Hydrogenation of Nitroarenes to Anilines in Flow Reactor Using Supported Rhodium in Catalyst-Cartridge (Cart-Rh@PS)

Saurabh Sharma,[a,b] Yamini[a] and Pralay Das*[a,b]

New Journal of Chemistry

[a]Natural Product Chemistry and Process Development Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur-176061, (H. P.), India, Fax:+91-1894-230433
E-mail: pdas@ihbt.res.in, pralaydas1976@gmail.com
[b]Academy of Scientific & Innovative Research, New Delhi, India

CONTENTS

Page No.

A. Methods and Materials

Reagents for synthesis were purchased from Sigma Aldrich and Techchem Solutions. Polymer resin Amberlite IRA-900 (chloride form) from Acros Organics. Silica gel (60-120) for column chromatography purchased from Sd Fine-chem Ltd. All solvents were used without further purification. Thin layer chromatography was performed using precoated silica gel plates 60 F254 (Merck) in UV light detector. ESI-MS spectra were analyzed using micromass Q-TOF ultima spectrometer.^{1}H and ^{13}C NMR spectra were recorded by using BrukerAvance 300 and 600 spectrometer operating at300 MHz (^{1}H) and 75 MHz (^{13}C)/ 600 MHz (^{1}H) and 150 MHz (^{13}C) respectively. Spectra were recorded at 25 °C in $CDCl_3$ [residual $CHCl_3$ (δ_H 7.26 ppm) or $CDCl_3$ (δ_C 77.00 ppm), DMSO-d_6(δ_H 2.50 and 2.80 ppm) or (δ_C 39.5 ppm) and CD_3OD (δ_H 3.33 and 4.88 ppm) or CD_3OD (δ_C48.00 ppm) as international standard] with TMS as internal standard. Chemical shifts were recorded in δ (ppm) relative to the TMS and NMR solvent signal, coupling constants (*J*) are given in Hz and multiplicities of signals are reported as follows: s, singlet; bs, broad singlet; d, doublet; t, triplet; m, multiplet.

B. Preparation of polystyrene supported rhodium (0) (Rh@PS) nanoparticles as catalyst

In 100 ml round bottom flask, 5 g of Amberlite® IRA-900 resin was taken and added into solution of $NaBH_4$(140 mg in 30 ml water). The mixture war stirred for 4 hours at room temperature after that the resin was washed with water till neutral pH and then with acetone to remove water from the resin. The borohydride exchanged resin was dried over rotary evaporator under reduced pressure. Dried resin was treated with $RhCl_3.3H_2O$ (10 mg/gm) in DMF at 100 ^{o}C till the yellowish solution turns colorless and white resin turns black indicated that the impregnation of rhodium metal in the solid resin. After complete immobilization of rhodium over solid resin, resin was washed with water and acetone then dried over the rotavapour under reduced pressure. The Rh@PS was used in several reduction reactionsup to 12 runs without loss in catalytic activity.

C. Recyclability test of Rh@PS

The recyclability experiment of Rh@PS was done for the hydrogenation of4-nitrotoluene. After completion of reaction, the reaction mixture was filtered off through a cotton bed, washed with water and acetone properly, dried over rotary evaporator. Finally, the recovered dried catalyst was repeatedly used for the same reaction. The catalyst retained its catalytic activity up to 12 cycles with negligible metal leaching.

TEM images of the rhodium nanopartciles at 20, 5 and 1 nm scale (Fig (a), (b) and (c)) respectively.

We have included the part of the original TEM image given below, into manuscript for high resolution of the images.

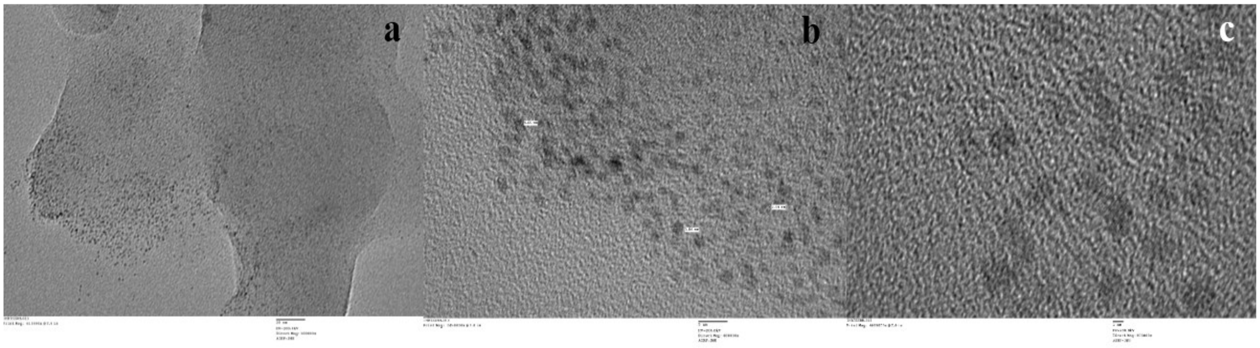


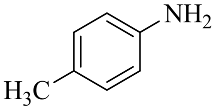
Figure S1. (a) TEM image at 20 nm, (b) TEM image at 5 nm, (c) HRTEM image

D. ICP-AES study of the reaction mixture

In the recyclability experiments, we have used 350 mg of Rh@PS (2 mol% Rh) for 100 mg of 4-nitrotolene (**1a**) as a model substrate for the reduction reaction, in 350 mg of Rh@PS contains 1.13 mg rhodium metal when 10 mg $RhCl_3.3H_2O$ was allowed to bind on 1 gm of borohydride exchanged polystyrene resin matrix, and finally got the reaction mixture. After digesting the reaction mixture with acid solution, it was analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). ICP-AES analysis carried out on ARCOS from M/S Spectro, Germany. We found that only 0.01 ppm metal was leached out during the reaction.

Experimental procedure for hydrogenation of 4-nitrotoluene using Rh@PSas catalyst under flow reactor:

4-Methylaniline[1a](2a)



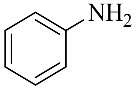
A solution of 4-nitrotoluene (100 mg, 0.7299 mmol) in 20 mL EtOAc:MeOH (1:1) was passed through the Cat-Cart containing solid supported rhodium (Cart-Rh@PS) catalyst (350 mg) in cartridge, for 20 minutes at 100 °C and the reaction was completed in single run. Monitoring of the reaction was observed by TLC, after completion of the reaction the solution containing product was dried over rotary evaporator and afforded the product 4-methylaniline (**2a**) as brown solid (75 mg, 96%).

^{1}H NMR (600 MHz; CDCl$_3$) δ2.25 (s, 3H), 6.61 (d, *J* = 8.22 Hz, 2H), 6.97 (d, *J* = 8.04 Hz, 2H).

^{13}CNMR (150 MHz, CDCl$_3$) δ20.40, 115.24, 127.77, 129.71, 143.72.

ESI-MS(m/z): [M+H]$^+$ calcd. for $C_7H_{10}N$ is 108.0808 and obsd. 108.0820. NMR data compared with reported compound

Aniline[1a] (Table3,**2b**)



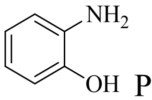
Prepared as described for **2a** starting from nitrobenzene (100 mg, 0.8130 mmol) (Cart-Rh@PS) catalyst (350 mg) for 10 minutes at 100 °C the reaction was completed in single run. On completion of the reaction the solution containing product (**2b**) was dried over rotary evaporator and afforded the product aniline (**2b**) as brown liquid (74 mg, 98%).

^{1}H NMR (600 MHz; CDCl$_3$) δ 6.68 (d, *J* = 7.8 Hz, 2H), 6.74-6.77 (t, *J* = 7.29 Hz, 1H), 7.14-7.17 (t, *J* = 7.71 Hz, 1H).

^{13}C NMR (150 MHz, CDCl3) δ115.09, 118.55, 129.25, 146.31.

ESI-MS(m/z): [M+H]$^+$ calcd. for C_6H_8N is 94.0651 and obsd. 94.0670. NMR data compared with reported compound.

2-Aminophenol[1b] (Table 3, **2c**)



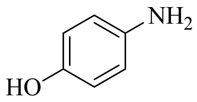
Prepared as described for **2a** starting from 2-nitrophenol (100 mg, 0.7194 mmol) (Cart-Rh@PS) catalyst (350 mg) for 20 minutes at 80 ^{o}C the reaction was completed in single run. After completion of the reaction the solution containing product (**2c**) was dried over rotary evaporator and afforded the product 4-aminophenol (**2c**) as yellow solid (75 mg, 96%).

^{1}H NMR (600 MHz; CD$_3$OD) δ6.56-6.61 (m, 1H), 6.64-6.67 (m, 1H), 6.70-6.72 (m, 1H), 6.75-6.76 (m, 1H).

^{13}CNMR (600 MHz, CD$_3$OD) δ114.57, 116.53, 119.25, 120.04, 135.00, 145.53.

ESI-MS(m/z): [M+H]$^+$ calcd. for C$_6$H$_8$NO is 110.0606 and obsd. 110.0608. NMR data compared with reported compound.

4-Aminophenol[1c]**(**Table3,**2d**)



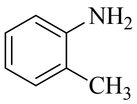
Prepared as described for **2a** starting from 4-nitrophenol (100 mg, 0.7194 mmol)(Cart-Rh@PS) catalyst (350 mg) for 20 minutes at 80 ^{o}C the reaction was completed in single run. After completion of the reaction the solution containing product (**2c**) was dried over rotary evaporator and afforded the product 4-aminophenol(**2c**) as yellow solid (74.5 mg, 95%).

^{1}H NMR (600 MHz; DMSO-d_6) δ6.39 (d, *J*= 8.64 Hz, 2H), 6.45 (d, *J*= 8.64 Hz, 2H).

^{13}CNMR (150 MHz, DMSO-d_6) δ 115.75, 116.00, 141.07, 148.69.

ESI-MS(m/z):[M+H]+ calcd. for C$_6$H$_8$NO is 110.0600 and obsd. 110.0595. NMR data compared with reported compound.

2-Methylaniline[1d](Table2,**2e**)



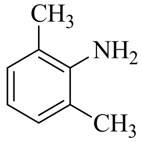
Prepared as described for **2a** starting from 2-nitrotoluene (100 mg, 0.7299 mmol)(Cart-Rh@PS) catalyst (350 mg) for 20 minutes at 80 ^{o}C the reaction was completed in two runs. After completion of the reaction the solution containing product (**2e**) was dried over rotary evaporator and afforded the product 2-toluidine (**2e**) as yellow liquid (75 mg, 96%).

^{1}H NMR (600 MHz; CDCl$_3$) δ2.22 (s, 3H), 6.72-6.77 (m, 2H), 7.08-7.11 (m, 2H).

^{13}CNMR (150 MHz, CDCl$_3$) δ 17.27, 114.86, 118.55, 122.25, 126.89, 130.37, 144.49.

ESI-MS(m/z): [M+H]+ calcd. for $C_7H_{10}N$ is 108.0808 and obsd. 108.0796. NMR data compared with reported compound.

2,6-Dimethylaniline[1f](Table3,**2f**)



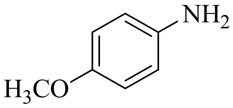
Prepared as described for **2a** starting from 2,6-dimethylnitrobenzene (100 mg, 0.6622mmol),Cart-Rh@PS catalyst (350 mg) for 10 minutes at 80 °C the reaction was completed in two runs. After completion of the reaction the solution containing product (**2f**) was dried over rotary evaporator and afforded the product 2,6-dimethylaniline (**2f**) as yellow liquid (78.5 mg, 98%).

^{1}H NMR (300 MHz; CDCl$_3$) δ2.22 (s, 6H), 3.60 (brs, 2H), 6.66-6.71 (t, *J* = 7.41 Hz, 1H), 6.97 (d, *J* = 7.35 Hz, 2H).

^{13}CNMR (75 MHz, CDCl$_3$) δ 17.54, 117.97, 121.65, 128.21, 142.68.

ESI-MS(m/z):[M+H]+ calcd. for $C_8H_{12}N$ is 122.0964 and obsd. 122.0953. NMR data compared with reported compound.

4-Anisidine[1a](Table3,**2g**)

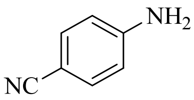


Prepared as described for **2a** starting from 4-methoxynitrobenzene (100 mg, 0.6535 mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 40 °Cthe reaction was completed in three run. After completion of the reaction the solution containing product (**2g**) was dried over rotary evaporator and afforded the product 4-anisidine (**2g**) as brown solid (78 mg, 97%).

^{1}H NMR (300 MHz; CDCl$_3$) δ 3.35 (brs, 2H), 3.75 (s, 3H), 6.63-6.67 (m, 2H), 6.75-6.79 (m, 2H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 55.52, 114.64, 116.22, 139.88, 152.56. NMR data compared with reported compound.

4-Aminobenzonitrile[1a](Table3,**2h**)



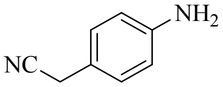
Prepared as described for **2a** starting from 4-nitrobenzonitrile (100 mg, 0.6757mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 40 °C the reaction was completed in single run. After completion of the reaction the solution containing product (**2h**) was dried over rotary evaporator and afforded the product 4-aminobenzonitrile (**2h**) as white solid (77 mg, 97%).

^{1}H NMR (600 MHz; CDCl$_3$) δ4.15 (brs, 2H), 6.64 (d, *J*= 8.4 Hz, 2H), 7.41 (d, *J*= 8.4 Hz, 2H).

^{13}CNMR (150 MHz, CDCl$_3$) δ 100.28, 114.41, 120.06, 133.79, 150.31.

ESI-MS (m/z): [M+H] $^+$ calcd. for $C_7H_7N_2$ is 119.0604 and obsd. 119.0607. NMR data compared with reported compound.

2-(4-Aminophenyl)acetonitrile[1g](Table3,**2i**)



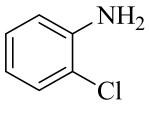
Prepared as described for **2a** starting from 4-acetylnitrobenzene (100 mg, 0.6173 mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 60 °C the reaction was completed in single run. After completion of the reaction the solution containing product (**2i**) was dried over rotary evaporator and afforded the product 2-(4-aminophenyl)acetonitrile (**2i**) as white solid (76.6 mg, 94%).

^{1}H NMR (600 MHz; CDCl$_3$) δ 3.60 (s, 2H), 6.64 (d, *J*= 8.4 Hz, 2H), 7.05 (d, *J*= 8.4 Hz, 2H).

^{13}CNMR (150 MHz, CDCl$_3$) δ 22.56, 115.27, 118.52, 119.03, 128.73, 146.14.

ESI-MS (m/z): [M+H] $^+$ calcd. for $C_8H_9N_2$ is 133.0760 and obsd. 133.0772. NMR data same as reported compound.

2-Chloroaniline[1b](Table3,**2j**)



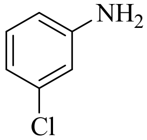
Prepared as described for **2a** starting from 2-chloronitrobenzene(100 mg, 0.6369 mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 80 °C the reaction was completed in single run. After completion of the reaction the solution containing product (**2j**) was dried over rotary evaporator and afforded the product 2-chloroaniline (**2j**) as brown liquid (75 mg, 93%).

^{1}H NMR (600 MHz; CDCl$_3$) δ4.00 (brs, 2H), 6.72-6.74 (t,*J* = 7.62 Hz, 1H), 6.78-6.80 (m, 1H), 7.09-7.12 (t, *J* = 7.65 Hz, 1H), 7.28 (d, *J* = 7.92 Hz, 1H).

^{13}CNMR (150 MHz, CDCl$_3$) δ 115.80, 118.94, 119.20, 127.55, 129.33, 142.84.

ESI-MS (m/z): [M+H] $^+$ calcd. for C_6H_7ClN is 128.0262 and obsd. 128.0265. NMR data compared with reported compound.

3-Chloroaniline[1d](Table3,**2k**)



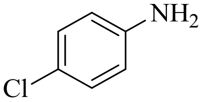
Prepared as described for **2a** starting from 3-chloronitrobenzene(100 mg, 0.6369 mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 100 °Cthe reaction was completed in single run. After completion of the reaction the solution containing product (**2k**) was dried over rotary evaporator and afforded the product 3-chloroaniline (**2k**) as brown liquid (77 mg, 95%).

^{1}H NMR (600 MHz; CD$_3$OD) δ 6.58-6.62 (m, 2H), 6.70 (s, 1H), 7.01-7.04 (t, J = 7.98 Hz, 1H)

^{13}CNMR (150 MHz, CD$_3$OD) δ 113.36, 114.69, 117.20, 130.17, 134.65, 149.72.

ESI-MS (m/z): [M+H] $^+$ calcd. for C_6H_7ClN is 128.0262 and obsd. 128.0255. NMR data compared with reported compound.

4-Chloroaniline[1a](Table3,**2l**)



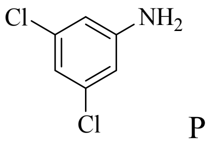
Prepared as described for **2a** starting from 4-chloronitrobenzene(100 mg, 0.6369 mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 100 °C the reaction was completed in single run. After completion of the reaction the solution containing product (**2l**) was dried over rotary evaporator and afforded the product 4-chloroaniline (**2l**) as brown liquid (76 mg, 94%).

^{1}H NMR (600 MHz; CDCl$_3$) δ 6.60-6.61 (m, 2H), 7.09-7.10 (m, 2H).

^{13}CNMR (150 MHz,CDCl$_3$) δ 116.21, 123.18, 129.10, 144.89.

ESI-MS (m/z): [M+H] $^+$ calcd. for C_6H_7ClN is 128.0262 and obsd. 128.0269. NMR data compared with reported compound.

3,5-Dichloroaniline[1e](Table3,**2m**)



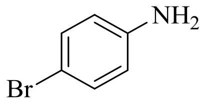
Prepared as described for **2a** starting from 1,3-dichloro-5-nitrobenzene (100 mg, 0.5236 mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 60 °C the reaction was completed in single run. After completion of the reaction the solution containing product (**2m**) was dried over rotary evaporator and afforded the product 5,6-Dichloroaniline(**2m**) as yellow liquid(75 mg, 93%).

^{1}H NMR (600 MHz; CDCl$_3$) δ 3.81 (brs, 2H), 6.52 (d, *J*= 1.74 Hz, 2H), 6.71 (d, *J*= 1.74 Hz, 1H).

^{13}CNMR (150 MHz, CDCl$_3$) δ 113.12, 118.18, 135.30, 148.19.

ESI-MS (m/z): [M+H]$^+$ calcd. for $C_6H_6Cl_2N$ is 161.9872 and obsd. 161.9879. NMR data compared with reported compound.

4-Bromoaniline[1a](Table3,**2n**)



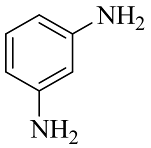
Prepared as described for **2a** starting from 1-bromo-4-nitrobenzene (100 mg, 0.4978 mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 80 °C the reaction was completed in single run. After completion of the reaction the solution containing product (**2n**) was dried over rotary evaporator and afforded the product 4-bromoaniline (**2n**) as brown solid (78 mg, 92%).

^{1}H NMR (600 MHz; CDCl$_3$) δ6.56 (d, *J* = 8.58 Hz, 2H), 7.22 (d, *J* = 8.64 Hz, 2H).

^{13}CNMR (150 MHz, CDCl$_3$) δ 110.23, 116.70, 132.00, 145.36.

ESI-MS (m/z): [M+H]$^+$ calcd. for C_6H_7BrN is 171.9756 and obsd. 171.9750. NMR data compared with reported compound.

Benezene-1,3-diamine[1a](Table3,**2o**)



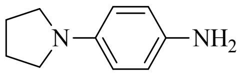
Prepared as described for **2a** starting from 3-aminonitrobenzene (100 mg, 0.7246mmol),Cart-Rh@PS catalyst (350 mg) for 20 minutes at 80 °C the reaction was completed in single run. After completion of the reaction the solution containing product (**2o**) was dried over rotary evaporator and afforded the product benezene-1,3-diamine(**2o**) a white solid(76 mg, 97%).

^{1}H NMR (600 MHz; CDCl$_3$) δ 3.57 (s, 4H), 6.03 (s, 1H), 6.14-6.15 (m, 2H), 6.96-6.99 (t, *J* = 7.86 Hz, 1H).

^{13}CNMR (150 MHz, CDCl$_3$) δ 101.86, 105.79, 130.00, 147.42.

ESI-MS (m/z): [M+H] $^+$ calcd. for $C_6H_9N_2$ is 109.0760 and obsd. 109.0768. NMR data compared with reported compound.

4-(pyrrolidine-1-yl)benzenamine[1k](Table3,**2p**)



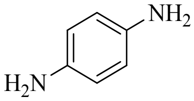
Prepared as described for **2a** starting from 1-(4-nitrophenyl)pyrrolidine (100 mg, 0.5208mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 100 °C the reaction was completed in single run. After completion of the reaction the solution containing product (**2p**) was dried over rotary evaporator and afforded the product 4-(pyrrolidine-1-yl)benzenamine (**2p**) as white solid(78 mg, 93%).

^{1}H NMR (600 MHz; CDCl$_3$) δ1.99-2.03 (m, 4H), 3.26 (s, 6H), 6.50 (d, *J* = 16.62 Hz, 2H), 6.70 (d, *J* = 16.44 Hz, 2H).

^{13}CNMR (150 MHz, CDCl$_3$) δ25.16, 48.23, 112.93, 117.04, 136.00, 142.33.

ESI-MS (m/z): [M+H] $^+$ calcd. for $C_{10}H_{15}N_2$ is 163.1230 and obsd. 163.1223. NMR data compared with reported compound.

Benezene-1,4-diamine[1a](Table3,**2q**)



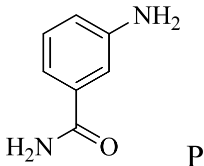
Prepared as described for **2a** starting from 1,4-dinitrobenzene (100 mg, 0.5952mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 100 °C the reaction was completed in single run. After completion of the reaction the solution containing product (**2q**) was dried over rotary evaporator and afforded the product 1,4-diaminobenene(**2q**) as white solid(62 mg, 96%).

^{1}H NMR (600 MHz; CDCl$_3$) δ3.33 (brs, 4H), 6.57 (s, 4H).

^{13}CNMR (150 MHz, CDCl$_3$) δ 116.73, 138.61.

ESI-MS (m/z): [M+H] $^+$ calcd. for $C_6H_9N_2$ is 109.0760 and obsd. 109.0750. NMR data compared with reported compound.

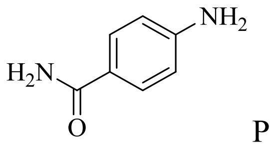
3-Aminobenzamide[1i](Table3,**2r**)



Prepared as described for **2a** starting from 3-nitrobenzamide (100 mg, 0.6024mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 90 °C the reaction was completed in two runs. After completion of the reaction the solution containing product (**2r**) was dried over rotary evaporator and afforded the product 3-aminobenzamide (**2r**) as yellowish solid (74 mg, 90%).

^{1}H NMR (600 MHz; DMSO-*d_6*) δ5.19 (brs, 2 NH), 6.68 (d, *J* = 7.32 Hz, 1H), 6.98 (d, *J* = 7.44 Hz, 1H), 7.05-7.07 (m, 2H), 7.15 (s, NH), 7.73 (s, NH).
^{13}CNMR (150 MHz, DMSO-*d_6*) δ113.61, 115.19, 116.99, 129.03, 135.69, 149.05, 169.26
ESI-MS (m/z): $[M+H]^+$ calcd. for $C_7H_9N_2O$ is 137.0709 and obsd. 137.0702. NMR data compared with reported compound.

4-Aminobenzamide[1a](Table3,**2s**)



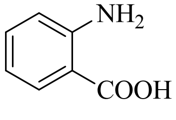
Prepared as described for **2a** starting from 4-nitrobenzamide (100 mg, 0.6024 mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 90 °C the reaction was completed in two runs. After completion of the reaction the solution containing product (**2s**) was dried over rotary evaporator and afforded the product 4-aminobenzamide (**2s**) as white solid (76 mg, 93%).

^{1}H NMR (600 MHz; CD_3OD) δ 6.65-6.66 (d, *J* = 8.64 Hz, 2H), 7.63-7.64 (d, *J* = 8.58 Hz, 2H).

^{13}CNMR (150 MHz,CD_3OD) δ 113.61, 121.25, 129.47, 152.52, 171.77.

ESI-MS (m/z): $[M+H]^+$ calcd. for $C_7H_9N_2O$ is 137.0709 and obsd. 137.0702. NMR data compared with reported compound.

2-aminobenzoic acid[1j](Table 3, **2t**)



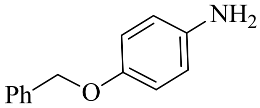
Prepared as described for **2a** starting from 2-nitrobenzoic acid (100 mg, 0.5988 mmol), Cart-Rh@PS catalyst (350 mg) for 20 minutes at 80 °C the reaction was completed in single run. After completion of the reaction the solution containing product (**2t**) was dried over rotary evaporator and afforded the product 4-aminobenzamide (**2t**) as white solid (75 mg, 92%).

^{1}H NMR (300 MHz; CD_3OD) δ6.55-6.60 (t, *J* = 7.54 Hz, 1H), 6.73 (d, *J* = 8.34 Hz, 1H), 7.21-7.26 (m, 1H), 7.80-7.83 (m, 1H).

^{13}CNMR (75 MHz,CD_3OD) δ 111.08, 115.58, 116.74, 131.66, 133.88, 151.75, 170.77.

ESI-MS (m/z): $[M+H]^+$ calcd. for $C_7H_8NO_2$ is 138.0550 and obsd. 138.0545. NMR data compared with reported compound.

4-(benzyloxy)aniline[1a](Table3,**2u**)



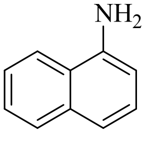
Prepared as described for **2a** starting from 1-(benzoxyl)-4-nitrobenzene (100 mg, 0.4366 mmol), catalyst Cart-Rh@PS (350 mg) for 20 minutes at 90 °Cthe reaction was completed in single run. After completion of the reaction the solution containing product (**2u**) was dried over rotary evaporator and afforded the product 4-(benzyloxy)aniline (**2u**) as brown liquid(74 mg, 85%).

^{1}H NMR (600 MHz; $CDCl_3$) δ5.00 (s, 2H), 6.64 (d, *J* = 8.64 Hz, 2H), 6.82 (d, *J* = 8.70 Hz, 2H), 7.31-7.33 (t, *J* = 7.32 Hz, 1H), 7.37-7.39 (t, *J* = 7.53 Hz, 2H), 7.42 (d, *J* = 7.44 Hz, 2H).

^{13}CNMR (150 MHz, $CDCl_3$) δ 70.74, 116.04, 116.37, 127.45, 127.75, 128.46, 137.47, 140.11, 151.99.

ESI-MS (m/z) $[M+H]^+$ calcd. for $C_{13}H_{14}NO$ is 200.1070 obsd. 200.1060.NMR data compared with reported compound.

Naphthalene-1-amine[1a](Table3,**2v**)



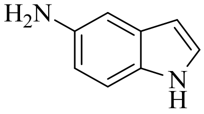
Prepared as described for **2a** starting from 1-nitronaphthalene (100 mg, 0.5780mmol), catalyst Cart-Rh@PS (350 mg) for 20 minutes at 80 °C the reaction was completed in single run. After completion of the reaction the solution containing product (**2v**) was dried over rotary evaporator and afforded the product naphthalene-1-amine (**2v**) as brown liquid(79 mg, 96%).

^{1}H NMR (600 MHz; CDCl$_3$) δ 6.81-6.83 (m, 1H), 7.32-7.38 (m, 2H), 7.48-7.52 (m, 2H), 7.84-7.86 (m, 2H).

^{13}CNMR (150 MHz, CDCl$_3$) δ 109.65, 118.94, 120.75, 123.62, 124.81, 125.80, 126.29, 128.51, 134.36, 142.02.

ESI-MS (m/z): [M+H] $^{+}$ calcd. for $C_{10}H_{10}N$ is 144.0808 and obsd. 144.0800. NMR data compared with reported compound.

1*H*-Idole-5-amine[1b](Table3,**2w**)



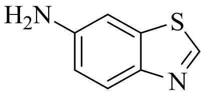
Prepared as described for **2a** starting from 5-nitro-1*H*-indole (100 mg, 0.6172mmol), catalyst Cart-Rh@PS (350 mg) for 20 minutes at 80 ^{o}C the reaction was completed in single run. After completion of the reaction the solution containing product (**2w**) was dried over rotary evaporator and afforded the product 1*H*-idole-5-amine (**2w**) as white solid (78 mg, 95%).

^{1}H NMR (600 MHz; DMSO-*d$_6$*) δ 4.49 (brs, 2H), 6.13 (s, 1H), 6.49 (d, *J* = 8.40 Hz, 1H), 6.69 (s, 1H), 7.08 (d, *J* = 8.40 Hz, 1H), 7.12 (s, 1H), 10.57 (s, 1H).

^{13}CNMR (150 MHz, DMSO-*d$_6$*) δ 100.08, 103.67, 111.83, 112.28, 125.17, 129.01, 130.22, 141.47

ESI-MS (m/z): [M+H]$^{+}$ calcd. for $C_{10}H_{10}N$ is 133.0760 and obsd. 133.0772. NMR data compared with reported compound.

Benzothiazole-6-amine[1g](Table3,**2x**)



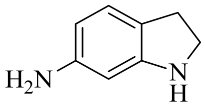
Prepared as described for **2a** starting from 6-nitrobenzo thiazole (100 mg, 0.5554 mmol), catalyst Cart-Rh@PS (350 mg) for 20 minutes at 80 ^{o}C the reaction was completed in single run. After completion of the reaction the solution containing product (**2x**) was dried over rotary evaporator and afforded the product benzothiazole-6-amine (**2x**) as white solid (78 mg, 94%).

^{1}H NMR (300 MHz; CDCl$_3$) δ 3.57 (brs, 2H), 6.86-6.90 (m, 1H), 7.17-7.18 (m, 1H), 7.89-7.92(m, 1H), 8.71 (s, 1H).

^{13}C NMR (75 MHz; CDCl$_3$) δ 105.62, 115.74, 123.92, 135.46, 144.79, 146.77, 149.74

ESI-MS (m/z) $[M+H]^+$ calcd. for $C_{10}H_{10}N$ is 151.0324 obsd. 151.0330.NMR data compared with reported compound.

Indolin-6-amine[1h](Table3,**2y**)

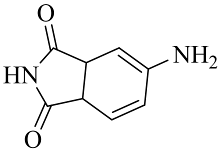


Prepared as described for **2a** starting from 6-nitroindoline (100 mg, 0.6098 mmol), catalyst Cart-Rh@PS (350 mg) for 20 minutes at 90 °C the reaction was completed in single run. After completion of the reaction the solution containing product (**2y**) was dried over rotary evaporator and afforded the product indolin-6-amine (**2y**) as white solid (78 mg, 95%).

^{1}H NMR (600 MHz; CDCl$_3$) δ 2.89-2.92 (t, *J* = 8.25 Hz, 2H), 3.49-3.52 (t, *J* = 8.25 Hz, 2H), 3.62 (s, 3 NH), 6.03-6.06 (m, 2H), 6.87 (d, *J* = 7.68 Hz, 1H).

^{13}CNMR (150 MHz, CDCl$_3$) δ 28.95, 47.66, 97.31, 105.46, 119.54, 124.83, 146.07, 152.70. NMR data compared with reported compound.

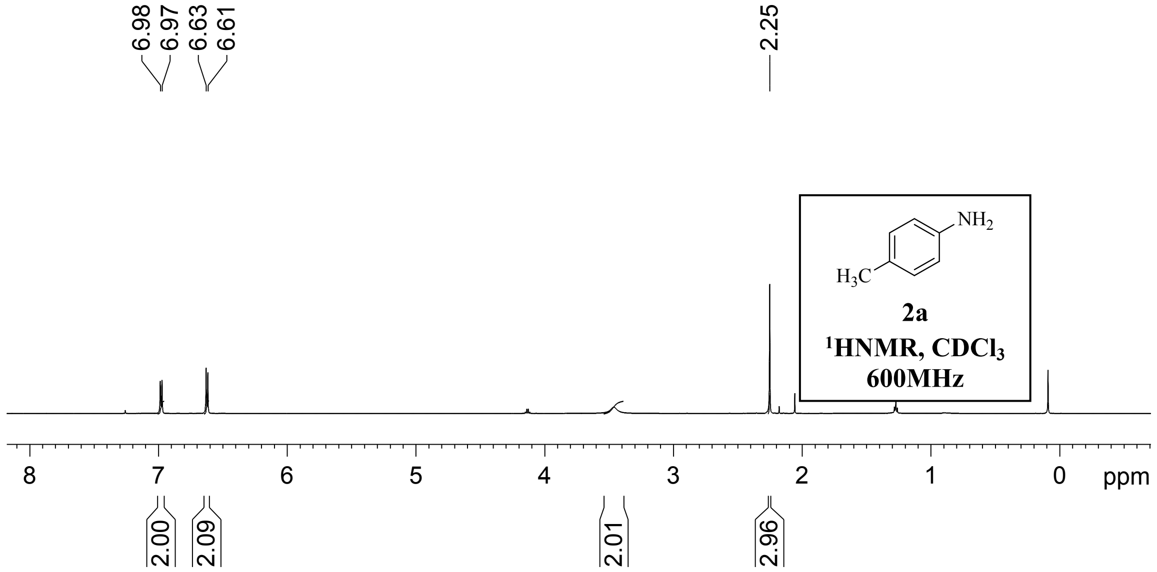
5-Amino-3a,7a-dihydro-1*H*-isoindole-1,3(2*H*)-dione[1j](Table3,**2z**)

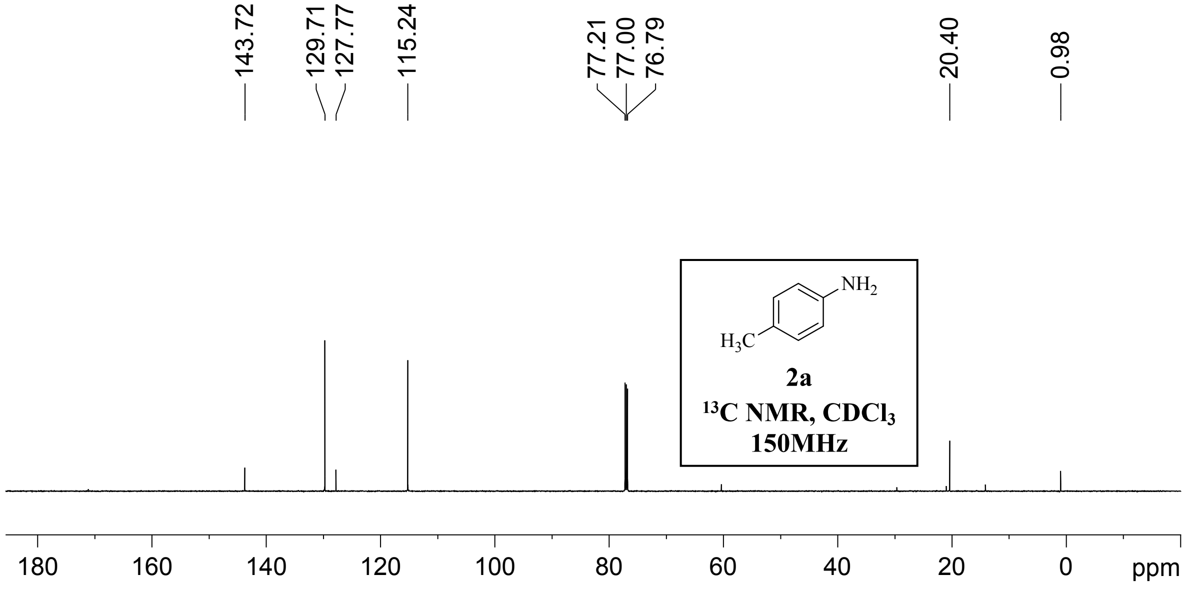


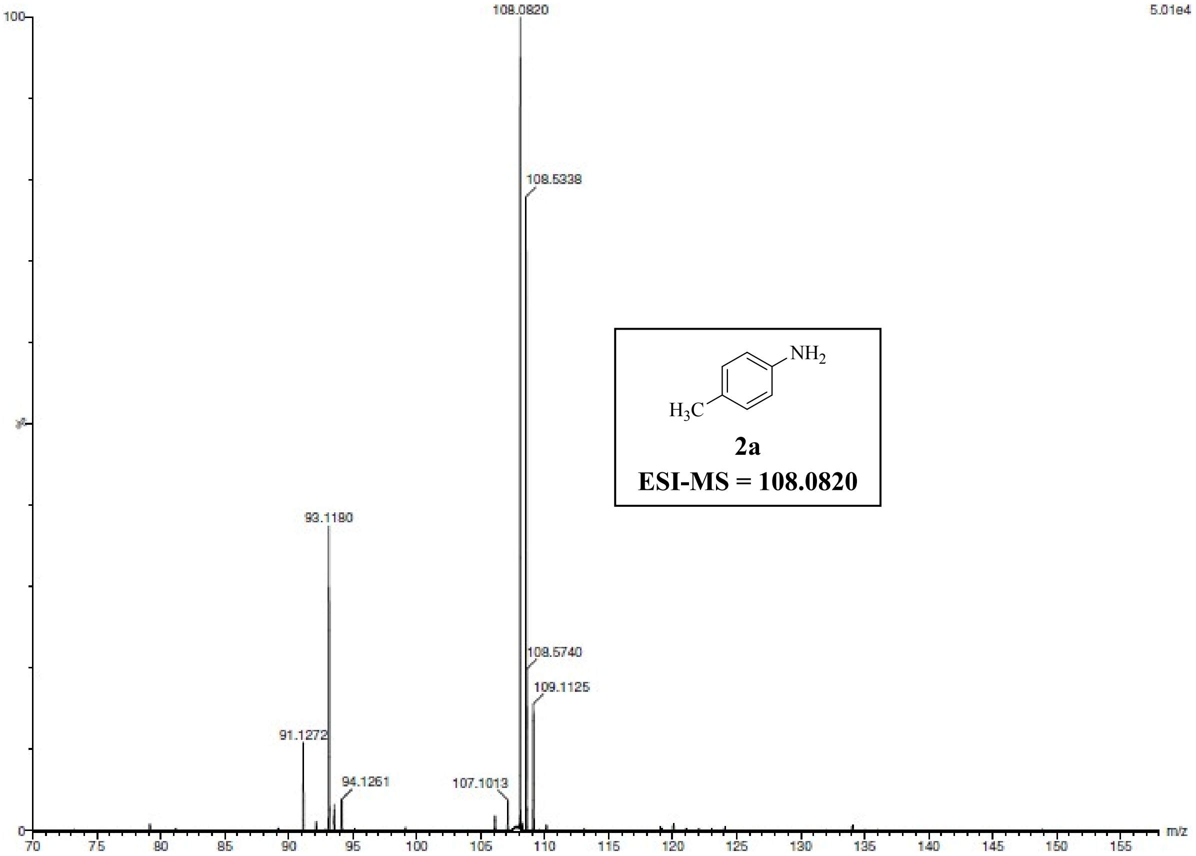
Prepared as described for **2a** starting from 5-nitro-3a,7a-dihydro-1*H*-isoindole-1,3 (2*H*)-dione (100 mg, 0.5208 mmol), catalyst Cart-Rh@PS (350 mg) for 20 minutes at 80 °Cthe reaction was completed in two runs. After completion of the reaction the solution containing product (**2z**) was dried over rotary evaporator and afforded the product indolin-6-amine (**2z**) as white solid (77 mg, 90%).

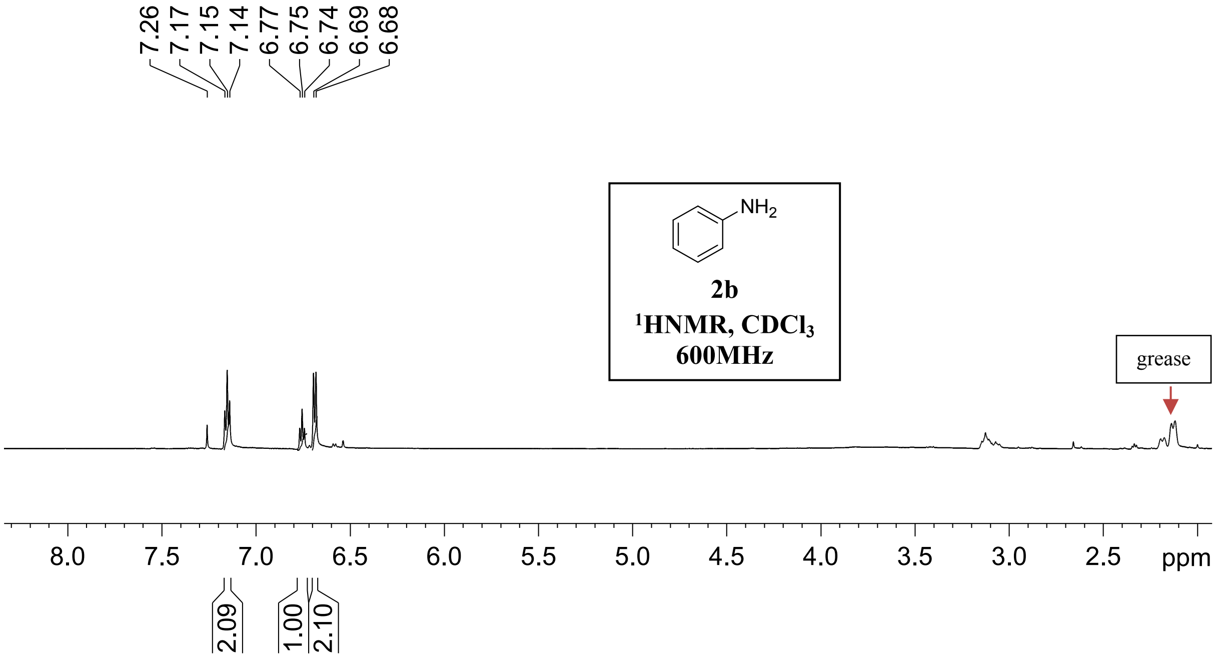
^{1}H NMR (600 MHz; DMSO-*d$_6$*) δ6.40 (s, 2H), 6.78 (d, *J*= 8.16 Hz, 1H), 6.86 (s, 1H), 7.43 (d, *J*= 8.16 Hz, 1H), 10.73 (s, 1H).

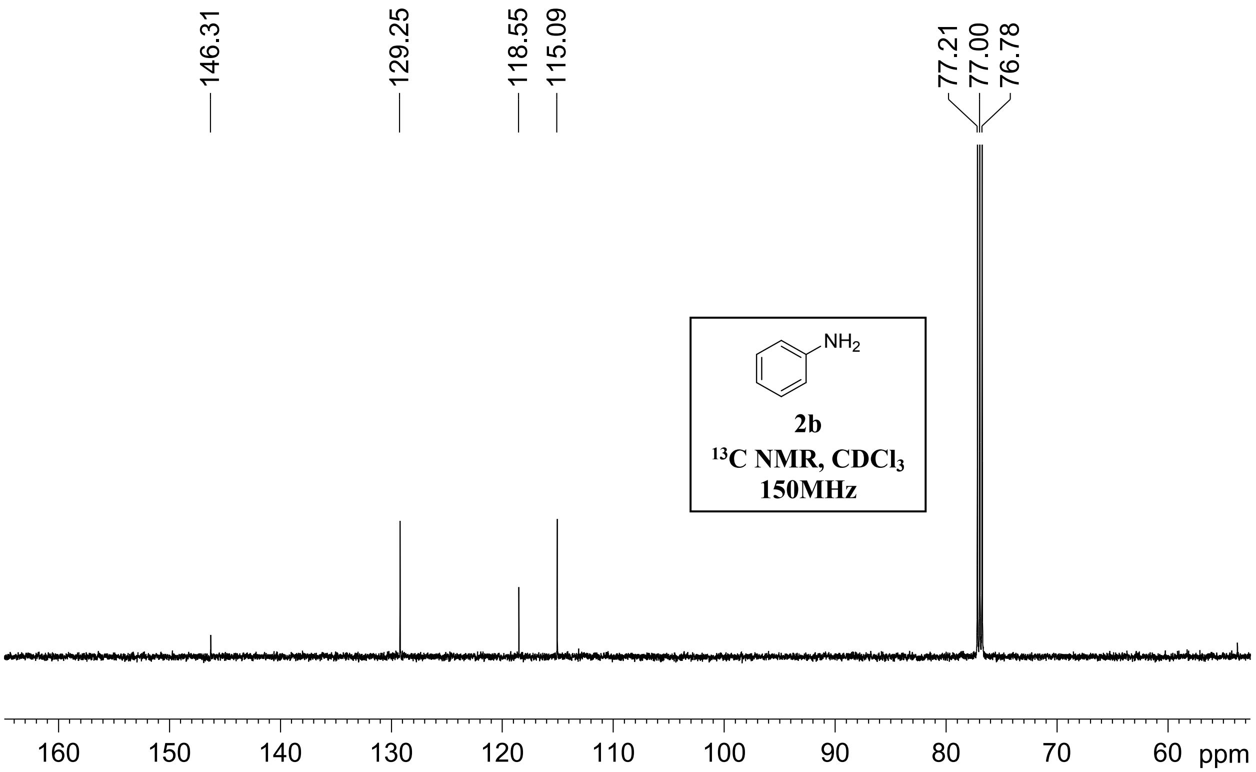
^{13}CNMR (150 MHz, DMSO-*d$_6$*) δ 107.08, 117.29, 118.36, 125.11, 135.91, 155.30, 169.83, 170.15. NMR data compared with reported compound.


6.98
6.97
6.63
6.61
2.25
NH$_2$
H$_3$C
2a
^{1}HNMR, CDCl$_3$
600MHz
8
7
6
5
4
3
2
1
0
ppm
2.00
2.09
2.01
2.96


143.72
129.71
127.77
115.24
77.21
77.00
76.79
20.40
0.98
NH$_2$
H$_3$C
2a
^{13}C NMR, CDCl$_3$
150MHz
180
160
140
120
100
80
60
40
20
0
ppm


100
%
0
5.01e4
108.0820
108.5338
93.1180
108.5740
109.1125
91.1272
94.1261
107.1013
m/z
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
NH2
H3C
2a
ESI-MS = 108.0820

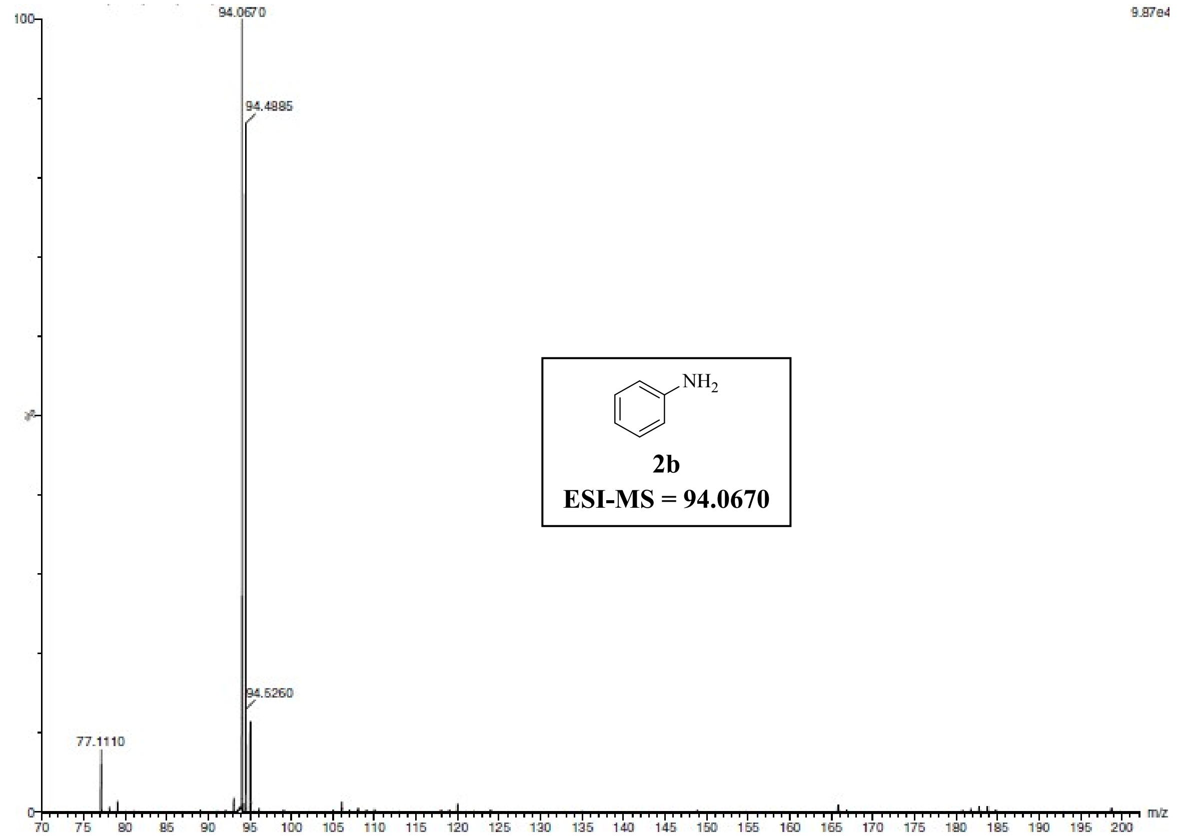

7.26
7.17
7.15
7.14
6.77
6.75
6.74
6.69
6.68
NH2
2b
1HNMR, CDCl3
600MHz
grease
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
2.09
1.00
2.10



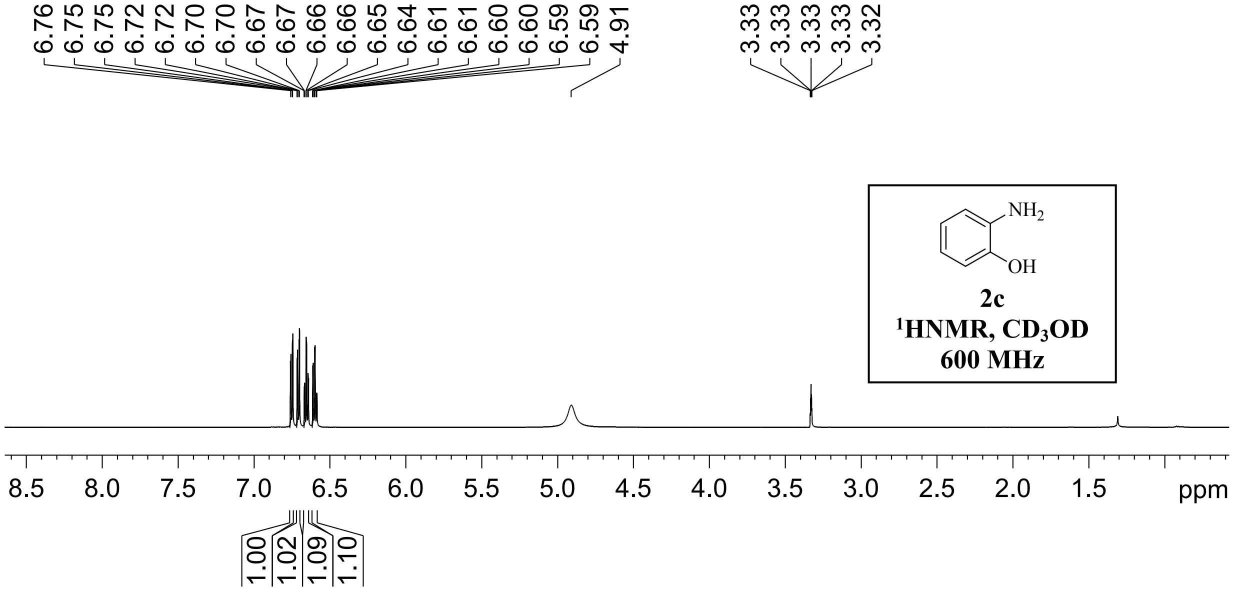
2b

^{13}C NMR, CDCl$_3$

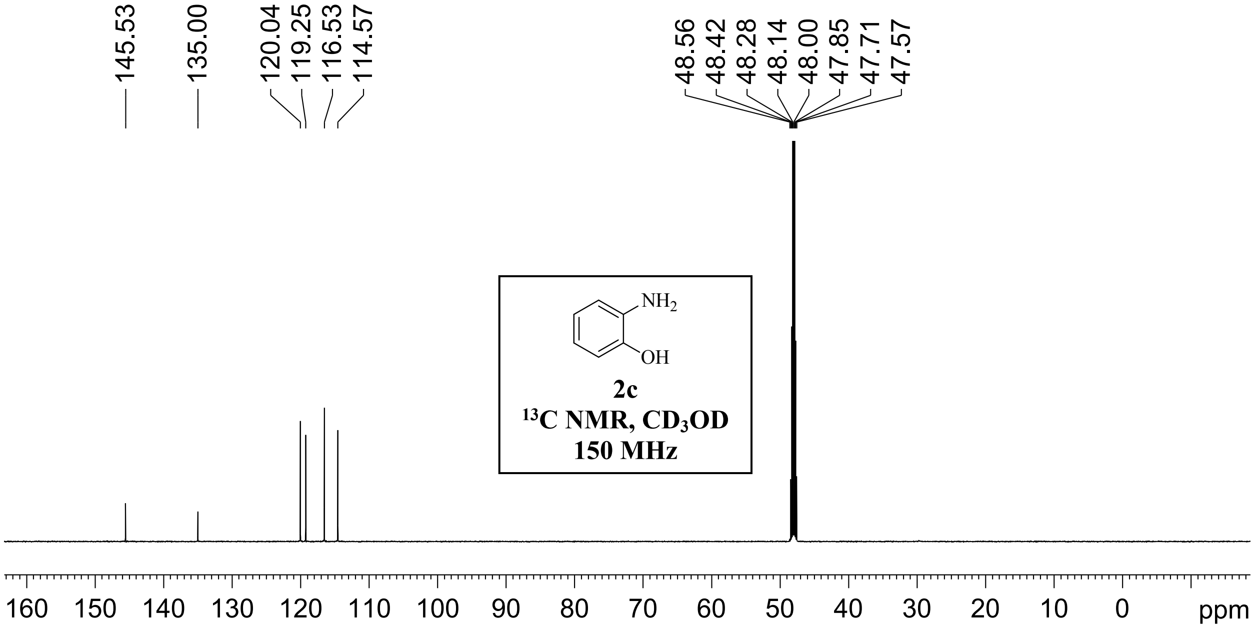
150MHz

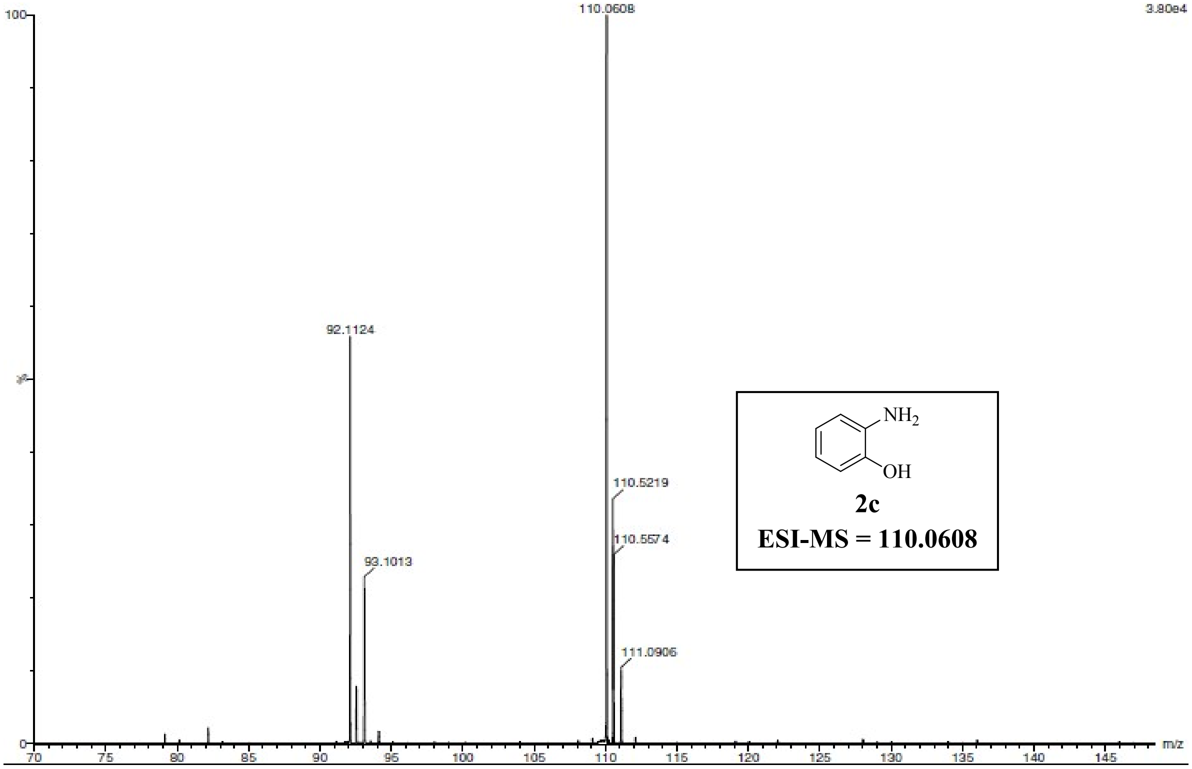


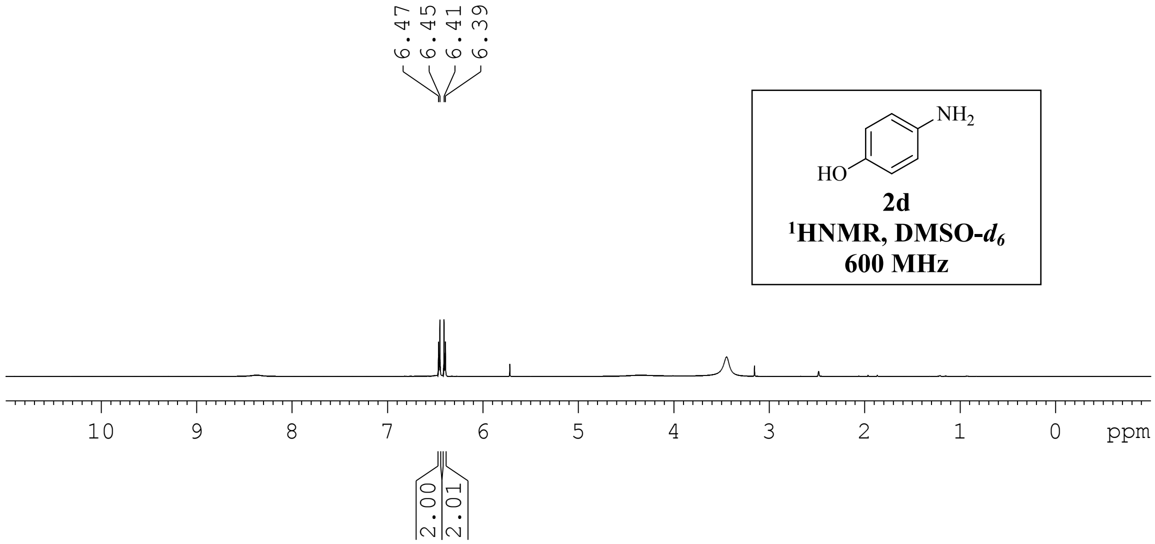
2b
ESI-MS = 94.0670

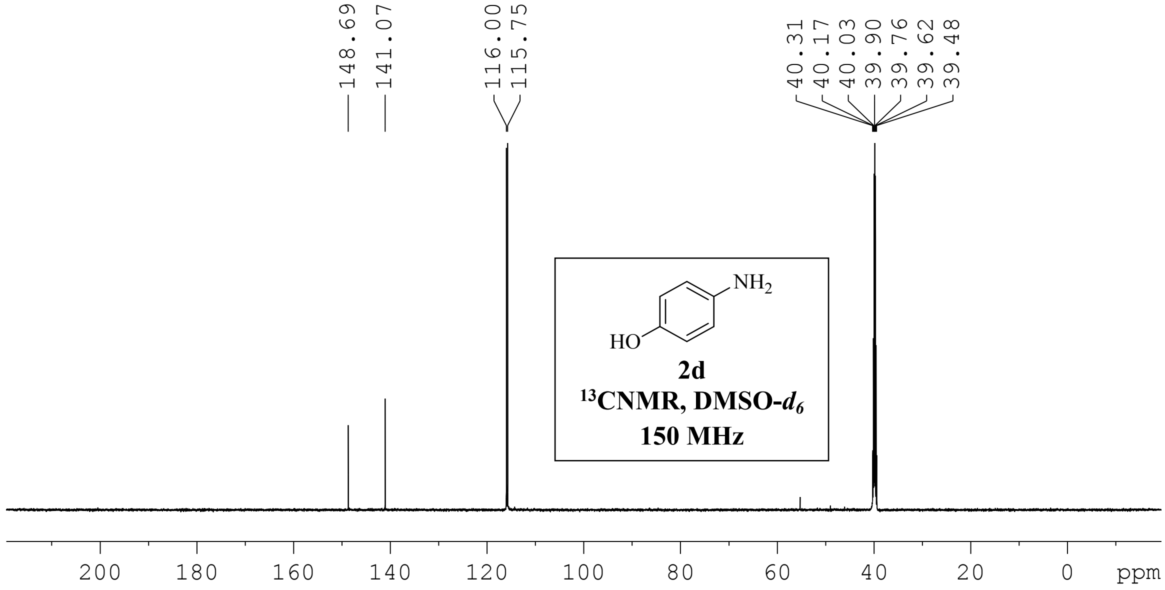


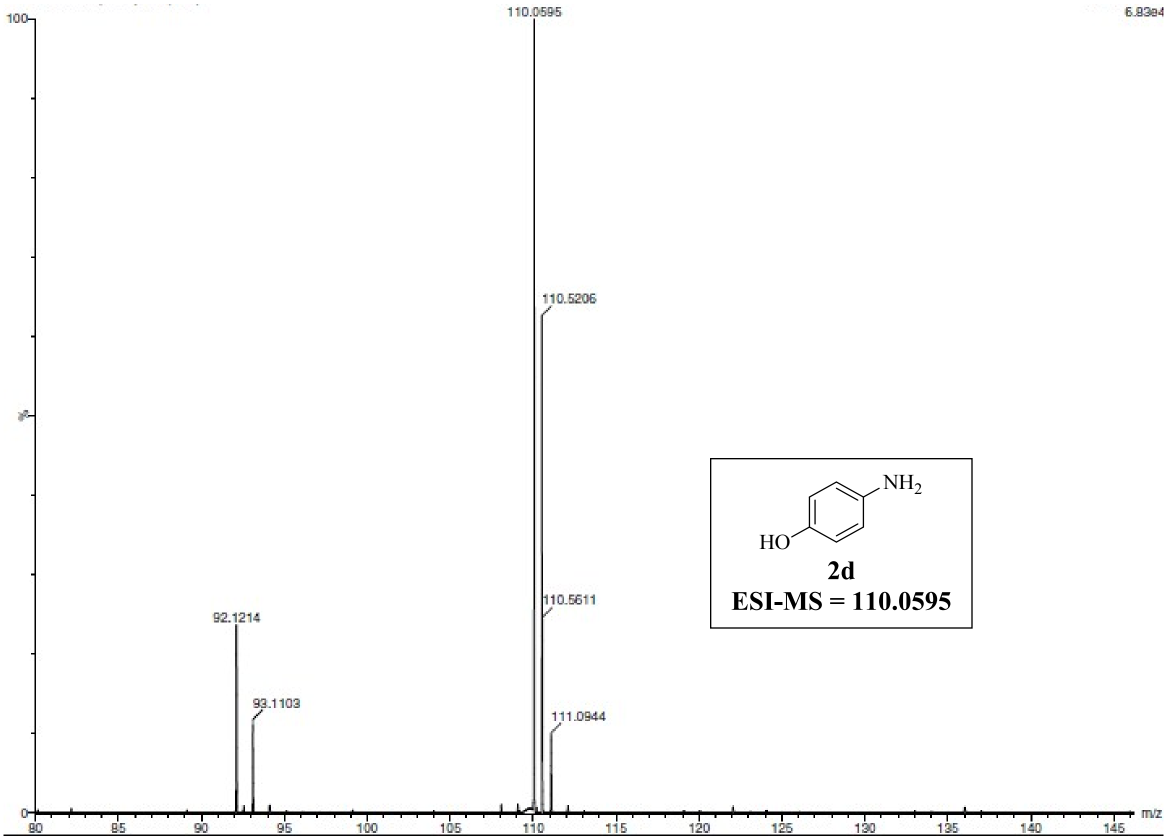
2c
^{1}HNMR, CD_3OD
600 MHz

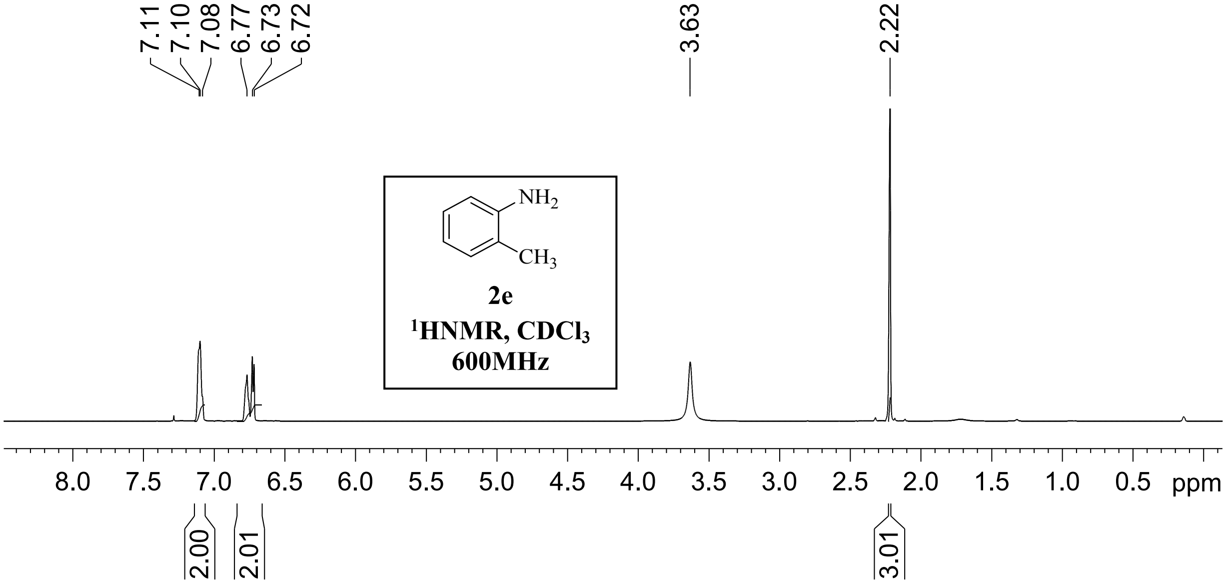

145.53
135.00
120.04
119.25
116.53
114.57
48.56
48.42
48.28
48.14
48.00
47.85
47.71
47.57
NH2
OH
2c
13C NMR, CD3OD
150 MHz
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

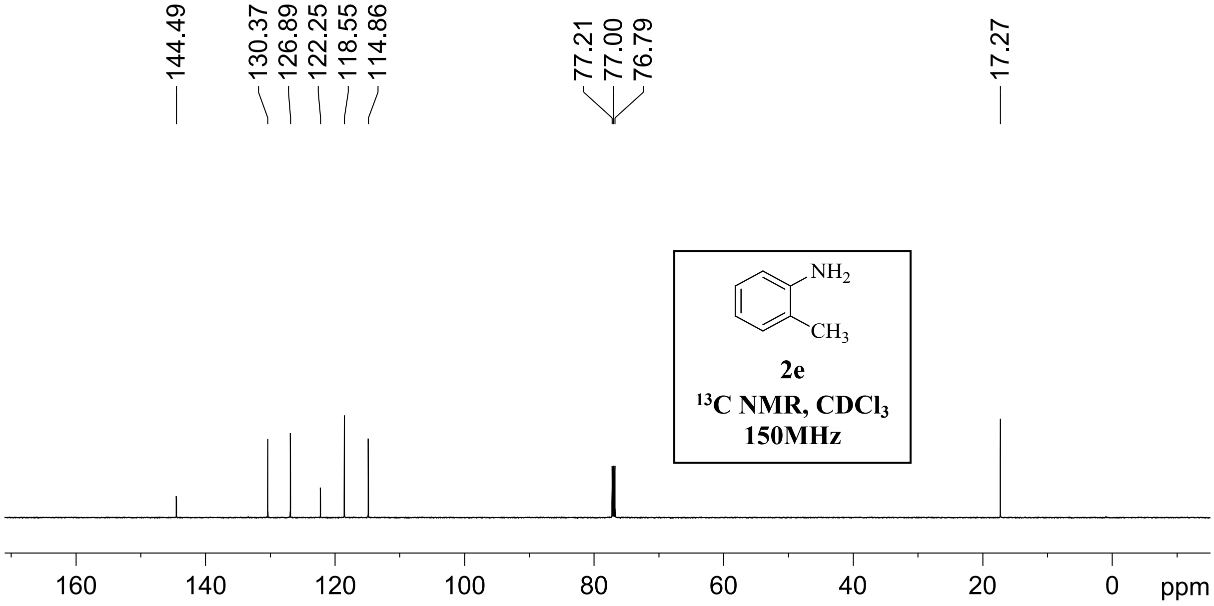

100
%
0
110.0608
3.80e4
92.1124
93.1013
110.5219
110.5574
111.0906
NH2
OH
2c
ESI-MS = 110.0608
70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 m/z

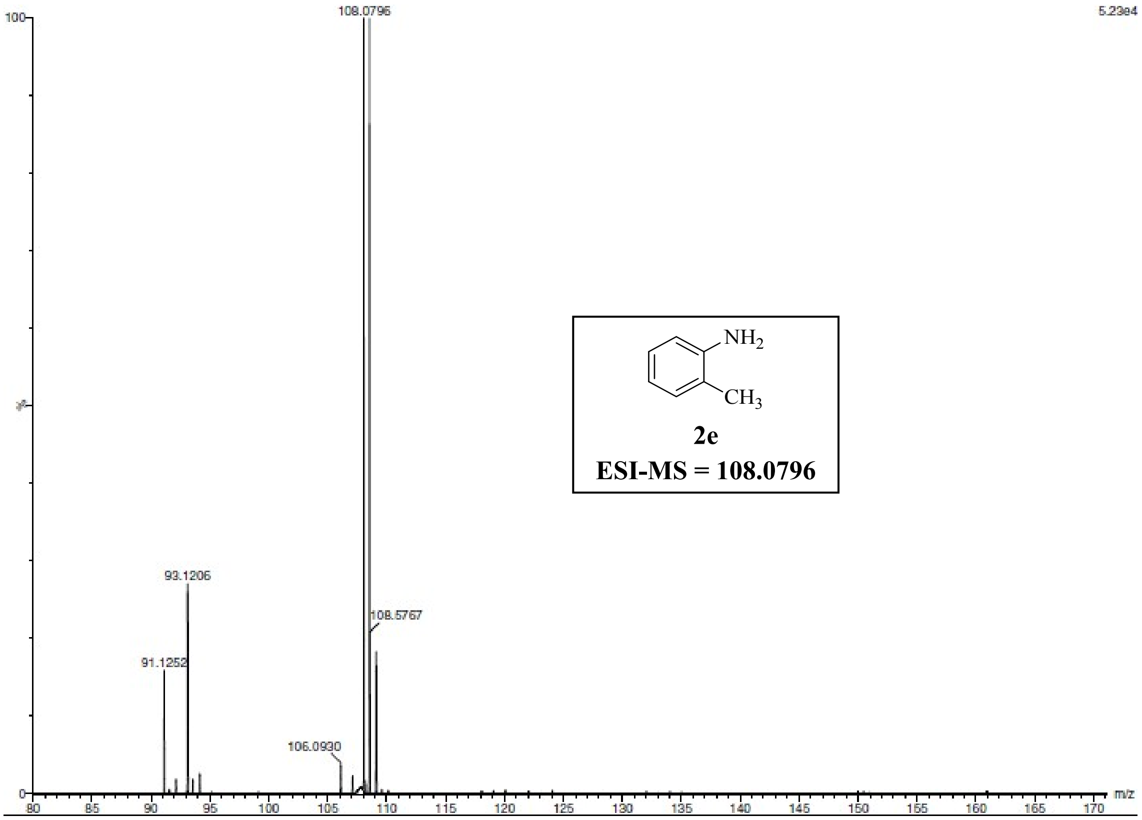

6.47
6.45
6.41
6.39
NH2
HO
2d
^{1}HNMR, DMSO-d_6
600 MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.01

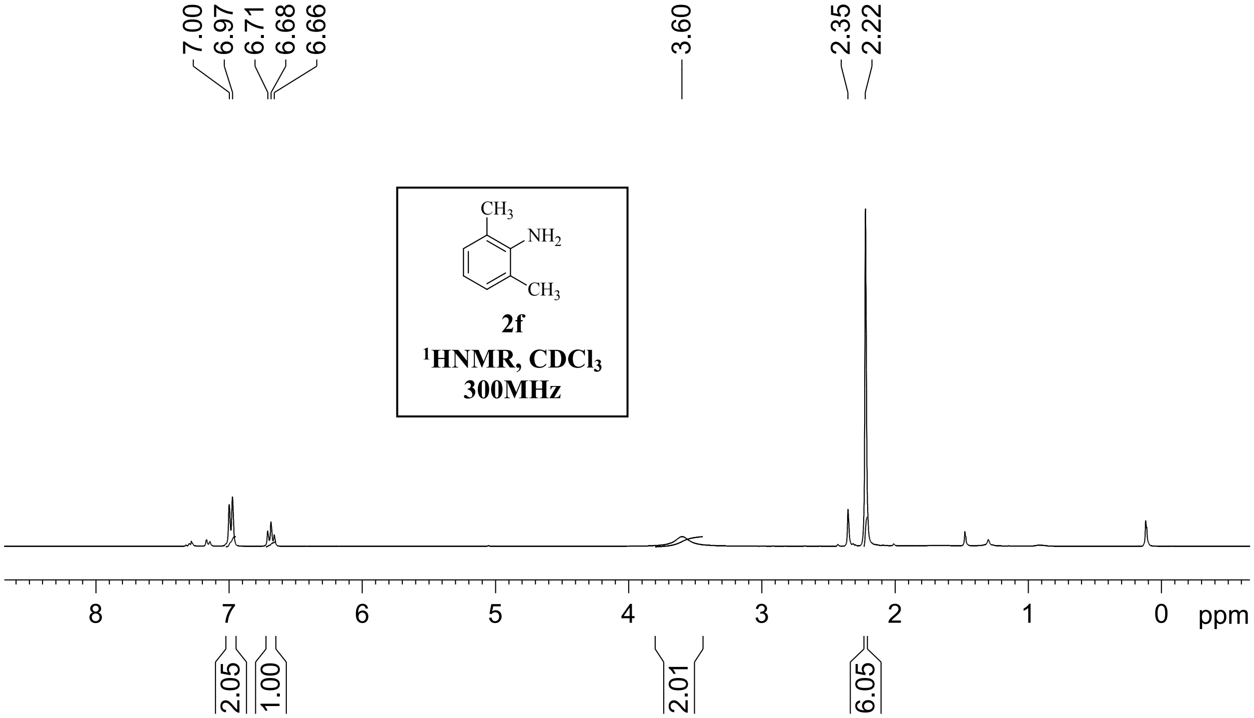

148.69
141.07
116.00
115.75
40.31
40.17
40.03
39.90
39.76
39.62
39.48
NH2
HO
2d
^{13}CNMR, DMSO-d_6
150 MHz
200
180
160
140
120
100
80
60
40
20
0
ppm

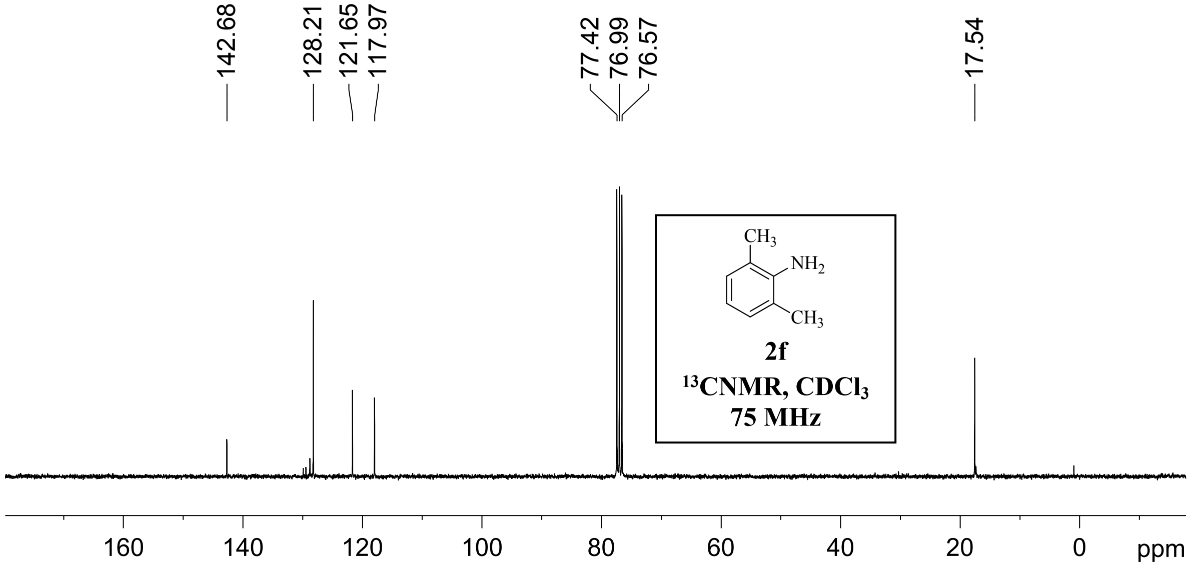

100
%
0
110.0595
6.83e4
110.5206
110.5611
111.0944
92.1214
93.1103
80
85
90
95
100
105
110
115
120
125
130
135
140
145
m/z
NH2
HO
2d
ESI-MS = 110.0595

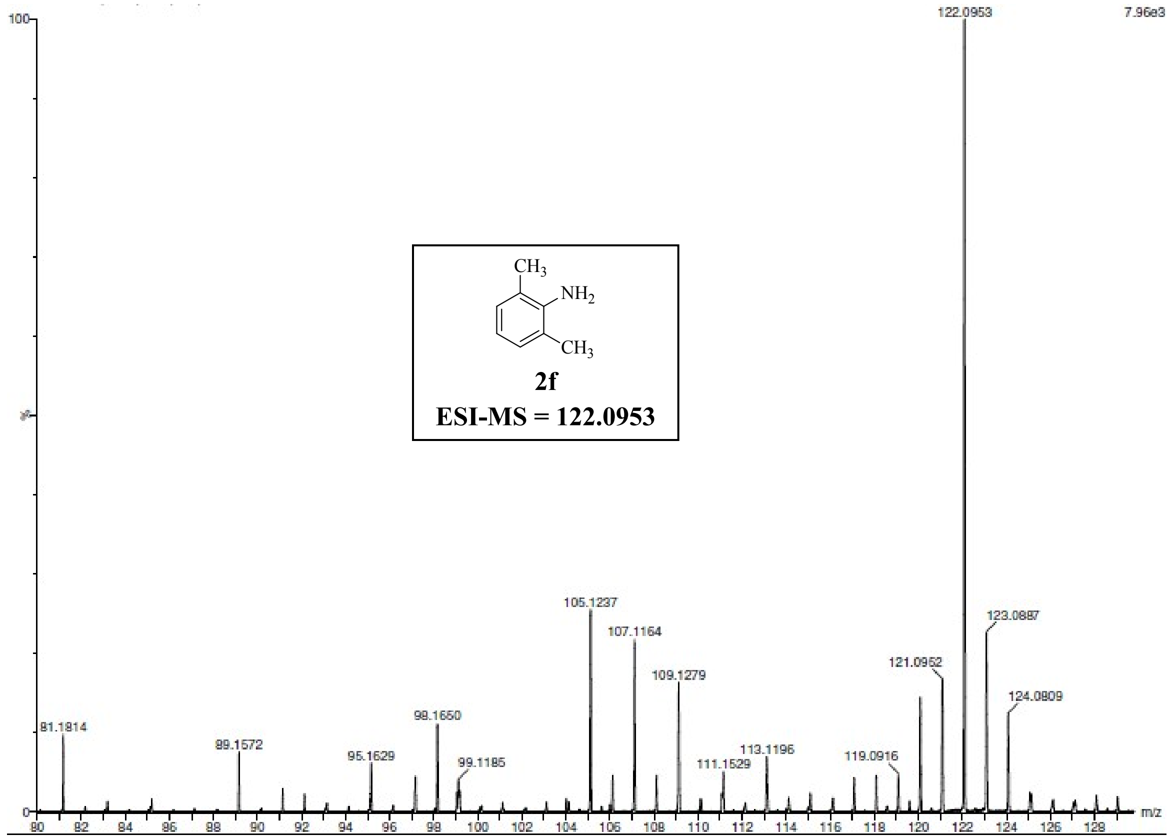

7.11
7.10
7.08
6.77
6.73
6.72
3.63
2.22
NH2
CH3
2e
1HNMR, CDCl3
600MHz
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.01
3.01


144.49
130.37
126.89
122.25
118.55
114.86
77.21
77.00
76.79
17.27
NH2
CH3
2e
13C NMR, CDCl3
150MHz
160
140
120
100
80
60
40
20
0
ppm

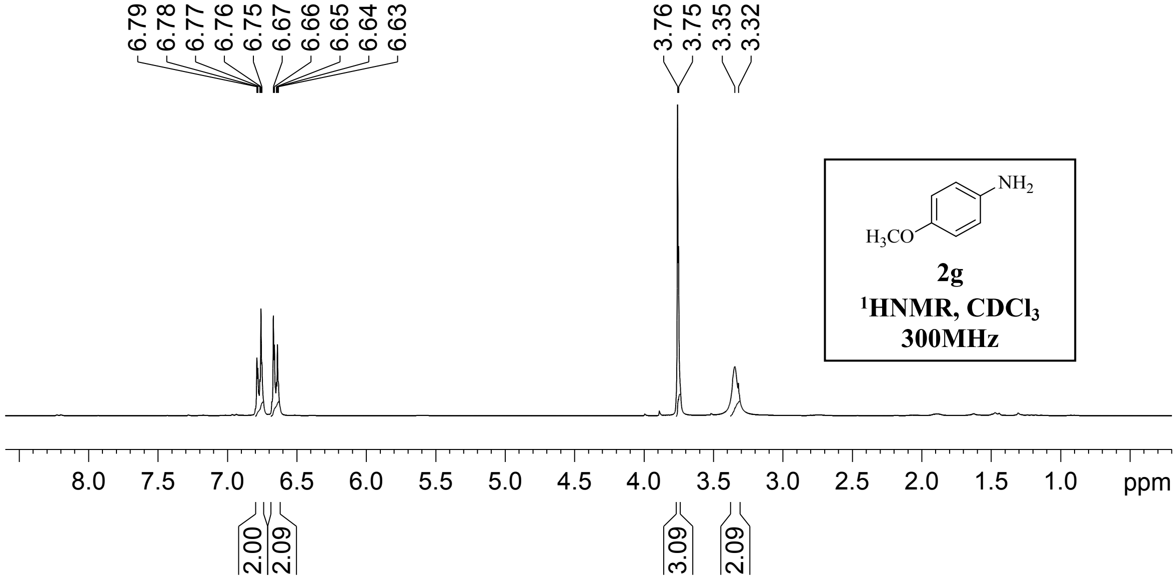

108.0796
5.23e4
100
%
0
93.1206
91.1252
108.5767
106.0930
NH2
CH3
2e
ESI-MS = 108.0796
m/z
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170


7.00
6.97
6.71
6.68
6.66
3.60
2.35
2.22
CH3
NH2
CH3
2f
1HNMR, CDCl3
300MHz
8
7
6
5
4
3
2
1
0
ppm
2.05
1.00
2.01
6.05

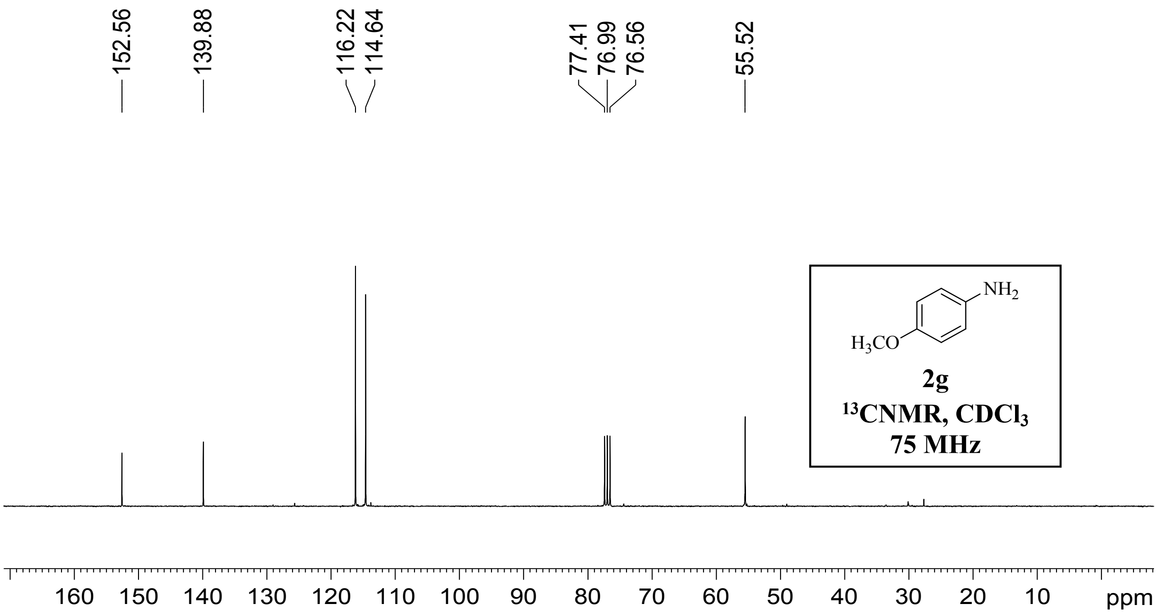

142.68
128.21
121.65
117.97
77.42
76.99
76.57
17.54
CH3
NH2
CH3
2f
13CNMR, CDCl3
75 MHz
160
140
120
100
80
60
40
20
0
ppm

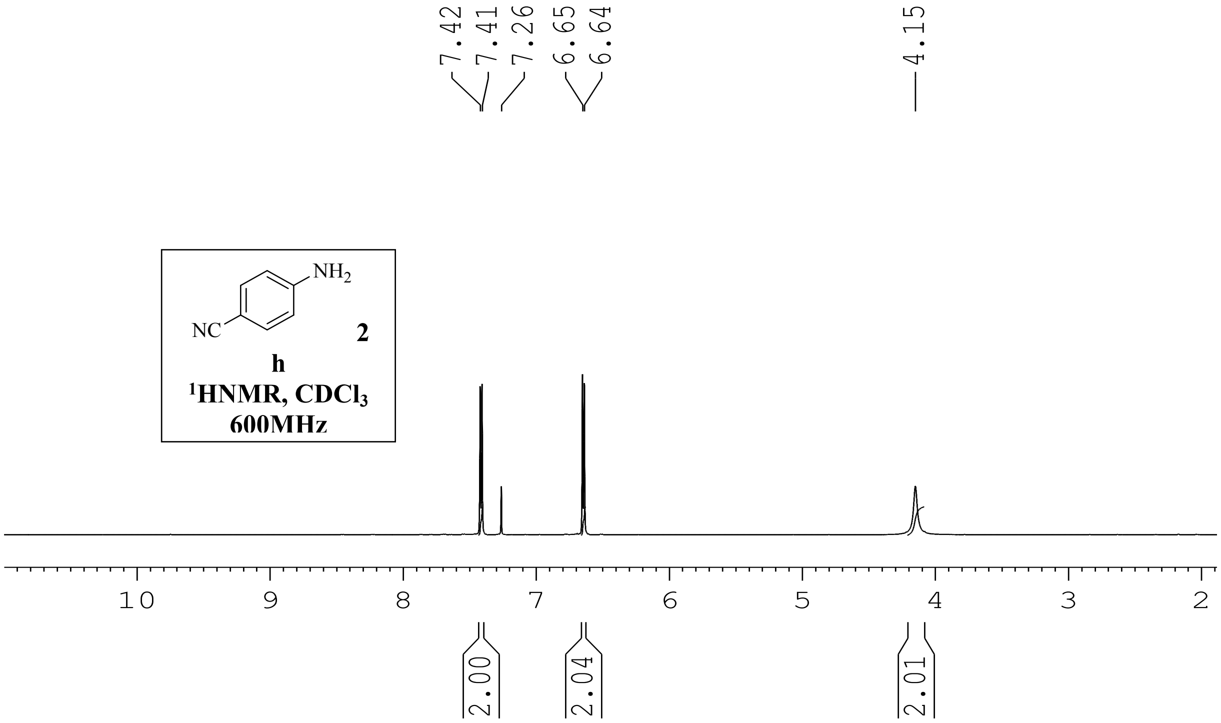


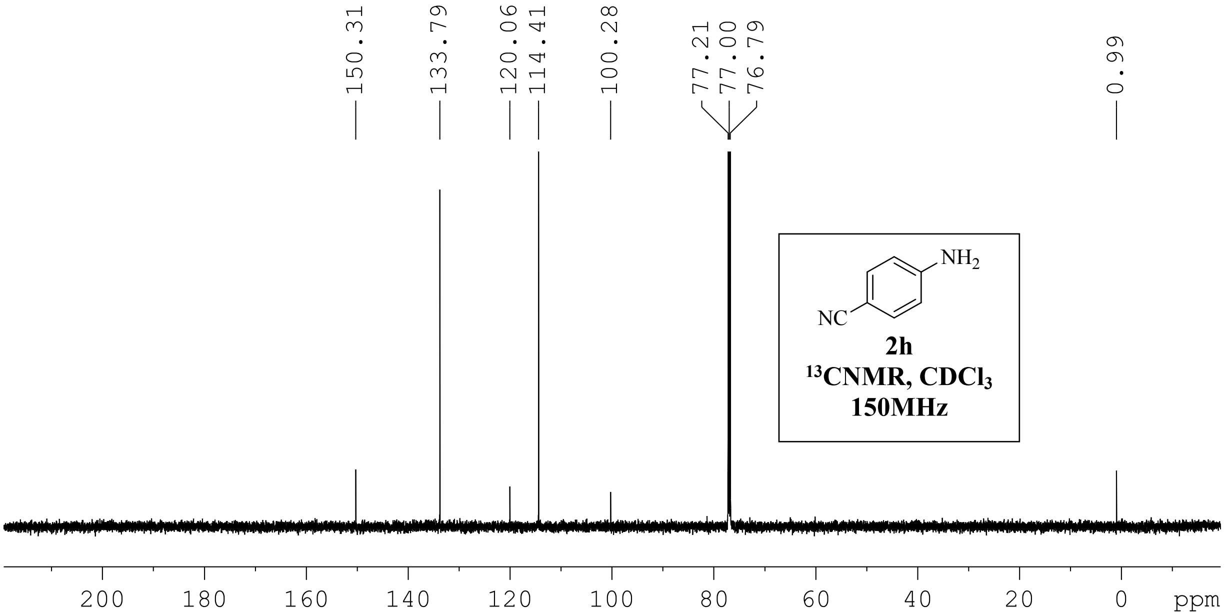
2f
ESI-MS = 122.0953

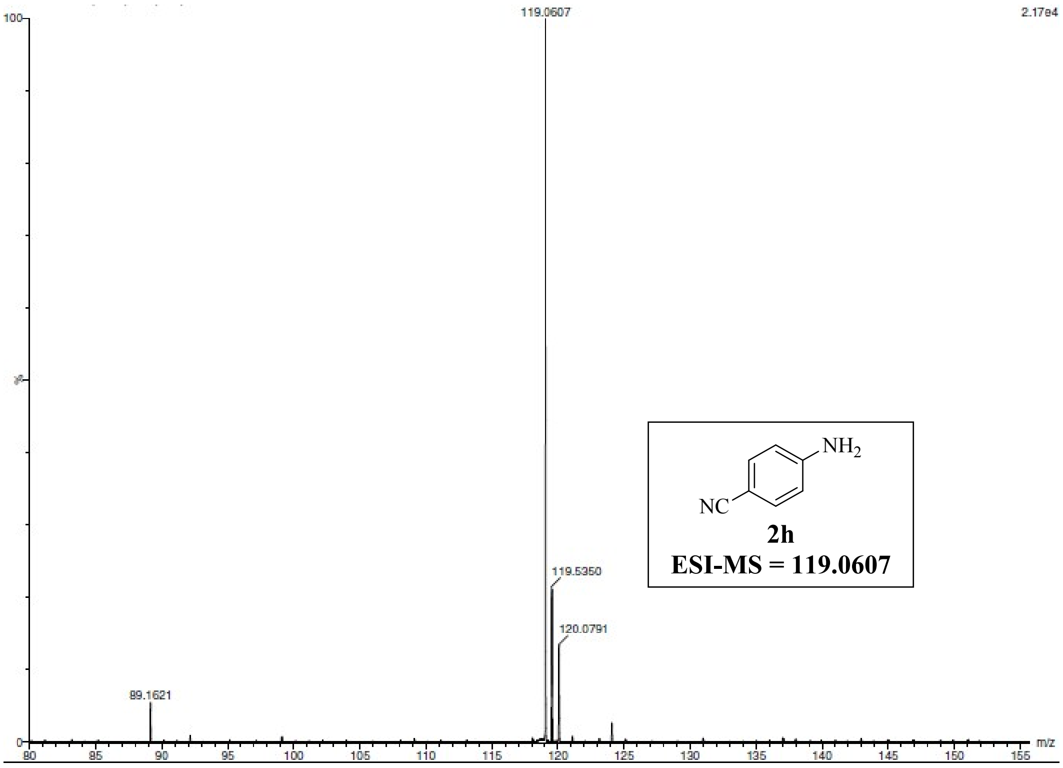


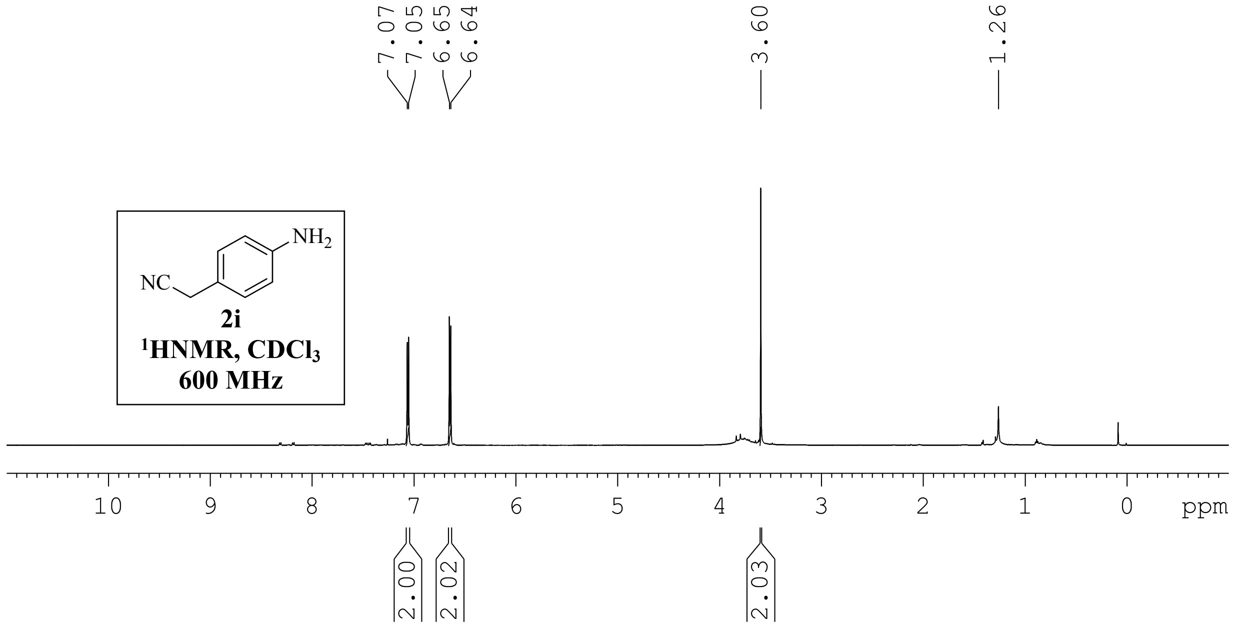
2g
^{1}HNMR, CDCl$_3$
300MHz

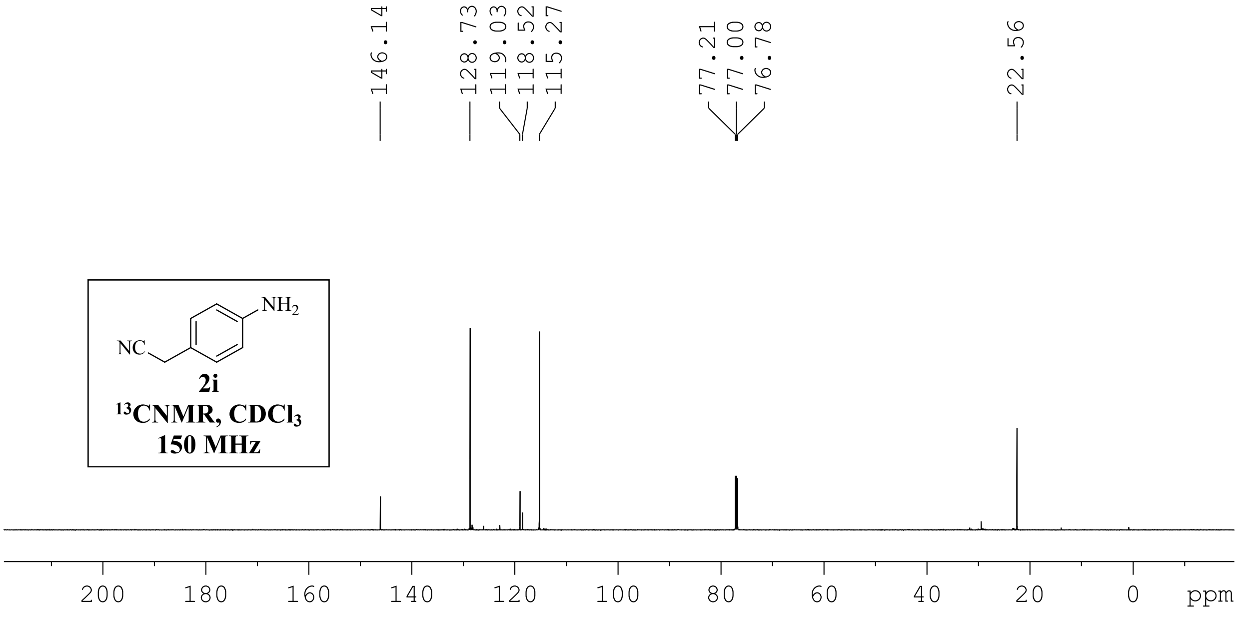

152.56
139.88
116.22
114.64
77.41
76.99
76.56
55.52
NH2
H3CO
2g
13CNMR, CDCl3
75 MHz
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

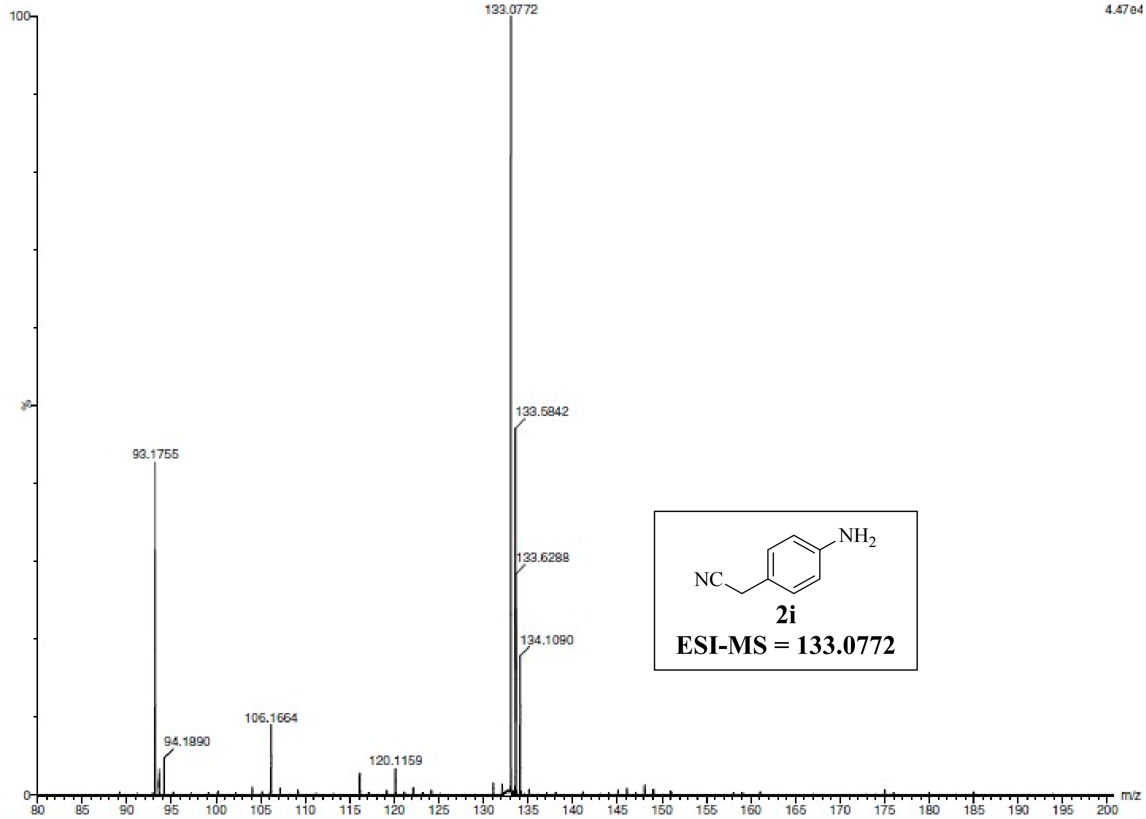

7.42
7.41
7.26
6.65
6.64
4.15
NH2
NC
2
h
1HNMR, CDCl3
600MHz
10 9 8 7 6 5 4 3 2
2.00
2.04
2.01


150.31
133.79
120.06
114.41
100.28
77.21
77.00
76.79
0.99
NH$_2$
NC
2h
^{13}CNMR, CDCl$_3$
150MHz
200
180
160
140
120
100
80
60
40
20
0
ppm


119.0607
2.17e4
100
%
0
119.5350
120.0791
89.1621
m/z
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
NH$_2$
NC
2h
ESI-MS = 119.0607

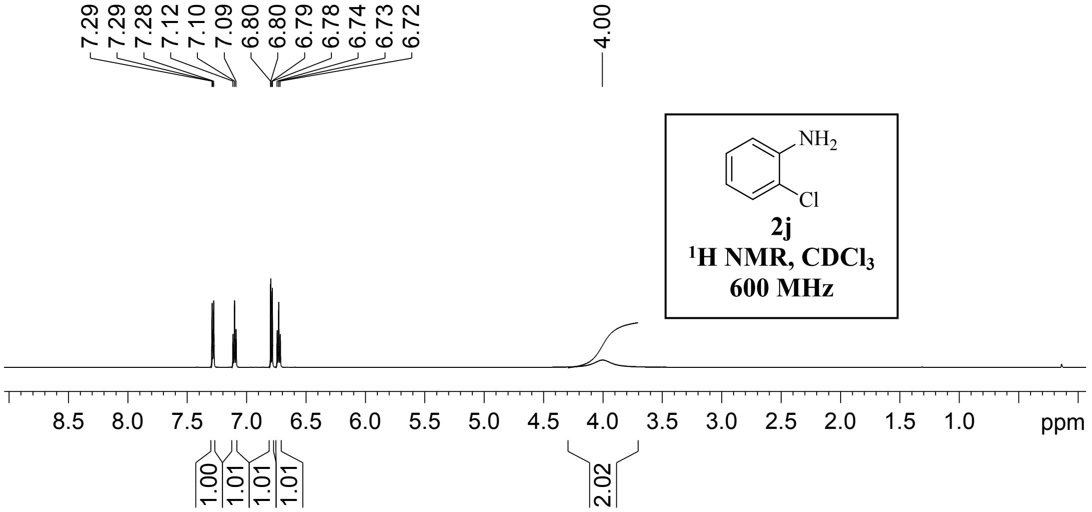

7.07
7.05
6.65
6.64
3.60
1.26
NH2
NC
2i
¹HNMR, CDCl3
600 MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
2.03


146.14
128.73
119.03
118.52
115.27
77.21
77.00
76.78
22.56
NH2
NC
2i
¹³CNMR, CDCl3
150 MHz
200
180
160
140
120
100
80
60
40
20
0
ppm



2i

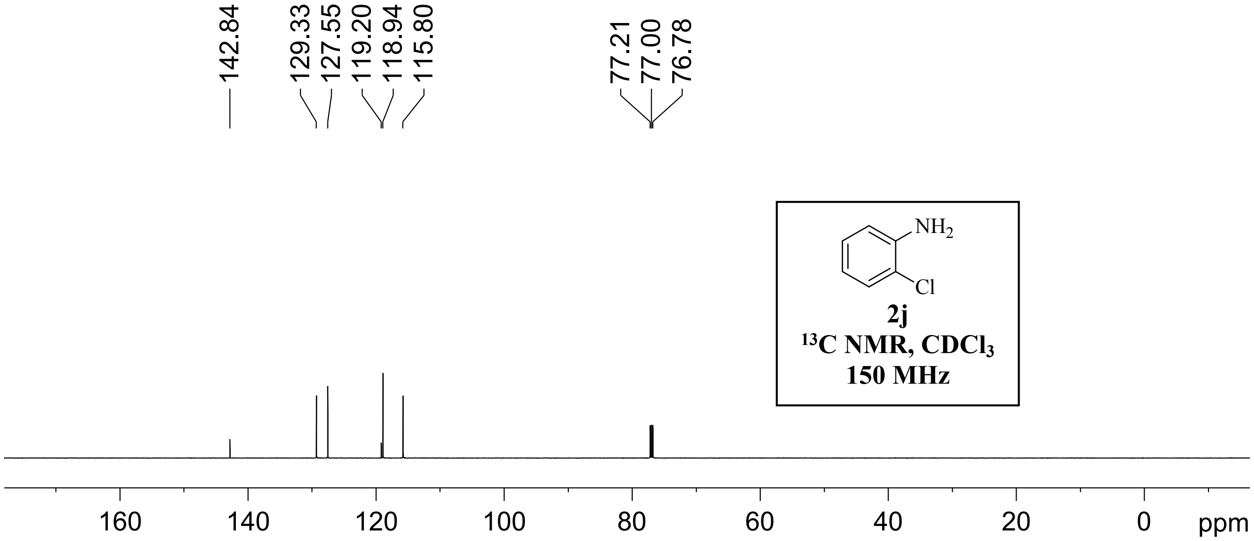
ESI-MS = 133.0772



2j

^{1}H NMR, CDCl$_3$

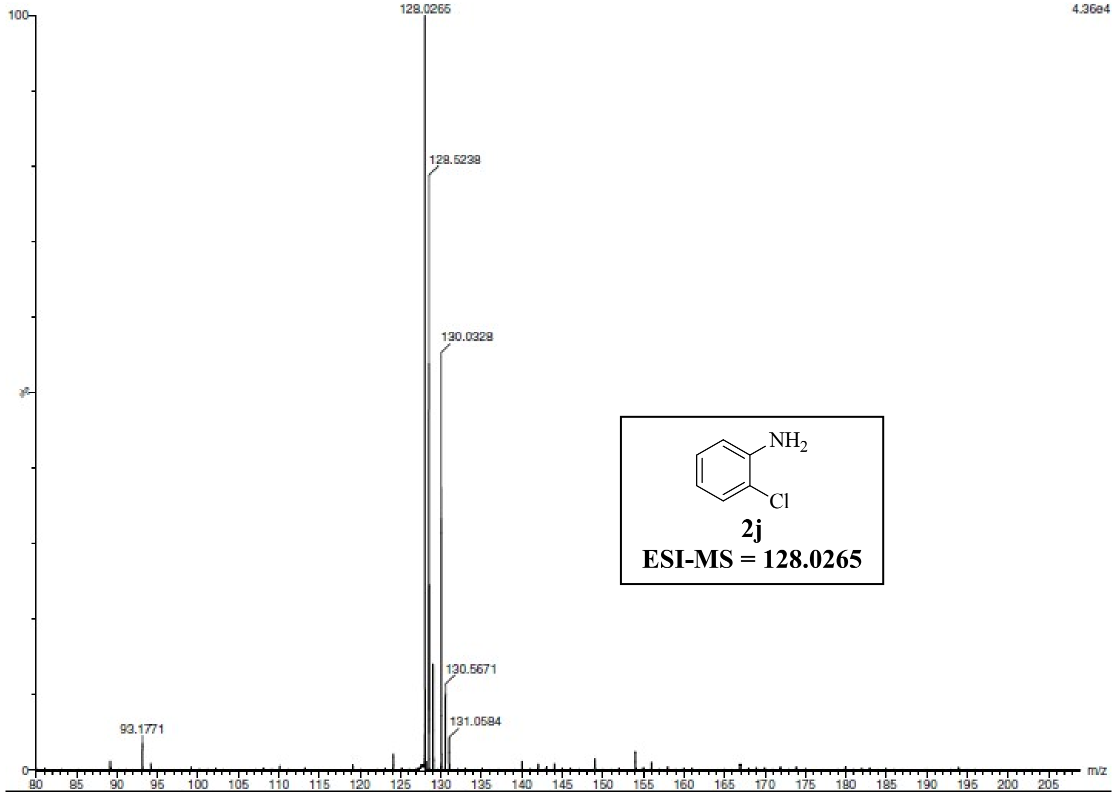
600 MHz



2j

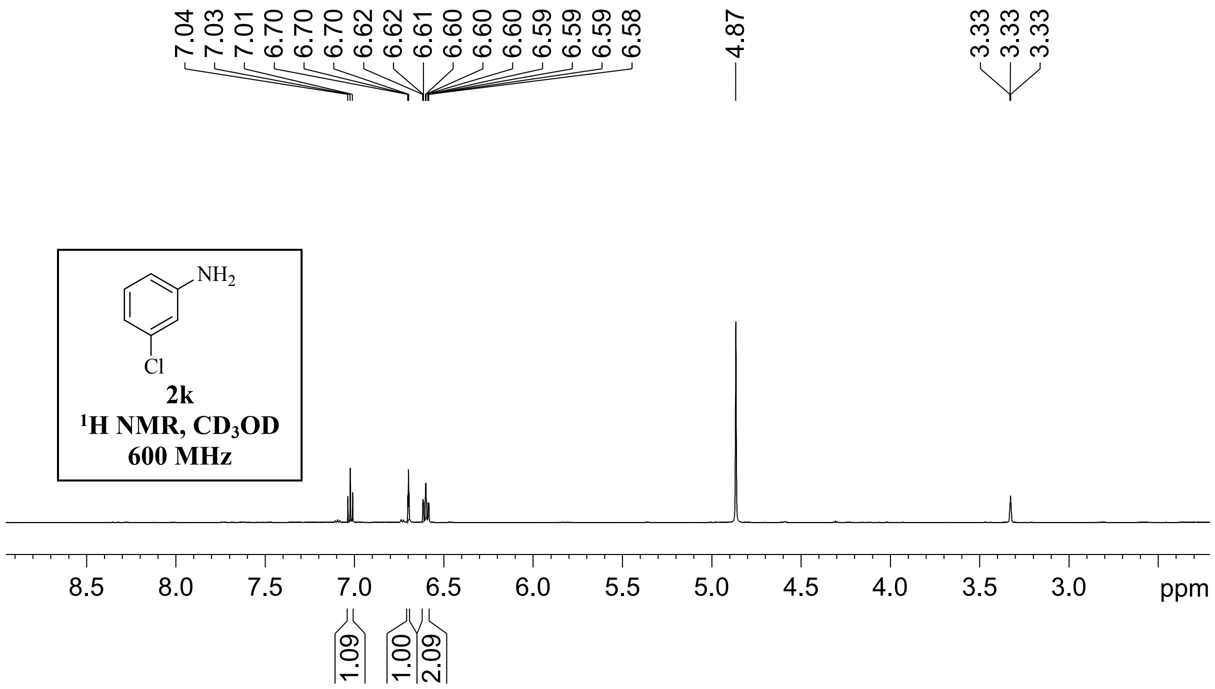
^{13}C NMR, $CDCl_3$

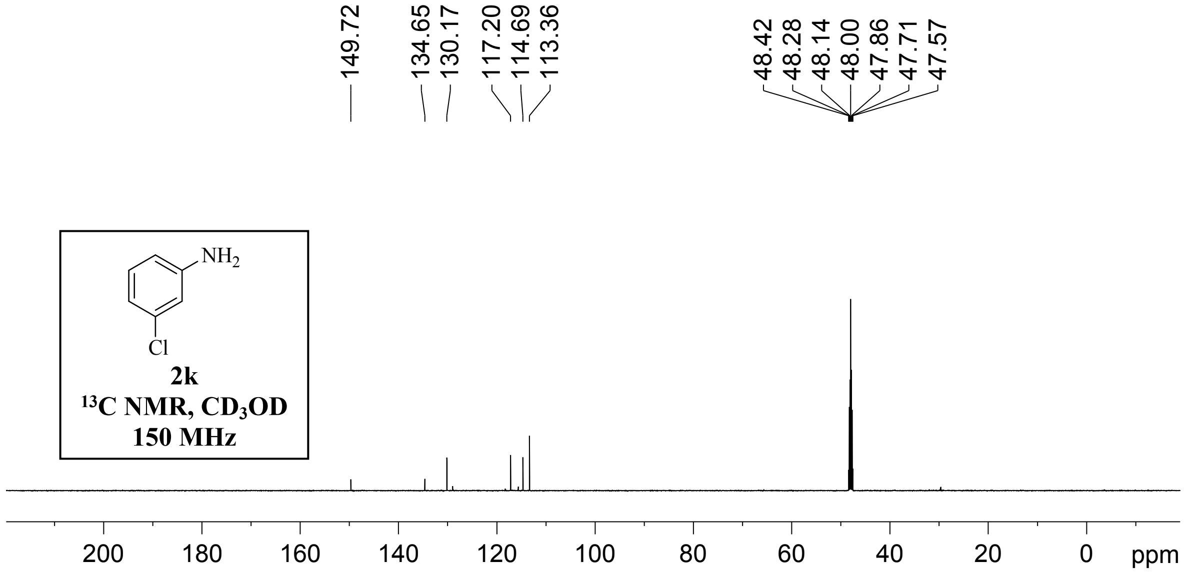
150 MHz

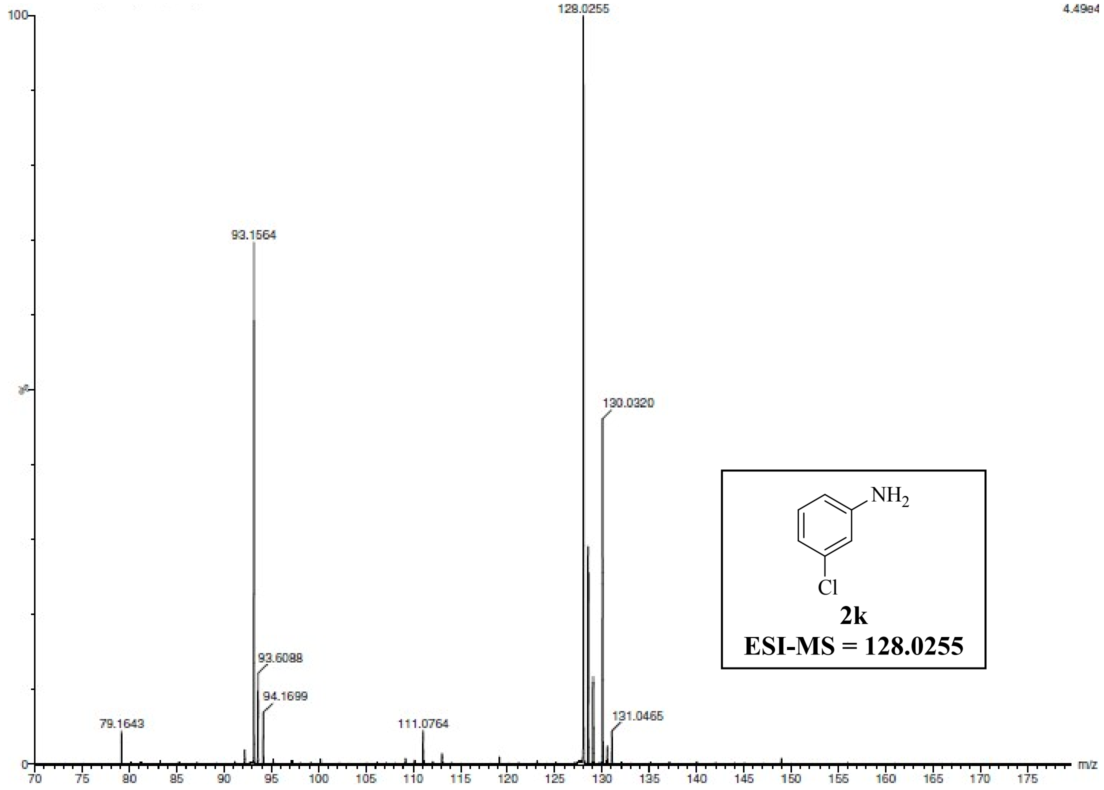


2j

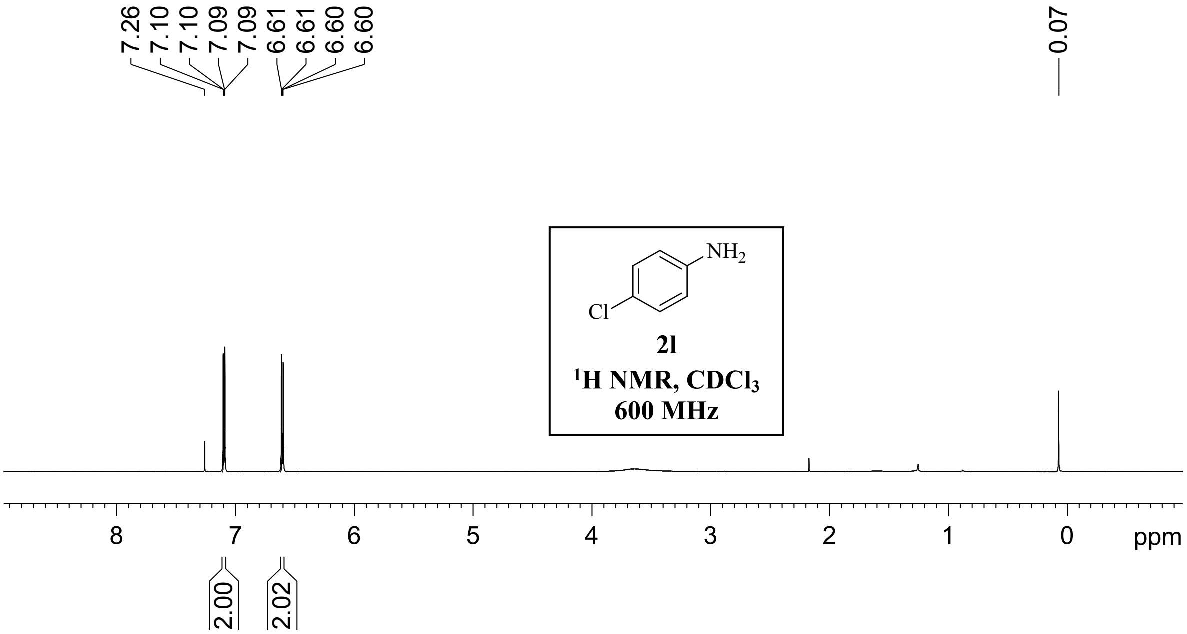
ESI-MS = 128.0265


7.04
7.03
7.01
6.70
6.70
6.70
6.62
6.62
6.61
6.60
6.60
6.60
6.59
6.59
6.59
6.58
4.87
3.33
3.33
3.33
NH2
Cl
2k
1H NMR, CD3OD
600 MHz
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
1.09
1.00
2.09

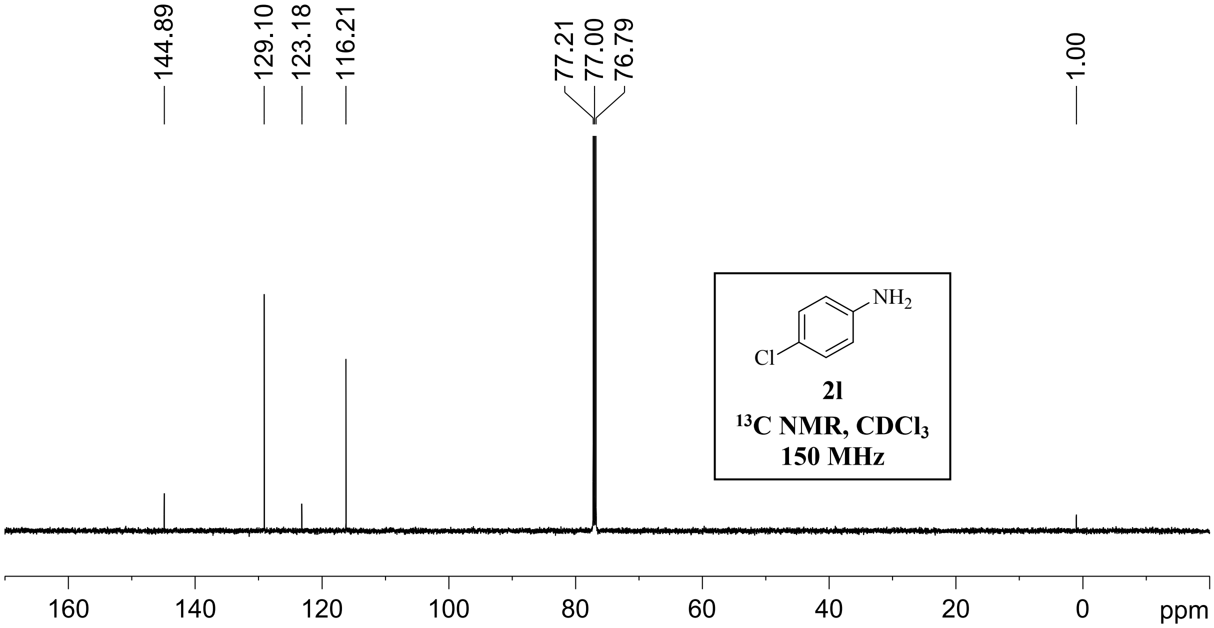

149.72
134.65
130.17
117.20
114.69
113.36
48.42
48.28
48.14
48.00
47.86
47.71
47.57
NH2
Cl
2k
13C NMR, CD3OD
150 MHz
200
180
160
140
120
100
80
60
40
20
0
ppm

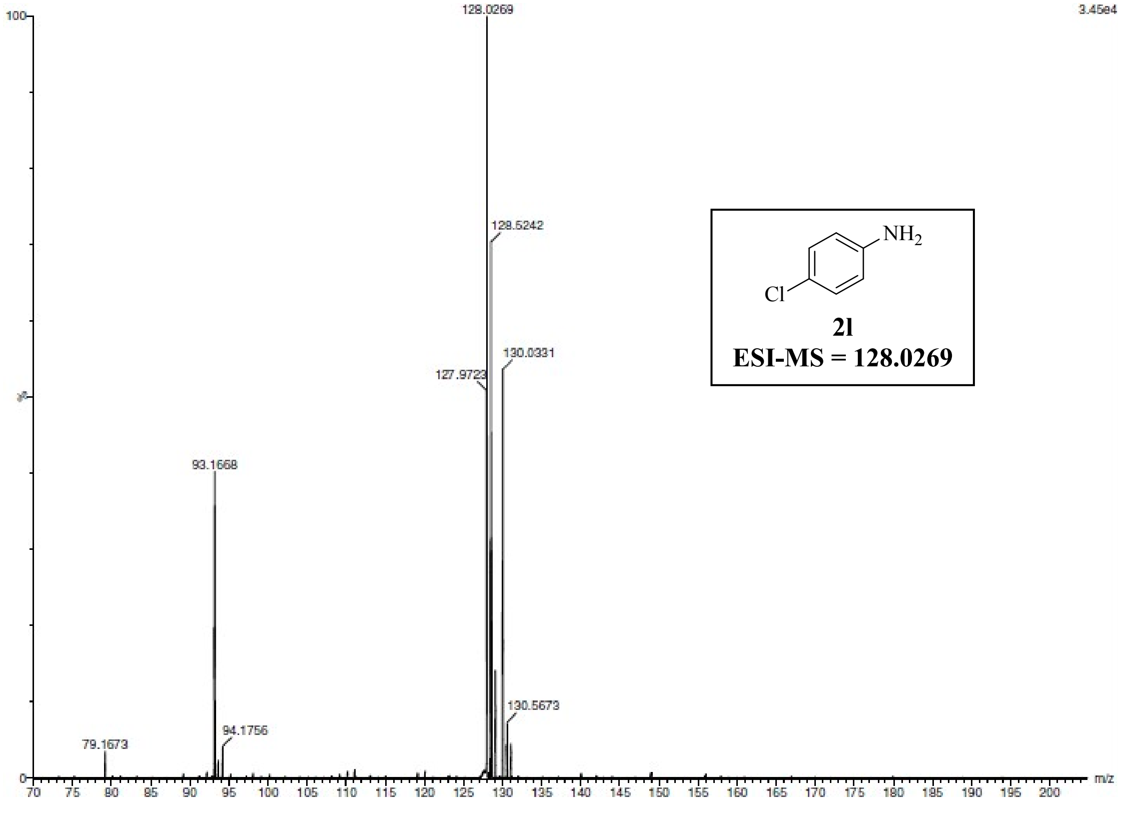


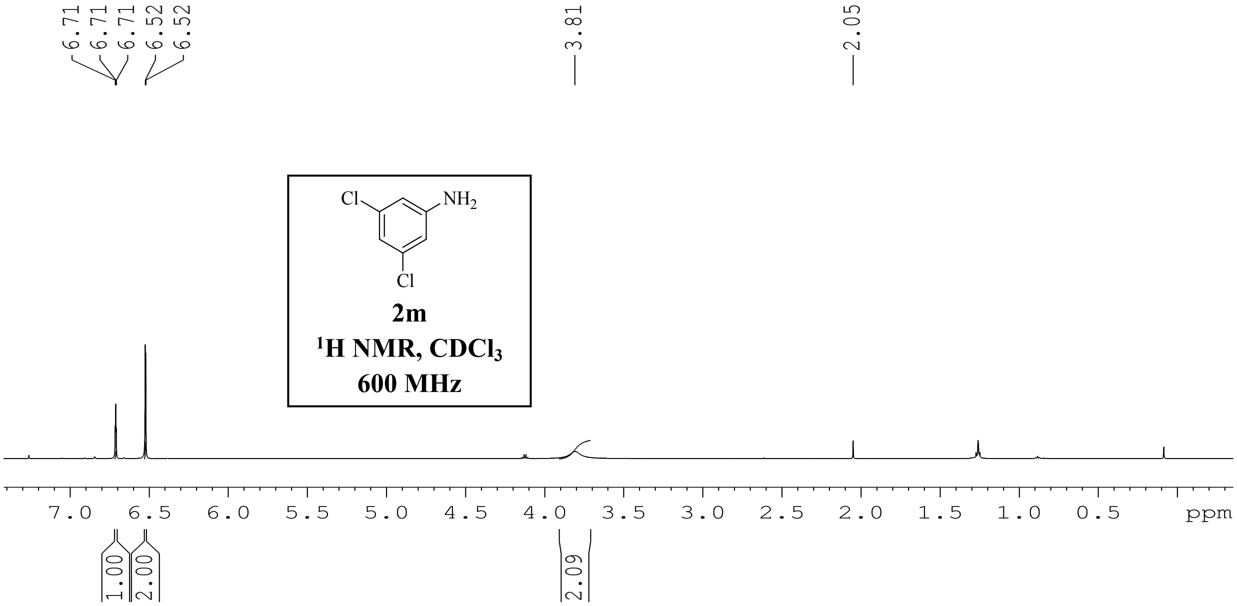
2k
ESI-MS = 128.0255

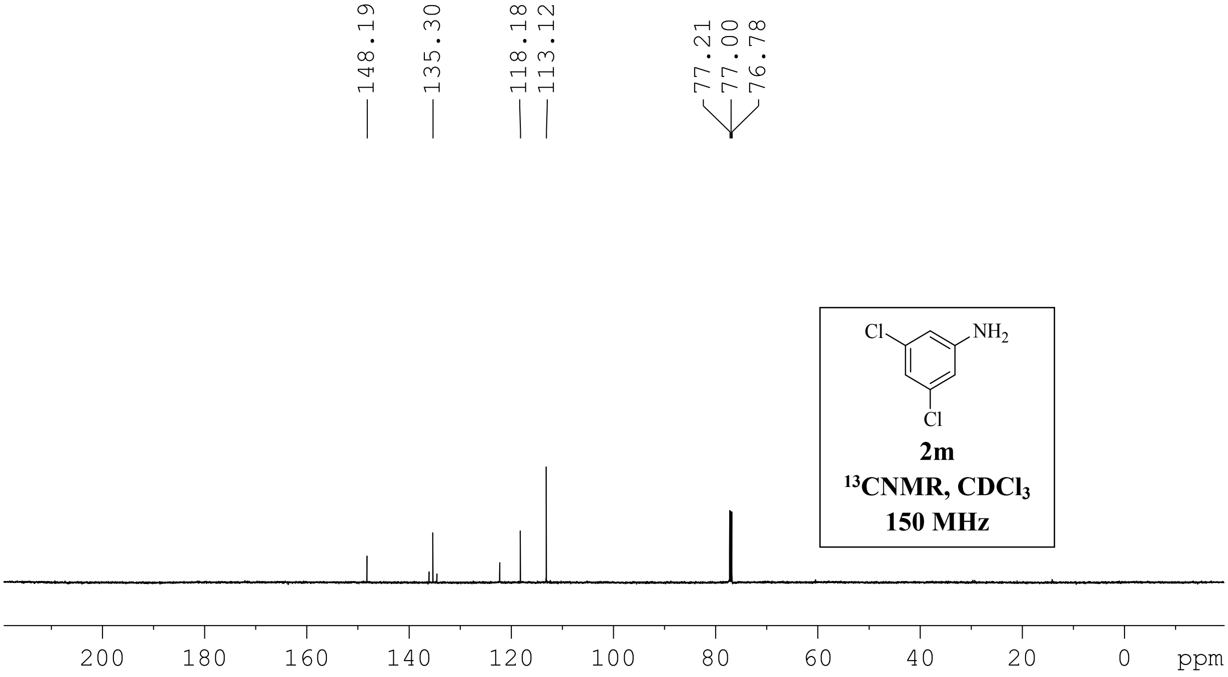


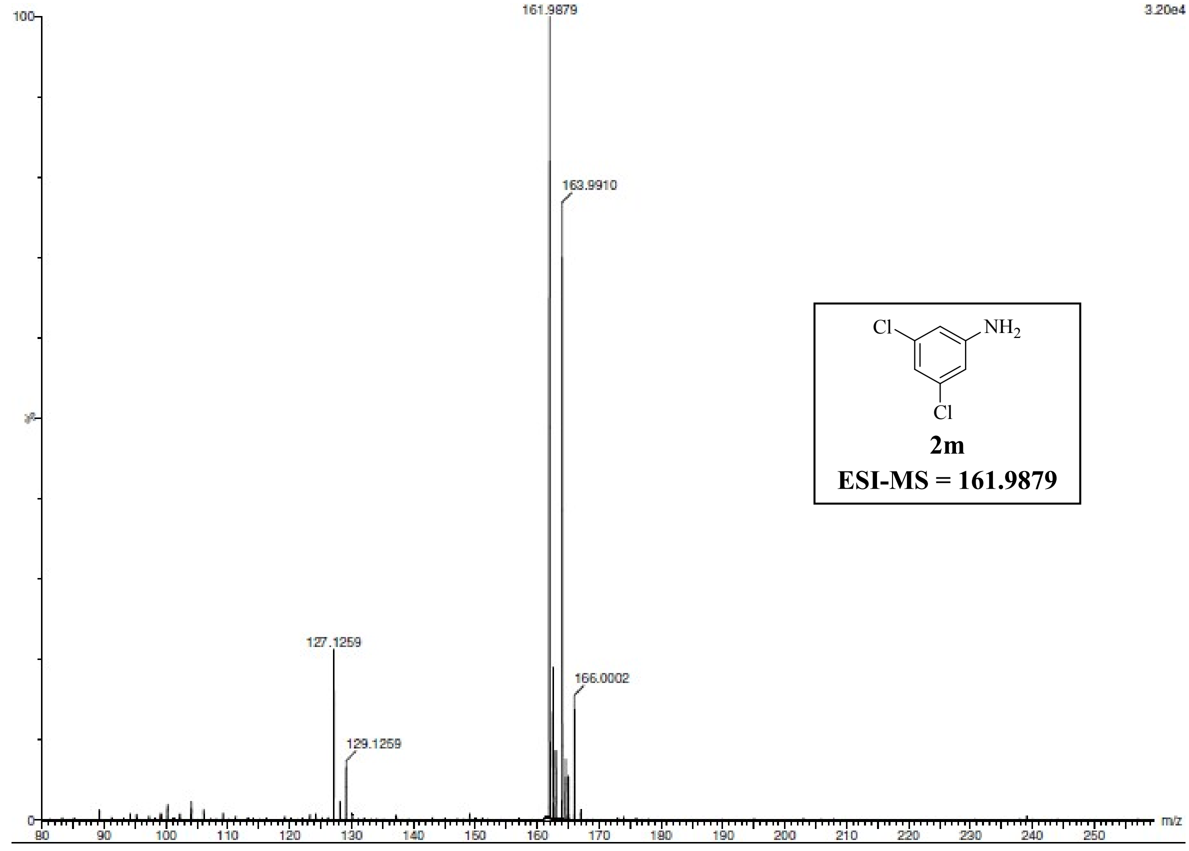
2l
^{1}H NMR, $CDCl_3$
600 MHz


144.89
129.10
123.18
116.21
77.21
77.00
76.79
1.00
NH2
Cl
2l
13C NMR, CDCl3
150 MHz
160
140
120
100
80
60
40
20
0
ppm


128.0269
3.45e4
128.5242
127.9723
130.0331
93.1668
94.1756
79.1673
130.5673
100
%
0
m/z
NH2
Cl
2l
ESI-MS = 128.0269
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
200

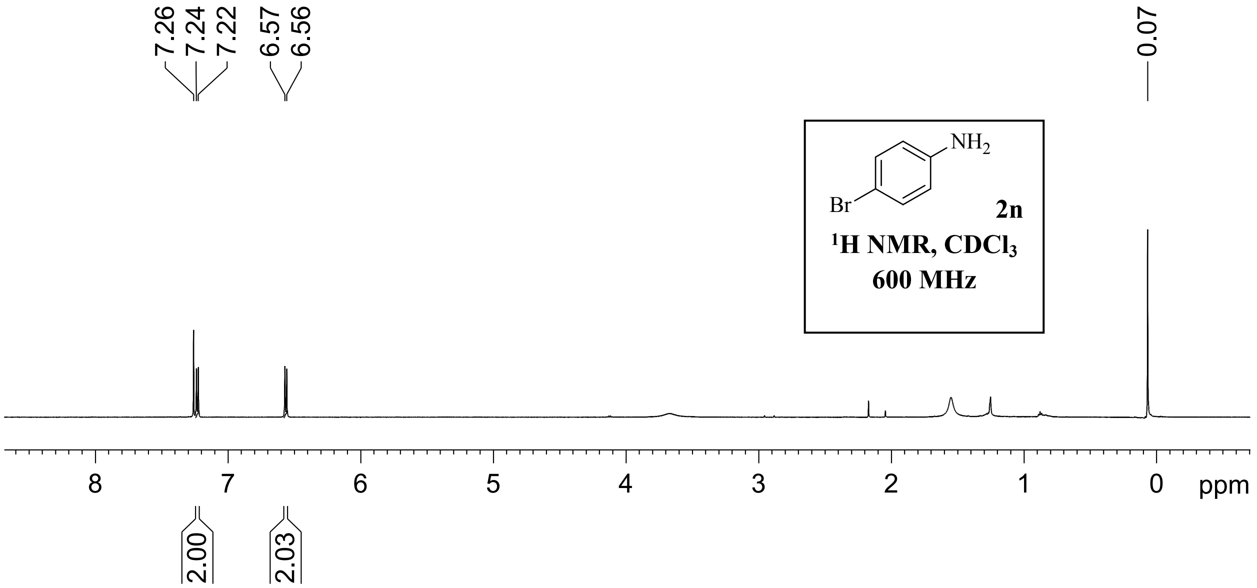

6.71
6.71
6.71
6.52
6.52
3.81
2.05
Cl
NH$_2$
Cl
2m
^{1}H NMR, CDCl$_3$
600 MHz
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.00
2.09


148.19
135.30
118.18
113.12
77.21
77.00
76.78
Cl
NH$_2$
Cl
2m
^{13}CNMR, CDCl$_3$
150 MHz
200
180
160
140
120
100
80
60
40
20
0
ppm



2m

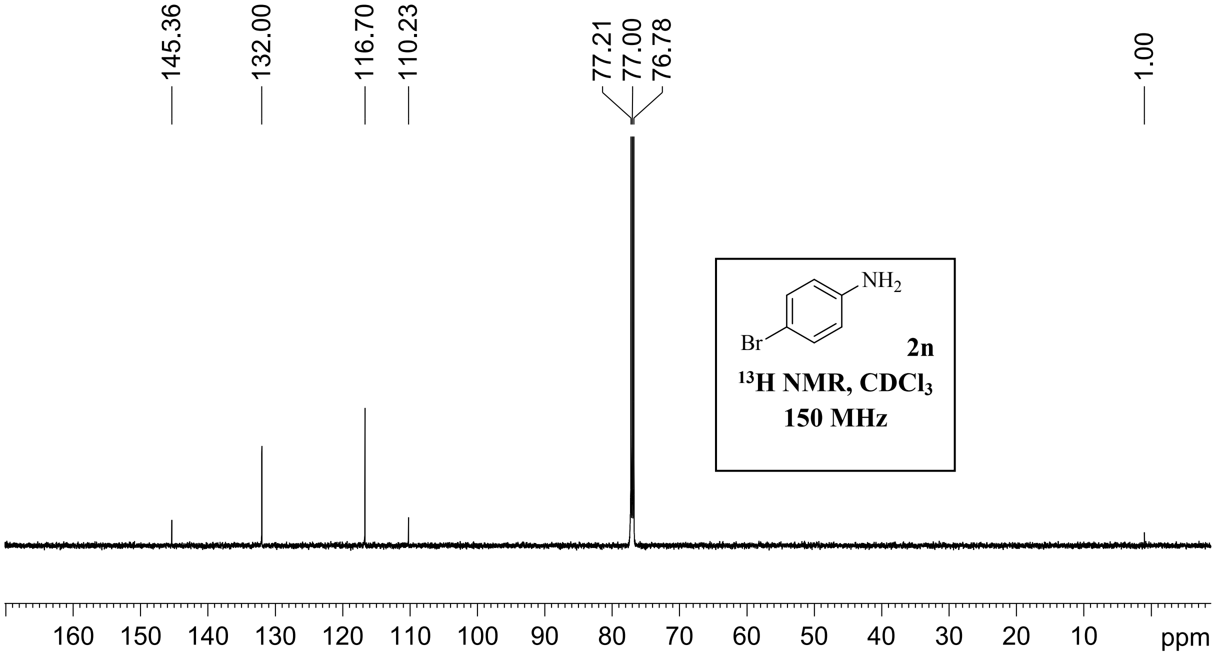
ESI-MS = 161.9879



2n

^{1}H NMR, CDCl$_3$

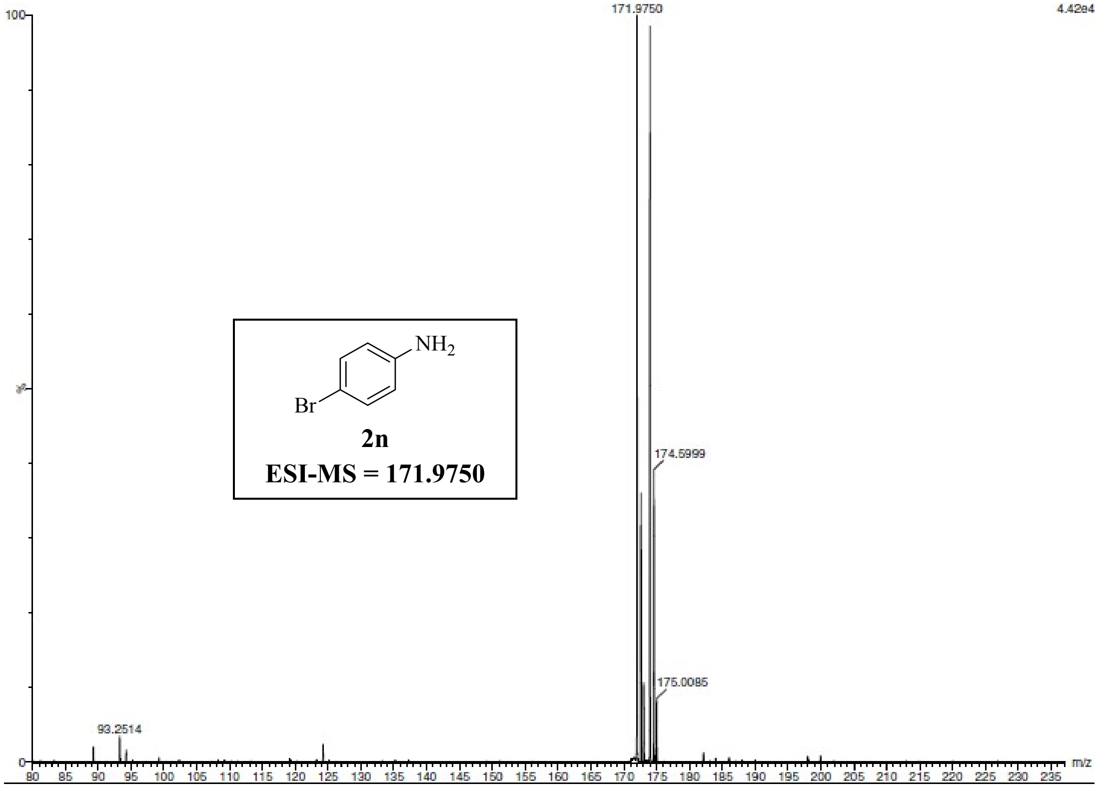
600 MHz



2n

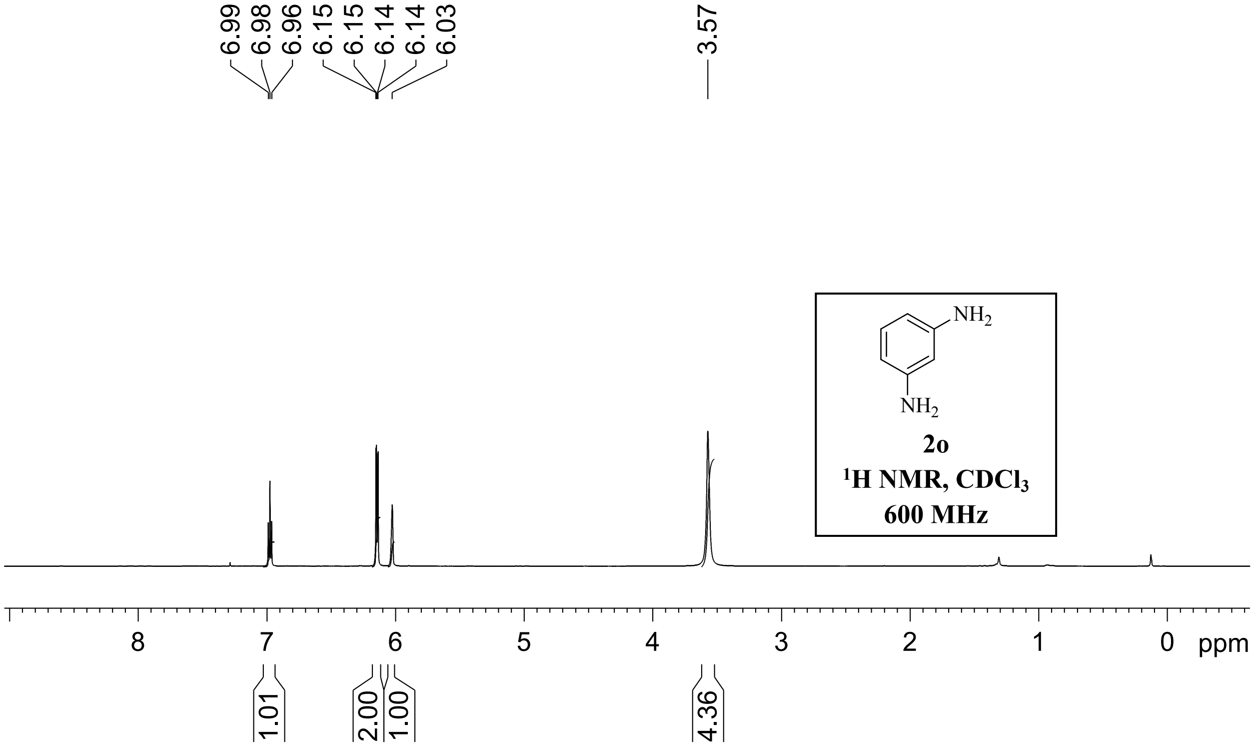
^{13}H NMR, CDCl$_3$

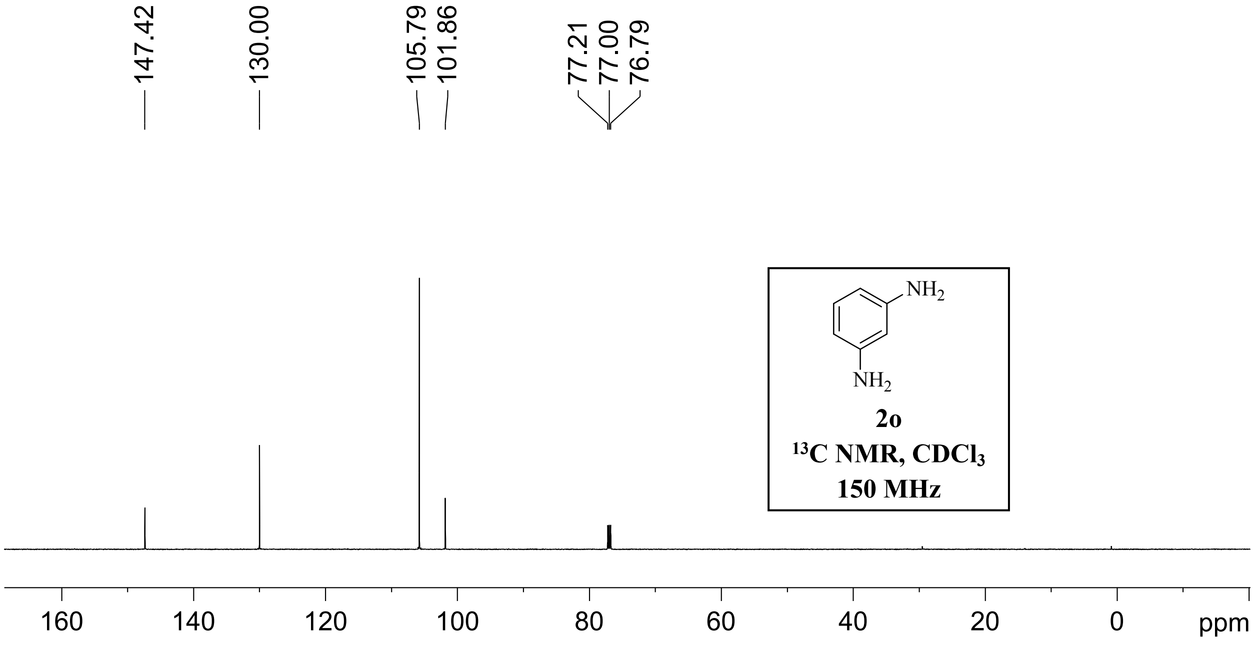
150 MHz

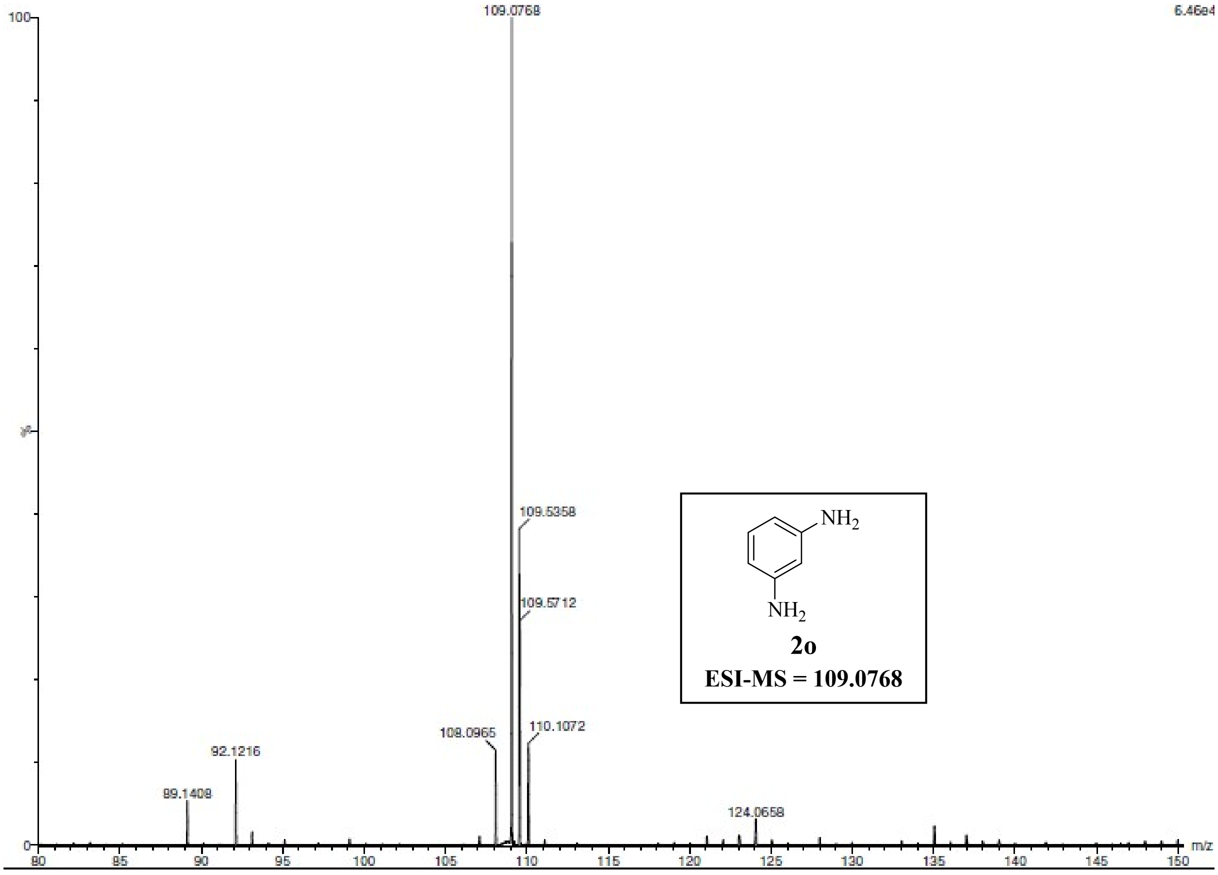


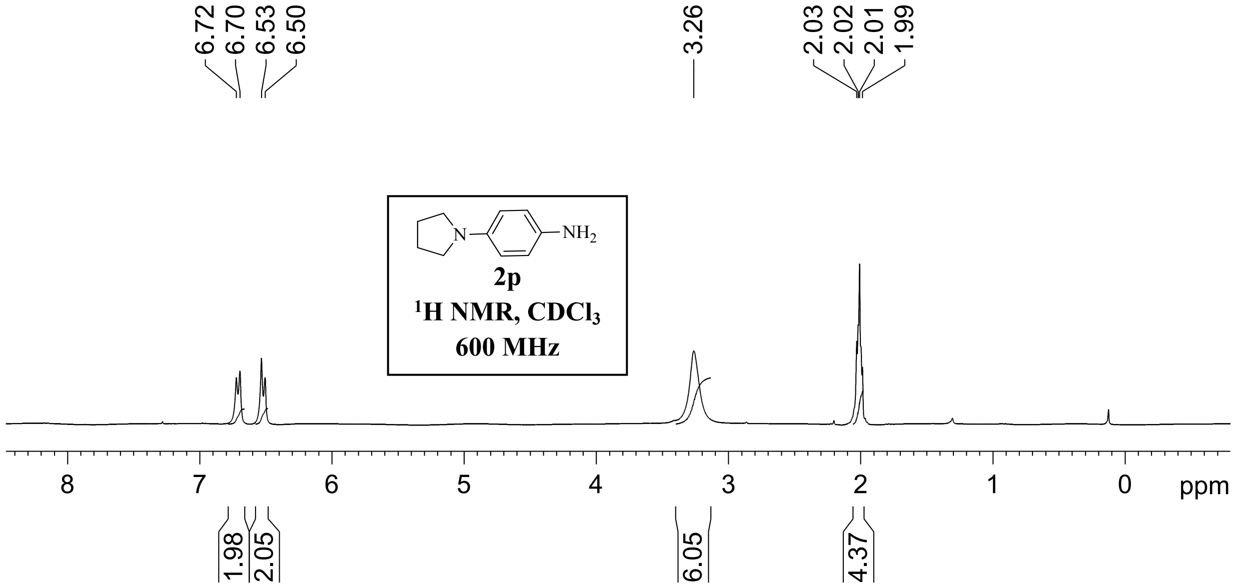
2n

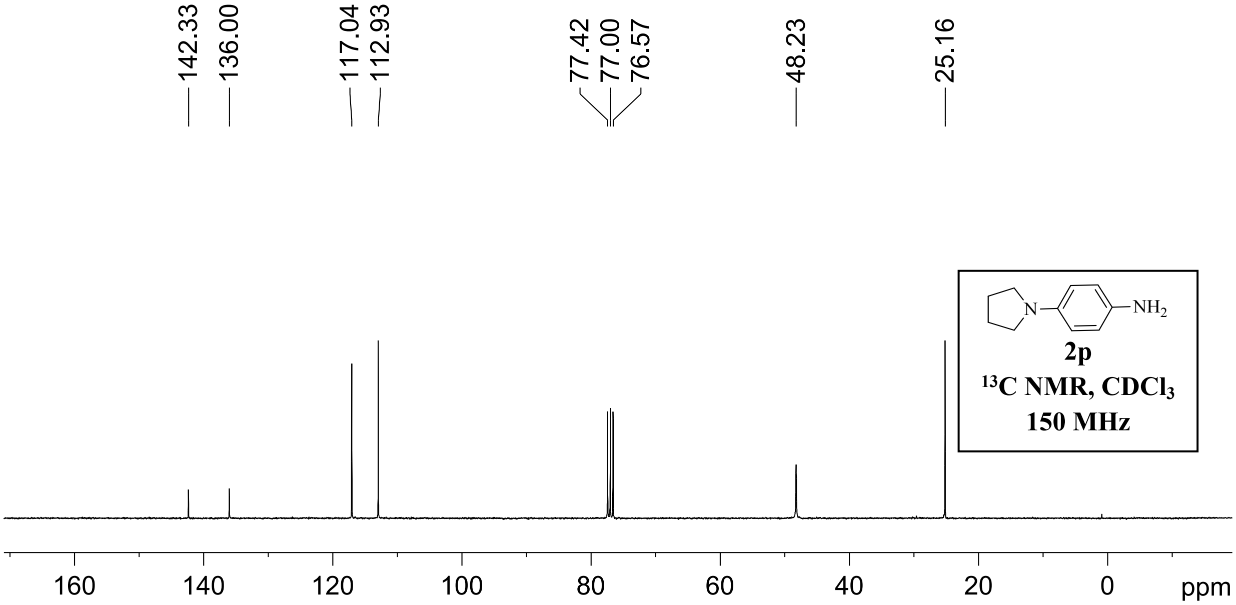
ESI-MS = 171.9750

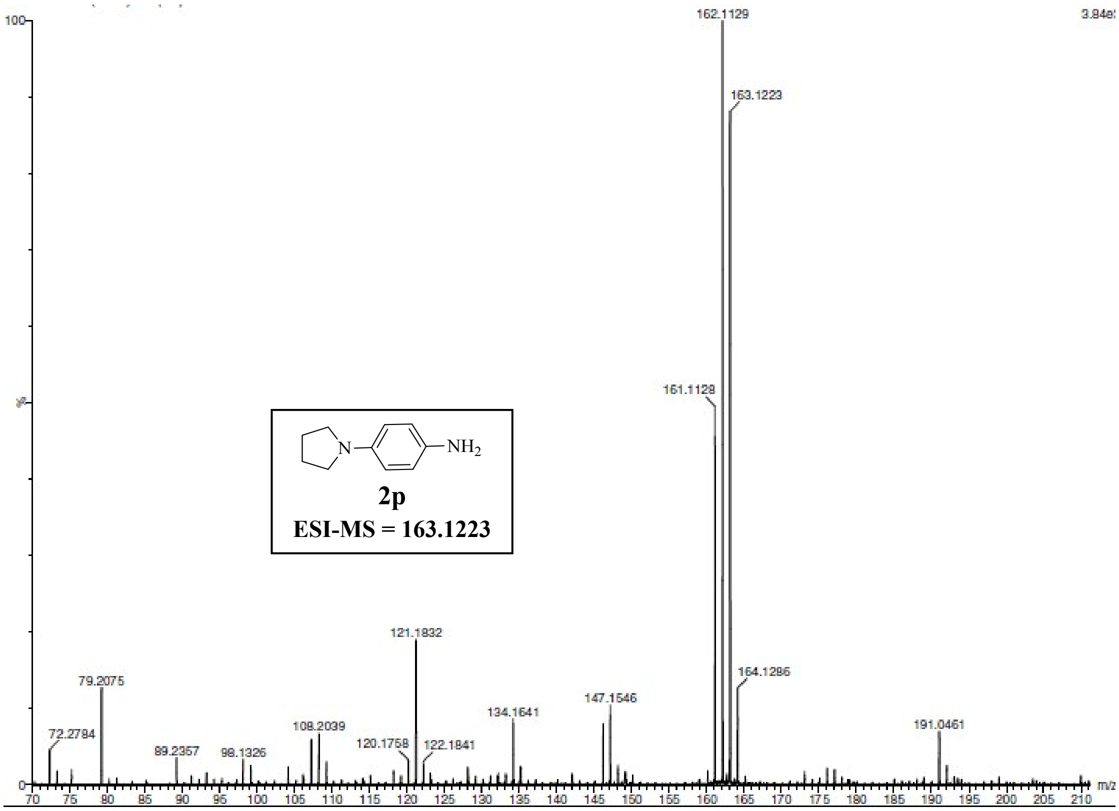

6.99
6.98
6.96
6.15
6.15
6.14
6.14
6.03
3.57
2o
^{1}H NMR, CDCl$_3$
600 MHz
NH$_2$
NH$_2$
8
7
6
5
4
3
2
1
0
ppm
1.01
2.00
1.00
4.36

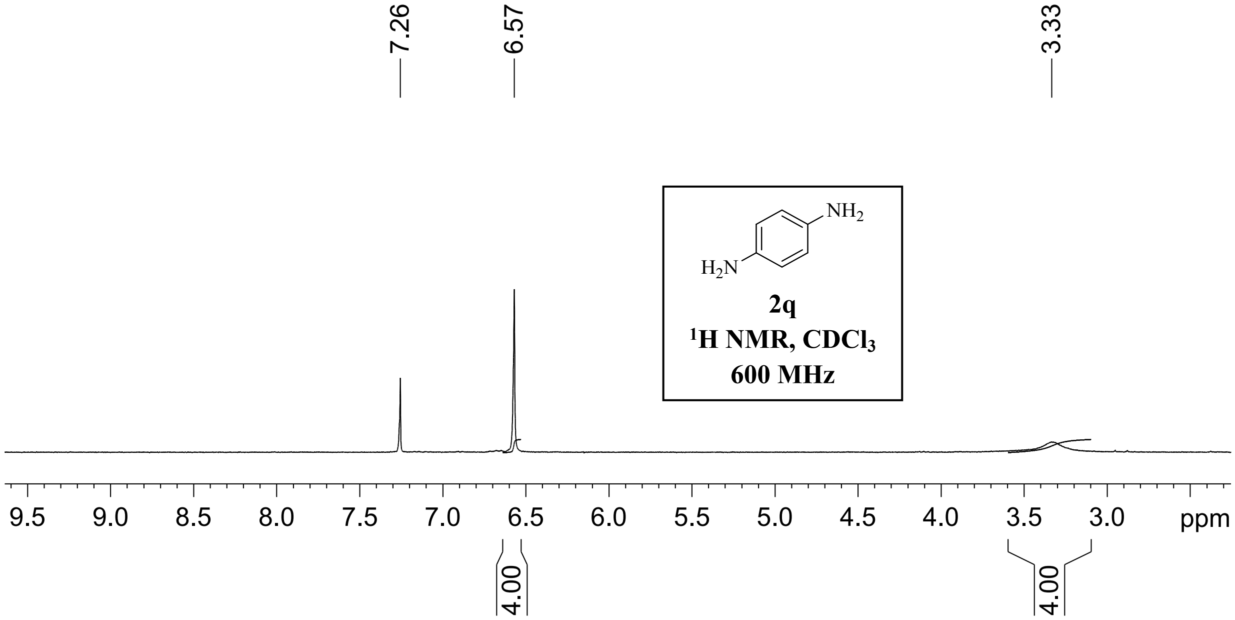

147.42
130.00
105.79
101.86
77.21
77.00
76.79
2o
^{13}C NMR, CDCl$_3$
150 MHz
NH$_2$
NH$_2$
160
140
120
100
80
60
40
20
0
ppm

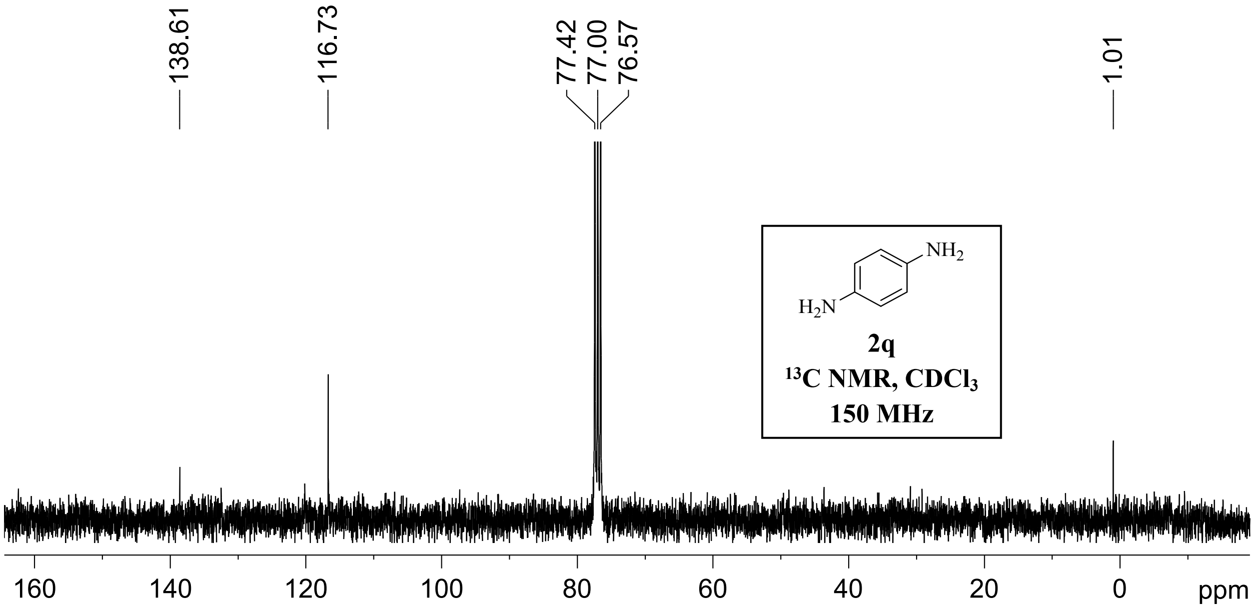

100
%
0
109.0768
6.46e4
109.5358
109.5712
108.0965
110.1072
92.1216
89.1408
124.0658
NH2
NH2
2o
ESI-MS = 109.0768
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
m/z

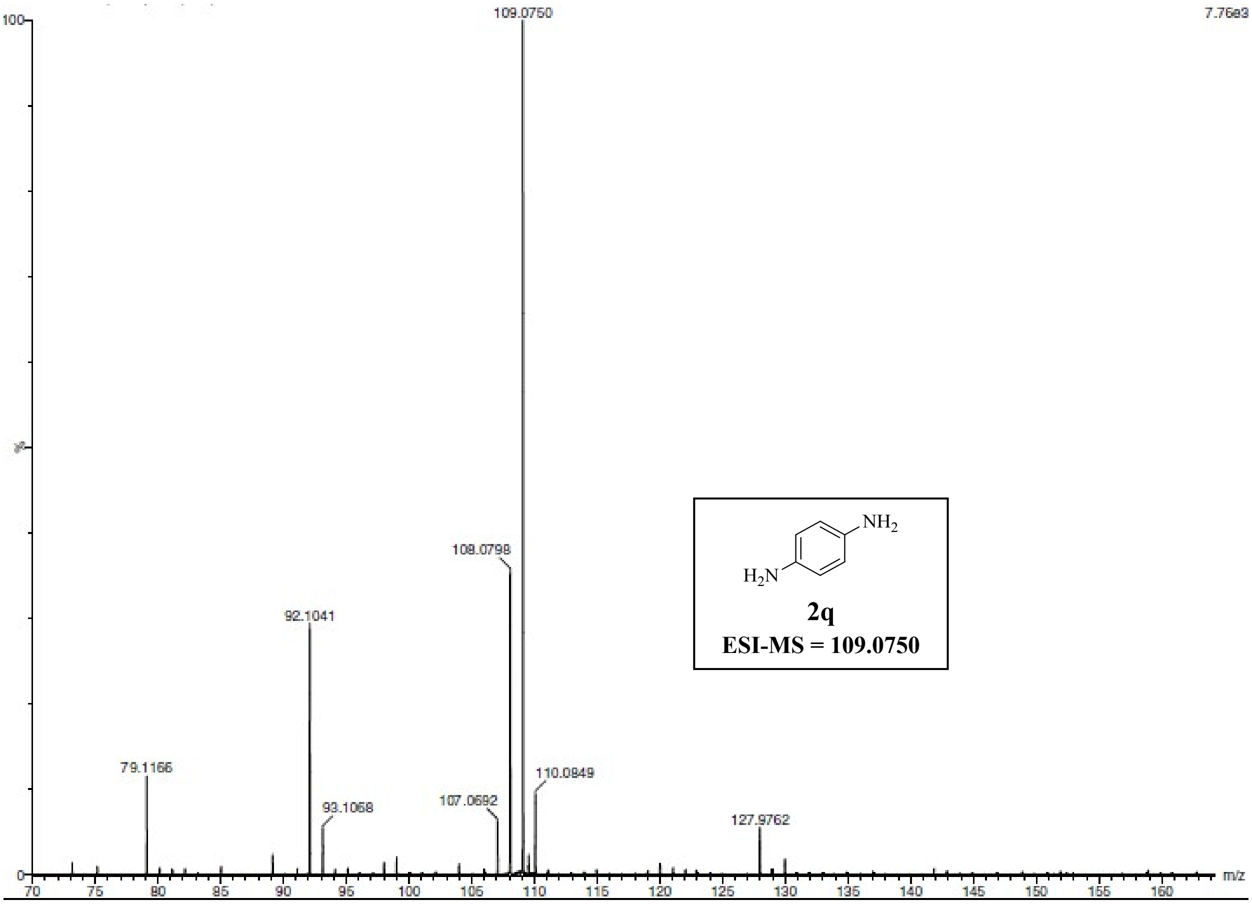

6.72
6.70
6.53
6.50
3.26
2.03
2.02
2.01
1.99
N
NH2
2p
1H NMR, CDCl3
600 MHz
8
7
6
5
4
3
2
1
0
ppm
1.98
2.05
6.05
4.37


142.33
136.00
117.04
112.93
77.42
77.00
76.57
48.23
25.16
N
NH2
2p
13C NMR, CDCl3
150 MHz
160
140
120
100
80
60
40
20
0
ppm


100
%
0
162.1129
3.84e
163.1223
161.1128
121.1832
164.1286
79.2075
147.1546
134.1641
72.2784
108.2039
191.0461
89.2357
98.1326
120.1758
122.1841
N
NH2
2p
ESI-MS = 163.1223
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
200
205
210
m/z

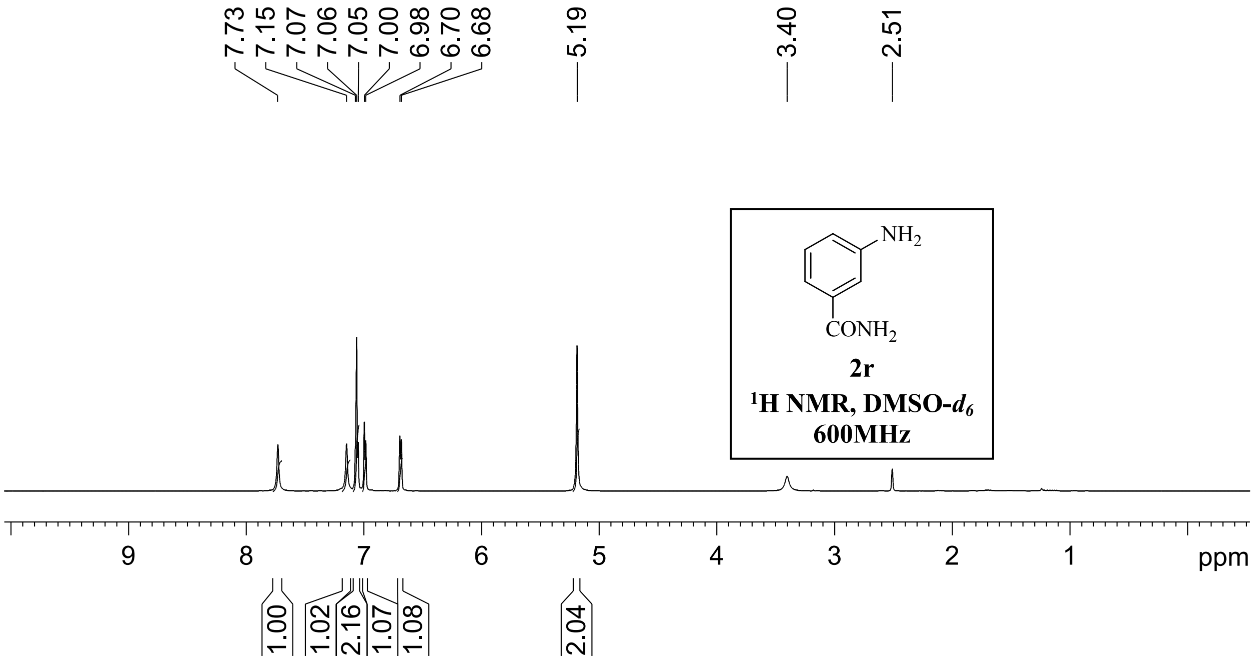

7.26
6.57
3.33
2q
^{1}H NMR, CDCl$_3$
600 MHz
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
4.00
4.00


138.61
116.73
77.42
77.00
76.57
1.01
2q
^{13}C NMR, CDCl$_3$
150 MHz
160
140
120
100
80
60
40
20
0
ppm



2q

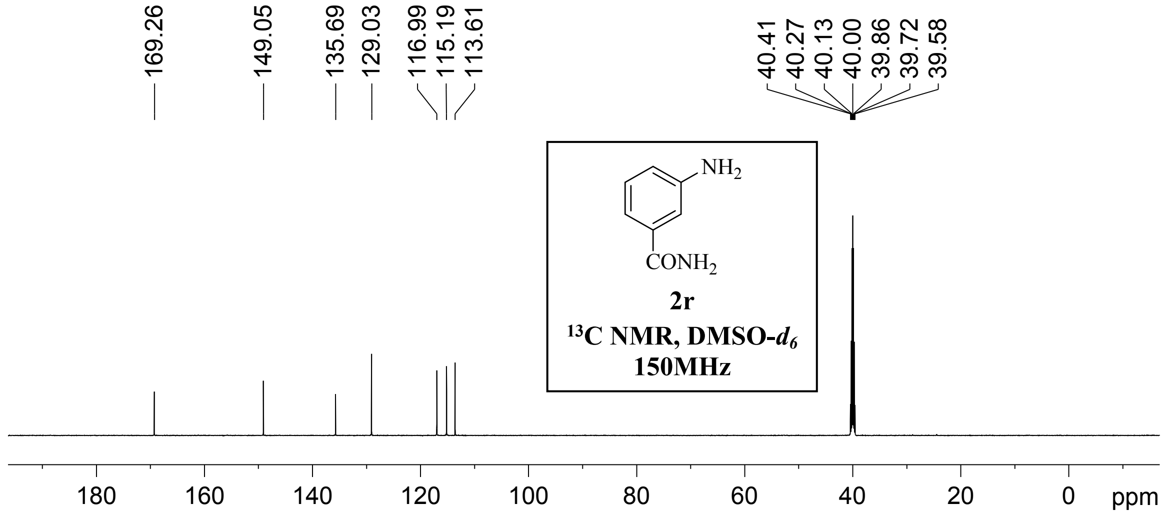
ESI-MS = 109.0750

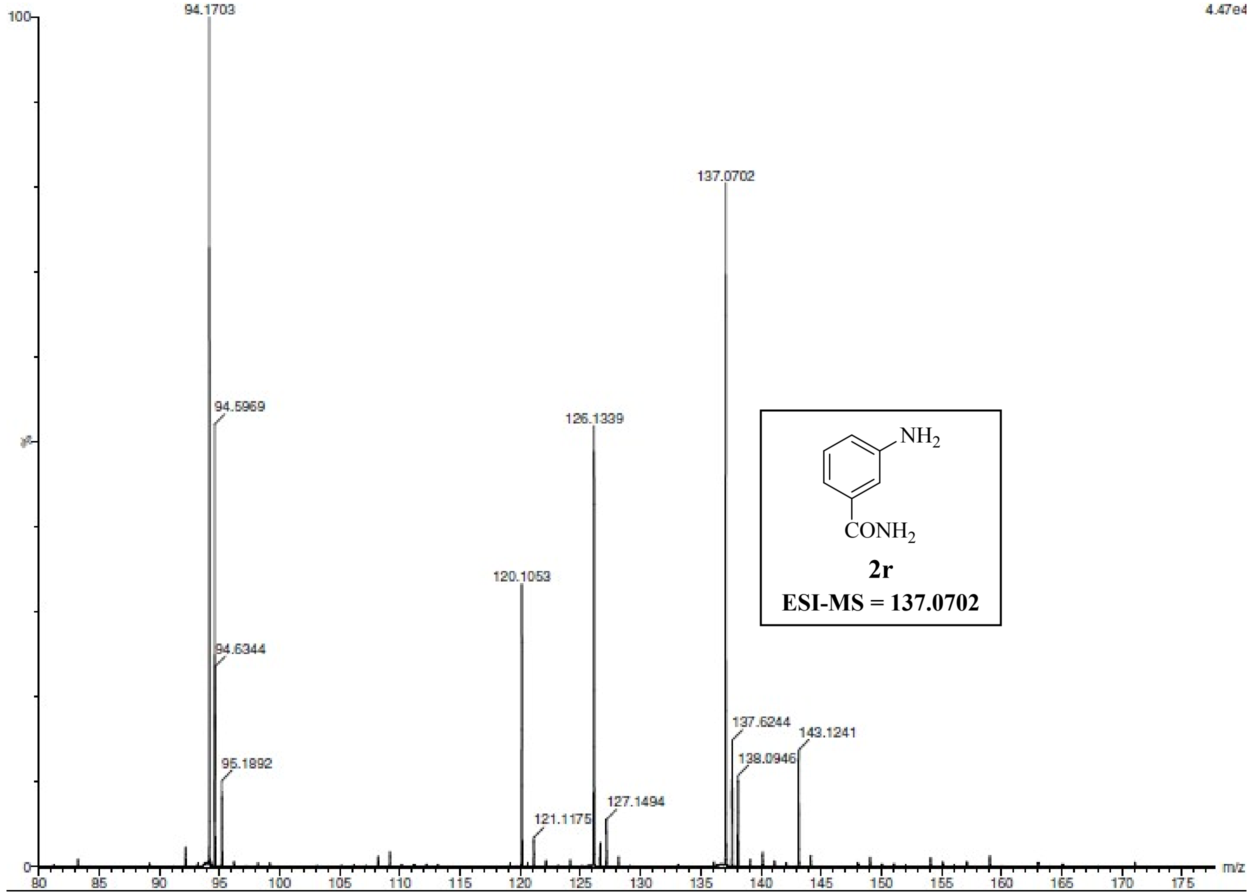


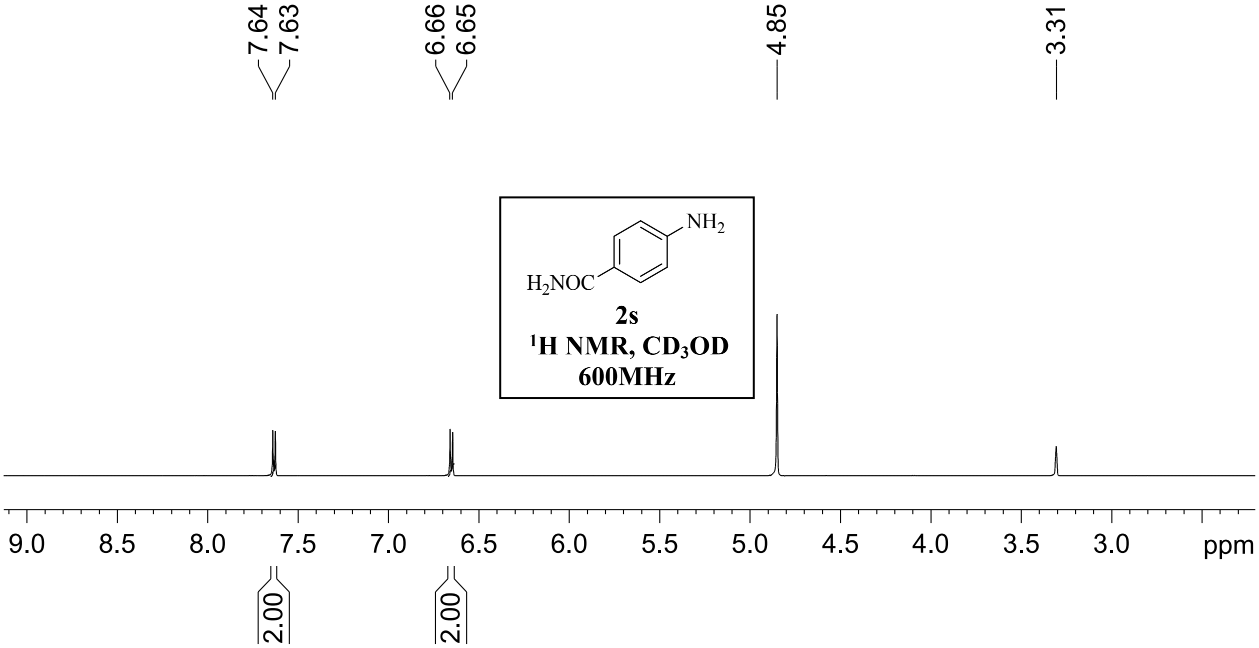
2r

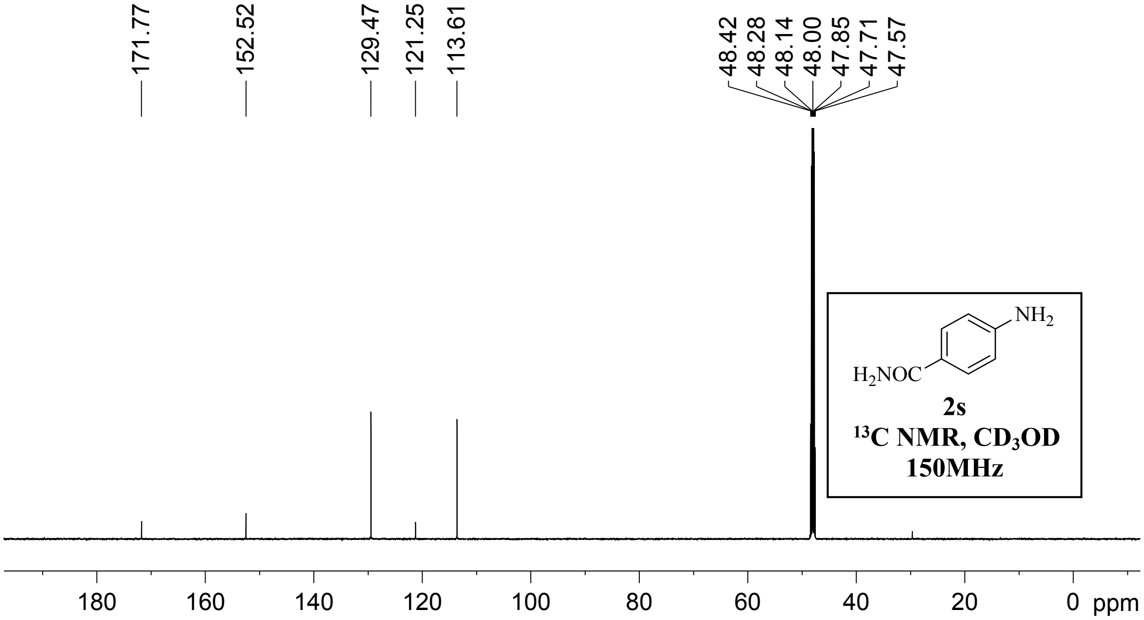
^{1}H NMR, DMSO-*d₆*

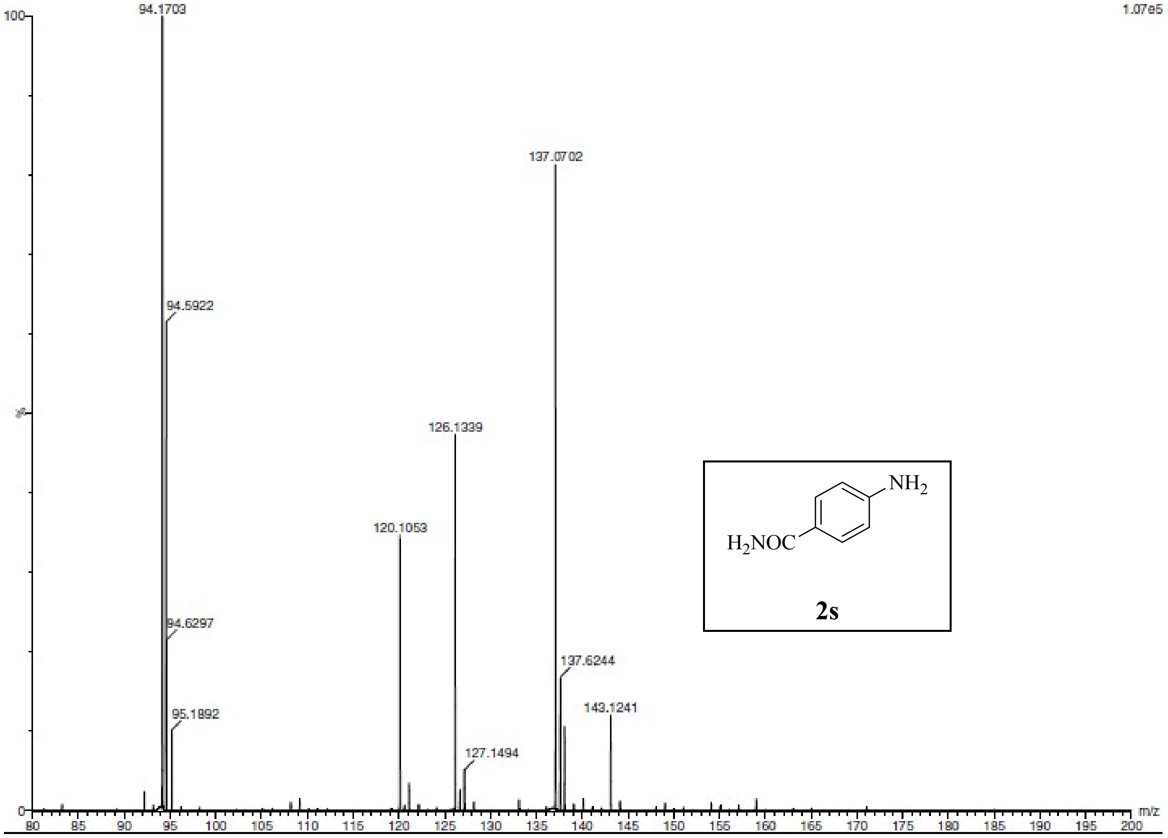
600MHz


169.26
149.05
135.69
129.03
116.99
115.19
113.61
40.41
40.27
40.13
40.00
39.86
39.72
39.58
NH2
CONH2
2r
13C NMR, DMSO-d6
150MHz
180
160
140
120
100
80
60
40
20
0
ppm

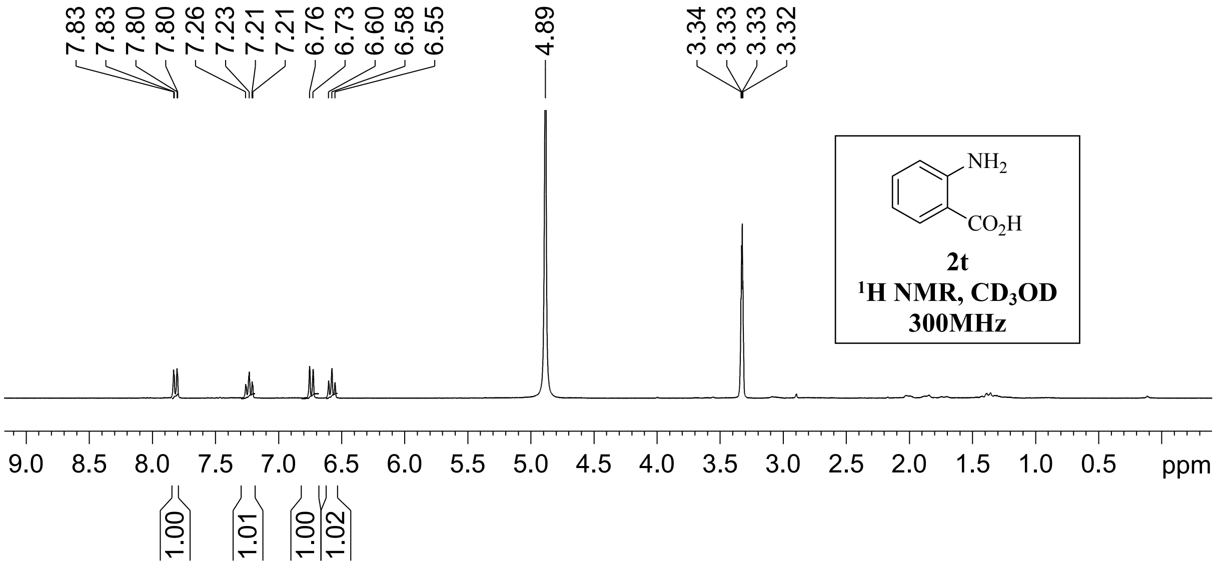

100
%
0
4.47e4
94.1703
94.5969
94.6344
95.1892
120.1053
121.1175
126.1339
127.1494
137.0702
137.6244
138.0946
143.1241
NH2
CONH2
2r
ESI-MS = 137.0702
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175
m/z


7.64
7.63
6.66
6.65
4.85
3.31
NH2
H2NOC
2s
1H NMR, CD3OD
600MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
2.00
2.00

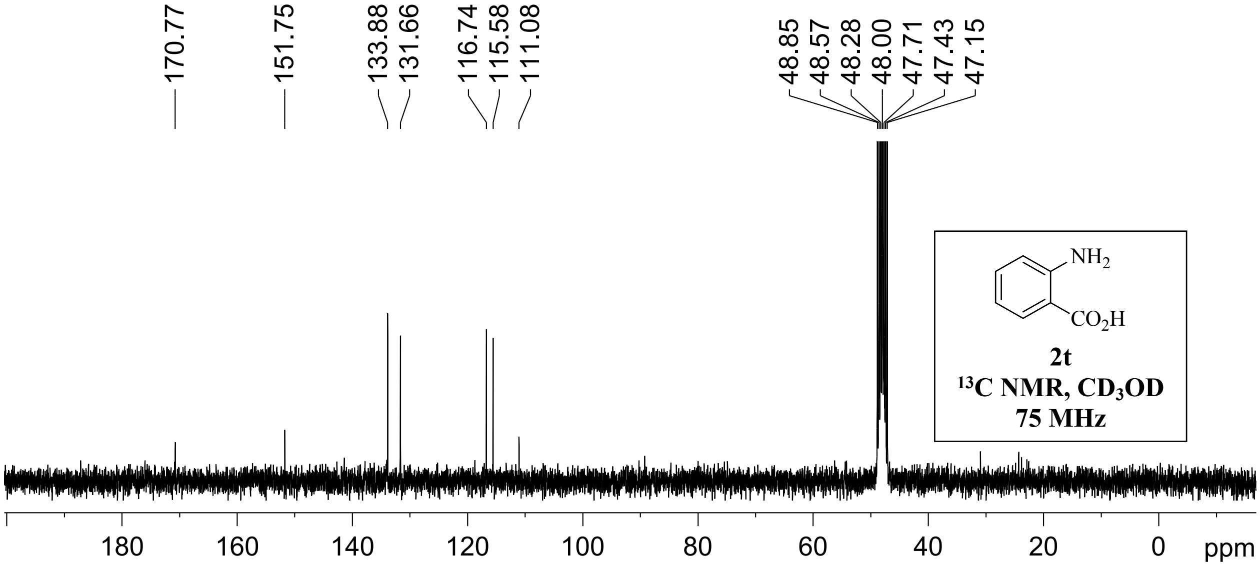

171.77
152.52
129.47
121.25
113.61
48.42
48.28
48.14
48.00
47.85
47.71
47.57
NH2
H2NOC
2s
13C NMR, CD3OD
150MHz
180
160
140
120
100
80
60
40
20
0
ppm

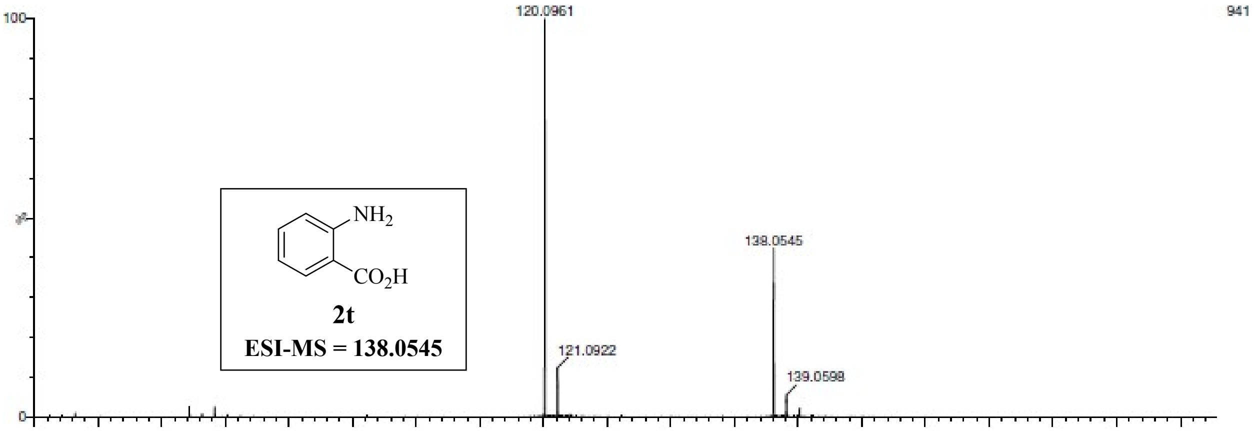


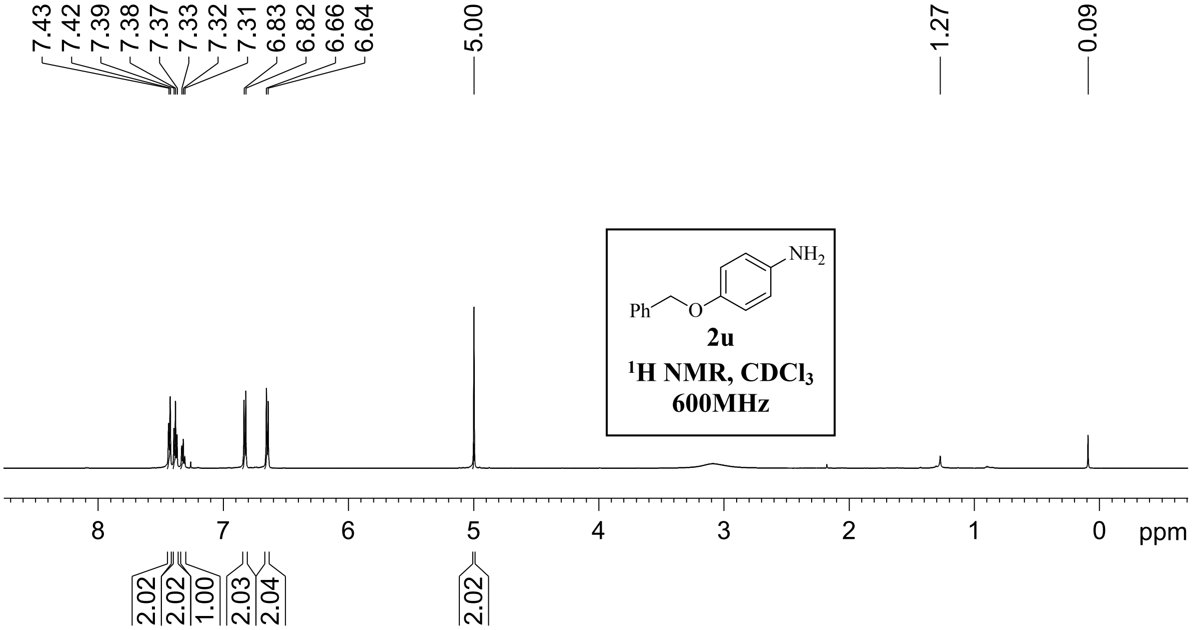
100
%
0
1.07e5
94.1703
94.5922
94.6297
95.1892
120.1053
126.1339
127.1494
137.0702
137.6244
143.1241
m/z
80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200
NH2
H2NOC
2s

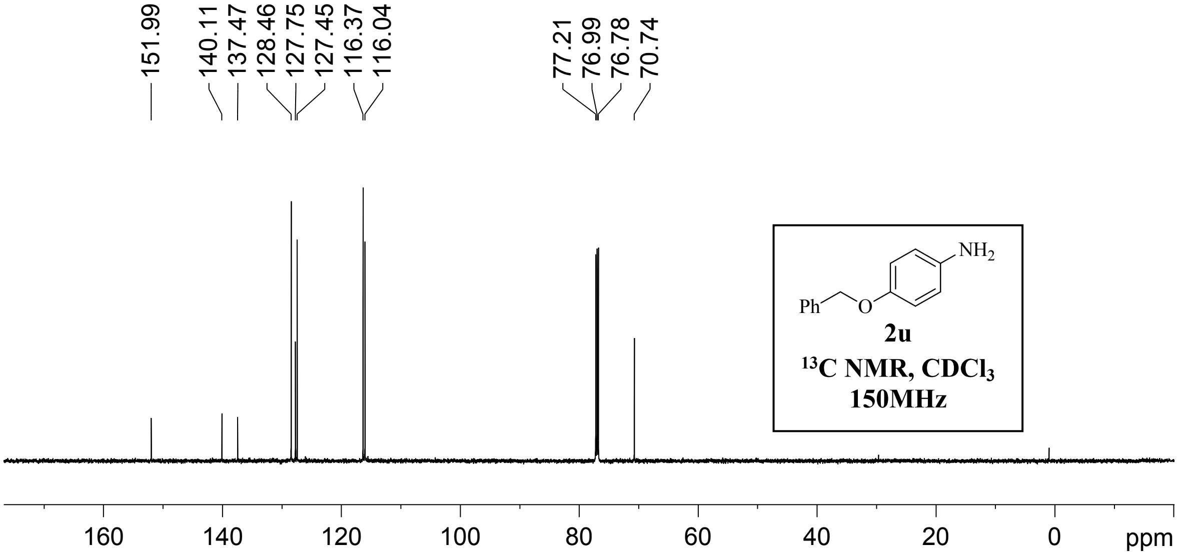


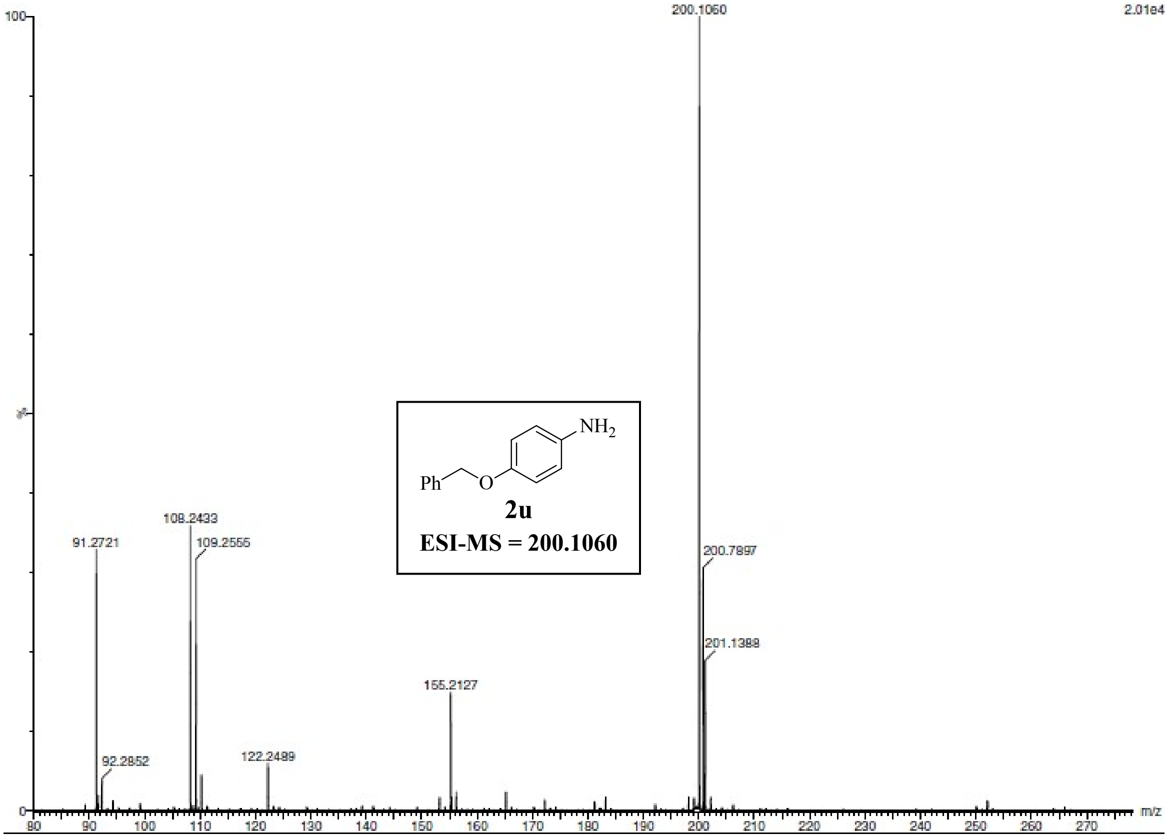
7.83 7.83 7.80 7.80 7.26 7.23 7.21 7.21 6.76 6.73 6.60 6.58 6.55
4.89
3.34 3.33 3.33 3.32
NH2
CO2H
2t
1H NMR, CD3OD
300MHz
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.01 1.00 1.02


170.77
151.75
133.88
131.66
116.74
115.58
111.08
48.85
48.57
48.28
48.00
47.71
47.43
47.15
NH2
CO2H
2t
13C NMR, CD3OD
75 MHz
180
160
140
120
100
80
60
40
20
0
ppm


100
%
0
120.0961
941
121.0922
138.0545
139.0598
NH2
CO2H
2t
ESI-MS = 138.0545

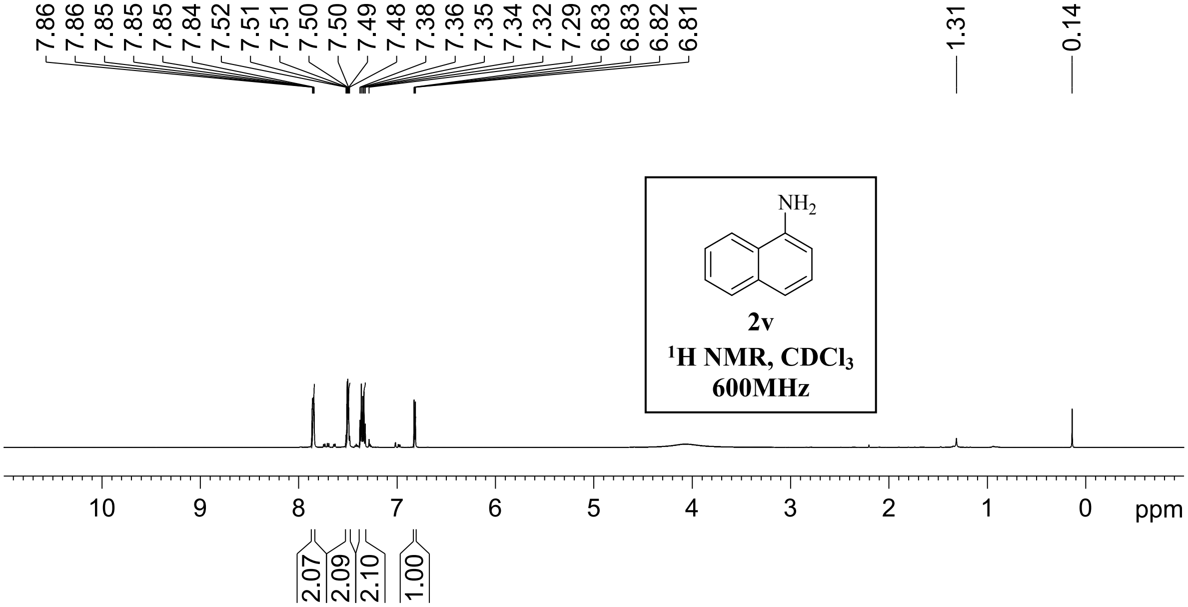

7.43
7.42
7.39
7.38
7.37
7.33
7.32
7.31
6.83
6.82
6.66
6.64
5.00
1.27
0.09
NH2
Ph
O
2u
1H NMR, CDCl3
600MHz
8
7
6
5
4
3
2
1
0
ppm
2.02
2.02
1.00
2.03
2.04
2.02


151.99
140.11
137.47
128.46
127.75
127.45
116.37
116.04
77.21
76.99
76.78
70.74
NH2
Ph
O
2u
13C NMR, CDCl3
150MHz
160
140
120
100
80
60
40
20
0
ppm



2u

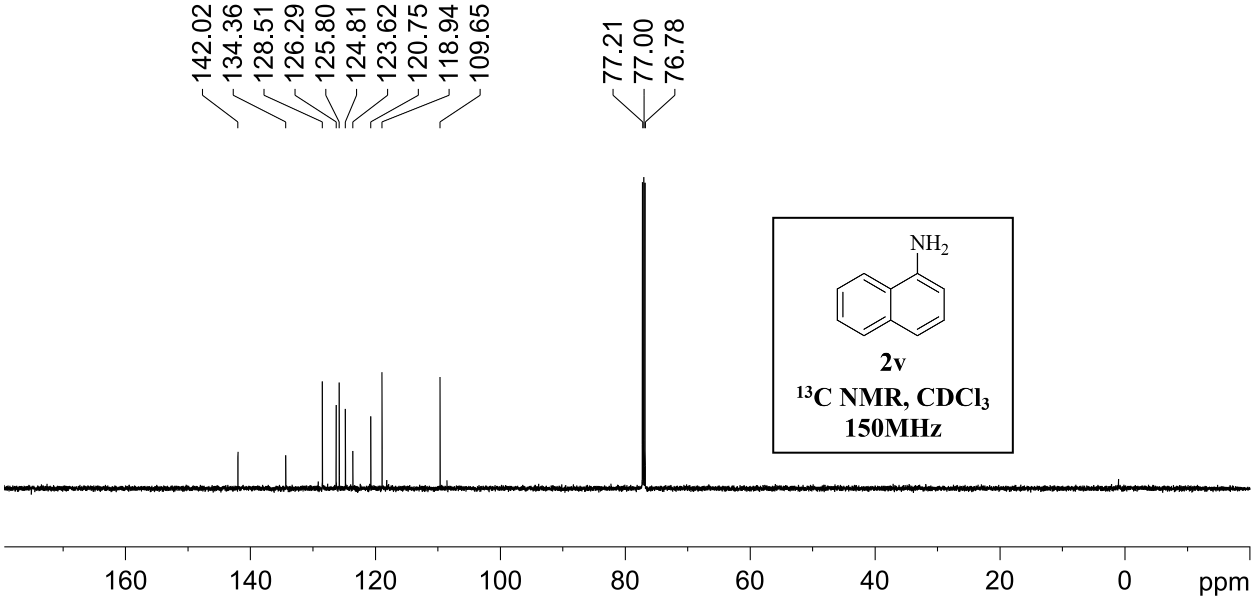
ESI-MS = 200.1060

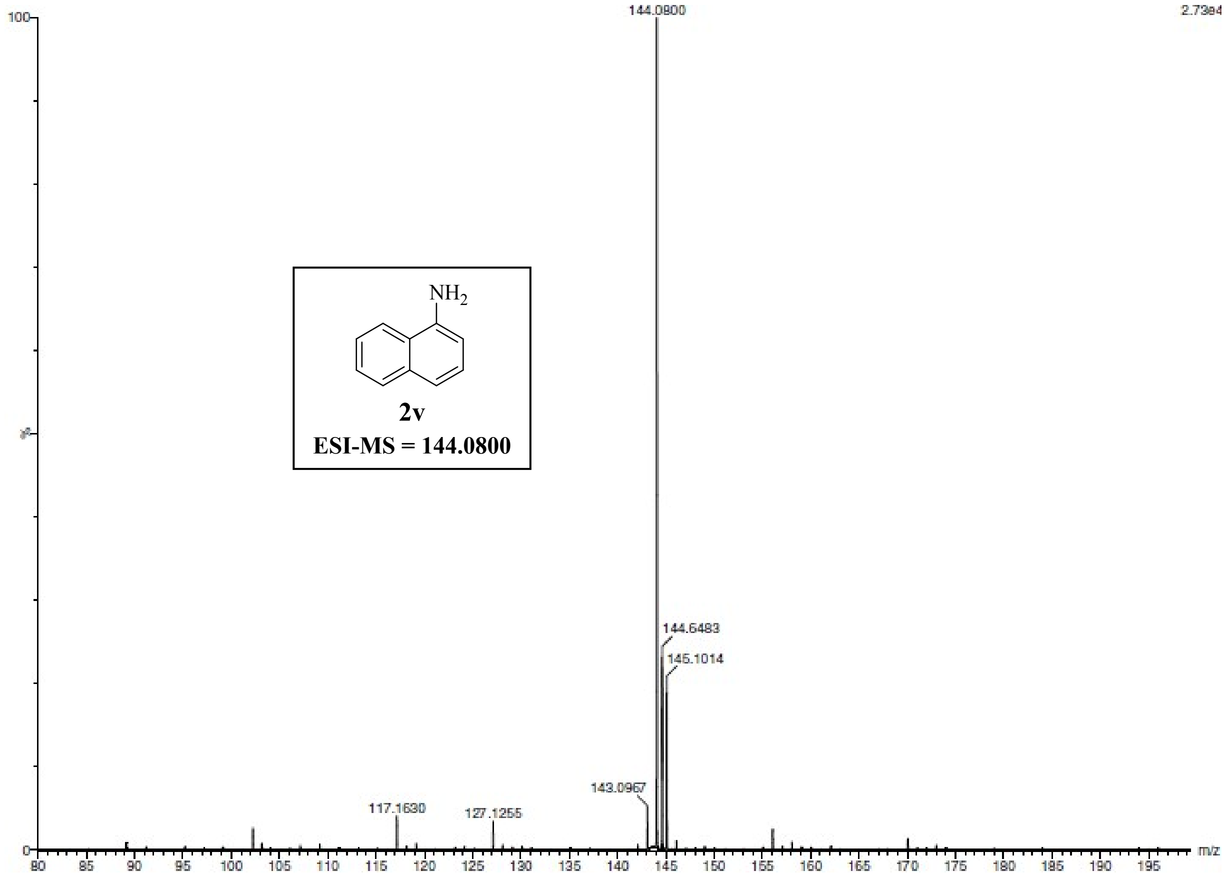


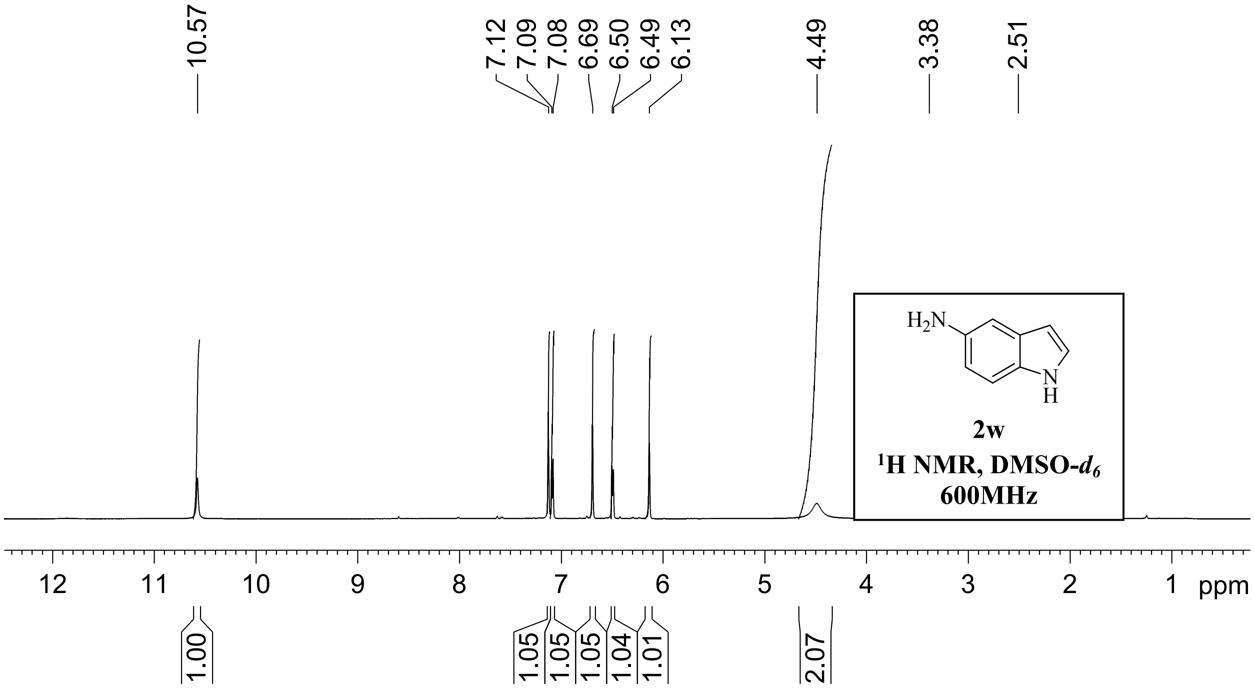
2v

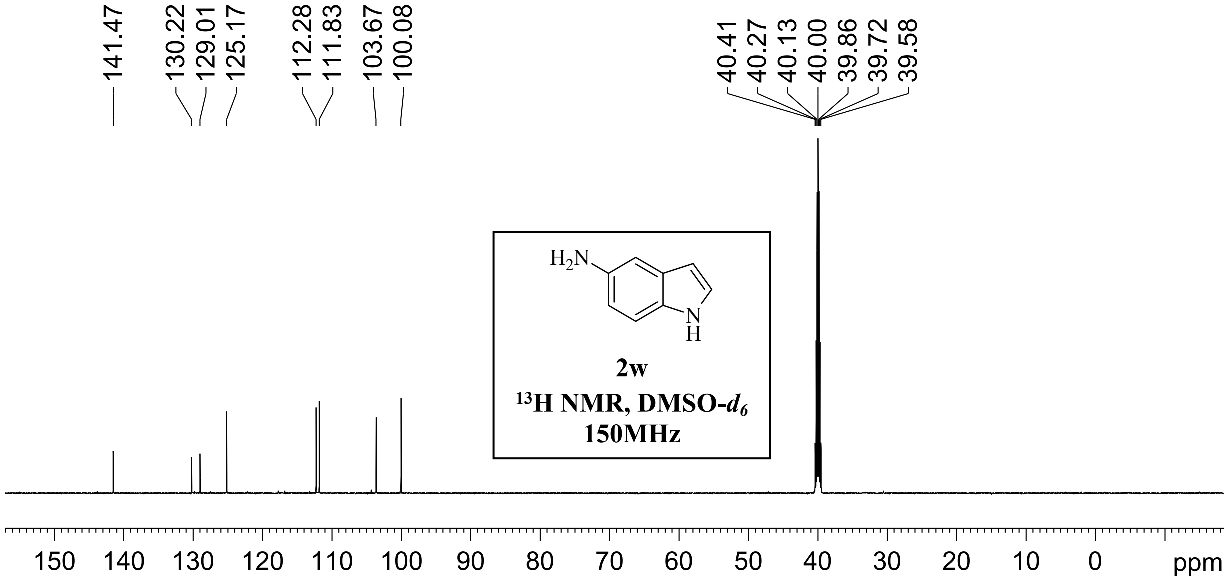
^{1}H NMR, $CDCl_3$

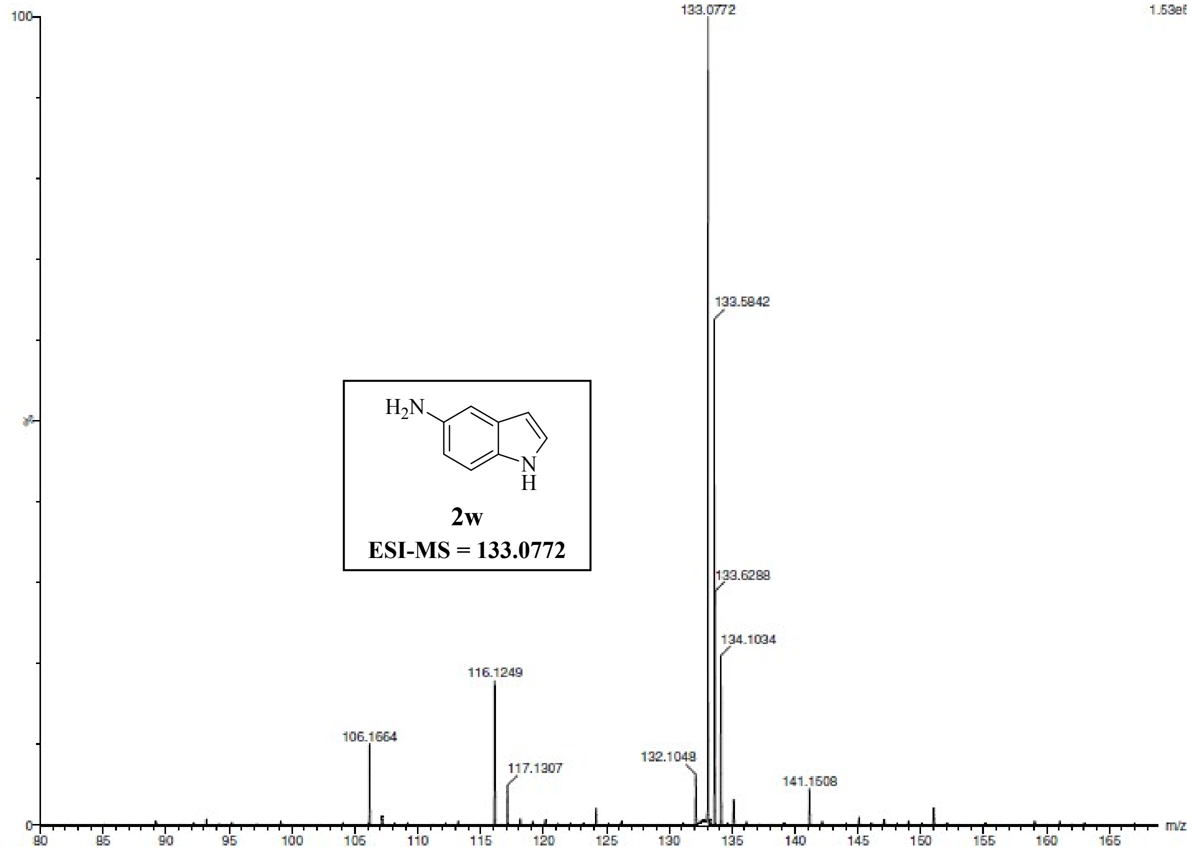
600MHz

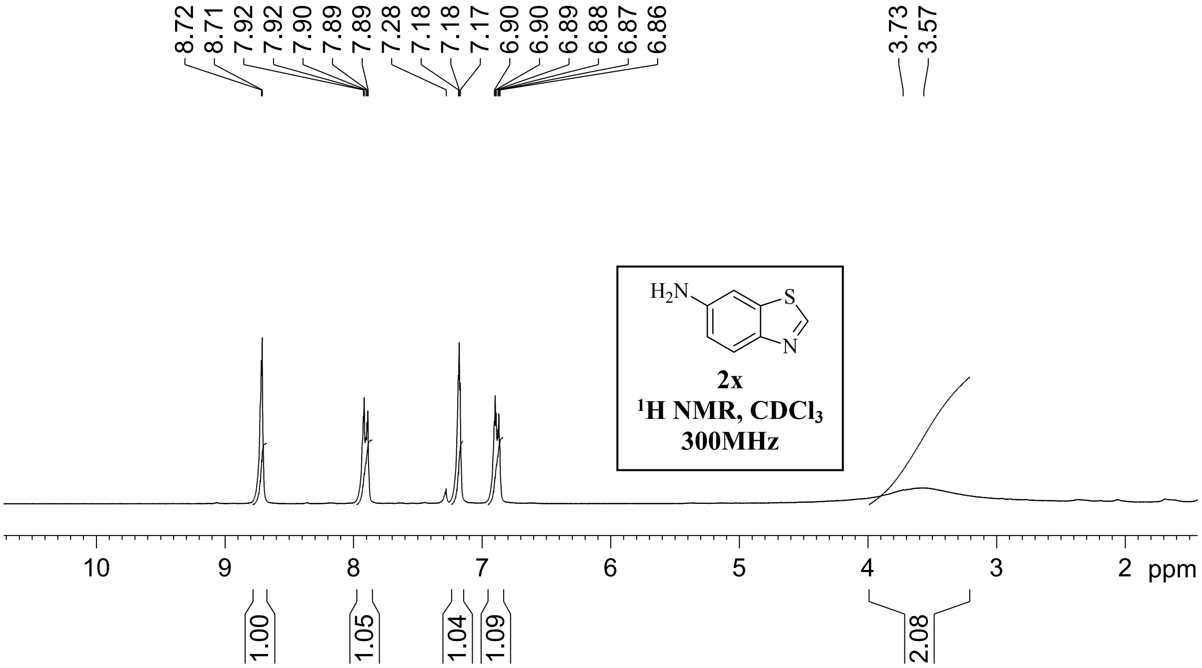

142.02
134.36
128.51
126.29
125.80
124.81
123.62
120.75
118.94
109.65
77.21
77.00
76.78
NH2
2v
13C NMR, CDCl3
150MHz
160
140
120
100
80
60
40
20
0
ppm

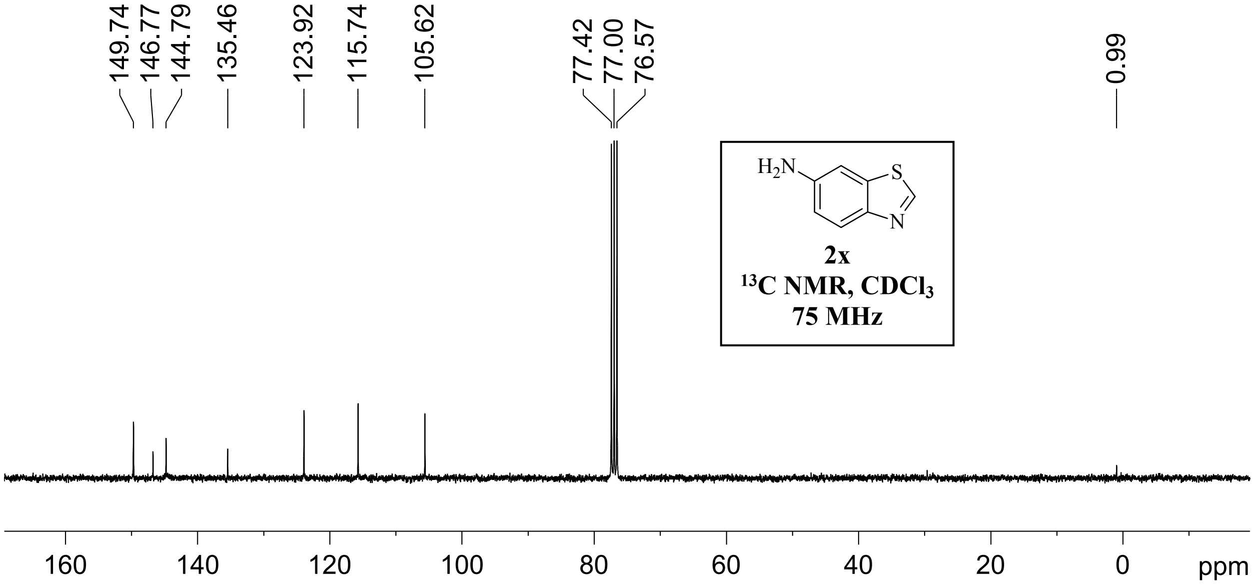

100
%
0
144.0800
2.73e4
NH2
2v
ESI-MS = 144.0800
144.6483
145.1014
143.0967
117.1630
127.1255
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
m/z

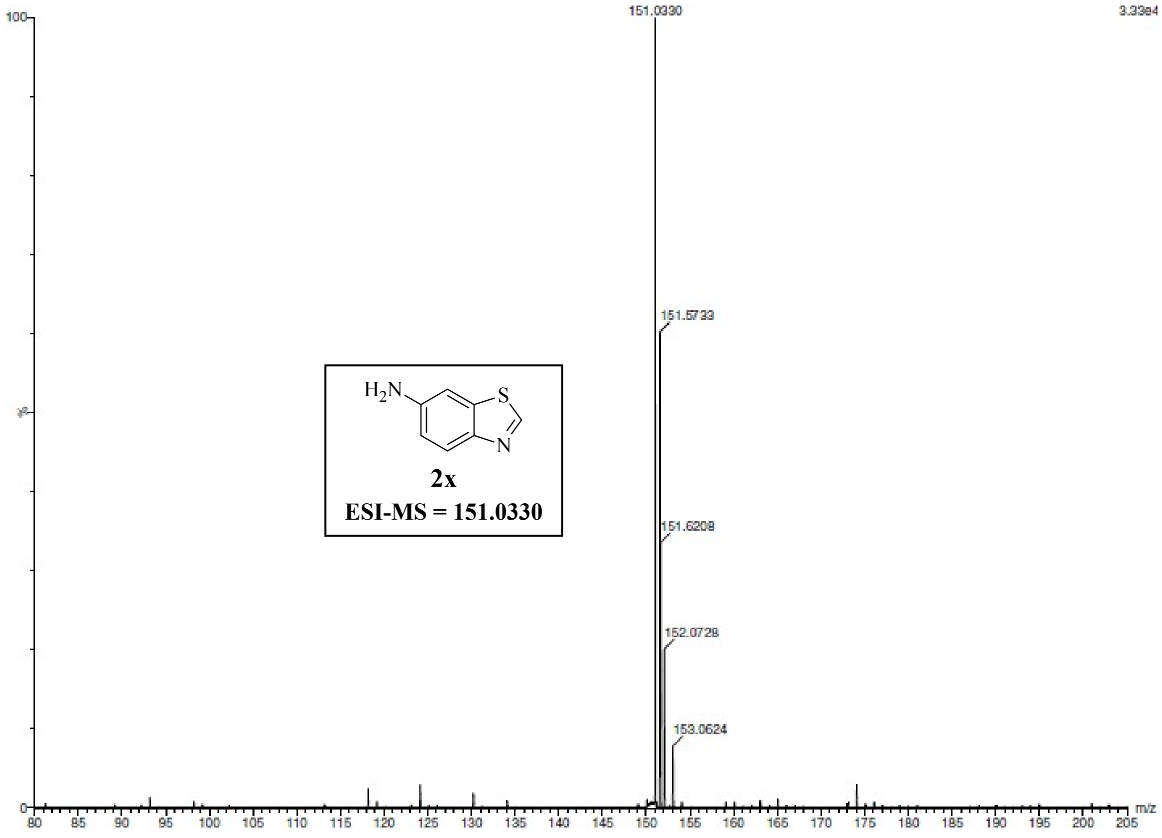

10.57
7.12
7.09
7.08
6.69
6.50
6.49
6.13
4.49
3.38
2.51
H_2N
N
H
2w
^{1}H NMR, DMSO-d_6
600MHz
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.05
1.05
1.05
1.04
1.01
2.07

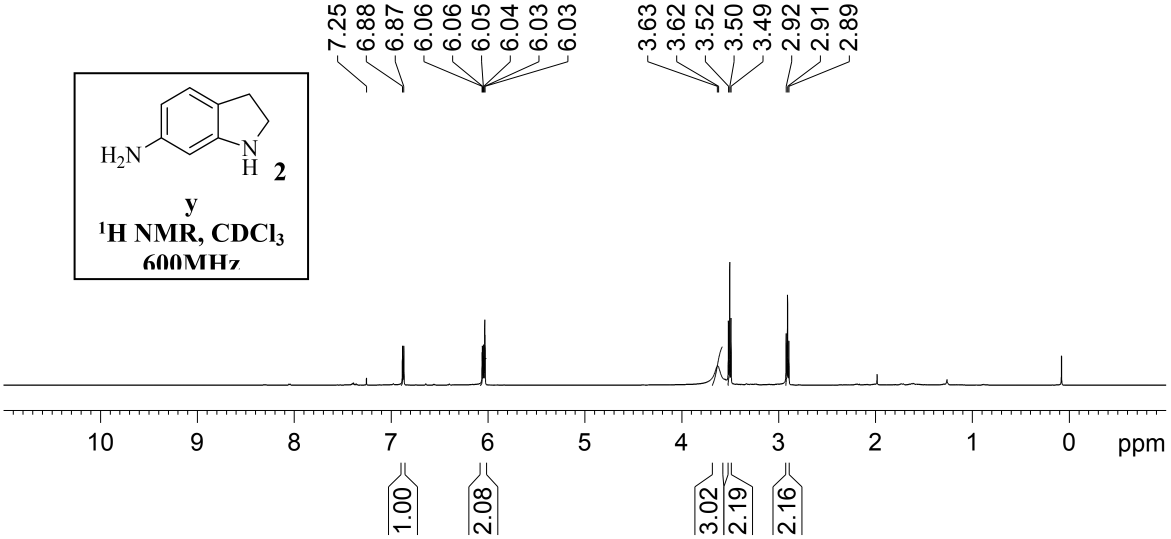

141.47
130.22
129.01
125.17
112.28
111.83
103.67
100.08
40.41
40.27
40.13
40.00
39.86
39.72
39.58
H_2N
N
H
2w
^{13}H NMR, DMSO-d_6
150MHz
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

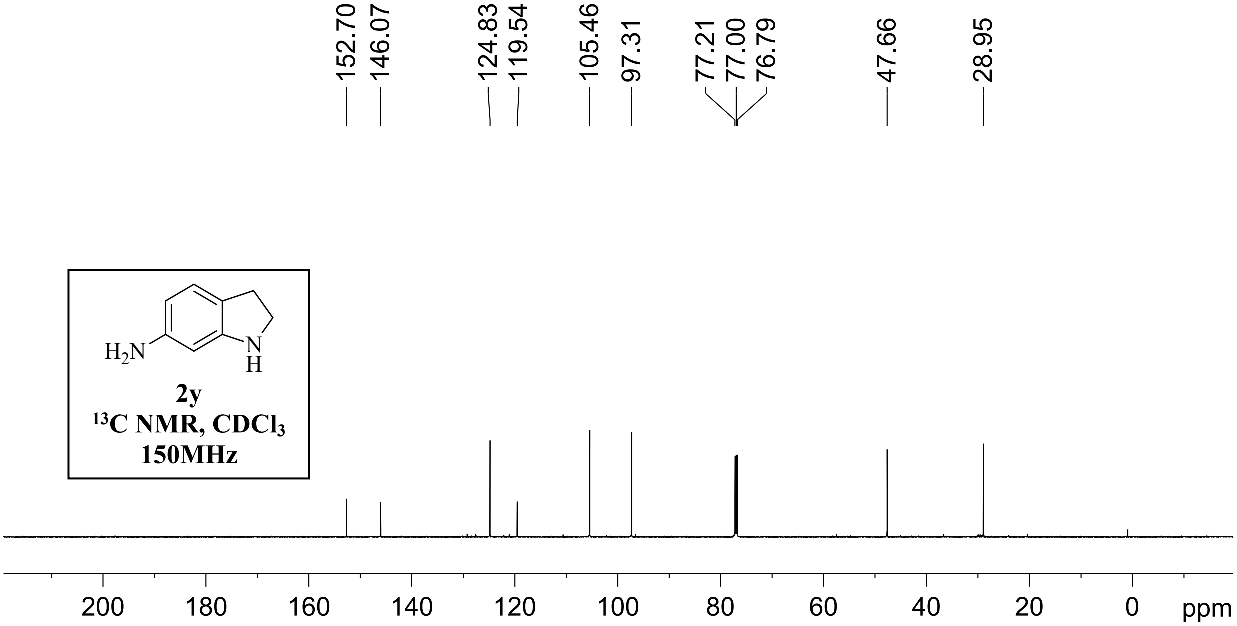

100
%
0
133.0772
1.53e6
133.5842
133.6288
134.1034
116.1249
106.1664
117.1307
132.1049
141.1508
m/z
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
165
H2N
N
H
2w
ESI-MS = 133.0772

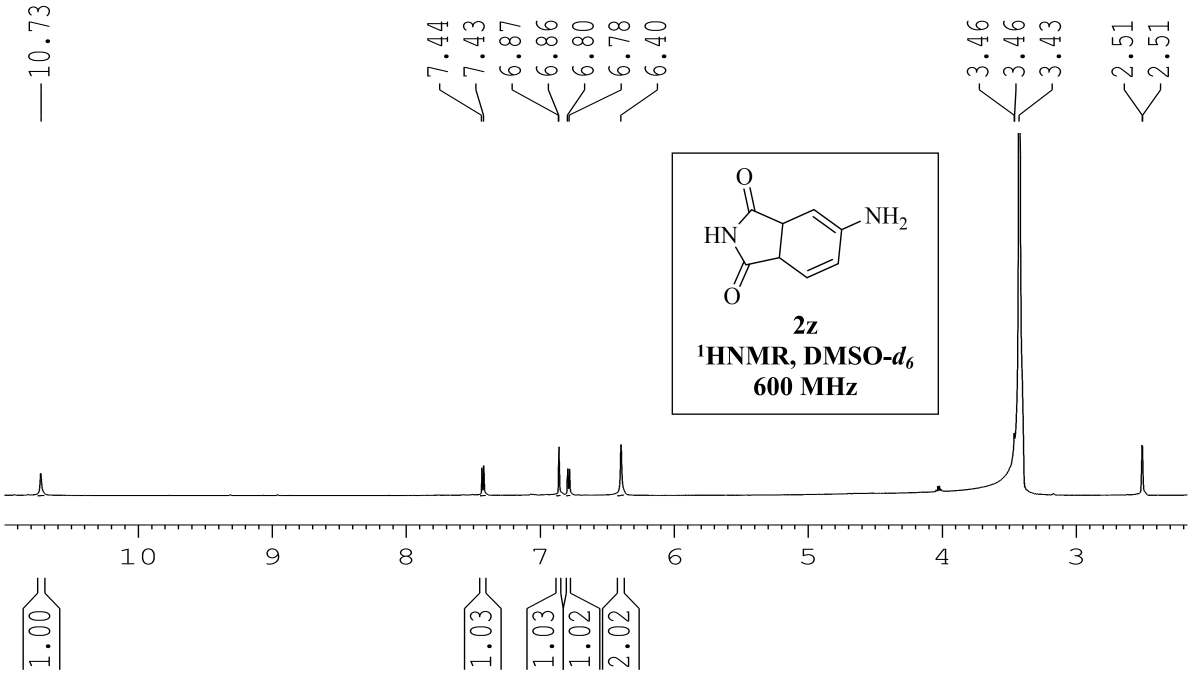

8.72
8.71
7.92
7.92
7.90
7.89
7.89
7.28
7.18
7.18
7.17
6.90
6.90
6.89
6.88
6.87
6.86
3.73
3.57
H2N
S
N
2x
1H NMR, CDCl3
300MHz
10
9
8
7
6
5
4
3
2
ppm
1.00
1.05
1.04
1.09
2.08

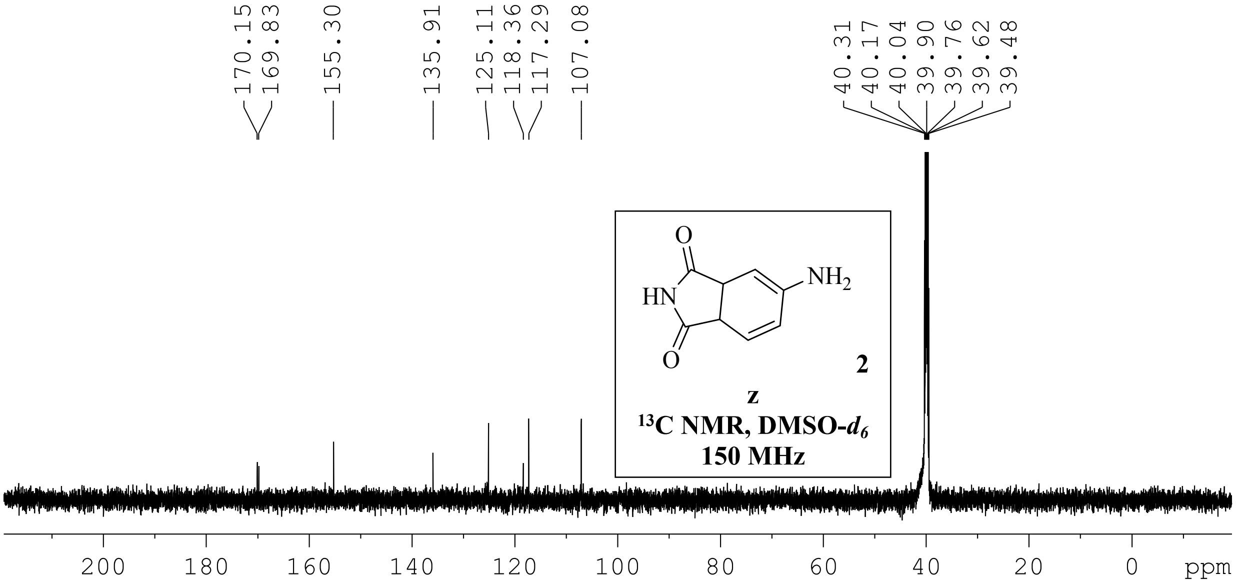

149.74
146.77
144.79
135.46
123.92
115.74
105.62
77.42
77.00
76.57
0.99
H2N
S
N
2x
13C NMR, CDCl3
75 MHz
160
140
120
100
80
60
40
20
0
ppm


151.0330
3.33e4
100
%
0
151.5733
151.6209
152.0728
153.0624
H2N
S
N
2x
ESI-MS = 151.0330
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
200
205
m/z


7.25
6.88
6.87
6.06
6.06
6.05
6.04
6.03
6.03
3.63
3.62
3.52
3.50
3.49
2.92
2.91
2.89
H2N
N
H
2
y
1H NMR, CDCl3
600MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.08
3.02
2.19
2.16

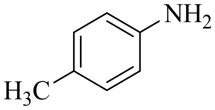

152.70
146.07
124.83
119.54
105.46
97.31
77.21
77.00
76.79
47.66
28.95
H2N
N
H
2y
13C NMR, CDCl3
150MHz
200
180
160
140
120
100
80
60
40
20
0
ppm


10.73
7.44
7.43
6.87
6.86
6.80
6.78
6.40
3.46
3.46
3.43
2.51
2.51
O
HN
NH2
O
2z
1HNMR, DMSO-d6
600 MHz
10
9
8
7
6
5
4
3
1.00
1.03
1.03
1.02
2.02


170.15
169.83
155.30
135.91
125.11
118.36
117.29
107.08
40.31
40.17
40.04
39.90
39.76
39.62
39.48
O
HN
NH2
O
2
z
13C NMR, DMSO-d6
150 MHz
200
180
160
140
120
100
80
60
40
20
0
ppm

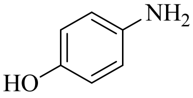
Experimental procedure for Scheme 1

4-Methylaniline (2a)



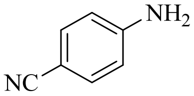
A solution of 4-nitrotoluene (1g, 7.2992 mmol) in 150 mL of EtOAc: MeOH (1:1) was passed through the Cat-Cart containing solid supported rhodium (Cart-Rh@PS) catalyst (350 mg) in cartridge at 100 ^{o}C and the reaction was completed in single run. Monitoring of the reaction was observed by TLC, after completion of the reaction the solution containing product was dried over rotary evaporator and afforded the product 4-methylaniline (**2a**) as brown solid (726 mg, 93%).

4-Aminophenol (2d)



Prepared as described for **2a** starting from 4-nitrophenol (1 g, 7.194 mmol) in 150 mL of EtOAc: MeOH (1:1), (Cart-Rh@PS) catalyst (350 mg) at 80 ^{o}Cthe reaction was completed in single run. After completion of the reaction the solution containing product (**2c**) was dried over rotary evaporator and afforded the product 4-aminophenol(**2c**) as yellow solid (737 mg, 95%).

4-Aminobenzonitrile(2h)



Prepared as described for **2a** starting from 4-nitrobenzonitrile (100 mg, 6.757 mmol)in 150 mL of EtOAc: MeOH (1:1), Cart-Rh@PS catalyst (350 mg) at 50 ^{o}Cthe reaction was completed in single run. After completion of the reaction the solution containing product (**2h**) was dried over rotary evaporator and afforded the product 4-aminobenzonitrile (**2h**) as white solid (677 mg, 85%).

References:

1. (a) A. K. Shil, D. Sharma, N. R. Guha and P. Das, *Tetrahedron Lett.*, 2012, **53**, 4858-4861; (b) D. Cantillo, M. Baghbanzadeh, and C. O. Kappe, *Angew. Chem. Int. Ed.*, 2012, **51**, 10190-10193. (c) N. R. Guha, D. Bhattacherjeeand P. Das, *Tetrahedron Letters*, 2014, **55**, 2912–2916; (e) W. G. Jia, S. Ling, H. N. Zhang, E. H. Sheng, and R. Lee, *Organometallics*, 2018, **37**, 40-47; (f)S. T. Yang, P. Shen, B. S. Liao, Y. H. Liu, S. M. Peng, and S. T. Liu, *Organometallics*, 2017, **36**, 3110-3116; (g) N. M. Patil, T. Sasaki, and B. M. Bhanage, *ACS Sustainable Chem. Eng.*, 2016, **4**, 429-436; (h) J. Spencer, R. P. Rathnam, H. Patel, N. Anjum, *Tetrahedron*, 2008, **64**, 10195-10200; (i) S. Chandrashekharappa, K. N. Venugopala, R. Venugopala and B. Odhav, *Asian J. Chem.*, 2016, **28**, 2177-2180; (j) X. Wang and Y. Li, *J. Mol. Catal. A: Chem.*, 2016, **420**, 56-65, (k) H. Gao, Z. Zhou, D.-Hyun. Kwon, J. Coombs, S. Jones, N. E. Behnke,D. H. Ess and L. Kürti, *Nat. Chem.*, 2017, **9**, 681-688.