Electronic Supplementary Information

Ammonolysis of Anilides Promoted by Ethylene Glycol and Phosphoric Acid

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General Considerations

All manipulations were carried out on the bench top unless otherwise noted. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker AC-300 MHz or a Varian-300 MHz spectrometer. The chemical shifts (δ) are given in parts per million and referenced to residual solvent peaks (2.48 ppm for DMSO-d_6) or a TMS internal standard. Gas chromatography was carried out on a Shimadzu GC-17A Gas Chromatograph Spectrometer with a Stabilwax®-DB column (Restek). Gas chromatography/mass spectrometry (GC/MS) was performed on a Shimadzu QP2010S using an RTX-5MS column. Flash column chromatography was carried out on an Isco Combiflash system using silica gel 60 (Silicylce) ethyl acetate/ hexanes mixtures for elution. Attenuated total reflectance (ATR) IR spectra (4000 - 400 cm^{-1}) were recorded with a Bruker Tensor 27 spectrometer outfitted with a single reflection ATR containing a Ge crystal with a refractive index of 4.0.

$ZrCl_4$ and $SmCl_3$ were purchased from Strem Chemicals Inc. and used without further purification. H_3PO_4, crystalline (99.999 %), $(NH_4)_2HPO_4$ (>99.99%) and $(NH_4)H_2PO_4$ (99.99 %) were purchased from Sigma Aldrich and used without further purification. Anhydrous ethylene glycol, used in the screening of Lewis acids was purchased from Sigma Aldrich. Ethylene glycol that was used in all other ammonolysis reactions was purchased from Fisher Scientific. 1,3,5-trimethoxybenzene was purchased from Sigma Aldrich and purified prior to use by silica gel chromatography using diethyl ether for elution.

Amide substrates: benzanilide, 1,3-diphenylurea, *N*-phenylphthalimide and *N*-Boc-aniline were purchased from Aldrich chemical company and used without further purification. Acetanilide was purchased from Aldrich as a brown solid and was purified by sublimation to a white solid. Amide substrates that were not commercially available were synthesized by combining the appropriate amines and acyl chlorides to provide the desired amide: *N*-ethylheptanilide,[1] 2-phenylacetanilide,[2] heptanilide,[3] *N*-(3,5-dimethoxyphenyl)heptanamide, *N*-8-quinolinyl-heptanamide,[4] *N*-(2-bromophenyl)heptanamide, *N*-benzylheptanamide,[5] *N,N*-benzylmethylhept-anamide,[6] 1-(2,3-dihydro-1H-indol-1-yl)-1-heptanamide,[7] 4-methoxybenzanilide,[8] and 4-nitro-benzanilide.[9] Synthesized amides were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, melting point (where appropriate), high resolution mass spectrometry and gas chromatography and compared with published characterization data when available. Benzylphenylcarbamate,[10] and 4-methylbenzenesulfonanilide[11] were prepared using known literature procedures.

Electronic grade, anhydrous ammonia (99.99 %) was purchased from Airgas Inc. All other commercially available materials were used without further purification.

CAUTION: Ammonia is a noxious and corrosive gas. All handling of ammonia should be carried out in a fume hood to prevent inhalation. Ammonia is incompatible with many standard laboratory materials including, but not limited to: brass, copper, natural rubber, polyurethane, Viton® Fluoroelastomers (FKM), silicone and hydrocarbon-based lubricants. Useful ammonia compatibility information can be found at the following websites (accessed July 27, 2014):

http://www.coleparmer.com/Chemical-Resistance
http://encyclopedia.airliquide.com/Encyclopedia.asp?GasID=2

Heating solutions containing dissolved ammonia will generate high pressures, and such operations should be carried out with care in an appropriate pressure vessel and behind a blast shield.

Experimental Procedures

General Heptanamide Synthesis (Table 1). Heptanoyl chloride (4 mmol) was added drop-wise with a syringe to a stirred solution of amine (4 mmol), trimethylamine (0.61g, 6 mmol) and dichloromethane (50 mL) at 0 °C. The mixture was allowed to stir at this temperature for 30 minutes and was then warmed to room temperature and stirred for an additional four hours. The dichloromethane solution was then washed with 2 M HCl solution (3 x 10 mL), 2 M NaOH solution (3 x 10 mL) and brine (1x 10 ml). The organic layer was dried with Na_2SO_4 and concentrated en vacuo. The crude amide was purified by silica gel chromatography (hexanes/EtOAc). The wash step with 2 M HCl solution was not used in the purification of *N*-8-quinolinylheptanamide.

General procedure for anilide synthesis (Table 2). Acyl chloride (22 mmol) was added dropwise with a syringe to a stirred solution of aniline (2.05g, 22 mmol), $NaHCO_3$ (2.02g, 24 mmol) and THF (50 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 5 h. Water was added slowly to the reaction mixture and the amide product was extracted with EtOAc. The combined EtOAc layers were washed with brine, dried with Na_2SO_4 and concentrated en vacuo. The crude amide product was purified by silica gel chromatography (hexanes/ EtOAc).

General Procedures for Ammonolysis Reactions

Method A. Ammonolysis Reaction with High Pressure Ammonia. In a nitrogen-filled glovebox, H_3PO_4 (1 mmol) was added to a 45 mL stainless steel (or Hastelloy) Parr pressure vessel equipped with a stir bar. The Parr vessel was removed from the glovebox, and amide (2 mmol) and ethylene glycol (5 mL) were added. The Parr vessel was sealed and cooled to -4 °C (temperature measured by an internal thermocouple) in an acetone/dry ice bath. Anhydrous ammonia was added to the vessel until the internal pressure of the vessel reached 7 atm. The Parr vessel was allowed to warm to room temperature with stirring and the mixture was heated at 145 °C. The pressure in the vessel during the reactions typically reached approx. 350 psi.

Product Analysis. Upon completion of the reaction, the Parr vessel was allowed to cool to room temperature and slowly vented while stirring vigorous. Upon releasing the ammonia pressure, the Parr vessel was carefully opened in a fume hood and the sides of the vessel washed with methanol or a 20% DMF in methanol solution. 1,3,5-trimethoxybenzne (internal standard) was weighed and added to the reaction mixture and the reaction mixture was analyzed by GC. Product yields were determined on the basis of calibration curves established independently for each of the amines, primary amides and the internal standard. For NMR analysis, 3 mL of the methanol-diluted reaction mixture was concentrated by rotary evaporation and diluted with brine (1 mL). The ethylene glycol/brine solution (which contains 1,3,5-trimethoxybenzene) was extracted 3-4 times with dichloromethane and the combined organic layers were dried with anhydrous Na_2SO_4, concentrated and then analyzed by NMR spectroscopy using DMSO-d_6 as solvent.

Determining Ammonia Concentration in Ammonolysis Reactions.
At 145 °C, all ammonia in the Parr vessel will be dissolved in ethylene glycol or in the headspace, and there should be no pure liquid phase (critical temperature of ammonia = 132 °C). By heating known concentrations of dissolved ammonia in ethylene glycol (0, 1, 2, and 4 M) at 145 °C in a Parr vessel, a linear relationship between [NH_3] and pressure at 145 °C was established (Figure S1). This chart was used to determine [NH_3] in our ammonolysis reactions unless otherwise noted.

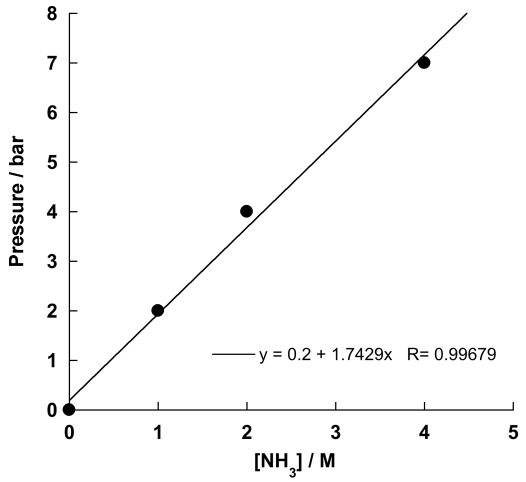


Figure S1. [NH_3] in ethylene glycol vs. pressure at 145 °C.

Method B. Ammonolysis Reaction with 5 M NH_3 Stock Solution in Ethylene Glycol
Phosphoric acid (1 mmol), amide (2 mmol) and a stir bar were placed in a 45 mL stainless steel (or Hastelloy) Parr vessel. The vessel was then cooled in an acetone/dry ice bath to minimize loss of ammonia. A 5 M titrated solution of ammonia dissolved in ethylene glycol[12] (5 ml) was then added to the reaction vessel using a gas-tight syringe. The vessel was then quickly sealed and allowed to warm to room temperature before heating to 145°C. The work-up procedure used is the same as that described above.

Effect of [H_3PO_4] on the Ammonolysis of Heptanilide

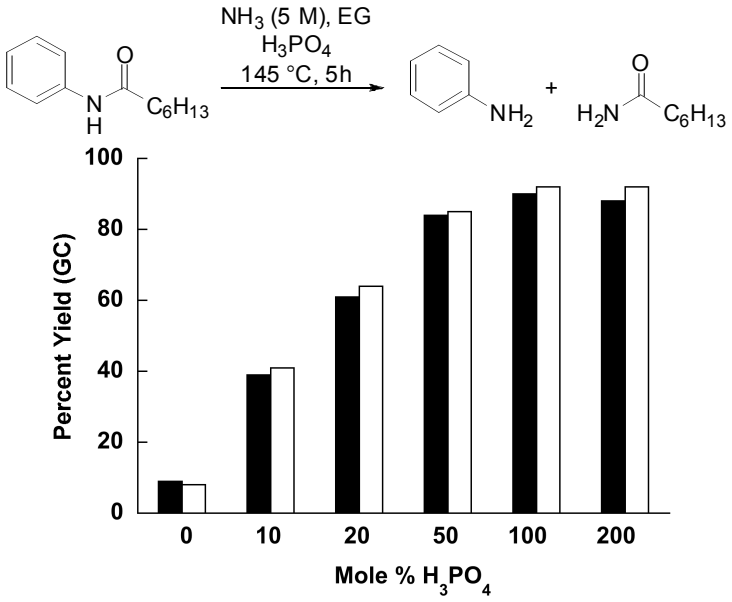


Figure S2. Effect of increasing [H_3PO_4] (0-4 mmol) in the ammonolysis of heptanilide (2 mmol) at 145 °C in ethylene glycol and dissolved ammonia (5 M). Reaction analyzed by GC using 1,3,5-trimethoxybenzene as internal standard. Black bars = aniline; white bars = heptanamide

Effect of [NH_3] on the Ammonolysis of Heptanilide

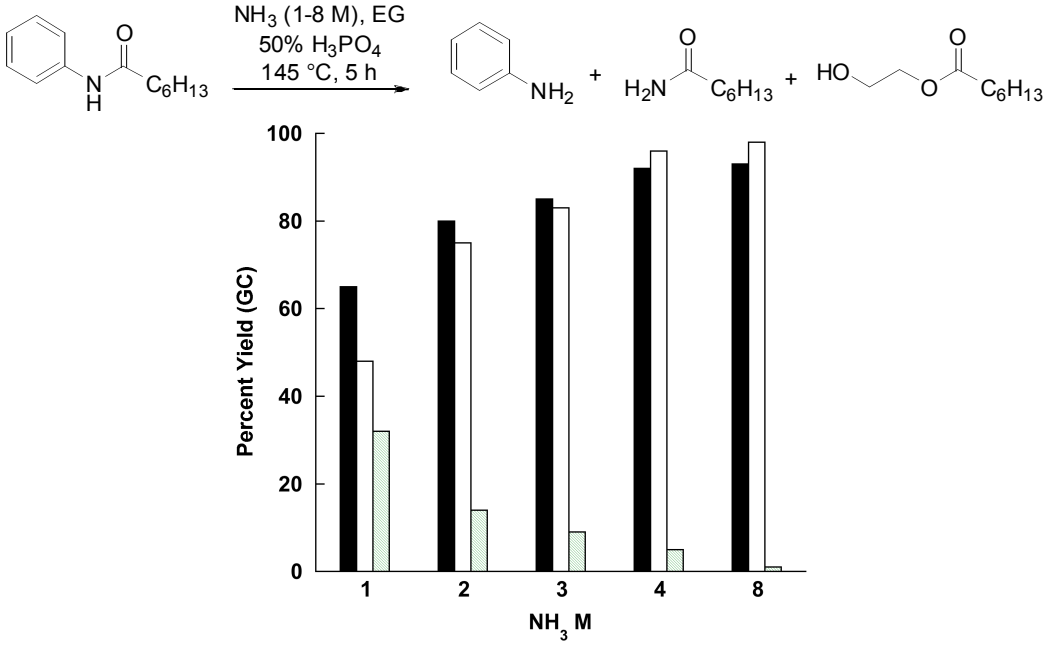
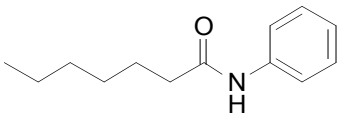
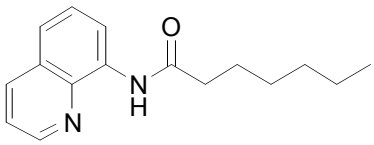


Figure S3. The effects of increasing [NH_3] on the ammonolysis of heptanilide (2 mmol) with H_3PO_4 (1 mmol) at 145 °C. Where molar equivalence is in reference to heptanilide. Black bars = aniline. White bars = heptanamide. Striped bars = 2-hydroxyethyl heptanoate (not independently calibrated**)**

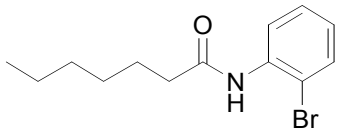
Substrate Characterization Data.



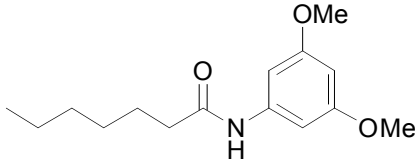
Heptanilide: White solid. mp = 64 °C [Lit mp = 63.7- 64 °C][13]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (d, J = 8.0 Hz, 2H), 7.31 (t and s, J = 7.6 Hz, 3H), 7.09 (t, J = 7.6 Hz, 1H), 2.35 (t, J = 7.4 Hz, 2H), 1.72 (p, J = 7.1 Hz, 2H), 1.33 (m, 6H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR: (75MHz, $CDCl_3$) δ 171.77, 138.24, 129.17, 124.35, 120.05, 38.04, 31.78, 29.16, 25.83, 22.72, 14.25. HRMS (ESI) [M + Na^+] /z calcd. 228.1359, found 228.1356



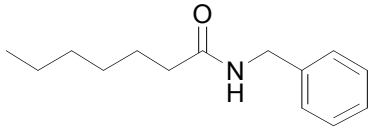
***N*-8-quinolinylheptanamide**: Slightly yellow oil, ^{1}HNMR (300 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.79 (m, 2H), 8.15 (dd, J = 9.2, 1.5 Hz, 1H), 7.49 (m, 3H), 2.56 (t, J = 7.4 Hz, 2H), 1.82 (p, J = 8.3 Hz, 2H), 1.39 (m, 6H), 0.90 (t, J = 5.8 Hz, 3H). ^{13}C NMR: (75MHz, $CDCl_3$) δ 172.14, 148.30, 138.58, 136.57, 134.82, 128.16, 127.67, 121.77, 121.51, 116.61, 38.50, 31.83, 29.21, 25.87, 22.75, 14.28. HRMS (ESI) [M + Na^+] /z calcd. 279.1468, found 279.1472



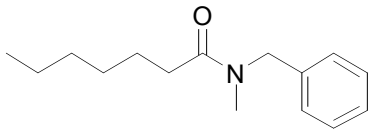
***N*-(2-bromophenyl)heptanamide:** white solid. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 8.36 (d, J = 7.9 Hz, 1H), 7.61 (s, 1H), 7.53 (dd, J = 8.0, 1.5 Hz, 1H), 7.31 (td, J = 7.9, 1.5 Hz, 1H), 6.97 (td, J = 7.9, 1.6 Hz, 1H), 2.43 (t, J = 7.4 Hz, 2H), 1.75 (p, J = 7.2 Hz, 2H), 1.35 m, J = Hz, 6H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C NMR: (75MHz, $CDCl_3$) δ 171.39, 135.97, 132.38, 128.61, 125.21, 122.09, 101.05, 38.25, 31.75, 29.07, 25.73, 22.71, 14.24. HRMS (ESI) [M + Na^+] /z calcd. 306.0464, found 306.0471



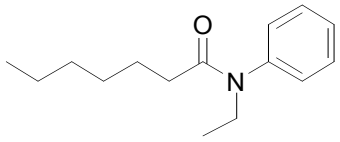
***N*-(3,5-dimethoxyphenyl)heptanamide:** White solid mp = 69-70 °C. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.17 (s, 1H), 6.78 (s, 2H), 6.22 (t, J = 2.2 Hz, 1H), 3.77 (s, 6H), 2.33 (t, J = 7.3 Hz, 2H), 1.71 (p, J = 7.3 Hz, 2H), 1.32 (m, 6H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C NMR: (75MHz, $CDCl_3$) δ171.94, 161.23, 140.06, 98.17, 96.80, 55.55, 38.09, 31.78, 29.14, 25.73, 22.70, 14.23. HRMS (ESI) [M + Na^+] /z calcd. 288.1571, found 288.1574



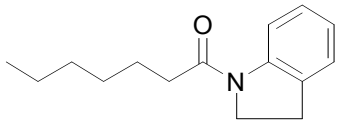
Benzylheptanamide, white solid. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.30 (m, 5H), 5.77 (s, 1H), 4.44 (d, J = 5.8 Hz, 2H), 2.20 (t, J = 7.3 Hz, 2H), 1.65 (p, J = 7.5 Hz, 2H), 1.29 (m, J = Hz, 6H), 0.88 (t, J = 6.7 Hz, 3H);). ^{13}C NMR: (75MHz, $CDCl_3$) δ 173.10, 138.67, 128.92, 128.05, 127.72, 43.80, 37.05, 31.74, 29.20, 25.94, 22.72, 14.23. HRMS (ESI) [M + Na^+] /z calcd. 242.1516, found 242.1523



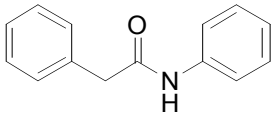
***N,N*-benzylmethylheptanamide,** colourless oil. ^{1}H NMR: (300 MHz, $CDCl_3$) major rotamer (60:40) δ 7.29 (m, J = Hz, 5H), 4.59 (s, 2H) , 2.91 (s, 3H), 2.37 (t, J = 7.2 Hz, 2H), 1.67 (p, J = 7.2 Hz, 2H), 7.1 (m, Hz, 6H), 0.88 (m, 3H); ^{13}C NMR: (75 MHz, $CDCl_3$) rotamers δ 173.84, 173.48, 137.84, 137.06, 129.10, 128.75, 128.22, 127.75, 127.45, 126.50, 53.57, 50.93, 35.00, 34.04, 33.79, 33.37, 31.87, 31.83, 29.38, 25.61, 25.36, 22.76, 14.26. HRMS (ESI) [M + Na^+] /z calcd. 256.1672, found 256.1673



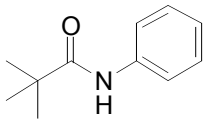
***N*-Ethylheptanilide:** Colourless oil**.** ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.40 (m, 3H), 7.15 (d, J = 7.9 Hz, 2H), 3.75 (q, J = 7.0 Hz, 2H), 2.00 (t, J = 7.3 Hz, 2H), 1.55 (p, J = 6.7 Hz, 2H), 1.17 (m, 6H), 1.11 (t, J = 7.0 Hz, 3H), 0.83 (t, J = 6.5 Hz, 3H); ^{13}C NMR: (75MHz, $CDCl_3$) δ172.85, 142.84, 129.78, 128.66, 127.94, 44.11, 34.67, 31.71, 29.14, 25.69, 22.64, 14.20, 13.31. HRMS (ESI) [M + H^+] /z calcd. 234.1853, found 234.1856



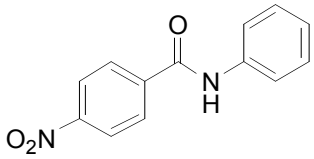
1-(2,3-dihydro-1H-indol-1-yl)-1-heptanamide: Off-white, waxy solid mp = 56 °C. ^{1}H NMR: (300 MHz, $CDCl_3$) major rotamer (89:11) δ 8.24 (d, J = 7.9 Hz, 1H), 7.18 (m, 2H), 6.99 (td, J = 7.0, 1.0 Hz, 1H), 4.04 (t, J = 8.4 Hz, 2H), 3.18 (, J = 8.4 Hz, 2H), 2.41 (t, J = 7.8 Hz, 2H), 1.73 (p, J = 7.2 Hz, 2H), 1.34 (m, J = Hz, 6H), 0.90 (t, J = 6.6 Hz, 3H). ^{13}C NMR: (75MHz, $CDCl_3$) δ 171.71, 131.21, 127.75, 124.68, 124.63, 123.63, 123.58, 117.22, 101.06, 61.61, 48.19, 36.22, 31.91, 29.33, 28.25, 24.77, 22.78, 14.28. HRMS (ESI) [M + H^+] /z calcd. 232.1696, found 232.1693



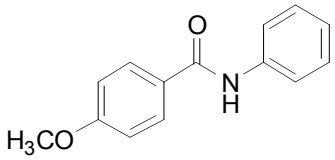
2-phenylacetanilide. White crystalline solid. mp = 118-119 °C [Lit mp = 118-119 °C][2] **.** ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.33 (m, 10 H), 7.07 (t, J = 7.3 Hz, 1 H), 3.71 (s, 2 H). ^{13}C NMR: (75MHz, $CDCl_3$) δ 169.41, 137.89, 134.71, 129.74, 129.43, 129.16, 127.86, 124.68, 120.11, 45.03. HRMS (ESI) [M + Na^+] /z calcd. 234.0890, found 234.0882



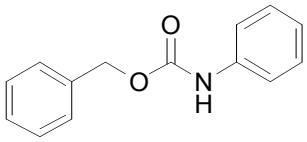
Pivalanilide. Fluffy white solid, mp = 133-134 °C [Lit mp = 130 – 131 °C] ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 2H), 7.31 (t, J = 7.8 Hz, 3H), 7.09 (t, J = 7.5 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR: (75MHz, $CDCl_3$) δ 176.78, 138.26, 129.16, 124.39, 120.19, 77.68, 77.25, 76.83, 39.81, 27.85. HRMS (ESI) [M + Na^+] /z calcd. 200.1046, found 200.1043



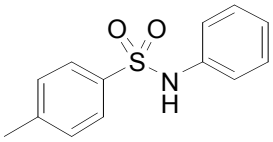
4-nitrobenzanilide. Light yellow solid. mp = 215- 216 °C [Lit mp = 214-216 °C]. ^{1}H NMR**:** (300 MHz, DMSO-d_6) δ 10.53 (s, 1H), 8.36 (d, J = 9.1 Hz, 2H), 8.16 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 7.4 Hz, 2H), 7.4 (t, J = 7.4 Hz, 1H); ^{13}C NMR: (75MHz, DMSO-d_6) δ 164.56, 149.82, 141.31, 139.39, 129.89, 129.39, 124.85, 124.22, 121.17. HRMS (ESI) [2M + Na^+] /z calcd. 507.1276, found 507.1270



4-Methoxybenzanilide.: Shiny white solid. mp = 170 - 172°C [lit mp = 170-171 °C]. ^{1}H NMR**:** (300 MHz, DMSO-d_6) δ 10.06 (s, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.04 (d + t, 3H), 3.82 (s, 3H). ^{13}C NMR: (75 MHz, DMSO-d_6) δ 165.57, 162.56, 140.04, 130.26, 129.21, 127.68, 124.08, 121.01, 114.26, 56.09. HRMS (ESI) [M + Na^+] /z calcd. 250.0839, found 250.0837

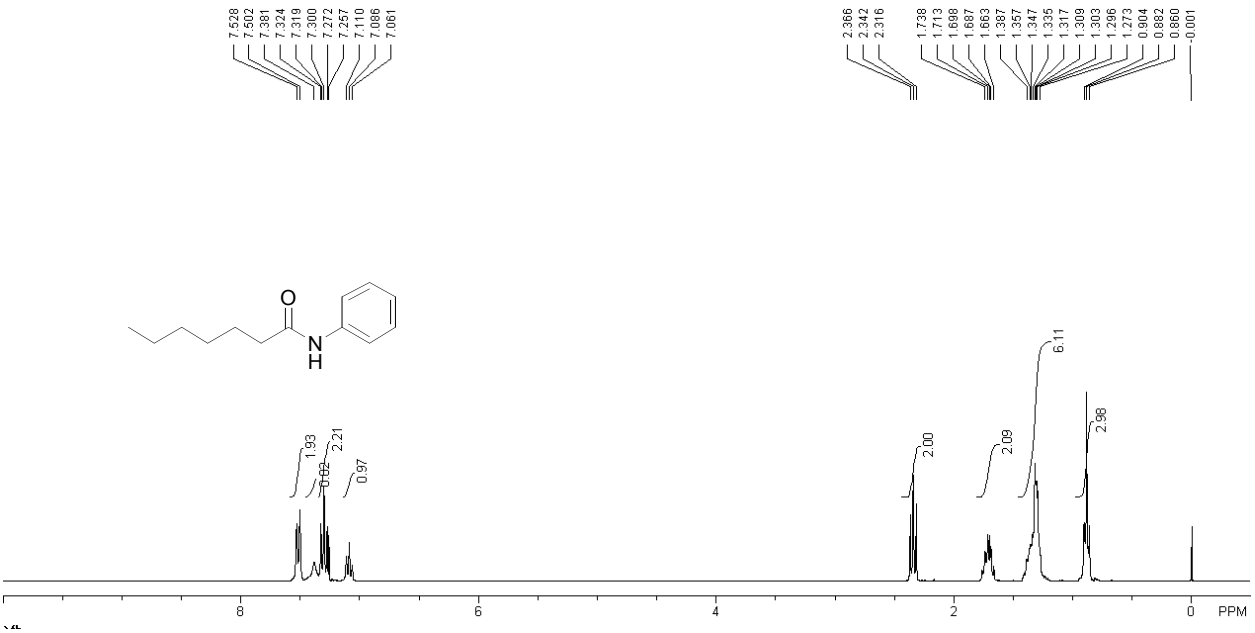


Benzylphenylcarbamate: Isolated as a yellow solid mp = 75-76 °C [Lit mp = 76 -77 °C]. ^{1}H NMR: (300 MHz, DMSO-d_6) δ 9.74 (s, 1H), 7.39 (m, 9H), 6.97 (t, J = 7.2 Hz, 1H), 5.13 (s, 2H); ^{13}C NMR: (75 MHz, DMSO-d_6) δ154.05, 139.77, 137.32, 129.43, 129.12, 128.77, 128.70, 123.10, 118.86, 66.38. HRMS (ESI) [M + Na^+] /z calcd. 250.0839, found 250.0831

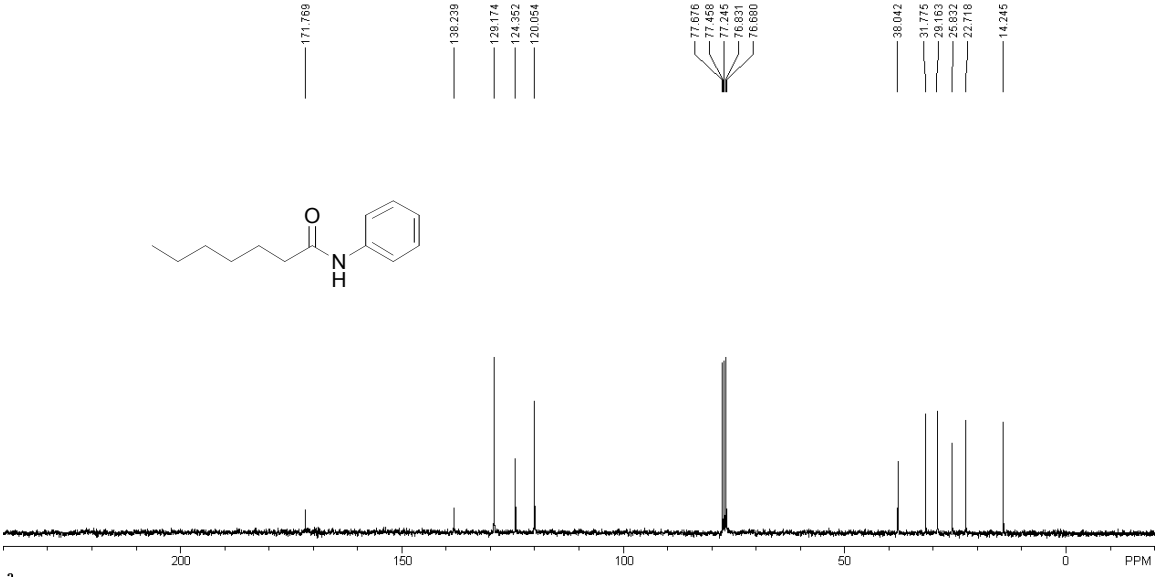


4-methylbenzenesulfonanilide. White solid, mp = 100 – 102 °C [Lit mp = 101 – 104 °C] ^{1}H NMR: (300 MHz, DMSO-d_6) δ 10.17 (s, 1H), 7.61 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.19 (t, J = 8.6 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 6.98 (t, J = 7.3 Hz, 1H), 2.30 (s, J = Hz, 3H) ^{13}C NMR: (75MHz, DMSO-d_6) δ 143.87, 138.49, 137.38, 130.32, 129.77, 127.37, 124.60, 120.58, 21.60. HRMS (ESI) [M + Na^+] /z calcd. 270.0560, found 270.0563

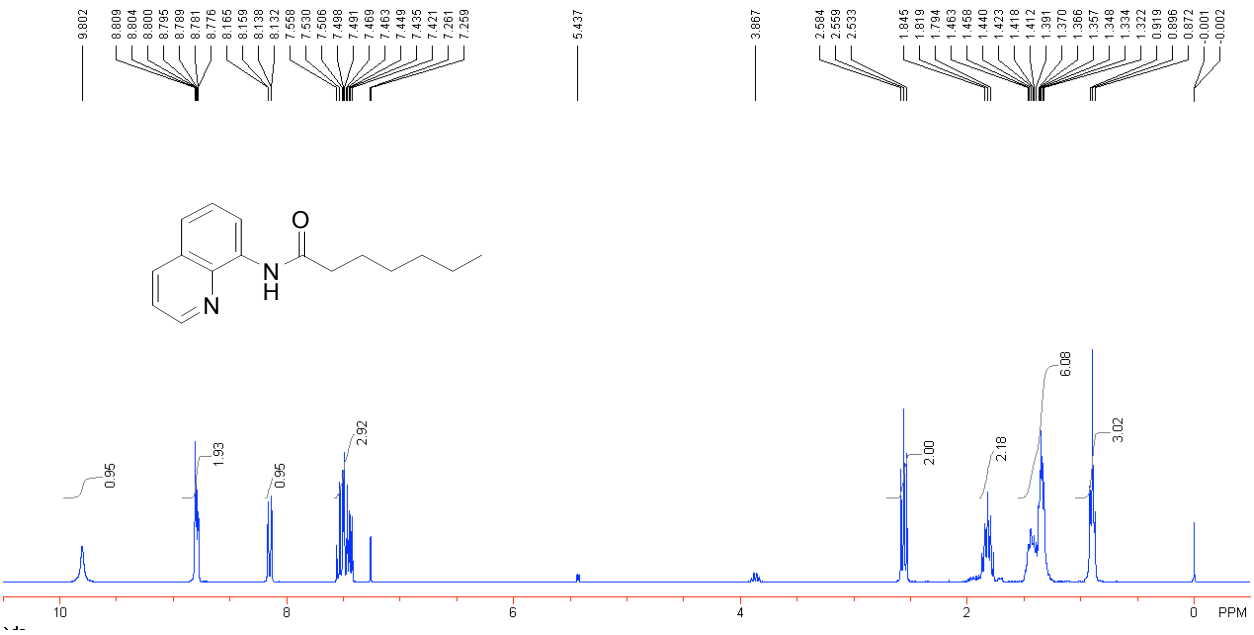
NMR Spectral Data



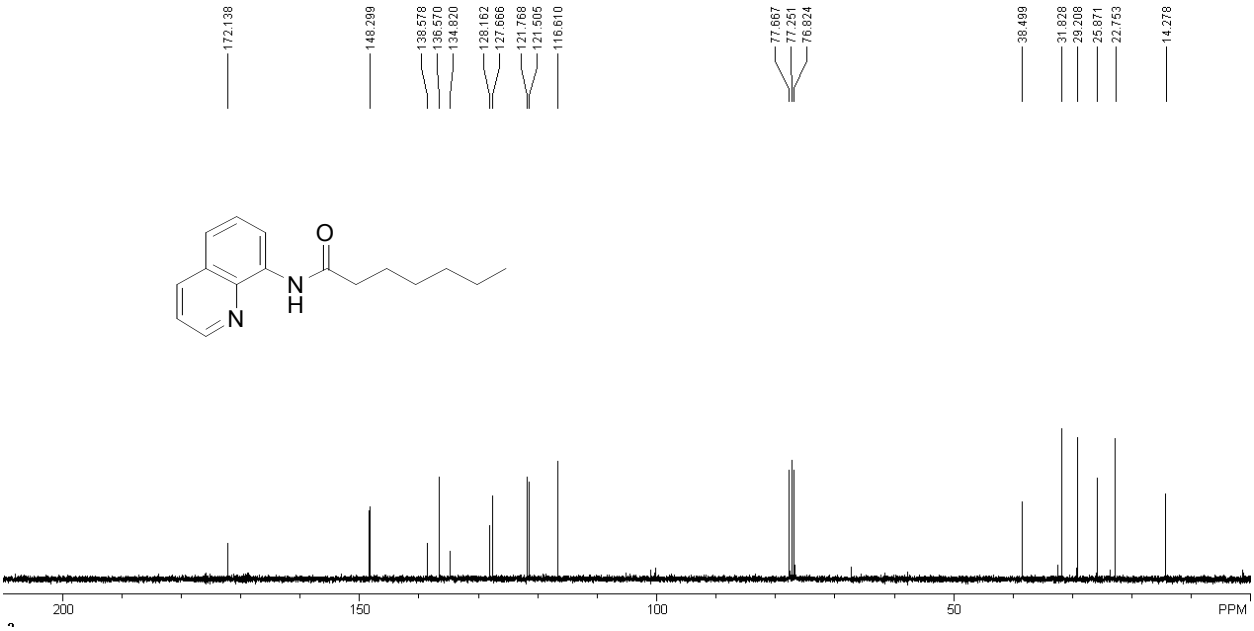
^{1}H NMR spectrum on heptanilide CDCl3 at 300 MHz



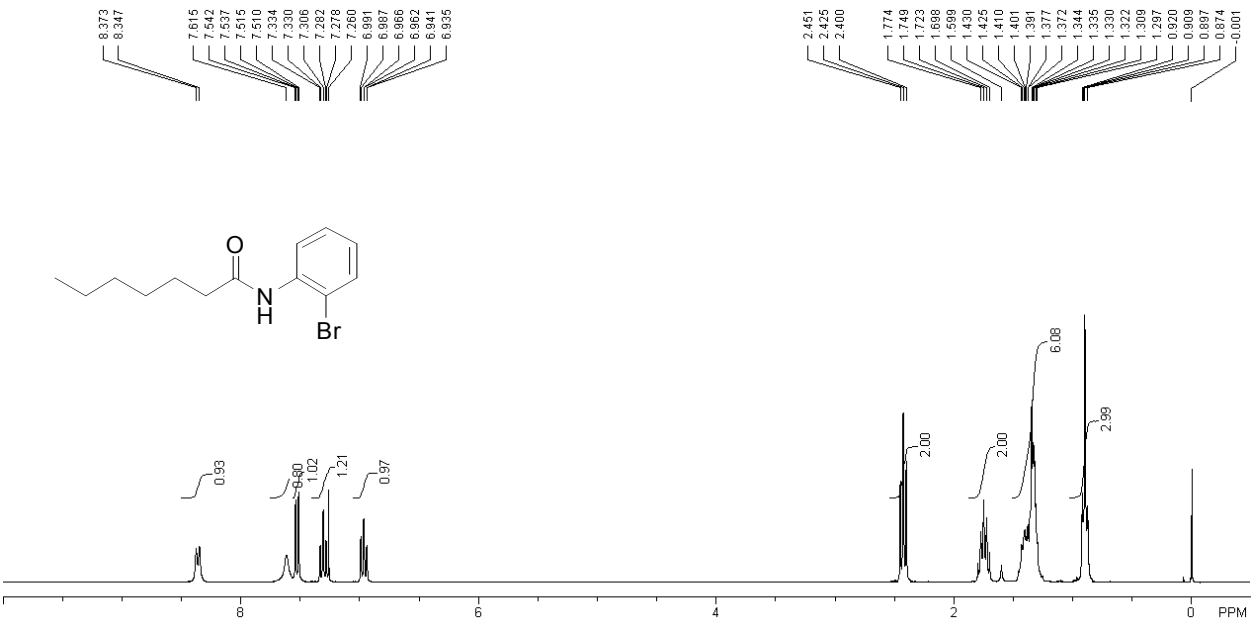
^{13}C {1H} NMR spectrum of heptanilide in $CDCl_3$ at 75 MHz



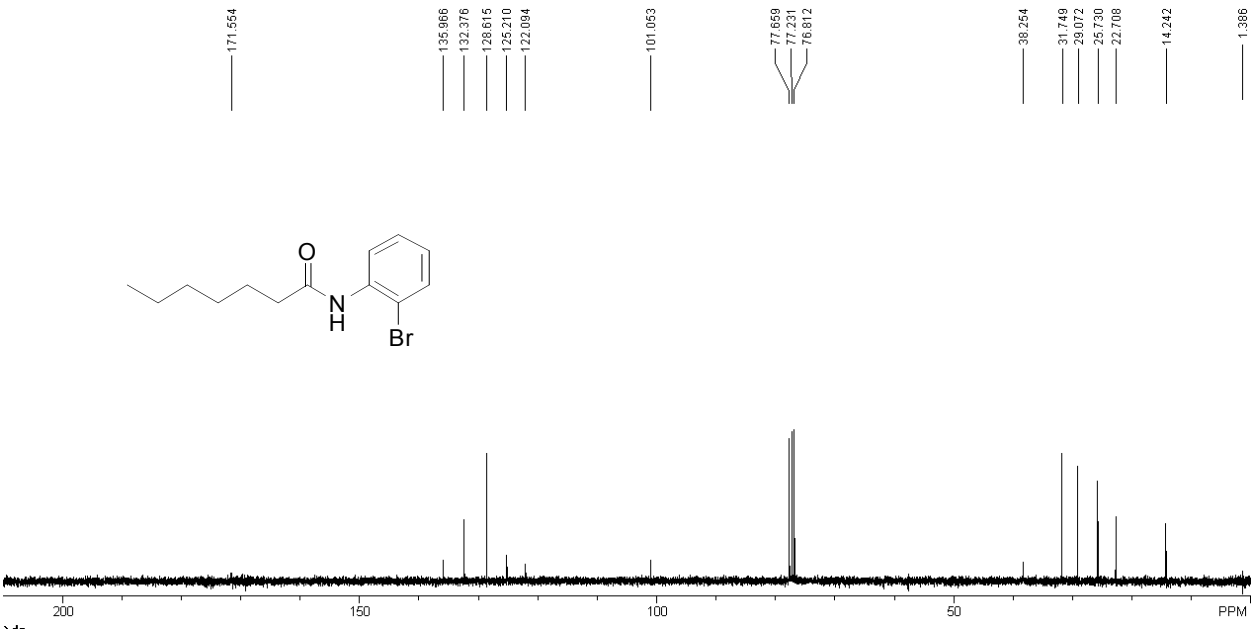
^{1}H NMR spectrum of *N*-8-quinolinylheptanamide in $CDCl_3$ at 300 MHz



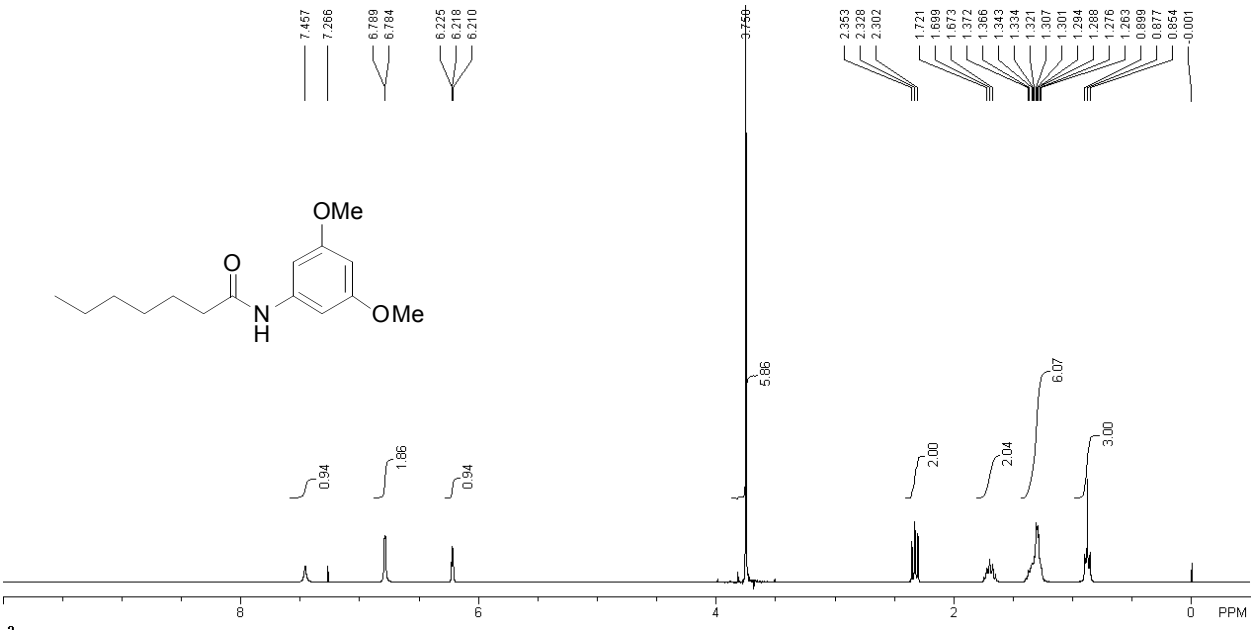
^{13}C NMR spectrum of *N*-8-quinolinylheptanamide in $CDCl_3$ at 75 MHz



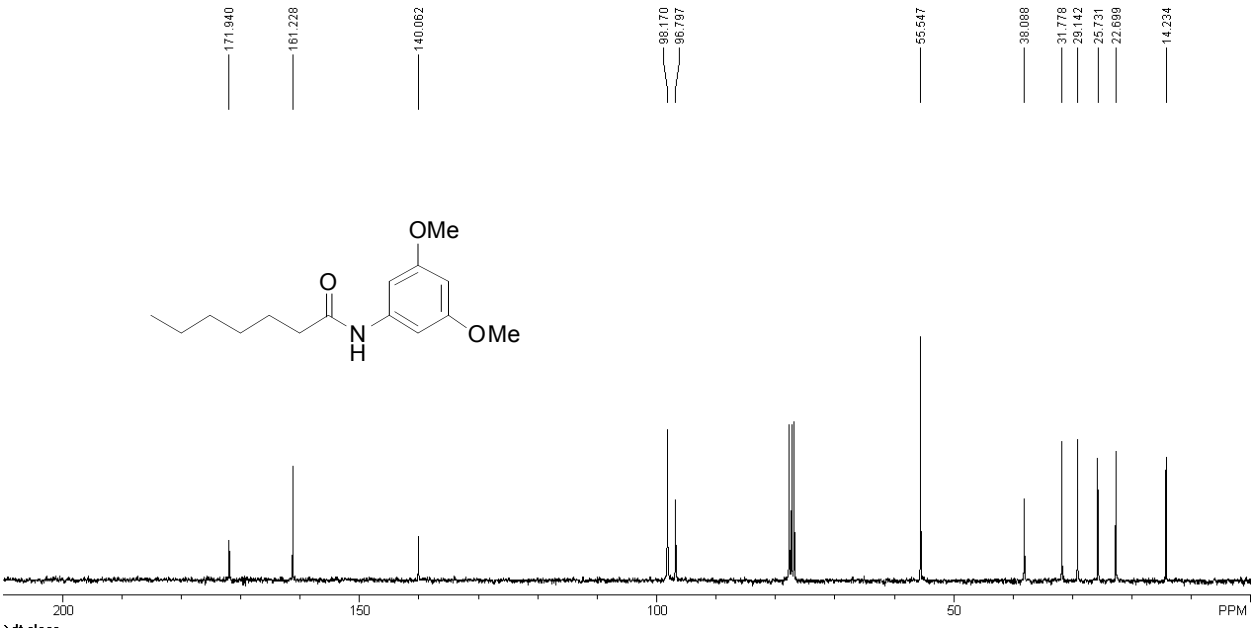
^{1}H NMR spectrum of *N*-(2-bromophenyl)heptanamide in $CDCl_3$ at 300 MHz



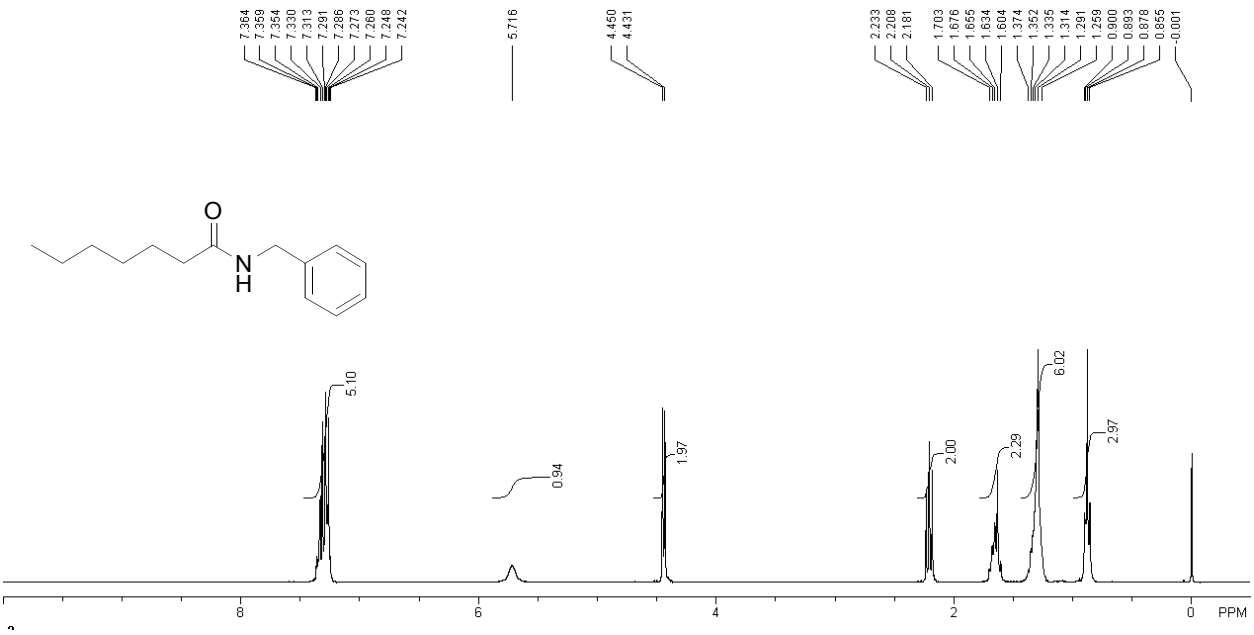
^{13}C NMR spectrum of *N*-(2-bromophenyl)heptanamide in $CDCl_3$ at 75 MHz



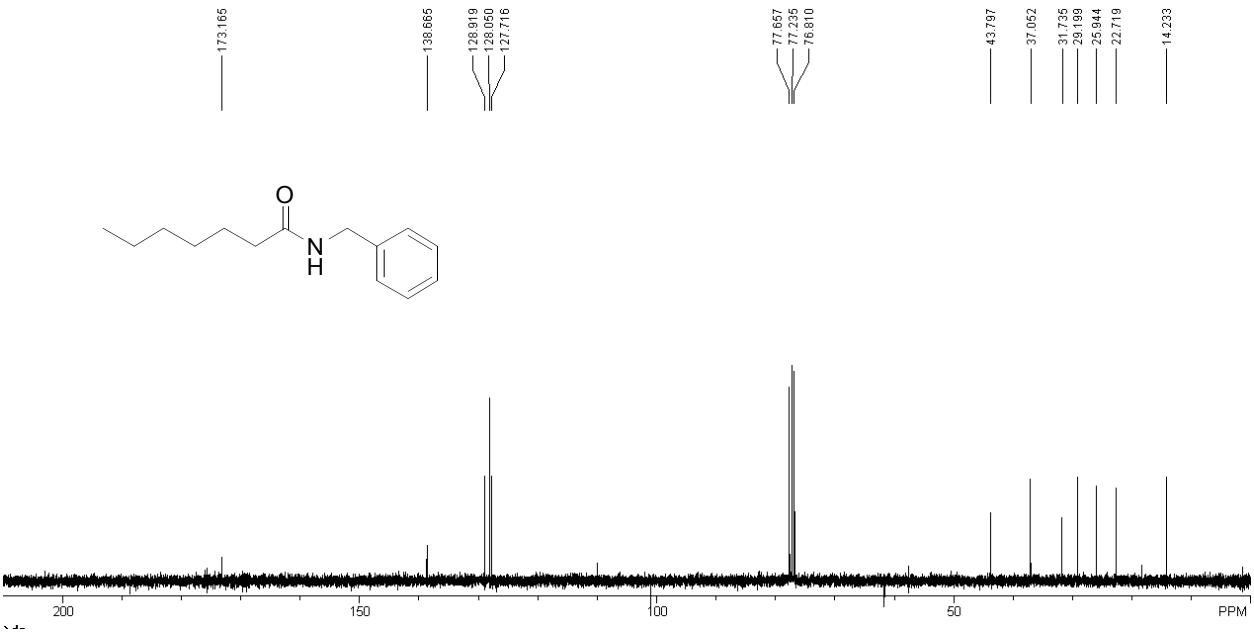
^{1}H NMR spectrum of *N*-(3,5-dimethoxyphenyl)heptanamide in $CDCl_3$ at 300MHz



^{13}C NMR spectrum of *N*-(3,5-dimethoxyphenyl)heptanamide in $CDCl_3$ at 75 MHz



^{1}H NMR spectrum of *N*-benzylheptanamide in $CDCl_3$ at 300MHz



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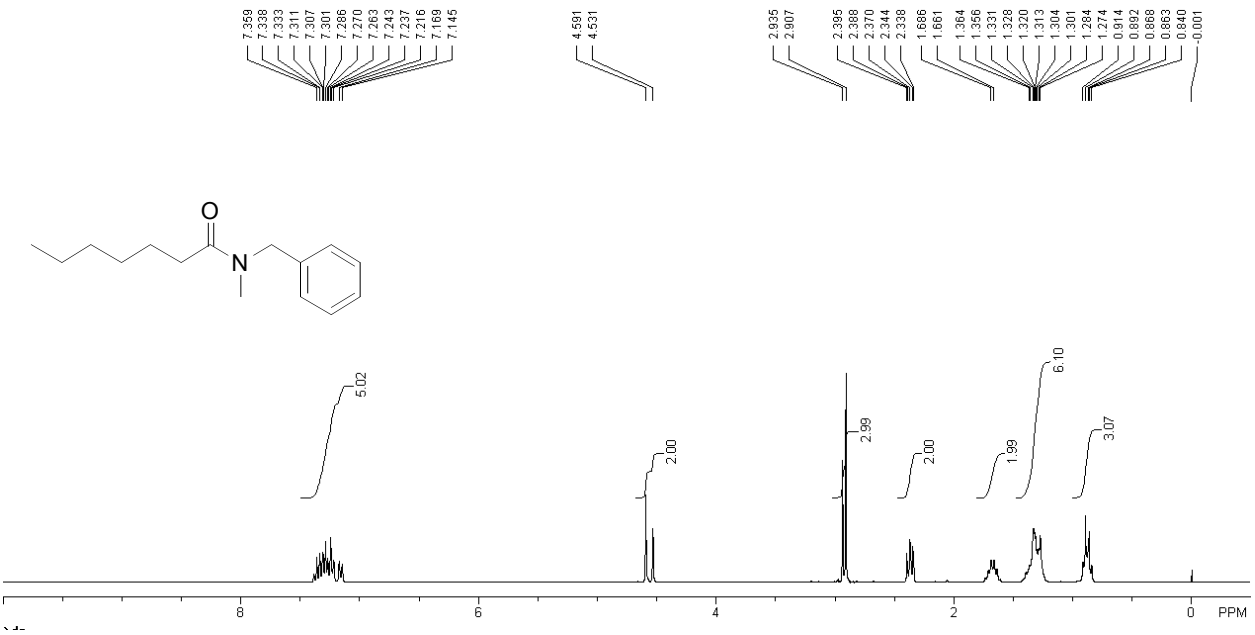
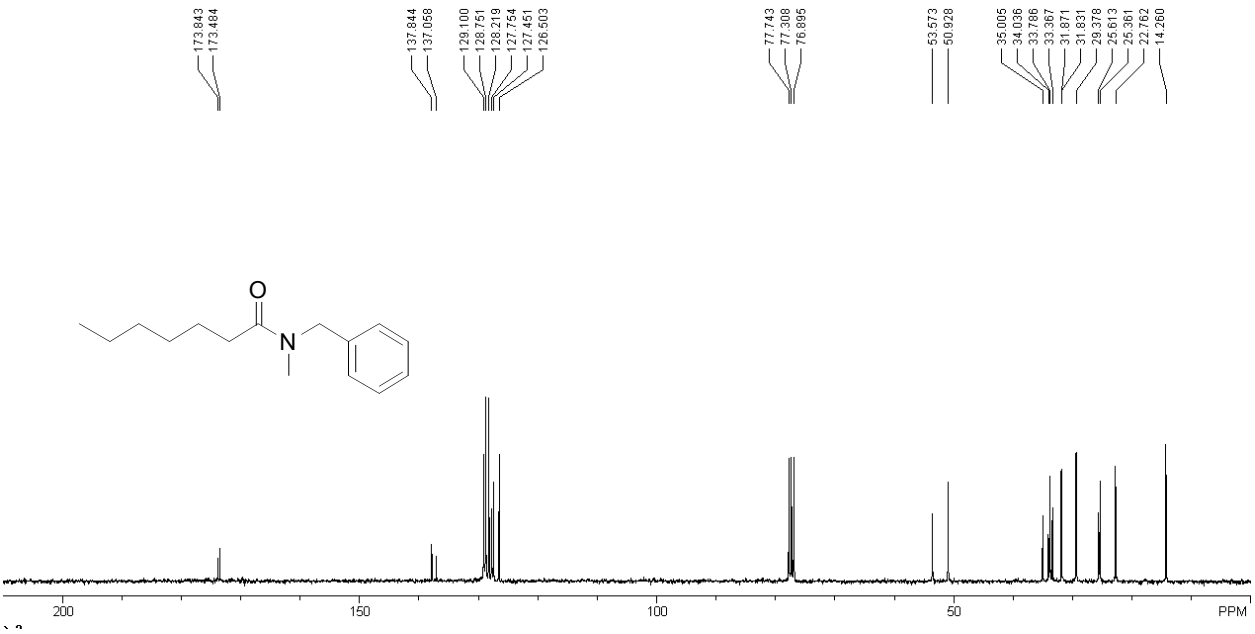
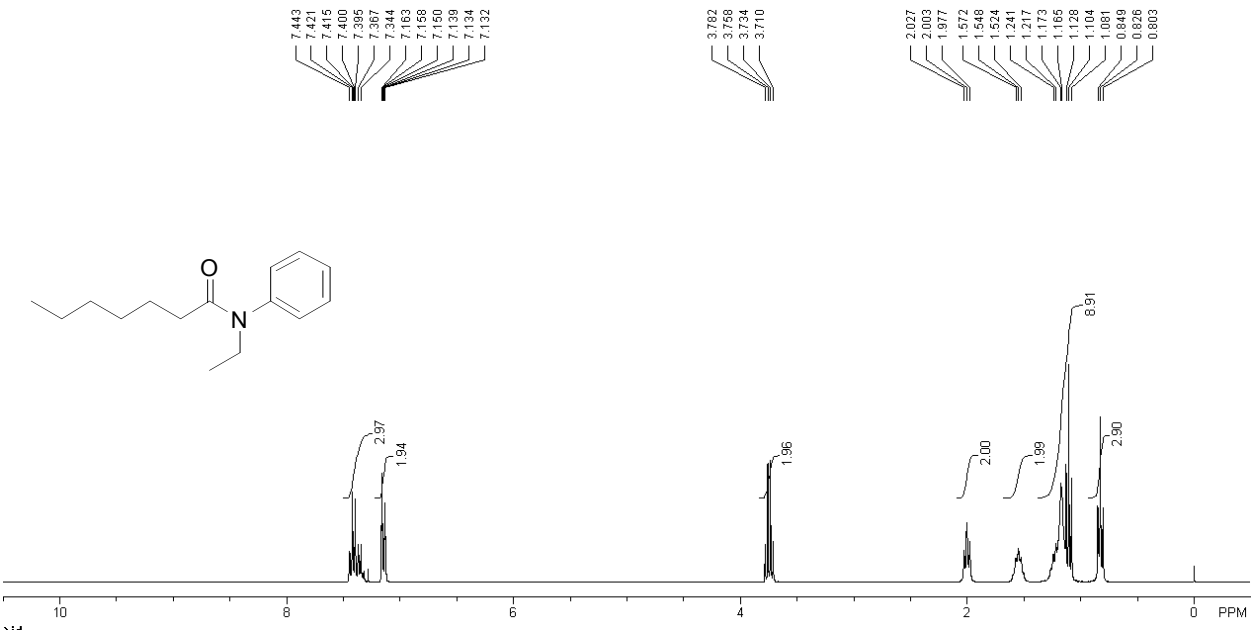


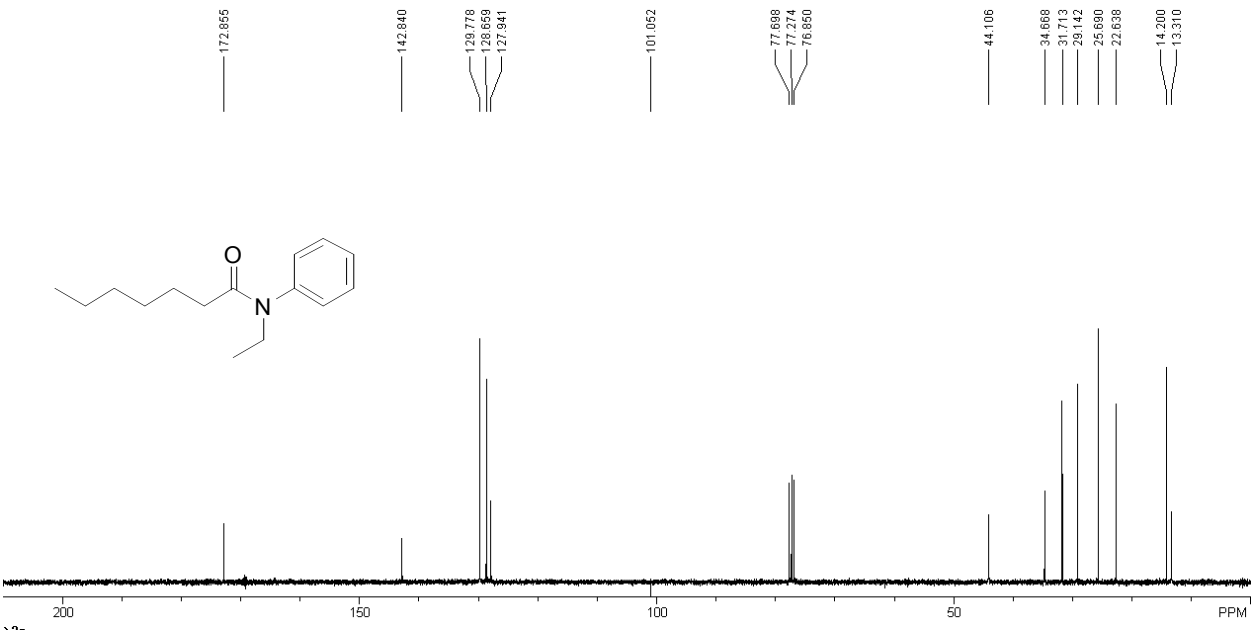
^{1}H NMR spectrum of *N,N*-benzylmethylheptanamide in $CDCl_3$ at 300MHz



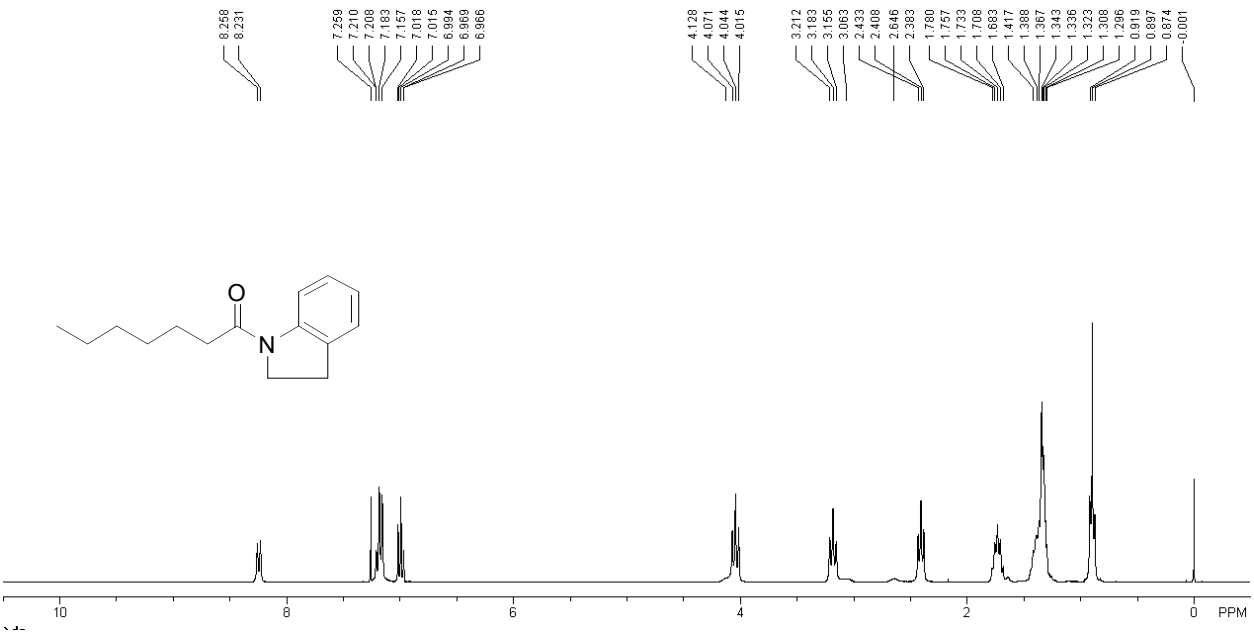
^{13}C NMR spectrum of *N, N*-benzylmethylheptanamide in $CDCl_3$ at 75MHz



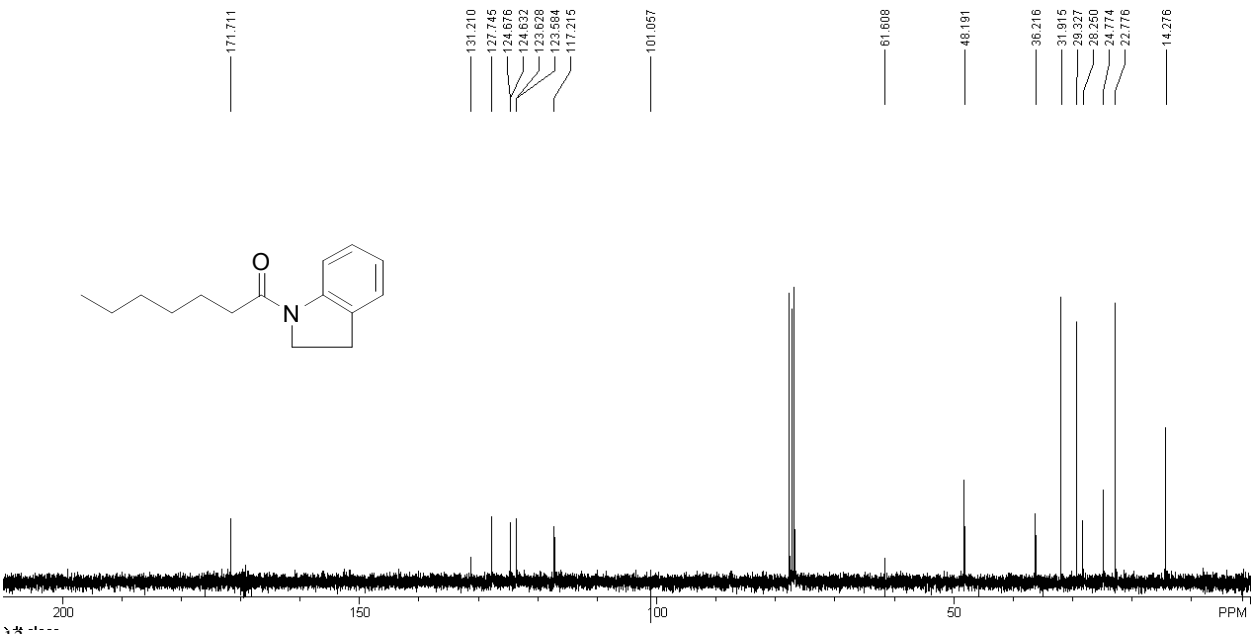
^{1}H NMR spectrum of *N*-Ethylheptanilide in $CDCl_3$ at 300MHz



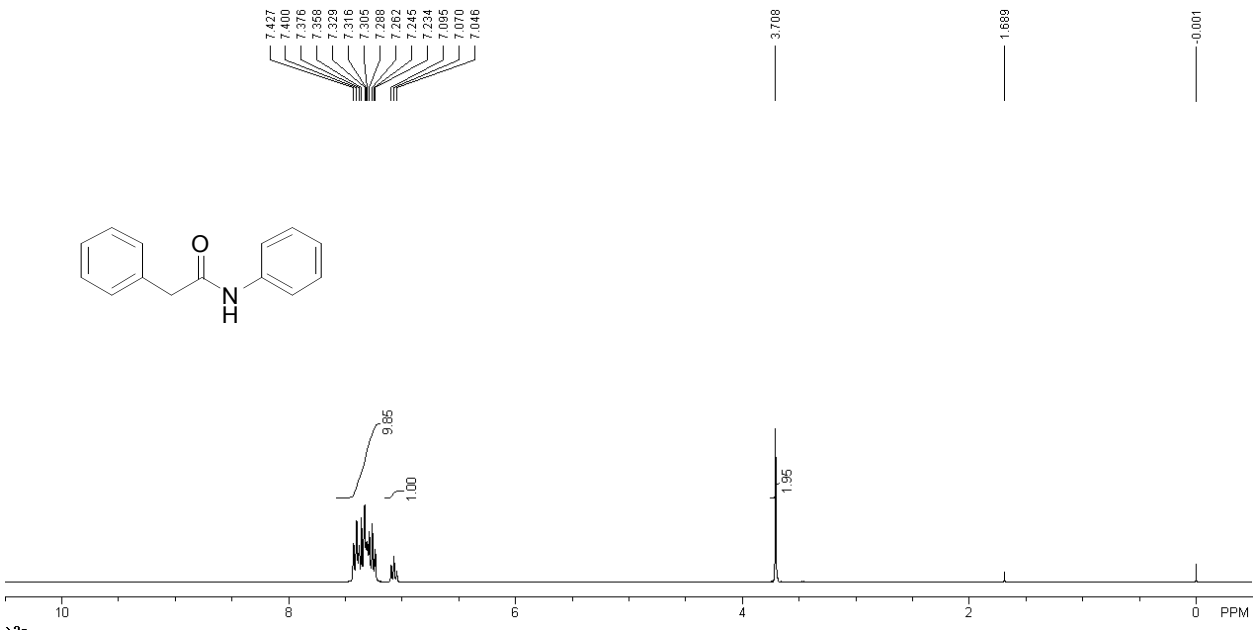
^{13}C NMR spectrum of *N*-Ethylheptanilide in $CDCl_3$ at 75MHz



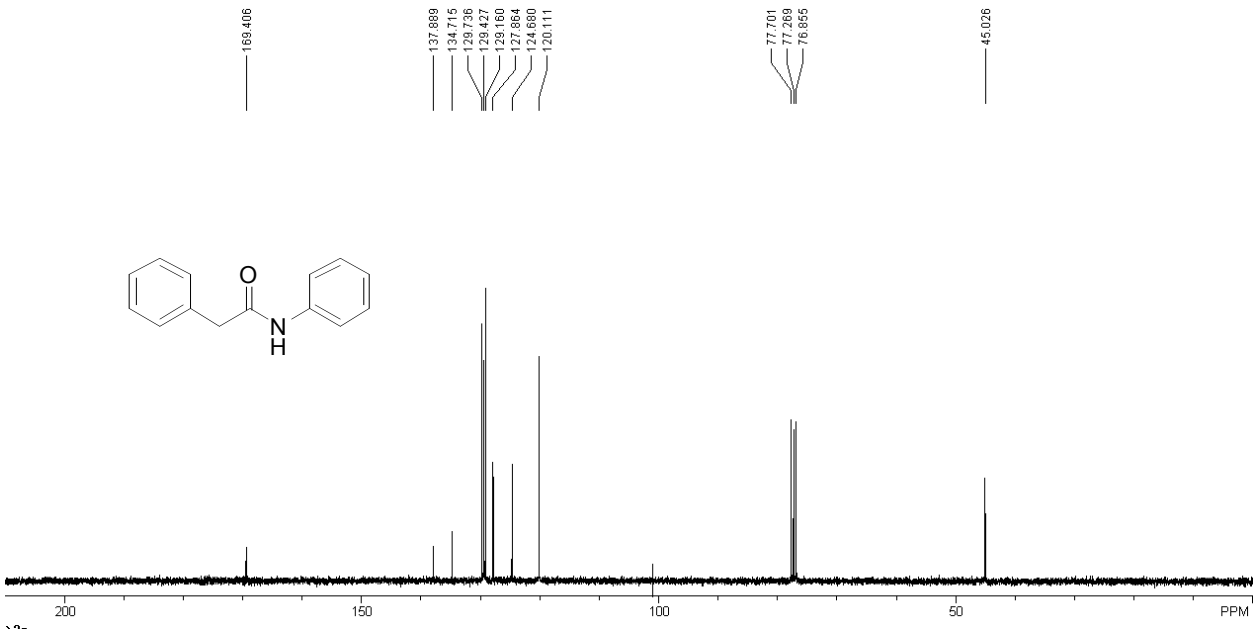
^{1}H NMR spectrum of 1-(2,3-dihydro-1H-indol-1-yl)-1-heptanamide in $CDCl_3$ at 300MHz



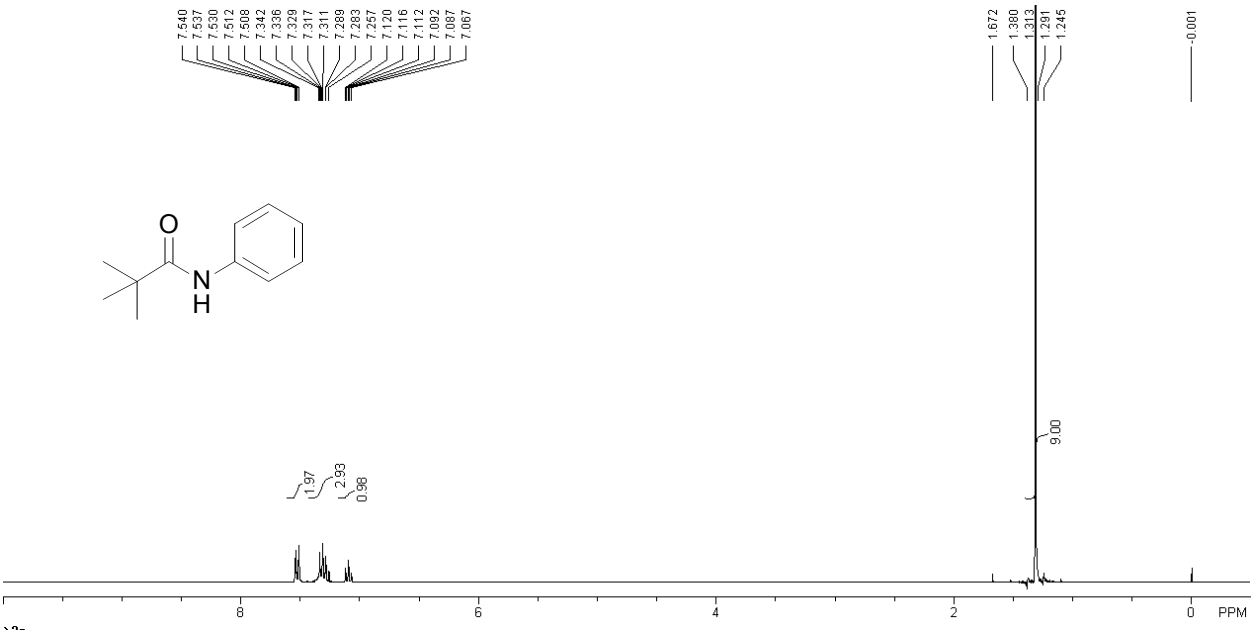
^{13}C NMR spectrum of 1-(2,3-dihydro-1H-indol-1-yl)-1-heptanamide in $CDCl_3$ at 75MHz



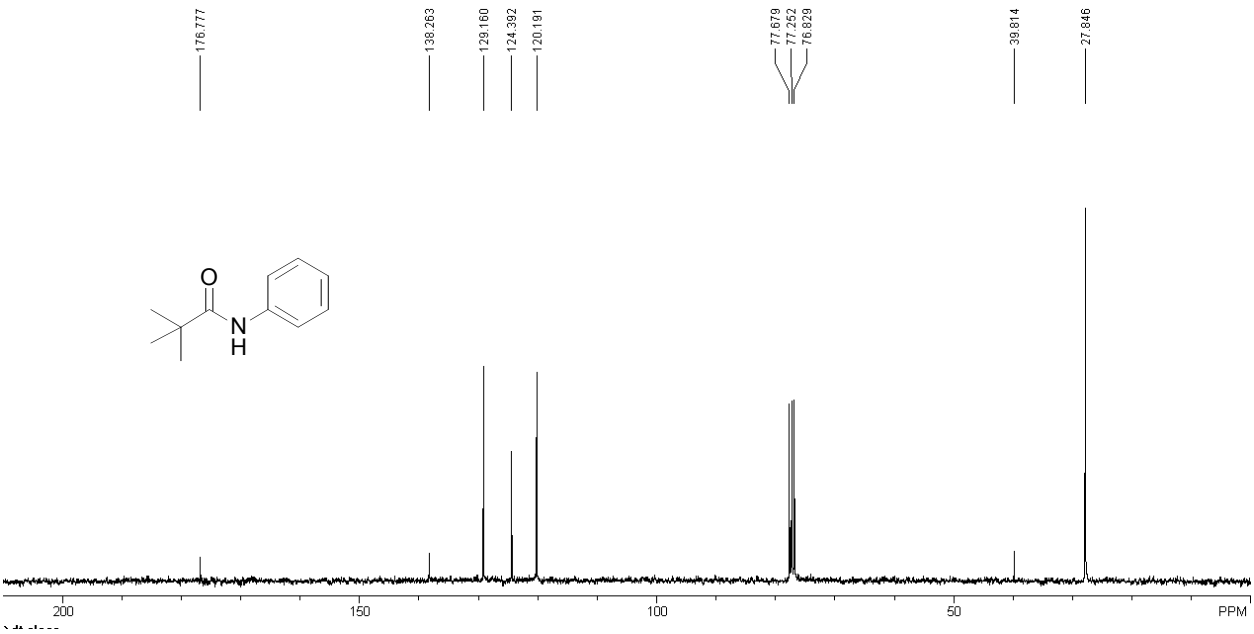
^{1}H NMR spectrum of 2-Phenylacetanilide in $CDCl_3$ at 300MHz



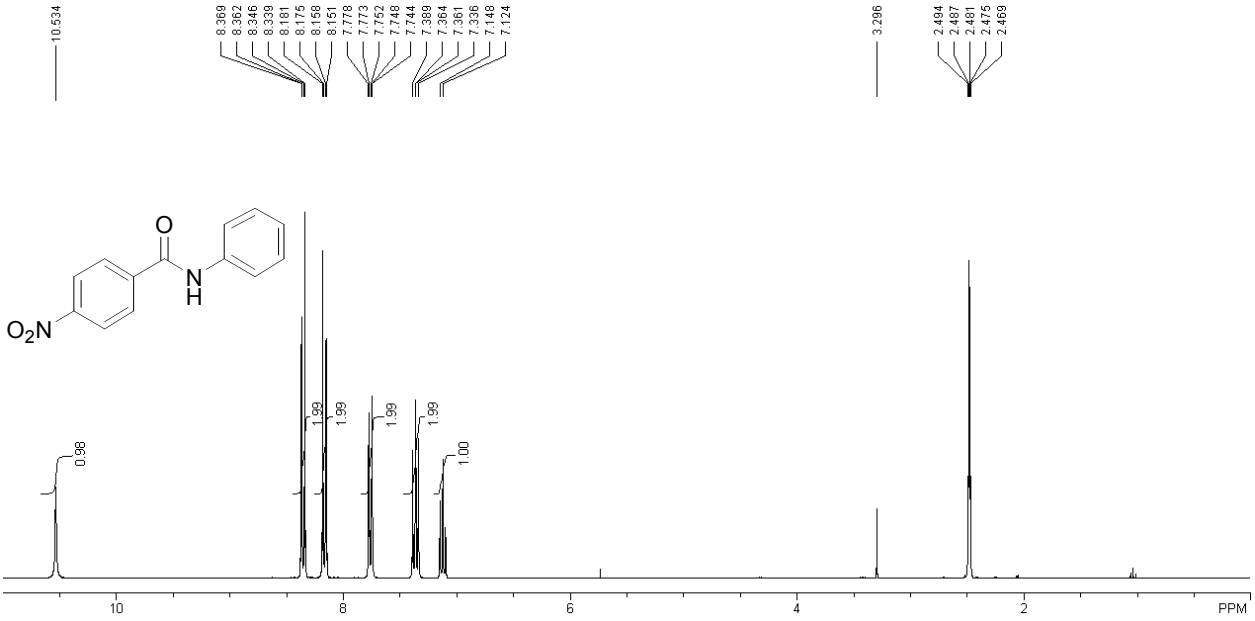
^{13}C NMR spectrum of 2-Phenylacetanilide in $CDCl_3$ at 75MHz



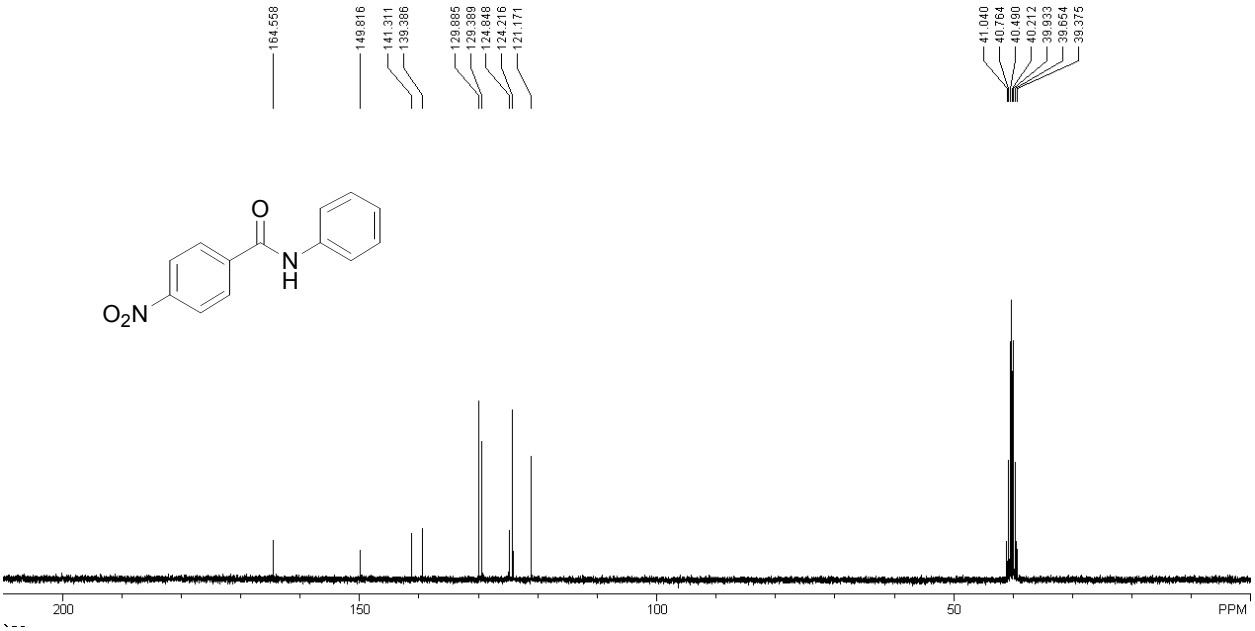
^{1}H NMR spectrum of Pivalanilide in $CDCl_3$ at 300 MHz



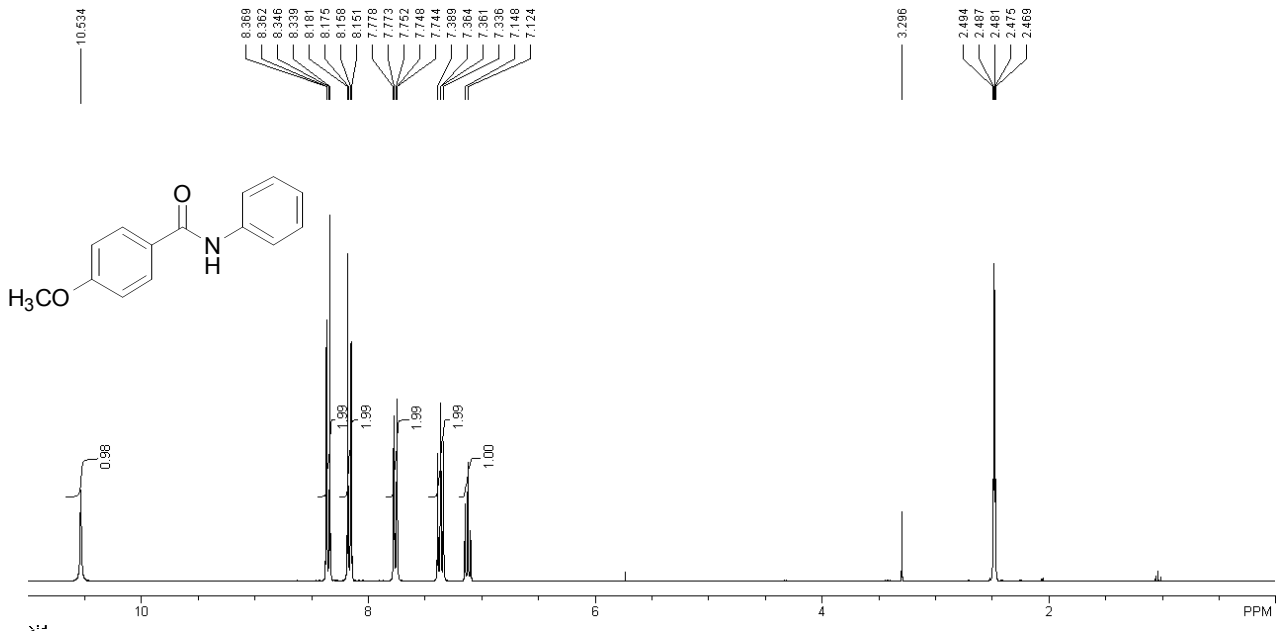
^{13}C NMR spectrum of Pivalanilide in $CDCl_3$ at 75 MHz



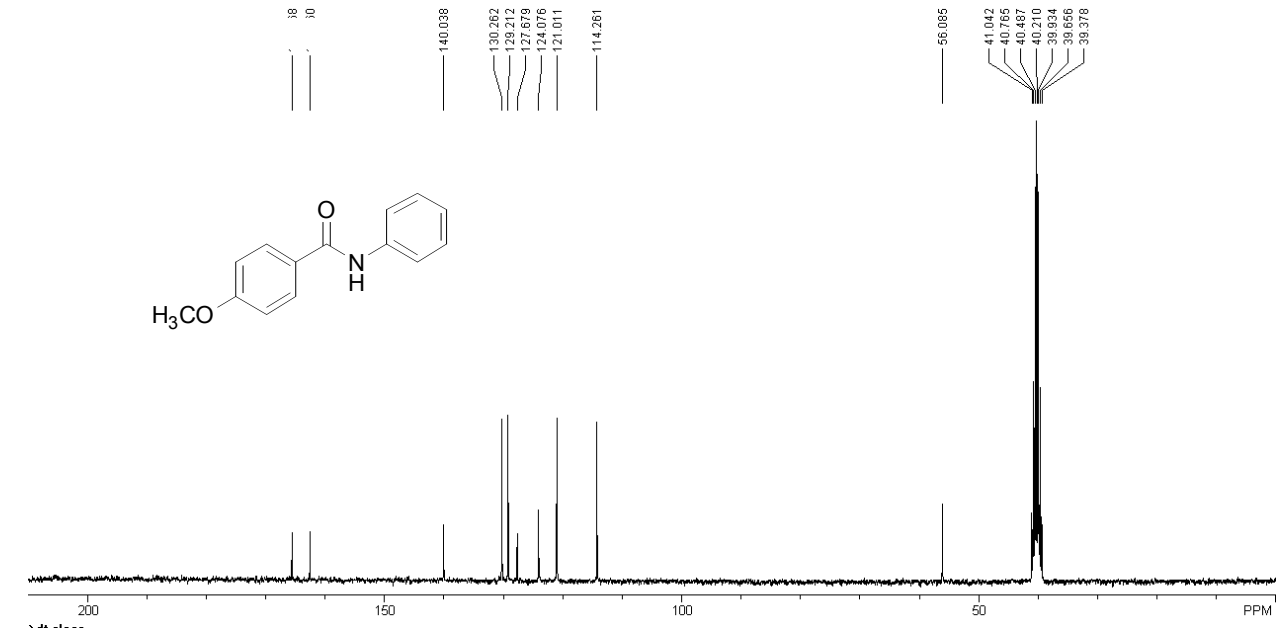
^{1}H NMR spectrum of 4-nitrobenzanilide in DMSO-d_6 at 300 MHz



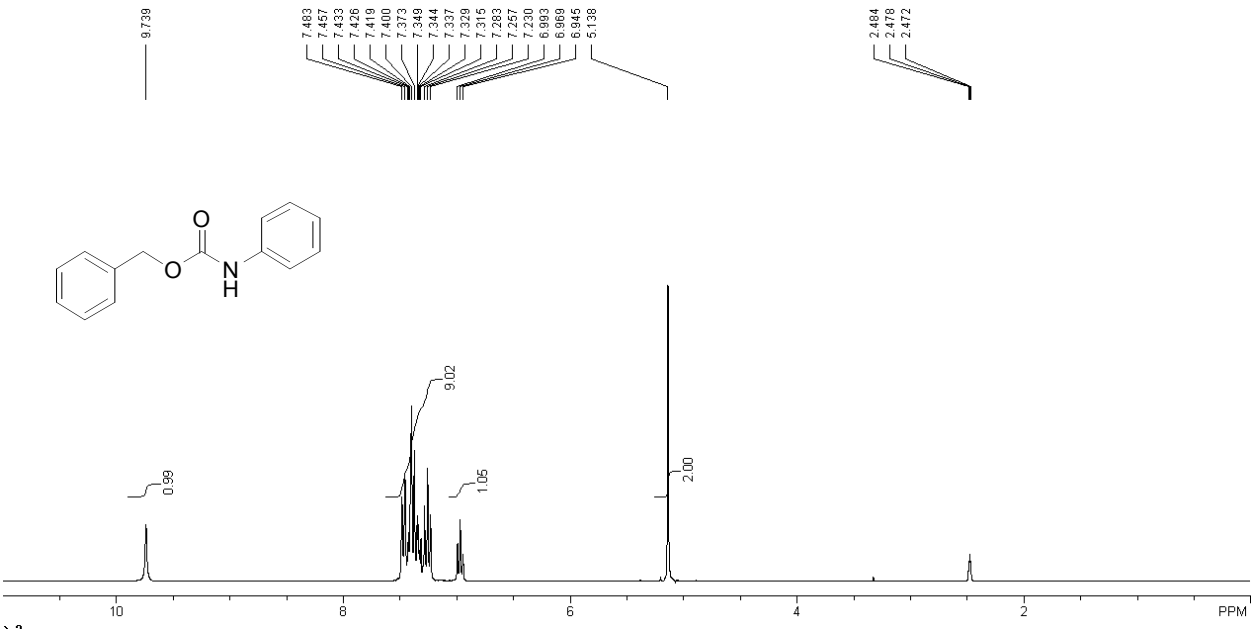
^{13}C NMR spectrum of 4-nitrobenzanilide in DMSO-d_6 at 75 MHz



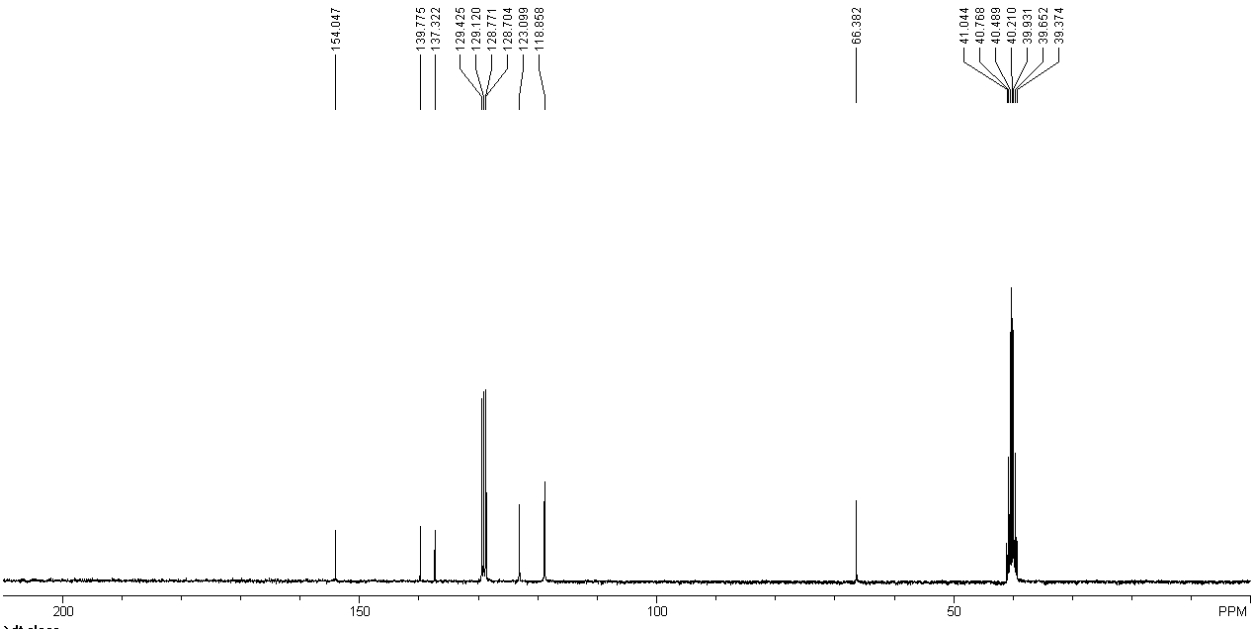
^{1}H NMR spectrum of 4-methoxybenzanilide in DMSO-d_6 at 300 MHz



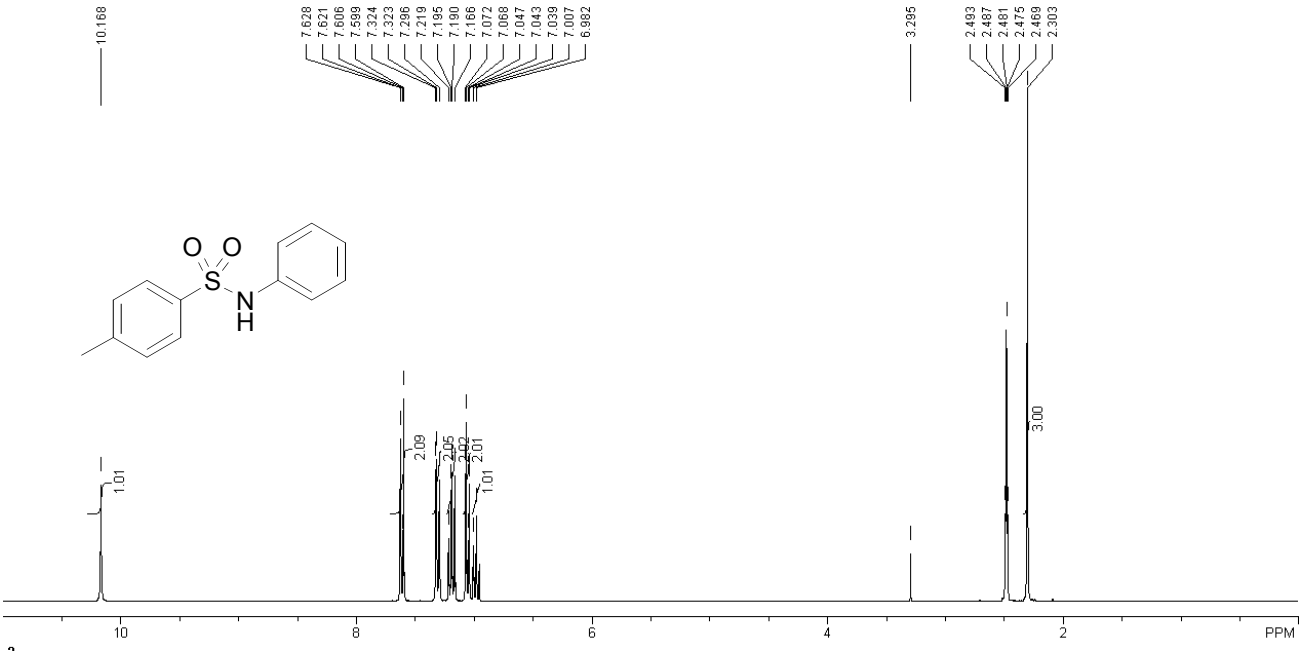
^{13}C NMR spectrum of 4-methoxybenzanilide in DMSO-d_6 at 75 MHz



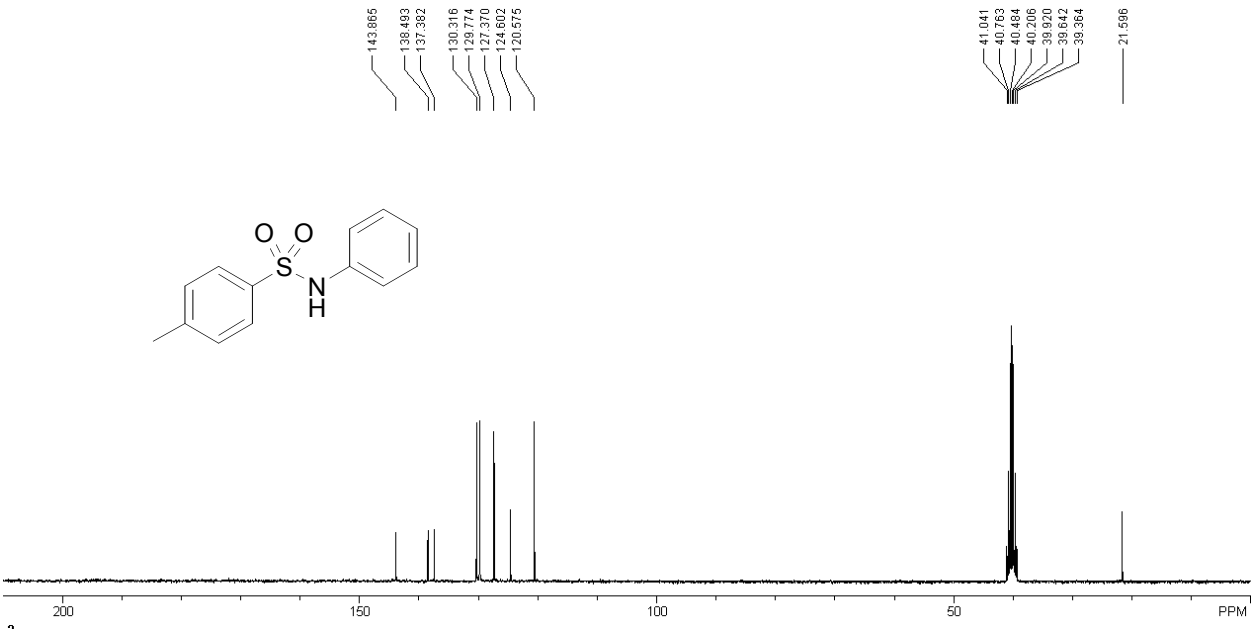
^{1}H NMR spectrum of Benzylphenylcarbamate in DMSO-d_6 at 300 MHz



^{13} C NMR spectrum of Benzylphenylcarbamate in DMSO-d_6 at 75 MHz



^{1}H NMR spectrum of 4-methylbenzenesulfonanilide in DMSO-d_6 at 300 MHz



^{13}C NMR spectrum of 4-methylbenzenesulfonanilide in DMSO-d_6 at 75 MHz

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