Supporting Information

Transamidation of Aromatic Amines with Formamides Using Cyclic Dihydrogen Tetrametaphosphate

Kishor Kumar Chouhan,[a] Deep Chowdhury,[a] and Arup Mukherjee[a,*]

[a]*Department of Chemistry, Indian Institute of Technology Bhilai, GEC Campus, Sejbahar, Raipur, Chhattisgarh 492015, India.*

E-mail: arup@iitbhilai.ac.in

General Consideration.

Unless otherwise mentioned, all reactions were performed without any precautions under aerobic conditions. All the chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, Merck, Avra, Loba Chemie, and TCI and were used without any further purifications. Deuterated solvents were procured from Sigma-Aldrich. Merck precoated 0.25 mm silica gel plates (60 F_{254}) were used to perform the analytical thin-layer chromatography (TLC). Visualization was achieved with short wave UV light. Column chromatography purifications were performed using silica gel 100–200 mesh size. UV studies were carried out on a Shimadzu UV-2600 instrument. FT-IR studies were carried out on a Perkin Elmer instrument. NMR spectroscopy was measured on Bruker Avance 500 MHz and 400 MHz spectrometers. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00) or chloroform (δ = 7.28, singlet). High-resolution mass spectrometric analysis was carried out on Agilent 6545XT AdvanceBio LC/Q-TOF.

(a) General procedure for the transamidation reaction with 2:

In a 15 mL oven-dried thick-walled pressure tube, amine (0.25 mmol), DMF (2 mL), and **2** (1 equiv.) were added. The pressure tube was sealed tightly and kept in a pre-heated oil bath. After the reaction gets over, the pressure tube was cooled down to room temperature and cold water (10 mL) was added. The reaction mixture was extracted with ethyl acetate (3 x 10 mL) and the

combined organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure. The crude product was purified through column chromatography using hexane and ethyl acetate as an eluent to get the desired product.

(b) Control Experiments

To understand the mechanistic process of the transamidation reaction, various control experiments were carried out, including FT-IR, UV-Vis spectroscopy etc.

(i) Interaction between DMF with $[PPN]_2[P_4O_{12}H_2]$ (2) through FT-IR:

Initially, FT-IR data was recorded for DMF and **2** separately. Subsequently, **2** and DMF were mixed and FT-IR of the mixture was recorded at 100 ^oC. It has been observed that the shifting of the >C=O group from 1660 cm^{-1} of DMF to 1656 cm^{-1} takes place in the reaction mixture. This may be attributed due to the weak interaction between the >C=O of DMF with **2** (Figure S1).

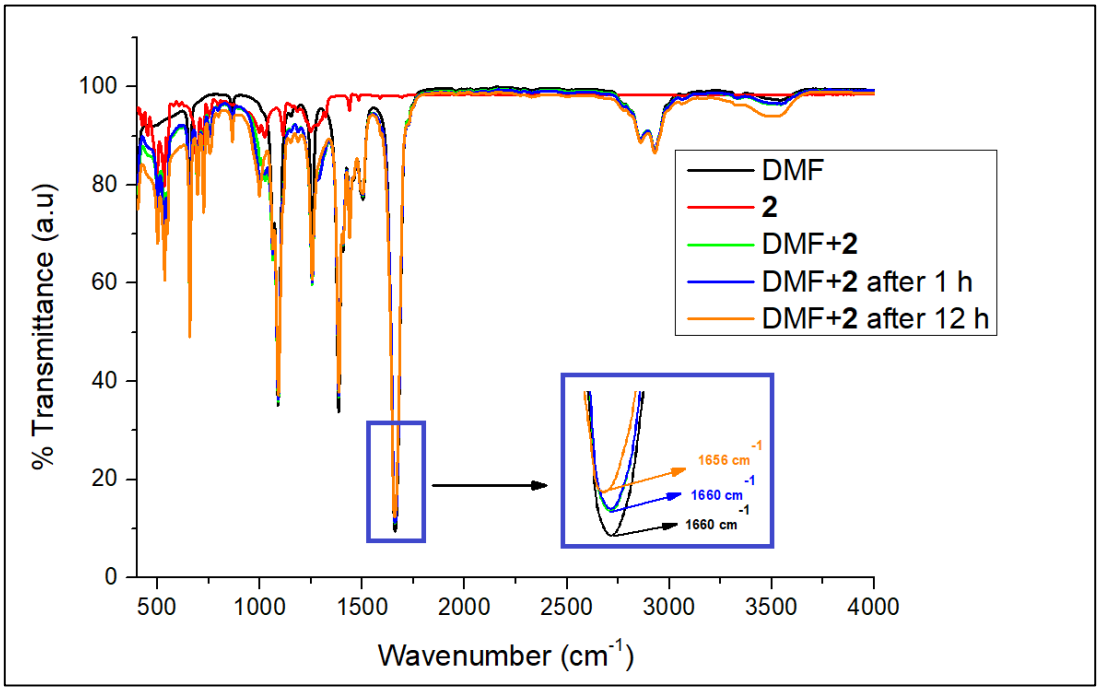


Figure S1. FT-IR spectrum of DMF with **2**.

(ii) Spectrophotometric study between DMF and 2:

At the outset, a stock solution of DMF (with different concentrations) and **2** (0.001mmol) was prepared in acetonitrile. A solution of **2** was taken in a cuvette and then various concentrations of DMF were added to it gradually (Figure S2). In every case, immediately after mixing, the absorption spectra were recorded. It has been observed that the absorbance of the mixture

gradually increased with increasing the concentration of DMF. A plot of $1/\Delta A$ (A = absorbance) versus 1/[DMF] provides a straight line with a positive slope as per the Benesi-Hildebrand equation (Figure S3).

Moreover, in order to obtain the stoichiometry of the **2** and DMF adduct, we have carried out Job's plot (ΔA *vs* mole fraction of DMF; where $\Delta A = A - A_0$; A_0 = absorbance of **2**, and A = absorbance of **2** in the presence of DMF) which demonstrates a 1:1 association between **2** and DMF (Figure S4).

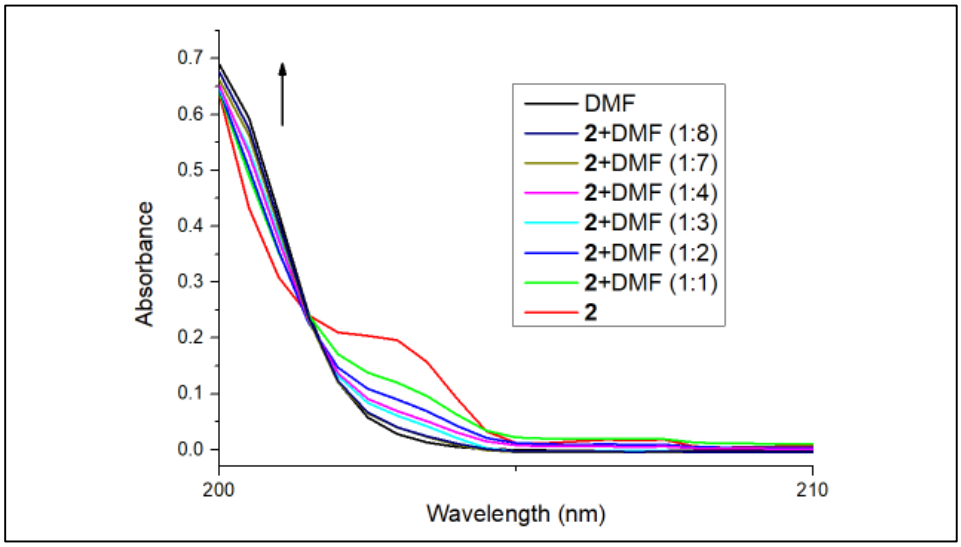


Figure S2. UV-Vis spectroscopy of DMF and the mixture having **2** with various concentrations of DMF in acetonitrile.

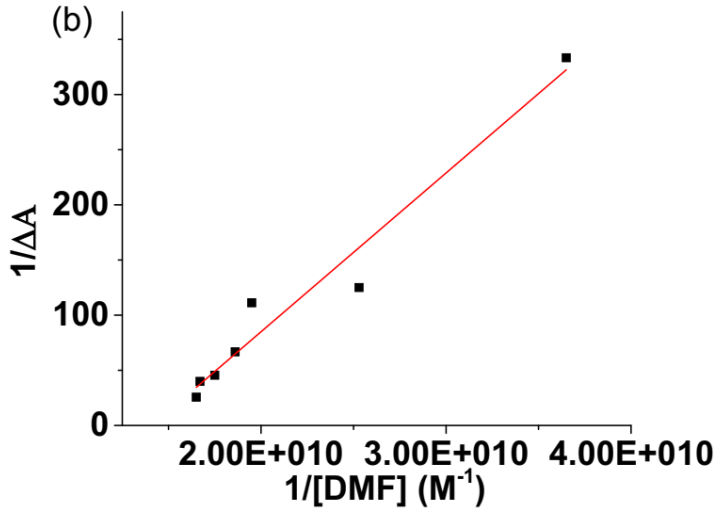


Figure S3. Benesi Hildebrand plot (plot of $1/\Delta A$ vs 1/[DMF], $\Delta A = A - A_0$).

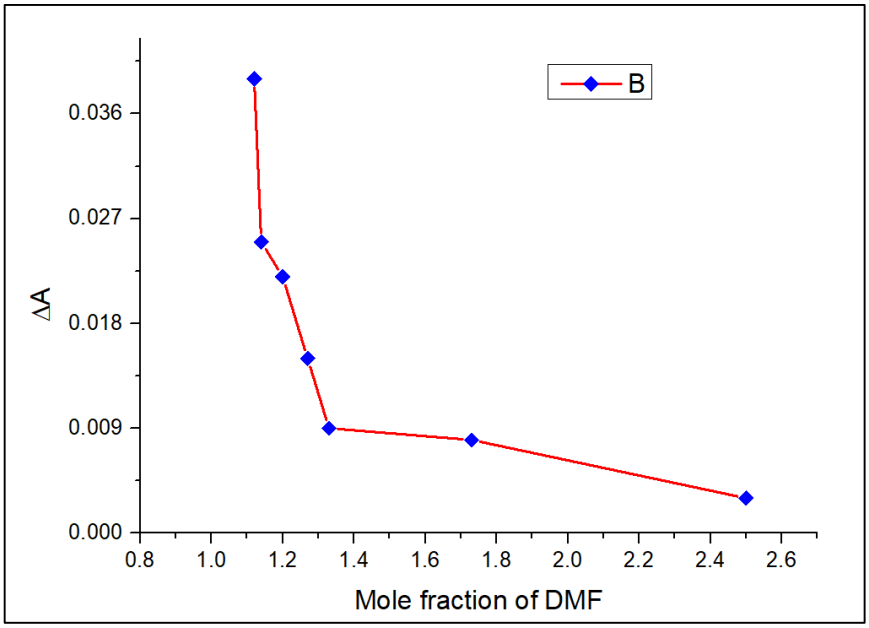


Figure S4. Job's plot (plot of ΔA vs Mole fraction of DMF, $\Delta A = A - A_0$).

(c) Kinetic Experiments:

The rate of the reaction was determined following the initial rate law method. By using GC-MS, multiple data points were collected at the initial state of the reaction. Finally, the rate of the reaction was determined by using the least square fit method with the formation of the product with respect to time.

General method: In an oven-dried 15 mL thick-walled reaction tube, aniline (**5b**) (various concentrations) was added. To this, 2 mL DMF and **2** (various concentrations) were added. The tube was sealed and placed in a preheated oil bath at 100 °C. At constant time intervals, an aliquot was collected from the reaction mixture and injected into the GC-MS. The yield of the product was calculated using dodecane as an internal standard.

(i) Determination of the reaction order with respect to aniline (5b):

To determine the order of the reaction with respect to aniline, the transamidation reaction from aniline to N-formylated product (**6b**) was carried out with two different concentrations of aniline (0.35 mmol and 0.45 mmol) keeping the concentration of **2** (0.35 mmol) and DMF (2 mL) constant.

Run	5b (mmol)	2 (mmol)	Initial rate (M/min.)
1	0.35	0.35	0.0029
2	0.45	0.35	0.0044

For each reaction, after a certain time interval, a small amount of aliquot was taken from the reaction mixture, and the yields were determined using GC-MS. For each reaction, the yield of the product was plotted against time where for both the cases linear equations were obtained and from the slope, the initial rates of these reactions were obtained.

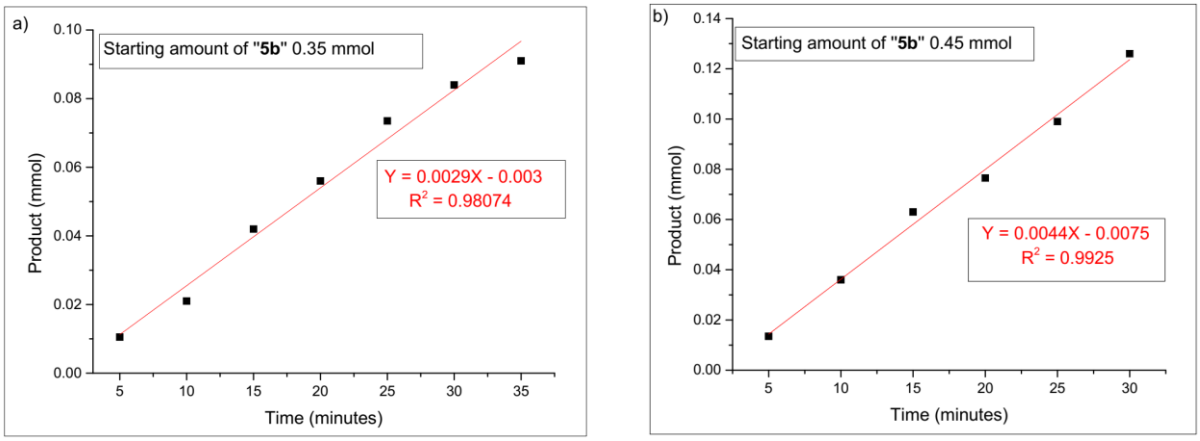


Figure S5. Plot of the amount of product (mmol) vs time for varying concentrations of **5b**: a) with 0.35 mmol and b) with 0.45 mmol.

For this transamidation reaction we can write,

Rate = Constant x $[\mathbf{5b}]^X$ x $[\mathbf{2}]^Y$

At a particular concentration of **2**, the ratio of rates of the reactions of Run 1 and Run 2 should be proportional to the ratio of the concentrations of **5b**.

So we can write, $R_1/R_2 = [0.35/0.45]^X$, where R_1 and R_2 are the initial rates of the reactions for Run 1 and Run 2.

So, $X = [\log (R_1) - \log (R_2)] / [\log (0.35) - \log (0.45)]$

$= [\log (0.0029) - \log (0.0044)] / [\log (0.35) - \log (0.45)]$

$= 1.66$

≈ 2

(ii) Determination of reaction order with respect to 2:

To determine the order of the transamidation reaction with respect to **2**, conversion from **5b** to **6b** was carried out at two different concentrations of **2** (0.35 mmol and 0.2625 mmol), keeping the concentration of **5b** (0.35 mmol) and DMF (2 mL) constant.

Run	5b (mmol)	2 (mmol)	Initial rate (M/min.)
1	0.35	0.35	0.0029
2	0.35	0.2625	0.0021

For each reaction, after certain time intervals, a small amount of an aliquot was taken from the reaction mixture, and yields were determined using GC-MS. For each reaction, the yield of the product was plotted against time wherein both the cases linear equations were obtained and from the slope, the initial rates of the reactions were determined.

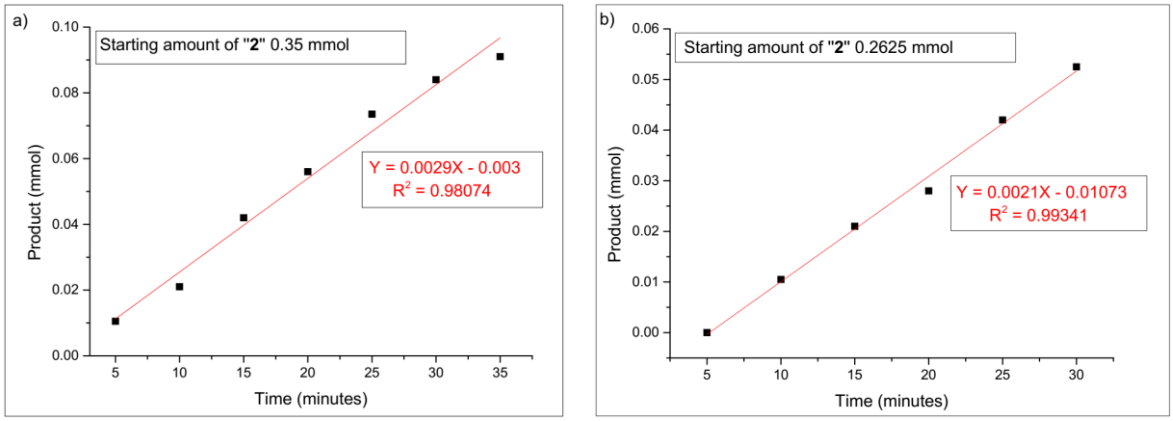


Figure S6. Plot of the amount of product (mmol) vs time for varying concentrations of **2**: a) with 0.35 mmol and b) with 0.2625 mmol.

For this transamidation reaction we can write,

Rate = Constant x $[\mathbf{5b}]^X$ x $[\mathbf{2}]^Y$

At a particular concentration of **5b**, the ratio of rates of the reactions of Run 1 and Run 2 should be proportional to the ratio of the concentrations of **2**.

So, we can write, $R_1/R_2 = [0.35/0.2625]^X$, where R_1 and R_2 are the initial rates of the reactions of Run 1 and Run 2:

So, X = [log (R_1)-log (R_2)] / [log (0.35)- log (0.2625)]

= [log (0.0029) – log (0.0021)] / [log (0.35) – log (0.2625)]

= 1.12

≈ 1

(iii) Hammett Studies

In an oven-dried 25 mL round bottom flask, an appropriate amount of aniline derivative and **2** were taken under aerobic conditions. To this, 2 mL DMF was added and the reaction vessel was sealed and placed in a preheated oil bath at 100 ºC. At constant time intervals, an aliquot was collected, and the yield of the desired product was monitored by GC-MS using dodecane as an internal standard. Reactivity for this reaction follows the following order *p*-Me > H > *p*-Cl. For this particular reaction, –1.12053 was obtained as a ρ value which signifies the reaction probably proceeds through the generation of a slight positive charge.

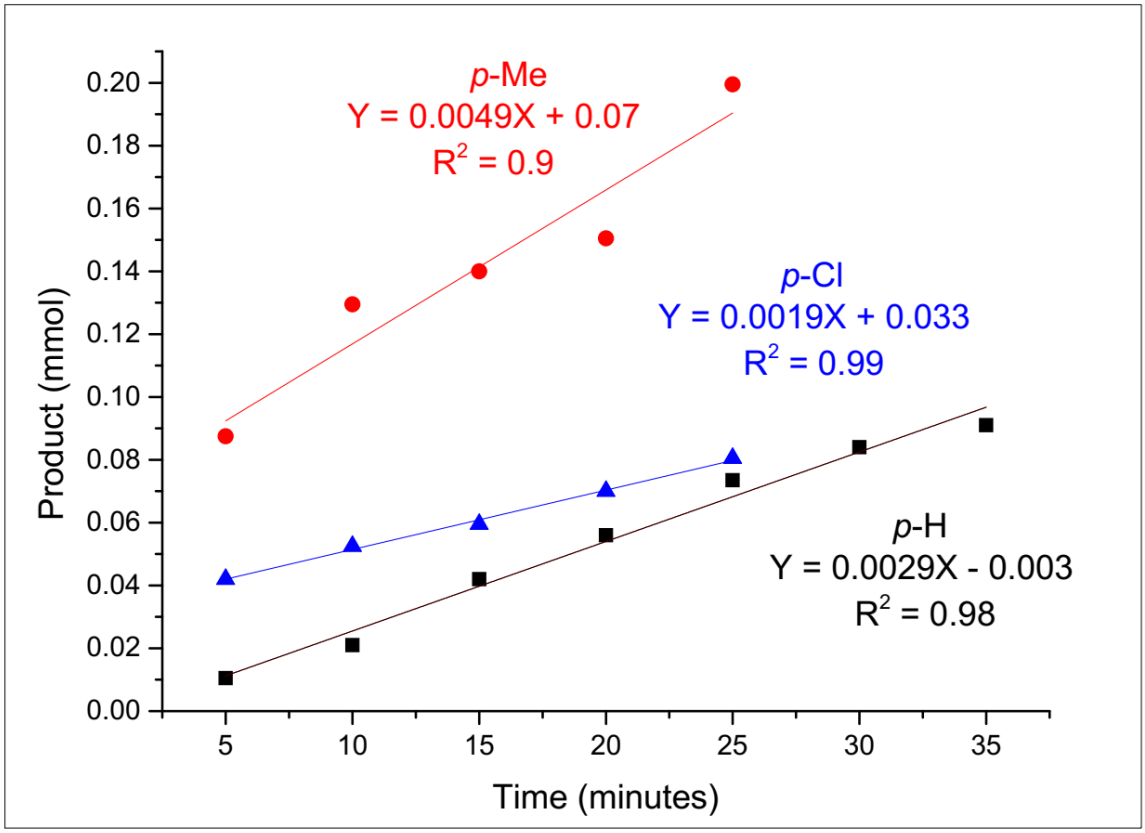


Figure S7. Kinetic data for the transamidation aniline derivatives with DMF in the presence of **2**.

Hammett Plot kinetic Study Data			
Substrate	**Slope**	**[log(k_X/k_H)]**	**σ_p**
p-Me	0.0071	0.389	–0.17
p-H	0.0029	0	0
p-Cl	0.0019	–0.184	0.227
ρ = –1.03			

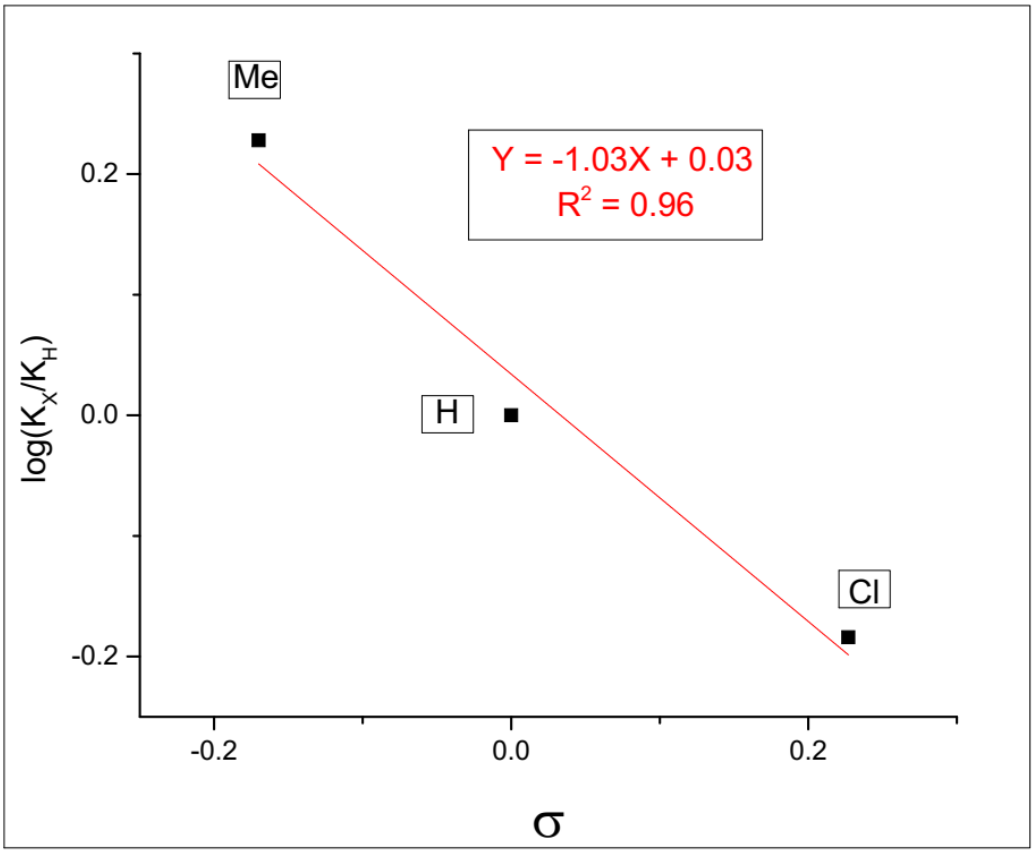
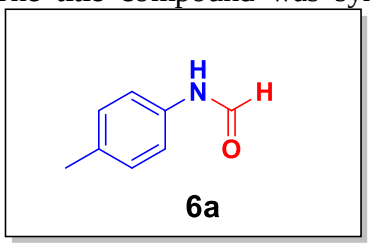


Figure S8. Hammett plot for the transamidation of aniline derivatives.

(d) Analytical data of the isolated compounds.

N-(4-Methylphenyl)formamide (6a)[1]: Reaction scale: *p*-toluidine (26.78 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

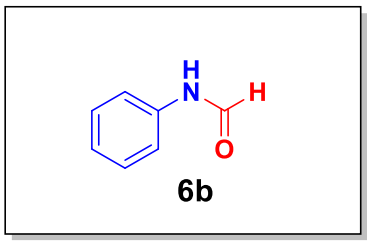
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 76% (26 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 5.4/4.6. Major rotamer: δ 8.60 (d, *J* = 11.5 Hz, 1H, CHO), 8.11 (br s, 1H, NH), 7.13 (dd, *J* = 9.4, 8.9 Hz, 2H), 7.01 – 6.93 (m, 2H), 2.32 (s, 3H); Minor rotamer: δ 8.33 (d, *J* = 1.6 Hz, 1H, CHO), 7.46 – 7.37 (m, 2H), 7.13 (dd, *J* = 9.4, 8.9 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 162.83, 135.28, 134.12, 130.33, 119.29, 20.87; Minor rotamer: δ 159.01, 134.61, 134.35, 129.66, 120.12, 20.96; HRMS (ESI) calcd for $C_8H_{10}NO$ $[M+H]^+$: 136.0757; Found: 136.0759.



6a

Phenylformamide (6b)[1]**:** Reaction scale: aniline (22.80 mg, 0.25 mmol), DMF (2 mL), [$PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

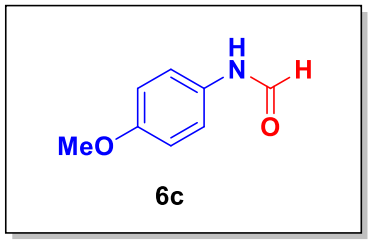
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 67% (20 mg). ^{1}H NMR (400 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 5.4/4.6. Major rotamer: δ 8.67 (d, *J* = 11.4 Hz, 1H, CHO), 8.23 (br s, 1H, NH), 7.53 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.21 – 7.16 (m, 1H), 7.10 – 7.06 (m, 1H); Minor rotamer: δ 8.37 (d, *J* = 1.3 Hz, 1H, CHO), 7.53 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.15 – 7.11 (m, 1H), 7.10 – 7.06 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): Major rotamer δ 162.77, 136.71, 129.87, 125.46, 118.98; Minor rotamer δ 159.10, 136.91, 129.21, 124.94, 120.07; HRMS (ESI) calcd for C_7H_8NO $[M+H]^+$: 122.0600; Found: 122.0601.



6b

N-(4-methoxyphenyl)formamide (6c)[1]: Reaction scale: 4-methoxyaniline (30.79 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

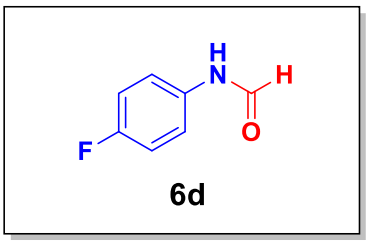
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 90% (34 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 5.6/4.4. Major rotamer: δ 8.34 (d, *J* = 8.4 Hz, 1H, CHO), 7.98 (br s, 1H, NH), 7.47 (d, *J* = 8.8 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 1H), 6.95 – 6.84 (m, 2H), 3.83 (s, 3H); Minor rotamer: δ 8.53 (d, *J* = 11.5 Hz, 1H, CHO), 7.33 (br s, 1H, NH), 7.47 (d, *J* = 8.8 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 1H), 6.95 – 6.84 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 158.87, 156.75, 129.52, 121.81, 114.91, 55.56, Minor rotamer: δ 163.06, 157.66, 129.92, 121.71, 114.24, 55.49; HRMS (ESI) calcd for $C_8H_{10}NO_2$ $[M+H]^+$: 152.0706; Found: 152.0708.



6c

N-(4-Fluorophenyl)formamide (6d)[1]: Reaction scale: 4-fluoroaniline (27.78 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

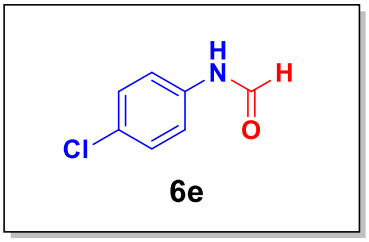
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 60% (21 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 6/4. Major rotamer: δ 8.37 (s, 1H, CHO), 7.53 (dd, *J* = 8.3, 4.7 Hz, 2H), 7.09 (d, *J* = 5.7 Hz, 1H), 7.05 (t, *J* = 8.5 Hz, 1H); Minor rotamer: δ 8.60 (d, *J* = 11.3 Hz, 1H, CHO), 7.53 (dd, *J* = 8.3, 4.7 Hz, 2H), 7.09 (d, *J* = 5.7 Hz, 1H), 7.05 (t, *J* = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 158.99, 160.59, 158.65, 132.84 (d, *J* = 2.3 Hz), 121.82 (d, *J* = 8.0 Hz), 116.49, 115.71; Minor rotamer: δ 162.89, 161.45, 159.50, 132.69 (d, *J* = 2.6 Hz), 121.23 (d, *J* = 8.2 Hz), 116.68, 115.89 HRMS (ESI) calcd for C_7H_7FNO $[M+H]^+$: 140.0506; Found: 140.0507.



6d

N-(4-Chlorophenyl)formamide (6e)[2]: Reaction scale: 4-chloroaniline (31.89 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 46% (18 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 6/4. Major rotamer: δ 8.39 (s, 1H, CHO), 7.52 (d, *J* = 8.6 Hz, 2H), 7.47 (br s, 1H, NH), 7.33 (dt, *J* = 20.0, 9.9 Hz, 2H); Minor rotamer: δ 8.67 (d, *J* = 11.3 Hz, 1H, CHO), 7.33 (dt, *J* = 20.0, 9.9 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 158.95, 135.39,

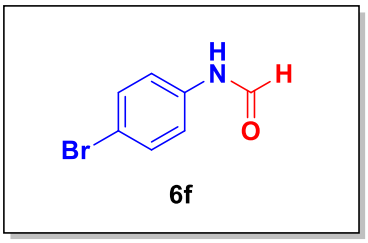


6e

130.82, 129.16, 121.21; Minor rotamer: δ 162.47, 135.26, 129.88, 120.13, HRMS (ESI) calcd for C_7H_7ClNO $[M+H]^+$: 156.0211; Found: 156.0211.

N-(4-bromophenyl)formamide (6f)[3]: Reaction scale: 4-bromoaniline (43 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

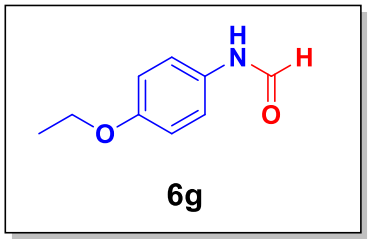
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 40% (20 mg). ^1H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 6.1/3.9. Major rotamer: δ 8.37 (s, 1H, CHO), 7.91 (br s, 1H, NH), 7.48 – 7.42 (m, 3H), 6.96 (d, *J* = 8.7 Hz, 1H); Minor rotamer: δ 8.64 (d, *J* = 11.3 Hz, 1H, CHO), 7.48 – 7.42 (m, 3H), 6.96 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 158.86, 135.93, 132.20, 121.54, 117.58, Minor rotamer: δ 162.12, 135.77, 132.92, 120.48, 118.41; HRMS (ESI) calcd for C_7H_7BrNO $[M+H]^+$: 199.9706; Found: 199.9707.



6f

N-(4-ethoxyphenyl)formamide (6g)[4]: Reaction scale: 4-ethoxyaniline (34.29 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

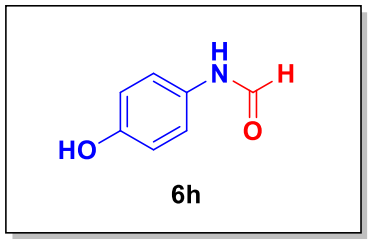
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 80% (33 mg). ^1H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 5.3/4.7. Major rotamer: δ 8.33 (s, 1H,CHO), 8.10 (br s, 1H, NH), 7.45 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.07 – 4.00 (m, 2H), 1.46 – 1.39 (m, 3H); Minor rotamer: δ 8.53 (d, *J* = 10.0 Hz, 1H, CHO), 7.04 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.07 – 4.00 (m, 2H), 1.46 – 1.39 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 158.92, 157.02, 129.82, 121.79, 114.85, 63.72, 14.80; Minor rotamer: δ 156.11, 129.39, 121.68, 115.49, 63.83, 14.78; HRMS (ESI) calcd for $C_9H_{12}NO_2$ $[M+H]^+$: 166.0863; Found: 166.0862.



6g

N-(4-hydroxyphenyl)formamide (6h)[5]**.** Reaction scale: 4-hydroxyaniline (28 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

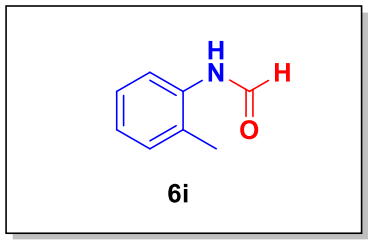
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 66% (23 mg). ^{1}H NMR (500 MHz, DMSO-d_6): A mixture of rotamers were observed, ratio: 7.6/2.4. Major rotamer: δ 9.89 (s, 1H,), 9.22 (s, 1H), 8.16 (d, J = 0.8 Hz, 1H), 7.43 – 7.31 (m, 2H), 6.72 (dd, J = 17.3, 10.3 Hz, 2H); Minor rotamer: δ 9.84 (d, J = 11.0 Hz, 1H,), 9.26 (s, 1H), 8.51 (d, J = 11.2 Hz, 1H), 7.03 – 6.94 (m, 2H), 6.72 (dd, J = 17.3, 10.3 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-d_6): Major rotamer: δ 159.28, 153.99, 130.45, 121.25, 115.63; Minor rotamer: δ 163.01, 154.66, 130.12, 120.65, 116.26; HRMS (ESI) calcd for $C_7H_8NO_2$ $[M+H]^+$: 138.0550; Found: 138.0547.



6h

N-(2-Methylphenyl)formamide (6i)[2]: Reaction scale: *o*-toluidine (26.79 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

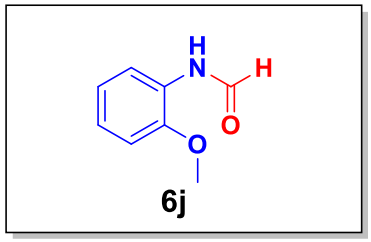
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 56% (19 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 6.6/3.4. Major rotamer: δ 8.54 (d, J = 11.3 Hz, 1H, CHO), 7.65 (br s, 1H, NH), 7.24 – 7.21 (m, 2H), 7.15 (t, J = 7.6 Hz, 2H), 2.29 (s, 3H); Minor rotamer: δ 8.44 (s, 1H, CHO), 7.90 (d, J = 7.9 Hz, 1H, NH), 7.20 (d, J = 6.6 Hz, 2H), 7.12 – 7.05 (m, 2H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 163.00, 134.88, 131.28, 129.45, 127.21, 126.06, 122.96, 17.73; Minor rotamer: 158.96, 134.60, 130.58, 128.37, 126.92, 125.53, 120.54, 17.70; HRMS (ESI) calcd for $C_8H_{10}NO$ $[M+H]^+$: 136.0757; Found: 136.0759.



6i

N-(2-methoxyphenyl)formamide (6j)[6]: Reaction scale: 2-methoxyaniline (30.79 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 58% (22 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 7/3. Major rotamer: δ 8.48 (s, 1H, CHO), 8.39 (d, J = 7.9 Hz, 1H), 7.85 (br s, 1H, NH), 7.10 (t, J = 7.7 Hz, 1H), 6.96 (ddd, J = 24.3, 15.3, 7.9 Hz, 2H), 3.91 (s, 3H); Minor rotamer: δ 8.77 (d, J = 11.6 Hz, 1H, CHO), 7.74 (br s, 1H, NH), 7.23 (d, J = 7.7 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H), 6.96 (ddd, J = 24.3, 15.3, 7.9 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (126 MHz,

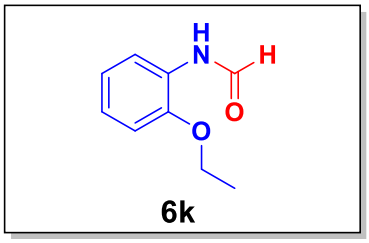


6j

$CDCl_3$): Major rotamer: δ 158.74, 147.77, 126.74, 124.29, 121.13, 120.46, 110.03, 55.73; Minor rotamer: δ 161.46, 148.72, 126.20, 125.22, 121.07, 116.60, 111.28. HRMS (ESI) calcd for $C_8H_{10}NO_2$ $[M+H]^+$: 152.0706; Found: 152.0704.

N-(2-ethoxyphenyl)formamide (6k)[7]: Reaction scale: 2-ethoxyaniline (34 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

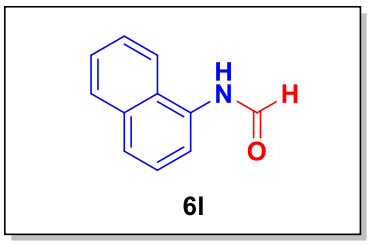
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 64% (26 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 6.7/3.3. Major rotamer: δ 8.50 (d, *J* = 1.0 Hz, 1H, CHO), 8.39 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.87 (br s, 1H, NH), 7.08 (td, *J* = 8.0, 1.4 Hz, 1H), 6.92 (dd, *J* = 14.4, 8.1 Hz, 2H), 4.17 – 4.12 (m, 2H), 1.47 (dt, *J* = 16.6, 5.8 Hz, 3H); Minor rotamer: δ 8.79 (d, *J* = 11.7 Hz, 1H, CHO), 7.79 (br s, 1H, NH), 7.23 (d, *J* = 7.8 Hz, 1H), 7.16 – 7.10 (m, 1H), 6.97 (dd, *J* = 14.0, 7.3 Hz, 2H), 4.12 – 4.07 (m, 2H), 1.47 (dt, *J* = 16.6, 5.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 158.75, 147.06, 126.78, 124.25, 120.96, 120.42, 110.86, 64.18, 14.89; Minor rotamer: δ 161.41, 147.93, 126.23, 125.11,120.90, 116.31, 112.06, 64.23, 14.81; HRMS (ESI) calcd for $C_9H_{12}NO_2$ $[M+H]^+$: 166.0863; Found: 166.0861.



6k

N-(Naphthalen-1-yl) formamide (6l)[4]: Reaction scale: *α*-naphthylamine (35.79 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

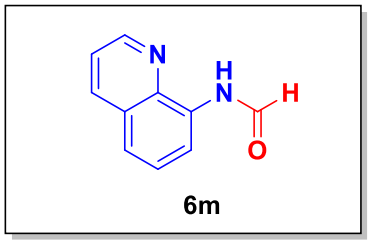
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 26% (11 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 6/4. Major rotamer: δ 8.66 (d, *J* = 11.0 Hz, 1H, CHO), 8.33 (br s, 1H, NH), 7.92 (dd, *J* = 17.7, 7.9 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.48 (m, 3H), 7.36 (d, *J* = 7.3 Hz, 1H); Minor rotamer: δ 8.04 (dd, *J* = 16.6, 7.8 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.48 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 163.89, 134.30, 132.00, 128.61, 127.78, 127.09 (d, *J* = 1.8 Hz), 126.56, 126.25, 125.54, 121.22, 119.19; Minor rotamer: δ 159.57, 134.09, 128.89, 126.84, 126.60, 126.16, 125.74, 120.89, 120.33; HRMS (ESI) calcd for $C_{11}H_{10}NO$ $[M+H]^+$: 172.0757; Found: 172.0753.



6l

N-(Quinolin-8-yl)formamide (6m)[2]: Reaction scale: 8-aminoquinoline (36 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

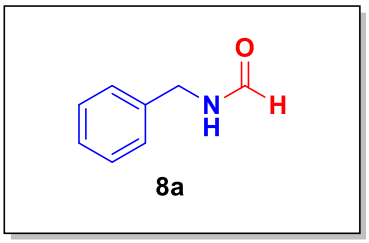
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 30% (13 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 9/1. Major rotamer: δ 9.80 (s, 1H), 8.86 – 8.79 (m, 1H), 8.74 (dd, *J* = 5.2, 3.6 Hz, 1H), 8.69 (s, 1H), 8.22 – 8.14 (m, 1H), 7.57 – 7.52 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H); Minor rotamer: δ 9.46 (s, 1H), 9.12 (d, *J* = 11.8 Hz, 1H), 8.86 – 8.79 (m, 1H), 8.74 (dd, *J* = 5.2, 3.6 Hz, 1H), 8.22 – 8.14 (m, 1H), 7.57 – 7.52 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.23, 148.46, 138.33, 136.41, 133.57, 127.98, 127.32, 122.24, 121.77, 117.59; HRMS (ESI) calcd for $C_{10}H_9N_2O$ $[M+H]^+$: 173.0709; Found: 173.0712.



6m

N-benzylformamide (8a)[8]: Reaction scale: benzylamine (26.79 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

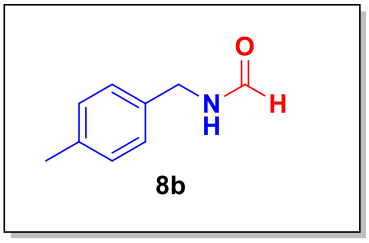
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 76% (26 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers was observed, ratio: 8.6/1.4. Major rotamer: δ 8.24 (s, 1H, CHO), 7.43 – 7.22 (m, 5H), 6.20 (br s, 1H, NH), 4.48 (d, *J* = 5.9 Hz, 2H); Minor rotamer: δ 8.16 (d, *J* = 11.9 Hz, 1H, CHO), 7.43 – 7.22 (m, 5H), 4.40 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 161.12, 137.61, 128.78, 127.78, 127.67, 42.16; Minor rotamer: δ 164.75, 137.50, 128.93, 127.97, 126.98, 45.67; HRMS (ESI) calcd for $C_8H_{10}NO$ $[M+H]^+$: 136.0757; Found: 136.0756.



8a

N-(4-methylbenzyl)formamide (8b)[9]. Reaction scale: 4-methylbenzylamine (30.29 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 86% (32 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.6/1.4. Major rotamer: δ 8.23 (s, 1H, CHO), 7.20 – 7.14 (m, 4H), 6.10 (br s, 1H, NH), 4.43 (d, *J* = 5.8 Hz, 2H), 2.35 (s, 3H); Minor rotamer: δ 8.15 (d, *J* = 11.9 Hz, 1H,

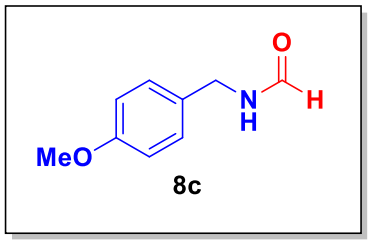


8b

CHO), 7.20 – 7.14 (m, 4H), 4.36 (d, J = 6.3 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 161.03, 137.40, 134.60, 129.43, 127.80, 41.93, 21.08; Minor rotamer: δ 164.67, 137.74, 134.47, 129.57, 126.95, 45.44; HRMS (ESI) calcd for $C_9H_{12}NO$ $[M+H]^+$: 150.0913; Found: 150.0911.

N-(4-Methoxybenzyl)formamide (8c)[8]: Reaction scale: 4-methoxylbenzylamine (34 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

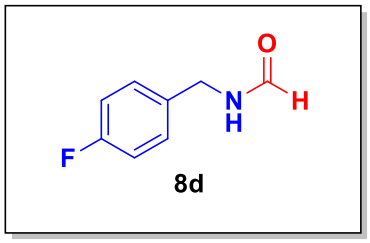
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 95% (39 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.5/1.5. Major rotamer: δ 8.25 (s, 1H, CHO), 7.33 – 7.12 (m, 2H), 6.90 (t, J = 10.0 Hz, 2H), 5.94 (br s, 1H, NH), 4.43 (d, J = 5.4 Hz, 2H), 3.82 (s, 3H); Minor rotamer: δ 8.10 (d, J = 7.3 Hz, 1H, CHO), 7.33 – 7.12 (m, 2H), 4.37 (d, J = 6.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 160.98, 159.17, 129.66, 129.21, 114.17, 55.32, 41.70; Minor Rotamer: δ 164.88, 159.36, 130.02, 128.34 (d, J = 2.8 Hz), 114.31, 45.29; HRMS (ESI) calcd for $C_9H_{12}NO_2$ $[M+H]^+$: 166.0863; Found: 166.0859.



8c

N-(4-Fluorobenzyl)formamide (8d)[8]: Reaction scale: 4-fluorobenzylamine (31.28 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

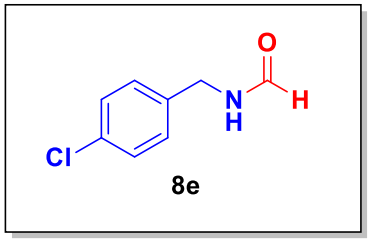
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 68% (26 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.6/1.4. Major rotamer: δ 8.25 (s, 1H, CHO), 7.25 (dd, J = 11.9, 6.5 Hz, 2H), 7.04 (dt, J = 17.0, 8.5 Hz, 2H), 6.45 (br s, 1H, NH), 4.44 (d, J = 4.8 Hz, 2H); Minor rotamer: δ 8.17 (d, J = 11.6 Hz, 1H, CHO), 7.25 (dd, J = 11.9, 6.5 Hz, 2H), 7.04 (dt, J = 17.0, 8.5 Hz, 2H), 4.39 (d, J = 5.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 163.48, 161.36, 129.52 (d, J = 8.1 Hz), 128.72, 115.52, 41.54; Minor rotamer: δ 164.75, 161.04, 133.30 (d, J = 3.2 Hz), 128.80, 115.74, 45.12; HRMS (ESI) calcd for C_8H_9FNO $[M+H]^+$: 154.0663; Found: 154.0662.



8d

N-(4-chlorobenzyl)formamide (8e)[8]: Reaction scale: 4-chlorobenzylamine (36 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

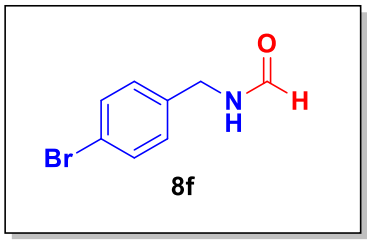
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 67% (29 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.8/1.2. Major rotamer: δ 8.28 (s, 1H, CHO), 7.34 (dd, *J* = 18.8, 8.3 Hz, 2H), 7.22 (dd, *J* = 13.3, 8.4 Hz, 2H), 6.07 (br s, 1H, NH), 4.46 (d, *J* = 6.0 Hz, 2H); Minor rotamer: δ 8.18 (d, *J* = 11.9 Hz, 1H, CHO), 7.34 (dd, *J* = 18.8, 8.3 Hz, 2H), 7.22 (dd, *J* = 13.3, 8.4 Hz, 2H), 4.41 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 161.04, 136.17, 133.52, 128.91, 128.63, 128.31 41.47; Minor rotamer: δ 135.99, 133.90, 129.13, 128.53, 45.00; HRMS (ESI) calcd for C_8H_9ClNO $[M+H]^+$: 170.0367; Found: 170.0366.



8e

N-(4-Bromobenzyl formamide (8f)[8]: Reaction scale: 4-bromobenzylamine (46.50 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

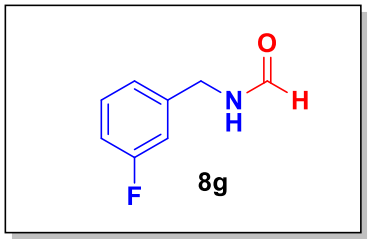
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 63% (34 mg).^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.7/1.3; Major rotamer: δ 8.29 (s, 1H), 7.49 (dd, *J* = 14.5, 8.1 Hz, 2H), 7.17 (t, *J* = 9.0 Hz, 2H), 6.35 (br s, 1H), 4.44 (d, *J* = 5.2 Hz, 2H); Minor rotamer: δ 8.17 (d, *J* = 11.7 Hz, 1H), 7.49 (dd, *J* = 14.5, 8.1 Hz, 2H), 7.17 (t, *J* = 9.0 Hz, 2H), 4.39 (d, *J* = 6.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 161.38, 136.49, 131.89, 129.49, 121.64, 41.65; Minor rotamer: δ 132.08, 128.70, 45.20; HRMS (ESI) calcd for C_8H_9BrNO $[M+H]^+$: 213.9862; Found: 213.9859.



8f

N-(3-Fluorobenzyl)formamide (8g)[10]: Reaction scale: 3-fluorobenzylamine (31.26 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 92% (35 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.8/1.2. Major rotamer: δ 8.26 (s, 1H, CHO), 7.29 (dd, *J* = 13.8, 7.7 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.11 (br s, 1H, NH), 4.46 (d, *J* = 6.1 Hz, 2H); Minor rotamer: δ 8.16 (d, *J* = 11.9 Hz, 1H, CHO), 7.29 (dd, *J* = 13.8, 7.7 Hz, 1H), 7.00 – 6.93

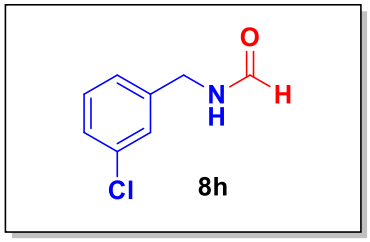


8g

(m, 2H), 4.40 (d, J = 6.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.09, 140.16 (d, J = 7.0 Hz), 130.31 (d, J = 8.2 Hz), 123.20, 114.66, 114.49, 41.60; HRMS (ESI) calcd for C_8H_9FNO $[M+H]^+$: 154.0663; Found: 154.0664.

N-(3-chlorobenzyl)formamide (8h)[10] Reaction scale: 3-chlorobenzylamine (35.40 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

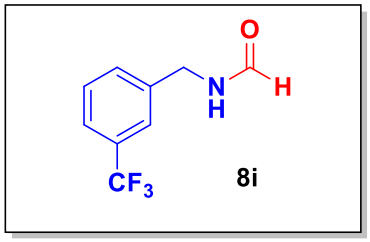
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 86% (36 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.8/1.2. Major rotamer: δ 8.26 (s, 1H, CHO), 7.37 – 7.20 (m, 3H), 7.19 – 7.10 (m, 1H), 6.10 (br s, 1H, NH), 4.45 (d, J = 6.0 Hz, 2H); Minor rotamer: δ 8.16 (d, J = 11.9 Hz, 1H, CHO), 7.37 – 7.20 (m, 3H), 7.19 – 7.10 (m, 1H), 4.39 (d, J = 6.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 161.09, 139.66, 134.61, 130.05, 127.81(d, J = 8.4 Hz), 125.83, 41.54; Minor rotamer: δ 130.24, 128.19, 125.02; HRMS (ESI) calcd for C_8H_9ClNO $[M+H]^+$: 170.0367; Found: 170.0366.



8h

N-(3-(trifluoromethyl)benzyl)formamide (8i)[8]: Reaction scale: 3-(trifluoromethyl)benzylamine (44 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

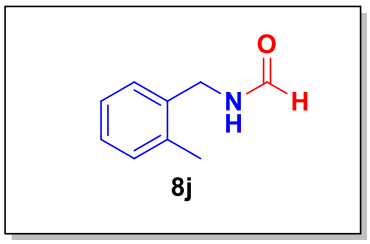
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 90% (46 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.9/1.1. Major rotamer: δ 8.25 (s, 1H, CHO), 7.56 – 7.41 (m, 4H), 6.38 (br s, 1H, NH), 4.50 (d, J = 6.1 Hz, 2H); Minor rotamer: δ 8.16 (d, J = 11.9 Hz, 1H, CHO), 7.56 – 7.41 (m, 4H), 4.46 (d, J = 6.6Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.26, 138.72, 131.06, 130.26, 129.49, 129.24, 124.37 (dd, J = 20.7, 3.5 Hz), 122.88, 41.5; HRMS (ESI) calcd for $C_9H_9F_3NO$ $[M+H]^+$: 204.0631; Found: 204.0632.



8i

N-(2-methylbenzyl)formamide (8j)[11]: Reaction scale: 2-methylbenzylamine (31 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

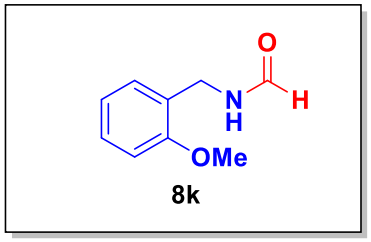
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 63% (24 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.6/1.4. Major rotamer: δ 8.24 (s, 1H, CHO), 7.26 – 7.17 (m, 4H), 6.14 (br s, 1H, NH), 4.49 (d, *J* = 4.4 Hz, 2H), 2.35 (s, 3H); Minor rotamer: 8.14 (d, *J* = 11.9 Hz, 1H, CHO), 7.26 – 7.17 (m, 4H), 4.40 (d, *J* = 6.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): Mixture of rotamers δ 160.67, 142.24, 128.99, 128.81, 127.88, 127.68, 126.18, 125.83, 48.02, 21.68; HRMS (ESI) calcd for $C_9H_{12}NO$ $[M+H]^+$: 150.0913; Found: 150.0906.



8j

N-(2-methoxybenzyl)formamide(8k)[12]: Reaction scale: 2-methoxybenzylamine (34 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

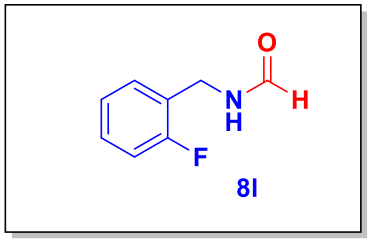
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 76% (31 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 9.4/0.6. Major rotamer: δ 8.16 (s, 1H, CHO), 7.27 (dd, *J* = 18.7, 11.2 Hz, 2H), 6.90 (dt, *J* = 17.1, 7.0 Hz, 2H), 6.22 (br s,1H, NH), 4.46 (d, *J* = 5.9 Hz, 2H), 3.84 (s, 3H); Minor rotamer: δ 8.13 (s, 1H, CHO), 7.16 (d, *J* = 7.3 Hz, 2H), 6.90 (dt, *J* = 17.1, 7.0 Hz, 2H), 6.08 (br. s, 1H, NH), 4.33 (d, *J* = 6.5 Hz, 2H), 3.83 (s, 3H) ; ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 160.90, 157.55, 129.78, 129.09, 125.67, 120.75, 110.34, 55.33, 38.04; Minor rotamer: δ 164.83, 129.47, 128.69, 120.67, 110.45, 55.29, 42.08; HRMS (ESI) calcd for $C_9H_{12}NO_2$ $[M+H]^+$: 166.0863; Found: 166.0862.



8k

N-(2-Fluorobenzyl)formamide (8l)[9]: Reaction scale: 2-fluorobenzylamine (31 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 92% (35 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 6.8/3.2. Major rotamer: δ 8.19 (s, 1H, CHO), 7.31 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.08 (dd, *J* = 14.7, 7.9 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.33 (br s, 1H, NH), 4.49 (d, *J* = 6.0 Hz, 2H); Minor rotamer: δ 8.15 (d, *J* = 12.0 Hz, 1H, CHO), 7.31 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.08 (dd, *J* = 14.7, 7.9 Hz, 1H), 7.05 – 7.00 (m, 1H), 4.41 (d,

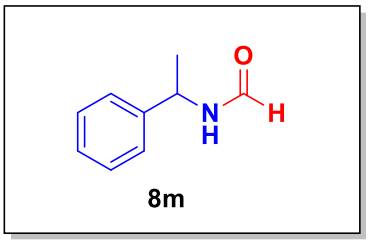


8l

J = 6.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 161.96, 161.19, 130.20 (d, *J* = 4.0 Hz), 129.49 (d, *J* = 8.1 Hz), 124.37 (d, *J* = 3.5 Hz), 115.77, 115.48, 36.13 (d, *J* = 3.5 Hz); Minor rotamer: δ 164.84, 160.01, 129.92 (d, *J* = 8.2 Hz), 129.11 (d, *J* = 3.8 Hz), 124.57 (d, *J* = 5.2 Hz), 115.60, 115.32, 39.98 (d, *J* = 3.9 Hz); HRMS (ESI) calcd for C_8H_9FNO $[M+H]^+$: 154.0663; Found: 154.0663.

N-(1-phenylethyl)formamide (8m)[8]: Reaction scale: 1-phenylethan-1-amine (30 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

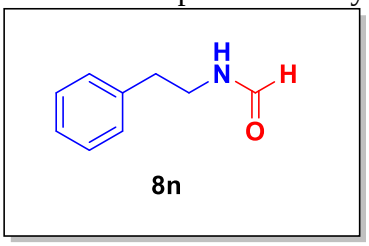
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 41% (15 mg). ^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 7.9/2.1. Major rotamer: δ 8.21 (s, 1H, CHO), 7.42 – 7.30 (m, 5H), 6.37 (br s, 1H, NH), 5.23 (p, *J* = 7.0 Hz, 1H), 1.56 (d, *J* = 6.9 Hz, 3H); Minor rotamer: δ 8.17 (d, *J* = 12.1 Hz, 1H, CHO), 7.42 – 7.30 (m, 5H), 4.72 (p, *J* = 7.2 Hz, 1H), 1.60 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 161.18, 136.44, 130.63, 128.03, 126.33, 40.45, 19.03; Minor rotamer: δ 135.02, 130.73, 128.59, 126.53, 43.77; HRMS (ESI) calcd for $C_9H_{12}NO$ $[M+H]^+$: 150.0913; Found: 150.0912.



8m

N-Phenethylformamide (8n)[7]: Reaction scale: Phenethylamine (30.29 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

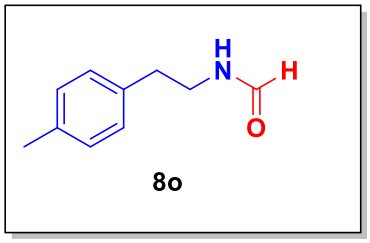
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 86% (32 mg).^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.3/1.7. Major rotamer: δ 8.16 (s, 1H, CHO), 7.37 – 7.18 (m, 5H), 6.03 (br s, 1H), 3.60 (dd, *J* = 12.9, 6.6 Hz, 2H), 2.87 (dd, *J* = 15.1, 8.1 Hz, 2H); Minor rotamer: 7.92 (d, *J* = 11.8 Hz, 1H, CHO), 7.37 – 7.18 (m, 5H), 3.50 (dd, *J* = 13.3, 6.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 161.46, 138.40, 128.74 (d, *J* = 2.6 Hz),126.70, 39.37, 35.43; Minor rotamer: δ 164.61, 128.86, 126.94, 43.31, 37.65; HRMS (ESI) calcd for $C_9H_{12}NO$ $[M+H]^+$: 150.0913; Found: 150.0909.



8n

N-(4-methylphenethyl)formamide (8o)[13]: Reaction scale: 2-(*p*-tolyl)ethylamine (33.80 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

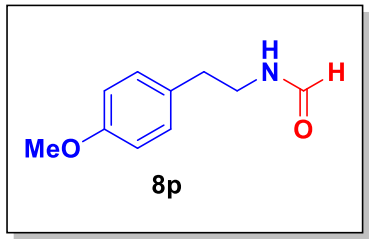
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 91% (37 mg).[1]H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.4/1.6. Major rotamer: δ 8.09 (s, 1H, CHO), 7.08 (dt, *J* = 17.1, 7.8 Hz, 4H), 5.79 (br s, 1H, NH), 3.53 (dd, *J* = 13.2, 6.6 Hz, 2H), 2.77 (dt, *J* = 13.9, 6.8 Hz, 2H), 2.32 (s, 3H); Minor rotamer: δ 7.88 (d, *J* = 11.8 Hz, 1H, CHO), 7.08 (dt, *J* = 17.1, 7.8 Hz, 4H), 3.43 (dd, *J* = 13.2, 6.6 Hz, 2H), 2.77 (dt, *J* = 13.9, 6.8 Hz, 2H); [13]C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 161.23, 136.21, 135.37, 129.52, 128.62, 39.26, 35.03, 21.01; Minor rotamer: δ 164.54, 136.49, 134.49, 129.38, 128.73, 43.25, 37.28; HRMS (ESI) calcd for $C_{10}H_{14}NO$ $[M+H]^+$: 164.1070; Found: 164.1071.



8o

N-(4-methoxyphenethyl)formamide (8p)[10]: Reaction scale: 4-methoxyphenethylamine (37.80 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

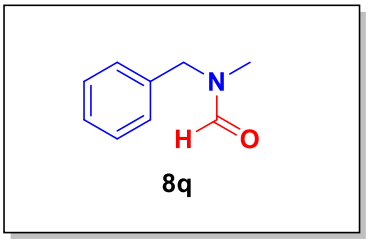
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 96% (43 mg). [1]H NMR (400 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.2/1.8. Major Rotamer: δ 8.14 (s, 1H, CHO), 7.13 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.01 (br s, 1H, NH), 3.80 (s, 3H), 3.55 (q, *J* = 6.7 Hz, 2H), 2.79 (dd, *J* = 15.3, 8.3 Hz, 2H); Minor rotamer, δ 7.89 (d, *J* = 12.0 Hz, 1H, CHO), 7.10 (d, *J* = 8.9 Hz, 2H), 3.49 – 3.39 (m, 2H); [13]C NMR (101 MHz, $CDCl_3$): Major rotamer: δ 161.47, 158.39, 130.36, 129.72, 114.13, 55.29, 39.54, 34.52; Minor rotamer: δ 164.65, 158.53, 129.87, 129.52, 114.26, 43.52, 36.75; HRMS (ESI) calcd for $C_{10}H_{14}NO_2$ $[M+H]^+$: 180.1019; Found: 180.1013.



8p

N-benzyl-N-methylformamide (8q)[14]: Reaction scale: N-methylbenzylamine (30.29 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 73% (27 mg).[1]H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 5.8/4.2. Major rotamer: δ 8.30 (s, 1H, CHO), 7.43 – 7.33 (m, 5H), 4.41 (s, 2H), 2.80 (s, 3H); Minor rotamer: 8.18 (s, 1H, CHO), 7.32 – 7.19 (m, 5H), 4.54 (s, 2H), 2.86 (s, 3H); [13]C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 162.77, 135.77, 128.92, 128.26, 127.41,

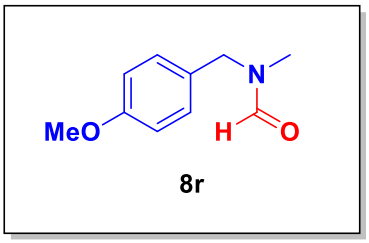


8q

53.50, 29.70; Minor Rotamer: δ 162.61, 136.03, 128.71, 128.12, 127.66, 47.79, 34.06; HRMS (ESI) calcd for $C_9H_{12}NO$ $[M+H]^+$: 150.0913; Found: 150.0902.

N-(4-methoxybenzyl)-N-methylformamide (8r)[15]: Reaction scale: 4-methoxy-N-methylbenzylamine (37.80 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 67% (30 mg).

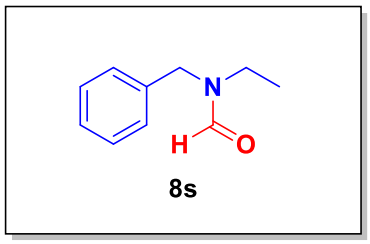


8r

^{1}H NMR (500 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 5.9/4.1. Major rotamer: δ 8.29 (s, 1H, CHO), 6.90 (dd, *J* = 15.6, 8.5 Hz, 4H), 4.34 (s, 2H), 3.83 (s, 3H), 2.77 (s, 3H); Minor rotamer: δ 8.15 (s, 1H, CHO), 7.17 (dd, *J* = 30.2, 8.5 Hz, 4H), 4.47 (s, 2H), 3.82 (s, 3H), 2.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): Major rotamer: δ 162.61, 159.49, 128.78, 127.64, 114.27, 55.30 (d, *J* = 5.4 Hz), 47.16, 29.25; Minor rotamer: δ 162.51, 159.15, 129.67, 128.16, 114.06, 52.99, 38.15, 33.92; HRMS (ESI) calcd for $C_{10}H_{14}NO_2$ $[M+H]^+$:180.1019; Found: 180.1003.

N-Benzyl-N-ethylformamide (8s)[15]: Reaction scale: N-Ethylbenzylamine (33.50 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 67% (27 mg).

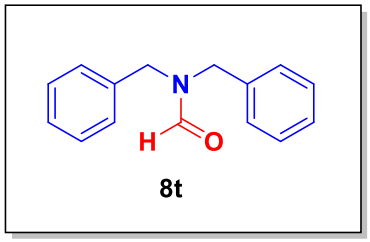


8s

^{1}H NMR (600 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 5.0/5.0. Major rotamer: δ 8.25 (s, 1H, CHO), 7.31 – 7.23 (m, 5H), 4.58 (s, 2H), 3.23 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); Minor rotamer: 8.28 (s, 1H, CHO), 7.40 – 7.33 (m, 5H), 4.42 (s, 2H), 3.32 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H) ; ^{13}C NMR (151 MHz, $CDCl_3$): Major rotamer: δ 162.62, 136.54, 128.66, 128.14, 127.48, 44.84, 41.52, 14.36 ; Minor rotamer: δ 136.24, 128.87, 128.06, 127.55, 50.89, 36.84, 12.22; HRMS (ESI) calcd for $C_{10}H_{14}NO$ $[M+H]^+$: 164.1070; Found: 164.1067.

N,N-Dibenzylformamide (8t)[16]: Reaction scale: Dibenzylamine (49.32 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

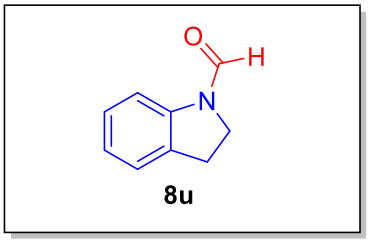
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 63% (35 mg).[1]H NMR (600 MHz, $CDCl_3$): A mixture of rotamers were observed, δ 8.45 (s, 1H, CHO), 7.44 – 7.17 (m, 10H), 4.45 (s, 2H), 4.29 (s, 2H); [13]C NMR (151 MHz, $CDCl_3$): δ 162.88, 136.03, 135.65, 128.95, 128.73, 128.55, 128.18, 127.74, 127.70, 50.28, 44.68. HRMS (ESI) calcd for $C_{15}H_{16}NO$ $[M+H]^+$: 226.1226; Found: 226.1222.



8t

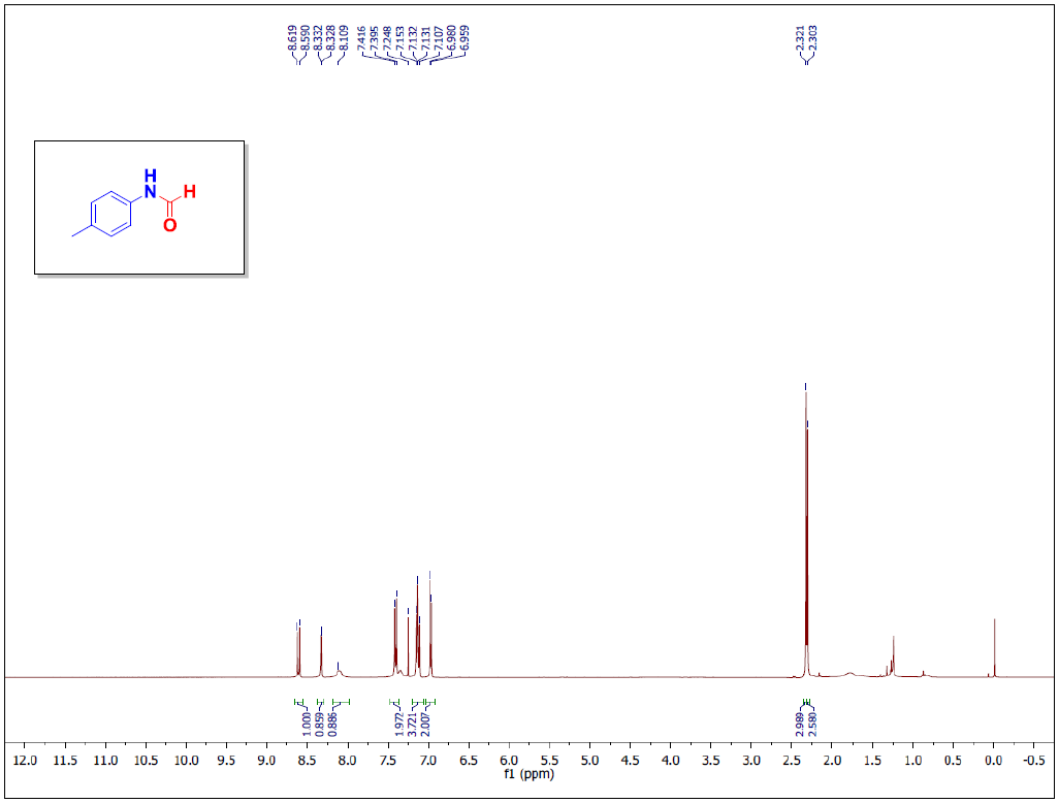
Indoline-1-carbaldehyde (8u)[12]: Reaction scale: Indoline (30 mg, 0.25 mmol), DMF (2 mL), $[PPN]_2[P_4O_{12}H_2]$ (348.76 mg, 0.25 mmol).

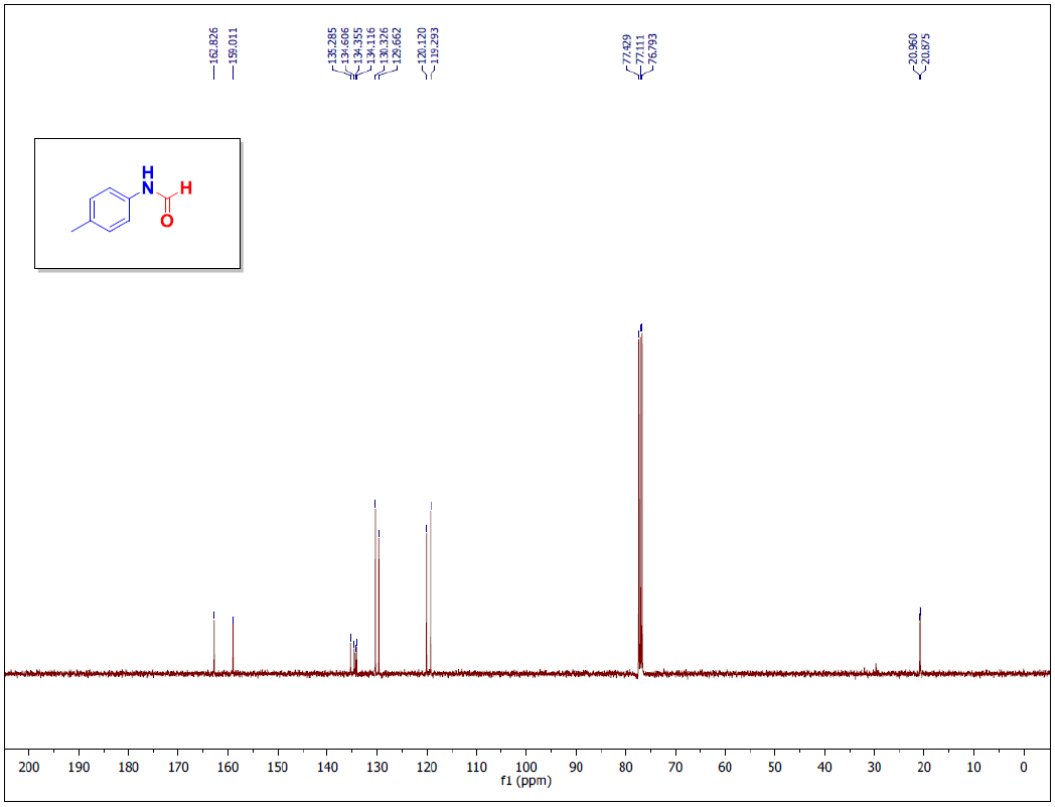
The title compound was synthesized according to general procedure and isolated though column chromatography. The isolated yield is 81% (30 mg).[1]H NMR (600 MHz, $CDCl_3$): A mixture of rotamers were observed, ratio: 8.3/1.7. δ 8.95 (s, 1H, CHO), 8.53 (s, 1H, CHO), 8.09 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.16 (m, 3H), 7.08 (dd, *J* = 10.0, 4.2 Hz, 1H), 4.11 (dt, *J* = 17.0, 8.3 Hz, 2H), 3.19 (dt, *J* = 16.9, 8.4 Hz, 2H); [13]C NMR (151 MHz, $CDCl_3$): δ 159.37, 157.64, 141.23, 141.07, 132.03, 131.97, 127.61, 126.10, 124.88, 124.64, 124.33, 116.70, 109.43, 47.00, 44.68, 27.77, 27.20. HRMS (ESI) calcd for $C_9H_{10}NO$ $[M+H]^+$: 148.0757; Found: 148.0751.



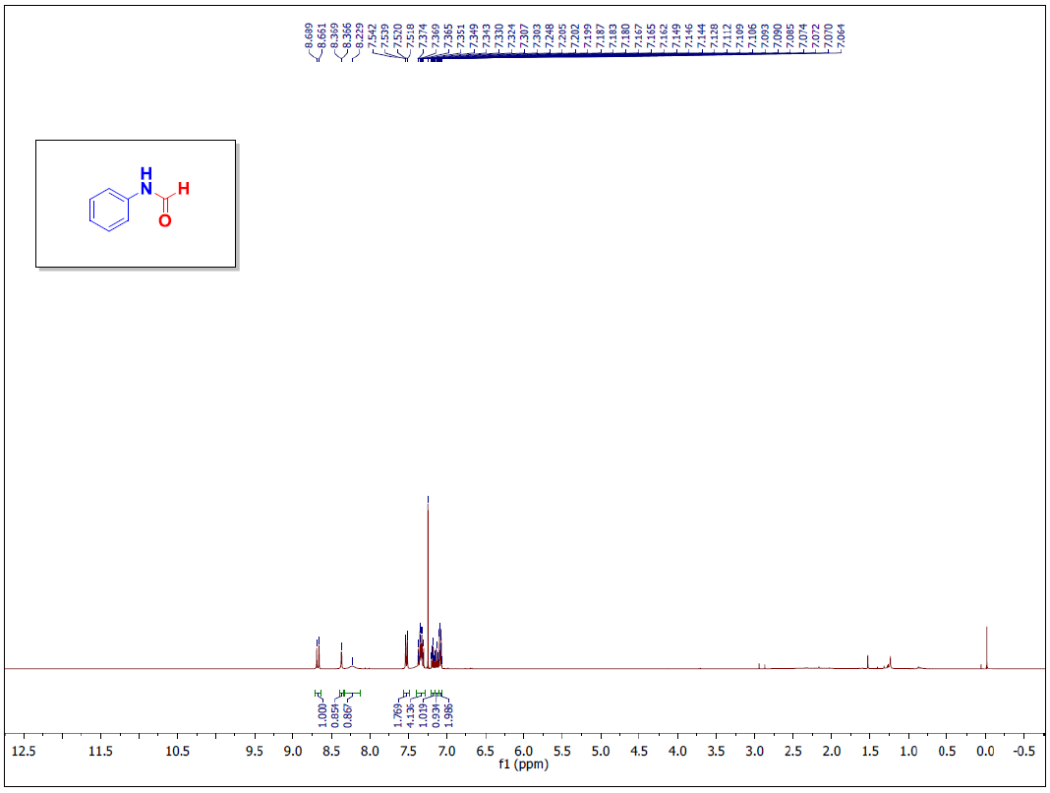
8u

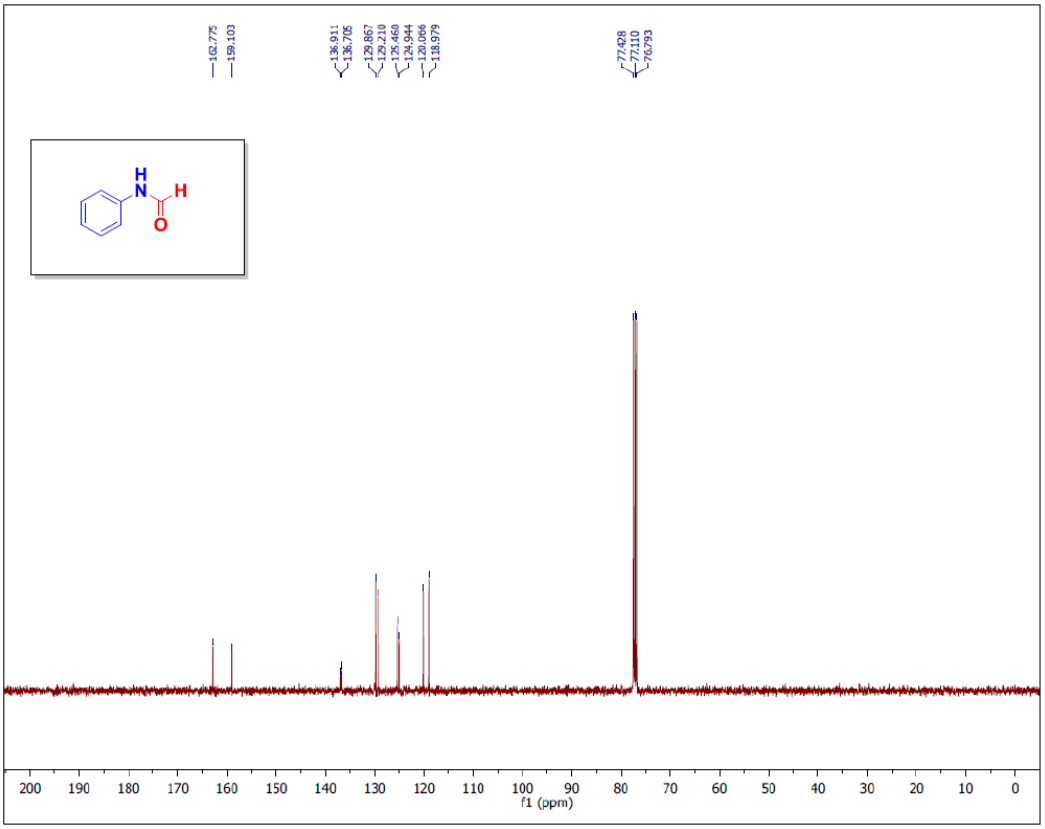
^{1}H and ^{13}C NMR spectra of compound 6a:



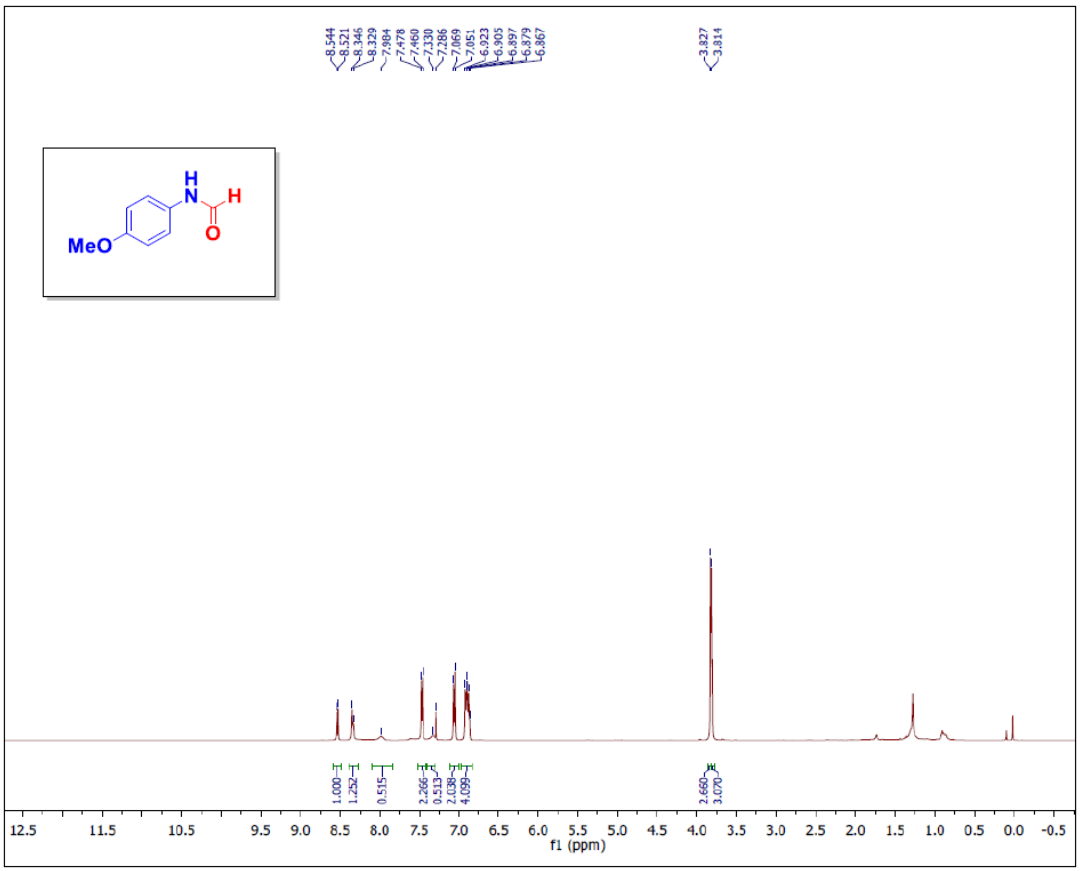


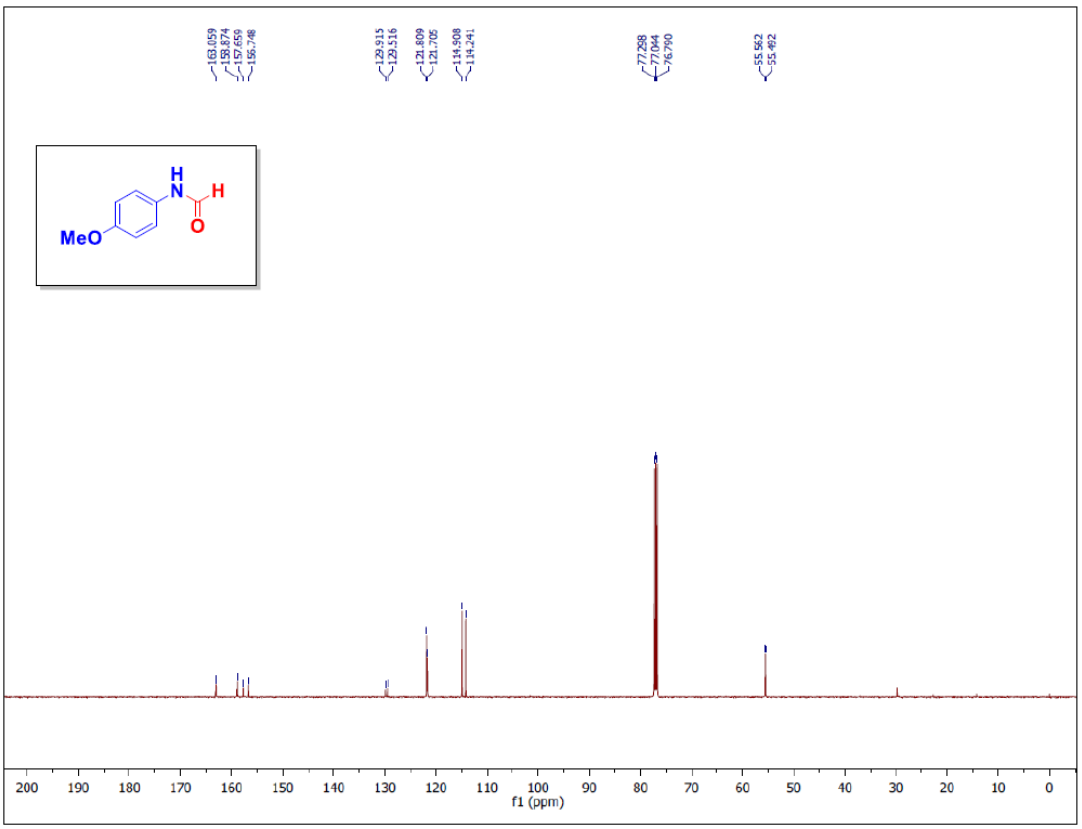
^{1}H and ^{13}C NMR spectra of compound 6b:



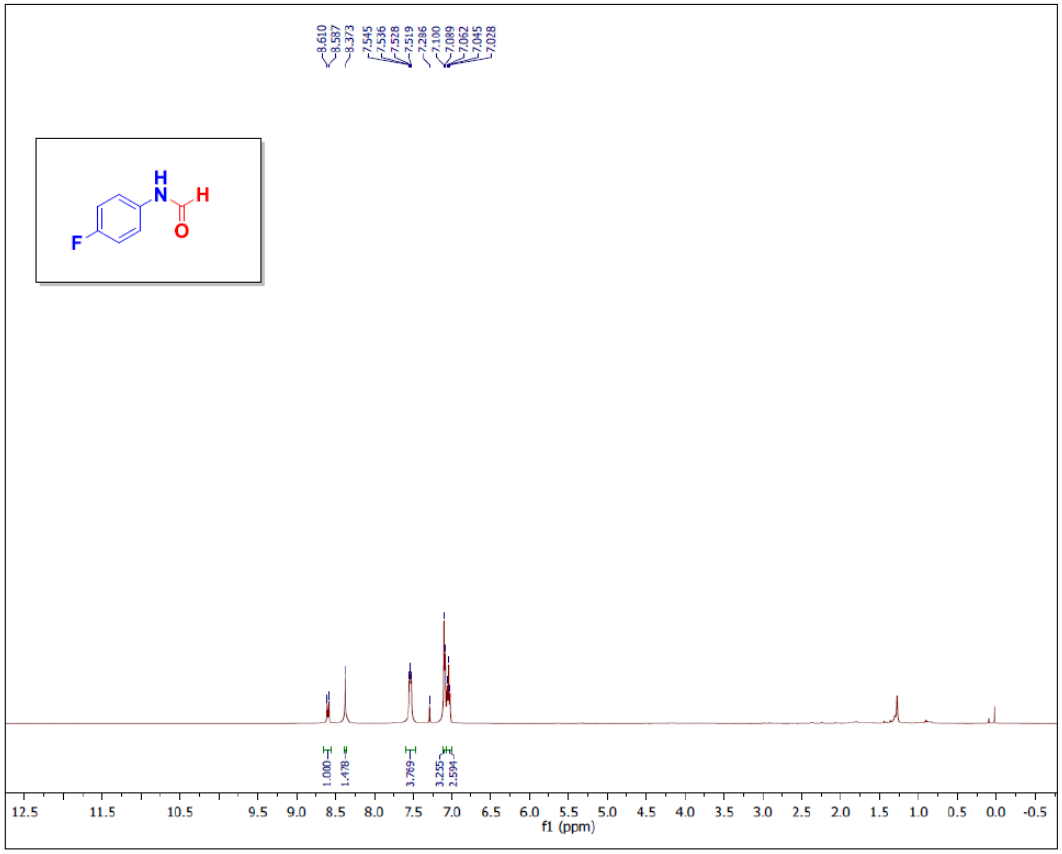


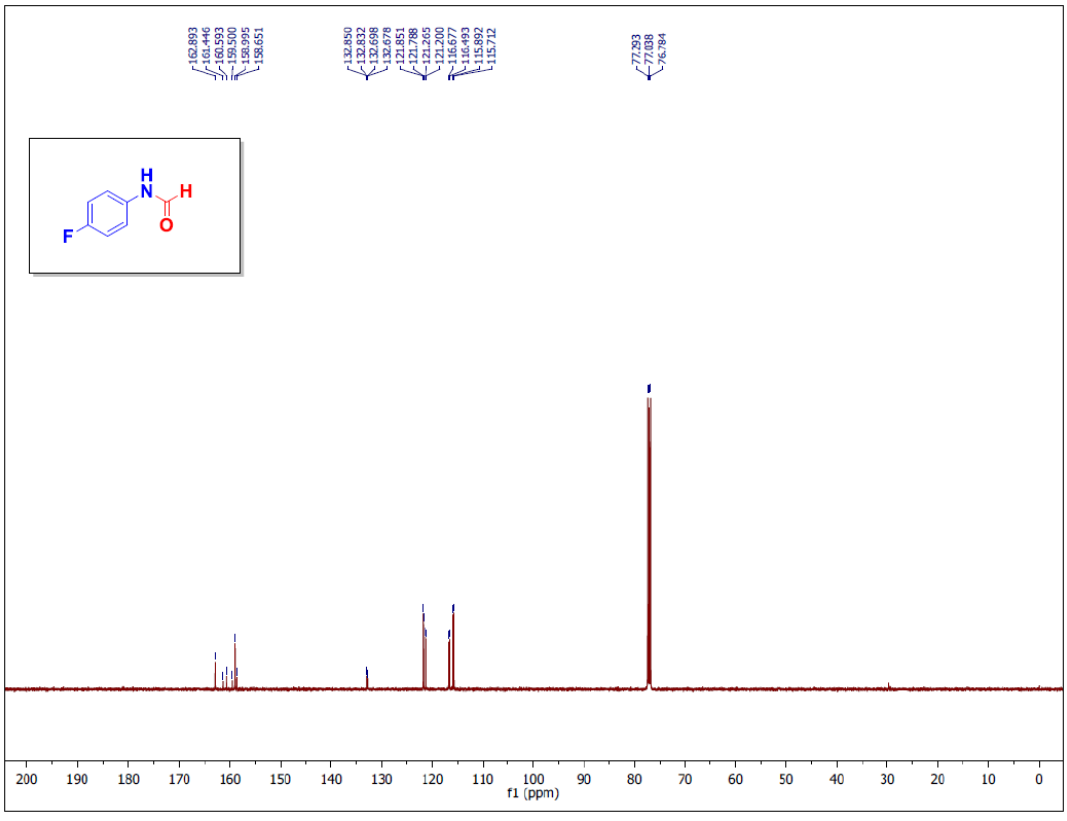
^{1}H and ^{13}C NMR spectra of compound 6c:



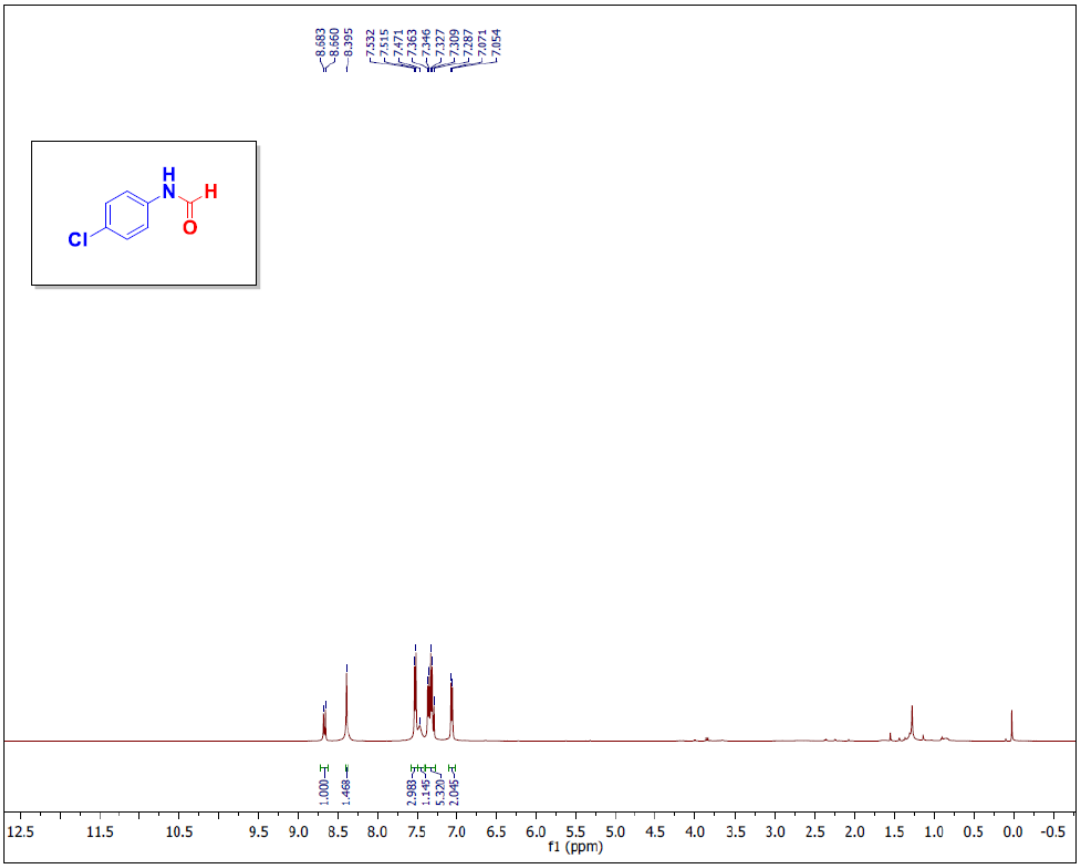


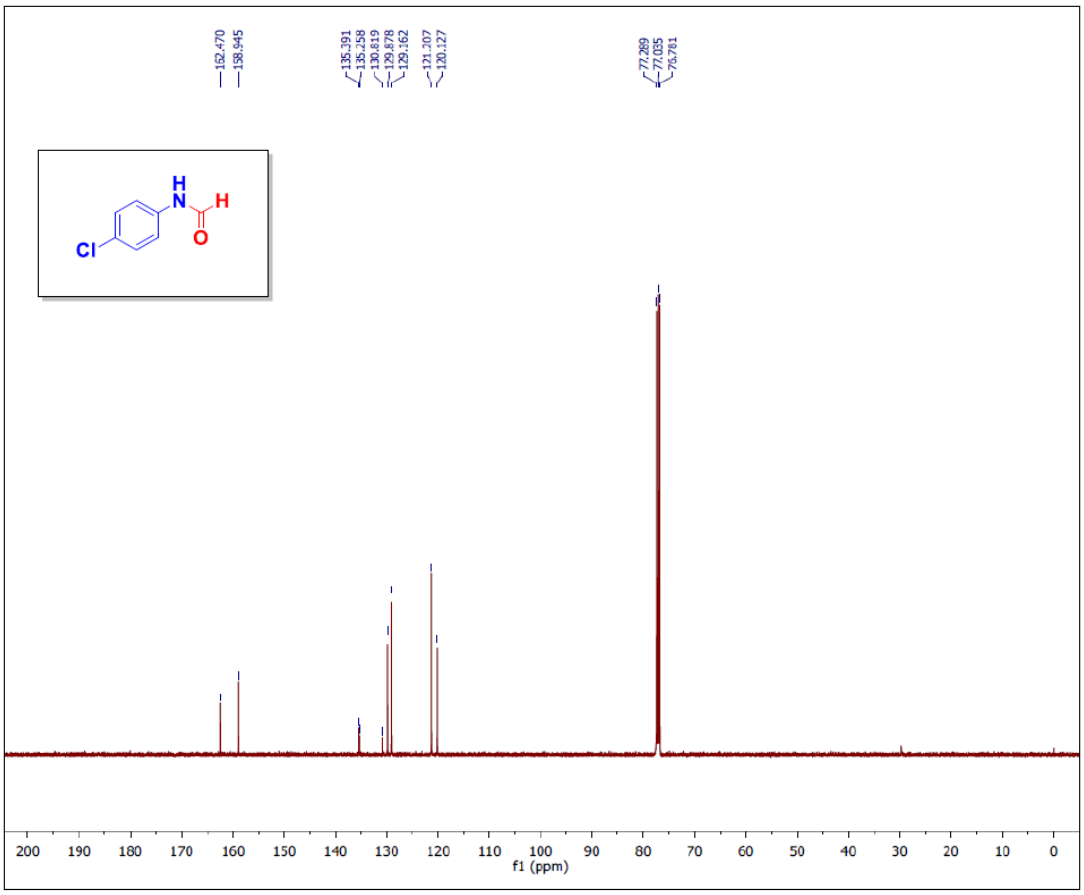
^{1}H and ^{13}C NMR spectra of compound 6d:



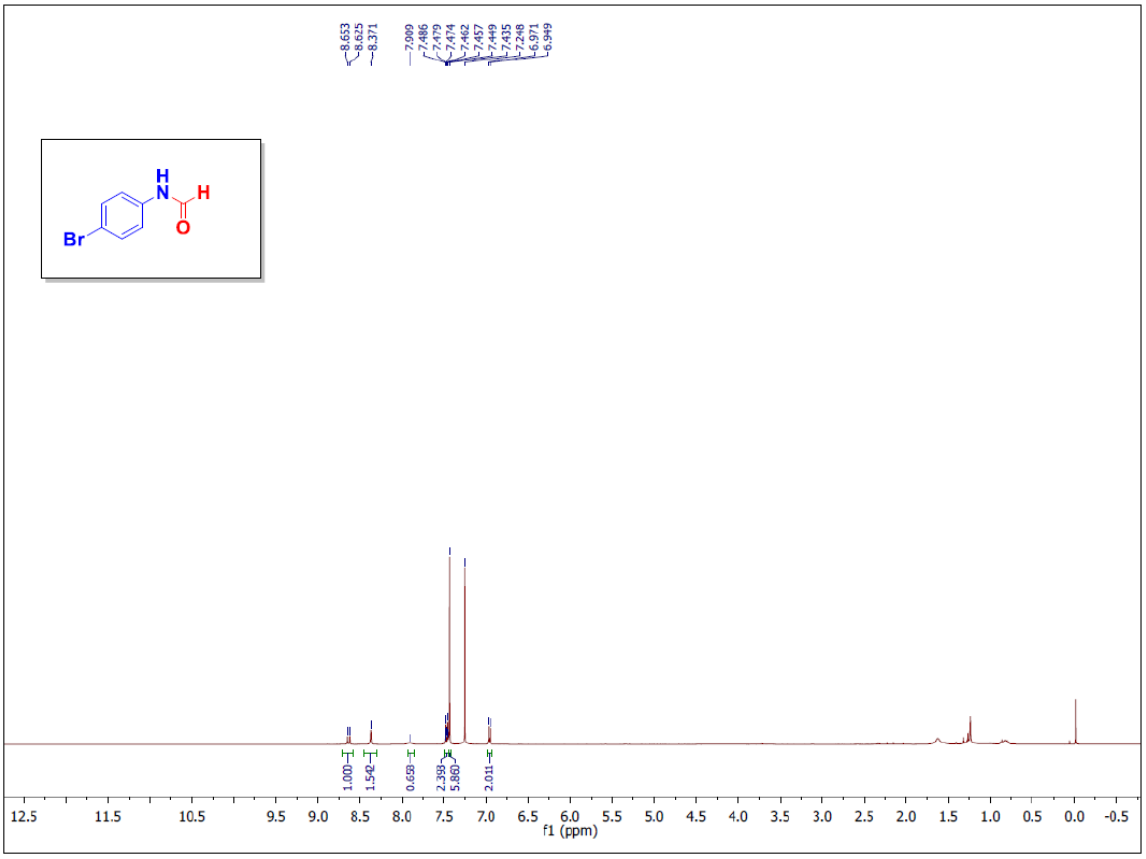


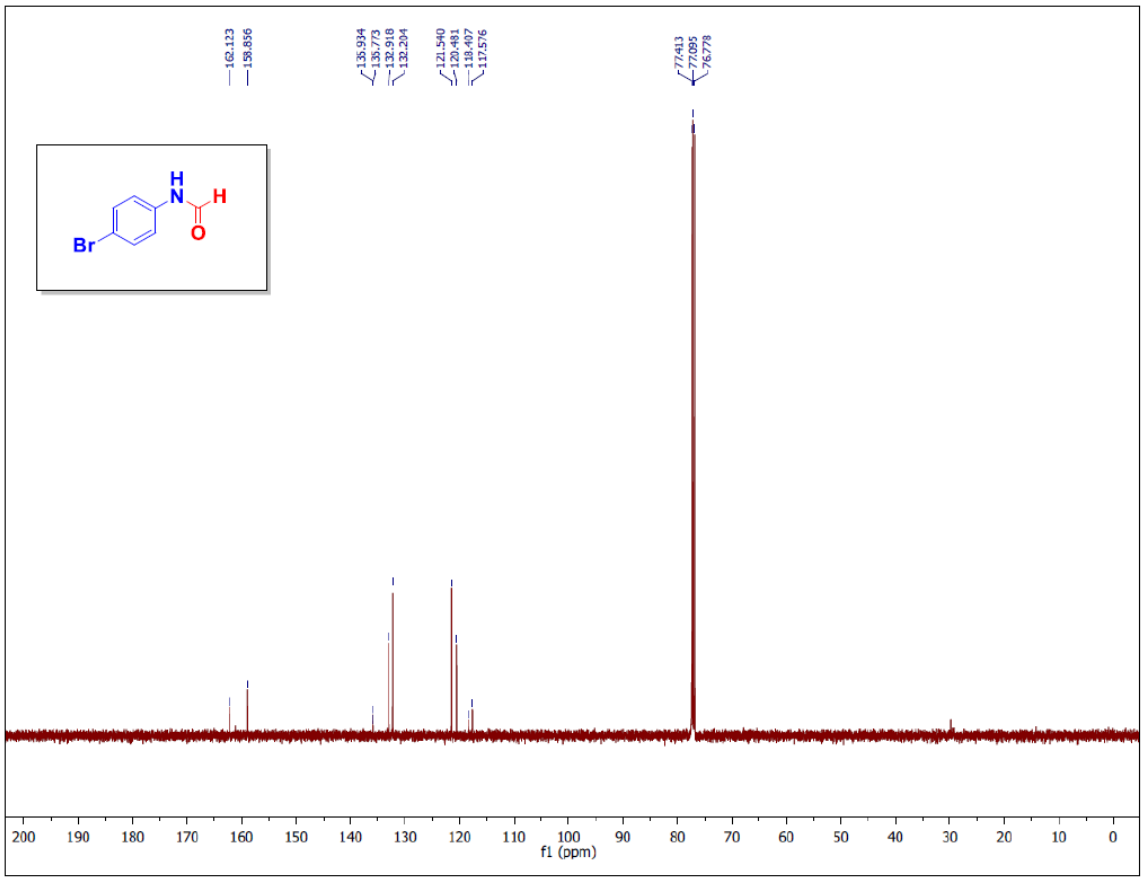
^{1}H and ^{13}C NMR spectra of compound 6e:



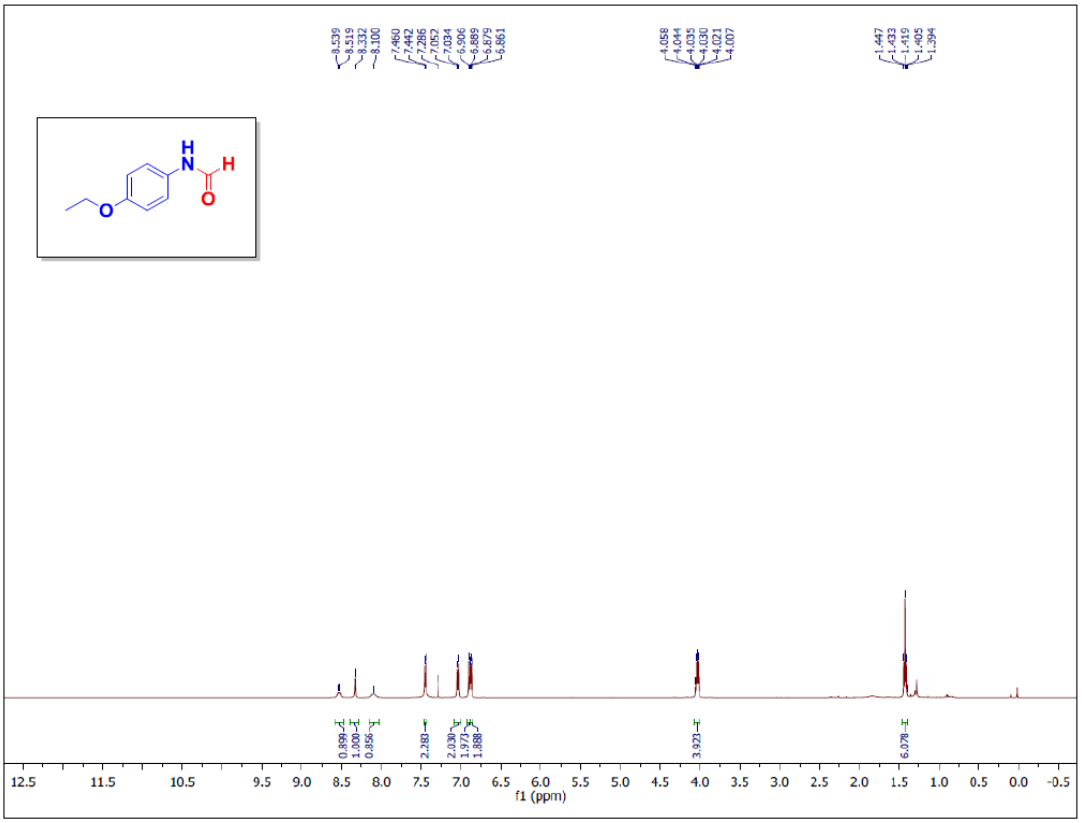


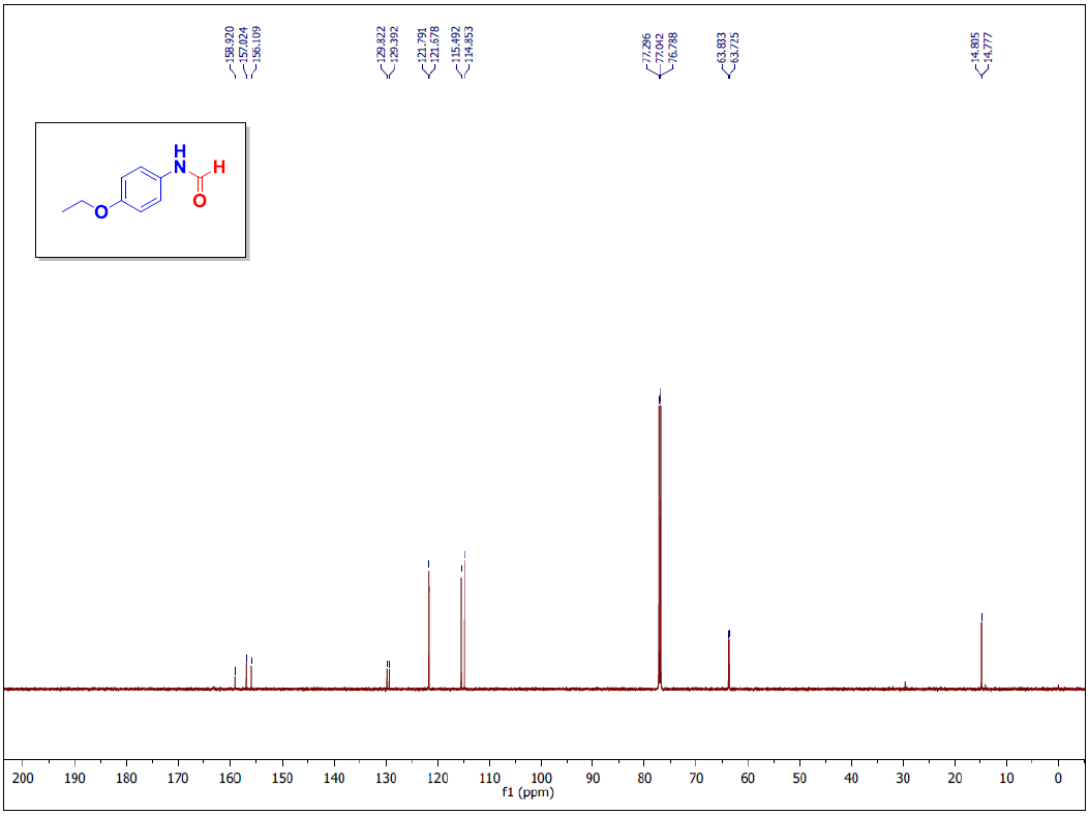
^{1}H and ^{13}C NMR spectra of compound 6f:



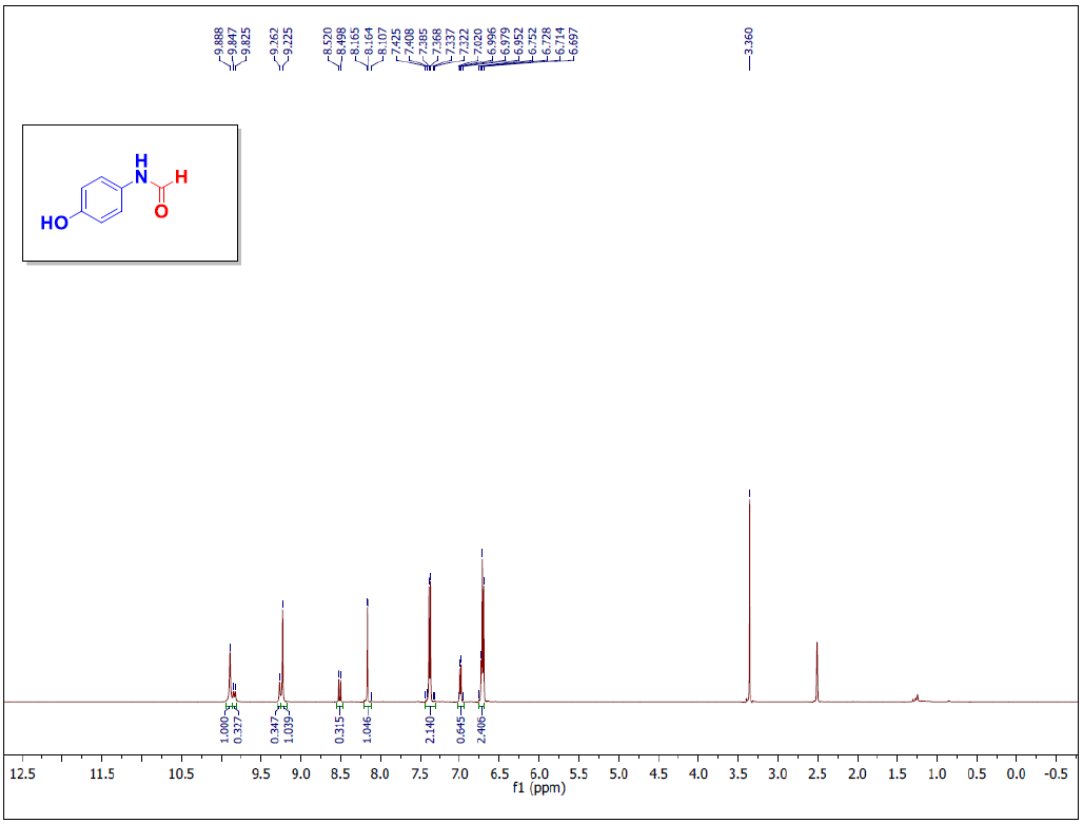


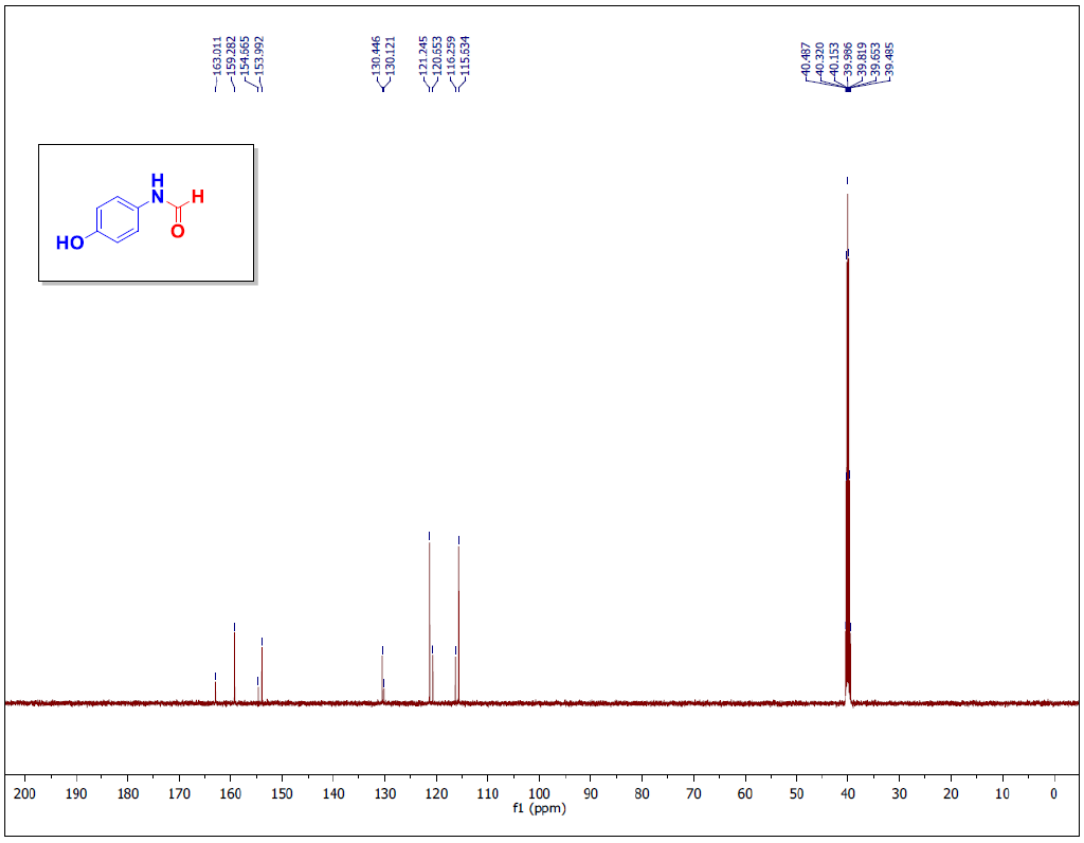
^{1}H and ^{13}C NMR spectra of compound 6g:



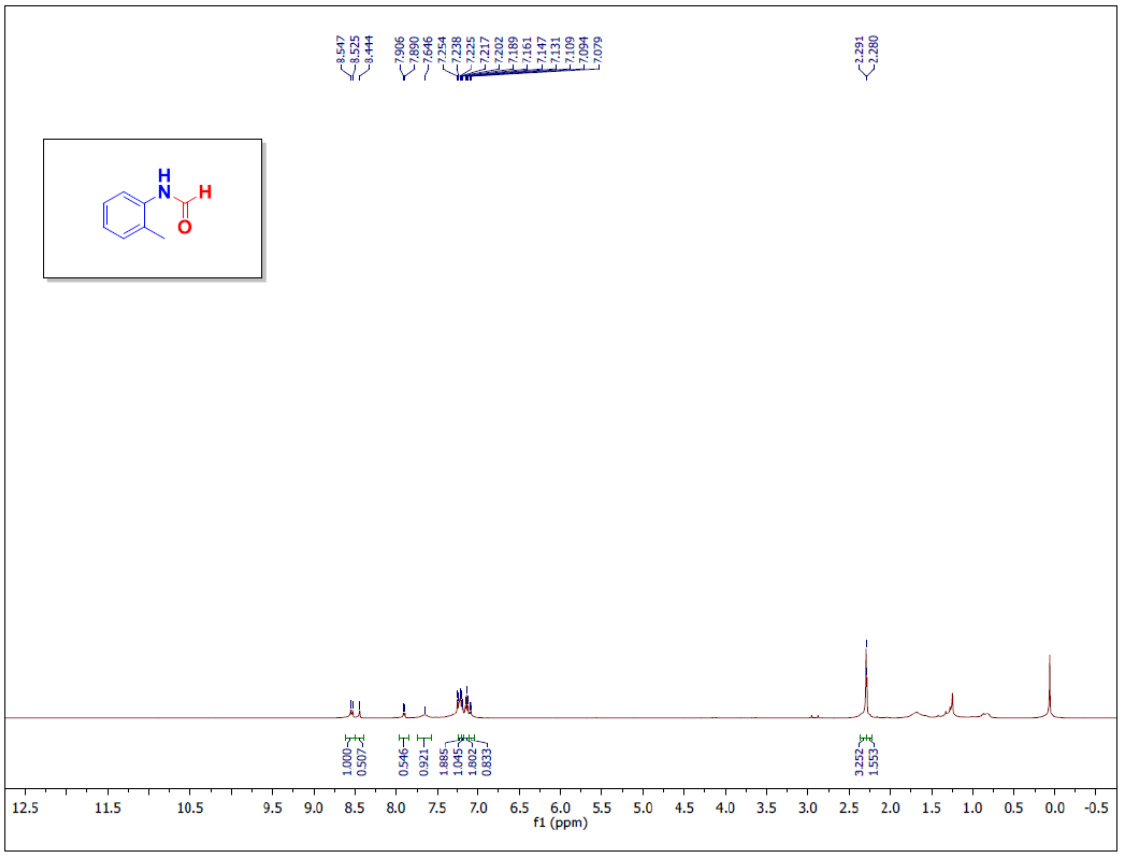


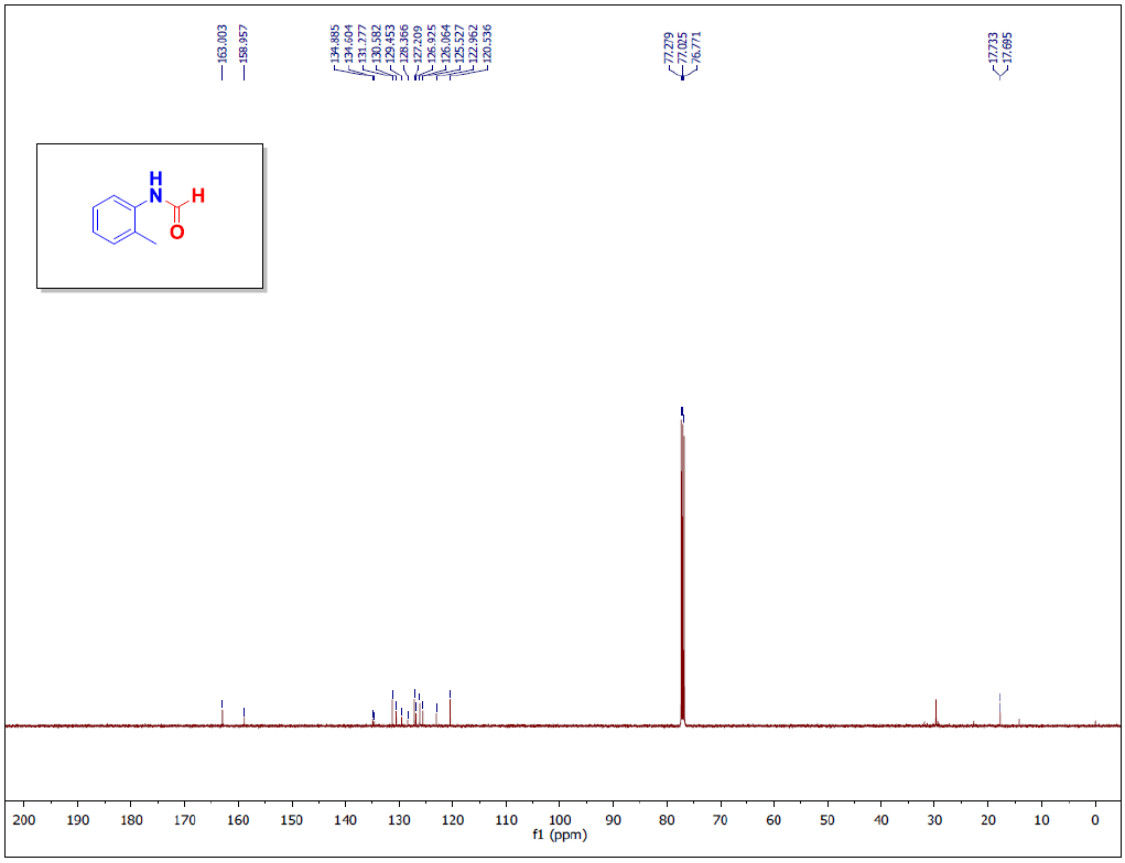
^{1}H and ^{13}C NMR spectra of compound 6h (DMSO-d_6):



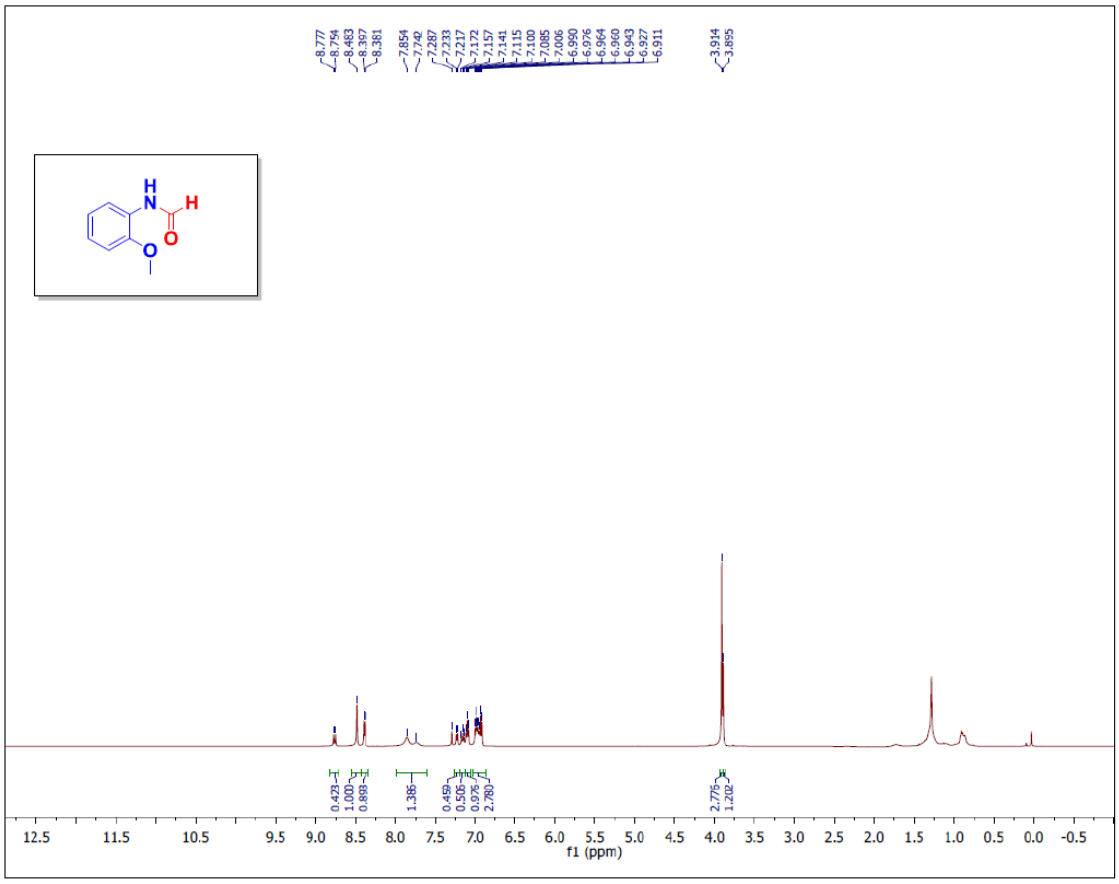


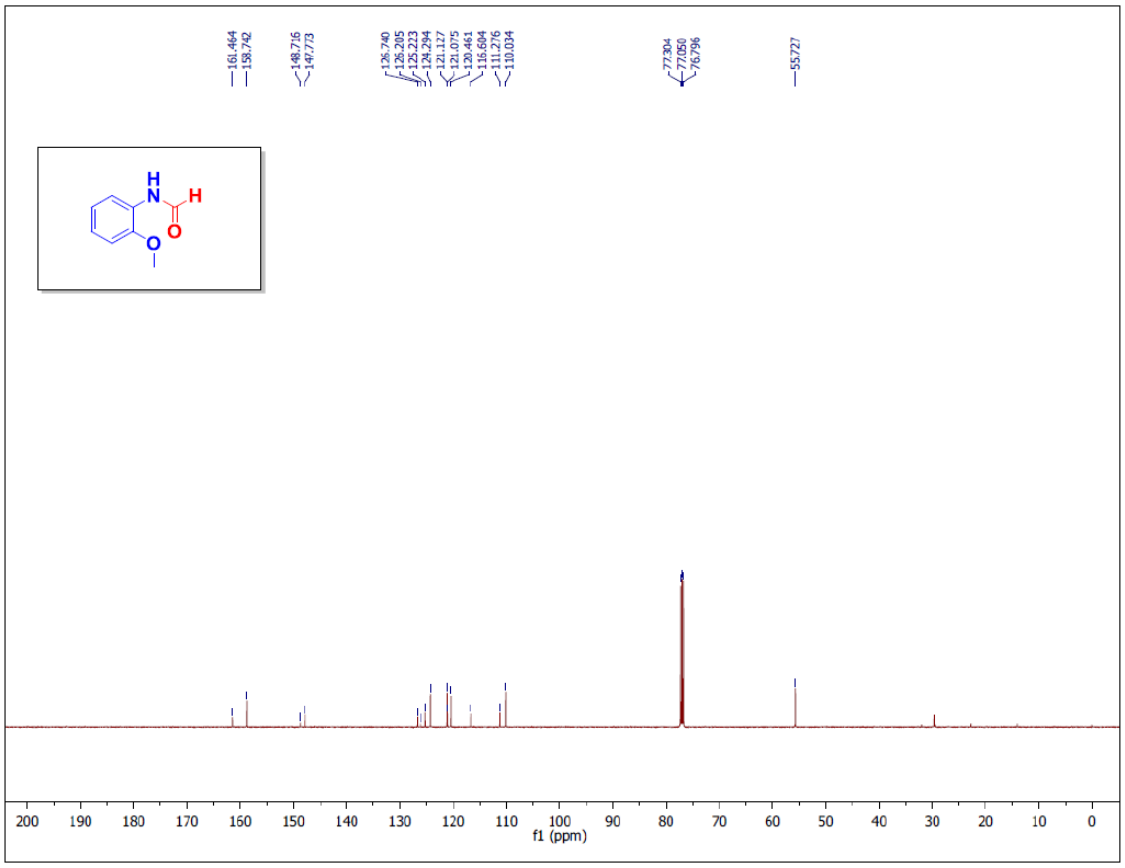
^{1}H and ^{13}C NMR spectra of compound 6i:



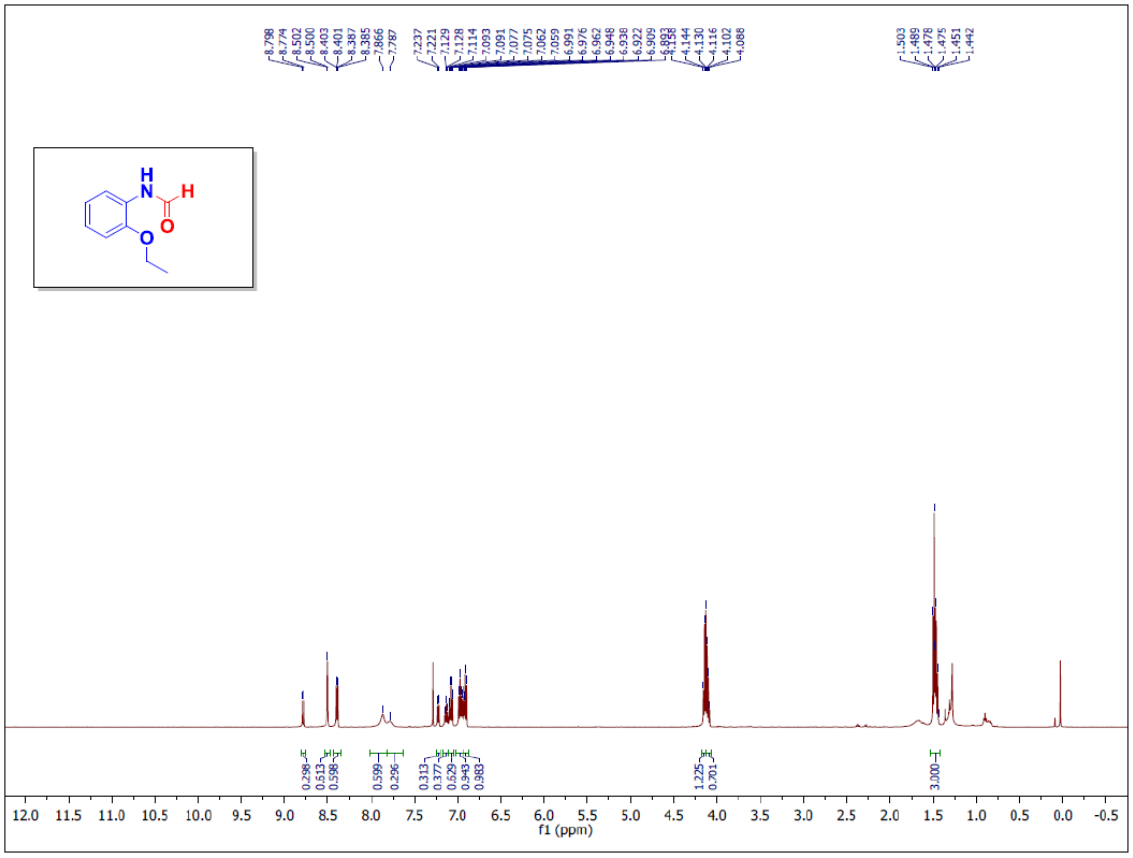


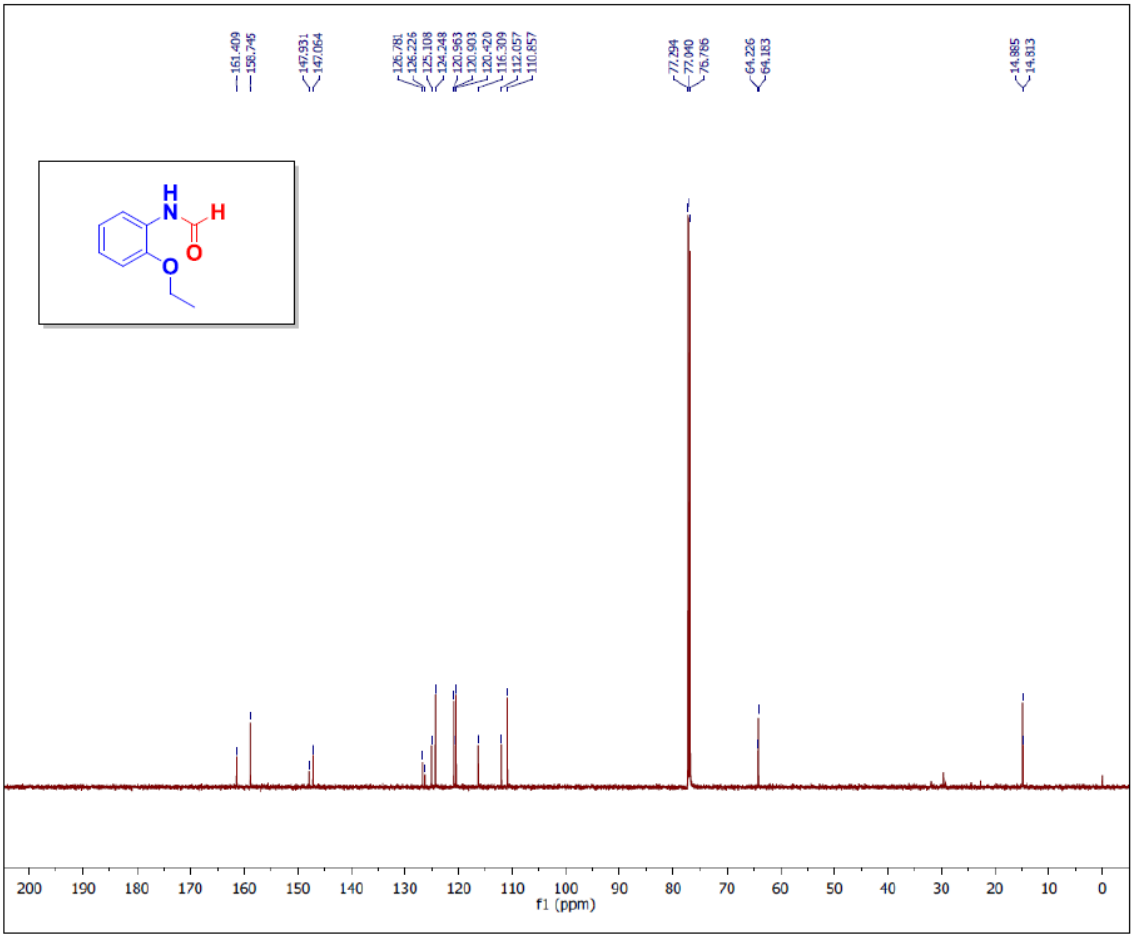
^{1}H and ^{13}C NMR spectra of compound 6j:



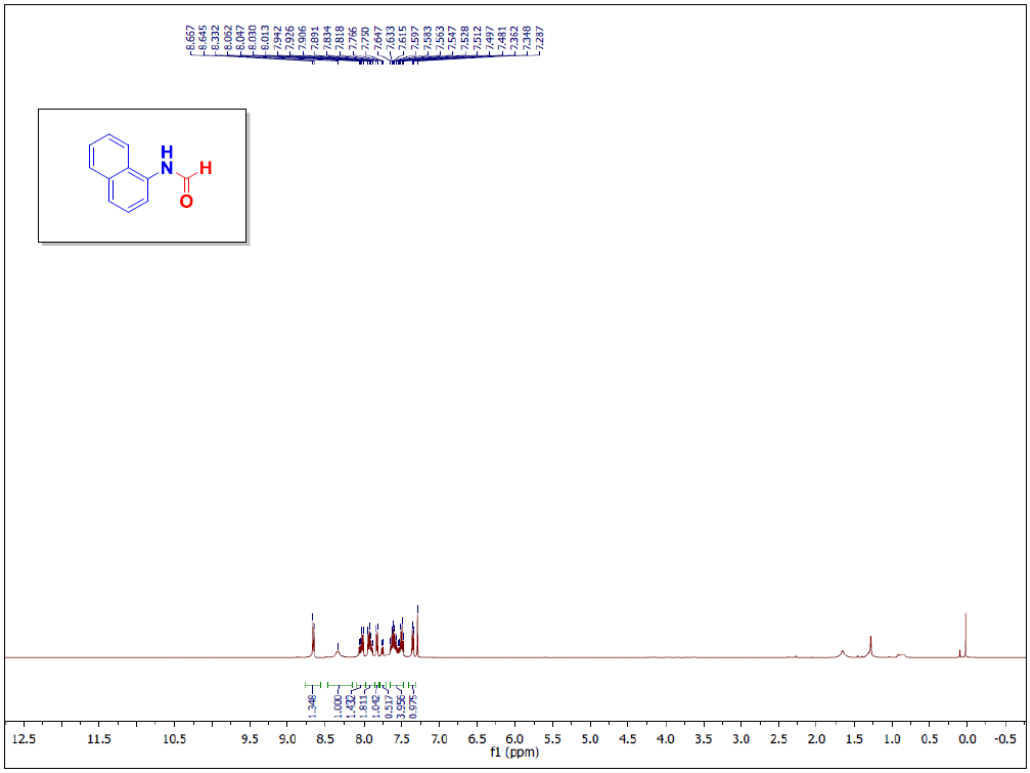


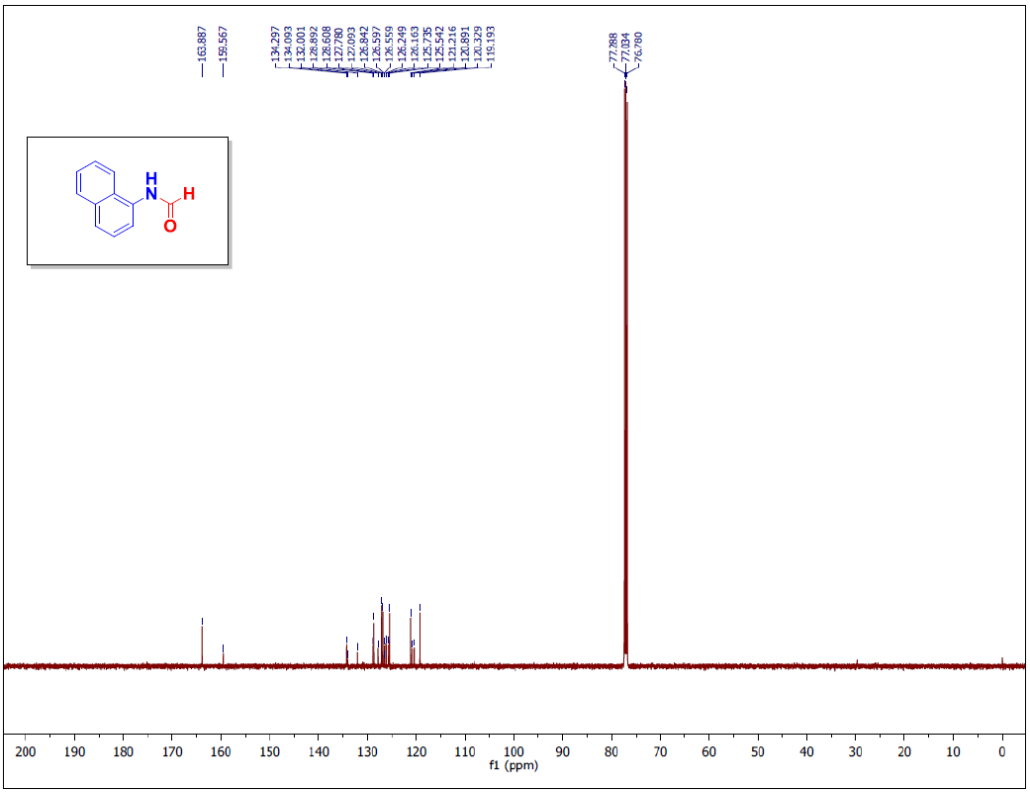
^{1}H and ^{13}C NMR spectra of compound 6k:



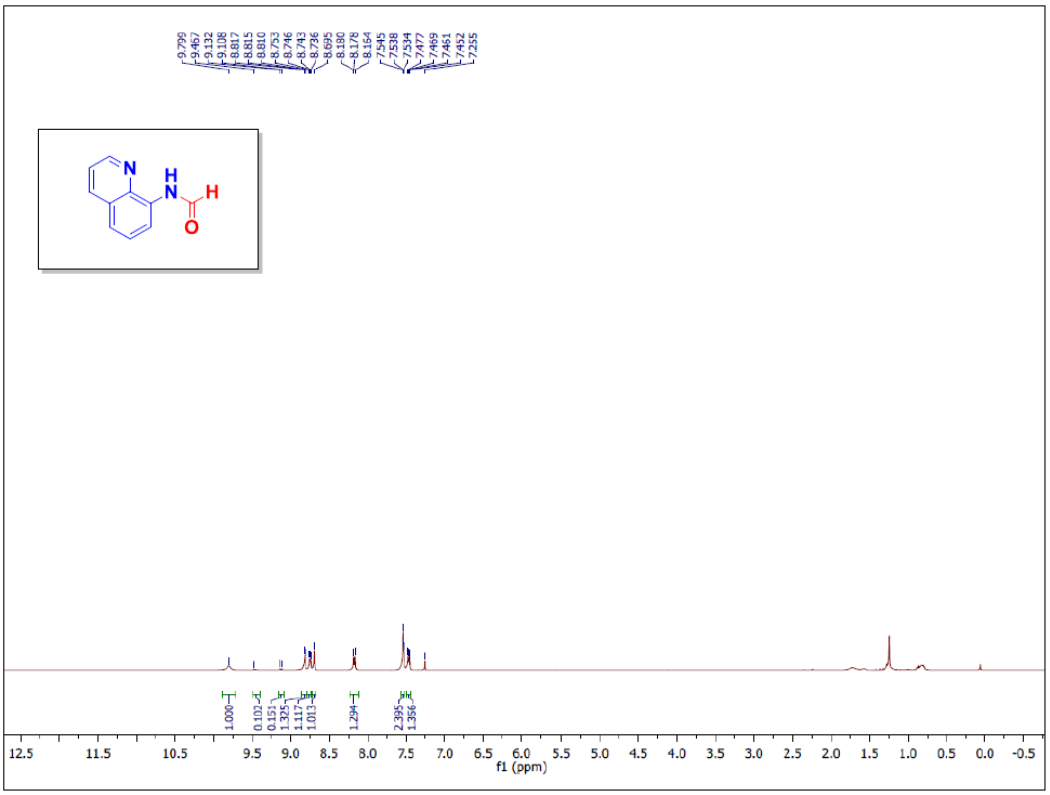


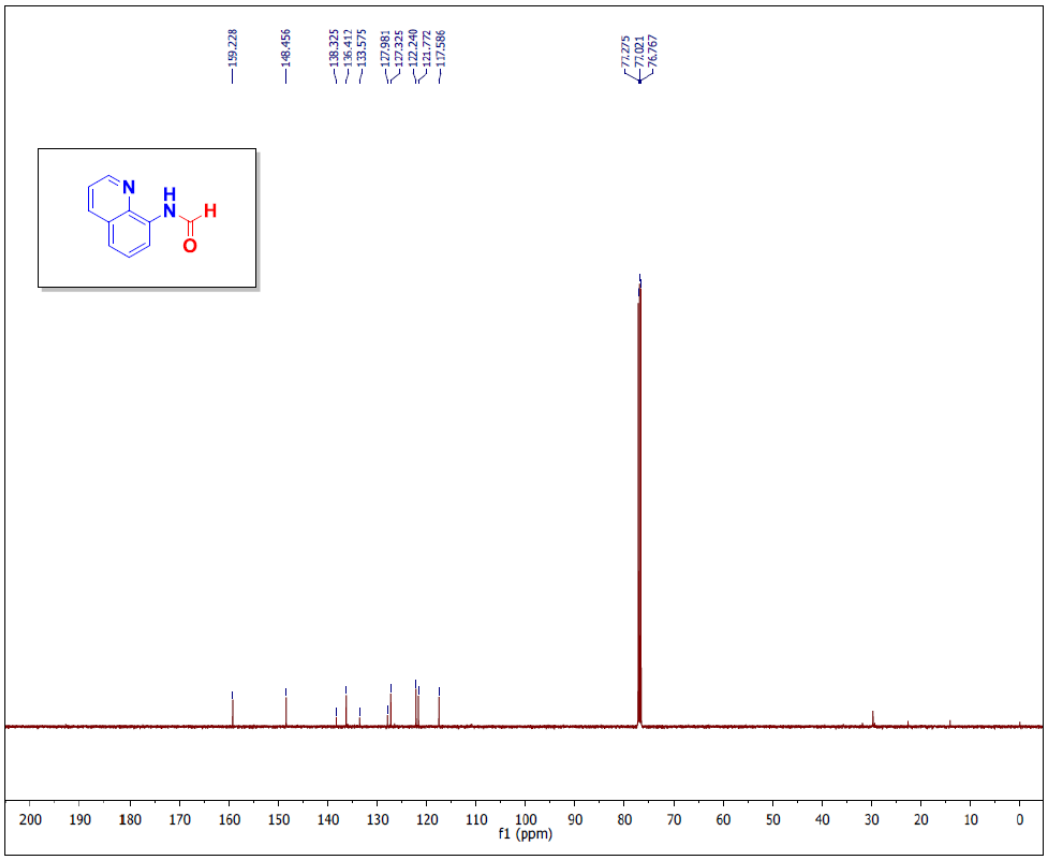
^{1}H and ^{13}C NMR spectra of compound 6l:



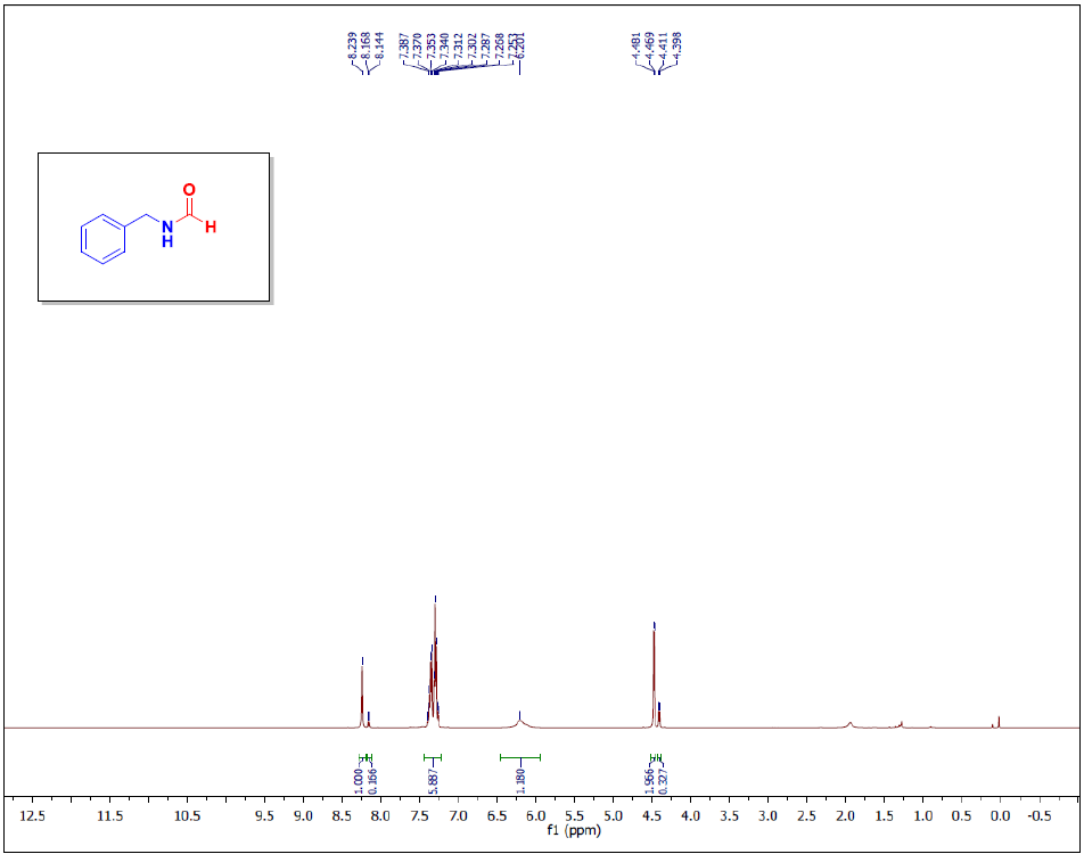


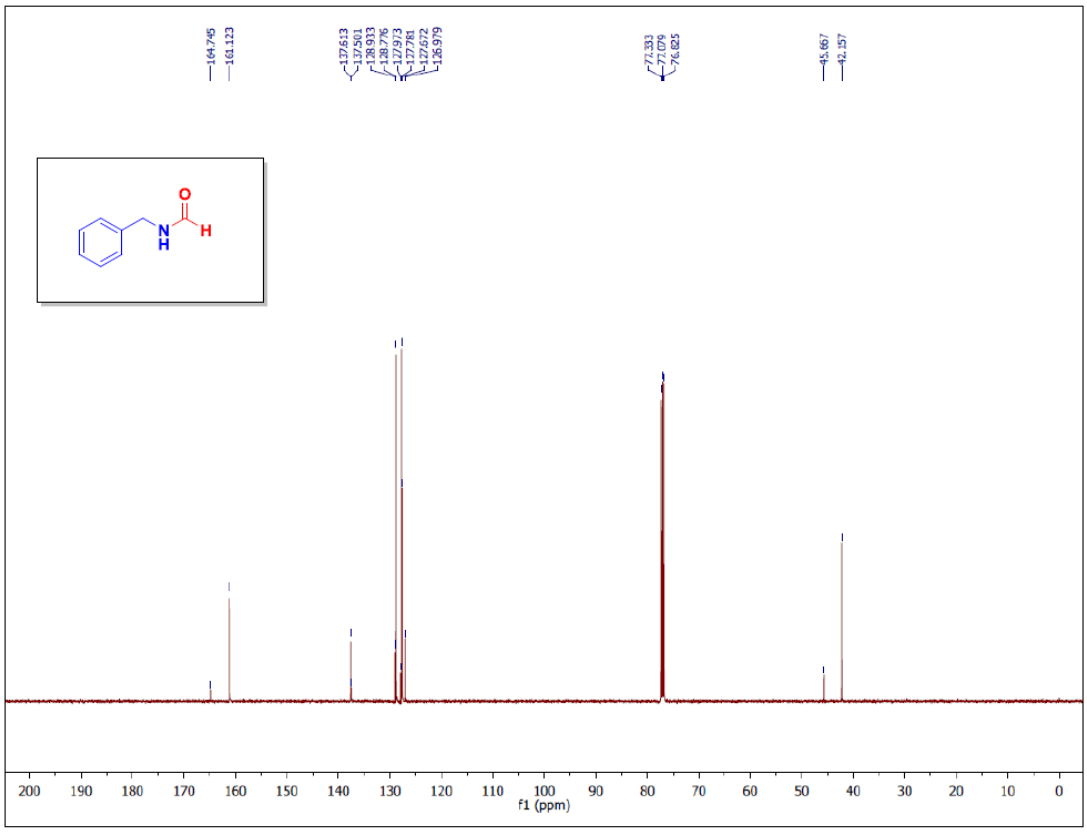
^{1}H and ^{13}C NMR spectra of compound 6m:



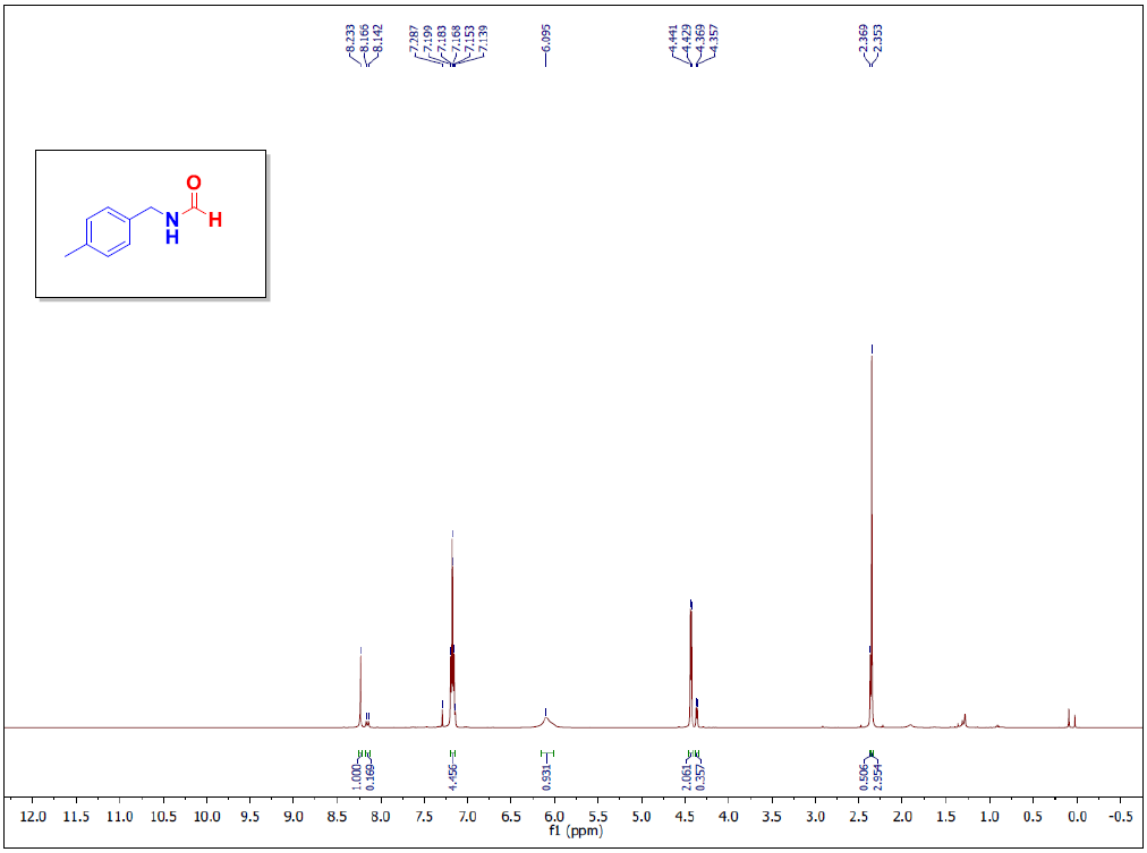


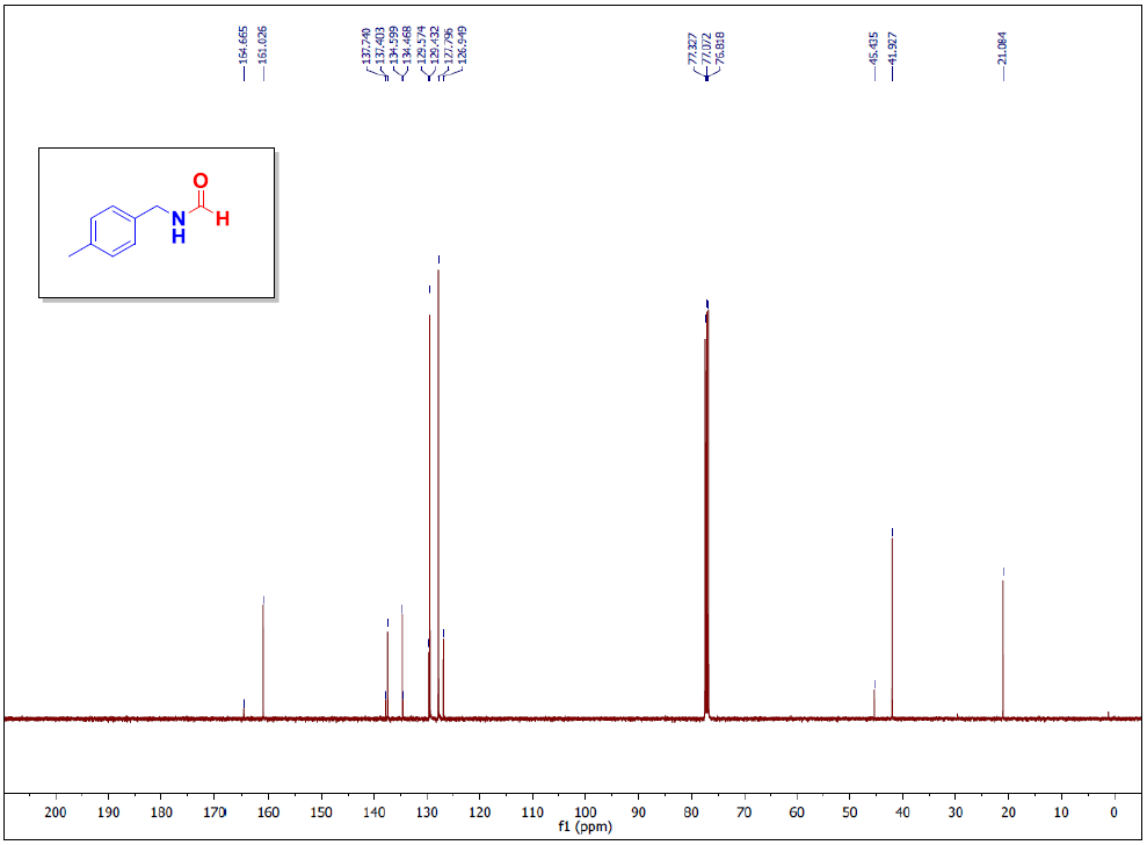
^{1}H and ^{13}C NMR spectra of compound 8a:



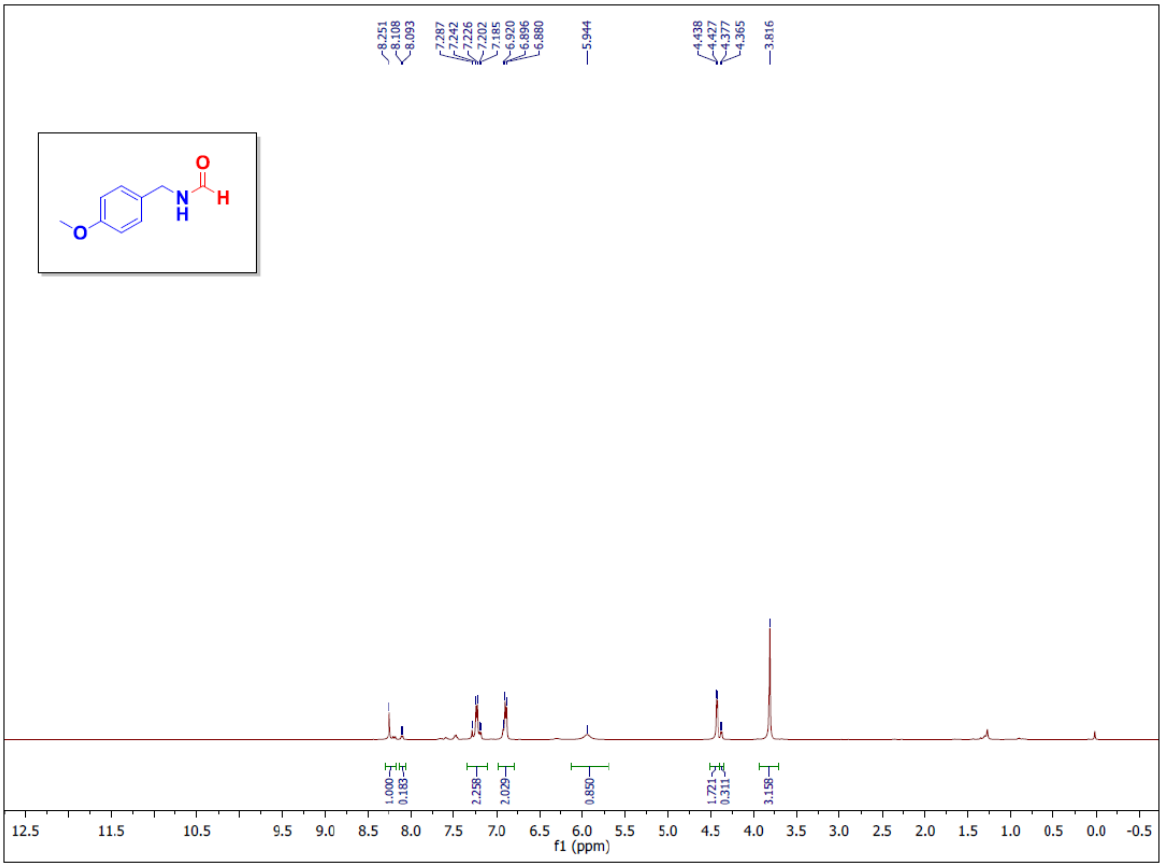


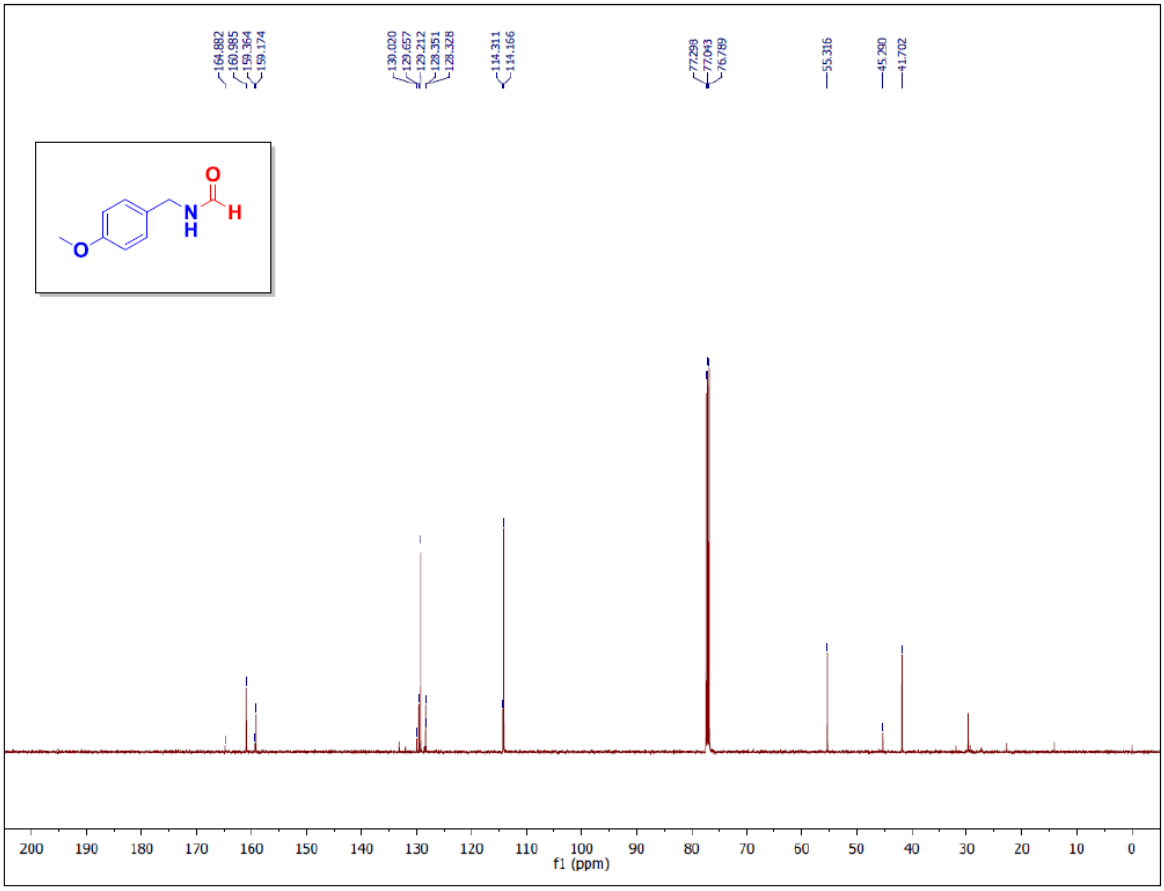
^{1}H and ^{13}C NMR spectra of compound 8b:



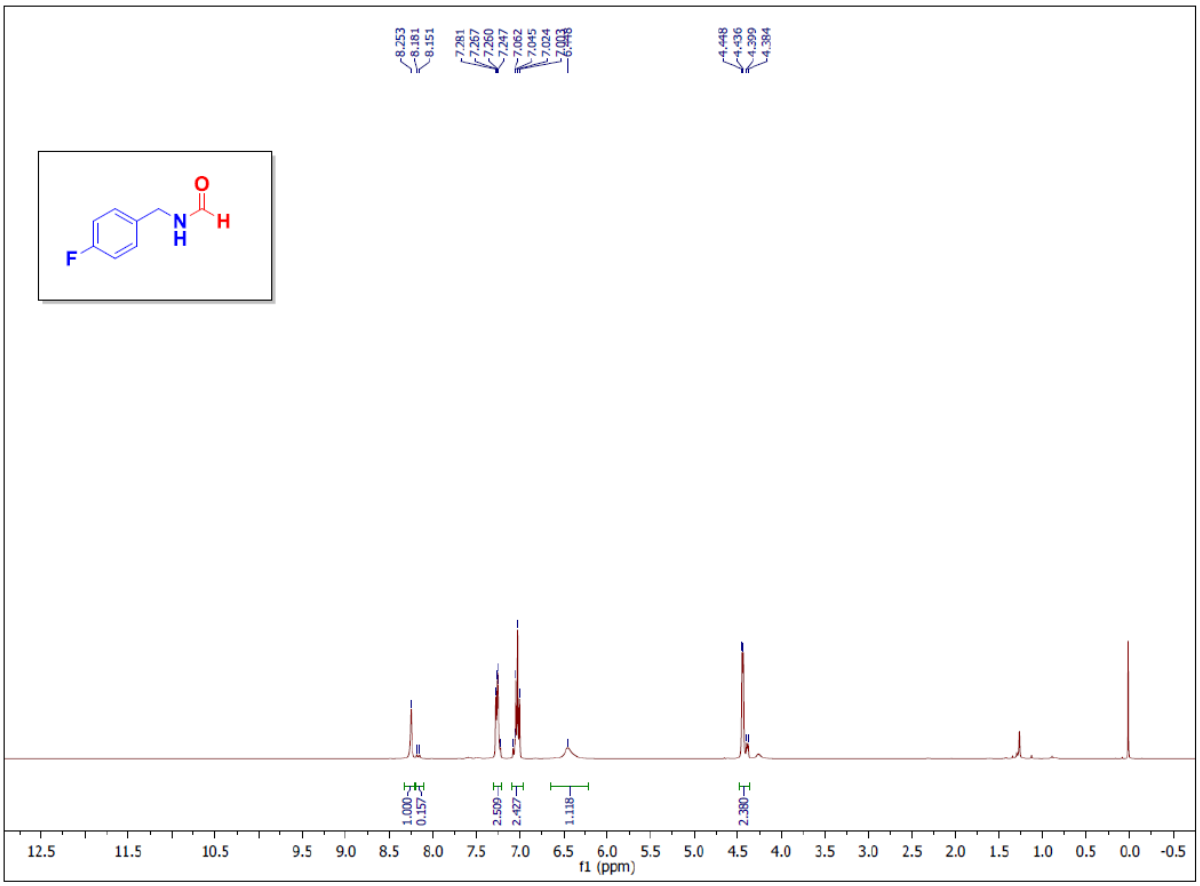


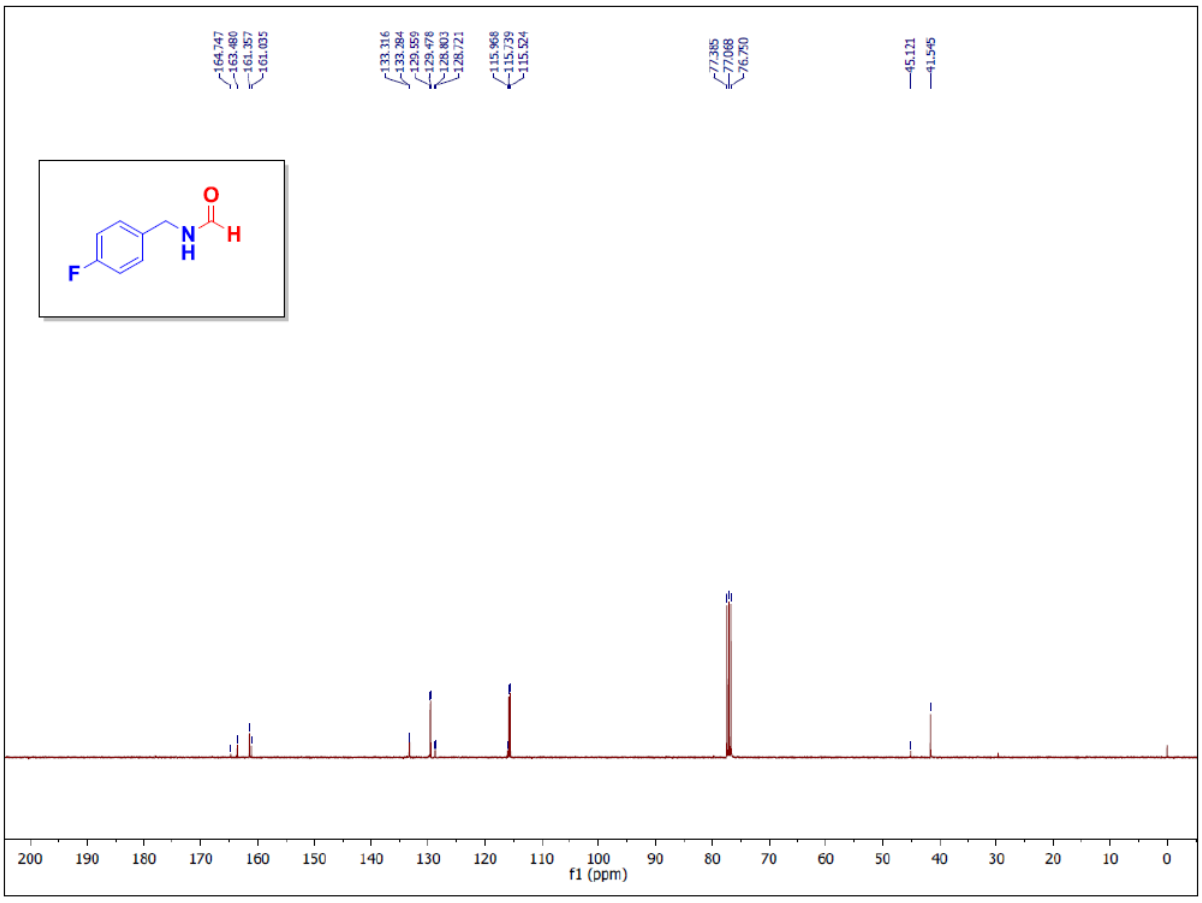
^{1}H and ^{13}C NMR spectra of compound 8c:



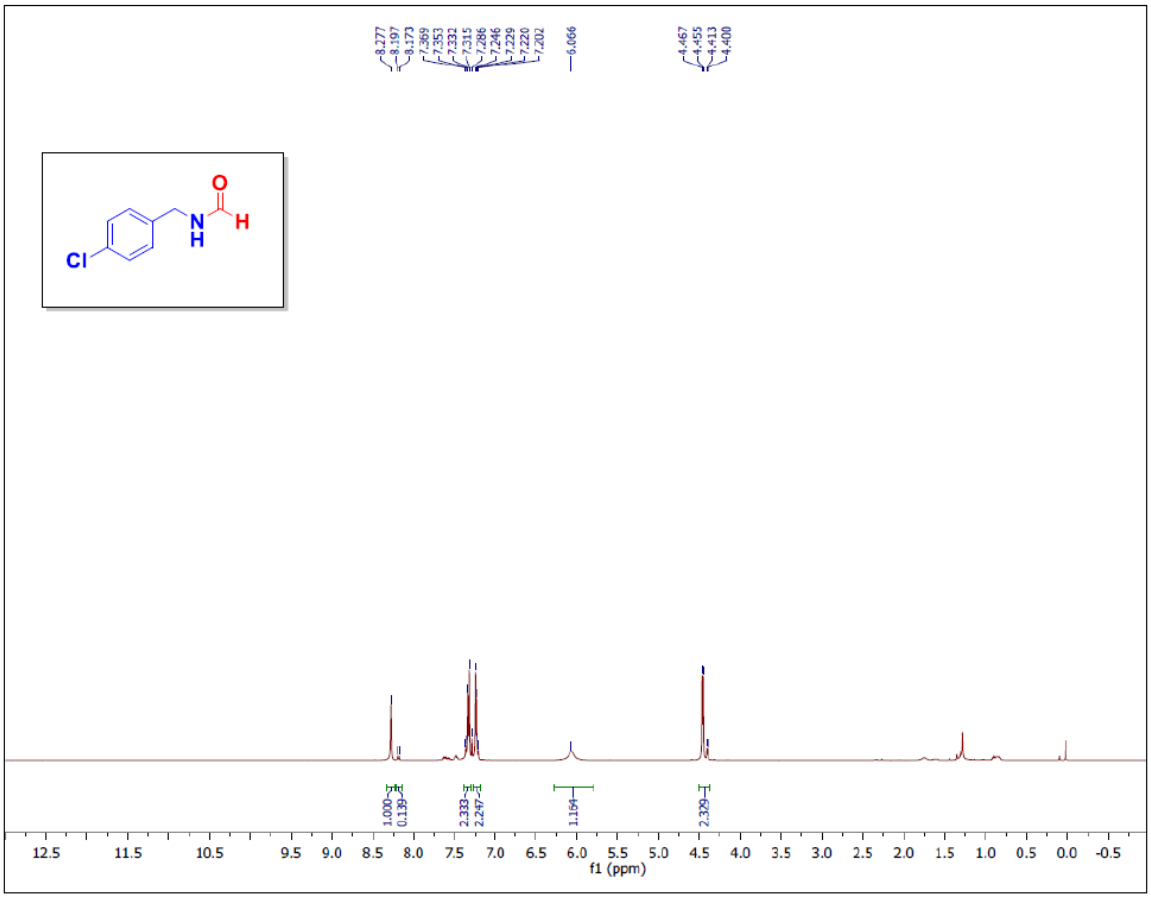


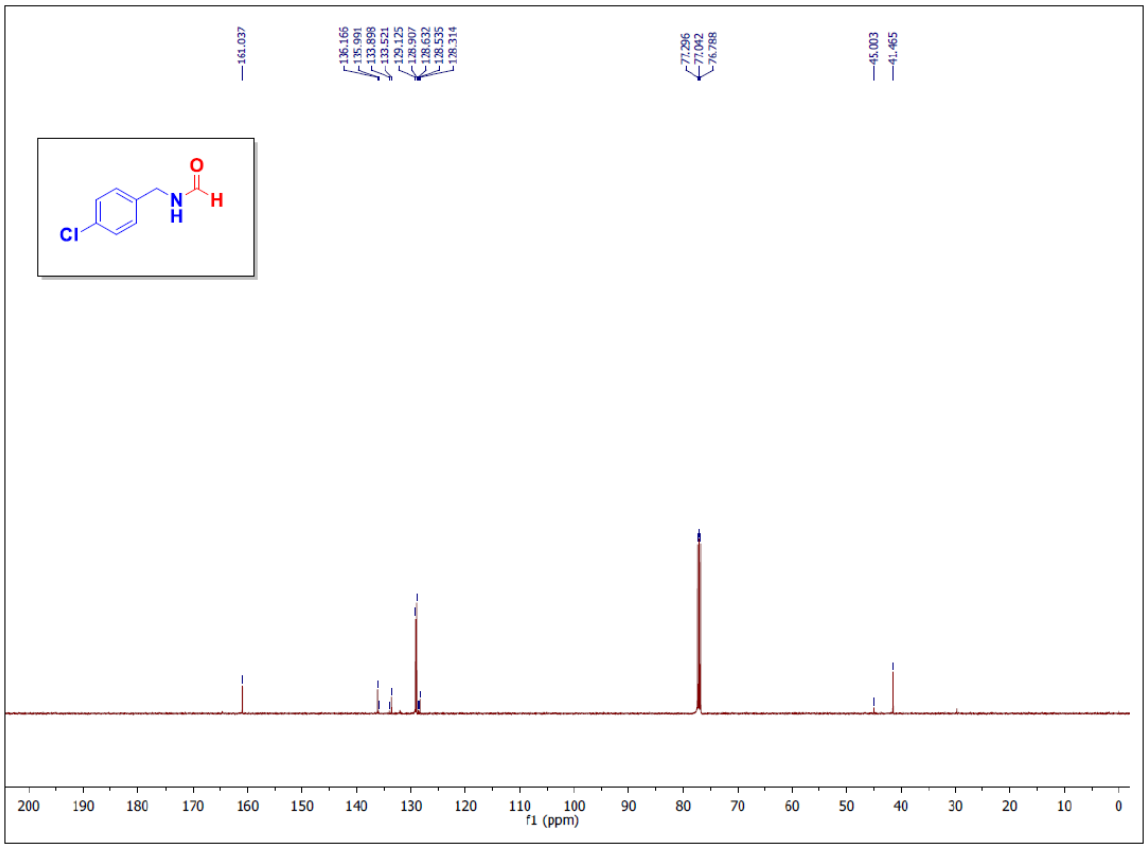
^{1}H and ^{13}C NMR spectra of compound 8d:



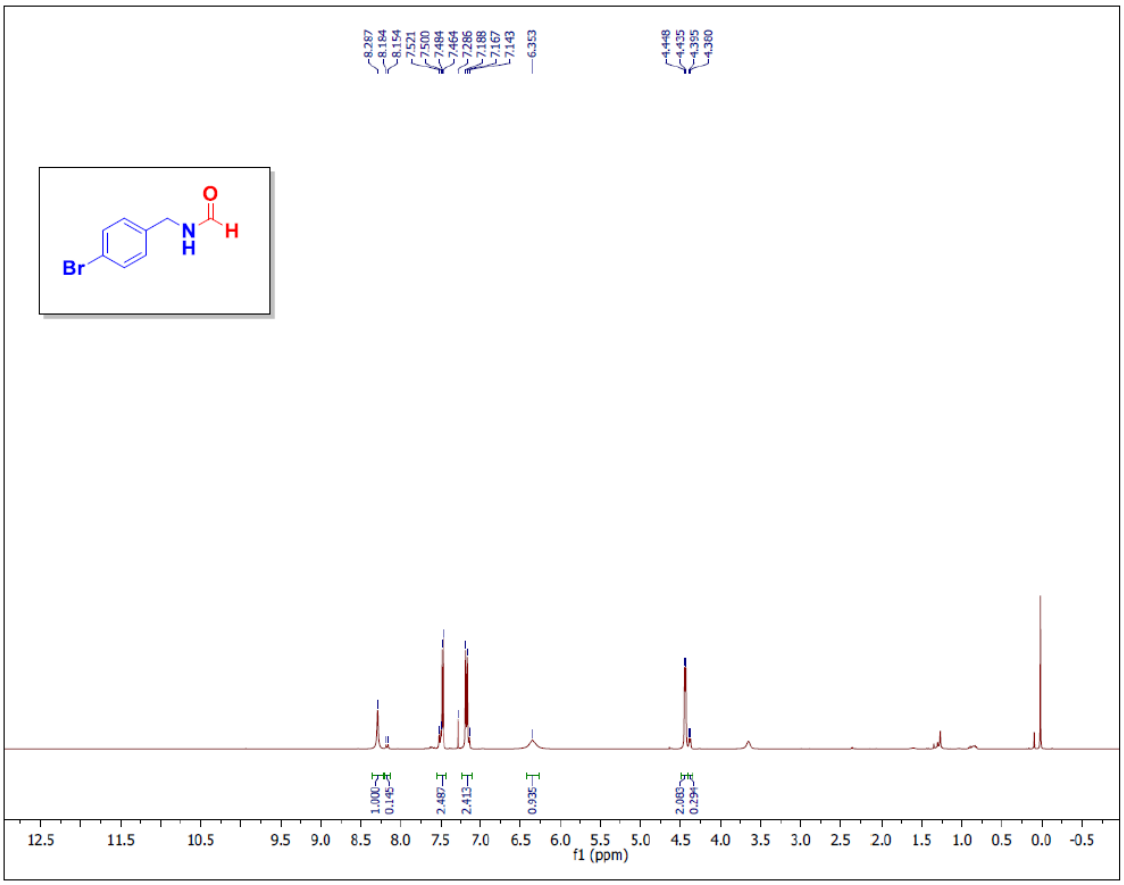


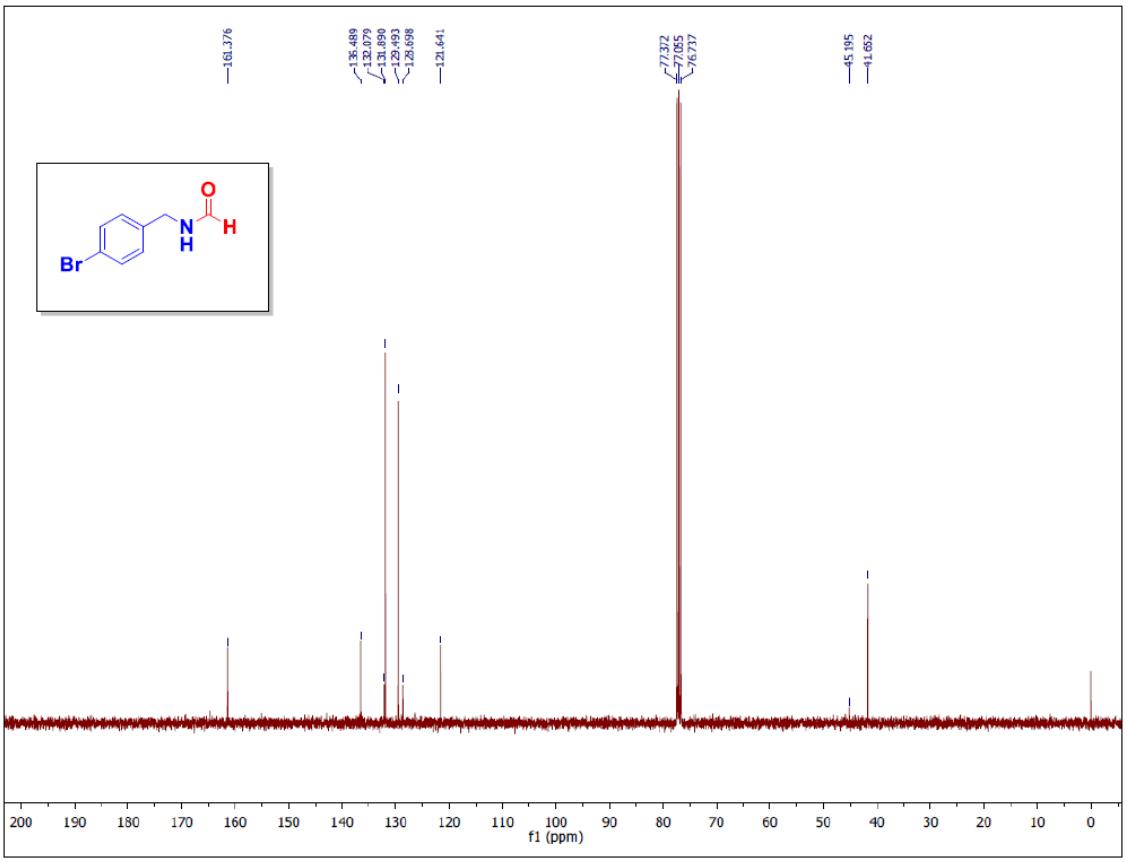
^{1}H and ^{13}C NMR spectra of compound 8e:



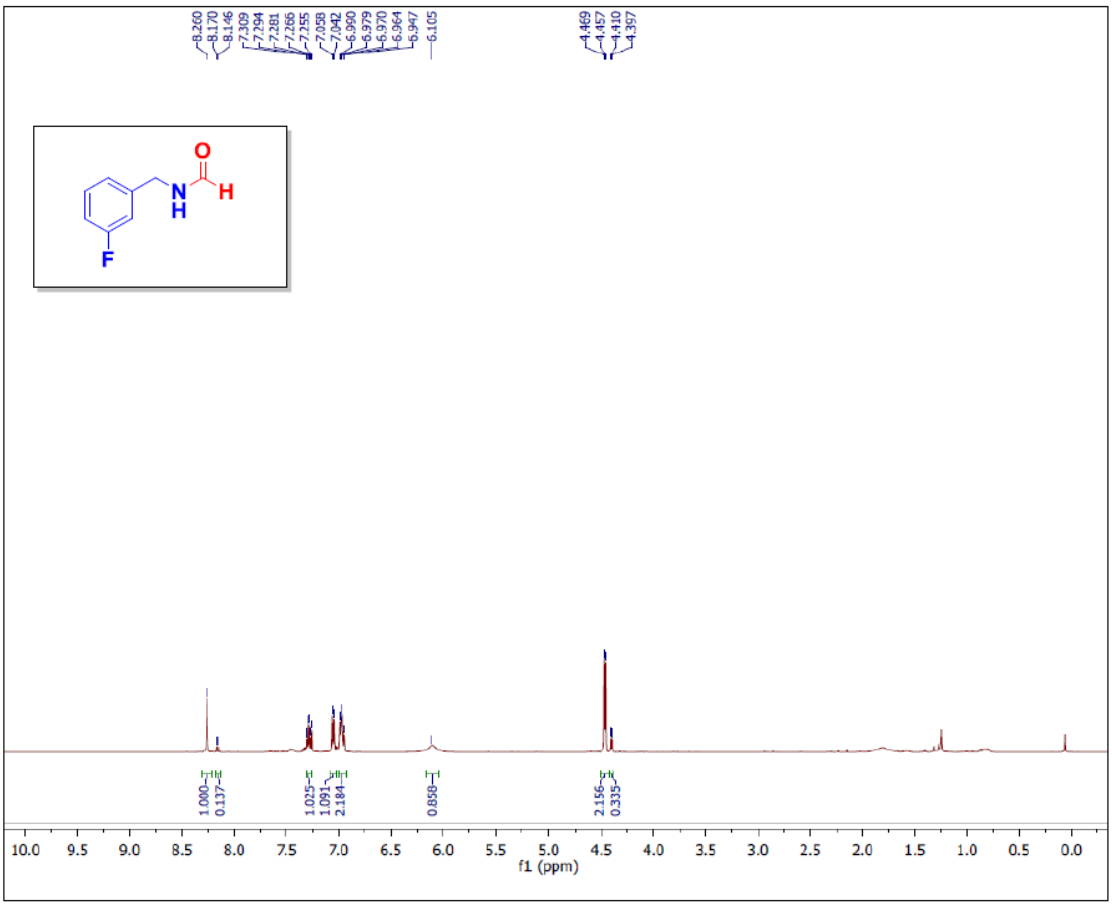


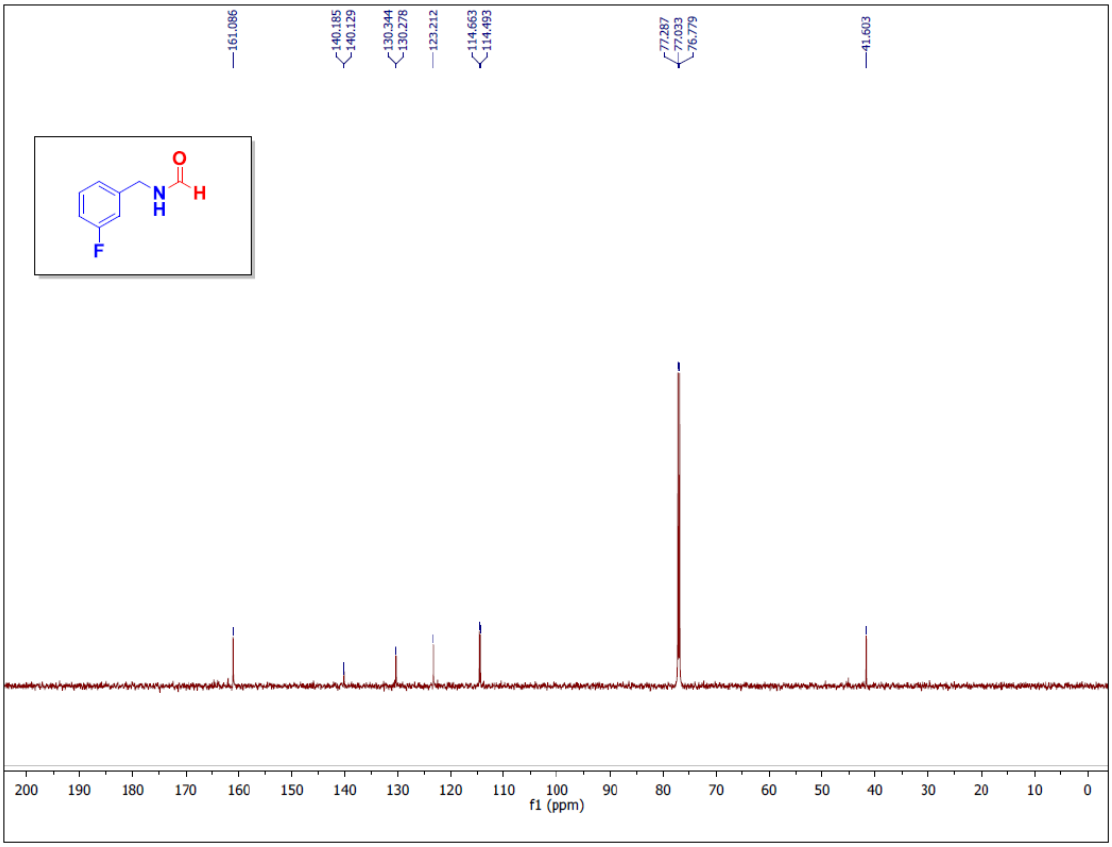
^{1}H and ^{13}C NMR spectra of compound 8f:



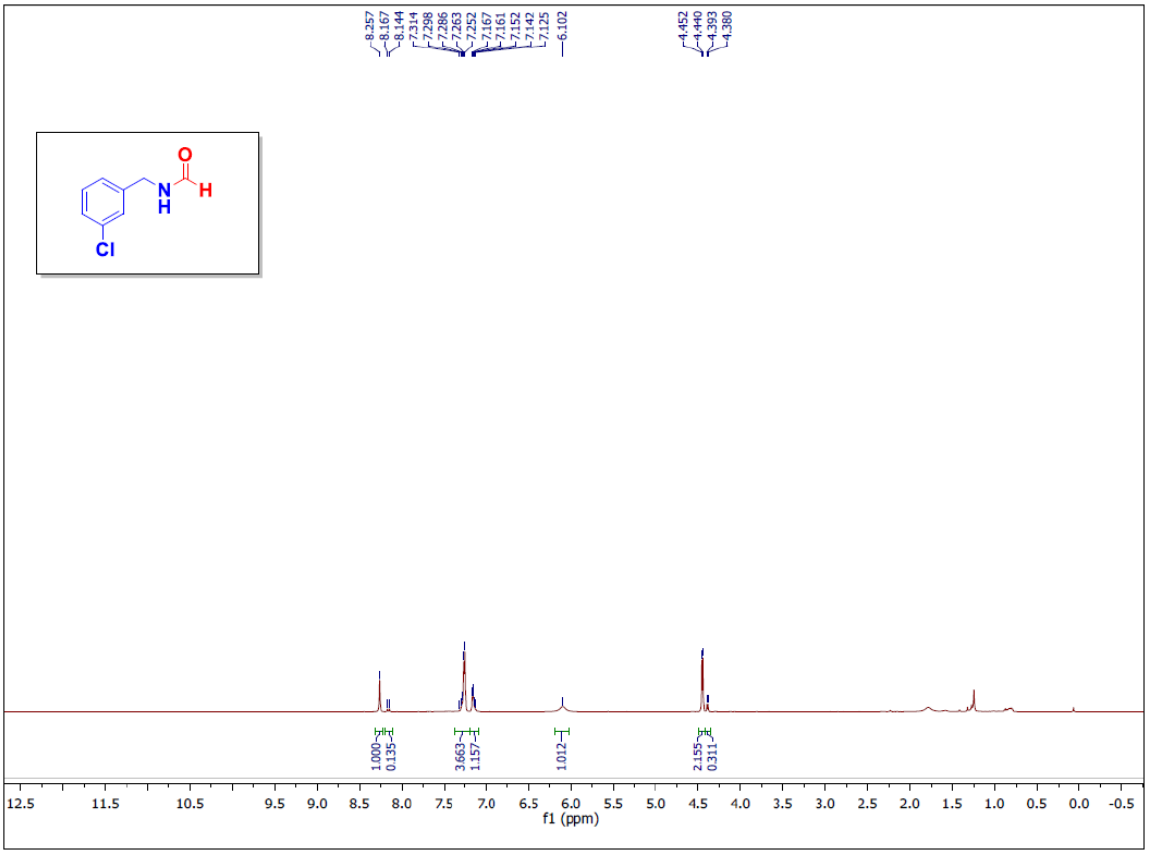


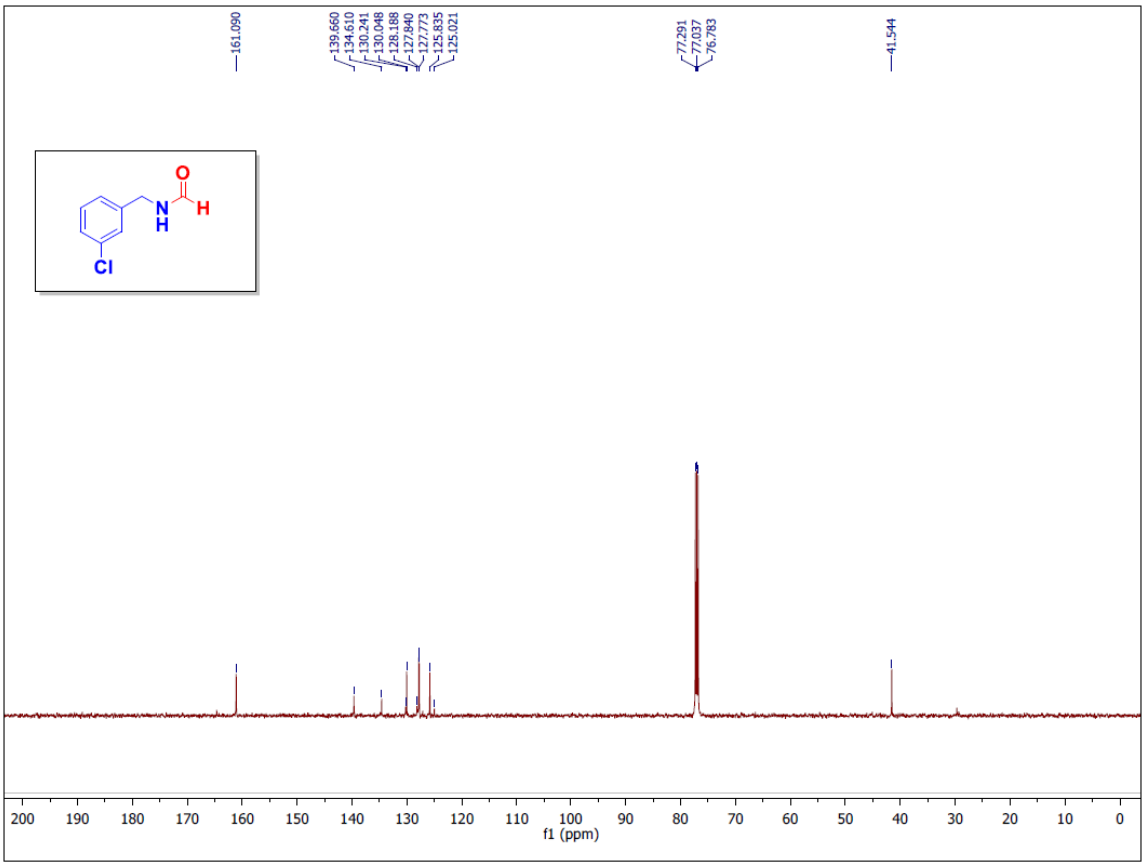
^{1}H and ^{13}C NMR spectra of compound 8g:



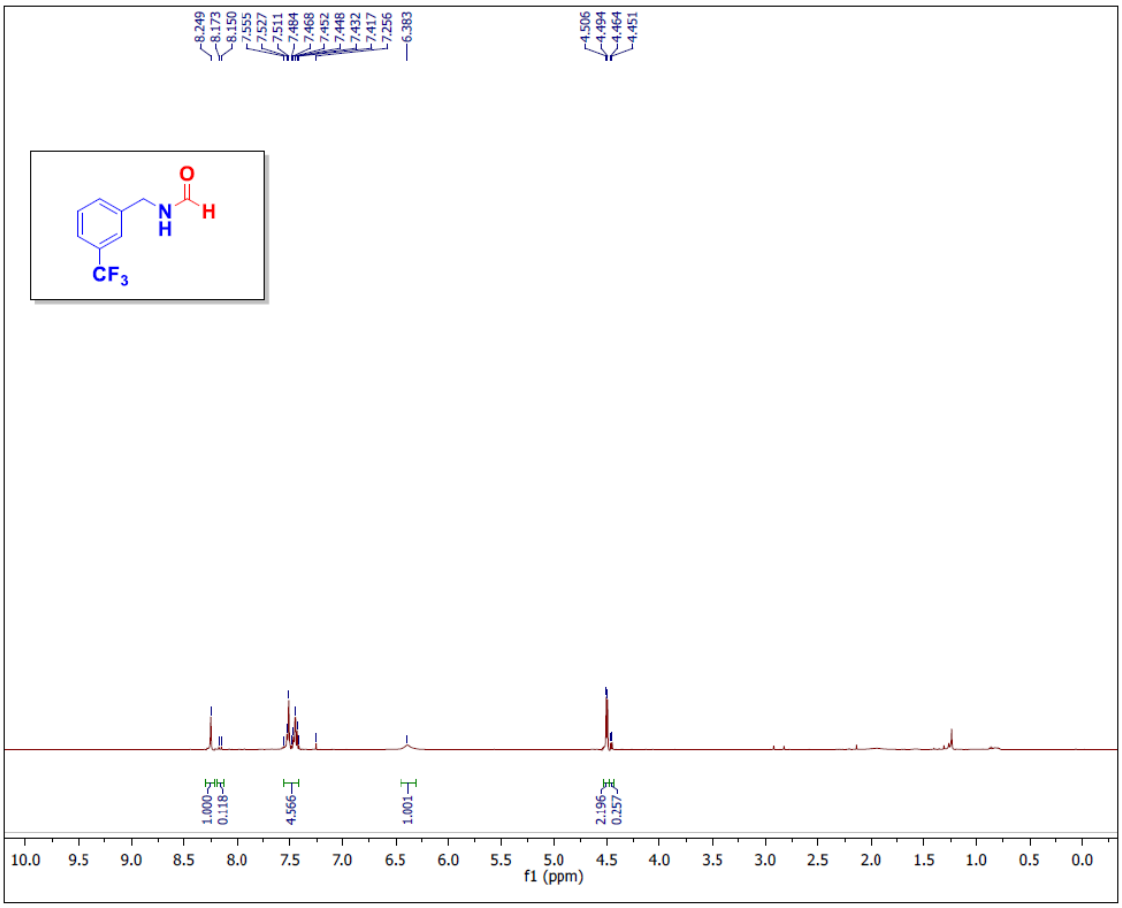


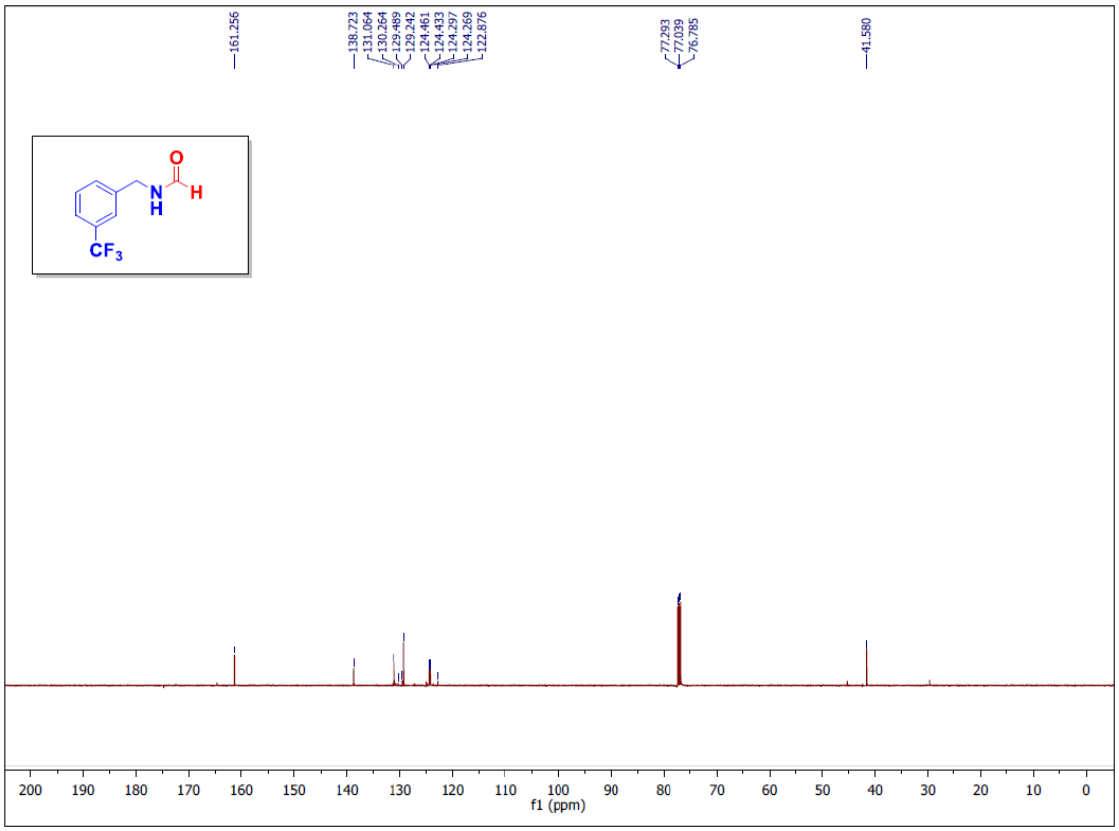
^{1}H and ^{13}C NMR spectra of compound 8h:



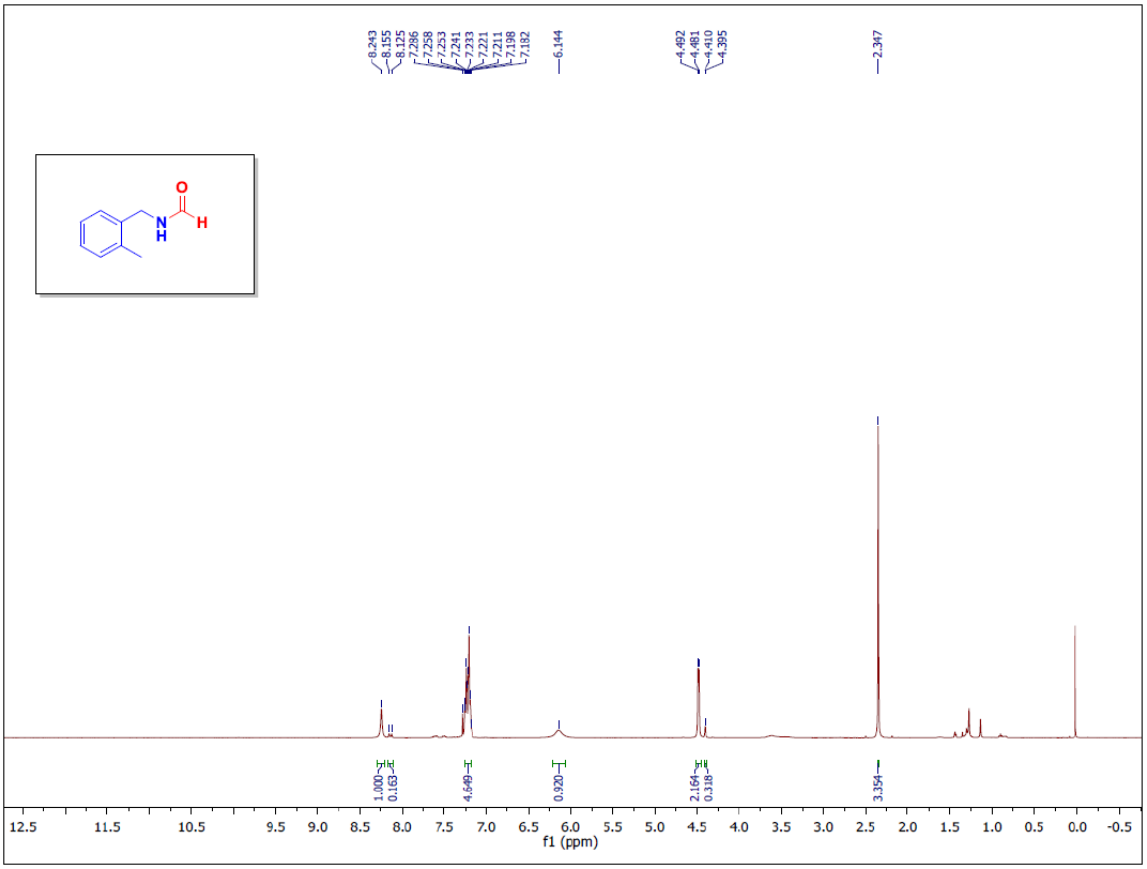


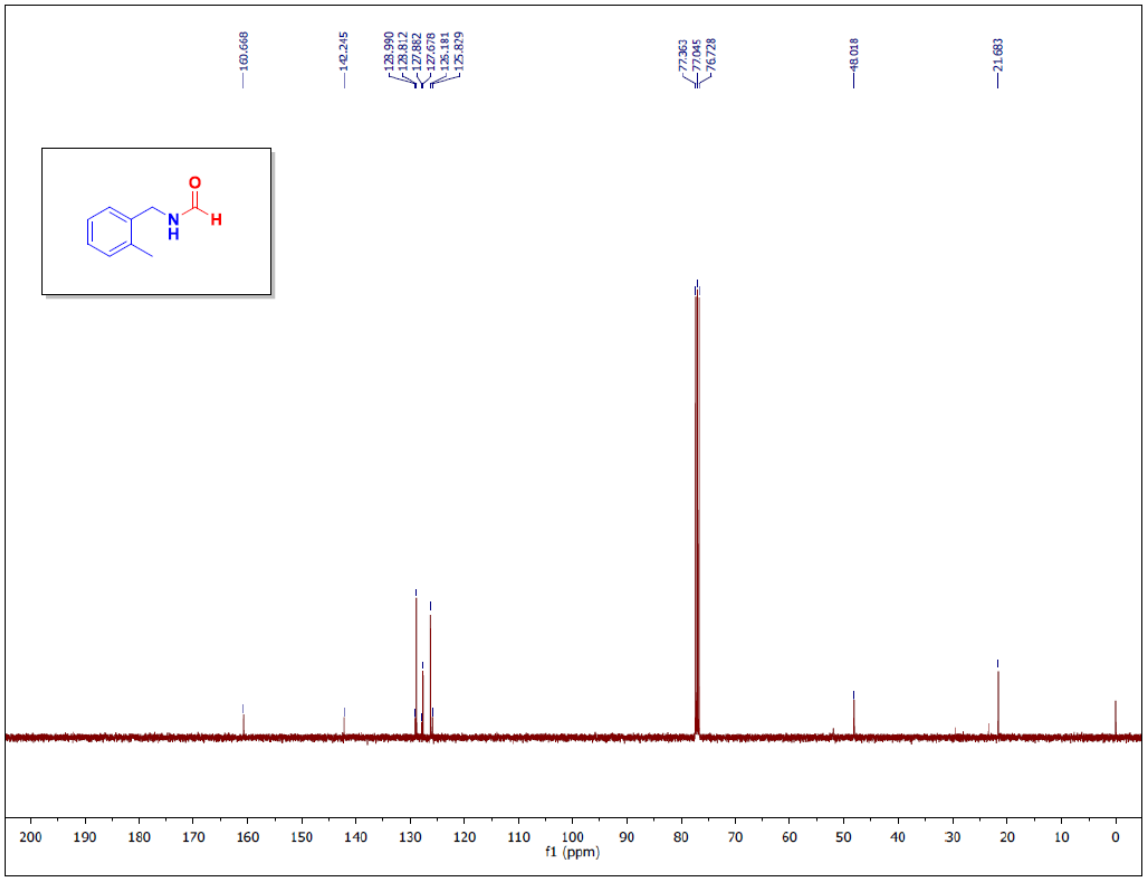
^{1}H and ^{13}C NMR spectra of compound 8i:



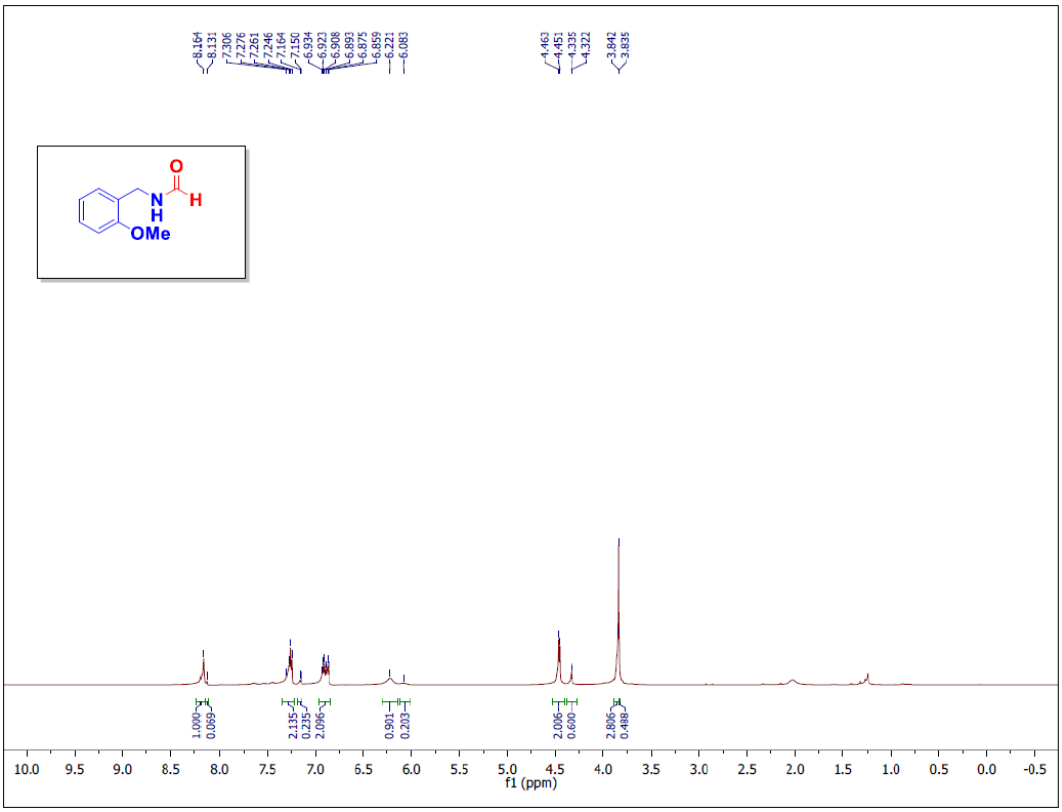


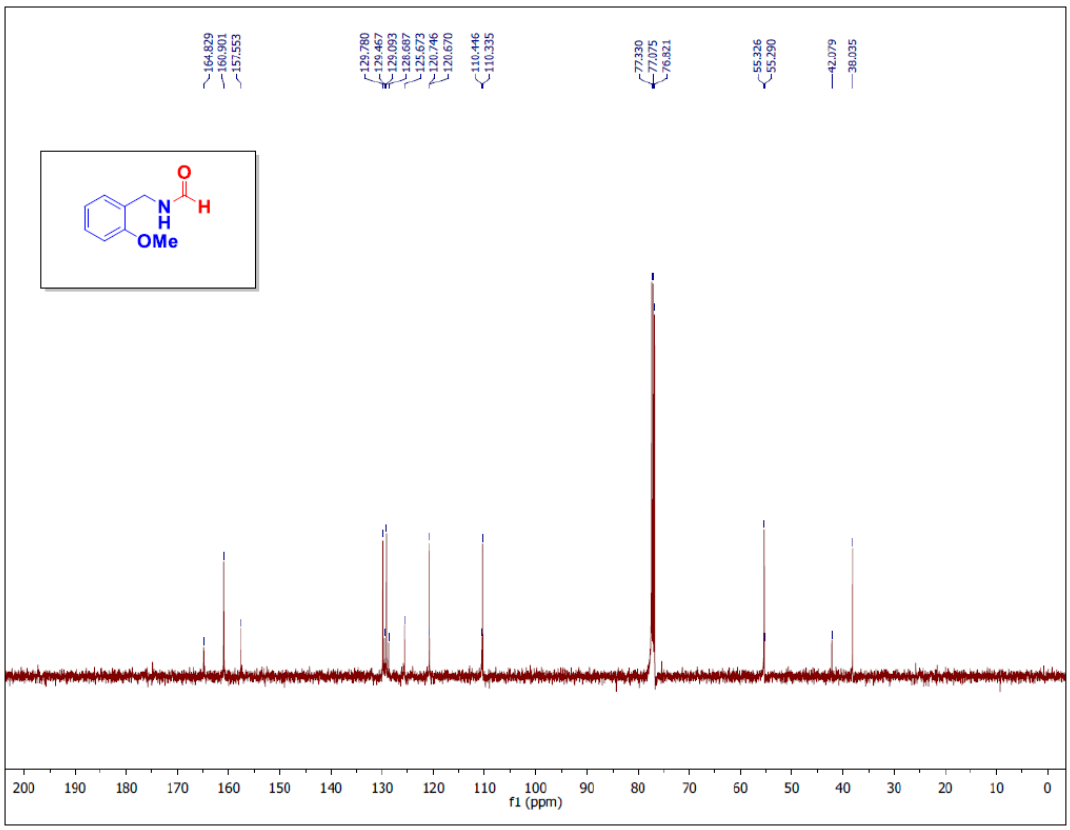
^{1}H and ^{13}C NMR spectra of compound 8j:



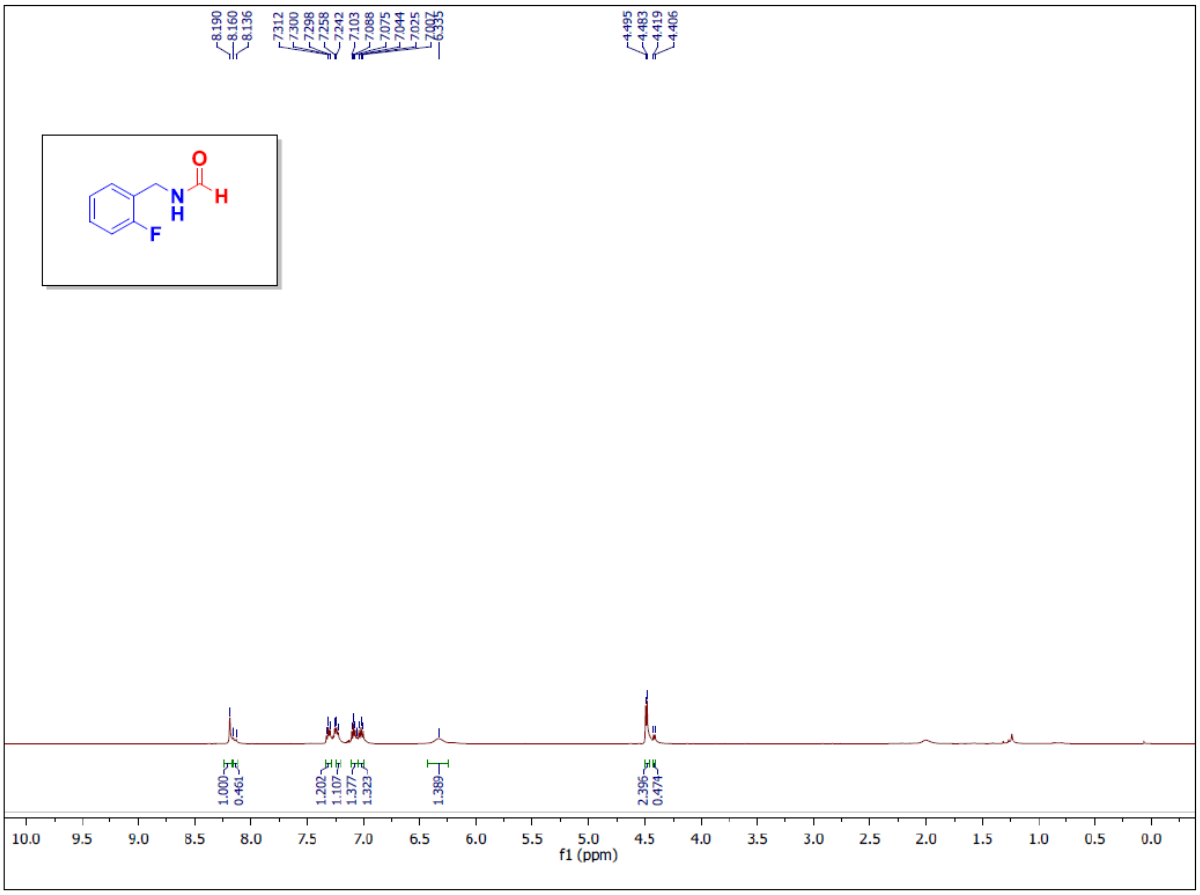


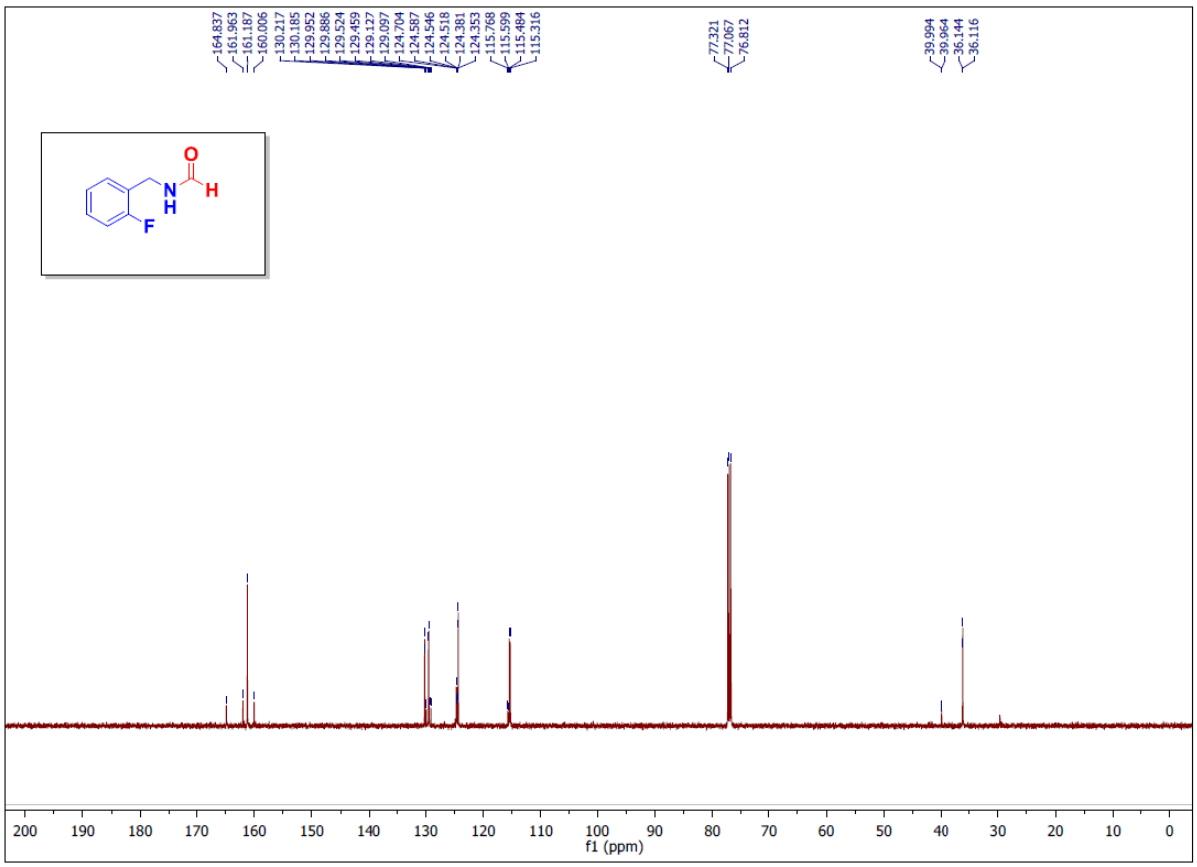
^{1}H and ^{13}C NMR spectra of compound 8k:



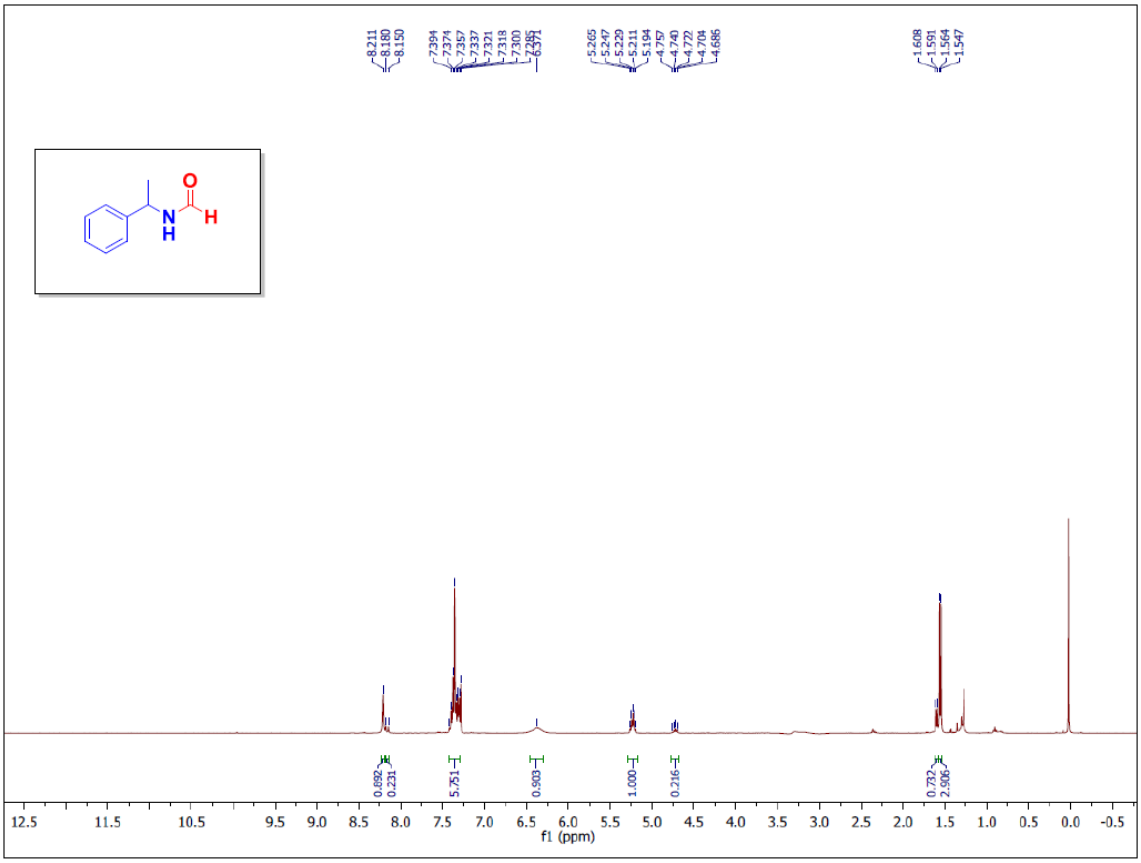


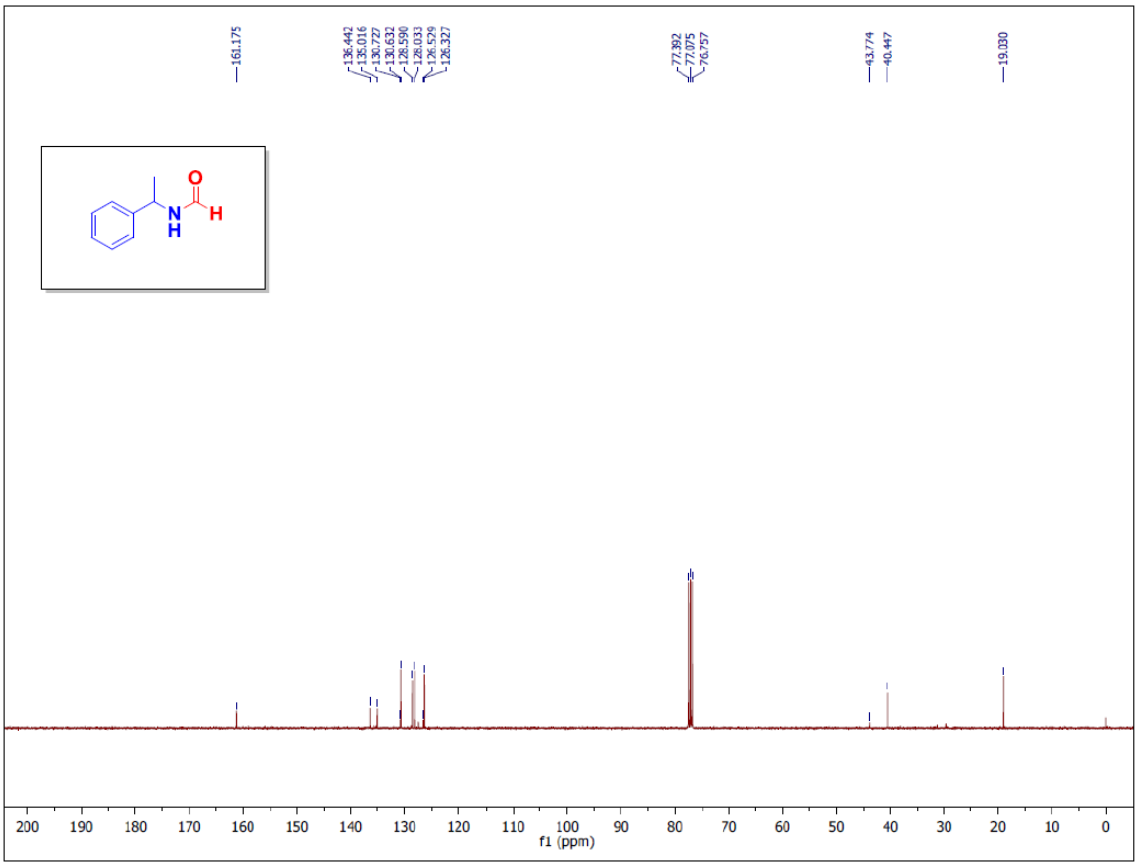
^{1}H and ^{13}C NMR spectra of compound 8l:



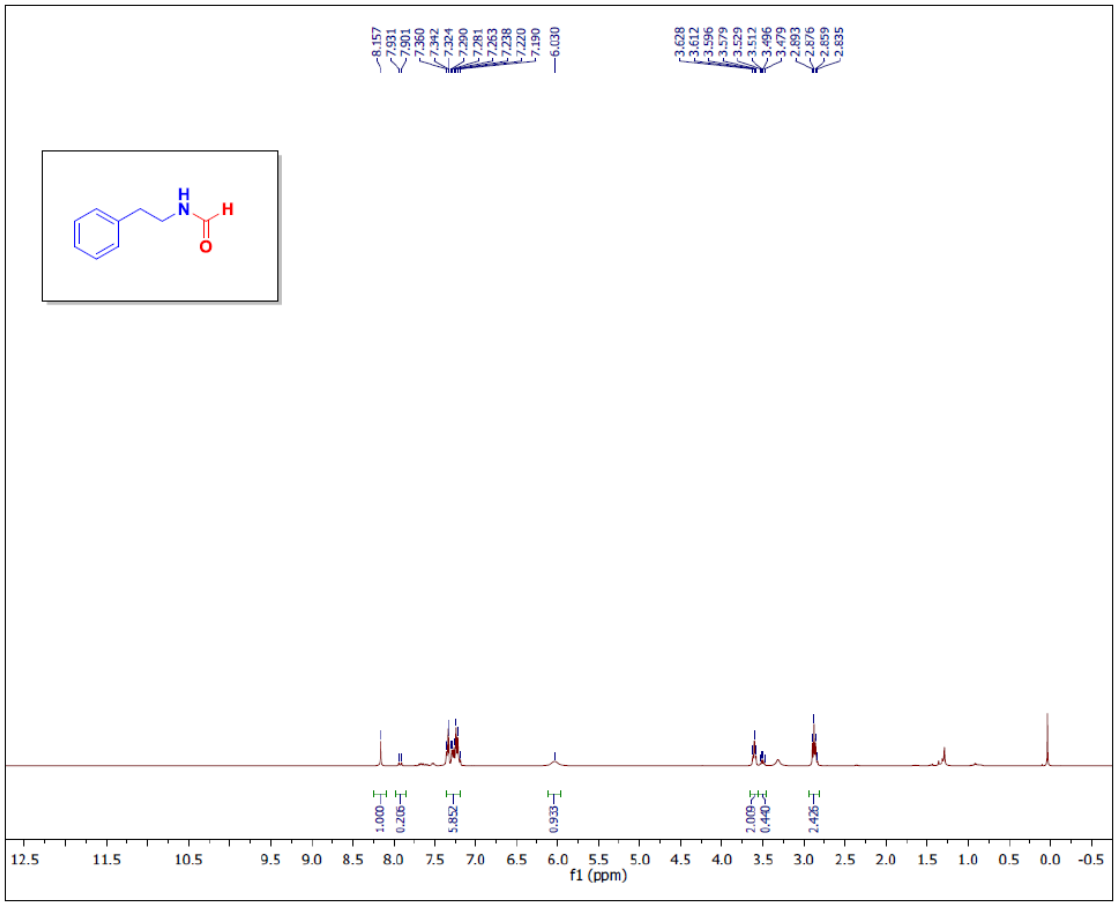


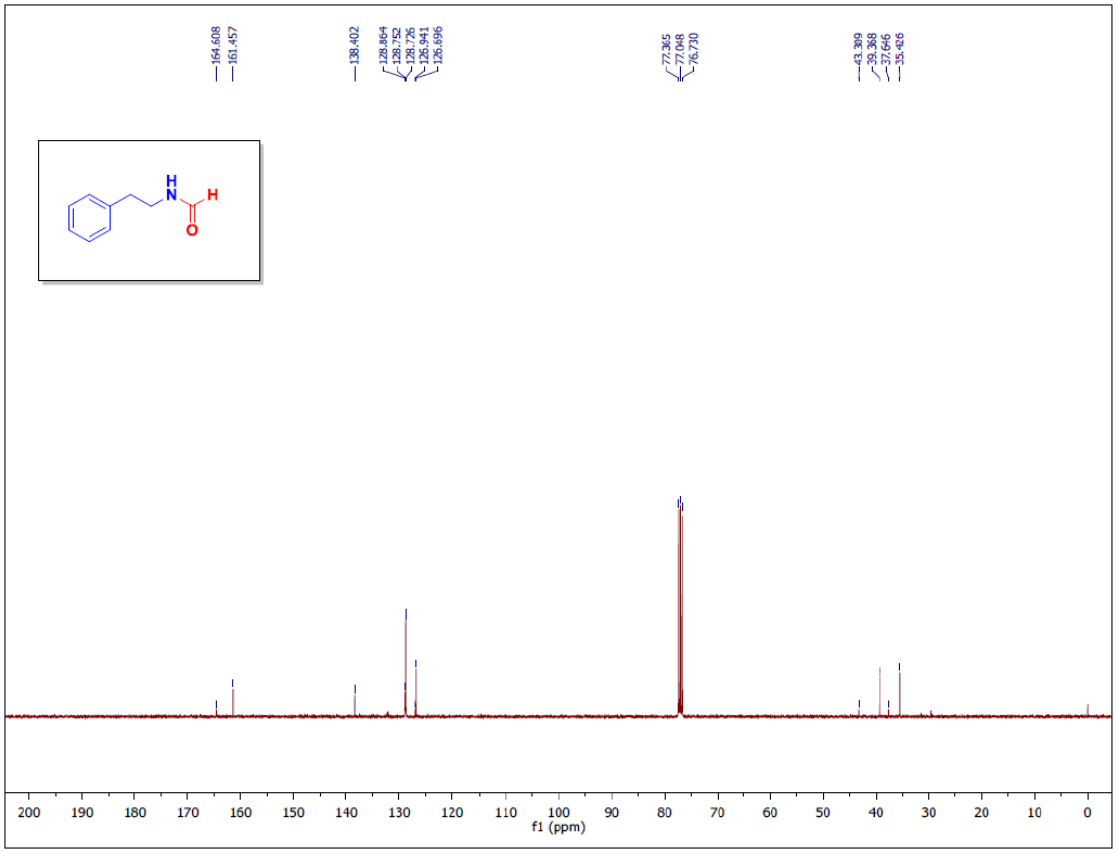
^{1}H and ^{13}C NMR spectra of compound 8m:



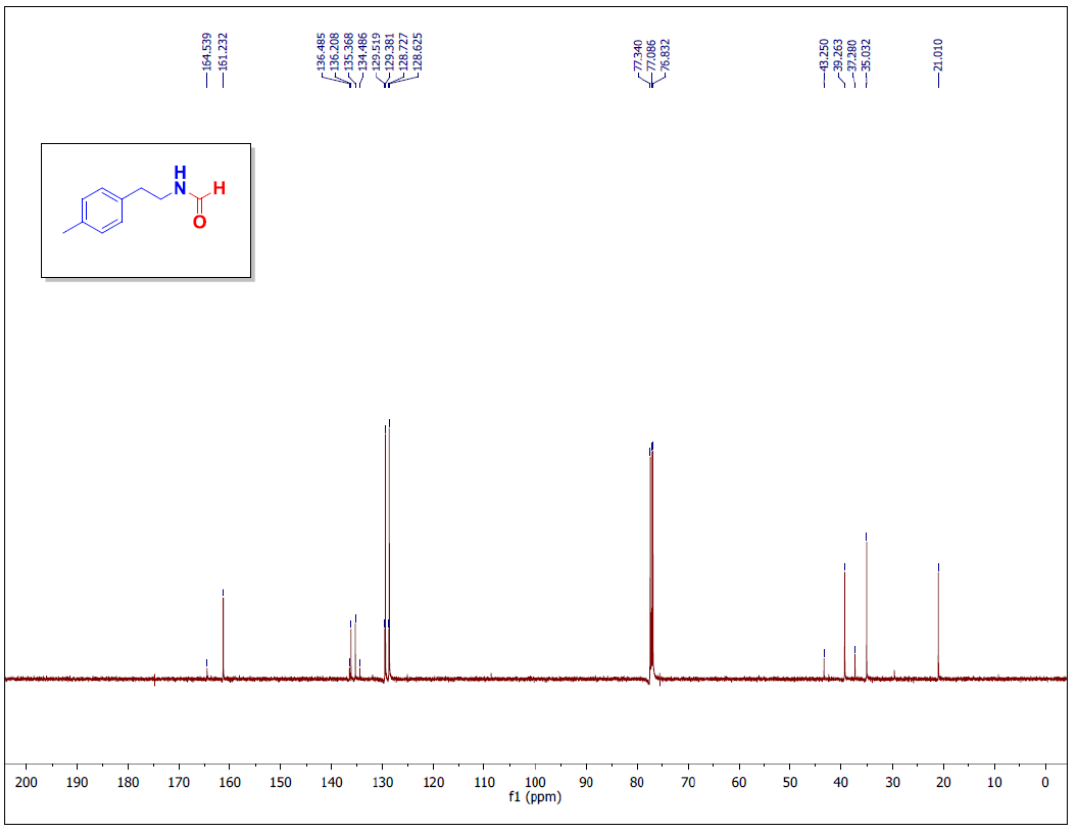


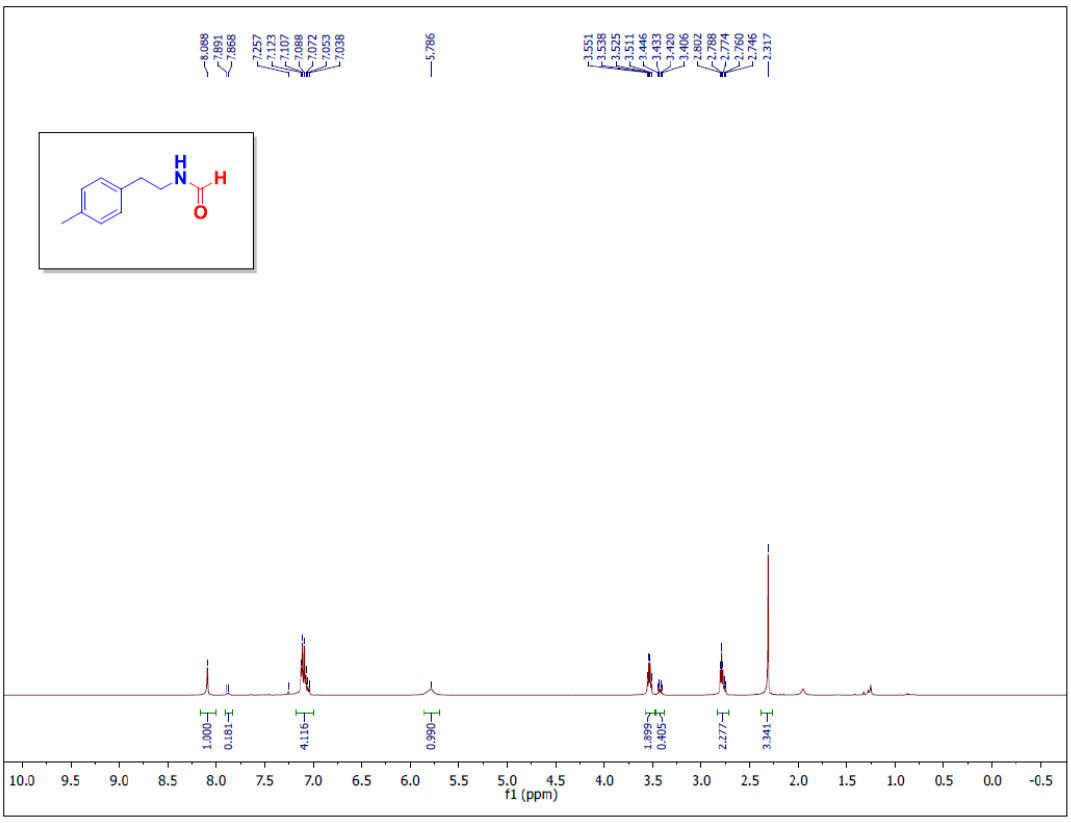
^{1}H and ^{13}C NMR spectra of compound 8n:



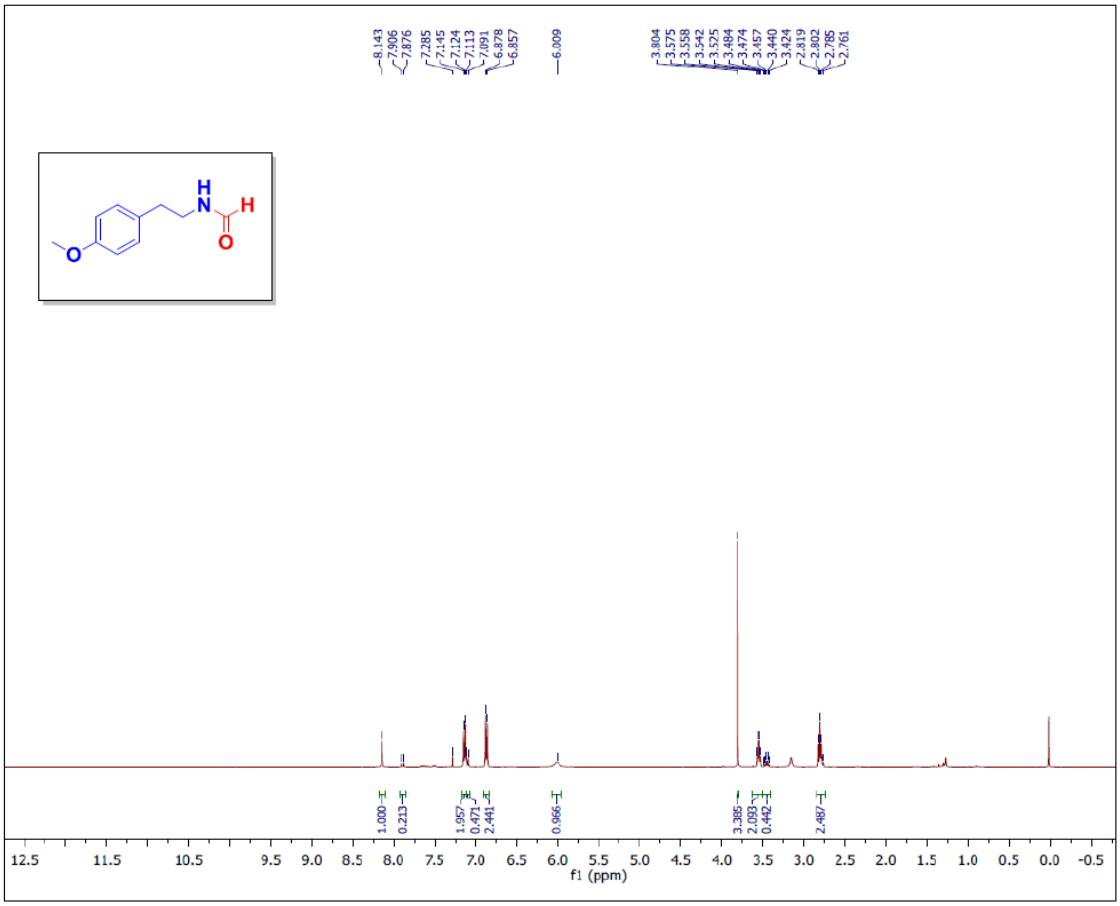


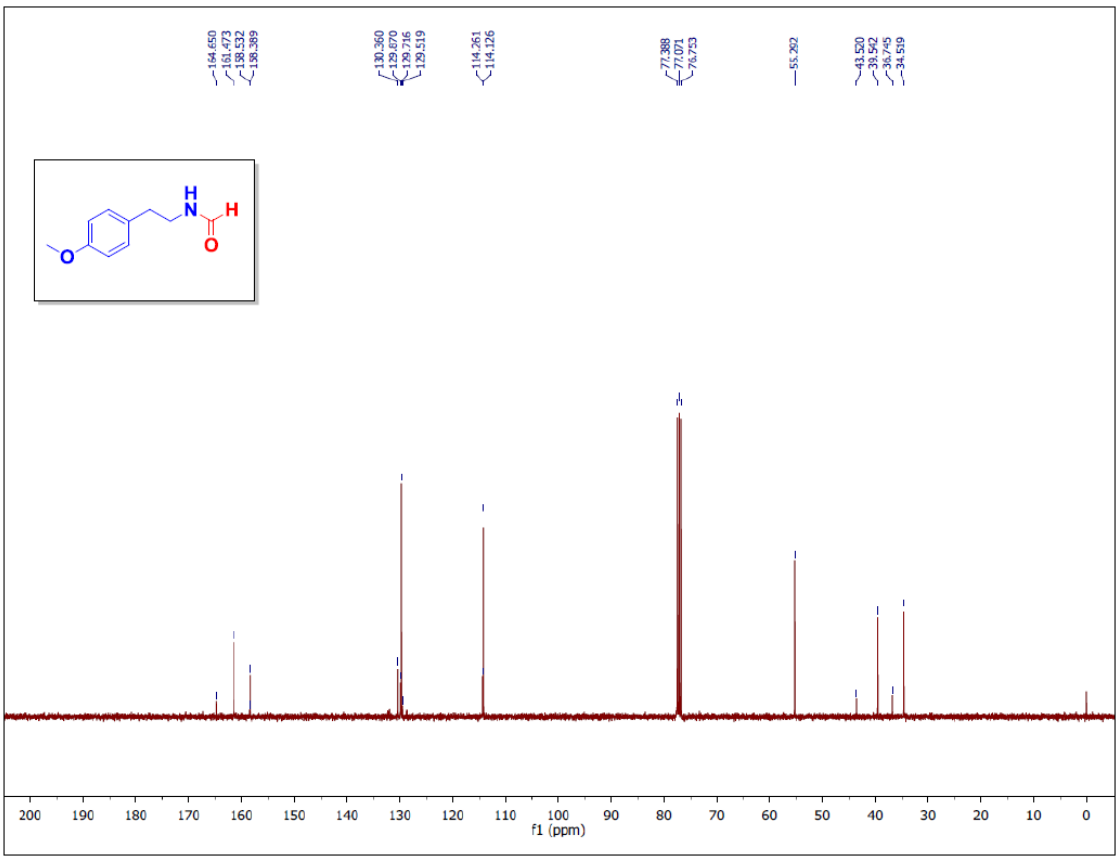
^{1}H and ^{13}C NMR spectra of compound 8o:



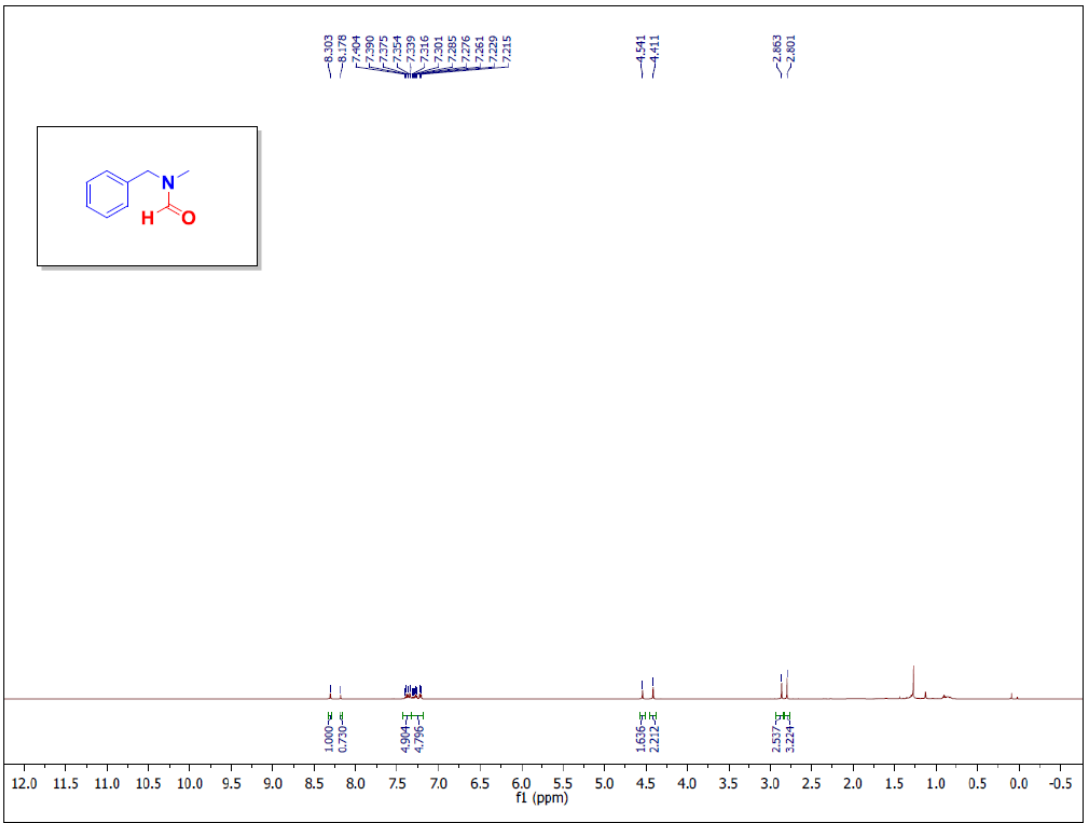


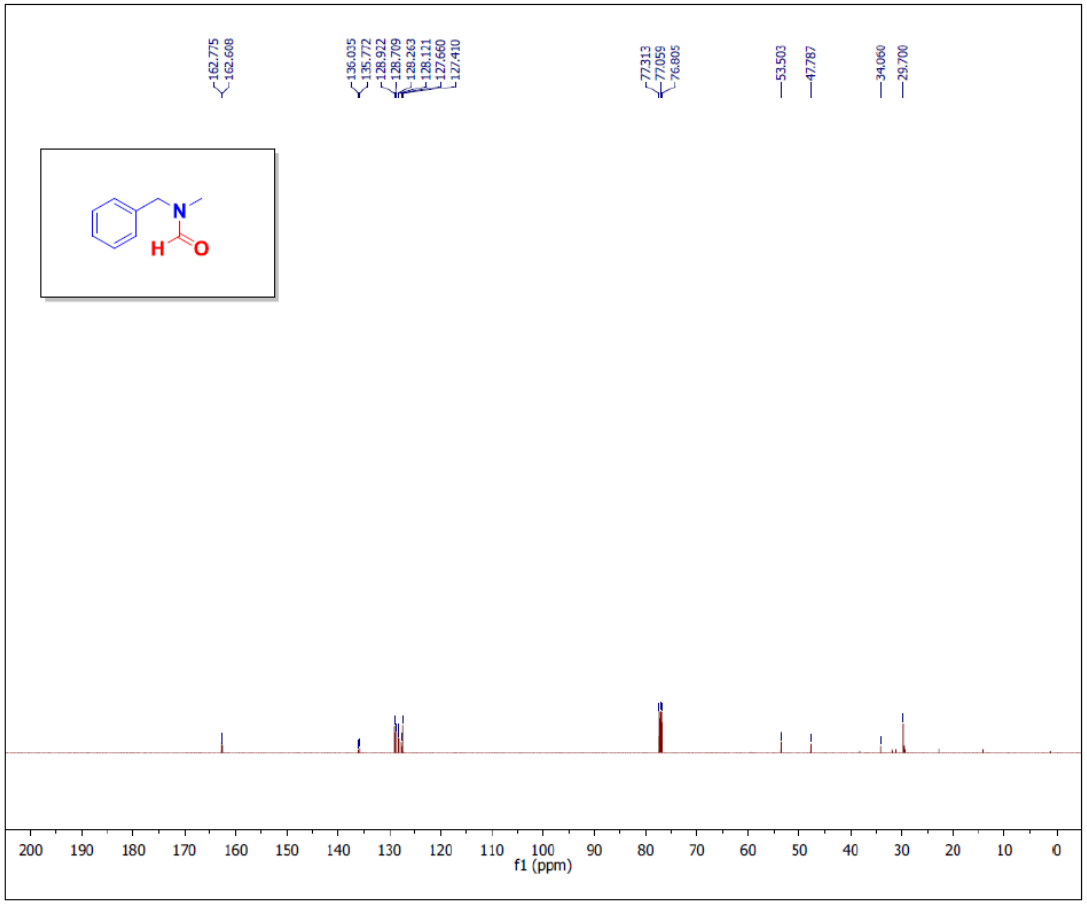
^{1}H and ^{13}C NMR spectra of compound 8p:



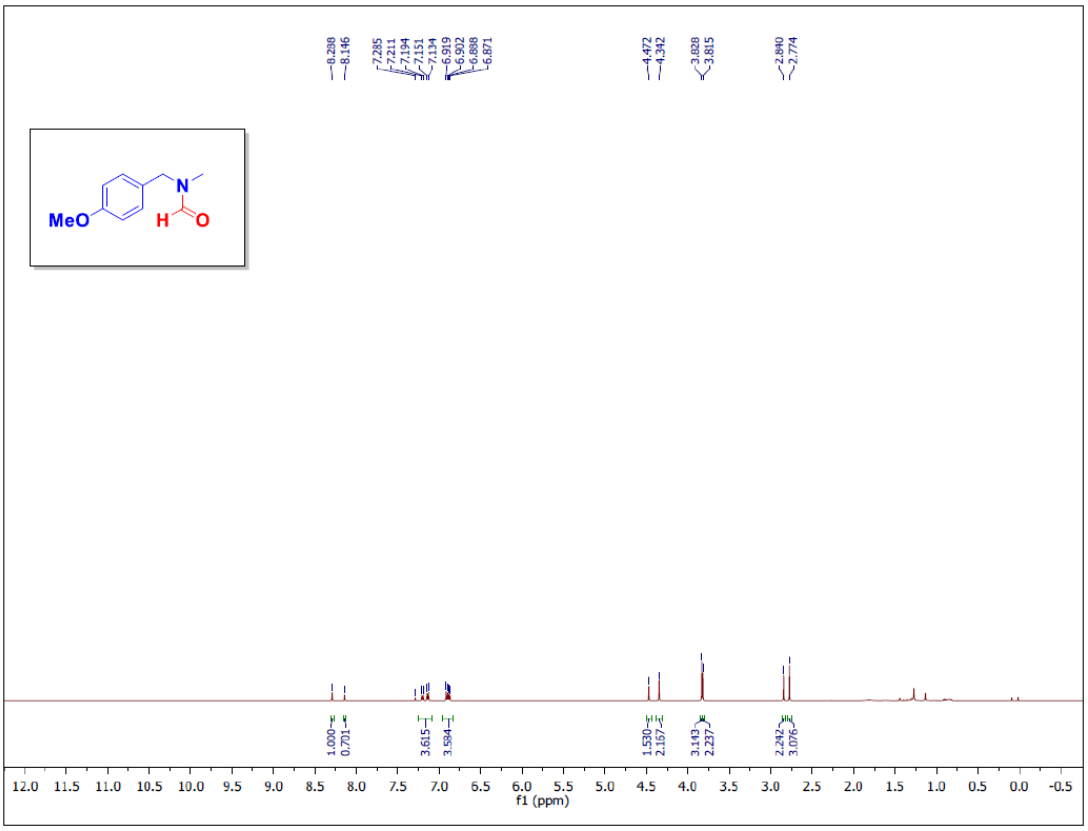


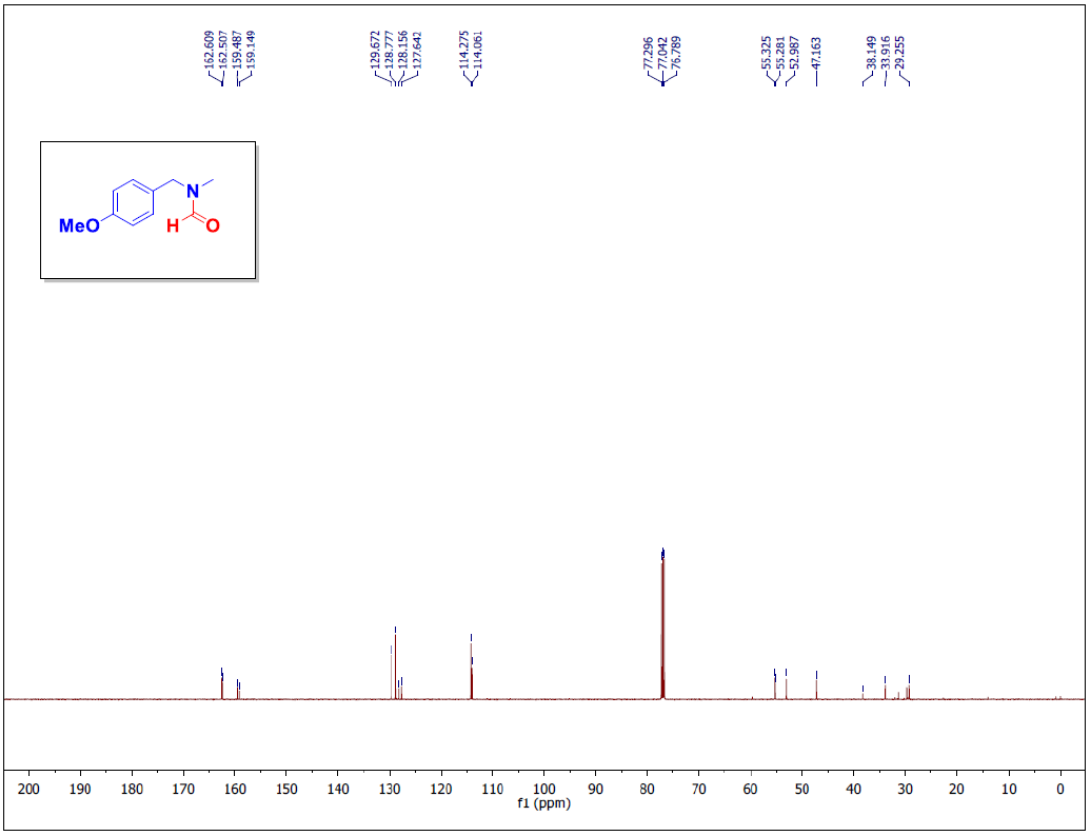
^{1}H and ^{13}C NMR spectra of compound 8q:



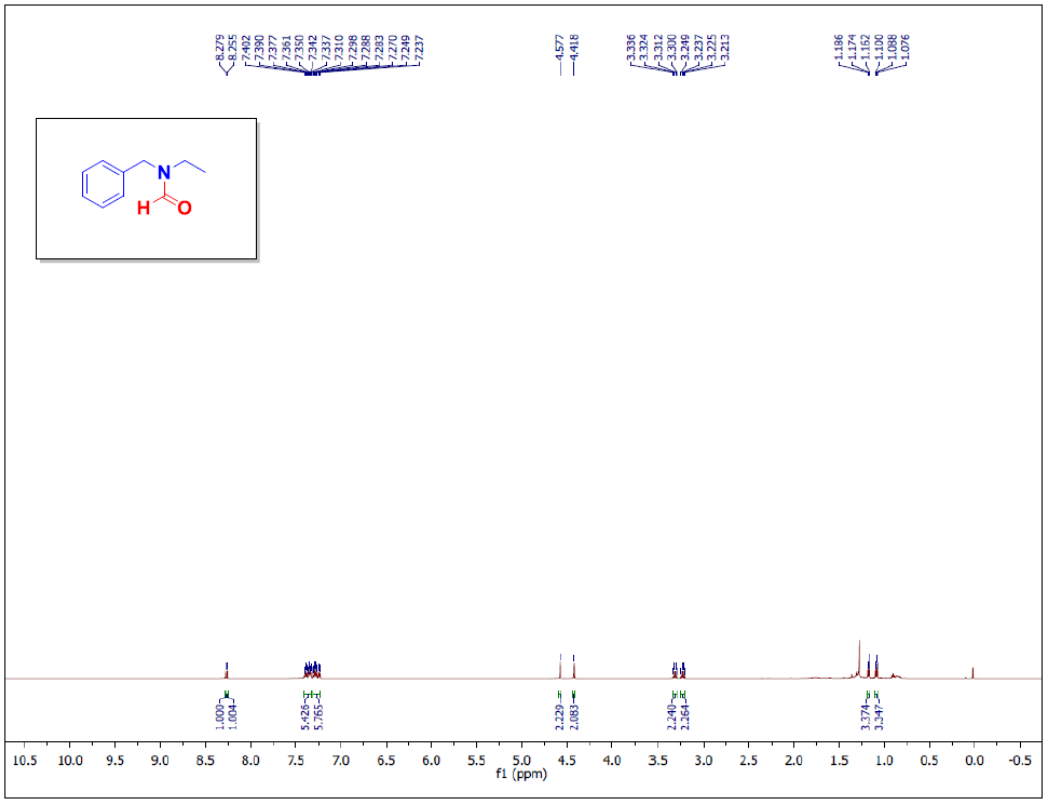


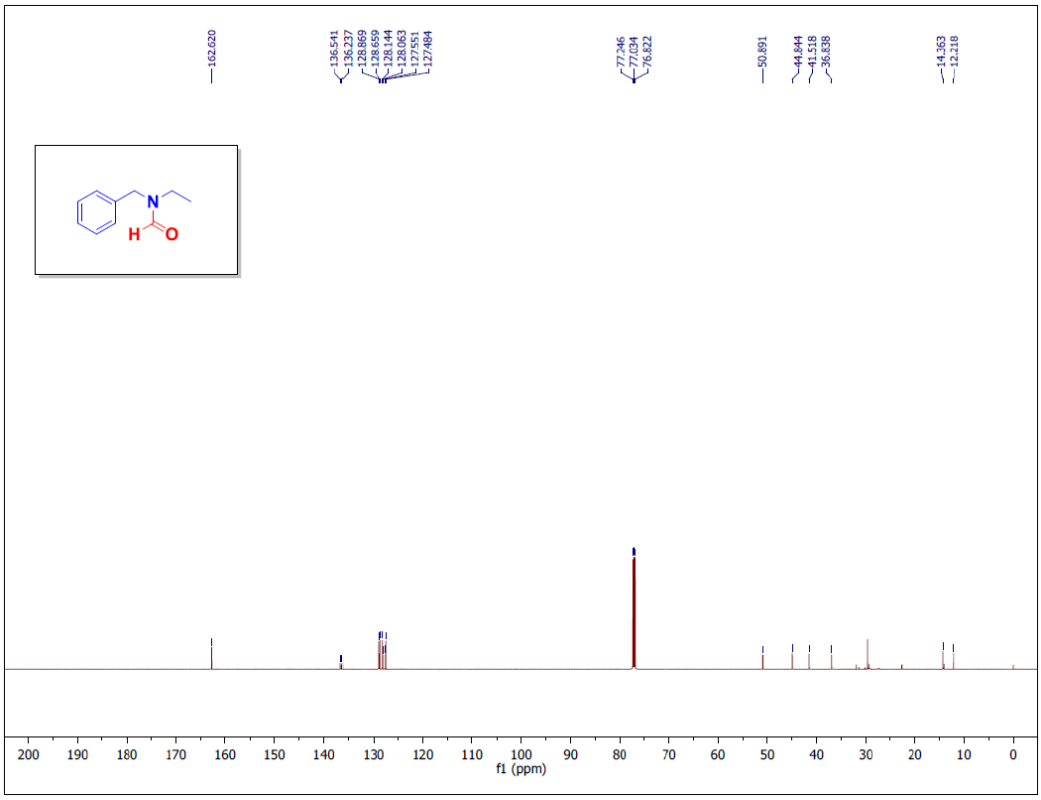
^{1}H and ^{13}C NMR spectra of compound 8r:



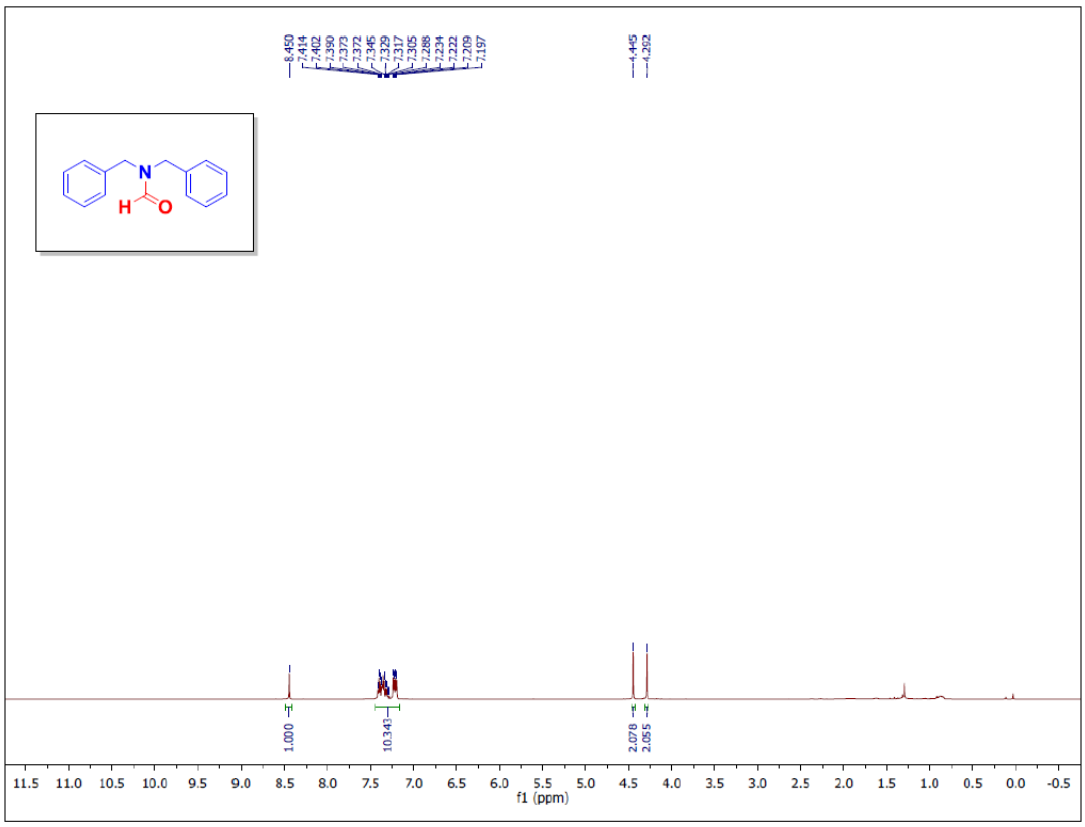


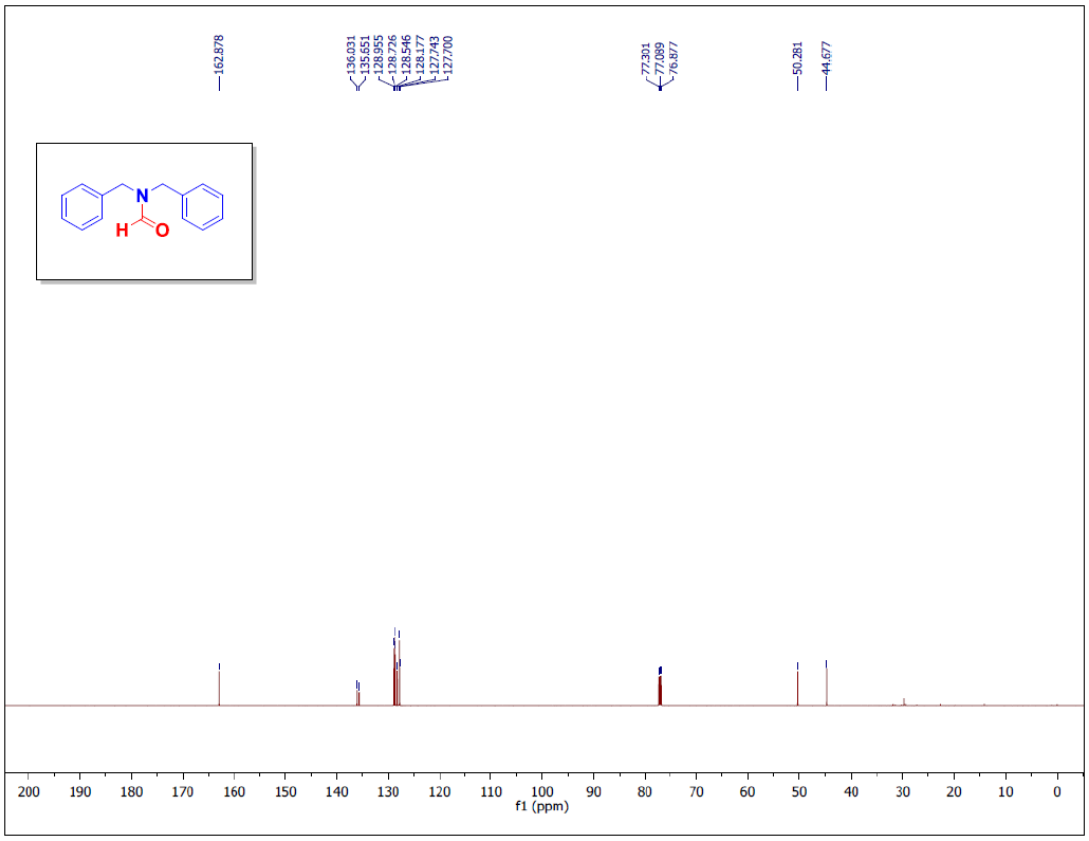
^{1}H and ^{13}C NMR spectra of compound 8s:



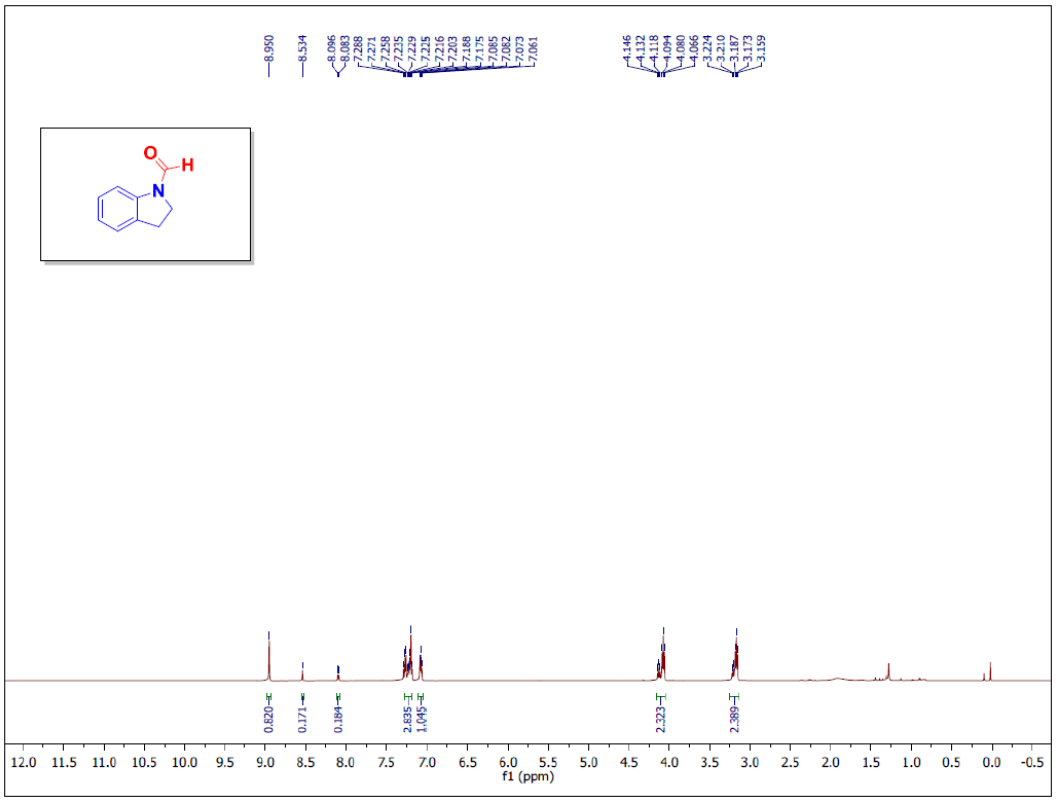


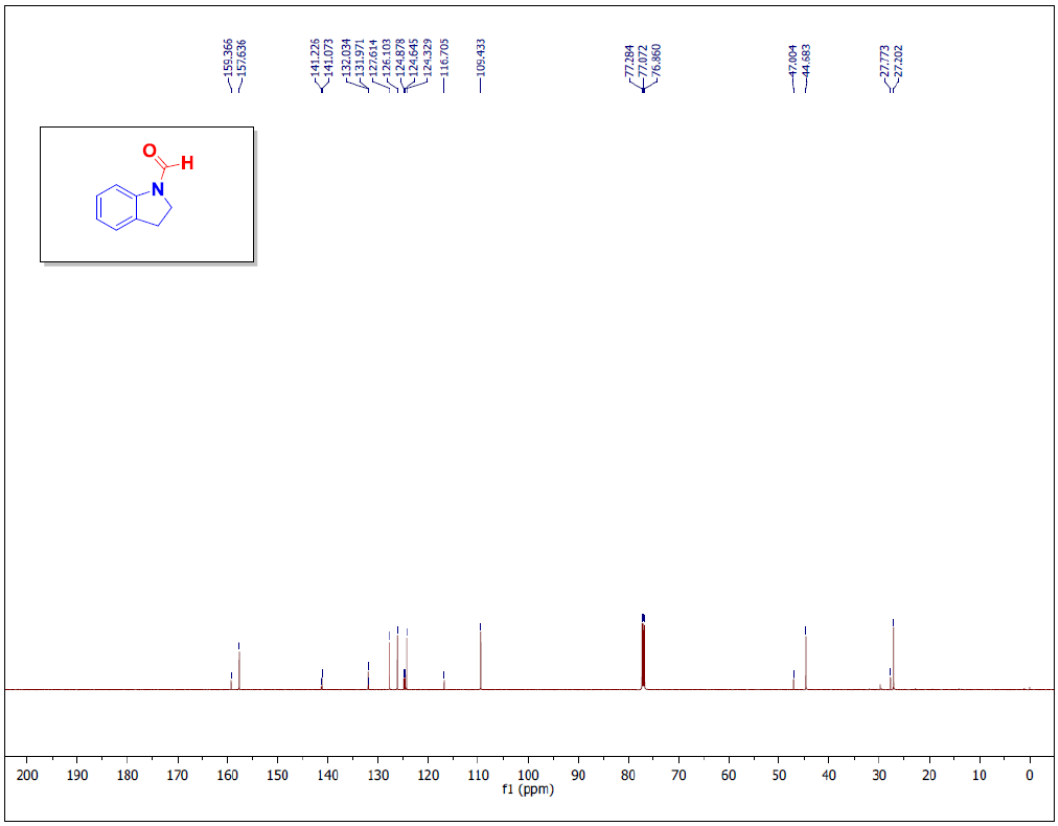
^{1}H and ^{13}C NMR spectra of compound 8t:





^{1}H and ^{13}C NMR spectra of compound 8u:





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