Cu-Catalyzed Transamidation of Unactivated Aliphatic Amides

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1.0 General Information

1.1 General Analytical Information. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 400 MHz instrument at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR). All ^{1}H NMR spectra were measured in parts per million (ppm) downfield, or were measured relative to the residual proton signals of d^{l}-chloroform ($CDCl_3$, 7.26 ppm) and dimethyl sulfoxide-d_6 (DMSO-d_6, 2.50 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual carbon signals of $CDCl_3$ (77.16 ppm) and DMSO-d_6 (39.52 ppm). Coupling constants (*J*) are reported in hertz (Hz). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet). Thin-layer chromatography (TLC) was performed on precoated Merck Silica gel 60 F254 plates and compounds were visualized with a UV light at 254 nm. Flash chromatography for purification of compounds were carried out using silica gel (100–200 mesh).

1.2 General Reagents Information. Unless otherwise noted, commercially available materials were obtained from Aldrich Chemical Co., Alfa Aesar and used without prior purification. Chlorotrimethylsilane (TMSCl, 98% purity) was purchased from Aldrich Chemical Co. and was stored in refrigerator for storage. $CuCl_2$ (99% purity) was purchased from Aldrich Chemical Co. Lab reagent (LR) grade solvents were used for extraction and column chromatography purchased from Loba-chem.

1.3 General Manipulation Considerations. Unless otherwise specified, all reagents were weighed and handled in air, and all reactions performed in a 20 mL sealed vial with an air atmosphere. The eluents used for column chromatography were presented as ratios of solvent volumes. $CuCl_2$ (99% purity) was used for scope study unless otherwise noted. Yields reported in the publication are isolated yields unless otherwise noted. All new starting materials and products were characterized by ^{1}H and ^{13}C NMR spectroscopies.

2.0 Optimization of Reaction Conditions of transamidation

2.1 General procedure for optimizations of reaction conditions. An oven-dried 20 mL Teflon screw-capped vial equipped with a stir bar was sequentially charged with amide **1I**, aniline **2A** and catalyst. TMSCl were transferred into the tube via a syringe. The resulting mixture was stirred in a preheated heat block. After full fill the reaction condition of experiment, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution and saturated brine, dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. The residue was purified by flash chromatography on silica gel using hexane and ethyl acetate as eluent to give the transamidated product **3I**.

Table S1:- Catalyst Study*

Entry	Catalyst (20 mol%)	Yield[#]
1	**$CuCl_2$**	**72**
2	$CuBr_2$	61
3	CuCl	5
4	CuBr	4
5	CuI	3
6	$Cu(OTf)_2$	41
7	$Cu(OAc)_2$	52
8	$PdCl_2$	traces
9	$NiCl_2$	20

*Reaction conditions: 1I (1.1 mmol), 2A (1.61 mmol) and TMSCl (1.61 mmol) were reacted in Toluene (1.0 mL) at 120 °C for 10 h. [#]Isolation by using column chromatography.

Table S2:- Lewis acid study*

Entry	Lewis acid (Equiv)	Yield (%)[#]
1	**TMSCl**	**72**
2	$FeCl_3$	13
3	$AlCl_3$	9

4	TiCl4	traces

*Reaction conditions: 1I (1.1 mmol), 2A (1.61 mmol) and $CuCl_2$ (0.22 mmol) were reacted in Toluene (1.0 mL) at 120 °C for 10 h. #Isolation by using column chromatography.

Table S3:- Solvent-Study*

Entry	Solvent	Yield (%)#
1	Toluene	72
2	Xylene	69
3	NMP	79
4	DMSO	traces
5$	**Neat**	**87**
6	Chlorobenzene	45
7	n-Butanol	0

*Reaction conditions: 1I (1.1 mmol), 2A (1.61 mmol) and $CuCl_2$ (0.22 mmol) were reacted in Toluene (1.0 mL) at 120 °C for 10 h. #Isolation by using column chromatography. $Without solvent under same condition.

Table S4:- Equiv, time and temperature study*

Entry	Aniline 2A (equiv)	$CuCl_2$ (mol%)	Temperature (°C)	TMSCl (equiv)	Time (hr)	Yield (%)#
1	1.0	20.0	120	1.5	10	56
2	1.5	20.0	120	1.5	10	87
3	2.0	20.0	120	1.5	10	88
4	1.5	0.0	120	1.5	10	10
5	1.5	10.0	120	1.5	10	70
6	1.5	15.0	120	1.5	10	81
7	1.5	30.0	120	1.5	10	86
8	1.5	40.0	120	1.5	10	87
9	1.5	20.0	80	1.5	10	0
10	1.5	20.0	100	1.5	10	35
11	1.5	20.0	110	1.5	10	72
12	1.5	20.0	130	1.5	10	85
13	1.5	20.0	140	1.5	10	88

14	1.5	20.0	120	0	10	0
15	1.5	20.0	120	0.5	10	10
16	1.5	20.0	120	1.0	10	55
17	1.5	20.0	120	2.0	10	89
18	1.5	20.0	120	1.5	2	60
19	**1.5**	**20.0**	**120**	**1.5**	**4**	**87**
20	1.5	20.0	120	1.5	6	85
21	1.5	20.0	120	1.5	8	89

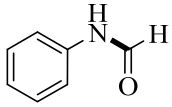
*Reaction conditions: 1A (1.0 eq). #Isolation by using column chromatography.

3.0 Cu-catalyzed transamidation of Aliphatic unactivated amides

3.1 Experimental Procedure (EP-1): An oven-dried 20 mL Teflon screw-capped vial equipped with a stir bar was sequentially charged with aliphatic amide (0.5 mmol, 1 equiv.), amine (0.75 mmol, 1.5 equiv.) and $CuCl_2$ (0.075 mmol, 0.15 equiv.). TMSCl (0.75 mmol, 1.5 equiv.) was transferred into the tube via a syringe. The resulting mixture was stirred under an argon atmosphere in a preheated heat block at 120 °C for 4 h. At this point, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution (~0.1 M, 2 x 30 mL; **note**: water was used for washing instead of HCl (aq) for pyridine/quinoline-containing amide products) and saturated brine (~30 mL), dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. The residue was purified by flash chromatography on silica gel using hexane and ethyl acetate as eluent to give the transamidated product.

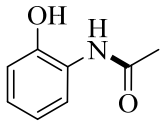
Scheme 1

N-phenylformamide[1] **(Scheme 1**, entry **3A)** (CAS No. **103-70-8**)



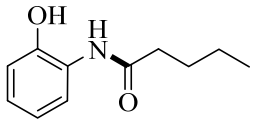
Using the experimental procedure EP-1, the product was obtained as light brown solid in 94% yield; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 9.20 (br, 1H), 8.68 (d, J = 11.3 Hz, 1H), 8.57 (br, 1H), 8.31 (s, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.34-7.27 (m, 4H), 7.16 (t, J = 7.5 Hz, 1H), 7.12-7.08 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 163.23, 159.89, 137.09, 136.85, 129.69, 129.01, 125.25, 124.74, 120.23, 118.78.

N-(2-hydroxyphenyl)acetamide[2] **(Scheme 1**, entry **3B)** (CAS No. **614-80-2**)



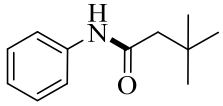
Using the experimental procedure EP-1, the product was obtained as light brown solid in 92% yield; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 9.73 (s, 1H), 9.30 (br, 1H), 7.67 (d, J = 8.1 Hz, 1H), 6.98 – 6.89 (m, 1H), 6.85 (d, J = 9.5 Hz, 1H), 6.75 (t, J = 7.6 Hz, 1H), 2.09 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = F3169.03, 147.90, 126.43, 124.66, 122.38, 118.98, 115.96, 23.60.

N-(2-hydroxyphenyl)pentanamide[3] **(Scheme 1**, entry **3C)** (CAS No. **105293-97-8**)



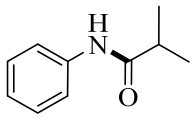
Using the experimental procedure EP-1, the product was obtained as light brown solid in 90% yield; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 9.72 (br, 1H), 9.25 (s, 1H), 7.67 (d, J = 9.3 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 6.6 Hz, 1H), 6.76 (td, J = 7.5, 1.6 Hz, 1H), 2.40 (t, J = 7.4 Hz, 2H), 1.58 (p, J = 7.4 Hz, 2H), 1.33 (h, J = 7.4 Hz, 2H), 0.90 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 172.05, 147.92, 126.47, 124.64, 122.30, 118.99, 116.11, 35.68, 27.44, 21.80, 13.71.

3,3-dimethyl-N-phenylbutanamide[3] **(Scheme 1**, entry **3D)** (CAS No. **72807-56-8**)



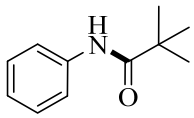
Using the experimental procedure EP-1, the product was obtained as light brown solid in 86% yield; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 9.77 (s, 1H), 7.59 (d, J = 7.6 Hz, 2H), 7.01 (t, J = 7.3 Hz, 2H), 2.18 (s, 2H), 1.02 (s, 9H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 169.96, 139.28, 128.59, 122.95, 119.18, 49.60, 30.83, 29.62.

N-phenylisobutyramide[4] **(Scheme 1**, entry **3E)** (CAS No. **4406-41-1**)



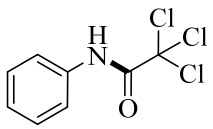
Using the experimental procedure EP-1, the product was obtained as light brown solid in 85% yield; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.53 (d, J = 8.3 Hz, 2H), 7.43 (br, 1H), 7.30 (t, J = 7.6 Hz, 2H), 7.09 (t, J = 7.4 Hz, 1H), 2.52 (hept, J = 7.0 Hz, 1H), 1.25 (s, 3H), 1.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 175.72, 138.24, 129.00, 124.23, 120.11, 36.65, 19.69.

N-phenylpivalamide[1] **(Scheme 1**, entry **3F)** (CAS No. **6625-74-7**)



Using the experimental procedure EP-1, the product was obtained as light brown solid in 78% yield; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.53 (d, J = 8.7 Hz, 2H), 7.31 (t, J = 7.5 Hz, 3H), 7.10 (t, J = 8.0 Hz, 1H), 1.32 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 176.72, 138.15, 129.01, 124.28, 120.16, 39.68, 27.71.

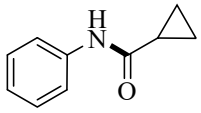
2,2,2-trichloro-N-phenylacetamide[5] **(Scheme 1**, entry **3G)** (CAS No. **2563-97-5**)



Using the experimental procedure EP-1, the product was obtained as light brown solid in 50% yield; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.34 (br, 1H), 7.58 (d, J = 8.7 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H),

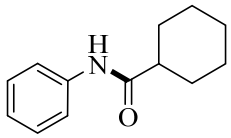
7.24 (t, J = 7.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 159.37, 136.06, 129.45, 126.18, 120.52, 92.96.

N-phenylcyclopropanecarboxamide[3] **(Scheme 1**, entry **3H)** (CAS No. **2759-52-6**)



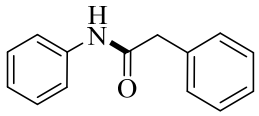
Using the experimental procedure EP-1, the product was obtained as light brown solid in 86% yield; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.67 (s, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.08 (t, J = 7.5 Hz, 1H), 1.55-1.49 (m, 1H), 1.13 – 0.97 (m, 2H), 0.83-0.79 (m, 2H).

N-phenylcyclohexanecarboxamide[1] **(Scheme 1**, entry **3I)** (CAS No. **2719-26-8**)



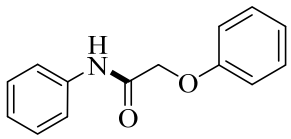
Using the experimental procedure EP-1, the product was obtained as light brown solid in 83% yield; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 9.79 (s, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.26 (t, J = 7.9 Hz, 2H), 2.31 (t, J = 11.6 Hz, 1H), 1.83 – 1.70 (m, 4H), 1.65 (d, J = 9.8 Hz, 1H), 1.51 – 1.33 (m, 2H), 1.33 – 1.13 (m, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 174.29, 139.52, 128.60, 122.83, 119.02, 44.87, 29.15, 25.42, 25.26.

N,2-diphenylacetamide[3] **(Scheme 1**, entry **3J)** (CAS No. **621-06-7**)



Using the experimental procedure EP-1, the product was obtained as light brown solid in 87% yield; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 10.19 (s, 1H), 7.61 (d, J = 8.7 Hz, 2H), 7.40 – 7.19 (m, 7H), 7.03 (t, J = 7.4 Hz, 1H), 3.64 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 169.11, 139.25, 136.04, 129.12, 128.72, 128.31, 126.53, 123.21, 119.10, 43.35.

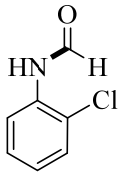
2-phenoxy-N-phenylacetamide[5] **(Scheme 1**, entry **3K)** (CAS No. **18705-01-6**)



Using the experimental procedure EP-1, the product was obtained as light brown solid in 89% yield; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 10.11 (s, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.9 Hz, 4H), 7.08 (t, J = 7.4 Hz, 1H), 7.02-6.95 (m, 3H), 4.70 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 166.59, 157.83, 138.41, 129.53, 128.74, 123.70, 121.19, 119.71, 114.66, 67.10.

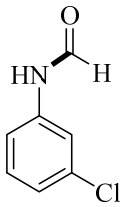
Scheme 2

N-(2-Hydroxy-4-methylphenyl)formamide[6] **(Scheme 2**, entry **3a)** (CAS No. **2843-27-8**)



Using the experimental procedure EP-1, the product was obtained as brown solid in 73% yield; 66:34 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.66 (d, J = 11.1 Hz, 0.47H), 8.45 (s, 1H), 8.35 (d, J = 8.3 Hz, 1H), 7.74 (br, 1.3H), 7.38 (d, J = 8.1 Hz, 0.45H), 7.33 (d, J = 8.1 Hz, 1H), 7.27 – 7.18 (m, 1H), 7.09 (dt, J = 8.3, 4.4 Hz, 0.48H), 7.02 (t, J = 7.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 161.73, 159.03, 133.81, 130.44, 129.24, 128.13, 127.93, 126.10, 125.27, 122.14, 118.87.

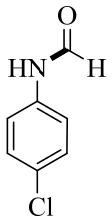
N-(3-chlorophenyl) formamide[7] (**Scheme 2**, entry **3b**) (CAS No. **139-71-9**)



Using the experimental procedure EP-1, the product was obtained as off white solid in 90%; 55:45 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.69 – 8.61 (m, 2H), 8.56 (s, 0H), 8.33 (s,

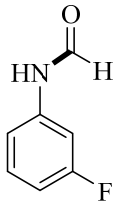
1H), 7.70 (s, 0H), 7.62 (s, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.28 – 7.15 (m, 4H), 7.12 (d, J = 8.1 Hz, 1H), 7.06 (d, J = 7.0 Hz, 2H), 6.95 (d, J = 7.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 162.60, 159.26, 138.08, 135.60, 134.88, 130.95, 130.25, 125.50, 125.05, 120.25, 118.92, 118.08, 116.84.

N-(4-chlorophenyl) formamide[6] (**Scheme 2**, entry **3c**) (CAS No. **2617-79-0**)



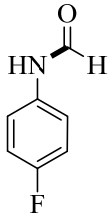
Using the experimental procedure EP-1, the product was obtained as off-white solid in 80% yield; 56:44 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.71 (br, 0.64H), 8.59 (d, J = 11.2 Hz, 0.77H), 8.31 (s, 1H), 7.75 (br, 0.82H), 7.44 (d, J = 8.9 Hz, 2H), 7.26 (d, J = 8.8 Hz, 1.58H), 7.22 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 1.56H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 162.83, 159.34, 135.54, 135.42, 130.91, 129.99, 129.95, 129.24, 121.40, 120.20.

N-(3-fluorophenyl)formamide[8] (**Scheme 2**, entry **3d**) (CAS No. **1428-10-0**)



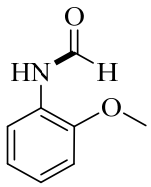
Using the experimental procedure EP-1, the product was obtained as yellow solid in 87% yield; 52:48 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.88 (br, 0.88H), 8.64 (d, J = 11.2 Hz, 0.95H), 8.30 (s, 1.17H), 8.03 (br, 1.06H), 7.41 (d, J = 10.6 Hz, 1.15H), 7.28 – 7.10 (m, 3.35H), 6.78 (m, 3.96H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 164.68, 164.20, 162.83, 162.22, 161.77, 159.59, 138.59, 138.52, 138.41, 131.29, 131.20, 130.39, 130.29, 115.41, 115.38, 114.18, 114.15, 112.24, 112.03, 111.78, 111.57, 107.89, 107.63, 106.16, 105.91.

N-(4-fluorophenyl) formamide[6] (**Scheme 2**, entry **3e**) (CAS No. **459-25-6**)



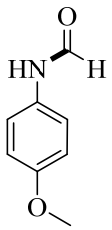
Using the experimental procedure EP-1, the product was obtained as off-white solid in 69% yield; 63:37 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.63 (br, 0.55H), 8.57 (d, J = 11.1 Hz, 0.82H), 8.34 (s, 1H), 7.76 (br, 0.86H), 7.50 (dd, J = 9.0, 4.9 Hz, 2H), 7.07 (m, 2.87H), 7.01 (t, J = 8.6 Hz, 2.14H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 163.20, 161.80, 160.95, 159.37, 159.30, 158.52, 133.00, 132.86, 122.04, 121.95, 121.34, 121.26, 116.79, 116.56, 116.00, 115.77.

N-(2-methoxyphenyl)formamide[6] (**Scheme 2,** entry **3f**) (CAS No. **23896-88-0**)



Using the experimental procedure EP-1, the product was obtained as brown solid in 92% yield; 69:31 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.89 (s, 0.25H), 8.47 (s, 1H), 8.35 (d, J = 7.9 Hz, 1H), 7.92 (s, 0.82H), 7.79 (s, 0.41H), 7.18 (d, J = 8.2 Hz, 0.43H), 7.12 (t, J = 7.9 Hz, 0.46H), 7.06 (t, J = 7.1 Hz, 1H), 6.99 – 6.85 (m, 3H), 3.87 (s, 3H), 3.85 (s, 1.29H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 161.60, 158.91, 148.89, 147.91, 126.81, 126.29, 125.34, 124.36, 121.14, 120.55, 116.85, 111.39, 110.16, 55.80.

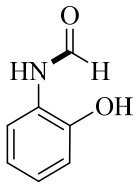
N-(4-methoxyphenyl) formamide[6] (**Scheme 2**, entry **3g**) (CAS No. **5470-34-8**)



Using the experimental procedure EP-1, the product was obtained as reddish brown solid in 93% yield; 51:49 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.55 (br, 0.63H), 8.50 (d, J = 11.4

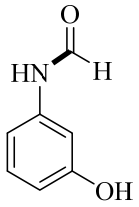
Hz, 1H), 8.28 (s, 1H), 7.88 (br, 0.83H), 7.43 (d, J = 9.0 Hz, 2H), 7.03 (d, J = 8.8 Hz, 1.91H), 6.85 (dd, J = 14.4, 8.9 Hz, 4H), 3.78 (s, 2.86H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.43, 159.34, 157.68, 156.77, 130.14, 129.74, 121.96, 121.61, 114.97, 114.29, 55.63, 55.55.

N-(2-Hydroxy-4-methylphenyl)formamide[9] **(Scheme 2**, entry **3h)** (CAS No. **2843-27-8**)



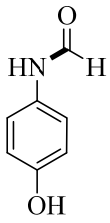
Using the experimental procedure EP-1, the product was obtained as brown solid in 90% yield; 85:15 mixture of rotamers: **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 9.93 (s, 1H), 9.56 (s, 1H), 9.24 (d, J = 11.1 Hz, 0.15H), 8.52 (d, J = 11.2 Hz, 0.17H), 8.28 (s, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.12 (d, J = 7.7 Hz, 0.17H), 6.98 (t, J = 7.6 Hz, 0.19H), 6.94 – 6.82 (m, 2H), 6.75 (t, J = 7.6 Hz, 1.2H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 163.48, 160.04, 148.97, 146.74, 126.01, 125.49, 124.20, 121.77, 120.84, 119.45, 119.01, 116.11, 115.11.

N-(3-hydroxyphenyl)formamide[7] (**Scheme 2**, entry **3i**) (CAS No. **24891-35-8**)



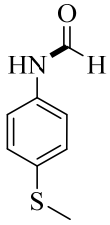
Using the experimental procedure EP-1, the product was obtained as brown oil in 89% yield; 73:27 mixture of rotamers: **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 10.03 (s, 1H), 10.00 (s, 0.25H), 9.51 (s, 0.37H), 9.41 (s, 1H), 8.72 (d, J = 11.0 Hz, 0.36H), 8.22 (s, 1H), 7.18 (s, 1H), 7.08 (t, J = 8.1 Hz, 1.44H), 6.93 (d, J = 10.0 Hz, 1H), 6.63 (d, J = 7.9 Hz, 0.38H), 6.57 (s, 0.38H), 6.48 (t, J = 7.0 Hz, 0.39H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 162.38, 159.46, 158.27, 157.70, 139.47, 139.25, 130.20, 129.57, 110.85, 110.80, 109.92, 108.02, 106.40, 104.77.

N-(4-hydroxyphenyl)formamide[9] (**Scheme 2**, entry **3j**) (CAS No. **41656-75-1**)



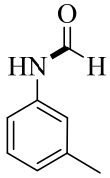
Using the experimental procedure EP-1, the product was obtained as brown solid in 93% yield; 77:23 mixture of rotamers: **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 9.88 (s, 1H), 9.83 (d, J = 11.2 Hz, 0.34H), 9.22 (s, 1.28H), 8.50 (d, J = 11.1 Hz, 0.28H), 8.16 (d, J = 2.2 Hz, 1H), 7.37 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 0.61H), 6.76 – 6.66 (m, 2.63H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 162.56, 158.84, 154.23, 153.55, 129.99, 129.66, 120.82, 120.22, 115.87, 115.19.

N-(4-(methylthio)phenyl)formamide[9] (**Scheme 2**, entry **3k**) (CAS No. **170288-29-6**)



Using the experimental procedure EP-1, the product was obtained as cream solid in 88% yield; 54:46 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.57 (d, J = 11.4 Hz, 0.92H), 8.51 (br, 0.7H), 8.29 (s, 1H), 7.61 (br, 0.83H), 7.42 (d, J = 8.7 Hz, 2H), 7.23 – 7.13 (m, 4H), 6.98 (d, J = 8.6 Hz, 1.80H), 2.41 (s, 2.56H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 162.82, 159.24, 135.43, 134.51, 134.47, 134.22, 128.52, 127.95, 120.76, 119.76, 16.60, 16.58.

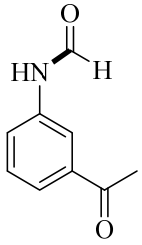
N-m-tolylformamide[6] (**Scheme 2**, entry **3l**) (CAS No. **3085-53-8**)



Using the experimental procedure EP-1, the product was obtained as brown oil in 85% yield; 55:45 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.96 (br, 0.86H), 8.68 (d, J = 11.3 Hz,

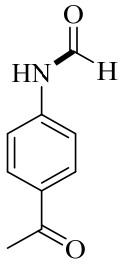
1H), 8.33 (d, J = 1.9 Hz, 0.8H), 8.09 (br, 0.66H), 7.40 (s, 0.82H), 7.33 (d, J = 8.1 Hz, 0.79H), 7.20 (dt, J = 12.0, 7.8 Hz, 1.88H), 6.99 (d, J = 7.7 Hz, 1H), 6.96 – 6.88 (m, 2.87H), 2.34 (s, 3.15H), 2.31 (s, 2.52H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 163.16, 159.57, 139.87, 139.06, 137.01, 136.82, 129.57, 128.91, 126.10, 125.61, 120.80, 119.55, 117.24, 115.81, 21.48, 21.42.

N-(3-acetylphenyl)formamide[9] (**Scheme 2**, entry **3m**) (CAS No. **72801-78-6**)



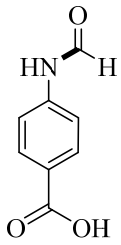
Using the experimental procedure EP-1, the product was obtained as white solid in 72% yield; 64:36 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.99 (br, 0.52H), 8.86 (d, J = 11.1 Hz, 0.6H), 8.43 (s, 1H), 8.39 (br, 0.71H), 7.96-7.90 (m, 3.17H), 7.67 (d, J = 8.7 Hz, 2H), 7.18 (d, J = 8.7 Hz, 1.24H), 2.57 (s, 1.72H), 2.56 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 197.39, 197.01, 162.26, 159.61, 141.55, 141.36, 133.74, 133.28, 130.51, 129.86, 119.39, 117.34, 26.56.

N-(4-acetylphenyl)formamide[5] (**Scheme 2,** entry **3n**) (CAS No. **41656-75-1**)



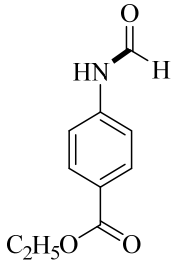
Using the experimental procedure EP-1, the product was obtained as white solid in 80% yield; 66:34 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.93 (d, J = 11.4 Hz, 0.46H), 8.76 (d, J = 11.2 Hz, 0.54H), 8.48 (br, 0.75H), 8.42 (s, 1H), 8.07 (s, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 7.5 Hz, 1.14H), 7.67 (d, J = 9.3 Hz, 1H), 7.52 – 7.37 (m, 1.57H), 7.32 (d, J = 5.6 Hz, 0.55H), 2.60 (s, 1.56H), 2.57 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 198.34, 197.66, 162.74, 159.83, 138.53, 137.81, 137.78, 137.61, 130.19, 129.53, 125.29, 124.85, 124.69, 123.20, 119.42, 117.84, 26.81.

4-formamidobenzoic acid[5] (**Scheme 2**, entry **3o**) (CAS No. **28533-43-9**)



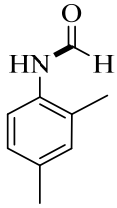
Using the experimental procedure EP-1, the product was obtained as brown oil in 68% yield; 55:45 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.85 (br, 0.49H), 8.69 (d, J = 11.4 Hz, 0.58H), 8.35 (s, 0.49H), 8.00 (br, 0.45H), 7.55 (d, J = 8.2 Hz, 1H), 7.33 (dt, J = 13.4, 8.1 Hz, 2.15H), 7.18 (t, J = 7.5 Hz, 0.57H), 7.12 (m, 1.6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 163.09, 159.55, 137.06, 136.87, 129.82, 129.15, 125.37, 124.87, 120.19, 118.91.

Ethyl 4-formamidobenzoate[5] (**Scheme 2**, entry **3p**) (CAS No. **5422-63-9**)



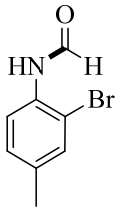
Using the experimental procedure EP-1, the product was obtained as white solid in 60% yield; 75:25 mixture of rotamers: **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 10.53 (s, 1H), 10.46 (d, J = 10.8 Hz, 0.27H), 8.96 (d, J = 10.6 Hz, 0.26H), 8.35 (d, J = 1.7 Hz, 1H), 7.91 (m,2.65H), 7.71 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.1 Hz, 0.77H), 4.28 (q, J = 7.1 Hz, 2.64H), 1.30 (t, J = 7.1 Hz, 4H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 165.24, 162.54, 160.11, 142.90, 142.43, 130.73, 130.33, 124.66, 118.62, 116.43, 60.45, 14.18.

N-(2,4-dimethylphenyl)formamide[10] (**Scheme 2**, entry **3q**) (CAS No. **60397-77-5**)



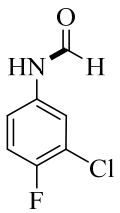
Using the experimental procedure EP-1, the product was obtained as off-white solid in 79% yield; 65:35 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.45 (d, J = 11.2 Hz, 0.91H), 8.39 (s, 0.53H), 8.18 (br, 0.77H), 7.66 (d, J = 8.7 Hz, 0.51H), 7.35 (br, 0.38H), 7.04 (s, 1H), 7.00 (s, 3H), 2.31 (s, 3H), 2.28 (s, 1.62H), 2.26 (s, 3H), 2.22 (s, 1.65H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 163.82, 159.50, 136.07, 135.45, 132.53, 131.96, 131.31, 130.22, 129.26, 127.63, 127.36, 123.51, 121.46, 20.94, 20.87, 17.79, 17.75.

N-(2-bromo-4-methylphenyl)formamide[9] (**Scheme 2**, entry **3r**) (CAS No. **353284-16-9**)



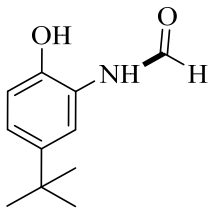
Using the experimental procedure EP-1, the product was obtained as off-white solid in 65% yield; 67:33 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.62 (d, J = 11.1 Hz, 0.49H), 8.46 (s, 1H), 8.22 (d, J = 8.3 Hz, 1H), 7.62 (br, 1H), 7.42 (s, 0.50H), 7.37 (s, 1H), 7.12 (s, 1H), 7.10 (s, 0.58H), 2.32 (s, 1.48H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 161.90, 158.88, 136.91, 135.93, 133.88, 132.72, 132.35, 129.42, 129.17, 122.24, 119.46, 114.78, 113.04, 20.67, 20.61.

N-(3-chloro-4-fluorophenyl)formamide[9] (**Scheme 2**, entry **3s**) (CAS No. **770-22-9**)



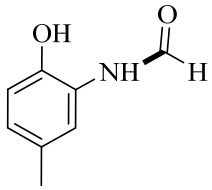
Using the experimental procedure EP-1, the product was obtained as off-white solid in 79% yield; 64:36 mixture of rotamers: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.66 (br, 0.42H), 8.58 (d, J = 11.1 Hz, 0.56H), 8.35 (s, 1H), 7.78 (br, 0.73H), 7.72 (dd, J = 6.5, 2.5 Hz, 1H), 7.36 (m, 1H), 7.18 (dd, J = 6.2, 2.6 Hz, 0.49H), 7.14 (t, J = 8.6 Hz, 0.57H), 7.08 (t, J = 8.7 Hz, 1H), 7.03 – 6.94 (m, 0.56H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 162.89, 159.30, 157.27, 156.42, 154.80, 153.97, 133.55, 122.47, 121.61, 119.88, 119.81, 119.13, 119.06, 117.81, 117.58, 117.00, 116.78.

N-(5-(tert-butyl)-2-hydroxyphenyl)formamide[5] (**Scheme 2**, entry **3t**) (CAS No. **2305056-85-1**)



Using the experimental procedure EP-1, the product was obtained as brown solid in 87% yield; 77:23 mixture of rotamers: **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 9.67 (s, 1H), 9.53 (s, 1H), 9.18 (d, J = 11.2 Hz, 0.14H), 8.52 (d, J = 11.2 Hz, 0.17H), 8.27 (s, 1H), 8.08 (s, 1H), 7.09 (s, 0.18H), 6.99 (dd, J = 8.5, 2.4 Hz, 0.2H), 6.93 (dd, J = 8.4, 2.4 Hz, 1H), 6.82 (s, 0.21H), 6.78 (d, J = 8.4 Hz, 1H), 1.23 (s, 11.58H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 163.64, 159.98, 146.67, 144.42, 141.89, 141.26, 125.41, 124.54, 122.04, 120.81, 119.06, 117.92, 115.62, 114.64, 33.79, 31.37, 31.29.

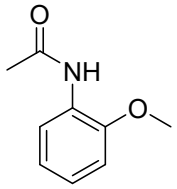
N-(2-hydroxy-5-methylphenyl)formamide[5] (**Scheme 2**, entry **3u**) (CAS No. **74642-14-1**)



Using the experimental procedure EP-1, the product was obtained as brown solid in 85% yield; 81:19 mixture of rotamers: **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 9.65 (s, 1H), 9.50 (s, 1H), 9.18 (d, J = 11.6 Hz, 0.15H), 8.51 (d, J = 11.1 Hz, 0.17H), 8.26 (s, 1H), 7.86 (s, 1H), 6.93 (s, 0.18H), 6.76 (d, J =

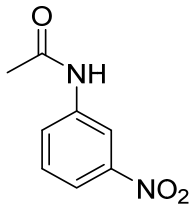
6.7 Hz, 0.63H), 6.73 (m, 1.8H), 2.18 (s, 3.72H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 163.40, 159.93, 146.52, 144.40, 128.16, 127.53, 124.98, 124.44, 122.12, 121.26, 115.96, 114.89, 20.49, 20.09.

N-(2-methoxyphenyl)acetamide[11] **(Scheme 2**, entry **3v) (**CAS No. **93-26-5)**



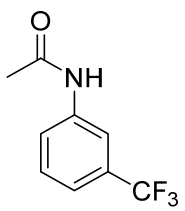
Using the experimental procedure EP-1, the product was obtained as white solid in 93% yield; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.34 (d, J = 9.7 Hz, 1H), 7.79 (br, 1H), 7.08 – 6.99 (m, 1H), 6.94 (t, J = 7.1 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 3.87 (s, 3H), 2.19 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 168.31, 147.79, 127.78, 123.73, 121.17, 119.92, 109.98, 55.74, 24.97.

N-(3-nitrophenyl)acetamide[12] **(Scheme 2**, entry **3w) (**CAS No. **121-89-1)**



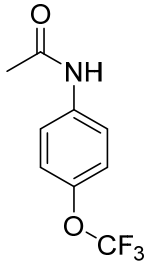
Using the experimental procedure EP-1, the product was obtained as yellow solid in 53% yield; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 10.44 (br, 1H), 8.60 (t, J = 2.2 Hz, 1H), 7.87 (dd, J = 8.2, 2.2 Hz, 2H), 7.57 (t, J = 8.2 Hz, 1H), 2.09 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 169.10, 147.95, 140.40, 130.08, 124.87, 117.50, 113.04, 112.94, 24.03.

N-(3-(trifluoromethyl)phenyl)acetamide[5] **(Scheme 2**, entry **3x) (**CAS No. **349-76-8)**



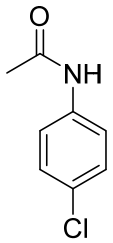
Using the experimental procedure EP-1, the product was obtained as white solid in 74% yield; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 10.26 (s, 1H), 8.07 (t, J = 2.0 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 168.93, 140.04, 129.91, 122.46, 119.36,119.32, 119.29, 119.25, 115.0, 114.96, 24.02, 20.57.

N-(4-(trifluoromethoxy)phenyl)acetamide[5] **(Scheme 2**, entry **3y) (**CAS No. **85013-98-5)**



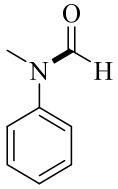
Using the experimental procedure EP-1, the product was obtained as Colourless Solid in 60% yield; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.95 (s, 1H), 7.53 (d, J = 9.0 Hz, 2H), 7.14 (d, J = 8.8 Hz, 2H), 2.16 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 169.00, 136.71, 121.77, 121.32, 42.44, 24.46.

N-(4-chlorophenyl)acetamide[5] **(Scheme 2**, entry **3z) (**CAS No. **99-91-2)**



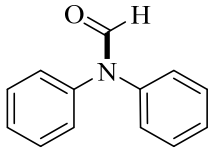
Using the experimental procedure EP-1, the product was obtained as light yellow solid in 68%; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 10.05 (br, 1H), 7.60 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.9 Hz, 2H), 2.04 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 168.43, 138.26, 128.53, 126.50, 120.48, 23.96.

N-methyl-N-phenylformamide[6] (**Scheme 2**, entry **3aa**) (CAS No. **93-61-8**)



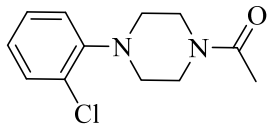
Using the experimental procedure EP-1, the product was obtained as yellow oil in 87% yield; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.34 (s, 1H), 7.28 (t, J = 8.0 Hz, 2H), 7.14 (t, J = 8.0 Hz, 1H), 7.04 (d, J = 8.6 Hz, 2H), 3.18 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 162.41, 142.21, 129.66, 126.46, 122.41, 32.08.

N,N-diphenylformamide[5] (**Scheme 2**, entry **3ab**) (CAS No. **607-00-1**)



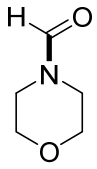
Using the experimental procedure EP-1, the product was obtained as yellow solid in 79% yield. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.60 (s, 1H), 7.33-7.30 (m, 4H), 7.28 – 7.15 (m, 4H), 7.10 (d, J = 7.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 161.85, 141.91, 139.76, 129.81, 129.29, 127.16, 126.97, 126.23, 125.21.

1-(4-(2-chlorophenyl)piperazin-1-yl)ethan-1-one[5] **(Scheme 2**, entry **3ac) (**CAS No. **150557-82-7)**



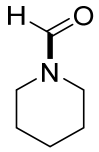
Using the experimental procedure EP-1, the product was obtained as light yellow solid in 85%; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 7.42 (d, J = 7.8 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.14 (d, J = 8.1 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 3.58 (q, J = 4.9 Hz, 4H), 2.96 (t, J = 4.9 Hz, 2H), 2.90 (t, J = 5.0 Hz, 2H), 2.04 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 168.33, 148.65, 130.31, 128.09, 127.73, 124.23, 121.09, 51.16, 50.74, 45.91, 45.48, 41.03, 21.19.

morpholine-4-carbaldehyde[6] **(Scheme 2**, entry **3ad) (**CAS No. **4394-85-8)**



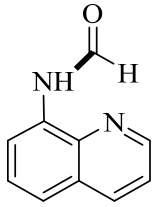
Using the experimental procedure EP-1, the product was obtained as yellow oil in 75%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.86 (s, 1H), 3.51-3.48 (m, 2H), 3.48 – 3.41 (m, 2H), 3.40 – 3.32 (m, 2H), 3.26 – 3.18 (m, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 160.56, 66.85, 66.01, 45.42, 40.20.

piperidine-1-carbaldehyde[6] **(Scheme 2**, entry **3ae) (**CAS No. **2591-86-8)**



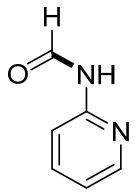
Using the experimental procedure EP-1, the product was obtained as yellow oil in 69%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.79 (s, 1H), 3.30 – 3.21 (m, 2H), 3.17 – 3.03 (m, 2H), 1.50 – 1.45 (m, 2H), 1.42 – 1.34 (m, 2H), 1.35 – 1.24 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 160.33, 46.34, 40.11, 26.14, 24.66, 24.23.

N-(quinolin-8-yl)formamide[5] (**Scheme 2**, entry **3af**) (CAS No. **62937-22-8**)



Using the experimental procedure EP-1, the product was obtained as brown solid in 60% yield; 88:12 mixture of rotamers; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 9.62 (br, 1H), 9.20 (br, 0.09H), 8.87 (d, J = 11.7 Hz, 0.11H), 8.56 (dd, J = 4.3, 1.6 Hz, 1.13H), 8.50 (p, J = 4.6 Hz, 1H), 8.45 (s, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.1 Hz, 0.15H), 7.29 (s, 1.15H), 7.28 (s, 1H), 7.26 (s, 0.18H), 7.22 (dd, J = 8.3, 4.3 Hz, 1.31H), 7.01 (s, 0.1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 159.39, 148.30, 138.05, 136.88, 133.52, 128.12, 127.51, 122.37, 121.81, 117.99.

N-(pyridin-2-yl)formamide[9] (**Scheme 2**, entry **3ag**) (CAS No. **34813-97-3**)



Using the experimental procedure EP-1, the product was obtained as brown solid in 70%; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 10.58 (s, 1H), 9.28 (d, J = 10.3 Hz, 0.57H), 8.33 (s, 0.82H), 8.25 (s, 0.64H), 7.82 – 7.69 (m, 1.11H), 7.08 (d, J = 5.6 Hz, 1.11H), 6.92 (d, J = 8.3 Hz, 0.61H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 162.14, 160.32, 151.65, 151.03, 148.08, 138.71, 138.33, 119.78, 119.24, 113.79, 111.14.

4.0 Optimization of Reaction Conditions of annulation

4.1 General procedure for optimizations of reaction conditions. An oven-dried 20 mL Teflon screw-capped vial equipped with a stir bar was sequentially charged with amide **4c**, aniline **5a** and catalyst. TMSCl were transferred into the tube via a syringe. The resulting mixture was stirred in a preheated heat block. After full fill the reaction condition of experiment, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution and saturated brine, dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. The residue was purified by flash chromatography on silica gel using hexane and ethyl acetate as eluent to give the transamidated product **6c**.

Table S5:- Equiv, time and temperature study*

Entry	Aniline 5a (equiv)	$CuCl_2$ (mol%)	Temperature (^{o}C)	TMSCl (equiv)	Time (hr)	Yield (%)$^{\#}$
1	1.5	20.0	100	1.5	12	0
2	1.5	20.0	110	1.5	12	0

3	1.5	20.0	130	1.5	12	11
4	1.5	20.0	140	1.5	12	17
5	1.5	20.0	150	1.5	12	45
6	1.5	20.0	**160**	1.5	12	51
7	1.5	20.0	160	1.5	14	61
8	1.5	20.0	160	1.5	**16**	65
9	1.5	20.0	160	1.5	18	65
10	1.5	20.0	160	1.5	20	64
11	1.5	20.0	160	0	16	0
12	1.5	20.0	160	0.5	16	8
13	1.5	20.0	160	1.0	16	40
14	1.5	20.0	160	**2.0**	16	76

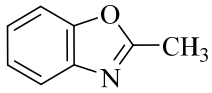
*Reaction conditions: 4c (1.0 eq). #Isolation by using column chromatography.

5.0 Cu-catalyzed annulation of aliphatic unactivated amides with substituted 2-aminophenols

5.1 Experimental Procedure (EP-2): An oven-dried 20 mL Teflon screw-capped vial equipped with a stir bar was sequentially charged with aliphatic amide (0.5 mmol, 1 equiv.), amine (0.75 mmol, 1.5 equiv.) and $CuCl_2$ (0.075 mmol, 0.15 equiv.). TMSCl (0.75 mmol, 1.5 equiv.) was transferred into the tube via a syringe. The resulting mixture was stirred under an argon atmosphere in a preheated heat block at 160 °C for 16 h. At this point, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution (~0.1 M, 2 x 30 mL; **note**: water was used for washing instead of HCl (aq) for pyridine/quinoline-containing amide products) and saturated brine (~30 mL), dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. The residue was purified by flash chromatography on silica gel using hexane and ethyl acetate as eluent to give the annulated benzoxazole product.

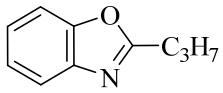
5.2 Analytical Data

2-methylbenzo[d]oxazole[13] (**Scheme 5a**, entry **6a**) (CAS No. **95-21-6**)



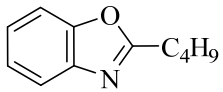
Using the experimental procedure EP-2, the product was obtained as light brown liquid in 80%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.66 (dd, J = 6.2, 2.9 Hz, 1H), 7.47 (dd, J = 6.4, 2.9 Hz, 1H), 7.29 (dd, J = 5.3, 3.9 Hz, 2H), 2.65 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 172.1, 145.4, 140.6, 138.2, 128.7, 122.9, 23.5.

2-propylbenzo[d]oxazole[14] (**Scheme 5a**, entry **6b**) (CAS No. **2008-05-1**)



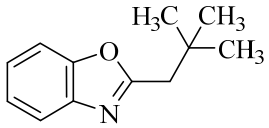
Using the experimental procedure EP-2, the product was obtained as light brown liquid in 76%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.64 (dd, J = 7.2, 4.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.26-7.24 (m, 2H), 2.88 (t, 2H), 1.92-1.87 (m, 2H), 1.03 (t, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 167.1, 150.6, 141.3, 123.9, 119.4, 110.3, 30.5, 20.3, 13.9.

2-butylbenzo[d]oxazole[14] (**Scheme 5a**, entry **6c**) (CAS No. **6797-49-5**)



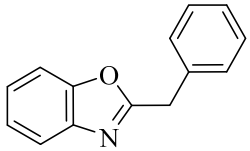
Using the experimental procedure EP-2, the product was obtained as light brown liquid in 75%; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 7.68 – 7.61 (m, 1H), 7.61 – 7.52 (m, 1H), 7.33 – 7.23 (m, 2H), 2.86 (t, J = 7.5 Hz, 2H), 1.73 (p, J = 7.5 Hz, 2H), 1.33 (dq, J = 14.8, 7.3 Hz, 2H), 0.85 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 166.69, 150.20, 141.02, 124.31, 123.91, 119.07, 110.18, 28.12, 27.35, 21.54, 13.29.

2-neopentylbenzo[d]oxazole[15] (**Scheme 5a**, entry **6d**) (CAS No. **143857-68-5**)



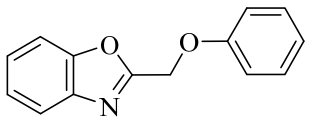
Using the experimental procedure EP-2, the product was obtained as light-yellow solid in 70%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.70 (d, J = 3.2 Hz, 1H), 7.55 – 7.43 (m, 1H), 7.32 – 7.24 (m, 2H), 2.82 (s, 2H), 1.08 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 166.05, 150.88, 141.38, 124.52, 124.15, 119.70, 110.40, 42.54, 32.20, 29.73.

2-benzylbenzo[d]oxazole[16] (**Scheme 5a**, entry **6e**) (CAS No. **2008-07-3**)



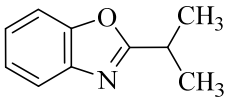
Using the experimental procedure EP-2, the product was obtained as light-yellow solid in 72%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.67 (dd, J = 5.9, 2.4 Hz, 1H), 7.49 – 7.38 (m, 1H), 7.34 (d, J = 7.1 Hz, 2H), 7.29 (t, J = 7.8 Hz, 2H), 7.24-7.19 (m, 3H), 4.22 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 165.18, 151.00, 141.29, 134.76, 128.97, 128.78, 127.27, 124.66, 124.16, 119.77, 110.40, 35.18.

2-(phenoxymethyl)benzo[d]oxazole[17] (**Scheme 5a**, entry **6f**) (CAS No. **7506-48-1**)



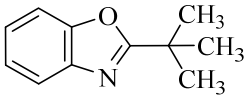
Using the experimental procedure EP-2, the product was obtained as white solid in 75%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.65 (dd, J = 5.3, 3.9 Hz, 1H), 7.43 (dd, J = 4.8, 3.2 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.19 (t, J = 7.6 Hz, 2H), 6.97 (s, 1H), 6.94 (s, 1H), 6.92 – 6.85 (m, 1H), 5.20 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 161.56, 157.93, 150.97, 140.74, 129.69, 125.64, 124.69, 121.97, 120.43, 114.87, 110.95, 62.80.

2-isopropylbenzo[d]oxazole[14] (**Scheme 5a**, entry **6g**) (CAS No. **6797-15-5**)



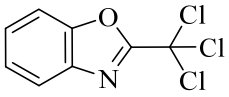
Using the experimental procedure EP-2, the product was obtained as light brown liquid in 60%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.70-7.66 (m, 1H), 7.47 (dd, J = 5.6, 3.7 Hz, 1H), 7.35 – 7.23 (m, 2H), 3.25 (hept, J = 7.0 Hz, 1H), 1.46 (d, J = 8.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 171.45, 150.84, 141.27, 124.57, 124.17, 119.72, 110.43, 29.01, 20.41.

2-(tert-butyl)benzo[d]oxazole[14] (**Scheme 5a**, entry **6h**) (CAS No. **54696-03-6**)



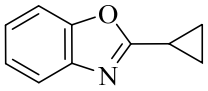
Using the experimental procedure EP-2, the product was obtained as brown liquid in 58%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.52-7.48 (m, 1H), 7.30-7.27 (m, 1H), 7.13 – 7.03 (m, 2H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 173.61, 150.94, 141.36, 124.51, 124.08, 119.82, 110.42, 34.28, 28.59.

2-(trichloromethyl)benzo[d]oxazole[17] (**Scheme 5a**, entry **6i**) (CAS No. **14468-53-2**)



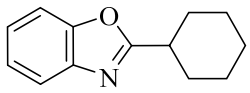
Using the experimental procedure EP-2, the product was obtained as brown solid in 35%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.56 (dd, J = 7.9, 1.7 Hz, 1H), 7.19 – 7.08 (m, 1H), 7.03 – 6.87 (m, 1H), 6.89 – 6.76 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 159.31, 149.86, 127.07, 123.84, 123.65, 119.10, 115.61, 92.74.

2-cyclopropylbenzo[d]oxazole[14] (**Scheme 5a**, entry **6j**) (CAS No. **63359-58-0**)



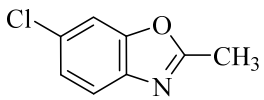
Using the experimental procedure EP-2, the product was obtained as brown liquid in 65%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.58 (d, J = 6.7 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.23-7.19 (m, 2H), 2.21-2.14 (m, 1H), 1.26-1.21 (m, 2H), 1.23 – 1.07 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 168.64, 150.45, 141.54, 124.11, 123.99, 118.98, 110.02, 9.30, 9.17.

2-cyclohexylbenzo[d]oxazole[18] (**Scheme 5a**, entry **6k**) (CAS No. **104462-82-0**)



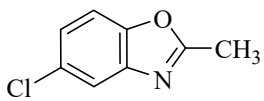
Using the experimental procedure EP-2, the product was obtained as brown solid in 57%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.70 – 7.63 (m, 1H), 7.63 – 7.55 (m, 1H), 7.35 – 7.24 (m, 2H), 2.92 (tt, J = 11.0, 3.7 Hz, 1H), 2.04 (dd, J = 12.9, 3.1 Hz, 2H), 1.71 (dt, J = 13.1, 3.8 Hz, 2H), 1.65 – 1.50 (m, 3H), 1.35 (qt, J = 12.2, 3.2 Hz, 2H), 1.28 – 1.13 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 169.50, 149.99, 140.85, 124.40, 123.96, 119.23, 110.32, 36.78, 29.85, 25.24, 24.82.

6-chloro-2-methylbenzo[d]oxazole[11] (**Scheme 5a**, entry **6l**) (CAS No. **63816-18-2**)



Using the experimental procedure EP-2, the product was obtained as brown solid in 57%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.54 (dd, J = 8.4 Hz, 1H), 7.47 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 2.63 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 168.9, 146.9, 120.6, 119.5, 107.1, 15.0.

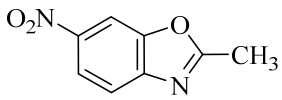
5-chloro-2-methylbenzo[d]oxazole[13] (**Scheme 5b**, entry **6m**) (CAS No. **19219-99-9**)



Using the experimental procedure EP-2, the product was obtained as light-yellow solid in 74%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.60 (s, 1H), 7.36 (d, J = 8.6 Hz, 1H), 7.24 (d, J = 8.6 Hz, 1H),

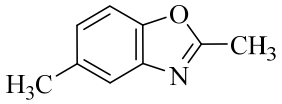
2.61 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 165.57, 149.53, 142.31, 129.48, 124.95, 119.39, 111.07, 14.56.

2-methyl-6-nitrobenzo[d]oxazole[19] (**Scheme 5b**, entry **6n**) (CAS No. **5683-43-2**)



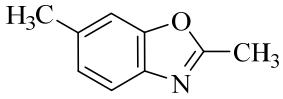
Using the experimental procedure EP-2, the product was obtained as off-white solid in 35%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.40 (s, 1H), 8.28 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 8.8 Hz, 1H), 2.73 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 168.97, 150.28, 146.98, 120.57, 119.53, 107.06, 15.02.

2,5-dimethylbenzo[d]oxazole[13] (**Scheme 5b**, entry **6o**) (CAS No. **5676-58-4**)



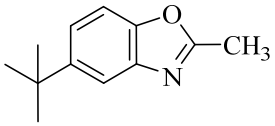
Using the experimental procedure EP-2, the product was obtained as yellow liquid in 80%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.41 (s, 1H), 7.31 (d, J = 8.2 Hz, 1H), 7.06 (d, J = 10.1 Hz, 1H), 2.59 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 163.99, 149.21, 141.51, 133.97, 125.56, 119.33, 109.60, 21.43, 14.51.

2,6-dimethylbenzo[d]oxazole[13] (**Scheme 5b**, entry **6p**) (CAS No. **53012-61-6**)



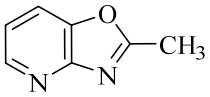
Using the experimental procedure EP-2, the product was obtained as yellow liquid in 81%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.48 (d, J = 8.2 Hz, 1H), 7.22 (s, 1H), 7.06 (d, J = 8.3 Hz, 1H), 2.56 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 163.28, 151.20, 139.05, 134.76, 125.26, 118.62, 110.40, 21.58, 14.37.

5-(tert-butyl)-2-methylbenzo[d]oxazole[20] (**Scheme 5b**, entry **6q**) (CAS No. **40874-54-2**)



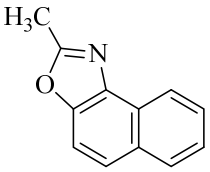
Using the experimental procedure EP-2, the product was obtained as yellow liquid in 79%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.70 (s, 1H), 7.44 – 7.34 (m, 2H), 2.65 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 164.12, 149.04, 147.85, 141.23, 122.26, 116.00, 109.45, 34.97, 31.89, 14.59.

2-methyloxazolo[4,5-b]pyridine[13] (**Scheme 5b**, entry **6r**) (CAS No. **86467-39-2**)



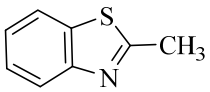
Using the experimental procedure EP-2, the product was obtained as off-white solid in 49%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 7.84 (d, J = 6.2 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.12 (dd, J = 8.1, 4.6 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 172.13, 145.36, 140.59, 138.15, 128.68, 122.86, 23.46.

2-methylnaphtho[1,2-d]oxazole[21] (**Scheme 5b**, entry **6s**) (CAS No. **85-15-4**)



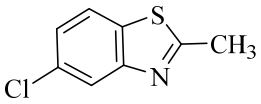
Using the experimental procedure EP-2, the product was obtained as brown liquid in 55%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ = 8.46 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.51 (t, J = 7.6 Hz, 1H), 2.72 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ = 162.94, 148.18, 136.63, 131.10, 128.58, 126.98, 126.31, 125.35, 125.19, 122.00, 110.70, 14.68.

2-methylbenzo[d]thiazole[16] (**Scheme 5b**, entry **6t**) (CAS No. **120-75-2**)



Using the experimental procedure EP-2, the product was obtained as brown liquid in 75%; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 8.00-7.97 (m, 1H), 7.93 – 7.90 (m, 1H), 7.47-7.43 (m, 1H), 7.39-7.34 (m, 1H), 2.77 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 166.8, 153.0, 135.2, 125.9, 124.6, 121.9, 121.8, 19.6.

5-chloro-2-methylbenzo[d]thiazole[16] (**Scheme 5b**, entry **6u**) (CAS No. **1006-99-1**)



Using the experimental procedure EP-2, the product was obtained as brown liquid in 70%; **^{1}H NMR** (400 MHz, DMSO-d_6, ppm): δ = 8.06 (d, J = 8.6 Hz, 1H), 7.97 (d, J = 2.0 Hz, 1H), 7.43 (dd, J = 8.6, 2.1 Hz, 1H), 2.80 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6, ppm): δ = 169.63, 153.84, 133.96, 130.73, 124.78, 123.38, 121.40, 19.80.

6.0 References

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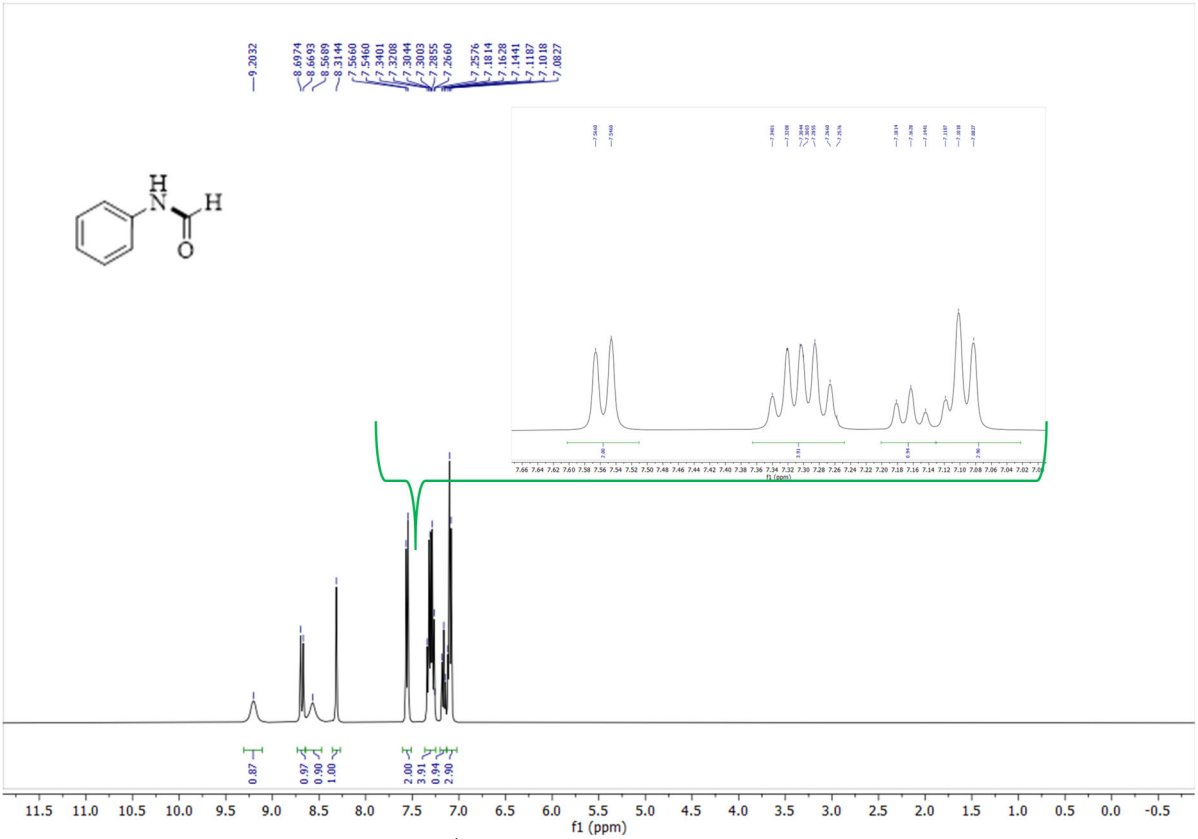
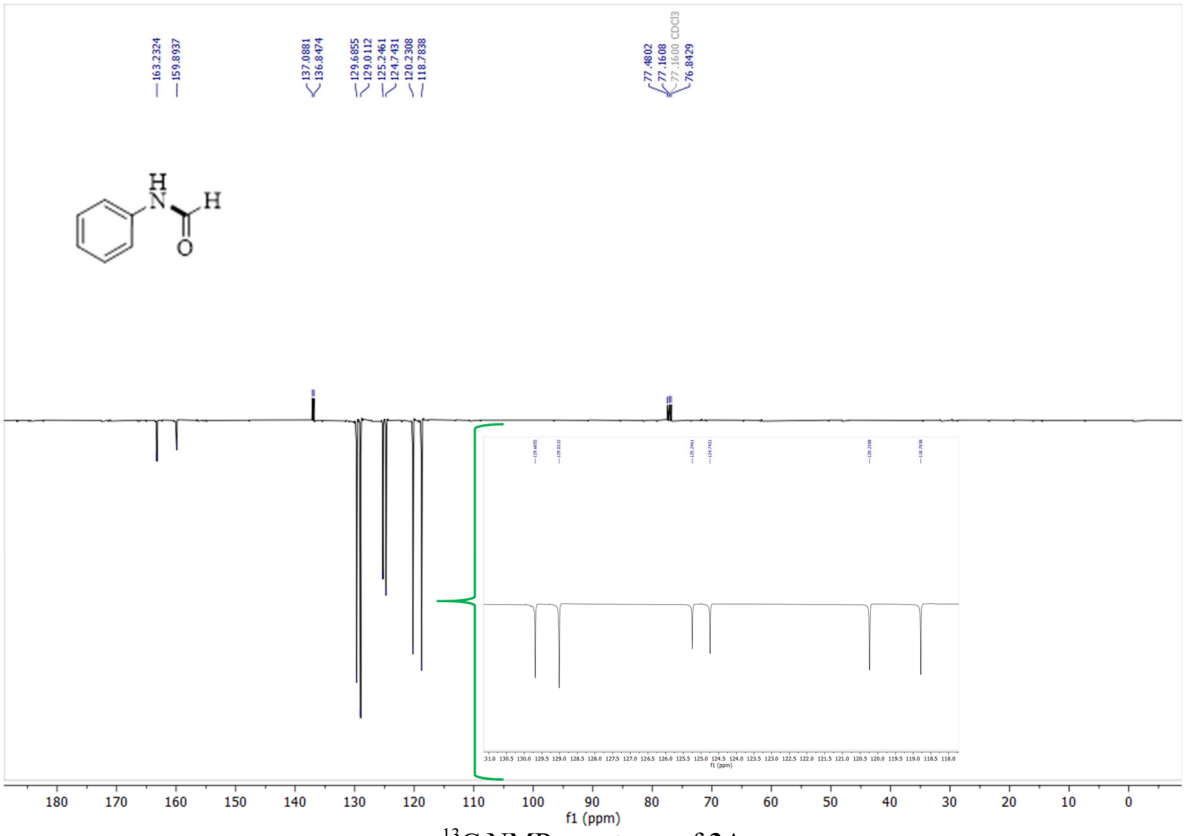
7.0 Copies of 1H and 13C spectra



^{1}H NMR spectrum of **3A**



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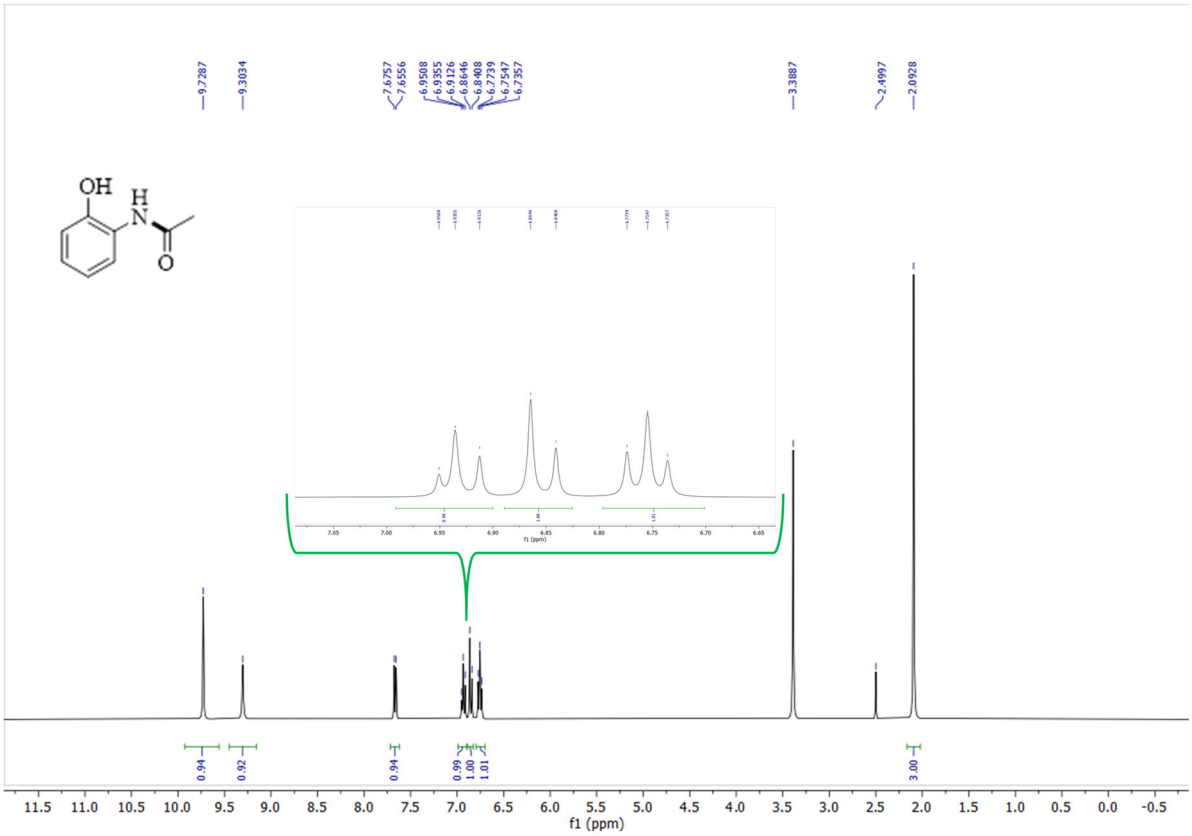

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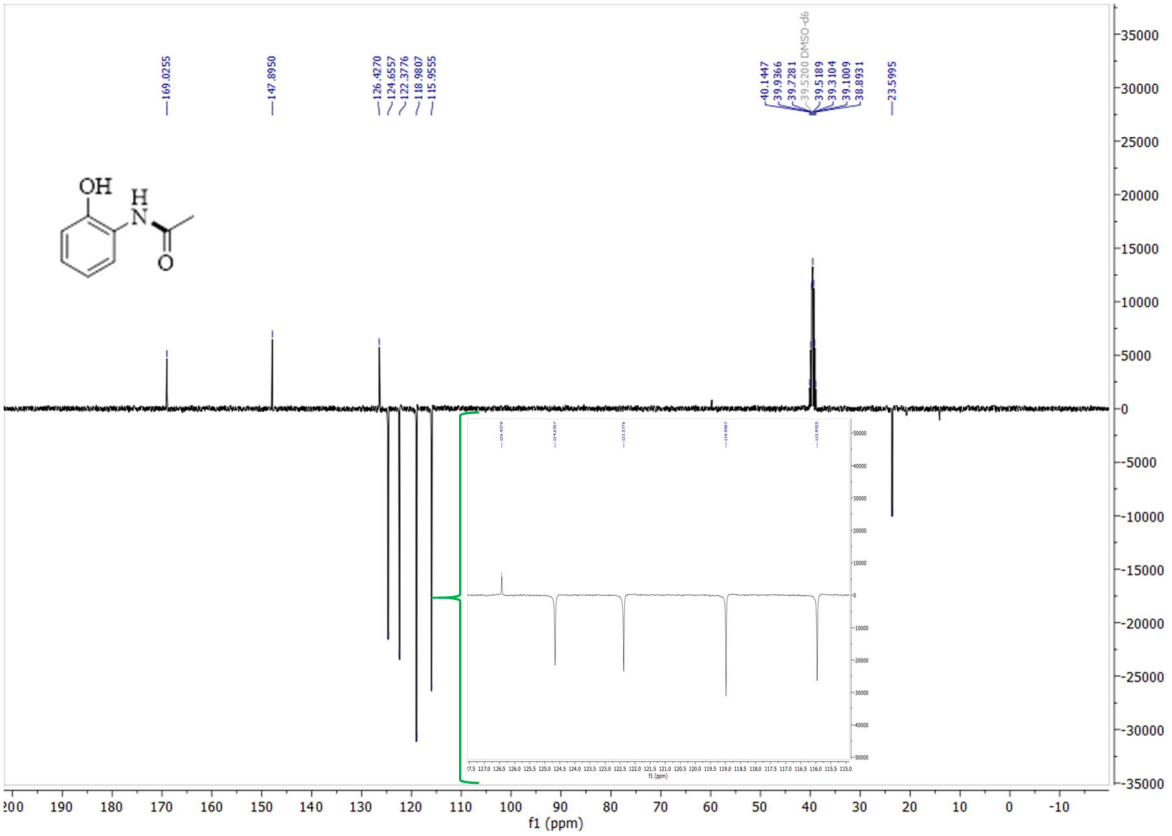

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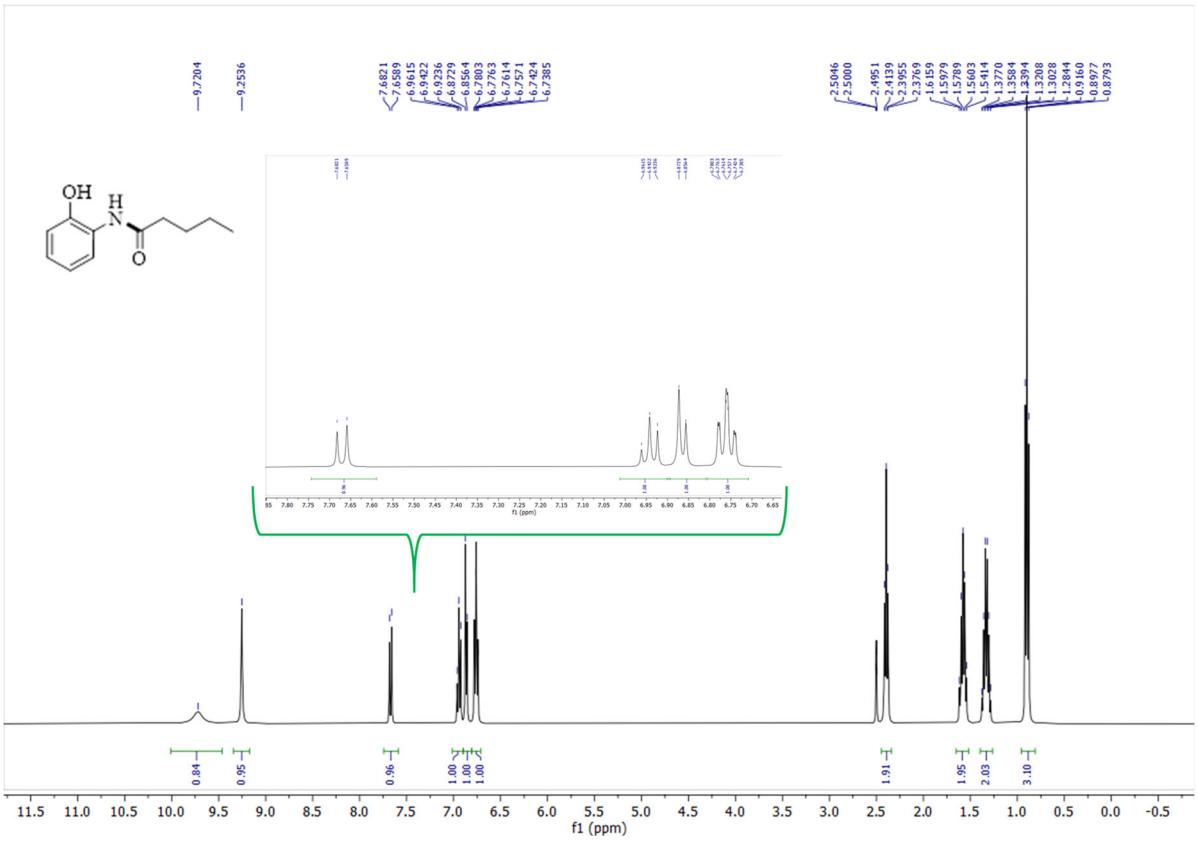

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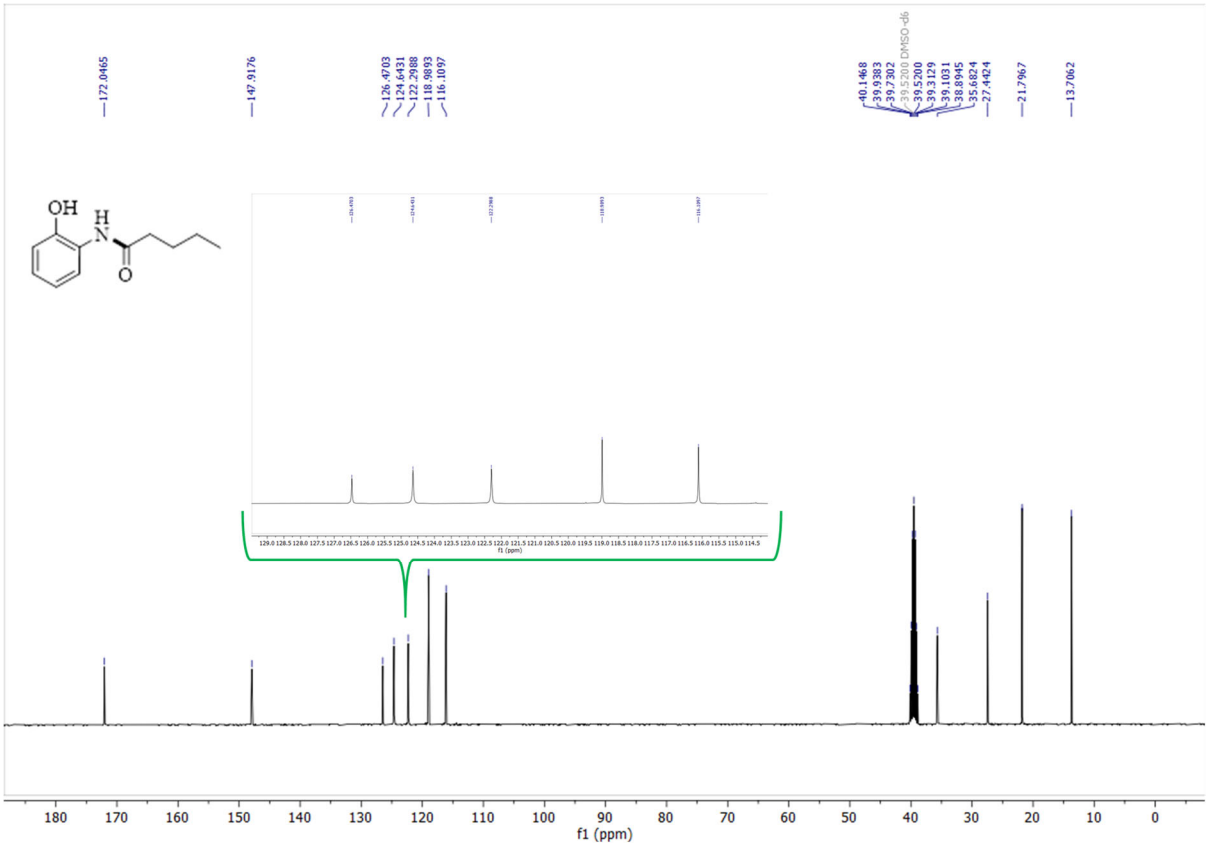
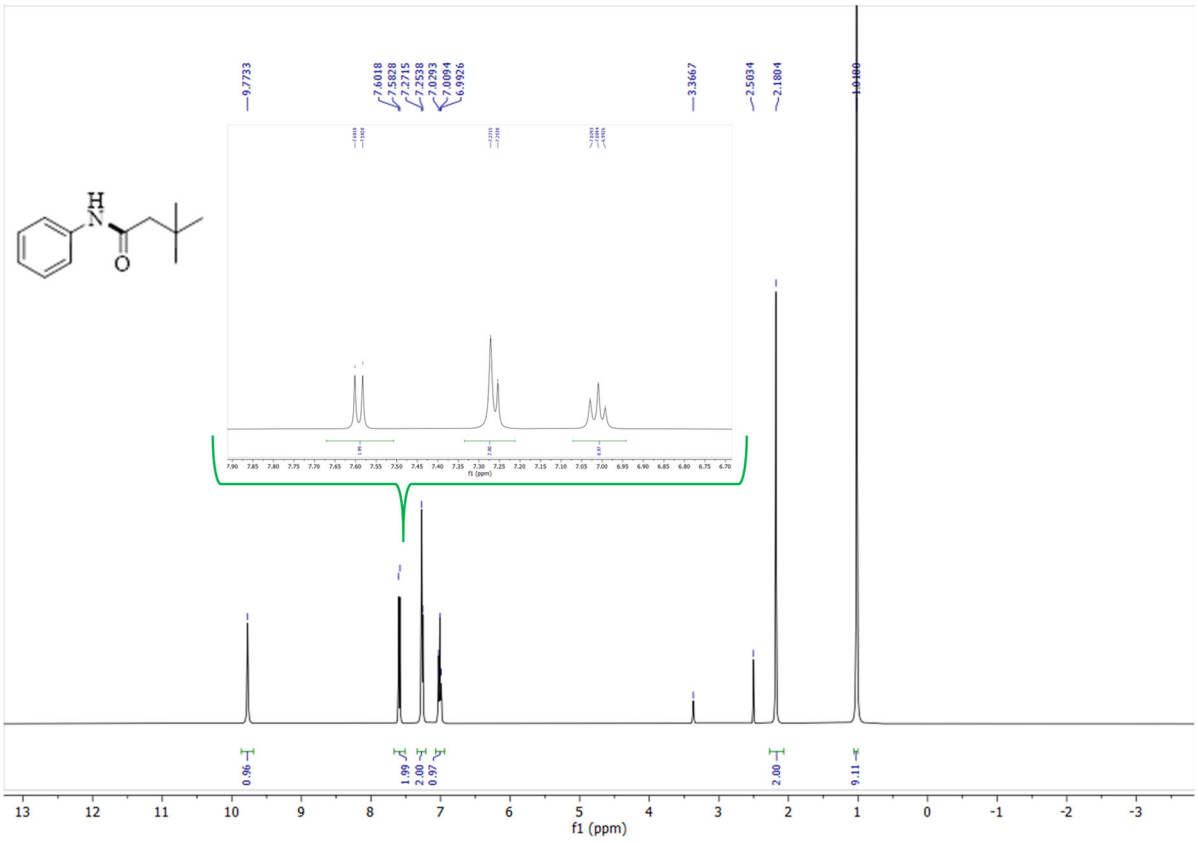


^{13}C NMR spectrum of **3C**



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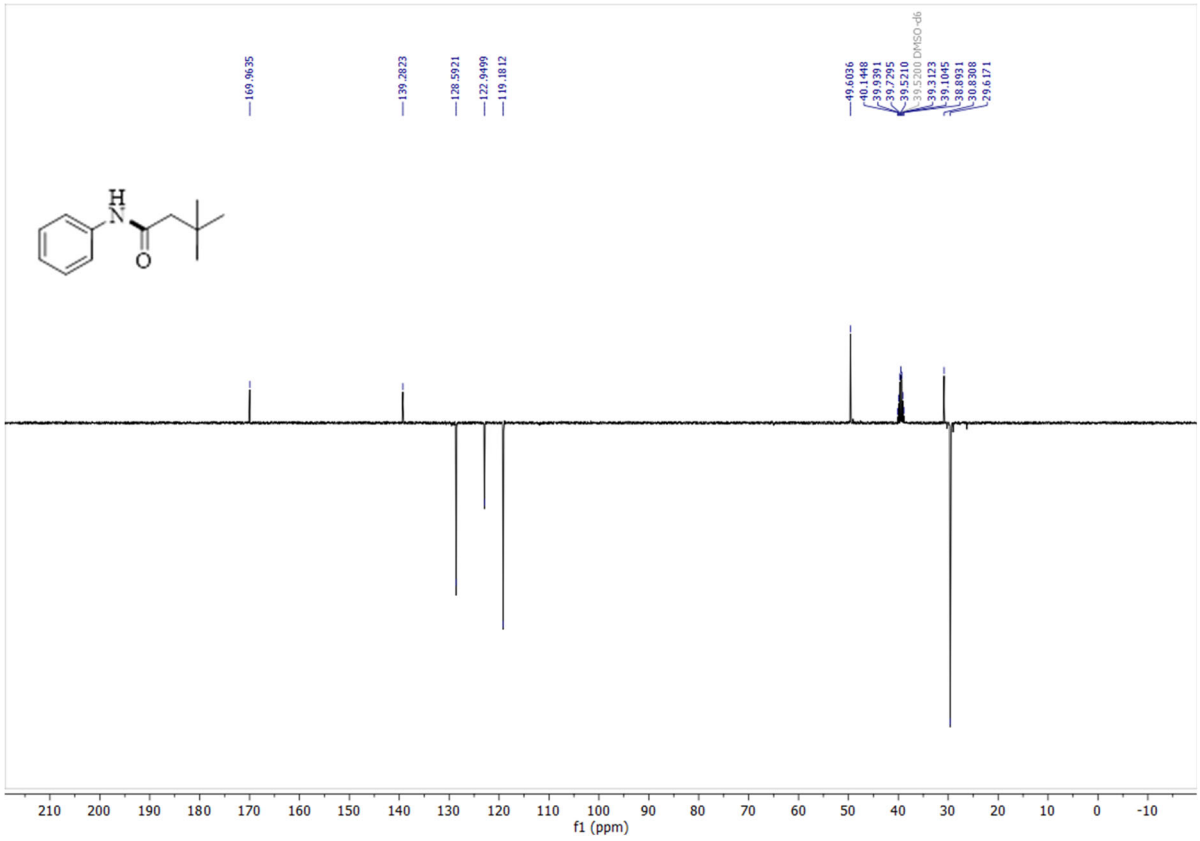
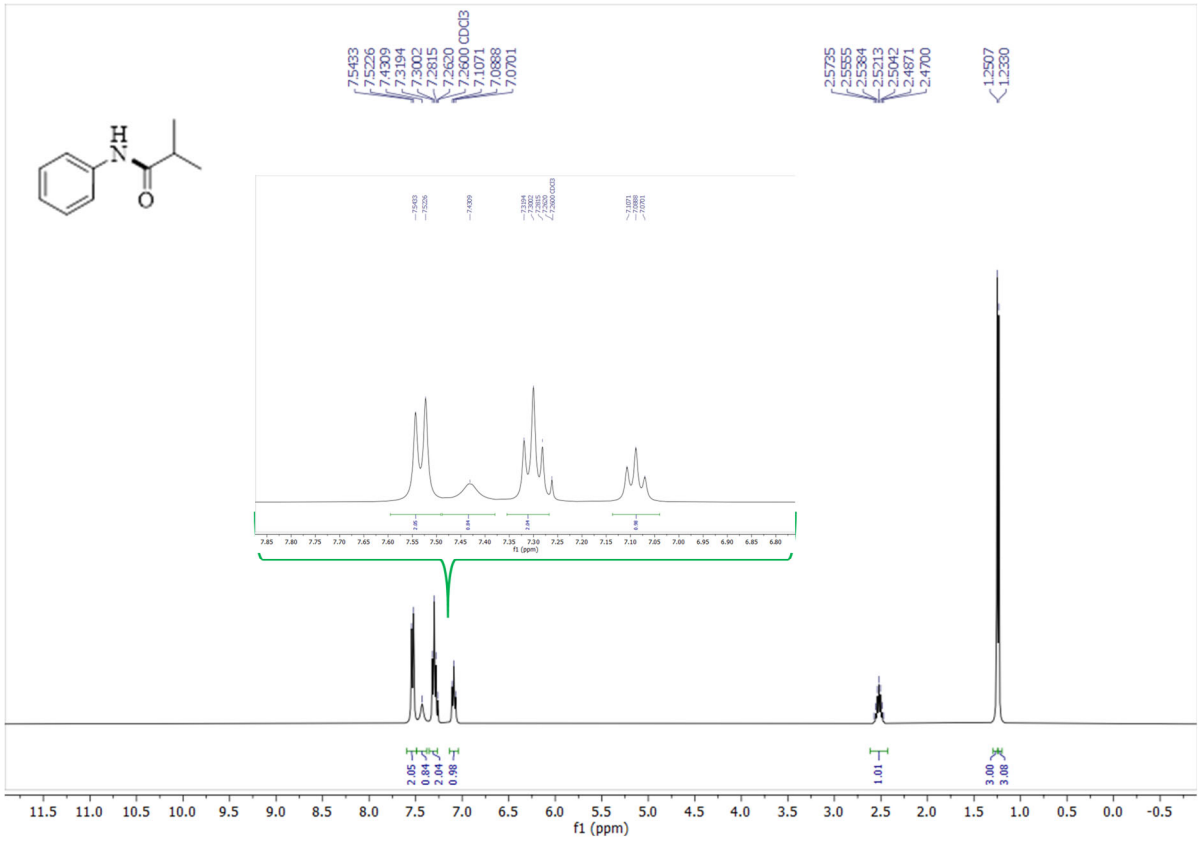


^{13}C NMR spectrum of **3D**



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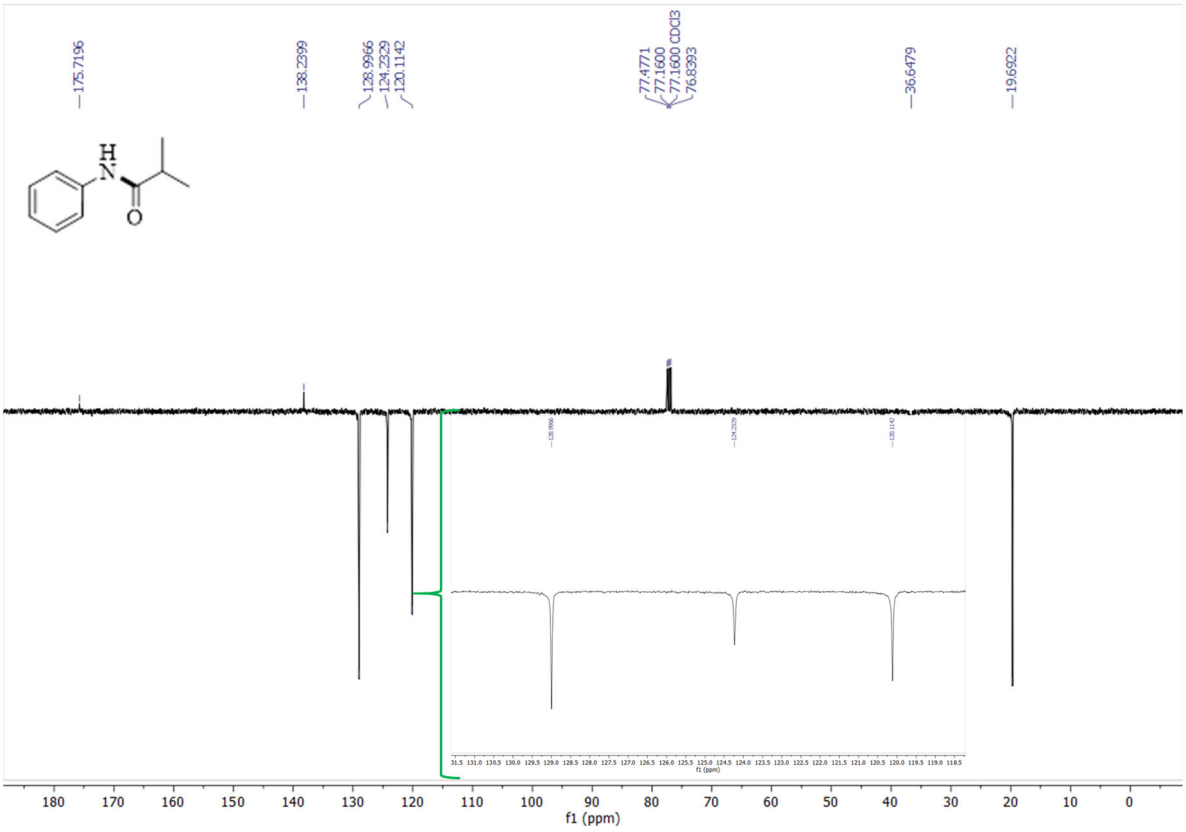
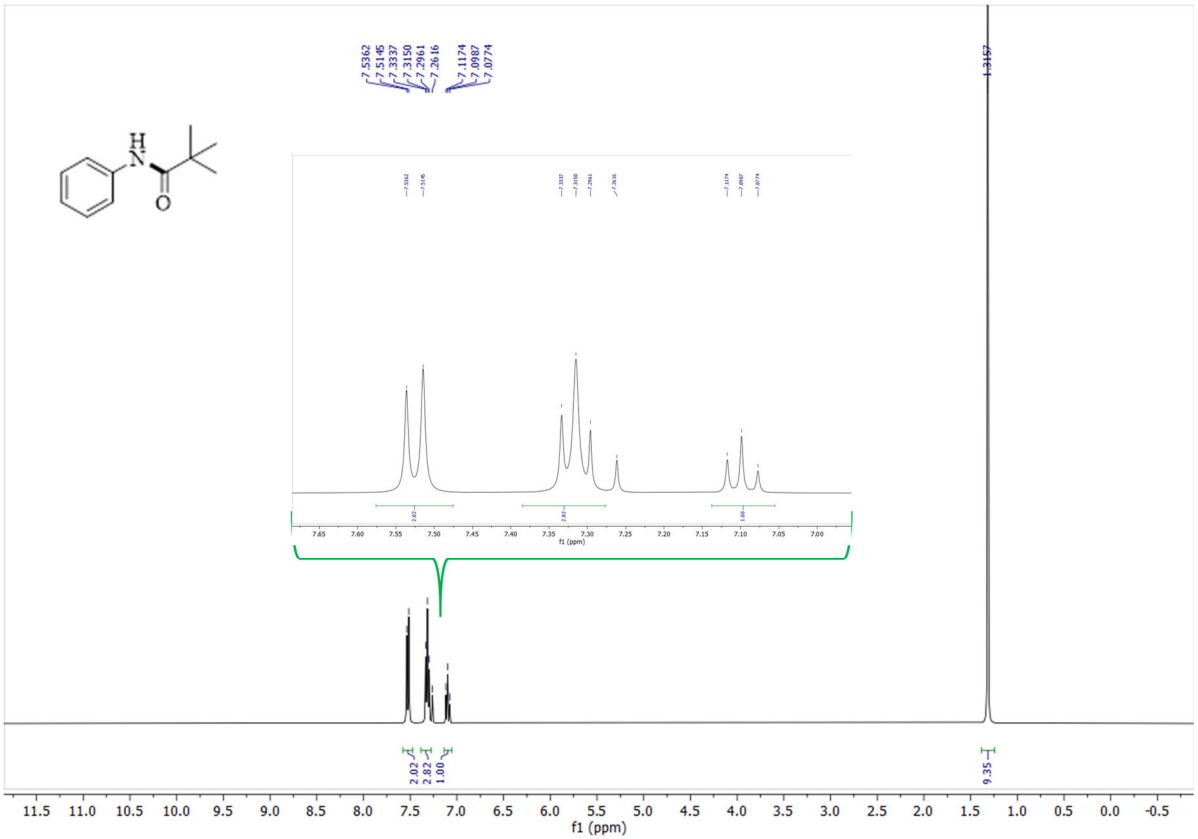


^{13}C NMR spectrum of **3E**



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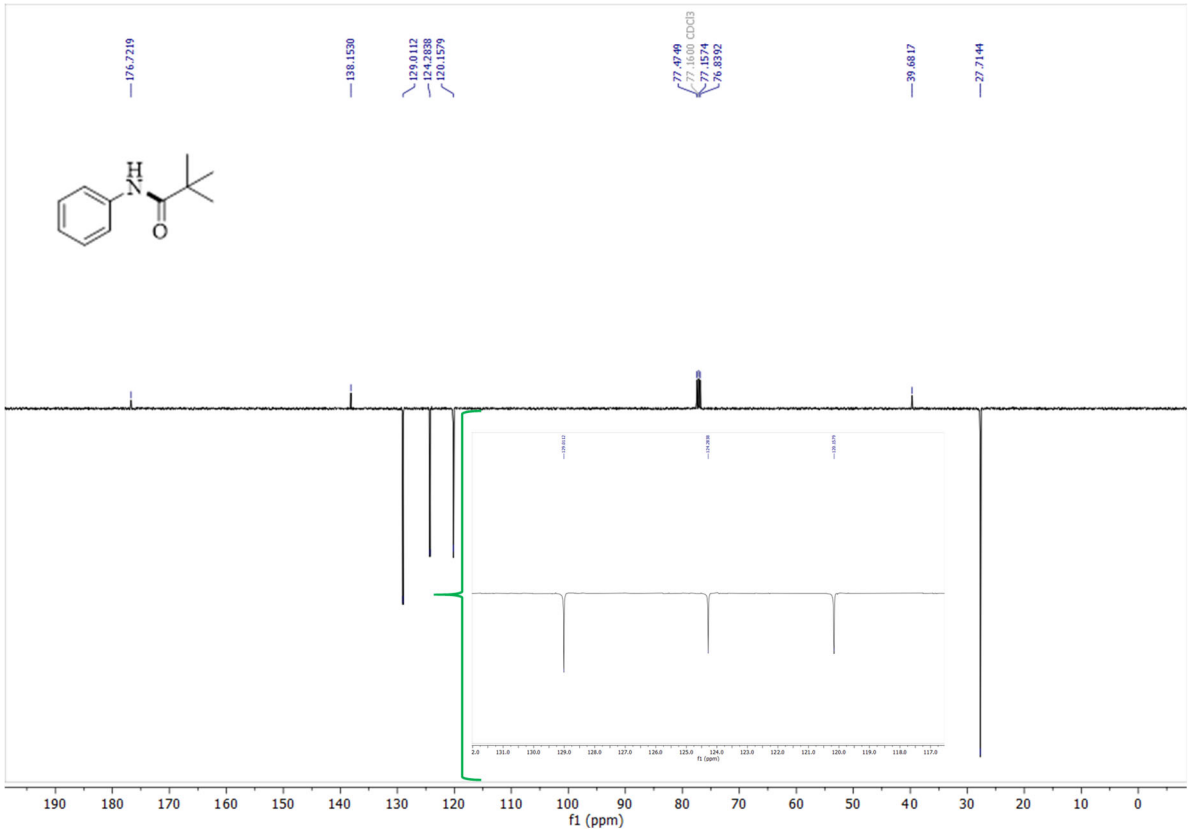
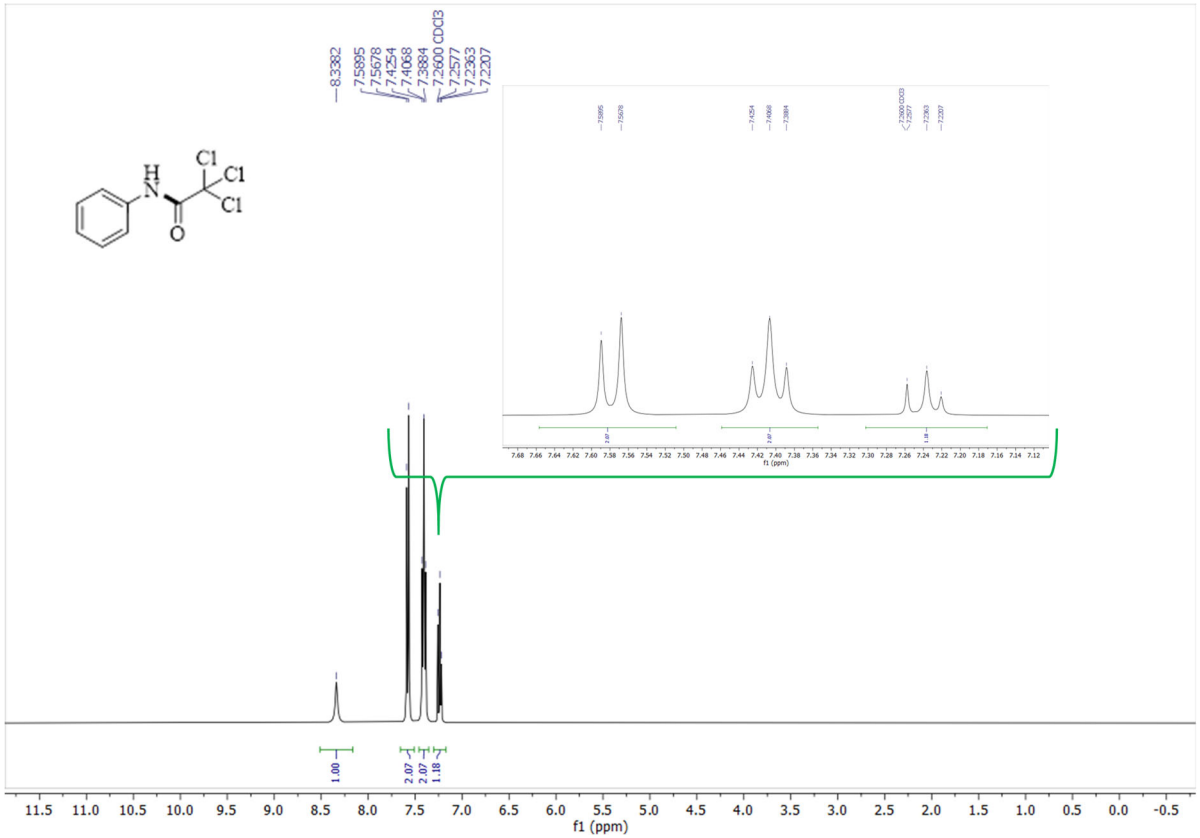


^{13}C NMR spectrum of **3F**



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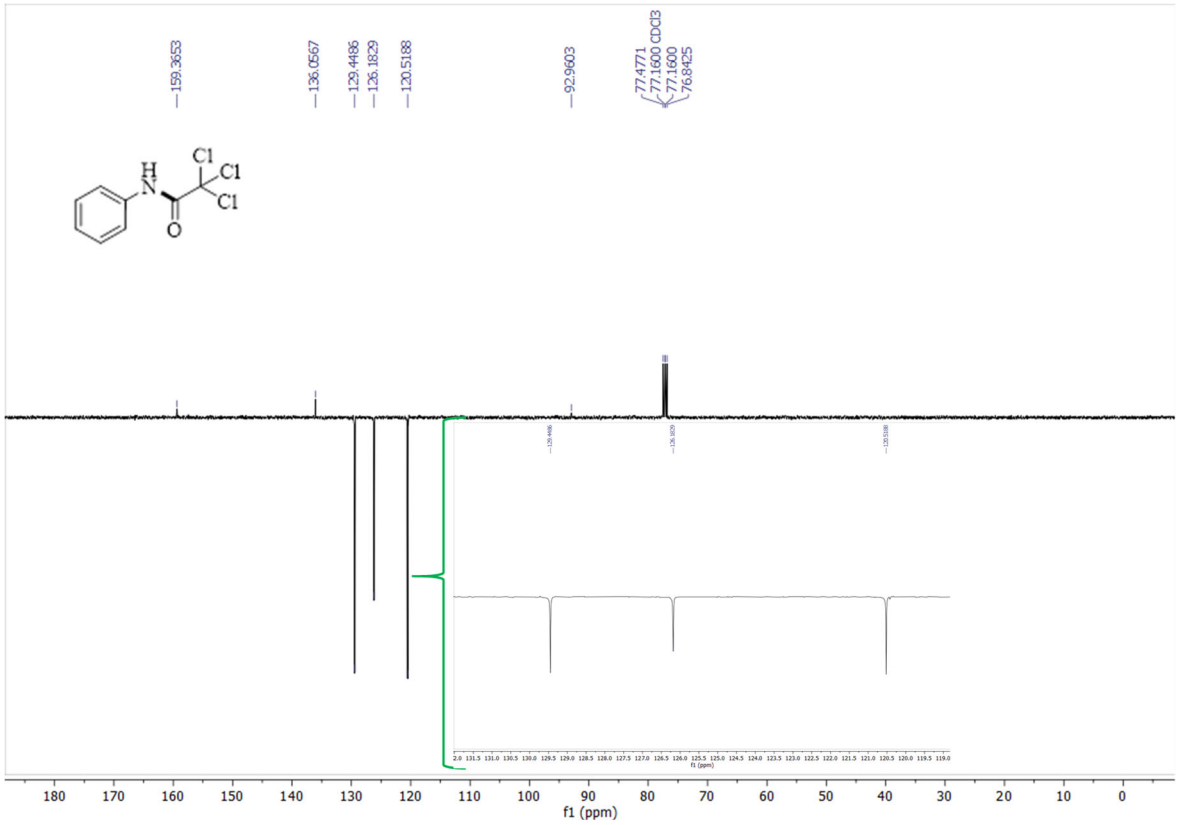

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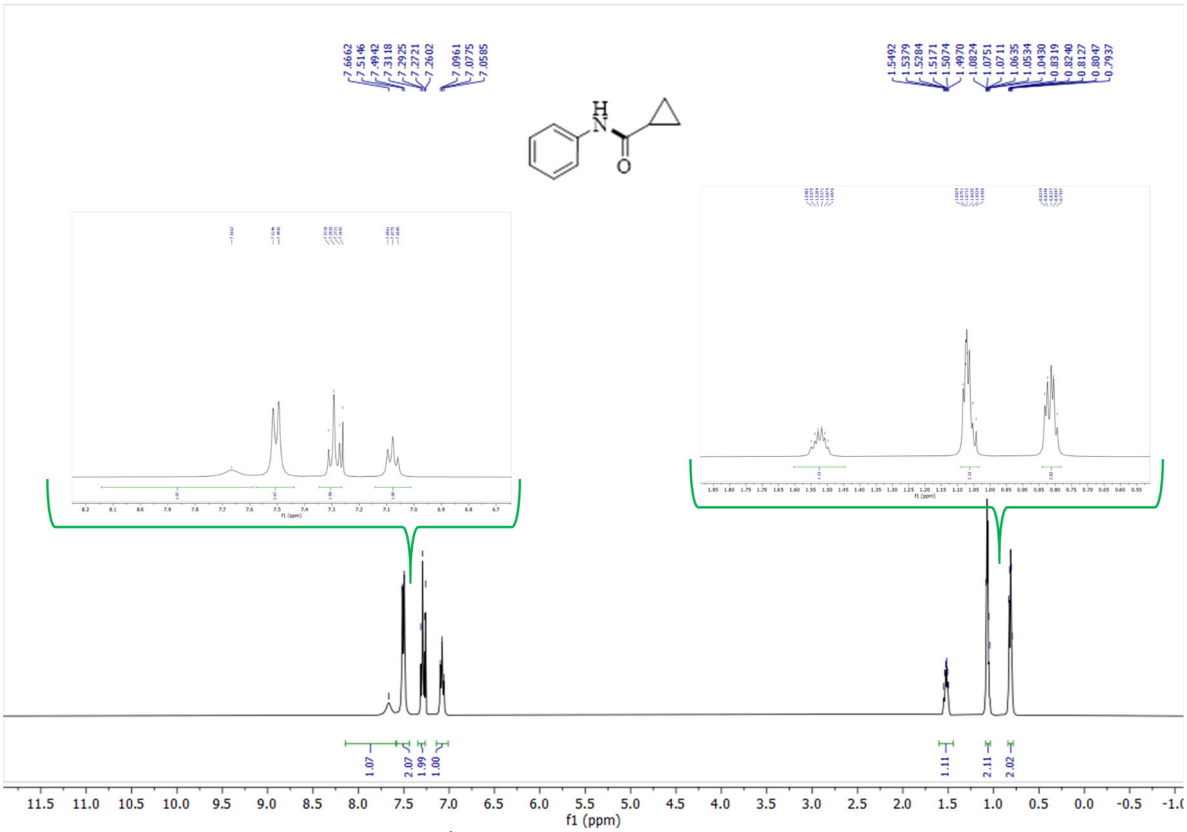

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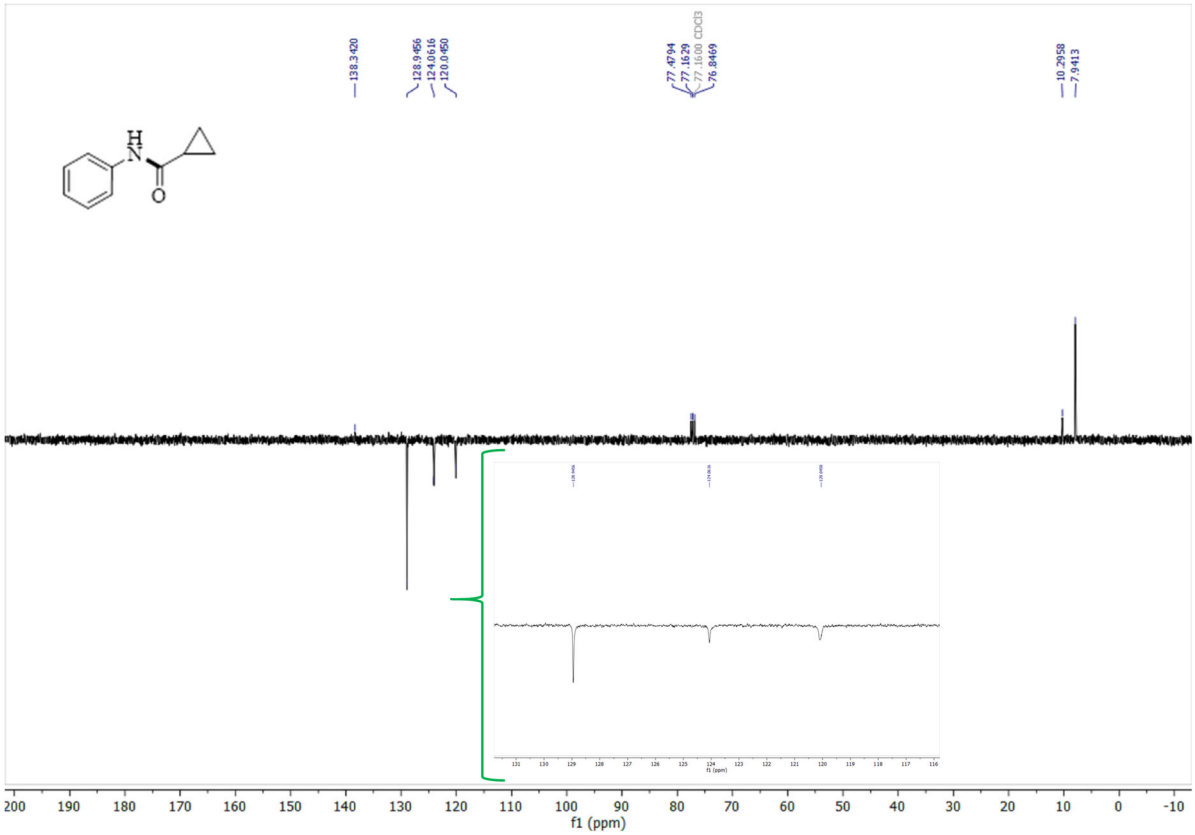

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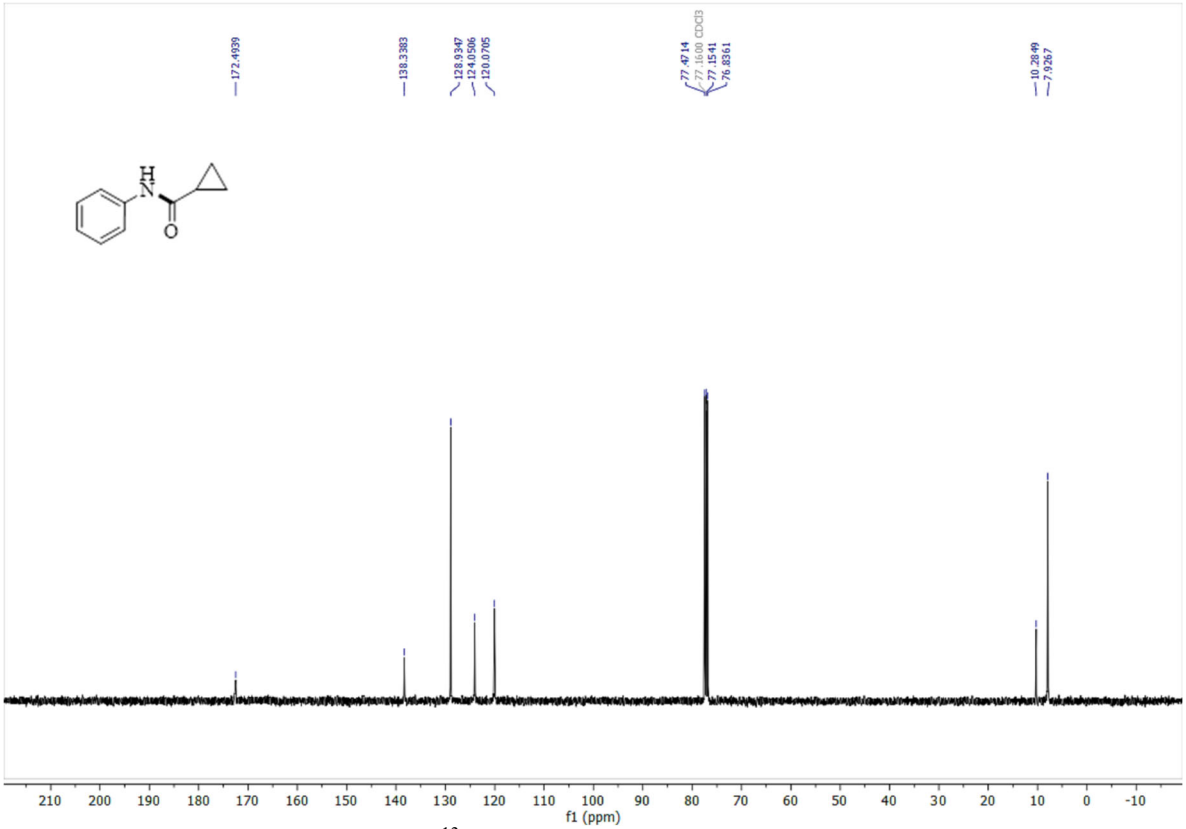
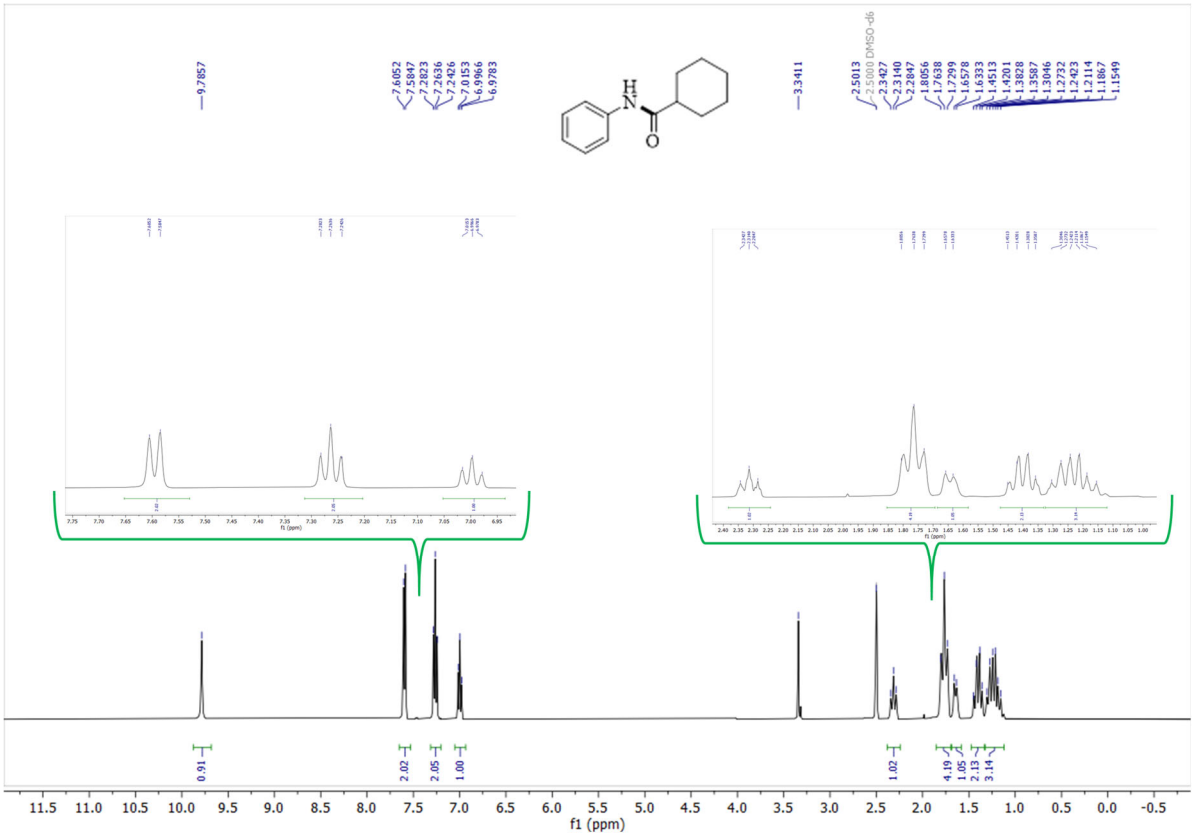
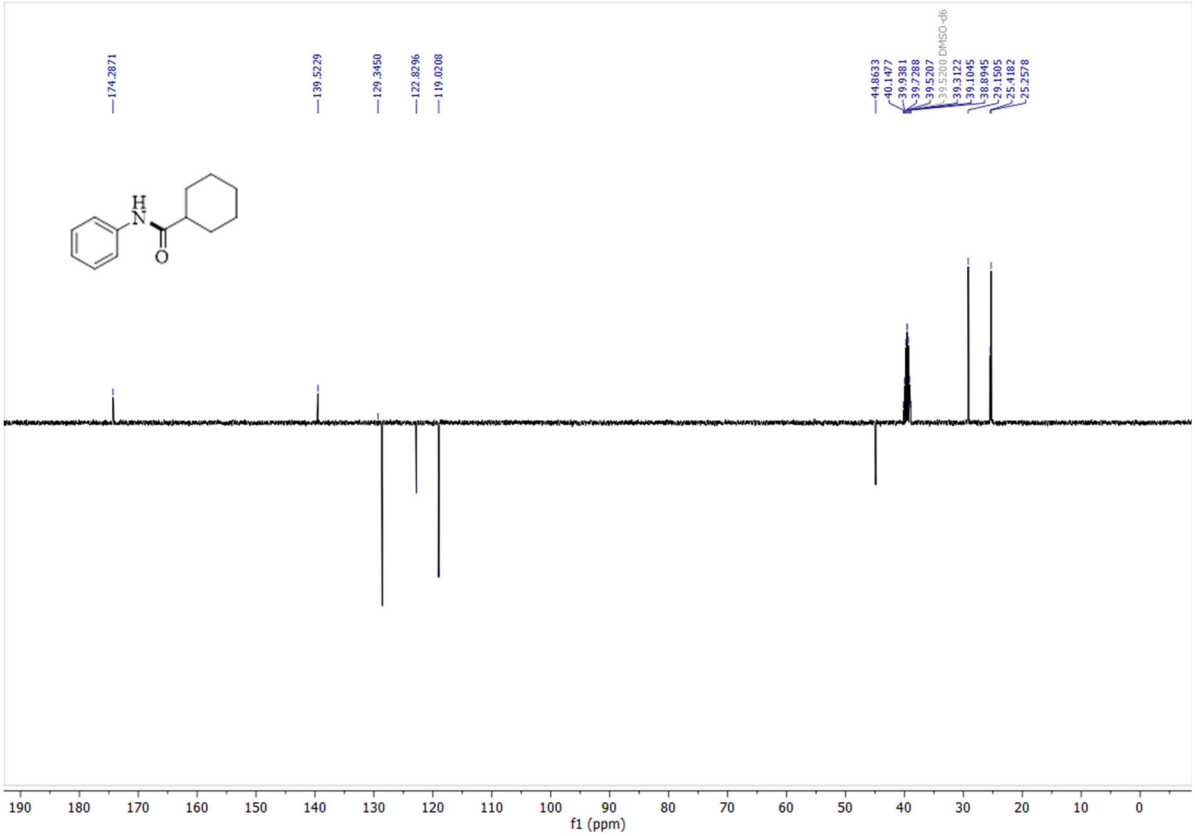


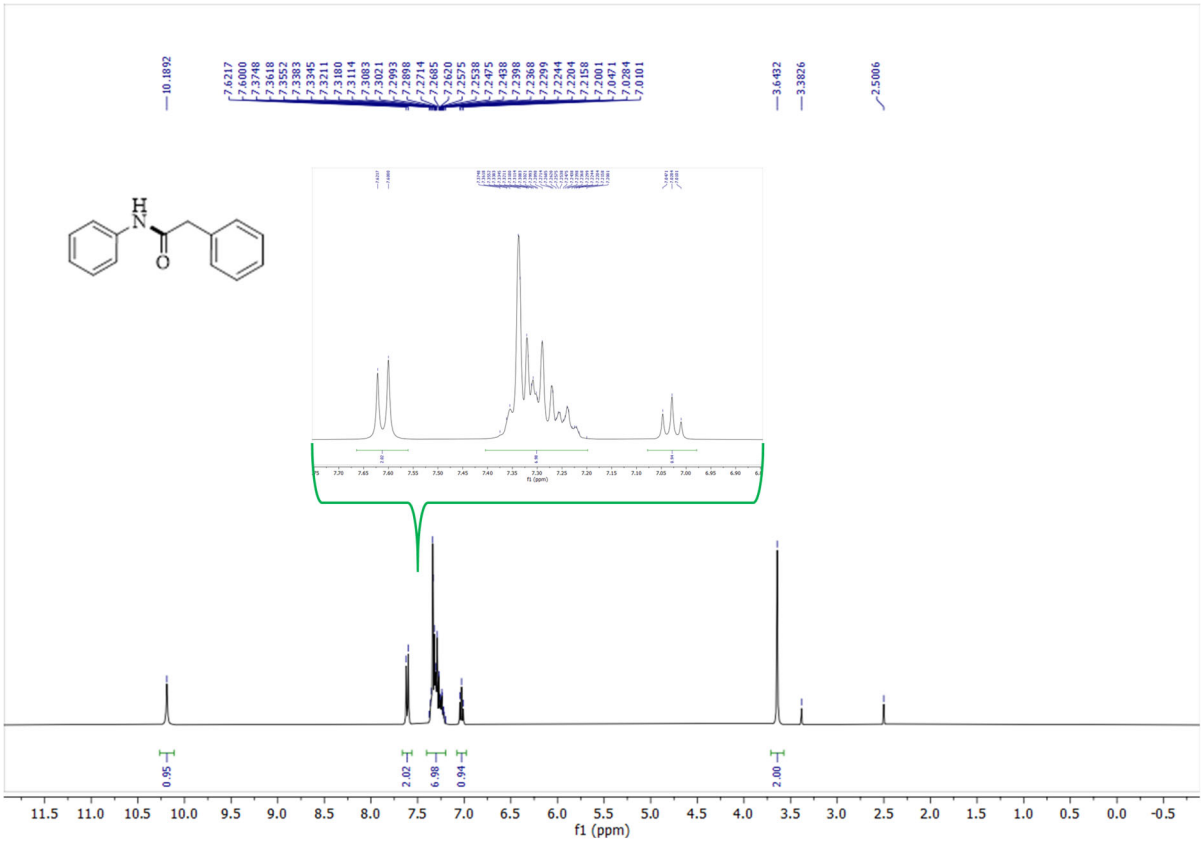
^{13}C NMR spectrum of **3H**



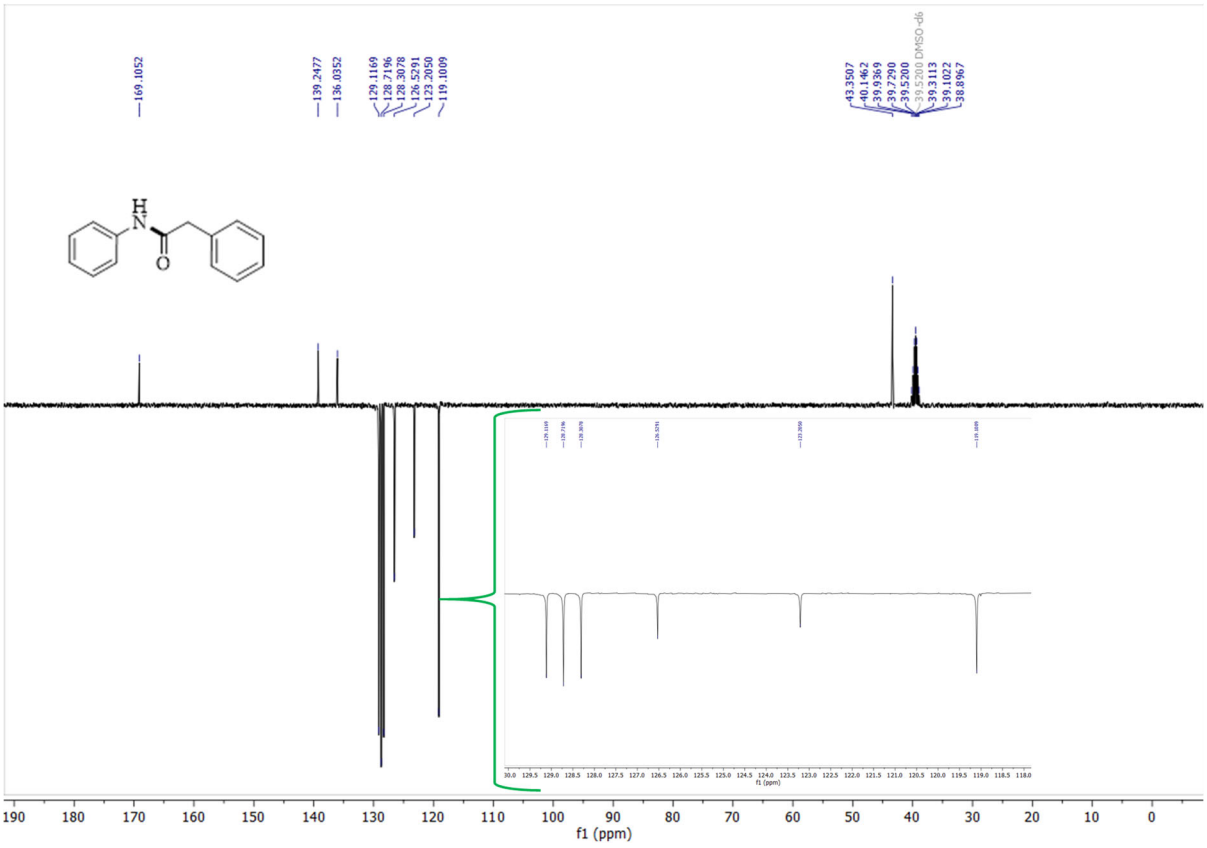
^{1}H NMR spectrum of **3I**



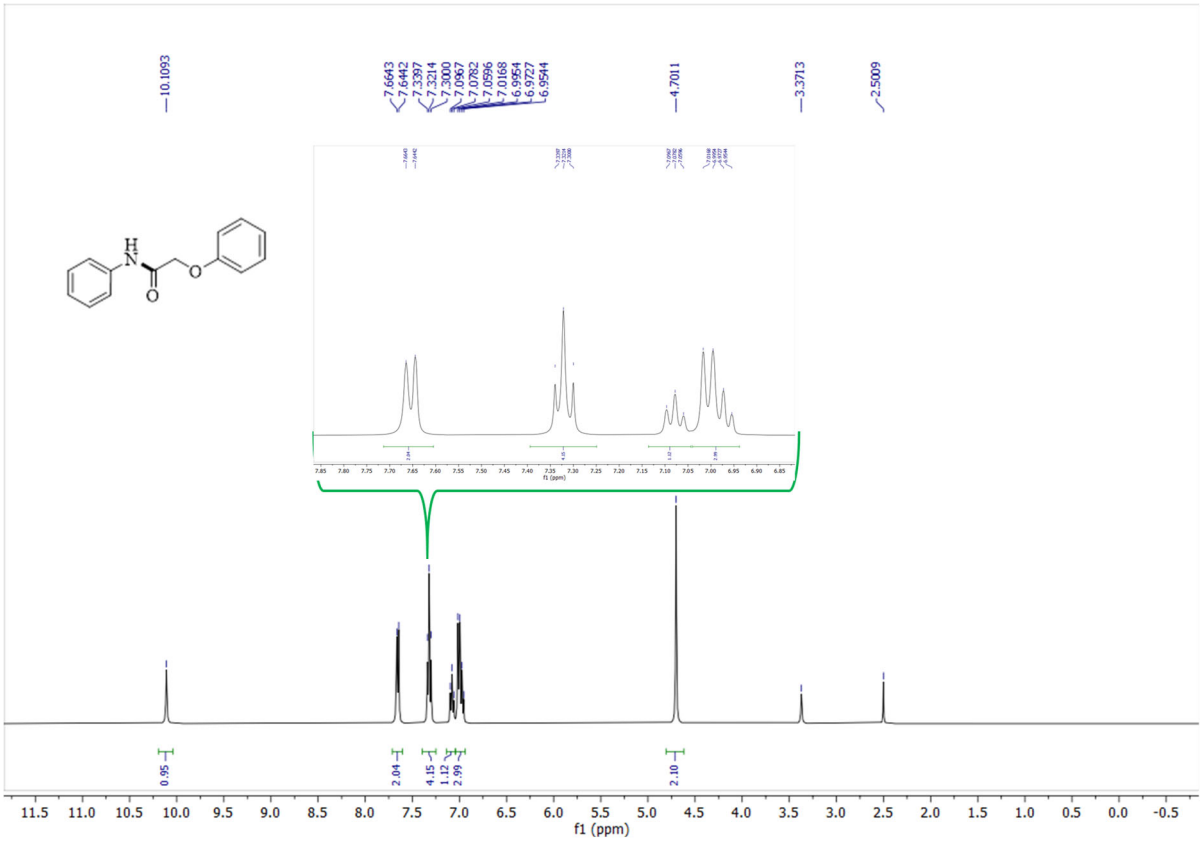
^{13}C NMR spectrum of **3I**



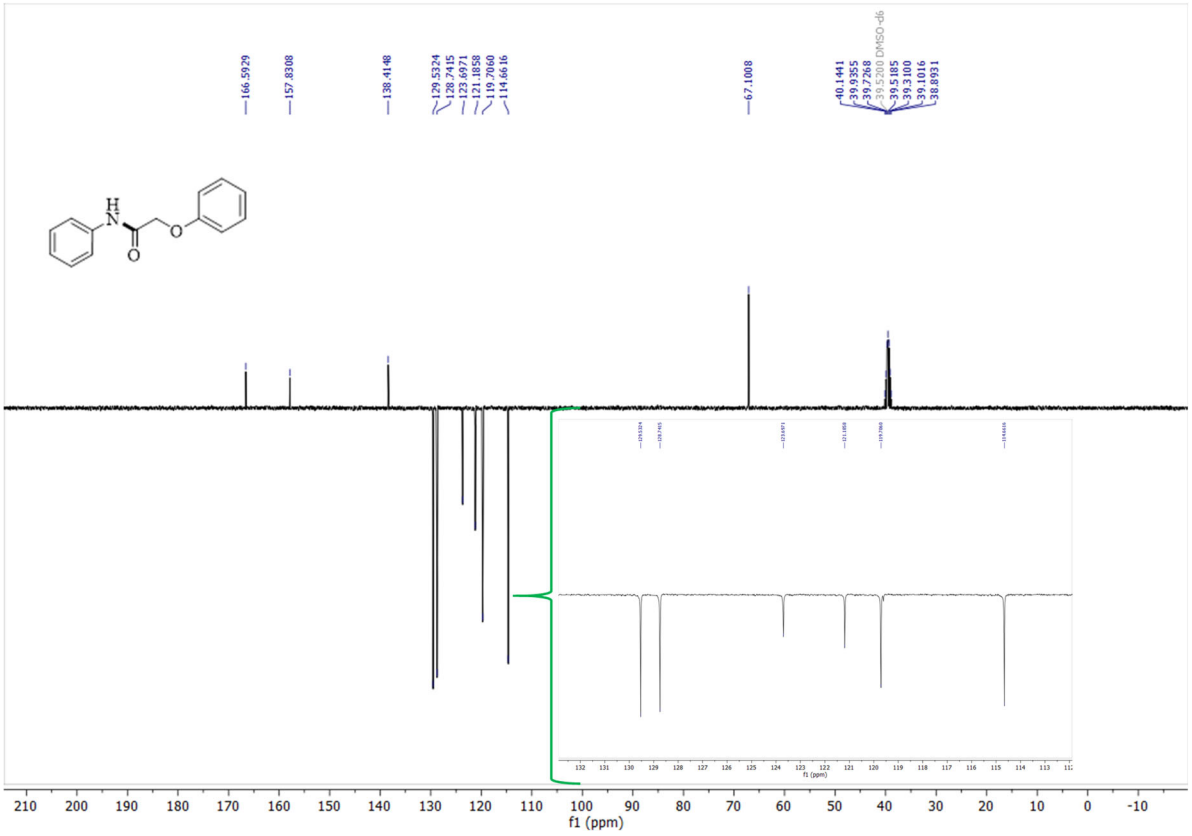
^{1}H NMR spectrum of **3J**



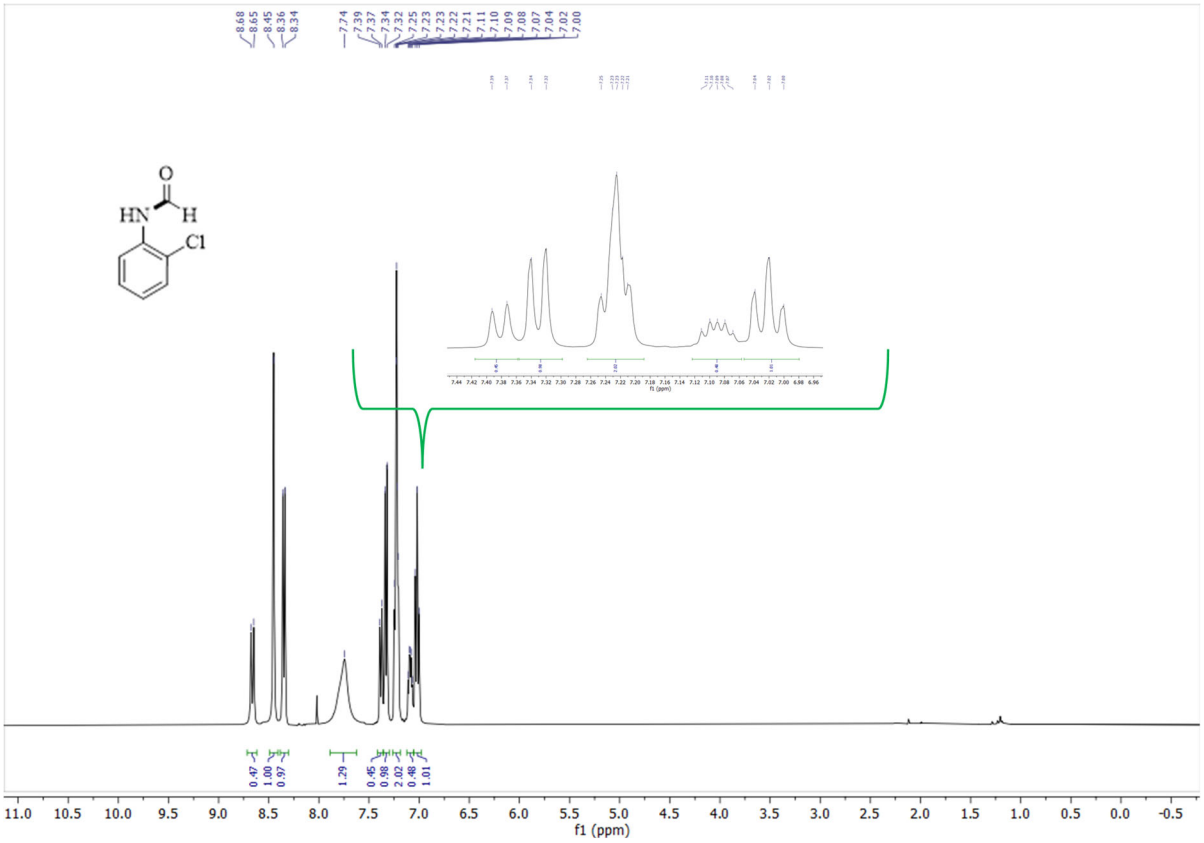
^{13}C NMR spectrum of **3J**



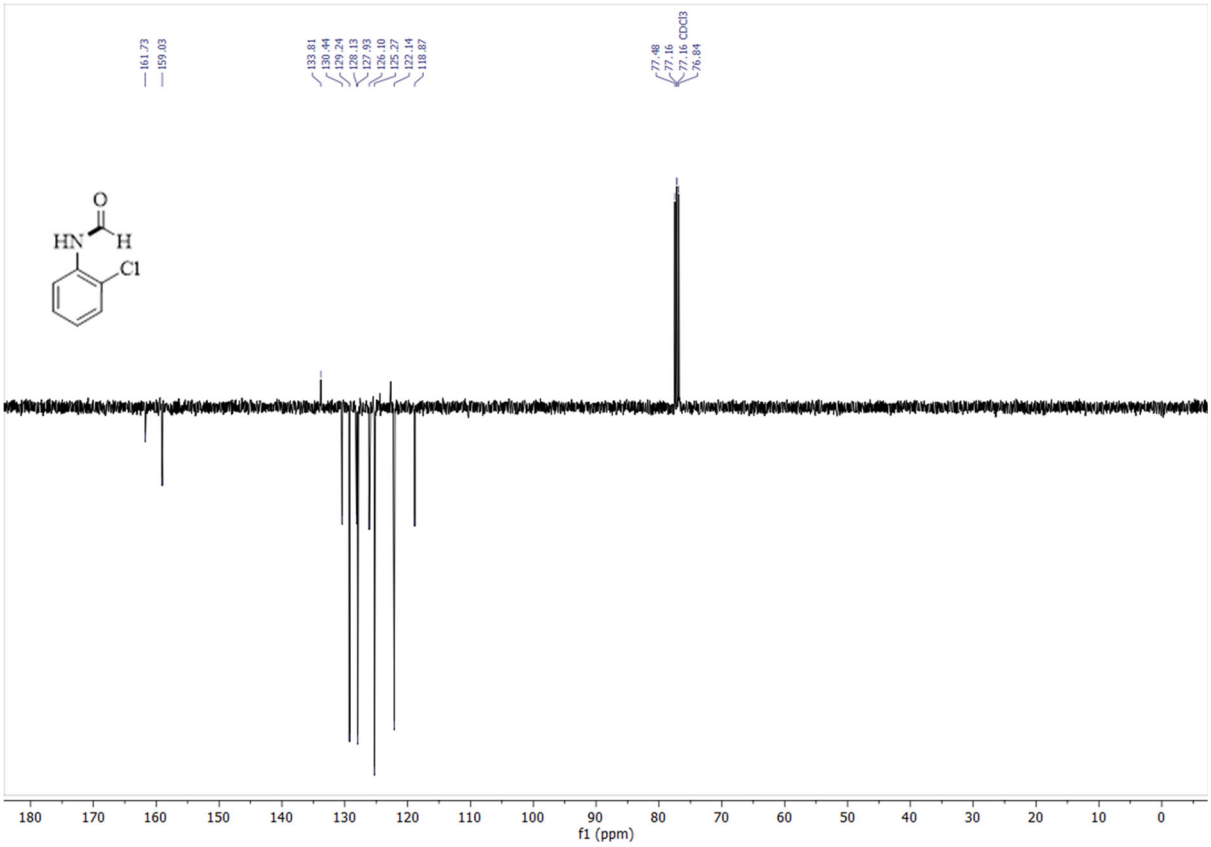
^{1}H NMR spectrum of **3K**



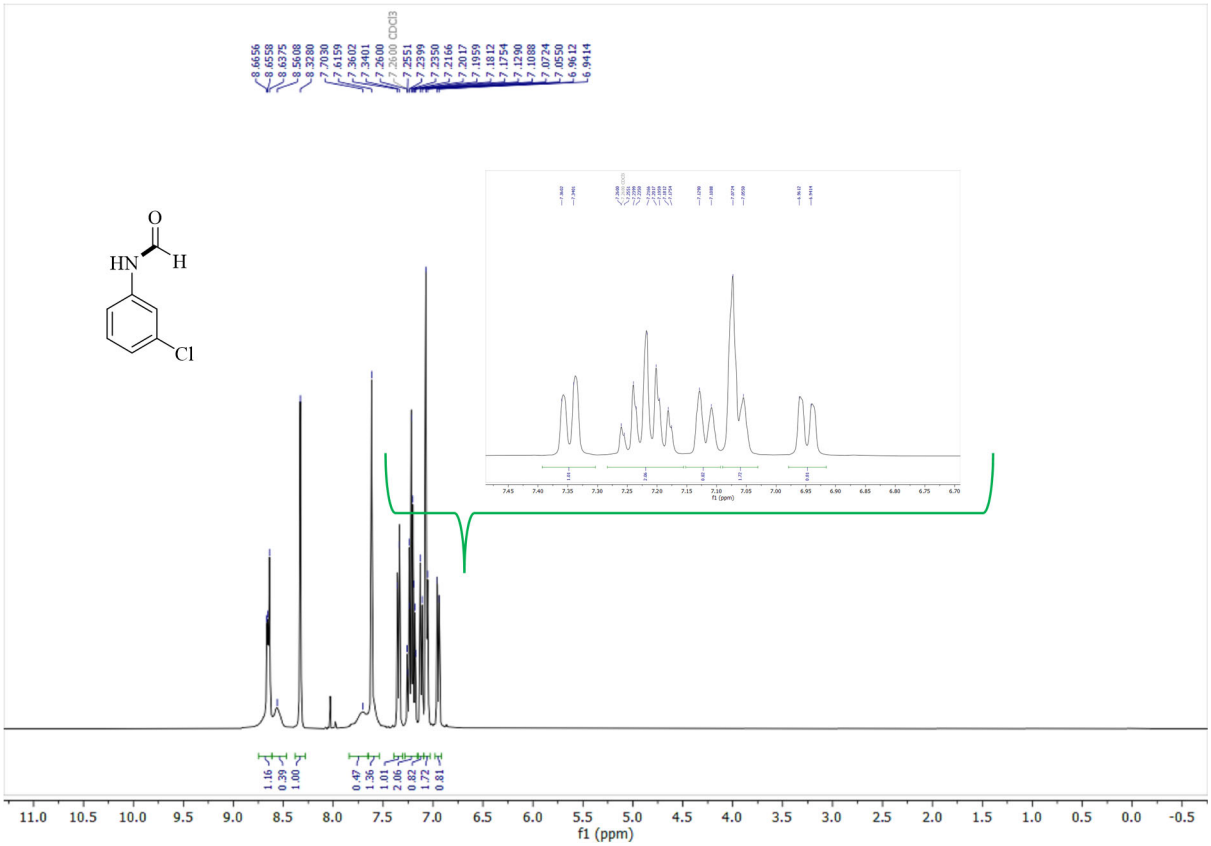
^{13}C NMR spectrum of **3K**



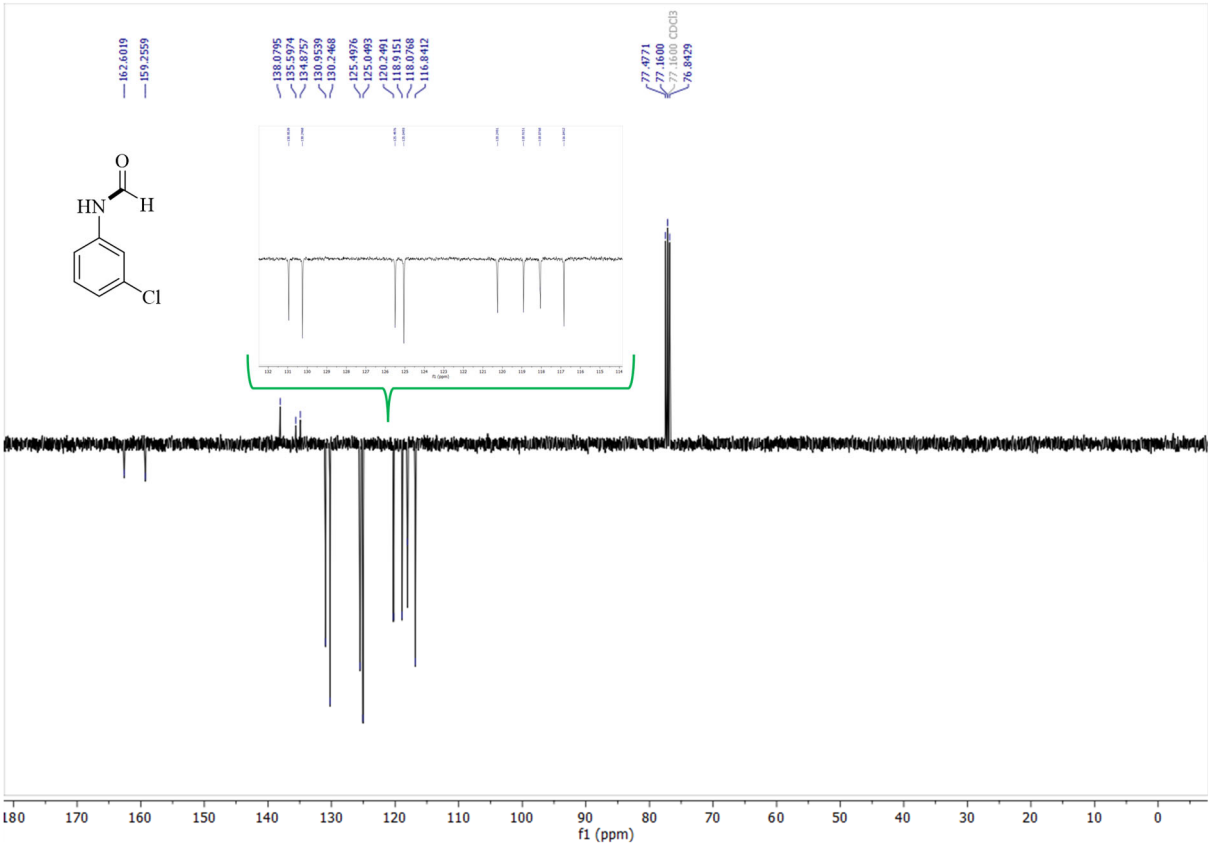
^{1}H NMR spectrum of **3a**



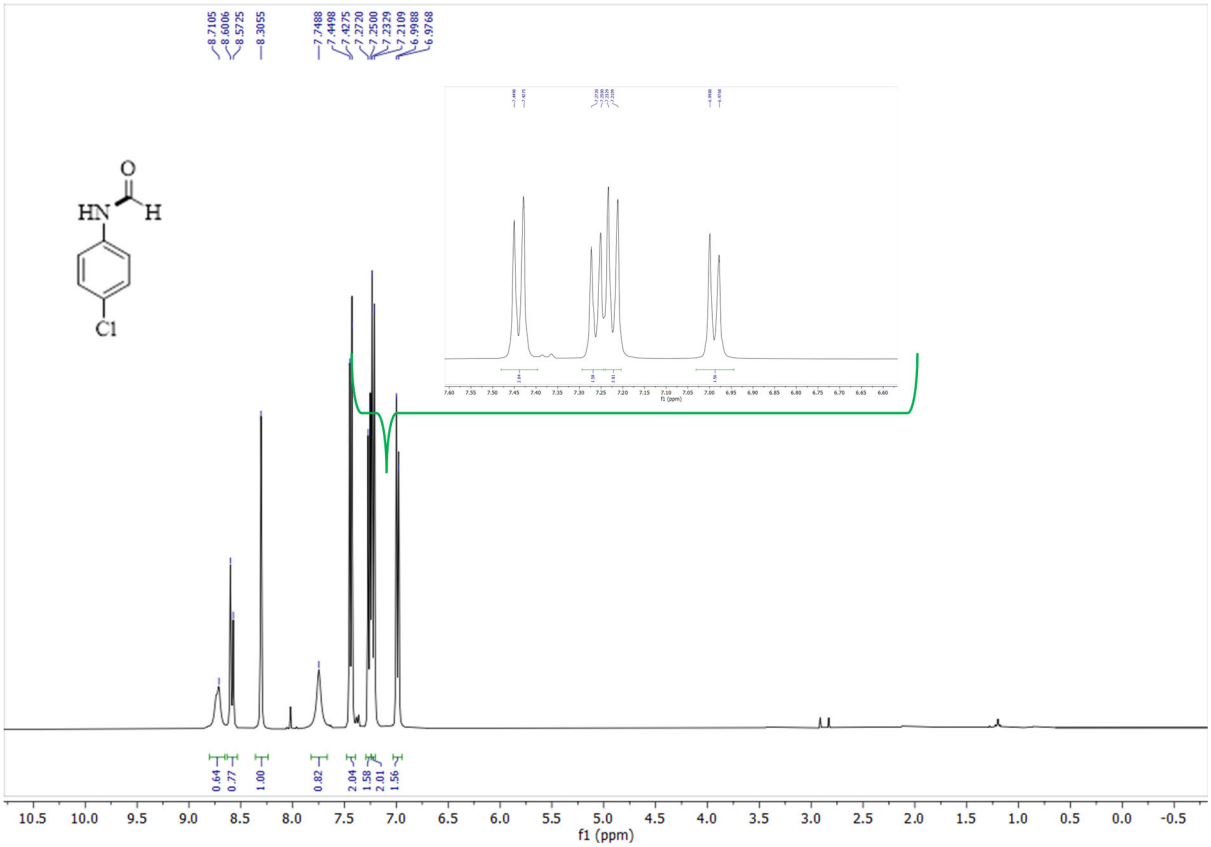
^{13}C NMR spectrum of **3a**



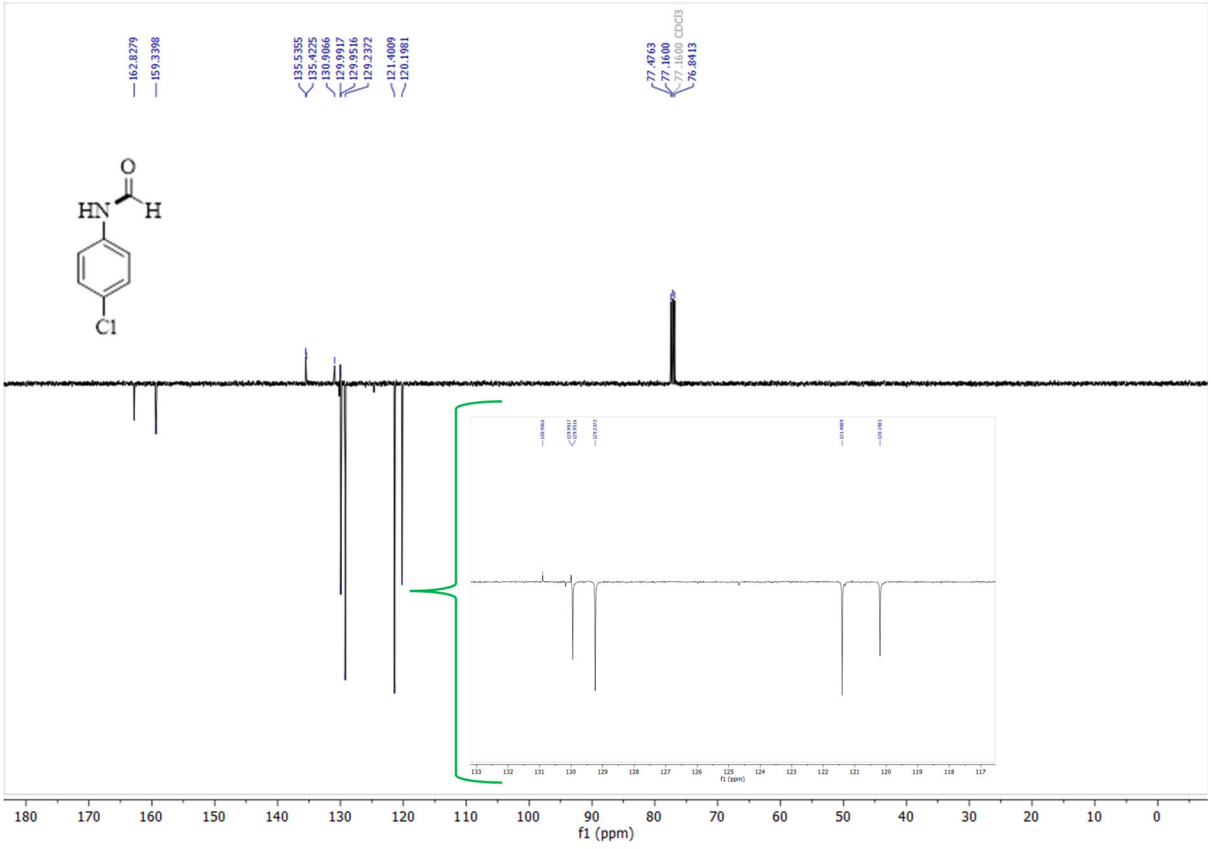
^{1}H NMR spectrum of **3b**



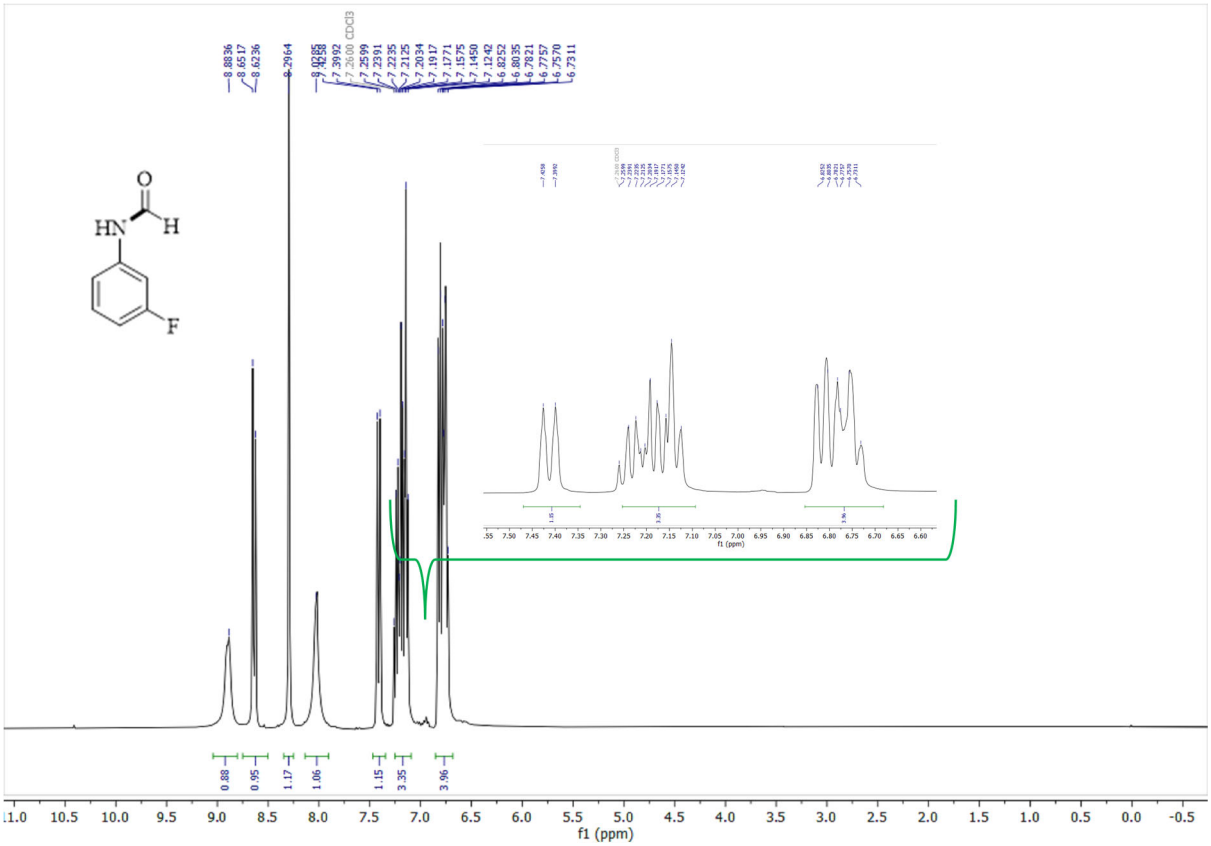
^{13}C NMR spectrum of **3b**



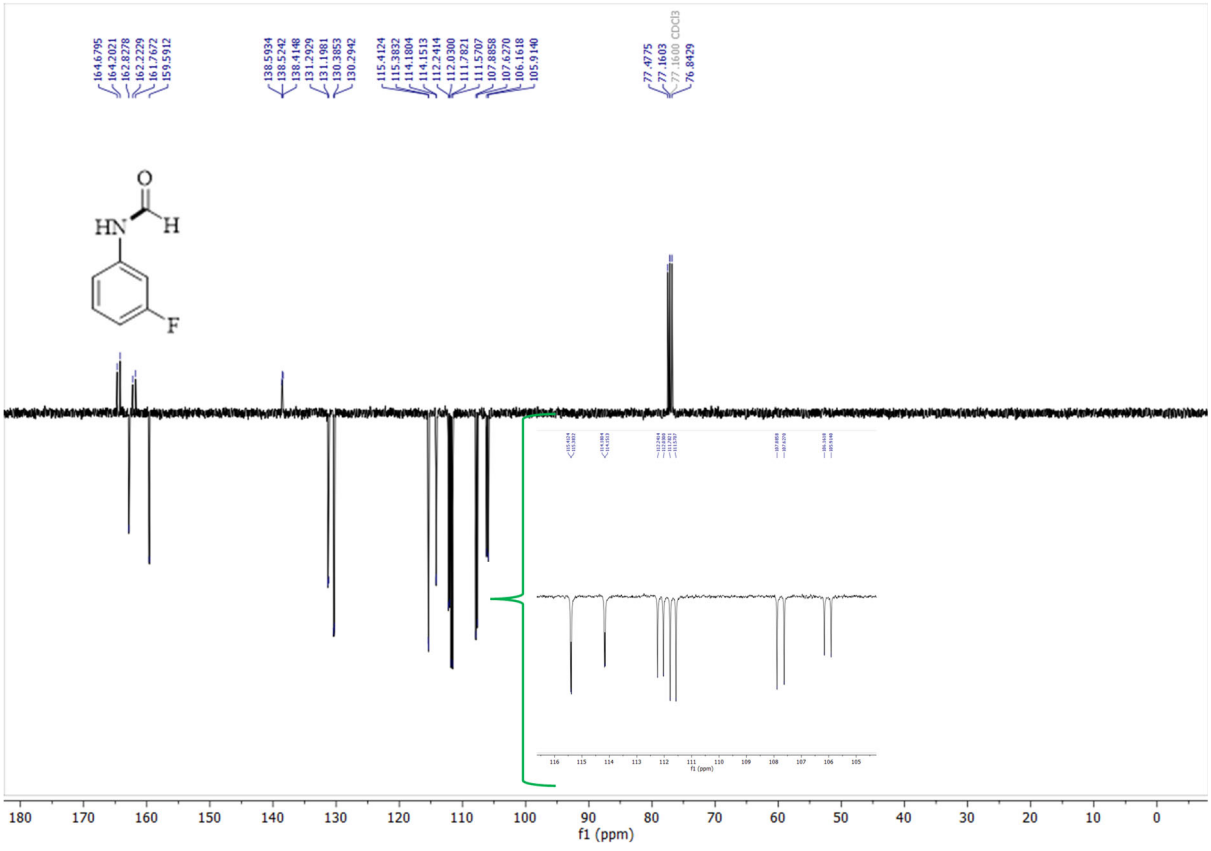
^{1}H NMR spectrum of **3c**



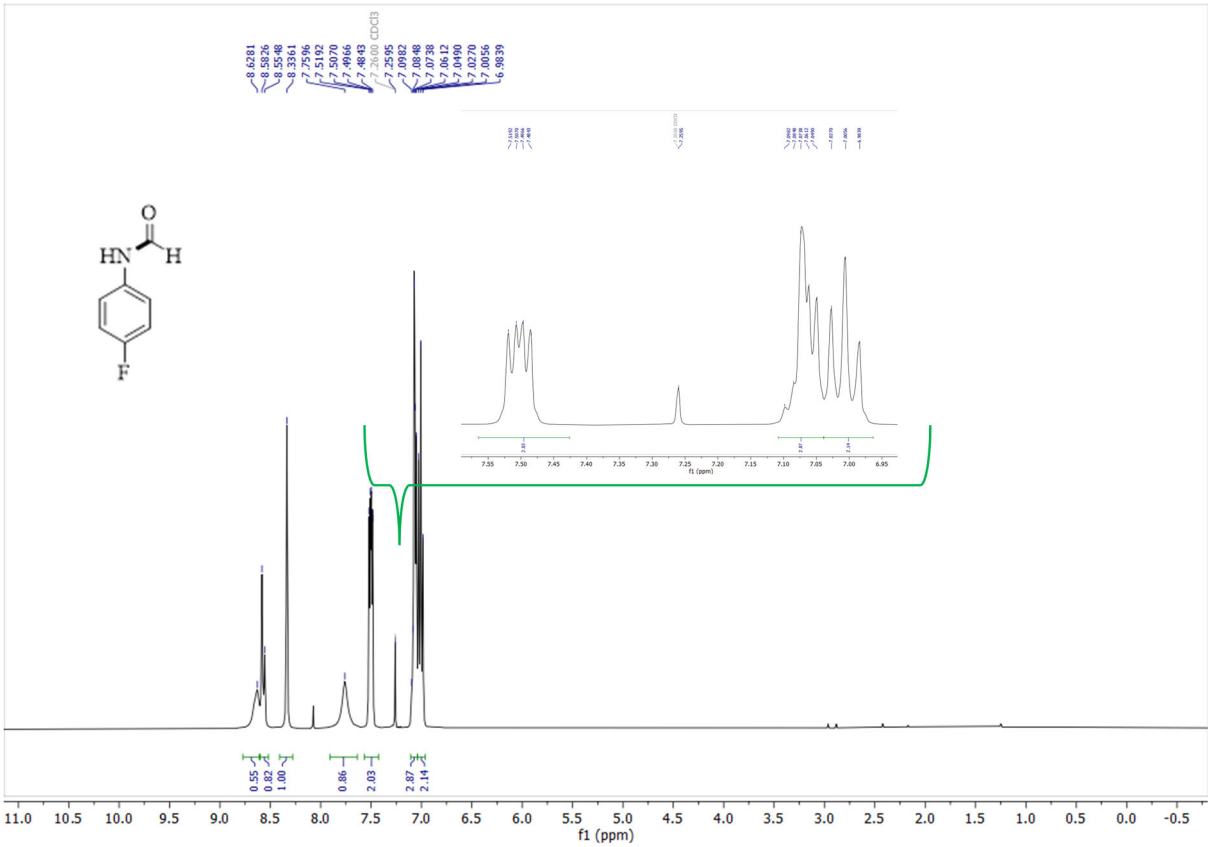
^{13}C NMR spectrum of **3c**



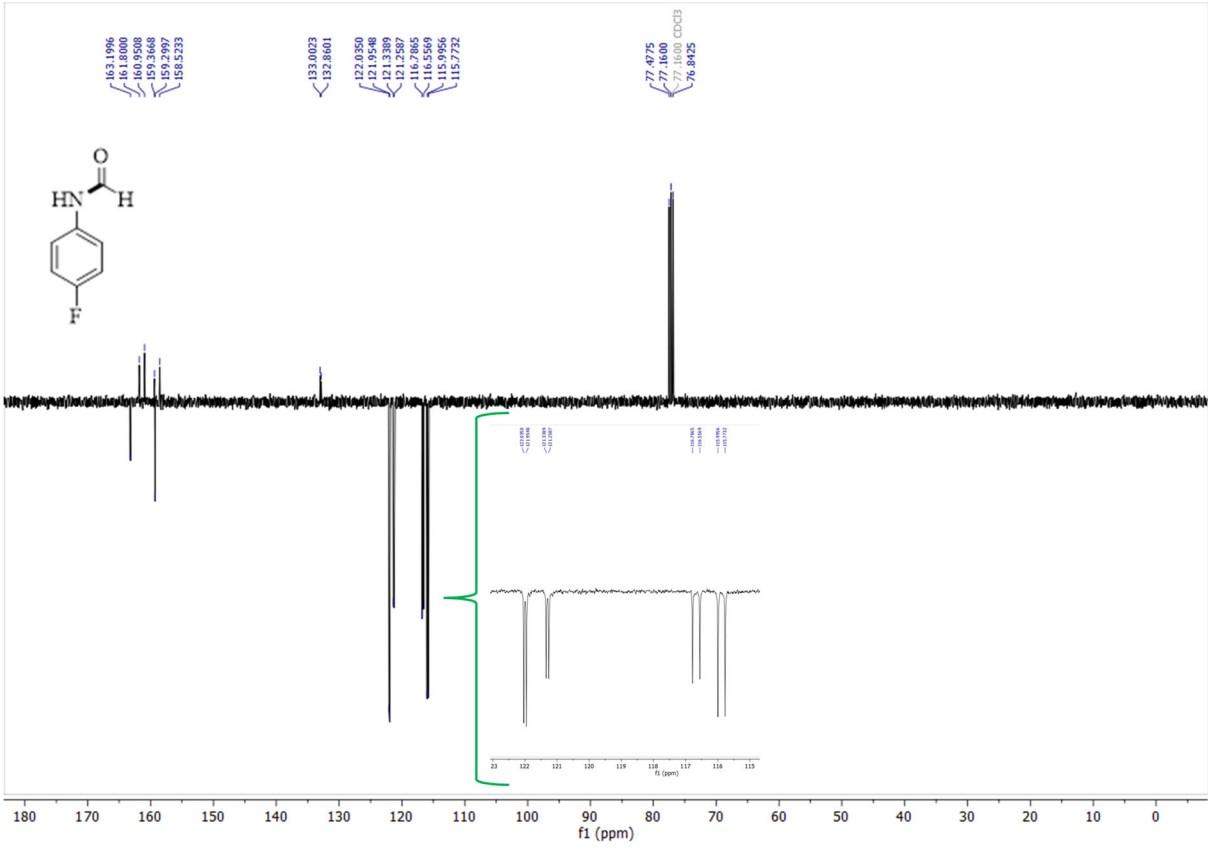
^{1}H NMR spectrum of **3d**



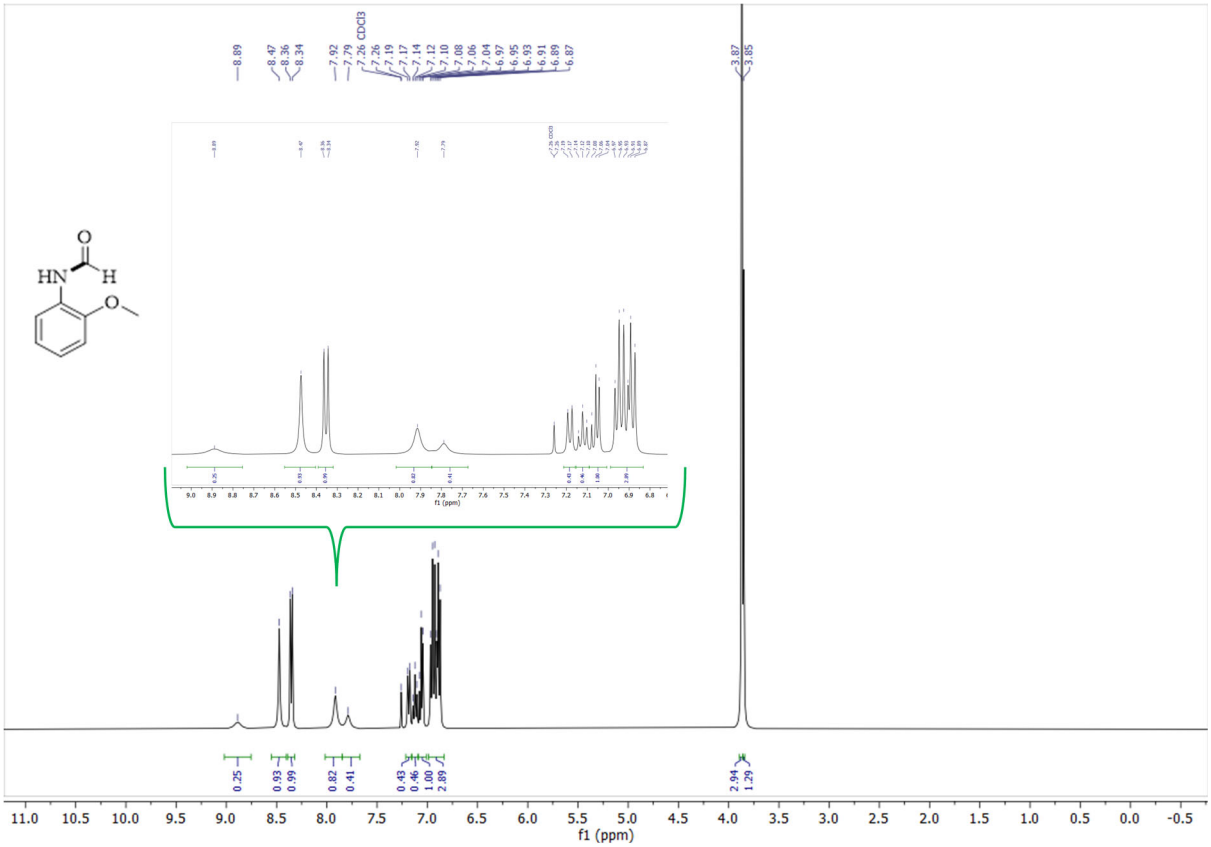
^{13}C NMR spectrum of **3d**



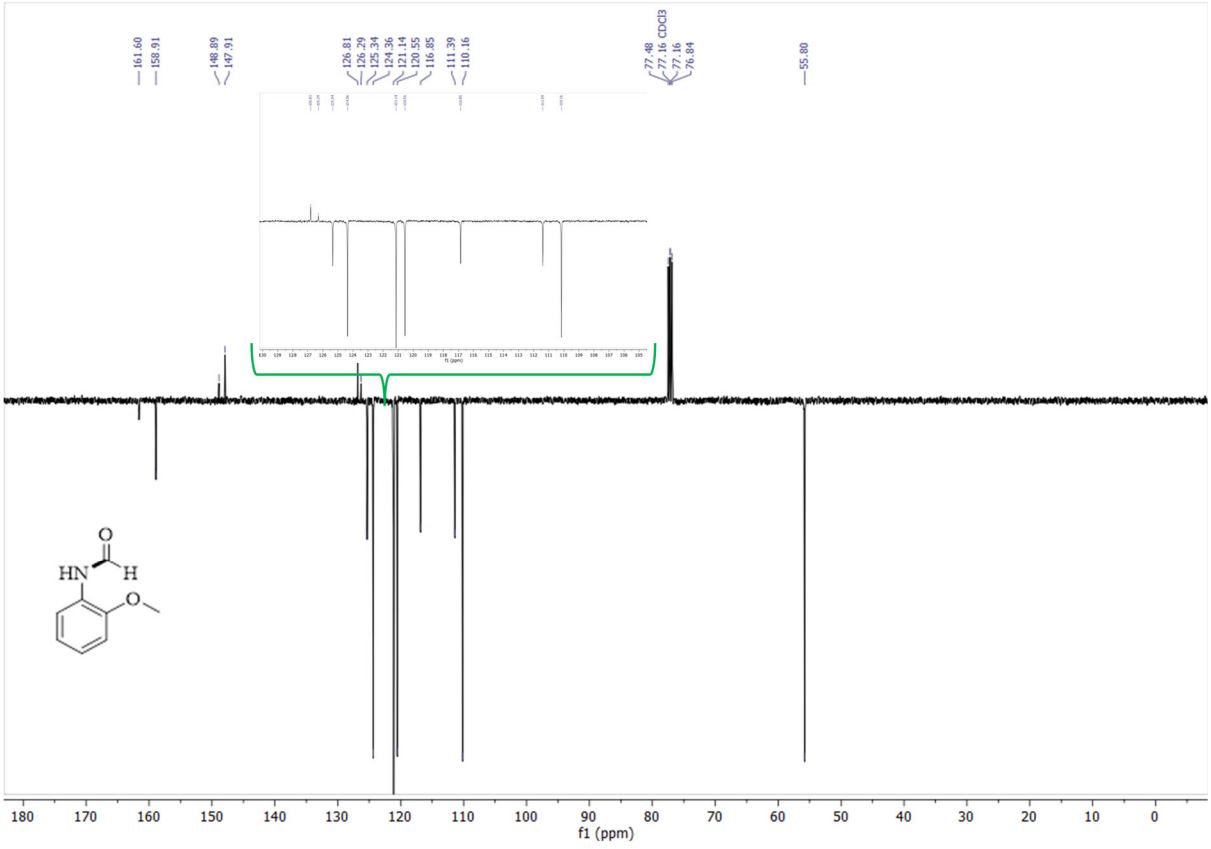
^{1}H NMR spectrum of **3e**



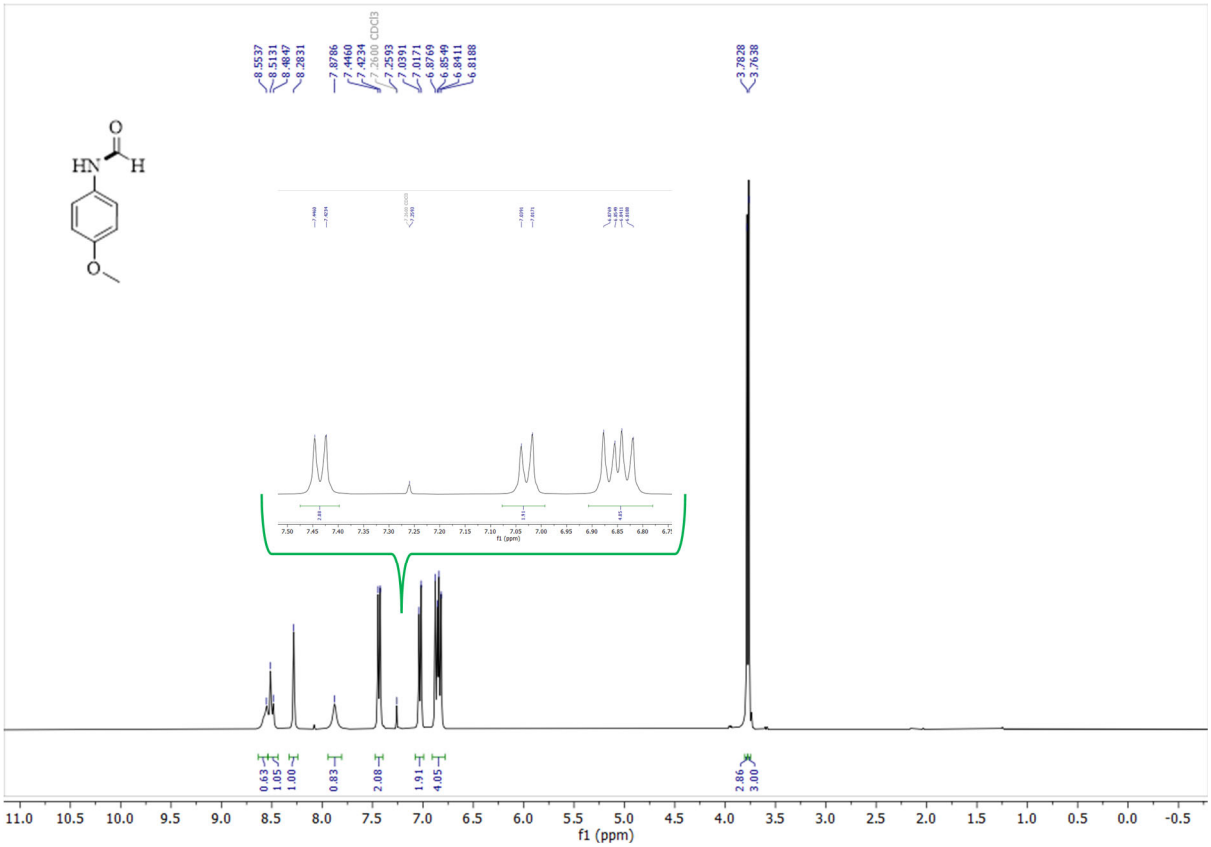
^{13}C NMR spectrum of **3e**



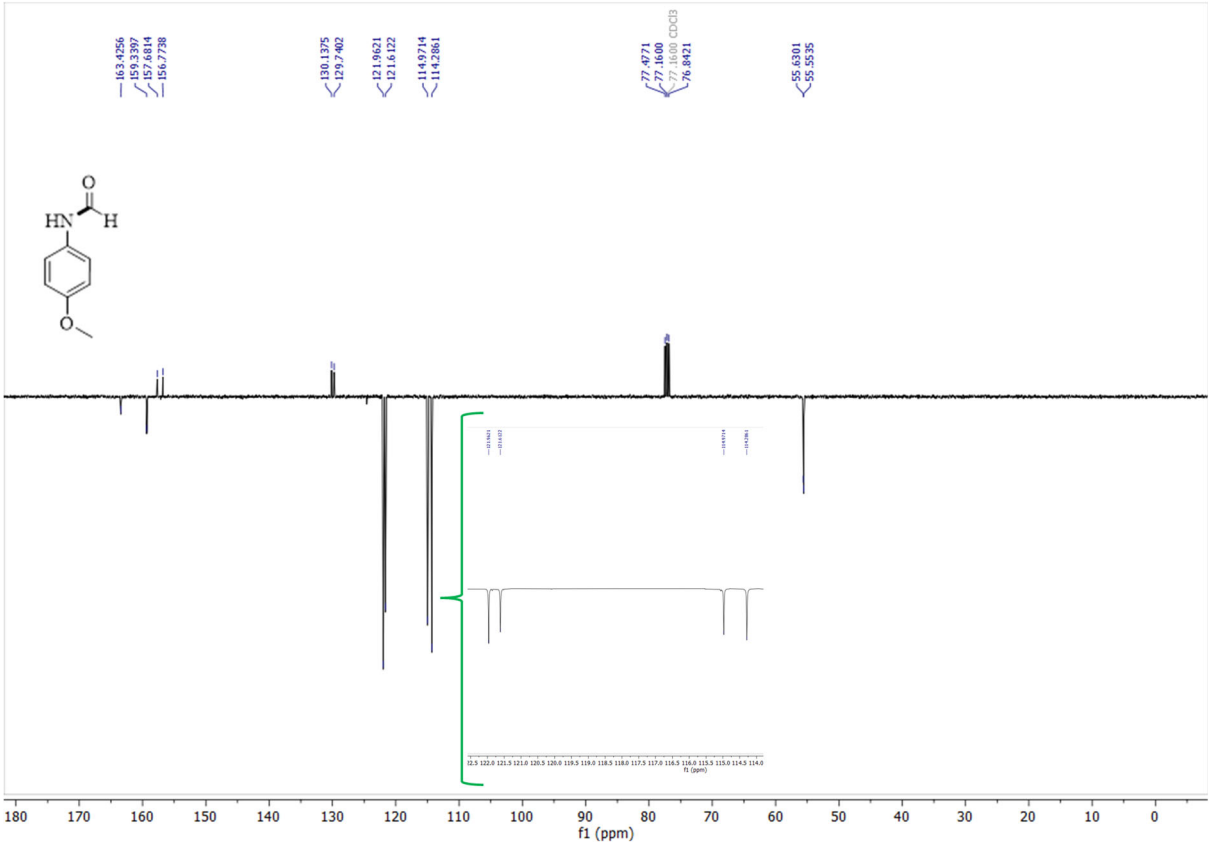
^{1}H NMR spectrum of **3f**



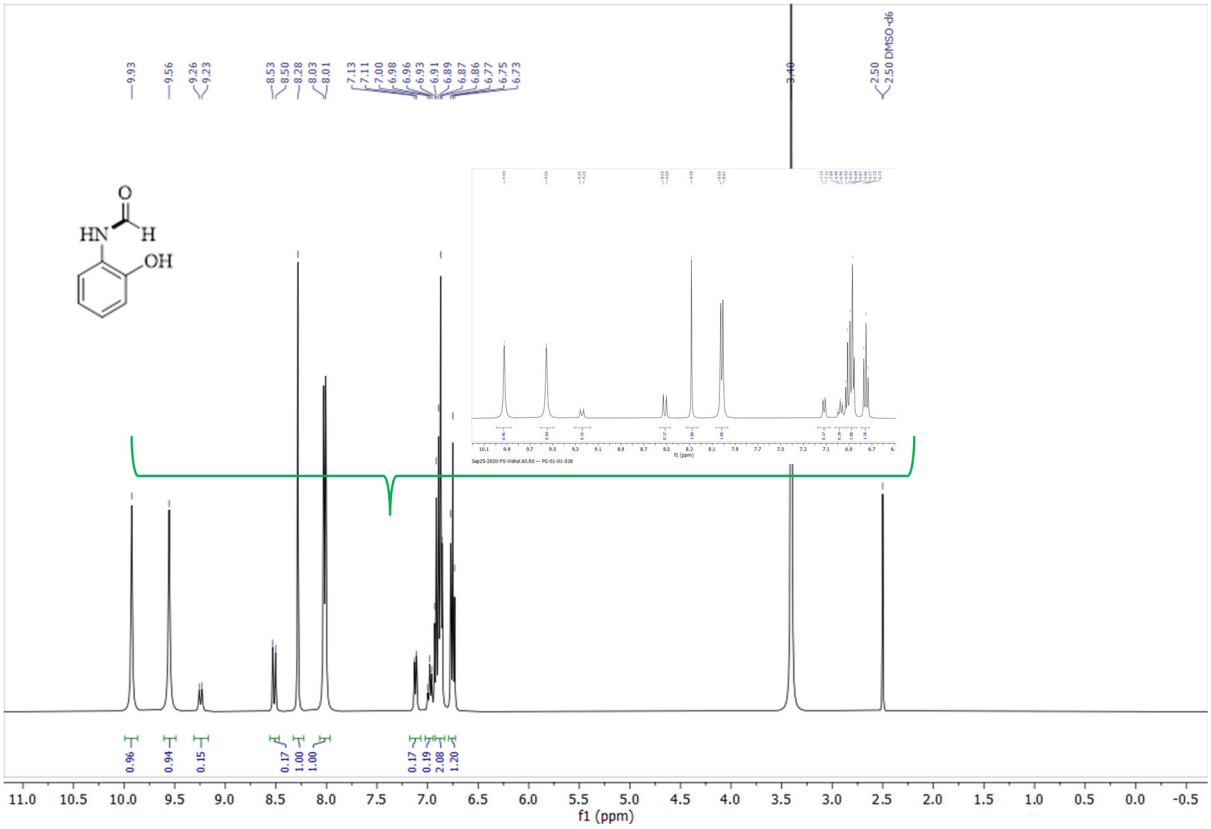
^{13}C NMR spectrum of **3f**



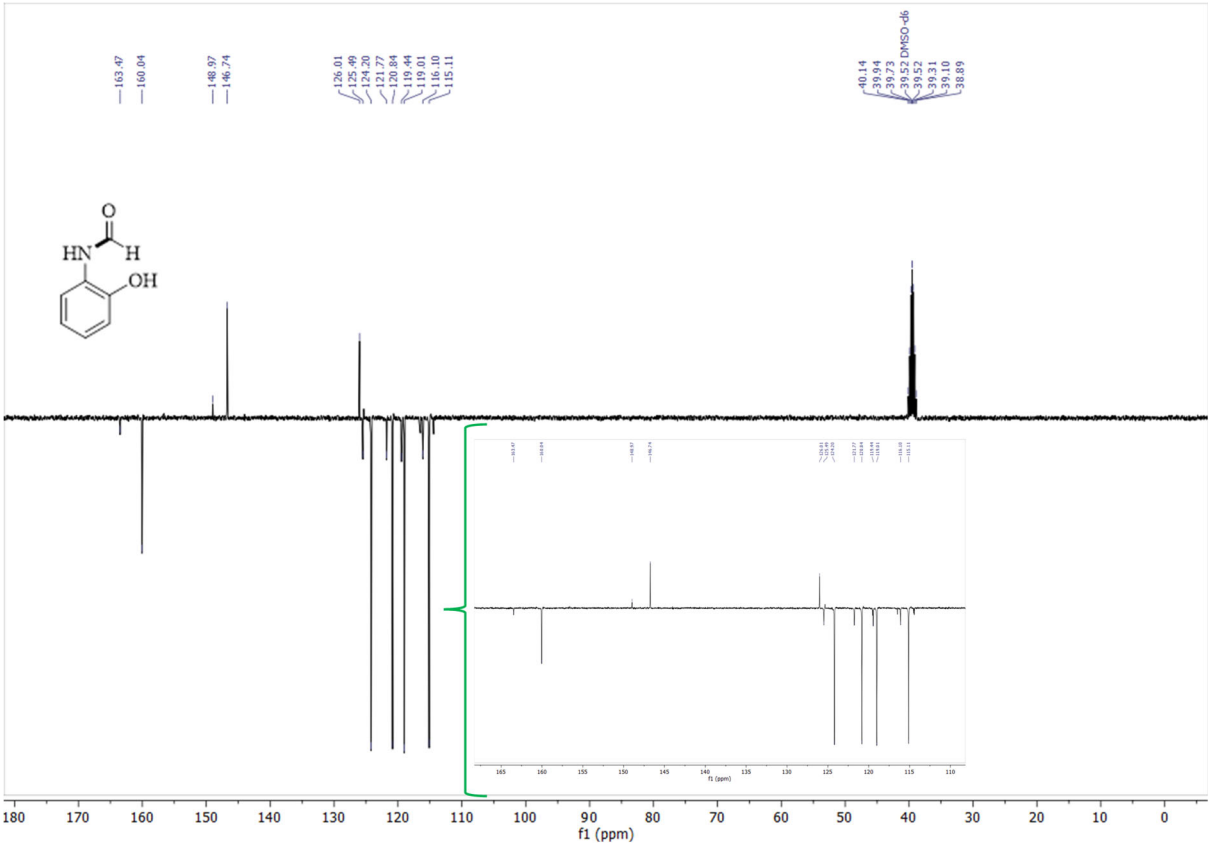
^{1}H NMR spectrum of **3g**



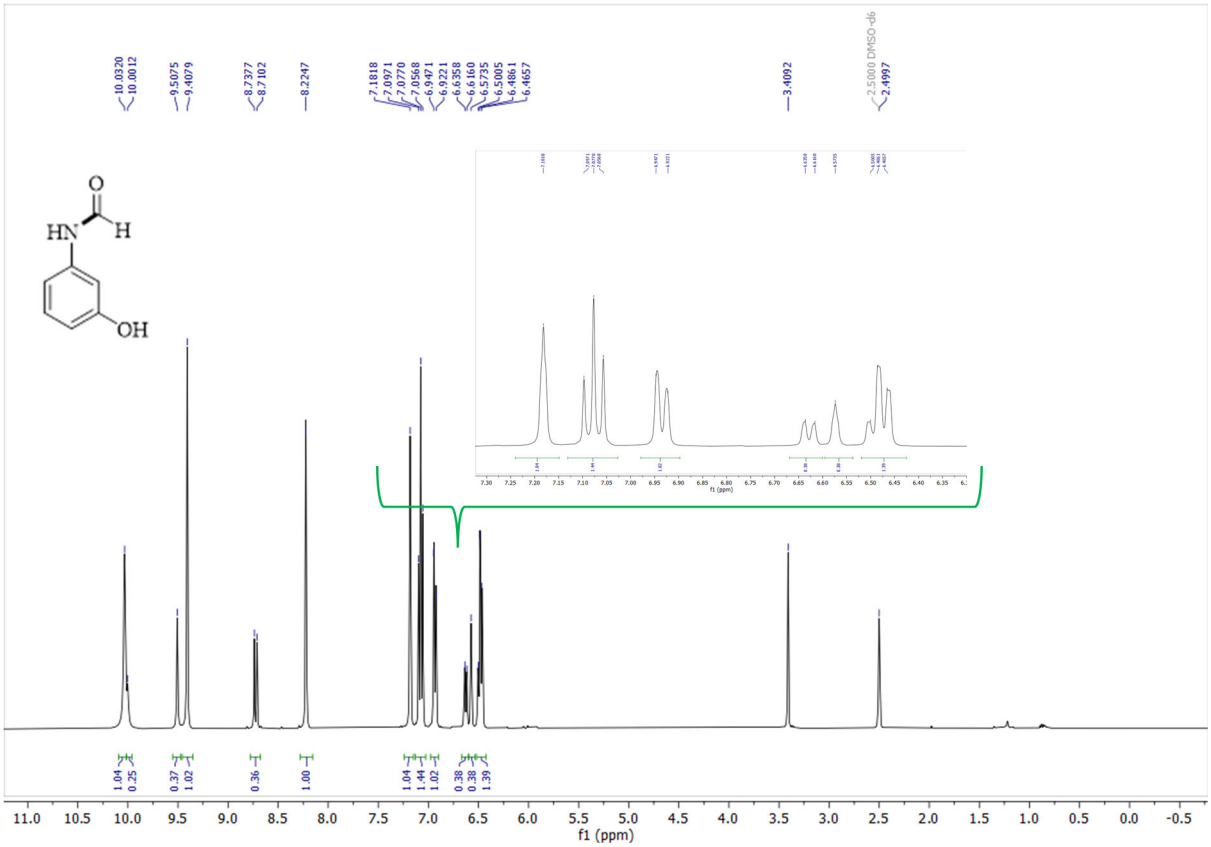
^{13}C NMR spectrum of **3g**



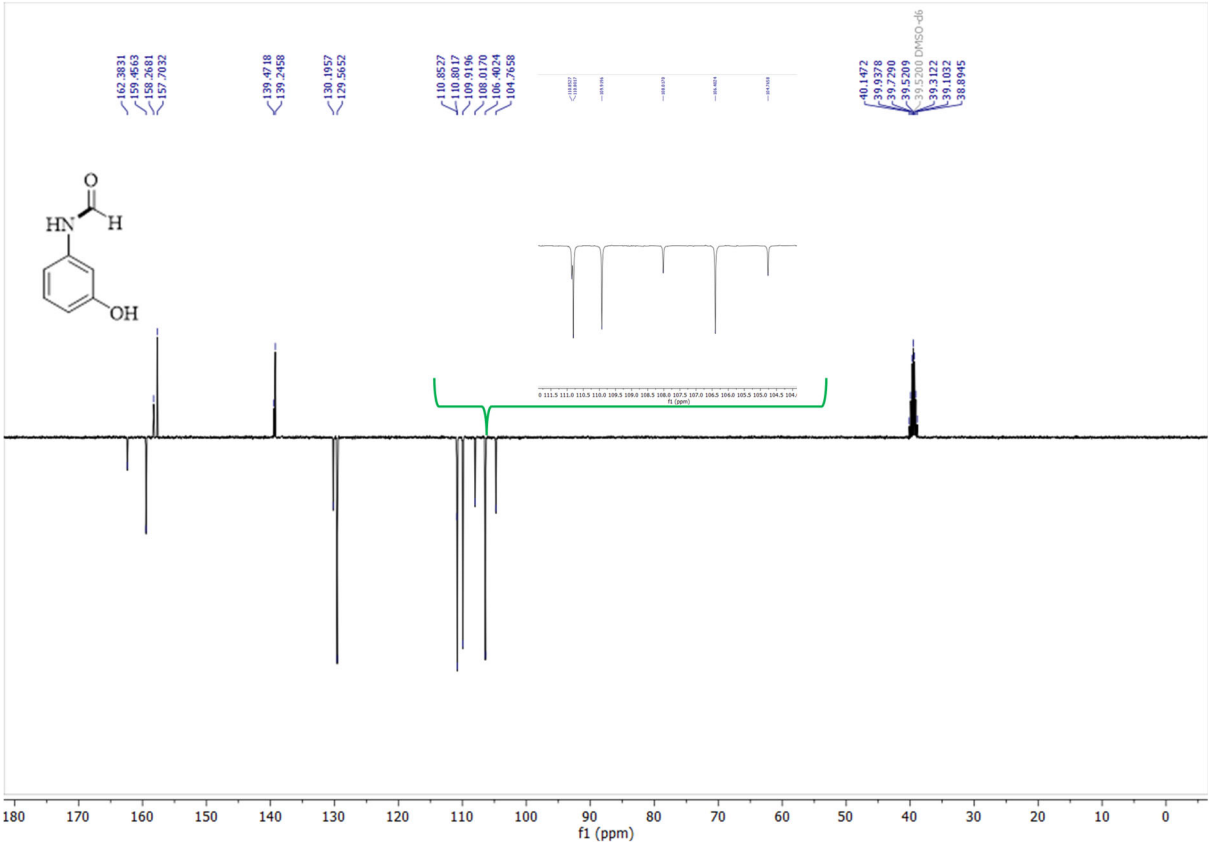
^{1}H NMR spectrum of **3h**



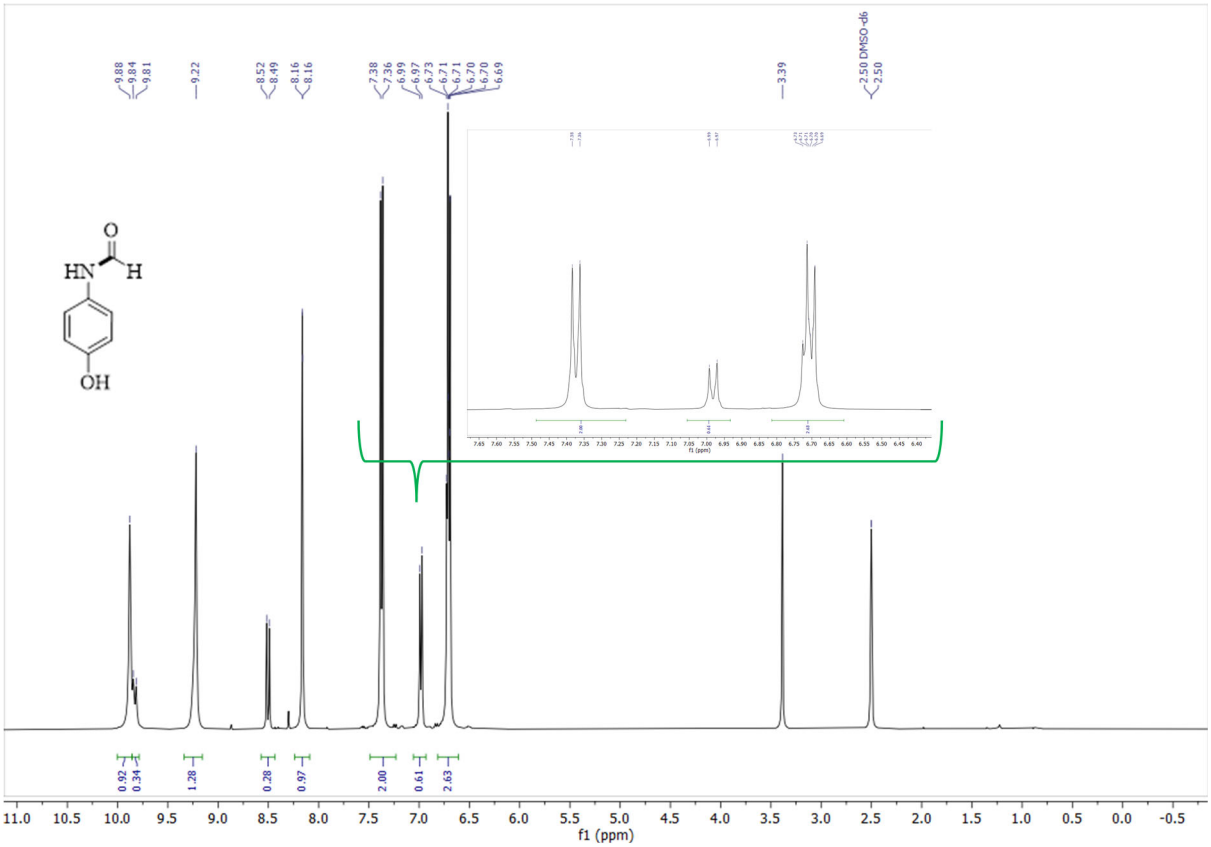
^{13}C NMR spectrum of **3h**



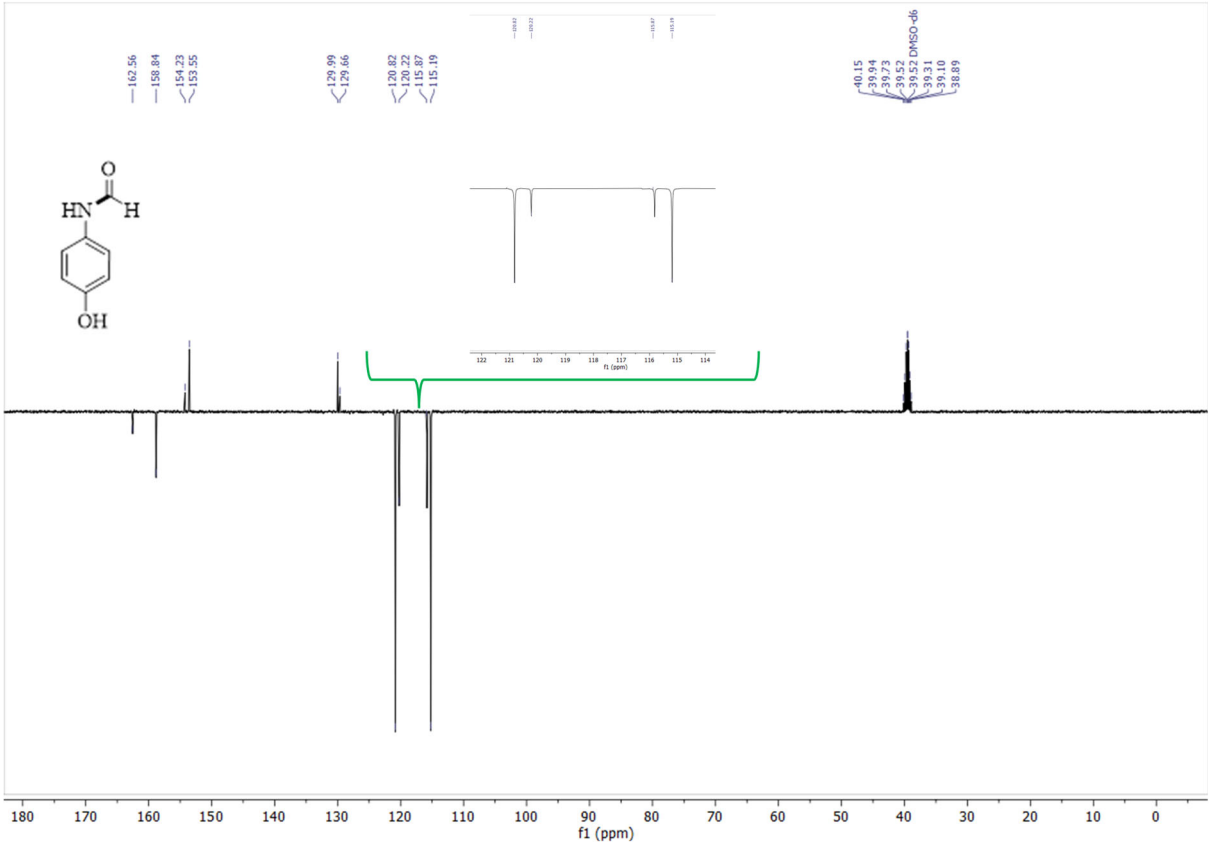
^{1}H NMR spectrum of **3i**



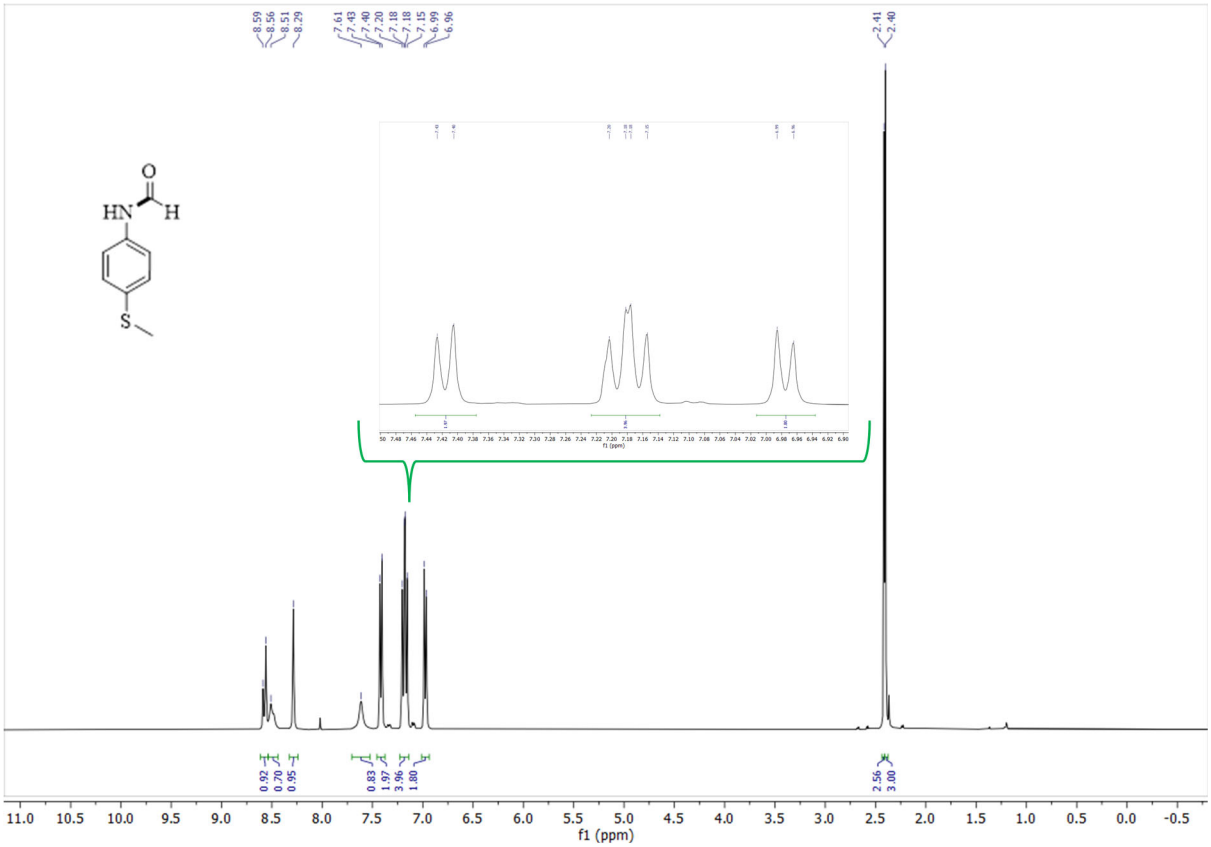
^{13}C NMR spectrum of **3i**



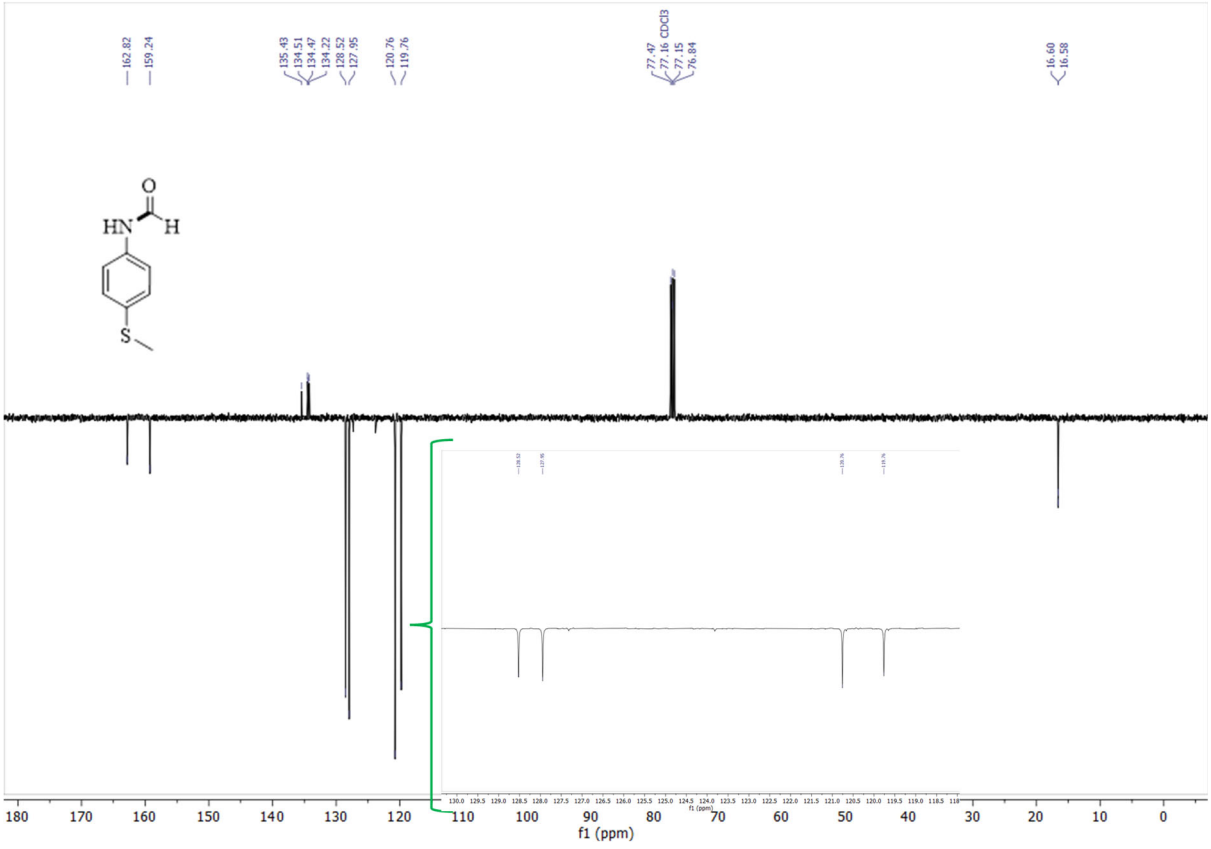
^{1}H NMR spectrum of **3j**



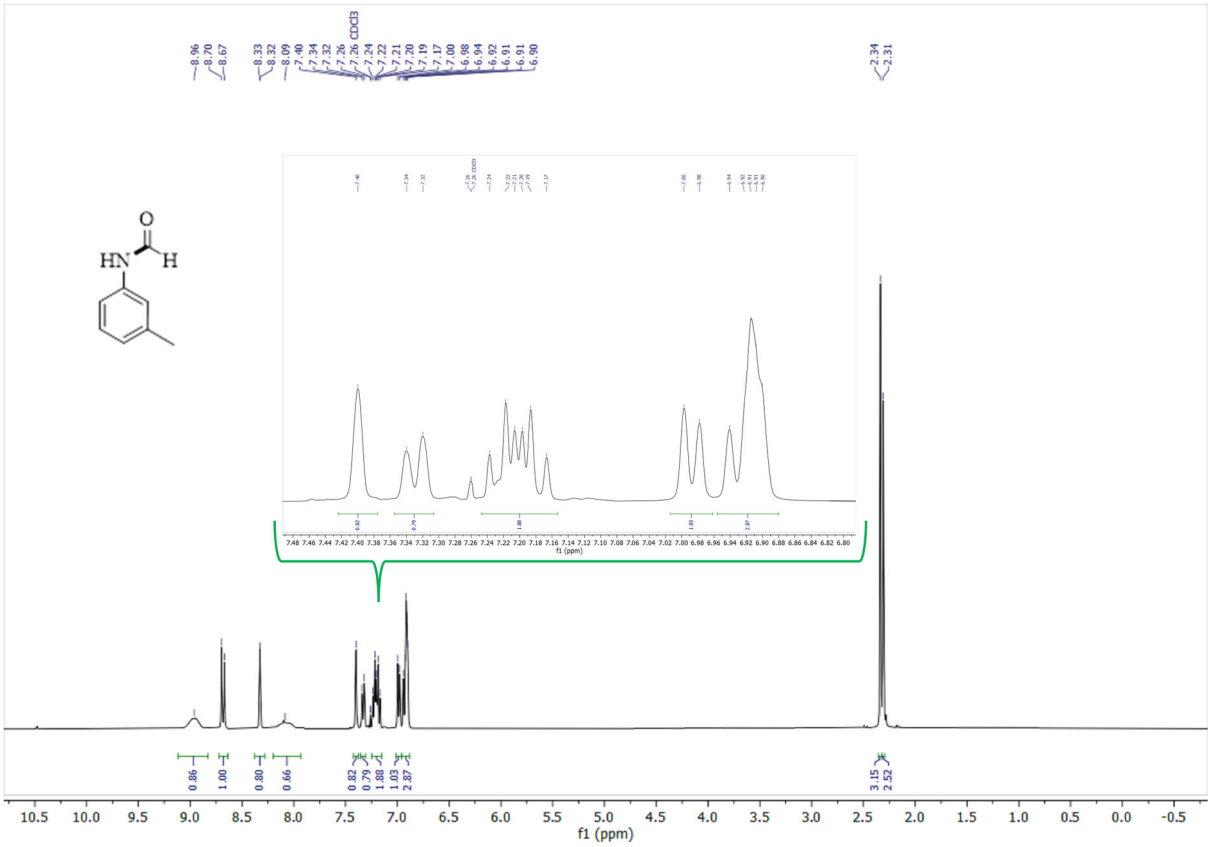
^{13}C NMR spectrum of **3j**



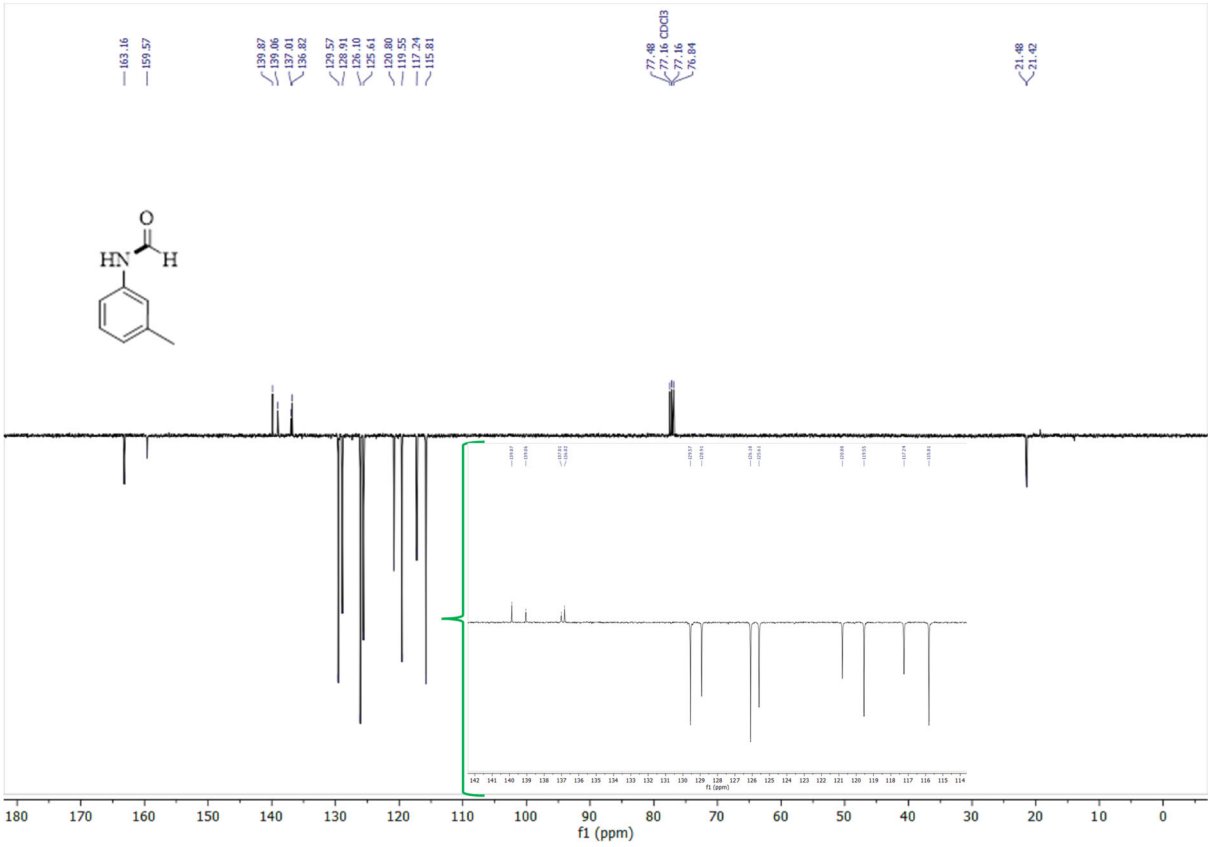
^{1}H NMR spectrum of **3k**



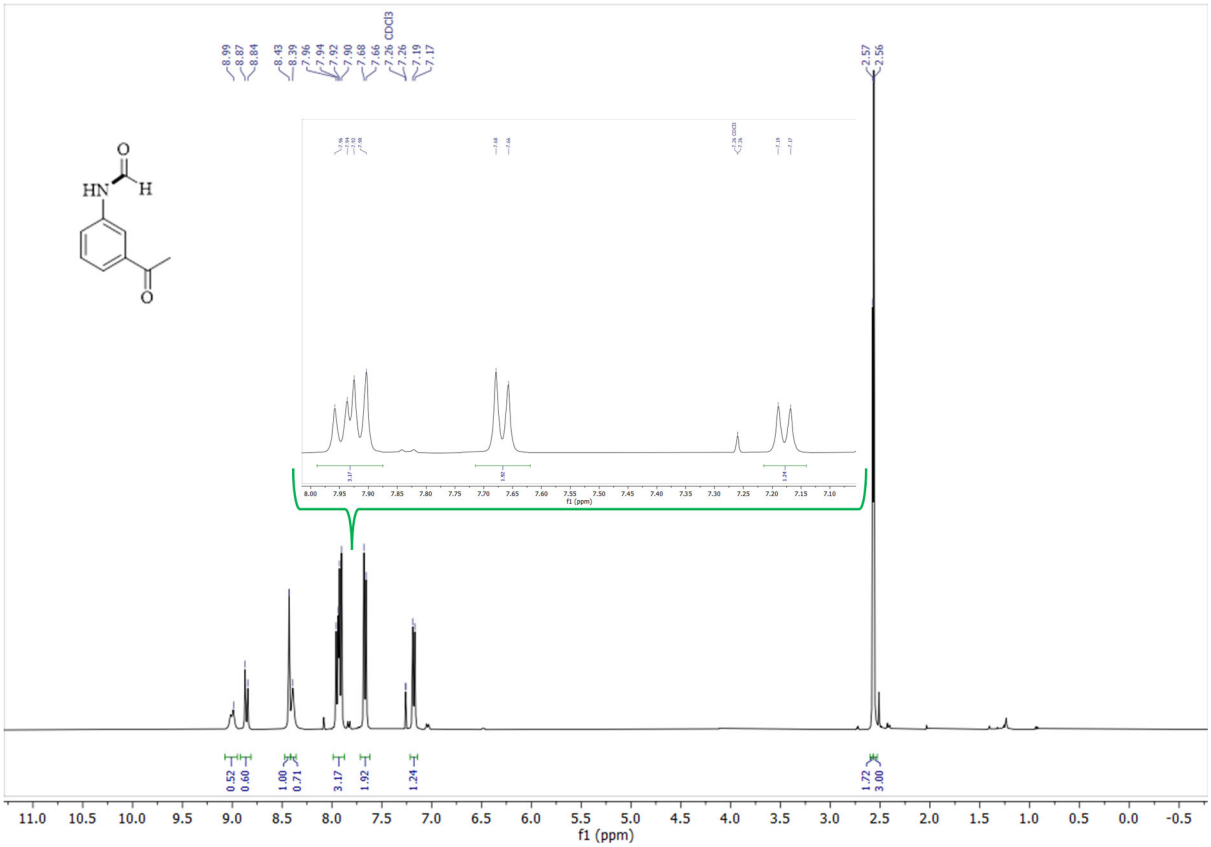
^{13}C NMR spectrum of **3k**



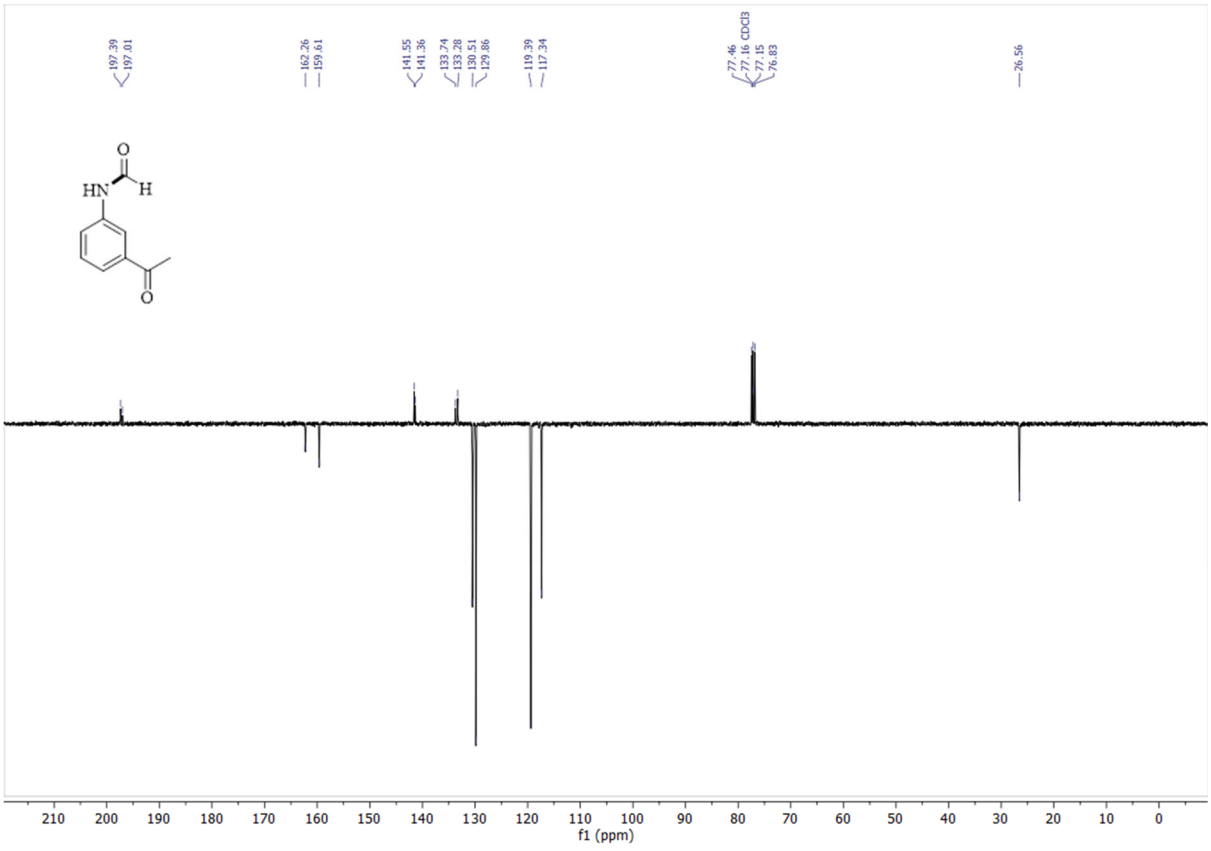
^{1}H NMR spectrum of **3l**



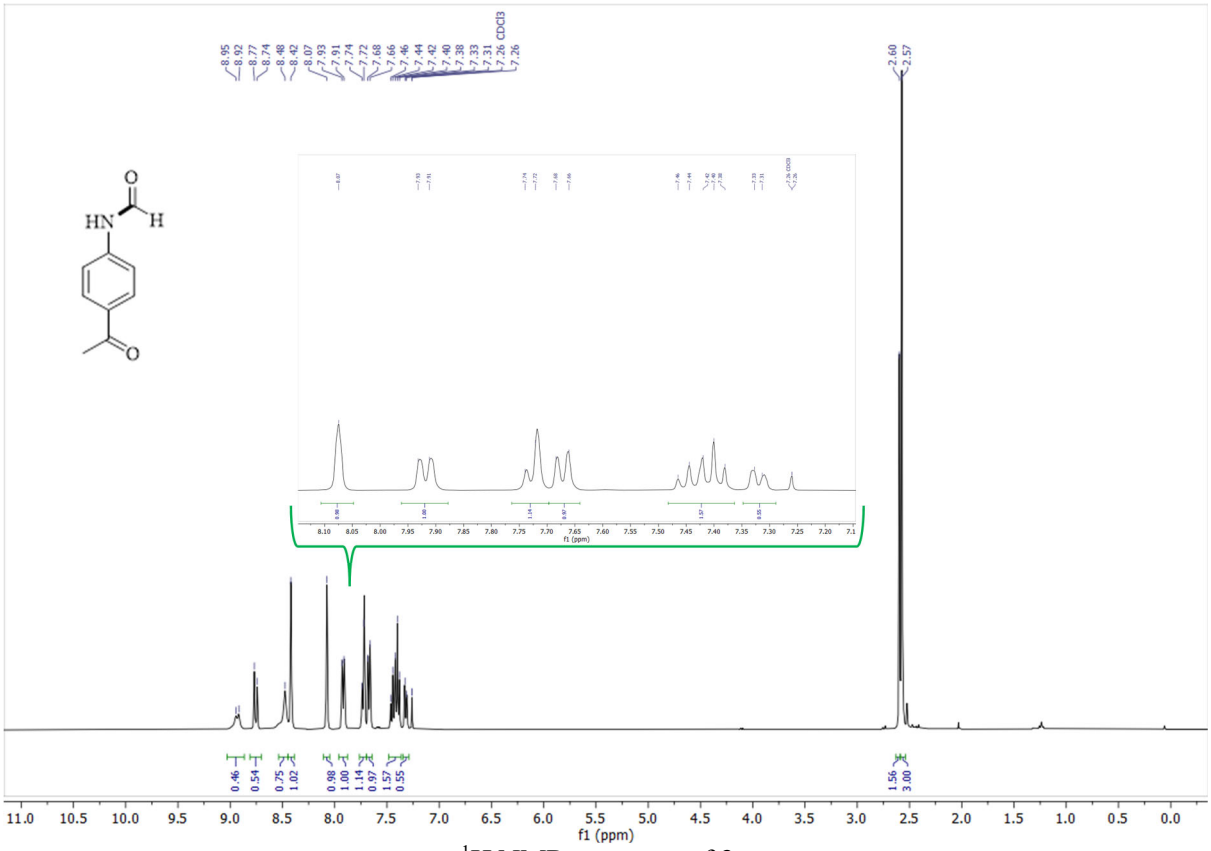
^{13}C NMR spectrum of **3l**



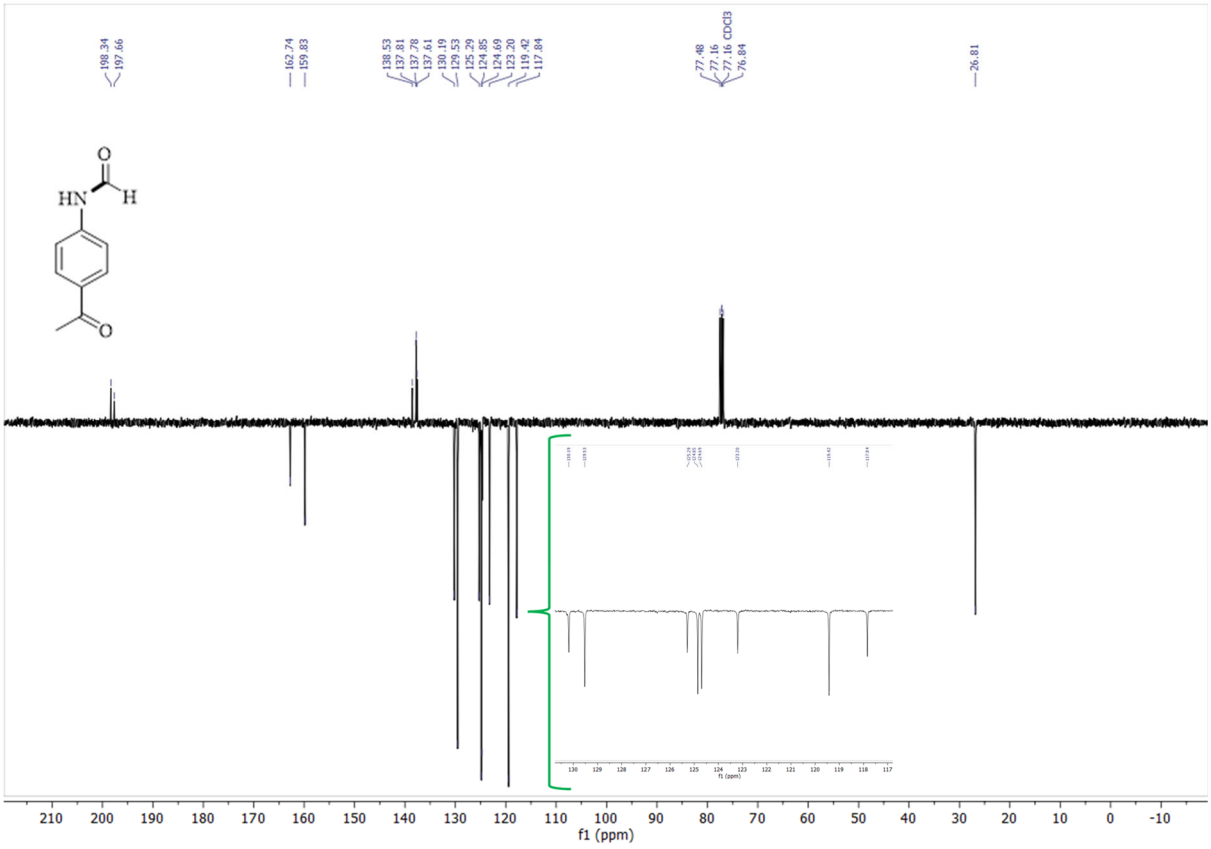
^{1}H NMR spectrum of **3m**



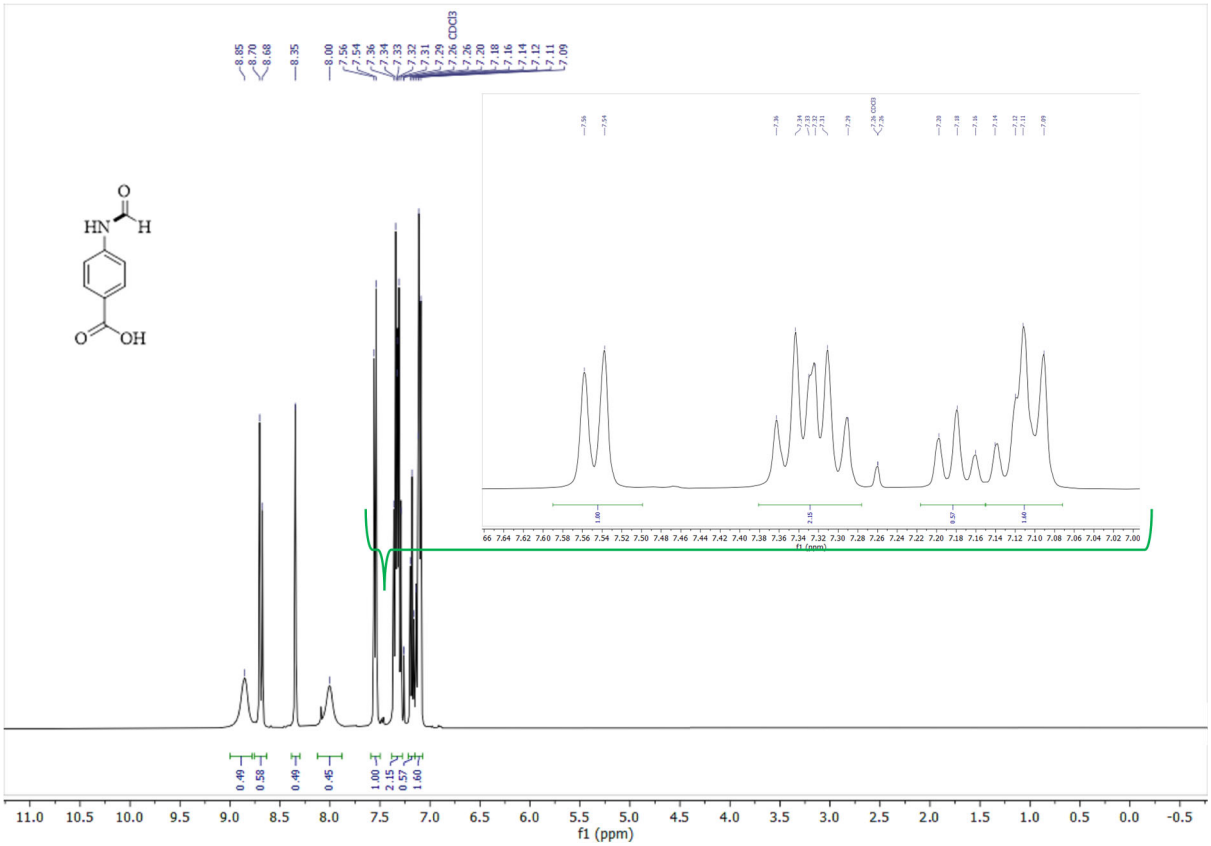
^{13}C NMR spectrum of **3m**



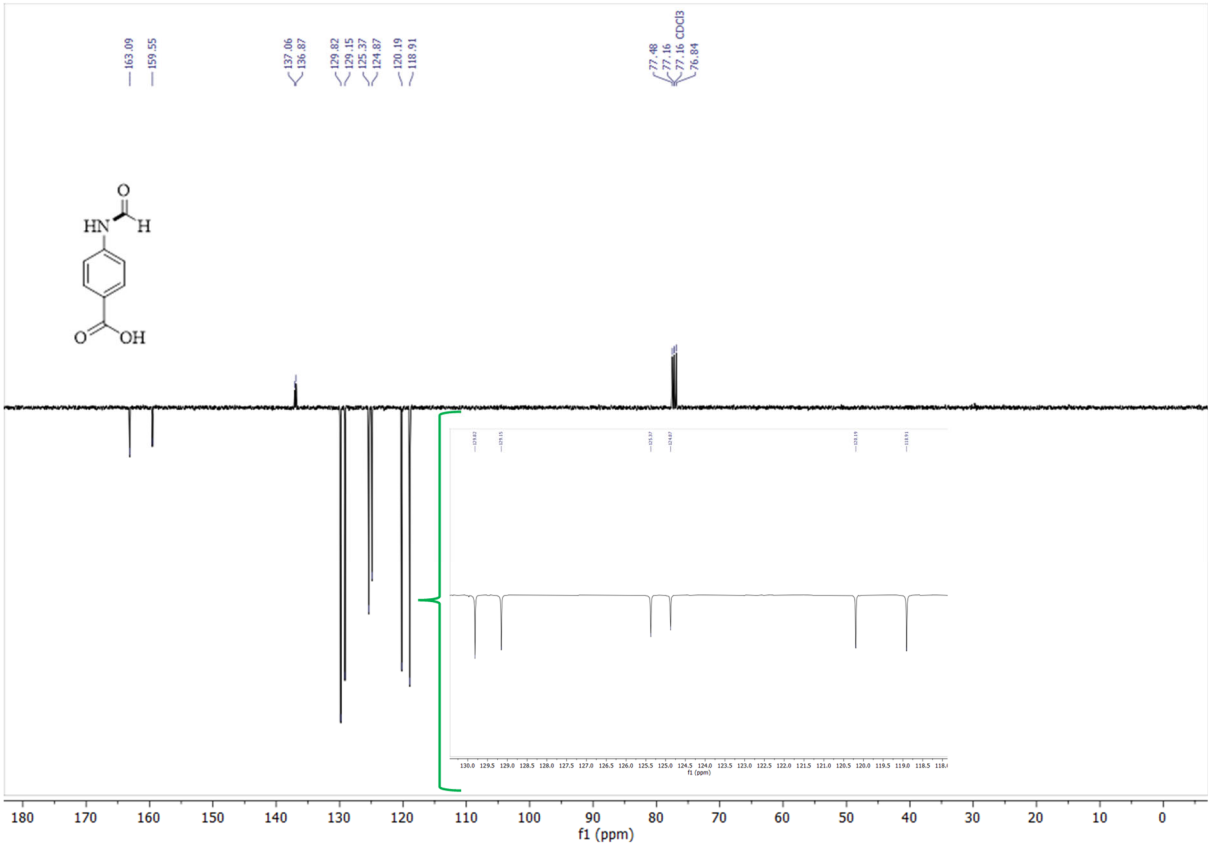
^{1}H NMR spectrum of **3n**



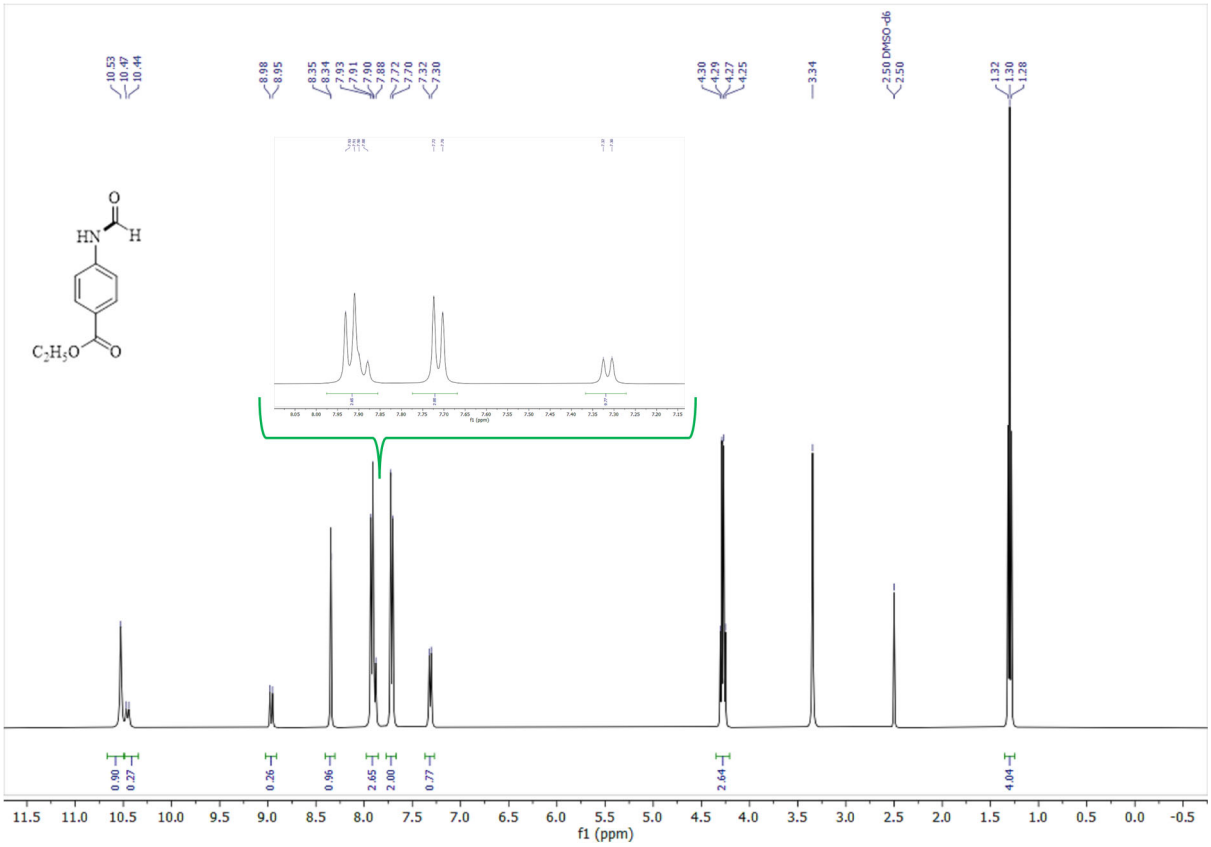
^{13}C NMR spectrum of **3n**



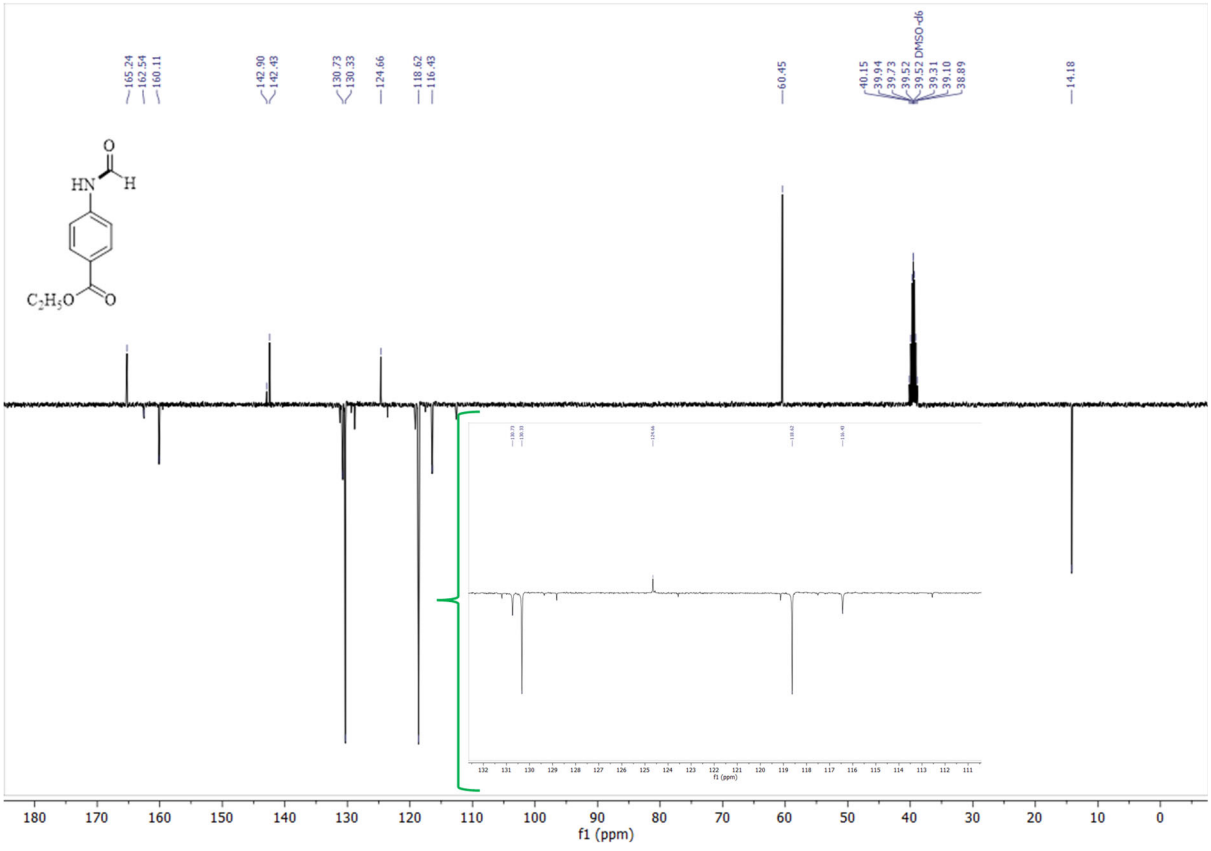
^{1}H NMR spectrum of **3o**



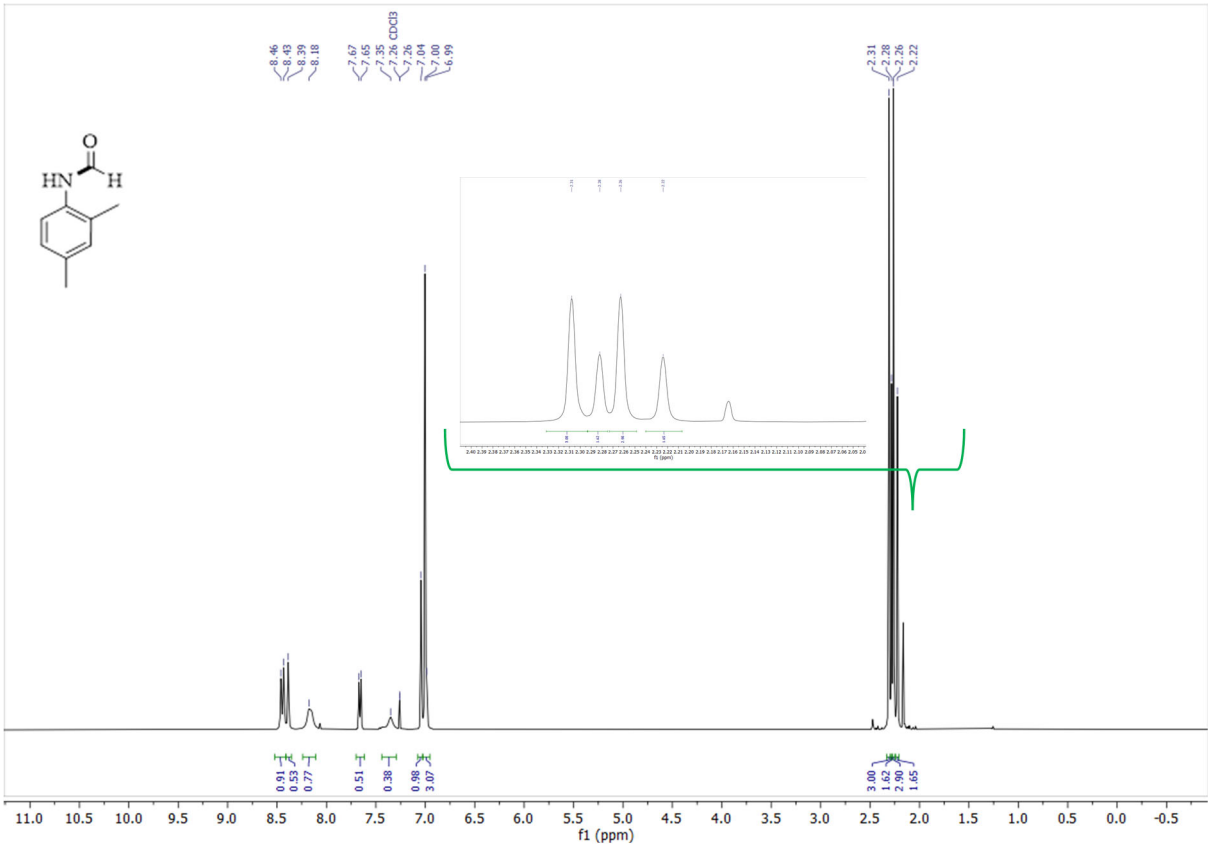
^{13}C NMR spectrum of **3o**



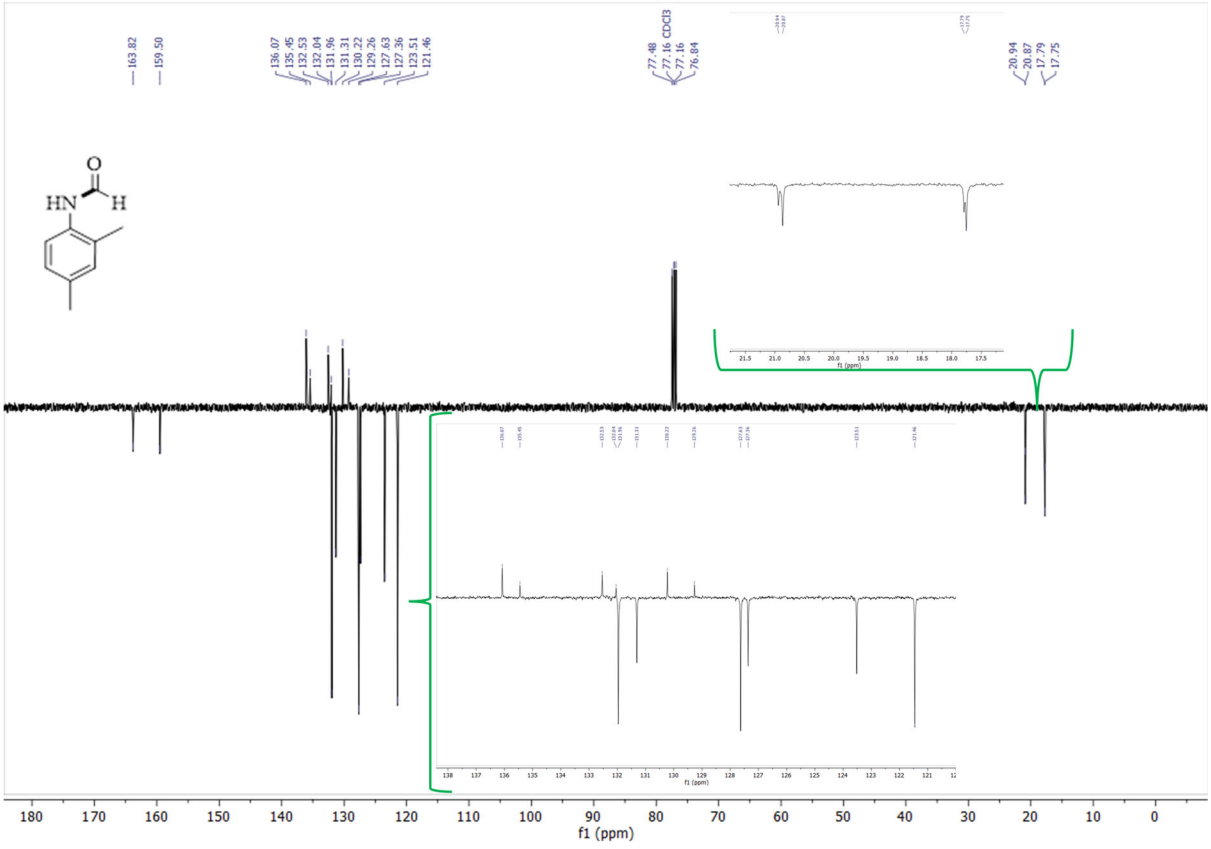
^{1}H NMR spectrum of **3p**



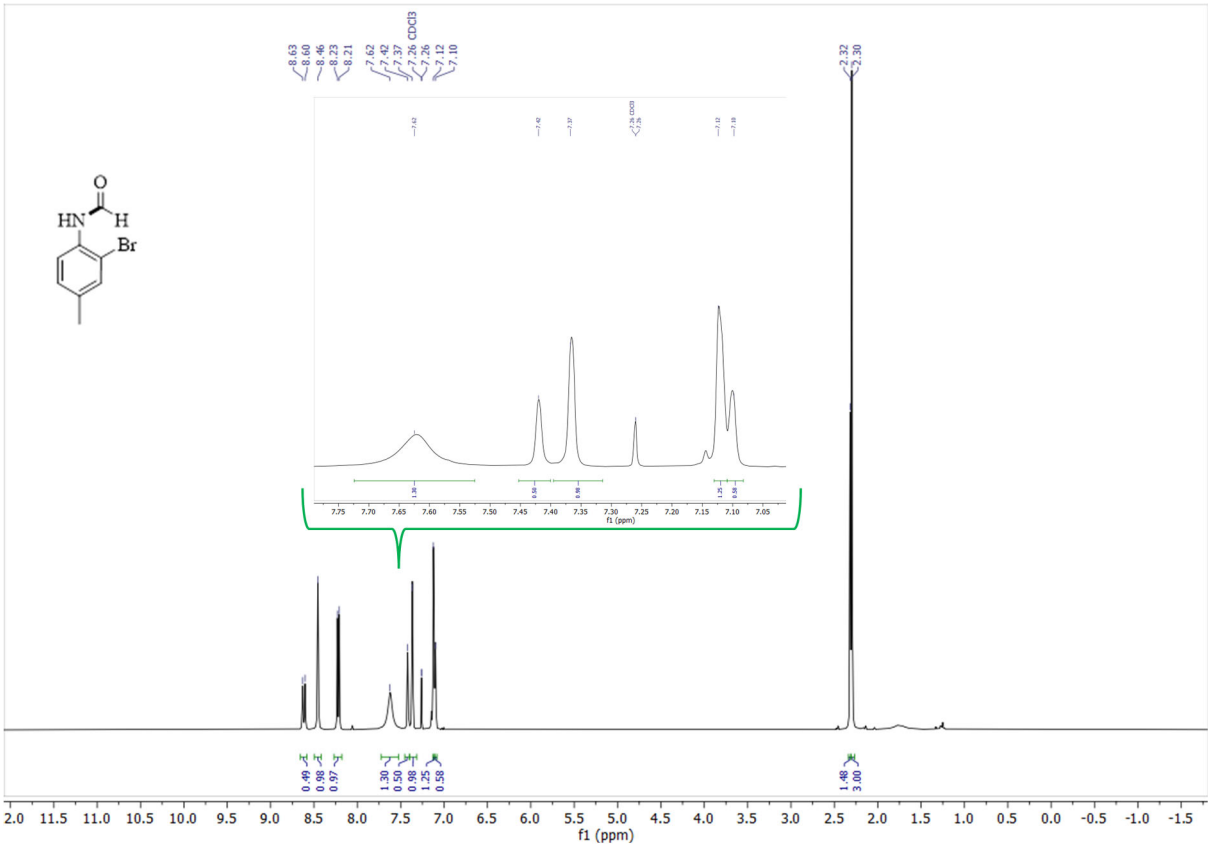
^{13}C NMR spectrum of **3p**



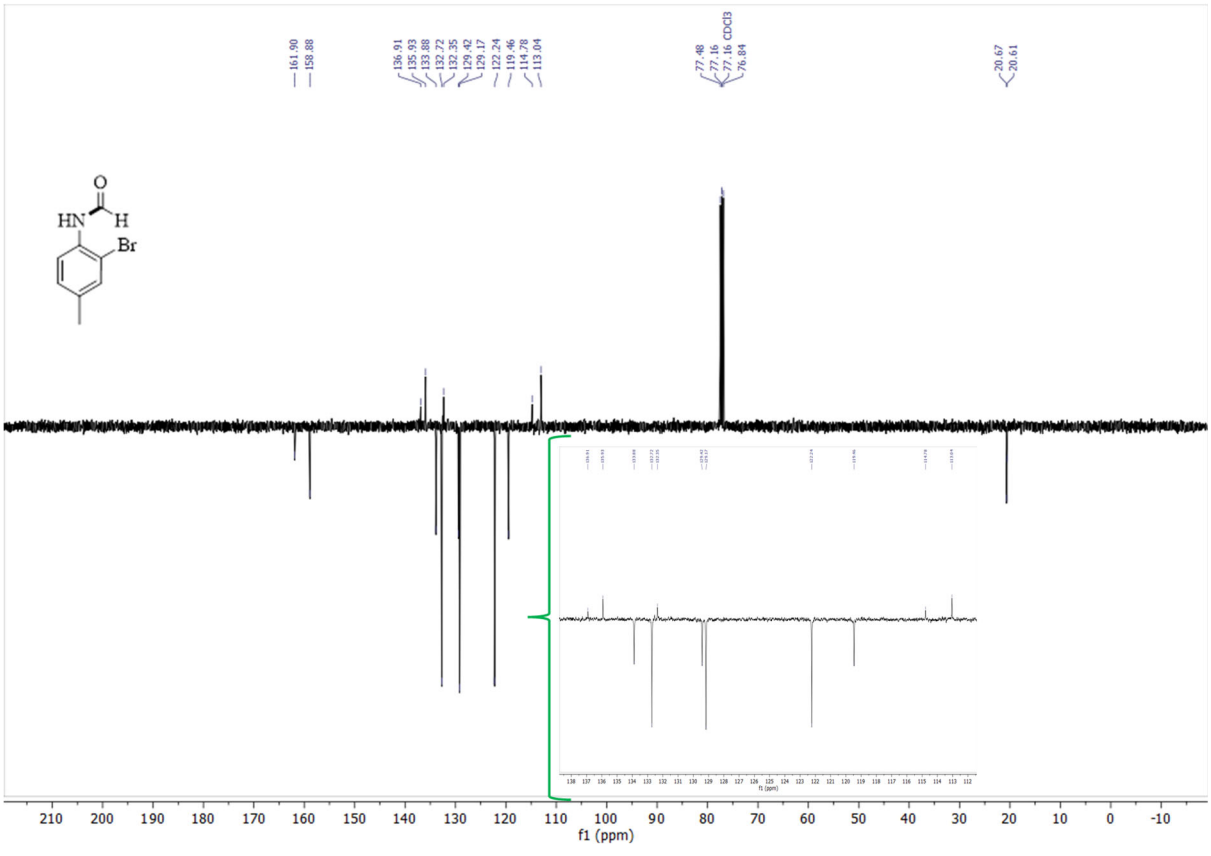
^{1}H NMR spectrum of **3q**



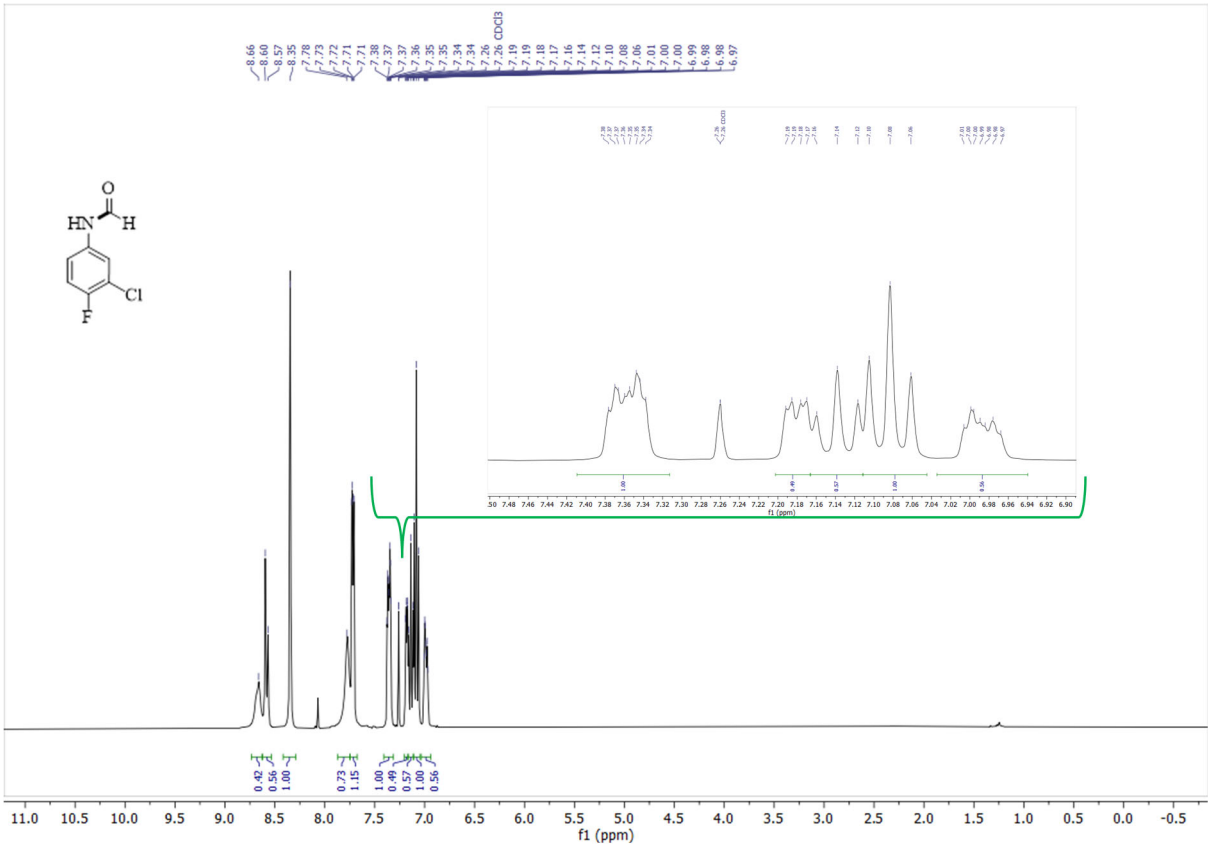
^{13}C NMR spectrum of **3q**



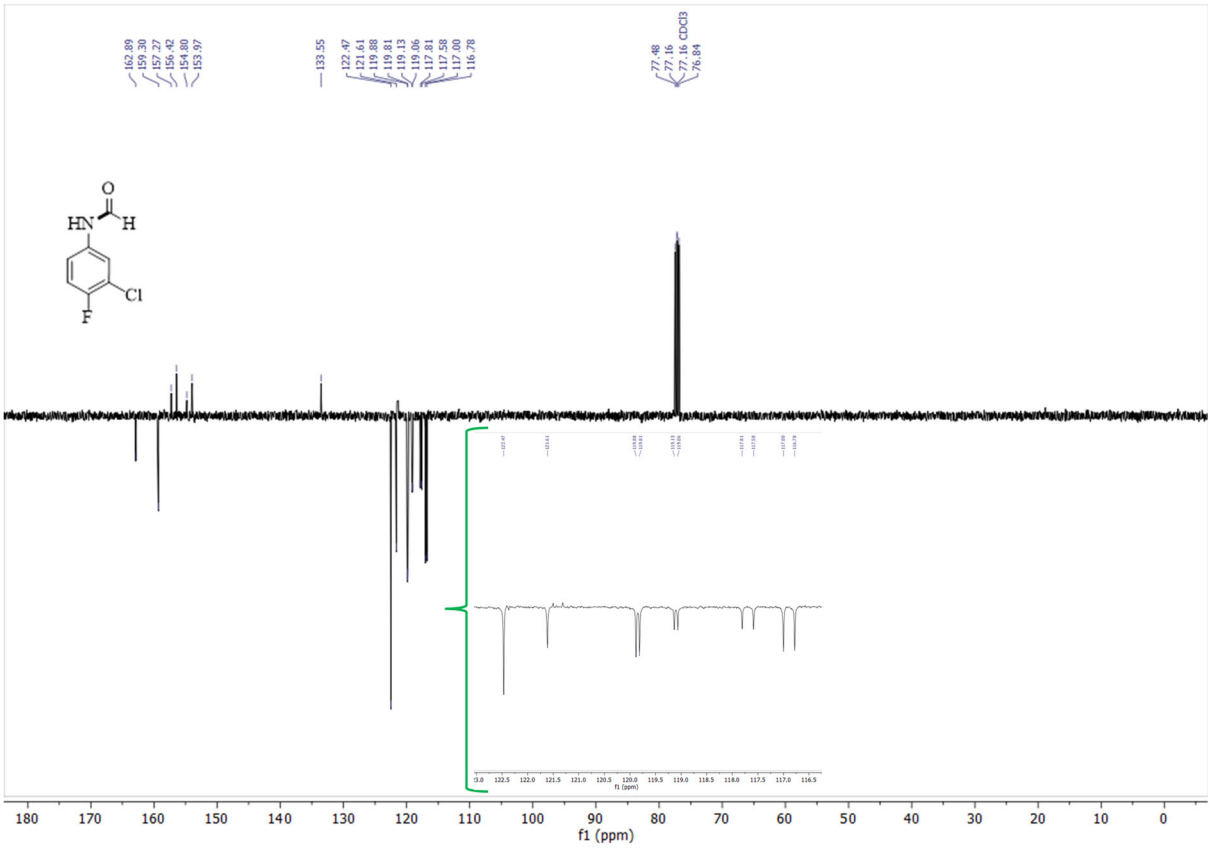
^{1}H NMR spectrum of **3r**



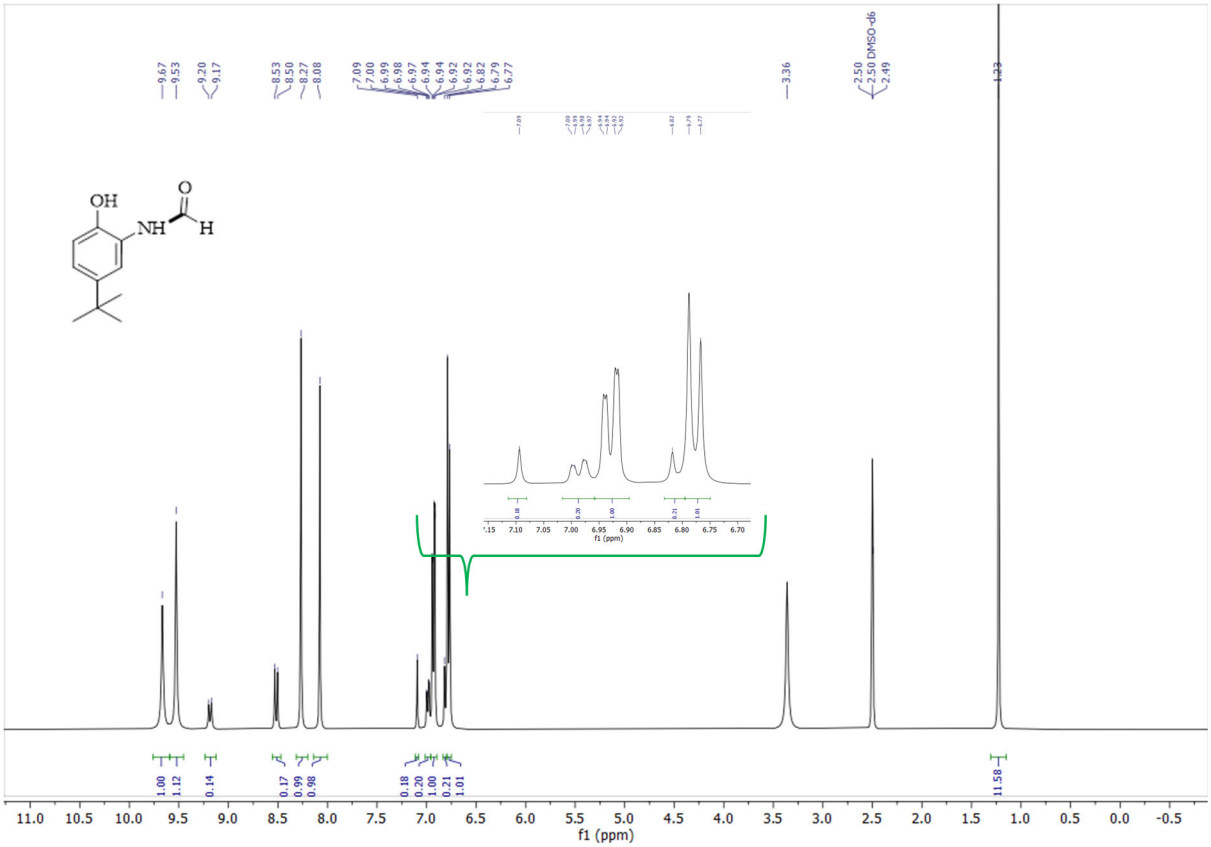
^{13}C NMR spectrum of **3r**



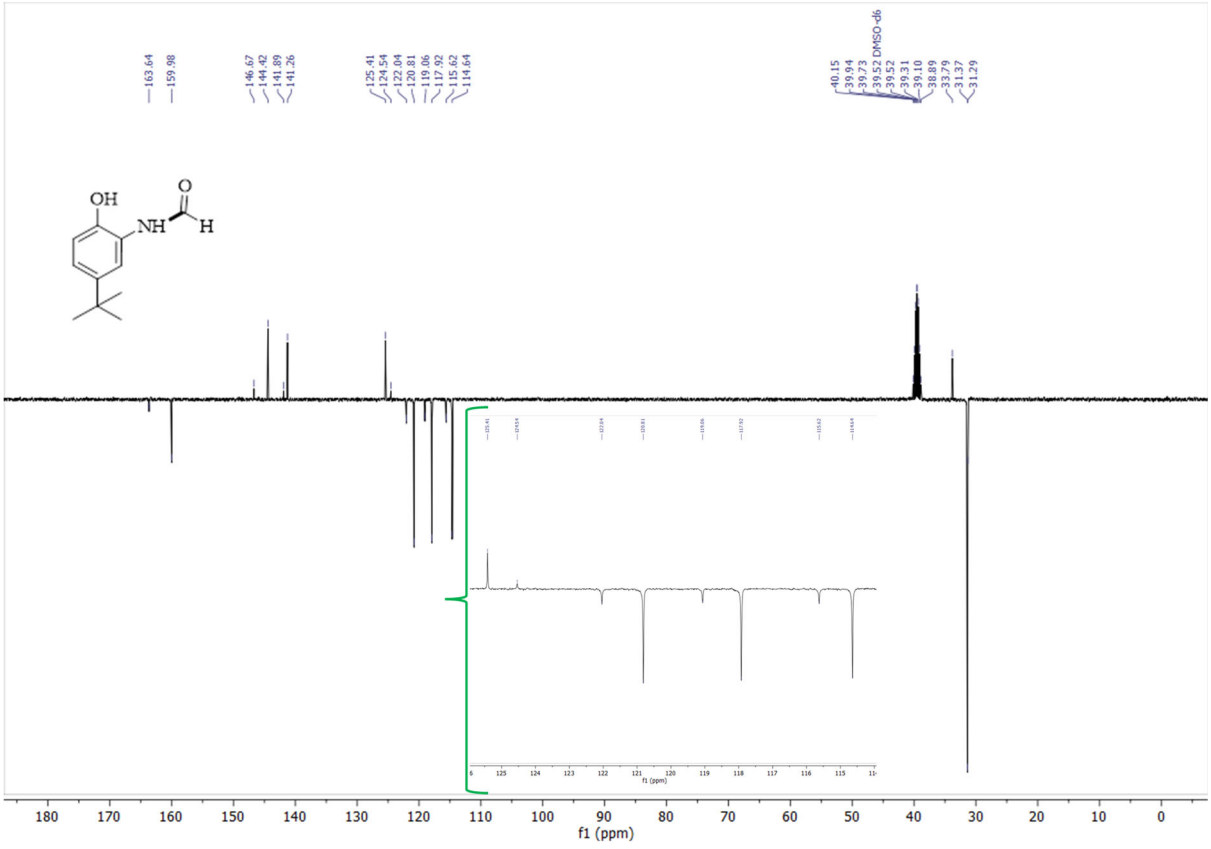
^{1}H NMR spectrum of **3s**



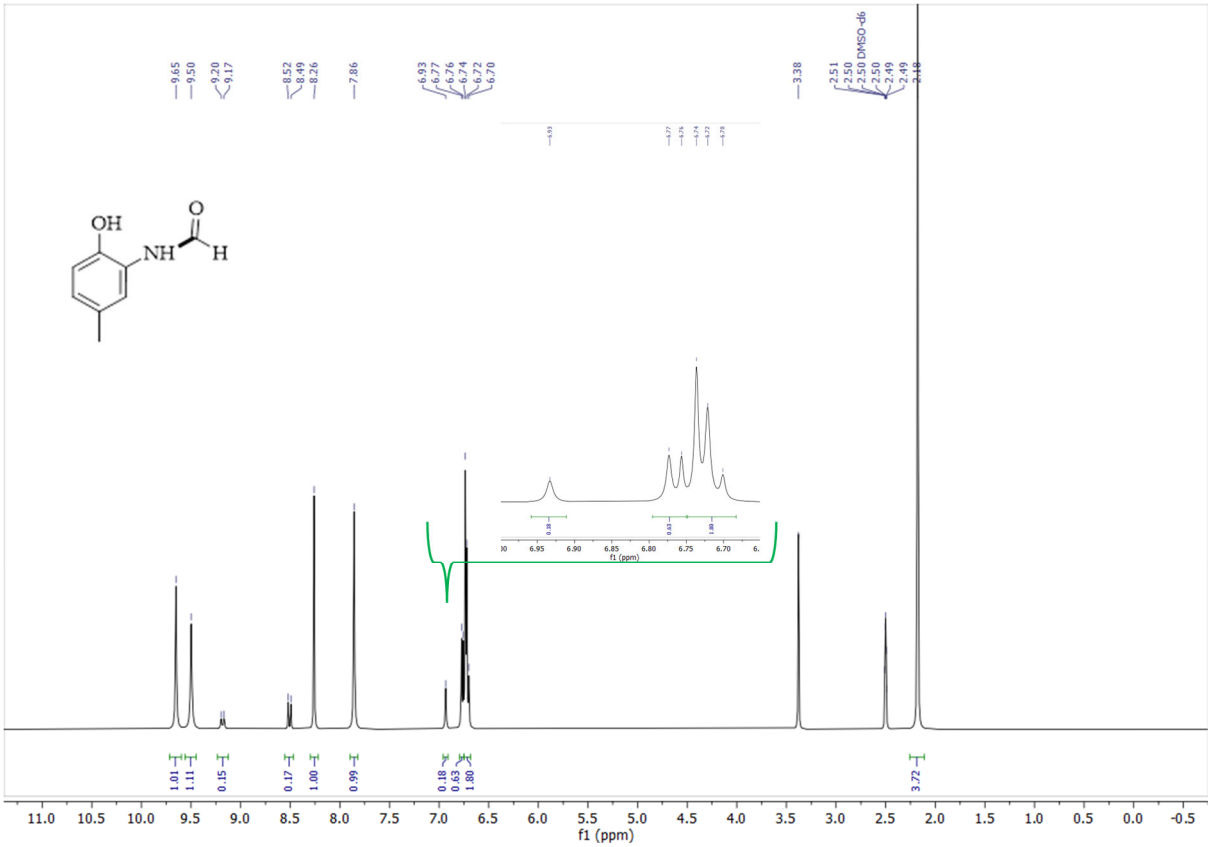
^{13}C NMR spectrum of **3s**



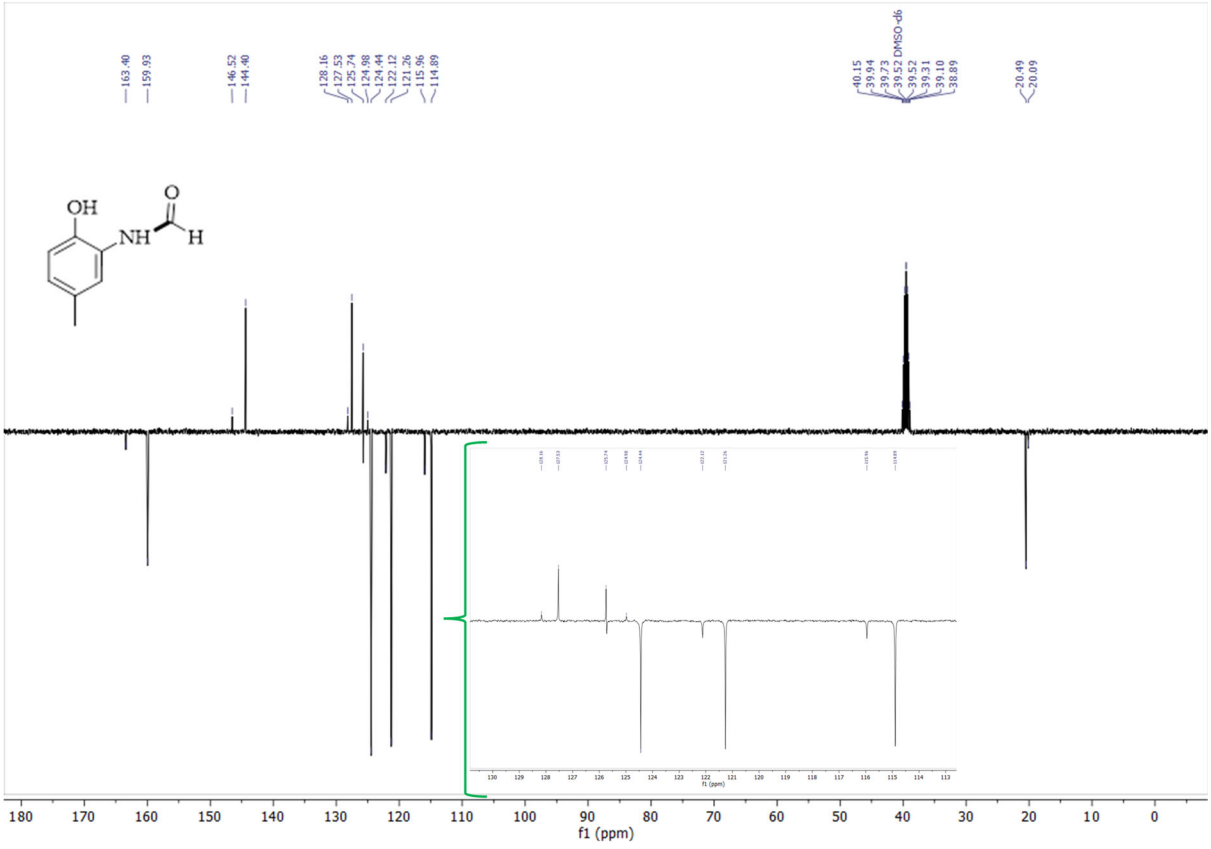
^{1}H NMR spectrum of **3t**



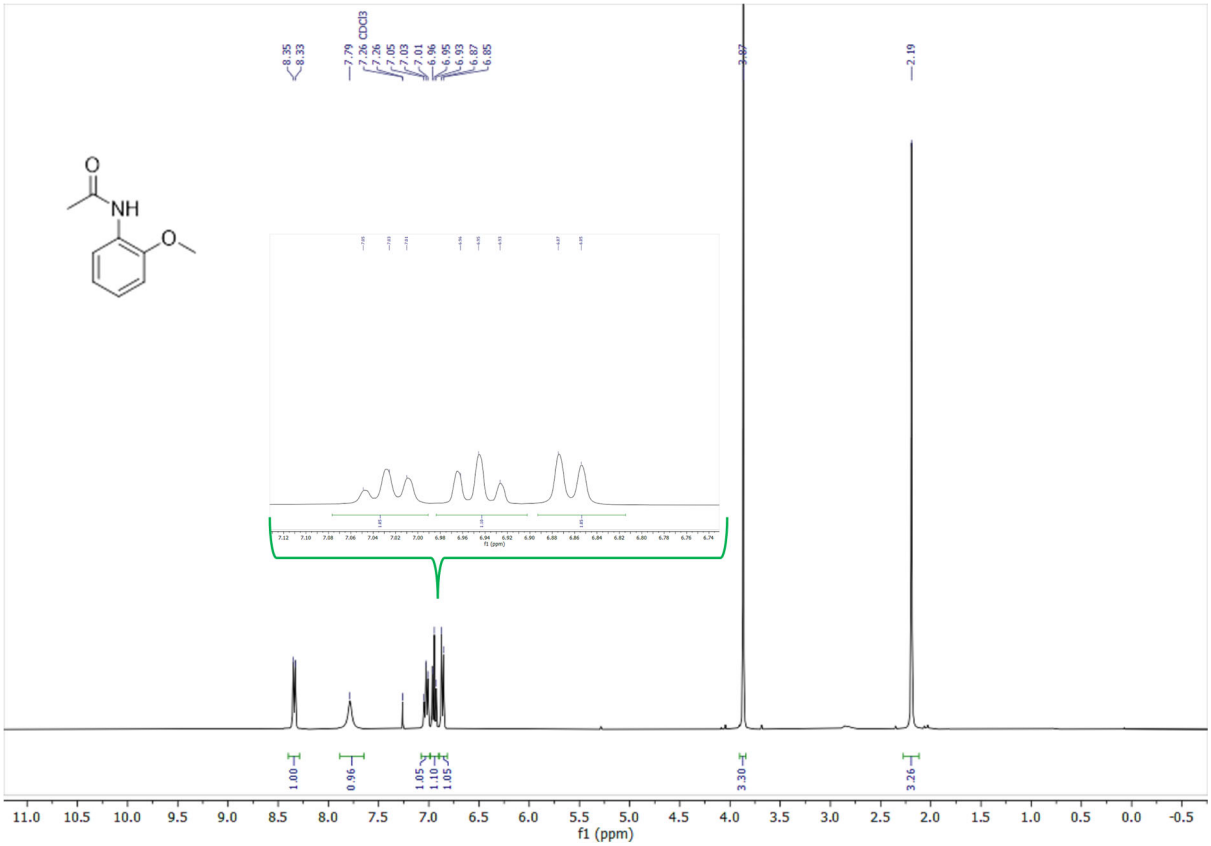
^{13}C NMR spectrum of **3t**



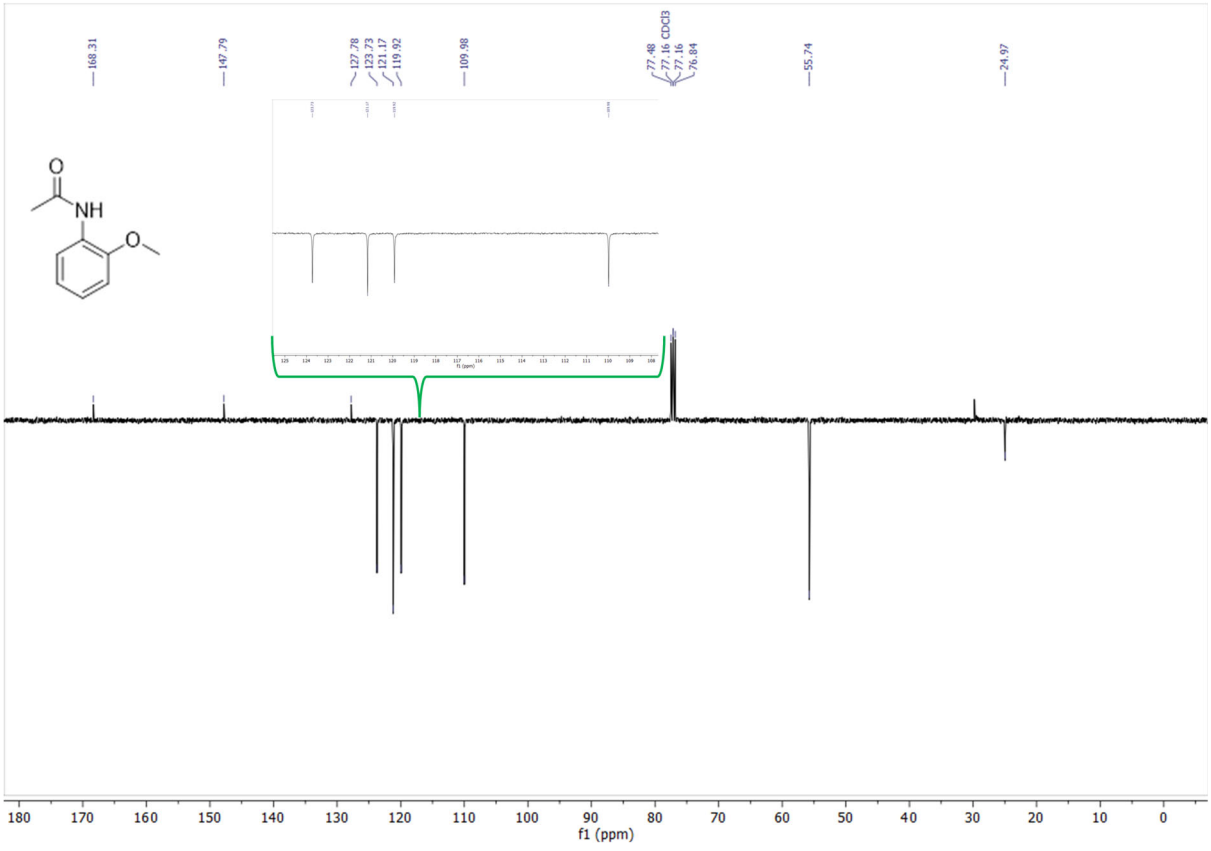
^{1}H NMR spectrum of **3u**



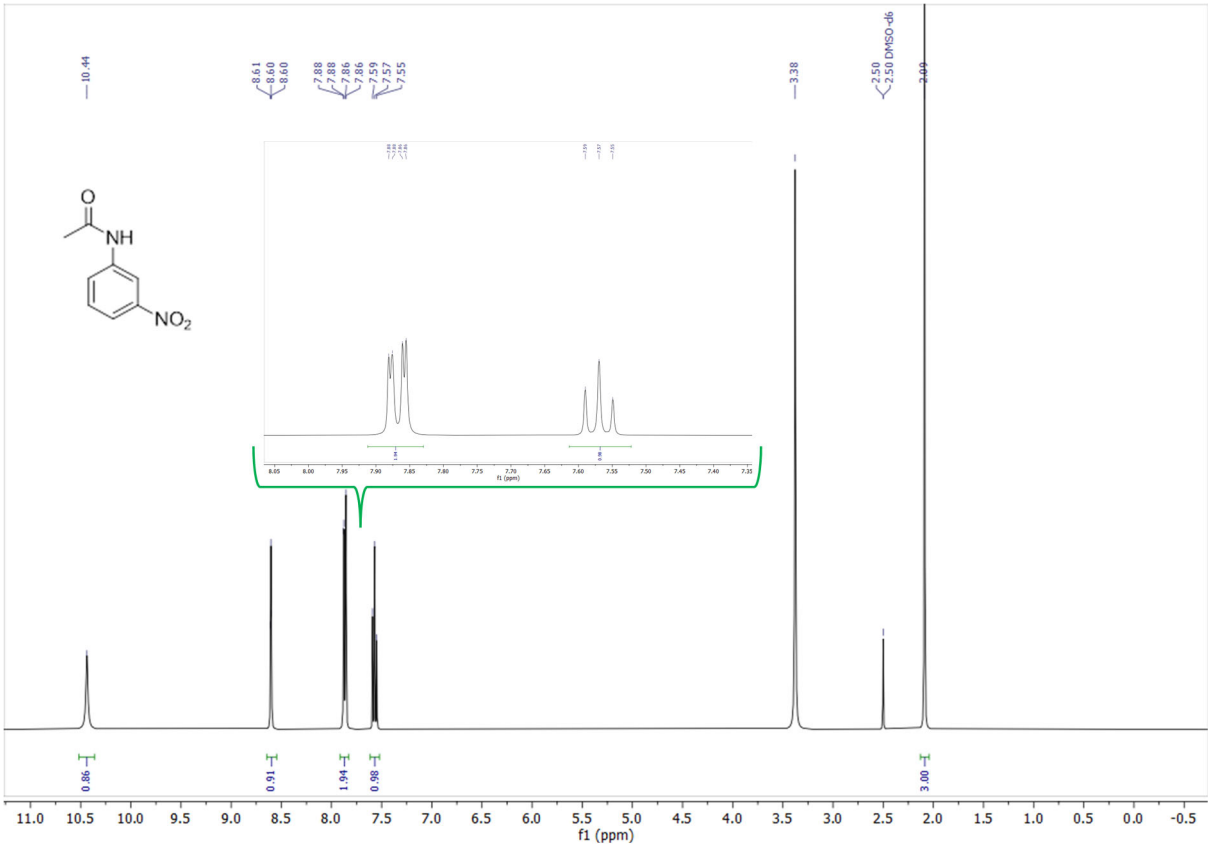
^{13}C NMR spectrum of **3u**



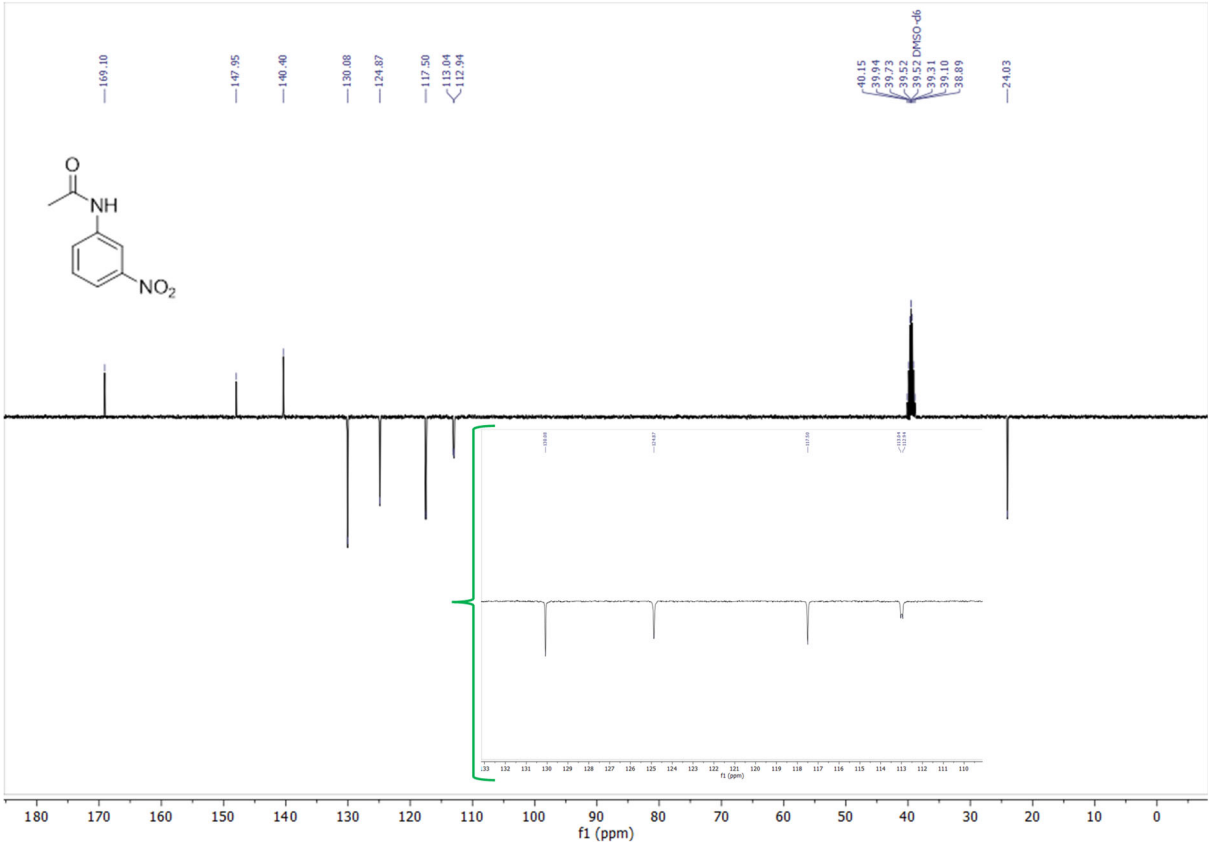
^{1}H NMR spectrum of **3v**



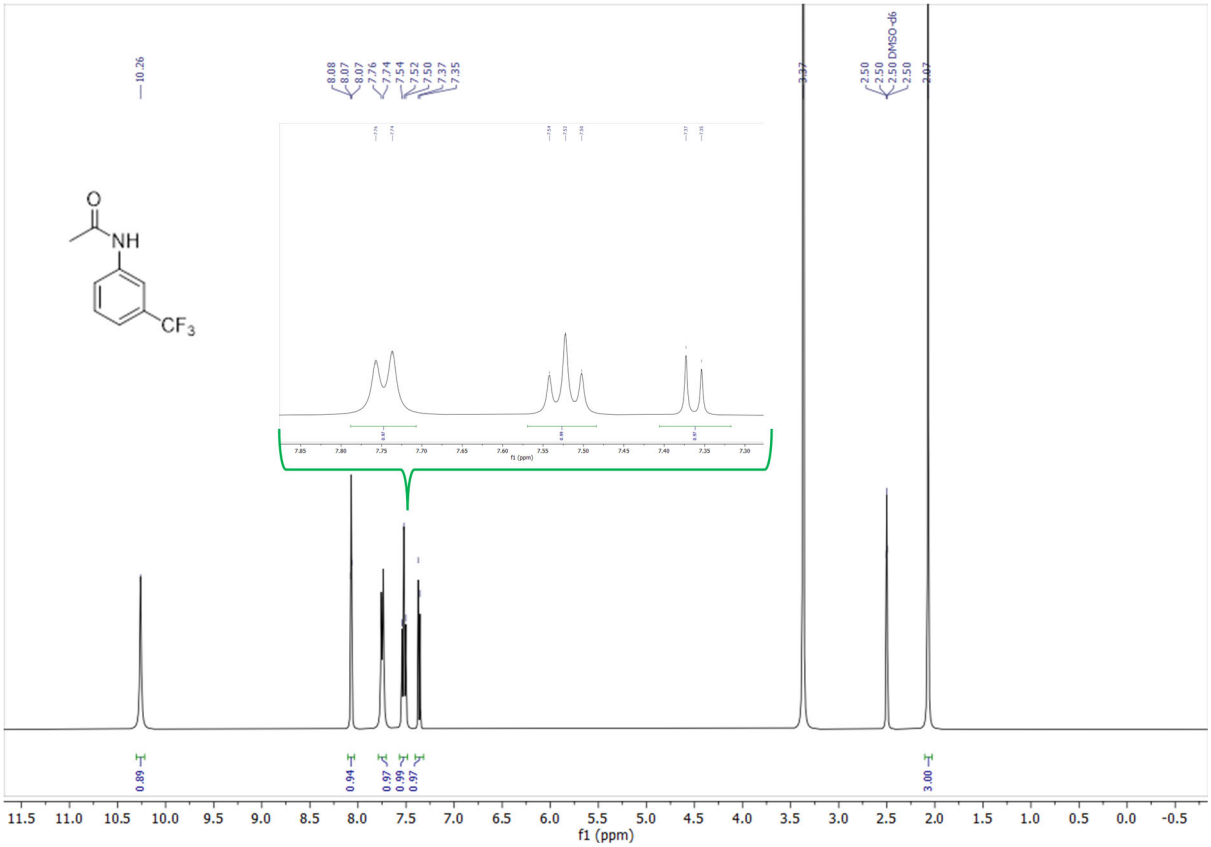
^{13}C NMR spectrum of **3v**



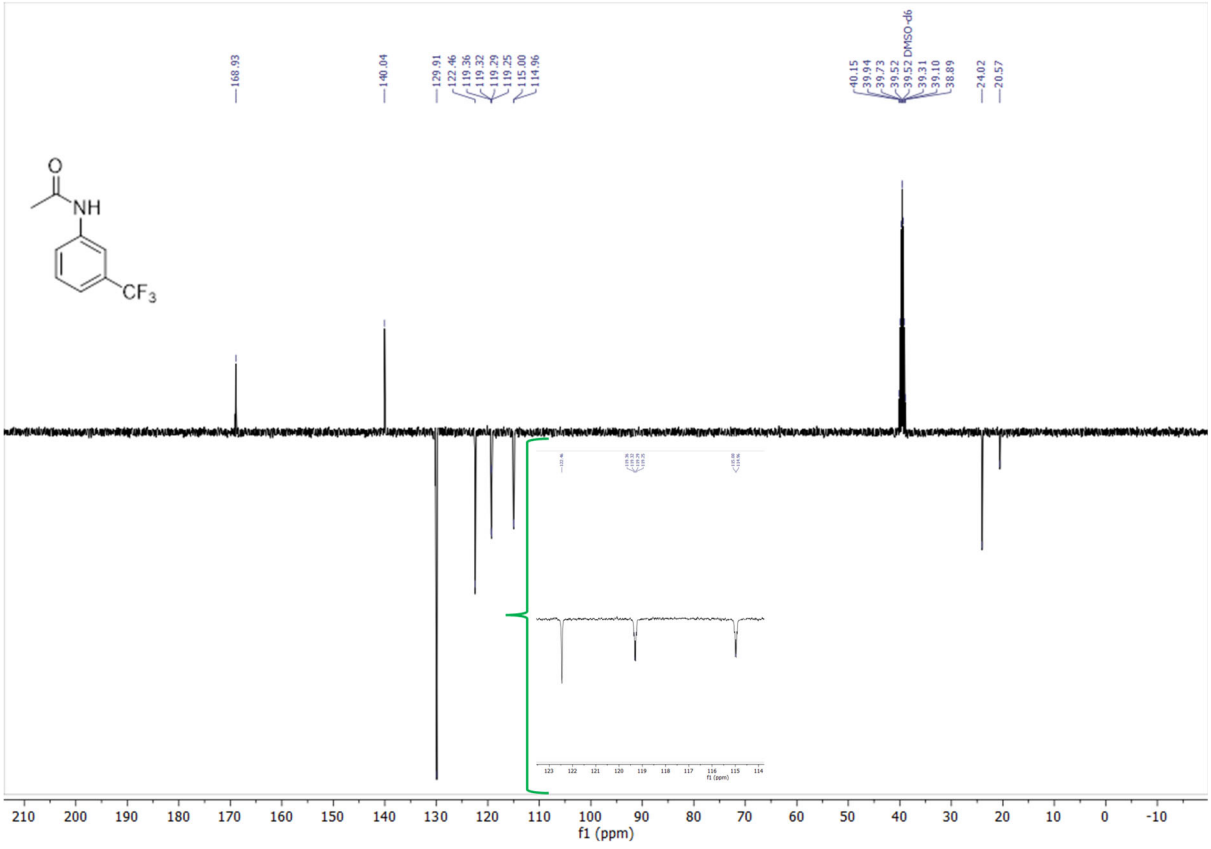
^{1}H NMR spectrum of **3w**



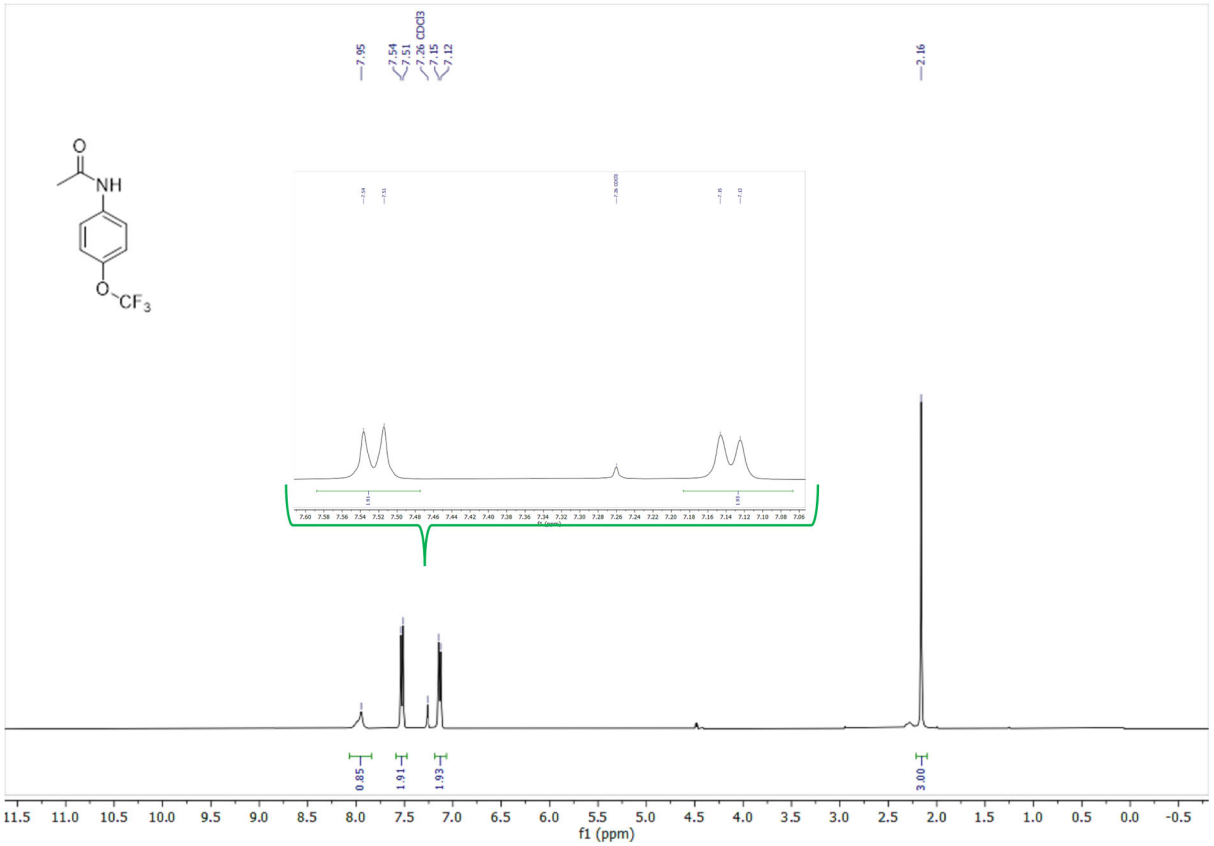
^{13}C NMR spectrum of **3w**



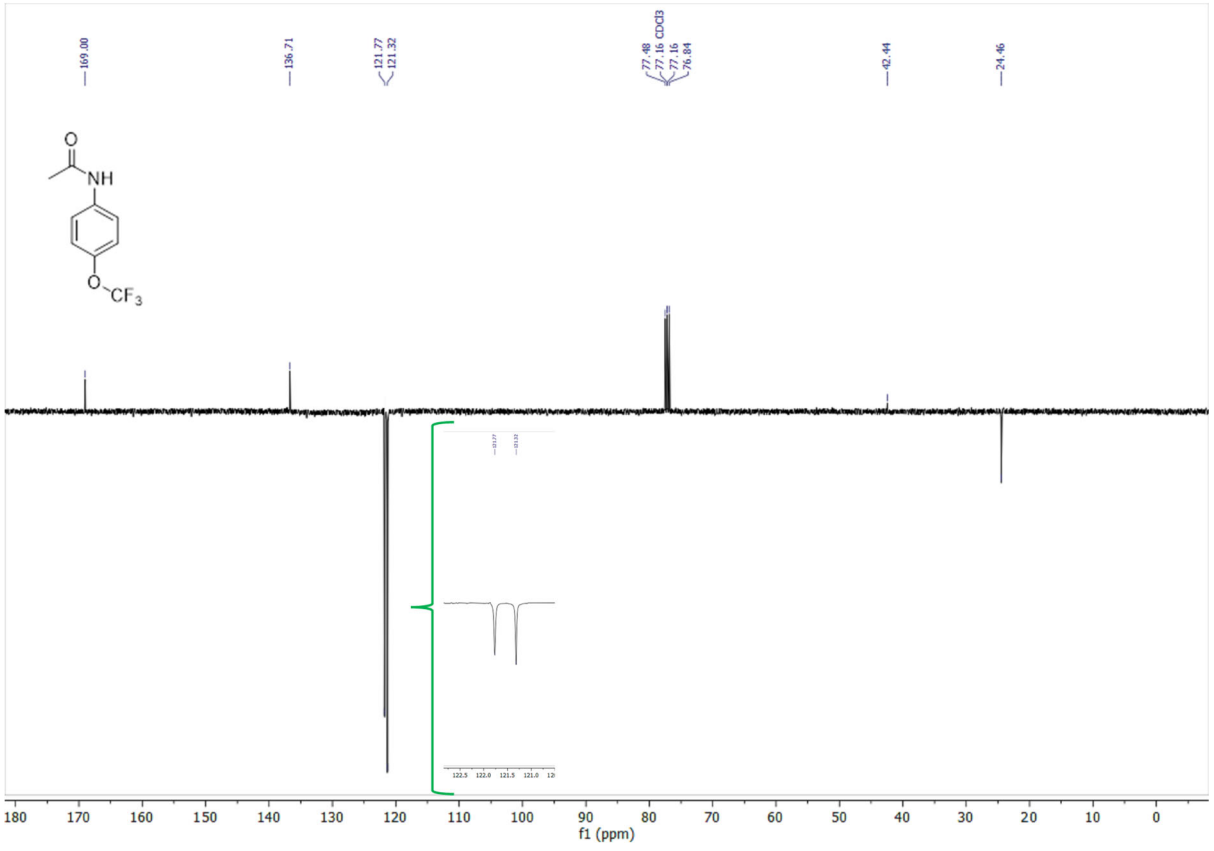
^{1}H NMR spectrum of **3x**



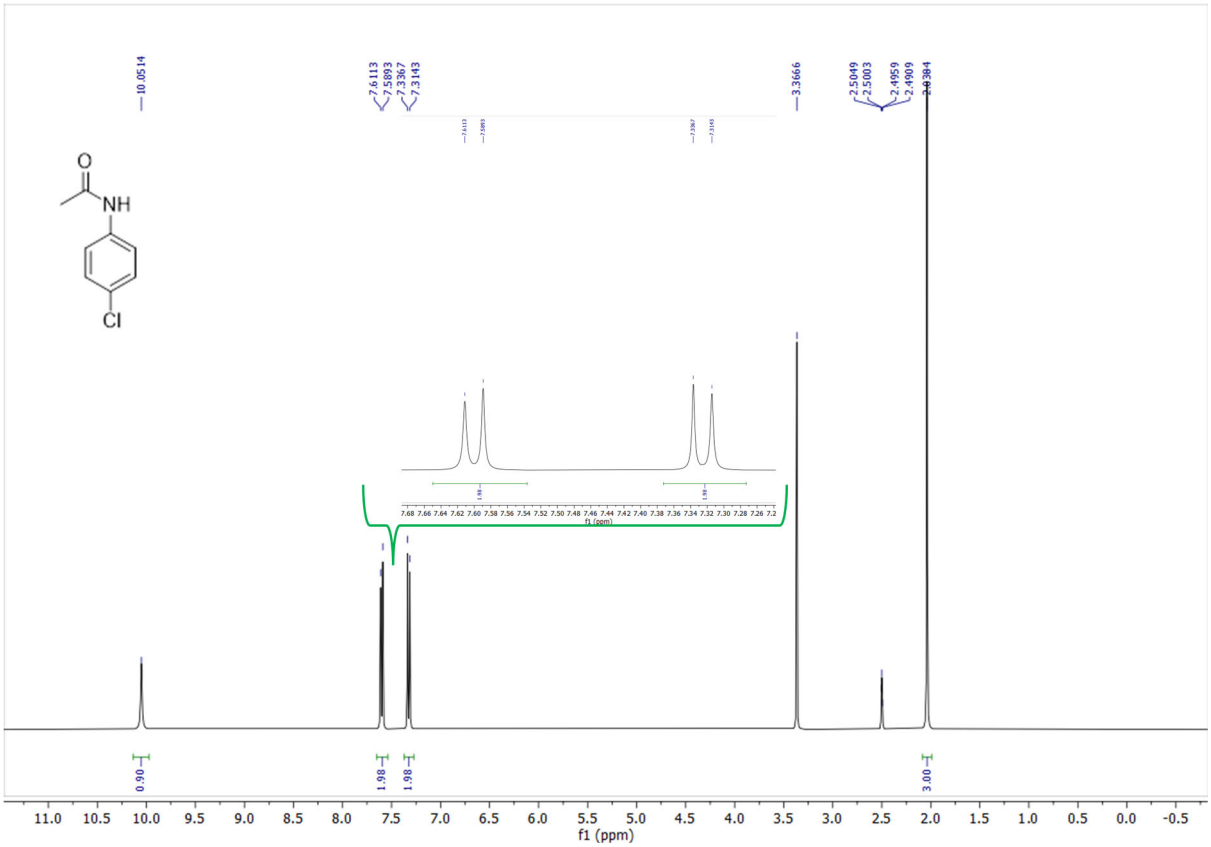
^{13}C NMR spectrum of **3x**



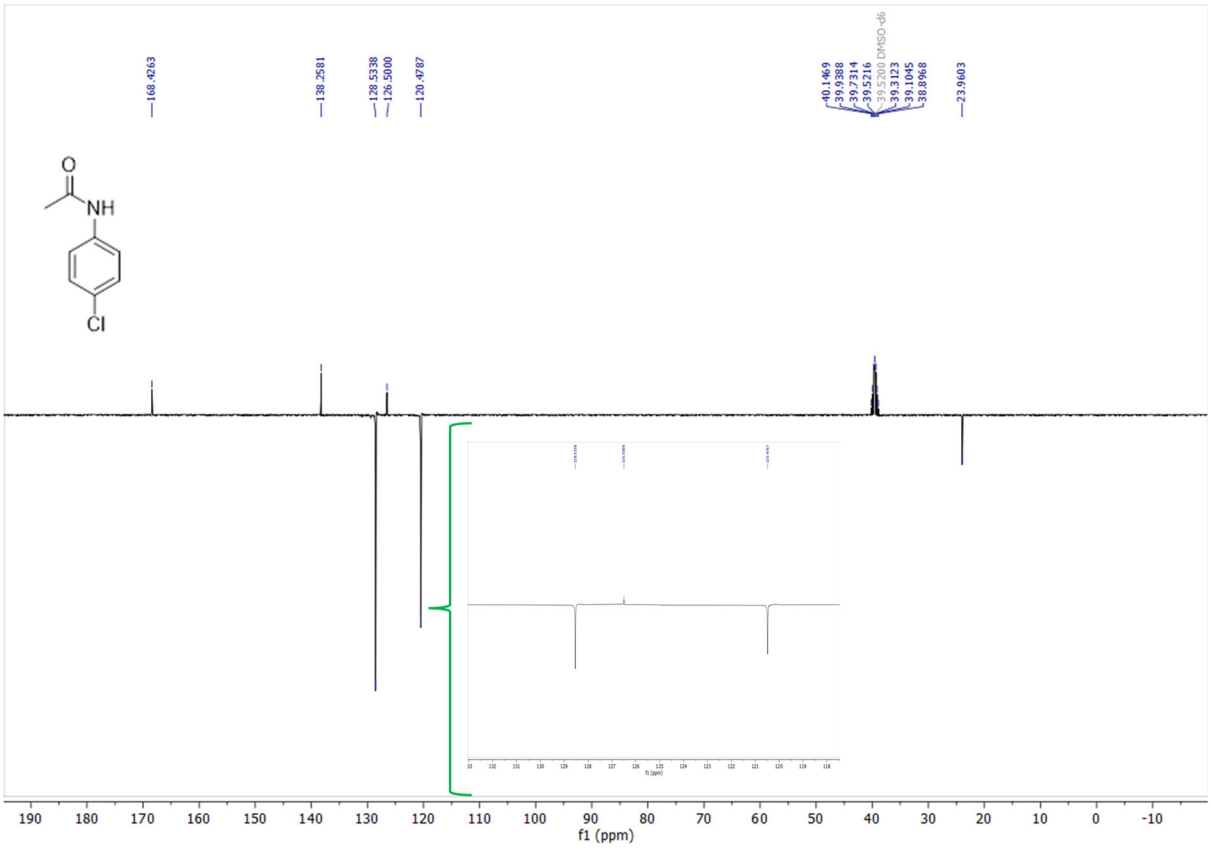
^{1}H NMR spectrum of **3y**



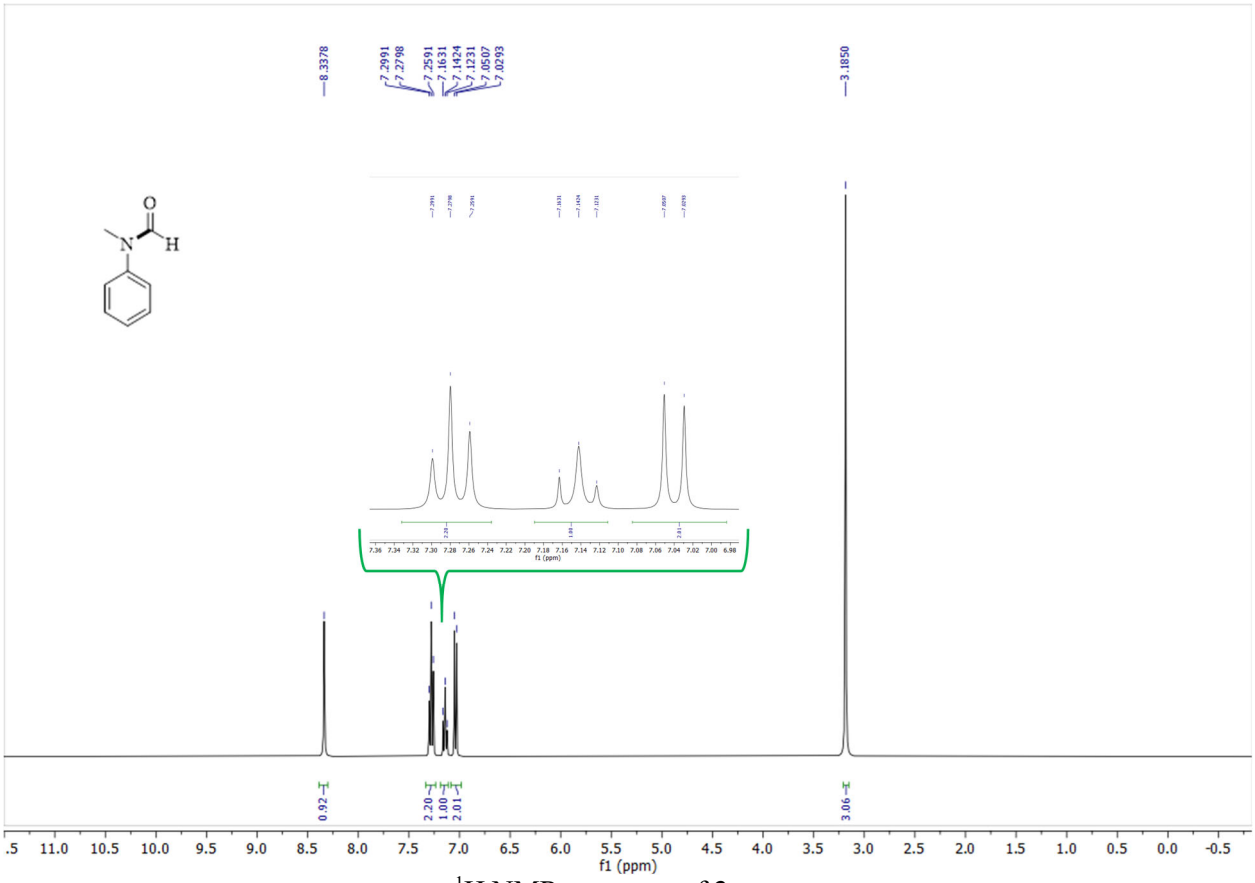
^{13}C NMR spectrum of **3y**



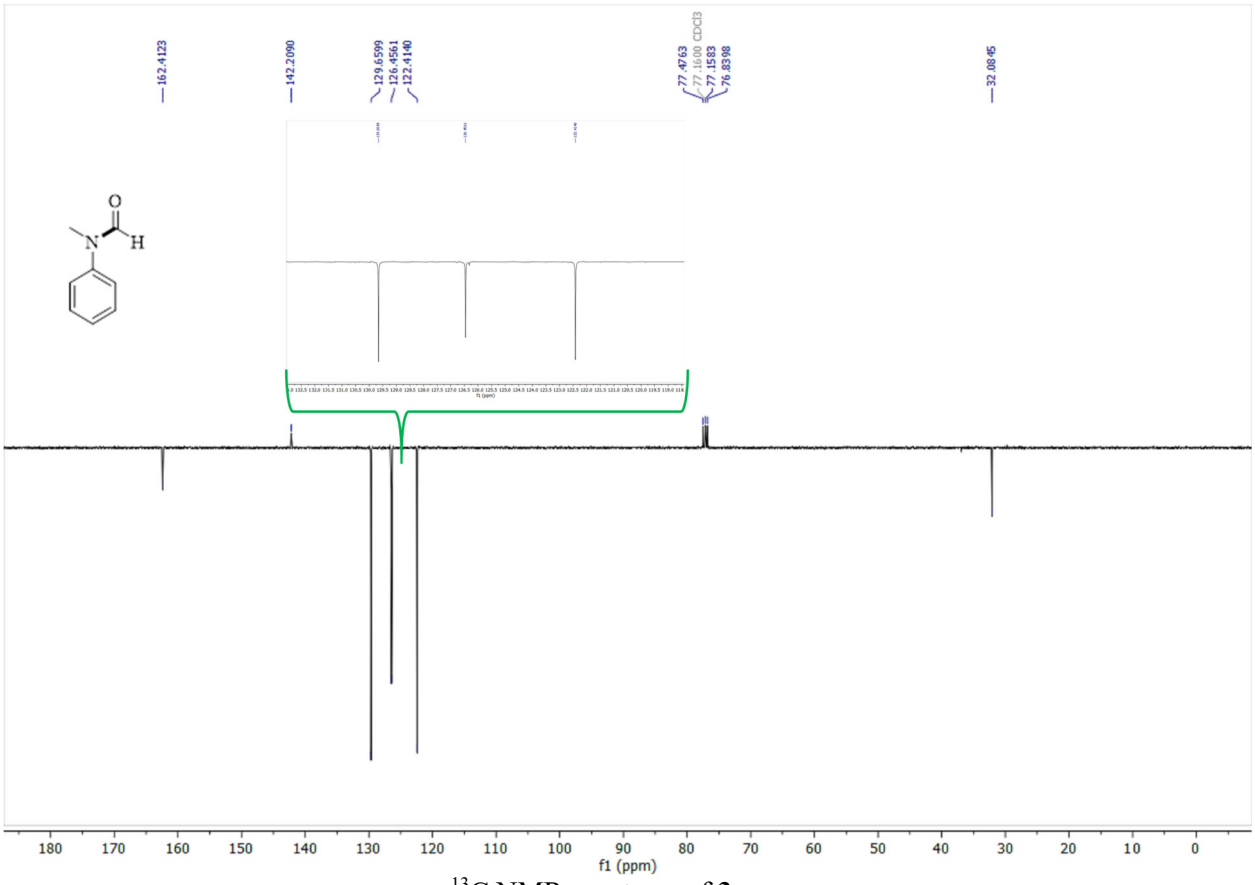
^{1}H NMR spectrum of **3z**



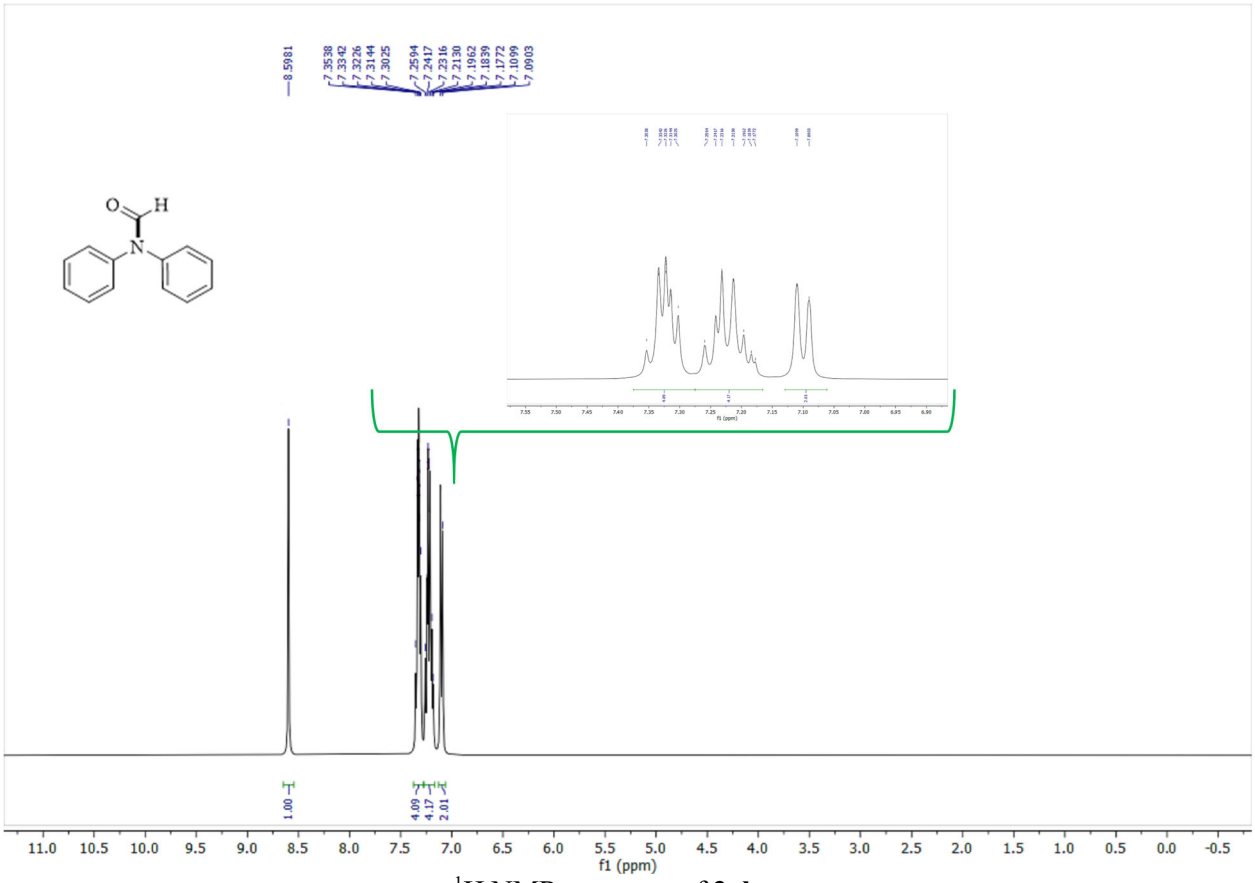
^{13}C NMR spectrum of **3z**



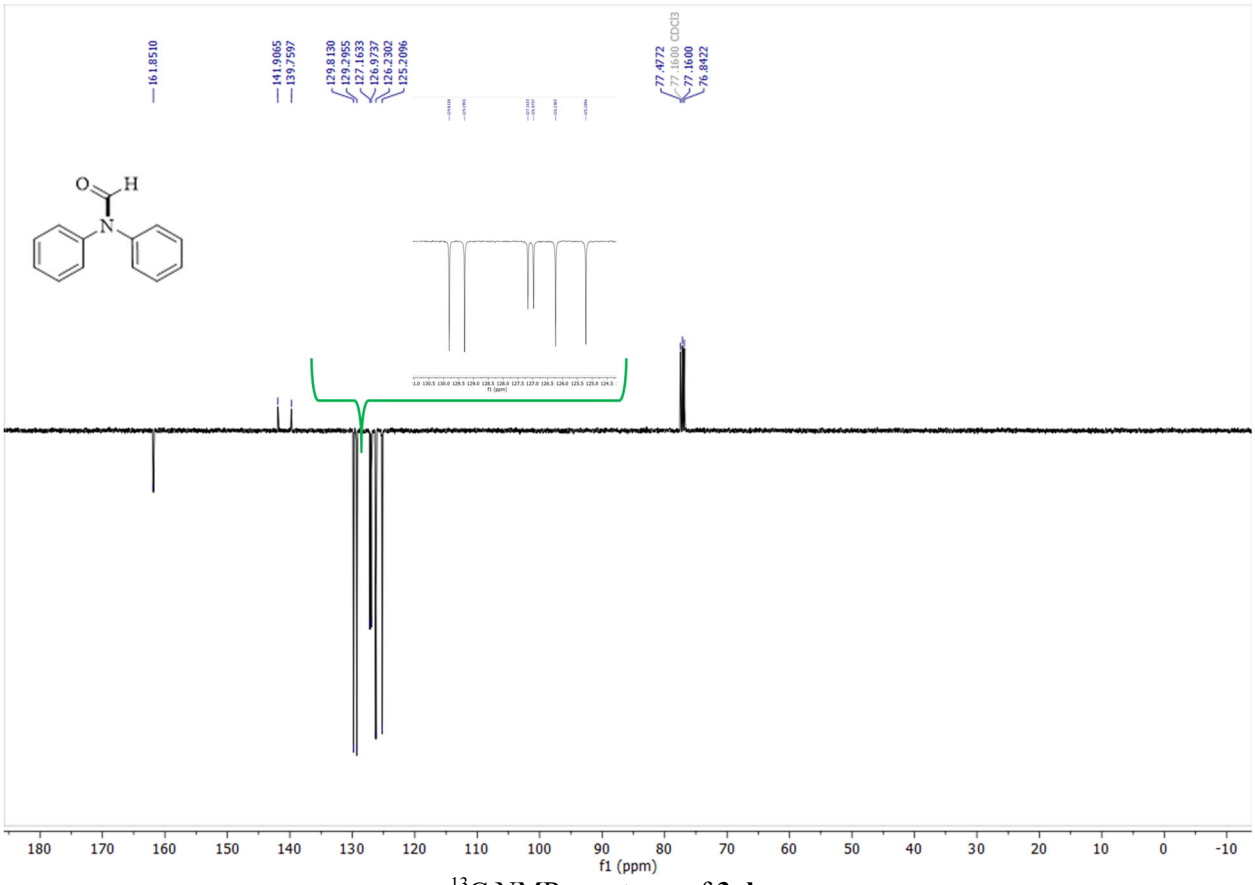
^{1}H NMR spectrum of **3aa**



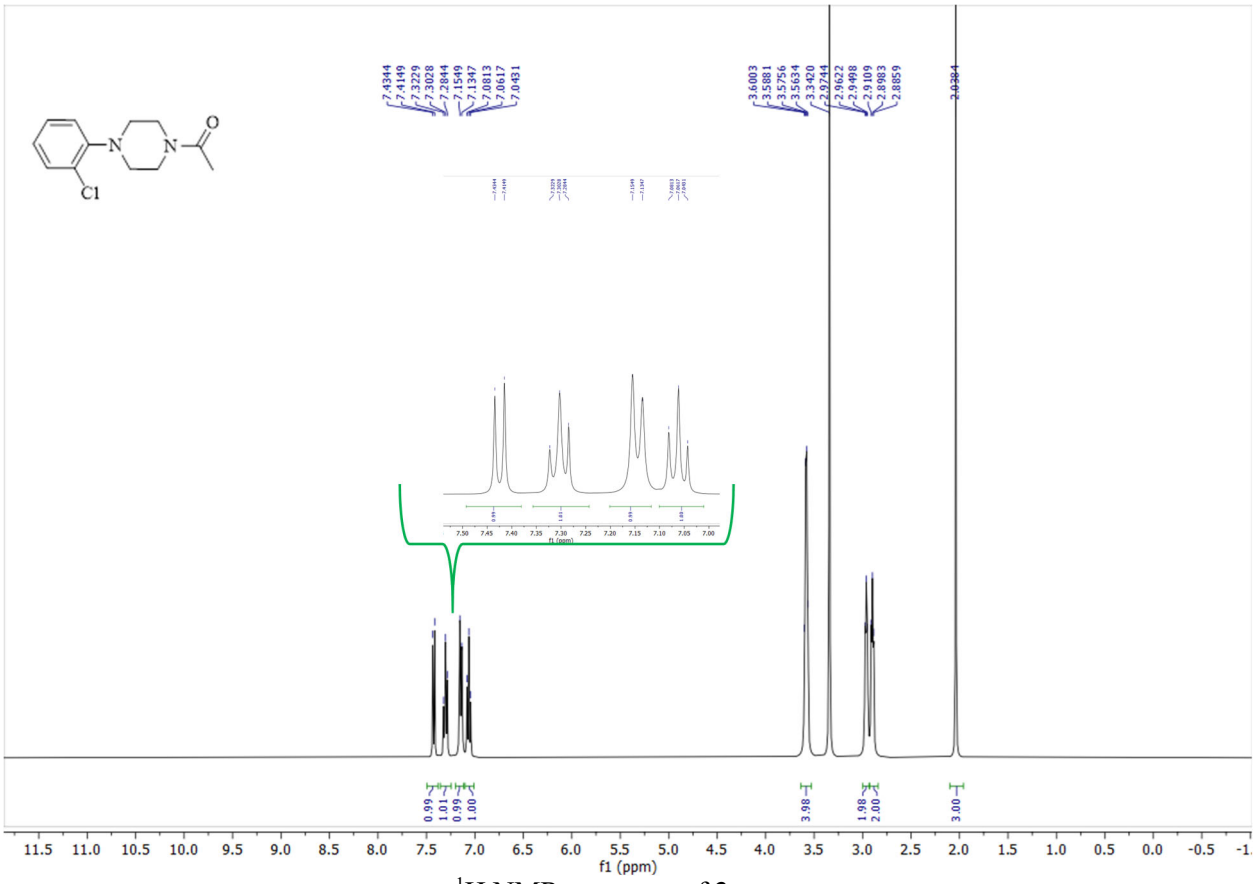
^{13}C NMR spectrum of **3aa**



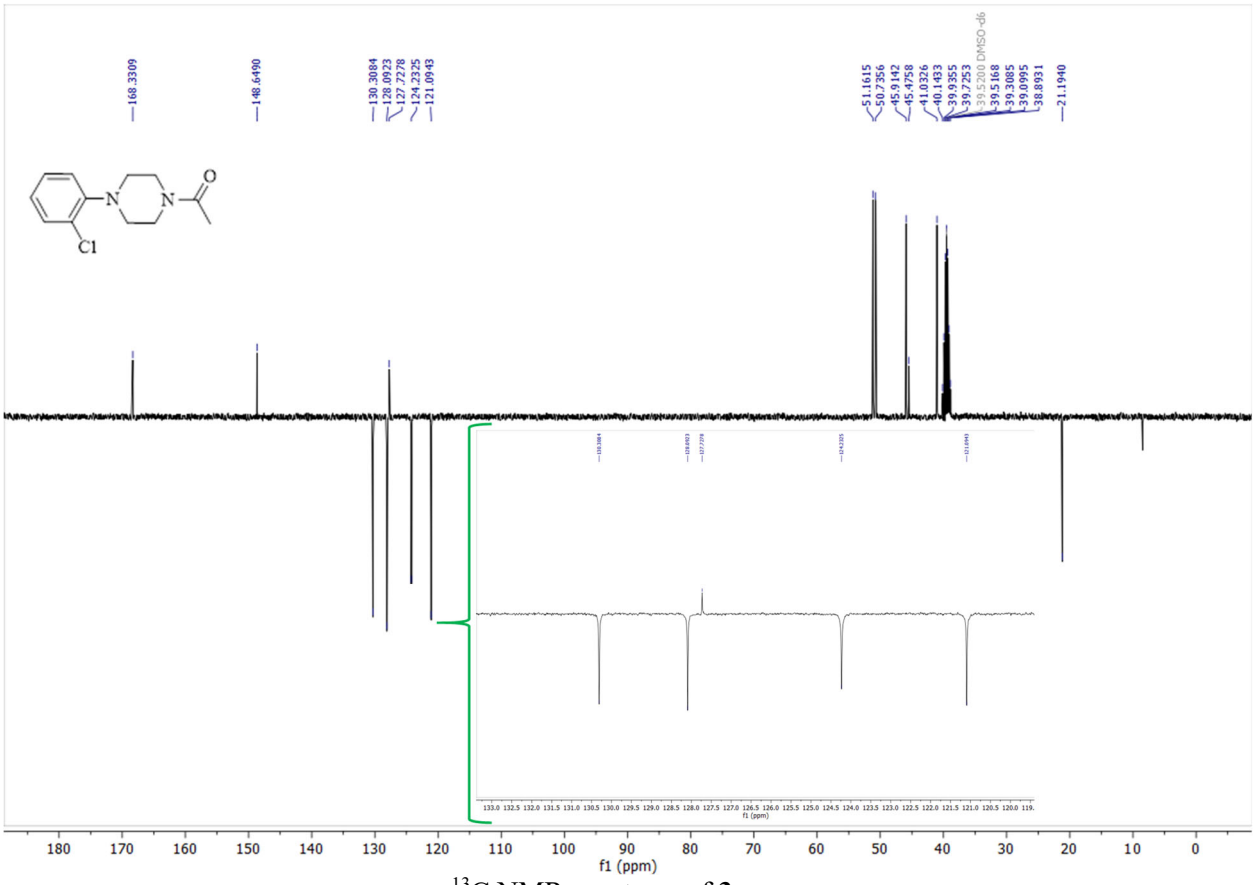
^{1}H NMR spectrum of **3ab**



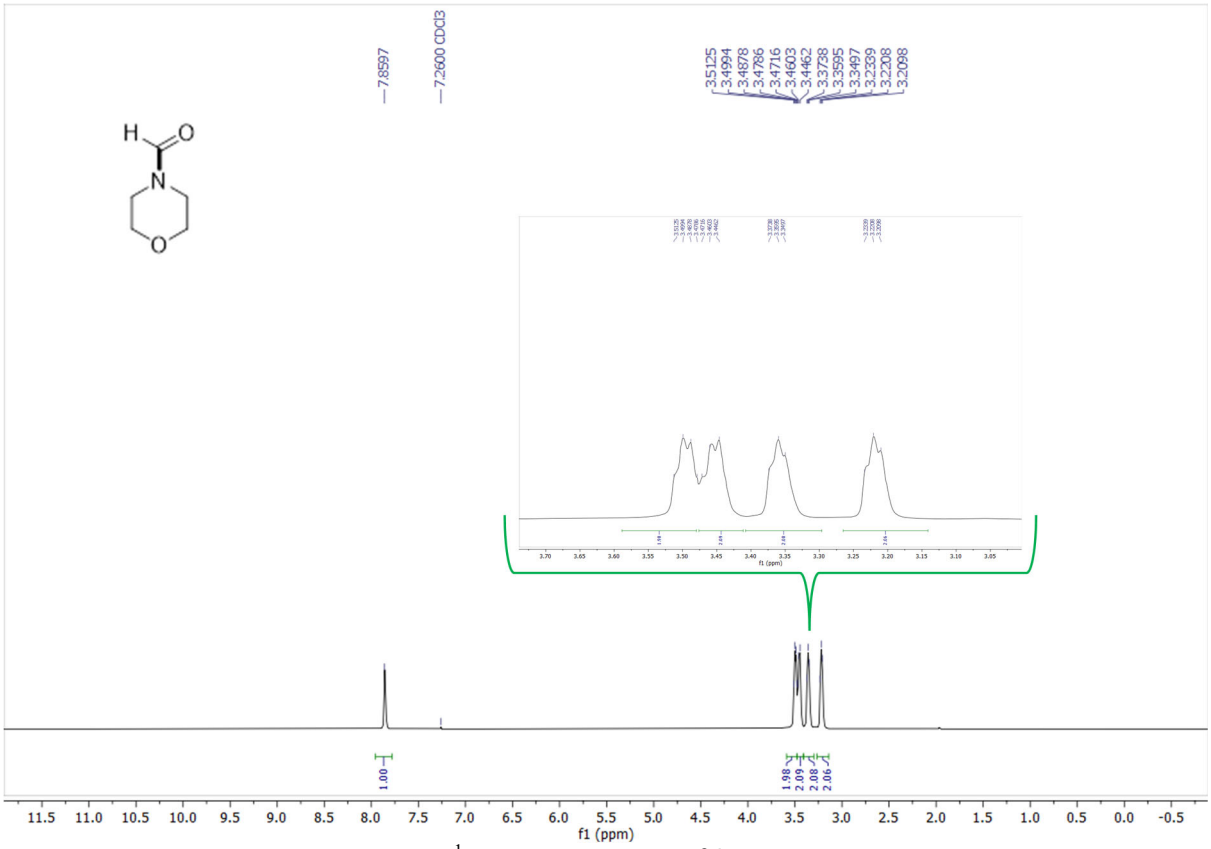
^{13}C NMR spectrum of **3ab**



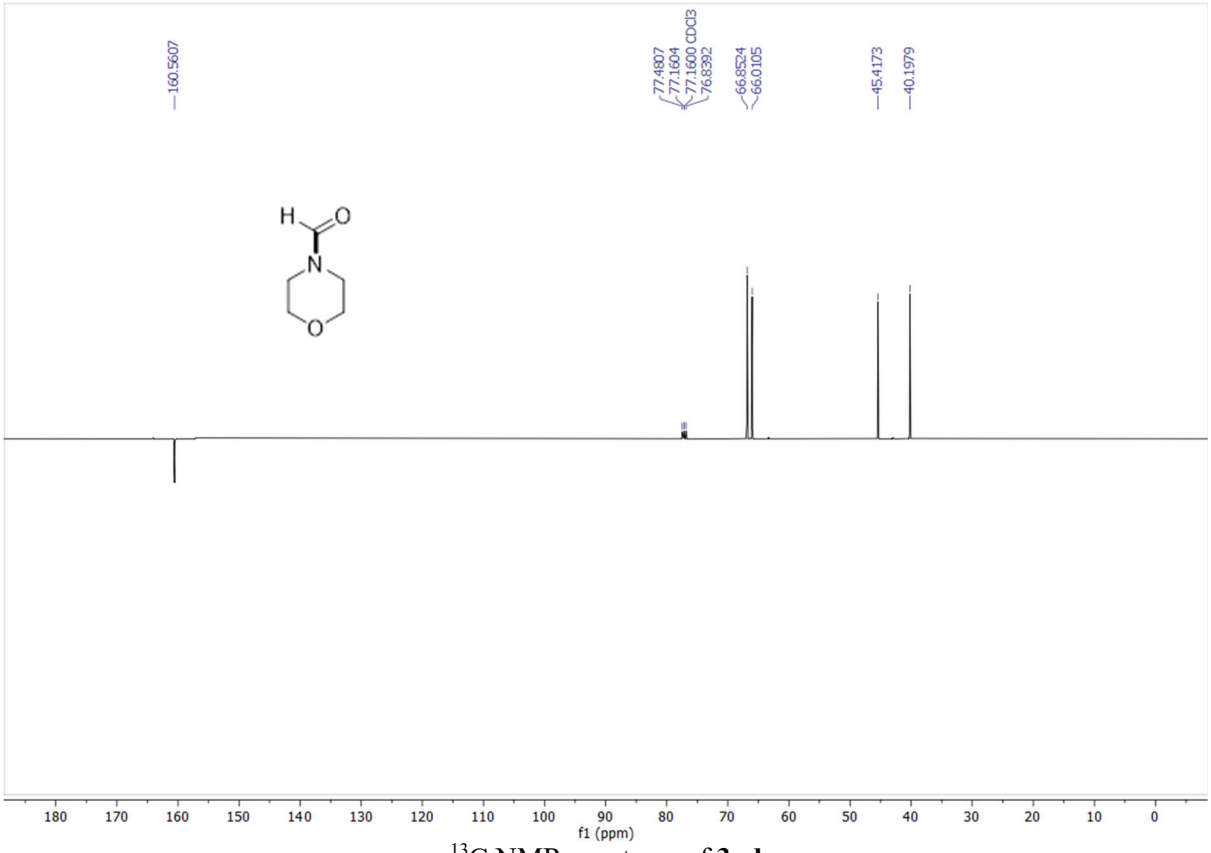
^{1}H NMR spectrum of **3ac**



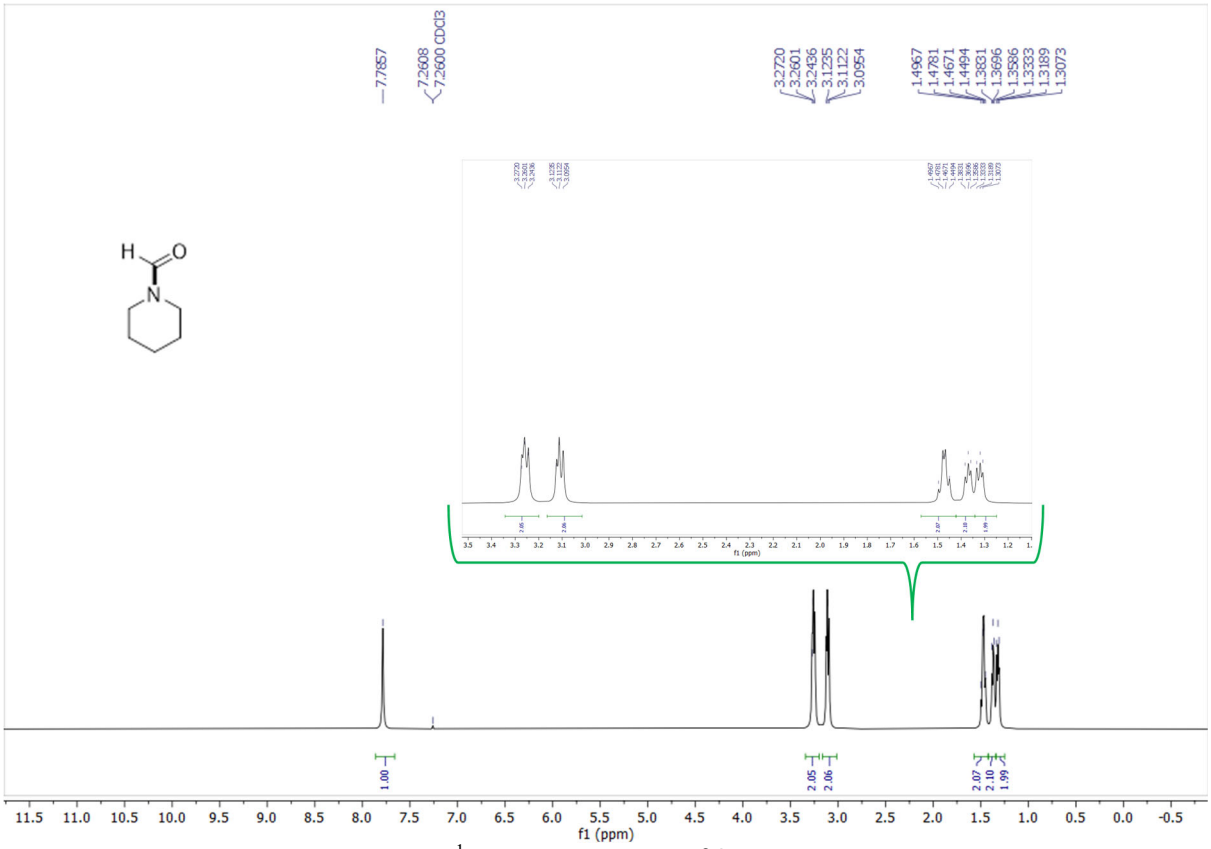
^{13}C NMR spectrum of **3ac**



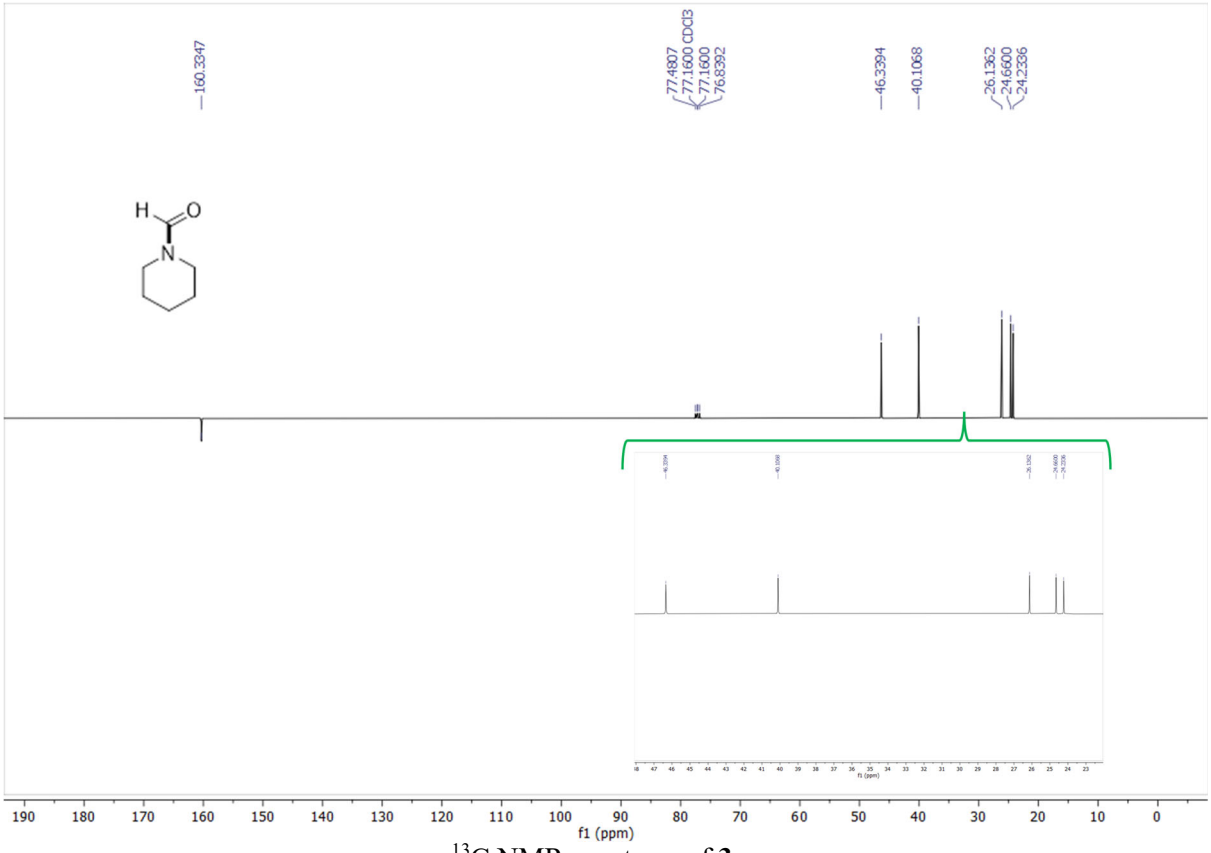
^{1}H NMR spectrum of **3ad**



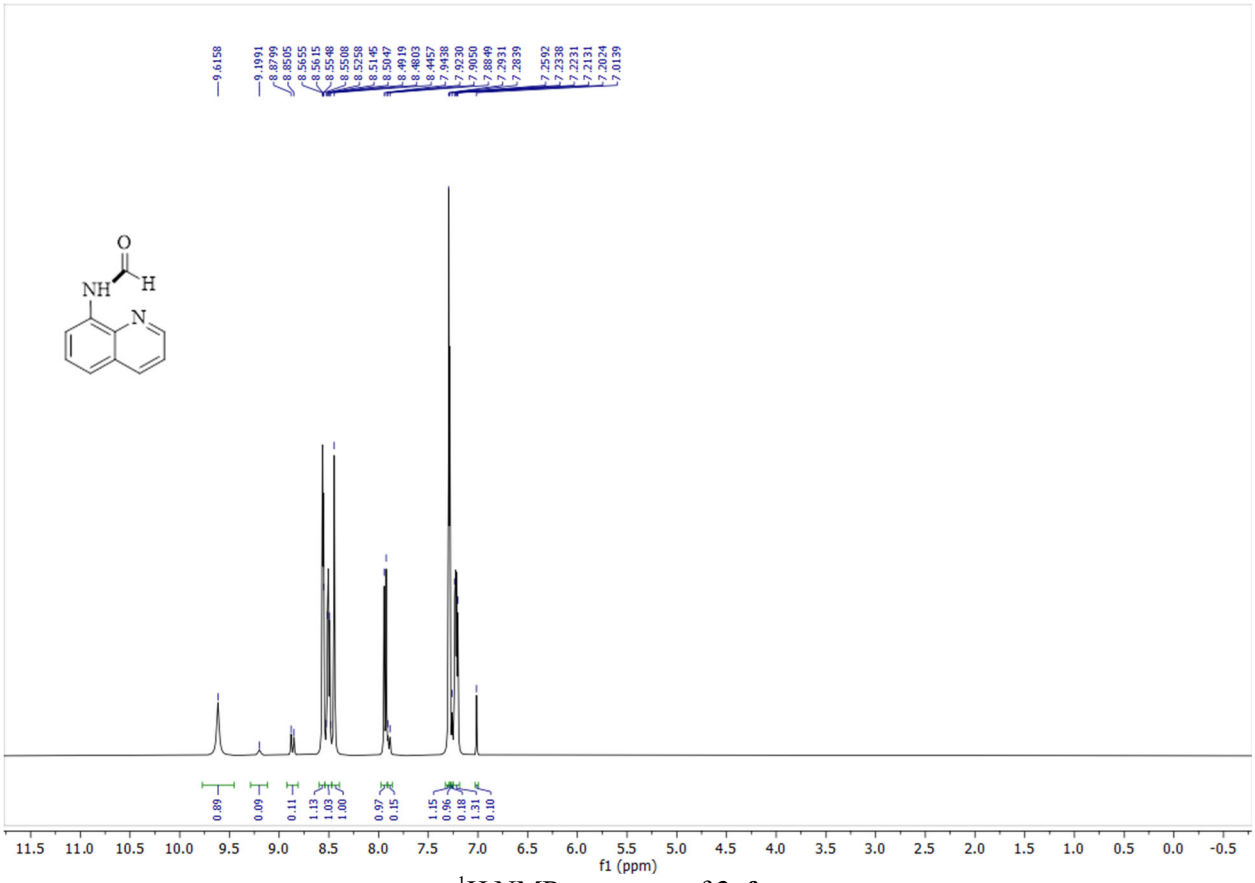
^{13}C NMR spectrum of **3ad**



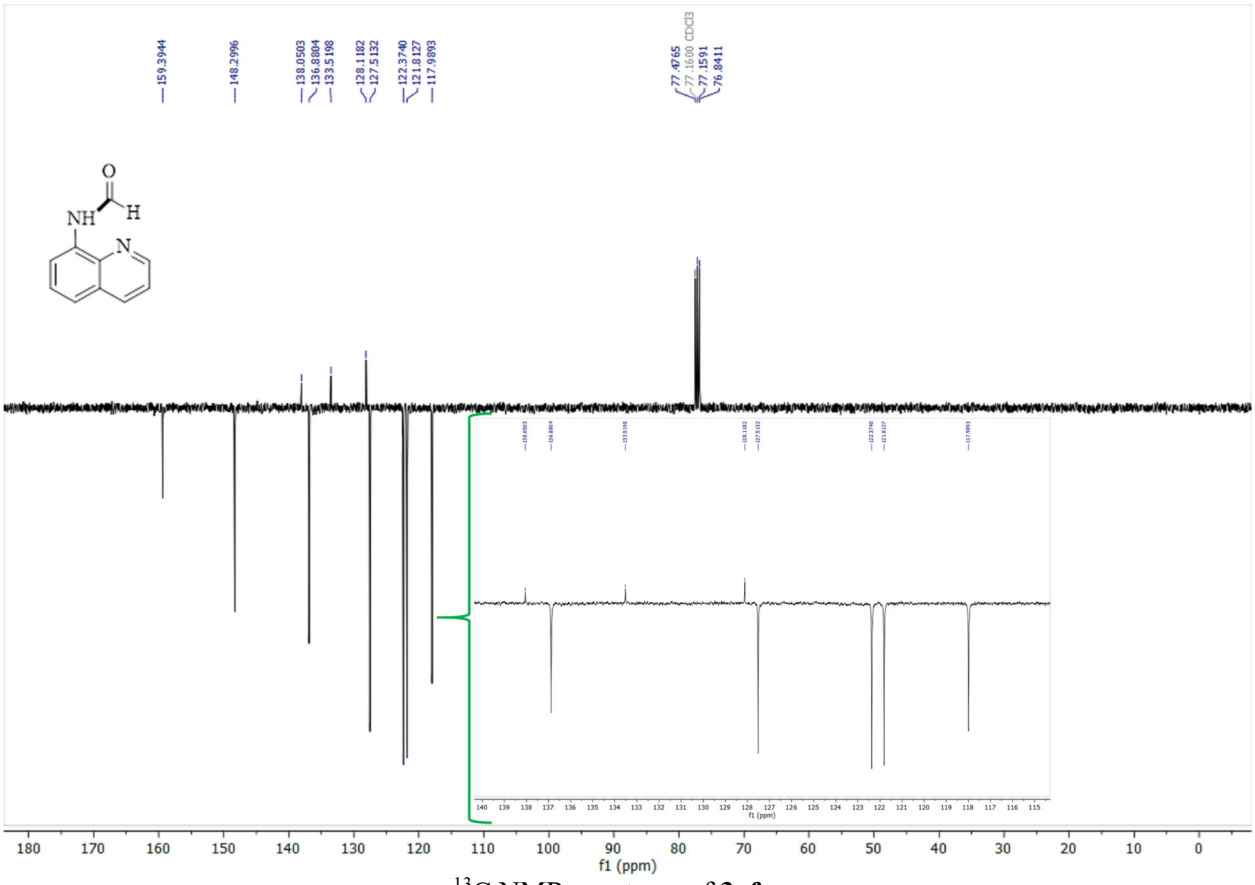
^{1}H NMR spectrum of **3ae**



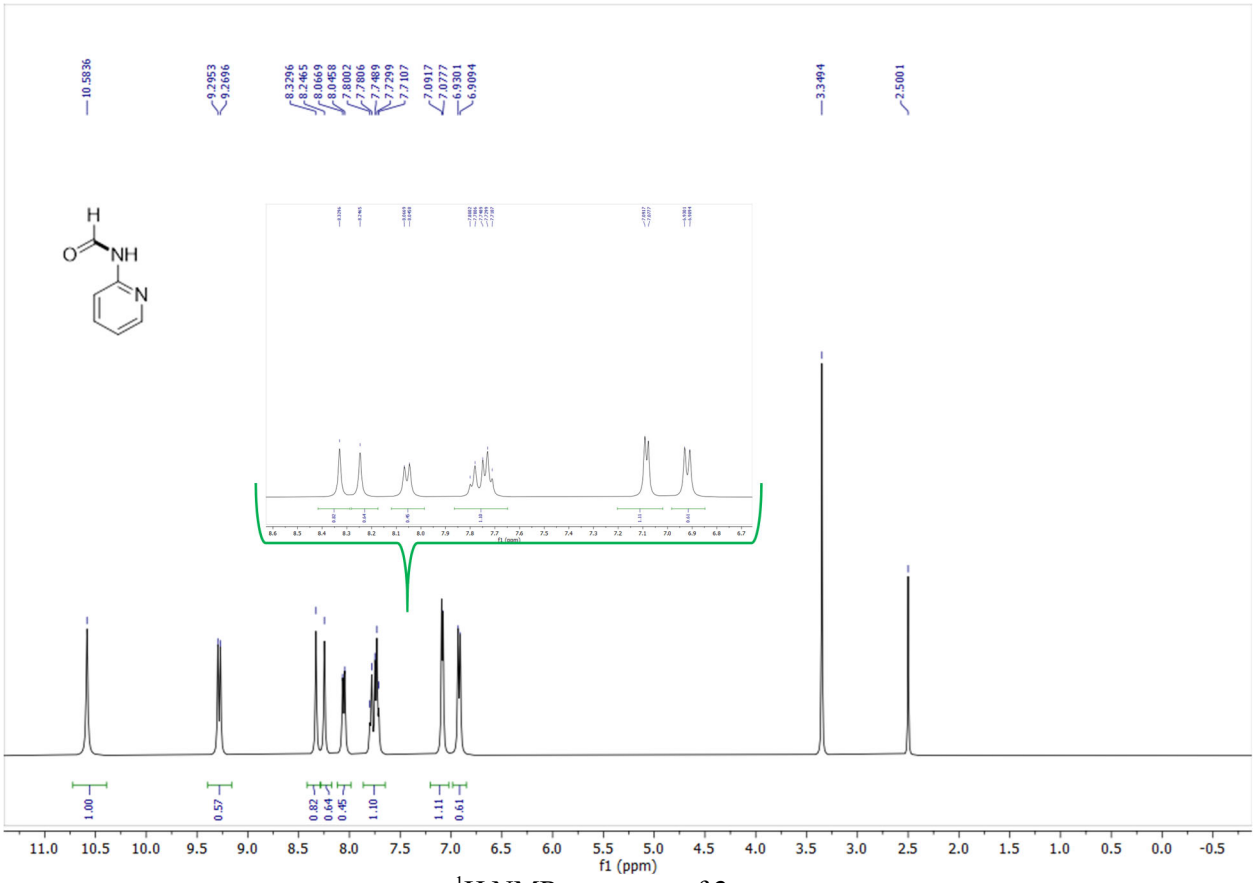
^{13}C NMR spectrum of **3ae**



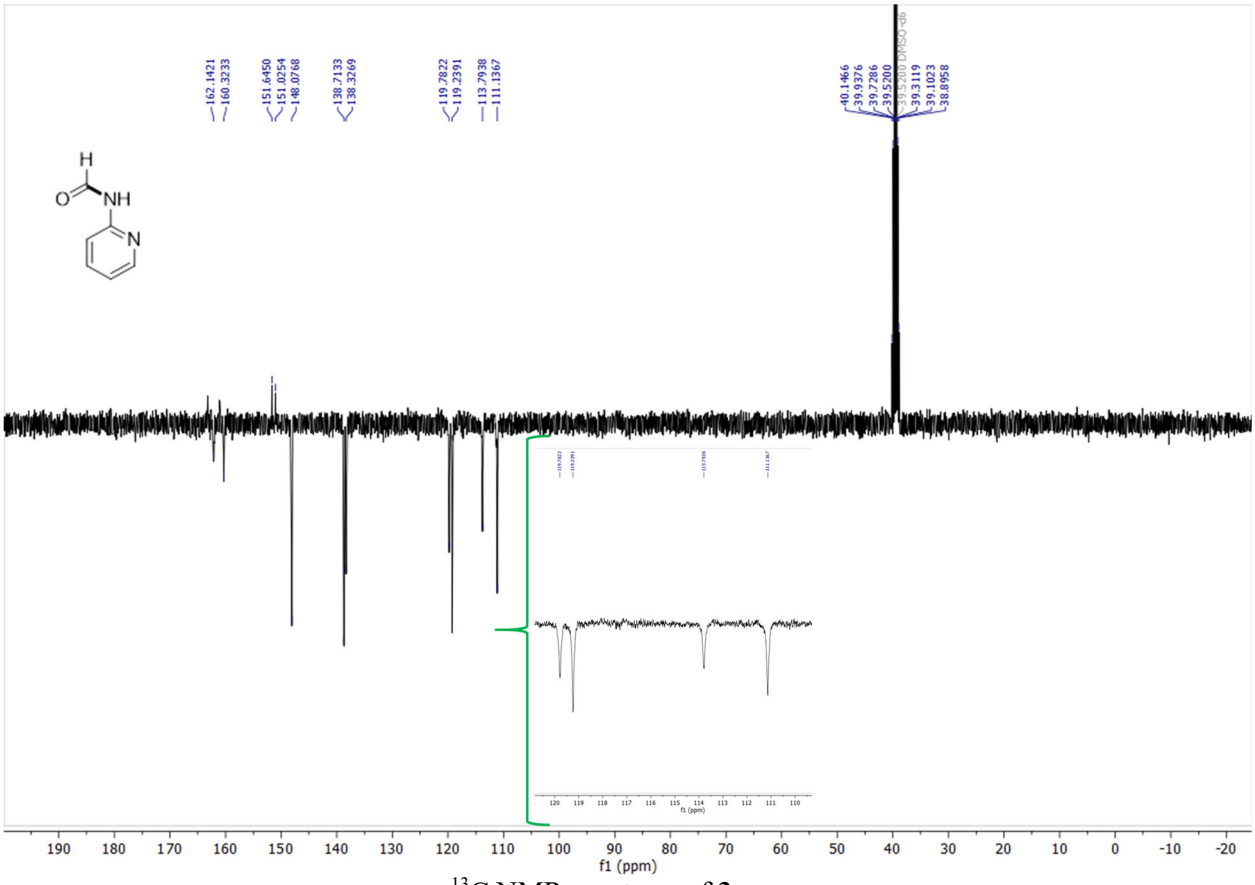
^{1}H NMR spectrum of **3af**



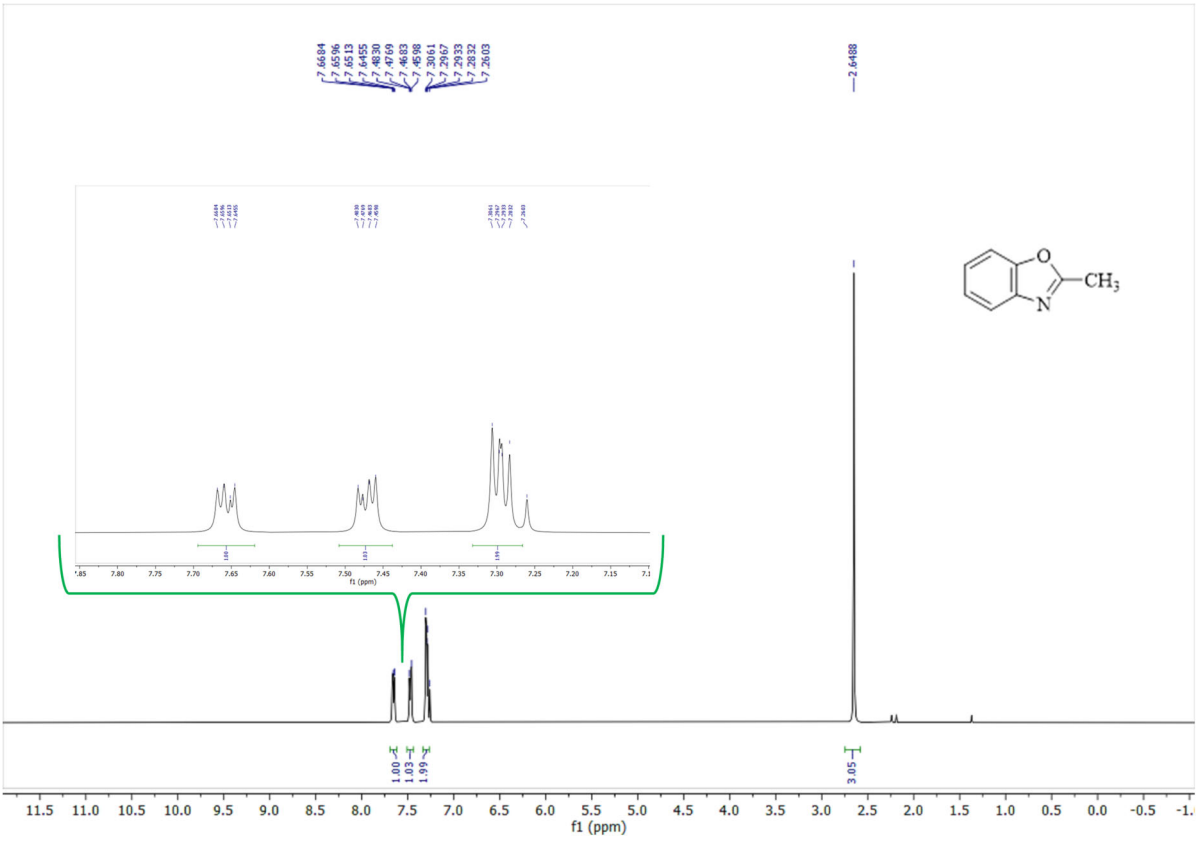
^{13}C NMR spectrum of **3af**



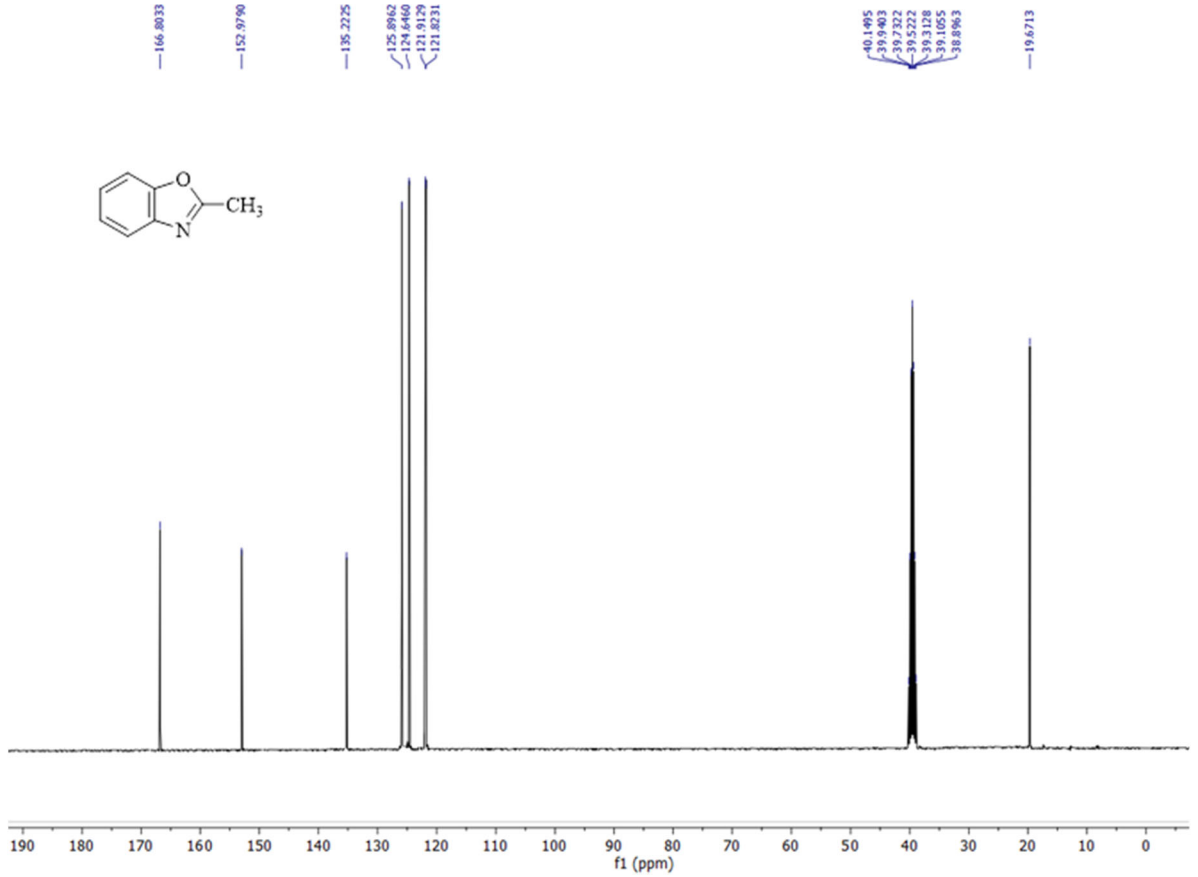
^{1}H NMR spectrum of **3ag**



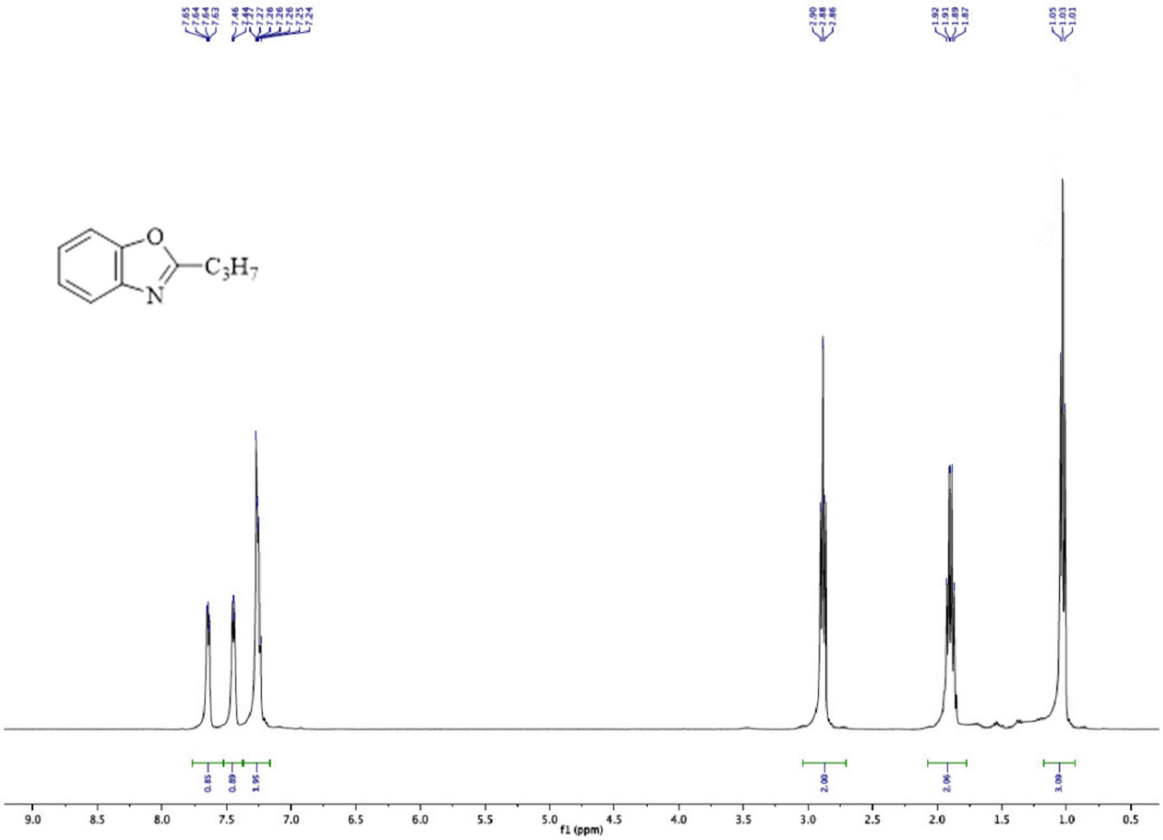
^{13}C NMR spectrum of **3ag**



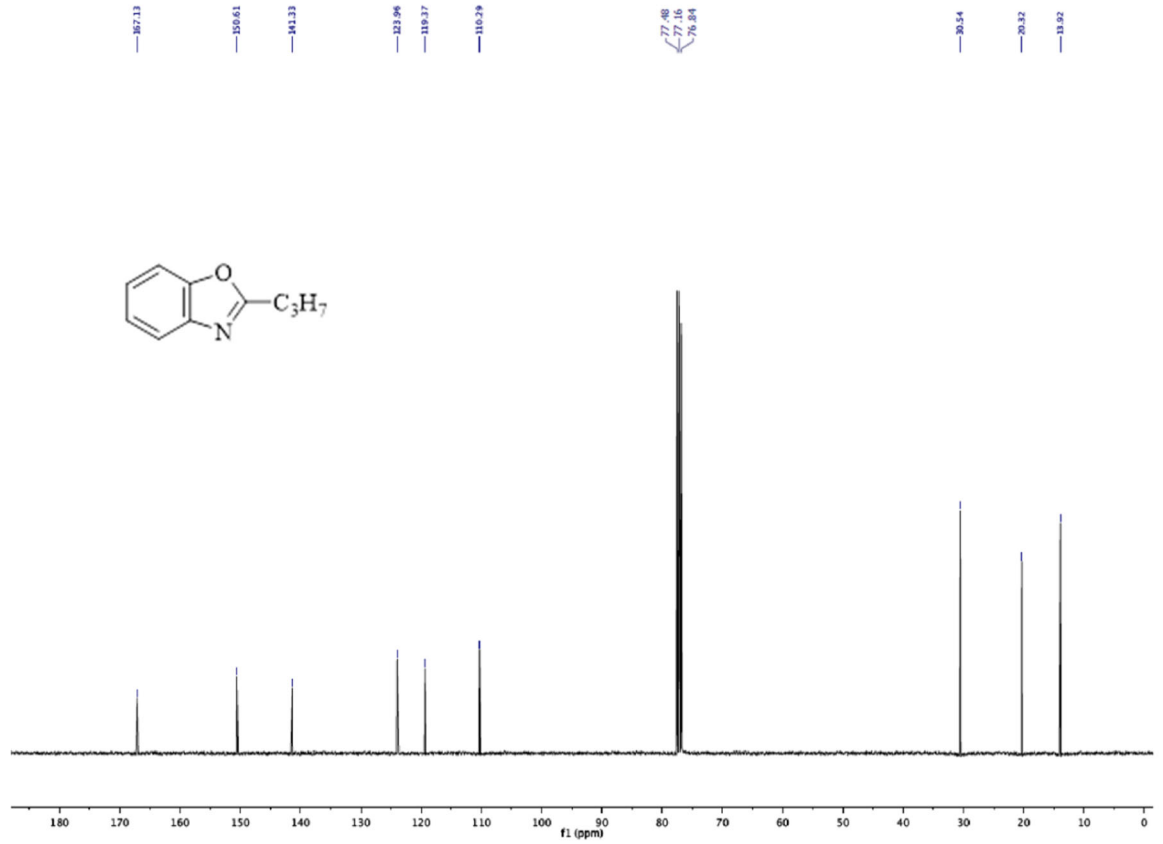
^{1}H NMR spectrum of **6a**



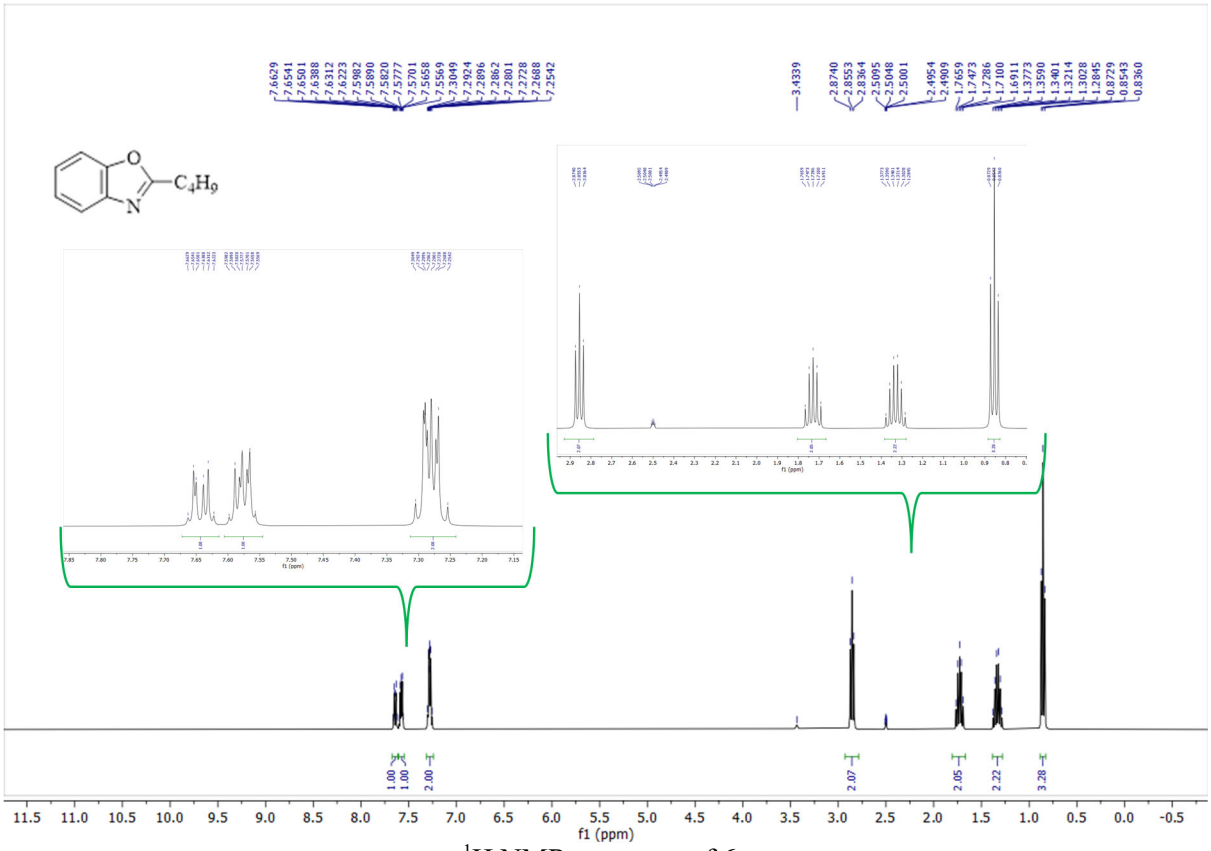
^{13}C NMR spectrum of **6a**



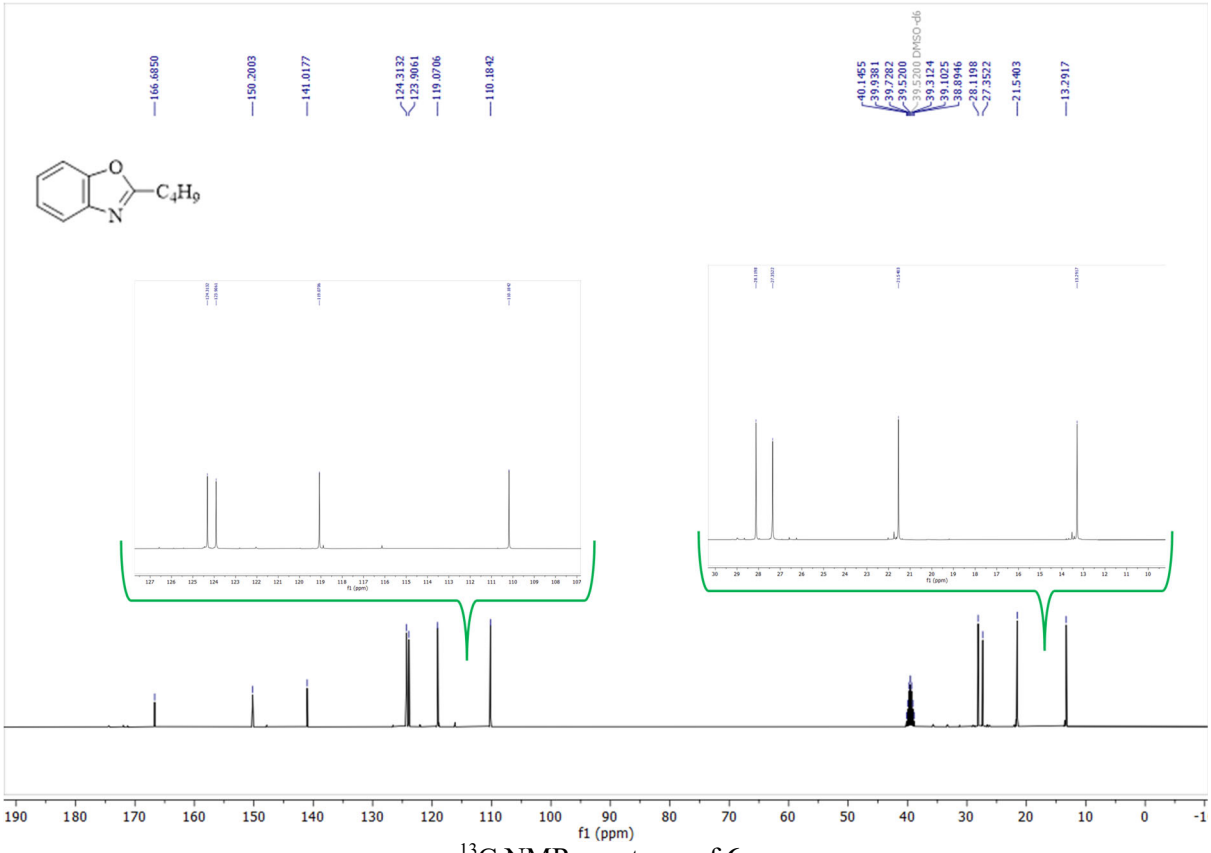
^{1}H NMR spectrum of **6b**



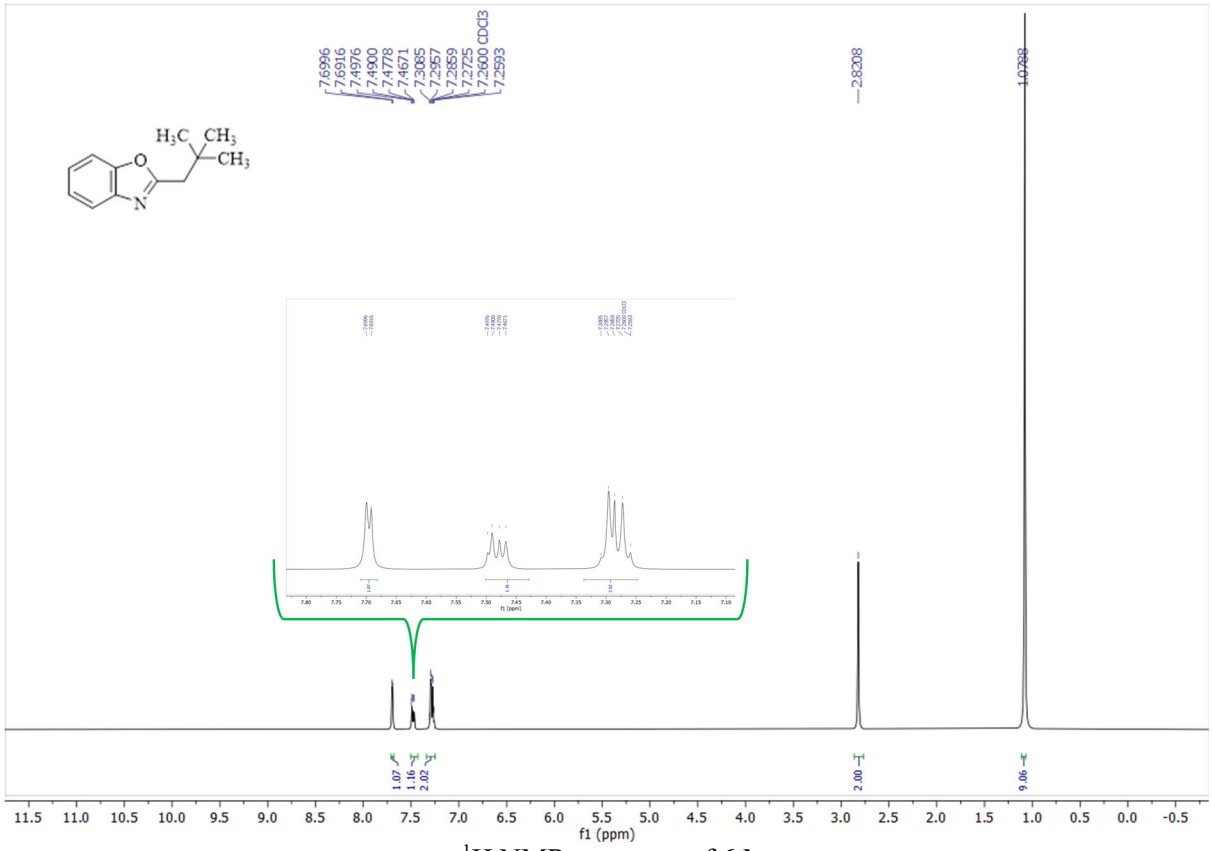
^{13}C NMR spectrum of **6b**



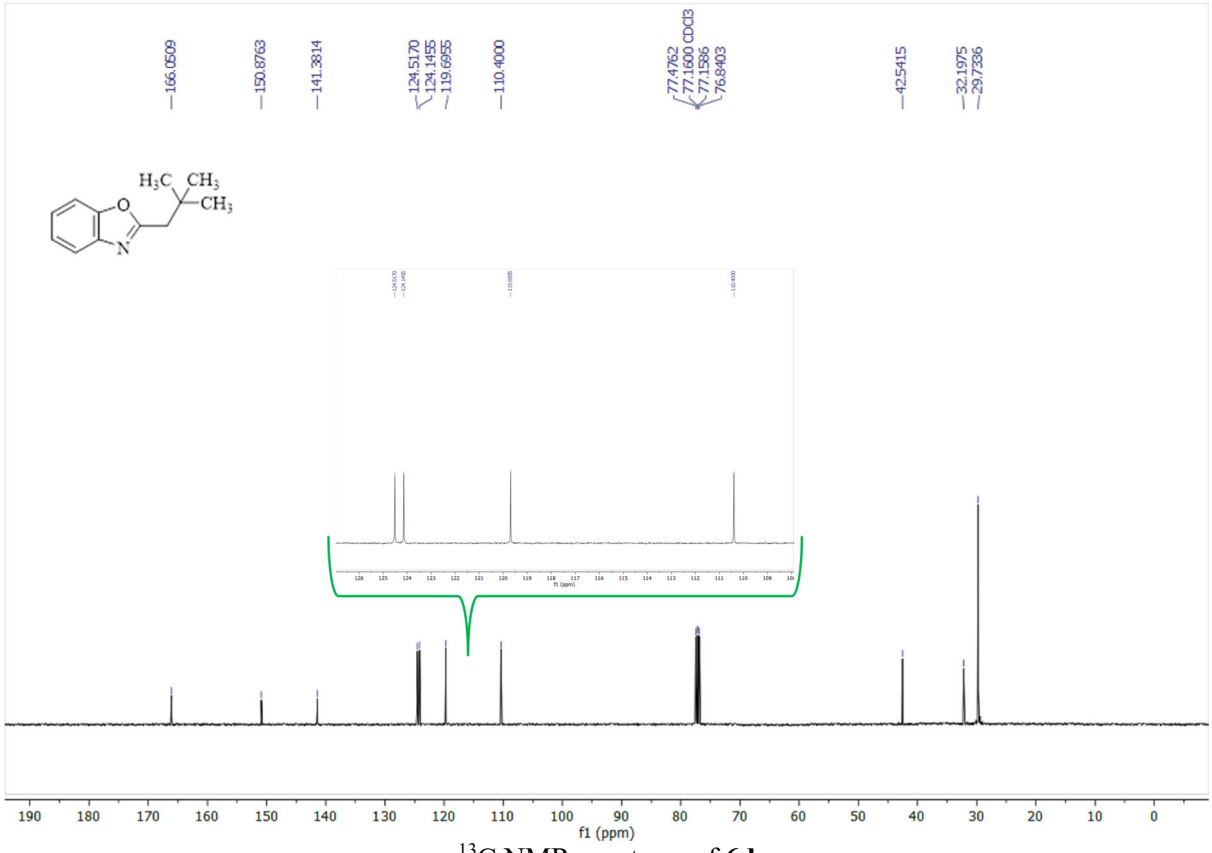
^{1}H NMR spectrum of **6c**



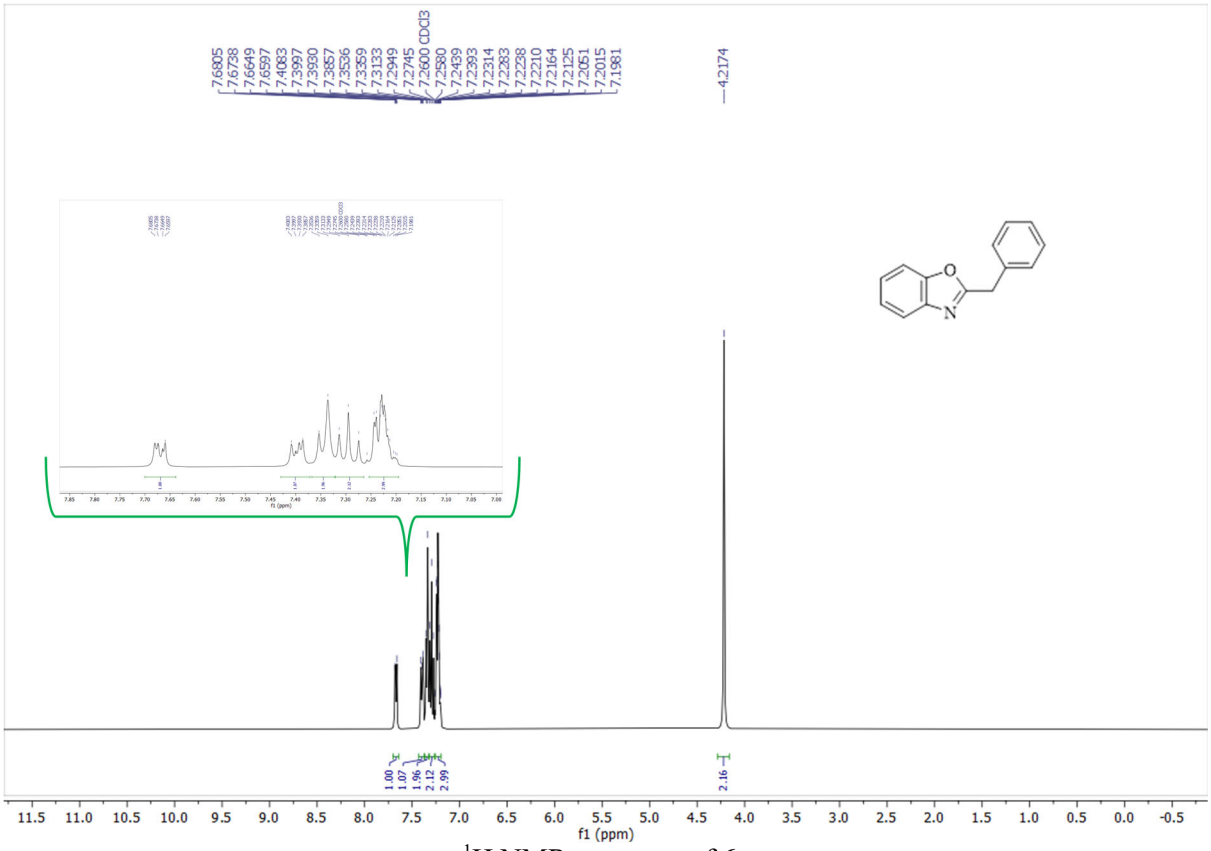
^{13}C NMR spectrum of **6c**



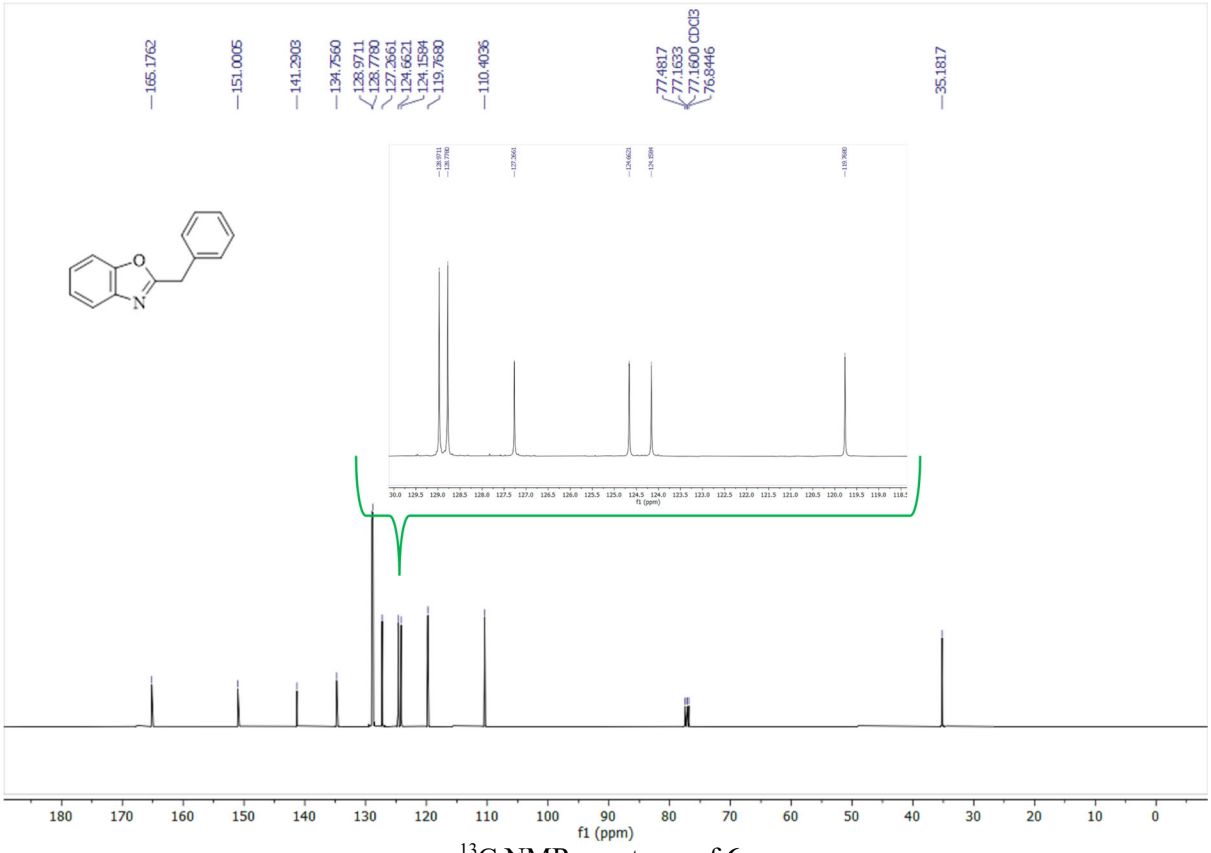
^{1}H NMR spectrum of **6d**



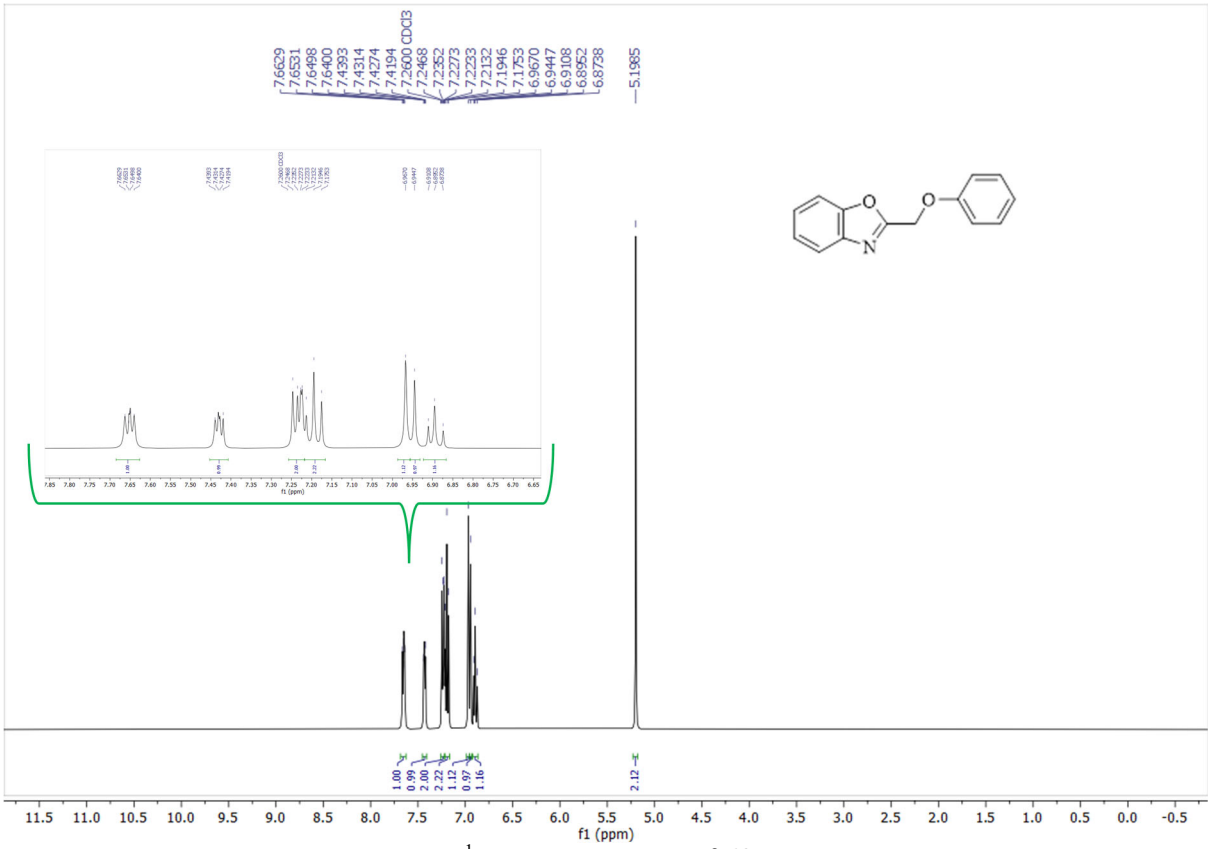
^{13}C NMR spectrum of **6d**



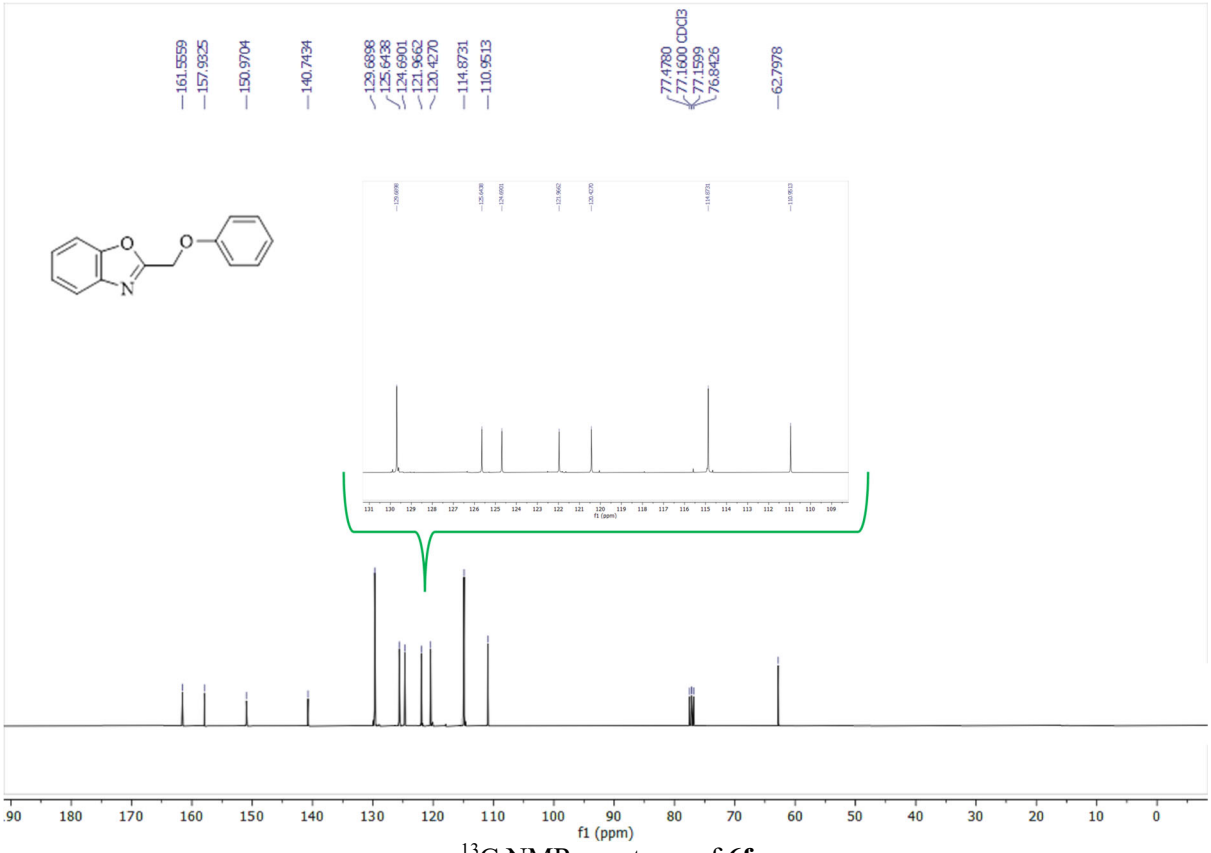
^{1}H NMR spectrum of **6e**



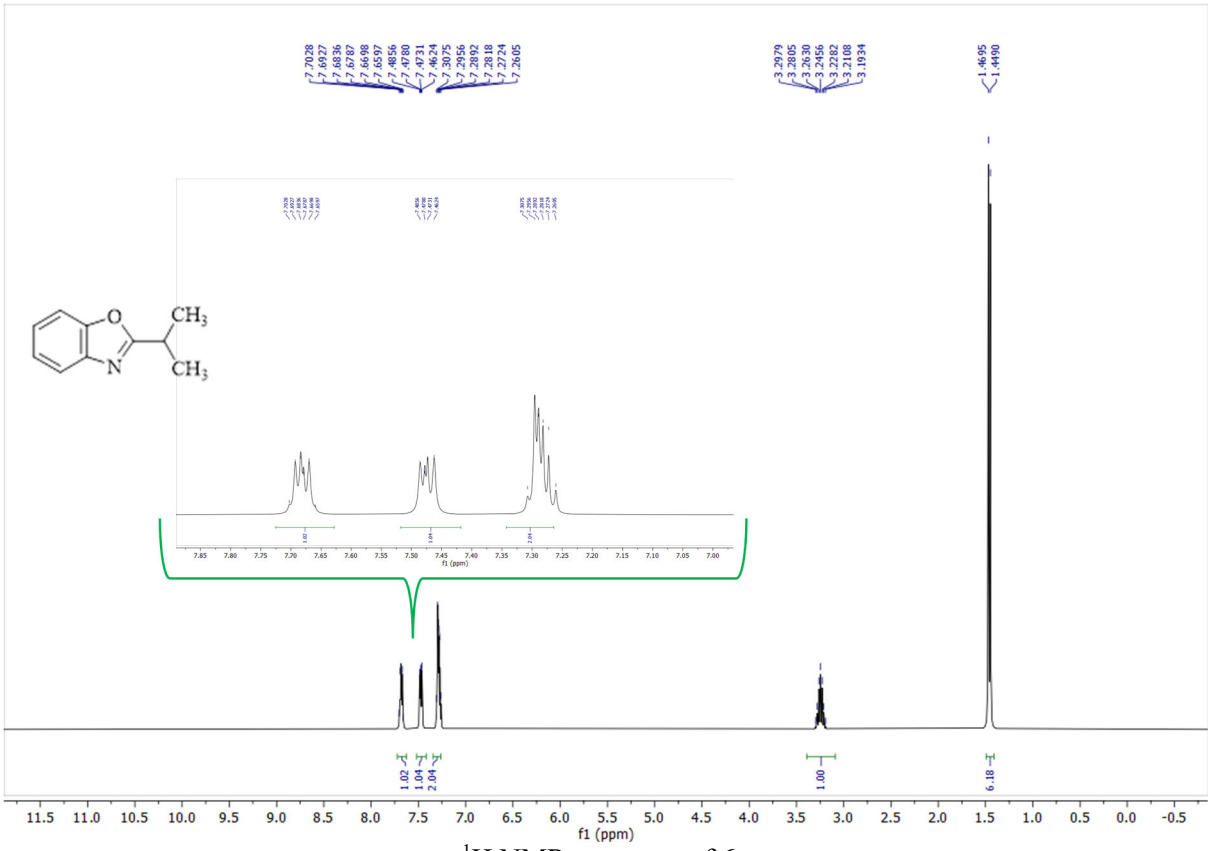
^{13}C NMR spectrum of **6e**



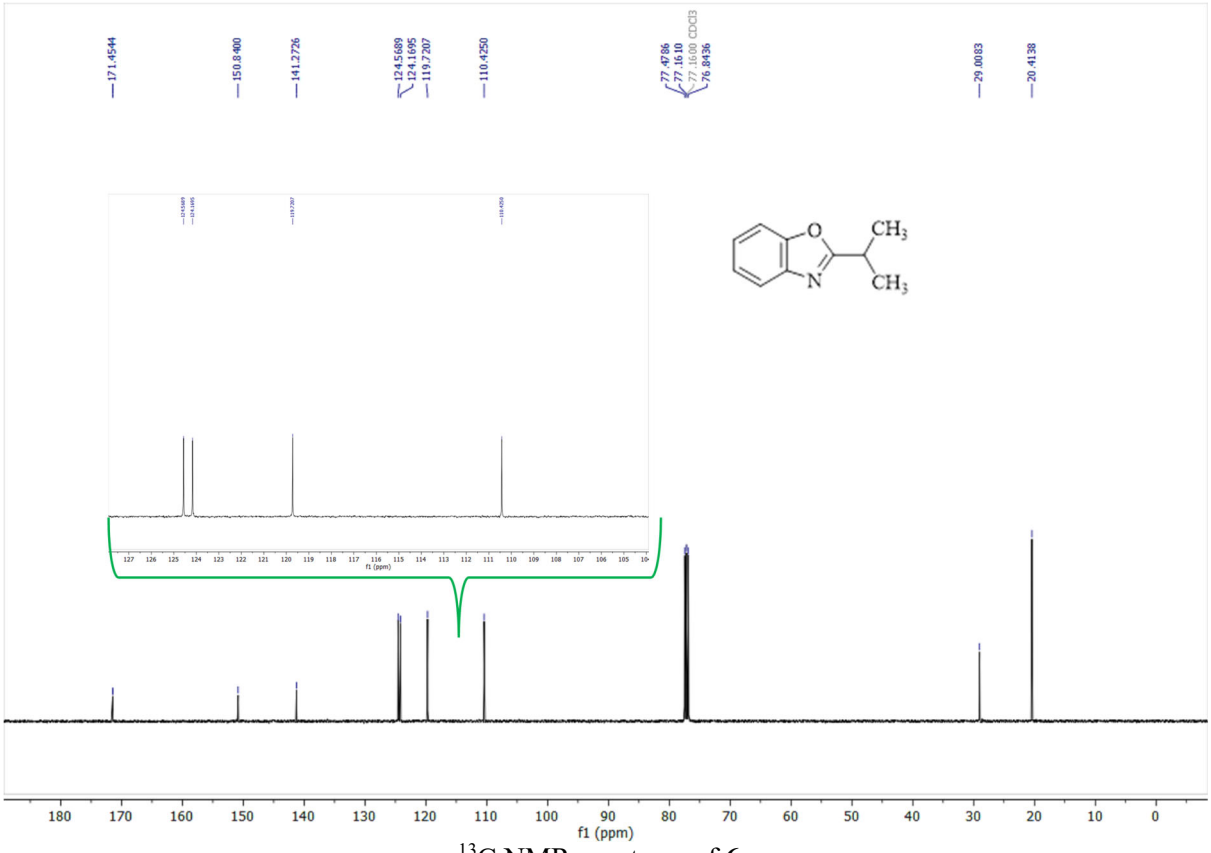
^{1}H NMR spectrum of **6f**



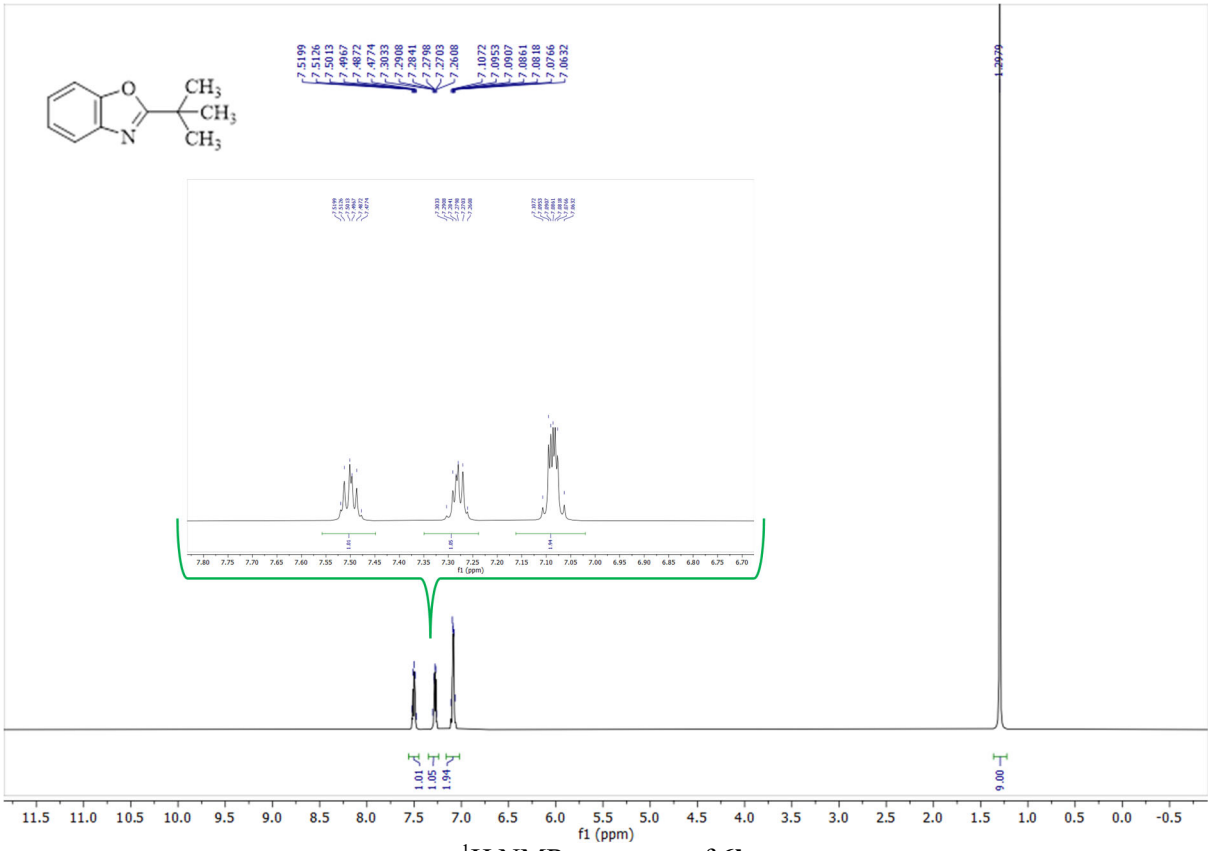
^{13}C NMR spectrum of **6f**



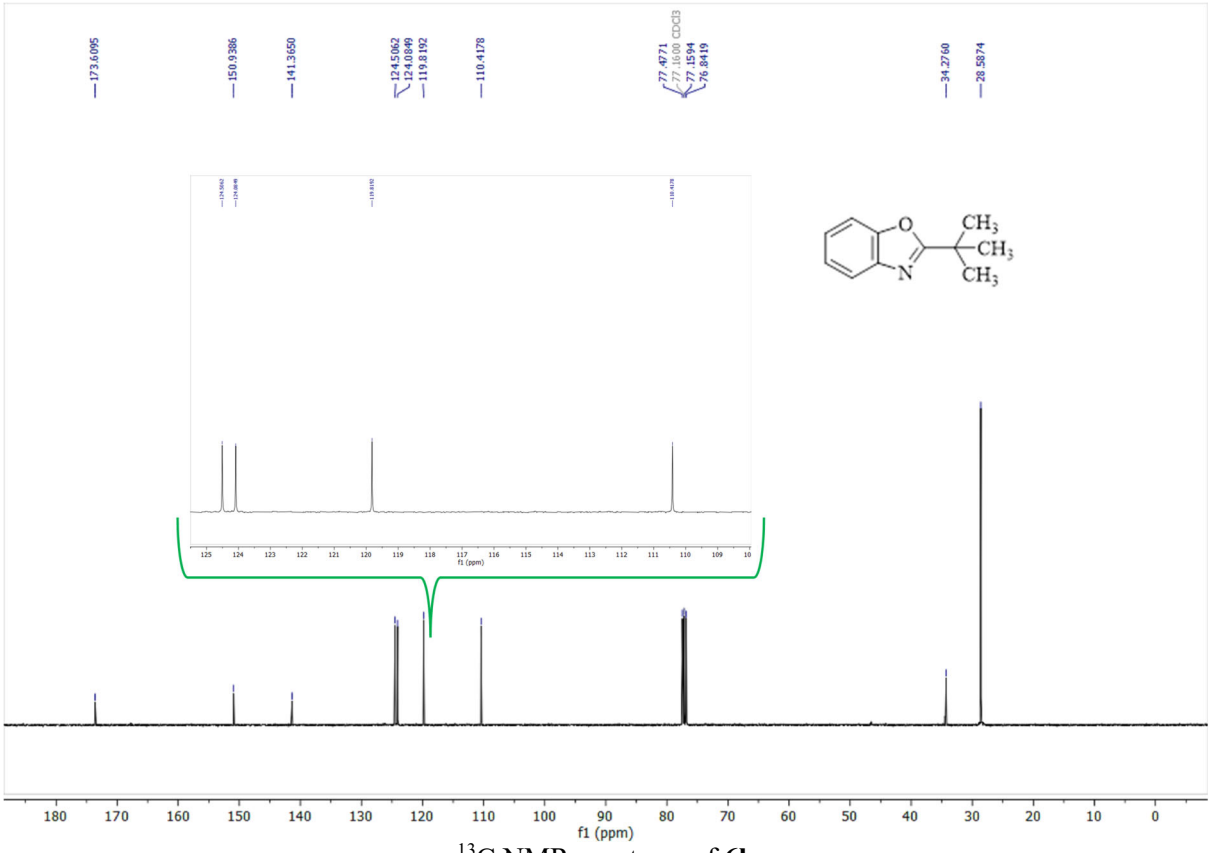
^{1}H NMR spectrum of **6g**



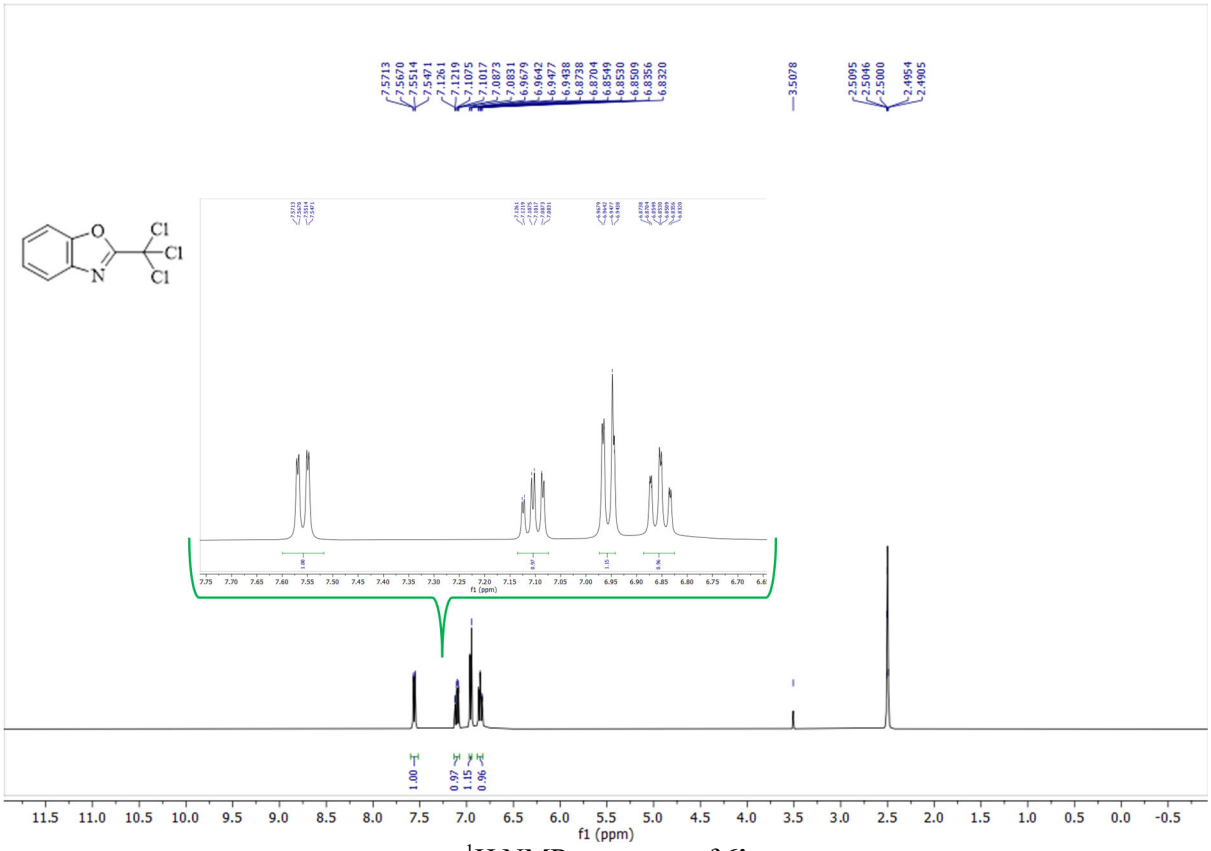
^{13}C NMR spectrum of **6g**



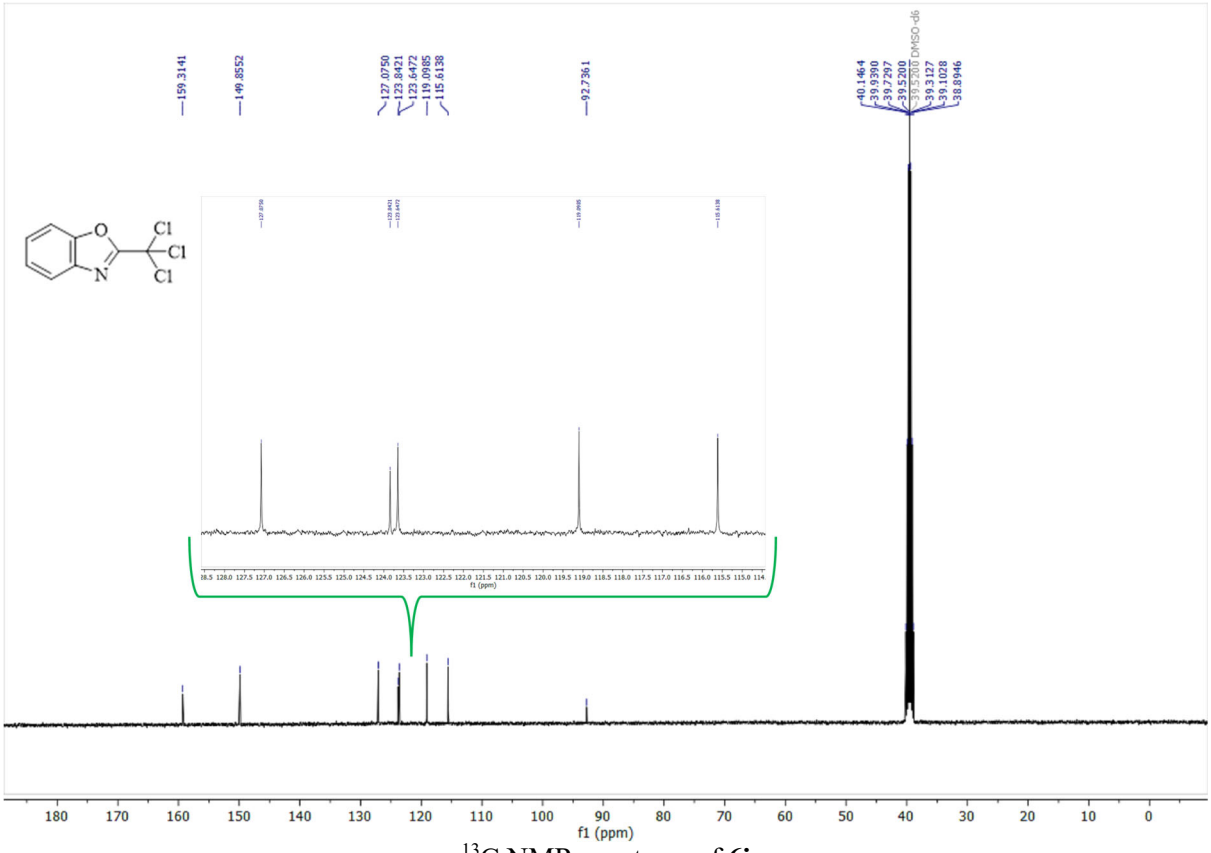
^{1}H NMR spectrum of **6h**



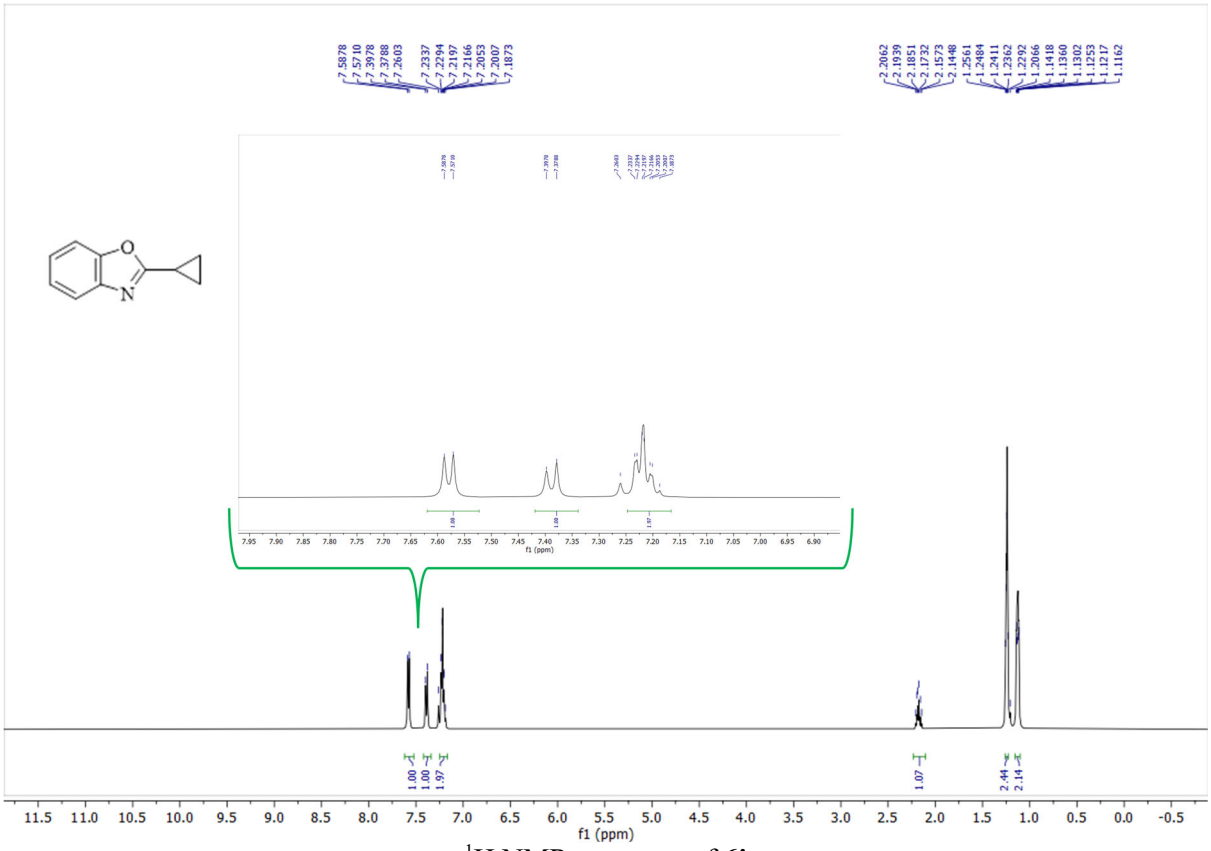
^{13}C NMR spectrum of **6h**



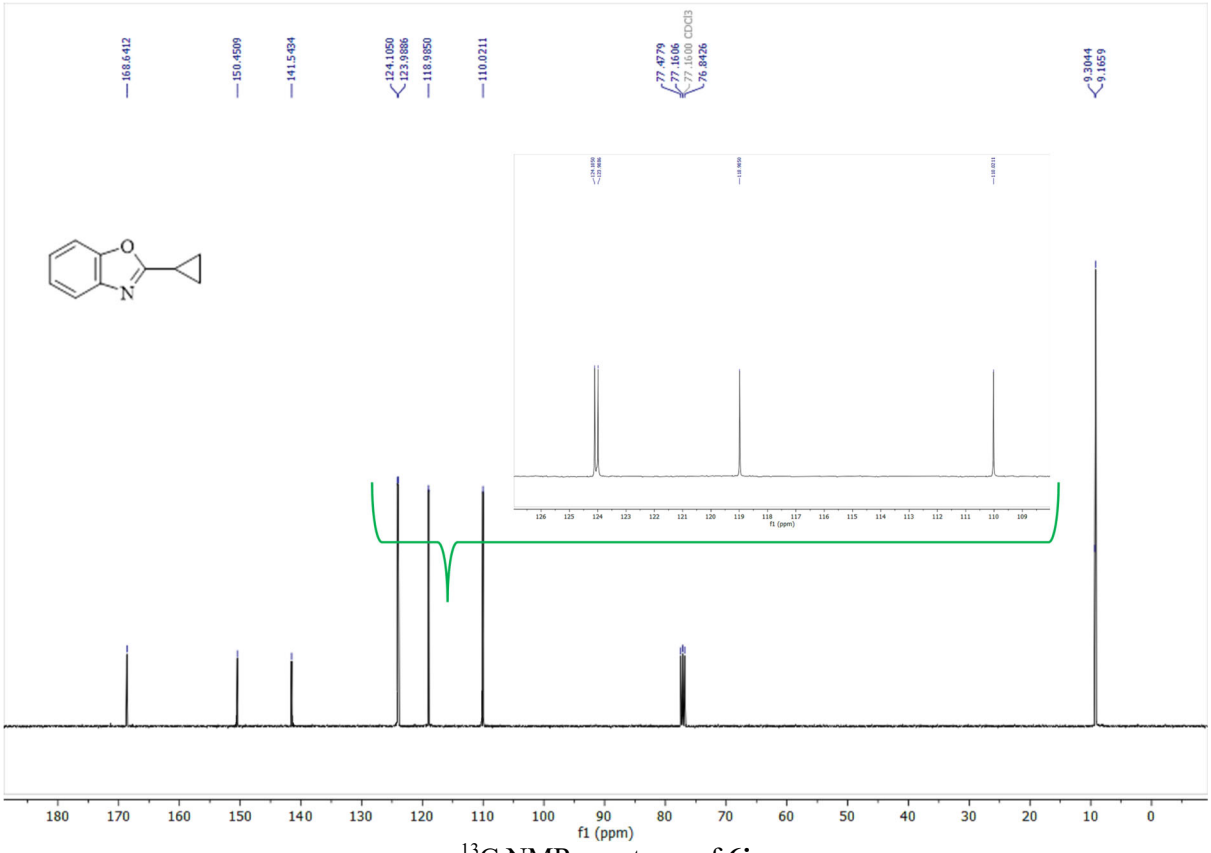
^{1}H NMR spectrum of **6i**



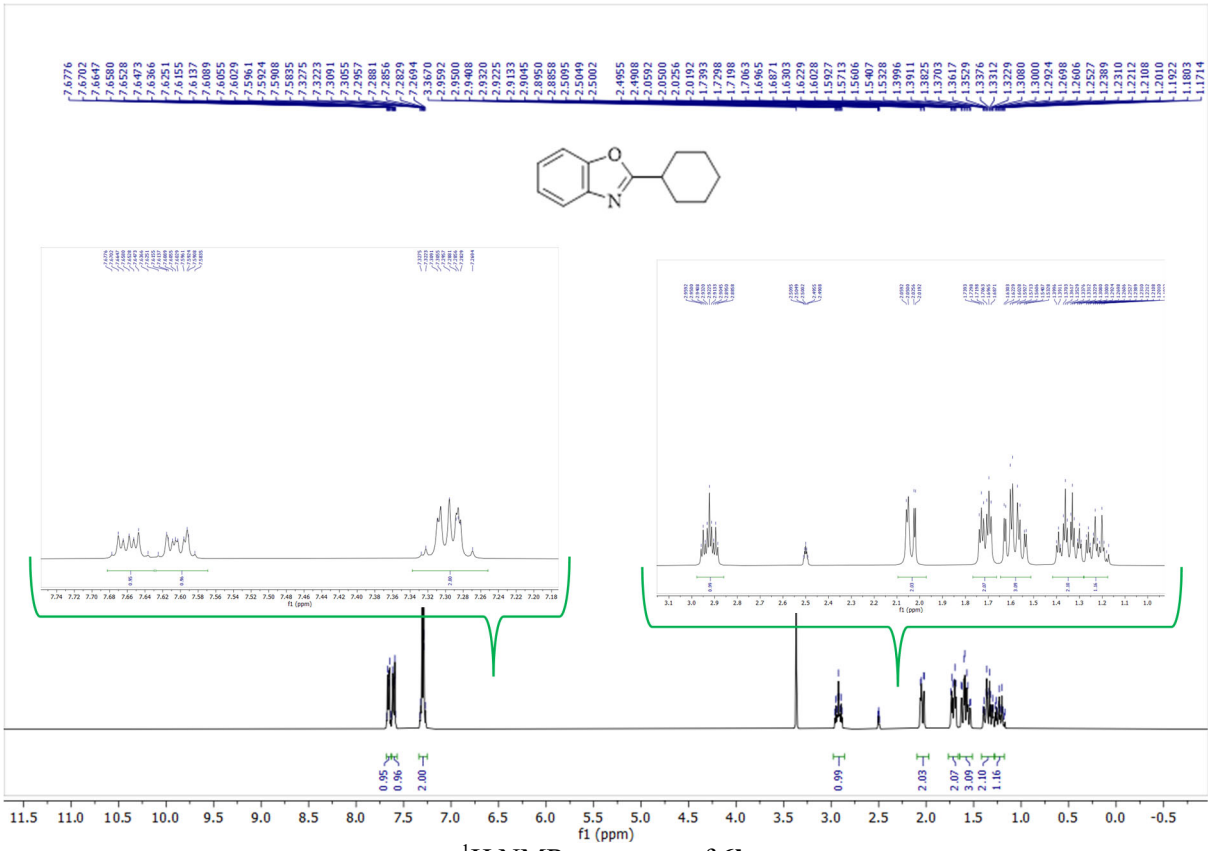
^{13}C NMR spectrum of **6i**



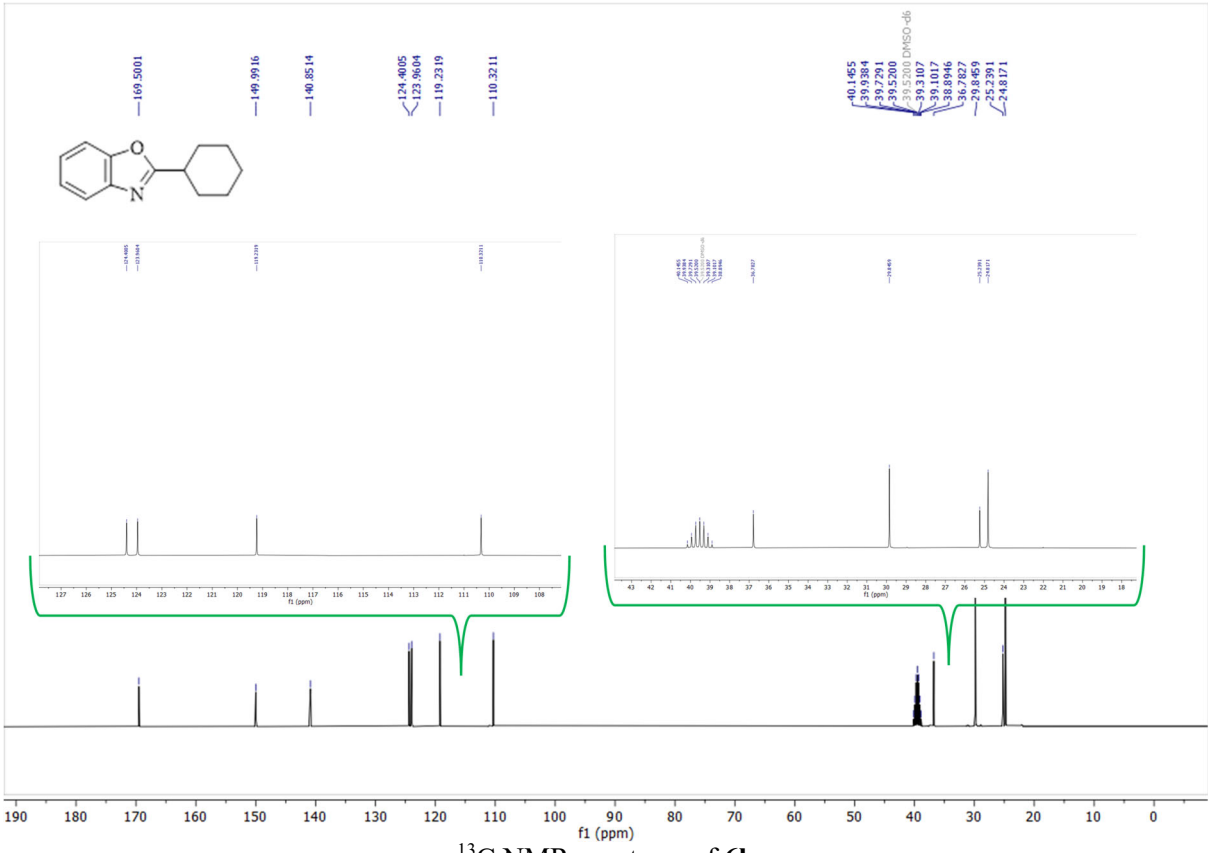
^{1}H NMR spectrum of **6j**



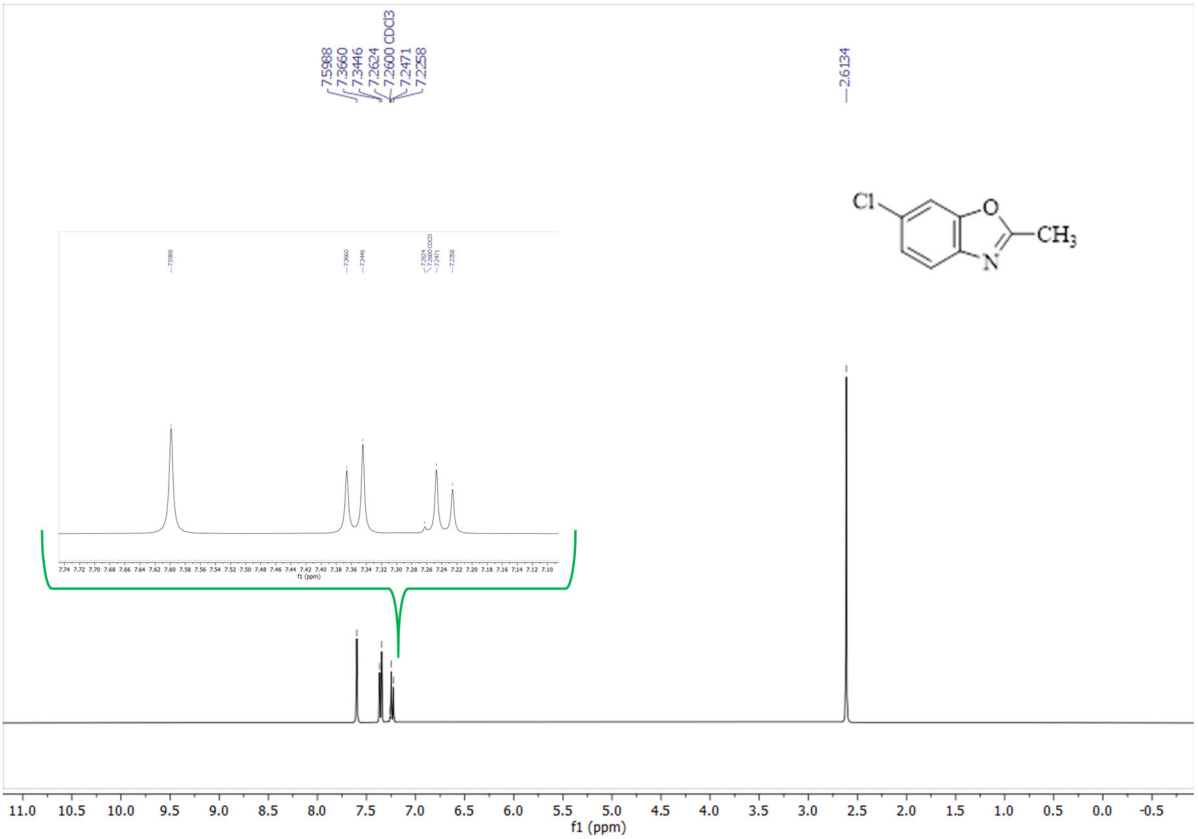
^{13}C NMR spectrum of **6j**



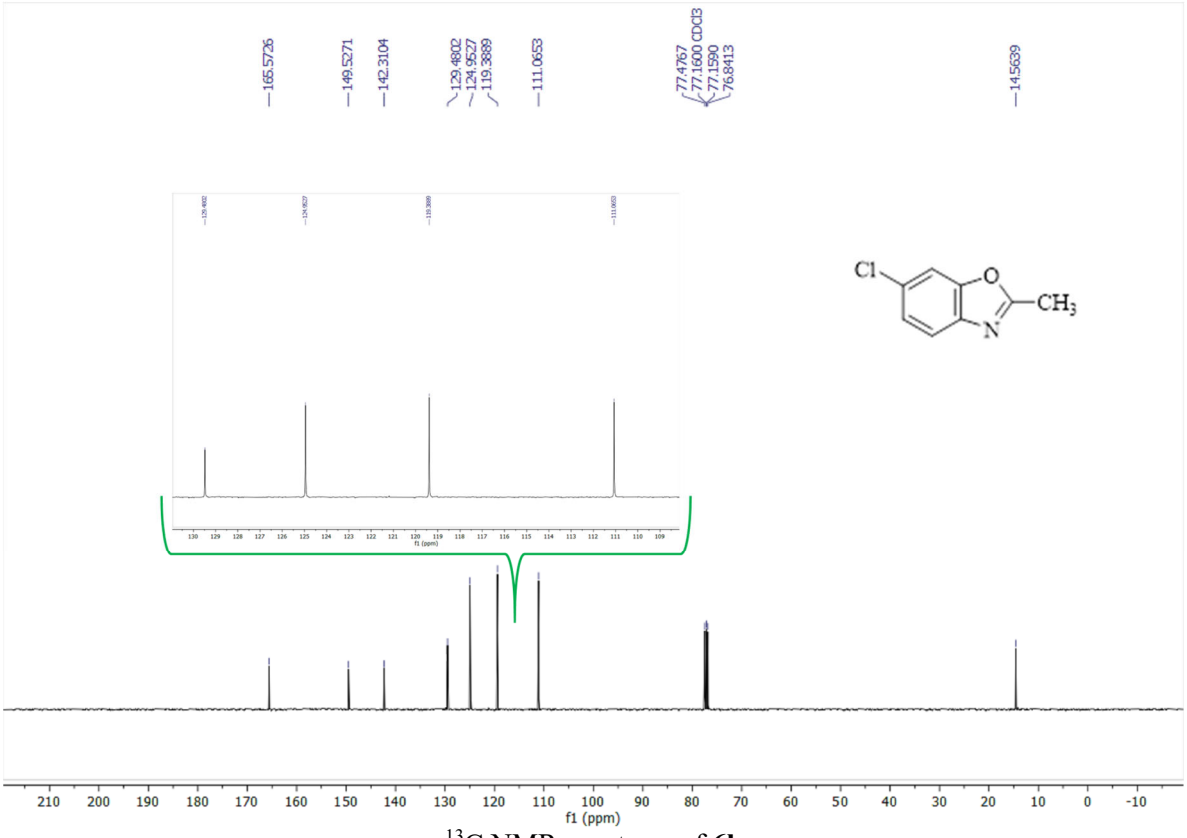
^{1}H NMR spectrum of **6k**



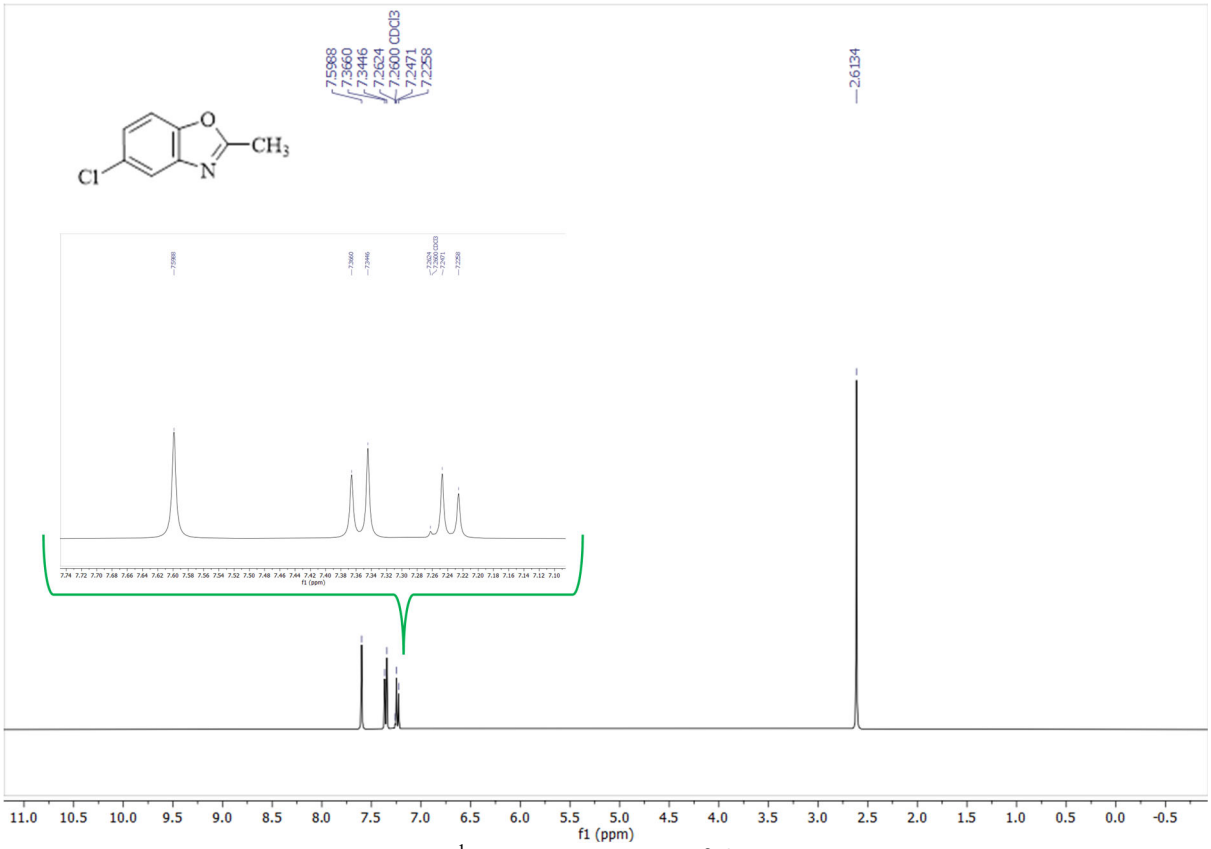
^{13}C NMR spectrum of **6k**



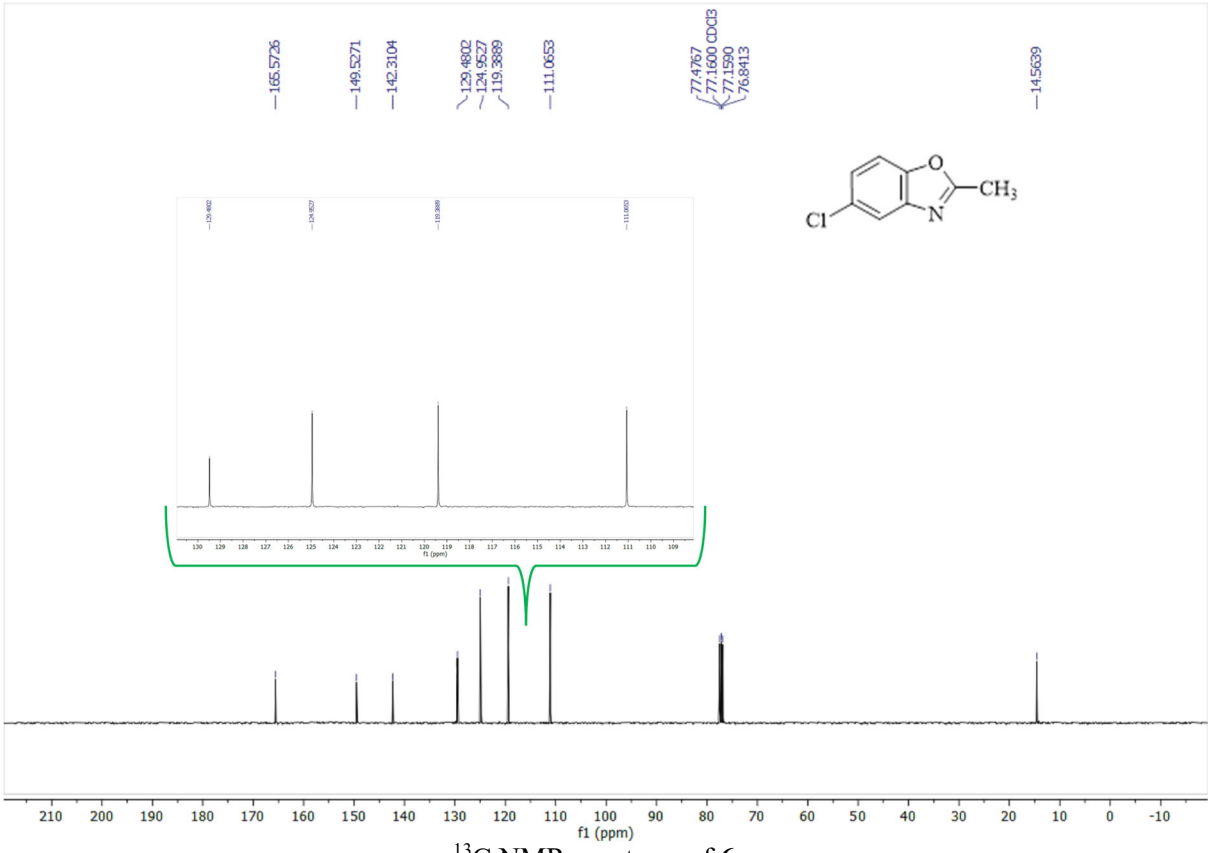
^{1}H NMR spectrum of **6l**



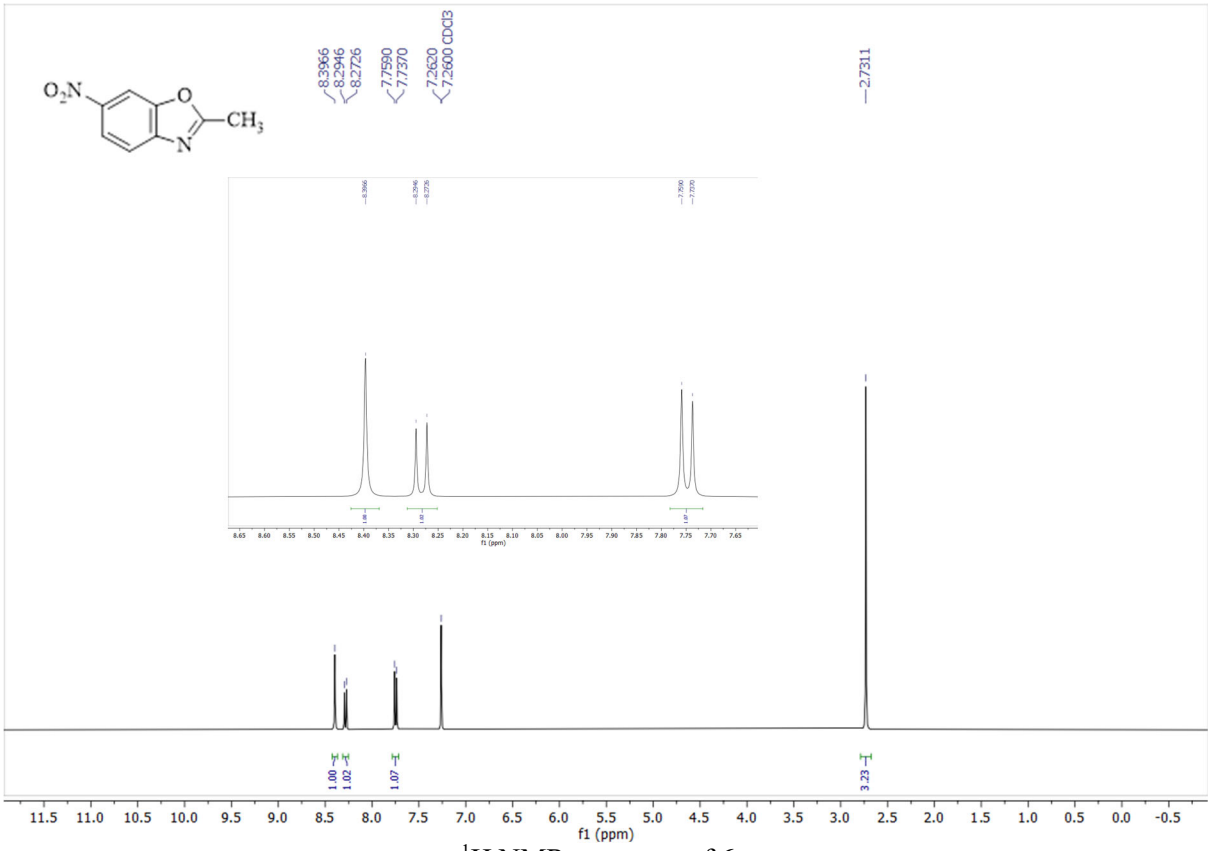
^{13}C NMR spectrum of **6k**



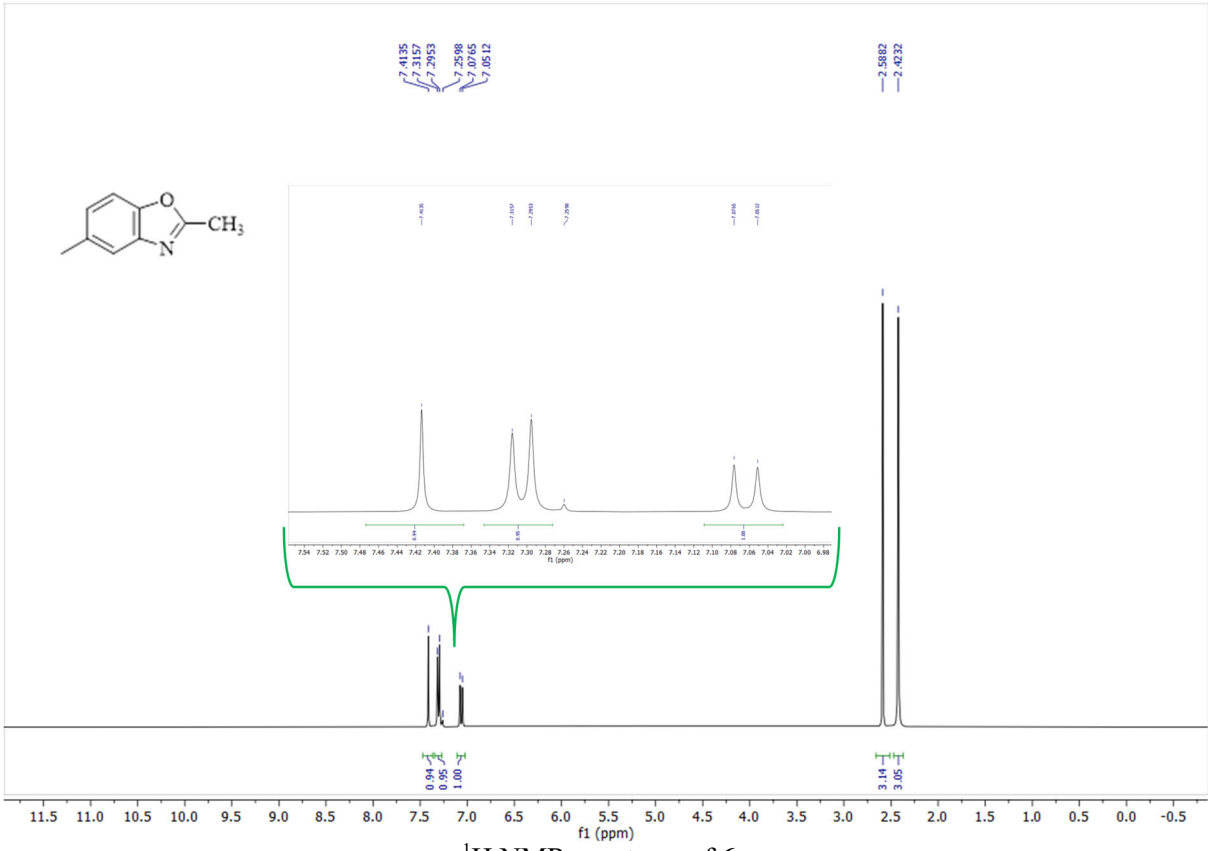
^{1}H NMR spectrum of **6m**



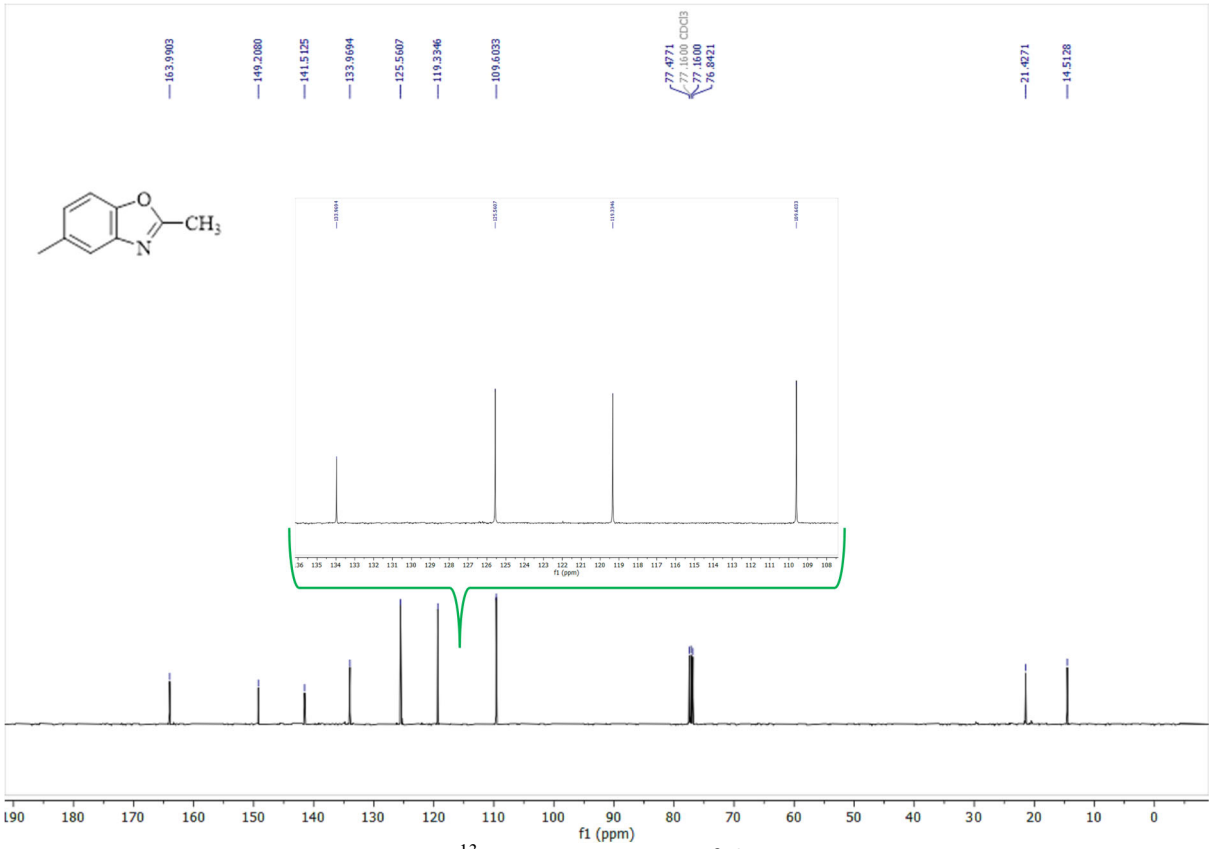
^{13}C NMR spectrum of **6m**



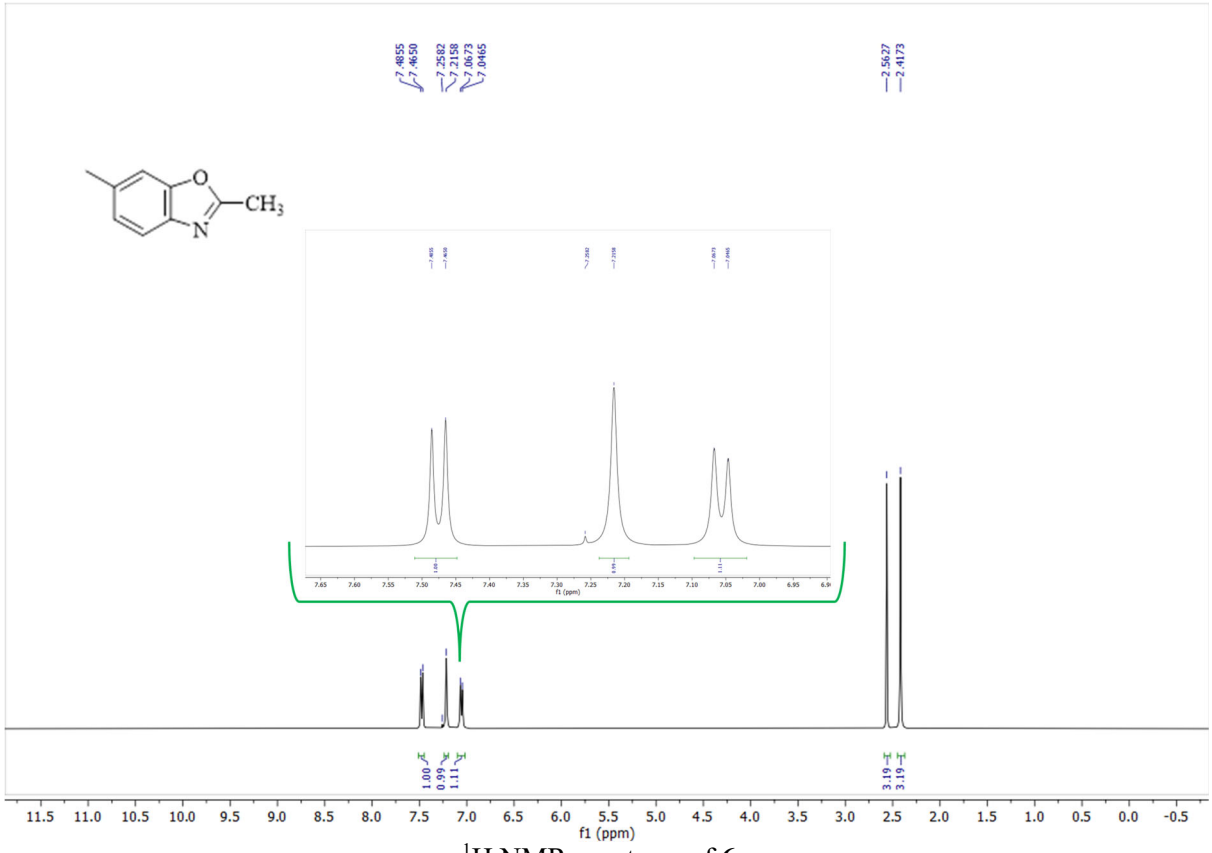
^{1}H NMR spectrum of **6n**



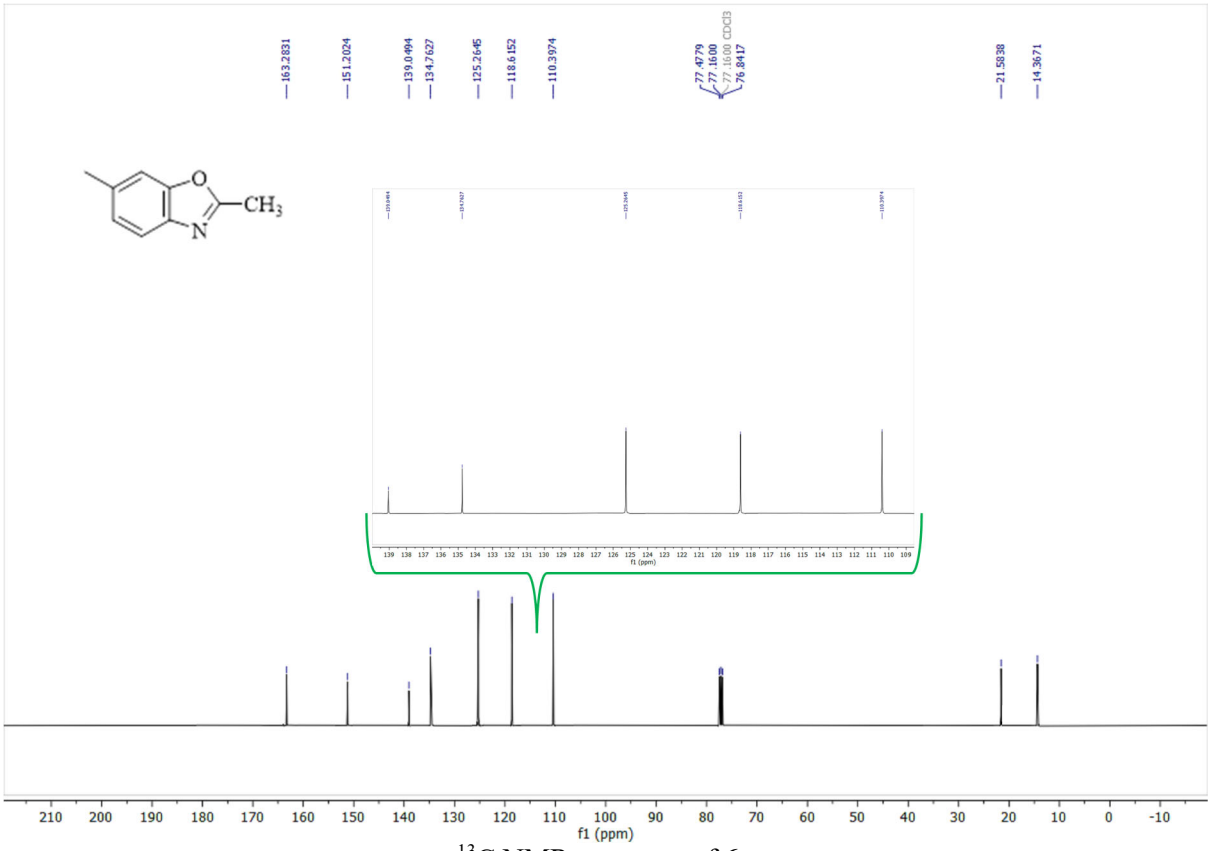
^{1}H NMR spectrum of **6o**



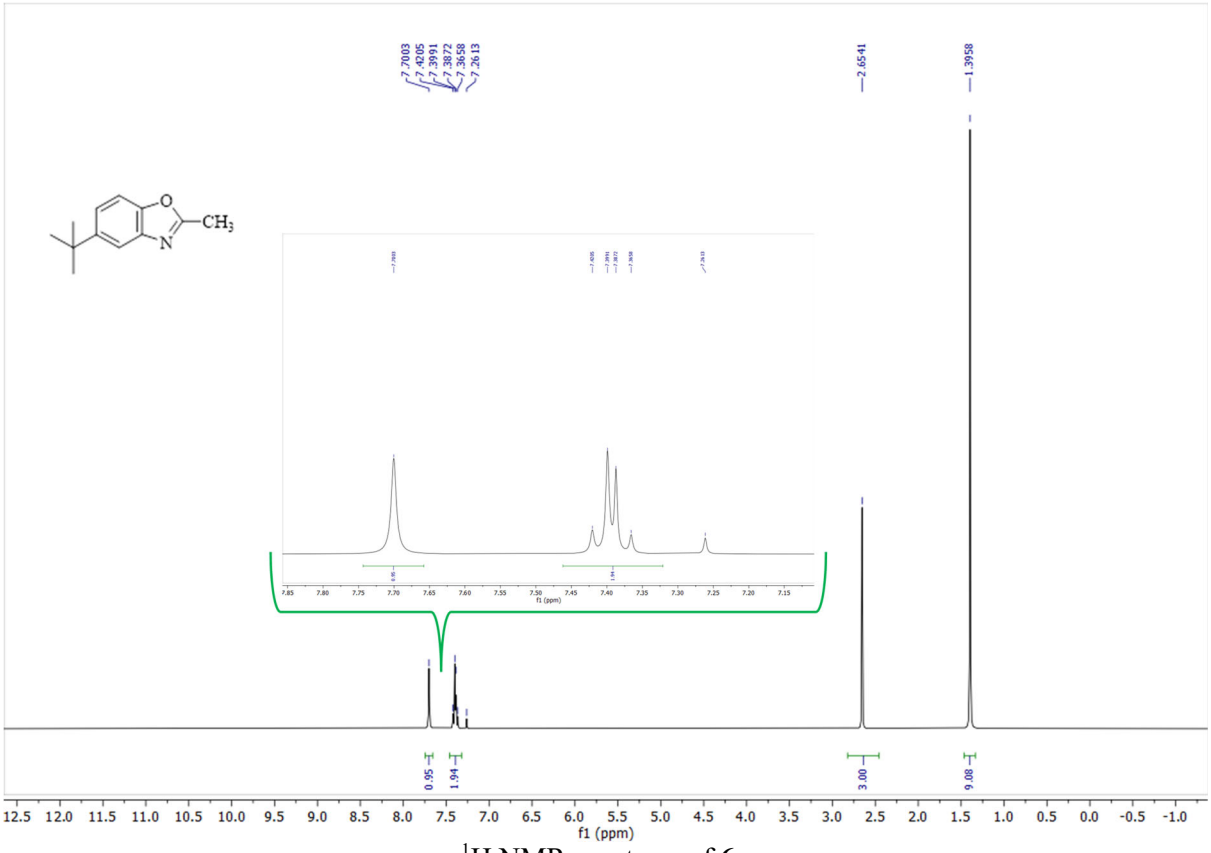
^{13}C NMR spectrum of **6o**



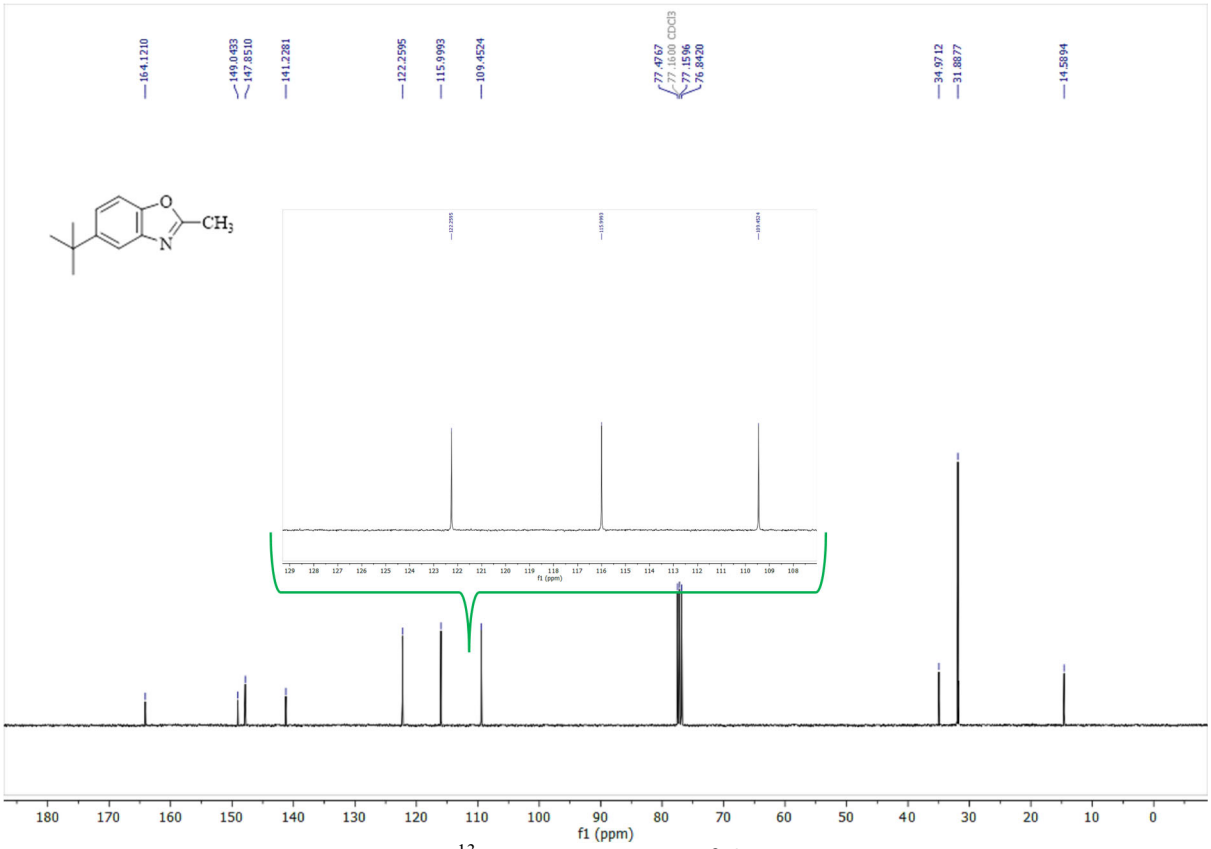
^{1}H NMR spectrum of **6p**



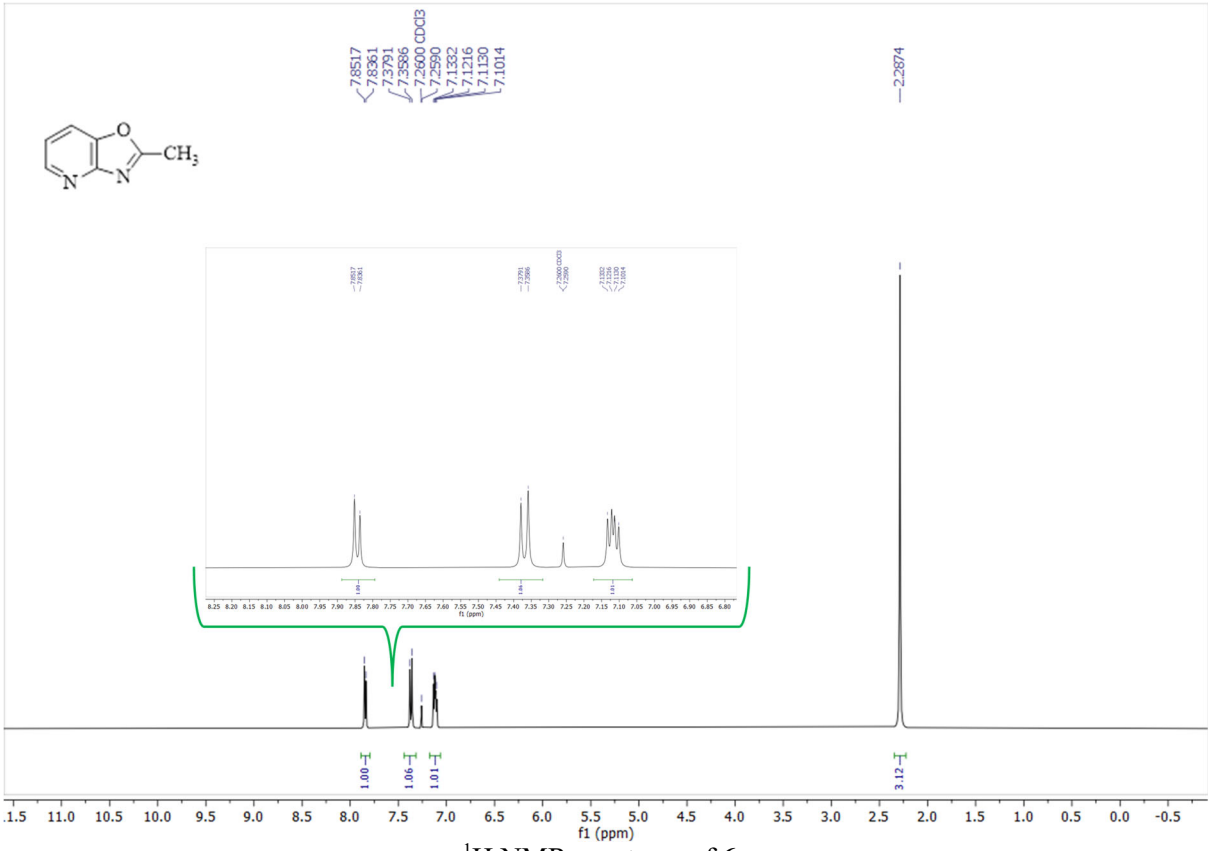
^{13}C NMR spectrum of **6p**



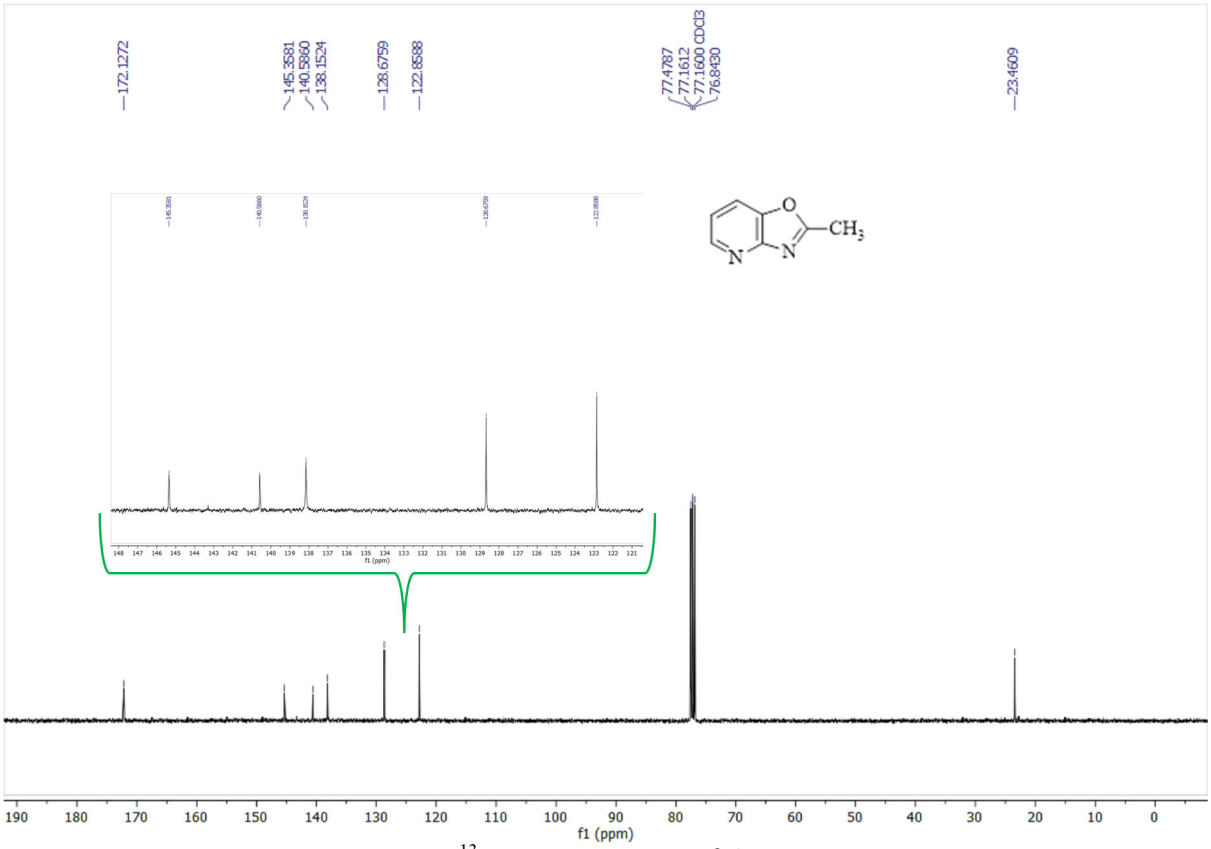
^{1}H NMR spectrum of **6q**



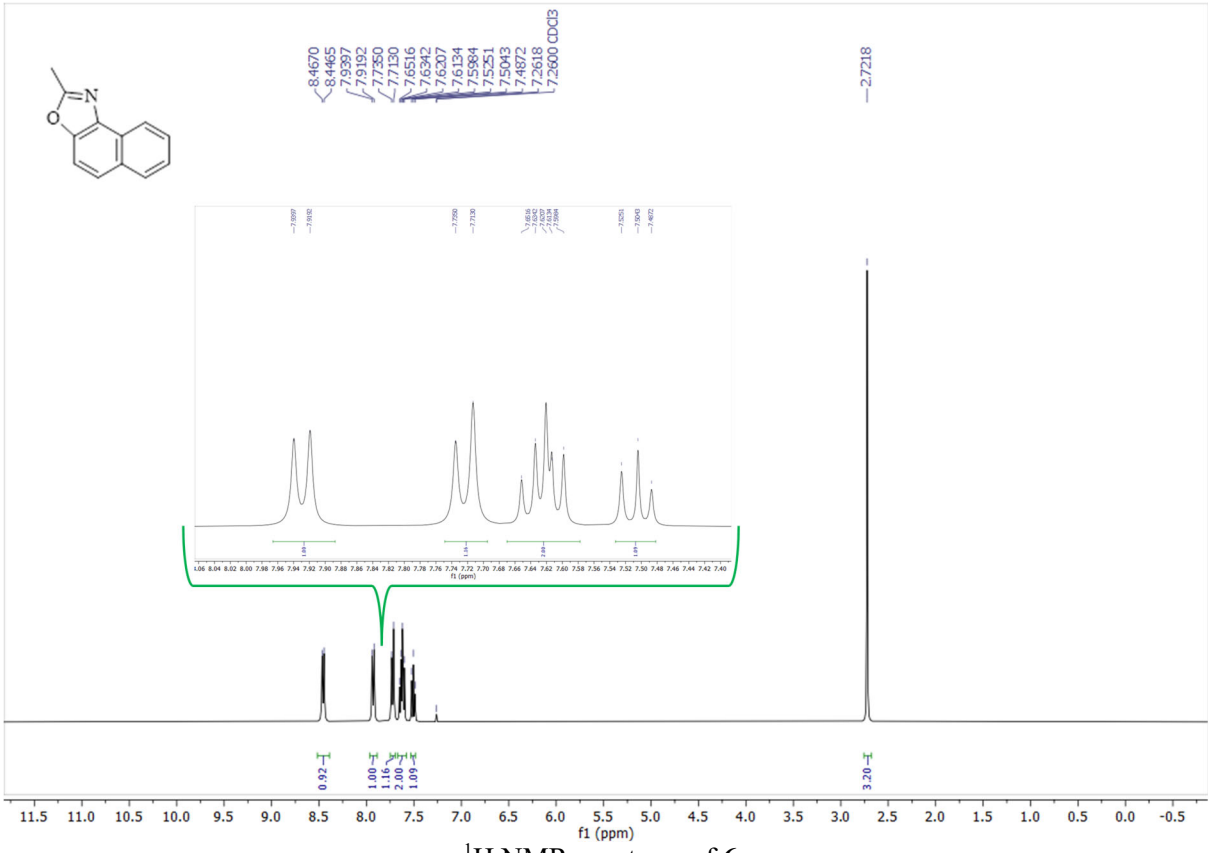
^{13}C NMR spectrum of **6q**



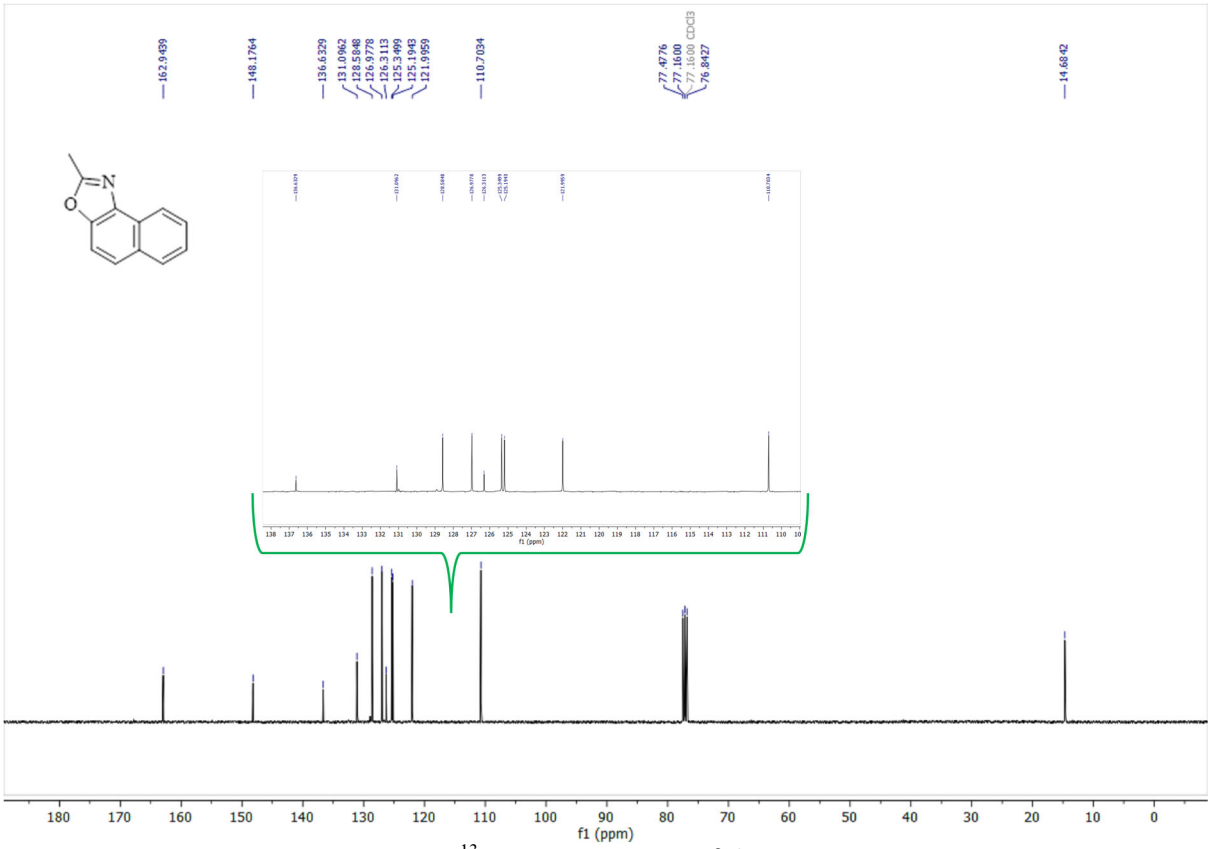
^{1}H NMR spectrum of **6r**



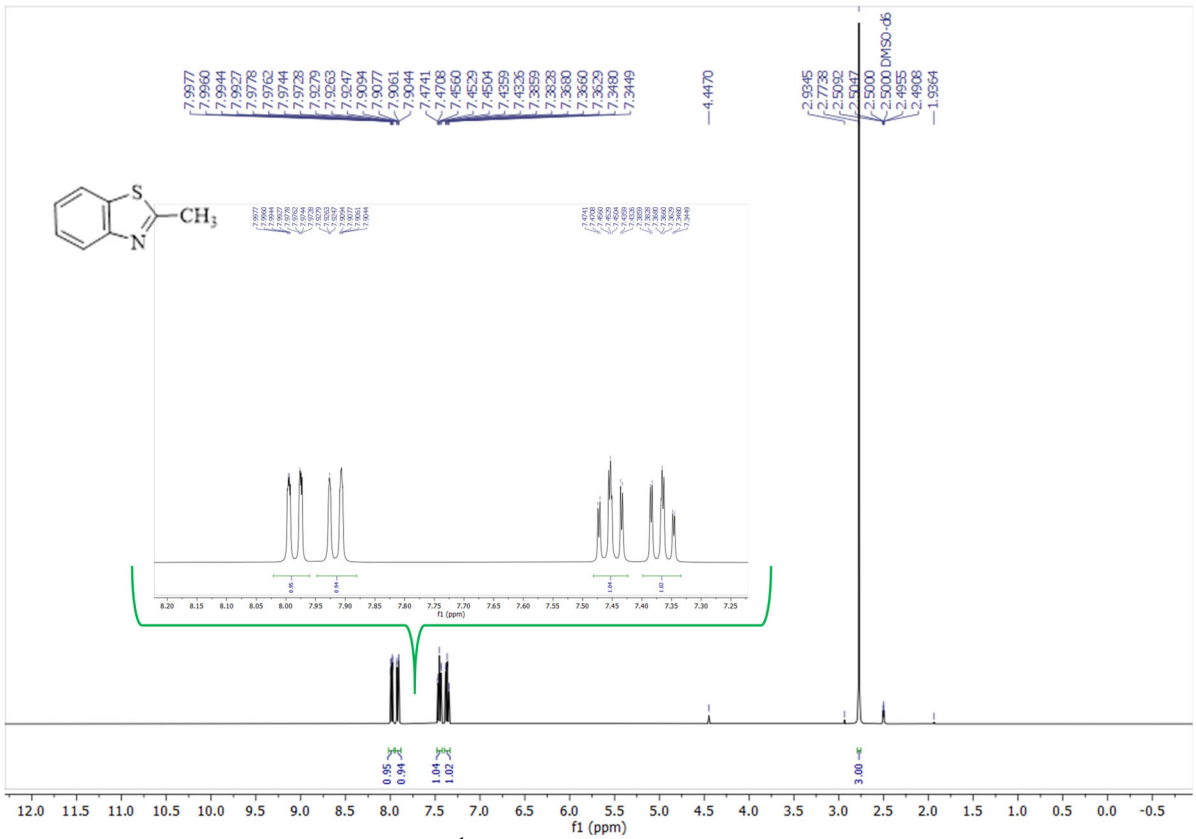
^{13}C NMR spectrum of **6r**



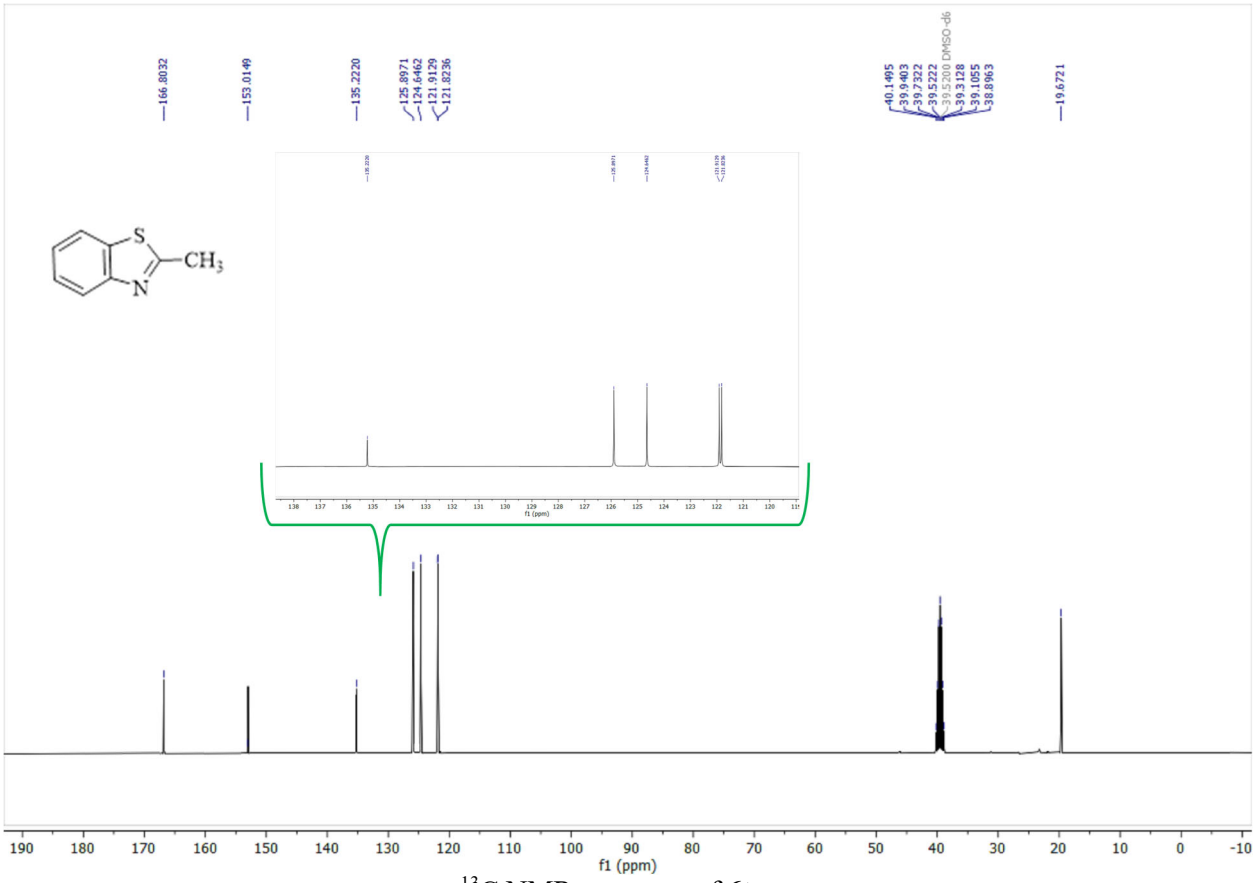
^{1}H NMR spectrum of **6s**



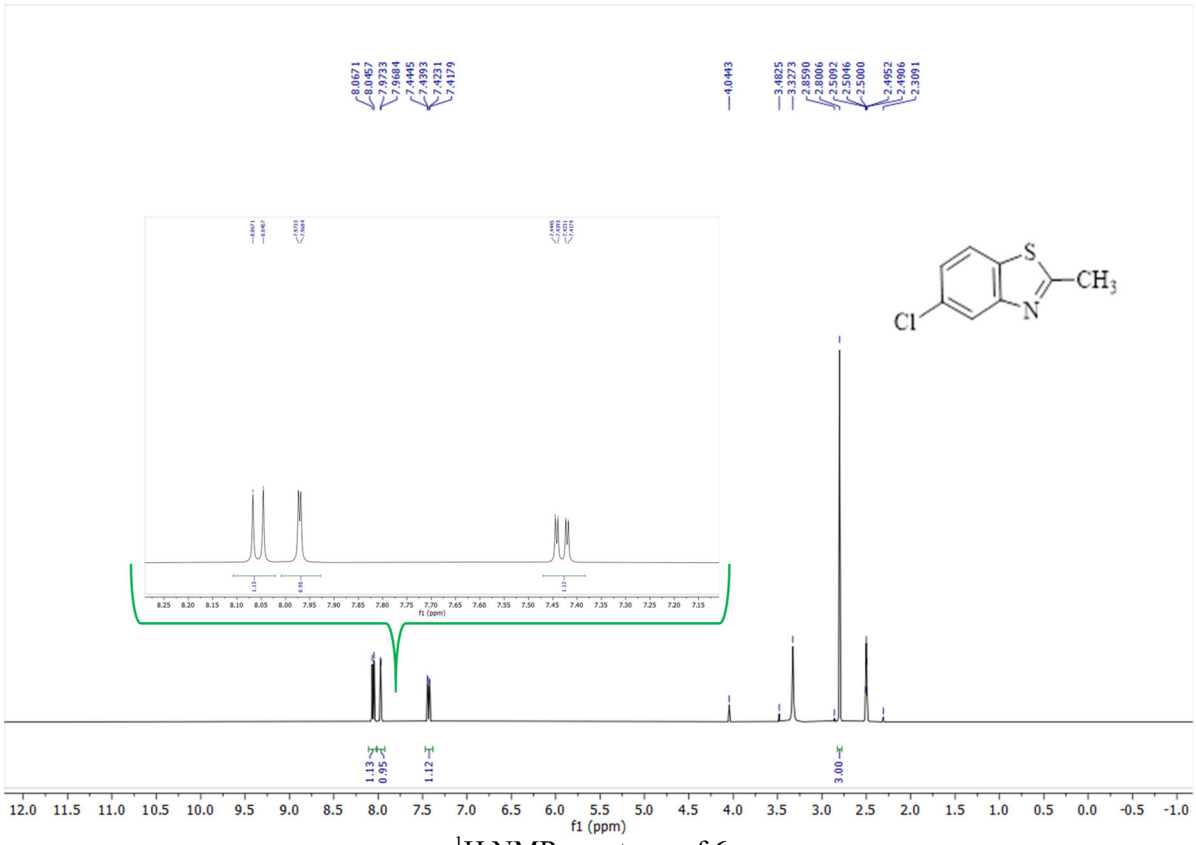
^{13}C NMR spectrum of **6s**



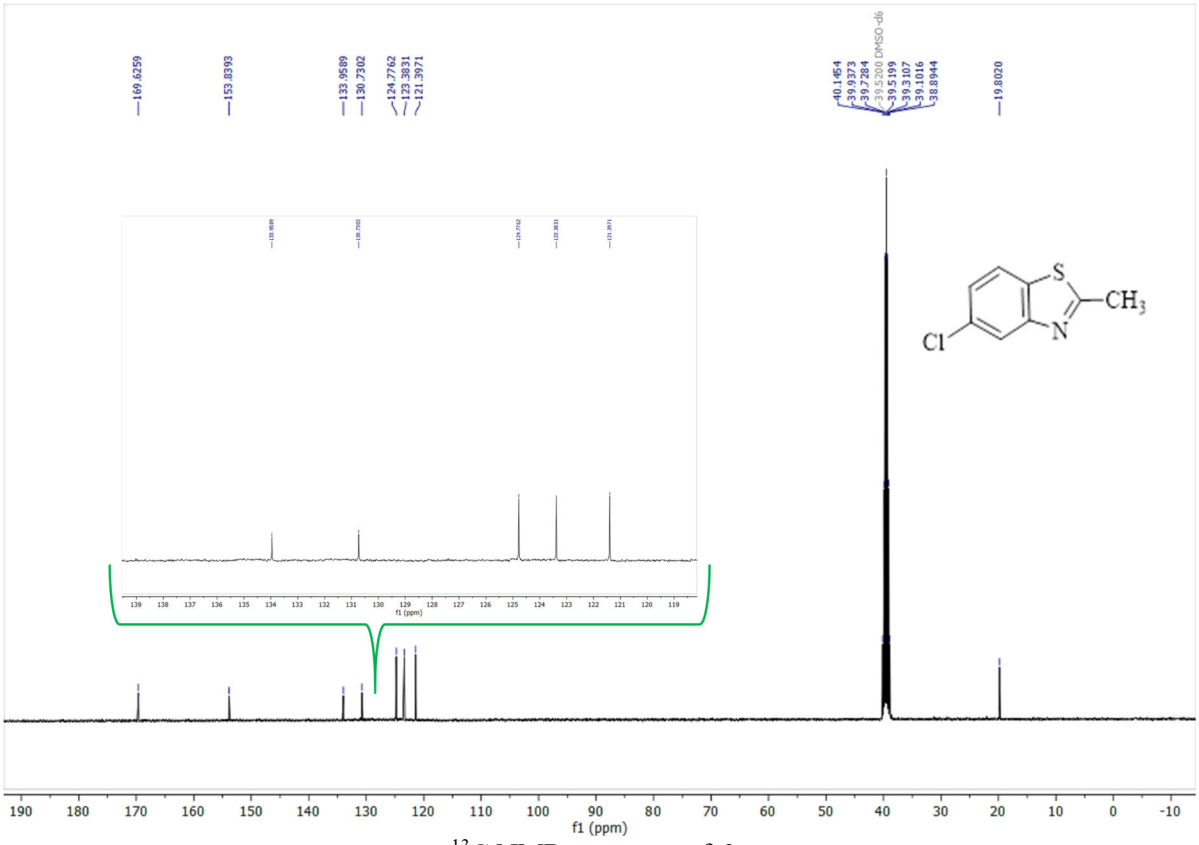
^{1}H NMR spectrum of **6t**



^{13}C NMR spectrum of **6t**



^{1}H NMR spectrum of **6u**



^{13}C NMR spectrum of **6u**