Supported Pd-catalyzed ring-opening and chemoselective aminocarbonylative coupling of benzoxazoles and aryl iodides

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A. General Information

High quality reagents and analytical grade solvents were purchased from Sigma Aldrich, TCI Chemicals, Merck and Sd Fine Chem. Ltd. Pd/C, Pd/Al_2O_3, and $Pd(OAc)_2$ and were purchased from TCI chemicals and Sigma Aldrich respectively. Reactions were monitored using TLC which was performed on pre-coated silica gel plates 60 F254 (purchased from Merck) in UV light detector. Silica gel (60-120 mesh size) for column chromatography purchased from Merck was used for the purification of compounds. ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance 600 spectrometer operating at Bruker Advance 600 spectrometer (600 MHz, ^1H at 600 MHz, ^{13}C at 151 MHz). Spectra were recorded at 25 °C in DMSO-*d6* [residual DMSO (δ_H 2.50 and 3.33 ppm) and DMSO (δ_C 39.52 ppm)] with TMS as an 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; m, multiplet; brs, broad singlet. Mass spectra were recorded on electrospray ionization (ESI) quadrupole time of flight (Q-TOF) mass spectrometer.

B. Procedure for the fabrication of polystyrene resin supported palladium (Pd@PS) catalyst.

The solution of 30 mg $NaBH_4$ in 10 mL of water was added to 1 g of Amberlite® IRA 900 Cl^- resin (PS) in a 50 mL flask. The resulting heterogeneous mixture was stirred for 4-5 h at room temperature. Then, partial borohydride exchanged resin was washed with water to neutralize the pH and later with acetone to remove excess of water from polymer. This exchanged polymer resin ($PS\text{-}BH_4^-$) was dried under reduced pressure. The $PS\text{-}BH_4^-$(1 g) was added into the warm (100 °C) solution of palladium acetate (10 mg) in DMF and the mixture was stirred for few minutes or till the brown colour solution changed to colourless and white $PS\text{-}BH_4^-$ simultaneously turned black giving Pd@PS catalyst. The Pd@PS catalyst was filtered through a cotton bed, washed with water and acetone, and dried under reduced pressure.

C. Optimization studies

Table S1: Effect of Oxalic acid equivalency:

Sr. No.	Oxalic acid (equiv.)	Isolated yield of 3a (%)
1	7	75
2	6	75
3	5	68
4	4	57

Reaction conditions: Inner vial: **1a** (1 equiv.), **2a** (1.5 equiv.), Pd@PS (3 mol%), K_2CO_3 (1.5 equiv.), Imidazole (1 equiv.), 1.5 mL of DMF; Outer vial: oxalic acid in 0.5 mL of DMF heated for 24 h at 130 °C

Table S2: Screening of solvent:

Sr. No.	Solvent	Isolated yield of 3a (%)
1	DMF	75
2	Toluene	nd
3	Xylene	nd
4	PEG-400	32
5	DMA	65
6	1,4 Dioxane	nd
7	Nitromethane	nd
8	Anisole	nd

Reaction conditions: Inner vial: **1a** (1 equiv.), **2a** (1.5 equiv.), Pd@PS (3 mol%), K_2CO_3 (1.5 equiv.), Imidazole (1 equiv.), 1.5 mL of solvent; Outer vial: oxalic acid (6 equiv.) in 0.5 mL of DMF heated for 24 h at 130 °C

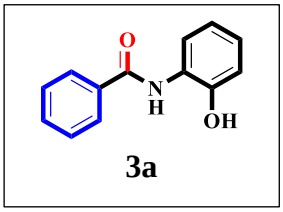
Table S3: Screening of time:

Sr. No.	Time (hrs)	Isolated yield of 3a (%)
1	8	40
2	16	64
3	20	70
4	24	75

Reaction conditions: Inner vial: **1a** (1 equiv.), **2a** (1.5 equiv.), Pd@PS (3 mol%), K_2CO_3 (1.5 equiv.), Imidazole (1 equiv.), 1.5 mL of DMF; Outer vial: oxalic acid (6 equiv.) in 0.5 mL of DMF.

D. General experimental procedure and characterization data for the synthesized compounds

N-(2-hydroxyphenyl)benzamide (3a)

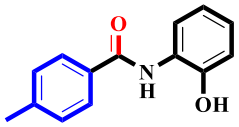


3a

We executed the reaction using Double-Vial (DV) system comprises of inner vial of 2 mL and outer vial of 5 mL and the entire system was fitted with PTFE faced black solid cap. Initially, the inner vial of the DV system was charged with Iodobenzene **1a** (0.245 mmol, 27.3 µL), benzoxazole **2a** (0.490 mmol, 58 mg), Pd@PS (0.007 mmol, 154 mg), K_2CO_3 (0.36 mmol, 50 mg), imidazole (0.245, 16.6 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.47 mmol, 132 mg) in 0.5 mL of DMF. Thereafter, the inner vial having contents was positioned carefully inside the outer vial (5 mL) containing oxalic acid/DMF (0.5 mL). Further, the entire system was capped with the solid PTFE faced

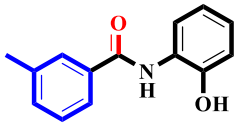
cap and further tightened with Teflon tape to check the leakage of gas. The whole system was allowed to heat in oil bath at 130 ^{o}C for 24 hrs. The reaction progress was observed with the help of TLC. After the accomplishment of the reaction, the inner vial containing contents was removed and the contents of the inner vial were transferred to a separatory funnel. Further, 3 mL of water was added in the reaction mixture and organic contents were extracted with ethyl acetate. The combined organic layer was passed over anhydrous Na_2SO_4 and concentrated under reduced pressure. The concentrated crude mixture was further purified by silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) afforded **3a** as light pink solid (39 mg, 75% yield); ^{1}H ($CDCl_3$, 600 MHz) δ *(ppm)* 9.75 (s, 1H), 9.52 (s, 1H), 7.97-7.98 (m, 2H), 7.68-7.70 (m, 1H), 7.58-7.61 (m, 1H), 7.52-7.55 (m, 1H), 7.03-7.06 (m, 1H), 6.92-6.94 (m, 1H), 6.83-6.85 (m, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ *(ppm)* 165.44, 149.51, 134.56, 131.84, 128.69, 127.67, 126.06, 125.87, 124.28, 119.22, 116.18. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{12}NO_2^+$ is 214.0863, obsd. 214.0856.

***N*-(2-hydroxyphenyl)-4-methylbenzamide (3b)**



Prepared as described for **3a**; reaction of 4-iodotoluene **1b** (0.229 mmol, 50 mg), benzoxazole **2a** (0.343 mmol, 41 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.343 mmol, 42 mg), imidazole (0.229, 15.5 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.37 mmol, 123 mg) in 0.5 mL of DMF gave **3b** after purification silica gel (mesh 60:120) column chromatography (15 % EtOAc in n-hexane) as Light pink solid (36 mg, 69% yield); ^{1}H ($CDCl_3$, 600 MHz) δ *(ppm)* 9.78 (s, 1H), 9.48 (s, 1H), 7.89 (d, *J*=7.86 Hz, 2H), 7.72 (d, *J*=7.80 Hz, 1H), 7.33 (d, *J*=7.86 Hz, 2H), 7.03-7.05 (t, *J*=7.62 Hz, 1H), 6.95 (d, *J*=7.92 Hz, 1H), 6.83-6.86 (t, *J*=7.56 Hz, 1H), 2.38 (s, 3H); ^{13}C ($CDCl_3$, 151 MHz) δ *(ppm)* 165.66, 149.61, 142.21, 131.99, 129.54, 128.01, 126.54, 126.01, 124.30, 119.57, 116.55, 21.48. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{14}H_{14}NO_2^+$ is 228.1019, obsd. 228.1024.

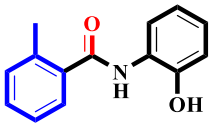
***N*-(2-hydroxyphenyl)-3-methylbenzamide (3c)**



Prepared as described for **3a**; reaction of 3-iodotoluene **1c** (0.229 mmol, 29.5 µL), benzoxazole **2a** (0.343 mmol, 41 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.343 mmol, 42 mg), imidazole (0.229, 15.5 mg) and DMF (1.5 mL) while the outer vial contained

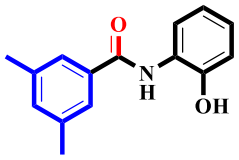
oxalic acid (1.37 mmol, 123 mg) in 0.5 mL of DMF gave **3c** after purification silica gel (mesh 60:120) column chromatography (15 % EtOAc in n-hexane) as Light pink solid (33 mg, 65% yield); ^{1}H ($CDCl_3$, 600 MHz) δ *(ppm)* 9.77 (s, 1H), 9.49 (s, 1H), 7.80 (s, 1H), 7.76-7.77 (m, 1H), 7.69 (d, *J*=7.86 Hz, 1H), 7.41-7.42 (m, 2H), 7.03-7.05 (t, *J*=7.68 Hz, 1H), 6.93 (d, *J*=7.98 Hz, 1H), 6.83-6.85 (t, *J*=7.62 Hz, 1H), 2.40 (s, 3H) ; ^{13}C ($CDCl_3$, 151 MHz) δ *(ppm)* 165.89, 149.74, 138.35, 134.85, (132.81-132.70), (128.97-128.86), 128.52, 126.43, 126.12, 125.10, 124.48, 119.54, 116.51, 21.44. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{14}H_{14}NO_2^+$ is 228.1019, obsd. 228.1024.

***N*-(2-hydroxyphenyl)-3-methylbenzamide (3d)**



Prepared as described for **3a**; reaction of 2-iodotoluene **1d** (0.229 mmol, 29.2 µL), benzoxazole **2a** (0.343 mmol, 41 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.343 mmol, 42 mg), imidazole (0.229, 15.5 mg) and DMF (1.5 mL), while the outer vial contained oxalic acid (1.37 mmol, 123 mg) in 0.5 mL of DMF gave **3d** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in n-hexane) as Light pink solid (30 mg, 58% yield); ^{1}H ($CDCl_3$, 600 MHz) δ *(ppm)* 9.78 (s, 1H), 9.44 (s, 1H), 7.74 (d, *J*=7.68 Hz, 1H), 7.54 (d, *J*=7.38 Hz, 1H), 7.39-7.41 (m, 1H), 7.29-7.32 (m, 2H), 7.03-7.06 (m, 1H), 6.93 (d, *J*=7.8 Hz, 1H), 6.84-6.86 (t, *J*=7.5 Hz, 1H), 2.44 (s, 3H); ^{13}C ($CDCl_3$, 151 MHz) δ *(ppm)* 168.46, 149.35, 137.08, 135.99, 131.13, 130.28, 127.72, 126.49, 126.16, 126.04, 123.95, 119.54, 116.61, 19.97. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{14}H_{14}NO_2^+$ is 228.1019, obsd. 228.1026.

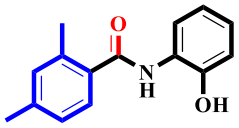
***N*-(2-hydroxyphenyl)-3,5-dimethylbenzamide (3e)**



Prepared as described for **3a**; the reaction of 1,3-Dimethyl-5-Iodobenzene **1e** (0.215 mmol, 31 µL), benzoxazole **2a** (0.323 mmol, 38 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.323 mmol, 44 mg), imidazole (0.215, 15 mg) and DMF (1.5 mL), while the outer vial contained oxalic acid (1.29 mmol, 116 mg) in 0.5 mL of DMF gave **3e** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as light pink solid (37 mg, 72% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.79 (s,1H), 9.47 (s,1H), 7.73 (d, *J*=7.86 Hz, 1H), 7.60 (s, 2H), 7.22 (s, 1H), 7.03-7.06 (t, *J*=7.68 Hz, 1H), 6.95 (d, *J*=7.98 Hz, 1H), 6.84-6.87 (t, *J*=7.62 Hz, 1H), 2.36 (s, 6H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 166.02,

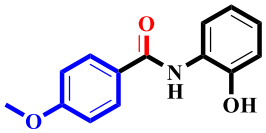
149.56, 138.19, 134.82, 133.47, 126.52, 126.00, 125.68, 124.24, 119.56, 116.54, 21.31. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{15}H_{16}NO_2^+$ is is 242.1176, obsd. 242.1184.

***N*-(2-hydroxyphenyl)-2,4-dimethylbenzamide (3f)**



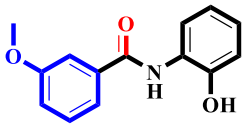
Prepared as described for **3a**; reaction of 2,4-Dimethyliodobenzene **1f** (0.215 mmol, 31 µL), benzoxazole **2a** (0.323 mmol, 38 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.323 mmol, 44 mg), imidazole (0.215, 15 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.29 mmol, 116 mg) in 0.5 mL of DMF gave **3f** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as light pink solid (31 mg, 60% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.80 (s, 1H), 9.32 (s, 1H), 7.73-7.74 (m, 1H), 7.43-7.45 (m, 1H), 7.09-7.11 (m, 2H), 7.01-7.03 (t, *J*=7.62 Hz, 1H), 6.91 (d, *J*=7.92 Hz, 1H), 6.82-6.84 (t, *J*=7.44 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 168.44, 149.15, 140.00, 136.17, 134.04, 131.85, 127.89, 126.66, 126.63, 125.88, 123.66, 119.55, 116.57, 21.27, 20.03. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{15}H_{16}NO_2^+$ is 242.1176, obsd. 242.1182.

***N*-(2-hydroxyphenyl)-4-methoxybenzamide (3g)**



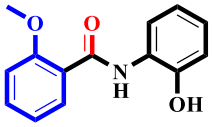
Prepared as described for **3a**; reaction of 4-iodoanisole **1g** (0.213 mmol, 50 mg), benzoxazole **2a** (0.319 mmol, 38 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.323 mmol, 44 mg), imidazole (0.215 mmol, 15 mg) and DMF (1.5 mL), while the outer vial contained oxalic acid (1.28 mmol, 115 mg) in 0.5 mL of DMF gave **3g** after purification silica gel (mesh 60:120) column chromatography (20% EtOAc in n-hexane) as light pink solid (39 mg, 76% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.74 (s, 1H), 9.44 (s, 1H), 7.96 (d, *J*=8.82 Hz, 2H), 7.64-7.66 (m, 1H), 7.06 (d, *J*=8.82 Hz, 2H), 7.01-7.04 (m, 1H), 6.91-6.92 (m, 1H), 6.81-6.84 (m, 1H), 3.84 (s, 3H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 165.29, 162.45, 149.68, 129.94, 126.83, 126.56, 125.99, 124.46, 119.55, 116.59, 114.21, 55.90. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{14}H_{14}NO_3^+$ is 244.0968, obsd. 244.0973.

***N*-(2-hydroxyphenyl)-3-methoxybenzamide (3h)**



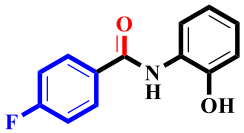
Prepared as described for **3a**; reaction of 3-iodoanisole **1h** (0.213 mmol, 25.4 µL), benzoxazole **2a** (0.319 mmol, 38 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.323 mmol, 44 mg), imidazole (0.215, 15 mg) and DMF (1.5 mL), while the outer vial contained oxalic acid (1.28 mmol, 115 mg) in 0.5 mL of DMF gave **3h** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as Light pink solid (37 mg, 72% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.76 (s, 1H), 9.54 (s, 1H), 7.66 (d, *J*=7.8 Hz, 1H), 7.55 (d, *J*=7.62 Hz, 1H), 7.53 (s, 1H), 7.43-7.45 (t, *J*=7.92 Hz, 1H), 7.15-7.17 (m, 1H), 7.04-7.06 (m, 1H), 6.94 (d, *J*=7.98 Hz, 1H), 6.83-6.86 (m, 1H), 3.83 (s, 3H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 165.53, 159.74, 149.98, 136.32, 130.14, 126.28, 126.25, 124.84, 128.11, 119.51, 117.98, 113.19, 55.78. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{14}H_{14}NO_3^+$ is 244.0968, obsd. 244.0973.

_N_-(2-hydroxyphenyl)-2-methoxybenzamide (3i)



Prepared as described for **3a**; reaction of 2-iodoanisole **1i** (0.213 mmol, 28 µL), benzoxazole **2a** (0.319 mmol, 38 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.323 mmol, 44 mg), imidazole (0.215, 15 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.28 mmol, 115 mg) in 0.5 mL of DMF gave **3i** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as light pink solid (29 mg, 56% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 10.59 (s, 1H), 10.23 (s, 1H), 8.38 (d, *J*=7.98 Hz, 1H), 8.09 (d, *J*=7.74 Hz, 1H), 7.56-7.59 (m, 1H), 7.26 (d, *J*=8.34 Hz, 1H), 7.13-7.15 (t, *J*=7.5 Hz, 1H), 6.92-6.93 (m, 2H), 6.81-6.83 (m, 1H), 4.04 (s, 3H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{14}H_{14}NO_3^+$ is 244.0968, obsd. 244.0970.

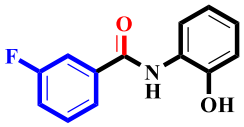
4-fluoro-_N_-(2-hydroxyphenyl)benzamide (3j)



Prepared as described for **3a**; reaction of 4-Fluoroiodobenzene **1j** (0.225 mmol, 26 µL), benzoxazole **2a** (0.33 mmol, 40 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.337 mmol, 47 mg), imidazole (0.225, 15 mg) and DMF (1.5 mL), while the outer vial contained oxalic acid (1.35 mmol, 121 mg) in 0.5 mL of DMF gave **3j** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in n-hexane) as Light pink solid (42

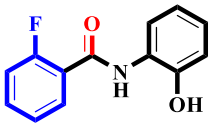
mg, 80% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.74 (s, 1H), 9.59 (s, 1H), 8.05-8.07 (m, 2H), 7.64 (d, *J*=7.86 Hz, 1H), 7.34-7.36 (t, *J*=8.64 Hz, 2H), 7.04-7.07 (m, 1H), 6.94 (d, *J*=8.04 Hz, 1H), 6.83-6.85 (t, *J*=7.56 Hz, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 165.41, (164.79-163.76), 150.12, (131.37-131.35), (130.79-130.73), 126.36, 126.18, 125.04, 119.49, 116.53, (115.93-115.79). ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{11}FNO_2^+$ is 232.0768, obsd. 232.0773.

3-fluoro-*N*-(2-hydroxyphenyl)benzamide (3k)



Prepared as described for **3a**; reaction of 3-Fluoroiodobenzene **1k** (0.225 mmol, 32 µL), benzoxazole **2a** (0.33 mmol, 40 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.337 mmol, 47 mg), imidazole (0.225, 15 mg) and DMF (1.5 mL), while the outer vial contained oxalic acid (1.35 mmol, 121 mg) in 0.5 mL of DMF gave **3k** after purification silica gel (mesh 60:120) column chromatography (15 % EtOAc in n-hexane) as Light pink solid (38 mg, 72% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.71 (s, 1H), 9.63 (s, 1H), 7.83 (d, *J*=7.74 Hz, 1H), 7.78 (d, *J*=9.78 Hz, 1H), 7.56-7.61 (m, 2H), 7.43-7.46 (m, 1H), 7.04-7.07 (m, 1H), 6.93-6.94 (m, 1H), 6.82-6.85 (m, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 164.44, (163.27-161.65), 150.37, (137.33-137.28), (131.13-131.08), 126.59, 125.87, 125.40, (124.18-124.17), 119.44, (119.02-118.88), 116.48, (114.99-114.84). ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{11}FNO_2^+$ is 232.0768, obsd. 232.0775.

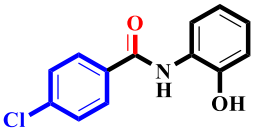
2-fluoro-*N*-(2-hydroxyphenyl)benzamide (3l)



Prepared as described for **3a**; reaction of 3-Fluoroiodobenzene **1l** (0.225 mmol, 32 µL), benzoxazole **2a** (0.33 mmol, 40 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.337 mmol, 47 mg), imidazole (0.225, 15 mg) and DMF (1.5 mL), while the outer vial contained oxalic acid (1.35 mmol, 121 mg) in 0.5 mL of DMF gave **3l** after purification silica gel (mesh 60:120) column chromatography (15 % EtOAc in n-hexane) as Light pink solid (31 mg, 61% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 10.09 (s, 1H), 9.45 (m, 1H), 8.06 (d, *J*=7.98 Hz, 1H), 7.89-7.92 (t, *J*=7.68 Hz, 1H), 7.61-7.64 (m, 1H), 7.36-7.40 (m, 2H), 6.98-7.01 (m, 1H), 6.92 (d, *J*=7.98 Hz, 1H), 6.82-6.85 (t, *J*=7.68 Hz, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 161.70, (160.79-159.16), 147.89, (134.04-133.99), 131.39, 126.59, (125.45-125.38), 123.03,

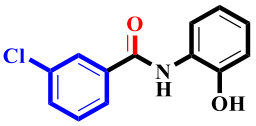
122.95, 121.97, 119.61, (116.92-116.76), 115.64. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{11}FNO_2^+$ is 232.0768, obsd. 232.0771.

4-chloro-*N*-(2-hydroxyphenyl)benzamide (3m)



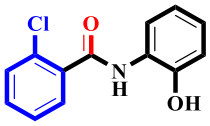
Prepared as described for **3a**; reaction of 4-Chloroiodobenzene **1m** (0.21 mmol, 50 mg), benzoxazole **2a** (0.31 mmol, 37 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.315 mmol, 43 mg), imidazole (0.21 mmol, 14 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.26 mmol, 113 mg) in 0.5 mL of DMF gave **3m** after purification silica gel (mesh 60:120) column chromatography (15 % EtOAc in n-hexane) as Light pink solid (33 mg, 64% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.73 (s, 1H), 9.62 (s, 1H), 8.00 (d, *J*=8.52 Hz, 2H), 7.63-7.65 (m, 1H), 7.59 (d, *J*=8.58 Hz, 2H), 7.04-7.07 (m, 1H), 6.93-6.95 (m, 1H), 6.82-6.85 (m, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 164.74, 150.19, 136.92, 133.67, 129.99, 128.99, 126.44, 126.04, 125.13, 119.46, 116.48. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{11}ClNO_2^+$ is 248.0473, obsd. 248.0476.

3-chloro-*N*-(2-hydroxyphenyl)benzamide (3n)



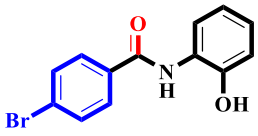
Prepared as described for **3a**; reaction of 4-Chloroiodobenzene **1n** (0.21 mmol, 50 mg), benzoxazole **2a** (0.31 mmol, 37 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.315 mmol, 43 mg), imidazole (0.21 mmol, 14 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.26 mmol, 113 mg) in 0.5 mL of DMF gave **3n** after purification silica gel (mesh 60:120) column chromatography (15 % EtOAc in n-hexane) as Light pink solid (31 mg, 59% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.69 (s, 2H), 8.02 (s, 1H), 7.93 (d, *J*=7.68 Hz, 1H), 7.66 (d, *J*=7.86 Hz, 1H), 7.54-7.59 (m, 2H), 7.05-7.07 (t, *J*=7.74 Hz, 1H), 6.93 (d, *J*=8.04 Hz, 1H), 6.82-6.85 (t, *J*=7.62 Hz, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 164.42, 150.50, 136.96, 133.73, 131.86, 130.90, 127.95, 126.78, 126.67, 125.81, 125.60, 119.43, 116.51. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{11}ClNO_2^+$ is 248.0473, obsd. 248.0480.

2-chloro-*N*-(2-hydroxyphenyl)benzamide (3o)



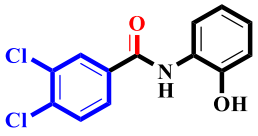
Prepared as described for **3a**; reaction of 4-Chloroiodobenzene **1o** (0.21 mmol, 50 mg), benzoxazole **2a** (0.31 mmol, 37 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.315 mmol, 43 mg), imidazole (0.21 mmol, 14 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.26 mmol, 113 mg) in 0.5 mL of DMF gave **3o** after purification silica gel (mesh 60:120) column chromatography (15 % EtOAc in n-hexane) as Light pink solid (27 mg, 53% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.77 (s, 1H), 9.63 (s, 1H), 7.79 (d, *J*=7.92 Hz, 1H), 7.62 (d, *J*=7.44 Hz, 1H), 7.55 (d, *J*=7.98 Hz, 1H), 7.49-7.51 (m, 1H), 7.43-7.46 (t, *J*=7.38 Hz, 1H), 7.01-7.04 (t, *J*=7.68 Hz, 1H), 6.91 (d, *J*=8.04 Hz, 1H), 6.82-6.84 (t, *J*=7.62 Hz, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 165.45, 149.14, 136.87, 131.67, 130.45, 130.19, 129.74, 127.68, 126.14, 126.05, 123.66, 119.49, 116.35. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{11}ClNO_2^+$ is 248.0473, obsd. 248.0477.

4-bromo-*N*-(2-hydroxyphenyl)benzamide (3p)



Prepared as described for **3a**; reaction of 1-Bromo-4-iodobenzene **1p** (0.176 mmol, 50 mg), benzoxazole **2a** (0.265 mmol, 32 mg), Pd@PS (0.005 mmol, 112 mg), K_2CO_3 (0.265 mmol, 36 mg), imidazole (0.176 mmol, 12 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.26 mmol, 113 mg) in 0.5 mL of DMF gave **3p** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as Light pink solid (29 mg, 57% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.72 (s, 1H), 9.61 (s, 1H), 7.92 (d, *J*=8.52 Hz, 2H), 7.74 (d, *J*=8.52 Hz, 2H), 7.62-7.63 (m, 1H), 7.03-7.06 (m, 1H), 6.92-6.93 (m, 1H), 6.82-6.84 (m, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 164.84, 150.19, 134.04, 131.94, 130.17, 126.45, 126.01, 125.84, 125.14, 119.45, 116.45. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{11}BrNO_2^+$ is 291.9968, obsd. 291.0006.

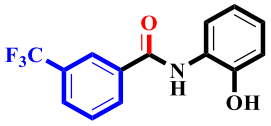
3,4-dichloro-*N*-(2-hydroxyphenyl)benzamide (3q)



Prepared as described for **3a**; reaction of 3,4-Dichloroiodobenzene **1q** (0.183 mmol, 50 mg), benzoxazole **2a** (0.274 mmol, 33 mg), Pd@PS (0.005 mmol, 112 mg), K_2CO_3 (0.274 mmol, 38 mg), imidazole (0.183 mmol, 12 mg) and DMF (1.5 mL) while the

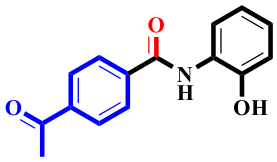
outer vial contained oxalic acid (1.095 mmol, 101 mg) in 0.5 mL of DMF gave **3q** after purification silica gel (mesh 60:120) column chromatography (20% EtOAc in n-hexane) as Light pink solid (26 mg, 51% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.77 (s, 1H), 9.68 (s, 1H), 8.217-8.220 (m, 1H), 7.93-7.95 (m, 1H), 7.81 (d, *J*=8.34 Hz, 1H), 7.54 (d, *J*=7.08 Hz, 1H), 7.05-7.08(m, 1H), 6.91-6.93 (m, 1H), 6.81-6.84 (m, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 163.60, 150.72, 135.36, 134.76, 131.75, 131.22, 130.14, 128.40, 126.85, 125.93, 125.56, 119.38, 116.48. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{10}Cl_2NO_2^+$is 282.0083, obsd. 282.0071.

_N_-(2-hydroxyphenyl)-3-(trifluoromethyl)benzamide (3r)



Prepared as described for **3a**; reaction of 3-iodobenzotrifluoride **1r** (0.183 mmol, 27 µL), benzoxazole **2a** (0.274 mmol, 33 mg), Pd@PS (0.005 mmol, 123 mg), K_2CO_3 (0.274 mmol, 38 mg), imidazole (0.183 mmol, 12 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.09 mmol, 98 mg) in 0.5 mL of DMF gave **3r** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as Light pink solid (34 mg, 67% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.87 (s, 1H), 9.68 (s, 1H), 8.32 (s, 1H), 8.27 (d, *J*=7.74 Hz, 1H), 7.96 (d, *J*=7.8 Hz, 1H), 7.76-7.79 (t, *J*=7.8 Hz, 1H), 7.56-7.57 (m, 1H), 7.06-7.09 (m, 1H), 6.93-6.95 (m, 1H), 6.83-6.85 (m, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 164.44, 150.77, 135.92, 132.17, 130.18, (129.76-129.54), (128.54-128.52), 126.82, 125.98, 125.69, (124.83-124.81), 123.57, 119.40, 116.53. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{14}H_{11}F_3NO_2^+$is 282.0736, obsd. 282.0728.

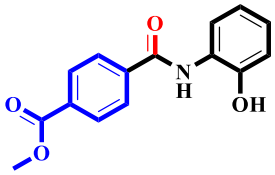
4-acetyl-_N_-(2-hydroxyphenyl)benzamide (3s)



Prepared as described for **3a**; reaction of 4-acetyliodobenzene **1s** (0.203 mmol, 50 mg), benzoxazole **2a** (0.274 mmol, 33 mg), Pd@PS (0.005 mmol, 112 mg), K_2CO_3 (0.274 mmol, 38 mg), imidazole (0.203 mmol, 14 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.21 mmol, 110 mg) in 0.5 mL of DMF gave **3s** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as light pink solid (39 mg, 76% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.75 (s, 1H), 9.71 (s, 1H), 8.09 (s, 4H), 7.64 (d, *J*=7.74 Hz, 1H), 7.05-7.07 (m, 1H), 6.93 (d, *J*=7.98 Hz, 1H), 6.83-6.85 (m, 1H), 3.89 (s, 3H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 166.17, 164.90, 150.25, 139.05, 132.51, 129.72, 128.45,

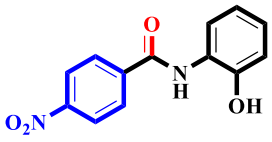
126.56, 125.92, 125.18, 119.46, 116.42, 52.89. MS $[M+H]^+$ *(m/z)* calcd. for $C_{15}H_{14}NO_3^+$ is 256.0968, obsd. 256.0972.

methyl 4-((2-hydroxyphenyl)carbamoyl)benzoate (3t)



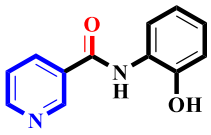
Prepared as described for **3a**; reaction of Methyl 4-iodobenzoate **1t** (0.190 mmol, 50 mg), benzoxazole **2a** (0.285 mmol, 39 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.285 mmol, 39 mg), imidazole (0.19 mmol, 13 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.09 mmol, 98 mg) in 0.5 mL of DMF gave **3t** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as light pink solid (36 mg, 70% yield); ^1H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.71 (s, 2H), 8.09 (s, 4H), 7.64 (d, *J*=7.8 Hz, 1H), 7.05-7.07 (m, 1H), 6.93 (d, *J*=8.04 Hz, 1H), 6.83-6.85 (t, *J*=7.56 Hz, 1H), 3.89 (s, 3H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 166.23, 164.96, 150.31, 139.09, 132.55, (129.85-129.71), (128.58-128.43), 126.61, 125.96, 120.01, 119.51, 116.47, 52.94. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{15}H_{14}NO_4^+$ is 272.0917, obsd. 272.0913.

***N*-(2-hydroxyphenyl)-4-nitrobenzamide (3u)**



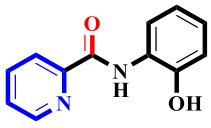
Prepared as described for **3a**; reaction of 1-iodo-4-nitrobenzene **1u** (0.2008 mmol, 50 mg), benzoxazole **2a** (0.301 mmol, 36 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.301 mmol, 42 mg), imidazole (0.20 mmol, 14 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.20 mmol, 108 mg) in 0.5 mL of DMF gave **3u** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as light pink solid (37 mg, 72% yield); ^1H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.84-9.76 (m, 2H), 8.35 (d, *J*=8.4 Hz, 2H), 8.19 (d, *J*=8.16 Hz, 2H), 7.62 (d, *J*=7.62 Hz, 1H), 7.06-7.09 (t, *J*=7.68 Hz, 1H), 6.94 (d, *J*=7.98 Hz, 1H), 6.83-6.86 (t, *J*=7.56 Hz, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 164.17, 150.51, 149.60, 140.72, 129.60, 126.81, 125.65, 125.51, 124.03, 119.43, 116.430. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{11}N_2O_4^+$ is 259.0713, obsd. 259.0705.

***N*-(2-hydroxyphenyl)nicotinamide (3v)**



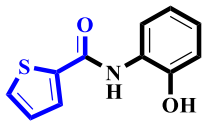
Prepared as described for **3a**; reaction of 3-Iodopyridine **1v** (0.243 mmol, 50 mg), benzoxazole **2a** (0.364 mmol, 43 mg), Pd@PS (0.007 mmol, 156 mg), K_2CO_3 (0.364 mmol, 50 mg), imidazole (0.243 mmol, 17 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.45 mmol, 130 mg) in 0.5 mL of DMF gave **3v** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as light pink solid (36 mg, 70% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.79 (s, 1H), 9.70 (s, 1H), 9.13 (s, 1H), 8.76 (s, 1H), 8.31-8.33 (m, 1H), 7.60-7.61 (m, 1H), 7.55-7.57 (m, 1H), 7.05-7.08 (t, *J*=7.38 Hz, 1H), 6.93 (d, *J*=7.86 Hz, 1H), 6.83-6.85 (t, *J*=7.44 Hz, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 164.41, 152.47, 150.51, 149.11, 135.94, 130.65, 126.72, 125.74, 125.61, 124.02, 119.43, 116.52. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{12}H_{11}N_2O_2^+$ is 215.0815, obsd. 215.0817.

***N*-(2-hydroxyphenyl)picolinamide (3w)**



Prepared as described for **3a**; reaction of 2-Iodopyridine **1w** (0.243 mmol, 50 mg), benzoxazole **2a** (0.364 mmol, 43 mg), Pd@PS (0.007 mmol, 156 mg), K_2CO_3 (0.364 mmol, 50 mg), imidazole (0.243 mmol, 17 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.45 mmol, 130 mg) in 0.5 mL of DMF gave **3w** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as light pink solid (32 mg, 61% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 10.48 (s, 1H), 10.31 (s, 1H), 8.73-8.75 (m, 1H), 8.38-8.39 (m, 1H), 8.19 (d, *J*=7.8 Hz, 1H), 8.07-8.10 (m, 1H), 7.68-7.70 (m, 1H), 6.94-6.98 (m, 2H), 6.84-6.87 (m, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 161.58, 149.86, (149.13-149.07), 147.00, 138.93, 127.52, 126.59, 124.57, 122.35, 119.75, 119.50, 115.17. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{12}H_{11}N_2O_2^+$ is 215.0815, obsd. 215.0816.

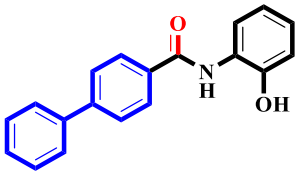
***N*-(2-hydroxyphenyl)thiophene-2-carboxamide (3x)**



Prepared as described for **3a**; reaction of 2-Iodothiophene **1x** (0.238 mmol, 26 µL), benzoxazole **2a** (0.357 mmol, 42 mg), Pd@PS (0.007 mmol, 156 mg), K_2CO_3 (0.357

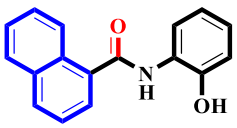
mmol, 49 mg), imidazole (0.238 mmol, 16 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.40 mmol, 126 mg) in 0.5 mL of DMF gave **3x** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as light pink solid (35 mg, 68% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.75 (s, 1H), 9.57 (s, 1H), 7.99-8.00 (m, 1H), 7.84 (d, *J*=4.98 Hz, 1H), 7.55 (d, *J*=7.86 Hz, 1H), 7.20-7.22 (m, 1H), 7.03-7.06 (m, 1H), 6.93 (d, *J*=8.04 Hz, 1H), 6.81-6.84 (m, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 160.42, 150.29, 140.13, 132.12, 129.60, 128.63, 126.48, 125.68, 125.43, 119.46, 116.45. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{11}H_{10}NO_2S^+$ is 220.0427, obsd. 220.0419.

***N*-(2-hydroxyphenyl)-[1,1'-biphenyl]-4-carboxamide (3y)**



Prepared as described for **3a**; reaction of 4-iodobiphenyl **1y** (0.225 mmol, 50 mg), benzoxazole **2a** (0.337 mmol, 40 mg), Pd@PS (0.006 mmol, 134 mg), K_2CO_3 (0.337 mmol, 47 mg), imidazole (0.225 mmol, 15 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.12 mmol, 101 mg) in 0.5 mL of DMF gave **3y** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as light pink solid (35 mg, 68% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.77 (s, 1H), 9.59 (s, 1H), 8.07 (d, *J*=8.28 Hz, 2H), 7.84 (d, *J*=8.34 Hz, 2H), 7.76 (d, *J*=7.26 Hz, 2H), 7.70 (d, *J*=7.8 Hz, 1H), 7.50-7.53 (m, 2H), 7.42-7.44 (t, *J*=7.38 Hz, 1H), 7.04-7.06 (m, 1H), 6.93-6.95 (m, 1H), 6.83-6.86 (m, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 165.40, 149.87, 143.66, 139.56, 133.64, 129.56, 128.71, 128.66, 127.40, 127.19, 126.37, 126.21, 124.66, 119.53, 116.51. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{19}H_{16}NO_2^+$ is 290.1176, obsd. 290.1185.

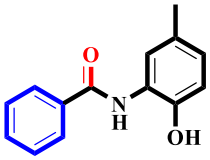
***N*-(2-hydroxyphenyl)-1-naphthamide (3z)**



Prepared as described for **3a**; reaction of 1-Iodonaphthalene **1z** (0.196 mmol, 29), benzoxazole **2a** (0.293 mmol, 35 mg), Pd@PS (0.006 mmol, 132 mg), K_2CO_3 (0.295 mmol, 41 mg), imidazole (0.196 mmol, 13 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.18 mmol, 106 mg) in 0.5 mL of DMF gave **3z** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as Light pink solid (30 mg, 58% yield); ^{1}H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.83 (s, 1H), 9.69 (s, 1H), 8.31 (d, *J*=7.86 Hz, 1H), 8.08 (d, *J*=8.1 Hz, 1H), 8.02 (d, *J*=7.2 Hz, 1H), 7.79-7.82 (m, 2H), 7.58-7.62 (m, 3H),

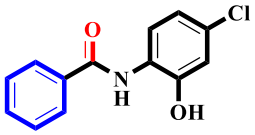
7.06-7.08 (t, *J*=7.44 Hz, 1H), 6.95 (d, *J*=7.86 Hz, 1H), 6.86-6.89 (m, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 167.88, 149.73, 134.80, 133.66, 130.76, 130.23, 128.80, 127.42, 126.83, 126.41, 126.27, 126.09, 125.75, 125.53, 124.49, 119.53, 116.51. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{17}H_{14}NO_2^+$ is 264.1019, obsd. 264.1021.

***N*-(2-hydroxy-5-methylphenyl)benzamide (3ab)**



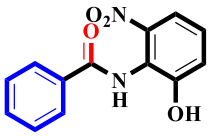
Prepared as described for **3a**; Iodobenzene **1a** (0.245 mmol, 27.3 µL), 5-methylbenzoxazole **2b** (0.367 mmol, 49 mg), Pd@PS (0.007 mmol, 156 mg), K_2CO_3 (0.36 mmol, 50 mg), imidazole (0.245, 16.6 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.47 mmol, 132 mg) in 0.5 mL of DMF gave **3ab** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as light pink solid (36 mg, 58% yield); ^1H ($CDCl_3$, 600 MHz) δ (*ppm*) 9.50 (s, 2H), 7.96-7.98 (m, 2H), 7.58-7.61 (m, 1H), 7.52-7.54 (m, 3H), 6.81-6.86 (m, 2H), 2.23 (s, 3H); ^{13}C ($CDCl_3$, 151 MHz) δ (*ppm*) 165.70, 147.42, 134.84, 132.14, 129.00, 128.13, 127.95, 126.54, 126.04, 124.88, 116.35, 20.80. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{14}H_{14}NO_2^+$ is 228.1019, obsd. 228.1026.

***N*-(4-chloro-2-hydroxyphenyl)benzamide (3ac)**



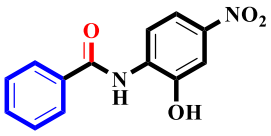
Prepared as described for **3a**; Iodobenzene **1a** (0.245 mmol, 27.3 µL), 6-chlorobenzoxazole **2c** (0.368 mmol, 56 mg), Pd@PS (0.007 mmol, 156 mg), K_2CO_3 (0.36 mmol, 50 mg), imidazole (0.245, 16.6 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.47 mmol, 132 mg) in 0.5 mL of DMF gave **3ac** after purification silica gel (mesh 60:120) column chromatography (20% EtOAc in n-hexane) as light pink solid (41 mg, 68% yield); ^1H ($CDCl_3$, 600 MHz) δ *(ppm)*; 10.40 (brs, 1H), 9.53(s, 1H),7.98 (d, *J*=7.68 Hz, 2H), 7.72 (d, *J*=8.46Hz, 1H), 7.60- 7.62 (m, 1H), 7.53-7.55 (m, 2H), 6.98 (s, 1H), 6.91 (d, *J*=8.58 Hz, 1H); ^{13}C ($CDCl_3$, 151 MHz) δ *(ppm)* 165.40, 150.68, 134.25, 131.85, 129.17, 128.60, 125.62, 125.10, 118.85, 115.60 ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{11}ClNO_2^+$ is 248.0473, obsd. 248.0474.

***N*-(2-hydroxy-6-nitrophenyl)benzamide (3ad)**



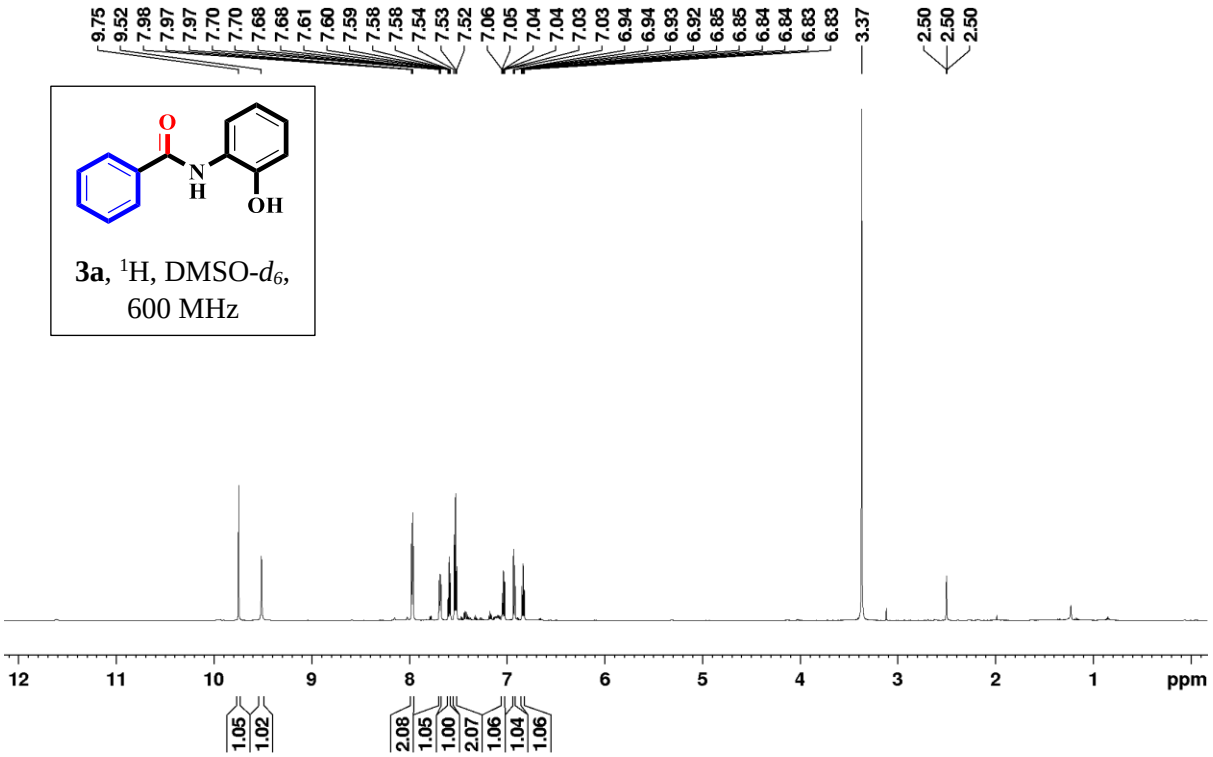
Prepared as described for **3a**; Iodobenzene **1a** (0.245 mmol, 27.3 µL), 4-nitrobenzoxazole **2d** (0.367 mmol, 60 mg), Pd@PS (0.007 mmol, 156 mg), K_2CO_3 (0.36 mmol, 50 mg), imidazole (0.245, 16.6 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.47 mmol, 132 mg) in 0.5 mL of DMF gave **3ad** after purification silica gel (mesh 60:120) column chromatography (25% EtOAc in n-hexane) as light pink solid (33 mg, 52% yield); ^{1}H ($CDCl_3$, 600 MHz) *δ (ppm)* 8.20 (d, *J*=7.74 Hz, 2H), 7.98-8.02 (m, 2H), 7.74-7.77 (m, 1H), 7.61-7.63(m, 2H), 6.89 (d, *J*=9.06 Hz 1H), 6.77 (s, 2H); ^{13}C ($CDCl_3$, 151 MHz) *δ (ppm)* 164.41, 148.41, 135.27, 134.68, 133.96, (130.23- 130.37), 128.97,(128.72-128.75), (123.71-123.82), (119.69-119.81), (114.04-114.07). ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{11}N_2O_4^+$ is 259.0713, obsd. 259.0708.

***N*-(2-hydroxy-4-nitrophenyl)benzamide (3ae)**

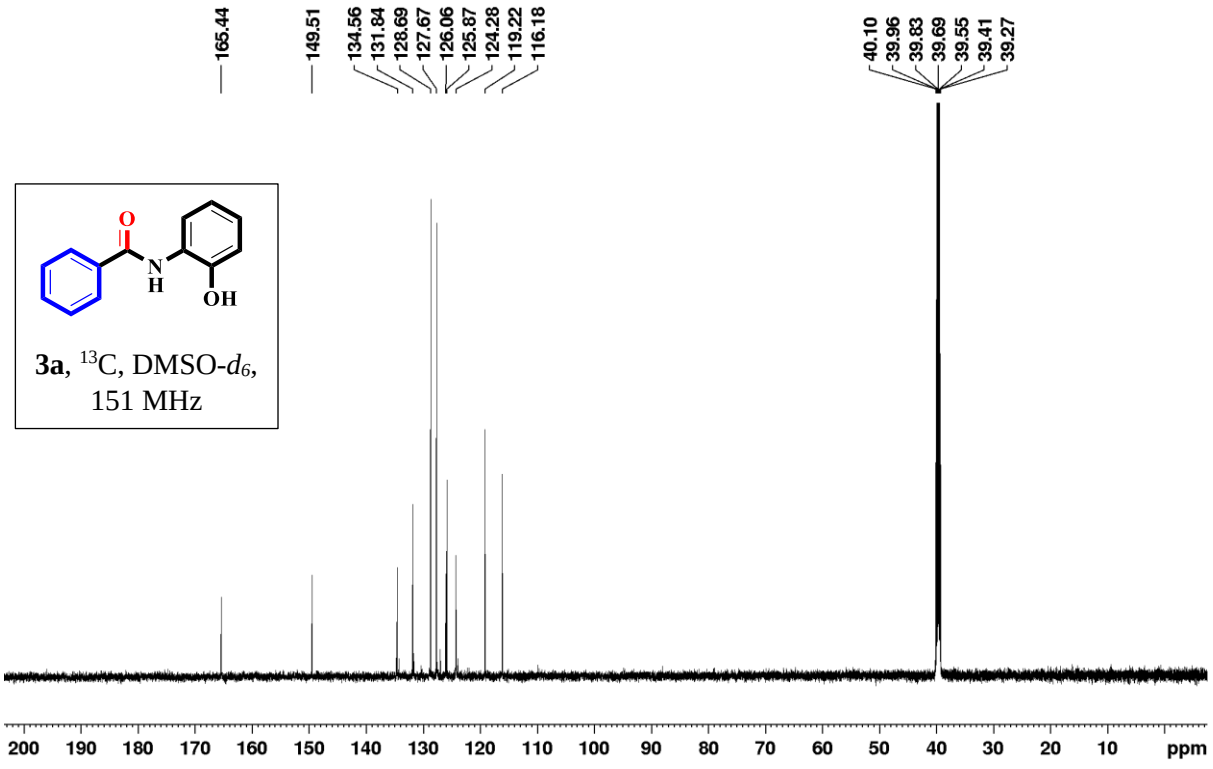


Prepared as described for **3a**; Iodobenzene **1a** (0.245 mmol, 27.3 µL), 6-nitrobenzoxazole **2e** (0.367 mmol, 60 mg), Pd@PS (0.007 mmol, 156 mg), K_2CO_3 (0.36 mmol, 50 mg), imidazole (0.245, 16.6 mg) and DMF (1.5 mL) while the outer vial contained oxalic acid (1.47 mmol, 132 mg) in 0.5 mL of DMF gave **3ae** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as light pink solid (42 mg, 67% yield); ^{1}H ($CDCl_3$, 600 MHz) *δ (ppm)* 10.54 (s,1H), 10.00 (s,1H), 7.98-7.99 (d, *J*=7.56 Hz, 2H), 7.59-7.61 (m, 1H),7.52-7.54 (m, 2H), 7.40-7.41(m, 1H), 7.31-7.34(t, *J*=8.16 Hz, 1H), 7.26-7.28 (m, 1H); ^{13}C ($CDCl_3$, 150 MHz) *δ (ppm)* 165.53, 153.80, 147.30, 133.65, 131.90, 128.42, 127.83, 127.10, 120.48, 118.59, 114.68. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{13}H_{11}N_2O_4^+$ is 259.0713, obsd. 259.0706.

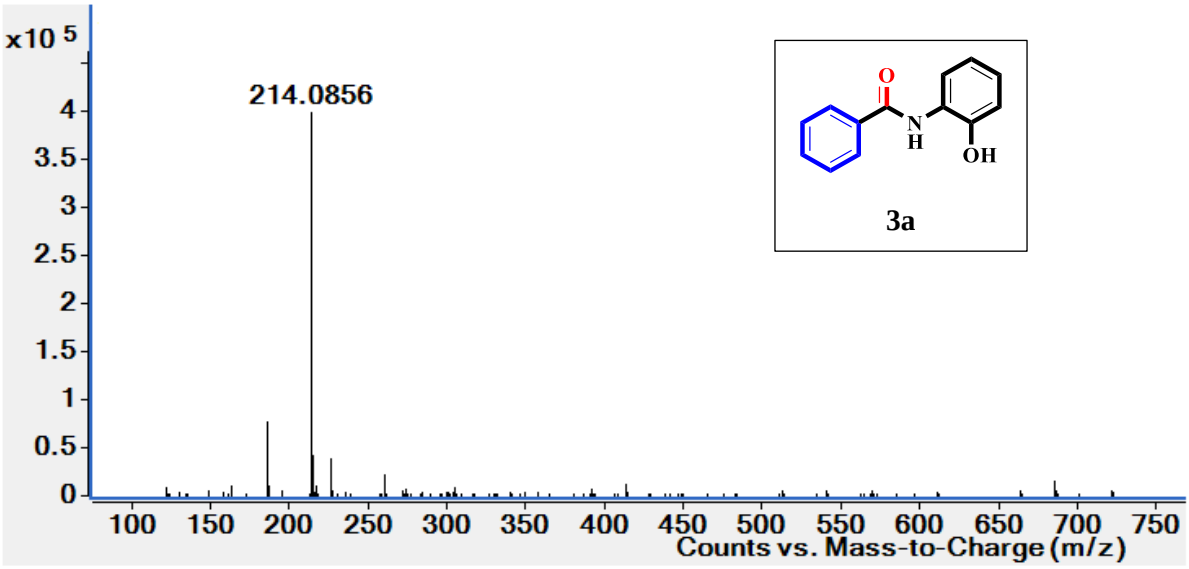
E. ^{1}H, ^{13}C and ESI-MS spectra of synthesized compounds



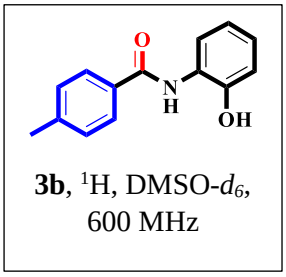
3a, ^{1}H, DMSO-d_6, 600 MHz



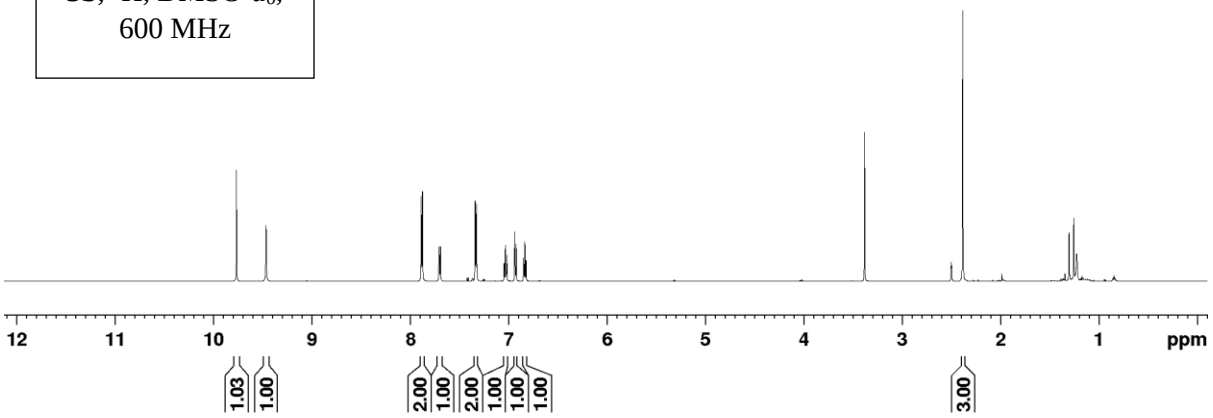
3a, ^{13}C, DMSO-d_6, 151 MHz

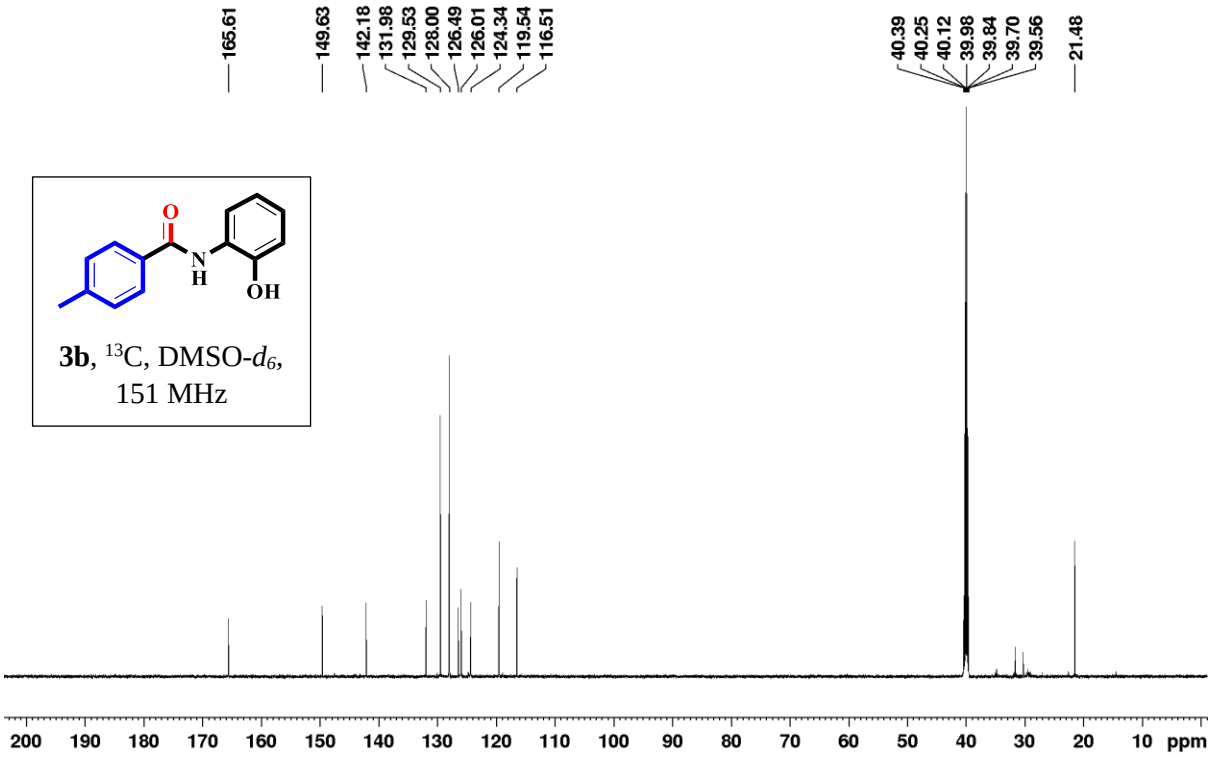


3a

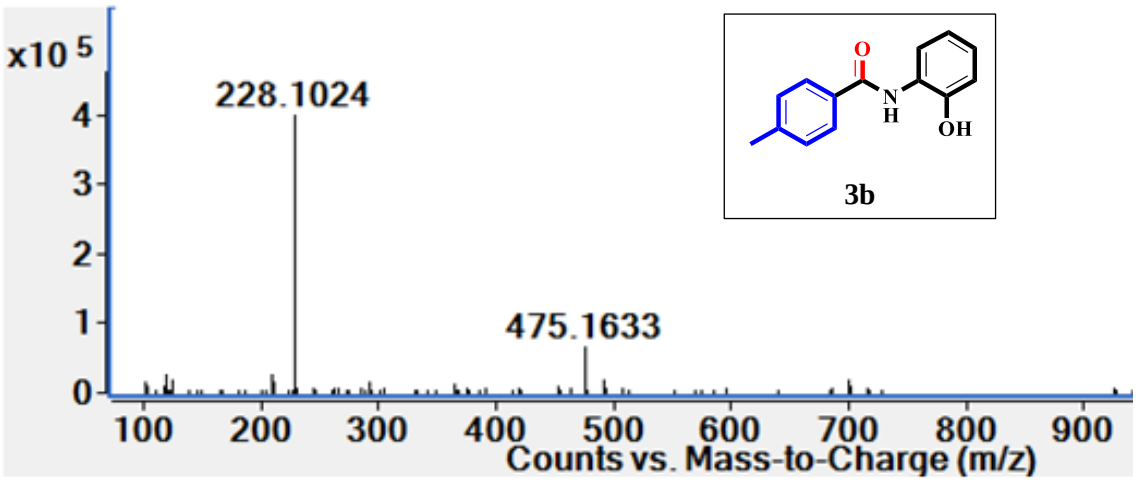


3b, ^{1}H, DMSO-d_6, 600 MHz

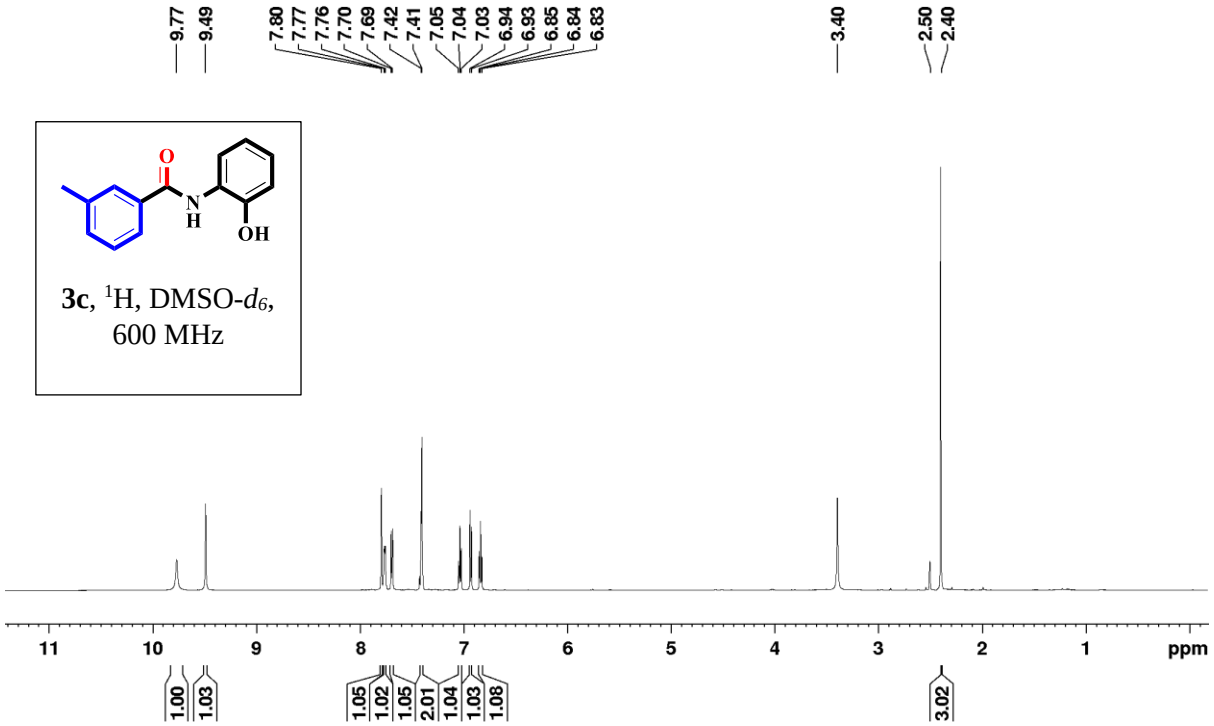




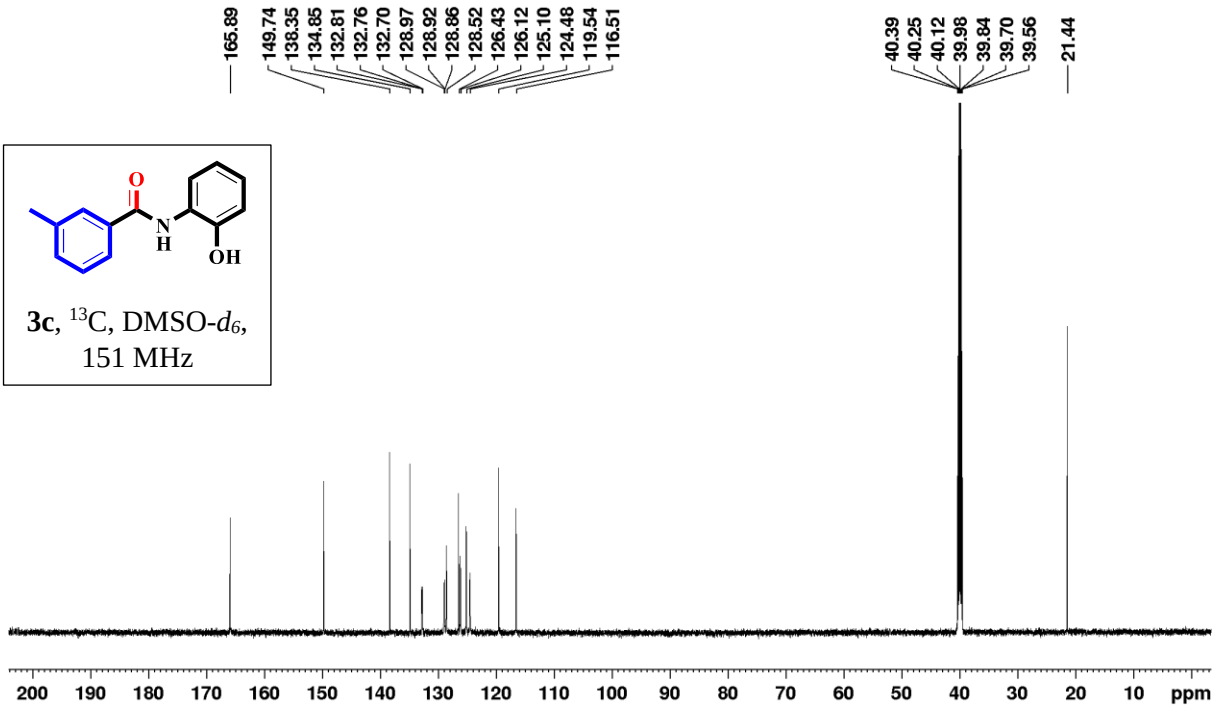
3b, ^{13}C, DMSO-d_6, 151 MHz



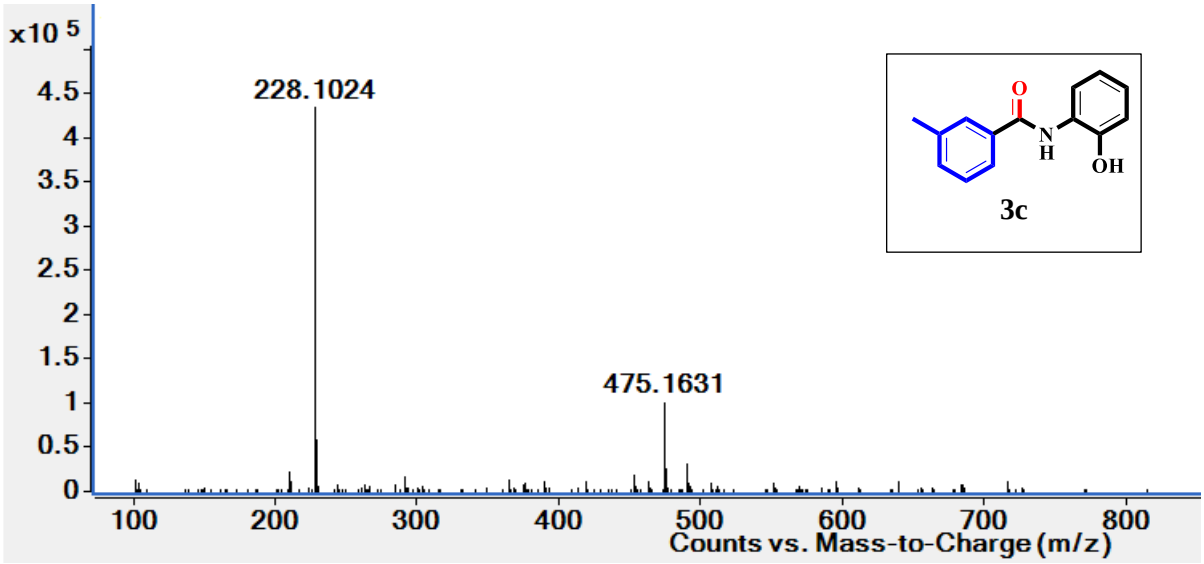
3b

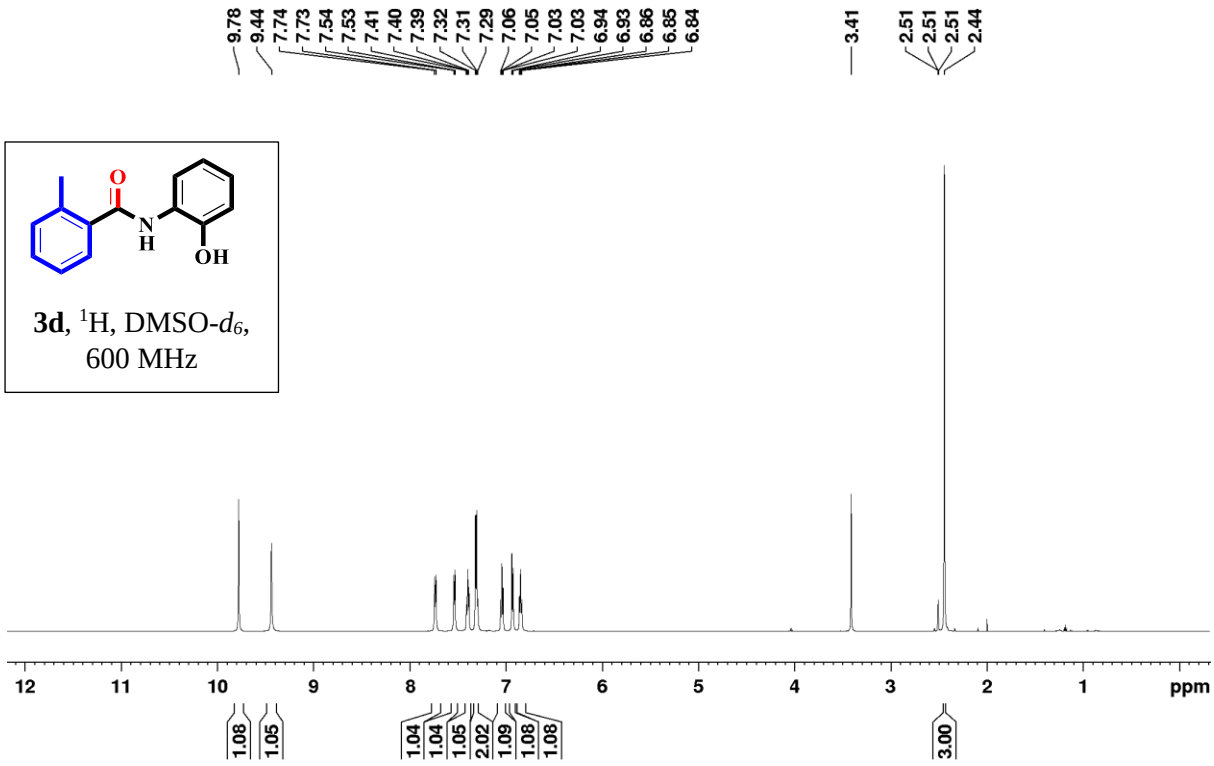


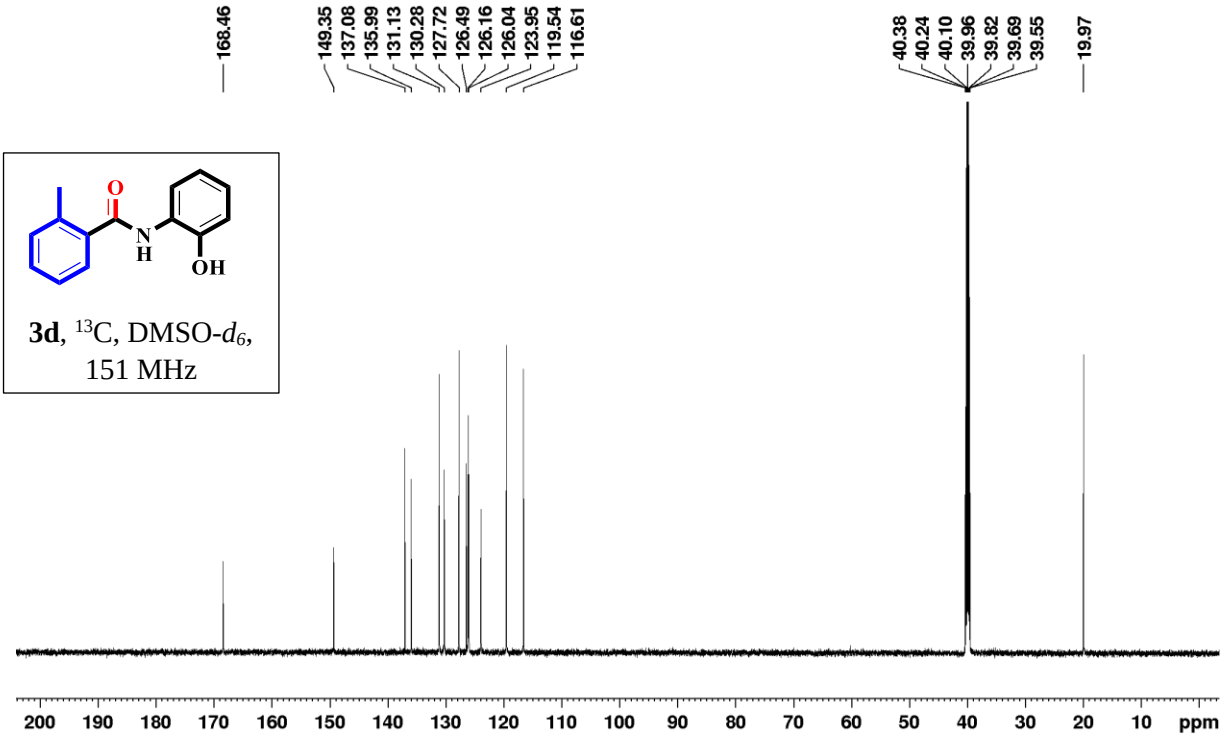
3c, ^{1}H, DMSO-d_6, 600 MHz

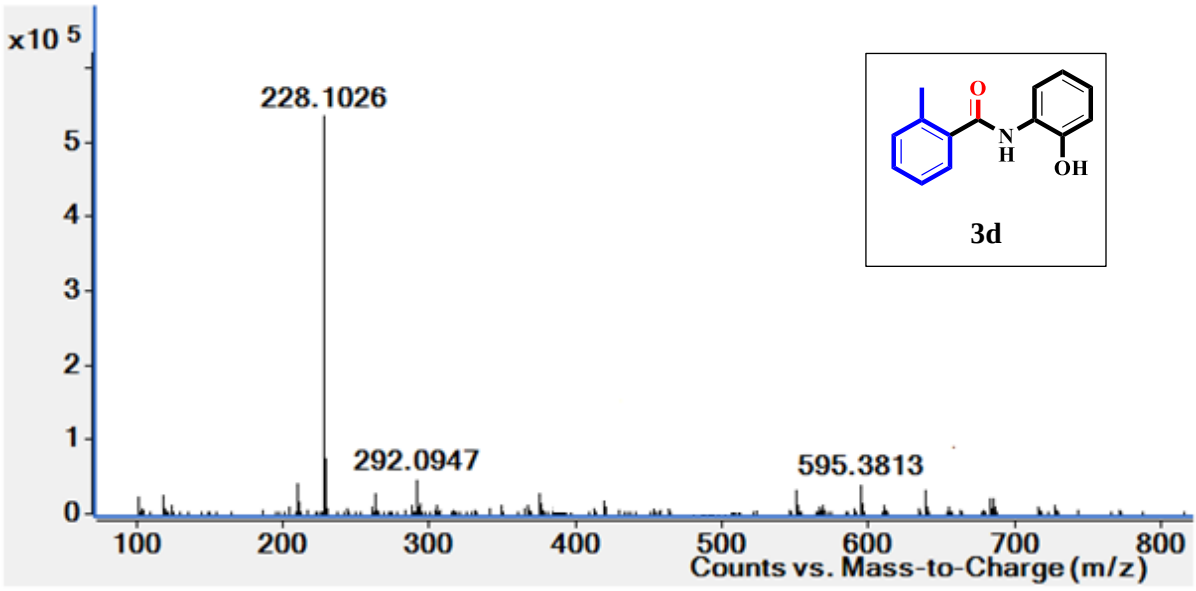


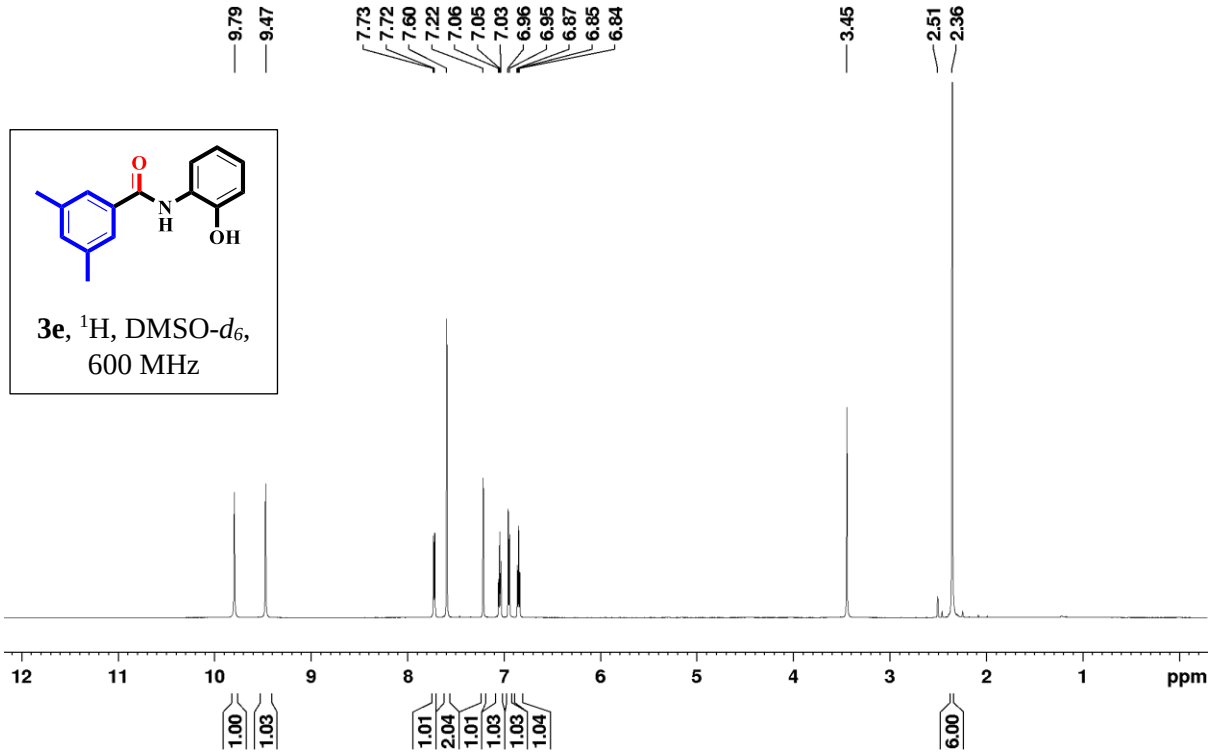
3c, ^{13}C, DMSO-d_6, 151 MHz


x10 5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
228.1024
475.1631
100
200
300
400
500
600
700
800
Counts vs. Mass-to-Charge (m/z)
O
N
H
OH
3c

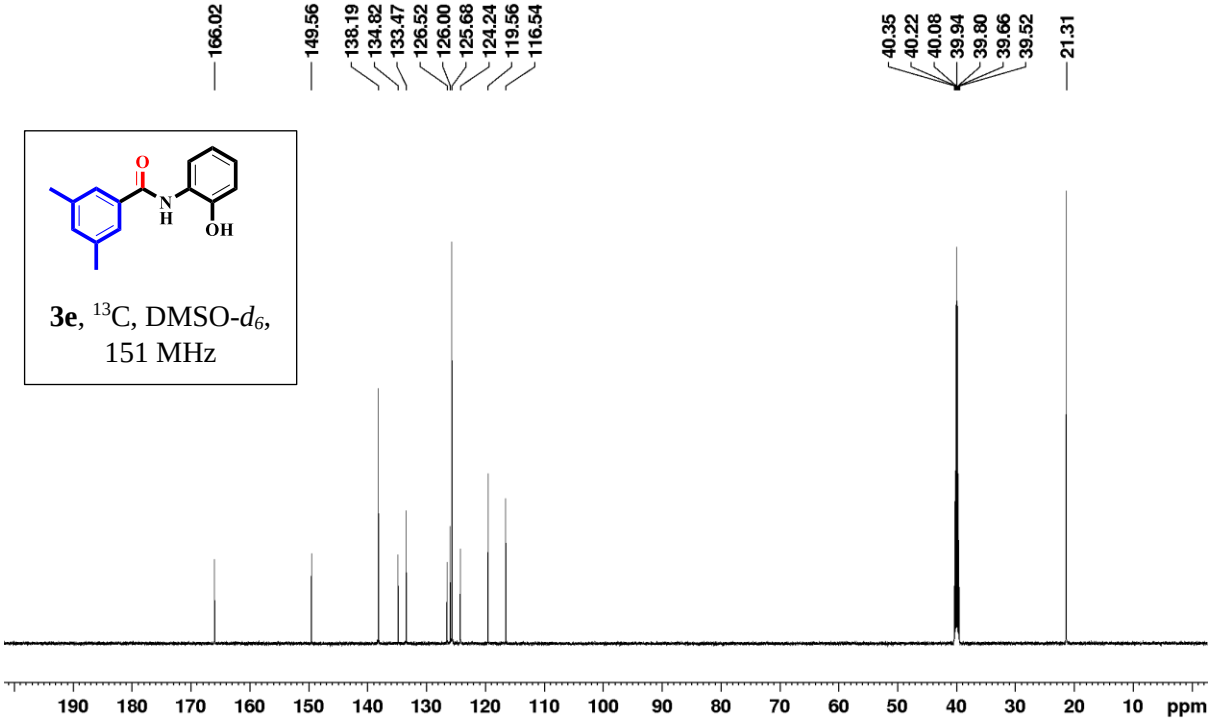

9.78
9.44
7.74
7.73
7.54
7.53
7.41
7.40
7.39
7.32
7.31
7.29
7.06
7.05
7.03
7.03
6.94
6.93
6.86
6.85
6.84
3.41
2.51
2.51
2.51
2.44
O
N
H
OH
3d, 1H, DMSO-d6,
600 MHz
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.08
1.05
1.04
1.04
1.05
2.02
1.09
1.08
1.08
3.00


168.46
149.35
137.08
135.99
131.13
130.28
127.72
126.49
126.16
126.04
123.95
119.54
116.61
40.38
40.24
40.10
39.96
39.82
39.69
39.55
19.97
O
N
H
OH
3d, 13C, DMSO-d6,
151 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

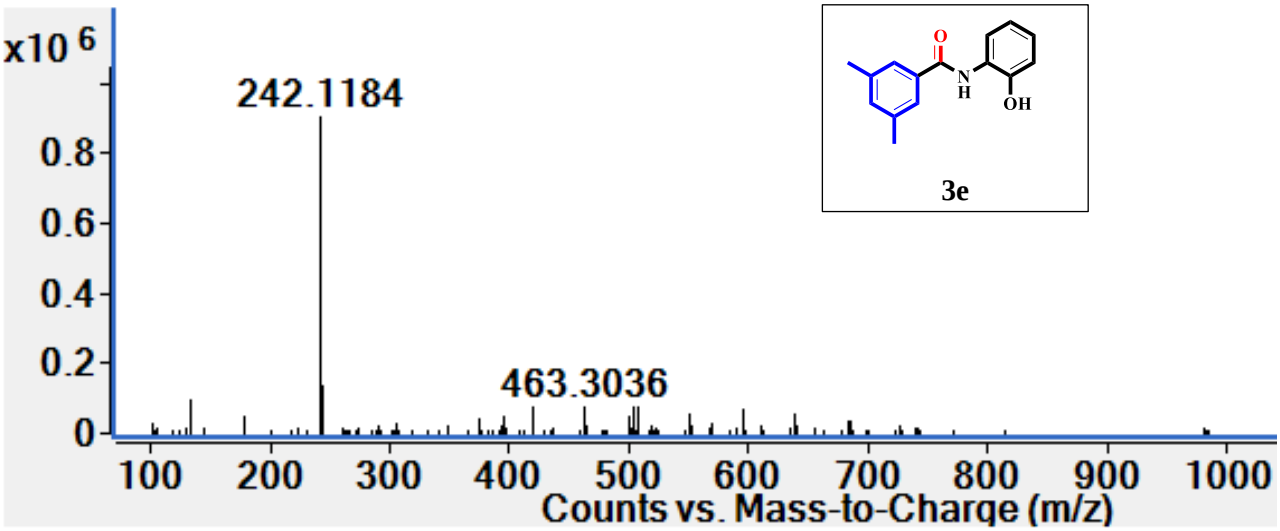

x10 5
5
4
3
2
1
0
228.1026
292.0947
595.3813
100 200 300 400 500 600 700 800
Counts vs. Mass-to-Charge (m/z)
O
N
H
OH
3d

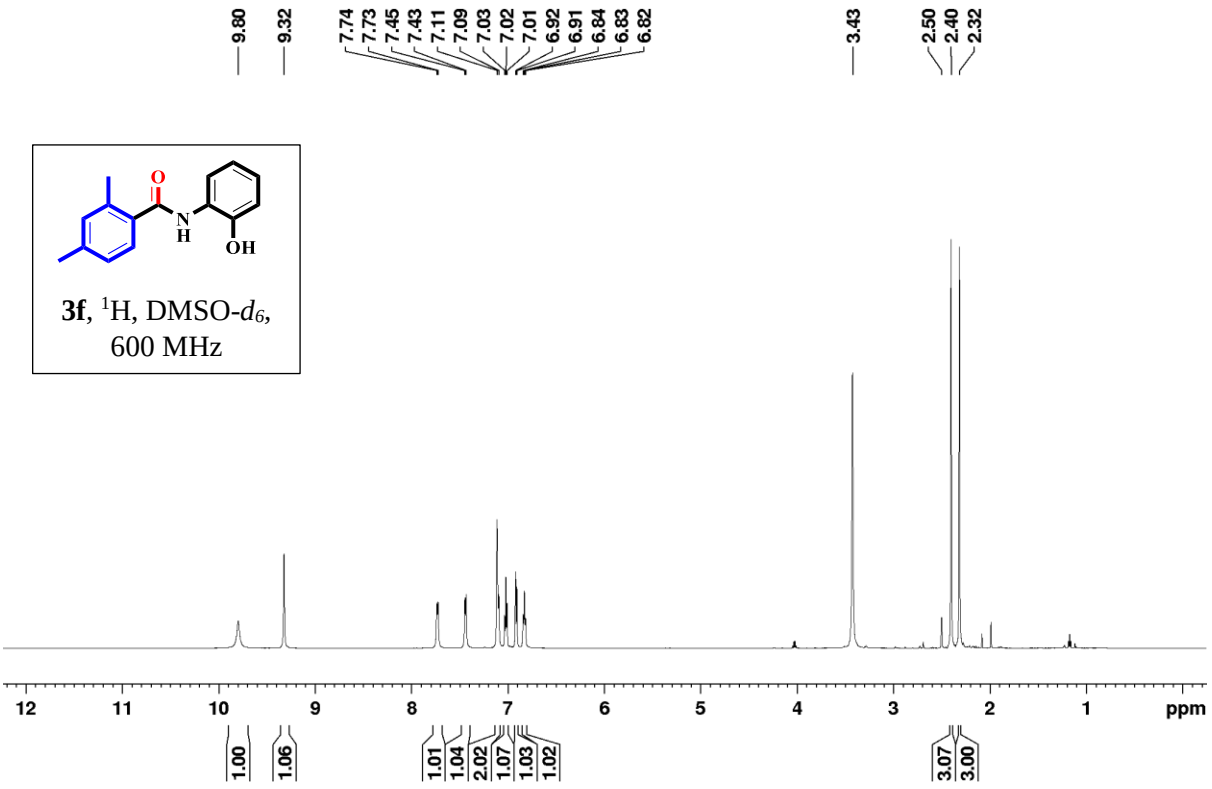


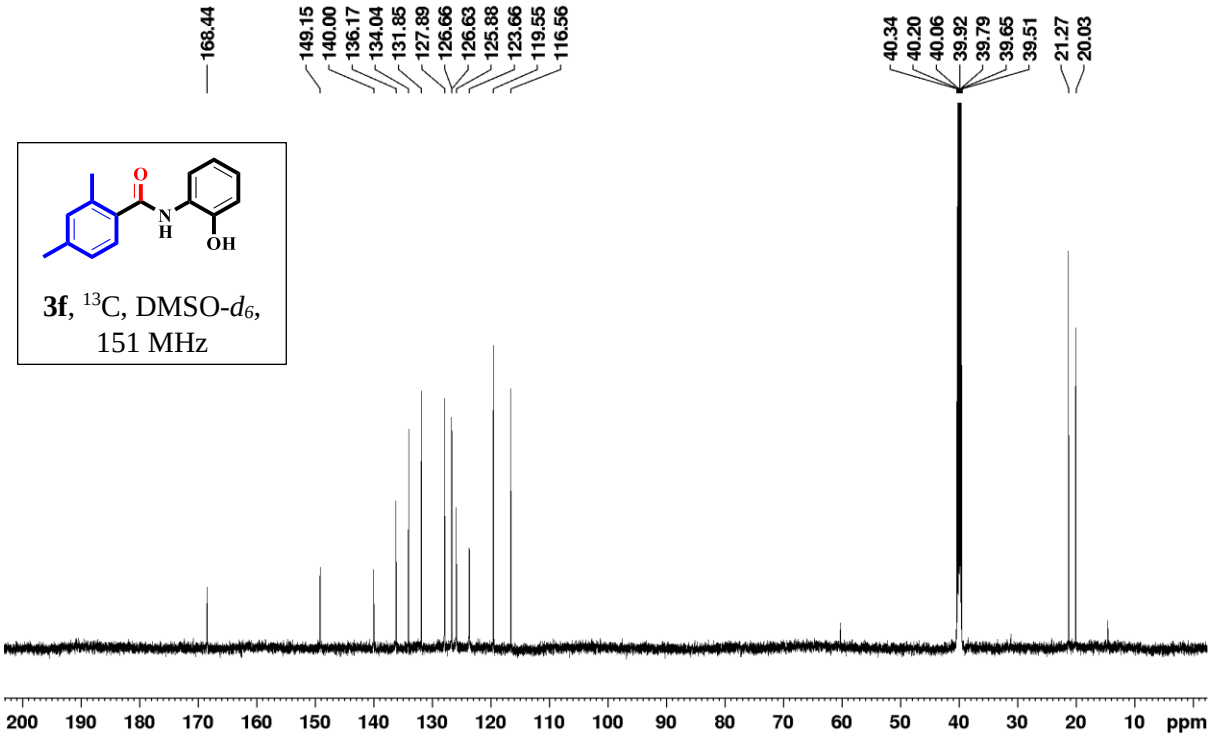
3e, ^{1}H, DMSO-*d*$_6$, 600 MHz



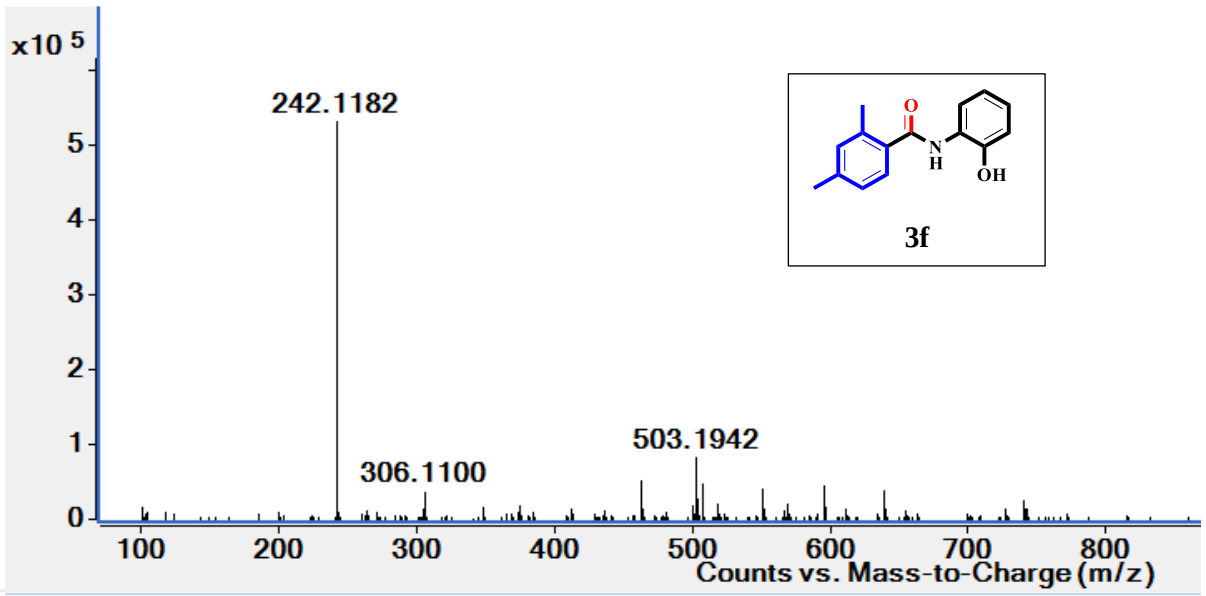
3e, ^{13}C, DMSO-*d*$_6$, 151 MHz

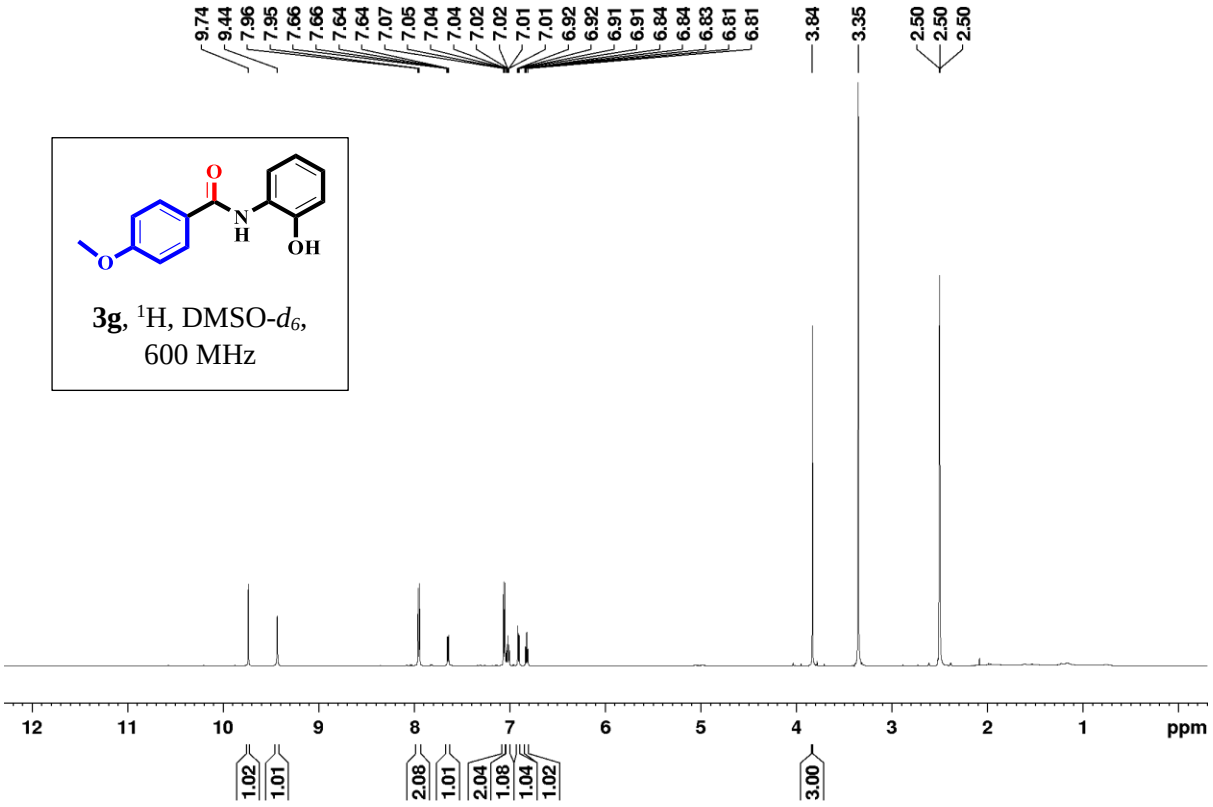

x10 6
242.1184
463.3036
0.8
0.6
0.4
0.2
0
100
200
300
400
500
600
700
800
900
1000
Counts vs. Mass-to-Charge (m/z)
O
N
H
OH
3e


9.80
9.32
7.74
7.73
7.45
7.43
7.11
7.09
7.03
7.02
7.01
6.92
6.91
6.84
6.83
6.82
3.43
2.50
2.40
2.32
O
N
H
OH
3f, 1H, DMSO-d6, 600 MHz
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.06
1.01
1.04
2.02
1.07
1.03
1.02
3.07
3.00

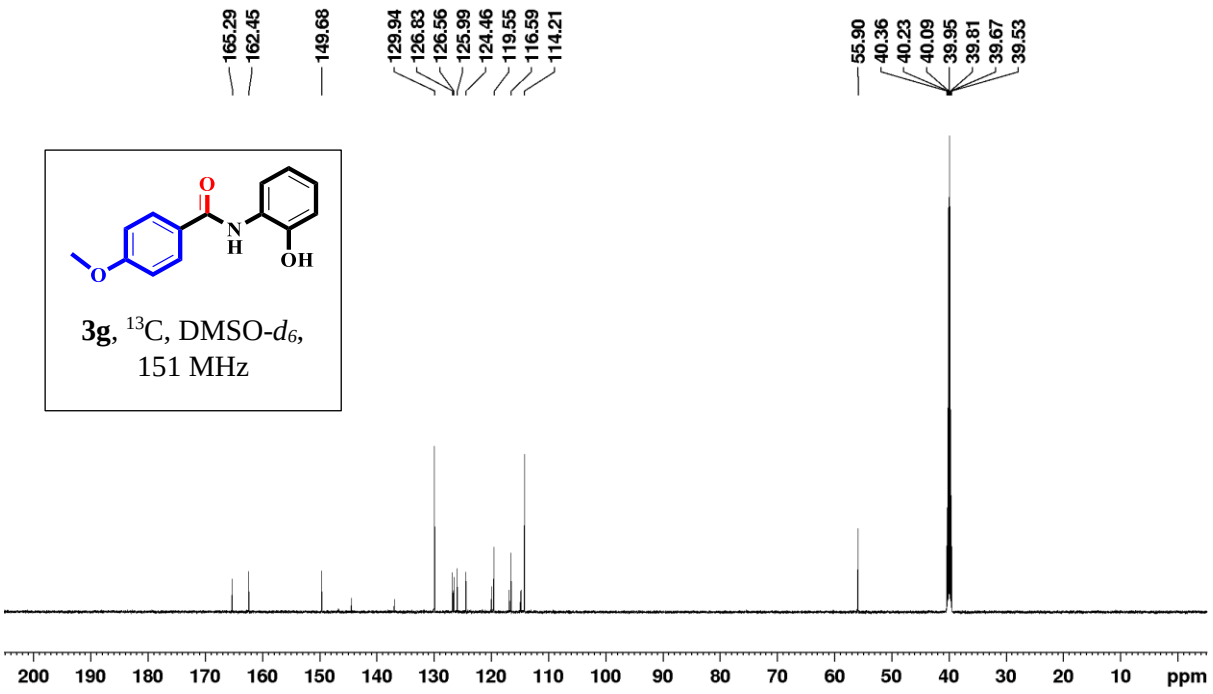


3f, ^{13}C, DMSO-d_6, 151 MHz

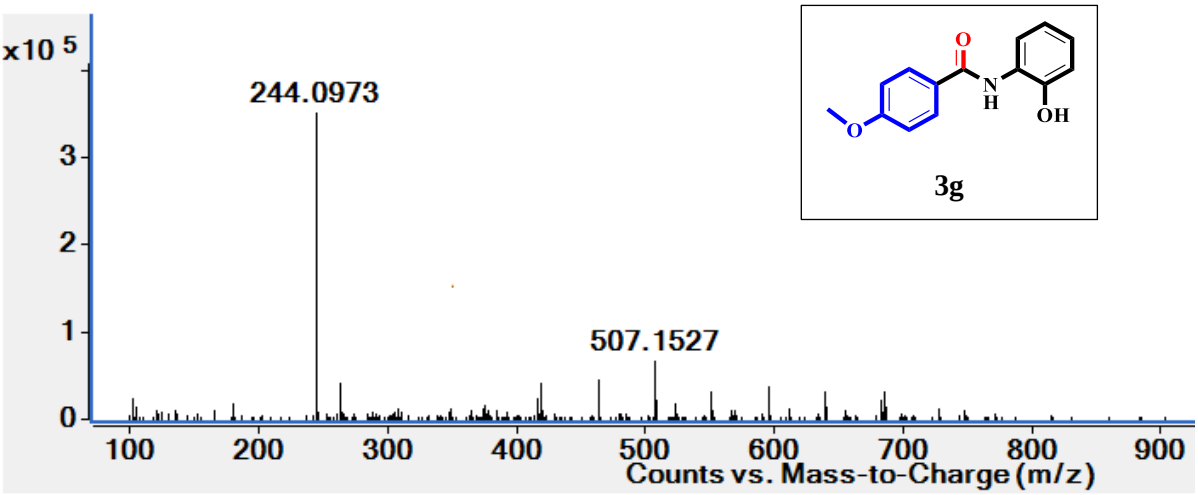


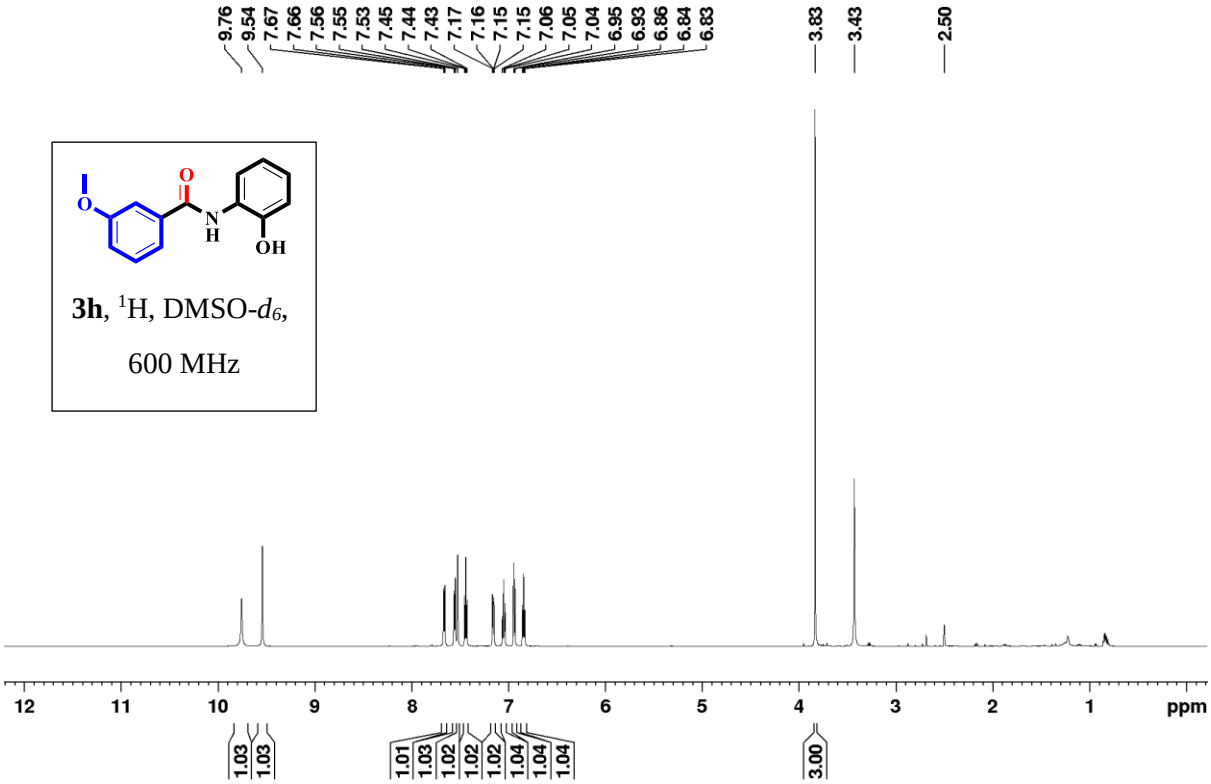


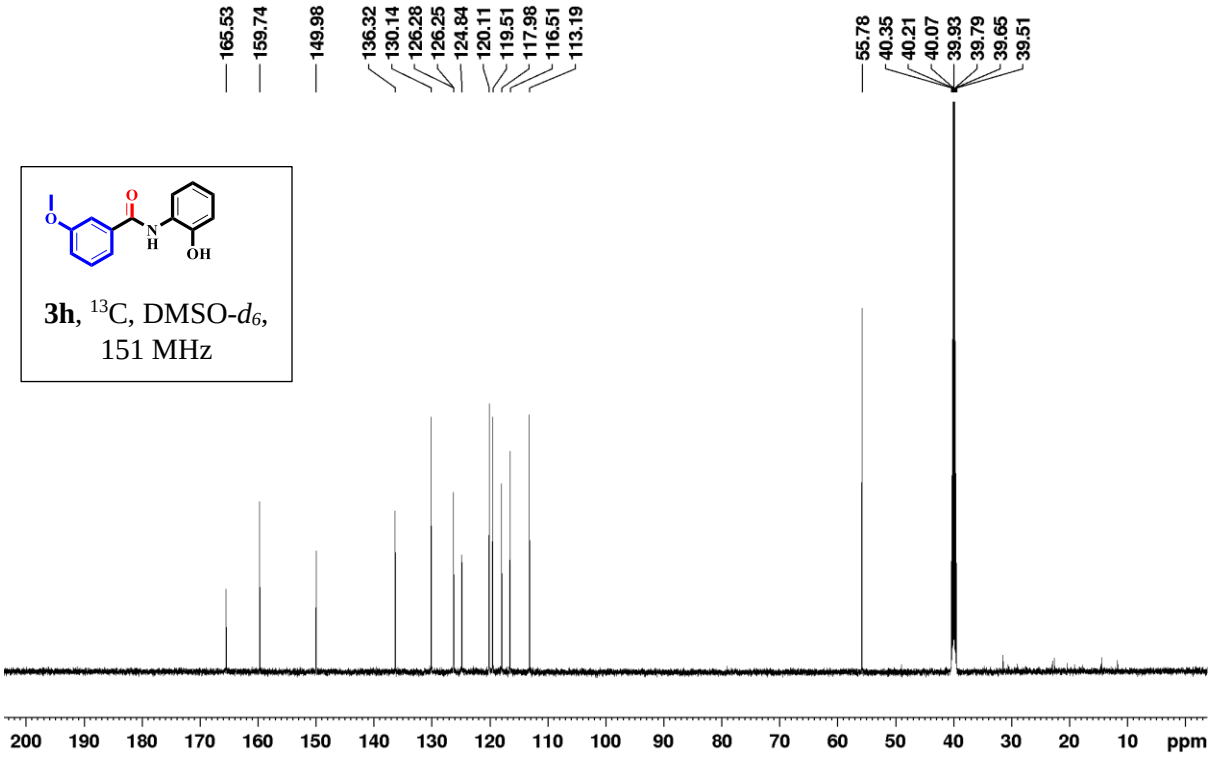
3g, ^{1}H, DMSO-d_6, 600 MHz

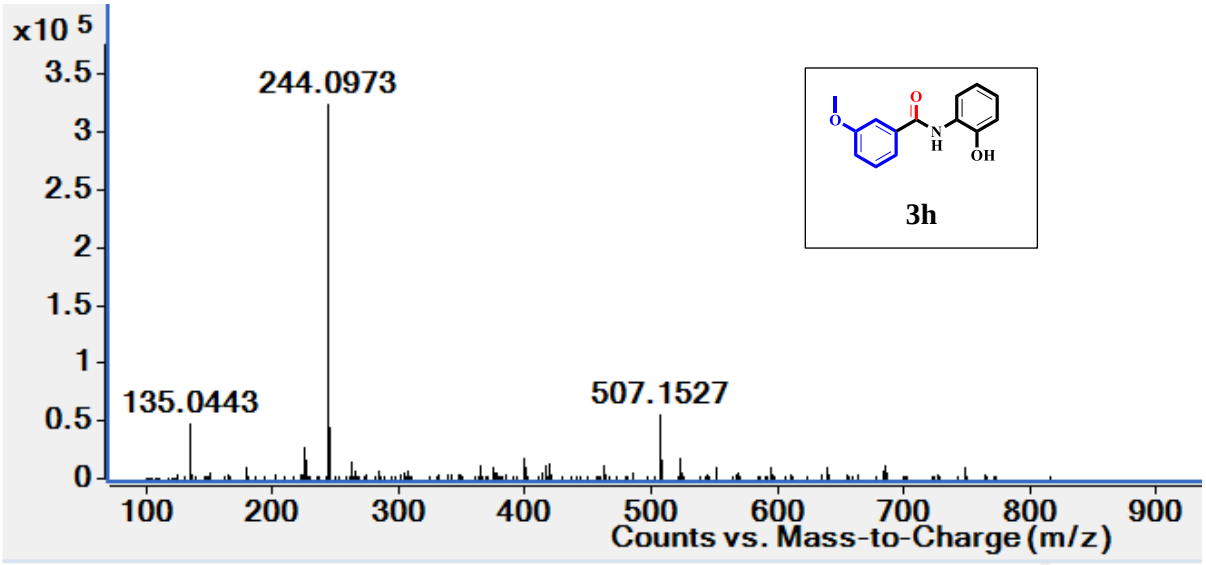


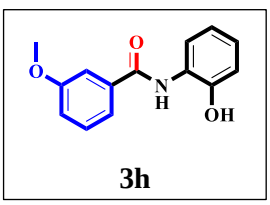
3g, ^{13}C, DMSO-d_6, 151 MHz

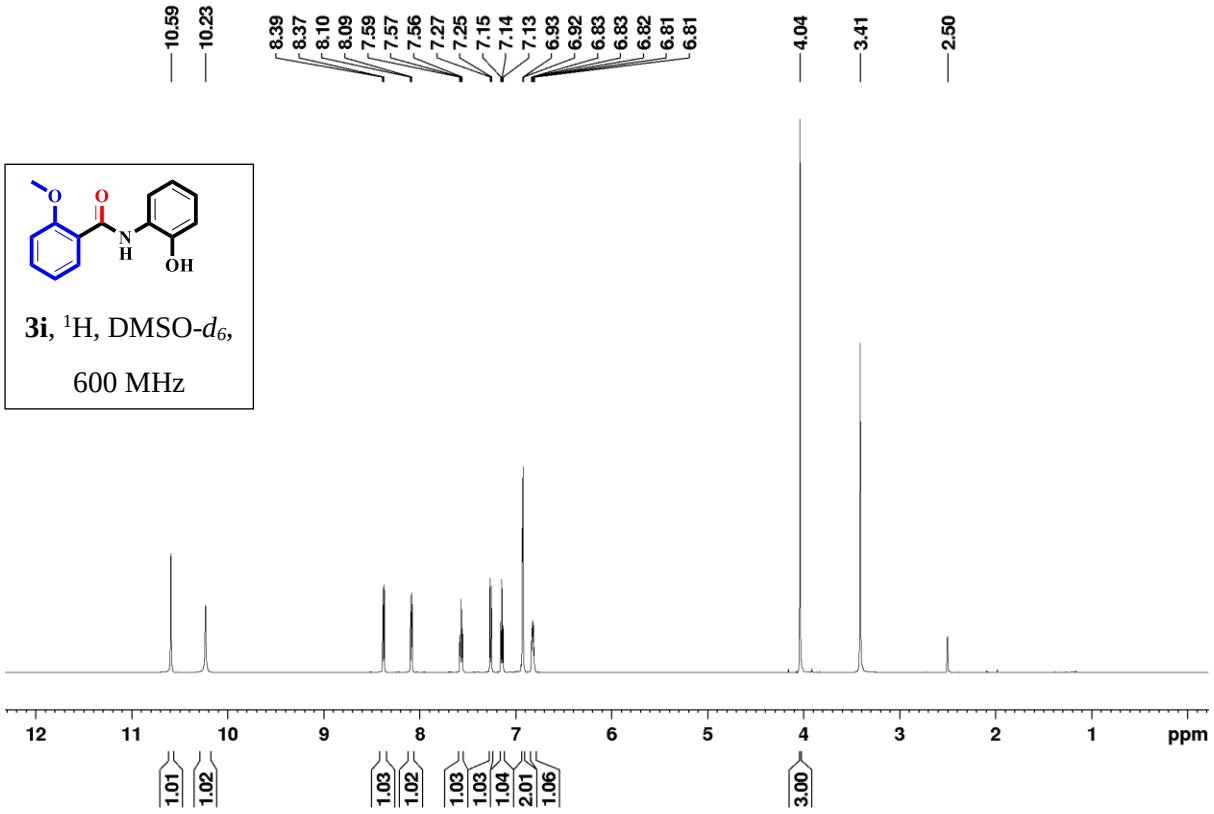

x10 5
244.0973
507.1527
Counts vs. Mass-to-Charge (m/z)
3g

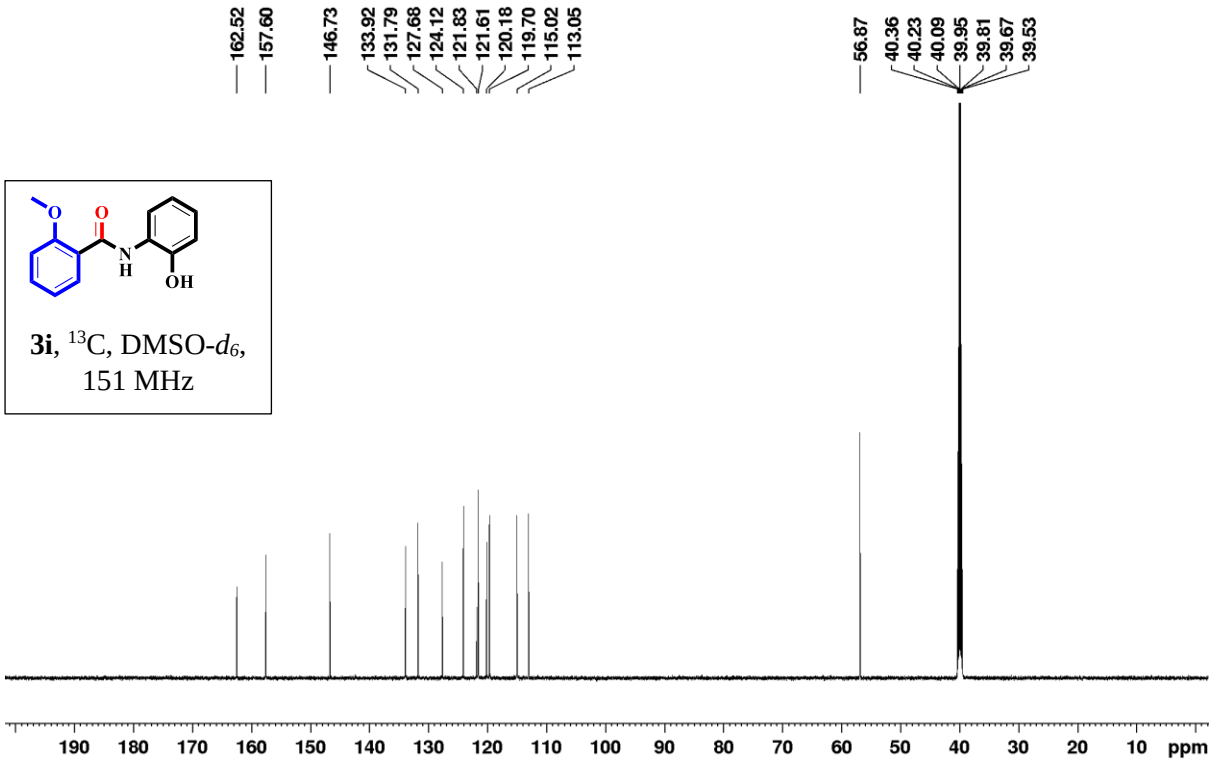

9.76
9.54
7.67
7.66
7.56
7.55
7.53
7.45
7.44
7.43
7.17
7.16
7.15
7.15
7.06
7.05
7.04
6.95
6.93
6.86
6.84
6.83
3.83
3.43
2.50
3h, 1H, DMSO-d6,
600 MHz
ppm
1.03
1.03
1.01
1.03
1.02
1.02
1.02
1.04
1.04
1.04
3.00

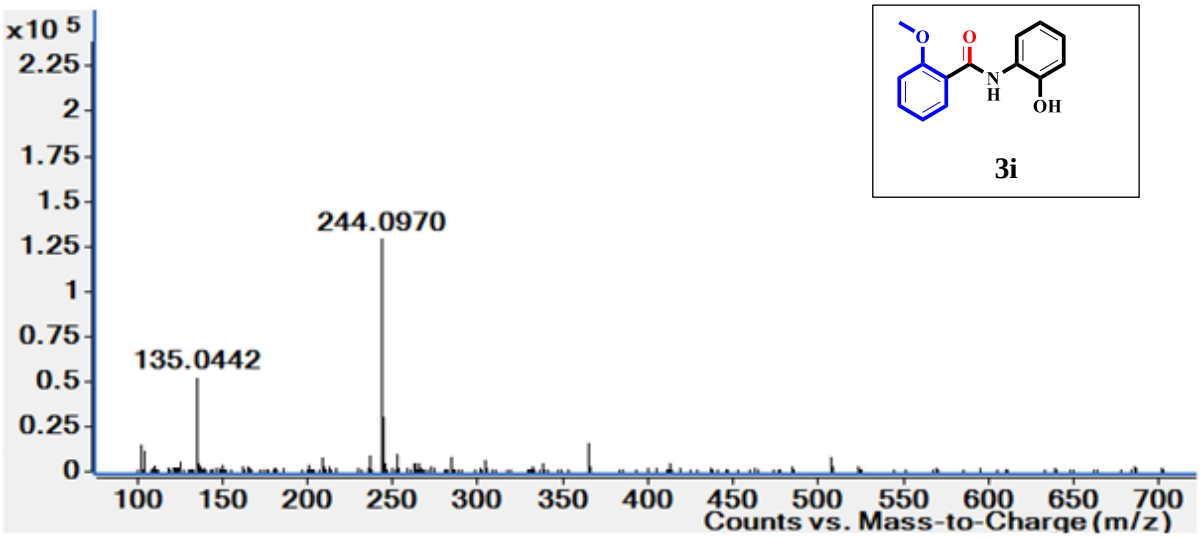

165.53
159.74
149.98
136.32
130.14
126.28
126.25
124.84
120.11
119.51
117.98
116.51
113.19
55.78
40.35
40.21
40.07
39.93
39.79
39.65
39.51
3h, 13C, DMSO-d6, 151 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


x10 5
3.5
3
2.5
2
1.5
1
0.5
0
244.0973
135.0443
507.1527
100 200 300 400 500 600 700 800 900
Counts vs. Mass-to-Charge (m/z)
3h

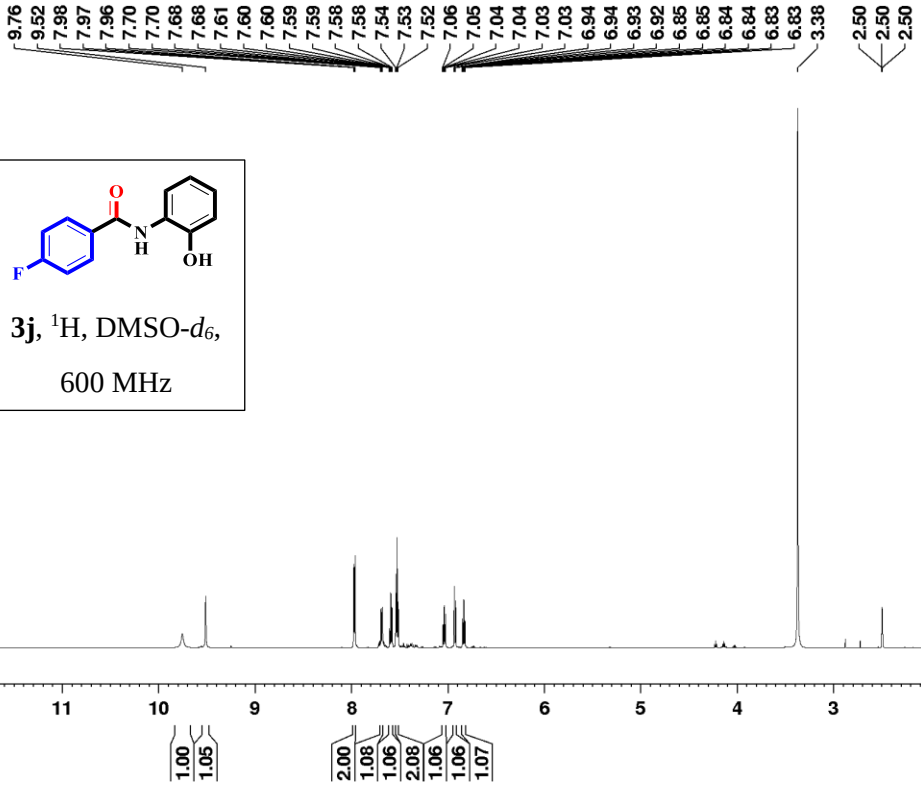

3h


10.59
10.23
8.39
8.37
8.10
8.09
7.59
7.57
7.56
7.27
7.25
7.15
7.14
7.13
6.93
6.92
6.83
6.83
6.82
6.81
6.81
4.04
3.41
2.50
3i, 1H, DMSO-d6,
600 MHz
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
1.02
1.03
1.02
1.03
1.03
1.04
2.01
1.06
3.00

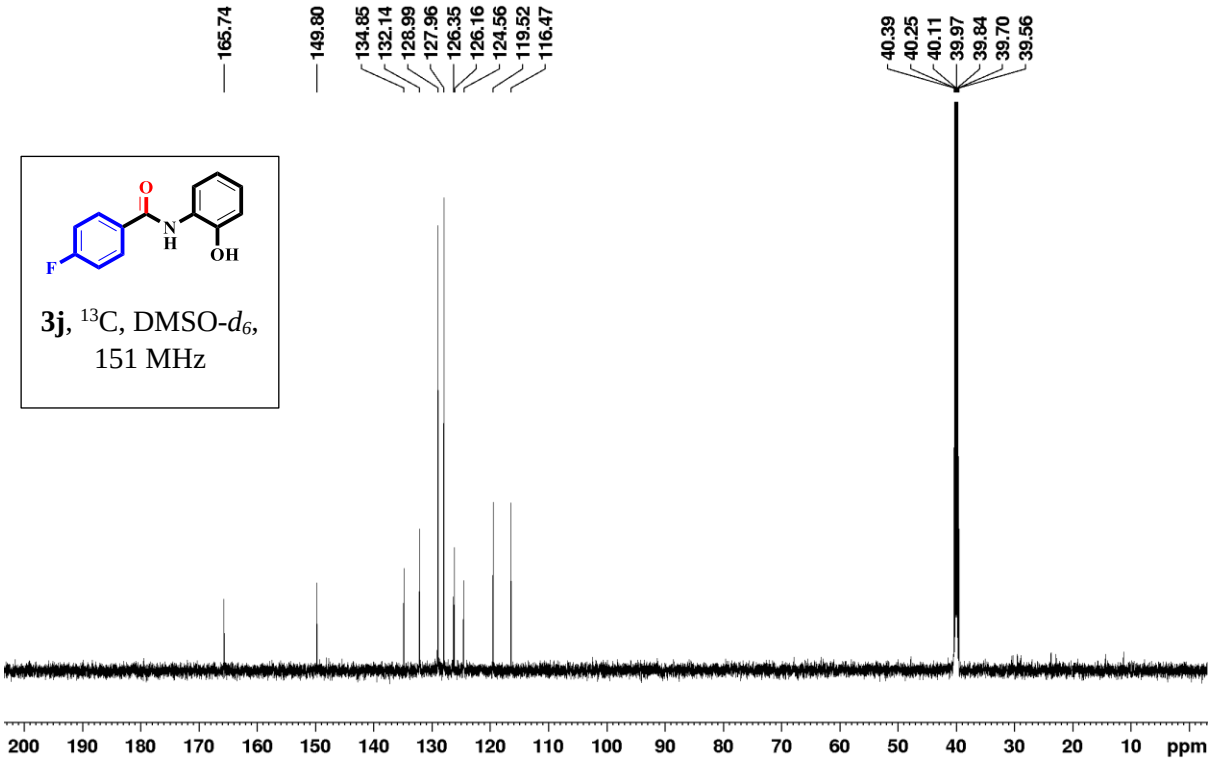

162.52
157.60
146.73
133.92
131.79
127.68
124.12
121.83
121.61
120.18
119.70
115.02
113.05
56.87
40.36
40.23
40.09
39.95
39.81
39.67
39.53
3i, 13C, DMSO-d6,
151 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



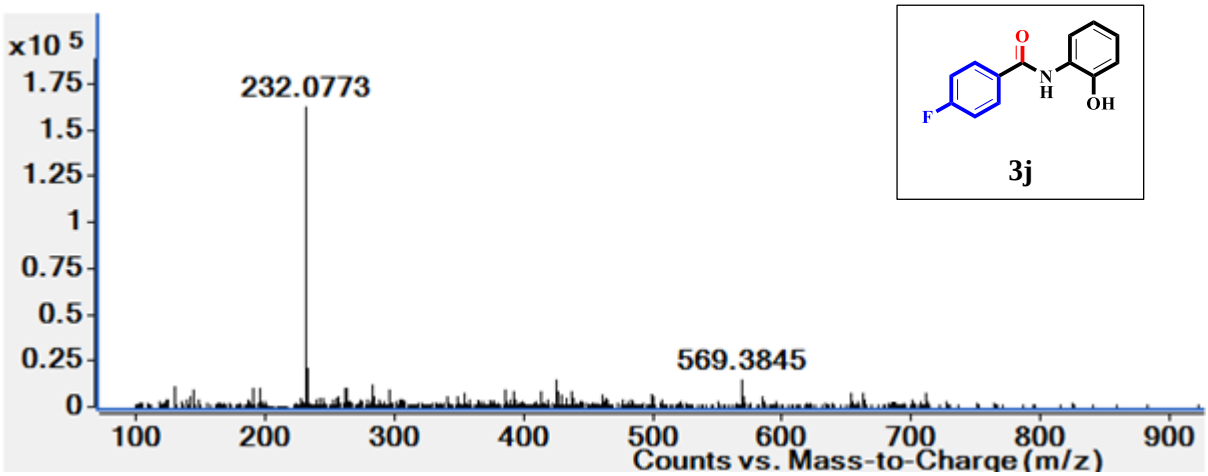
3i

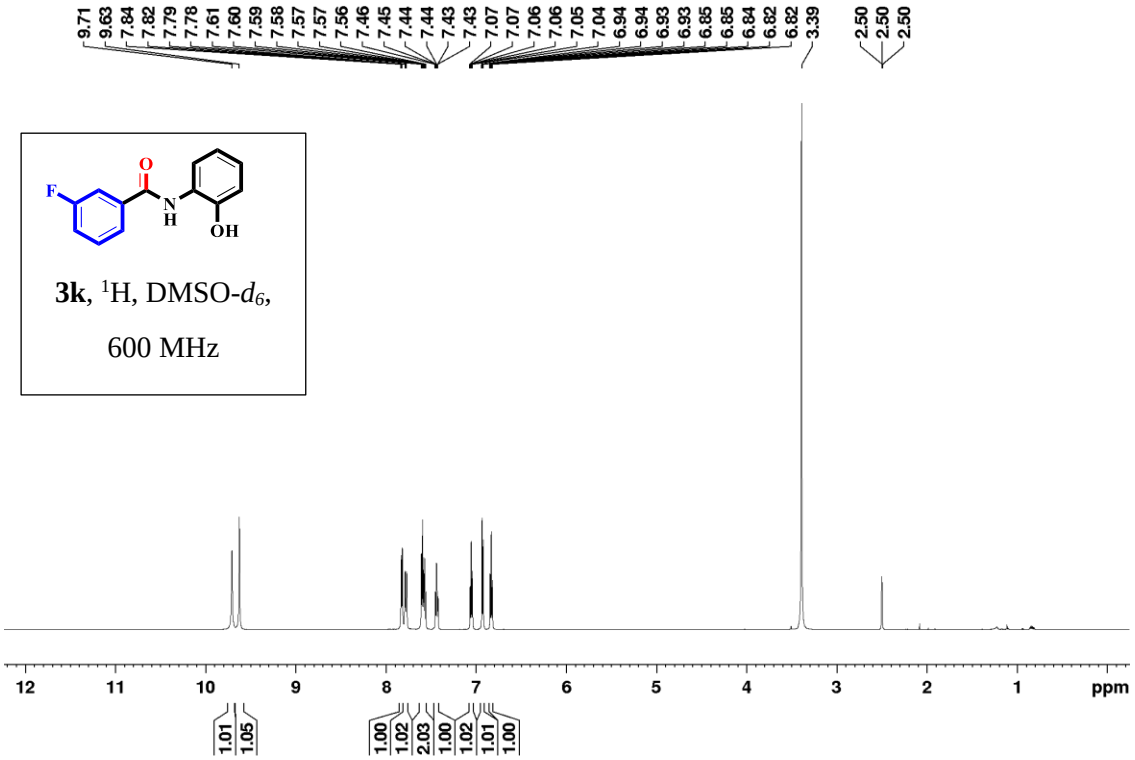


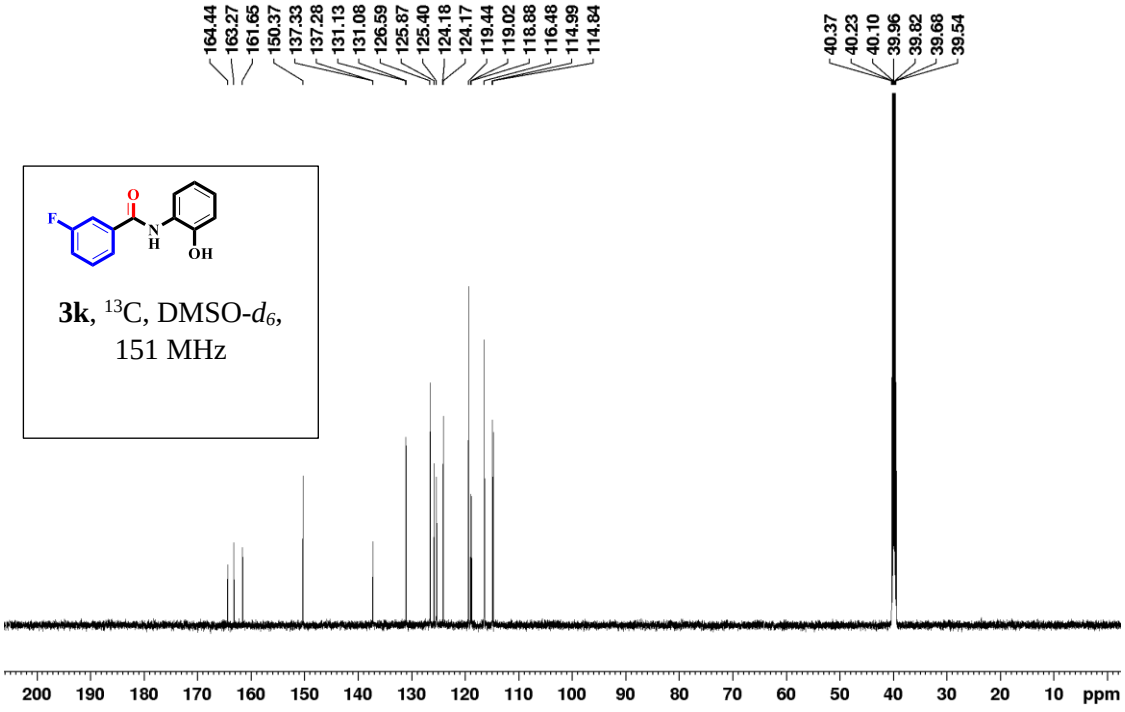
3j, ^{1}H, DMSO-d_6, 600 MHz

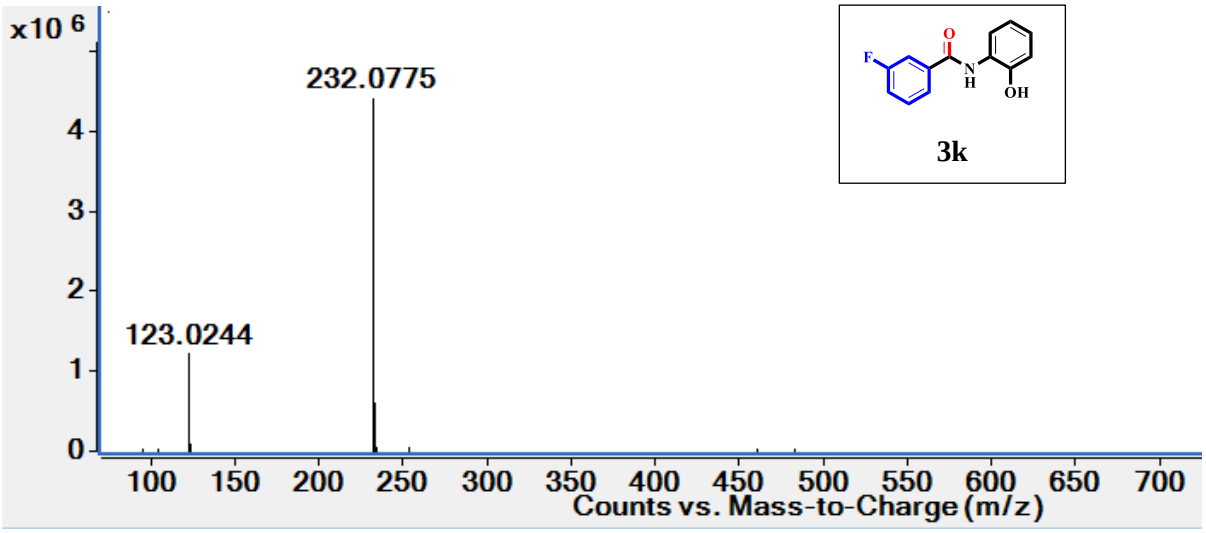


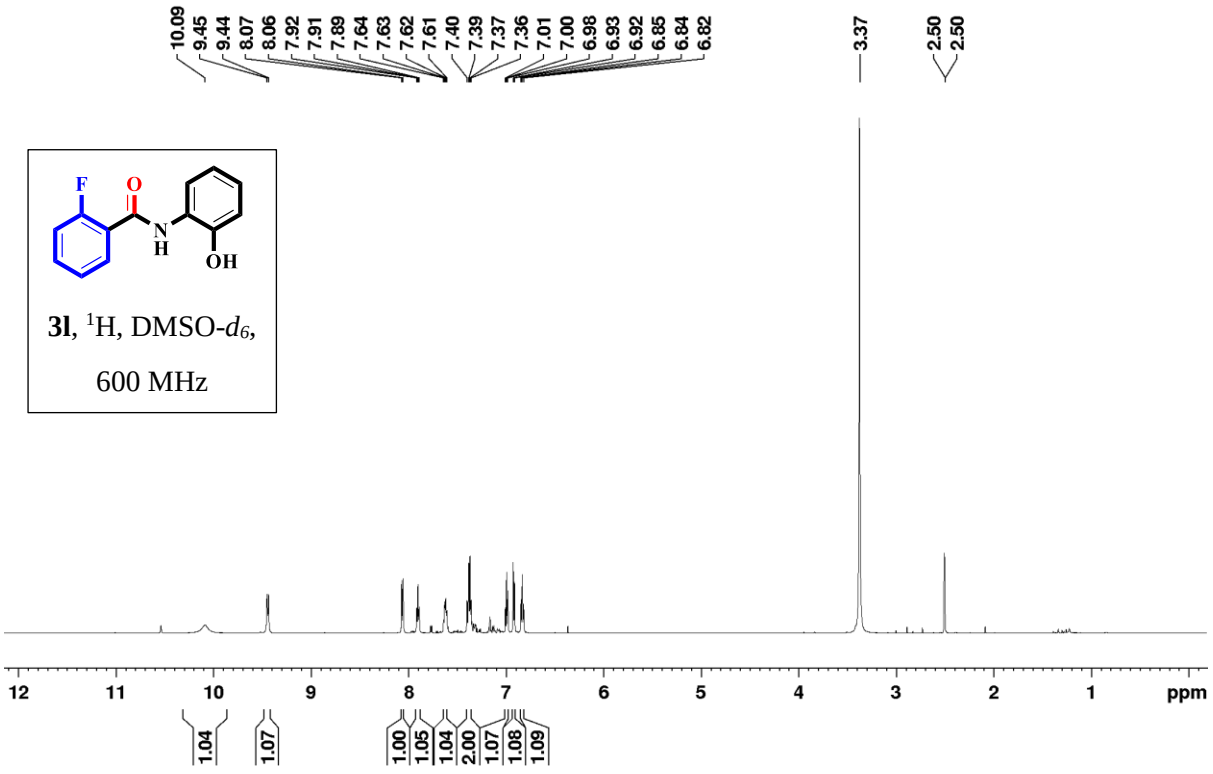
3j, ^{13}C, DMSO-d_6, 151 MHz

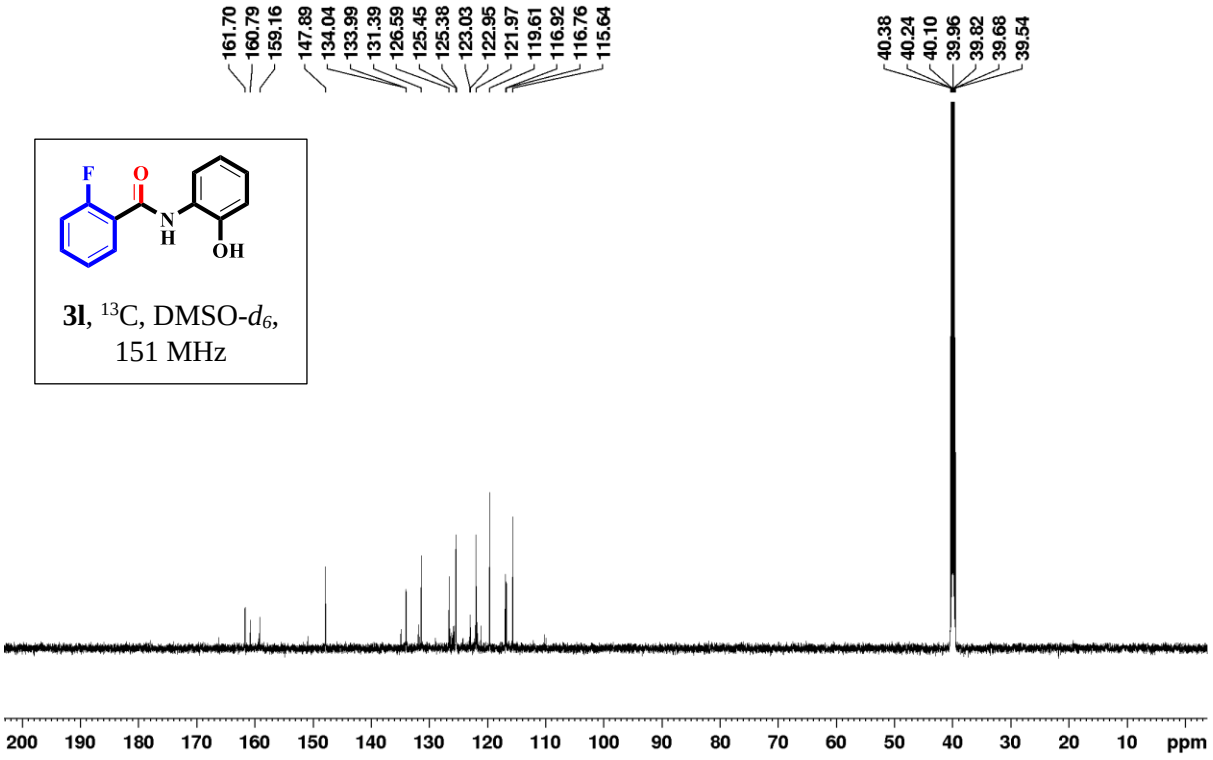



9.71
9.63
7.84
7.82
7.79
7.78
7.61
7.60
7.59
7.58
7.57
7.57
7.56
7.46
7.45
7.44
7.44
7.43
7.43
7.07
7.07
7.06
7.06
7.05
7.04
6.94
6.94
6.93
6.93
6.85
6.85
6.84
6.82
6.82
3.39
2.50
2.50
2.50
F
O
N
H
OH
3k, 1H, DMSO-d6,
600 MHz
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
1.05
1.00
1.02
2.03
1.00
1.02
1.01
1.00

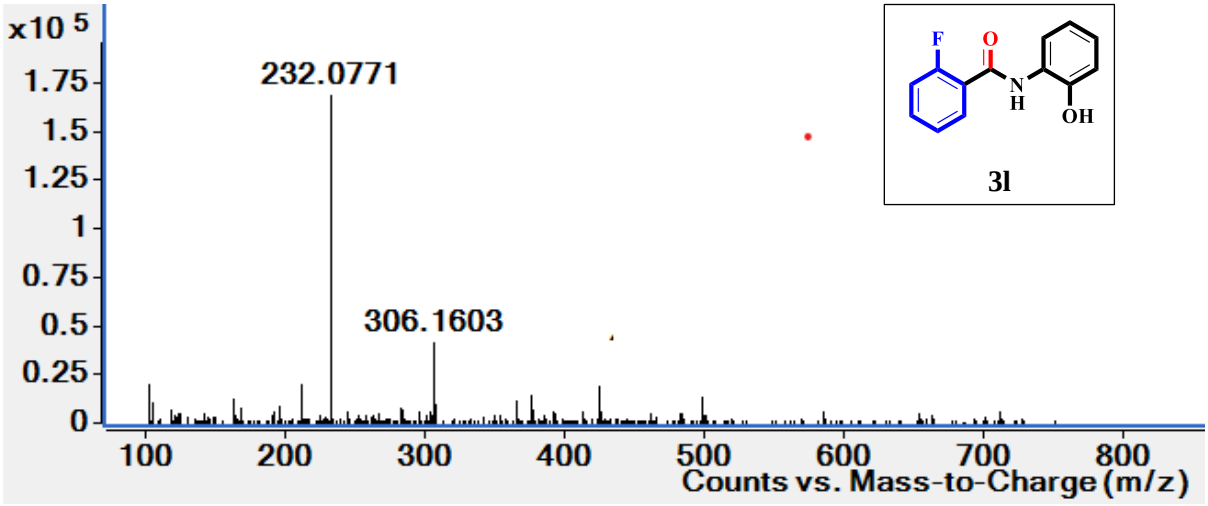

164.44
163.27
161.65
150.37
137.33
137.28
131.13
131.08
126.59
125.87
125.40
124.18
124.17
119.44
119.02
118.88
116.48
114.99
114.84
40.37
40.23
40.10
39.96
39.82
39.68
39.54
F
O
N
H
OH
3k, 13C, DMSO-d6,
151 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


x10 6
232.0775
123.0244
Counts vs. Mass-to-Charge (m/z)
3k

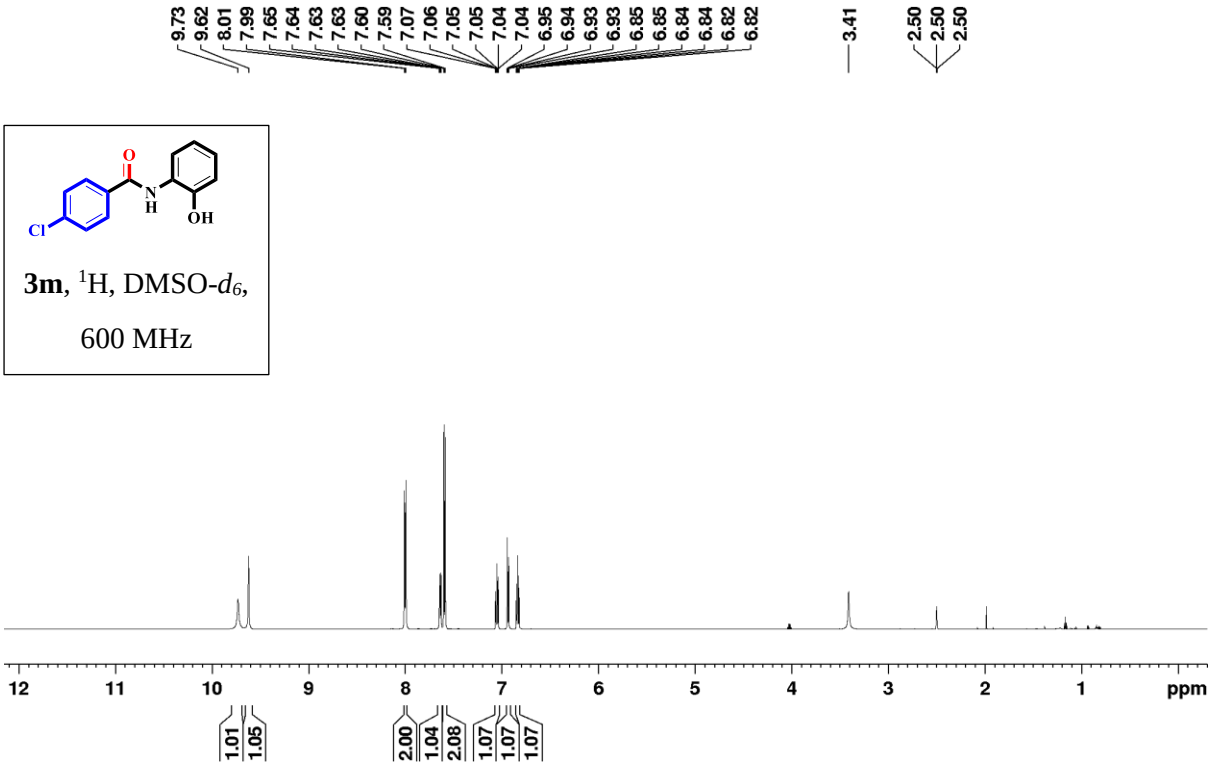

10.09
9.45
9.44
8.07
8.06
7.92
7.91
7.89
7.64
7.63
7.62
7.61
7.40
7.39
7.37
7.36
7.01
7.00
6.98
6.93
6.92
6.85
6.84
6.82
3.37
2.50
2.50
3l, 1H, DMSO-d6,
600 MHz
ppm

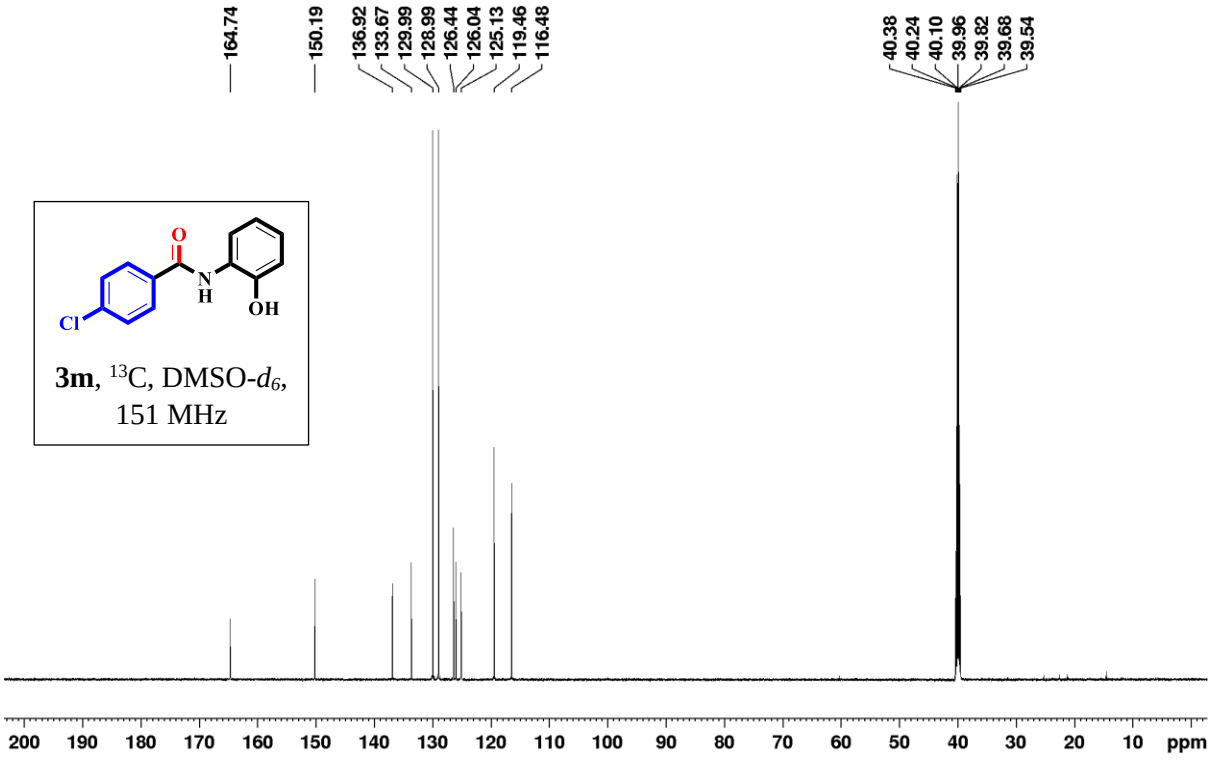


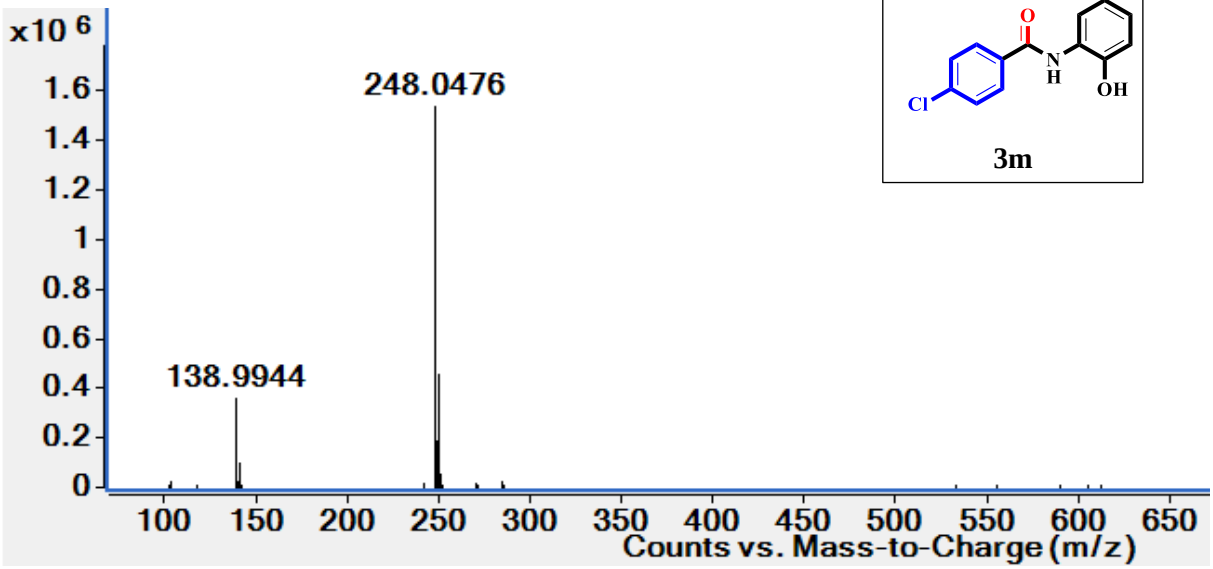
3l, ^{13}C, DMSO-d_6, 151 MHz

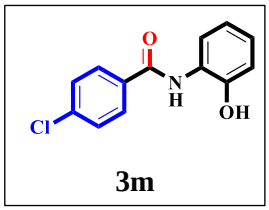


3l

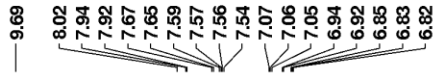

9.73
9.62
8.01
7.99
7.65
7.64
7.63
7.63
7.60
7.59
7.07
7.06
7.05
7.05
7.04
7.04
6.95
6.94
6.93
6.93
6.85
6.85
6.84
6.84
6.82
6.82
3.41
2.50
2.50
2.50
O
N
H
OH
Cl
3m, 1H, DMSO-d6,
600 MHz
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
1.05
2.00
1.04
2.08
1.07
1.07
1.07

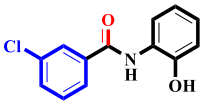

164.74
150.19
136.92
133.67
129.99
128.99
126.44
126.04
125.13
119.46
116.48
40.38
40.24
40.10
39.96
39.82
39.68
39.54
O
N
H
OH
Cl
3m, 13C, DMSO-d6,
151 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



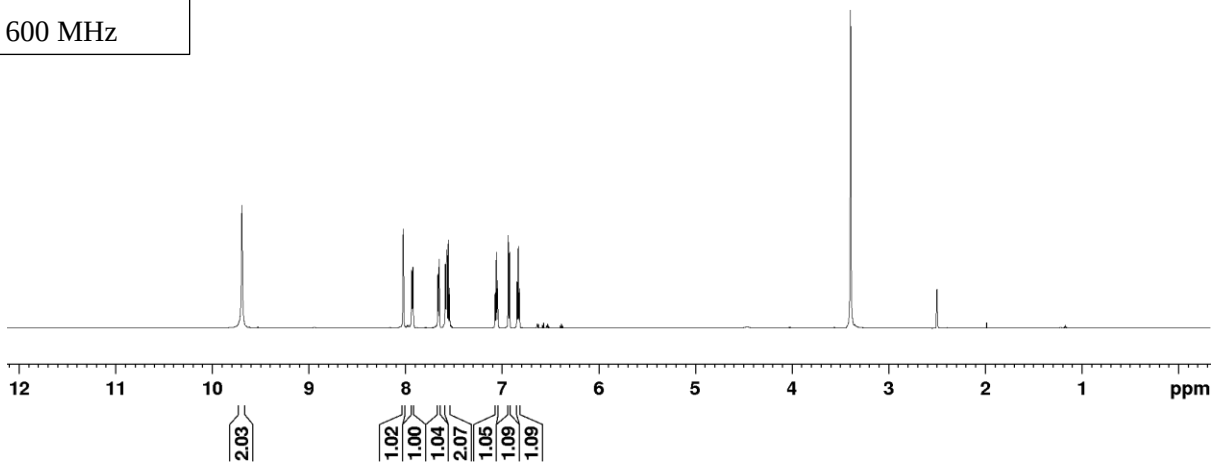


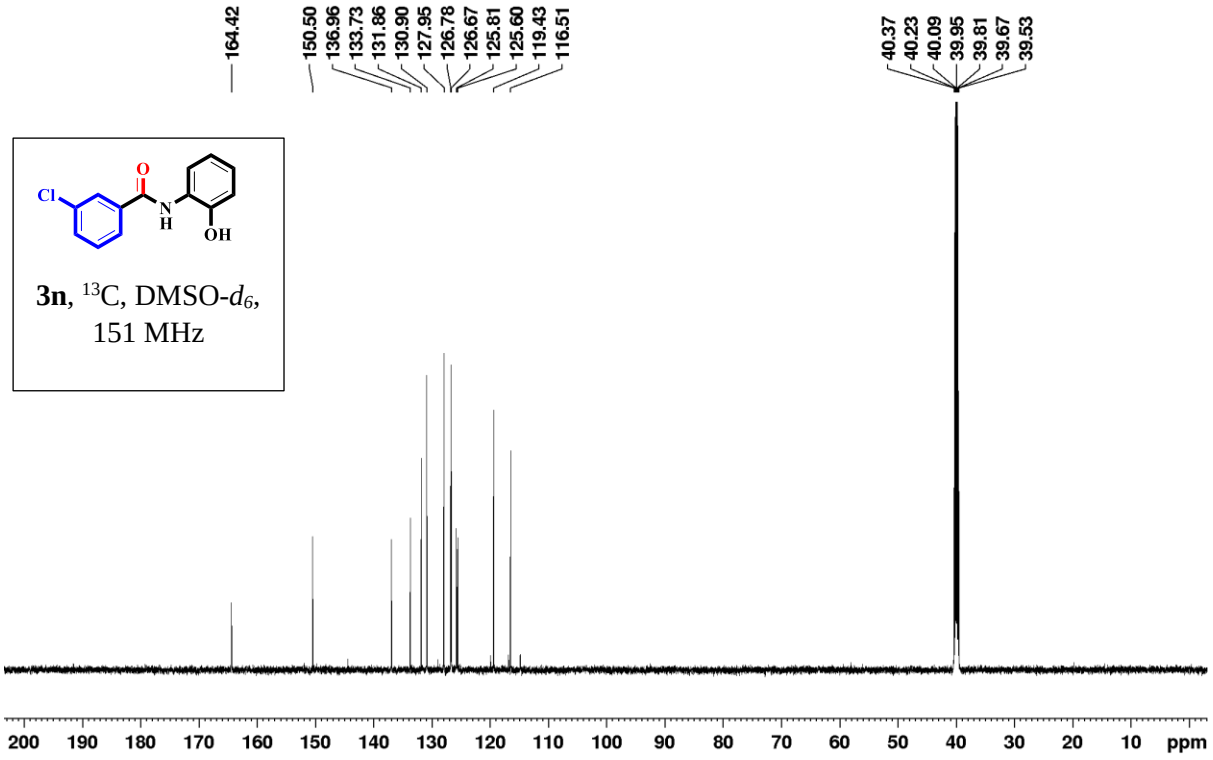
3m

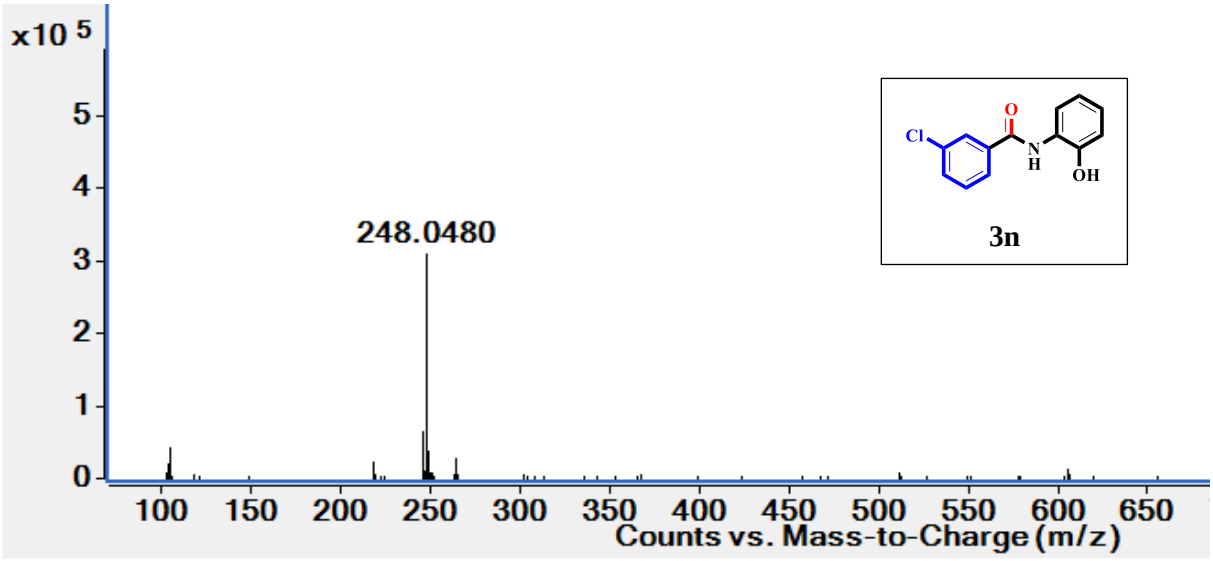


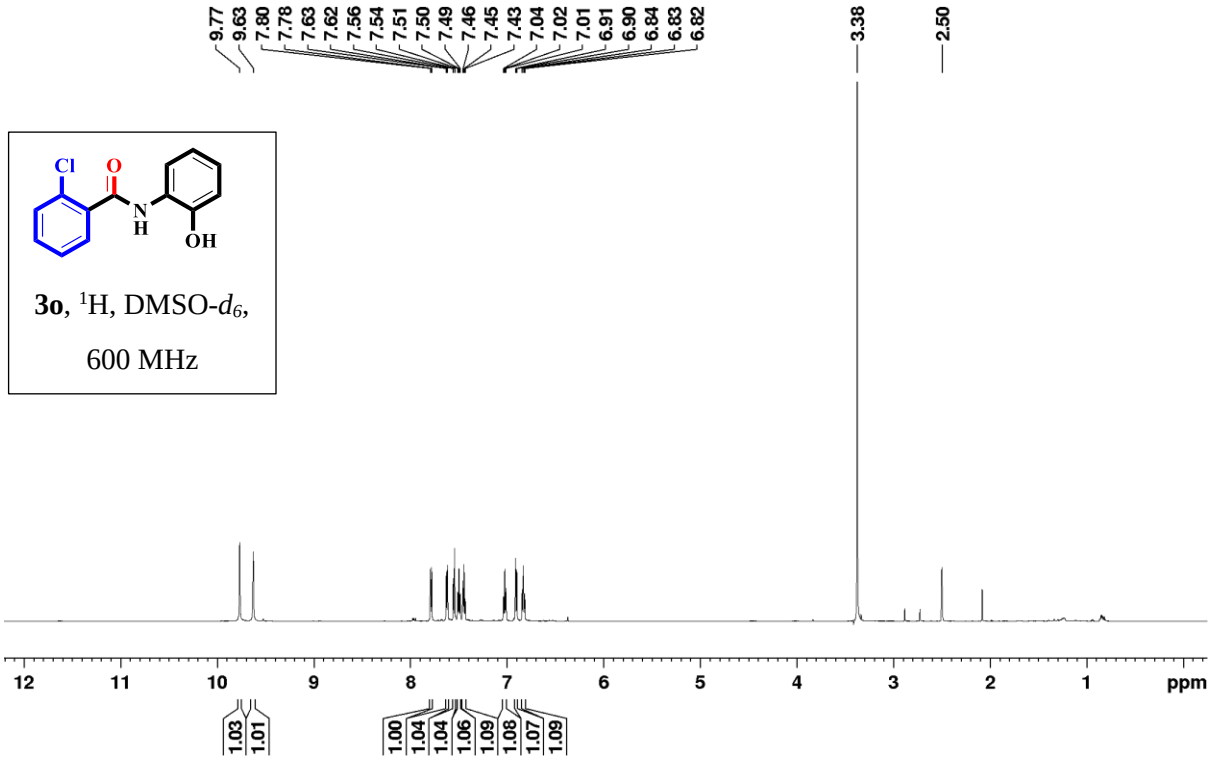


3n, ^{1}H, DMSO-d_6, 600 MHz

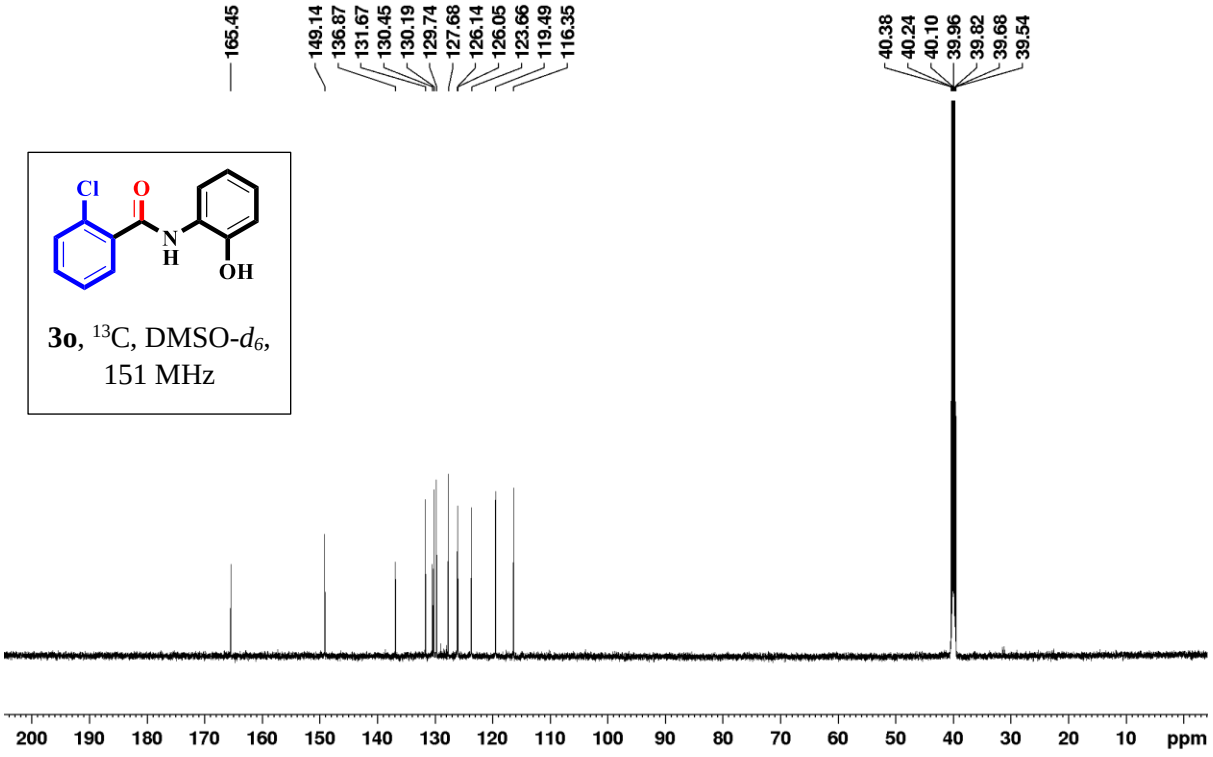



164.42
150.50
136.96
133.73
131.86
130.90
127.95
126.78
126.67
125.81
125.60
119.43
116.51
40.37
40.23
40.09
39.95
39.81
39.67
39.53
Cl
O
N
H
OH
3n, 13C, DMSO-d6, 151 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

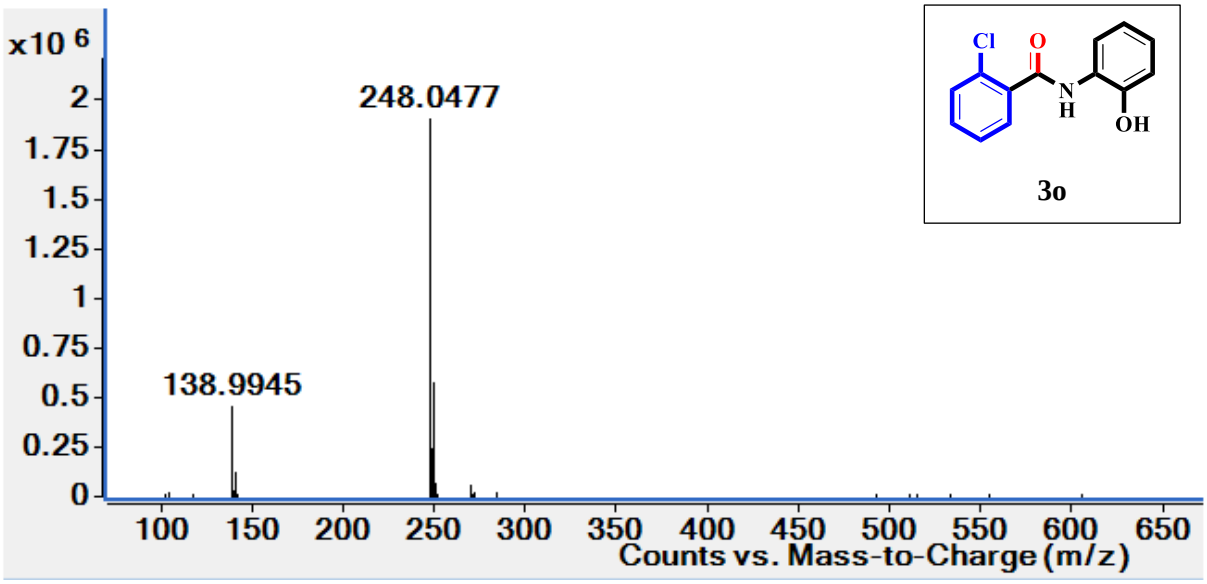

x10 5
5
4
3
2
1
0
248.0480
Cl
O
N
H
OH
3n
100 150 200 250 300 350 400 450 500 550 600 650
Counts vs. Mass-to-Charge (m/z)



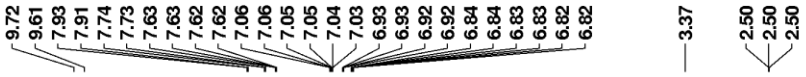
3o, ^{1}H, DMSO-d_6, 600 MHz

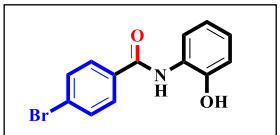


3o, ^{13}C, DMSO-d_6, 151 MHz

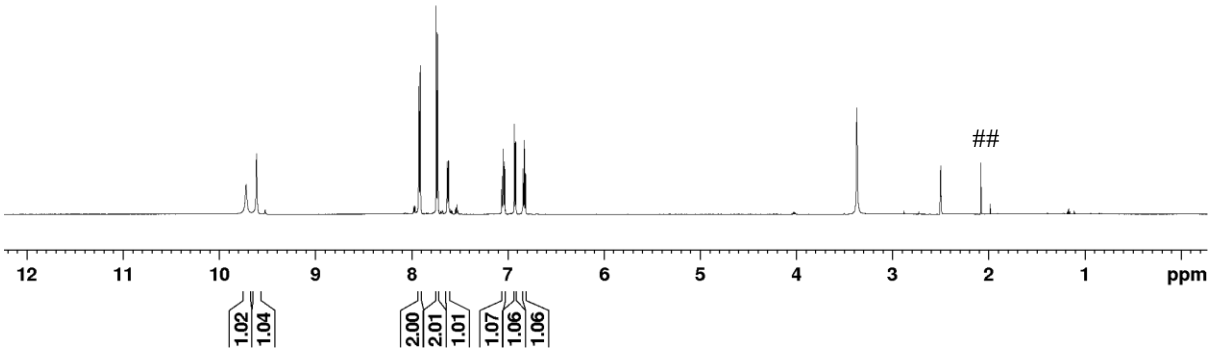


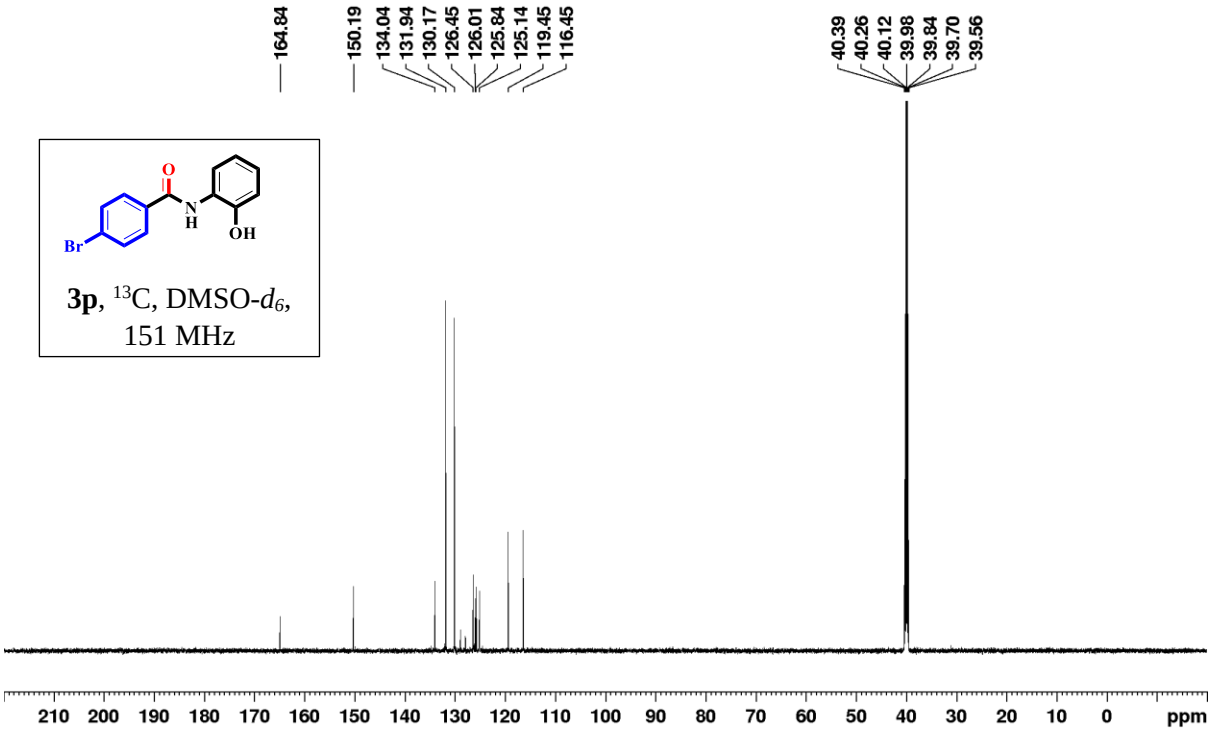
3o

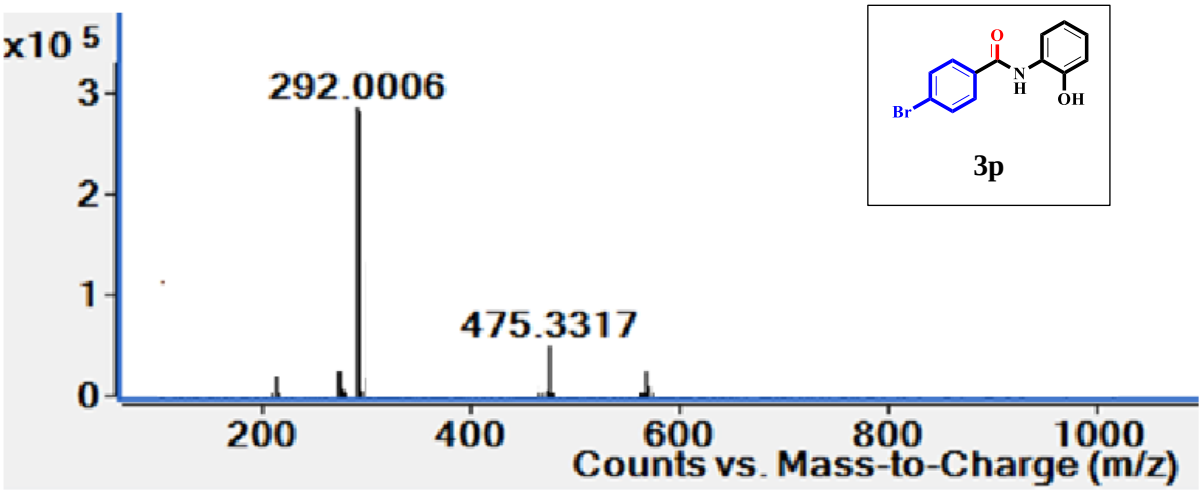


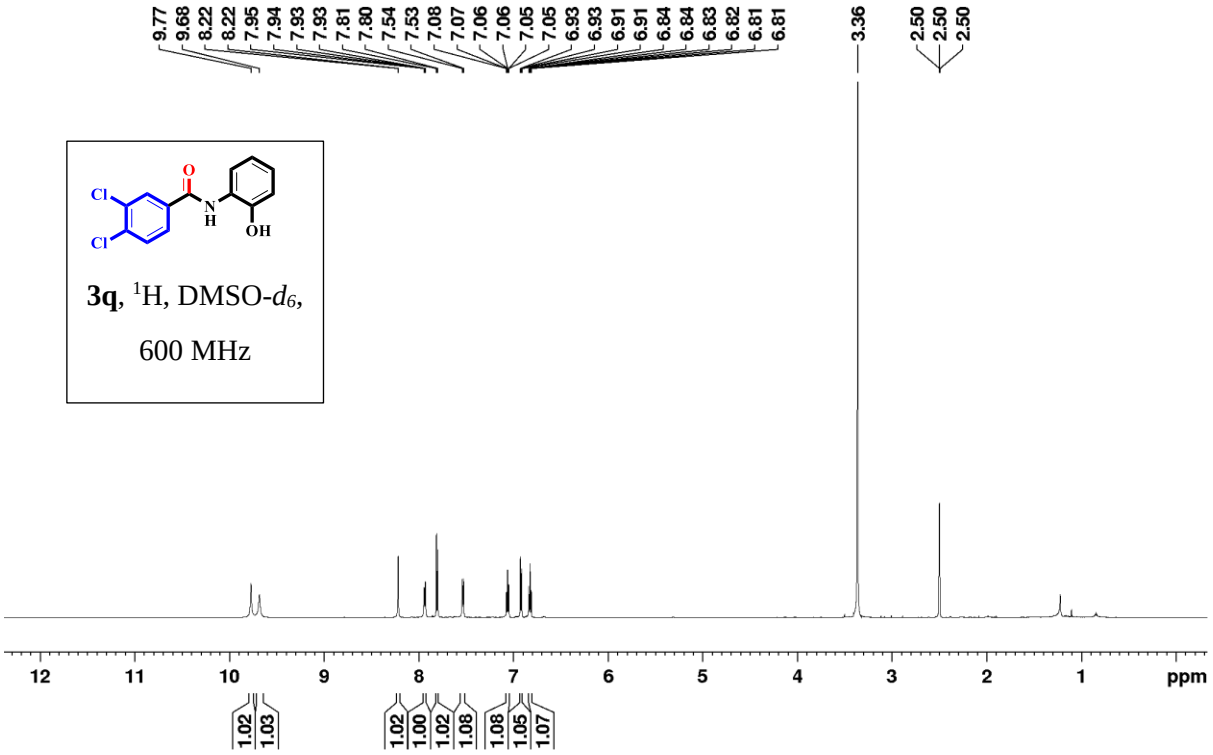


3p, ^{1}H, DMSO-d_6, 600 MHz

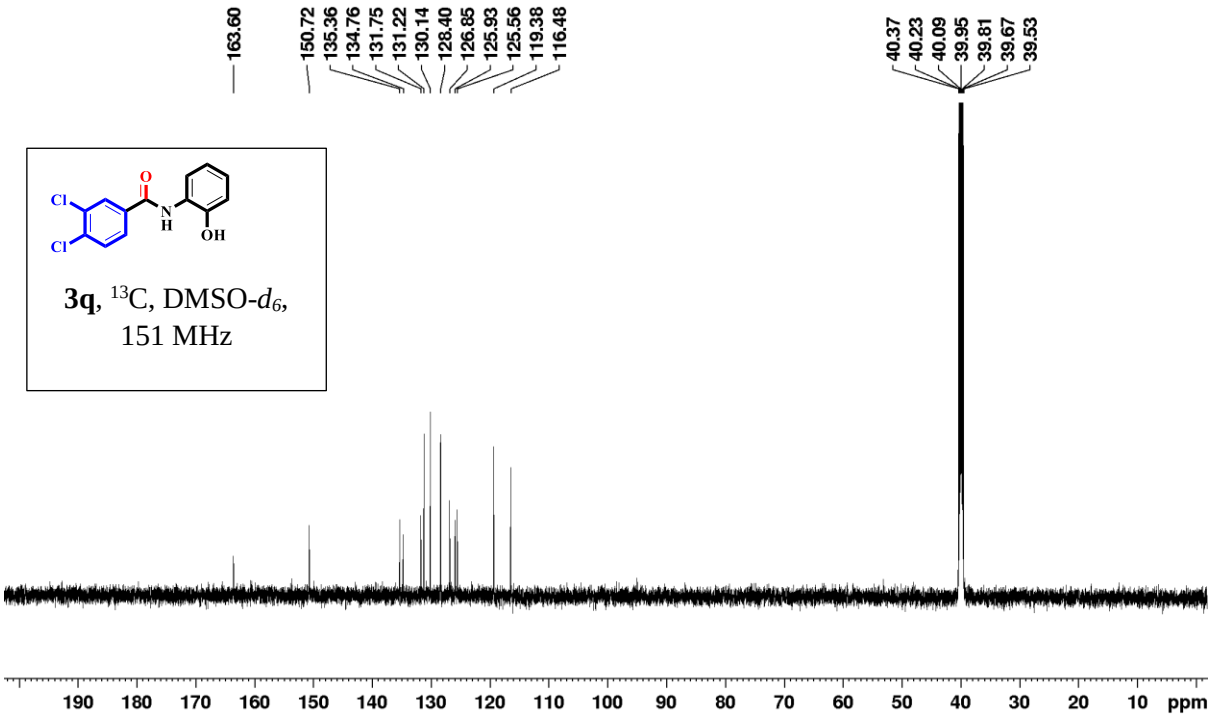



164.84
150.19
134.04
131.94
130.17
126.45
126.01
125.84
125.14
119.45
116.45
40.39
40.26
40.12
39.98
39.84
39.70
39.56
Br
O
N
H
OH
3p, 13C, DMSO-d6, 151 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

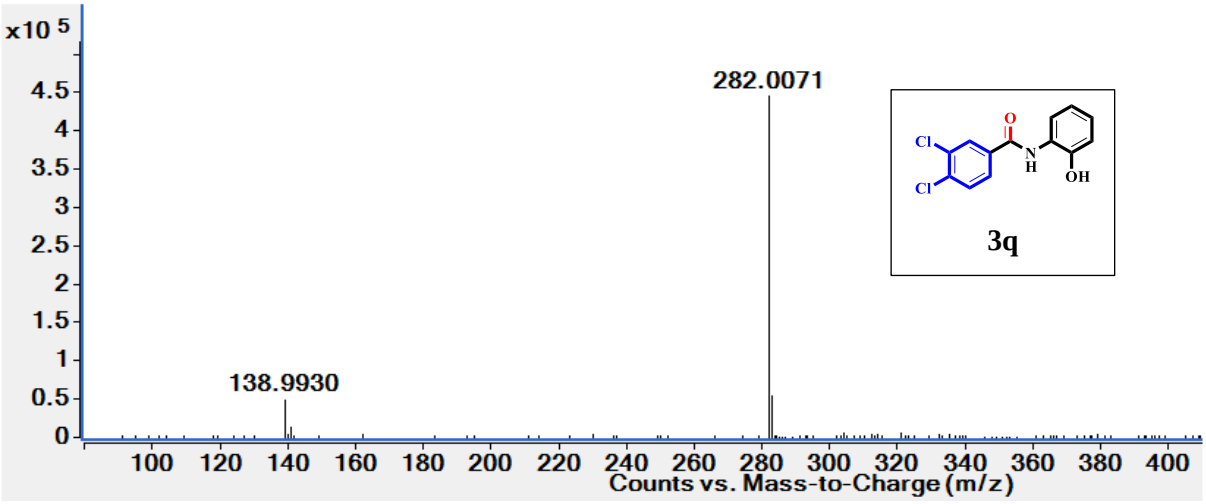

x10 5
3
2
1
0
292.0006
475.3317
200
400
600
800
1000
Counts vs. Mass-to-Charge (m/z)
Br
O
N
H
OH
3p

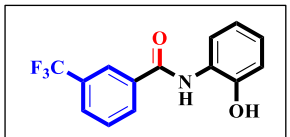


3q, ^{1}H, DMSO-d_6, 600 MHz

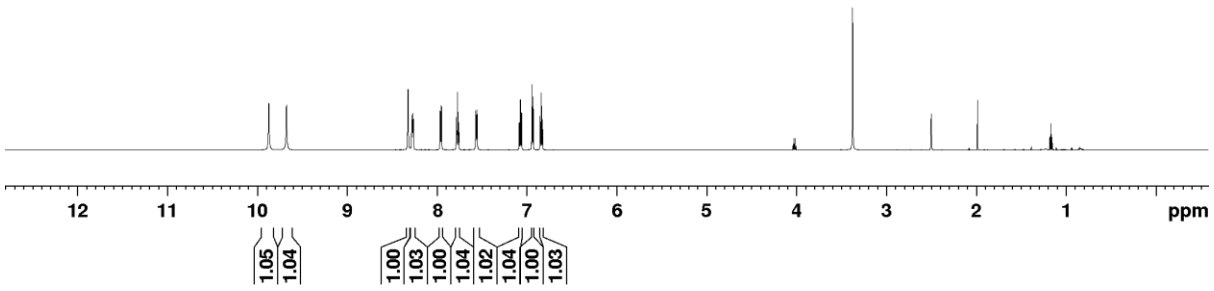


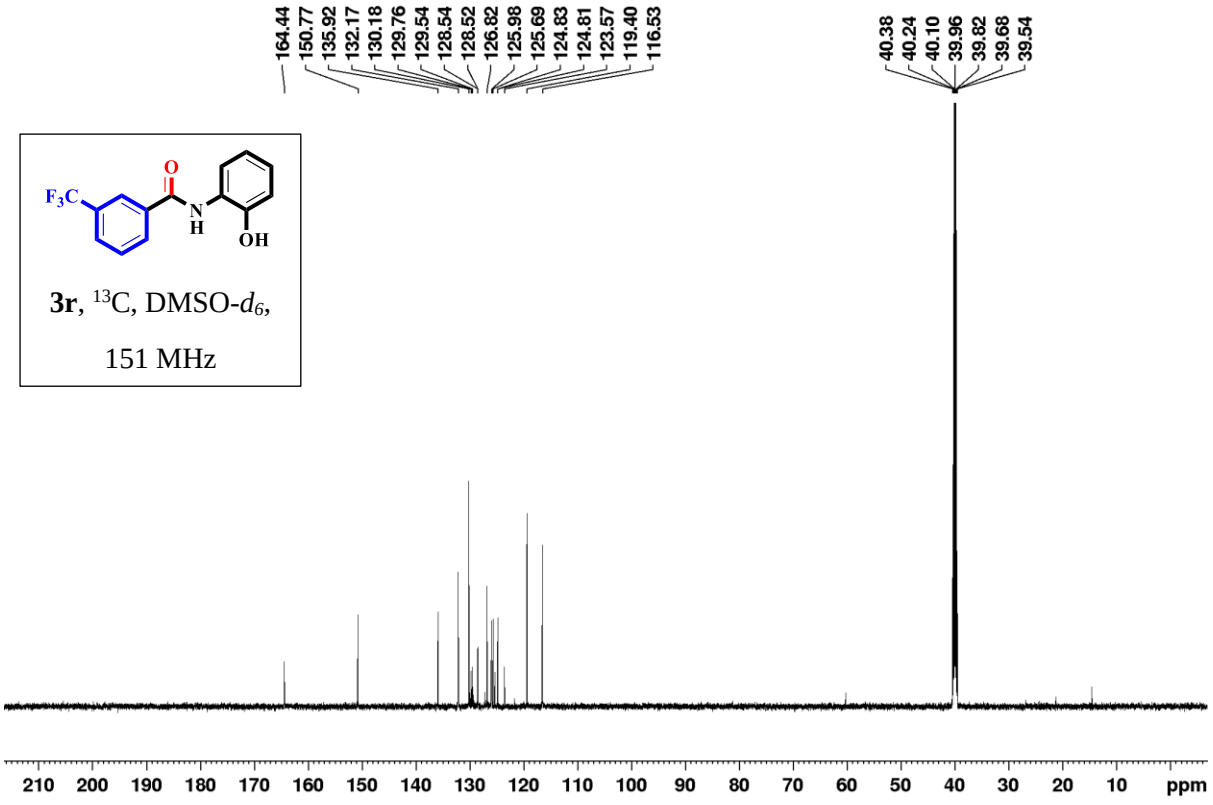
3q, ^{13}C, DMSO-d_6, 151 MHz

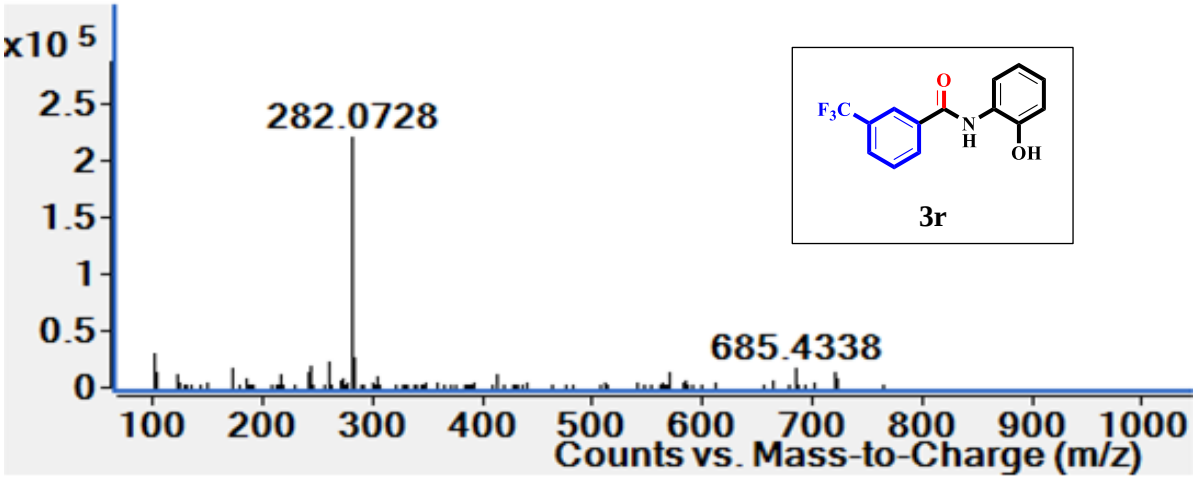


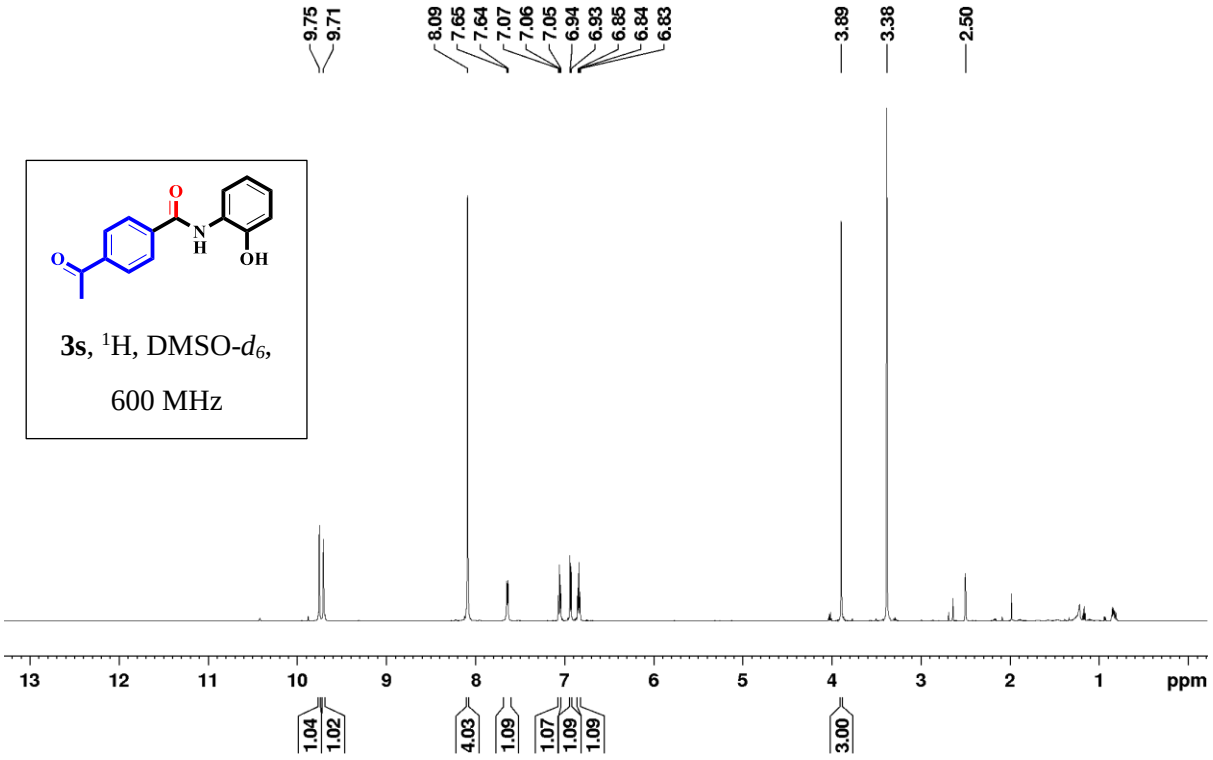


3r, ^{1}H, DMSO-d_6, 600 MHz

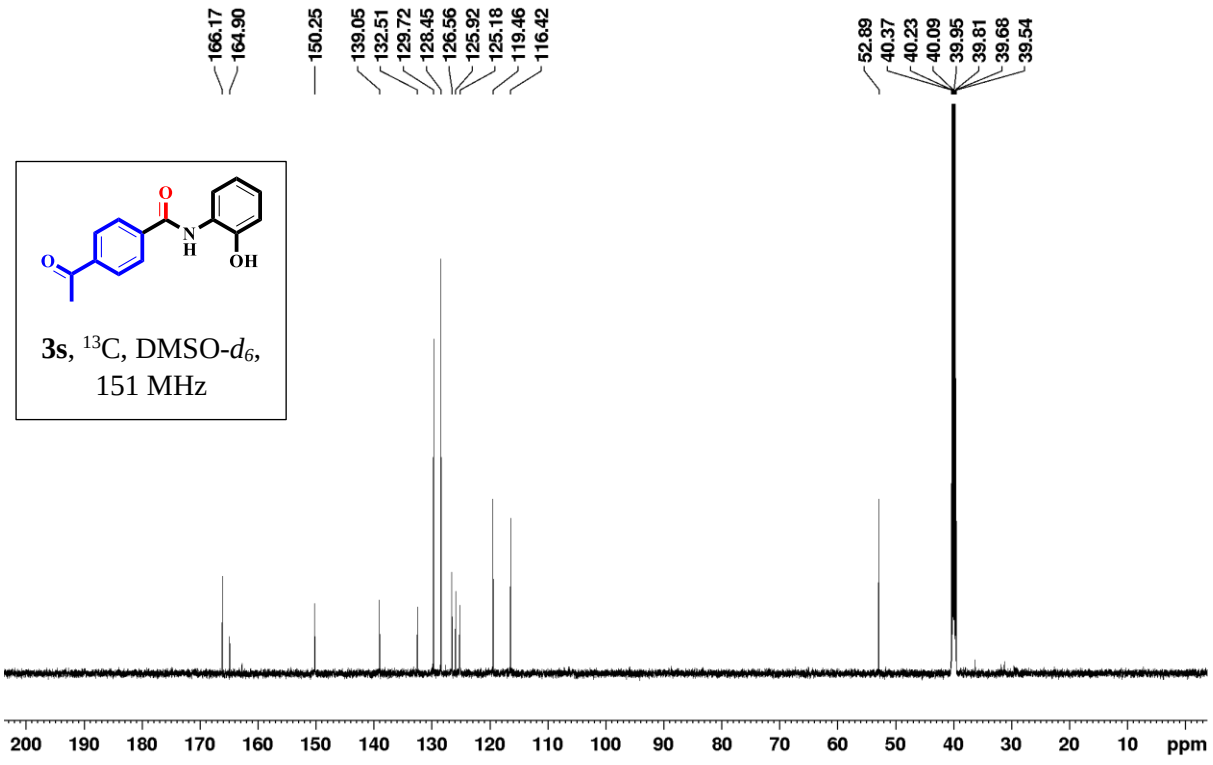



164.44
150.77
135.92
132.17
130.18
129.76
129.54
128.54
128.52
126.82
125.98
125.69
124.83
124.81
123.57
119.40
116.53
40.38
40.24
40.10
39.96
39.82
39.68
39.54
O
F3C
N
H
OH
3r, 13C, DMSO-d6,
151 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

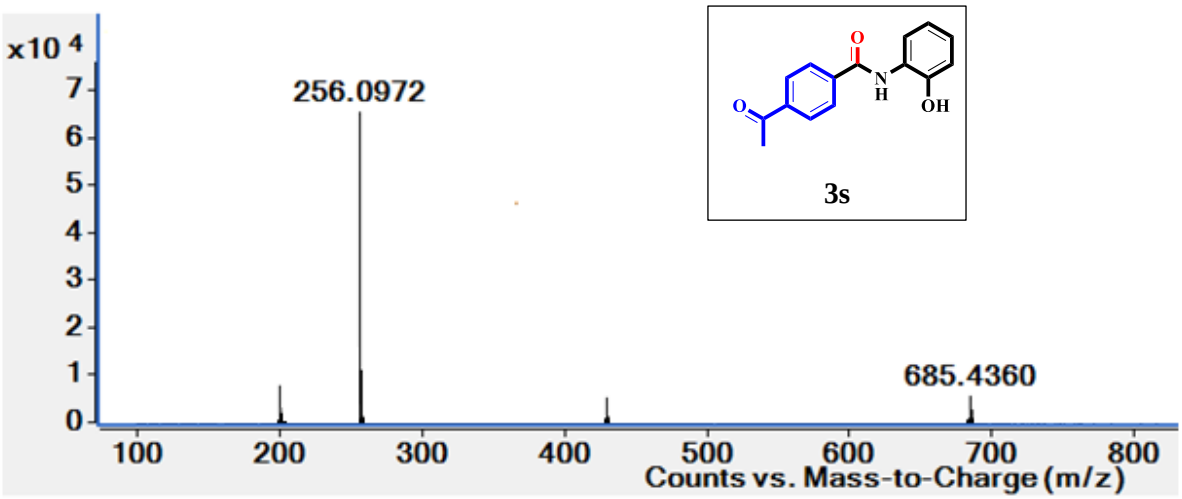

x10 5
2.5
2
1.5
1
0.5
0
282.0728
685.4338
100 200 300 400 500 600 700 800 900 1000
Counts vs. Mass-to-Charge (m/z)
O
F3C
N
H
OH
3r



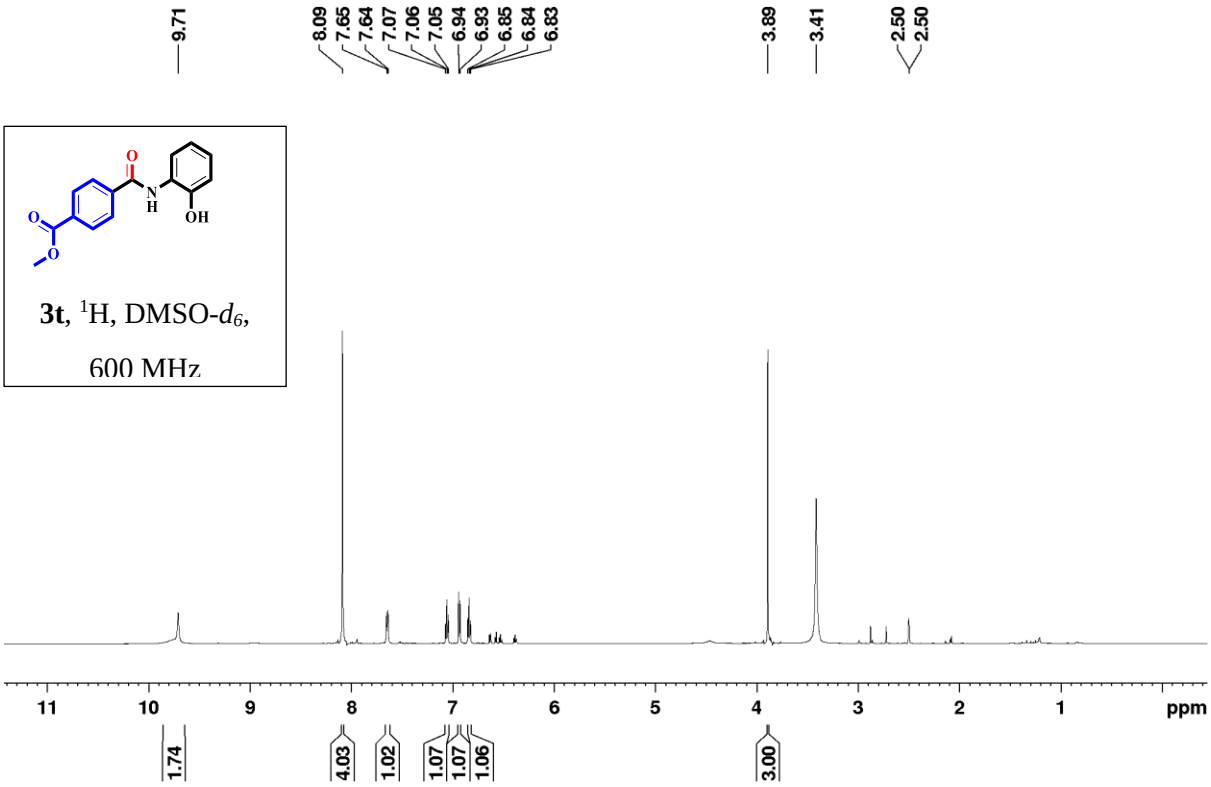
3s, ^{1}H, DMSO-d_6, 600 MHz



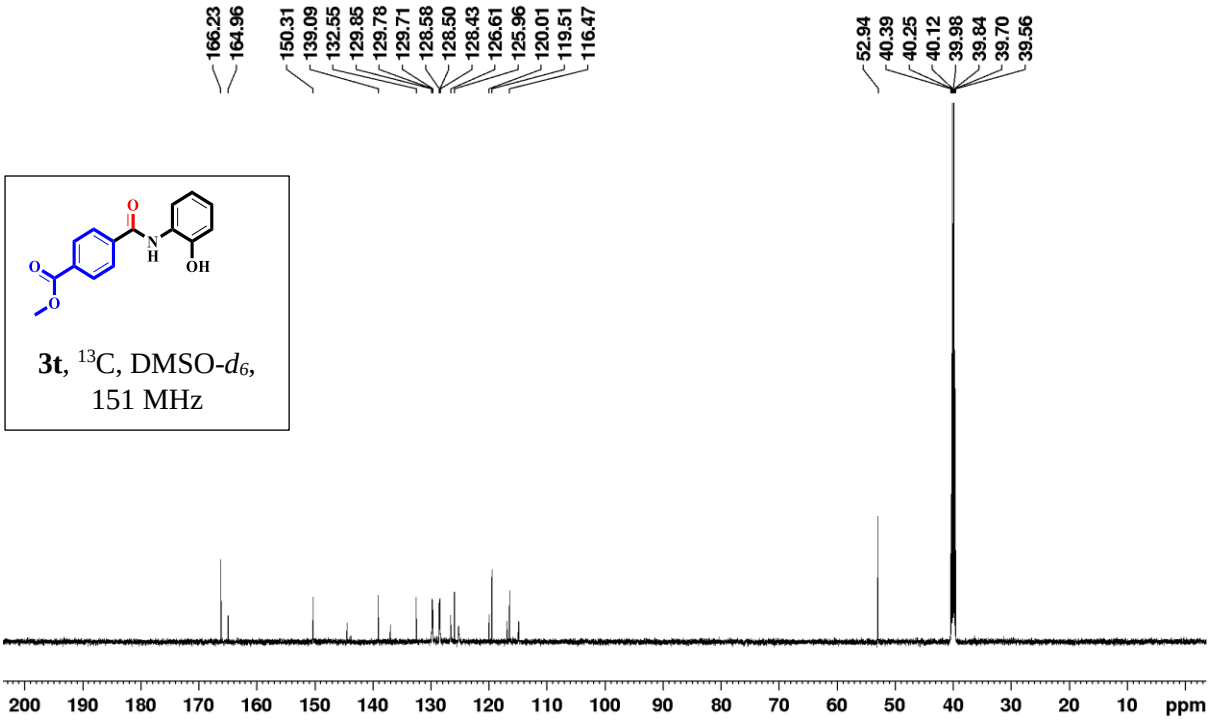
3s, ^{13}C, DMSO-d_6, 151 MHz



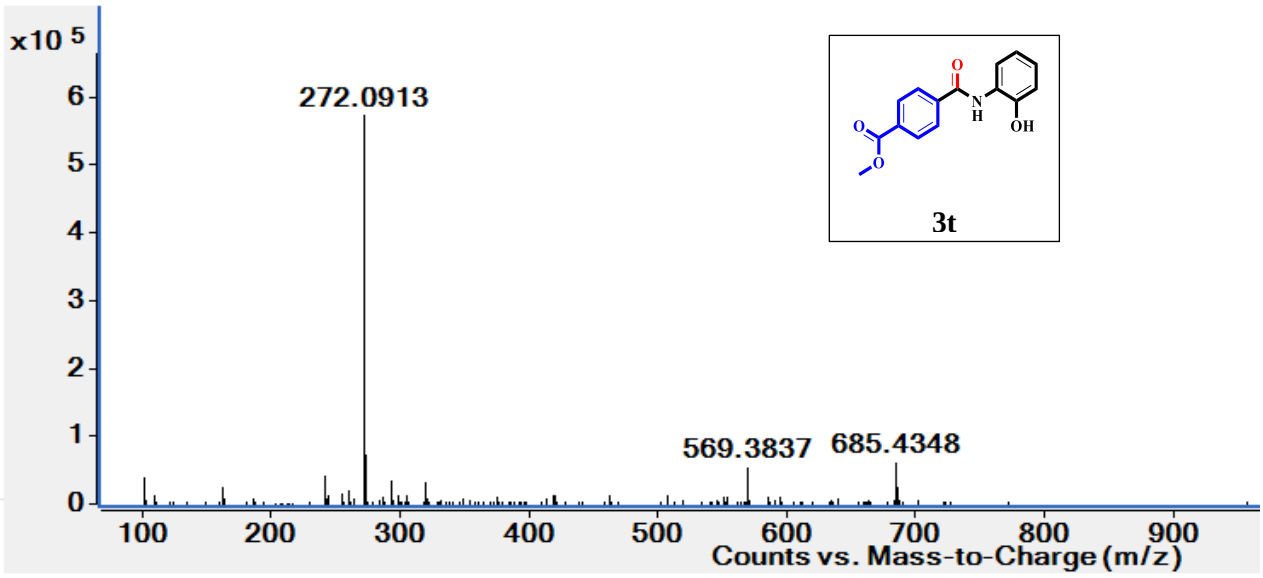
3s



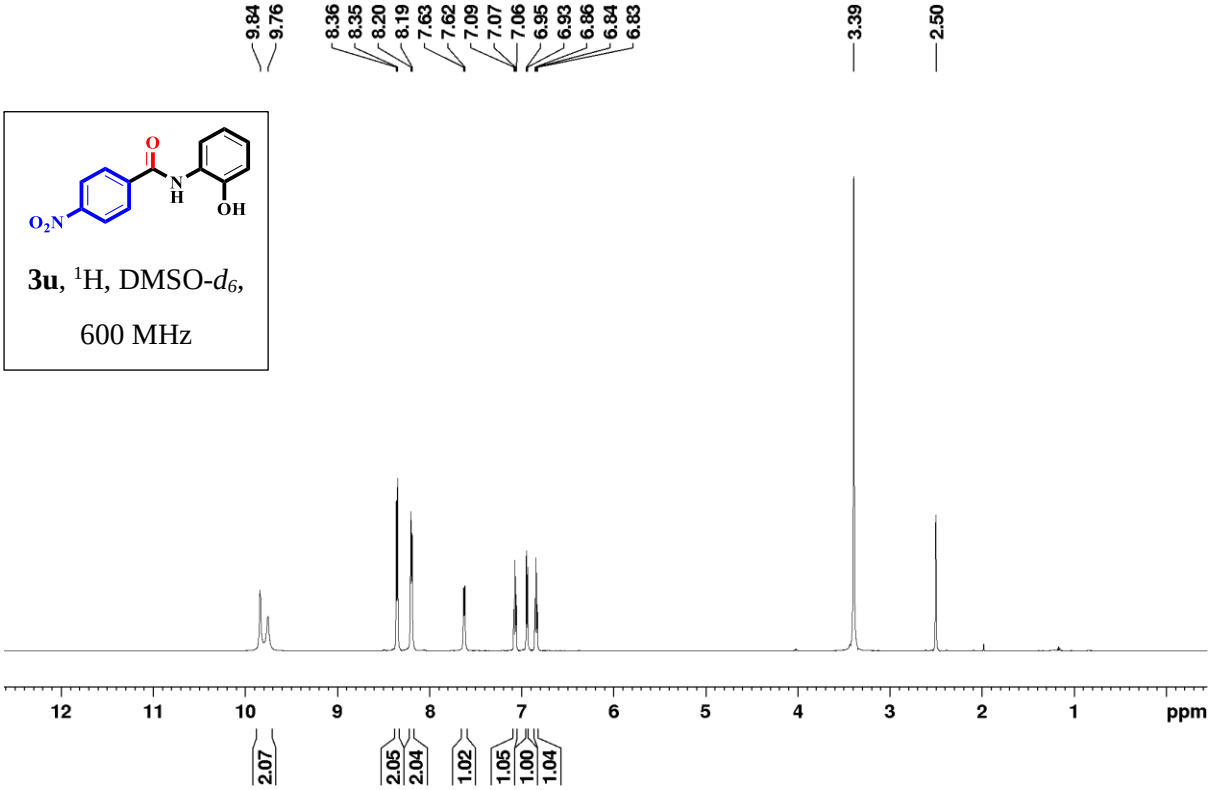
3t, ^{1}H, DMSO-d_6, 600 MHz

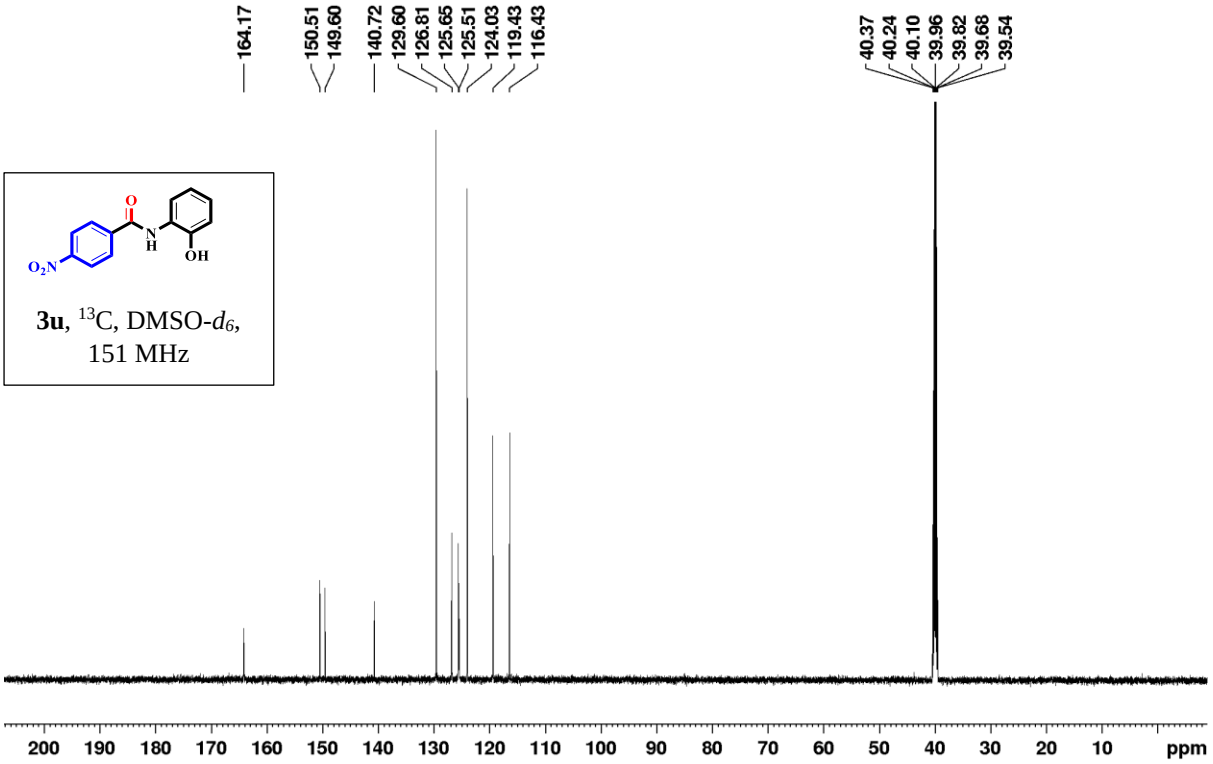


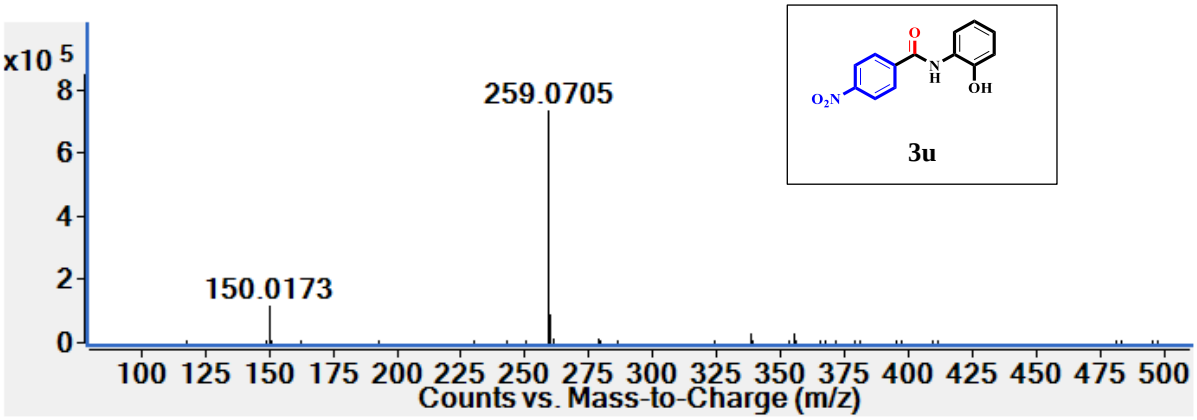
3t, ^{13}C, DMSO-d_6, 151 MHz



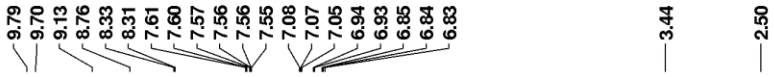
3t

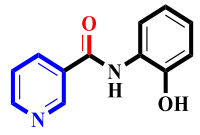

9.84
9.76
8.36
8.35
8.20
8.19
7.63
7.62
7.09
7.07
7.06
6.95
6.93
6.86
6.84
6.83
3.39
2.50
O
N
H
OH
O2N
3u, 1H, DMSO-d6,
600 MHz
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.07
2.05
2.04
1.02
1.05
1.00
1.04


164.17
150.51
149.60
140.72
129.60
126.81
125.65
125.51
124.03
119.43
116.43
40.37
40.24
40.10
39.96
39.82
39.68
39.54
O
N
H
OH
O2N
3u, 13C, DMSO-d6,
151 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

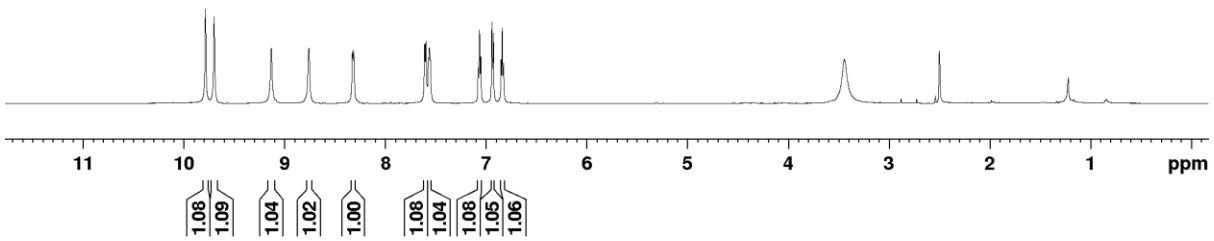


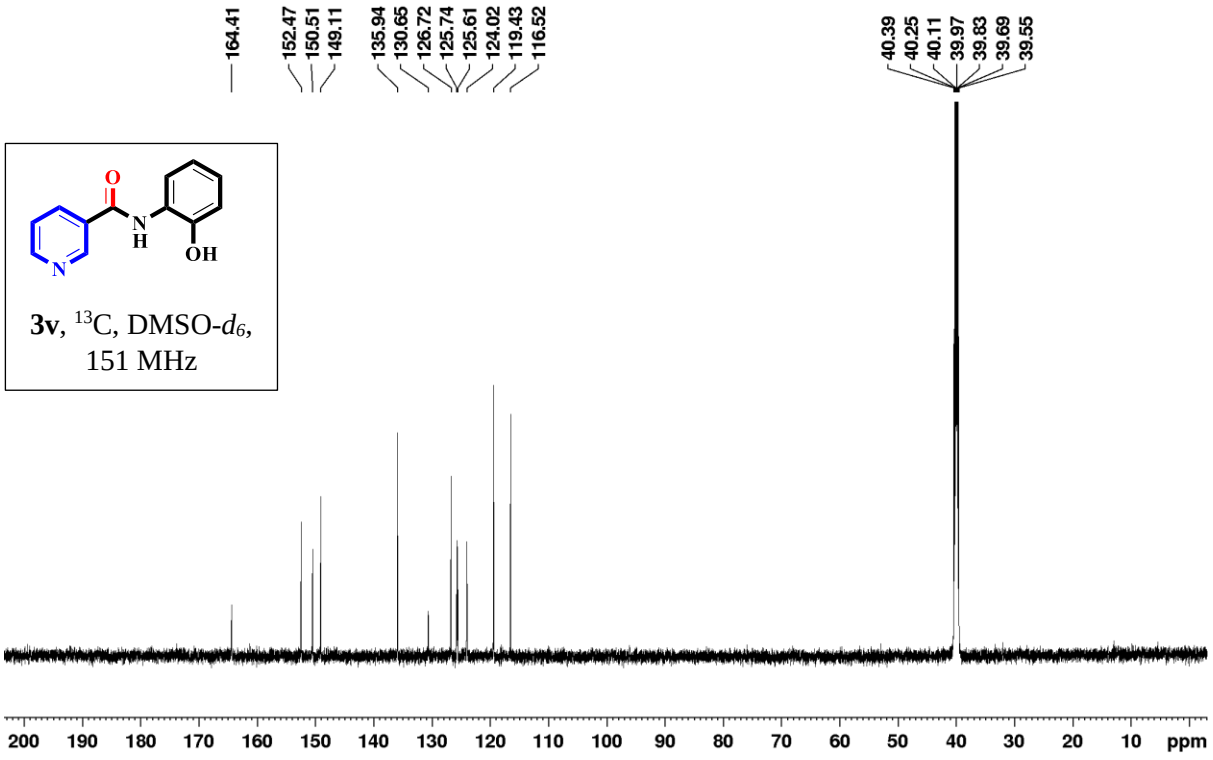
3u

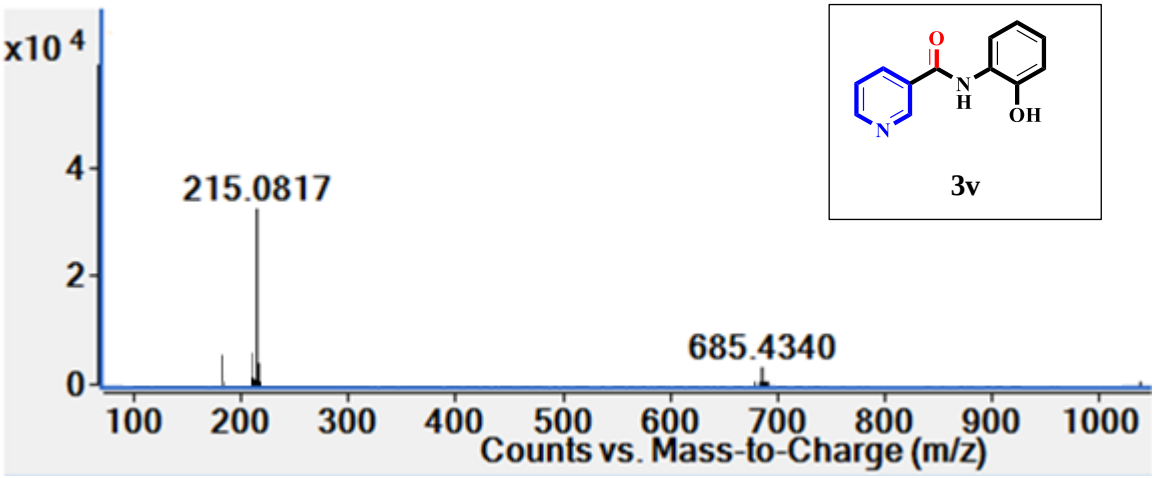


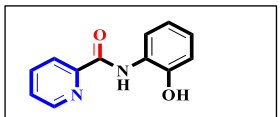


3v, ^{1}H, DMSO-*d*$_6$, 600 MHz

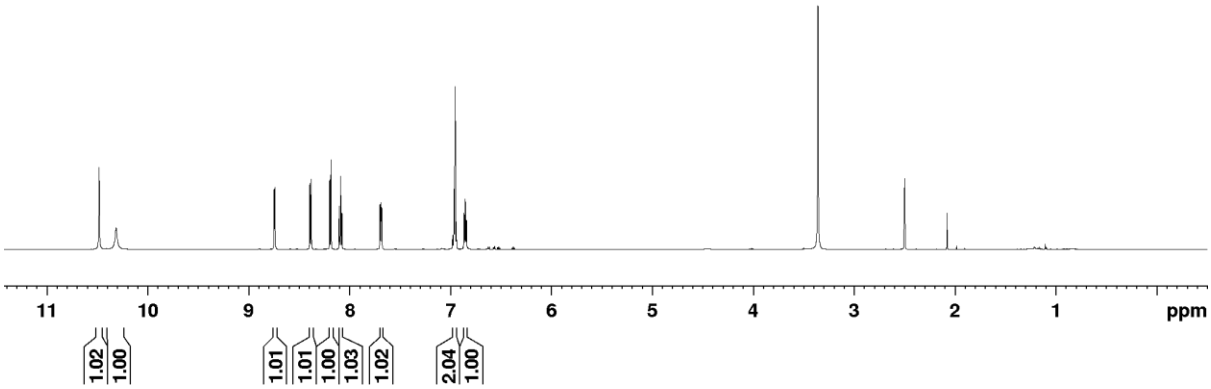


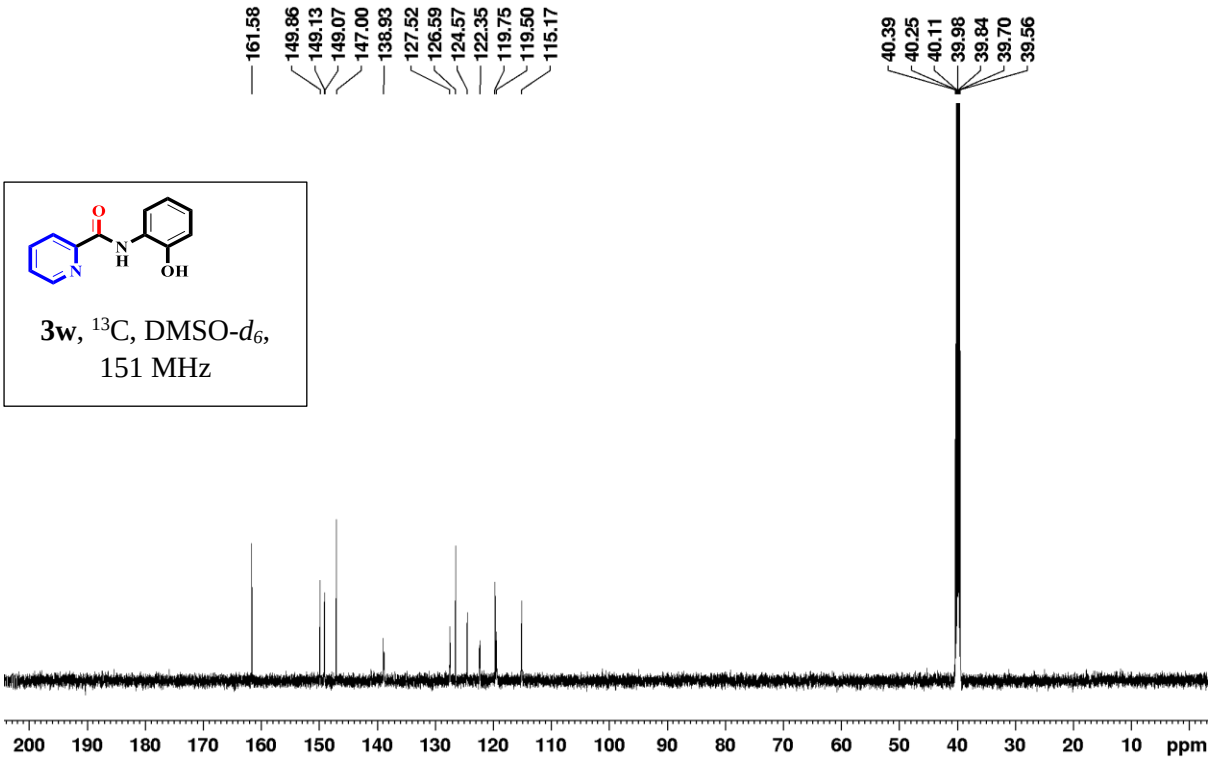

164.41
152.47
150.51
149.11
135.94
130.65
126.72
125.74
125.61
124.02
119.43
116.52
40.39
40.25
40.11
39.97
39.83
39.69
39.55
O
N
H
OH
N
3v, 13C, DMSO-d6, 151 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


x10 4
4
2
0
215.0817
685.4340
100 200 300 400 500 600 700 800 900 1000
Counts vs. Mass-to-Charge (m/z)
O
N
H
OH
N
3v

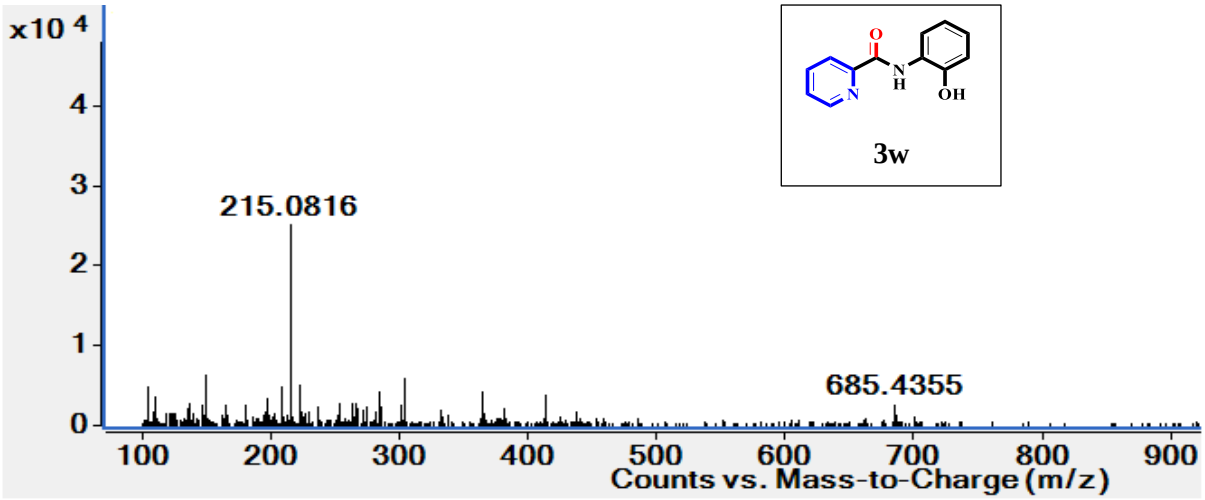


3w, ^{1}H, DMSO-d_6, 600 MHz

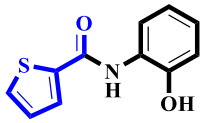




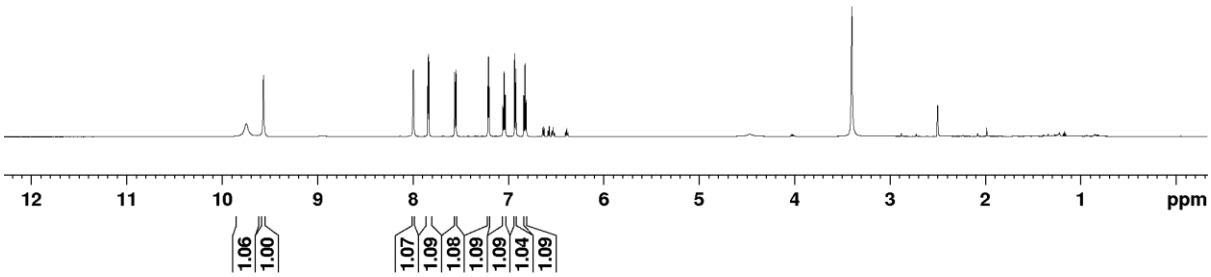
3w, ^{13}C, DMSO-d_6, 151 MHz

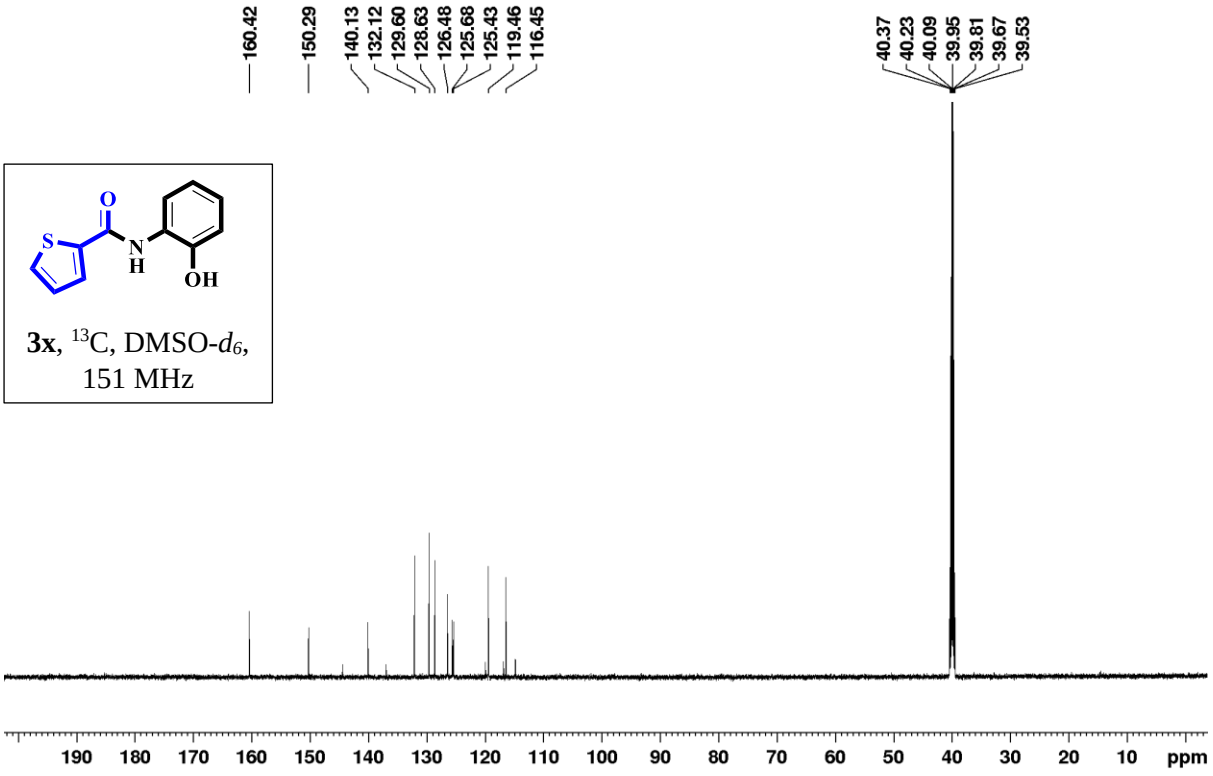


3w

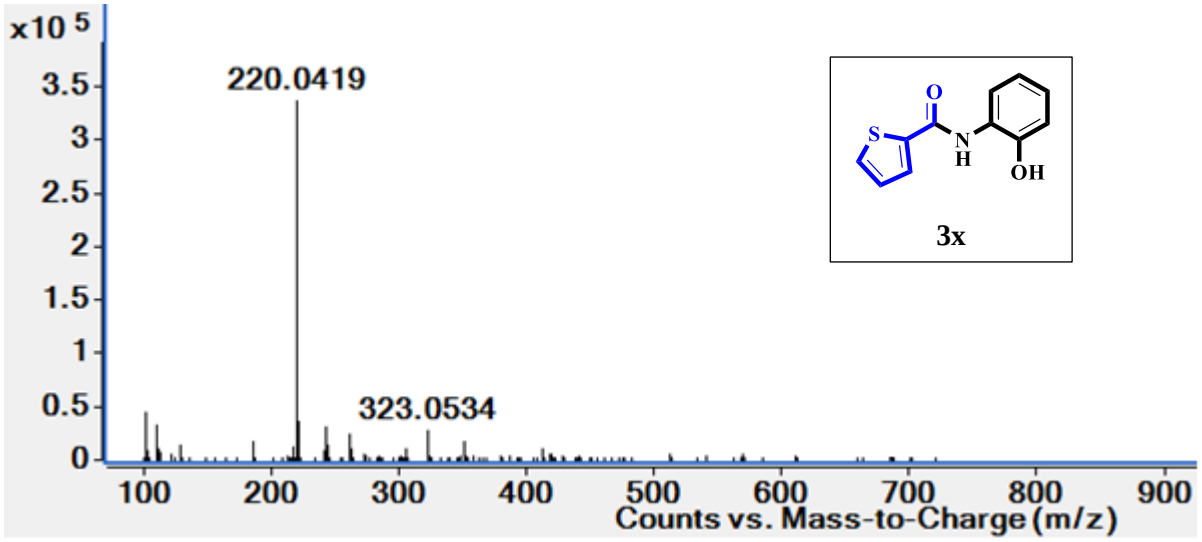


3x, ^{1}H, DMSO-d_6, 600 MHz

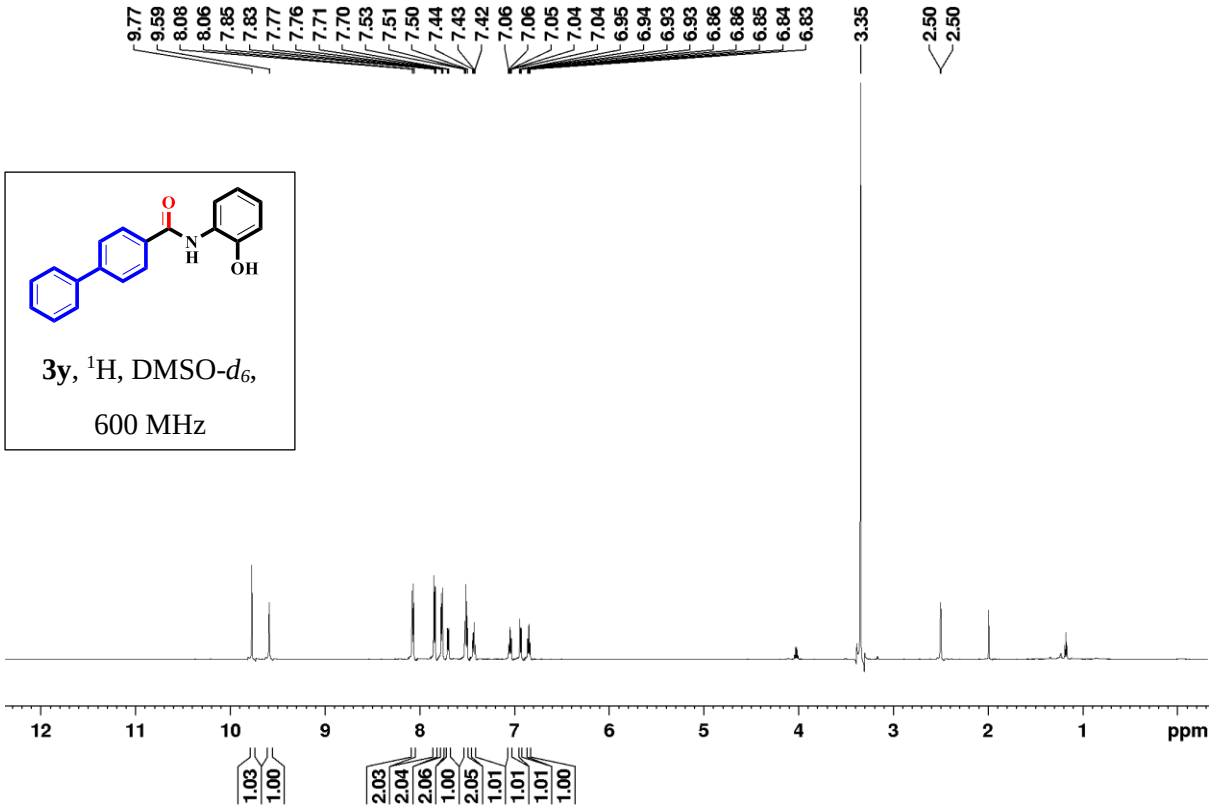




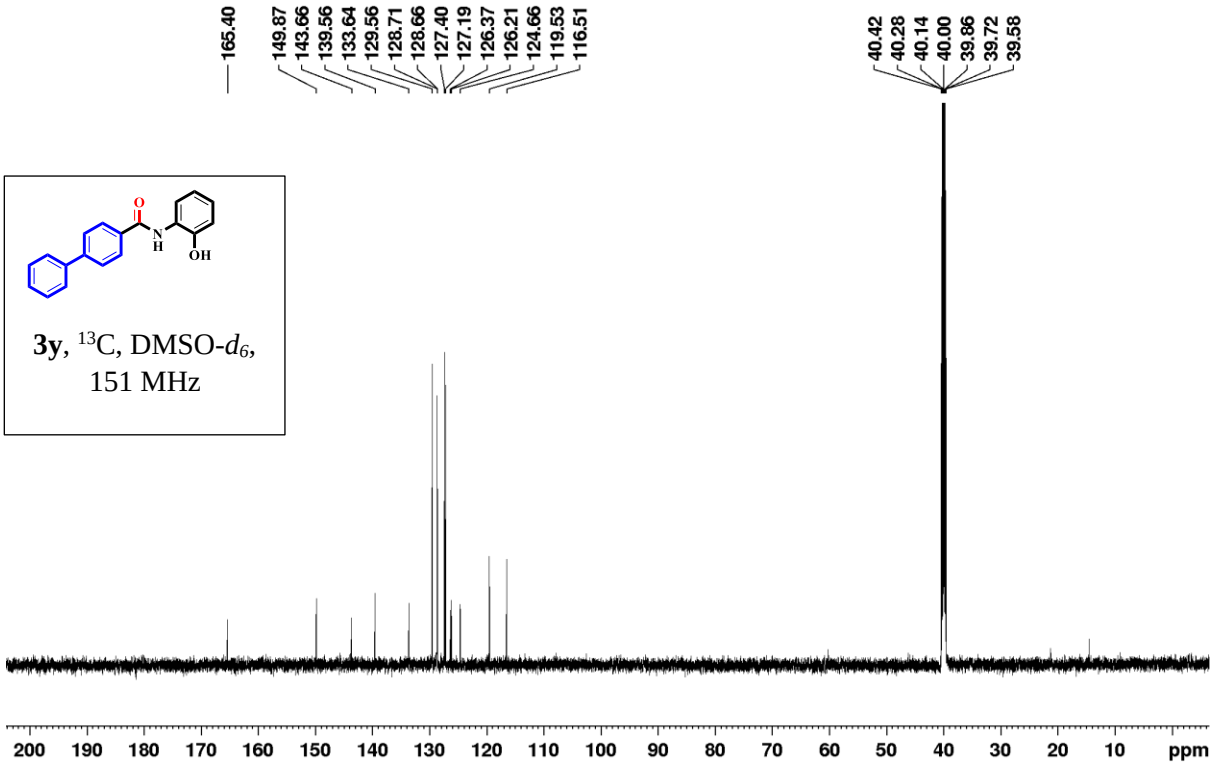
3x, ^{13}C, DMSO-d_6, 151 MHz



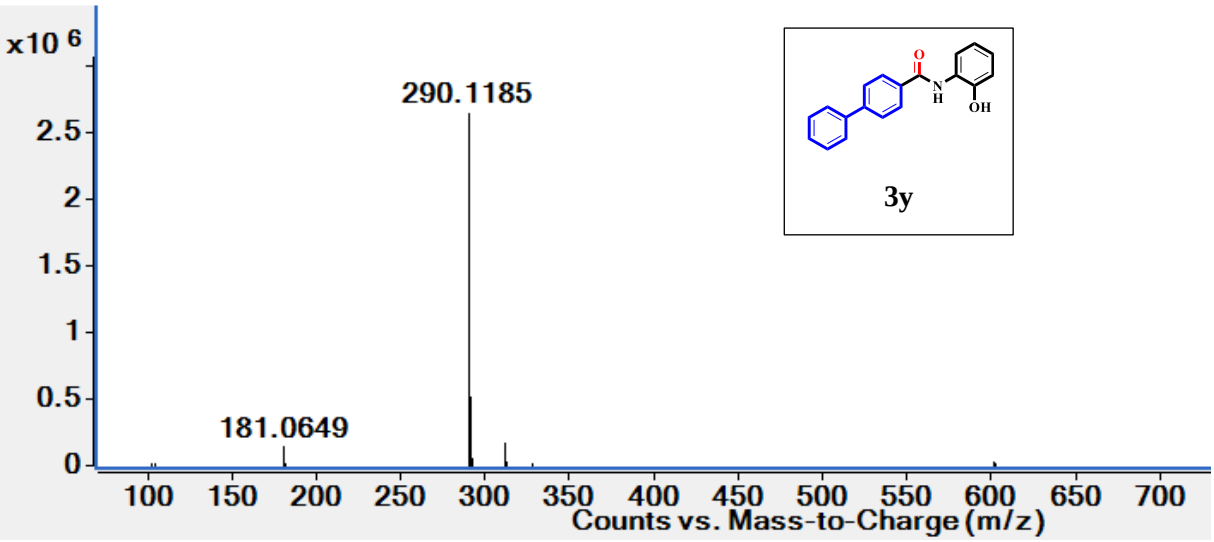
3x

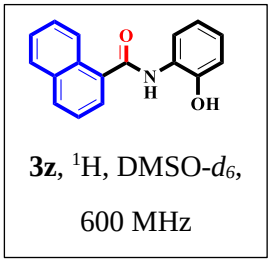


3y, ^{1}H, DMSO-d_6, 600 MHz

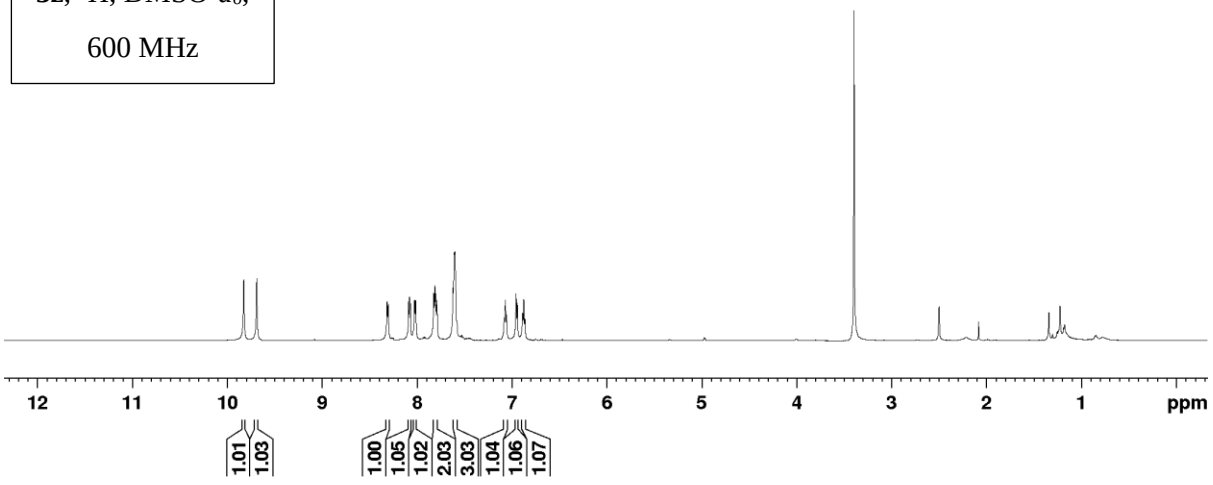


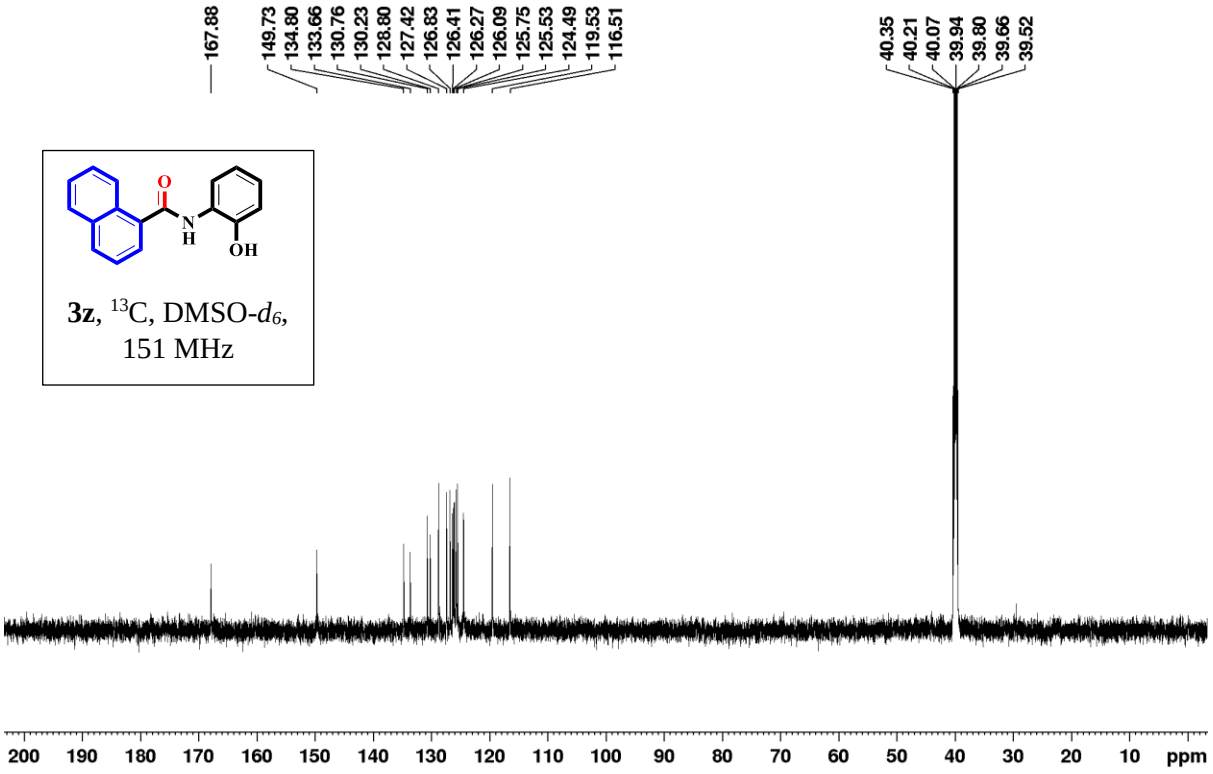
3y, ^{13}C, DMSO-d_6, 151 MHz

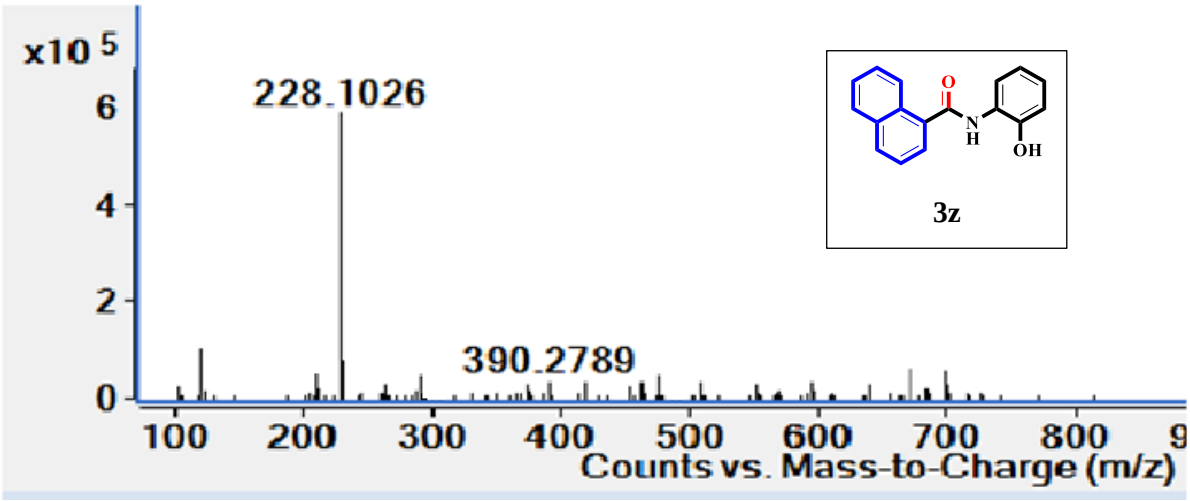


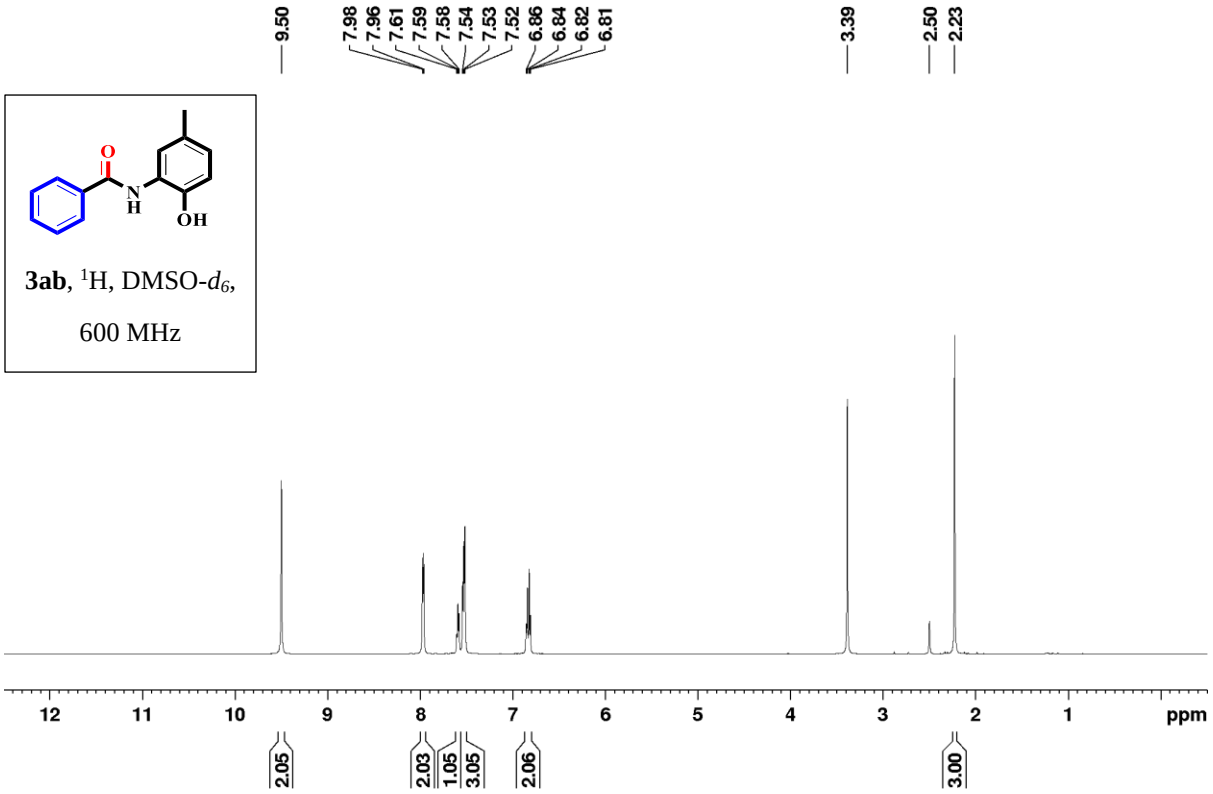


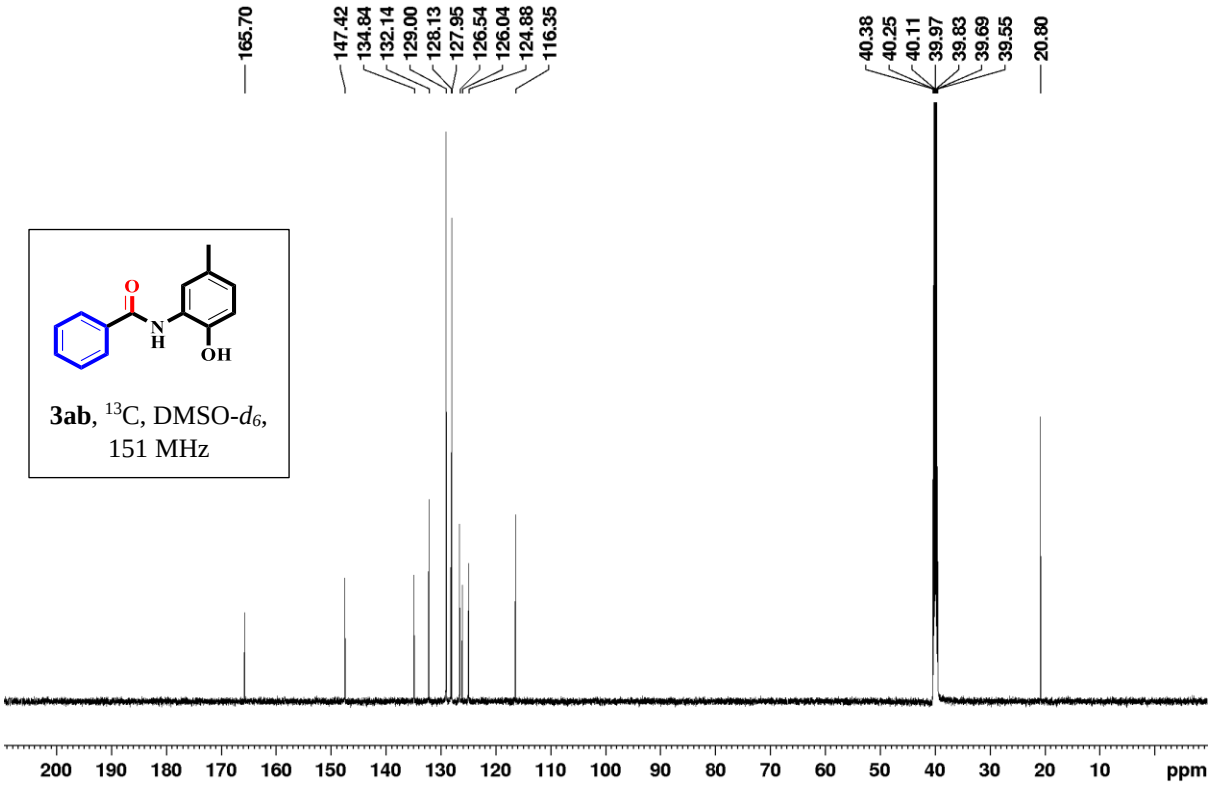
3z, ^{1}H, DMSO-d_6, 600 MHz

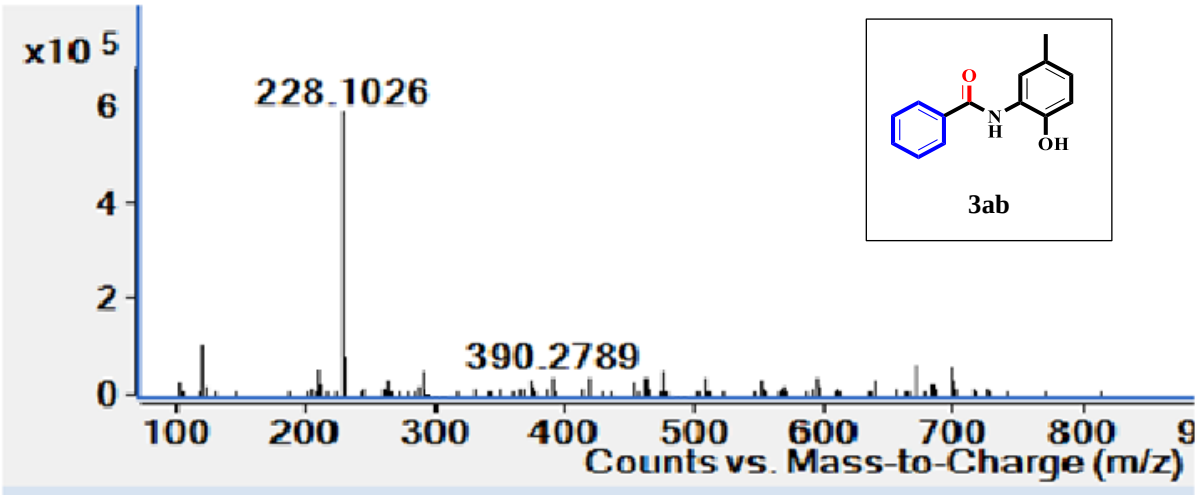


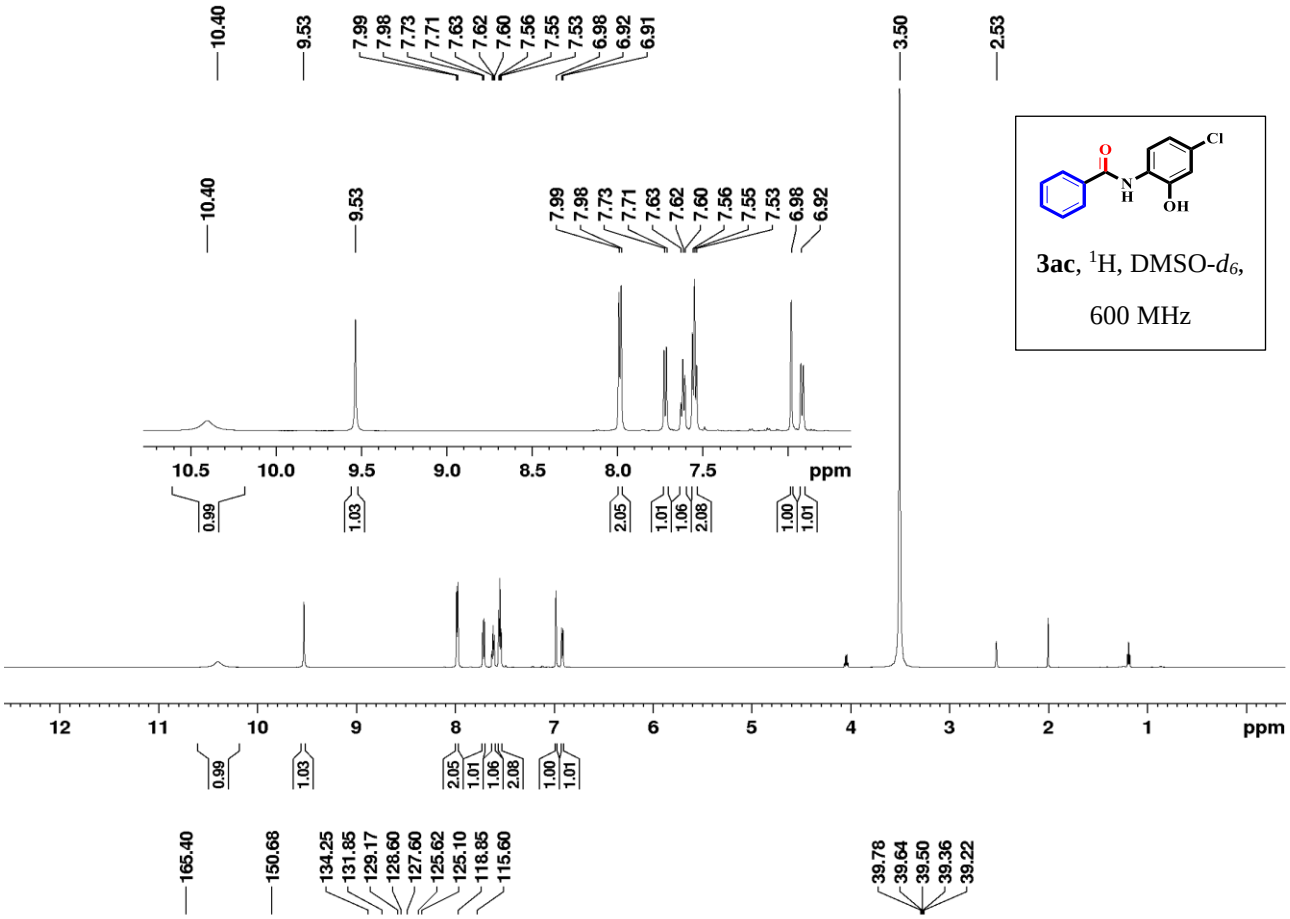

167.88
149.73
134.80
133.66
130.76
130.23
128.80
127.42
126.83
126.41
126.27
126.09
125.75
125.53
124.49
119.53
116.51
40.35
40.21
40.07
39.94
39.80
39.66
39.52
O
N
H
OH
3z, 13C, DMSO-d6, 151 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


x10 5
6
4
2
0
228.1026
390.2789
100 200 300 400 500 600 700 800
Counts vs. Mass-to-Charge (m/z)
O
N
H
OH
3z

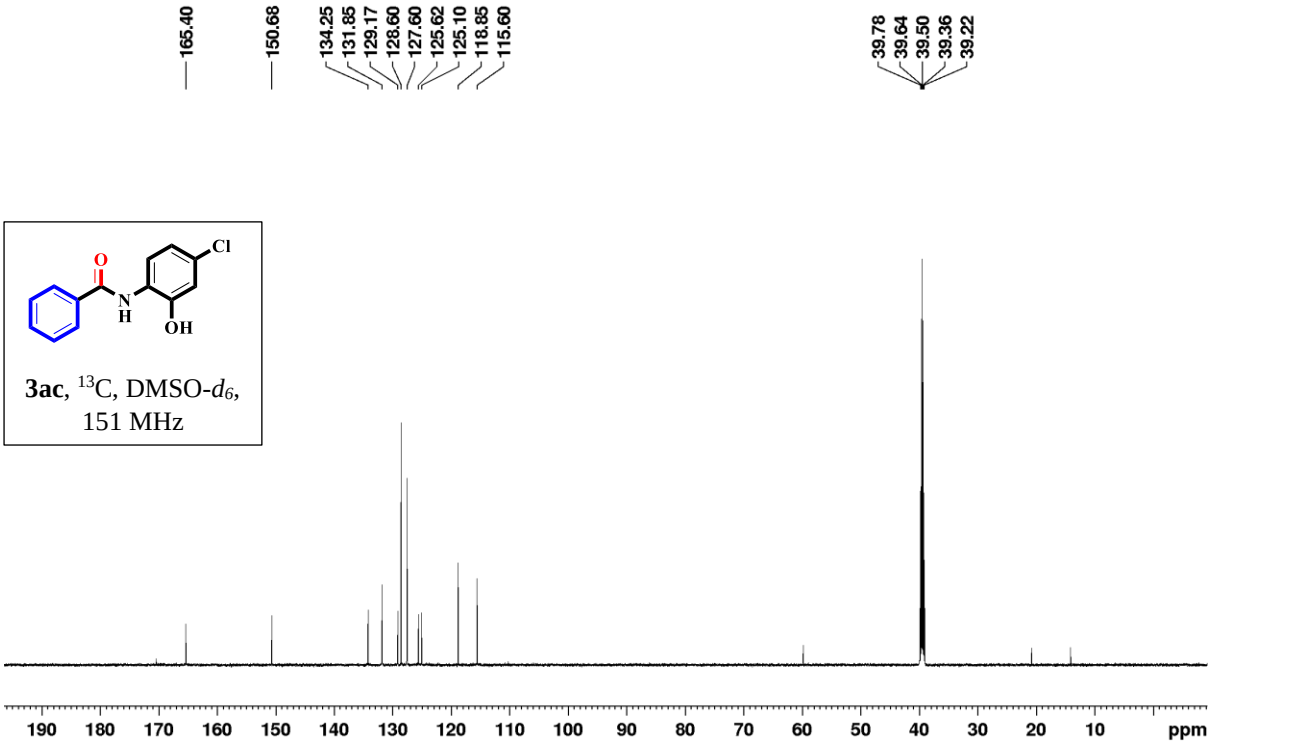

9.50
7.98
7.96
7.61
7.59
7.58
7.54
7.53
7.52
6.86
6.84
6.82
6.81
3.39
2.50
2.23
O
N
H
OH
3ab, 1H, DMSO-d6,
600 MHz
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.05
2.03
1.05
3.05
2.06
3.00


165.70
147.42
134.84
132.14
129.00
128.13
127.95
126.54
126.04
124.88
116.35
40.38
40.25
40.11
39.97
39.83
39.69
39.55
20.80
O
N
H
OH
3ab, 13C, DMSO-d6,
151 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

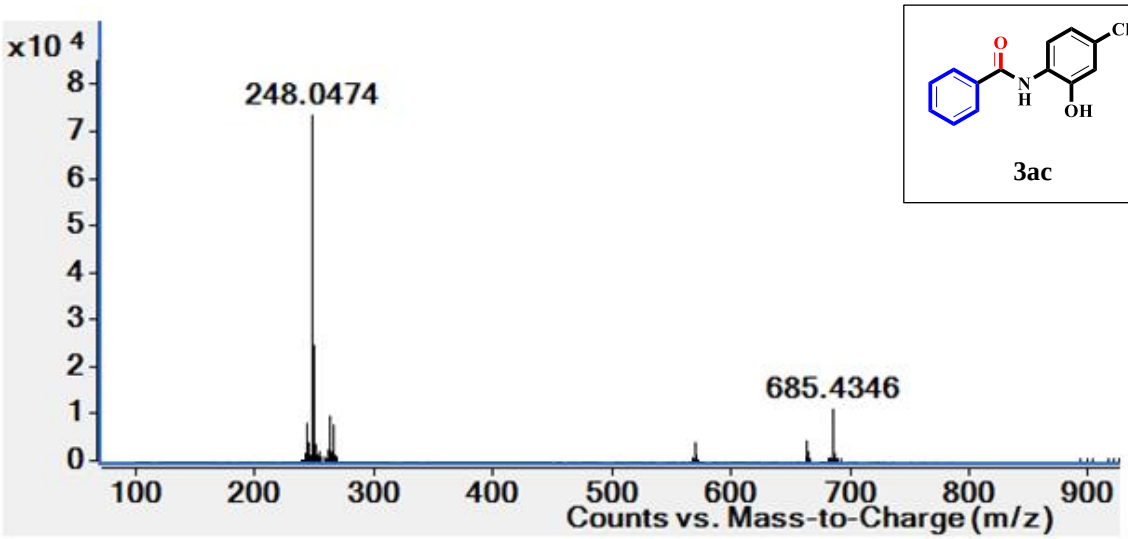

x10 5
6
4
2
0
228.1026
390.2789
100
200
300
400
500
600
700
800
Counts vs. Mass-to-Charge (m/z)
O
N
H
OH
3ab

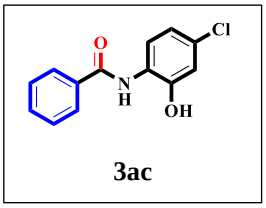


3ac, ^{1}H, DMSO-*d*$_6$, 600 MHz

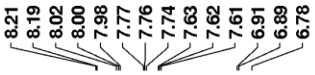


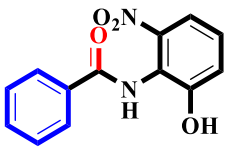
3ac, ^{13}C, DMSO-*d*$_6$, 151 MHz



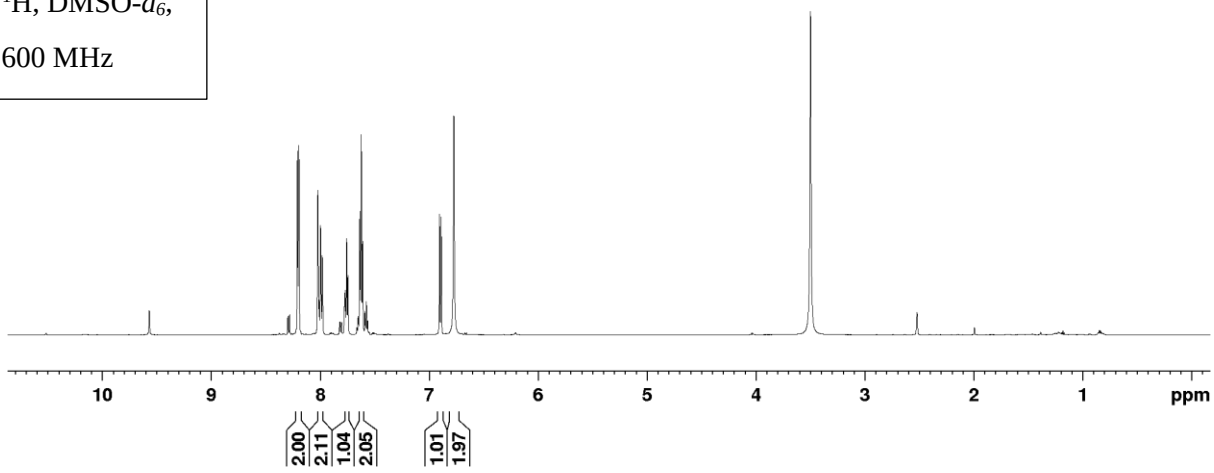


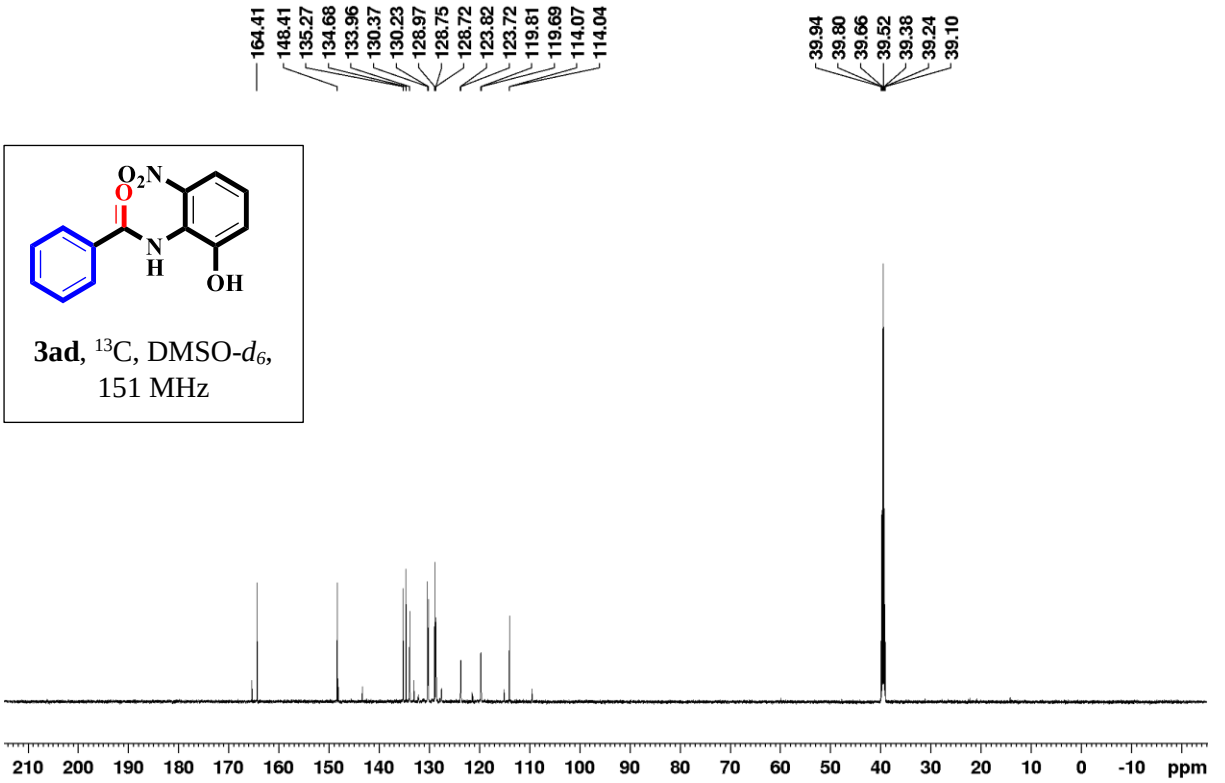
3ac

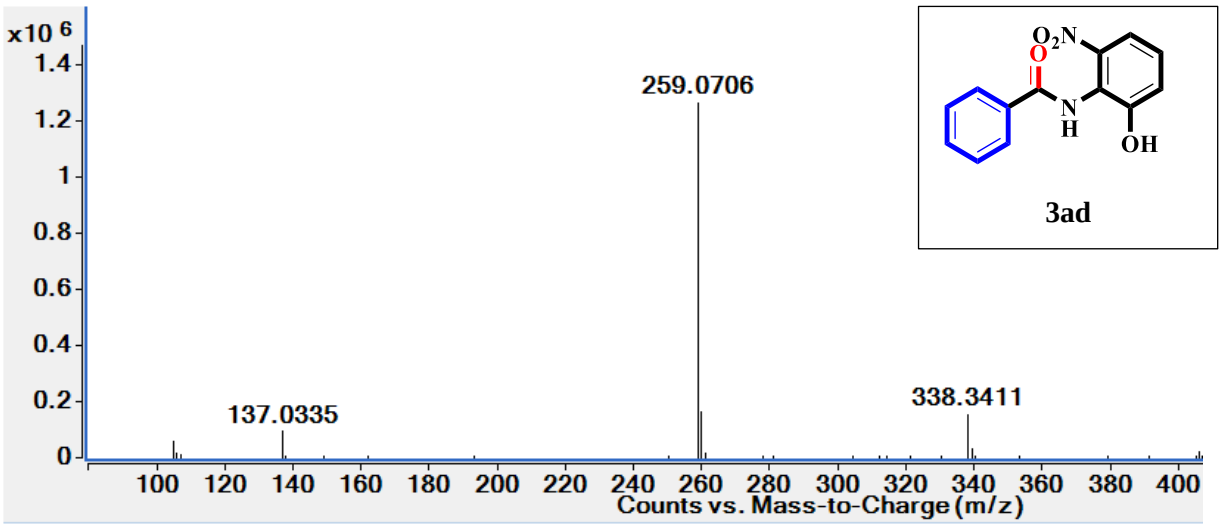


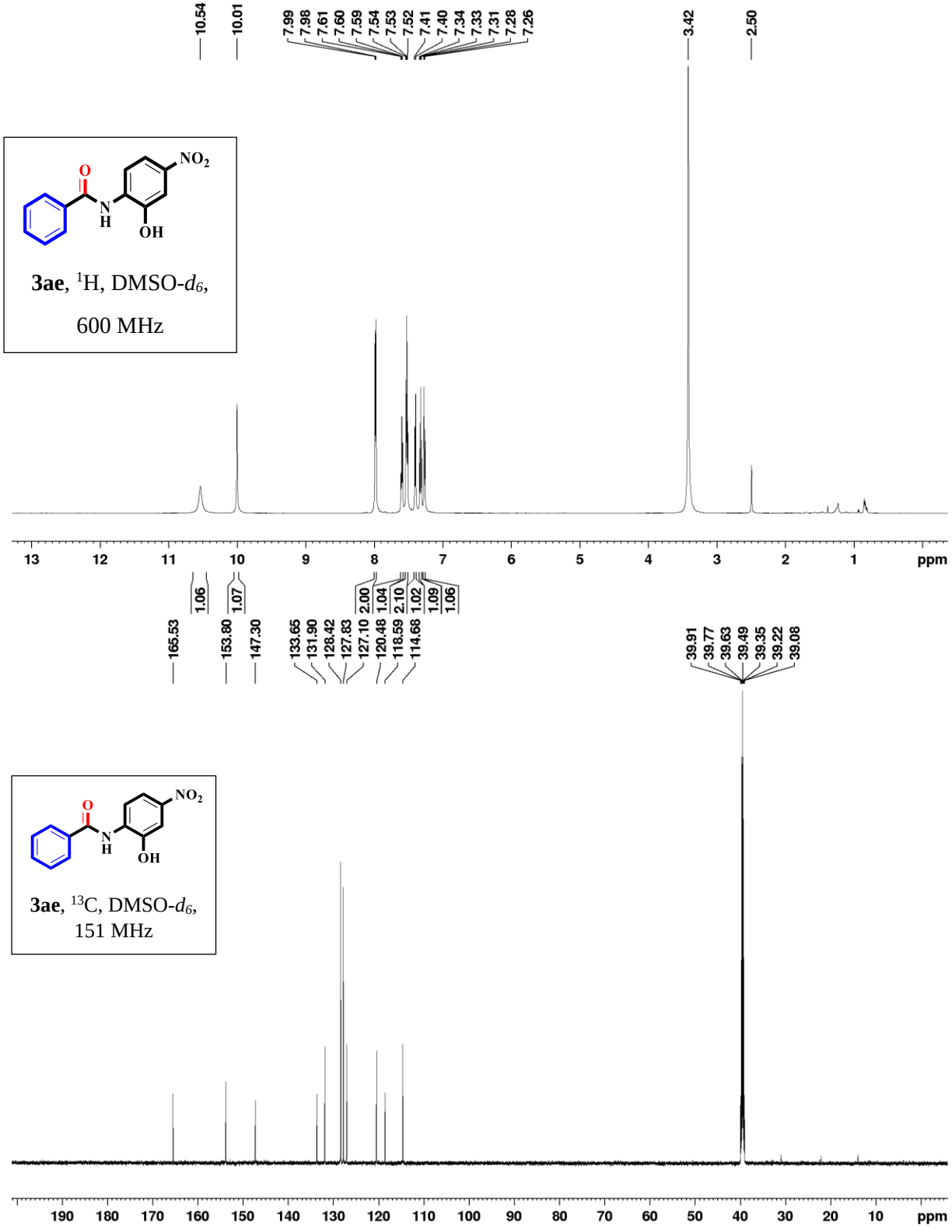


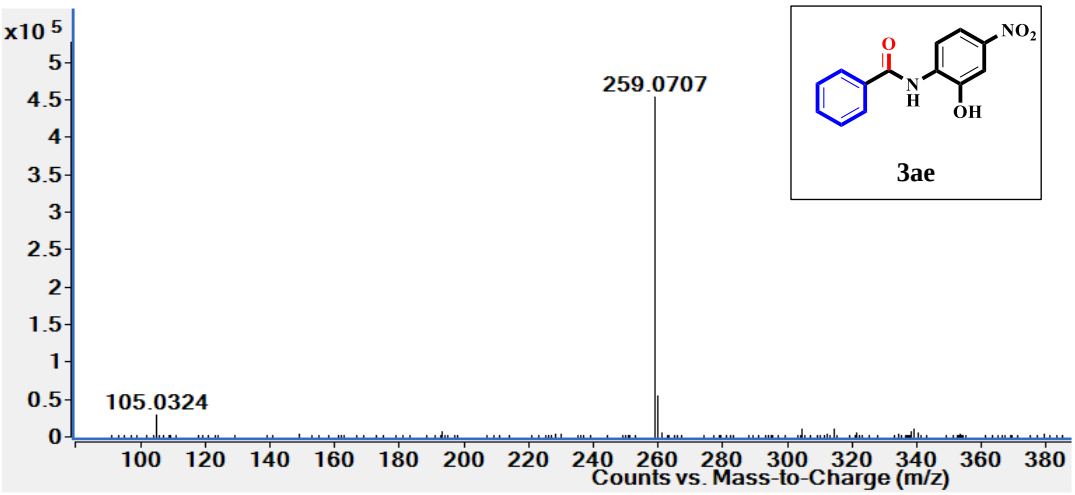
3ad, ^{1}H, DMSO-d_6, 600 MHz



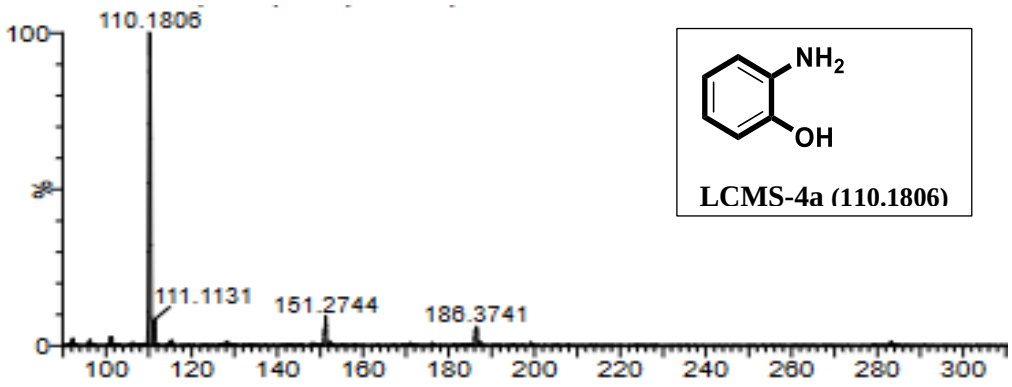

164.41
148.41
135.27
134.68
133.96
130.37
130.23
128.97
128.75
128.72
123.82
123.72
119.81
119.69
114.07
114.04
39.94
39.80
39.66
39.52
39.38
39.24
39.10
O2N
O
N
H
OH
3ad, 13C, DMSO-d6, 151 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

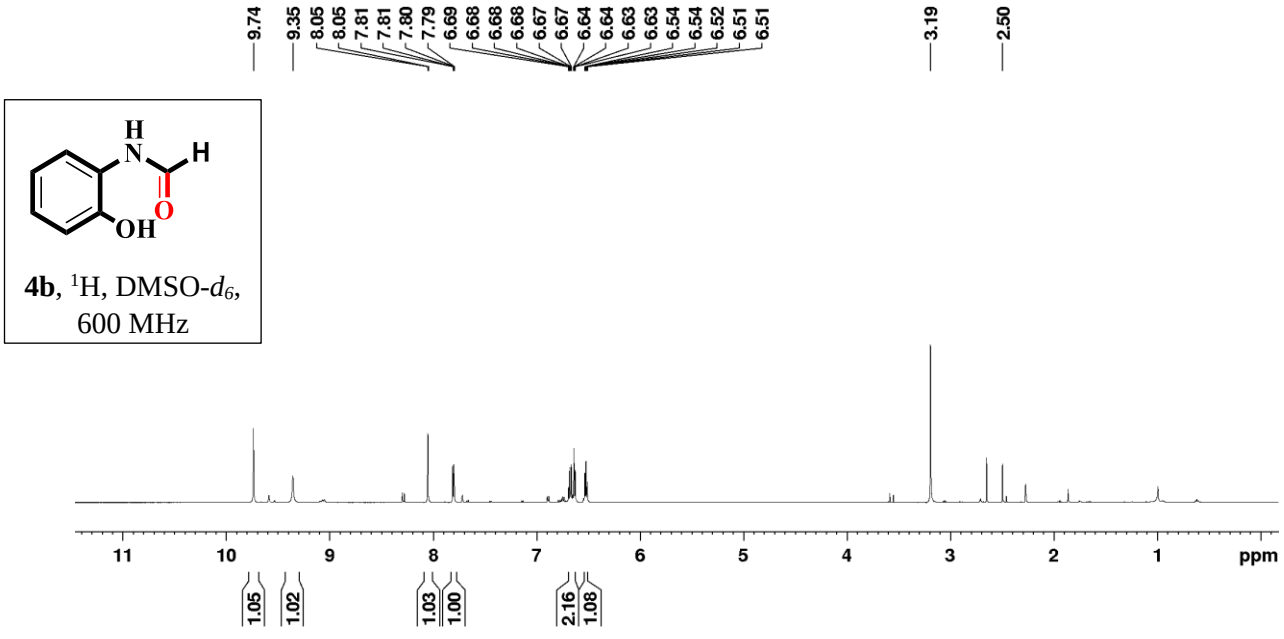

x10 6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
259.0706
137.0335
338.3411
100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
Counts vs. Mass-to-Charge (m/z)
O2N
O
N
H
OH
3ad

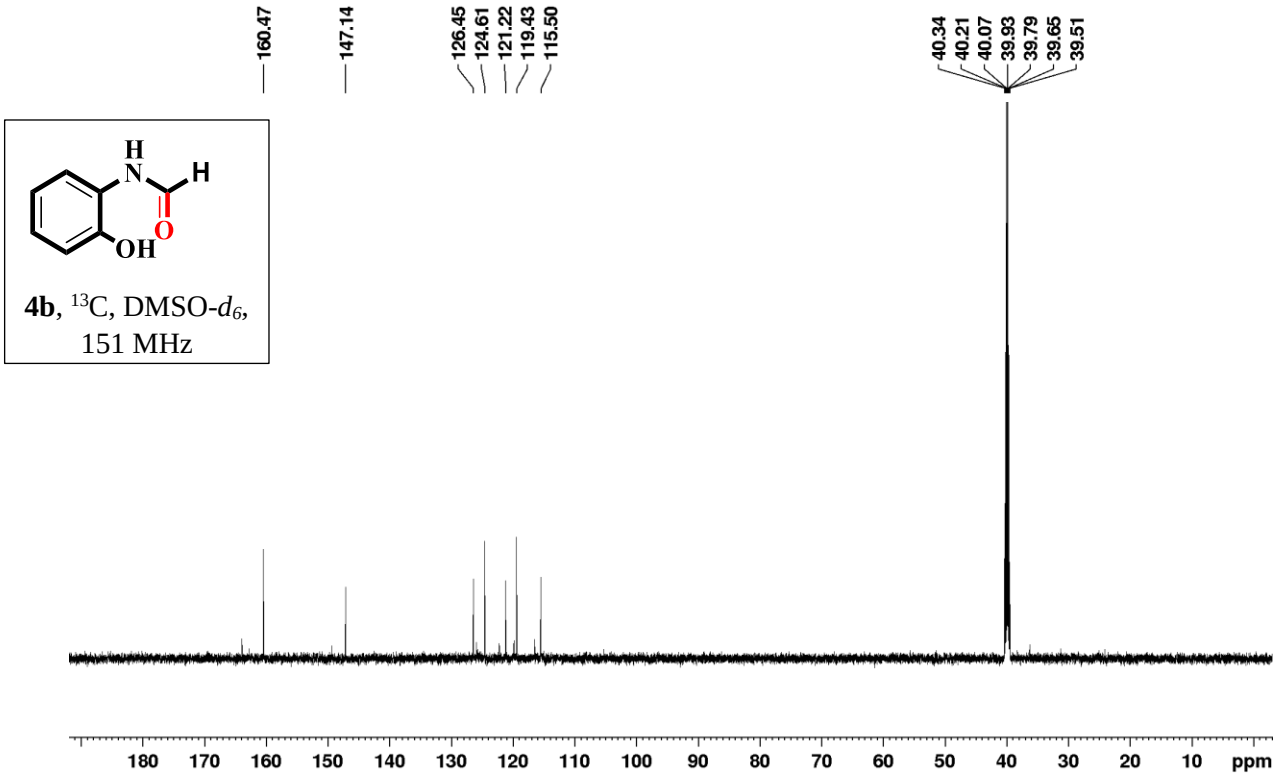

10.54
10.01
7.99
7.98
7.61
7.60
7.59
7.54
7.53
7.52
7.41
7.40
7.34
7.33
7.31
7.28
7.26
3.42
2.50
NO2
O
N
H
OH
3ae, 1H, DMSO-d6,
600 MHz
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.06
1.07
2.00
1.04
2.10
1.02
1.09
1.06
165.53
153.80
147.30
133.65
131.90
128.42
127.83
127.10
120.48
118.59
114.68
39.91
39.77
39.63
39.49
39.35
39.22
39.08
3ae, 13C, DMSO-d6,
151 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



F. Spectral data of compounds 4a and 4b







4b, ^{13}C, DMSO-d_6, 151 MHz

^{1}H ($CDCl_3$, 600 MHz) δ *(ppm)* 9.74 (s, 1H), 9.35 (s, 1H), 8.04-8.05 (m, 1H), 7.79-7.81 (m, 1H), 6.63-6.69 (m, 2H), 7.52-7.55 (m, 1H); **^{13}C ($CDCl_3$, 151 MHz)** δ *(ppm)* 160.47, 147.14, 126.45, 124.61, 121.22, 119.43, 115.50.