Supporting information

Supported palladium catalyzed aminocarbonylation of aryl iodides employing bench-stable CO and NH_3 surrogates

Shaifali, [a], [b] Sheetal, [a], [b], Rohit Bains, [a], [b] Ajay Kumar, [a], [b] Shankar Ram, [a], [b] Pralay Das*[a], [b]

[a]Natural Product Chemistry & Process Development Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur 176061, HP, India

[b]Academy of Scientific & Innovative Research, New Delhi 110025, India.

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A. General method and materials

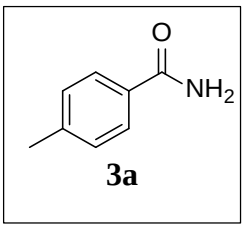
High quality reagents were purchased from Sigma Aldrich, Tech Chem Solutions (TCI, India), Loba Chemie, alpha aesar and Sd Fine-chem Ltd. Thin layer chromatography was performed using pre-coated silica gel plates $60F_{254}$ (Merck) in UV light detector. ESI-MS spectra were determined using a Waters micro mass Q-TOF Ultima Spectrometer. Mass spectra were recorded on electrospray ionization (ESI)quadrupole time of flight (Q-TOF) mass spectrometer. Melting points were recorded using LAB INDIA MR-VIS^{+}. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 600 spectrometer operating at 600 MHz (^{1}H) and 150 MHz (^{13}C) and Bruker Avance 300 spectrometer operating at 300 MHz (^{1}H) and 75 MHz (^{13}C). Spectra were recorded at 25 ºC in DMSO-*d6* [residual DMSO (δ_H 2.50 and 3.42 ppm) and DMSO (δ_C 39.52 ppm)] 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; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad singlet.

B. Synthesis of (1H-imidazol-1-yl) (p-tolyl)methanone (**5**)

The benzoyl imidazole was prepared by following the literature.[1] In a 25 mL round bottom flask, imidazole (2 mmol) was dissolved in anhydrous CH_2Cl_2 (2 mL). Further, benzoyl chloride (1mmol) was in added in solution of imidazole slowly and dropwise, resulting in precipitation of imidazolium chloride. The resultant mixture was allowed to stir for 2-3 h at room temperature. The reaction mixture was filtered, washed with cold water and extracted using dichloromethane as solvent. The organic layer was dried over sodium sulphate and solvent was evaporated under reduced pressure yielding crude benzoyl imidazole (**5**) as viscous oil. The crude was crystallized with the help of hexanes. The formation of the product was confirmed with the help of ESI-MS $[M+H]^+$ for $C_{11}H_{11}N_2O^+$ 187.1066 and found 187.0864.

C. Typical Experimental procedure

1. 4-methylbenzamide [2]



3a

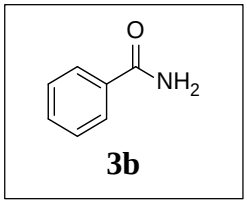
In a double vial system (inner vial is of 2mL and another which is outer is of 5mL), 4-methyl iodobenzene (0.229 mmol, 50 mg), ammonium carbamate (0.917 mmol, 69.7mg), Pd@PS (0.0069 mmol, 70 mg), TEA (0.573 mmol, 79.7 µl), imidazole (0.172 mmol, 13 mg) and DMF (1.5 mL) were added in inner vial (2 mL) while the outer vial was charged with oxalic acid (1.37 mmol, 123.8 mg) and DMF (0.3 mL). After completion of the addition, the inner vial containing contents was placed carefully inside outer vial (5 mL) having oxalic acid. Further, the 5 mL reaction vessel tighten with the solid PTFE faced solid cap and Teflon tape. The system was further stirred in oil bath heated at 130 ^{o}C for the required time. The reaction progress was monitored by TLC and after the completion of the reaction, the inner vial was removed. The contents of the inner vial in a separatory funnel. Further, water was added in the reaction mixture and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was further purified by silica gel column chromatography using hexane:ethyl acetate (60:40) as elutent, afforded **3a** as white solid (23 mg, 75%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 2.34(s, 3H), 2.34 (s, 3H), 7.245 (d, *J* = 7.98 Hz, 2H), 7.28 (brs, 1H), 7.775 (d, *J* = 8.1 Hz, 2H), 7.90 (brs, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 21.40, 127.90, 129.19, 131.94, 141.51, 168.25.

The expected ESI-MS, $[M+H]^+$ for $C_8H_{10}NO^+$ was 136.0757 and observed is 136.0755.

2. benzamide [2]



3b

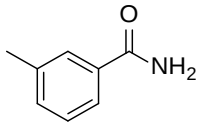
Prepared as general procedure described for **3a** from iodobenzene (0.245 mmol, 50 mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (35:65) as elutents **3b** as white solid (19 mg, 65%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.37 (brs, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.51-7.53 (m, 1H), 7.875 (d, *J* = 15, 7.32 Hz, 2H), 7.98 (brs, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 127.90, 128.66, 131.67, 134.71, 168.34

The calculated ESI-MS+H^+ for $C_7H_8NO^+$122.06 and found 122.0602.

3-methylbenzamide[2]



3c

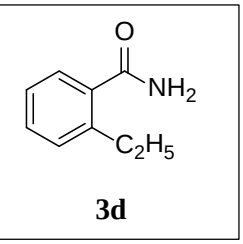
Prepared as general procedure described for **3a** from 3-iodotoluene (0.229 mmol, 50 mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (35:65) as elutents **3c** as white solid (16 mg, 52%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 2.35 (s, 3H), 7.32 (d, *J* = 4.5 Hz, 3H), 7.65-7.67 (m, 1H), 7.70 (s, 1H), 7.93 (brs, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 21.41, 125.04, 128.52, 128.54, 132.22, 134.71, 137.88, 168.48.

The expected ESI-MS, $[M+H]^+$ for $C_8H_{10}NO^+$ was 136.0757 and observed is 136.0755

2-ethylbenzamide[3]



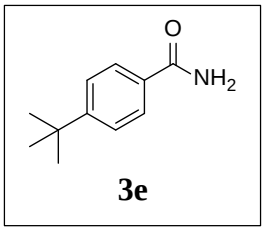
3d

Prepared as general procedure described for **3a** from 1-ethyl 2-iodobenzne (0.215 mmol, 50 mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (35:65) as elutents **3d** as white solid (14 mg, 45%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 1.14-1.16 (t, *J* = 7.5, 15Hz, 3H), 2.71-2.75 (q, *J* = 7.4 Hz, 2H), 7.21-7.22 (m, 1H), 7.25 (d, *J* = 7.5 Hz), 7.30-7.35 (m, 3H), 7.73 (brs, 1H).

The expected ESI-MS $[M+H]^+$ for $C_9H_{12}NO^+$ is 150.0913 and observed is 150.0912.

4-(*tert*-butyl)benzamide[2]



3e

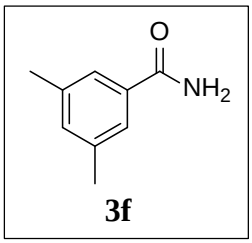
Prepared as general procedure described for **3a** from 4-*tert*-butyliodobenzene (0.192 mmol, 50 mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (40:60) as elutents **3e** as white solid (18 mg, 53%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 1.29 (s, 9H), 7.29 (brs, 1H), 7.45-7.46 (m, 2H), 7.79-7.81 (m, 2H), 7.91 (brs, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 31.42, 35.05, 125.42, 127.78, 132.00, 154.41, 168.26.

The calculated ESI-MS$[M+H]^+$ for $C_{11}H_{16}NO^+$ 178.1226 and found 178.1223.

3, 5-dimethylbenzamide[2]



3f

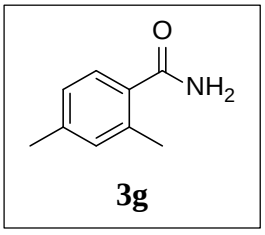
Prepared as general procedure described for **3a** from 1-iodo 3, 5 dimethylbenzene (0.215 mmol, 50 mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (40:60) as elutents **3d** as white solid (17 mg, 54%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 2.30 (s, 6H), 7.14 (s, 1H), 7.23 (brs, 1H), 7.48 (s, 2H), 7.85 (brs, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 21.31, 125.71, 132.89, 134.75, 137.70, 168.59.

The calculated ESI-MS $[M+H]^+$ for $C_9H_{12}NO^+$ 150.0913 and found 150.0910

2,4-dimethylbenzamide[2]



3g

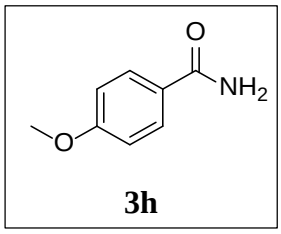
Prepared as general procedure described for **3a** from 1-iodo 3, 5 dimethylbenzene (0.215 mmol, 50 mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (40:60) as elutents **3g** as white solid (20 mg, 63%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 2.28 (s, 3H), 2.34 (s, 3H), 7.00-7.03 (m, 2H), 7.26-7.28 (m, 2H), 7.62 (s, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 21.02, 21.20, 126.33, 127.72, 131.62, 134.43, 135.83, 139.15, 171.46.

The calculated ESI-MS $[M+H]^+$ for $C_9H_{12}NO^+$ 150.0913 and found 150.0910.

4-methoxybenzamide[2]



3h

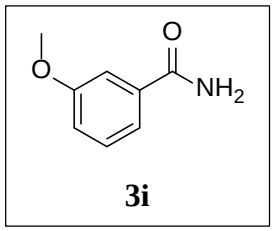
Prepared as general procedure described for **3a** from 4 -iodoanisole (0.213 mmol, 50 mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (1:1) as elutents **3h** as white solid (20 mg, 61%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 3.80 (s, 3H), 6.96-6.98 (m, 2H), 7.18 (brs, 1H), 7.84-7.86 (m, 3H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 55.77, 113.83, 126.98, 129.80, 162.04, 167.88.

The expected ESI-$[MS+H]^+$ $C_8H_{10}NO_2^+$ for 152.0706 is and observed is 152.0706.

3-methoxybenzamide



3i

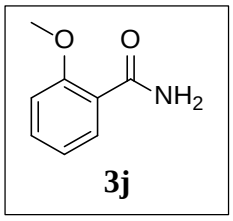
Prepared as general procedure described for **3a** from 3 -iodoanisole (0.213 mmol, 50 mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (1:1) as elutents **3i** as white solid (25mg, 77%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 3.79 (s, 3H), 7.07-7.09 (m, 1H), 7.34-7.37 (m, 2H), 7.42-7.43 (m, 1H), 7.45-7.46 (m, 1H), 7.96 (brs, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 55.68, 113.10,117.52, 120.15, 129.78, 136.19, 159.60, 168.10.

The calculated ESI-$[MS+H]^+$ $C_8H_{10}NO_2^+$ for 152.0706 and found 152.0707.

2-methoxybenzamide[3]



3j

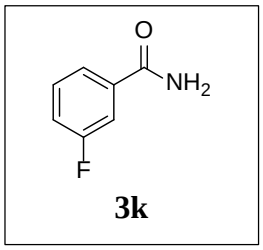
Prepared as general procedure described for **3a** from 2 -iodoanisole (0.213 mmol, 50 mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (1:1) as elutents **3j** as white solid (21mg, 65%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 3.89 (s, 3H), 7.02 (t, *J* = 7.6 Hz, 1H), 7.125 (d, *J* = 8.2 Hz, 1H), 7.46-7.48 (m, 1H), 7.52 (brs, 1H), 7.64 (brs, 1H), 7.80-7.81 (m, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 56.26, 112.43, 120.85, 123.17, 127.95, 131.91, 157.69, 167.77

The calculated ESI-$[MS+H]^+$ $C_8H_{10}NO_2^+$ for 152.0706 and found 152.0703.

3-fluorobenzamide[3]



3k

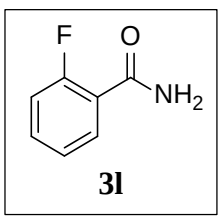
Prepared as general procedure described for **3a** from 3-Fluoroiodobenzene (0.225 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (60:40) as elutents **3k** as crystalline solid (16mg, 51%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.37-7.38 (m, 1H), 7.49-7.52 (m, 2H), 7.64-7.67 (m, 1H), 7.72-7.73 (m, 1H), 8.05 (brs, 1H)

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 119.34-119.49 (d, *J*=22.6 Hz), 123.28 (m), 128.82, 132.56-135.61 (m), 141.92-141.96 (d, *J*=6.0 Hz), 166.38-167.99 (d, *J*=241 Hz),171.71-171.72 (d, *J*=1.5 Hz).

The calculated ESI-$[M+H]^+$ for $C_7H_7FNO^+$ is 140.0506 and found 140.0505.

2-fluorobenzamide



3l

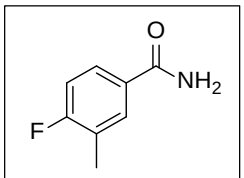
Prepared as general procedure described for **3a** from 2-Fluoroiodobenzene (0.225 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (60:40) as elutents **3l** as crystalline solid (26mg, 82%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.25-7.28 (m, 2H), 7.51-7.53 (m, 1H), 7.64-7.67 (m, 2H), 7.71 (brs, 1H)

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 116.55 (d, *J* = 22.4 Hz), 124.27-124.36 (d, *J* = 14.2 Hz), 124.85-124.88 (d, *J* = 3.4 Hz), 130.68-130.70 (d, *J* = 2.9 Hz), 132.90-132.96 (d, *J* = 8.6 Hz), 130.68-130.70 (d, *J* = 29 Hz), 159.75 (d, *J* = 3.4 Hz), 165.72.

The calculated ESI-$[M+H]^+$ for $C_7H_7FNO^+$ 140.0506 and found 140.0506.

3-fluoro-4-methylbenzamide



3m

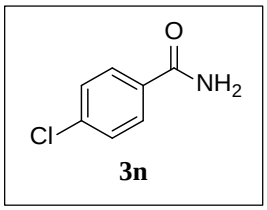
Prepared as general procedure described for **3a** from 4-Fluoro-3-iodotoluene (0.212 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (60:40) as elutents **3m** as white solid (18mg, 56%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 2.27 (s, 3H), 7.18-7.21 (t, *J* = 9.0 Hz, 1H), 7.30 (brs, 1H), 7.73-7.76 (m, 1H), 7.82-7.83 (m, 1H), 7.91 (s, 1H)

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 14.62, 115.10-115.25 (d *J* = 22.4 Hz), 124.47-124.58 (d, *J* = 17.5 Hz), 127.76-127.82 (d, *J* = 8.9 Hz), 130.84-130.86 (d, *J* = 3.8 Hz), 131.75 -131.79 (d, *J*=5.7 Hz), 162.06-163.70 (d, *J* = 246 Hz), 167.40.

The calculated ESI-$[MS+H]^+$ for $C_8H_9FNO^+$ 154.0663 and found 154.0663.

4-chlorobenzamide[2]



3n

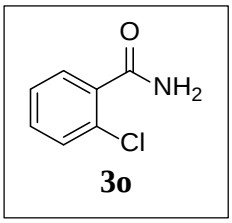
Prepared as general procedure described for **3a** from 1-Chloro-4-iodobenzene (0.210 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (60:40) as elutents **3n** as white solid (25mg, 76%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.46 (brs, 1H), 7.51-7.53 (m, 2H), 7.88-7.89(m, 2H), 8.04 (brs, 1H)

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 128.96, 129.87, 133.51, 136.54, 167.28.

The calculated ESI-$[MS+H]^+$ for $C_7H_7ClNO^+$ 156.0211 and found 156.0210.

2-chlorobenzamide



3o

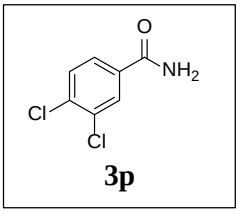
Prepared as general procedure described for **3a** from 1-Chloro-2-iodobenzene (0.210 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (40:60) as elutents **3o** as crystalline solid (24mg, 74%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.36-7.39 (m, 1H), 7.41-7.45 (m, 2H), 7.47-7.48 (m, 1H), 7.55 (brs, 1H), 7.84 (brs, 1H)

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 127.48, 129.11, 130.06, 130.07, 131.02, 137.62, 168.64.

The expected ESI-$[MS+H]^+$ for $C_7H_7ClNO^+$ 156.0211 and found 156.0209

3,4-dichlorobenzamide



3p

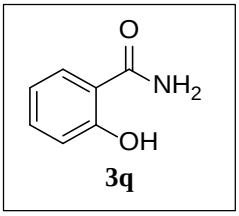
Prepared as general procedure described for **3a** from 3,4-Dichloroiodobenzene (0.183mmol, 50 mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (40:60) as elutents **3p** as white solid (17mg, 49%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.58 (brs, 1H), 7.74-7.75 (d, J=8.3 Hz, 1H), 7.84-7.85 (d, *J*=8.28 Hz, 1H), 8.10-8.12 (m, 2H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 128.21, 19.93, 131.11, 131.67, 134.52, 135.18, 166.63.

The expected ESI-$[MS+H]^+$ for $C_7H_6Cl_2NO^+$ is 189.9821 and observed is 189.9821

2-hydroxybenzamide



3q

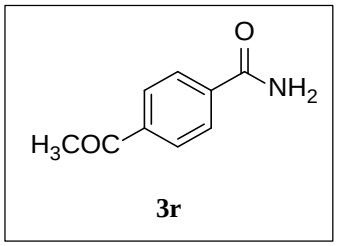
Prepared as general procedure described for **3a** from 2-iodophenol (0.227 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (3:1) as elutents **3q** as brownish solid (25mg, 80%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 6.84-6.88 (m, 2H), 7.38-7.41 (m, 1H), 7.83-7.84 (m, 1H), 7.87 (brs, 1H), 8.38 (brs, 1H), 13.02 (brs, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 114.82, 117.87, 118.82, 128.55, 134.55, 161.38, 172.54.

The calculated ESI-MS[M+H]$^{+}$ for $C_7H_8NO_2^{+}$ 138.055 and found 138.0551.

4-acetylbenzamide[2]



3r

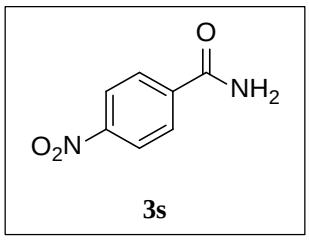
Prepared as general procedure described for **3a** from 4'-iodoacetophenone (0.203 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (40:60) as elutents **3d** as white solid (21mg, 65%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 2.62 (s, 3H), 7.59 (brs, 1H), 7.98-7.99 (m, 2H), 8.01-8.02 (m, 2H), 8.16 (brs, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 27.45, 128.22, 128.57, 138.55, 139.09, 167.54, 198.23

The calculated ESI-MS+H^{+} for $C_9H_{10}NO_2^{+}$ 164.0706 and found 164.706.

4-nitrobenzamide[2]



3s

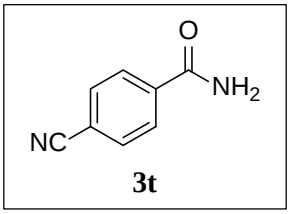
Prepared as general procedure described for **3a** from 1-Iodo-4-nitrobenzene (0.200 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (40:60) as elutents **3s** as white solid (19mg, 57%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.72 (brs, 1H), 8.09-8.10 (d, *J*=8.76 Hz, 2H), 8.27 (brs, 1H), 8.30-8.31 (d, *J*=8.76 Hz, 2H)

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 123.94, 129.38, 140.44, 149.52, 166.68

The calculated ESI-[MS+H]$^+$ for $C_7H_7N_2O_3^+$ 167.0451 and found 169.0458.

4-cyanobenzamide[2]



3t

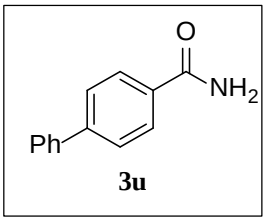
Prepared as general procedure described for **3a** from 4-Iodobenzonitrile (0.218 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (40:60) as elutents **3t** as white solid (23mg, 72%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.64 (brs, 1H), 7.94 (d, *J* = 8.28 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 8.19 (brs, 1H)

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 114.11, 118.82, 128.72, 132.82, 138.79, 166.91.

The calculated ESI-[MS+H]$^+$ for $C_8H_7N_2O^+$ 147.0553 and found 147.0459.

[1,1'-biphenyl]-4-carboxamide



3u

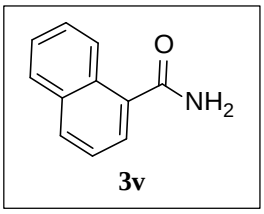
Prepared as general procedure described for **3a** from 4-iodobiphenyl (0.178 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (60:40) as elutents **3u** as white solid (21mg, 60%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.38-7.42 (m, 2H), 7.48-7.51 (t, *J*=7.56, 15.4 Hz, 2H), 7.72-7.76 (m, 4H), 7.97 (d, *J*=8.3 Hz, 2H), 8.02 (brs, 1H)

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 126.91, 127.34, 128.48, 128.63, 129.48, 133.57, 139.71, 143.23, 168.02

The calculated ESI-MS [M+H]$^+$ for $C_{13}H_{12}NO^+$ 198.0913 and found 198.0912.

1-naphthamide[2]



3v

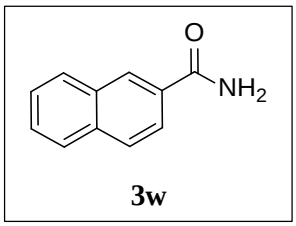
Prepared as general procedure described for **3a** from 1-Iodonaphthalene (0.196 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (40:60) as elutents **3v** as white solid (18mg, 55%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.55-7.59 (m, 4H), 7.64-7.65 (m, 1H), 7.96-8.01 (m, 3H), 8.31-8.32 (m, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 125.42, 126.61, 127.09, 128.56, 128.75, 130.15, 130.19, 130.35, 133.68, 135.14, 171.07.

The calculated ESI-MS $[M+H]^+$ for $C_{11}H_{10}NO^+$ is 172.0757 and found 172.0754.

2-naphthamide[2]



3w

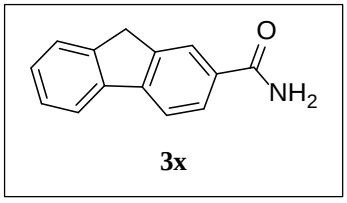
Prepared as general procedure described for **3a** from 2-Iodonaphthalene (0.196 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (40:60) as elutents **3w** as white solid (15mg, 45%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.43 (brs, 1H), 7.57-7.62 (m, 2H), 7.97-8.01 (m, 4H), 8.11 (brs, 1H), 8.49 (s, 1H)

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 124.86, 127.099, 128.01, 128.05, 128.21, 128.25, 129.31, 132.14, 132.63, 134.64, 168.42.

The calculated ESI-MS $[M+H]^+$ for $C_{11}H_{10}NO^+$ 172.0757 and found 172.0756.

9H-fluorene-2-carboxamide



3x

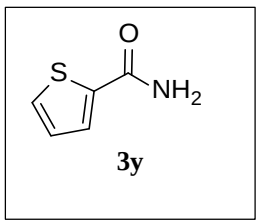
Prepared as general procedure described for **3a** from **2-Iodofluorene** (0.171 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (60:40) as elutents **3x** as white solid (15mg, 42%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 3.98 (s, 2H), 7.20 (brs, 1H), 7.36-7.38(t, *J* = 7.3, 14.7 Hz, 1H), 7.41-7.43 (t, *J* = 7.38, 14.8 Hz, 1H), 7.63 (d, *J* = 7.38 Hz, 1H), 7.93-7.97 (m, 4H), 8.11 (s, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 120.05, 121.19, 124.82, 125.76, 126.96, 127.39, 128.01, 133.05, 140.74, 143.31, 144.33, 144.39, 168.47.

The calculated ESI-$[M+H]^+$ for $C_{14}H_{12}NO^+$ 210.0913 and found 210.0913.

thiophene-2-carboxamide[3]



3y

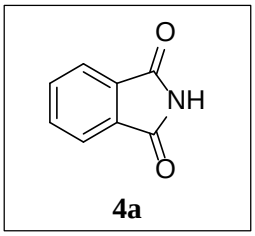
Prepared as general procedure described for **3a** from 2-Iodothiophene (0.238 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (60:40) as elutents **3y** as white solid (20mg, 66%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.12-7.139 (t, *J* = 4.0 Hz, 8.6 Hz, 1H), 7.36 (brs, 1H), 7.73-7.74 (m, 2H), 7.95 (brs, 1H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 128.33, 129.11, 131.42, 140.79, 163.33.

The calculated ESI-$[M+H]^+$ for $C_5H_6NOS^+$ 128.0165 and found 128.0159.

isoindoline-1,3-dione[4]



4a

Prepared as general procedure described for **3a** from 1,2-Diiodobenzene (0.152 mmol, 50mg) or 2-Bromoiodobenzene (0.176 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (60:40) as elutents **4a** as white solid (20mg, 66%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.83 (s,1H), 11.35 (brs, 1H)

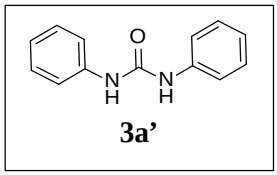
^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 123.41, 133.06, 134.80,169.71.

Prepared as general procedure described for **3a** from 2-Iodobenzoic acid (0.201 mmol, 50mg) or Methyl 2-iodobenzoate (0.190 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (60:40) as elutents **4a** as white solid (20mg, 66%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 7.82 (s,1H), 11.35 (brs, 1H)

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 123.40, 133.06, 134.79,169.71.

1,3-diphenylurea



3a'

Prepared as general procedure described for **3a** from 2-Iodoaniline (0.229 mmol, 50mg), gave after purification with silica gel column chromatography in Hexane: ethyl acetate (40:60) as elutents **3a'** as white solid (20mg, 80%).

^{1}H (600MHz, DMSO-*d6*), (δ ppm) 6.95-6.98 (m, 2H), 7.26-7.29 (m, 4H), 7.44-7.45 (m, 4H), 8.65 (s, 2H).

^{13}C (150 MHz, DMSO-*d6*), δ (ppm) 118.64, 122.27, 129.45, 140.15, 152.99.

The calculated ESI-$[M+H]^+$ for $C_5H_6NOS^+$ 213.1022 and found 213.1020.

D. References:

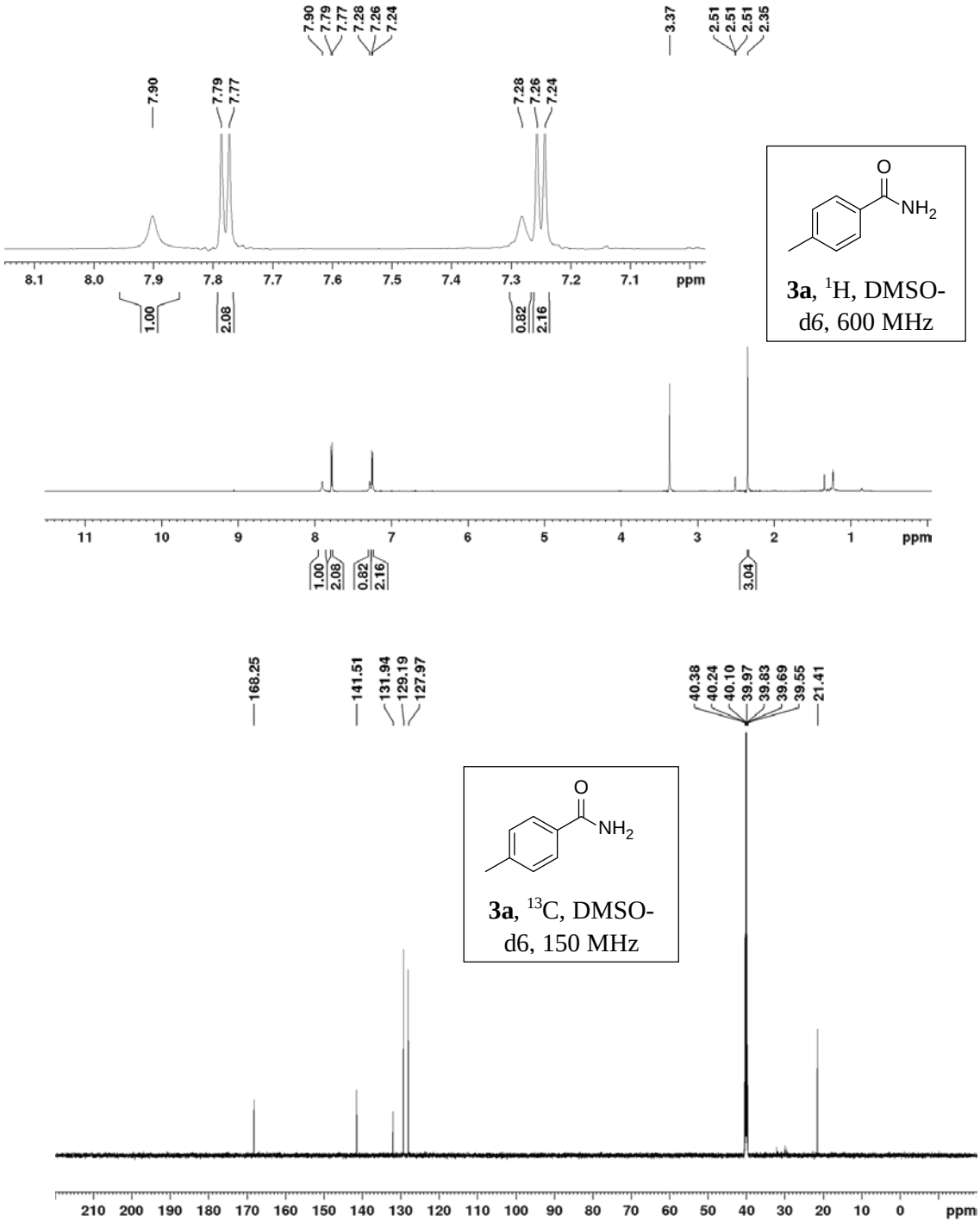
1. S. Zaramella, R. Strömberg, and E. Yeheskiely, *Eur. J. Org. Chem.* **2002**, 2633-2639.

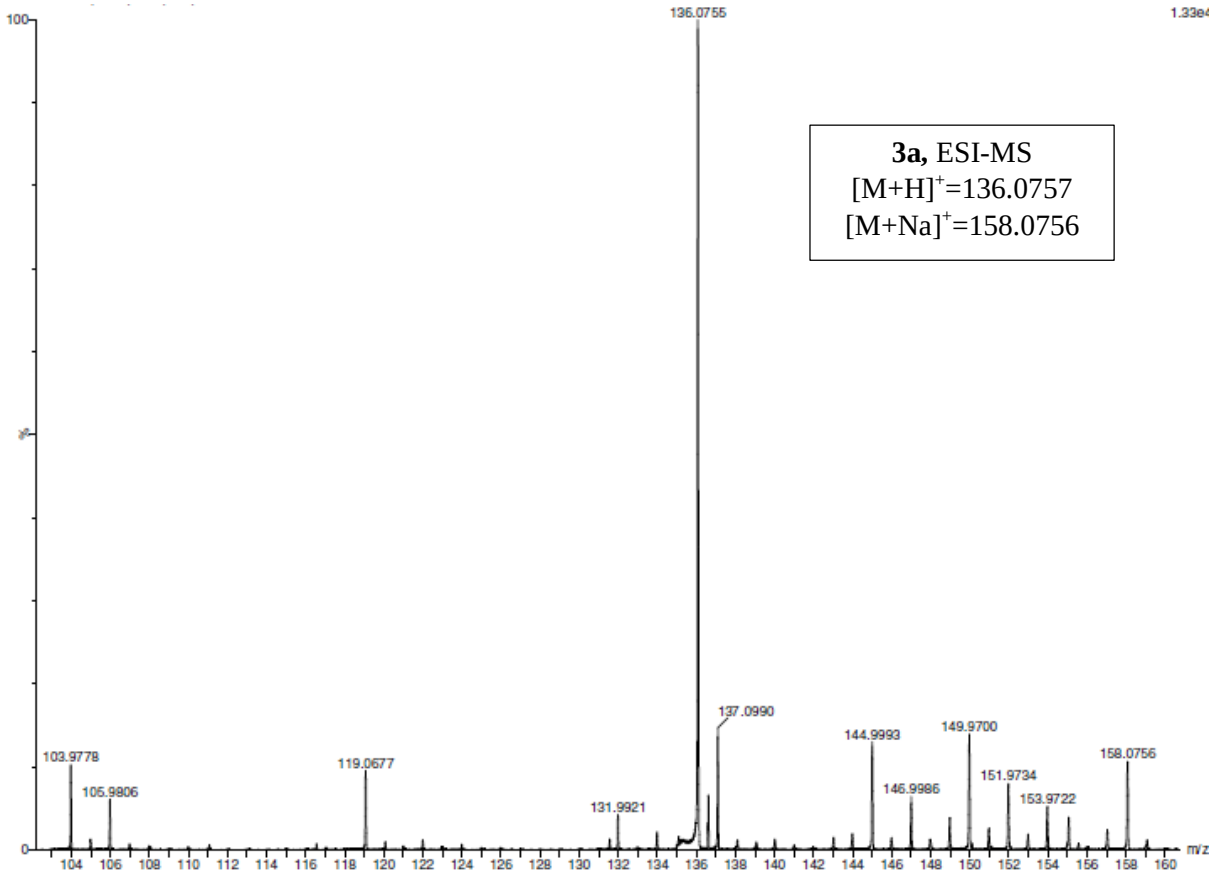
2. X. Qi, H.-J. Ai, C.-X. Cai, J.-B. Peng, J. Ying, X.-F. Wu, *Eur. J. Org. Chem*. **2017**, 7222–7225.

3. R. S. Mane, B. M. Bhanage, *RSC Adv*., **2015**, *5*, 76122.

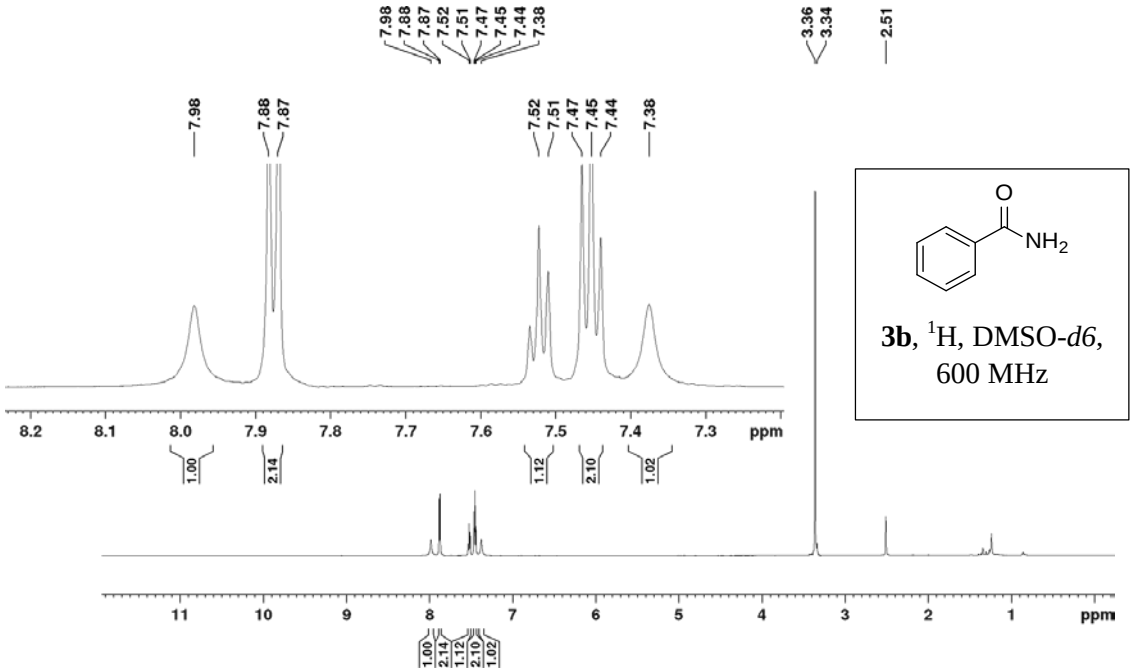
4. D. N. Sawant, Y. S. Wagh, K. D. Bhatte, B. M. Bhanage, *Eur. J. Org. Chem.* **2011**, 6719–6724.

(E) Copies of ^{1}H, ^{13}C and ESI-MS

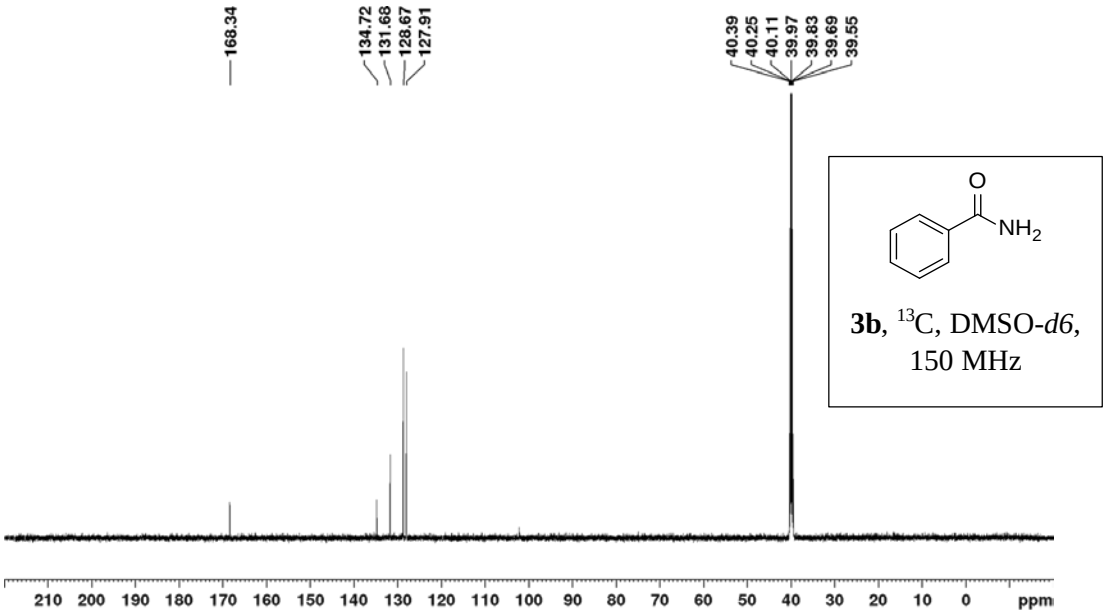




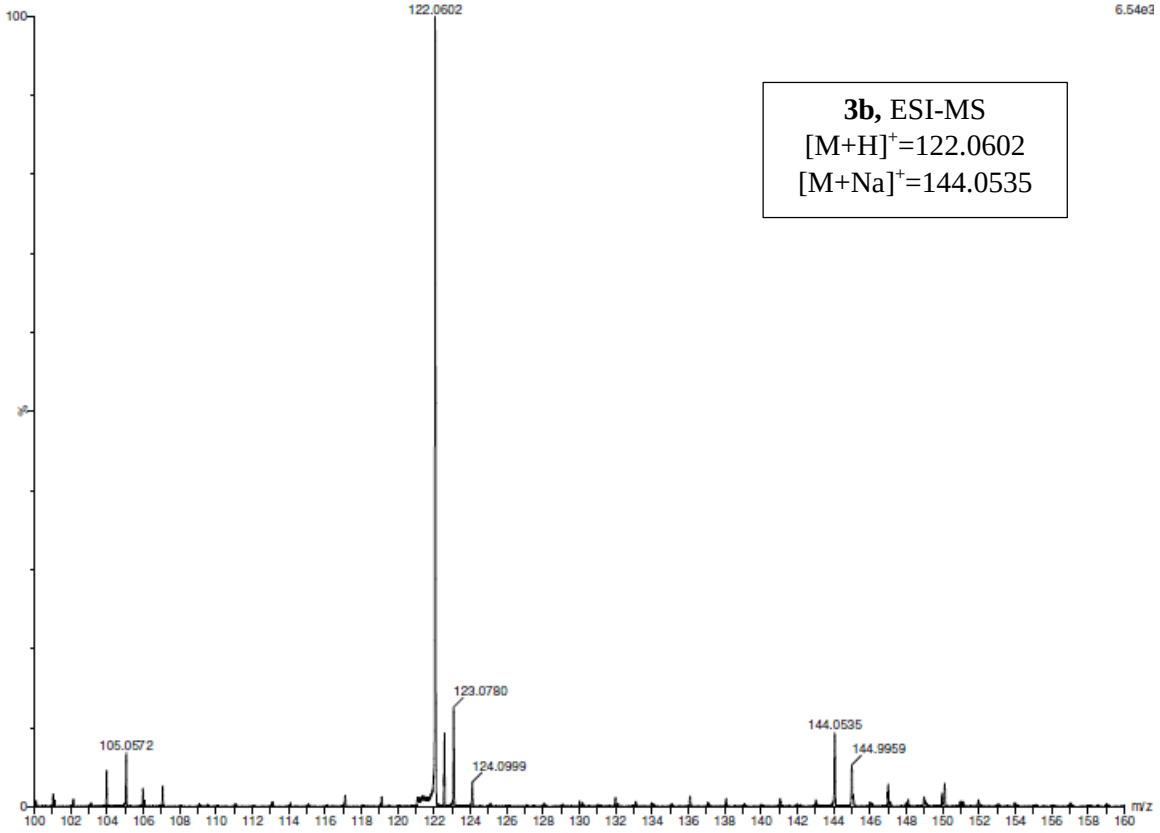
3a, ESI-MS
$[M+H]^+$=136.0757
$[M+Na]^+$=158.0756



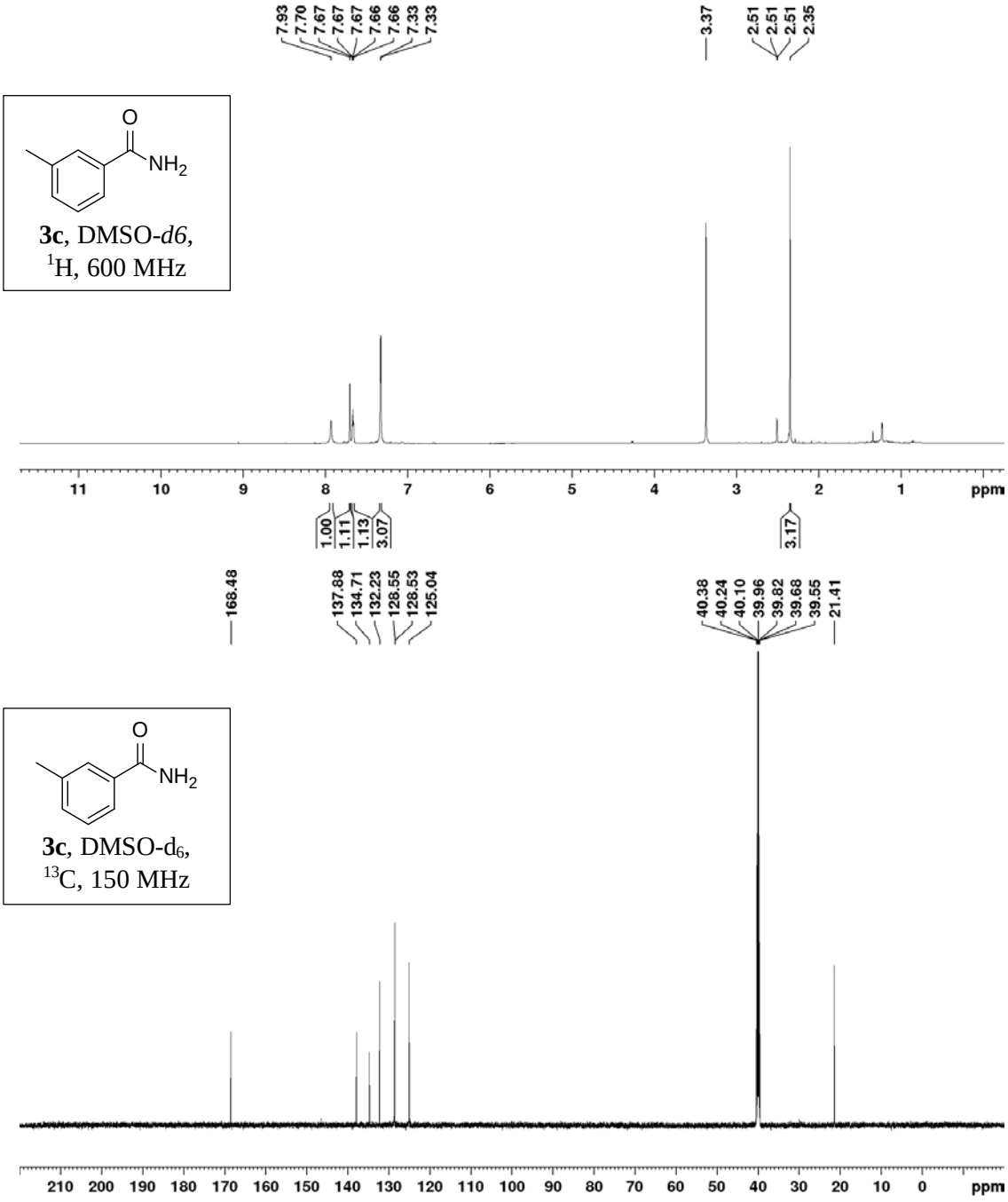
3b, ^{1}H, DMSO-*d6*, 600 MHz

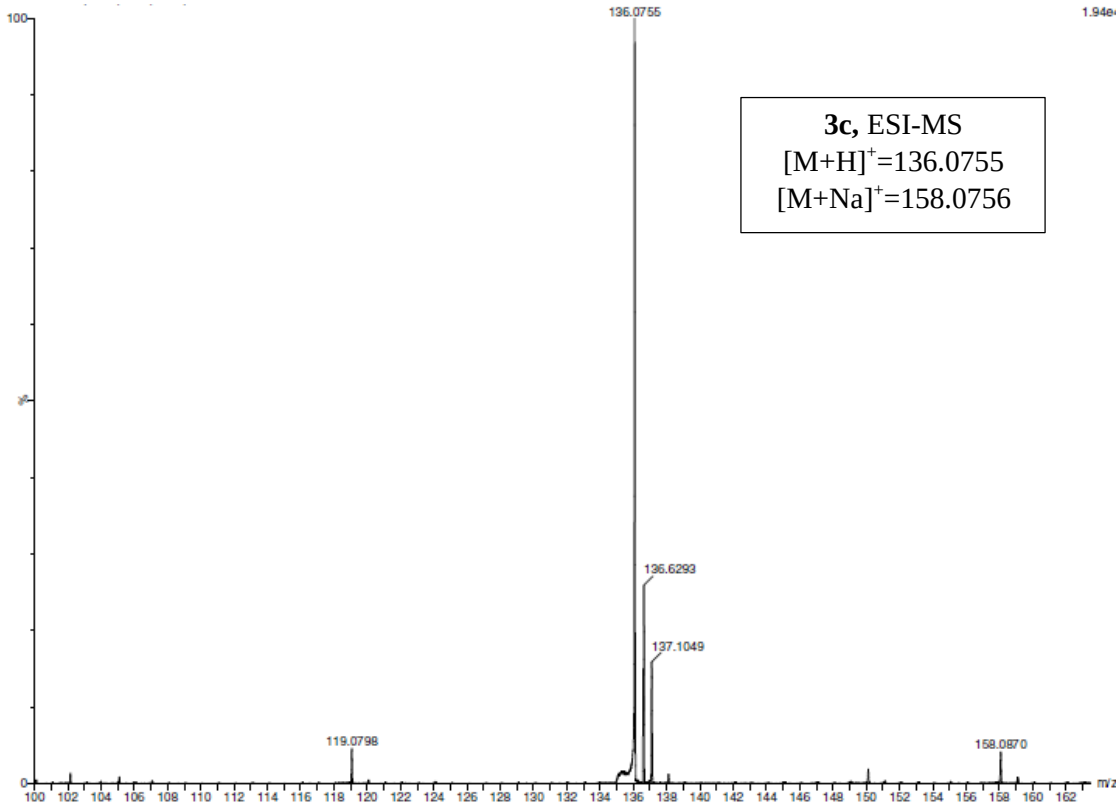


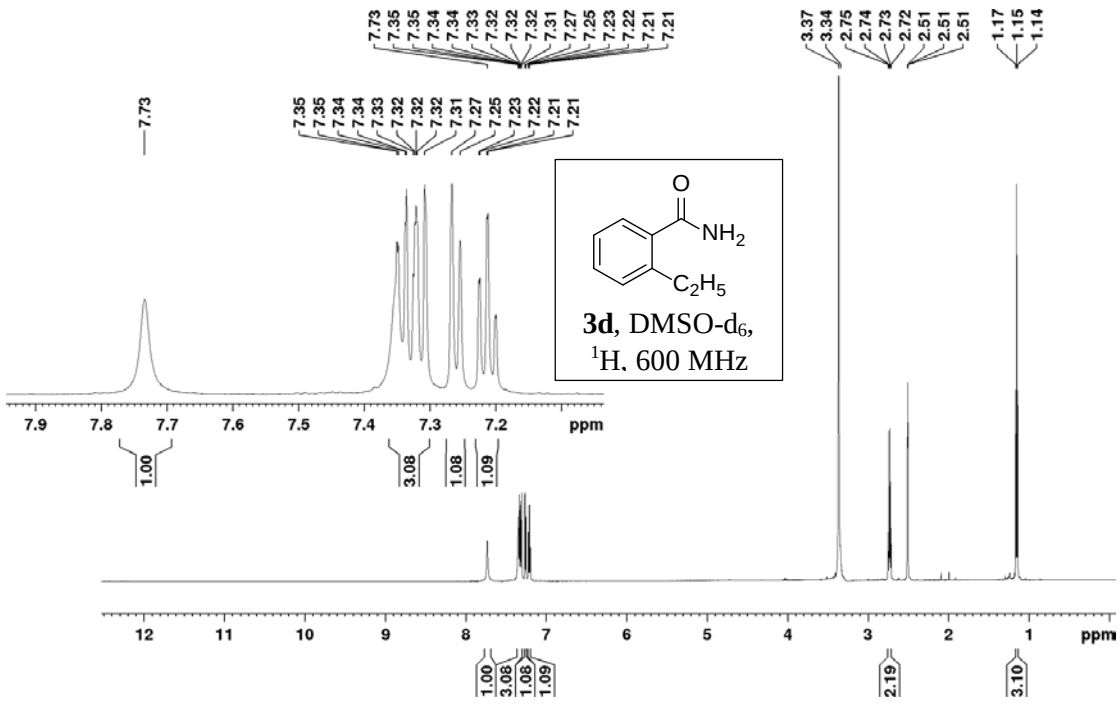
3b, ^{13}C, DMSO-*d6*, 150 MHz

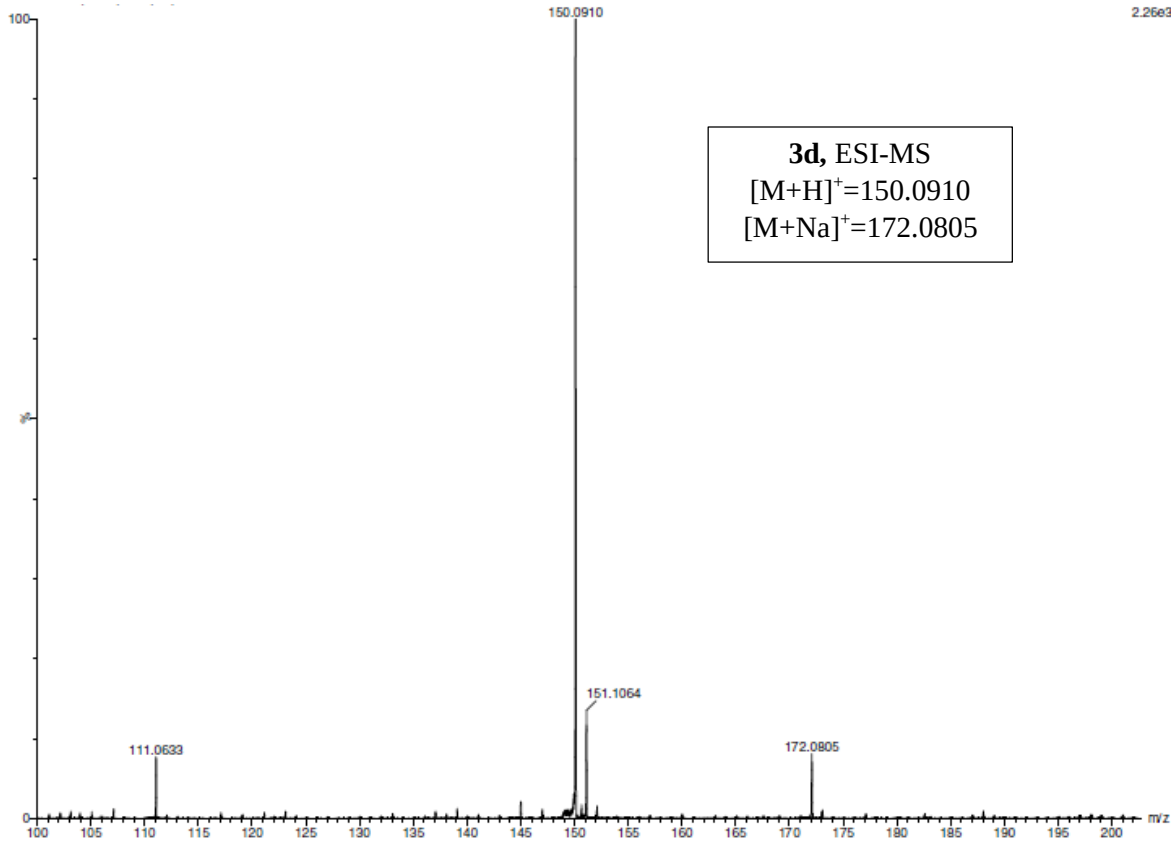


3b, ESI-MS
$[M+H]^+$=122.0602
$[M+Na]^+$=144.0535

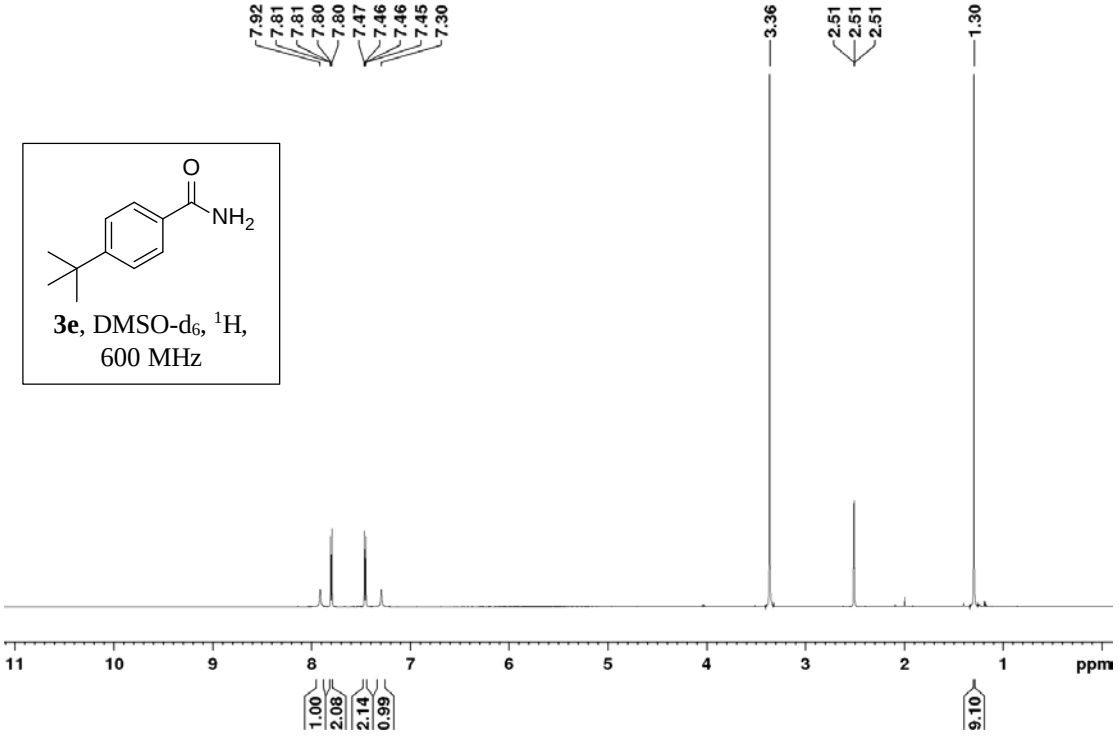

7.93
7.70
7.67
7.67
7.67
7.66
7.66
7.33
7.33
3.37
2.51
2.51
2.51
2.35
O
NH2
3c, DMSO-d6,
1H, 600 MHz
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.11
1.13
3.07
3.17
168.48
137.88
134.71
132.23
128.55
128.53
125.04
40.38
40.24
40.10
39.96
39.82
39.68
39.55
21.41
O
NH2
3c, DMSO-d6,
13C, 150 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


136.0755
136.6293
137.1049
119.0798
158.0870
3c, ESI-MS
$[M+H]^+$=136.0755
$[M+Na]^+$=158.0756

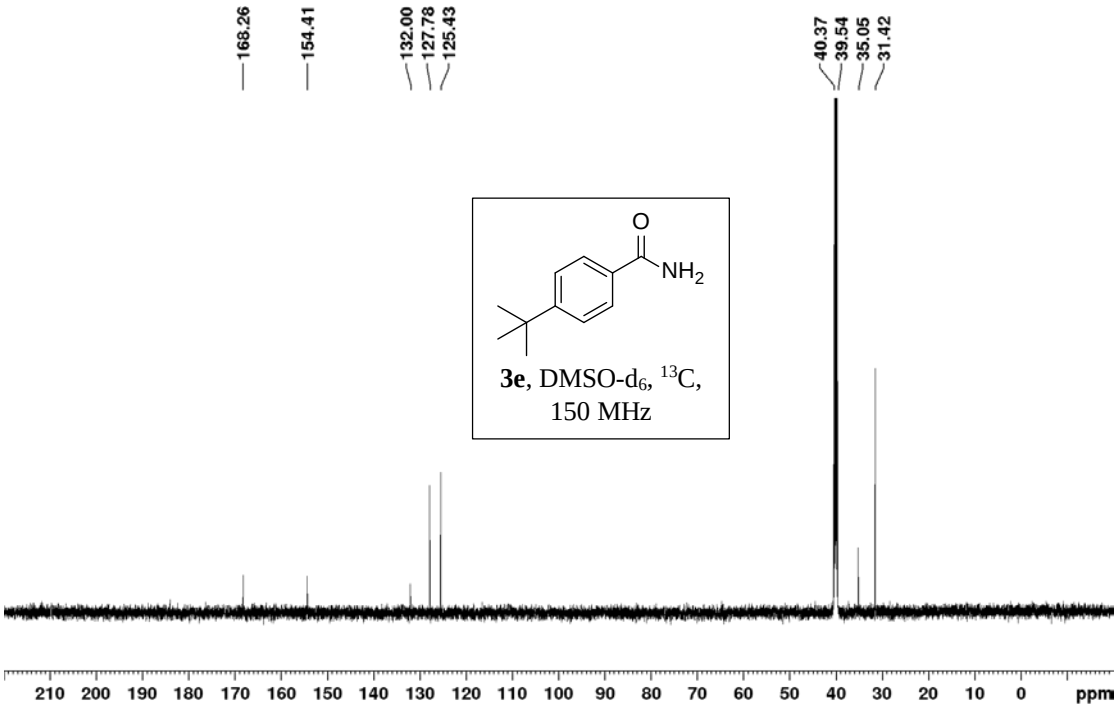

3d, DMSO-d_6,
^{1}H, 600 MHz
ppm



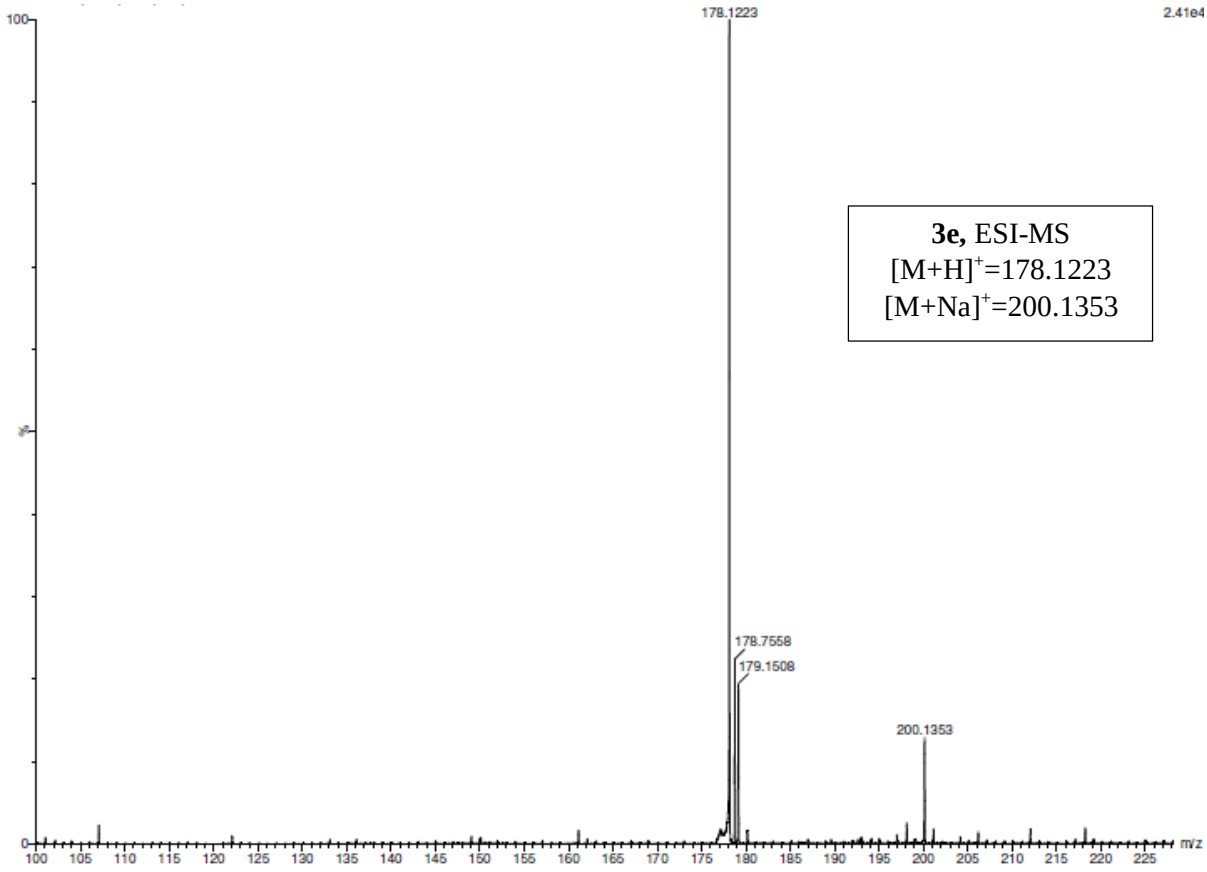
3d, ESI-MS
$[M+H]^+$=150.0910
$[M+Na]^+$=172.0805



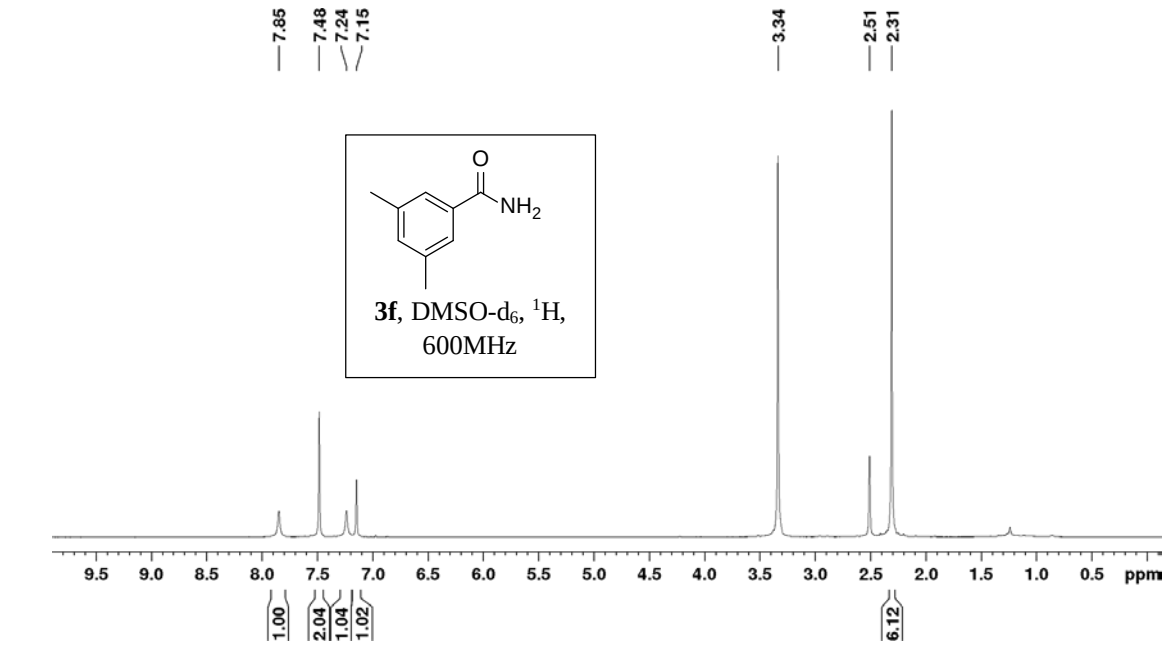
3e, DMSO-d_6, ^1H, 600 MHz



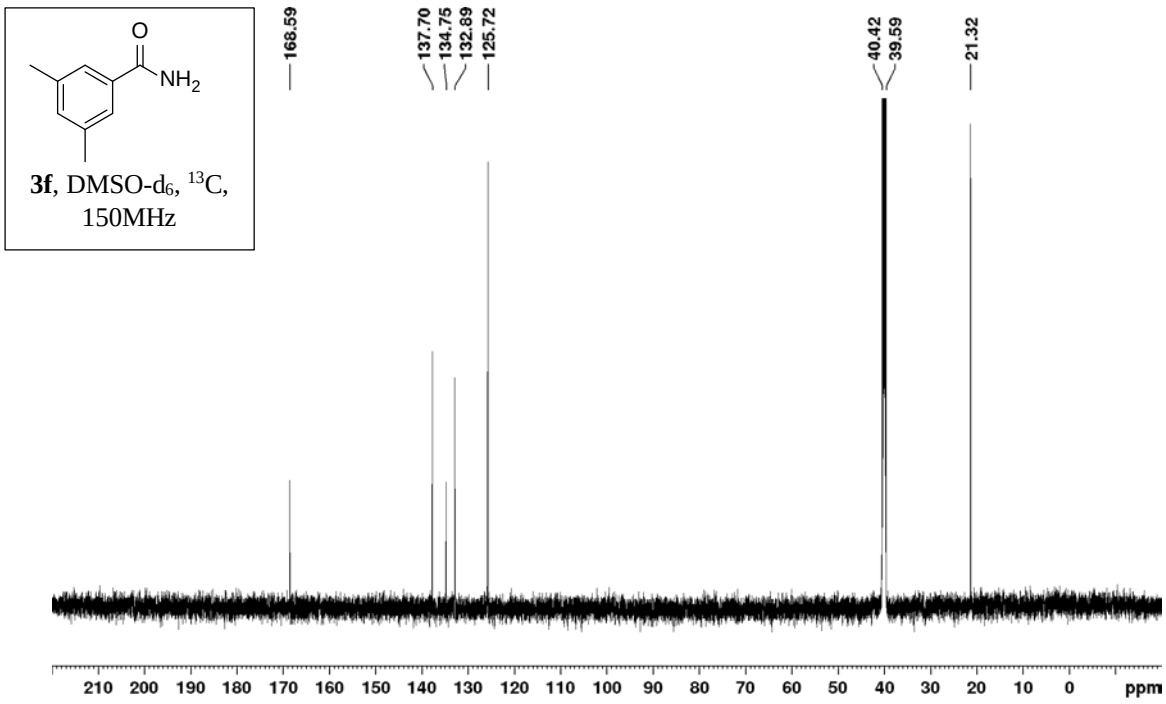
3e, DMSO-d_6, ^{13}C, 150 MHz



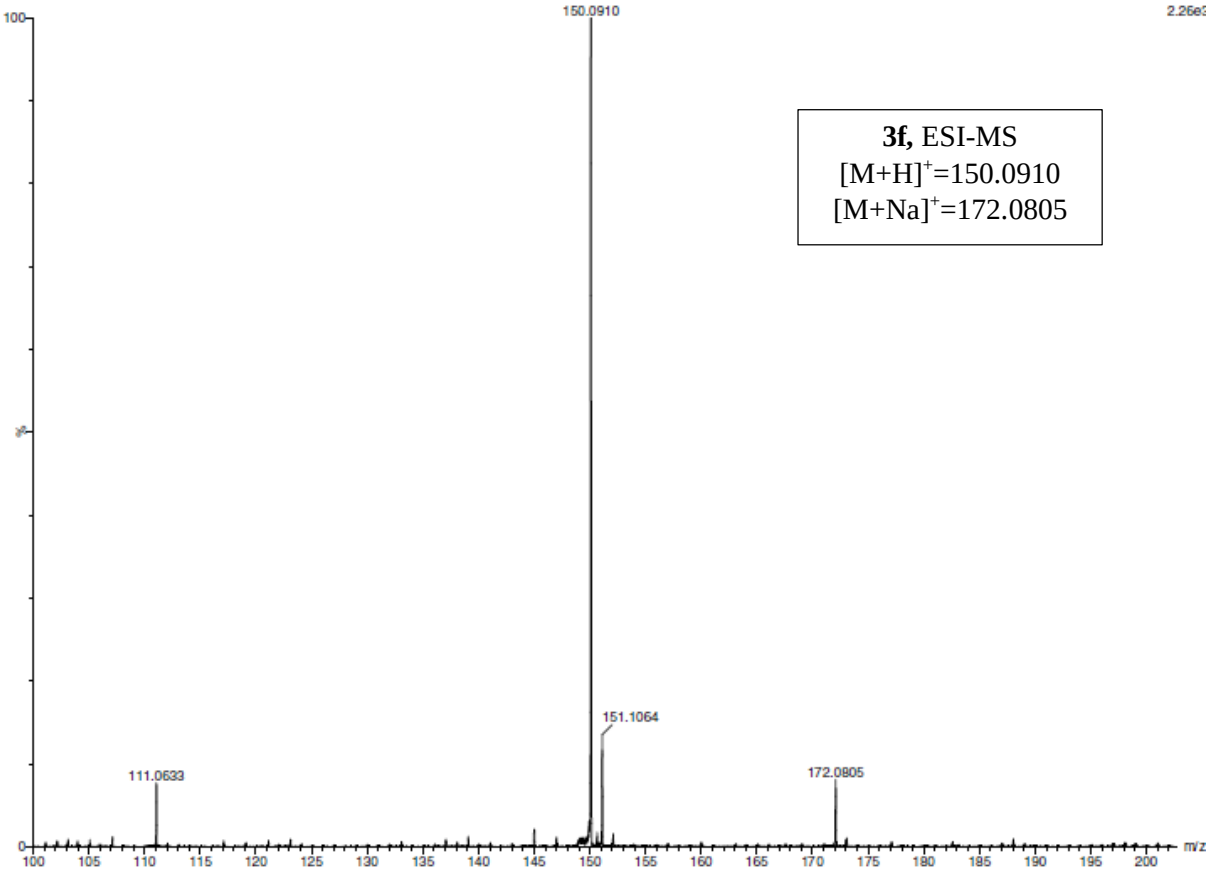
3e, ESI-MS
$[M+H]^+$=178.1223
$[M+Na]^+$=200.1353



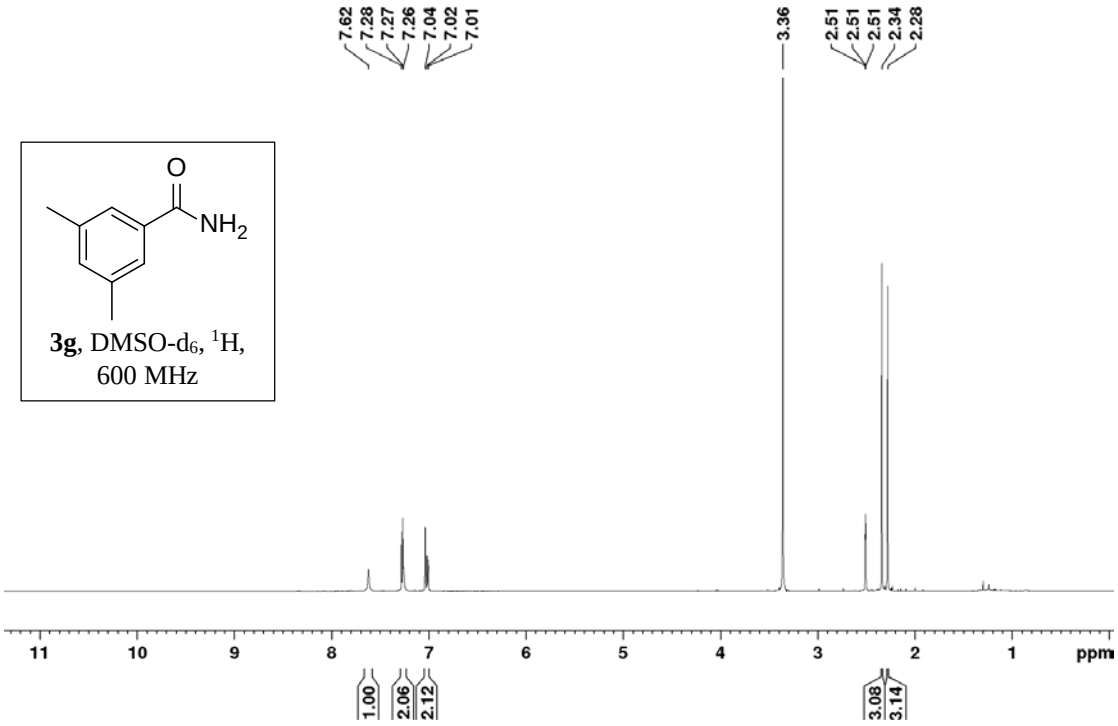
3f, DMSO-d_6, ^{1}H, 600MHz



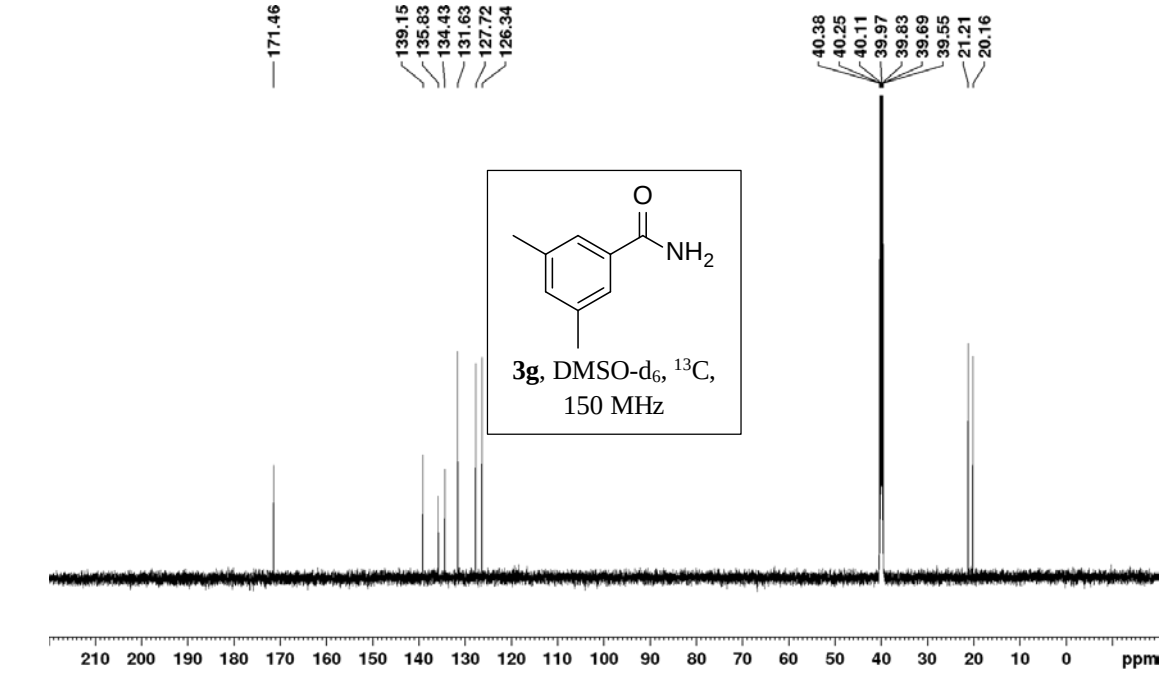
3f, DMSO-d_6, ^{13}C, 150MHz

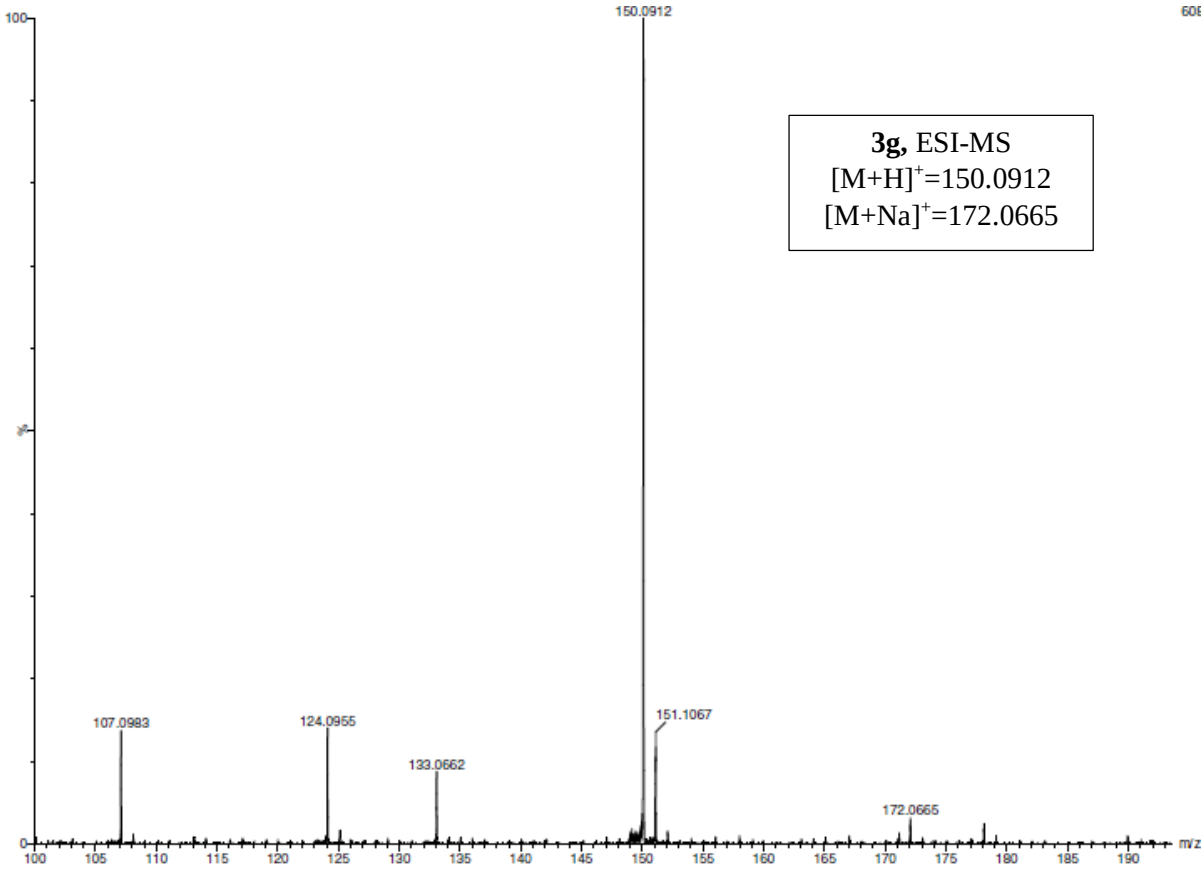


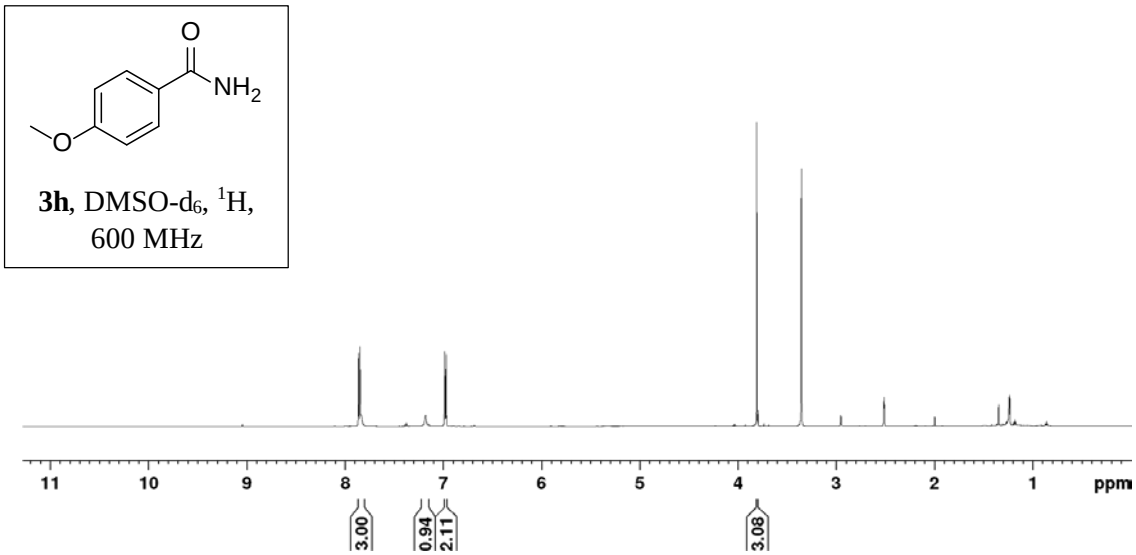
3f, ESI-MS
$[M+H]^+$=150.0910
$[M+Na]^+$=172.0805

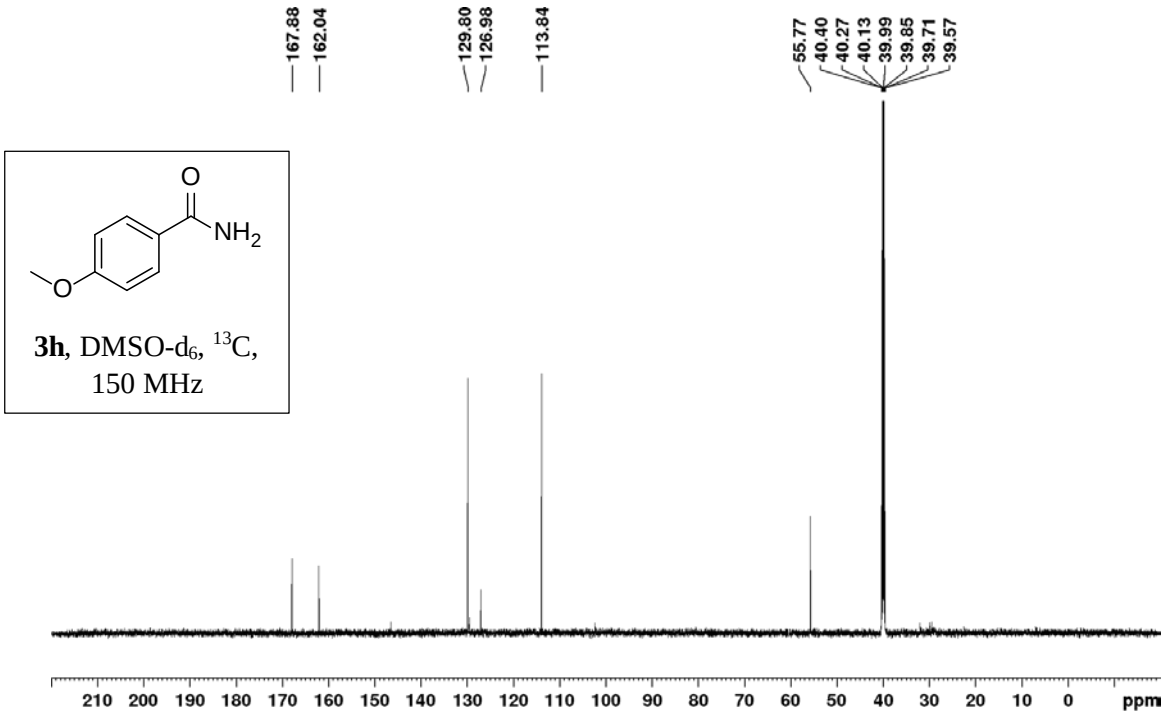


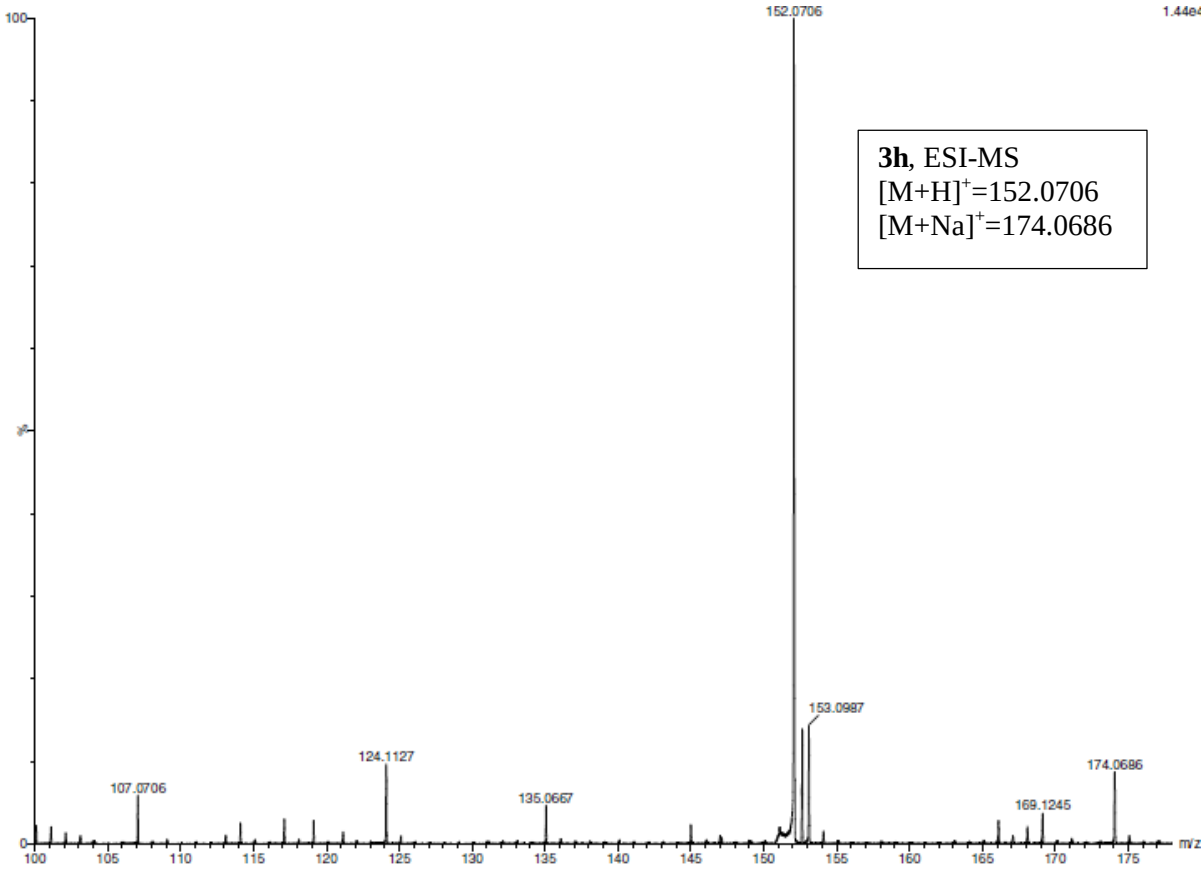
3g, DMSO-d_6, ^{1}H, 600 MHz


171.46
139.15
135.83
134.43
131.63
127.72
126.34
40.38
40.25
40.11
39.97
39.83
39.69
39.55
21.21
20.16
O
NH2
3g, DMSO-d6, 13C,
150 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

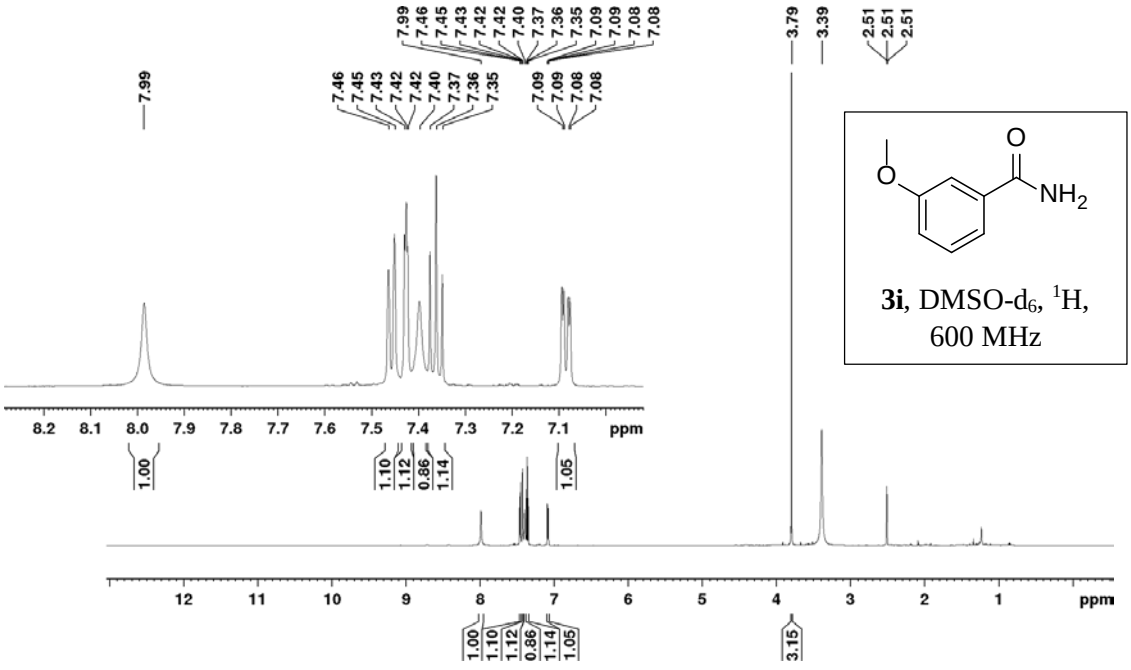

150.0912
3g, ESI-MS
[M+H]+=150.0912
[M+Na]+=172.0665
107.0983
124.0955
133.0662
151.1067
172.0665
m/z


7.86
7.86
7.85
7.84
6.98
6.98
6.97
6.97
3.81
3.35
2.51
2.51
2.51
O
NH2
O
3h, DMSO-d6, 1H,
600 MHz
11
10
9
8
7
6
5
4
3
2
1
ppm
3.00
0.94
2.11
3.08

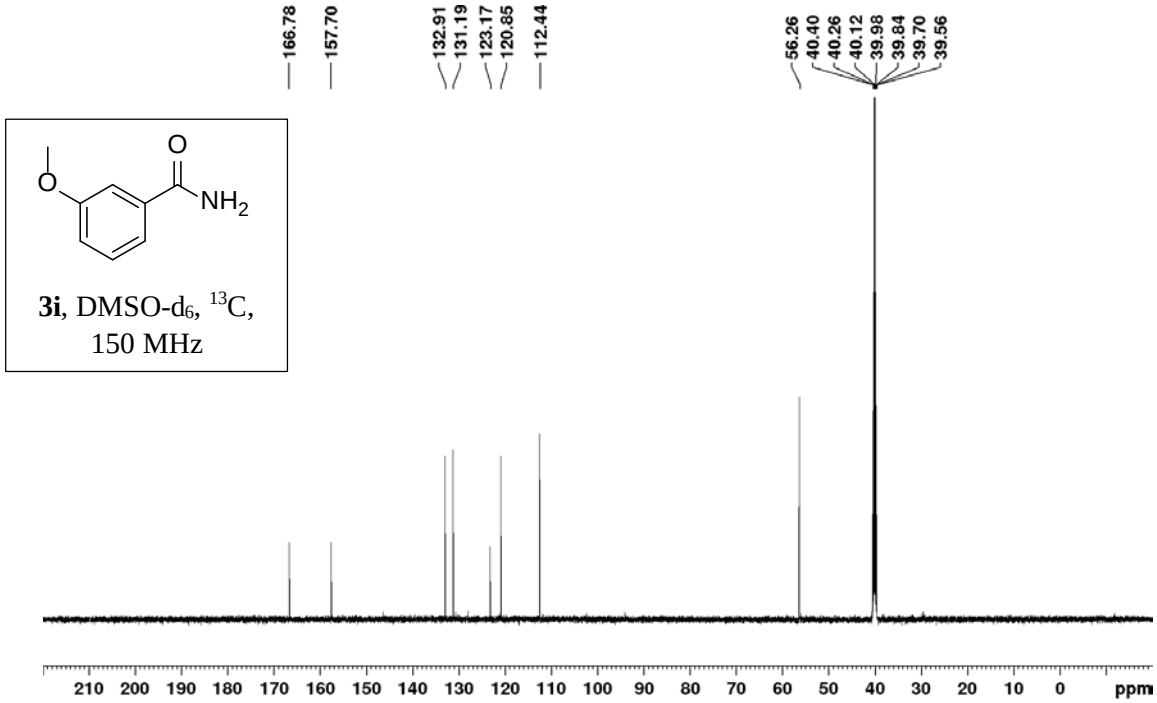

167.88
162.04
129.80
126.98
113.84
55.77
40.40
40.27
40.13
39.99
39.85
39.71
39.57
O
NH2
O
3h, DMSO-d6, 13C,
150 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



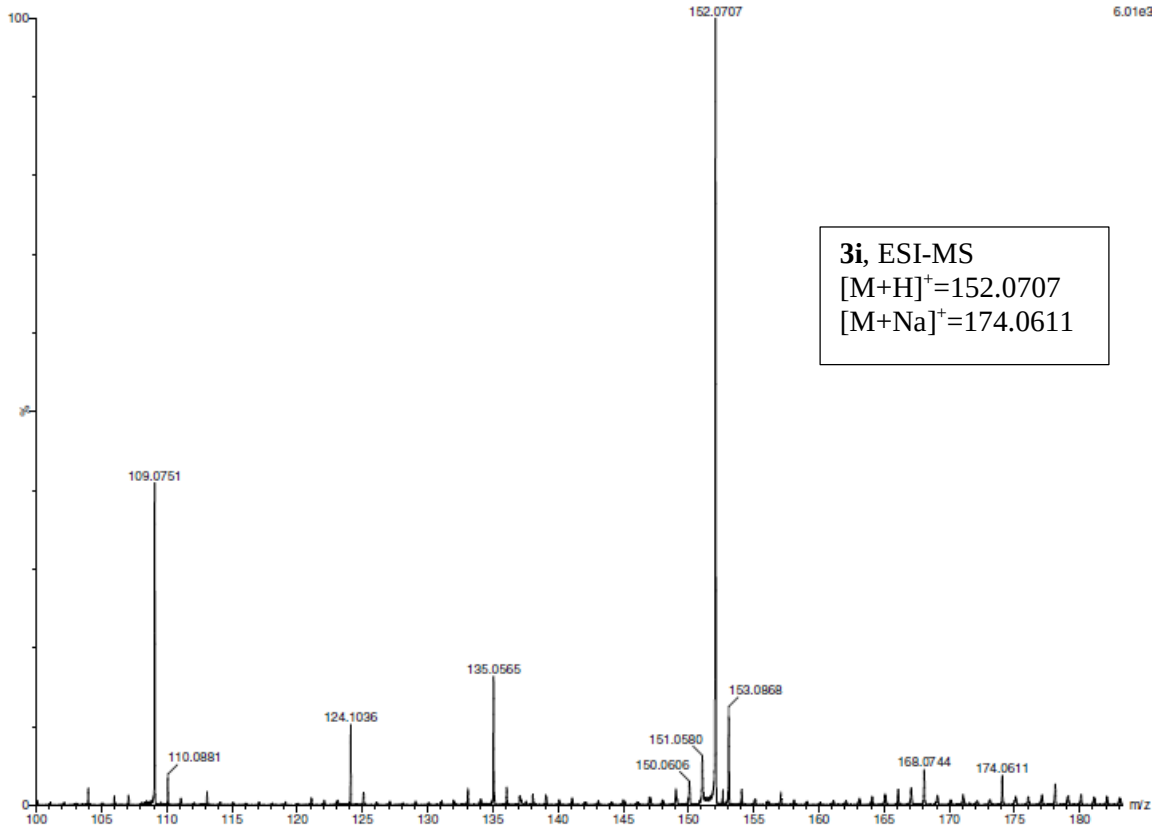
3h, ESI-MS
$[M+H]^+$=152.0706
$[M+Na]^+$=174.0686



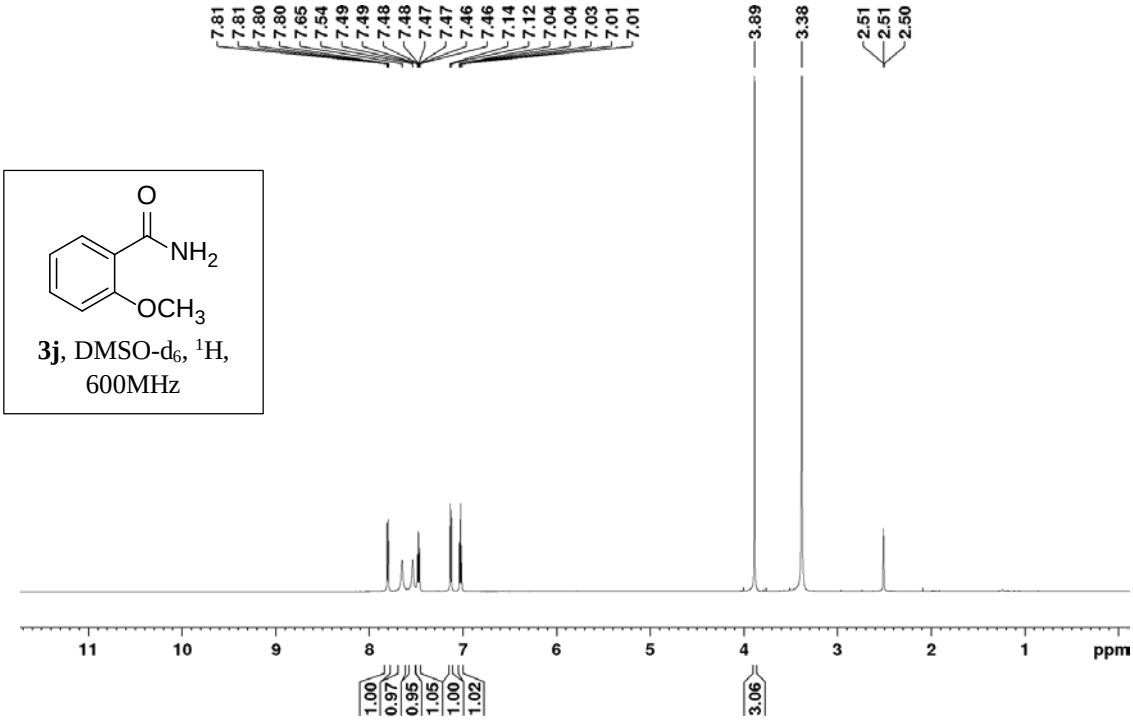
3i, DMSO-d_6, ^{1}H, 600 MHz



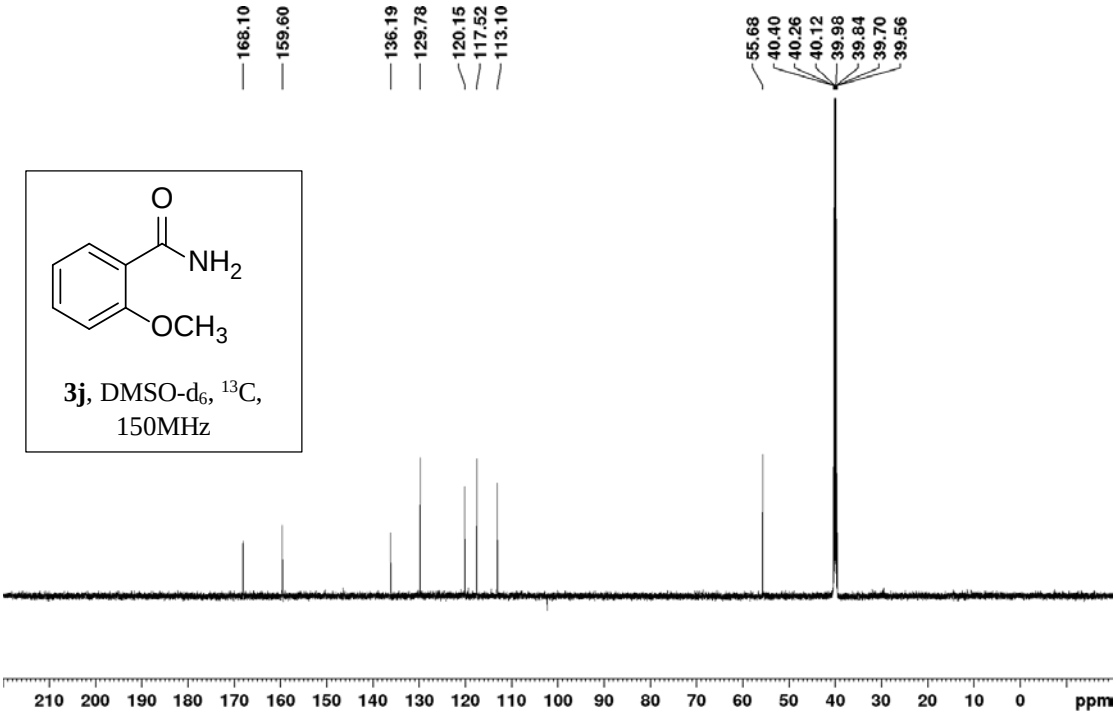
3i, DMSO-d_6, ^{13}C, 150 MHz



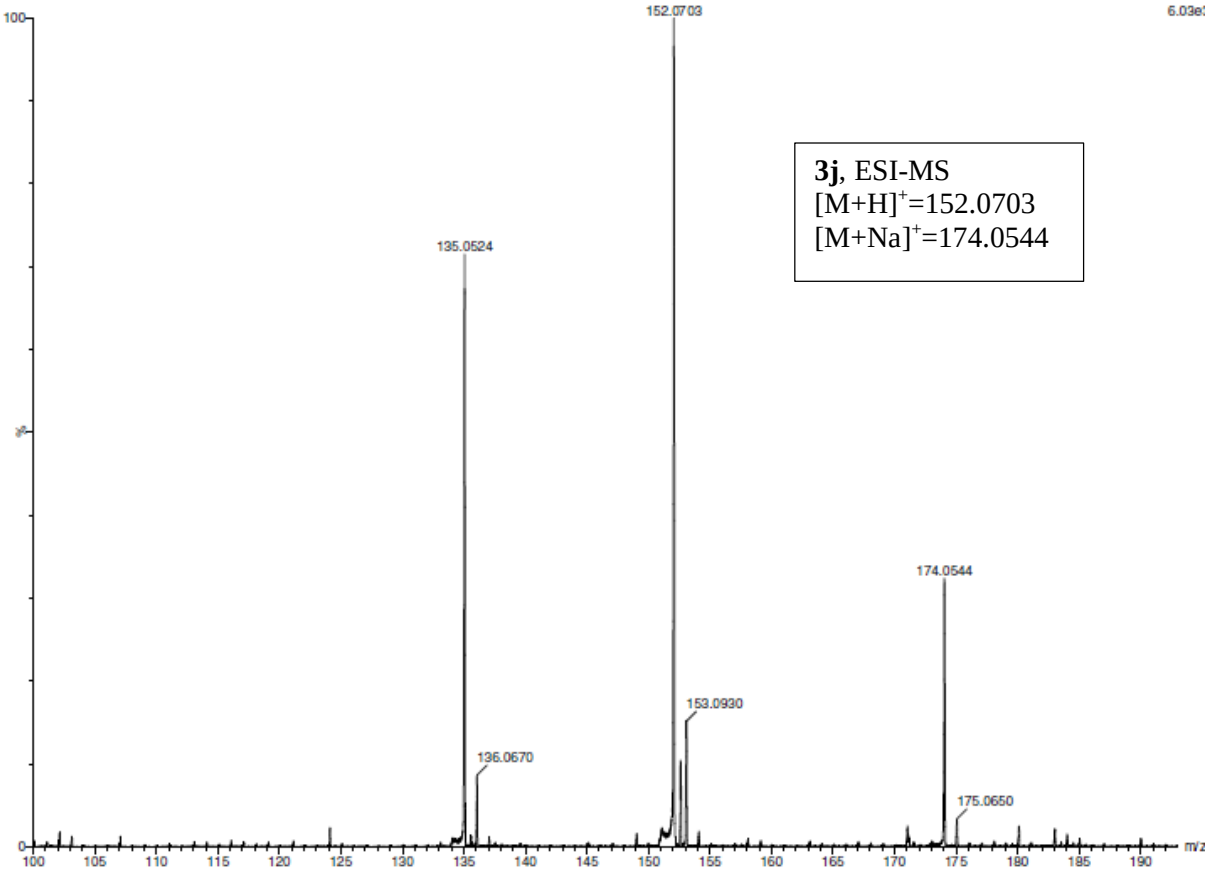
3i, ESI-MS
$[M+H]^+$=152.0707
$[M+Na]^+$=174.0611

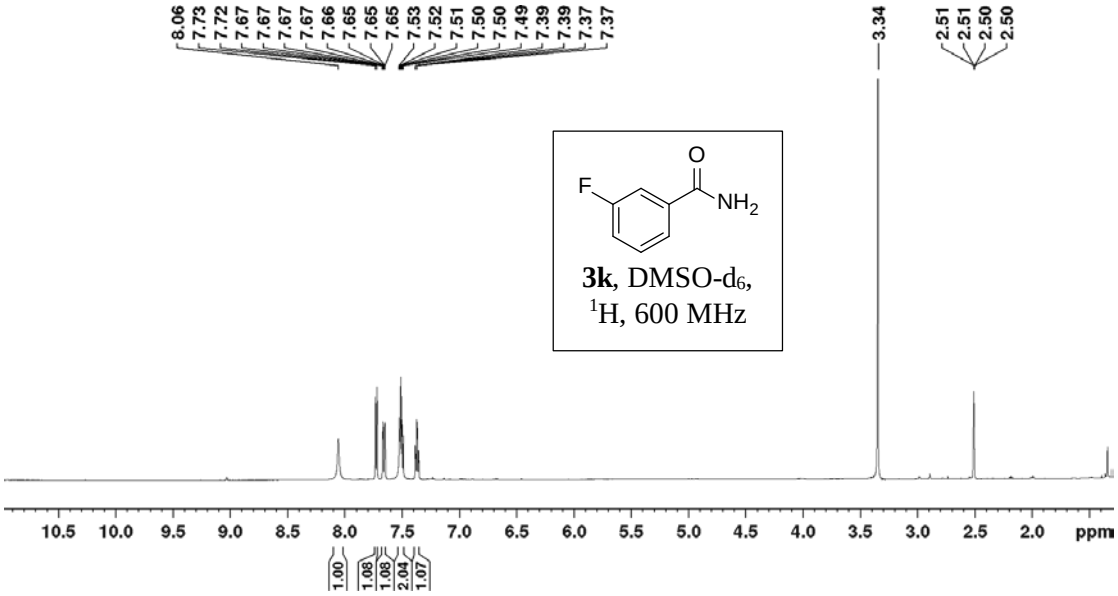


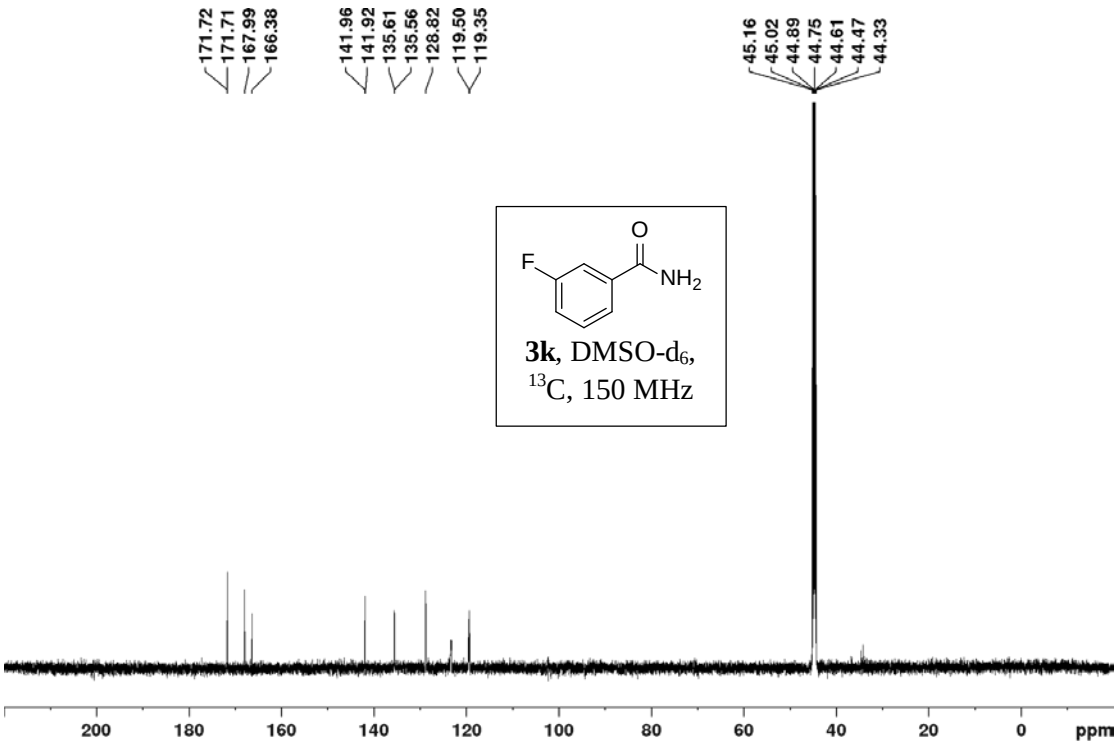
3j, DMSO-d_6, ^{1}H, 600MHz



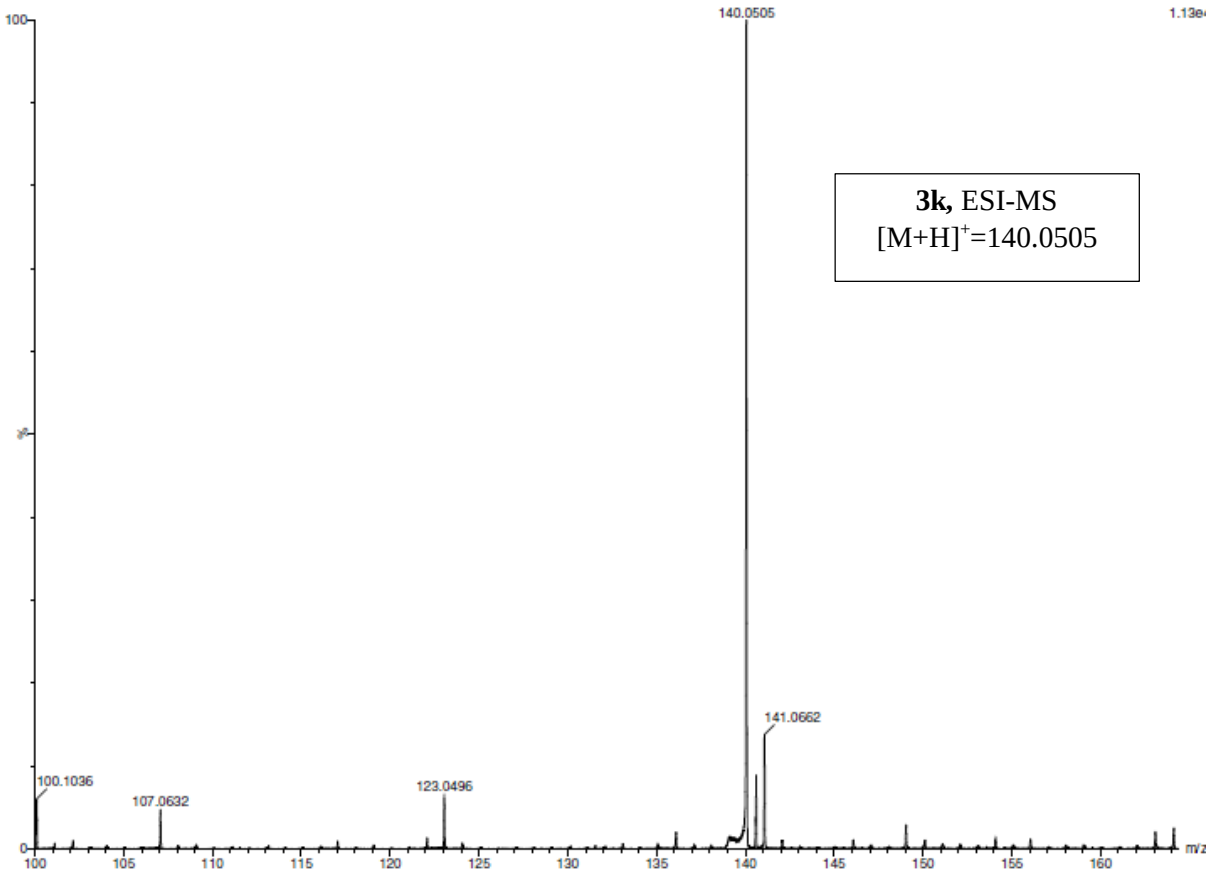
3j, DMSO-d_6, ^{13}C, 150MHz


152.0703
135.0524
174.0544
153.0930
136.0670
175.0650
3j, ESI-MS
$[M+H]^+$=152.0703
$[M+Na]^+$=174.0544

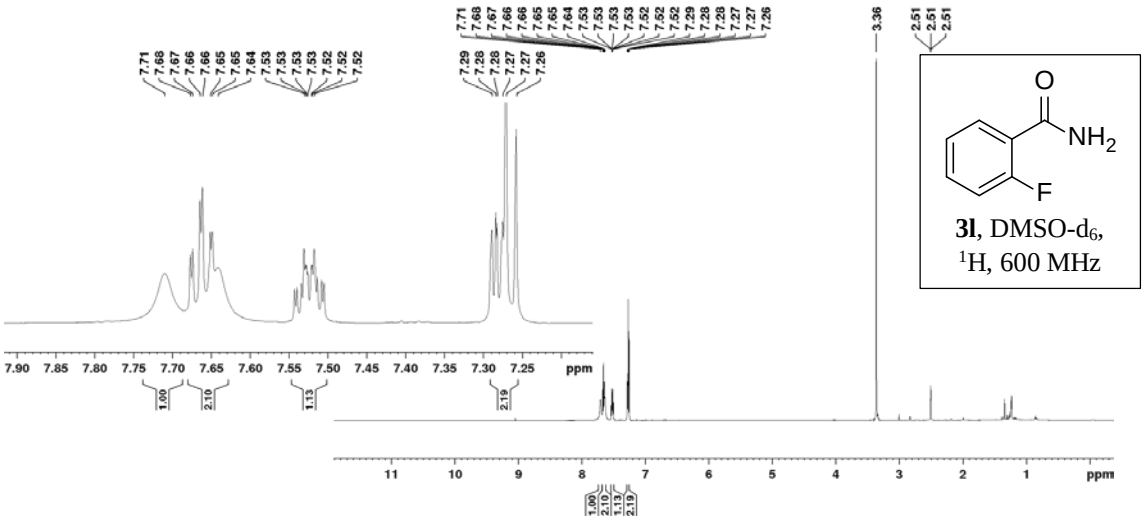

8.06
7.73
7.72
7.67
7.67
7.67
7.67
7.66
7.65
7.65
7.65
7.53
7.52
7.51
7.50
7.50
7.49
7.39
7.39
7.37
7.37
3.34
2.51
2.51
2.50
2.50
F
O
NH2
3k, DMSO-d_6,
^{1}H, 600 MHz
1.00
1.08
1.08
2.04
1.07
ppm

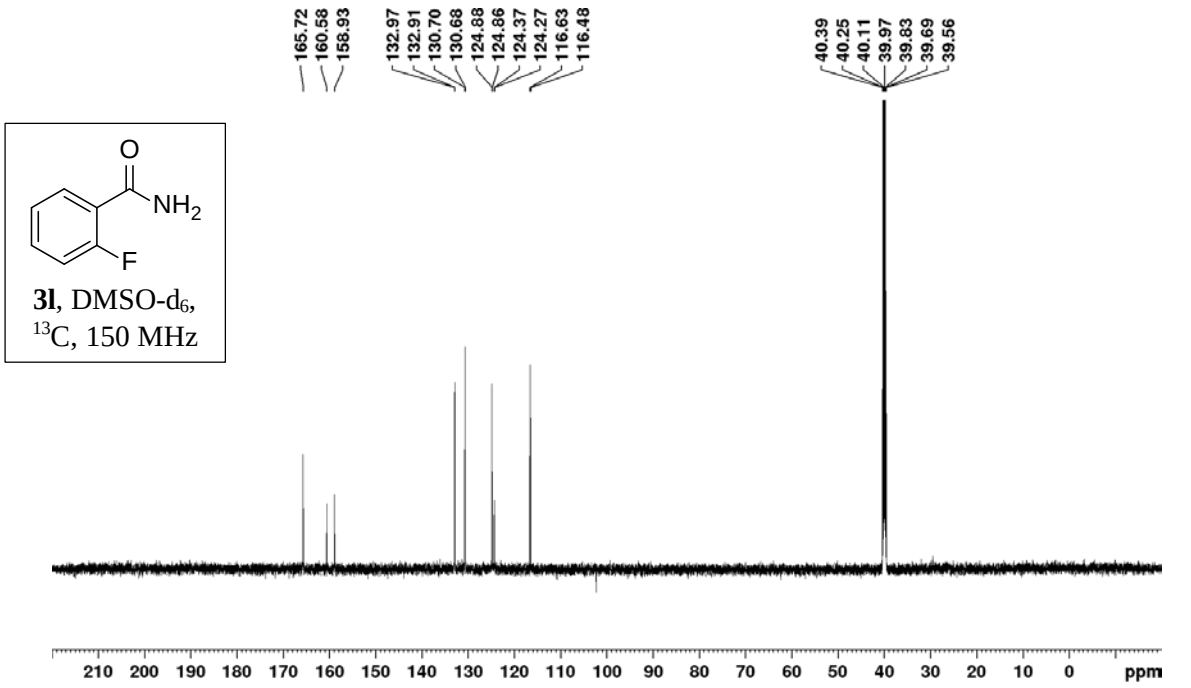


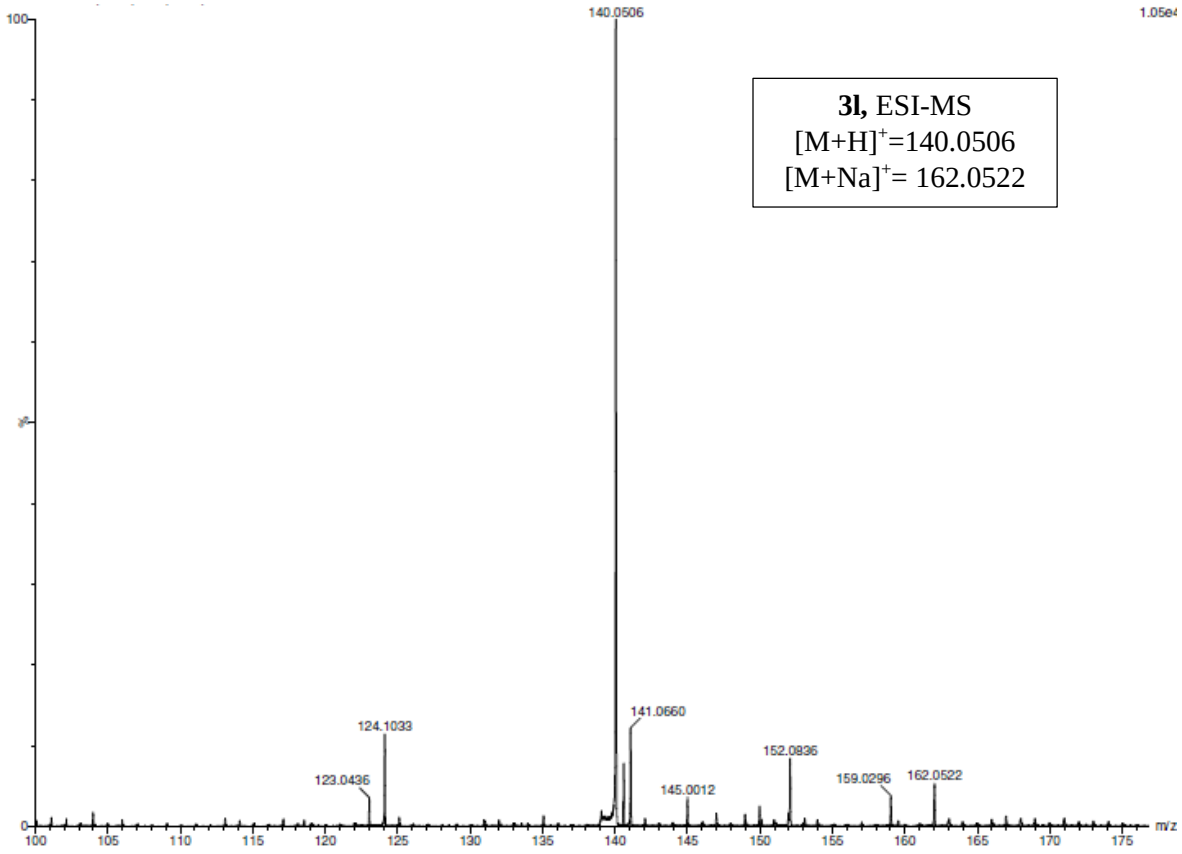
3k, DMSO-d_6, ^{13}C, 150 MHz



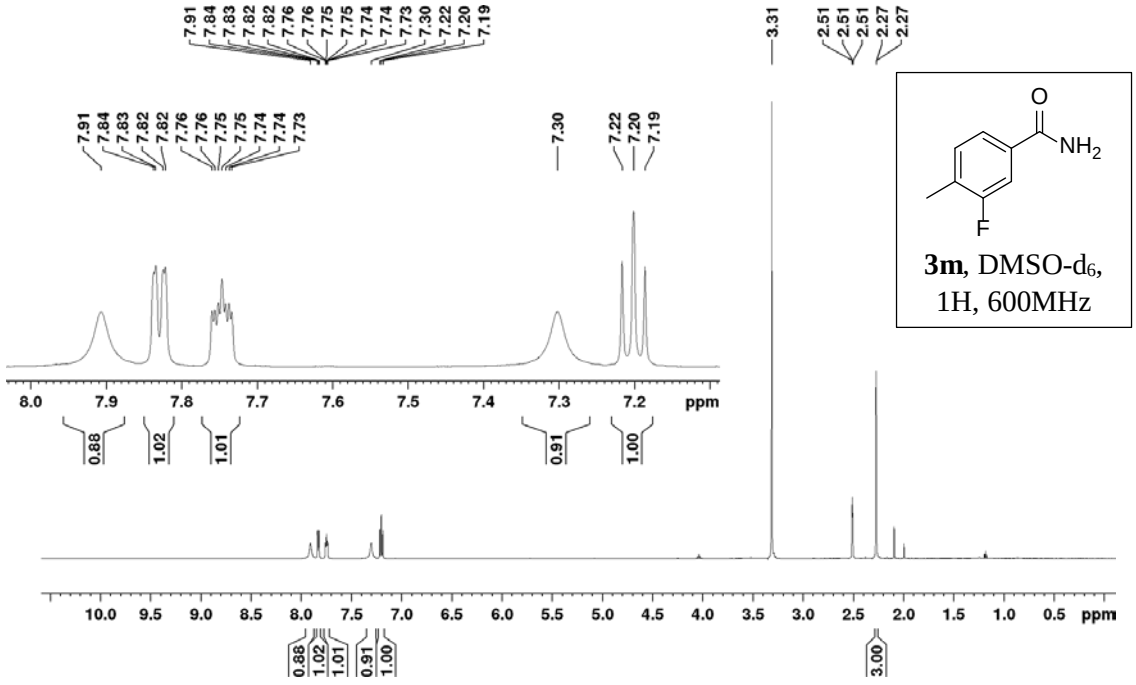
3k, ESI-MS
$[M+H]^+$=140.0505


7.71 7.68 7.67 7.66 7.66 7.65 7.65 7.64 7.53 7.53 7.53 7.53 7.52 7.52 7.52
7.71 7.68 7.67 7.66 7.66 7.65 7.65 7.64 7.53 7.53 7.53 7.52 7.52 7.29 7.28 7.28 7.27 7.27 7.26
3.36
2.51 2.51 2.51
7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 ppm
1.00 2.10 1.15 2.19
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 2.10 1.15 2.19
O
NH2
F
3l, DMSO-d6,
1H, 600 MHz

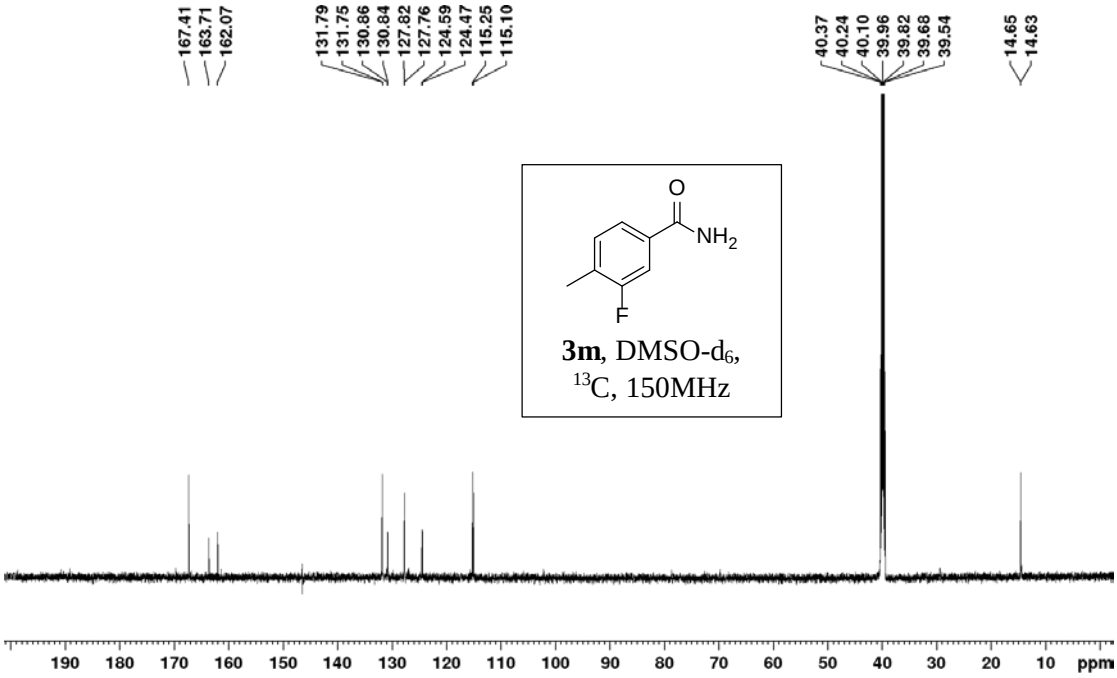

165.72 160.58 158.93
132.97 132.91 130.70 130.68 124.88 124.86 124.37 124.27 116.63 116.48
40.39 40.25 40.11 39.97 39.83 39.69 39.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
O
NH2
F
3l, DMSO-d6,
13C, 150 MHz



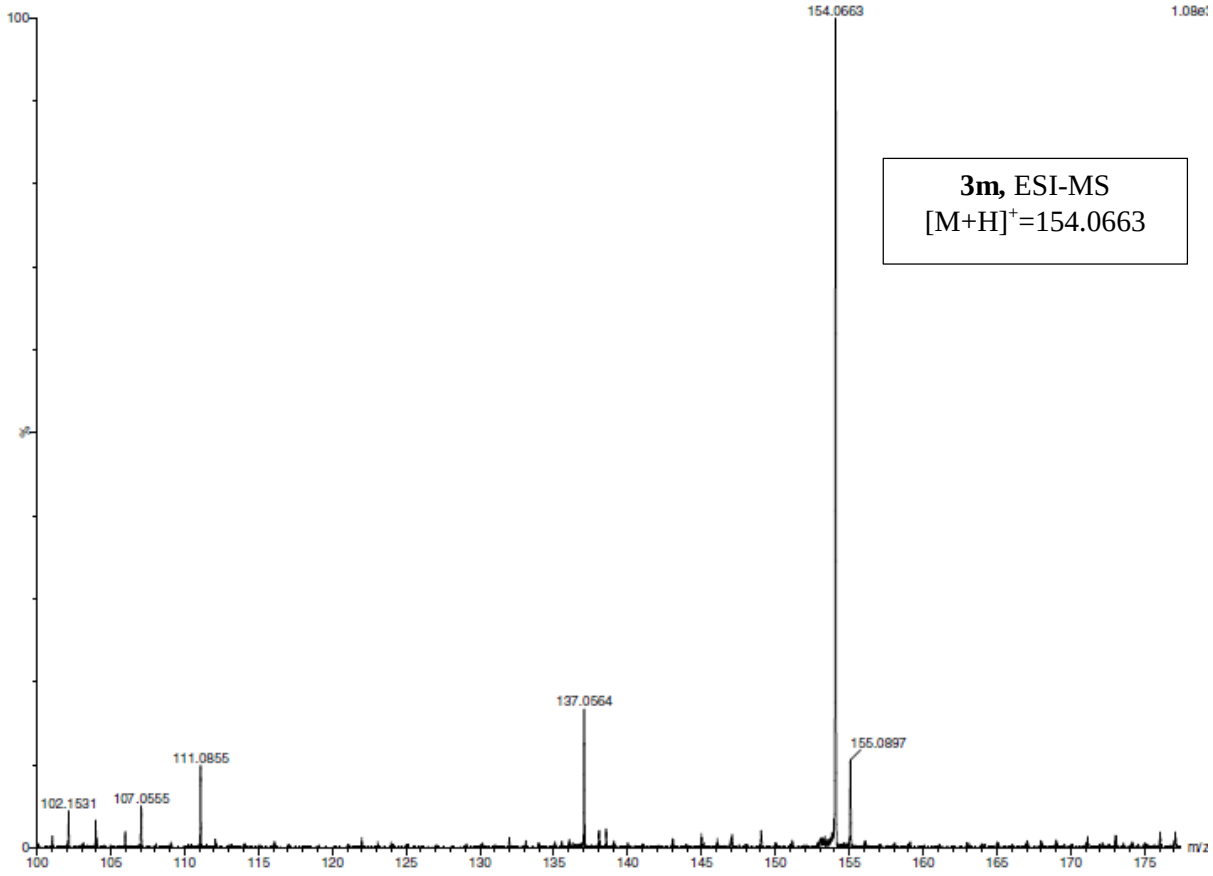
3l, ESI-MS
$[M+H]^+$=140.0506
$[M+Na]^+$= 162.0522



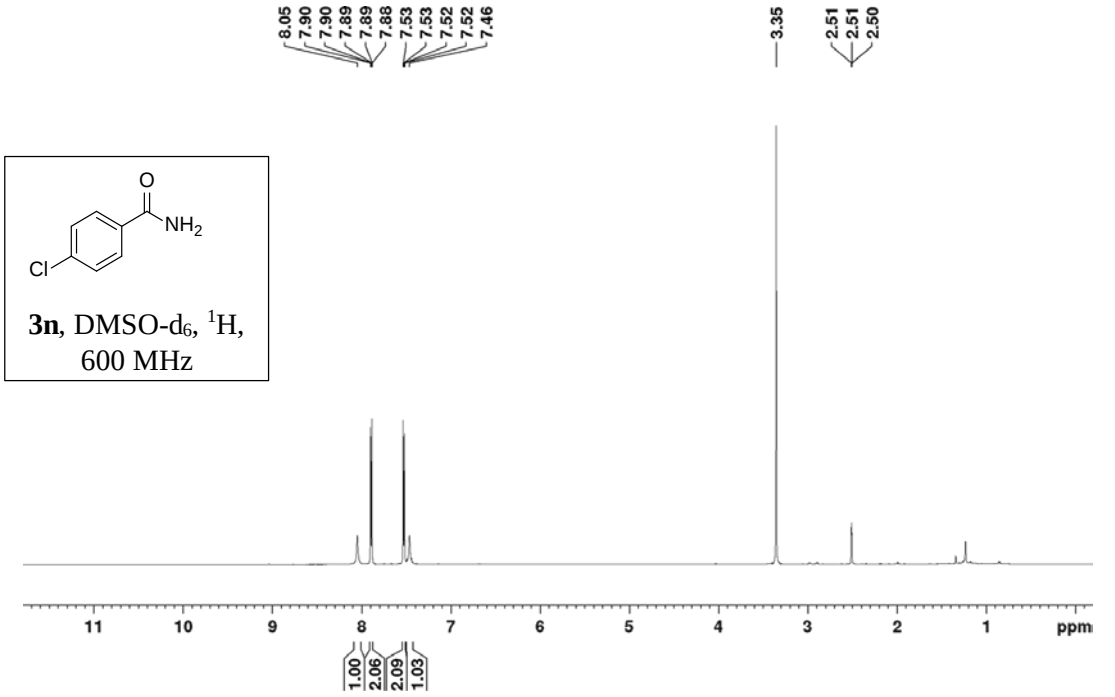
3m, DMSO-d_6,
1H, 600MHz



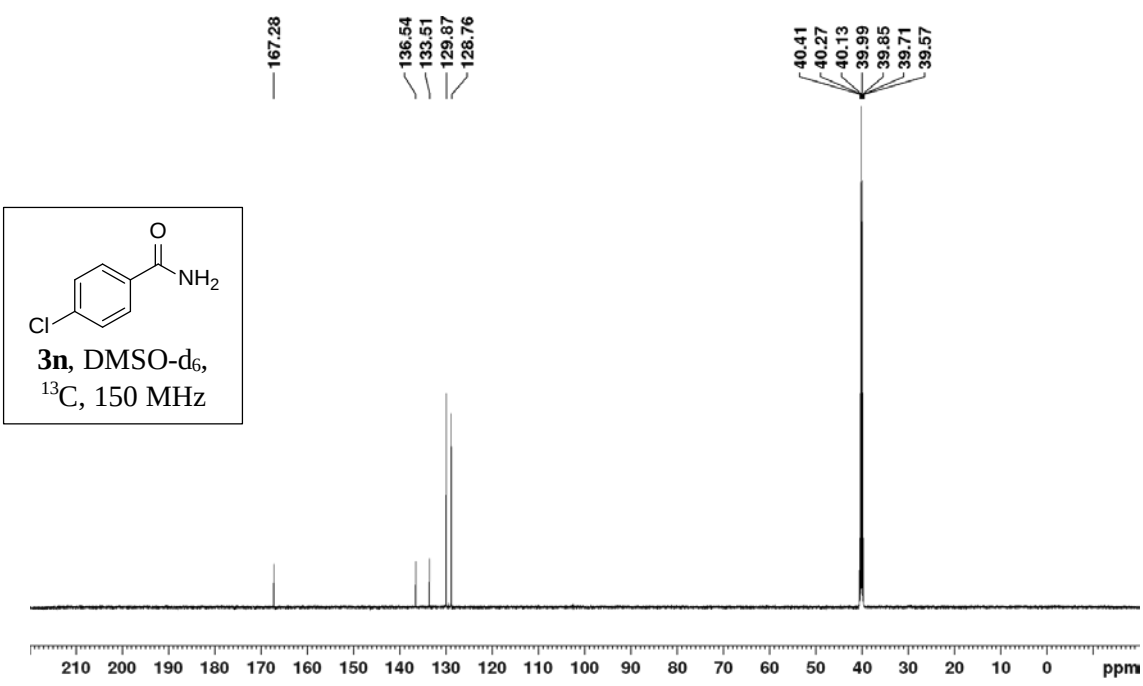
3m, DMSO-d_6, ^{13}C, 150MHz



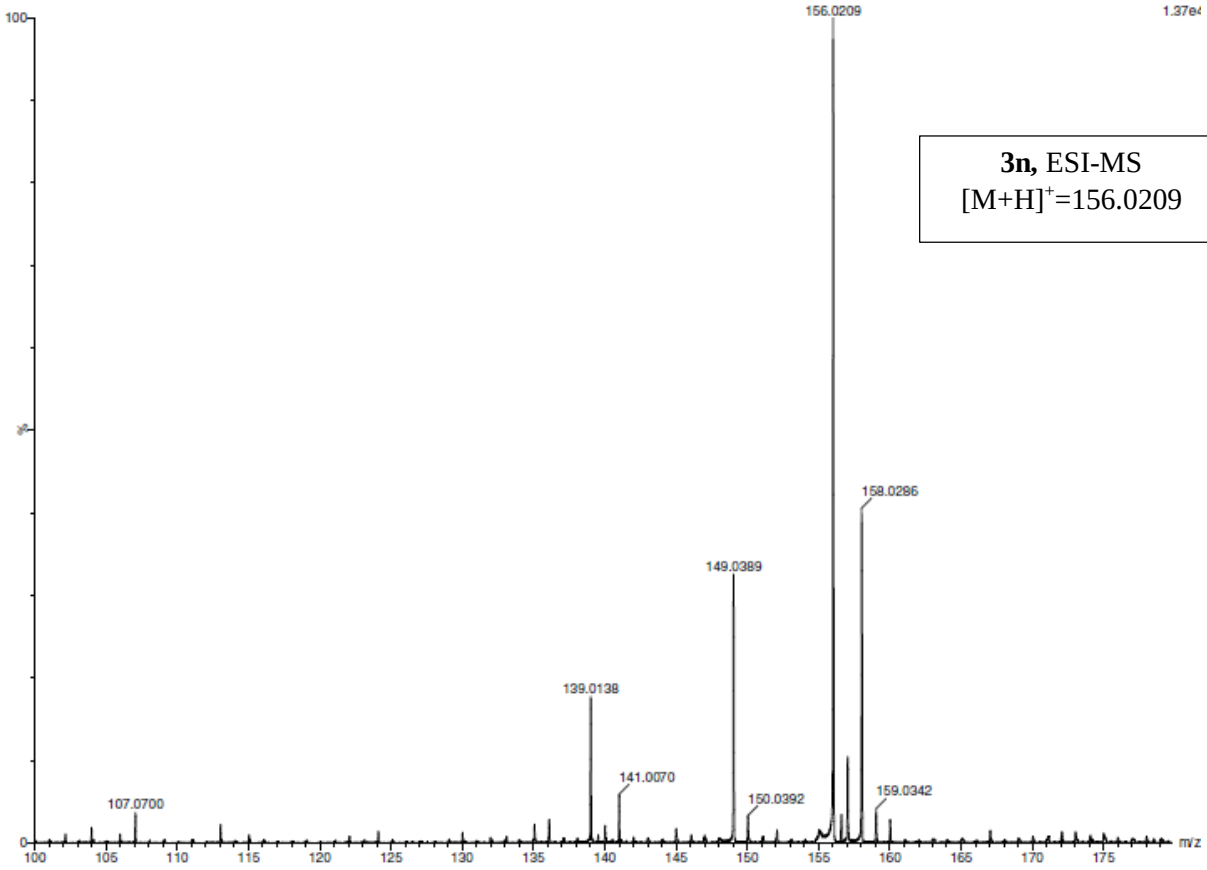
3m, ESI-MS
$[M+H]^+$=154.0663



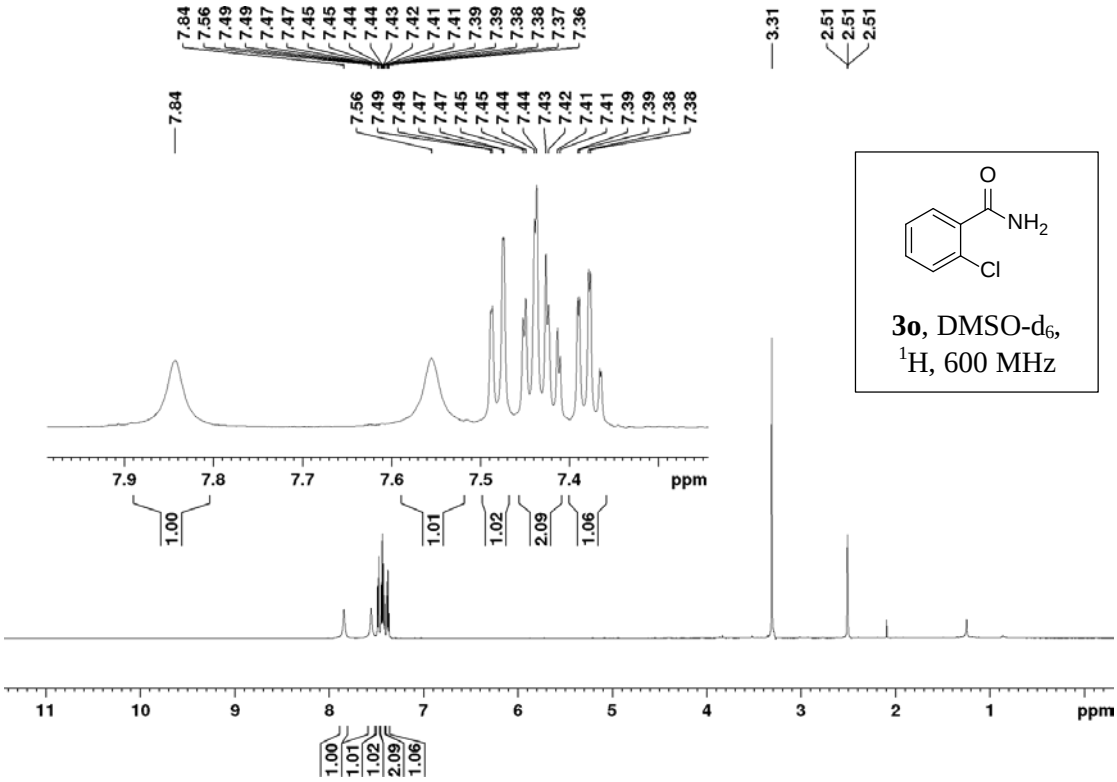
3n, DMSO-d_6, ^{1}H, 600 MHz



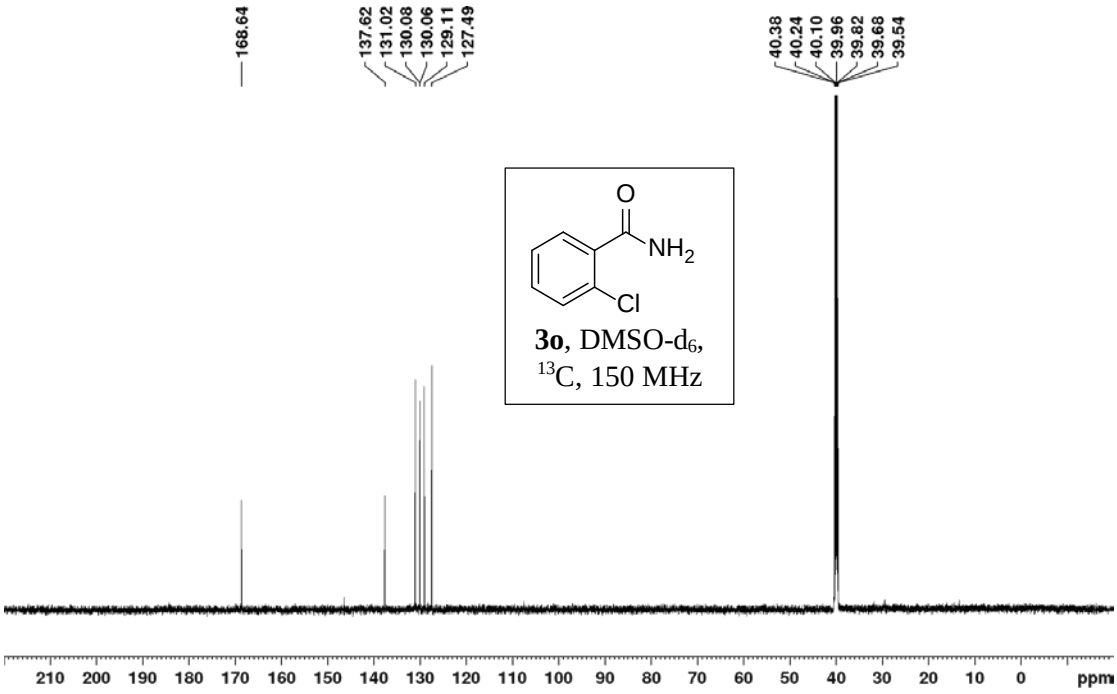
3n, DMSO-d_6, ^{13}C, 150 MHz

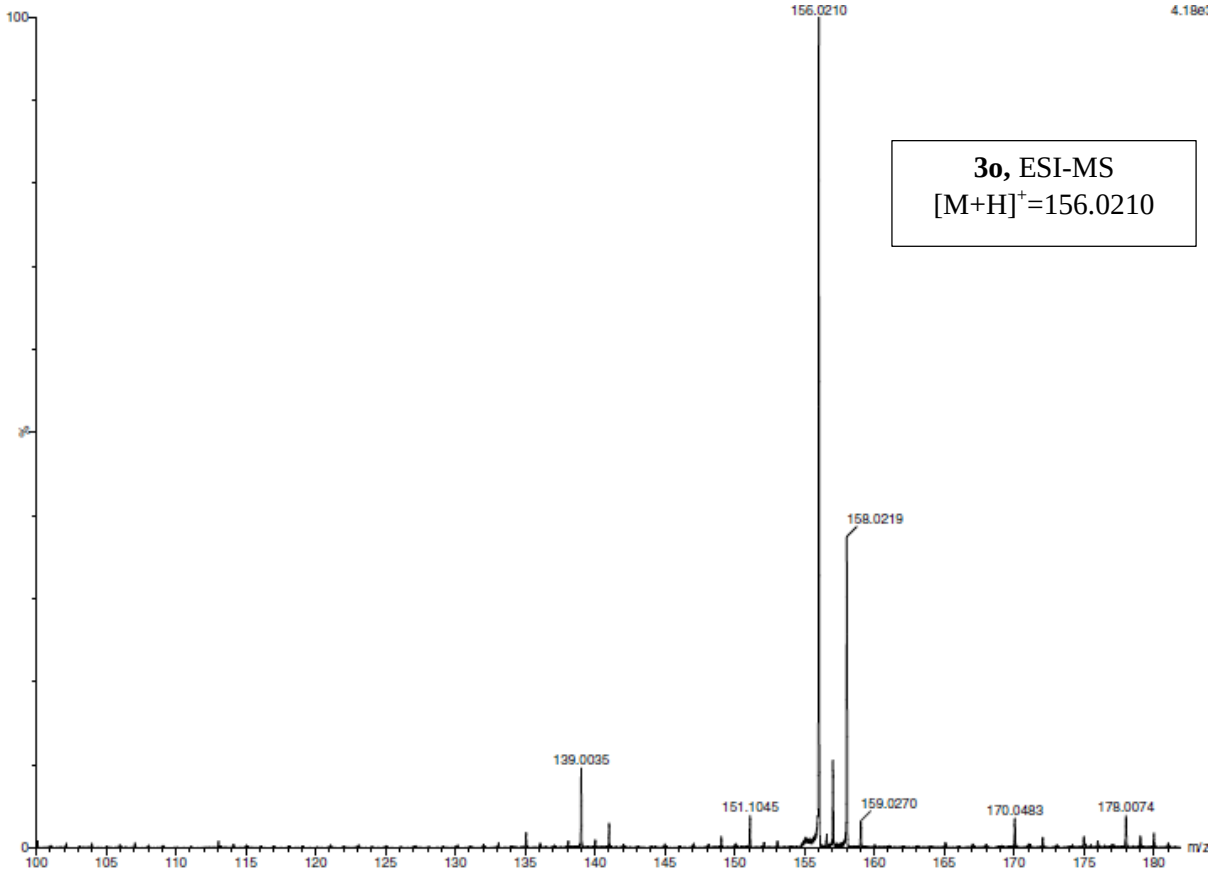


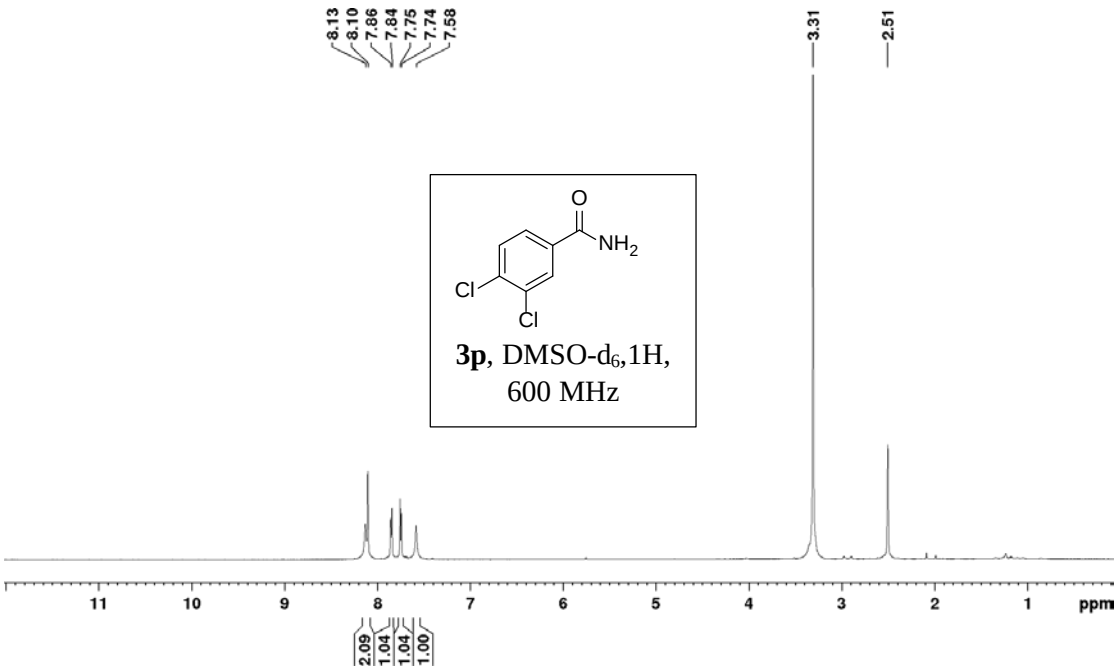
3n, ESI-MS
$[M+H]^+$=156.0209

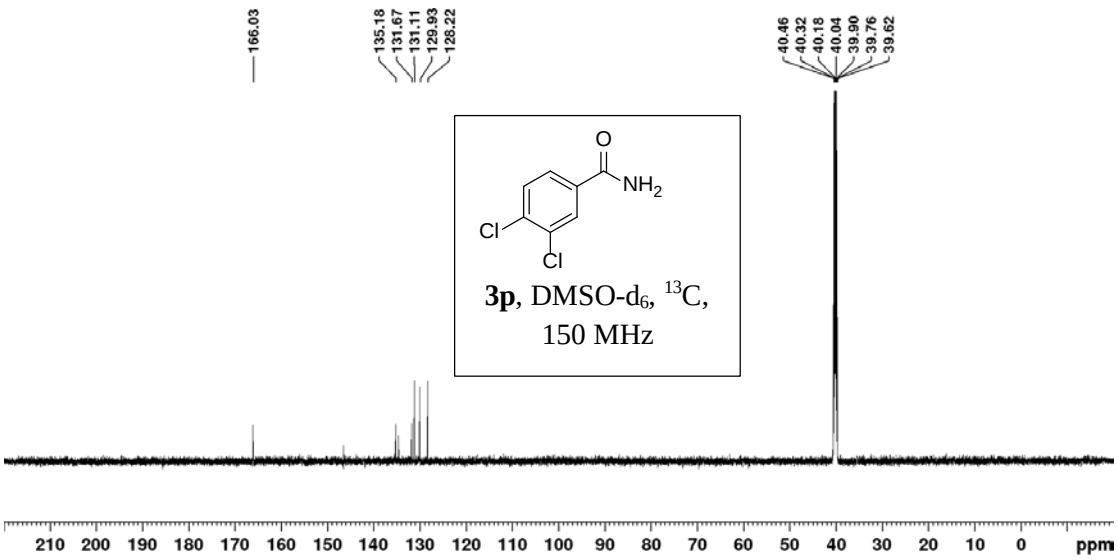


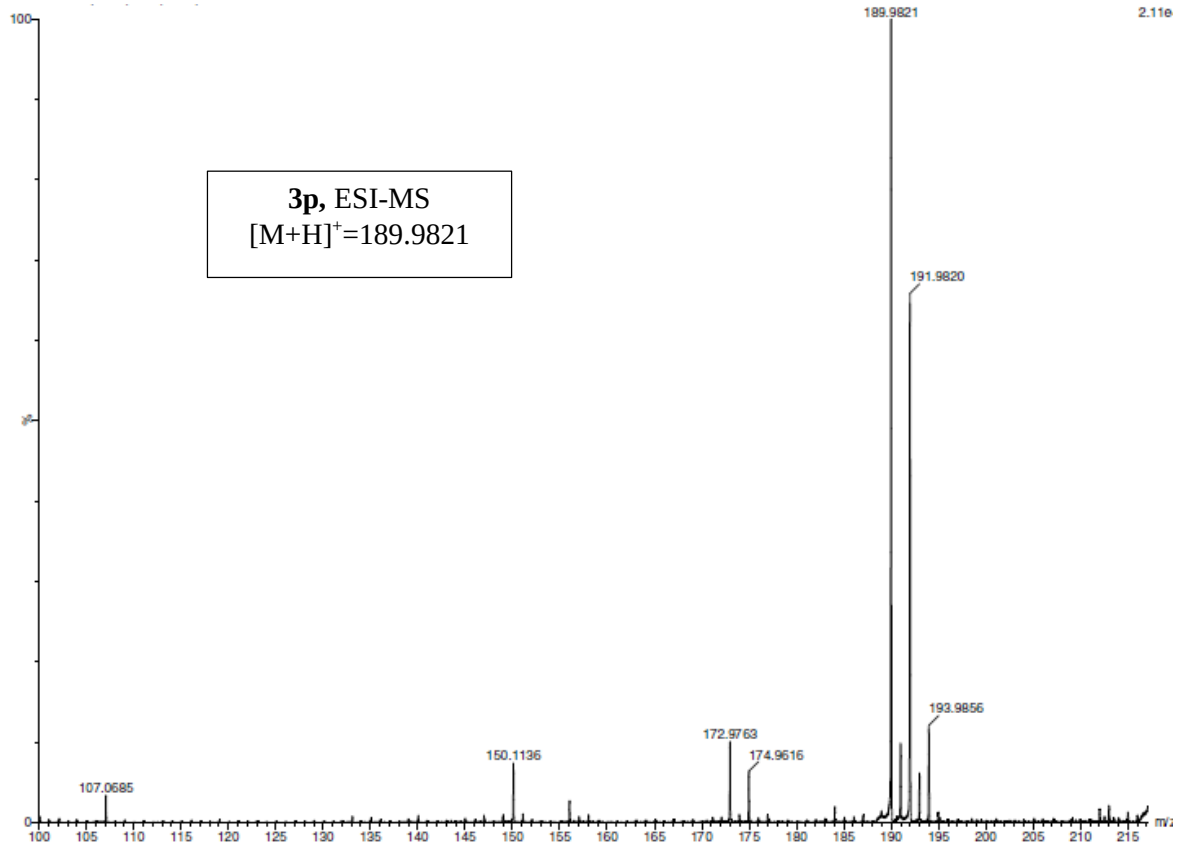
3o, DMSO-d_6,
^{1}H, 600 MHz

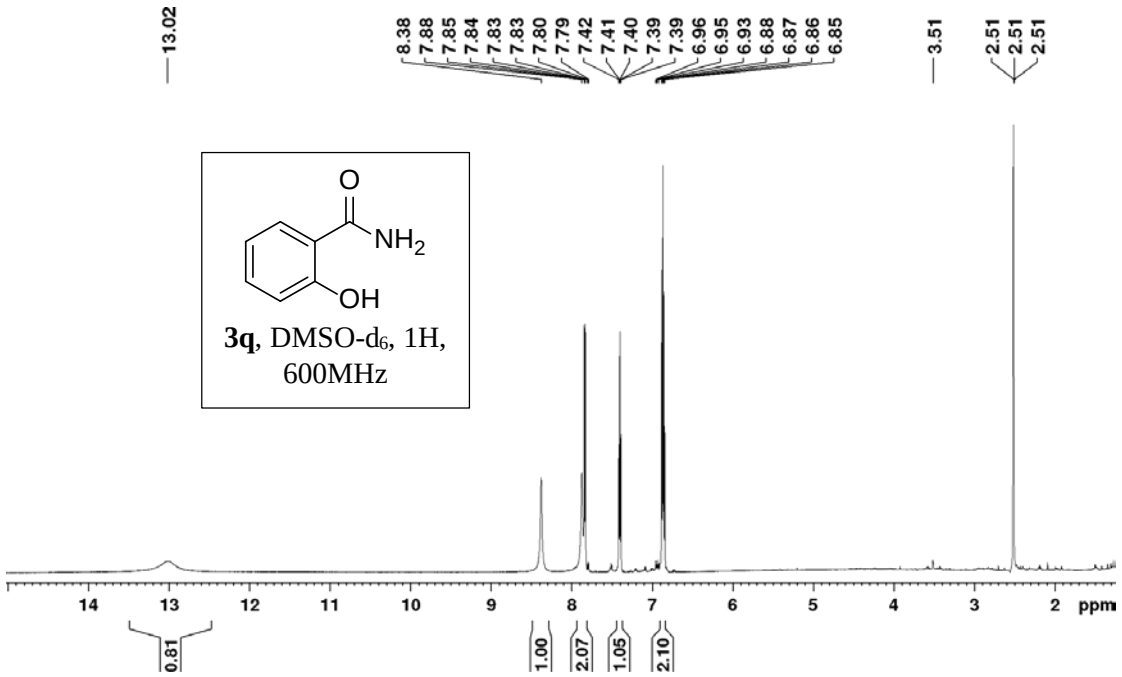

168.64
137.62
131.02
130.08
130.06
129.11
127.49
40.38
40.24
40.10
39.96
39.82
39.68
39.54
O
NH2
Cl
3o, DMSO-d6,
13C, 150 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

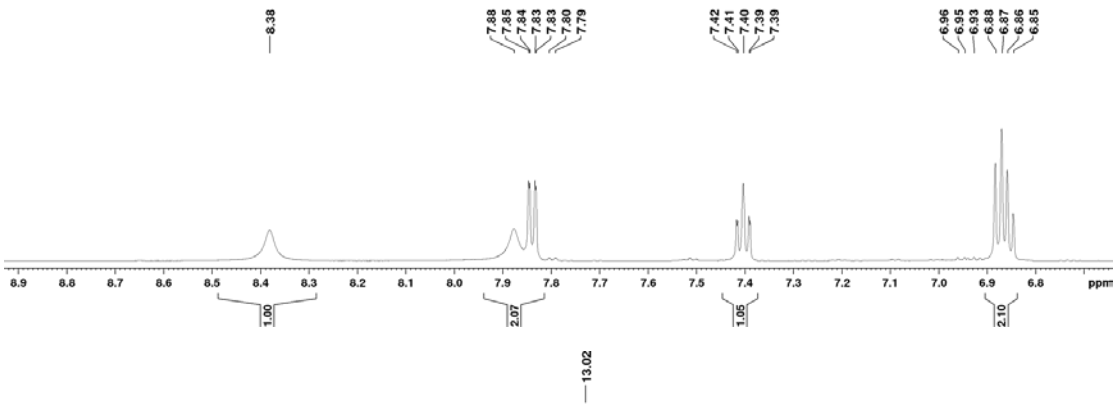

100
%
0
156.0210
158.0219
139.0035
151.1045
159.0270
170.0483
178.0074
100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 m/z
3o, ESI-MS
[M+H]+=156.0210

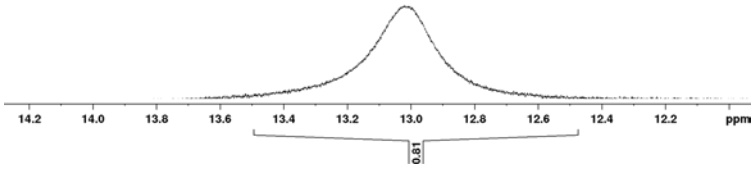

8.13
8.10
7.86
7.84
7.75
7.74
7.58
3.31
2.51
O
NH2
Cl
Cl
3p, DMSO-d6,1H,
600 MHz
11
10
9
8
7
6
5
4
3
2
1
ppm
2.09
1.04
1.04
1.00

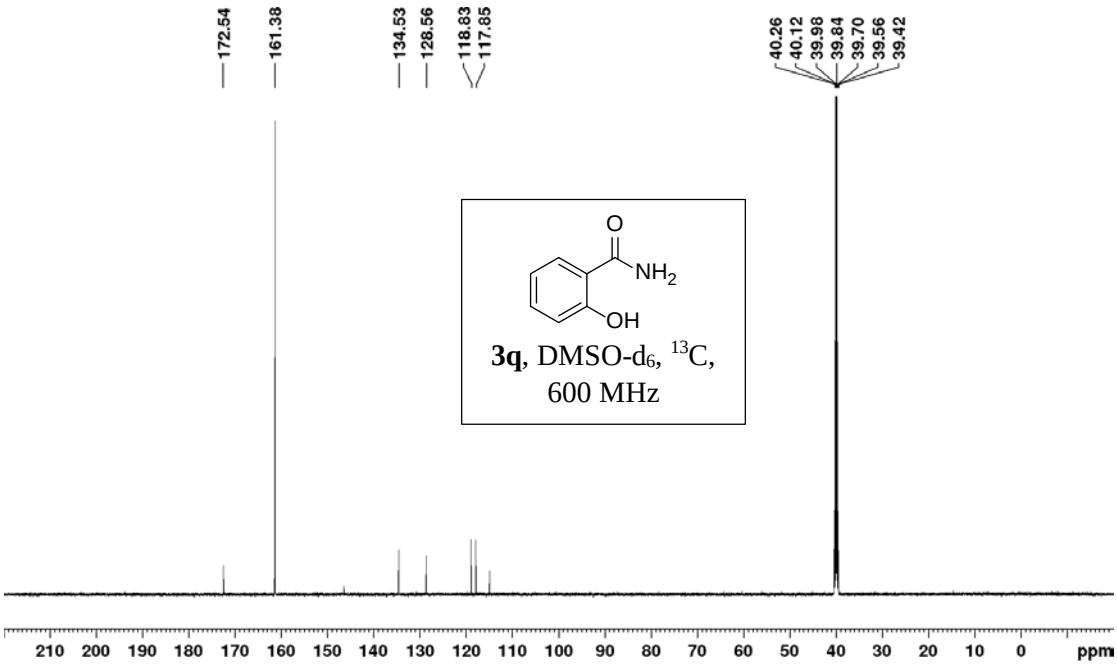

166.03
135.18
131.67
131.11
129.93
128.22
40.46
40.32
40.18
40.04
39.90
39.76
39.62
O
NH2
Cl
Cl
3p, DMSO-d6, 13C,
150 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

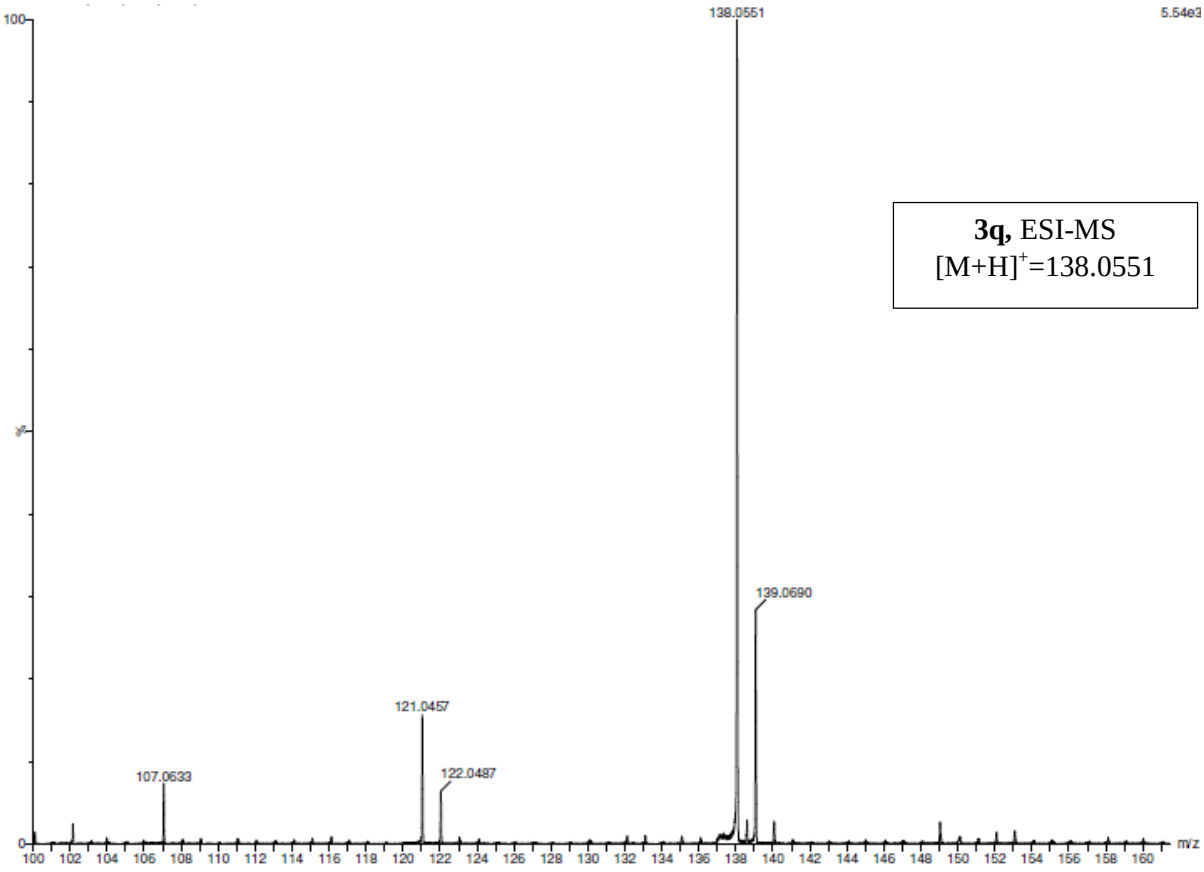

3p, ESI-MS
[M+H]+=189.9821
189.9821
191.9820
193.9856
172.9763
174.9616
150.1136
107.0685


13.02
8.38
7.88
7.85
7.84
7.83
7.83
7.80
7.79
7.42
7.41
7.40
7.39
7.39
6.96
6.95
6.93
6.88
6.87
6.86
6.85
3.51
2.51
2.51
2.51
O
NH2
OH
3q, DMSO-d6, 1H, 600MHz
14
13
12
11
10
9
8
7
6
5
4
3
2
ppm
0.81
1.00
2.07
1.05
2.10

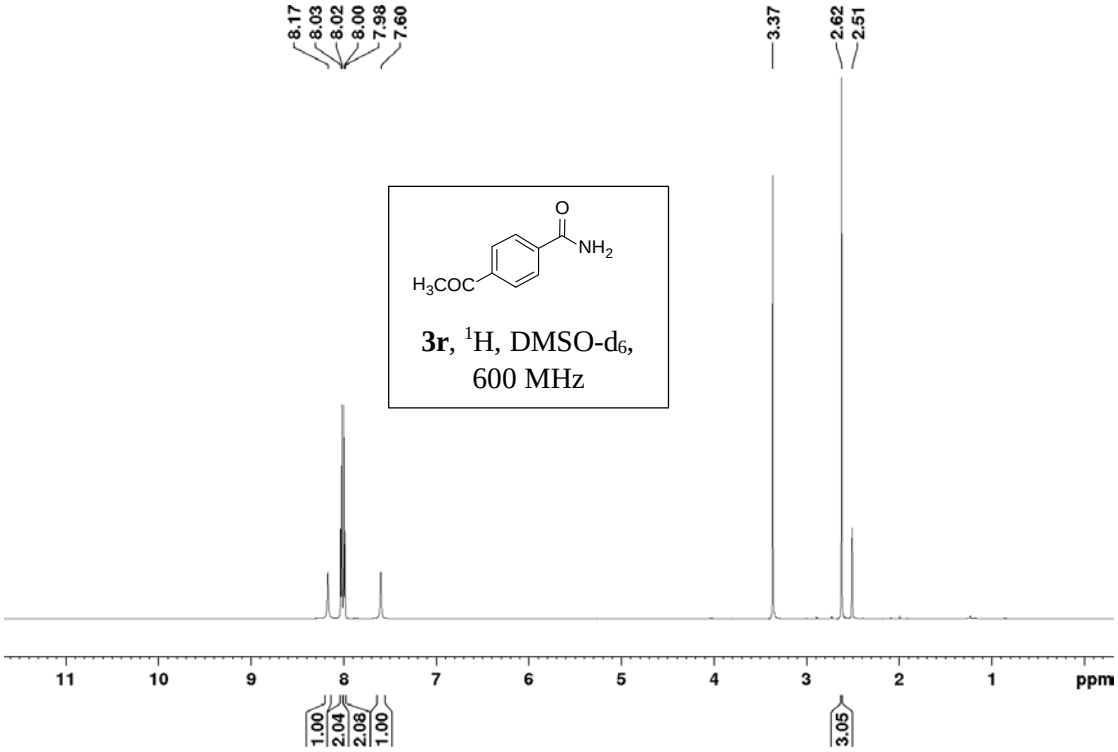

8.38
7.88
7.85
7.84
7.83
7.83
7.80
7.79
7.42
7.41
7.40
7.39
7.39
6.96
6.95
6.93
6.88
6.87
6.86
6.85
1.00
2.07
1.05
2.10
13.02


0.61

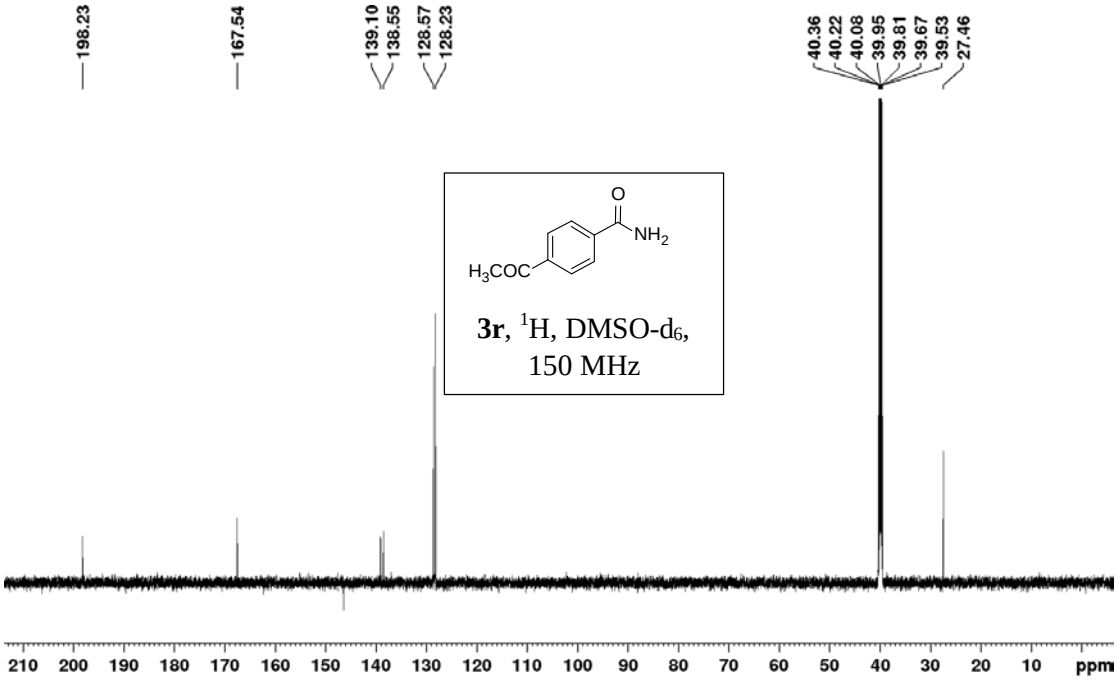

172.54
161.38
134.53
128.56
118.83
117.85
40.26
40.12
39.98
39.84
39.70
39.56
39.42
O
NH2
OH
3q, DMSO-d6, 13C, 600 MHz

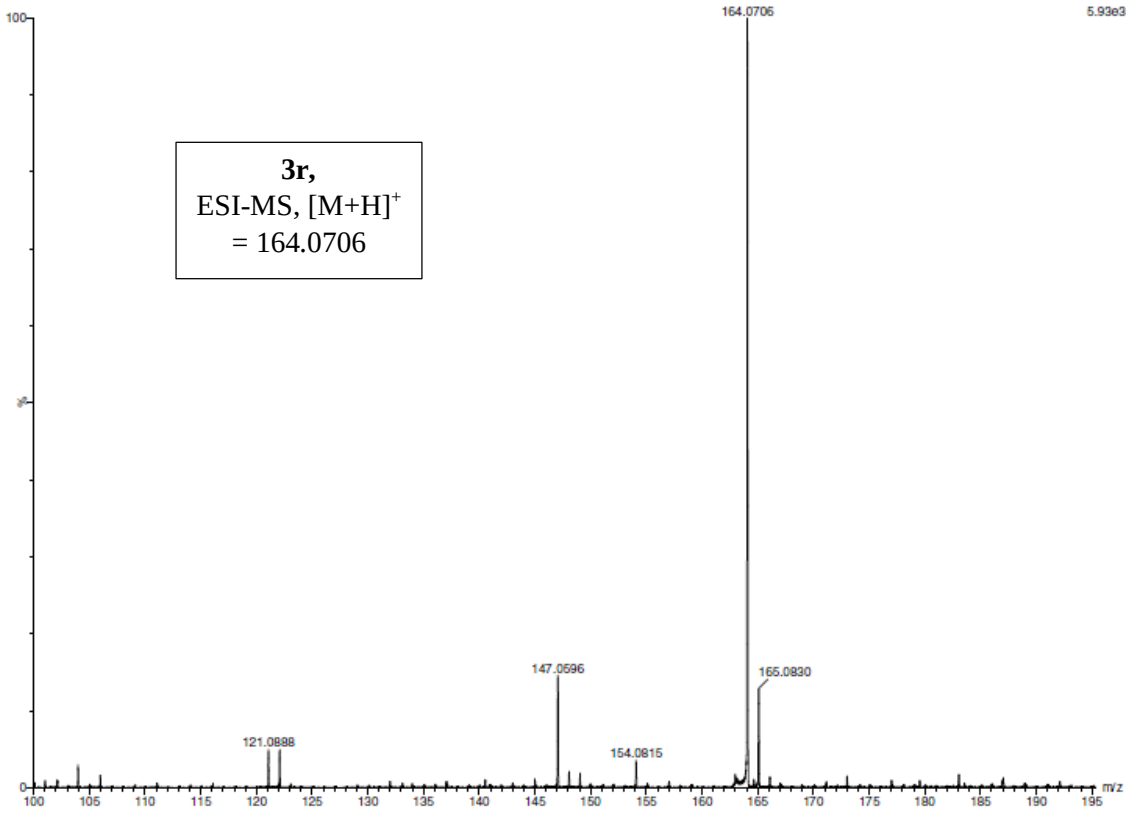


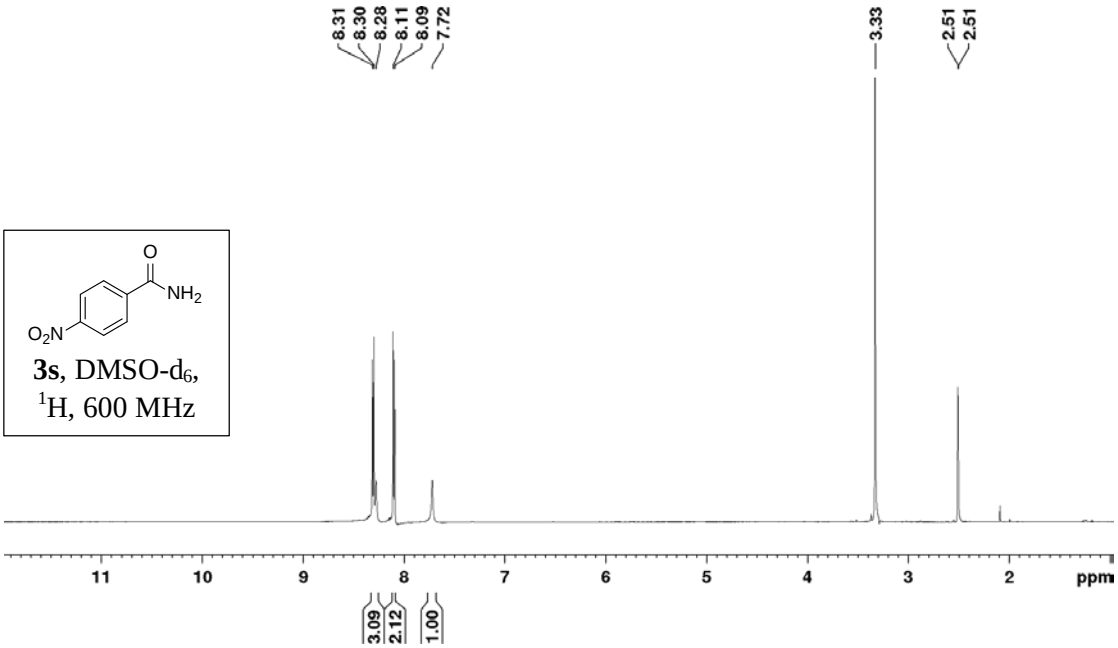
3q, ESI-MS
$[M+H]^+$=138.0551

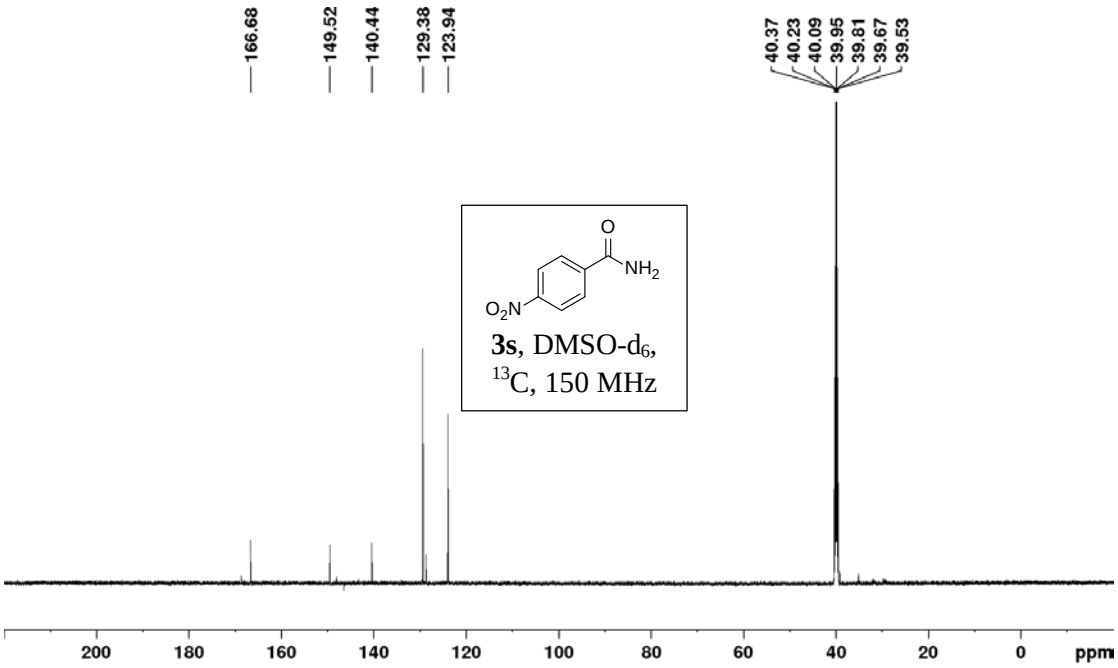


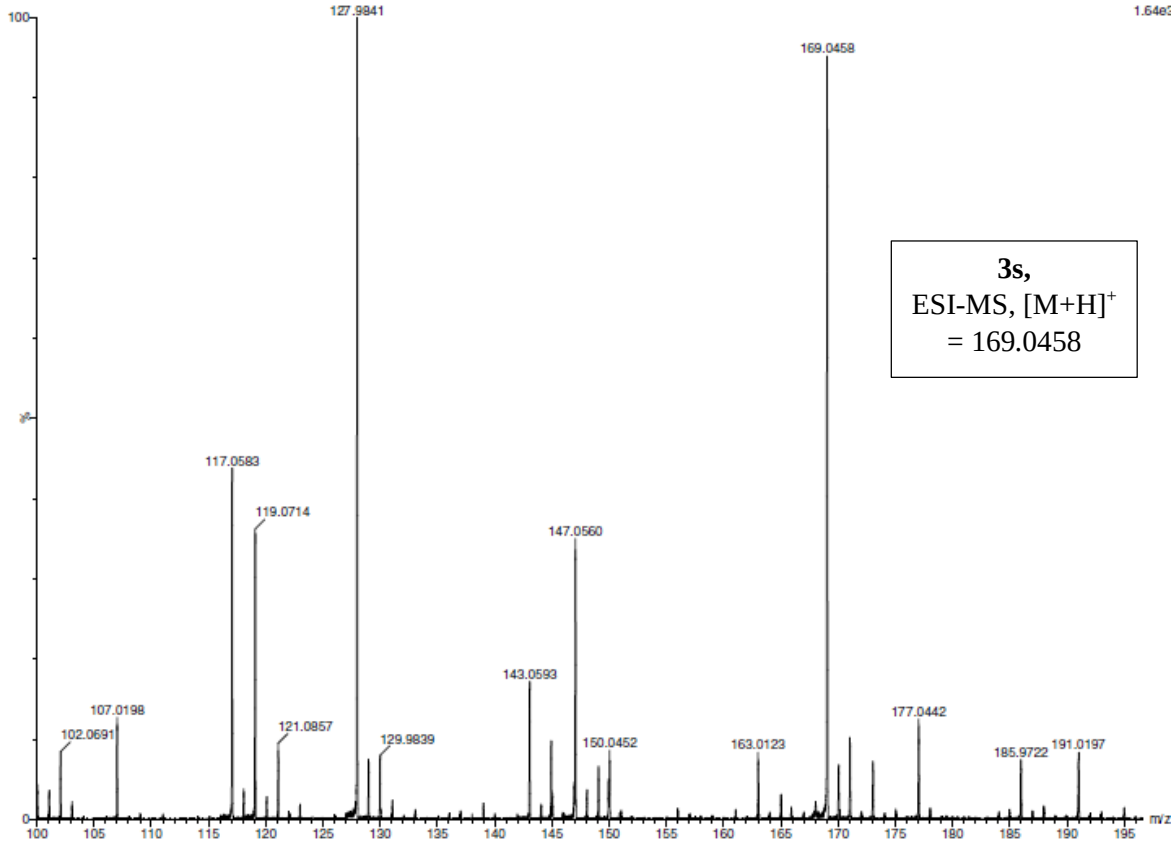
3r, ^{1}H, DMSO-d_6, 600 MHz


198.23
167.54
139.10
138.55
128.57
128.23
40.36
40.22
40.08
39.95
39.81
39.67
39.53
27.46
O
NH2
H3COC
3r, 1H, DMSO-d6,
150 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

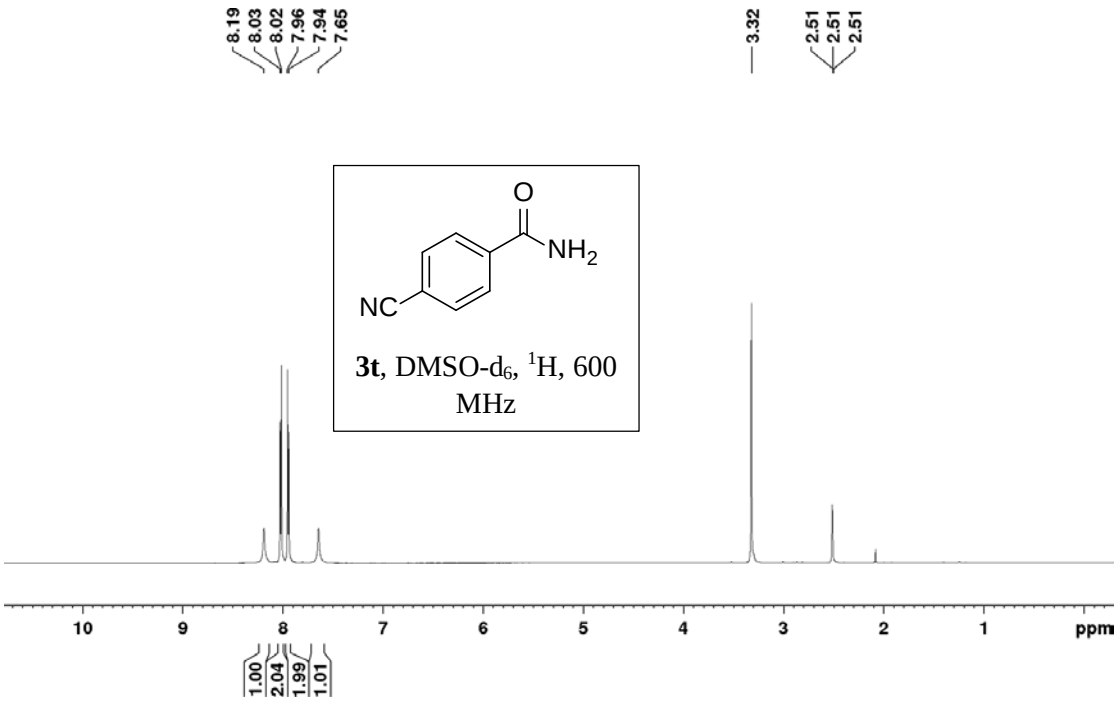

3r,
ESI-MS, [M+H]+
= 164.0706
164.0706
5.93e3
147.0596
165.0830
121.0888
154.0815
m/z


8.31
8.30
8.28
8.11
8.09
7.72
3.33
2.51
2.51
O
NH2
O2N
3s, DMSO-d6,
1H, 600 MHz
11
10
9
8
7
6
5
4
3
2
ppm
3.09
2.12
1.00

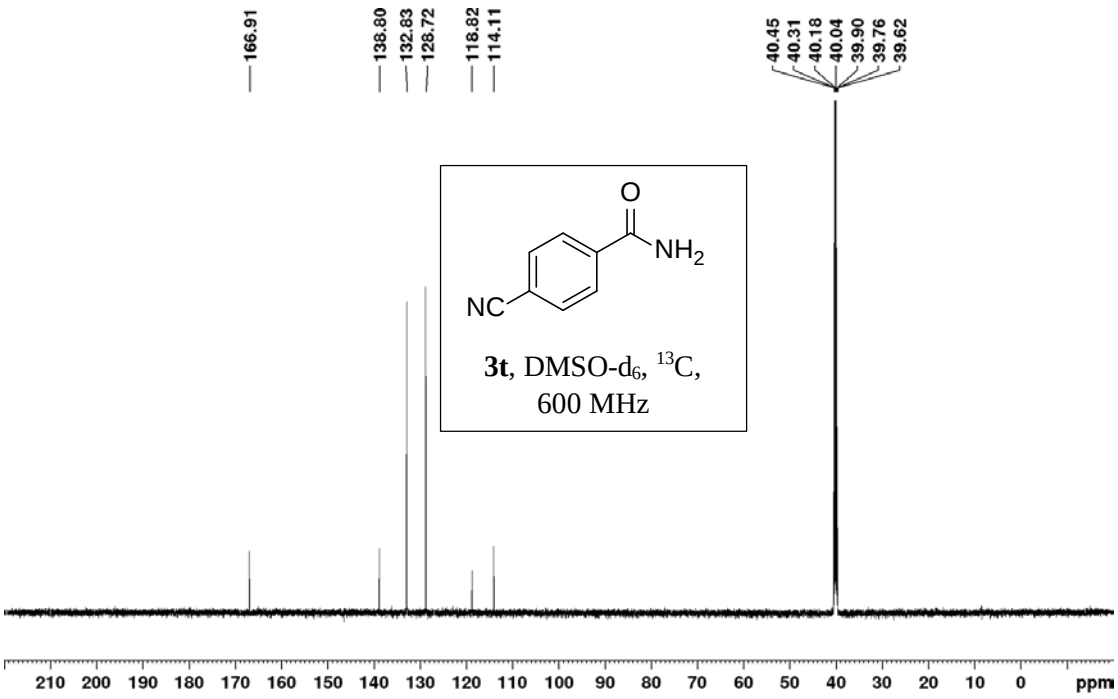

166.68
149.52
140.44
129.38
123.94
40.37
40.23
40.09
39.95
39.81
39.67
39.53
O
NH2
O2N
3s, DMSO-d6,
13C, 150 MHz
200
180
160
140
120
100
80
60
40
20
0
ppm



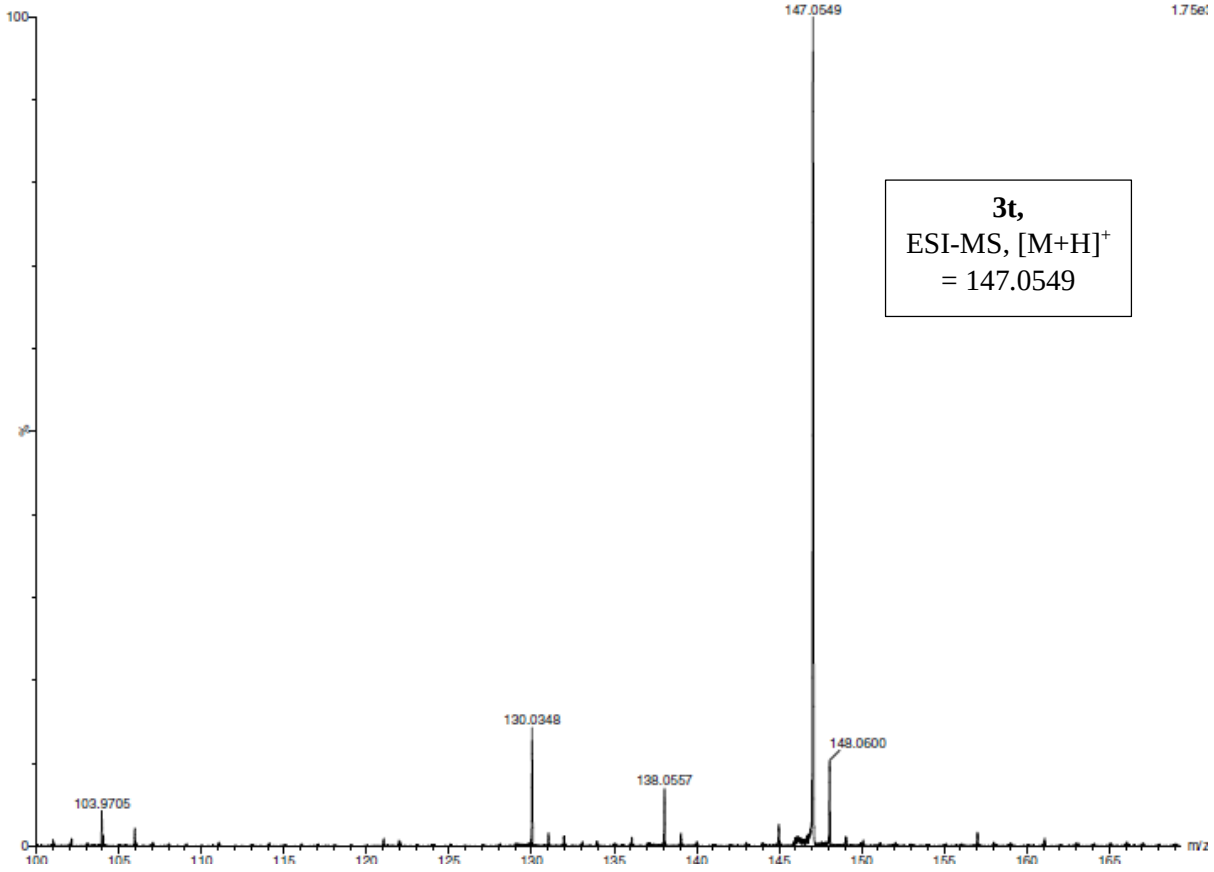
3s,
ESI-MS, $[M+H]^+$ = 169.0458



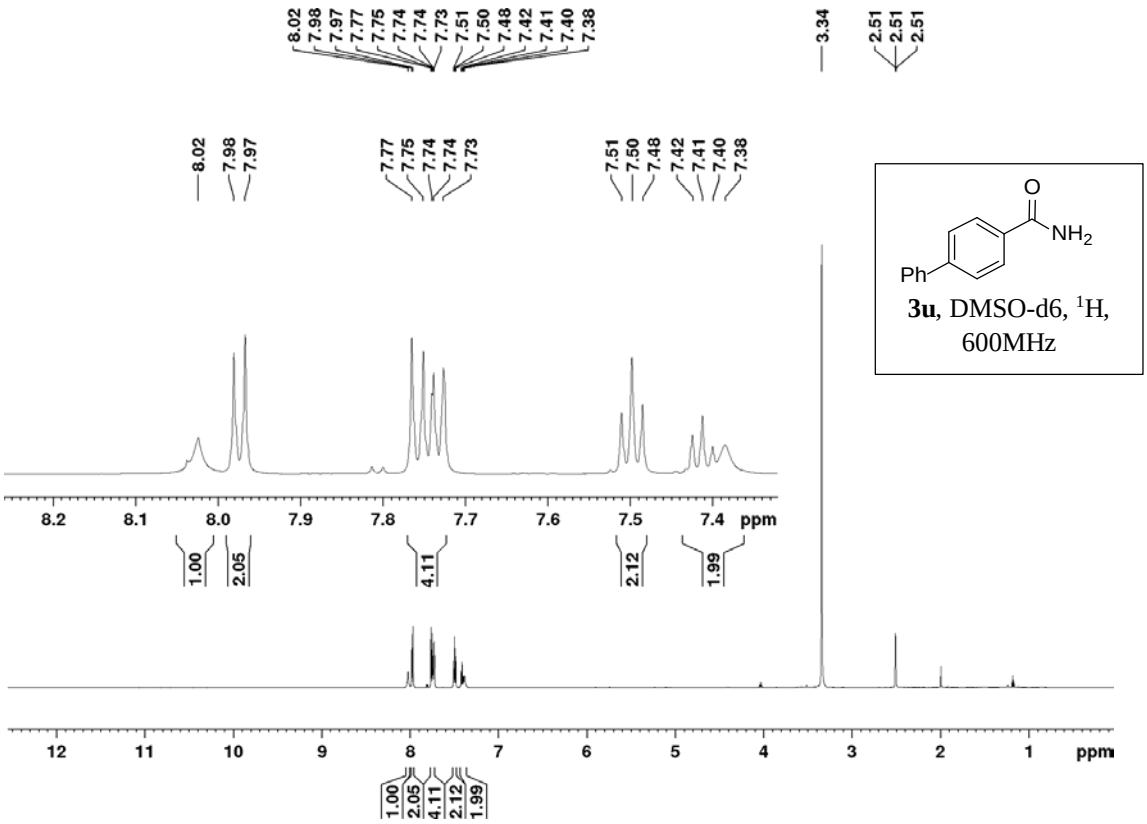
3t, DMSO-d_6, ^{1}H, 600 MHz

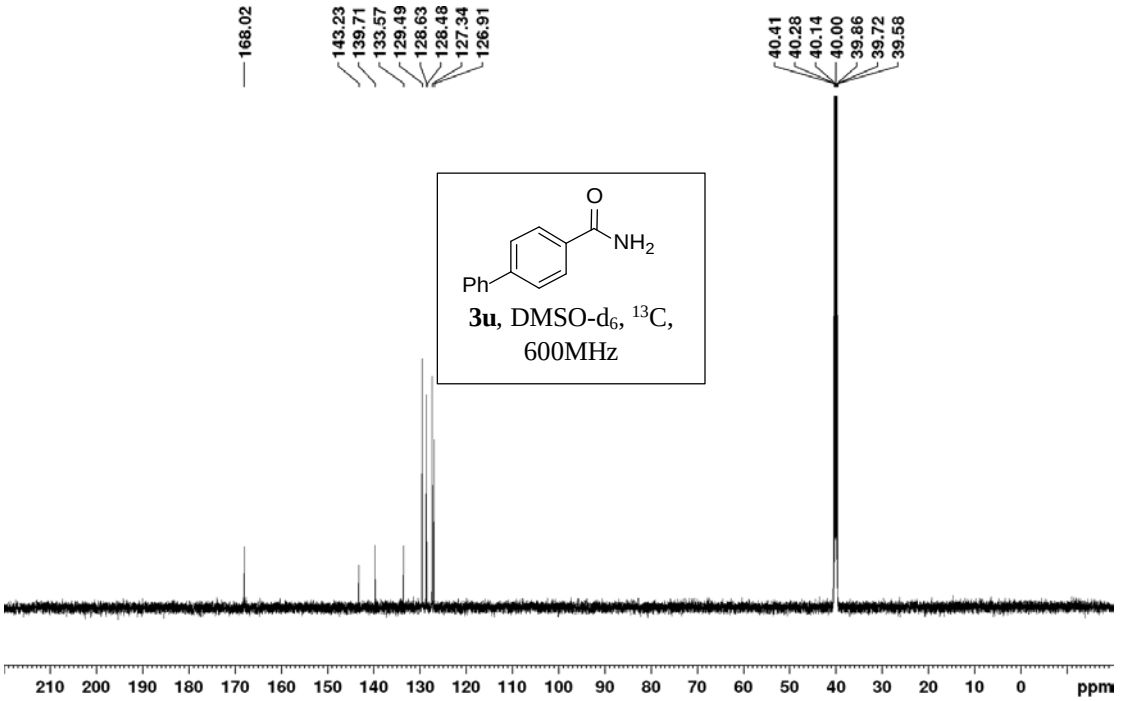


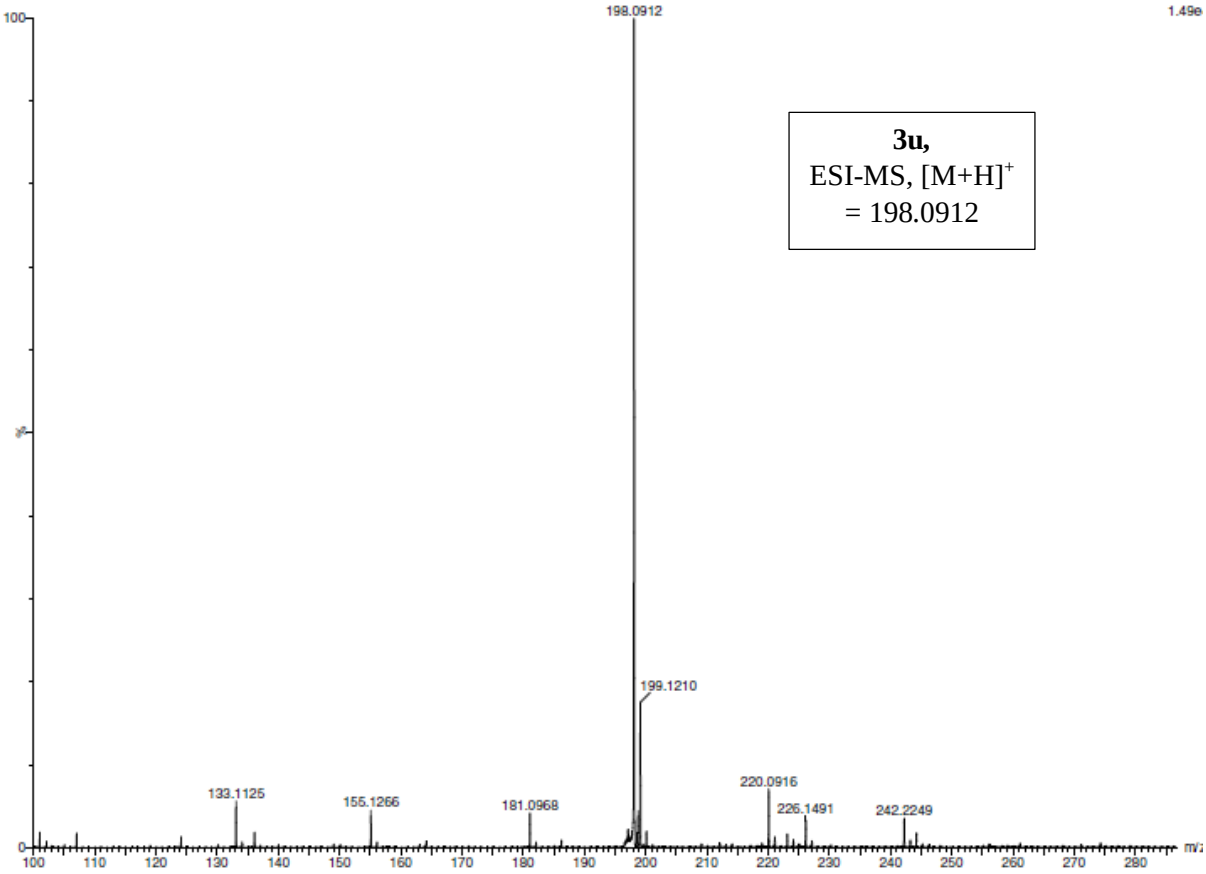
3t, DMSO-d_6, ^{13}C, 600 MHz



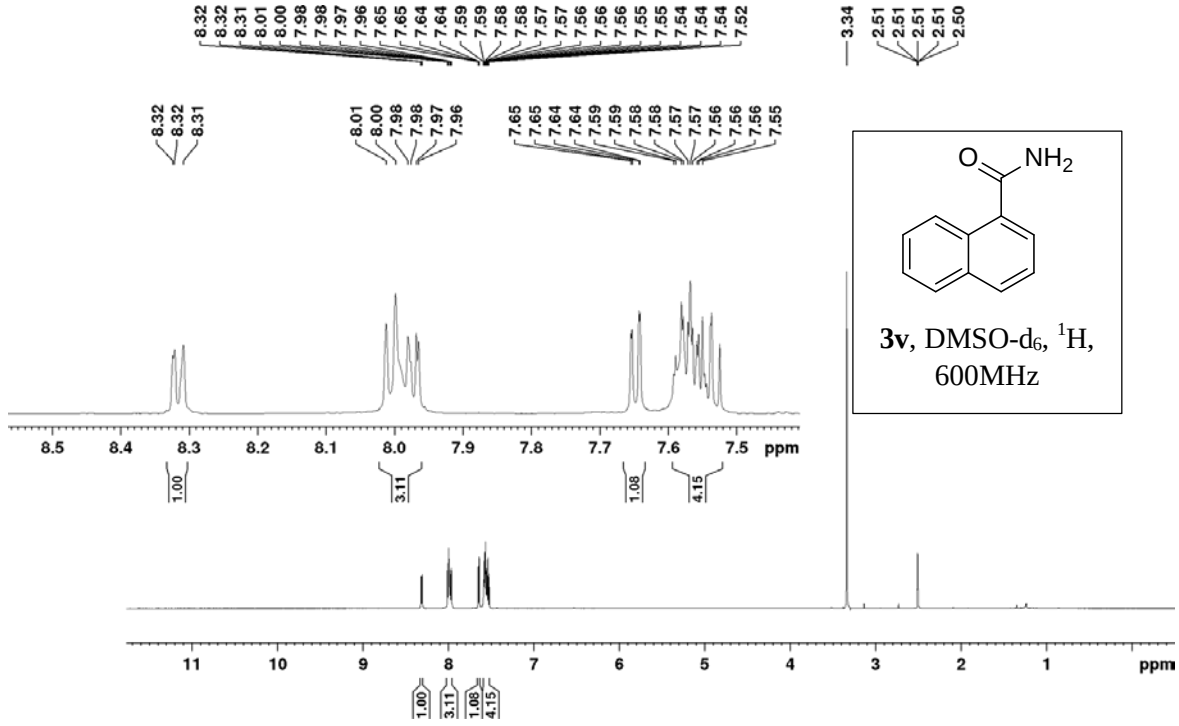
3t,
ESI-MS, $[M+H]^+$ = 147.0549


8.02
7.98
7.97
7.77
7.75
7.74
7.74
7.73
7.51
7.50
7.48
7.42
7.41
7.40
7.38
3.34
2.51
2.51
2.51
O
NH2
Ph
3u, DMSO-d6, 1H, 600MHz
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
ppm
1.00
2.05
4.11
2.12
1.99
12
11
10
9
8
7
6
5
4
3
2
1
ppm

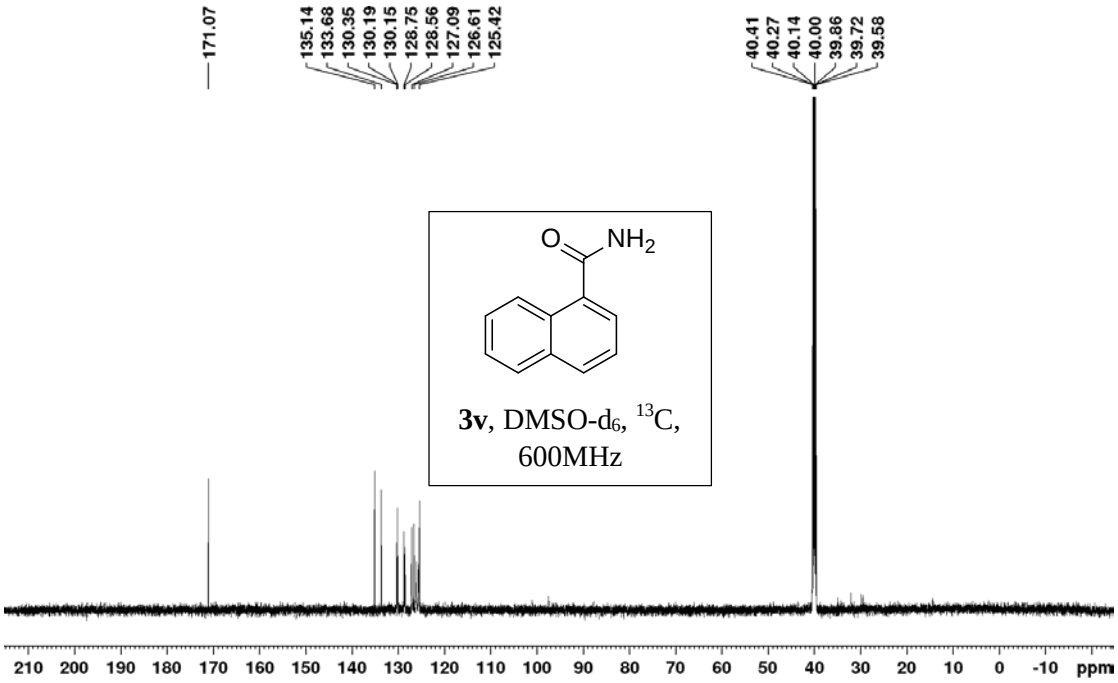

168.02
143.23
139.71
133.57
129.49
128.63
128.48
127.34
126.91
40.41
40.28
40.14
40.00
39.86
39.72
39.58
O
NH2
Ph
3u, DMSO-d6, 13C, 600MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



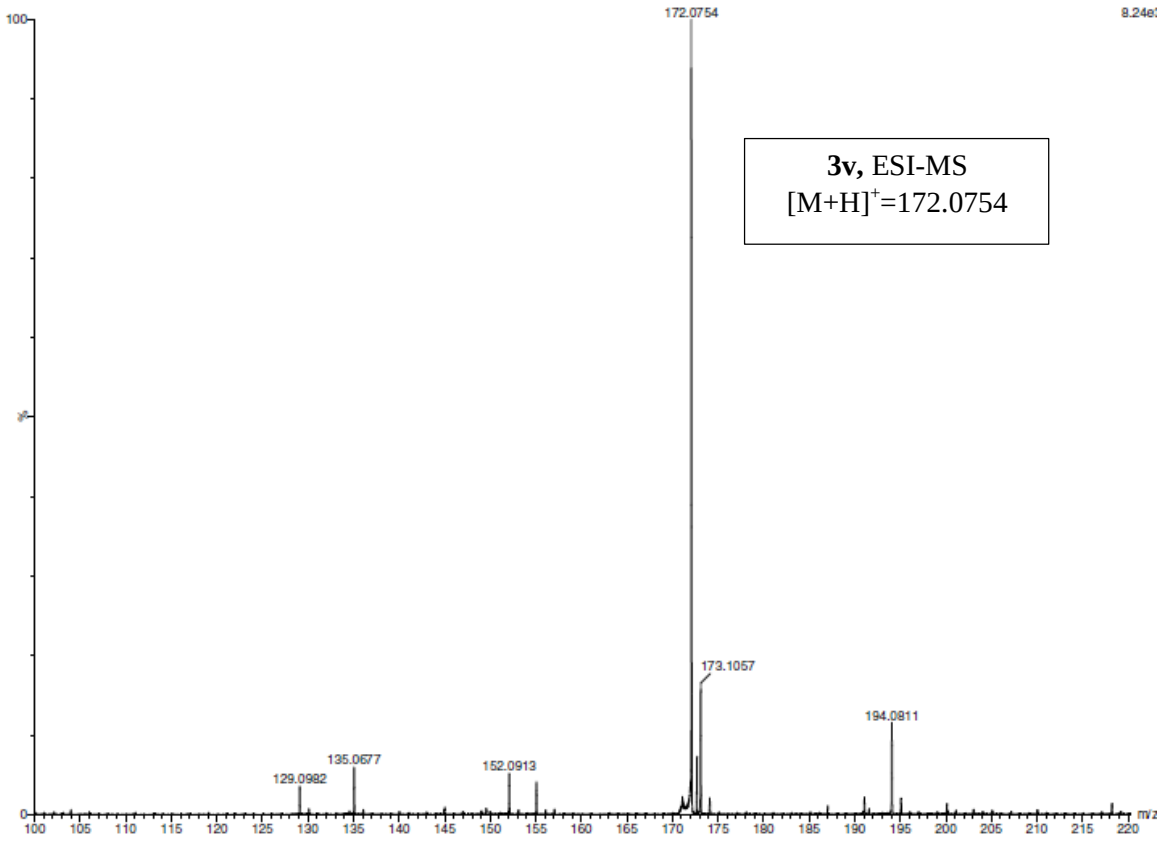
3u,
ESI-MS, $[M+H]^+$
= 198.0912



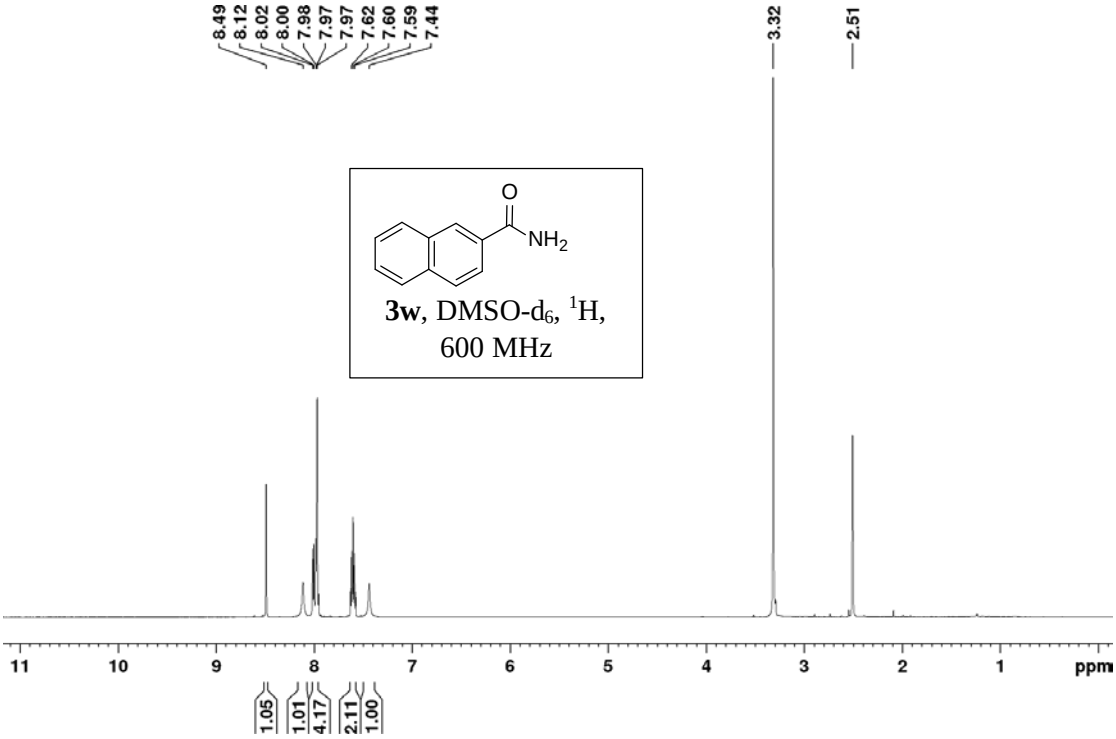
3v, DMSO-d_6, ^{1}H,
600MHz

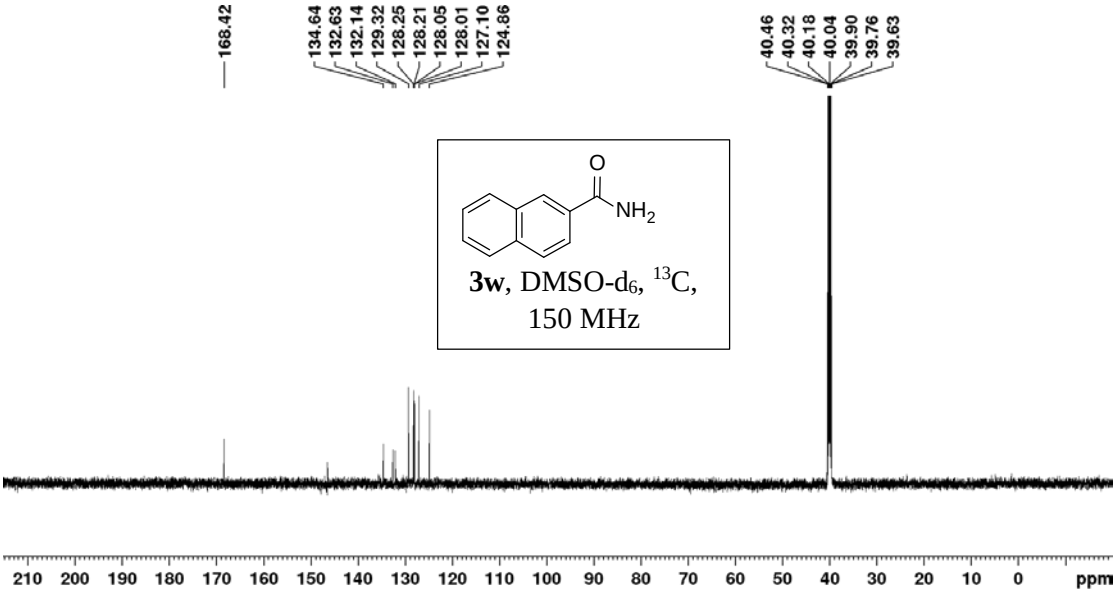


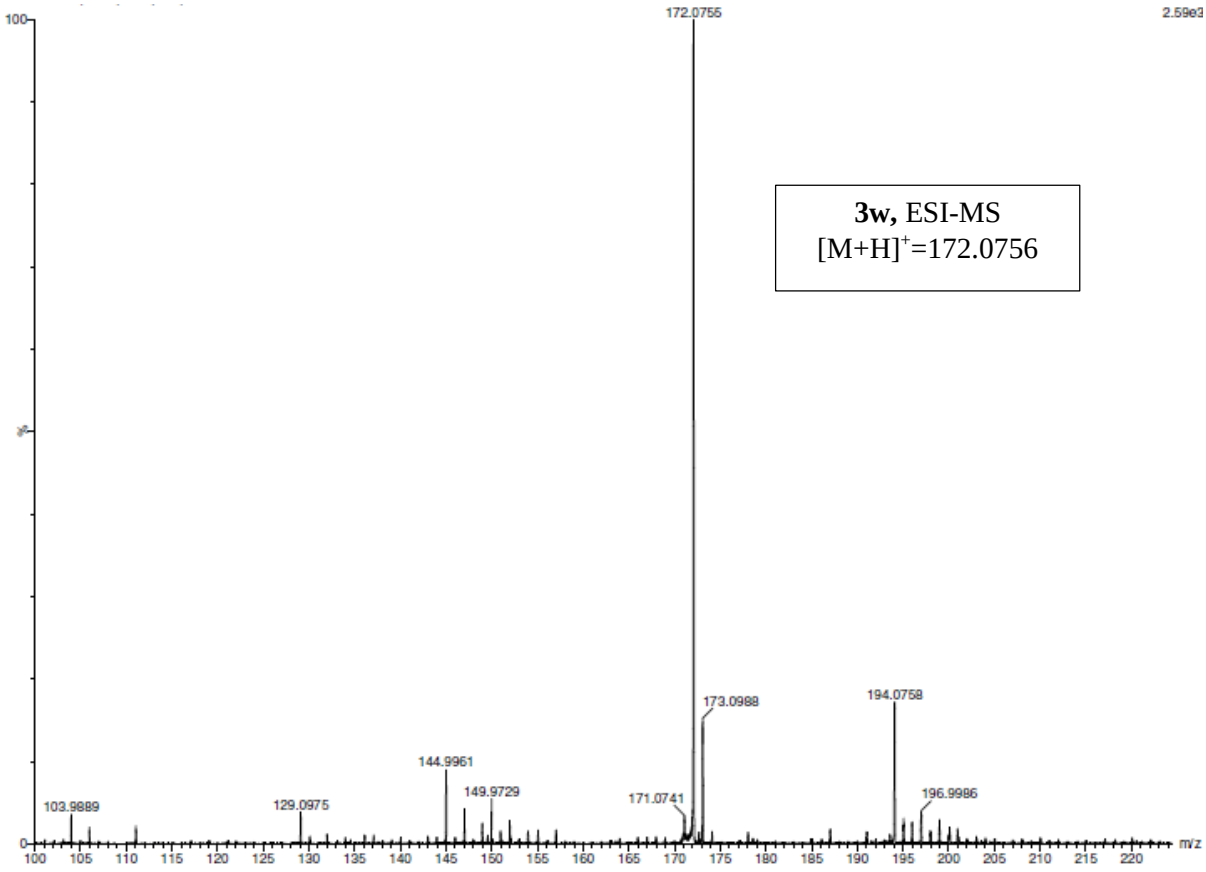
3v, DMSO-d_6, ^{13}C, 600MHz



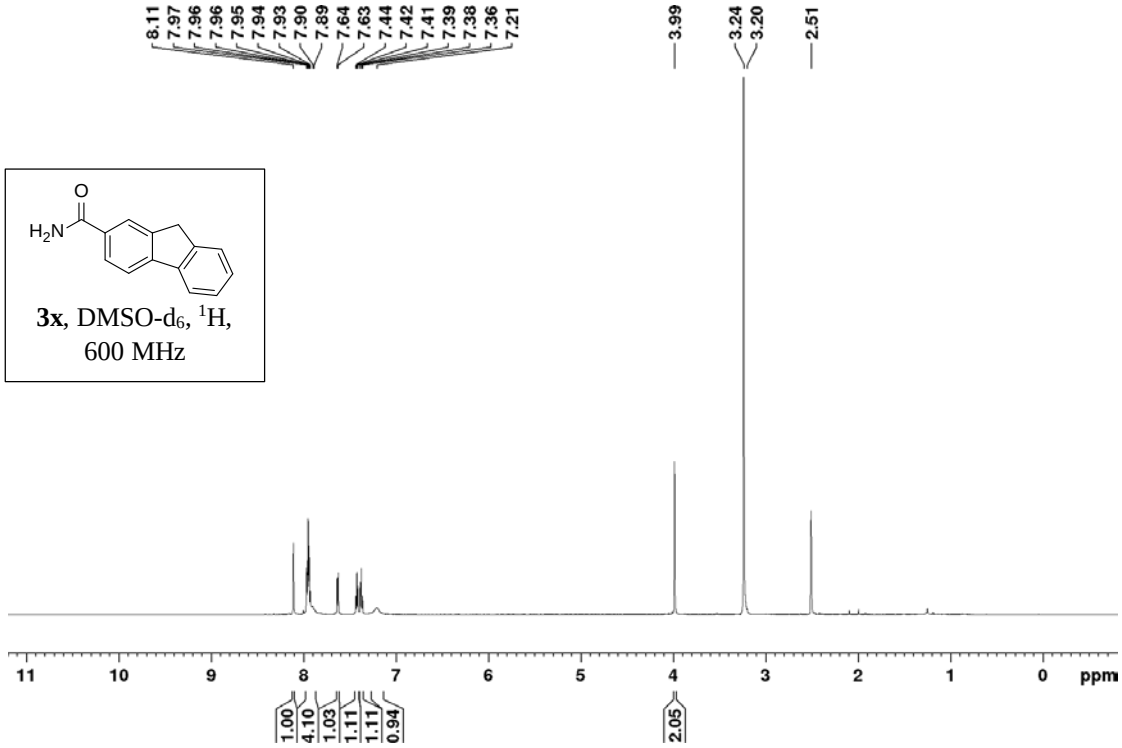
3v, ESI-MS
$[M+H]^+$=172.0754


8.49
8.12
8.02
8.00
7.98
7.97
7.97
7.62
7.60
7.59
7.44
3.32
2.51
O
NH2
3w, DMSO-d6, 1H,
600 MHz
11
10
9
8
7
6
5
4
3
2
1
ppm
1.05
1.01
4.17
2.11
1.00

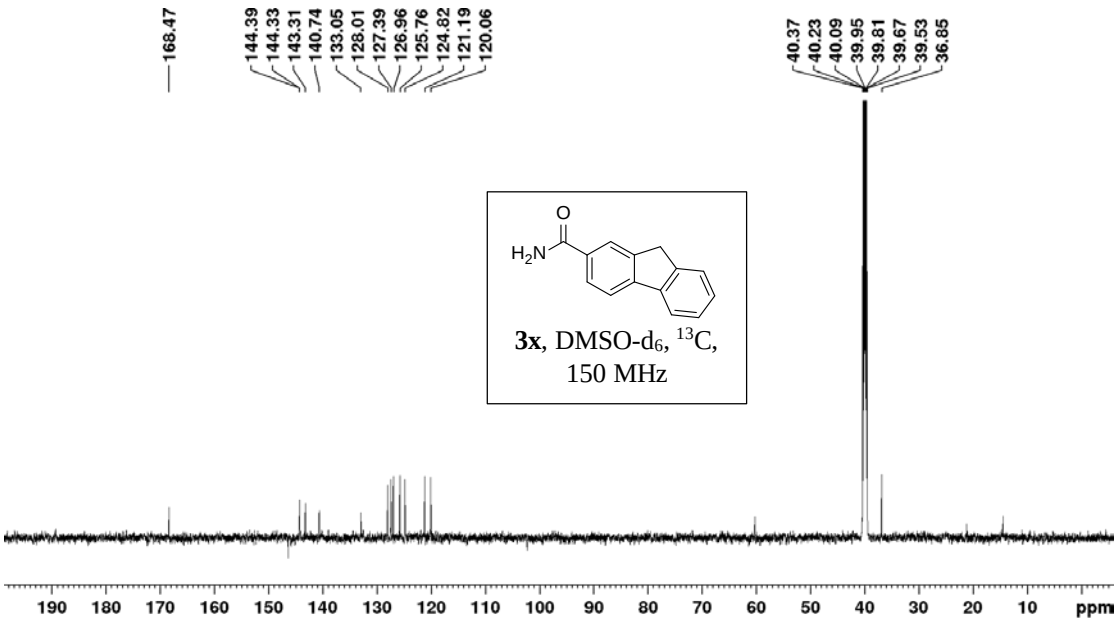

168.42
134.64
132.63
132.14
129.32
128.25
128.21
128.05
128.01
127.10
124.86
40.46
40.32
40.18
40.04
39.90
39.76
39.63
O
NH2
3w, DMSO-d6, 13C,
150 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

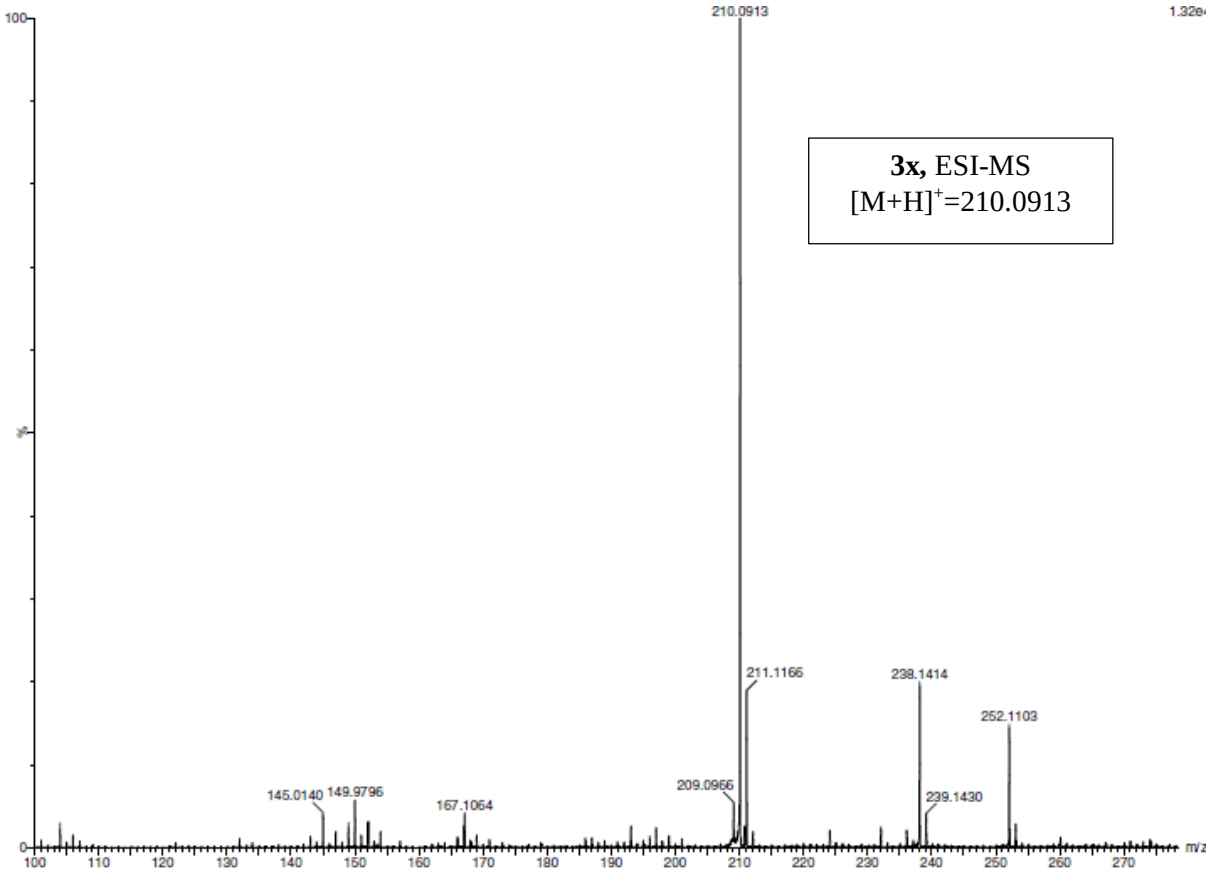


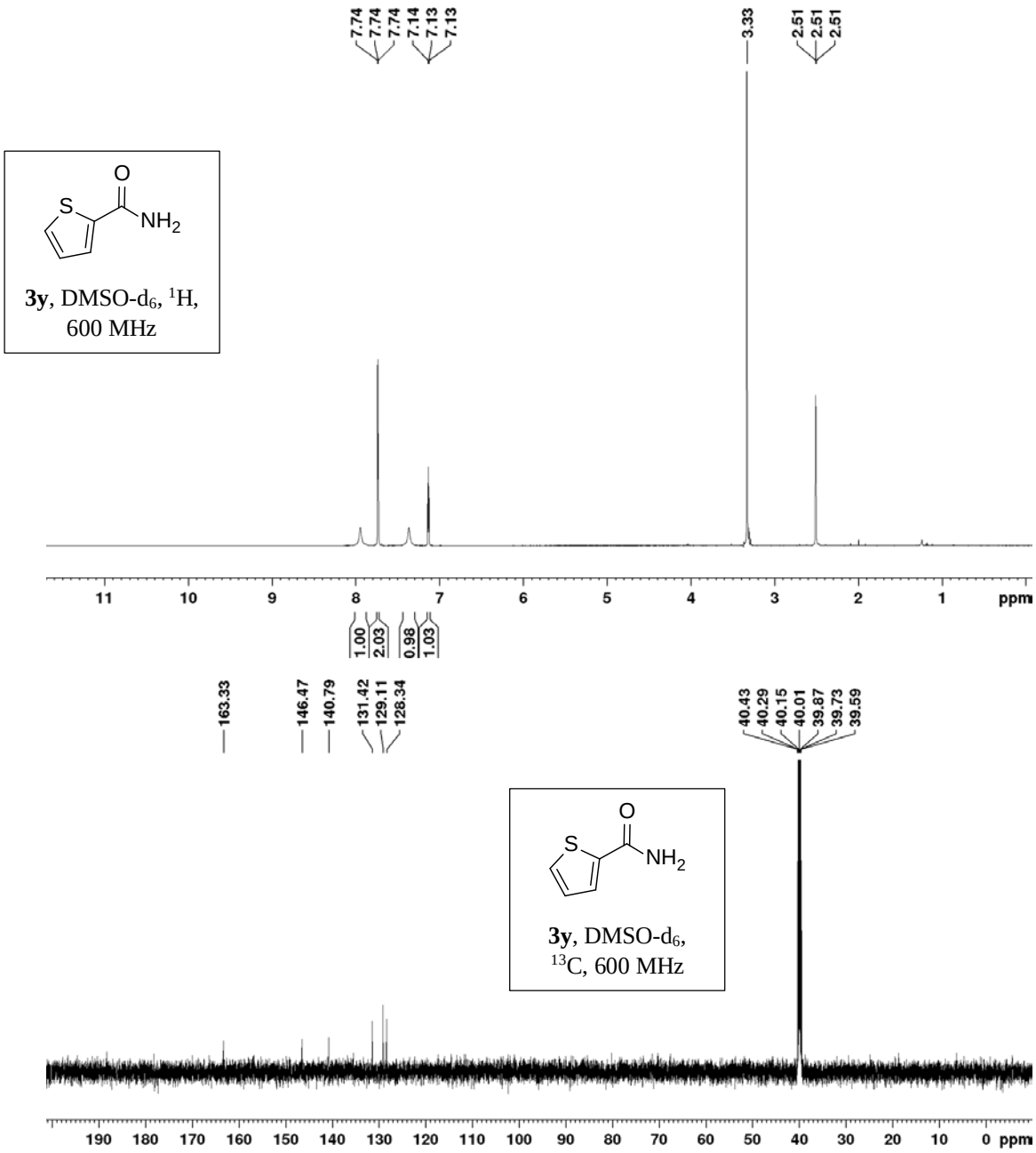
3w, ESI-MS
$[M+H]^+$=172.0756

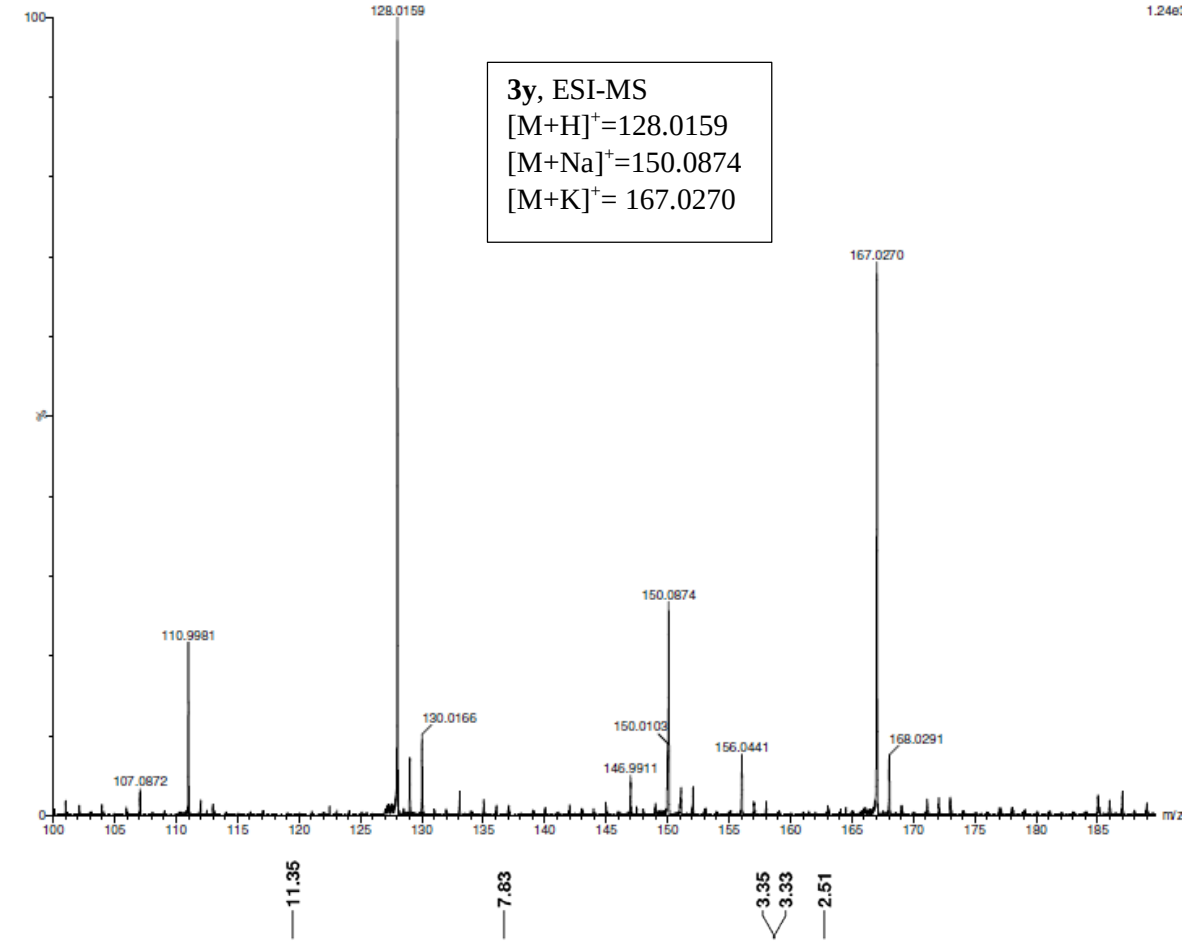


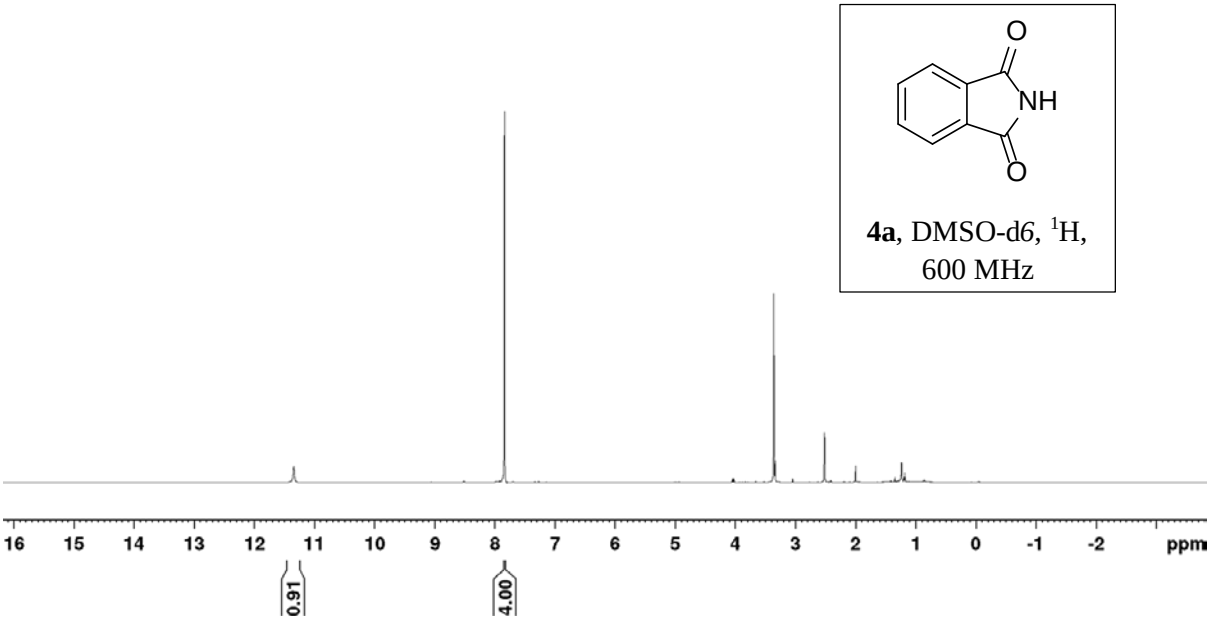
3x, DMSO-d_6, ^{1}H,
600 MHz

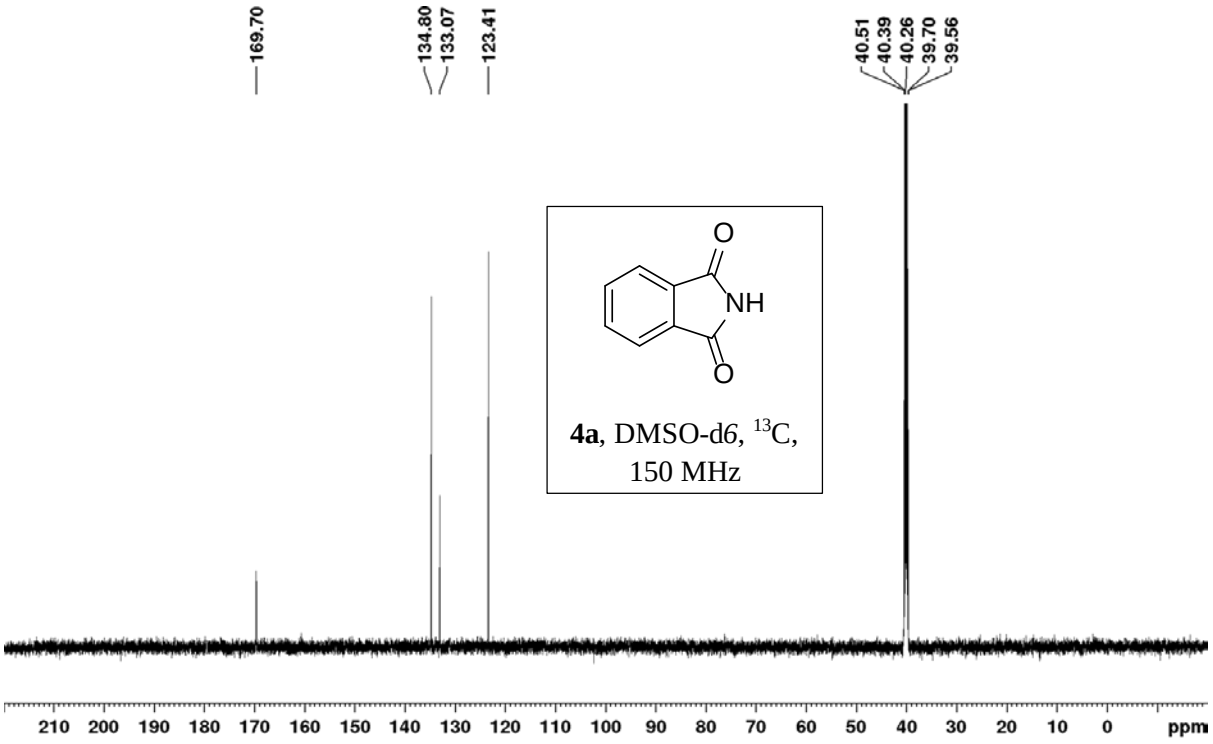

168.47
144.39
144.33
143.31
140.74
133.05
128.01
127.39
126.96
125.76
124.82
121.19
120.06
40.37
40.23
40.09
39.95
39.81
39.67
39.53
36.85
O
H2N
3x, DMSO-d6, 13C,
150 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


100
210.0913
1.326e
3x, ESI-MS
[M+H]+=210.0913
211.1166
238.1414
252.1103
145.0140
149.9796
167.1064
209.0966
239.1430
0
100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270
m/z

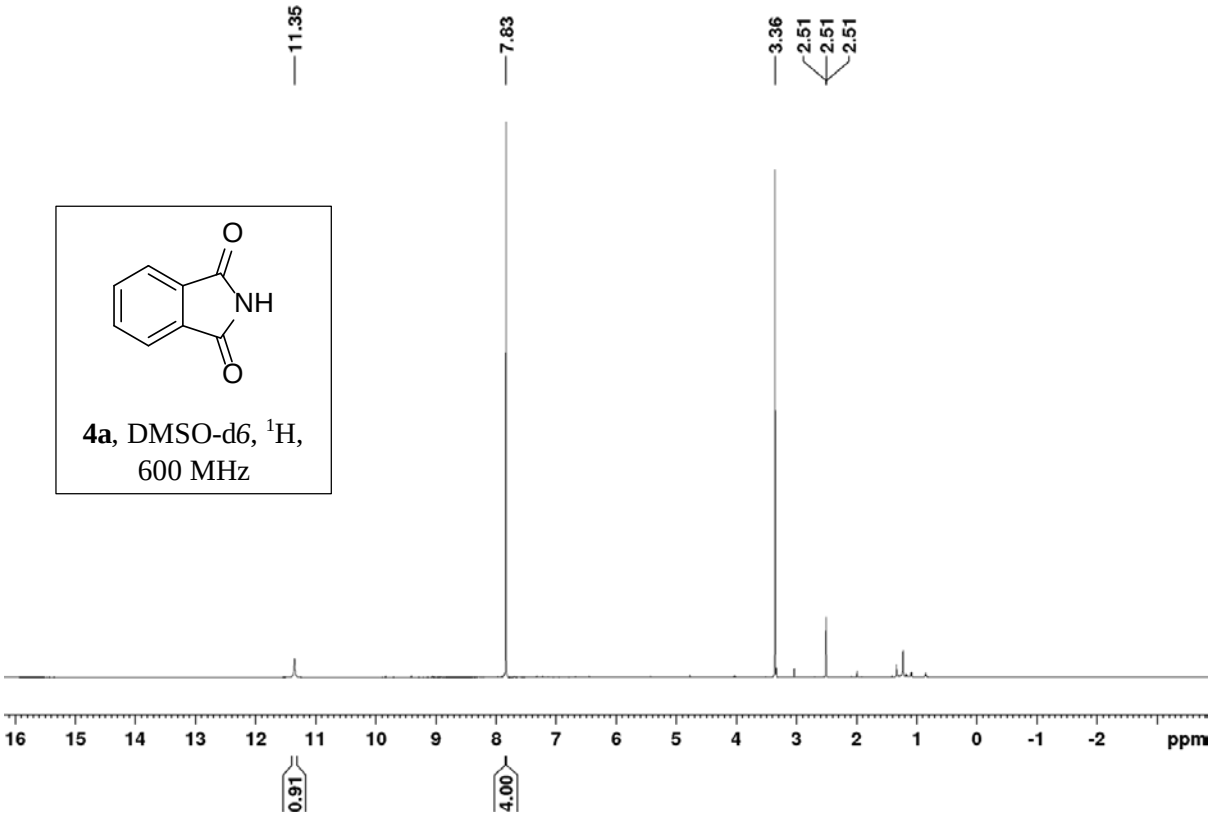

7.74
7.74
7.74
7.14
7.13
7.13
3.33
2.51
2.51
2.51
O
S
NH2
3y, DMSO-d6, 1H, 600 MHz
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.03
0.98
1.03
163.33
146.47
140.79
131.42
129.11
128.34
40.43
40.29
40.15
40.01
39.87
39.73
39.59
O
S
NH2
3y, DMSO-d6, 13C, 600 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


3y, ESI-MS
[M+H]+=128.0159
[M+Na]+=150.0874
[M+K]+= 167.0270
128.0159
167.0270
150.0874
110.9981
130.0166
150.0103
156.0441
168.0291
146.9911
107.0872
11.35
7.83
3.35
3.33
2.51

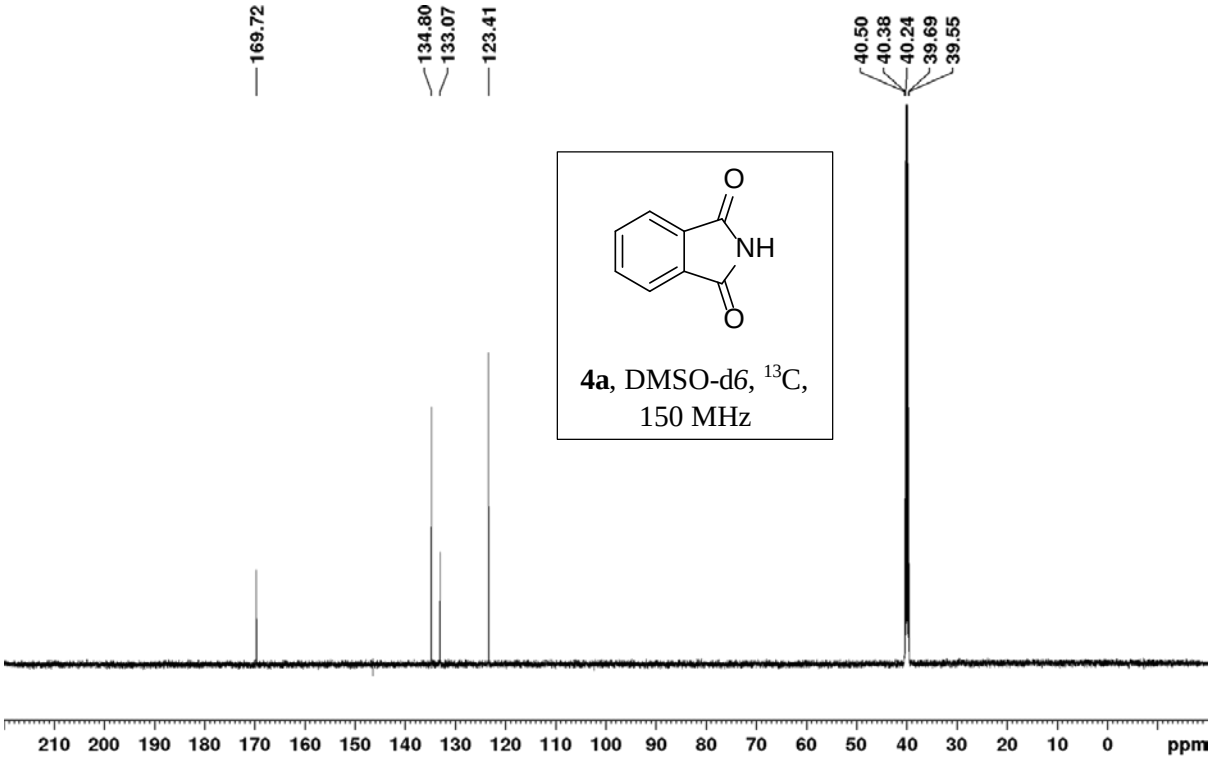

O
NH
O
4a, DMSO-d6, 1H, 600 MHz
0.91
4.00
ppm



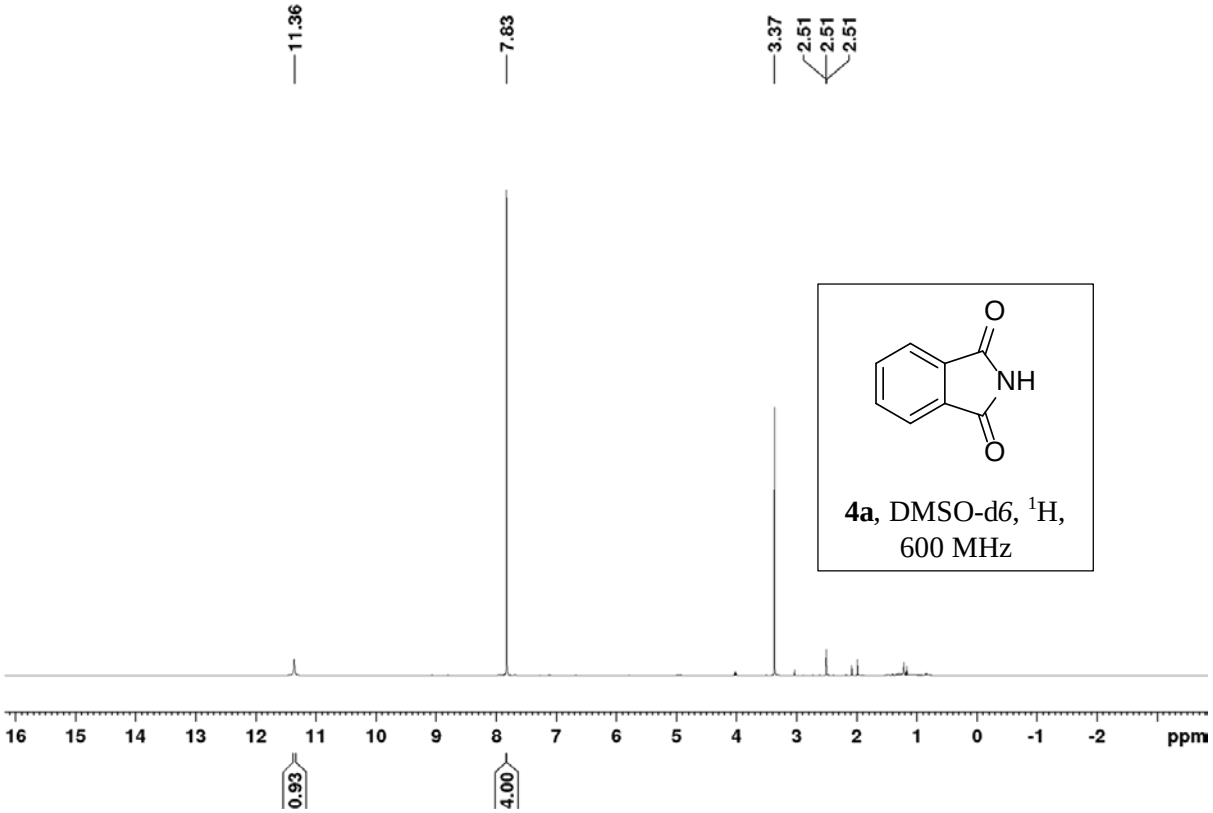
4a, DMSO-d*6*, ^{13}C, 150 MHz



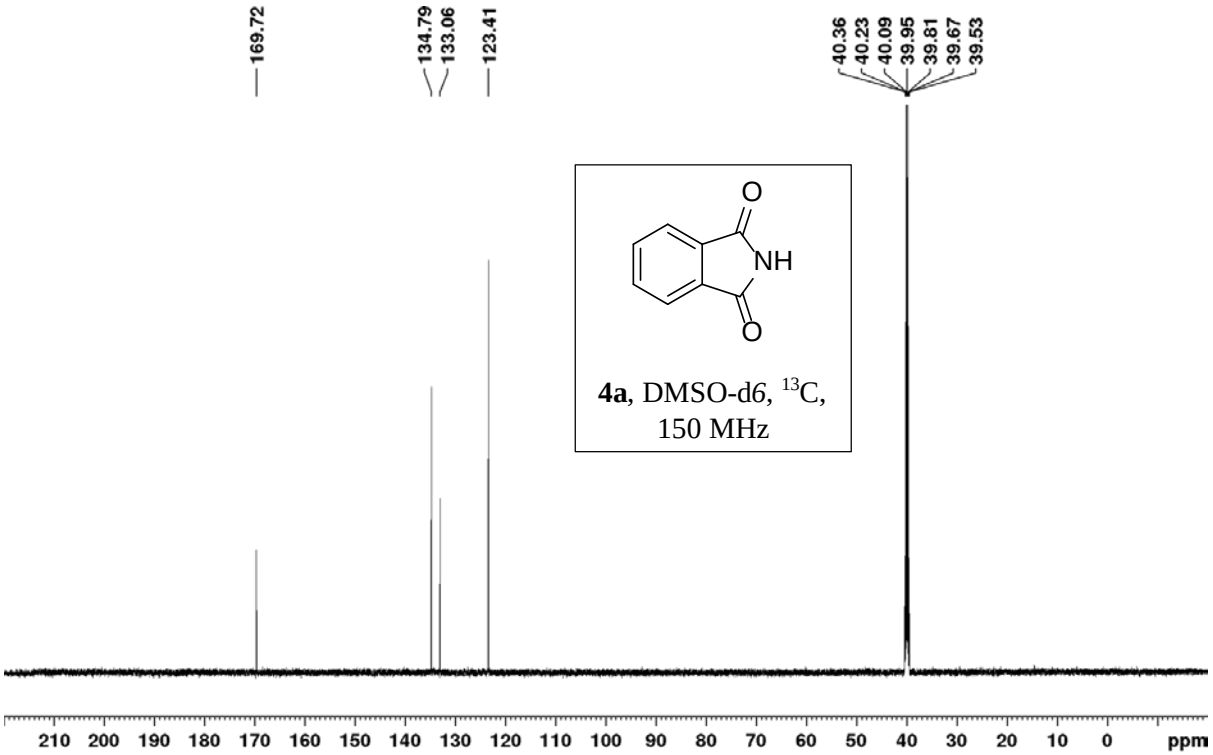
4a, DMSO-d*6*, ^{1}H, 600 MHz



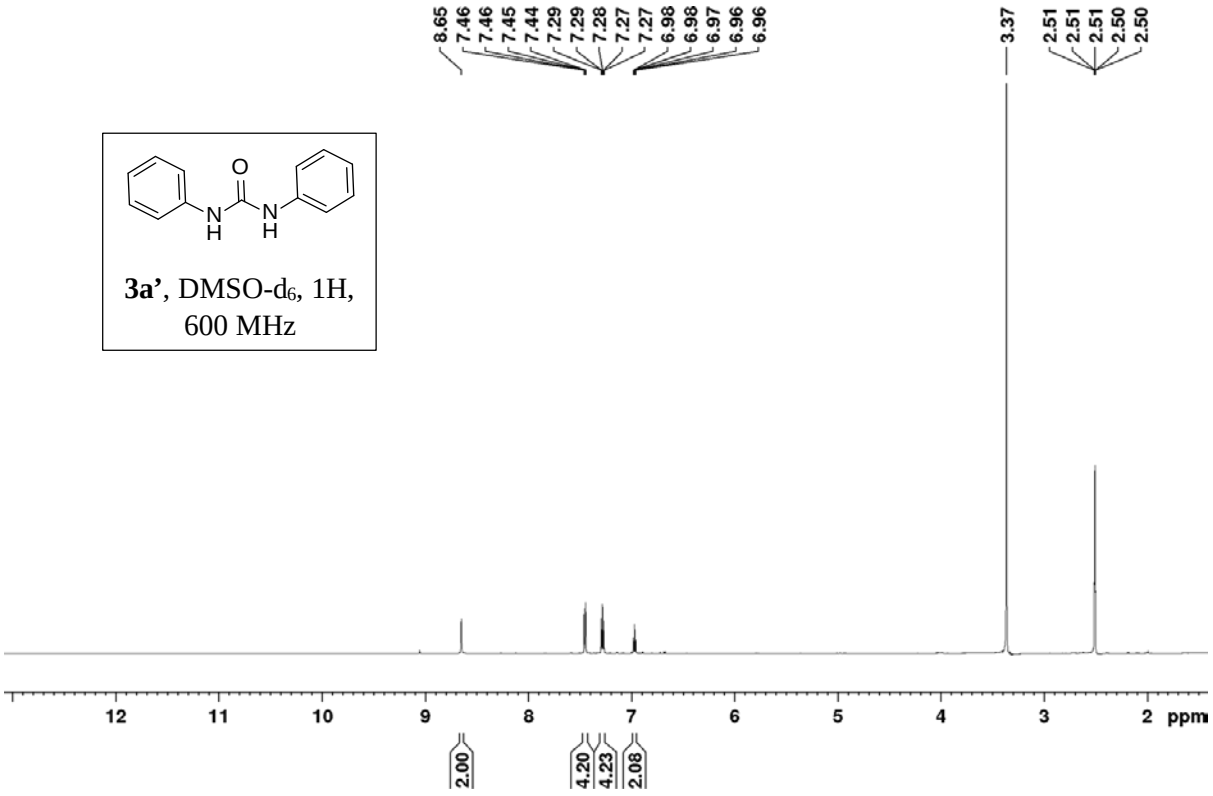
4a, DMSO-d*6*, ^{13}C, 150 MHz



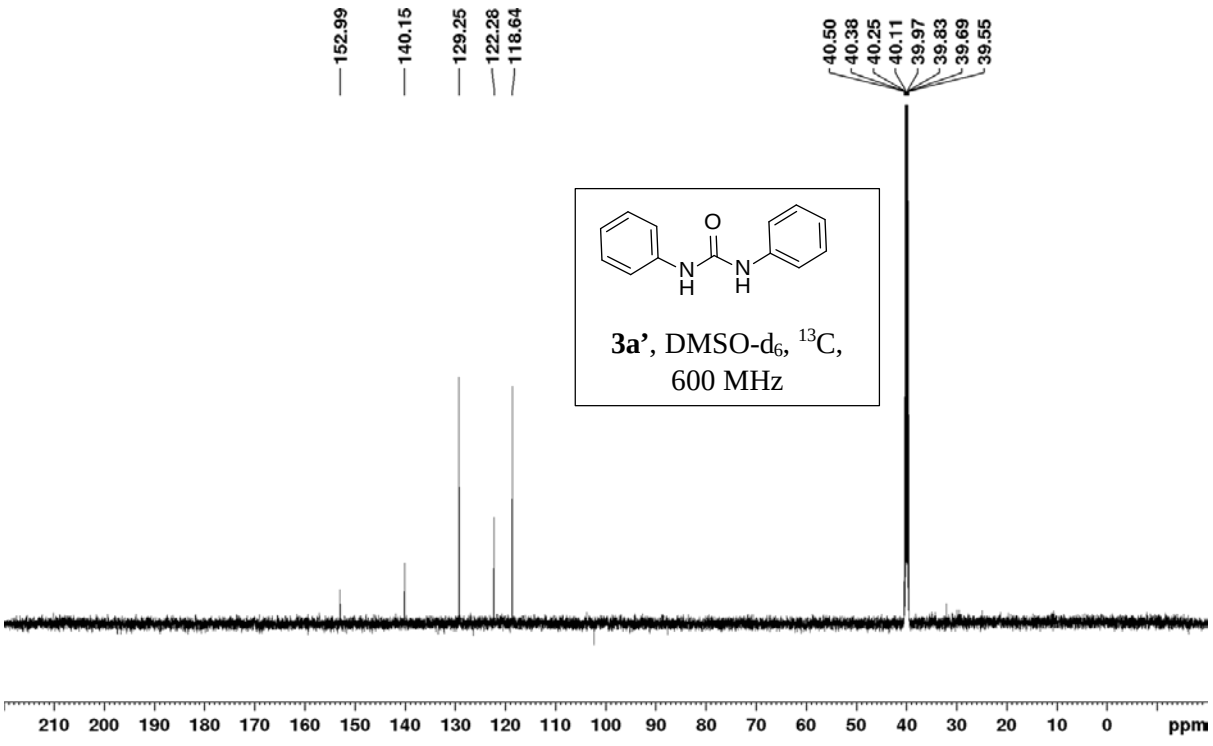
4a, DMSO-d*6*, ^{1}H, 600 MHz

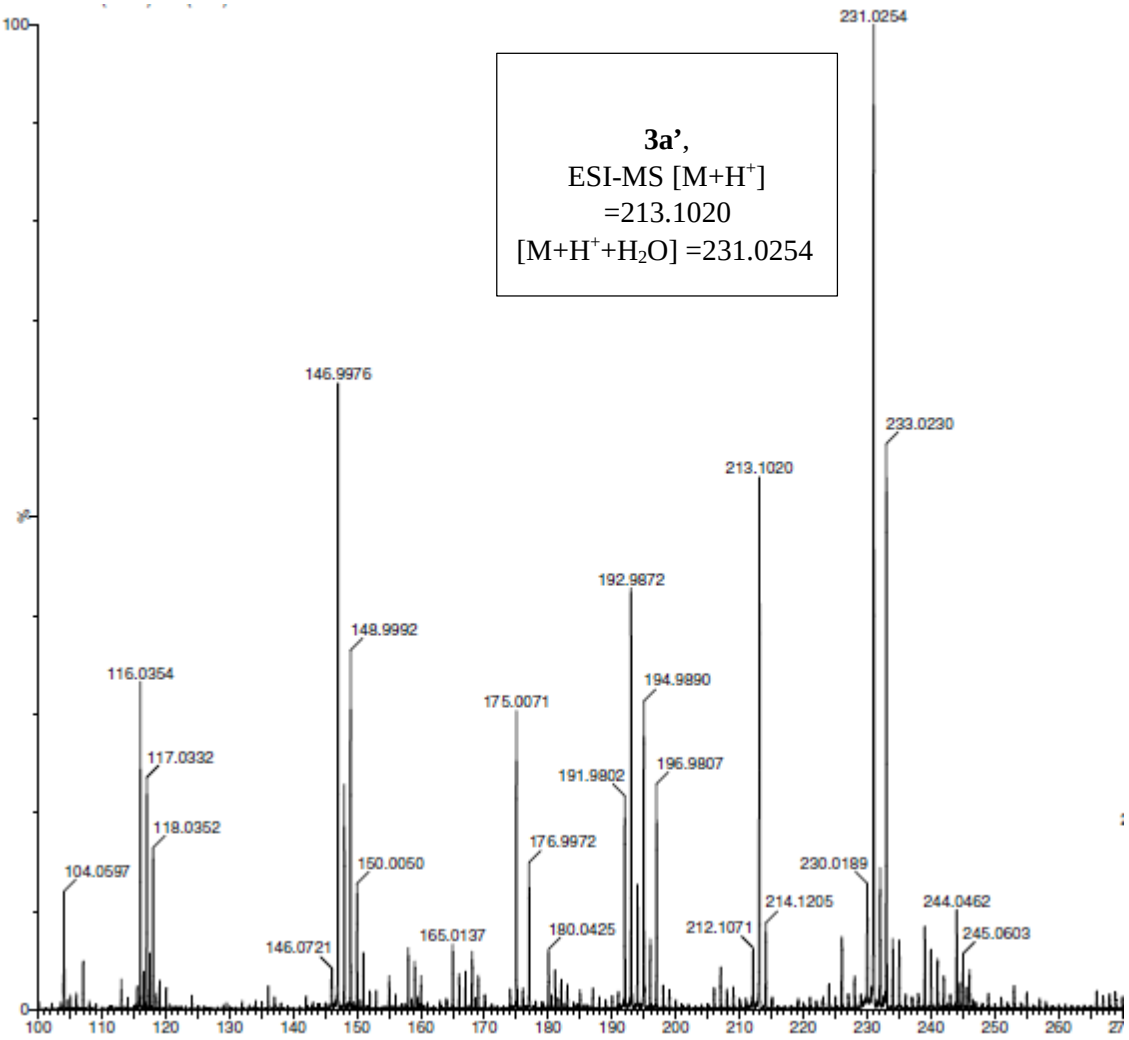


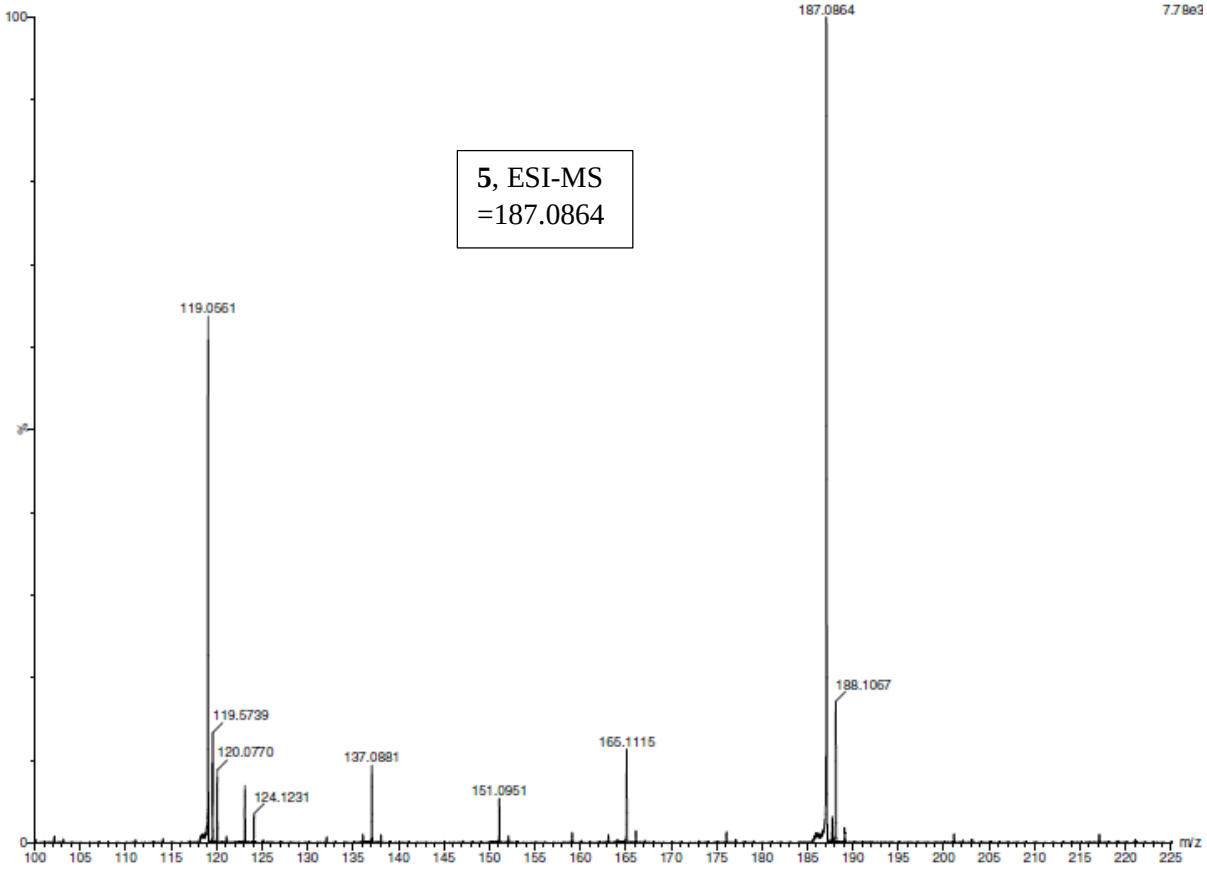
4a, DMSO-d*6*, ^{13}C, 150 MHz



3a', DMSO-d_6, 1H, 600 MHz


152.99
140.15
129.25
122.28
118.64
40.50
40.38
40.25
40.11
39.97
39.83
39.69
39.55
O
N
H
N
H
3a', DMSO-d6, 13C,
600 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


3a',
ESI-MS [M+H+]
=213.1020
[M+H+ +H2O] =231.0254
100
%
0
231.0254
233.0230
213.1020
146.9976
192.9872
148.9992
194.9890
116.0354
175.0071
117.0332
191.9902
196.9807
118.0352
176.9972
104.0597
150.0050
230.0189
214.1205
244.0462
212.1071
180.0425
165.0137
245.0603
146.0721
100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260



5, ESI-MS =187.0864