Electronic Supplementary Material (ESI) for Green Chemistry.
This journal is © The Royal Society of Chemistry 2019

An Efficient Way for the N-Formylation of Amines by Inorganic-ligand Supported Iron Catalysis

Zhikang Wu,[a†] Yongyan Zhai,[a†] Wenshu Zhao,[c†] Zheyu Wei,[a] Han Yu,[a,b*] Sheng Han [a*] and Yongge Wei[b,d*]

[a.] *School of Chemical and Environmental Engineering Shanghai Institute of Technology,No. 100 Haiquan Road, Shanghai 201418 (P.R. China) E-mail: hanyu0220@tsinghua.edu.cn*

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

[c.] *Longhua Hospital Shanghai University of Traditional Chinese Medicine*

[d] *State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing 100191, P.R. China.* E-mail: ygwei@pku.edu.cn

† These authors contributed equally to this work.

* E-mail: hanyu0220@tsinghua.edu.cn, hansheng654321@sina.com, yonggewei@ tsinghua.edu.cn,

Table of contents

I. General information

The catalyst was prepared according to published literature methods.[1] All reagents were purchased from Sigma-Aldrich and Adamas-beta, which were used without further purification. FT-IR spectra were recorded on a Thermo Fisher Nicolet 6700. XRD were explored on D/max 2200 PC of Janpan. GC analyses were performed on Shimadzu GC-2014 with a flame ionization detector equipped with an Rtx-1 capillary column (internal diameter = 0.25 mm, length = 30 m) or a Stabil wax capillary column (internal diameter = 0.25 mm, length = 30 m). GC mass spectra were recorded on Shimadzu GCMS-QP2010 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 $CDCl_3$ and DMSO 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

$[NH_4]_3[FeMo_6O_{18}(OH)_6]$ was prepared according to the published literature methods and what we previously reported[1,2]. Firstly, $(NH_4)_6Mo_7O_{24}\times 4\cdot H_2O$ (5.0 g, 4 .0 mmol) was dissolved in water (80 ml) under stirring in an oil bath at 100 ^{o}C. Then, an aqueous solution of $Fe_2(SO_4)_3$ (2.3 g, 5.75 mmol) dissolved in 20 ml of water was added drop by drop to the above solution. The pH of the solution needs to be controlled at around 4.0 to 6.5 in this process strictly. After the dropwise addition is completed, the mixed solution is further stirred at a constant temperature of 100 ^{o}C for 2 hour. Following by, the solution is filtered immediately. The obtained solution was cooling at room temperature for 12 hours and precipitated the white crystals [1]. After recrystallized, filtered and vacuum dried, the white crystals (5.1 g) was deposited and collected. IR: 3174.36 (vasNH, m), 1635.68 (δOH m), 1400.75 (δNH, s), 947.41 (ν Mo=O, νs), 891.89 (ν Mo=O, νs), 650.93 (ν Mo-O-Mo, νs), 572.87 (ν M-O-Mo, w) cm^{-1}.

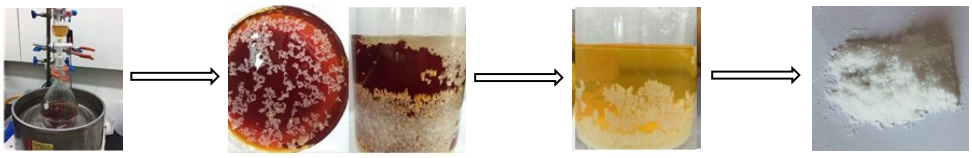


Figure S1. $[NH_4]_3[FeMo_6O_{18}(OH)_6]$

III. FT-IR spectra of catalyst 1

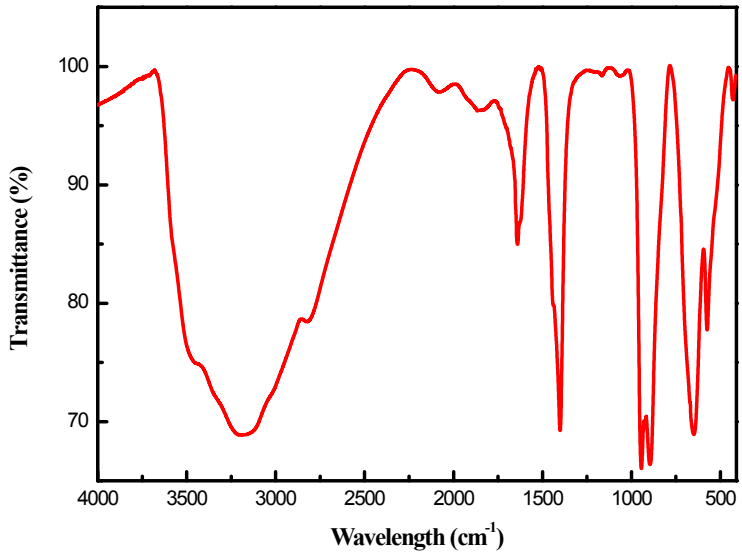


Figure S2. FT-IR spectra of catalyst **1**

IV. XRD spectra of catalyst 1

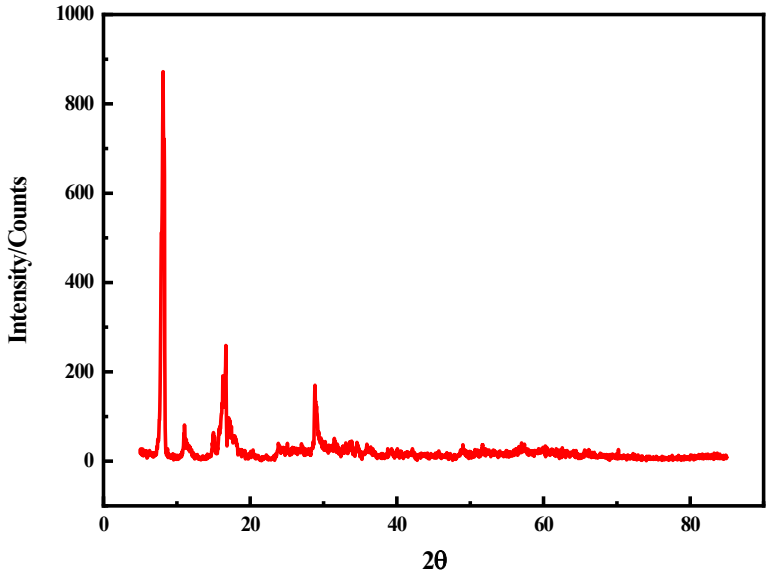


Figure S3. XRD spectra of catalyst **1**

V. ESI-MS spectra of catalyst 1

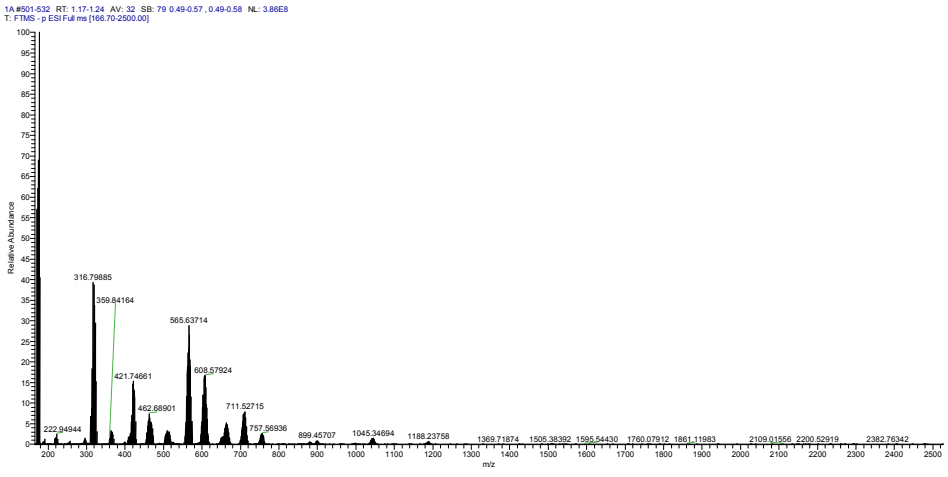


Figure S4. ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$.

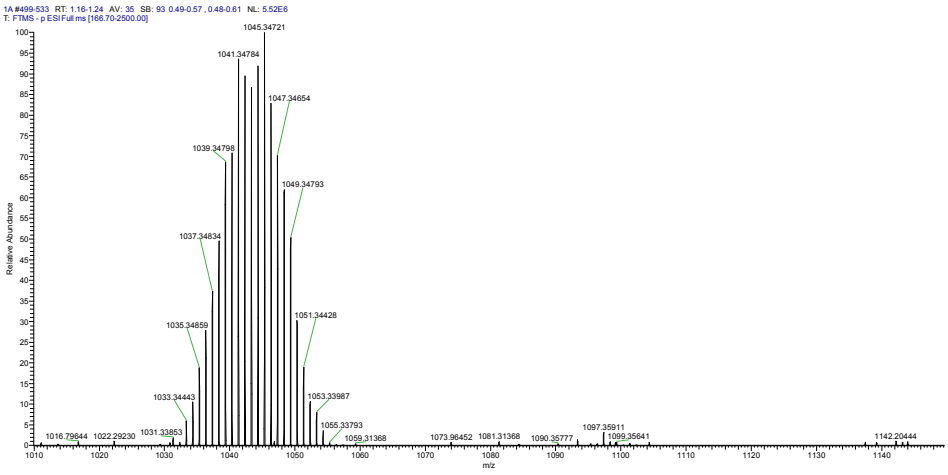


Figure S5. Zoom the area of ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$, (m/z = 1010-1500, $\{NH_4H[FeMo_6O_{24}H_6]\}^{1-}$ = 1043.34 g/mol).

VI. General procedure for N-Formylation of Amines with Formic acid

The Cat.**1** (1.0 mol%), amines (1.0 mmol), formic acid (2.0 ml), Na_2SO_3 (0.05 eq.) stirring at a reaction tube at 80 ^oC for 2 h (diamines for 12 h). Afterwards, a small amount of ethyl acetate was added into the reaction mixture and the solution was quickly filtered. The filtered solid was washed, dried and then recycled. Reaction mixture was analyzed by GC-MS analysis. Finally, the solvent was removed in vacuo, and the corresponding Formamides was purified by washing through base-washed

silica gel column. (Petrol: EtOAc = 1:2).

VII. Recycling experiments of catalyst 1

The POM catalyst was filtered and dried after the direct coupling experiment. The recovered catalyst was characterized by FTIR and X-RD. The infrared image contains a new catalyst and the sixth catalyst.

Figure S6. The catalyst recovery

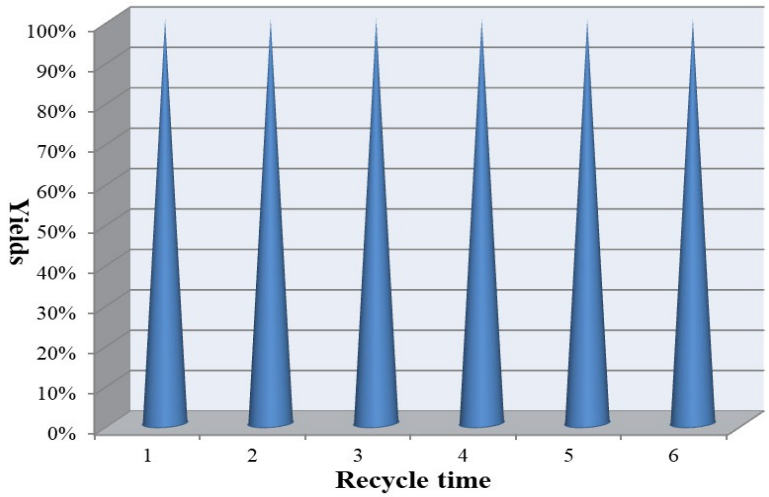


Figure S7. Recycling experiments for the Cat. **1**

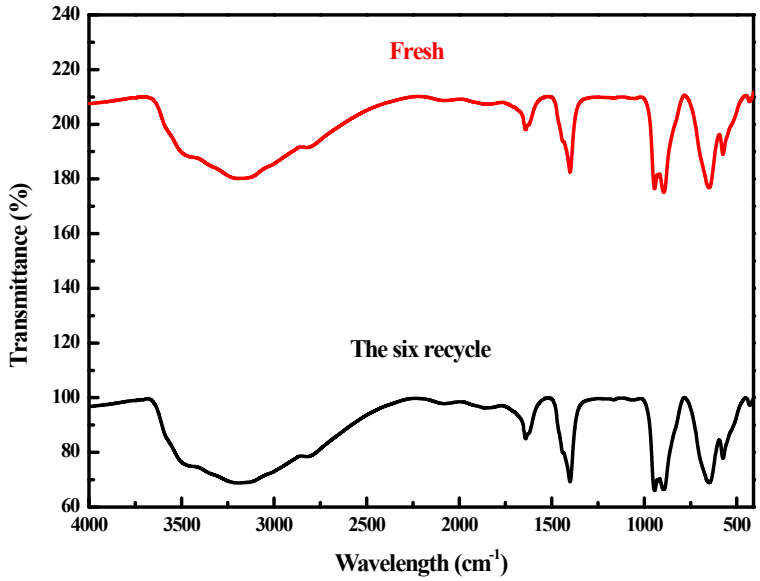


Figure S8. FT-IR spectra of the Cat. **1** before and after reaction

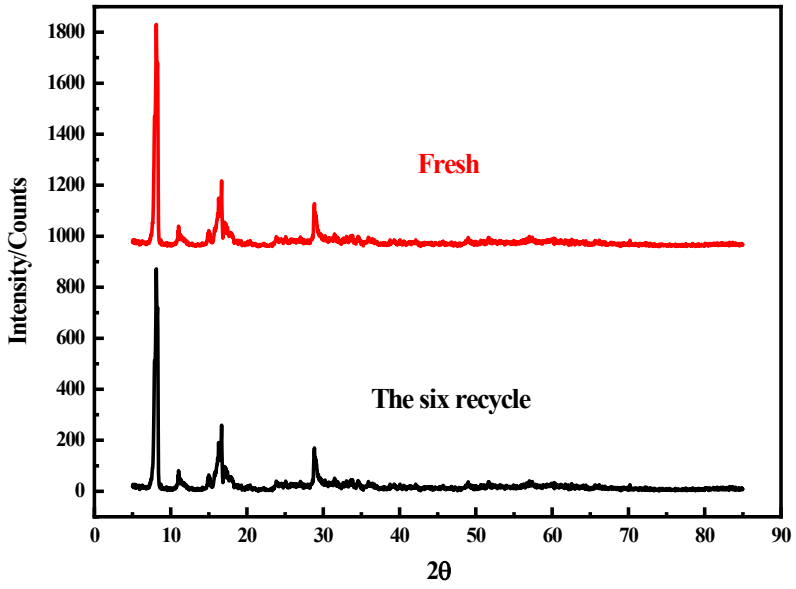
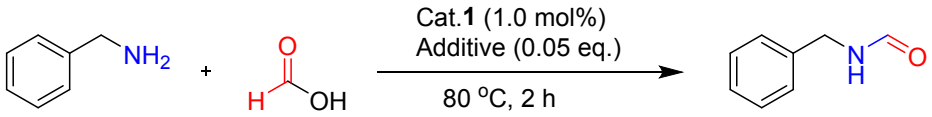


Figure S9. XRD of Cat. **1** before and after reaction

VIII. Optimization of reaction conditions

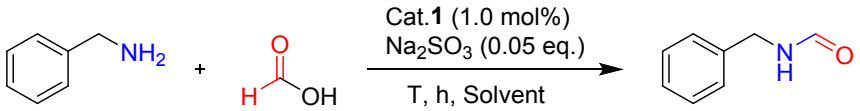
Table S1： Effect of the amount of catalyst, additive on *N*-Formylation of Amines



Entry	Catalyst [mol%]	Additive [eq.]	Yield[j] [%]
1	**1** (1.0)	NaBr	24
2	**1** (1.0)	NaI	45
3	**1** (1.0)	Na_2CO_3	77
4	**1** (1.0)	KCl	32
5	**1** (1.0)	K_2SO_4	53
6	**1** (1.0)	KBr	45
7	**1** (1.0)	KI	64
8	**1** (1.0)	$NaHCO_3$	72
9	**1 (1.0)**	**Na_2SO_3**	**>99**
10[b]	**1** (1.0)	Na_2SO_3	86
11[c]	**1** (1.0)	Na_2SO_3	89
12[d]	**1** (0.1)	Na_2SO_3	63
13[e]	**1** (0.5)	Na_2SO_3	76
14[f]	**1** (1.5)	Na_2SO_3	93

[a] Reaction conditions: Cat. **1** (1.0 mol%), benzylamine (1.0 mmol), formic acid (2.0 ml), 80 °C, 2 h. [b] Na_2SO_3 (0.01 eq.). [c]Na_2SO_3 (0.1 eq.). [d] Cat. **1** (0.1 mol%). [e] Cat. **1** (0.5 mol%). [f] Cat. **1** (1.5 mol%). [g] Substrate conversion and yield were determined by GC-MS (internal standard is toluene) analysis.

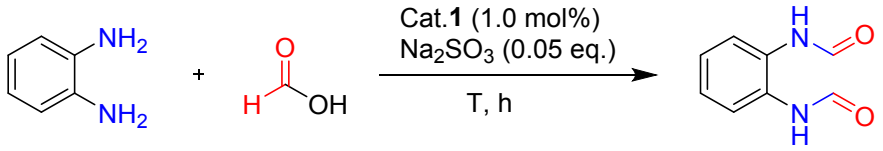
Table S2: Effect of temperature, solvent and time on *N*-formylation of Amines



Entry	T [°C]	Solvent [2.0 mL]	Time [h]	Yield[b] [%]
1	50	none	4	43
2	60	none	4	66
3	70	none	4	78
4	75	none	4	83
5	80	none	4	92
6	85	none	4	90
7	90	none	4	74
8	**80**	none	**2**	**>99**
9	80	none	6	94
10[b]	80	diethyl ether	2	75
11[c]	80	MeCN	2	68
12[d]	80	Toluene	2	81
13[e]	80	DMF	2	83

[a]Reaction conditions: Cat. **1** (1.0 mol%), benzylamine (1.0 mmol), formic acid (2.0 ml), Na_2SO_3 (0.05 eq.) stirring at a reaction tube at 80 °C for 2 h. [b-e] Cat. **1** (1.0 mol%), benzylamine (1.0 mmol), formic acid (2.0 mmol), Na_2SO_3 (0.05 eq.) stirring at a reaction tube at 80 °C for 2 h. [f]Substrate conversion and yield were determined by GC-MS (internal standard is toluene) analysis.

Table S3: Optimization of *N*-formylation on diamine



Entry	T [°C]	HCOOH (ml)	T [h]	Yield[b] [%]
1	60	1.0	12	38
2	70	1.0	12	45
3	75	1.0	12	51
4	80	1.0	12	63
5	85	1.0	12	60
6	90	1.0	12	56
7	80	1.0	12	67
8	80	1.5	12	78
9	80	1.8	12	80
10	**80**	**2.0**	**12**	**82**
11	80	2.5	12	60
12	80	3.0	12	75
13	80	2.0	6	59
15	80	2.0	18	78

[a] Reaction conditions: Cat. **1** (1.0 mol%), phenylenediamine (1.0 mmol), formic acid (2.0 mL), Na_2SO_3 (0.05 eq.) stirring at a reaction tube at 80 °C for 12 h. [b] Yields were determined by ^{1}H-NMR, values in parentheses are the isolated yield.

IX. References

[1] K, Nomiya; T, Takahashi; T, Shirai; M, Miwa. Anderson-type heteropolyanions of molybdenum(VI) and tungsten(VI) *Polyhedron*. **1987**, *6*, 213-218.

[2] H, Yu.; Q, Zhao.; Z, Wei.; Z, Wu.; Q, L.; S, Han.; Y, Wei. Iron-catalyzed oxidative functionalization of C(sp^3)–H bonds under bromide-synergized mild conditions. *Chem. Commun*. **2019**, *55*, 7840.

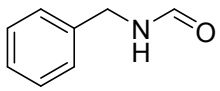
[3] C, C, Chong; R, Kinjo. Hydrophosphination of CO_2 and Subsequent Formate Transfer in the 1,3,2-Diazaphospholene-Catalyzed N-Formylation of Amines. *Angew. Chem. Int. Ed.* **2015**, *54*, 12116.

[4] B, Kang; S, H, Hong. *Cheminform*. **2015**, *357*, 834.

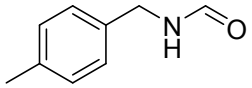
[5] S, Chakraborty; U, Gellrich; Y, Diskin-Posner. Manganese-Catalyzed N-Formylation of Amines by Methanol Liberating H_2: A Catalytic and Mechanistic Study. *Angew. Chem. Int. Ed. Engl.* **2017**, *56*, 4229.

[6] O, Jacquet; C, D, N, Gomes; M, Ephritikhine; T, Cantat. Recycling of Carbon and Silicon Wastes: Room Temperature Formylation of N-H Bonds Using Carbon Dioxide and Polymethylhydrosiloxane. *J. Am. Chem. Soc*. **2012**, *134*, 2934-2937.

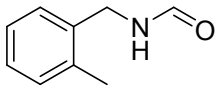
X. NMR data of products



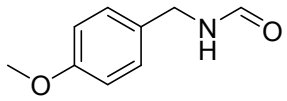
N-benzylformamide(2)[3-6]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.37 – 7.27 (m, 3H), 7.24 (t, *J* = 7.3 Hz, 2H), 6.99 (s, 1H), 4.37 (s, 2H). ^{3}C NMR (125 MHz, $CDCl_3$) δ 160.81 (s), 137.74 (s), 129.35 (s), 128.08 (s), 42.37 (s).



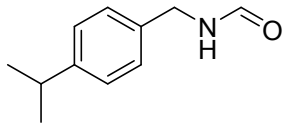
N-(4-methylbenzyl)formamide(3) [3-6]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.18 (dd, *J* = 15.2, 7.5 Hz, 4H), 6.09 (s, 1H), 4.44 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.06 (s), 137.43 (s), 134.59 (s), 129.45 (s), 127.81 (s), 126.96 (s), 41.95 (s), 21.10 (s).



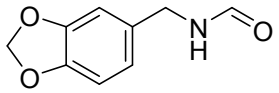
N-(2-methylbenzyl)formamide(4) [3-6]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.35 (s, 4H), 6.02 (s, 1H), 5.23 (s, 2H), 1.53 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.38 (s), 142.51 (s), 128.79 (s), 127.60 (s), 126.17 (s), 47.65 (s), 21.74 (s).



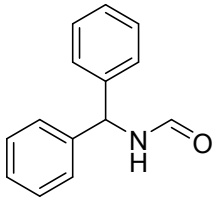
N-(4-methoxybenzyl)formamide(5) [3-6]: ^{1}H NMR (500 MHz, DMSO) δ 8.45 (s, 1H), 8.22 (s, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 4.34 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ 161.51 (s), 158.88 (s), 131.30 (s), 129.10 (s), 114.10 (s), 55.24 (s), 40.82(s).



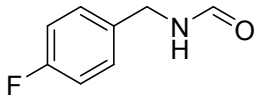
N-(4-isopropylbenzyl)formamide(6) [3-6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.20 (d, *J* = 5.8 Hz, 4H), 6.52 (s, 1H), 4.40 (s, 2H), 2.90 (s, 1H), 1.23 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.40 (s), 148.39 (s), 134.95 (s), 127.86 (s), 127.33 (d, *J* = 129.7 Hz), 41.91 (s), 33.82 (s), 23.85 (s).



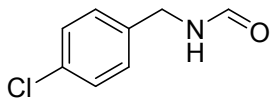
N-(benzo[d][1,3]dioxol-5-ylmethyl)formamide(7) [3-6]**:** ^{1}H NMR (500 MHz, DMSO) δ 8.44 (s, 1H), 8.12 (s, 1H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.98 (s, 2H), 4.22 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.38 (s), 147.96 (s), 147.09 (s), 131.39 (s), 121.12 (s), 108.39 (d, *J* = 7.1 Hz), 101.13 (s), 42.03 (s).



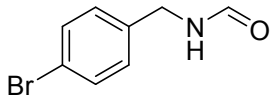
N-benzhydrylformamide(8) [3-6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.37 – 7.34 (m, 4H), 7.31 (d, *J* = 7.1 Hz, 2H), 7.26 (d, *J* = 7.1 Hz, 4H), 6.39 (s, 1H), 6.35 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.22 (s), 140.93 (s), 128.97 (s), 128.76 (s), 128.03 (s), 127.66 (s), 127.32 (d, *J* = 18.7 Hz), 55.72 (s).



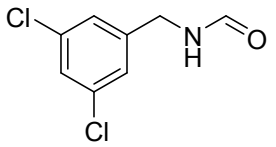
N-(4-fluorobenzyl)formamide(9) [3-6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.12 (s, 1H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.98 (s, 2H), 4.22 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.04 (s), 129.49 (d, *J* = 8.1 Hz), 115.71 (s), 115.54 (s), 41.46 (s).



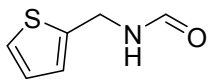
N-(4-chlorobenzyl)formamide(10) [3-6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 5.96 (s, 1H), 4.47 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.96 (s), 136.14 (s), 133.58 (s), 129.14 (s), 128.93 (s), 128.31 (s), 41.50 (s).



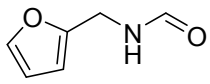
N-(4-bromobenzyl)formamide(11) [3-6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.12 (s, 1H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.98 (s, 2H), 4.22 (d, *J* = 6.0 Hz, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 161.03 (s), 136.65 (s), 131.90 (s), 129.49 (s), 121.63 (s), 41.56 (s).



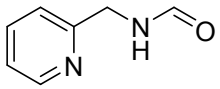
N-(3,5-dichlorobenzyl)formamide(12) [3-6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.39 (s, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.28 (s, 1H), 7.24 (s, 1H), 6.33 (s, 1H), 4.52 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.21 (s), 134.20 (s), 133.69 (s), 131.00 (s), 129.39 (s), 127.46 (s), 39.59 (s).



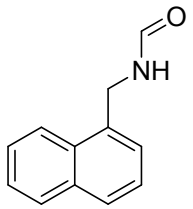
N-(thiophen-2-ylmethyl)formamide(13) [3-6]**:** ^{1}H NMR (500 MHz, DMSO) δ 8.52 (s, 1H), 8.02 (s, 1H), 7.30 (d, *J* = 6.0 Hz, 1H), 6.92 – 6.85 (m, 2H), 4.40 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (125 MHz, DMSO) δ 161.40 (s), 142.30 (s), 127.18 (s), 126.05 (s), 125.55 (s), 36.20 (s).



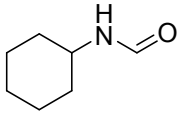
N-(furan-2-ylmethyl)formamide(14) [3-6]**:** ^{1}H NMR (500 MHz, DMSO) δ 8.17 (s, 1H), 7.32 (s, 1H), 6.78 (s, 1H), 6.26 (d, *J* = 34.9 Hz, 2H), 4.44 (d, *J* = 5.1 Hz, 2H). ^{13}C NMR (125 MHz, DMSO) δ 161.38 (s), 152.26 (s), 142.63 (s), 110.89 (s), 107.40 (s), 34.43 (s).



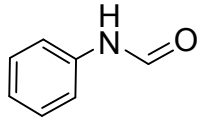
N-(pyridin-2-ylmethyl)formamide(15) [3-6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.60 (s, 1H), 8.21 (s, 1H), 7.68 (s, 1H), 7.37 (s, 1H), 7.21 (s, 1H), 4.82 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (125 MHz, CDCl3) δ 164.65 (s), 156.97 (s), 149.22 (s), 137.35 (s), 126.28 (s), 122.34 (s), 44.69 (s).



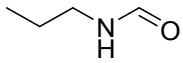
N-(naphthalen-1-ylmethyl)formamide(16) [3-6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.99 (s, 1H), 7.90 – 7.77 (m, 3H), 7.55 (s, 1H), 7.43 (s, 1H), 6.09 (s, 1H), 4.90 (s, 2H). ^{13}C NMR (120 MHz, $CDCl_3$) δ 160.95 (s), 133.88 (s), 132.82 (s), 131.25 (s), 128.84 (s), 126.78 (d, *J* = 8.1 Hz), 126.12 (s), 125.41 (s), 123.36 (s), 40.30 (s).



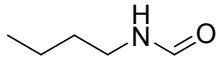
N-(cyclohexylmethyl)formamide(17) [3-6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 6.81 (s, 1H), 3.67 (s, 1H), 1.77 (d, *J* = 12.3 Hz, 2H), 1.59 (d, *J* = 3.6 Hz, 2H), 1.21 (t, *J* = 12.5 Hz, 3H), 1.13 – 0.98 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.15 (s), 32.68 (d, *J* = 5.4 Hz), 31.64 (s), 24.62 (s).



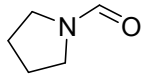
N-phenylformamide(18) [3-6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.32 (s, 1H), 7.32 (dt, *J* = 16.0, 8.0 Hz, 4H), 7.19 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.88 (s), 130.41 (s), 129.74 (s), 129.12 (s), 128.39 (s), 119.67 (s).



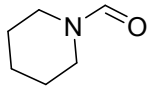
N-propylformamide(19) [3-6]**:** ^{1}H NMR (500 MHz, DMSO) δ 8.85 (s, 1H), 8.00 (s, 1H), 2.98 (s, 2H), 1.28 (s, 2H), 1.18 (s, 2H), 0.75 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ 161.46 (s), 39.33 (s), 22.69 (s), 11.69 (s).



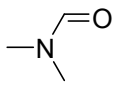
N-butylformamide(20) [3-6]**:** ^{1}H NMR (500 MHz, DMSO) δ 8.85 (s, 1H), 8.00 (s, 1H), 2.98 (s, 2H), 1.28 (s, 2H), 1.18 (s, 2H), 0.75 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ 161.30 (s), 37.18 (s), 31.52 (s), 19.91 (s), 13.79 (s).



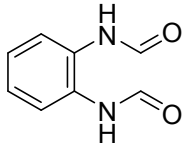
pyrrolidine-1-carbaldehyde(21) [3-6]**:** ^{1}H NMR (500 MHz, DMSO) δ 8.06 (s, 1H), 3.33 (s, 2H), 3.11 (s, 2H), 1.69 (s, 4H).^{13}C NMR (125 MHz, DMSO) δ 161.13 (s), 45.84 (s), 43.11 (s), 24.87 (s), 24.19 (s).



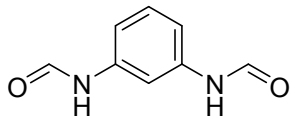
piperidine-1-carbaldehyde(22) [3-6]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 3.42 (dd, *J* = 74.1, 14.0 Hz, 4H), 1.84 – 1.33 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.09 (s), 47.02 (s), 40.80 (s), 26.58 (s), 25.09 (s), 24.68 (s).



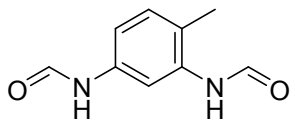
N,N-dimethylformamide(23) [3-6]**:** ^{1}H NMR (500 MHz, DMSO) δ 7.88 (s, 1H), 2.80 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ 162.46 (s), 35.78 (s), 30.69 (s).



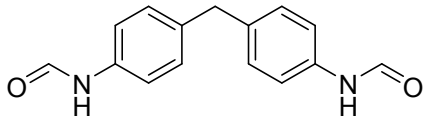
N,N'-(1,2-phenylene)diformamide(24): ^{1}H NMR (500 MHz, DMSO) δ 8.28 (s, 1H), 8.16 (s, 1H), 7.61 (s, 2H), 7.20 (d, *J* = 4.8 Hz, 2H), 6.45 (s, 2H). ^{13}C NMR (125 MHz, DMSO) δ 163.56 (s), 122.39 (s), 115.74 (s).



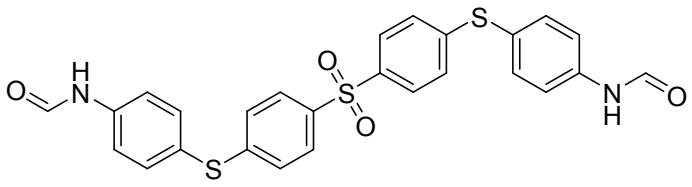
N,N'-(1,3-phenylene)diformamide(25): ^{1}H NMR (500 MHz, DMSO) δ 10.04 (s, 2H), 8.27 (s, 1H), 8.10 (s, 1H), 7.98 (s, 1H), 7.31 (s, 1H), 7.18 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (125 MHz, DMSO) δ 160.21 (s), 138.82 (s), 130.18 (s), 129.60 (s), 115.31 (s), 110.90 (s), 109.54 (s).



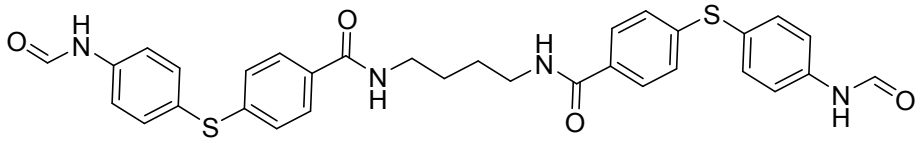
N,N'-(4-methyl-1,3-phenylene)diformamide(26): ^{13}C NMR (125 MHz, DMSO) δ 160.21 (s), 138.82 (s), 130.18 (s), 129.60 (s), 115.31 (s), 110.90 (s), 109.54 (s). ^{13}C NMR (125 MHz, DMSO) δ 160.22 (s), 159.79 (s), 136.73 (s), 136.21 (s), 131.51 (s), 130.91 (s), 124.80 (s), 116.09 (s), 17.79 (s).



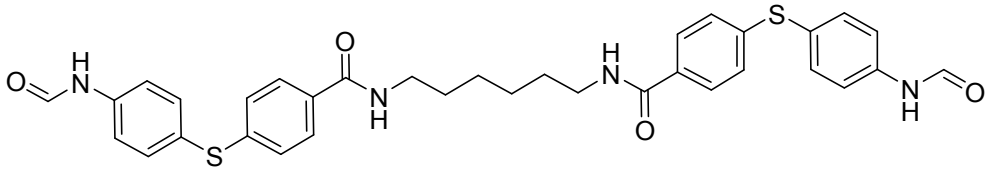
N,N'-(methylenebis(4,1-phenylene))diformamide(27): ^{1}H NMR (500 MHz, DMSO) δ 10.11 (s, 2H), 8.24 (d, *J* = 1.4 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 4H), 7.15 (d, *J* = 8.1 Hz, 4H), 3.84 (s, 2H). ^{13}C NMR (125 MHz, DMSO) δ 159.86 (s), 137.33 – 137.13 (m), 136.91 (d, *J* = 49.1 Hz), 129.99 (s), 129.46 (s), 119.75 (s), 118.29 (s).



N,N'-(((sulfonylbis(4,1-phenylene))bis(sulfanediyl))bis(4,1-phenylene))diformamide(28): ^{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), 146.73 (s), 140.17 (s), 138.24 (s), 136.29 (s), 128.48 (s), 127.00 (s), 121.01 (s).

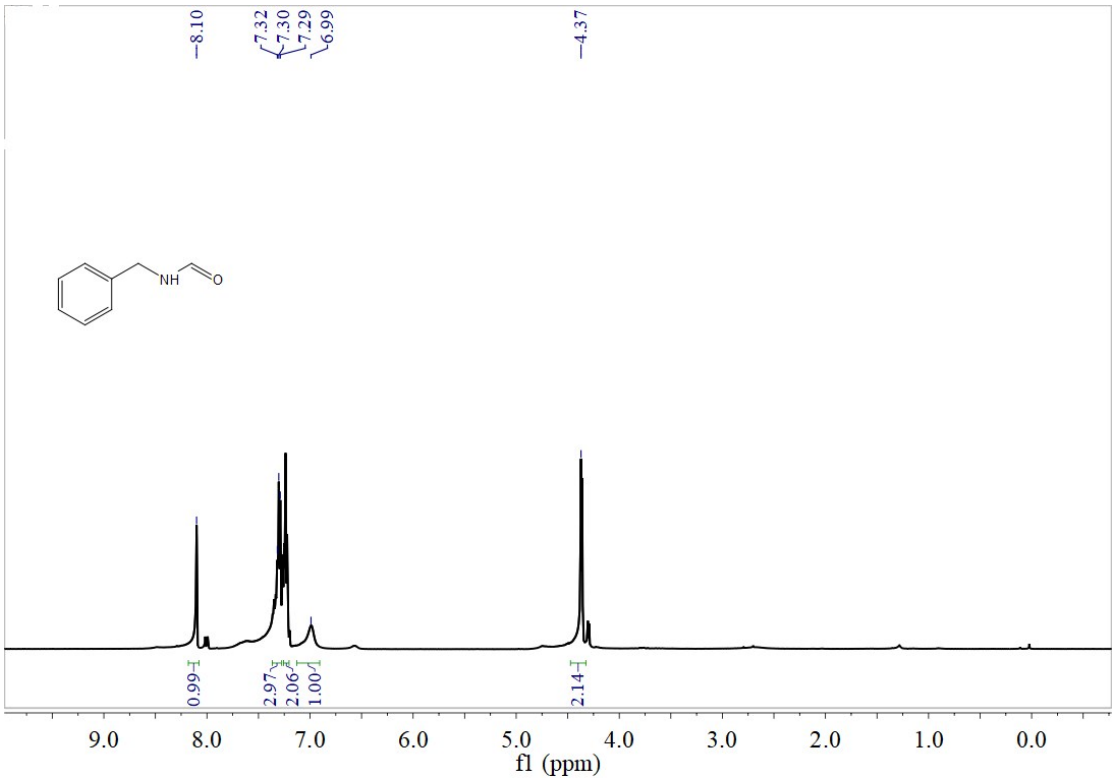


N,N'-(butane-1,4-diyl)bis(4-((4-formamidophenyl)thio)benzamide)(29): 1H NMR (500 MHz, DMSO) δ 10.41 (s, 2H), 8.43 (s, 2H), 8.33 (s, 2H), 7.76 (d, J = 8.2 Hz, 4H), 7.69 (d, J = 8.4 Hz, 4H), 7.46 (d, J = 8.3 Hz, 4H), 7.18 (d, J = 8.2 Hz, 4H), 3.26 (d, J = 4.4 Hz, 4H), 1.54 (s, 4H). ^{13}C NMR (125 MHz, DMSO) δ 165.93 (s), 160.35 (s), 141.54 (s), 139.36 (s), 134.95 (s), 128.52 (s), 127.58 (s), 120.82 (s), 118.90 (s), 27.17 (s).

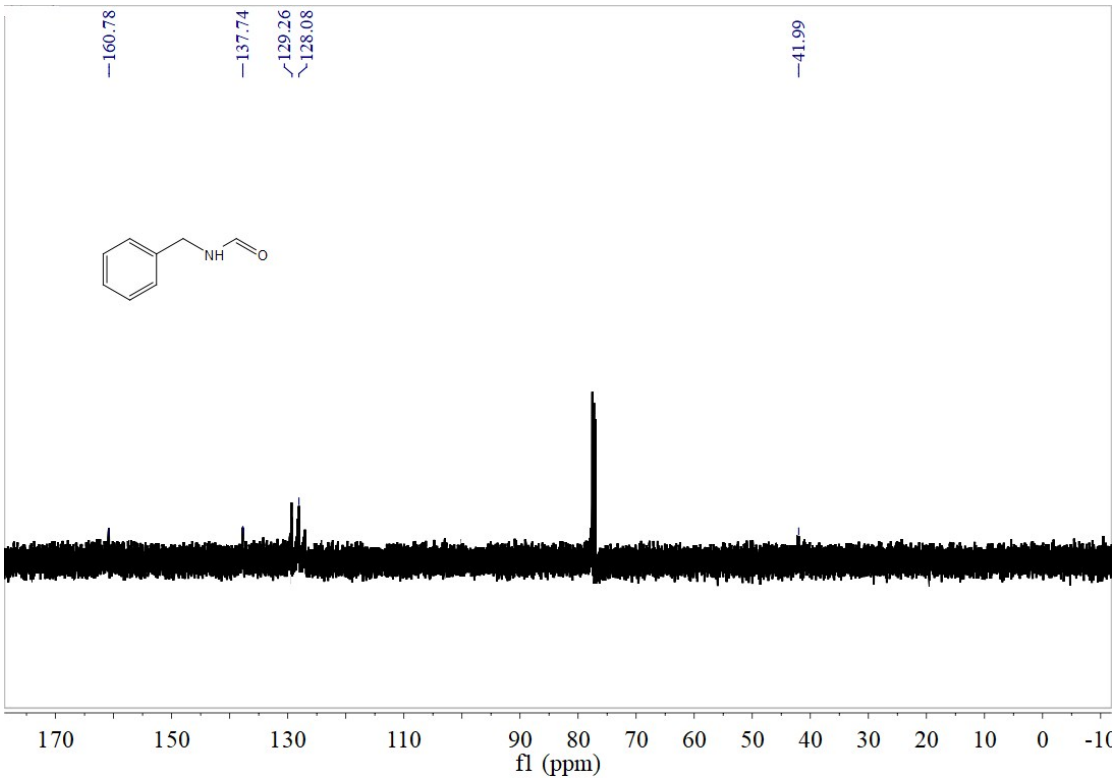


N,N'-(hexane-1,6-diyl)bis(4-((4-formamidophenyl)thio)benzamide)(30): ^{1}H NMR (500 MHz, DMSO) δ 10.41 (s, 2H), 8.39 (s, 2H), 8.32 (s, 2H), 7.75 (d, *J* = 8.2 Hz, 5H), 7.68 (s, 4H), 7.44 (d, *J* = 6.5 Hz, 5H), 7.18 (d, *J* = 8.2 Hz, 5H), 3.35 (s, 4H), 1.48 (s, 4H), 1.25 (s, 4H). ^{13}C NMR (125 MHz, 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), 118.88 (s), 29.49 (d, *J* = 17.0 Hz), 29.24 (s), 26.95 (s).

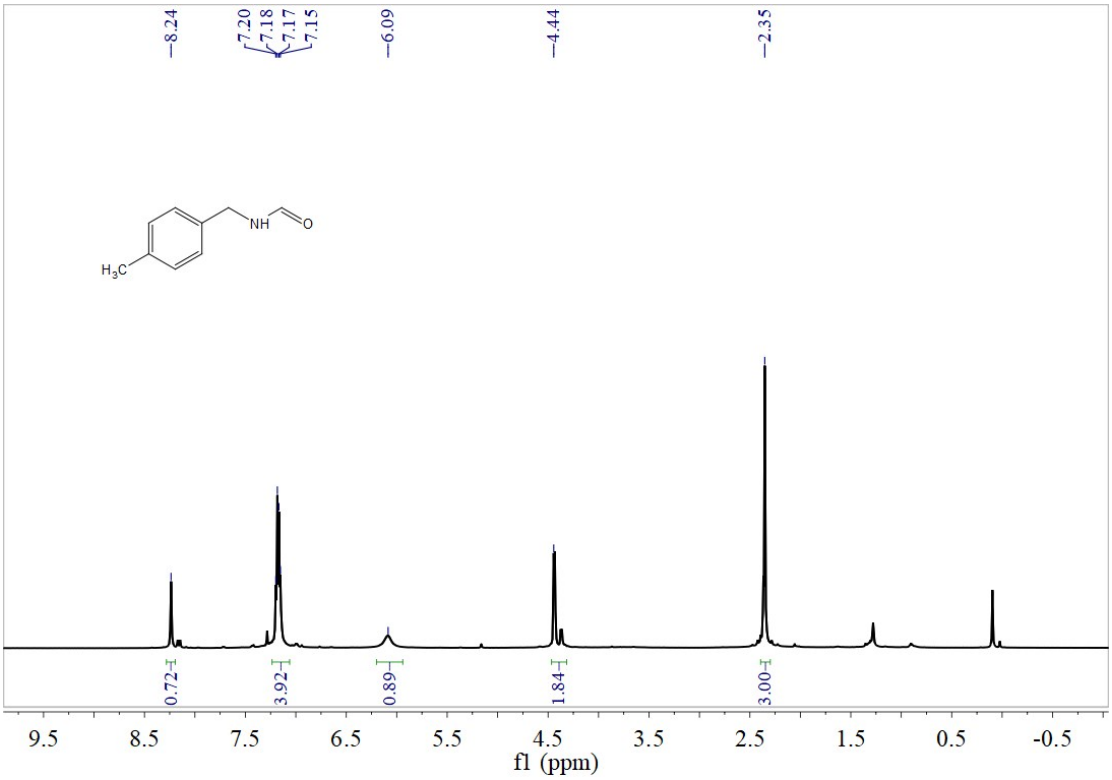
Ⅸ. NMR spectra



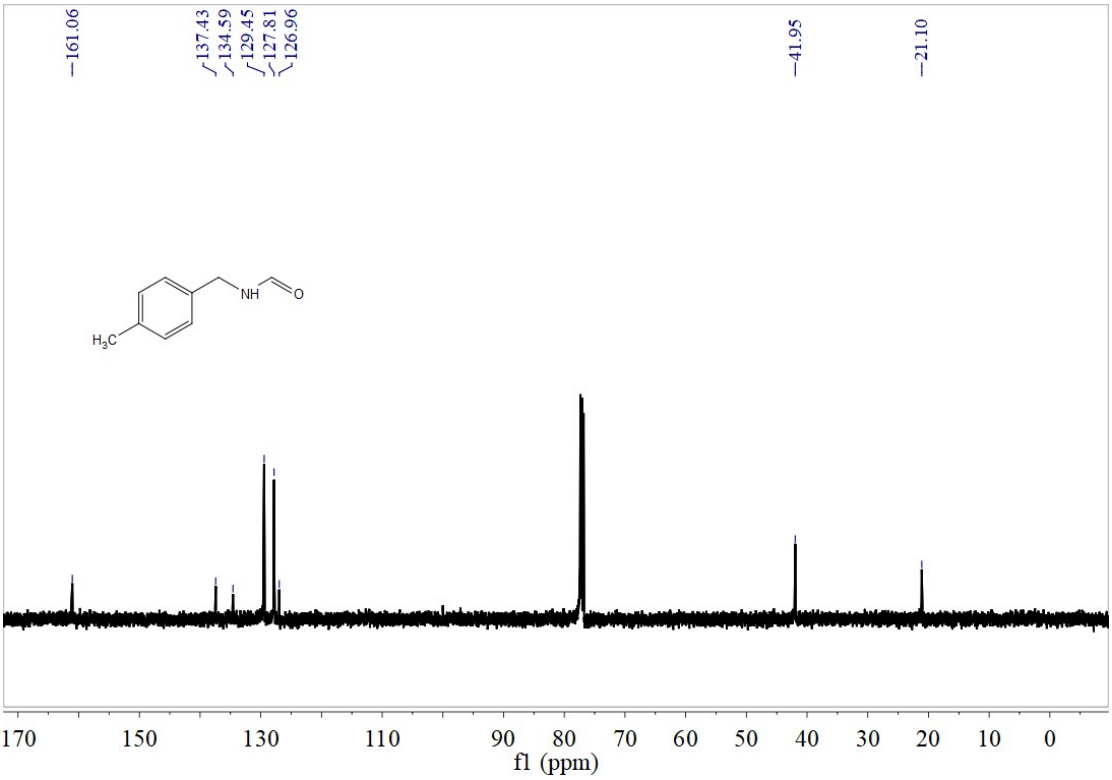
^{1}H NMR spectra of **2** (500 MHz, $CDCl_3$)



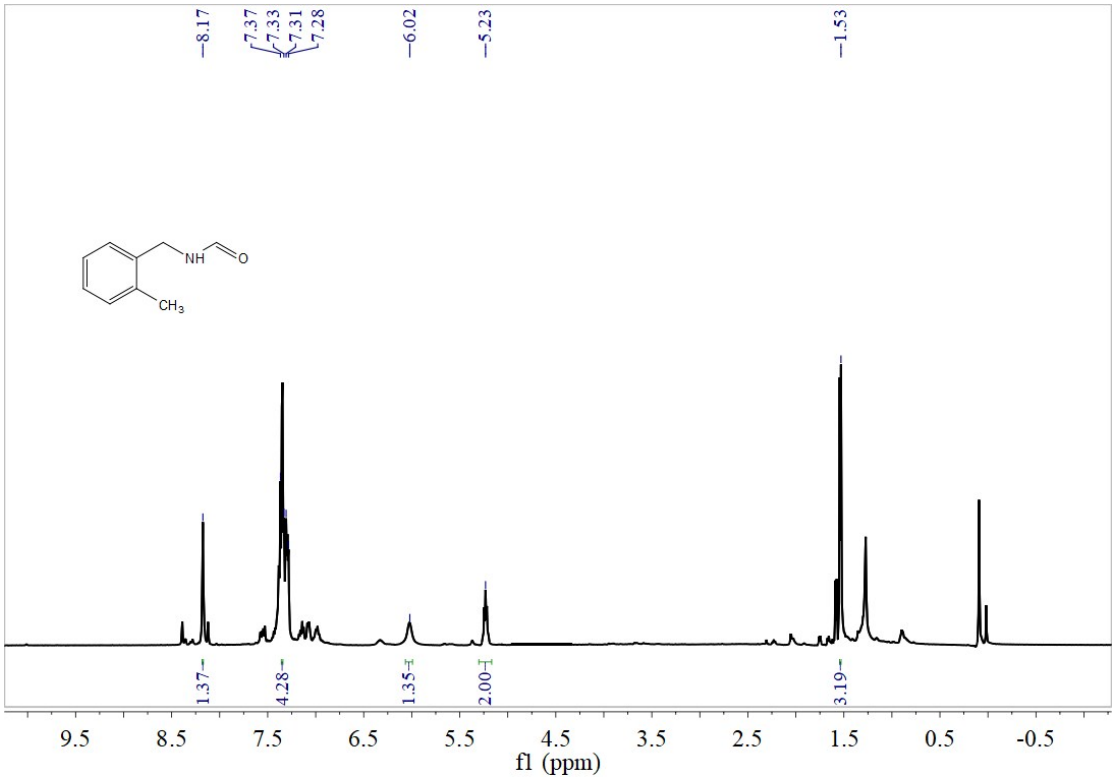
^{1}C NMR spectra of **2** (125 MHz, $CDCl_3$)



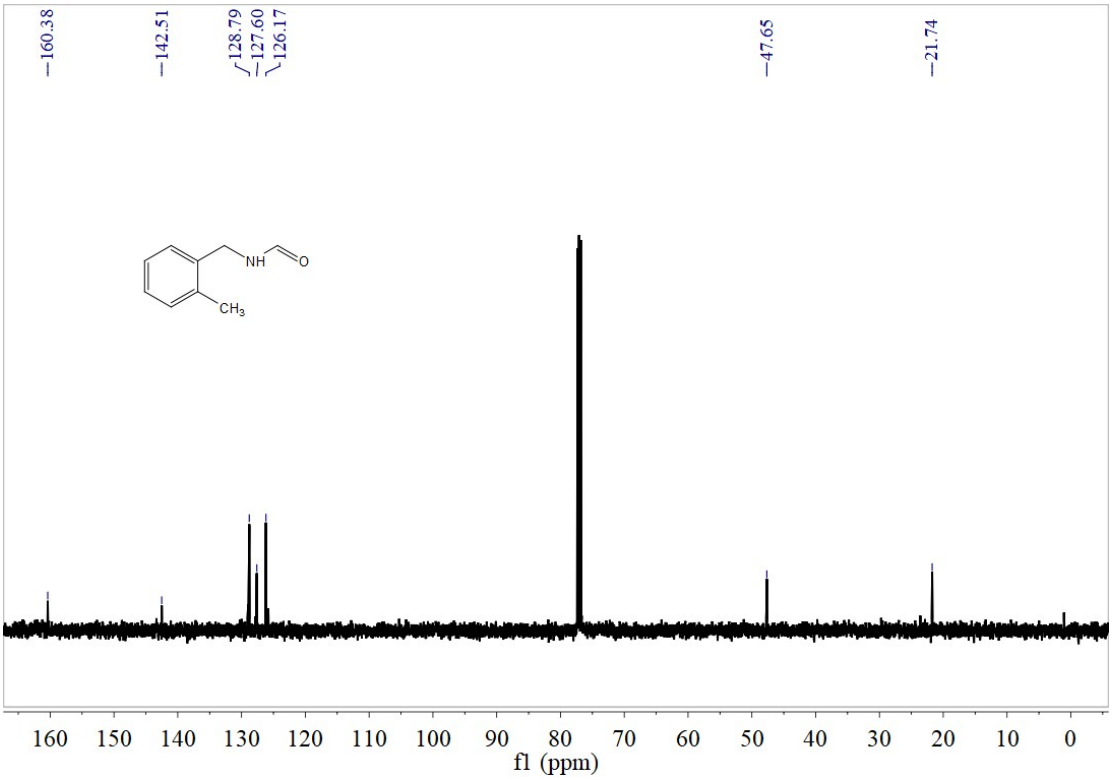
^{1}H NMR spectra of **3** (500 MHz, $CDCl_3$)



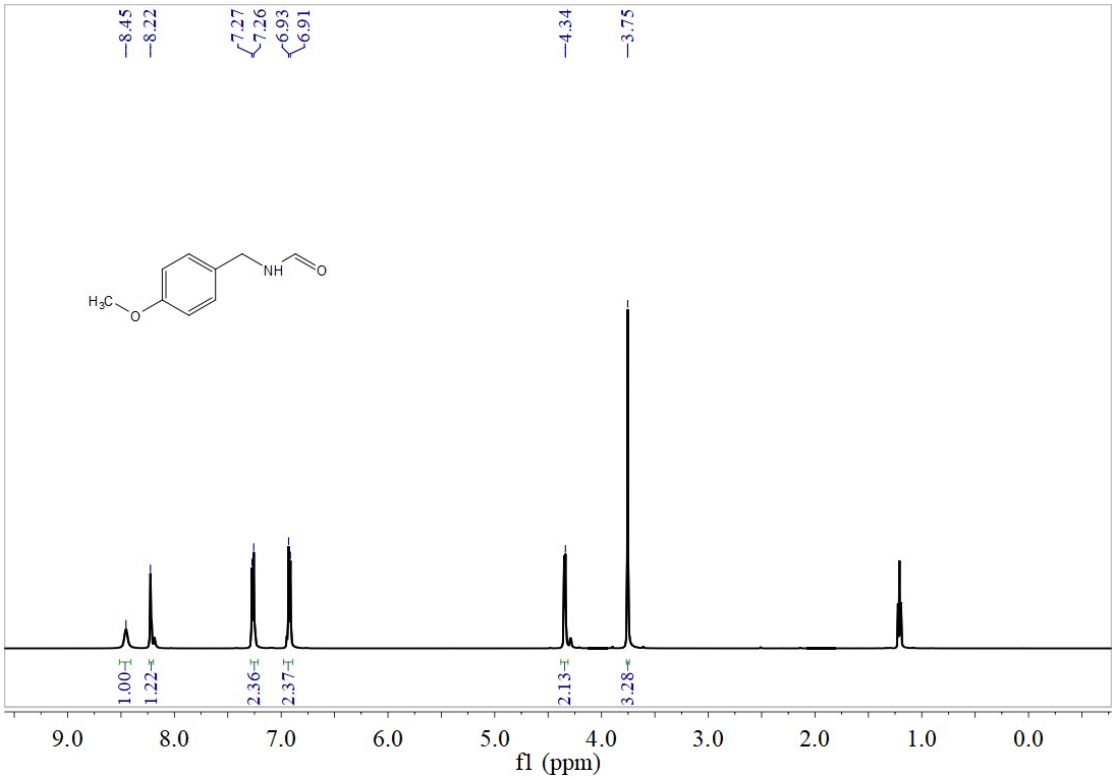
^{1}C NMR spectra of **3** (125 MHz, $CDCl_3$)



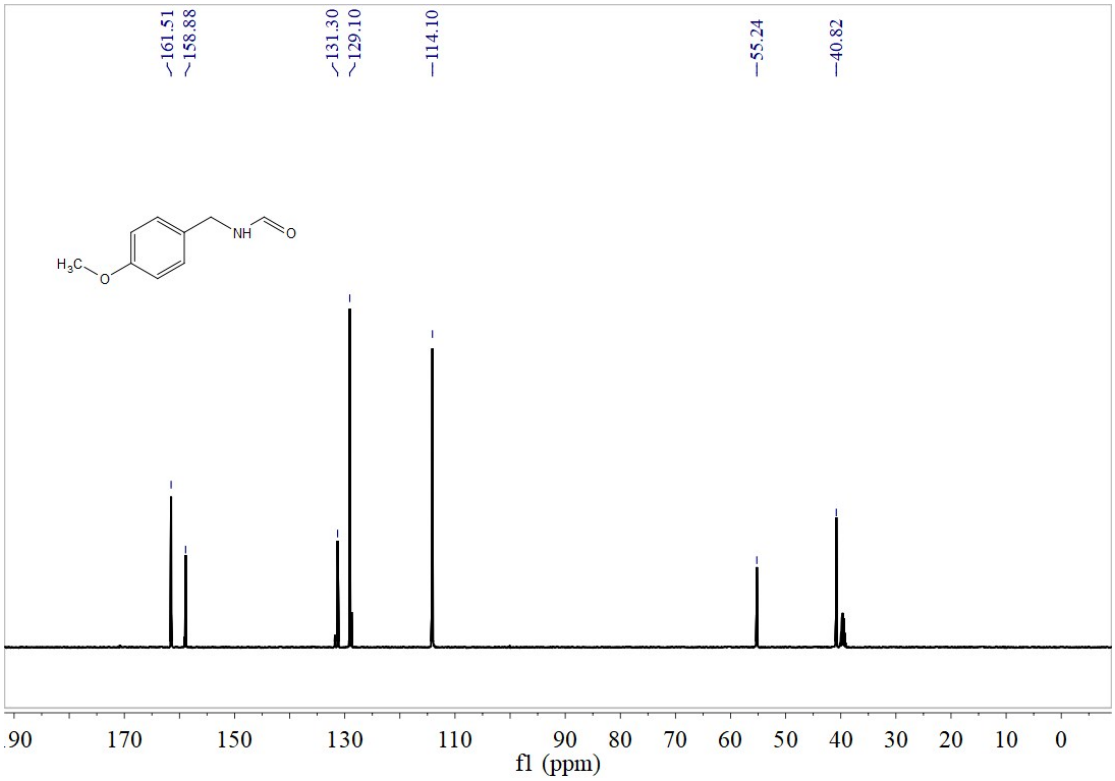
^{1}H NMR spectra of **4** (500 MHz, CDCl3)



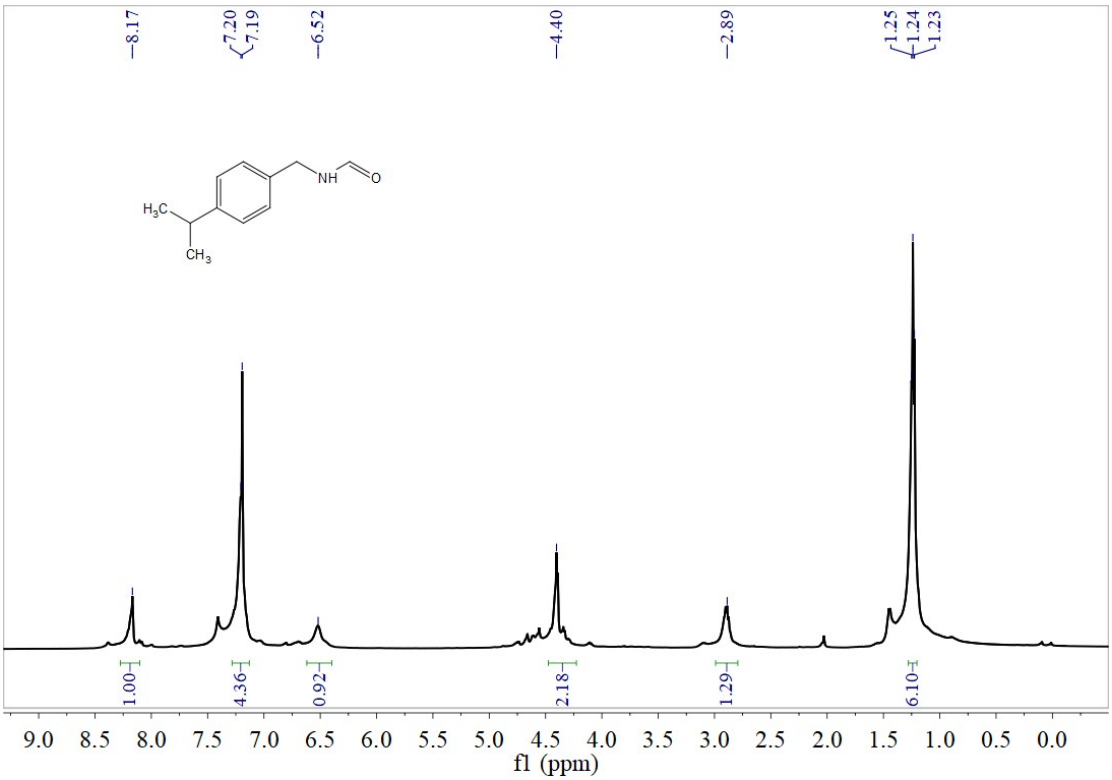
^{1}C NMR spectra of **4** (125 MHz, $CDCl_3$)



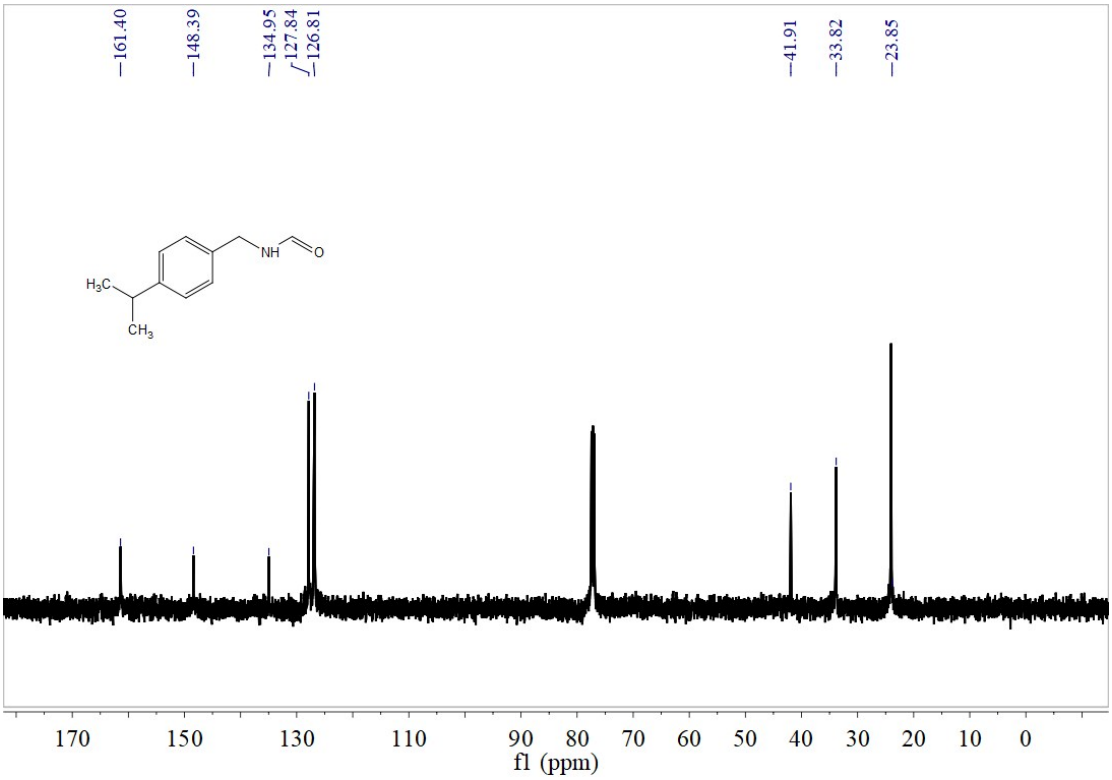
^{1}H NMR spectra of **5** (500 MHz, DMSO)



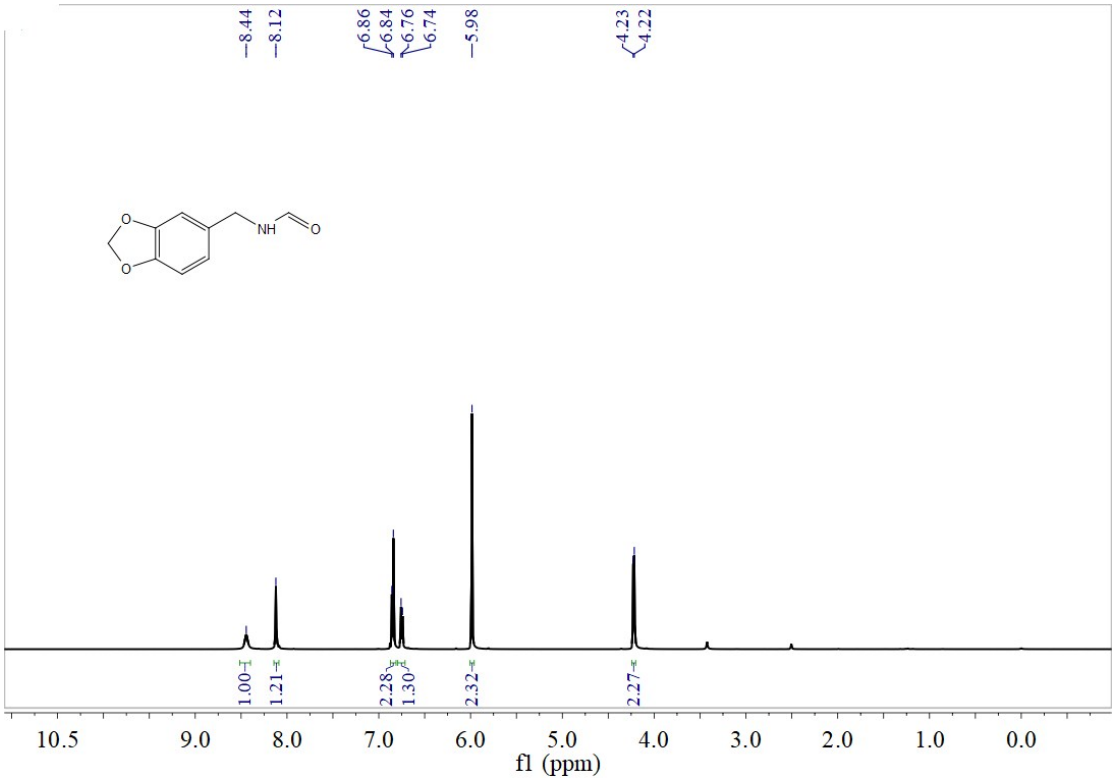
^{1}C NMR spectra of **5** (125 MHz, DMSO)



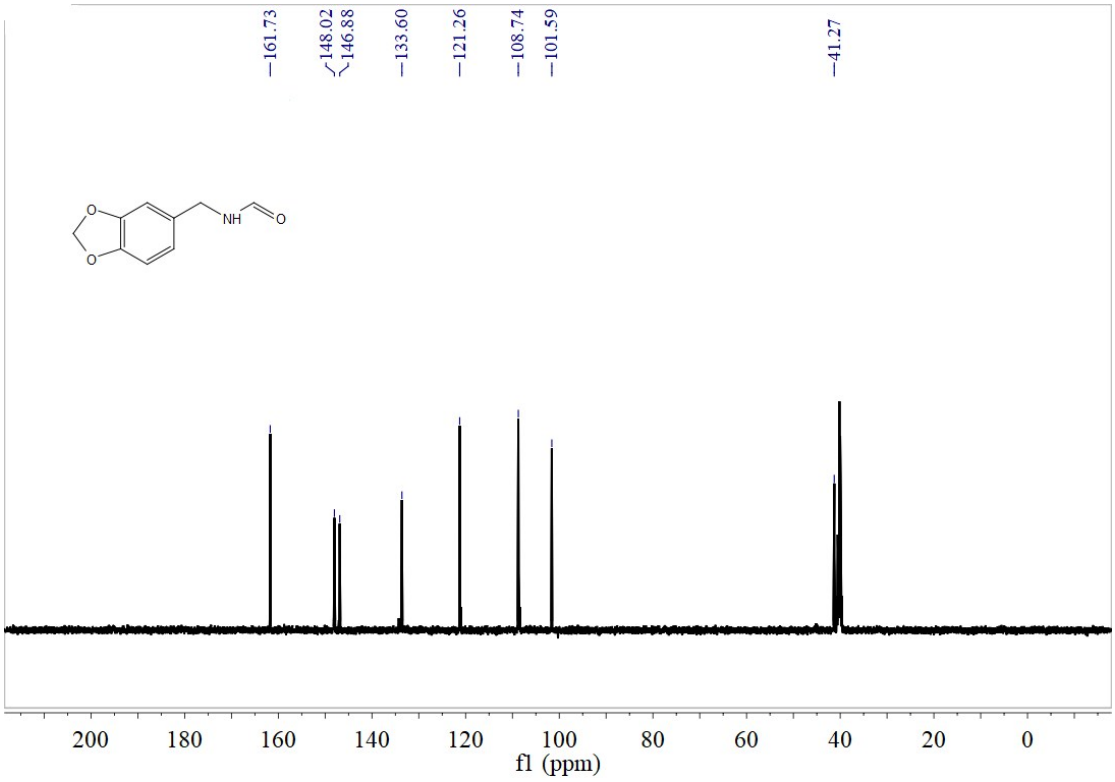
^{1}H NMR spectra of **6** (500 MHz, $CDCl_3$)



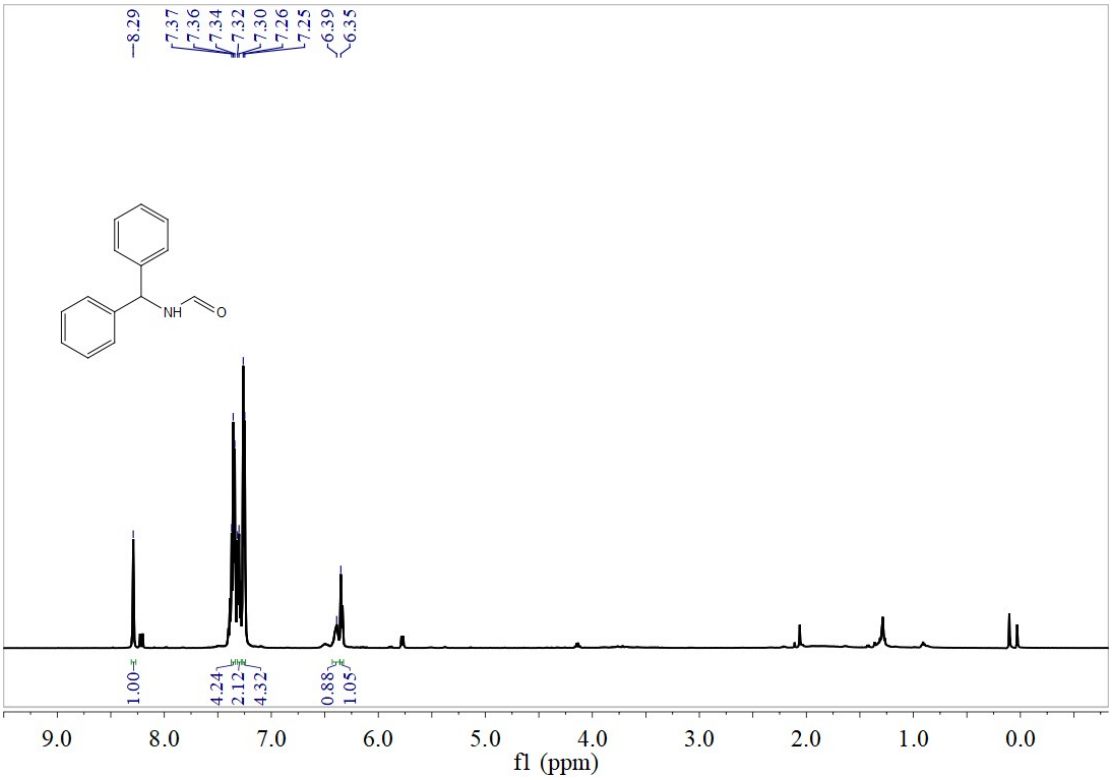
^{1}C NMR spectra of **6** (125 MHz, $CDCl_3$)



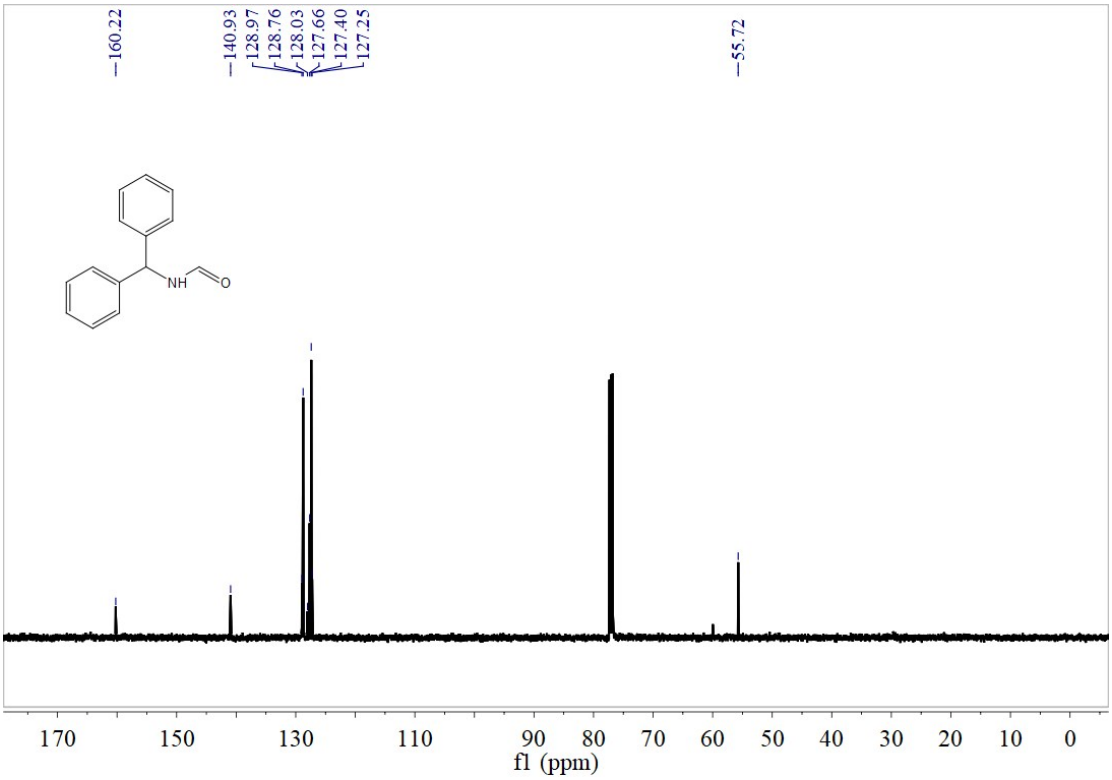
^{1}H NMR spectra of **7** (500 MHz, DMSO)



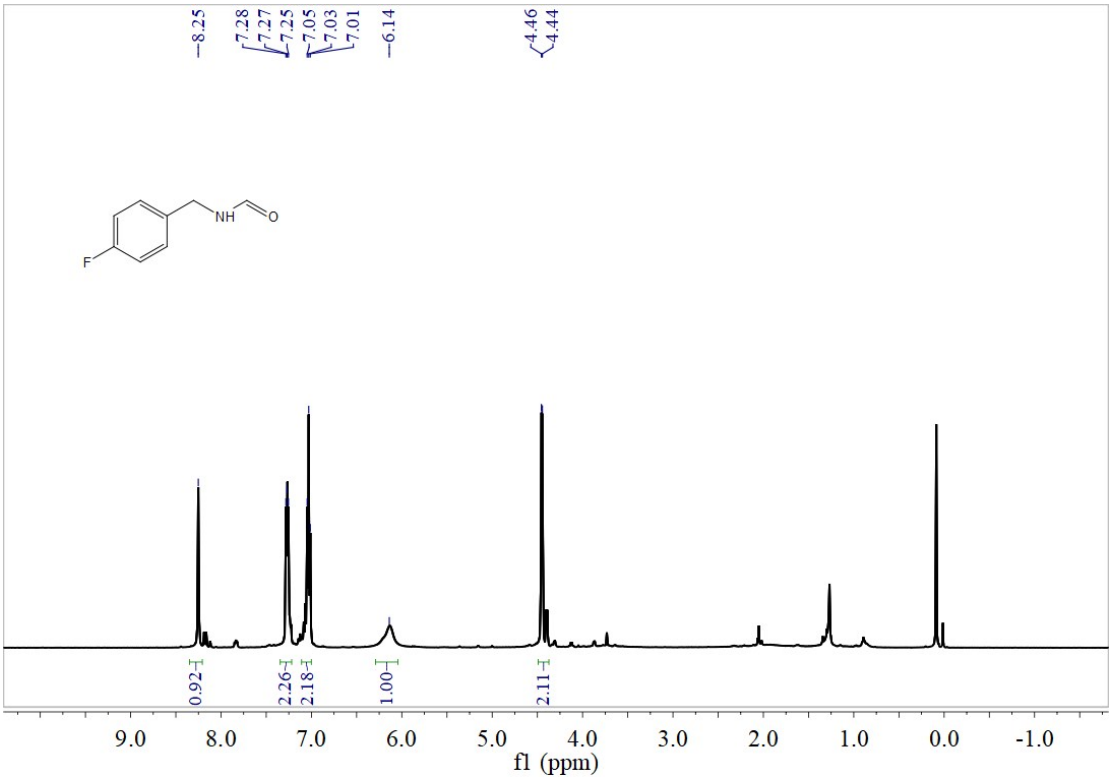
^{1}C NMR spectra of **7** (125 MHz, DMSO)



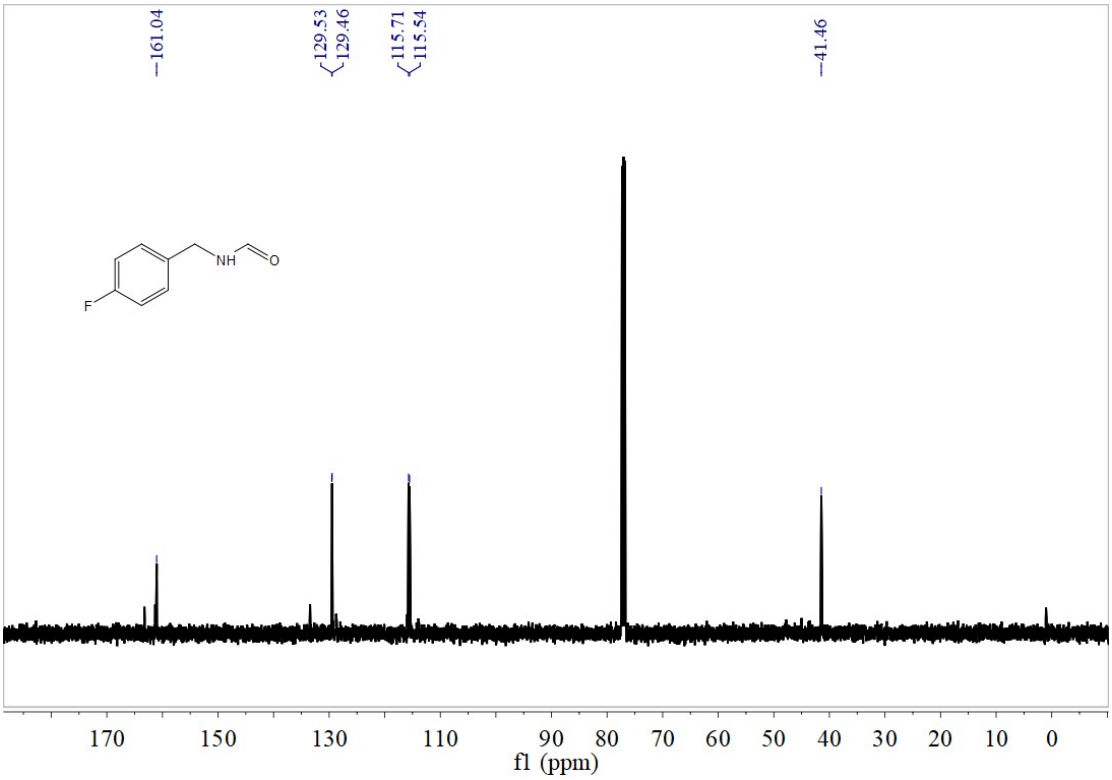
^{1}H NMR spectra of **8** (500 MHz, $CDCl_3$)



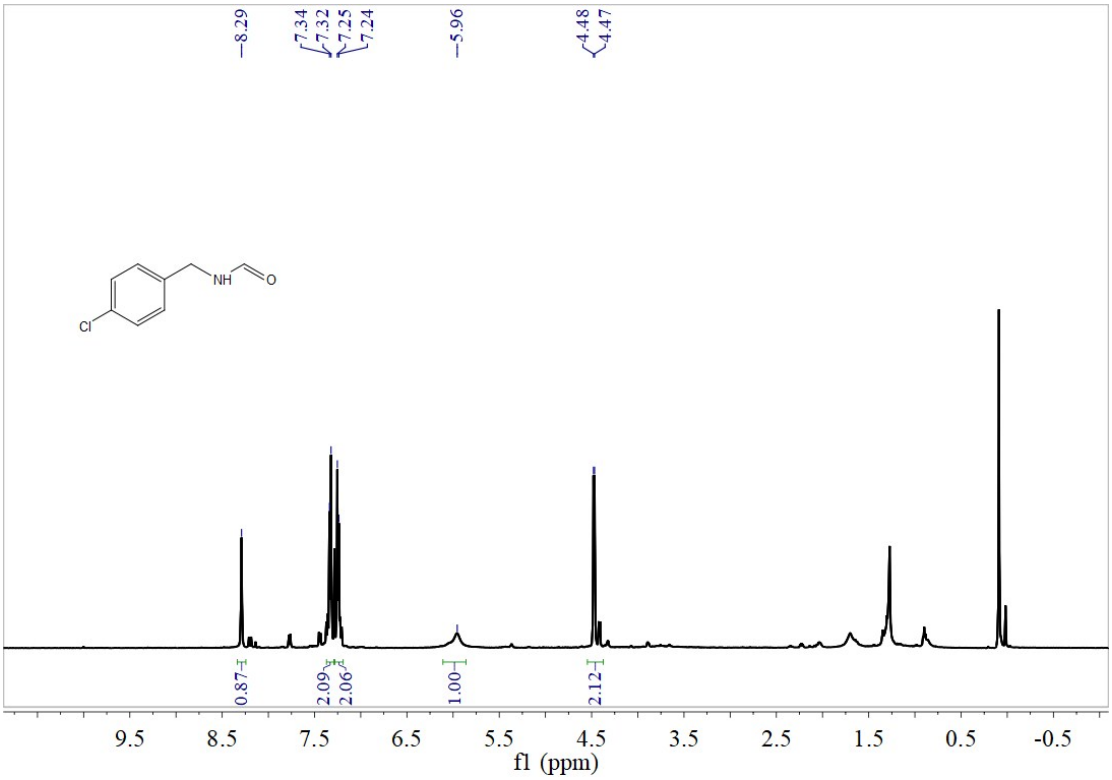
^{1}C NMR spectra of **8** (125 MHz, $CDCl_3$)



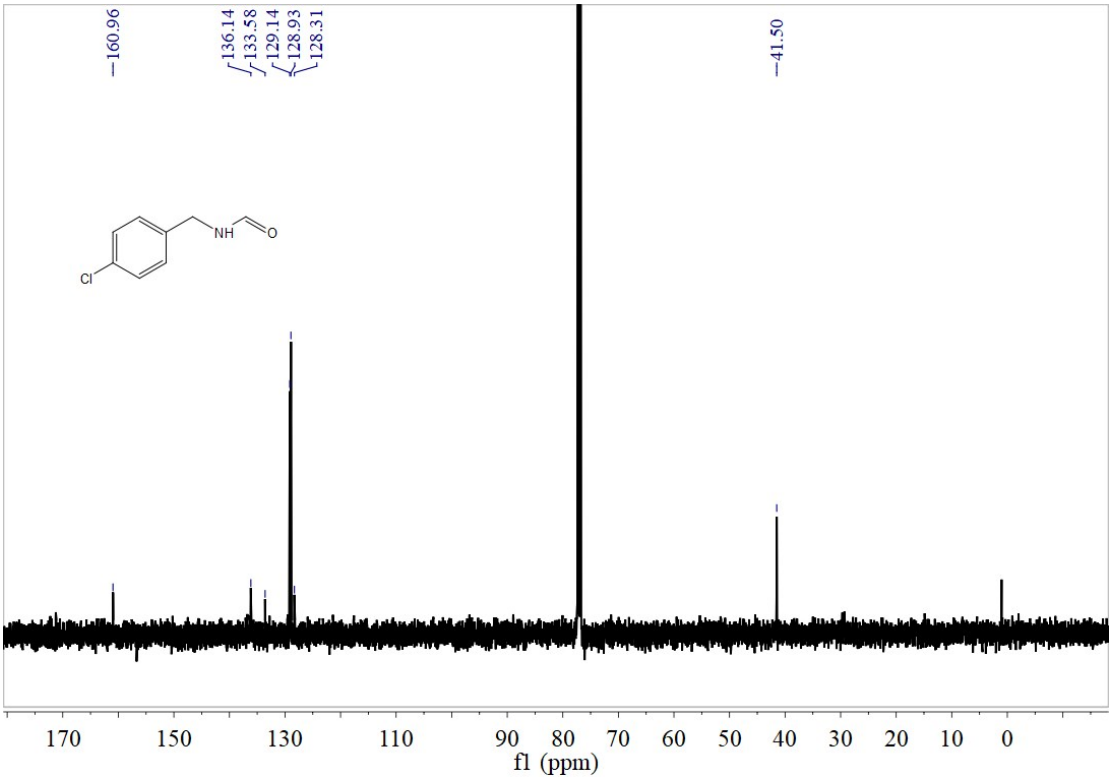
^{1}H NMR spectra of **9** (500 MHz, $CDCl_3$)



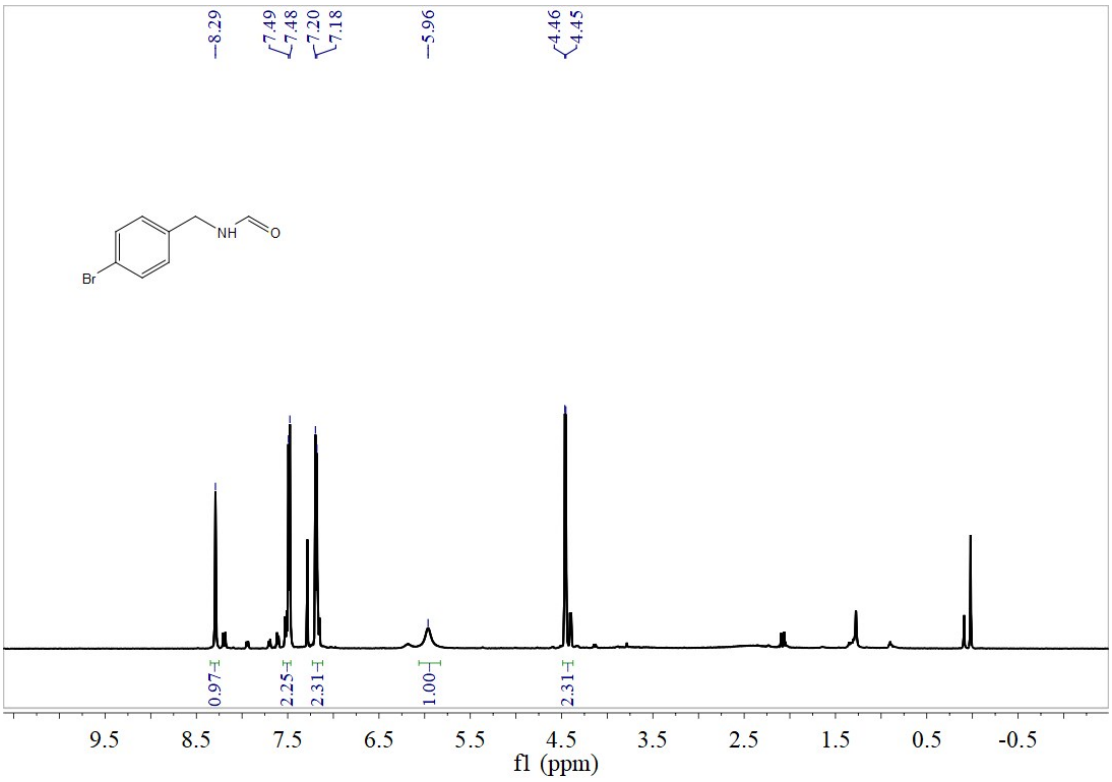
^{1}C NMR spectra of **9** (125 MHz, $CDCl_3$)



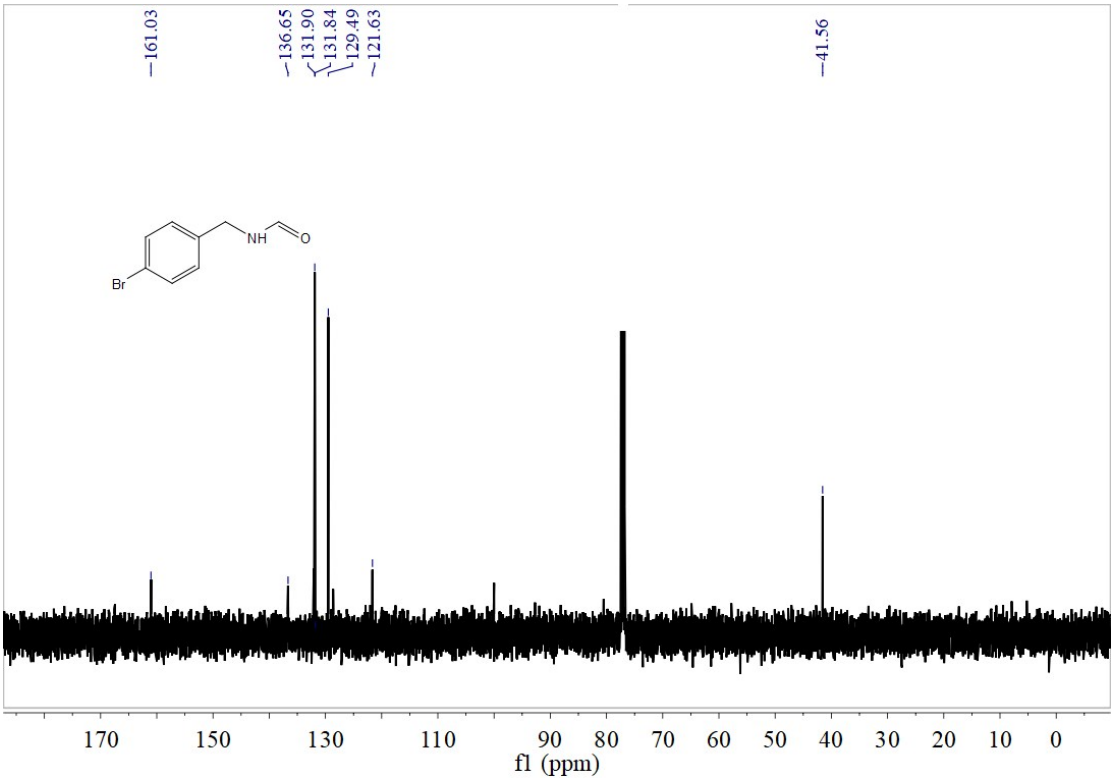
^{1}H NMR spectra of **10** (500 MHz, $CDCl_3$)



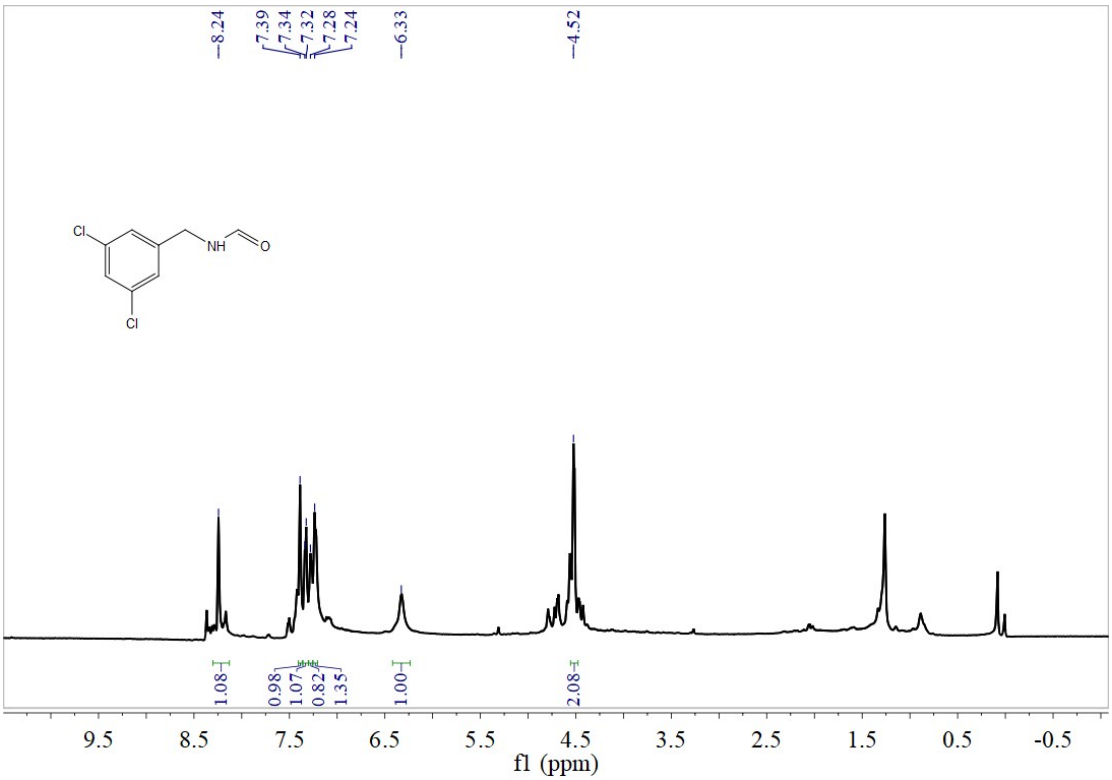
^{1}C NMR spectra of **10** (125 MHz, $CDCl_3$)



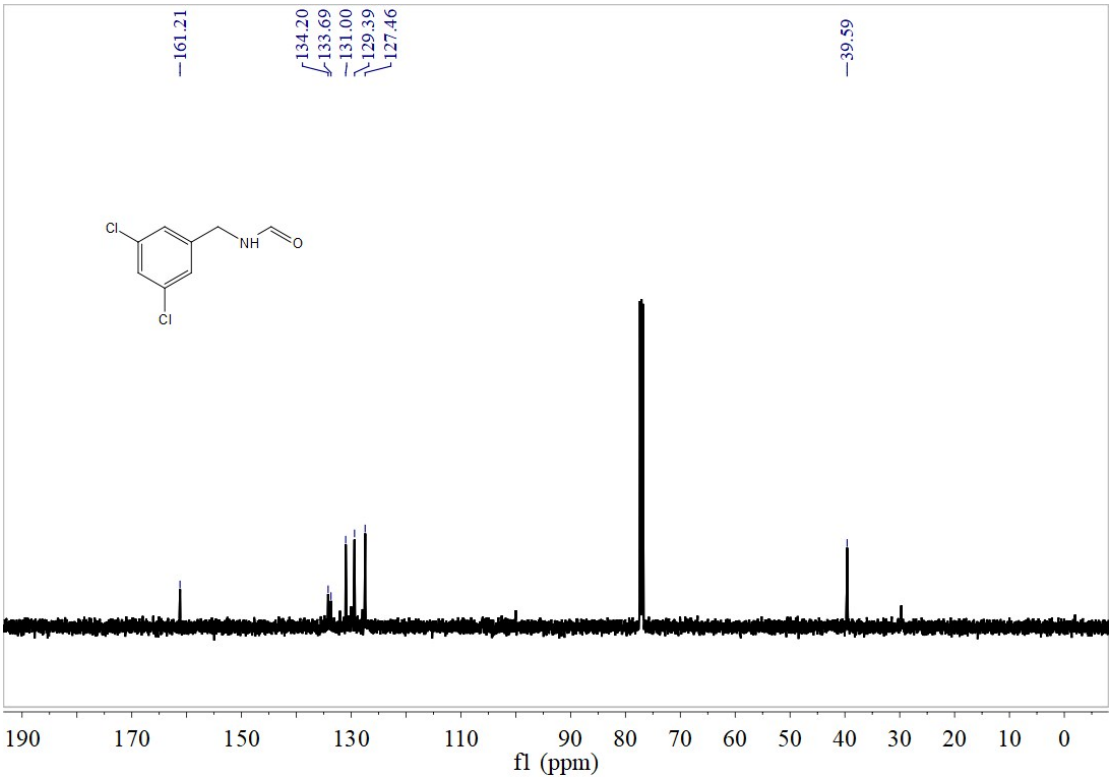
^{1}H NMR spectra of **11** (500 MHz, $CDCl_3$)



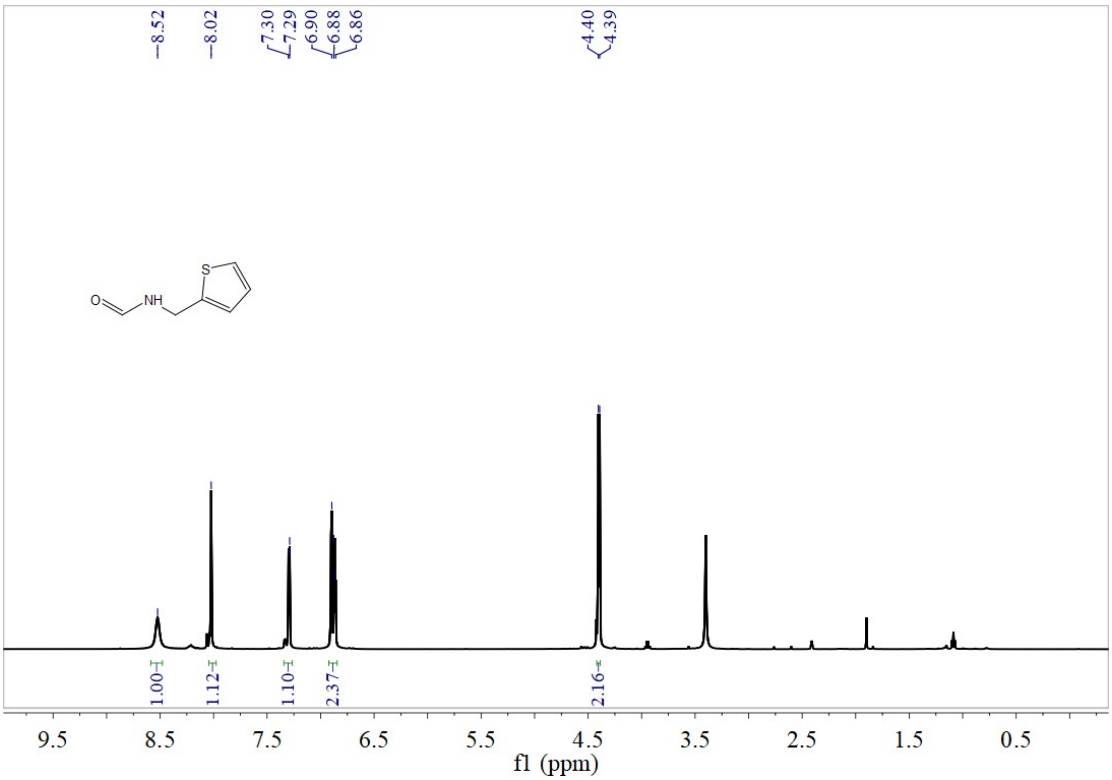
^{1}C NMR spectra of **11** (125 MHz, $CDCl_3$)



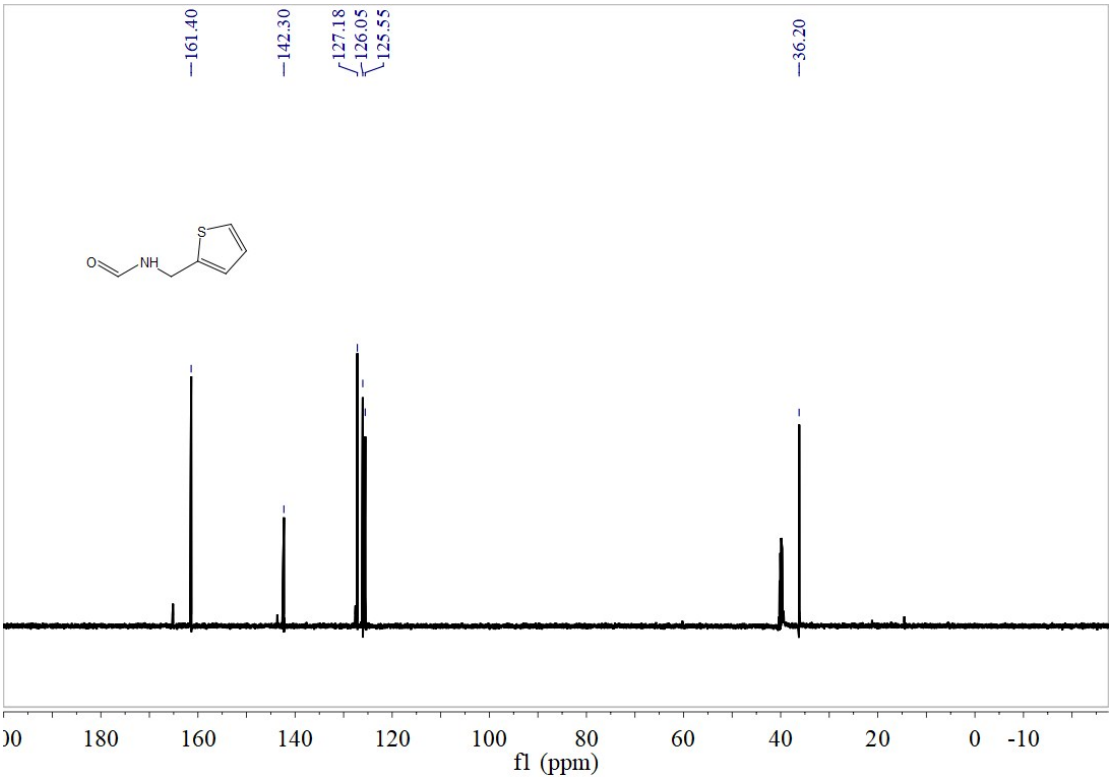
^{1}H NMR spectra of **12** (500 MHz, $CDCl_3$)



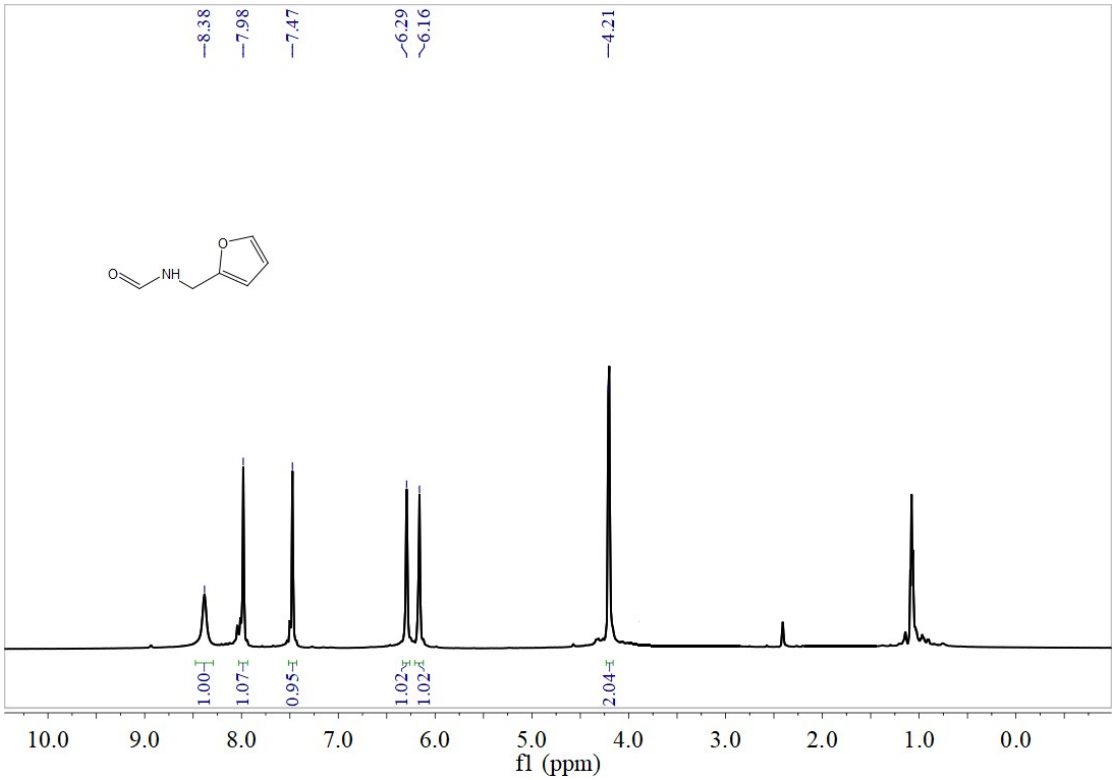
^{1}C NMR spectra of **12** (125 MHz, $CDCl_3$)



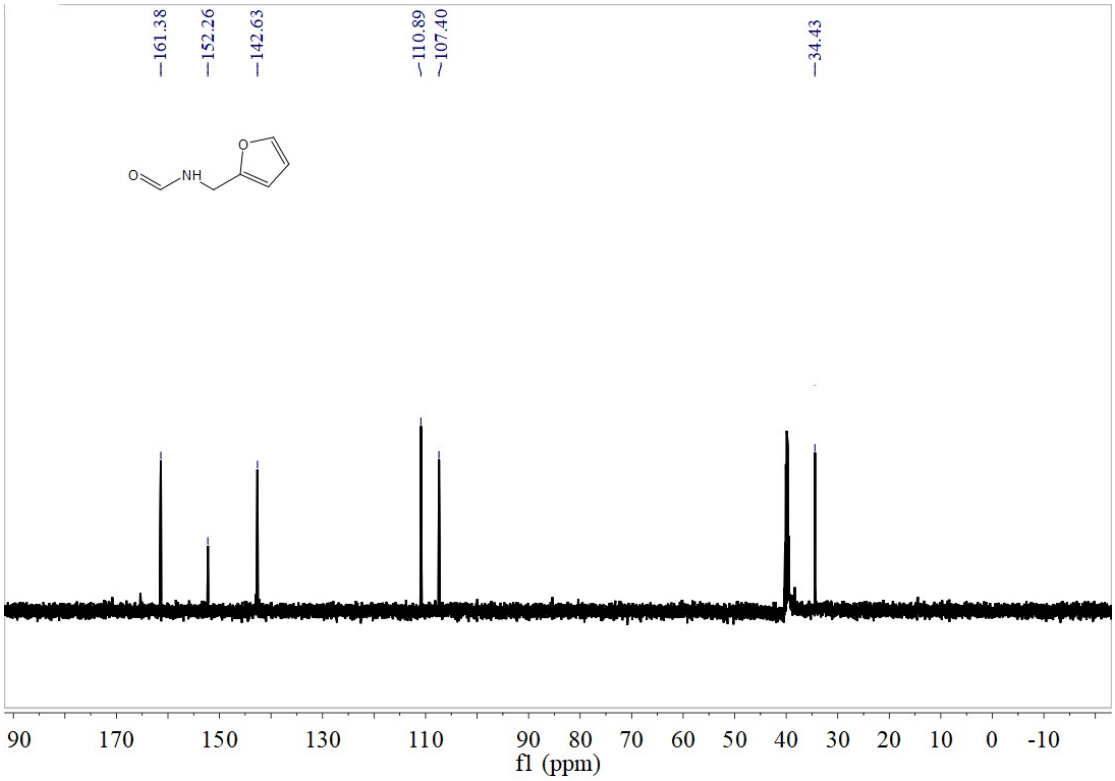
^{1}H NMR spectra of **13** (500 MHz, DMSO)



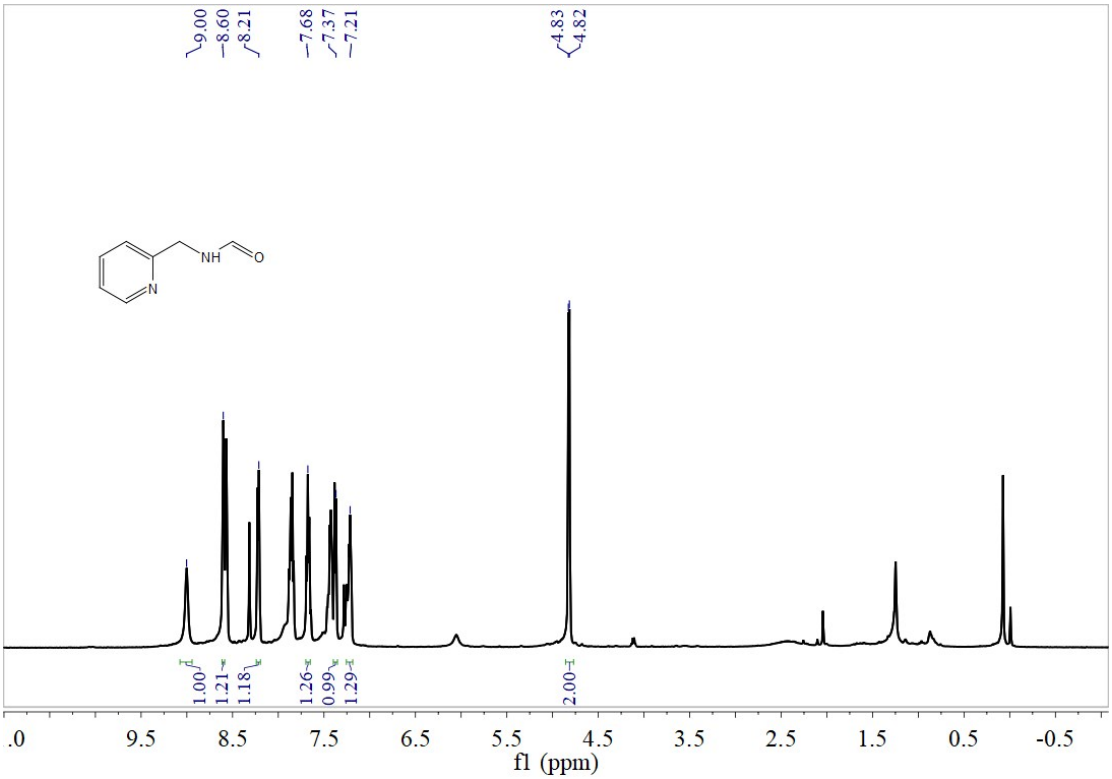
^{1}C NMR spectra of **13** (125 MHz, DMSO)



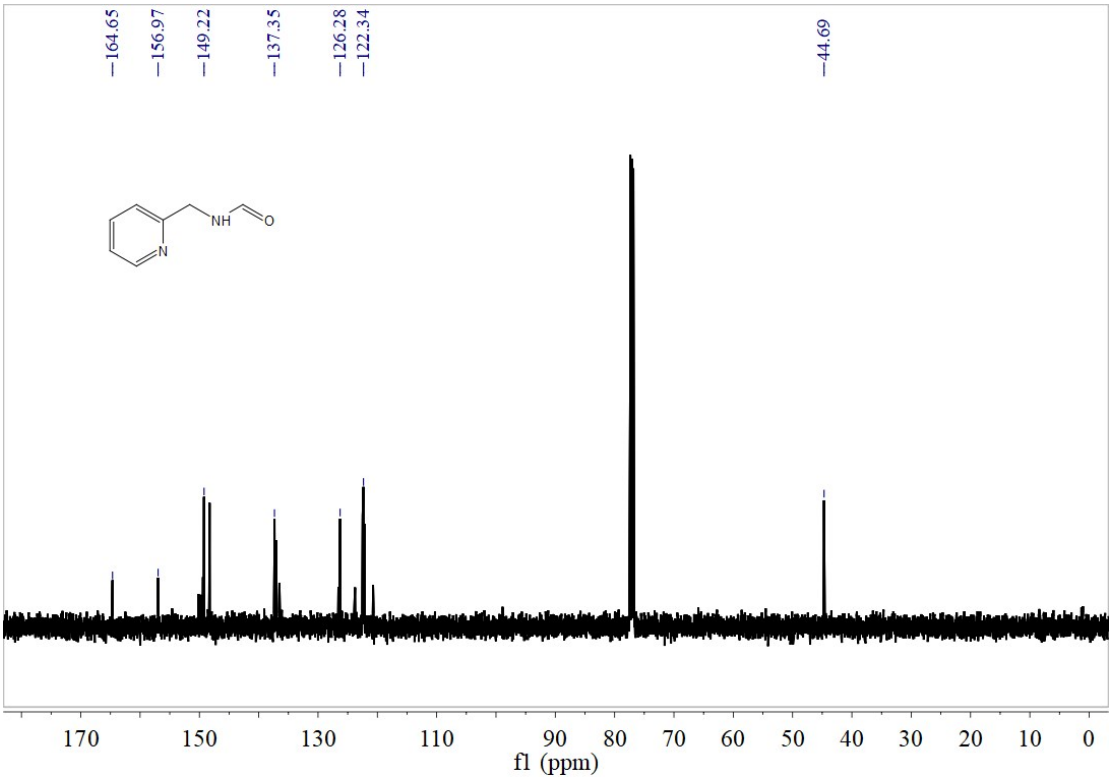
^{1}H NMR spectra of **14** (500 MHz, DMSO)



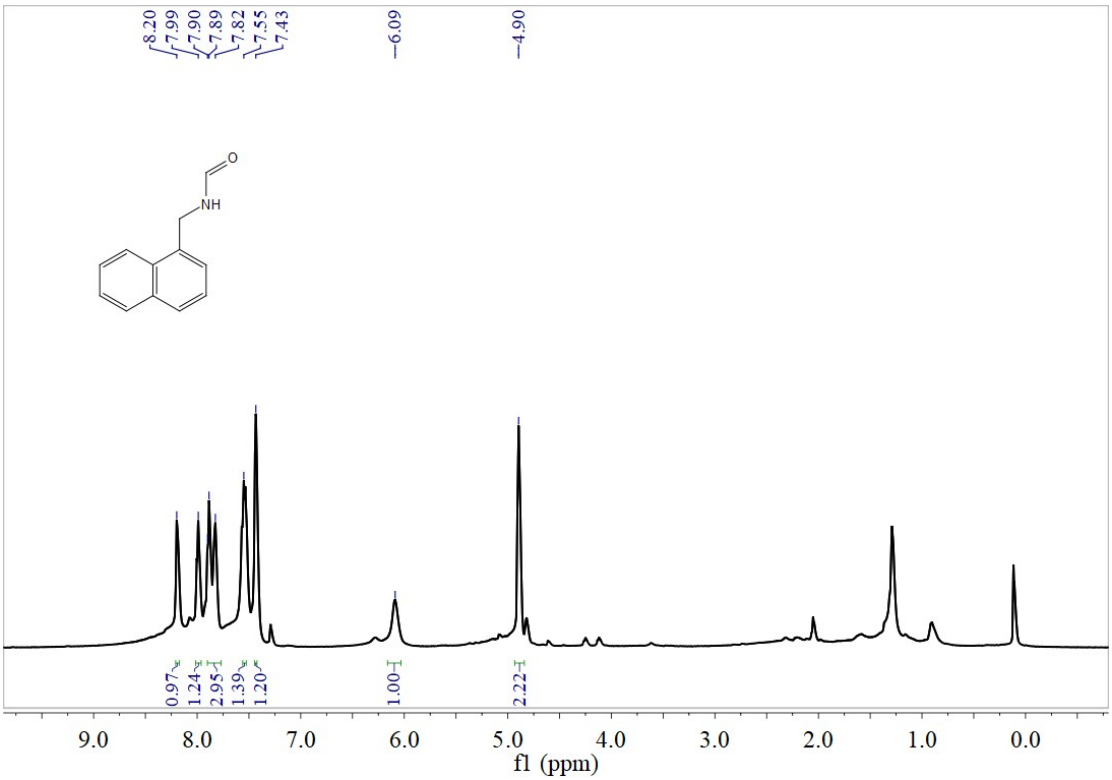
^{1}C NMR spectra of **14** (125 MHz, DMSO)



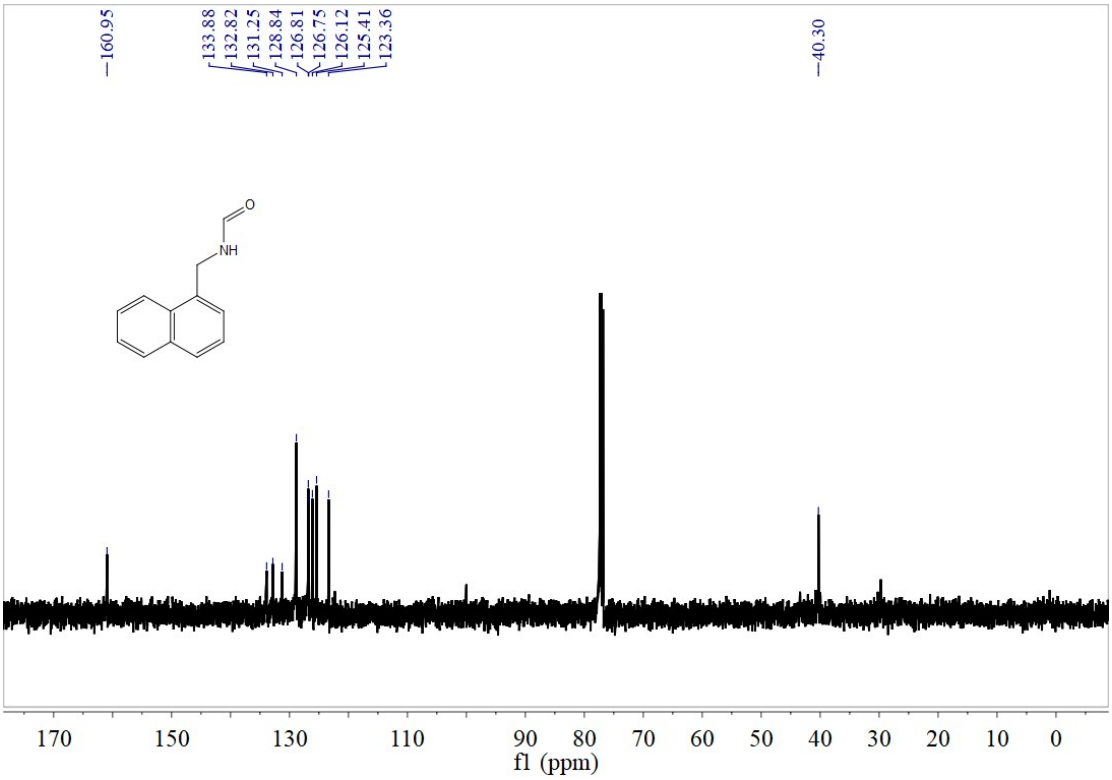
^{1}H NMR spectra of **15** (500 MHz, $CDCl_3$)



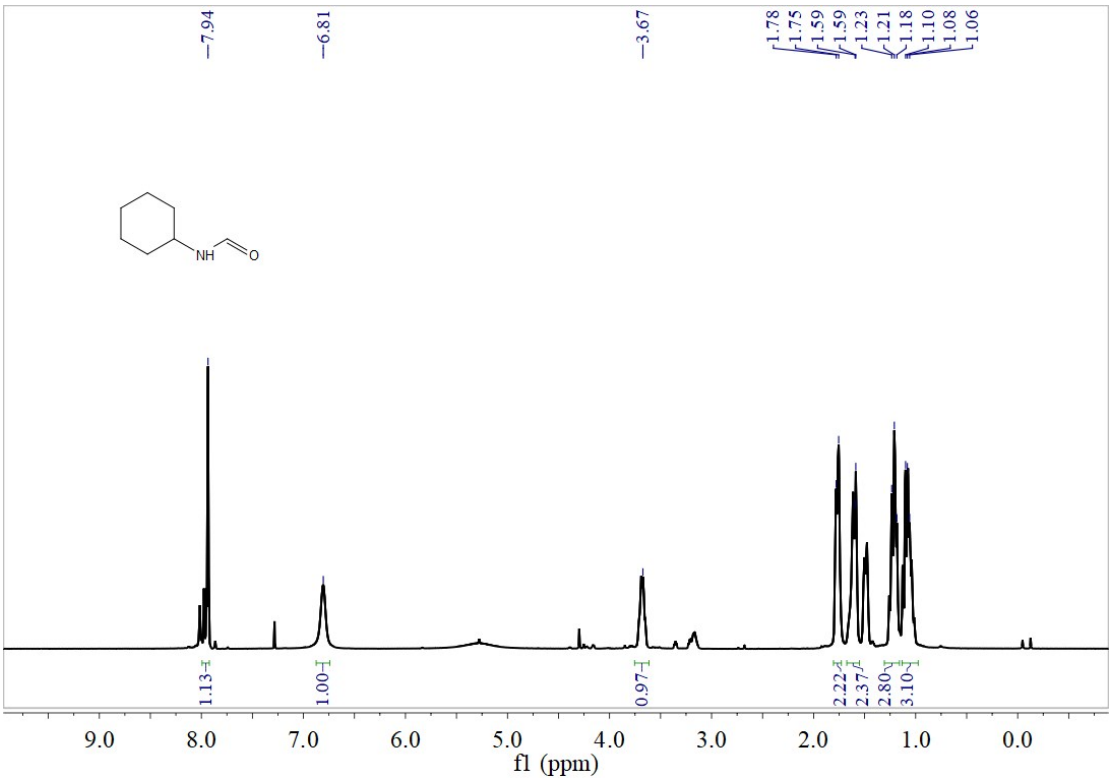
^{1}C NMR spectra of **15** (125 MHz, $CDCl_3$)



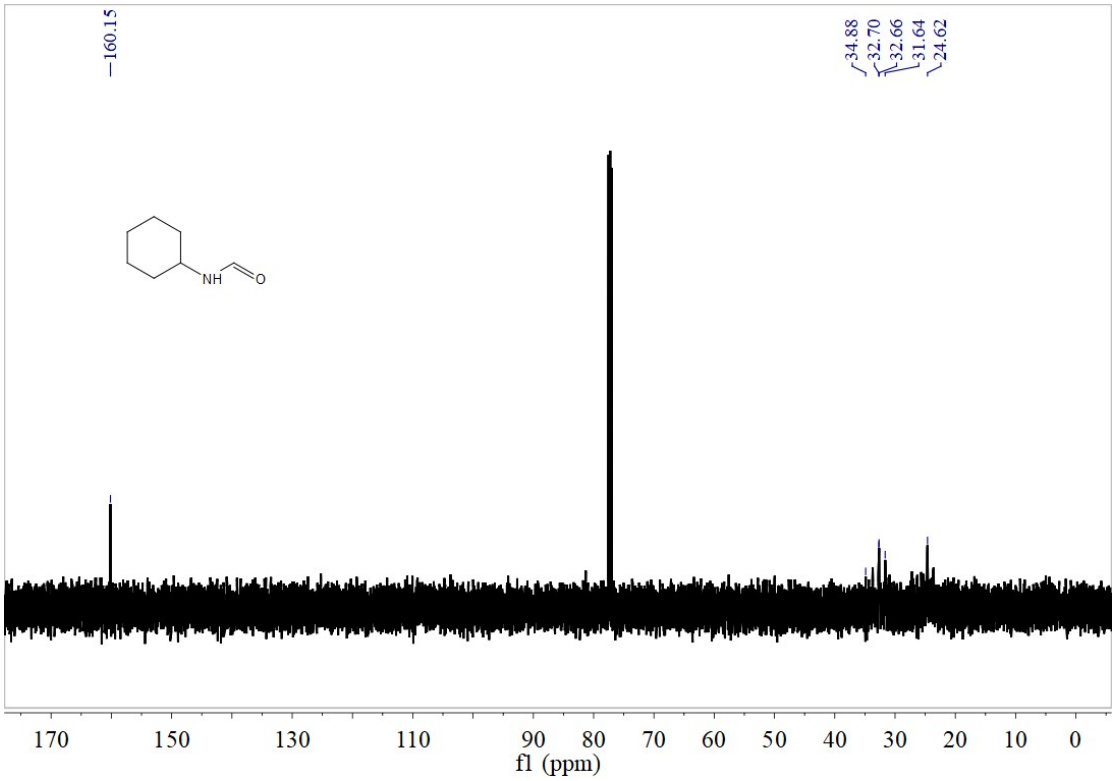
^{1}H NMR spectra of **16** (500 MHz, $CDCl_3$)



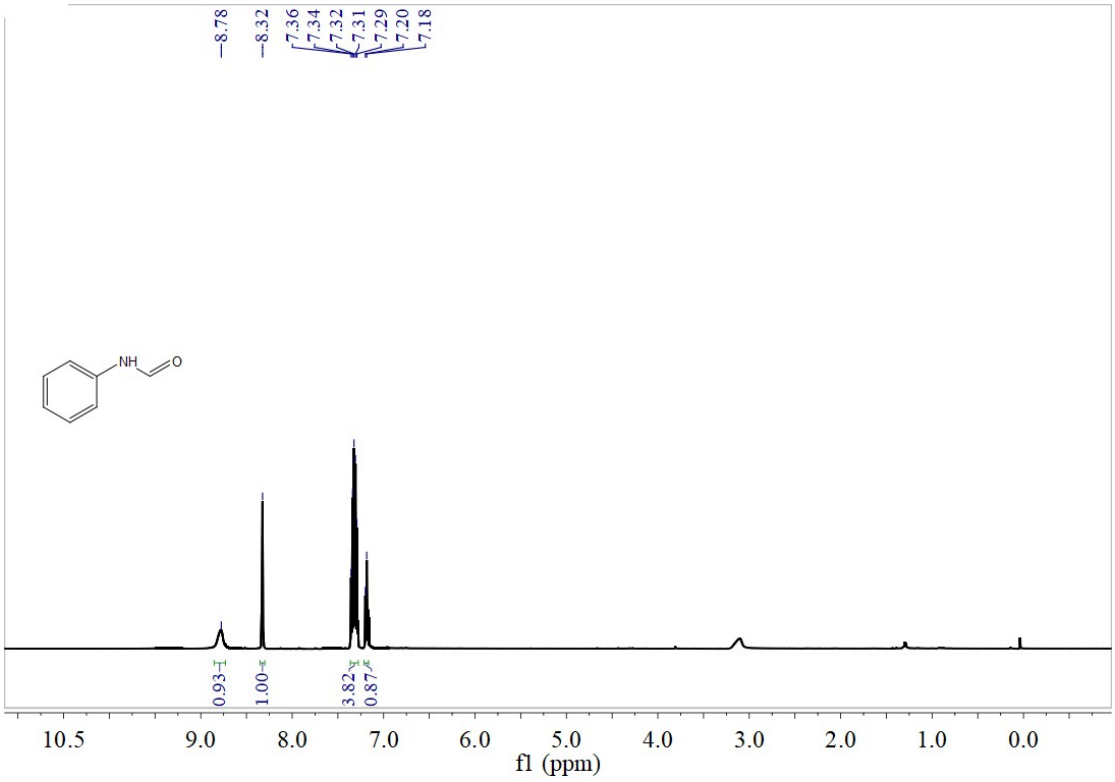
^{1}C NMR spectra of **16** (125 MHz, $CDCl_3$)



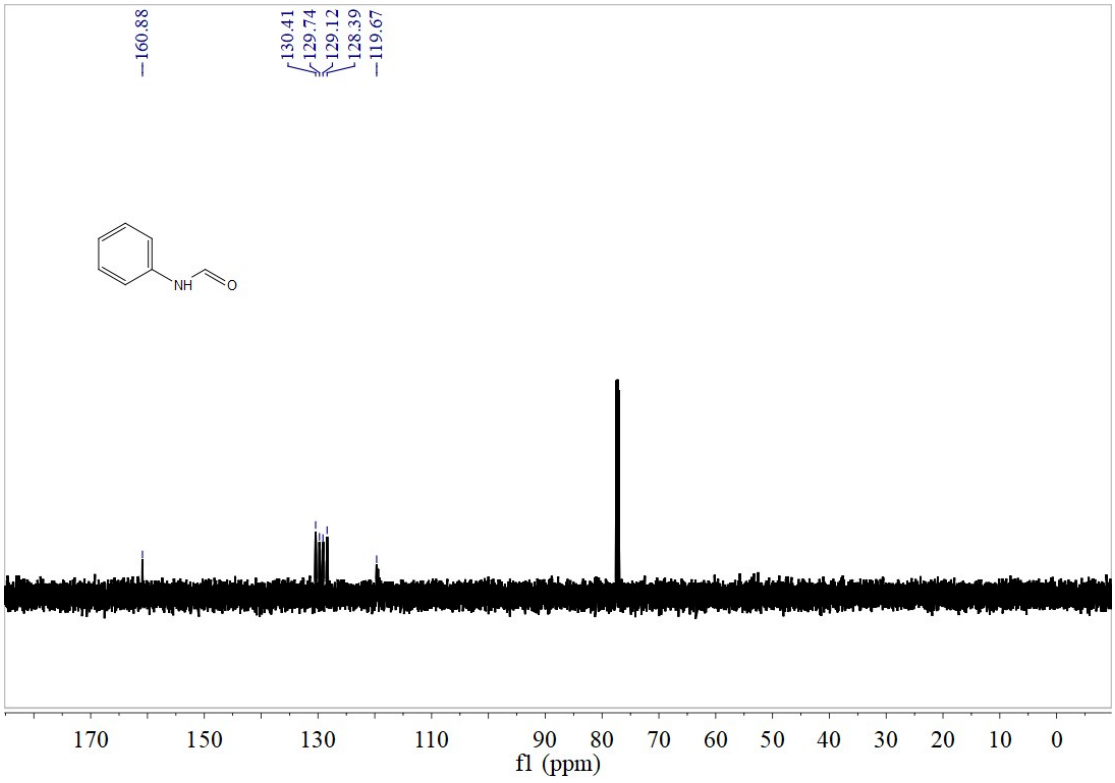
^{1}H NMR spectra of **17** (500 MHz, $CDCl_3$)



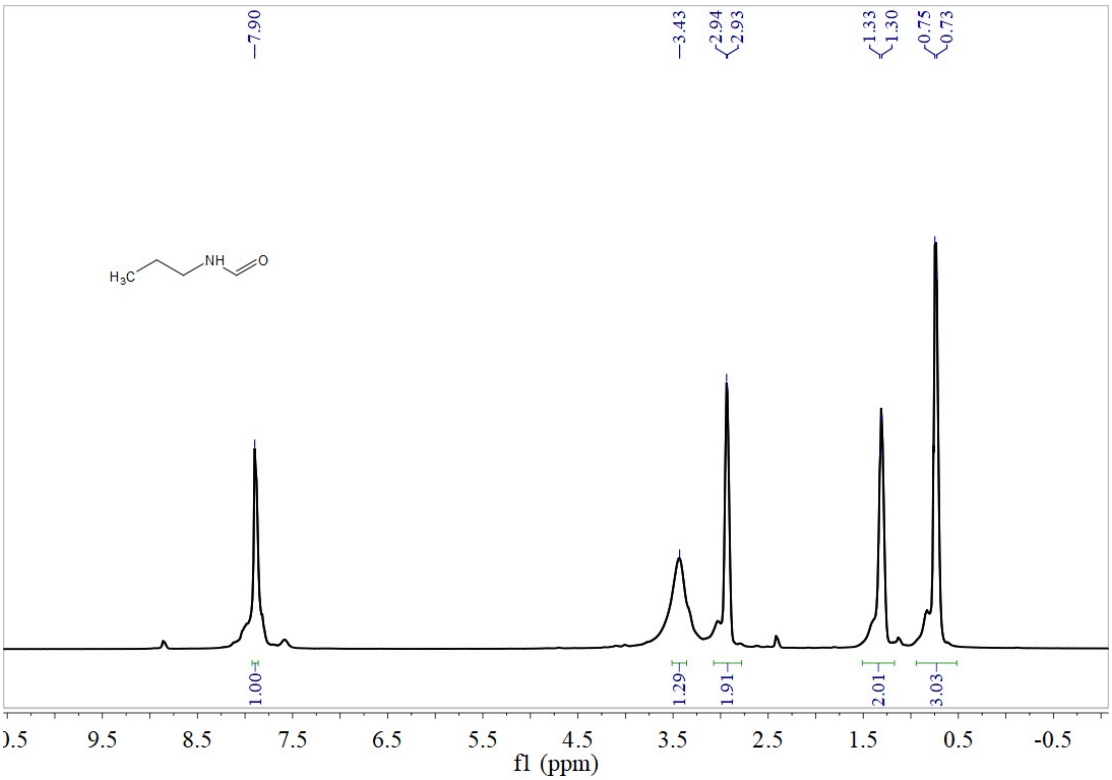
^{1}C NMR spectra of **17** (125 MHz, $CDCl_3$)



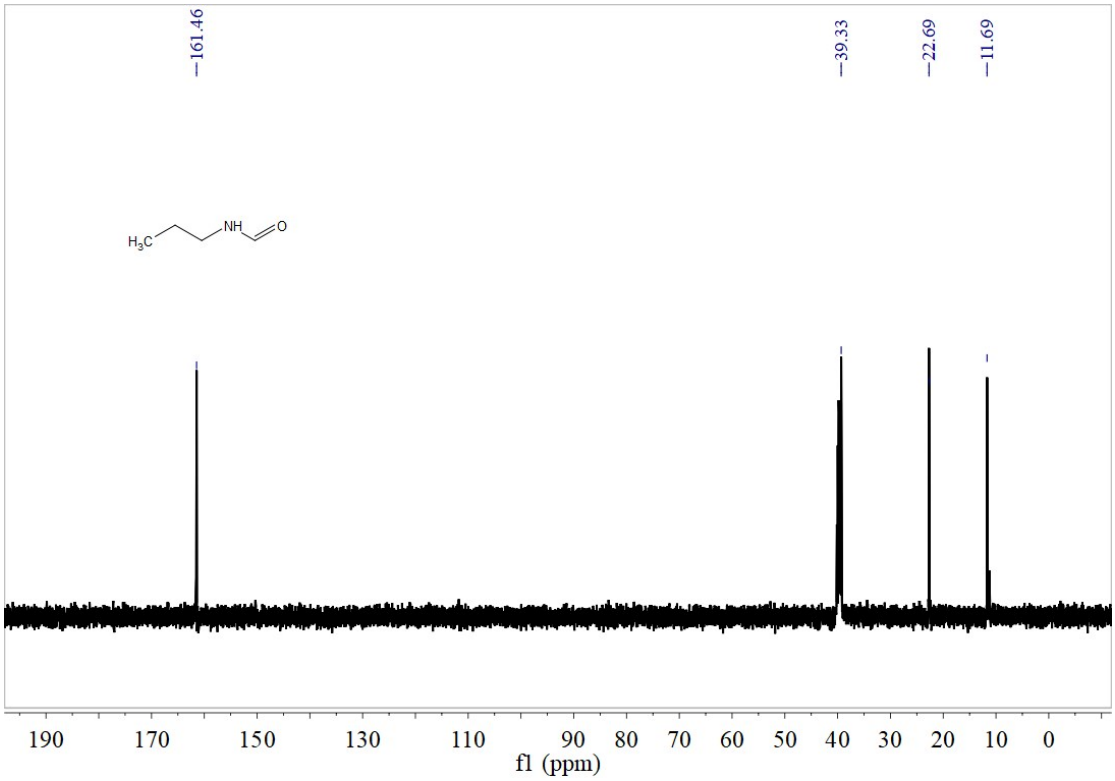
^{1}H NMR spectra of **18** (500 MHz, $CDCl_3$)



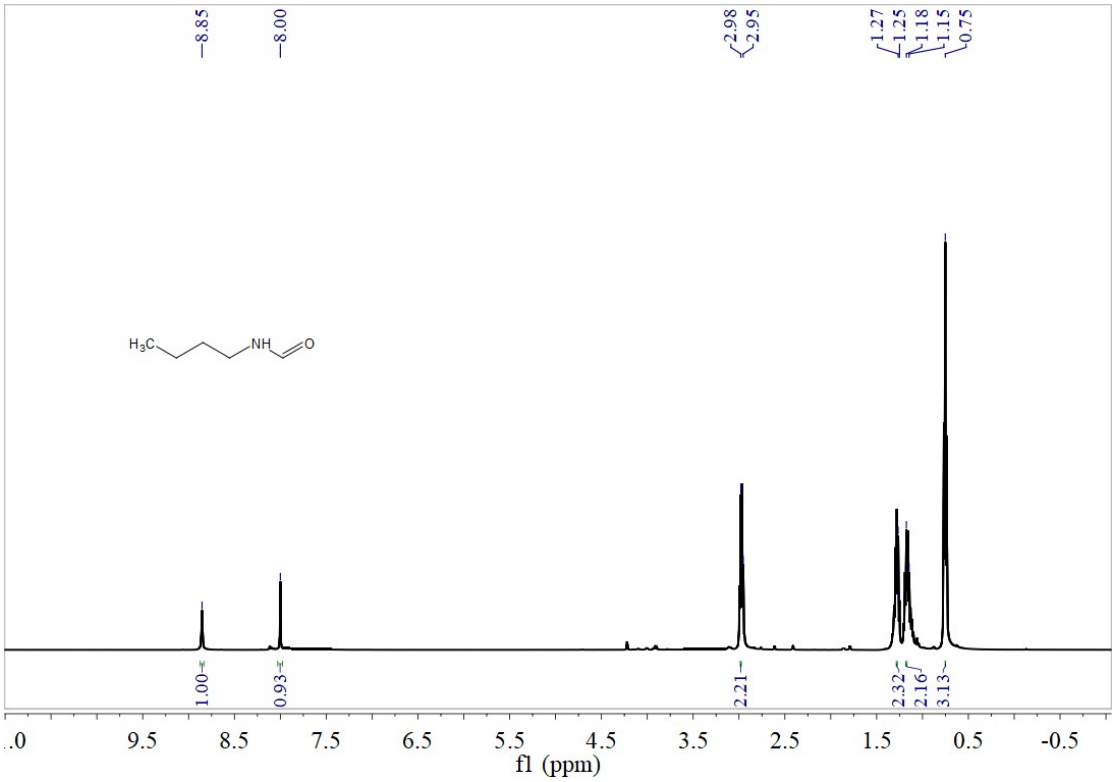
^{1}C NMR spectra of **18** (125 MHz, $CDCl_3$)



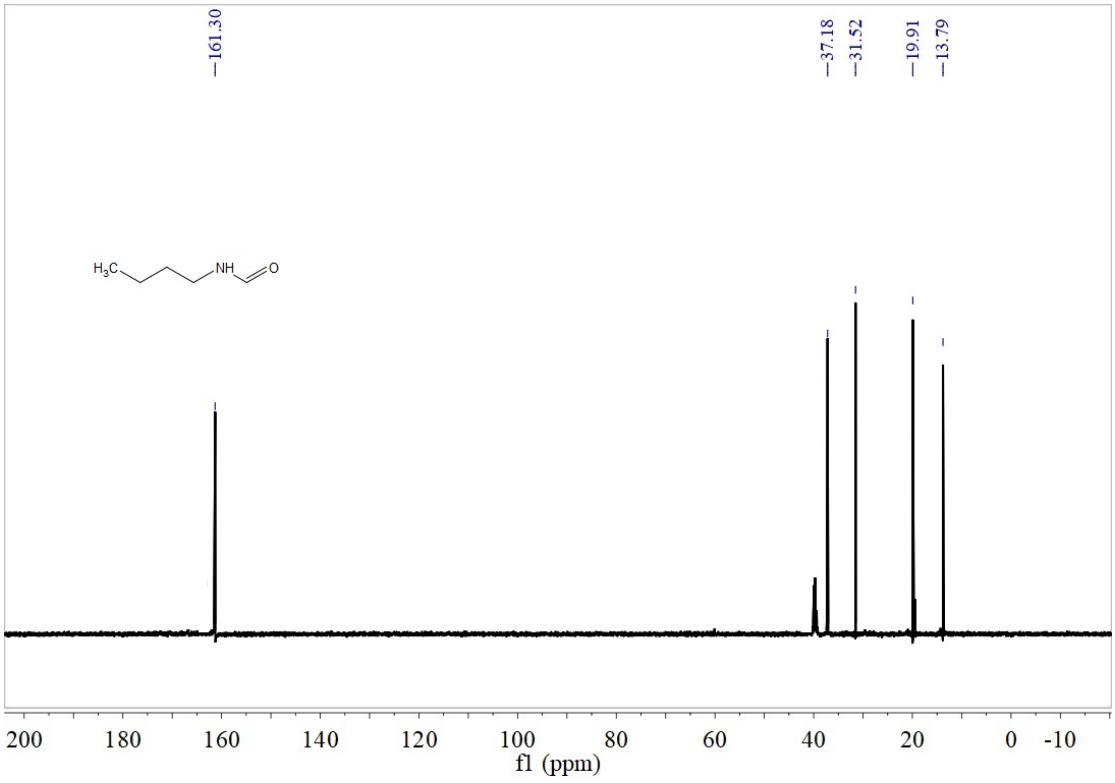
^{1}H NMR spectra of **19** (500 MHz, DMSO)



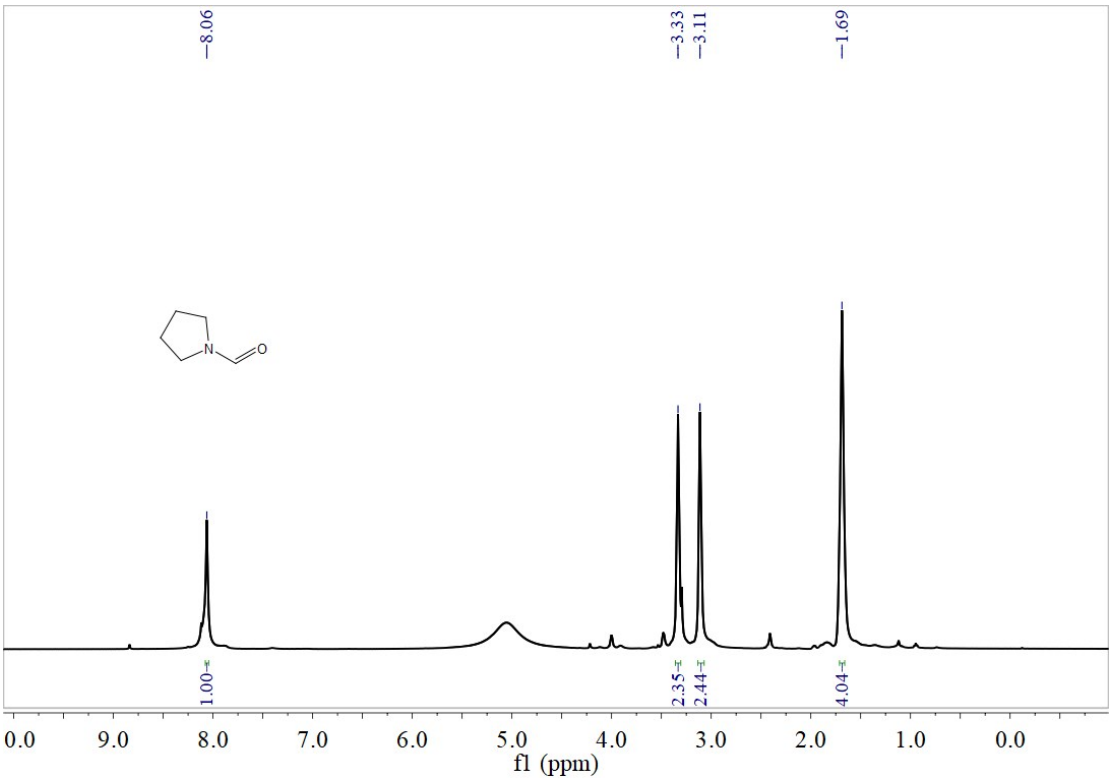
^{1}C NMR spectra of **19** (125 MHz, DMSO)



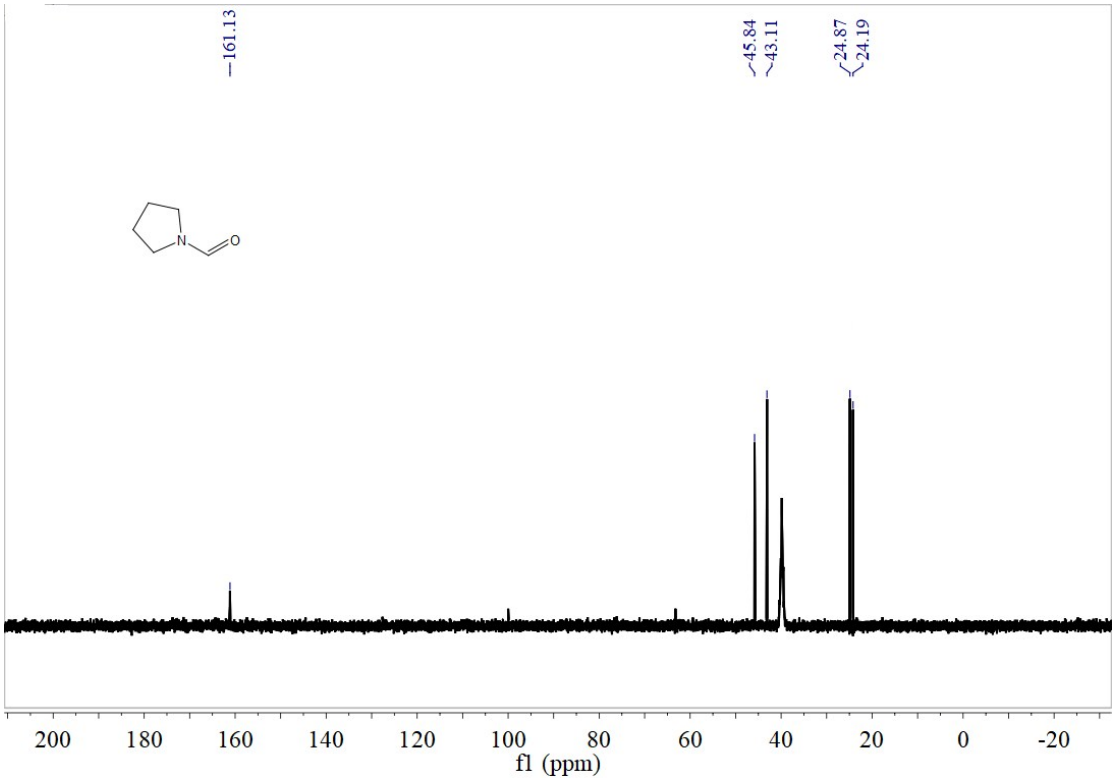
^{1}H NMR spectra of **20** (500 MHz, DMSO $_{3}$)



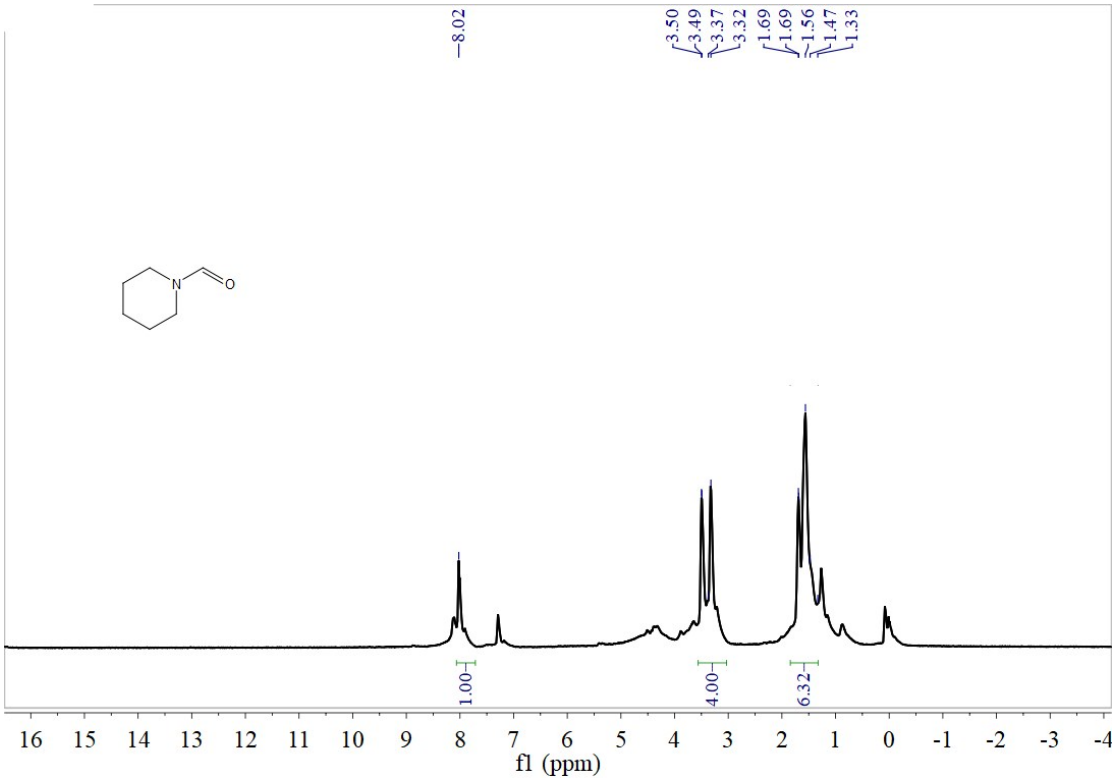
^{1}C NMR spectra of **20** (125 MHz, DMSO)



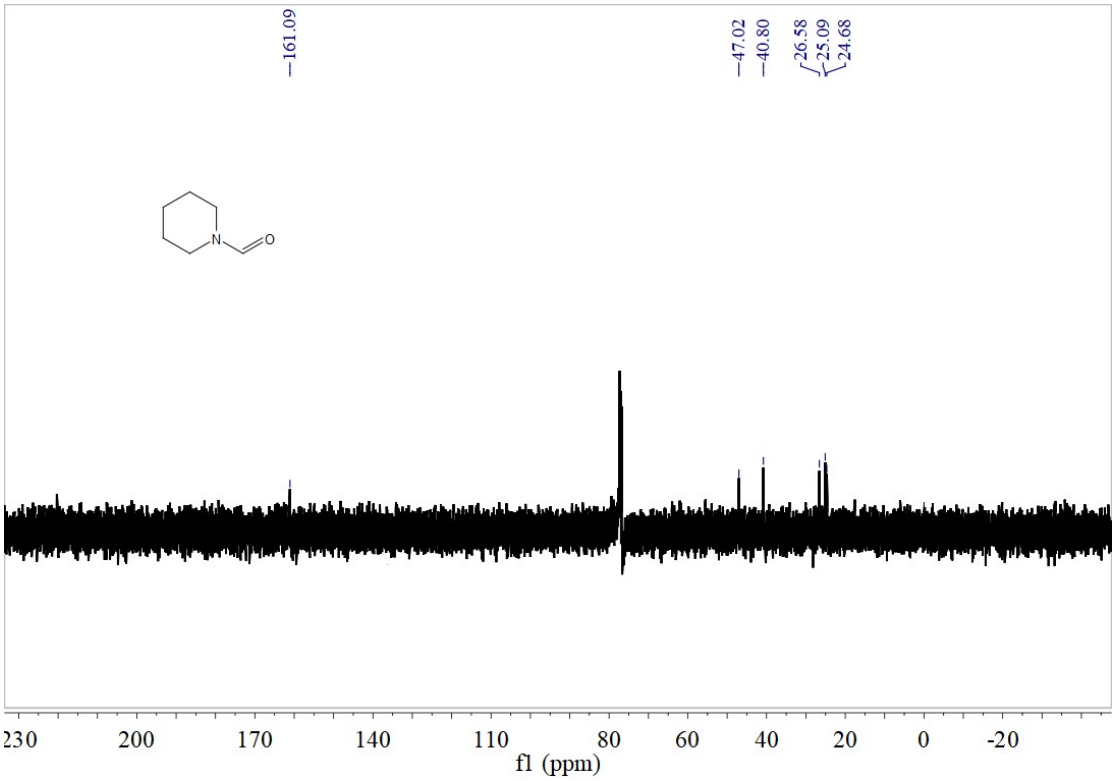
^{1}H NMR spectra of **21** (500 MHz, DMSO)



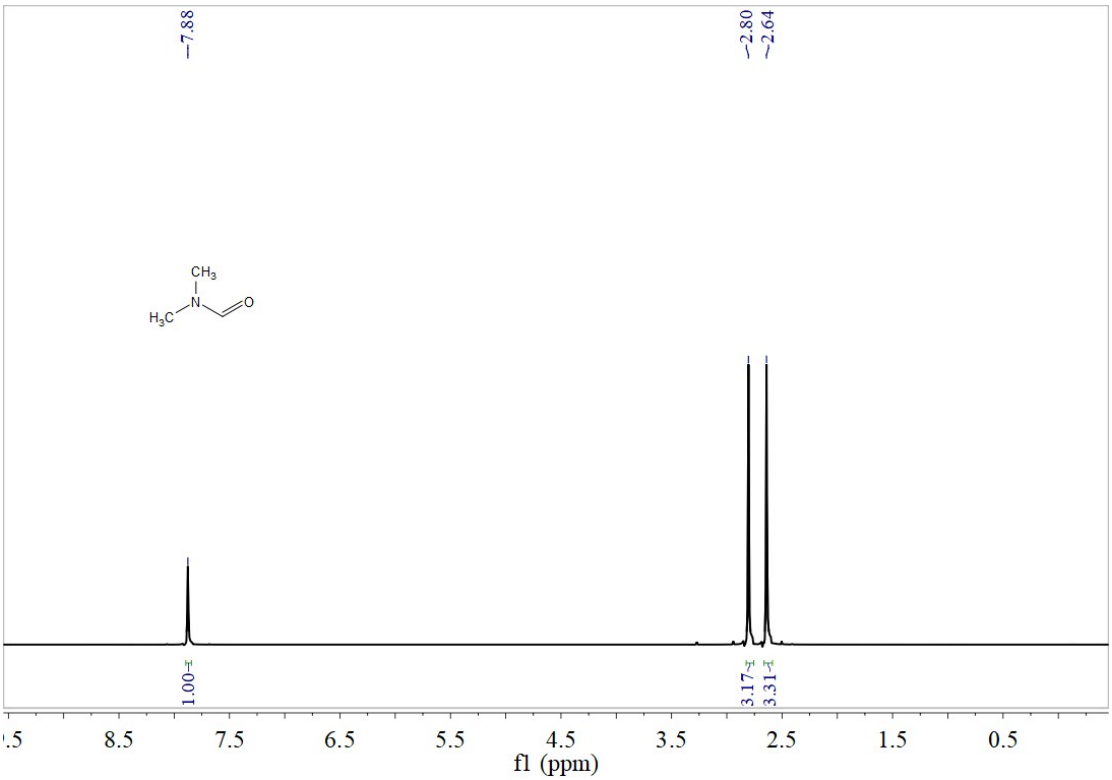
^{1}C NMR spectra of **21** (125 MHz, DMSO)



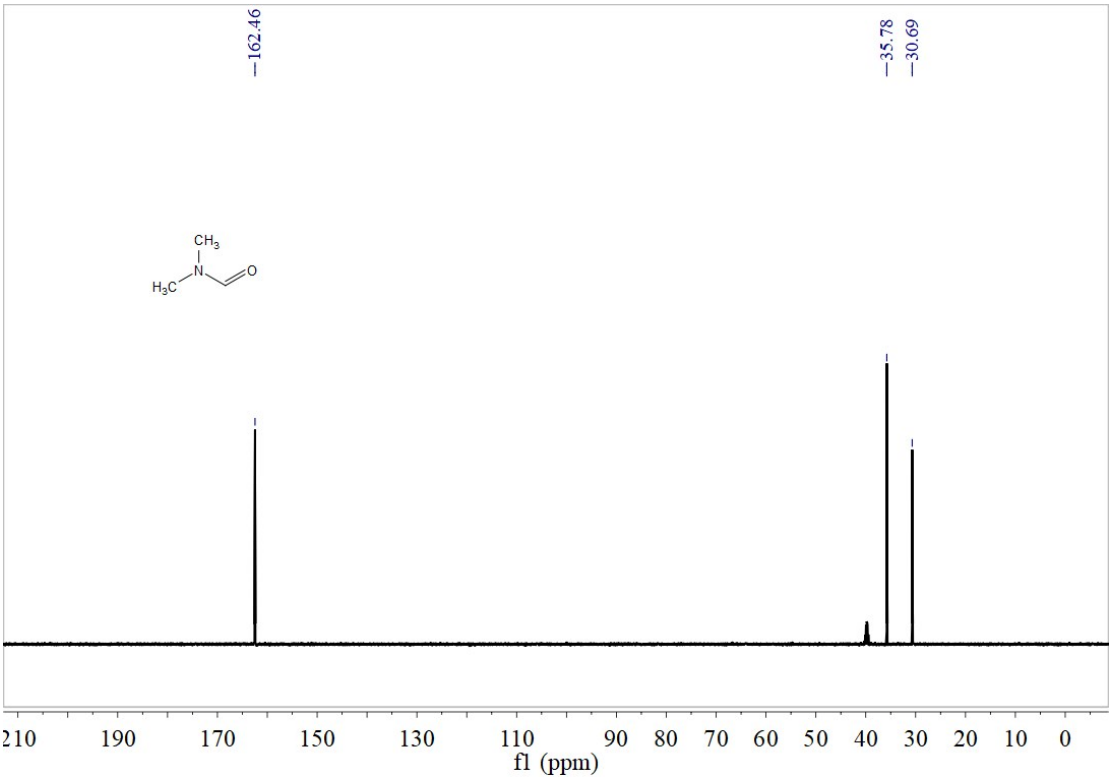
^{1}H NMR spectra of **22** (500 MHz, $CDCl_3$)



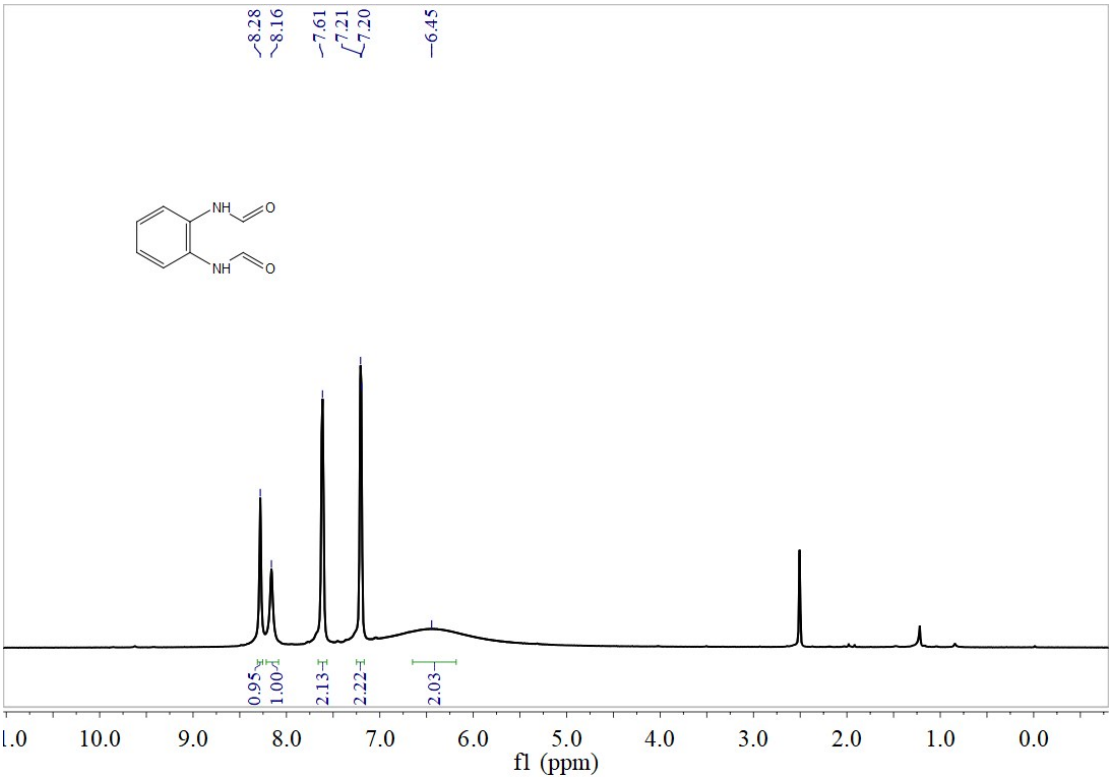
^{1}C NMR spectra of **22** (125 MHz, $CDCl_3$)



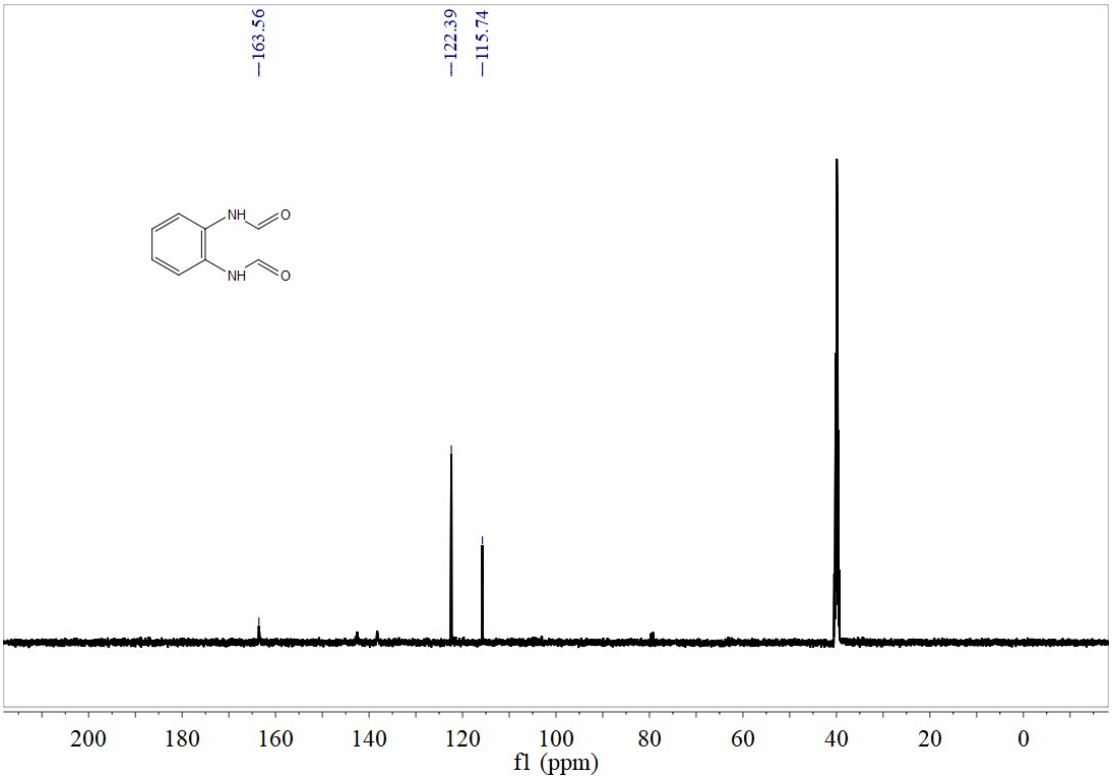
^{1}H NMR spectra of **23** (500 MHz, DMSO)



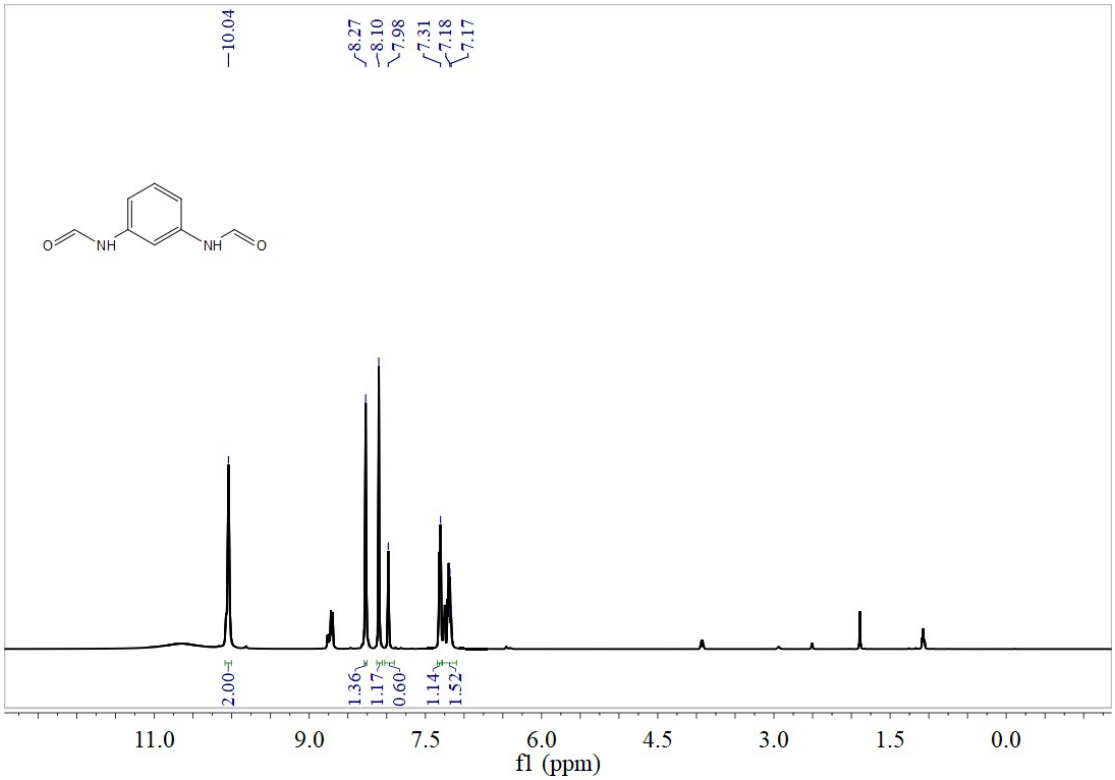
^{1}C NMR spectra of **23** (125 MHz, DMSO)



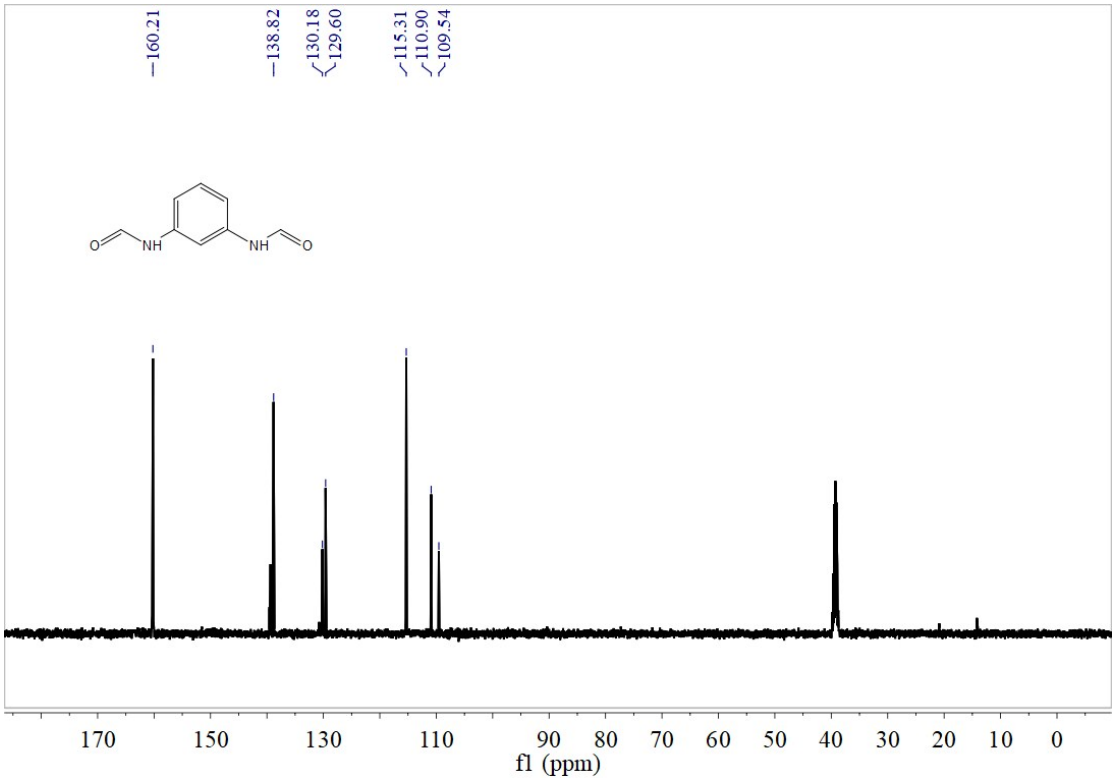
^{1}H NMR spectra of **24** (500 MHz, DMSO)



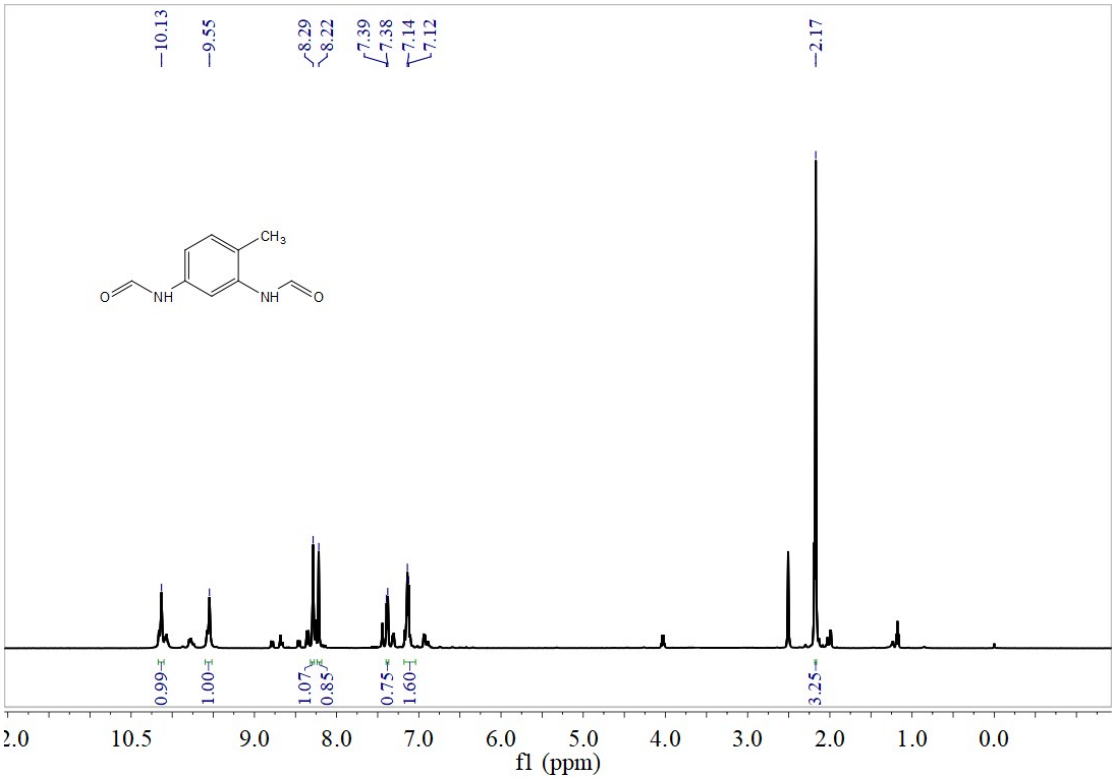
^{1}C NMR spectra of **24** (125 MHz, DMSO)



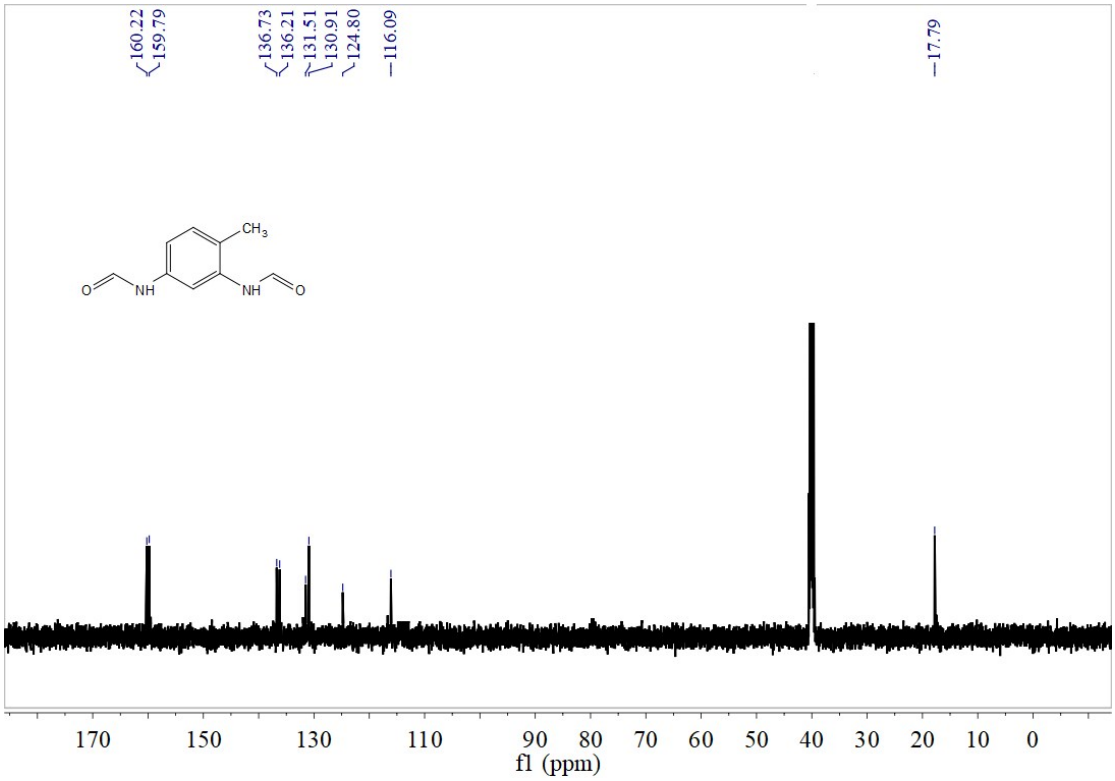
^{1}H NMR spectra of **25** (500 MHz, DMSO)



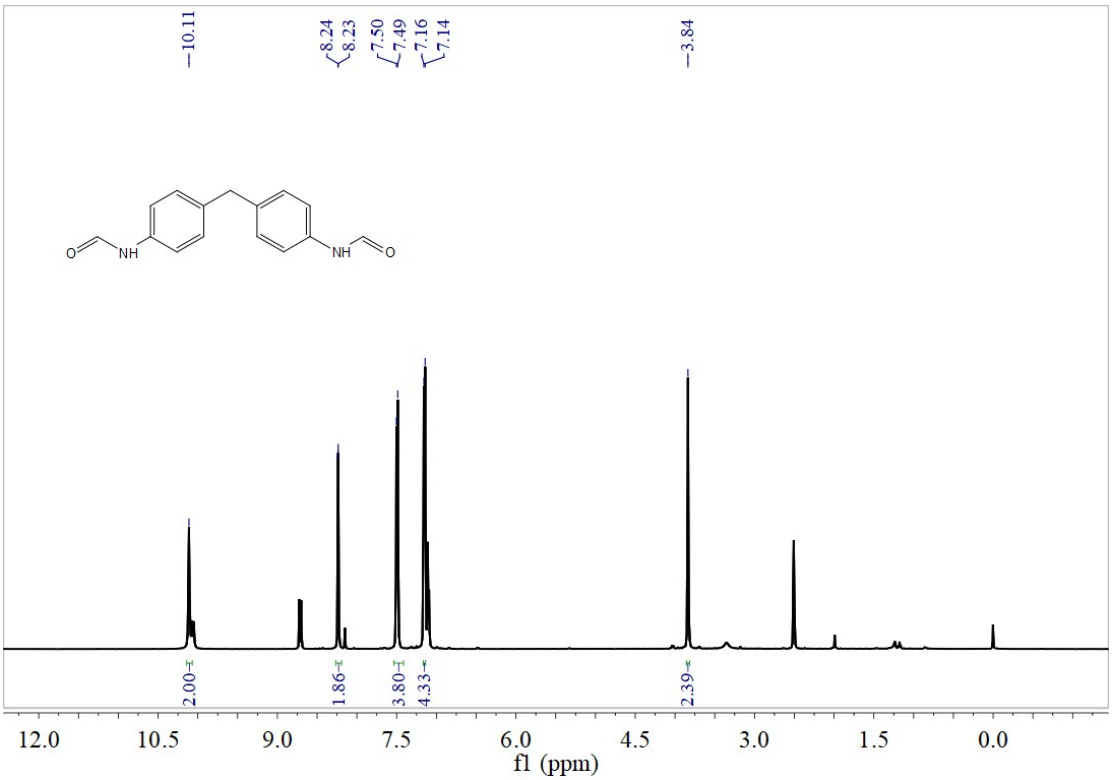
^{1}C NMR spectra of **25** (125 MHz, DMSO)



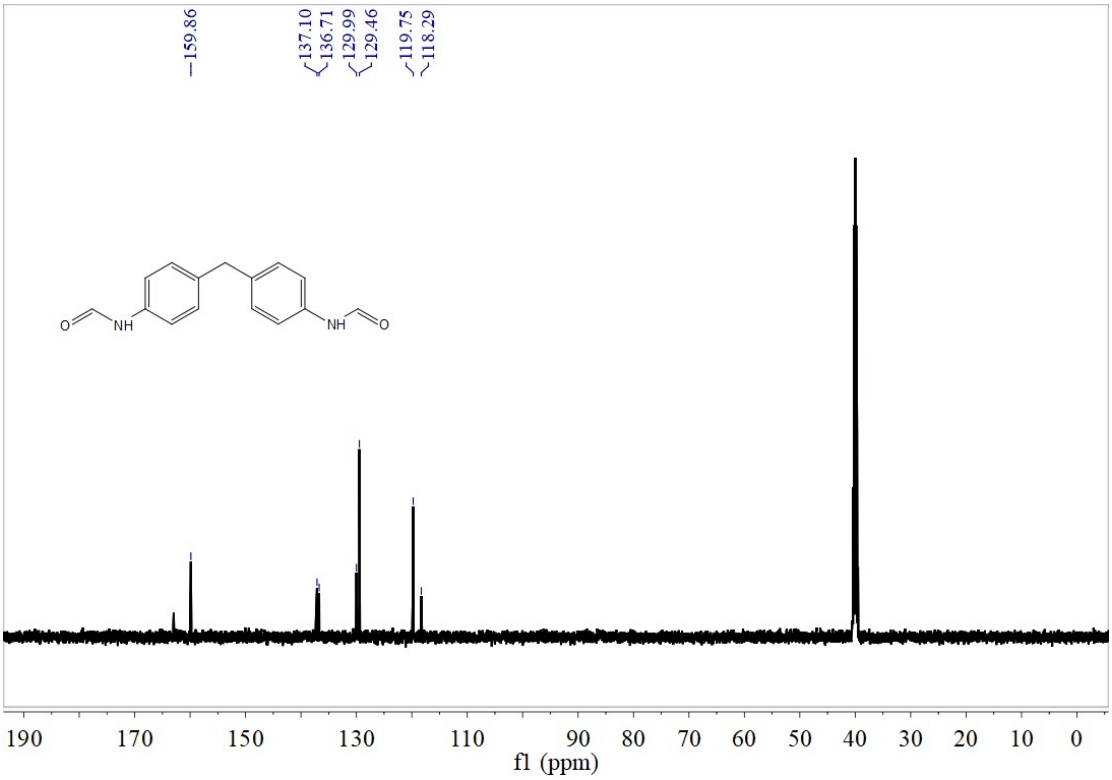
^{1}H NMR spectra of **26** (500 MHz, DMSO)



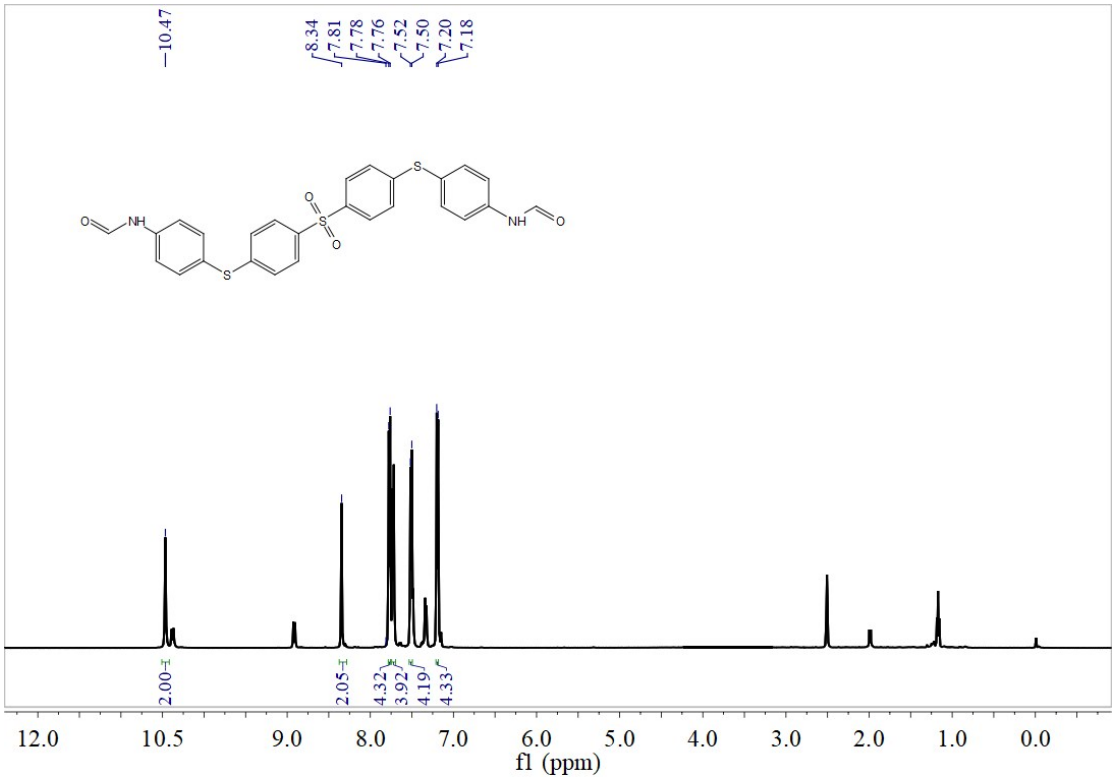
^{1}C NMR spectra of **26** (125 MHz, DMSO)



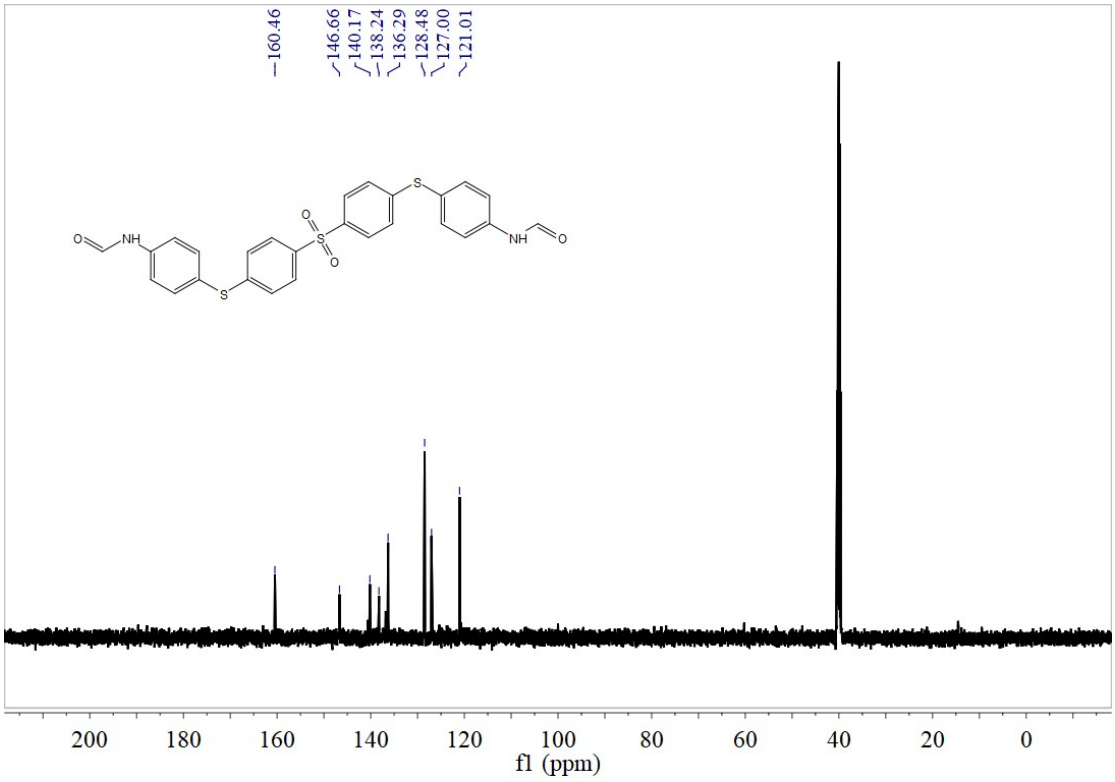
^{1}H NMR spectra of **27** (500 MHz, DMSO)



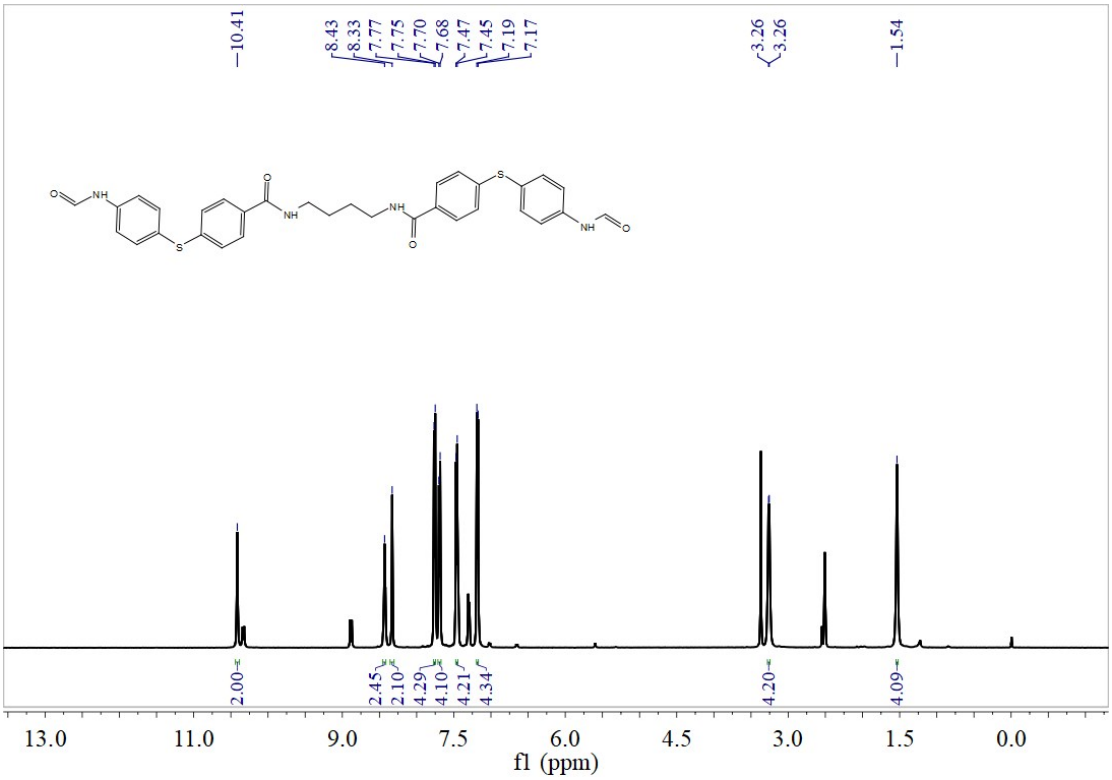
^{1}C NMR spectra of **27** (125 MHz, DMSO)



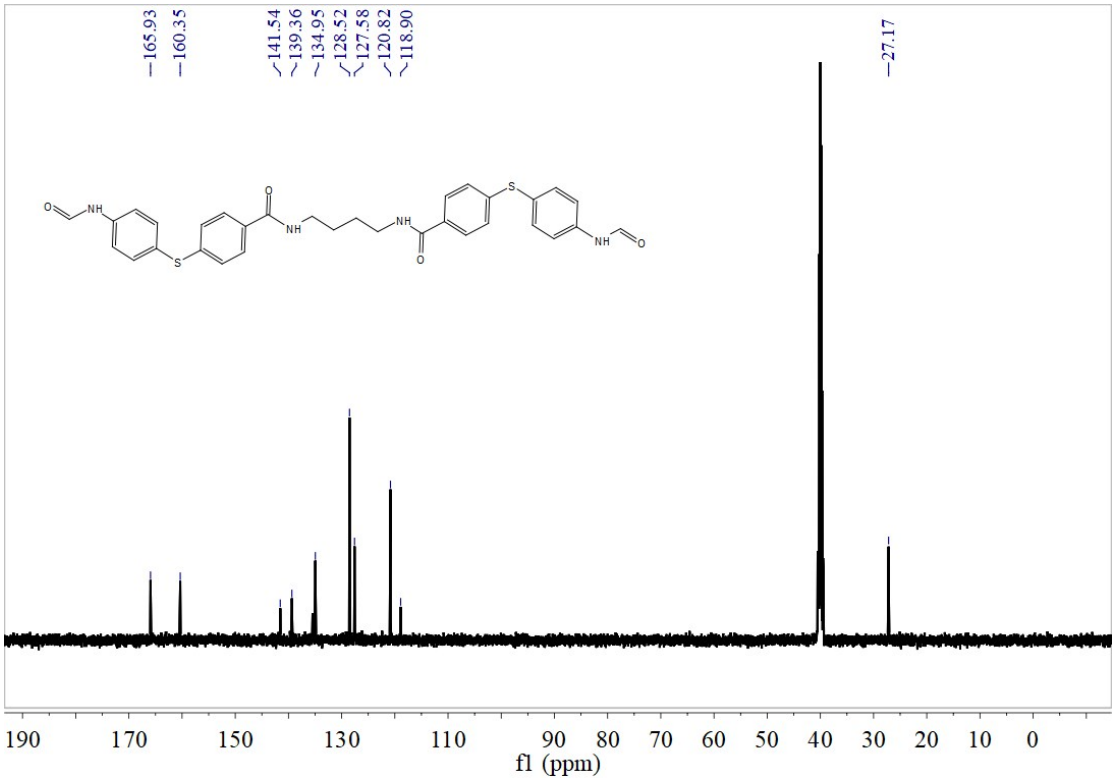
^{1}H NMR spectra of **28** (500 MHz, DMSO)



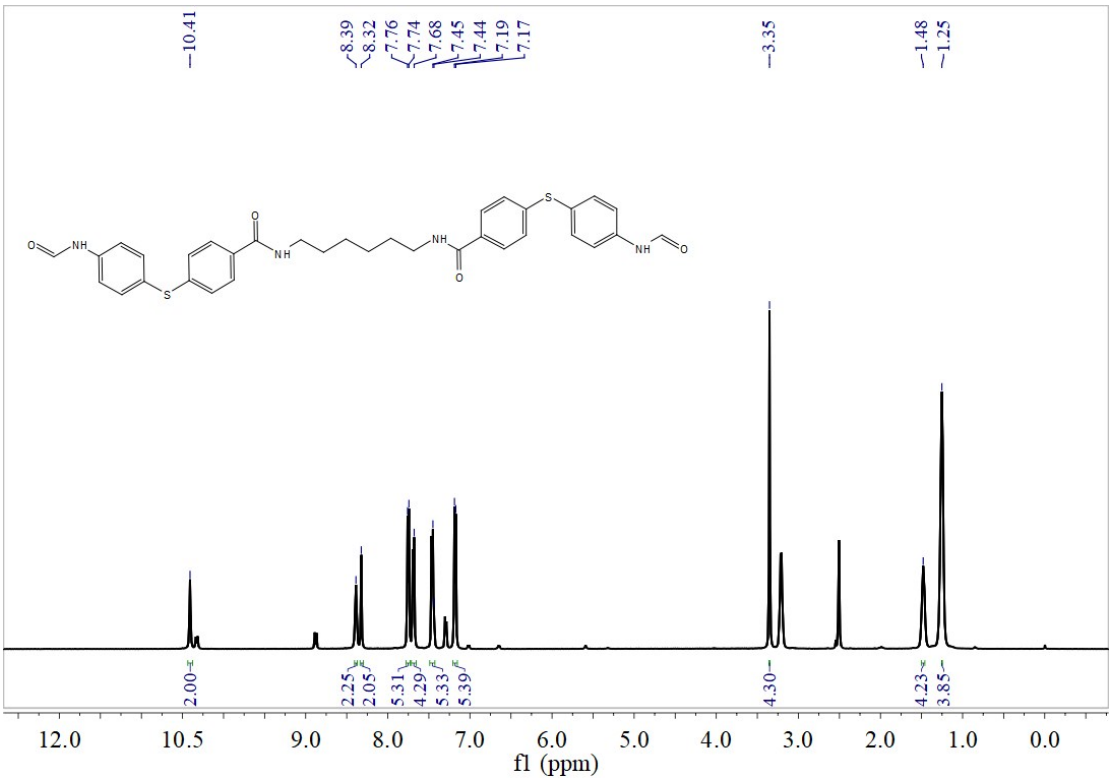
^{1}C NMR spectra of **28** (125 MHz, DMSO)



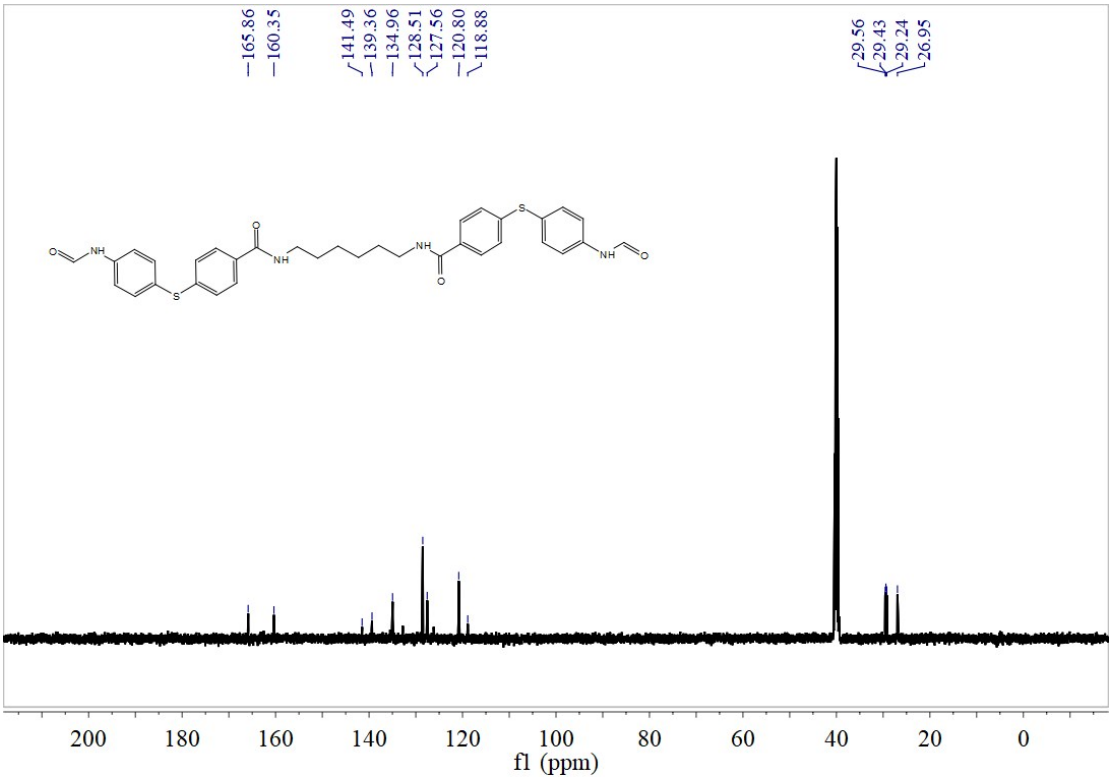
^{1}H NMR spectra of **29** (500 MHz, DMSO)



^{1}C NMR spectra of **29** (125 MHz, DMSO)



^{1}H NMR spectra of **30** (500 MHz, DMSO)



^{1}C NMR spectra of **30** (125 MHz, DMSO)