Supporting Information

Biomass-derived glucose-mediated nitro-reductive cyclization: Modular synthesis of pyrrole-fused heterocycles

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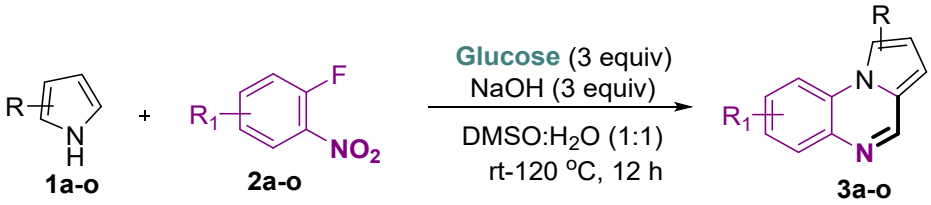
1. GENERAL CONSIDERATION

Unless noted otherwise, all reagents and solvents were purchased from commercial sources and used as received. The glassware to be used in the reaction was thoroughly washed and dried in an oven and the experiments were carried out with the required precautions. Reactions were monitored by TLC, which was performed with 0.2 mm Merck pre-coated silica gel 60 F254 Aluminium sheets. TLC plates were visualized with UV light and column chromatography was performed using silica gel (60-120, 100-200, or 230-400 mesh). New compounds were characterized by melting point, ^{1}H NMR, ^{13}C NMR, IR, and HRMS data. High-Resolution Mass Spectra (HRMS) were obtained using the Electron spin ionization (ESI) technique and as a TOF mass analyzer. All melting points were taken using a melting point apparatus equipped with a calibrated thermometer and are uncorrected. ^{1}H and ^{13}C spectra were recorded on Jeol 500, 600 MHz, and 125, 150 MHz NMR spectrometers in $CDCl_3$ and DMSO-d_6 with residual undeuterated solvent ($CDCl_3$: 7.26/7.00) using Me_3SiCl as an internal standard. Chemical shifts (δ) are given in ppm and *J* values are given in Hz, pattern was designated as s, singlet; bs, broad singlet; d, doublet; dd, doublet of doublet; dt, triplet of doublet; t, triplet; m, multiplet.

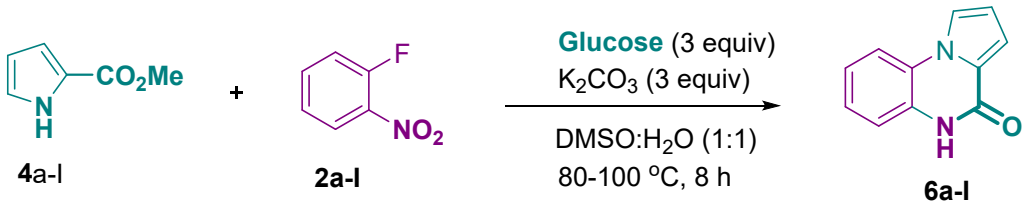
2. EXPERIMENTAL SECTION

Representative procedure for one-pot synthesis of pyrrolo[*1,2-a*] quinoxalines (3a-o)[1]



To a stirred solution of pyrrole/substituted pyrrole (1 mmol) in DMSO (1 mL), NaOH (1.5 mmol) and 1-fluoro-2-nitrobenzene derivatives (1.1 mmol) were added slowly. The reaction mixture was then stirred vigorously for 2 h at room temperature. Then D-glucose (3 mmol), NaOH (1.5 mmol), and H_2O (1 mL) were added to the reaction mixture and heated at 120 °C for 12h. After completion of the reaction, as monitored by TLC, the reaction mixture was diluted with saturated brine solution and extracted with EtOAc (20 mL × 3). The organic layer was combined and dried over anhydrous sodium sulfate (Na_2SO_4). Finally, the solvent was evaporated under reduced pressure and purified by silica gel column chromatography to obtain the desired product **3a-o** in a quantitative yield of about 70-90%.

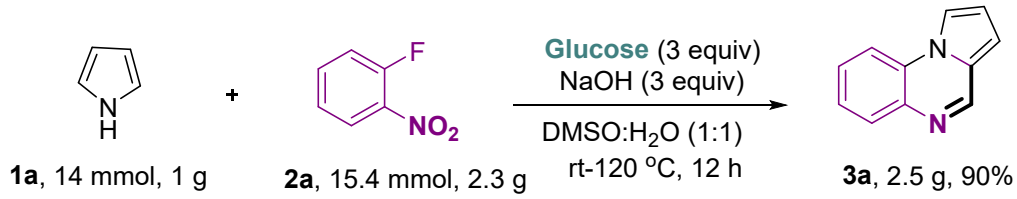
Representative procedure for one-pot synthesis of pyrrolo[*1,2-a*] quinoxaline-4(*5H*)-one (6a-o)[1]



To a stirred solution of methyl pyrrole-2-carboxylate (1 mmol) in DMSO (1 mL), K_2CO_3 (1.5 mmol) and 1-fluoro-2-nitrobenzene derivatives (1.1 mmol) were added slowly sequentially. The reaction mixture was then stirred vigorously for 2 h at 80 °C. Then D-glucose (3 mmol), K_2CO_3/NaOH (1.5 mmol), and H_2O (1 mL) were added to the reaction mixture and kept for heating at 100 °C for 8 h. After completion of the reaction, as monitored by TLC, the reaction mixture was diluted with saturated brine solution and extracted with EtOAc (20 mL × 3). The organic layer was combined and dried over anhydrous sodium sulfate (Na_2SO_4). Finally, the

solvent was evaporated under reduced pressure and purified by silica gel column chromatography to obtain the desired product **6a-i** in a quantitative yield of about 75-90%.

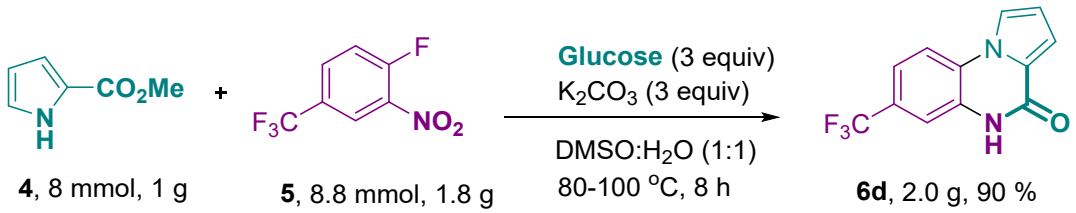
Representative procedure for one-pot gram scale synthesis of pyrrolo[*1,2-a*] quinoxalines (3a)[1]



1a, 14 mmol, 1 g + **2a**, 15.4 mmol, 2.3 g → **3a**, 2.5 g, 90%

To a stirred solution of pyrrole/substituted pyrrole (14 mmol, 1 g) in DMSO (14 mL), NaOH (21 mmol, 0.840 g) and 1-fluoro-2-nitrobenzene derivatives (16 mmol) were added slowly. The reaction mixture was then stirred vigorously for 2 h at room temperature. Then D-glucose (42 mmol, 7.5 g), NaOH (21 mmol, 0.840) and H_2O (10 mL) were added to the reaction mixture and heated at 120 °C for 12h. After completion of the reaction, as monitored by TLC, the reaction mixture was diluted with saturated brine solution and extracted with EtOAc (20 mL × 3). The organic layer was combined and dried over anhydrous sodium sulfate (Na_2SO_4). Finally, the solvent was evaporated under reduced pressure and purified by silica gel column chromatography to obtain the desired product **3a** in a quantitative yield of about 90%.

Representative procedure for one-pot synthesis of 7-(trifluoromethyl)pyrrolo[1,2-a] quinoxaline-4(5H)-one (6d)[1]



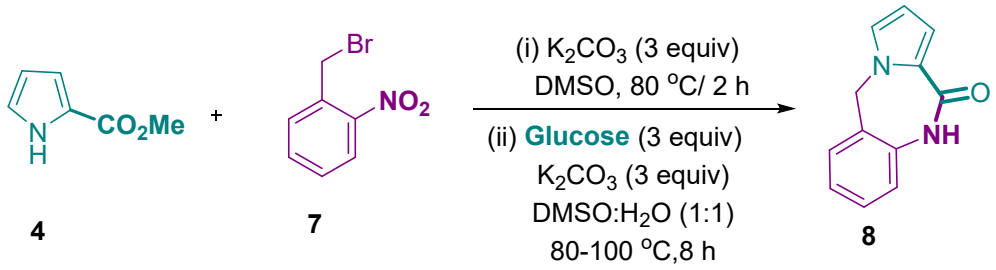
4, 8 mmol, 1 g + **5**, 8.8 mmol, 1.8 g → **6d**, 2.0 g, 90 %

To a stirred solution of methyl pyrrole-2-carboxylate (8 mmol, 1 g) in DMSO (8 mL), K_2CO_3 (12 mmol, 1.5 g) and 1-fluoro-2-nitro-4-(trifluoromethyl)benzene (8.8 mmol, 1.8 g) were added slowly sequentially. The reaction mixture was then stirred vigorously for 2 h at 80 °C. Then D-glucose (24 mmol, 4 g), K_2CO_3 (12 mmol, 1.5 g), and H_2O (8 mL) were added to the reaction mixture and kept for heating at 100 °C for 8 h. After completion of the reaction, as monitored by TLC, the reaction mixture was diluted with saturated brine solution and extracted with EtOAc (20 mL × 3). The organic layer was combined and dried over anhydrous sodium sulfate (Na_2SO_4). Finally, the solvent was evaporated under reduced pressure and purified by

silica gel column chromatography to obtain the desired product **6a-i** in a quantitative yield of about 75-90%.

Representative procedure for one-pot synthesis of bioactive pyrrole fused moieties (8, 10,12)

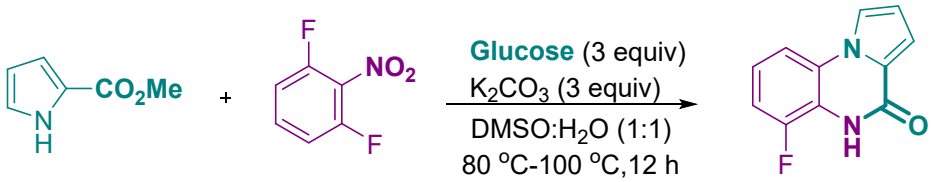
(i) Representative procedure for one-pot synthesis of Pyrrolo[*1,2-a*][1,4]diazepin-11-one (8)[2]



4 **7** **8**

To a stirred solution of pyrrole/substituted pyrrole-2-carboxylate (1 mmol) in DMSO (1 mL), K_2CO_3 (1.5 mmol) and 2- nitrobenzyl bromide (1.1 mmol) was added slowly. The reaction mixture was then stirred vigorously for 2 h at 80 °C. Then D-glucose (3 mmol), K_2CO_3 (1.5 mmol), and H_2O (1 mL) were added to the reaction mixture and kept for heating at 100 °C for 8h. After completion of the reaction, as monitored by TLC, the reaction mixture was diluted with saturated brine solution and extracted with EtOAc (20 mL × 3). The organic layer was combined and dried over anhydrous sodium sulfate (Na_2SO_4). Finally, the solvent was evaporated under reduced pressure and purified by silica gel column chromatography to obtain the desired product **8** in a quantitative yield of about 80%.

(ii) Representative procedure for the synthesis of 6-fluoropyrrolo[*1,2-a*]quinoxaline-4(5*H*)-one (12)[3]

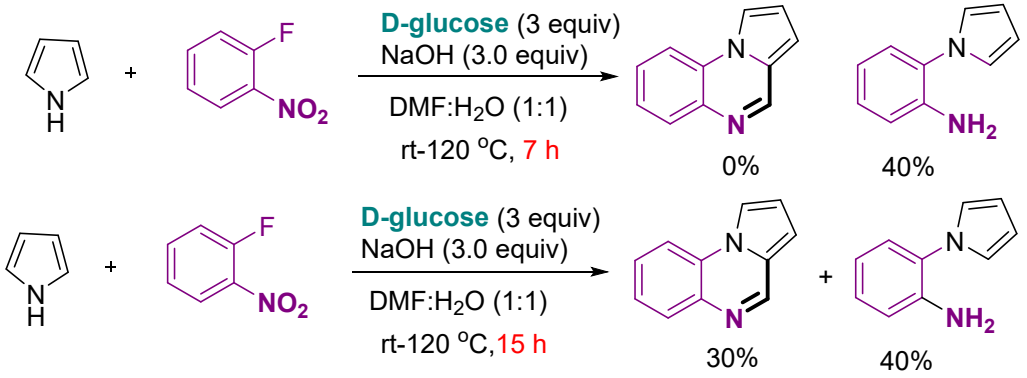


(**10,** 82%)

To a stirred solution of pyrrole (1 mmol) in DMSO (1 mL), K_2CO_3/NaOH (1.5 mmol) and 1,3-difluoro-2-nitrobenzene (1.1 mmol) were added slowly. The reaction mixture was then stirred vigorously for 2 h at 80 °C. Then D-glucose (3 mmol), K_2CO_3/NaOH (1.5 mmol), and H_2O (1 mL) were added to the reaction mixture and heated at 100 °C for 10h. After completion of the

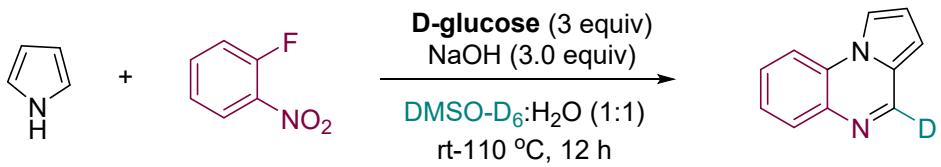
reaction, as monitored by TLC, the reaction mixture was diluted with saturated brine solution and extracted with EtOAc (20 mL × 3). The organic layer was combined and dried over anhydrous sodium sulfate (Na_2SO_4). Finally, the solvent was evaporated under reduced pressure and purified by silica gel column chromatography to obtain the desired product **10** in a quantitative yield of about 82%.

Representative procedure for the experimental evidence for 2-pyrrolyl aniline (2a)



To a stirred solution of pyrrole (1 mmol) in DMF (1 mL), NaOH (1.5 mmol) and 1-fluoro-2-nitrobenzene derivatives (1.1 mmol) were added slowly. The reaction mixture was then stirred vigorously for 2 h at room temperature. Then D-glucose (3 mmol), NaOH (1.5 mmol) and H_2O (1 mL) were added to the reaction mixture and heated at 120 °C for 7h. The pyrrolyl aniline was seen as a fluorescent spot in the TLC with an R_f different from the pyrroloquinoxaline (also seen as a fluorescent spot). After completion of the reaction, as monitored by TLC, the reaction mixture was diluted with saturated brine solution and extracted with EtOAc (20 mL × 3). The organic layer was combined and dried over anhydrous sodium sulfate (Na_2SO_4). Finally, the solvent was evaporated under reduced pressure and purified by silica gel column chromatography to obtain the desired product in a quantitative yield of about 40%. Furthermore, again the same reaction was set up and kept for 15 h, and the corresponding pyrroloquinoxaline formation could be seen to the extent of 30 %.

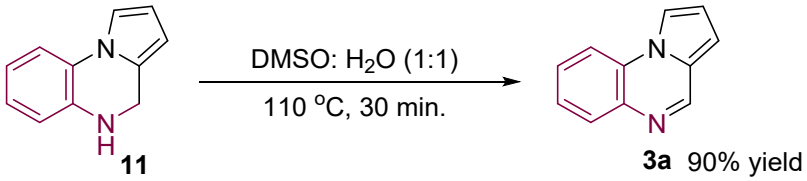
Representative procedure for the experimental evidence for deuterium incorporation



3p, 65%,(**75% D-incorporation)**

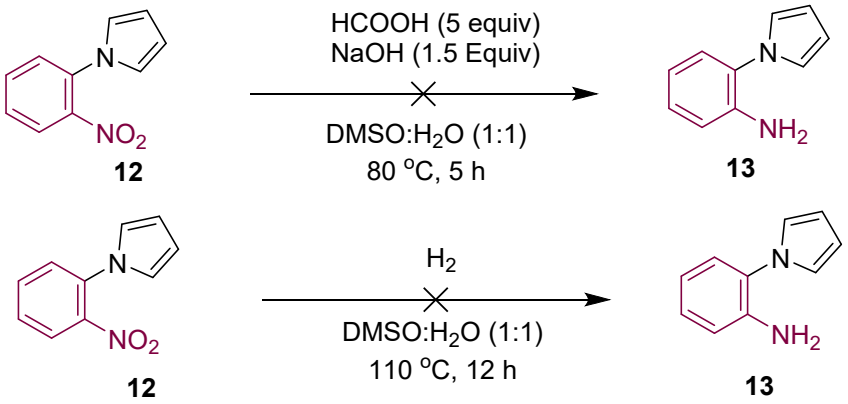
To a stirred solution of pyrrole (1 mmol) in DMSO-D_6 (1 mL), NaOH (1.5 mmol) and 1-fluoro-2-nitrobenzene derivatives (1.1 mmol) were added slowly. The reaction mixture was then stirred vigorously for 2 h at room temperature. Then D-glucose (3 mmol), NaOH (1.5 mmol) and D_2O (1 mL) were added to the reaction mixture and heated at 120 °C for 12h. The deuterated pyrroloquinoxaline was seen as a fluorescent spot in the TLC. After completion of the reaction, as monitored by TLC, the reaction mixture was diluted with saturated brine solution and extracted with EtOAc (20 mL × 3). The organic layer was combined and dried over anhydrous sodium sulfate (Na_2SO_4). Finally, the solvent was evaporated under reduced pressure and purified by silica gel column chromatography to obtain the desired product in a quantitative yield of about 65%.

Representative procedure for the test for the intermediates in the reaction



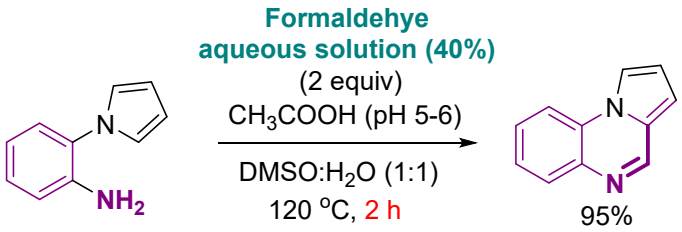
A solution of 4,5-dihydropyrroloquinoxaline (**11**) (1 mmol) in DMSO: H_2O (2 mL). The reaction mixture was then stirred vigorously for 30 min at 110 °C. After half an hour of reaction, it was seen that 4,5-dihydropyrroloquinoxaline (**11**) was oxidised to pyrroloquinoxaline (**3a**). completion of the reaction, as monitored by TLC, the reaction mixture was diluted with saturated brine solution and extracted with EtOAc (20 mL × 3). The organic layer was combined and dried over anhydrous sodium sulfate (Na_2SO_4). Finally, the solvent was evaporated under reduced pressure and purified by silica gel column chromatography to obtain the desired product in a quantitative yield (**3a**) of about 90%.

Representative procedure for the control experiment with formic acid



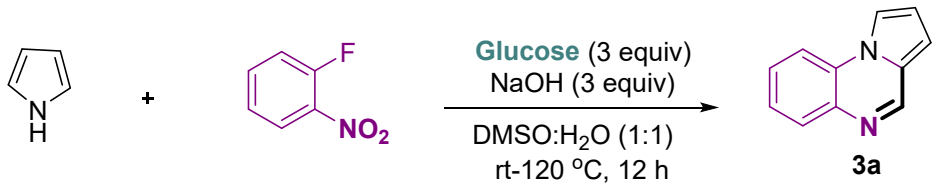
To a stirred solution of 1-(2-nitrophenyl)-1H-pyrrole (**12**) (1 mmol) in DMSO: H_2O (2 mL). was added Formic acid (5 mmol) and NaOH (1.5 mmol). The reaction mixture was then stirred vigorously for 5 h at 80 °C. However, no reduced product formation could be seen. Hence forth, same reaction was kept in the absence of formic acid and NaOH, purging the hydrogen gas (H_2) and heated for 120 °C for 12 h but the 2-pyrrolyl aniline formation could not be seen.

Representative procedure for the experimental setup required to investigate the pH needed for the standard reaction



To a stirred solution of pyrrole aniline (0.5 mmol) in DMSO: H_2O (1:1, 2 mL), NaOH (1.5 mmol) and 1-fluoro-2-nitrobenzene derivatives (1.1 mmol) were added slowly. Further Aq. formaldehyde solution (40%,1 mL) was added and pH of 5 was maintained with CH_3COOH monitored by pH paper.The reaction mixture was then stirred vigorously for 2 h at room temperature. After completion of the reaction, as monitored by TLC, the fluorescent spot of pyrroloquinoxaline was seen. The reaction mixture was diluted with saturated brine solution and extracted with EtOAc (20 mL × 3), the organic layer was combined and dried over anhydrous sodium sulfate (Na_2SO_4). Finally, the solvent was evaporated under reduced pressure and purified by silica gel column chromatography to obtain the desired product in a quantitative yield of about 95%.

Representative procedure for the experimental investigation to check the change of pH during the course of the reaction



To a stirred solution of pyrrole/substituted pyrrole (0.5 mmol) in DMSO (0.5 mL), NaOH (0.75 mmol) and 1-fluoro-2-nitrobenzene derivatives (0.6 mmol) were added slowly. The reaction mixture was then stirred vigorously for 2 h at room temperature. Then D-glucose (1.5 mmol), NaOH (0.75 mmol), and H_2O (0.5 mL) were added to the reaction mixture and heated at 120

°C for 12 h. The aliquots of the sample were withdrawn followed by the dilution of the reaction mixture with ethylacetate (EtOAc) and checked the pH using pH meter. As recorded the pH was found to decrease from 8.0 to 6.8.

Sr.No.	Time Interval	pH measured (from pH meter)
1.	2 h	8.0
2.	4 h	7
3.	6 h	6.8
4.	8 h	6

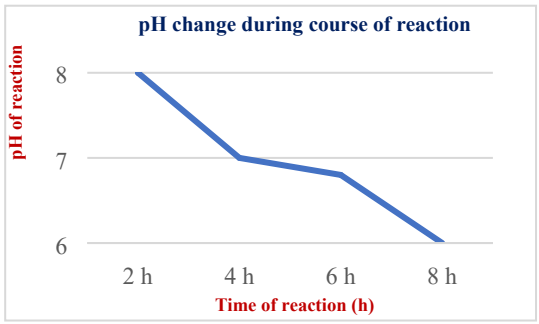
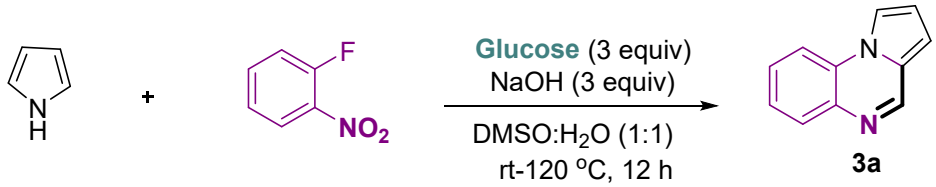


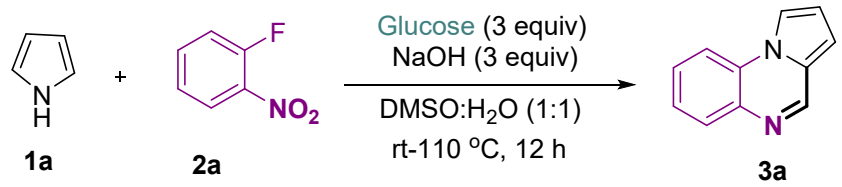
Figure 1. Graphical presentation of change of pH during reaction

Representative procedure for the mass studies to investigate the formation of intermediates for the synthesis of pyrrole fused *N* heterocycles



To a stirred solution of pyrrole/substituted pyrrole (0.5 mmol) in DMSO (0.5 mL), NaOH (0.75 mmol) and 1-fluoro-2-nitrobenzene derivatives (0.6 mmol) were added slowly. The reaction mixture was then stirred vigorously for 2 h at room temperature. Then D-glucose (1.5 mmol), NaOH (0.75 mmol), and H_2O (0.5 mL) were added to the reaction mixture and heated at 120 °C for 12h. The aliquots of the sample were withdrawn and the samples were prepared for a crude mixture using HPLC grade MeOH and mass spectra were recorded.

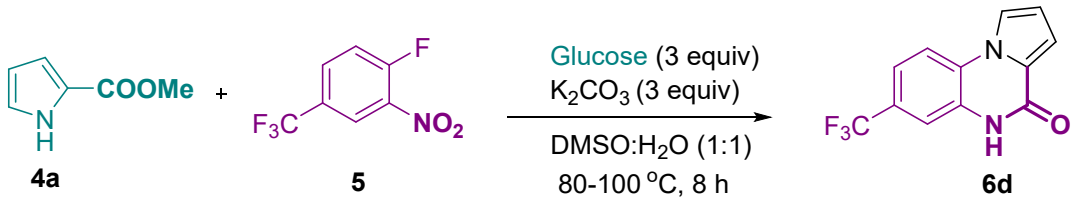
3. GREEN CHEMISTRY METRICS



1a 2a 3a

A) Reaction Stage				
i)	**Substrate**	**Mass (g)**	**Mol. Wt.**	**Mol**
	1a	**1.00**	67	0.014
	2a	**2.31**	141	0.016
ii)	**Reagents**	**Mass (g)**	**Mol. Wt.**	**Mol**
	Glucose	**7.56**	180	0.042
	NaOH	**1.68**	40	0.042
iii)	**Reaction Solvents**	**Vol. (mL)**	**Density (g/mL)**	**Mass (g)**
	DMSO	14	1.1	15.4
	H_2O	14	1.0	14
	Total solvents			**29.4**
	Total Reaction Materials	**41.95 g**		
B) Work-up Stage (Filtration and Recrystallization)				
	Materials	**Vol. (mL)**	**Density (g/mL)**	**Mass (g)**
	H_2O	15	1.0	15
	AcOEt	15	0.902	13.5
	Cyclohexane	10	0.779	7.79
	Total Workup Materials	**36.29 g**		
	Total Input Materials	**78.24 g**		
	Output Target Product	**Mass (g)**	**Mol. Wt.**	
	3a	**2.2**	168.20	

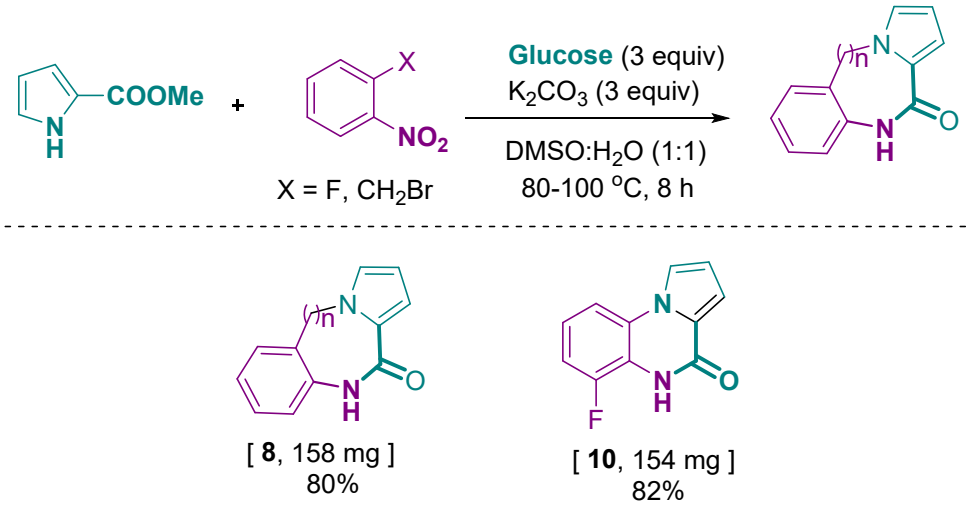
	Green Metrics Analysis			
	Yield (%)	**95**		
	Conversion (%)	**100**		
	AE (%)	**80.7**		
	RME (%)	**66.4**		
	$PMI_{[Reaction]}$	**19.00**		
	$PMI_{[Workup]}$	**16.49**		
	$PMI_{[Total]}$	**35.49**		



C) Reaction Stage				
i)	**Substrate**	**Mass (g)**	**Mol. Wt.**	**Mol**
	4a	**1.00**	125	0.014
	5	**1.83**	209	0.016
ii)	**Reagents**	**Mass (g)**	**Mol. Wt.**	**Mol**
	Glucose	**4.32**	180	0.042
	K_2CO_3	**3.32**	40	0.042
iii)	**Reaction Solvents**	**Vol. (mL)**	**Density (g/mL)**	**Mass (g)**
	DMSO	8	1.1	8.8
	H_2O	8	1.0	8
	Total solvents			**16.8**
	Total Reaction Materials	**27.27 g**		

D) Work-up Stage (Filtration and Recrystallization)				
	Materials	**Vol. (mL)**	**Density (g/mL)**	**Mass (g)**
	H_2O	15	1.0	15
	AcOEt	15	0.902	13.5
	Cyclohexane	10	0.779	7.79
	Total Workup Materials	**36.29 g**		
	Total Input Materials	**63.56 g**		
	Output Target Product	**Mass (g)**	**Mol. Wt.**	
	6d	**2.0**	184	
	Green Metrics Analysis			
	Yield (%)	**90**		
	Conversion (%)	**100**		
	AE (%)	**75.44**		
	RME (%)	**70.7**		
	$PMI_{[Reaction]}$	**13.6**		
	$PMI_{[Workup]}$	**18.1**		
	$PMI_{[Total]}$	**31.7**		

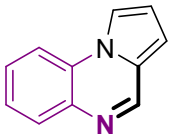
The PMI, AE, E-Factors, and reaction mass efficiency (RME) were also calculated for other KSMs prepared using the developed protocol, as shown below.



Compounds	AE (%)	$PMI_{[Reaction]}$	$PMI_{[Workup]}$	$PMI_{[Total]}$	E-Factor
8	58	10.0	29.0	39.0	9
10	67	9.8	21.8	39.6	8.8

4. CHARACTERIZATION DATA

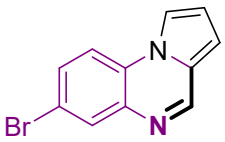
Pyrrolo[1,2-a]quinoxaline (3a)[3]



3a

Yellow solid (151 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.89 (s, 1H), 7.82 (d, J = 7.4 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.45 – 7.41 (m, 1H), 6.88 (dd, J = 11.9, 2.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 135.8, 130.1, 128.0, 127.9, 126.5, 125.2, 114.2, 114.3, 107.4.

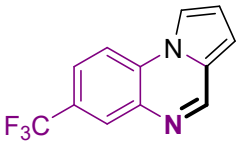
7-Bromo Pyrrolo[1,2-a]quinoxaline (3b)[5]



3b

Yellow solid (215 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.10 (d, J = 2.2 Hz, 1H), 7.93 – 7.86 (m, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.60 (dd, J = 8.7, 2.2 Hz, 1H), 6.92 (dd, J = 3.9, 1.1 Hz, 1H), 6.89 (dd, J = 3.9, 2.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2, 137.5, 133.0, 131.0, 127.5, 126.8, 118.2, 115.7, 114.9, 108.5, 77.7, 77.5, 77.2.

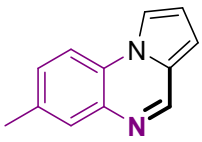
7-(Trifluoromethyl)-Pyrrolo[1,2-a]quinoxaline (3c)[3]



3c

Yellow solid (212 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.23 (s, 1H), 7.99 – 7.92 (m, 2H), 7.74 (dd, J = 8.6, 1.7 Hz, 1H), 6.97 (dd, J = 3.9, 1.1 Hz, 1H), 6.94 (dd, J = 3.9, 2.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$ δ 147.1, 135.6, 130.2, 127.7, 126.6, 124.2 115.0 (d, 2JC−F = 14.4 Hz), 114.6, 108.5.

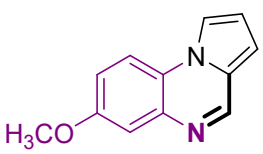
7-Methyl Pyrrolo[1,2-a]quinoxaline (3d)[3]



3d

Yellow solid (163 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.86 (s, 1H), 7.75 (d, J = 7.6 Hz, 2H), 7.31 (d, J = 8.5 Hz, 1H), 6.86 (dd, J = 3.9, 1.2 Hz, 1H), 6.84 (dd, J = 3.9, 2.6 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 135.8, 135.0, 129.9, 128.9, 126.4, 125.9, 114.0, 113.8, 113.5, 107.1, 21.1.

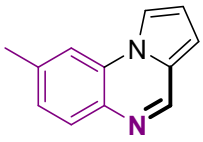
7-Methoxy Pyrrolo[1,2-a]quinoxaline (3e)[3]



3e

Orange solid (174 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.86 (d, J = 8.9 Hz, 1H), 7.80 (s, 1H), 7.23 (d, J = 1.4 Hz, 1H), 7.02 (ddd, J = 8.9, 2.7, 0.6 Hz, 1H), 6.87 – 6.84 (m, 2H), 3.94 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 143.3, 131.3, 130.2, 128.8, 126.4, 114.1, 113.7, 112.8, 106.7, 97.6, 55.8.

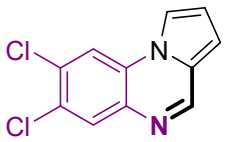
8-Methyl Pyrrolo[1,2-a]quinoxaline (3f)[3]



3f

Yellow solid (163 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.85 (s, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.62 (s, 1H), 7.23 (d, J = 8.2 Hz, 1H), 6.87 – 6.79 (m, 2H), 2.52 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.8, 138.3, 133.8, 129.8, 127.8, 126.6, 126.5, 126.4, 113.8, 106.9, 21.8.

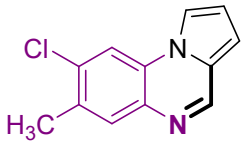
7,8-Dichloro Pyrrolo[1,2-a]quinoxaline (3g)[3]



3g

Light brown solid (46 mg, 80%); ^{1}H NMR (600 MHz, DMSO) δ 8.89 (s, 1H), 8.71 (s, 1H), 8.61 – 8.52 (m, 1H), 8.07 (s, 1H), 7.04 (dd, J = 4.0, 1.0 Hz, 1H), 6.96 (dd, J = 3.9, 2.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.9, 135.3, 131.5, 131.1, 131.0, 128.9, 127.2, 126.3, 115.5, 115.0, 108.6.

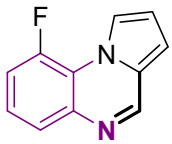
8-Chloro-7-methyl Pyrrolo[1,2-a]quinoxaline (3h)[3]



3h

Brown solid (192 mg, 89%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.80 (s, 1H), 7.79 (d, J = 1.1 Hz, 1H), 7.76 (s, 1H), 6.85 (dt, J = 3.8, 3.4 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 134.5, 133.6, 133.2, 131.5, 126.7, 126.2, 114.3, 114.2, 107.7, 19.9. HRMS (ESI) *m/z* calcd for $C_{12}H_9ClN_2$ $[M+H]^+$ 217.0532 found 217.0543.

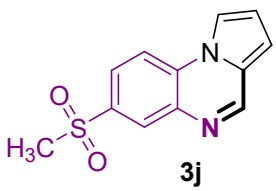
9-Fluoro-Pyrrolo[1,2-a]quinoxaline (3i)[7]



3i

Yellow solid (164 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.94 – 7.90 (m, 1H), 7.64 (d, J = 8.3 Hz, 1H), 7.46 (td, J = 8.3, 5.5 Hz, 1H), 7.22 – 7.13 (m, 1H), 6.96 (dd, J = 4.0, 1.0 Hz, 1H), 6.91 (dd, J = 3.9, 2.8 Hz, 1H). NMR (151 MHz, $CDCl_3$) δ 145.83 (s), 127.79 (s), 125.10 (s), 114.7 (d, 2JC−F = 25.8 Hz), 111.2 (d, 2JC−F = 20.1 Hz), 109.5, 108.3. ^{19}F NMR:(565 MHz, $CDCl_3$) δ -121.60.

7-(Methyl sulfonyl) Pyrrolo[1,2-a]quinoxaline (3j)

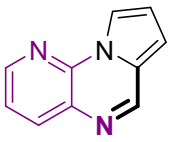


3j

Orange solid (172 mg, 70%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.56 (d, J = 2.4 Hz, 1H), 8.51 (d, J = 8.7 Hz, 1H), 8.31 (d, J = 2.0 Hz, 1H), 8.05 (dd, J = 8.6, 2.1 Hz, 1H), 7.08 (dd, J = 3.9, 0.8 Hz, 1H), 7.00 (dd, J = 3.8, 2.8 Hz, 1H), 3.30 (s, 1H). ^{13}C NMR (151 MHz,

$CDCl_3$) δ 148.0, 137.6, 135.4, 131.3, 128.9, 126.4, 126.2, 117.7, 116.7, 115.7, 109.4, 44.1. HRMS (ESI) *m/z* calcd for $C_{11}H_9N_2O_2S$ $[M+H]^+$ 234.0463 found 234.0459.

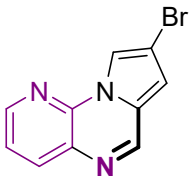
Pyrido[3,2-e]Pyrrolo[1,2-a]Pyrazine (3k)[3]



3k

Yellow solid (149 mg, 88%); ^1H NMR (600 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.52 (dd, J = 4.6, 1.4 Hz, 1H), 8.37 – 8.36 (m, 1H), 8.22 (dd, J = 8.0, 1.6 Hz, 1H), 7.42 (dd, J = 8.0, 4.7 Hz, 1H), 6.96 (dd, J = 3.9, 1.2 Hz, 1H), 6.90 (dd, J = 3.8, 2.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.0, 146.6, 140.0, 137.5, 130.8, 128.0, 121.5, 115.6, 114.6, 108.9.

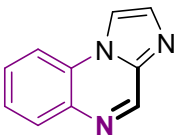
8-BromoPyrido[3,2-e]Pyrrolo[1,2-a]Pyrazine (3l)



3l

Yellow solid (179 mg, 85%); ^1H NMR (600 MHz, $CDCl_3$) NMR (600 MHz,) δ 8.66 (dd, J = 8.4, 1.3 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.64 – 7.57 (m, 1H), 7.54 – 7.46 (m, 1H), 6.81 (dd, J = 3.9, 2.8 Hz, 1H), 6.73 (dd, J = 3.9, 1.2 Hz, 1H), 2.75 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) NMR (151 MHz,) δ 138.6, 131.0, 129.6, 128.2, 126.1, 125.6, 121.6, 114.9, 114.0, 106.8, 77.3, 77.1, 76.9, 14.2. HRMS (ESI) *m/z* calcd for $C_{13}H_{10}N_2O$ $[M+1]^+$ 247.9823 found 247.9820, $[M+2]^+$ 249.9803 found 249.9802.

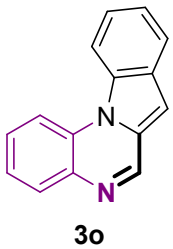
Immidazo[1,2-a]quinoxaline (3n)[3]



3n

White solid (139 mg, 82%); ^1H NMR (600 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.12 (dd, J = 7.1, 0.9 Hz, 2H), 7.90 (dd, J = 8.2, 1.1 Hz, 1H), 7.80 (d, J = 1.1 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.59 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.3, 138.9, 135.9, 134.5, 130.8, 129.1, 127.4, 126.6, 114.9, 112.3.

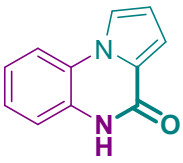
Indolo[1,2-a]quinoxaline (3o)[3]



3o

White solid (153 mg, 70%); ^1H NMR (600 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.44 (ddd, J = 15.9, 8.5, 0.9 Hz, 2H), 8.01 – 7.94 (m, 2H), 7.61 (ddd, J = 8.6, 7.3, 1.6 Hz, 1H), 7.55 (ddd, J = 8.6, 7.0, 1.3 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.15 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 135.8, 130.3, 129.0, 128.6, 124.2, 124.0, 122.7, 122.5, 114.7, 114.8, 100.7.

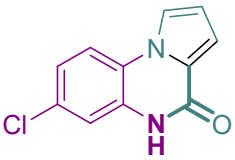
Pyrrolo[1,2-a]quinoxaline-4(5H)-one (6a)[6]



6a

White solid (36 mg, 90%); ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 11.20 (s, 1H), 8.14 (s, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.18 – 7.14 (m, 1H), 6.99 (dd, J = 3.8, 1.4 Hz, 1H), 6.65 – 6.64 (m, 1H). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 155.4, 128.9, 126.0, 123.7, 123.0, 123.0, 118.4, 116.9, 115.4, 113.1, 111.8.

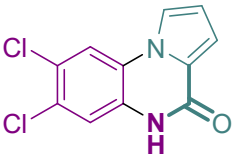
7-Chloro-Pyrrolo[1,2-a]quinoxaline-4(5H)-one (6b)[6]



6b

White solid (187 mg, 86%); ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 11.29 (s, 1H), 8.15 (dd, J = 2.8, 1.5 Hz, 1H), 8.04 (d, J = 8.7 Hz, 1H), 7.26 (d, J = 2.3 Hz, 1H), 7.22 (dd, J = 8.7, 2.3 Hz, 1H), 7.01 (dd, J = 3.8, 1.4 Hz, 1H), 6.66 (dd, J = 3.8, 2.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 155.2, 130.3, 129.7, 123.3, 122.5, 122.1, 118.9, 117.1, 116.1, 113.4, 112.2.

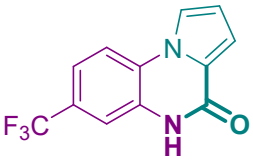
7,8-Dichloro-Pyrrolo[1,2-a]quinoxaline-4(5H)-one (6c)[7]



6c

White solid (223 mg, 89%); ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 11.34 (s, 1H), 8.39 (s, 1H), 8.21 (dd, J = 2.8, 1.4 Hz, 1H), 7.02 (dd, J = 3.8, 1.4 Hz, 1H), 6.67 (dd, J = 3.8, 2.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 155.0, 129.1, 127.6, 124.6, 123.4, 123.0, 119.5, 117.6, 117.3, 113.8, 112.7.

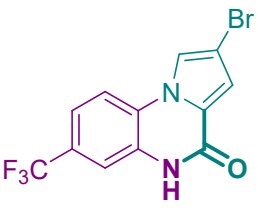
7-(Trifluoromethyl)Pyrrolo[1,2-a]quinoxaline-4(5H)-one (6d)[6]



6d

White solid (226 mg, 90%); ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 11.42 (s, 1H), 8.24 (dd, J = 18.2, 4.3 Hz, 2H), 7.56 (d, J = 4.6 Hz, 1H), 7.51 (dd, J = 14.0, 8.5 Hz, 1H), 7.07 (d, J = 3.8 Hz, 1H), 6.72 (dd, J = 6.9, 3.9 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 150.6, 132.4, 130.5, 129.9, 128.9, 127.6 126.6, 120.8, 120.0. ^{19}F NMR (565 MHz, DMSO) δ -56.84.

2-Bromo-7(Trifluoromethyl)Pyrrolo[1,2-a]quinoxaline-4(5H)-one (6f)

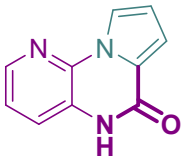


6f

White solid (273 mg, 83%); ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 11.59 (d, J = 15.7 Hz, 1H), 8.45 (t, J = 16.8 Hz, 2H), 8.32 – 8.15 (m, 1H), 7.69 – 7.38 (m, 1H), 7.21 – 7.00 (m, 1H). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 154.5, 129.7, 127.1, 126.9, 125.6, 125.3, 124.9, 123.8, 120.1, 119.5,

117.1, 114.3 (d, 2*J*C−F *J* = 23.6 Hz), 102.6. HRMS (ESI) *m/z* calcd for $C_{12}H_6BrF_3N_2O$ $[M+1]^+$ 330.9694 found 330.9690, $[M+2]^+$ 332.9673 found 332.9670.

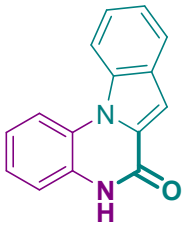
Pyrido[3,2-e]pyrrolo[1,2-a]pyrazin-6(5H)-one (6g)



6g

White solid (162 mg, 88%); ^{1}H NMR (600 MHz, DMSO-d$_6$) 11.14 (s, 1H), 7.95 (dd, J = 4.6, 1.2 Hz, 1H), 7.86 (dd, J = 2.7, 1.6 Hz, 1H), 7.42 (dd, J = 11.3, 10.2 Hz, 1H), 7.12 (dd, J = 8.0, 4.7 Hz, 1H), 6.87 (dd, J = 3.7, 1.5 Hz, 1H), 6.63 – 6.34 (m, 1H). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 155.7, 142.5, 135.8, 125.3, 125.1, 124.8, 122.8, 118.3, 114.3, 113.8, 40.6, 40.5, 40.4. HRMS (ESI) *m/z* calcd for $C_{10}H_7N_3O$ $[M+Na]^+$ 208.0847 found 208.0843.

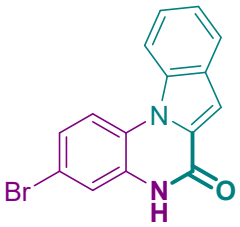
Indolo[1,2-a]quinoxaline-4(5H)-one (6i)[8]



6i

White solid (205 mg, 88%); ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 11.55 (s, 1H), 8.46 (d, *J* = 8.6 Hz, 1H), 8.42 (dd, *J* = 6.8, 2.6 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.41 (s, 1H), 7.31 (dt, *J* = 5.9, 5.4 Hz, 2H), 7.22 (qt, *J* = 8.0, 3.9 Hz, 2H). NMR (151 MHz, DMSO-d$_6$) δ 156.0, 134.0, 128.8, 128.6, 128.4, 125.6, 125.1, 124.6, 123.4, 123.1, 122.5, 117.0, 115.7, 114.8, 105.6, 40.1, 40.0, 39.8, 39.7, 39.5, 39.4, 39.3.

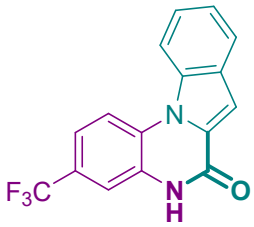
3-Bromo-indolo[1,2-a]quinoxaline-4(5H)-one (6j)[8]



6j

White solid (250 mg, 80%); ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 11.83 (s, 1H), 8.44 (d, *J* = 8.6 Hz, 1H), 8.39 (d, *J* = 8.8 Hz, 1H), 7.91 (dd, *J* = 10.4, 4.4 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.48 (s, 1H), 7.46 (d, *J* = 2.3 Hz, 1H), 7.40 – 7.34 (m, 1H). NMR (151 MHz, DMSO-d$_6$) δ 157.4, 135.5, 131.6, 130.1, 129.9, 127.4, 127.1, 125.9, 124.7, 124.3, 120.4, 119.1, 117.5, 116.2, 107.7, 42.1, 41.6, 41.5, 41.3, 41.2, 41.1, 40.9, 40.8.

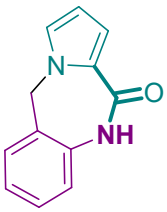
3-(Trifluoromethyl)-indolo[1,2-a]quinoxaline-4(5H)-one (6k)[8]



6k

White solid (239 mg, 79%); ^{1}H NMR (600 MHz, DMSO-d$_6$) ^{1}H NMR (600 MHz,) δ 11.72 (s, 1H), 8.60 (d, *J* = 8.6 Hz, 1H), 8.47 (d, *J* = 8.6 Hz, 1H), 7.91 (t, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 1.8 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.50 (s, 1H), 7.38 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 155.8, 134.2, 129.0, 128.8, 128.6, 127.8, 126.2, 123.3, 123.1, 119.8, 116.4, 114.8, 113.3, 106.9.

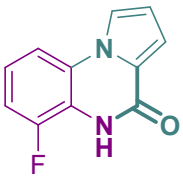
5,10-Dihydro-11H-benzo[e]pyrrolo[1,2-a][1,4]diazepin-11-one (8)[9]



(**8**)

White solid (156 mg, 79%); ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 9.97 (s, 1H), 7.31 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.10 (dt, *J* = 4.3, 2.1 Hz, 1H), 7.05 – 7.02 (m, 1H), 7.01 – 6.99 (m, 1H), 6.66 (dd, *J* = 3.8, 1.8 Hz, 1H), 6.03 (dd, *J* = 3.8, 2.5 Hz, 1H), 5.08 (s, 2H). ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 161.1, 138.8, 129., 129.3, 128.9, 126.9, 125.6, 124.6, 121.5, 116.7, 108.8, 50.4, 40.5, 40.4, 40.2, 40.1, 40.0, 39.8, 39.7.

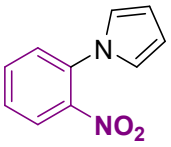
6-Fluoro-Pyrrolo[1,2-a]quinoxaline-4(5H)-one (12)[8]



(**12**)

White solid (166 mg, 82%); ^{1}H NMR (600 MHz, DMSO-d$_6$), δ 11.22 (s, 1H), 8.12 (dd, *J* = 2.7, 1.4 Hz, 1H), 7.81 (dd, *J* = 6.0, 3.2 Hz, 1H), 7.17 – 7.10 (m, 2H), 7.03 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.64 (dd, *J* = 3.7, 2.9 Hz, 1H). NMR (151 MHz, DMSO-d$_6$) δ 155.6, 151.4, 149.8, 125.1 (d, 4*J*C−F = 4.5 Hz), 124.0, 123.2 (d, 3*J*C−F = 8.0 Hz), 119.6, 118.6 (d, 2*J*C−F *J* = 16.3 Hz), 114.0, 113.1, 112.5 (d, 2*J*C−F *J* = 17.8 Hz), 111.8. ^{19}F NMR (565 MHz, DMSO) δ -124.68.

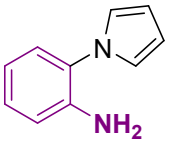
1-(2-nitrophenyl)-1H-pyrrole (2a)[3]



2a

Brown oily liquid (166 mg, 98%); ^{1}H NMR (600 MHz, CDCl$_3$-d$_6$), δ 7.87 – 7.82 (m, 1H), 7.65 (td, J = 7.8, 1.5 Hz, 1H), 7.47 (ddd, J = 7.1, 3.9, 1.2 Hz, 2H), 6.83 – 6.76 (m, 2H), 6.38 – 6.32 (m, 2H). ^{13}C NMR (151 MHz, CDCl$_3$-d$_6$) δ 134.2, 134.2, 133.3, 127.9, 127.7, 125.0, 121.4, 111.1, 77.3, 77.1, 76.9.

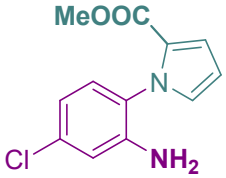
2-(1H-pyrrol-1-yl)aniline (2a')[3]



2a'

White solid (150 mg, 95%); ^{1}H NMR (600 MHz, CDCl$_3$-d$_6$), δ 7.21 – 7.10 (m, 1H), 6.85 (dd, *J* = 4.9, 2.8 Hz, 1H), 6.83 – 6.74 (m, 1H), 6.36 (t, *J* = 2.1 Hz, 1H), 3.67 (s, 2H).^{13}C NMR (151 MHz, CDCl$_3$-d$_6$) δ NMR (151 MHz,) δ 142.1, 128.6, 127.2, 121.8, 118.5, 116.2, 109.4.

Methyl 1-(2-amino-4-chlorophenyl)-1H-pyrrole-2-carboxylate(6b')[6]

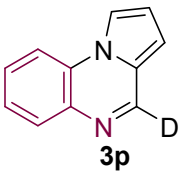


6b'

Yellow solid (150 mg, 92%); ^{1}H NMR (600 MHz,DMSO-d$_6$) δ 7.06 (dd, *J* = 3.8, 1.6 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 2.3 Hz, 1H), 6.60 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.37 (dd, *J* = 3.6, 2.9 Hz, 1H), 4.97 (s, 2H), 3.64 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 160.9, 147.5, 134.3, 131.4,

130.7, 125.8, 124.0, 119.4, 116.4, 115.5, 111.0, 52.2, 41.4, 41.3, 41.1, 41.0, 40.9, 40.7, 40.6, 40.5.

Deuterated Pyrrolo[1,2-a]quinoxaline (3p)



3p

Yellow solid (109 mg, 65%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (s), 7.96 (dd, *J* = 8.0, 1.4 Hz), 7.94 (dd, *J* = 2.5, 1.1 Hz), 7.87 (dd, *J* = 8.2, 1.0 Hz), 7.53 (m), 7.45 (m), 6.91 (dd, *J* = 4.0, 1.1 Hz), 6.89 (dd, *J* = 3.9, 2.7 Hz). ^{1}H NMR (151 MHz, $CDCl_3$) δ 145.9, 135.9, 130.2, 127.9, 125.3, 114.3, 114.1, 113.9, 107.4, 107.4. HRMS (ESI) *m/z* calcd for $C_{11}H_7N_2O$ $[M+H]^+$ 170.0829 found 170.0818.

5. References

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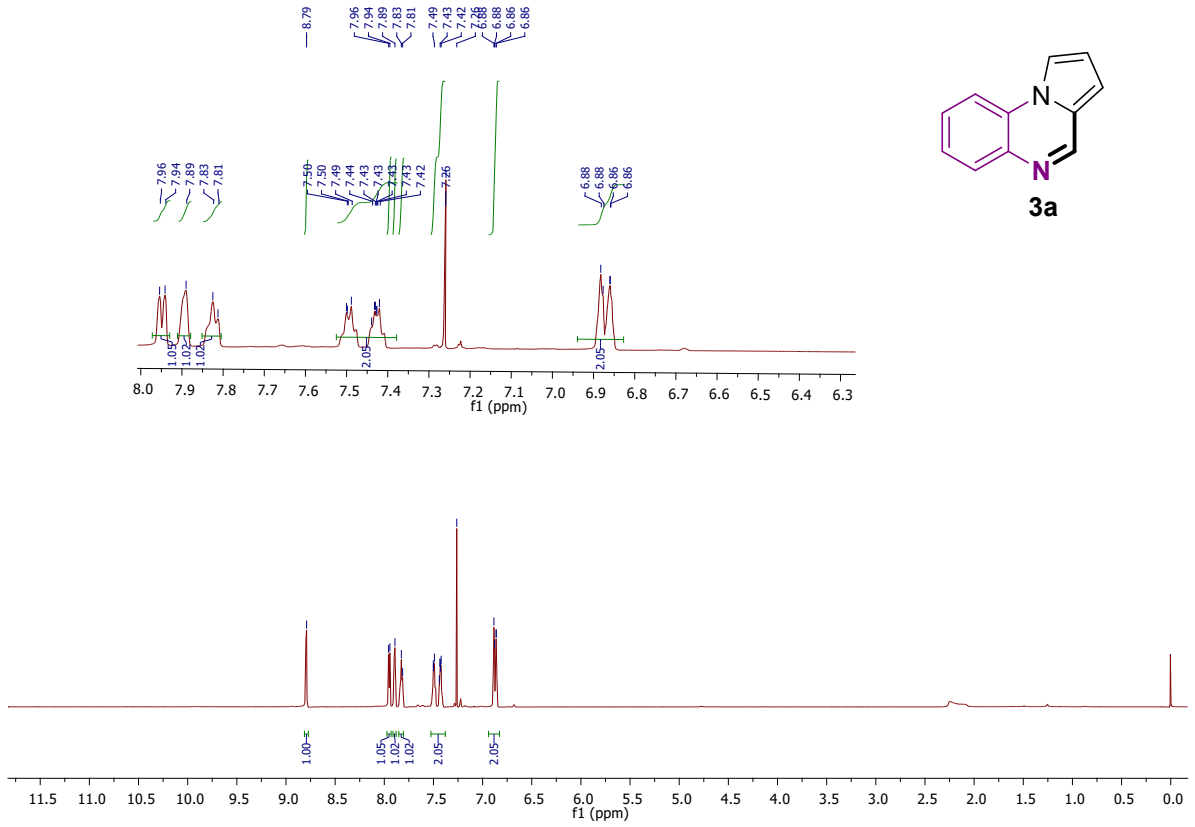
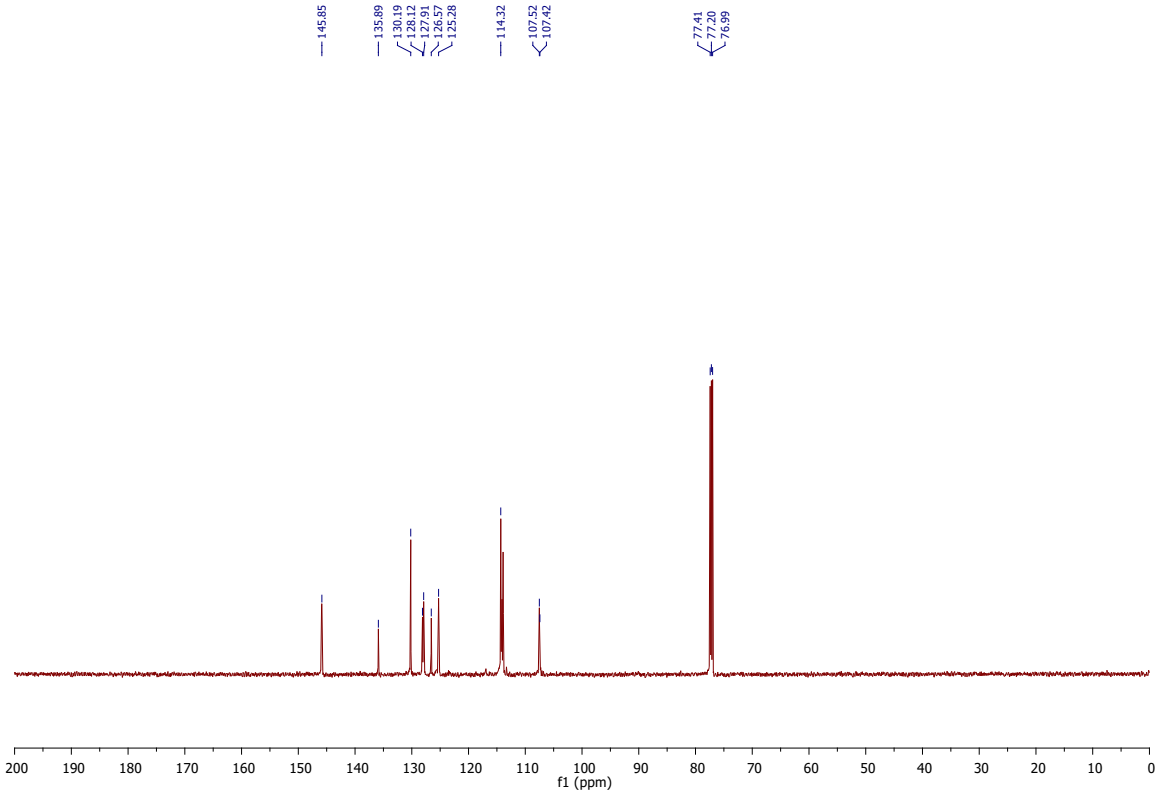
6. ^{1}H and ^{13}C Spectra

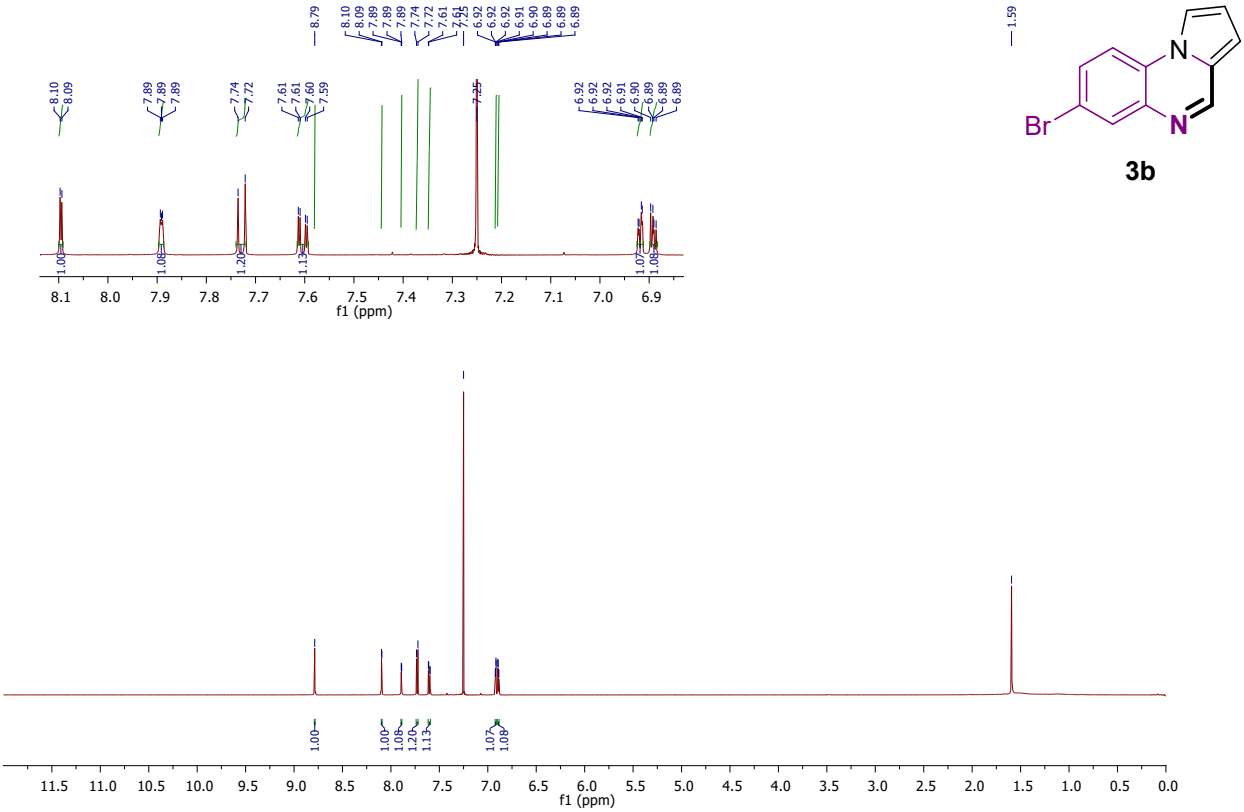
3a ^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

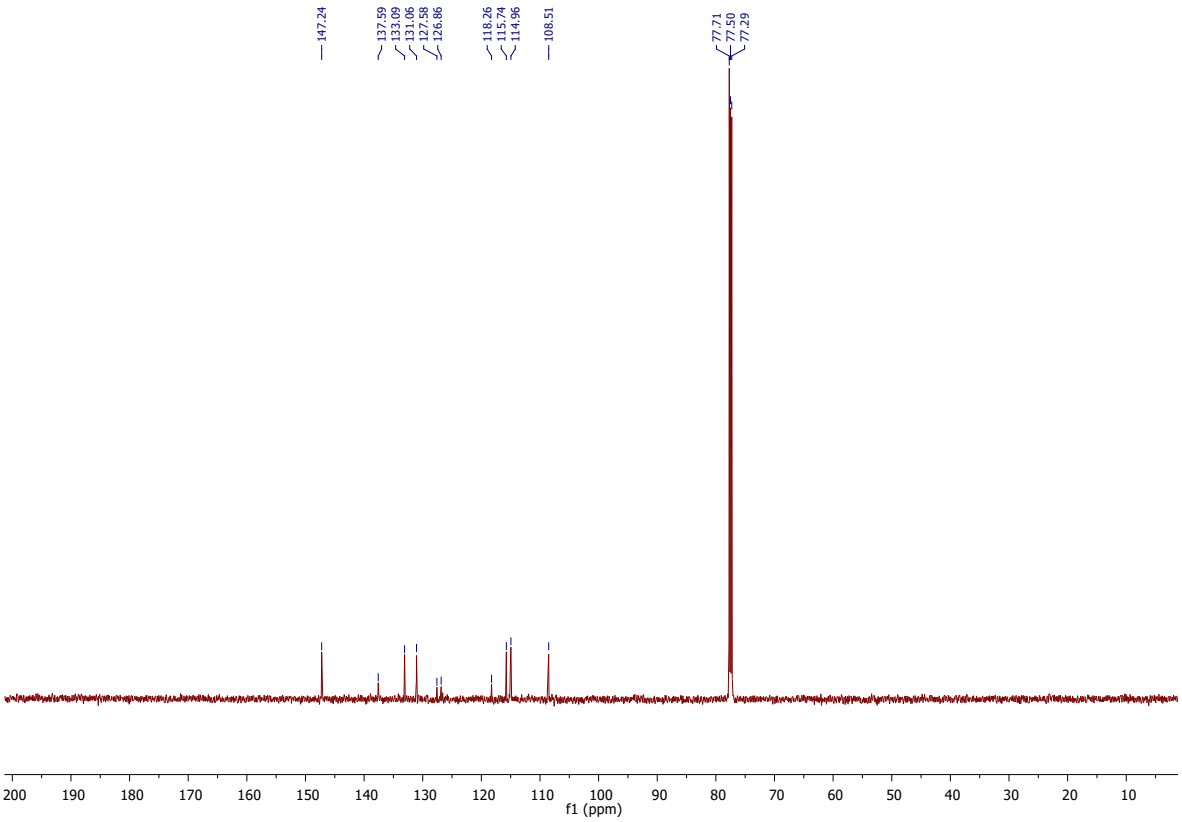


3b ^{1}H NMR ($CDCl_3$)

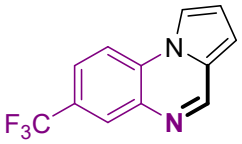


3b

^{13}C NMR ($CDCl_3$)

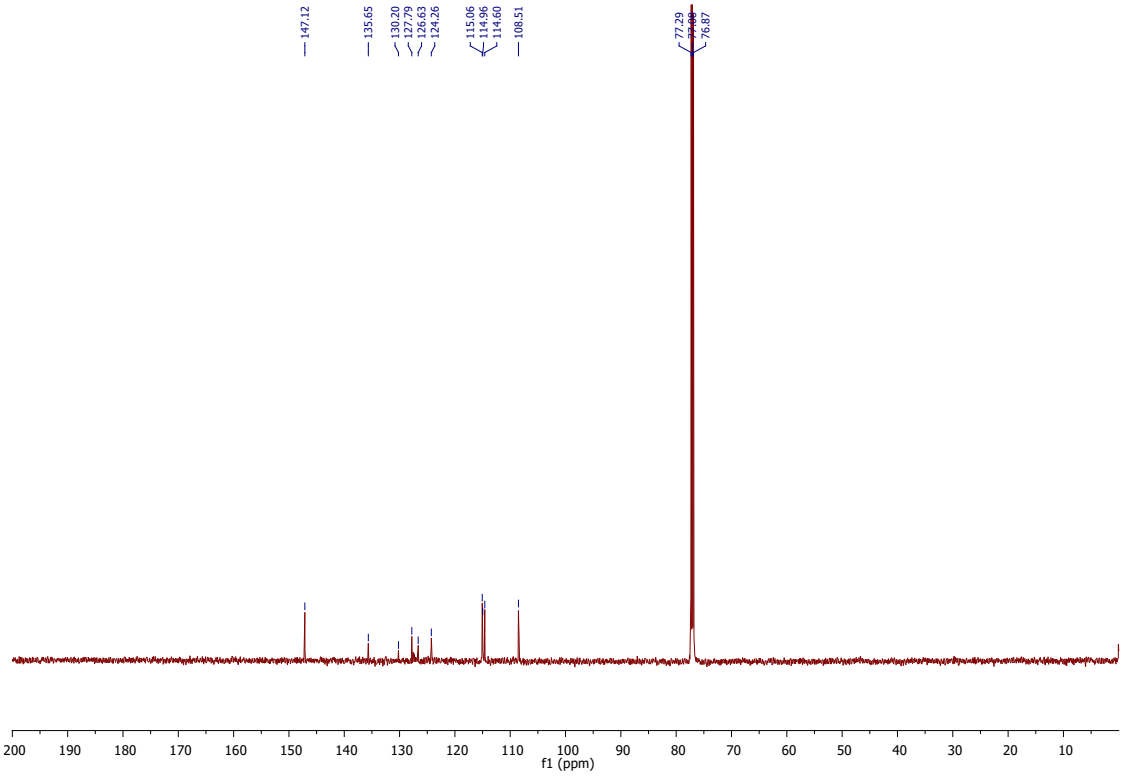


3c ^{1}H NMR ($CDCl_3$)

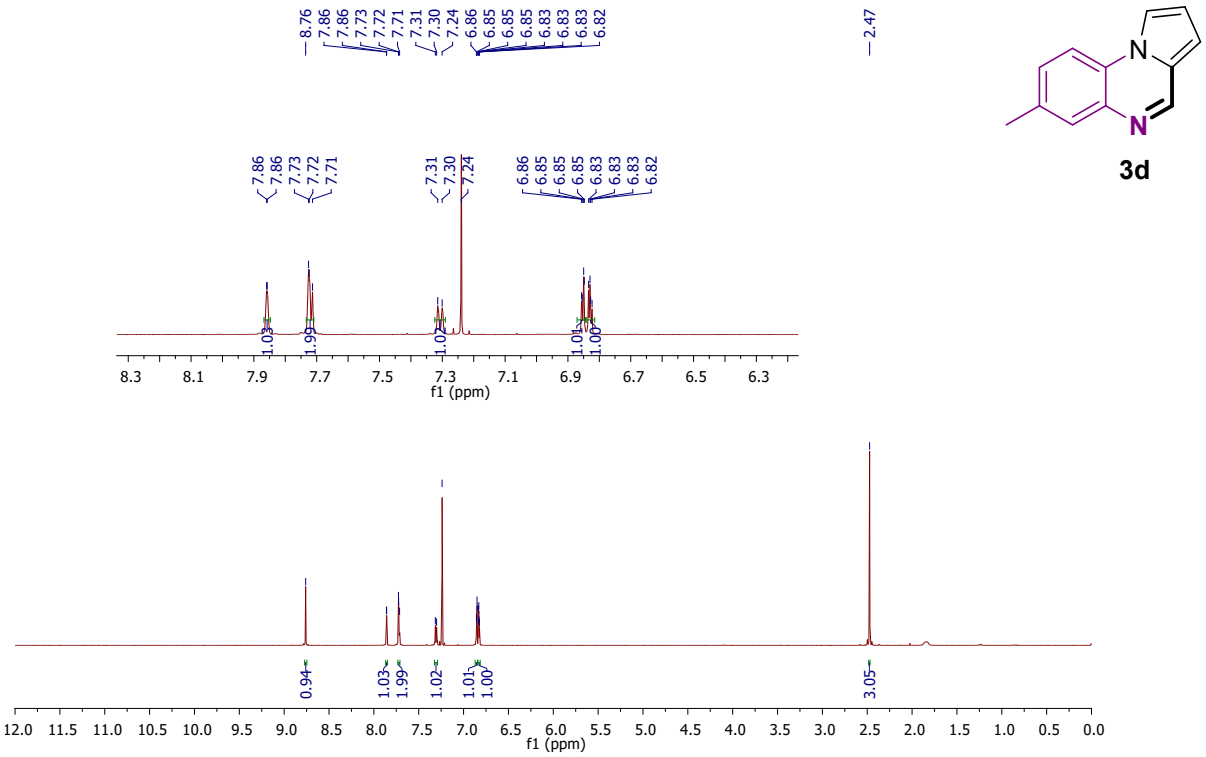


3c

^{13}C NMR ($CDCl_3$)

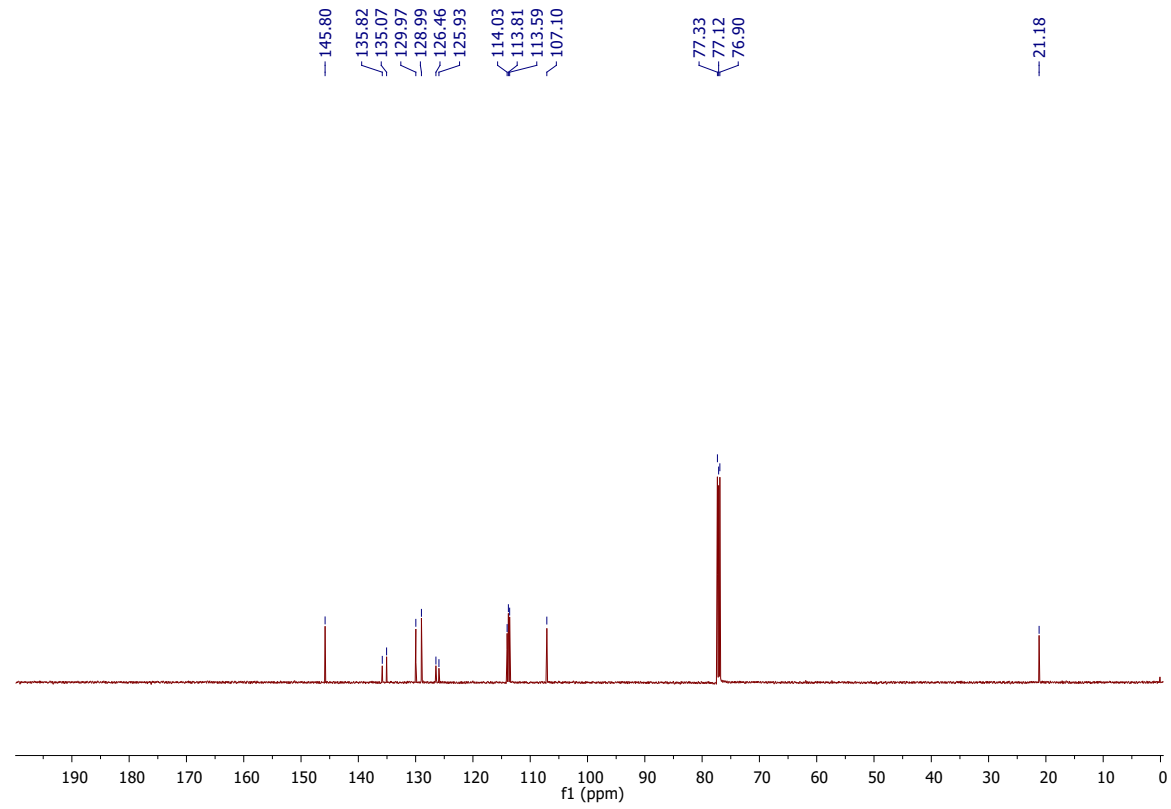


3d ^{1}H NMR ($CDCl_3$)

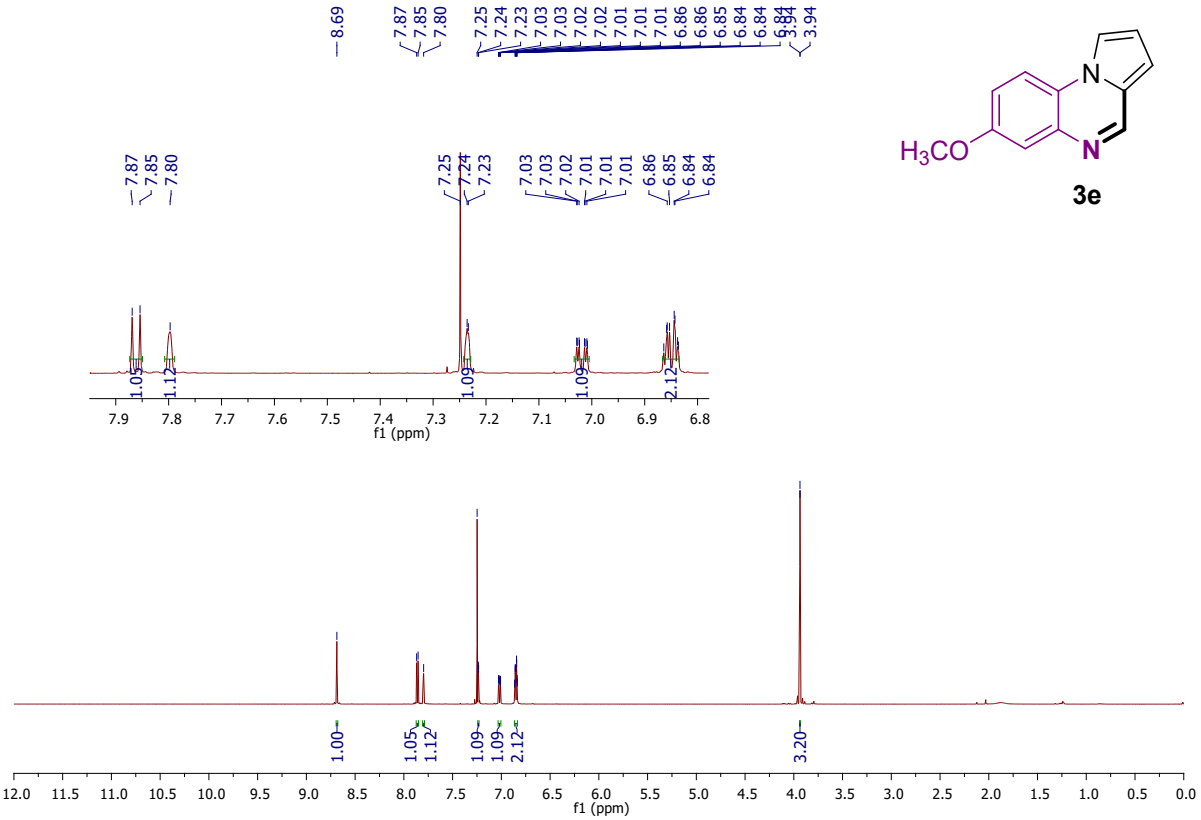


3d

^{13}C NMR ($CDCl_3$)

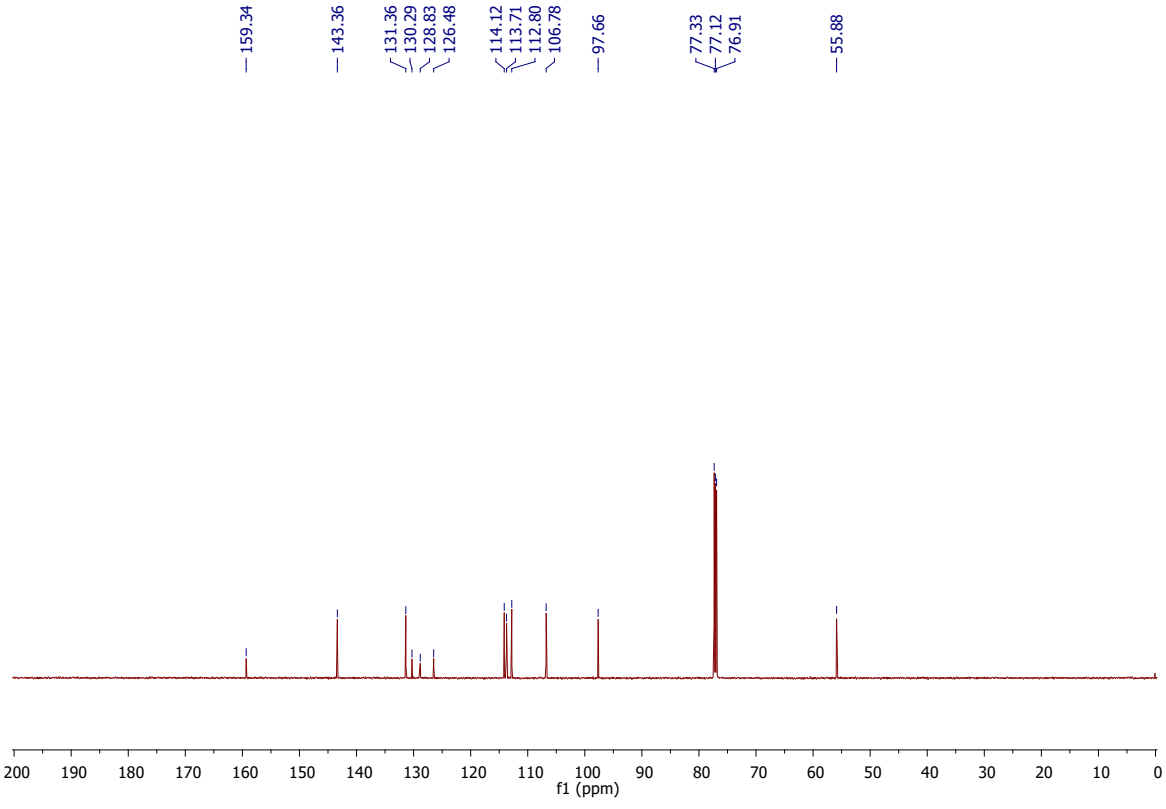


3e ^{1}H NMR ($CDCl_3$)

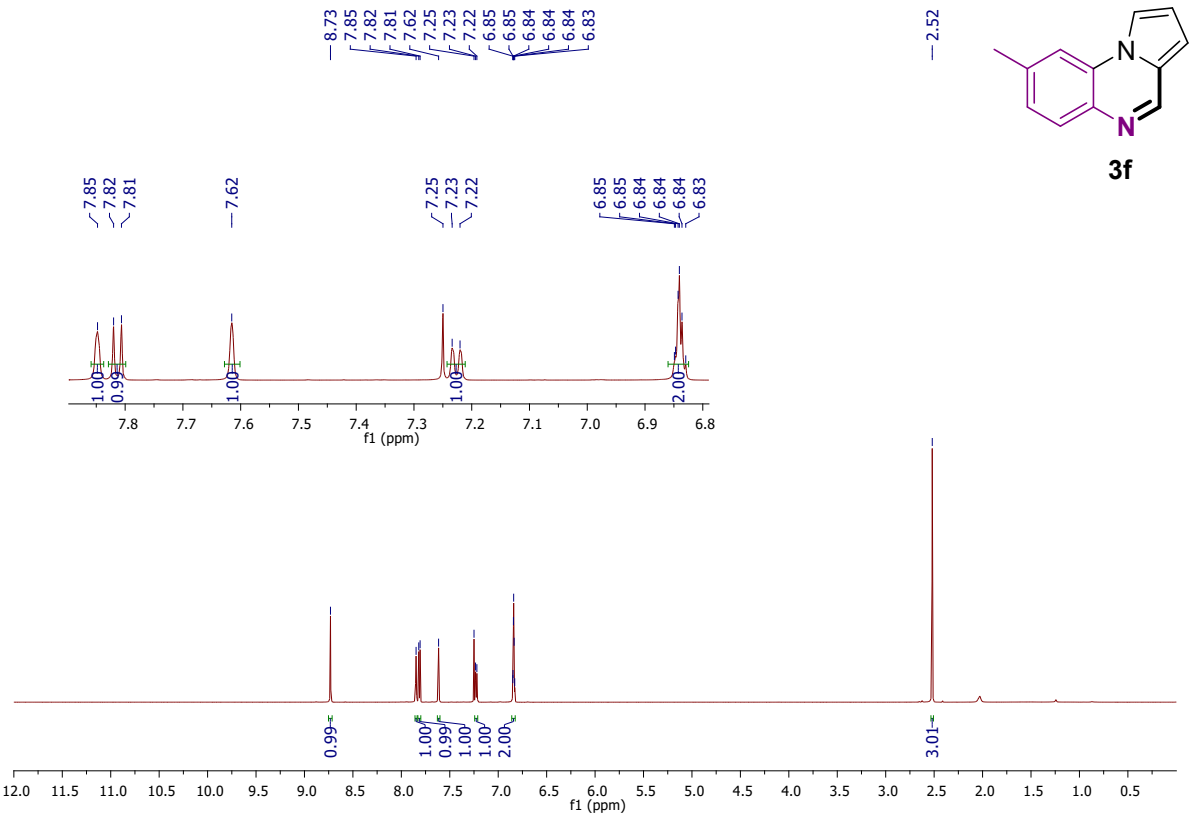


3e

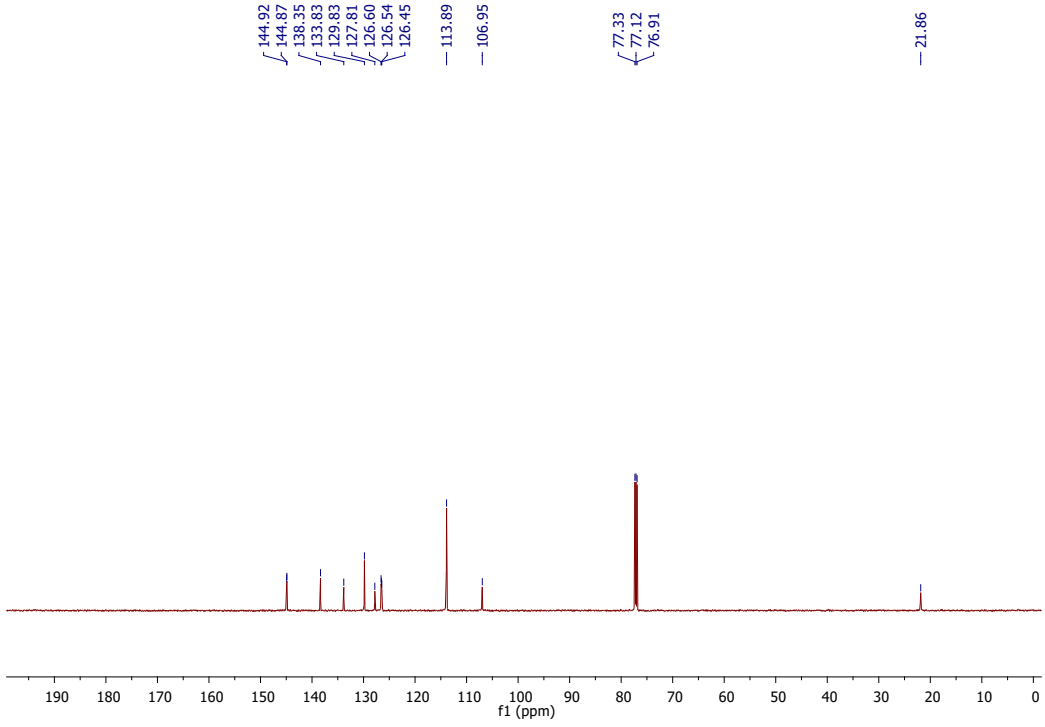
^{13}C NMR ($CDCl_3$)



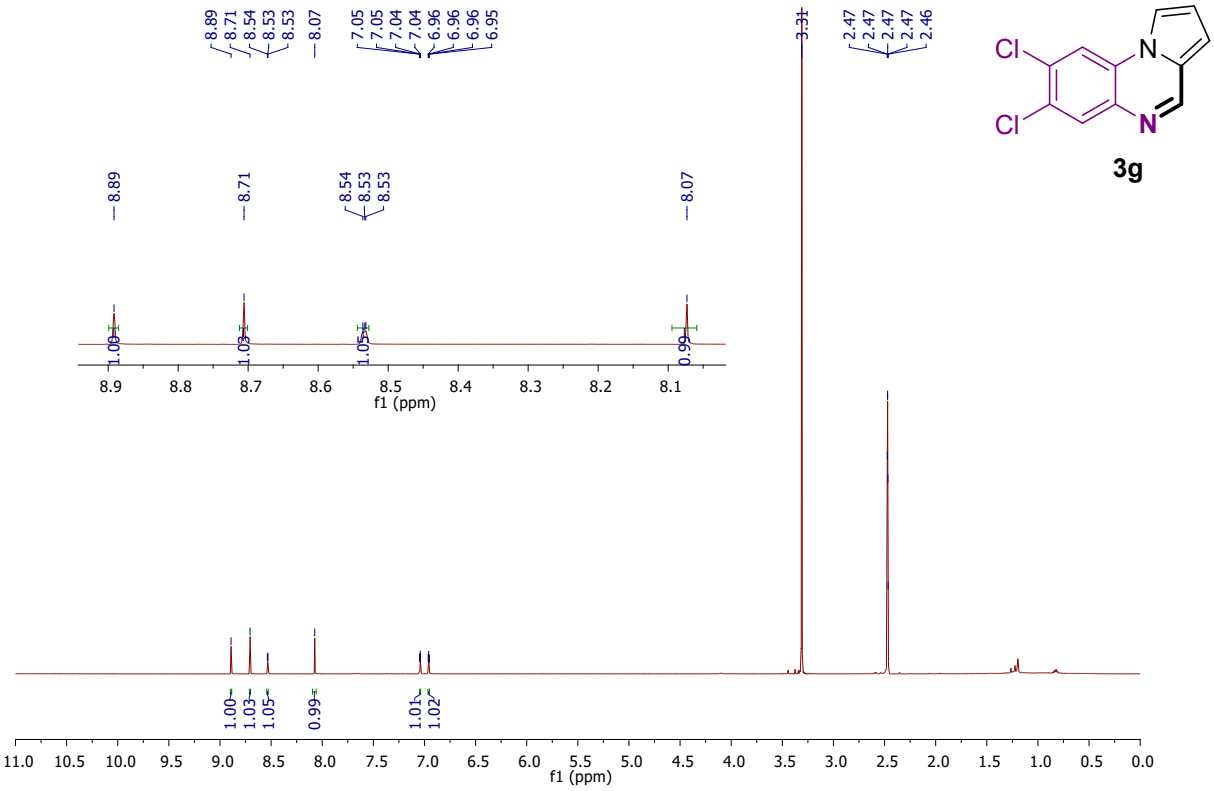
3f ^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

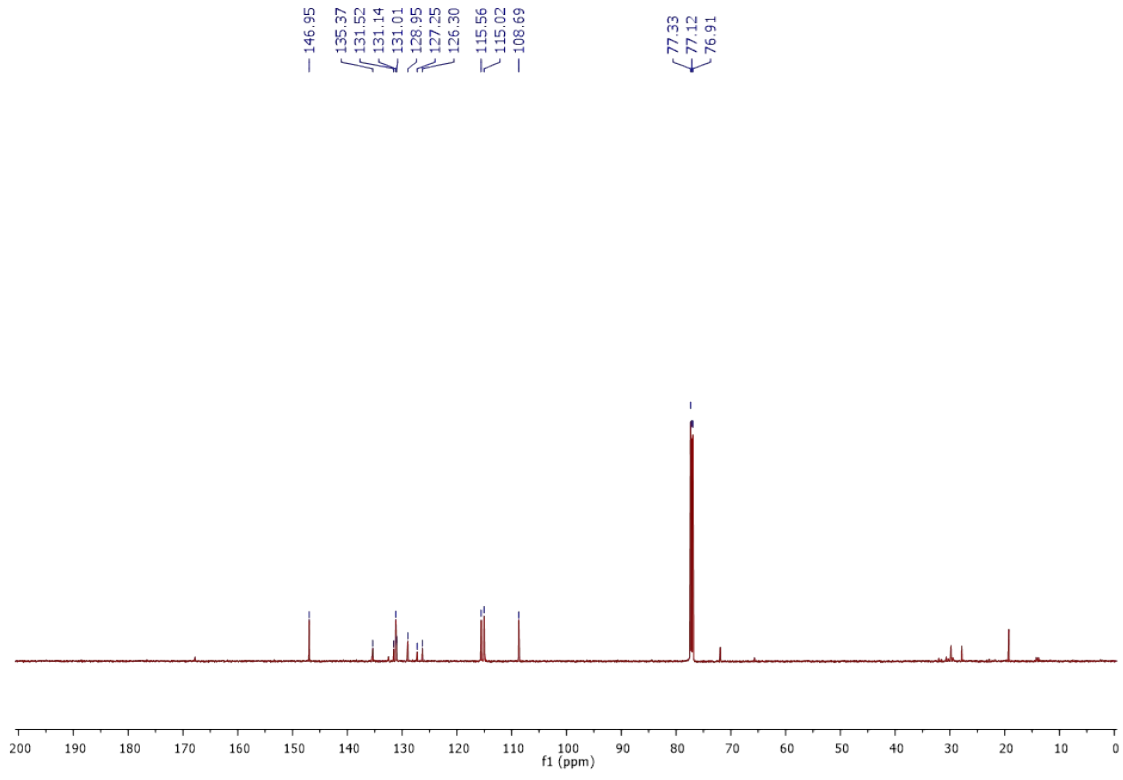


3g ^{1}H NMR (DMSO)

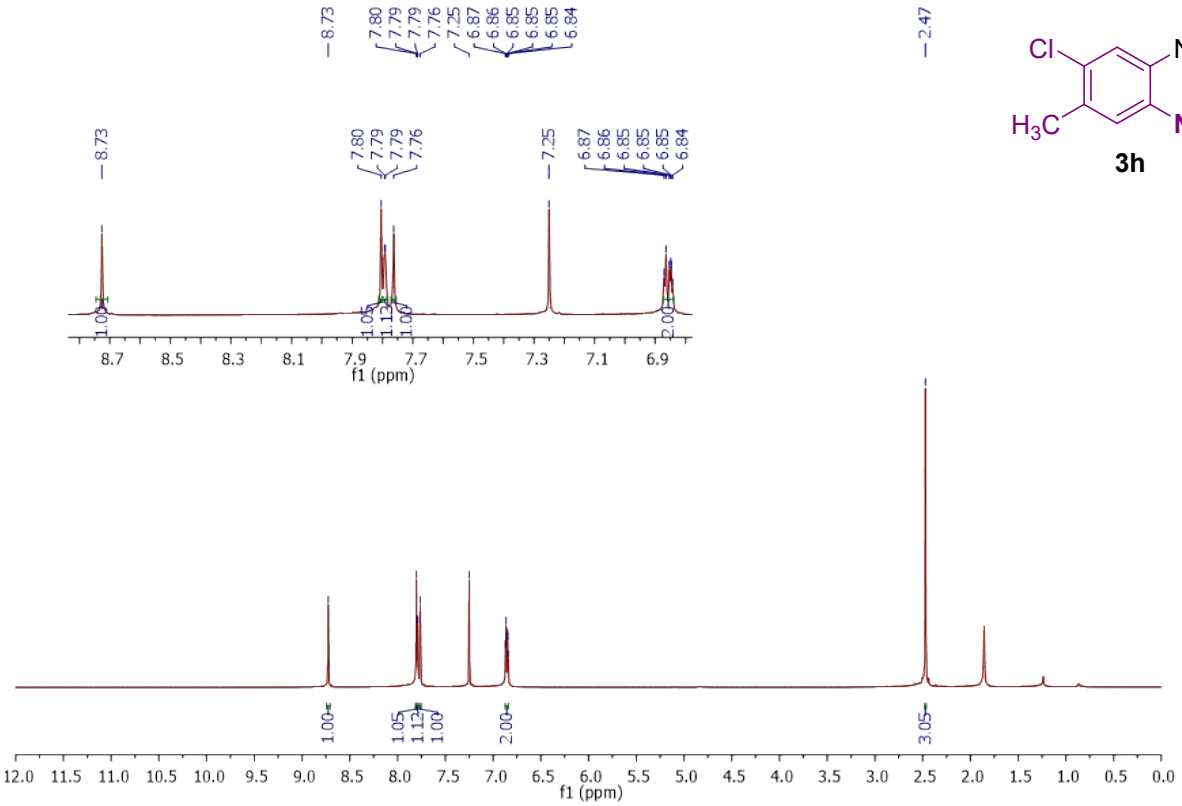


3g

^{13}C NMR ($CDCl_3$)

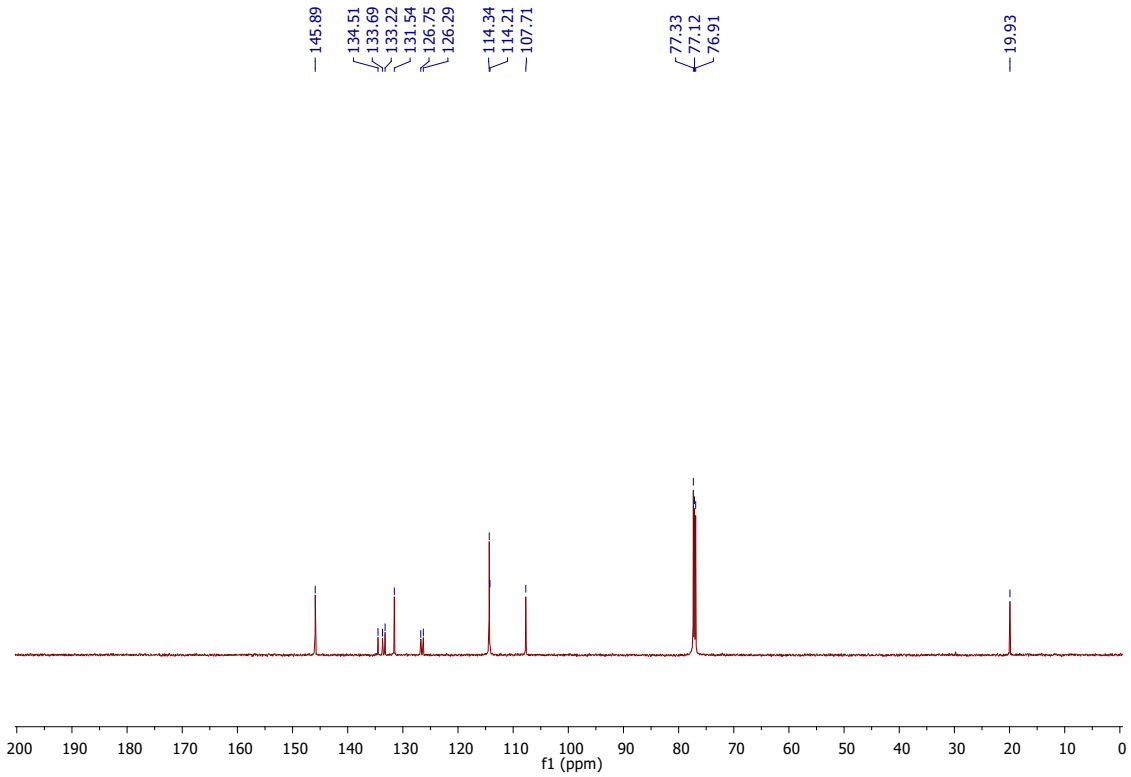


3h ^{1}H NMR ($CDCl_3$)

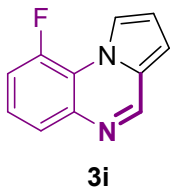


3h

^{13}C NMR ($CDCl_3$)

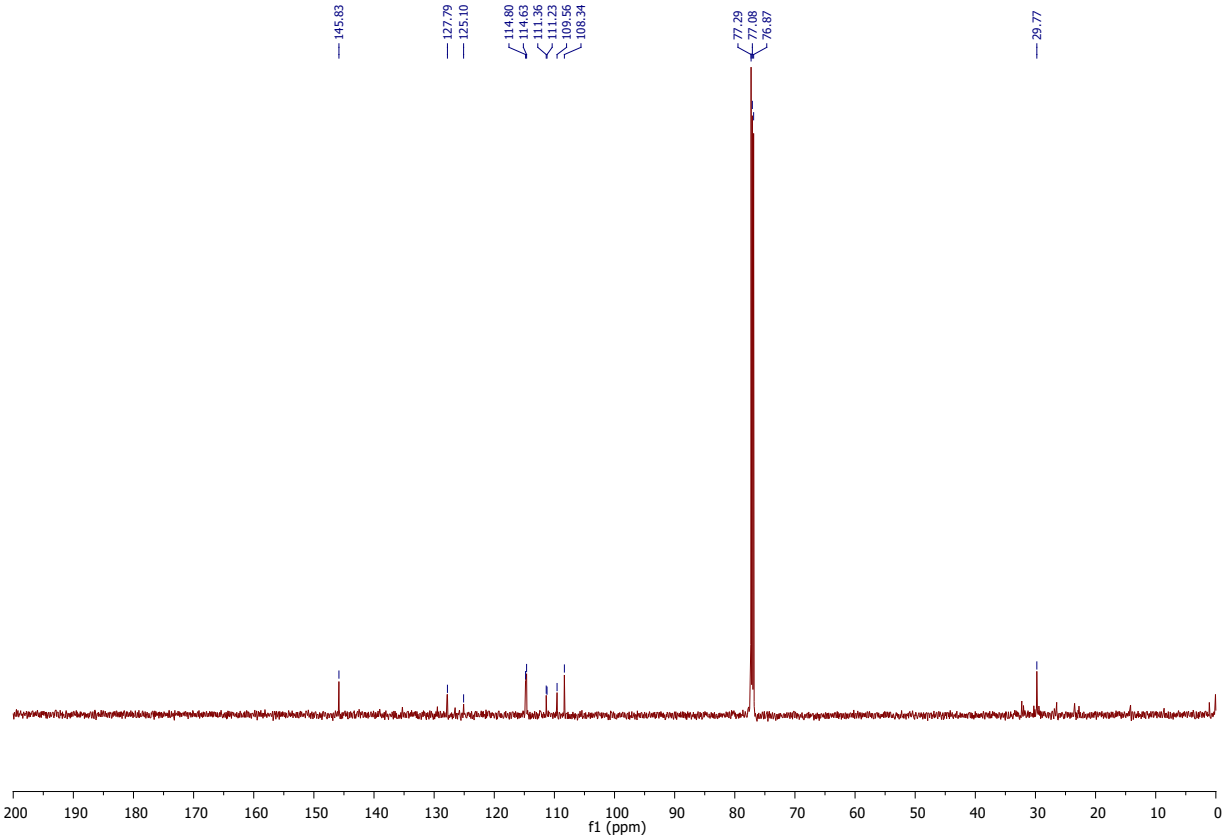


3i ^{1}H NMR ($CDCl_3$)

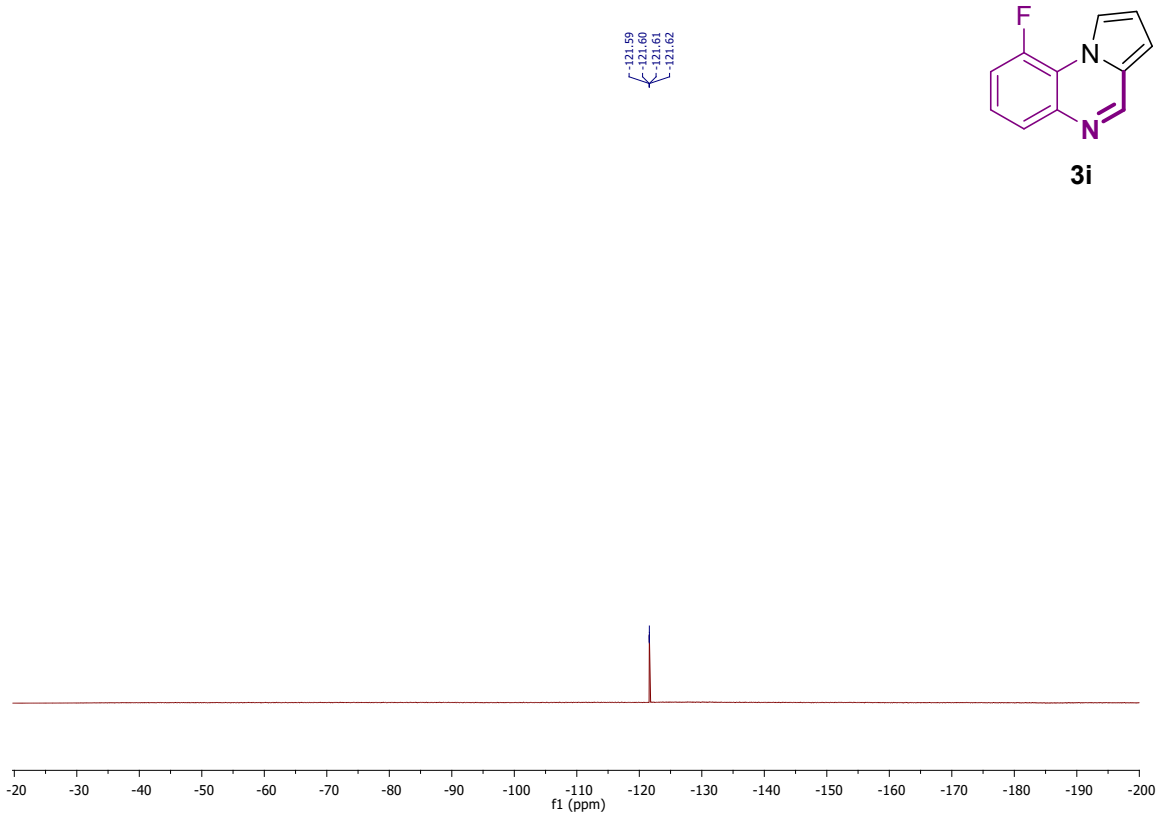


3i

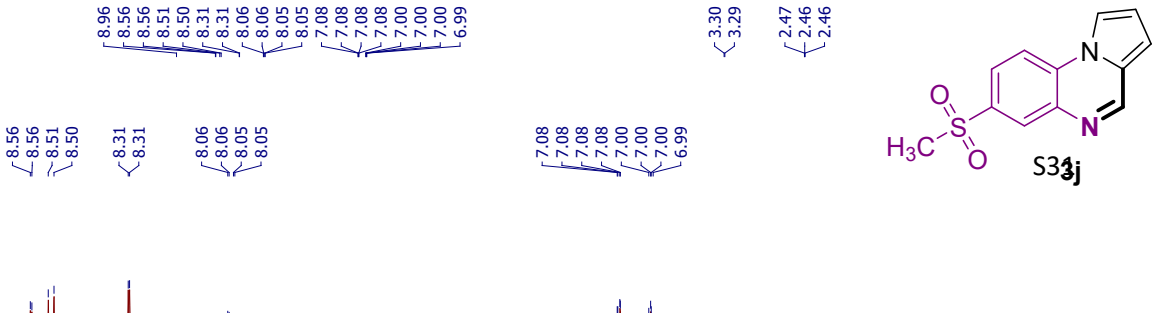
^{13}C NMR ($CDCl_3$)



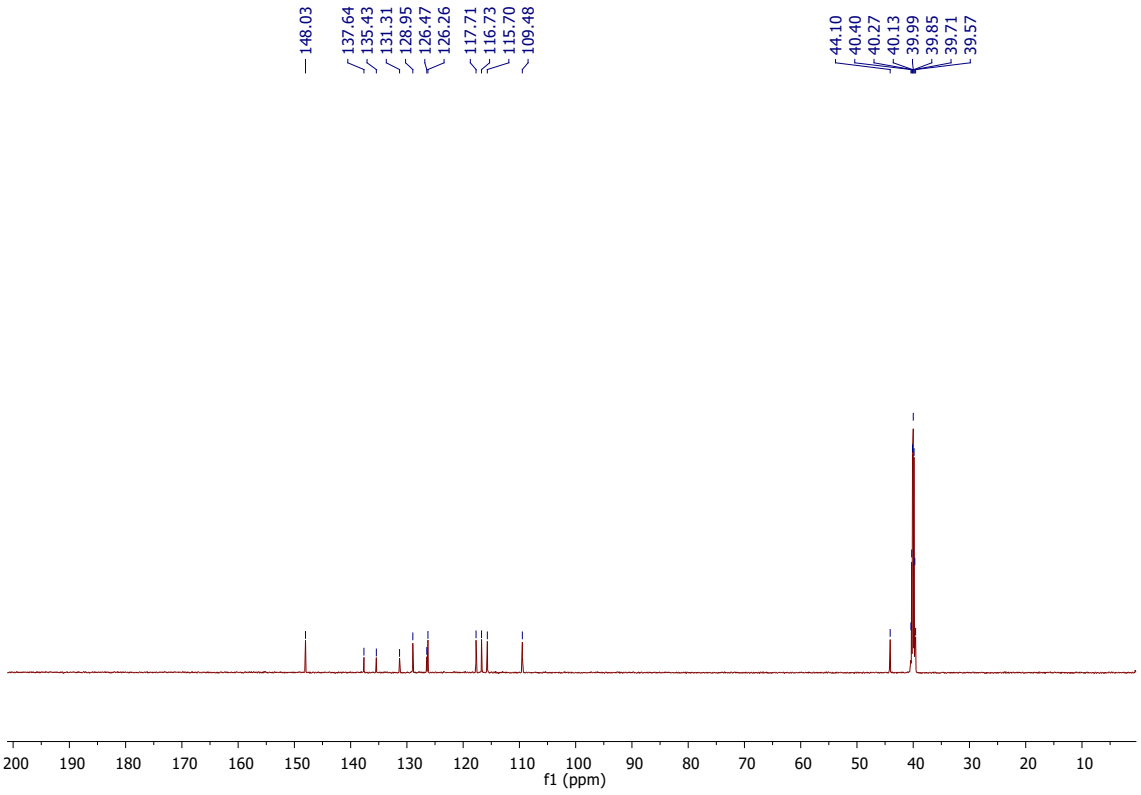
$^{19}F\{1H\}$ NMR ($CDCl_3$)



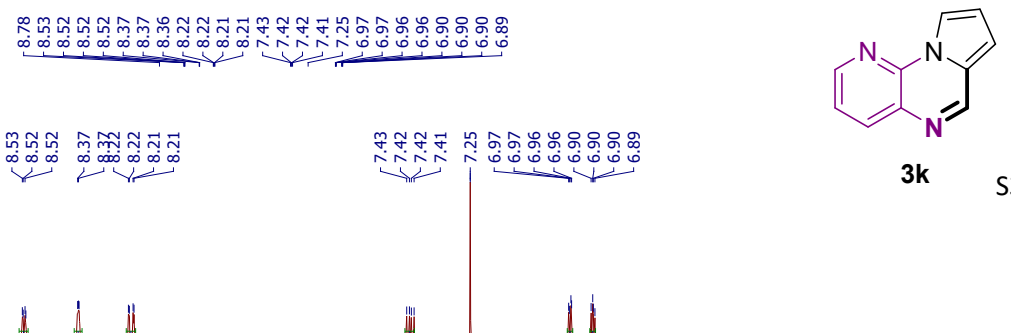
3j ^{1}H NMR (DMSO)



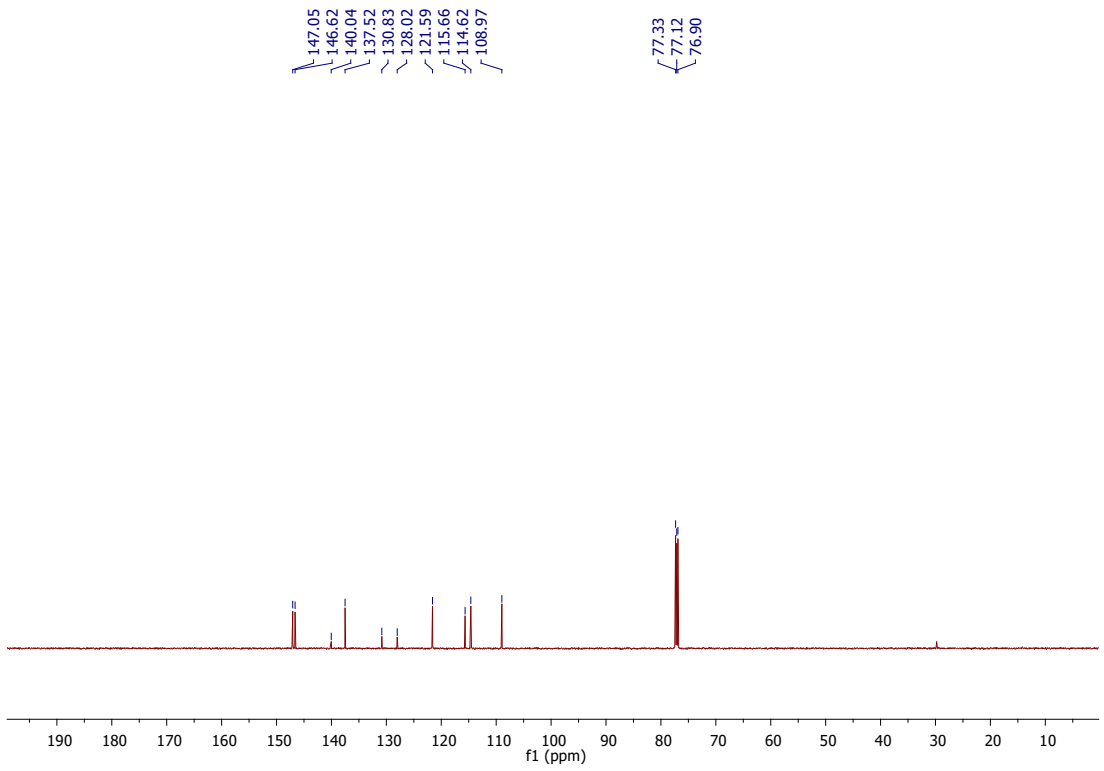
^{13}C NMR (DMSO)



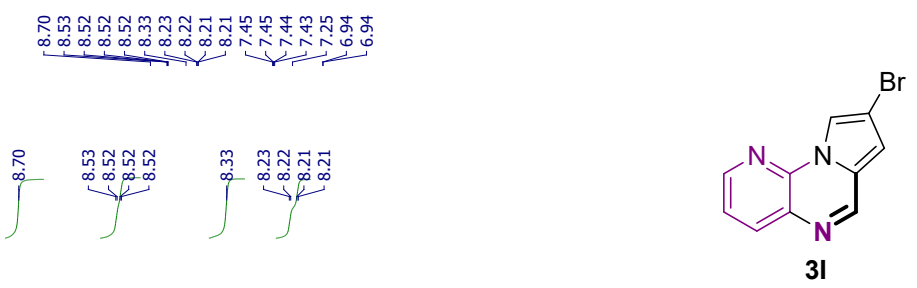
3k ^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

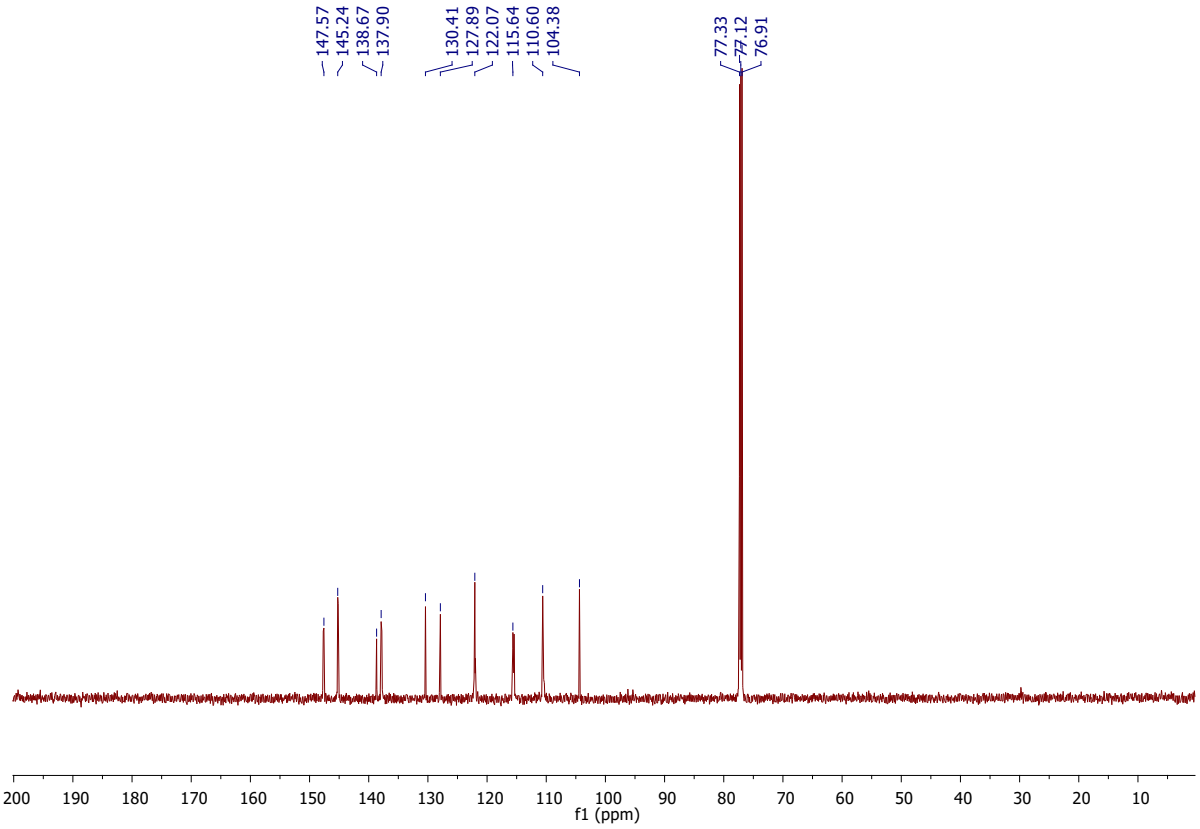


3l ^{1}H NMR ($CDCl_3$)

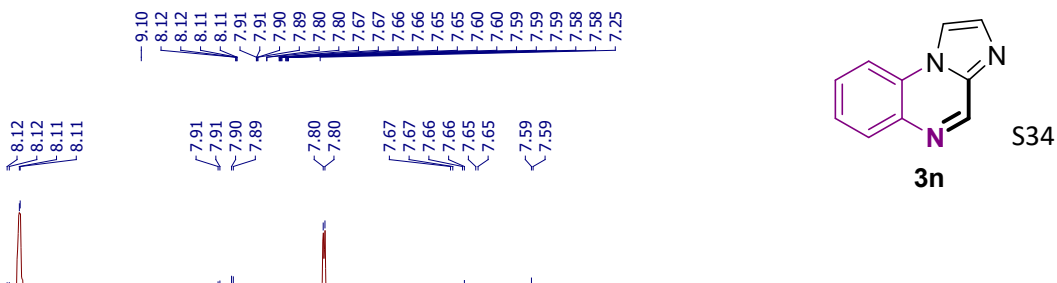


3l

^{13}C NMR ($CDCl_3$)

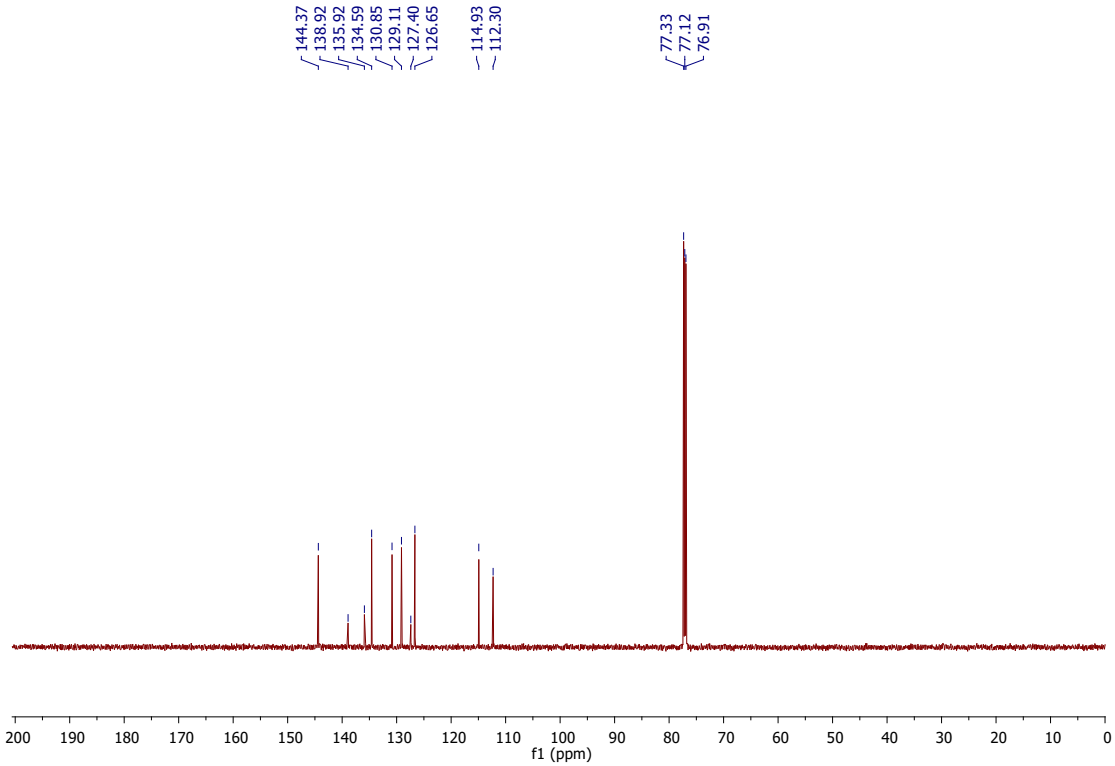


3n ^{1}H NMR ($CDCl_3$)

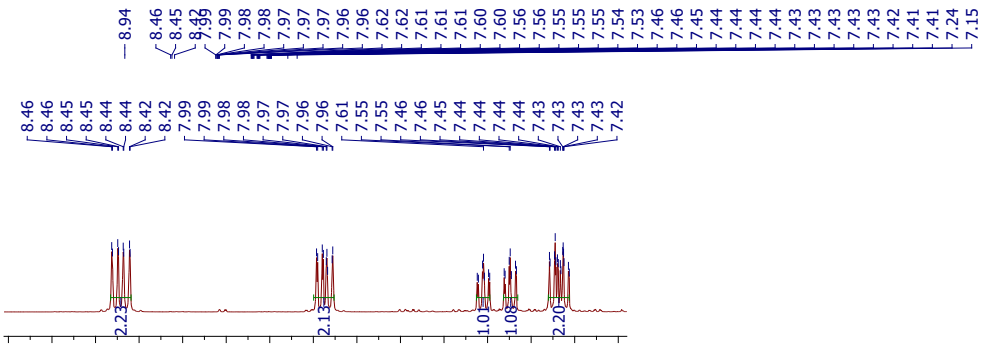


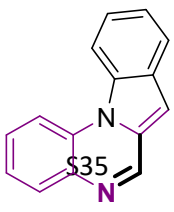
3n

^{13}C NMR ($CDCl_3$)



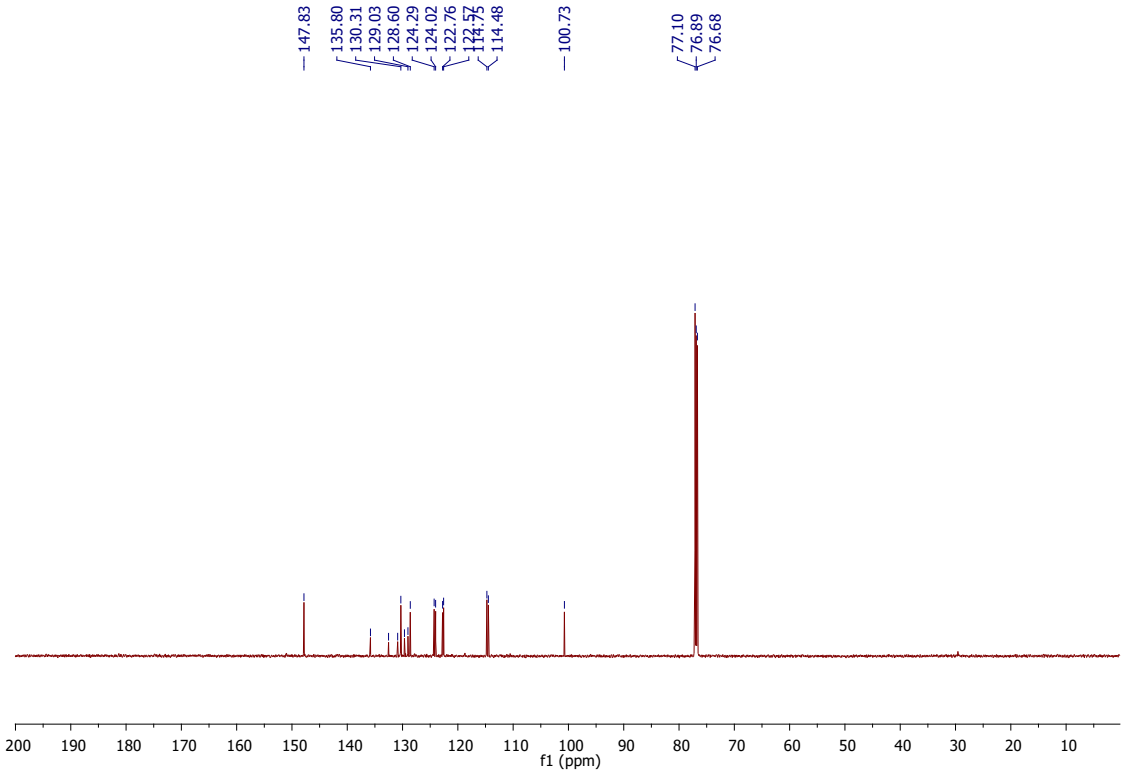
3o ^{1}H NMR ($CDCl_3$)



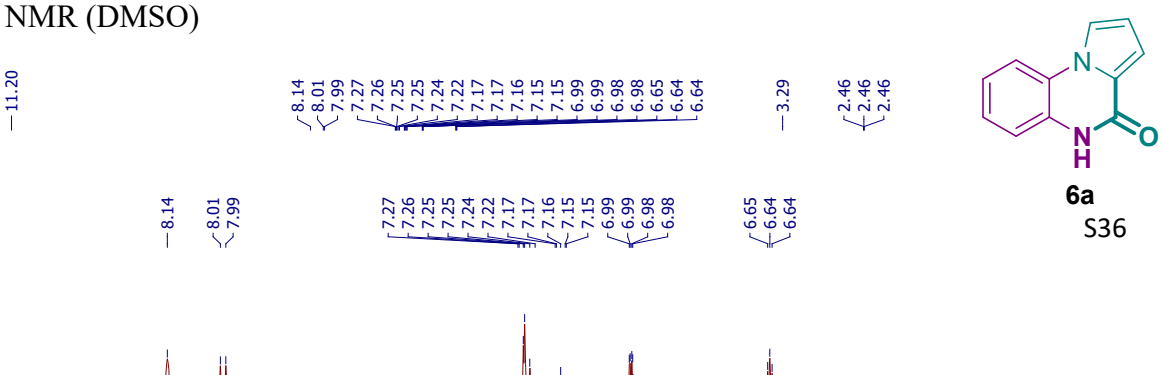


3o

^{13}C NMR ($CDCl_3$)

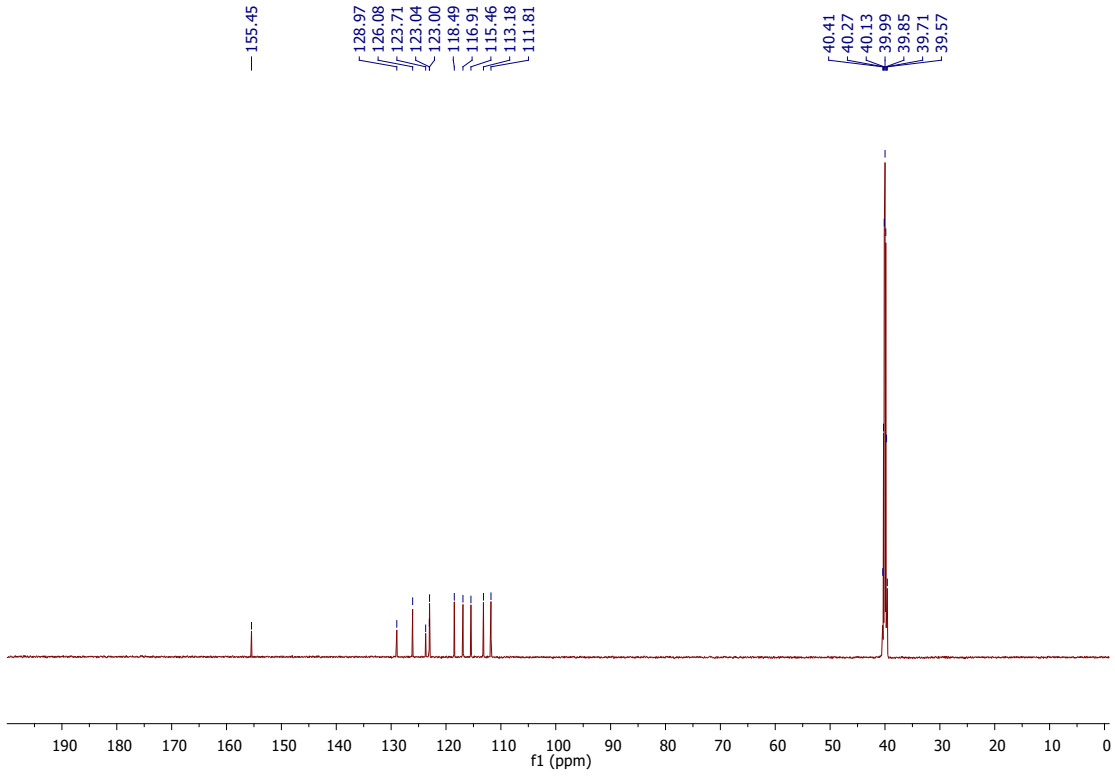


6a ^{1}H NMR (DMSO)

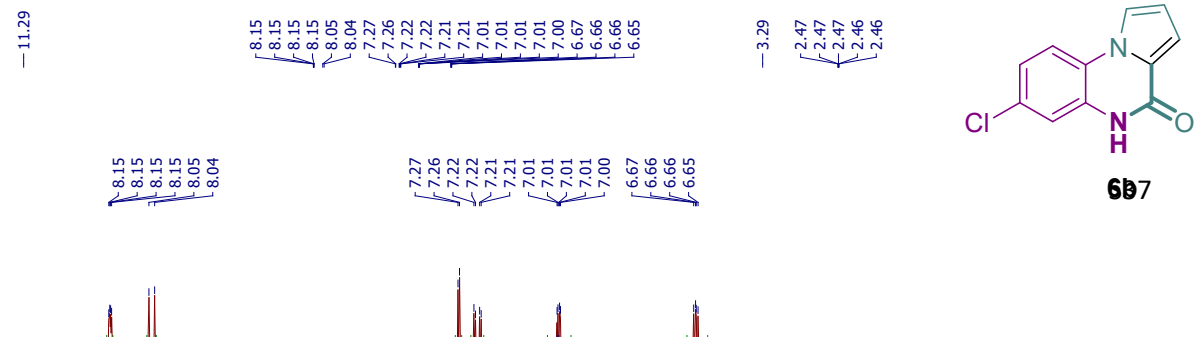


6a

^{13}C NMR (DMSO)



6b ^{1}H NMR (DMSO)



6b

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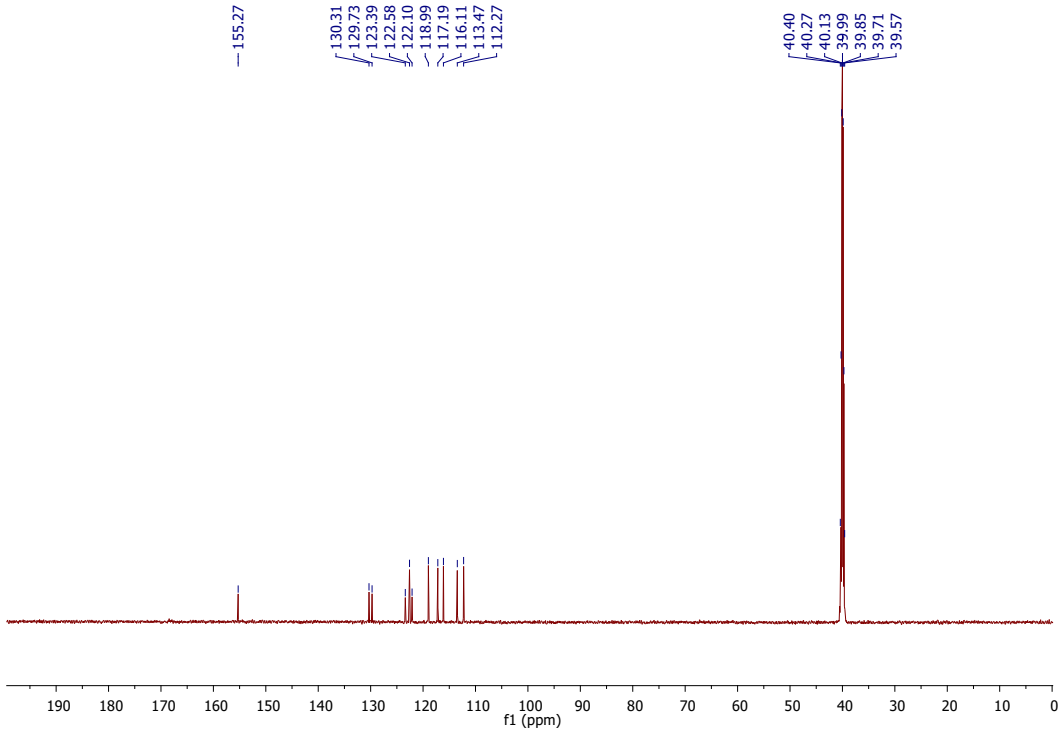
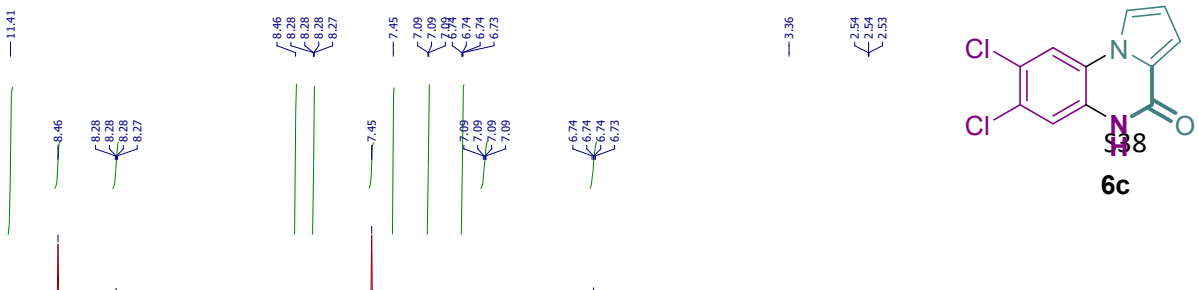
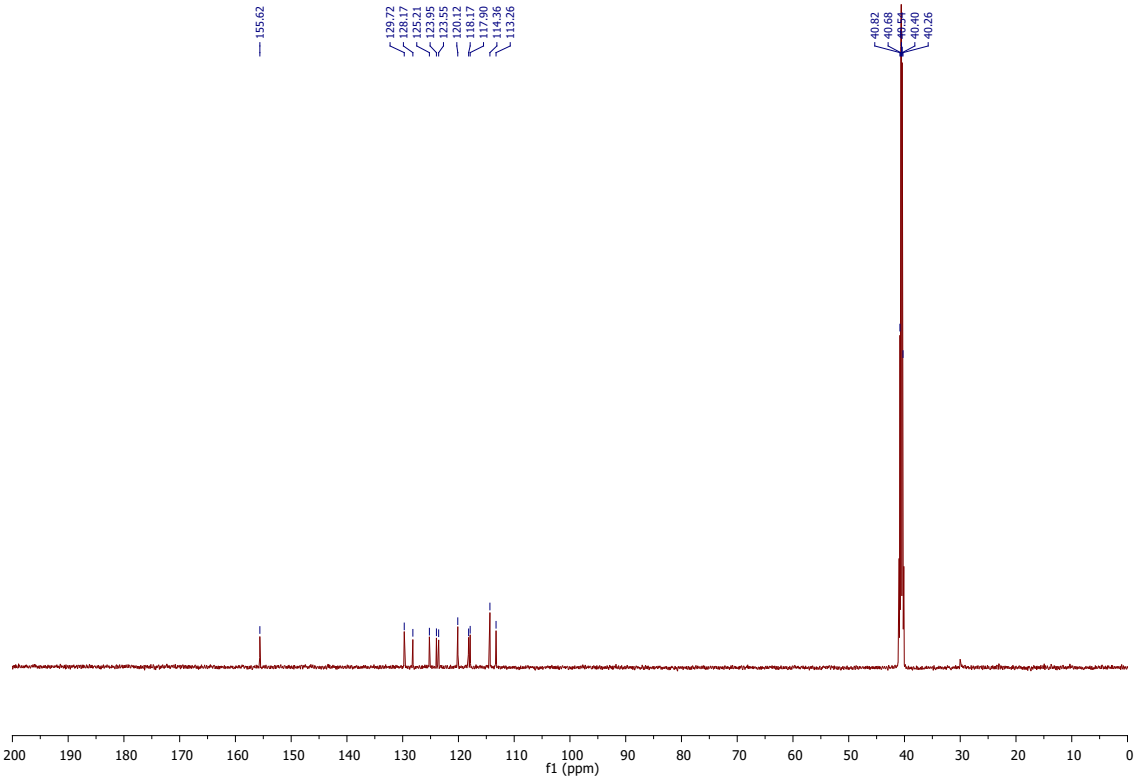


6c ^{1}H NMR (DMSO)

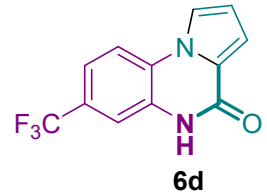


6c

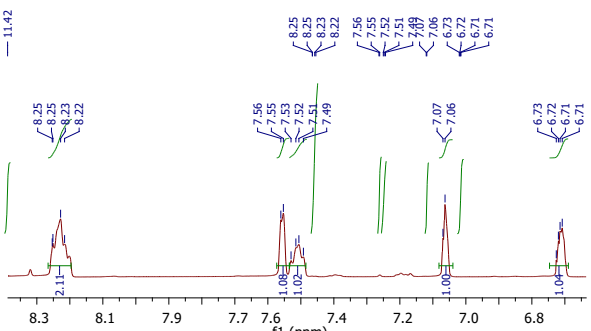
^{13}C NMR (DMSO)



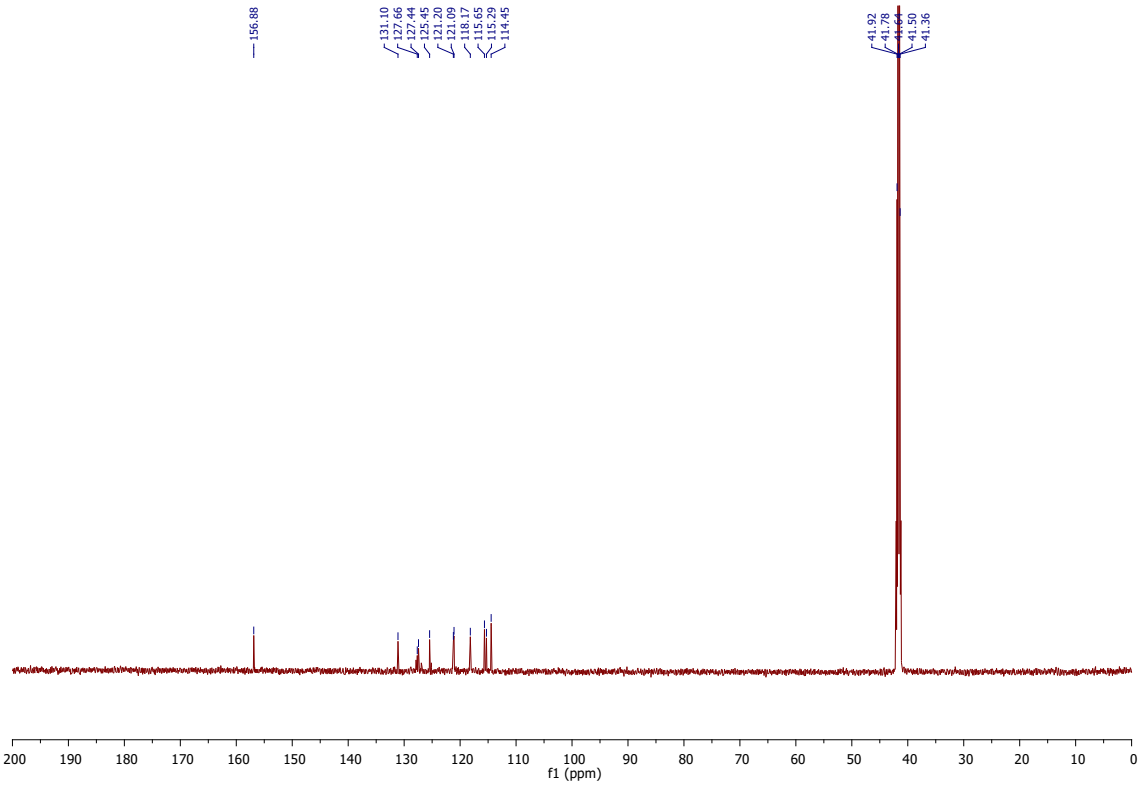
6d ^{1}H NMR (DMSO)



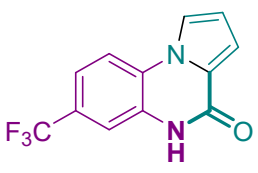
6d



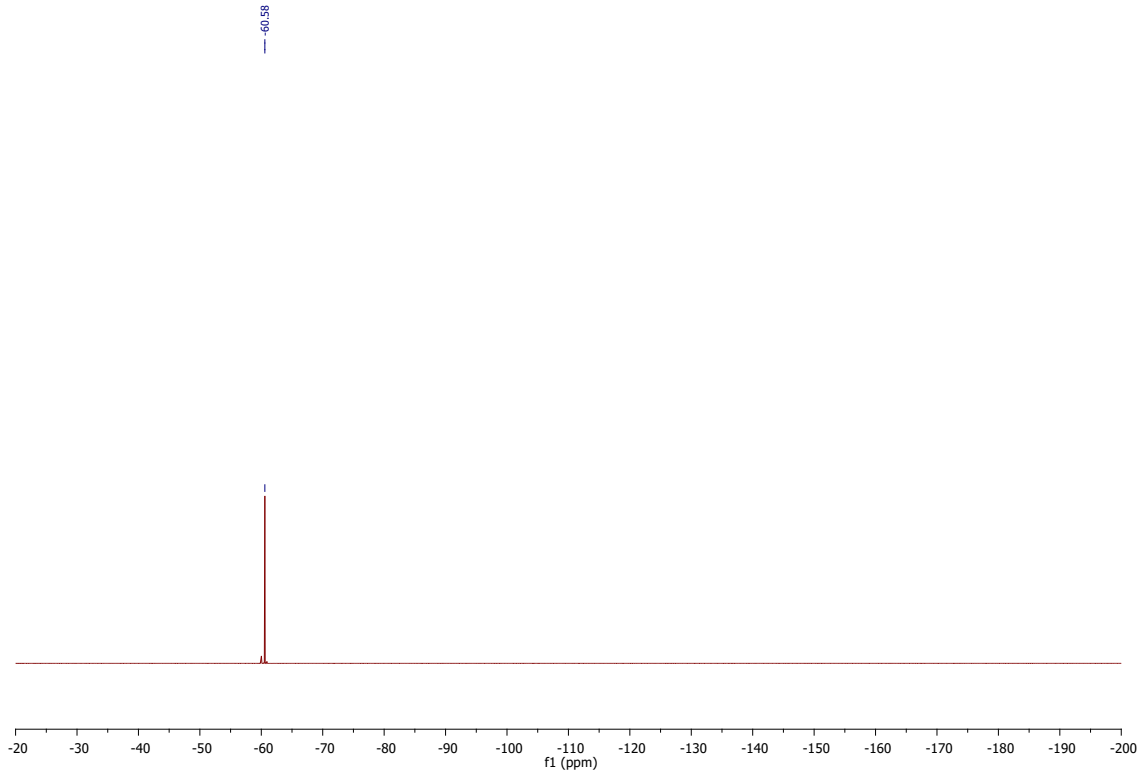
^{13}C NMR (DMSO)



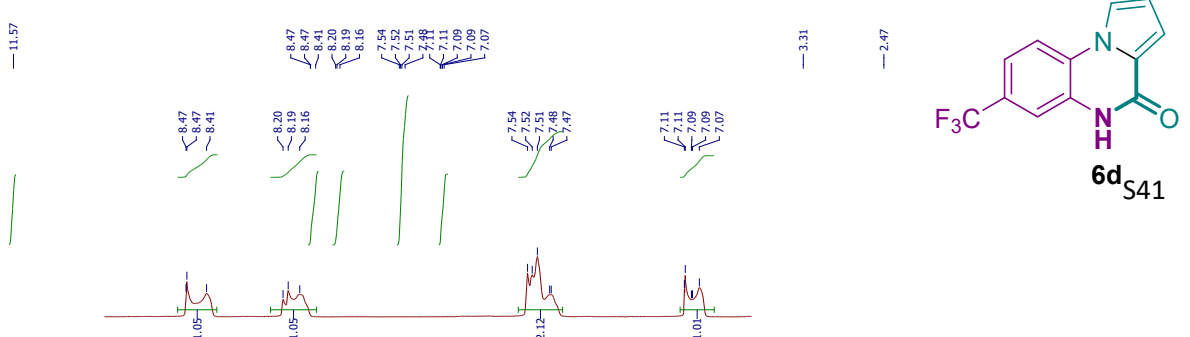
6d ^{19}F{1H} NMR (DMSO)



6d

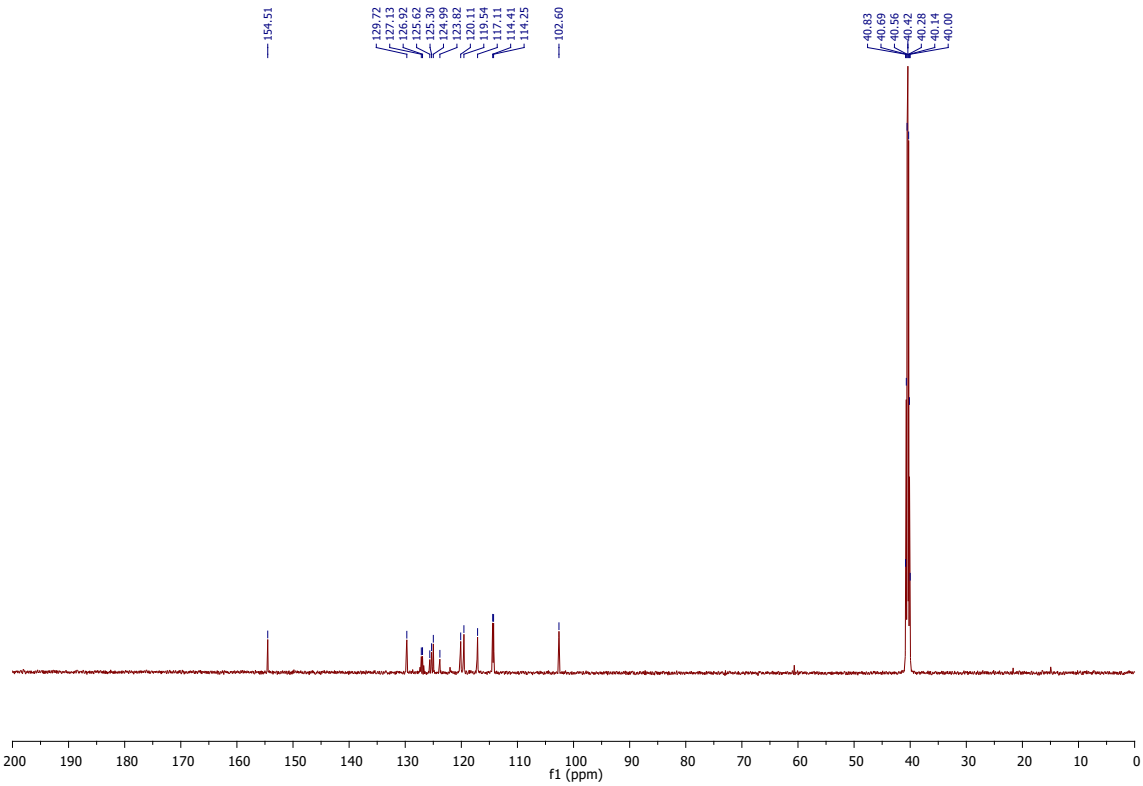


6f ^{1}H NMR (DMSO)

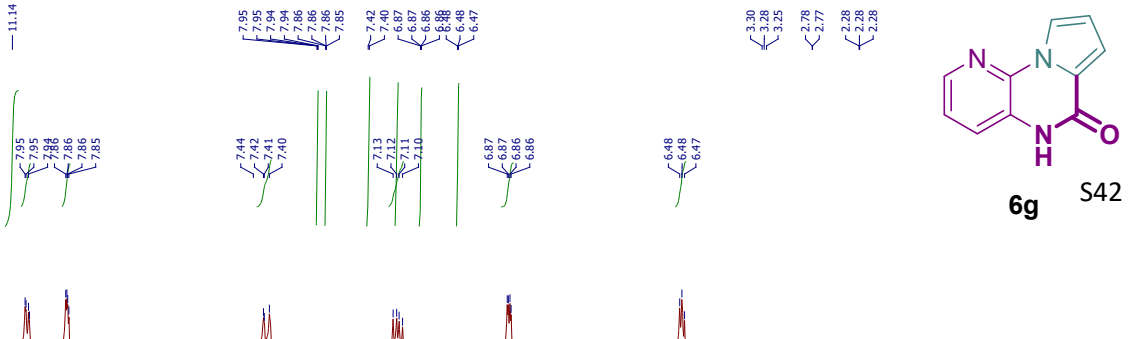


6d S41

^{13}C NMR (DMSO)

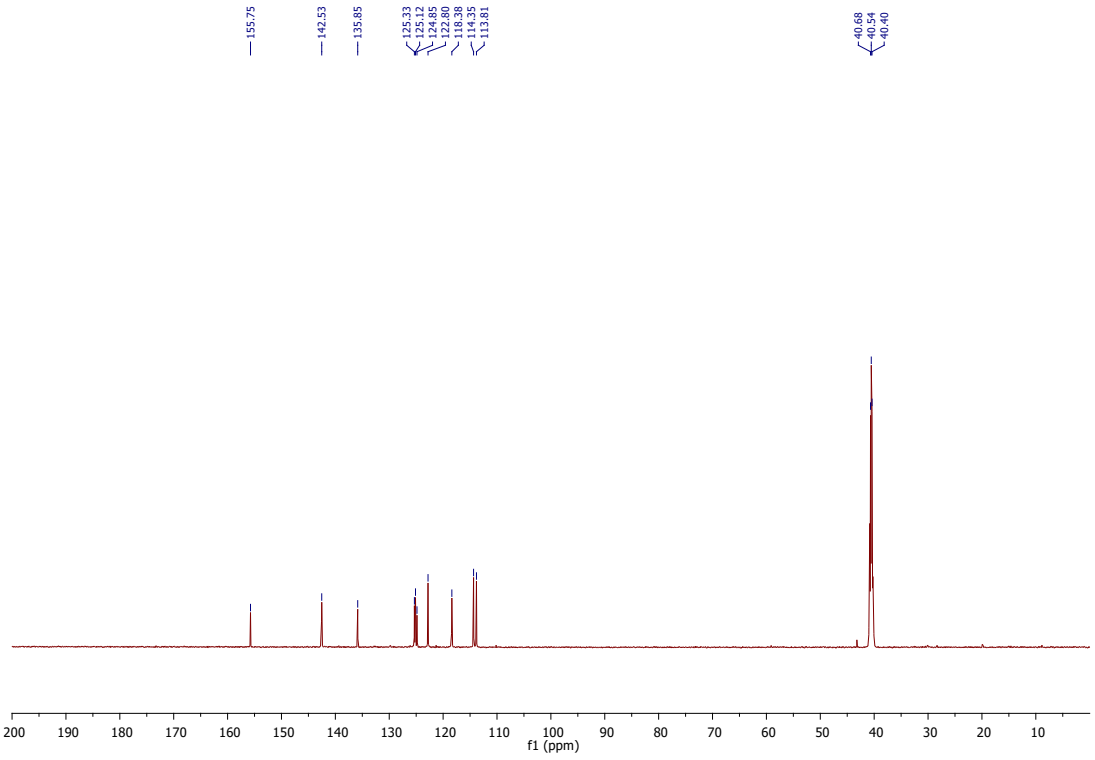


6g ^{1}H NMR (DMSO)

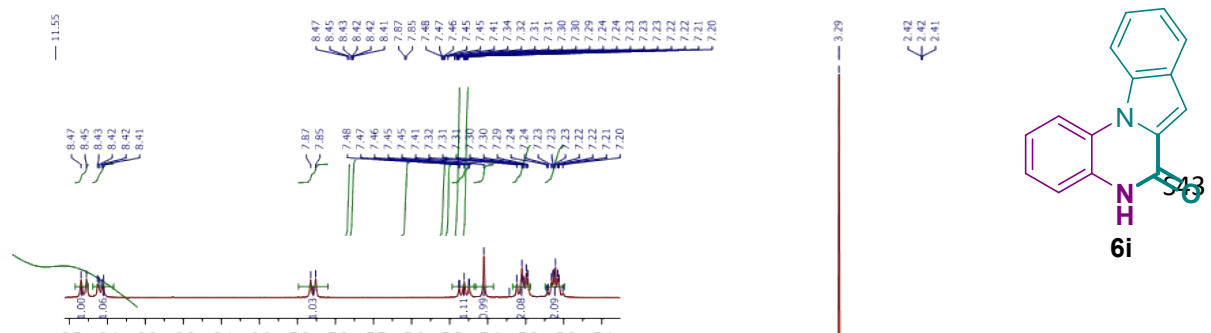


6g

^{13}C NMR (DMSO)

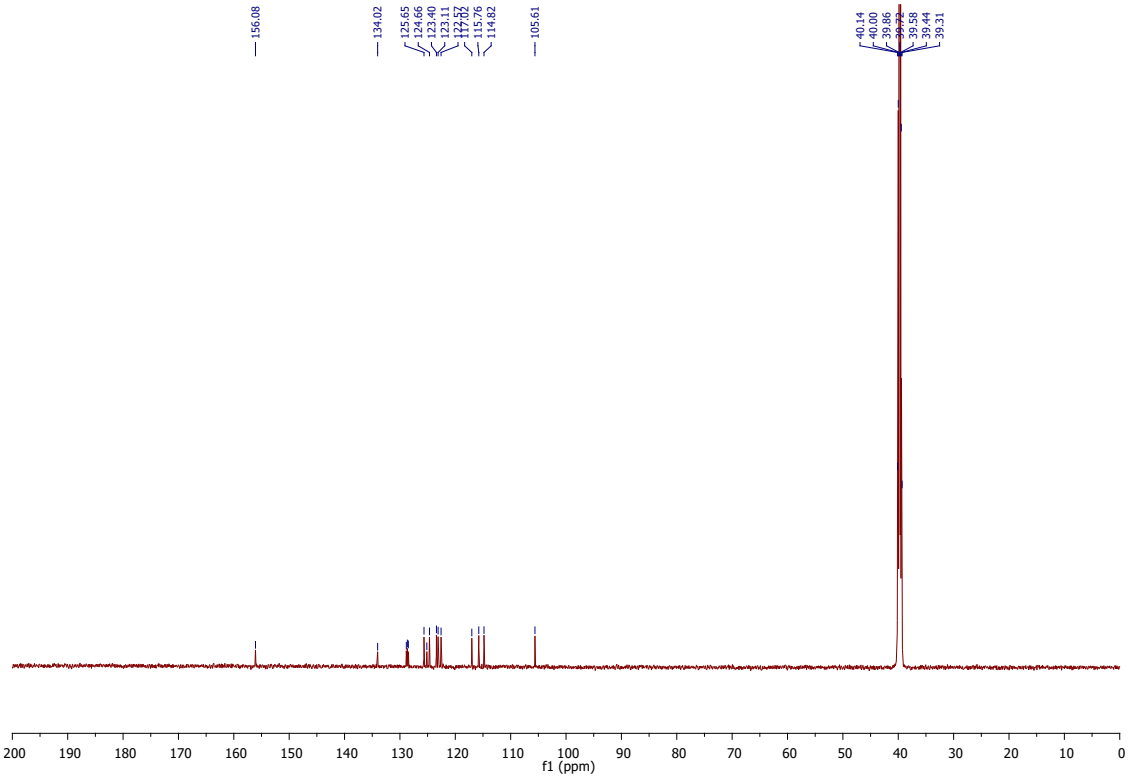


6i ^{1}H NMR (DMSO)

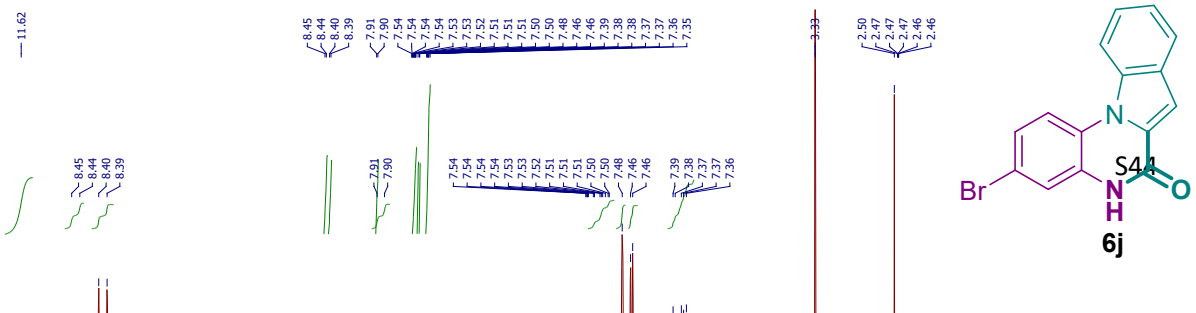


6i

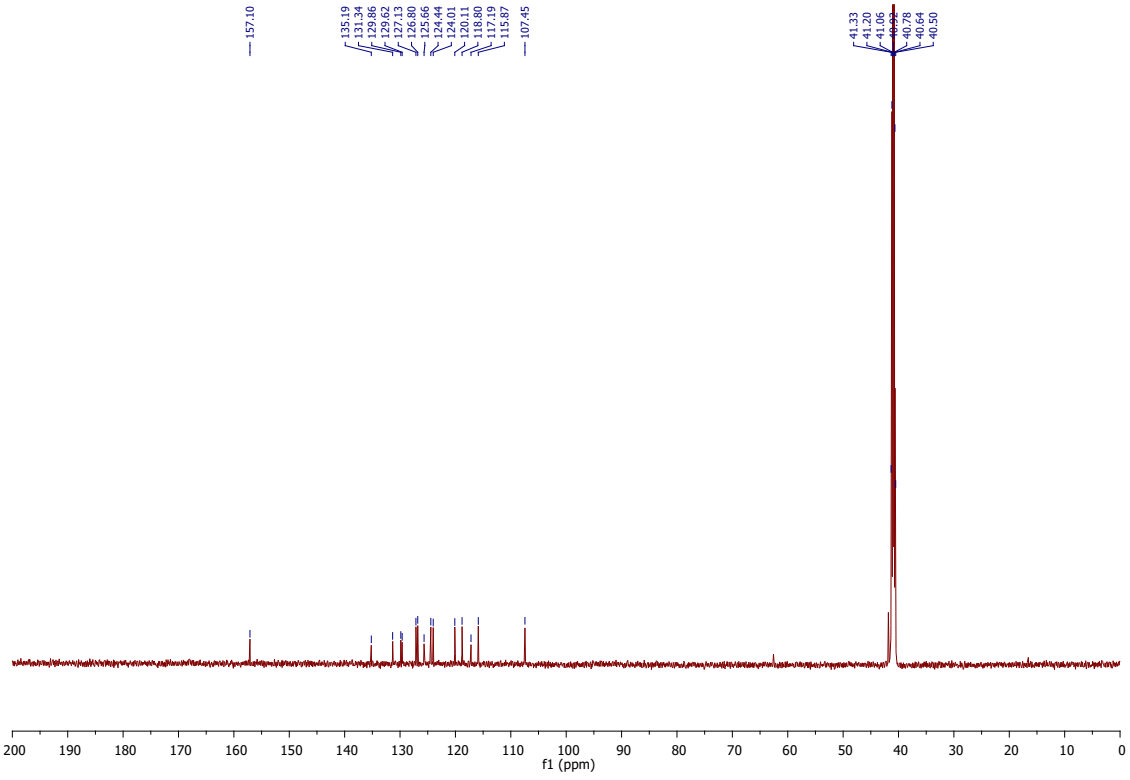
^{13}C NMR (DMSO)



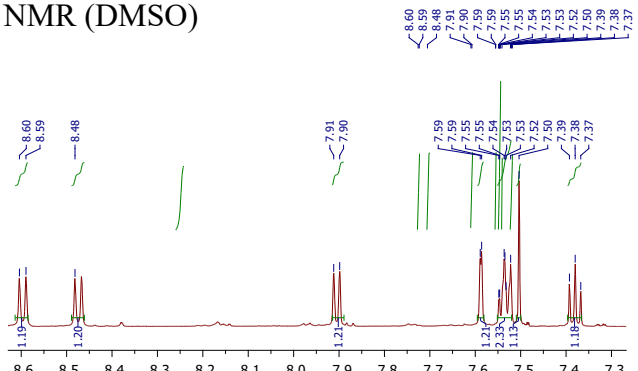
6j ^{1}H NMR (DMSO)

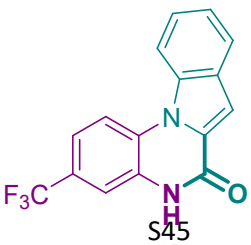


^{13}C NMR (DMSO)



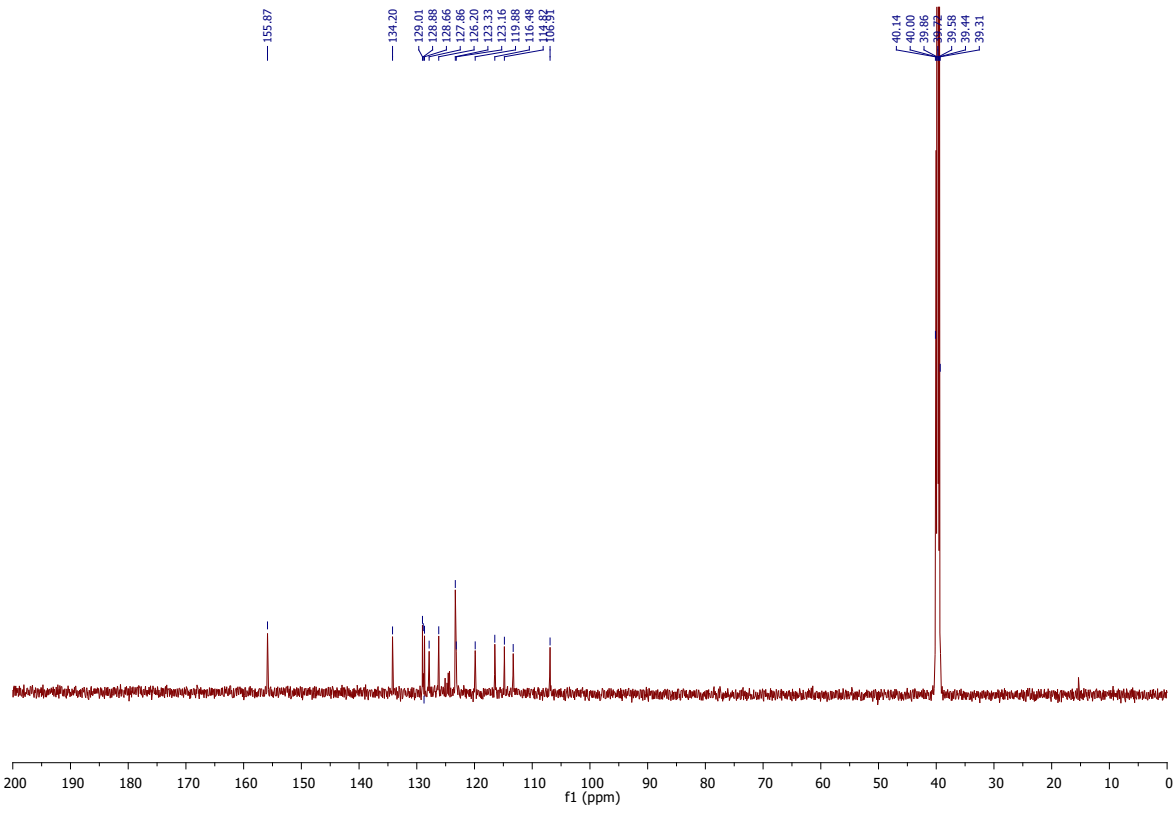
6k ^{1}H NMR (DMSO)



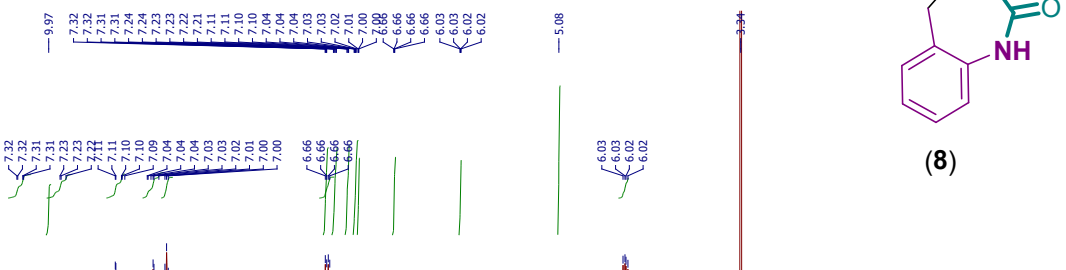


6k

^{13}C NMR (DMSO)

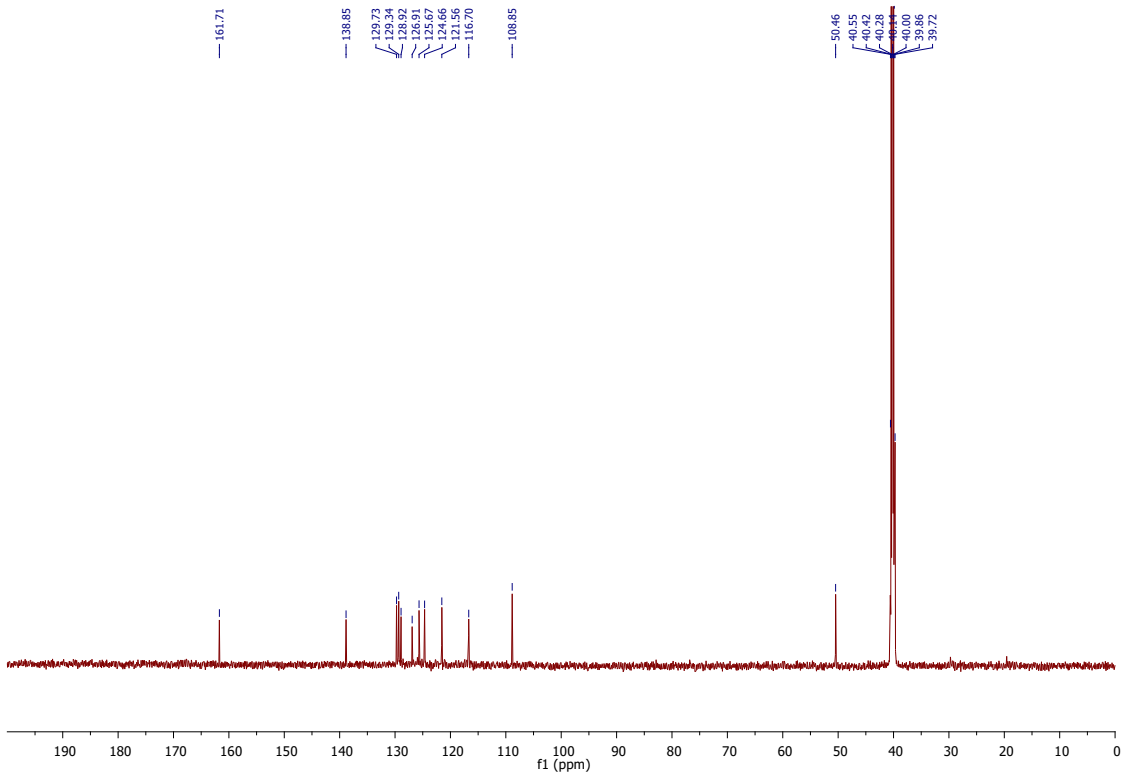


8 ^{1}H NMR (DMSO)

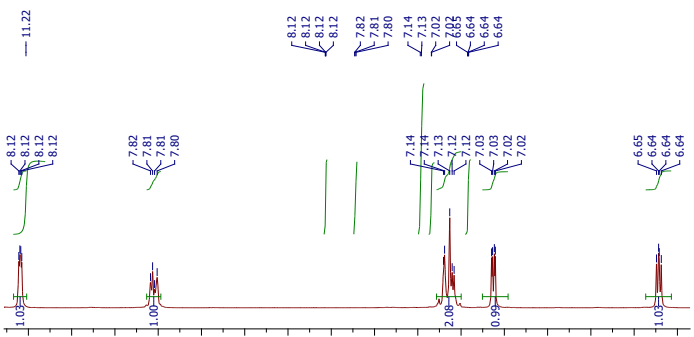


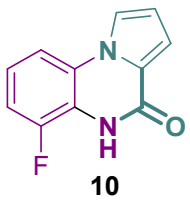
(**8**)

^{13}C NMR (DMSO)



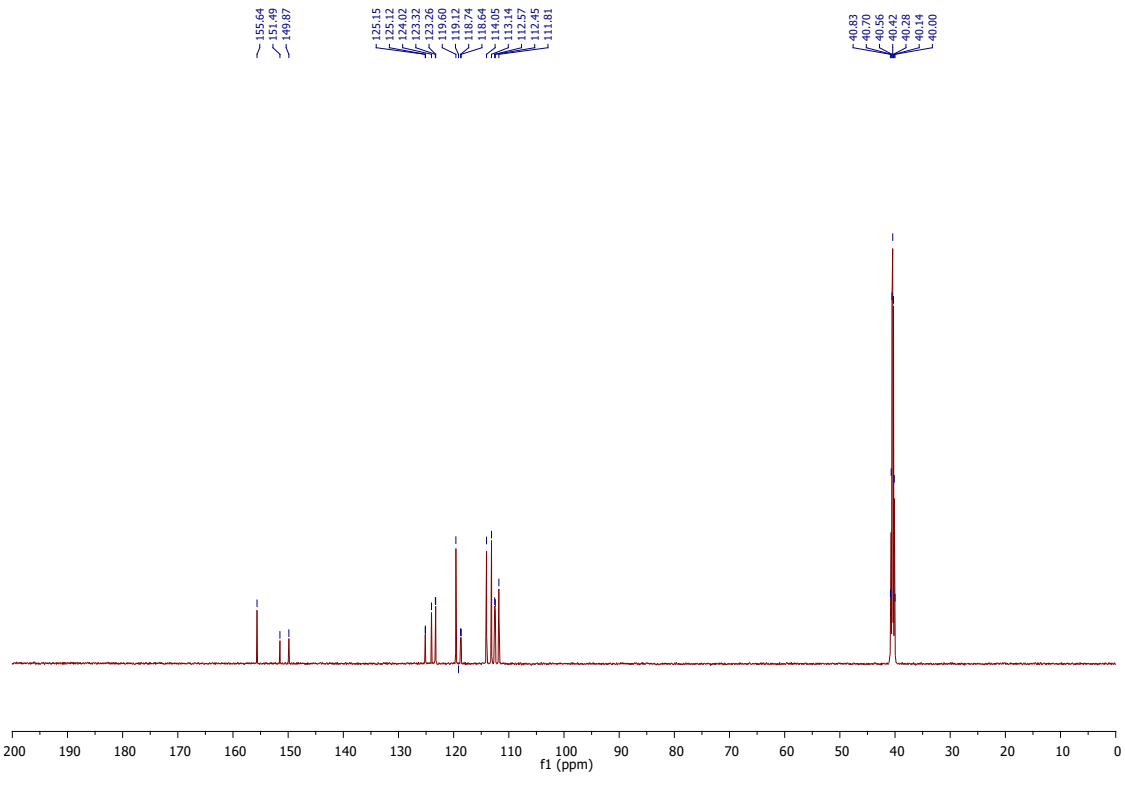
10 ^{1}H NMR (DMSO)



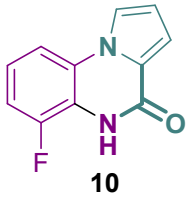


10

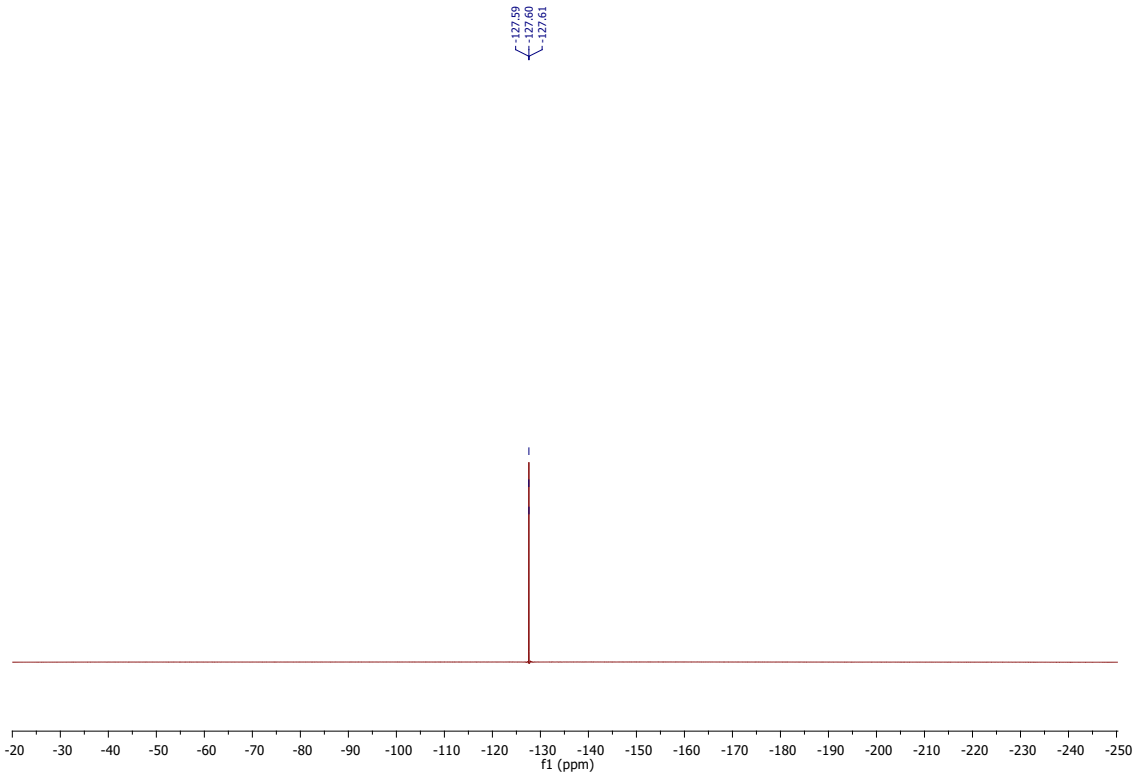
^{13}C NMR (DMSO)



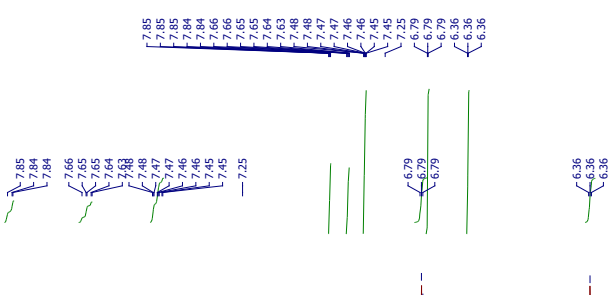
10 ^{19}F{1H} NMR (DMSO)

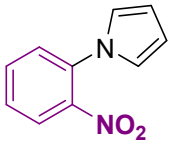


10



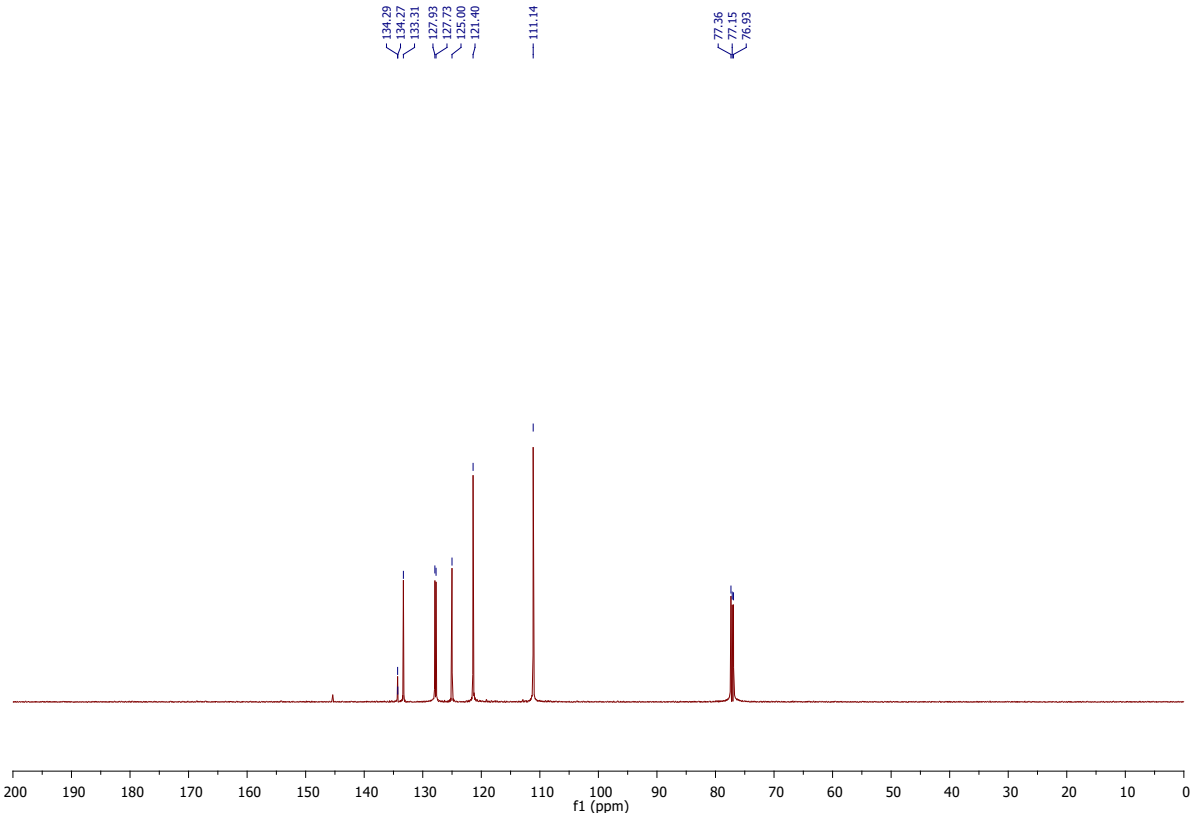
2a ^{1}H NMR ($CDCl_3$)



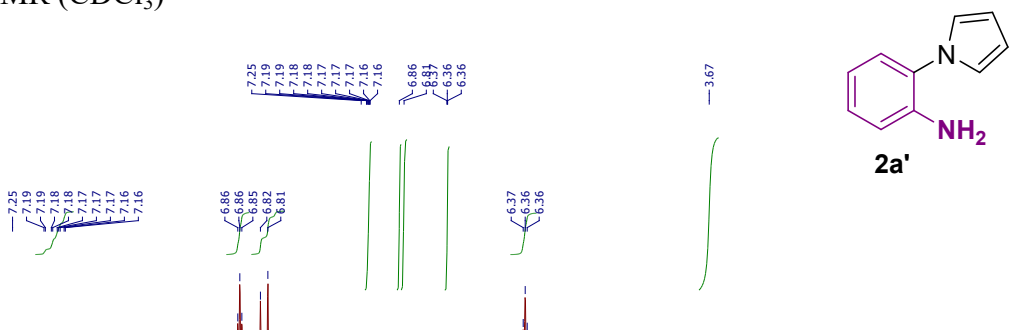


2a

^{13}C NMR ($CDCl_3$)

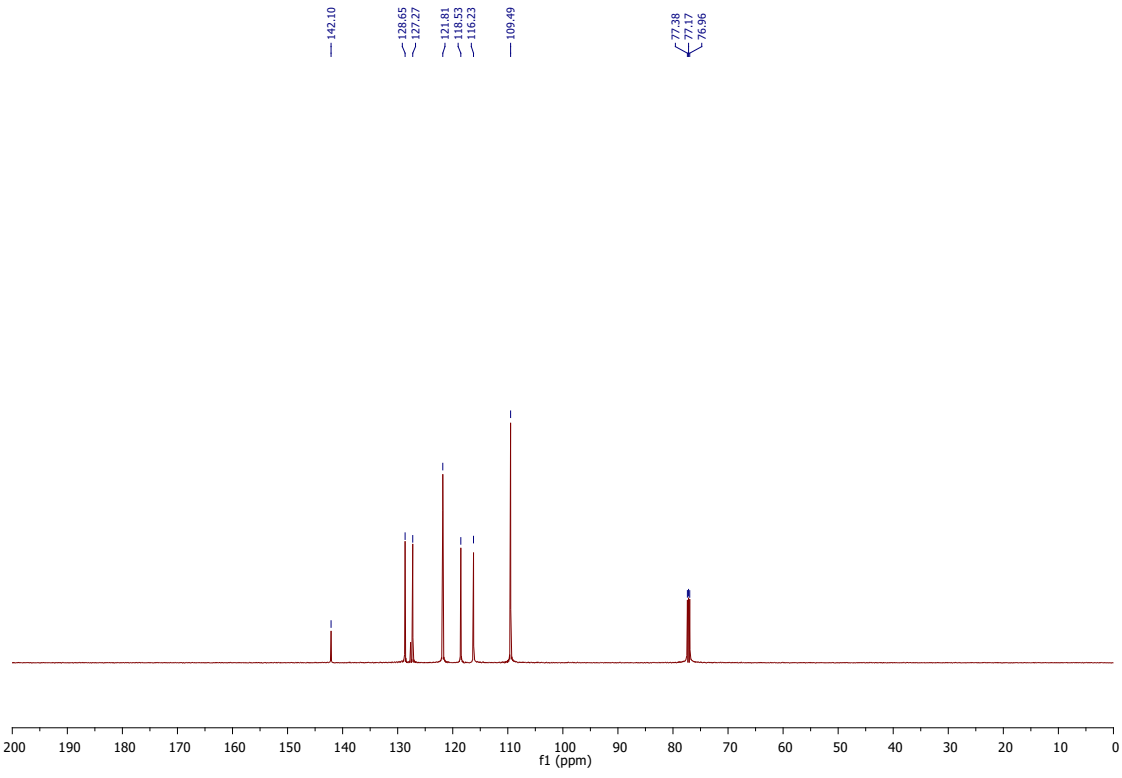


2a´ ^{1}H NMR ($CDCl_3$)

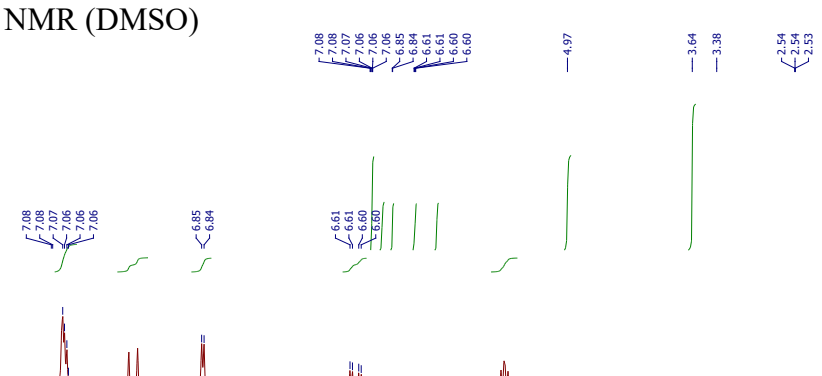


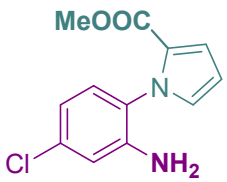
2a'

^{13}C NMR ($CDCl_3$)



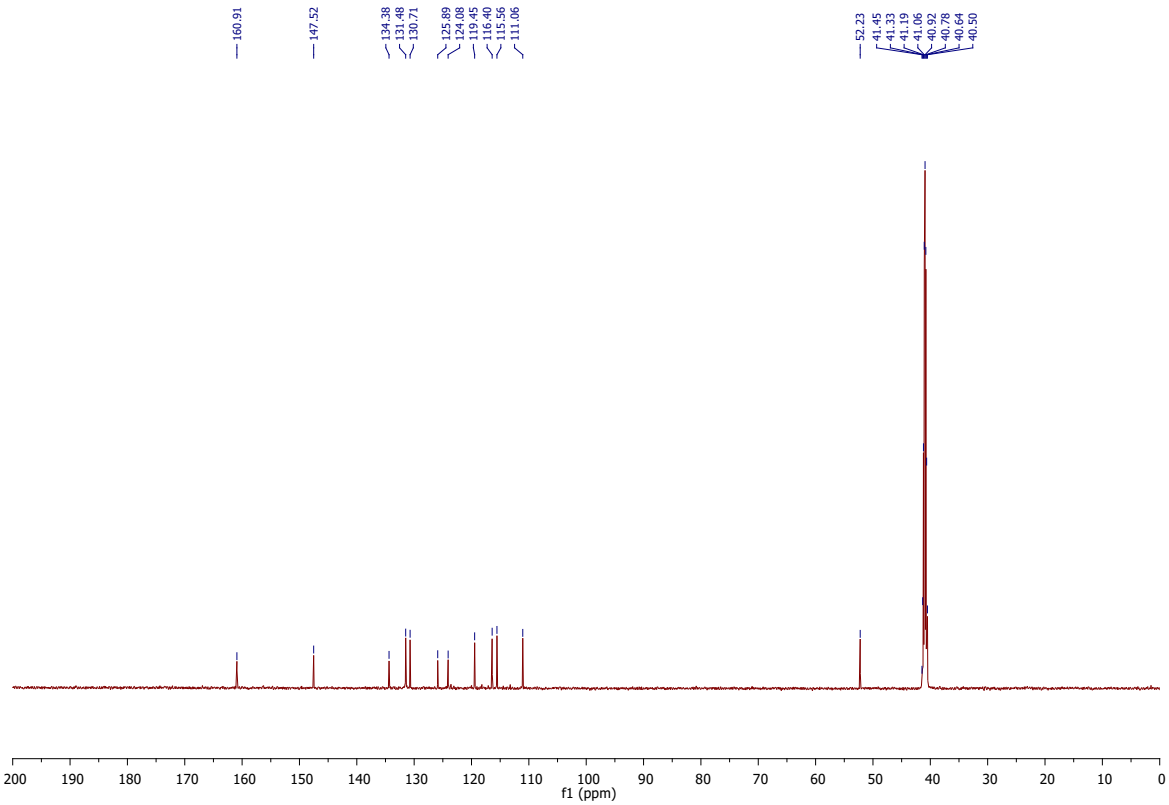
6b´ ^{1}H NMR (DMSO)



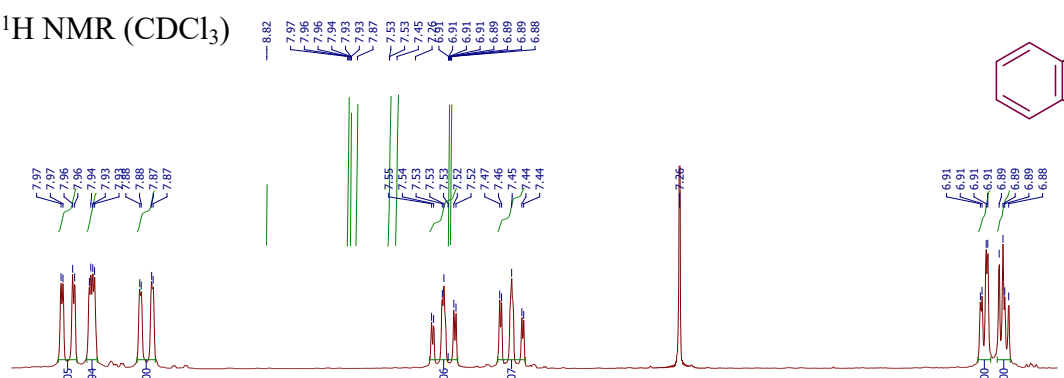


6b'

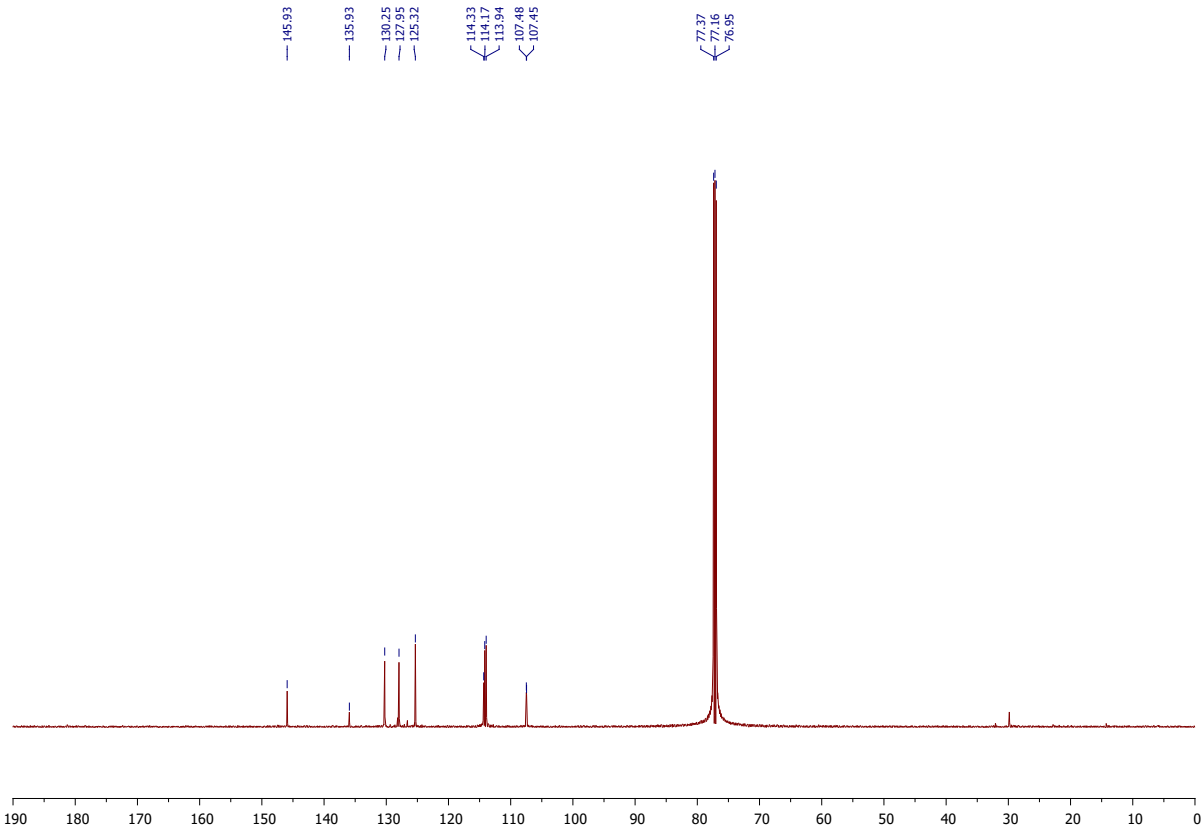
^{13}C NMR (DMSO)



3p ^{1}H NMR ($CDCl_3$)



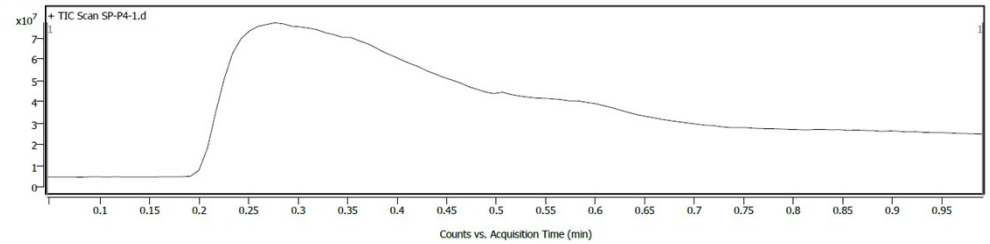
^{13}C NMR ($CDCl_3$)

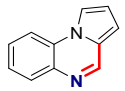


7. MASS SPECTRA

HRMS data of 3a

Sample Chromatograms

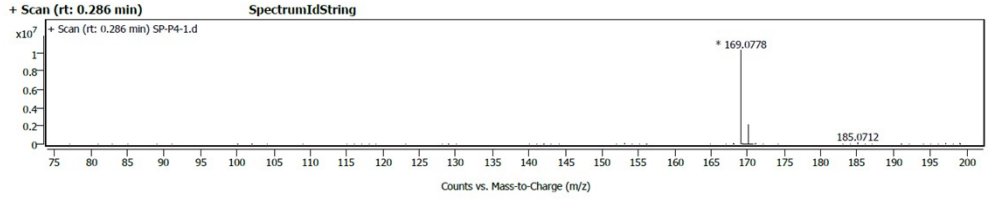




Molecular Formulae $C_{22}H_{16}N_4O$
Exact Mass : 168.0867
$(M+H)^+$: 169.0778 (observed)

Peak Spec

+ Scan (rt: 0.286 min) **SpectrumIdString**

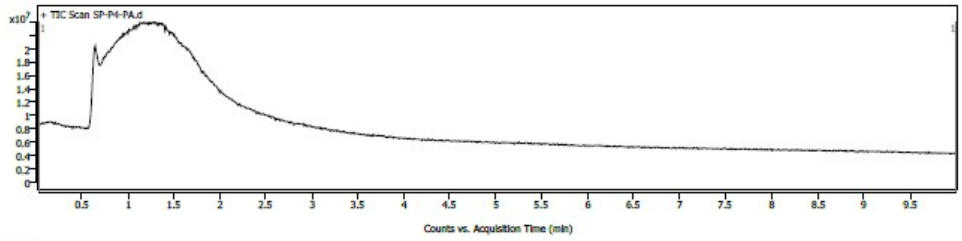


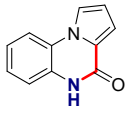
SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
169.0778	1	10325208	100.00					
170.0800	1	2145435	20.78					
171.0829	1	106114	1.03					
185.0712		147543	1.43					

HRMS data of 6a

Sample Chromatograms

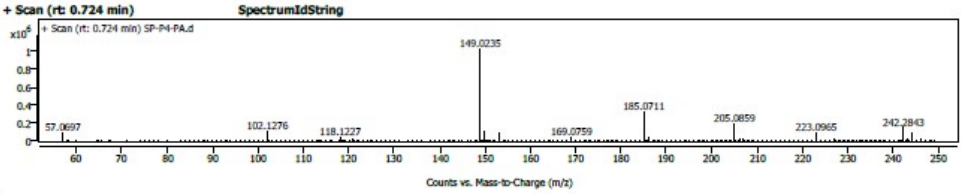




Molecular Formulae $C_{11}H_8N_2O$
Exact Mass : 184.0637
$(M+H)^+$: 185.0711 (observed)

Peak Spec

+ Scan (rt: 0.724 min) **SpectrumIdString**

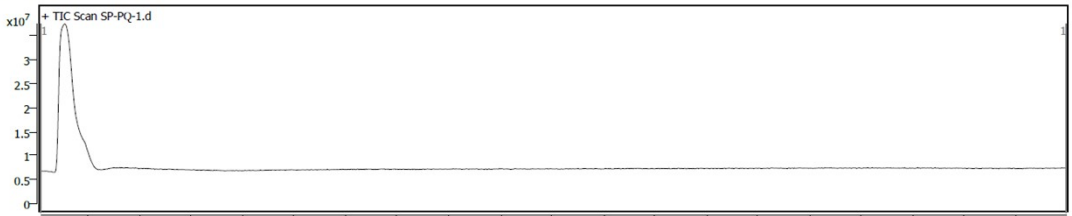


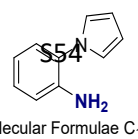
SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
57.0697		83310	8.19					
102.1276		108903	10.71					
118.1227		36737	3.61					
121.0284		27398	2.69					
149.0235	1	1016968	100.00					
149.0387		41942	4.12					
149.0509		49203	4.84					
150.0268	1	98409	9.68					
153.1386		85277	8.39					
169.0759		41311	4.06					
185.0711	1	323808	31.84					
186.0744	1	45037	4.43					

HRMS data of 2a’

Sample Chromatograms

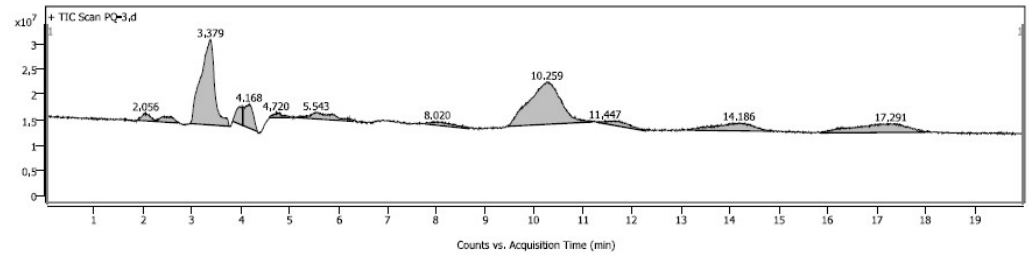


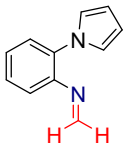


Molecular Formulae $C_{10}H_{10}N_2$
Exact Mass : 158.0844
$(M+H)^+$: 159.0919 (observed)

LCMS data of standard reaction to form 3a

Sample Chromatograms





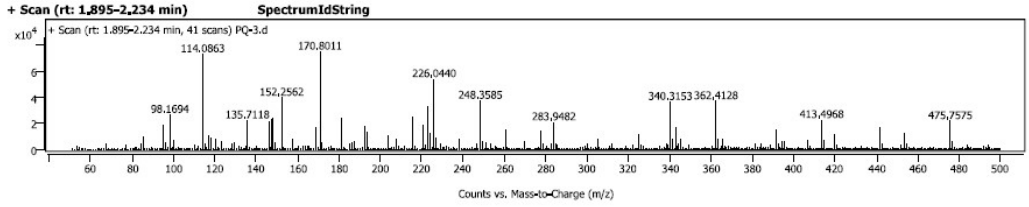
Molecular Formulae $C_{11}H_{10}N_2$
Exact Mass: 170.0844

Chromatogram Peaks

Peak	RT	Height	Area	Area %
1	2.056	1560180	17899572	4.69
2	2,438	1173505	21260012	5,57
3	3,379	17005193	337750619	88,49
4	3,999	3633901	31424129	8.23
5	4.168	4790685	59840670	15.68
6	4.720	1024214	12844032	3.37
7	5,543	1311083	47066883	12,33
8	8.020	795119	24962492	6,54
9	10.259	8434135	381678943	100.00
10	11.447	604176	29866075	7.82
11	14,186	1627907	84351486	22,10
12	17,291	1755375	130761199	34,26

Peak Spec

+ Scan (rt: 1,895-2,234 min) **SpectrumIdString**



SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
95.0350		18983	25,34					
98.1694		26530	35,41					
114.0863		73031	97,47					
135.7118	2	22191	29.62					
146.0312		20923	27,93					
147.1565		22967	30,65					
148.1724		23520	31.39					
152.2562		39632	52.90					
170.8011		74925	100.00					