Supplementary Information

1. Screening of the base

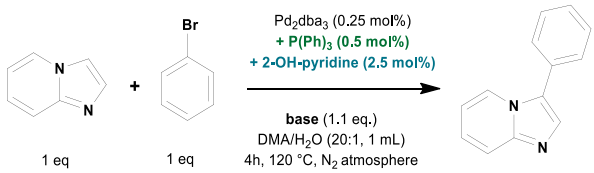


Table S1. Screening of stoichiometric bases in the coupling reaction of bromobenzene and imidazo[1,2-a]pyridine. Reaction conditions: Pd_2dba_3 (0.00025 mmol), PPh_3 (0.0005 mmol), 2-hydroxypyridine (0.0025 mmol), imidazo[1,2-a]pyridine (0.1 mmol), bromobenzene (0.1 mmol), base (0.11 mmol) in aqueous DMA (1 mL, 5 vol% H_2O)

Entry	Base	GC Yield (%)
1	Potassium hydroxide (KOH)	**91.2**
2	Potassium hydrogen carbonate ($KHCO_3$)	28.8
3	Potassium acetate (KOAc)	48.7
4	Potassium benzoate (KBZA)	25.7
5	Potassium pivalate (KOPiv)	44.6
6	Potassium phosphate (K_3PO_4)	50.7
7	Potassium tert-butoxide (KOtBu)	79.9
8	Potassium carbonate (K_2CO_3)	60.8

2. Screening of the solvent

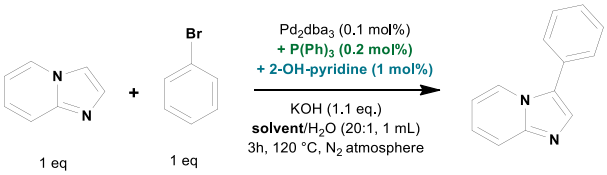


Table S2. Screening of the organic solvent in the coupling reaction of bromobenzene and imidazo[1,2-a]pyridine. Reaction conditions: Pd_2dba_3 (0.0001 mmol), PPh_3 (0.0002 mmol), 2-hydroxypyridine (0.001 mmol), imidazo[1,2-a]pyridine (0.1 mmol), bromobenzene (0.1 mmol), KOH (0.11 mmol) in aqueous solvent (1 mL, 5 vol% H_2O)

Entry	Organic solvent	GC Yield (%)
1	Dimethylacetamide (DMA)	67.7
2	Diglyme	<5
3	Mesitylene	<5
4	Dimethyl sulfoxide (DMSO)	<5
5	Sulfolane	<5
6	Dimethylformamide (DMF)	9.3
7	*N*-methyl-2-pyrrolidone (NMP)	33.4
8	*N*,*N*'-dimethylpropyleneurea (DMPU)	56.4
9	Tetramethylurea (TMU)	67.6

3. Screening of the 2-hydroxypyridine ligand concentration

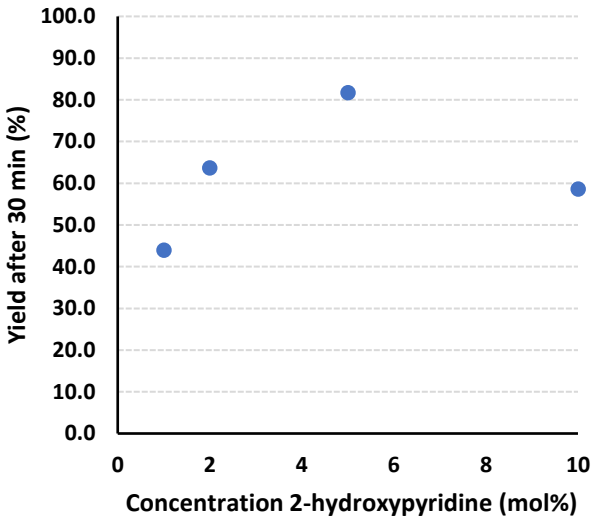


Figure S1. Variation of the 2-hydroxypyridine concentration. Reaction conditions: Pd_2dba_3 (0.0005 mmol, 0.5 mol%), PPh3 (0.001 mmol, 1 mol%), 2-hydroxypyridine (0.001-0.01 mmol), imidazo[1,2-a]pyridine (0.1 mmol), bromobenzene (0.1 mmol), KOH (0.11 mmol) in aqueous solvent (1 mL, 5 vol% H2O)

4. X-Ray Absorption Spectroscopy

General experimental procedure

The XAS data was collected *in situ* at the BM23 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) in frame of proposal MA-4926. The measurements were performed in transmission geometry exploiting Si(311) double-crystal monochromator operated in the continuous scanning mode. The sampling interval was 1 eV. The total time for the full spectrum from 24100 to 25700 eV took 40 s. Rh coated mirrors were used for the higher harmonics rejection. The intensity of the beam before and after the sample was registered by ionization chambers (after the reference palladium foil was measured simultaneously with the sample for energy calibration). The 1st, 2nd and 3rd ionization chambers were filled with inert gas mixture in order to obtain the absorption of the beam of 20%, 80%, and 80%, respectively at 24350 eV.

The samples were prepared in an identical way to the standard reaction procedure. The samples were kept in the closed glass vials of 13 mm thickness, flushed with nitrogen gas prior to the measurements and heating of the sample. The concentration of Pd (and the ligands) was increased by a 100-fold compared to the standard conditions used in the reaction to improve the quality of XAS spectra in transmission mode. The resulting edge-jump at Pd *K*-edge was ca. 0.05 - 0.1. The vials were put in the oil bath and placed on the heating plate under stirring, with the temperature measured inside the oil bath. Under each of the reported conditions, the spectra accumulation took around 30 minutes.

Table S3. List of *in situ* XAS experiments. Reaction conditions: 0.03 mmol Pd_2dba_3, 0.06 mmol phosphine ligand and 0.3 mmol 2-hydroxypyridine in 3 mL DMA

Entry	Phosphine ligand	Pyridine ligand	Temperature
1	Triphenylphosphine (0.02 M)	2-Hydroxypyridine (0.1M)	rt
2	SPhos (0.02M)	2-Hydroxypyridine (0.1M)	rt
3	SPhos (0.02M)	2-Hydroxypyridine (0.1M)	90°C[a]

[a]0.1 mmol of 4-bromothioanisole was added

Data analysis

The data processing and analysis was done in Demeter software.[1] At the first step, all spectra were aligned in energy according to the spectra of the reference channel (palladium foil). Then, the spectra were averaged as non-normalized μ(*E*)*d* signals. The obtained data were converted into the normalized spectra by subtraction of the linear function of the pre-edge (24150-24260 eV) and dividing by a parabolic function of the post-edge range (24400-24850 eV). The extraction of the χ(*k*) functions was done by subtraction of a spline background with spline range from 0 to 12.5 $Å^{-1}$ (ca.24950 eV). The 3-9 $Å^{-1}$ *k*-range was typically used for the Fourier-transformation. The fitting was performed in the *R*-space (typically from 1 to 3 Å) on $k^{1,2,3}$-weighted data (k^2-weighting was used for data visualization). Photoelectron scattering phases and amplitudes were calculated by FEFF6 code[2] using DFT geometries as an input. For each scattering path, its interatomic distance and Debye-Waller parameters were set as variables. To reduce the number of fitting parameters, the zero-potential correction (ΔE_0) was set common for all paths and the coordination numbers were fixed according to the DFT models.

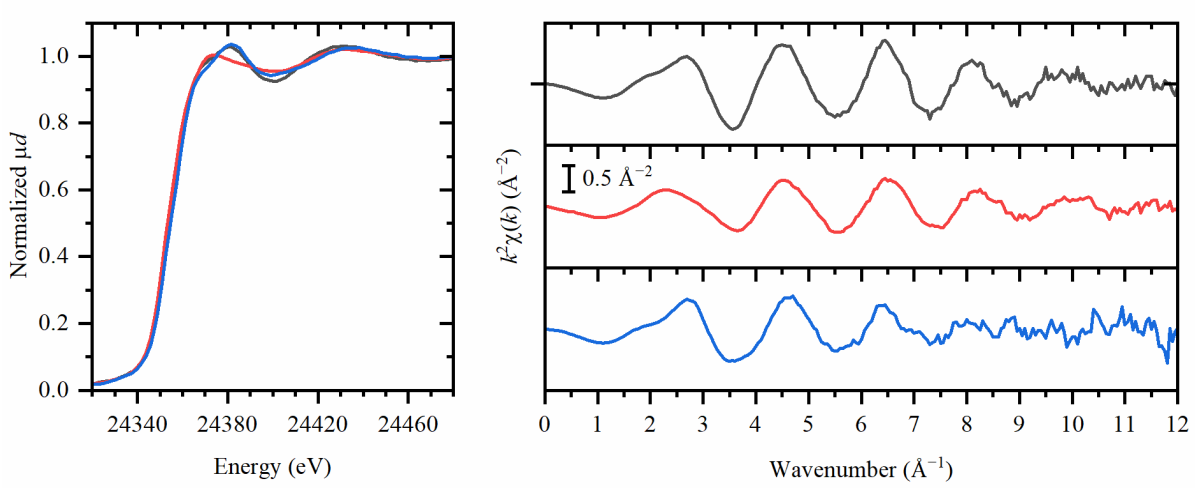


Figure S2. XANES spectra (left) and k^2-weighted χ(*k*)-functions for the spectra presented in Scheme 3 of the main text (black, red and blue lines for top, middle and bottom respectively).

Due to the limited k-interval several constrains were used. In particular, the coordination numbers were fixed according to the atomic DFT models obtained and the zero-energy correction was set to 0 for all paths. The structural parameters obtained from the fits are reported in Tables S4-S6, while the best-fit curves are shown in Scheme 3 of the main text.

Table S4. Structural parameters obtained from the fitting of EXAFS data shown in Scheme 3 (top).

Path	***R***	**σ^2**
Pd–N	2.09 ± 0.01	0.005 ± 0.001
Pd–P	2.35 ± 0.01	0.003 ± 0.001
Pd–C	3.00 ± 0.02	0.001 ± 0.002
Pd–N–C	3.32 ± 0.04	0.002 ± 0.006

Table S5. Structural parameters obtained from the fitting of EXAFS data shown in Scheme 3 (center).

Path	***R***	**σ^2**
Pd–N	2.12 ± 0.01	0.009 ± 0.005
Pd–P	2.29 ± 0.01	0.006 ± 0.003
Pd–C	3.04 ± 0.06	0.011 ± 0.013
Pd–N–C	3.20 ± 0.08	0.006 ± 0.018

Table S6. Structural parameters obtained from the fitting of EXAFS data shown in Scheme 3 (bottom).

Path	***R***	**σ^2**
Pd–N	2.03 ± 0.02	0.004 ± 0.002
Pd–P	2.38 ± 0.04	0.008 ± 0.003
Pd–C	2.54 ± 0.05	0.009 ± 0.008

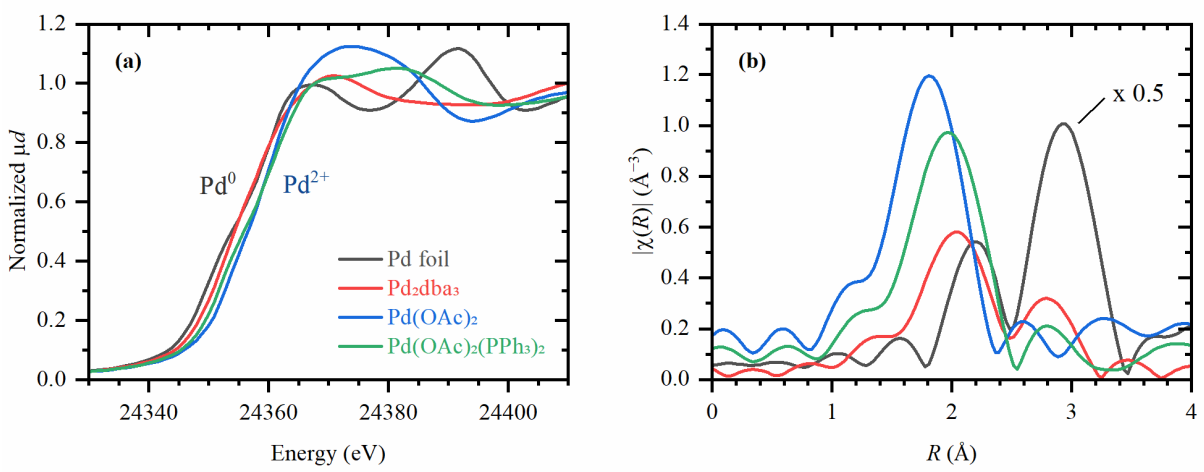


Figure S3. XANES spectra (left) and phase-corrected EXAFS data (right) for the reference Pd(0) foil (black), Pd_2dba_3 (red), $Pd(OAc)_2$ (blue) and $Pd(OAc)_2(PPh_3)_2$ (green).

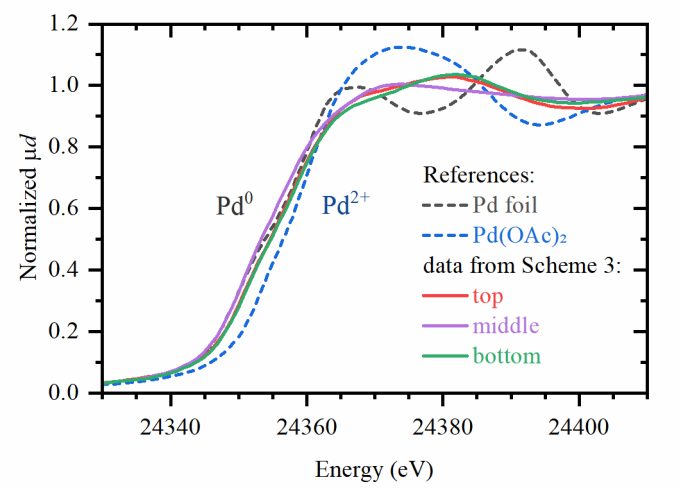


Figure S4. XANES spectra three states of the catalytic system shown in Scheme 3, in comparison to the reference Pd(0) and Pd(II) states.

1. Ravel, B. & Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.*, **12**, 537-541 (2005).
2. Rehr, J.J. & Albers, R.C. Theoretical approaches to x-ray absorption fine structure. *Rev. Mod. Phys.*, **72**, 621-654 (2000).

5. NMR Study of Catalyst Speciation

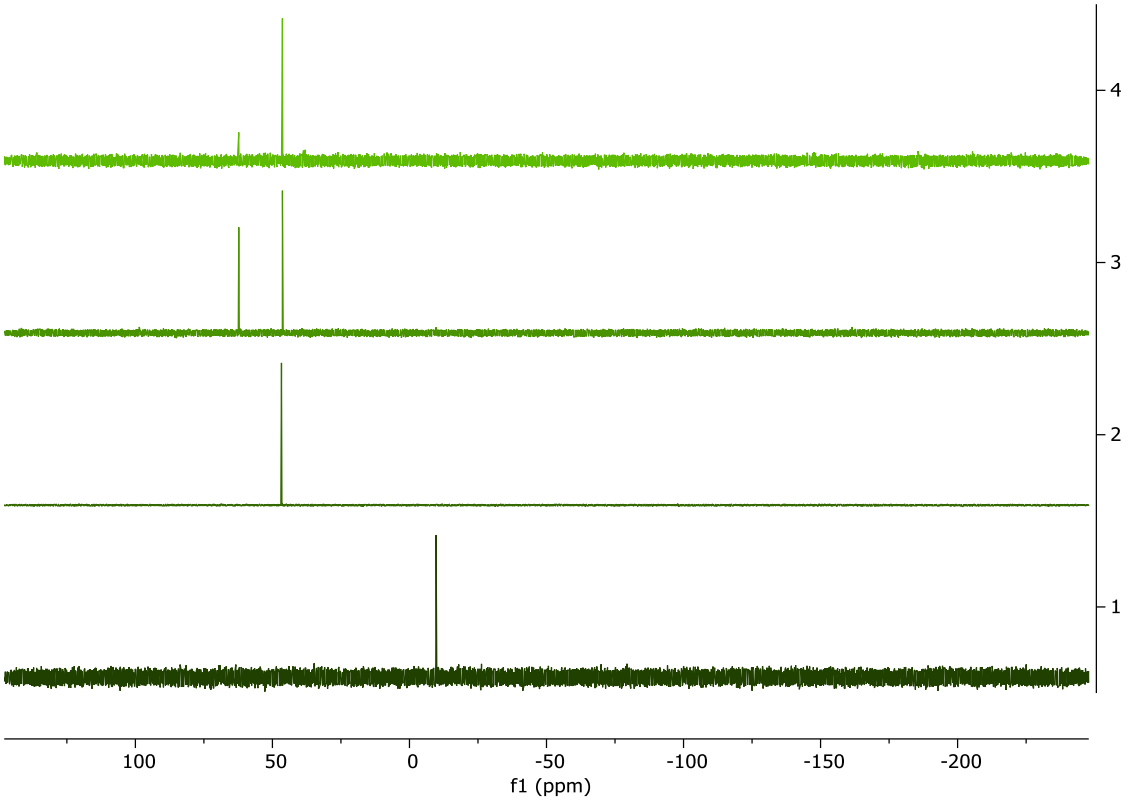


Figure S5. Inverse-gated ^{1}H decoupled ^{31}P NMR spectra of (in 10-fold increased concentration): 1) free SPhos ligand, 2) the corresponding oxide of SPhos, 3) upon addition of Pd precursor (without 2-hydroxypyridine ligand) and 4) with 4-fluoro-2-hydroxypyridine present. Conditions: 1) 0.002 mmol SPhos, 0.11 mmol KOH, H_2O (0.05 mL), DMSO-d_6 (0.10 mL) and DMA (0.85 mL), 2) 0.002 mmol SPhos, 0.11 mmol KOH, 35% H_2O_2 in H_2O (0.02 mL), H_2O (0.03 mL), DMSO-d_6 (0.10 mL) and DMA (0.85 mL), 3) 0.002 mmol Pd(cod)$(TMS)_2$, 0.002 mmol SPhos, 0.11 mmol KOH, H_2O (0.05 mL), DMSO-d_6 (0.10 mL) and DMA (0.85 mL), and 4) 0.002 mmol Pd(cod)$(TMS)_2$, 0.01 mmol 4-fluoro-2-hydroxypyridine, 0.002 mmol SPhos, 0.11 mmol KOH,H_2O (0.05 mL), DMSO-d_6 (0.10 mL) and DMA (0.85 mL).

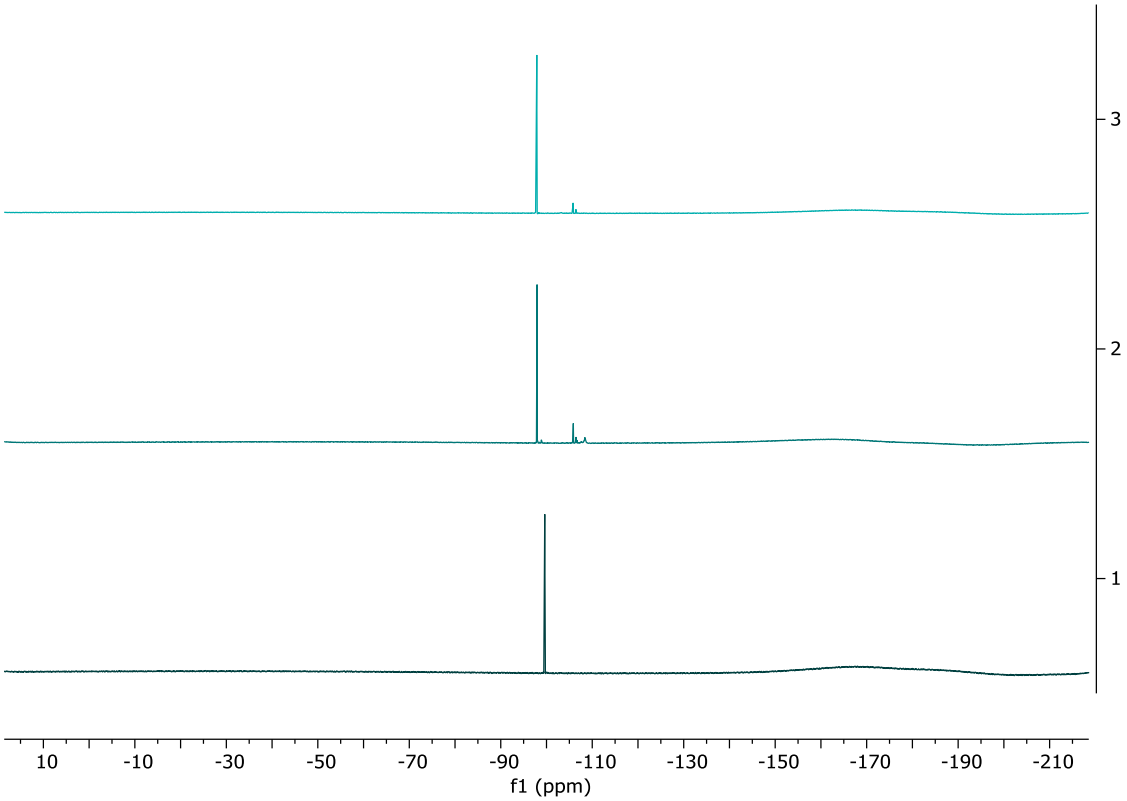
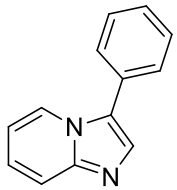


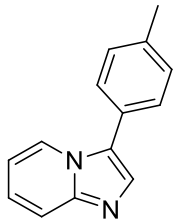
Figure S6. Inverse-gated ^{1}H decoupled ^{19}F NMR spectra of (in 10-fold increased concentration): 1) free 4-fluoro-2-hydroxypyridine ligand, 2) upon addition of Pd precursor (without SPhos ligand) and 3) with SPhos present. Conditions: 1) 0.010 mmol 4-fluoro-2-hydroxypyridine, 0.11 mmol KOH, H_2O (0.05 mL), DMSO-d_6 (0.10 mL) and DMA (0.85 mL), 2) 0.002 mmol Pd(cod)$(TMS)_2$, 0.010 mmol 4-fluoro-2-hydroxypyridine, 0.11 mmol KOH, H_2O (0.05 mL), DMSO-d_6 (0.10 mL) and DMA (0.85 mL), and 3) 0.002 mmol Pd(cod)$(TMS)_2$, 0.01 mmol 4-fluoro-2-hydroxypyridine, 0.002 mmol SPhos, 0.11 mmol KOH,H_2O (0.05 mL), DMSO-d_6 (0.10 mL) and DMA (0.85 mL).

6. Synthetic procedures and chemical details of isolated compounds



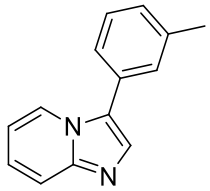
3-phenylimidazo[1,2-a]pyridine (1): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), triphenylphosphine (0.26 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and phenyl bromide (52.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 90/10 EtOAc/PEt) obtaining **1** (91.6 mg, 94% yield) as a brown oil.

^{1}H NMR (400 MHz, DMSO-d^6) δ 6.97 (m, 1H), 7.30 (m, 1H), 7.45 (m, 1H), 7.56 (m, 2H), 7.67 (m, 3H), 7.78 (s, 1H), 8.56 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 111.3, 118.0, 124.5, 125.0, 125.5, 128.0 (2C), 128.4, 129.4, 129.8 (2C), 133.0, 146.0. **MS** (ES+): m/z (%) = 51.0 (7), 63.0 (6), 78.0 (18), 89.0 (5), 167.0 (7), 194.0 (100)



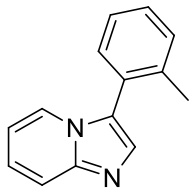
3-(4'-methylphenyl)imidazo[1,2-a]pyridine (2): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), triphenylphosphine (0.26 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 4-bromotoluene (85.5 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 90/10 EtOAc/PEt) obtaining **2** (94.9 mg, 91% yield) as a beige powder.

^{1}H NMR (400 MHz, DMSO-d^6) δ 2.38 (s, 3H), 6.95 (m, 1H), 7.28 (m, 1H), 7.36 (m, 2H), 7.54 (m, 2H), 7.64 (m, 1H), 7.72 (s, 1H), 8.51 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 21.3, 113.2, 118.0, 124.4, 124.8, 125.5, 126.4, 127.9 (2C), 130.3 (2C), 132.6, 137.9, 145.8. **MS** (ES+): m/z (%) = 51.0 (5), 63.0 (4), 78.0 (12), 91 (3), 103.0 (8), 115.0 (3), 130.0 (4), 180.0 (4), 192.0 (6), 208.1 (100)



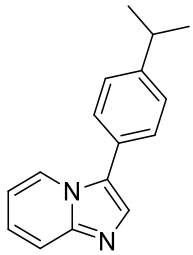
3-(3'-methylphenyl)imidazo[1,2-a]pyridine (3): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), triphenylphosphine (0.26 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 3-bromotoluene (60.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 1: 85/15 2: 60/40 EtOAc/PEt) obtaining **3** (92.7 mg, 89% yield) as a slightly yellow oil.

^{1}H NMR (400 MHz, DMSO-d^6) δ 2.40 (s, 3H), 6.96 (m, 1H), 7.18-7.33 (m, 2H), 7.39-7.48 (m, 3H), 7.65 (m, 1H), 7.75 (s, 1H), 8.56 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 21.5, 113.3, 118.0, 124.5, 124.9, 125.1, 125.6, 128.5, 129.1, 129.3, 129.6, 132.9, 139.1, 145.9. **MS** (ES+): m/z (%) = 51.0 (4), 63.0 (3), 78.0 (14), 103.0 (11), 115.0 (3), 130.0 (3), 180.0 (5), 192.0 (8), 208.1 (100)



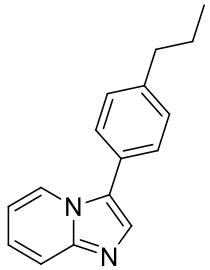
3-(2'-methylphenyl)imidazo[1,2-a]pyridine (4): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), triphenylphosphine (0.26 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 2-bromotoluene (60.2 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 1: 85/15 2: 60/40 EtOAc/PEt) obtaining **4** (82.2 mg, 79% yield) as a slightly yellow oil.

^{1}H NMR (400 MHz, DMSO-d^6) δ 2.12 (s, 3H), 6.91 (m, 1H), 7.29 (m, 1H), 7.33-7.47 (m, 4H), 7.60-7.72 (m, 2H), 7.93 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 19.9, 113.0, 117.9, 124.4, 124.6, 124.8, 126.8, 128.4, 129.5, 131.1, 131.2, 133.2, 138.0, 145.2. **MS** (ES+): m/z (%) = 39.0 (4), 51.0 (9), 78.0 (17), 89.0 (5), 103.0 (14), 115.0 (10), 130.0 (26), 152.0 (3), 180.0 (22), 208.0 (100)



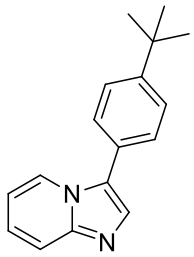
3-(4'-isopropylphenyl)imidazo[1,2-a]pyridine (5): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), SPhos (0.41 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 1-bromo-4-isopropylbenzene (77.4 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 1: 85/15 2: 50/50 EtOAc/PEt) obtaining **5** (98.8 mg, 84% yield) as a beige flaky solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 1.26 (d, 6H), 2.96 (spt, 1H), 6.95 (m, 1H), 7.29 (m, 1H), 7.42 (m, 2H), 7.58 (m, 2H), 7.65 (m, 1H), 7.73 (s, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 24.2 (2C), 33.7, 113.2, 118.0, 124.4, 124.8, 126.7, 127.6, 128.0, 132.8, 145.9, 148.7. **MS** (ES+): m/z (%) = 51.0 (4), 63.0 (3), 78.0 (12), 115.0 (5), 194.0 (9), 221.0 (100), 236.1 (54)



3-(4'-*n*-propylphenyl)imidazo[1,2-a]pyridine (6): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), SPhos (0.41 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 1-bromo-4-*n*-propylbenzene (77.4 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 1: 80/20 2: 50/50 EtOAc/PEt) obtaining **6** (97.3 mg, 82% yield) as a light brown powder.

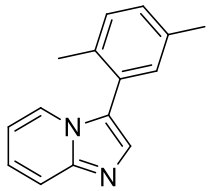
^{1}H NMR (400 MHz, DMSO-d^6) δ 0.94 (t, 3H), 1.65 (sxt, 2H), 2.63 (t, 2H), 6.95 (m, 1H), 7.29 (m, 1H), 7.37 (m, 2H), 7.57 (m, 2H), 7.65 (m, 1H), 7.73 (s, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 14.1, 24.4, 37.6, 113.2, 117.9, 124.5, 124.8, 126.7, 127.9 (2C), 129.7 (2C), 132.7, 142.6, 145.8. **MS** (ES+): m/z (%) = 78.0 (9), 192.0 (4), 207.0 (100), 236.0 (42)



3-(4'-*tert*-butylphenyl)imidazo[1,2-a]pyridine (7): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), SPhos (0.41 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 1-bromo-4-*tert*-butylbenzene (86.7 µL,

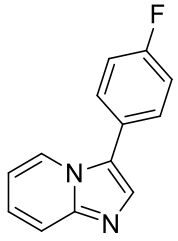
0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 1: 80/20 2: 50/50 EtOAc/PEt) obtaining **7** (91.7 mg, 73% yield) as pale brown, crystalline solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 1.34 (s, 9H), 6.95 (m, 1H), 7.30 (m, 1H), 7.53-7.62 (m, 4H), 7.65 (m, 1H), 7.73 (s, 1H), 8.55 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 31.5 (3C), 34.9, 113.2, 117.4, 118.0, 124.5, 124.9, 126.5 (2C), 127.7 (2C), 132.8, 133.6, 145.9, 151.0. **MS** (ES+): m/z (%) = 51.0 (3), 78.0 (11), 103.3 (8), 115.0 (4), 192.0 (6), 220.0 (17), 235.0 (100), 250.1 (47)



3-(2',5'-dimethylphenyl)imidazo[1,2-a]pyridine (8): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), SPhos (0.41 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 2-bromo-1,4-dimethylbenzene (69.1 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 1: 80/20 2: 50/50 EtOAc/PEt) obtaining **8** (96.6 mg, 87% yield) as a pale brown powder.

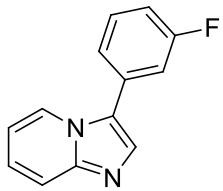
^{1}H NMR (400 MHz, DMSO-d^6) δ 2.06 (s, 3H), 2.33 (s, 3H), 6.90 (m, 1H), 7.18-7.34 (m, 4H), 7.59-7.70 (m, 2H), 7.89-7.96 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 19.4, 20.9, 34.9, 113.0, 117.8, 124.6, 124.7, 128.2, 130.1, 131.0, 131.7, 133.1, 134.8, 135.8, 145.2. **MS** (ES+): m/z (%) = 39.0 (4), 51.0 (8), 63.0 (5), 78.0 (15), 91.0 (4), 103.1 (9), 115.0 (11), 128.0 (6), 144.0 (31), 194.0 (19), 207.0 (16), 222.0 (100)



3-(4'-fluorophenyl)imidazo[1,2-a]pyridine (9): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), triphenylphosphine (0.26 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 1-bromo-4-fluorobenzene (54.9 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The

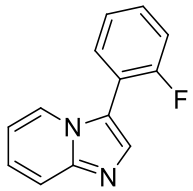
product was purified by flash column chromatography (Eluent: 70/30 EtOAc/PEt) obtaining **9** (83.2 mg, 78% yield) as a beige powder.

^{1}H NMR (400 MHz, DMSO-d^{6}) δ 6.95 (m, 1H), 7.30 (m, 1H), 7.39 (m, 2H), 7.66 (m, 1H), 7.69-7.74 (m, 2H), 7.76 (s, 1H), 8.50 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^{6}) δ 113.3, 116.6, 116.9, 118.0, 124.5, 125.1, 125.9, 130.4, 130.5, 133.1, 145.9, 161.0, 163.4. **^{19}F NMR** (400 MHz, DMSO-d^{6}) -113.6. **MS** (ES+): m/z (%) = 51.0 (7), 63.0 (5), 78.0 (26), 94.0 (3), 107.0 (7), 120.0 (4), 134.0 (4), 185.0 (6), 212.0 (100)



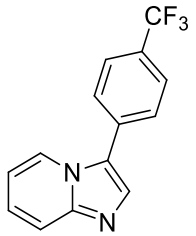
3-(3'-fluorophenyl)imidazo[1,2-a]pyridine (10): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), triphenylphosphine (0.26 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 1-bromo-3-fluorobenzene (55.8 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na2SO4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 70/30 EtOAc/PEt) obtaining **10** (94.7 mg, 89% yield) as a tan powder.

^{1}H NMR (400 MHz, DMSO-d^{6}) δ 6.99 (m, 1H), 7.22-7.36 (m, 2H), 7.50-7.62 (m, 3H), 7.68 (m, 1H), 7.85 (s, 1H), 8.62 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^{6}) δ 113.5, 114.4, 114.7, 114.9, 115.2, 118.0, 123.8, 124.8, 125.4, 133.8, 146.2, 161.8, 164.3. **^{19}F NMR** (400 MHz, DMSO-d^{6}) -111.9. **MS** (ES+): m/z (%) = 51.0 (7), 63.0 (5), 78.0 (21), 107.0 (5), 120.0 (3), 185.0 (5), 212.0 (100)



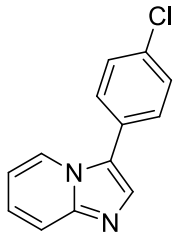
3-(2'-fluorophenyl)imidazo[1,2-a]pyridine (11): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), triphenylphosphine (0.26 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 1-bromo-2-fluorobenzene (54.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 70/30 EtOAc/PEt) obtaining **11** (96.0 mg, 90% yield) as a dark yellow oil.

^{1}H NMR (400 MHz, DMSO-d^{6}) δ 6.99 (m, 1H), 7.30-7.48 (m, 3H), 7.51-7.58 (m, 1H), 7.61-7.72 (m, 2H), 7.78 (s, 1H), 8.21 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^{6}) δ 113.2, 116.6, 116.9, 117.9, 119.7, 125.4, 125.8, 131.2, 131.7, 134.3, 146.1, 158.5, 161.0. **^{19}F NMR** (400 MHz, DMSO-d^{6}) -112.2. **MS** (ES+): m/z (%) = 51.0 (7), 63.0 (5), 78.0 (24), 94.0 (3), 107.0 (6), 120.0 (3), 185.0 (5), 212.0 (100)



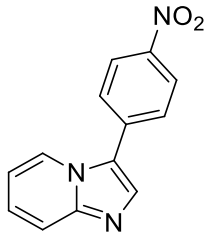
3-(4'-trifluoromethylphenyl)imidazo[1,2-a]pyridine (12): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), triphenylphosphine (0.26 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 4-bromobenzotrifluoride (70.0 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 90/10 EtOAc/PEt) obtaining **12** (118.7 mg, 91% yield) as a beige crystalline solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 7.02 (m, 1H), 7.36 (m, 1H), 7.70 (m, 1H), 7.85-7.96 (m, 5H), 8.68 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 113.9, 118.2, 124.1, 124.8, 125.8, 126.5, 128.2, 133.6, 134.4, 146.5, 134.3, 146.1, 158.5, 161.0. **^{19}F NMR** (400 MHz, DMSO-d^6) -61.0 **MS** (ES+): m/z (%) = 51.0 (5), 63.0 (3), 78.0 (20), 192.0 (6), 243.0 (7), 262.0 (100)



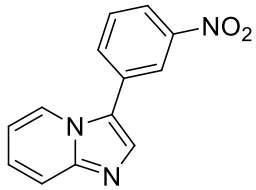
3-(4'-chlorophenyl)imidazo[1,2-a]pyridine (13): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), triphenylphosphine (0.26 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 1-bromo-4-chlorobenzene (95.7 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 90/10 EtOAc/PEt) obtaining **13** (97.0 mg, 85% yield) as a beige crystalline solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 6.98 (m, 1H), 7.32 (m, 1H), 7.56-7.63 (m, 2H), 7.65-7.74 (m, 3H), 7.81 (s, 1H), 8.56 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 113.5, 118.1, 124.4, 124.6, 125.3, 129.7, 129.8, 132.8, 133.4, 146.2. **MS** (ES+): m/z (%) = 28.0 (3), 51.0 (9), 62.9 (6), 78.0 (24), 101.0 (3), 113.9 (4), 138.9 (4), 149.9 (3), 166.0 (4), 192.0 (14), 228.0 (100)



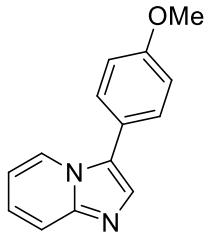
3-(4'-nitrophenyl)imidazo[1,2-a]pyridine (14): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), triphenylphosphine (0.26 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 1-bromo-4-nitrobenzene (101.0 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 95/5 EtOAc/PEt) obtaining **14** (102.5 mg, 86% yield) as an orange crystalline solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 7.07 (m, 1H), 7.40 (m, 1H), 7.73 (m, 1H), 7.97-8.06 (m, 3H), 8.36 (m, 2H), 8.76 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 114.0, 118.1, 123.4, 124.9 (2C), 125.2, 126.3, 127.7 (2C), 135.6, 136.1, 146.3, 147.2. **MS** (ES+): m/z (%) = 30.0 (5), 51.0 (7), 63.0 (7), 78.0 (12), 88.0 (4), 114.8 (3), 138.9 (5), 165.8 (7), 192.0 (87), 209.0 (22), 239.0 (100)



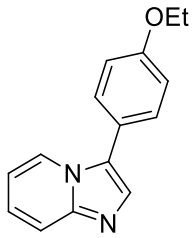
3-(3'-nitrophenyl)imidazo[1,2-a]pyridine (15): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), triphenylphosphine (0.26 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 1-bromo-3-nitrobenzene (101.0 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 95/5 EtOAc/PEt) obtaining **15** (96.5 mg, 81% yield) as an dark yellow crystalline solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 7.03 (m, 1H), 7.36 (m, 1H), 7.71 (m, 1H), 7.84 (m, 1H), 7.95 (s, 1H), 8.14 (m, 1H), 8.24 (m, 1H), 8.44 (m, 1H), 8.66 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 113.8, 118.1, 122.2, 122.7, 123.5, 124.8, 125.9, 131.0, 131.3, 134.0, 134.4, 146.6, 148.9. **MS** (ES+): m/z (%) = 30.0 (3), 51.0 (7), 63.0 (6), 78.0 (11), 139.0 (6), 164.0 (7), 192.0 (99), 239.0 (100)



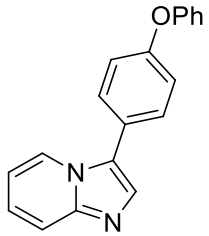
3-(4'-methoxyphenyl)imidazo[1,2-a]pyridine (16): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), SPhos (0.41 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 4-bromoanisole (62.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 90/10 EtOAc/PEt) obtaining **16** (86.4 mg, 77% yield) as a tan crystalline solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 3.83 (s, 3H), 6.94 (m, 1H), 7.12 (m, 2H), 7.27 (m, 1H), 7.58 (m, 2H), 7.64 (m, 1H), 7.68 (s, 1H), 8.46 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 55.5, 113.1, 115.2 (2C), 117.8, 121.6, 124.4, 124.6, 125.3, 129.7 (2C), 132.2, 145.5, 159.5. **MS** (ES+): m/z (%) = 51.0 (5), 63.0 (5), 78.0 (9), 127.0 (4), 154.0 (5), 181.0 (21), 192.0 (3), 209.0 (100), 210.0 (16), 224.1 (93), 225.1 (16)



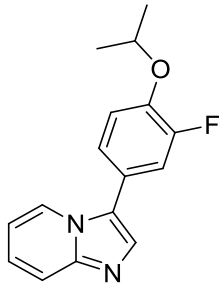
3-(4'-methoxyphenyl)imidazo[1,2-a]pyridine (17): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), SPhos (0.41 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 4-bromophenetole (71.4 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 90/10 EtOAc/PEt) obtaining **17** (81.0 mg, 68% yield) as a a tan powder.

^{1}H NMR (400 MHz, DMSO-d^6) δ 1.37 (t, 3H), 4.11 (q, 2H), 6.94 (m, 1H), 7.10 (m, 2H), 7.27 (m, 1H), 7.56 (m, 2H), 7.64 (m, 1H), 7.67 (s, 1H), 8.45 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 15.1, 63.7, 113.1, 115.6 (2C), 118.0, 121.4, 124.3, 124.6, 125.4, 129.7 (2C), 132.3, 145.6, 158.8. **MS** (ES+): m/z (%) = 29.0 (4), 51.0 (5), 78.0 (11), 79.0 (4), 131.9 (4), 179.0 (7), 181.0 (17), 209.0 (100), 210.0 (43), 238.0 (83), 239.0 (15)



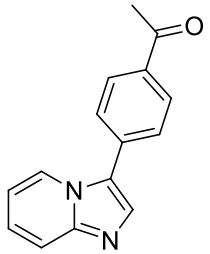
3-(4'-phenoxyphenyl)imidazo[1,2-a]pyridine (18): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), SPhos (0.41 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 4-bromodiphenyl ether (87.5 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 80/20 EtOAc/PEt) obtaining **18** (93.2 mg, 65% yield) as pale yellow solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 6.96 (m, 1H), 7.09-7.22 (m, 5H), 7.30 (m, 1H), 7.44 (m, 2H), 7.66 (m, 3H), 7.74 (s, 1H), 8.52 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 113.3, 118.0, 119.4, 119.5 (2C), 124.2 (2C), 124.4, 124.5, 124.9, 125.0, 129.9 (2C), 130.5 (2C), 132.7, 145.8, 156.5, 157.0. **MS** (ES+): m/z (%) = 51.0 (7), 77.0 (8), 180.0 (10), 209.0 (32), 286.1 (100)



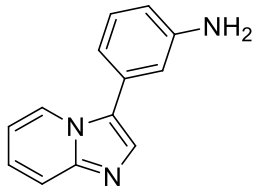
3-(3'-fluoro-4-isopropoxyphenyl)imidazo[1,2-a]pyridine (19): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), SPhos (0.41 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 4-bromo-2-fluoro-1-isopropoxybenzene (116.5 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 60/40 EtOAc/PEt) obtaining **19** (83.8 mg, 62% yield) as a slightly yellow oil.

^{1}H NMR (400 MHz, DMSO-d^6) δ 6.96 (m, 1H), 7.26-7.36 (m, 2H), 7.40 (m, 1H), 7.54 (m, 1H), 7.65 (m, 1H), 7.73 (s, 1H), 8.53 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 22.3 (2C), 71.9, 113.2, 116.0, 116.2, 117.8, 122.2, 122.3, 124.3, 124.6, 125.0, 132.9, 145.3, 145.5, 145.8, 152.0, 154.3. **^{19}F NMR** (400 MHz, DMSO-d^6) -132.7. **MS** (ES+): m/z (%) = 50.9 (3), 77.9 (15), 78.9 (4), 149.9 (4), 178.9 (4), 197.9 (4), 227.0 (20), 228.0 (100), 229.0 (20), 270.0 (32), 271.0 (6).



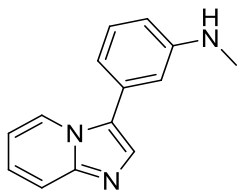
3-(4'-acetylphenyl)imidazo[1,2-a]pyridine (20): To a solution of Pd_2dba_3 (0.46 mg, 0.0005 mmol, 0.1 mol%), SPhos (0.26 mg, 0.001 mmol, 0.2 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 1 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 4'-bromoacetophenone (99.5 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 5/95 MeOH/DCM) obtaining **20** (106.5 mg, 90% yield) as a light brown, crystalline solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 7.03 (m, 1H), 7.36 (m, 1H), 7.70 (m, 1H), 7.85 (m, 2H), 7.94 (s, 1H), 8.10 (m, 2H), 8.69 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 27.2, 113.8, 118.0, 124.6, 124.9, 125.8, 127.3 (2C), 129.6 (2C), 133.9, 134.5, 136.0, 146.7, 197.7. **MS** (ES+): m/z (%) = 39.0 (3), 43.0 (10), 62.9 (8), 78.0 (12), 114.9 (4), 140.0 (6), 164.0 (6), 192.0 (80), 221.0 (88), 236.0 (100)



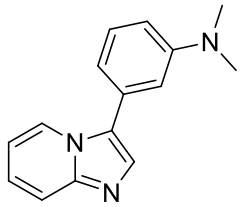
3-(imidazo[1,2-a]pyridin-3-yl)aniline (21): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), SPhos (0.82 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 3-bromoaniline (54.5 µL, 0.55 mmol, 110 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 5/95 MeOH/DCM) obtaining **21** (68.0 mg, 65% yield) as a dark brown oil.

^{1}H NMR (400 MHz, DMSO-d^6) δ 6.65 (m, 1H), 6.77 (m, 1H), 6.85 (m, 1H), 6.95 (m, 1H), 7.19 (m, 1H), 7.28 (m, 1H), 7.58 (m, 1H), 7.66 (s, 1H), 8.51 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 112.5, 113.0, 113.1, 114.1, 115.3, 117.3, 118.0, 124.6, 124.7, 124.9, 130.3, 132.3, 150.0. **MS** (ES+): m/z (%) = 51.0 (6), 63.1 (5), 78.0 (12), 90.9 (3), 104.1 (6), 131.0 (6), 181.0 (9), 192.0 (5), 209.0 (100)



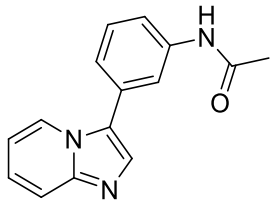
3-(imidazo[1,2-a]pyridin-3-yl)-*N*-methylaniline (22): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), SPhos (0.82 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 3-bromo-N-methylaniline (63.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 5/95 MeOH/DCM) obtaining **22** (97.6 mg, 87% yield) as a dark brown oil.

^{1}H NMR (400 MHz, DMSO-d^6) δ 2.74 (s, 3H), 6.62 (m, 1H), 6.78 (m, 2H), 6.95 (m, 1H), 7.26 (m, 2H), 7.64 (m, 1H), 7.70 (s, 1H), 8.54 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 30.2, 110.9, 111.9, 113.1, 115.0, 117.9, 124.6, 124.7, 126.5, 129.8, 130.3, 132.6, 145.8, 151.1. **MS** (ES+): m/z (%) = 51.0 (4), 63.0 (4), 78.0 (9), 111.1 (3), 131.0 (4), 180.0 (5), 192.0 (13), 207.0 (5), 223.0 (100)



3-(imidazo[1,2-a]pyridin-3-yl)-*N,N*-dimethylaniline (23): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), SPhos (0.82 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 3-bromo-N,N-dimethylaniline (71.4 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc) obtaining **21** (92.4 mg, 78% yield) as a yellow oil.

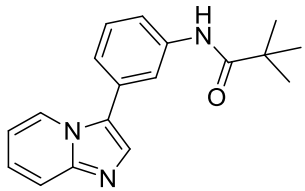
^{1}H NMR (400 MHz, DMSO-d^6) δ 2.96 (s, 3H), 6.81 (m, 1H), 6.84-7.00 (m, 3H), 7.21-7.39 (m, 2H), 7.64 (m, 1H), 7.73 (s, 1H), 8.56 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 111.6, 112.5, 113.2, 115.7, 117.9, 124.6, 124.8, 126.4, 129.8, 130.2, 132.5, 145.8, 151.5. **MS** (ES+): m/z (%) = 51.0 (3), 63.0 (3), 78.0 (8), 118.1 (7), 181.0 (3), 192.0 (18), 221.0 (17), 237.1 (100)



3-(imidazo[1,2-a]pyridin-3-yl)-acetanilide (24): To a solution of Pd_2dba_3 (0.92 mg, 0.0025 mmol, 0.5 mol%), SPhos (2.05 mg, 0.005 mmol, 1 mol%), 2-hydroxypyridine (2.40 mg, 0.025 mmol, 5 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 3-bromoacetanilide (107.0 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product

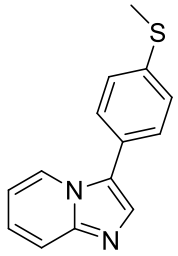
was purified by flash column chromatography (Eluent: 5/95 MeOH/DCM) obtaining **24** (67.8 mg, 54% yield) as a a tan, crystalline powder.

^{1}H NMR (400 MHz, DMSO-d^{6}) δ 2.08 (s, 3H), 6.99 (m, 1H), 7.33 (m, 2H), 7.48 (m, 1H), 7.64 (m, 2H), 7.75 (s, 1H), 7.91 (m, 1H), 8.55 (m, 1H), 10.12 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^{6}) δ 25.2, 113.3, 118.0, 118.1, 119.0, 122.6, 124.5, 125.2, 125.5, 129.6, 130.1, 132.8, 140.4, 146.0, 169.1. **MS** (ES+): m/z (%) = 43.0 (22), 51.0 (5), 63.0 (4), 78.0 (13), 79.0 (13), 79.0 (4), 131.0 (4), 154.0 (4), 180.0 (9), 181.0 (21), 182.0 (9), 207.0 (9), 208.1 (21), 209.0 (100), 210.1 (16), 251.1 (97), 252.1 (18).



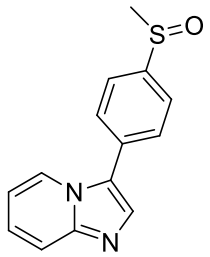
3-(imidazo[1,2-a]pyridin-3-yl)-N-pivaloylaniline (25): To a solution of Pd_2dba_3 (0.92 mg, 0.0025 mmol, 0.5 mol%), SPhos (2.05 mg, 0.005 mmol, 1 mol%), 2-hydroxypyridine (2.40 mg, 0.025 mmol, 5 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and *N*-(3-bromophenyl)pivalamide (128.1 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 80/20) obtaining **25** (90.5 mg, 62% yield) as a tan powder.

^{1}H NMR (400 MHz, DMSO-d^{6}) δ 1.25 (s, 9H), 7.01 (m, 1H), 7.33 (m, 2H), 7.48 (m, 1H), 7.67 (m, 1H), 7.75 (s, 1H), 7.98 (m, 1H), 8.58 (m, 1H), 9.36 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^{6}) δ 27.7 (3C), 113.4, 118.1, 119.3, 119.9, 120.8, 122.8, 124.5, 125.1, 129.3, 130.0, 132.9, 140.6, 146.0, 177.3. **MS** (ES+): m/z (%) 41.0 (9), 57.0 (40), 78 (8), 180.0 (5), 181.0 (14), 208.0 (11), 209.0 (57), 210.0 (10), 235.0 (5), 293.1 (100)



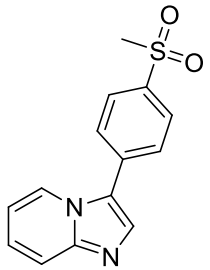
3-(4'-(methylthio)phenyl)imidazo[1,2-a]pyridine (26): To a solution of Pd2dba3 (0.92 mg, 0.001 mmol, 0.2 mol%), SPhos (0.82 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 4-bromothioanisole (101.6 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc) obtaining **26** (95.5 mg, 79% yield) as a brown crystalline compound.

^{1}H NMR (400 MHz, DMSO-d^6) δ 2.55 (s, 3H), 6.97 (m, 1H), 7.22 (m, 1H), 7.29 (m, 1H), 7.45 (m, 2H), 7.61 (m, 2H), 7.75 (s, 1H), 8.54 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 15.1, 112.4, 113.3, 117.4, 118.1, 124.5, 125.0, 127.0 (2C), 128.2, 128.5 (2C), 132.2, 132.8. **MS** (ES+): m/z (%) = 51.0 (5), 63.0 (4), 78.0 (11), 89.0 (3), 120.0 (5), 145.9 (3), 181.0 (5), 192 (21), 225.0 (97), 240.0 (100)



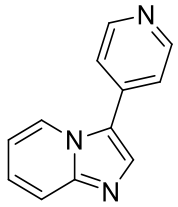
3-(4'-methylsulfinylphenyl)imidazo[1,2-a]pyridine (27): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), SPhos (0.82 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 4-bromophenyl methyl sulfoxide (109.5 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc) obtaining **27** (77.3 mg, 60% yield) as a tan powder.

^{1}H NMR (400 MHz, DMSO-d^6) δ 3.29 (s, 3H), 7.05 (m, 1H), 7.39 (m, 2H), 7.72 (m, 2H), 7.99 (m, 2H), 8.08 (m, 2H), 8.72 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 44.0, 113.9, 118.3, 125.0, 126.0, 126.3, 128.0 (2C), 128.4 (2C), 132.7, 134.4, 134.8, 139.8.



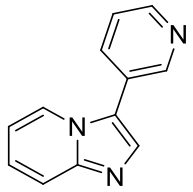
3-(4'-methylsulfonylphenyl)imidazo[1,2-a]pyridine (28): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), SPhos (0.82 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 4-bromophenyl methyl sulfone (117.5 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc) obtaining **28** (121.3 mg, 89% yield) as a tan powder.

^{1}H NMR (400 MHz, DMSO-d^6) δ 3.30 (s, 3H), 7.03 (m, 1H), 7.38 (m, 1H), 7.71 (m, 1H), 7.87 (s, 1H), 7.99 (m, 2H), 8.07 (m, 2H), 8.71 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 44.2, 114.0, 118.3, 125.0, 125.9, 128.0 (2C), 128.4 (2C), 129.4, 133.0, 134.4, 134.8, 139.8. **MS** (ES+): m/z (%) = 63.0 (9), 78.0 (9), 139.0 (4), 164.0 (6), 192.0 (68), 209.0 (28), 272.0 (100)



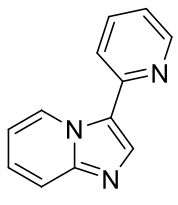
3-(4'-pyridyl)imidazo[1,2-a]pyridine (29): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), triphenylphosphine (0.52 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and K_3PO_4 (222.9 mg, 1.05 mmol, 210 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 4-bromopyridine hydrochloride (96.7 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 5/95 MeOH/DCM) obtaining **29** (85.7 mg, 88% yield) as a beige crystalline solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 6.99 (m, 1H), 7.35 (m, 1H), 7.57 (m, 1H), 7.69 (m, 1H), 7.89 (s, 1H), 8.13 (m, 1H), 8.62 (m, 2H), 8.90 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 113.6, 117.9, 122.5, 124.5, 124.7, 125.6, 125.7, 133.8, 135.2, 146.4, 148.6, 149.1. **MS** (ES+): m/z (%) = 51.0 (10), 63.0 (10), 78.0 (19), 142.0 (4), 168.0 (8), 195.0 (100)



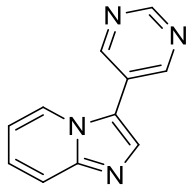
3-(3'-pyridyl)imidazo[1,2-a]pyridine (30): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), triphenylphosphine (0.52 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 3-bromopyridine (48.2 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 5/95 MeOH/DCM) obtaining **30** (88.9 mg, 91% yield) as an orange oil.

^{1}H NMR (400 MHz, DMSO-d^6) δ 6.99 (m, 1H), 7.35 (m, 1H), 7.57 (m, 1H), 7.69 (m, 1H), 7.89 (s, 1H), 8.13 (m, 1H), 8.62 (m, 2H), 8.90 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 113.6, 117.9, 122.5, 124.5, 124.7, 125.6, 125.7, 133.8, 135.2, 146.4, 148.6, 149.1. **MS** (ES+): m/z (%) = 51.0 (6), 63.0 (5), 78.0 (18), 79.0 (3), 142.0 (4), 168.0 (6), 193.0 (4), 194.0 (27), 195.0 (100), 196.0 (16)



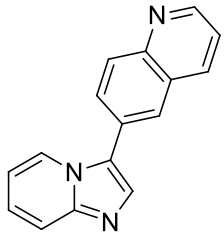
3-(2'-pyridyl)imidazo[1,2-a]pyridine (31): To a solution of Pd_2dba_3 (0.92 mg, 0.0025 mmol, 0.5 mol%), SPhos (2.05 mg, 0.005 mmol, 1 mol%), 2-hydroxypyridine (2.40 mg, 0.025 mmol, 5 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 2-bromopyridine (47.7 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 5/95 MeOH/DCM) obtaining **31** (70.2 mg, 72% yield) as a white solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 7.11 (m, 1H), 7.28 (m, 1H), 7.40 (m, 1H), 7.72 (m, 1H), 7.89 (m, 1H), 8.02 (m, 1H), 8.42 (s, 1H), 8.68 (m, 1H), 9.94 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 113.7, 117.8, 121.0, 121.6, 123.4, 126.2, 128.3, 135.8, 137.5, 147.2, 149.1, 150.4. **MS** (ES+): m/z (%) = 51.0 (9), 63.0 (6), 78.0 (16), 104.0 (3), 167.0 (3), 194.0 (100)



3-(5'-pyrimidinyl)imidazo[1,2-a]pyridine (32): To a solution of Pd_2dba_3 (0.92 mg, 0.0025 mmol, 0.5 mol%), SPhos (2.05 mg, 0.005 mmol, 1 mol%), 2-hydroxypyridine (2.40 mg, 0.025 mmol, 5 mol%) and K_3PO_4 (222.9 mg, 1.05 mmol, 210 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 5-bromopyrimidine (79.5 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 5/95 MeOH/DCM) obtaining **32** (78.3 mg, 80% yield) as a white crystalline solid.

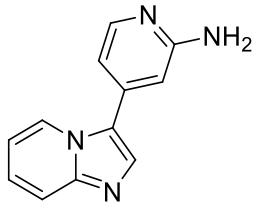
^{1}H NMR (400 MHz, DMSO-d^6) δ 7.03 (m, 1H), 7.38 (m, 1H), 7.72 (m, 1H), 8.01 (s, 1H), 8.71 (m, 1H), 9.18 (m, 2H), 9.23 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 113.8, 118.0, 119.6, 124.5, 125.2, 126.2, 135.0, 147.0, 155.6 (2C), 157.6. **MS** (ES+): m/z (%) = 38.0 (3), 51.0 (9), 63.0 (7), 78.0 (18), 115.0 (6), 142.0 (44), 168.0 (8), 196.0 (100)



6-(imidazo[1,2-a]pyridine-3-yl)quinoline (33): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), triphenylphosphine (0.52 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 6-bromoquinoline (104.0 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude

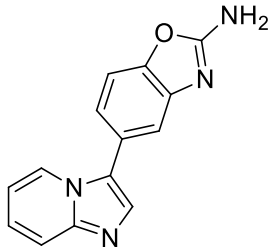
product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc) obtaining **34** (90.9 mg, 74% yield) as a beige solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 7.04 (m, 1H), 7.36 (m, 1H), 7.60 (m, 1H), 7.72 (m, 1H), 7.97 (s, 1H), 8.06 (m, 1H), 8.16 (m, 1H), 8.32 (m, 1H), 8.47 (m, 1H), 8.78 (m, 1H), 8.95 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 113.5, 117.9, 122.6, 124.8, 124.9, 125.6, 126.2, 127.3, 128.9, 129.7, 130.4, 133.9, 136.5, 146.6, 147.7, 151.2.



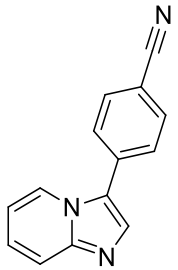
4-(imidazo[1,2-a]pyridine-3-yl)pyridin-2-amine (34): To a solution of Pd_2dba_3 (0.92 mg, 0.0025 mmol, 0.5 mol%), SPhos (2.05 mg, 0.005 mmol, 1 mol%), 2-hydroxypyridine (2.40 mg, 0.025 mmol, 5 mol%) and K_3PO_4 (222.9 mg, 1.05 mmol, 210 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 2-amino-4-bromopyridine (86.5 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 5/95 MeOH/DCM) obtaining **35** (69.5 mg, 66% yield) as a brown powder.

^{1}H NMR (400 MHz, DMSO-d^6) δ 6.09 (m, 2H), 6.77 (m, 2H), 7.03 (m, 1H), 7.35 (m, 1H), 7.69 (m, 1H), 7.88 (s, 1H), 8.04 (m, 1H), 8.63 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 104.9, 110.0, 113.6, 118.1, 124.1, 125.2, 125.6, 134.0, 137.4, 146.5, 149.3, 161.0. **MS** (ES+): m/z (%) = 51.0 (7), 63.0 (5), 79.0 (17), 91.0 (4), 104.9 (9), 155.0 (9), 170.0 (6), 182.0 (9), 194.0 (6), 209.0 (36), 210.0 (100)



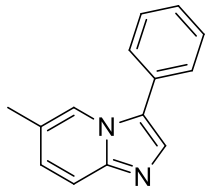
3-(4'-pyrimidinyl)imidazo[1,2-a]pyridine (35): To a solution of Pd_2dba_3 (0.92 mg, 0.0025 mmol, 0.5 mol%), SPhos (2.05 mg, 0.005 mmol, 1 mol%), 2-hydroxypyridine (2.40 mg, 0.025 mmol, 5 mol%) and K_3PO_4 (222.9 mg, 1.05 mmol, 210 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 5-bromobenzo[d]oxazol-2-amine (106.5 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: 5/95 MeOH/DCM) obtaining **35** (98.9 mg, 79% yield) as a dark red powder.

^{1}H NMR (400 MHz, DMSO-d^6) δ 6.88 (m, 1H), 7.10 (m, 1H), 7.22 (m, 1H), 7.36 (m, 1H), 7.58 (m, 1H), 7.95 (s, 1H), 8.55 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 109.0, 110.5, 112.4, 113.5, 116.0, 117.4, 118.2, 122.7, 124.8, 127.5, 133.5, 146.2, 147.7, 164.2.



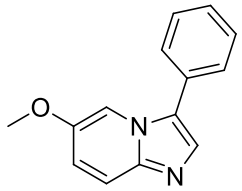
3-(4'-cyanophenyl)imidazo[1,2-a]pyridine (36): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), triphenylphosphine (0.52 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and K_3PO_4 (116.7 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyridine (50.7 µL, 0.50 mmol, 100 mol%) and 4-bromobenzonitrile (91.0 mg, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 95/5) obtaining **36** (99.3 mg, 91% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 7.03 (m, 1H), 7.38 (m, 1H), 7.70 (m, 1H), 7.92 (m, 2H), 7.99 (m, 3H), 8.70 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 110.1, 113.9, 118.2, 119.3, 124.1, 125.0, 126.0, 127.9 (2C), 133.6 (2C), 134.0, 135.0, 146.9. **MS** (ES+): m/z (%) = 51.0 (7), 63.0 (6), 78.0 (20), 114.0 (3), 192.0 (4), 219.0 (100)



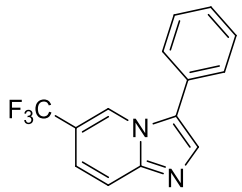
3-phenyl-6-methylimidazo[1,2-a]pyridine (37): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), triphenylphosphine (0.52 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added 6-methylimidazo[1,2-a]pyridine (66.1 mg, 0.50 mmol, 100 mol%) and bromobenzene (52.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 90/10) obtaining **37** (76.5 mg, 73% yield) as a light brown oil.

^{1}H NMR (400 MHz, DMSO-d^6) δ 2.30 (m, 3H), 7.16 (m, 1H), 7.43 (m, 1H), 7.49-7.60 (m, 3H), 7.65 (m, 2H), 7.70 (s, 1H), 8.34 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 18.2, 117.4, 121.8, 122.50, 125.5, 127.8, 127.9 (2C), 128.2, 129.4, 129.7 (2C), 132.8, 145.0. **MS** (ES+): m/z (%) = 39.0 (3), 51.0 (4), 65.0 (8), 77.0 (5), 92.0 (8), 103.1 (4), 180.0 (7), 192.0 (4), 208.0 (100)



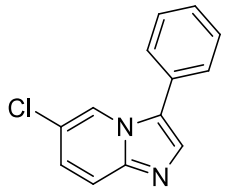
3-phenyl-6-methoxyimidazo[1,2-a]pyridine (38): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), triphenylphosphine (0.52 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) in hydrous DMA (5 vol% H_2O) was added 6-methoxyimidazo[1,2-a]pyridine (74.1 mg, 0.50 mmol, 100 mol%) and bromobenzene (52.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc) obtaining **38** (93.0 mg, 83% yield) as a brown oil.

^{1}H NMR (400 MHz, DMSO-d^6) δ 3.80 (s, 3H), 7.10 (m, 1H), 7.45 (m, 1H), 7.58 (m, 3H), 7.70 (m, 2H), 7.72 (m, 1H), 8.00 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 56.1, 105.9, 118.3, 119.6, 120.0, 127.7 (2C), 128.3, 129.5, 129.8 (2C), 133.2, 143.1, 149.4. **MS** (ES+): m/z (%) = 51.0 (5), 63.0 (4), 76.0 (5), 89.0 (4), 102.0 (7), 127.0 (9), 154.0 (8), 181.0 (24), 209.0 (31), 224.0 (100)



3-phenyl-6-trifluoromethylimidazo[1,2-a]pyridine (39): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), triphenylphosphine (0.52 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added 6-trifluoromethylimidazo[1,2-a]pyridine (93.1 mg, 0.50 mmol, 100 mol%) and bromobenzene (52.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 80/20) obtaining **39** (98.3 mg, 75% yield) as a dark yellow solid.

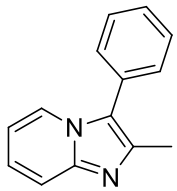
^{1}H NMR (400 MHz, DMSO-d^6) δ 7.46-7.63 (m, 4H), 7.74 (m, 2H), 7.89 (m, 1H), 7.94 (s, 1H), 8.80 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 115.7, 119.2, 120.4, 122.9, 124.0, 125.6, 127.3, 128.5 (2C), 129.0, 130.0 (2C), 134.7, 145.6. **^{19}F NMR** (400 MHz, DMSO-d^6) -60.7. **MS** (ES+): m/z (%) = 63.0 (6), 76.0 (4), 89.0 (6), 116.0 (11), 145.9 (7), 192.0 (6), 243.0 (7), 262.0 (100)



3-phenyl-6-chloroimidazo[1,2-a]pyridine (40): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), triphenylphosphine (0.52 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added

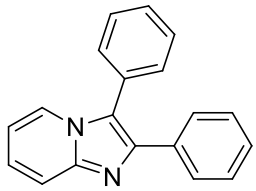
6-chloroimidazo[1,2-a]pyridine (76.3 mg, 0.50 mmol, 100 mol%) and bromobenzene (52.6 µL, 0.50 mmol, 100 mol%).The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 85/15) obtaining **40** (92.6 mg, 81% yield) as a beige solid.

^{1}H NMR (400 MHz, DMSO-d^6) δ 7.35 (m, 1H), 7.46 (m, 1H), 7.57 (m, 2H), 7.70 (m, 3H), 7.82 (s, 1H), 8.59 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 118.8, 120.4, 122.3, 125.8, 126.4, 128.2 (2C), 128.7, 128.8, 129.9 (2C), 133.9, 144.0. **MS** (ES+): m/z (%) = 51.0 (4), 63.0 (10), 76.0 (11), 89.0 (7), 112.0 (11), 166.0 (6), 192.0 (10), 228.0 (100)



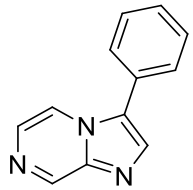
2-methyl-3-phenylimidazo[1,2-a]pyridine (41) : To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), triphenylphosphine (0.52 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added 2-methylimidazo[1,2-a]pyridine (66.1 mg, 0.50 mmol, 100 mol%) and bromobenzene (52.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 90/10) obtaining **41** (73.9 mg, 71% yield) as an orange oil.

^{1}H NMR (400 MHz, DMSO-d^6) δ 3.36 (s, 3H), 6.87 (m, 1H), 7.25 (m, 1H), 7.46 (m, 1H), 7.50-7.62 (m, 5H), 8.25 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 14.2, 111.8, 117.2, 121.8, 123.6, 125.0, 128.2, 129.4, 129.6 (2C), 129.7 (2C), 140.7, 143.9. **MS** (ES+): m/z (%) = 51.0 (6), 63.0 (5), 78.0 (10), 103.1 (8), 115.0 (3), 130.0 (3), 192.0 (4), 208.1 (100)



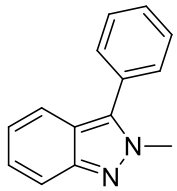
2,3-diphenylimidazo[1,2-a]pyridine (42): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), triphenylphosphine (0.52 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added 2-phenylimidazo[1,2-a]pyridine (97.1 mg, 0.50 mmol, 100 mol%) and bromobenzene (52.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 75/25) obtaining **42** (106.8 mg, 79% yield) as a brown powder.

^{1}H NMR (400 MHz, DMSO-d^6) δ 6.91 (m, 1H), 7.20-7.38 (m, 4H), 7.45 (m, 2H), 7.54-7.65 (m, 5H), 7.68 (m, 1H), 8.01 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 113.3, 117.5, 121.3, 124.2, 125.7, 127.9, 128.0 (2C), 128.7 (2C), 129.5, 129.9, 130.1 (2C), 131.2 (2C), 134.7, 141.6, 144.5. **MS** (ES+): m/z (%) = 51.0 (4), 78.0 (4), 134.3 (8), 165.0 (14), 165.0 (14), 166.0 (14), 190.0 (5), 241.0 (4), 269.1 (100)



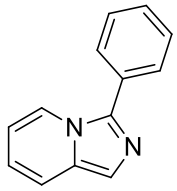
3-phenylimidazo[1,2-a]pyrazine (43): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), triphenylphosphine (0.52 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,2-a]pyrazine (59.6 mg, 0.50 mmol, 100 mol%) and bromobenzene (52.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 95/5) obtaining **43** (88.8 mg, 91% yield) as a beige powder.

^{1}H NMR (400 MHz, DMSO-d^6) δ 7.49 (m, 1H), 7.59 (m, 2H), 7.75 (m, 2H), 7.95 (m, 1H), 8.07 (s, 1H), 8.61 (m, 1H), 9.15 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 118.0, 126.7, 128.0, 128.1 (2C), 129.2, 129.9 (2C), 130.2, 135.0, 141.3, 144.0. **MS** (ES+): m/z (%) = 39.0 (4), 52.0 (10), 63.0 (6), 79.0 (9), 89.0 (8), 102.0 (6), 116.0 (10), 140.0 (6), 168.0 (6), 195.0 (100)



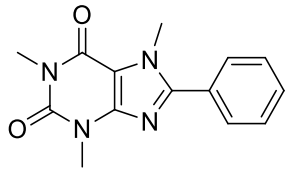
2-methyl-3-phenyl-2H-indazole (44): To a solution of Pd_2dba_3 (0.92 mg, 0.001 mmol, 0.2 mol%), triphenylphosphine (0.52 mg, 0.002 mmol, 0.4 mol%), 2-hydroxypyridine (0.96 mg, 0.01 mmol, 2 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added 2-methyl-2H-indazole (66.1 mg, 0.50 mmol, 100 mol%) and bromobenzene (52.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 160 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 85/15) obtaining **44** (43.7 mg, 42% yield) as a light yellow oil.

^{1}H NMR (400 MHz, DMSO-d^6) δ 4.16 (s, 3H), 7.08 (m, 1H), 7.29 (m, 1H), 7.50-7.72 (m, 7H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 39.1, 117.3, 120.4, 121.0, 122.0, 126.3, 129.2, 129.6 (2C), 129.7, 129.9 (2C), 135.4, 147.6. **MS** (ES+): m/z (%) = 77.0 (6), 104.0 (5), 139.0 (4), 165.0 (9), 180.0 (7), 206.1 (5), 207.1 (31), 208.1 (100), 209.1 (17).



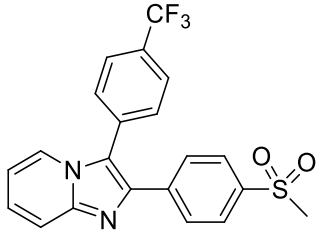
3-phenylimidazo[1,5-*a*]pyridine (45) : To a solution of Pd_2dba_3 (0.92 mg, 0.0025 mmol, 0.5 mol%), SPhos (2.05 mg, 0.005 mmol, 1 mol%), 2-hydroxypyridine (2.40 mg, 0.025 mmol, 5 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added imidazo[1,5-*a*]pyridine (59.1 mg, 0.50 mmol, 100 mol%) and bromobenzene (52.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 160 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 85/15) obtaining **45** (52.4 mg, 54% yield) as a tan crystal.

^{1}H NMR (400 MHz, DMSO-d^6) δ 6.72 (m, 1H), 6.84 (m, 1H), 7.46 (m, 1H), 7.56 (m, 3H), 7.64 (m, 1H), 7.84 (m, 2H), 8.45 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 113.9, 118.9, 119.7, 120.9, 122.3, 128.0 (2C), 128.9, 129.5 (2C), 130.5, 131.8, 137.7.



1,3,7-trimethyl-8-phenylpurine-2,6-dione (46) : To a solution of Pd_2dba_3 (0.92 mg, 0.0025 mmol, 0.5 mol%), SPhos (2.05 mg, 0.005 mmol, 1 mol%), 2-hydroxypyridine (2.40 mg, 0.025 mmol, 5 mol%) and KOH (30.86 mg, 0.55 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added caffeine (97.1 mg, 0.50 mmol, 100 mol%) and bromobenzene (52.6 µL, 0.50 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 160 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 50/50) obtaining **46** (96.0 mg, 71% yield) as a tan crystal.

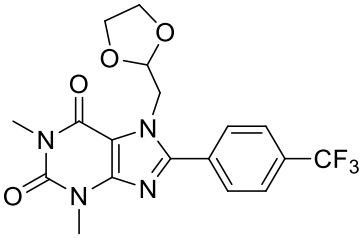
^{1}H NMR (400 MHz, DMSO-d^6) δ 3.25 (s, 3H), 3.45 (s, 3H), 3.99 (s, 3H), 7.58 (m, 3H), 7.79 (m, 2H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 28.1, 29.9, 34.1, 108.4, 128.7, 129.3 (2C), 129.6 (2C), 130.7, 148.1, 151.4, 151.7, 155.2. **MS** (ES+): m/z (%) = 42.0 (3), 67.0 (31), 76.0 (5), 77.0 (4), 82.0 (29), 102.9 (9), 169.9 (6), 192.9 (5), 212.9 (4), 241.0 (5), 269.0 (34), 270.0 (100), 271.0 (16).



2-(4-(methylsulfonyl)phenyl)-3-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (47): To a solution of Pd_2dba_3 (0.18 mg, 0.0005 mmol, 0.5 mol%), SPhos (0.41 mg, 0.001 mmol, 1 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 5 mol%) and KOH (6.17 mg, 0.11 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added 2-(4-(methylsulfonyl)phenyl)imidazo[1,2-*a*]pyridine (27.2 mg,

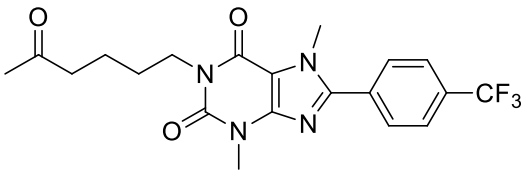
0.10 mmol, 100 mol%) and 4-bromobenzotrifluoride (14.0 µL, 0.10 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 120 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 50/50) obtaining **47** (35.4 mg, 85% yield) as a tan powder.

^{1}H NMR (400 MHz, DMSO-d^6) δ 3.22 (s, 3H), 6.96 (m, 1H), 7.41 (m, 1H), 7.74 (m, 1H), 7.80 (m, 3H), 7.90 (m, 2H), 7.98 (m, 3H), 8.17 (m, 1H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 43.7, 117.6, 121.0, 121.5, 121.6, 124.7, 126.7, 127.1, 127.7 (2C), 128.3, 128.6 (2C), 129.5, 132.0 (2C), 139.3, 140.1, 145.0, 170.0 (2C). **^{19}F NMR** (400 MHz, DMSO-d^6) -61.1.



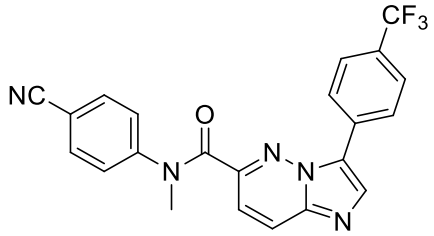
7-((1,3-dioxolan-2-yl)methyl)-1,3-dimethyl-8-(4-(trifluoromethyl)phenyl)purine-2,6-dione (48): To a solution of Pd_2dba_3 (0.18 mg, 0.0005 mmol, 0.5 mol%), SPhos (0.41 mg, 0.001 mmol, 1 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 5 mol%) and KOH (6.17 mg, 0.11 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added doxofylline (26.6 mg, 0.10 mmol, 100 mol%) and 4-bromobenzotrifluoride (14.0 µL, 0.10 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 160 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 30/70) obtaining **48** (12.7 mg, 31% yield) as a slightly yellow powder.

^{1}H NMR (400 MHz, DMSO-d^6) δ 3.27 (s, 3H), 3.49 (s, 3H), 3.68 (m, 4H), 4.54 (d, 2H), 5.16 (t, 1H), 7.94 (m, 2H), 8.03 (m, 2H). **^{13}C NMR** (400 MHz, DMSO-d^6) δ 28.1, 30.0, 48.4, 64.8 (2C), 101.2, 108.4, 123.0, 125.8, 126.1, 126.2, 130.8 (2C), 133.1, 148.0, 151.1, 151.4, 155.2. **^{19}F NMR** (400 MHz, DMSO-d^6) -61.3.



3,7-dimethyl1-(5-oxohexyl)-8-(4-(trifluoromethyl)phenyl)purine-2,6-dione (49): To a solution of Pd_2dba_3 (0.18 mg, 0.0005 mmol, 0.5 mol%), SPhos (0.41 mg, 0.001 mmol, 1 mol%), 2-hydroxypyridine (0.48 mg, 0.005 mmol, 5 mol%) and KOH (6.17 mg, 0.11 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added pentoxifylline (27.8 mg, 0.10 mmol, 100 mol%) and 4-bromobenzotrifluoride (14.0 µL, 0.10 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 160 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 30/70) obtaining **49** (12.2 mg, 29% yield) as a green powder.

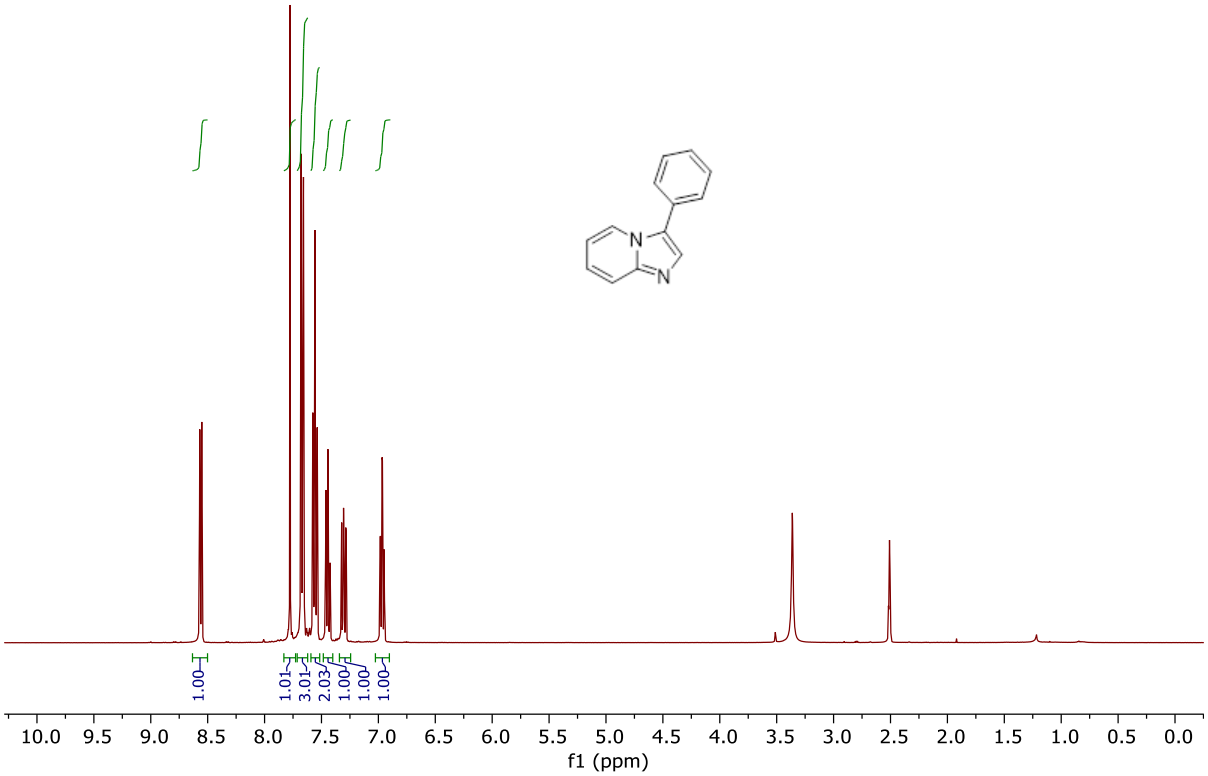
^{1}H NMR (400 MHz, DMSO-d^{6}) δ 1.50 (m, 4H), 2.08 (s, 3H), 2.48 (t, 2H), 3.48 (s, 3H), 3.89 (t, 2H), 4.04 (s, 3H), 7.94 (m, 2H), 8.05 (m, 2H). **^{13}C NMR** (400 MHz, DMSO-d^{6}) δ 21.0, 27.5, 29.9, 30.2, 34.2, 40.7, 42.7, 108.8, 126.1, 126.2, 130.4 (2C), 132.6, 147.8, 149.9, 150.9, 155.1, 208.6. **^{19}F NMR** (400 MHz, DMSO-d^{6}) -61.3.

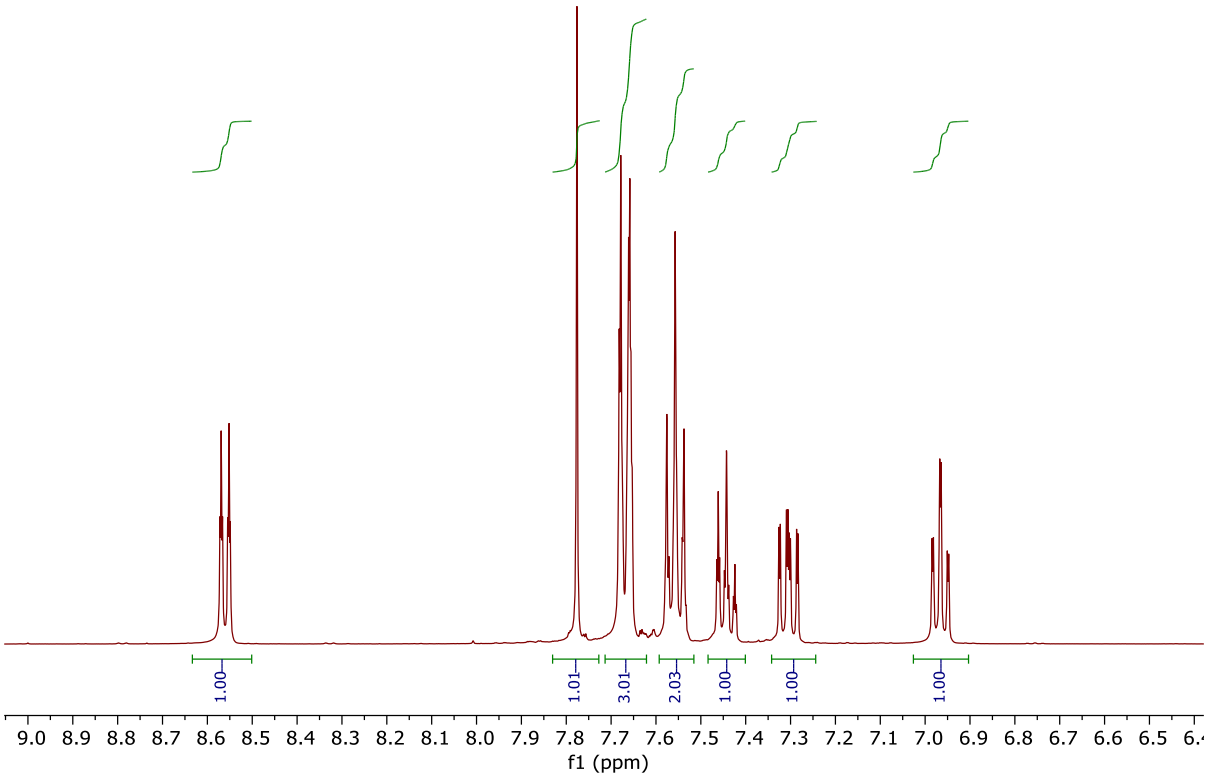


***N*-(4-cyanophenyl)-*N*-methyl-3-(4-(trifluoromethyl)phenyl)imidazo[1,2-*b*]pyridazine-6-carboxamide (50)**: To a solution of Pd_2dba_3 (0.09 mg, 0.00025 mmol, 0.5 mol%), SPhos (0.21 mg, 0.0005 mmol, 1 mol%), 2-hydroxypyridine (0.24 mg, 0.0025 mmol, 5 mol%) and KOH (3.09 mg, 0.055 mmol, 110 mol%) in hydrous DMA (5 vol% H_2O) was added *N*-(4-cyanophenyl)-*N*-methylimidazo[1,2-*b*]pyridazine-6-carboxamide (13.9 mg, 0.05 mmol, 100 mol%) and 4-bromobenzotrifluoride (7.0 µL, 0.05 mmol, 100 mol%). The reaction mixture was flushed with Ar and heated to 160 °C for 24h. The crude product mixture was allowed to cool down, quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash column chromatography (Eluent: EtOAc/PEt 50/50) obtaining **50** (11.0 mg, 52% yield) as a white powder. NMR spectra were in agreement with the data previously reported in literature (McNamara, C. W. et al. *Nature* **504**, 248–253 (2013))

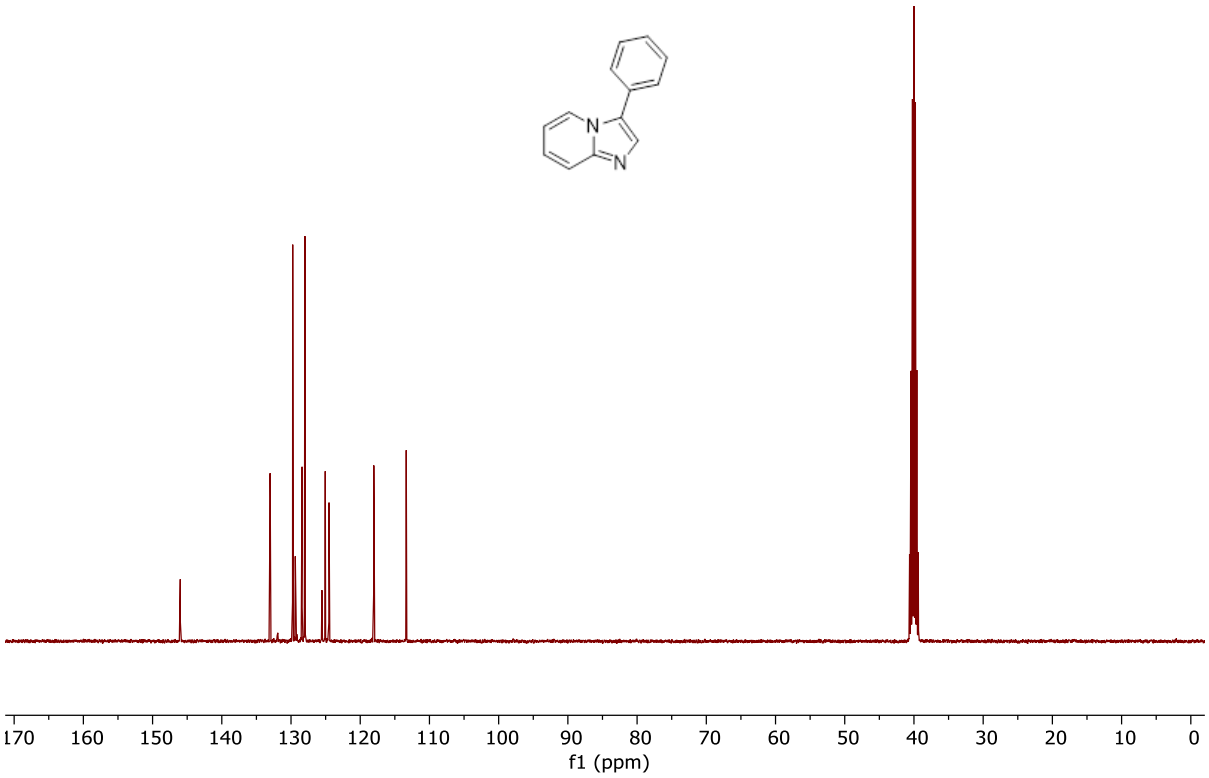
1. Characterization of isolated compounds (NMR + MS)

^{1}H NMR Spectrum of (**1**) (400 MHz, DMSO-d^{6}):

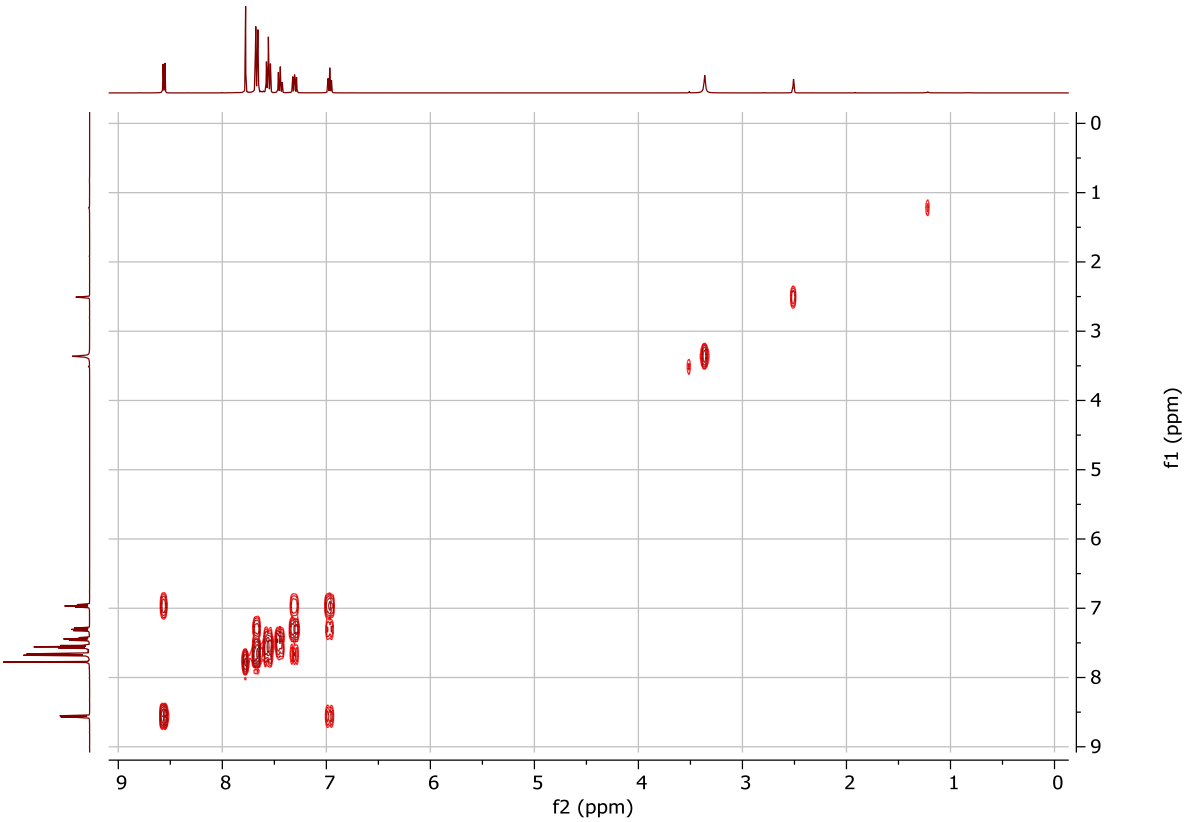


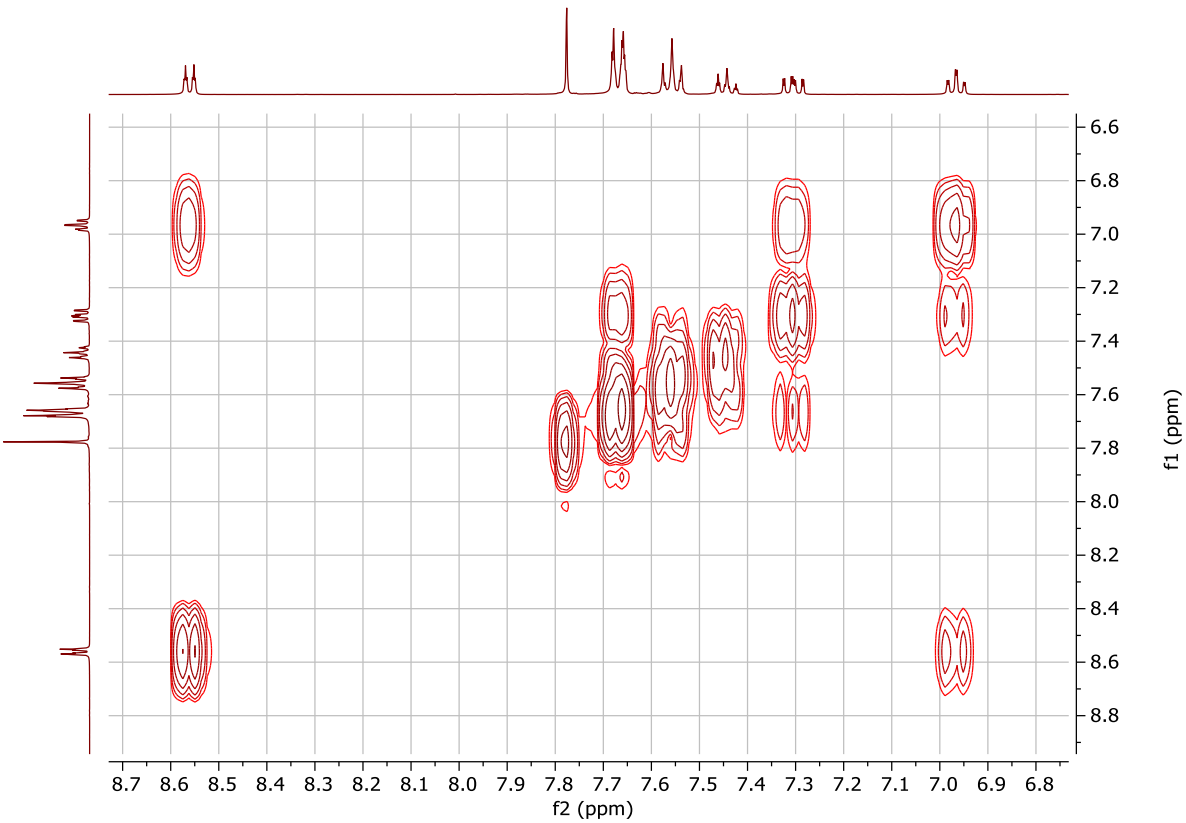


^{13}C NMR Spectrum of (**1**) (400 MHz, DMSO-d^{6}):

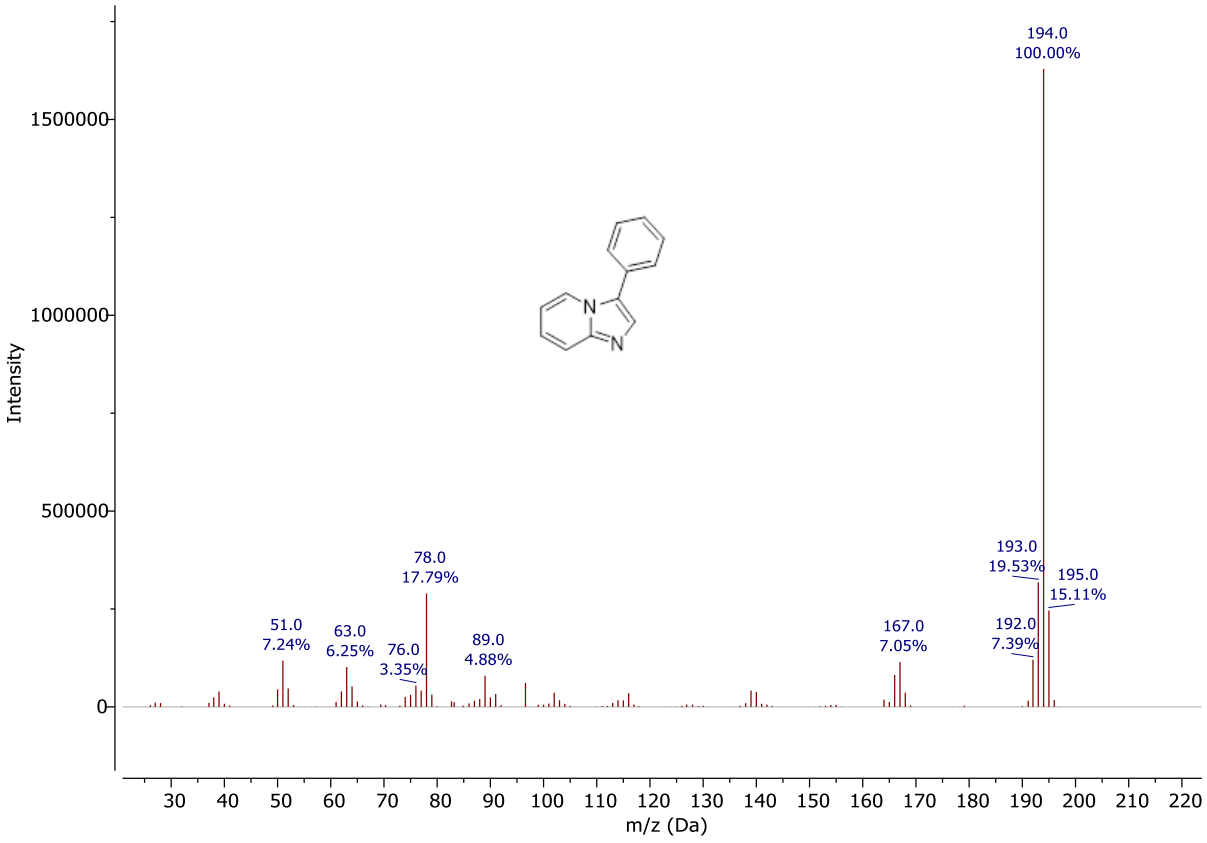


^{1}H/^{1}H COSY NMR Spectrum of (**1**) (400 MHz, DMSO-d^{6}):

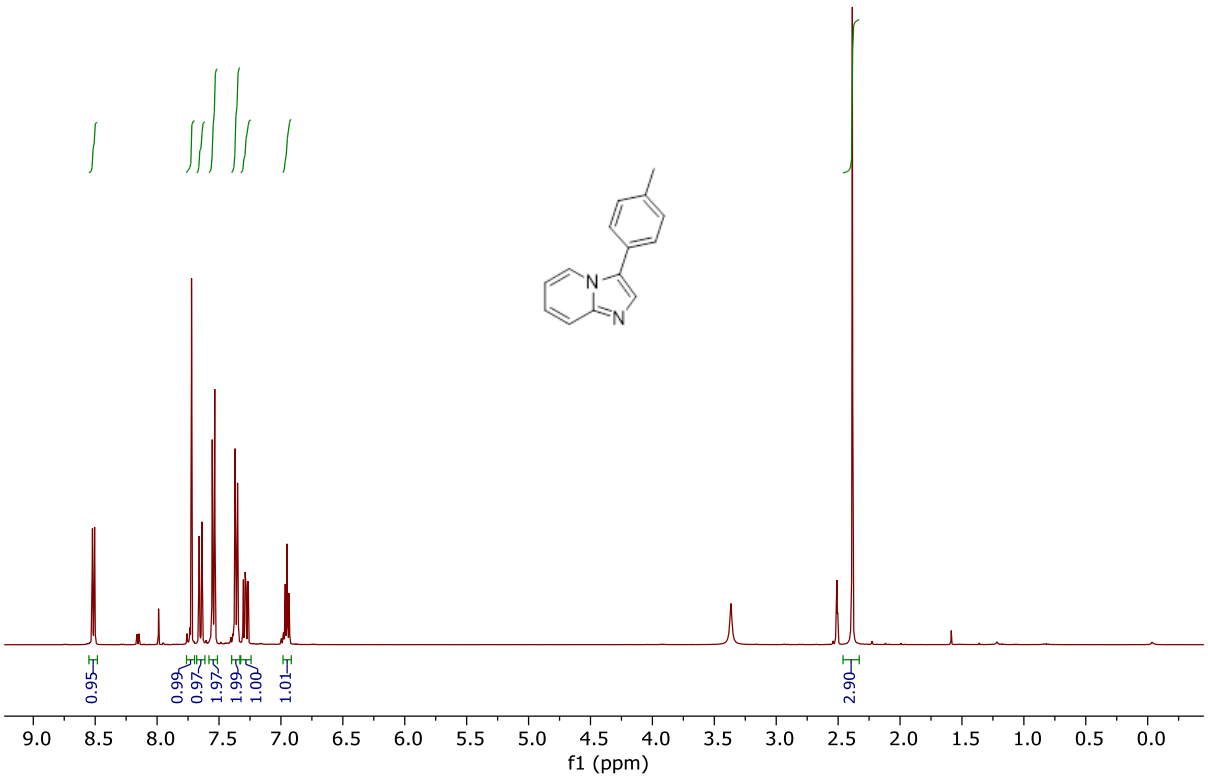


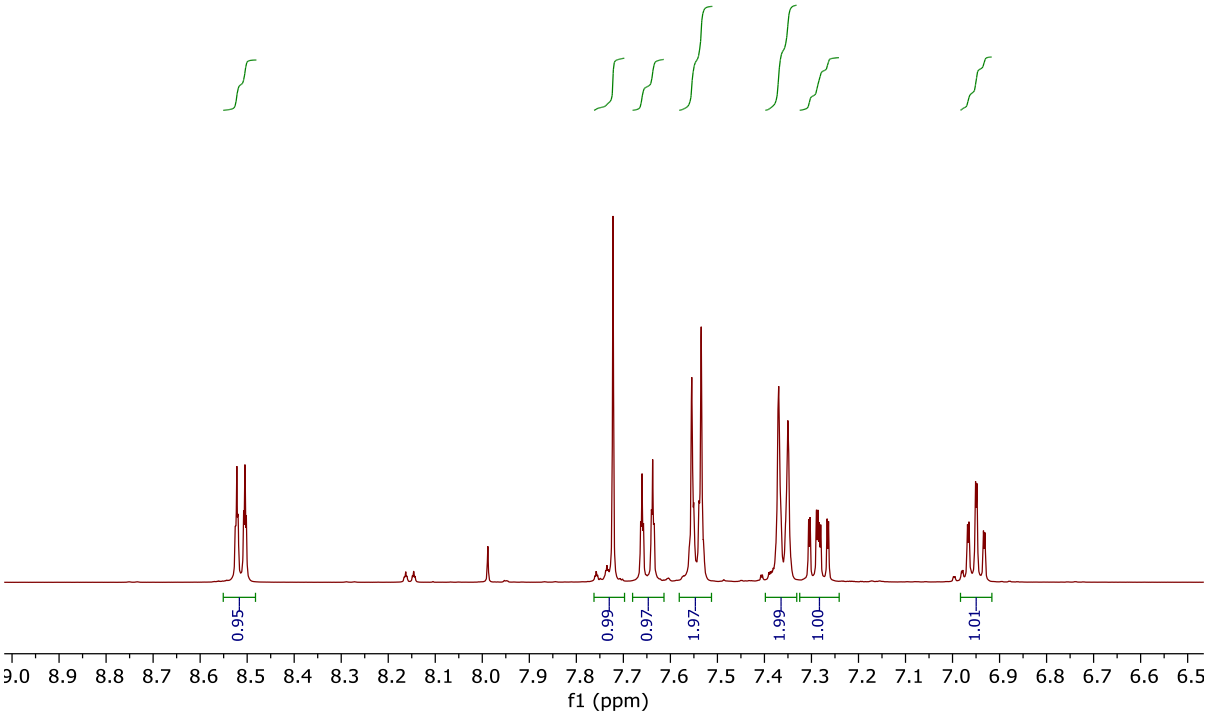


MS Spectrum of (**1**) (EI):

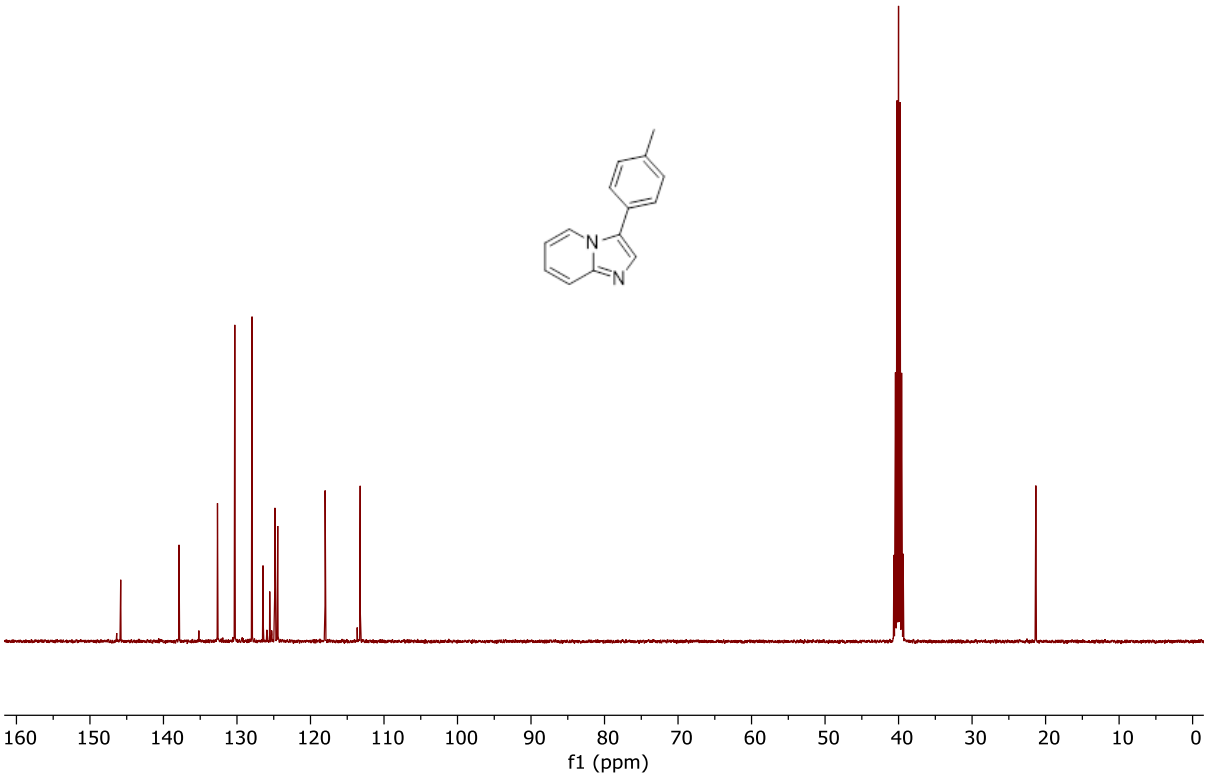


^{1}H NMR Spectrum of (**2**) (400 MHz, DMSO-d^{6}):

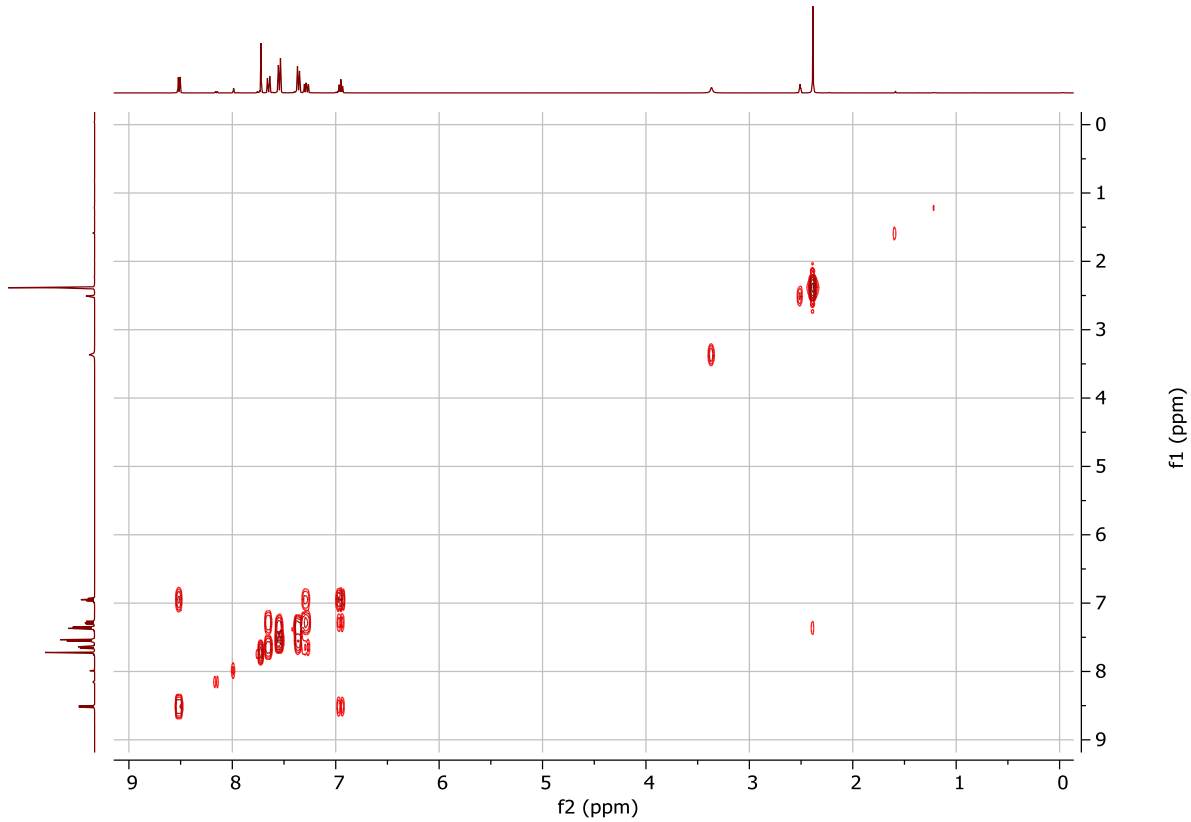


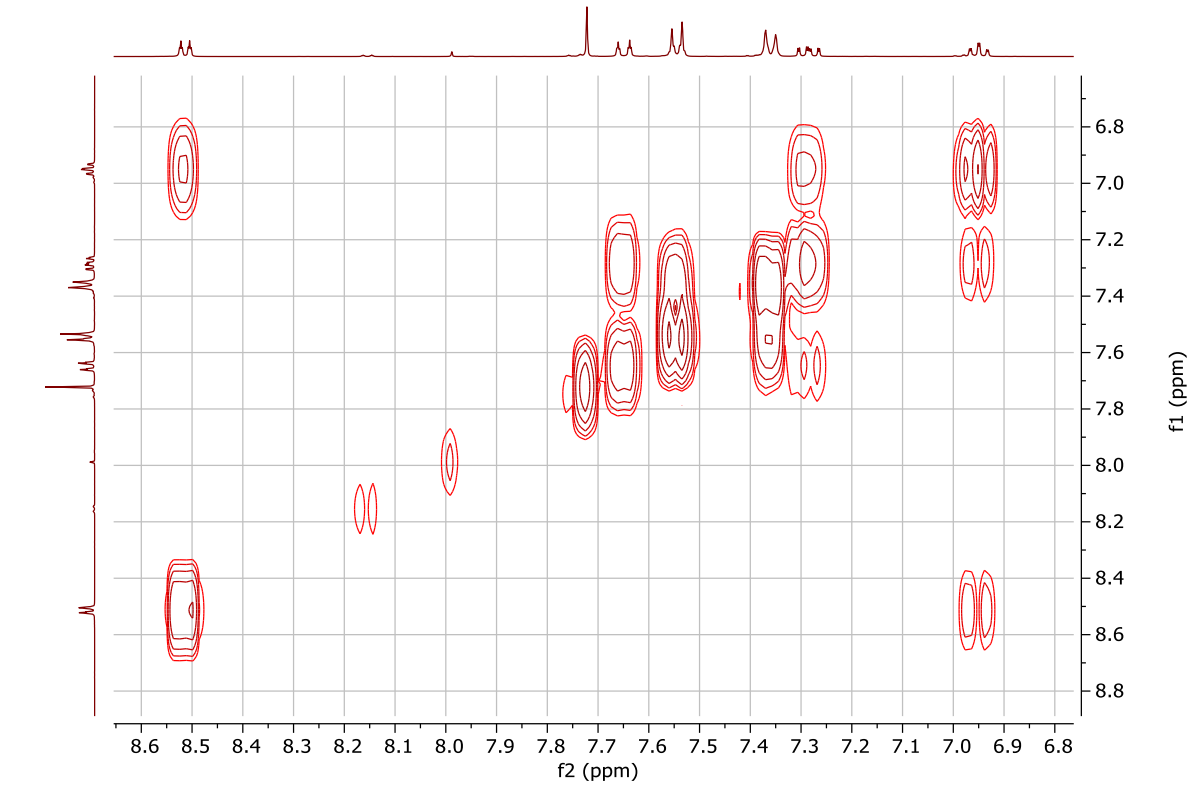


^{13}C NMR Spectrum of (**2**) (400 MHz, DMSO-d^{6}):

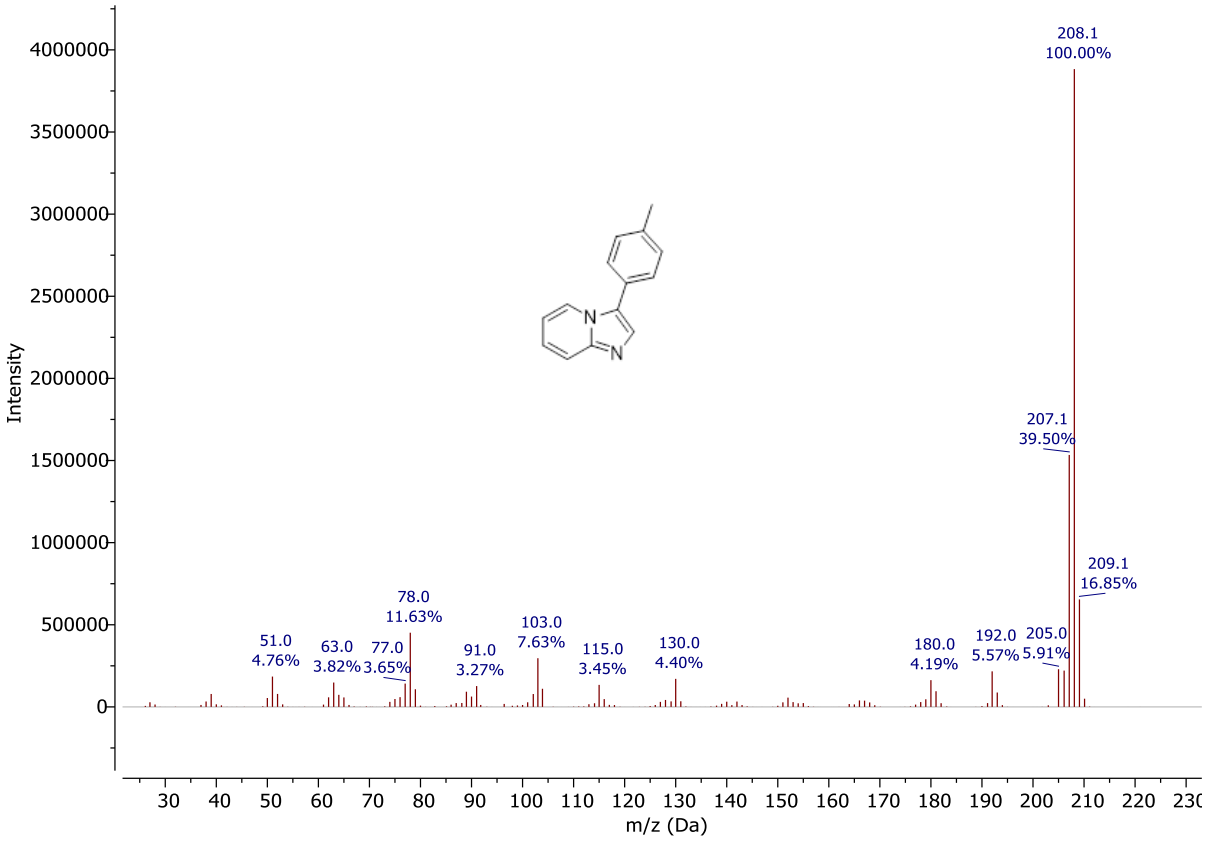


^{1}H/^{1}H COSY NMR Spectrum of (**2**) (400 MHz, DMSO-d^{6}):

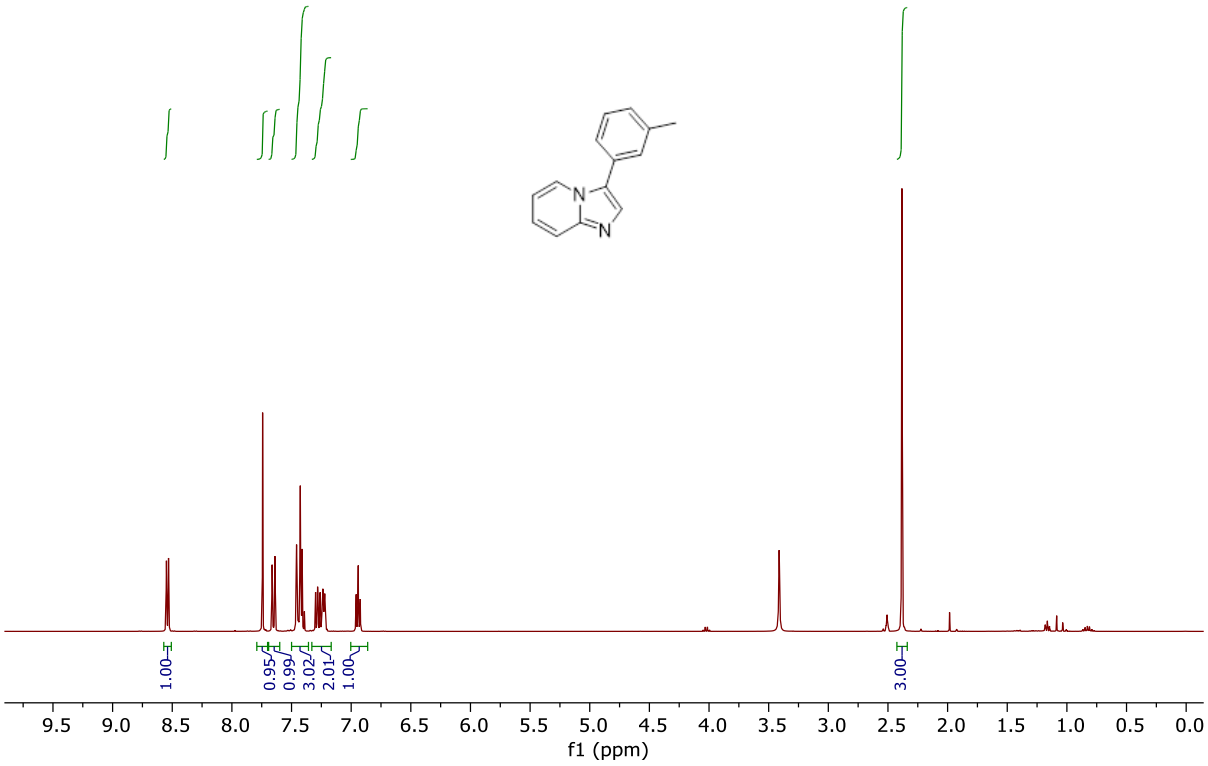


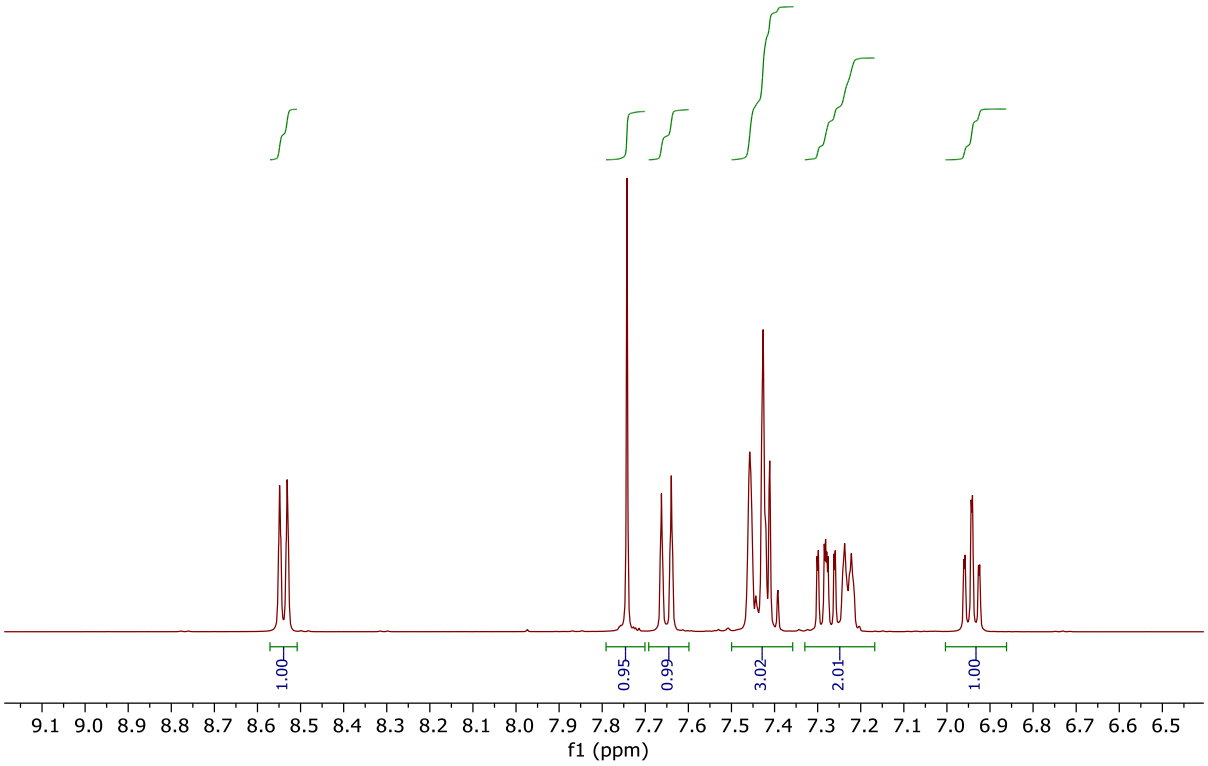


MS Spectrum of (**2**) (EI):

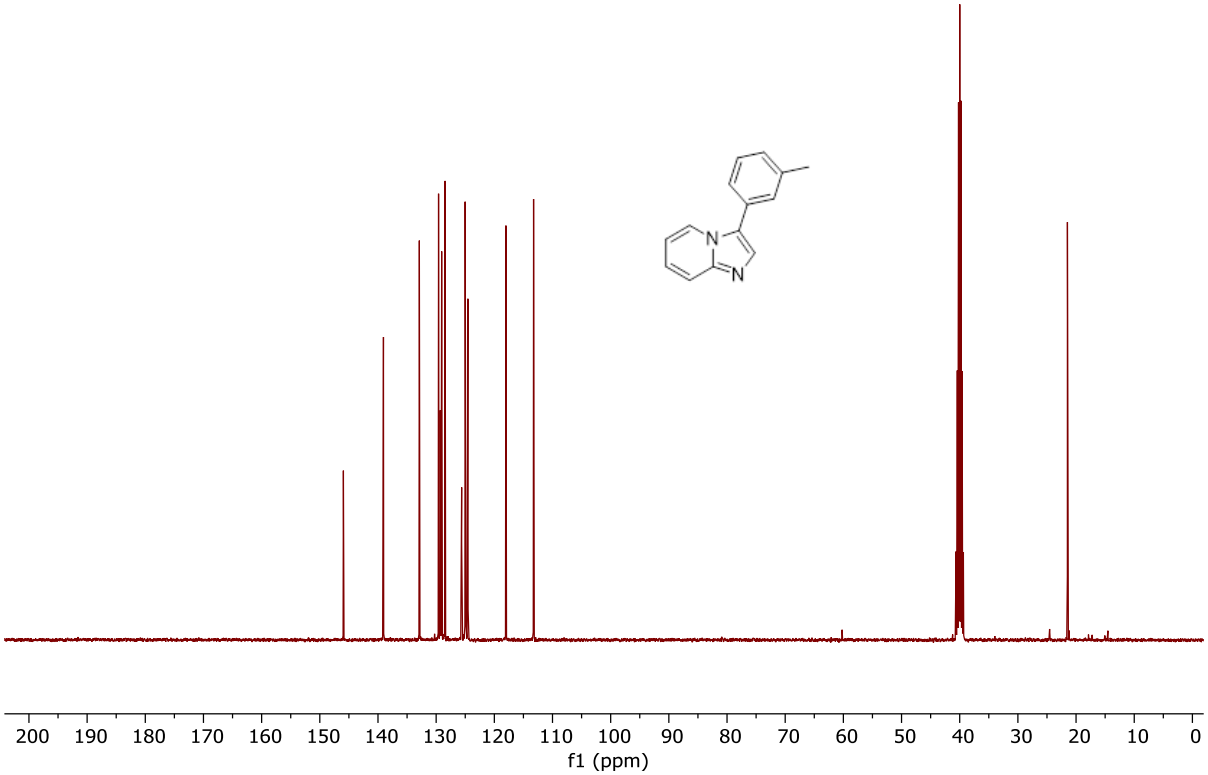


^{1}H NMR Spectrum of (**3**) (400 MHz, DMSO-d^{6}):

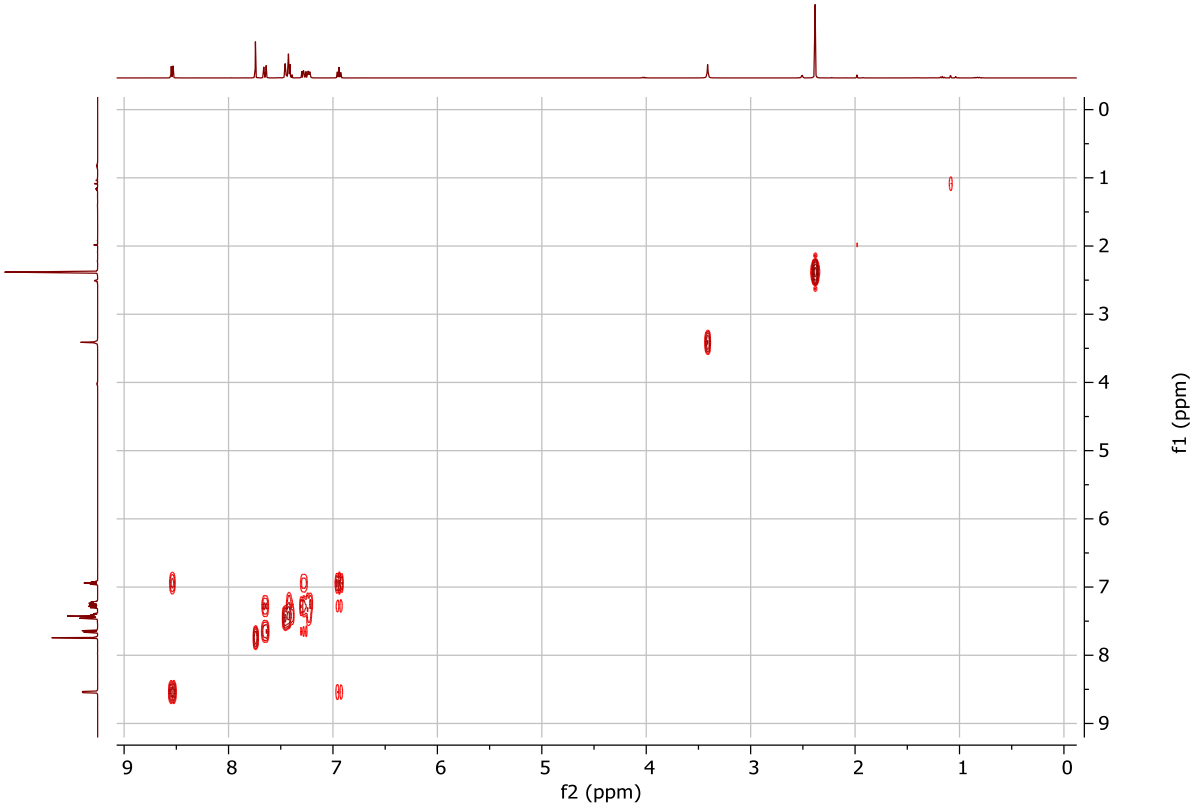




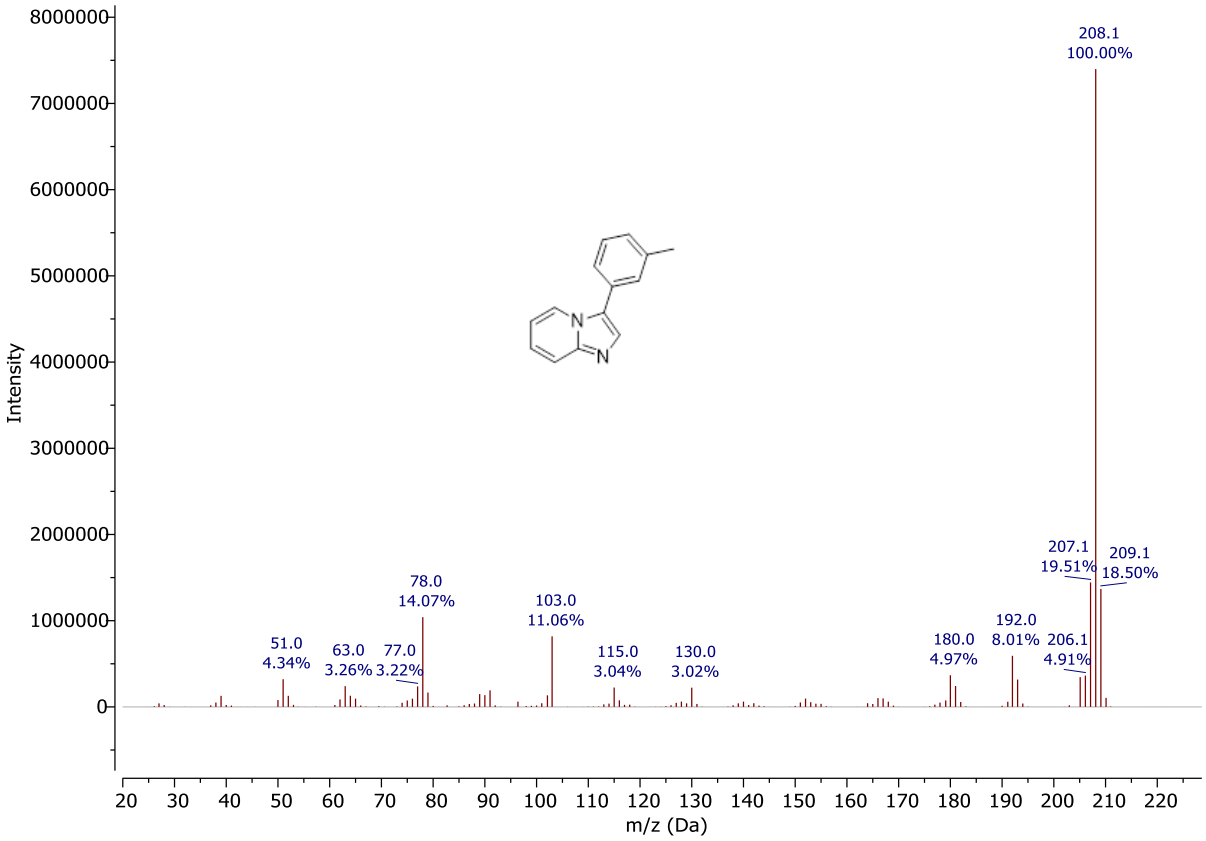
^{13}C NMR Spectrum of (**3**) (400 MHz, DMSO-d^{6}):



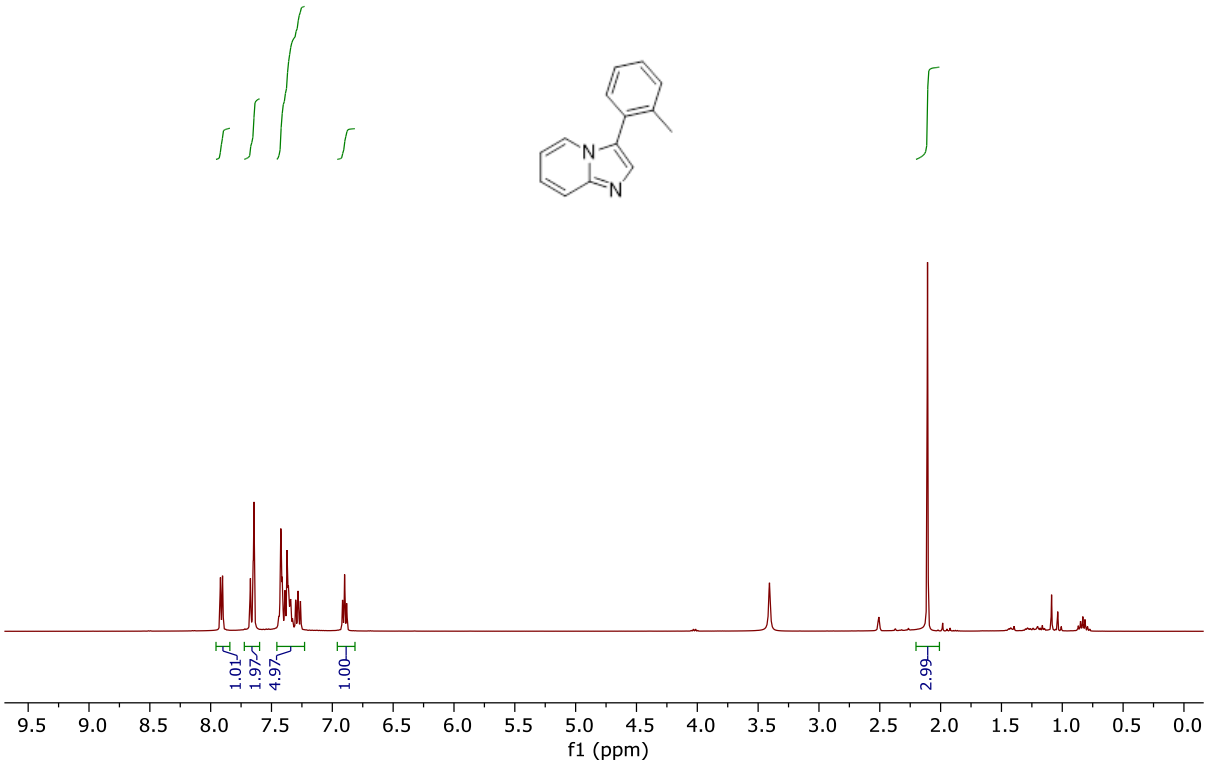
^{1}H/^{1}H COSY NMR Spectrum of (**3**) (400 MHz, DMSO-d^{6}):

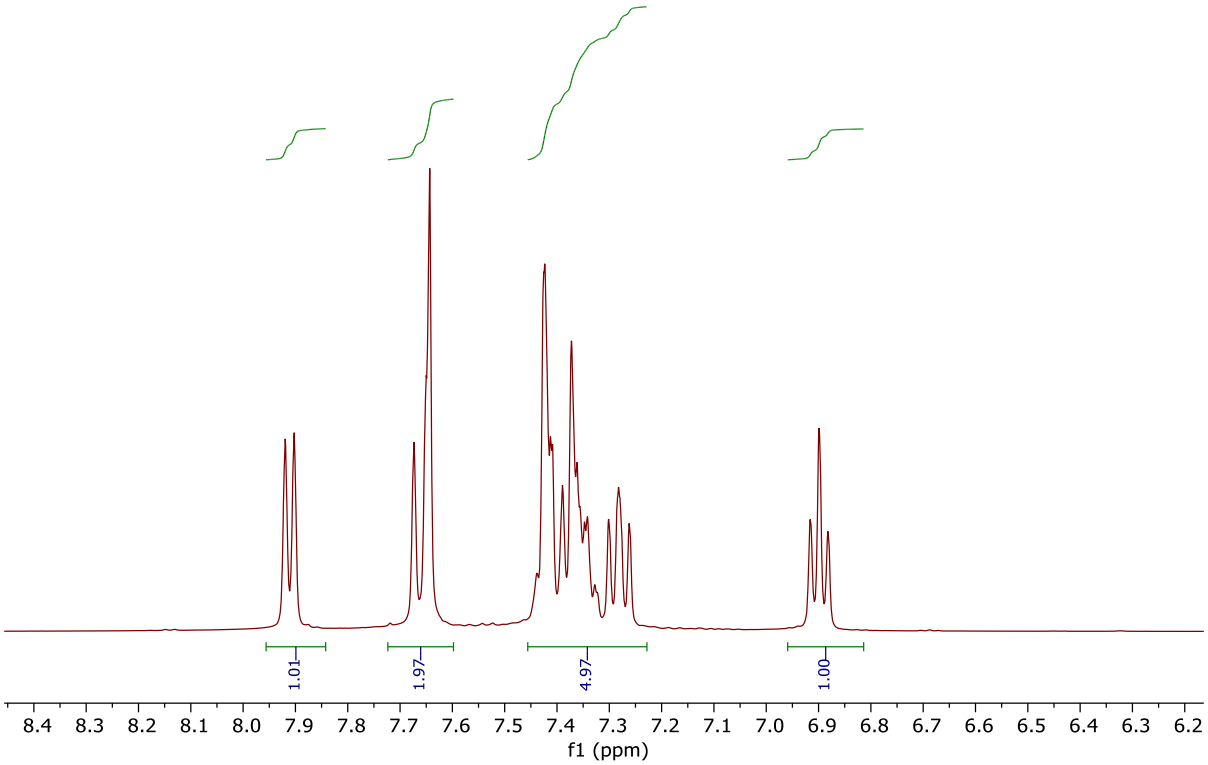


MS Spectrum of (**3**) (EI):

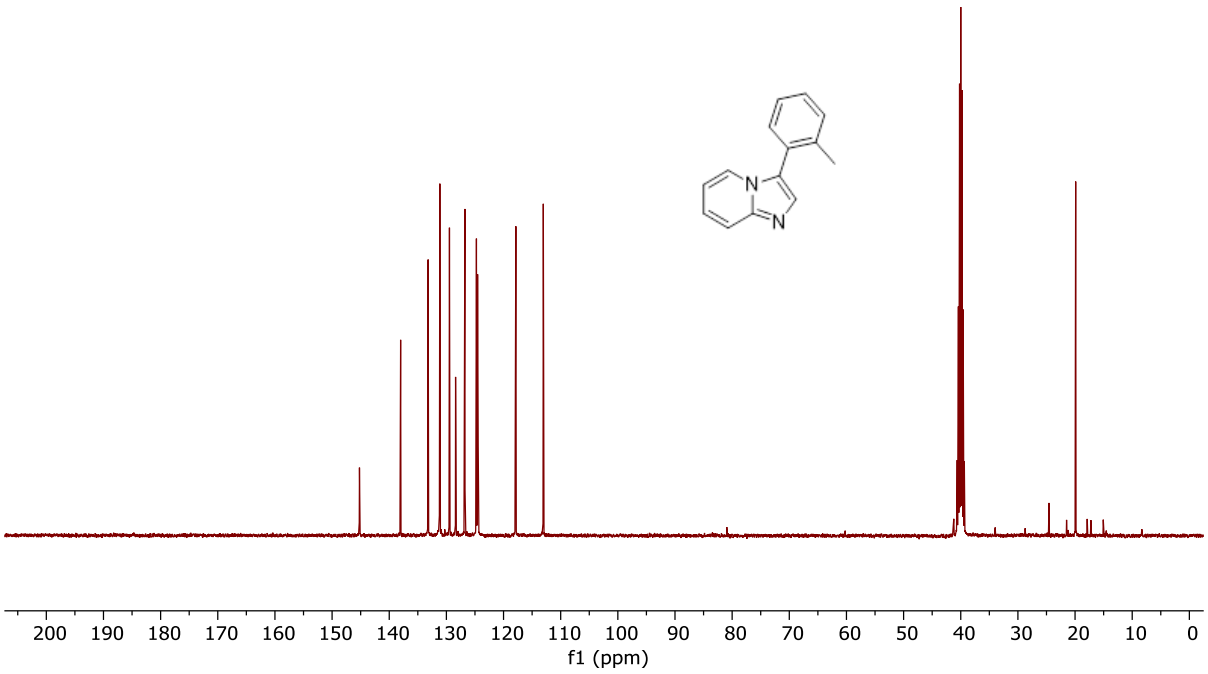


^{1}H NMR Spectrum of (**4**) (400 MHz, DMSO-d^{6}):

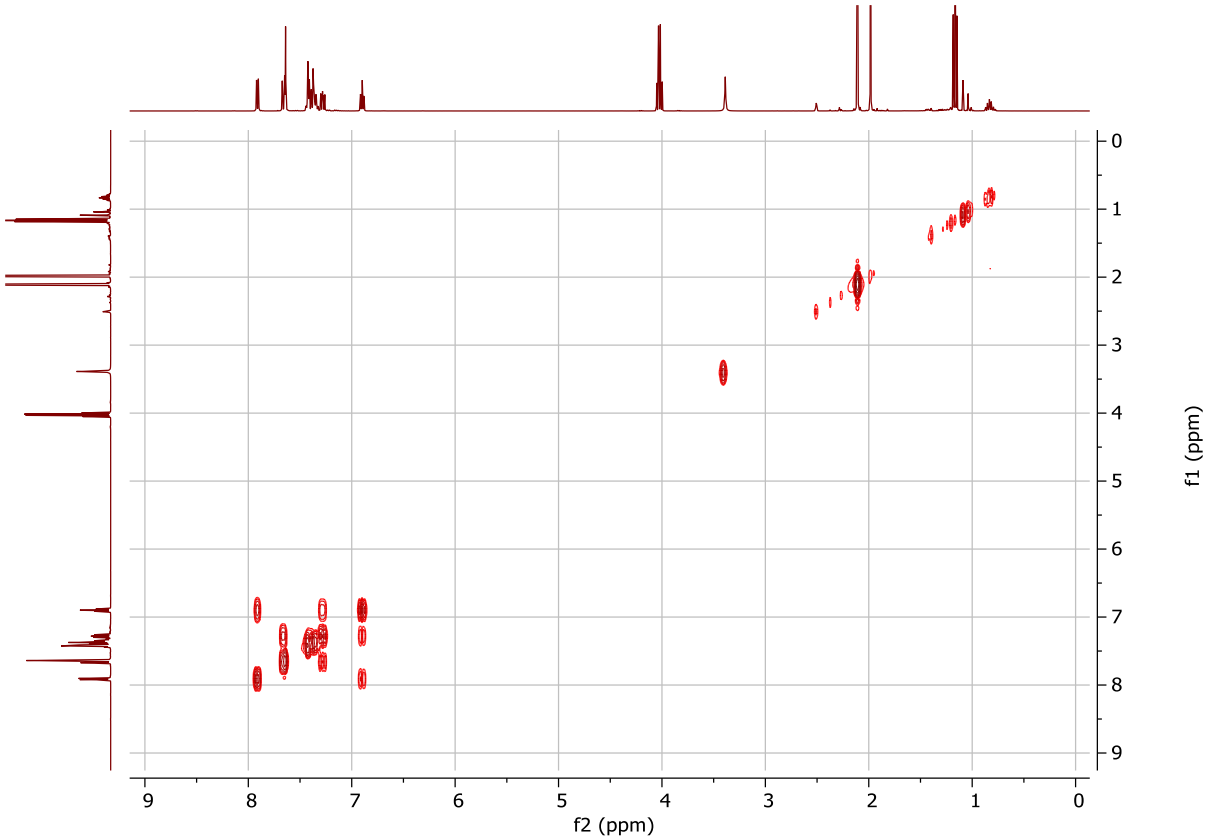




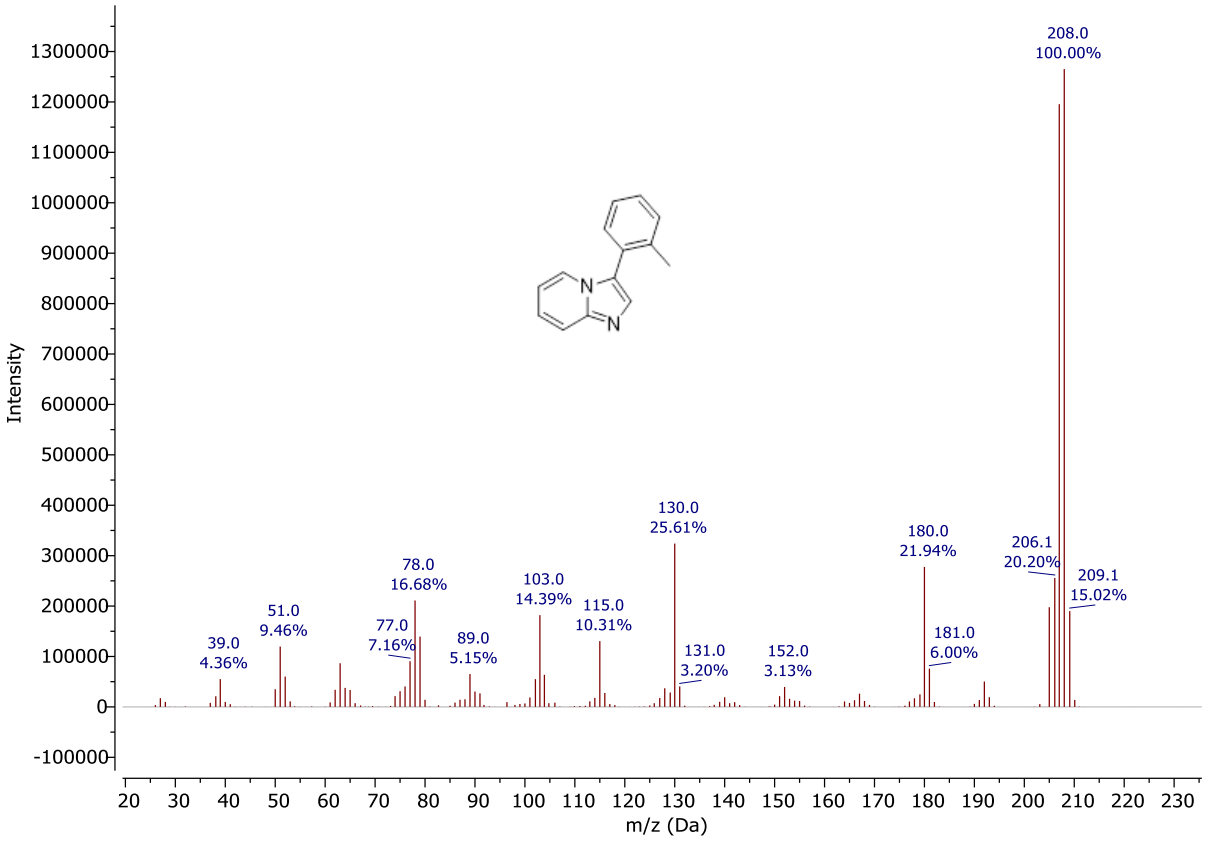
^{13}C NMR Spectrum of (**4**) (400 MHz, DMSO-d^{6}):



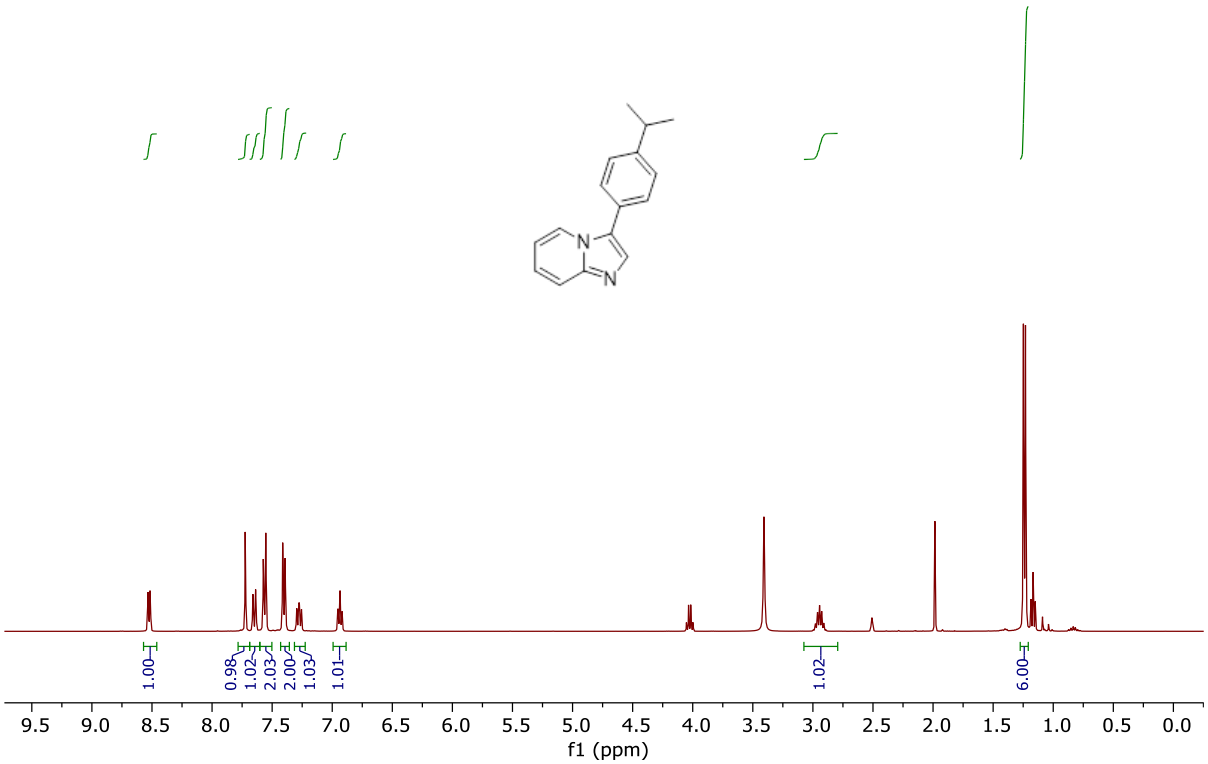
^{1}H/^{1}H COSY NMR Spectrum of (**4**) (400 MHz, DMSO-d^{6}):

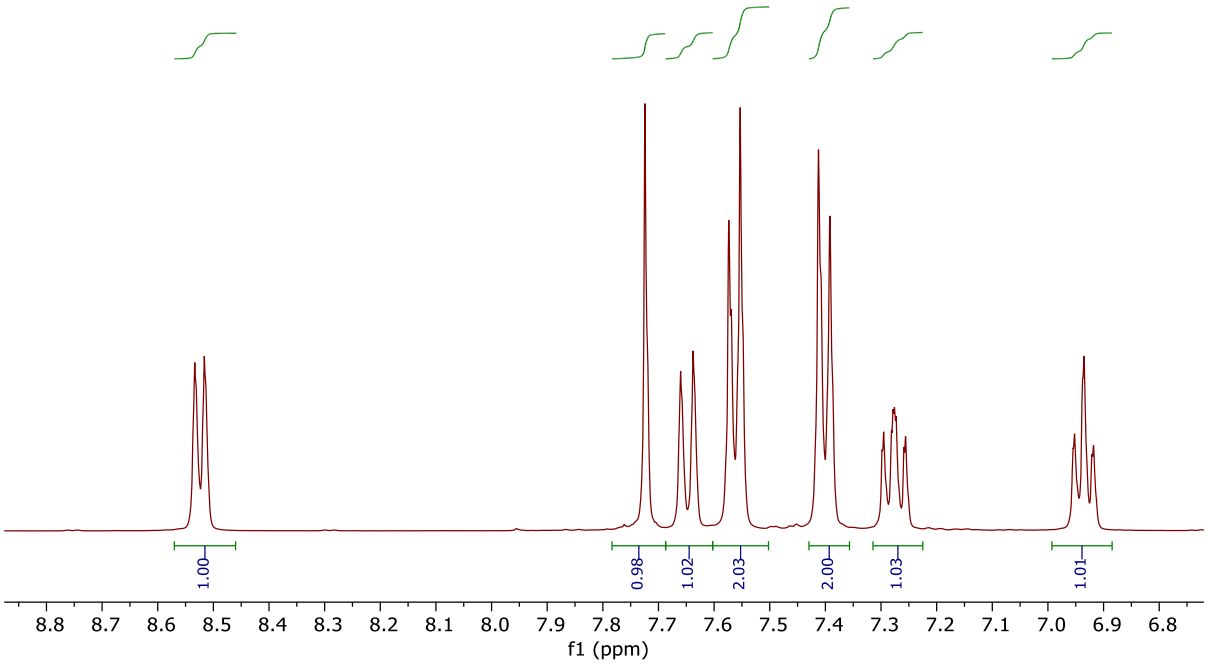


MS Spectrum of (**4**) (EI):

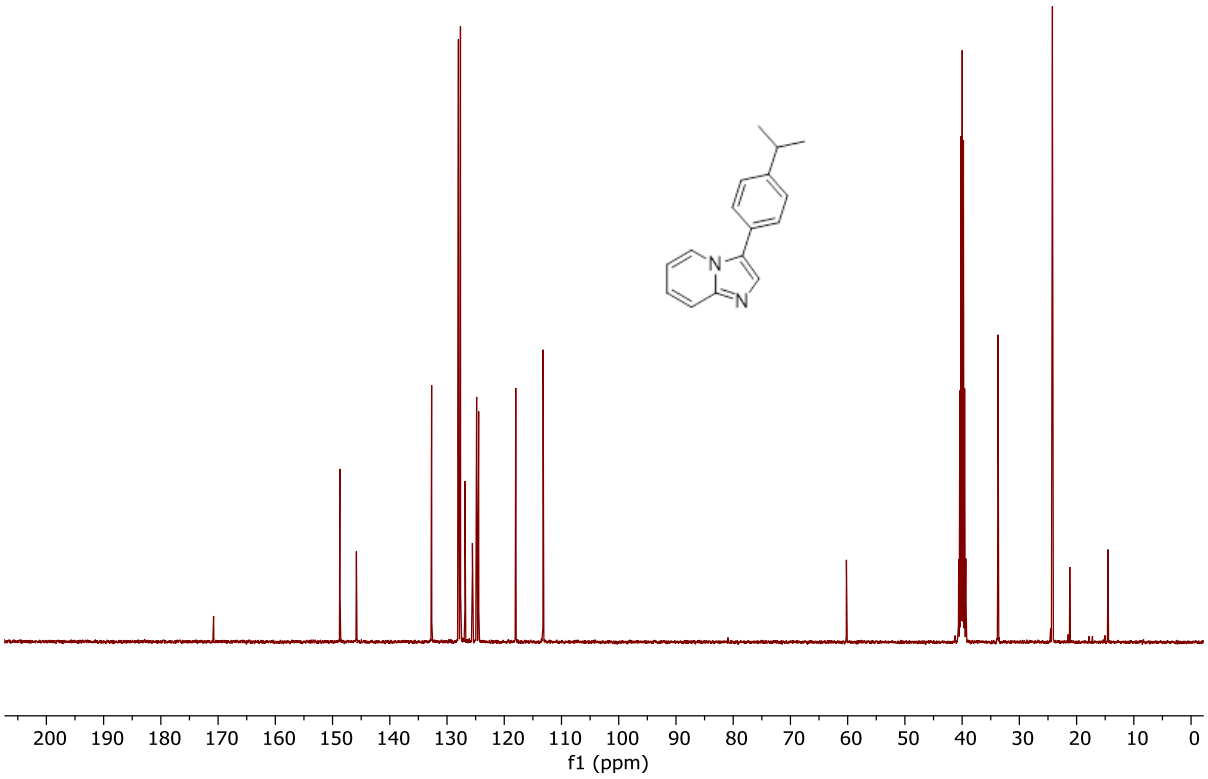


^{1}H NMR Spectrum of (**5**) (400 MHz, DMSO-d^{6}):

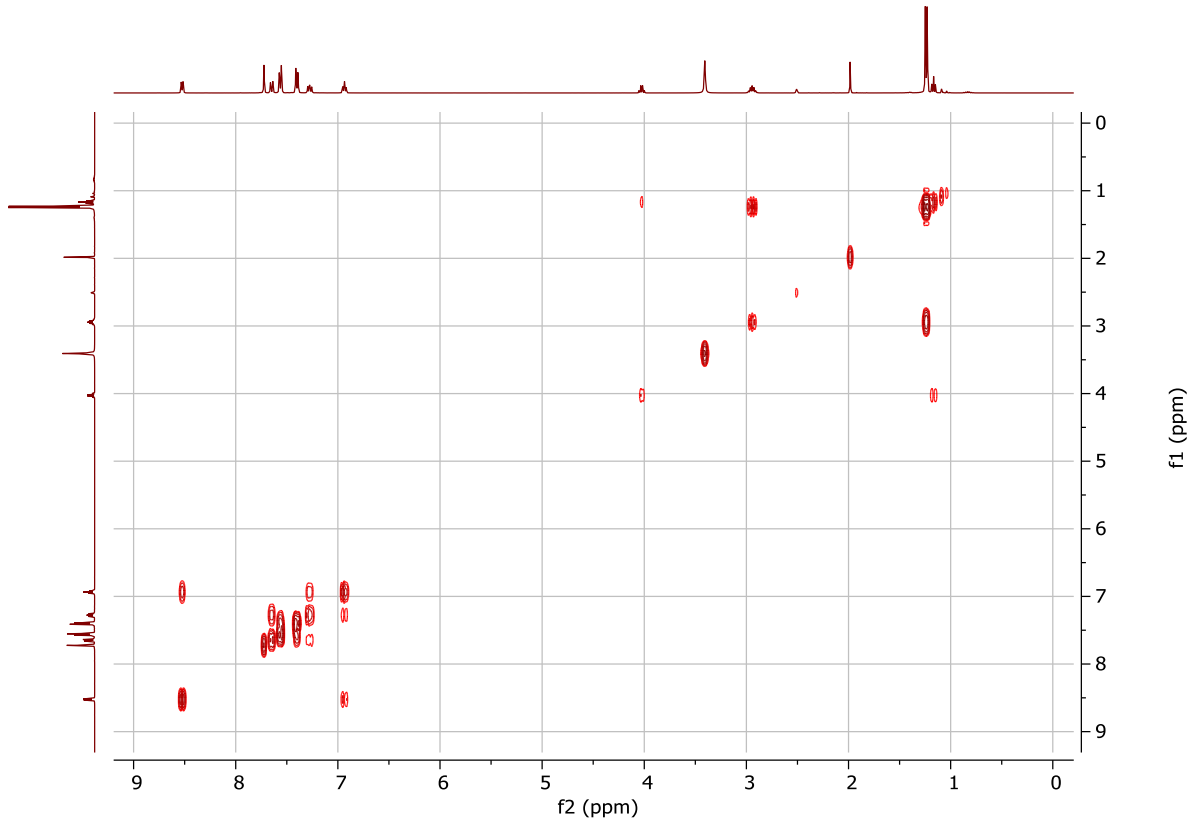




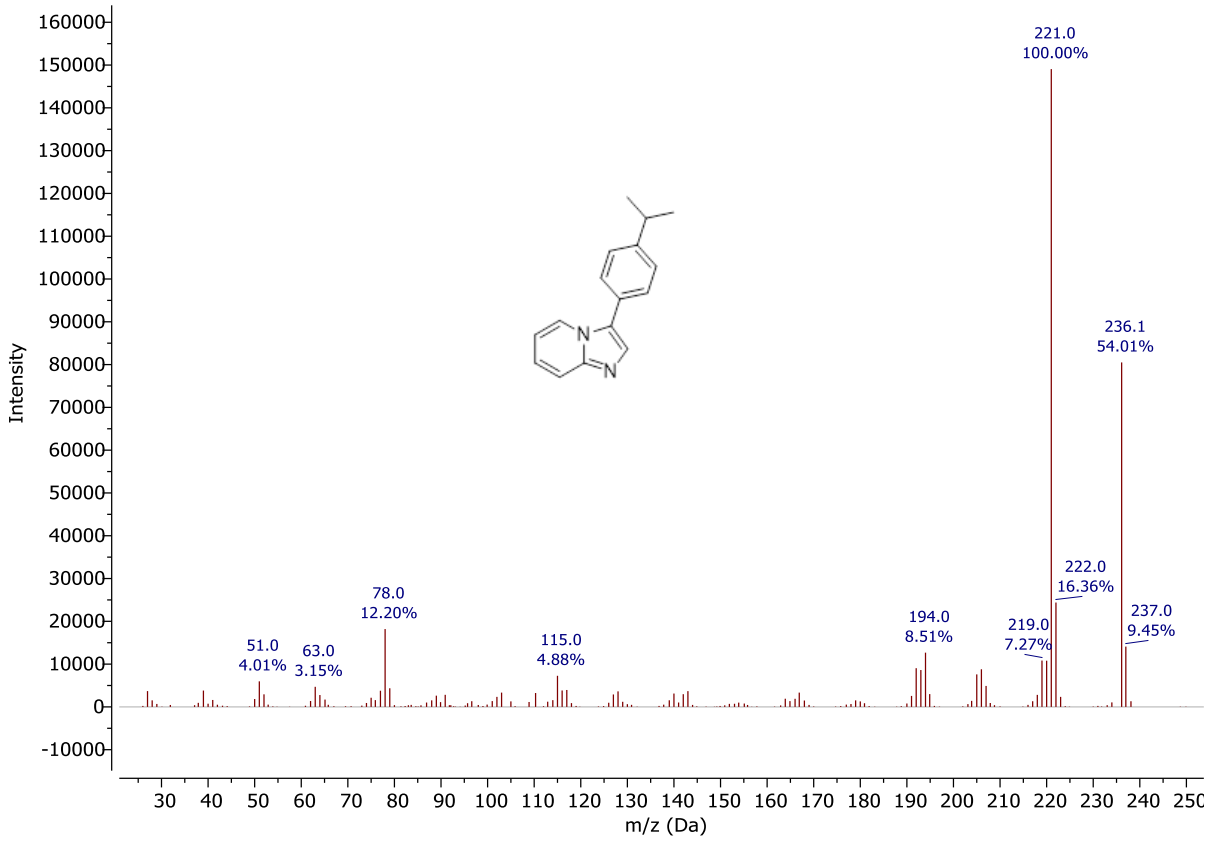
^{13}C NMR Spectrum of (**5**) (400 MHz, DMSO-d^{6}):



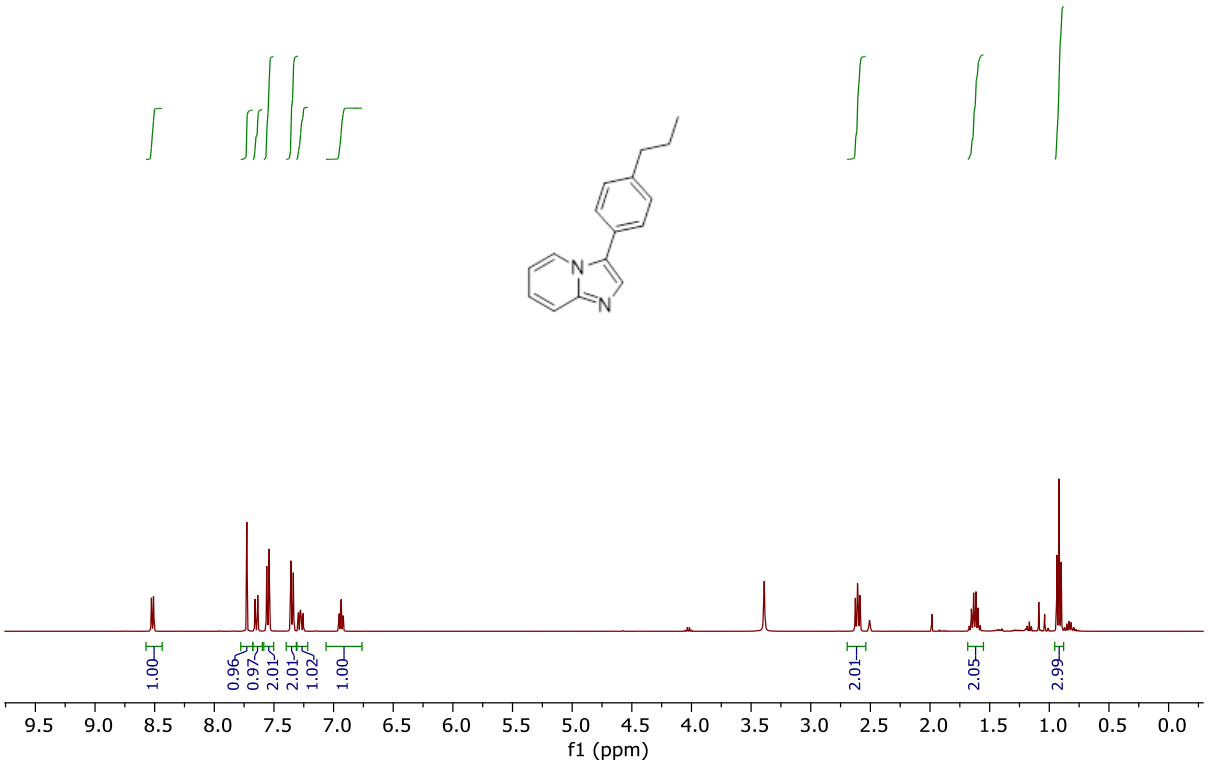
^{1}H/^{1}H COSY NMR Spectrum of (**5**) (400 MHz, DMSO-d^{6}):

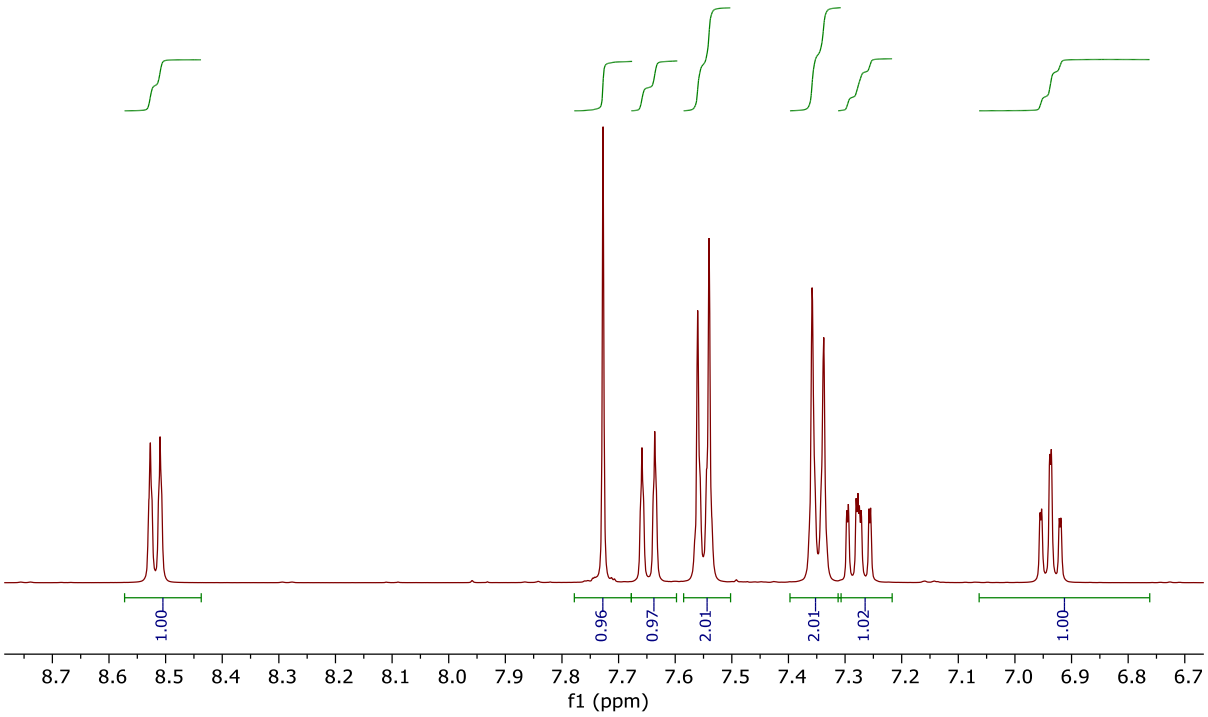


MS Spectrum of (**5**) (EI):

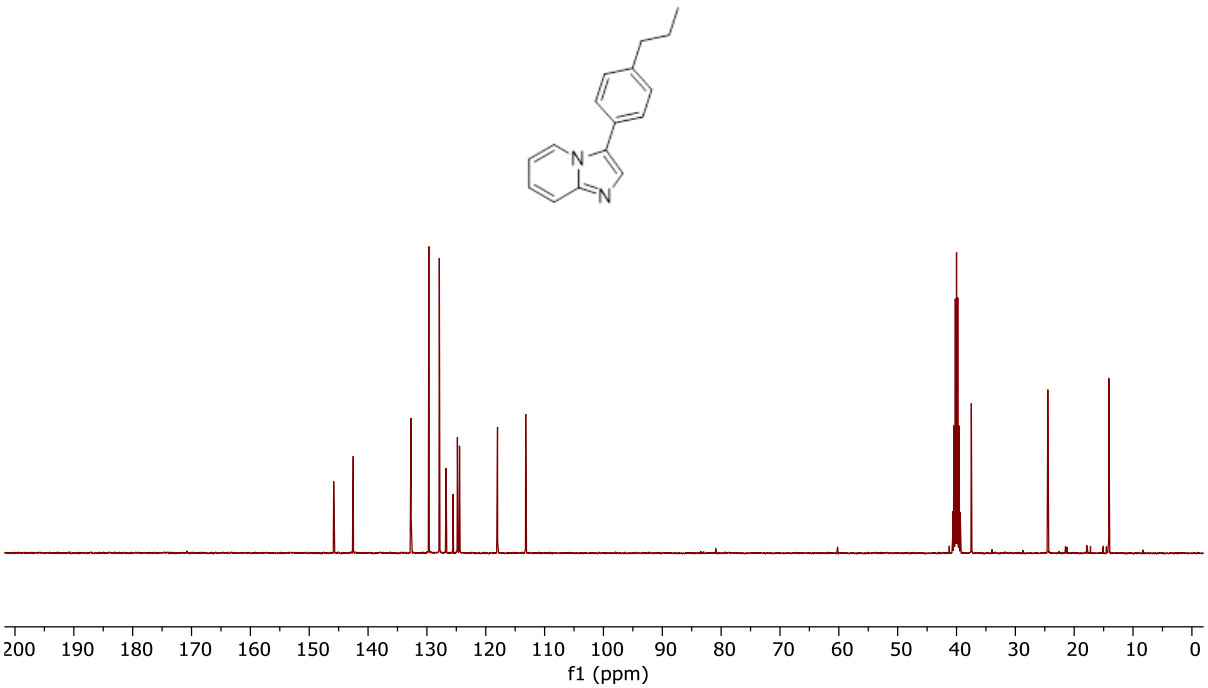


^{1}H NMR Spectrum of (**6**) (400 MHz, DMSO-d^{6}):

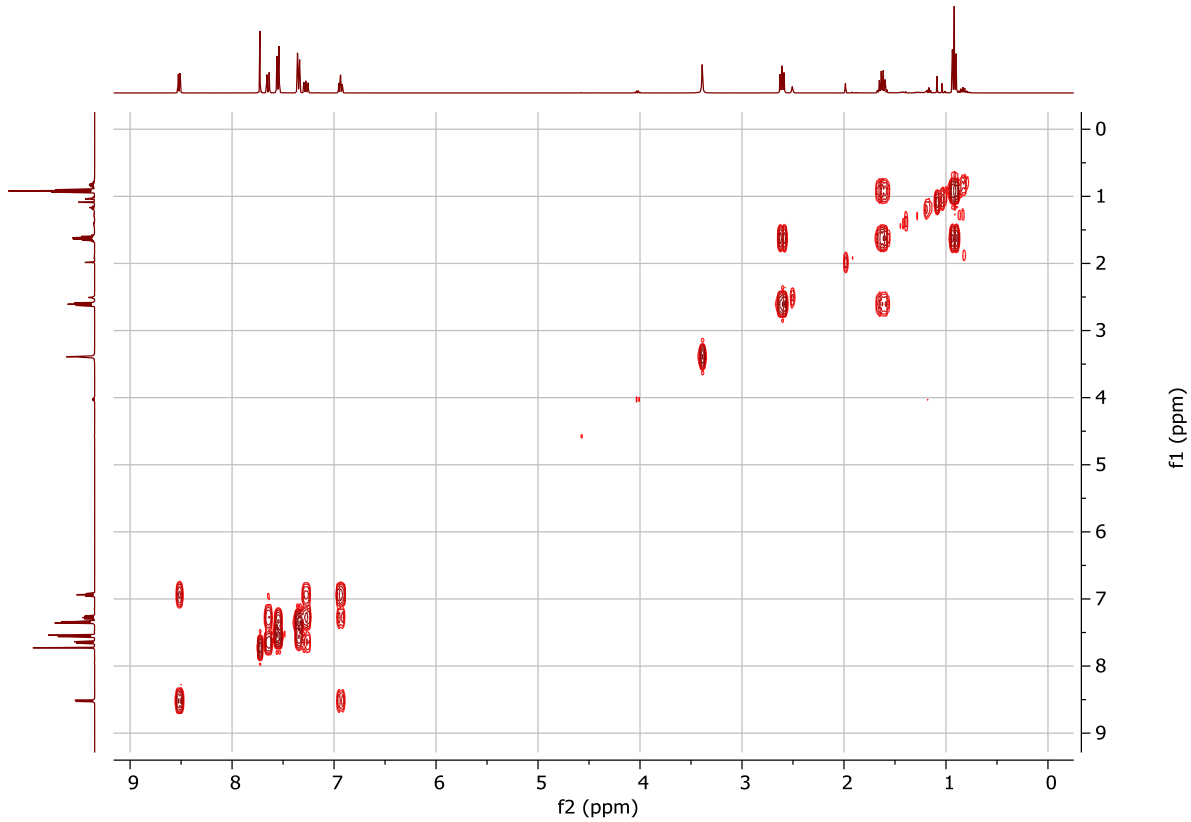




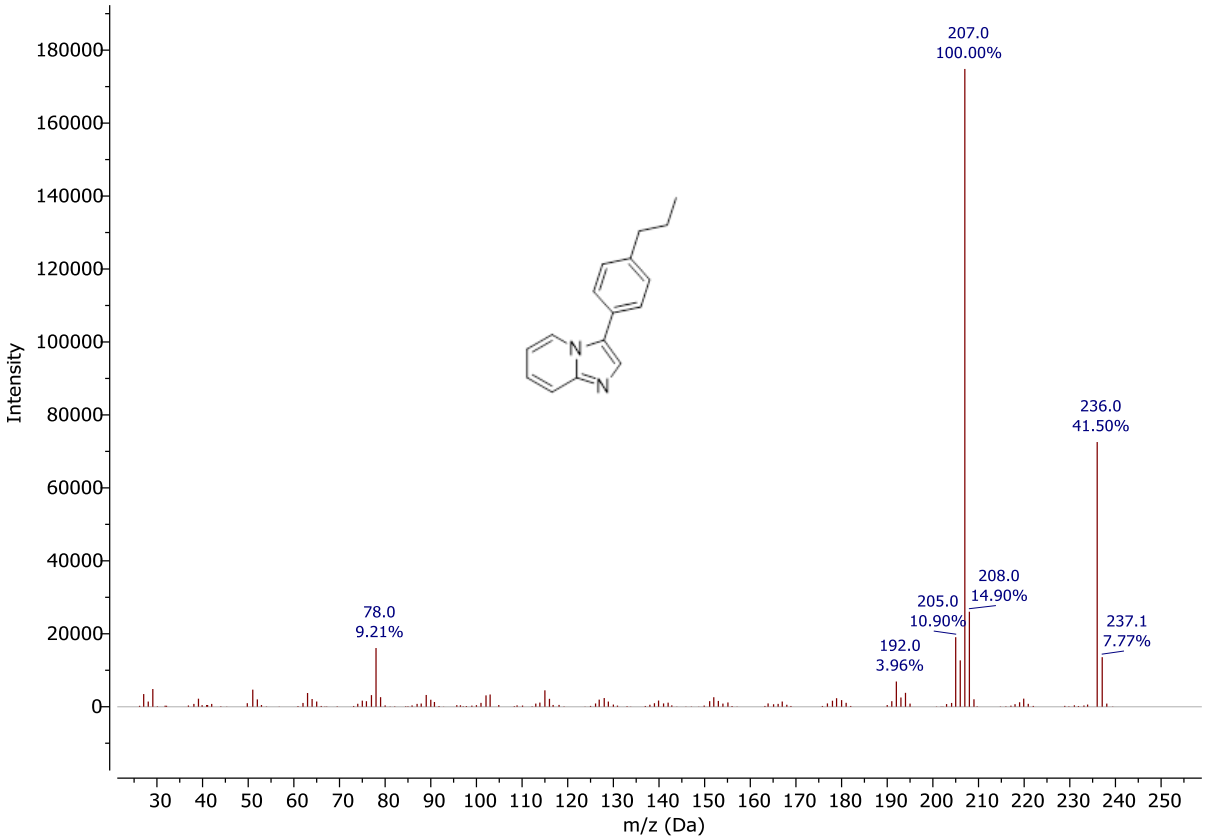
^{13}C NMR Spectrum of (**6**) (400 MHz, DMSO-d^{6}):



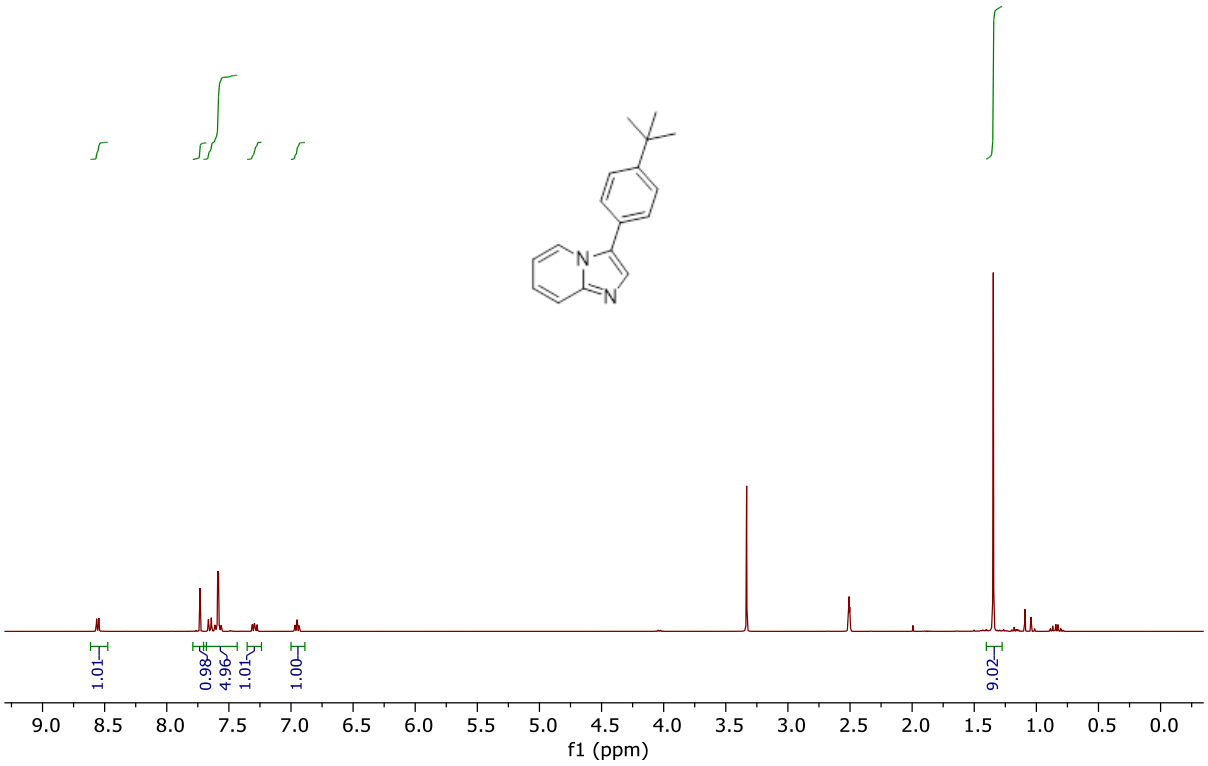
^{1}H/^{1}H COSY NMR Spectrum of (**6**) (400 MHz, DMSO-d^{6}):

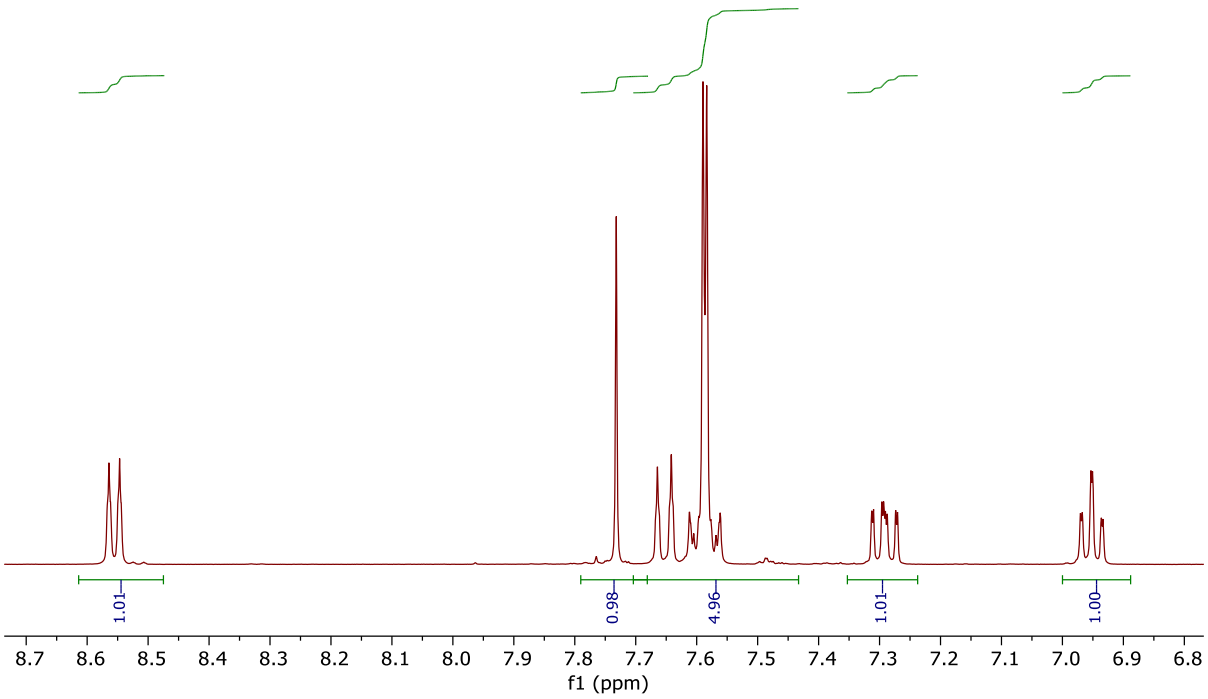


MS Spectrum of (**6**) (EI):

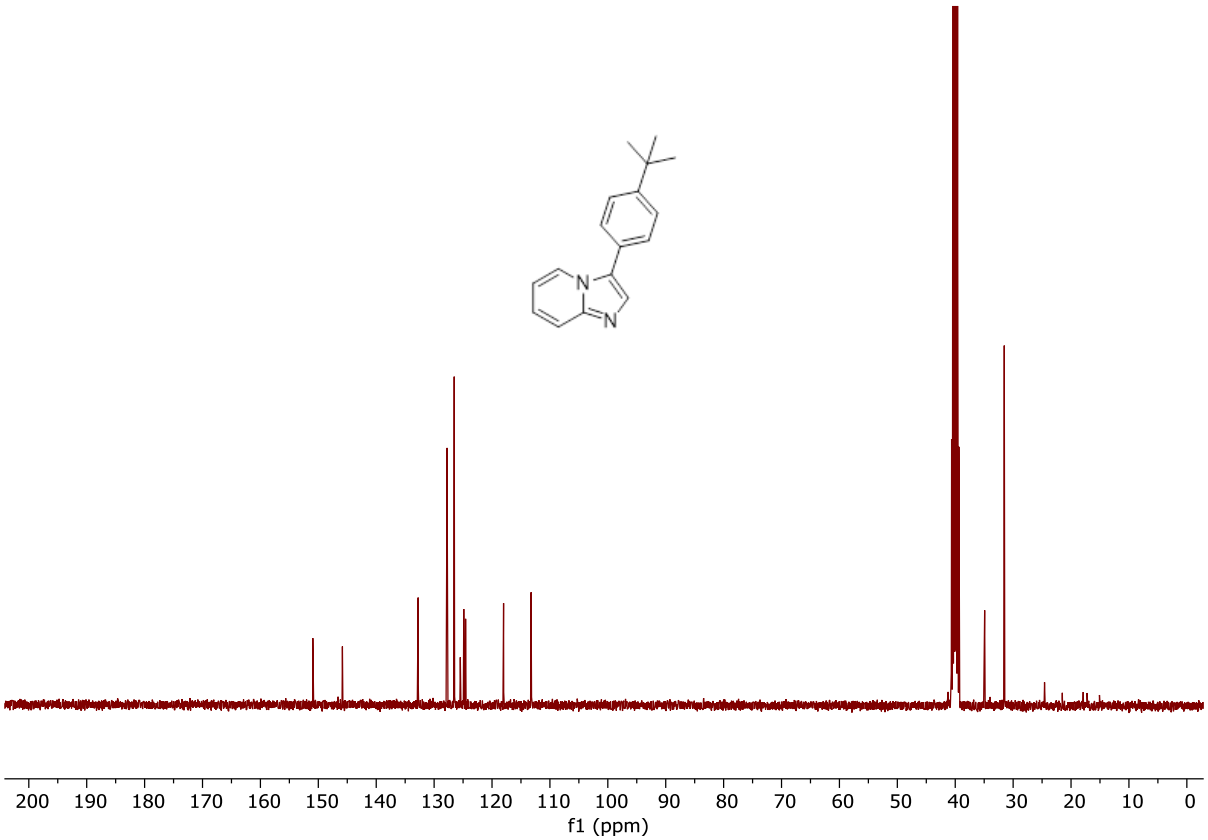


^{1}H NMR Spectrum of (**7**) (400 MHz, DMSO-d^{6}):

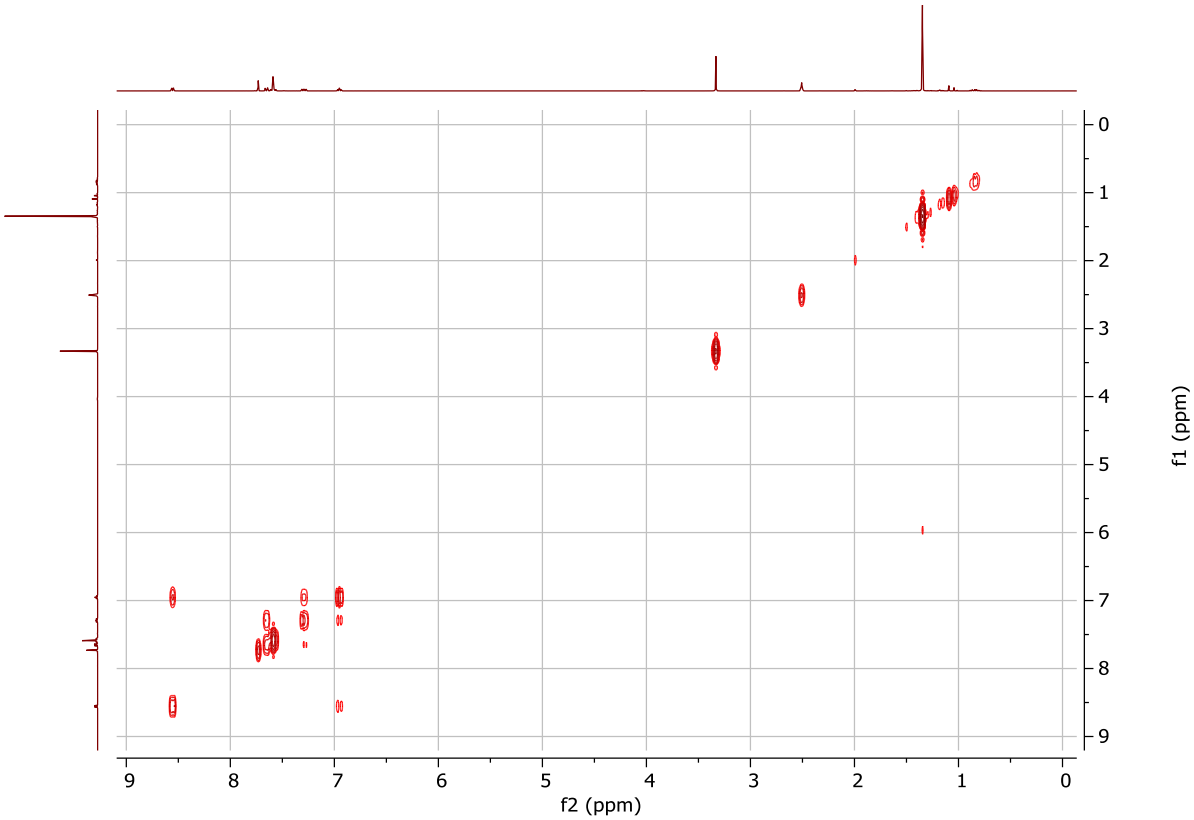




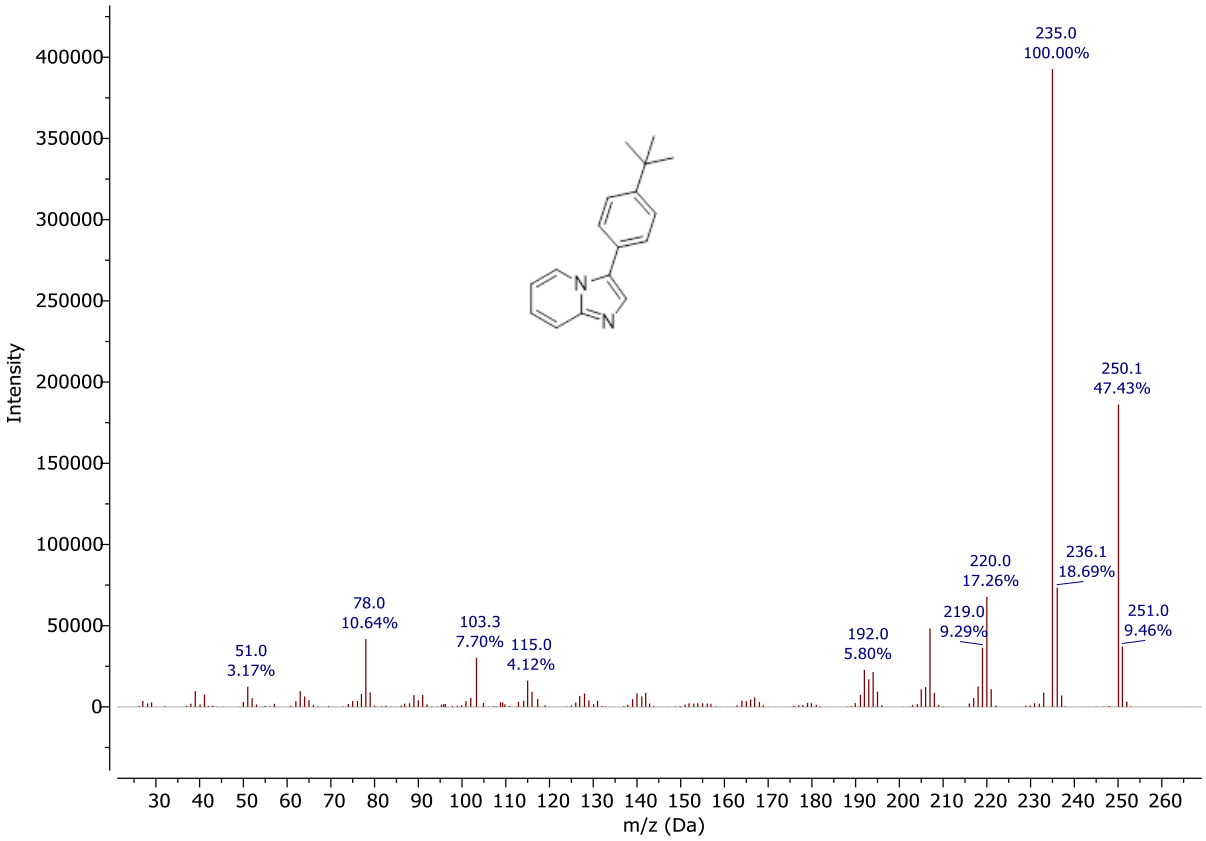
^{13}C NMR Spectrum of (**7**) (400 MHz, DMSO-d^{6}):



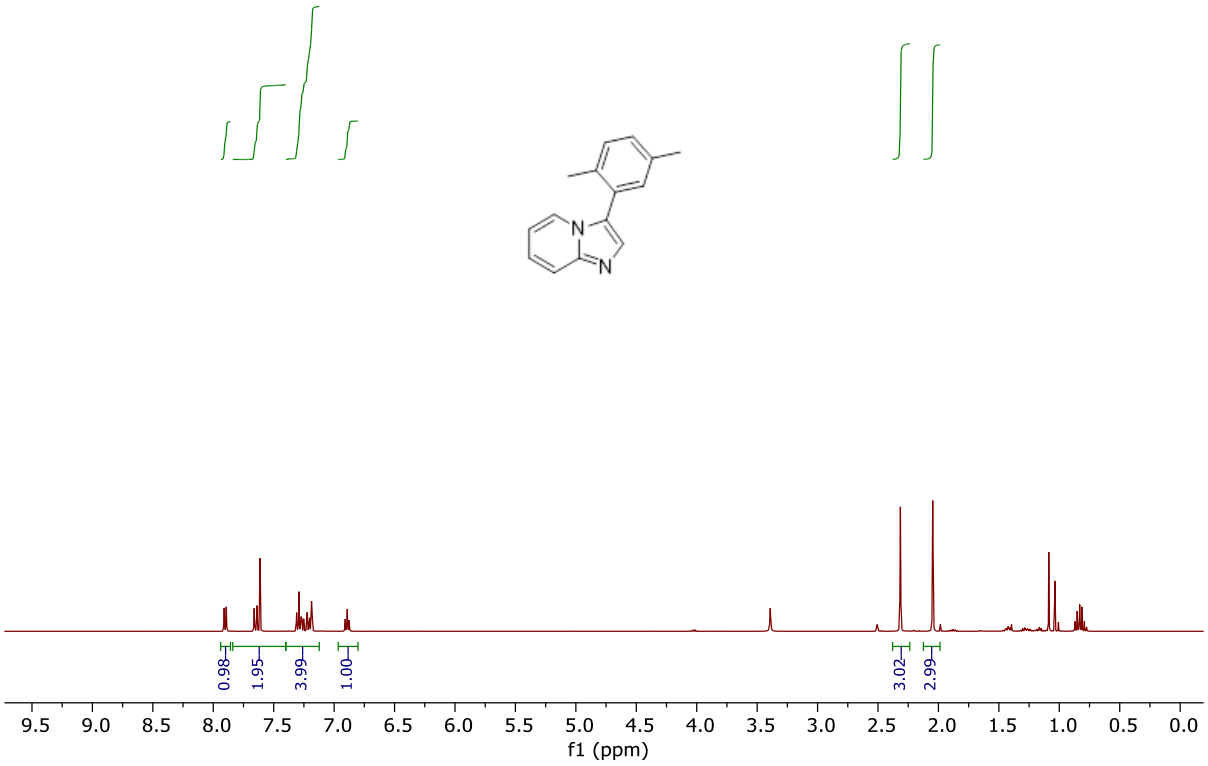
^{1}H/^{1}H COSY NMR Spectrum of (**7**) (400 MHz, DMSO-d^{6}):

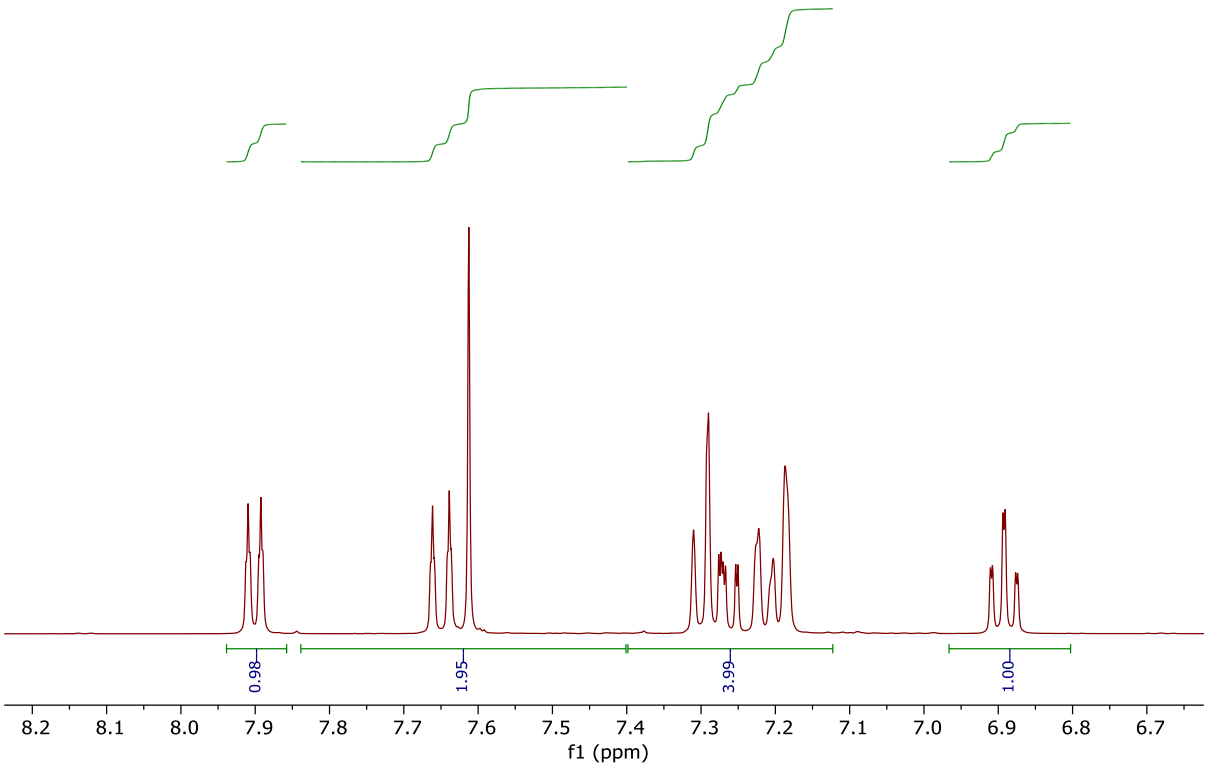


MS Spectrum of (**7**) (EI):

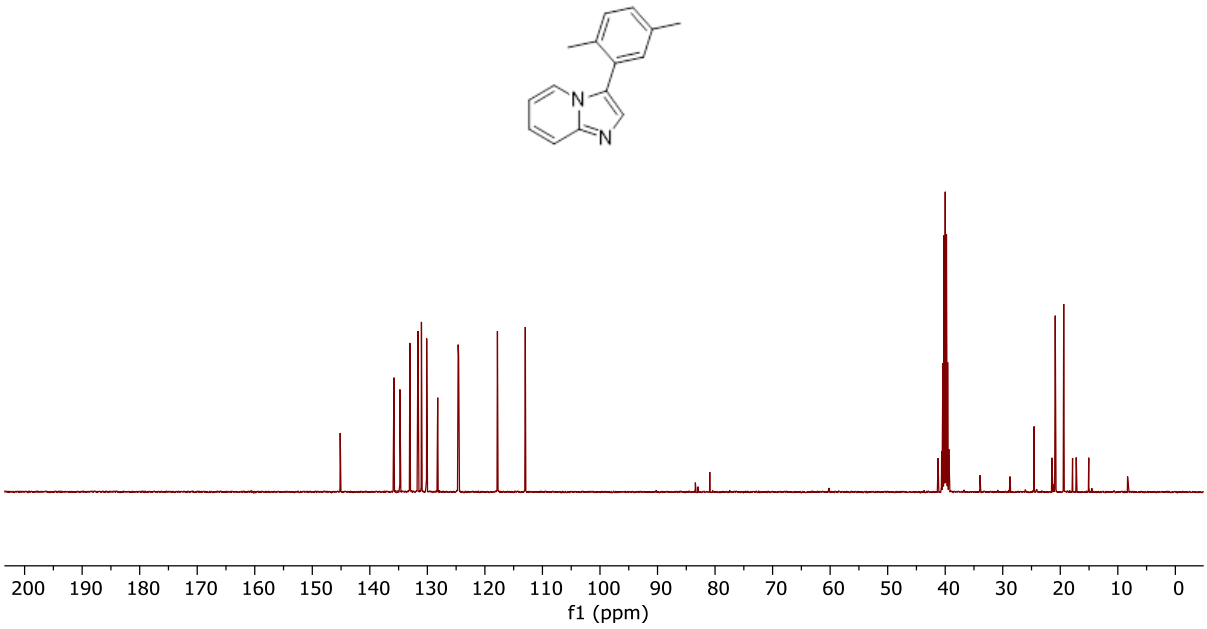


^{1}H NMR Spectrum of (**8**) (400 MHz, DMSO-d^{6}):

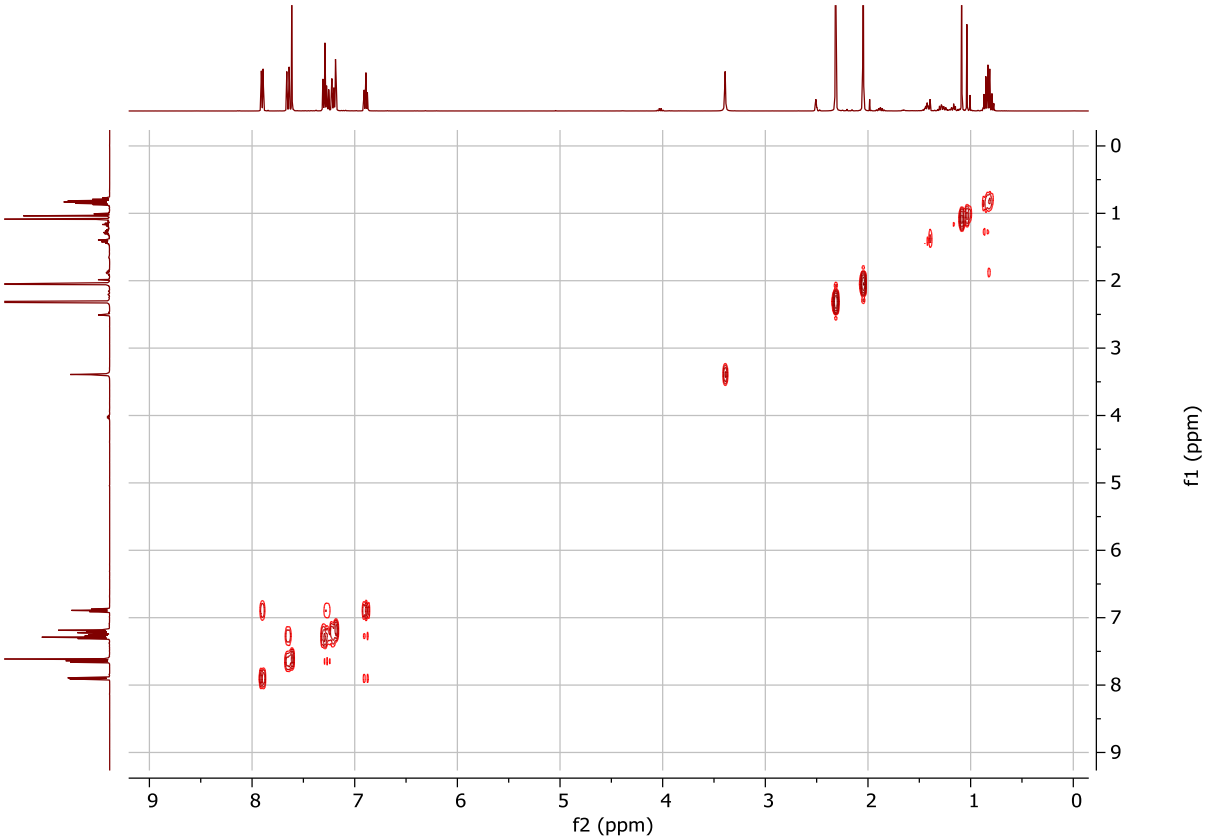




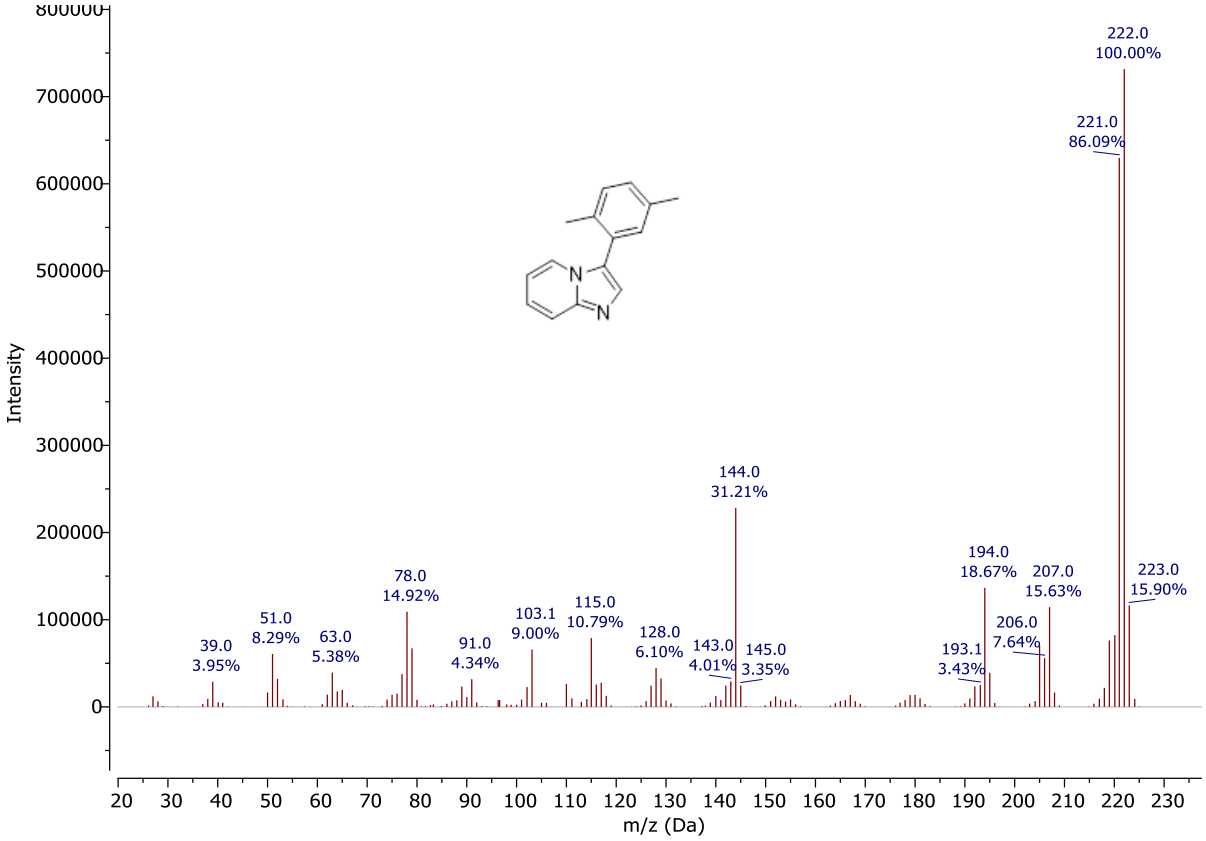
^{13}C NMR Spectrum of (**8**) (400 MHz, DMSO-d^{6}):



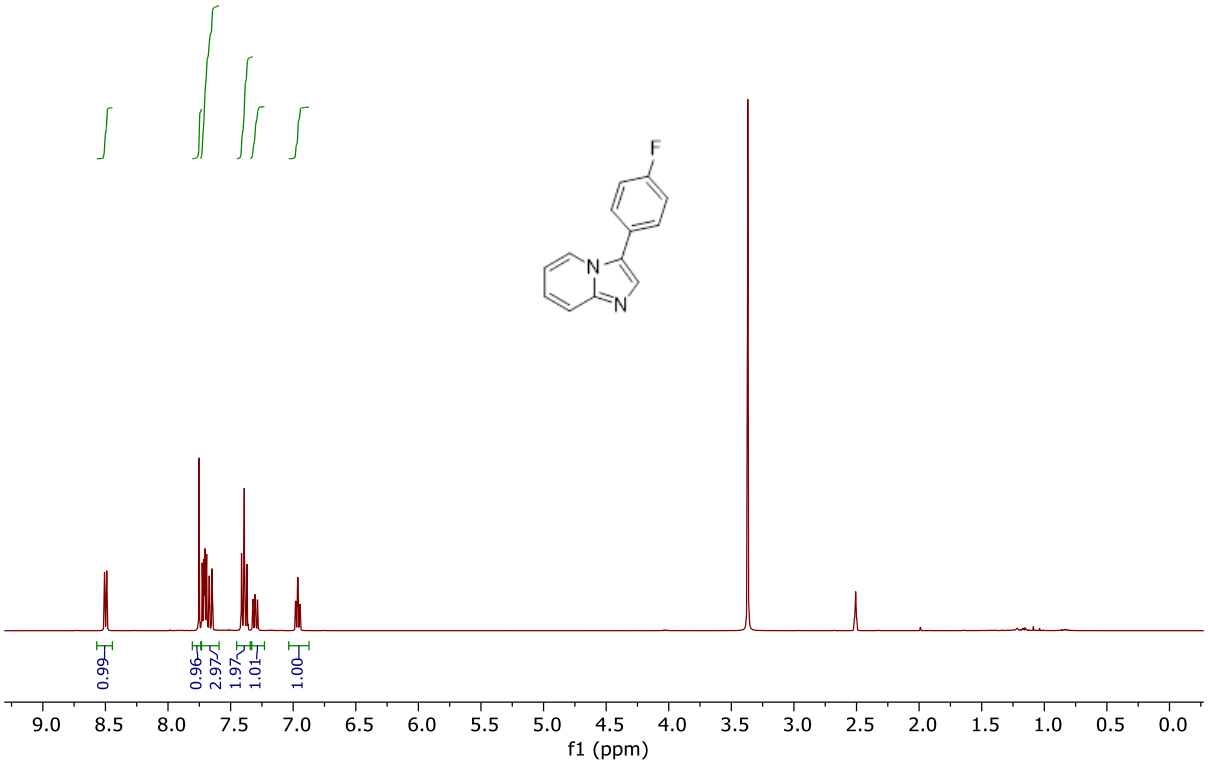
^{1}H/^{1}H COSY NMR Spectrum of (**8**) (400 MHz, DMSO-d^{6}):

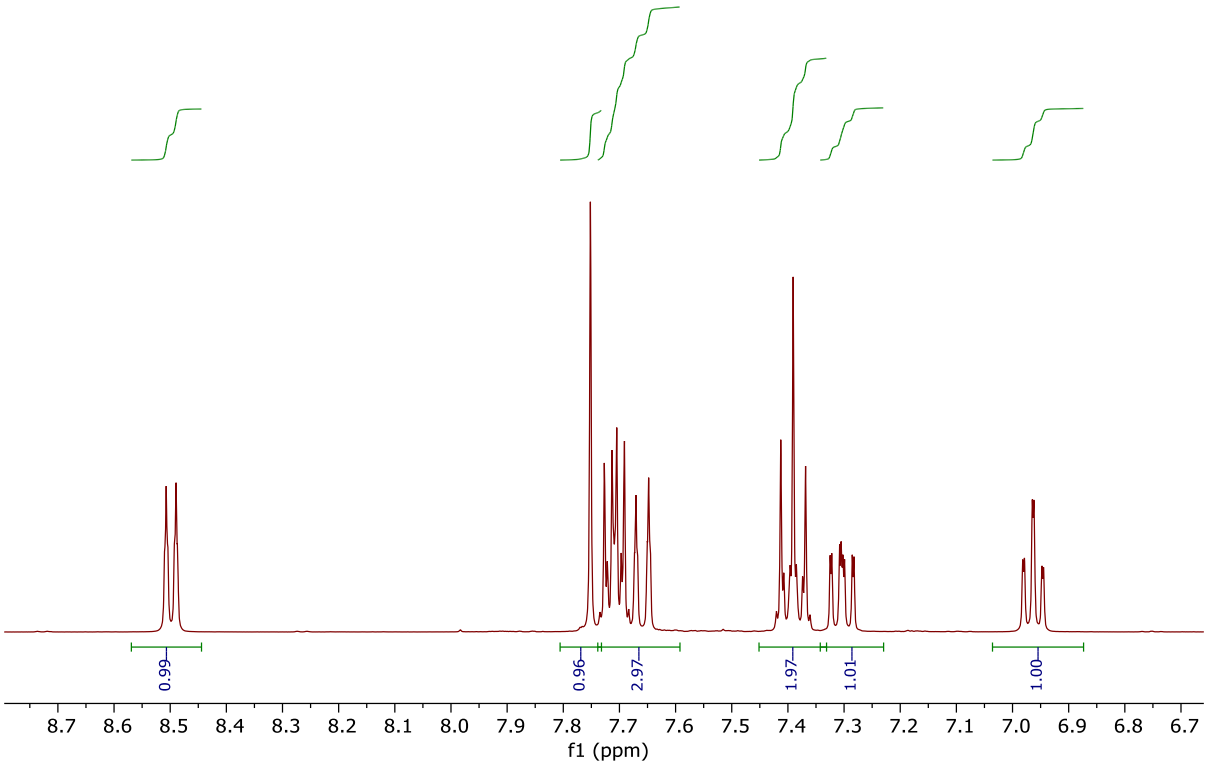


MS Spectrum of (**8**) (EI):

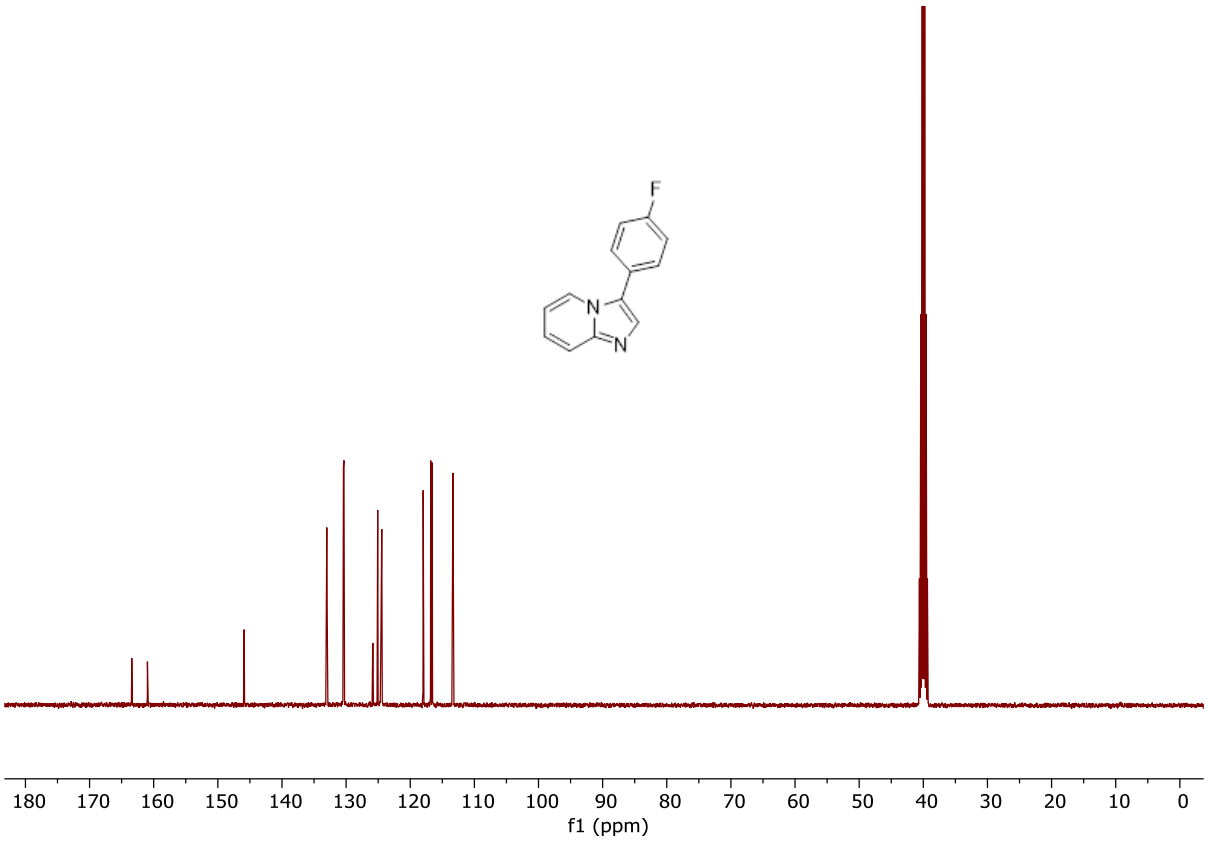


^{1}H NMR Spectrum of (**9**) (400 MHz, DMSO-d^{6}):

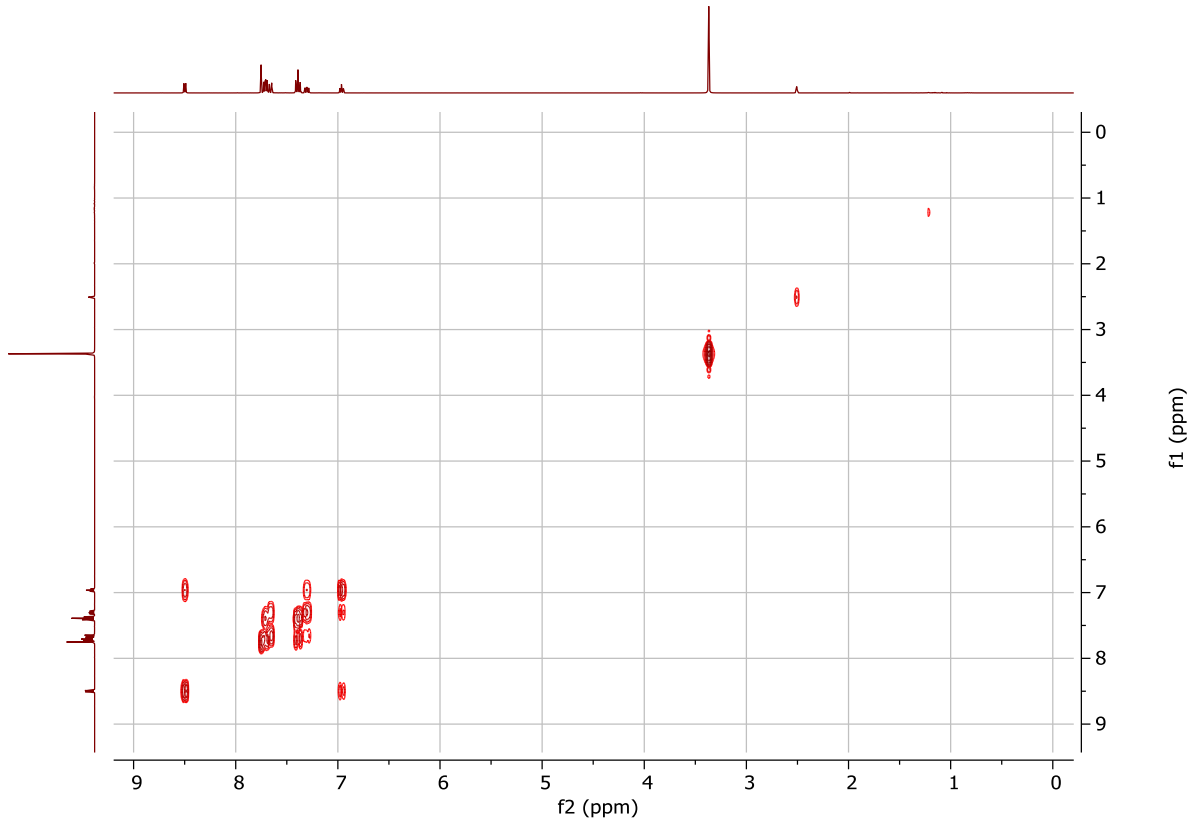




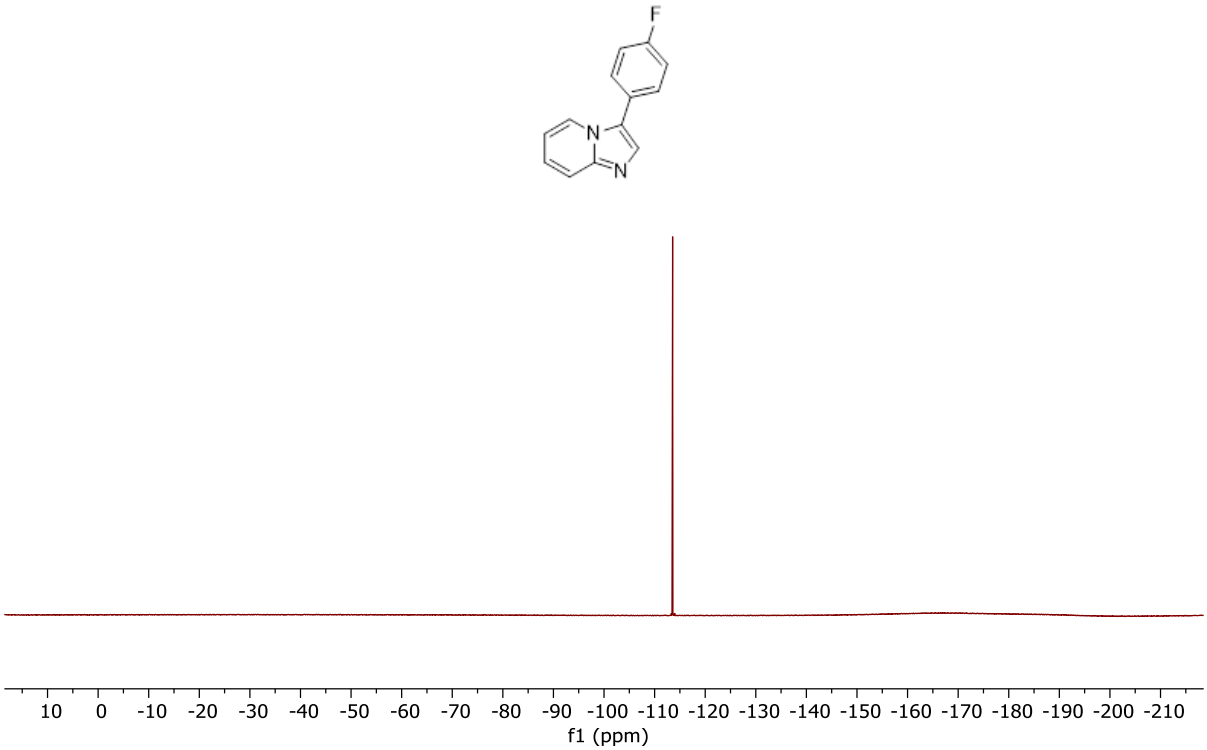
^{13}C NMR Spectrum of (**9**) (400 MHz, DMSO-d^{6}):



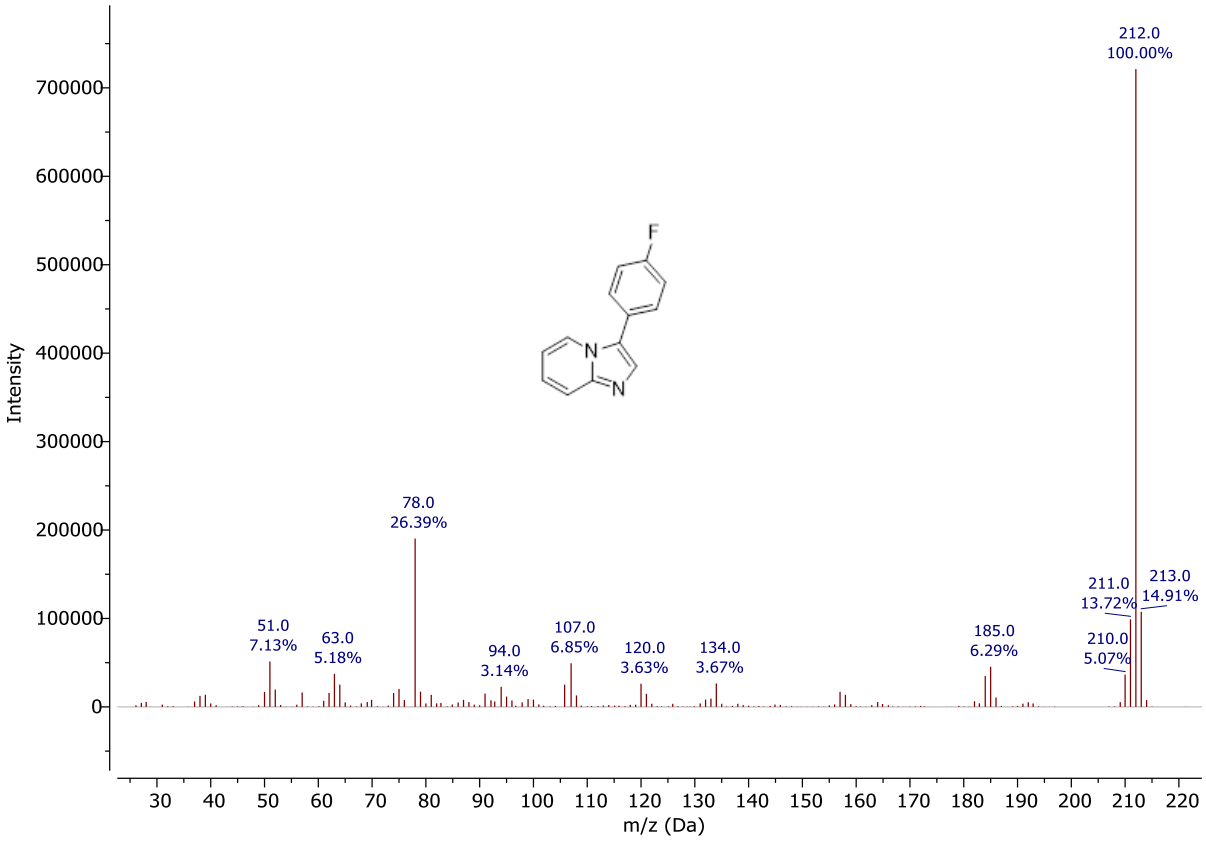
^{1}H/^{1}H COSY NMR Spectrum of (**9**) (400 MHz, DMSO-d^{6}):



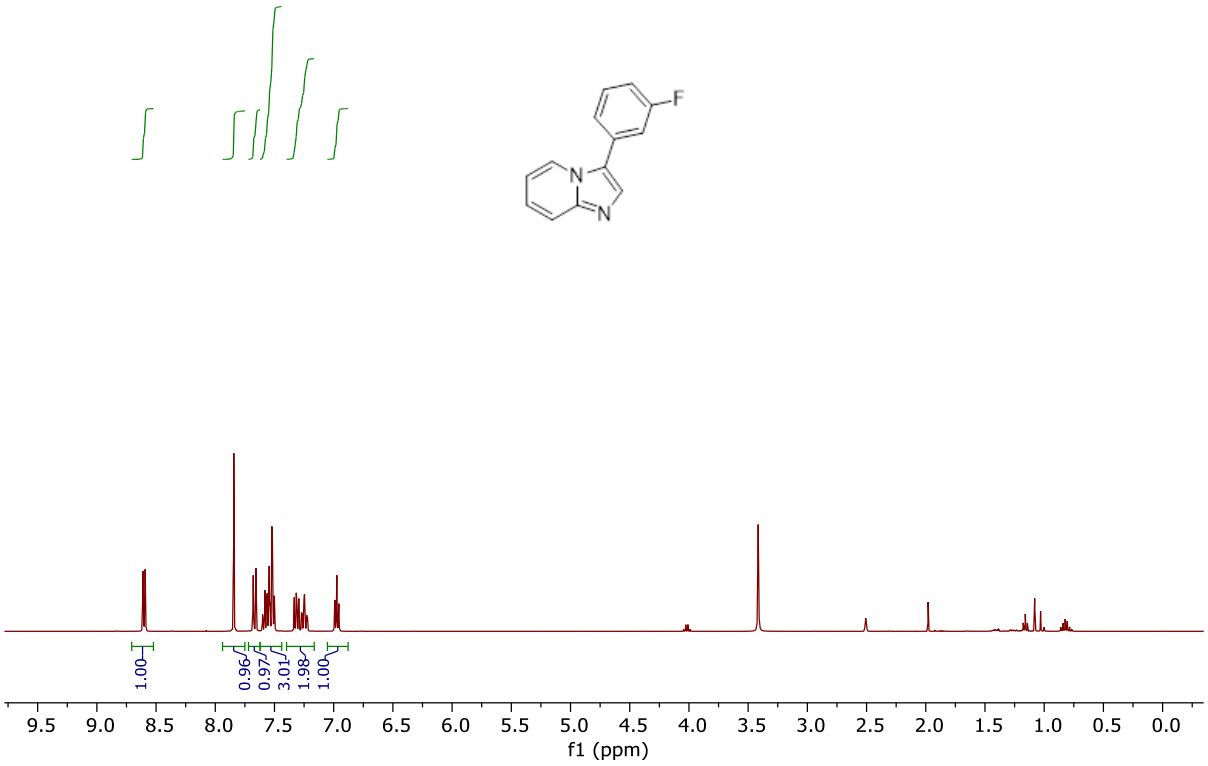
^{19}F NMR Spectrum of (**9**) (400 MHz, DMSO-d^{6}):

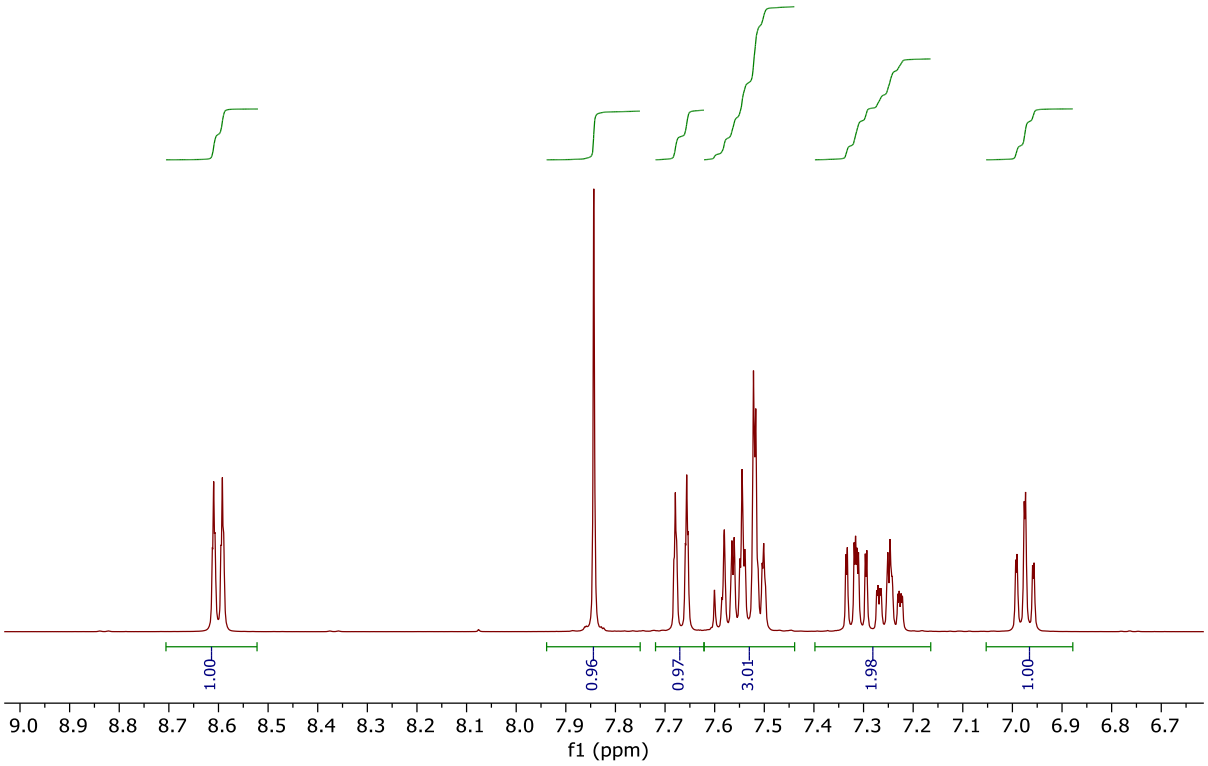


MS Spectrum of (**9**) (EI):

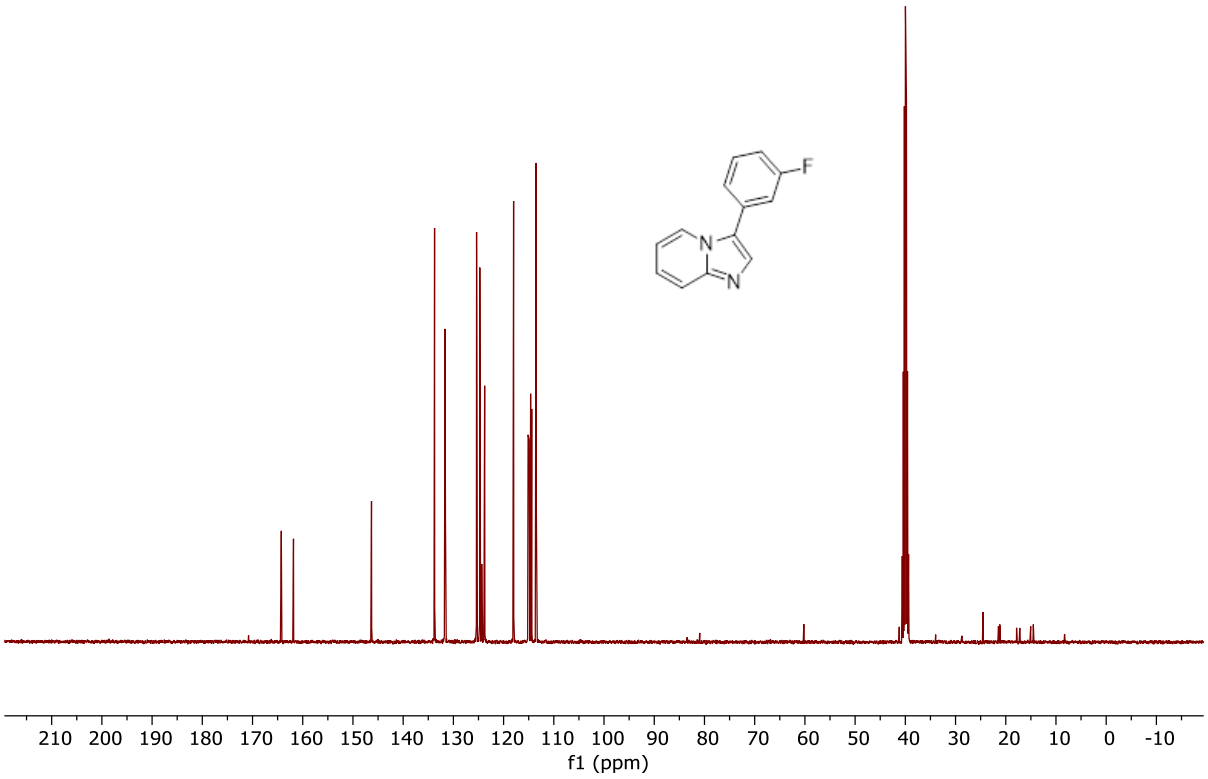


^{1}H NMR Spectrum of (**10**) (400 MHz, DMSO-d^{6}):

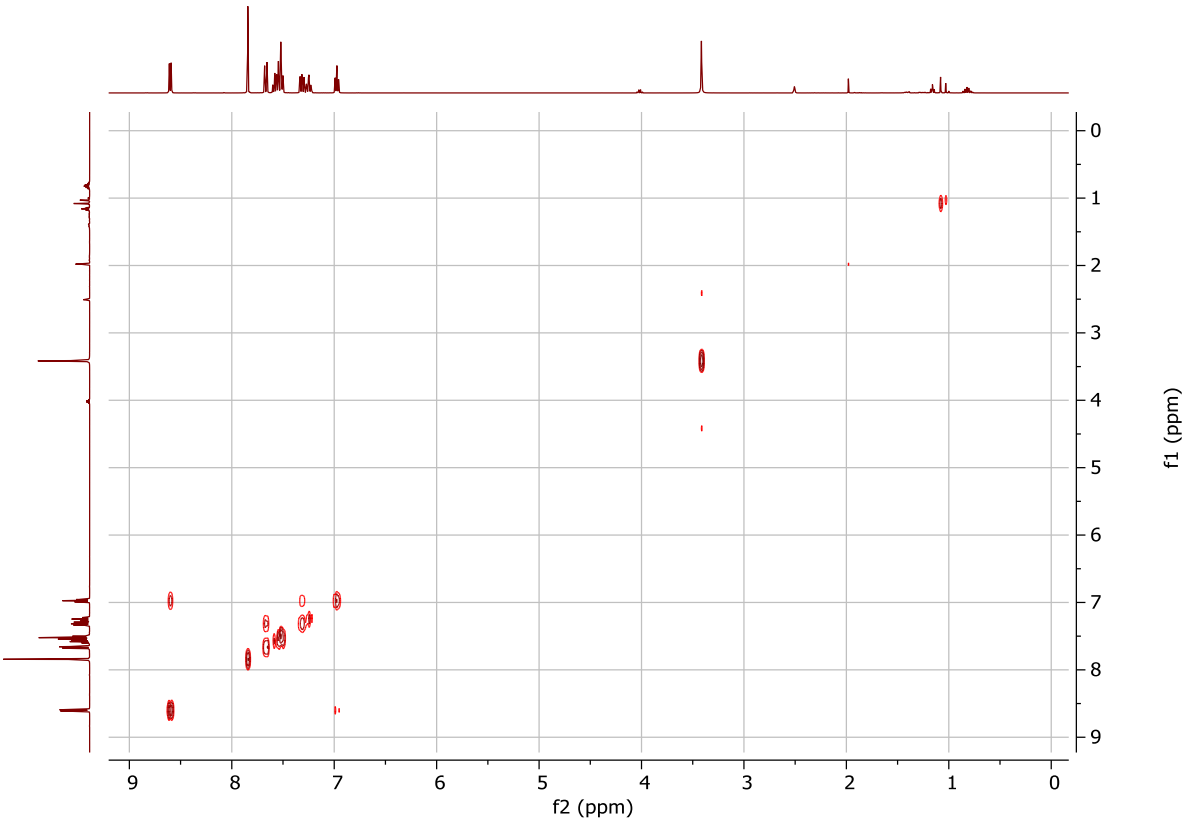




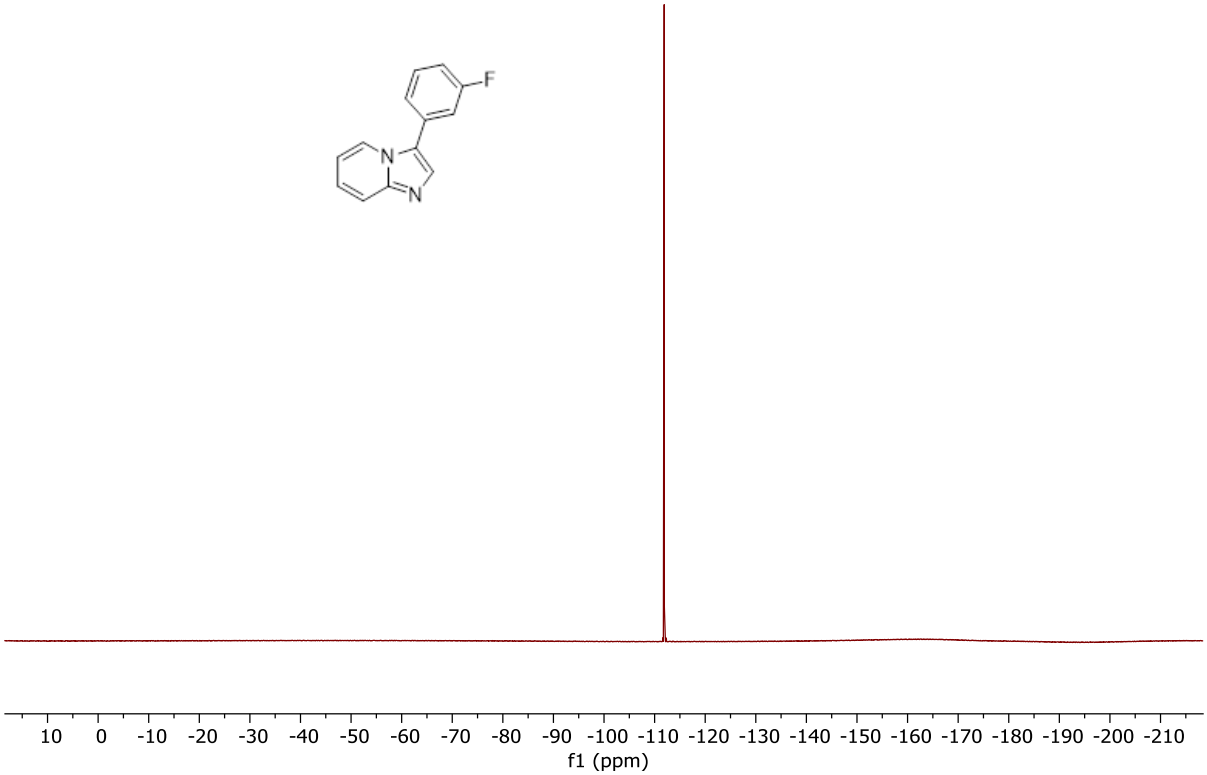
^{13}C NMR Spectrum of (**10**) (400 MHz, DMSO-d^{6}):



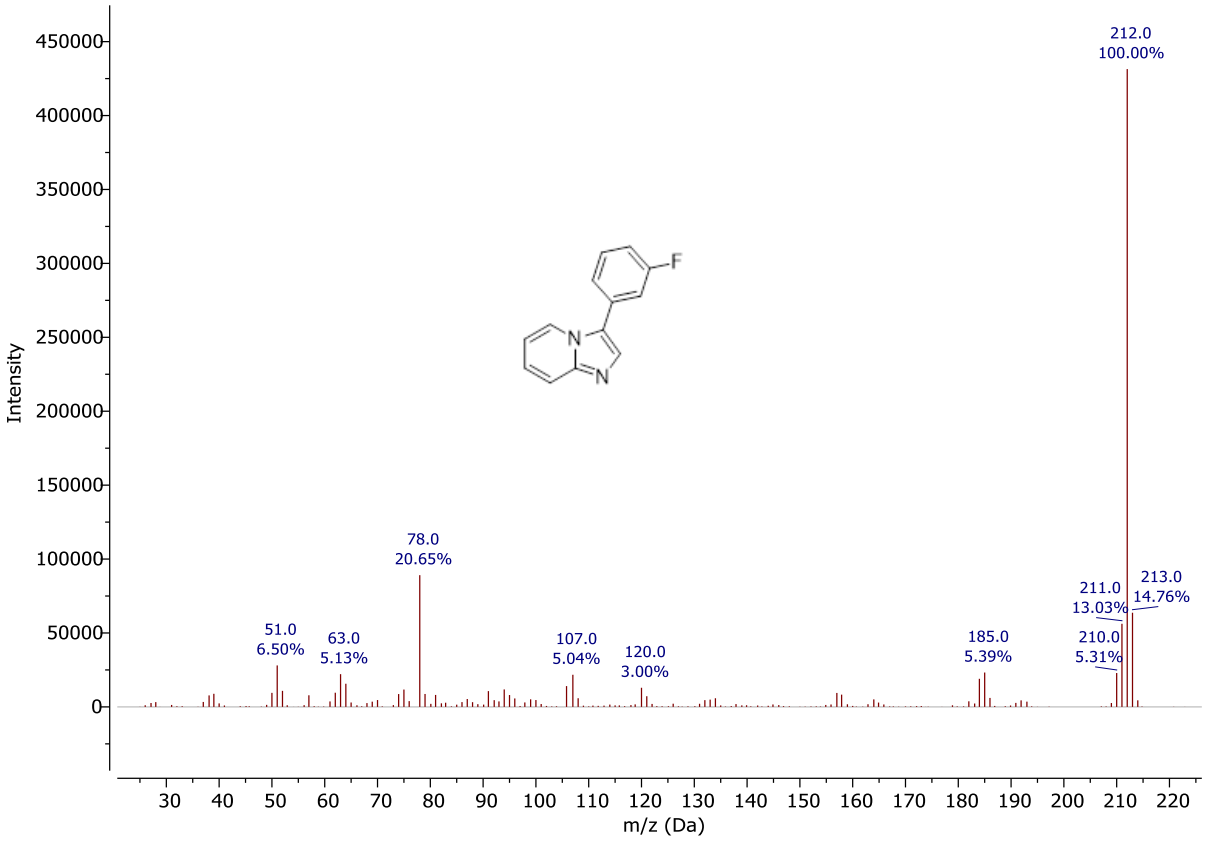
^{1}H/^{1}H COSY NMR Spectrum of (**10**) (400 MHz, DMSO-d^{6}):



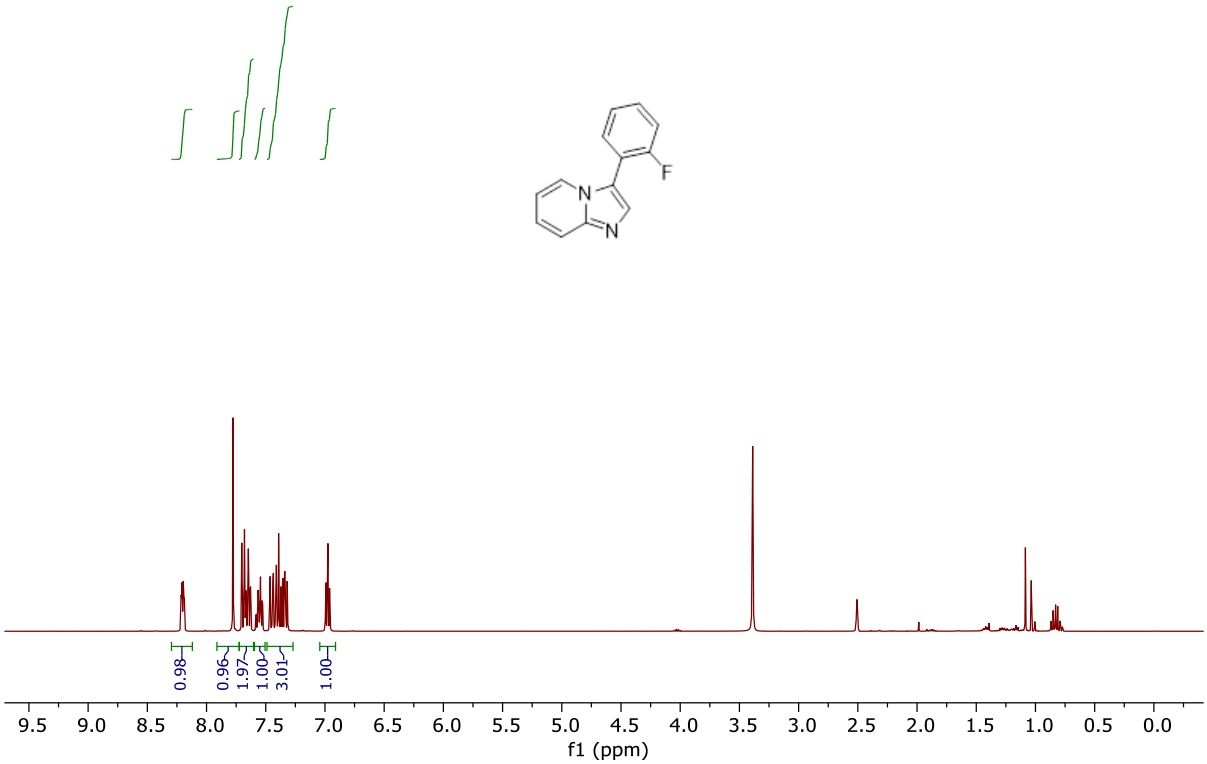
^{19}F NMR Spectrum of (**10**) (400 MHz, DMSO-d^6):

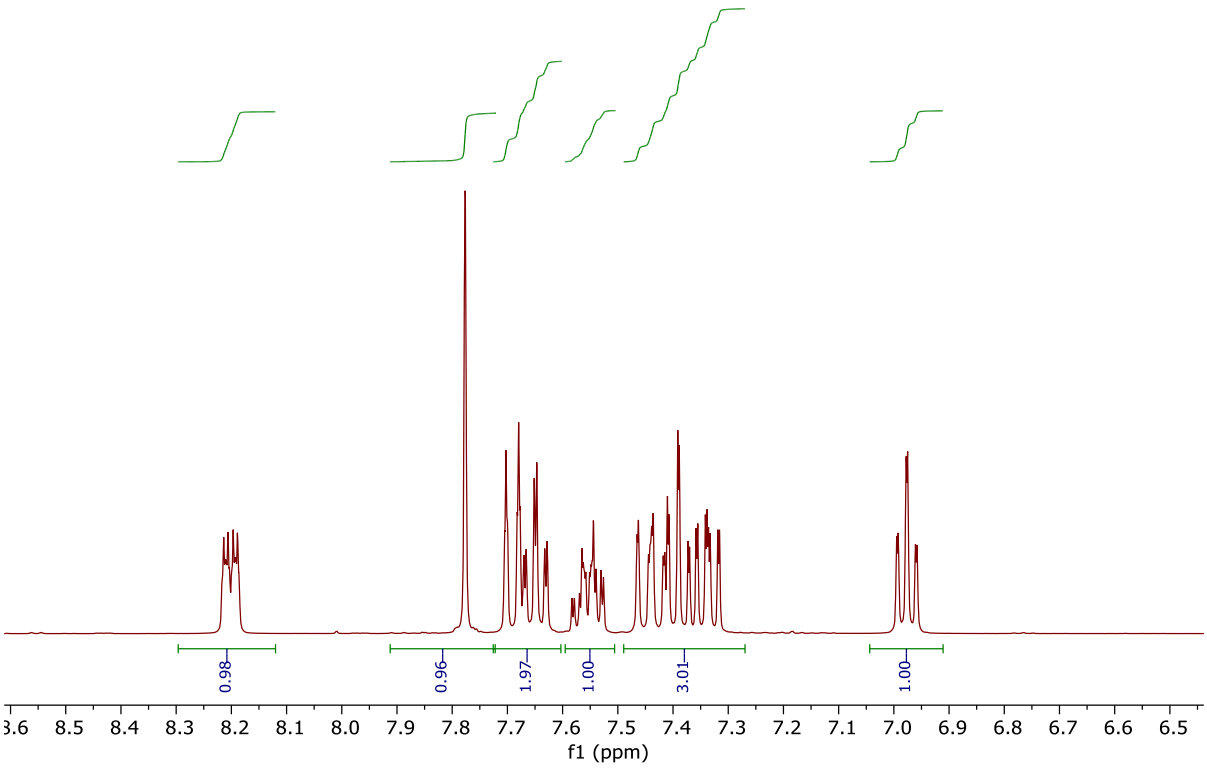


MS Spectrum of (**10**) (EI):

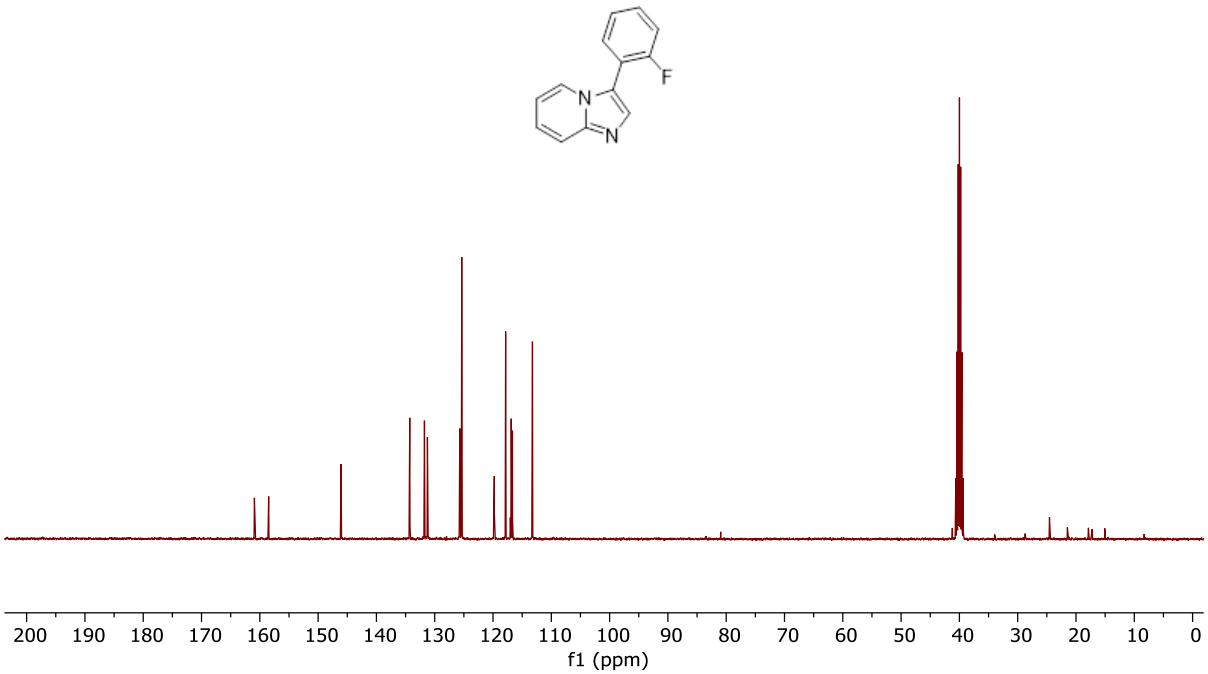


^{1}H NMR Spectrum of (**11**) (400 MHz, DMSO-d^{6}):

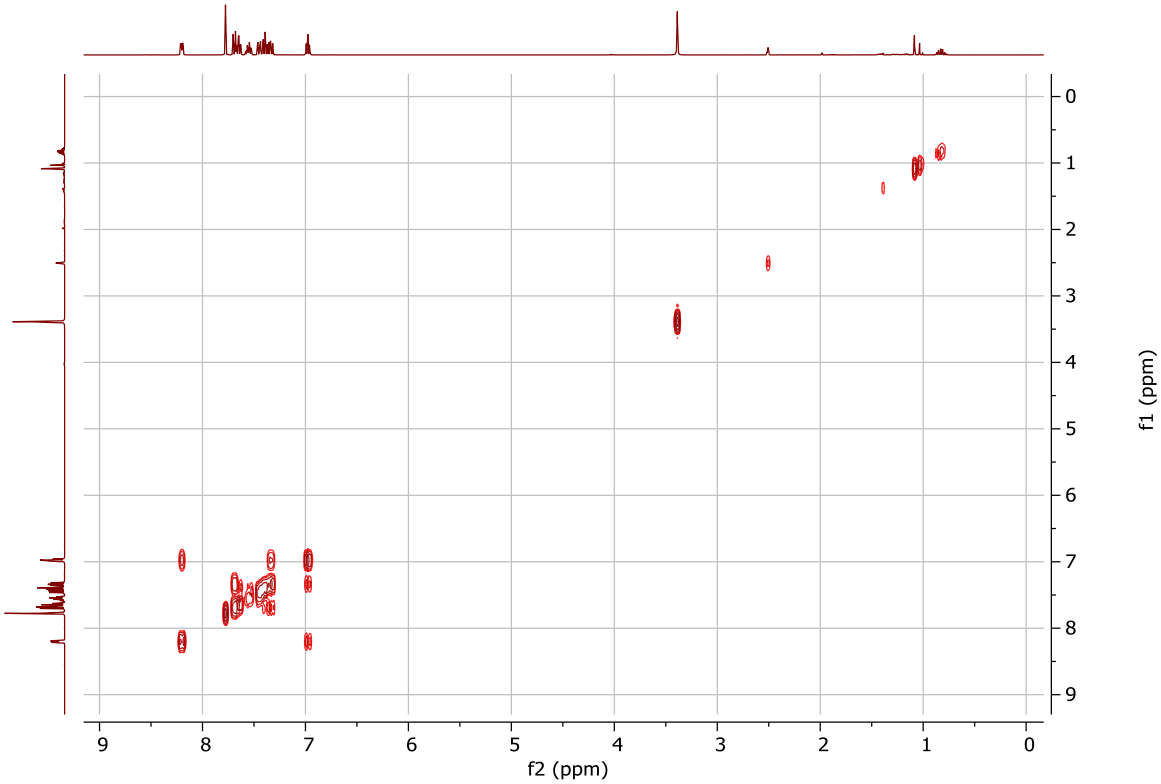




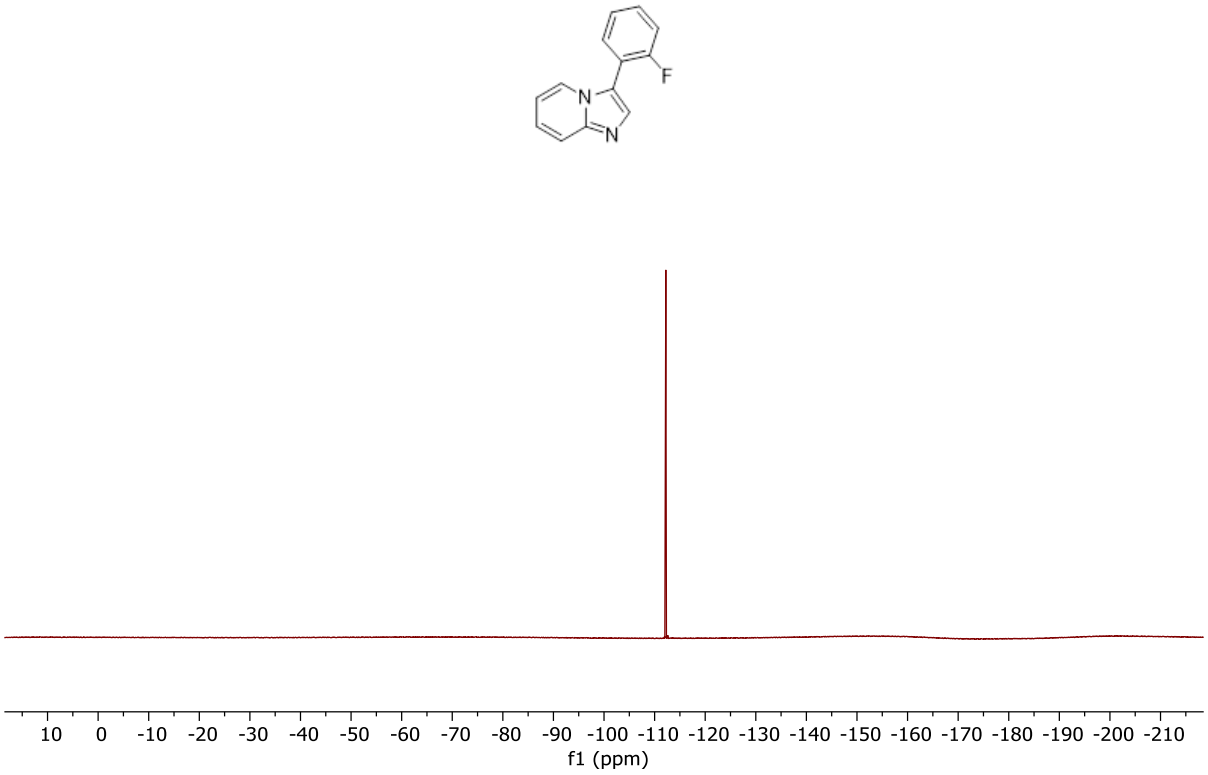
^{13}C NMR Spectrum of (**11**) (400 MHz, DMSO-d^{6}):



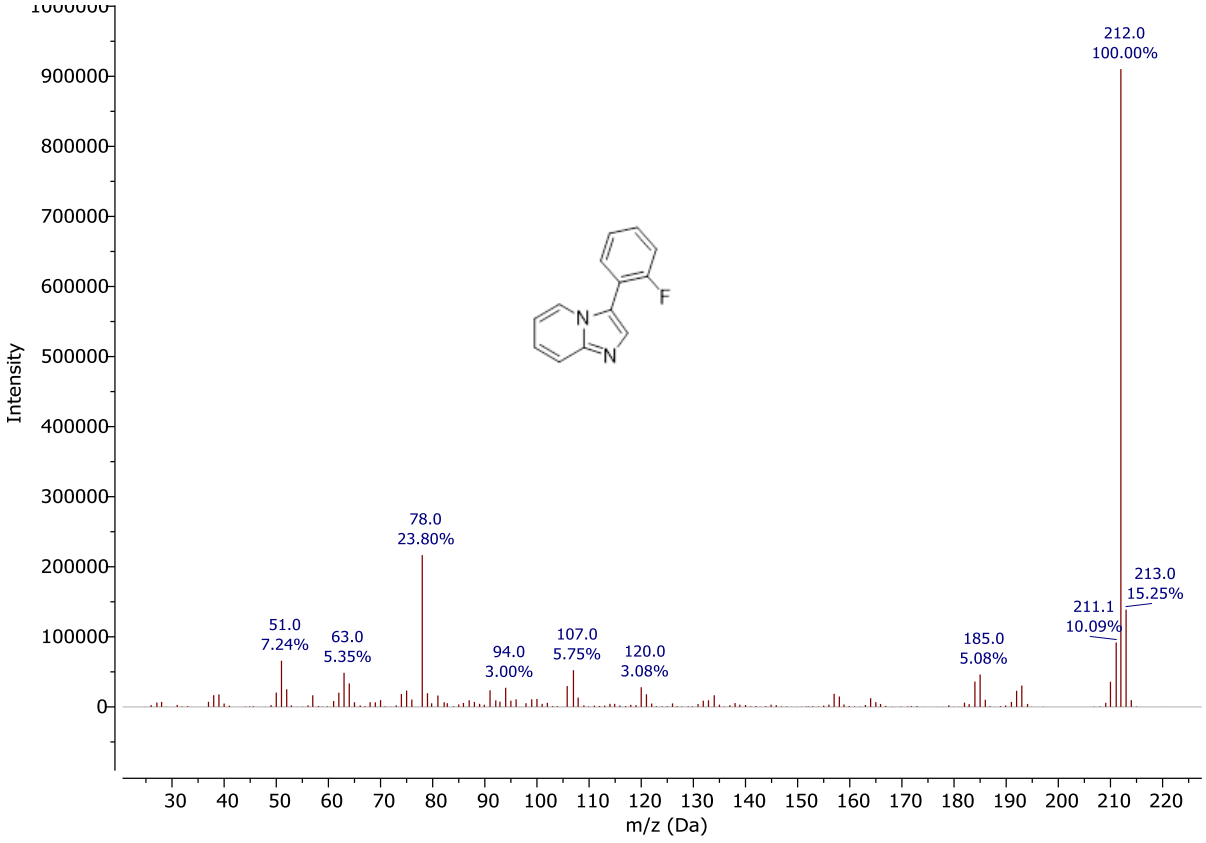
^{1}H/^{1}H COSY NMR Spectrum of (**11**) (400 MHz, DMSO-d^{6}):



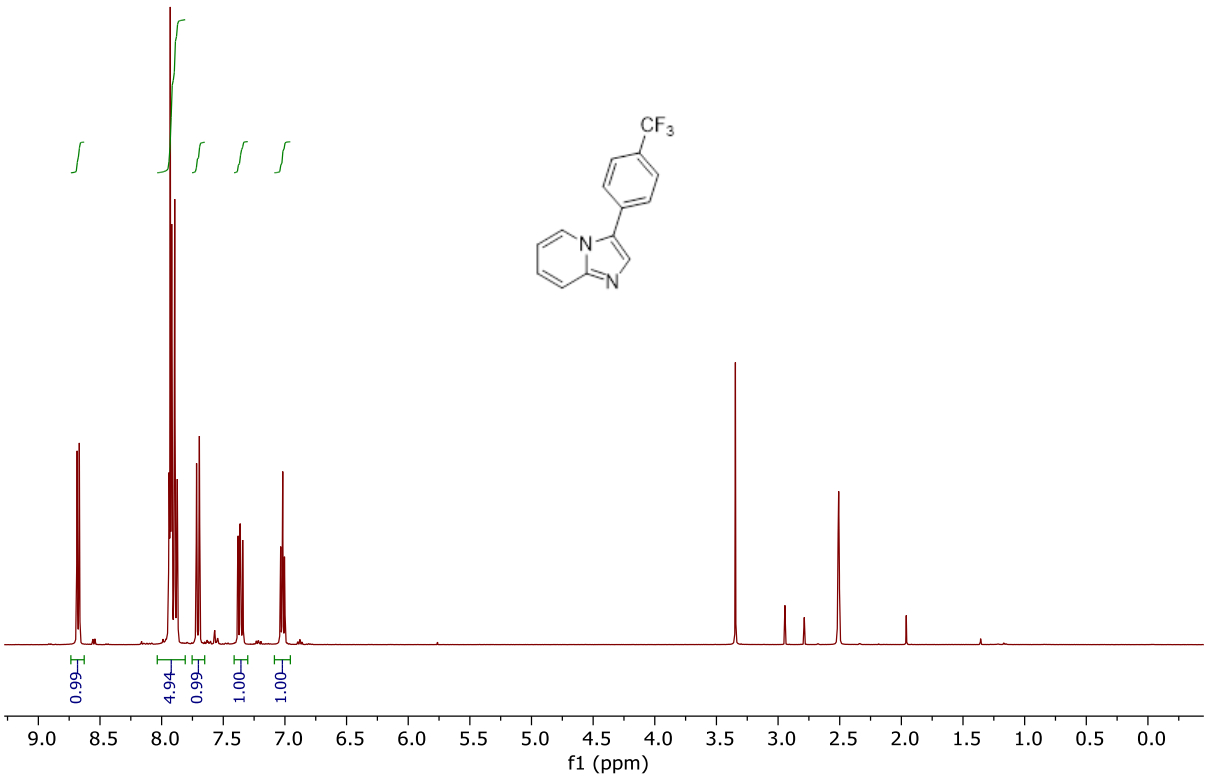
^{19}F NMR Spectrum of (**11**) (400 MHz, DMSO-d^{6}):

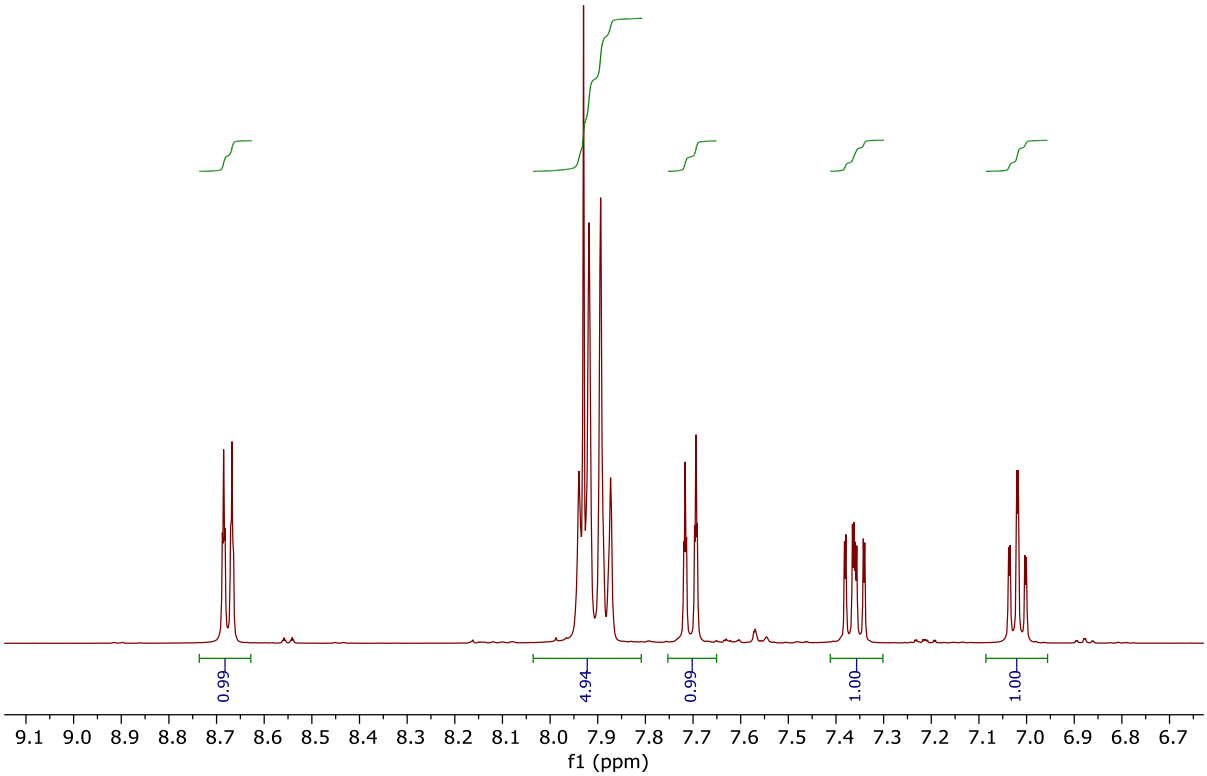


MS Spectrum of (**11**) (EI):

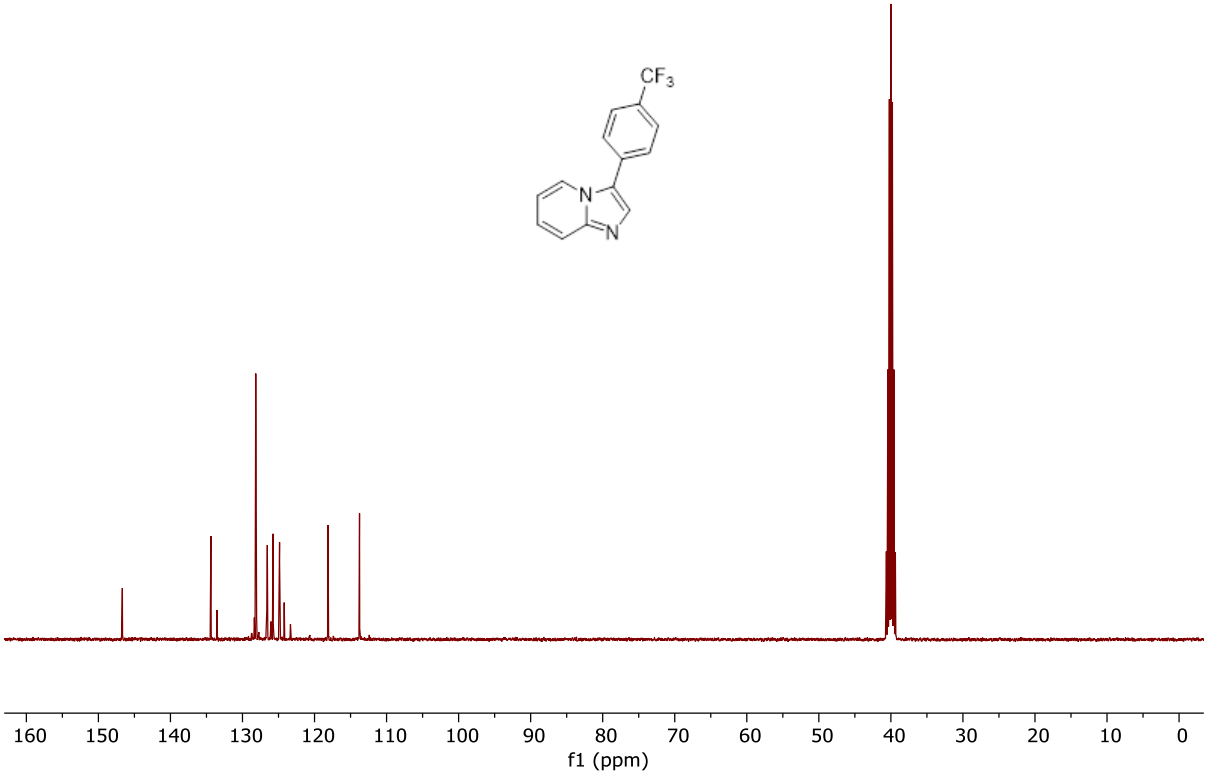


^{1}H NMR Spectrum of (**12**) (400 MHz, DMSO-d^{6}):

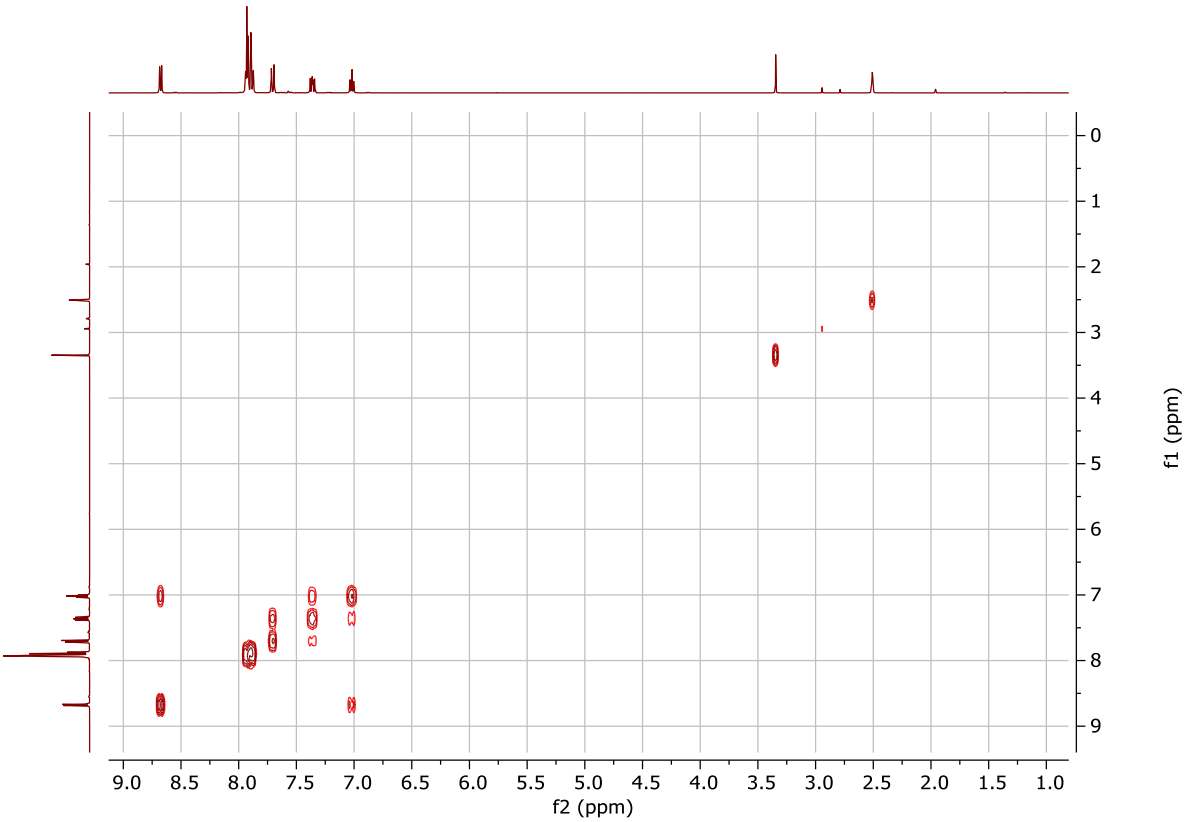


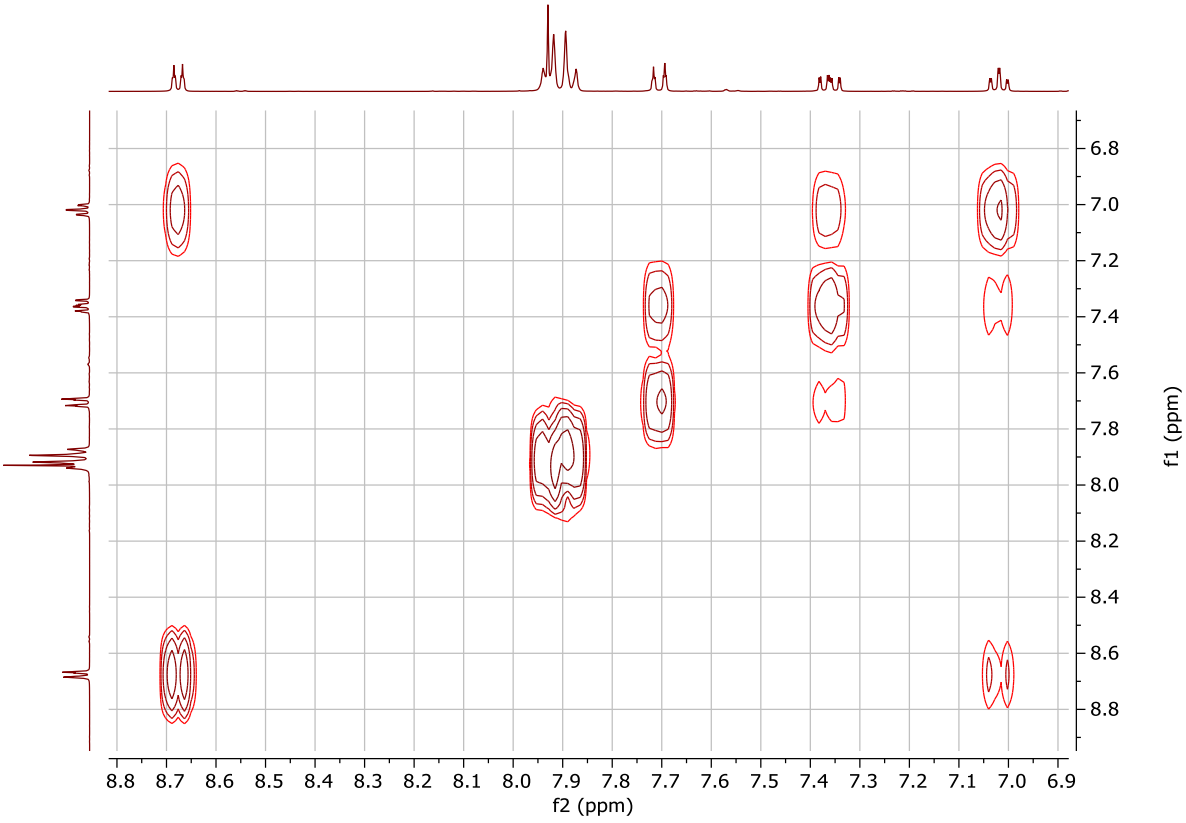


^{13}C NMR Spectrum of (**12**) (400 MHz, DMSO-d^{6}):

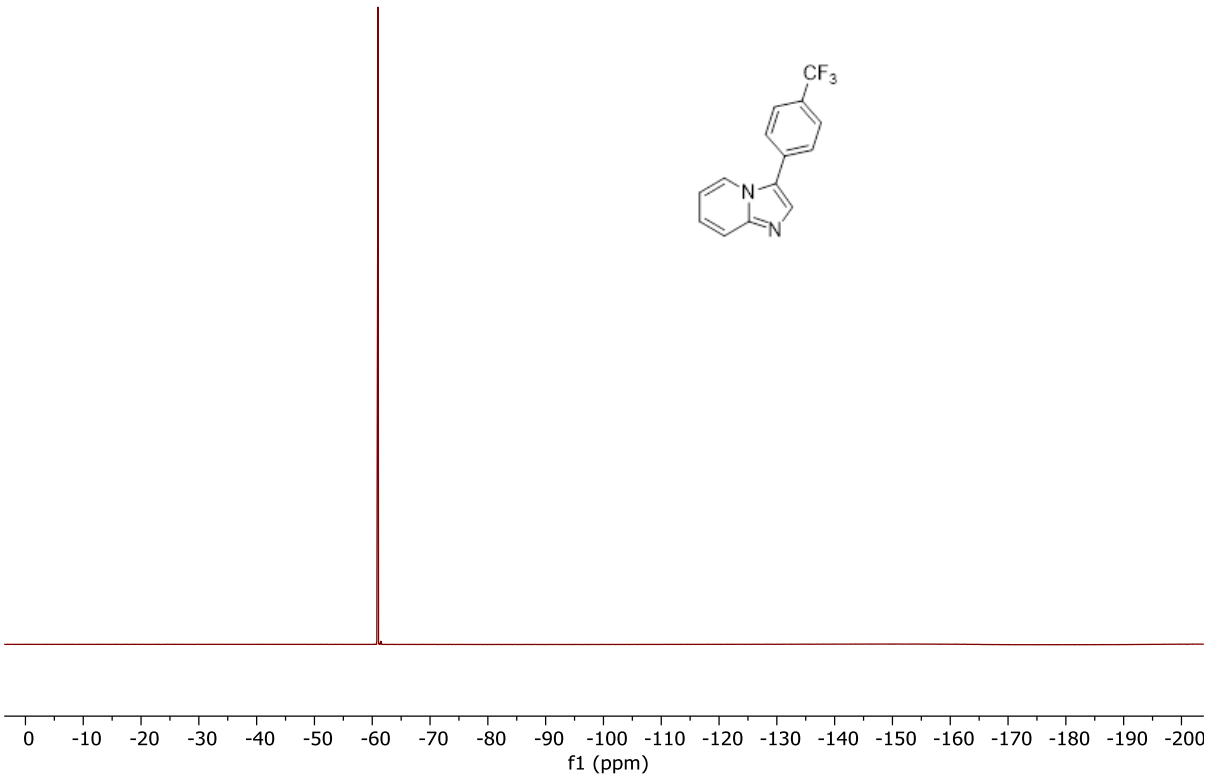


^{1}H/^{1}H COSY NMR Spectrum of (**12**) (400 MHz, DMSO-d^{6}):

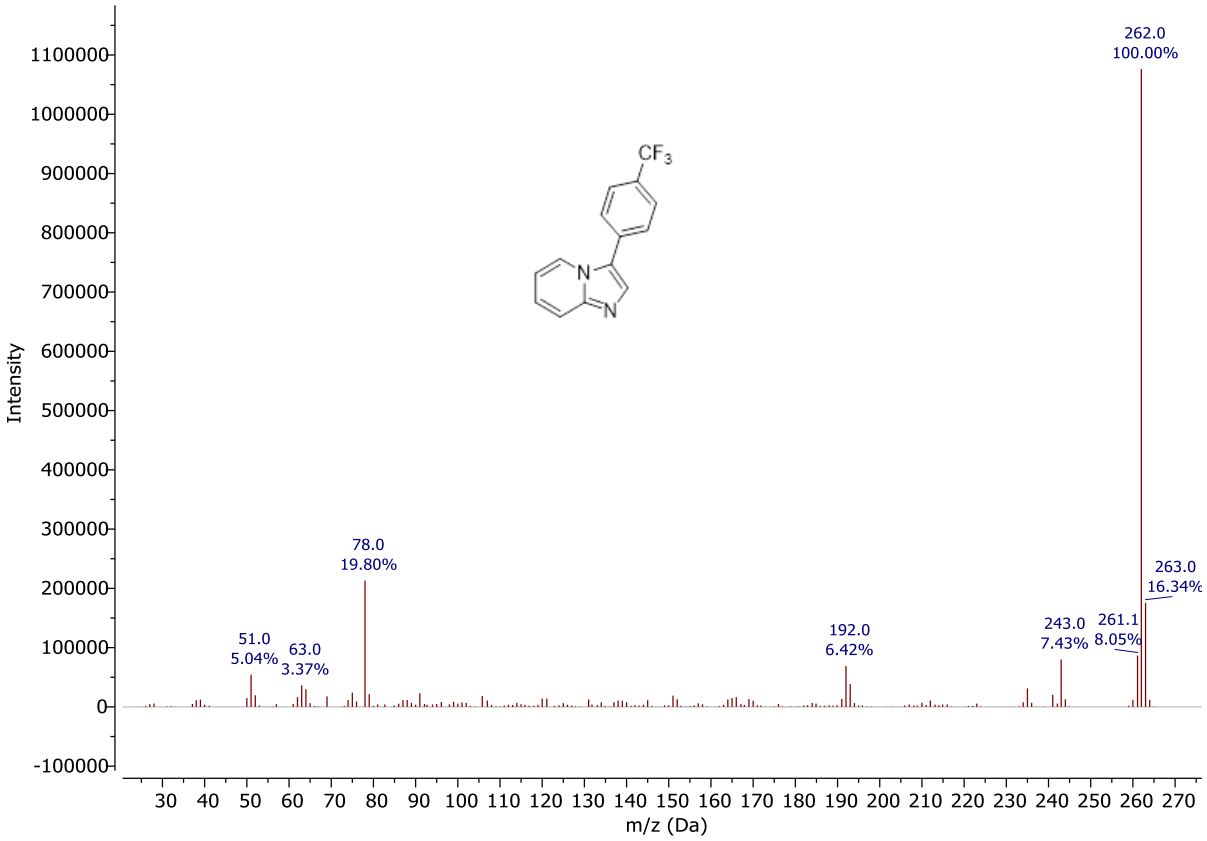




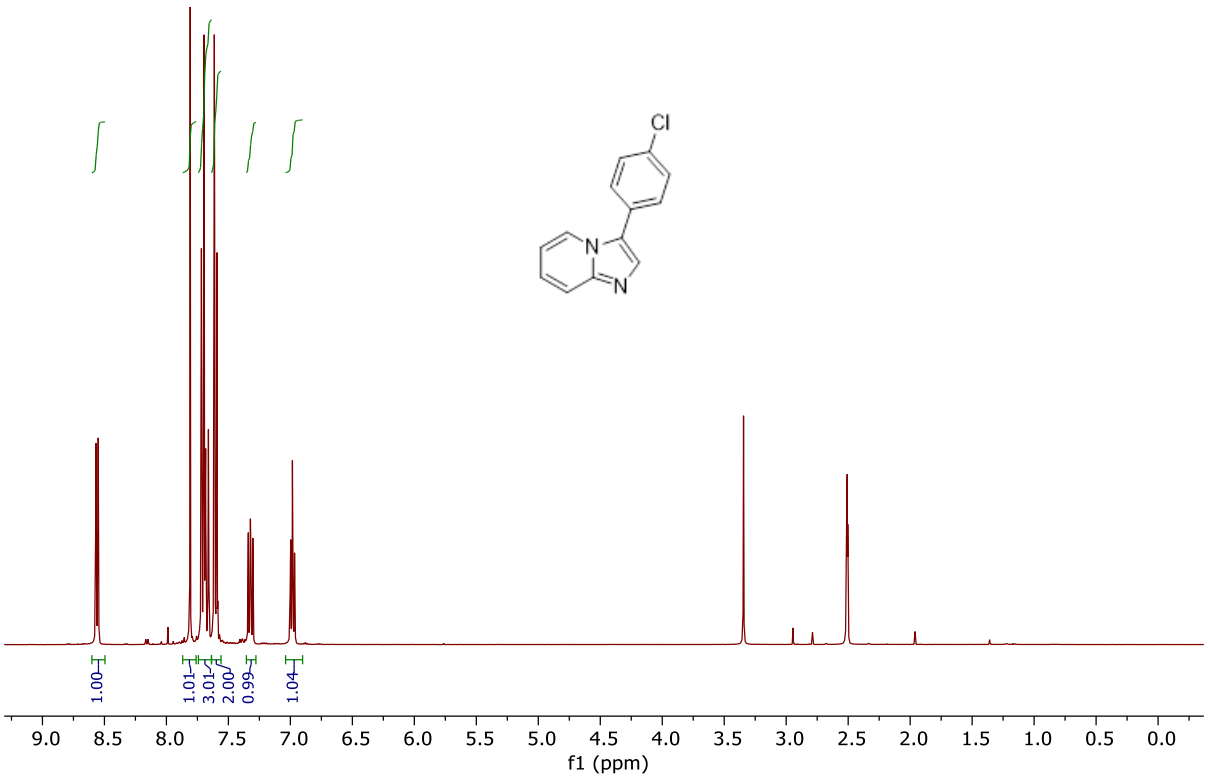
^{19}F NMR Spectrum of (**12**) (400 MHz, DMSO-d^{6}):

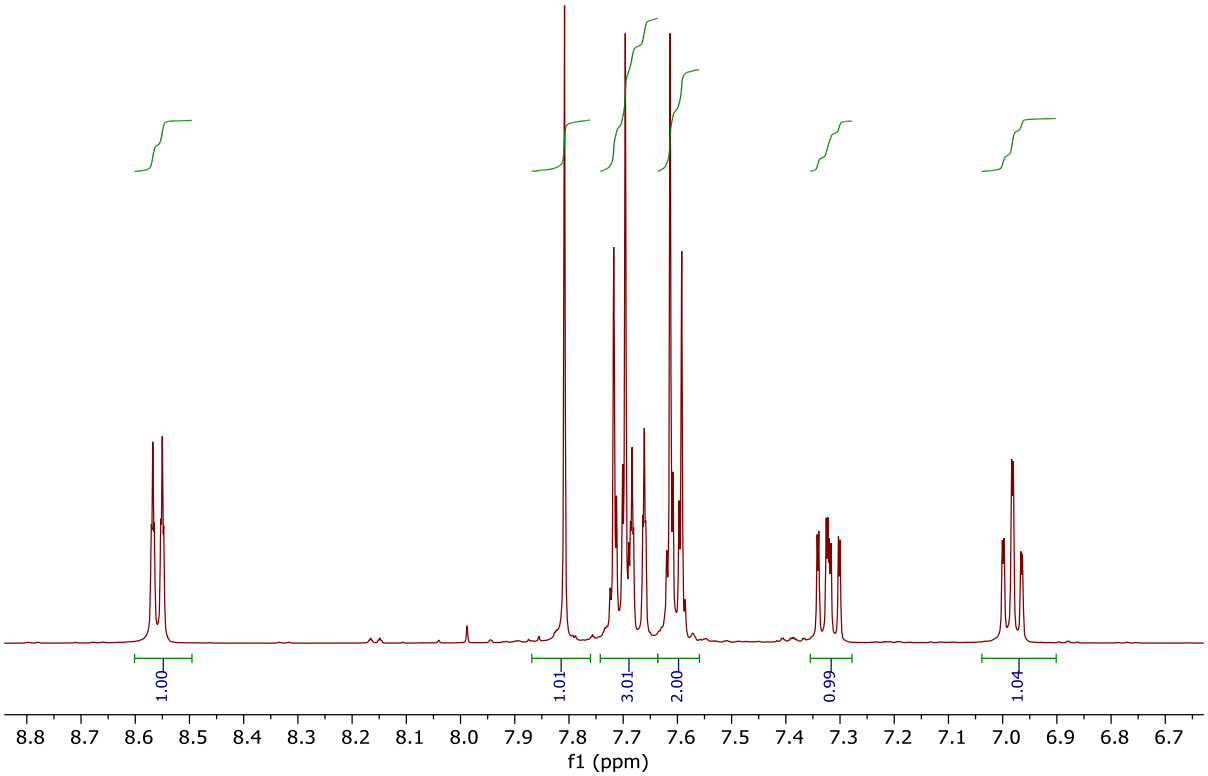


MS Spectrum of (**12**) (EI):

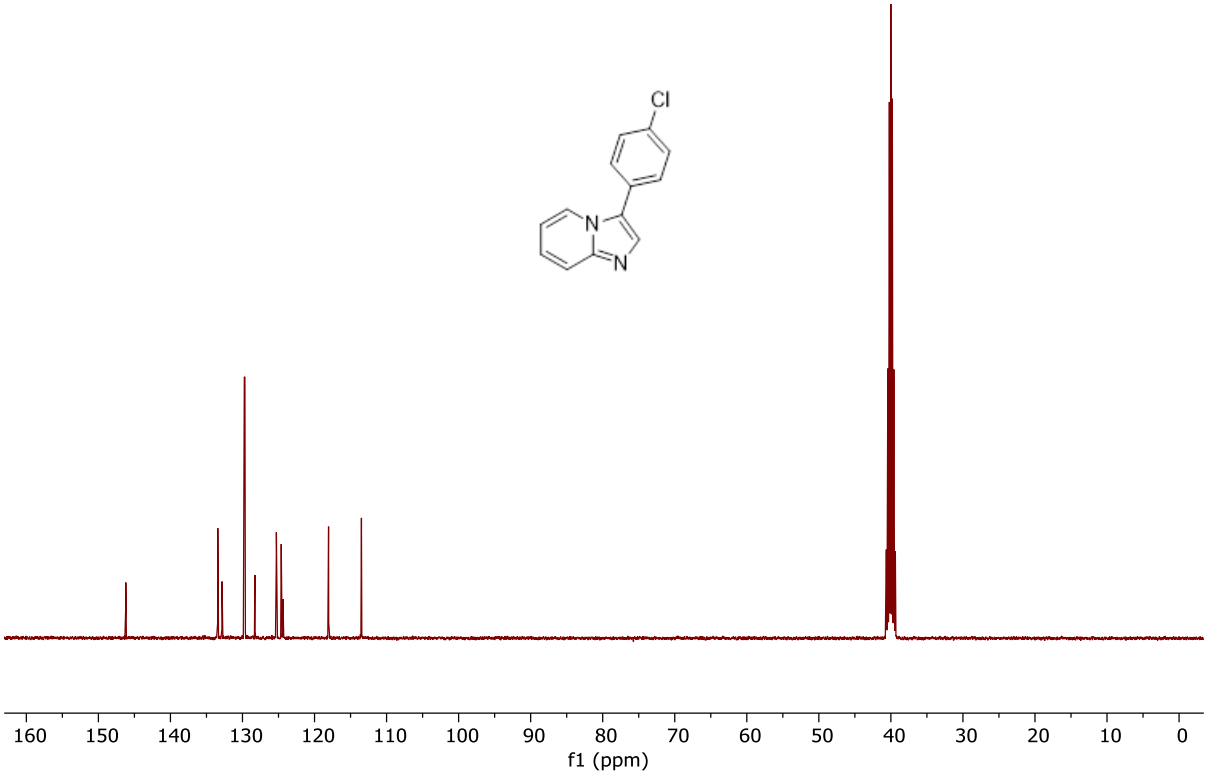


^{1}H NMR Spectrum of (**13**) (400 MHz, DMSO-d^{6}):

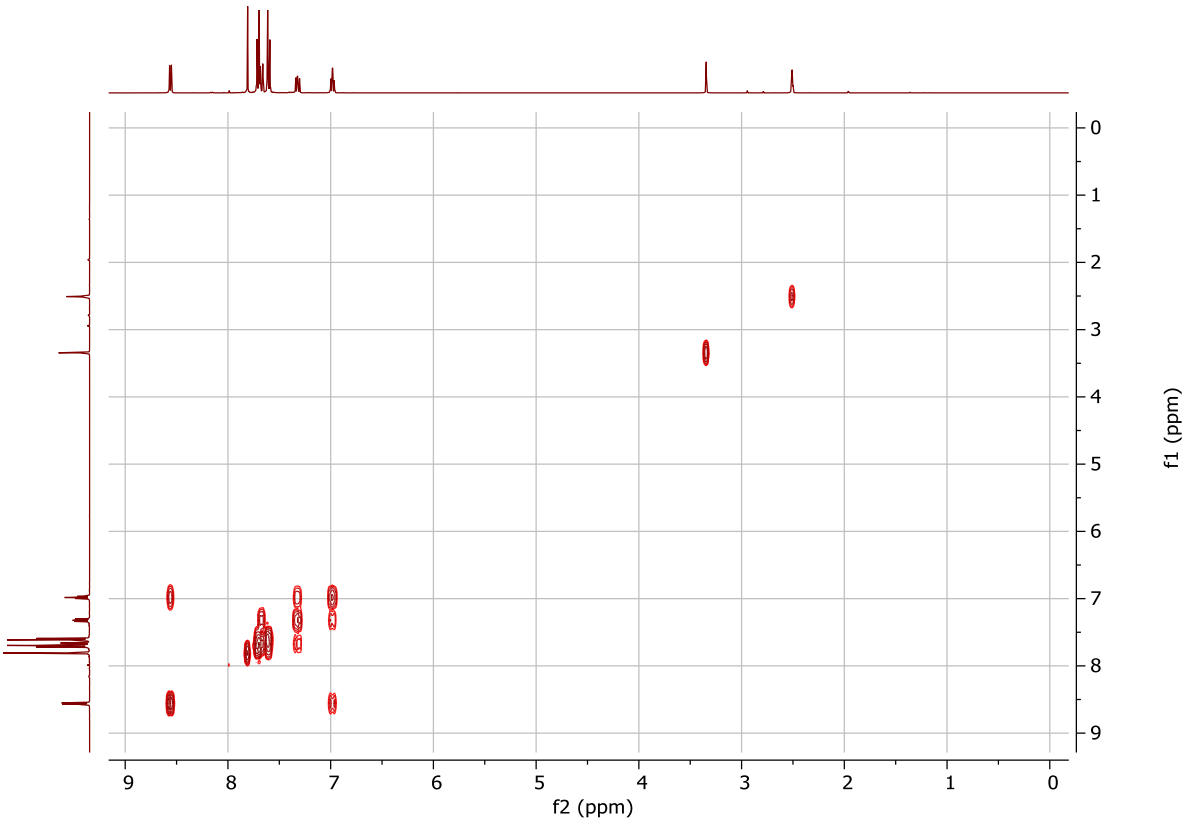


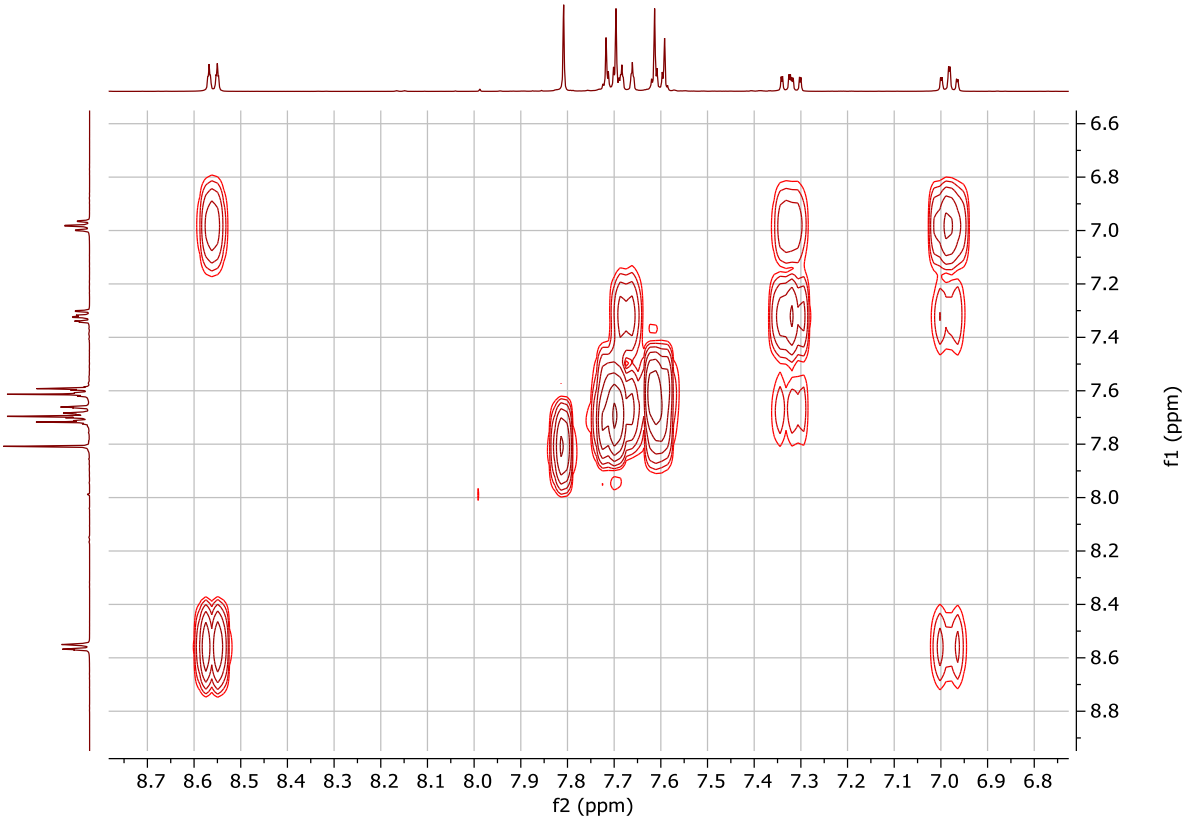


^{13}C NMR Spectrum of (**13**) (400 MHz, DMSO-d^{6}):

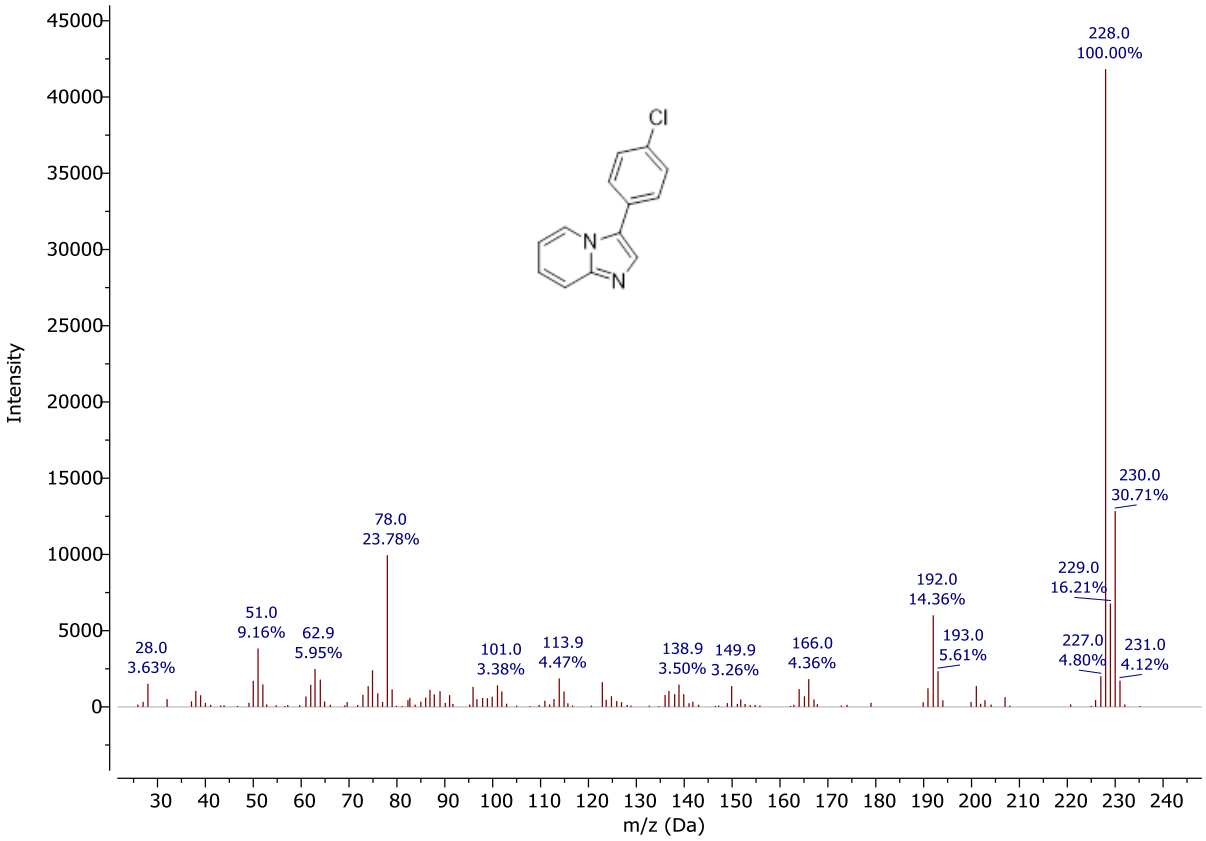


^{1}H/^{1}H COSY NMR Spectrum of (**13**) (400 MHz, DMSO-d^{6}):

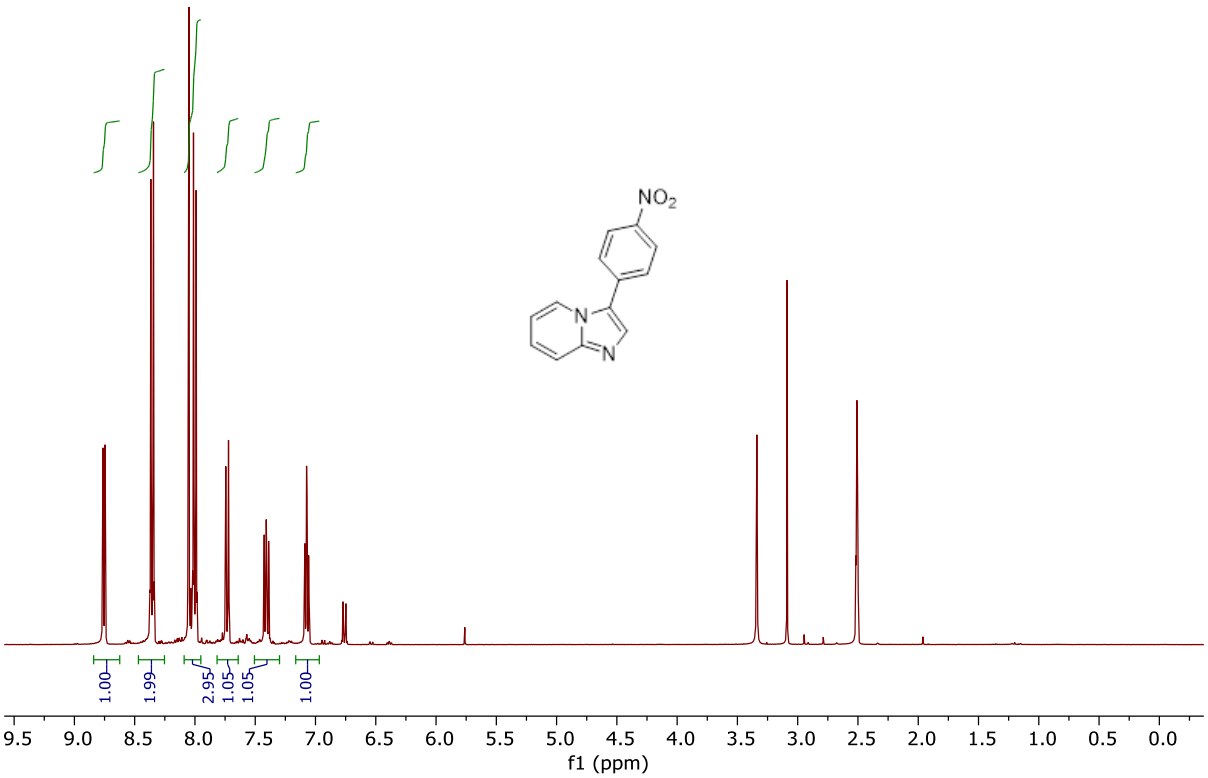


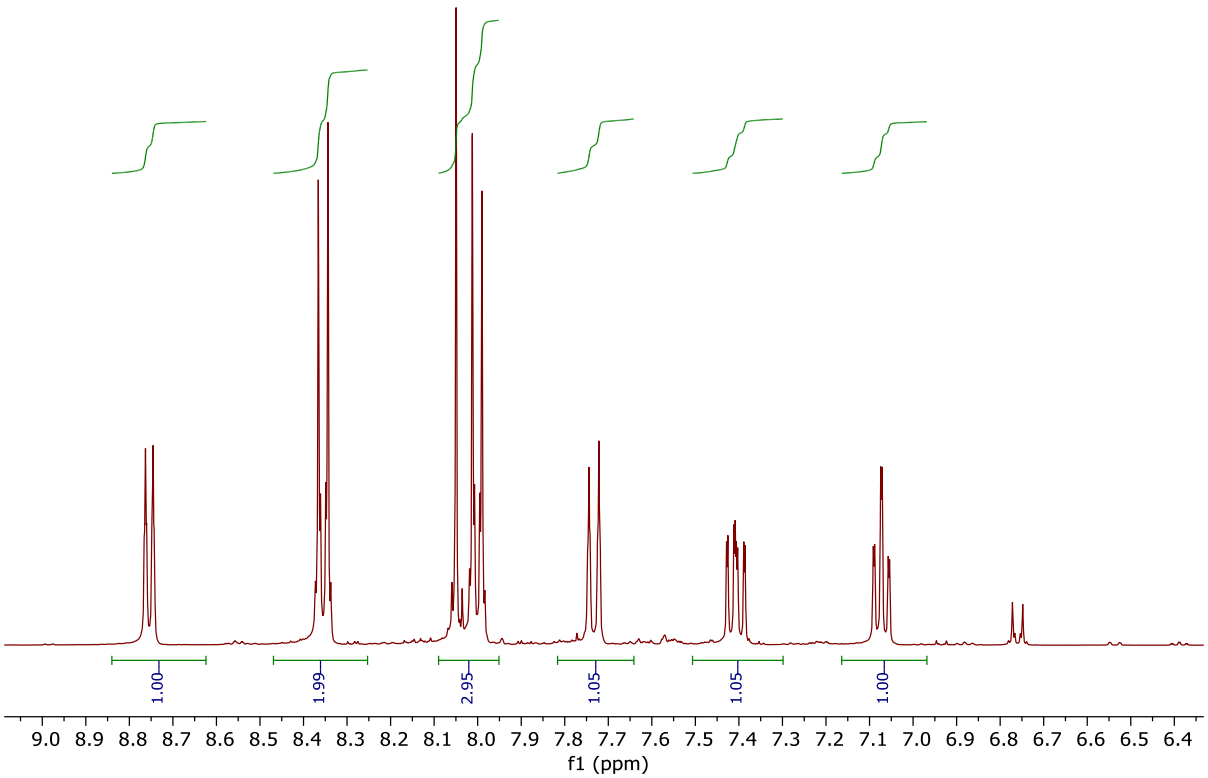


MS Spectrum of (**13**) (EI):

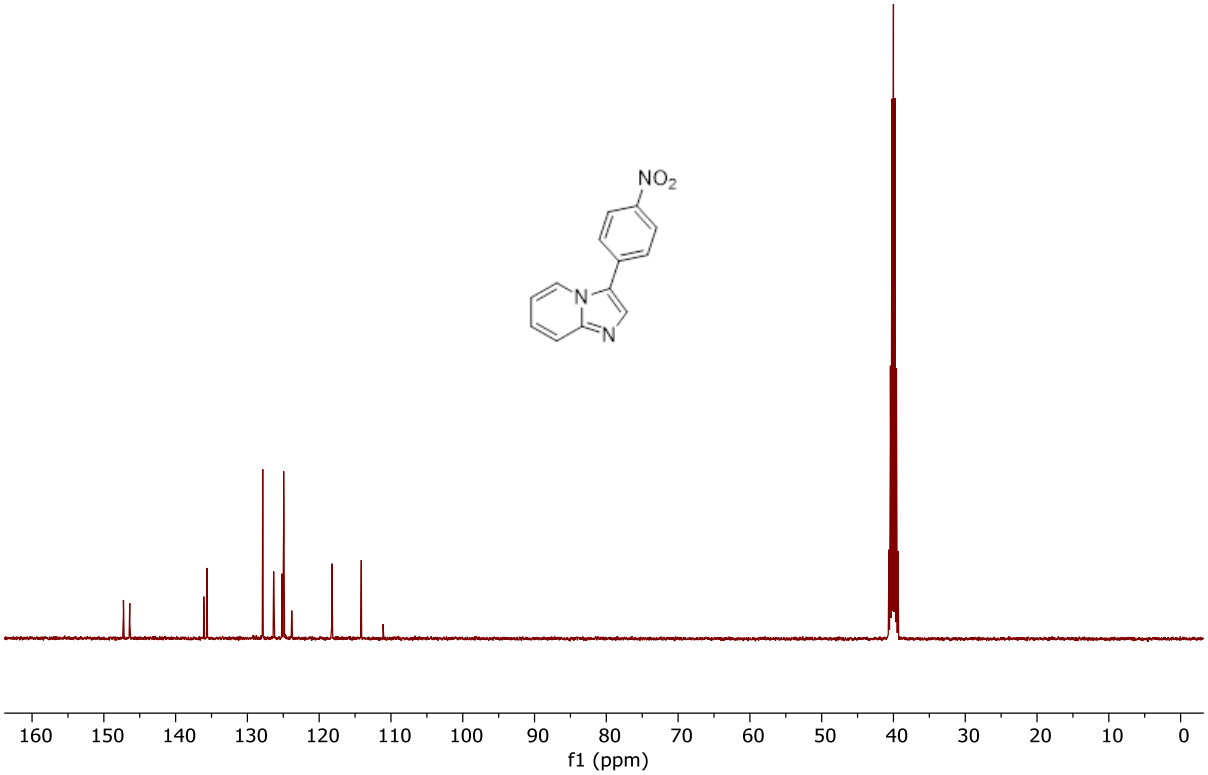


^{1}H NMR Spectrum of (**14**) (400 MHz, DMSO-d^{6}):

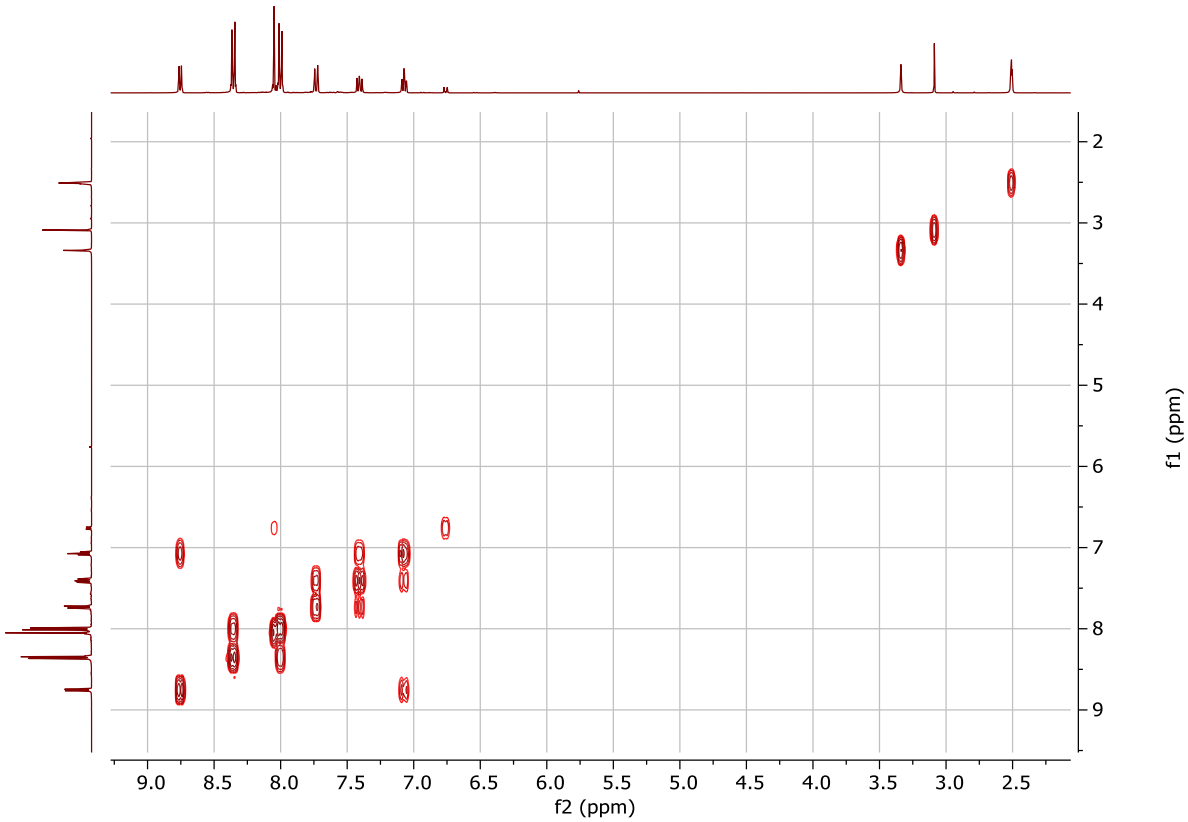


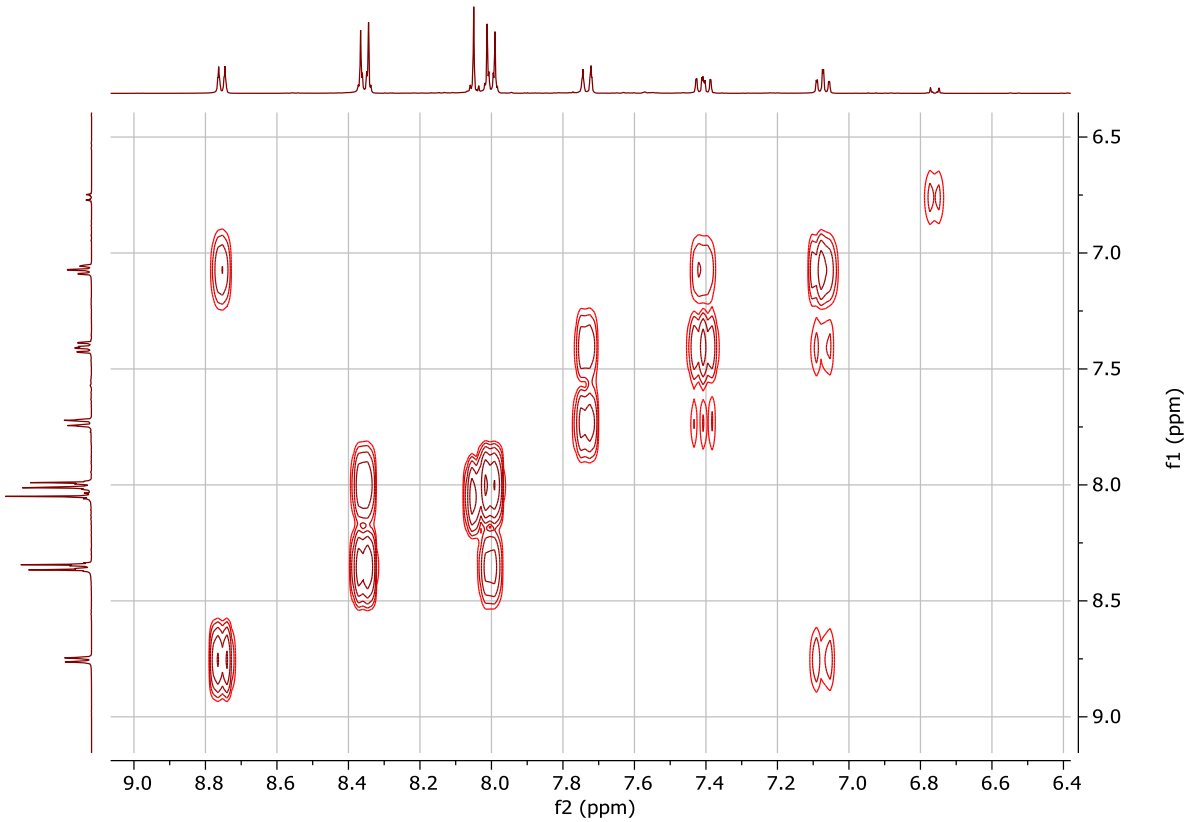


^{13}C NMR Spectrum of (**14**) (400 MHz, DMSO-d^{6}):

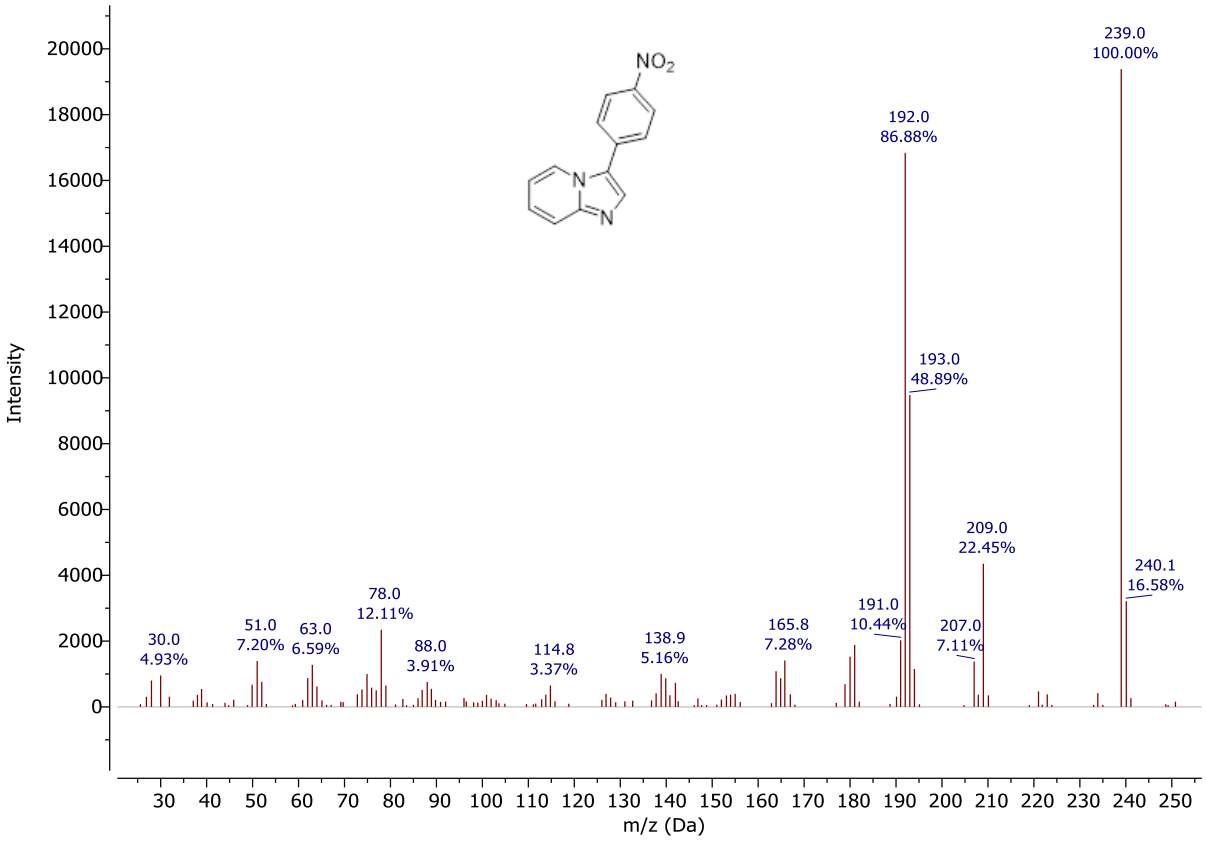


^{1}H/^{1}H COSY NMR Spectrum of (**14**) (400 MHz, DMSO-d^{6}):

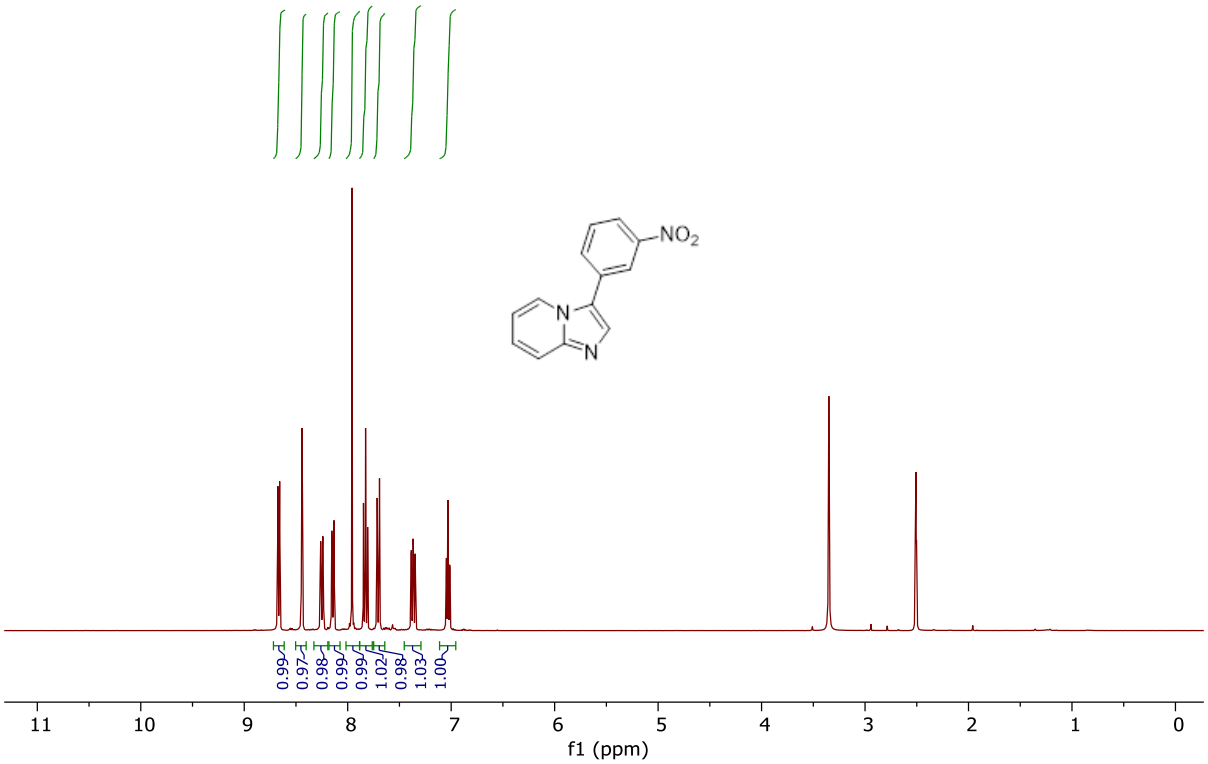


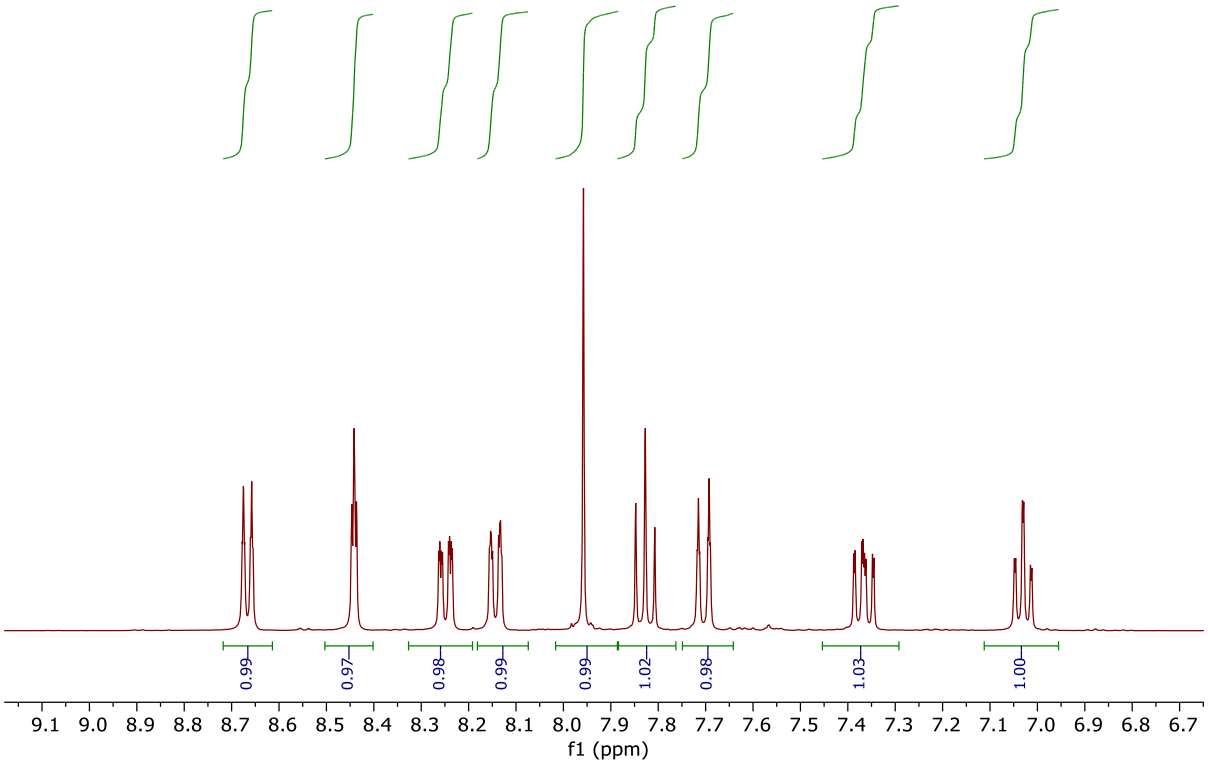


MS Spectrum of (**14**) (EI):

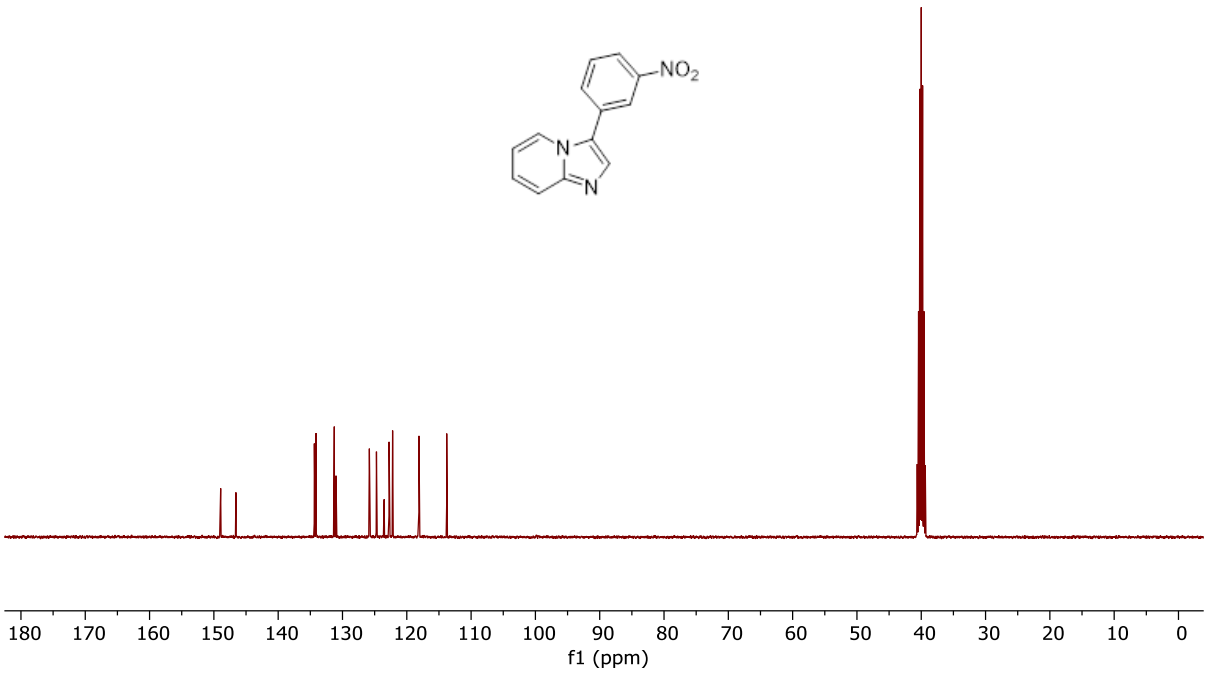


^{1}H NMR Spectrum of (**15**) (400 MHz, DMSO-d^{6}):

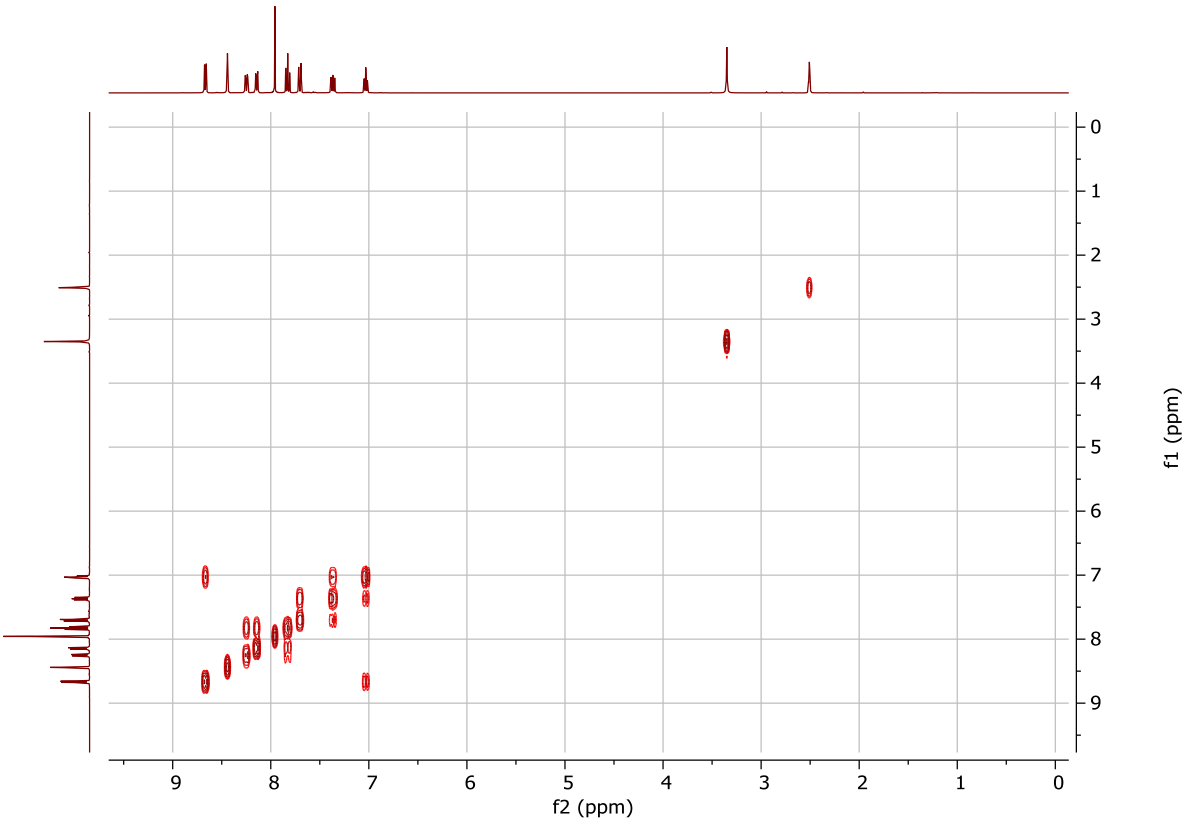


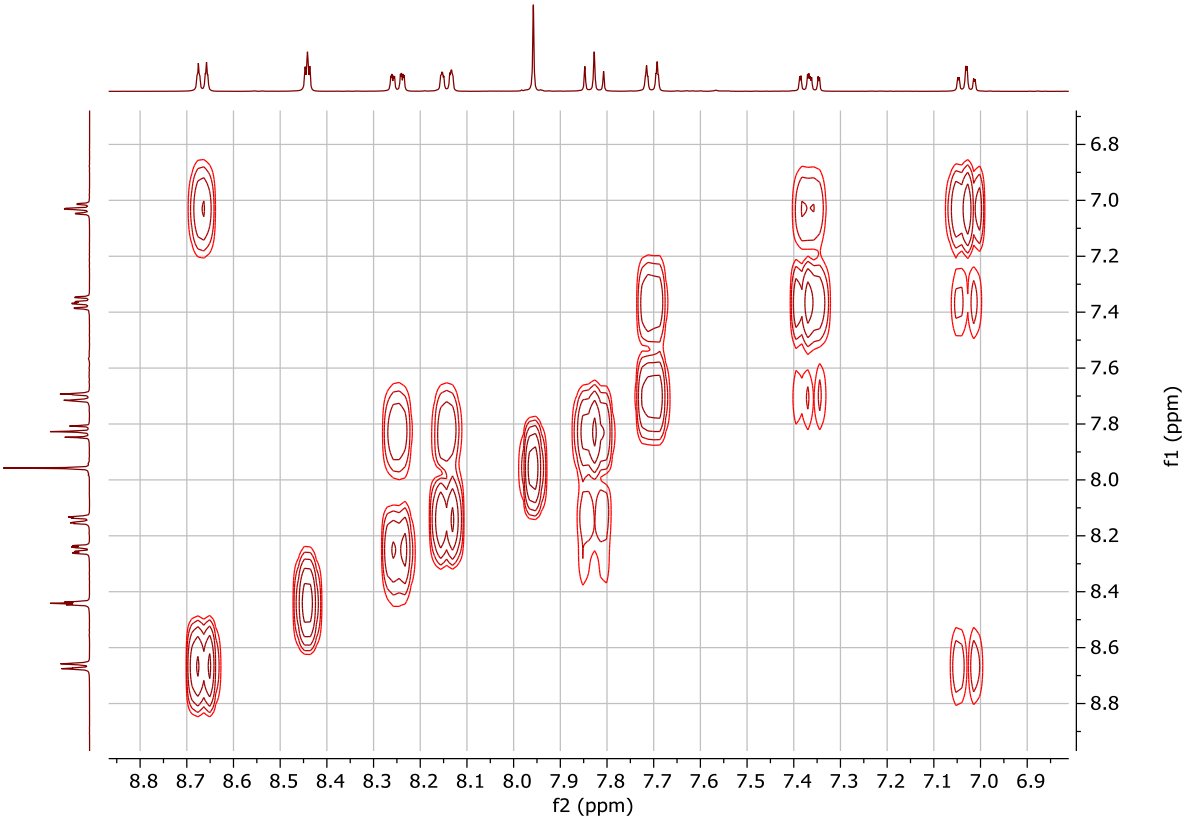


^{13}C NMR Spectrum of (**15**) (400 MHz, DMSO-d^{6}):

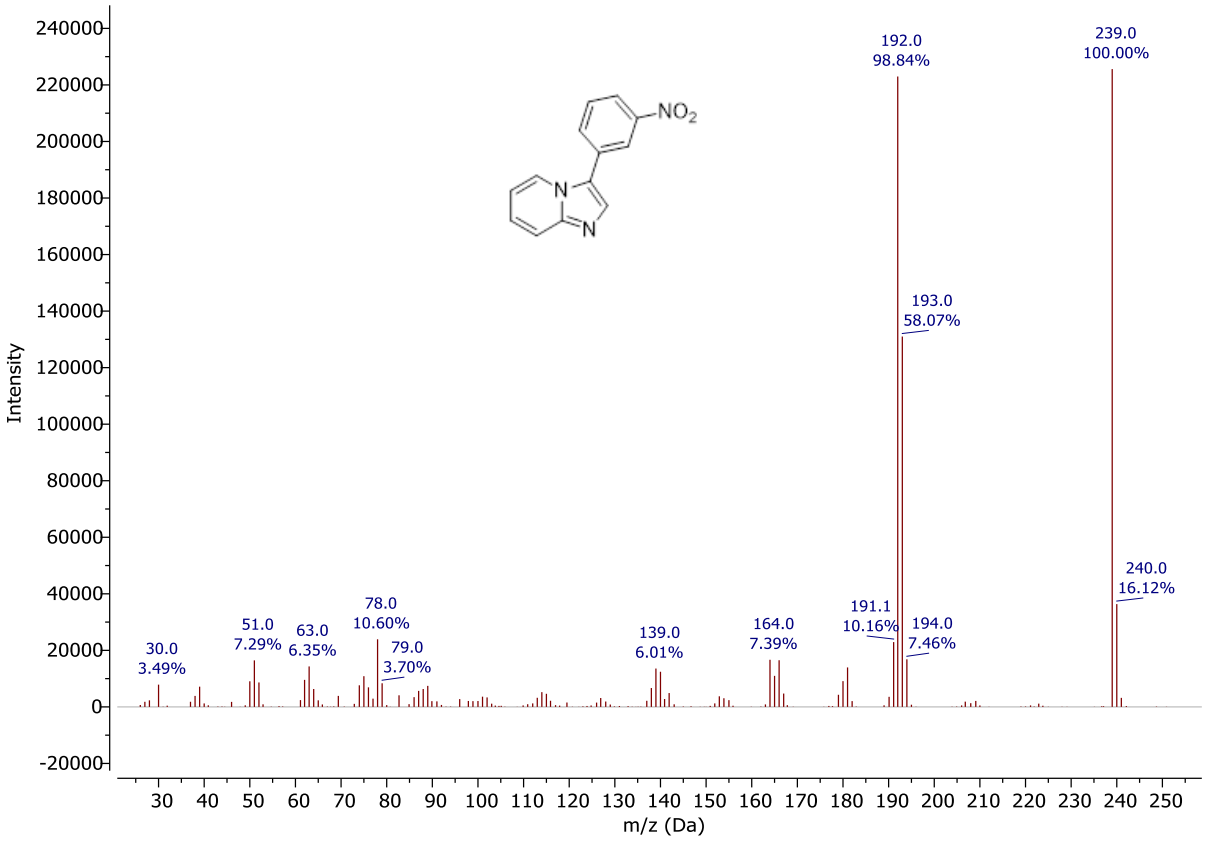


^{1}H/^{1}H COSY NMR Spectrum of (**15**) (400 MHz, DMSO-d^{6}):

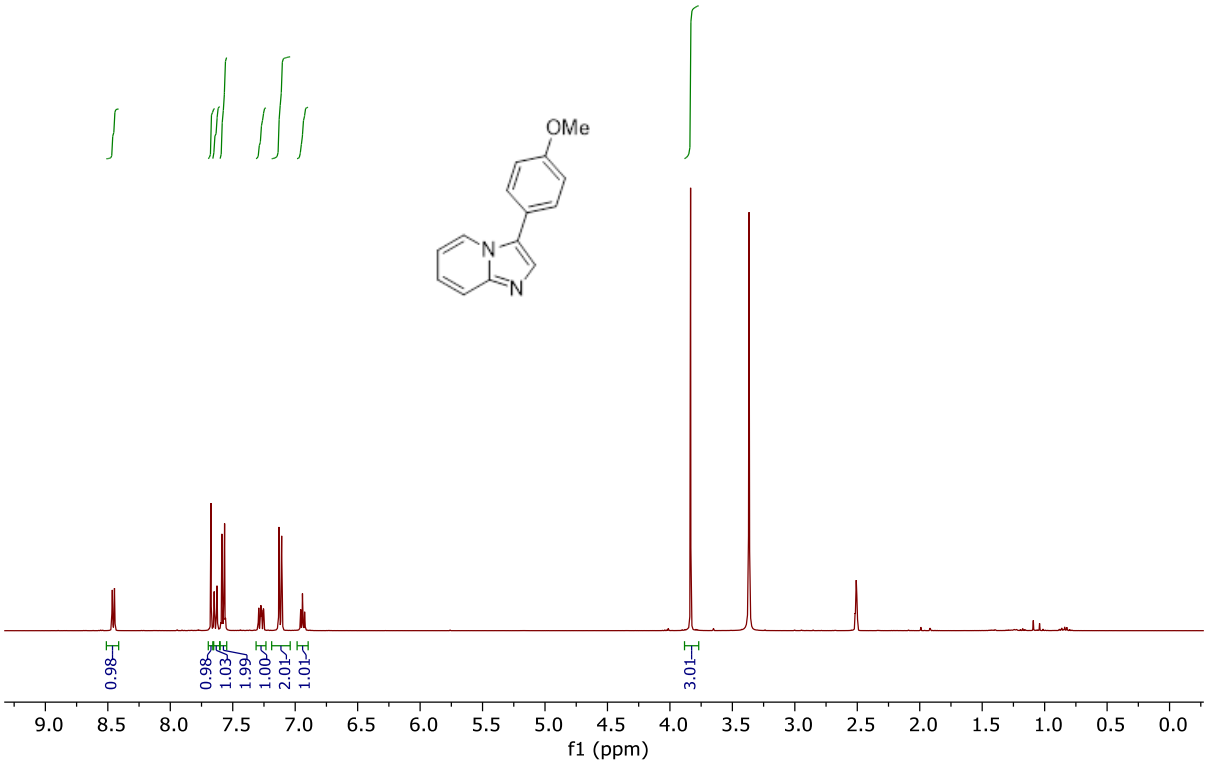


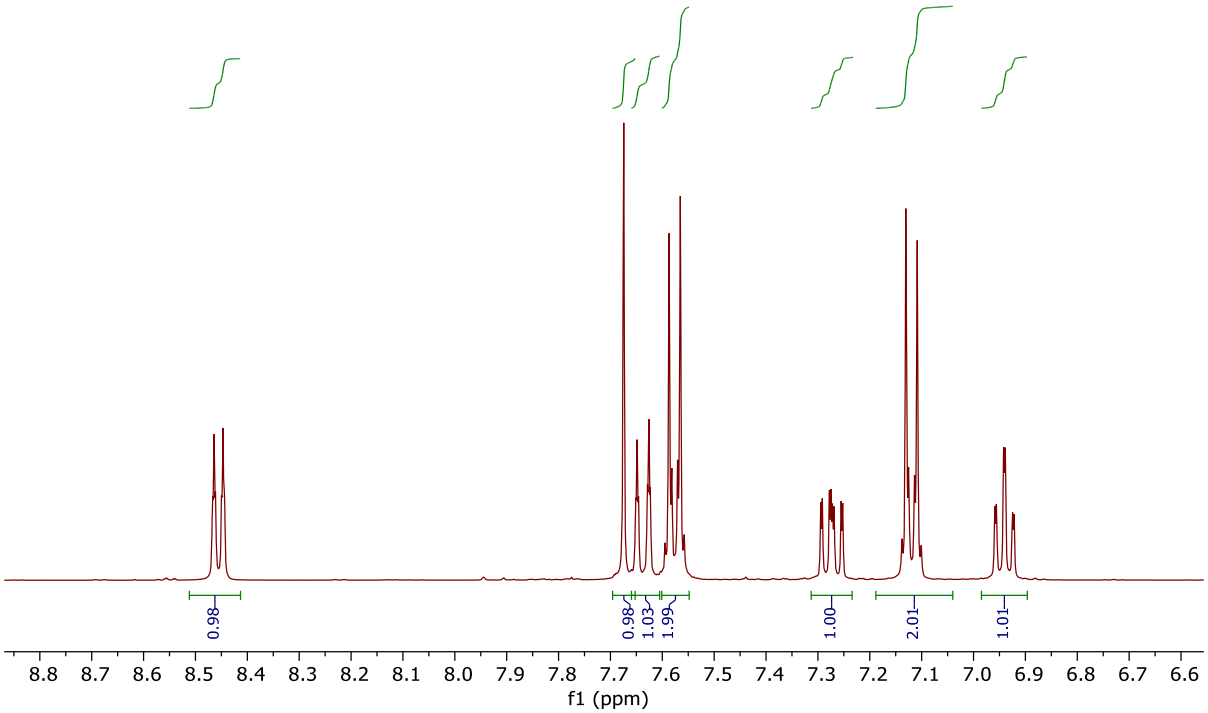


MS Spectrum of (**15**) (EI):

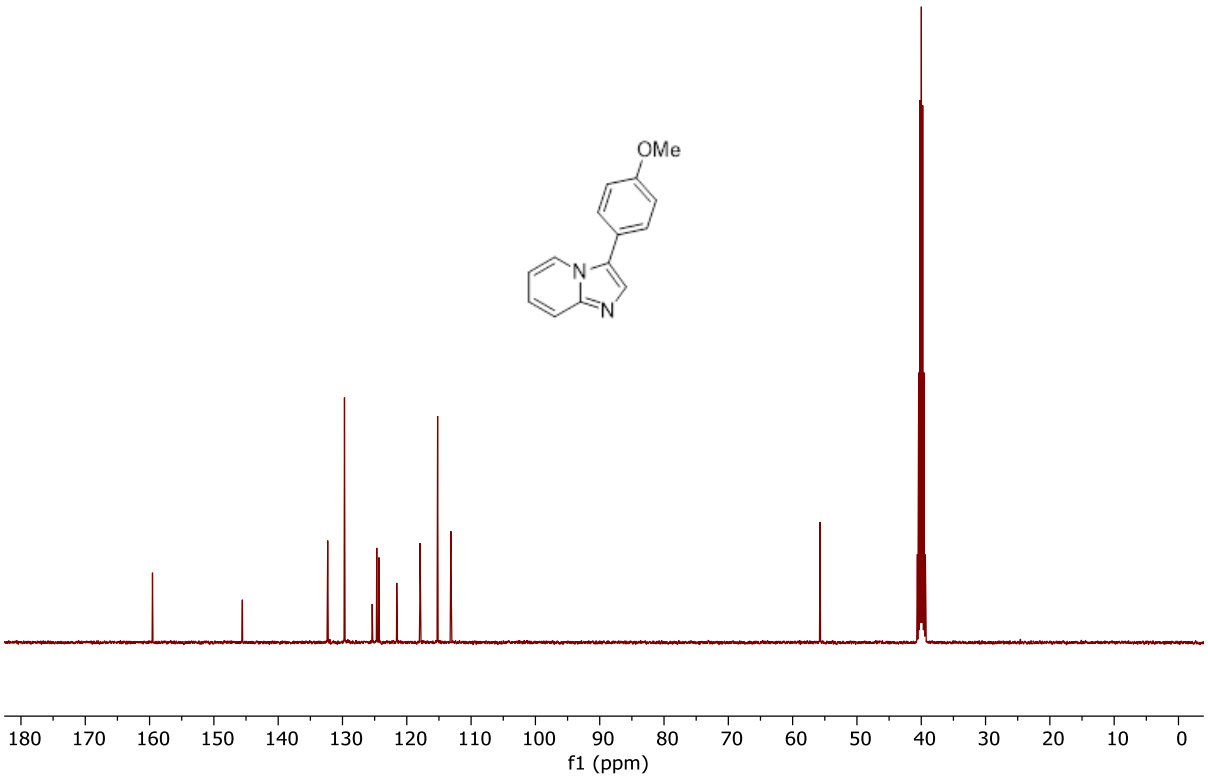


^{1}H NMR Spectrum of (**16**) (400 MHz, DMSO-d^{6}):

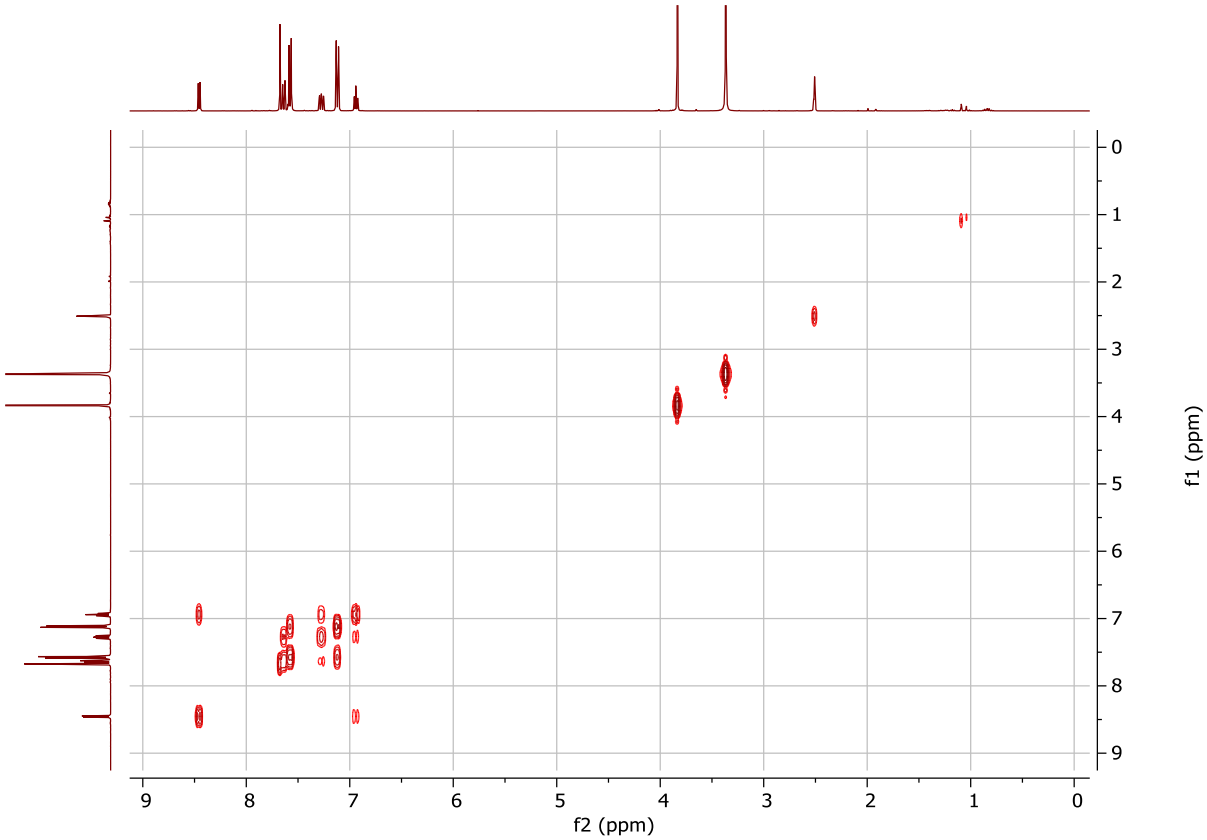


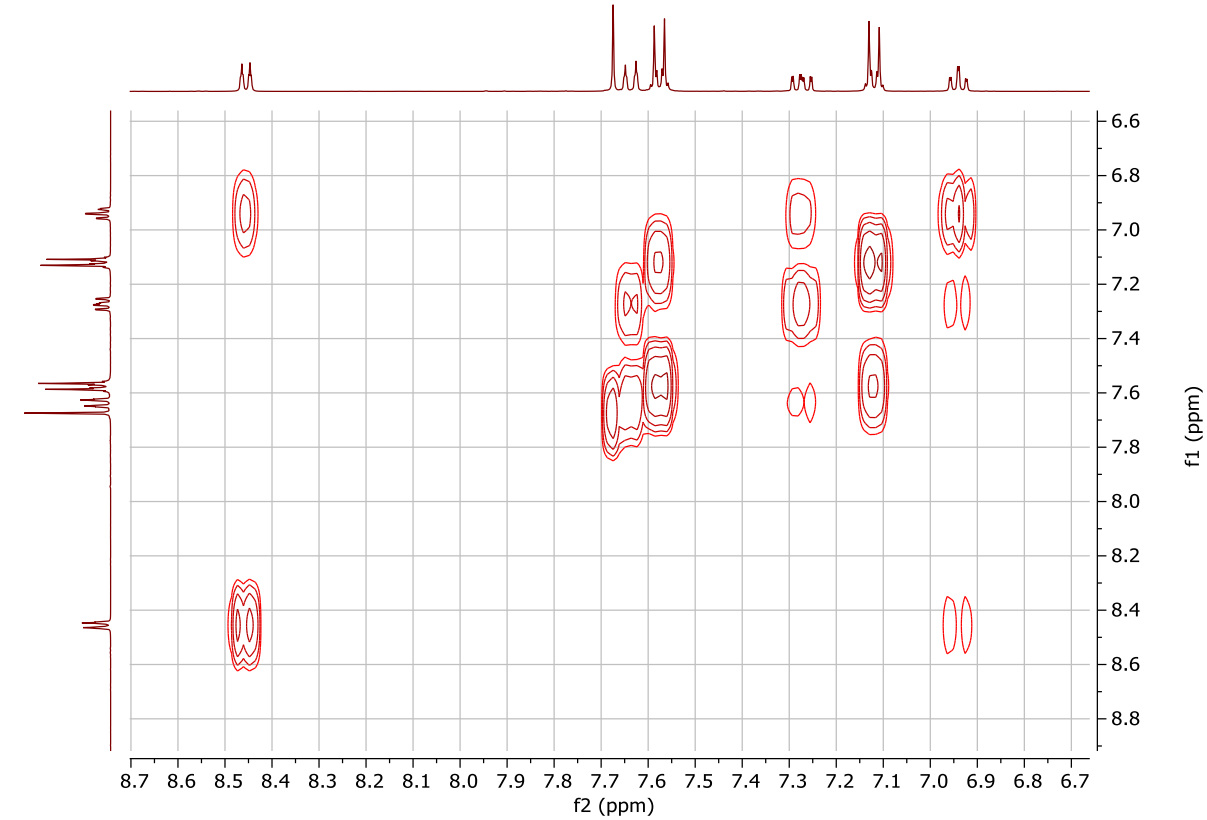


^{13}C NMR Spectrum of (**16**) (400 MHz, DMSO-d^{6}):

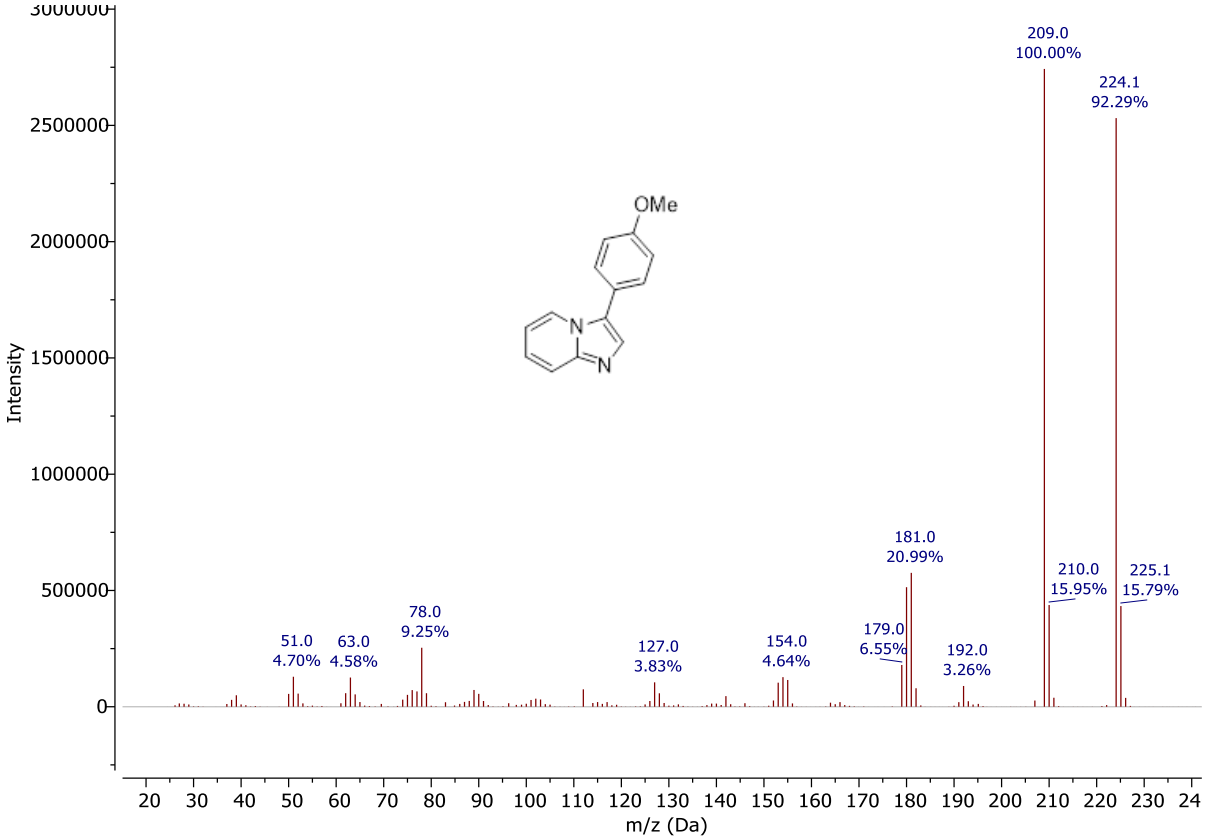


^{1}H/^{1}H COSY NMR Spectrum of (**16**) (400 MHz, DMSO-d^{6}):

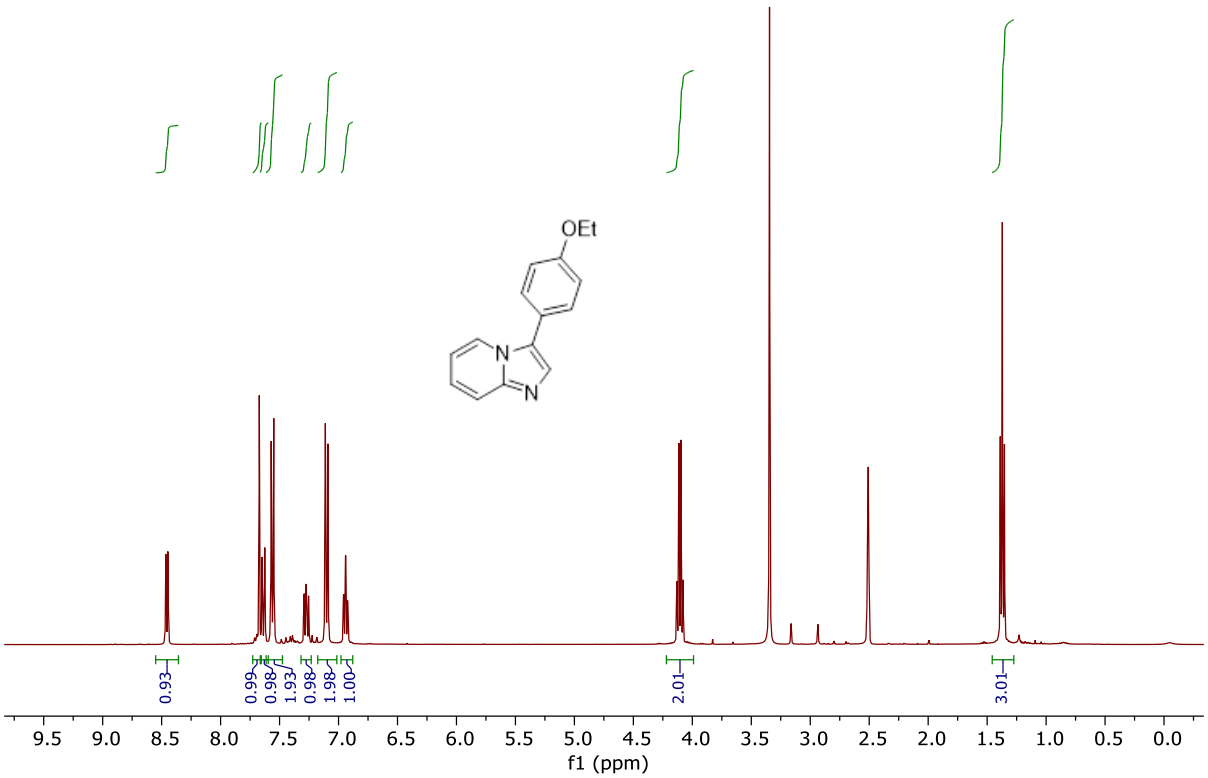


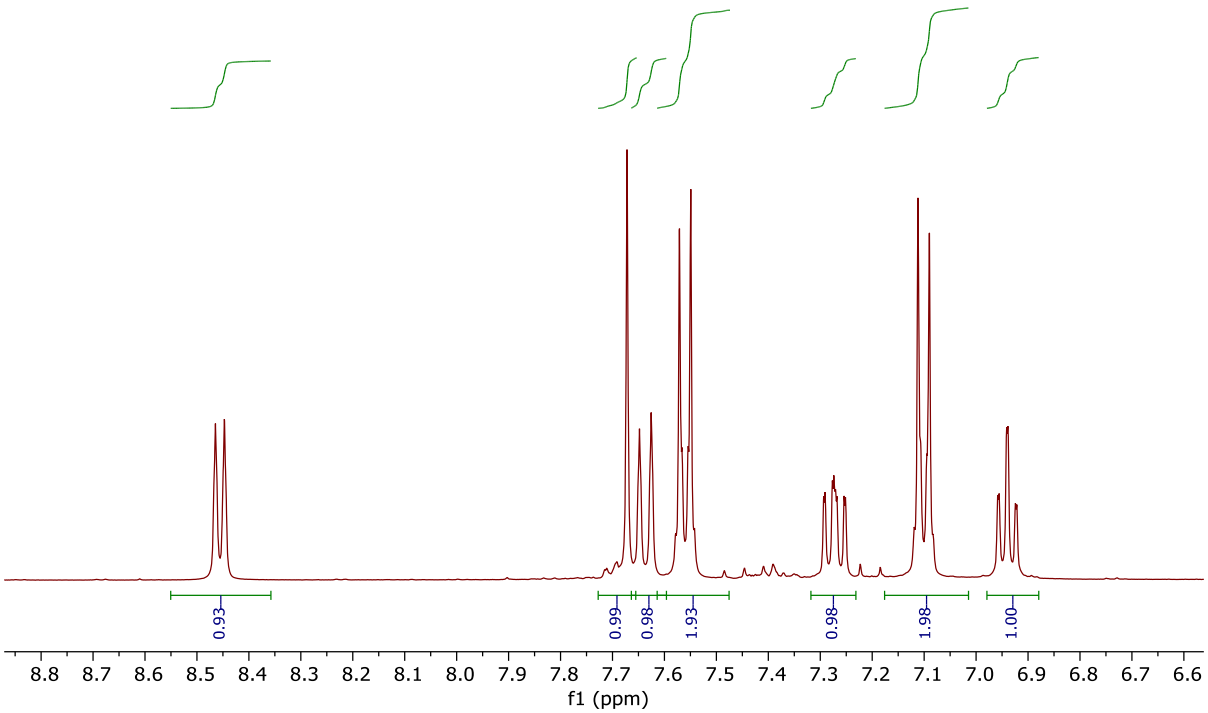


MS Spectrum of (**16**) (EI):

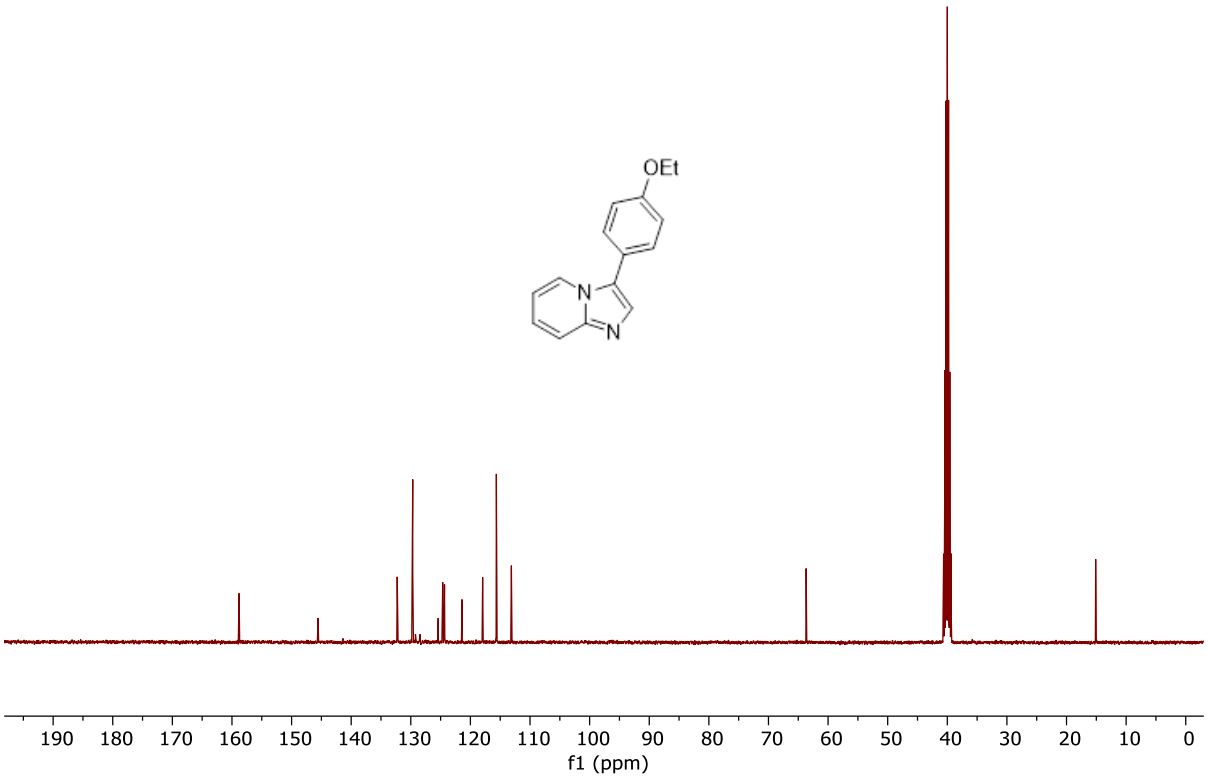


^{1}H NMR Spectrum of (**17**) (400 MHz, DMSO-d^{6}):

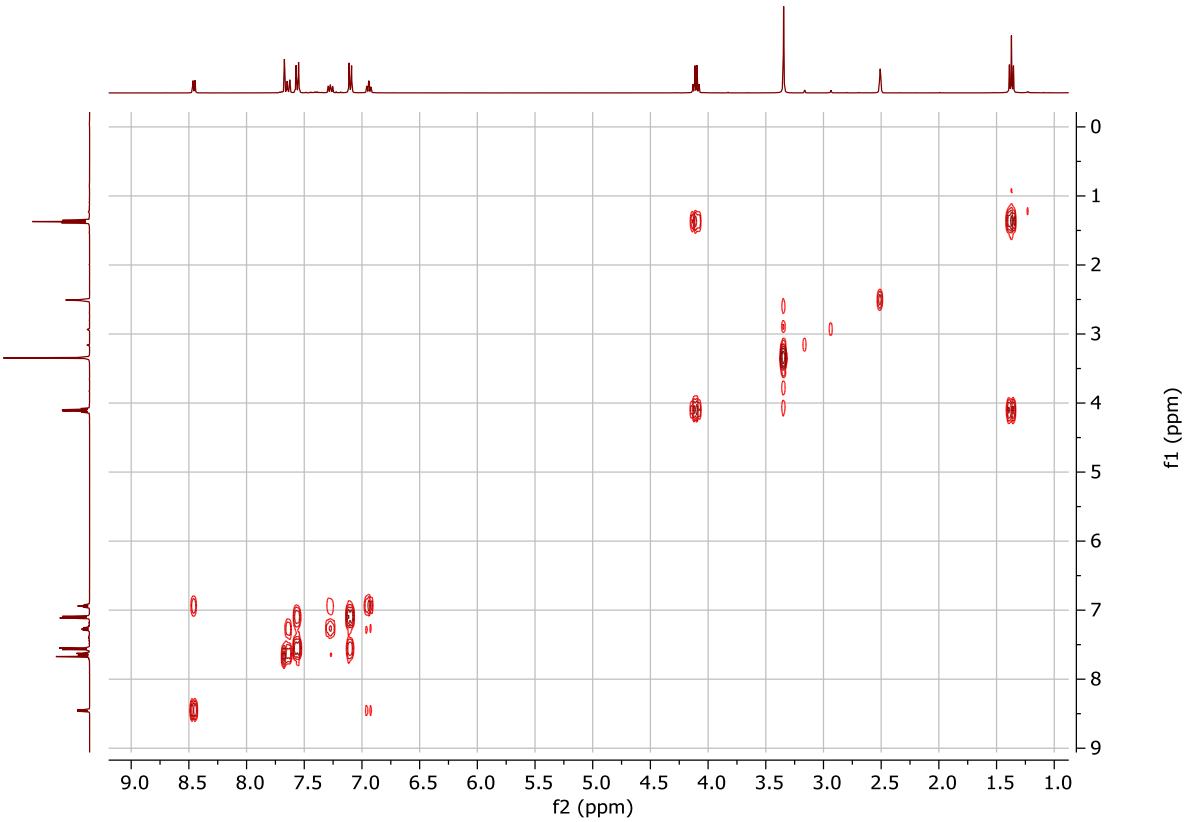


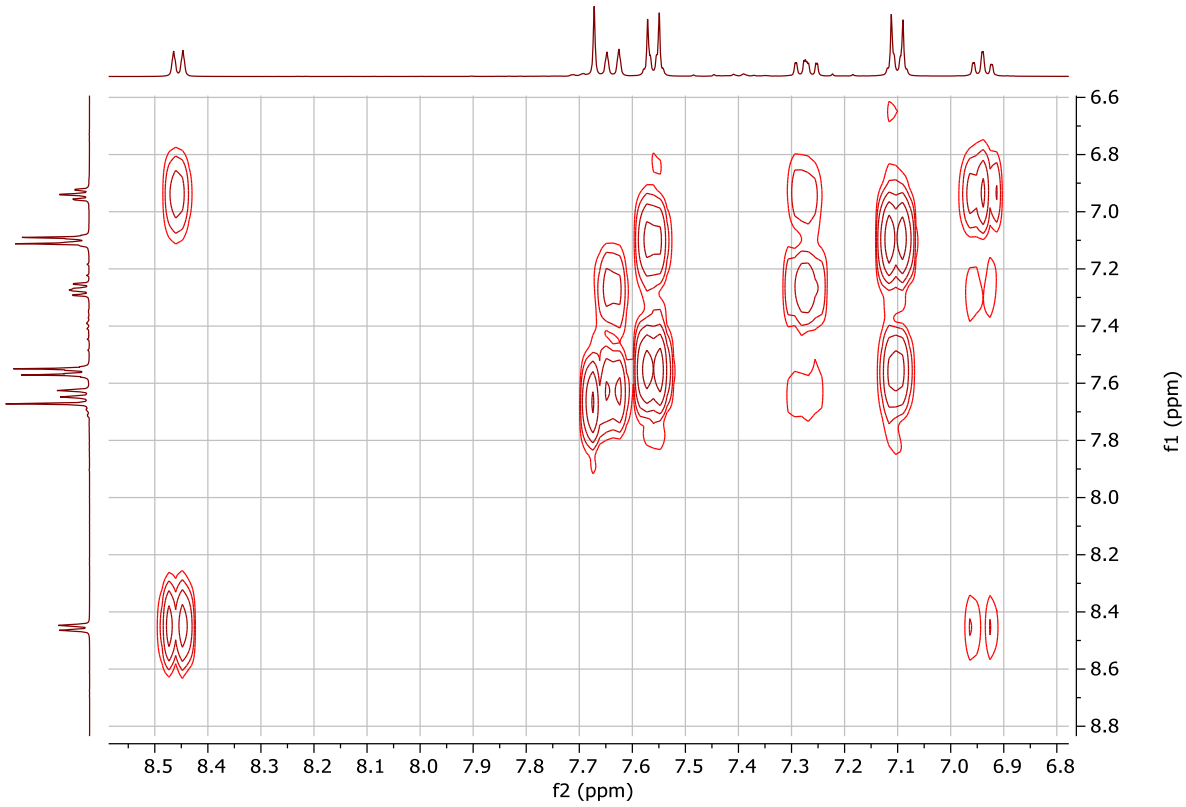


^{13}C NMR Spectrum of (**17**) (400 MHz, DMSO-d^{6}):

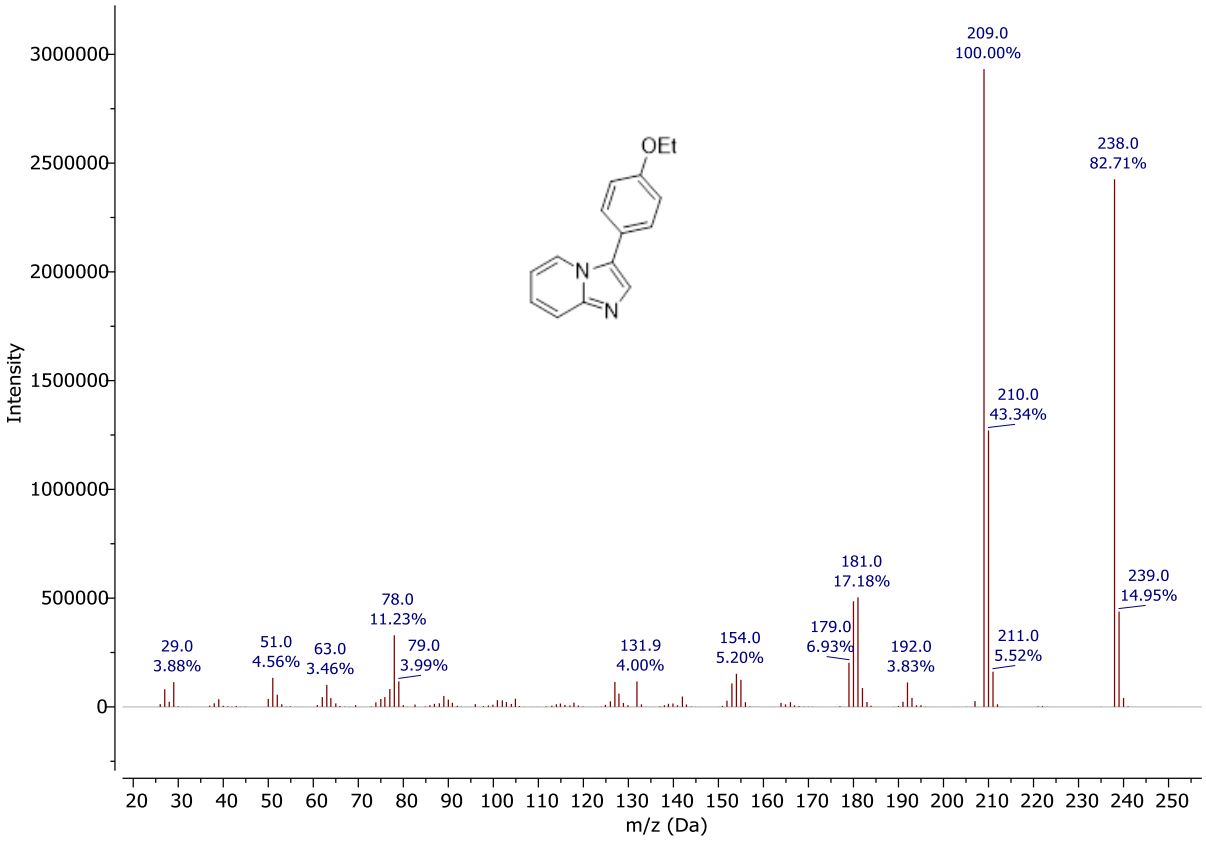


^{1}H/^{1}H COSY NMR Spectrum of (**17**) (400 MHz, DMSO-d^{6}):

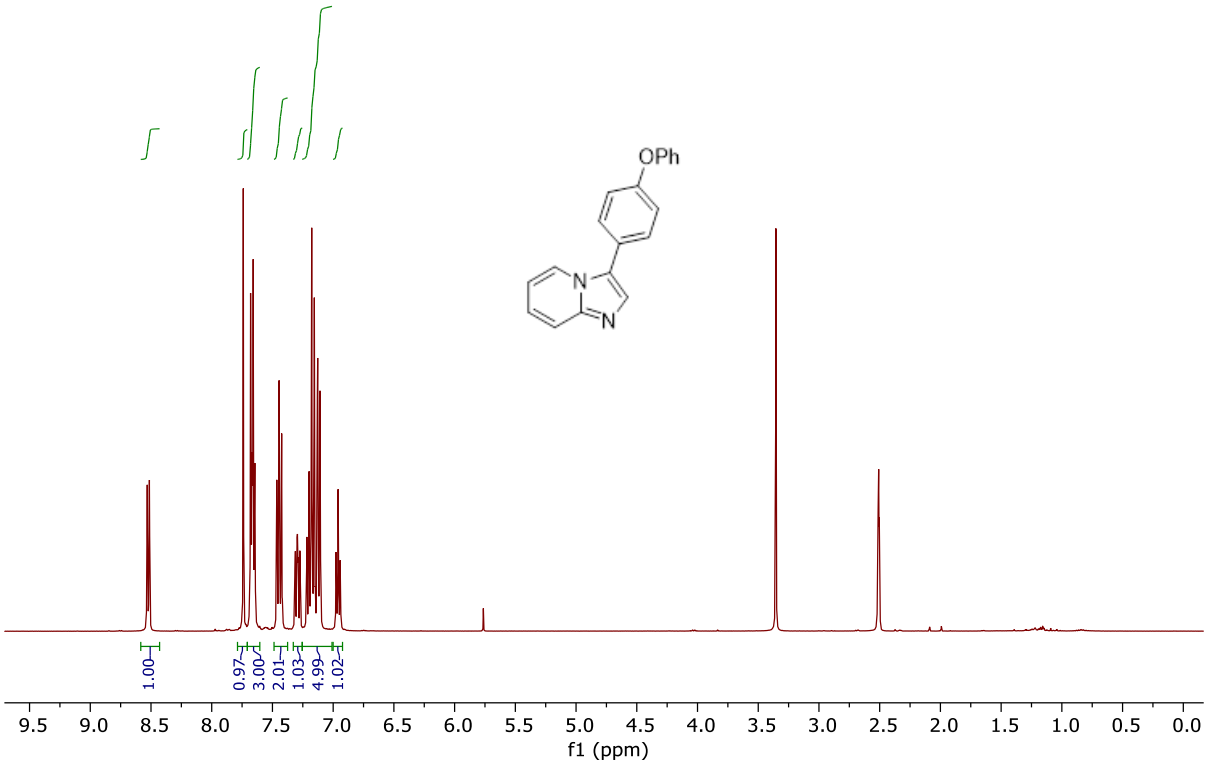


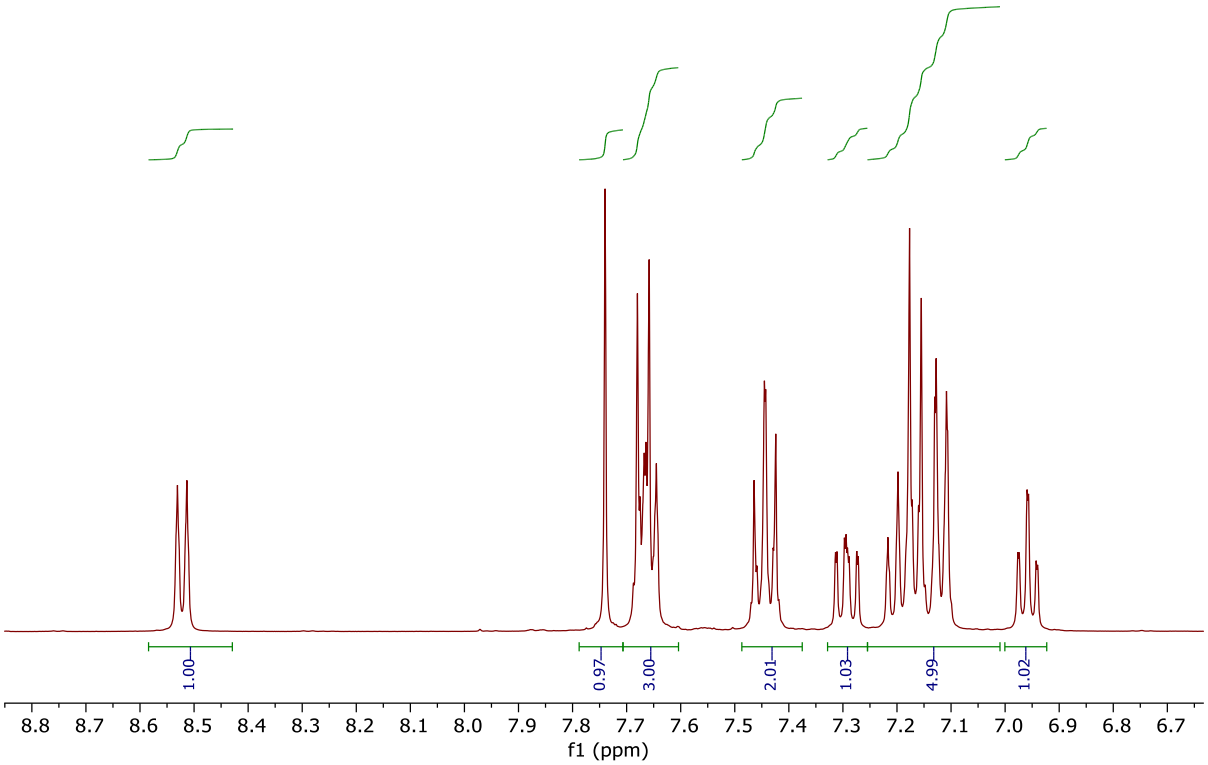


MS Spectrum of (**17**) (EI):

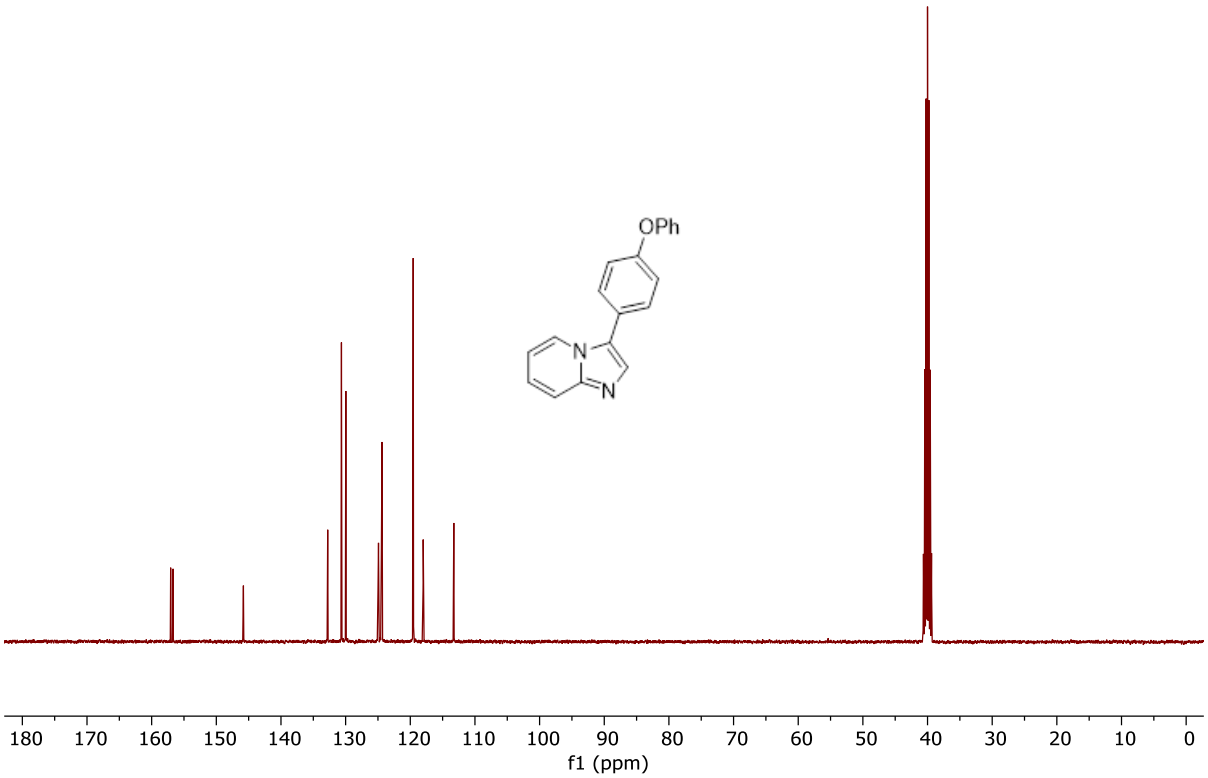


^{1}H NMR Spectrum of (**18**) (400 MHz, DMSO-d^{6}):

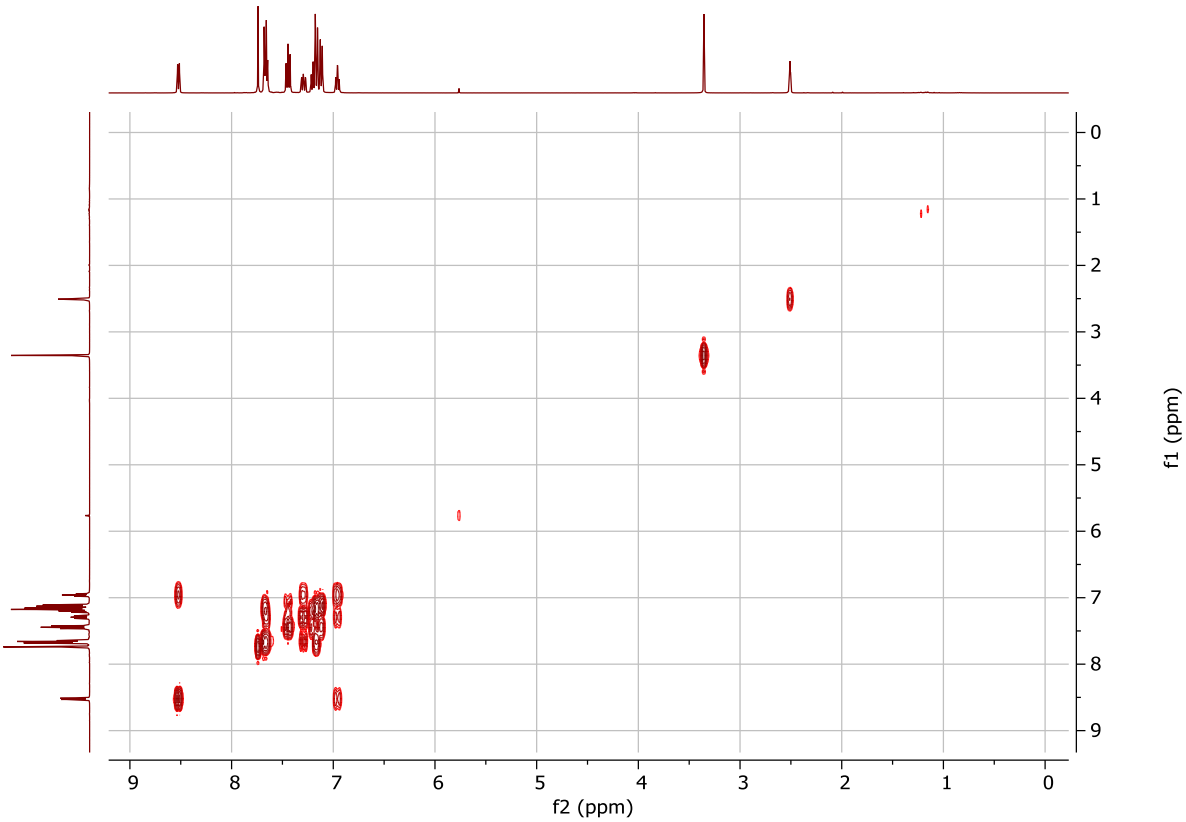


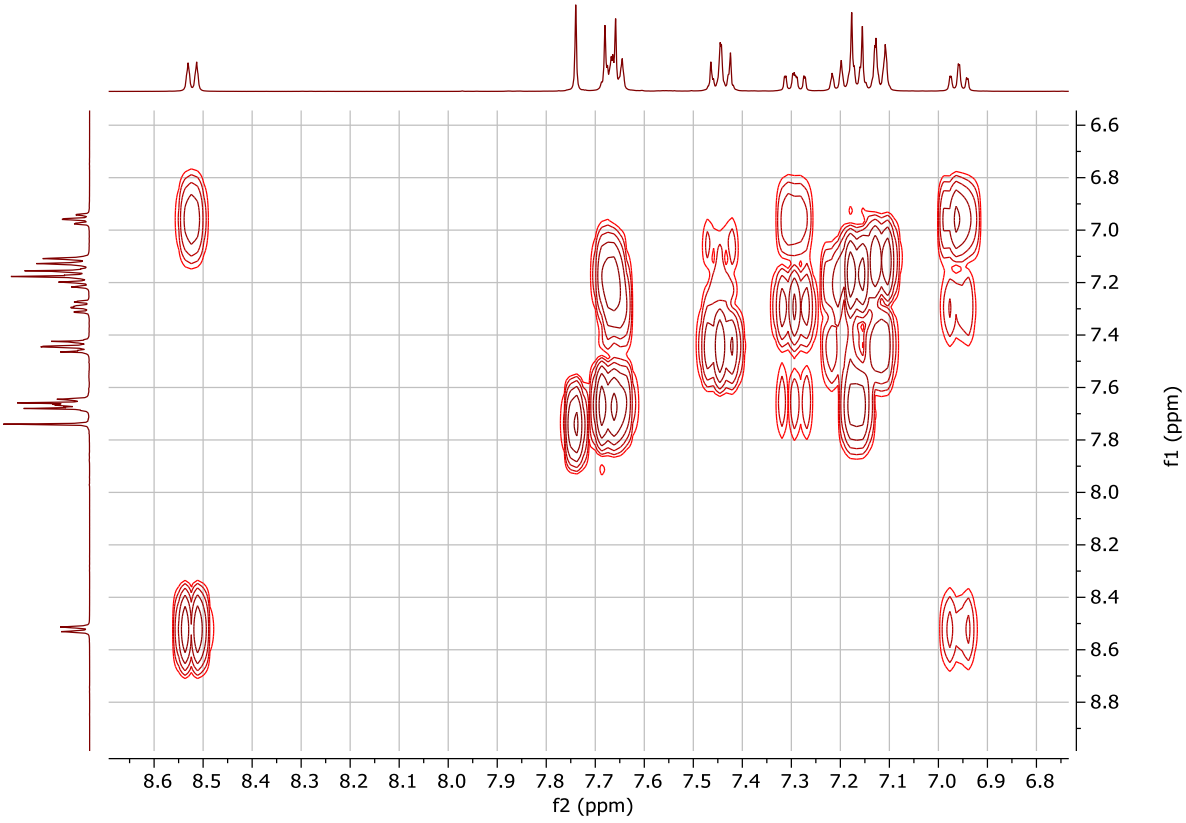


^{13}C NMR Spectrum of (**18**) (400 MHz, DMSO-d^{6}):

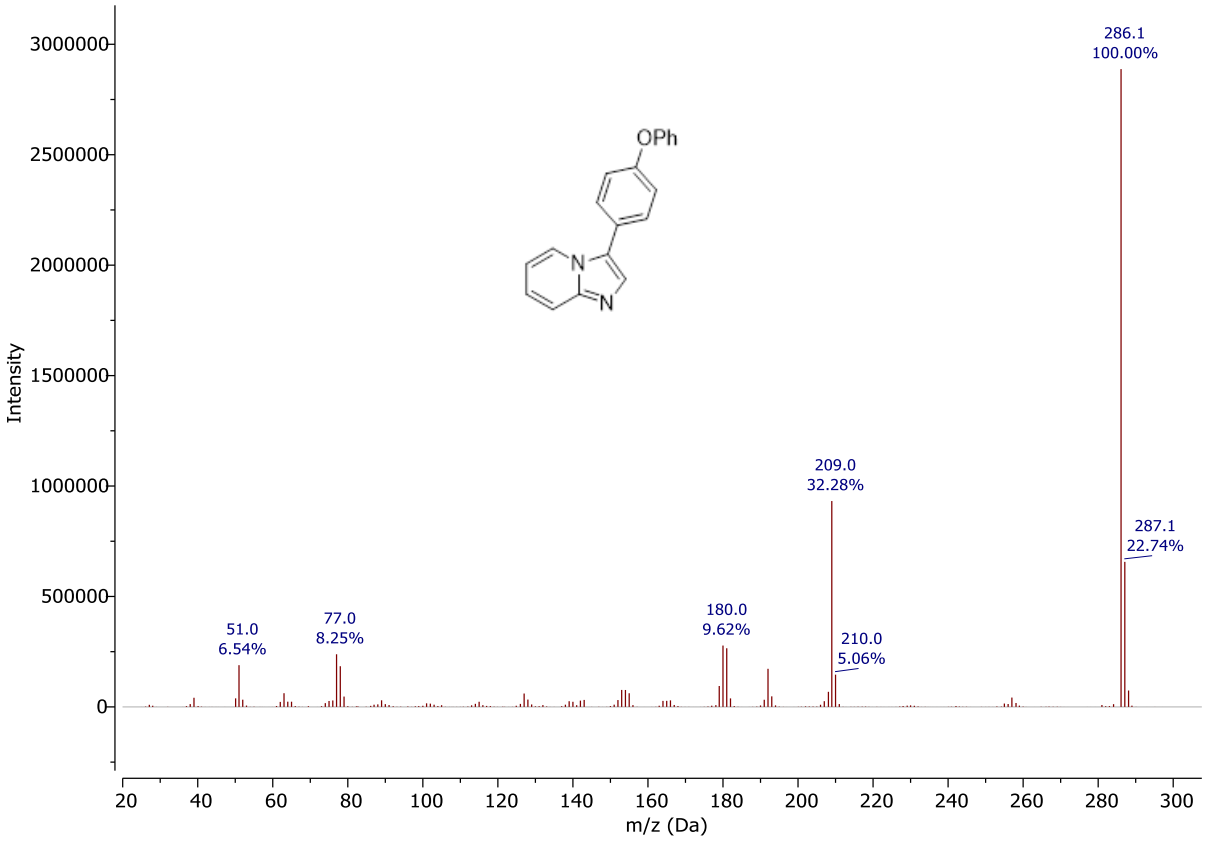


^{1}H/^{1}H COSY NMR Spectrum of (**18**) (400 MHz, DMSO-d^{6}):

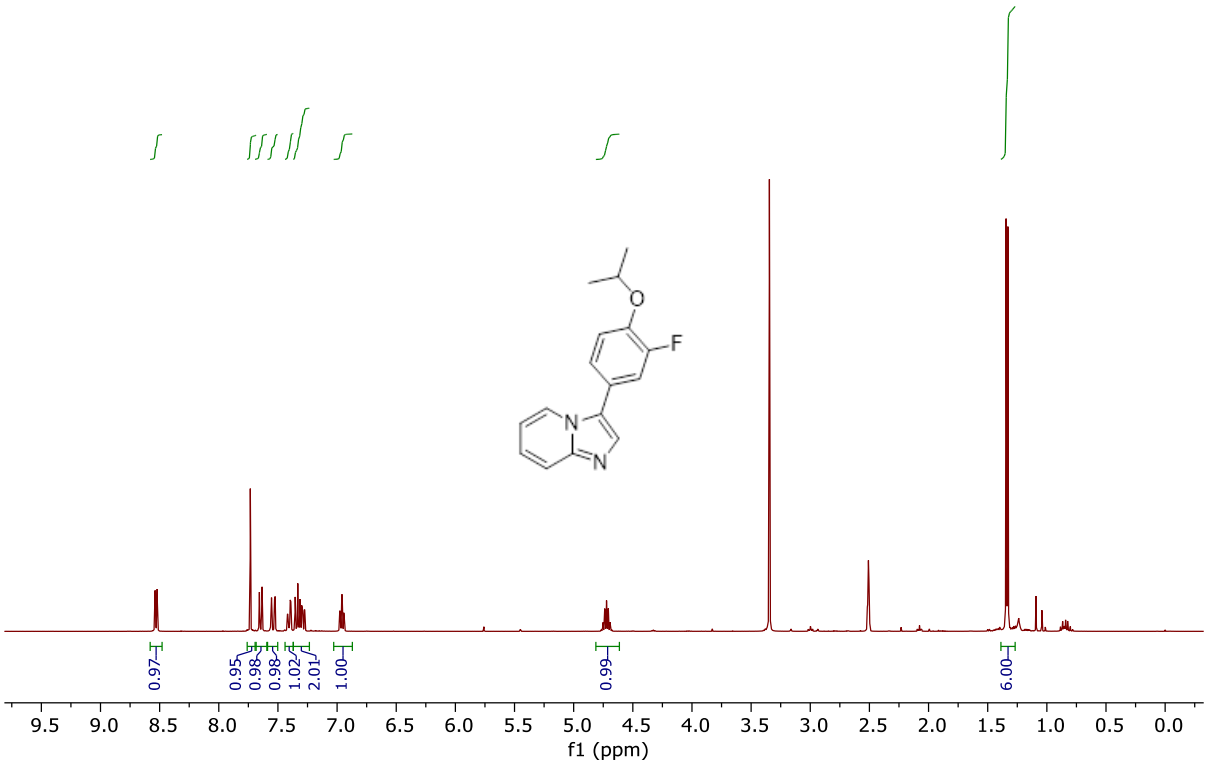


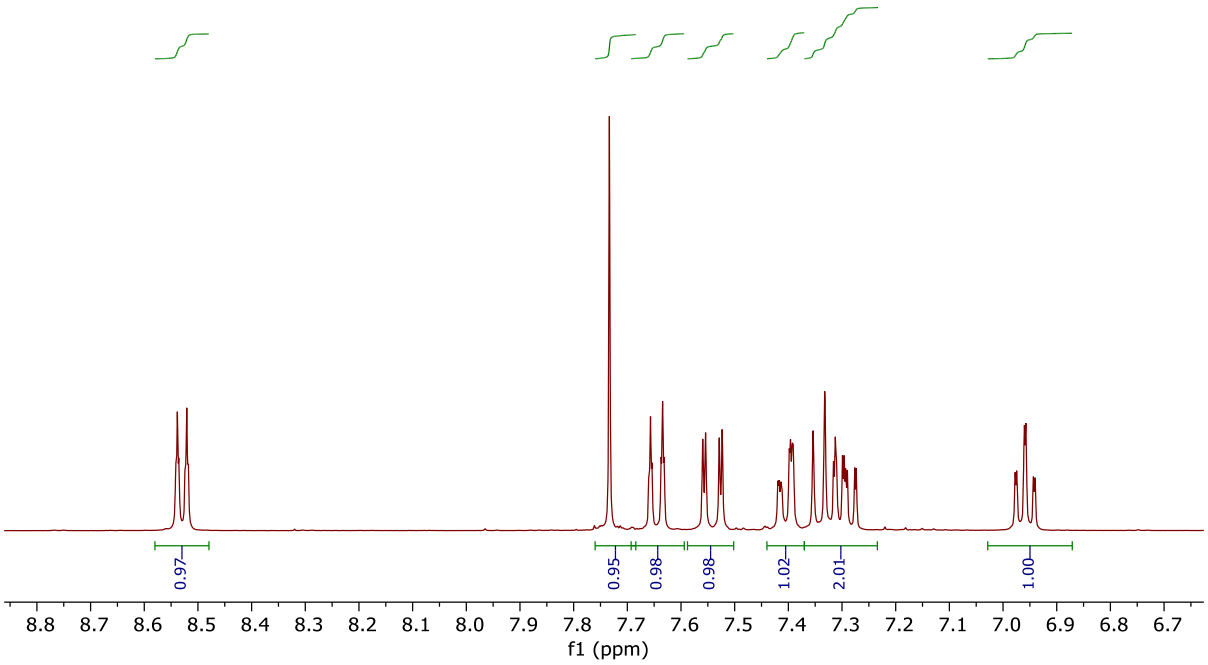


MS Spectrum of (**18**) (EI):

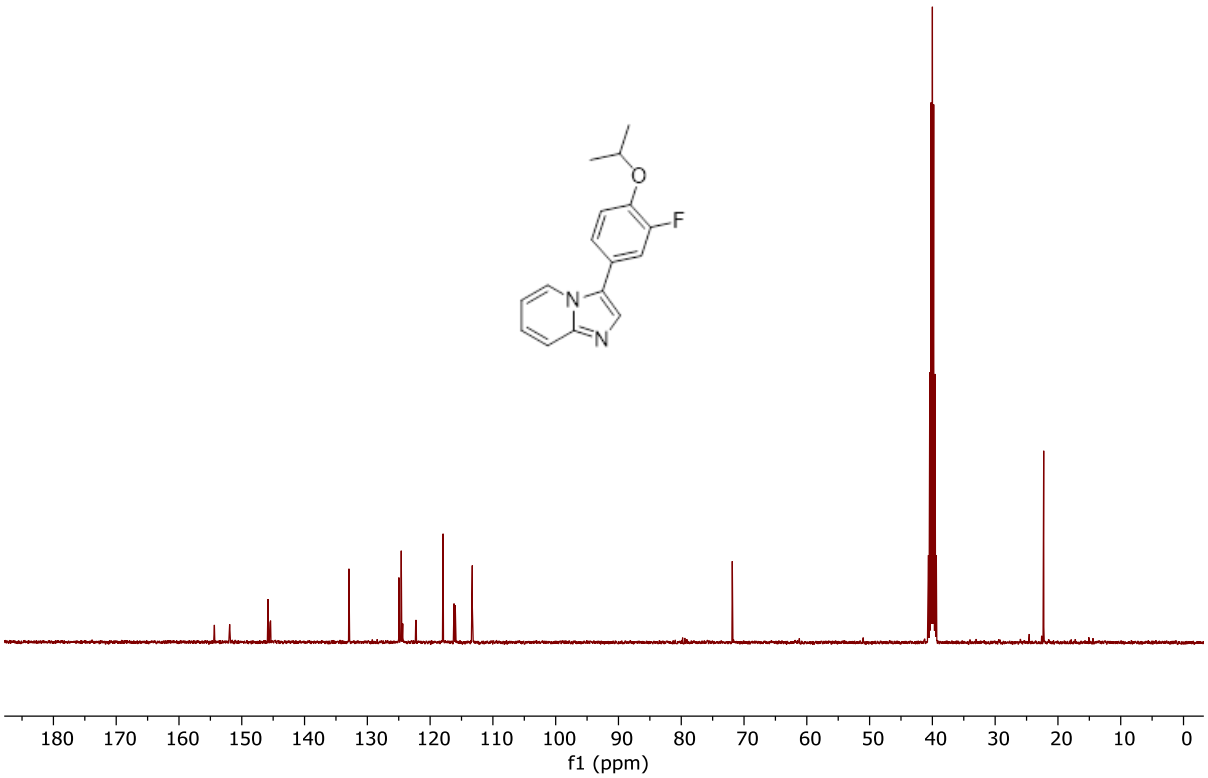


^{1}H NMR Spectrum of (**19**) (400 MHz, DMSO-d^{6}):

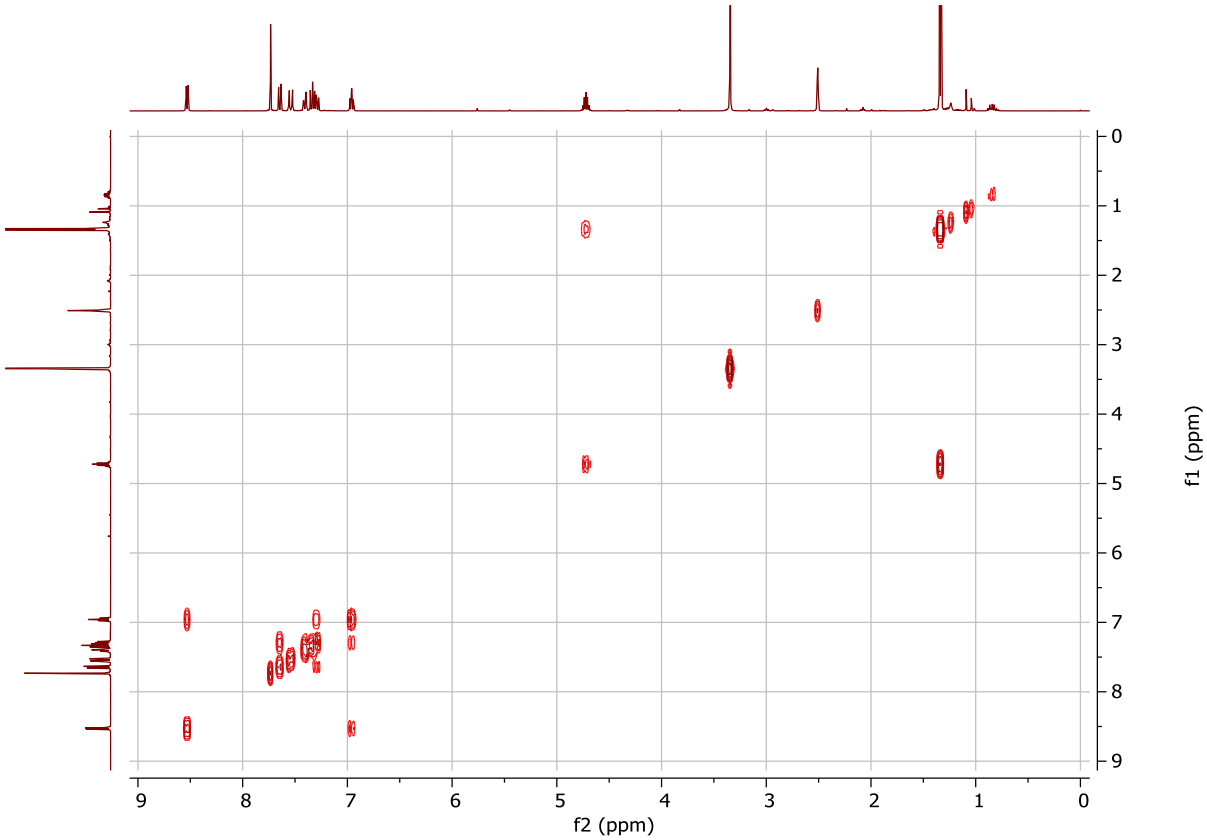


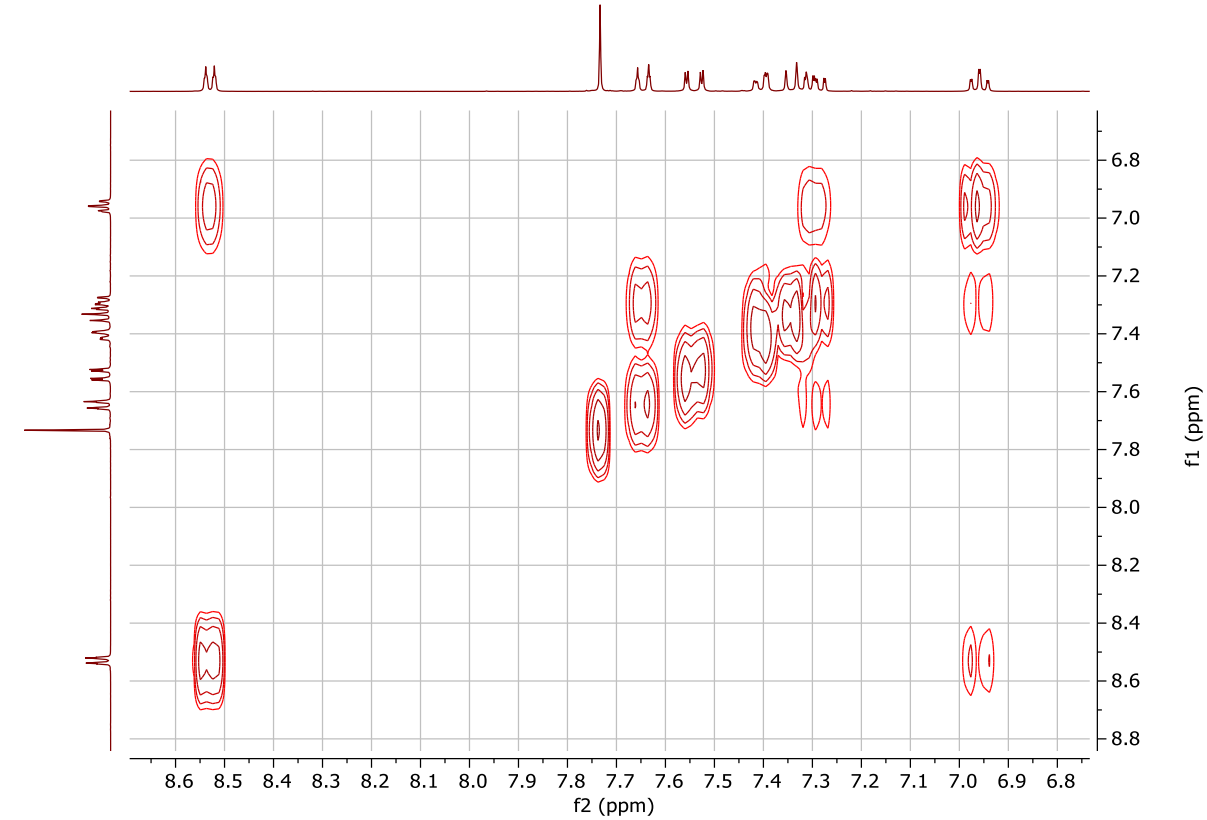


^{13}C NMR Spectrum of (**19**) (400 MHz, DMSO-d^{6}):

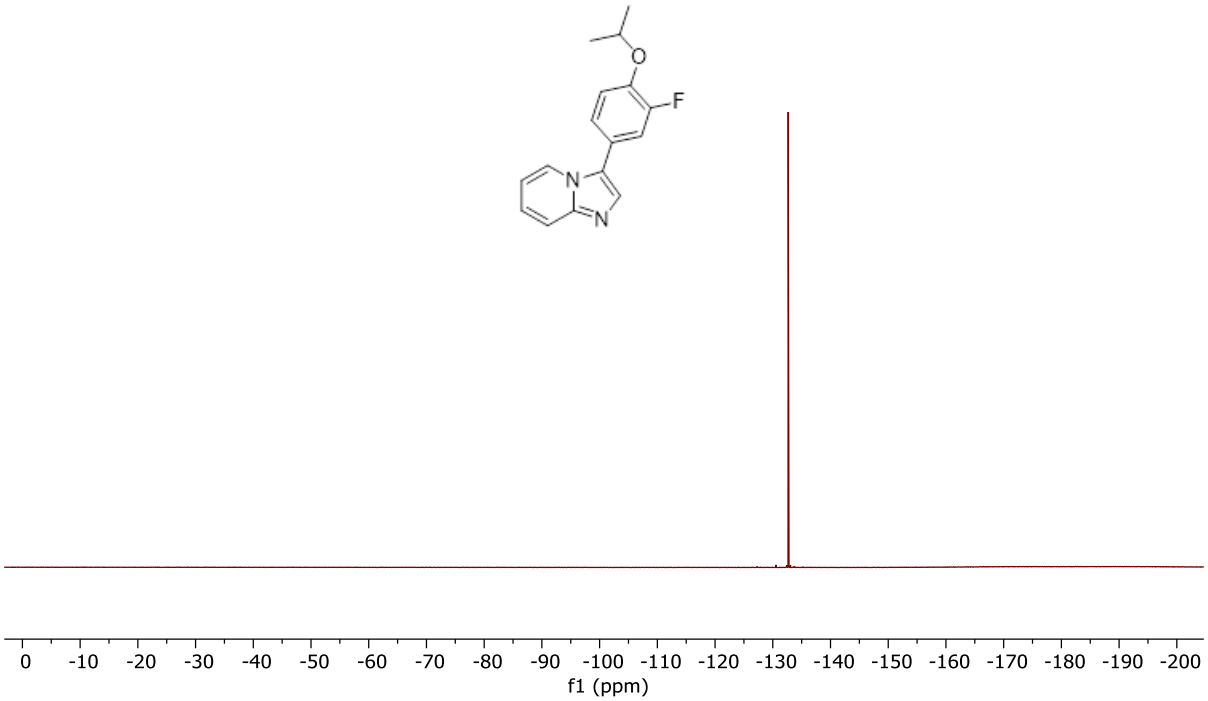


^{1}H/^{1}H COSY NMR Spectrum of (**19**) (400 MHz, DMSO-d^{6}):

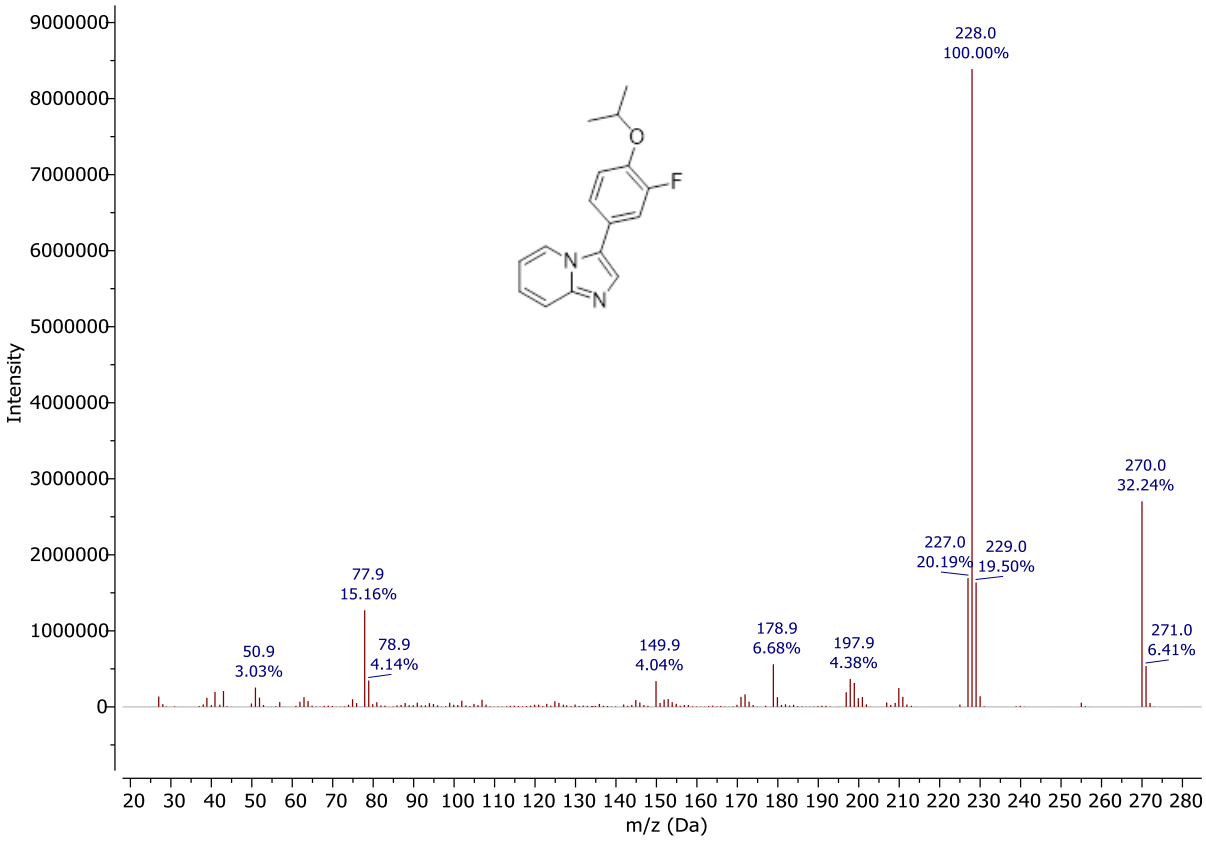




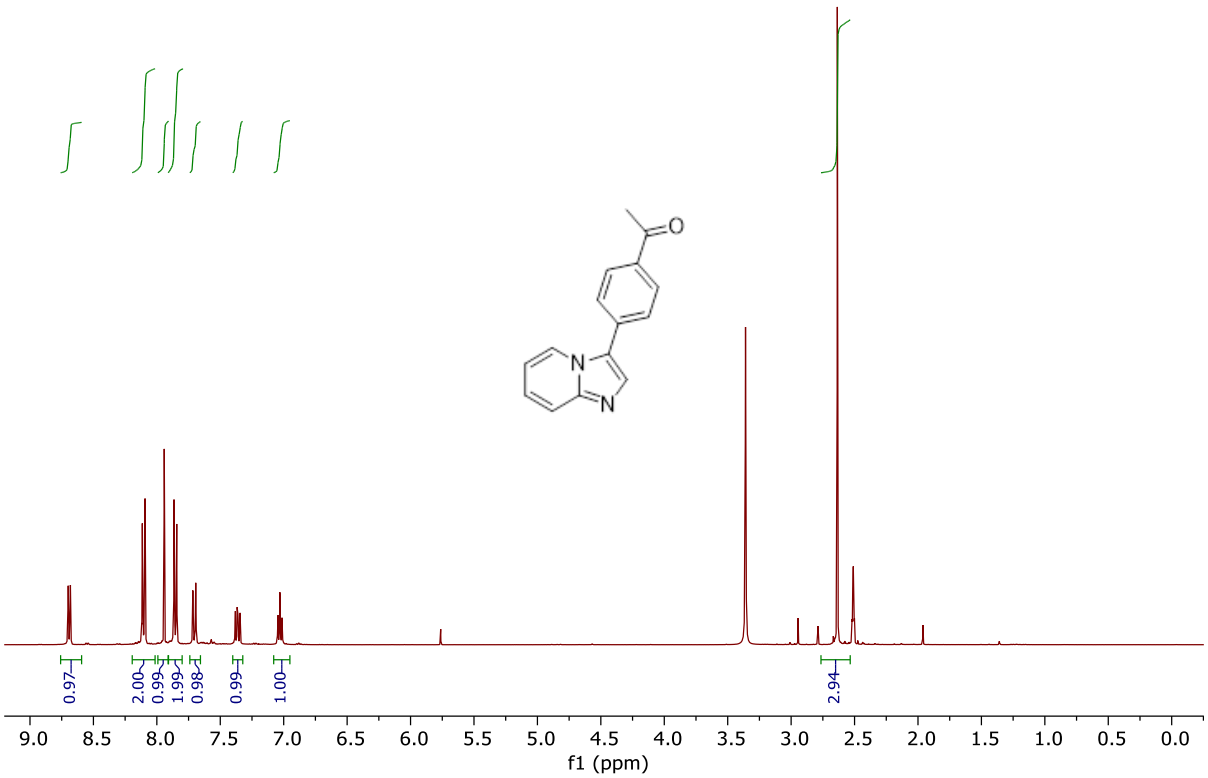
^{19}F NMR Spectrum of (**19**) (400 MHz, DMSO-d^{6}):

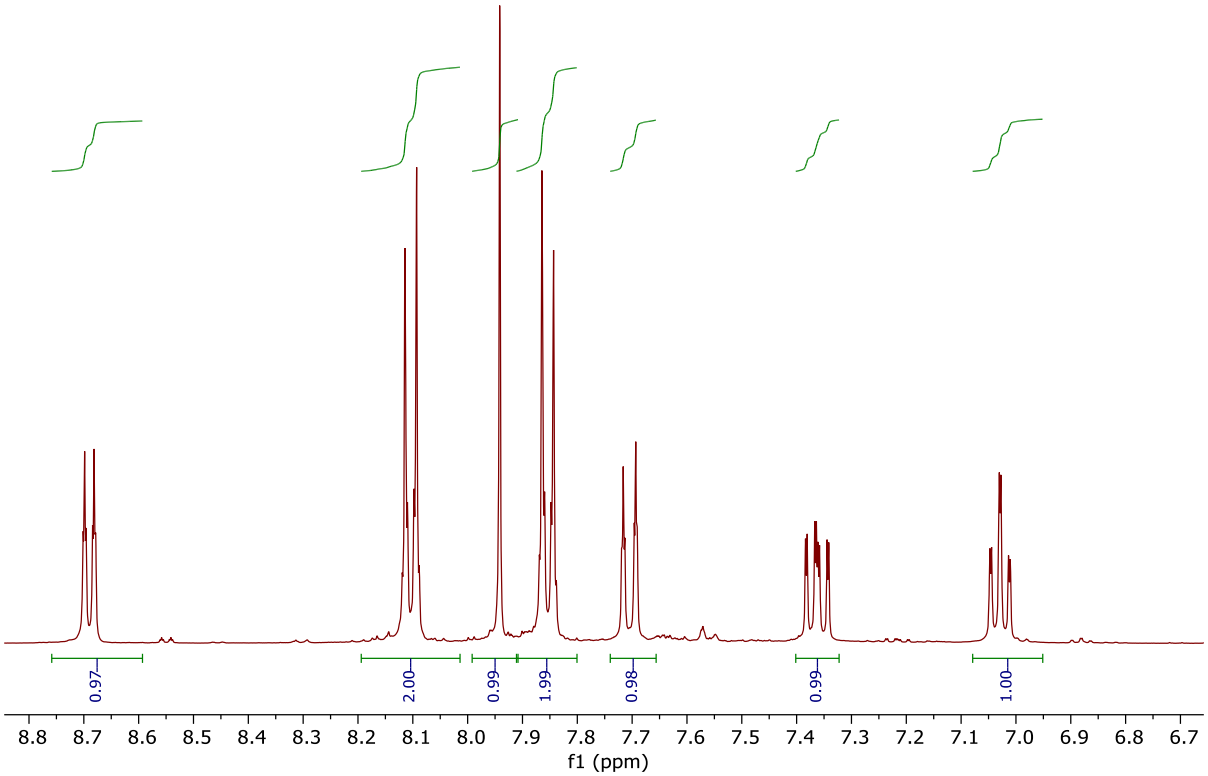


MS Spectrum of (**19**) (EI):

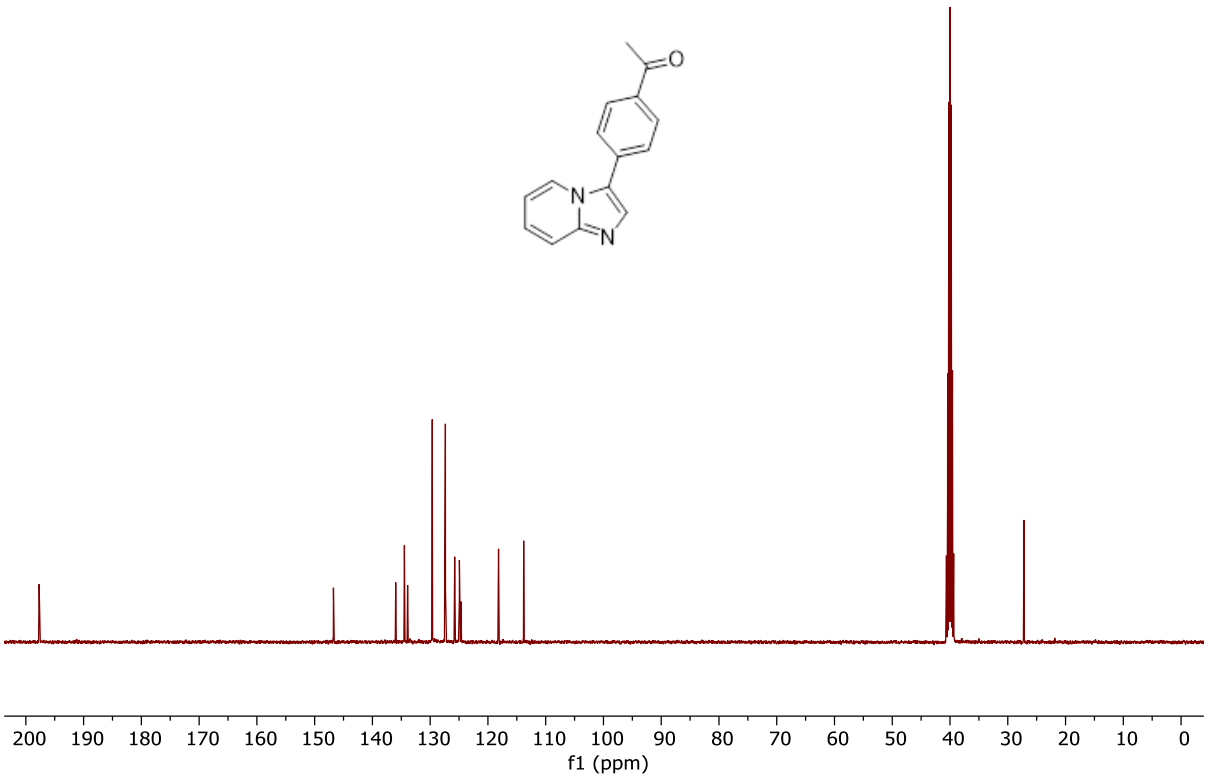


^{1}H NMR Spectrum of (**20**) (400 MHz, DMSO-d^{6}):

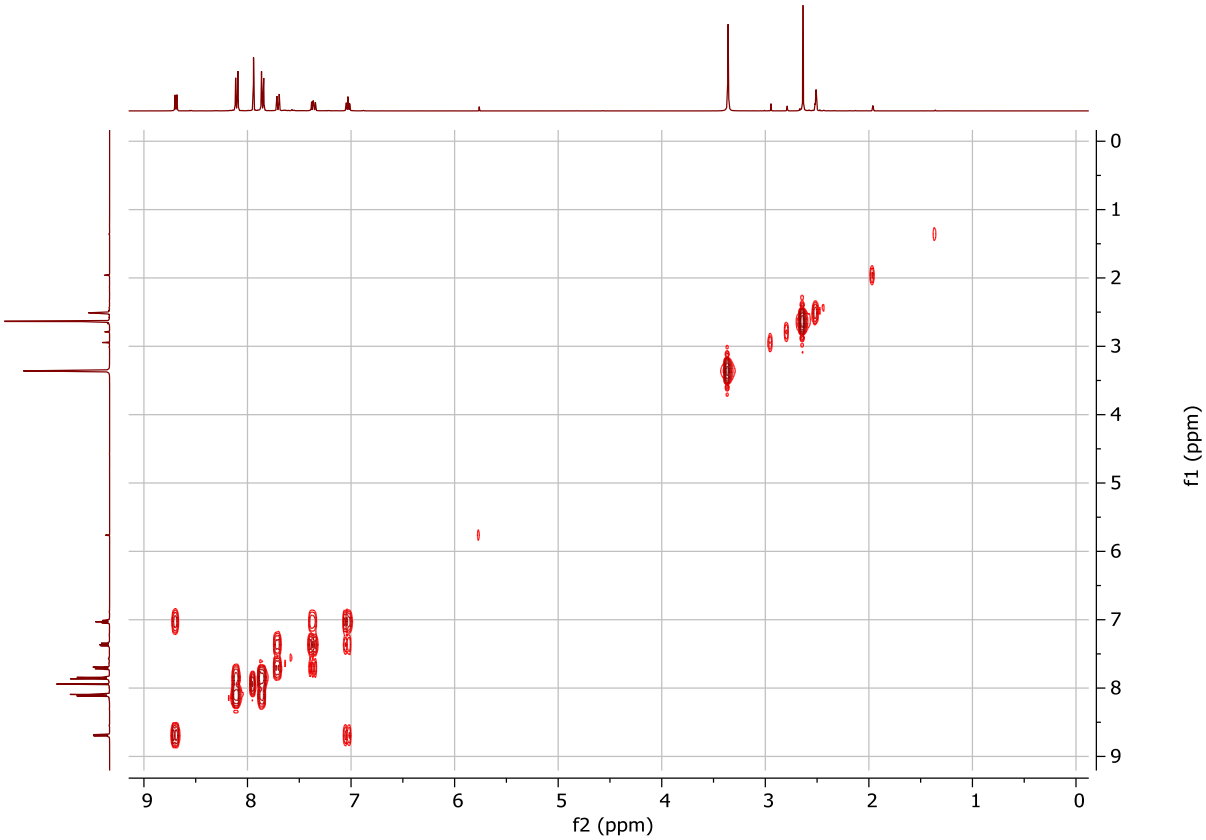


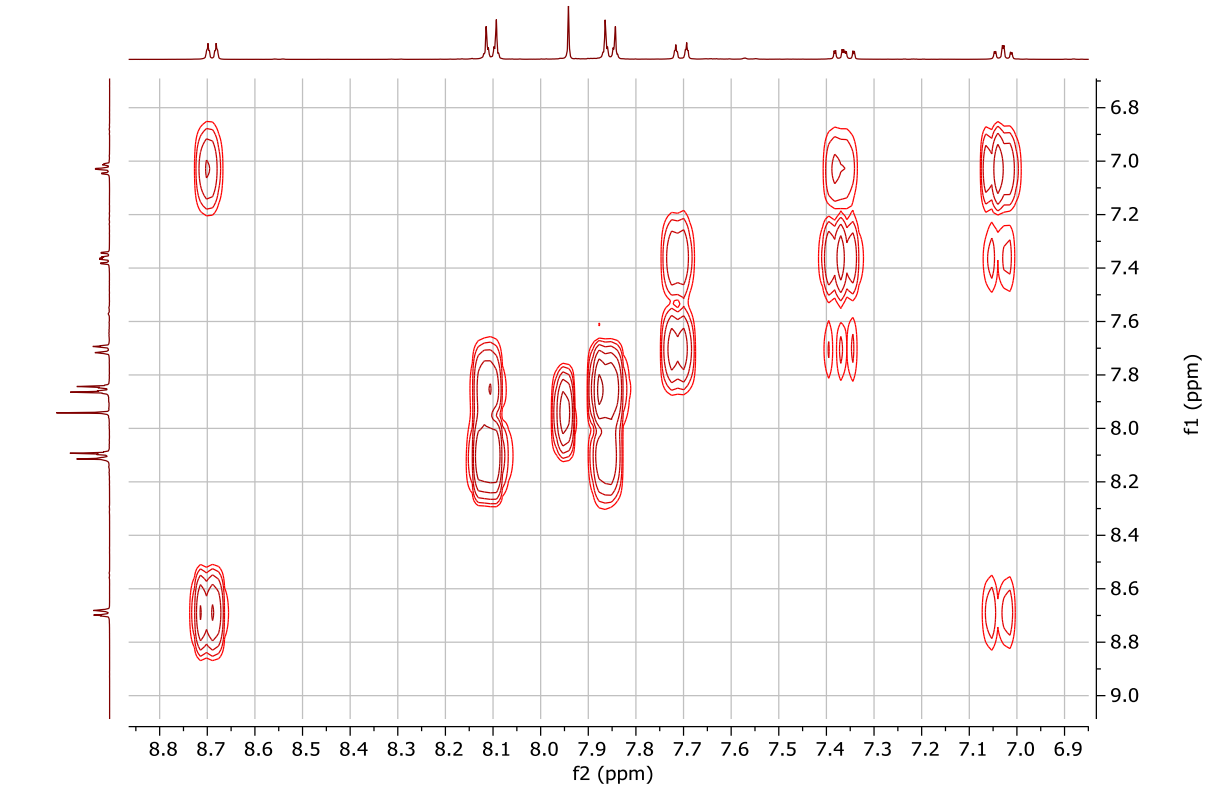


^{13}C NMR Spectrum of (**20**) (400 MHz, DMSO-d^{6}):

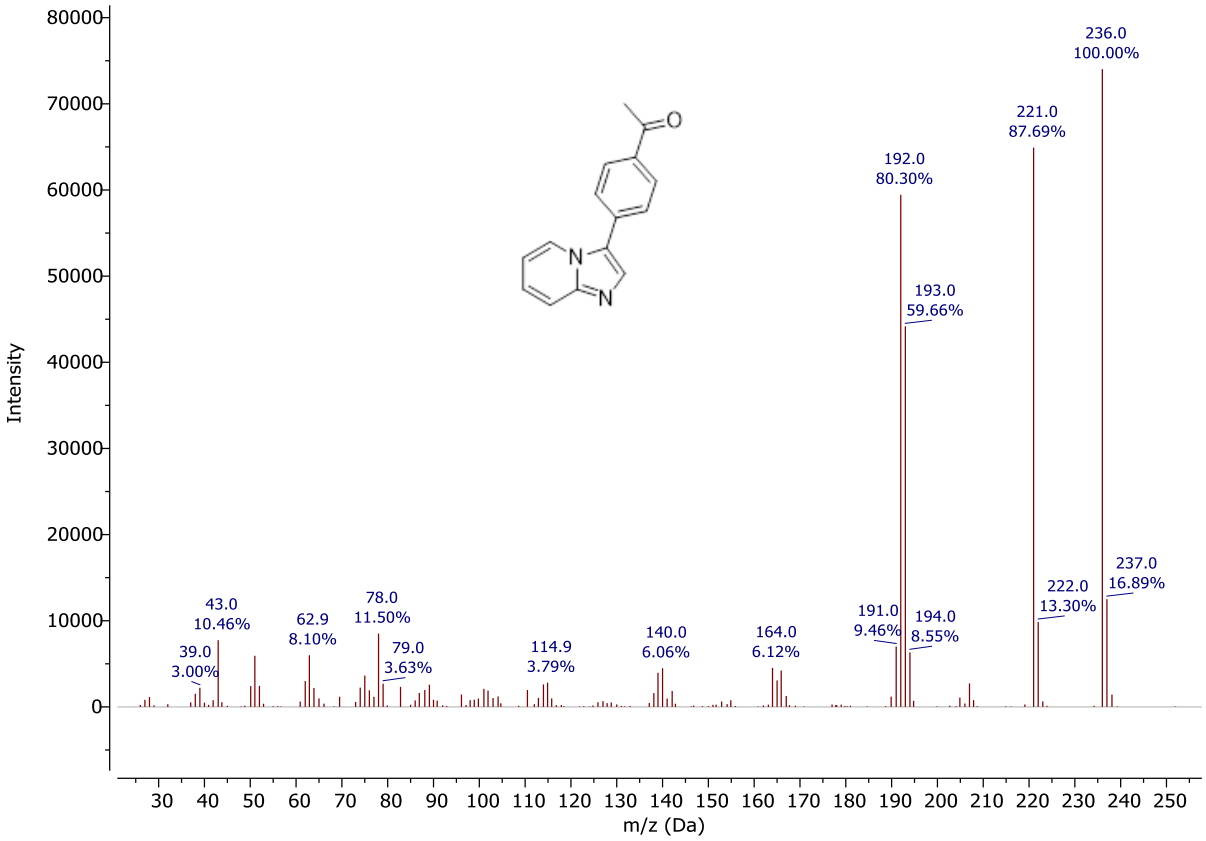


^{1}H/^{1}H COSY NMR Spectrum of (**20**) (400 MHz, DMSO-d^{6}):

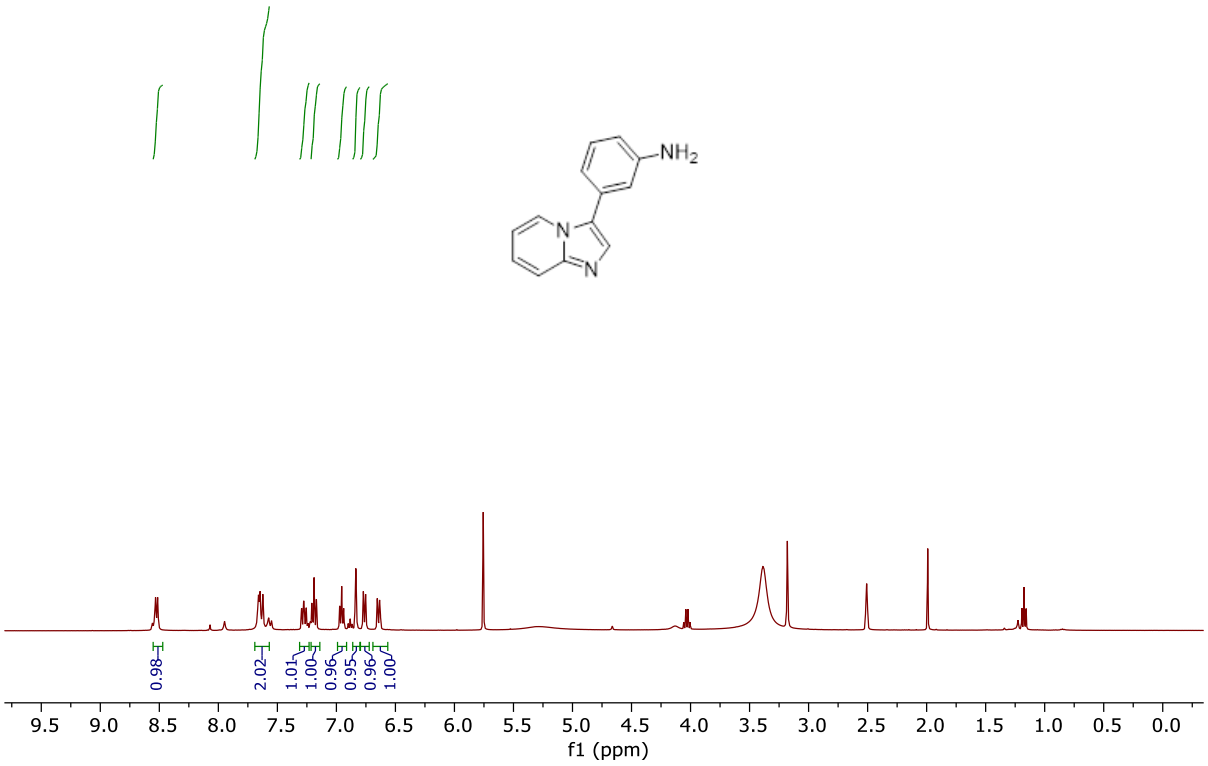


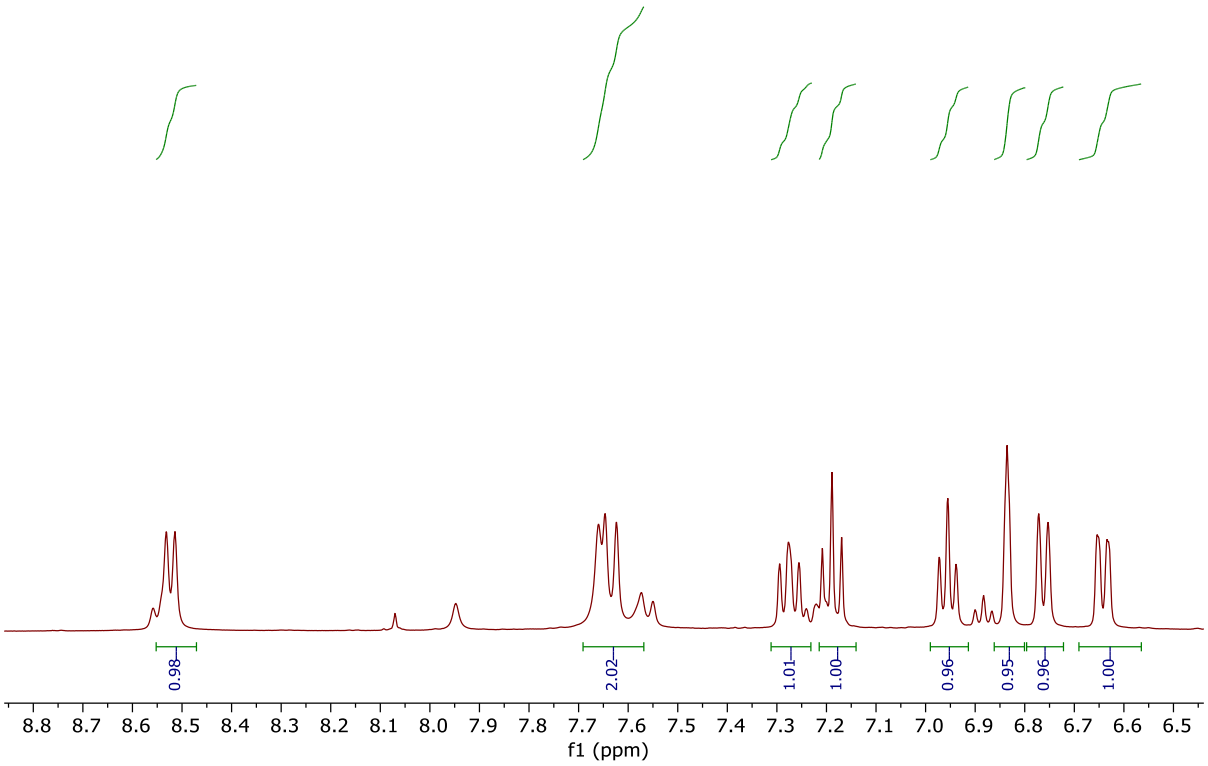


MS Spectrum of (**20**) (EI):

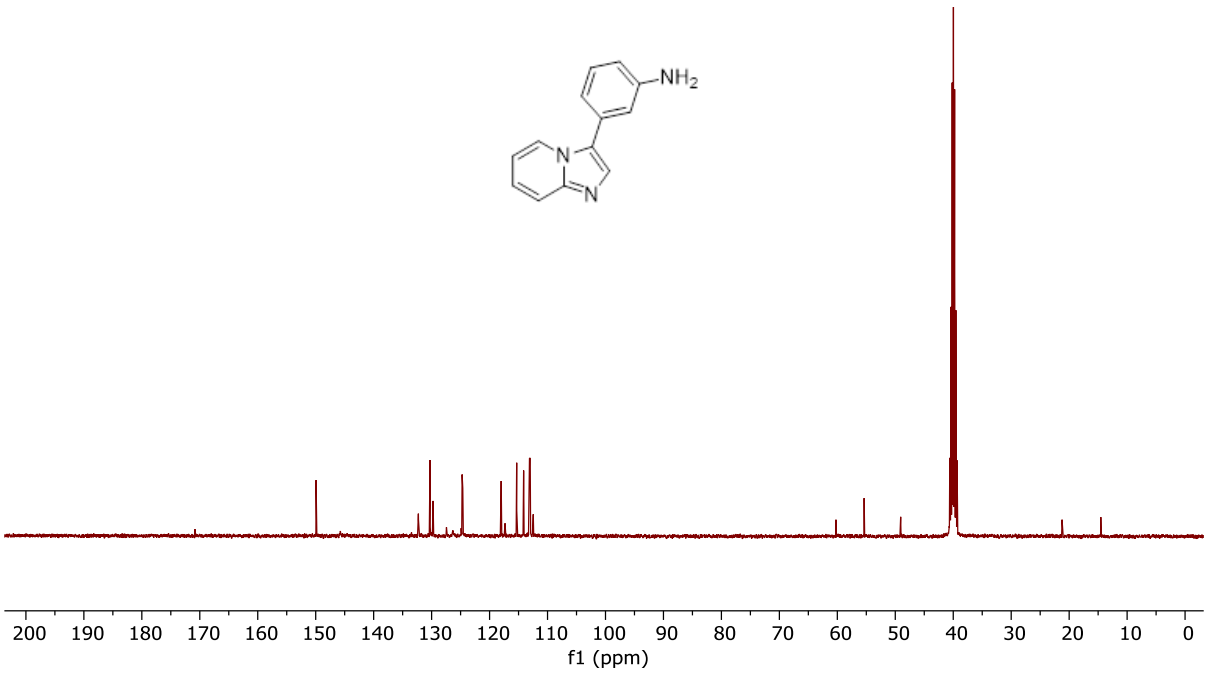


^{1}H NMR Spectrum of (**21**) (400 MHz, DMSO-d^{6}):

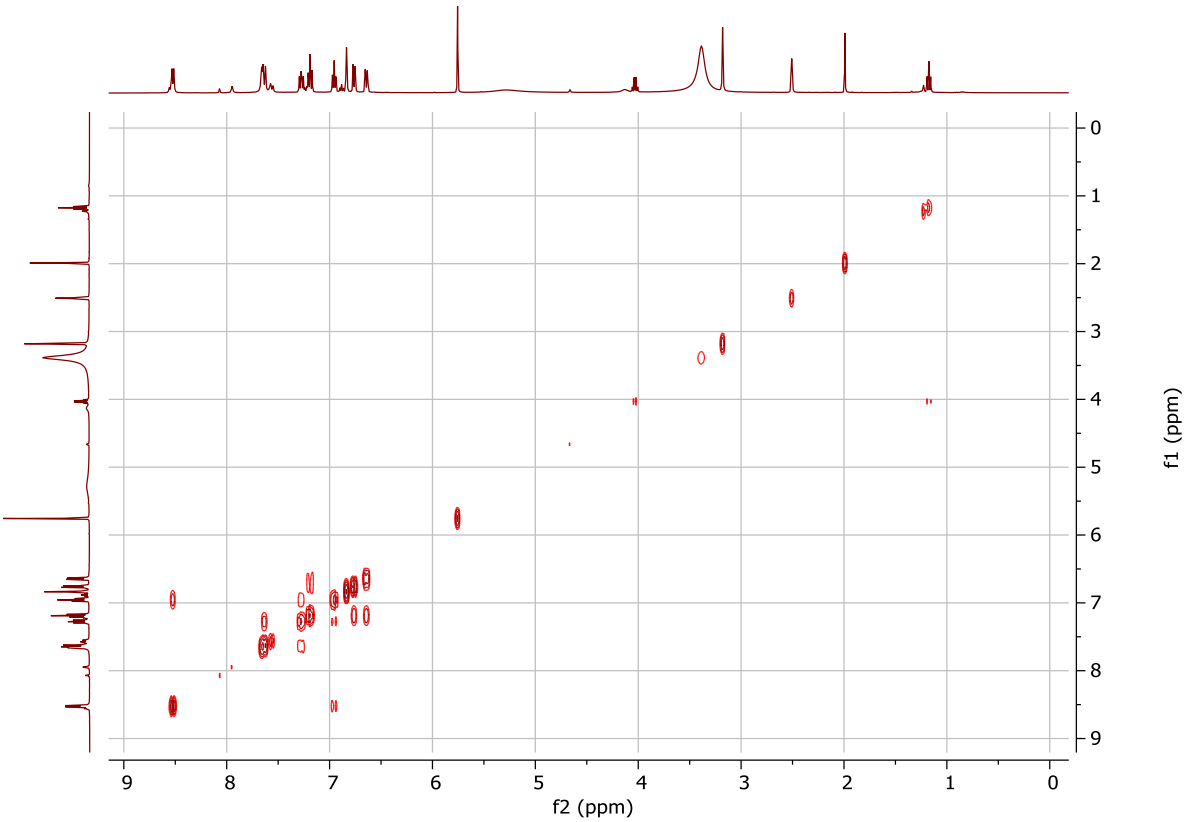




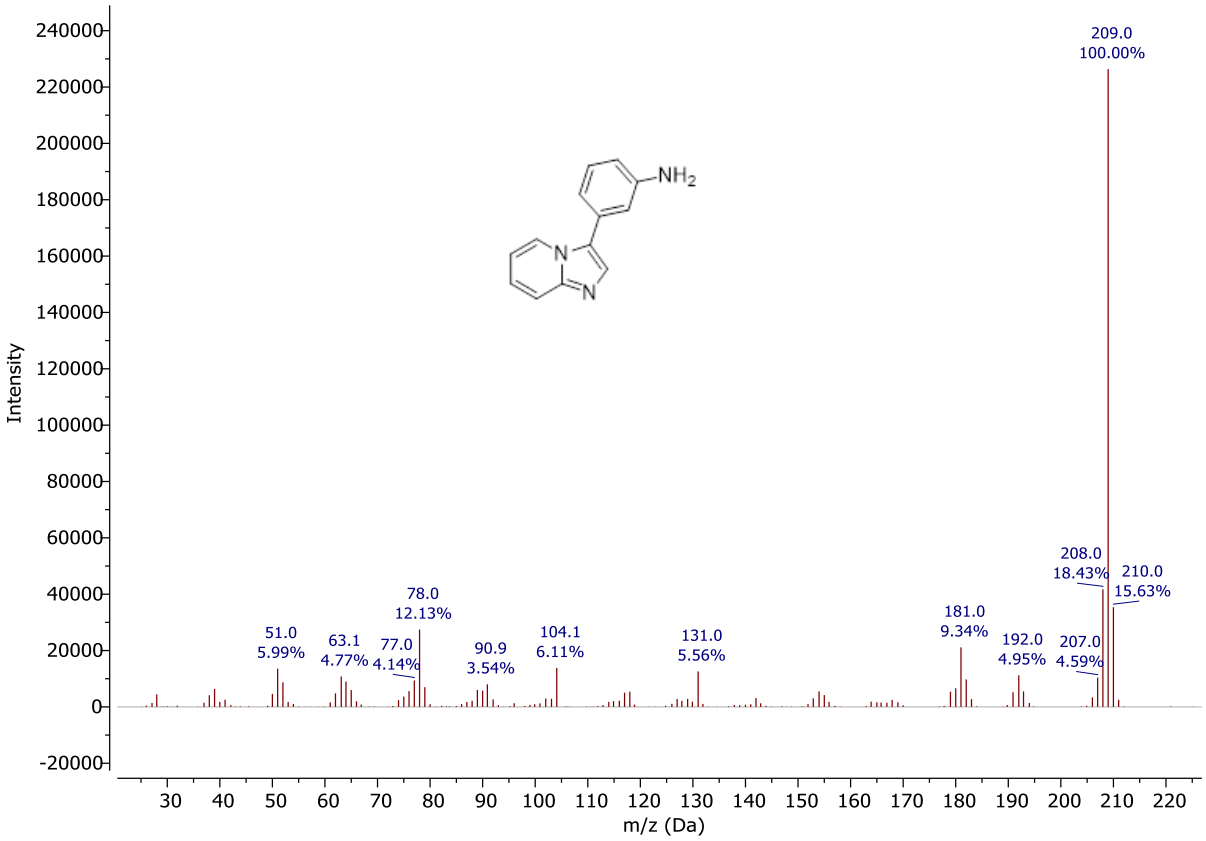
^{13}C NMR Spectrum of (**21**) (400 MHz, DMSO-d^{6}):



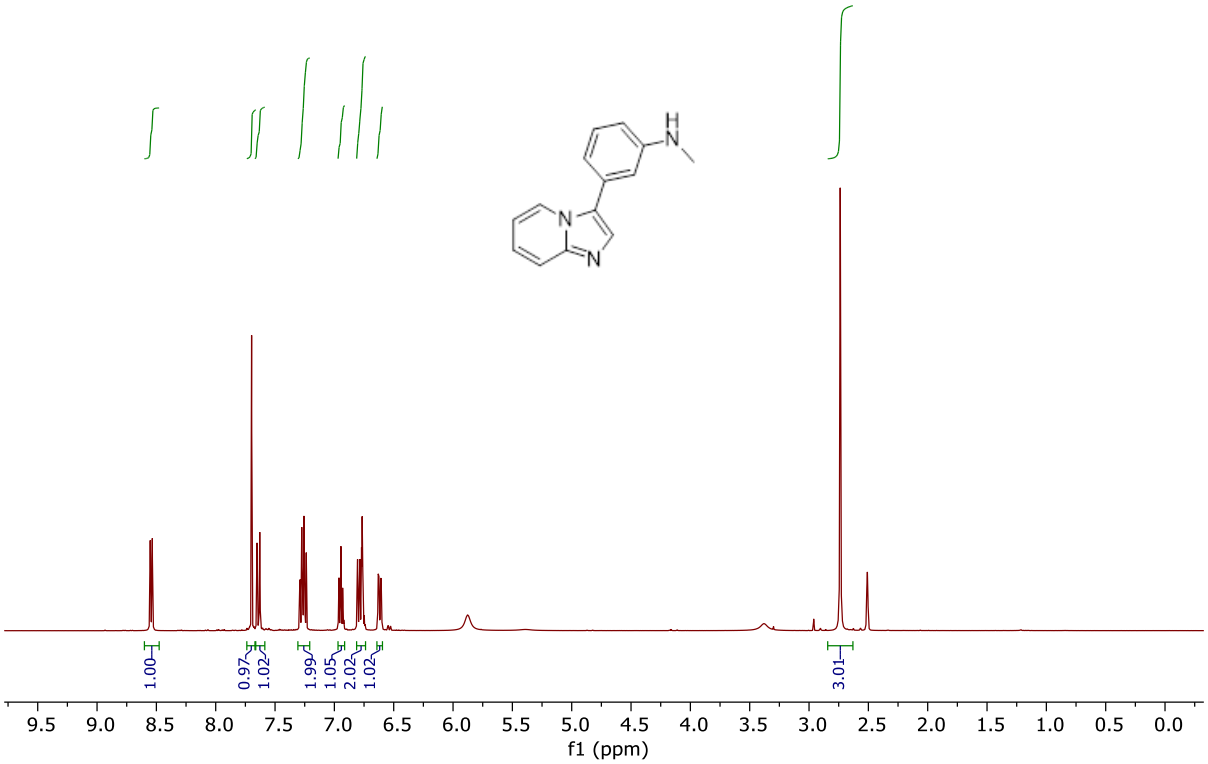
^{1}H/^{1}H COSY NMR Spectrum of (**21**) (400 MHz, DMSO-d^{6}):

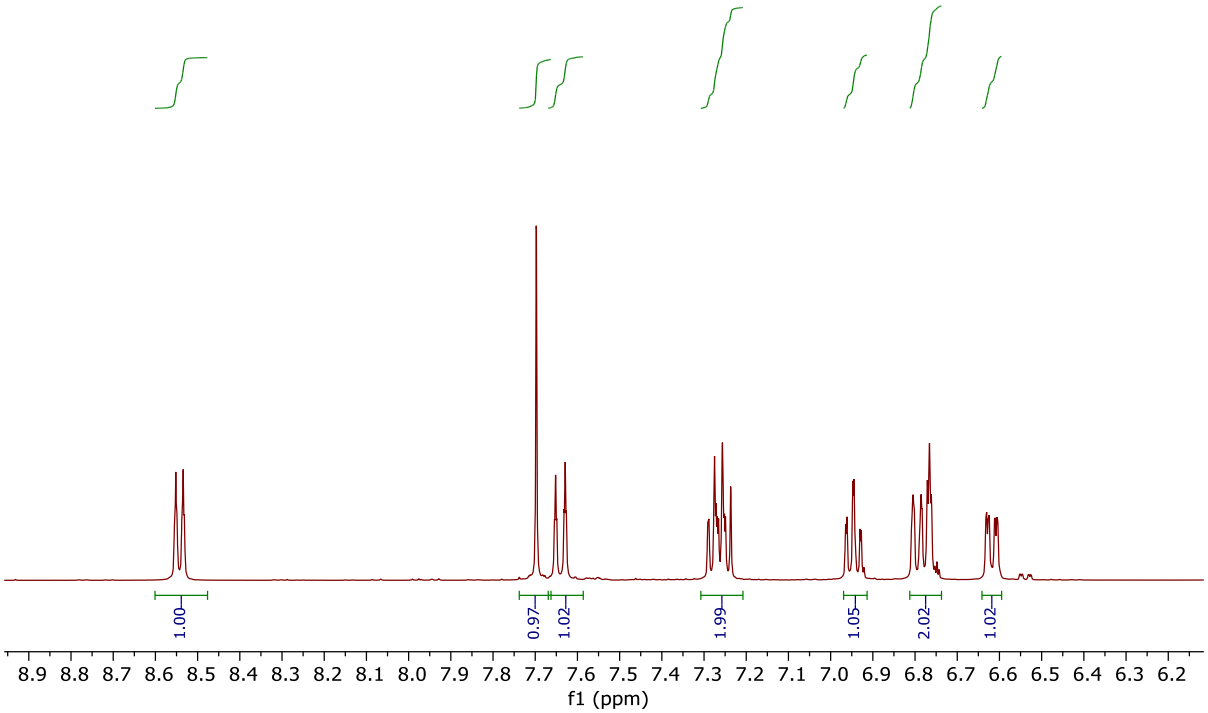


MS Spectrum of (**21**) (EI):

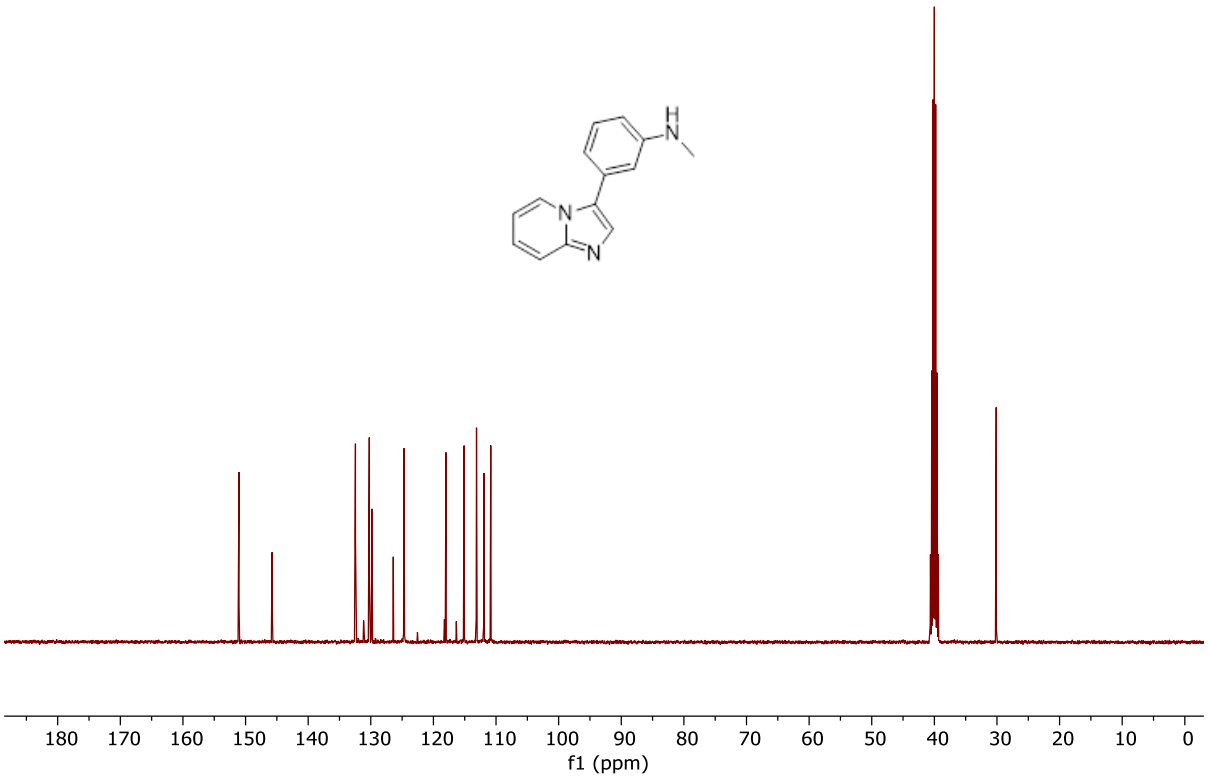


^{1}H NMR Spectrum of (**22**) (400 MHz, DMSO-d^{6}):

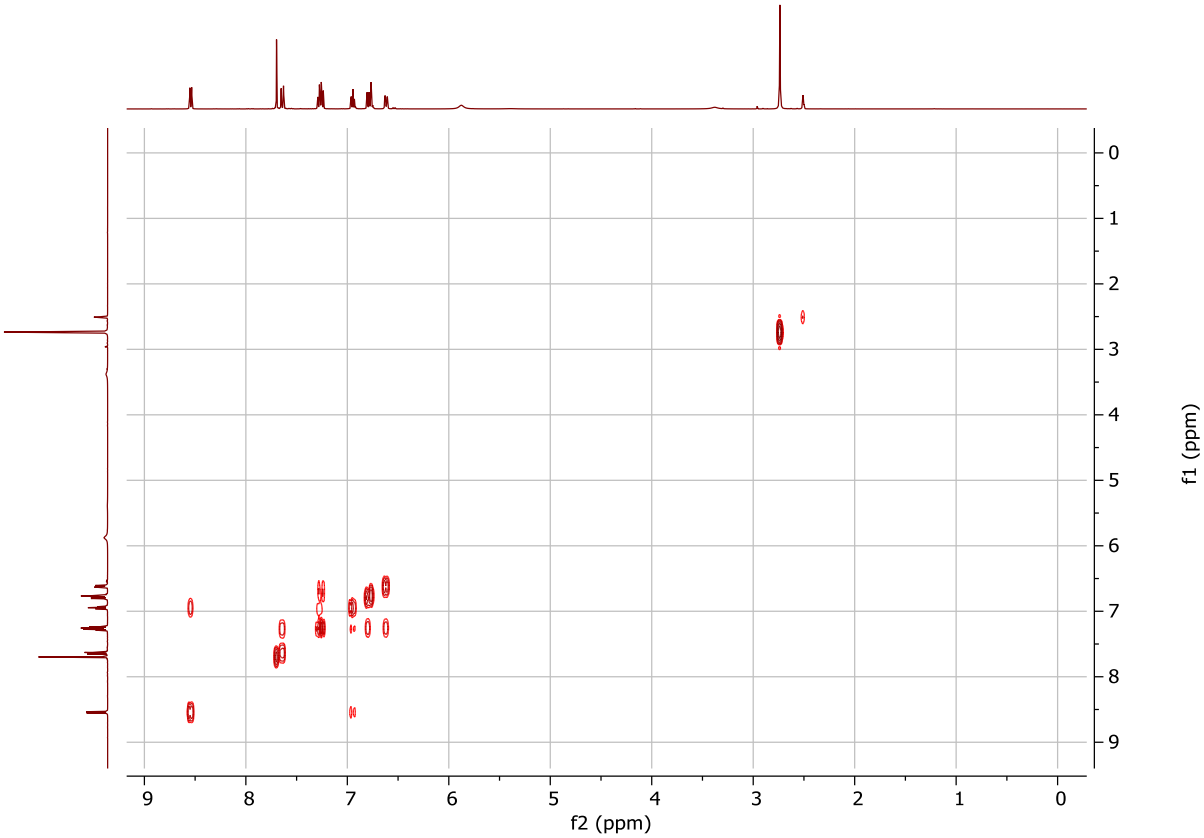


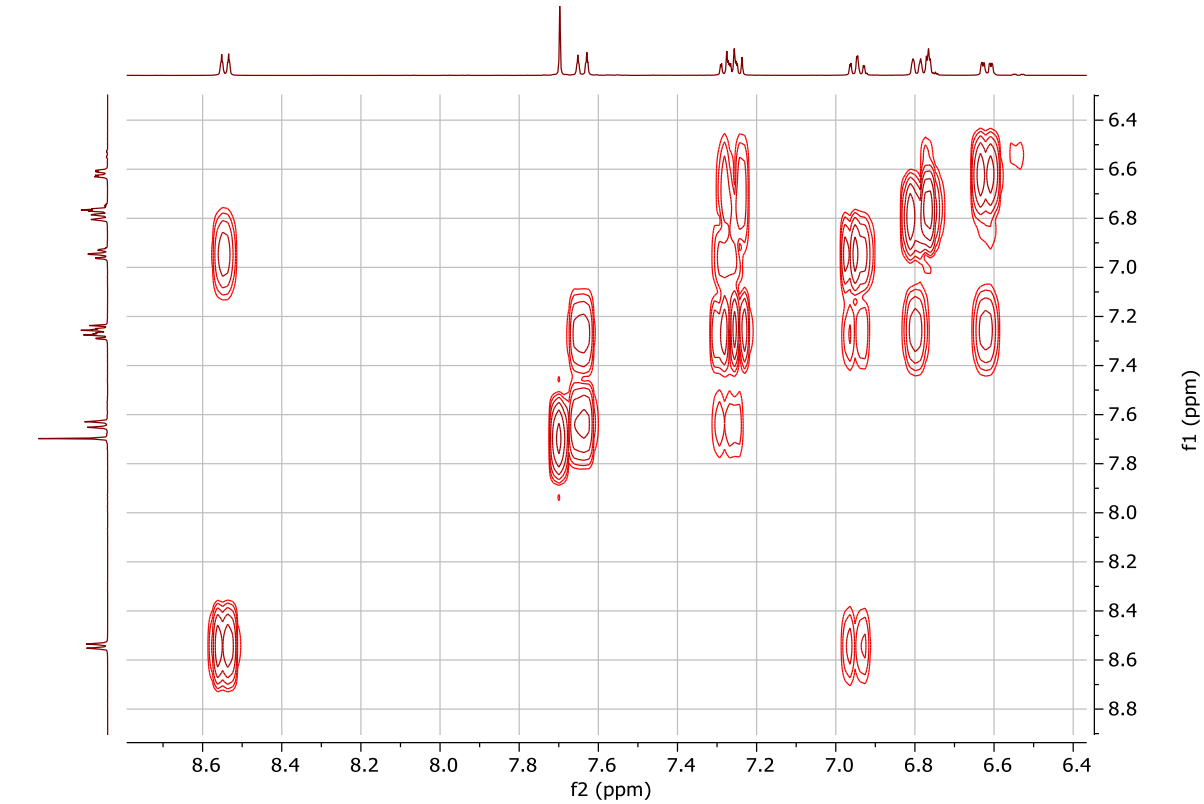


^{13}C NMR Spectrum of (**22**) (400 MHz, DMSO-d^{6}):

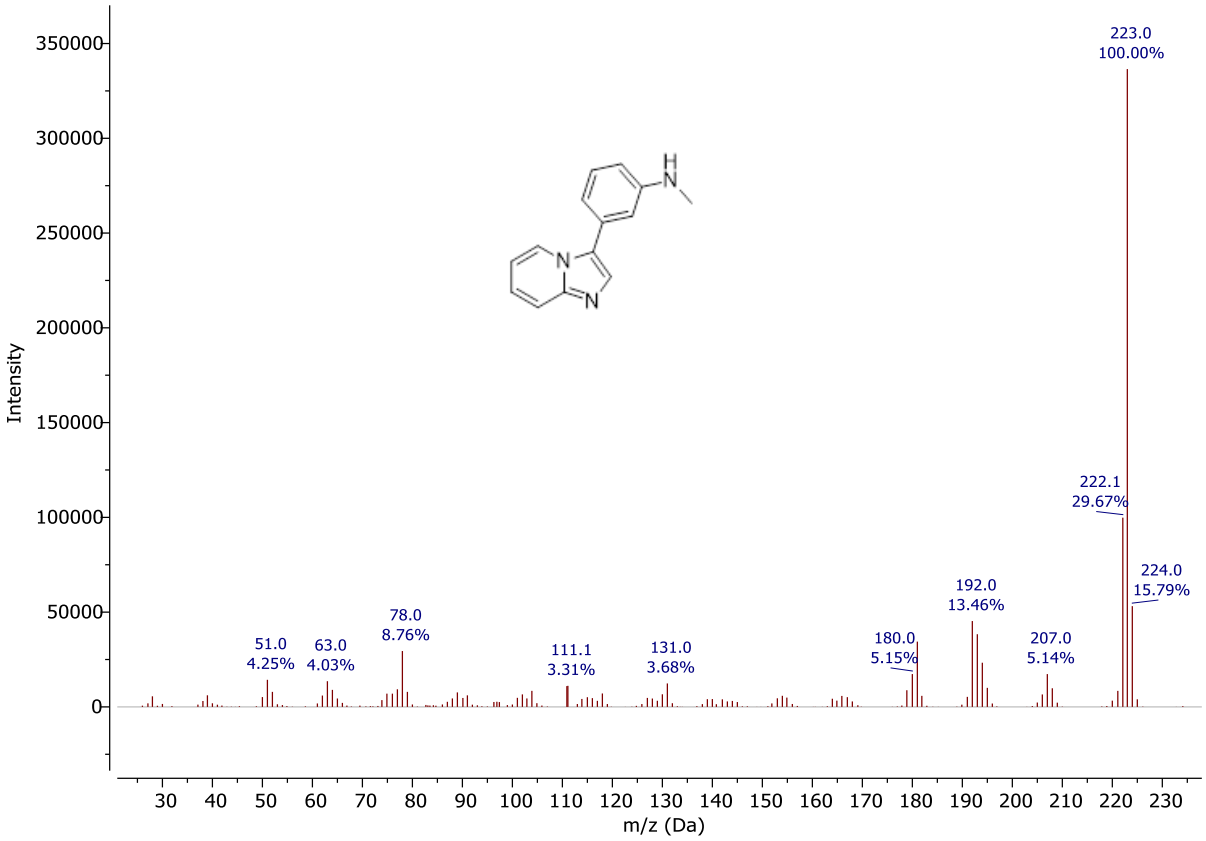


^{1}H/^{1}H COSY NMR Spectrum of (**22**) (400 MHz, DMSO-d^{6}):

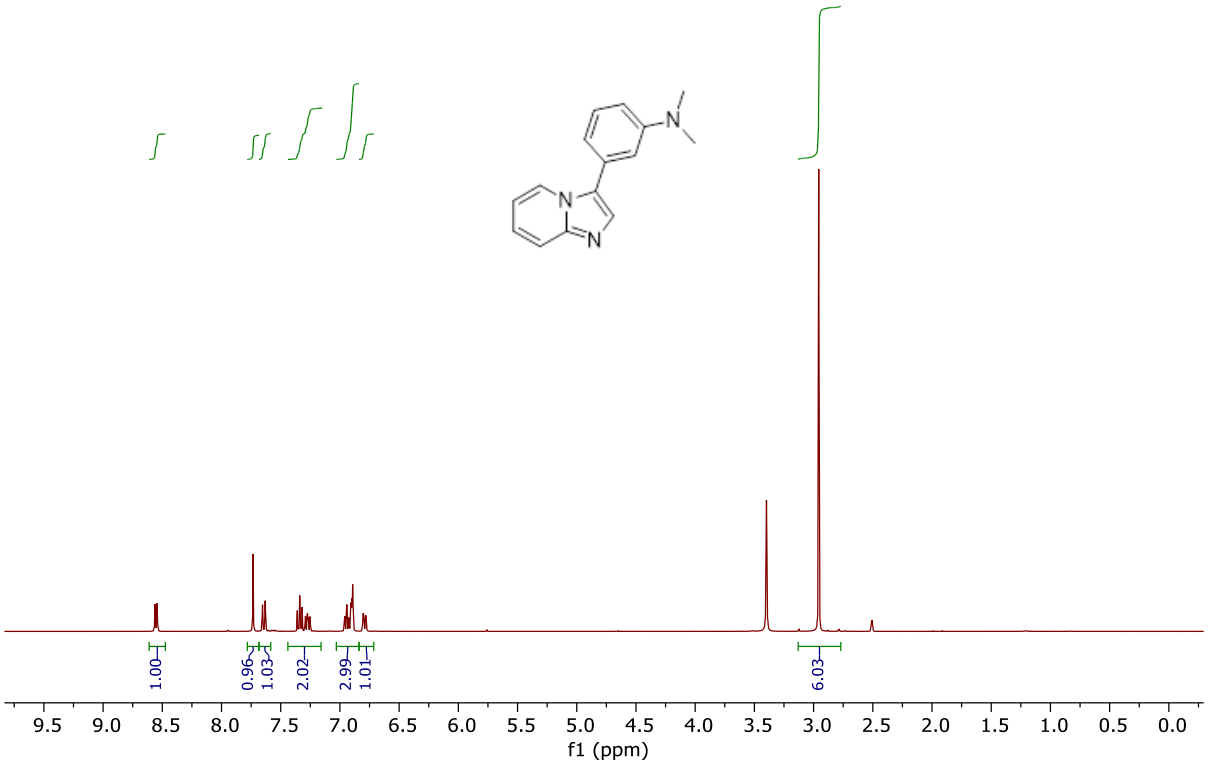


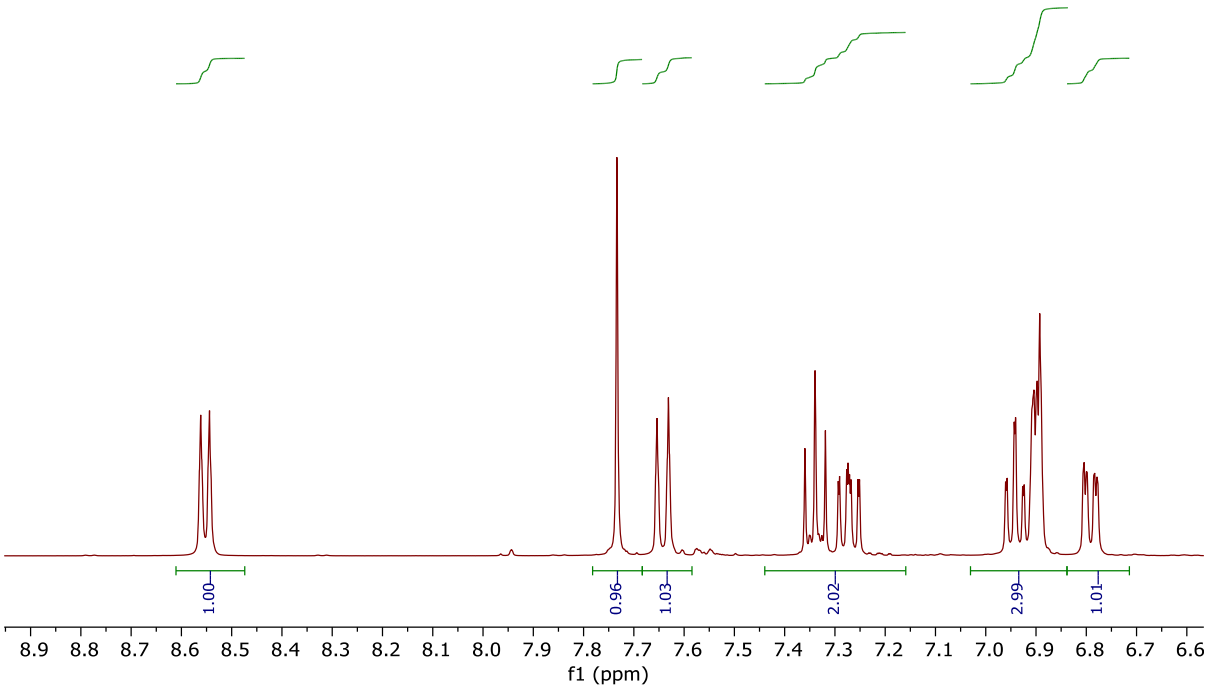


MS Spectrum of (**22**) (EI):

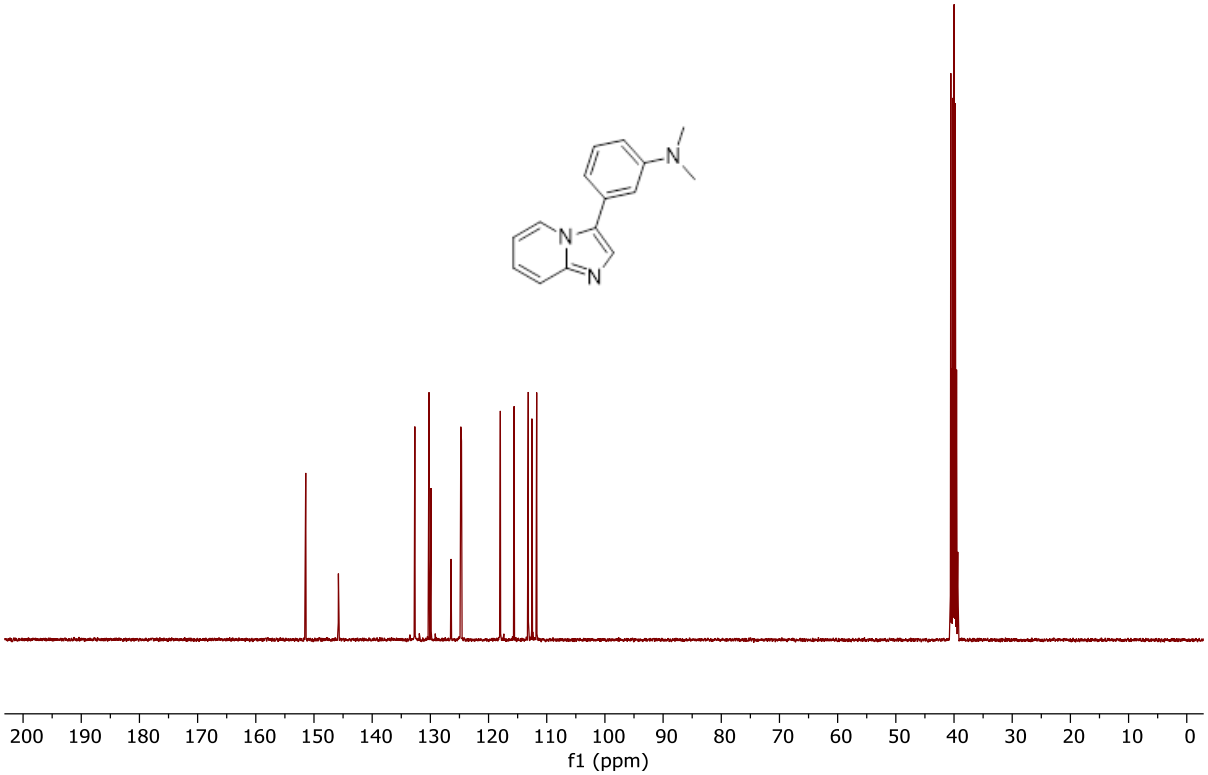


^{1}H NMR Spectrum of (**23**) (400 MHz, DMSO-d^{6}):

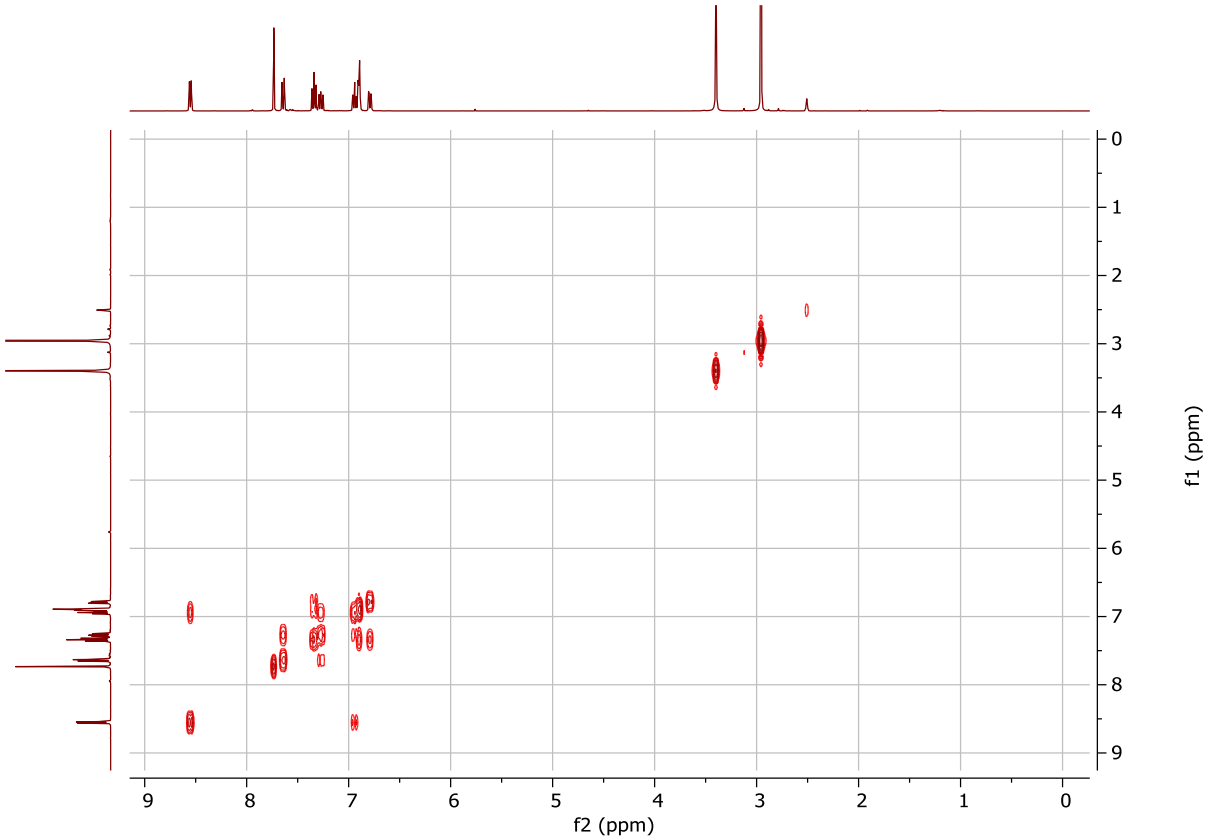




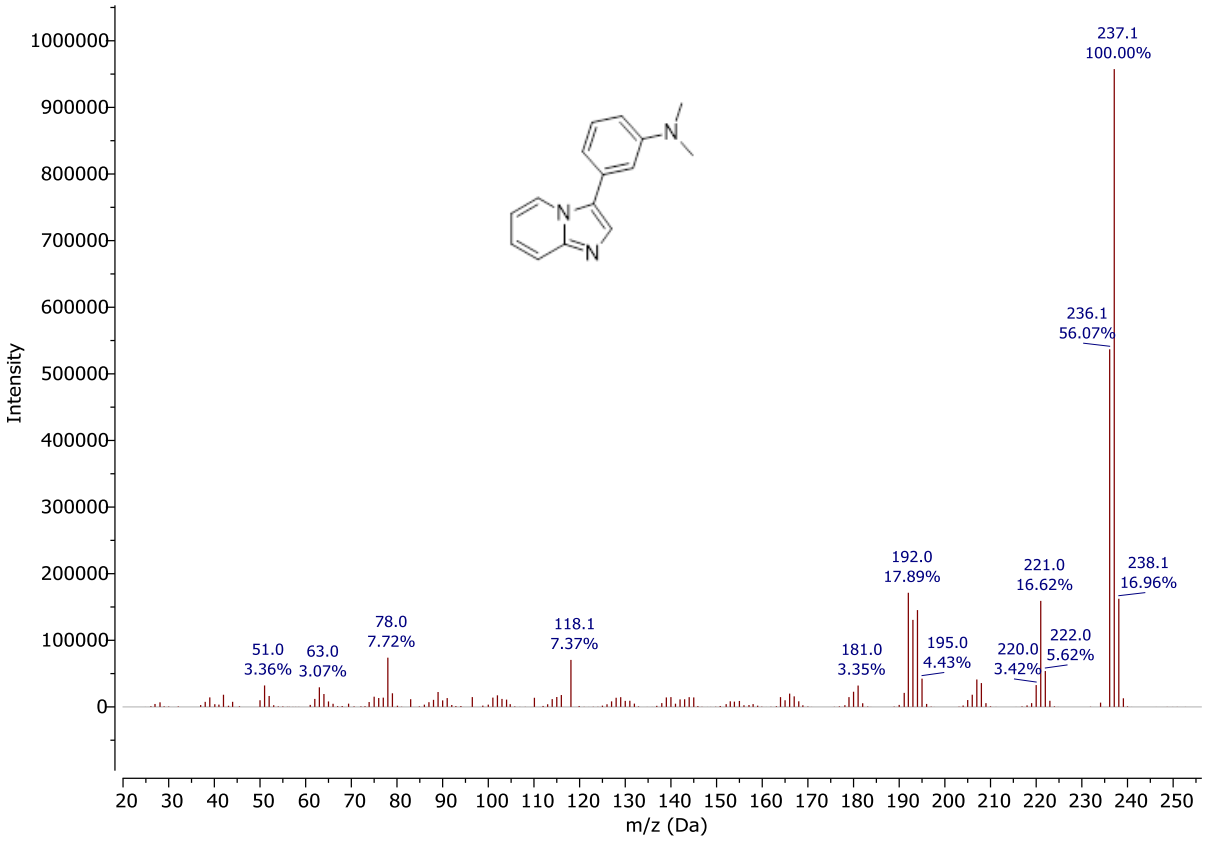
^{13}C NMR Spectrum of (**23**) (400 MHz, DMSO-d^{6}):



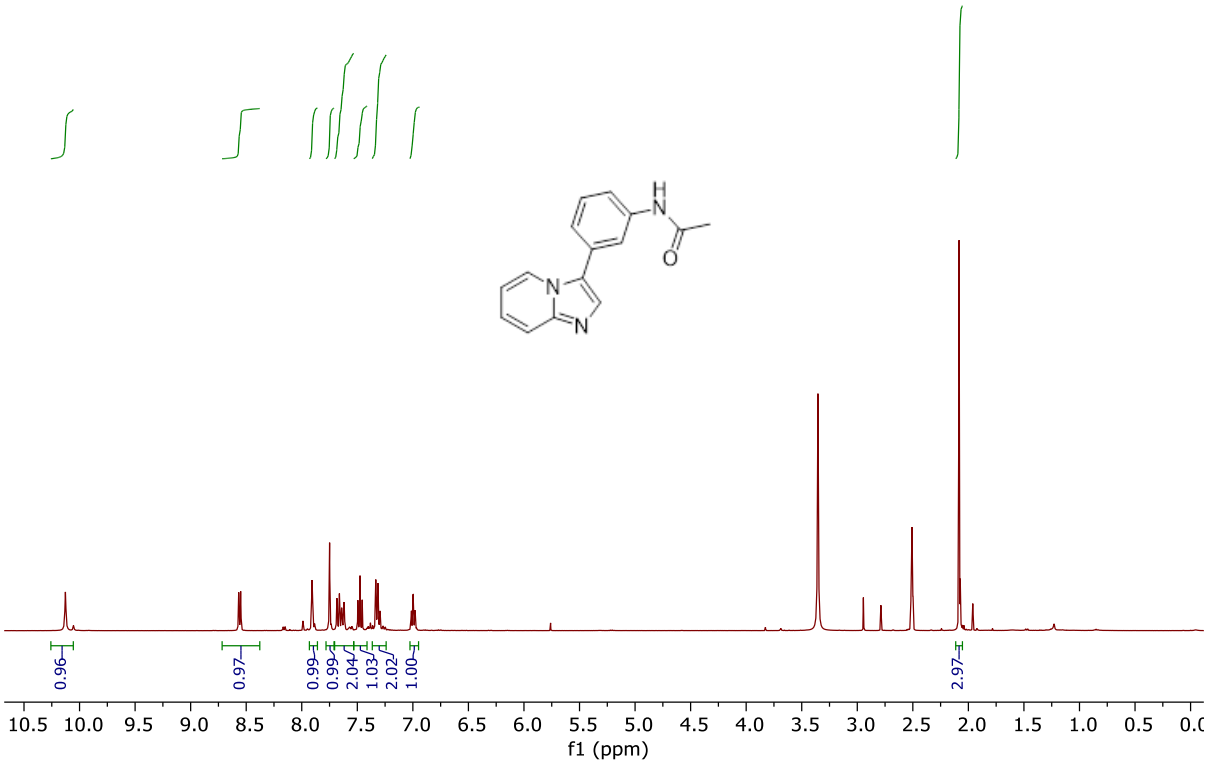
^{1}H/^{1}H COSY NMR Spectrum of (**23**) (400 MHz, DMSO-d^{6}):

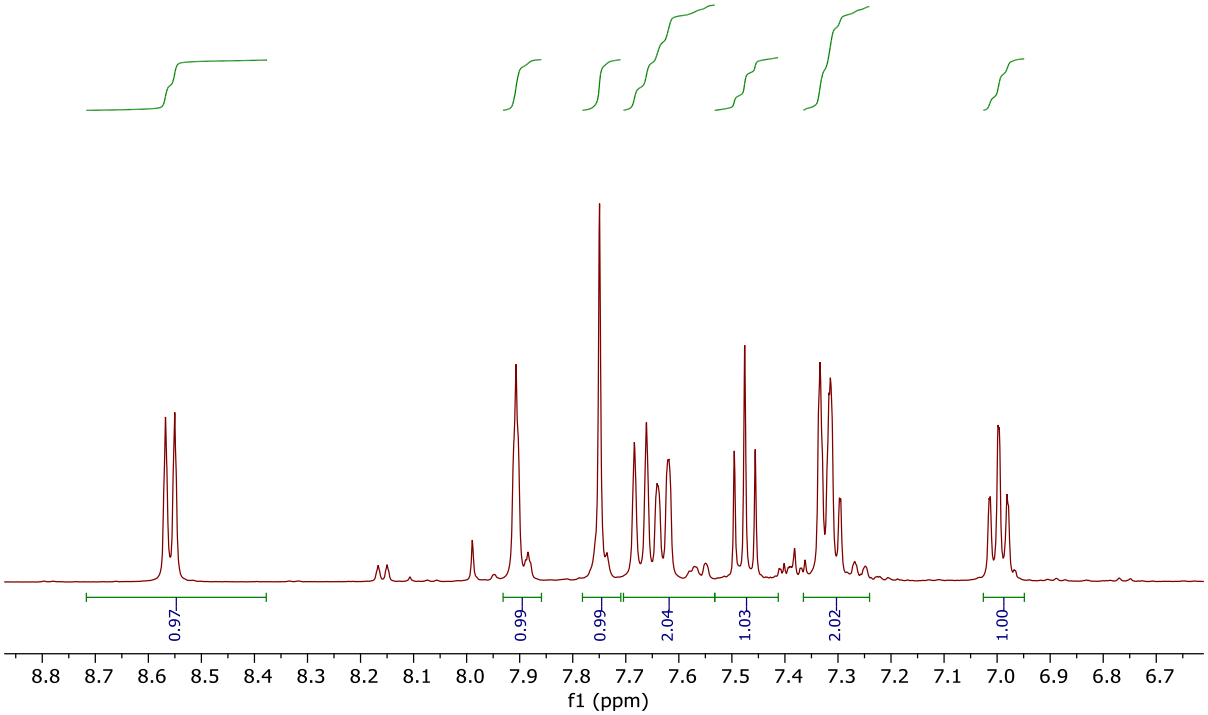


MS Spectrum of (**23**) (EI):

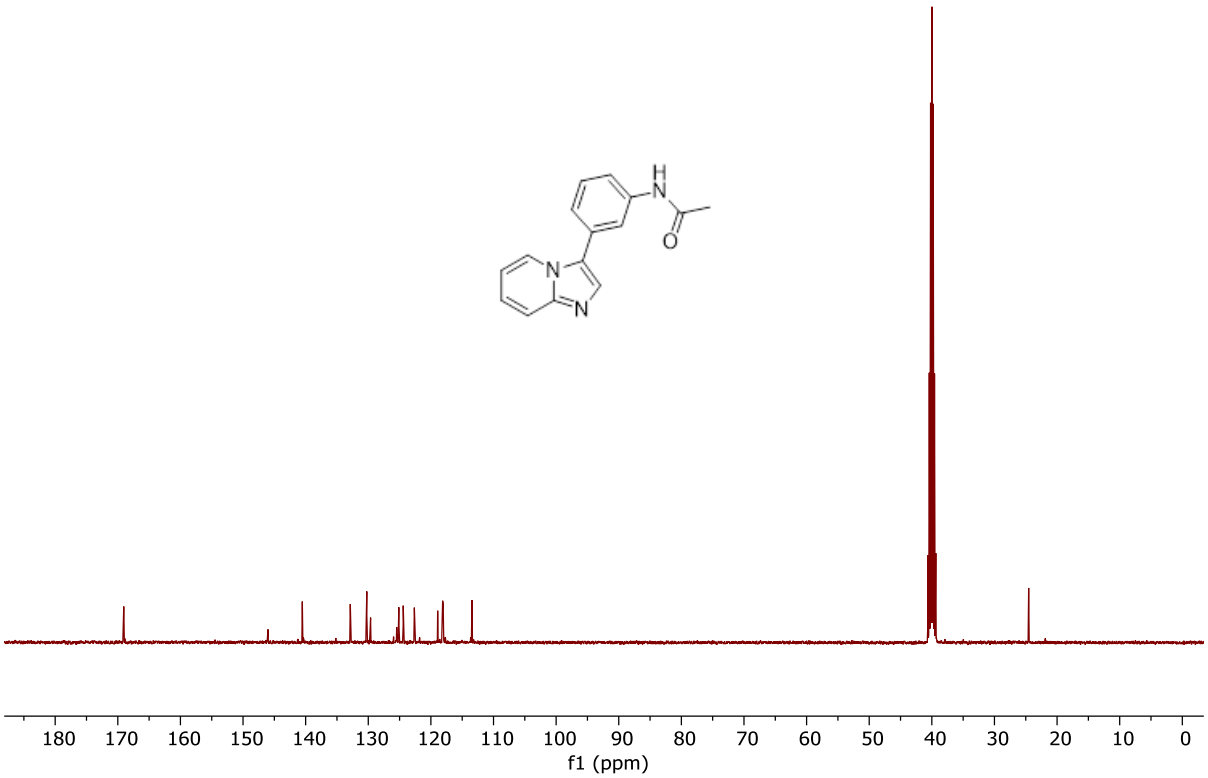


^{1}H NMR Spectrum of (**24**) (400 MHz, DMSO-d^{6}):

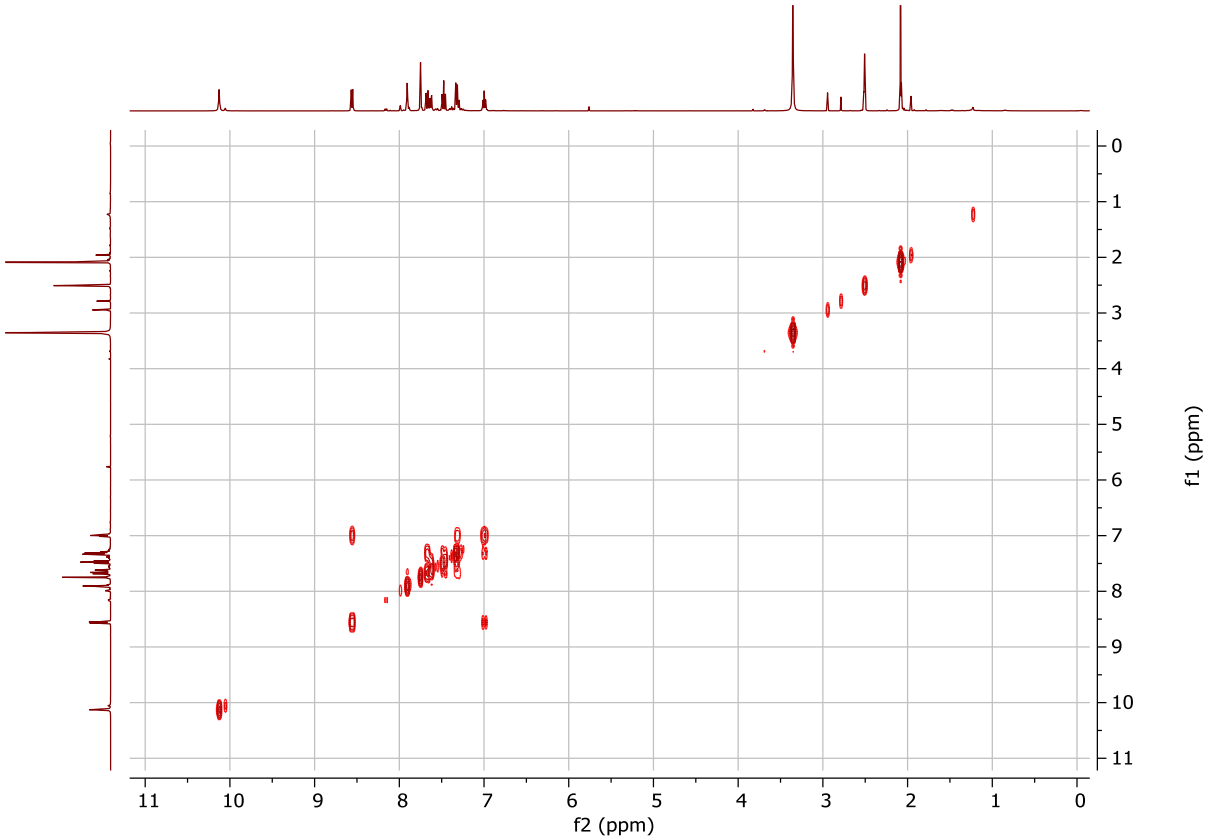


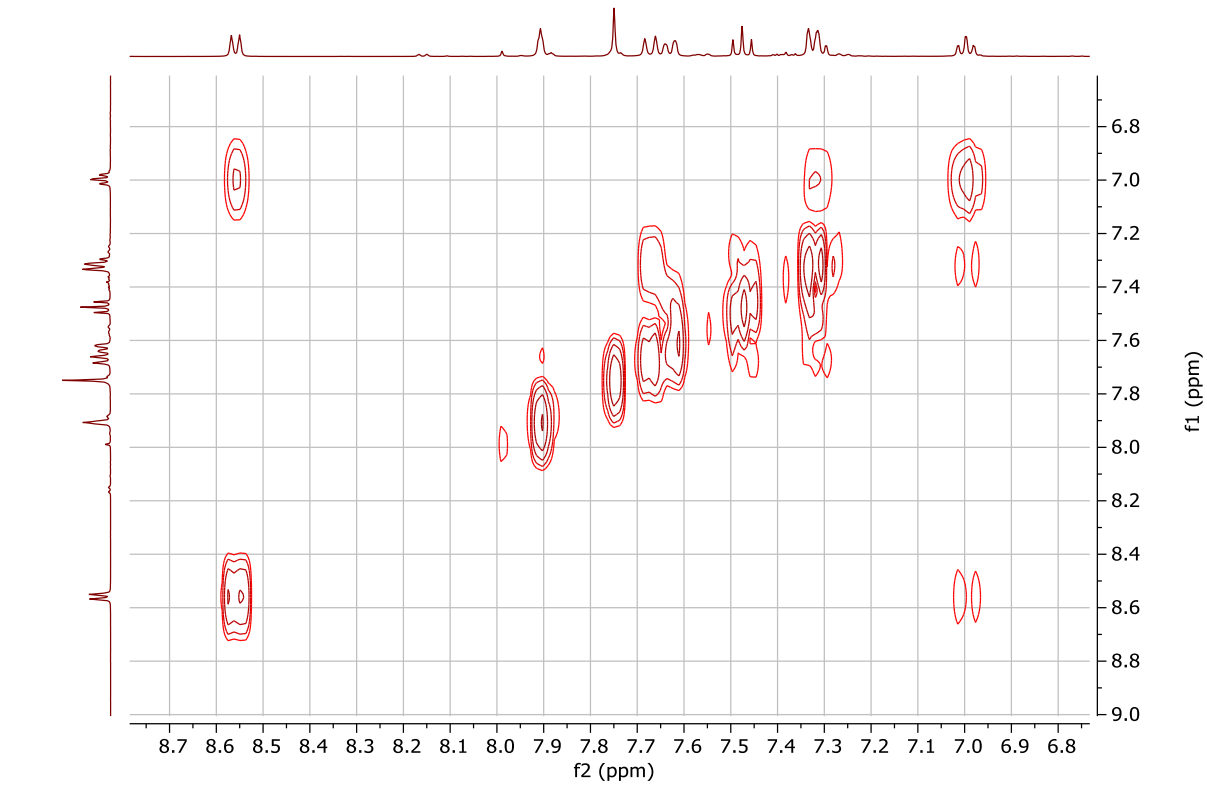


^{13}C NMR Spectrum of (**24**) (400 MHz, DMSO-d^{6}):

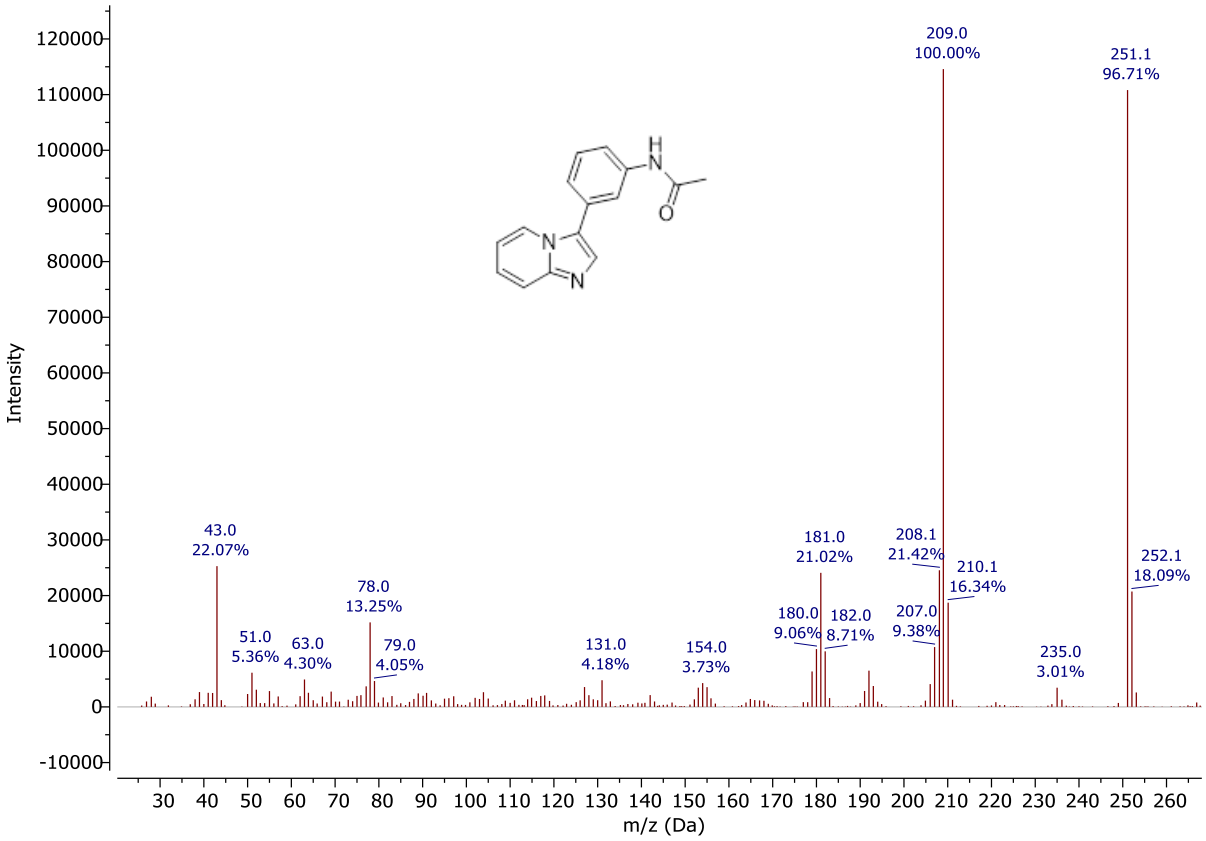


^{1}H/^{1}H COSY NMR Spectrum of (**24**) (400 MHz, DMSO-d^{6}):

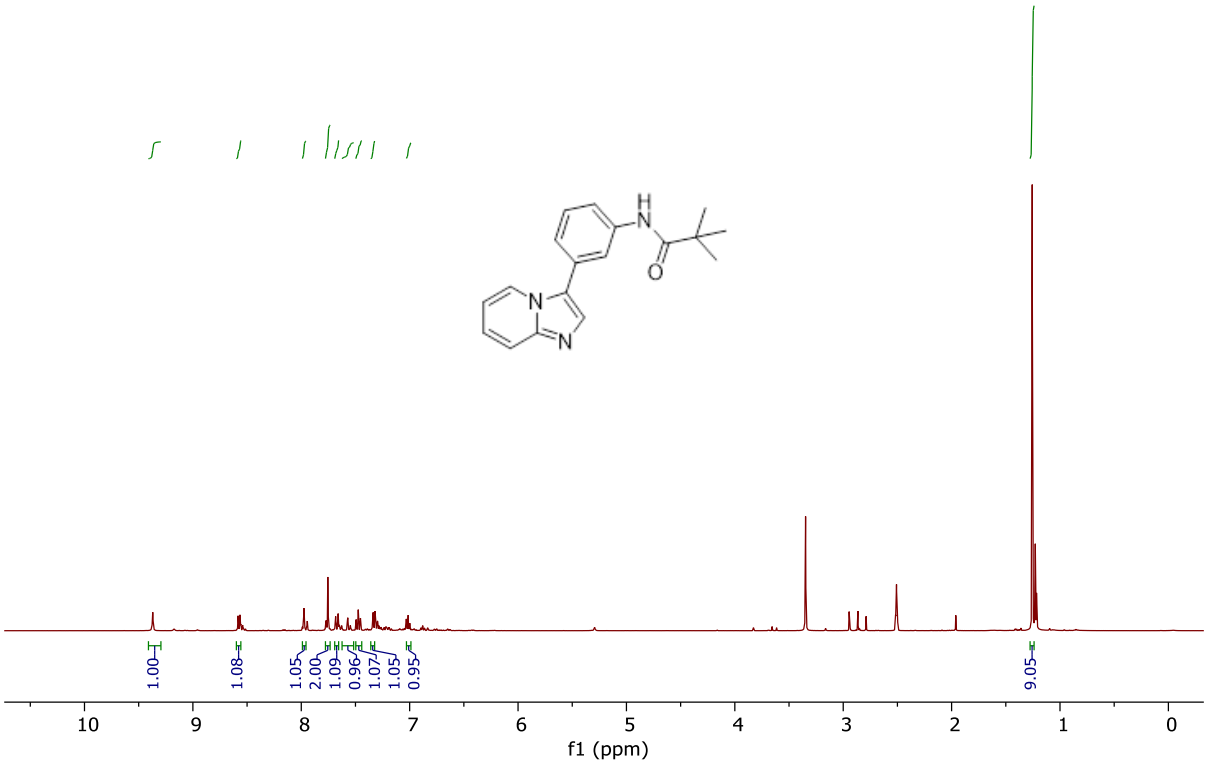




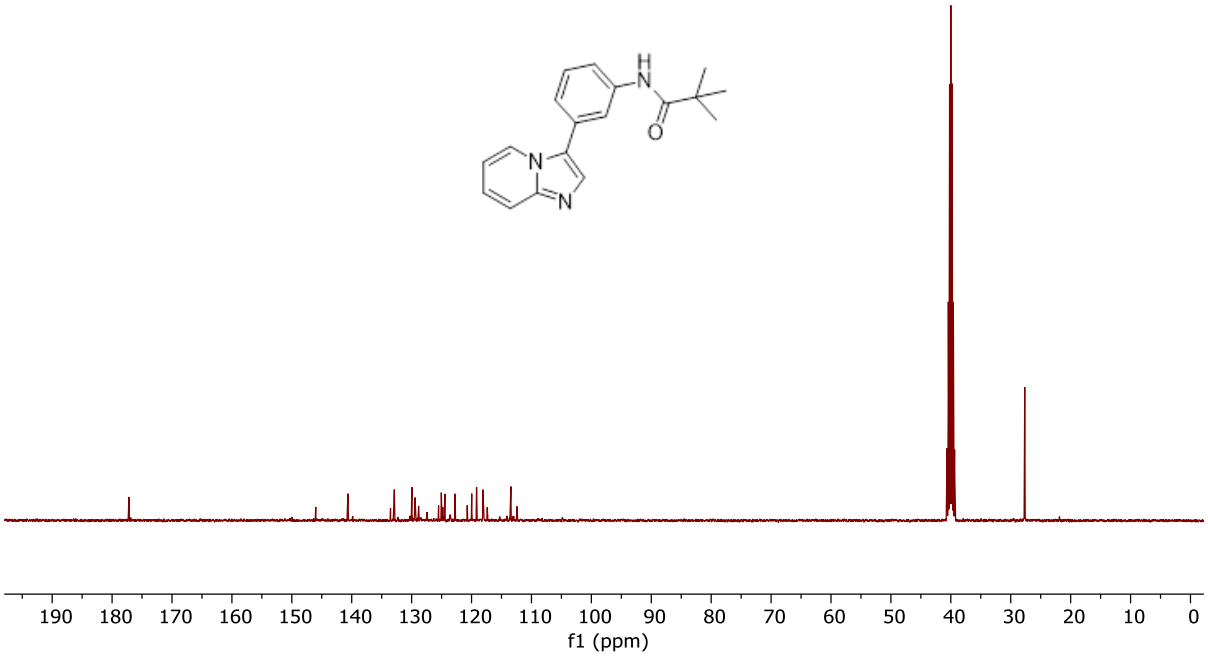
MS Spectrum of (**24**) (EI):



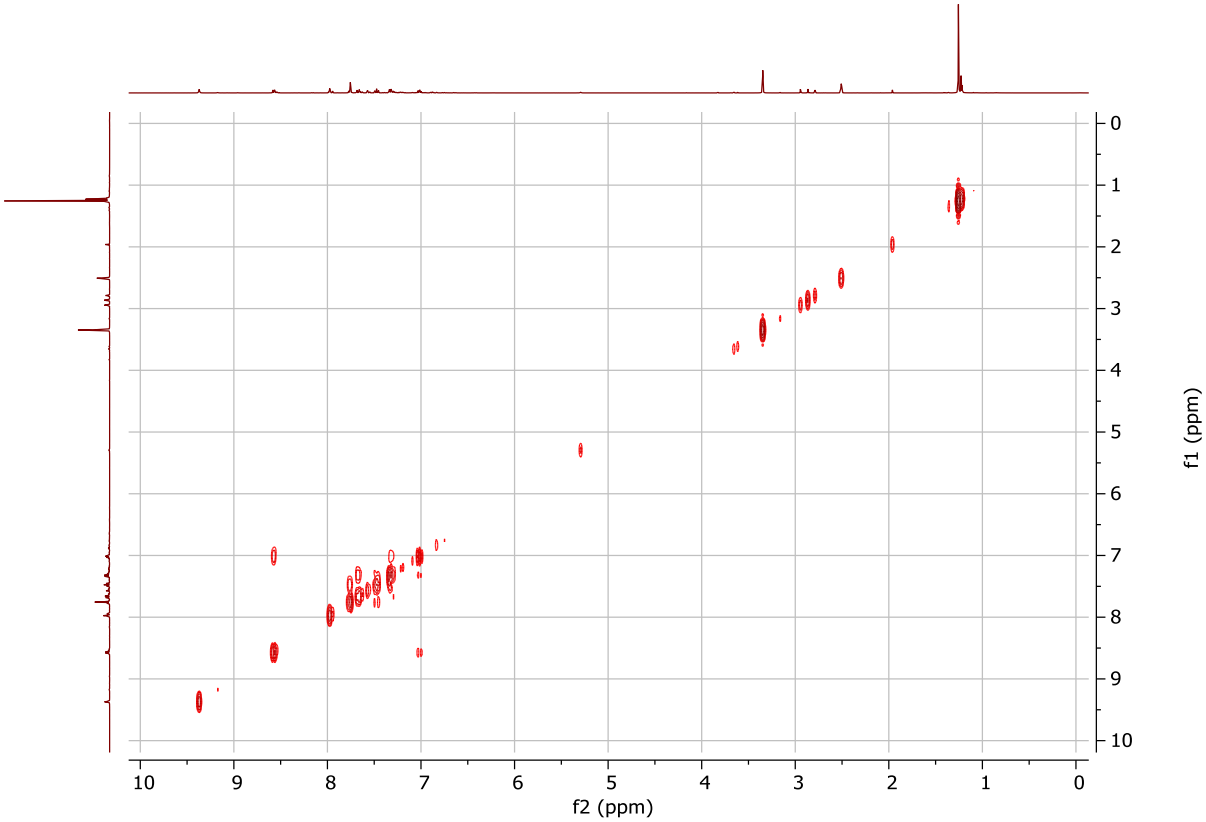
^{1}H NMR Spectrum of (**25**) (400 MHz, DMSO-d^{6}):



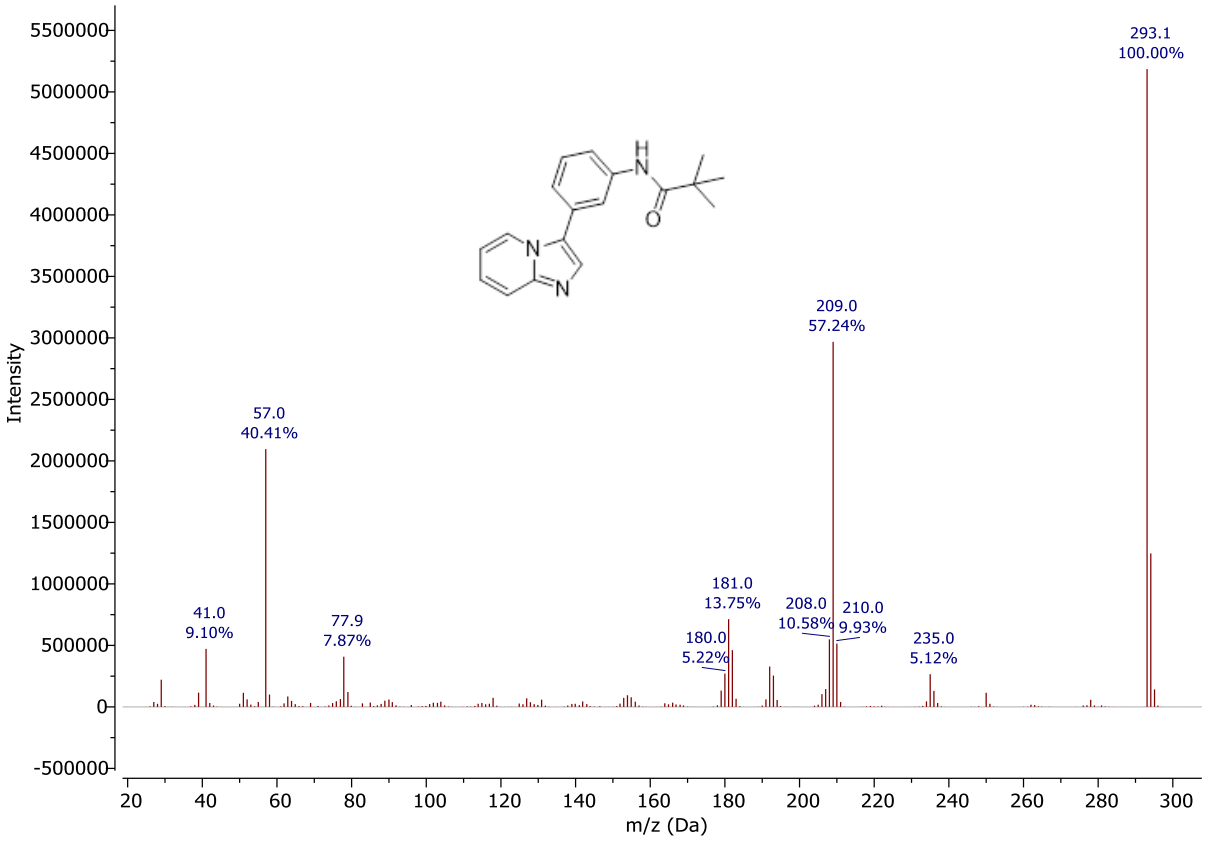
^{13}C NMR Spectrum of (**25**) (400 MHz, DMSO-d^{6}):



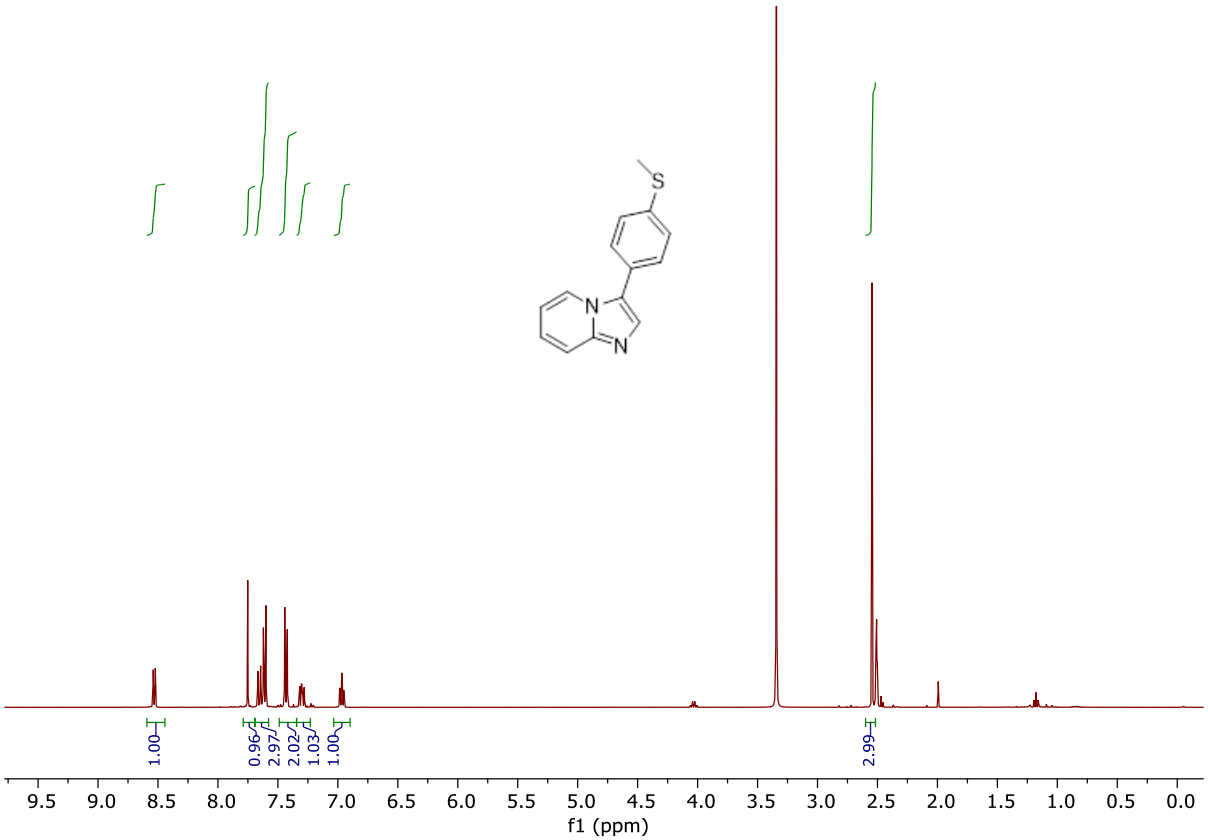
^{1}H/^{1}H COSY NMR Spectrum of (**25**) (400 MHz, DMSO-d^{6}):

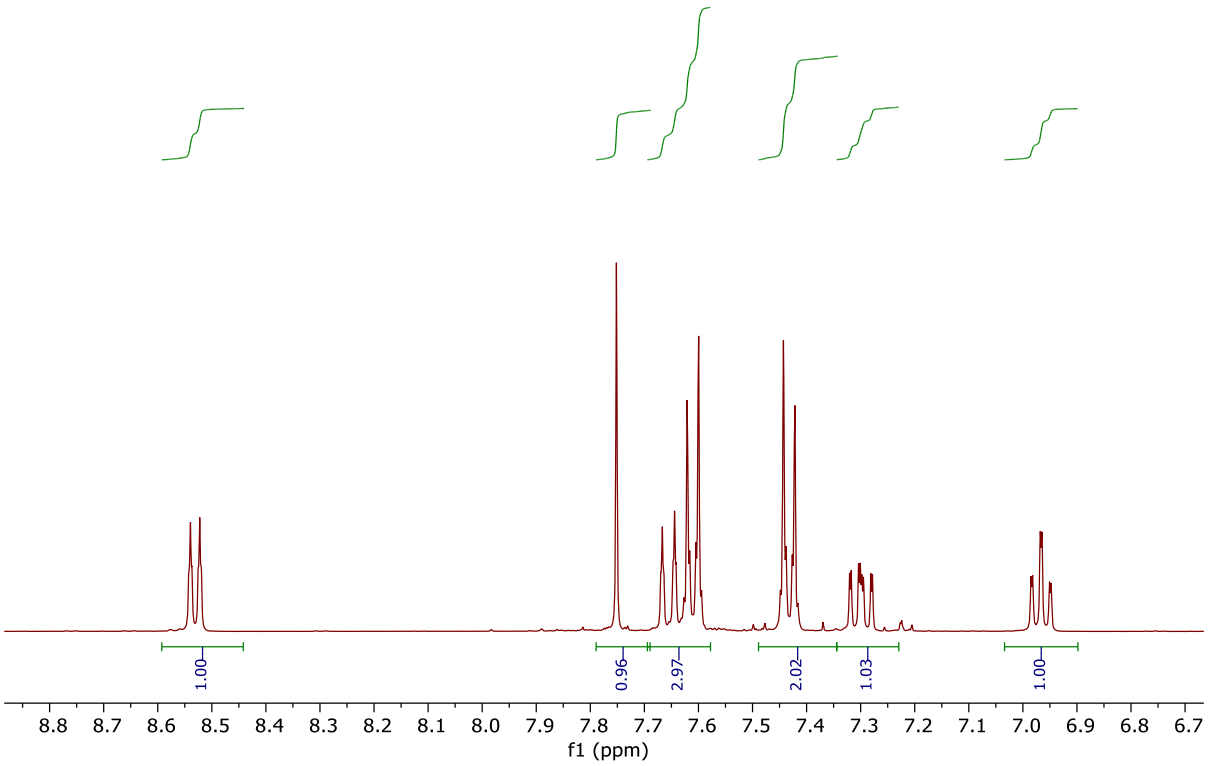


MS Spectrum of (**25**) (EI):

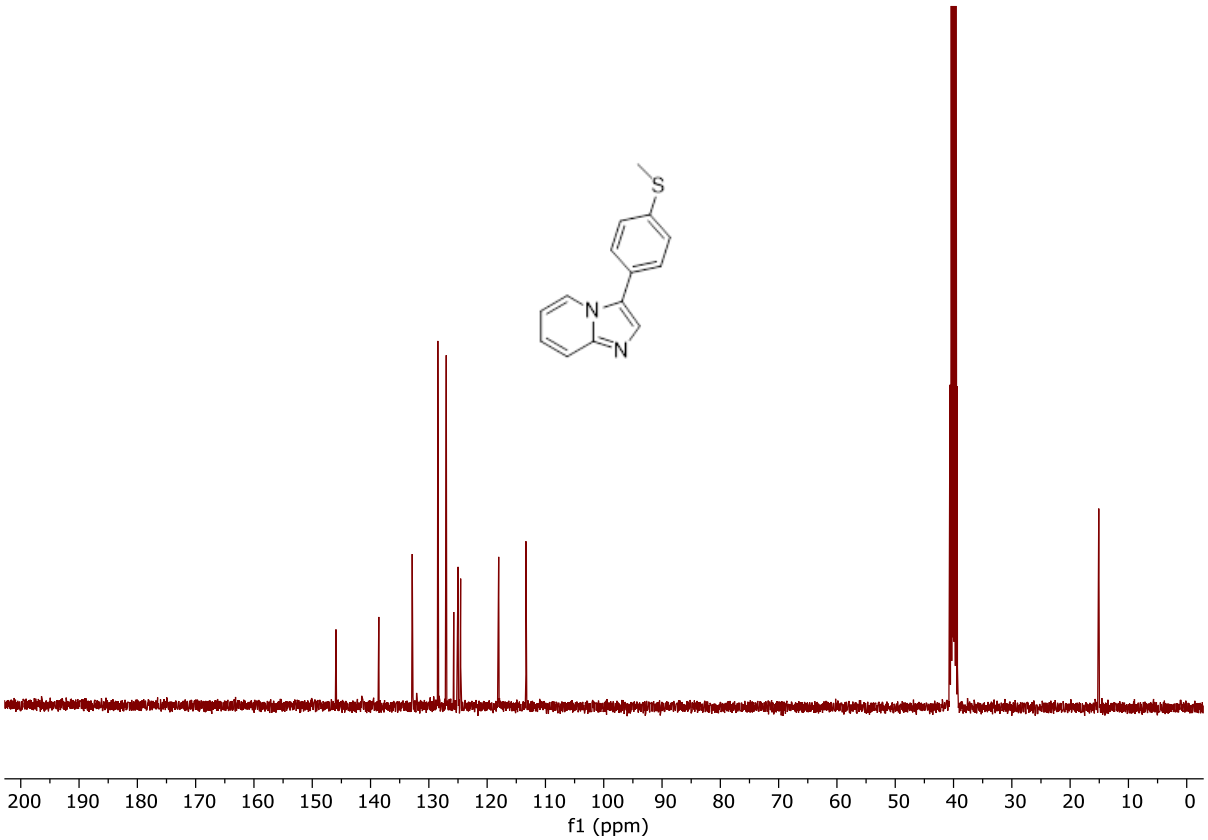


^{1}H NMR Spectrum of (**26**) (400 MHz, DMSO-d^{6}):

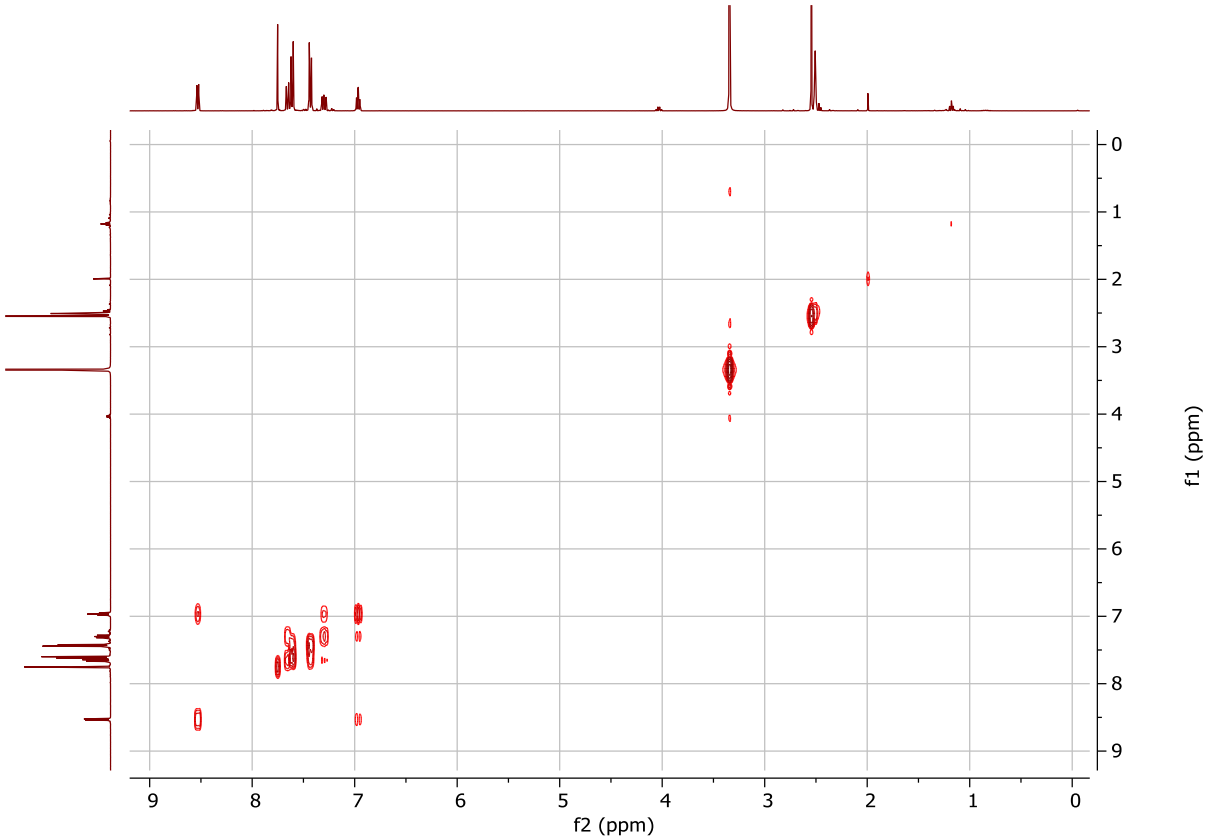




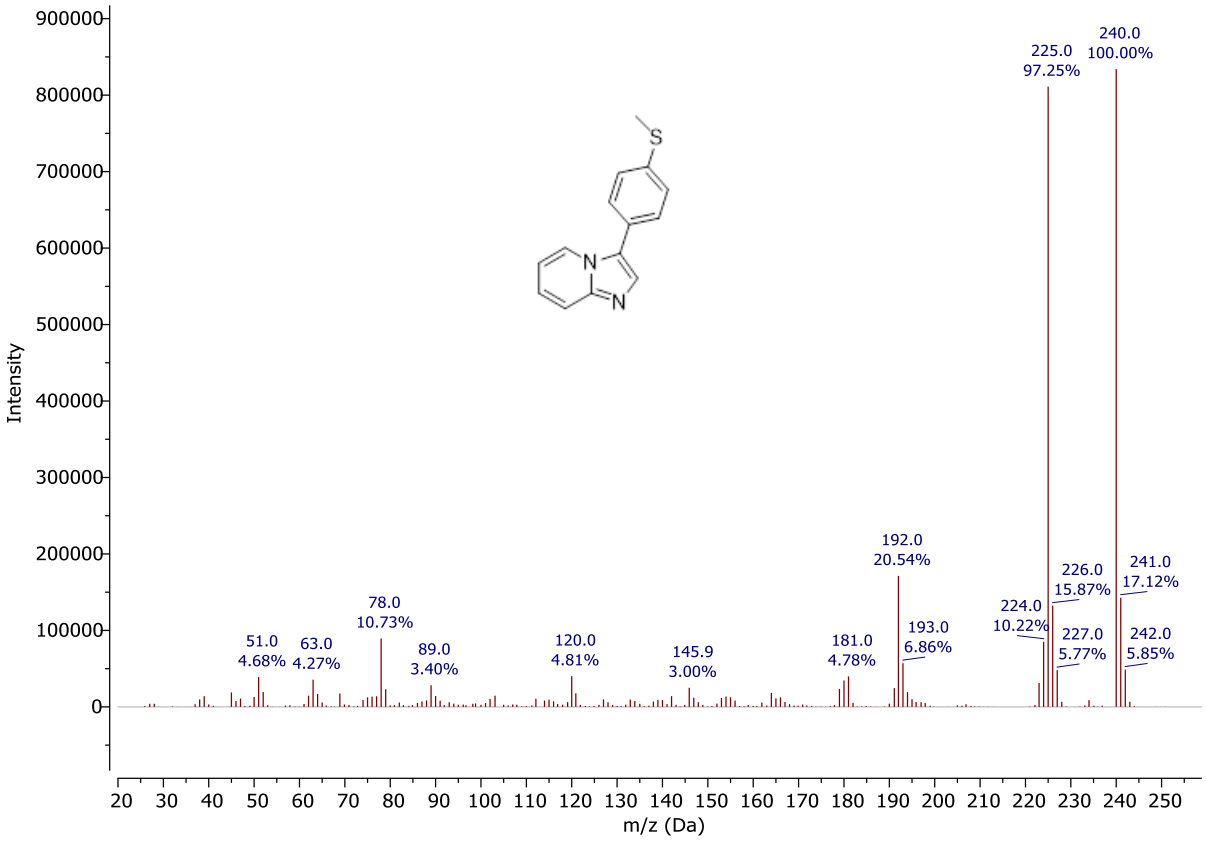
^{13}C NMR Spectrum of (**26**) (400 MHz, DMSO-d^{6}):



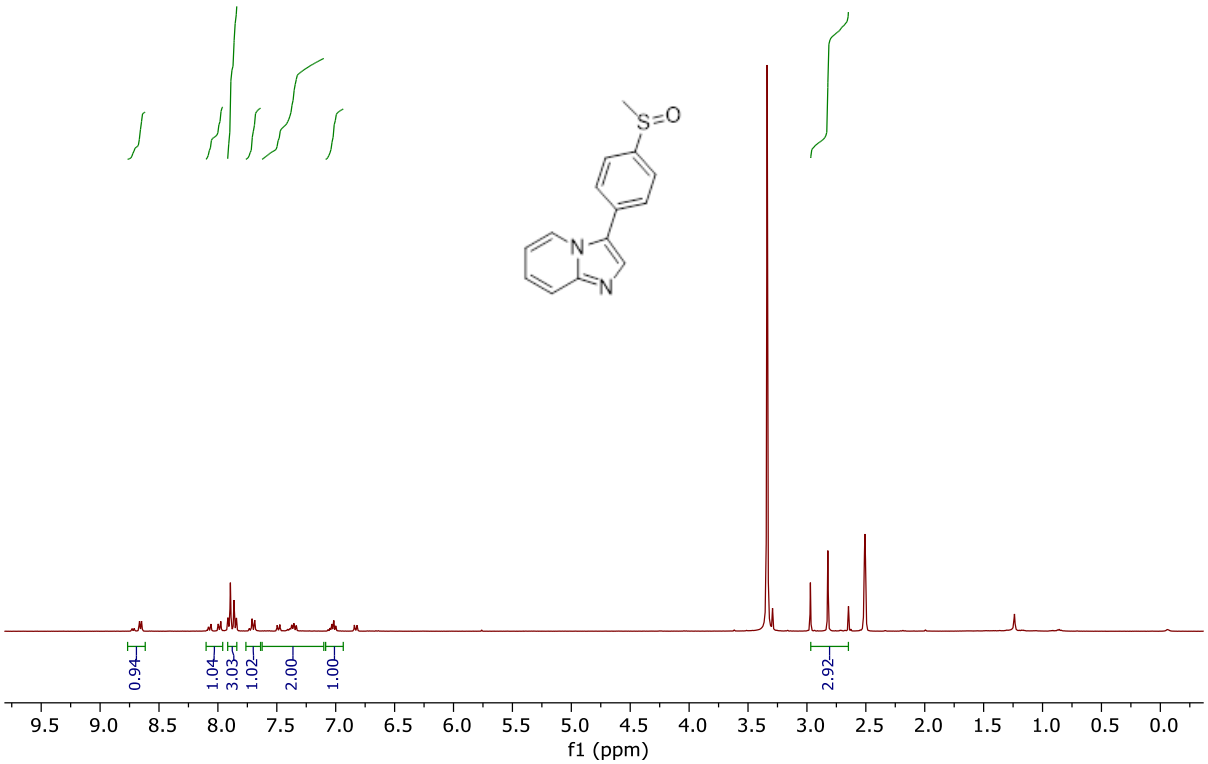
^{1}H/^{1}H COSY NMR Spectrum of (**26**) (400 MHz, DMSO-d^{6}):

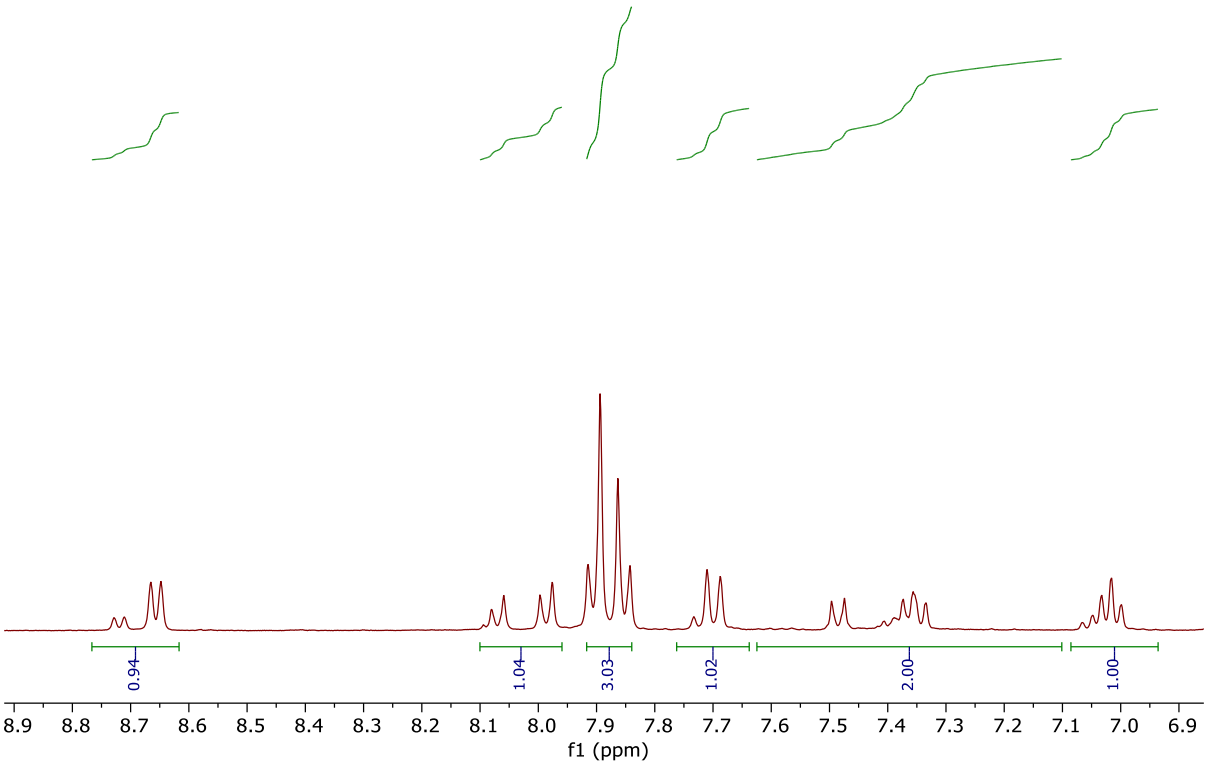


MS Spectrum of (**26**) (EI):

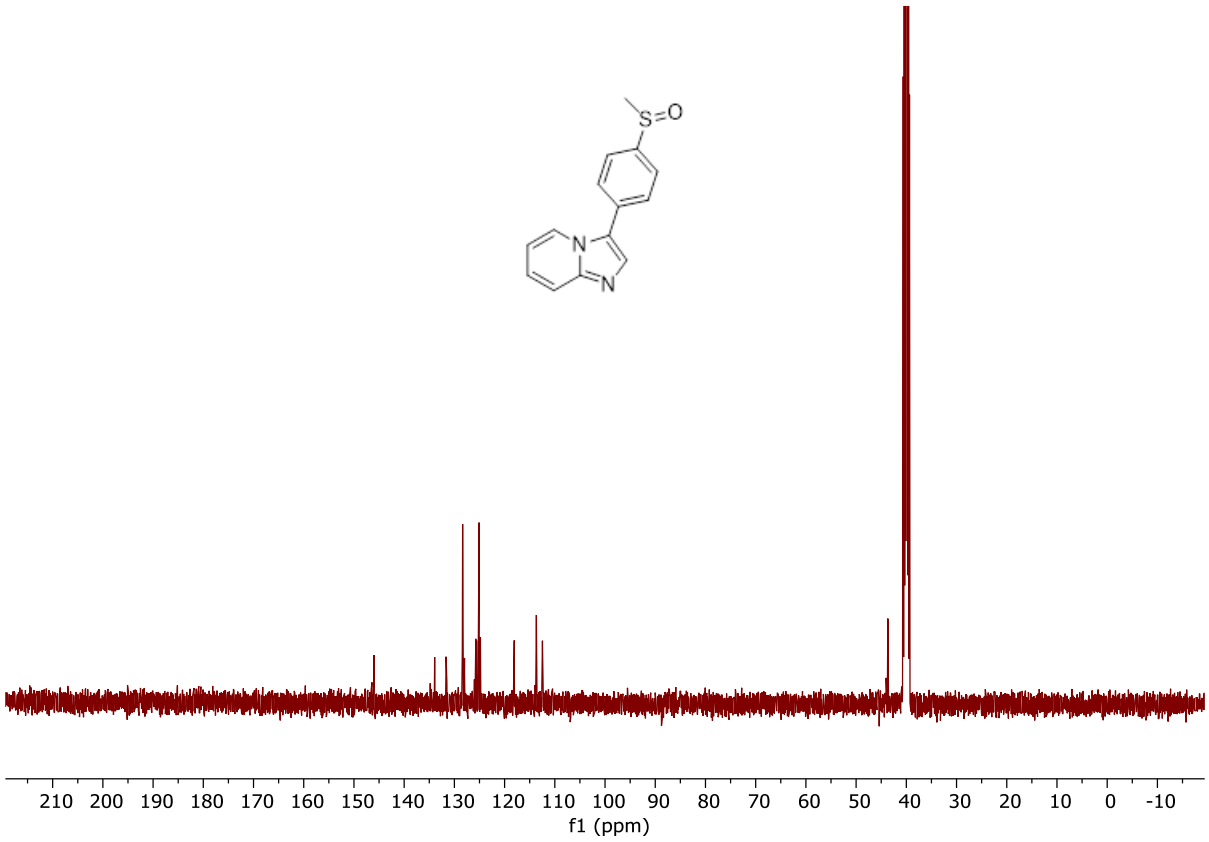


^{1}H NMR Spectrum of (**27**) (400 MHz, DMSO-d^{6}):

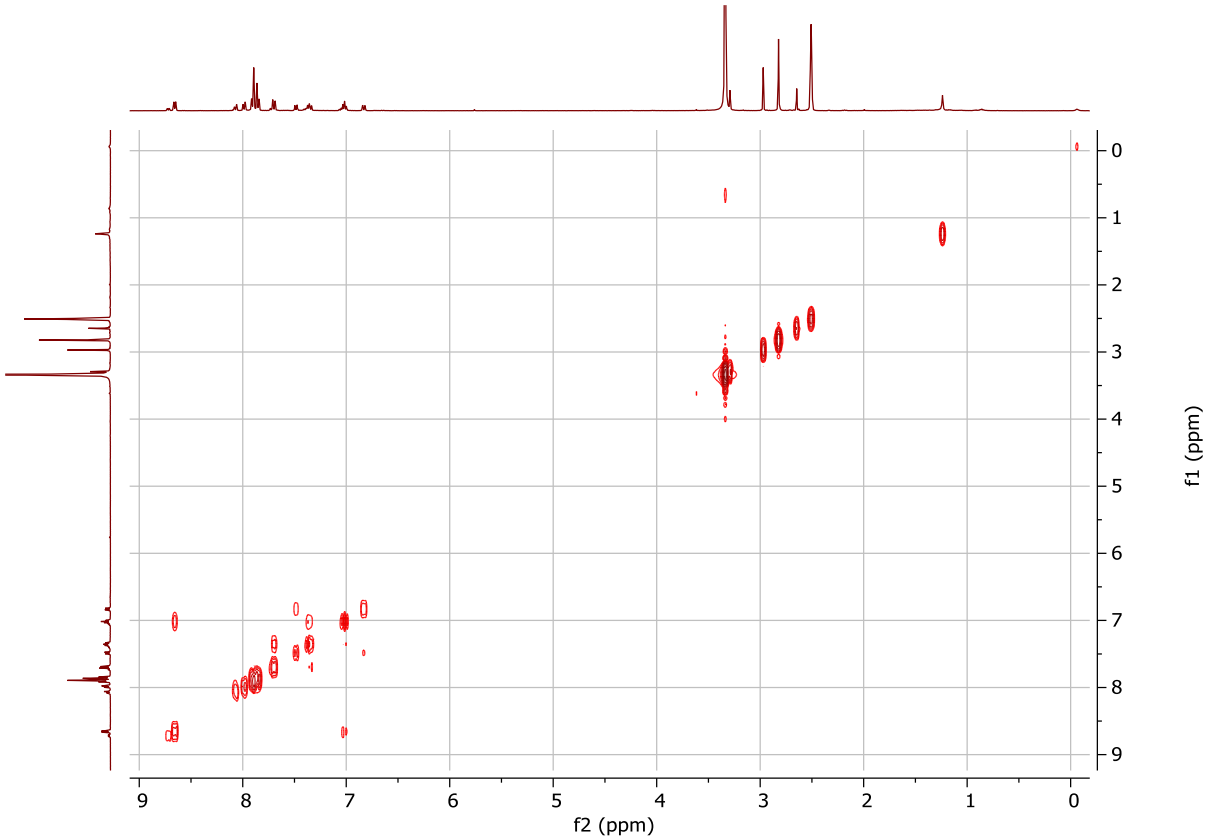




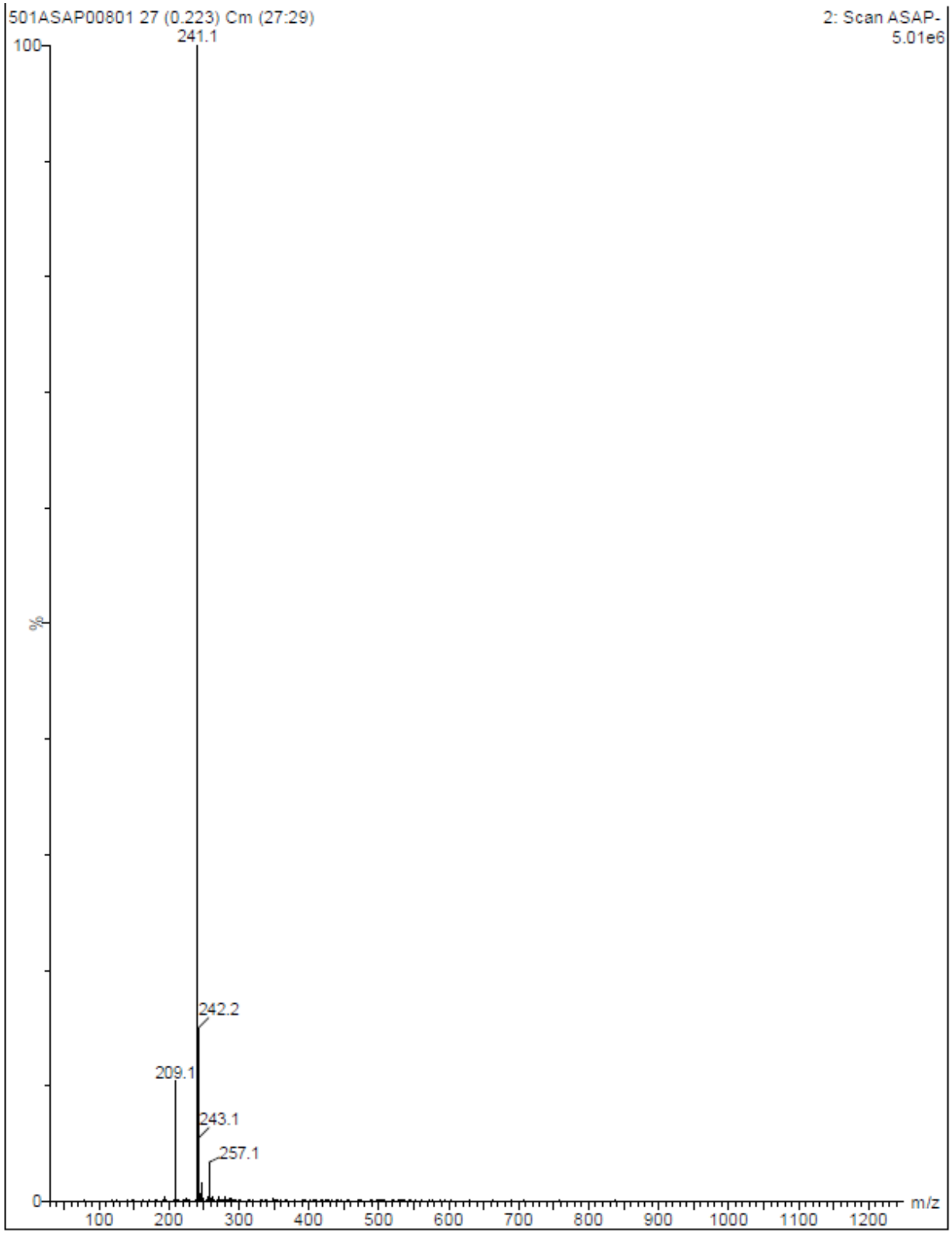
^{13}C NMR Spectrum of (**27**) (400 MHz, DMSO-d^{6}):



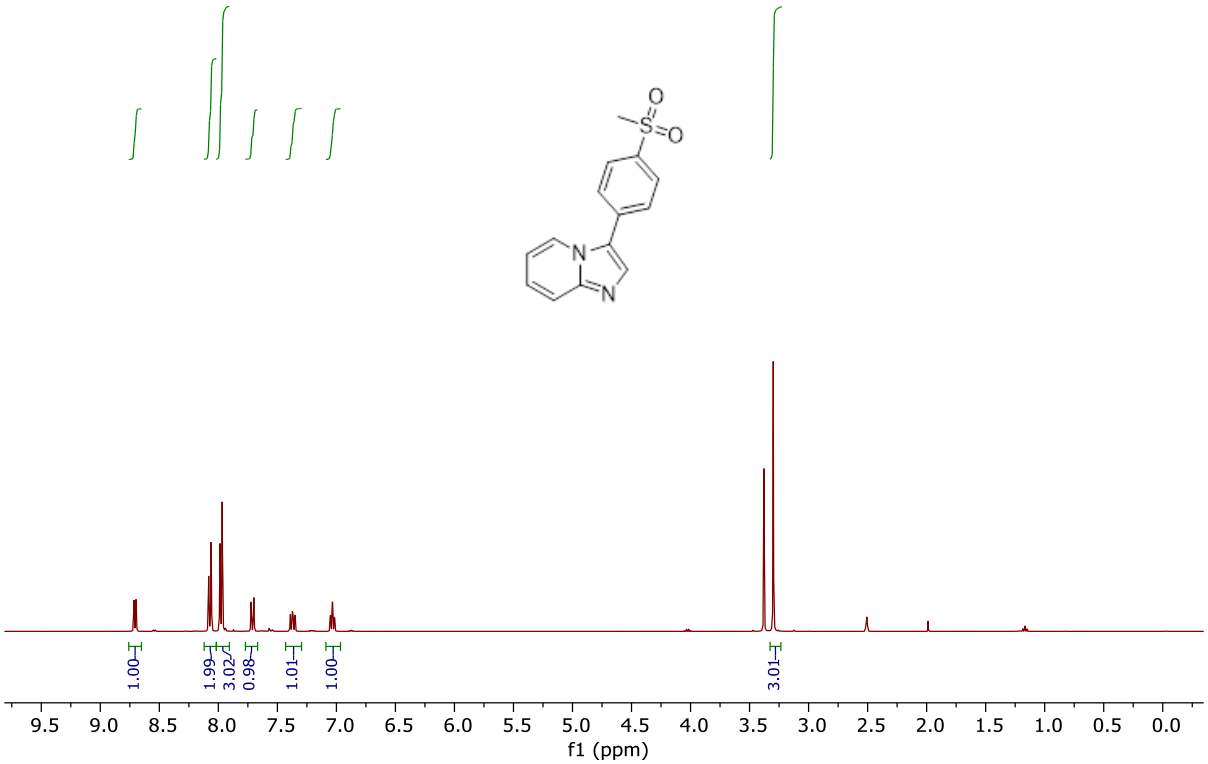
^{1}H/^{1}H COSY NMR Spectrum of (**27**) (400 MHz, DMSO-d^{6}):

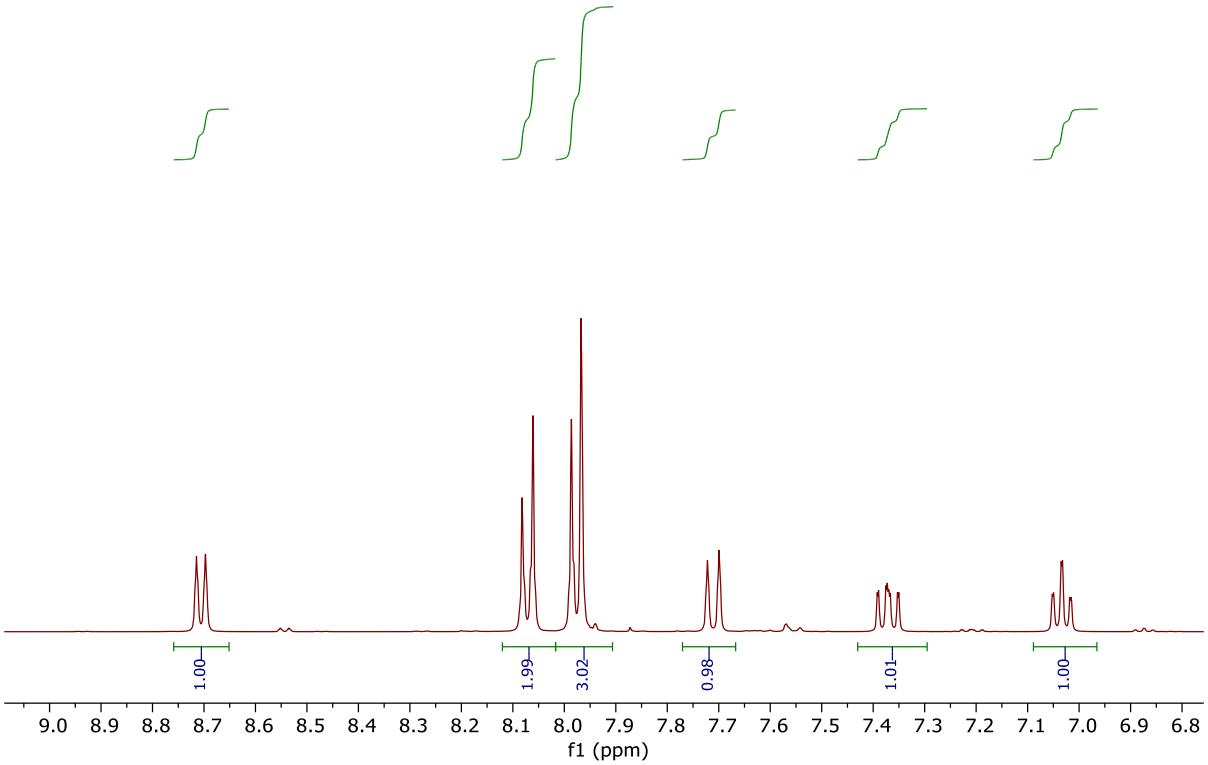


MS Spectrum of (**27**):

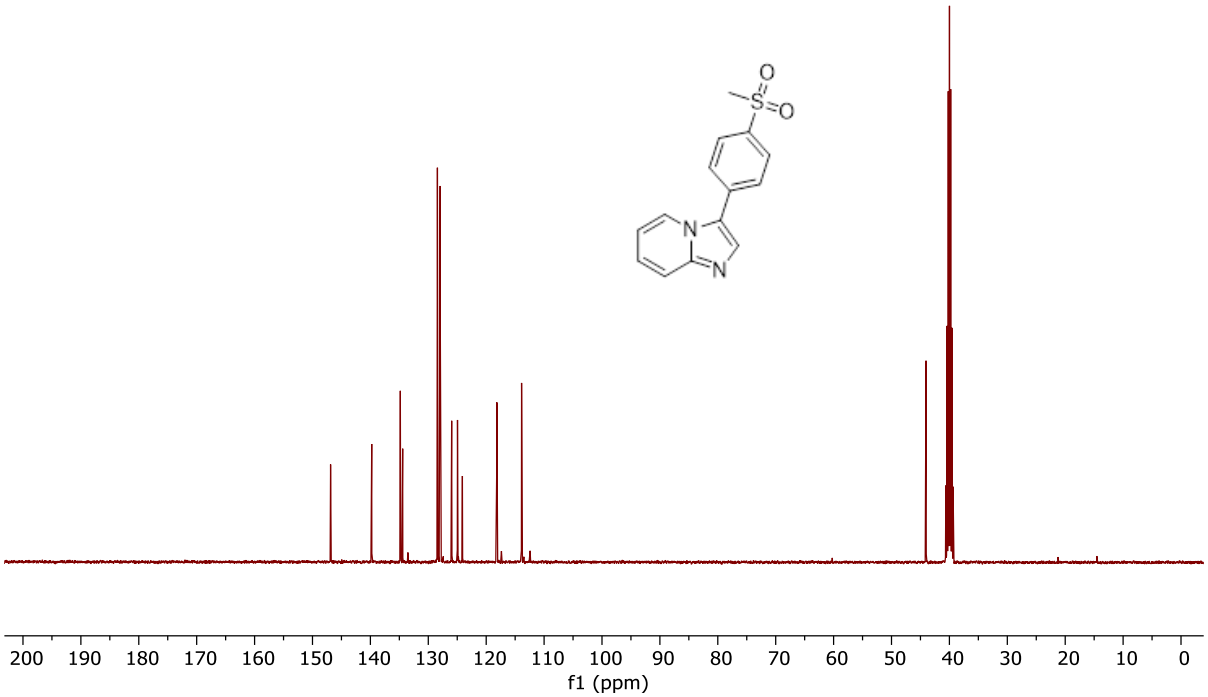


^{1}H NMR Spectrum of (**28**) (400 MHz, DMSO-d^{6}):

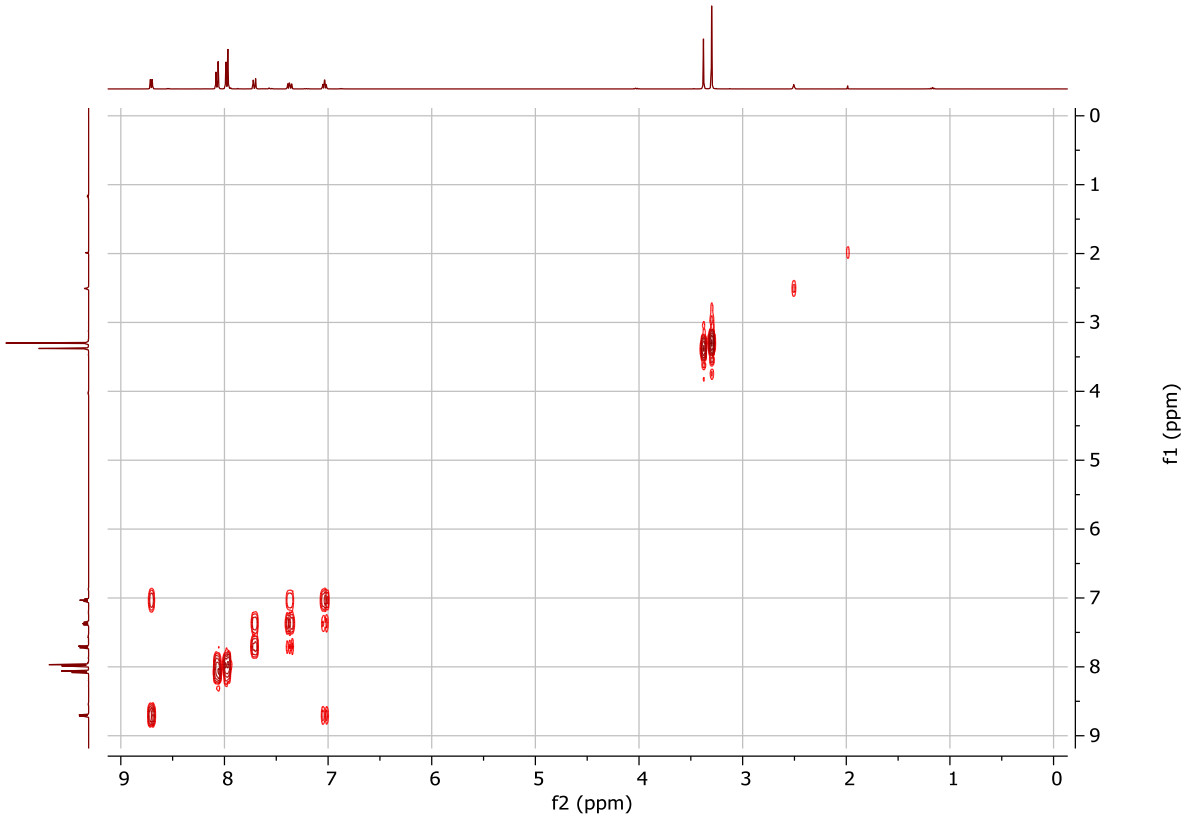




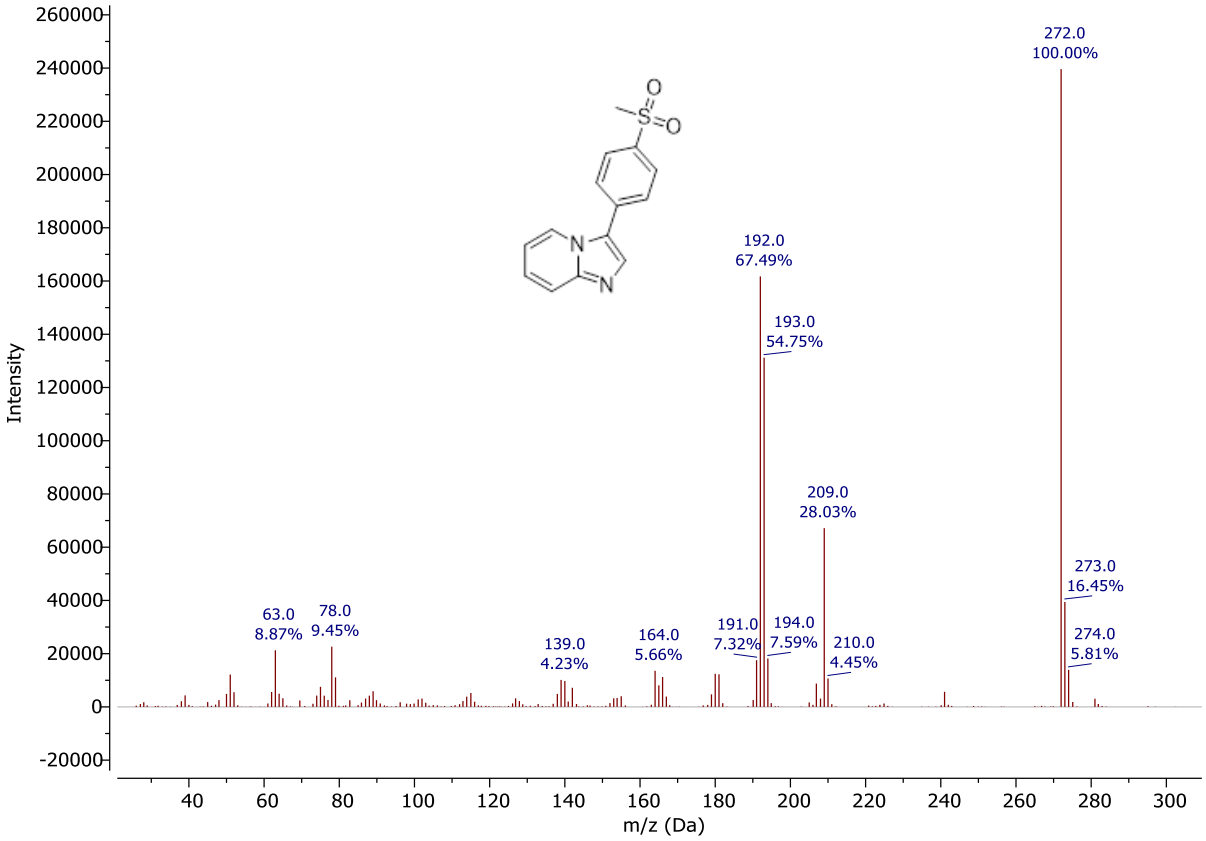
^{13}C NMR Spectrum of (**28**) (400 MHz, DMSO-d^{6}):



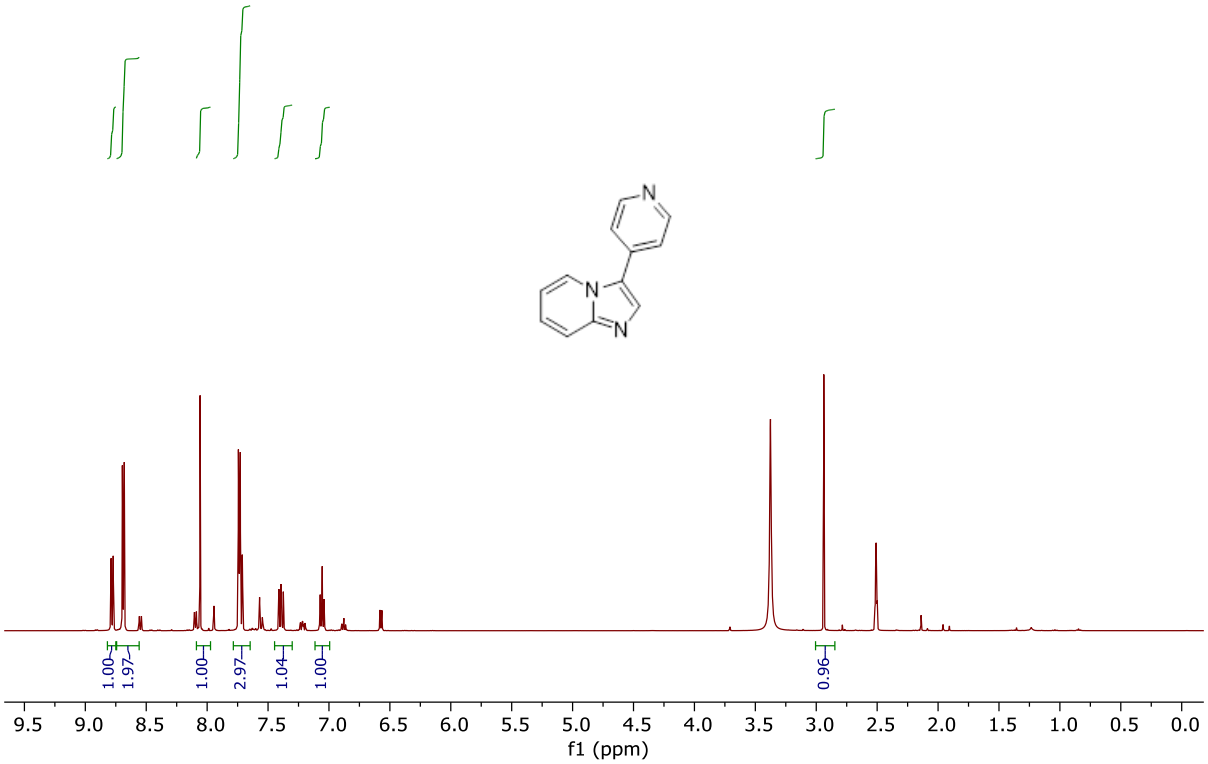
^{1}H/^{1}H COSY NMR Spectrum of (**28**) (400 MHz, DMSO-d^{6}):



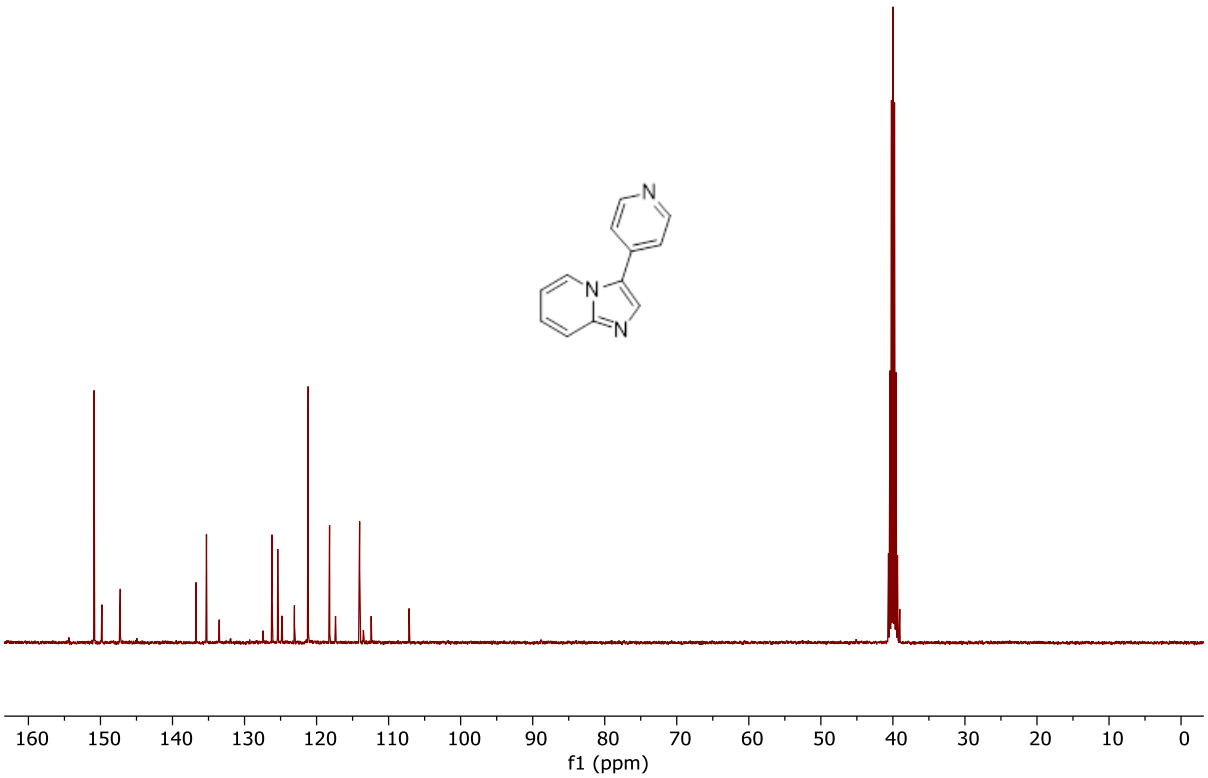
MS Spectrum of (**28**) (EI):



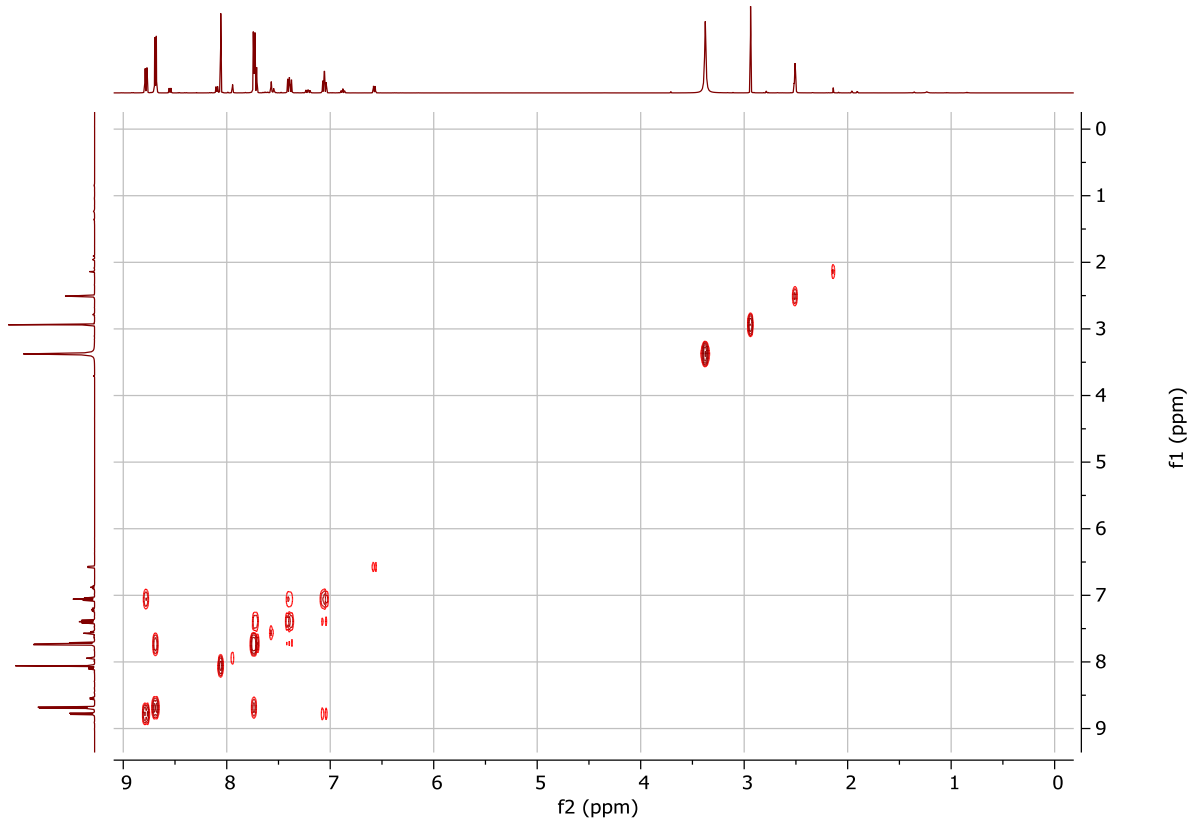
^{1}H NMR Spectrum of (**29**) (400 MHz, DMSO-d^{6}):



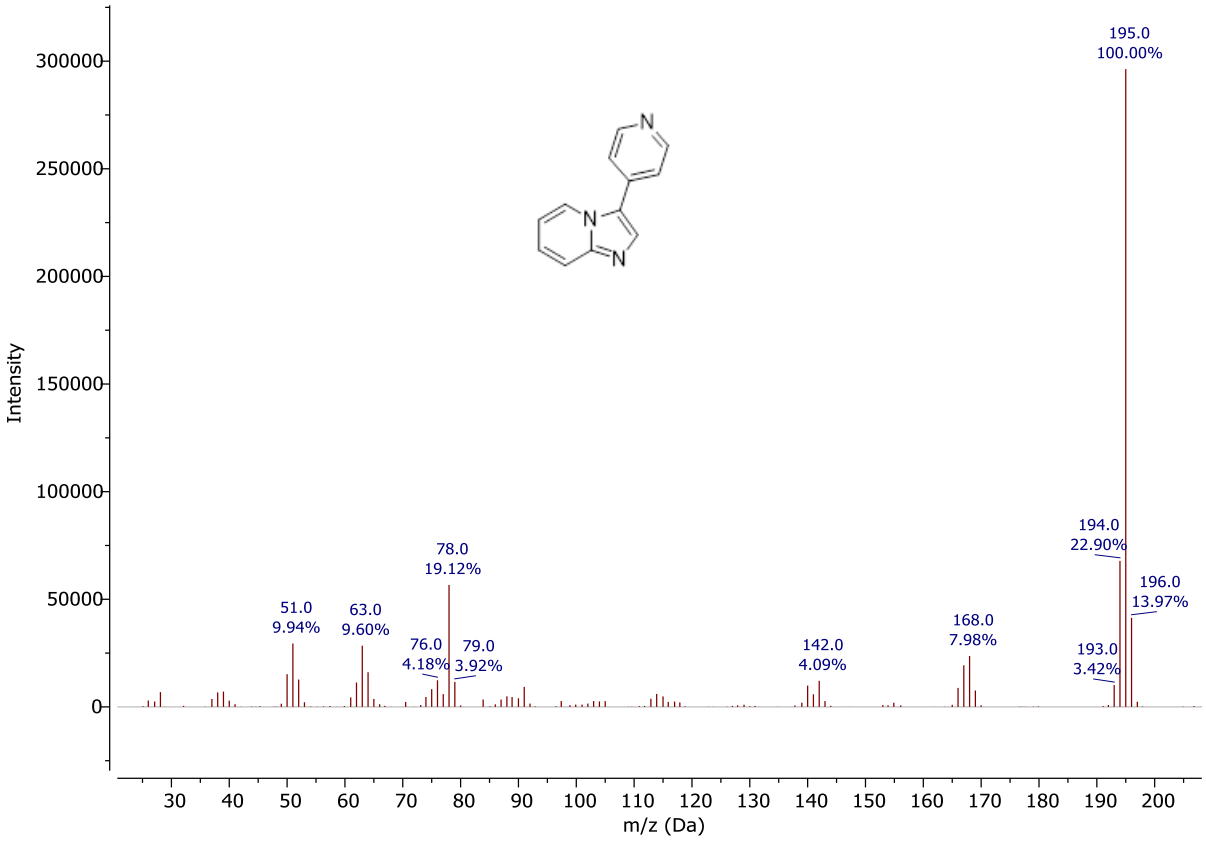
^{13}C NMR Spectrum of (**29**) (400 MHz, DMSO-d^{6}):



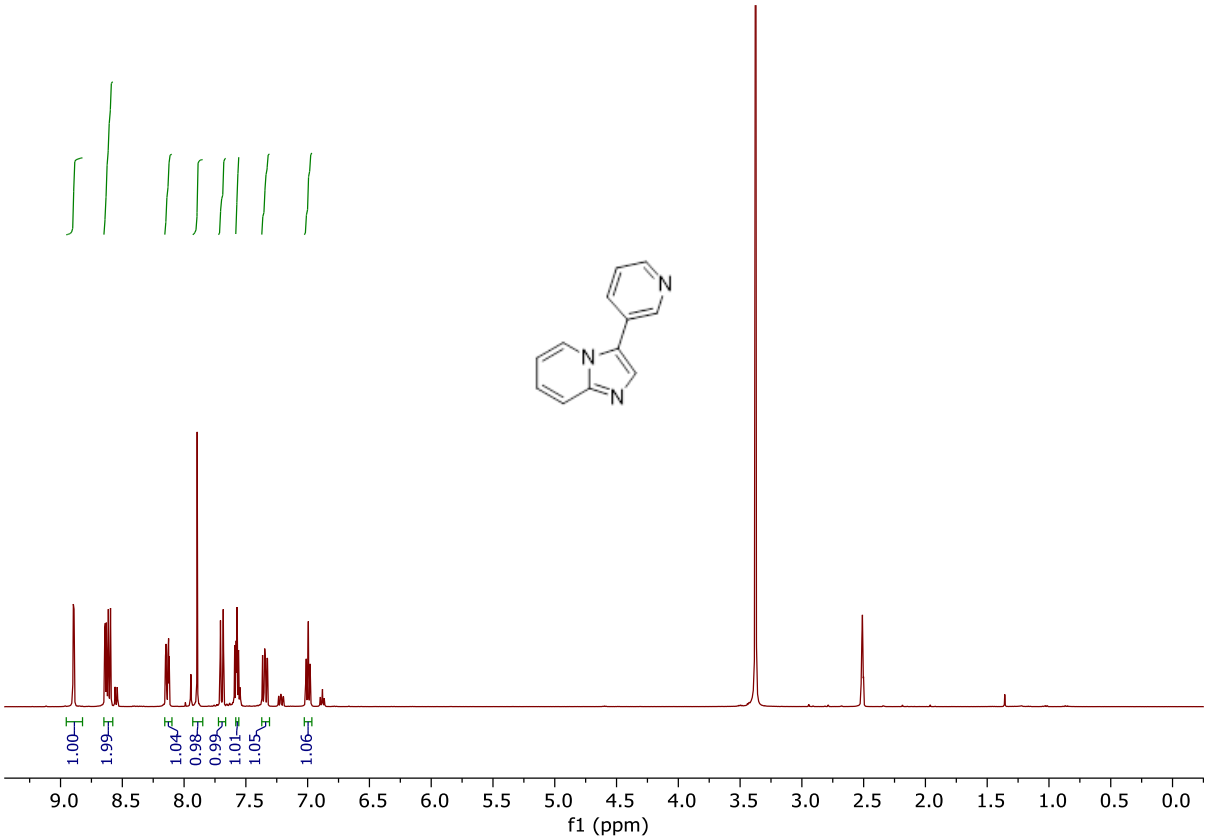
^{1}H/^{1}H COSY NMR Spectrum of (**29**) (400 MHz, DMSO-d^{6}):



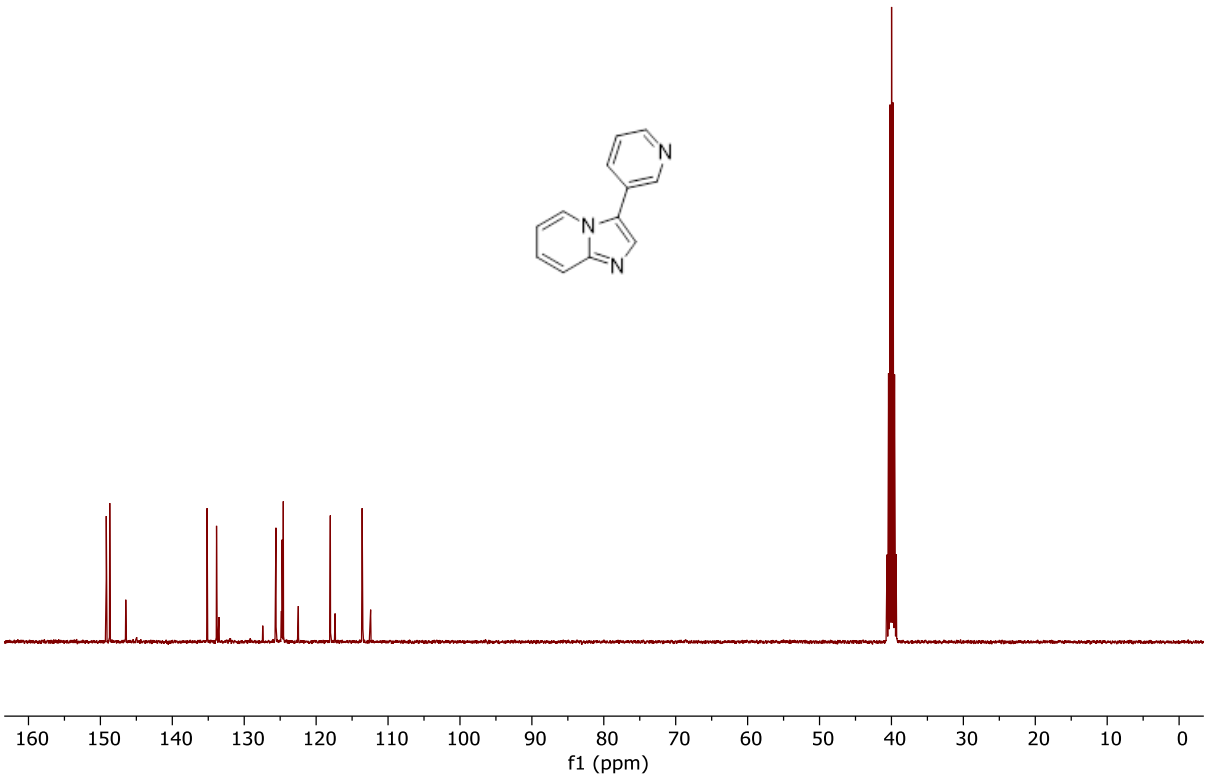
MS Spectrum of (**29**) (EI):



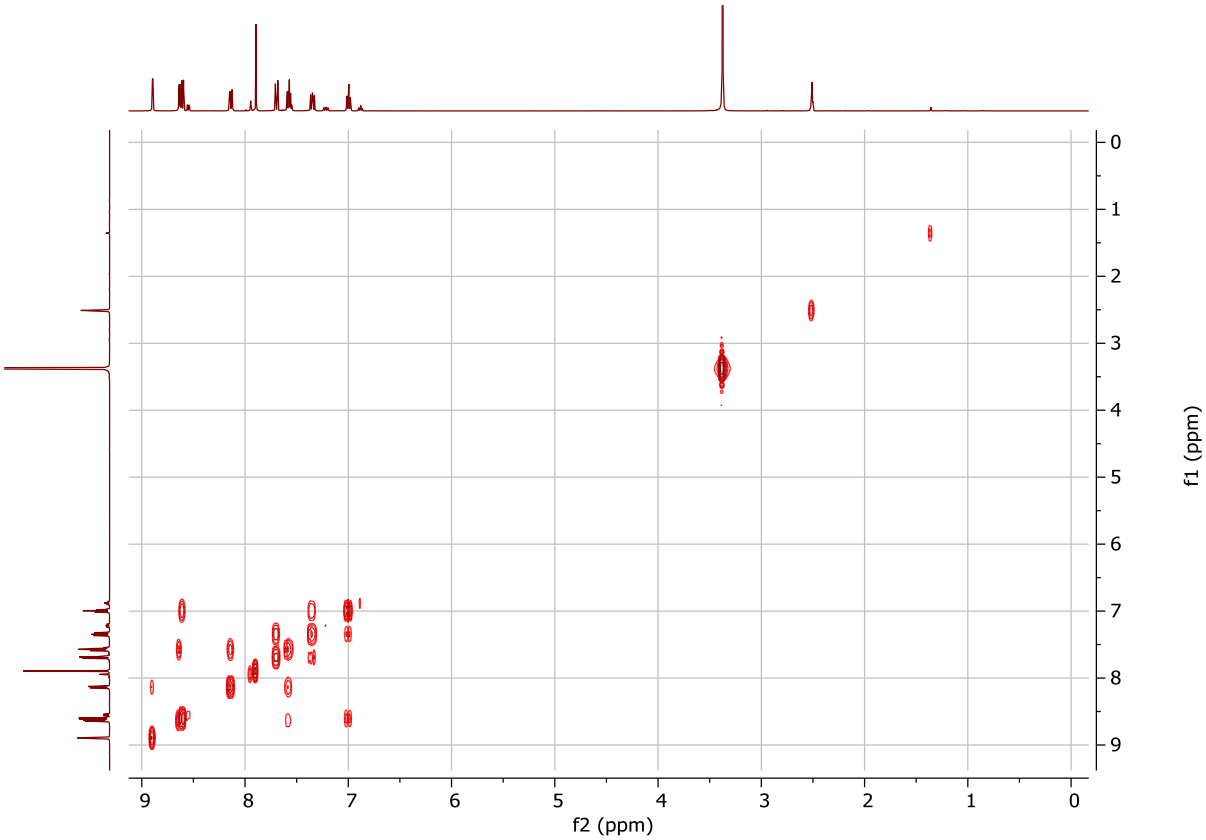
^{1}H NMR Spectrum of (**30**) (400 MHz, DMSO-d^{6}):



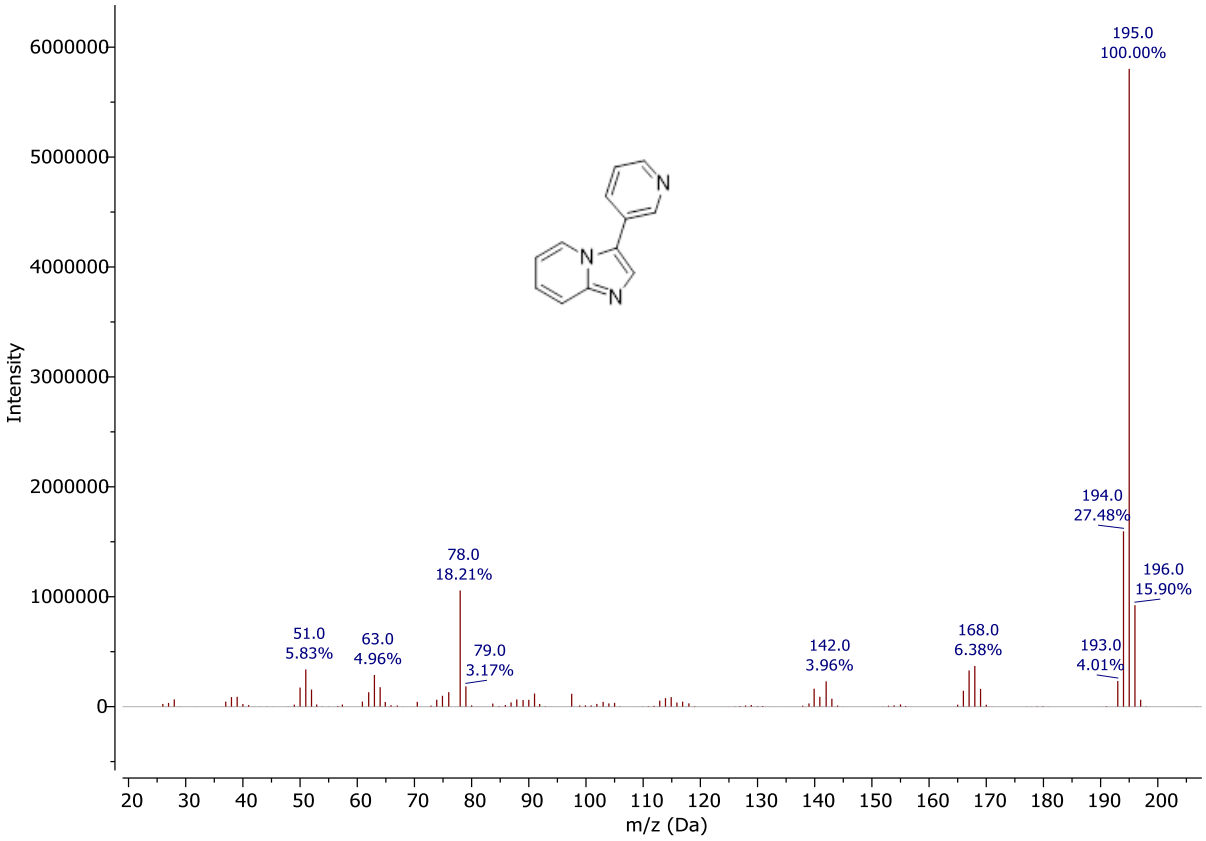
^{13}C NMR Spectrum of (**30**) (400 MHz, DMSO-d^{6}):



^{1}H/^{1}H COSY NMR Spectrum of (**30**) (400 MHz, DMSO-d^{6}):

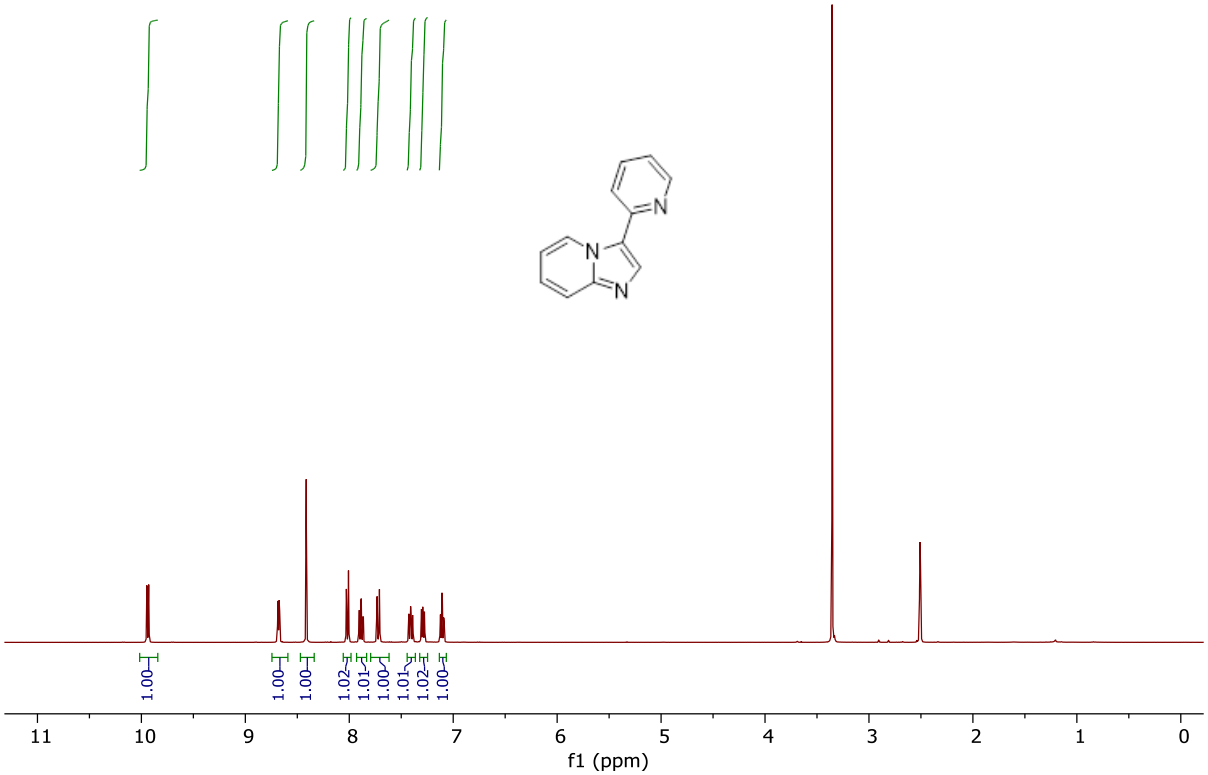


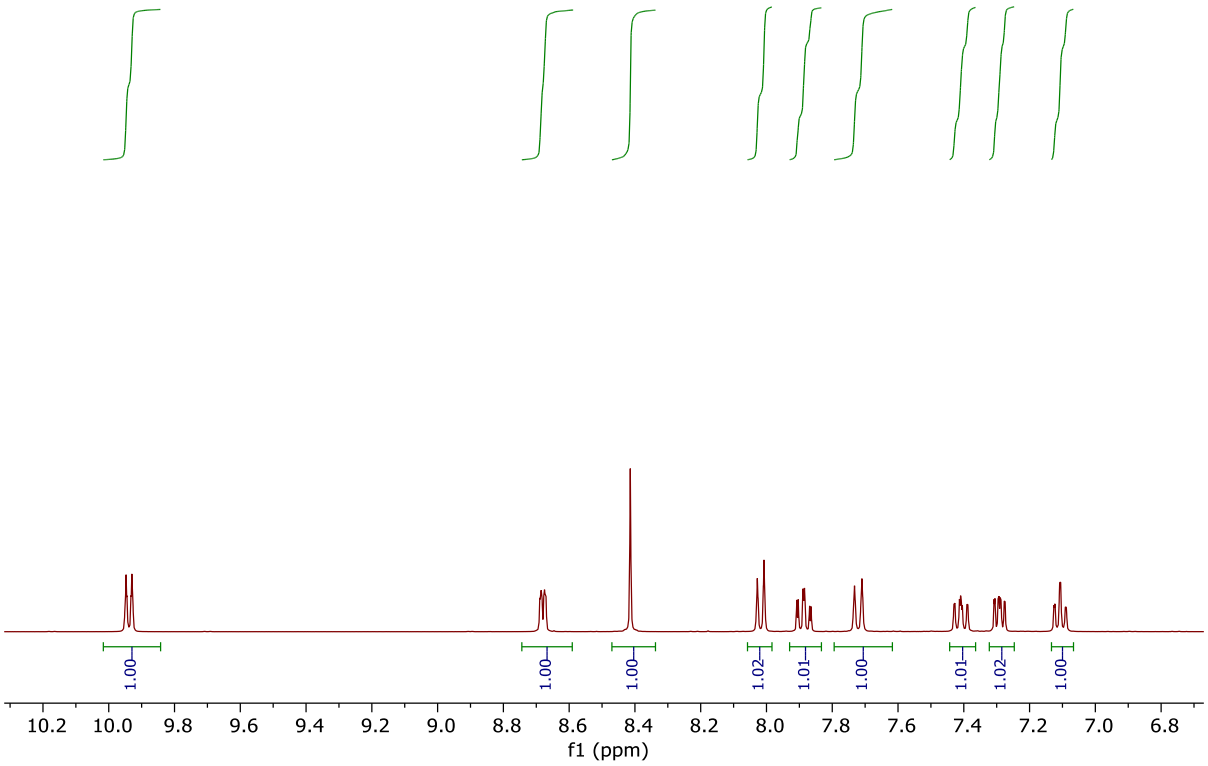
MS Spectrum of (**30**) (EI)



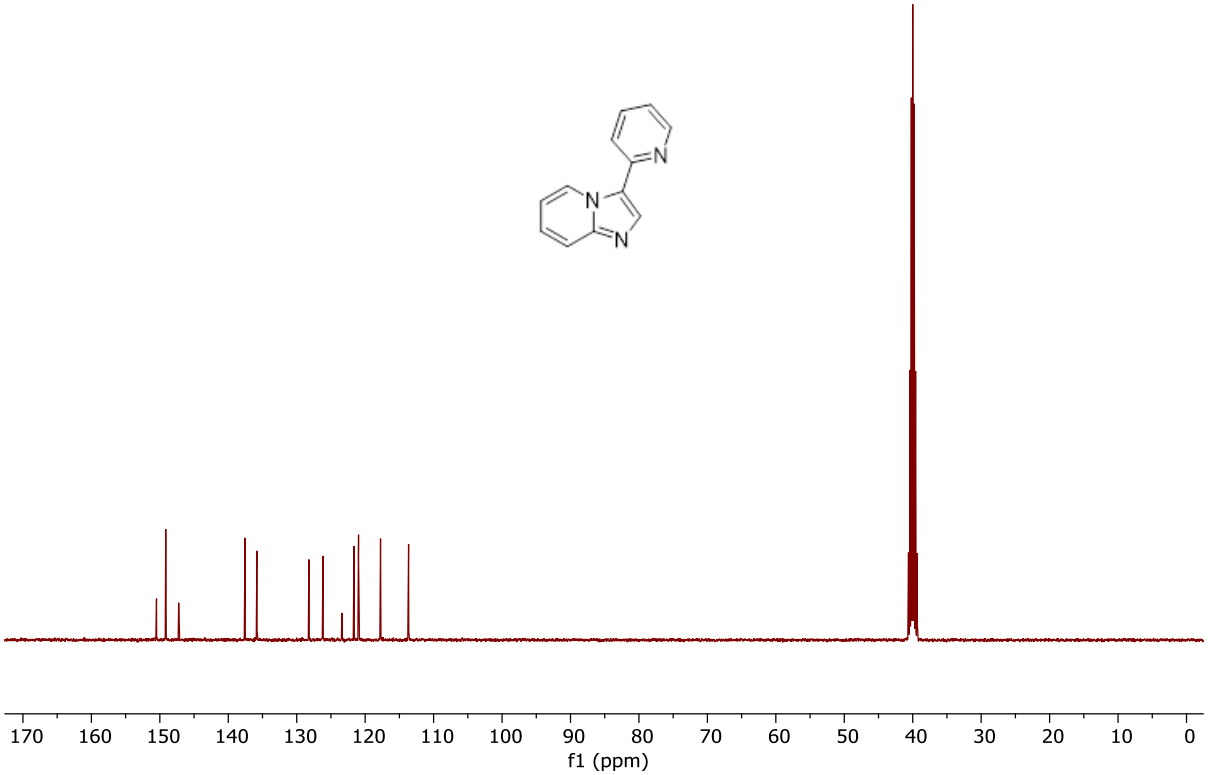
:

^{1}H NMR Spectrum of (**31**) (400 MHz, DMSO-d^{6}):

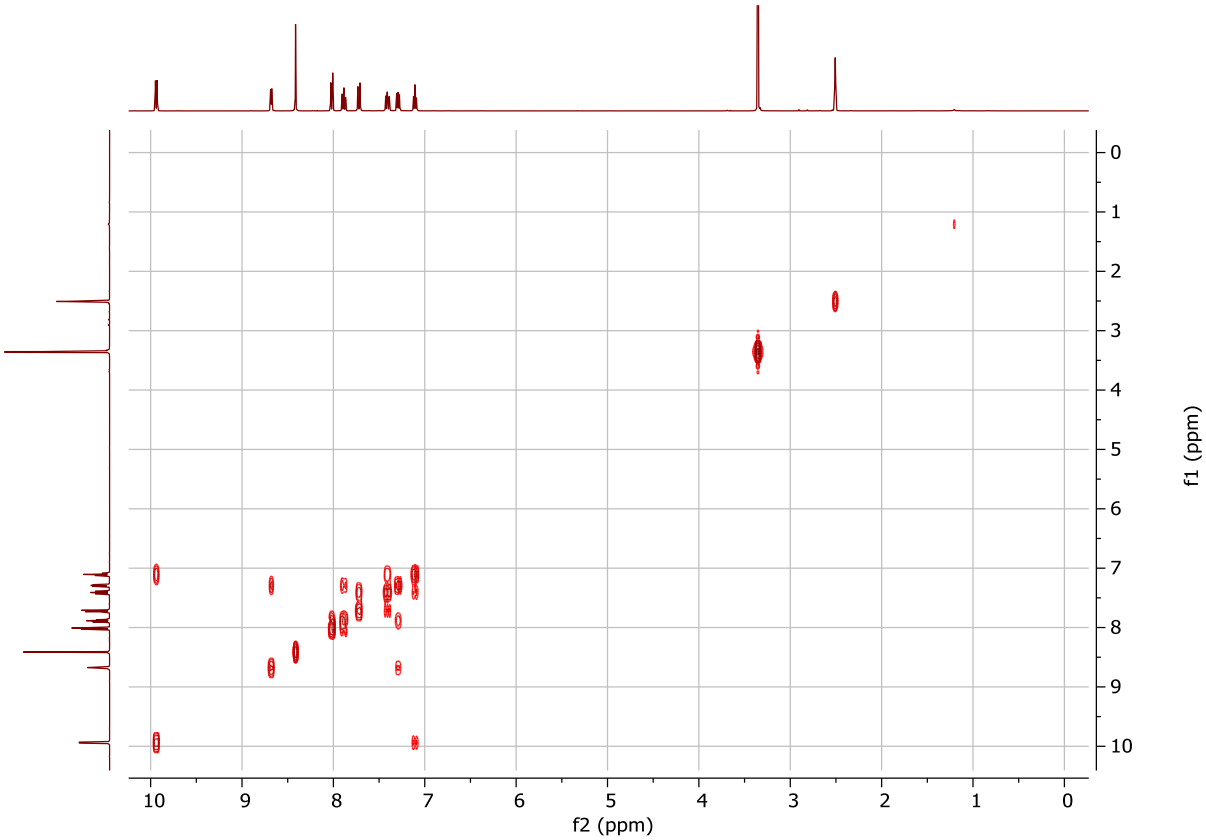


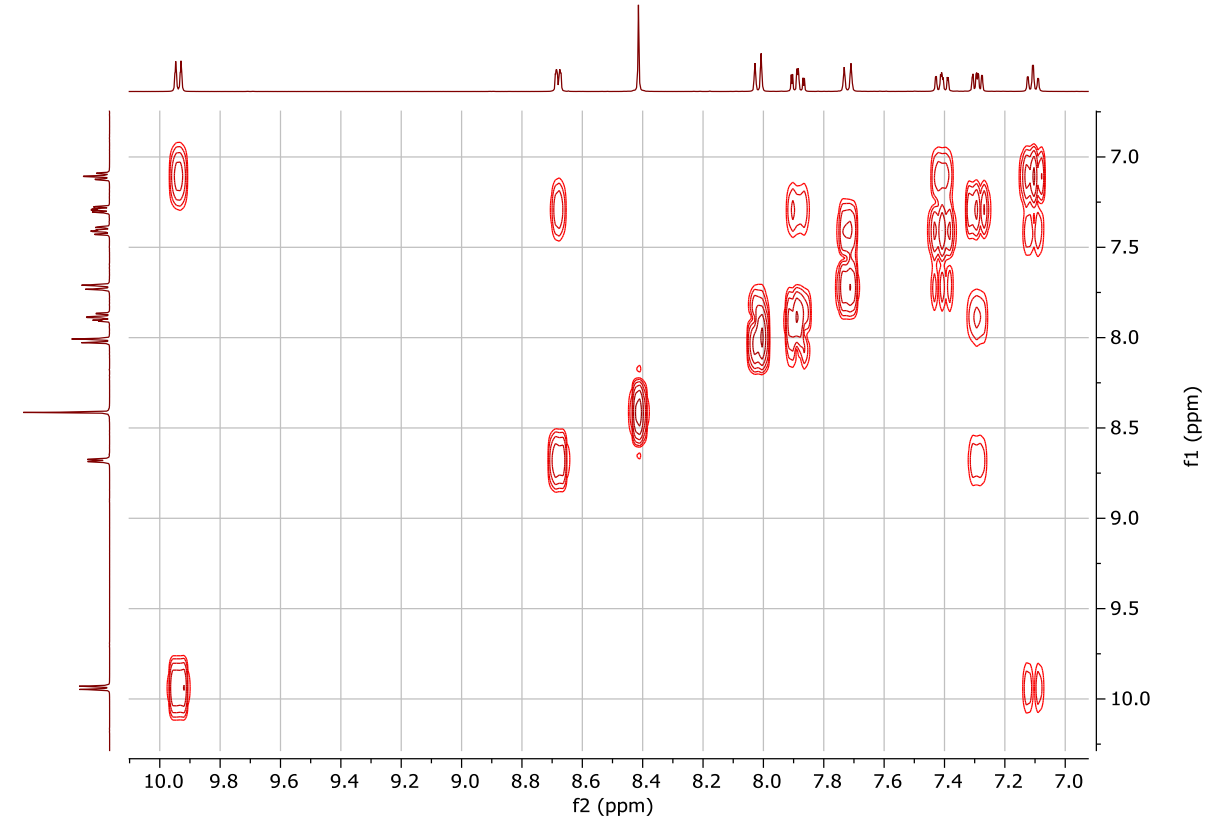


^{13}C NMR Spectrum of (**31**) (400 MHz, DMSO-d^{6}):

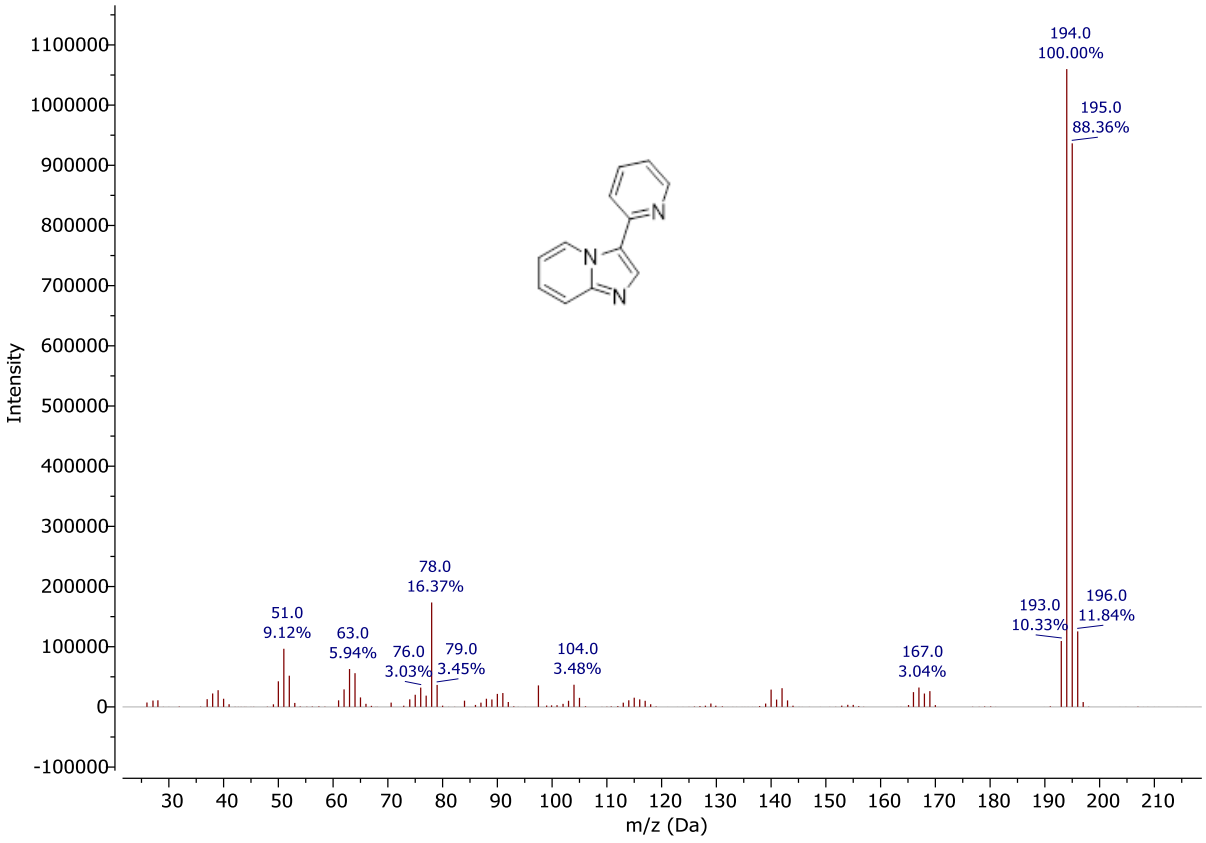


^{1}H/^{1}H COSY NMR Spectrum of (**31**) (400 MHz, DMSO-d^{6}):

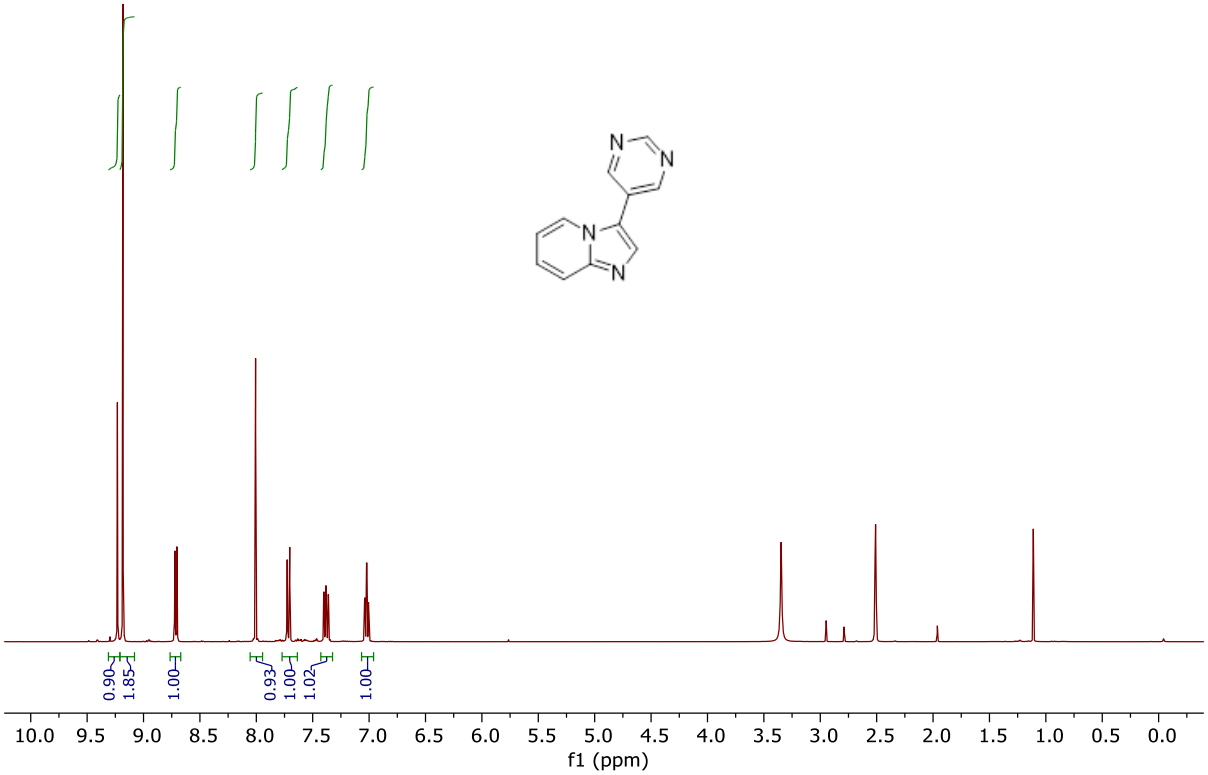


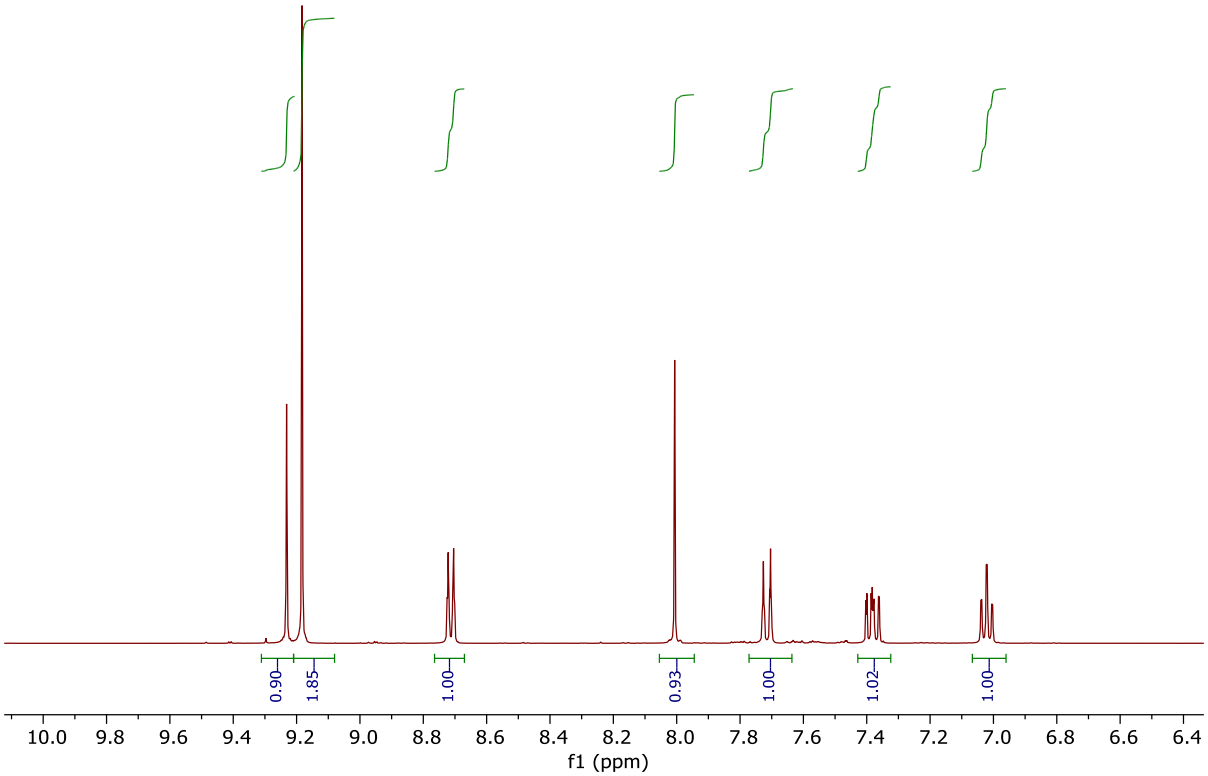


MS Spectrum of (**31**) (EI):

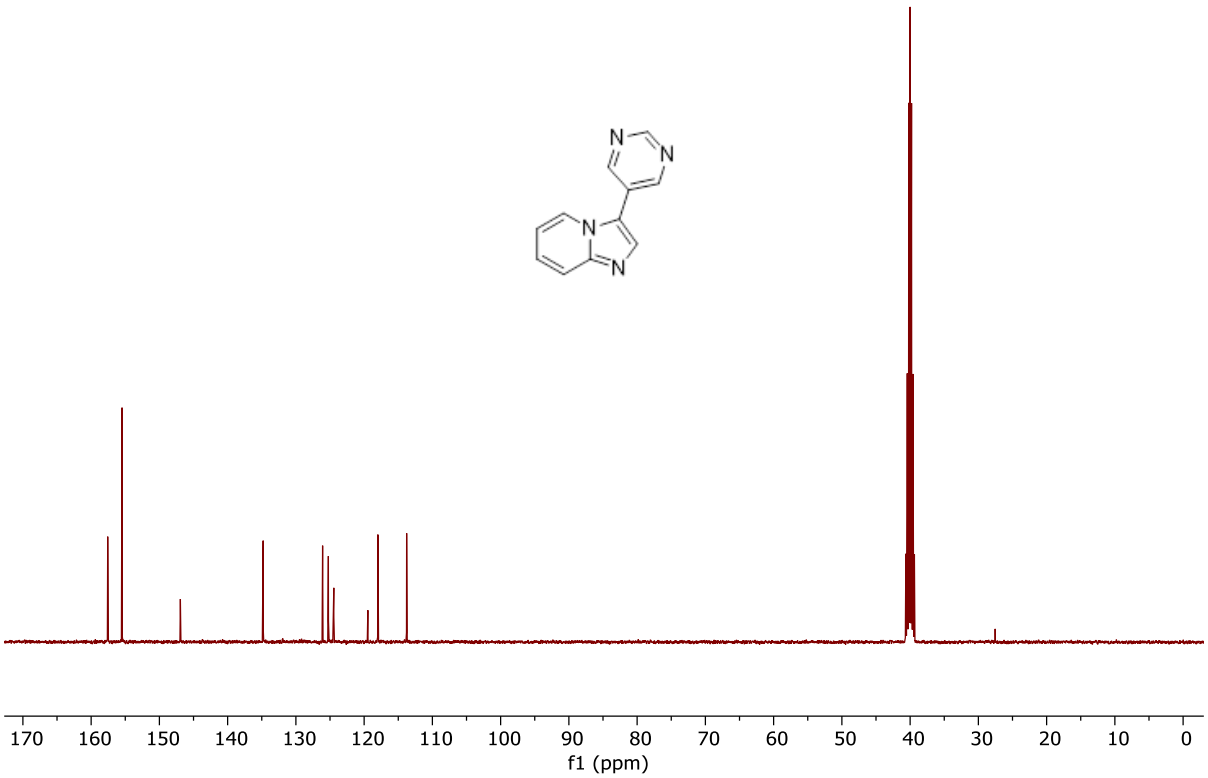


^{1}H NMR Spectrum of (**32**) (400 MHz, DMSO-d^{6}):

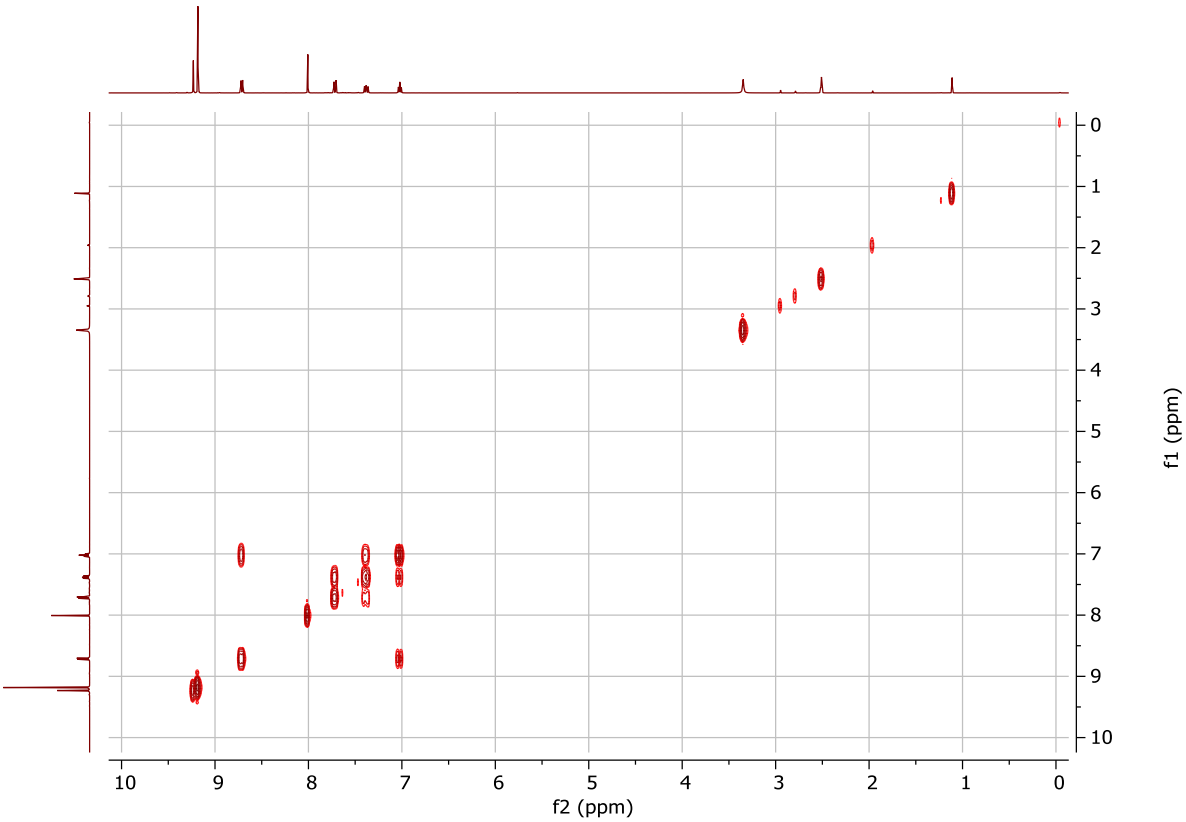


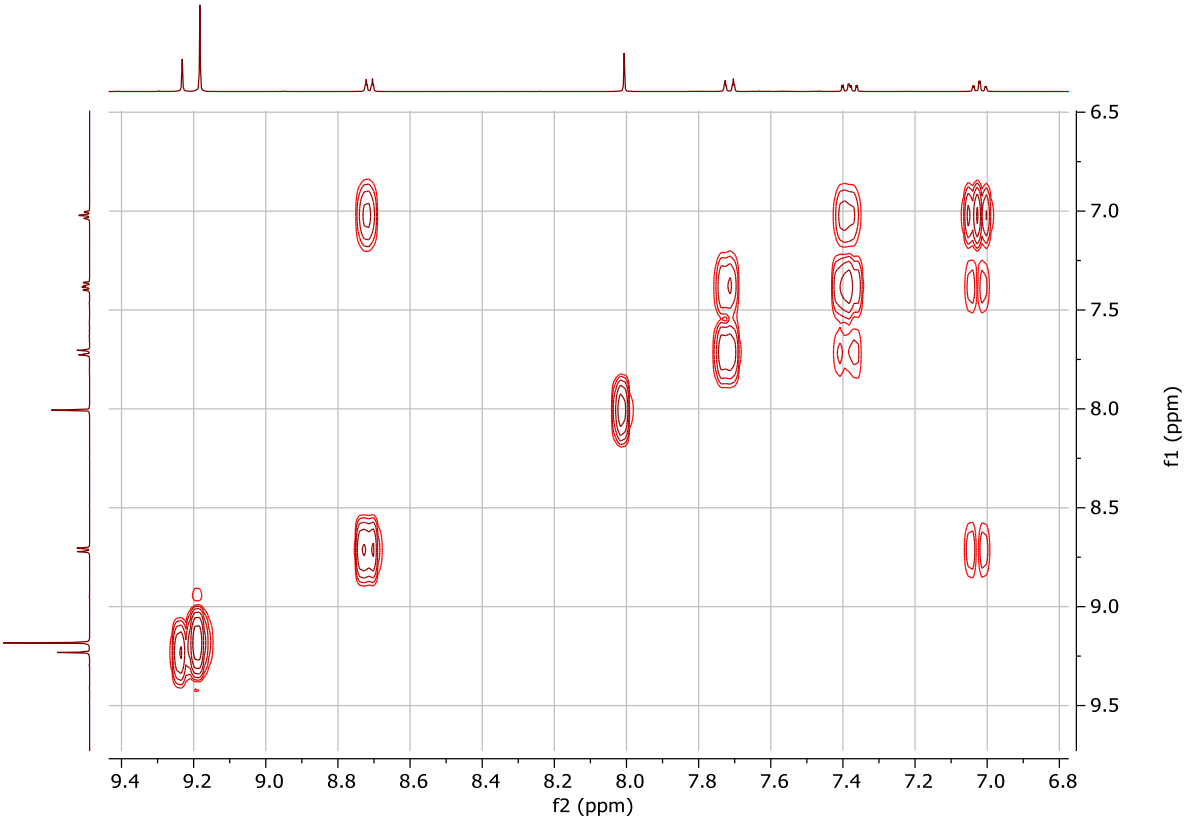


^{13}C NMR Spectrum of (**32**) (400 MHz, DMSO-d^{6}):

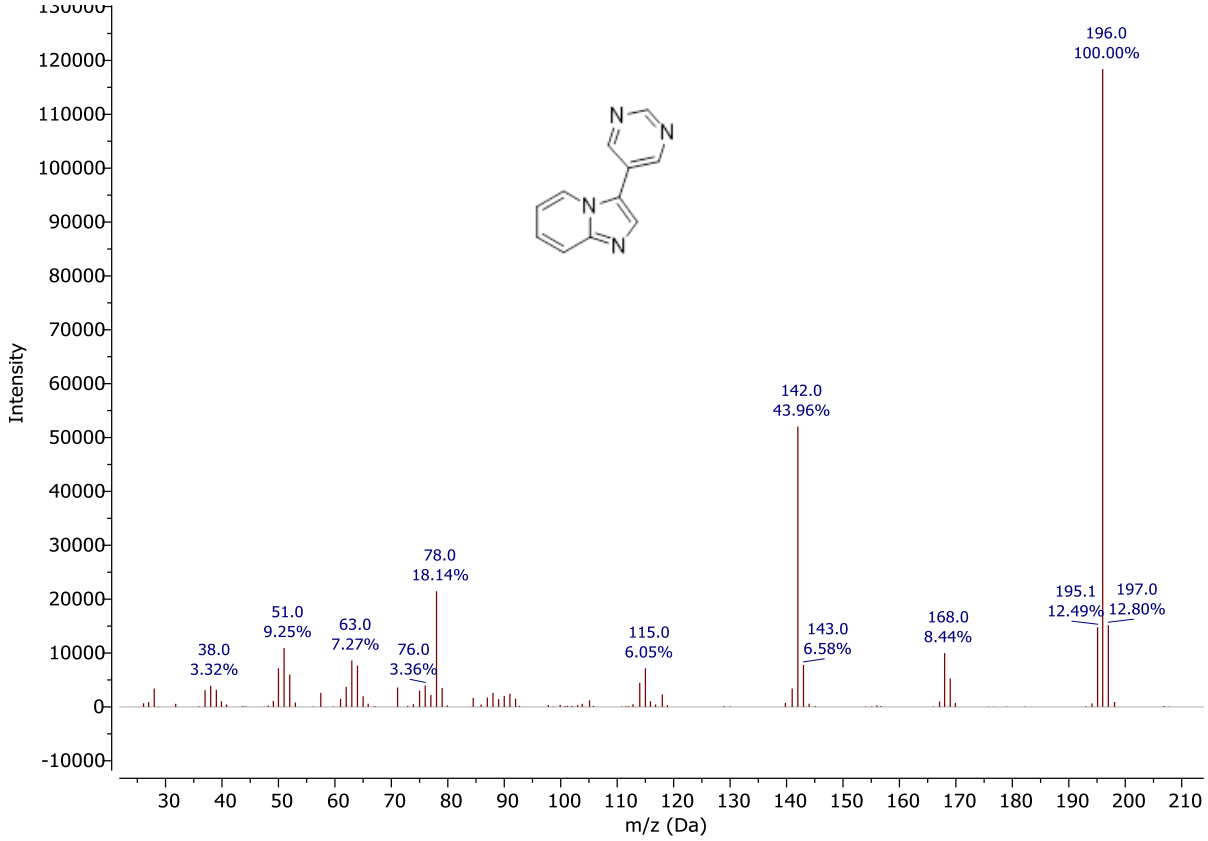


^{1}H/^{1}H COSY NMR Spectrum of (**32**) (400 MHz, DMSO-d^{6}):

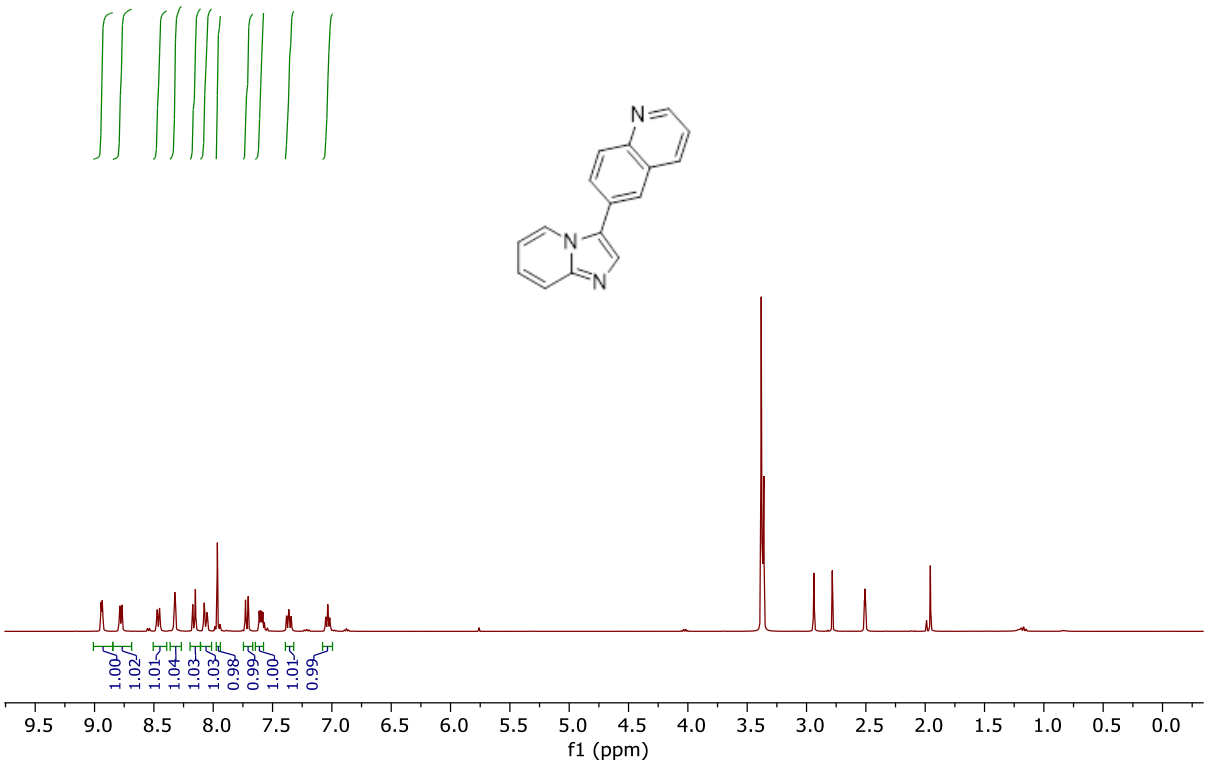


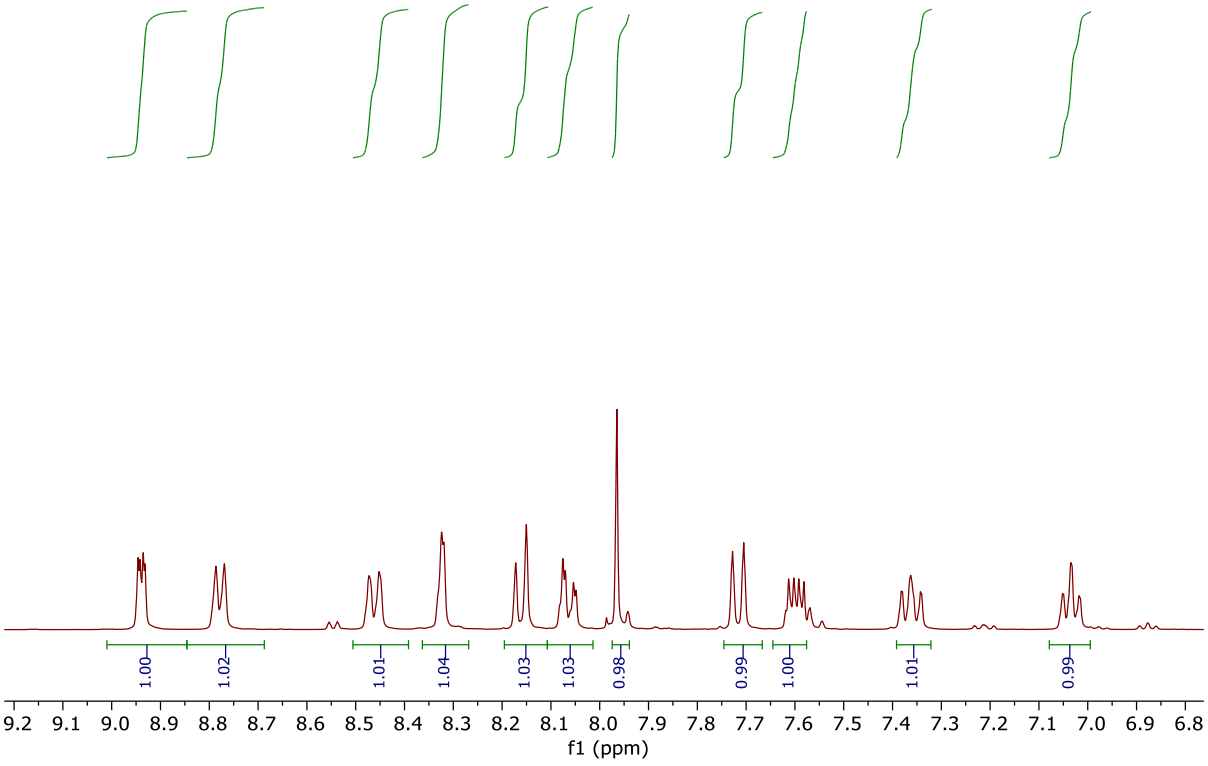


MS Spectrum of (**32**) (EI):

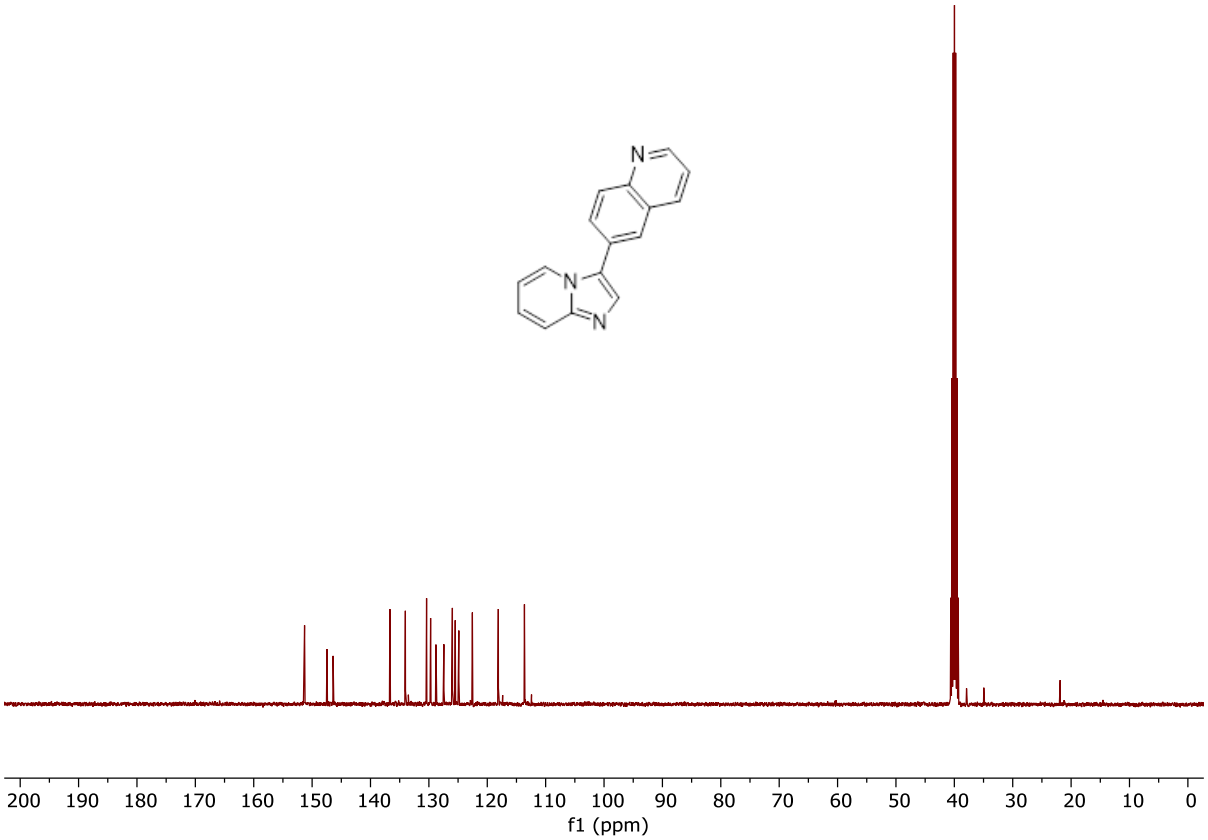


^{1}H NMR Spectrum of (**33**) (400 MHz, DMSO-d^{6}):

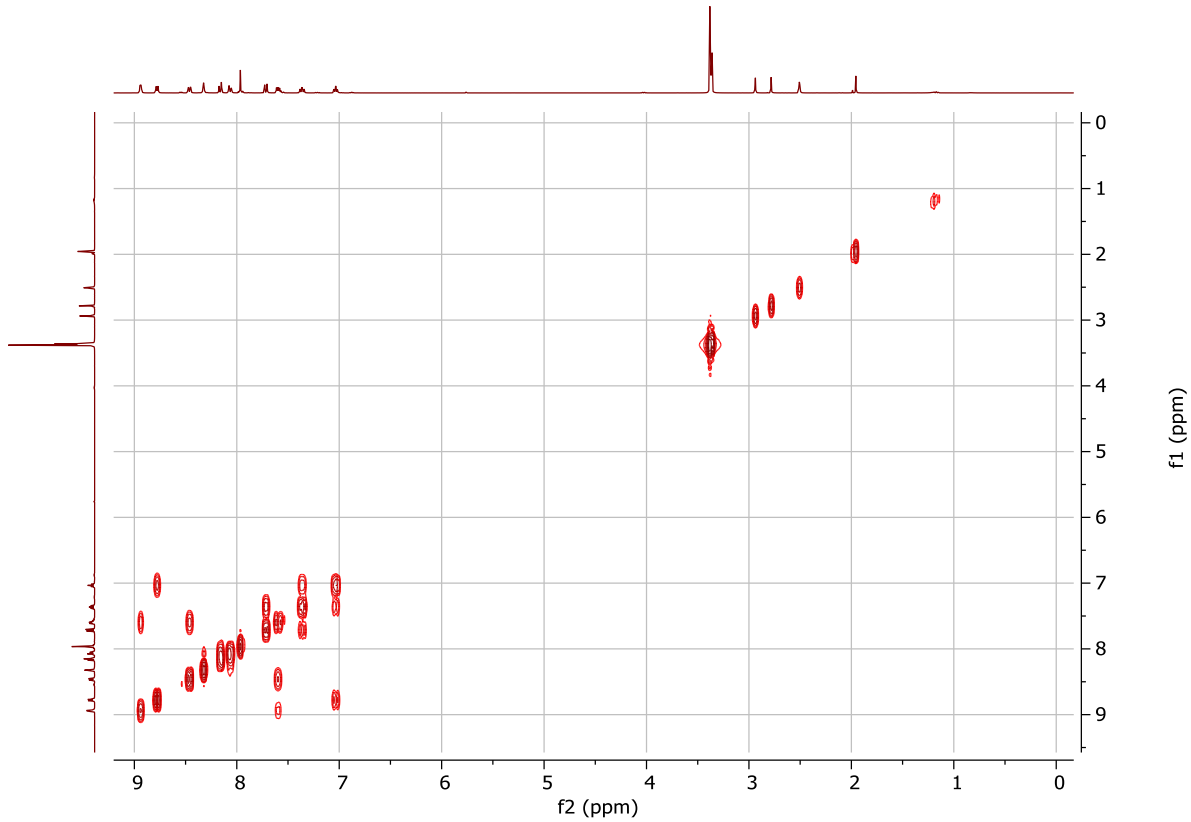




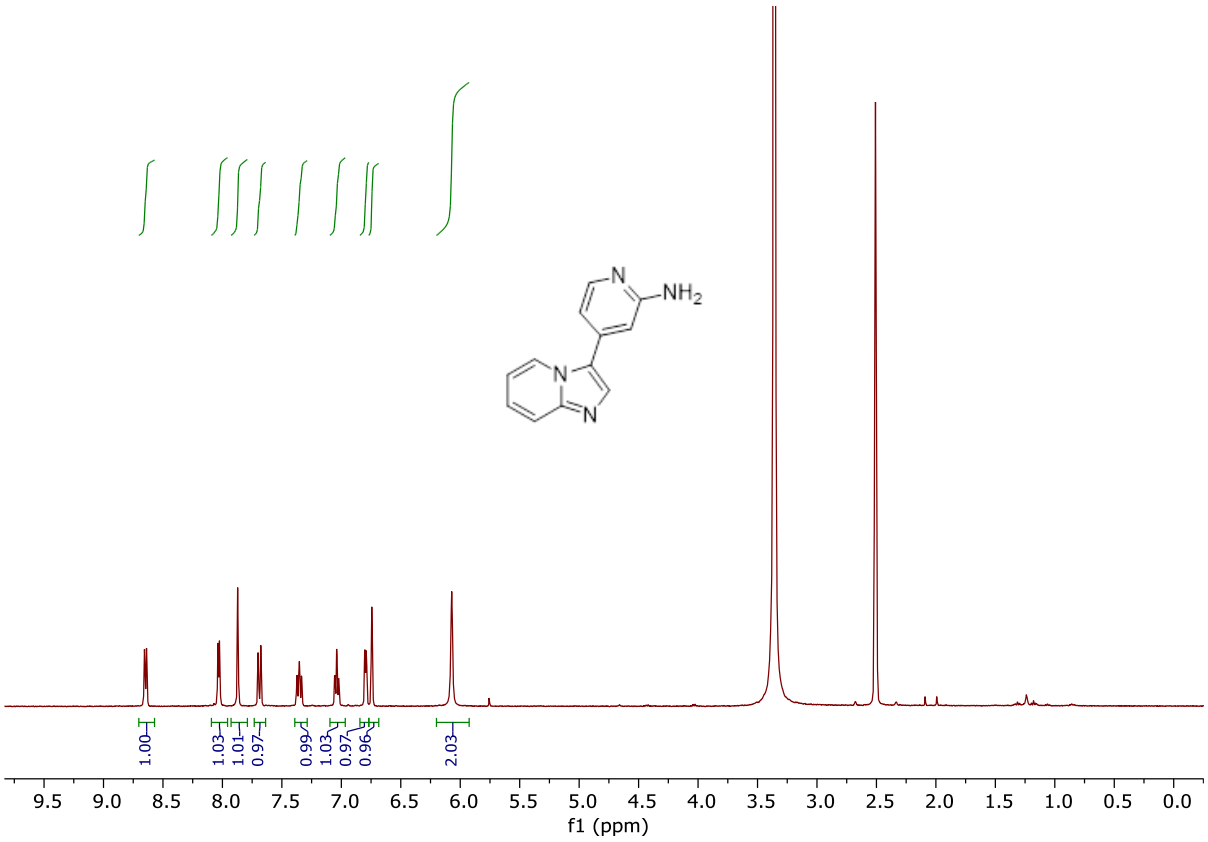
^{13}C NMR Spectrum of (**33**) (400 MHz, DMSO-d^{6}):

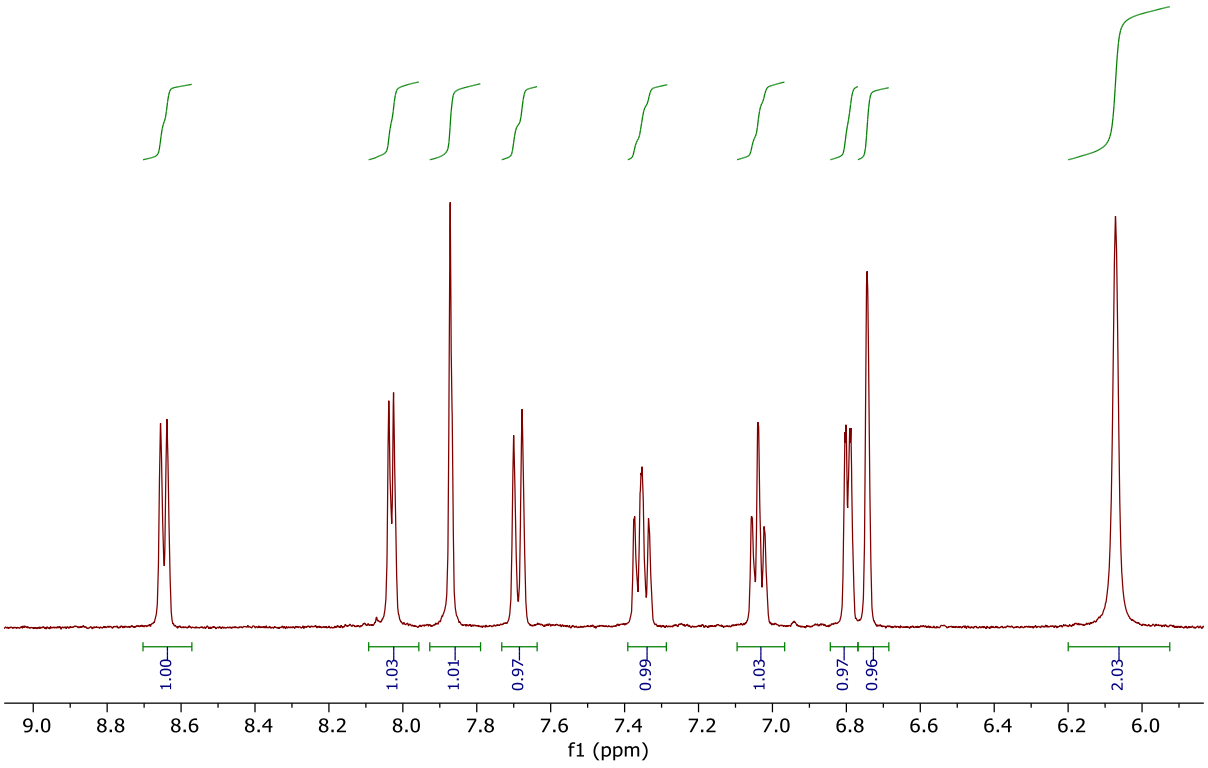


^{1}H/^{1}H COSY NMR Spectrum of (**33**) (400 MHz, DMSO-d^{6}):

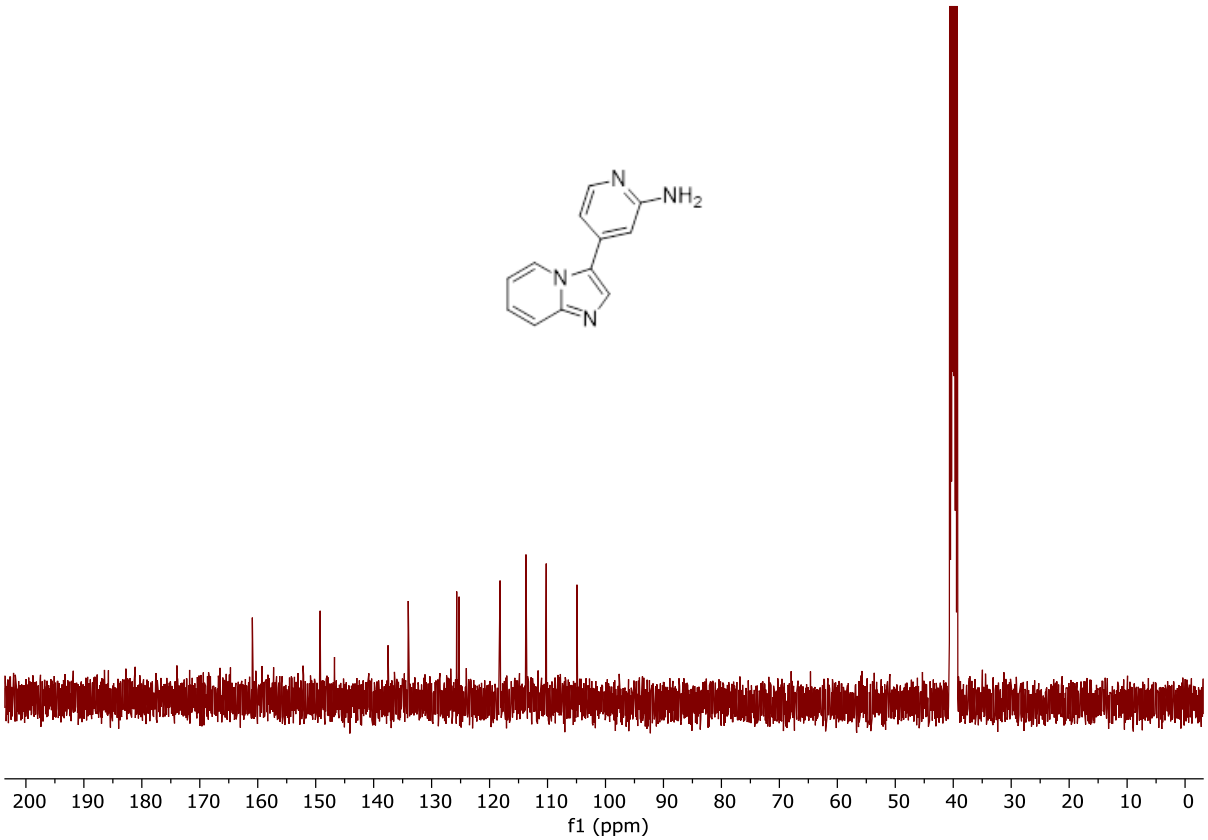


^{1}H NMR Spectrum of (**34**) (400 MHz, DMSO-d^{6}):

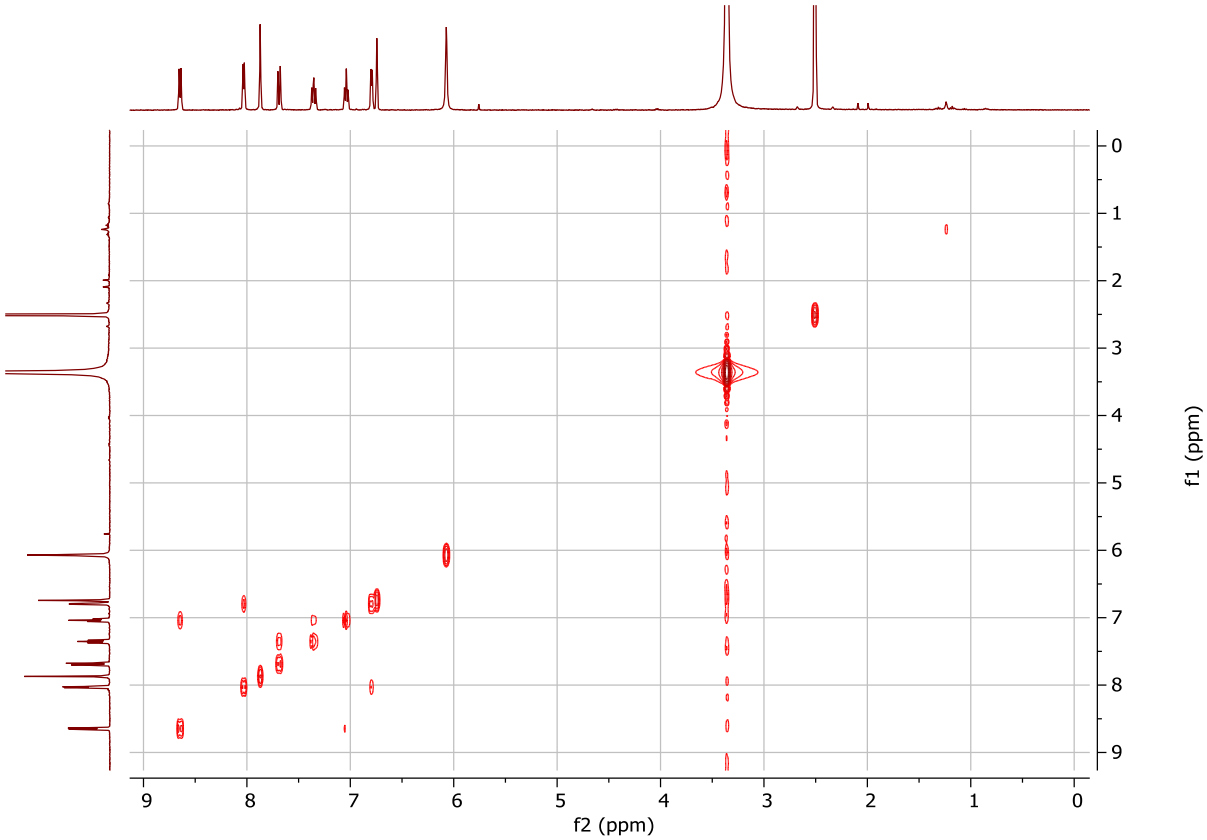




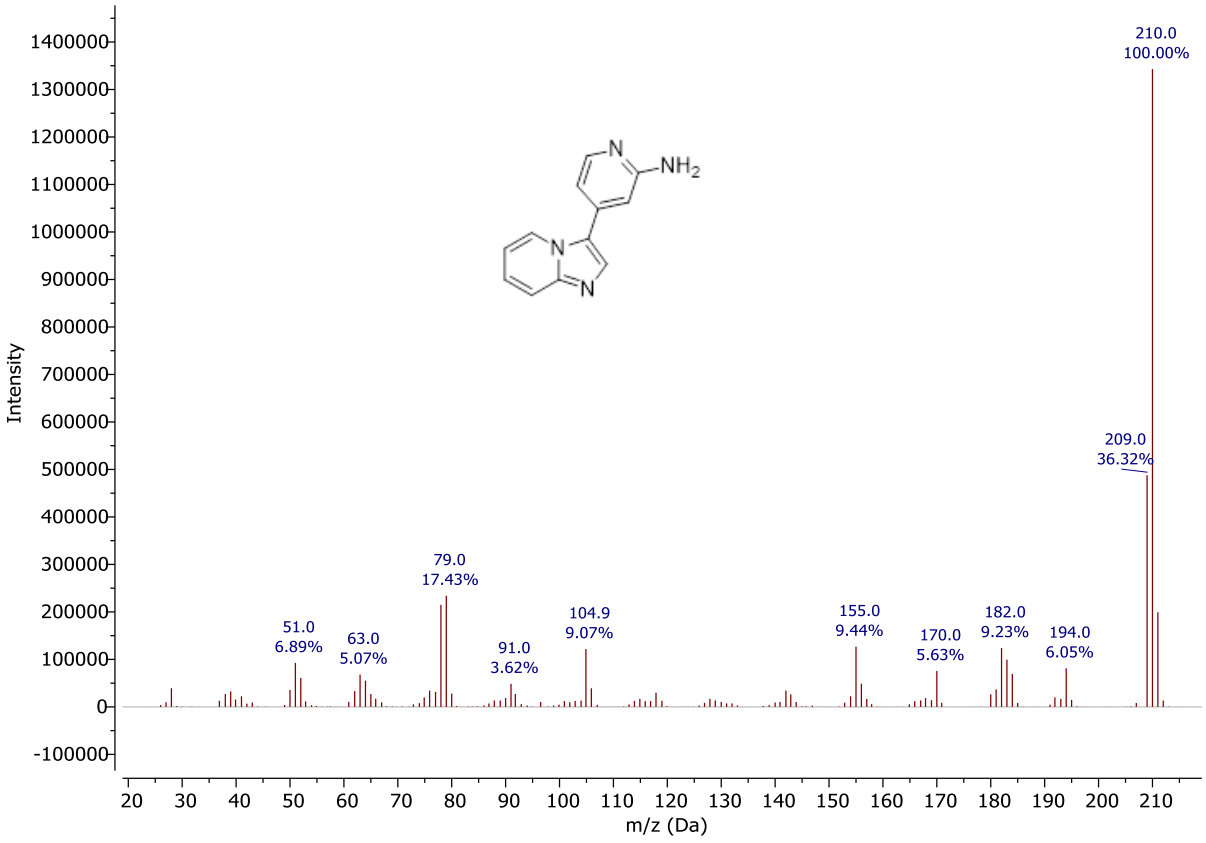
^{13}C NMR Spectrum of (**34**) (400 MHz, DMSO-d^{6}):



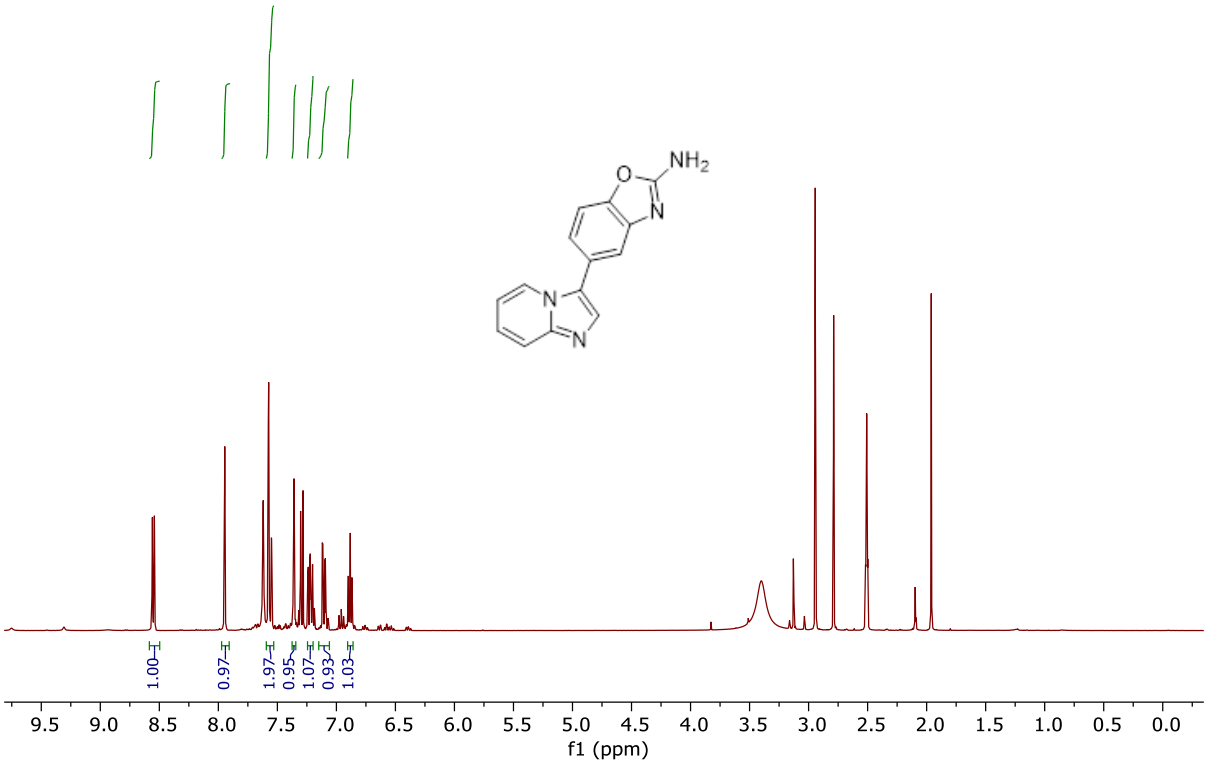
^{1}H/^{1}H COSY NMR Spectrum of (**34**) (400 MHz, DMSO-d^{6}):



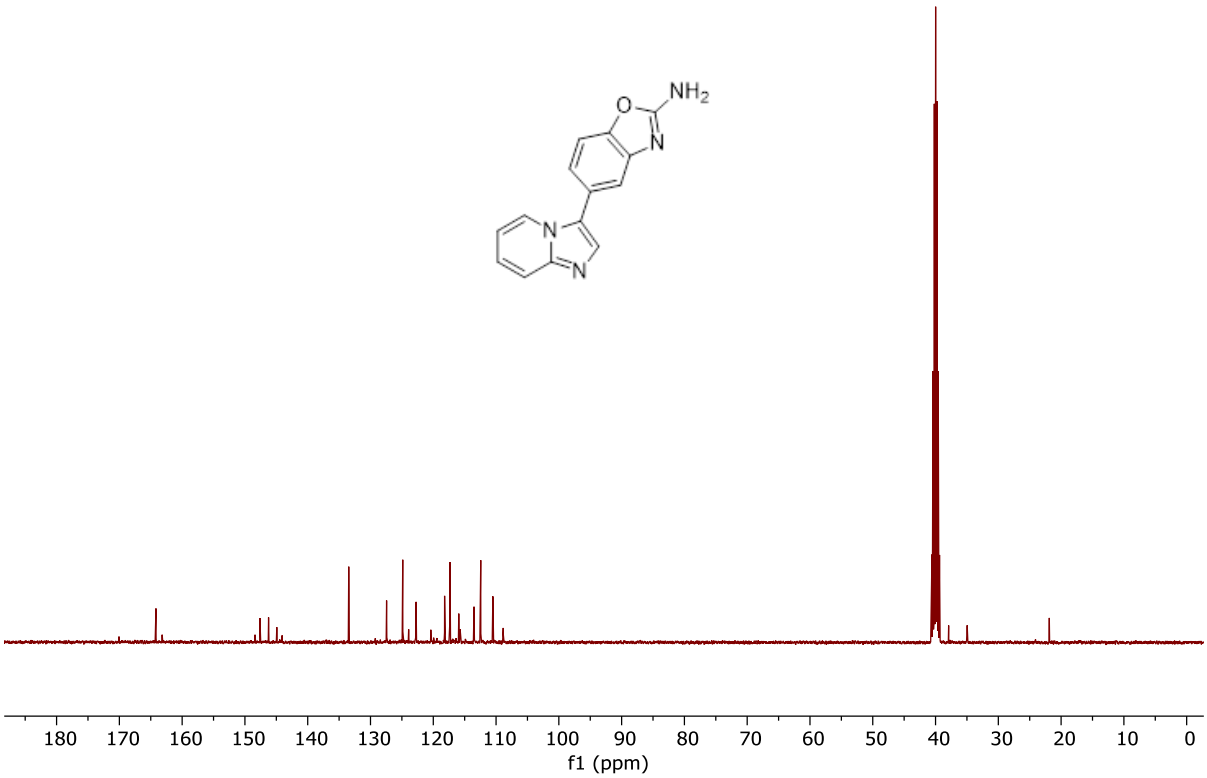
MS Spectrum of (**34**) (EI):



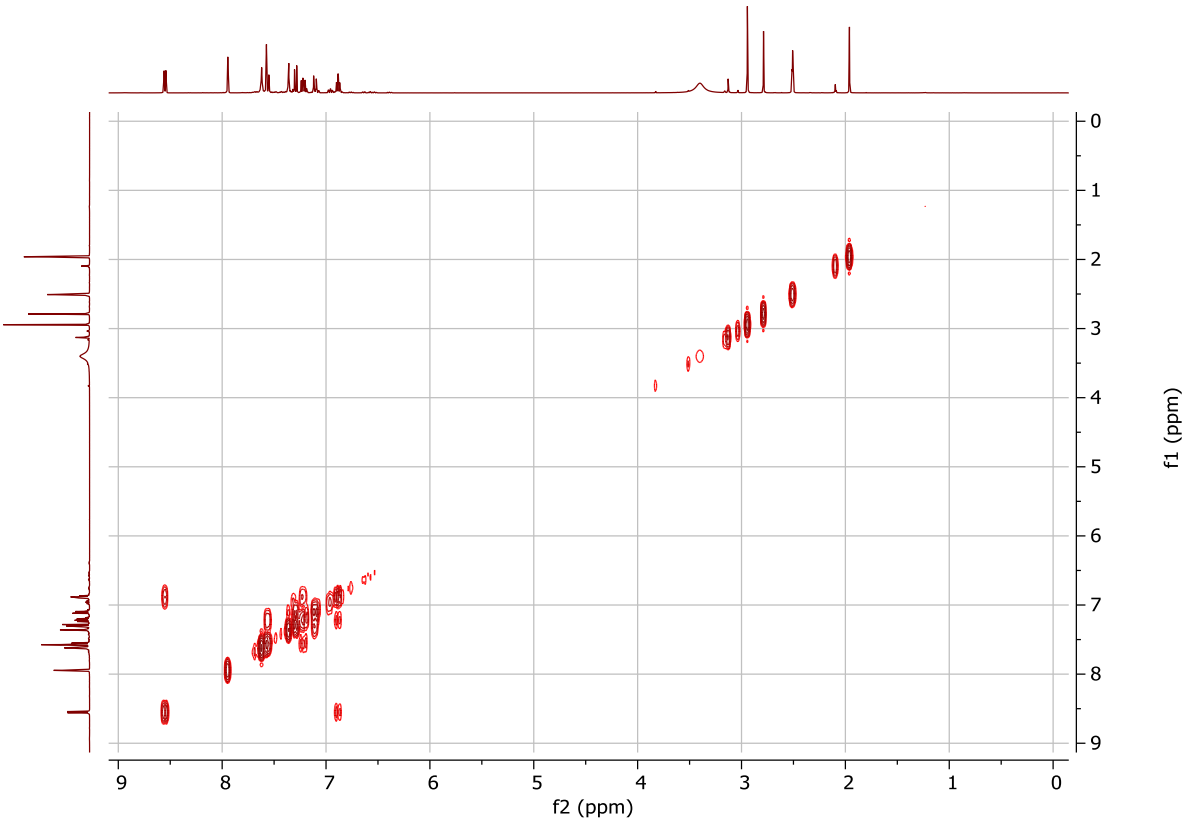
^{1}H NMR Spectrum of (**35**) (400 MHz, DMSO-d^{6}):



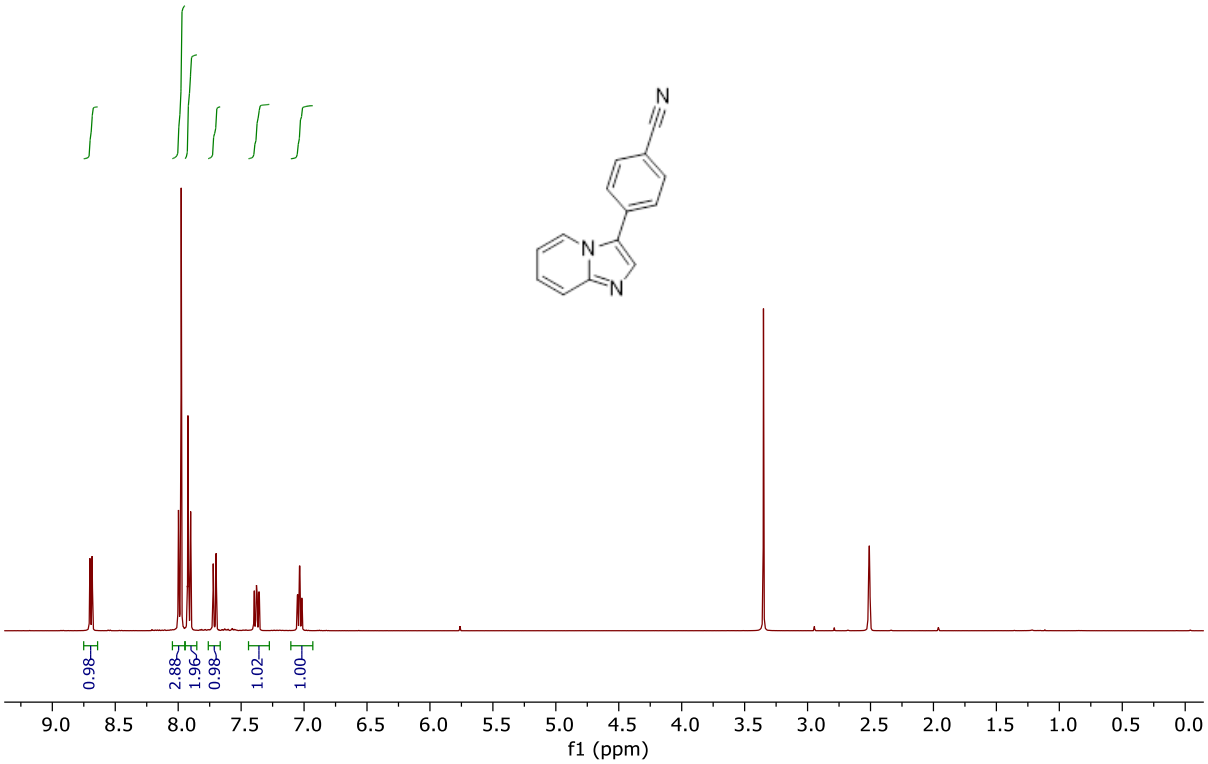
^{13}C NMR Spectrum of (**35**) (400 MHz, DMSO-d^{6}):

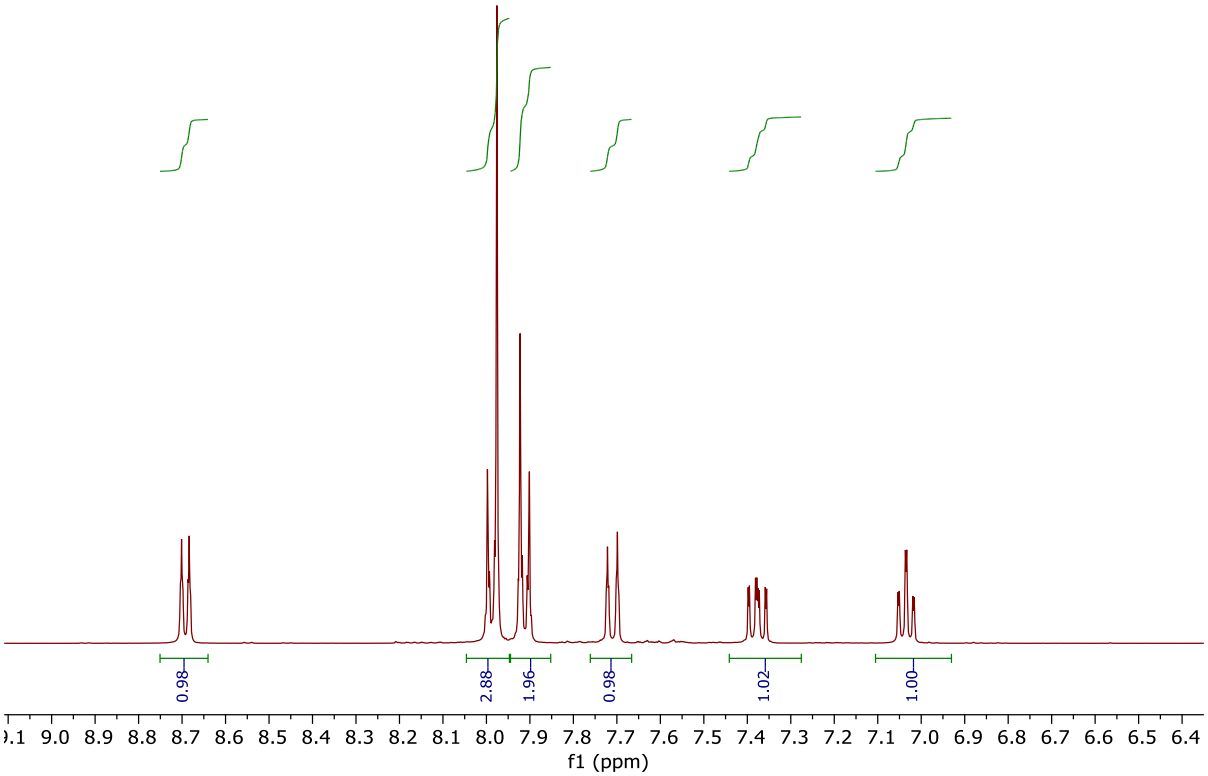


^{1}H/^{1}H COSY NMR Spectrum of (**35**) (400 MHz, DMSO-d^{6}):

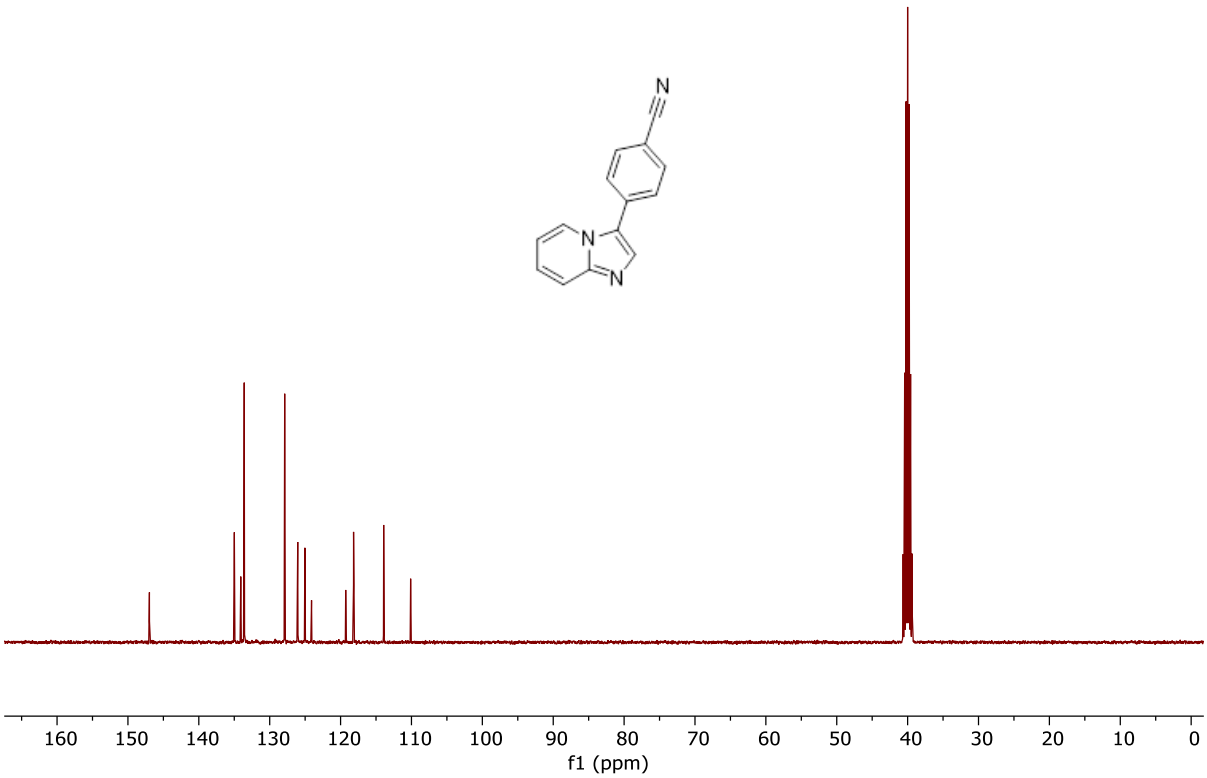


^{1}H NMR Spectrum of (**36**) (400 MHz, DMSO-d^{6}):

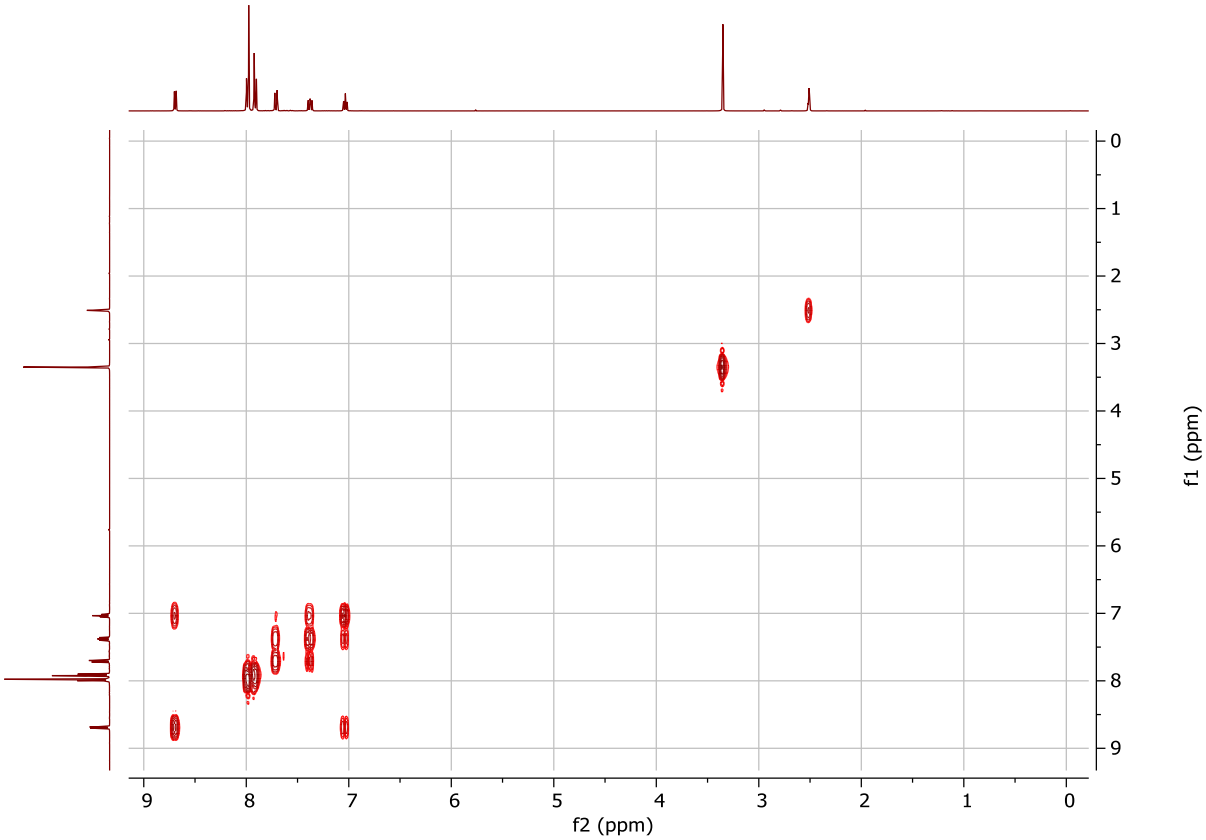


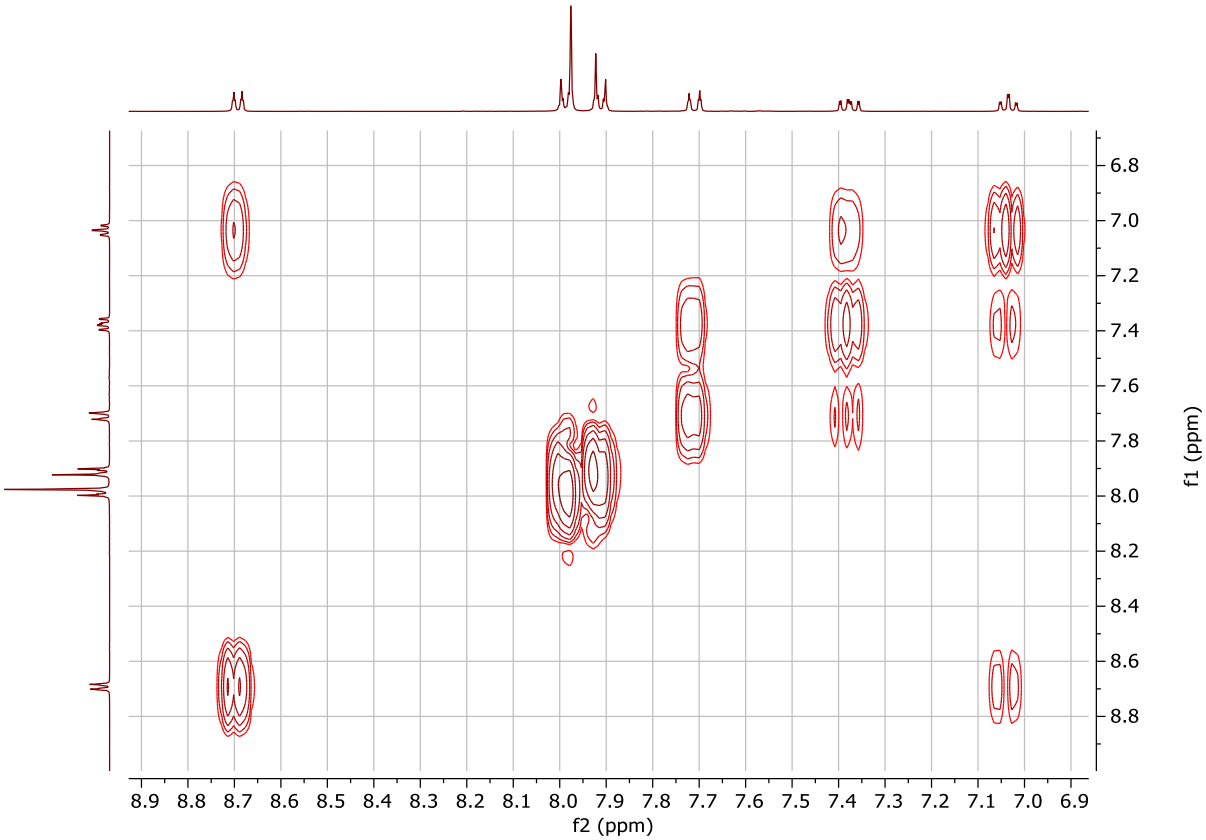


^{13}C NMR Spectrum of (**36**) (400 MHz, DMSO-d^{6}):

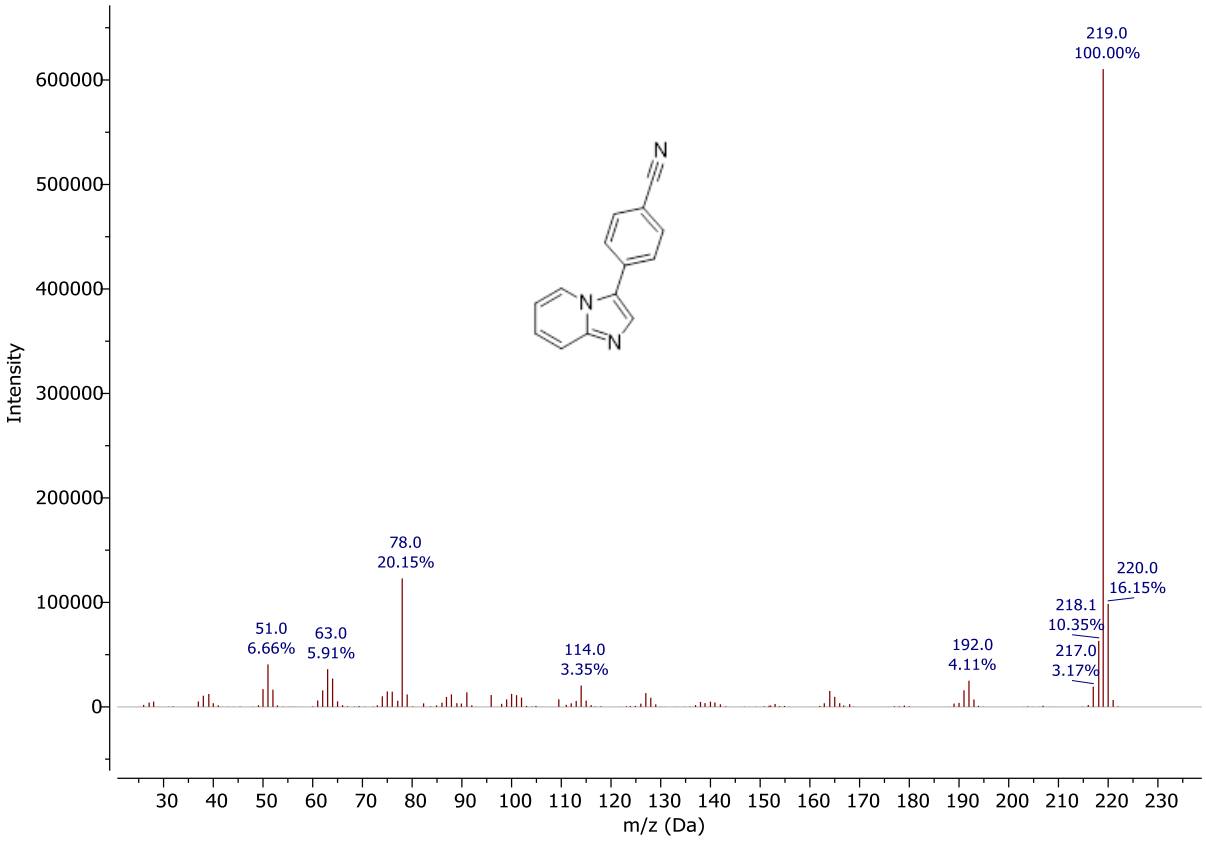


^{1}H/^{1}H COSY NMR Spectrum of (**36**) (400 MHz, DMSO-d^{6}):

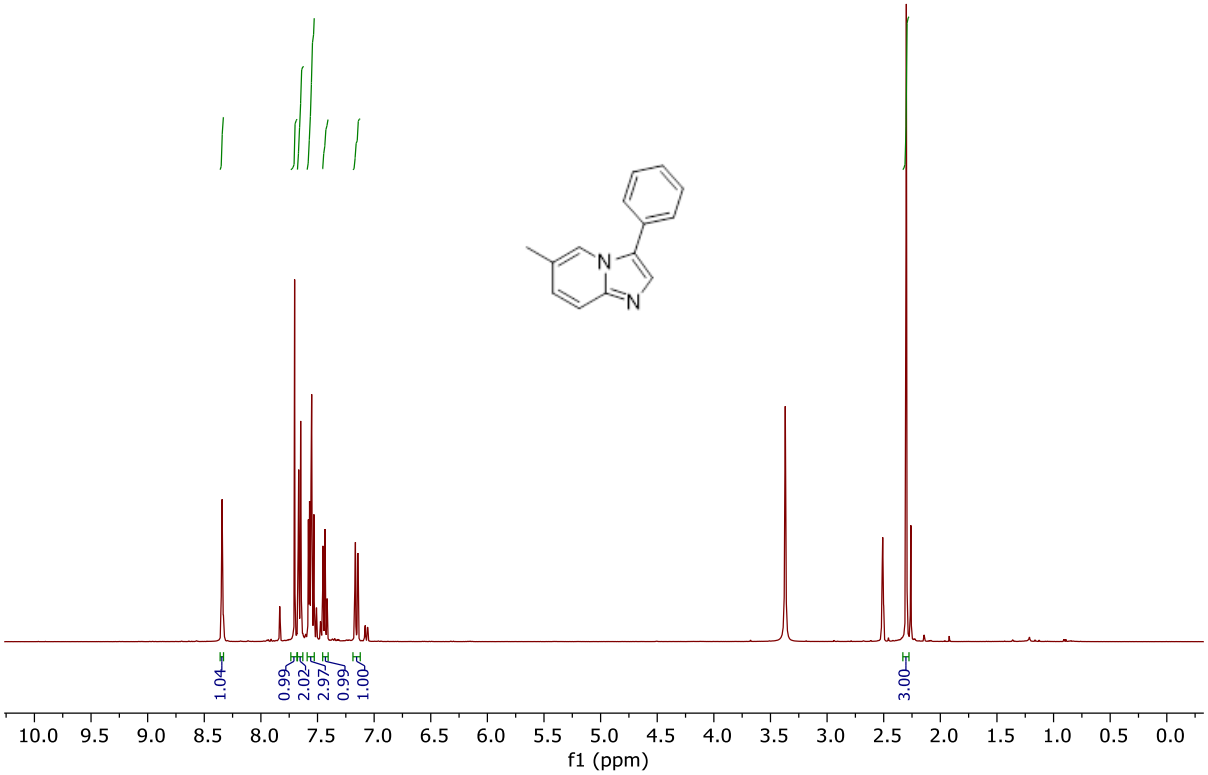


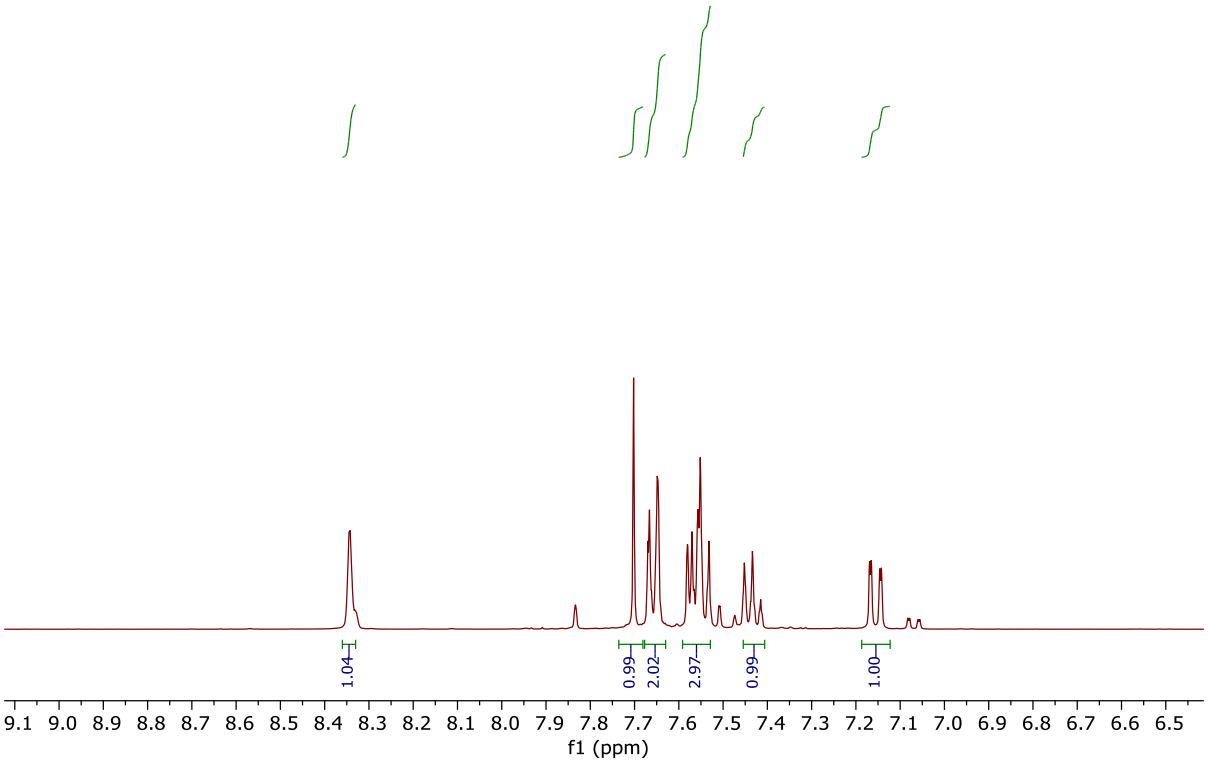


MS Spectrum of (**36**) (EI):

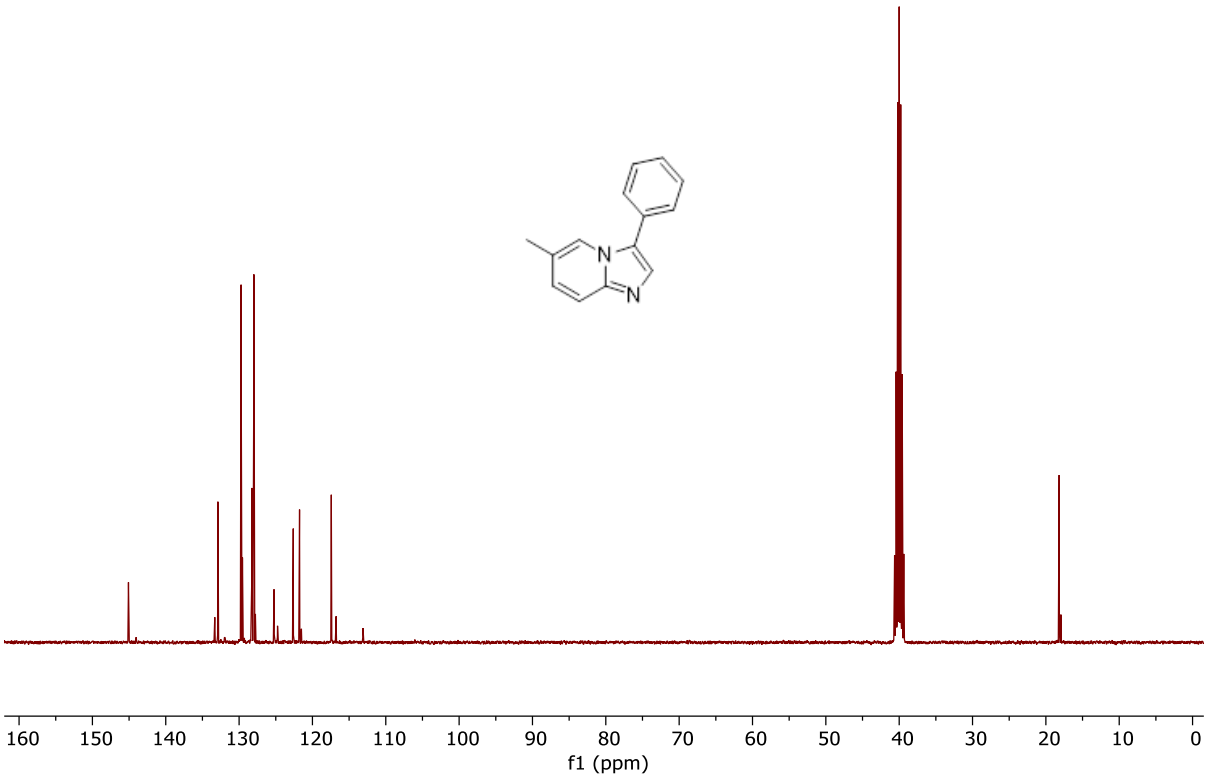


^{1}H NMR Spectrum of (**37**) (400 MHz, DMSO-d^{6}):

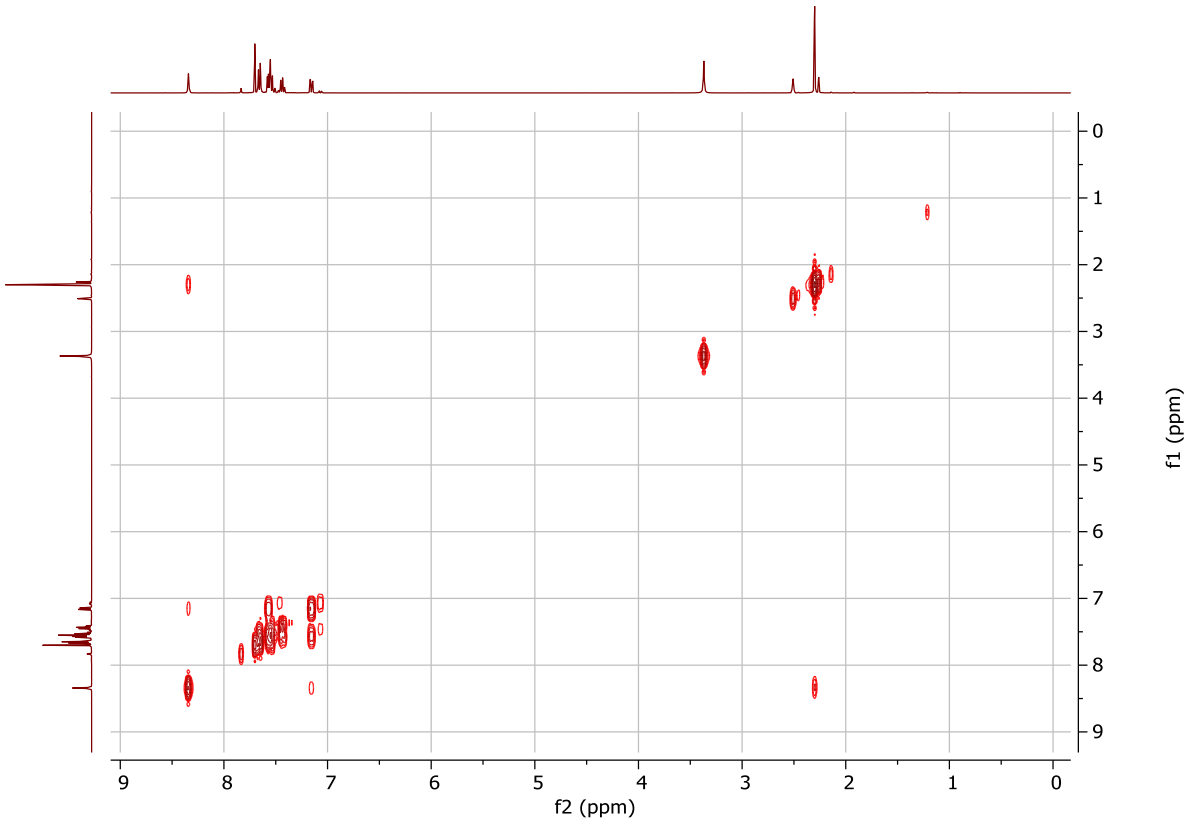


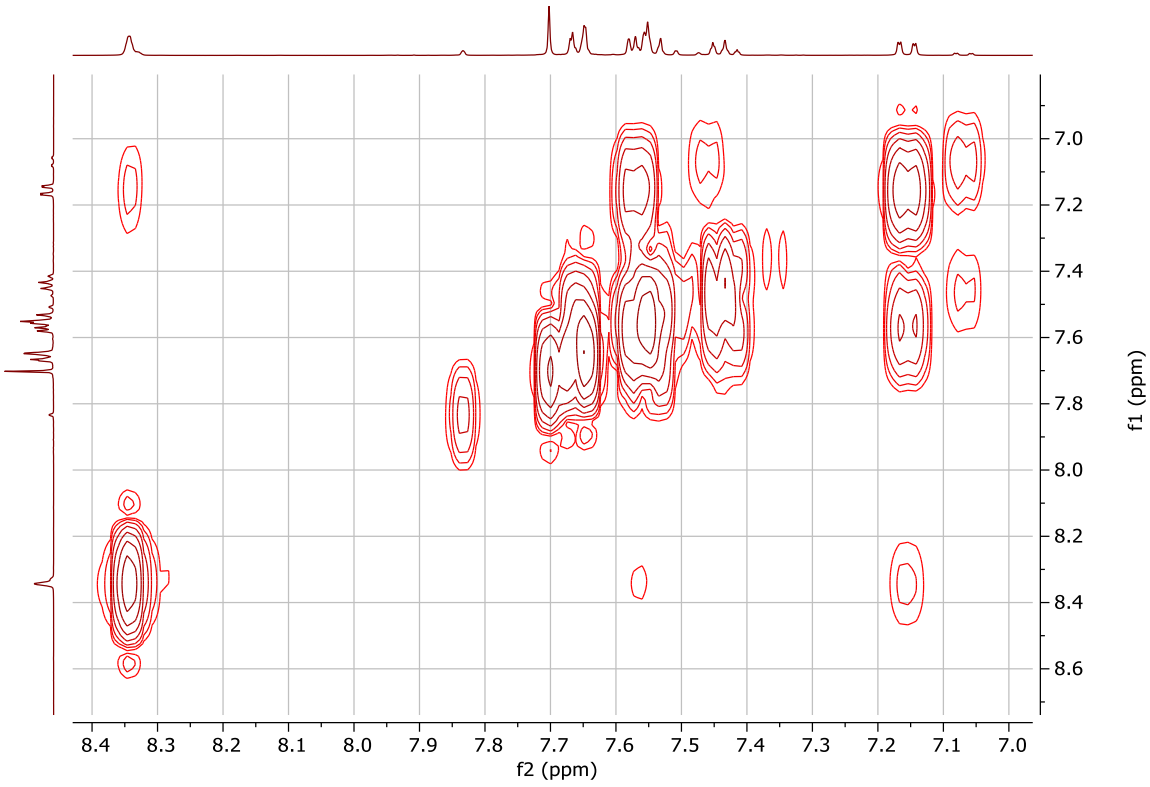


^{13}C NMR Spectrum of (**37**) (400 MHz, DMSO-d^{6}):

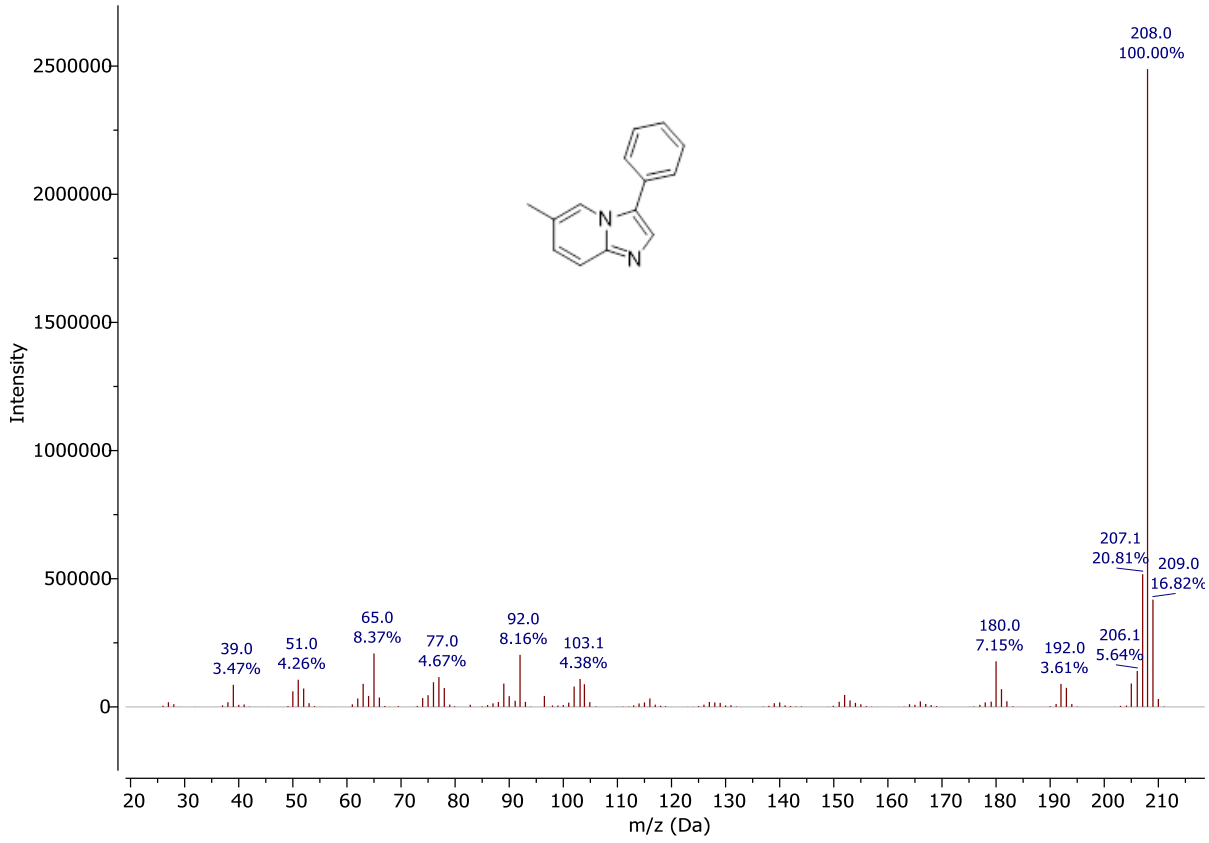


^{1}H/^{1}H COSY NMR Spectrum of (**37**) (400 MHz, DMSO-d^{6}):

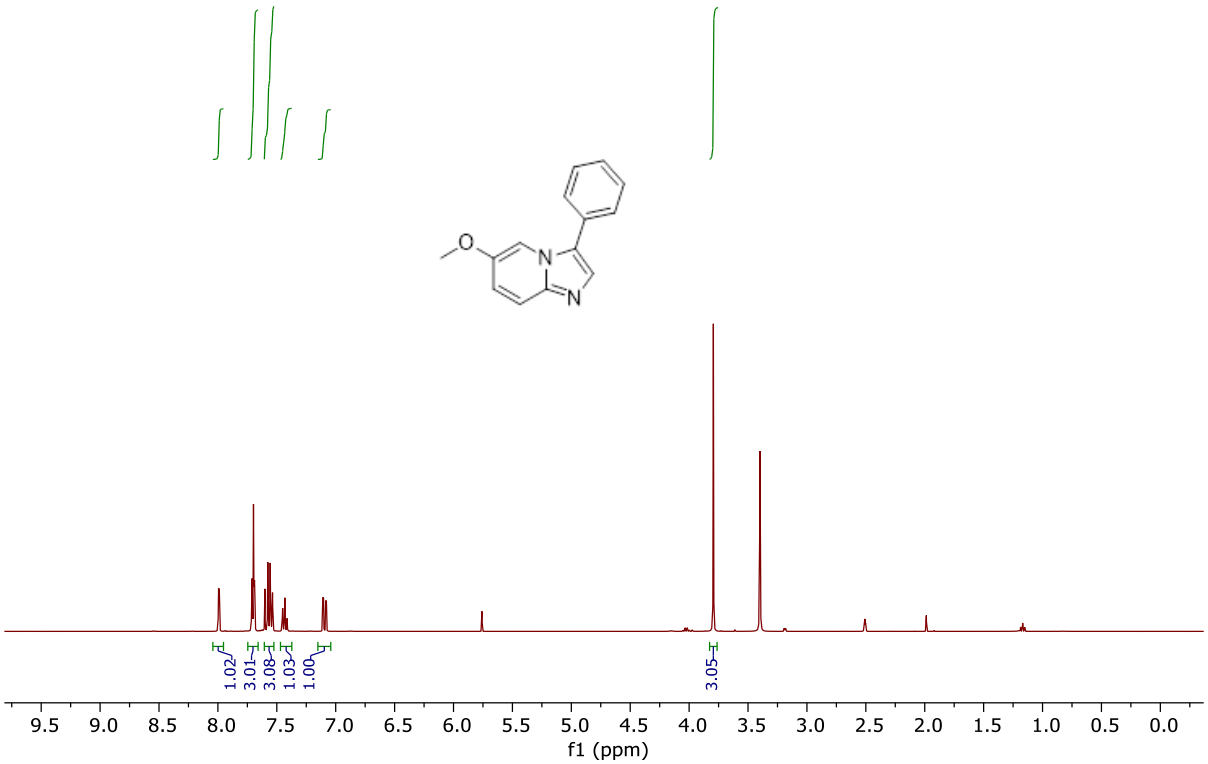


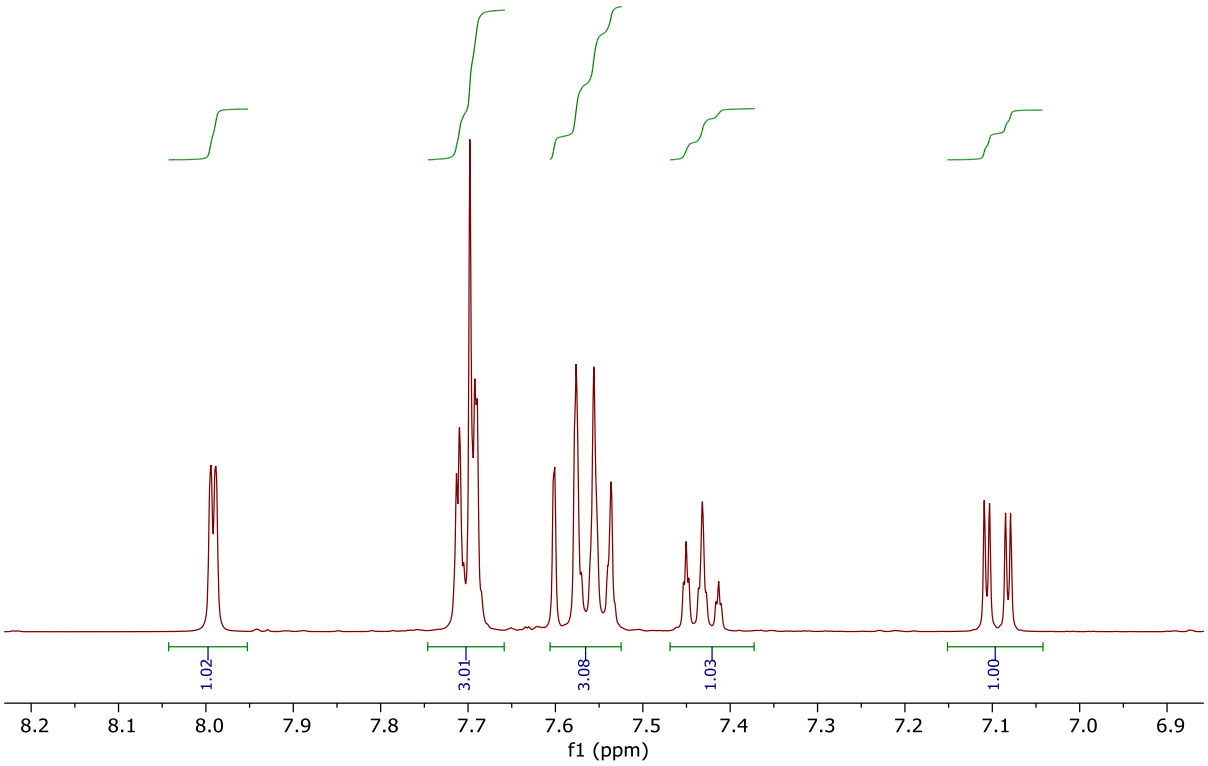


MS Spectrum of (**37**) (EI):

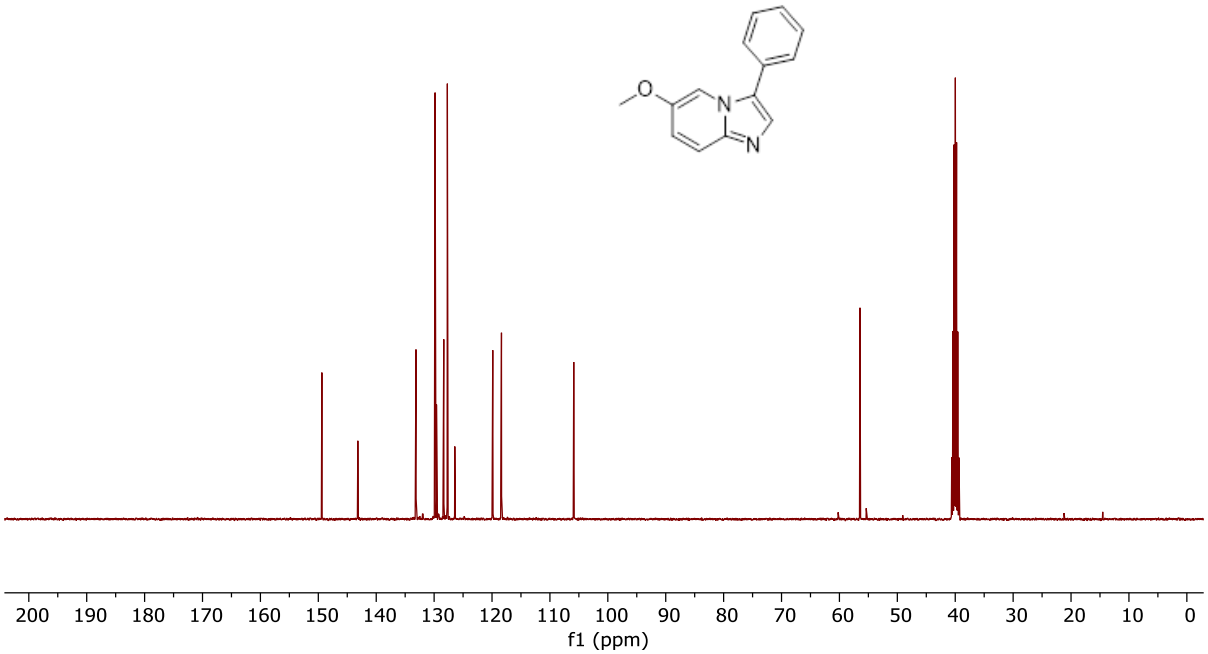


^{1}H NMR Spectrum of (**38**) (400 MHz, DMSO-d^{6}):

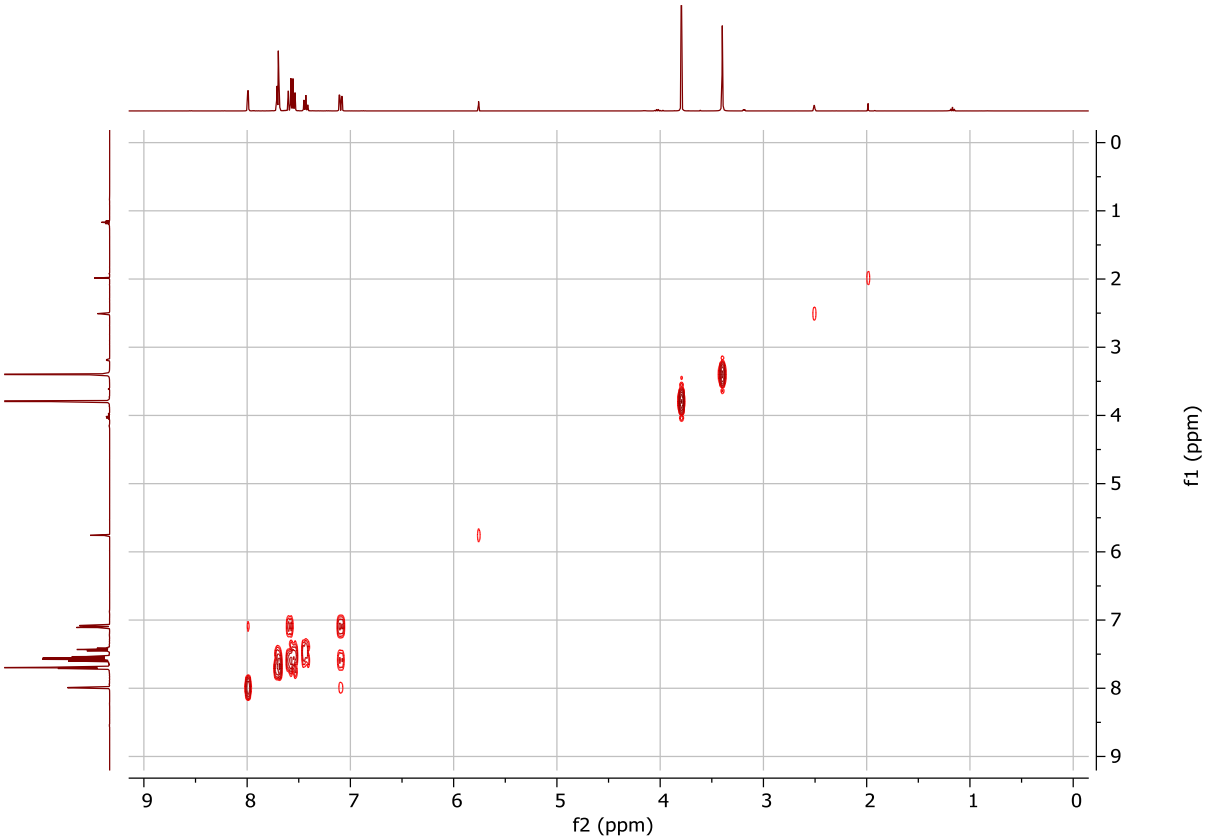




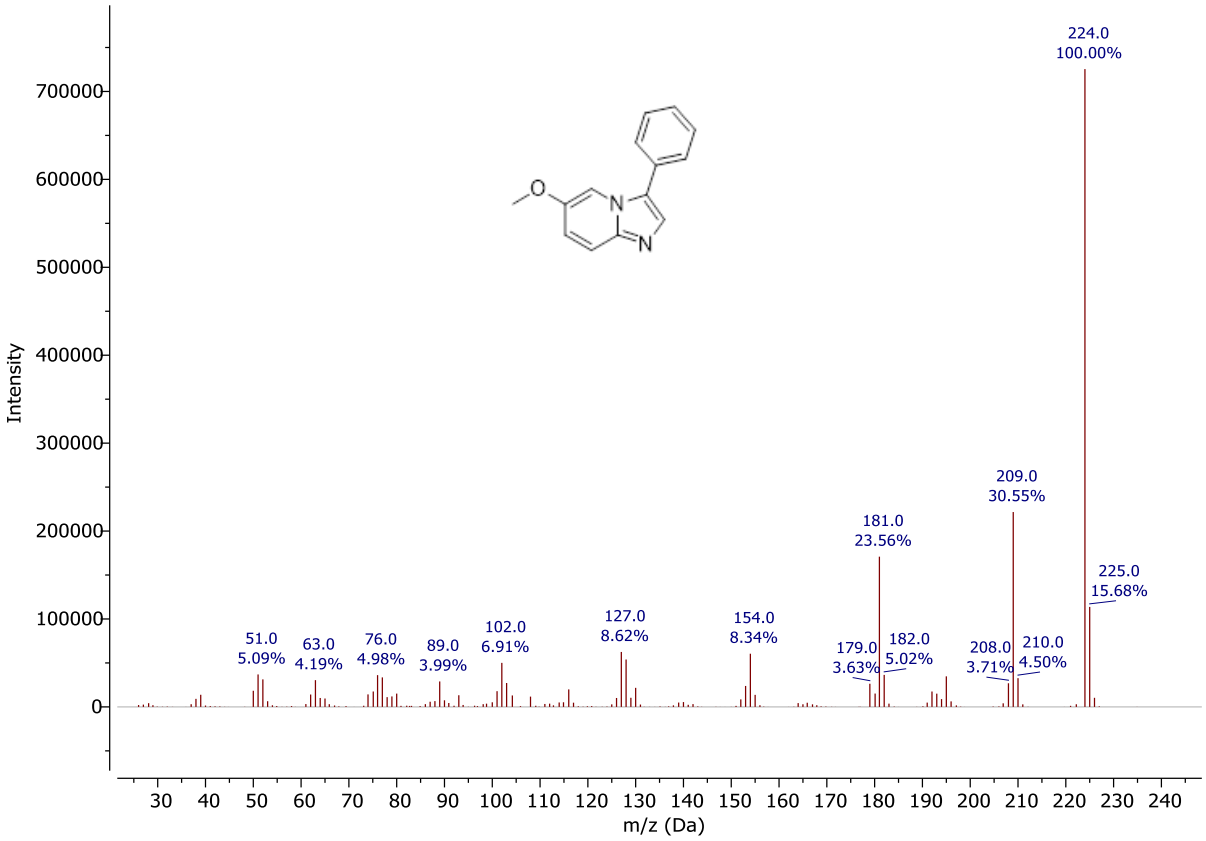
^{13}C NMR Spectrum of (**38**) (400 MHz, DMSO-d^{6}):



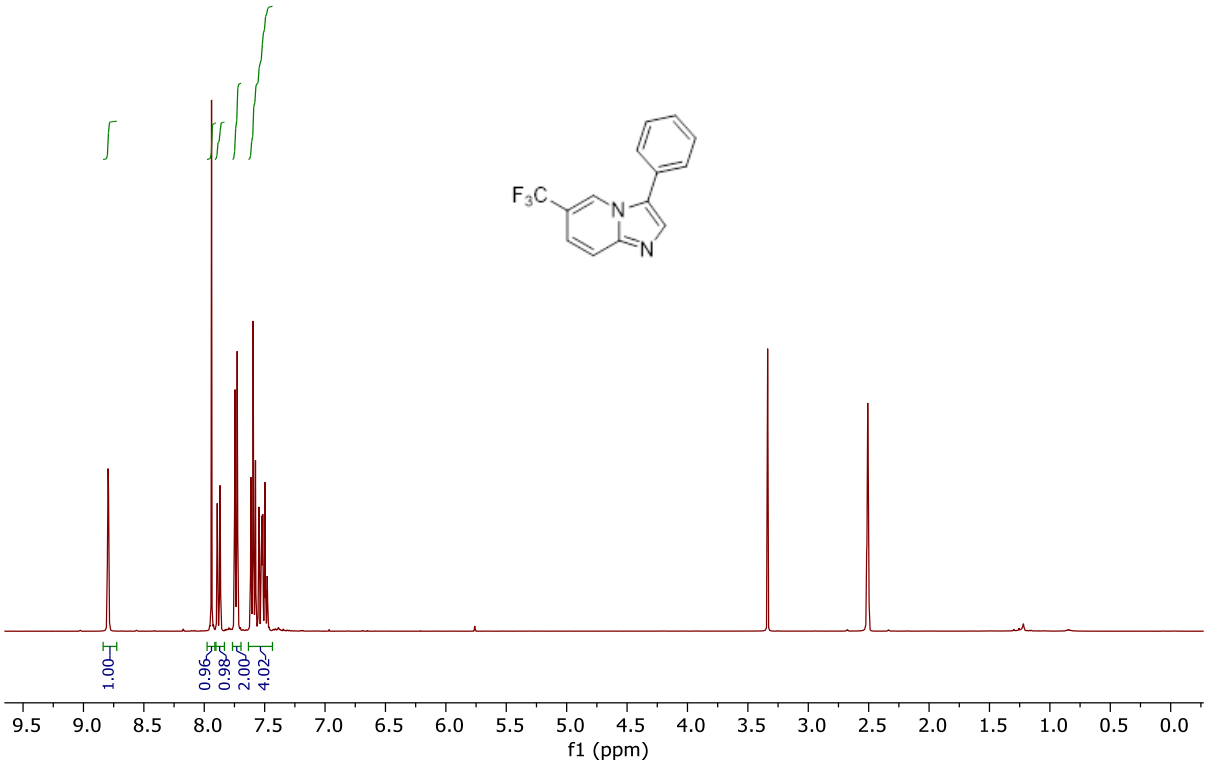
^{1}H/^{1}H COSY NMR Spectrum of (**38**) (400 MHz, DMSO-d^{6}):

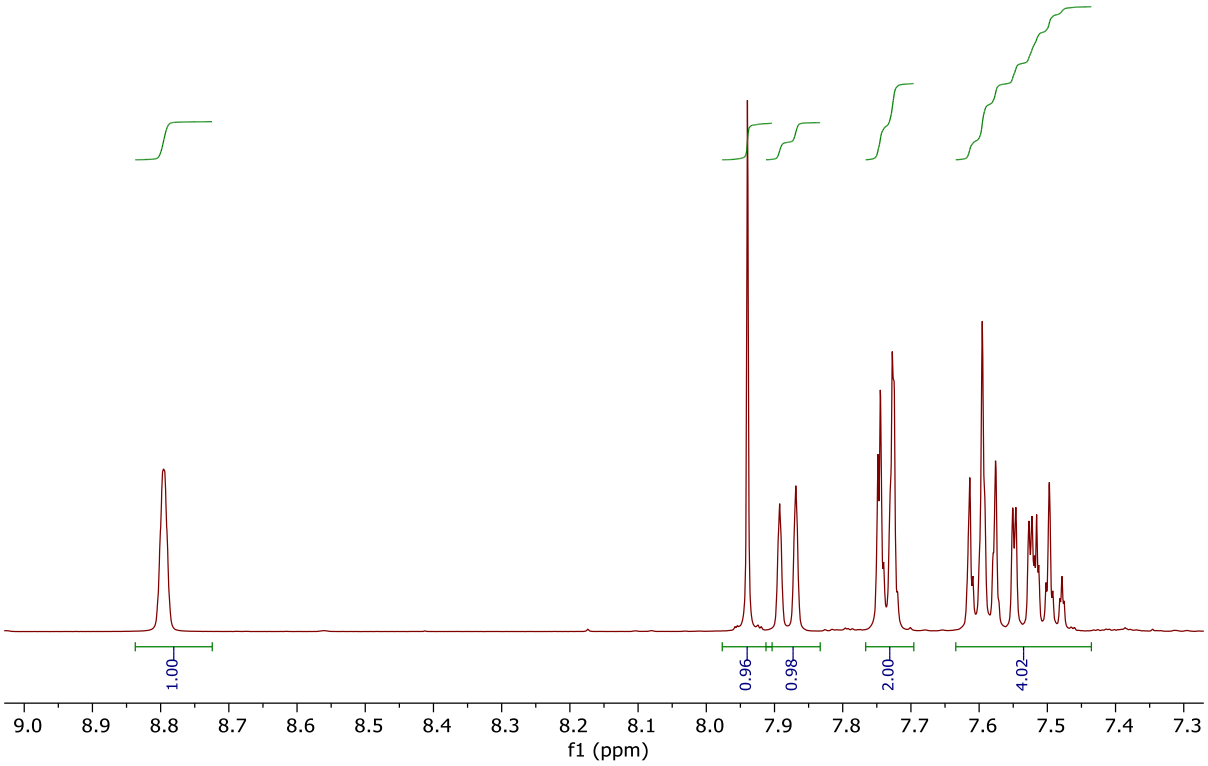


MS Spectrum of (**38**) (EI):

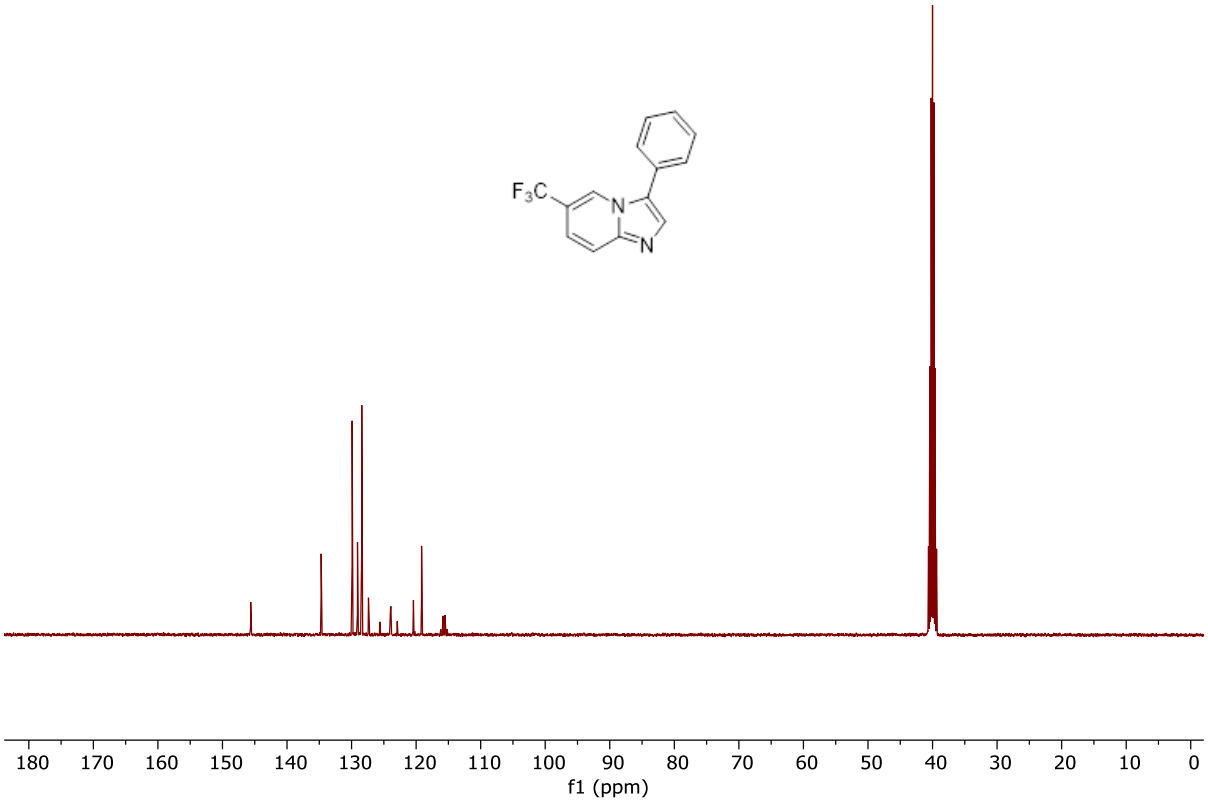


^{1}H NMR Spectrum of (**39**) (400 MHz, DMSO-d^{6}):

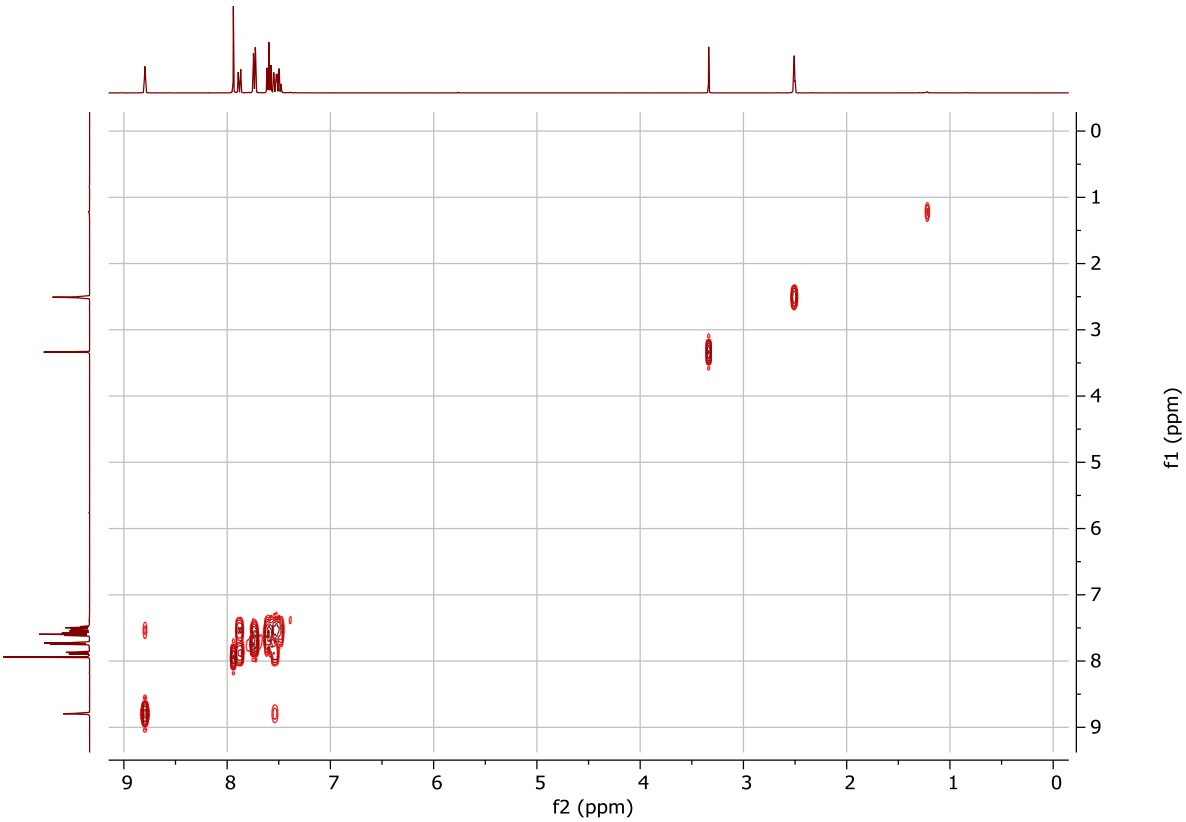


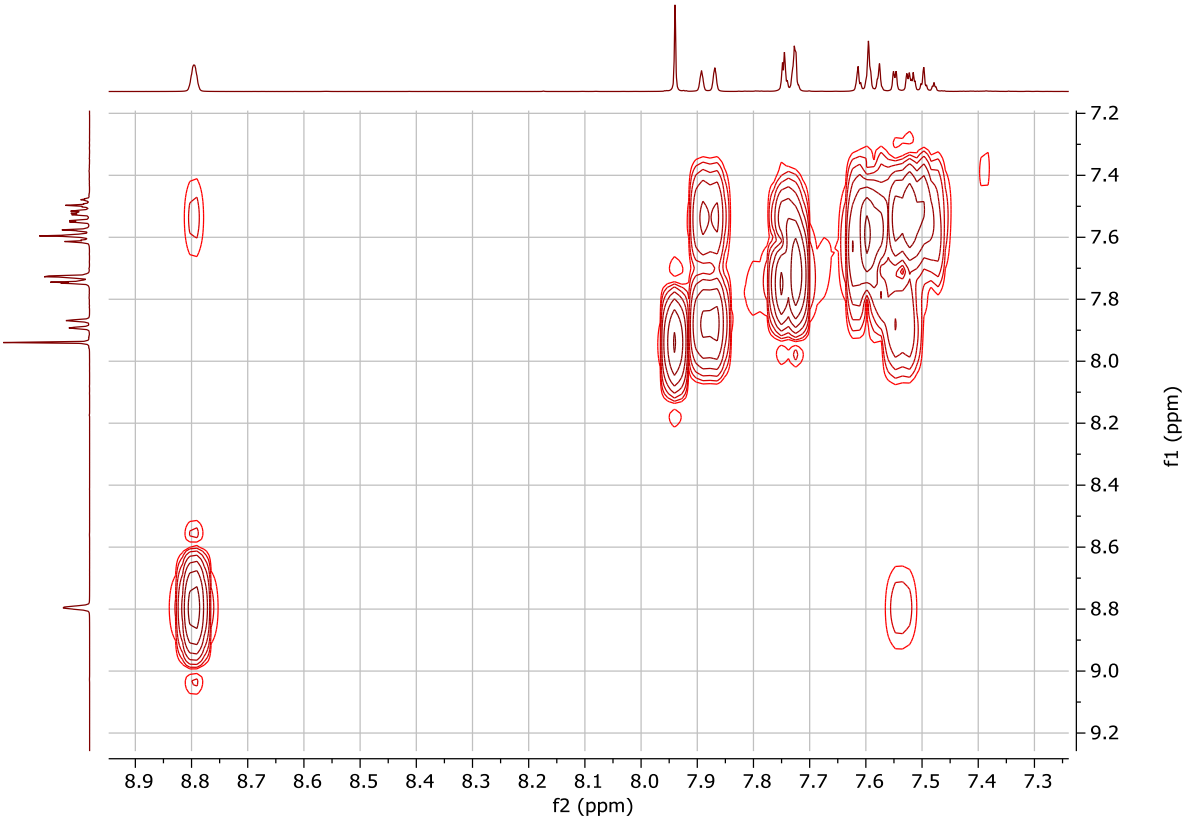


^{13}C NMR Spectrum of (**39**) (400 MHz, DMSO-d^{6}):

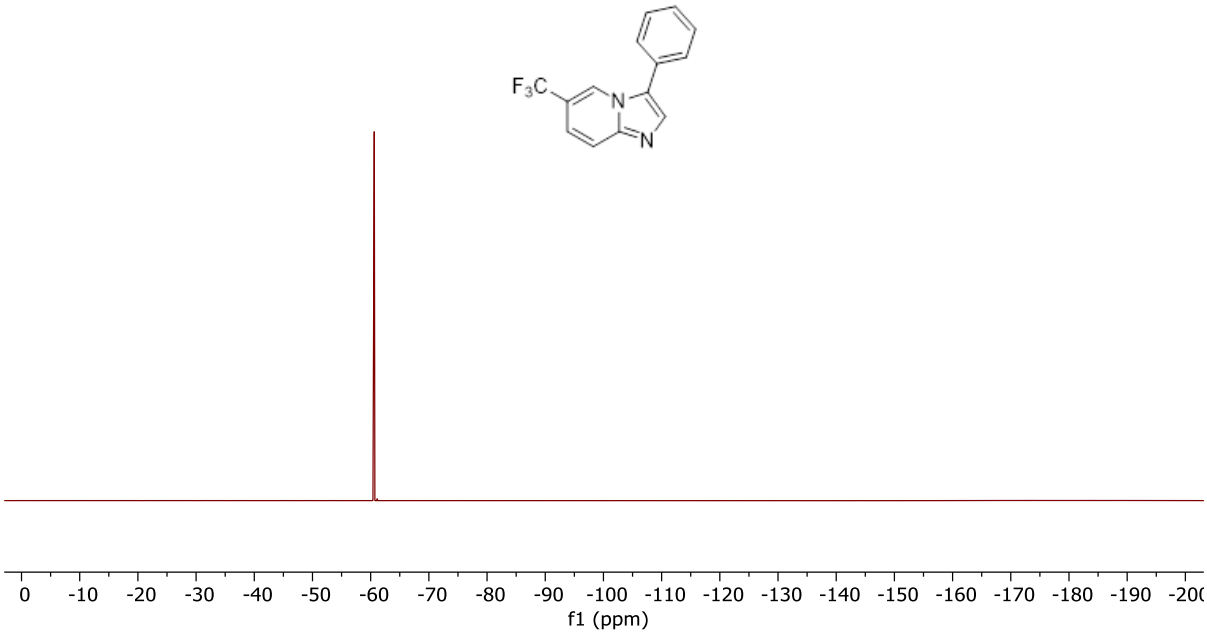


^{1}H/^{1}H COSY NMR Spectrum of (**39**) (400 MHz, DMSO-d^{6}):

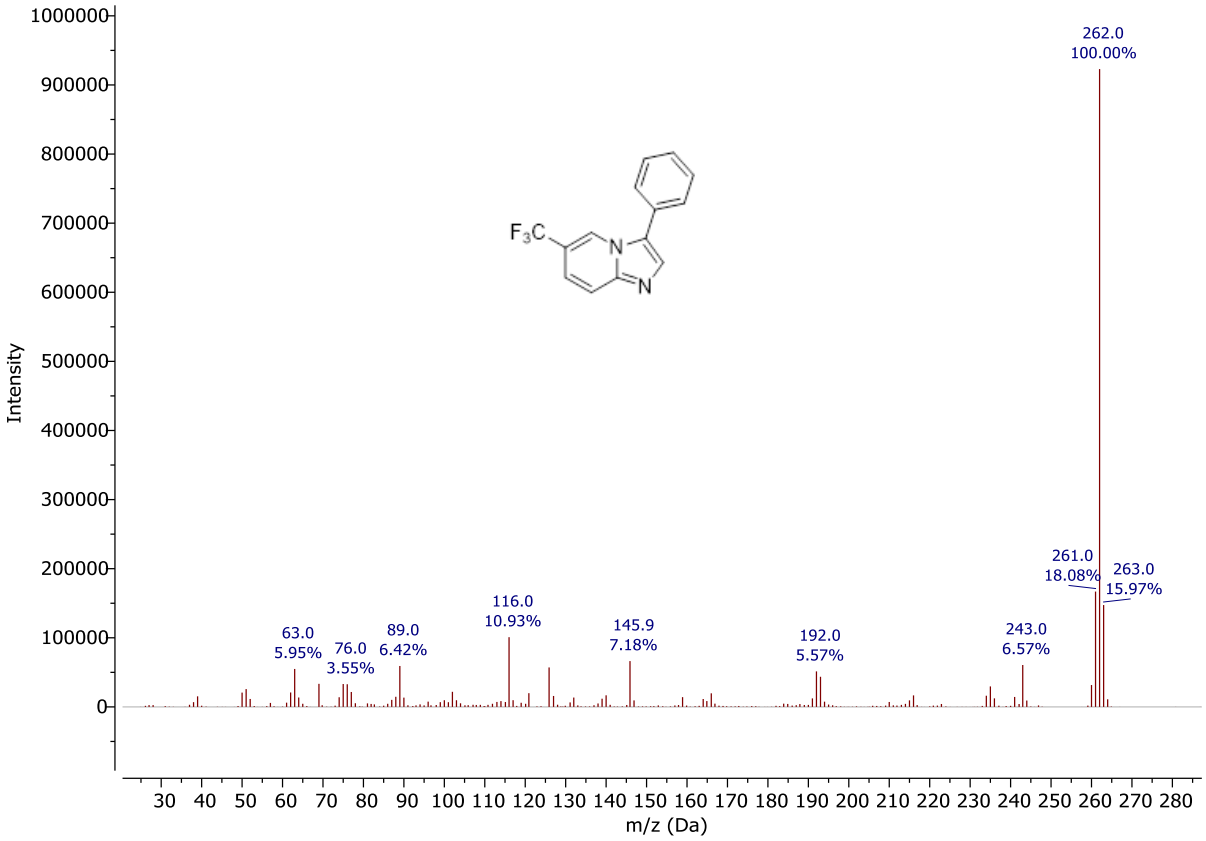




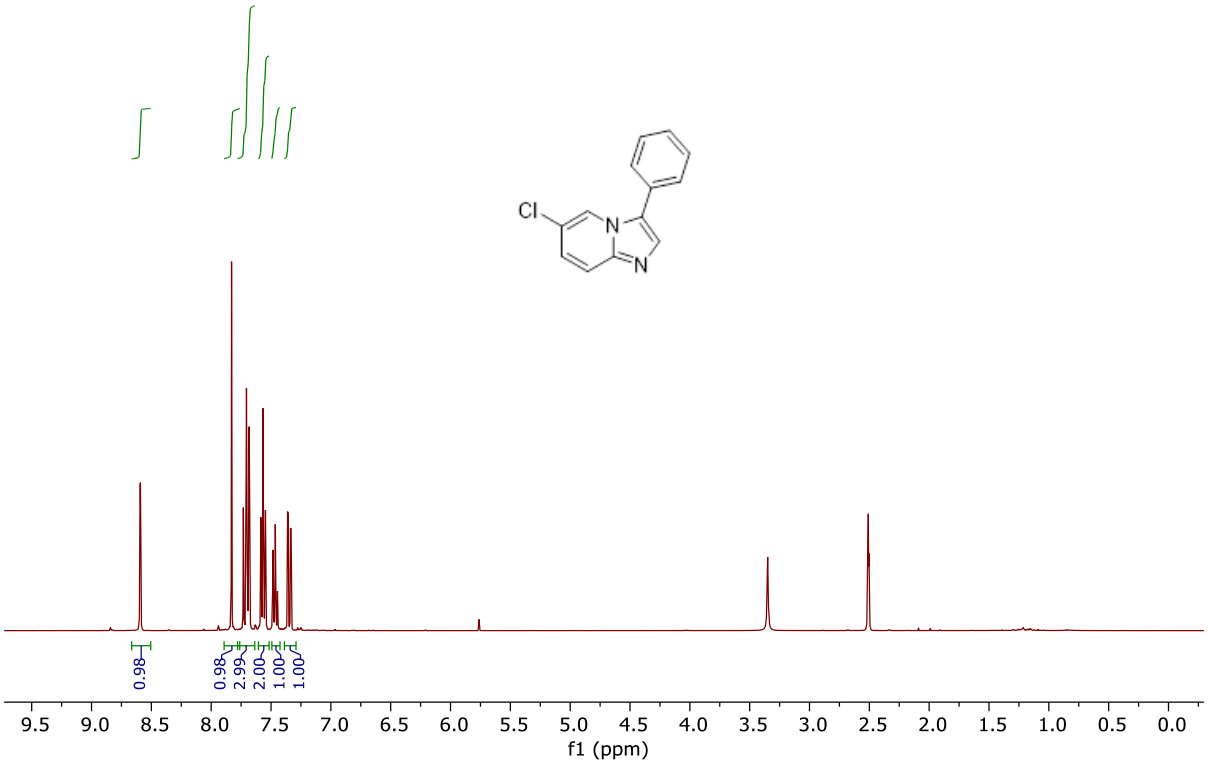
^{19}F NMR Spectrum of (**39**) (400 MHz, DMSO-d^{6}):

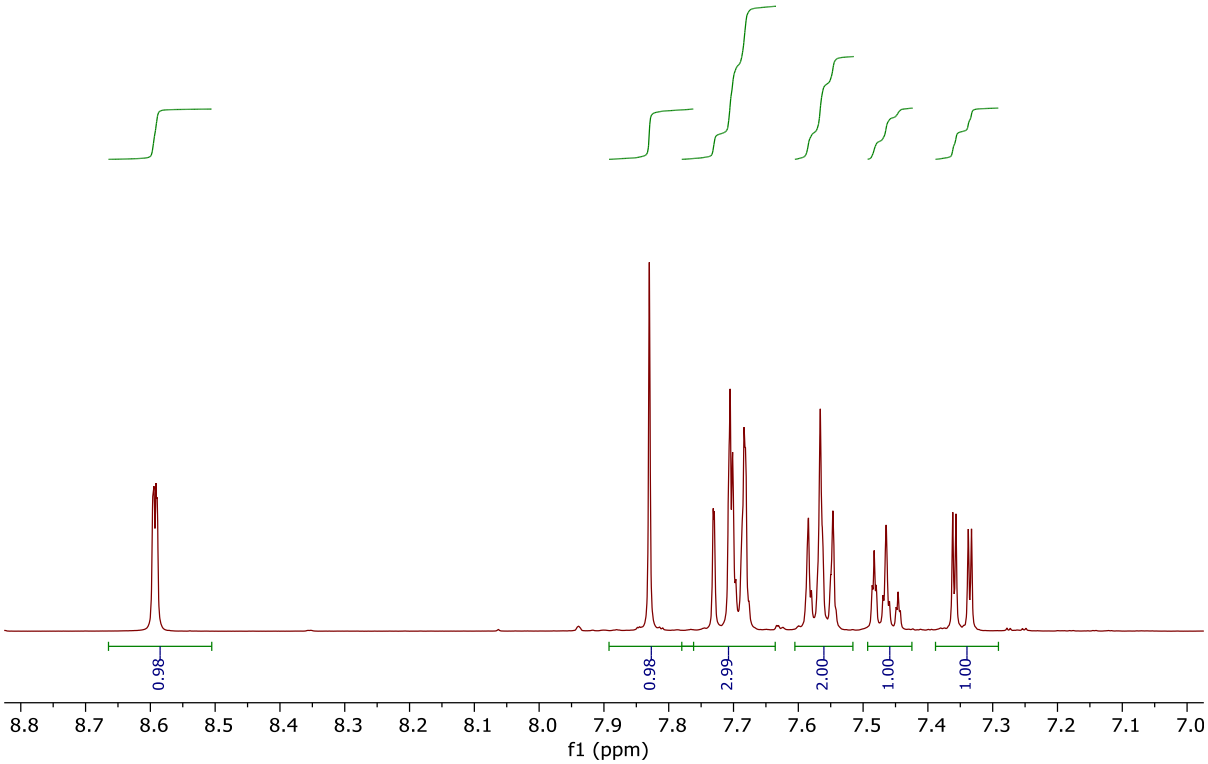


MS Spectrum of (**39**) (EI):

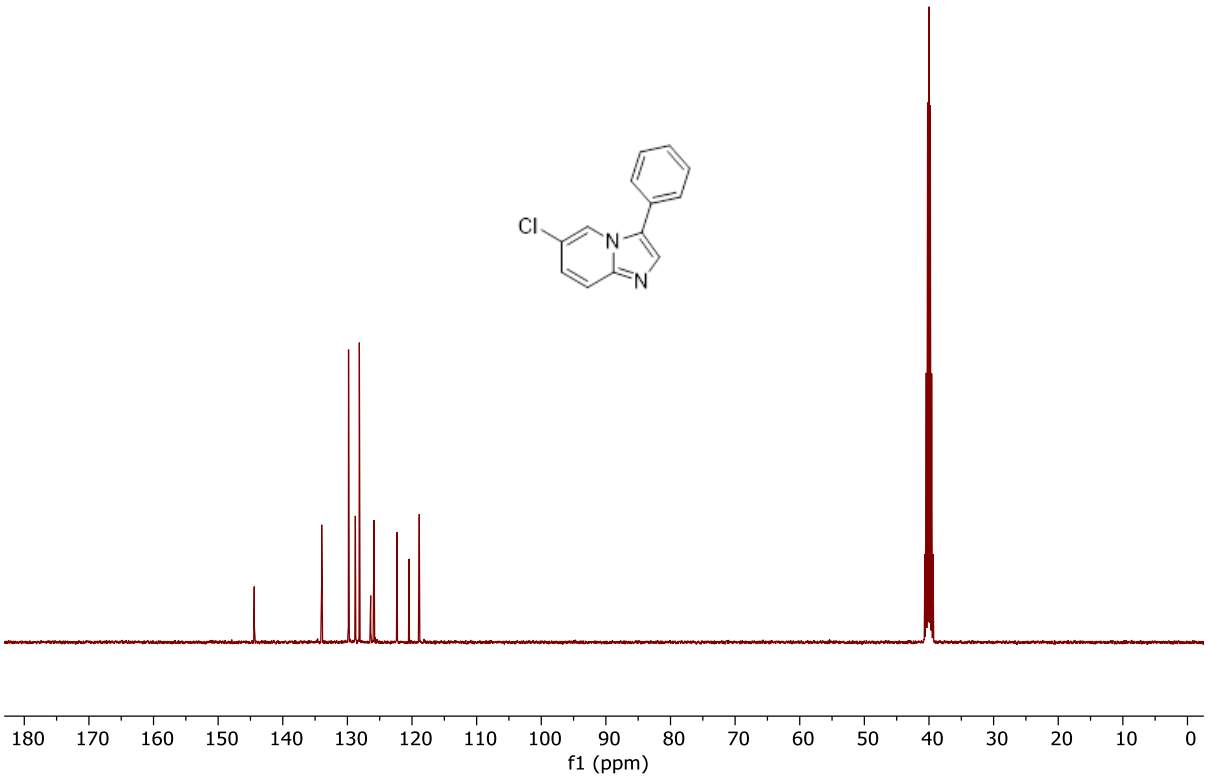


^{1}H NMR Spectrum of (**40**) (400 MHz, DMSO-d^{6}):

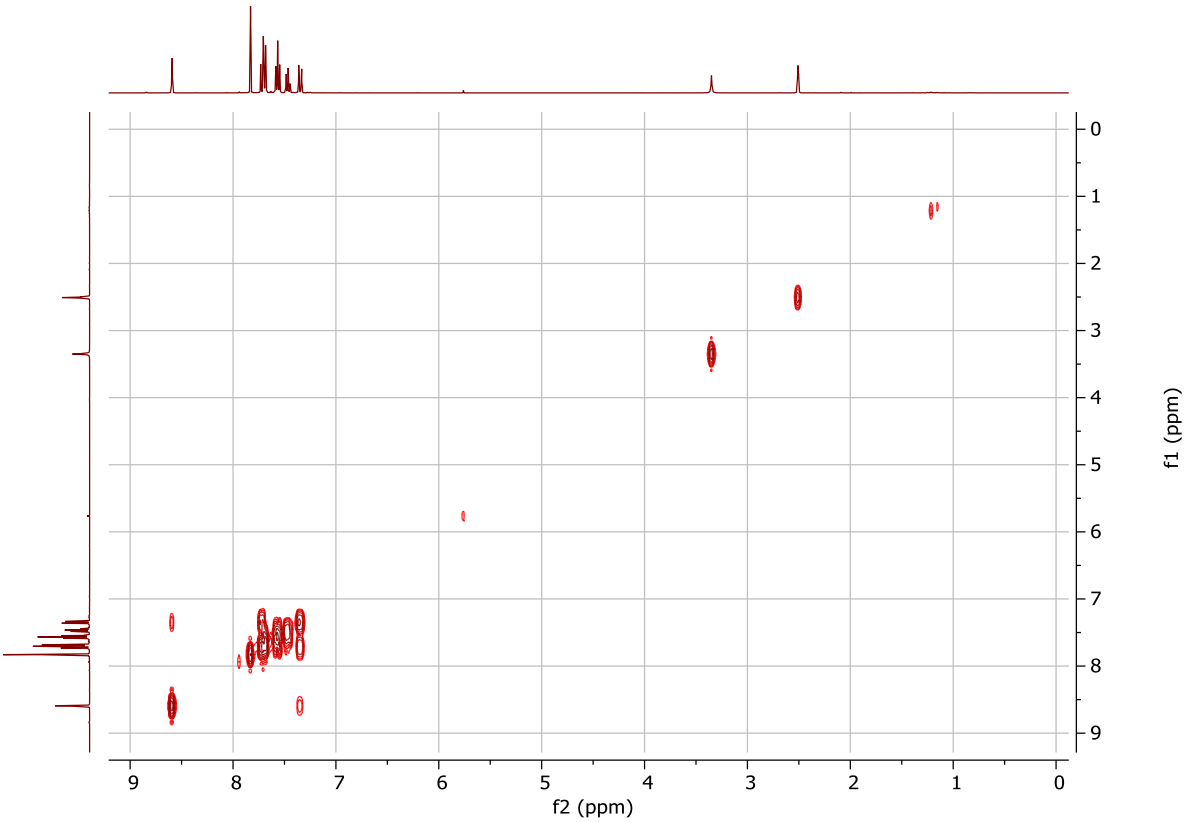


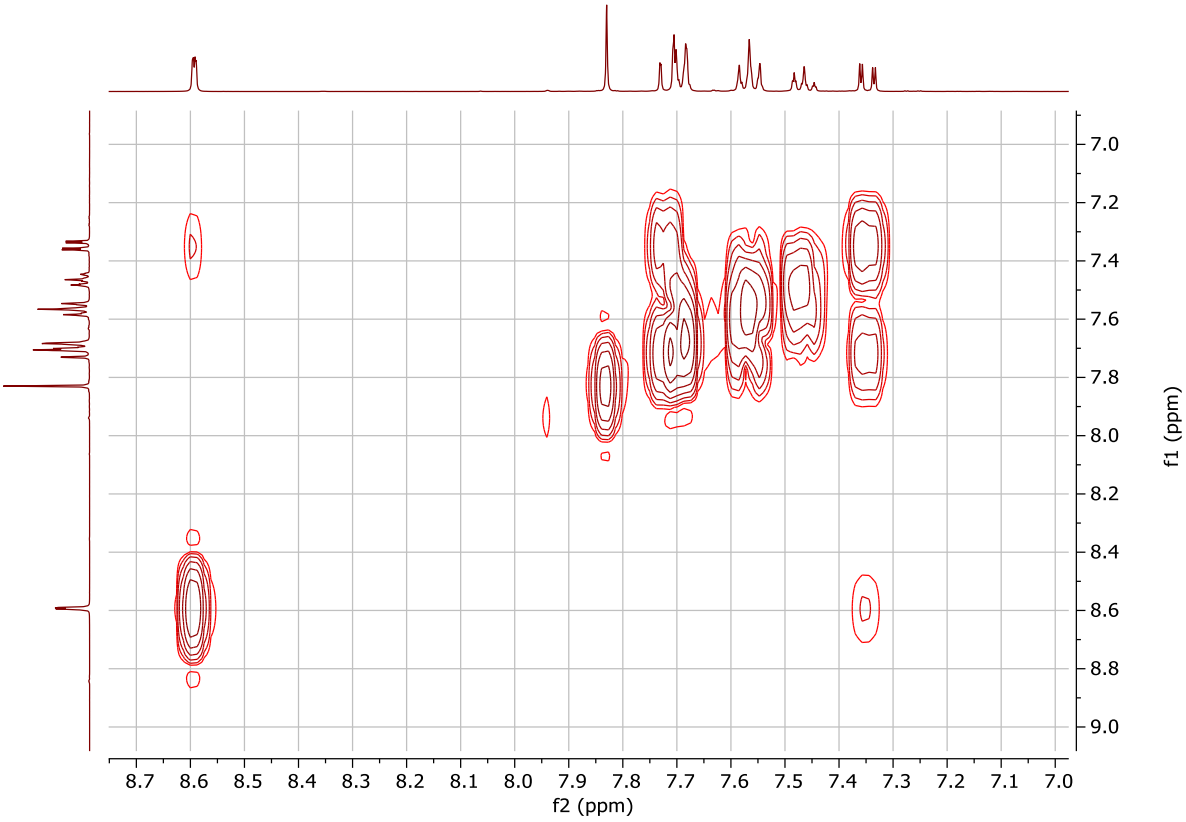


^{13}C NMR Spectrum of (**40**) (400 MHz, DMSO-d^{6}):

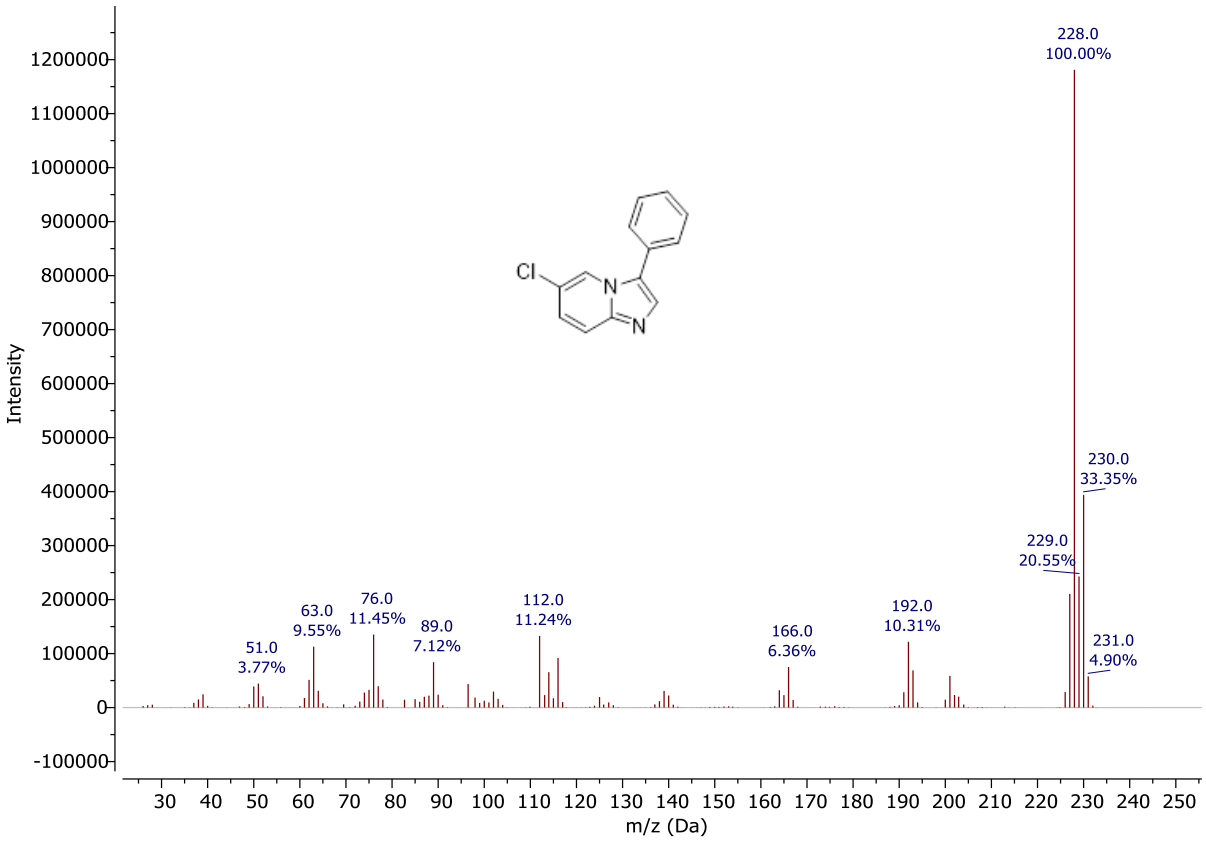


^{1}H/^{1}H COSY NMR Spectrum of (**40**) (400 MHz, DMSO-d^{6}):

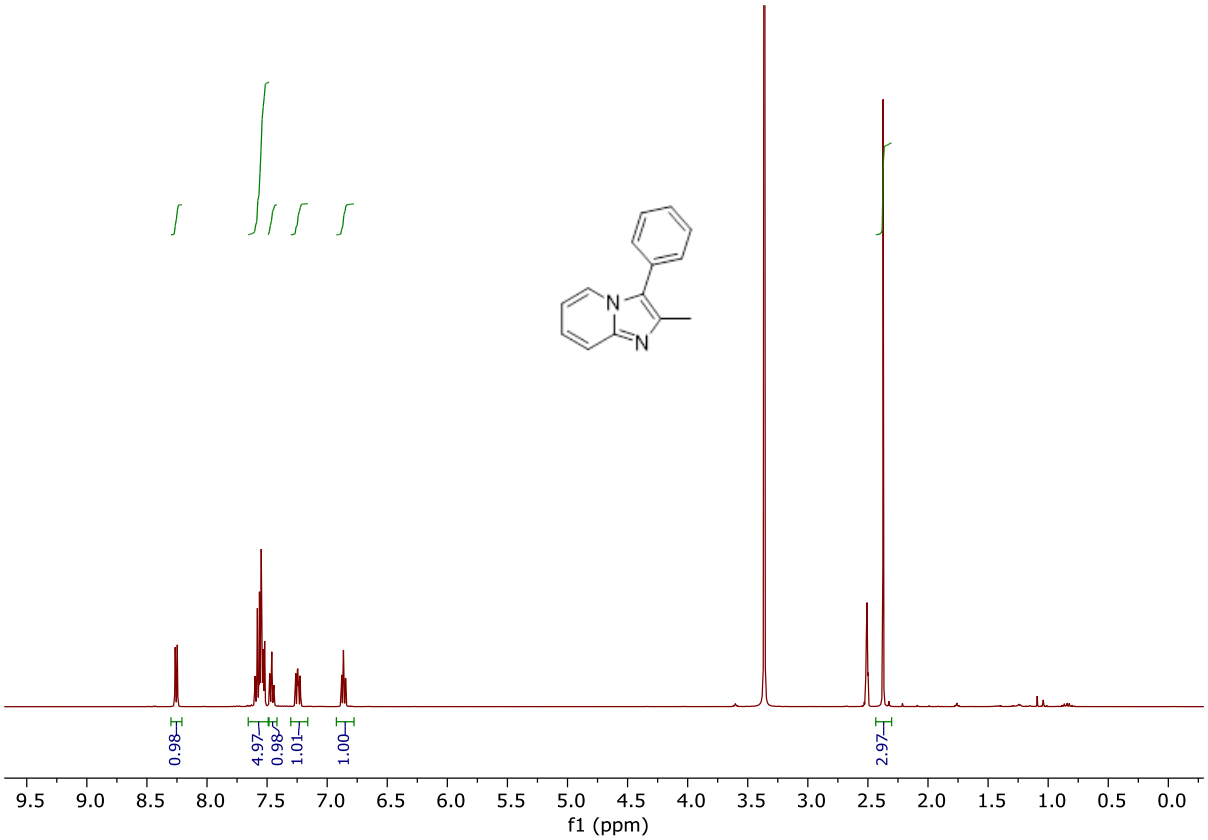


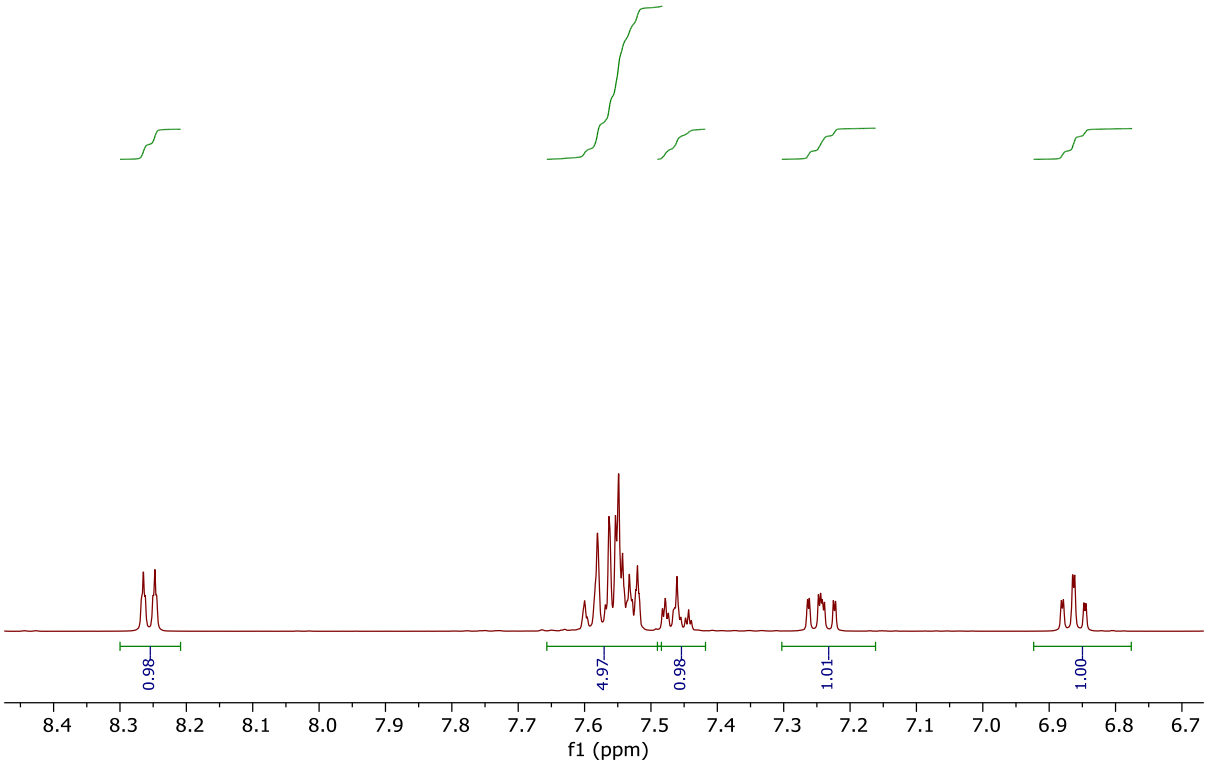


MS Spectrum of (**40**) (EI):

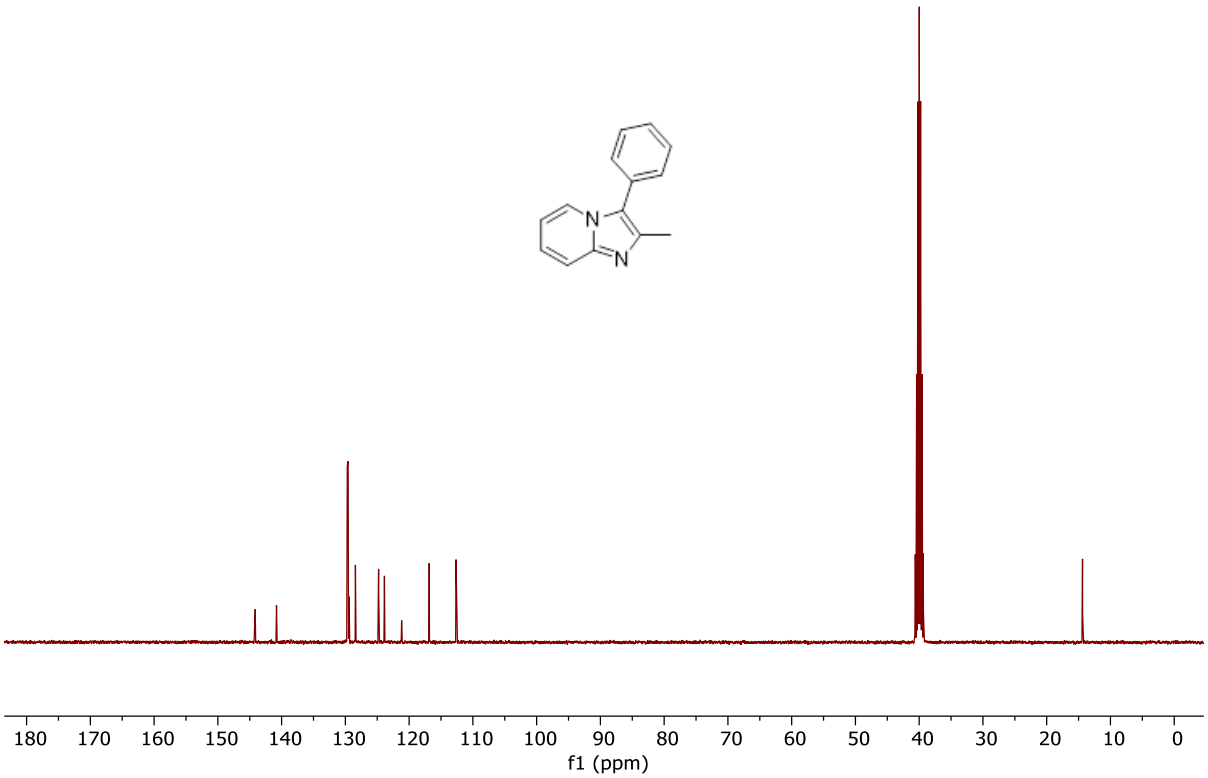


^{1}H NMR Spectrum of (**41**) (400 MHz, DMSO-d^{6}):

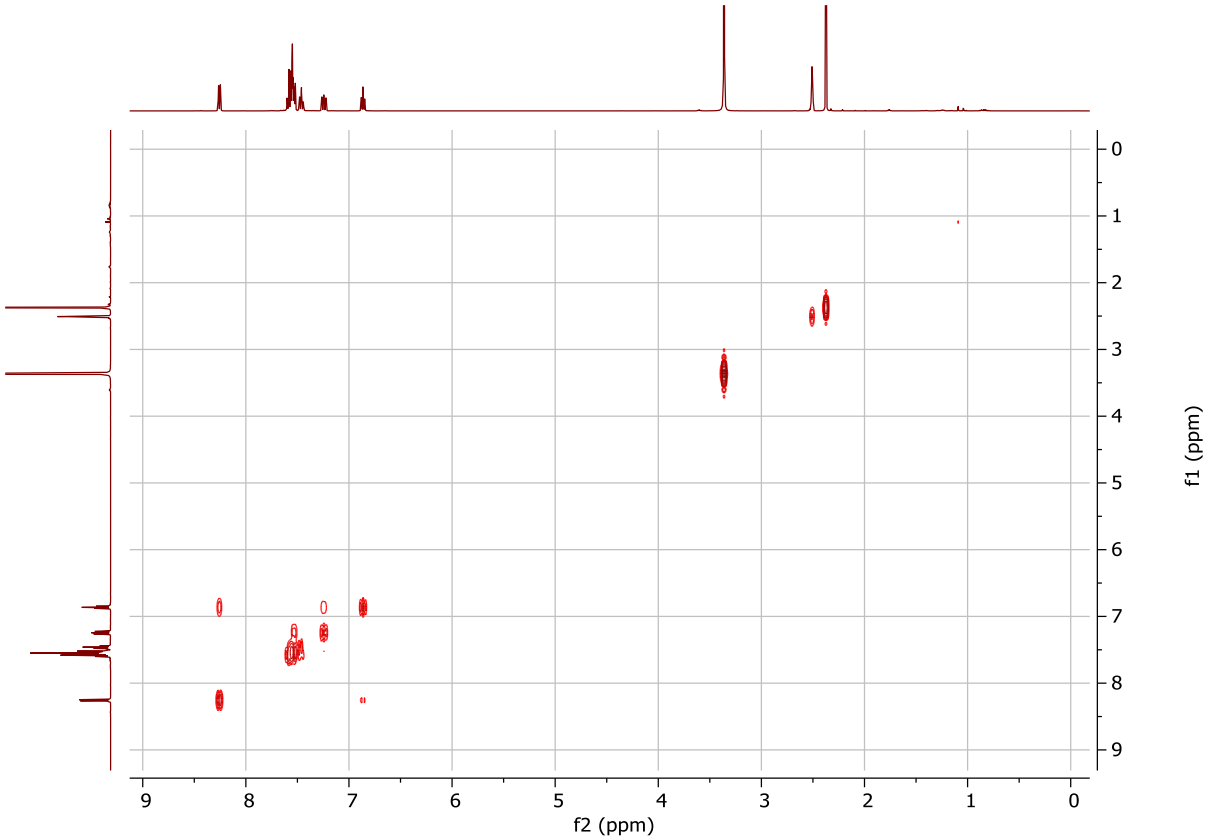


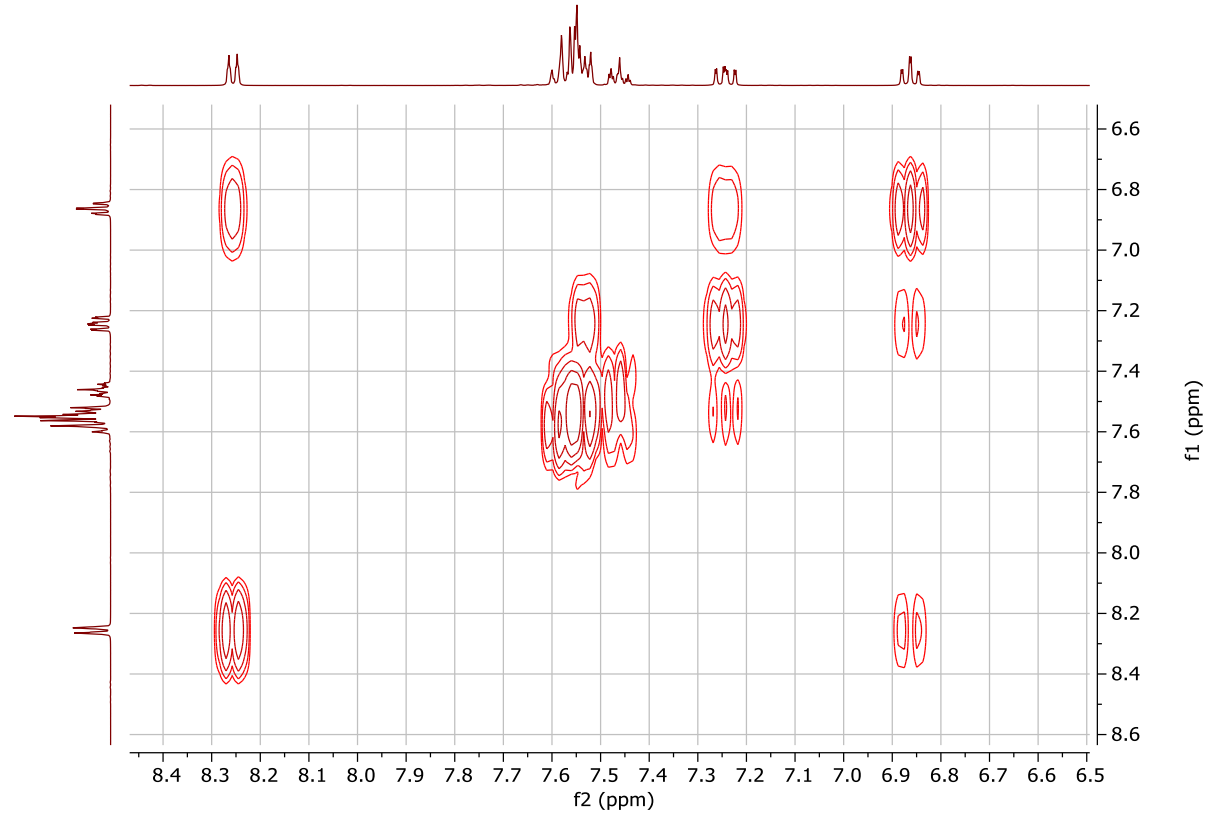


^{13}C NMR Spectrum of (**41**) (400 MHz, DMSO-d^{6}):

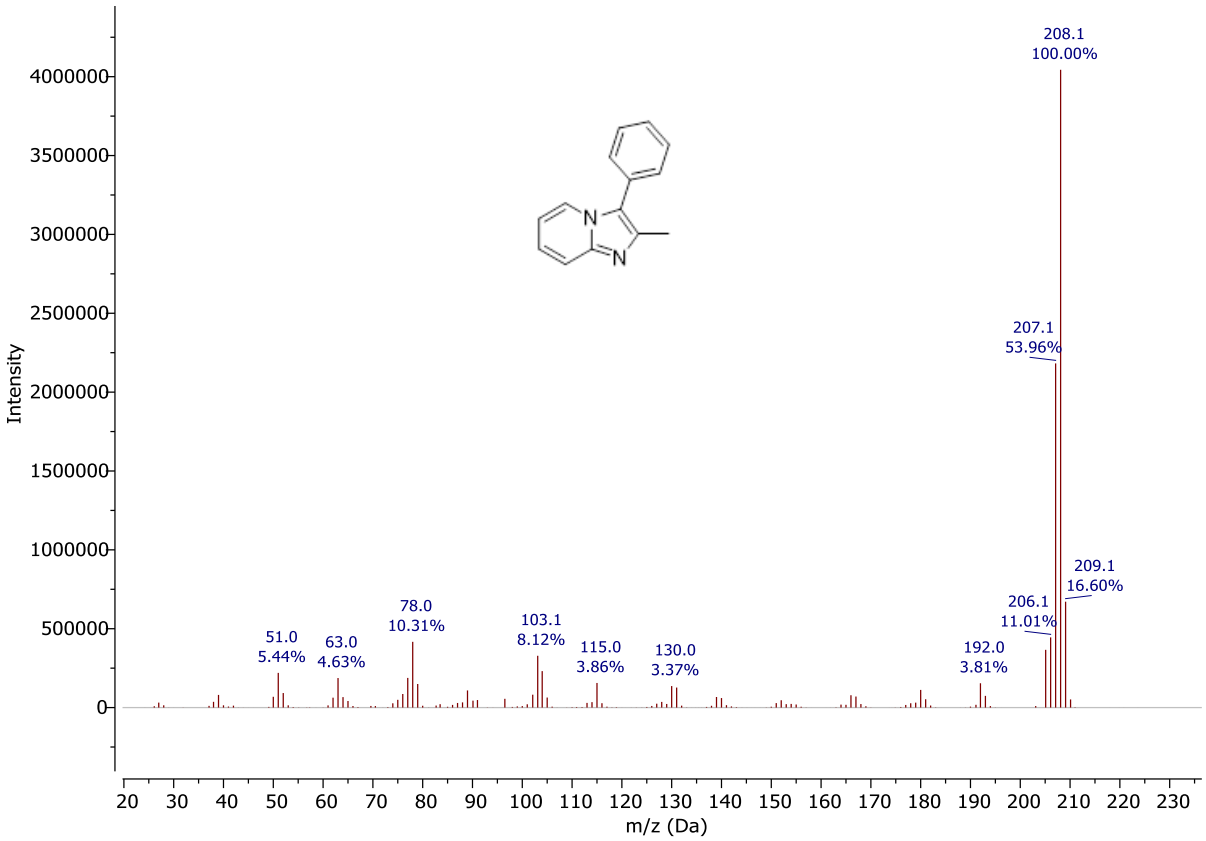


^{1}H/^{1}H COSY NMR Spectrum of (**41**) (400 MHz, DMSO-d^{6}):

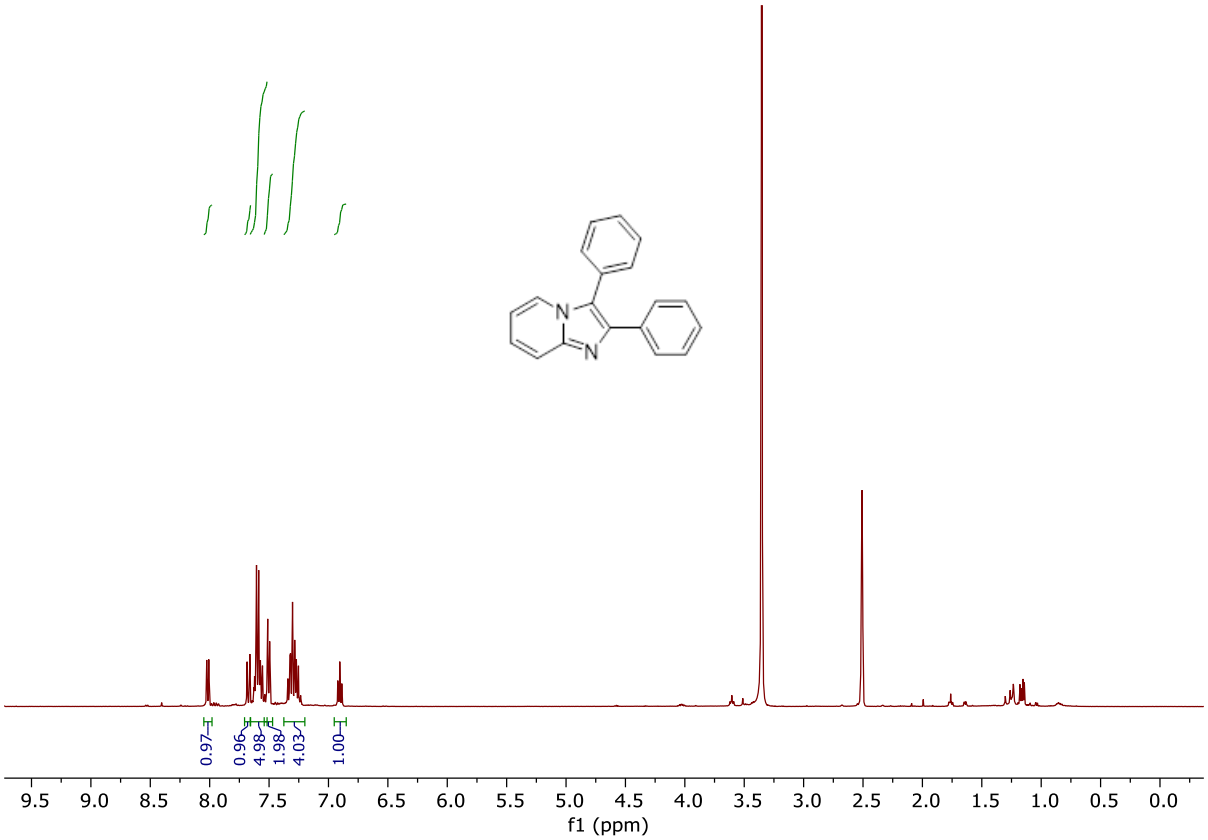




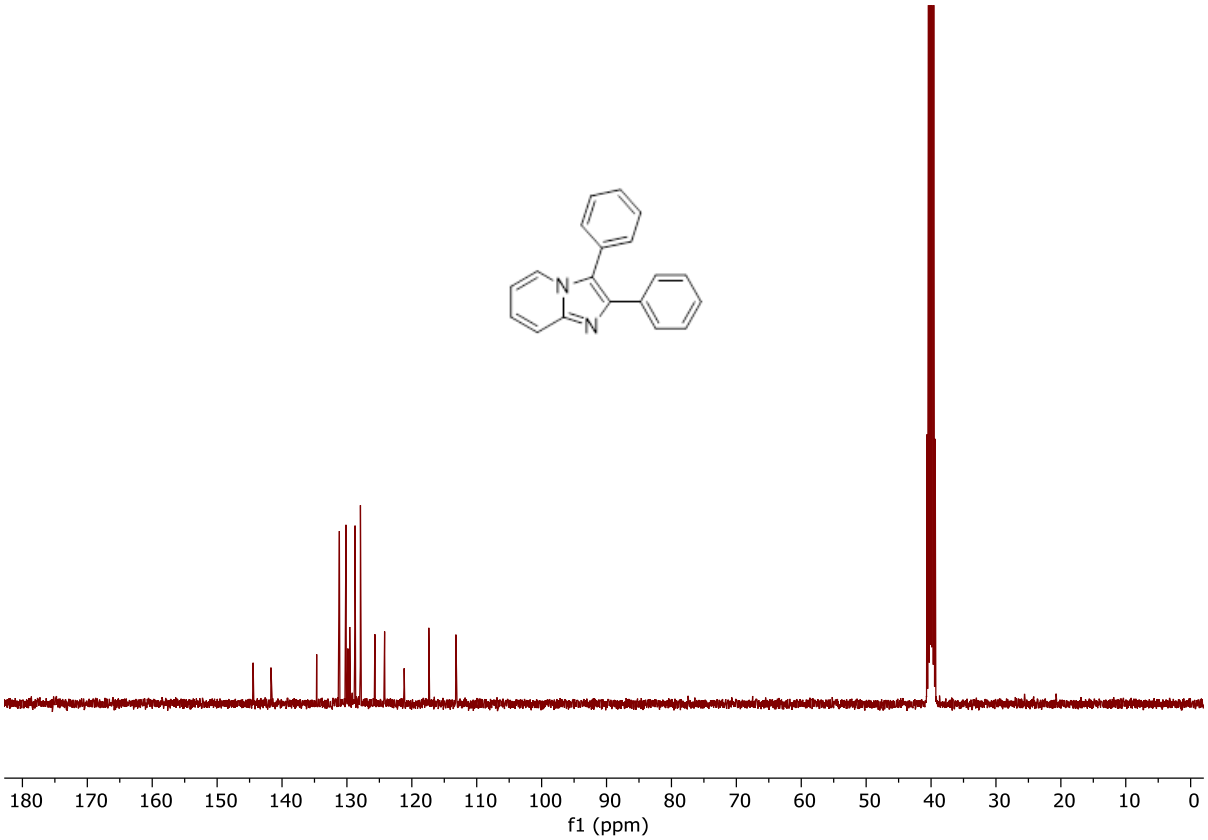
MS Spectrum of (**41**) (EI):



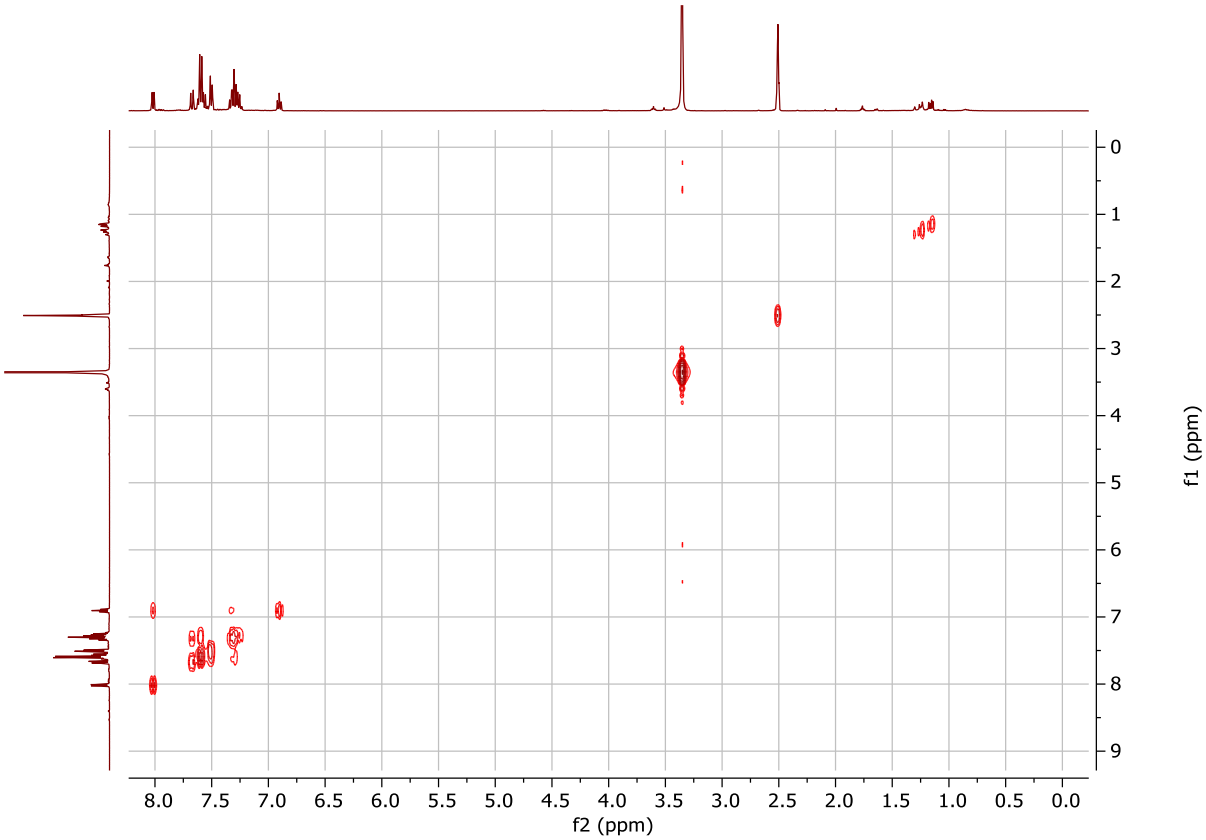
^{1}H NMR Spectrum of (**42**) (400 MHz, DMSO-d^{6}):



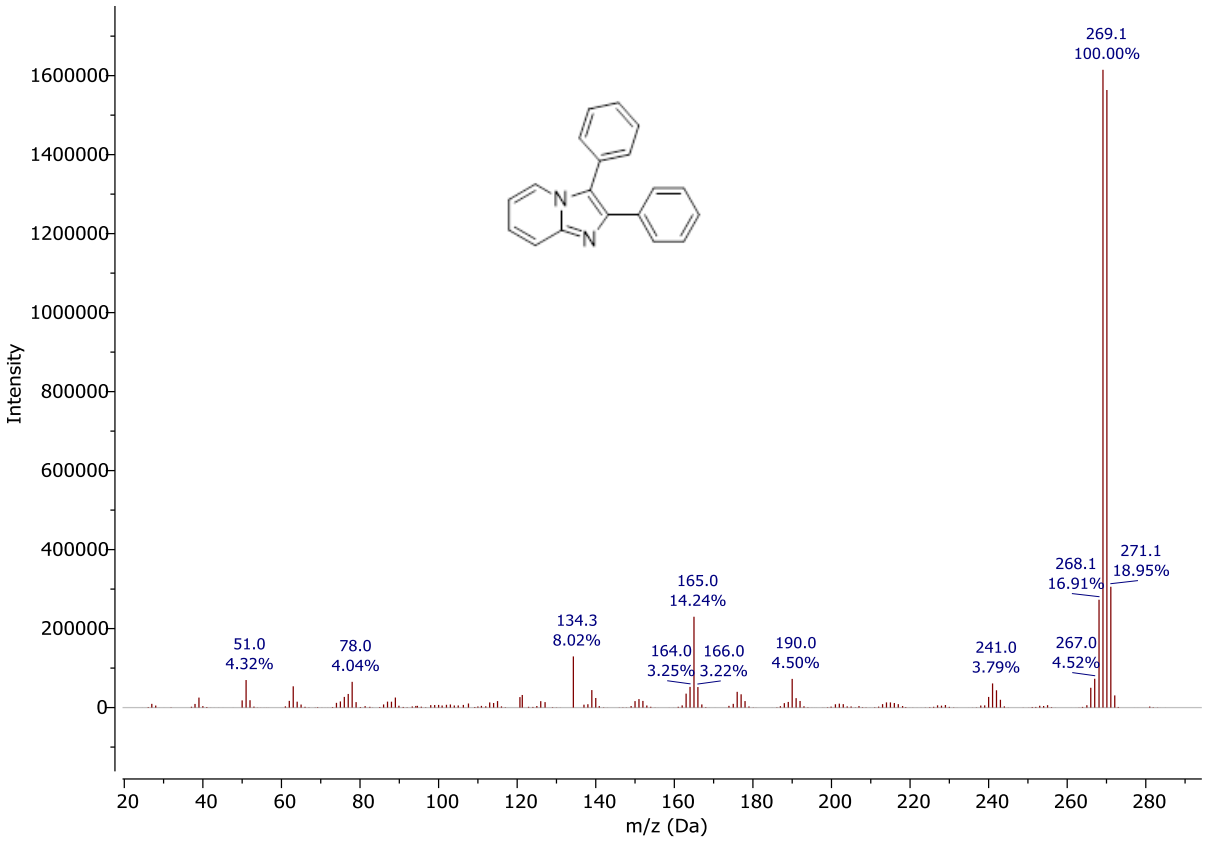
^{13}C NMR Spectrum of (**42**) (400 MHz, DMSO-d^{6}):



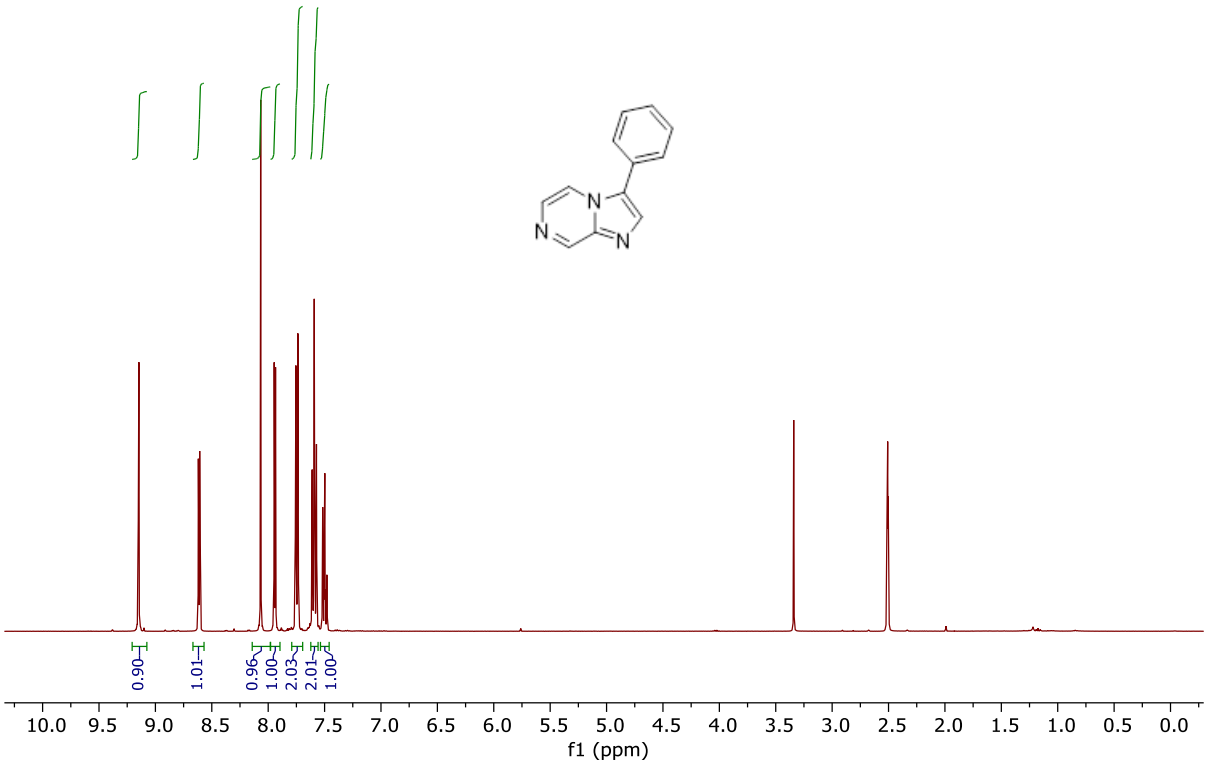
^{1}H/^{1}H COSY NMR Spectrum of (**42**) (400 MHz, DMSO-d^{6}):

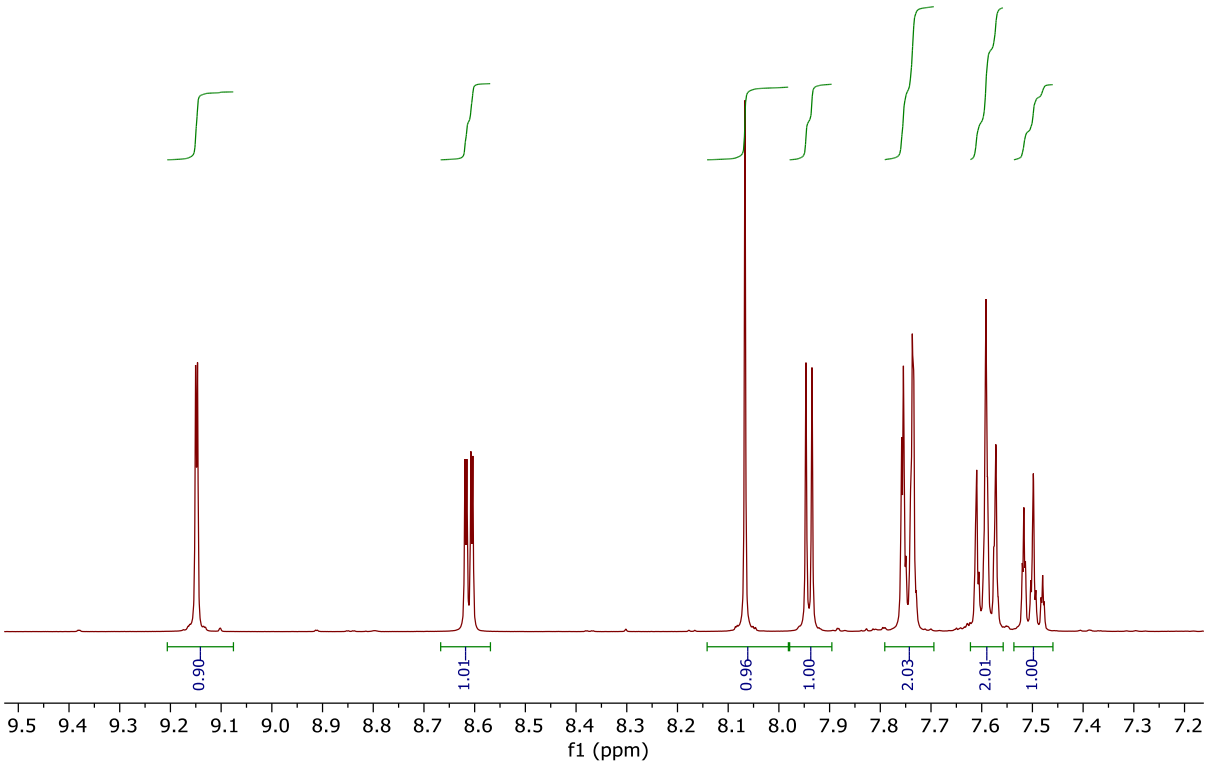


MS Spectrum of (**42**) (EI):

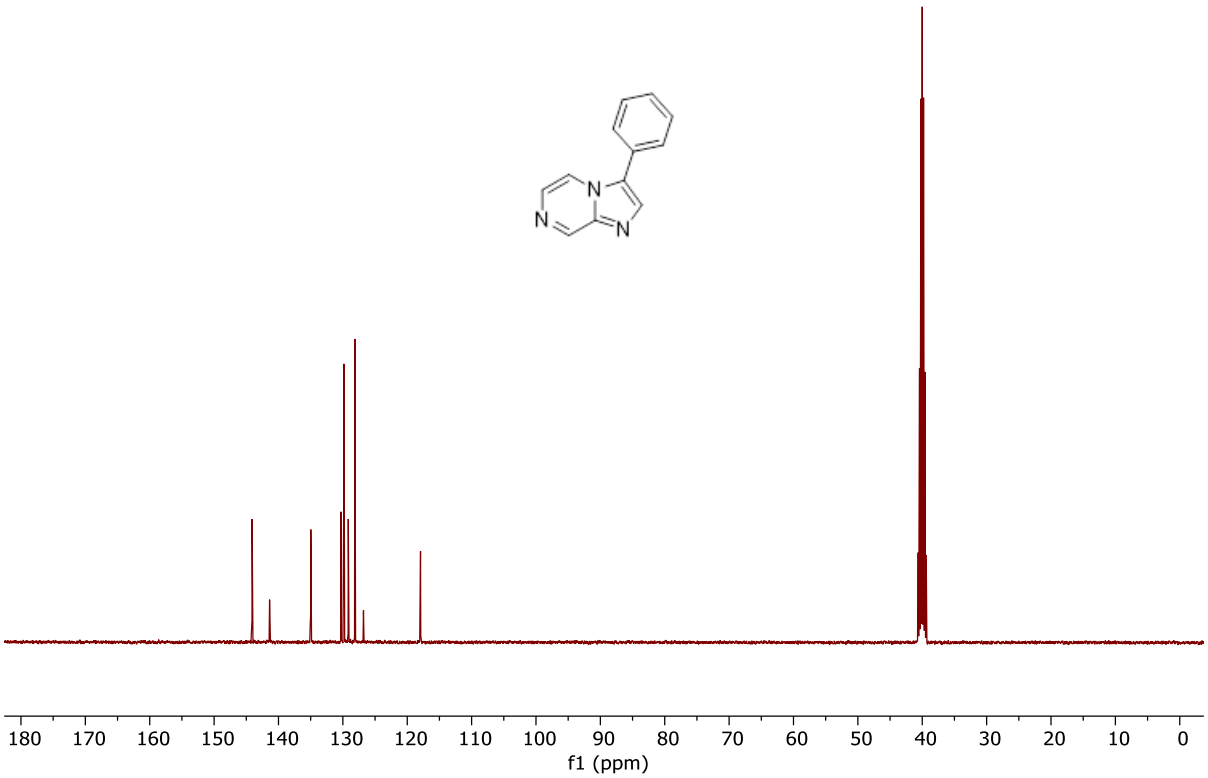


^{1}H NMR Spectrum of (**43**) (400 MHz, DMSO-d^{6}):

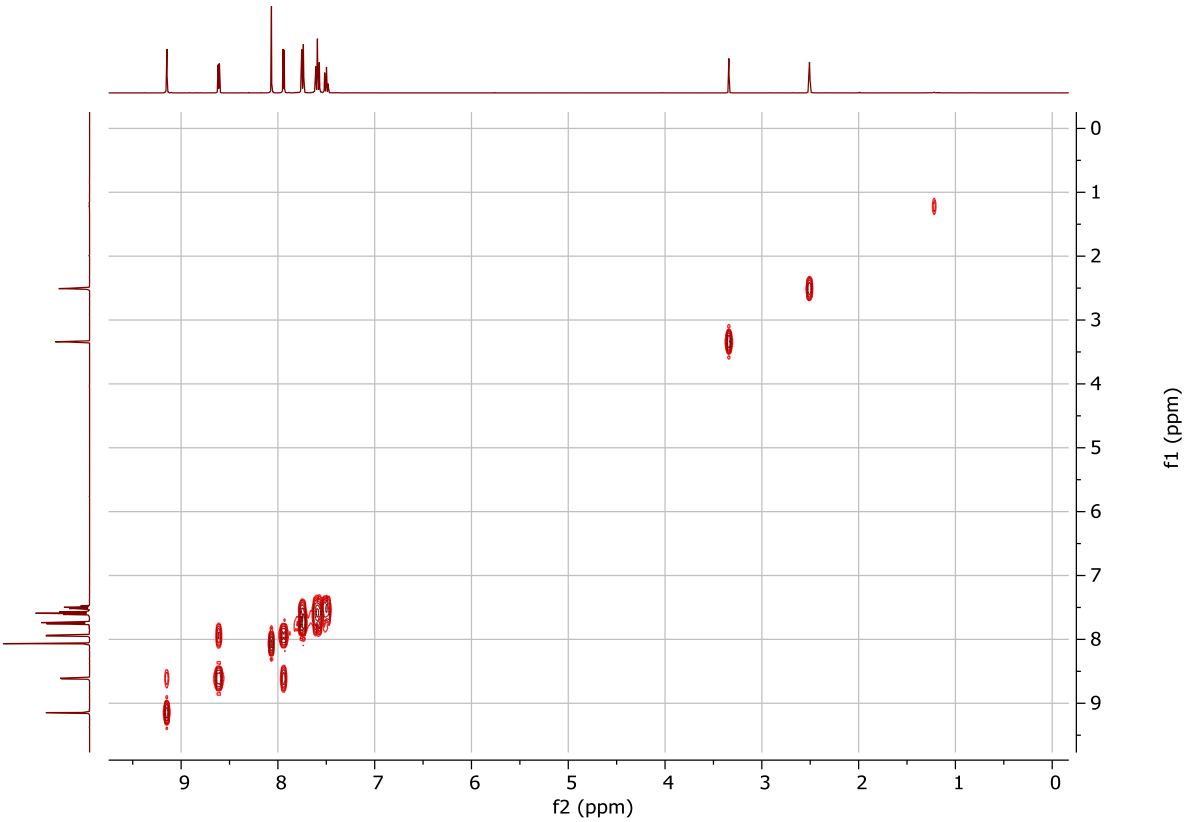


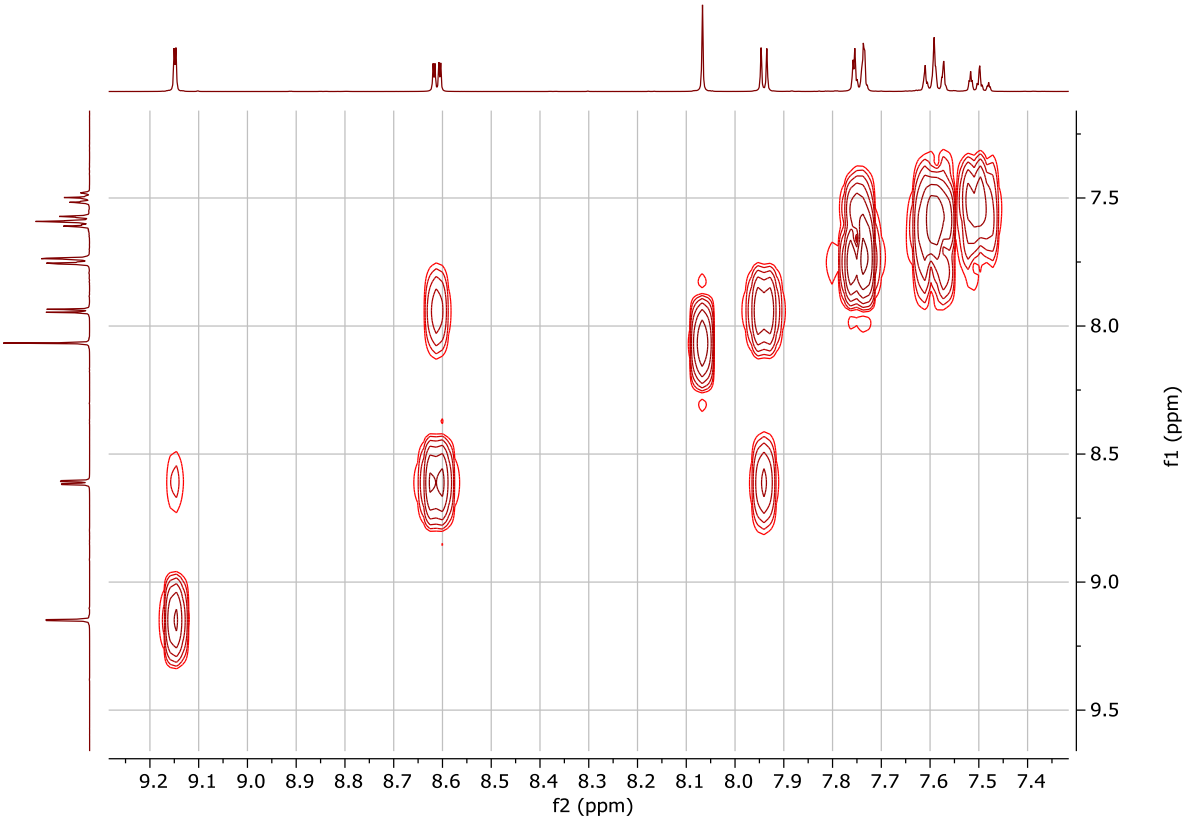


^{13}C NMR Spectrum of (**43**) (400 MHz, DMSO-d^{6}):

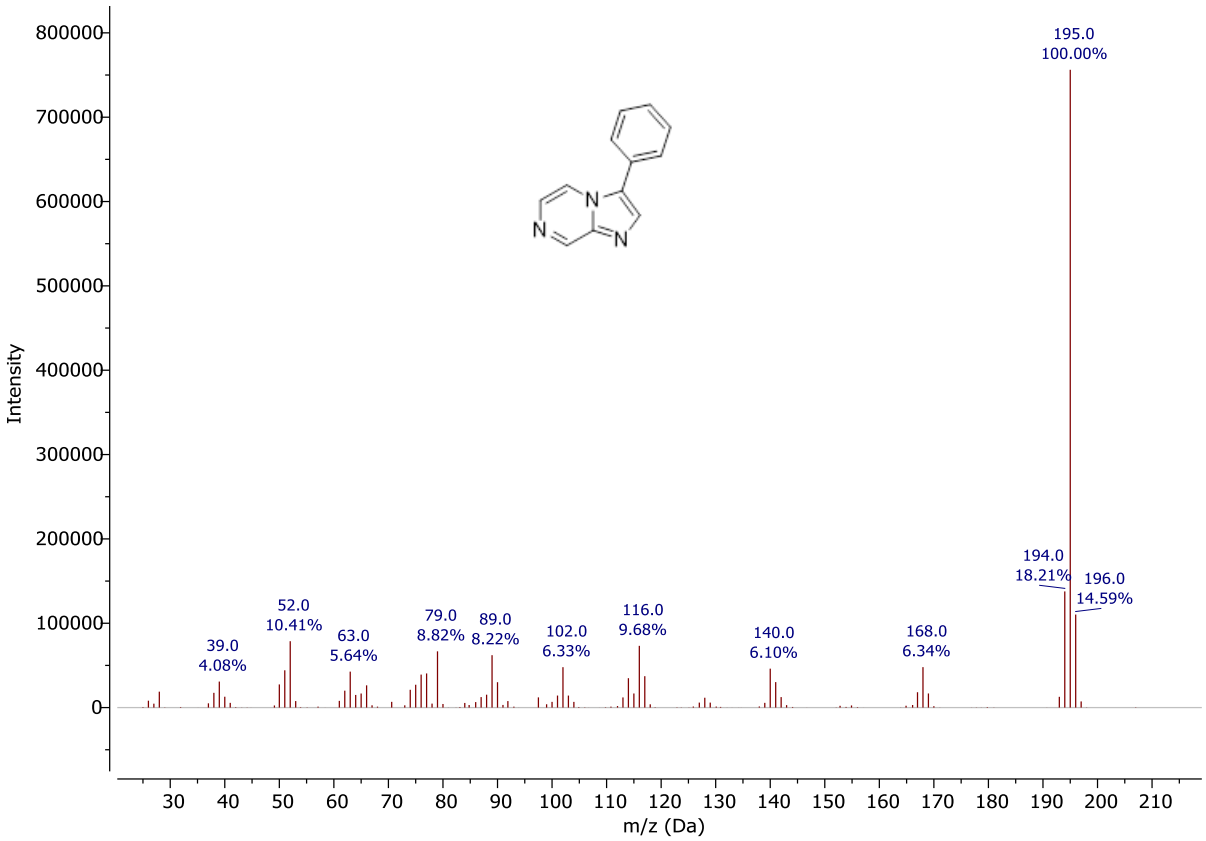


^{1}H/^{1}H COSY NMR Spectrum of (**43**) (400 MHz, DMSO-d^{6}):

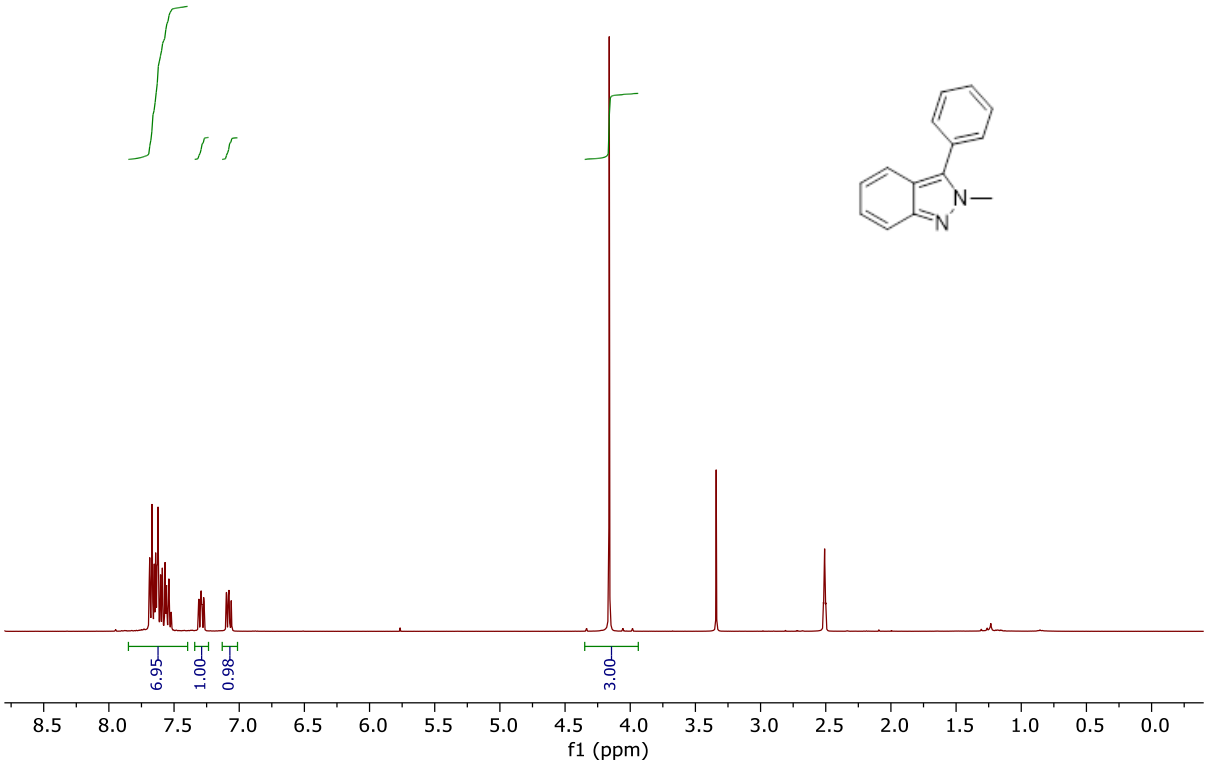


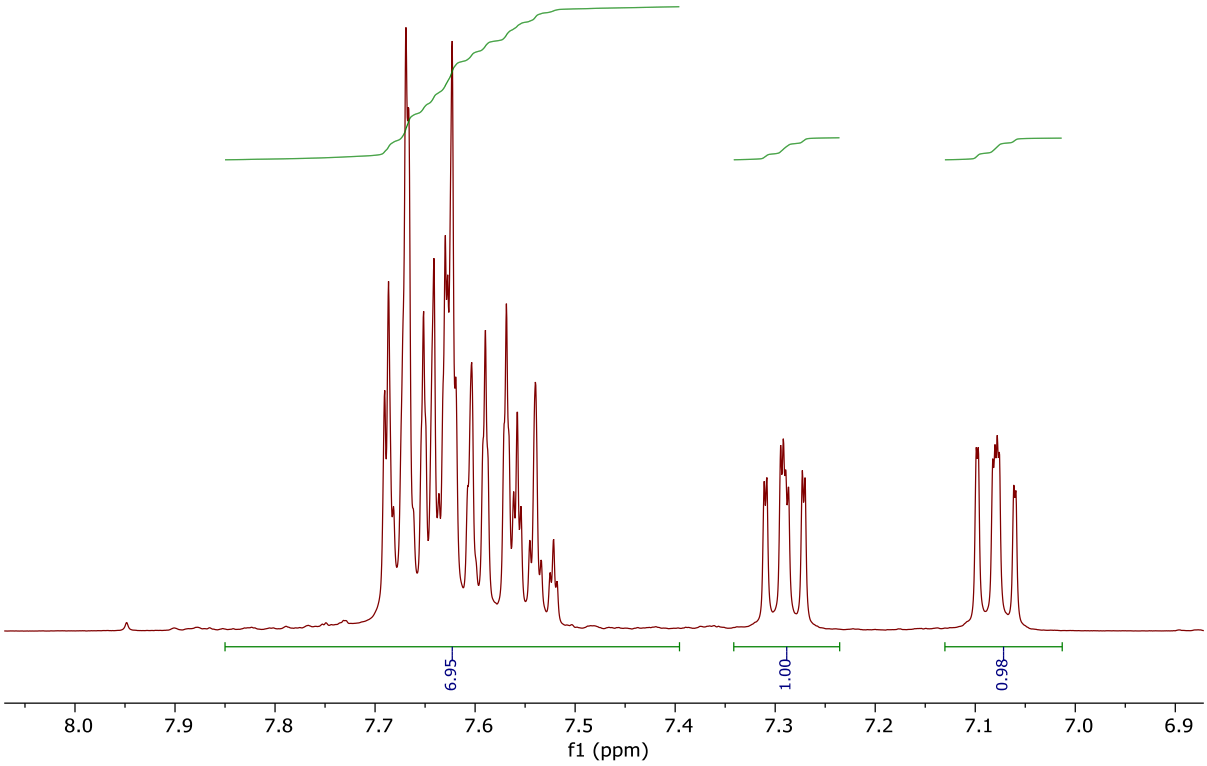


MS Spectrum of (**43**) (EI):

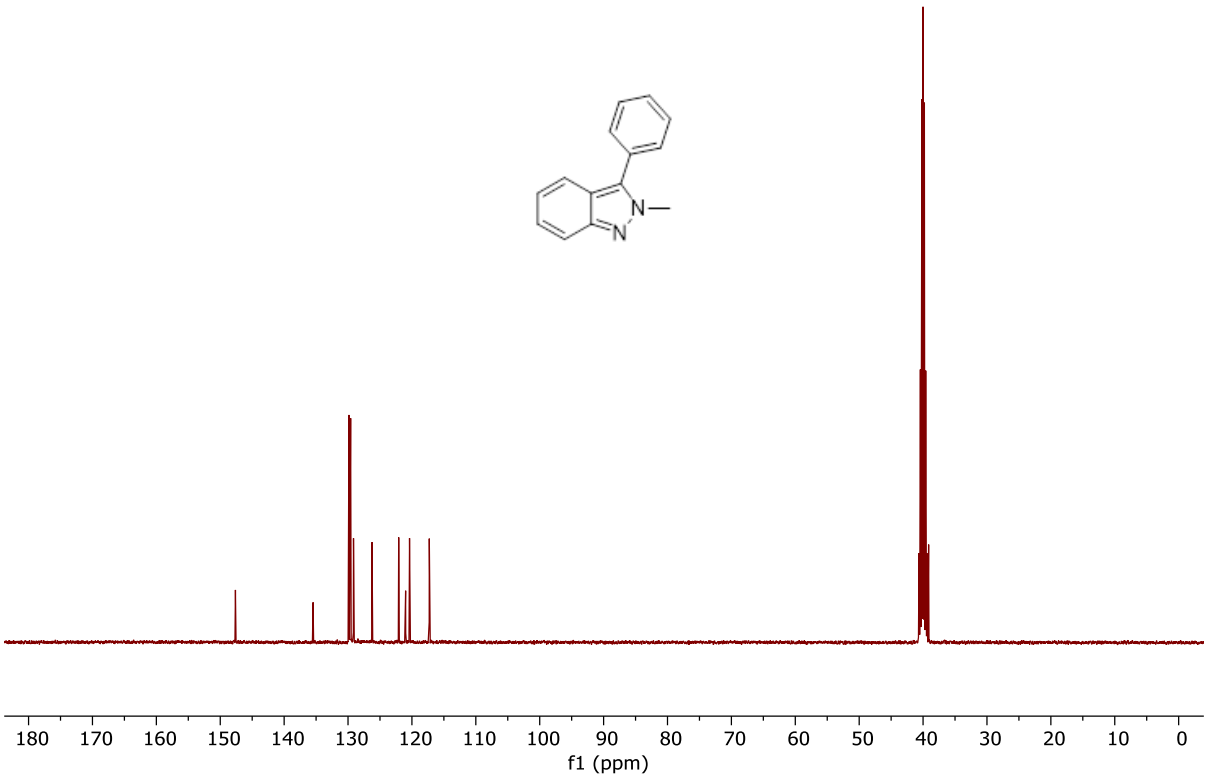


^{1}H NMR Spectrum of (**44**) (400 MHz, DMSO-d^{6}):

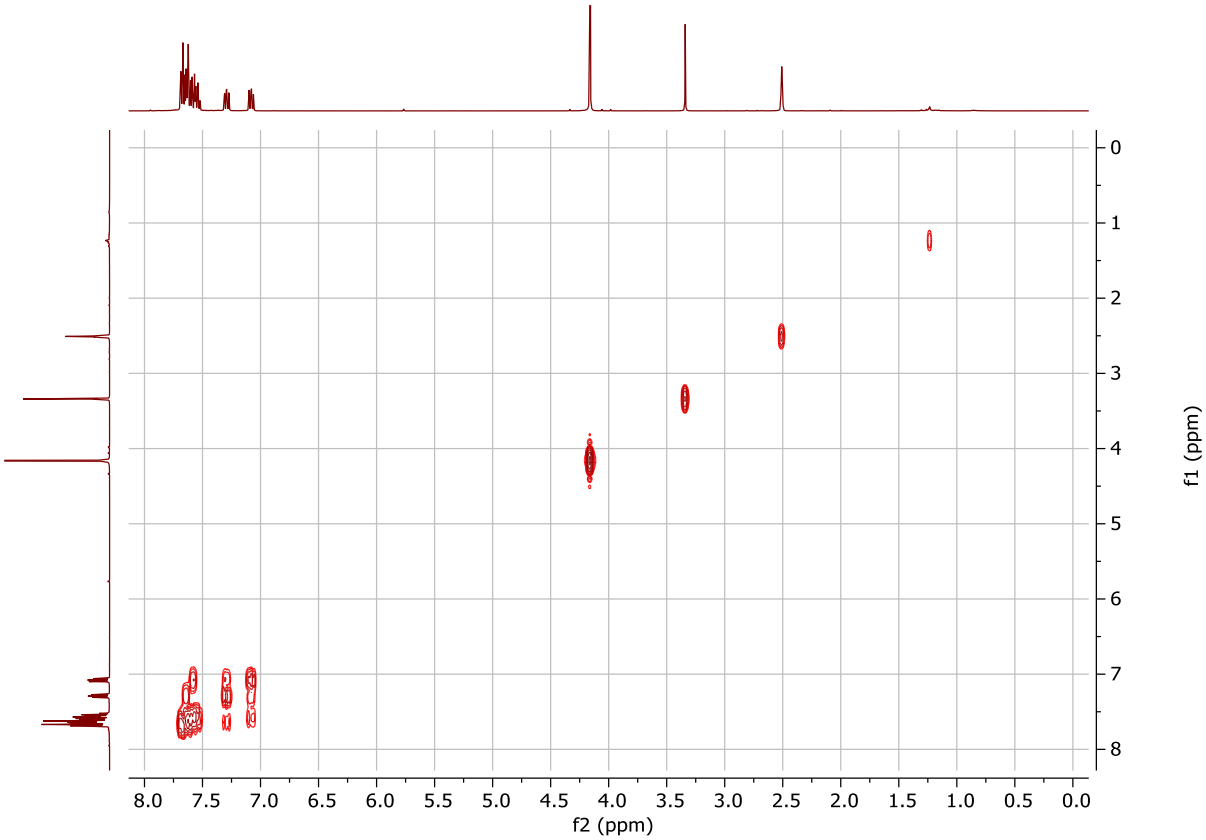


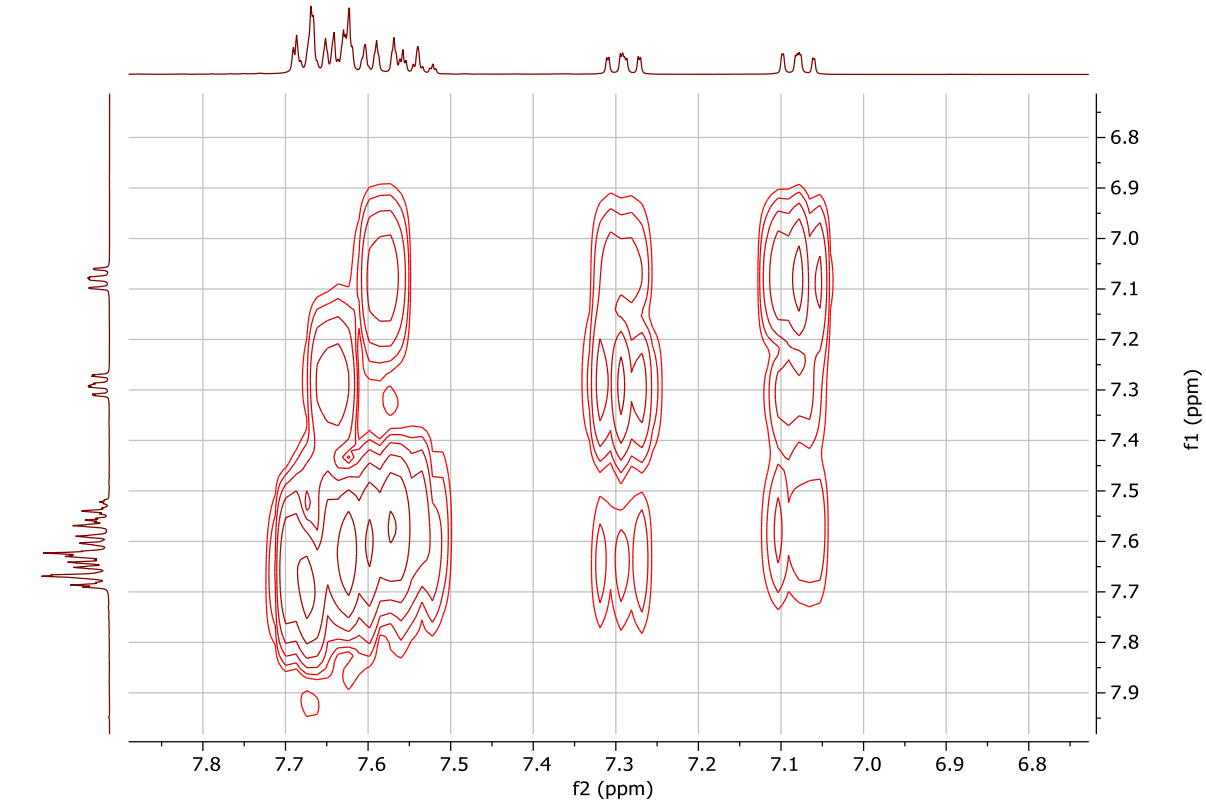


^{13}C NMR Spectrum of (**44**) (400 MHz, DMSO-d^{6}):

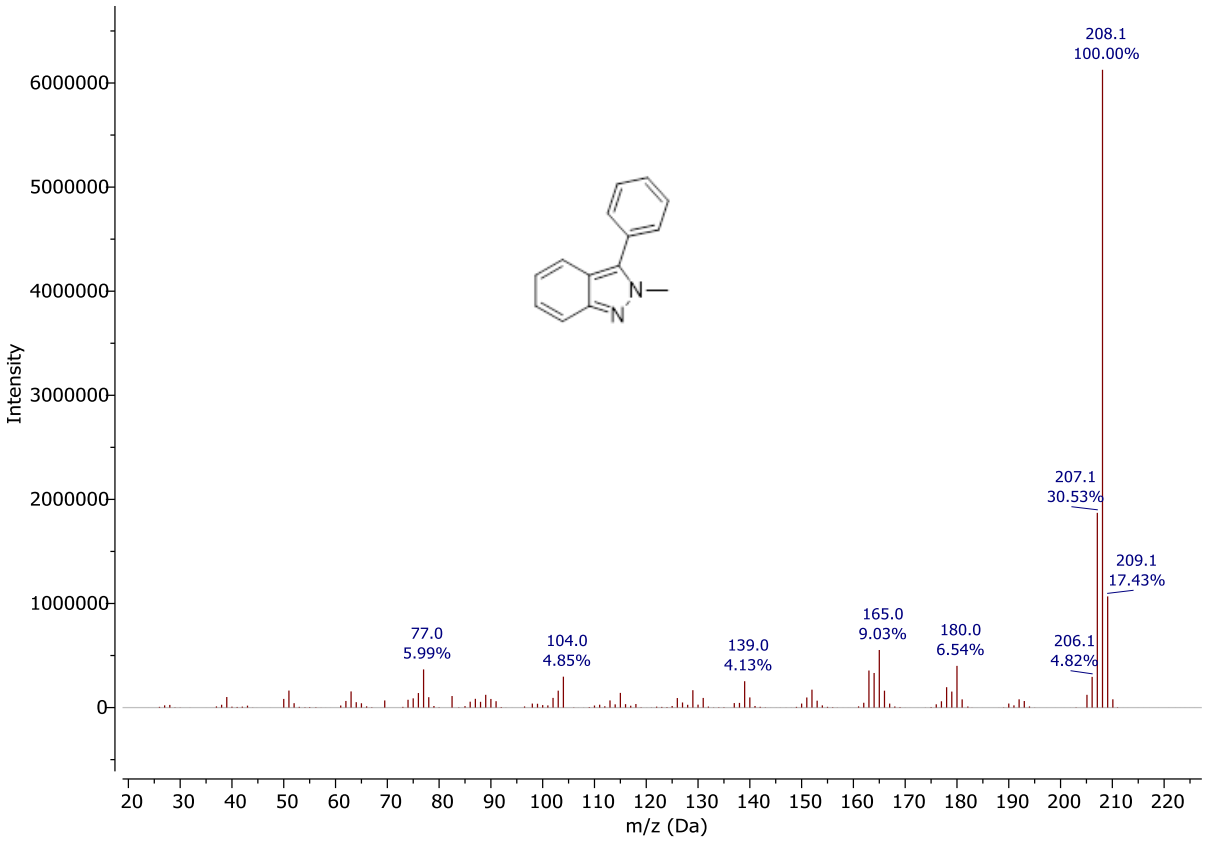


^{1}H/^{1}H COSY NMR Spectrum of (**44**) (400 MHz, DMSO-d^{6}):

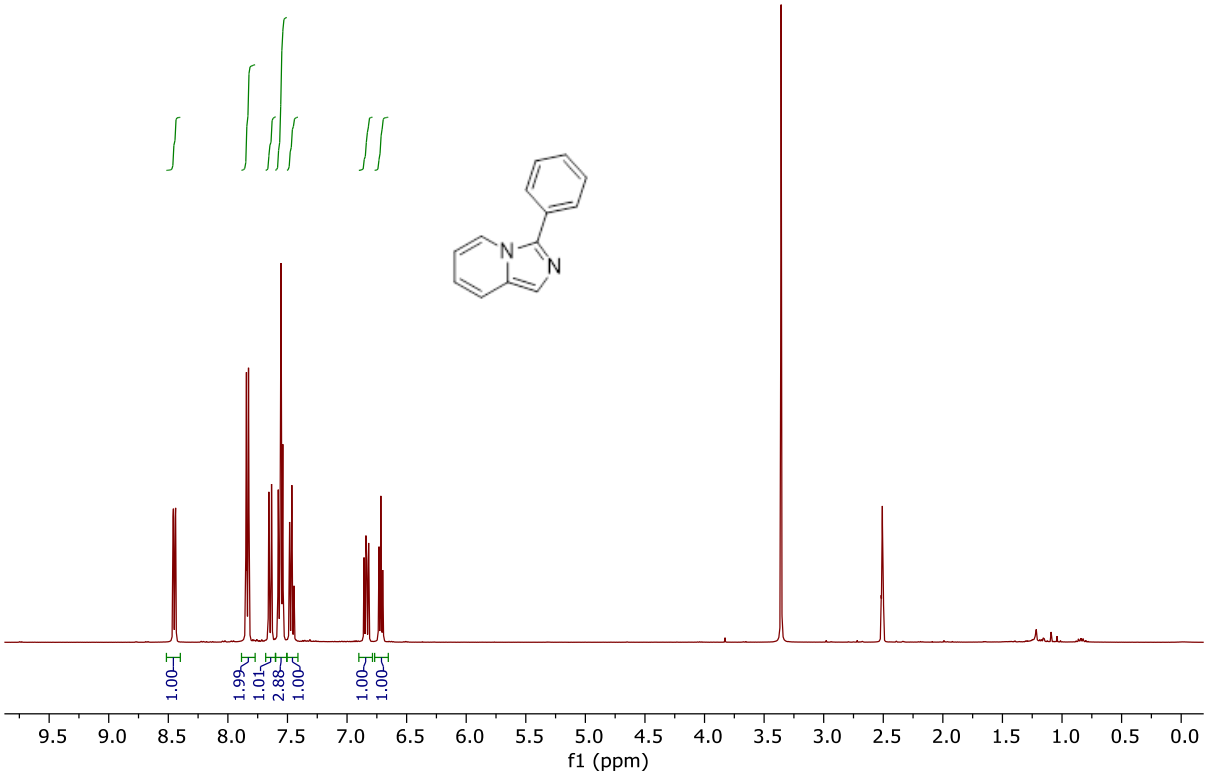


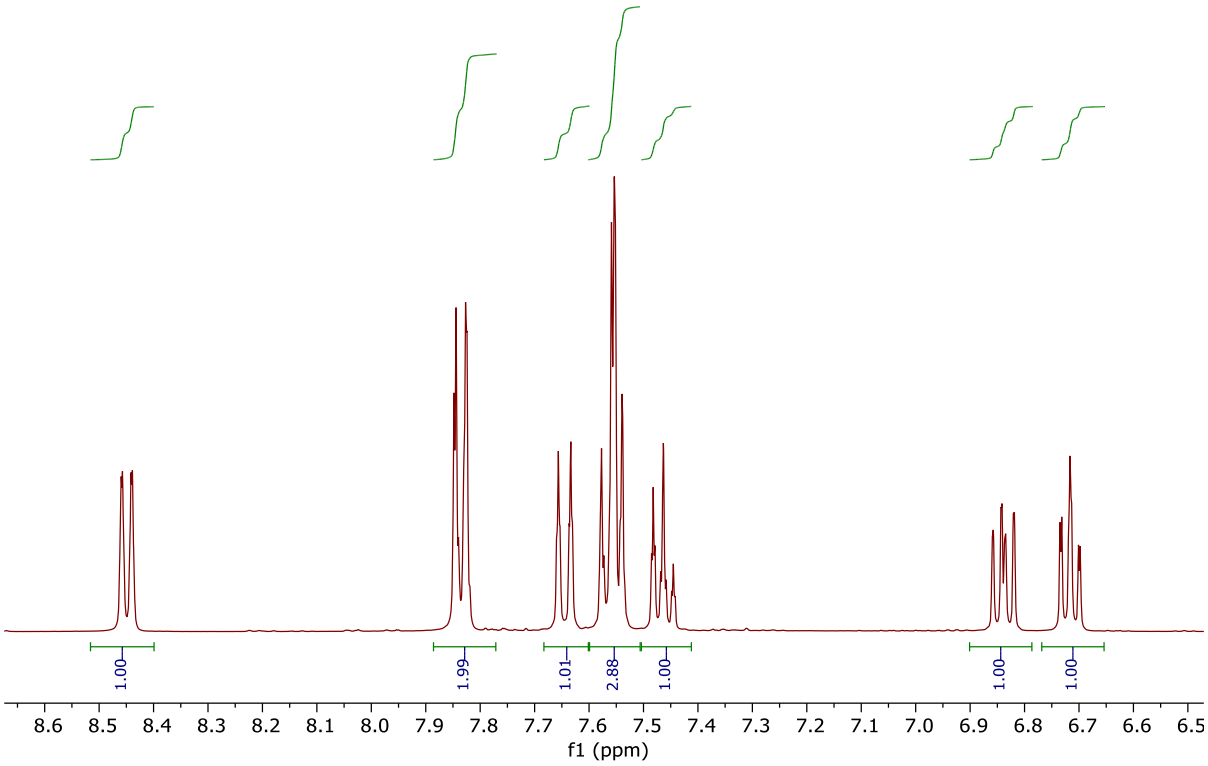


MS Spectrum of (**44**) (EI):

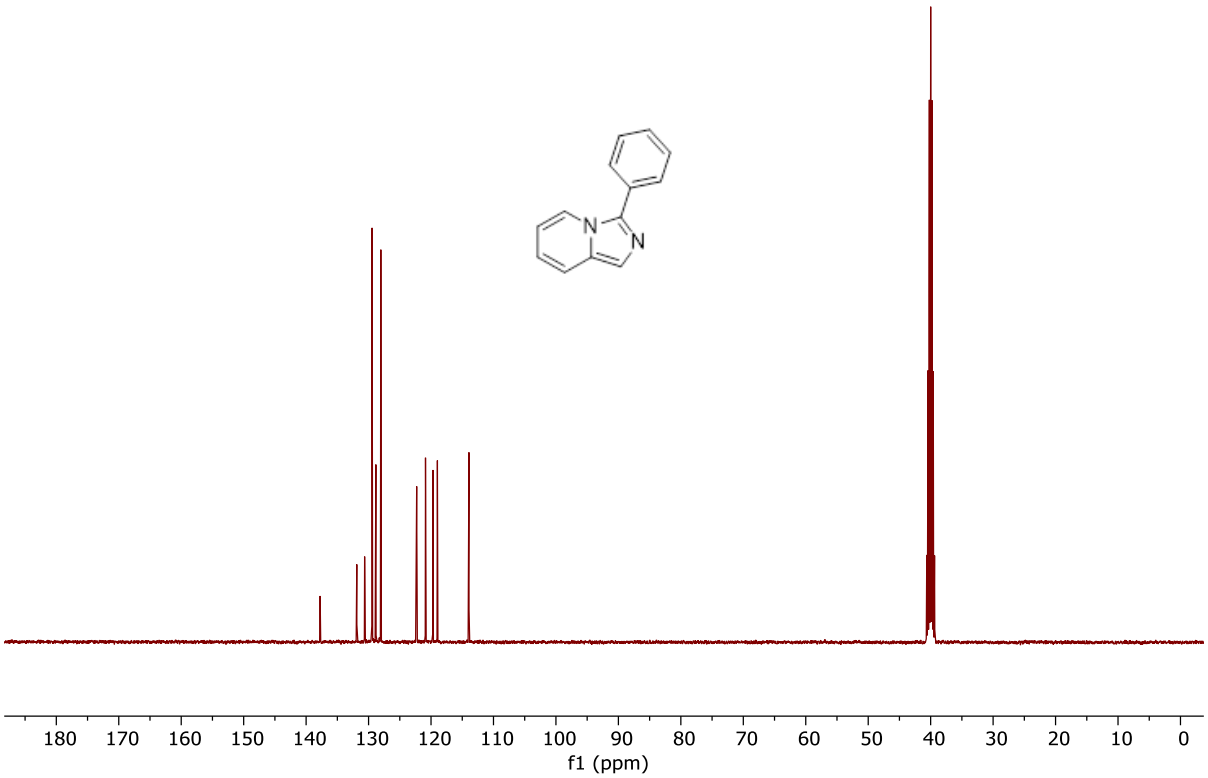


^{1}H NMR Spectrum of (**45**) (400 MHz, DMSO-d^{6}):

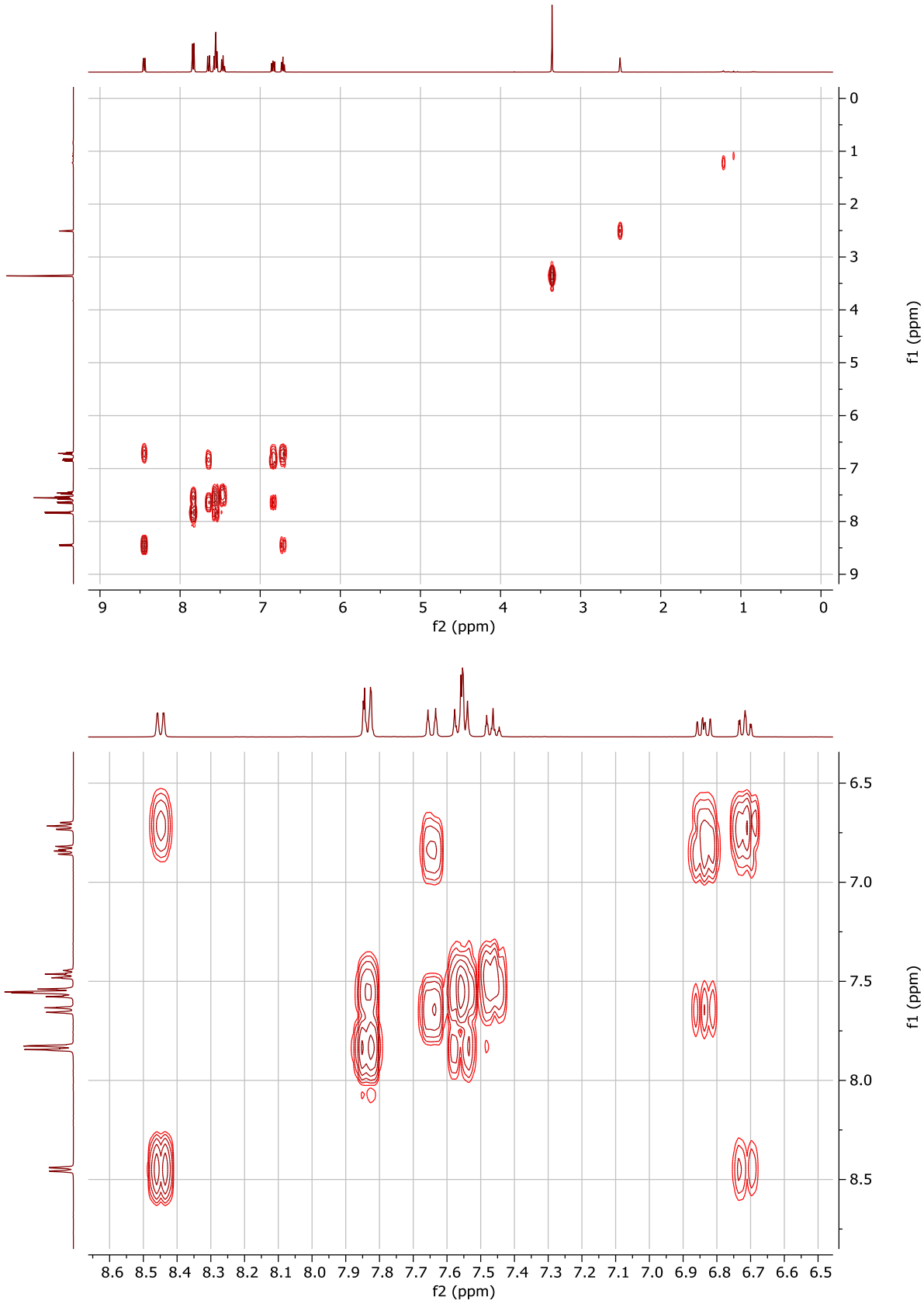




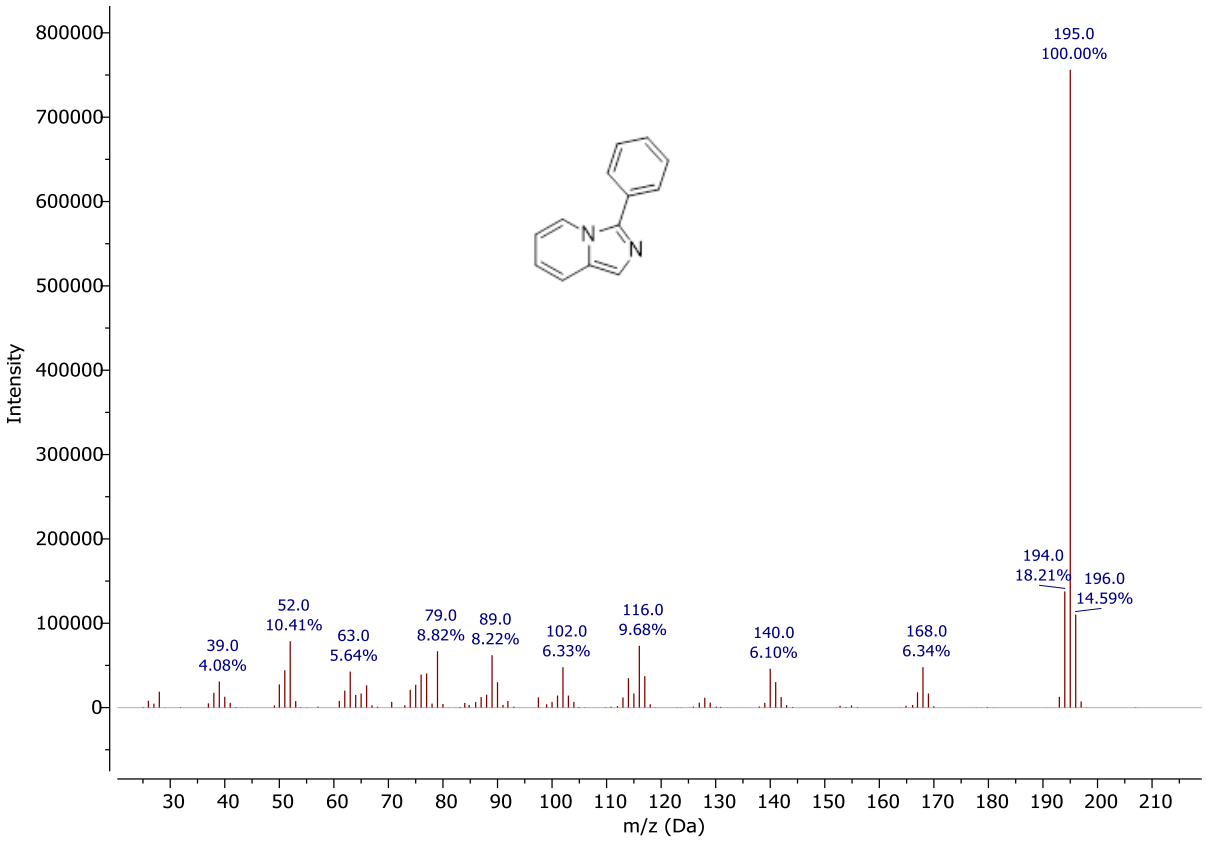
^{13}C NMR Spectrum of (**45**) (400 MHz, DMSO-d^{6}):



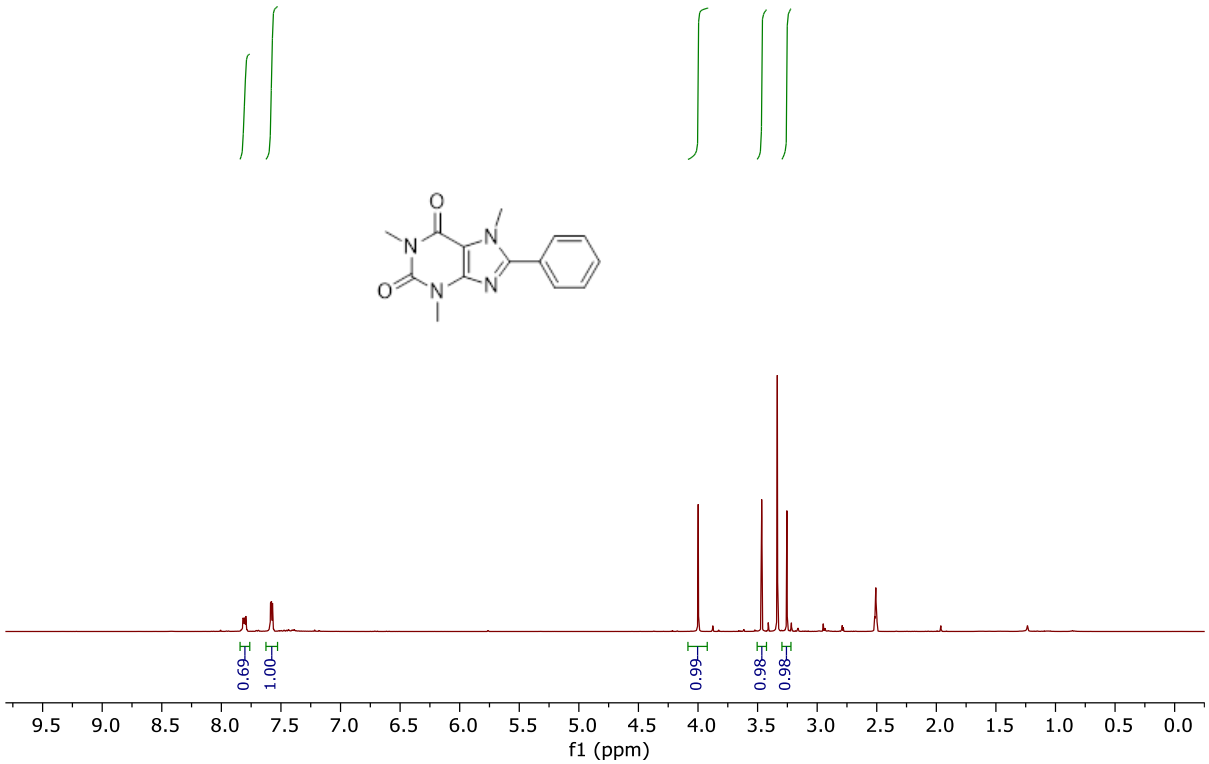
^{1}H/^{1}H COSY NMR Spectrum of (**45**) (400 MHz, DMSO-d^{6}):



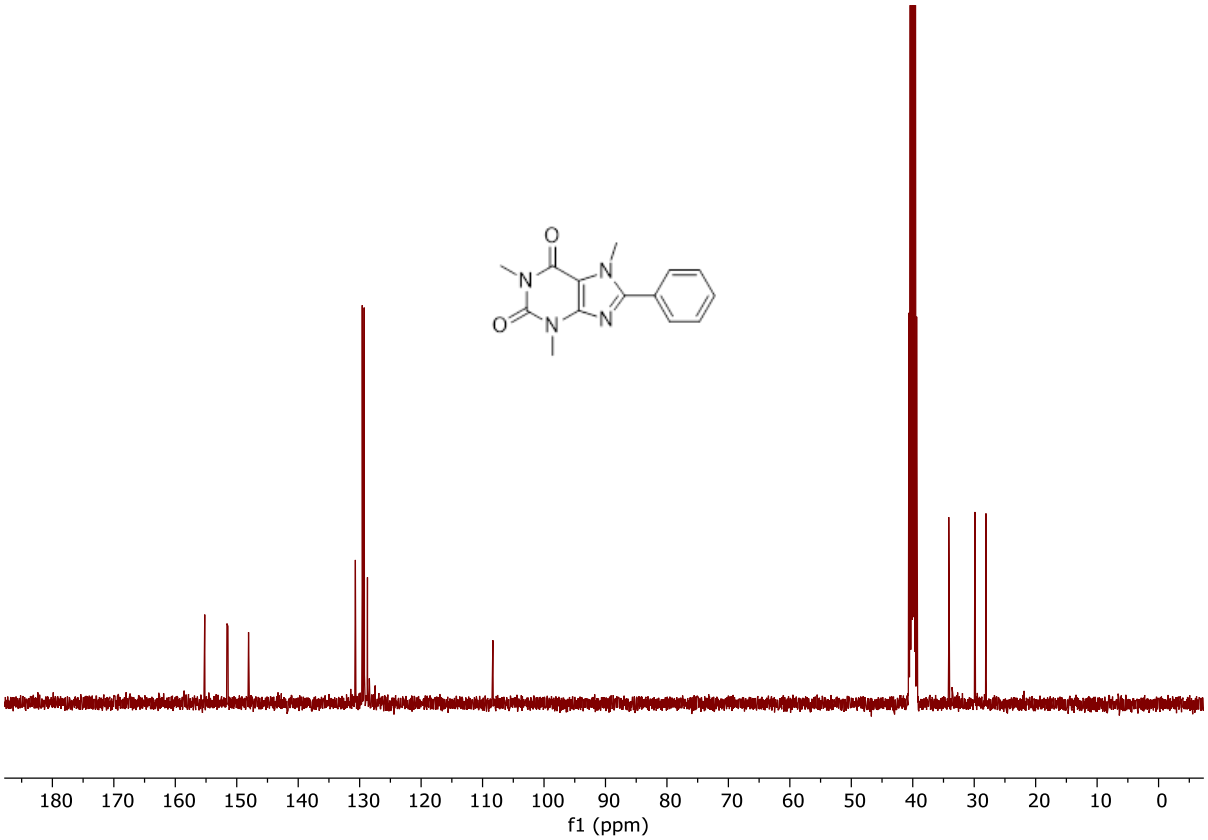
MS Spectrum of (**45**) (EI):



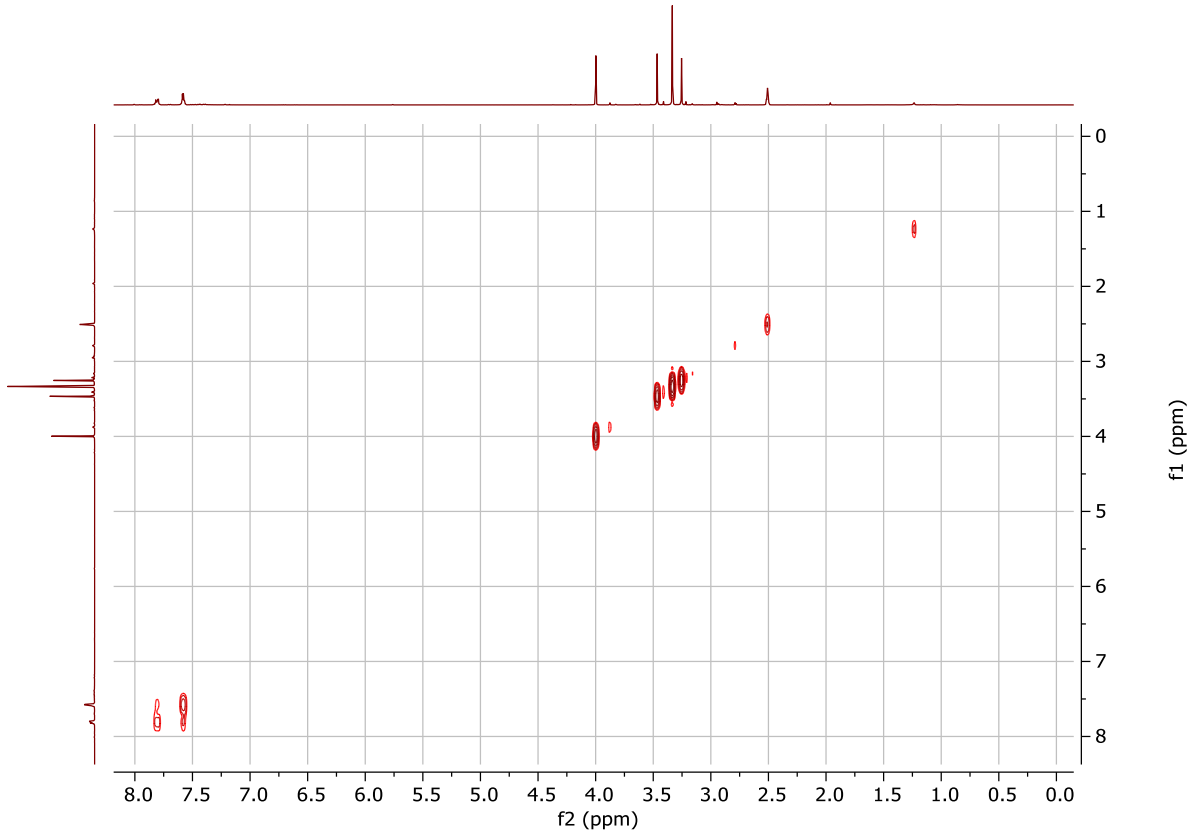
^{1}H NMR Spectrum of (**46**) (400 MHz, DMSO-d^{6}):



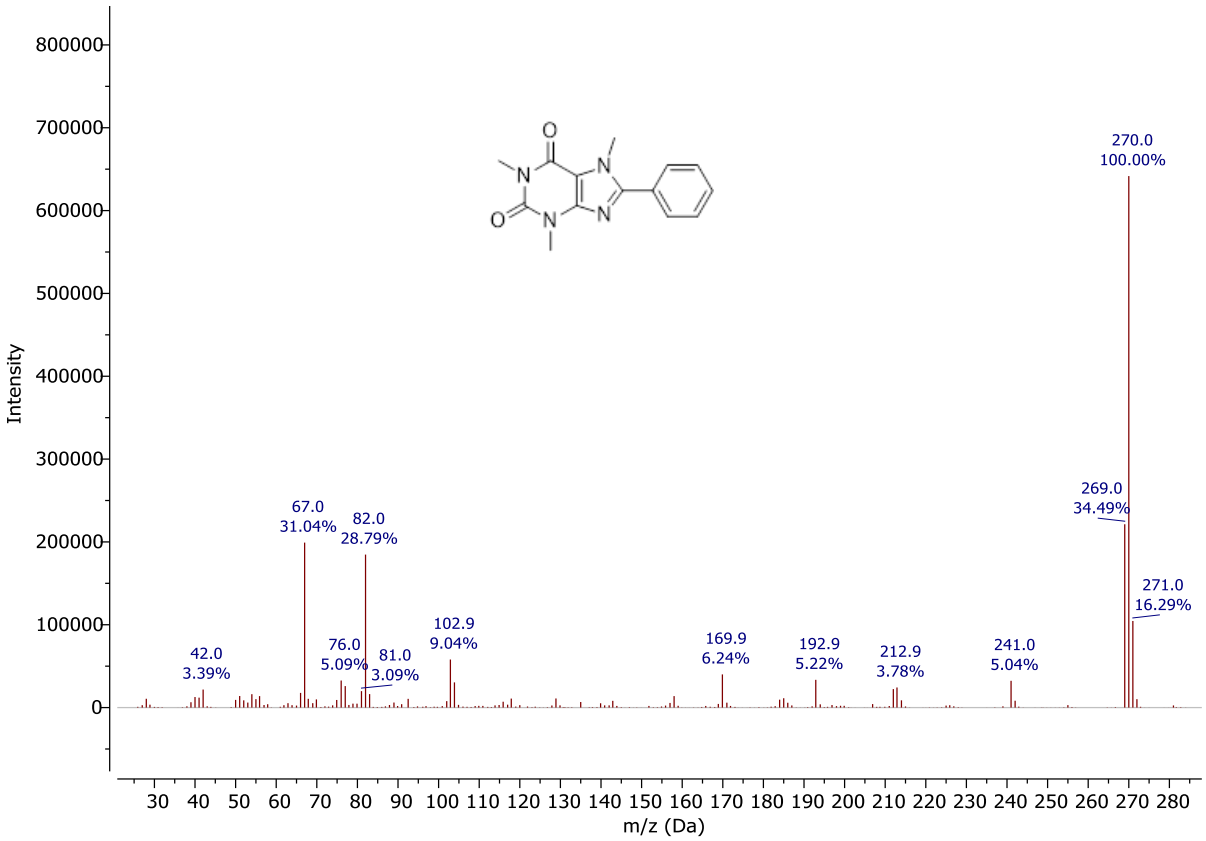
^{13}C NMR Spectrum of (**46**) (400 MHz, DMSO-d^{6}):



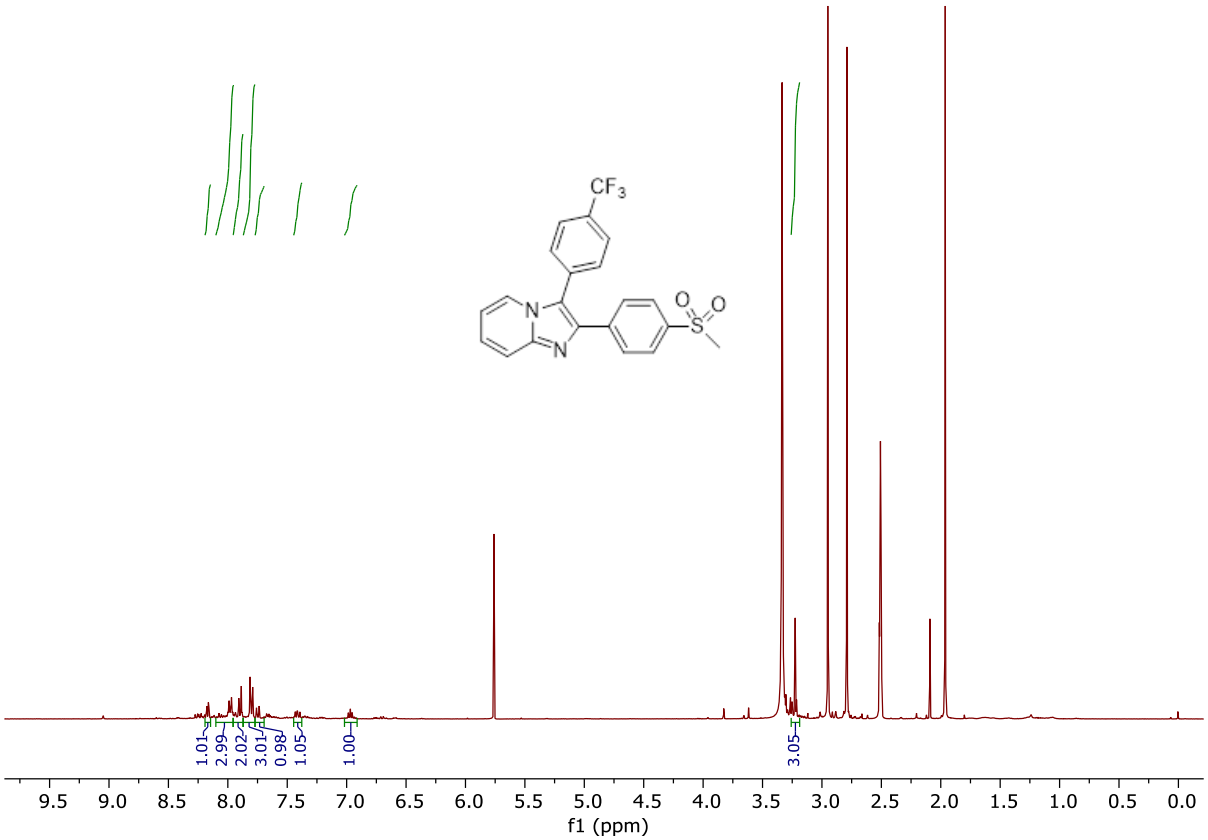
^{1}H/^{1}H COSY NMR Spectrum of (**46**) (400 MHz, DMSO-d^{6}):



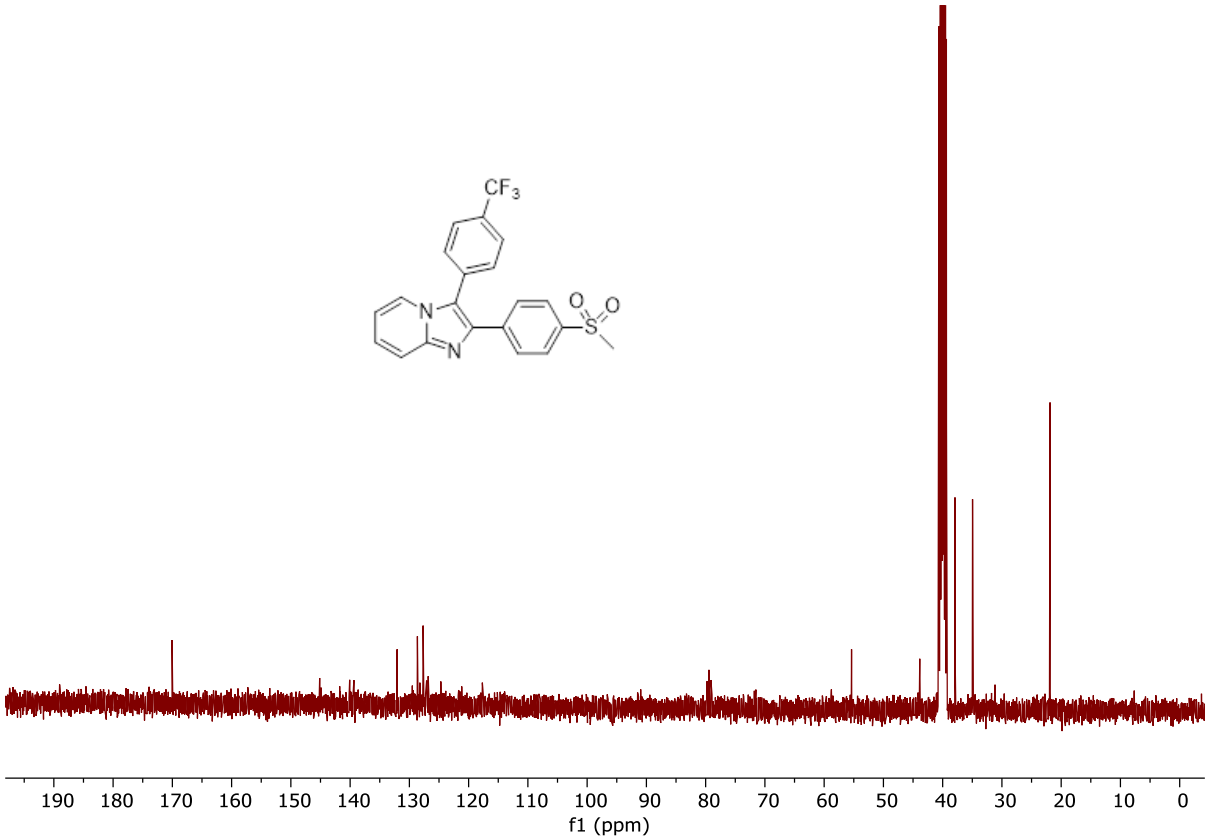
MS Spectrum of (**46**) (EI):



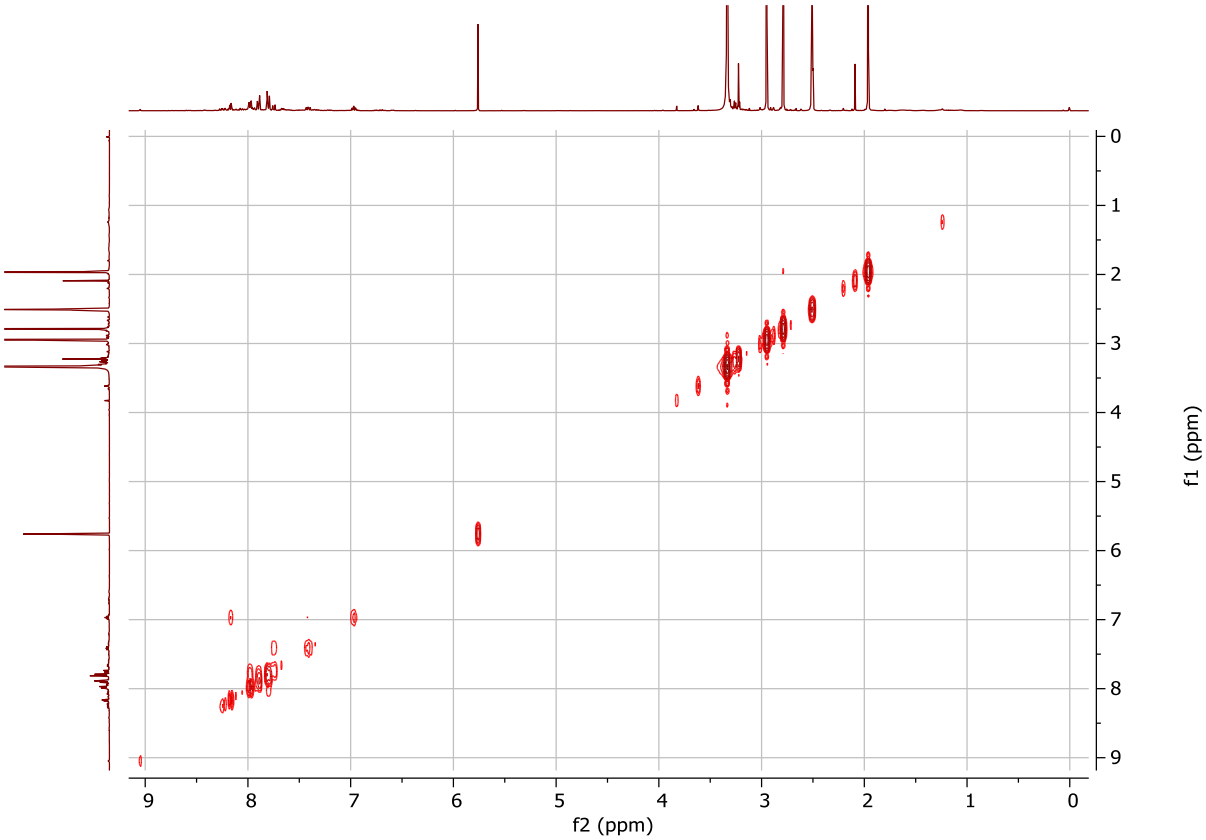
^{1}H NMR Spectrum of (**47**) (400 MHz, DMSO-d^{6}):



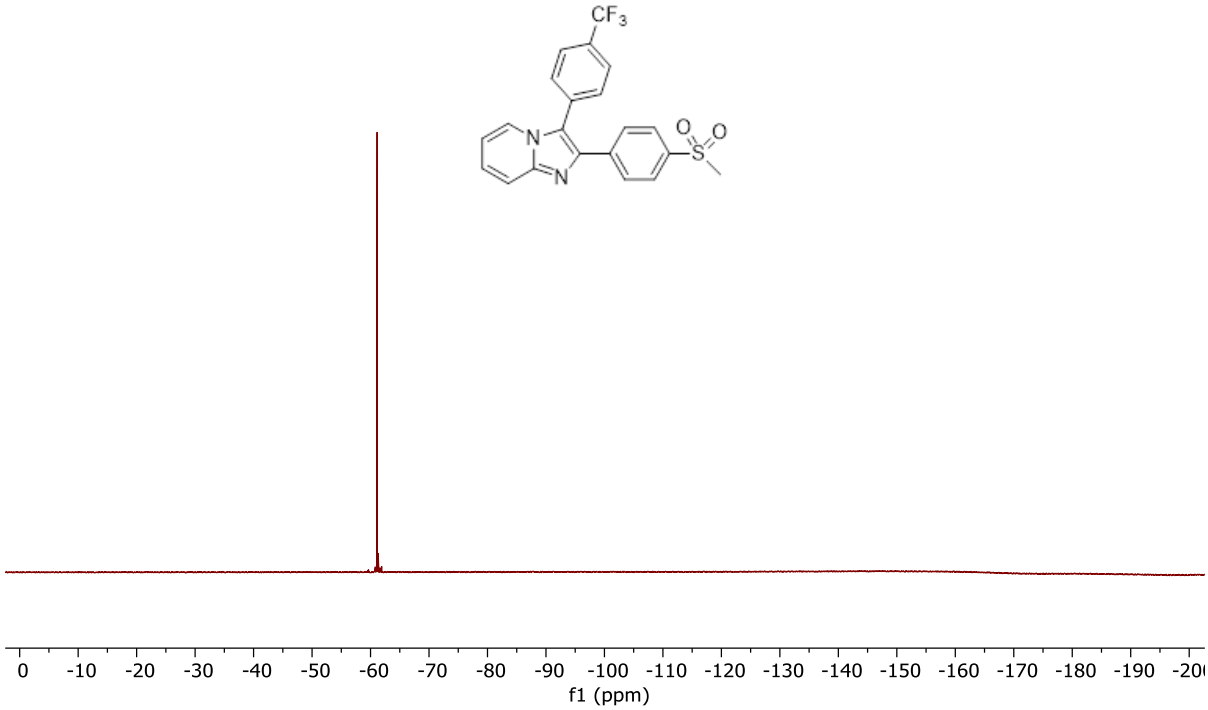
^{13}C NMR Spectrum of (**47**) (400 MHz, DMSO-d^{6}):



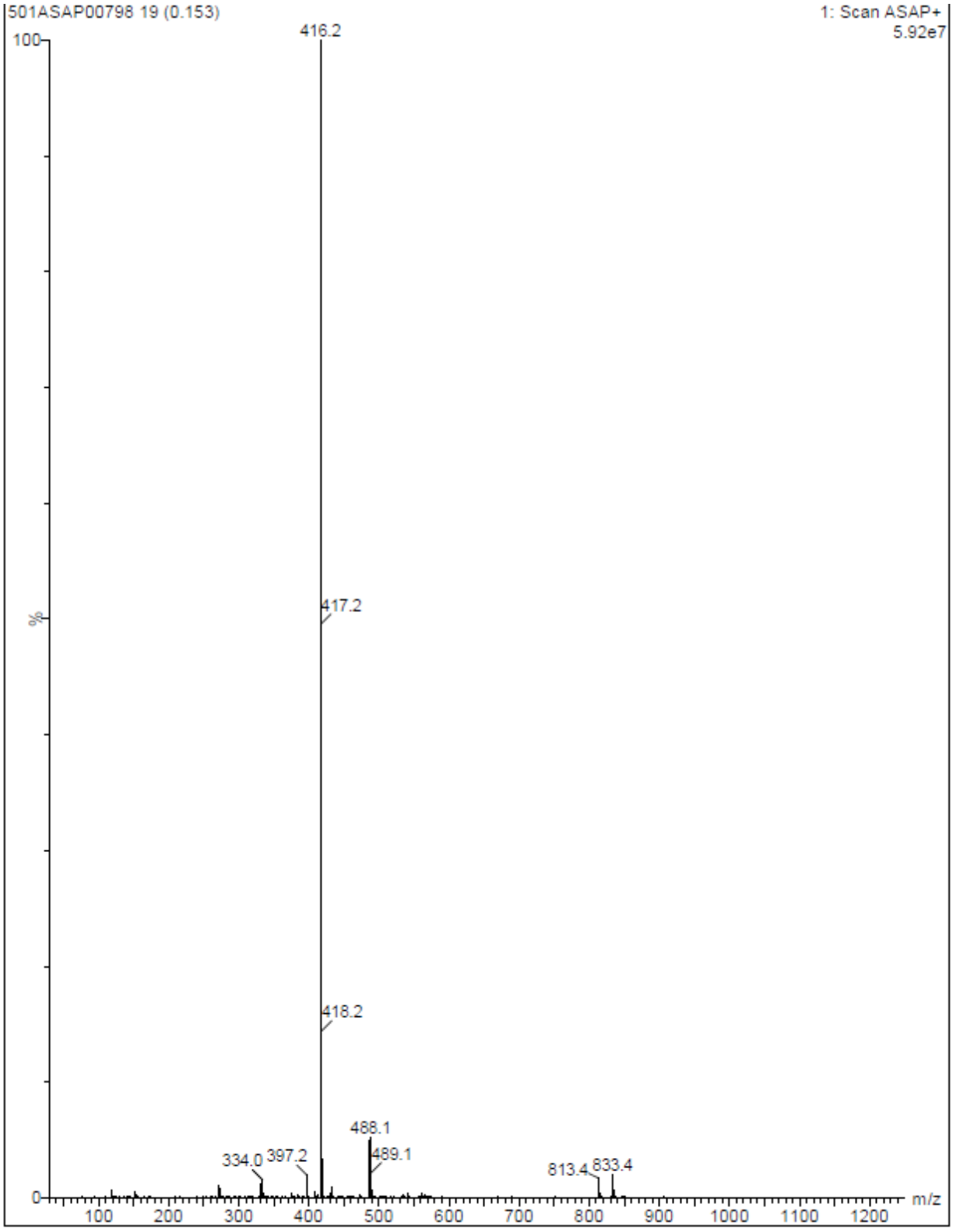
^{1}H/^{1}H COSY NMR Spectrum of (**47**) (400 MHz, DMSO-d^{6}):



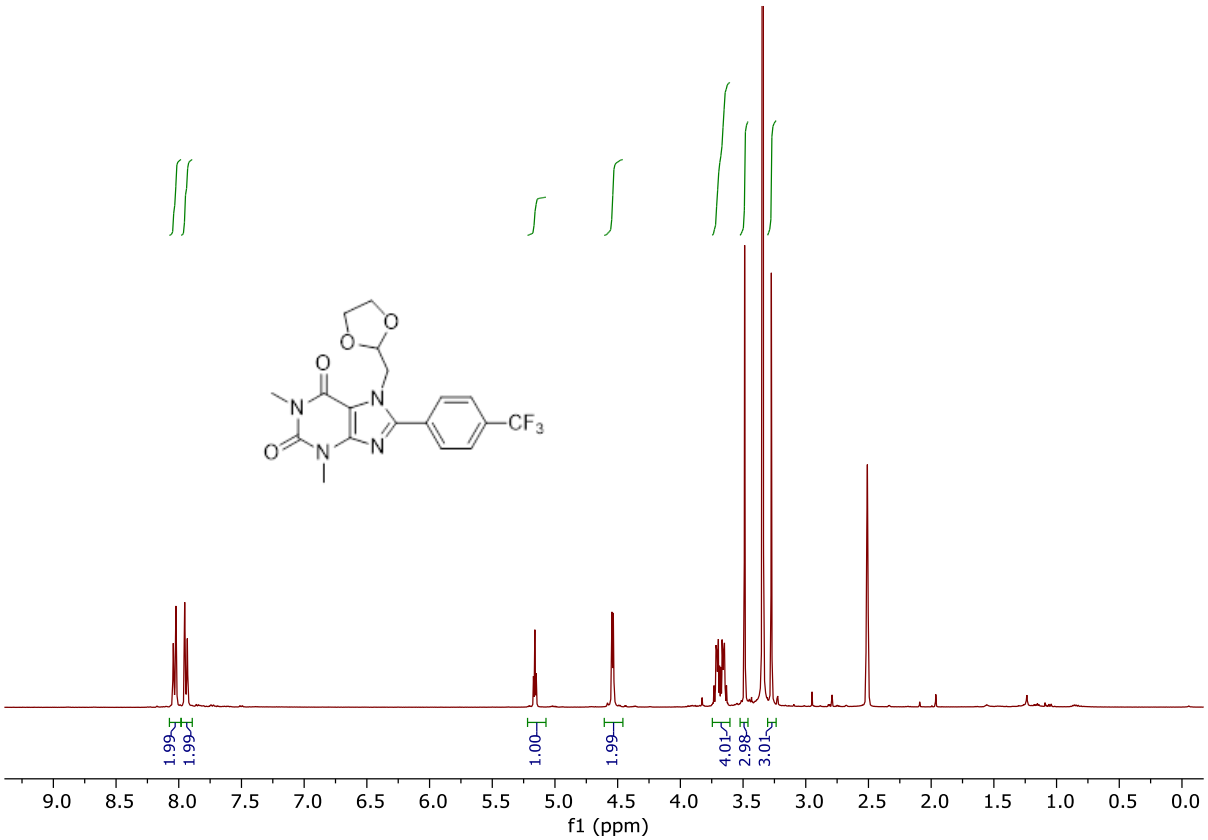
^{19}F NMR Spectrum of (**47**) (400 MHz, DMSO-d^{6}):



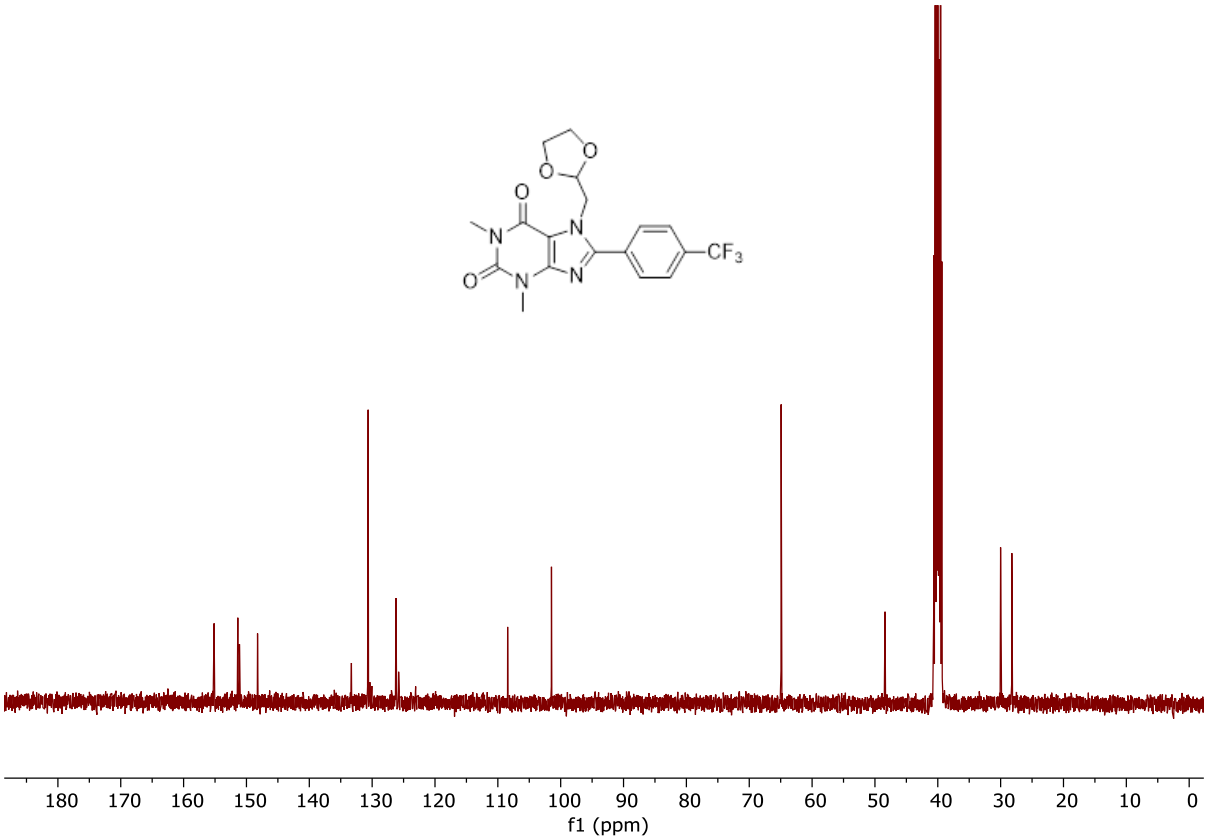
MS Spectrum of (**47**):



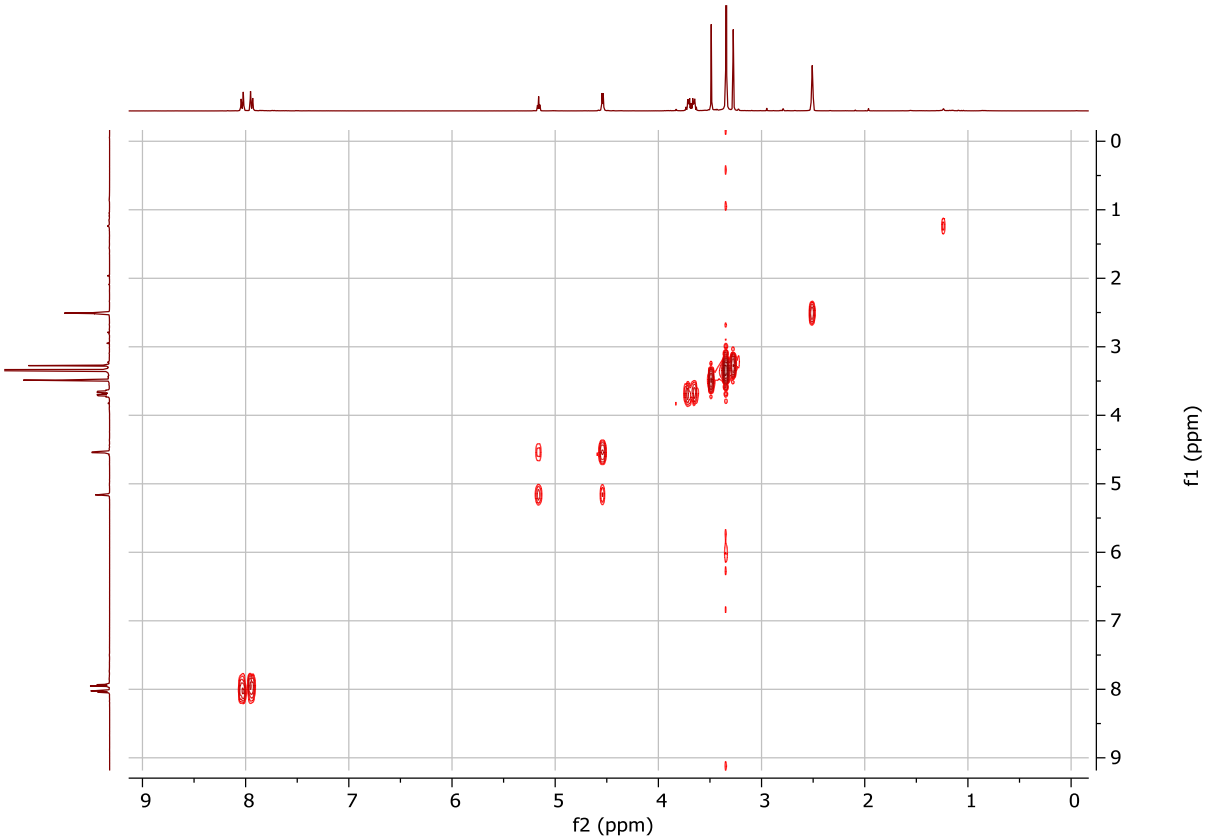
^{1}H NMR Spectrum of (**48**) (400 MHz, DMSO-d^{6}):



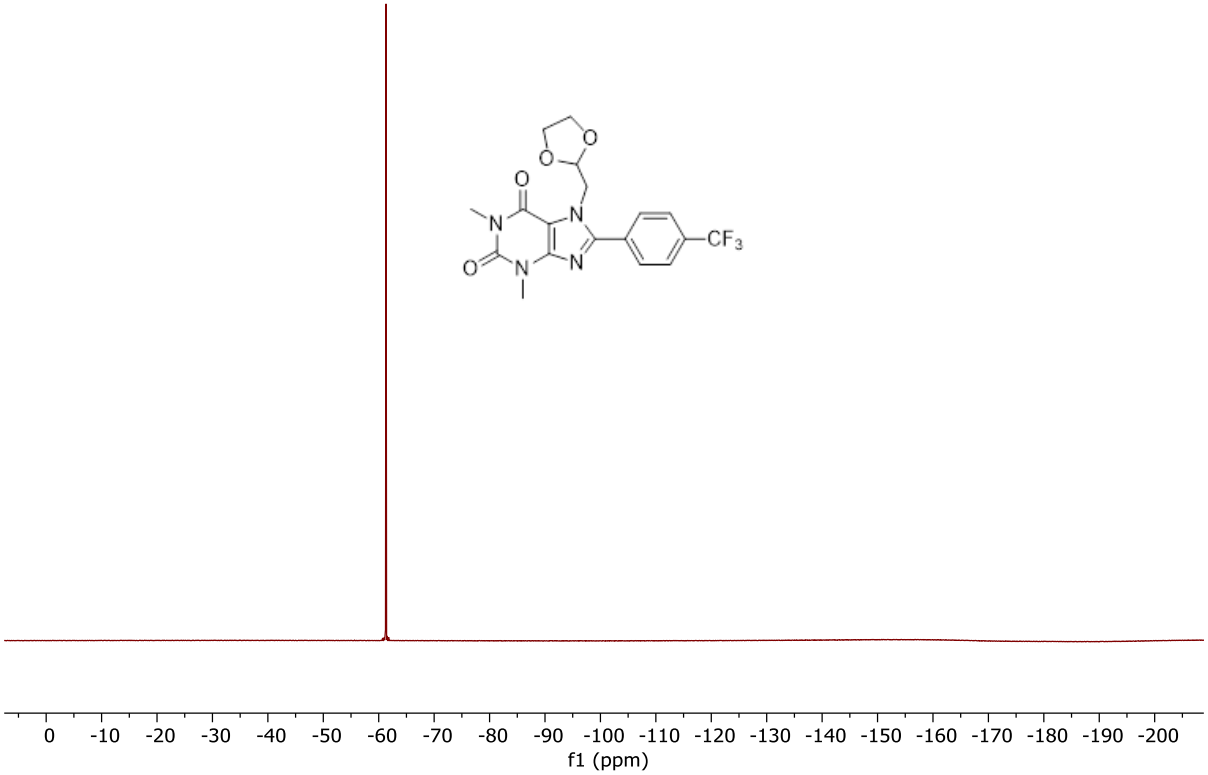
^{13}C NMR Spectrum of (**48**) (400 MHz, DMSO-d^{6}):



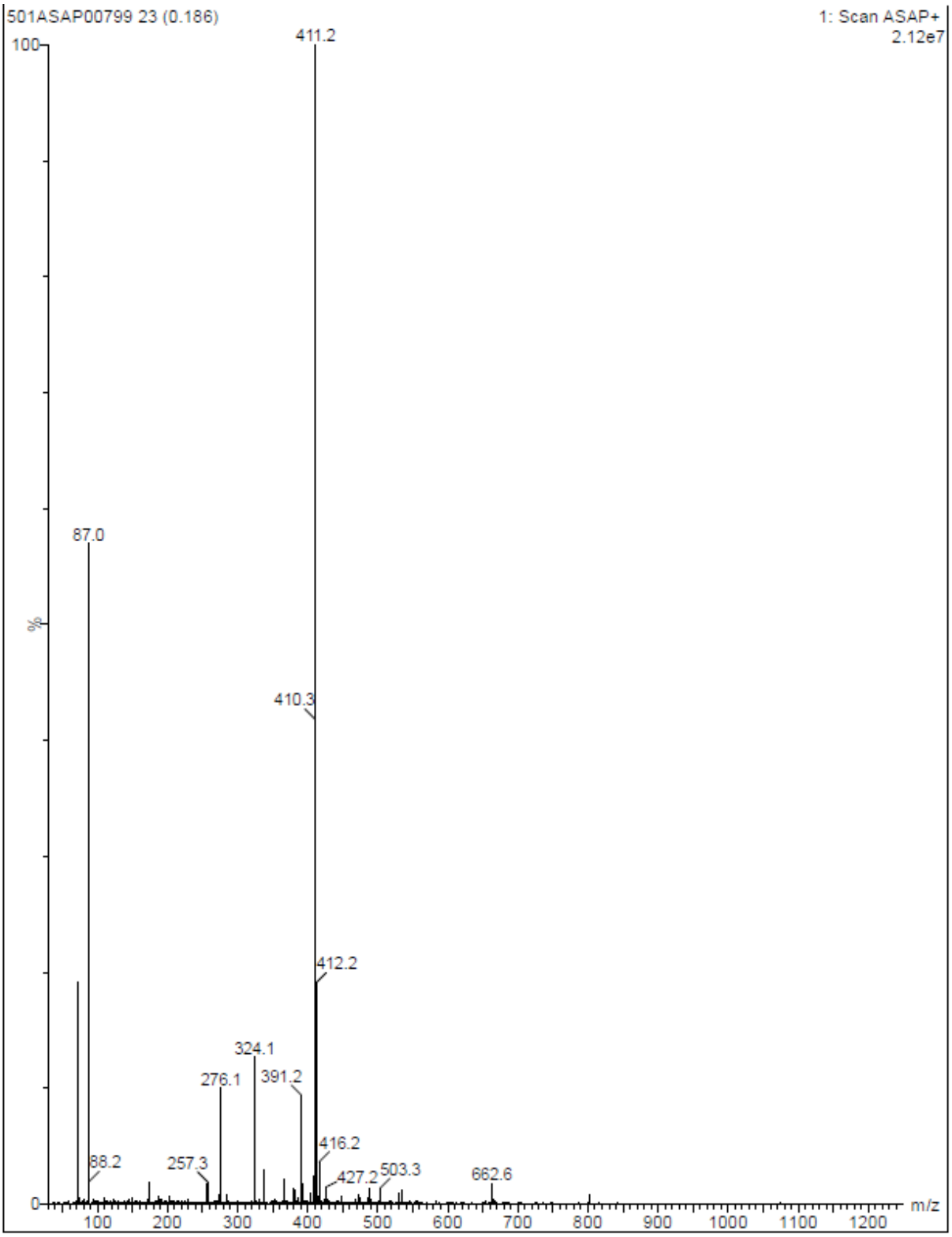
^{1}H/^{1}H COSY NMR Spectrum of (**48**) (400 MHz, DMSO-d^{6}):



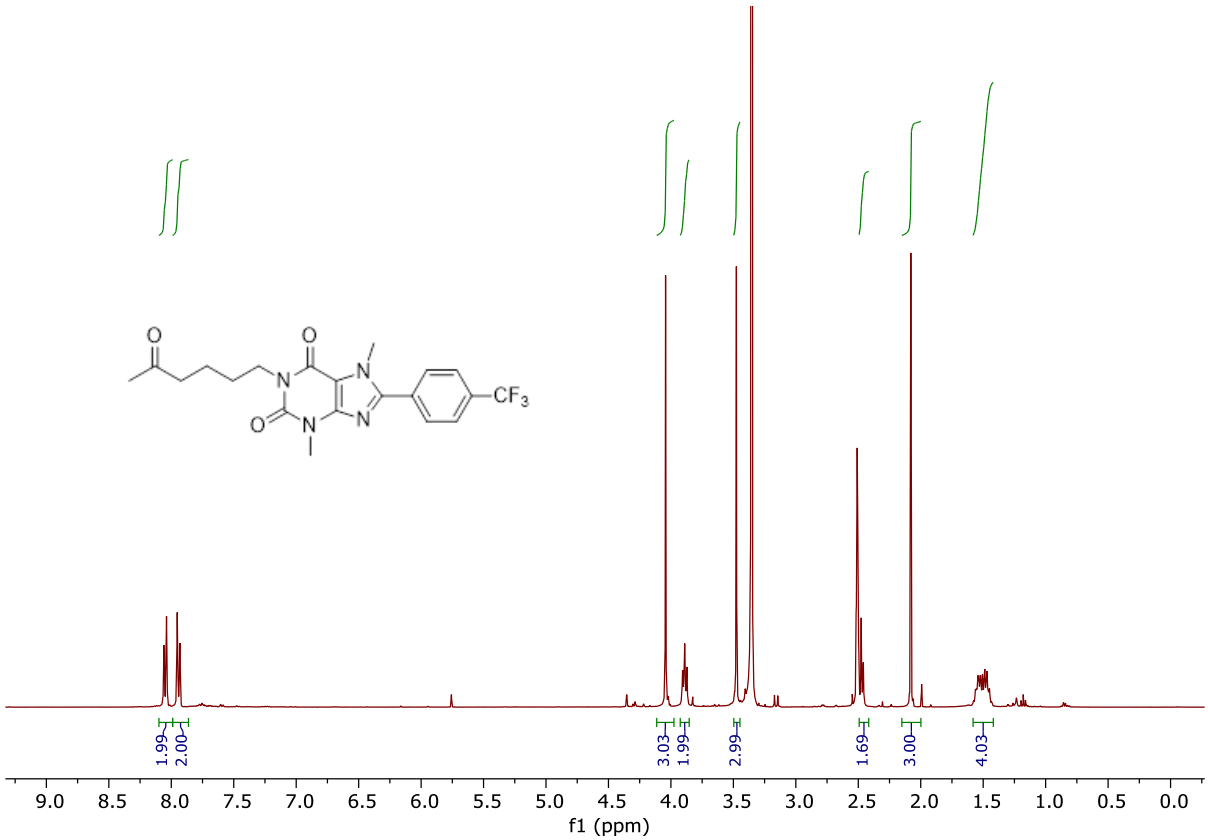
^{19}F NMR Spectrum of (**48**) (400 MHz, DMSO-d^{6}):



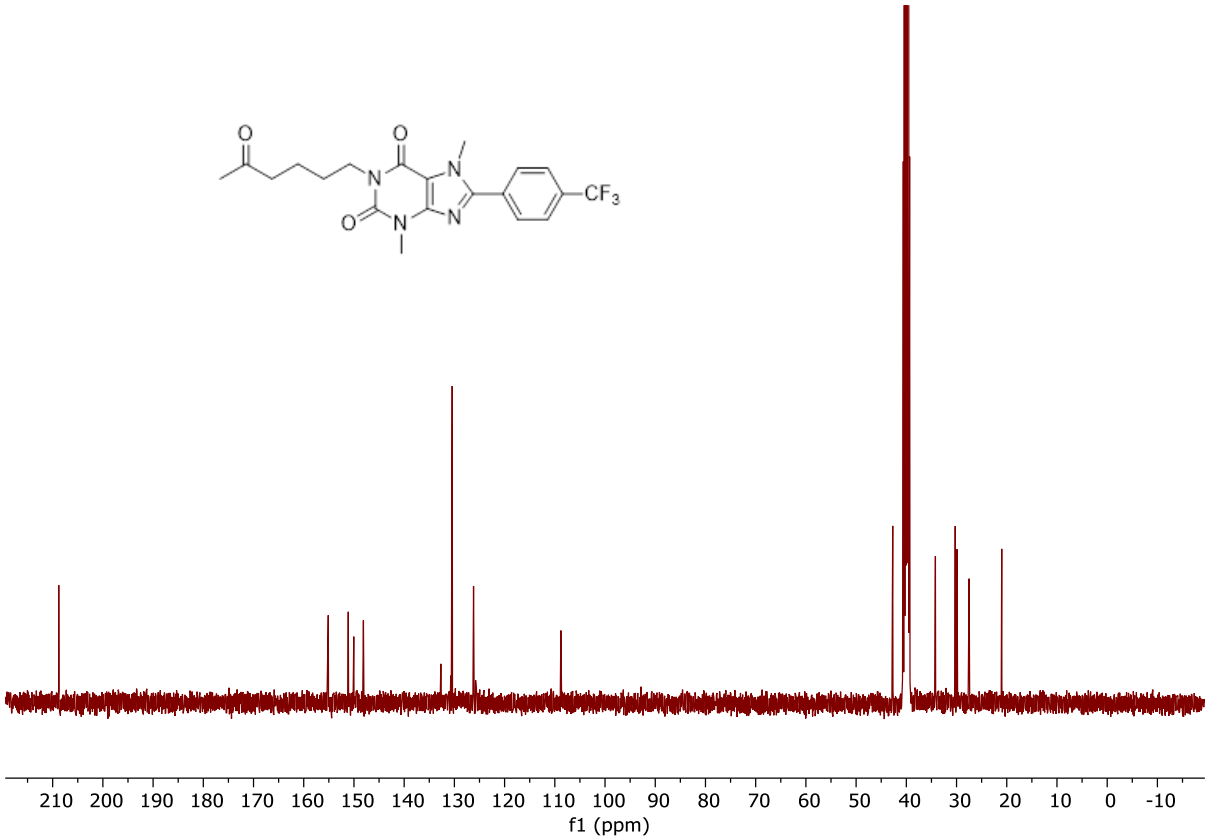
MS Spectrum of (**48**):



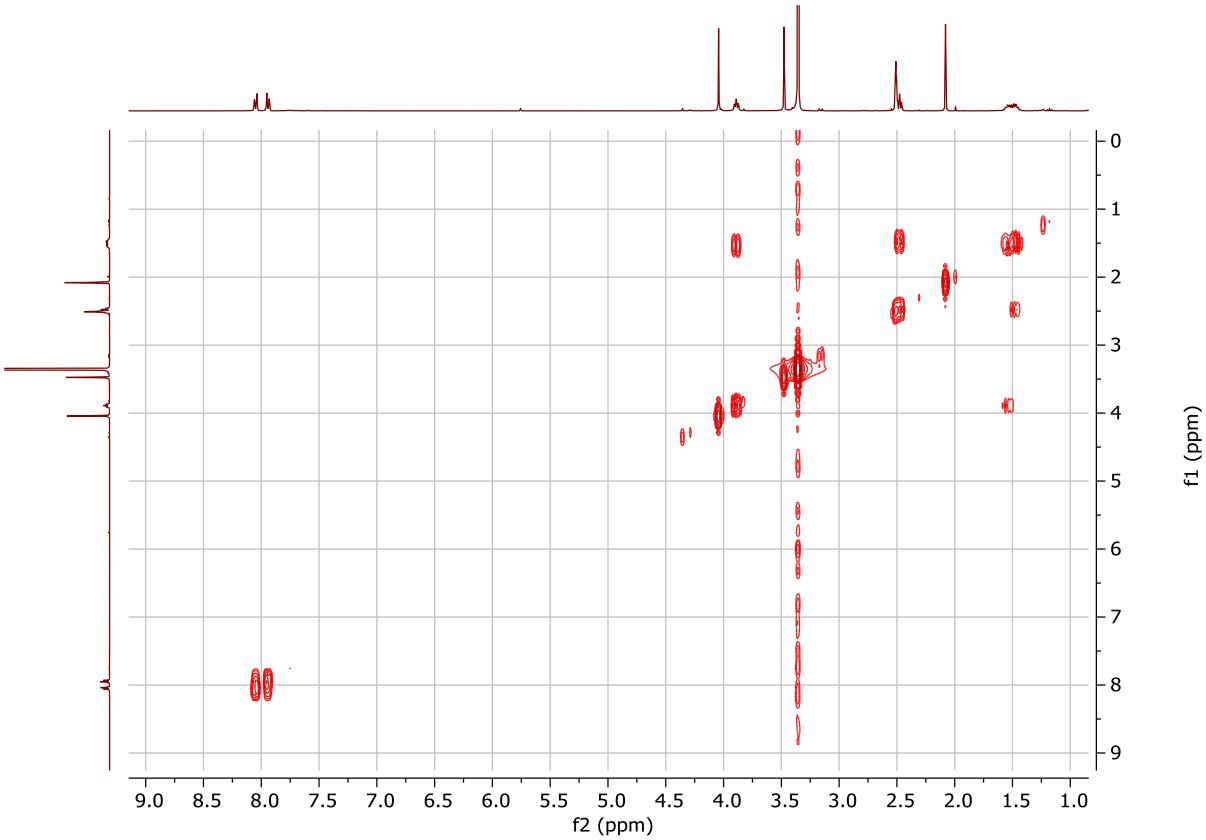
^{1}H NMR Spectrum of (**49**) (400 MHz, DMSO-d^{6}):



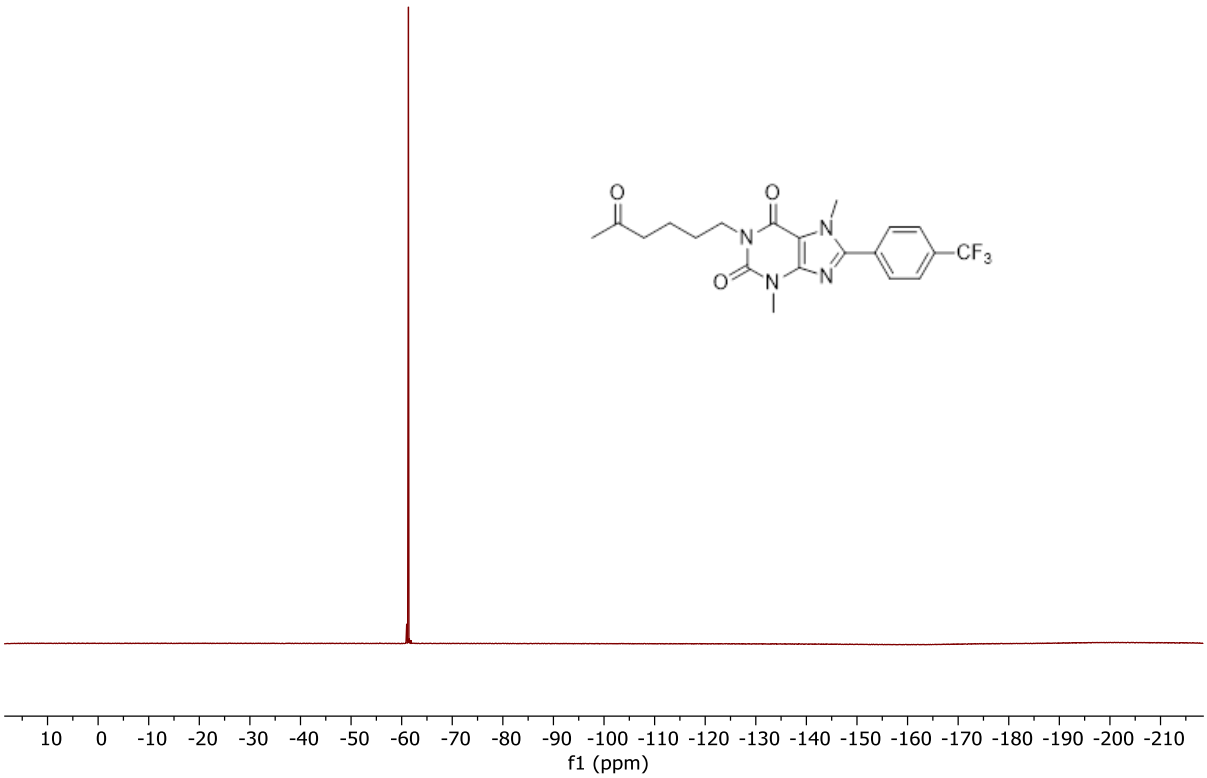
^{13}C NMR Spectrum of (**49**) (400 MHz, DMSO-d^{6}):



^{1}H/^{1}H COSY NMR Spectrum of (**49**) (400 MHz, DMSO-d^{6}):



^{19}F NMR Spectrum of (**49**) (400 MHz, DMSO-d^{6}):



MS Spectrum of (**49**):