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Supporting Information

CuO decorated magnetic reduced graphene oxide: a robust and promising heterogeneous catalyst for oxidative amidation of methylarenes in water via benzylic sp^3 C-H activation

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General

All chemicals used in this study were analytical grade, commercially available and used without further purification. Graphite (CAS No. 7782-42-5, particle size: <50μm) was purchased from Merck. Most of the products were purified by column chromatography from appropriate solvents and were identified by ^{1}H NMR and ^{13}C NMR. Progress of the reactions was monitored by TLC using silica gel polygrams SIL G/UV 254 plates. FT-IR spectra were recorded on Shimadzu DR-8001 Spectrometer and employed for characterization of the catalysts. NMR spectra were recorded on a Bruker Avance DPX 400 MHz Instrument in $CDCl_3$ or DMSO-*d6* solvents using TMS as internal standard. Chemical shifts were reported in ppm (δ), and coupling constants (*J*), in Hz. X-ray diffraction (XRD) patterns were recorded on a XRD-D8 (BRUKER, Germany) employing a scanning rate of 0.05° s^{-1} from 10° to 80° with Cu$K\alpha$ radiation. The absorbance of the material solutions was detected by UV-Vis Spectrophotometer (Pharmacia Biotech Ultraspec 4000). The surface morphology of graphene oxide and its nanocomposites was analyzed by using field emission scanning electron microscopy (JEOL, JSM-7610F) and transmission electron microscopy (JEOL, JEM-2100F, 200KV TEM).The analysis system was equipped with high-energy laser diodes. Melting points were determined in open capillaries with a Galen-Kamp melting point apparatus and are not corrected. The thermal degradation pattern of the synthesized nanocomposite was determined by thermogravimetric analysis (TGA) using a thermal analyzer TA-SDT Q-600. The magnetic properties of the prepared catalyst were investigated by using a VSM with an applied field between -8,000 and 8,000 Oe at room temperature (MDKF, Iran). ICPOES spectrometer (Thermo Scientific, IRIS Intrepid II, USA) were used for determination the loading amounts of Cu on the surface of prepared nanocomposites. The specific surface area of the hybrids was obtained by using gas adsorption analyzer (BELSORP, BELCo., Japan) and Brunauer-Emmett Teller (BET) method.

Experimental

Synthesis of Fe_3O_4 nanoparticles: The magnetic Fe_3O_4 nanoparticles were synthesized using a solvothermal reaction described as follows: 3.0 g of $FeCl_3.6H_2O$ and

12.0 g sodium acetate were dissolved in a 90 ml ethylene glycol and 10 ml ethylenediamine under magnetic stirring. After stirring for 1 h, a yellow solution was obtained. The resultant solution was then transferred into a Teflon-lined stainless-steel autoclave and sealed and heated at 200 °C for 2 h, and cooled to room temperature. The black magnetic particles were collected with the help of a magnet, followed by washing with ethanol several times. The product was dried under vacuum at 60 °C for 12 h.[1]

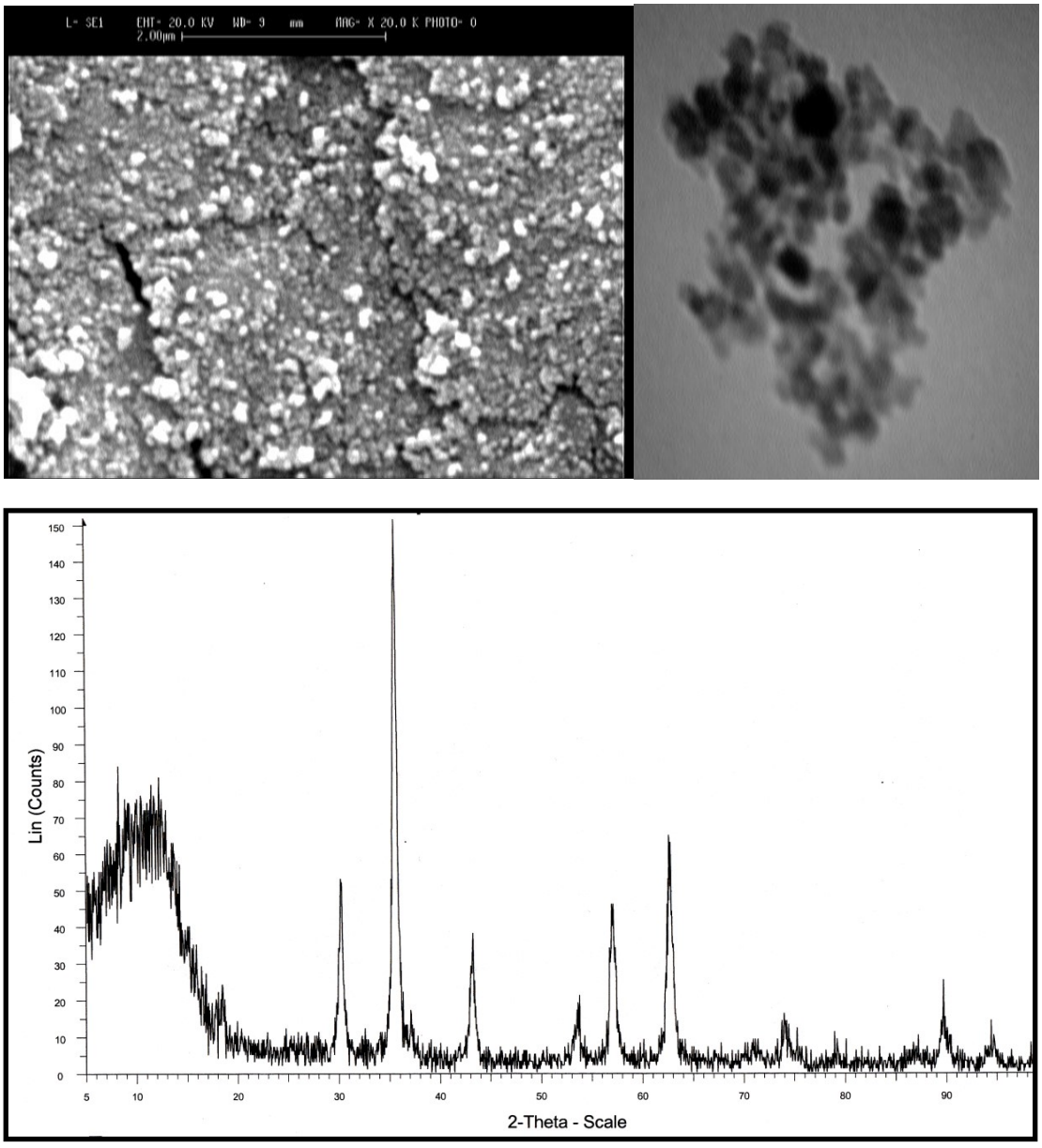


Fig. 1: (a) SEM, (b) TEM images and (c) XRD of the as-prepared Fe_3O_4 nanoparticles

Synthesis of the Fe_3O_4-CuO nanocomposite: At first, 0.9 g of copper chloride was dissolved in 50 mL of distilled water on magnetic stirrer, and pH was adjusted to 11 by NaOH (1 M). The solution was thoroughly agitated at 50 °C for 1 h. After that, the mixture was filtered and rinsed several times with distilled water, and dried in an oven at 250 °C. Then, the obtained CuO (0.5 g) was combined with the Fe_3O_4 NPs (0.3 g), which were dispersed in 80 mL of distilled water and 20 mL of polyethylene glycol, respectively. The mixture was then stirred for 22 h. The precipitate was harvested by filtration and rinsed with with distilled water and then dried in an oven at the temperature of 60 °C for 2 h. Finally, the powder was calcinated at 400 °C.[2]

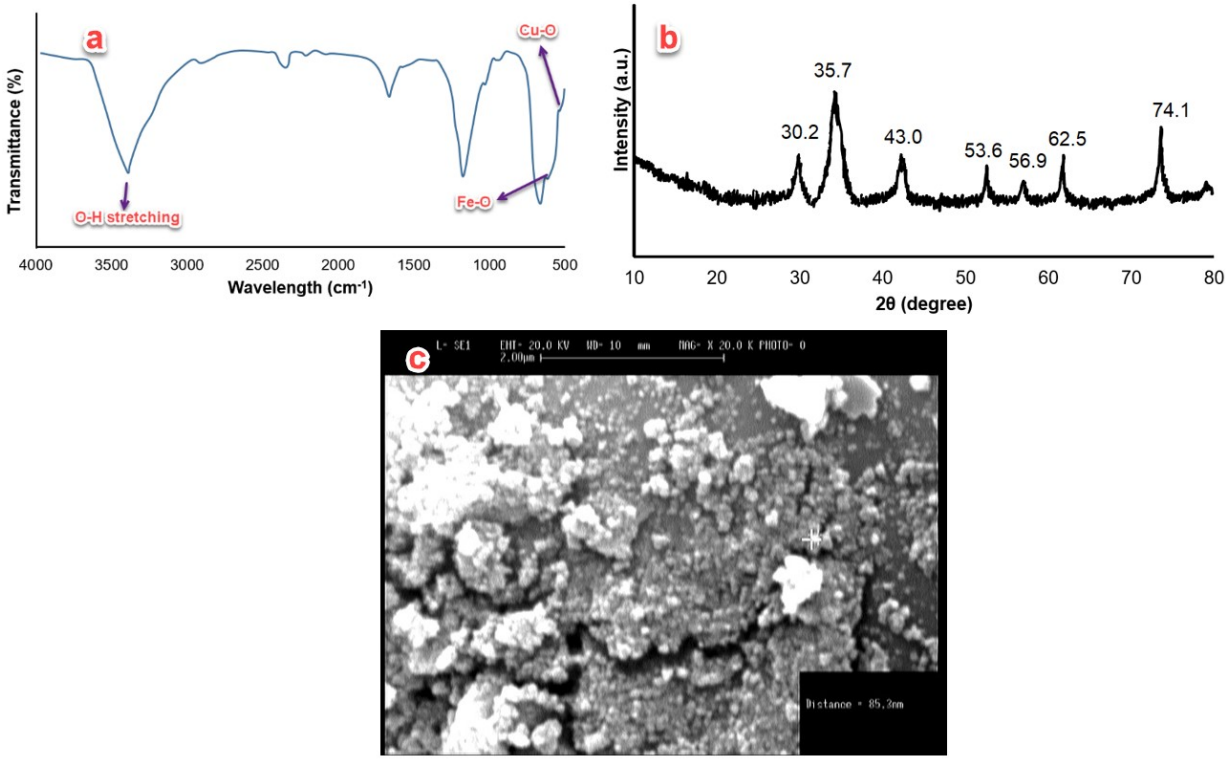


Fig. 2: (a) FT-IR, (b) XRD and (c) SEM images of Fe_3O_4-CuO nanocomposite nanoparticles

Synthesis of the CNT/Fe_3O_4-CuO nanocomposite: The functionalized CNTs was synthesized according to the reported literature.[3] Then the obtained functionalized CNTs (0.50 g) was mixed with Fe_3O_4-CuO nanocomposite (0.25 g) dispersed in ethanol, distilled

water, and polyethylene glycol, respectively (50 mL: 30 mL: 20 mL). After stirring for 24 h, the resulting product was isolated by using an external magnet, washed several times with deionized water and dried at 50 °C.[2]

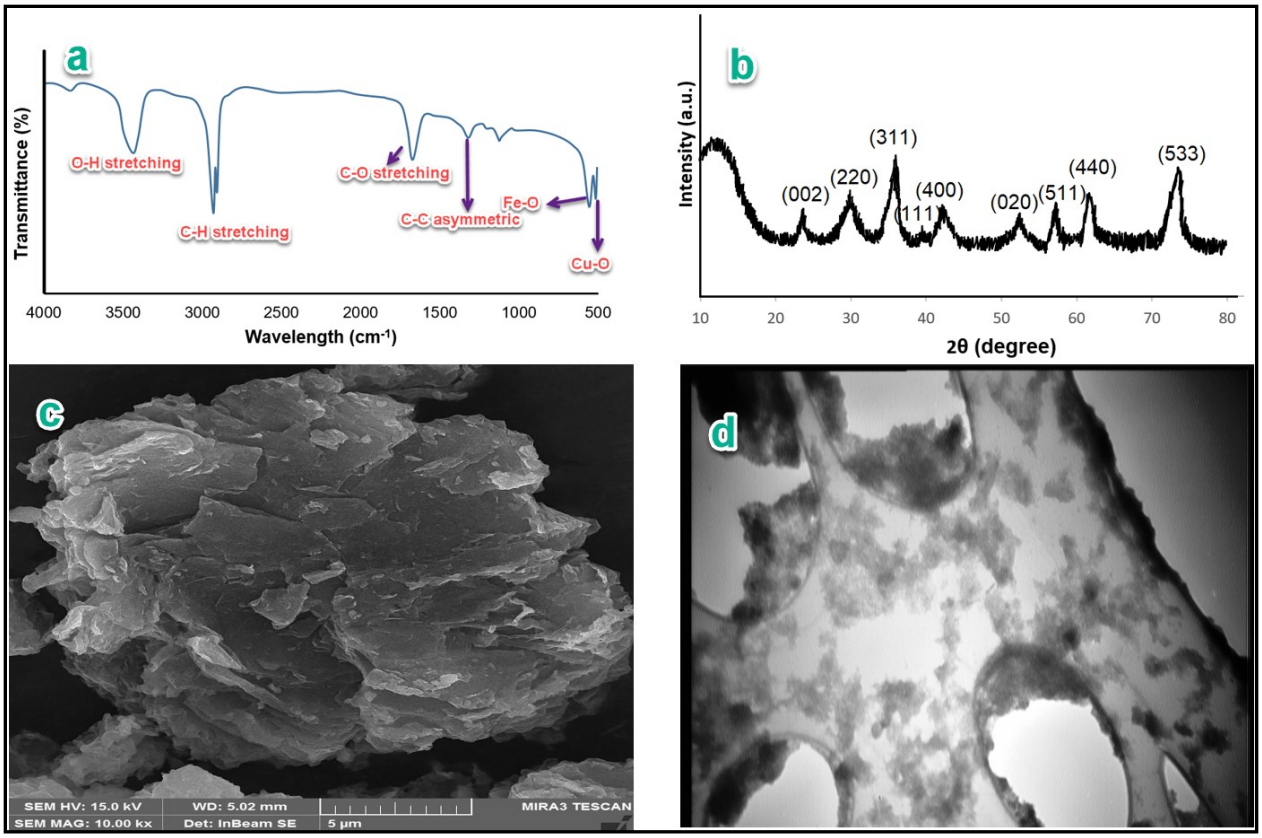


Fig. 3: (a) FT-IR, (b) XRD and (c) FESEM and (d) TEM images of CNT/Fe_3O_4-CuO nanocomposite nanoparticles

Adsorption kinetics experiments: A solution of 1000 mg/L of standardized Cu^{2+} was prepared from copper sulfate. The adsorption experiments were performed by stirring 0.1 g of reduced graphene oxide (rGO) with 100 mL of the experimental solution of known concentration in a water bath at 25 °C. At different time intervals, the supernatant was taken out and filtered, and the Cu^{2+} concentration in each flask was determined using an atomic absorption spectrophotometer. The amount of adsorbed Cu^{2+} by reduced

graphene oxide and carbon nanotube (CNT) at the equilibrium, (q_e (mg/g)) was calculated as follows:

$$qe = \frac{(C0 - C)V}{W}$$

where C_0 and C are the initial and equilibrium concentrations of the Cu^{2+} in aqueous phase (mg/L), V is the volume of the aqueous phase and W (g) is the weight of the adsorbent. Kinetics studies were carried out at initial Cu^{2+} concentrations of 40, and 60 mg/L. The adsorption isotherms of reduced graphene oxide for different metal ions were shown in Fig. 4.

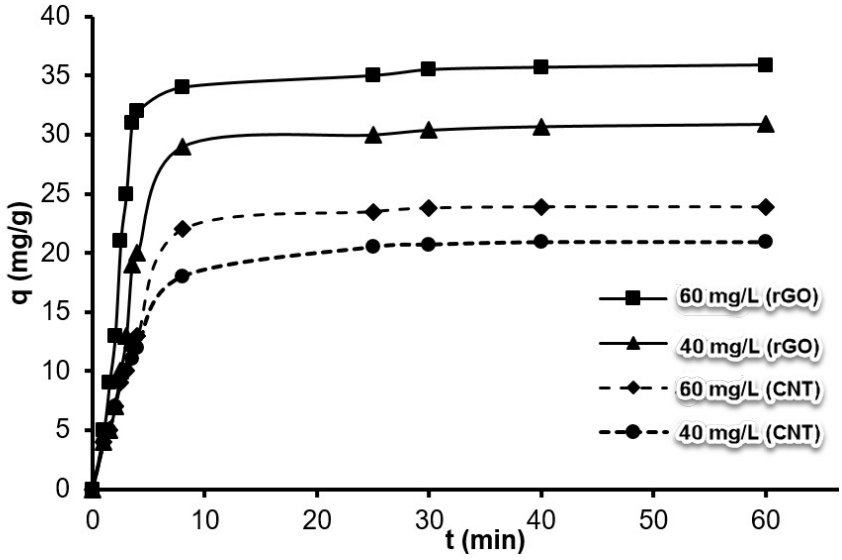
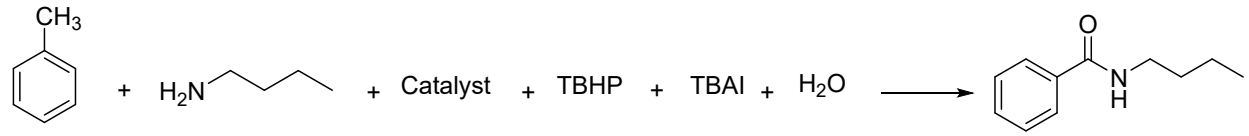


Fig. 4: Effect of contact time and comparison of different kinetic models for Cu^{2+} adsorption onto rGO and CNT at two different initial Cu^{2+} concentrations (C_0 = 40 and 60 mg/L; pH = 6; T = 25 °C)

It can be seen that the adsorption of Cu(II) onto reduced graphene oxide increases sharply within the first 25 min, then it rises slowly and reaches equilibrium in 1 h. The experimental q_e of rGO is about 35 mg/g and needed about 25 min to reach. For CNT, it needs 30 min to get the q_e of 23.8 mg/g. The process of adsorption achieved equilibrium in such a short time, suggested that reduced graphene oxide had higher adsorption efficiency than CNT.

Calculation of the E-factor[4]



920 mg 73 mg 15 mg 827 mg 111 mg 300 mg 154 mg

Total amount of the reactants (taking into account a loss of 10% of the solvent used) = 920 mg + 73 mg + 15 mg + 920 mg + 827 mg + 300 mg = 2246 mg.

Amount of the final product = 154 mg.

Amount of waste = 2246 - 154 = 2092 mg

E-factor = Amount of waste [kg]/Amount of product [kg] = 2092/154 = 13.58 kg kg^{-1}.

Calculation of the atom economy[5]

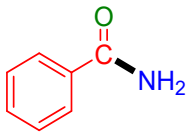
The atom economy of the reaction was calculated according to the following equation:

$$\% \text{ Atom economy} = 100 \times \frac{Molecular\ weight\ of\ the\ desired\ produc}{Molecular\ weight\ all\ of\ reactants}$$

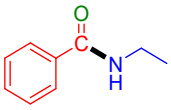
92 $gmol^{-1}$ 73 $gmol^{-1}$ 90 $gmol^{-1}$ 177 $gmol^{-1}$

Atom economy = 100 × 177/255 = 69%

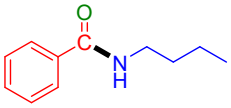
Spectroscopic data of products



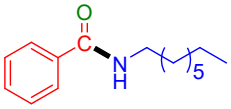
Benzamide **(3a)**: white solid, mp = 126-128 °C (lit.[6] 125-127 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 8.02 (brs, 1H), 7.87-7.91 (m, 2H), 7.39-7.48 (m, 4H); ^{13}C NMR (62.5 MHz, DMSO): *δ* (ppm) = 168.2. 134.0, 131.1, 128.1, 127.4.



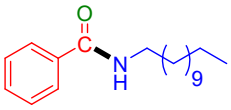
N-Ethylbenzamide **(3b)**: white solid, mp = 65-67 °C (lit.[6] 62-65 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 7.74-7.78 (m, 2H), 7.40-7.49 (m, 3H), 6.16 (brs, 1H), 3.46 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 2.5 Hz, 3H). ^{13}C NMR (62.9 MHz, DMSO): δ (ppm) = 166.5, 134.1, 131.0, 128.1, 127.0, 34.2, 14.5.



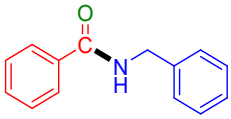
N-buthylbenzamide **(3c)**: yellow solid, mp = 39-41 °C (lit.[7] 38-39 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 7.74-7.77 (m, 2H), 7.39-7.49 (m, 3H), 6.12 (1H, brs), 3.42-3.50 (m, 2H), 1.55-1.64 (m, 2H), 1.37-1.49 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 167.6, 134.9, 131.3, 128.6, 126.8, 39.8, 31.8, 20.2, 13.8.



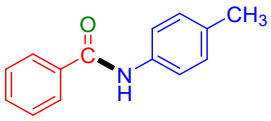
N-octylbenzamide **(3d)**: white solid, mp = 41-43 °C (lit.[7] 40-42 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.67-7.71 (m, 2H), 7.29-7.40 (m, 3H), 6.31 (brs, 1H), 3.31-3.39 (m, 2H), 1.47-1.58 (m, 2H), 1.19-1.24 (m, 10H), 0.80 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 167.7, 134.8, 131.2, 128.4, 127.0, 40.2, 31.8, 29.7, 29.3, 29.2, 27.1, 22.7, 14.1.



N-dodecylbenzamide **(3e)**: white solid, mp = 67-69 °C (lit.[7] °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.74-7.77 (m, 2H), 7.41-7.46 (m, 3H), 6.12 (brs, 1H), 3.40-3.48 (m, 2H), 1.58-1.63 (m, 2H), 1.25-1.39 (m, 18H), 0.85-0.89 (t, *J* = 5 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 167.5, 134.9, 131.3, 128.5, 126.8, 40.1, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 27.0, 14.1.

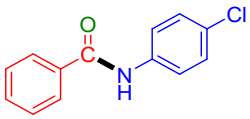


N-benzylbenzamide **(3f)**: white solid, mp = 108-110 °C (lit.[7] 106-108 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.69-7.73 (m, 2H), 7.18-7.42 (m, 8H), 6.47 (brs, 1H), 4.55 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 167.5, 138.3, 134.4, 131.6, 128.8, 128.6, 127.9, 127.6, 127.1, 44.1.

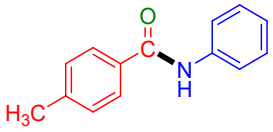


N-(*p*-tolyl)benzamide **(3g)**: white solid, mp = 156-158 °C (lit.[8] 153-155 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 10.15 (s, 1H), 7.91-7.95 (m, 2H), 7.63-7.67 (m, 2H), 7.48-7.55 (m,

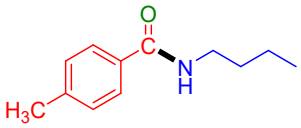
3H), 7.11-7.15 (m, 2H), 2.25 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 168.8, 136.6, 136.0, 132.0, 129.0, 128.2, 126.4, 119.0, 21.3.



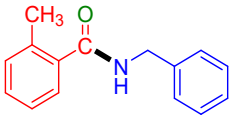
N-(4-chlorophenyl)benzamide **(3h)**: white solid, mp = 197-199 °C (lit.[9] 199-200 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.79 (d, *J* = 7.5 Hz, 2H), 7.75 (brs, 1H), 7.40-7.75 (m, 5H), 7.27 (d, *J* = 10.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 165.7, 136.5, 134.6, 132.1, 129.6, 129.2, 128.9, 127.0, 121.4.



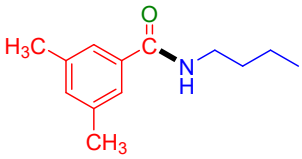
4-Methyl-*N*-phenylbenzamide **(3i)**: white solid, mp = 142-144 °C (lit.[9] 143-144 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.79 (s, 1H), 7.69 (d, *J* = 10.0 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.21-7.32 (m, 4H), 7.06-7.10 (m, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$): 165.8, 142.4, 138.1, 132.1, 129.4, 129.0, 127.1, 124.4, 120.2, 21.5.



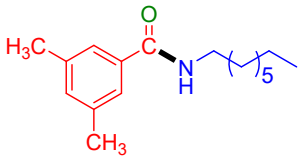
N-butyl-4-methylbenzamide **(3j)**: white solid, mp = 55-57 °C (lit.[10] 53-55 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.65 (d, *J* = 7.5 Hz, 2H), 7.19-7.23 (m, 2H), 6.11 (s, 1H), 3.40-3.48 (m, 2H), 2.38 (s, 3H), 1.53-1.62 (m, 2H), 1.36-1.44 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): *δ* (ppm) = 167.4, 141.3, 133.6, 129.2, 126.8, 39.8, 31.8, 21.4, 20.2, 13.8.



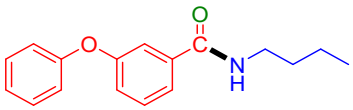
N-benzyl-2-methylbenzamide **(3k)**: white solid, mp = 106-108°C (lit.[11] 105 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.26-7.30 (m, 7H), 7.14-7.22 (m, 2H), 6.15 (brs, 1H), 4.61 (d, *J* = 7.5 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): *δ* (ppm) = 170.2, 138.6, 136.3, 136.1, 130.9, 129.8, 128.7, 127.7, 127.4, 126.9, 125.7, 43.6, 19.8.



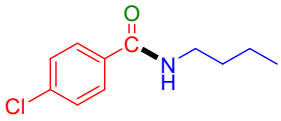
N-butyl-3,5-dimethylbenzamide **(3l)**: yellow solid, mp = 52-54 °C (lit.[12] 55-56 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.35 (s, 2H), 7.11 (s, 1H), 6.06 (brs, 1H), 3.40-3.48 (m, 2H), 2.35 (s, 6H), 1.57-1.63 (m, 2H), 1.37-1.46 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) = 167.9, 138.2, 134.9, 132.9, 124.6, 39.8, 31.8, 21.3, 20.2, 13.8.



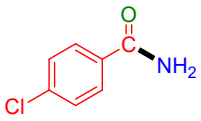
3,5-dimethyl-*N*-octylbenzamide **(3m)**: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (s, 2H), 7.14 (s, 1H), 6.24 (brs, 1H), 3.32-3.46 (m, 2H), 2.37 (s, 6H), 1.55-1.63 (m, 2H), 1.23-1.38 (m, 10H), 0.89-0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) = 168.1, 138.2, 134.8, 133.0, 124.7, 40.2, 31.8, 29.7, 29.3, 29.2, 27.0, 22.7, 21.3, 14.1.



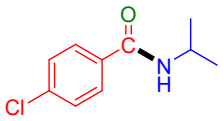
N-butyl-3-phenoxybenzamide **(3n)**: yellow solid, mp = 50-52 °C (lit.[13] 47-48 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.24-7.40 (m, 5H), 7.01-7.09 (m, 2H), 6.92-6.96 (m, 2H), 6.00 (brs, 1H), 3.32-3.40 (td, *J* = 7.5, 5 Hz, 2H), 1.44-1.55 (m, 2H), 1.25-1.37 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) = 166.9, 157.7, 156.7, 136.8, 130.0, 129.8, 123.8, 121.5, 121.4, 119.2, 117.2, 39.9, 31.7, 20.2, 13.8.



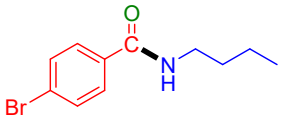
4-Chloro-*N*-butylbenzamide **(3o)**: yellow solid, mp = 79-81 °C (lit.[14] 81-82 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.60-7.70 (m, 2H), 7.30-7.35 (m, 2H), 6.08 (brs, 1H), 3.33-3.41 (m, 2H), 1.47-1.56 (m, 2H), 1.26-1.41 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): *δ* (ppm) = 166.5, 137.5, 133.2, 128.8, 128.3, 39.2, 31.7, 20.2, 13.8.



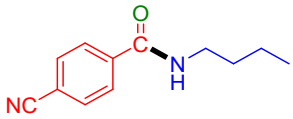
4-Chlorobenzamide **(3p)**: white solid, mp = 177-179 °C (lit.[15] 180-182 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 8.11 (s, 1H), 7.84-7.87 (d, *J* = 7.5 Hz, 2H), 7.40-7.59 (m, 2H); ^{13}C NMR (62.5 MHz, DMSO): *δ* (ppm) = 166.9, 136.1, 131.0, 129.3, 128.1.



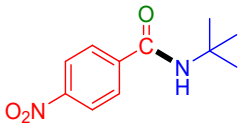
4-Chloro-*N*-isopropylbenzamide **(3q)**: yellow solid, mp = 139-141 °C (lit.[16] 142 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 7.80-7.88 (m, 2H), 7.35-7.49 (m, 2H), 5.13 (brs, 1H), 3.97-4.05 (m, 1H), 1.13 (d, *J* = 7.5 Hz, 6H); ^{13}C NMR (62.5 MHz, DMSO): *δ* (ppm) = 164.2, 135.7, 133.3, 129.1, 128.0, 42.9, 22.1.



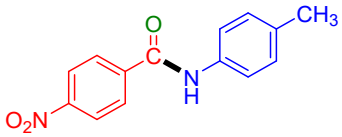
4-Bromo-*N*-butylbenzamide **(3r)**: yellow solid, mp = 91-93 °C (lit.[17] 88.5-89 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.48-7.58 (m, 4H), 5.97 (brs, 1H), 3.34-3.42 (m, 2H), 1.50-1.57 (m, 2H), 1.30-1.39 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): *δ* (ppm) = 166.9, 136.8, 130.0, 129.8, 123.4, 39.4, 31.3, 20.0, 13.7.



N-butyl-4-cyanobenzamide **(3s)**: white solid, mp = 53-55 °C (lit.[18] 45-50 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.86 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 2H), 6.12 (brs, 1H), 3.43-3.51 (m, 2H), 1.56-1.67 (m, 2H), 1.37-1.49 (m, 2H), 0.94-0.99 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) = 165.7, 138.8, 132.5, 127.6, 118.0, 115.0, 40.1, 31.6, 20.1, 13.8.

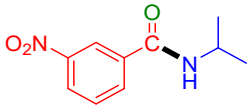


N-(*tert*-butyl)-4-nitrobenzamide **(3t)**: yellow solid, mp = 162-164 °C (lit.[16] 159-161 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 8.23-8.27 (m, 2H), 8.11 (s, 1H), 7.97-8.01 (m, 2H), 1.37 (s, 9H); ^{13}C NMR (62.5 MHz, DMSO): *δ* (ppm) = 164.6, 148.6, 141.5, 128.8, 123.2, 51.1, 28.3.

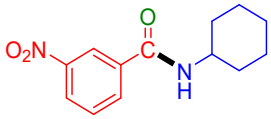


4-Nitro-*N*-(p-tolyl)benzamide **(3u)**: white solid, mp = °C (lit.[19] 198-199 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 10.46 (s, 1H), 8.33 (d, *J* = 7.5 Hz, 2H), 8.15 (d, *J* = 7.5 Hz, 2H),

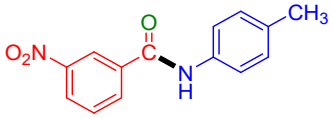
7.63 (d, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO): *δ* (ppm) = 163.6, 149.0, 140.6, 136.1, 136.0, 133.1, 129.1, 129.0, 123.5, 120.4, 120.3, 20.4.



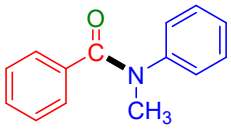
N-isopropyl-3-nitrobenzamide **(3v)**: white solid, mp = 210-212 °C (lit.[20] 210-212 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 8.59-8.64 (m, 2H), 8.24-8.30 (m, 2H), 7.66-7.72 (m, 1H), 4.02-4.15 (m, 1H), 1.14 (d, *J* = 7.5 Hz, 6H); ^{13}C NMR (62.5 MHz, DMSO): *δ* (ppm) = 163.0, 147.5, 136.0, 133.6, 129.7, 125.4, 121.8, 41.3, 22.0.



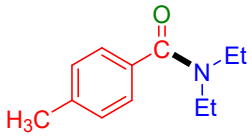
N-cyclohexyl-3-nitrobenzamide **(3w)**: yellow solid, mp = 150-152 °C (lit.[21] 146 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 8.37-8.44 (m, 2H), 8.06 (d, J = 7.5 Hz, 2H), 7.45-7.52 (m, 1H), 3.54 (s, 1H), 0.90-1.59 (m, 10H); ^{13}C NMR (62.5 MHz, DMSO): *δ* (ppm) = 163.0, 147.5, 136.1, 133.7, 129.7, 125.4, 121.9, 48.6, 32.2, 25.1, 24.8.



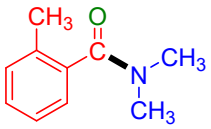
3-Nitro-*N*-(p-tolyl)benzamide **(3x)**: white solid, mp = 164-166 °C (lit.[22] 160-161 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 10.49 (s, 1H), 8.75-8.77 (m, 1H), 8.35-8.42 (m, 2H), 7.78-8.84 (t, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO): *δ* (ppm) = 163.0, 147.7, 136.3, 134.1, 133.1, 130.1, 129.0, 126.0, 122.3, 120.5, 120.4, 20.4.



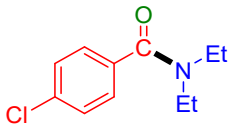
N-methyl-*N*-phenylbenzamide **(3y)**: white solid, mp = 64-66 °C (lit.[23] 61-63 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.47-7.90 (m, 2H), 7.12-7.30 (m, 6H), 7.01-7.04 (m, 2H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) = 170.7, 144.9, 135.9, 131.8, 129.2, 128.7, 127.7, 126.9, 124.5, 120.3, 38.4.



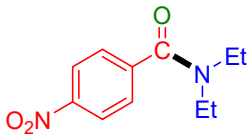
N,N-diethyl-4-methylbenzamide **(3z)**: white solid, mp = 44-46 °C (lit.[24] 43-44 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.51-7.67 (m, 1H), 7.28-7.33 (m, 1H), 7.16-7.20 (m, 2H), 3.27-3.54 (m, 4H), 2.36 (s, 3H), 1.21-1.25 (m, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): *δ* (ppm) = 170.9, 142.5, 134.3, 130.1, 128.9, 45.7, 21.5, 13.6.



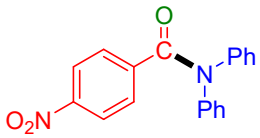
2-Methyl-*N,N*-dimethylbenzamide **(3z1)**:[25] yellow oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.40 (s, 1H), 7.17-7.23 (m, 3H), 3.13 (s, 3H), 2.83 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): *δ* (ppm) = 171.7, 140.8, 140.2, 130.9, 128.3, 127.1, 126.2, 39.2, 38.5, 20.5.



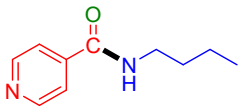
4-Chloro-*N,N*-diethylbenzamide **(3z2)**: white solid, mp = 45-47 °C (lit.[26] 44-47 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 7.44-7.48 (m, 2H), 7.32-7.35 (m, 2H), 3.37-3.39 (m, 2H), 3.09-3.12 (m, 2H), 1.16 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (62.5 MHz, DMSO): *δ* (ppm) = 171.1, 142.5, 135.8, 134.3, 133.4, 133.2, 132.8, 45.9, 15.6.



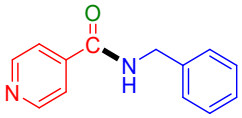
N,N-diethyl-4-nitrobenzamide **(3z3)**: white solid, mp = 64-66 °C (lit.[27] 66-68 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 7.69 (d, *J* = 10.0 Hz, 2H), 7.02 (d, *J* = 10.0 Hz, 2H), 2.99 (d, *J* = 5.0 Hz, 2H), 2.67 (d, *J* = 5.0 Hz, 2H), 0.55-0.68 (m, 6H); ^{13}C NMR (62.5 MHz, DMSO): *δ* (ppm) = 168.5, 147.6, 143.2, 127.1, 123.5, 43.0, 39.2, 13.8, 12.4.



4-Nitro-*N,N*-diphenylbenzamide **(3z4)**: white solid, mp = 149-152 °C (lit.[28] 150-152 °C). ^{1}H NMR (250 MHz, DMSO): δ (ppm) 8.06-8.10 (m, 2H), 7.68 (d, J = 7.5 Hz, 2H), 7.20-7.30 (m, 10H); ^{13}C NMR (62.5 MHz, DMSO): *δ* (ppm) = 167.8, 147.5, 142.7, 129.6, 129.2, 127.7, 126.9, 123.0.

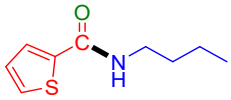


N-butylisonicotinamide **(5a)**: white solid, mp = 68-70 °C (lit.[29] 65-66 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 8.69-8.70 (m, 2H), 7.53 (d, *J* = 5.0 Hz, 2H), 6.11 (brs, 1H), 3.37-3.45 (m, 2H), 1.49-1.61 (m, 2H), 1.31-1.43 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): *δ* (ppm) = 165.5, 150.5, 141.9, 120.9, 40.0, 31.6, 20.1, 13.8.

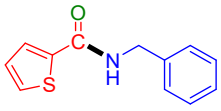


N-benzylisonicotinamide **(5b)**: white solid, mp = 87-88 °C (lit.[30] 86-88°C). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.71-7.74 (d, *J* = 7.5 Hz, 2H), 7.29-7.47 (m, 7H), 6.33 (brs, 1H),

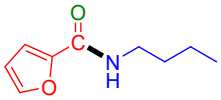
4.59 (d, *J* = 5.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) = 167.5, 138.1, 134.3, 131.6, 128.8, 128.7, 128.0, 127.7, 127.0, 44.2.



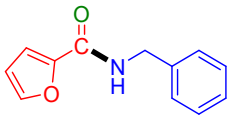
N-butylthiophene-2-carboxamide **(5c)**: yellow solid, mp = 70-72 °C (lit.[27] 67-69 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J* = 2.5 Hz, 1H), 7.45 (d, *J* = 2.5 Hz, 1H), 7.05-7.07 (m, 1H), 6.56 (brs, 1H), 3.44 (q, *J* = 5 Hz, 2H), 1.42-1.63 (m, 2H), 1.35-1.40 (m, 2H), 0.94 (t, *J* = 5.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) = 162.2, 139.2, 129.8, 128.0, 127.6, 39.9, 31.7, 20.1, 13.8.



N-benzylthiophene-2-carboxamide **(5d)**: yellow solid, mp = 119-121 °C (lit.[31] 120-122 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59 (s, 1H), 7.48 (d, *J* = 2.5 Hz, 1H), 7.31-7.34 (m, 5H), 7.06 (s, 1H), 6.92 (brs, 1H), 4.60 (d, *J* = 2.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) = 162.1, 138.9, 138.2, 130.2, 128.7, 127.9, 127.7, 127.6, 127.1, 43.9.



N-butylfuran-2-carboxamide **(5e)**: white solid. mp = 46-48 °C (lit.[32] 40-43 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50-7.51 (m, 1H), 7.46-7.47 (m, 1H), 6.95-6.97 (m, 1H), 6.17 (brs, 1H), 3.42-3.46 (m, 2H), 1.56-1.61 (m, 2H), 1.30-1.42 (m, 2H), 0.94 (t, *J* = 5.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) = 160.6, 146.8, 143.5, 120.0, 114.7, 39.5, 31.9, 20.0, 13.9.



N-benzylfuran-2-carboxamide **(5f)**: yellowish brown solid, mp = 108-110 °C (lit.[33] 108-110 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.34-7.45 (m, 6H), 7.18-7.19 (m, 1H), 6.73 (brs, 1H), 6.53 (s, 1H), 4.65 (d, *J* = 2.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) = 158.3, 147.9, 143.9, 138.0, 128.8, 127.9, 127.7, 114.5, 112.2, 43.2.

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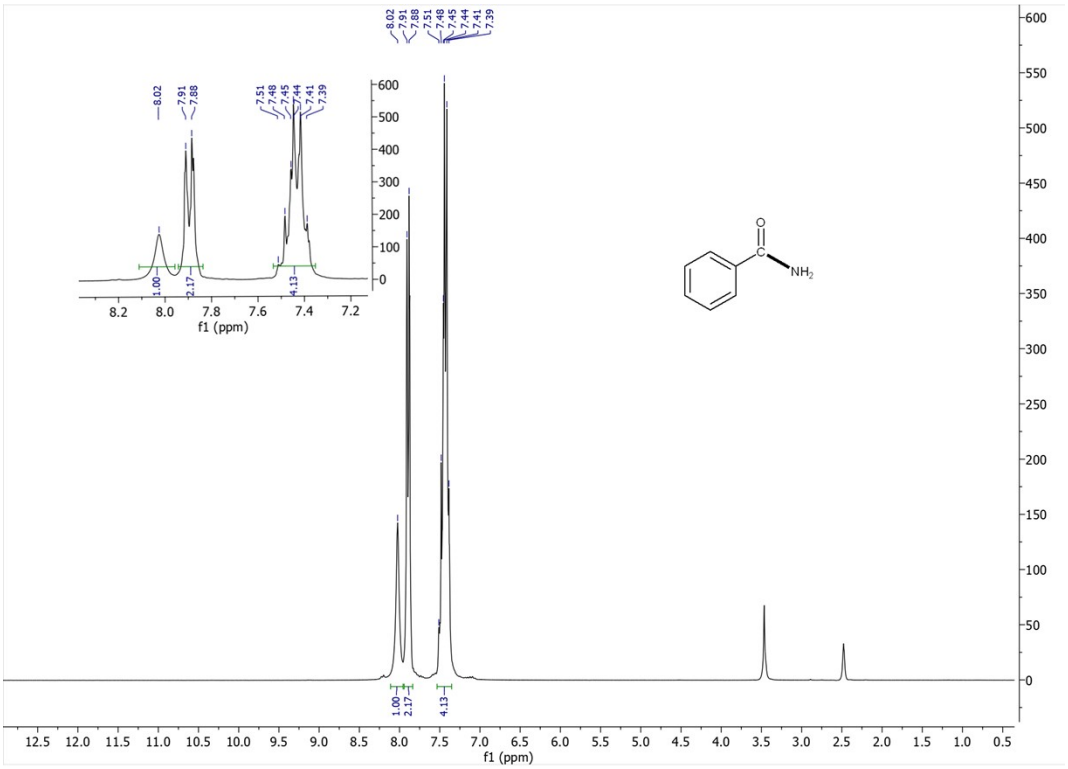
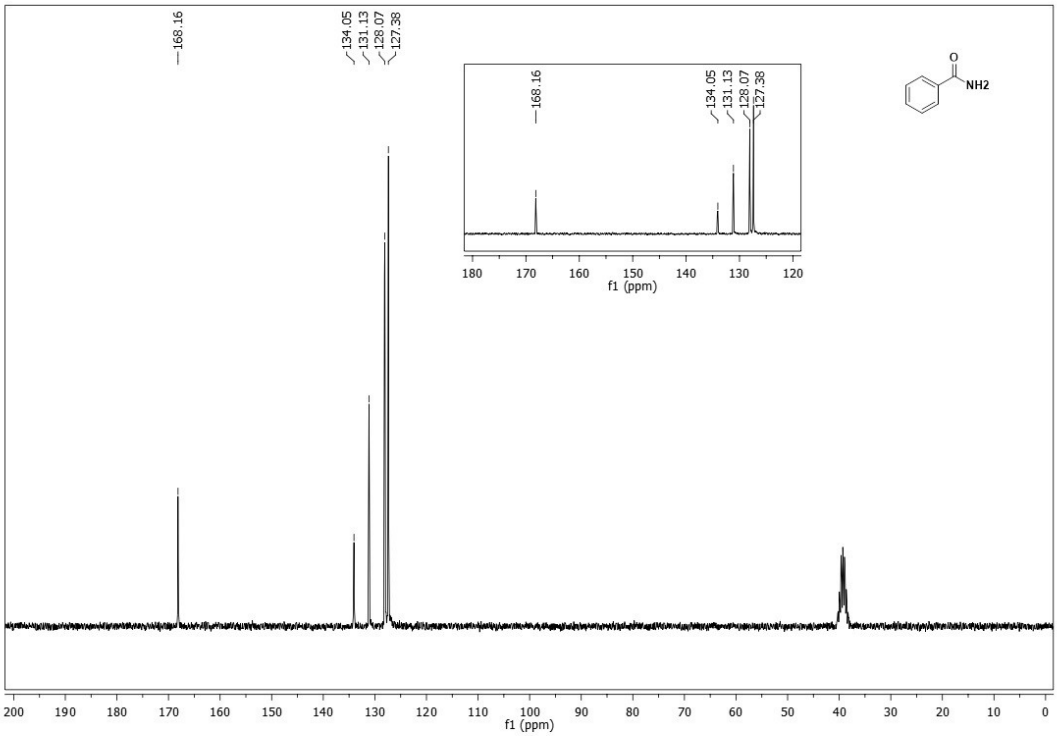
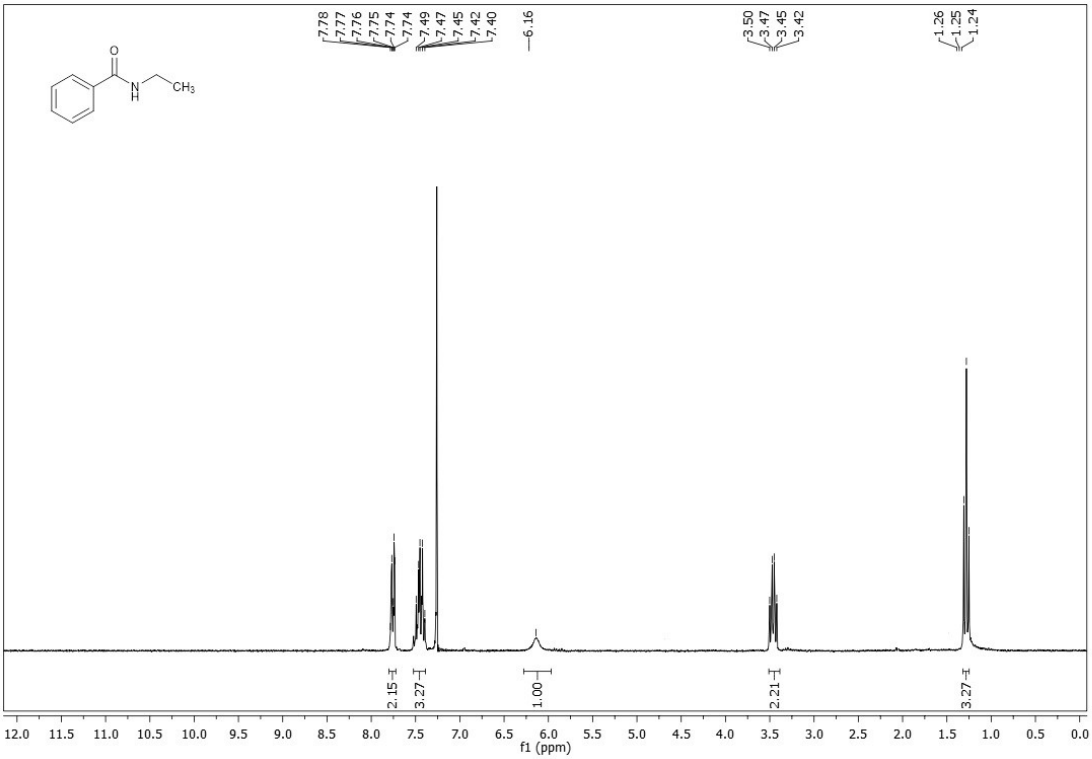
Copy of ^{1}H-NMR and ^{13}C-NMR of products



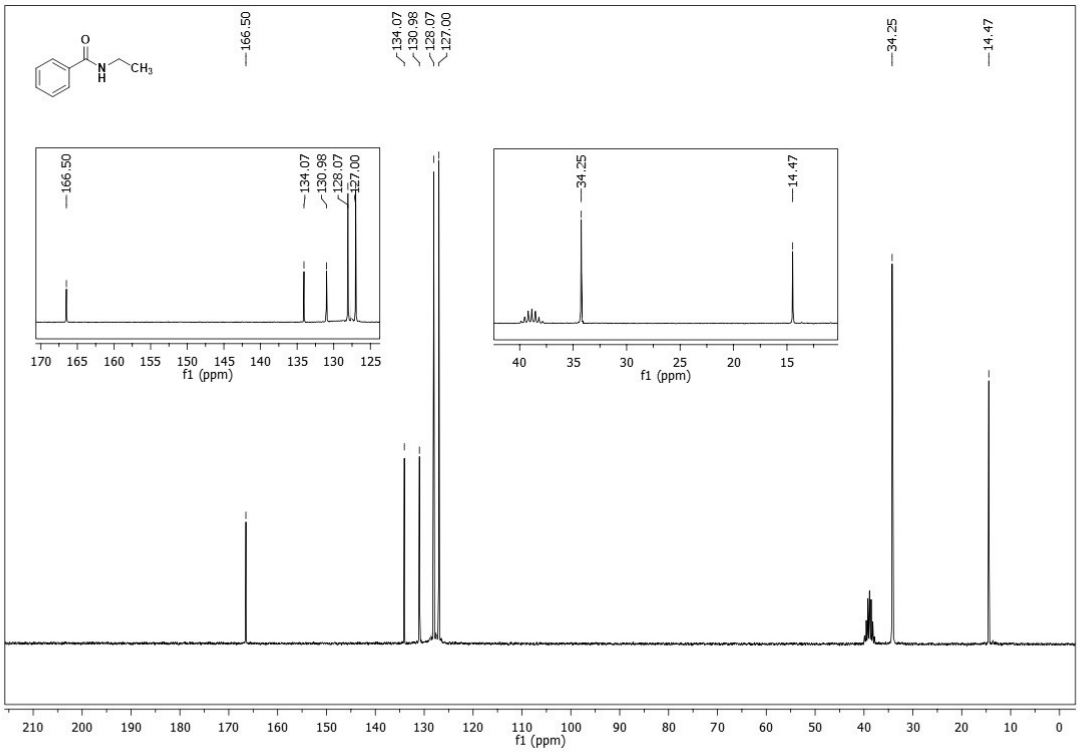
^{1}H-NMR of **3a**



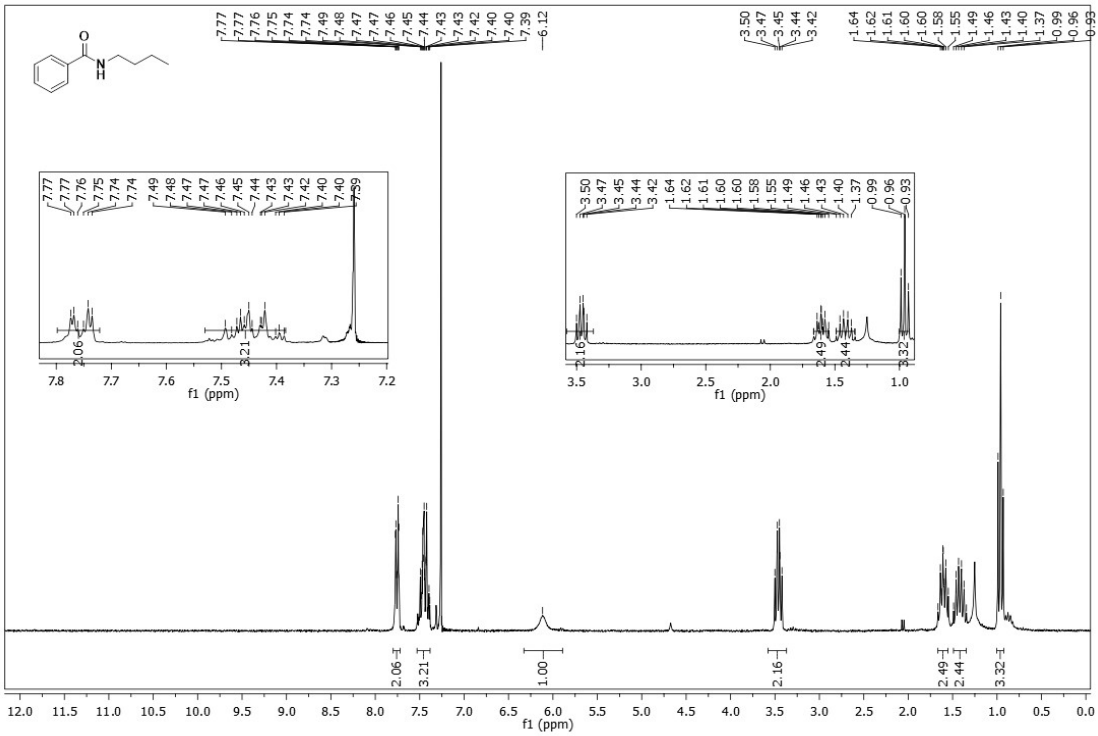
^{13}C-NMR of **3a**



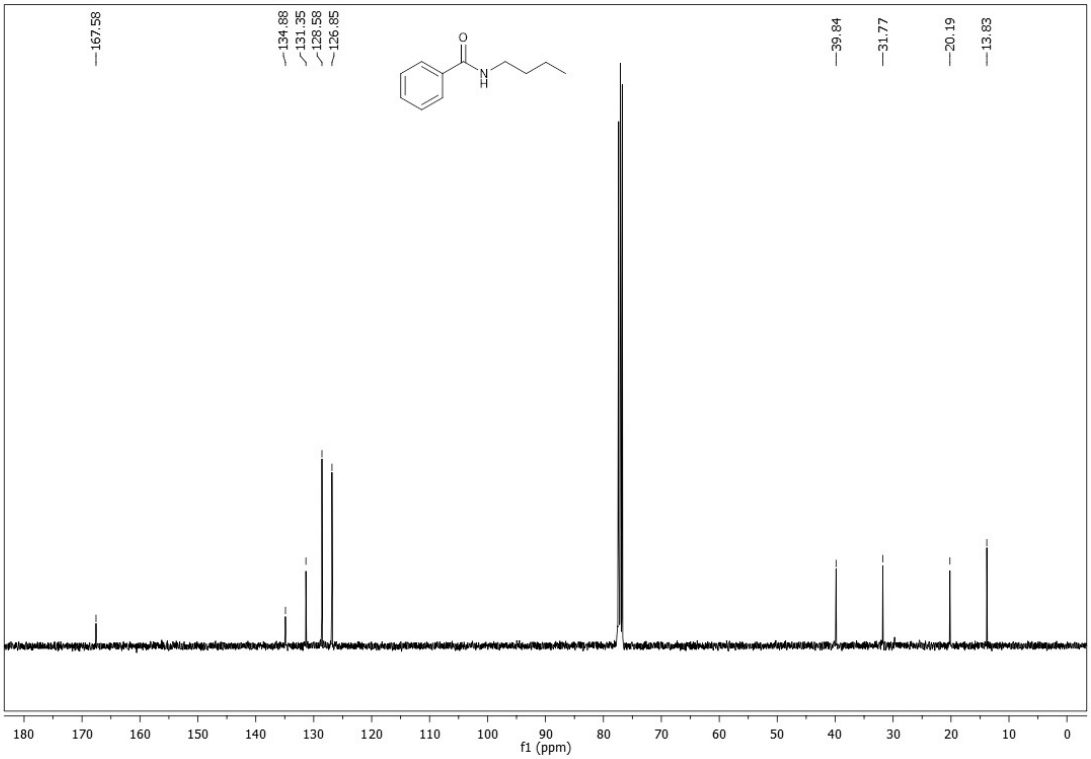
^{1}H-NMR of **3b**



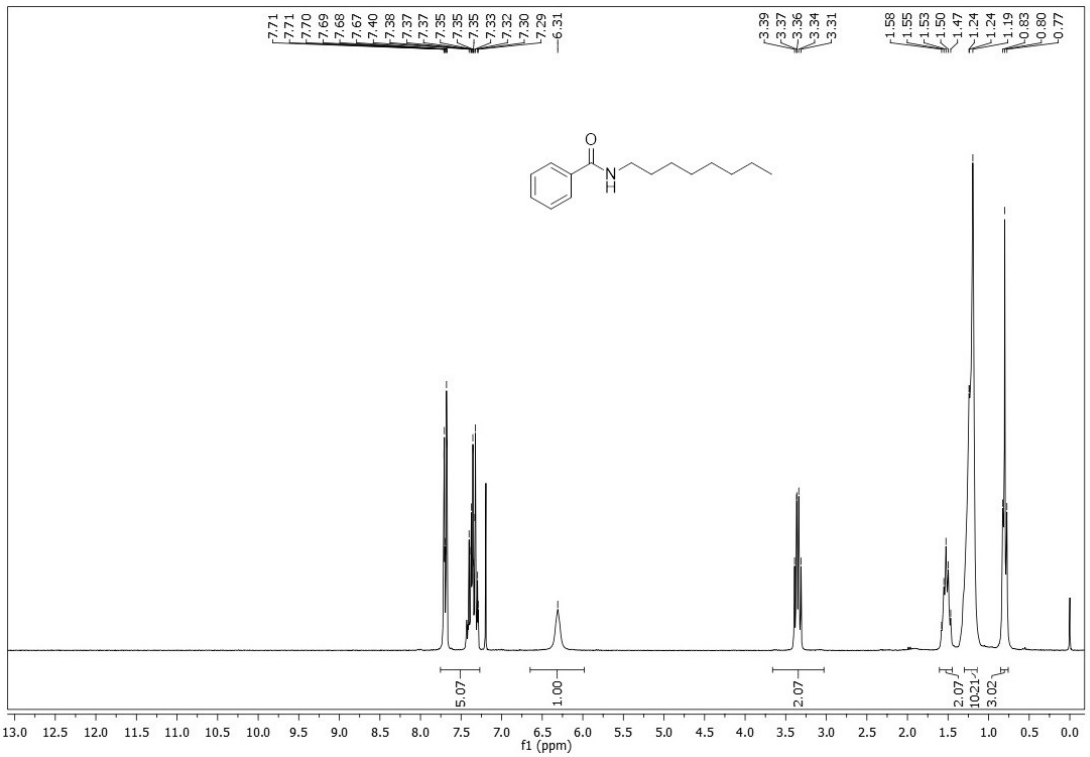
^{13}C-NMR of **3b**



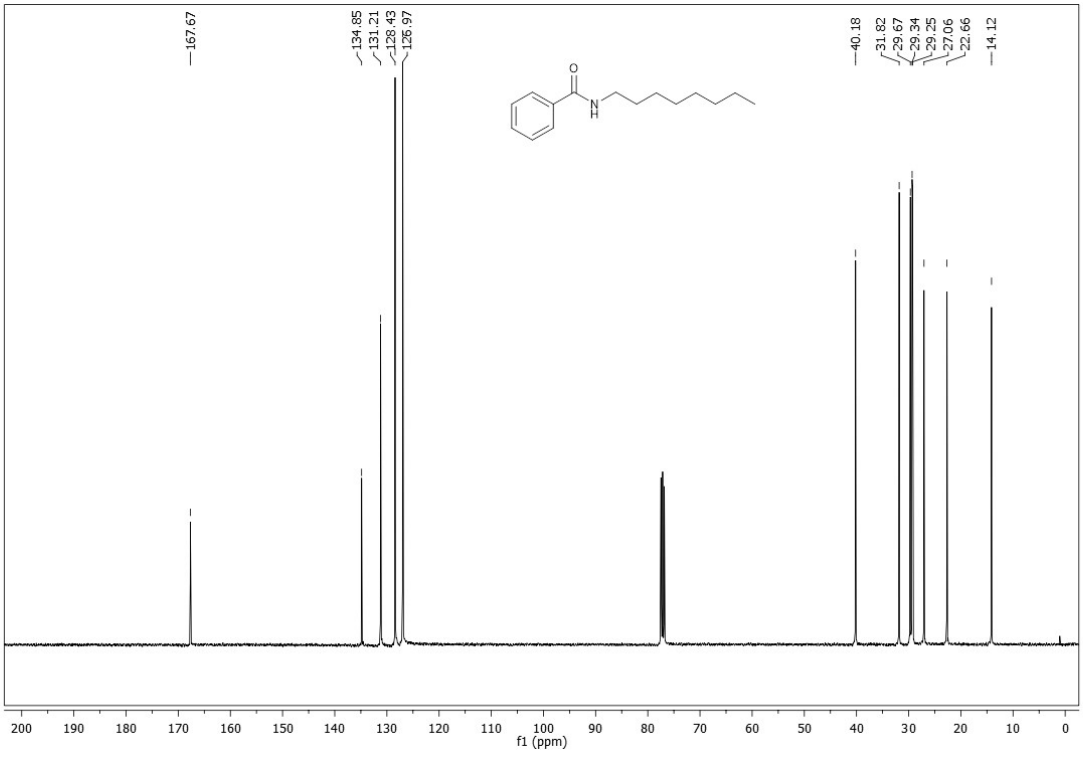
^{1}H-NMR of **3c**



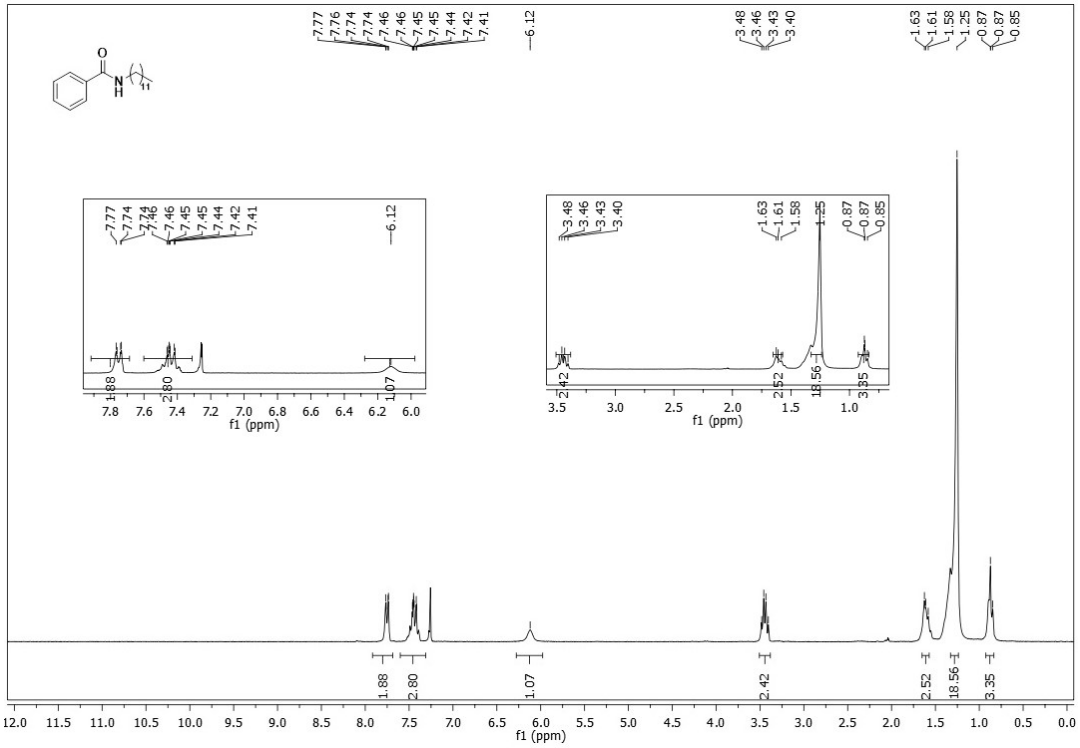
^{13}C-NMR of **3c**



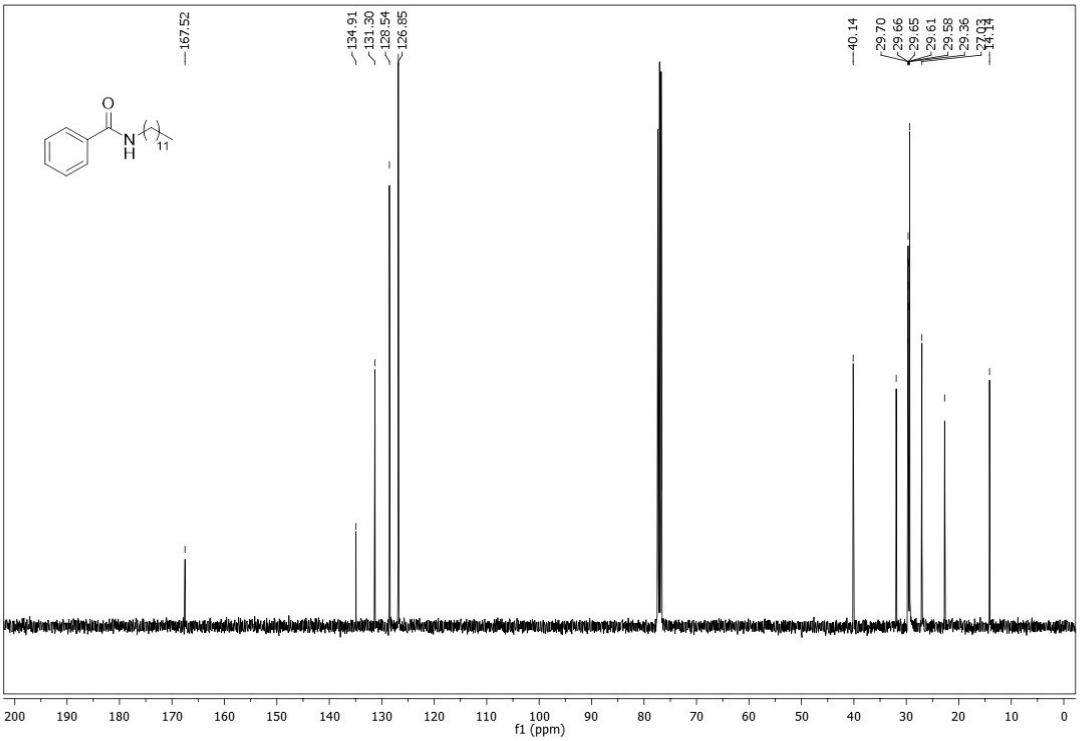
^{1}H-NMR of **3d**



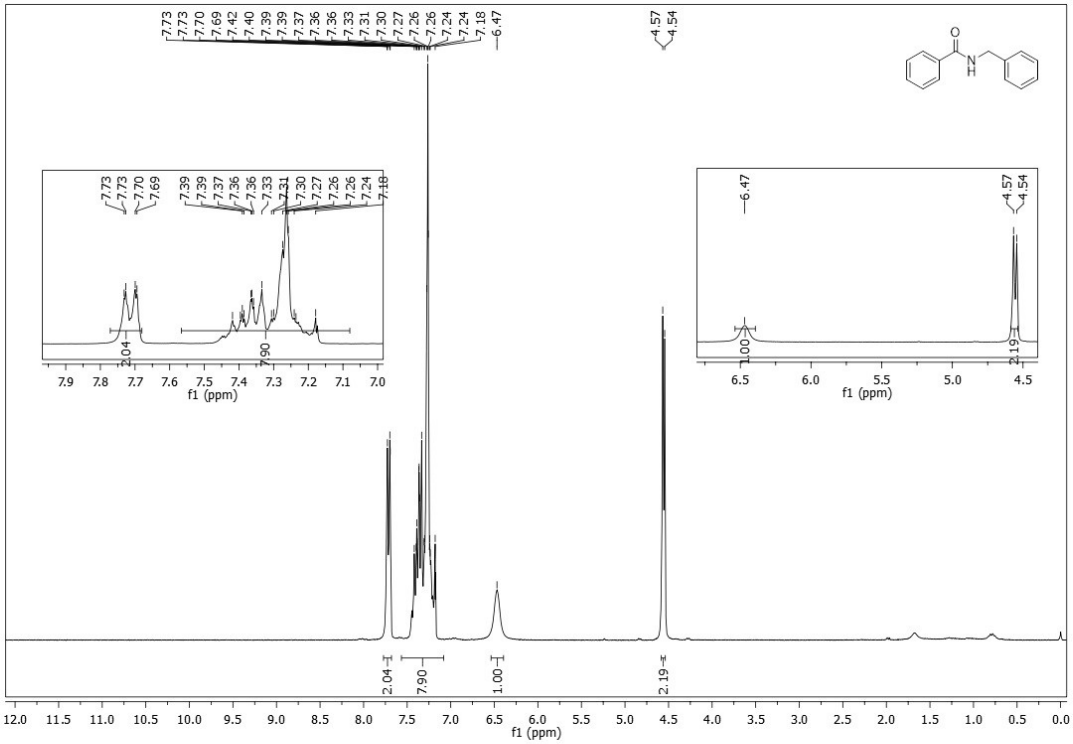
^{13}C-NMR of **3d**



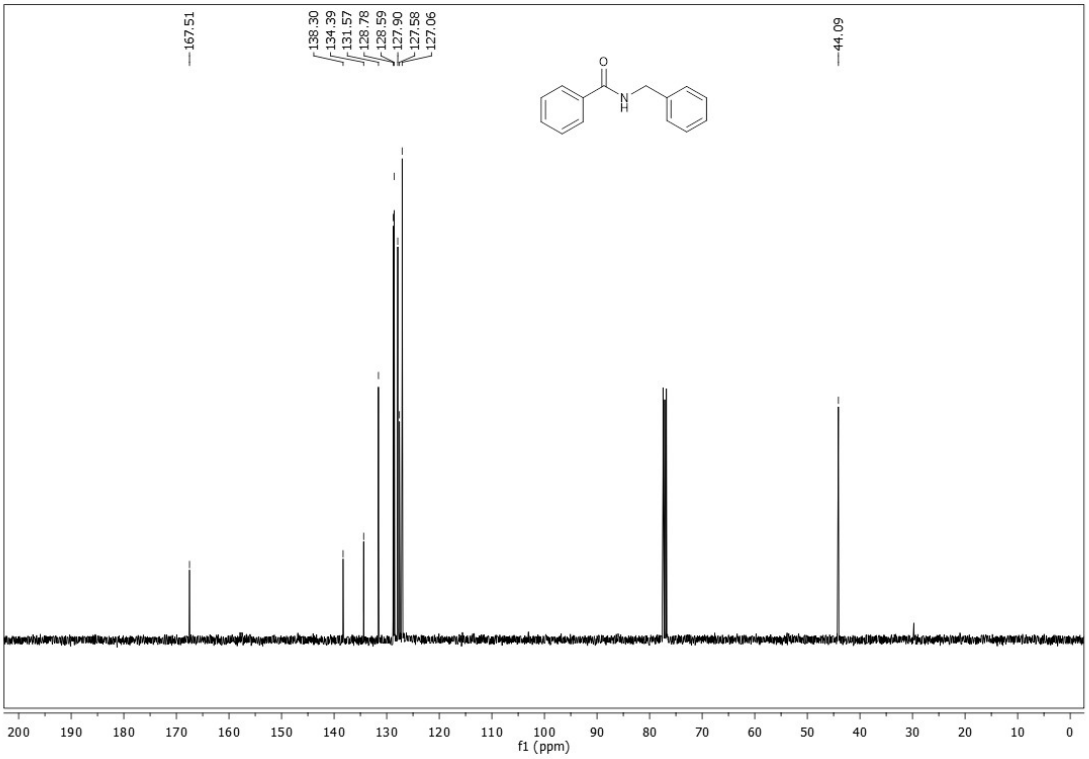
^{1}H-NMR of **3e**



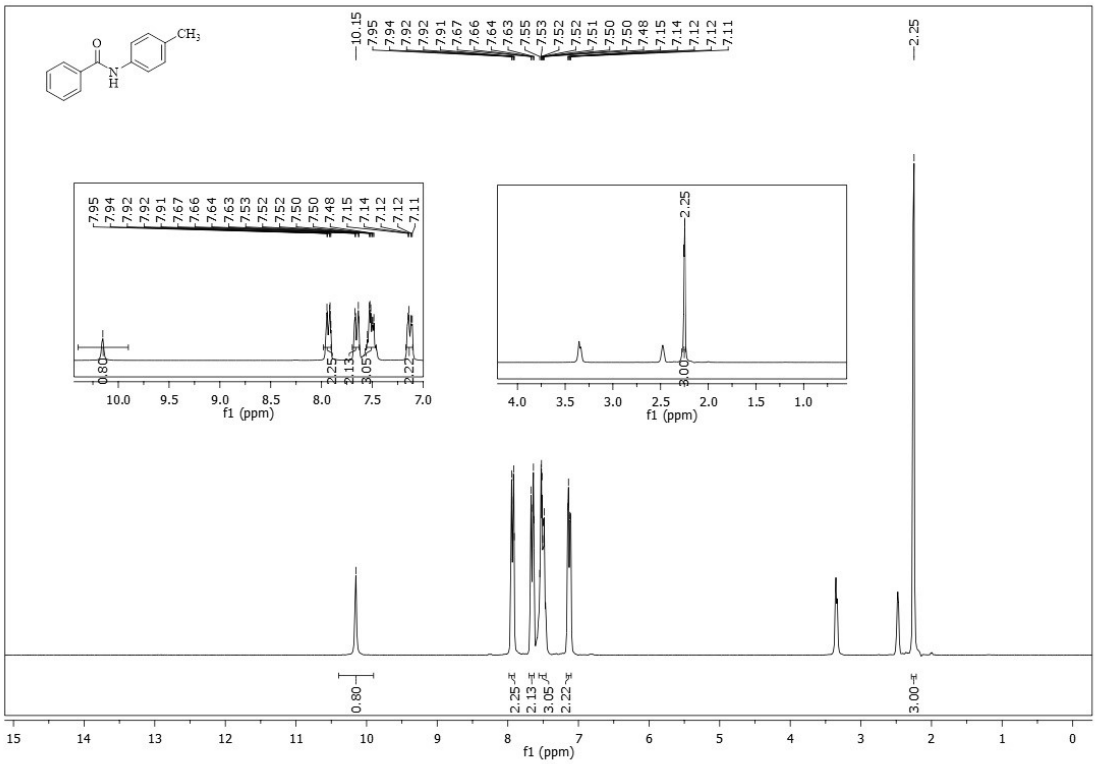
^{13}C-NMR of **3e**



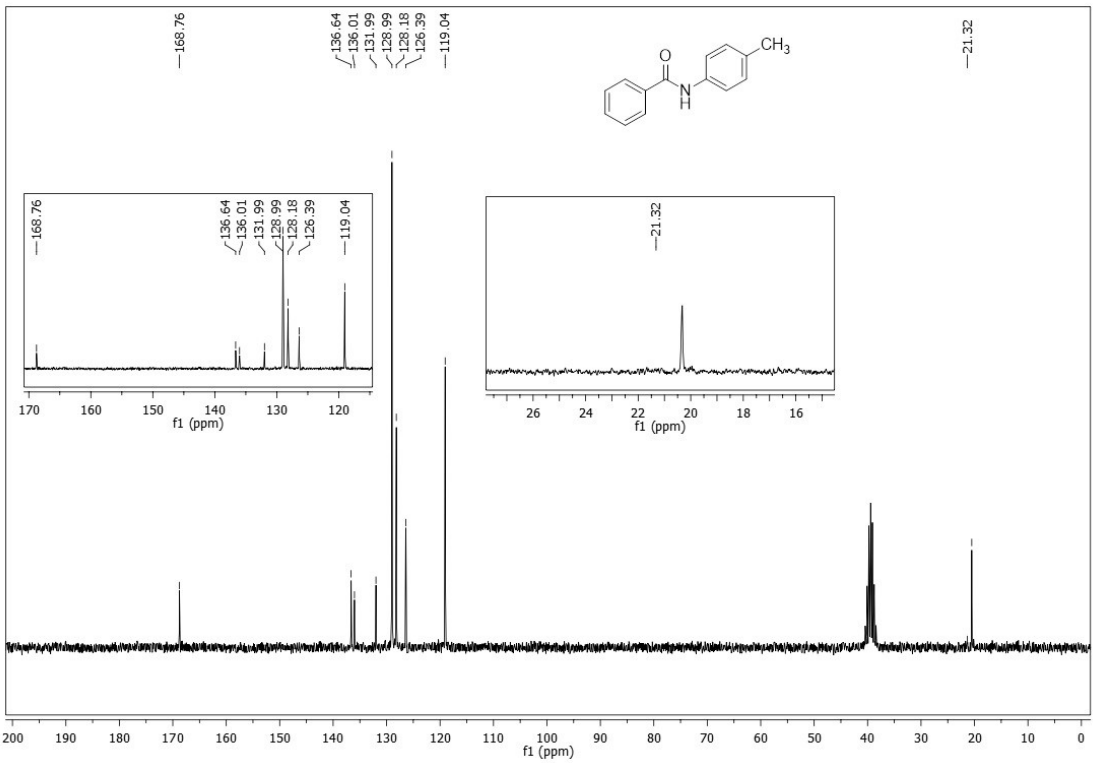
^{1}H-NMR of **3f**



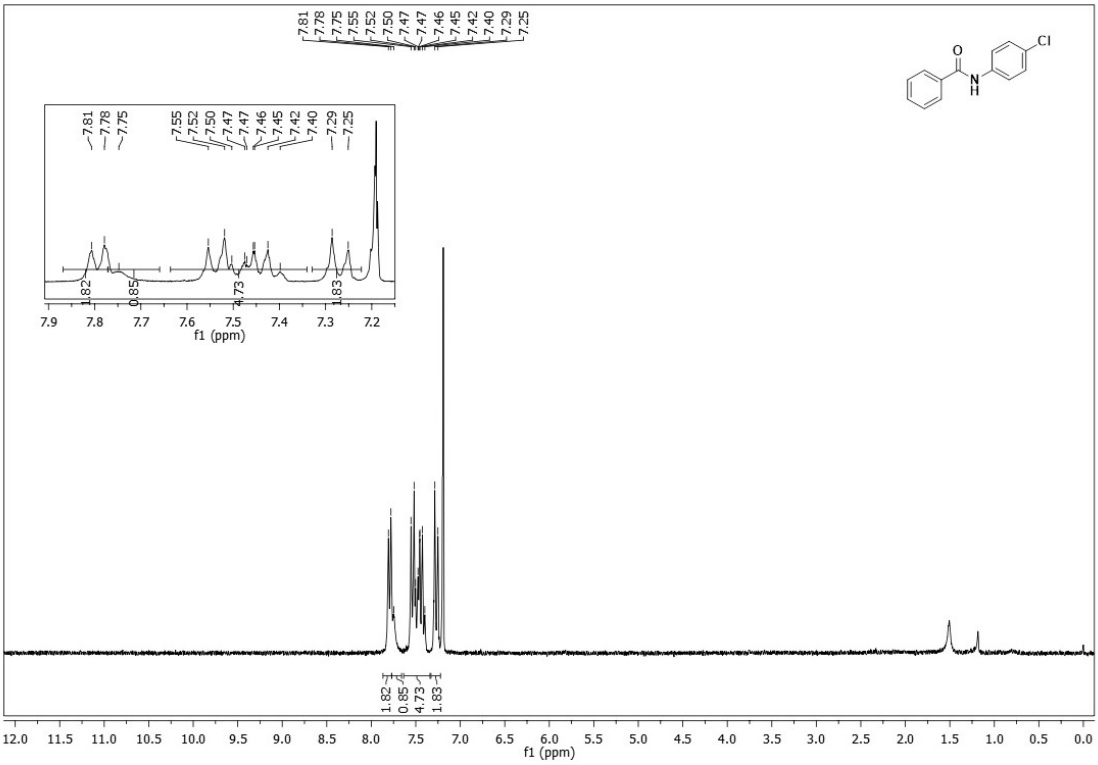
^{13}C-NMR of **3f**



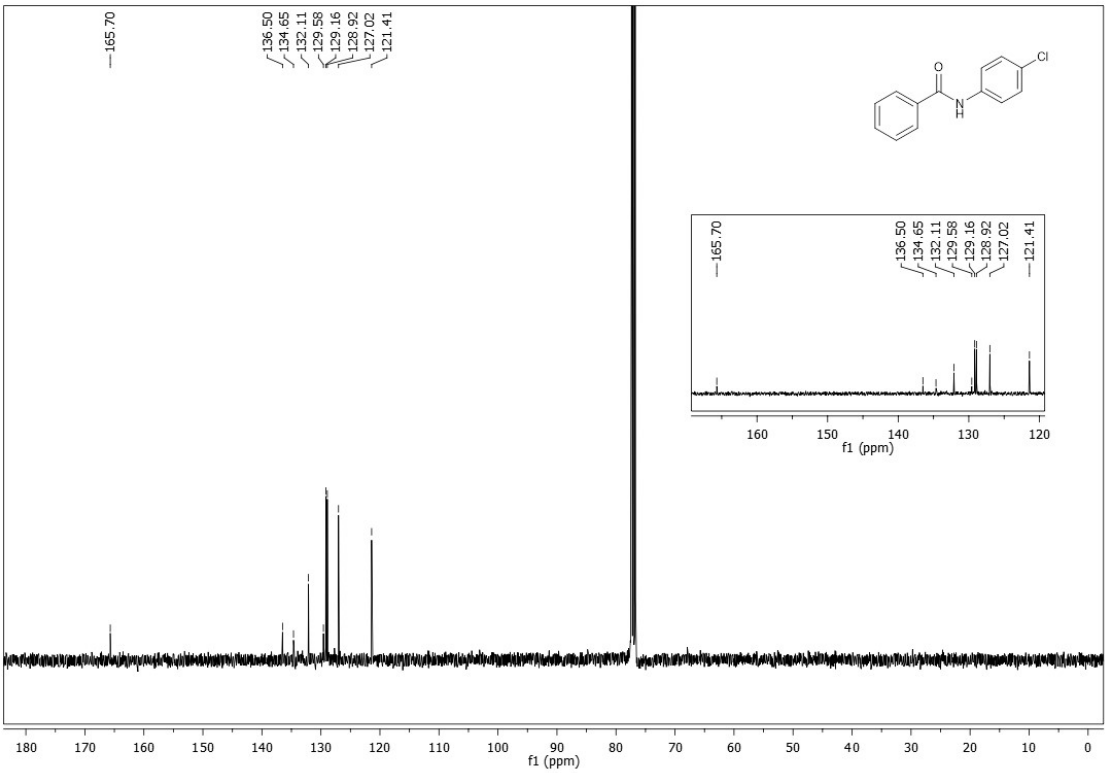
^{1}H-NMR of **3g**



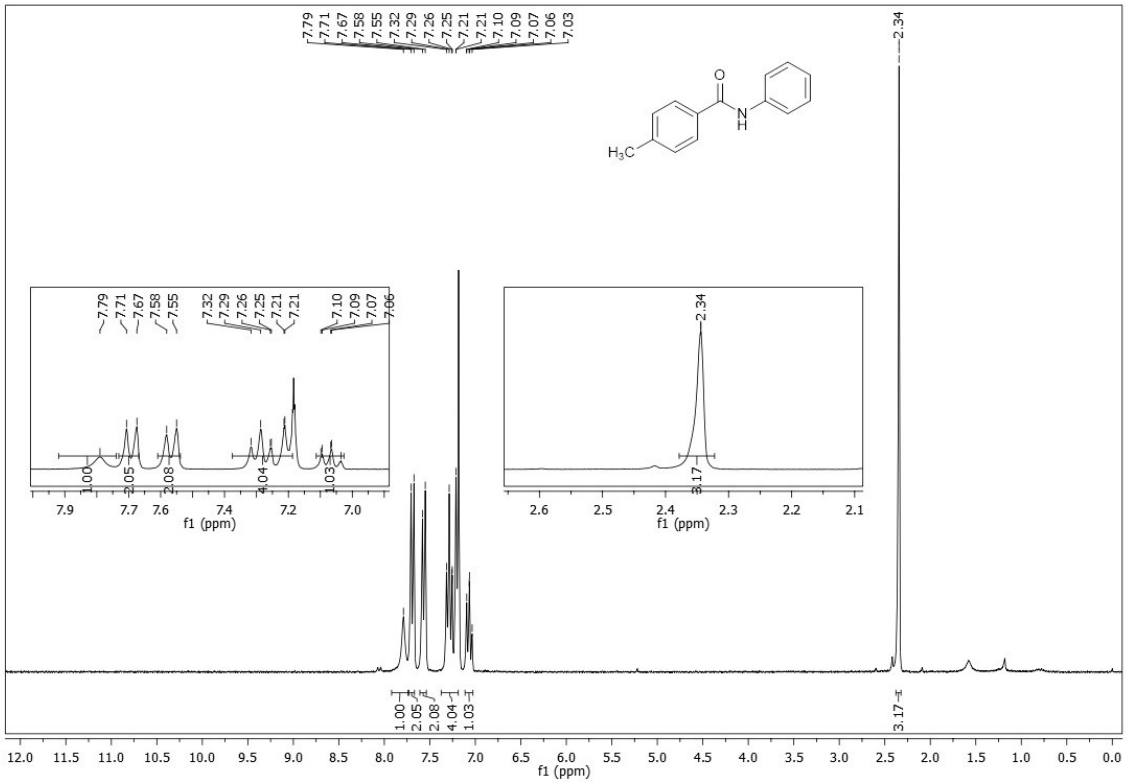
^{13}C-NMR of **3g**



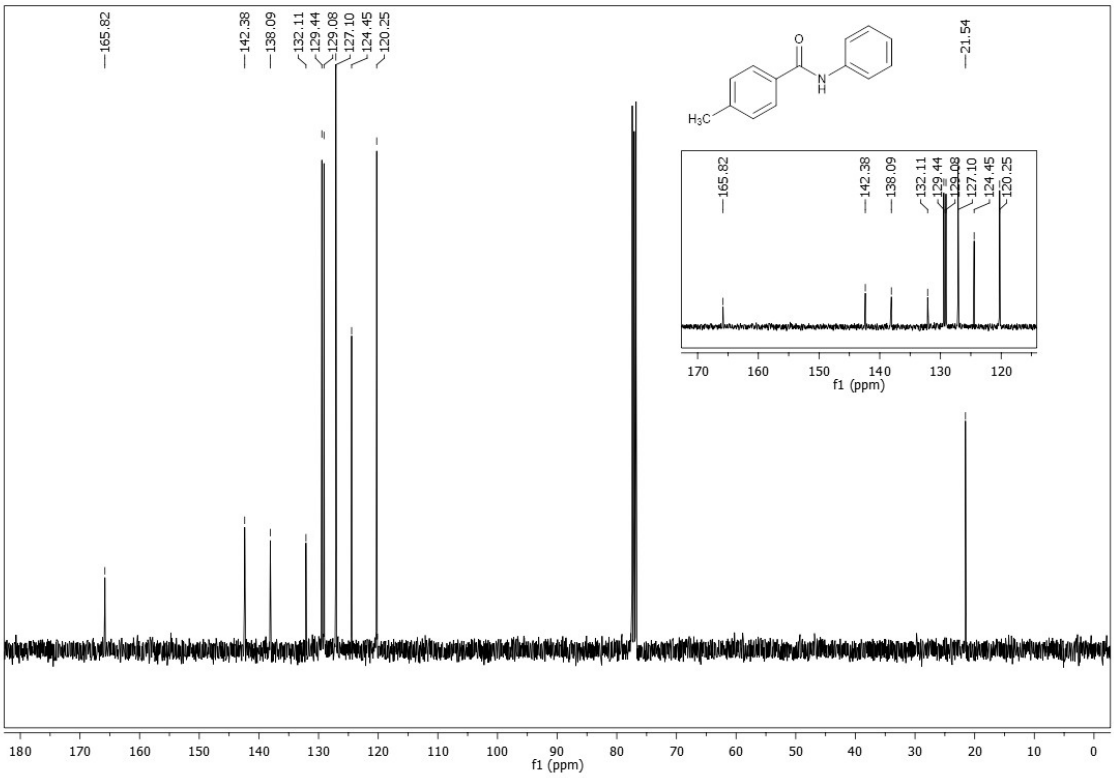
^{1}H-NMR of **3h**



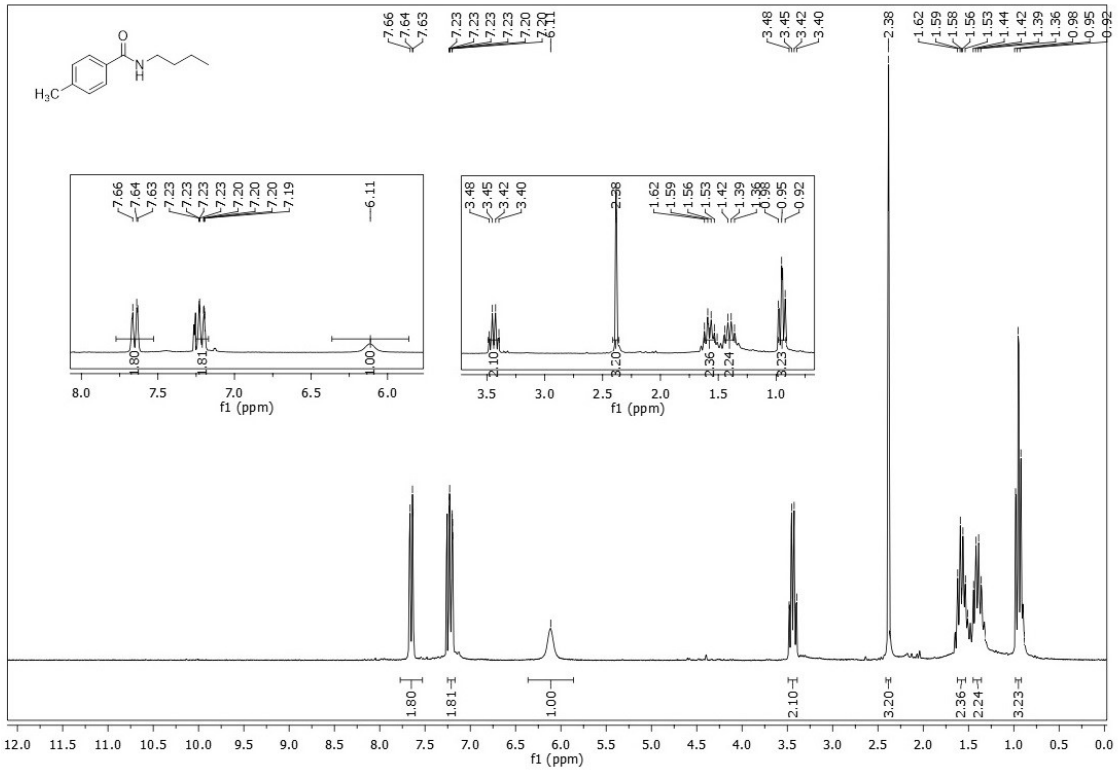
^{13}C-NMR of **3h**



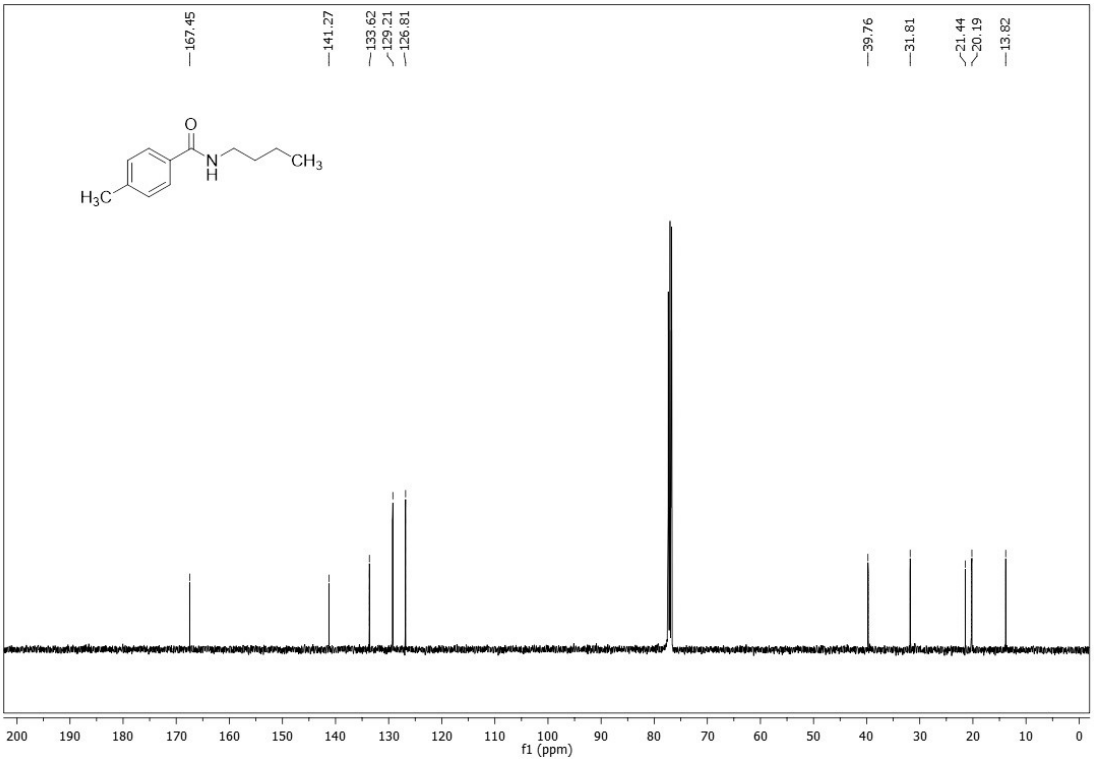
^{1}H-NMR of **3i**



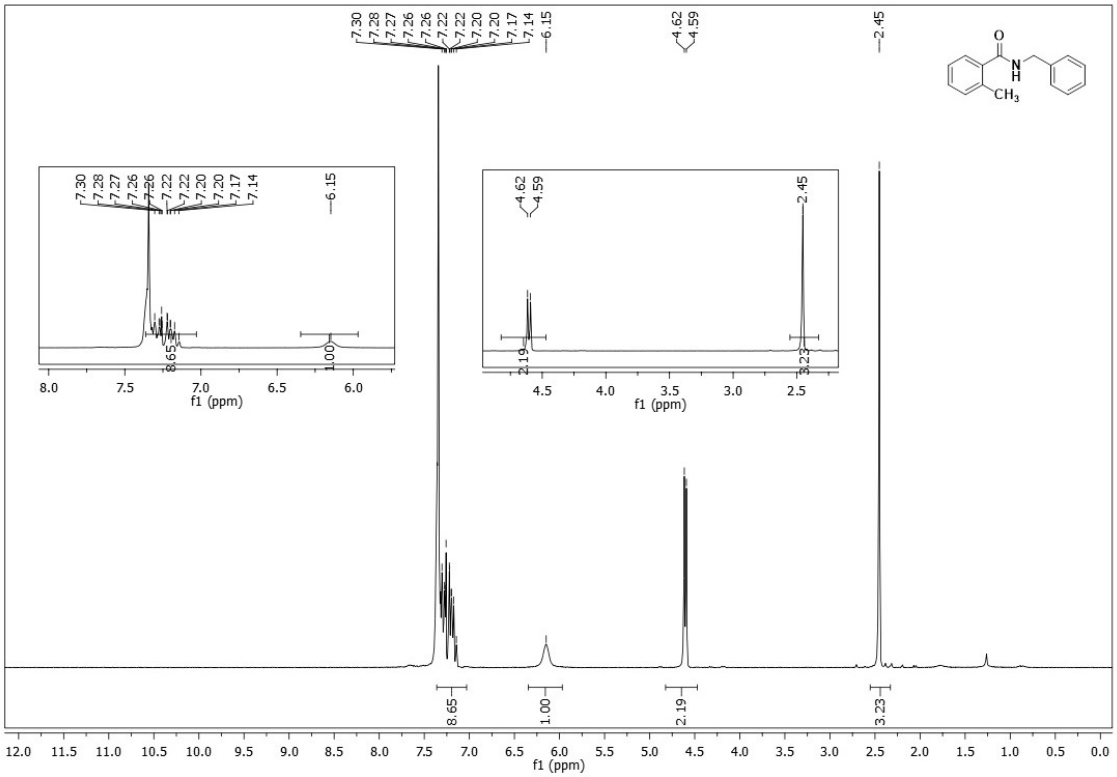
^{13}C-NMR of **3i**



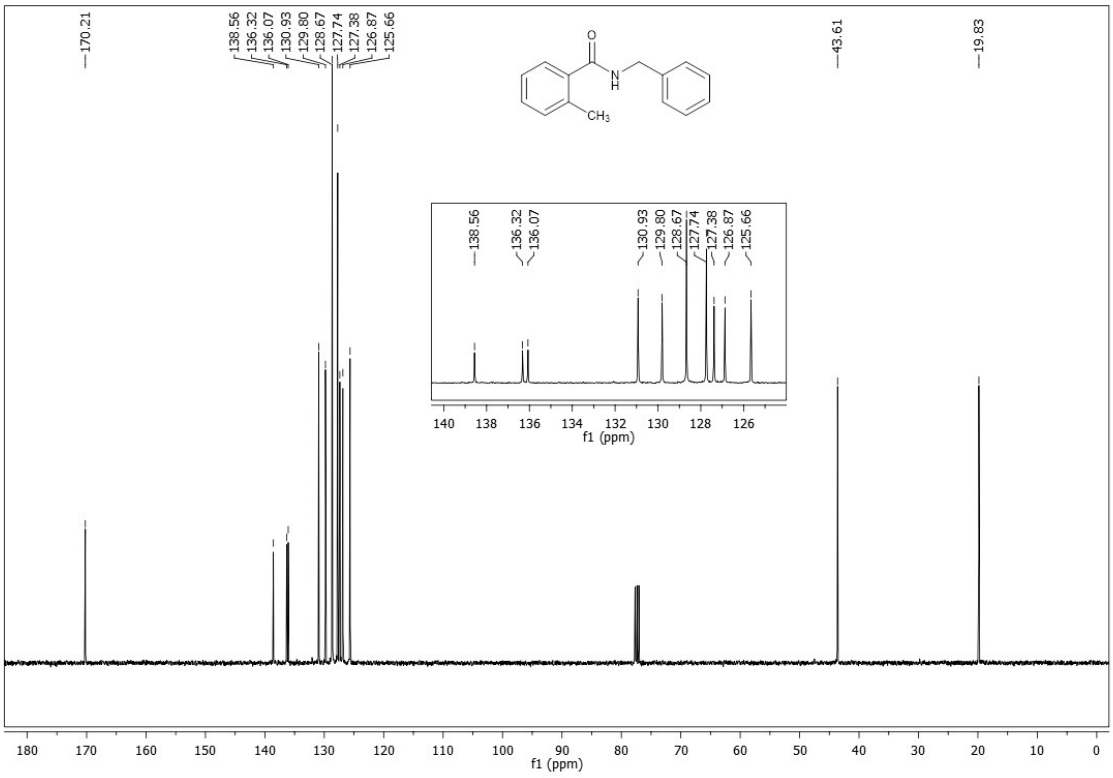
^{1}H-NMR of **3j**



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



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



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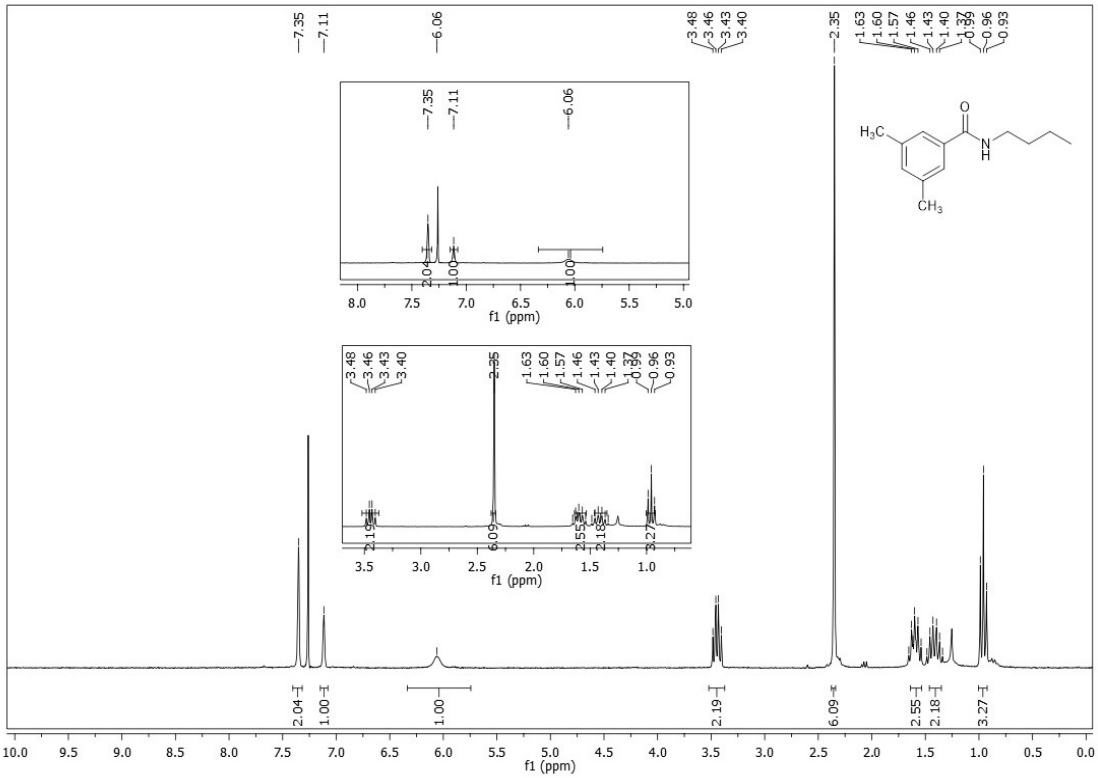
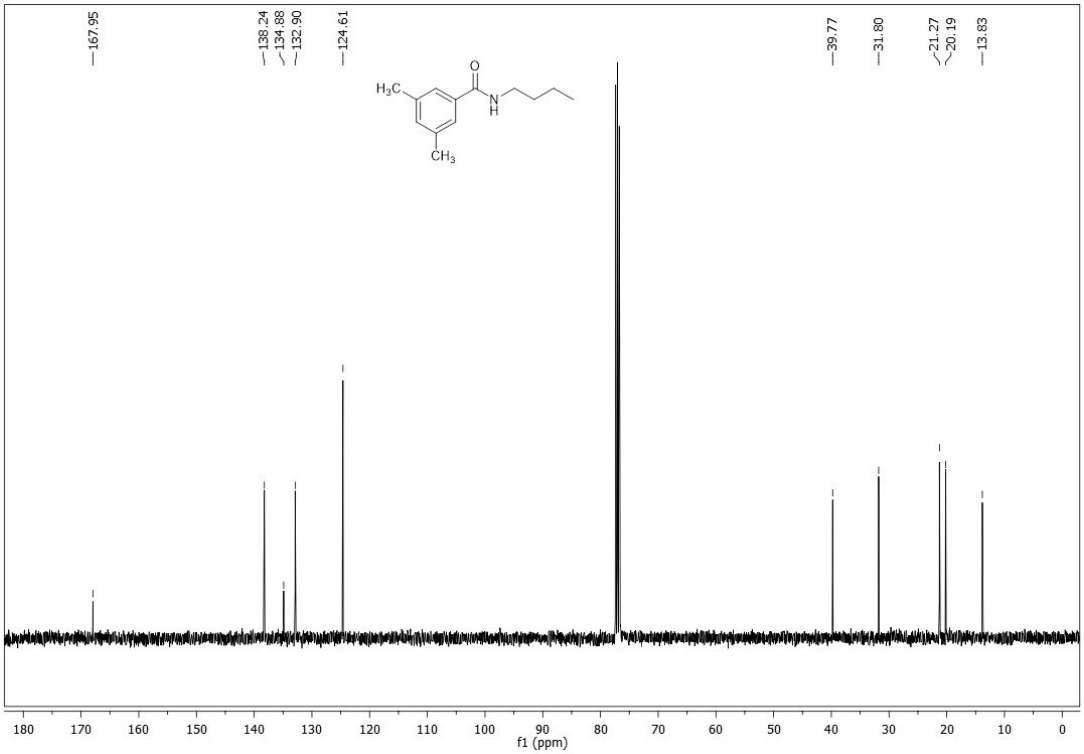
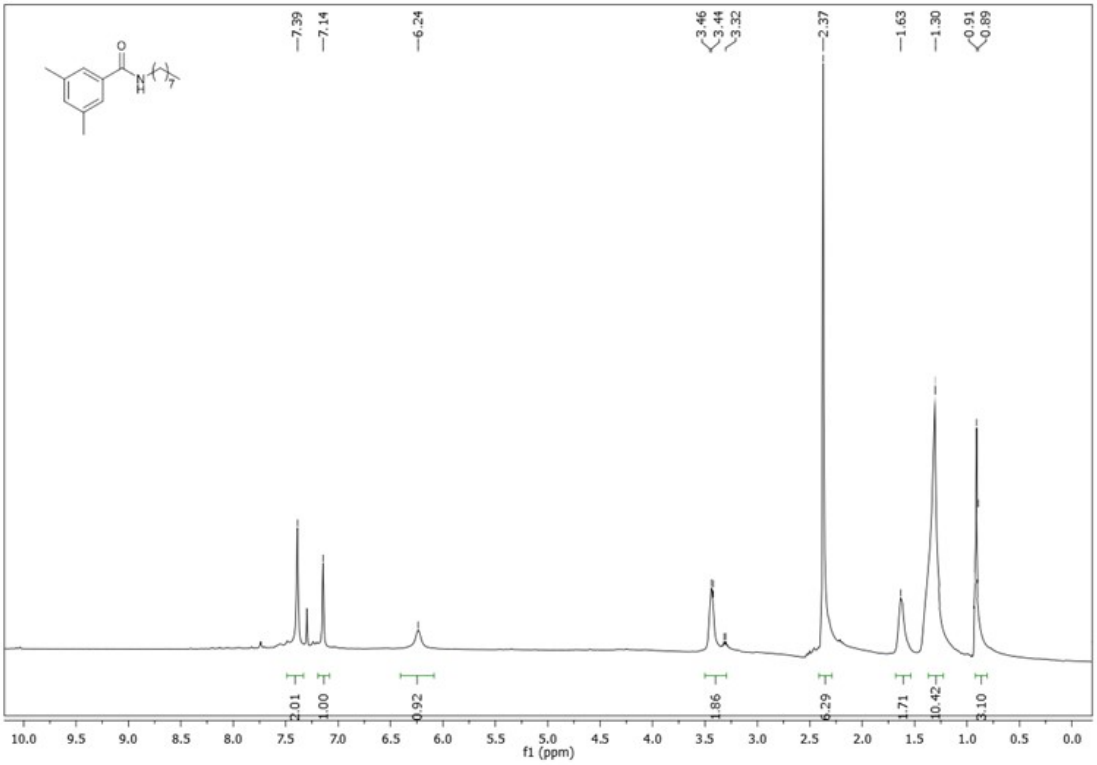


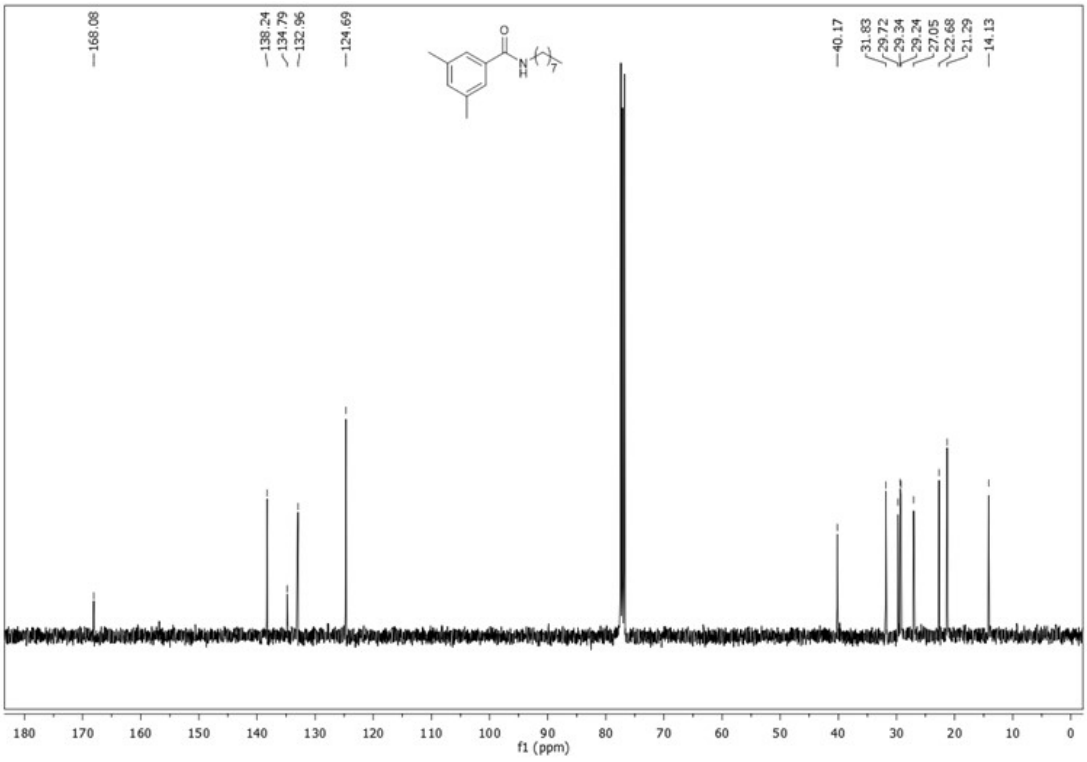
^{1}H-NMR of **3l**



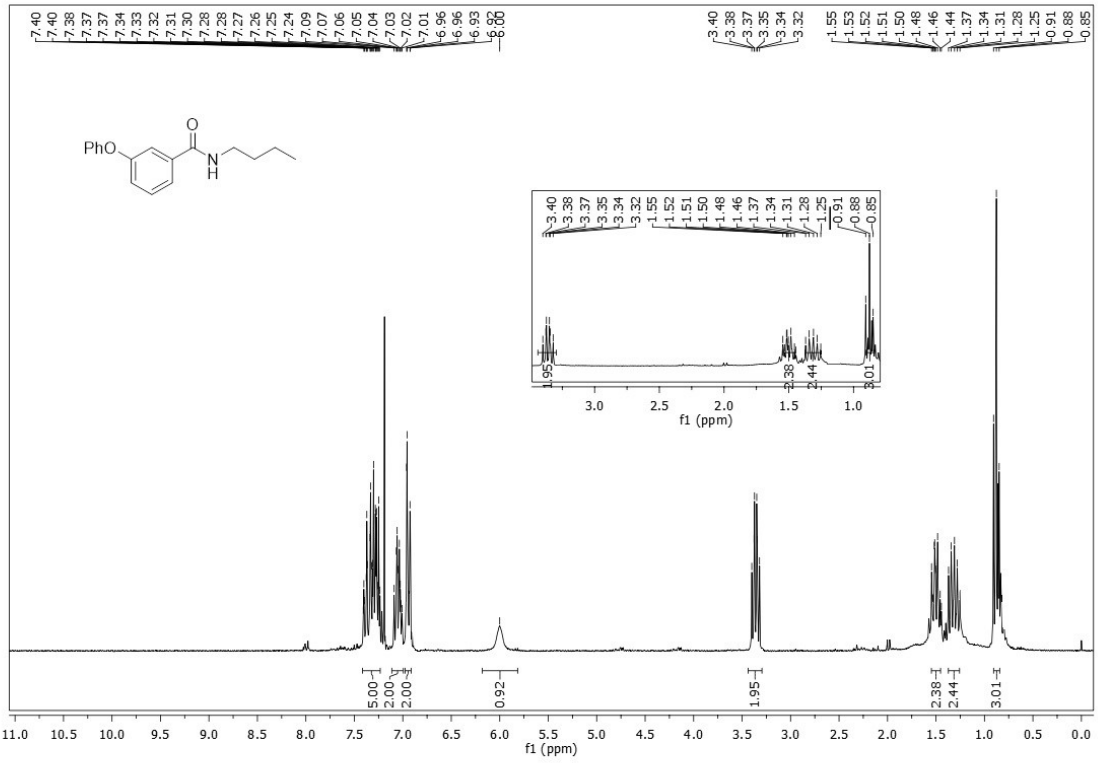
^{13}C-NMR of **3l**



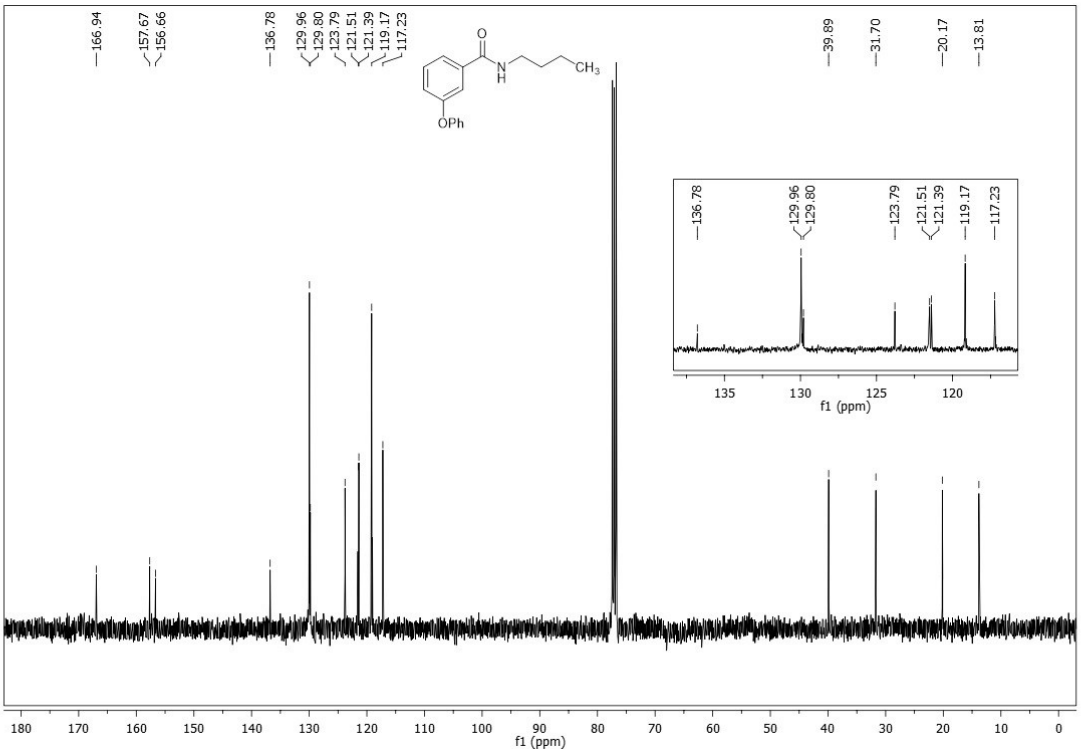
^{1}H-NMR of **3m**



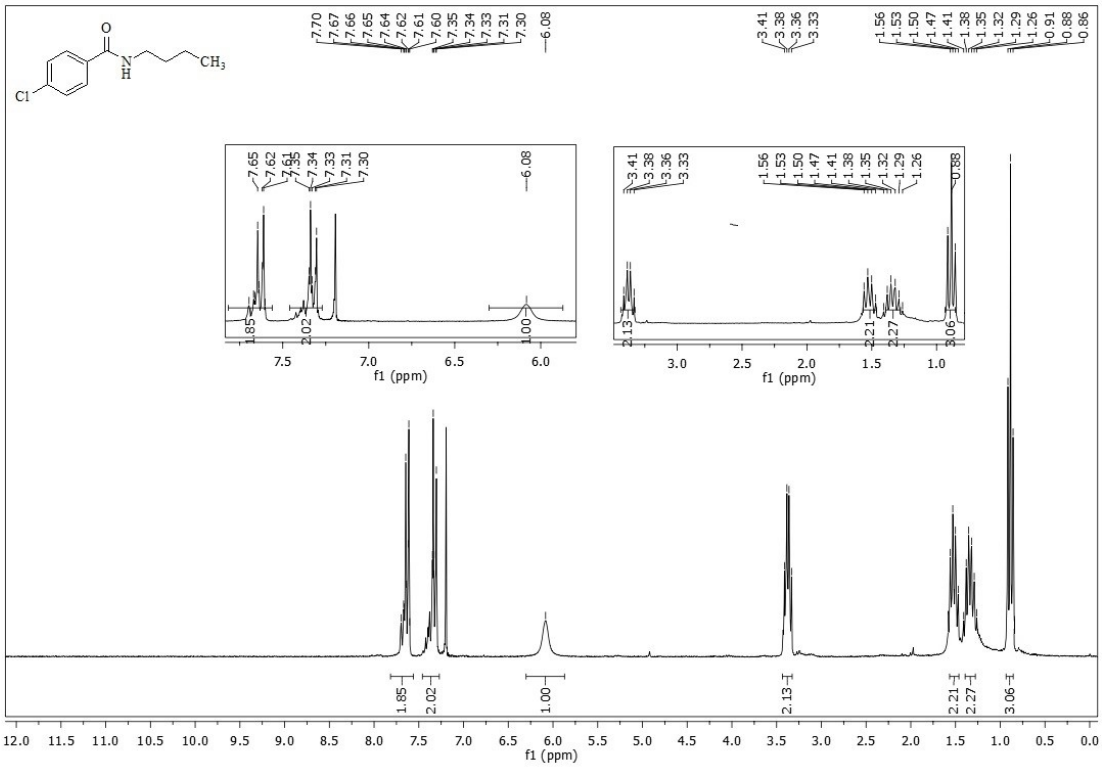
^{13}C-NMR of **3m**



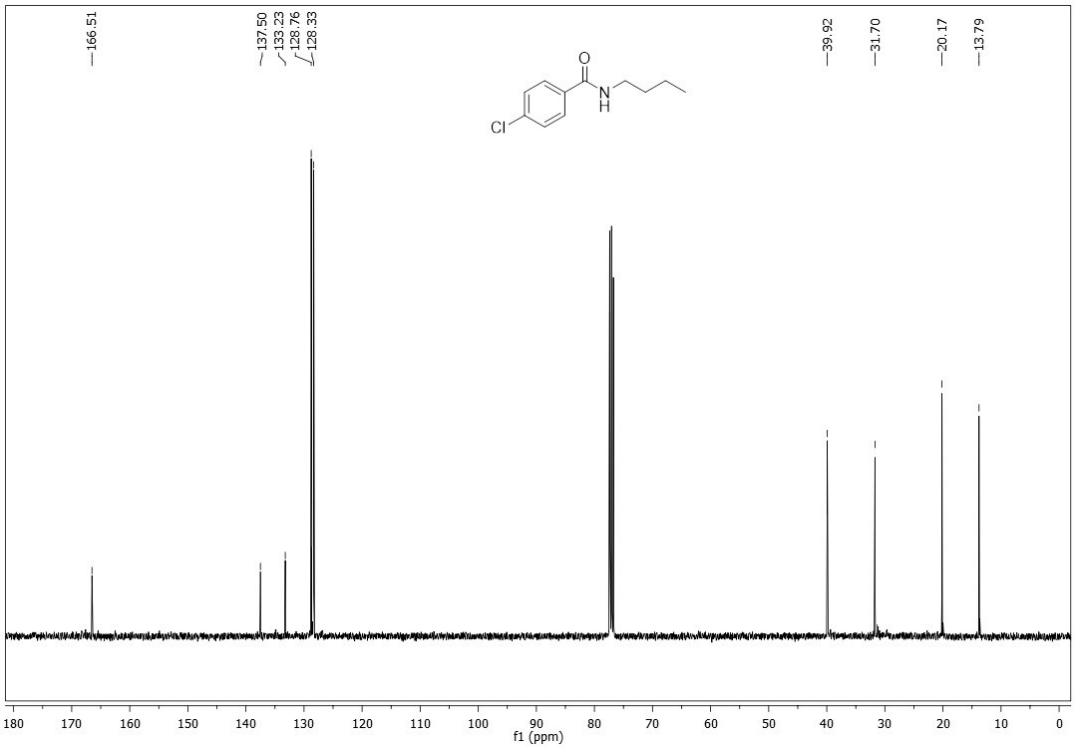
^{1}H-NMR of **3n**



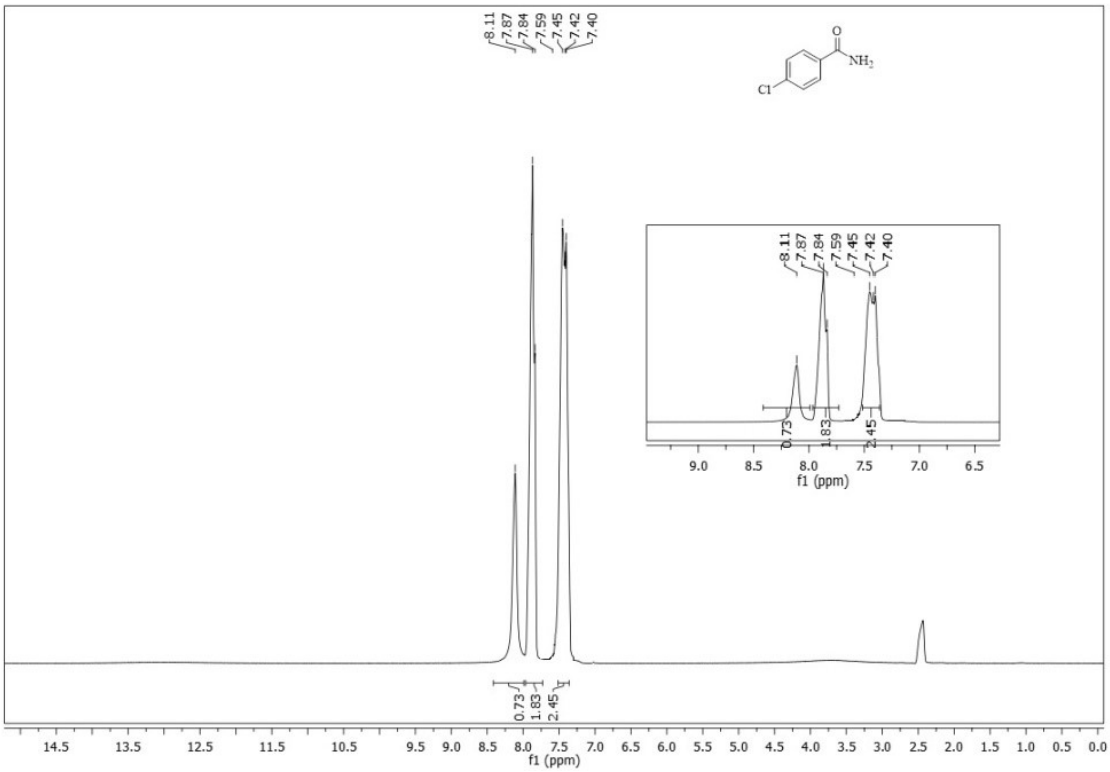
^{13}C-NMR of **3n**



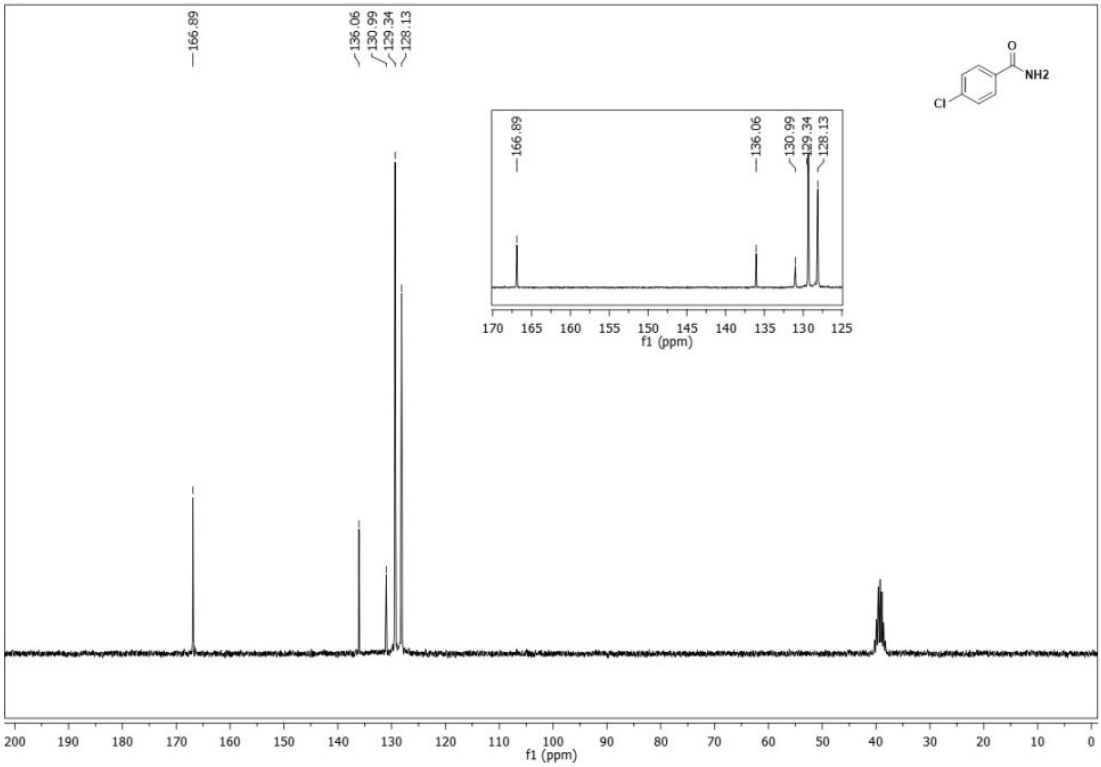
^{1}H-NMR of **3o**



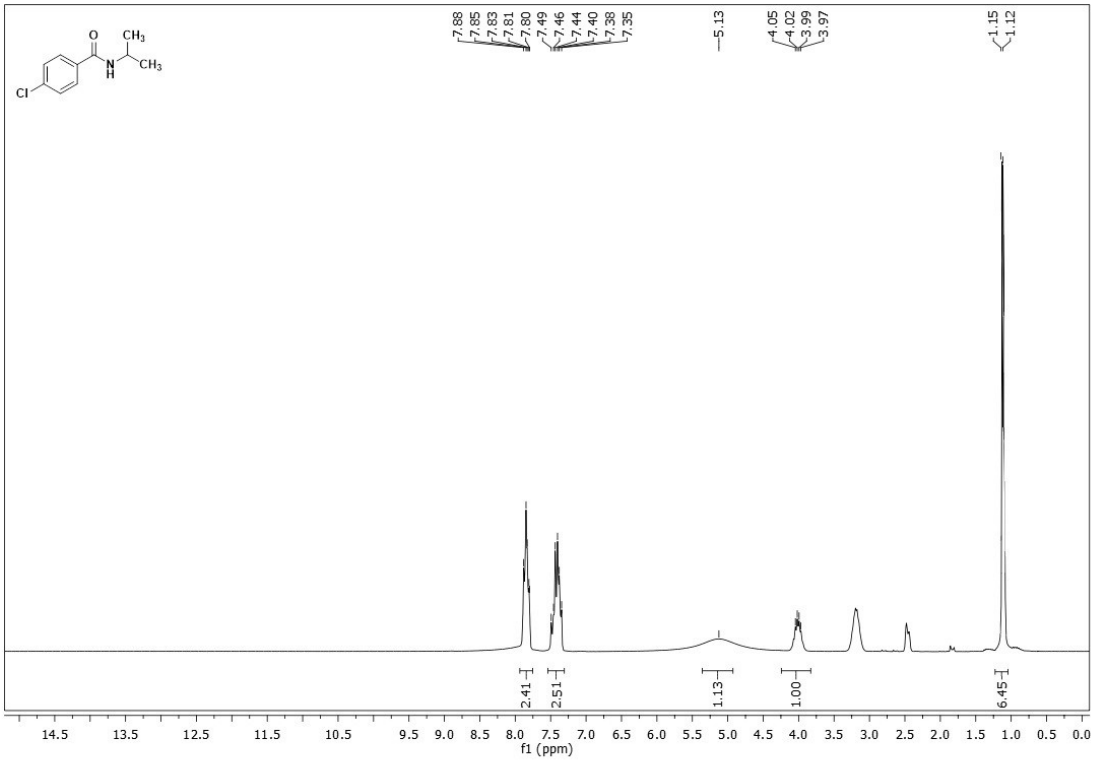
^{13}C-NMR of **3o**



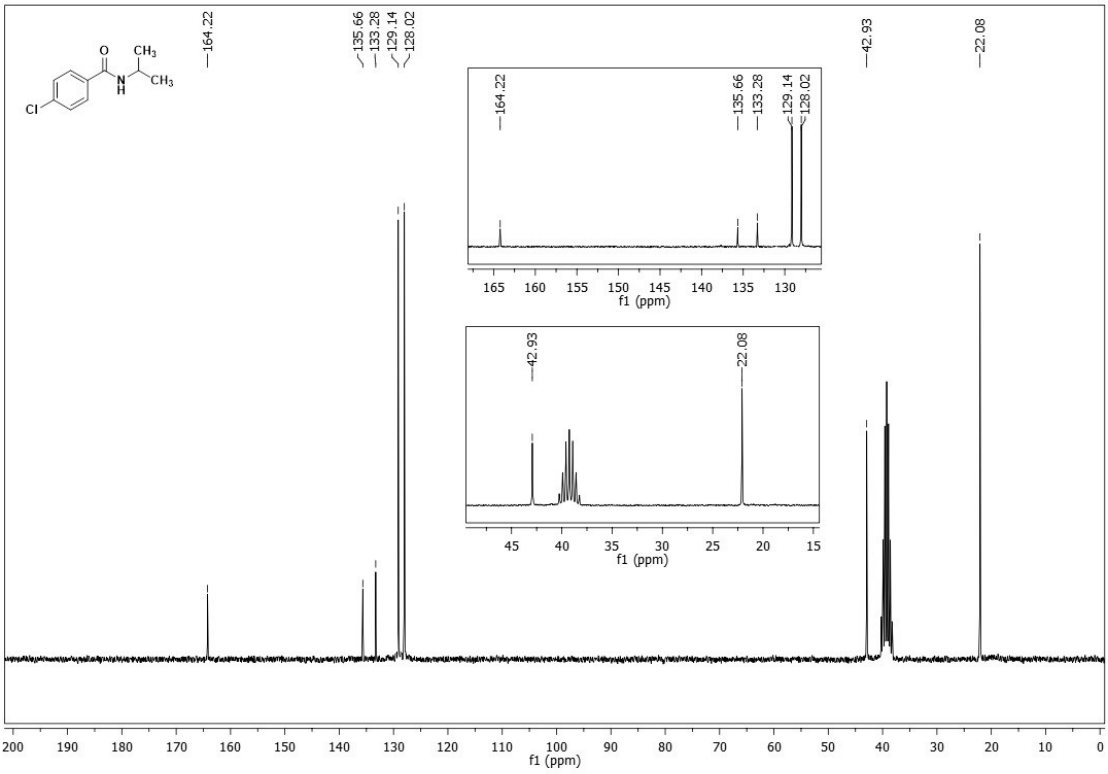
^{1}H-NMR of **3p**



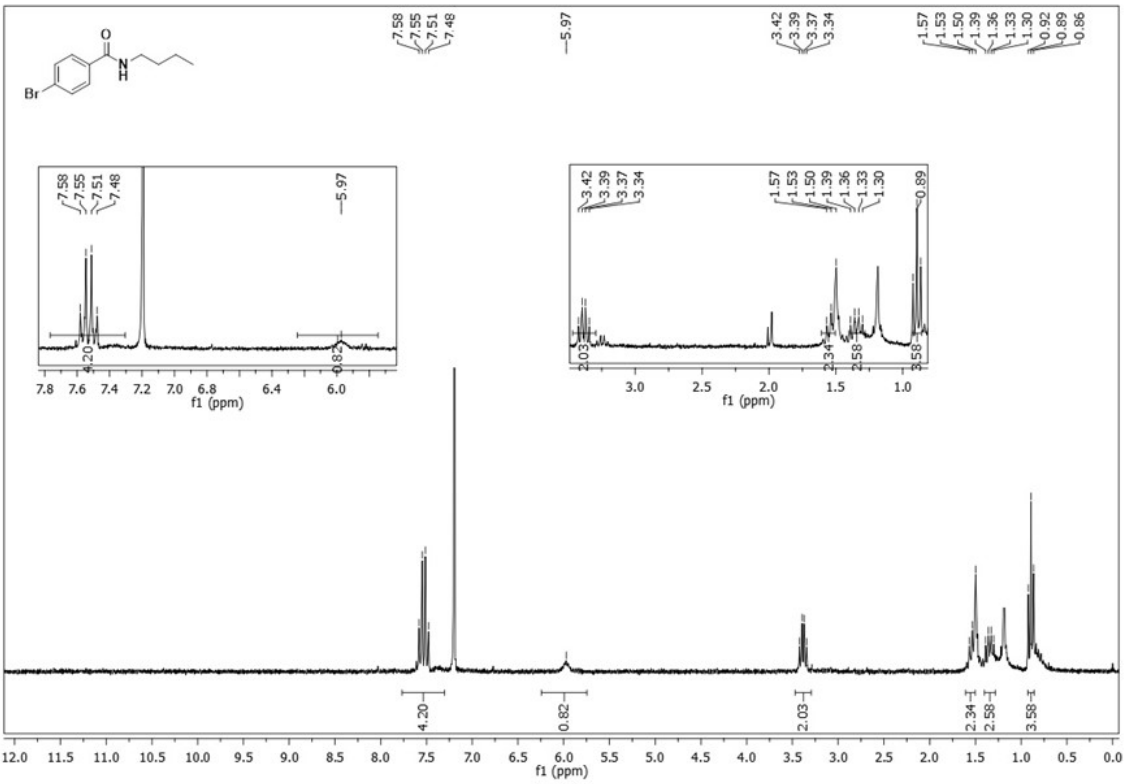
^{13}C-NMR of **3p**



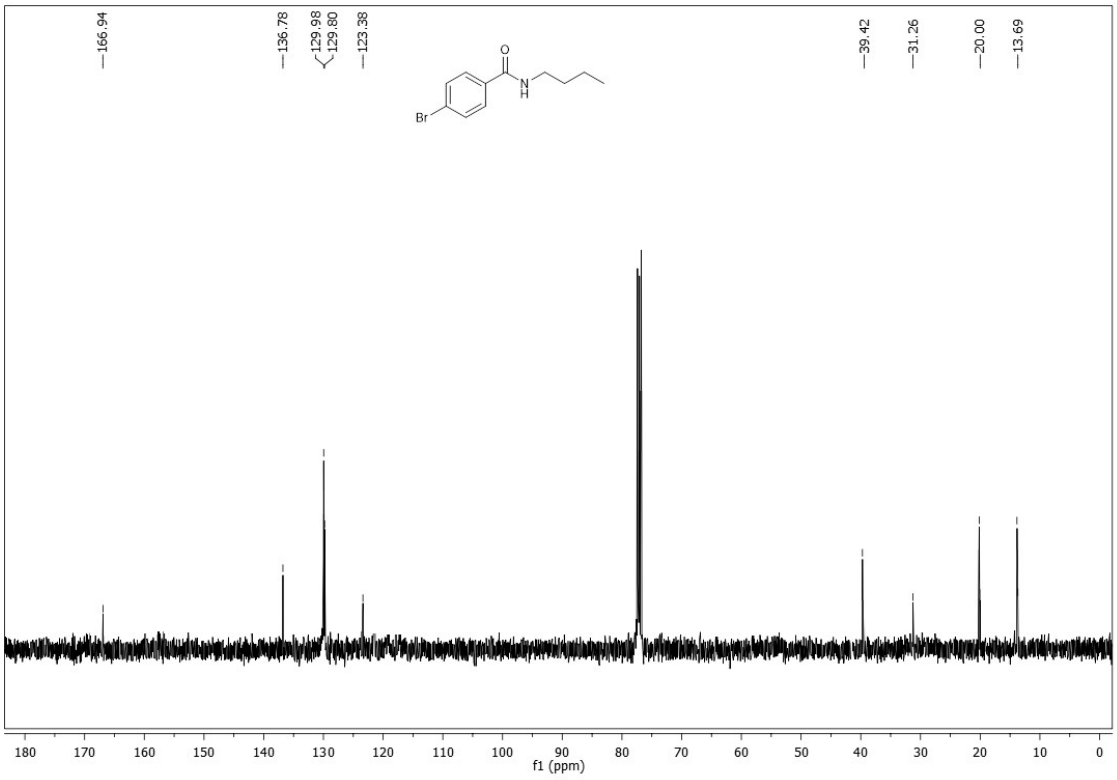
^{1}H-NMR of **3q**



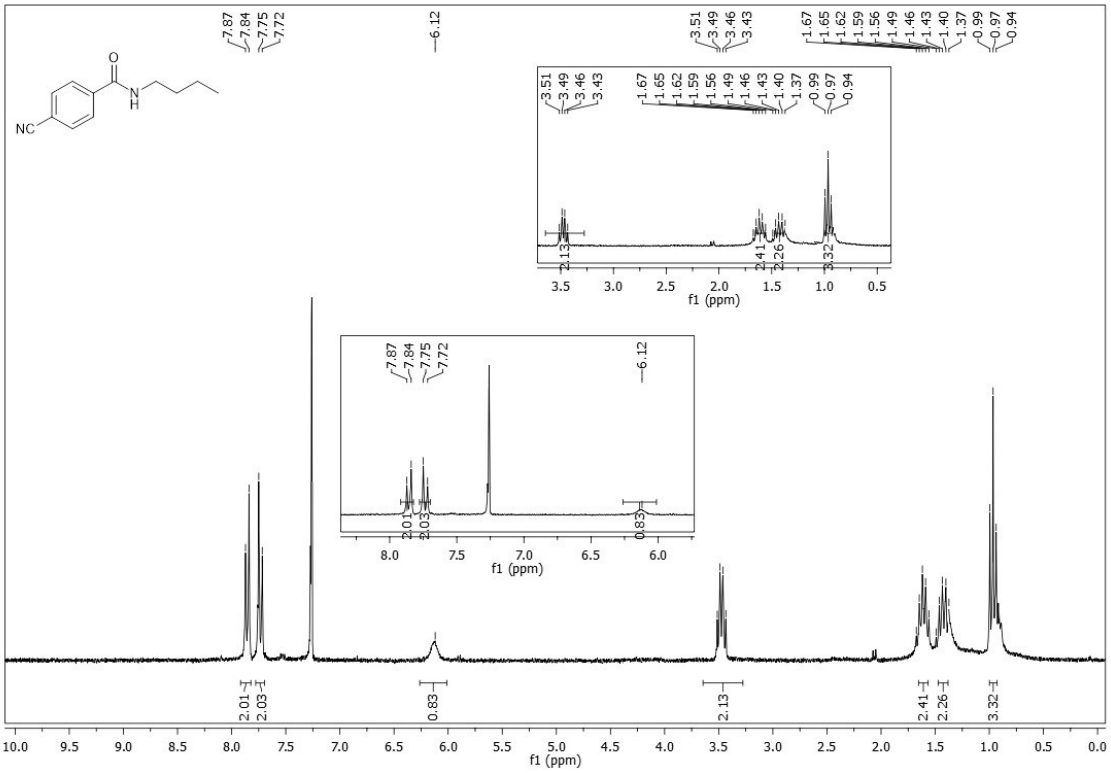
^{13}C-NMR of **3q**



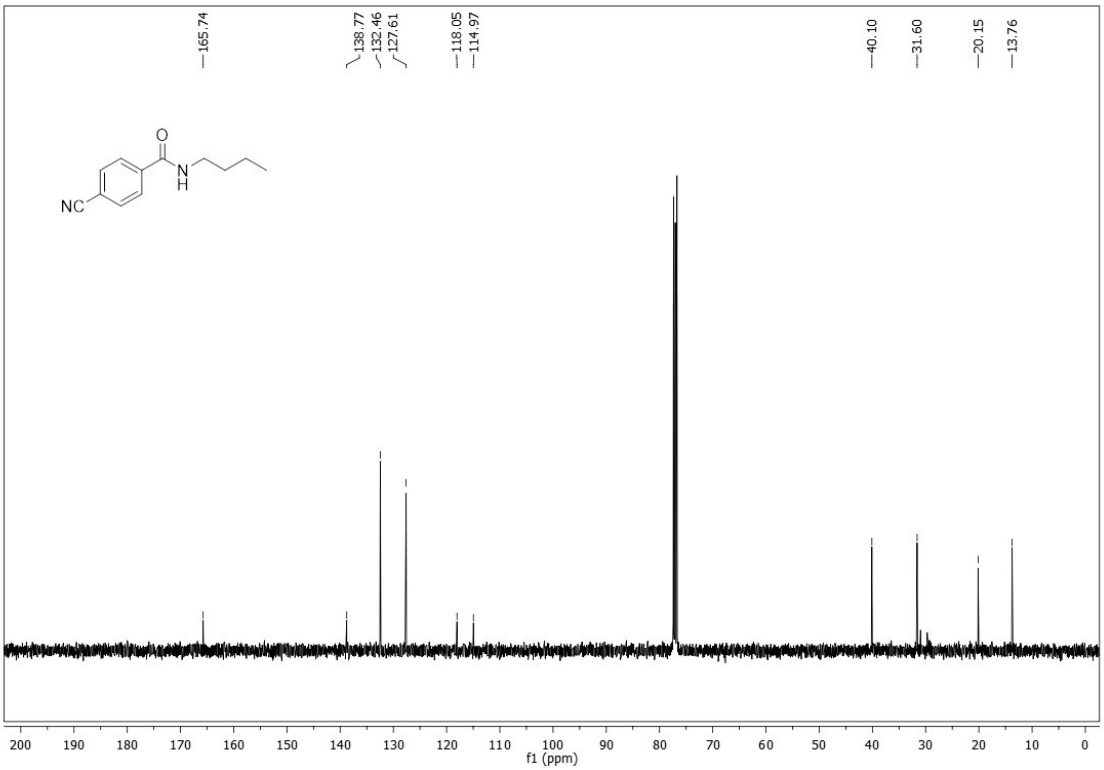
^{1}H-NMR of **3r**



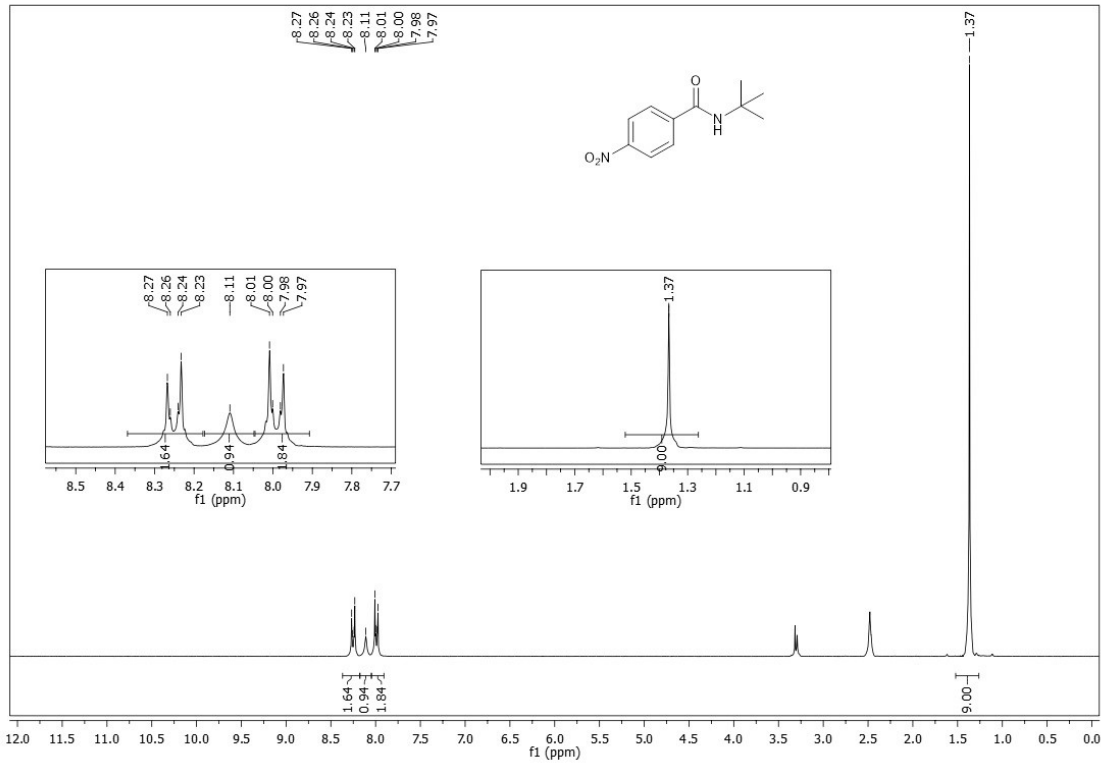
^{13}C-NMR of **3r**



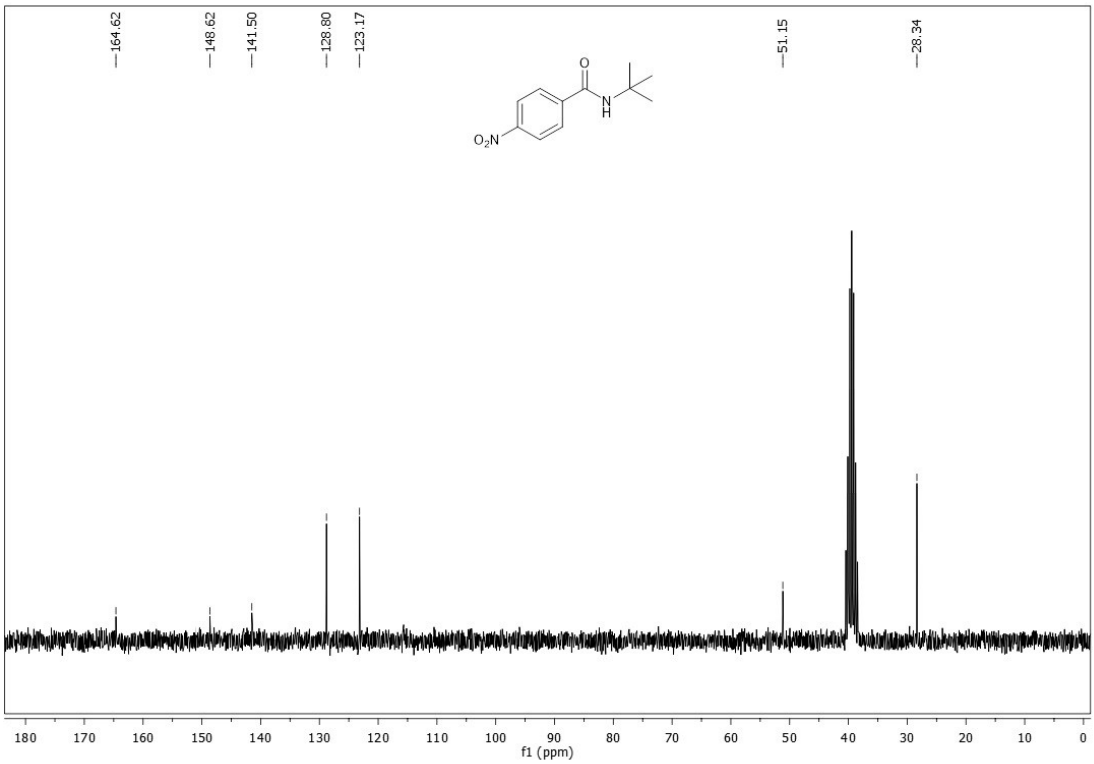
^{1}H-NMR of **3s**



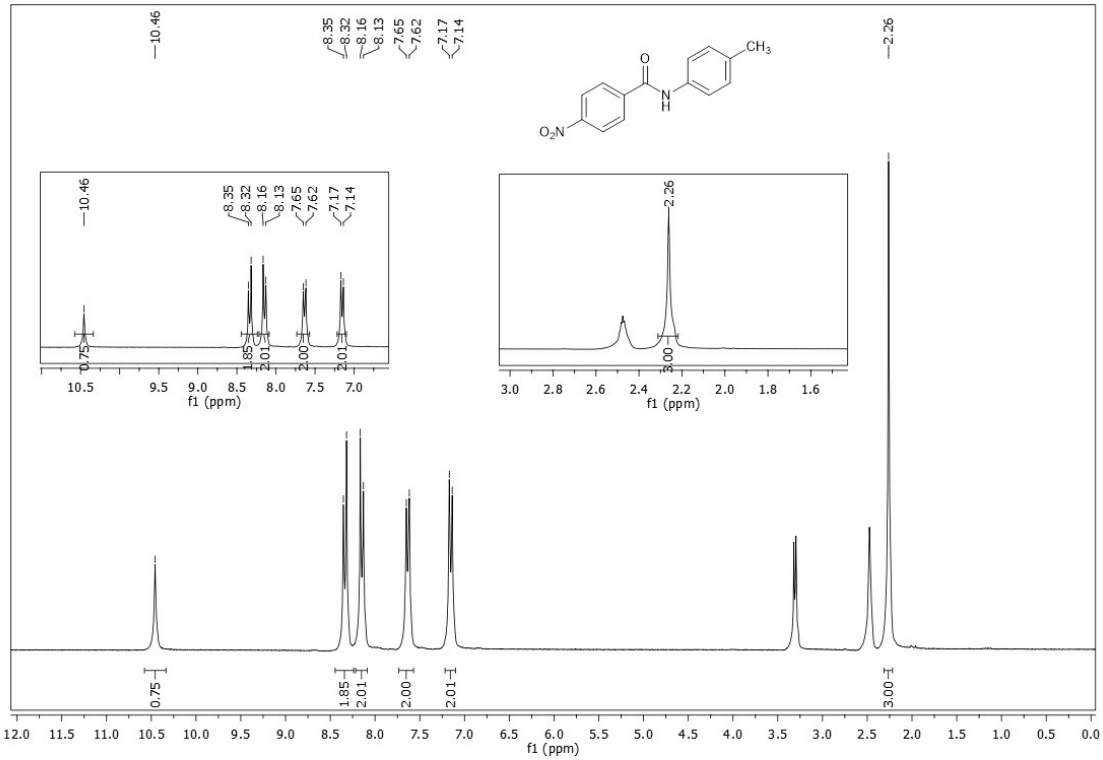
^{13}C-NMR of **3s**



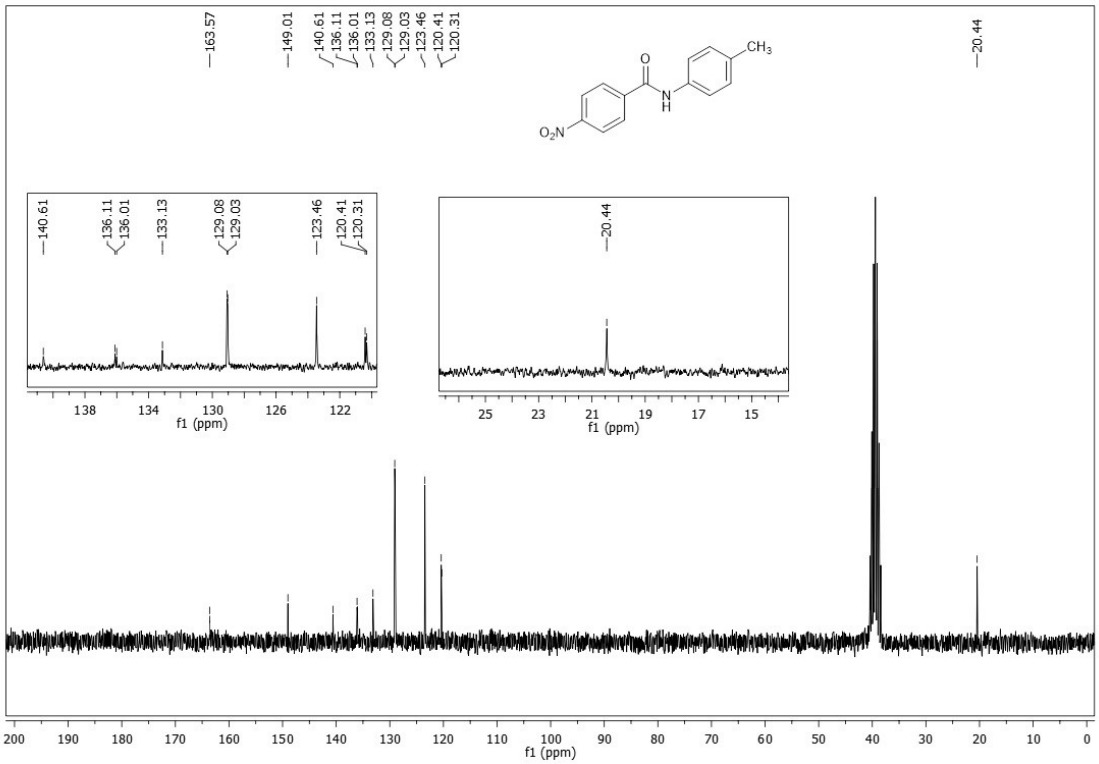
^{1}H-NMR of **3t**



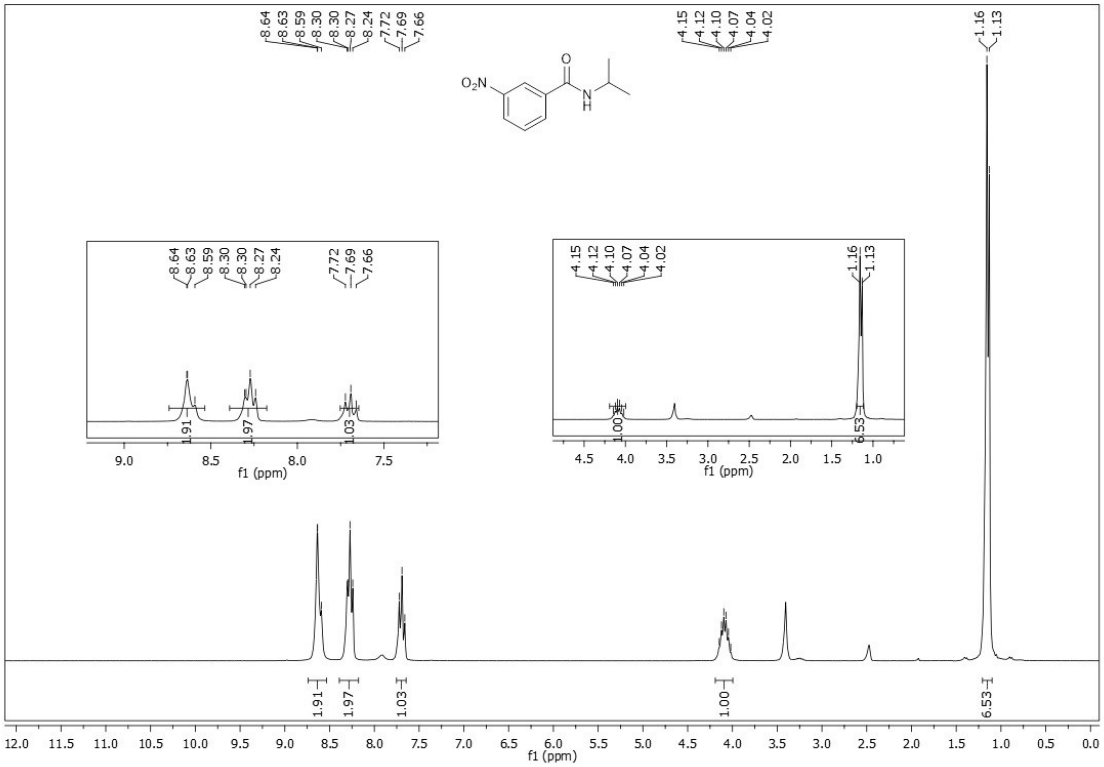
^{13}C-NMR of **3t**



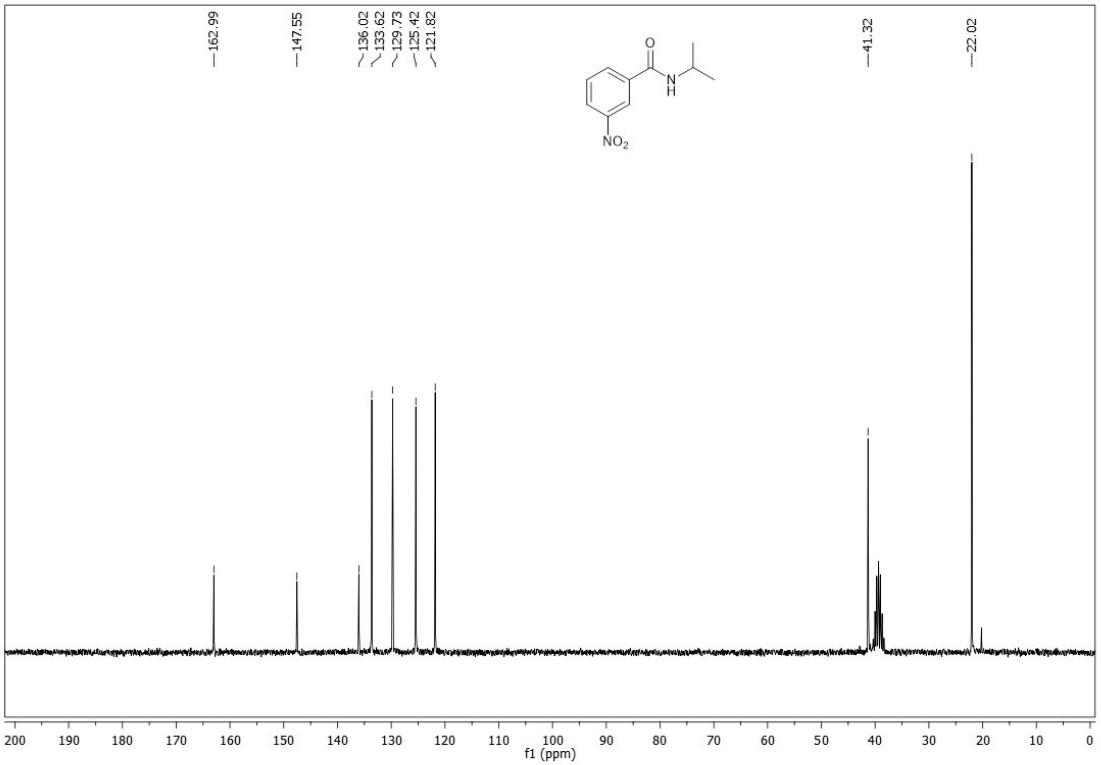
^{1}H-NMR of **3u**



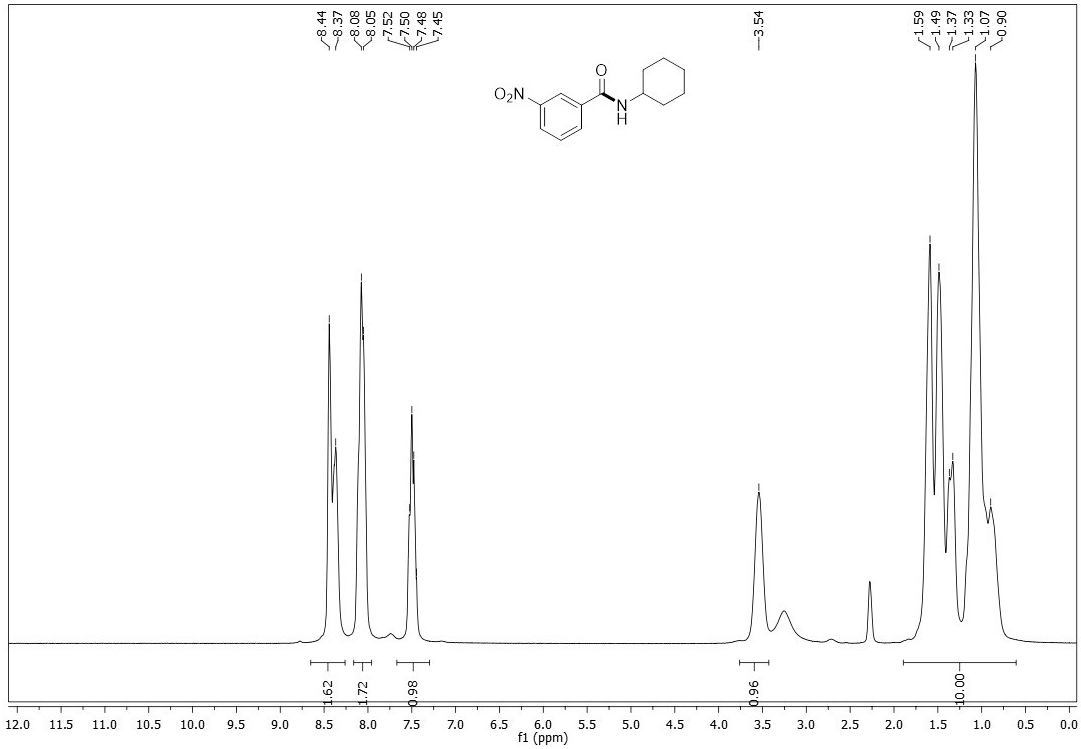
^{13}C-NMR of **3u**



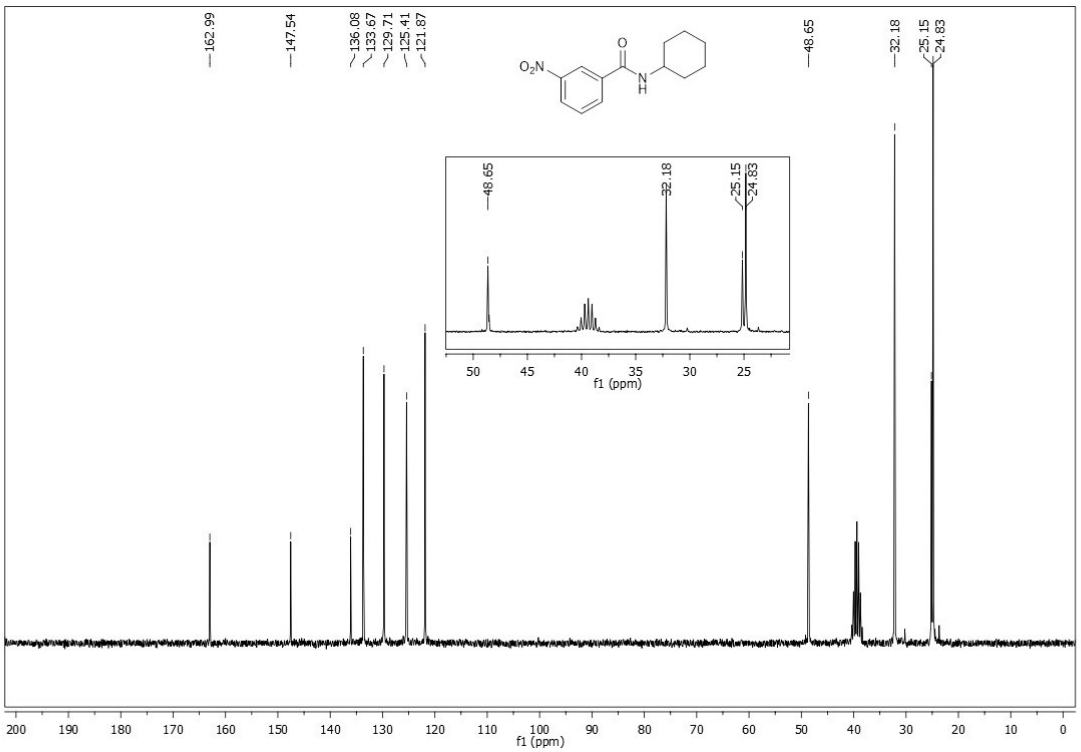
^{1}H-NMR of **3v**



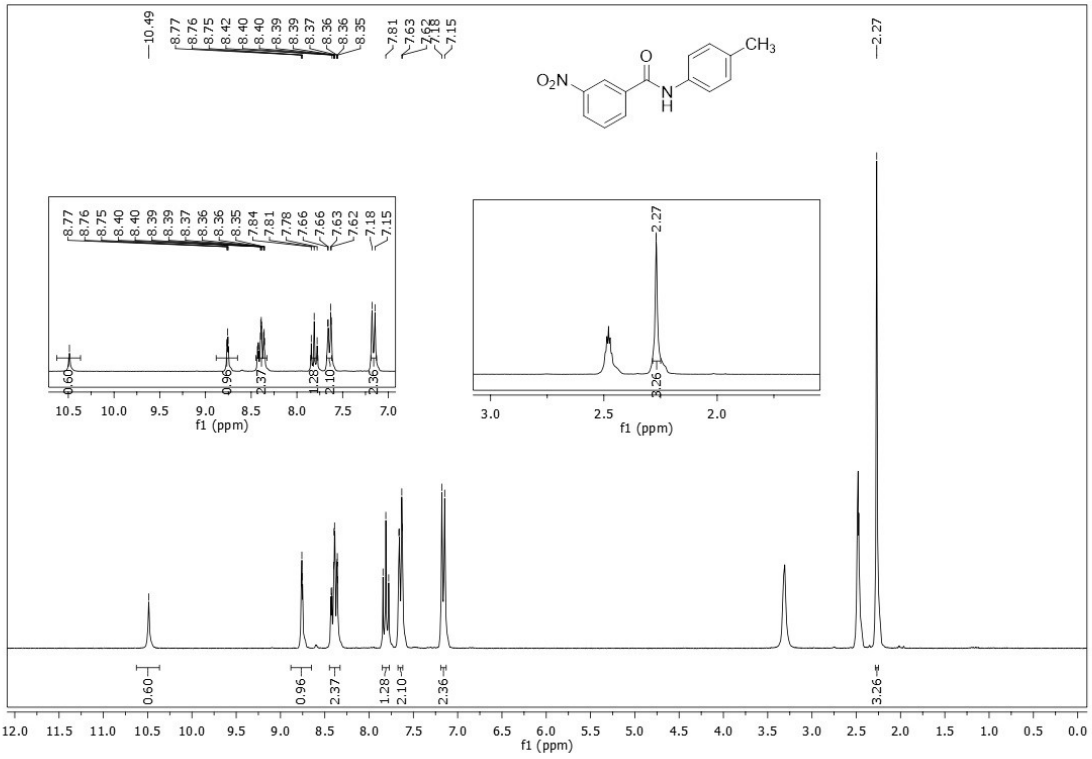
^{13}C-NMR of **3v**



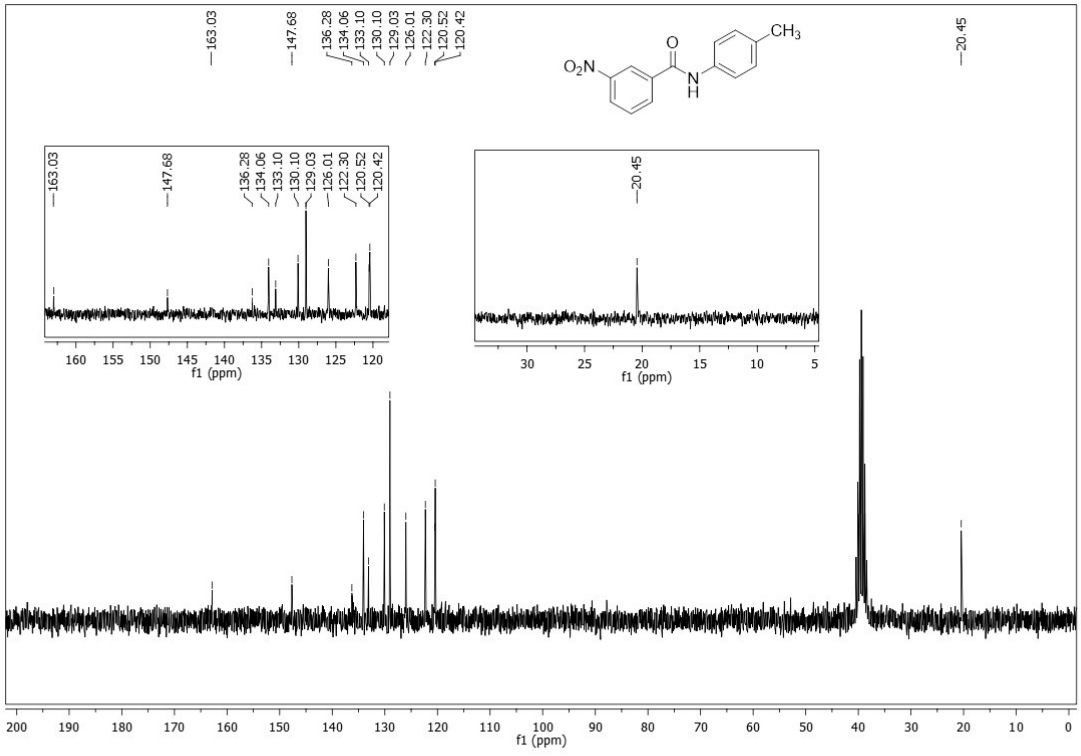
^{1}H-NMR of **3w**



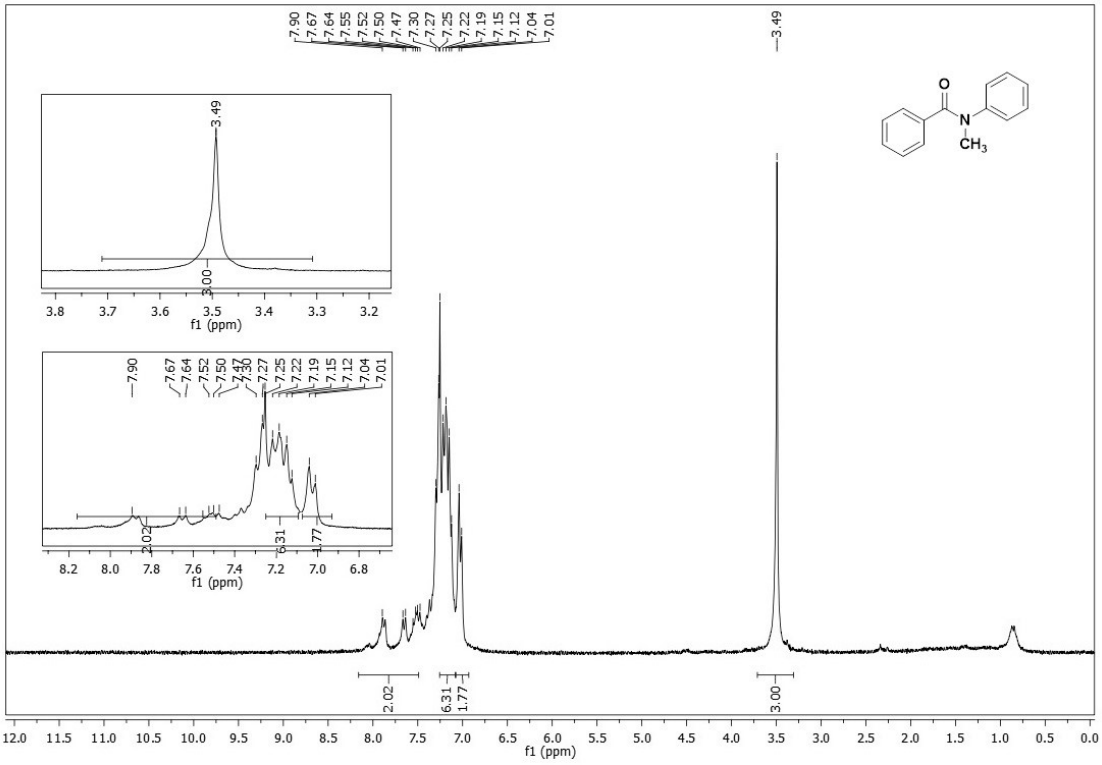
^{13}C-NMR of **3w**



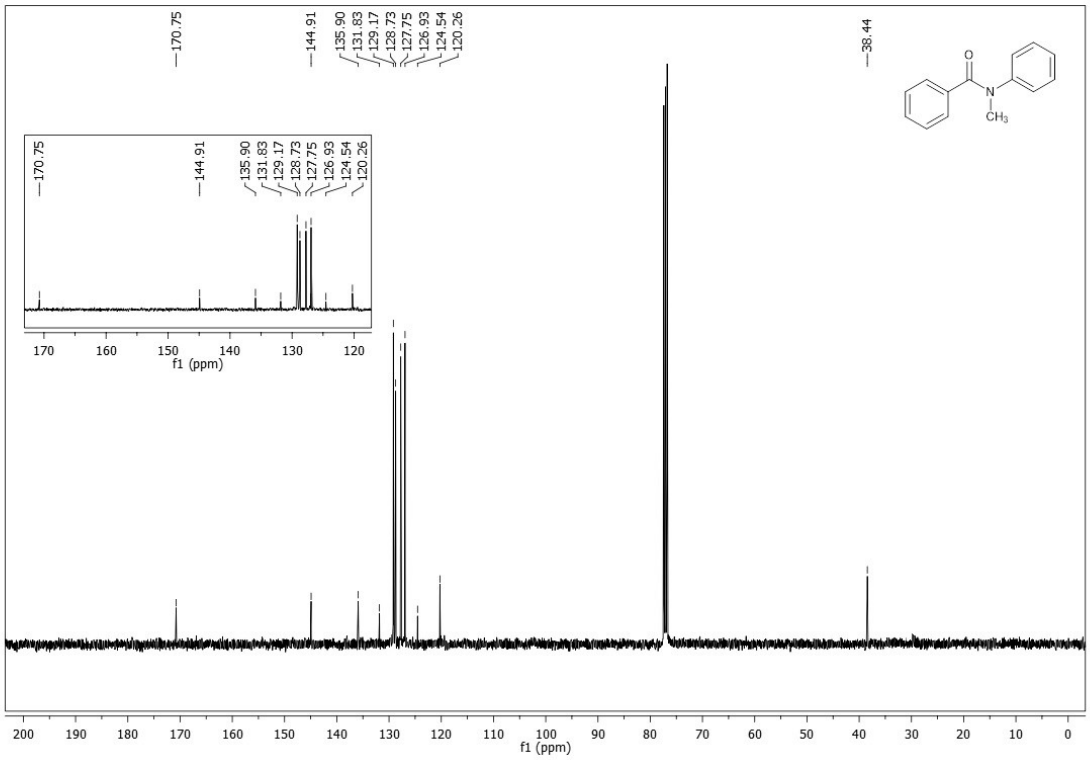
^{1}H-NMR of **3x**



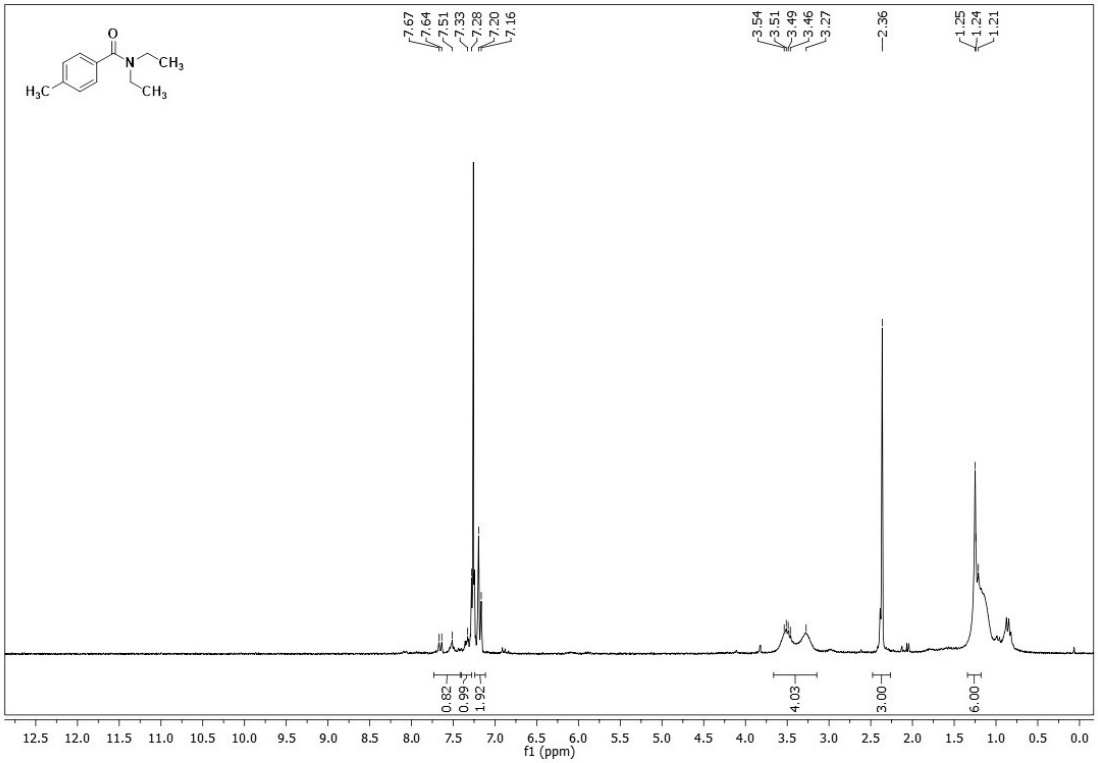
^{13}C-NMR of **3x**



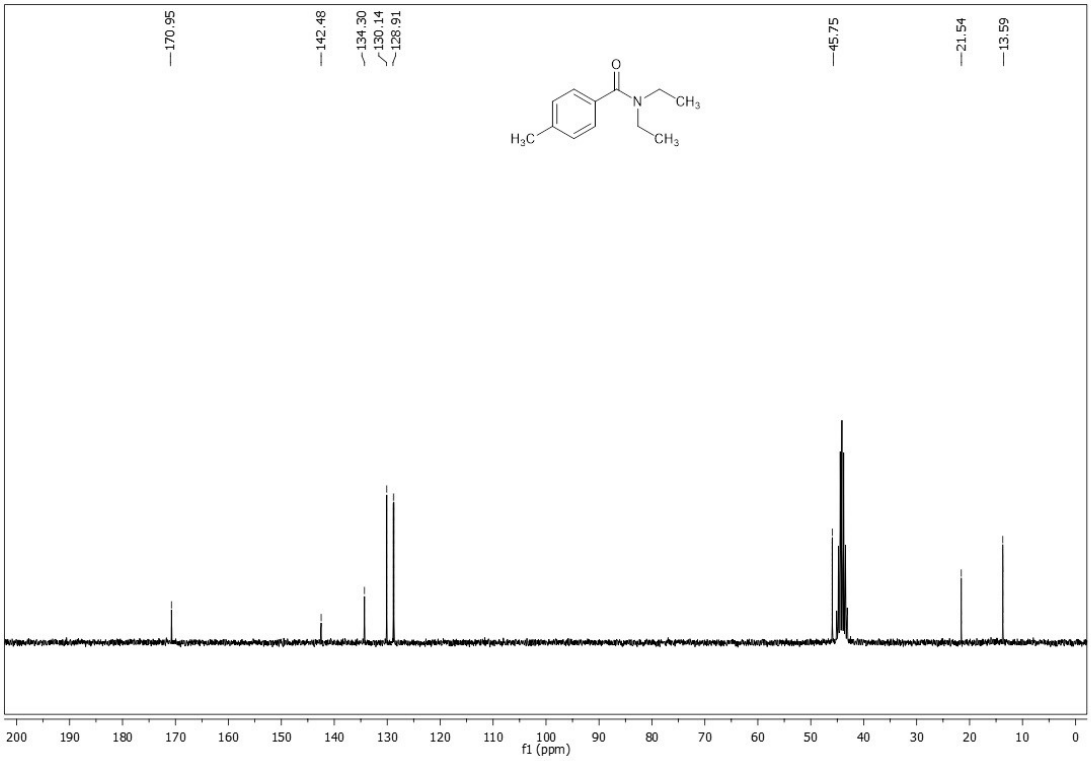
^{1}H-NMR of **3y**



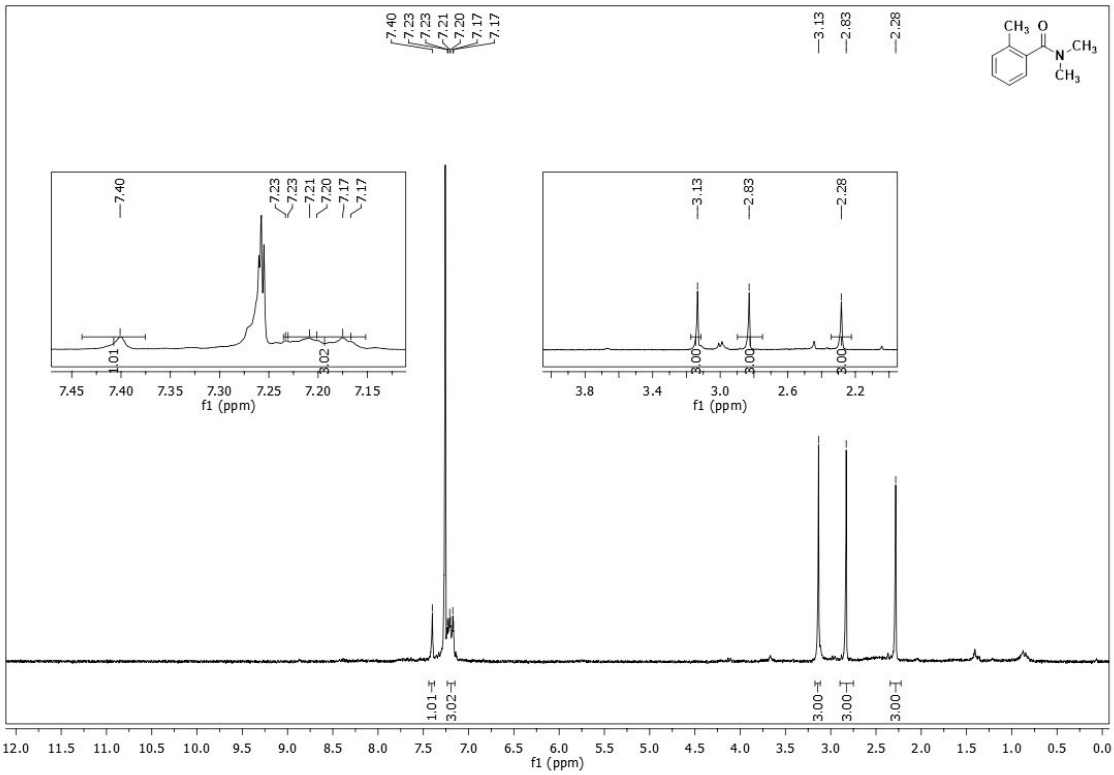
^{13}C-NMR of **3y**



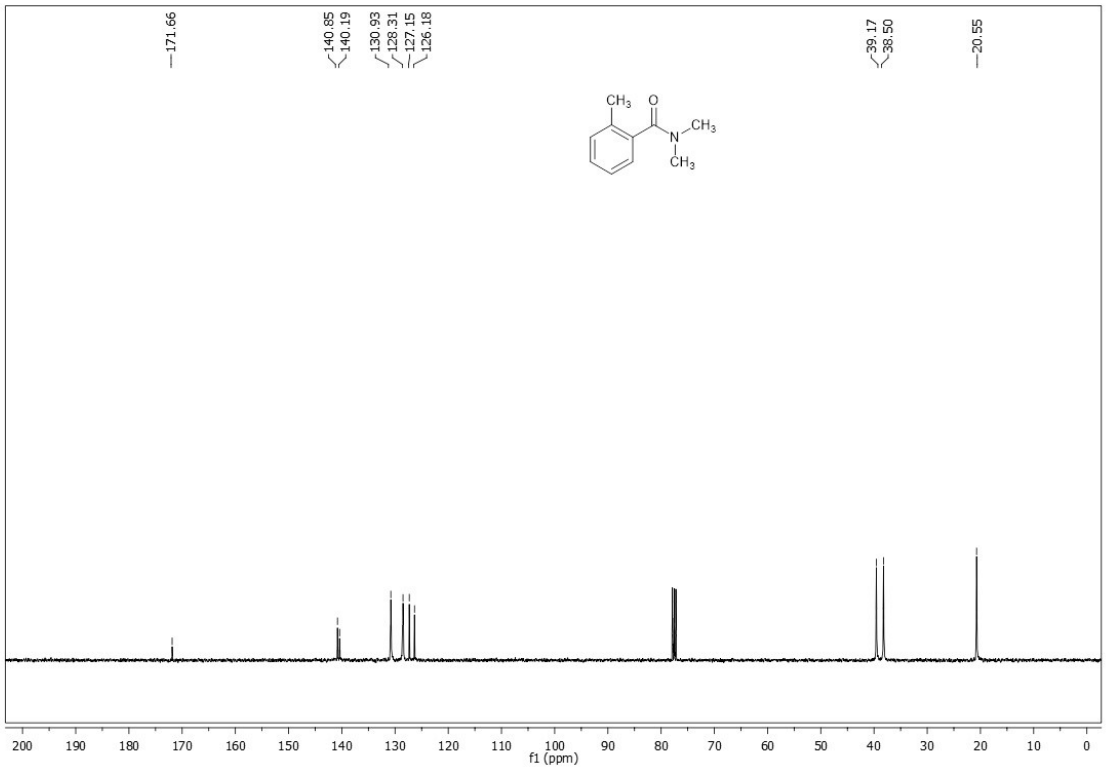
^{1}H-NMR of **3z**



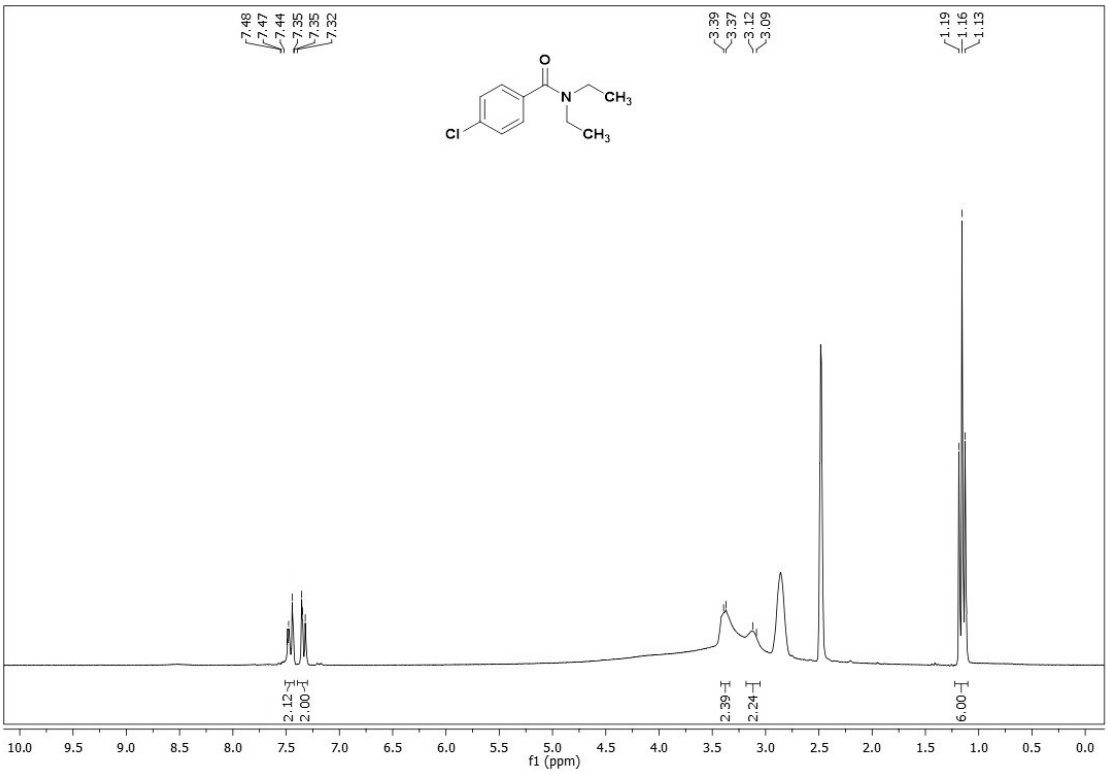
^{13}C-NMR of **3z**



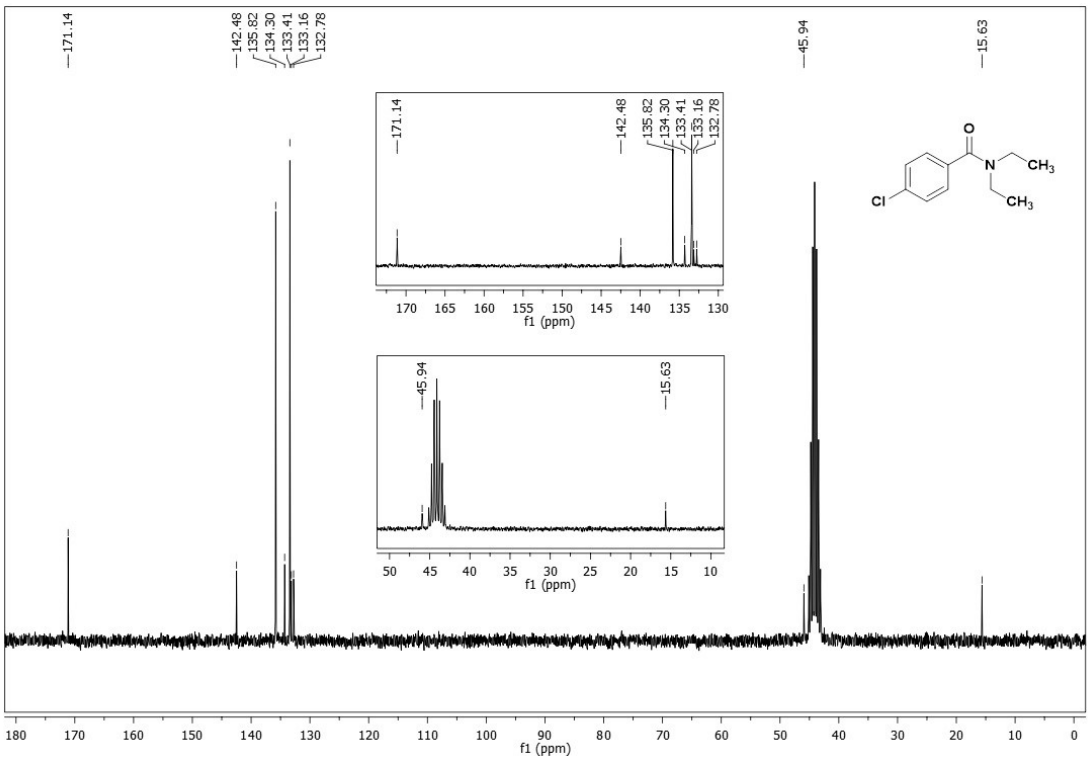
^{1}H-NMR of **3z1**



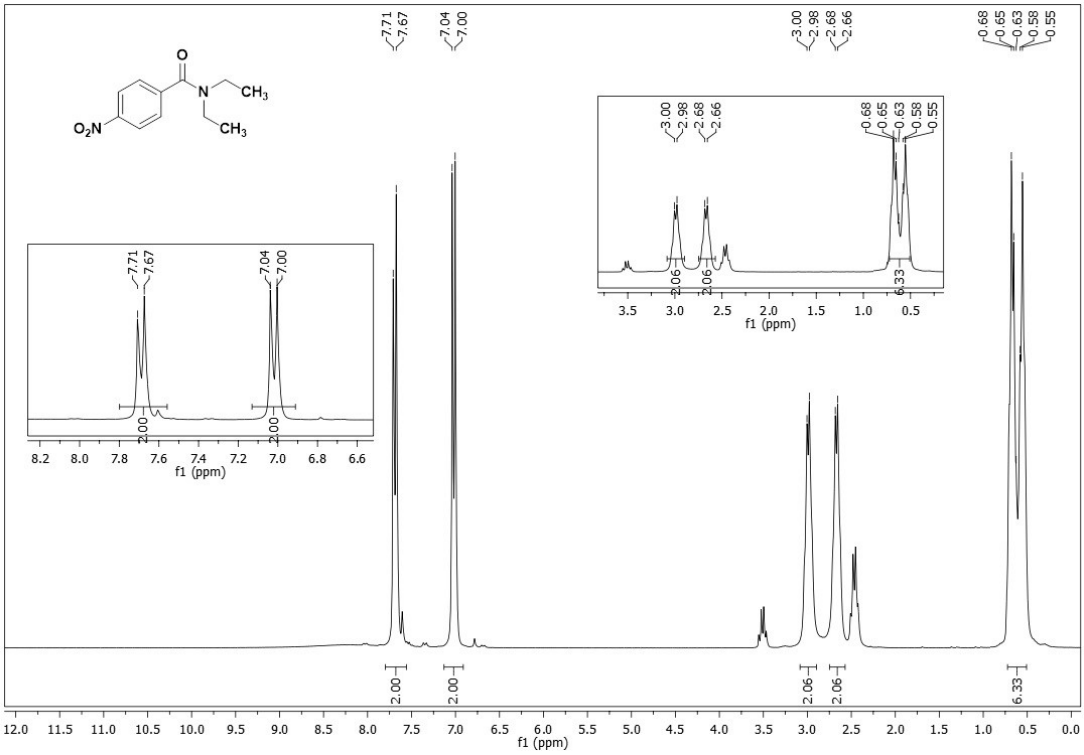
^{13}C-NMR of **3z1**



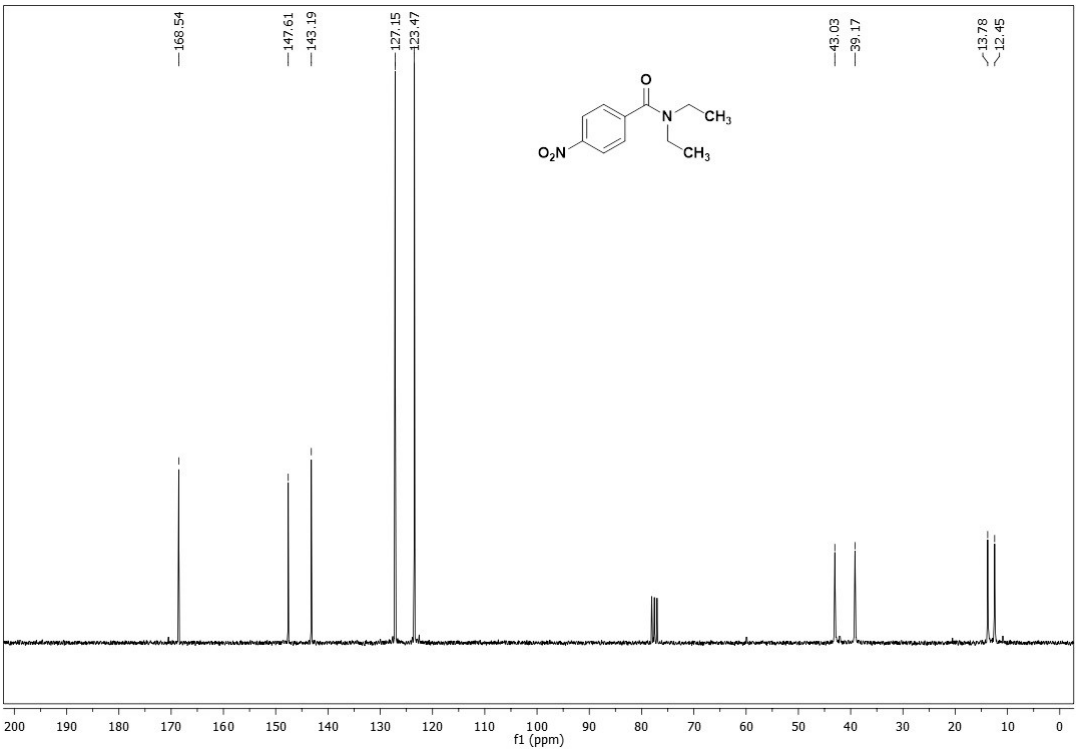
^{1}H-NMR of **3z2**



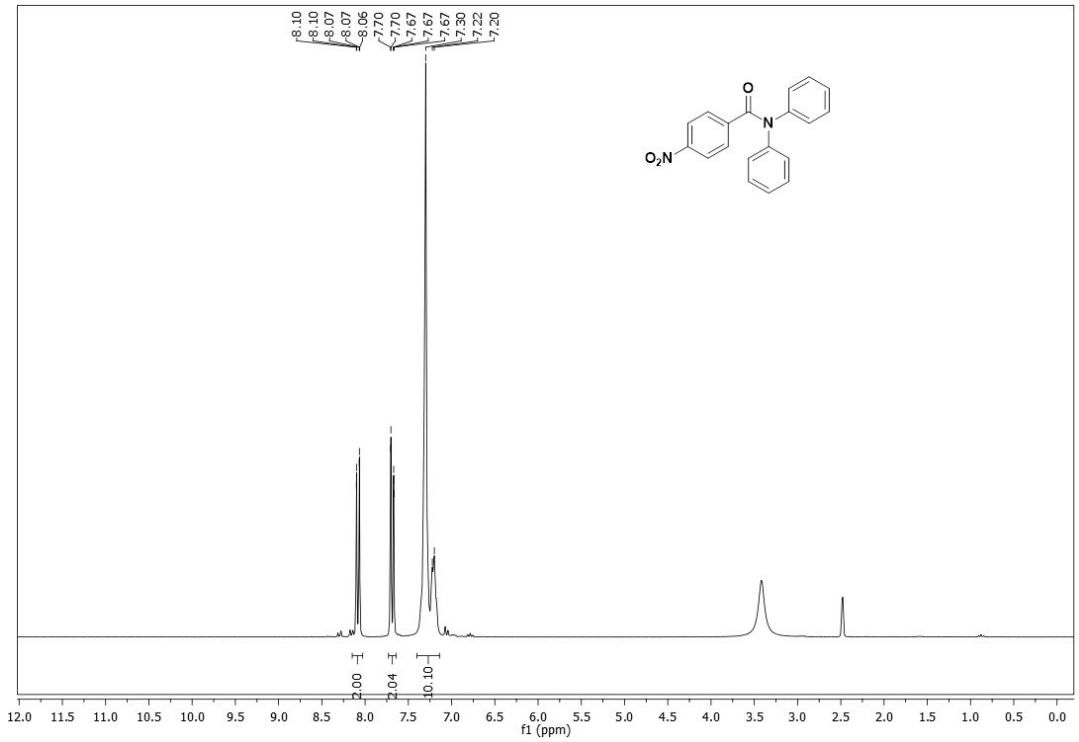
^{13}C-NMR of **3z2**



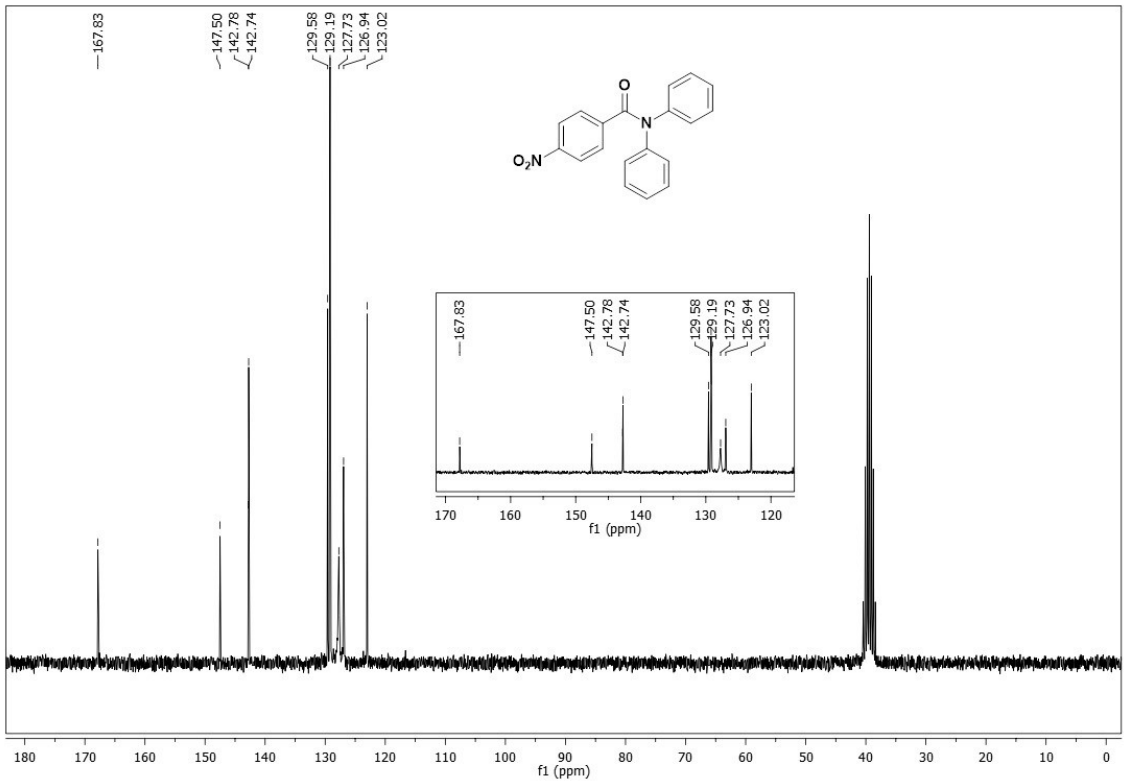
^{1}H-NMR of **3z3**



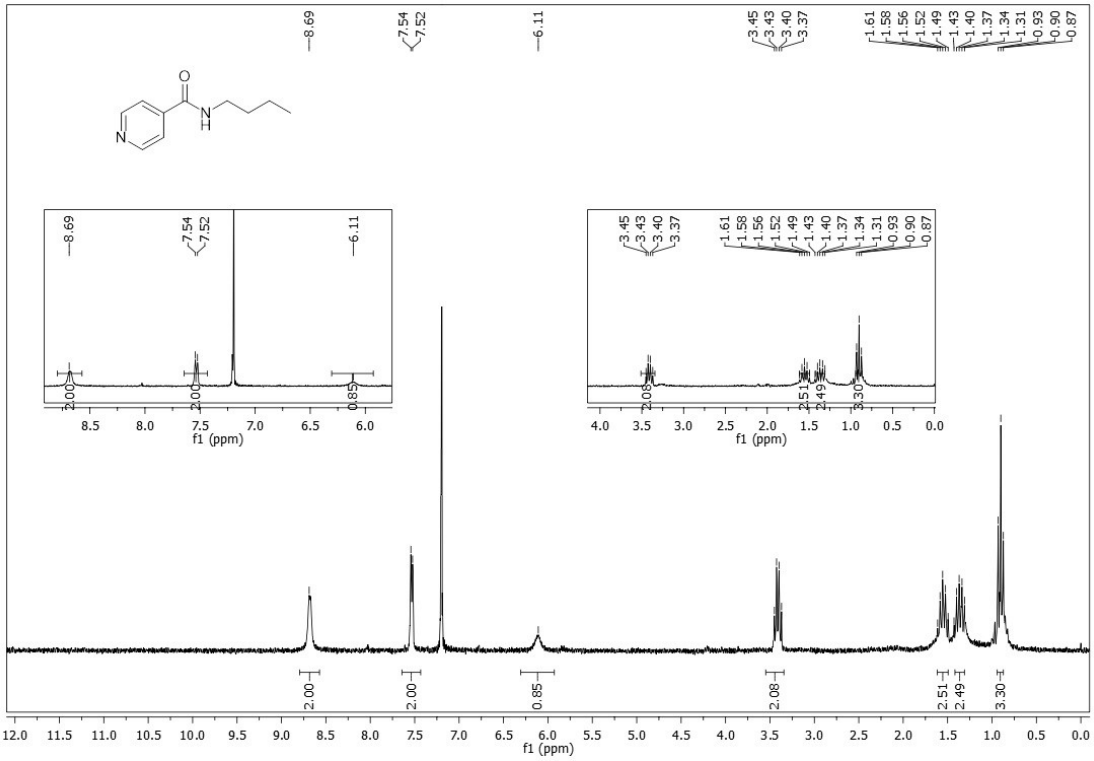
^{13}C-NMR of **3z3**


8.10
8.10
8.07
8.07
8.06
7.70
7.70
7.67
7.67
7.67
7.30
7.22
7.20
O
N
O2N
2.00
2.04
10.10
f1 (ppm)

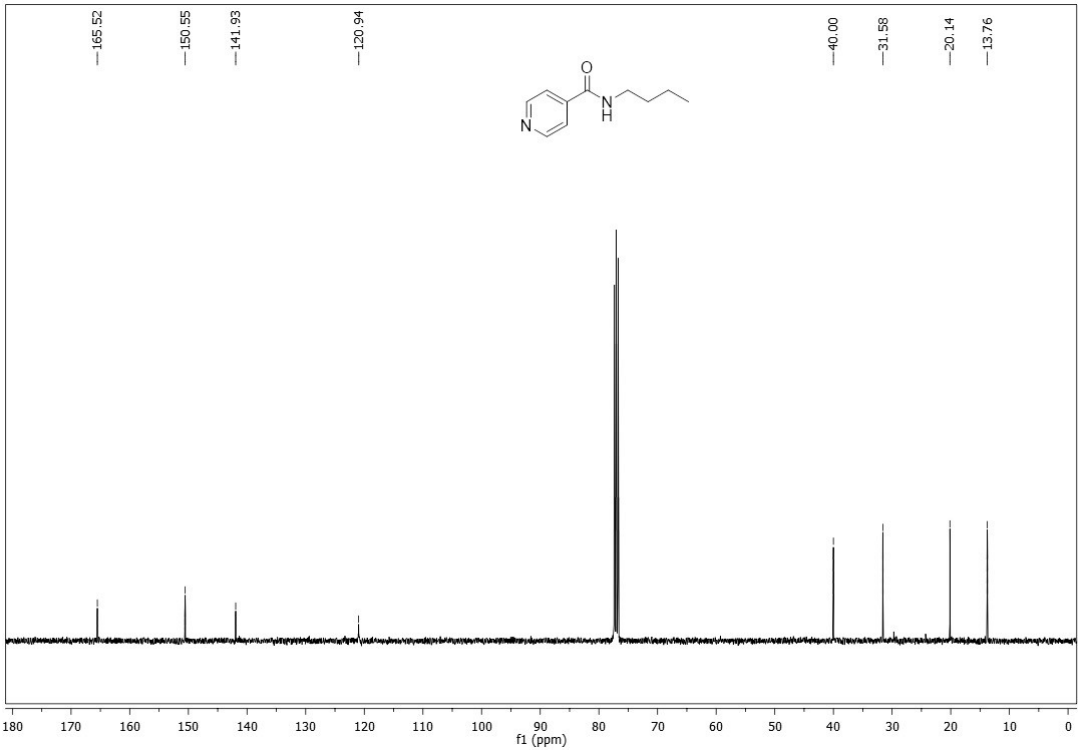
^{1}H-NMR of **3z4**


167.83
147.50
142.78
142.74
129.58
129.19
127.73
126.94
123.02
O
N
O2N
f1 (ppm)

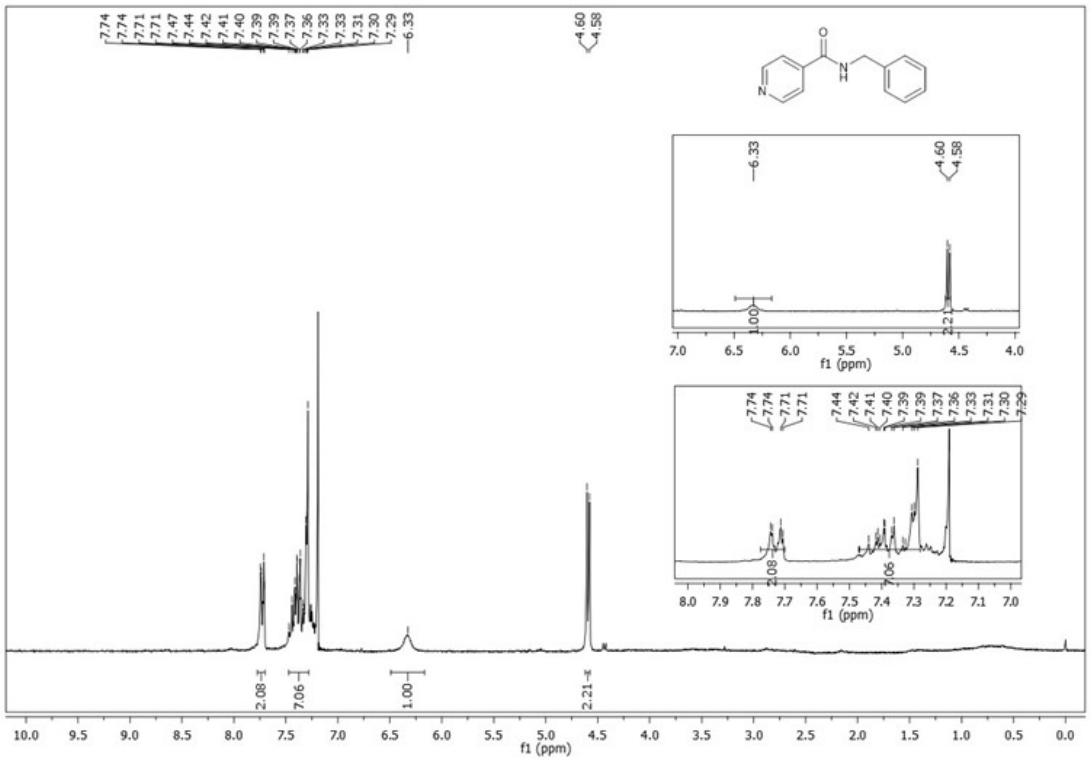
^{13}C-NMR of **3z4**



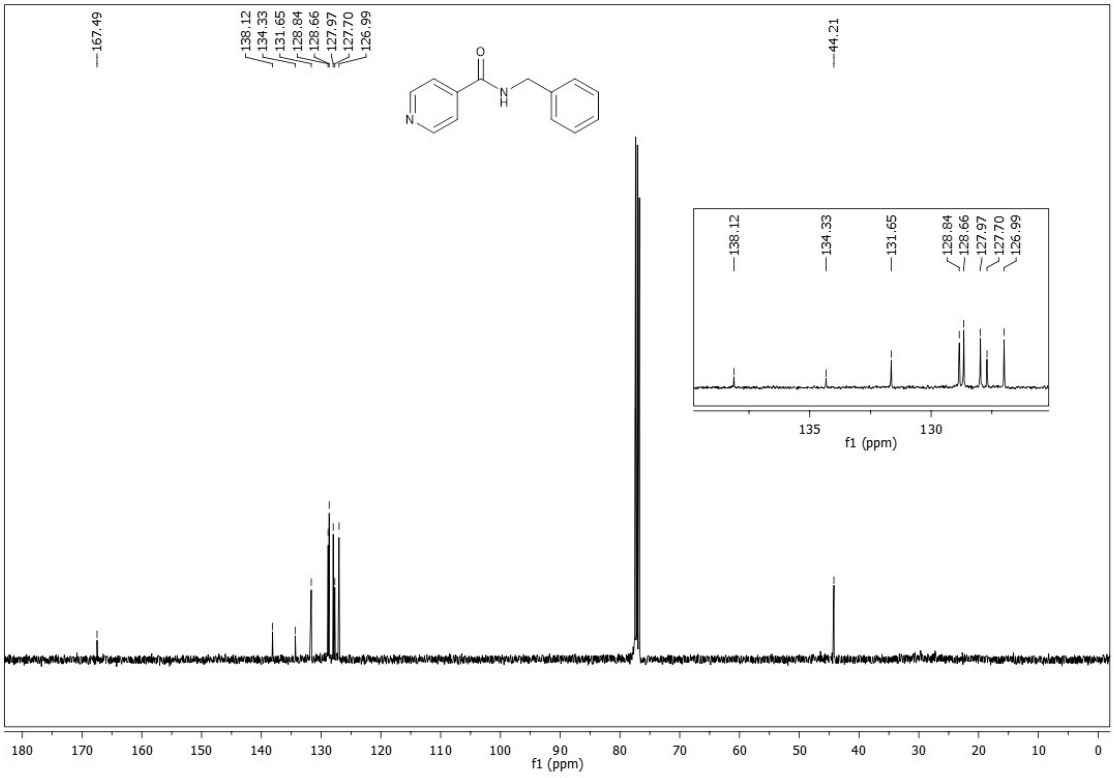
^{1}H-NMR of **5a**



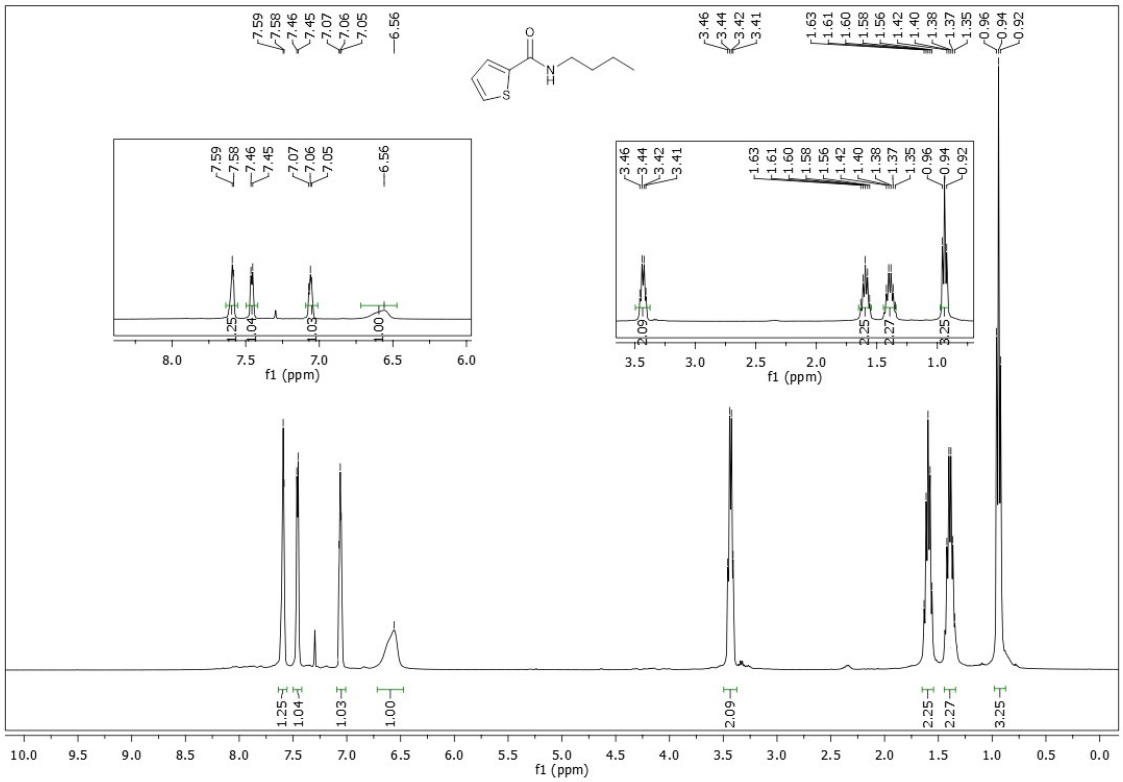
^{13}C-NMR of **5a**



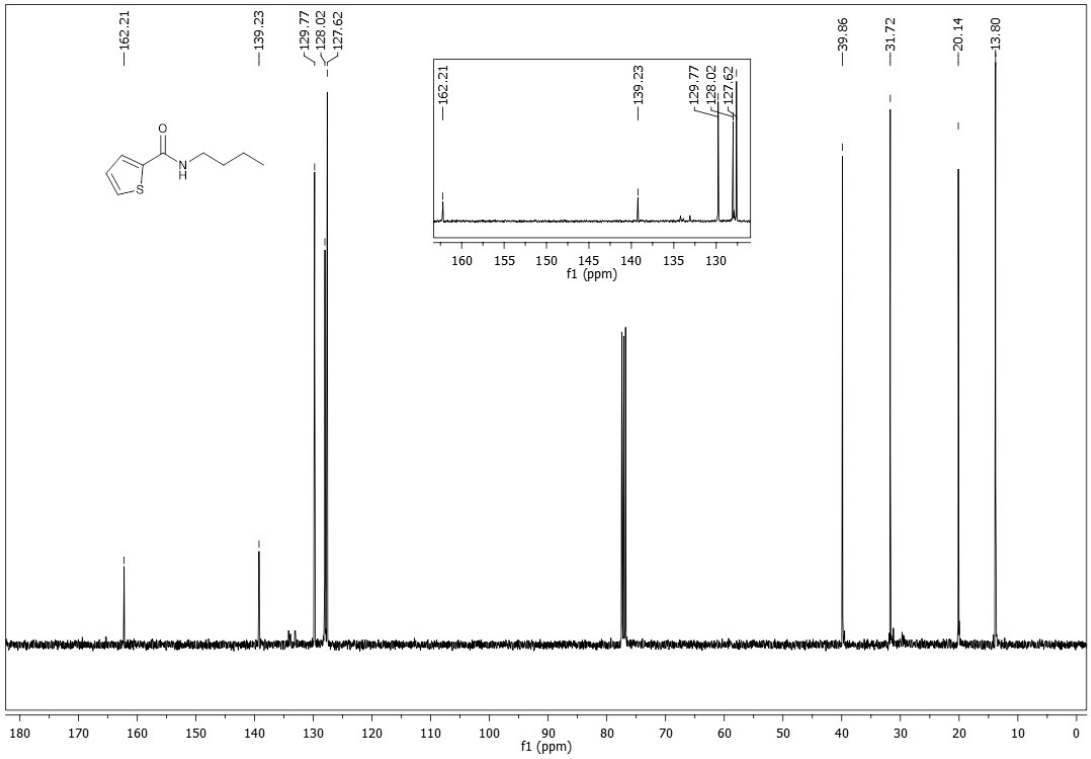
^{1}H-NMR of **5b**



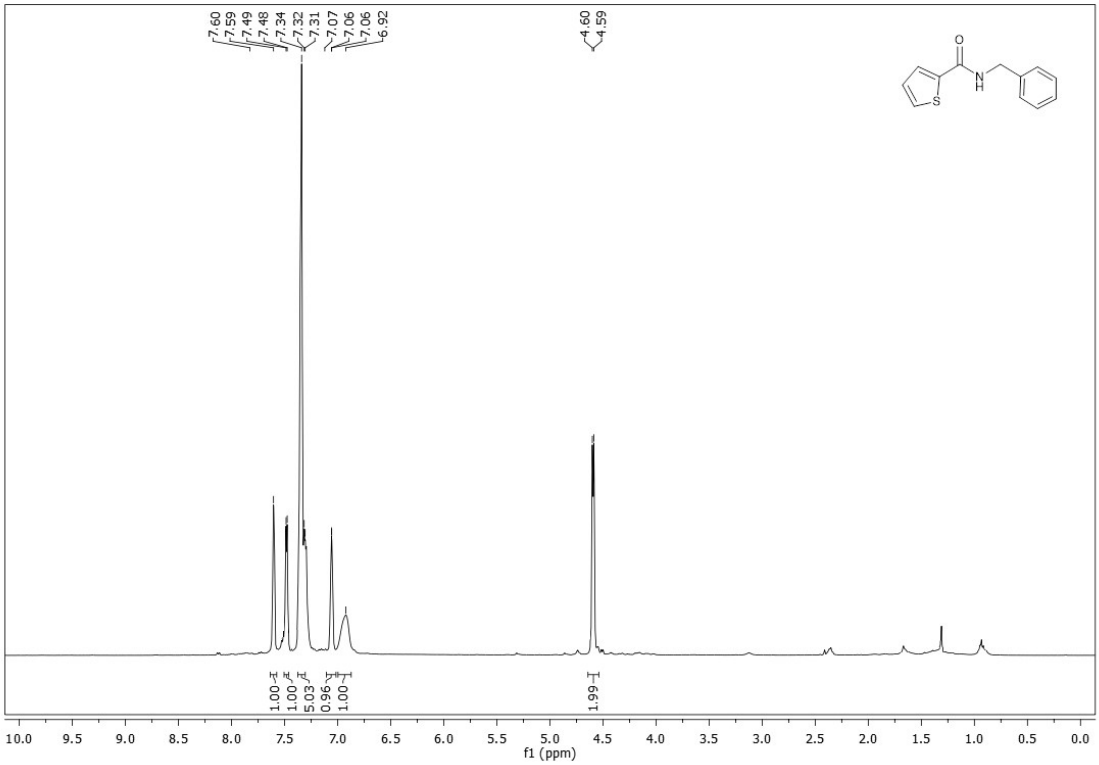
^{13}C-NMR of **5b**



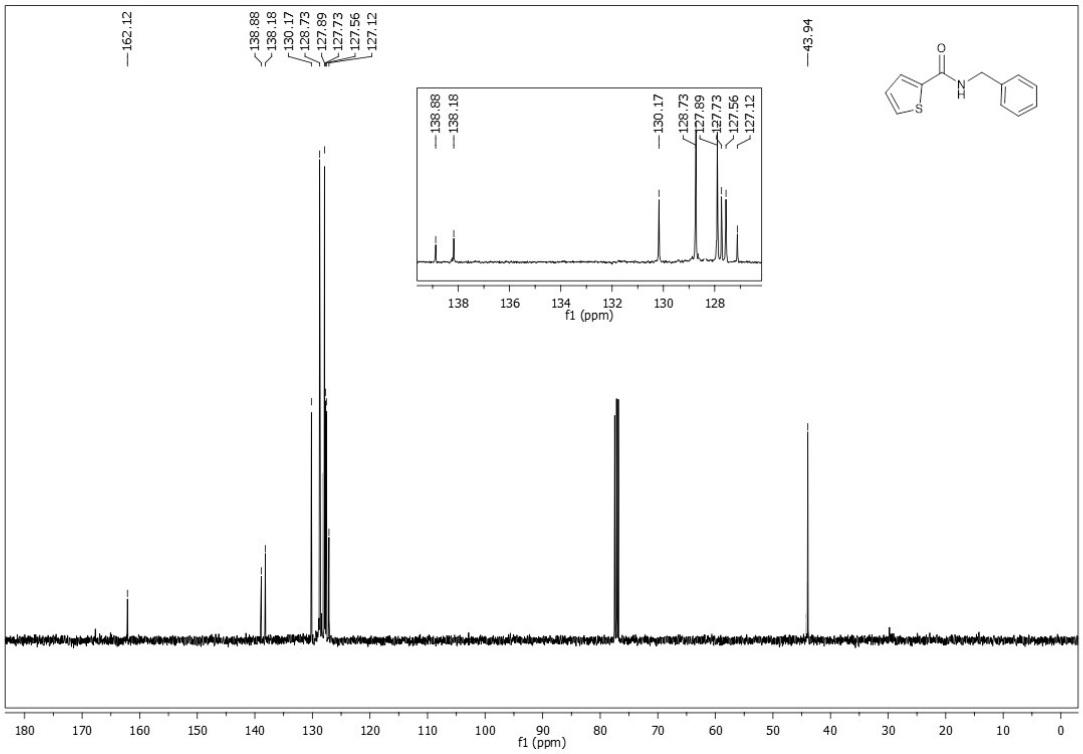
^{1}H-NMR of **5c**



^{13}C-NMR of **5c**

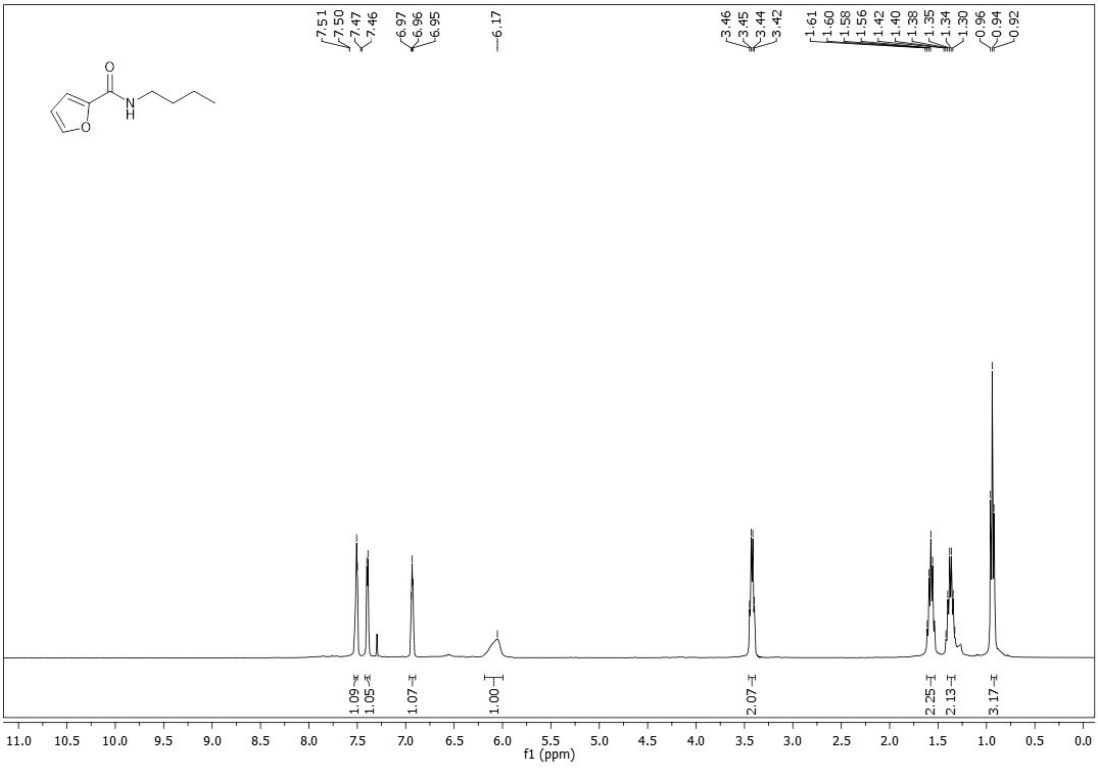


^{1}H-NMR of **5d**

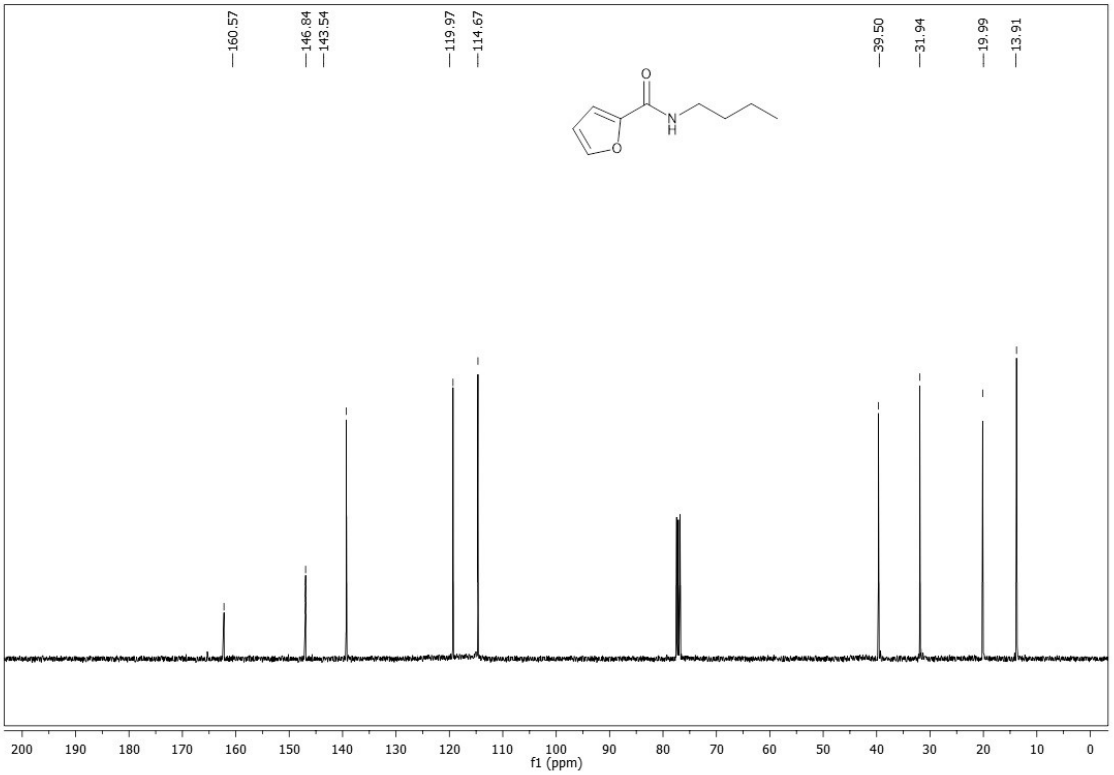


^{13}C-NMR of **5d**

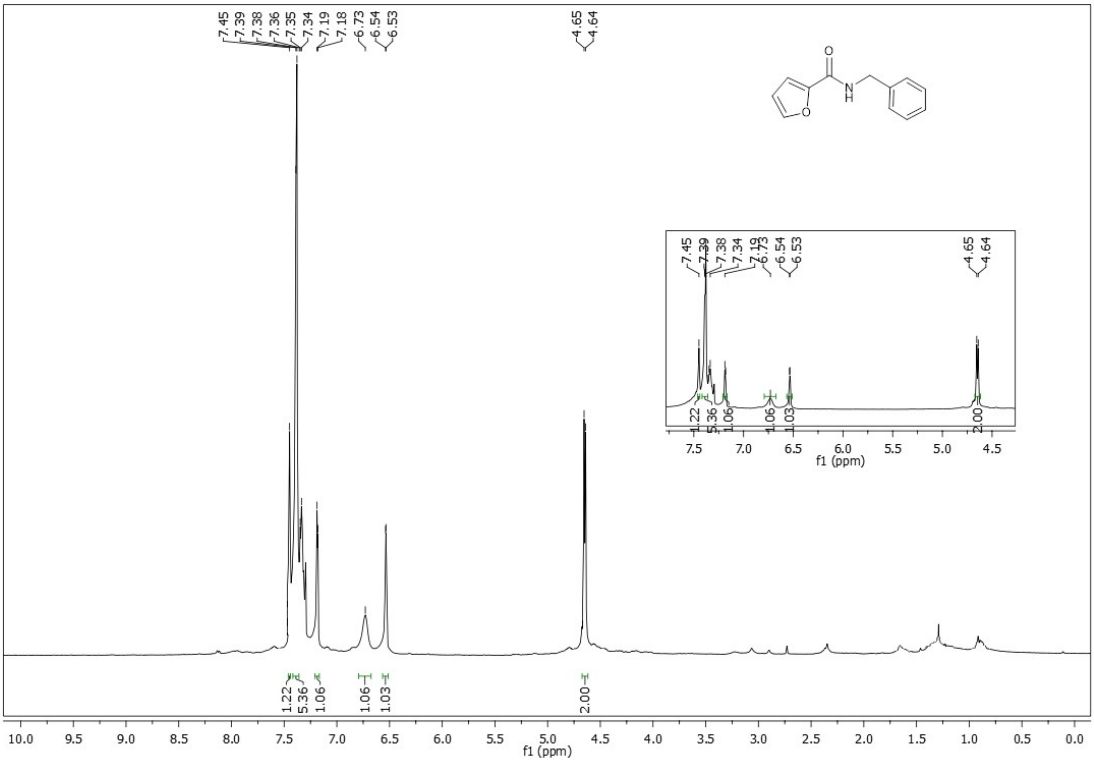
^{13}C-NMR of **5d**



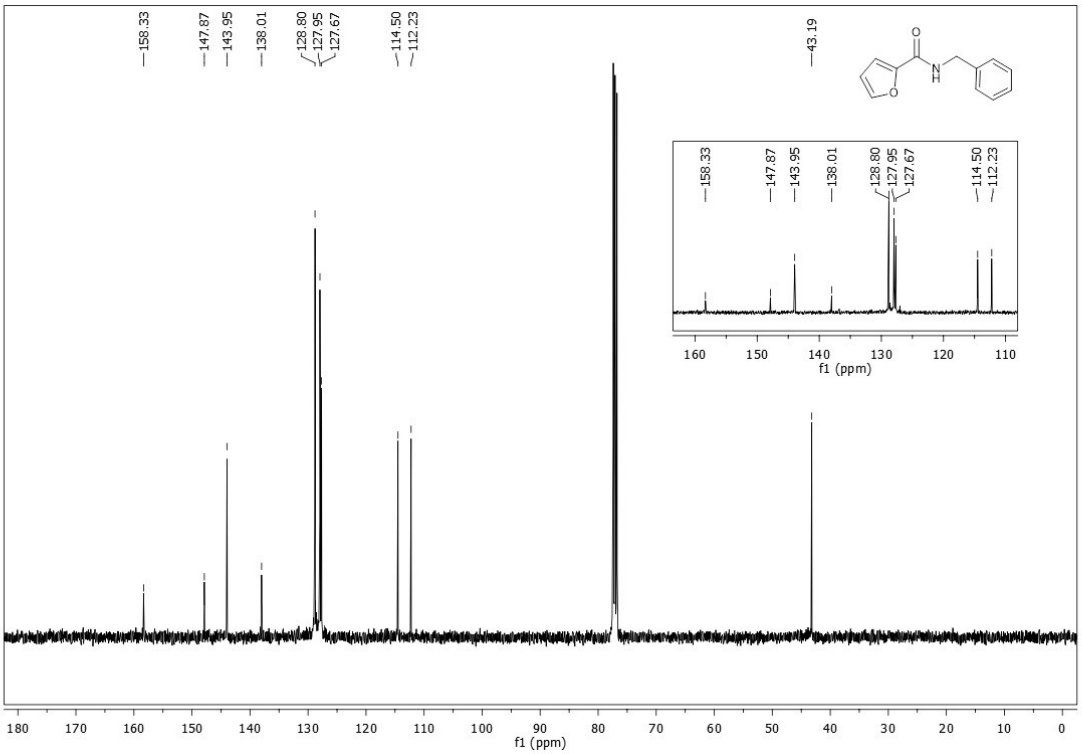
^{1}H-NMR of **5e**



^{13}C-NMR of **5e**



^{1}H-NMR of **5f**



^{13}C-NMR of **5f**