

# **A reaction of aroyl(heteroaroyl)pyruvic acid esters with 3,3-diaminoacrylonitriles: a new method for the synthesis of pyrroles with conjugated exocyclic double bonds**

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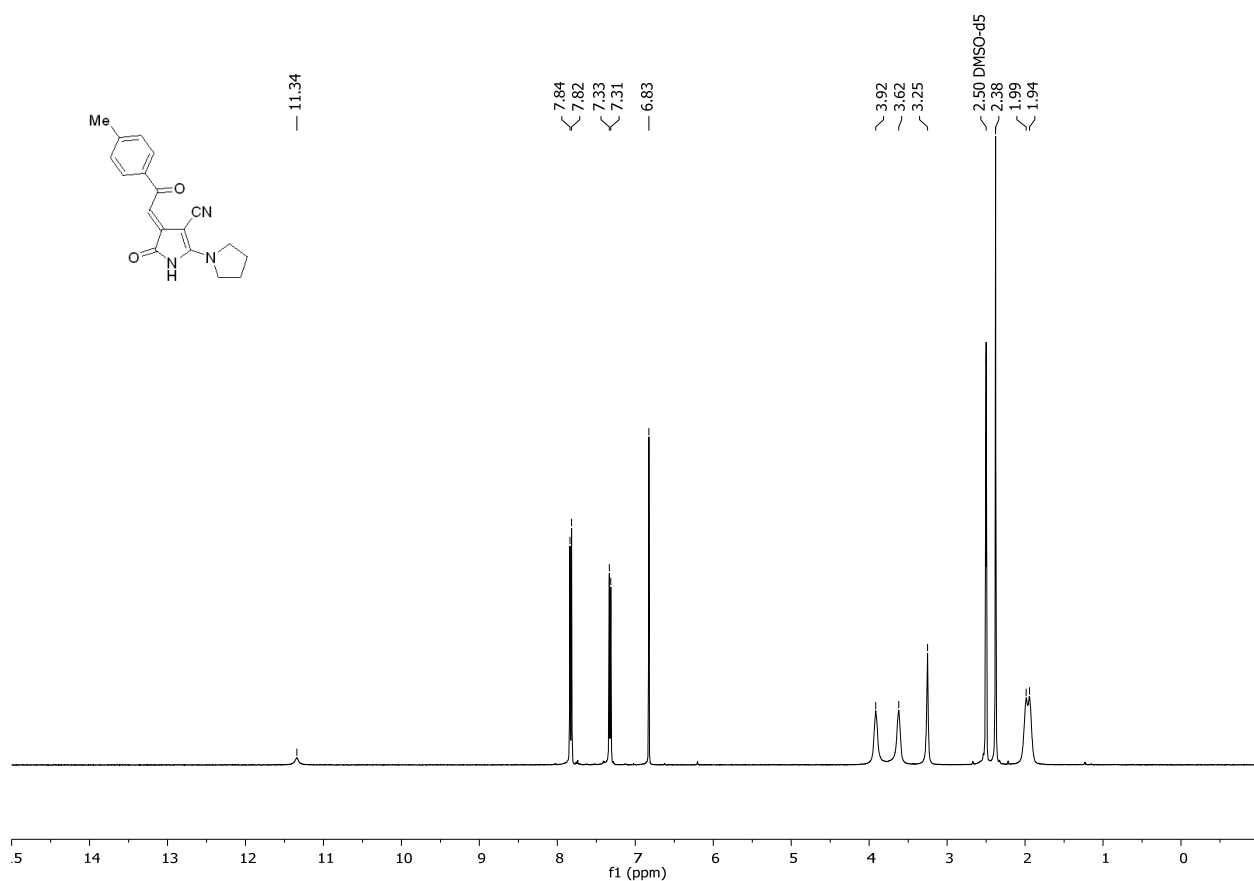
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<sup>2</sup> Perm Institute (branch) of the Russian University of Economics named after G. V. Plekhanov,  
57 Gagarin Blvd., Perm 614070, Russia; e-mail: lanselot2001@inbox.ru

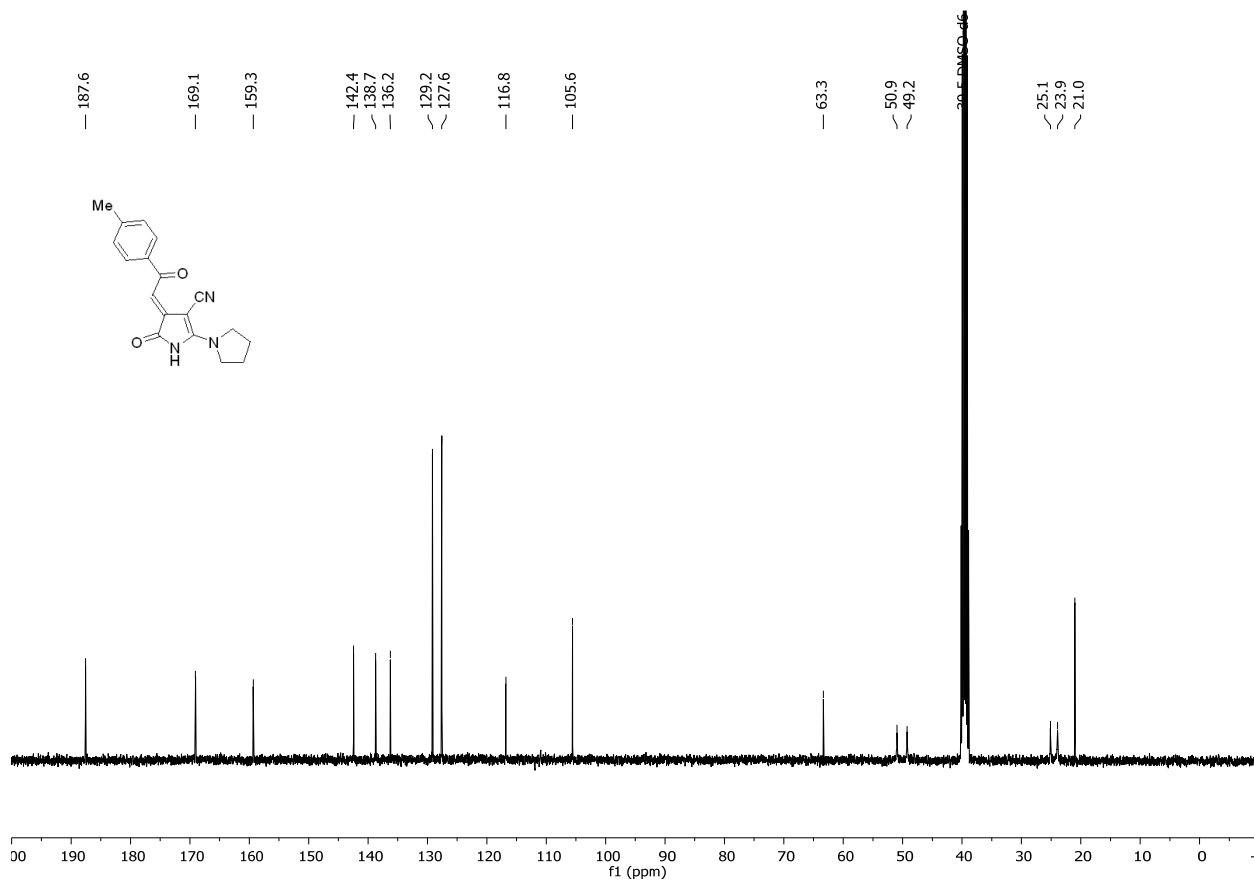
<sup>3</sup> Ural Federal University,  
19 Mira St., Yekaterinburg 620002, Russia; e-mail: v.a.bakulev@urfu.ru

SUPPLEMENTARY INFORMATION

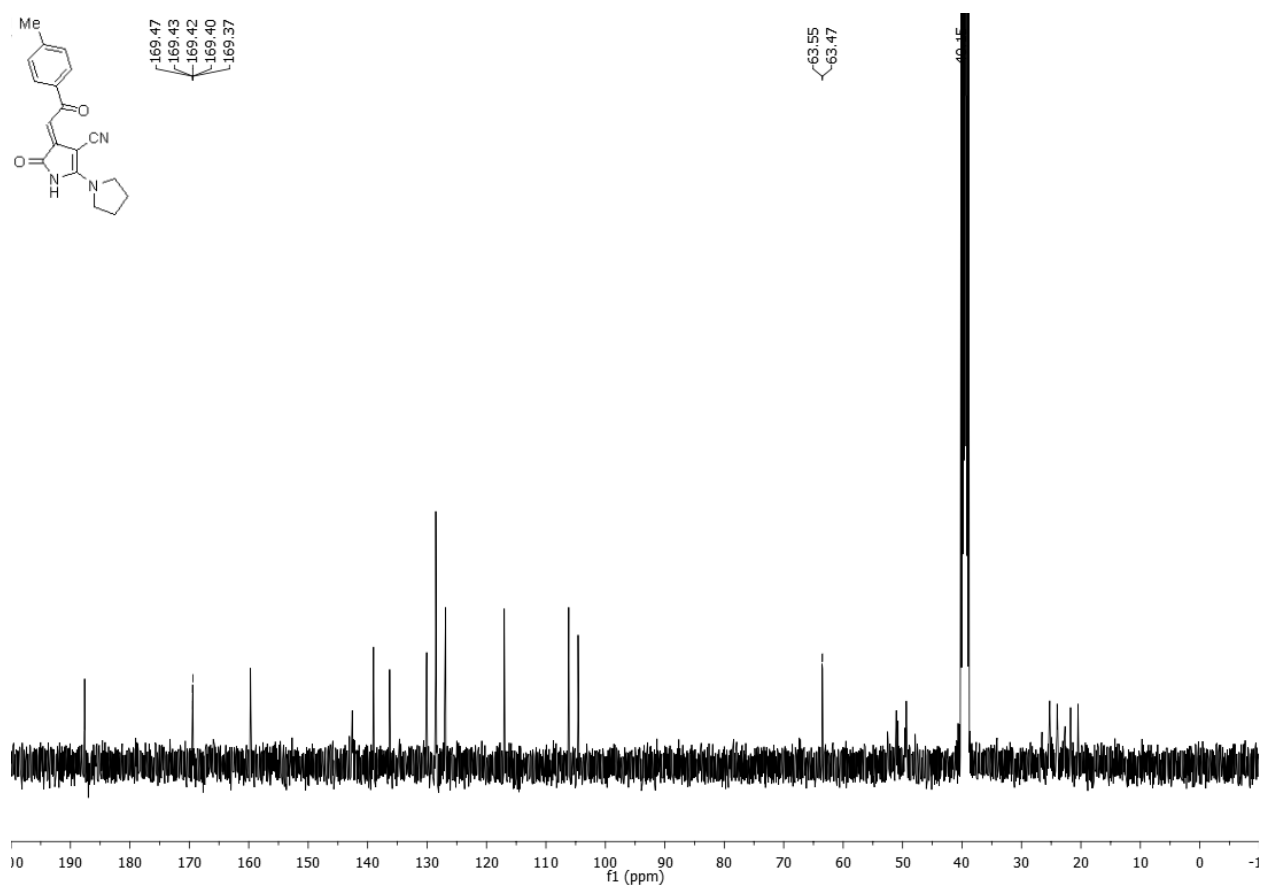
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3a**



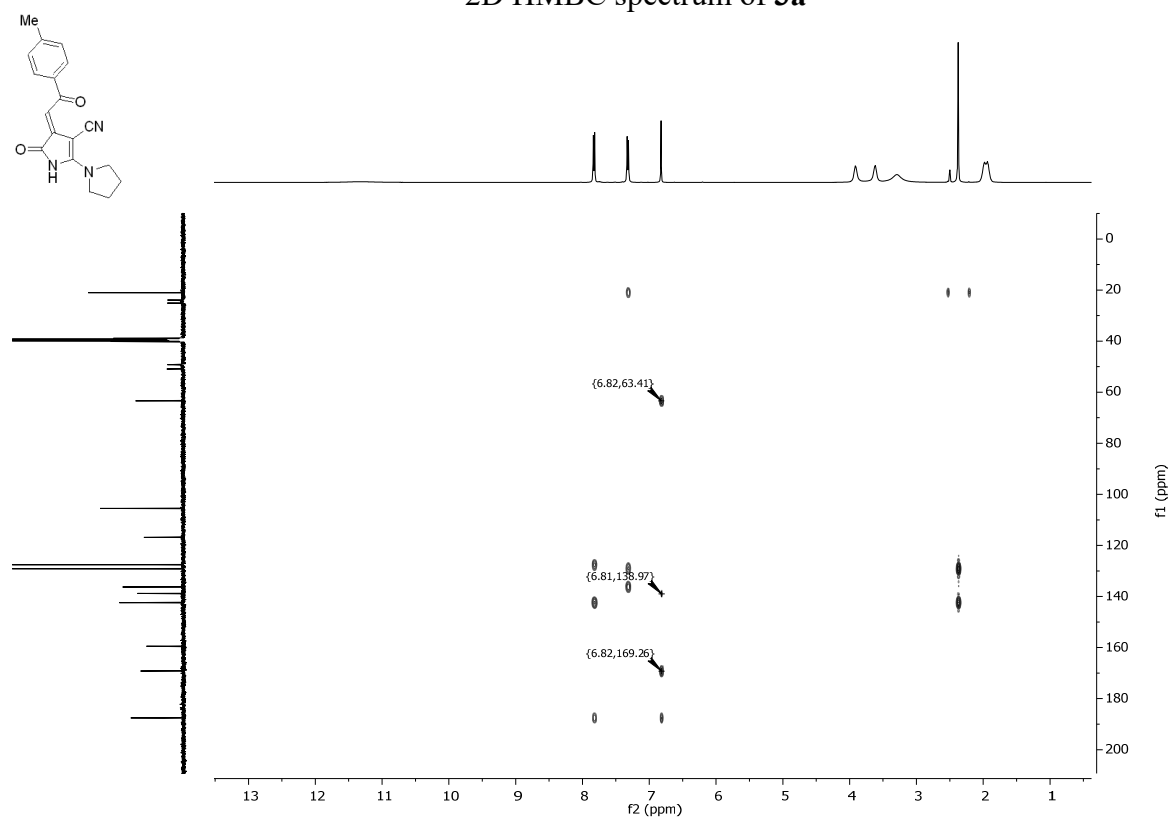
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3a**



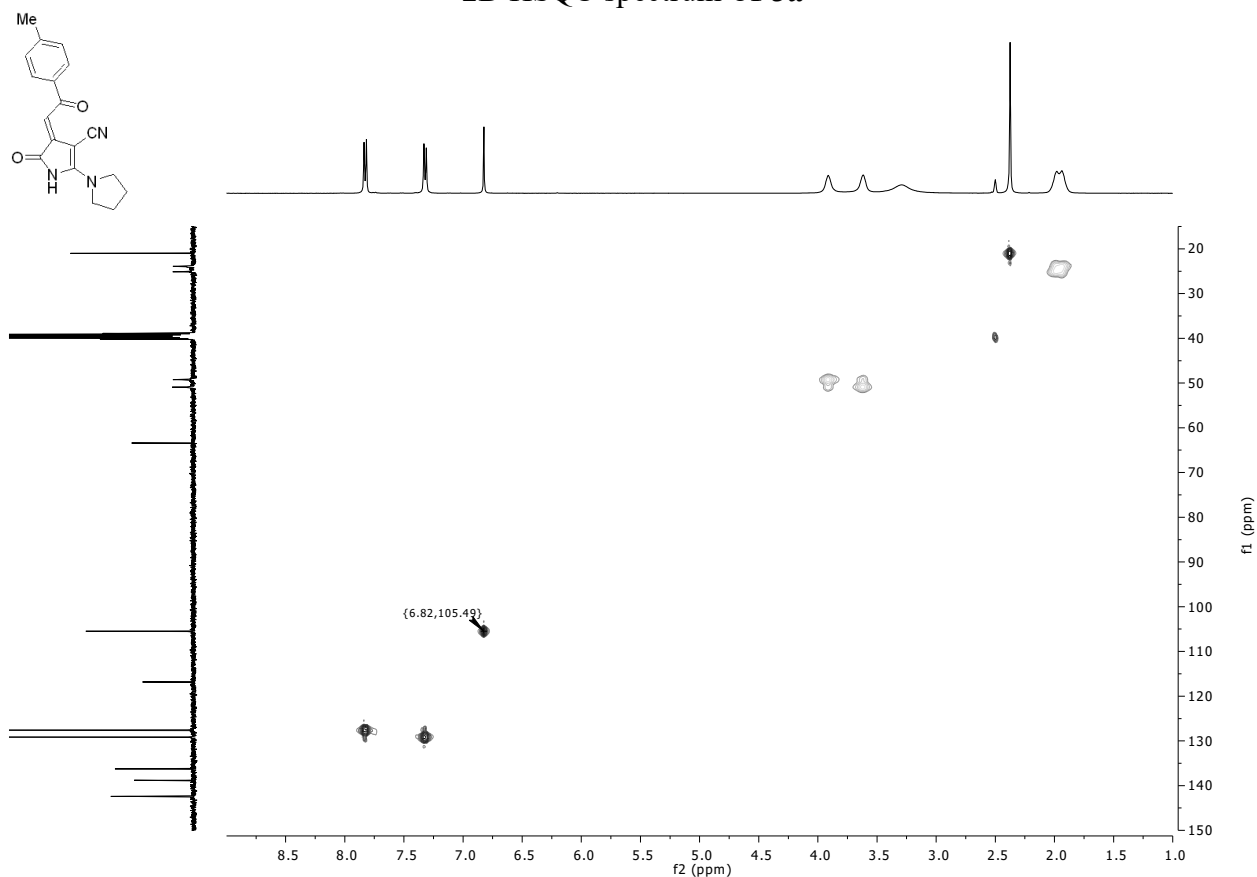
<sup>13</sup>C GATE NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3a**



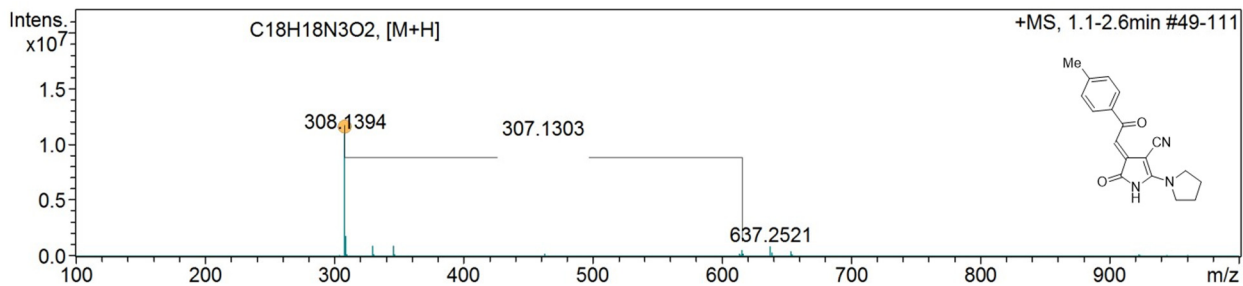
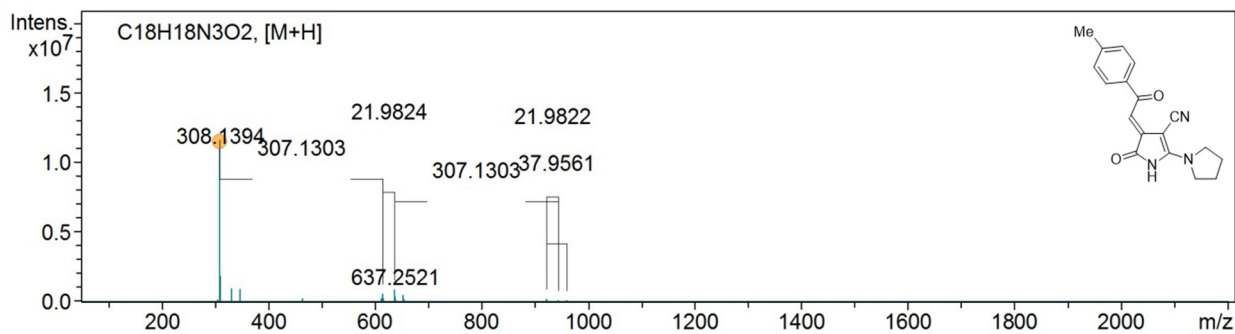
2D HMBC spectrum of **3a**



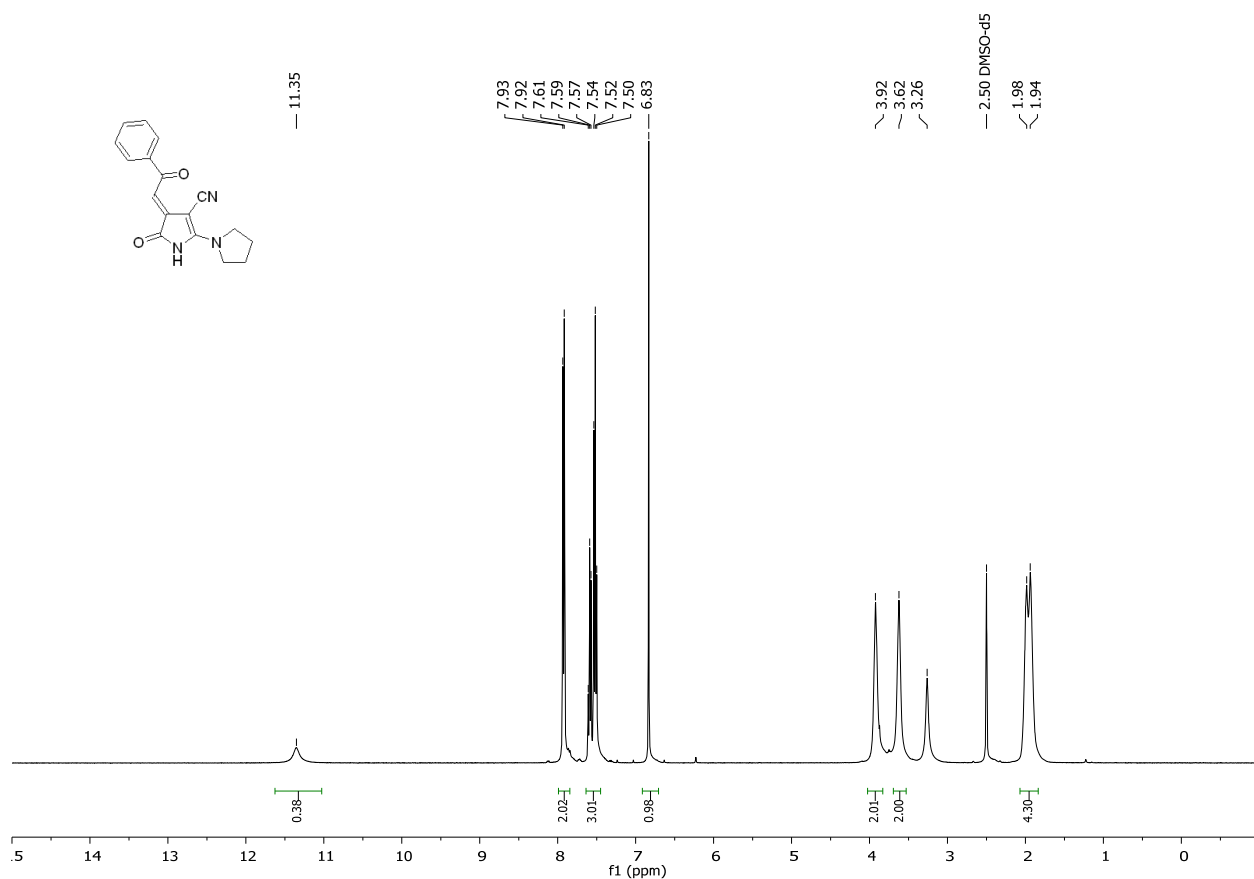
### 2D HSQC spectrum of 3a



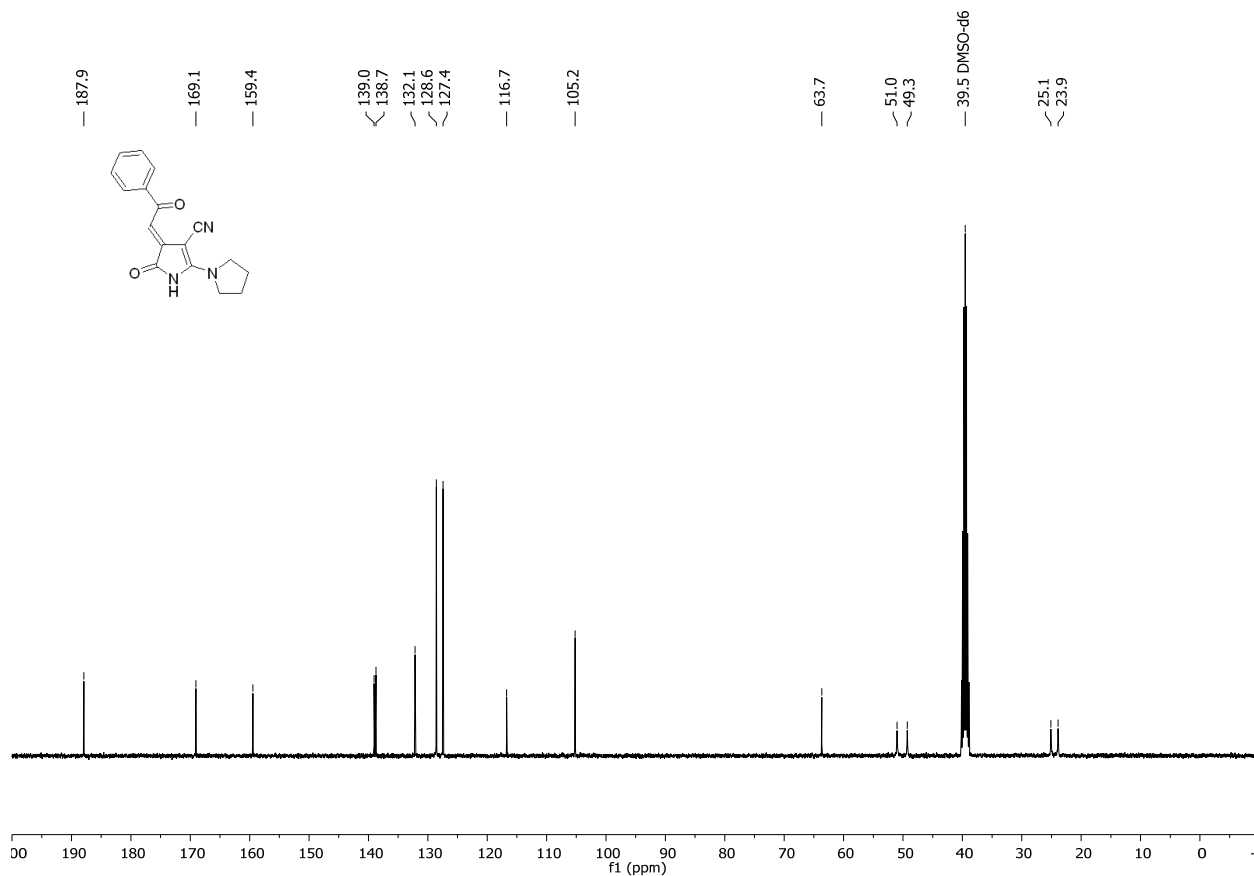
### HRMS spectrum of 3a



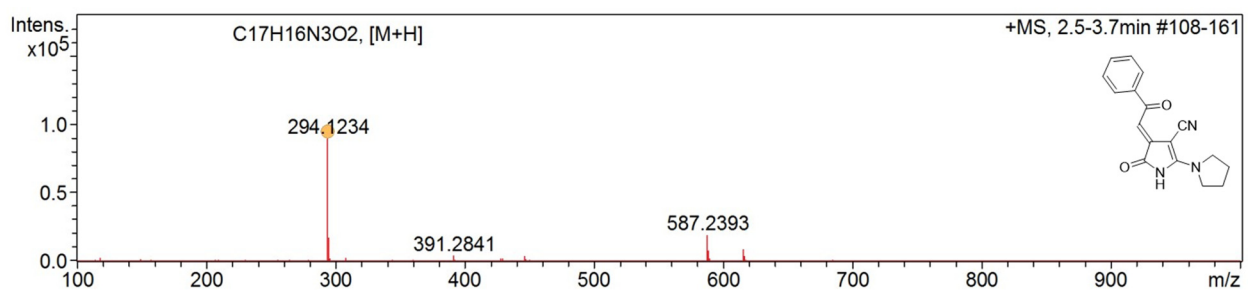
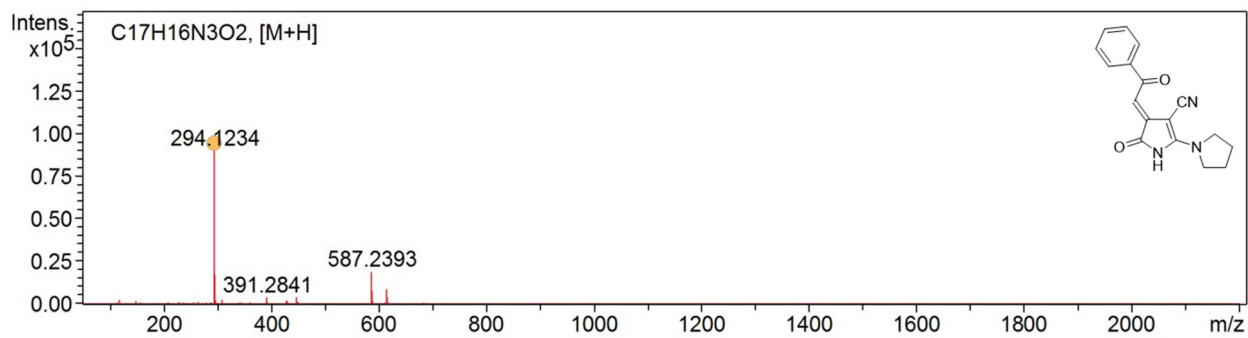
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3b**



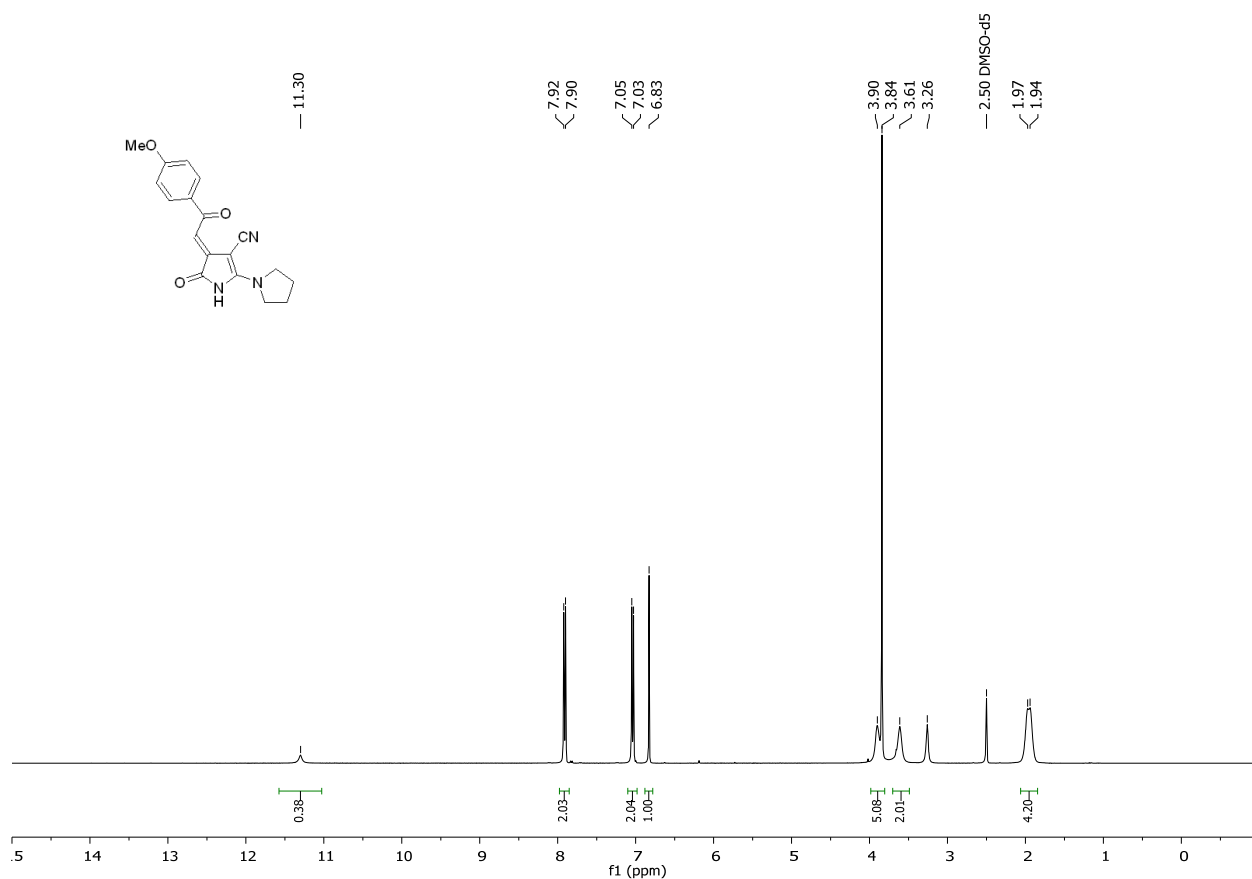
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3b**



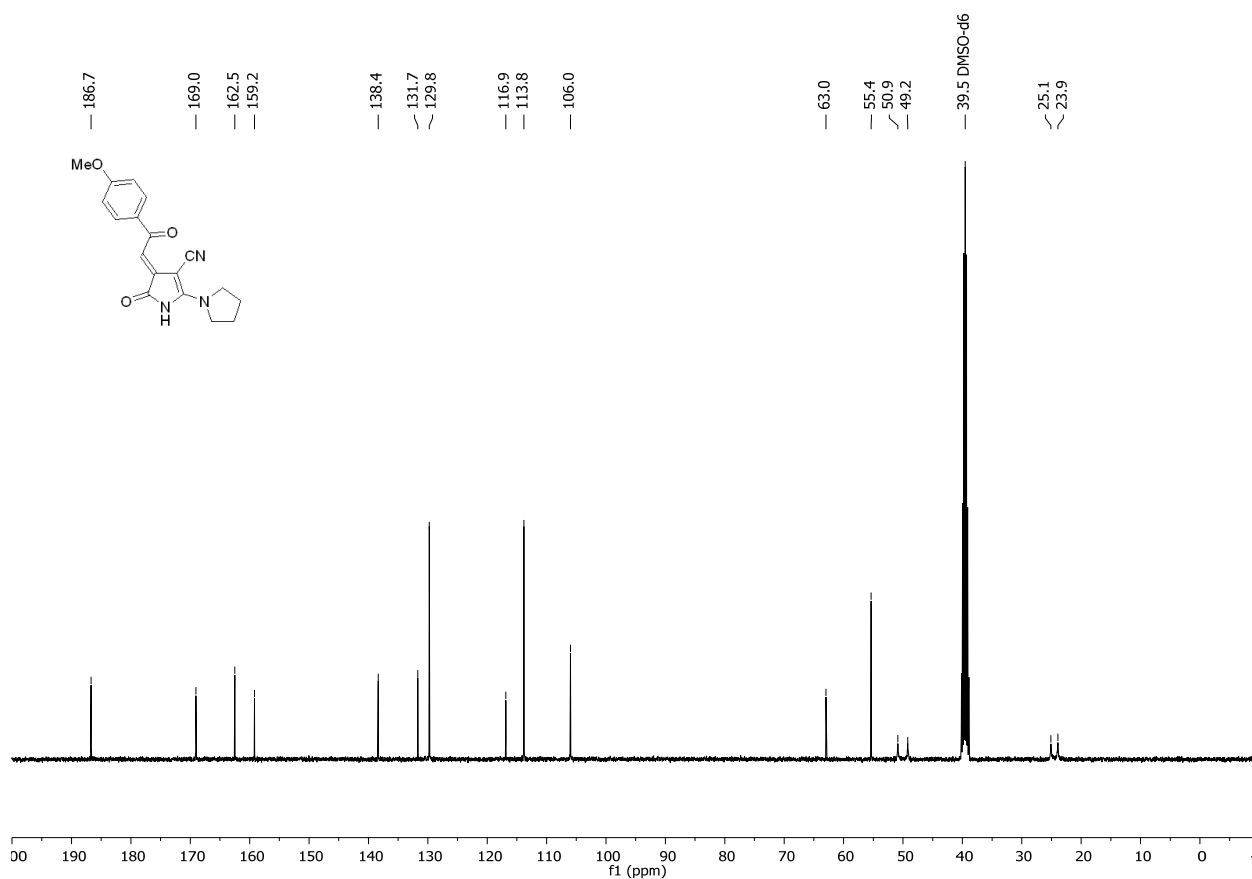
# HRMS spectrum of **3b**



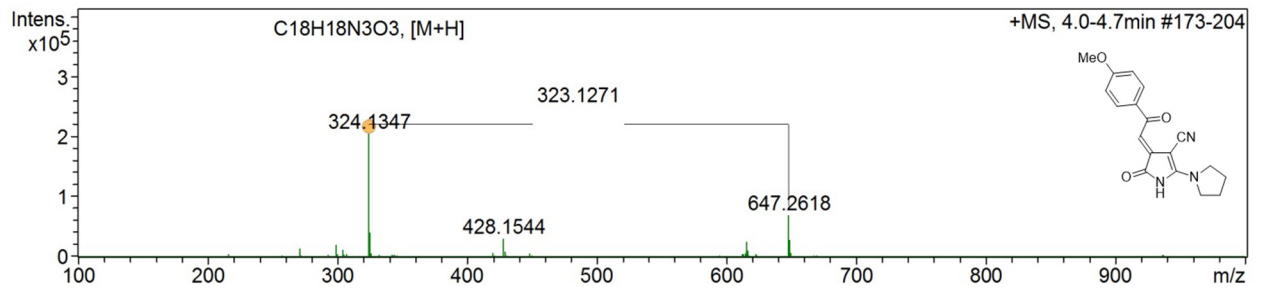
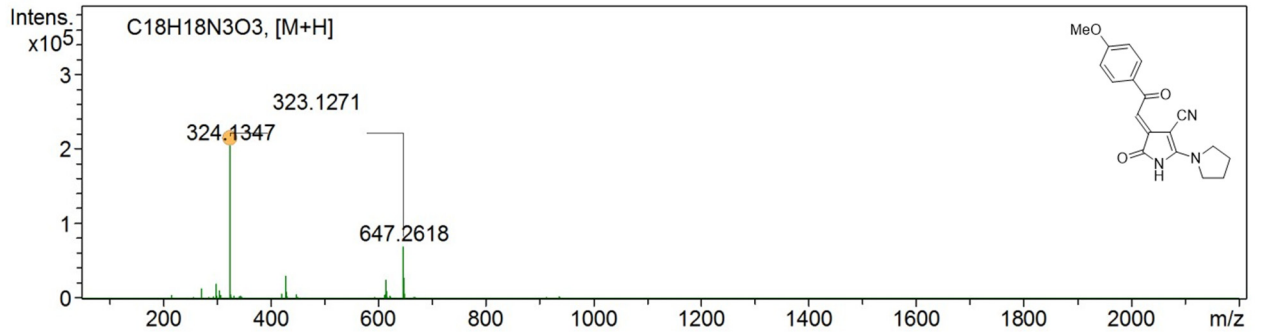
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3c**



<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3c**

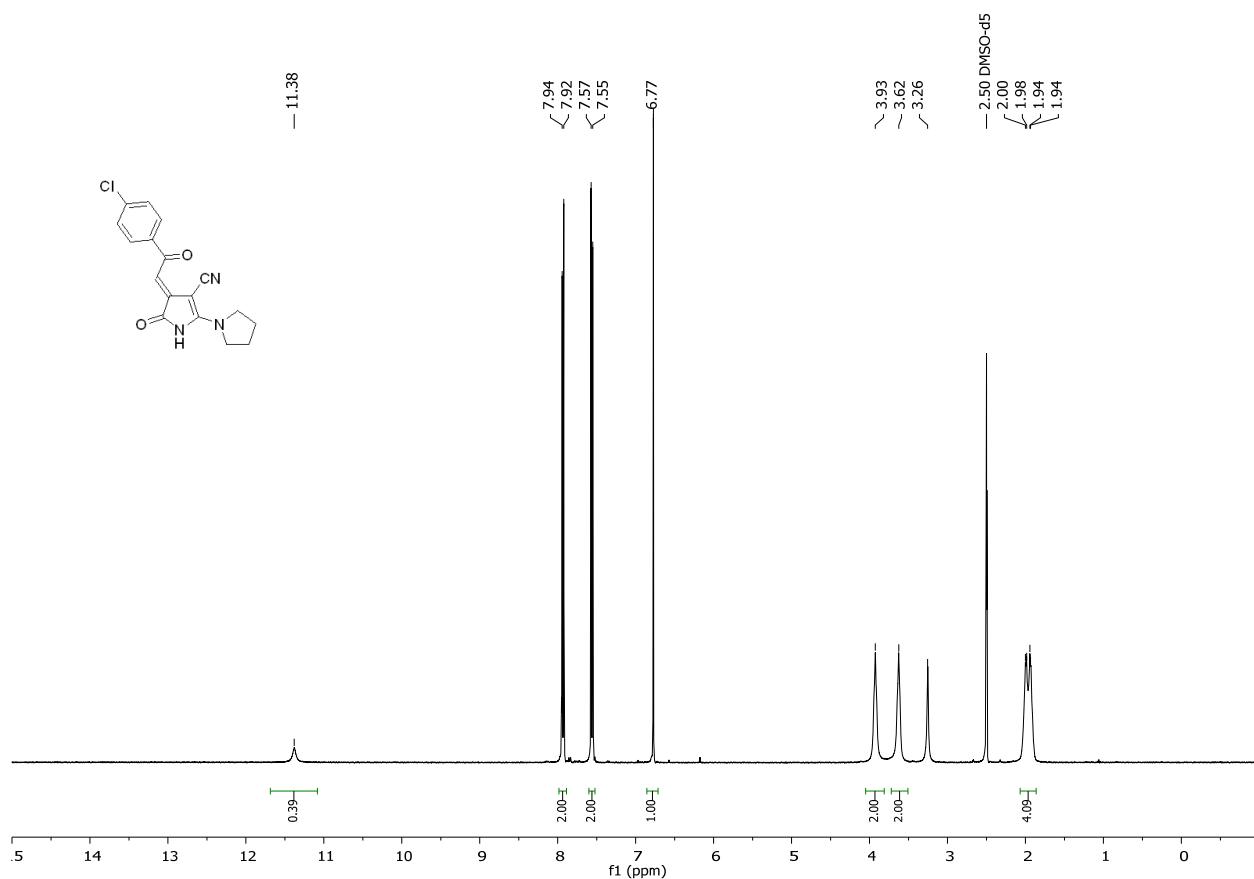


# HRMS spectrum of 3c

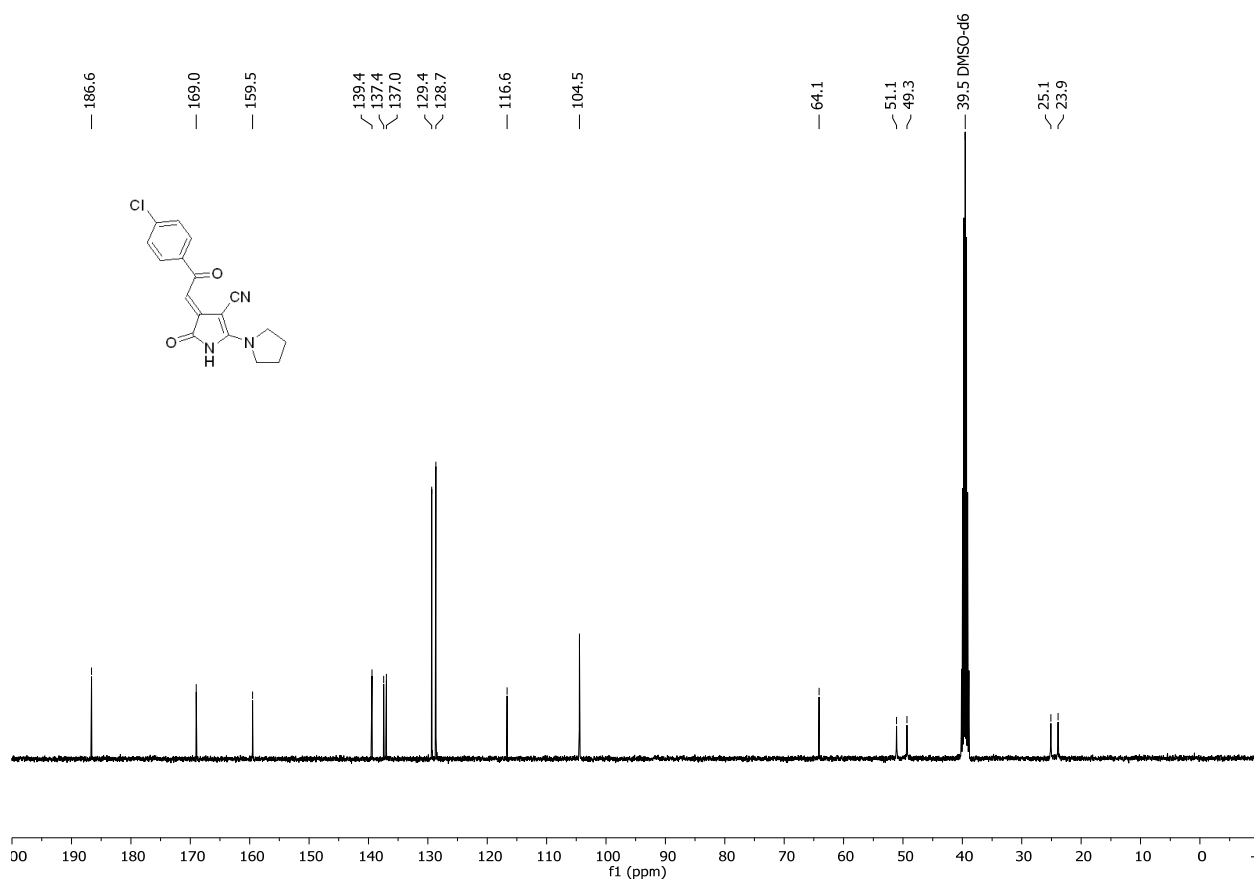




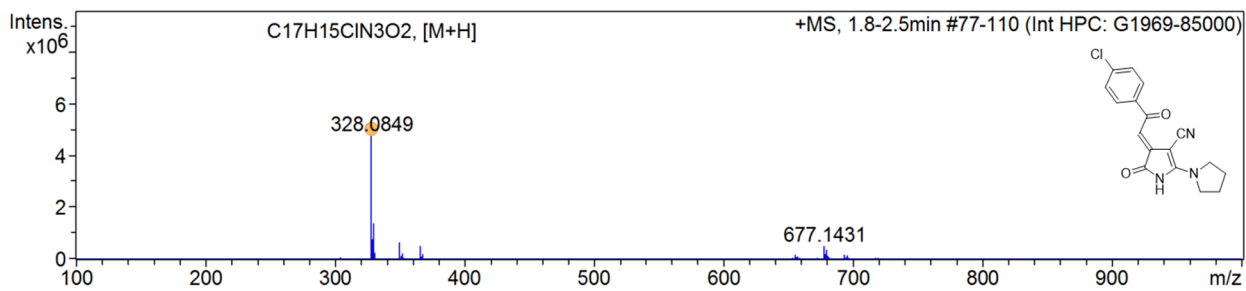
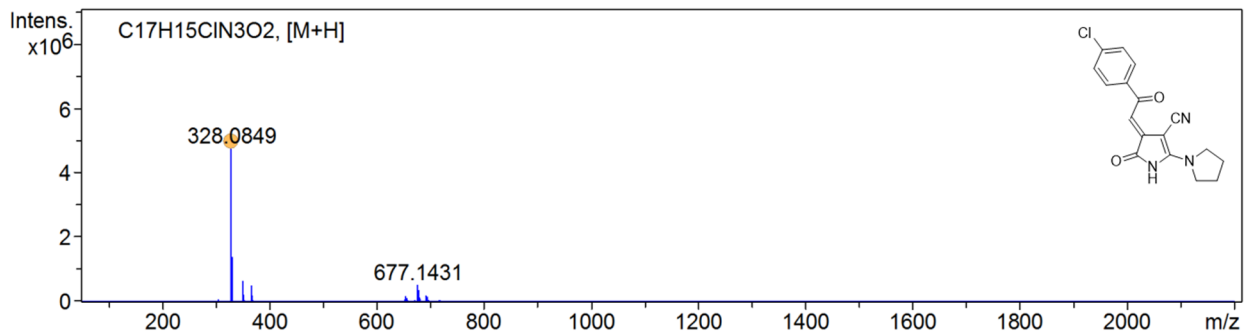
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3d**



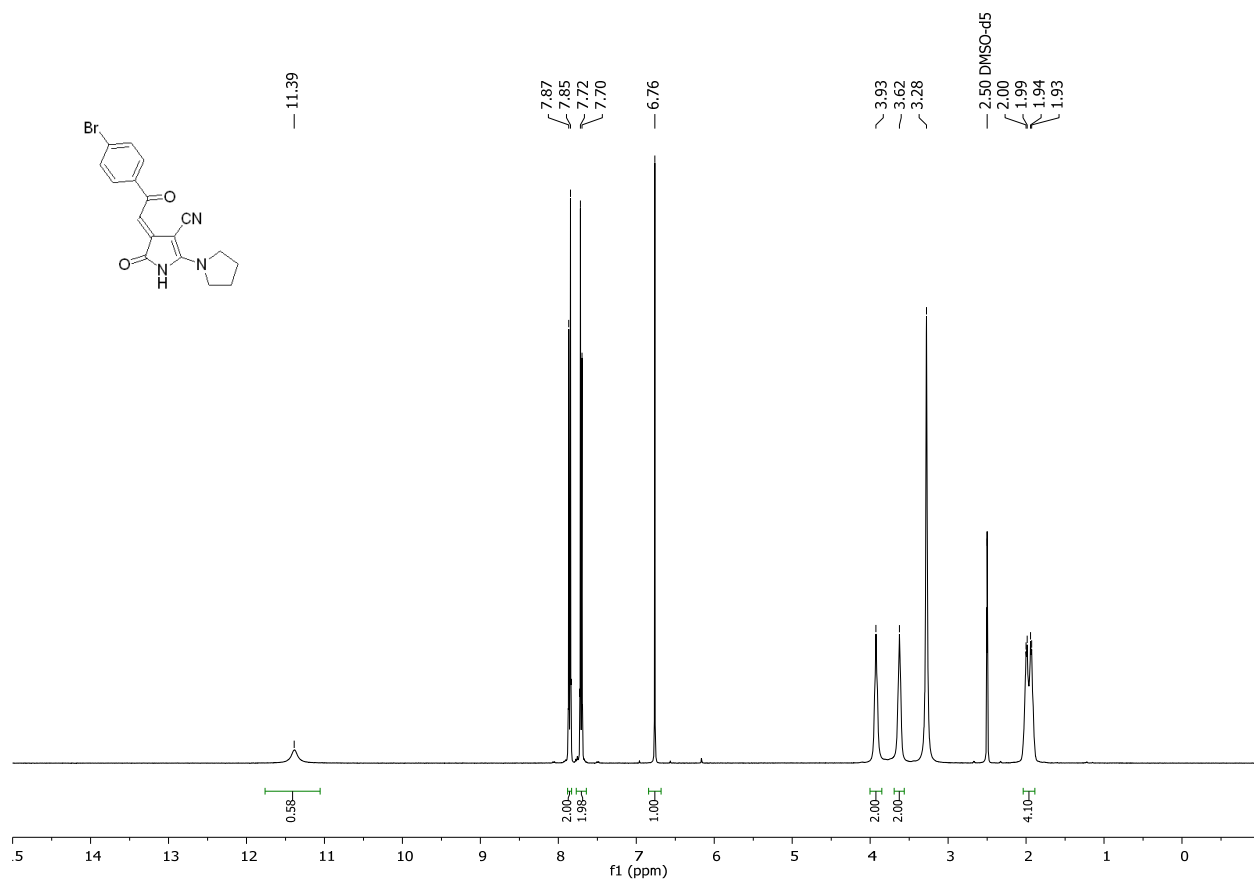
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3d**



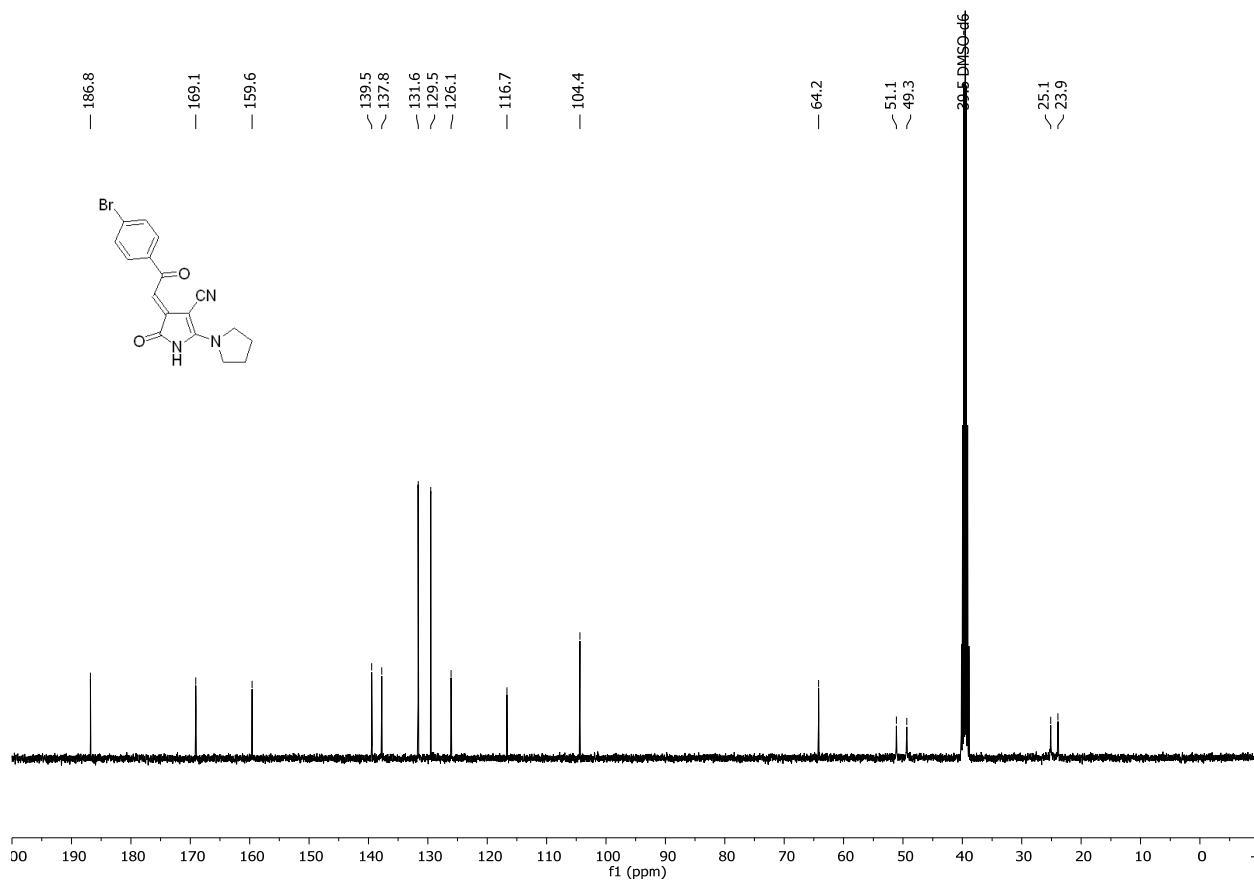
# HRMS spectrum of **3d**



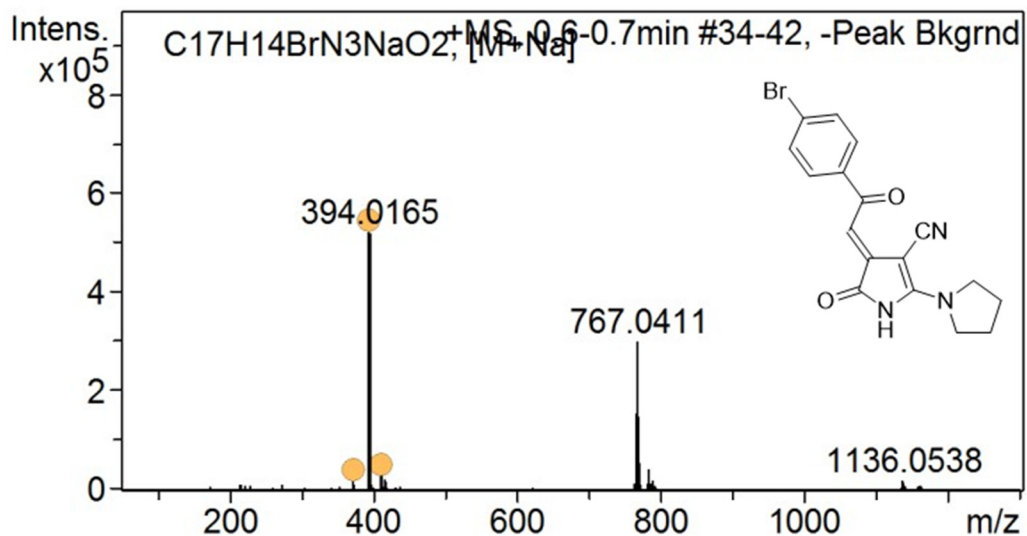
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3e**



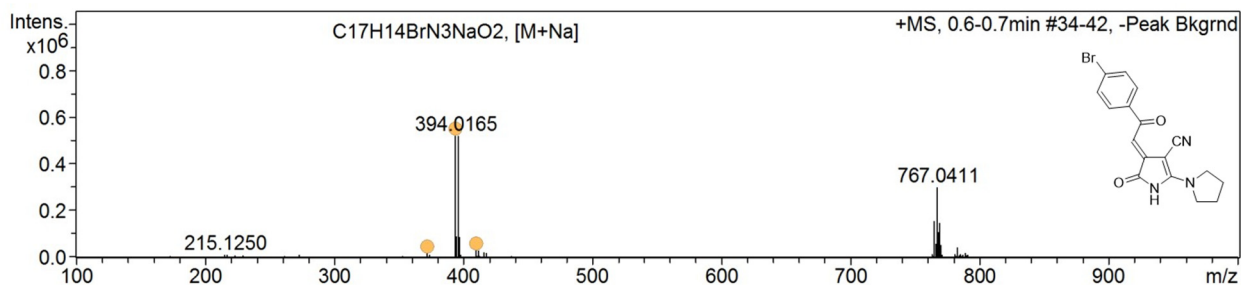
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3e**



HRMS spectrum of **3e**

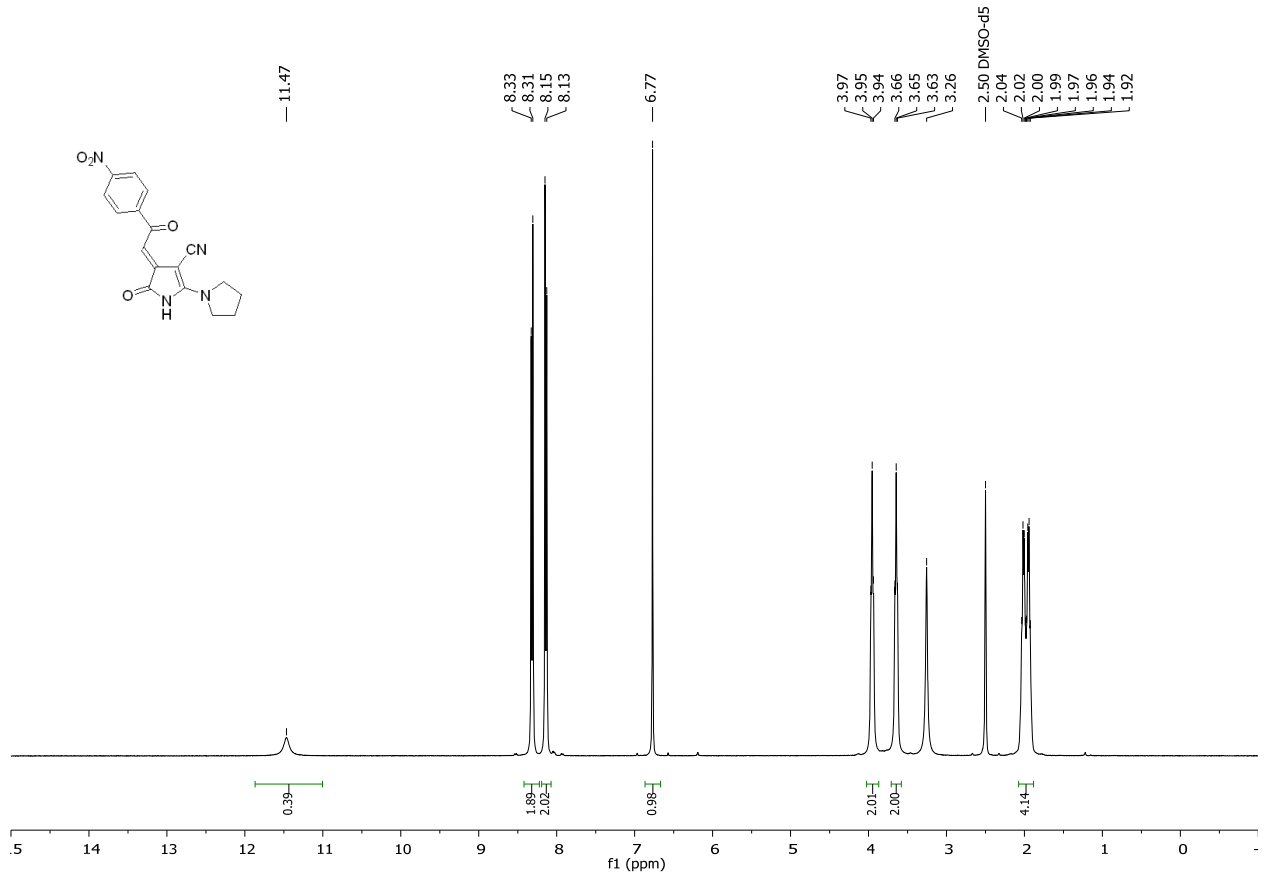


#	m/z	Res.	S/N	I	I %	FWHM
1	394.0165	29871	450789472.0	518467	100.0	0.0132

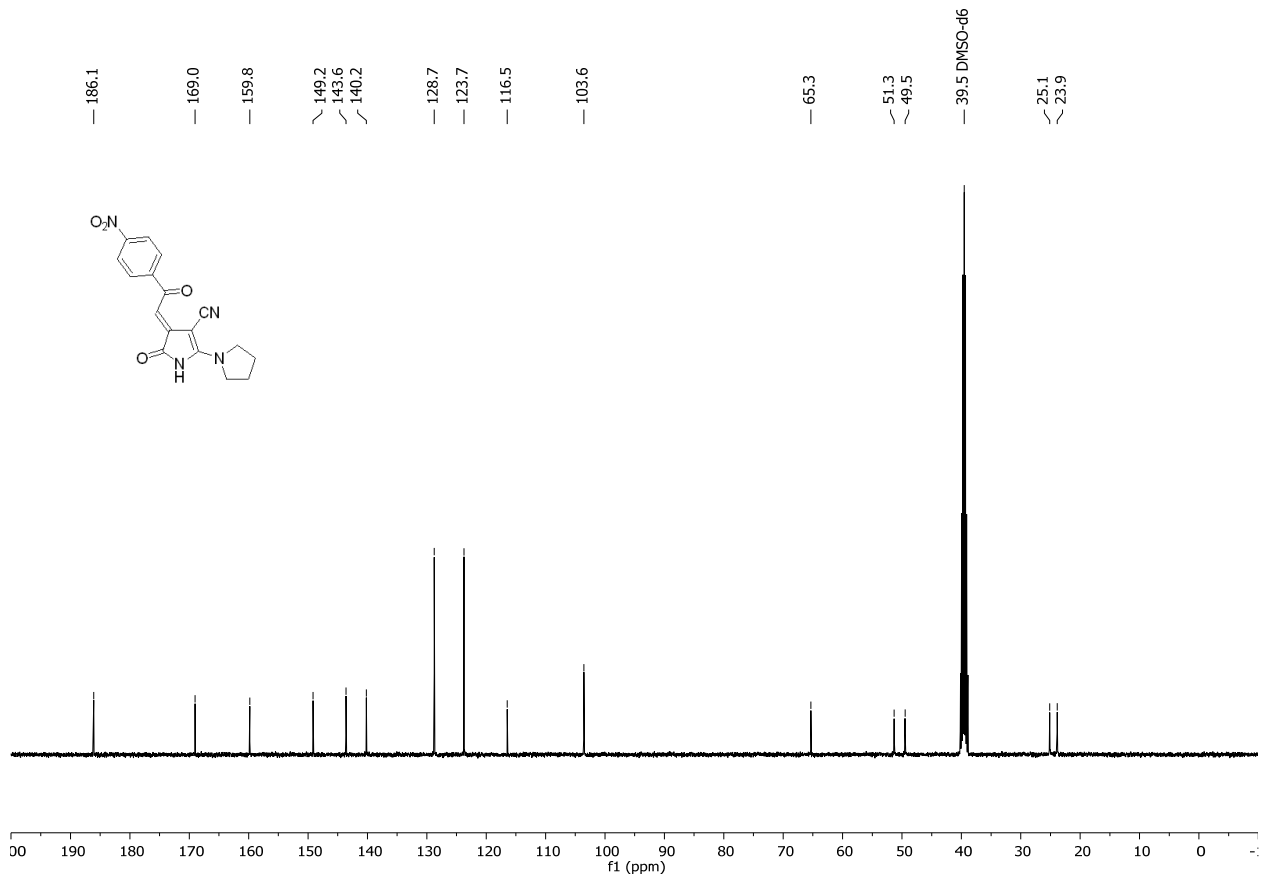


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
372.0329	1	C17H15BrN3O2	372.0342	3.7	157.5	1	100.00	11.5	even	ok

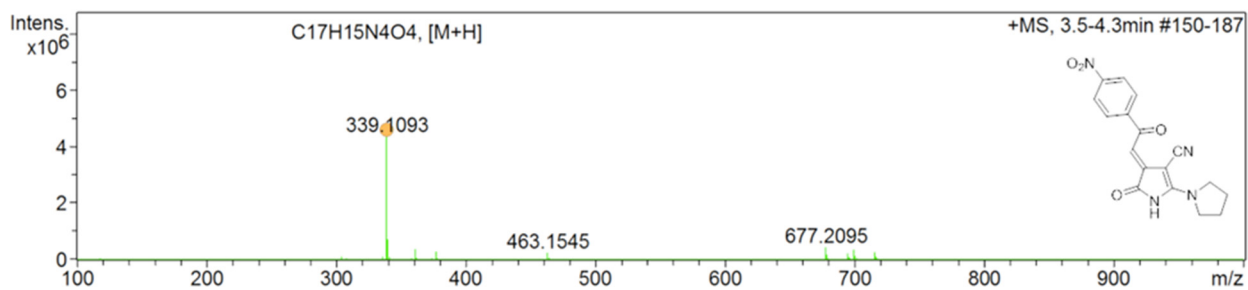
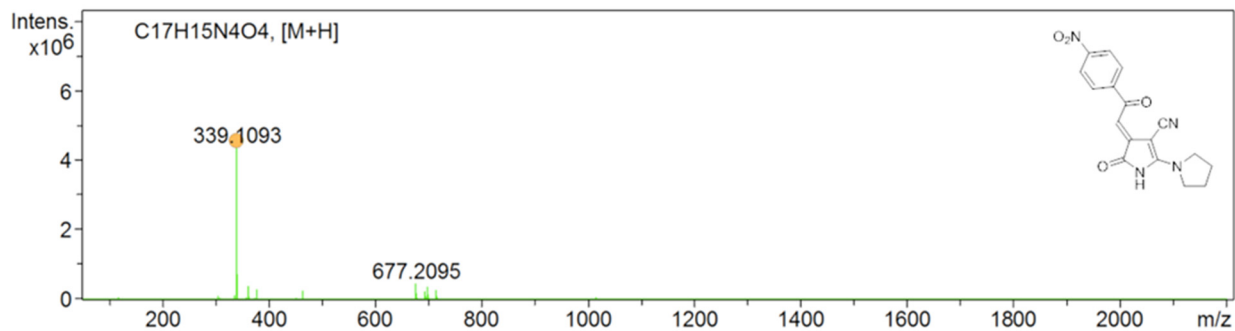
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3f**



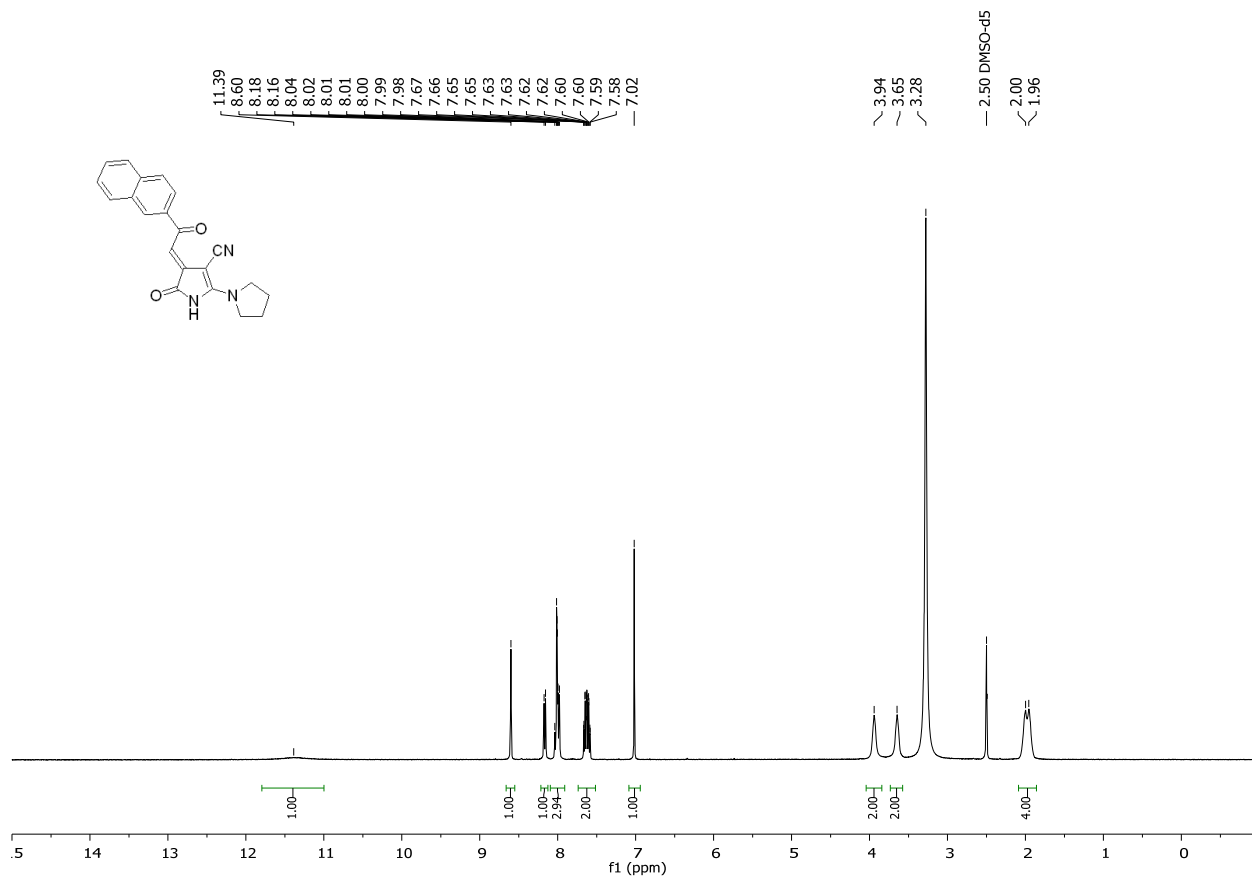
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3f**



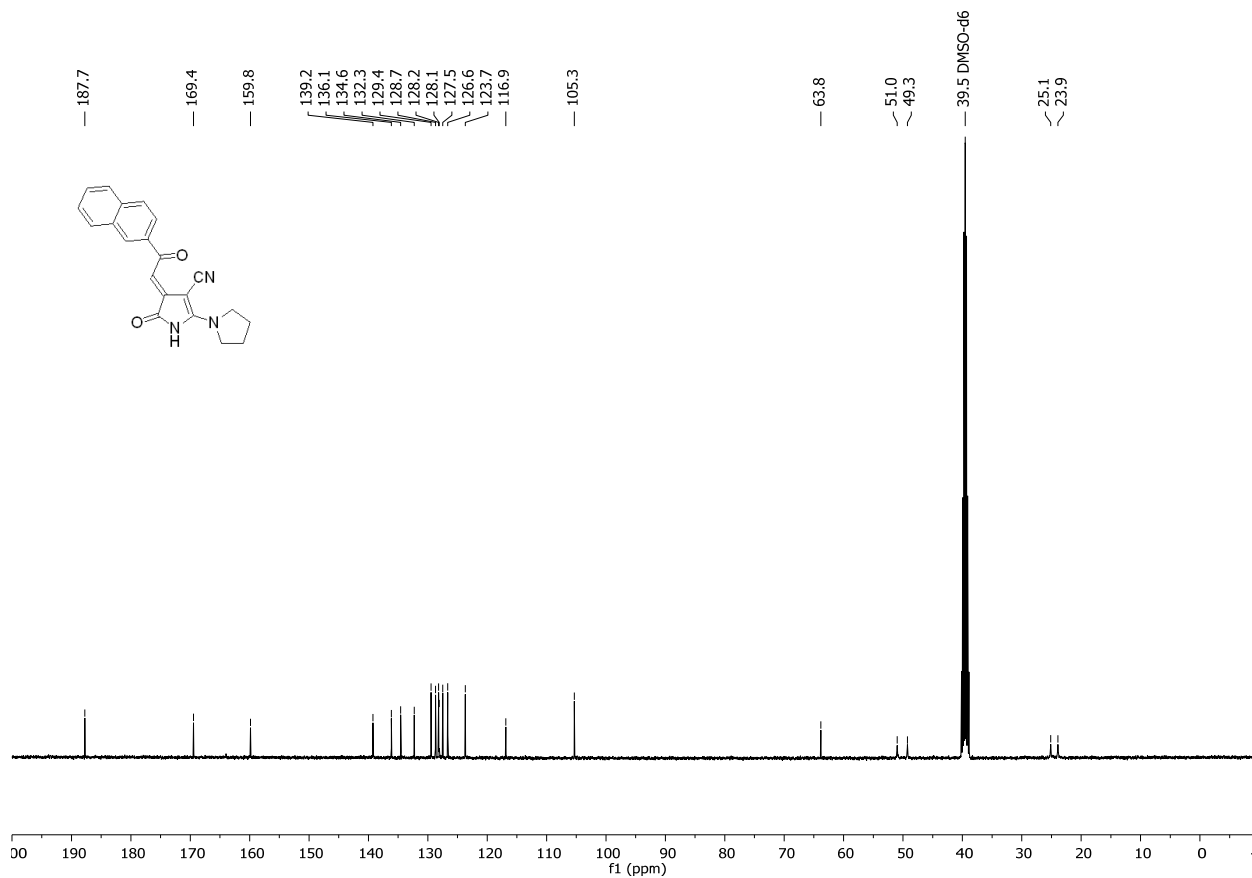
# HRMS spectrum of **3f**



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3g**

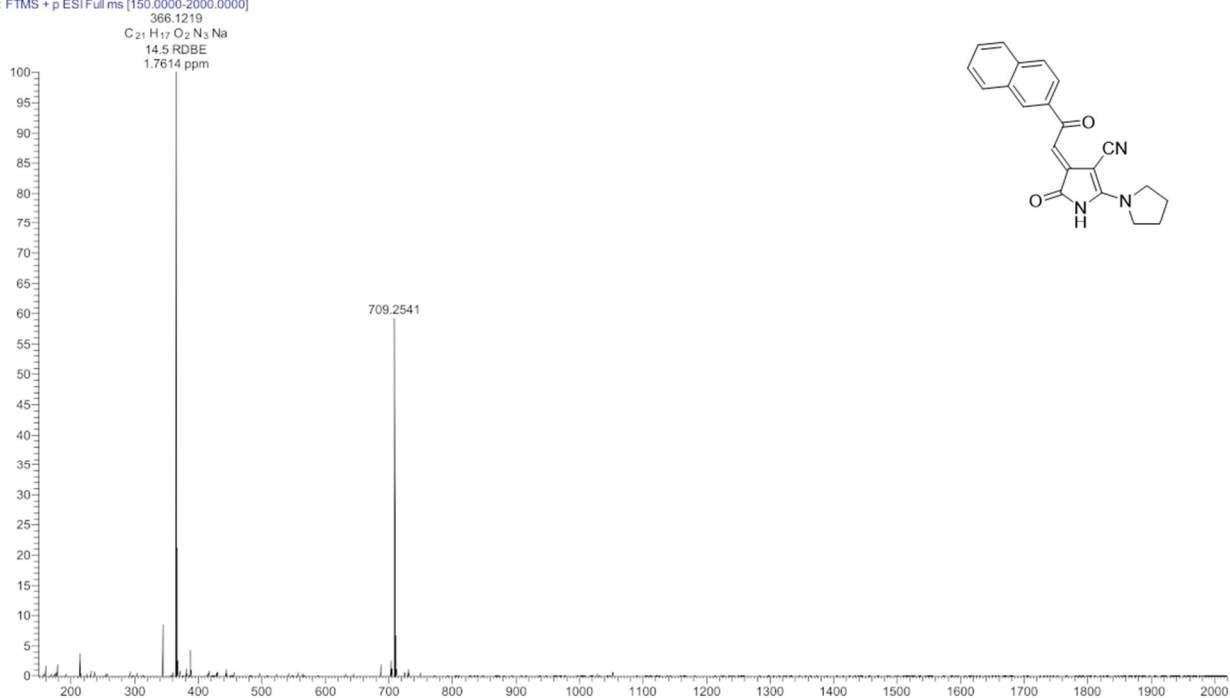


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3g**

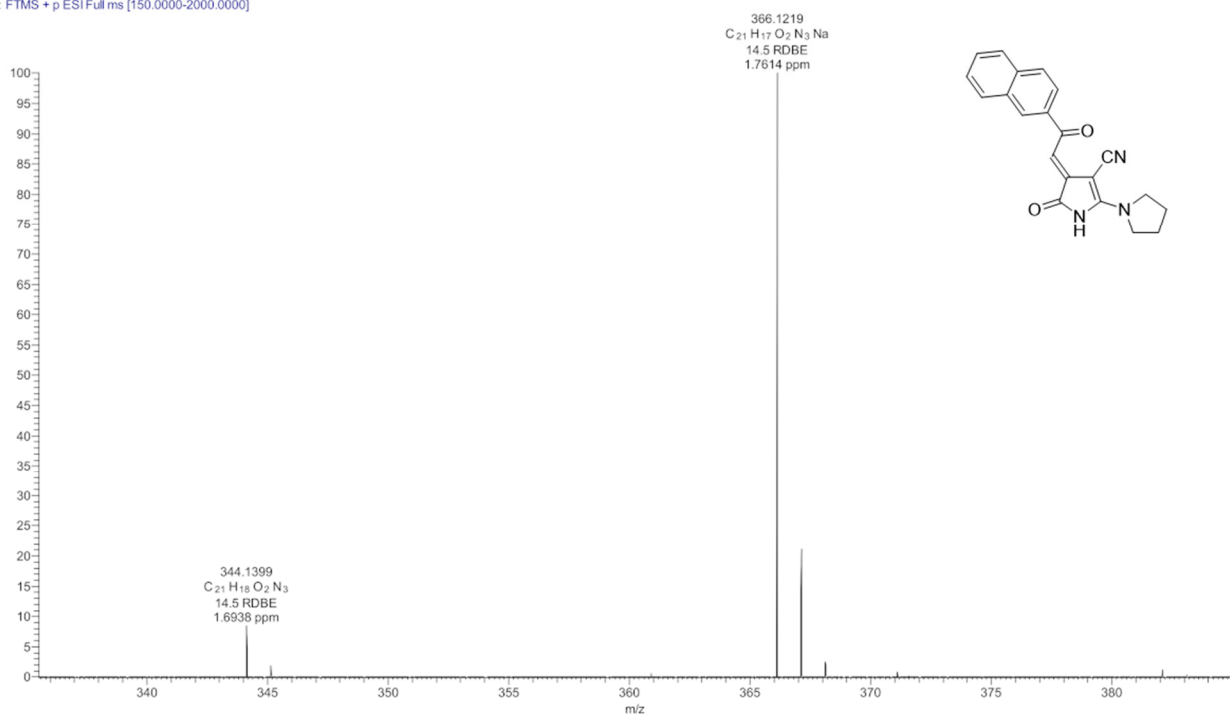


# HRMS spectrum of **3g**

PSG83 #54-96 RT: 0.24-0.42 AV: 43 SB: 54 0.07-0.15, 0.83-0.97 NL: 2.92E7  
T: FTMS + p ESI Full ms [150.0000-2000.0000]

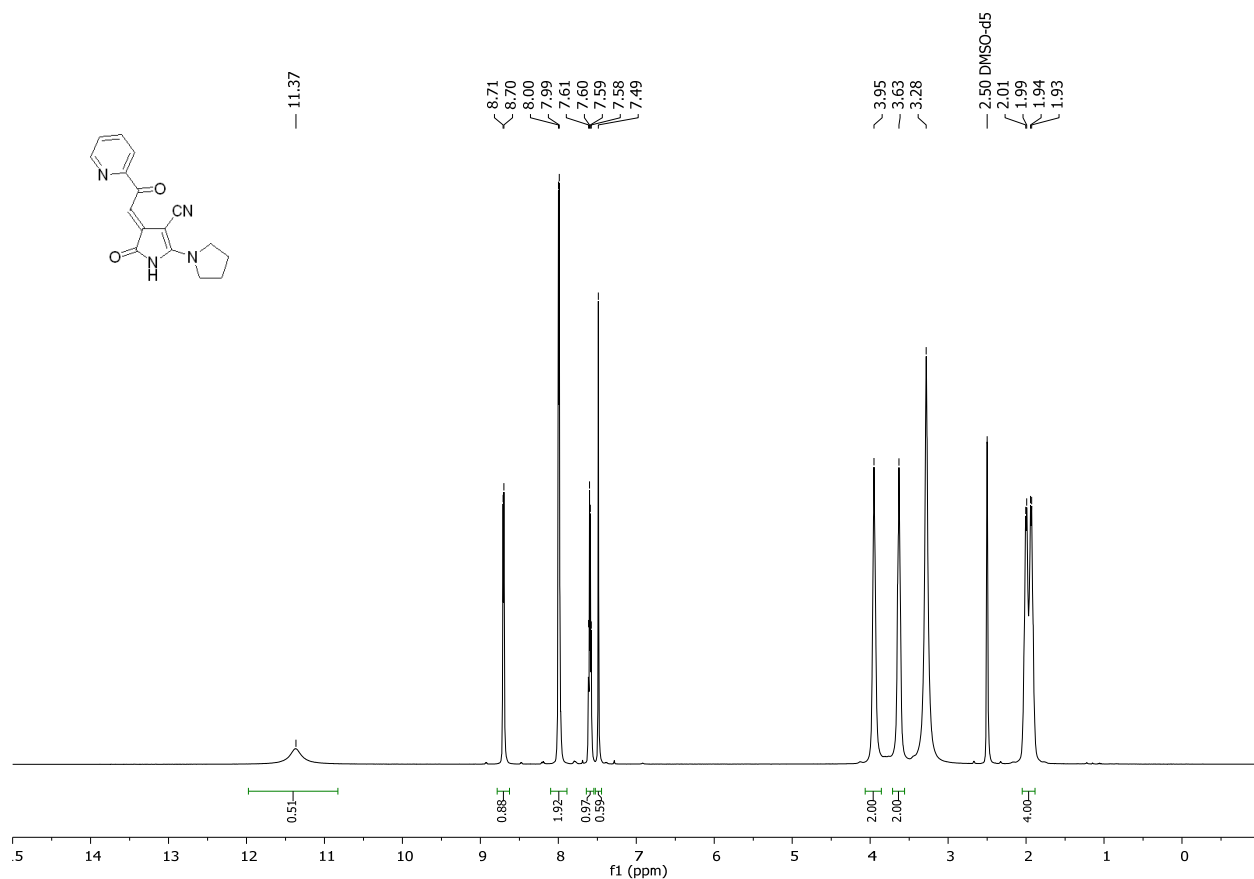


PSG83 #54-96 RT: 0.24-0.42 AV: 43 SB: 54 0.07-0.15, 0.83-0.97 NL: 2.92E7  
T: FTMS + p ESI Full ms [150.0000-2000.0000]

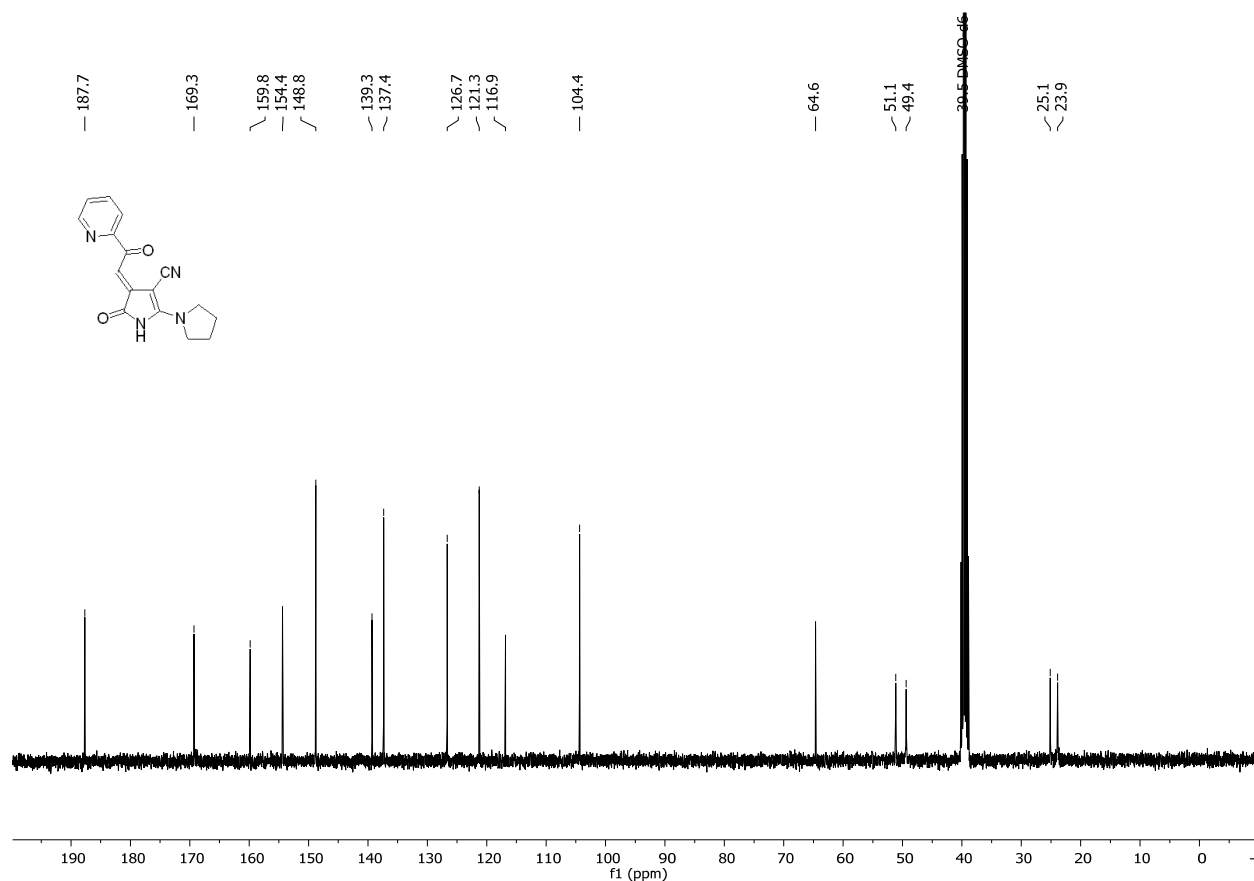




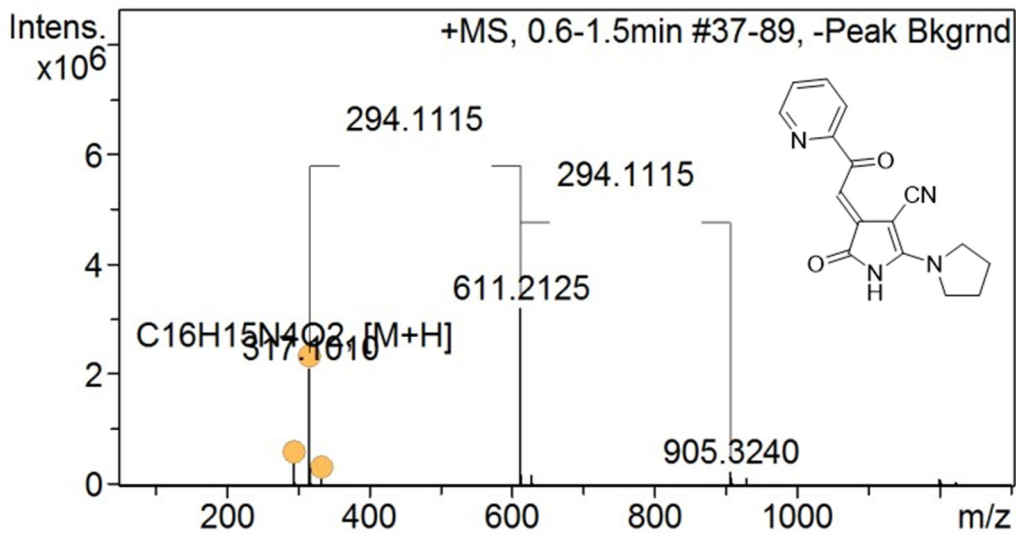
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3h**



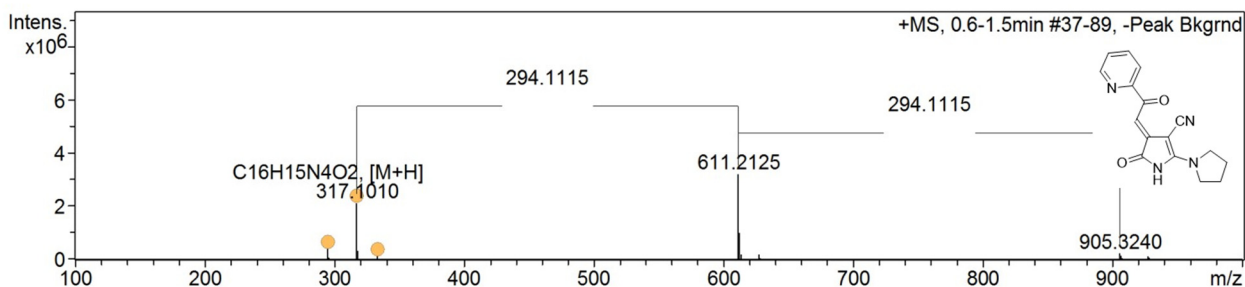
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3h**



### HRMS spectrum of 3h

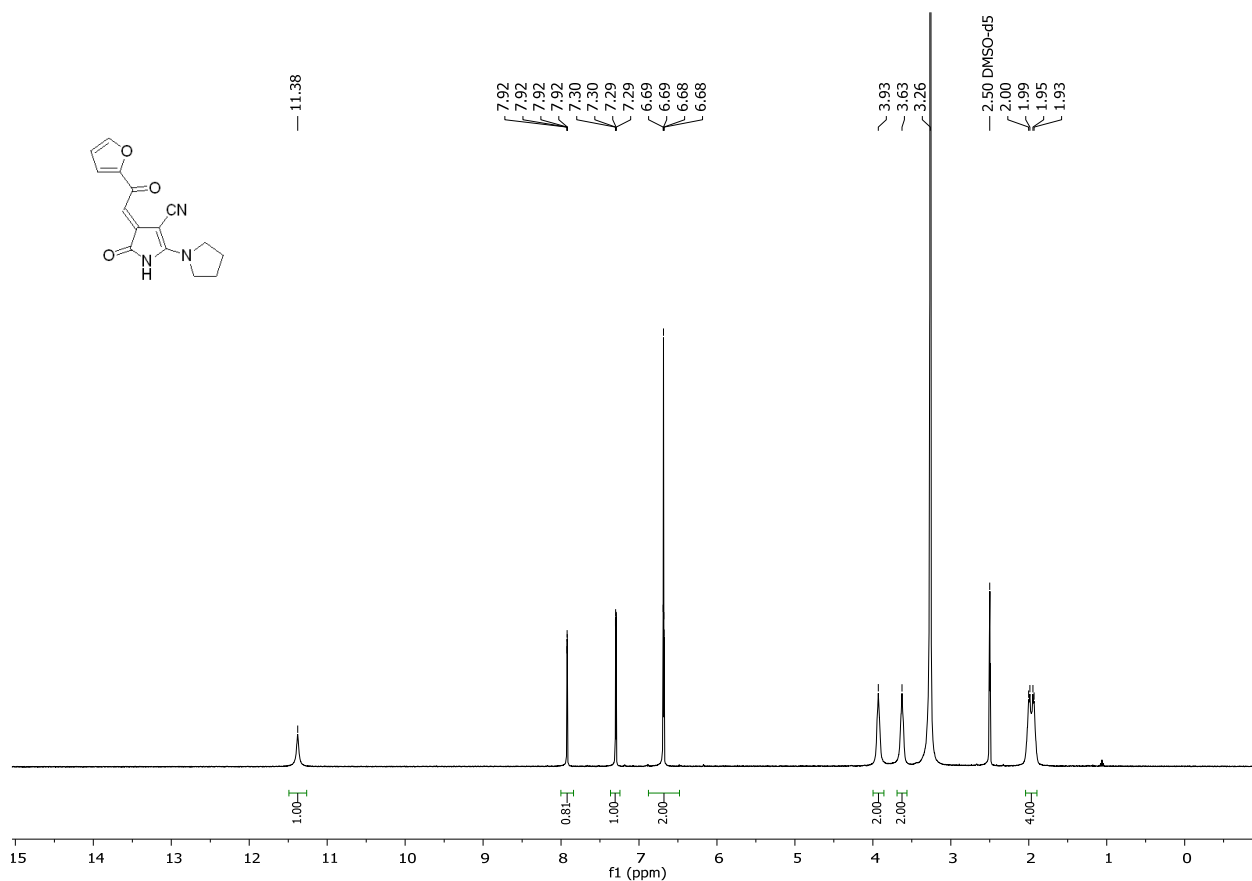


#	m/z	Res.	S/N	I	I%	FWHM
1	295.1188	25131	14857250.0	384263	12.0	0.0117

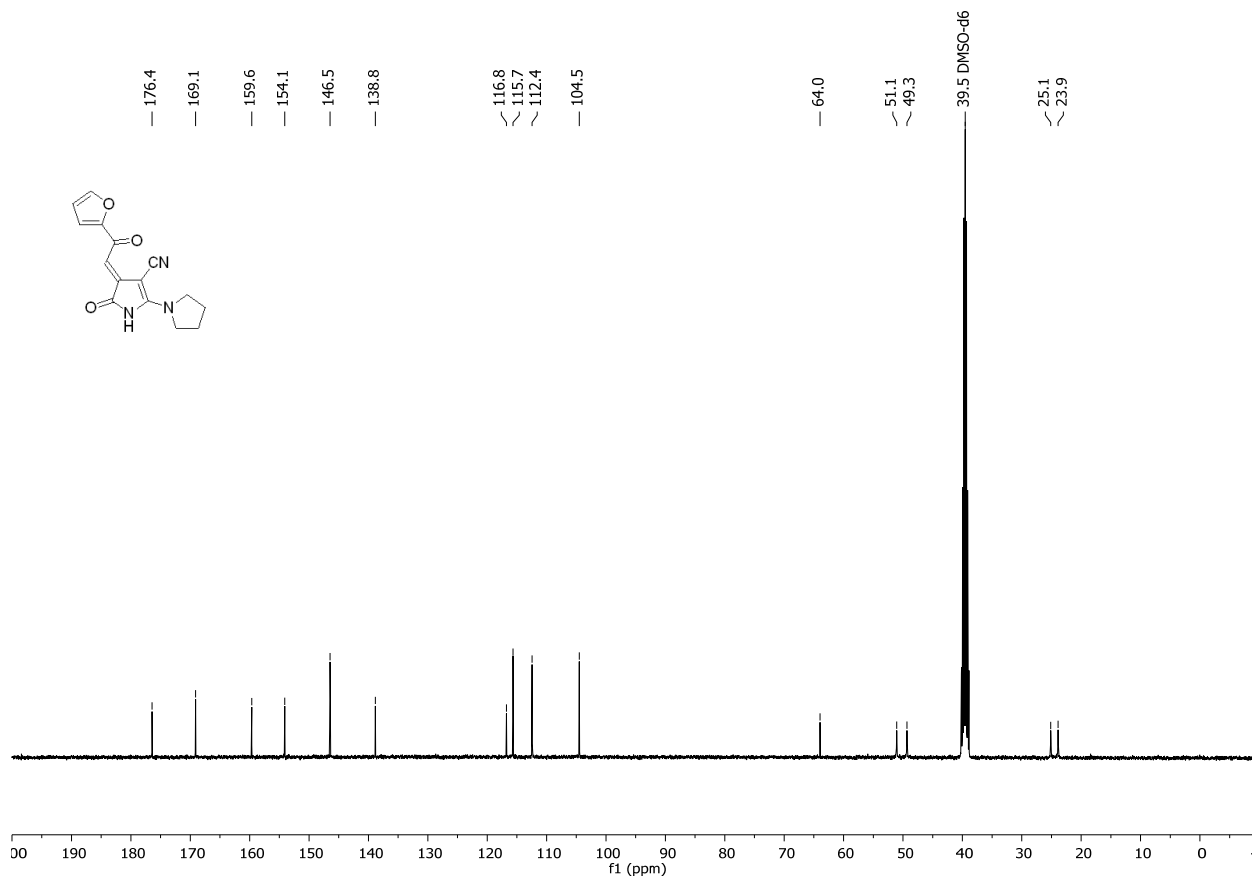


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
295.1188	1	C15H19O6	295.1176	-4.1	4.8	1	68.58	6.5	even	ok
	2	C14H13N7O	295.1176	-4.1	7.8	2	64.83	12.0	odd	ok
	3	C16H15N4O2	295.1190	0.4	14.5	3	100.00	11.5	even	ok

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3i**

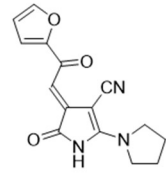
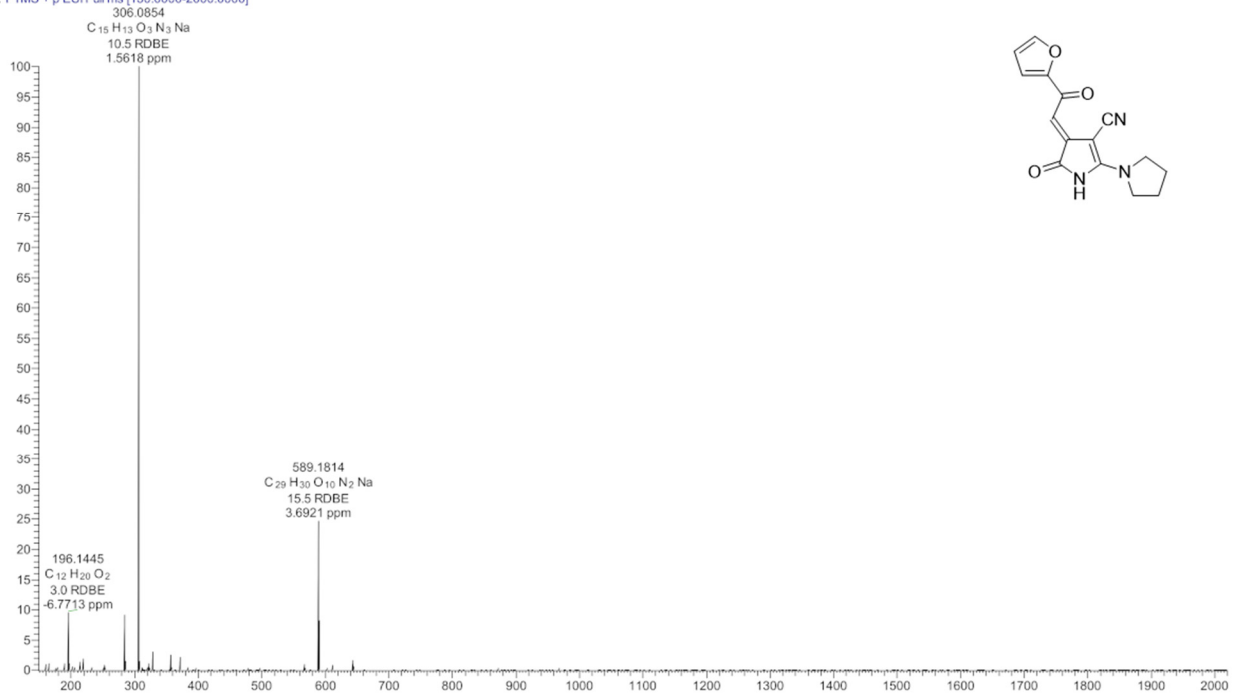


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3i**

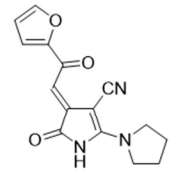
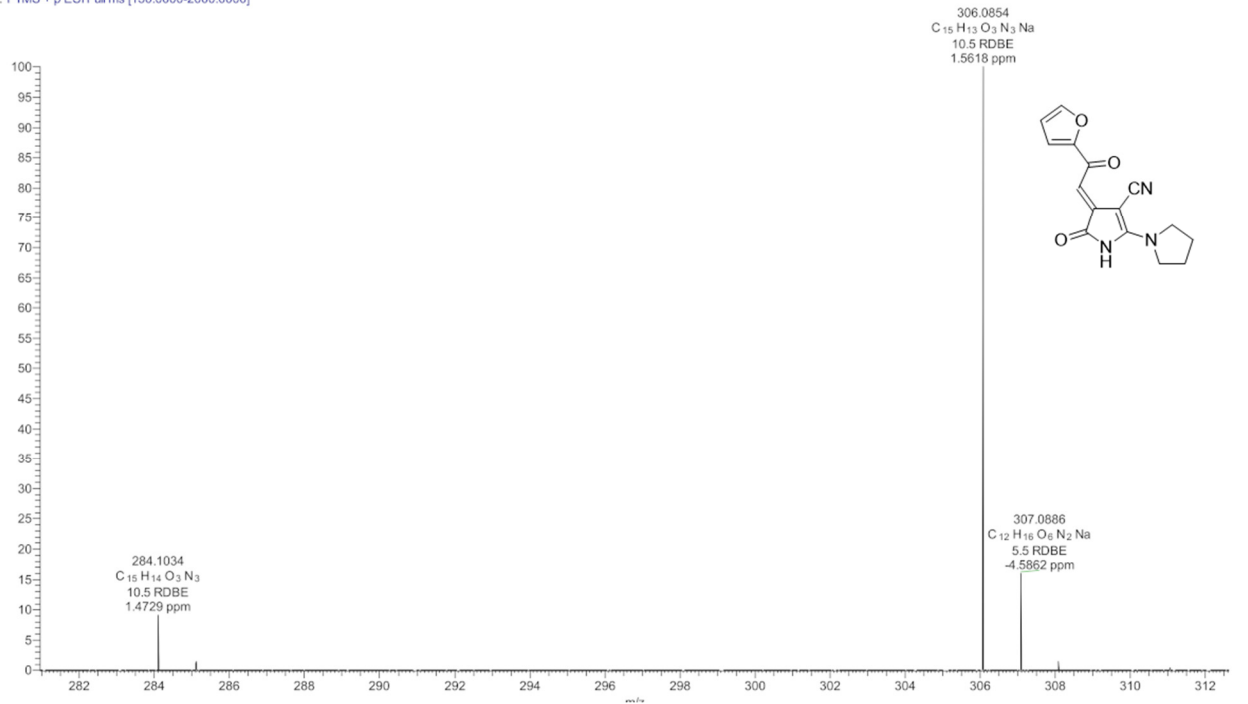


# HRMS spectrum of **3i**

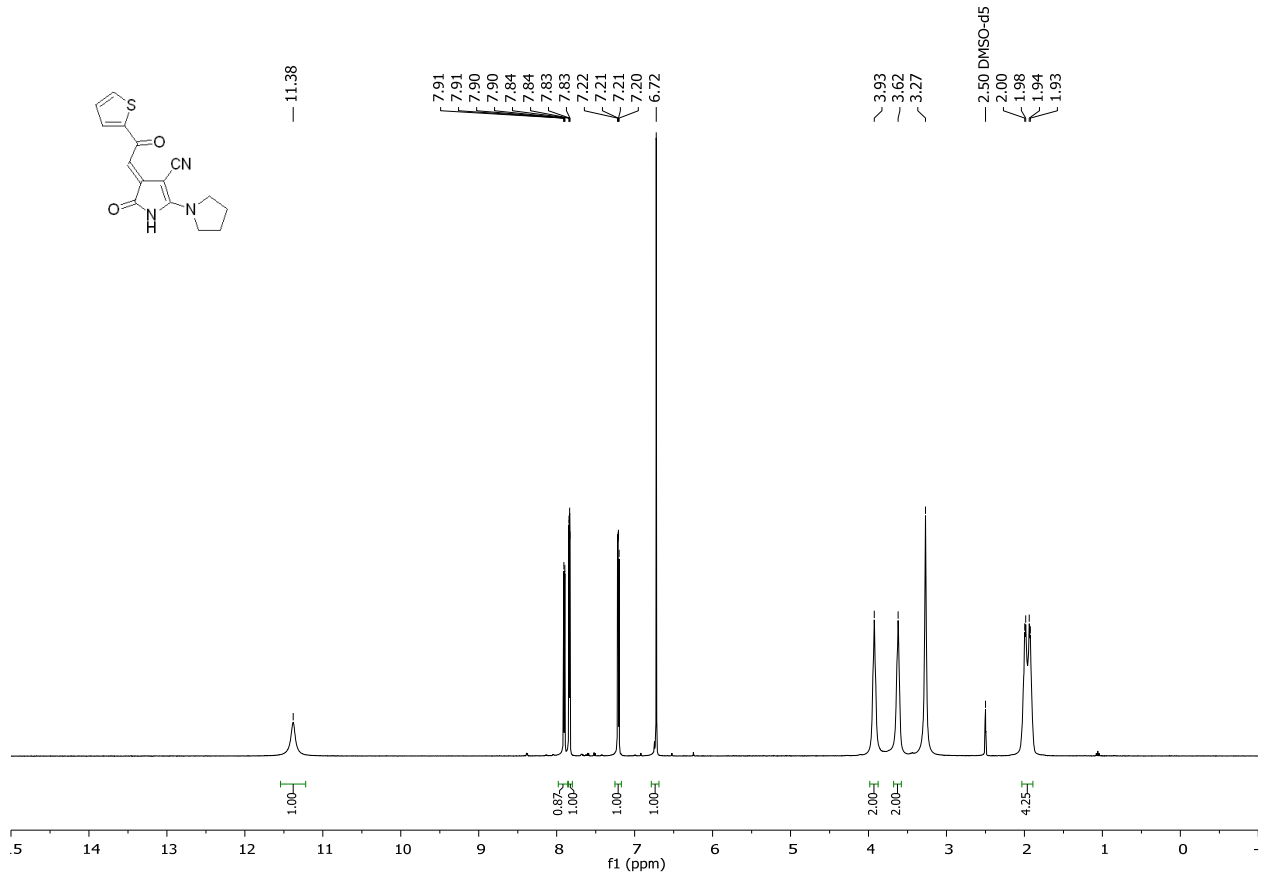
PSG79 #54-96 RT: 0.24-0.42 AV: 43 SB: 54 0.07-0.15, 0.83-0.97 NL: 5.34E7  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



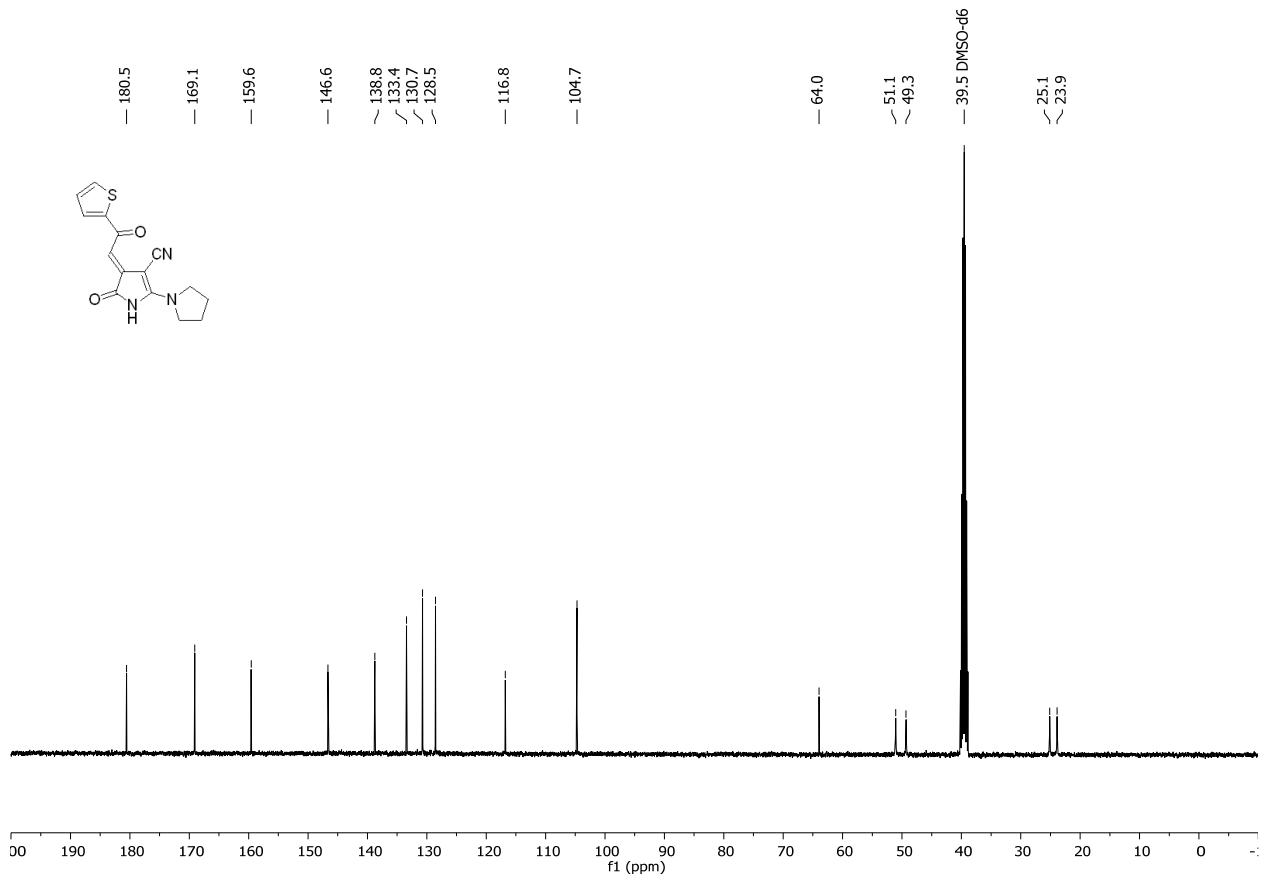
PSG79 #54-96 RT: 0.24-0.42 AV: 43 SB: 54 0.07-0.15, 0.83-0.97 NL: 5.34E7  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3j**

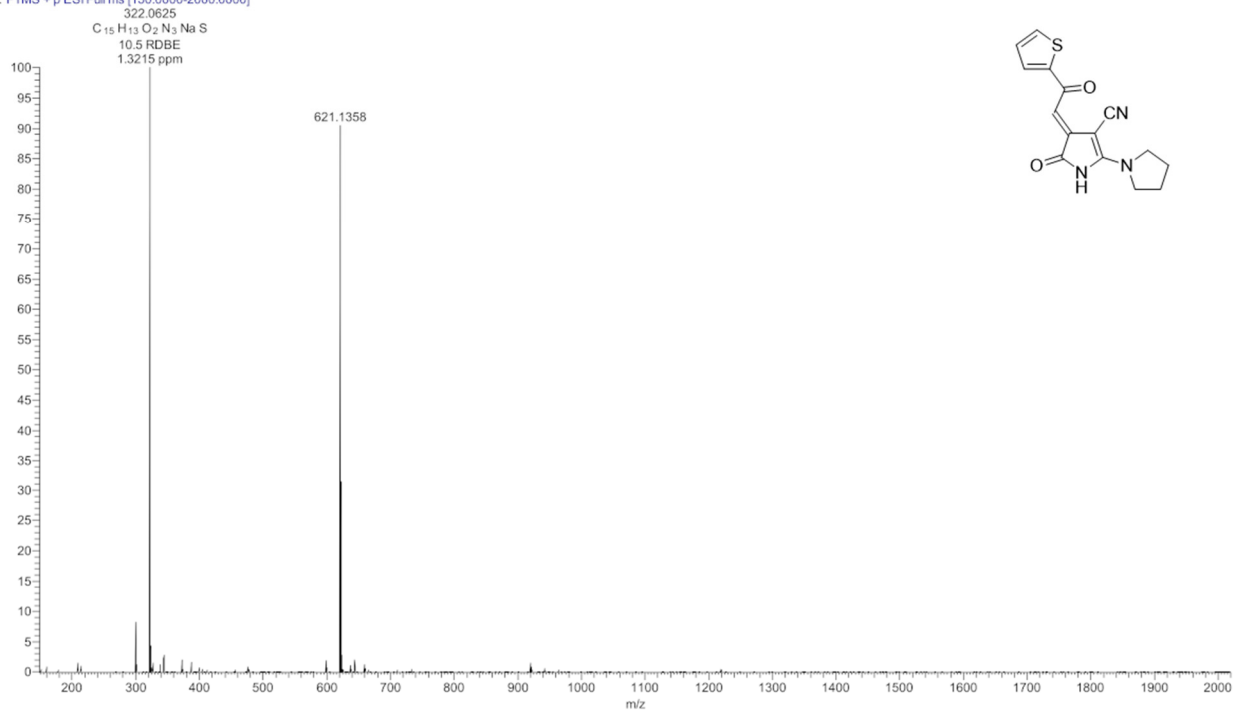


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3j**

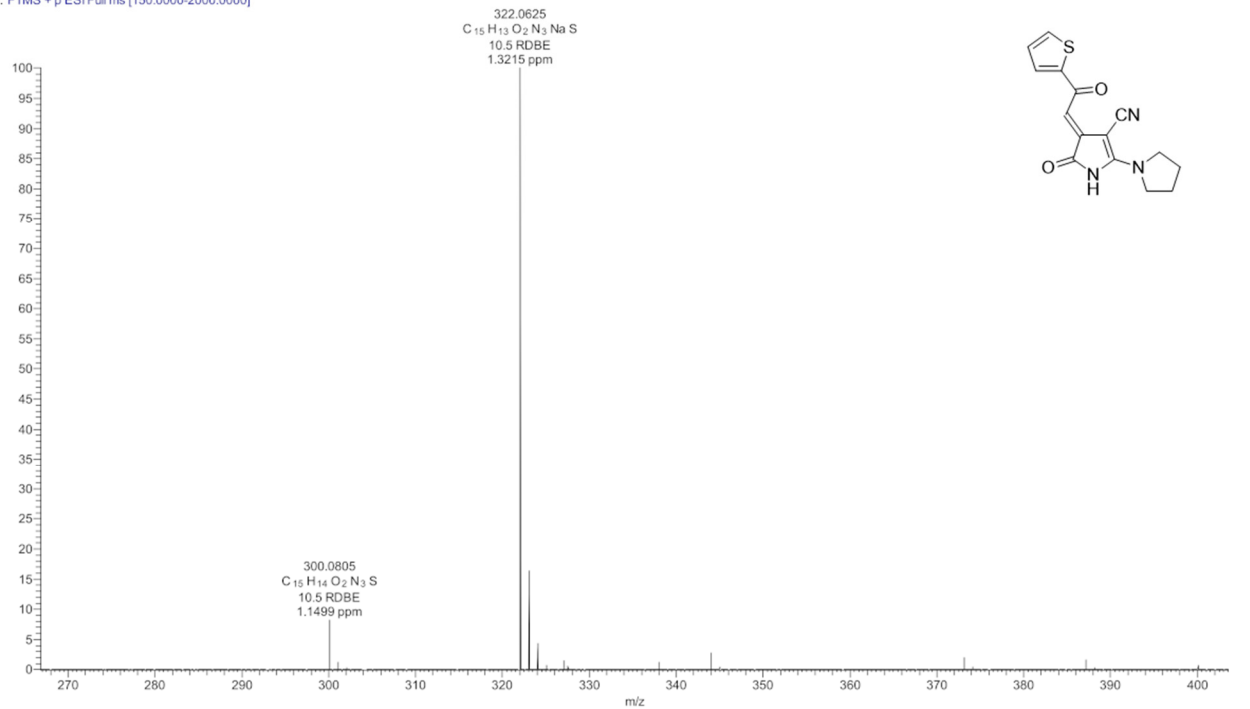


# HRMS spectrum of **3j**

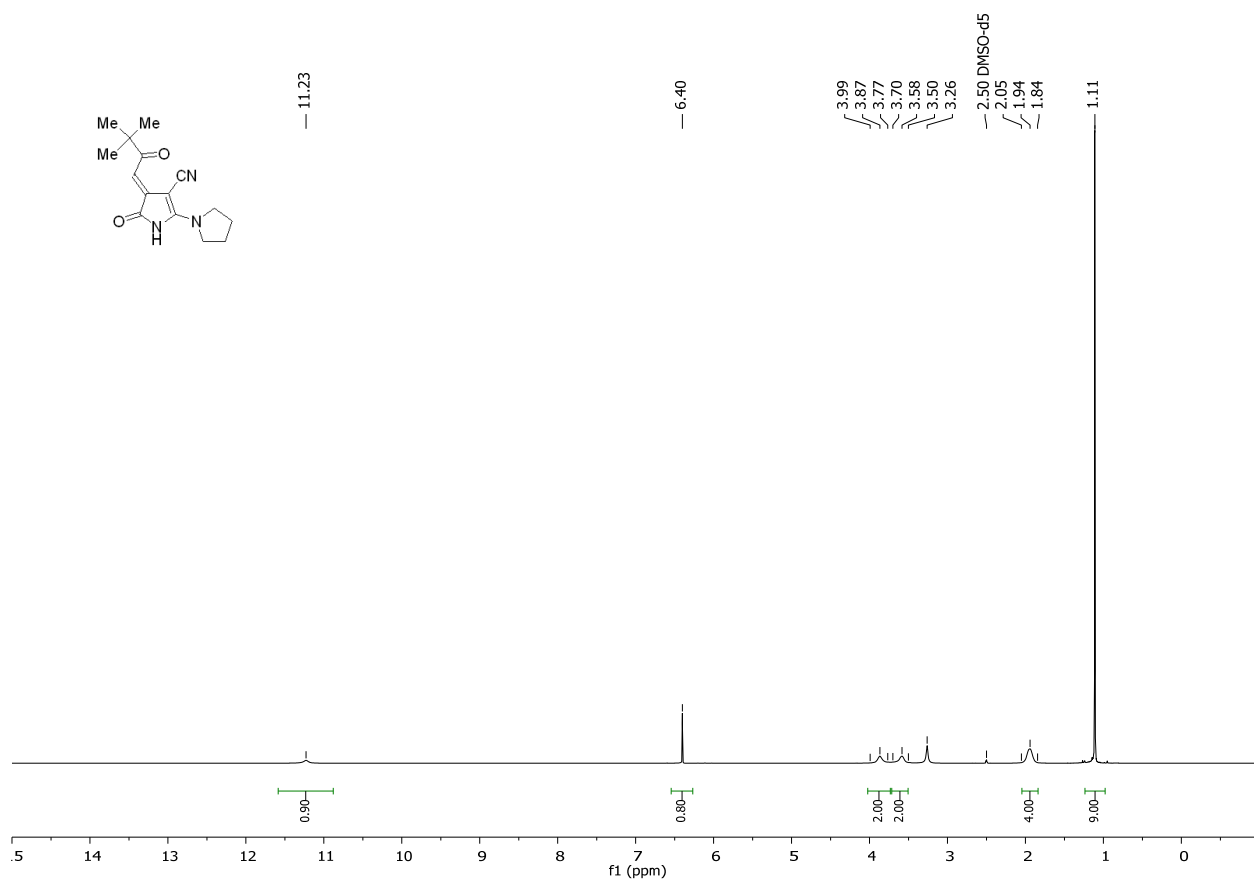
PSG102 #51-102 RT: 0.23-0.45 AV: 52 SB: 54 0.07-0.15, 0.83-0.97 NL: 9.72E7  
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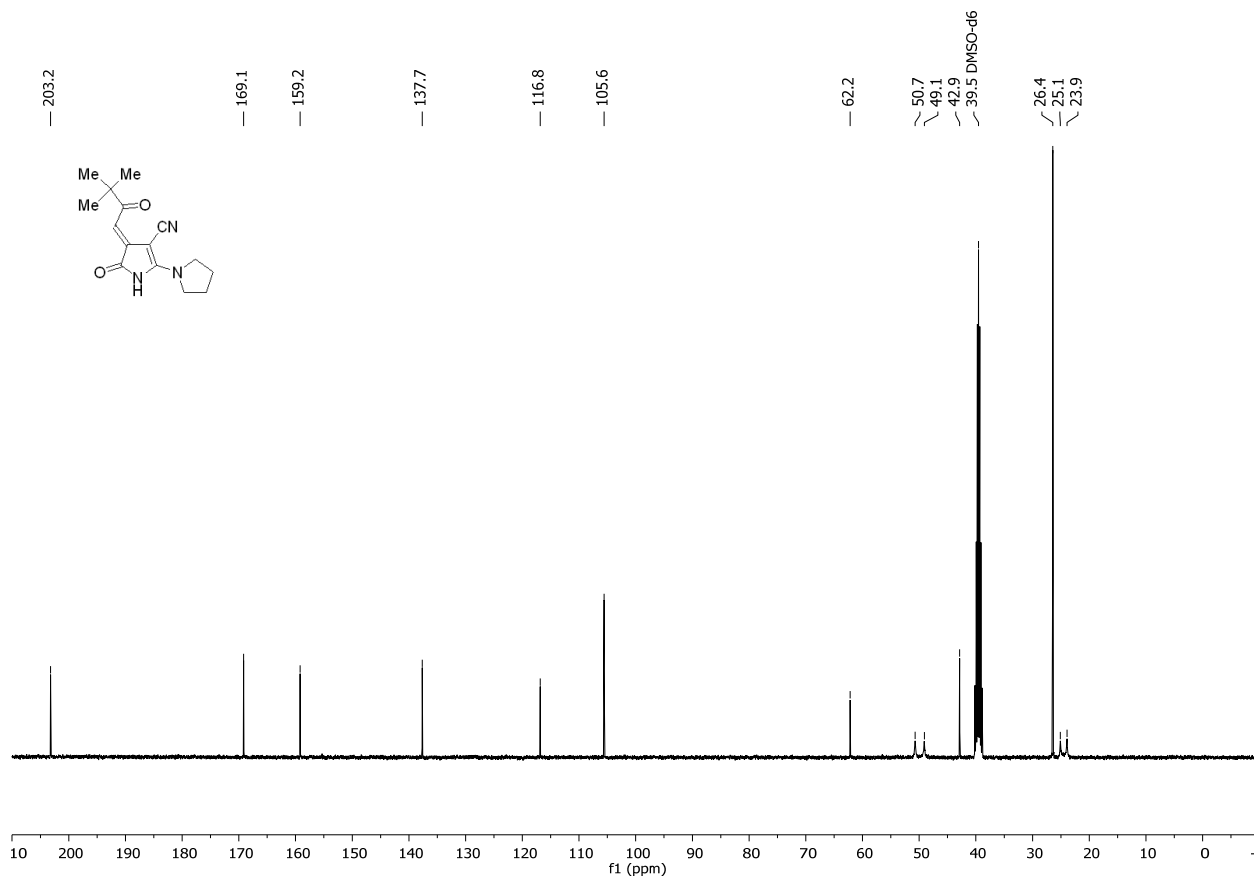
PSG102 #51-102 RT: 0.23-0.45 AV: 52 SB: 54 0.07-0.15, 0.83-0.97 NL: 9.72E7  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



### <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3k**

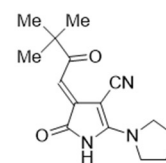
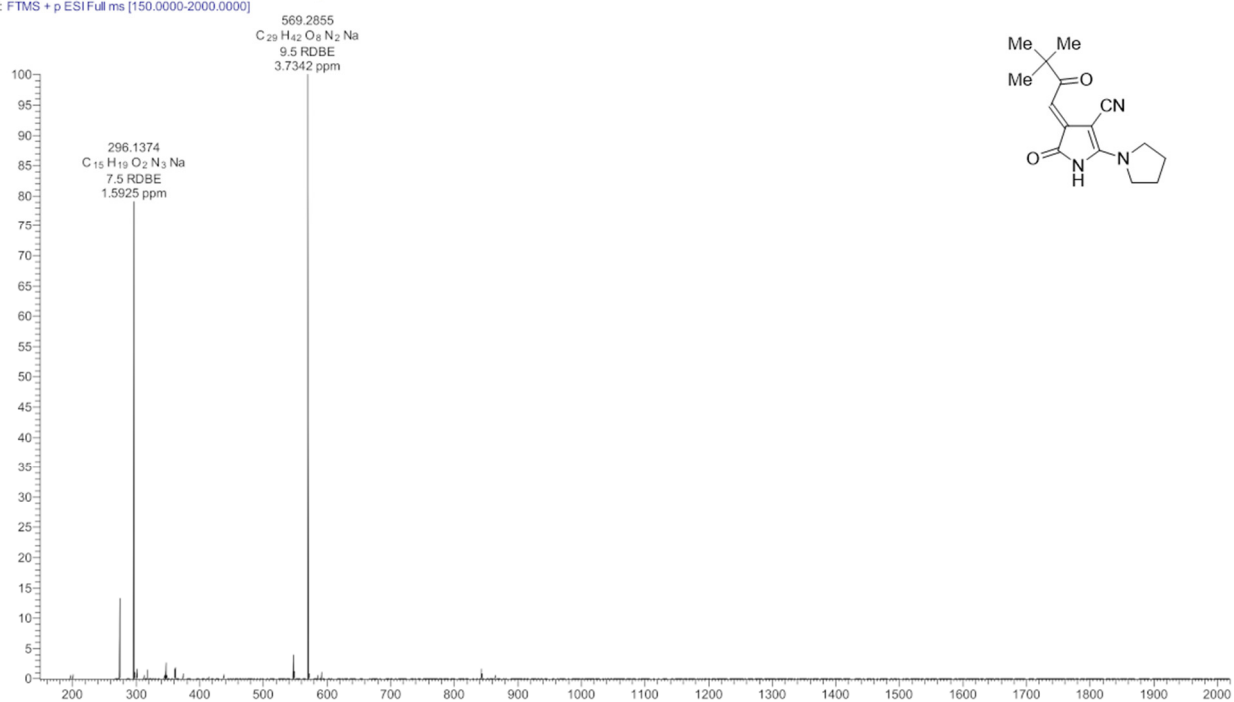


### <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3k**

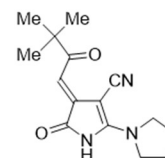
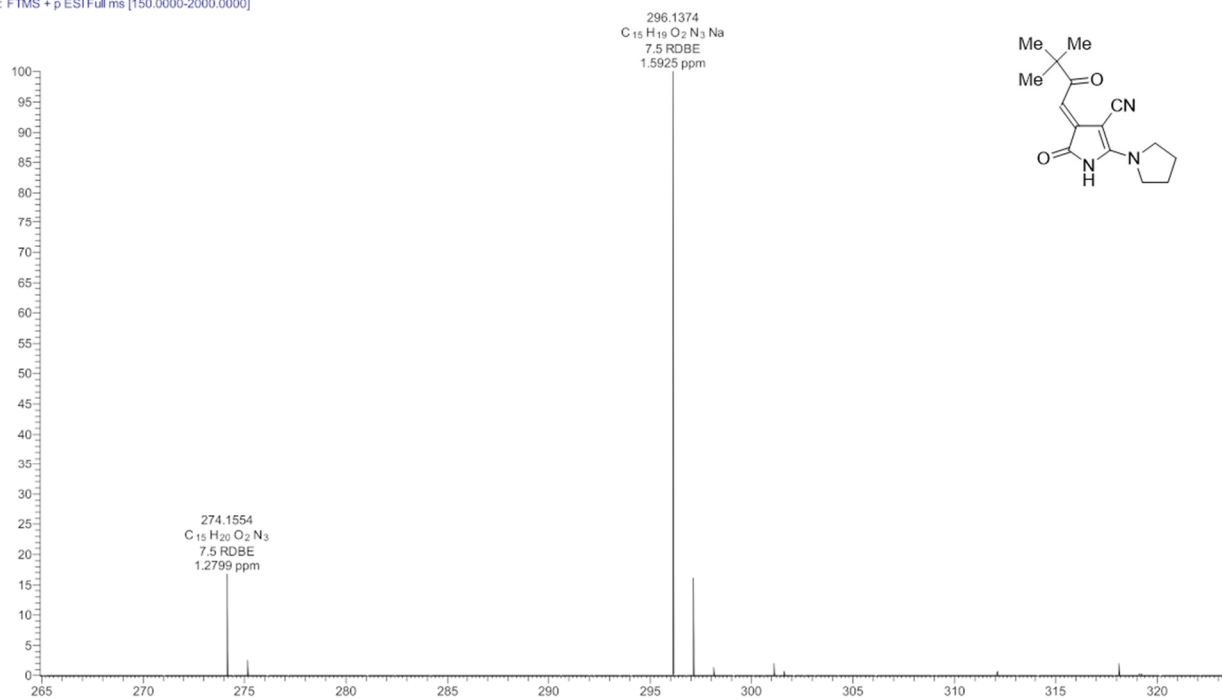


# HRMS spectrum of **3k**

PSG80 #54-96 RT: 0.24-0.42 AV: 43 SB: 54 0.07-0.15, 0.83-0.97 NL: 3.44E8  
T: FTMS + p ESI Full ms [150.0000-2000.0000]

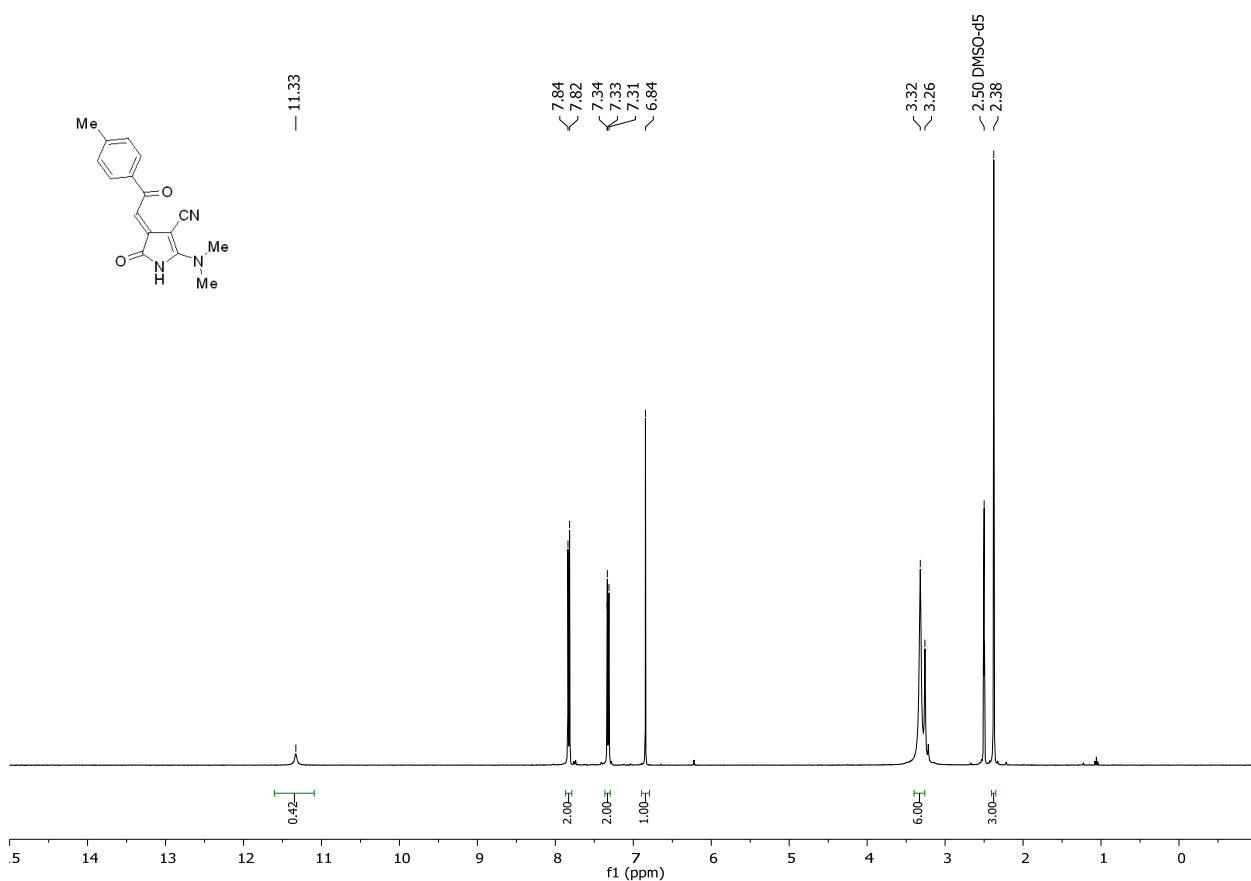


PSG80 #54-96 RT: 0.24-0.42 AV: 43 SB: 54 0.07-0.15, 0.83-0.97 NL: 2.72E8  
T: FTMS + p ESI Full ms [150.0000-2000.0000]

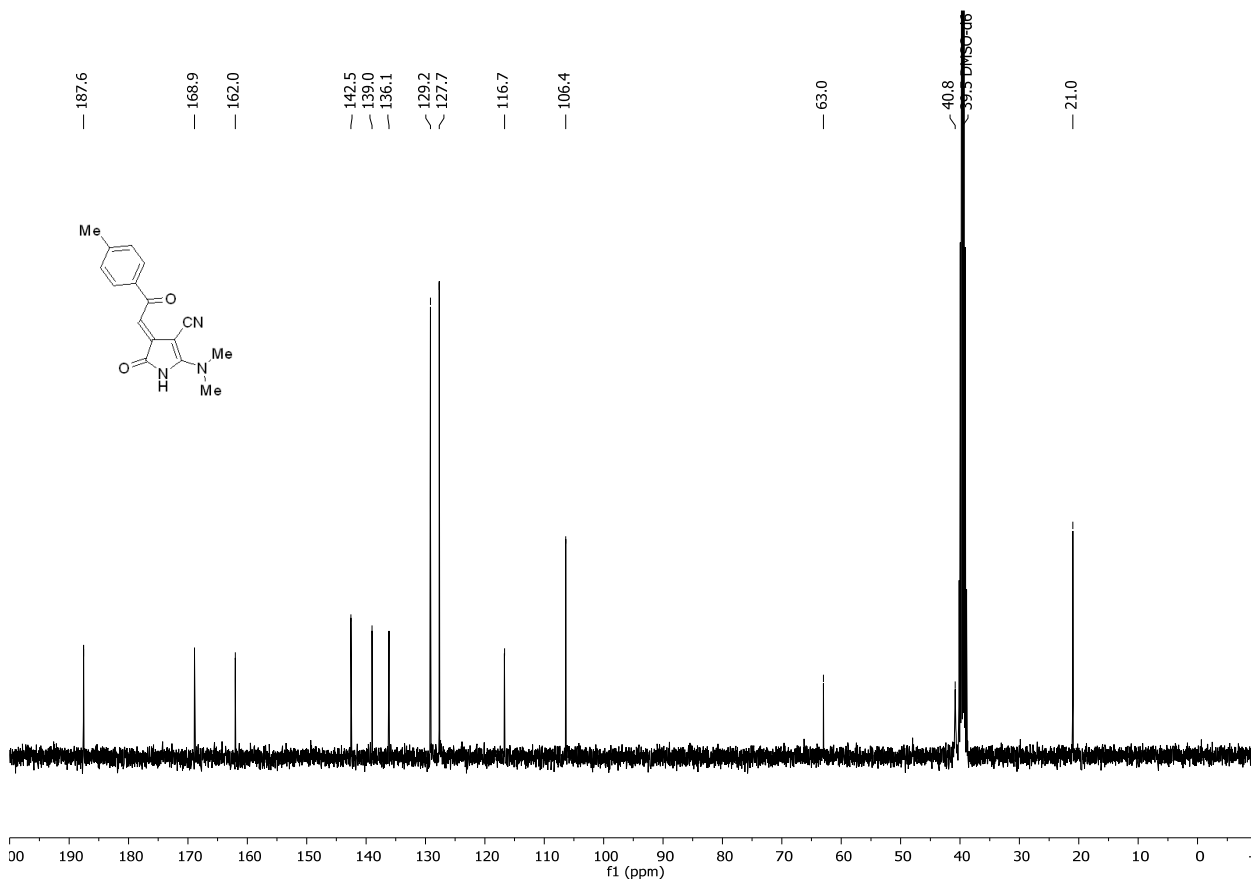




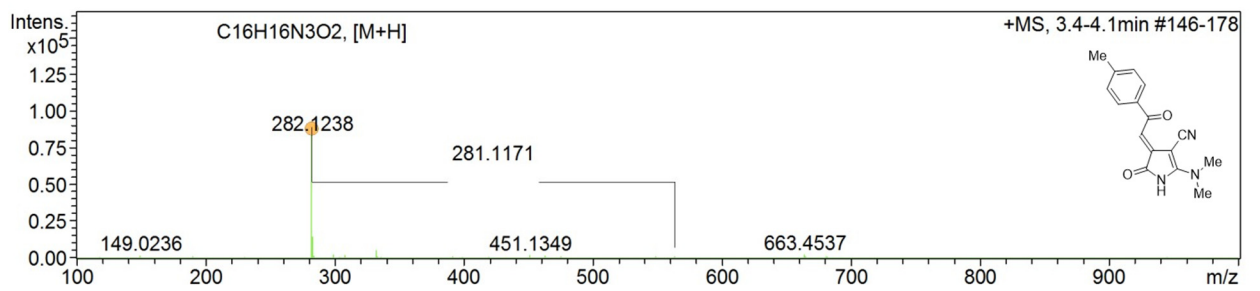
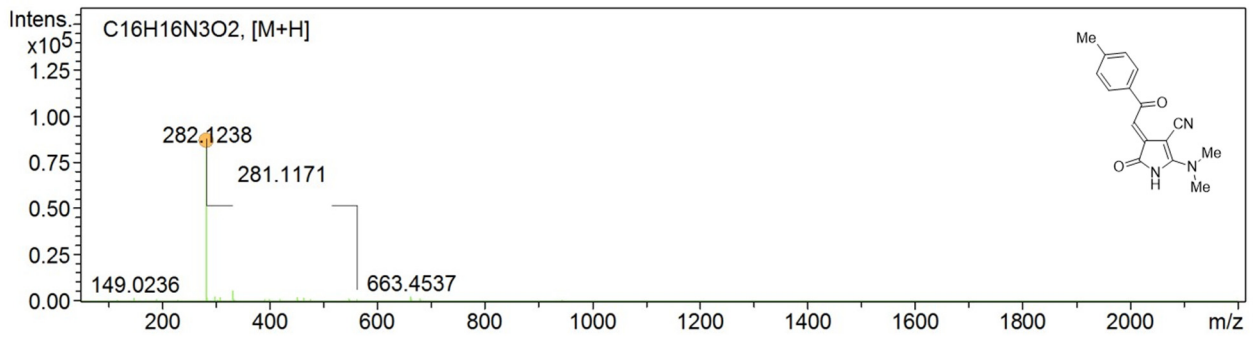
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **31**



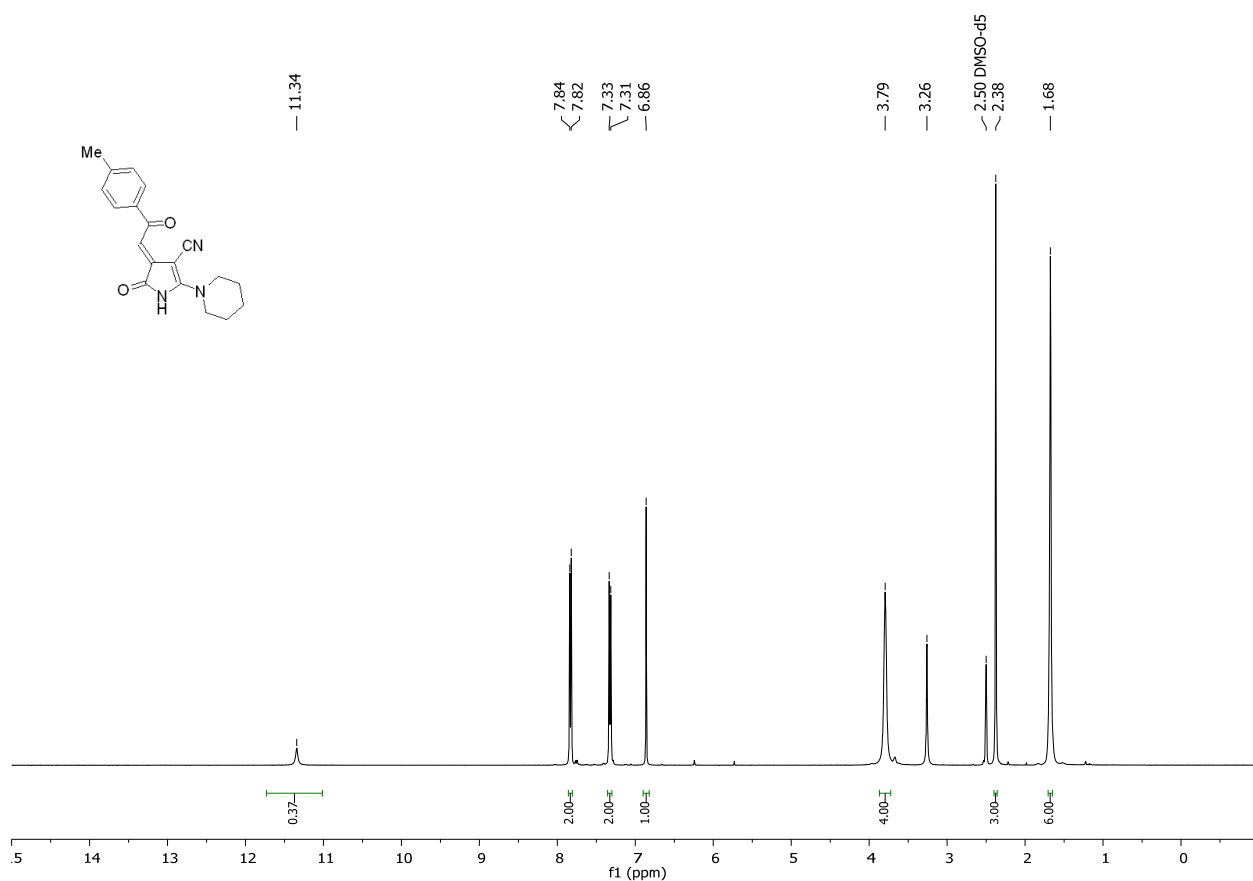
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **31**



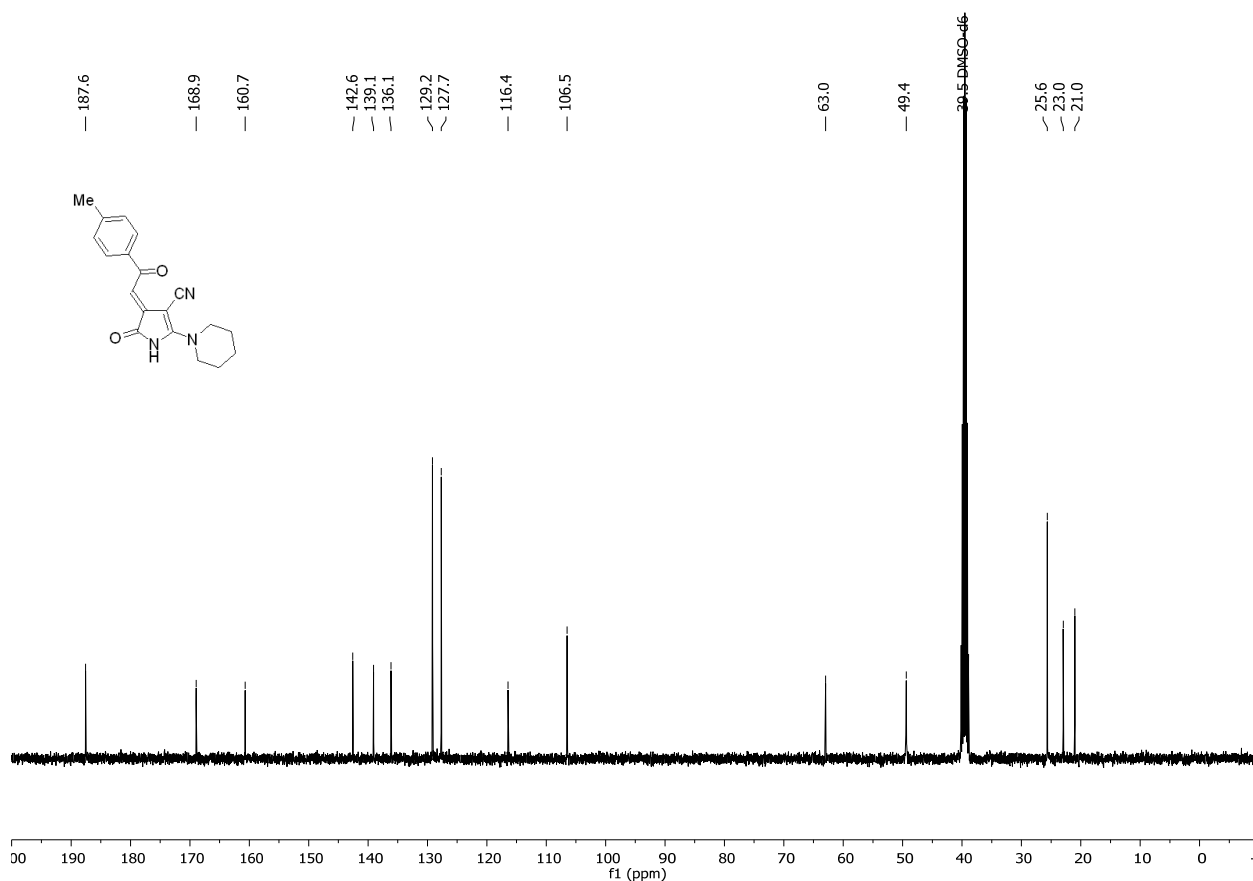
# HRMS spectrum of **31**



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3m**

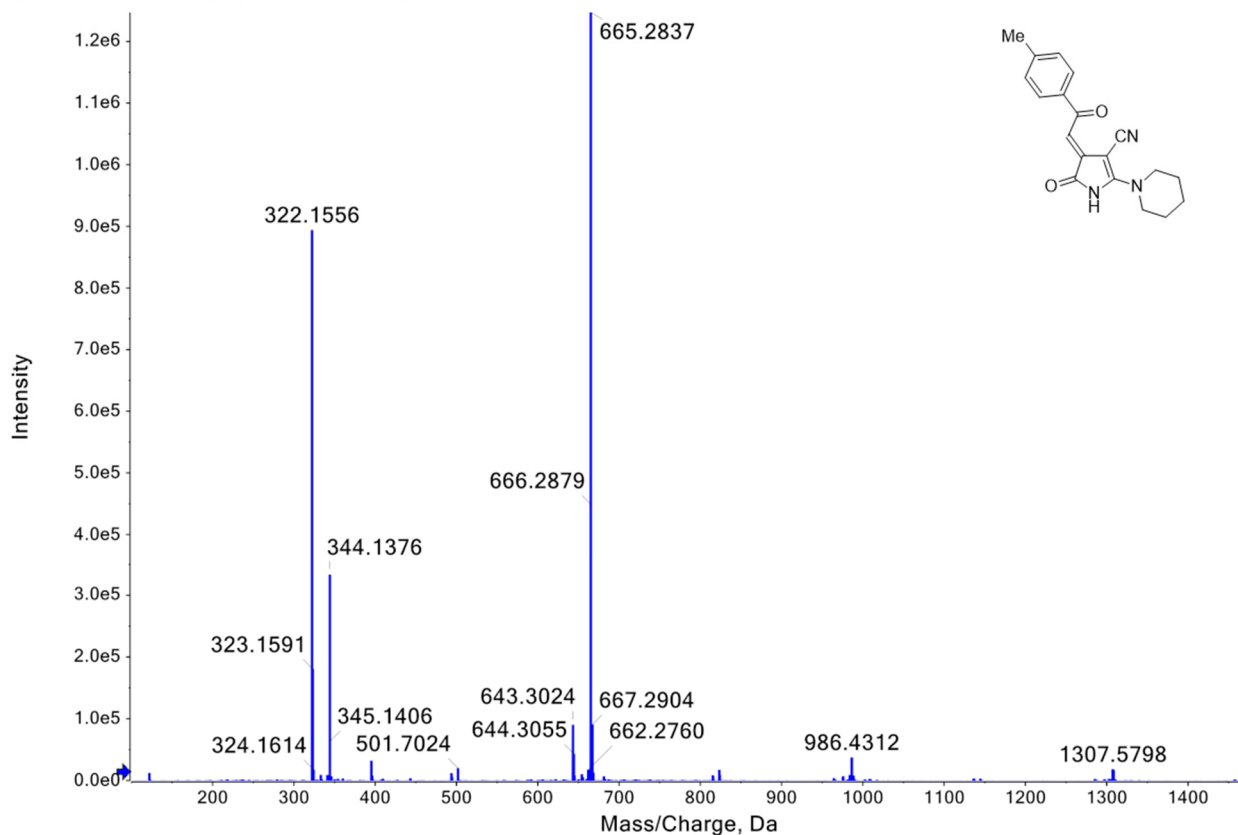


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3m**

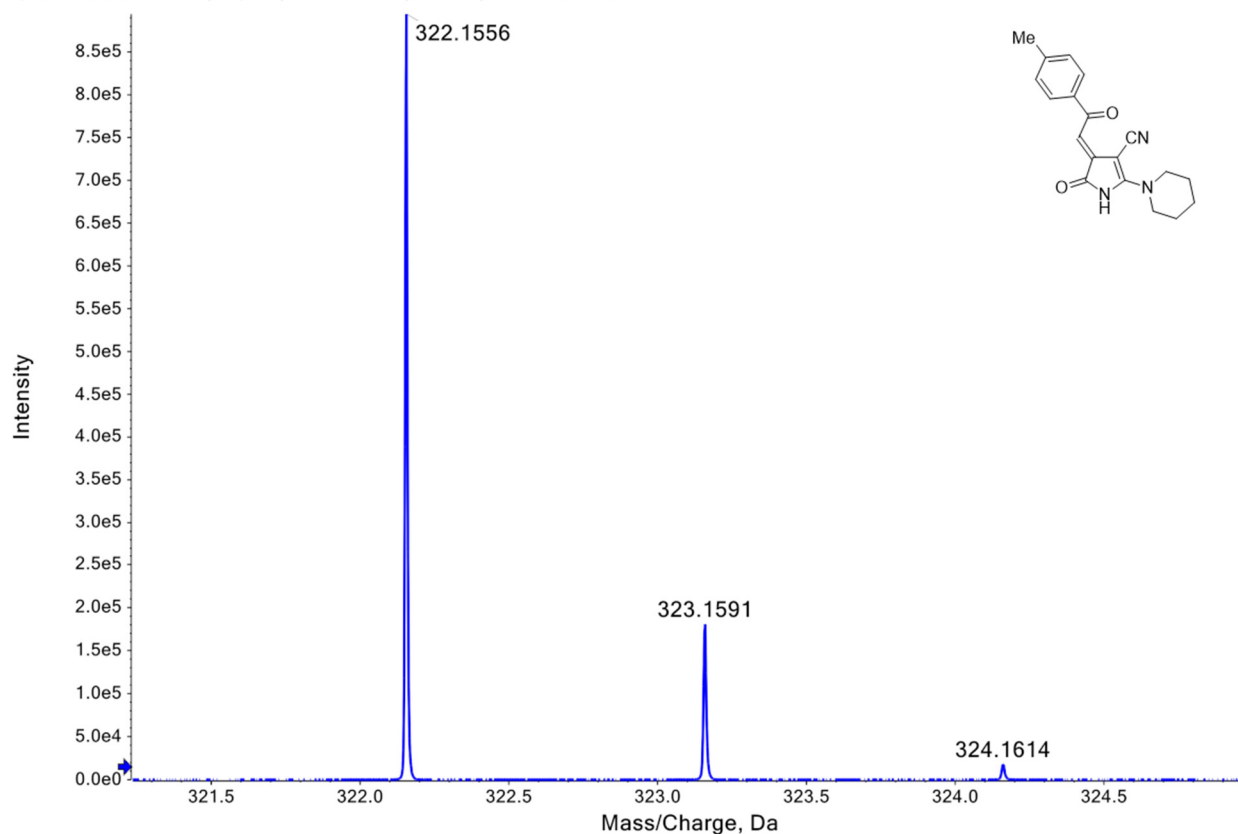


# HRMS spectrum of 3m

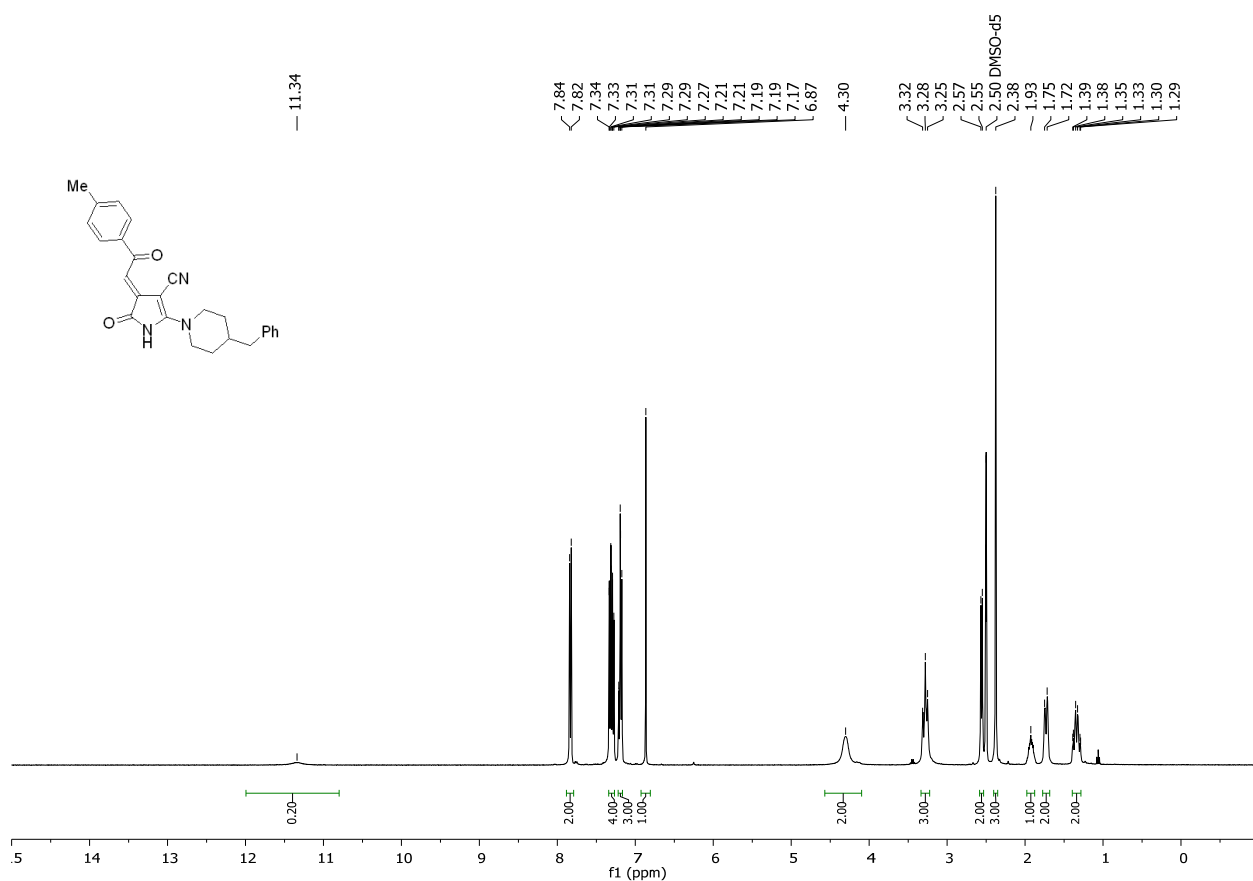
Spectrum from ESI POS.wiff (sample 44) - 473, +TOF MS (100 - 3000) from 0.618 to 0.660 min



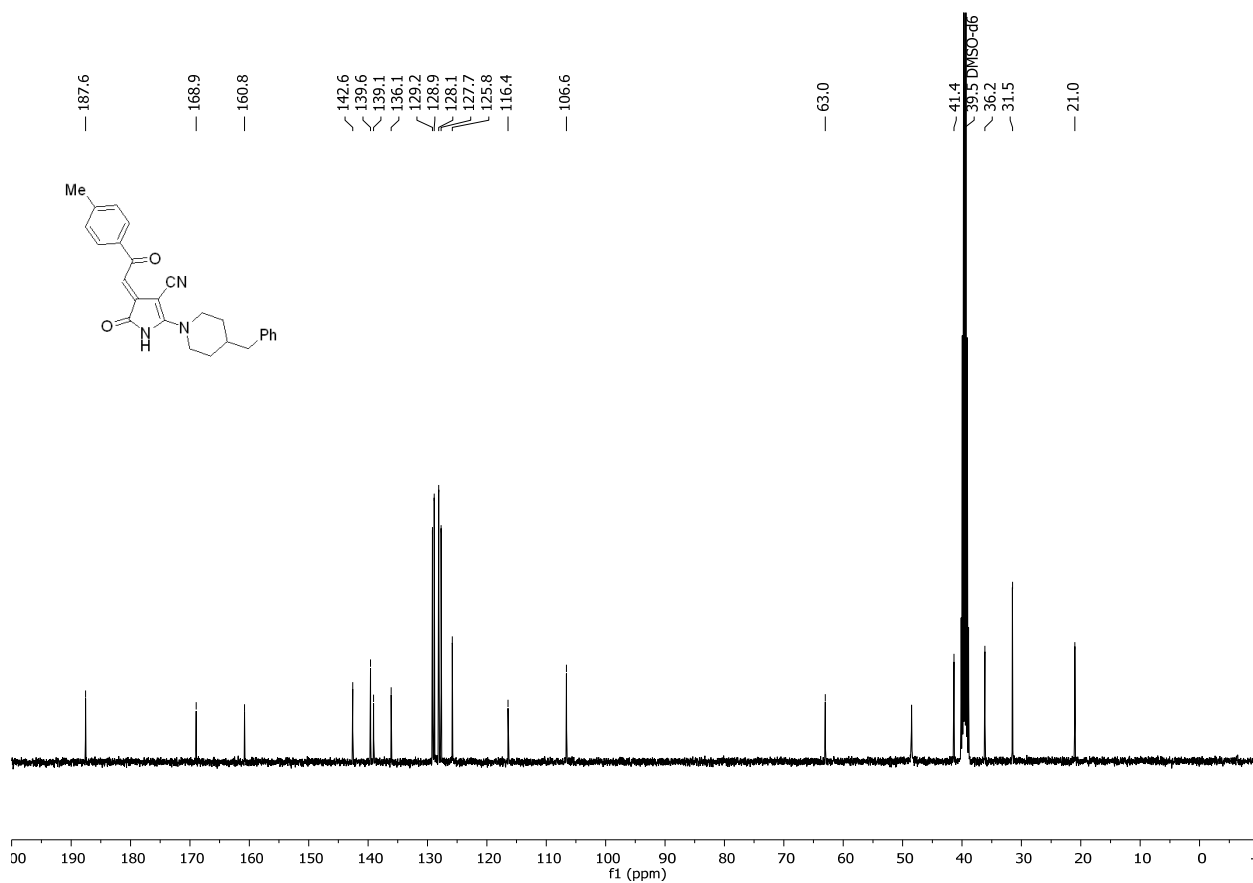
Spectrum from ESI POS.wiff (sample 44) - 473, +TOF MS (100 - 3000) from 0.618 to 0.660 min



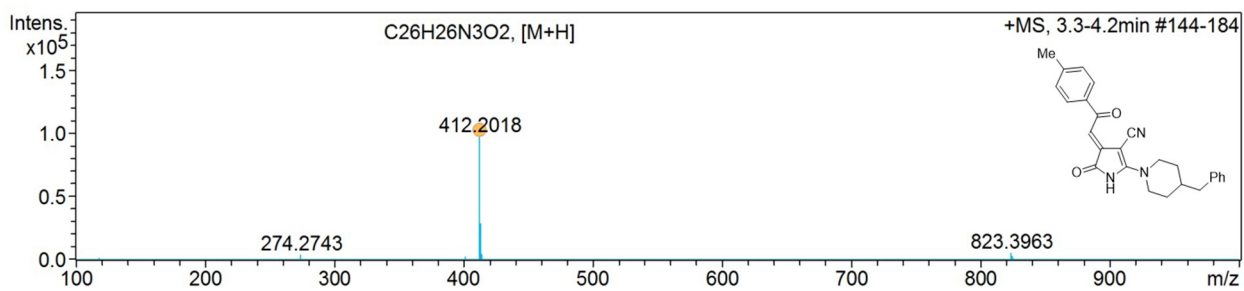
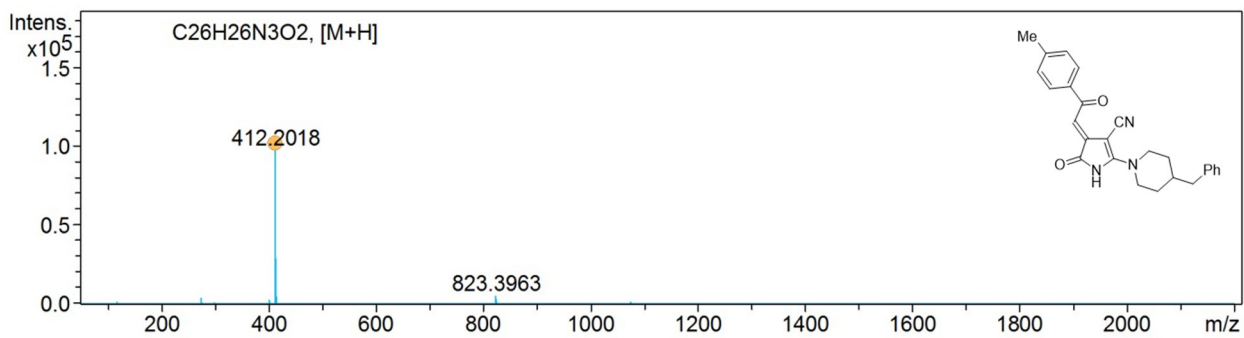
### <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3n**



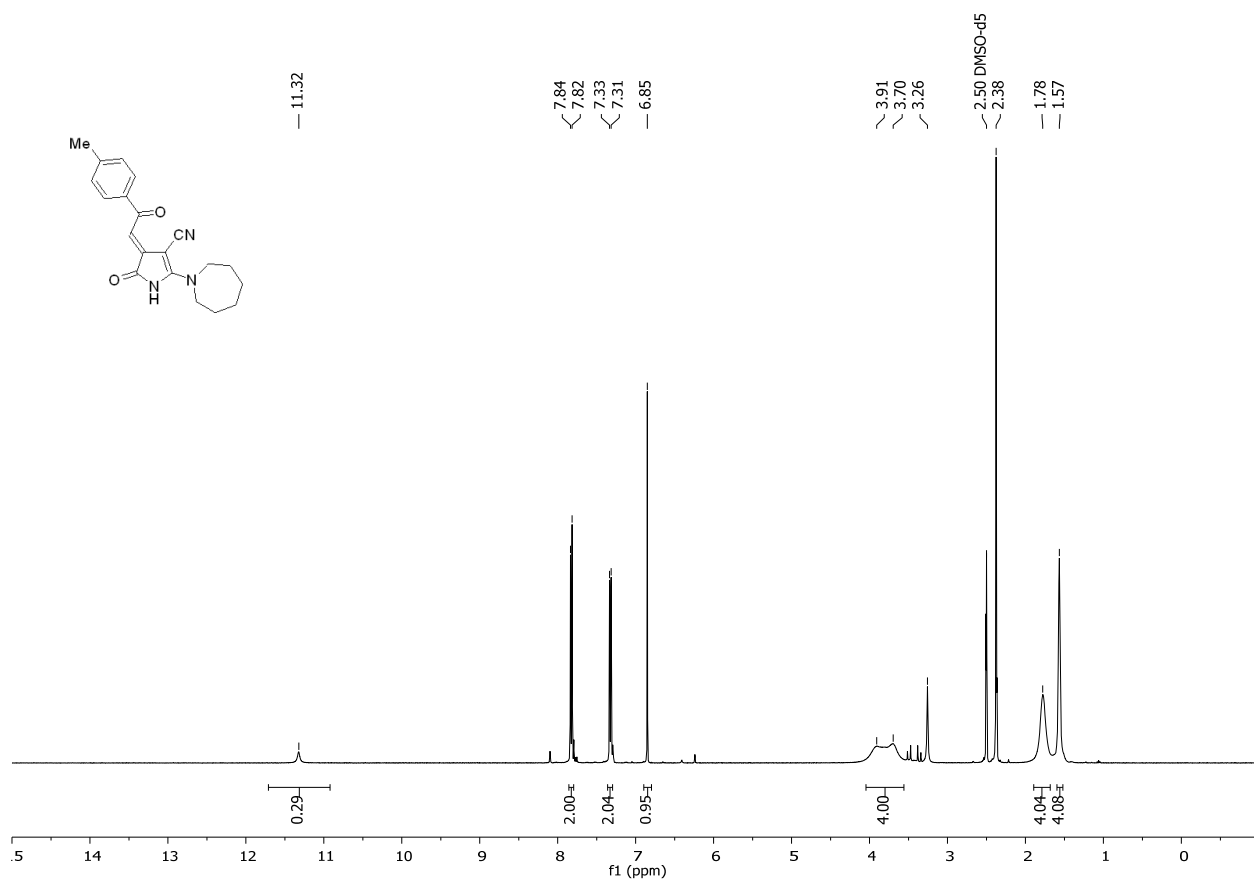
### <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3n**



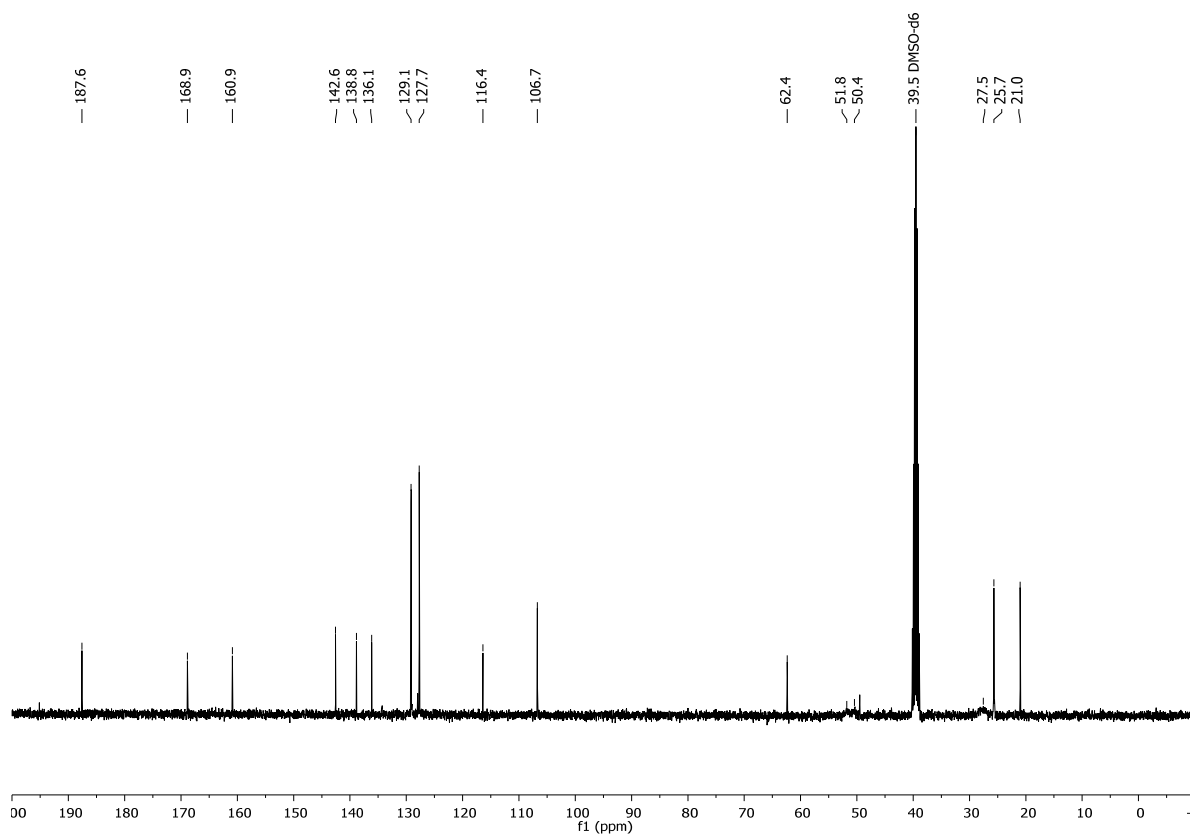
# HRMS spectrum of 3n



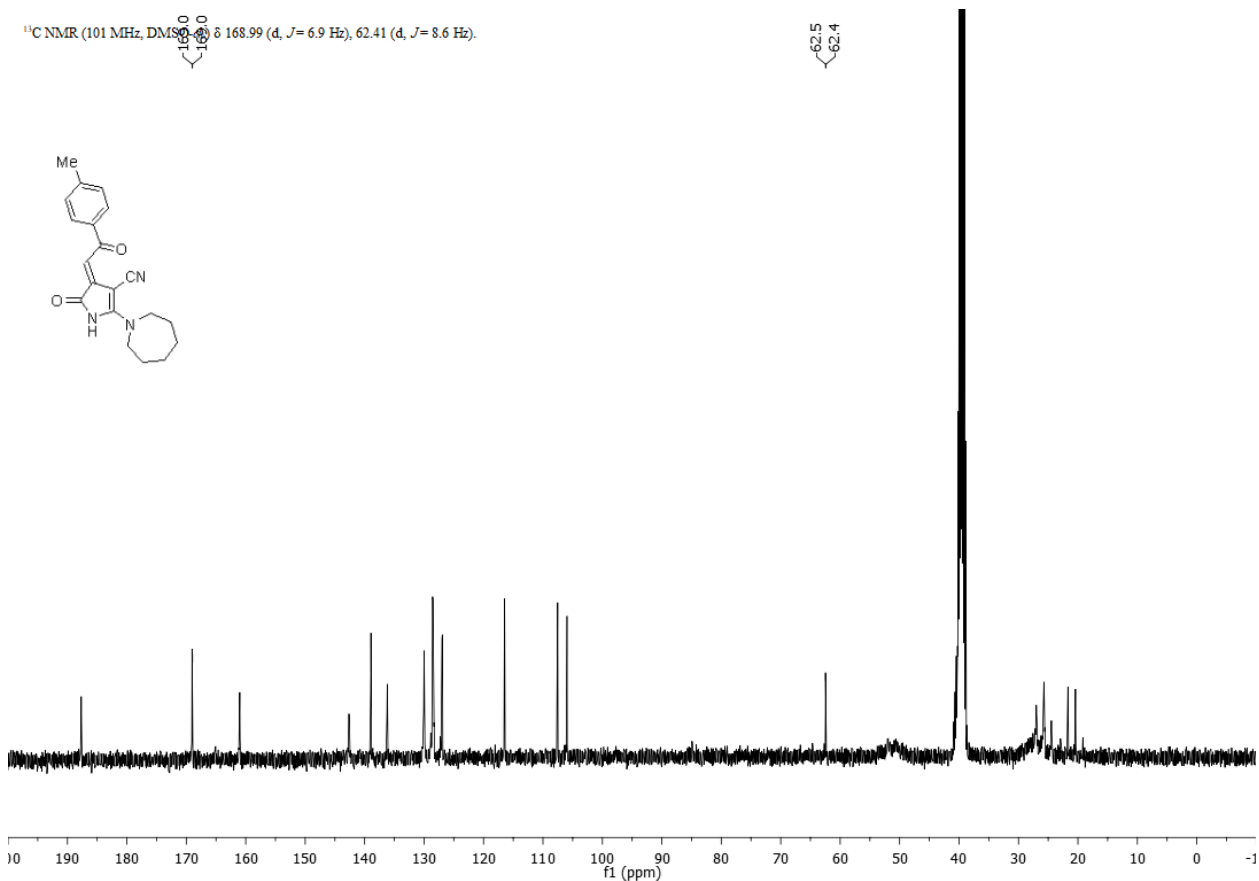
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3o**



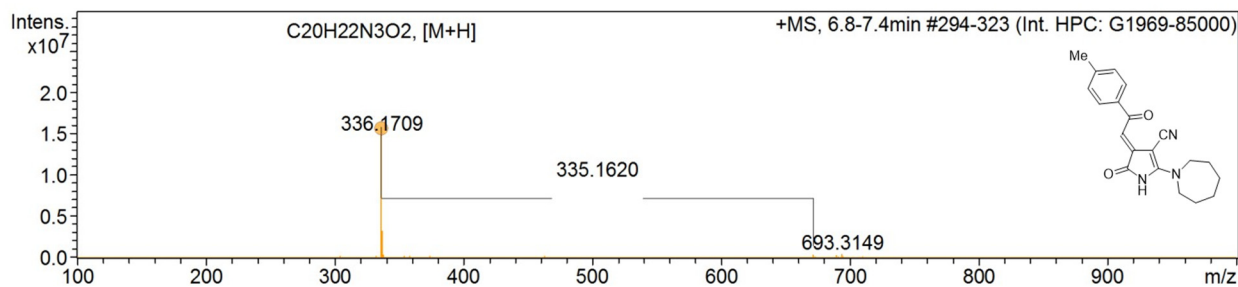
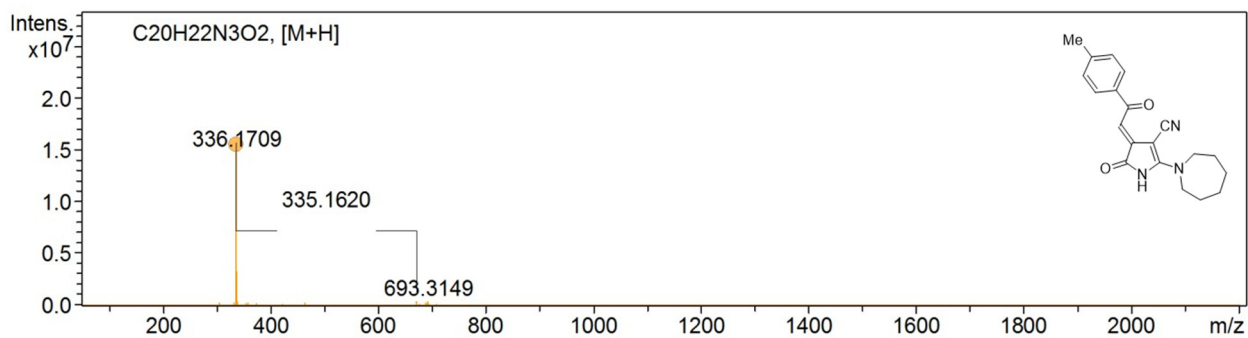
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3o**



# <sup>13</sup>C GATE NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3o**

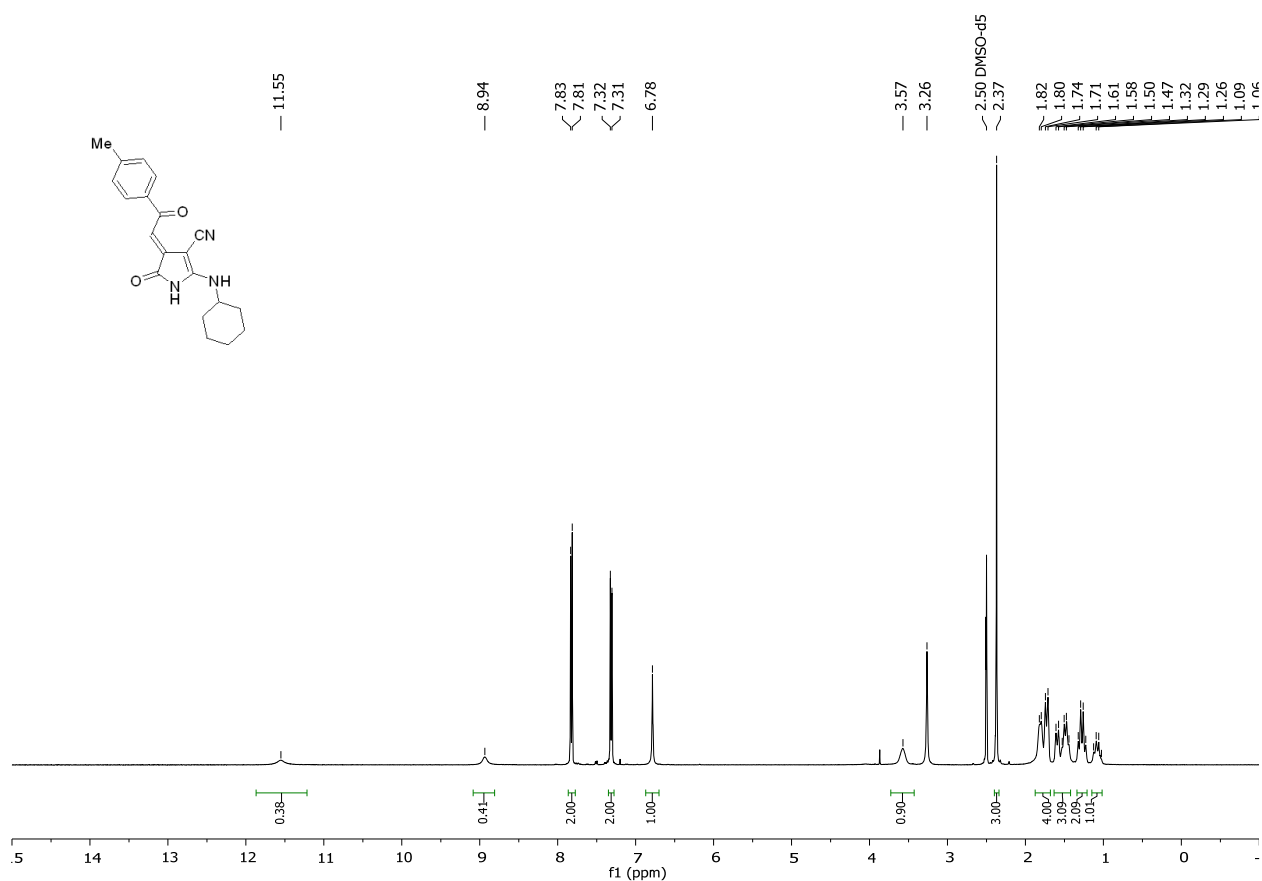


## HRMS spectrum of **3o**

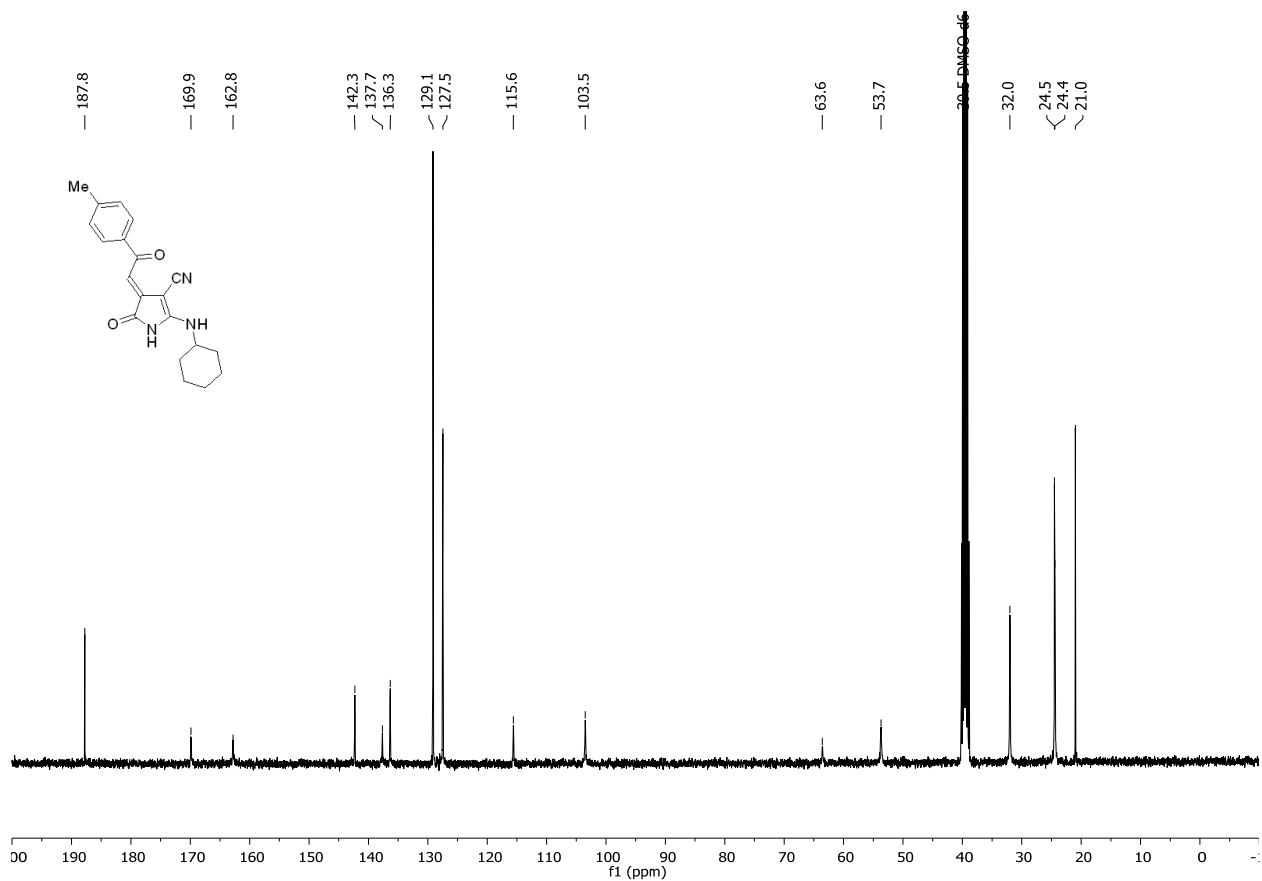




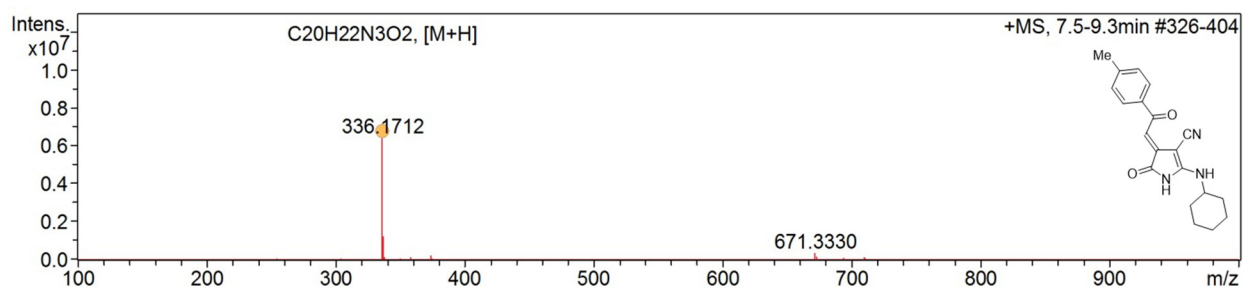
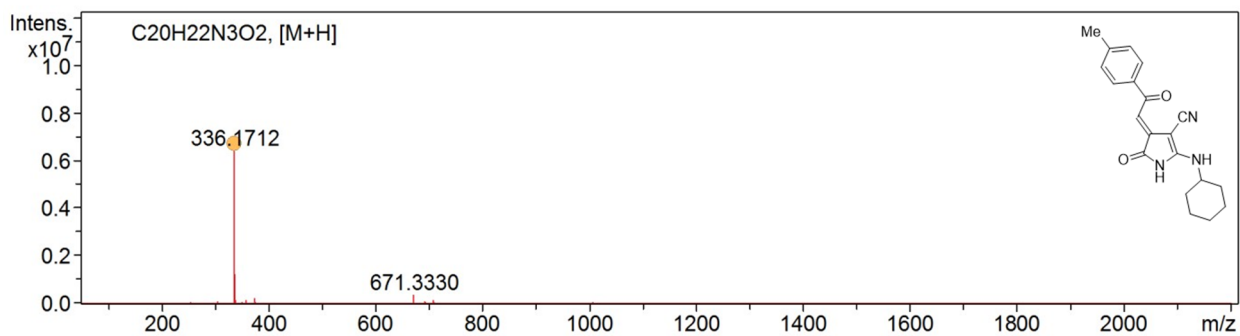
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **3p**



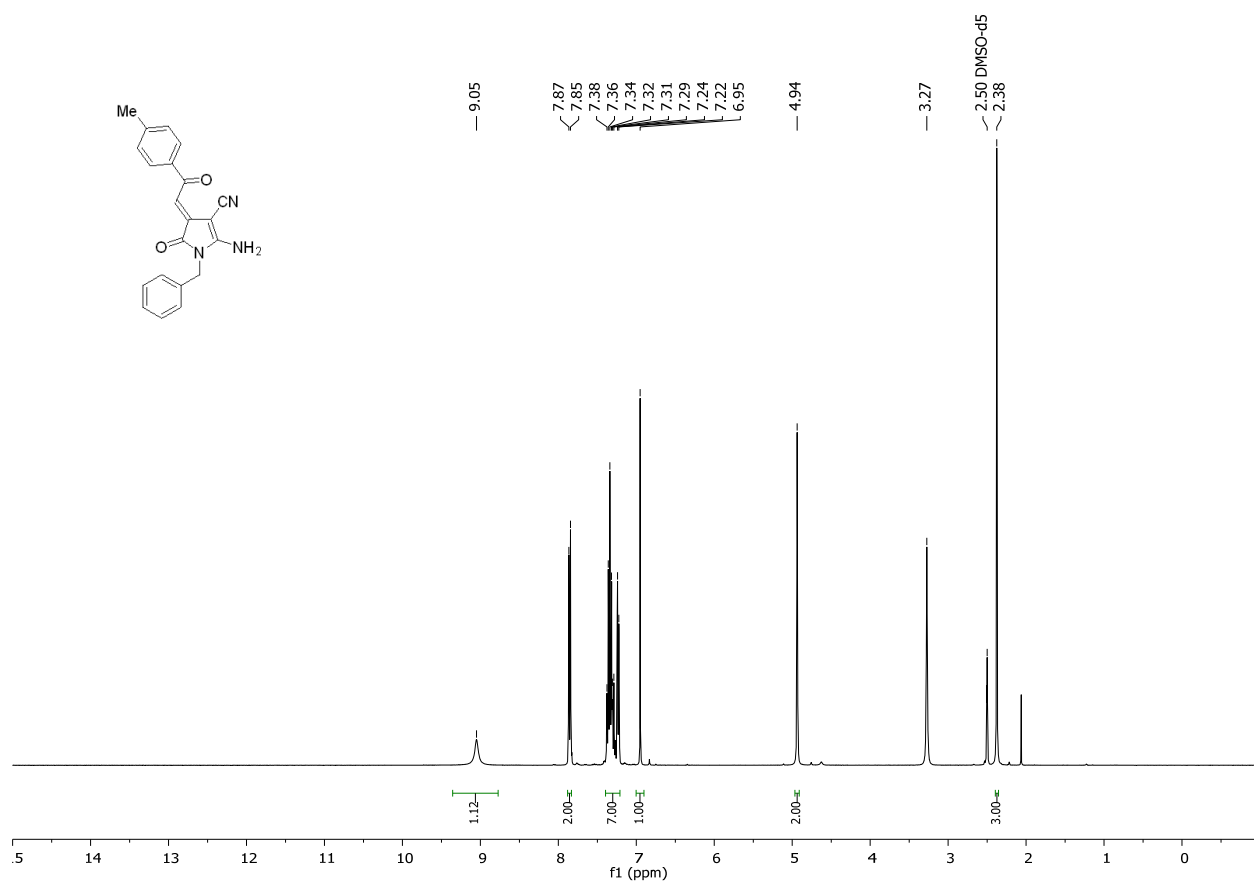
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **3p**



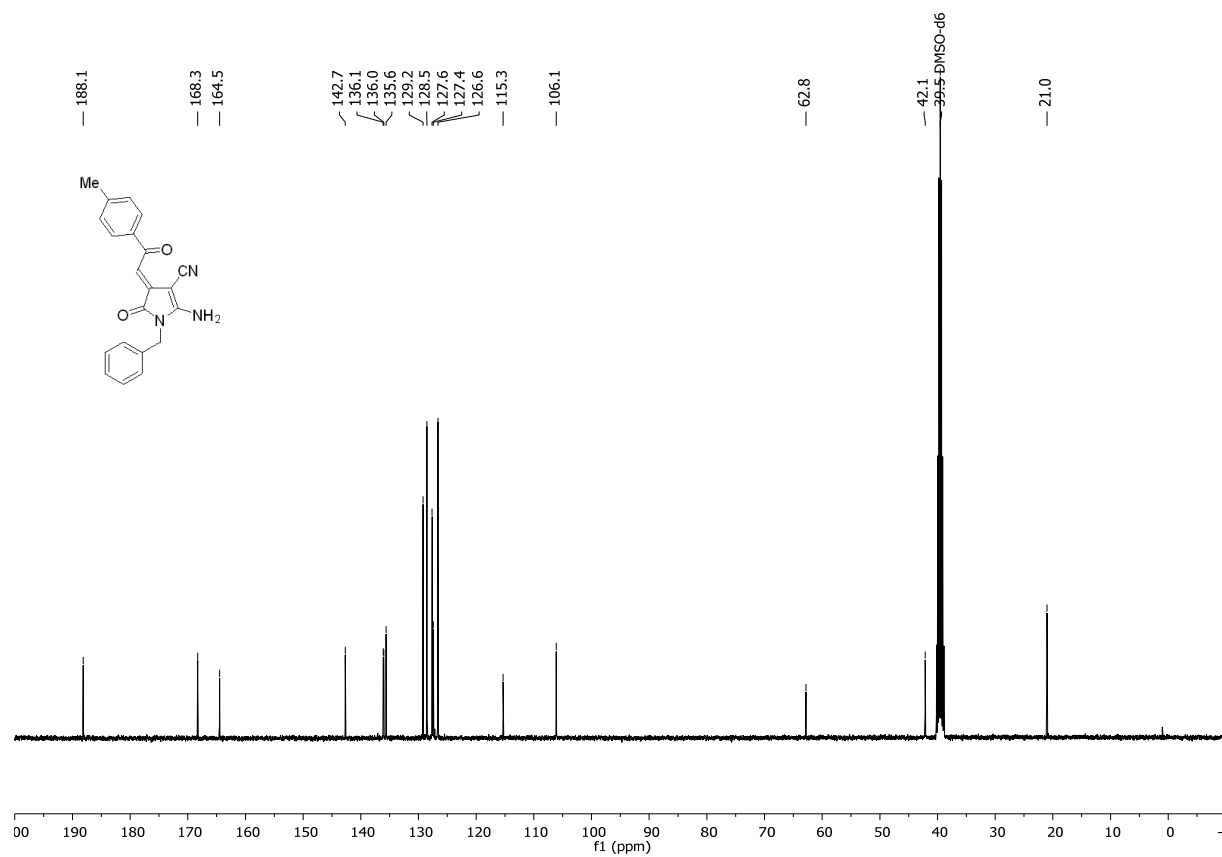
# HRMS spectrum of 3p



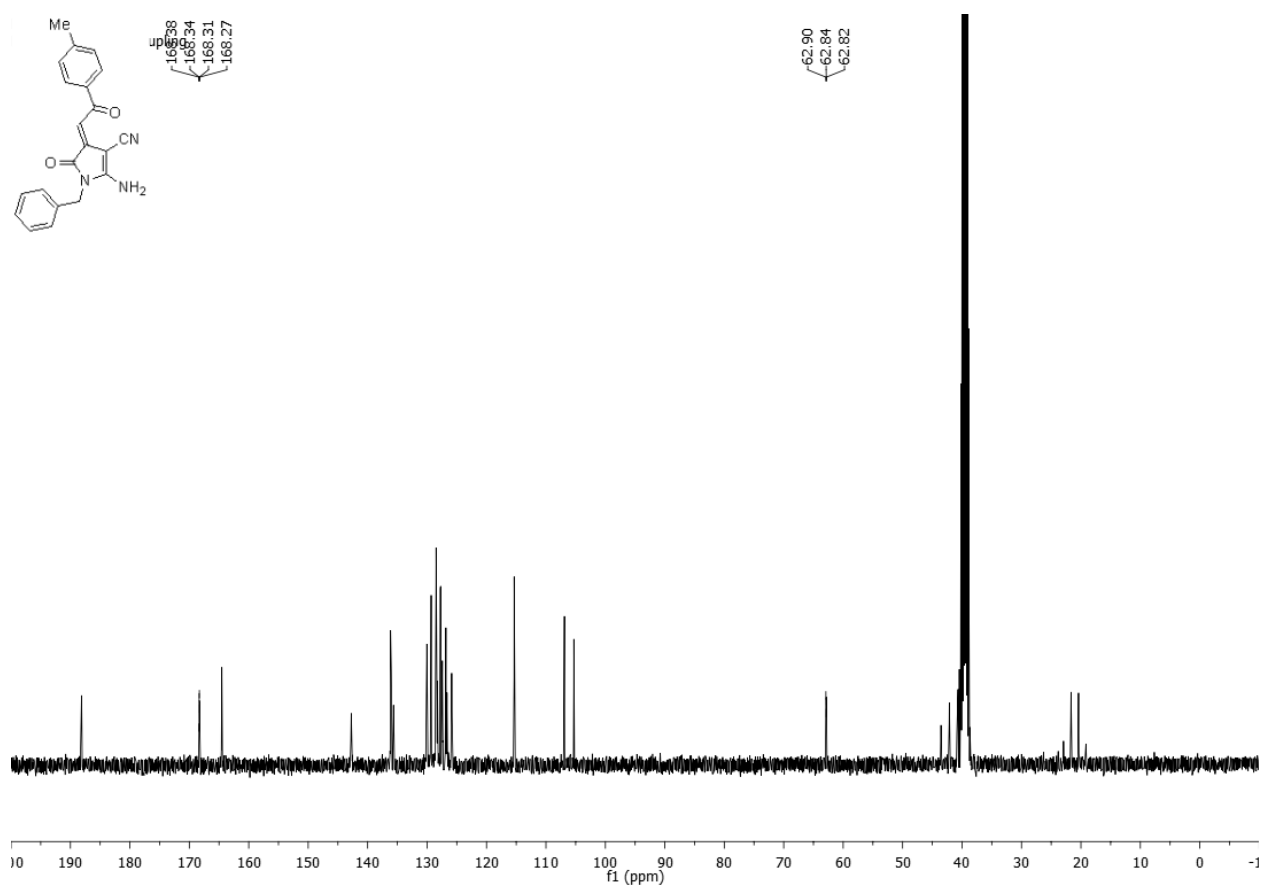
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **4a**



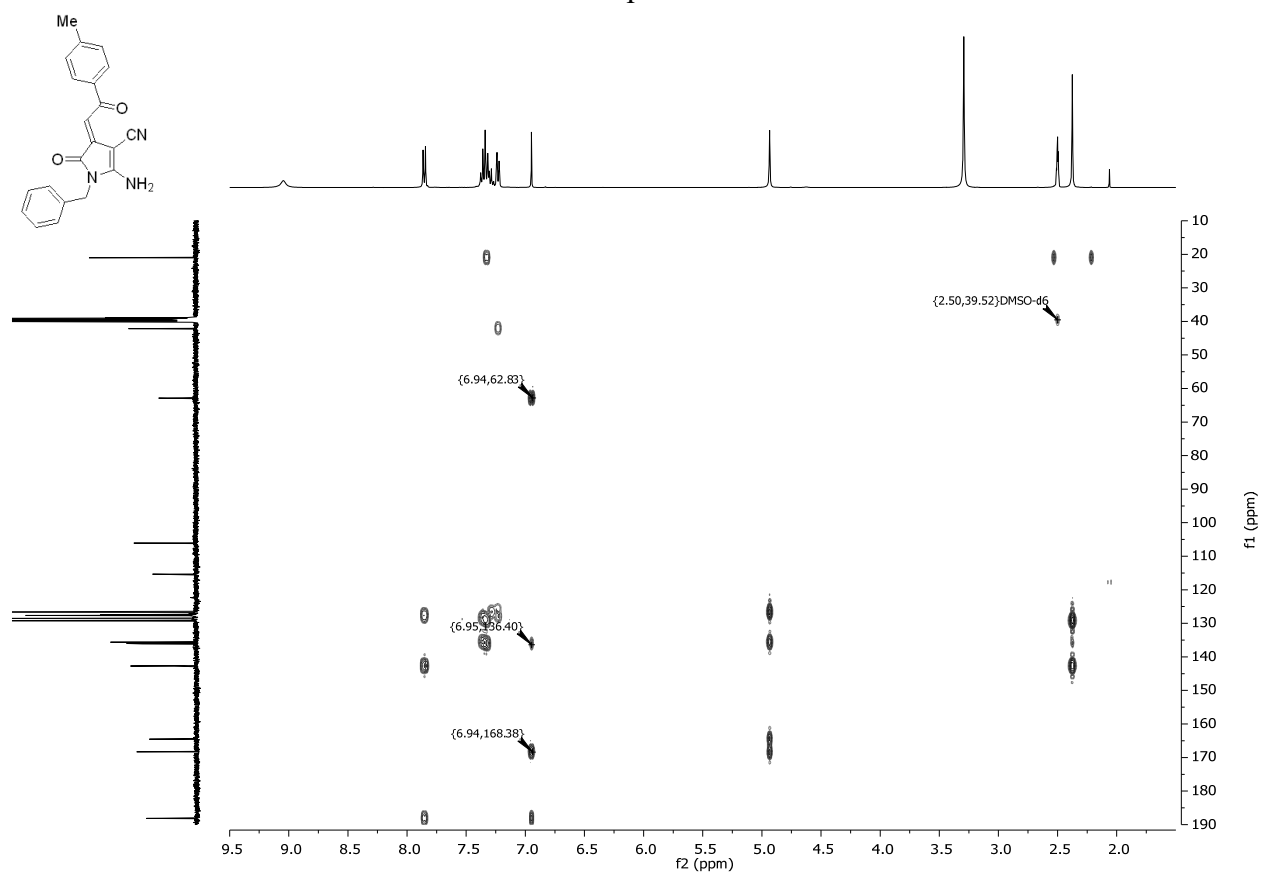
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **4a**



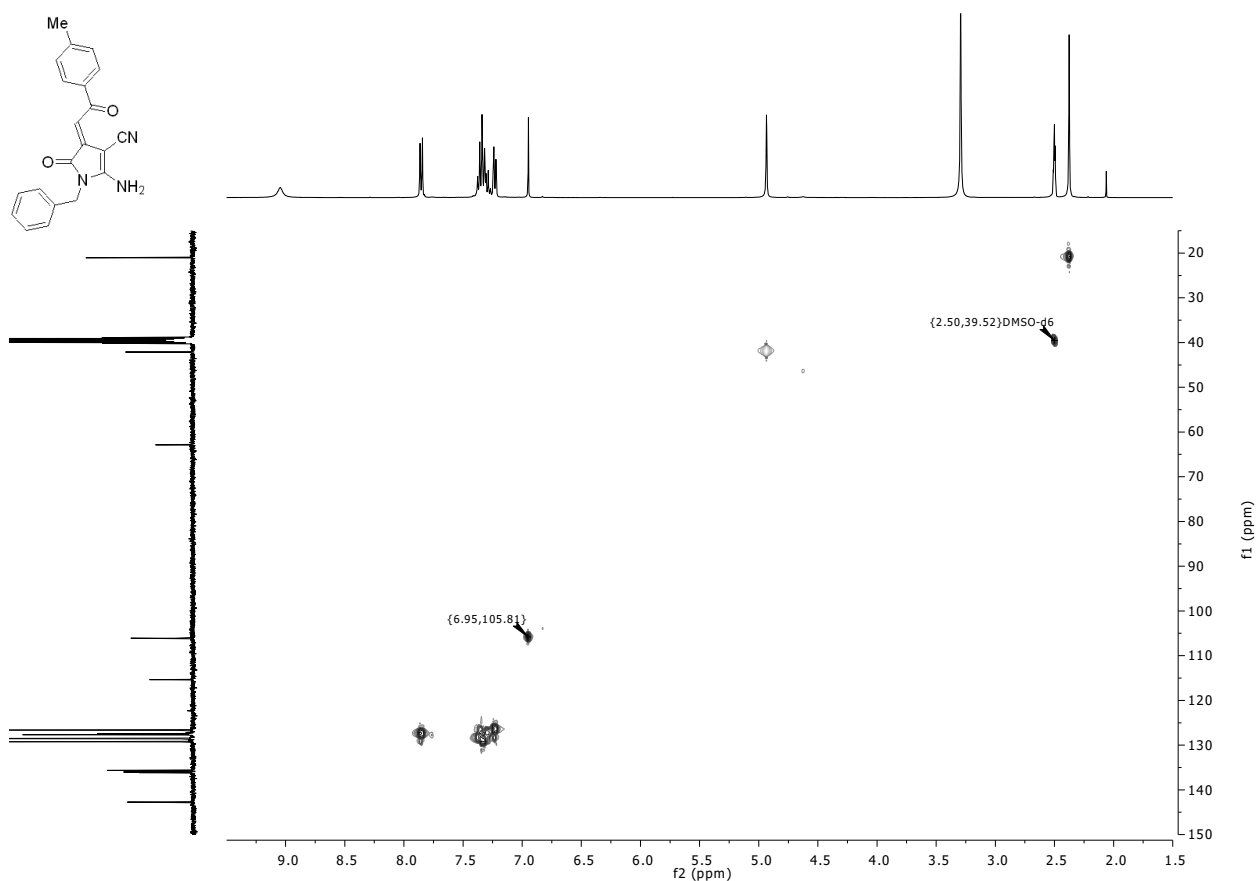
$^{13}\text{C}$  GATE NMR (100 MHz, DMSO- $d_6$ ) spectrum of **4a**



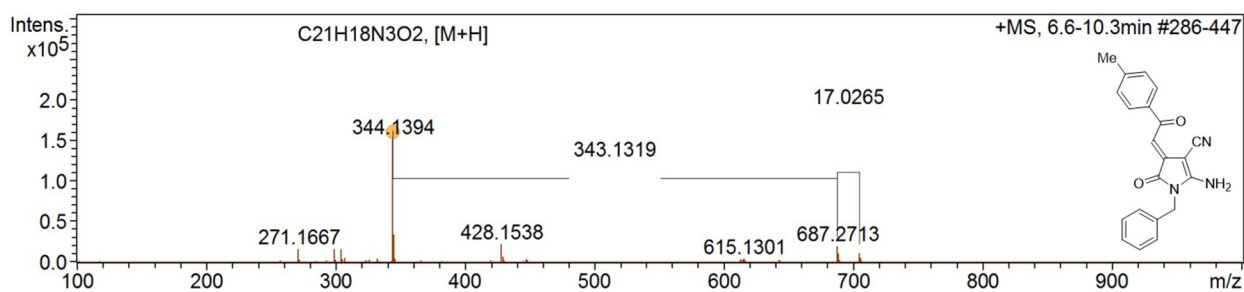
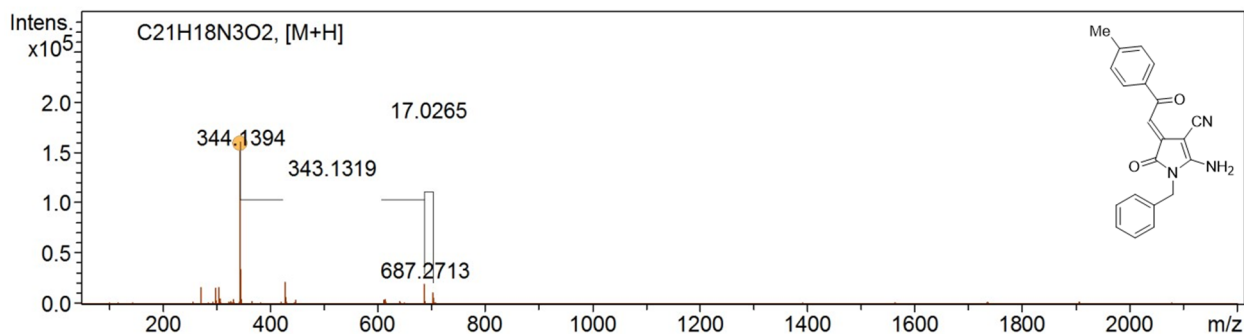
2D HMBC spectrum of **4a**



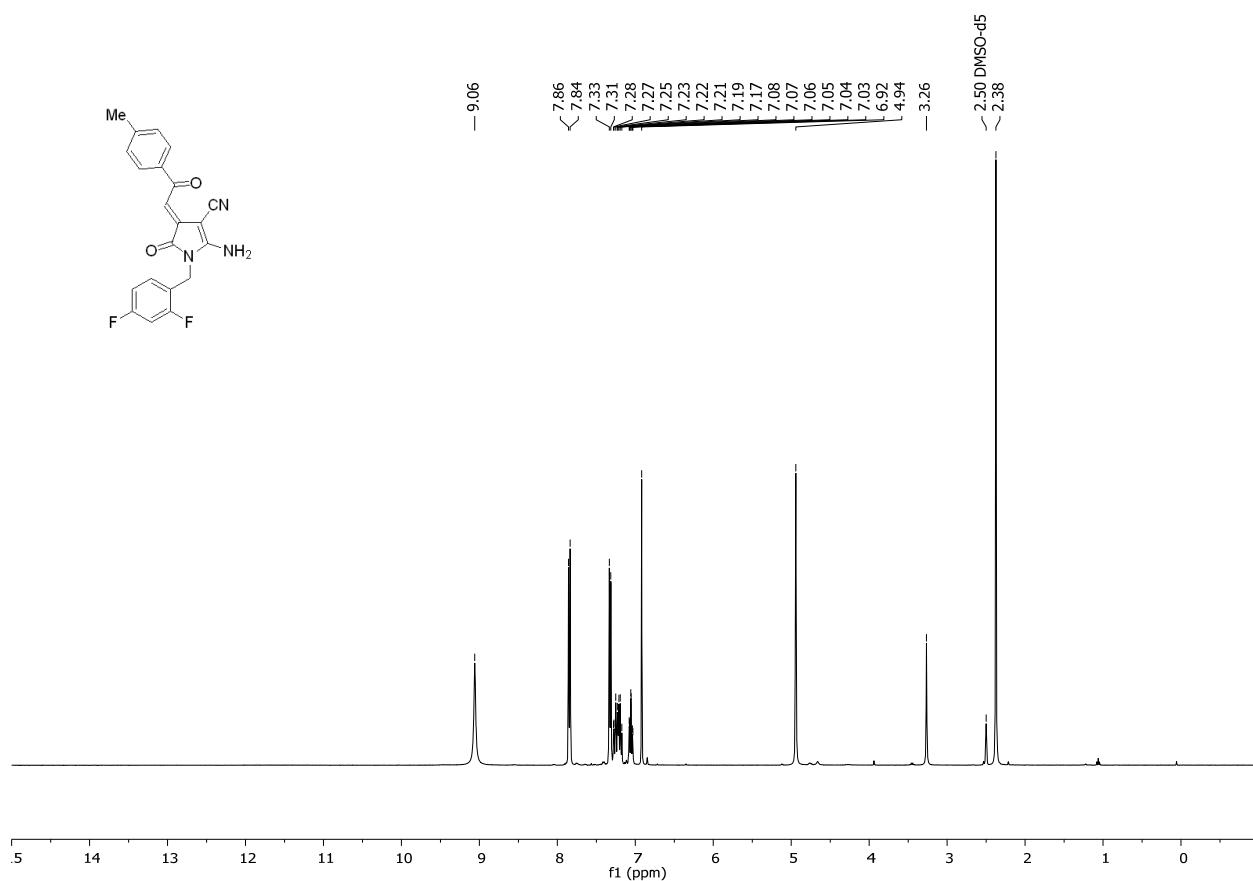
### 2D HSQC spectrum of 4a



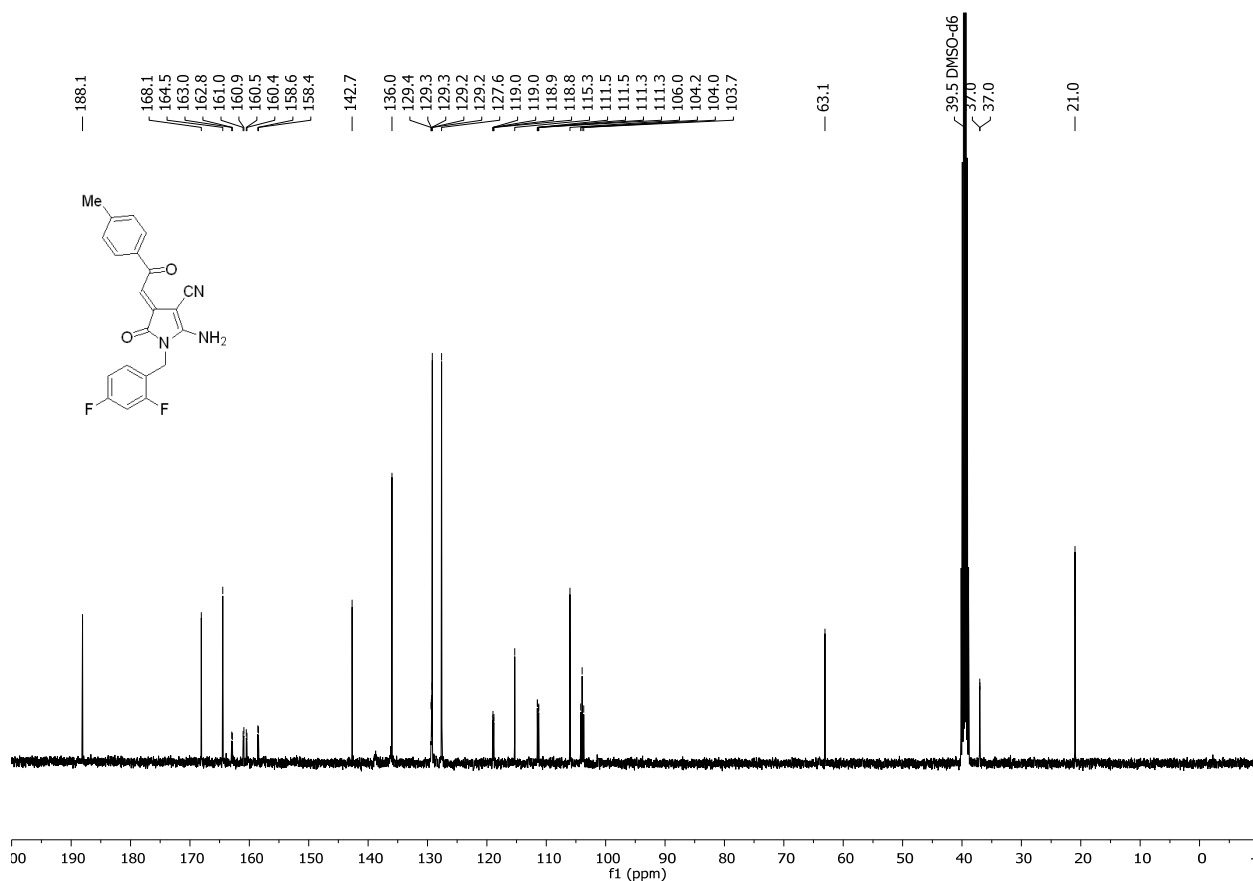
### HRMS spectrum of 4a



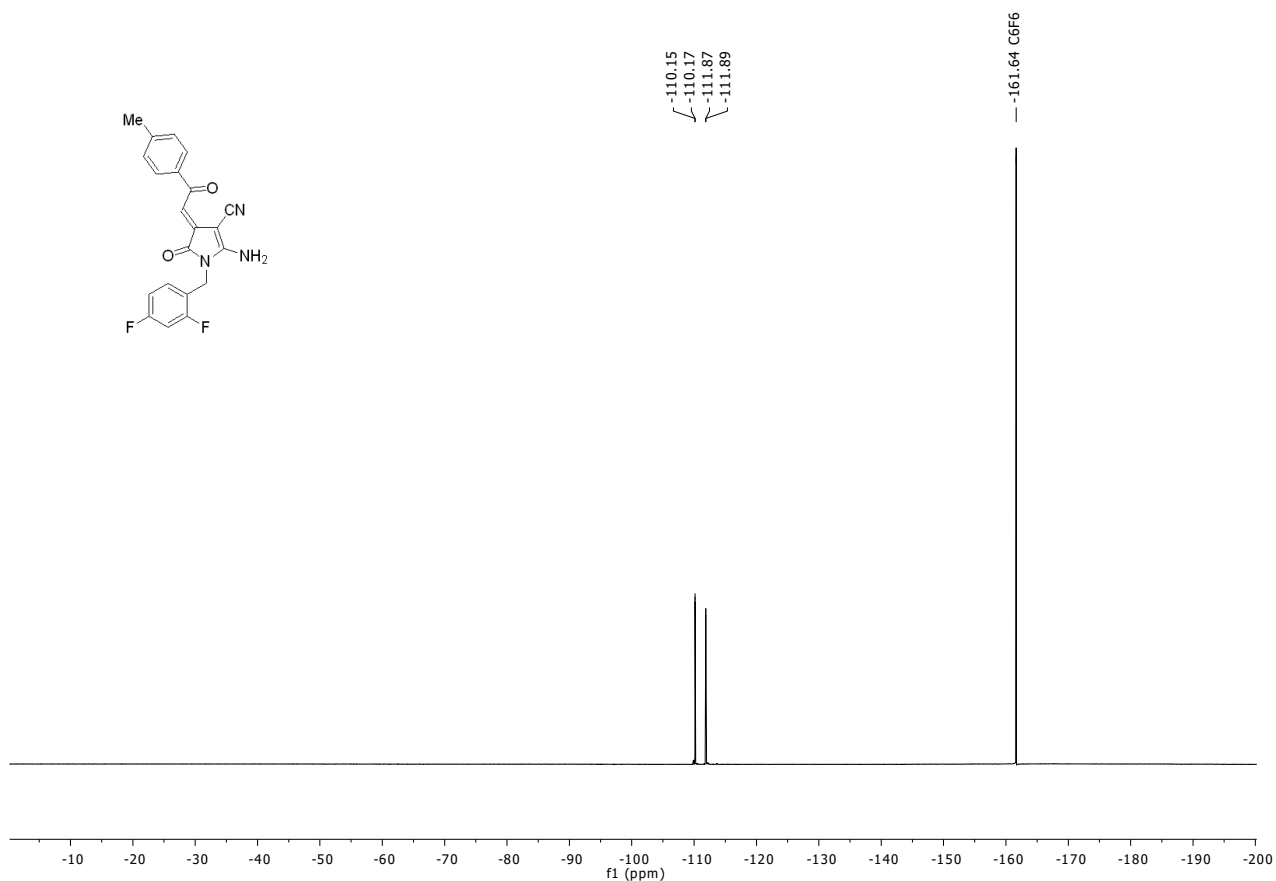
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **4b**



<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **4b**

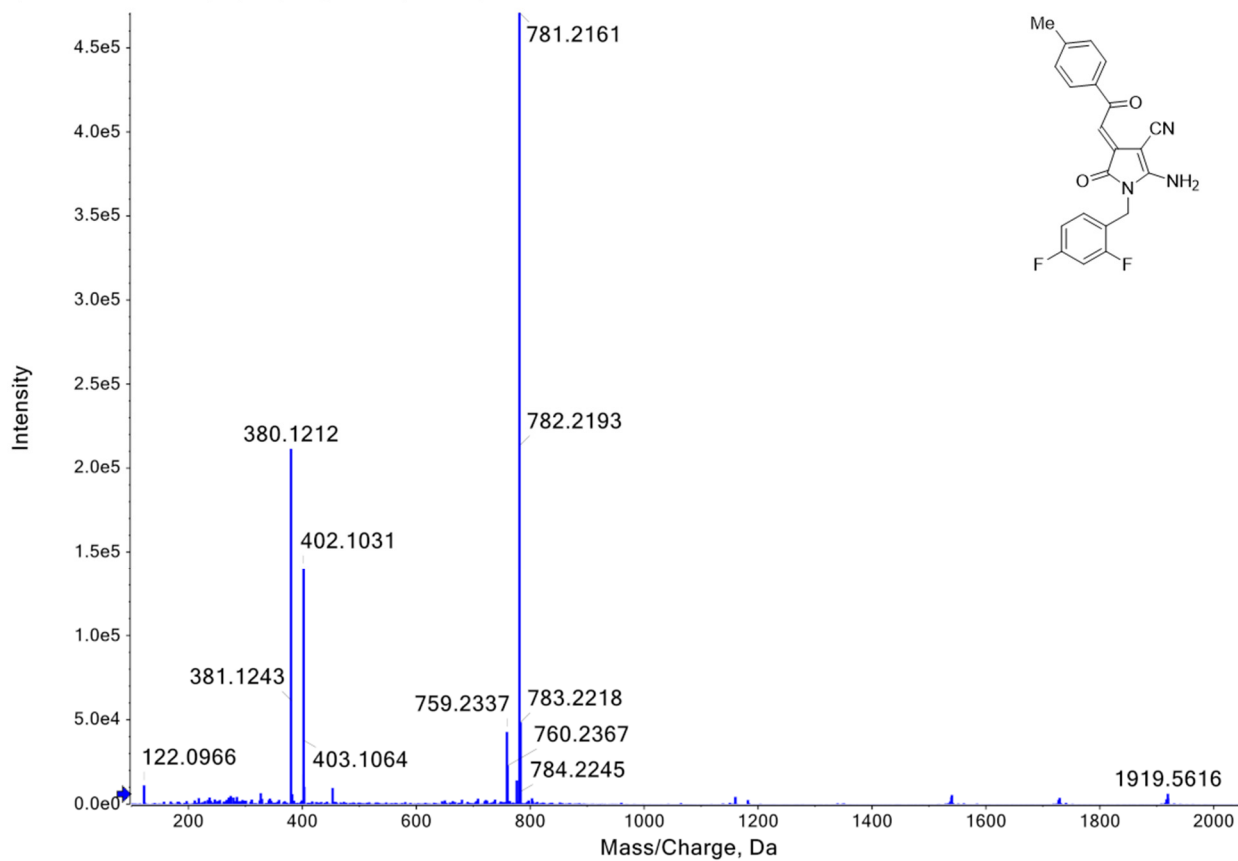


# $^{19}\text{F}$ NMR (377 MHz, DMSO- $d_6$ ) spectrum of **4b**

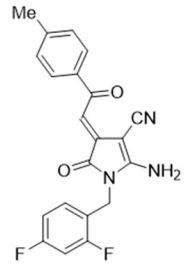
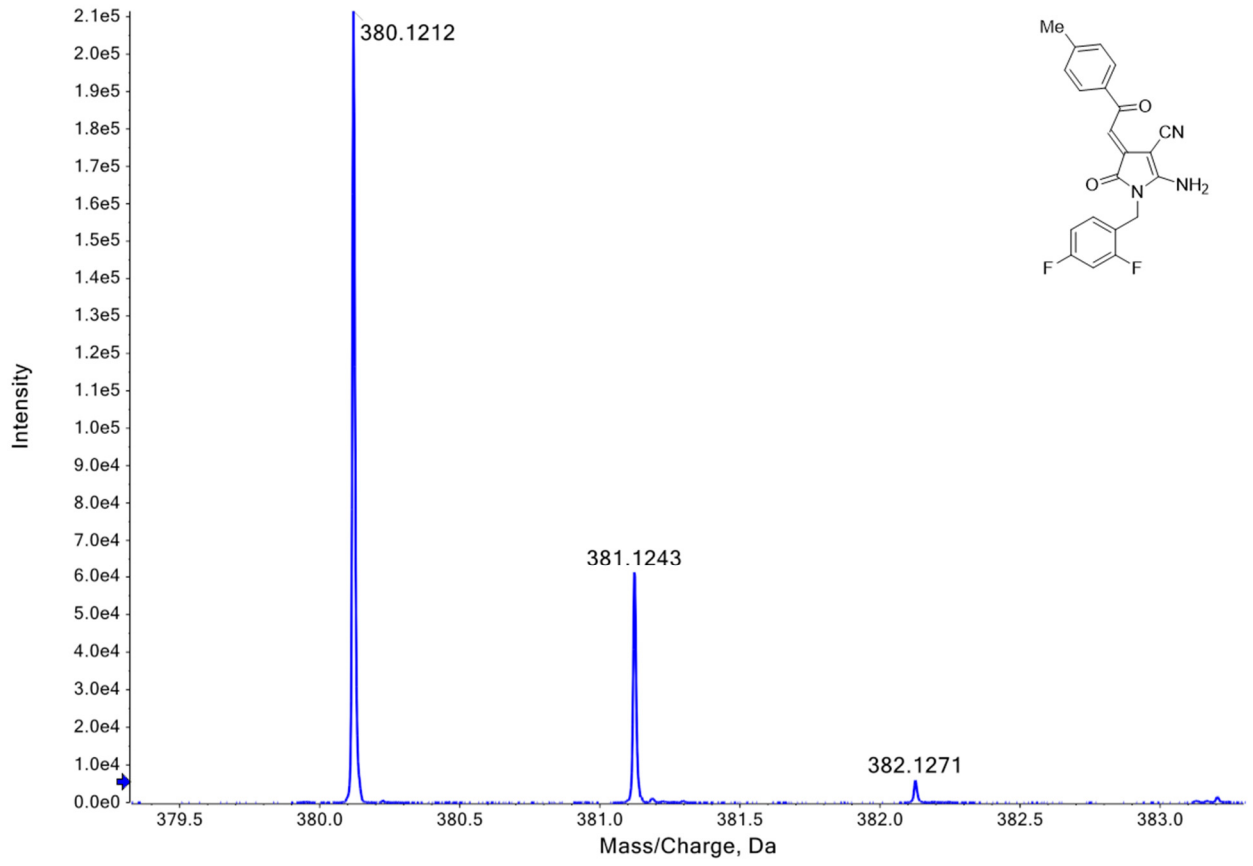


# HRMS spectrum of **4b**

Spectrum from ESI POS.wiff (sample 42) - 325, +TOF MS (100 - 3000) from 0.618 to 0.660 min

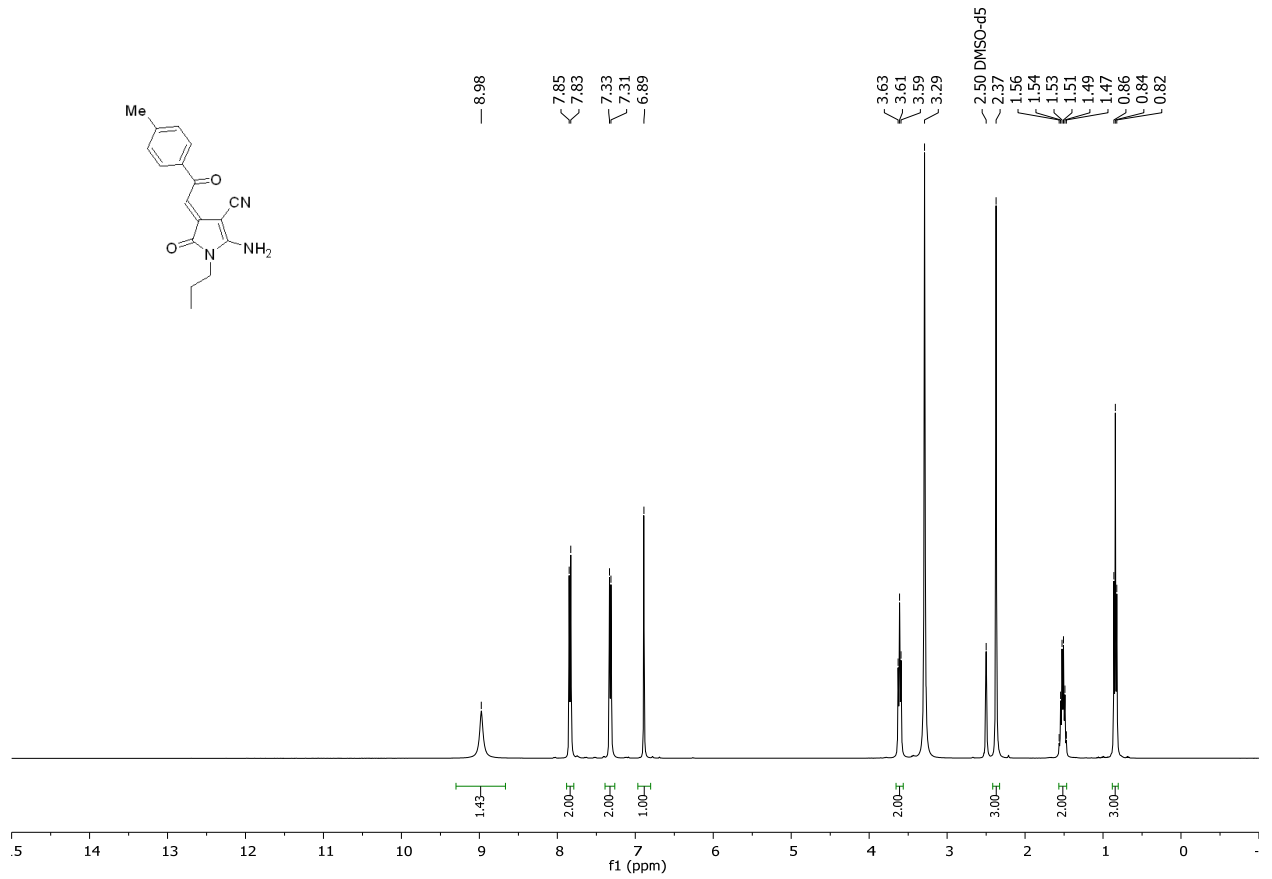


Spectrum from ESI POS.wiff (sample 42) - 325, +TOF MS (100 - 3000) from 0.618 to 0.660 min

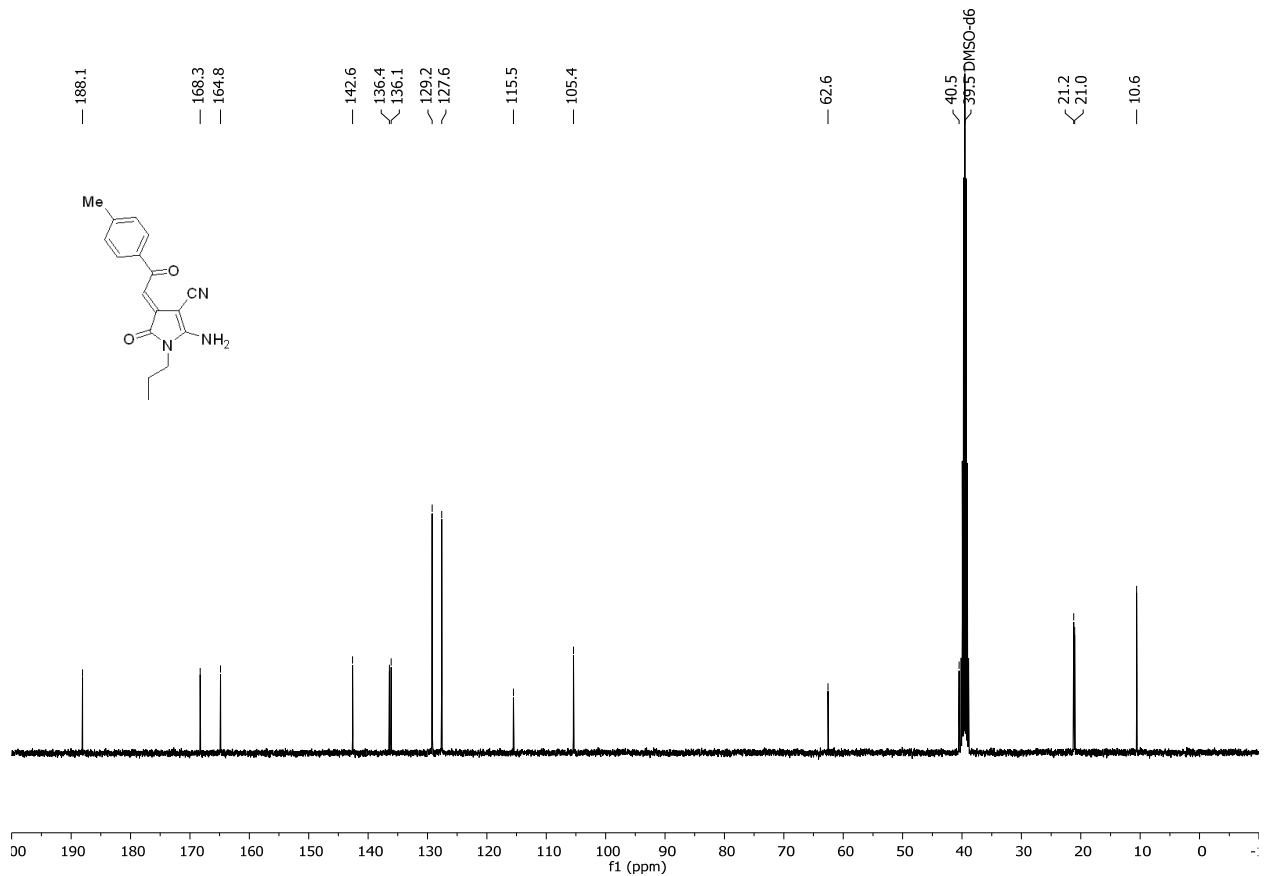




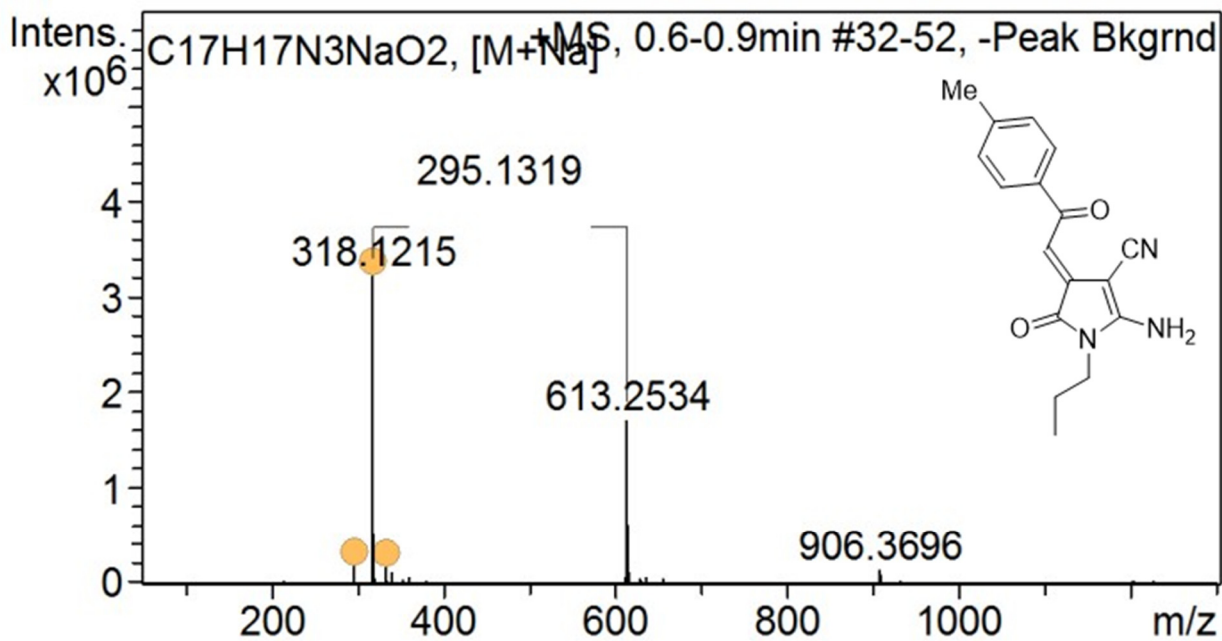
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **4c**



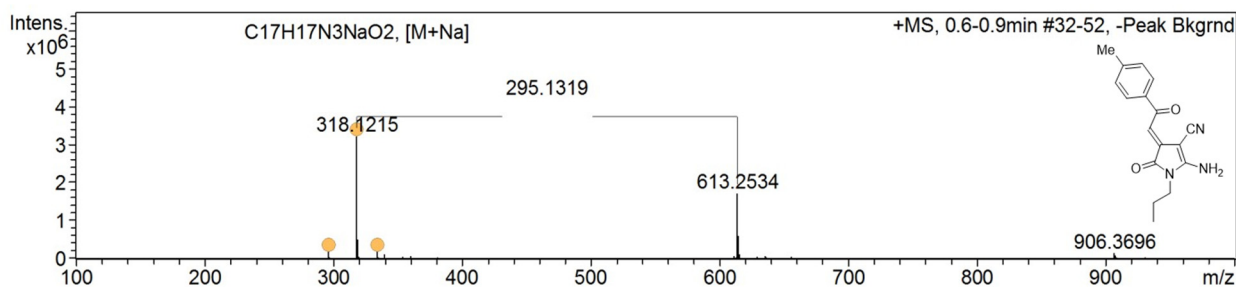
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **4c**



HRMS spectrum of **4c**

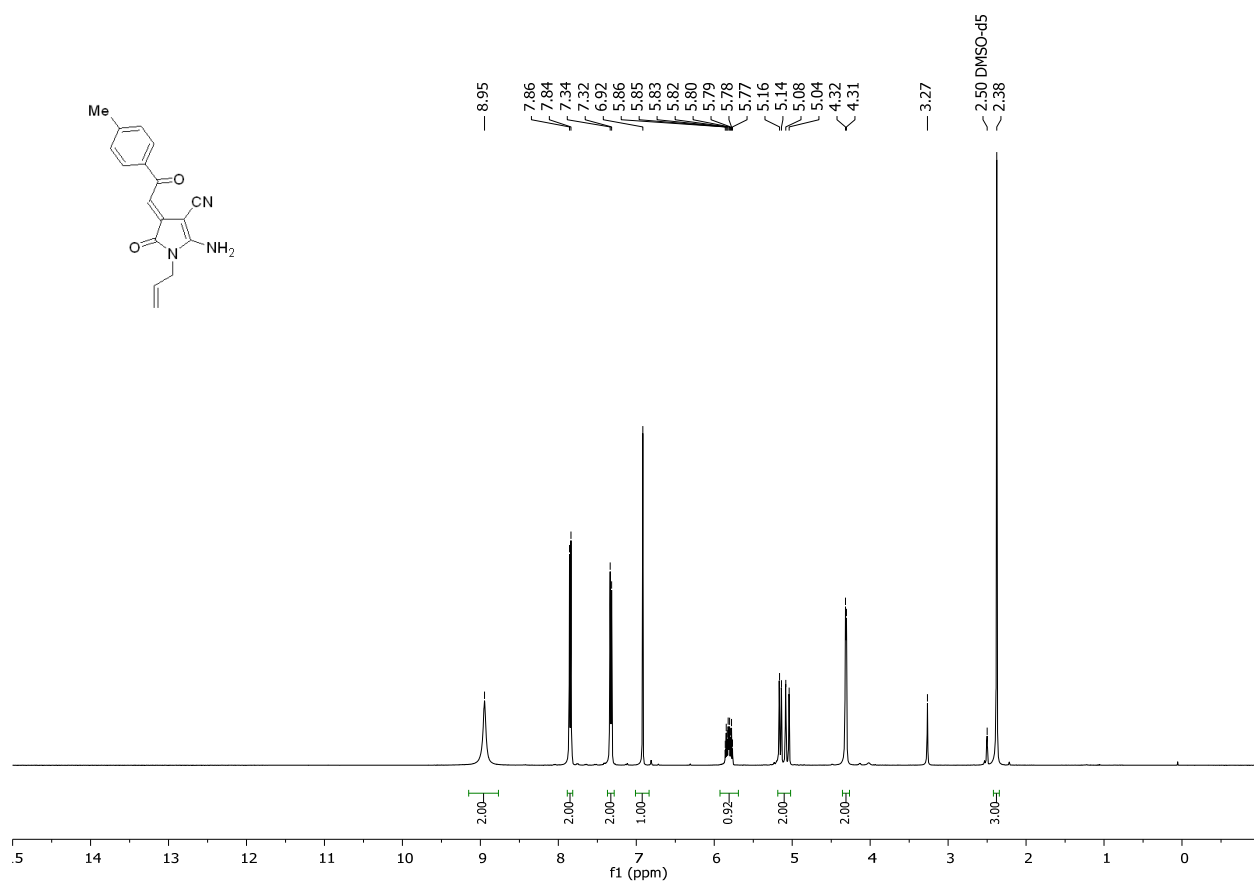


#	m/z	Res.	S/N	I	I %	FWHM
1	296.1390	22613	95207144.0	179414	5.6	0.0131

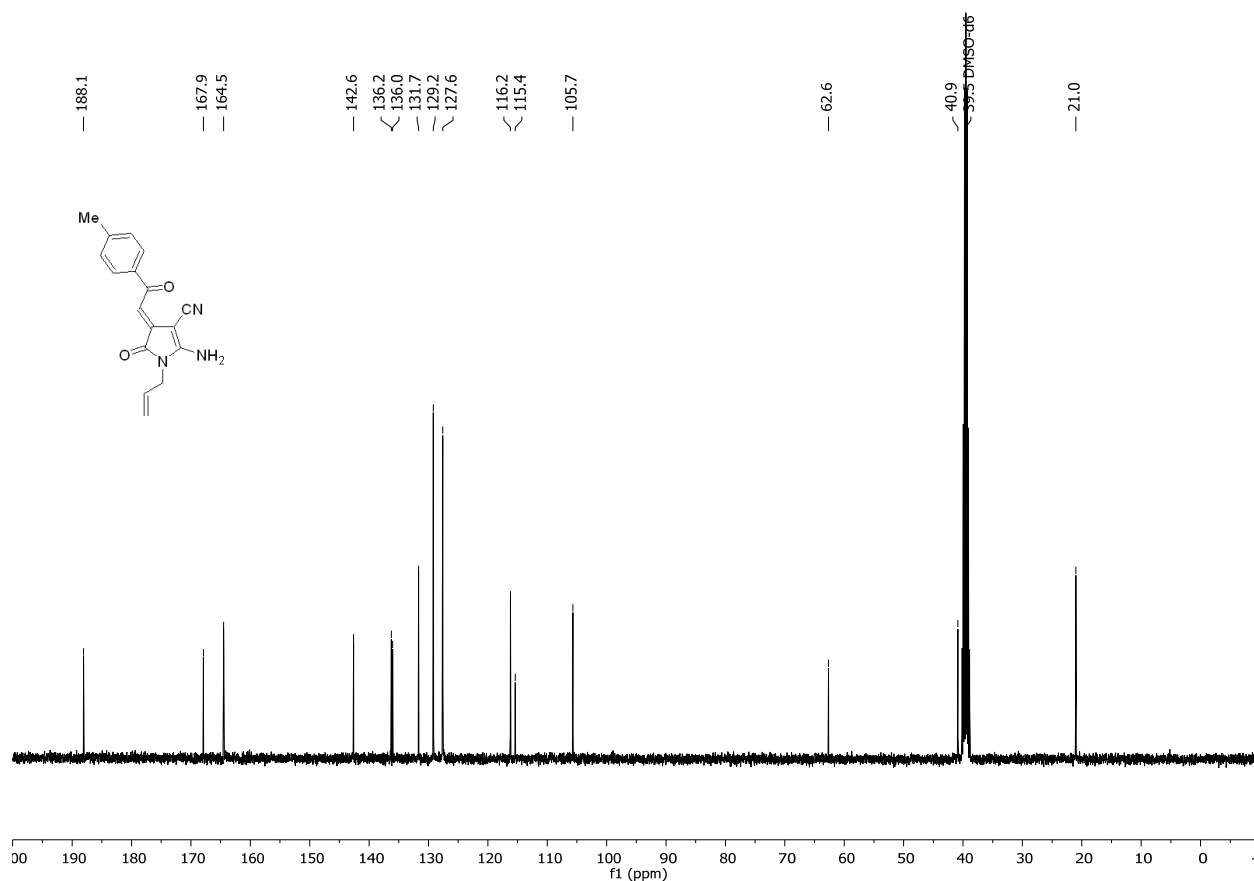


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
296.1390	1	C <sub>17</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub>	296.1394	1.2	8.7	1	100.00	10.5	even	ok

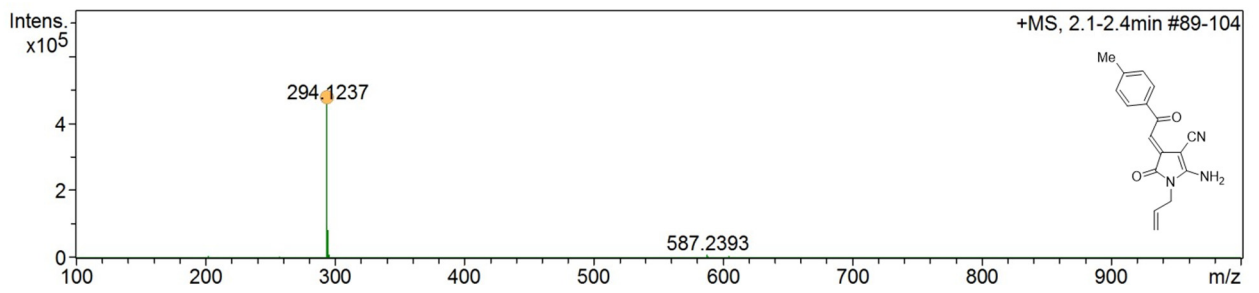
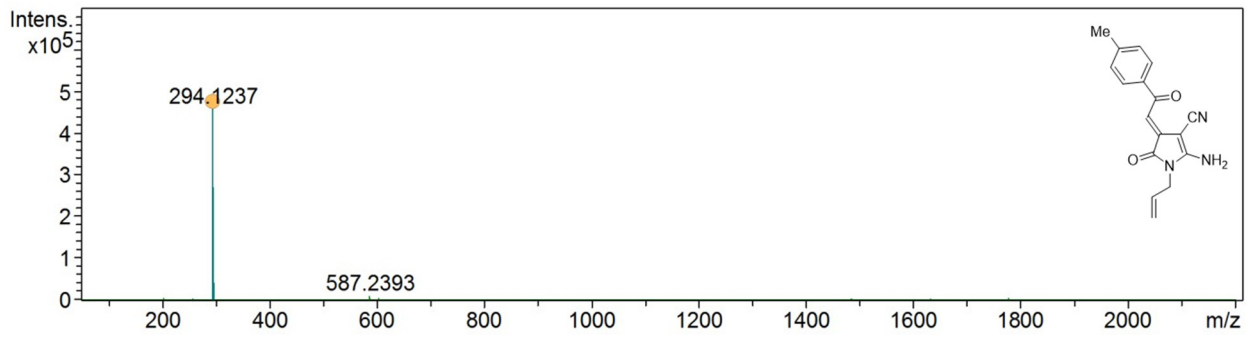
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **4d**



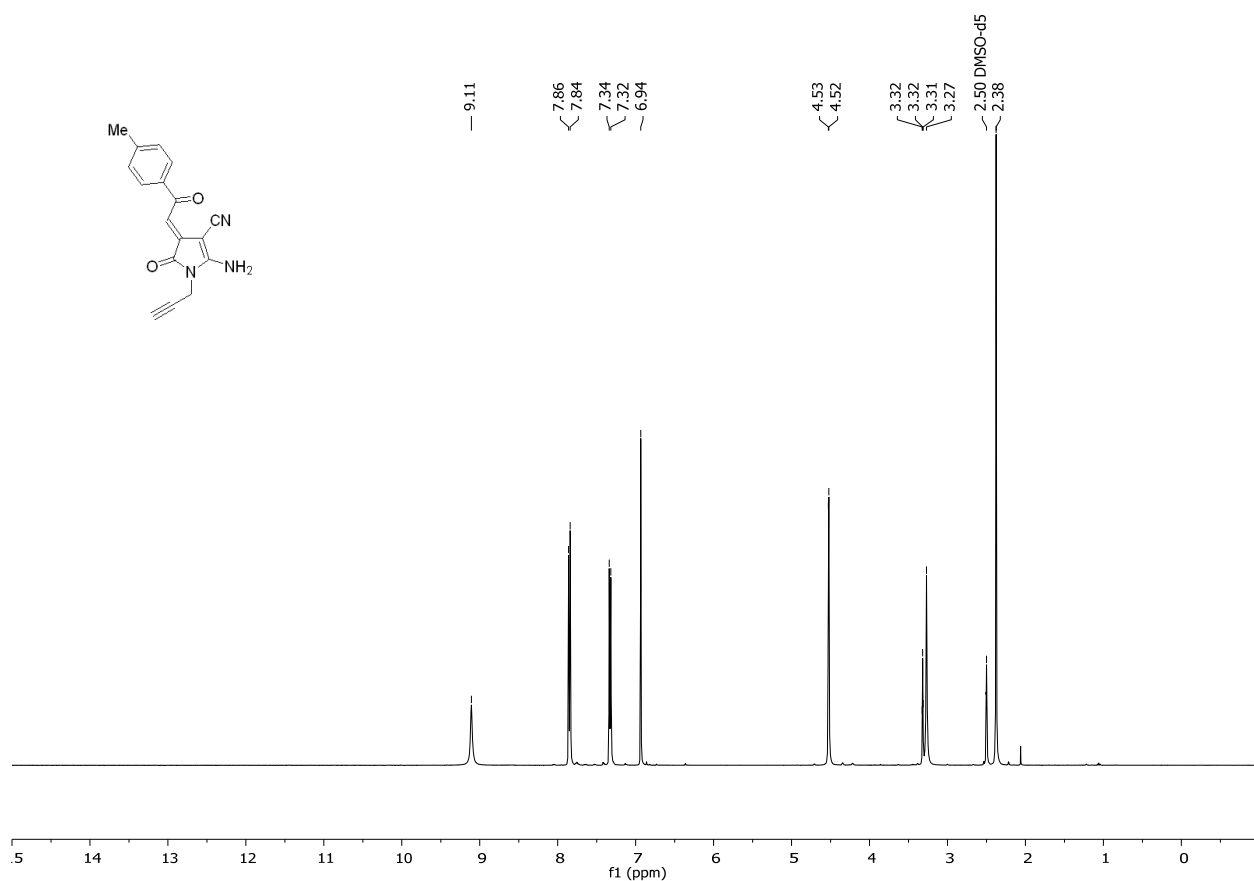
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **4d**



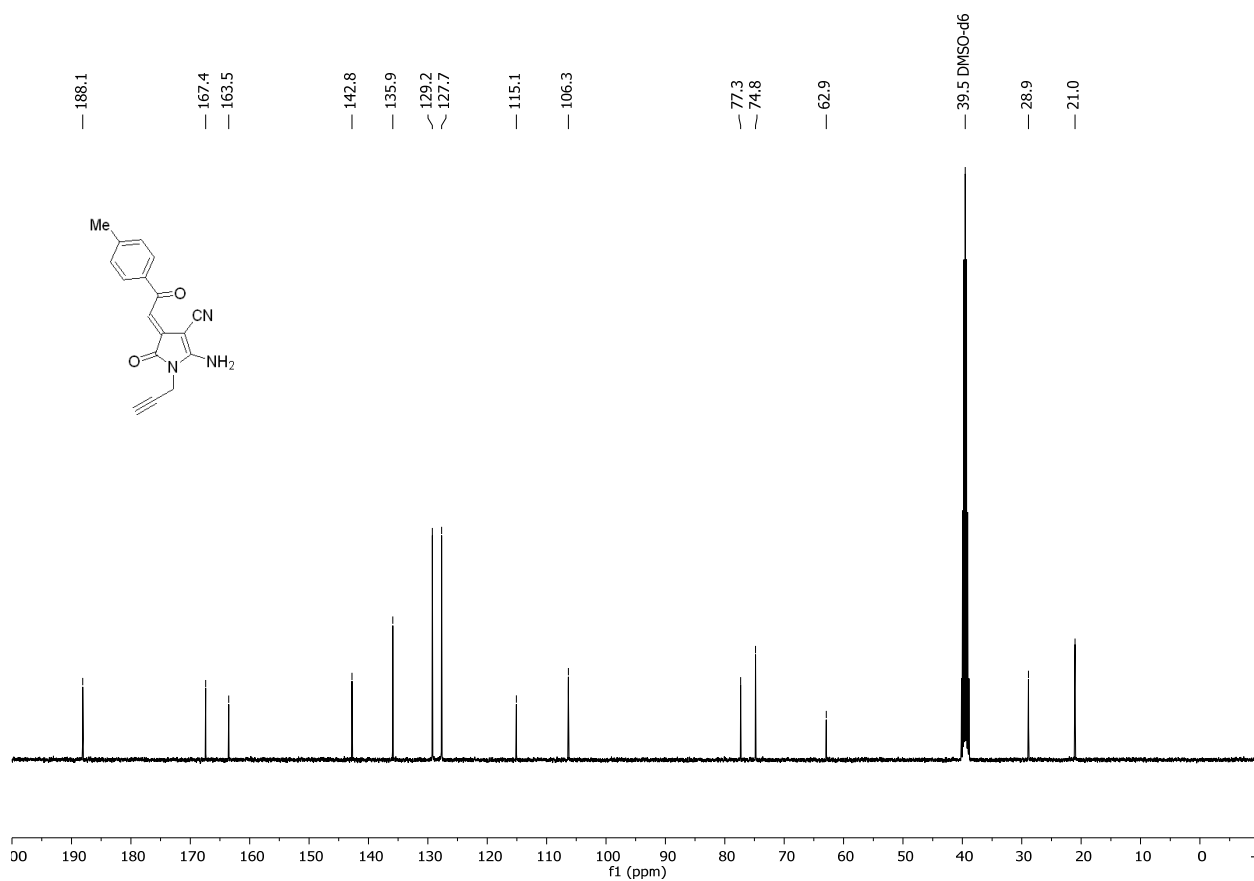
# HRMS spectrum of 4d



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **4e**

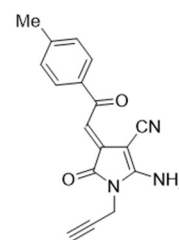
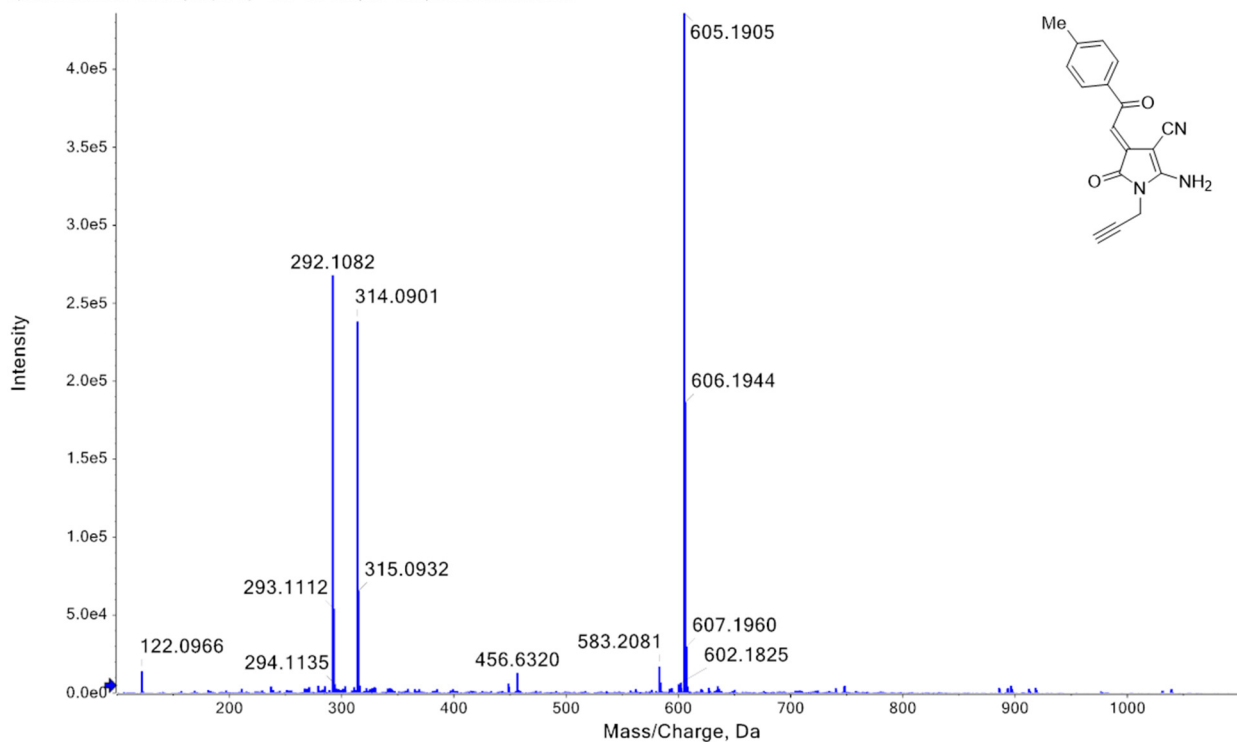


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **4e**

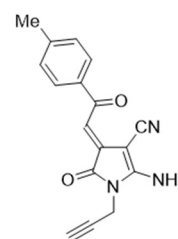
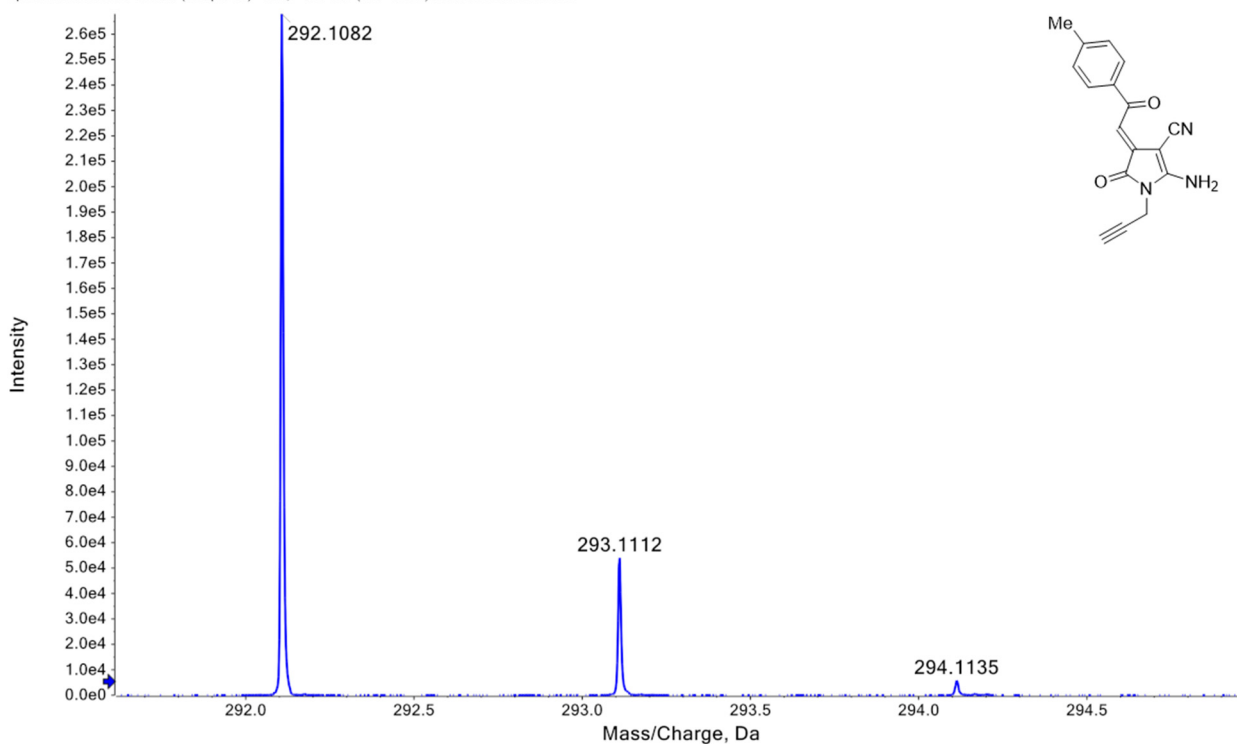


# HRMS spectrum of 4e

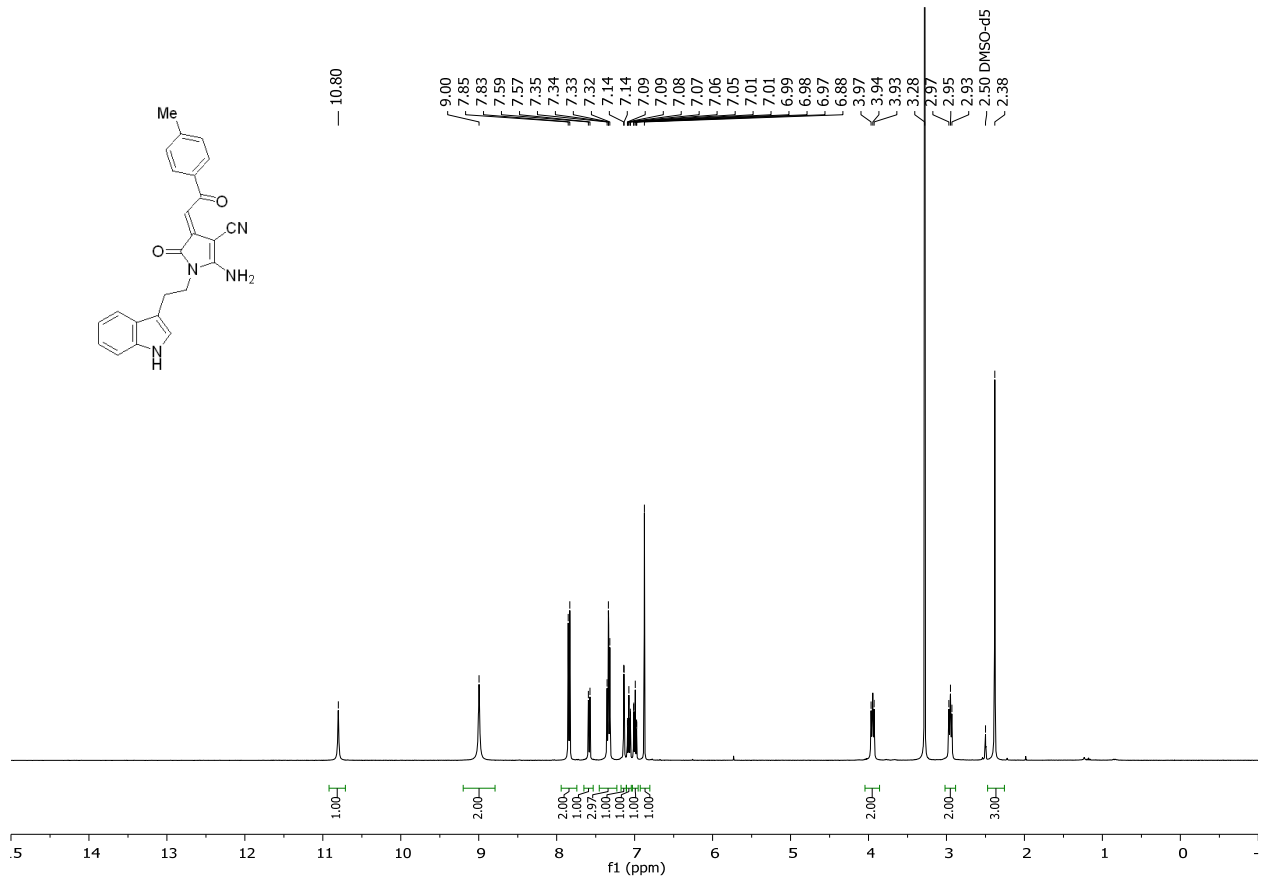
Spectrum from ESI POS.wiff (sample 45) - 491, +TOF MS (100 - 3000) from 0.618 to 0.660 min



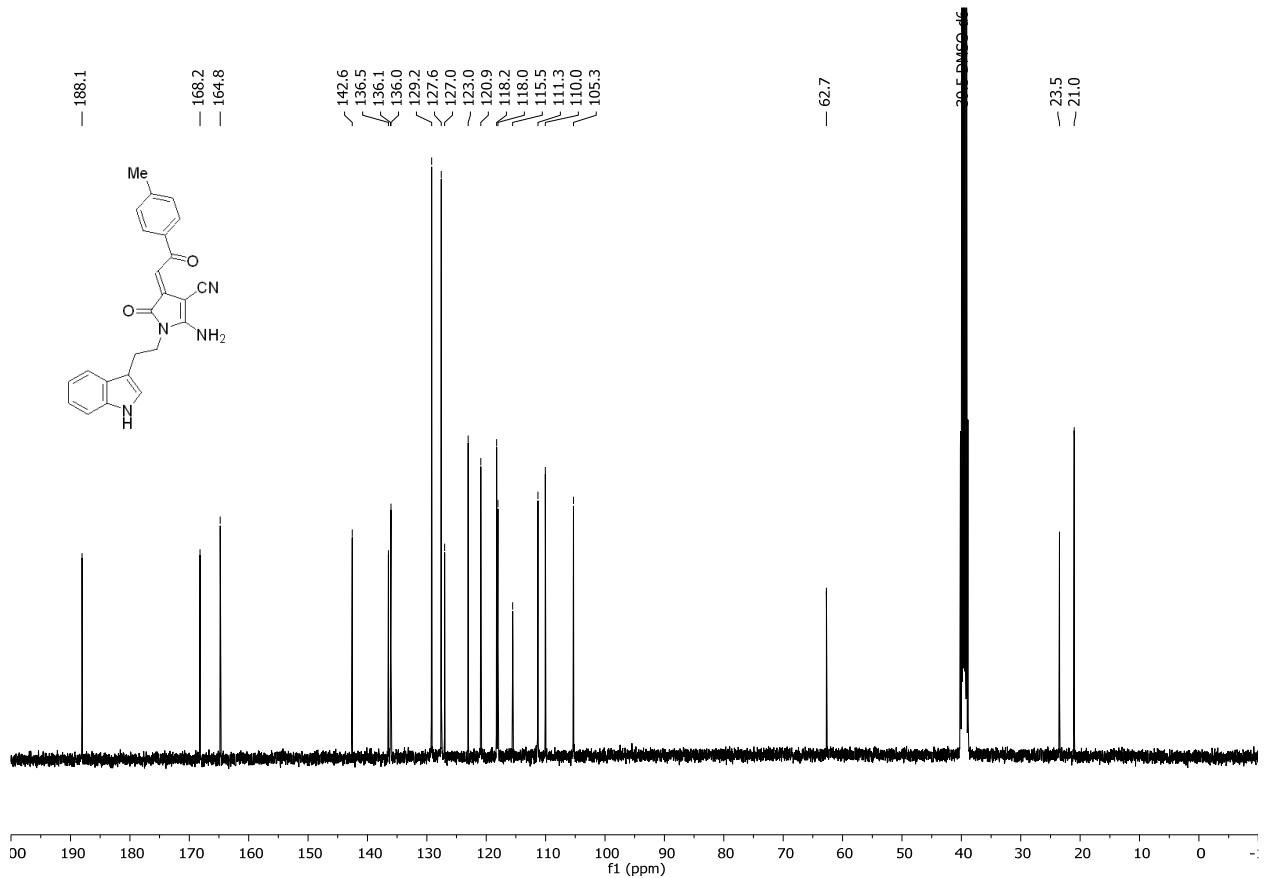
Spectrum from ESI POS.wiff (sample 45) - 491, +TOF MS (100 - 3000) from 0.618 to 0.660 min



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of **4f**

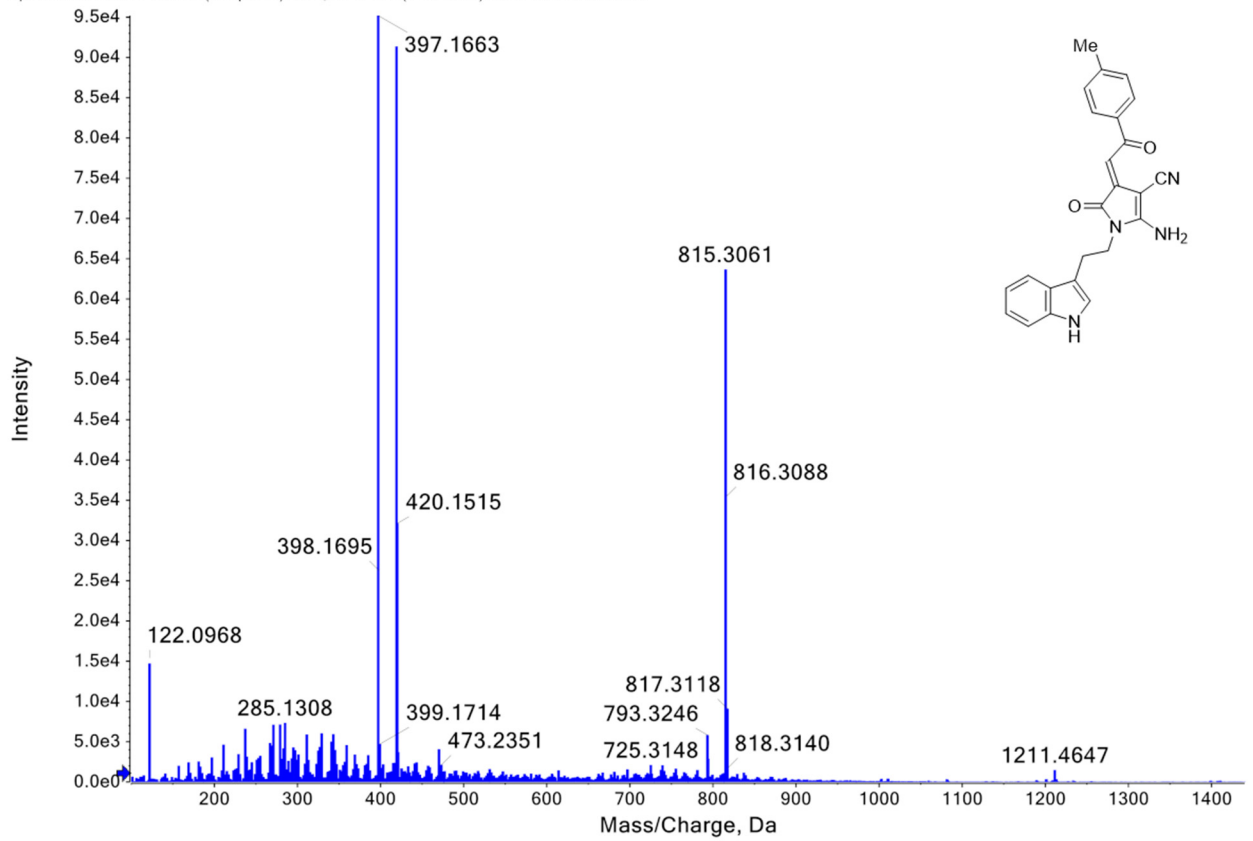


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of **4f**



# HRMS spectrum of 4f

Spectrum from ESI POS.wiff (sample 43) - 515, +TOF MS (100 - 3000) from 0.618 to 0.660 min



Spectrum from ESI POS.wiff (sample 43) - 515, +TOF MS (100 - 3000) from 0.618 to 0.660 min

