

## Supporting Information

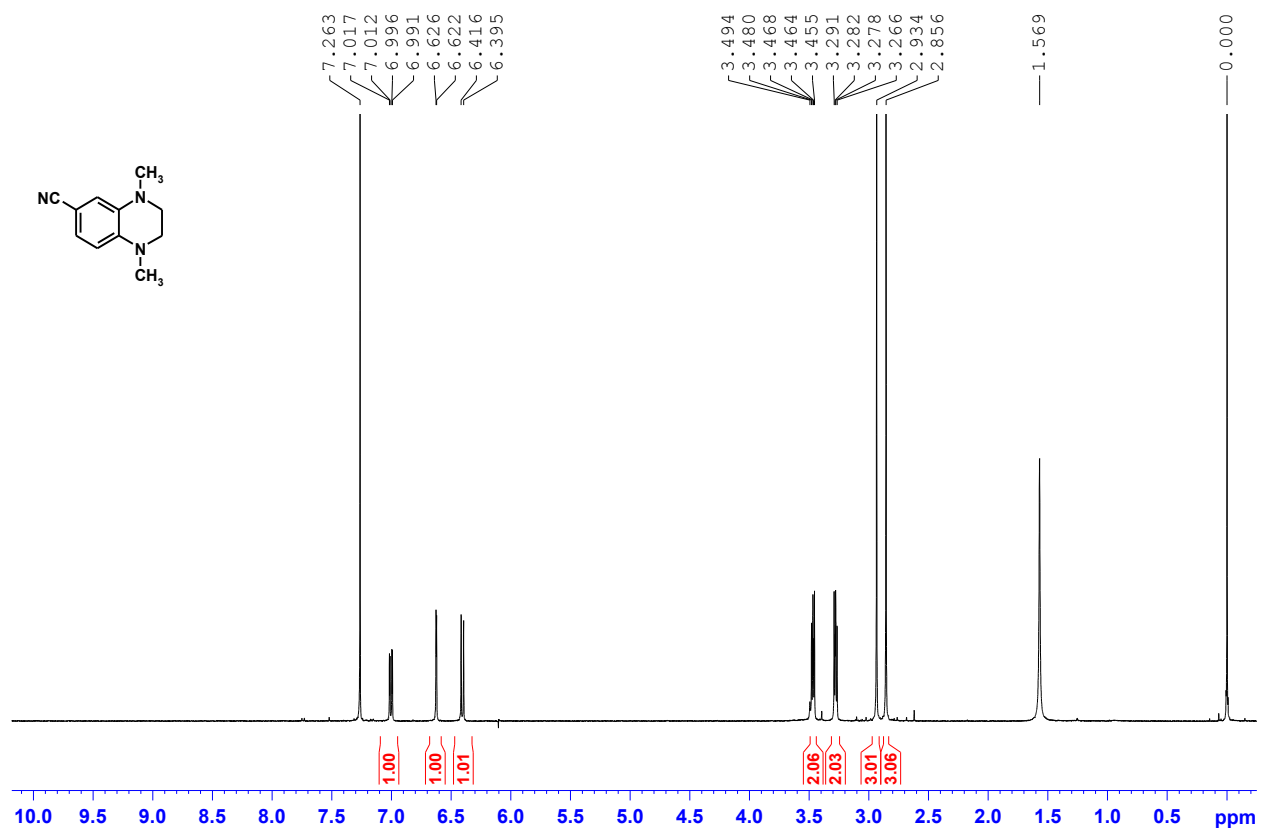
### **Dual S<sub>N</sub>Ar reaction in activated ortho-halonitrobenzene: Direct one-pot synthesis of substituted 1,2,3,4-tetrahydroquinoxalines, 2,3-dihydro-1,4-benzoxazines, and 1,4-benzodioxines**

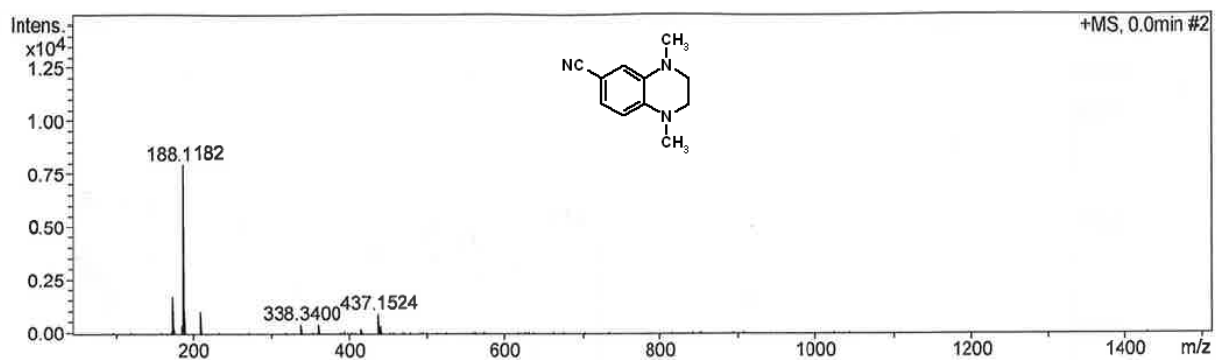
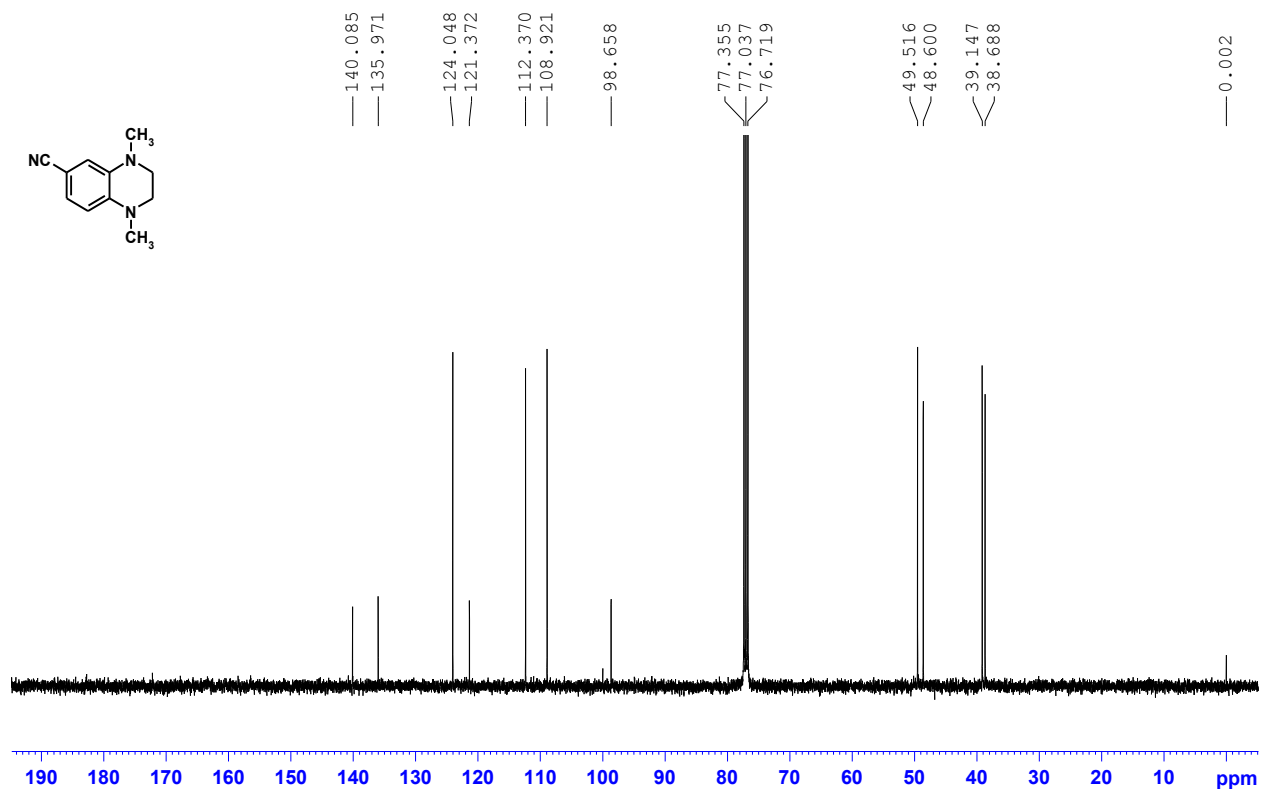
**Mahesh S. Deshmukh, Biswajit Das, Nidhi Jain\***

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### Copies of $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and HRMS:

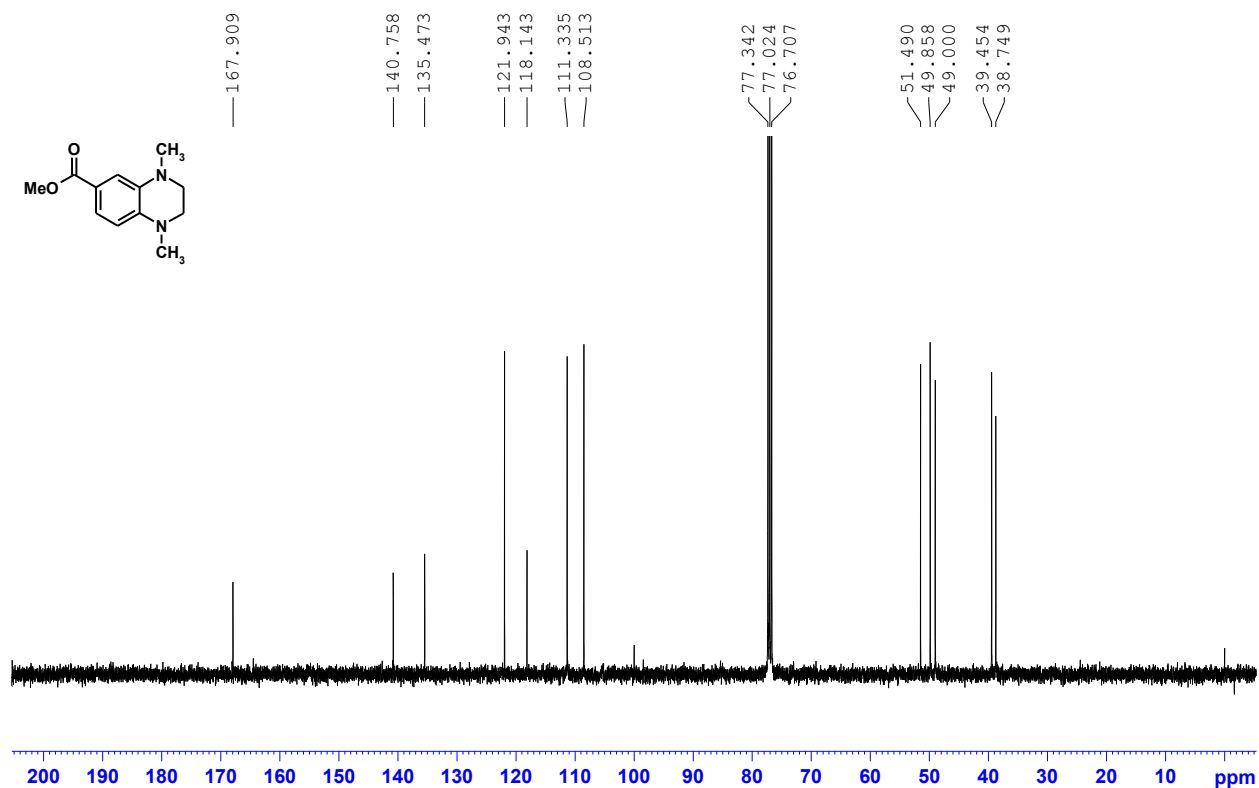
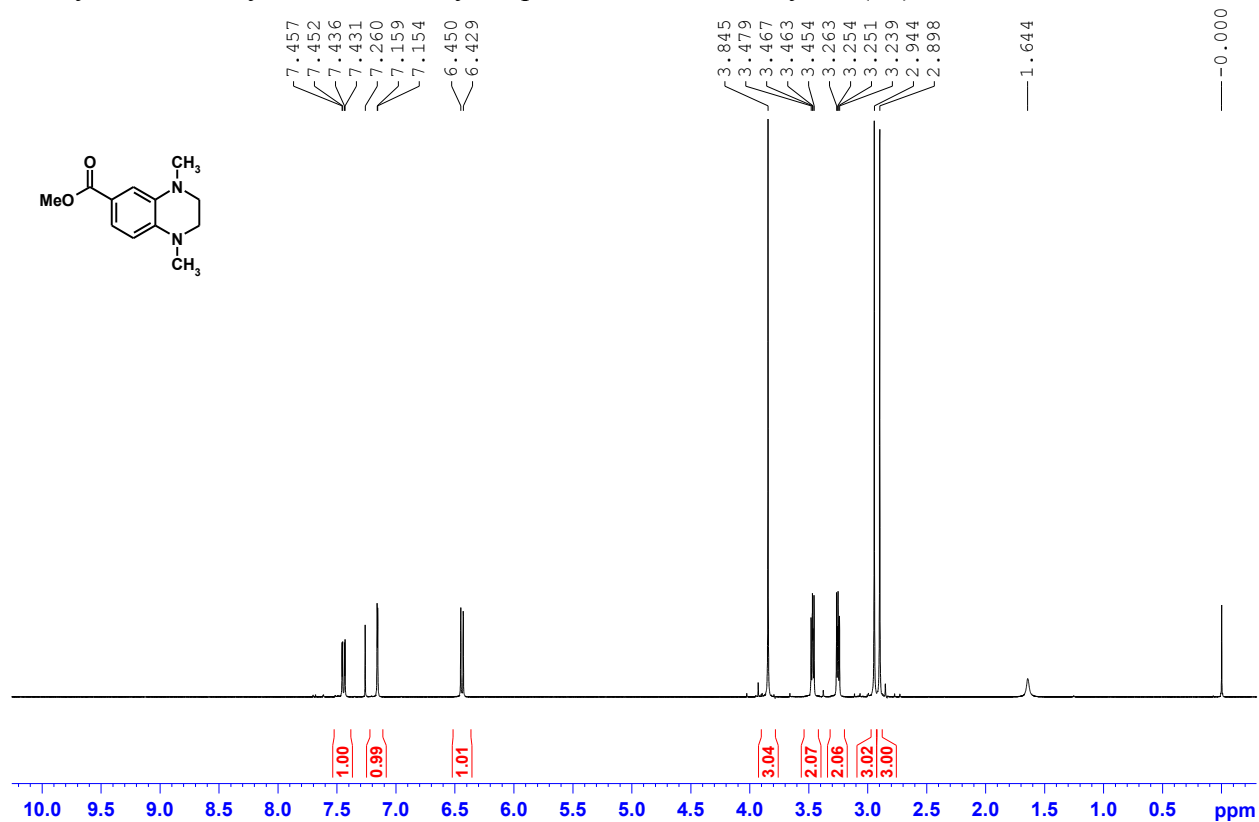
#### 1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-6-carbonitrile (**3a**)

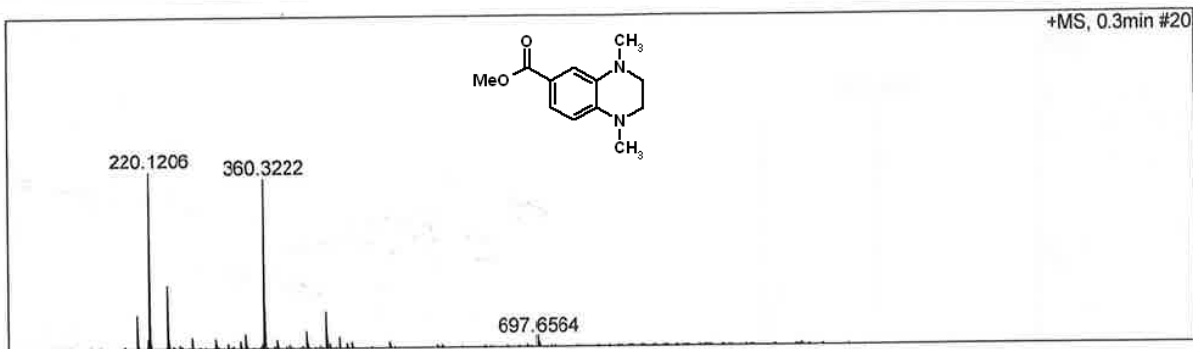




Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
188.1182	1	C 11 H 14 N 3	100.00	188.1182	-0.0	-0.0	7.2	6.5	even	ok

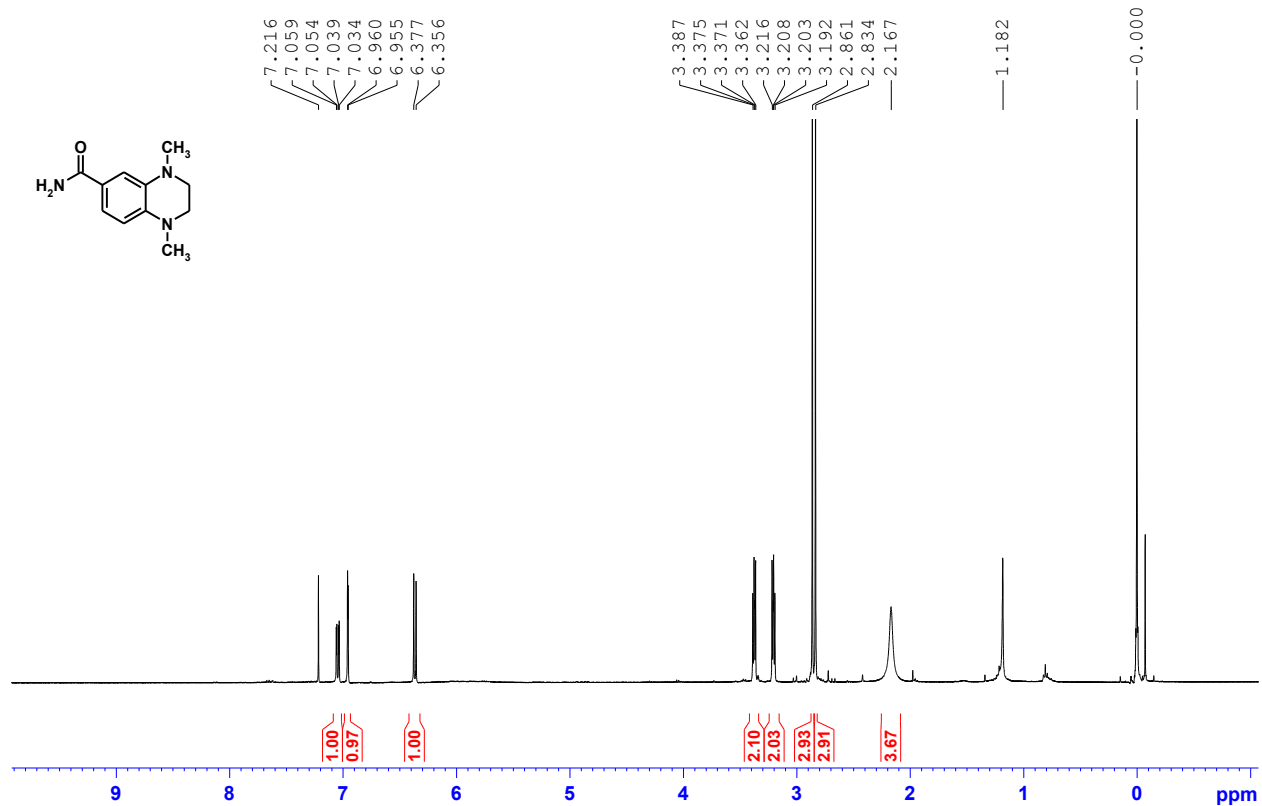
methyl 1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-6-carboxylate (**3b**)

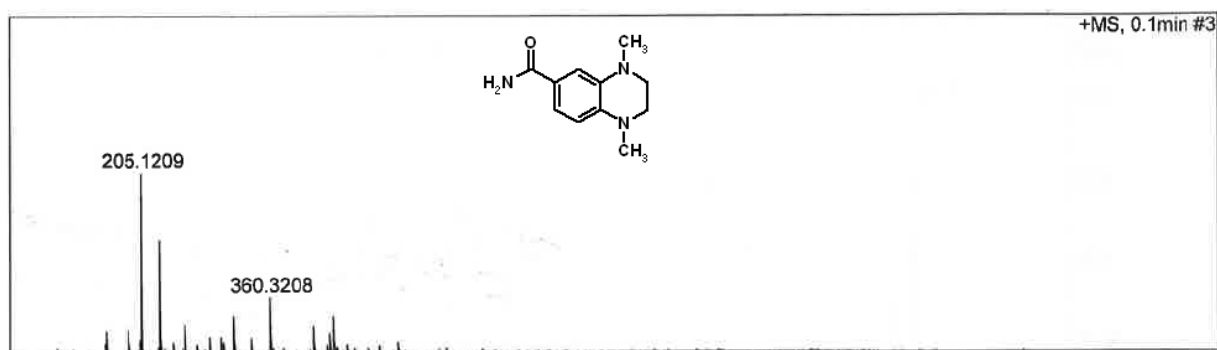
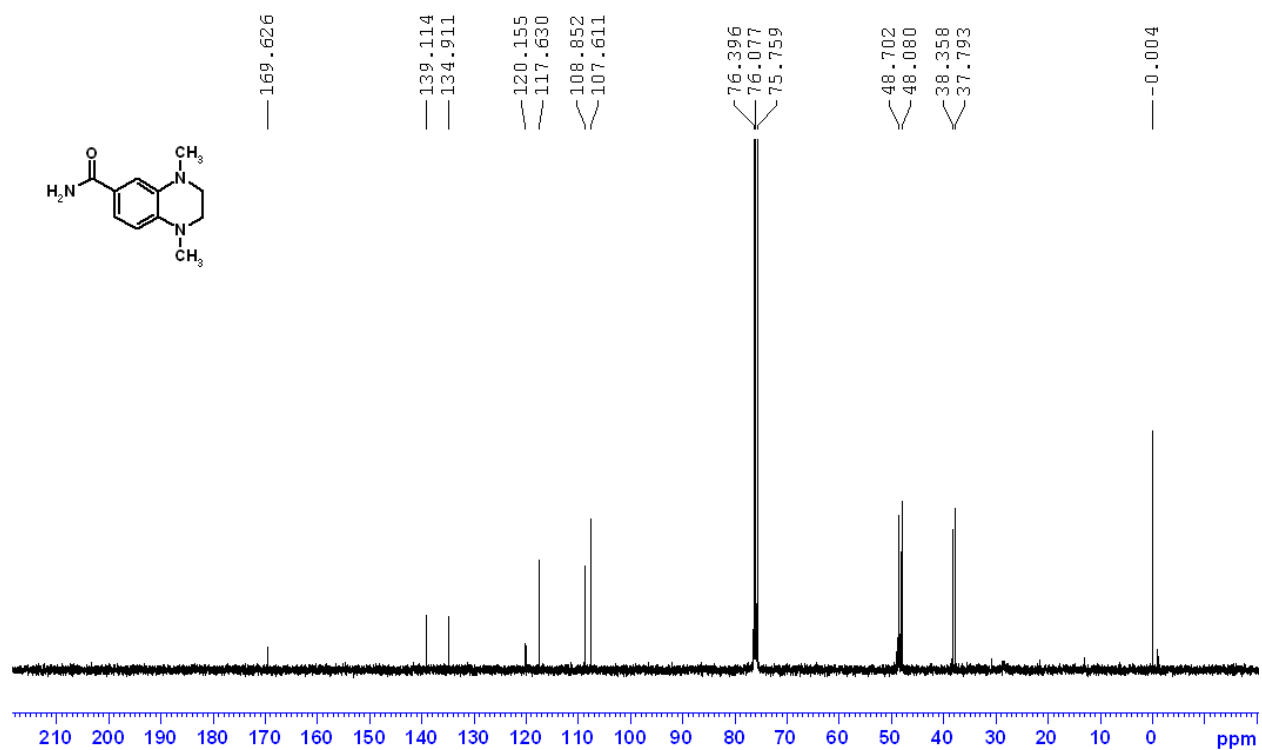




Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
220.1206	1	C 12 H 16 N 2 O 2	100.00	220.1206	-0.0	-0.0	177.9	6.0	odd	ok

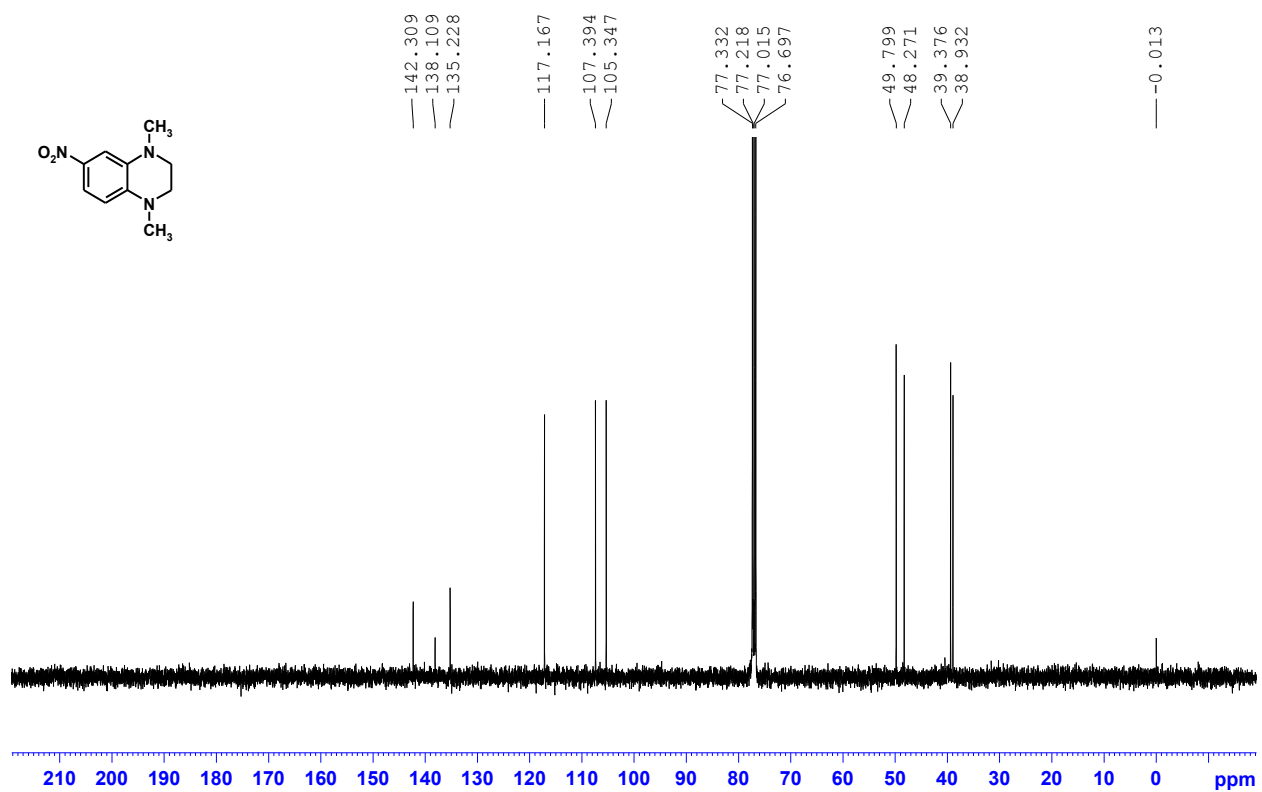
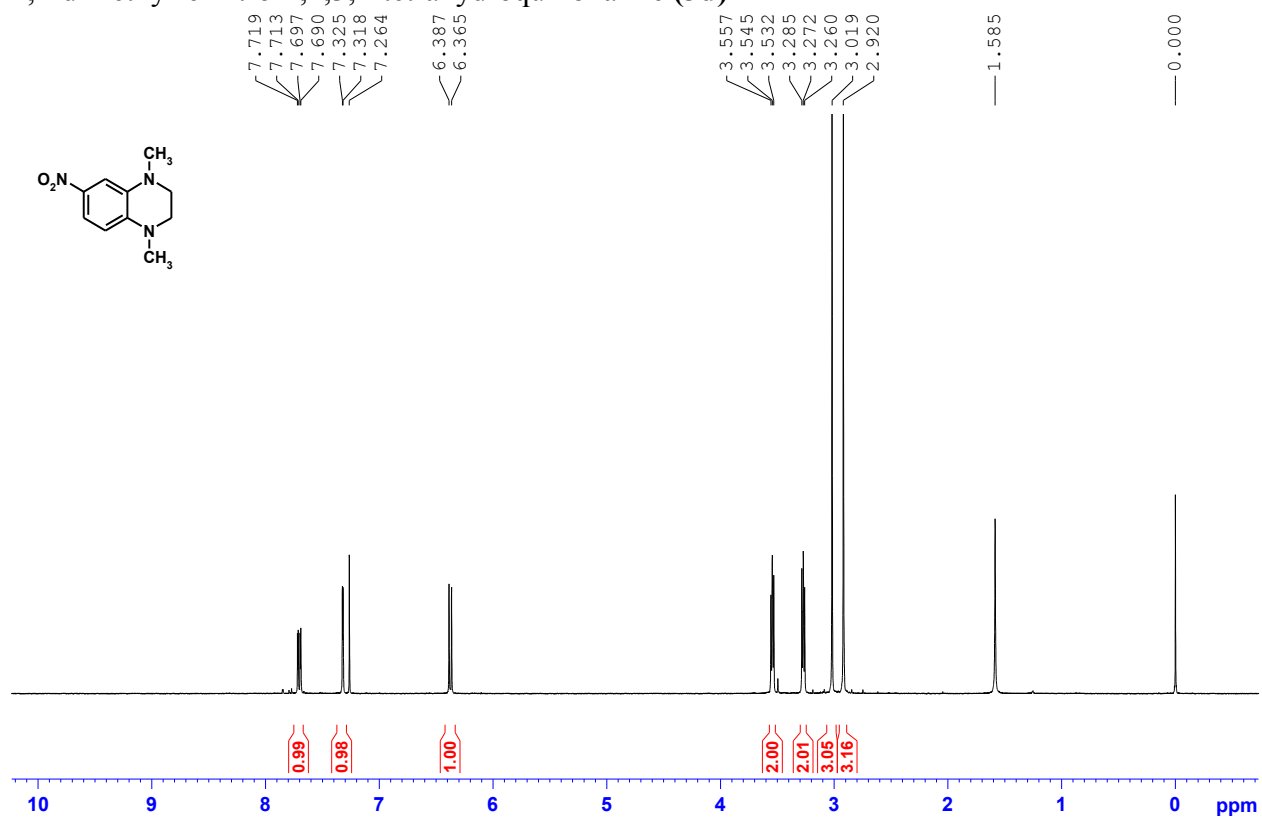
1,4-dimethyl-1,2,3,4-tetrahydroquinoline-6-carboxamide (**3c**)

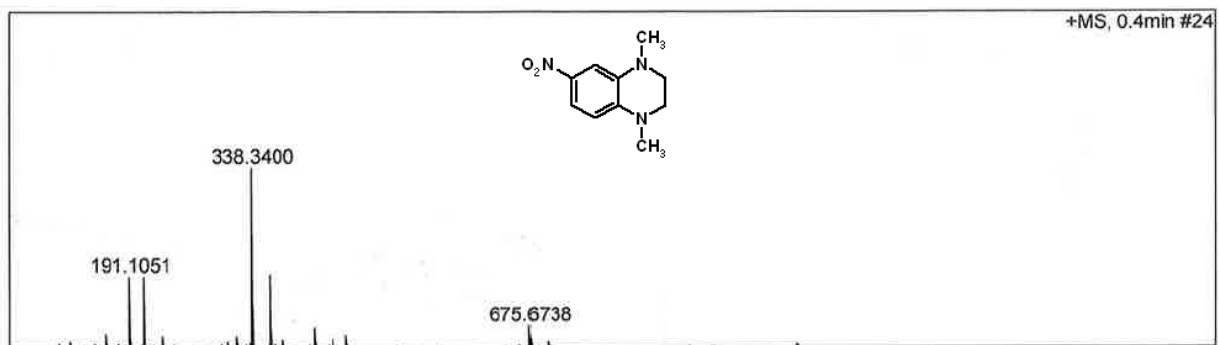




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205.1209	1	C 11 H 15 N 3 O	100.00	205.1210	0.1	0.5	110.5	6.0	odd	ok

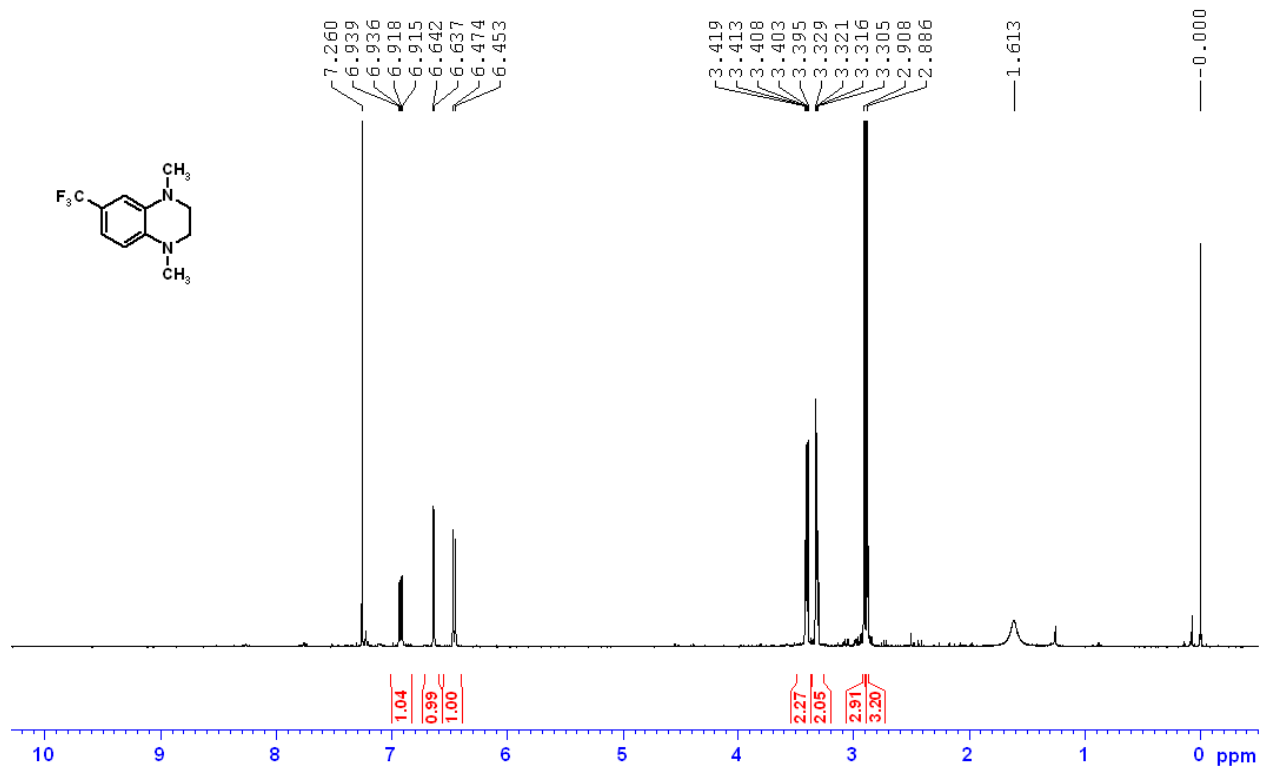
### 1,4-dimethyl-6-nitro-1,2,3,4-tetrahydroquinoxaline (**3d**)



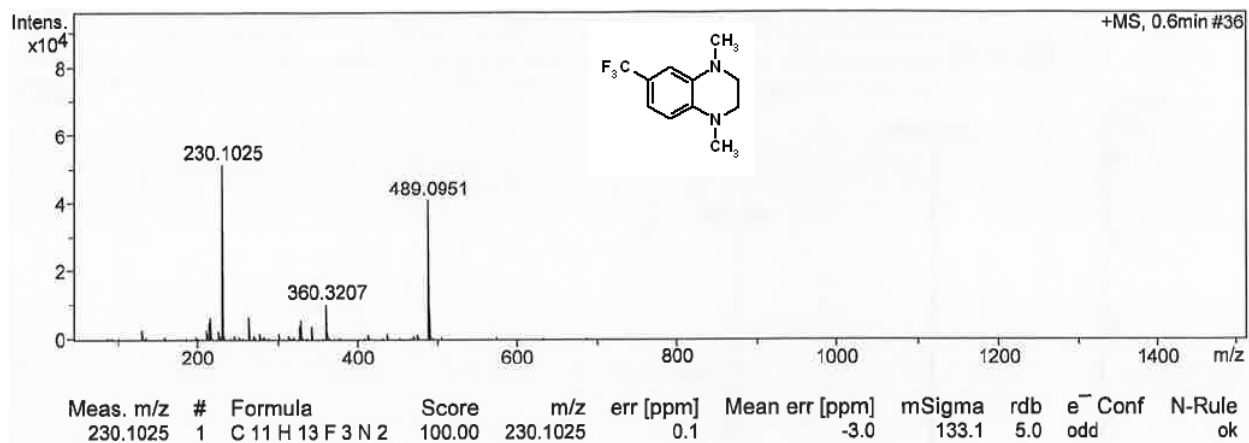
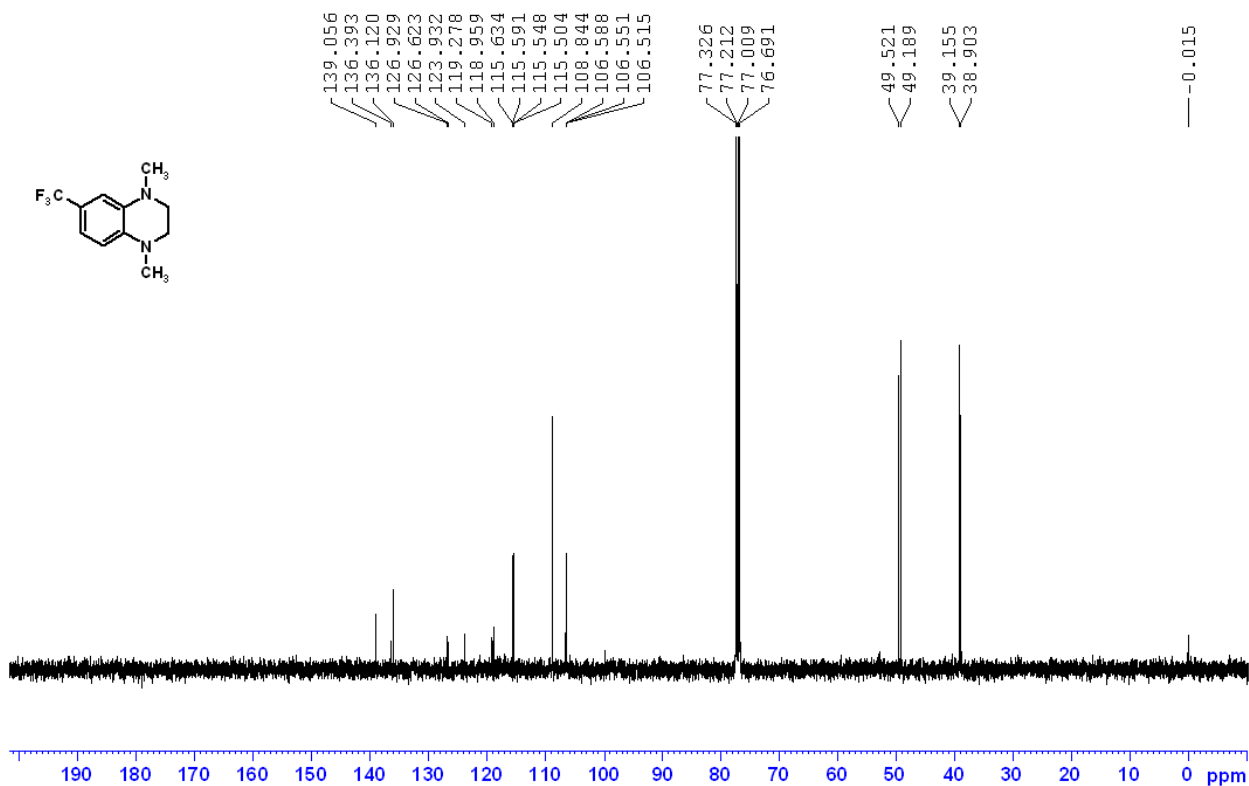


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
208.1080	1	C 10 H 14 N 3 O 2	100.00	208.1081	0.1	0.3	3.2	5.5	even	ok

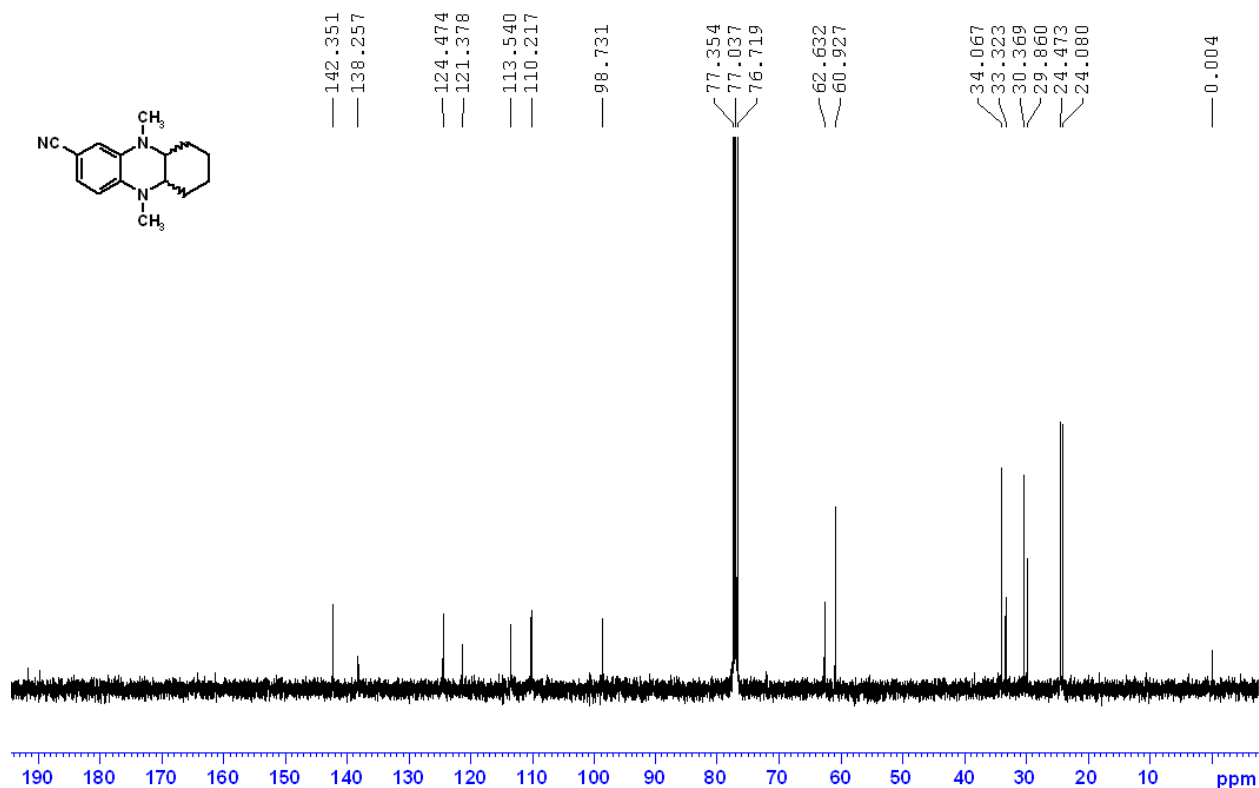
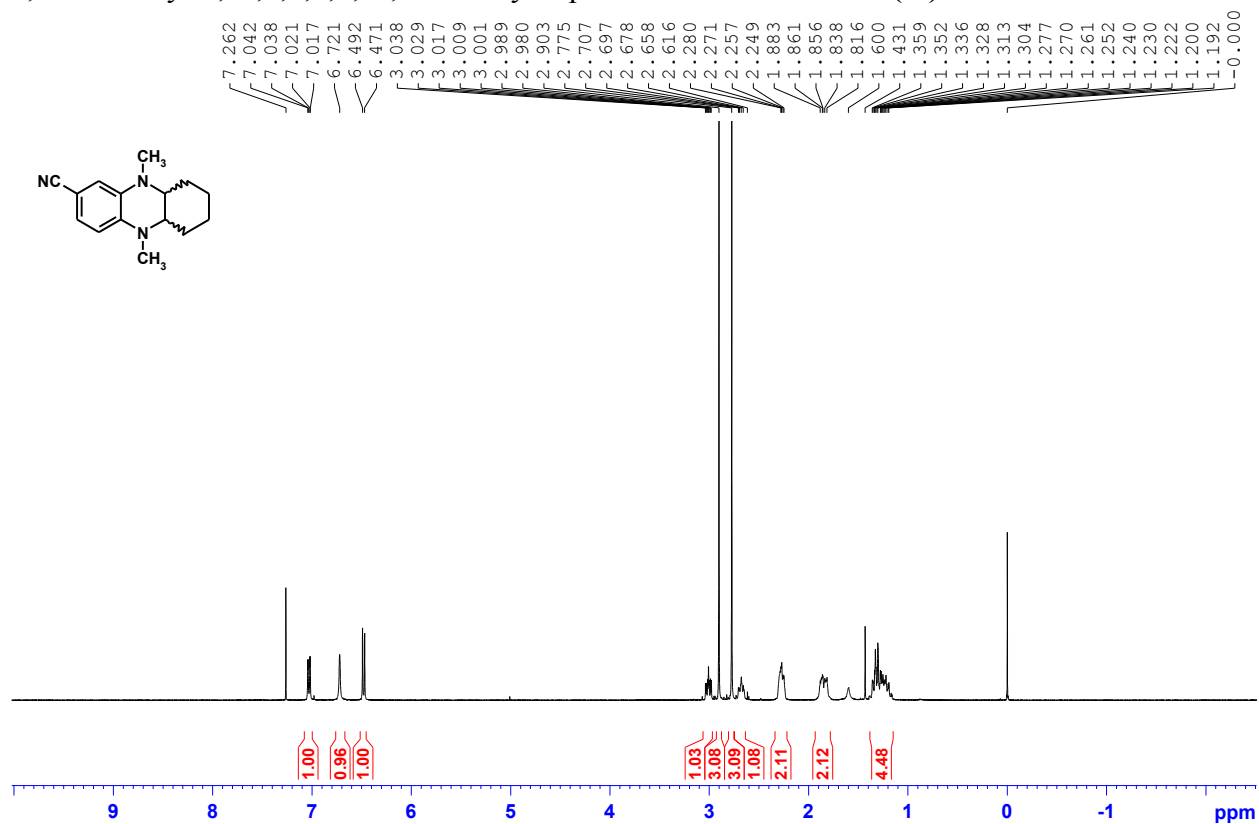
1,4-dimethyl-6-(trifluoromethyl)-1,2,3,4-tetrahydroquinoxaline (**3e**)

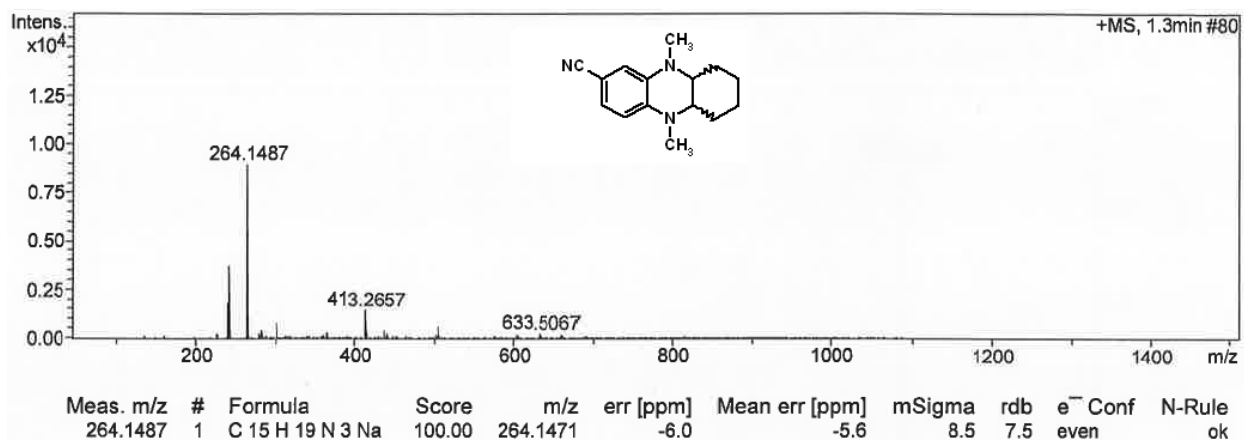




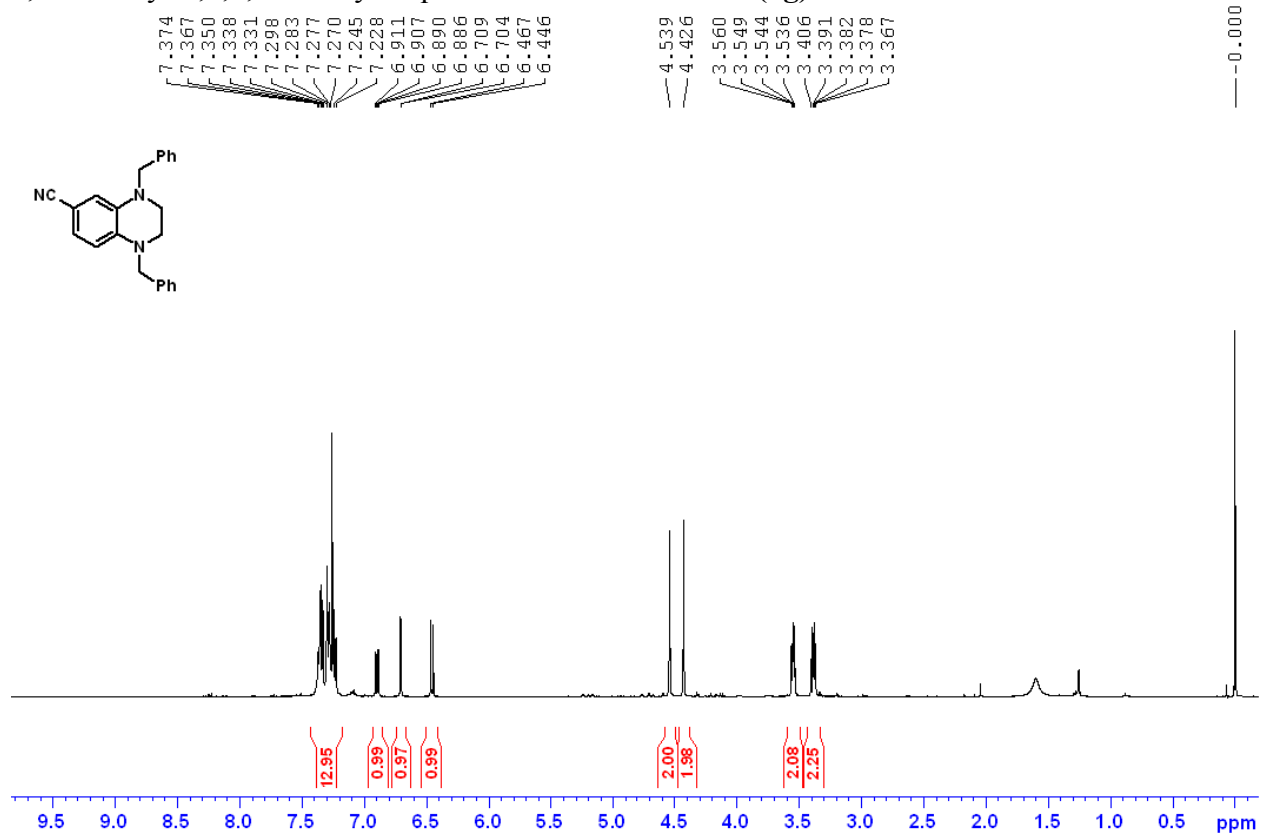


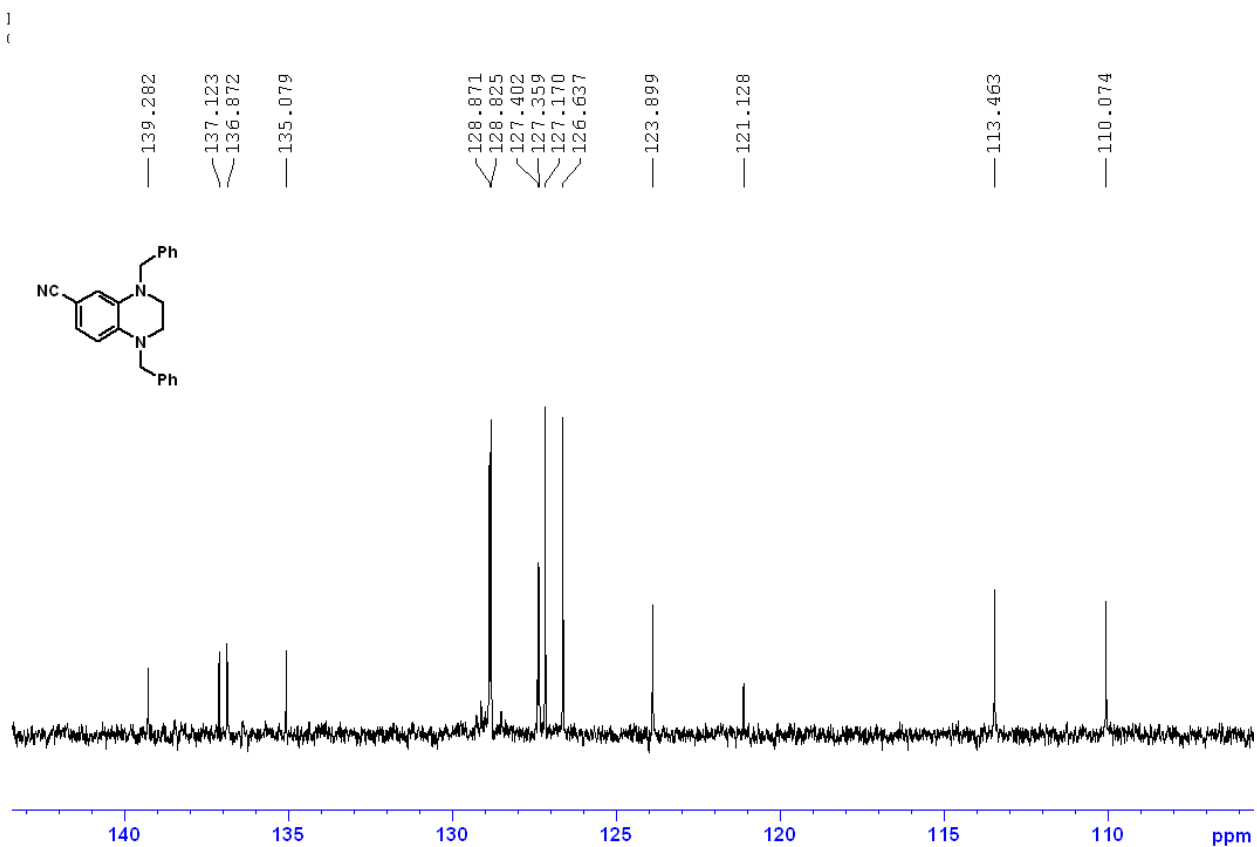
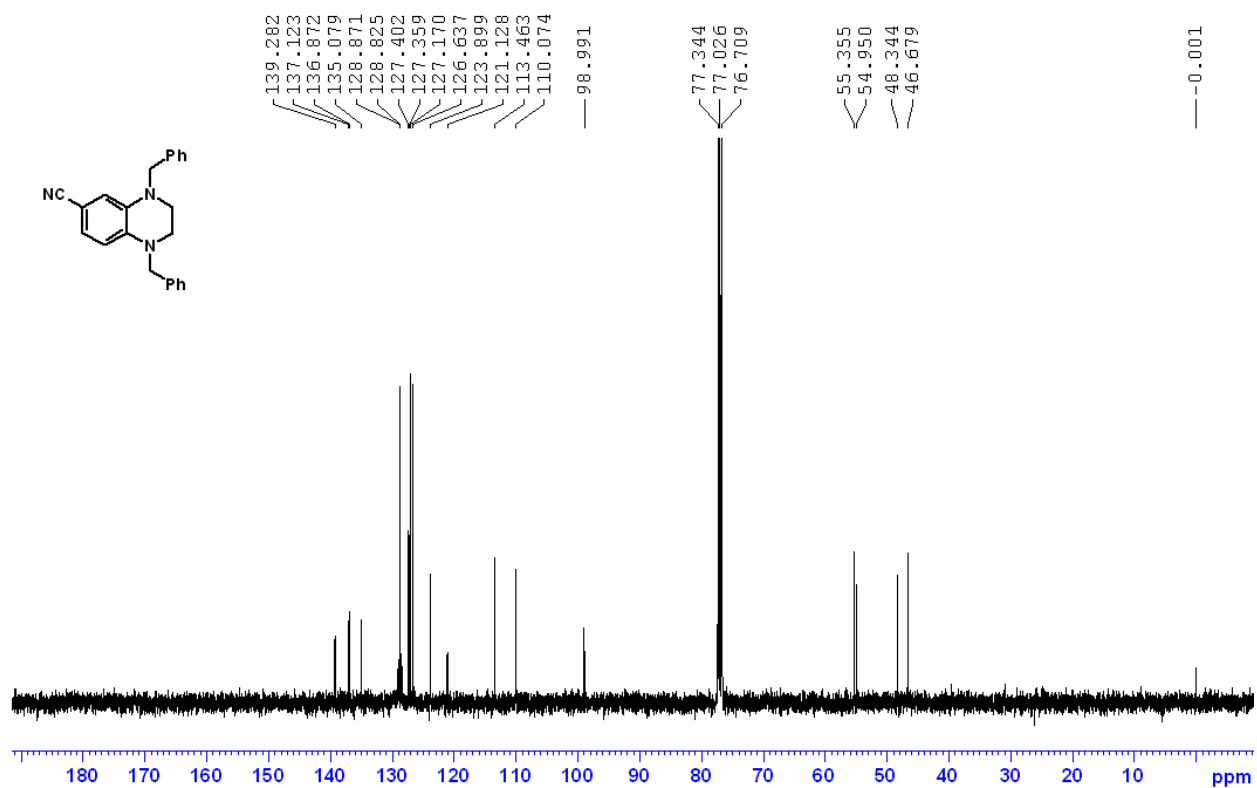
### 5,10-dimethyl-5,5a,6,7,8,9,9a,10-octahydrophenazine-2-carbonitrile (**3f**)

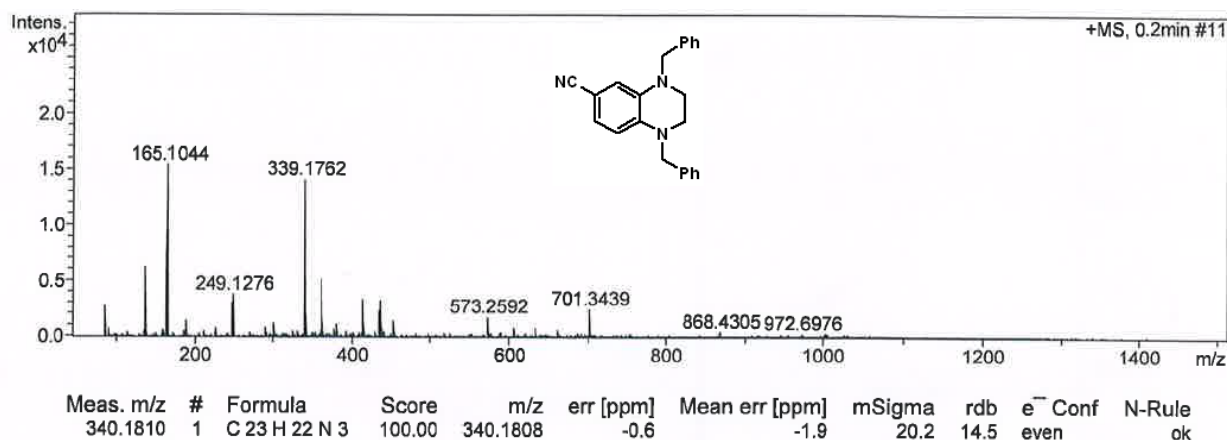




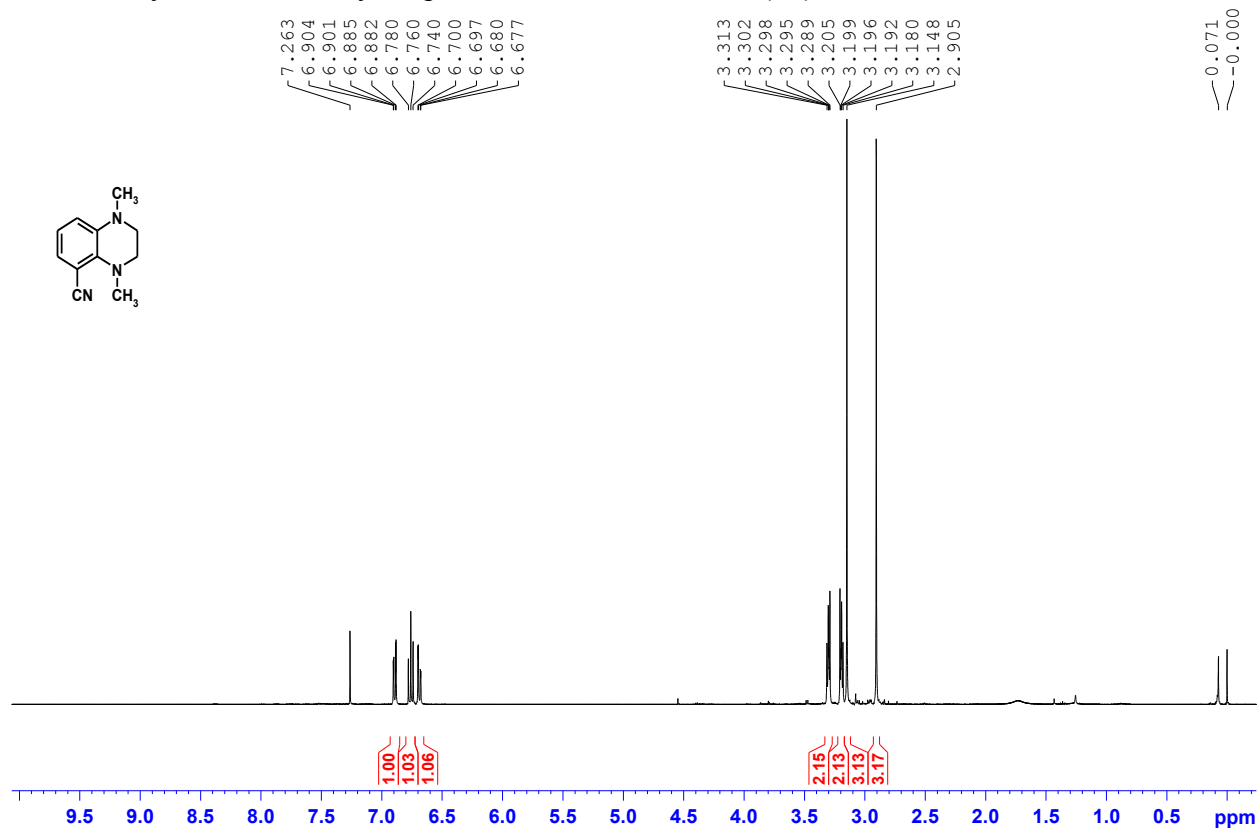
1,4-dibenzyl-1,2,3,4-tetrahydroquinoline-6-carbonitrile (**3g**)

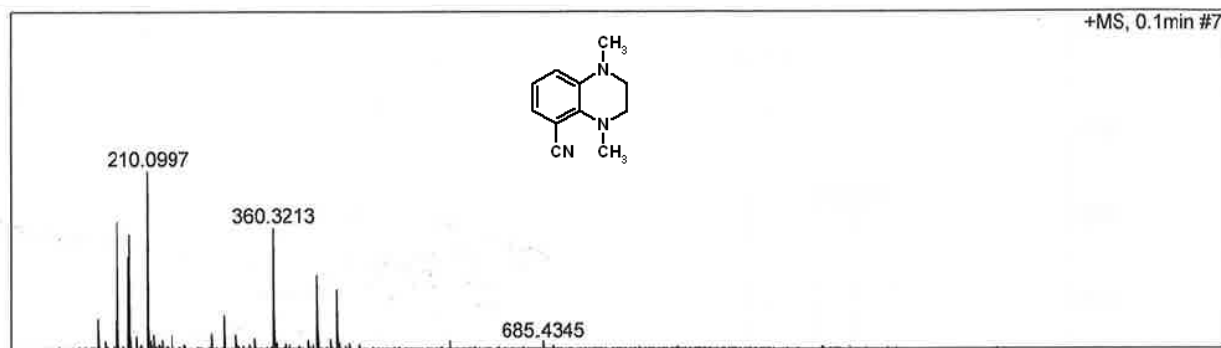
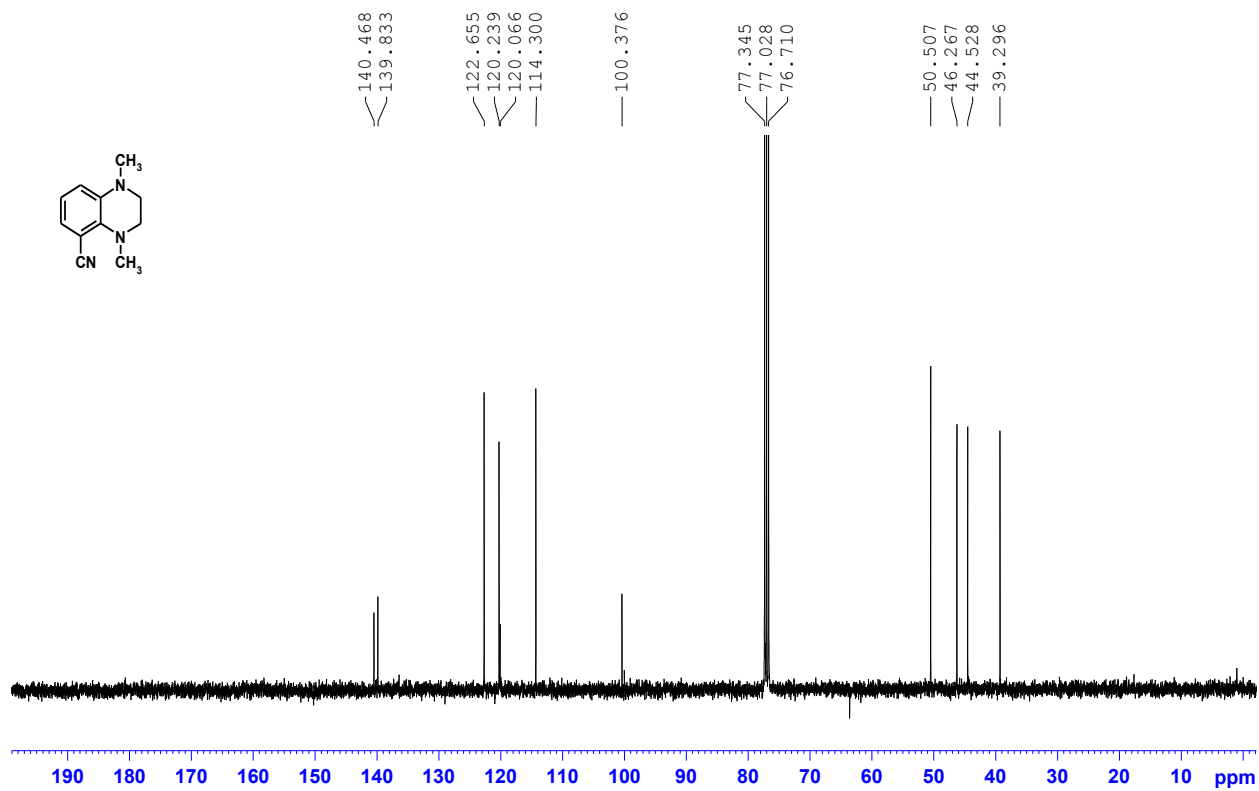






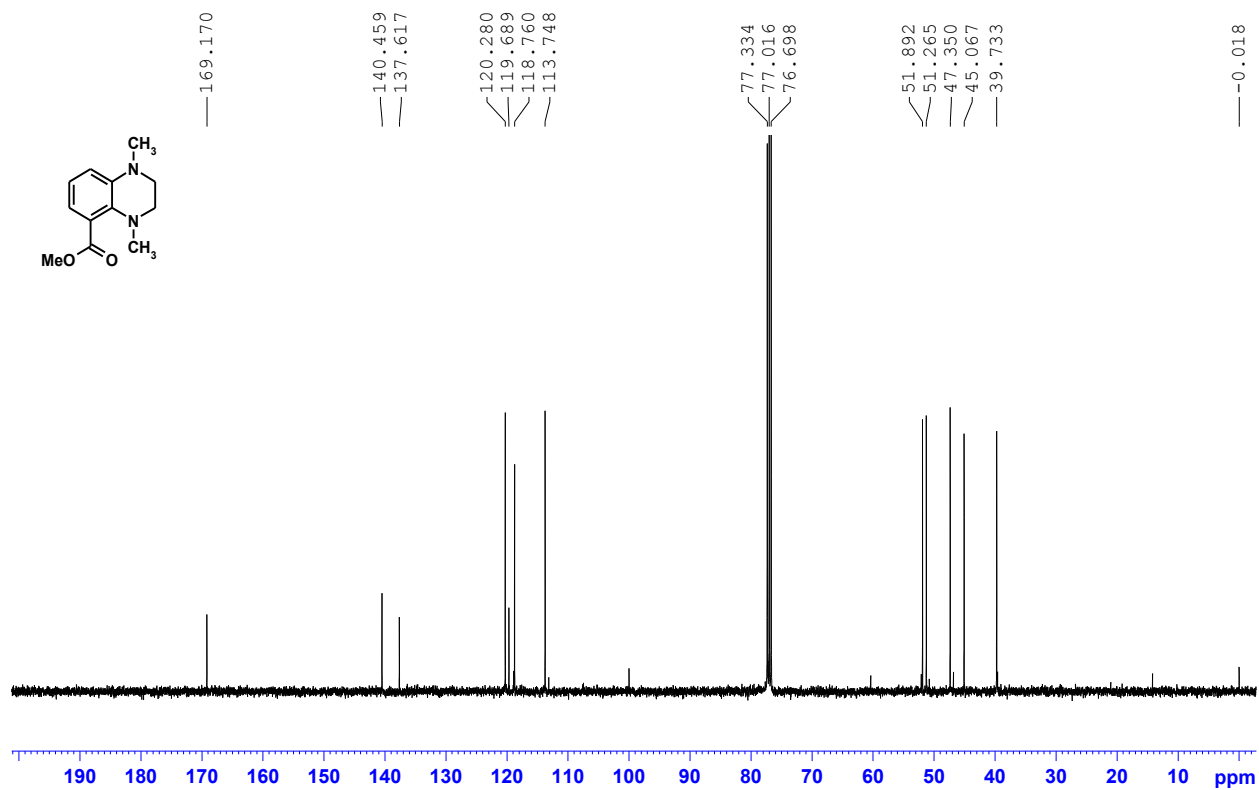
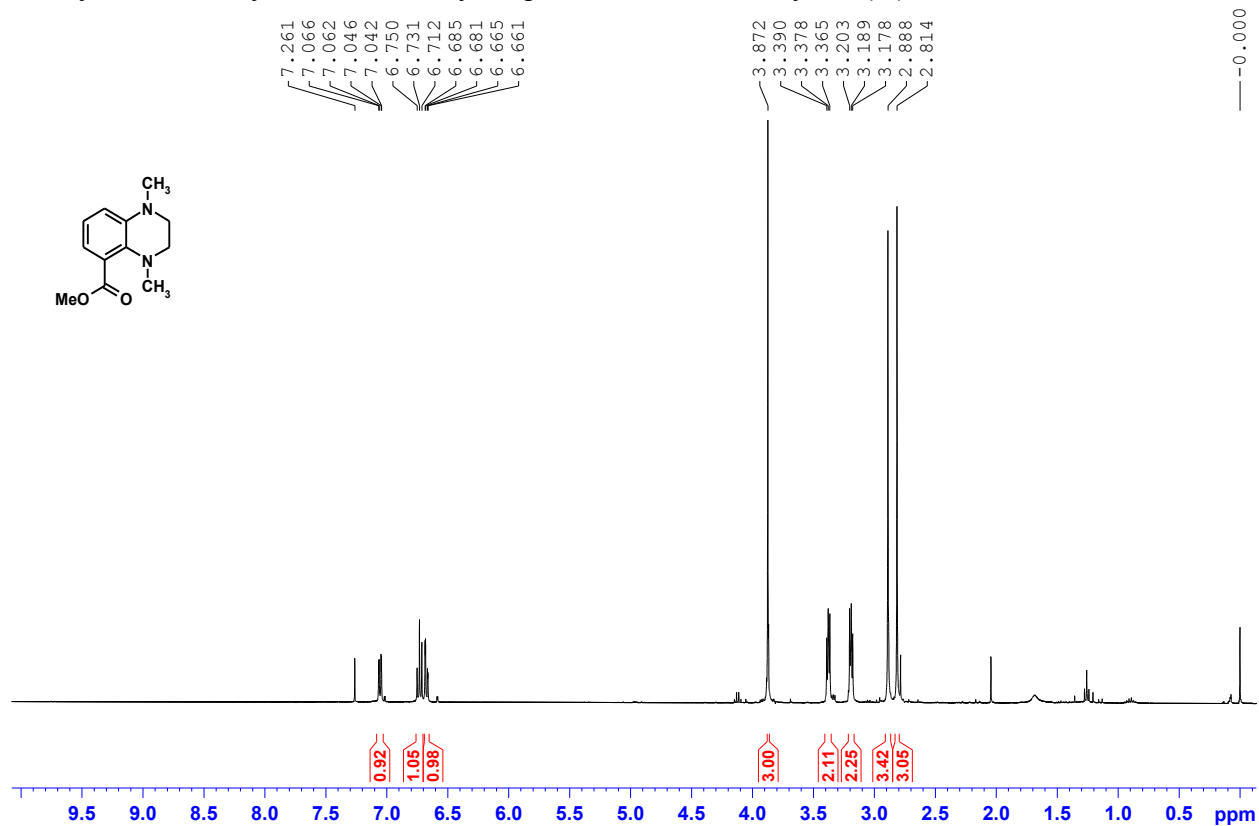
1,4-dimethyl-1,2,3,4-tetrahydroquinoline-5-carbonitrile (**3h**)

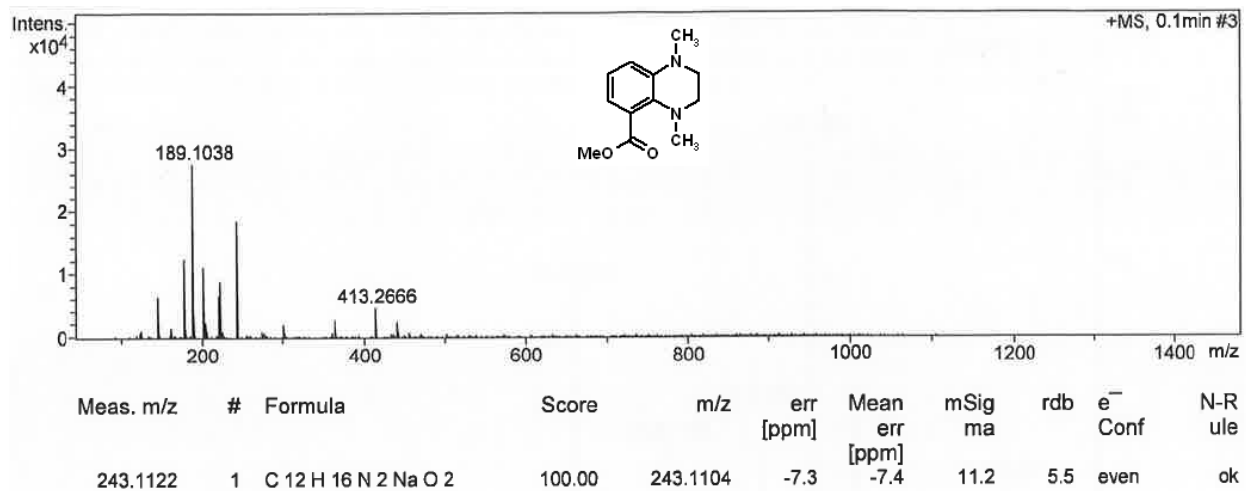




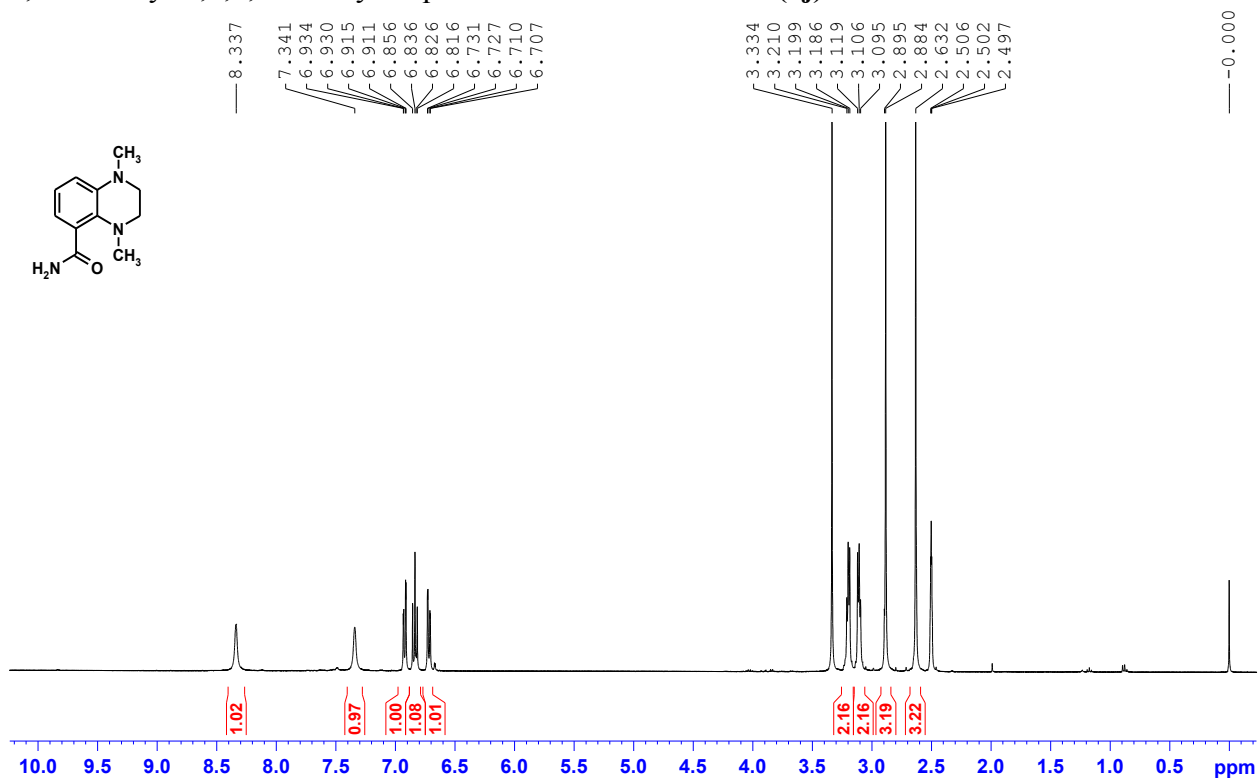
Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
210.0997	1	C 11 H 13 N 3 Na	100.00	210.1002	2.4	1.9	6.3	6.5	even	ok

### Methyl 1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-5-carboxylate (**3i**)

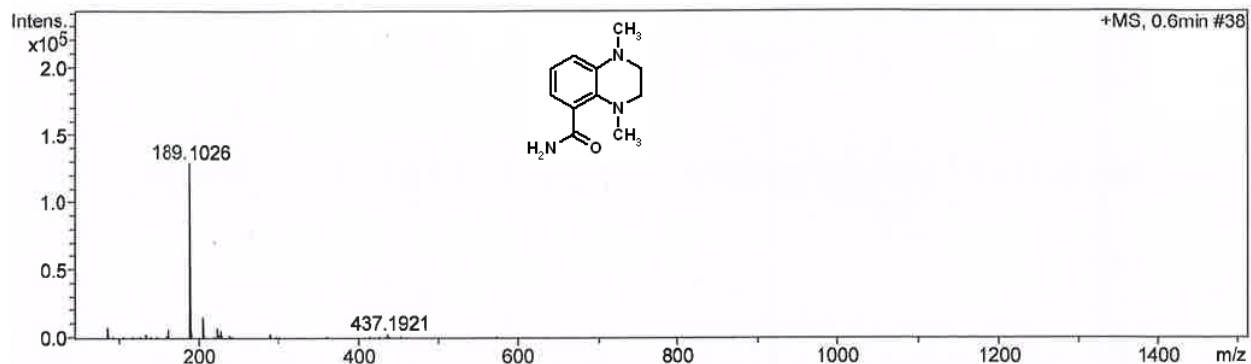
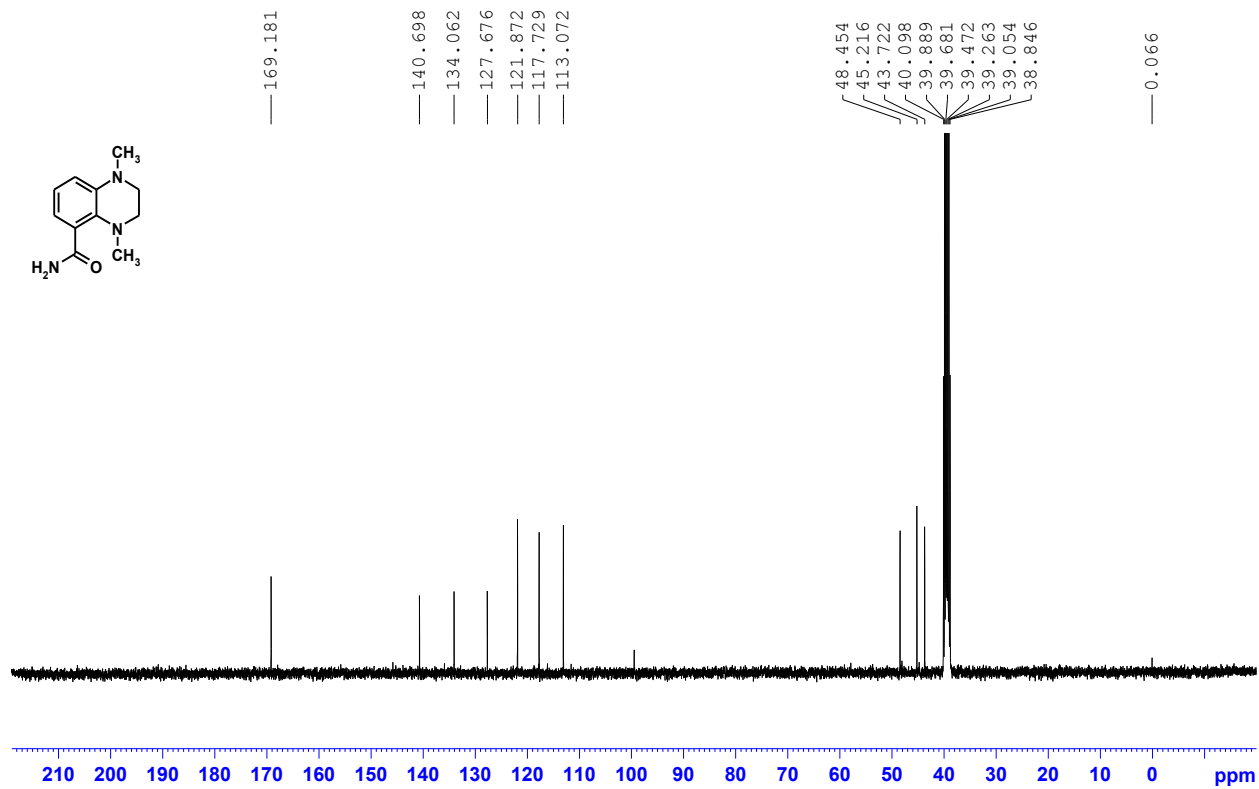




1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-5-carboxamide (**3j**)

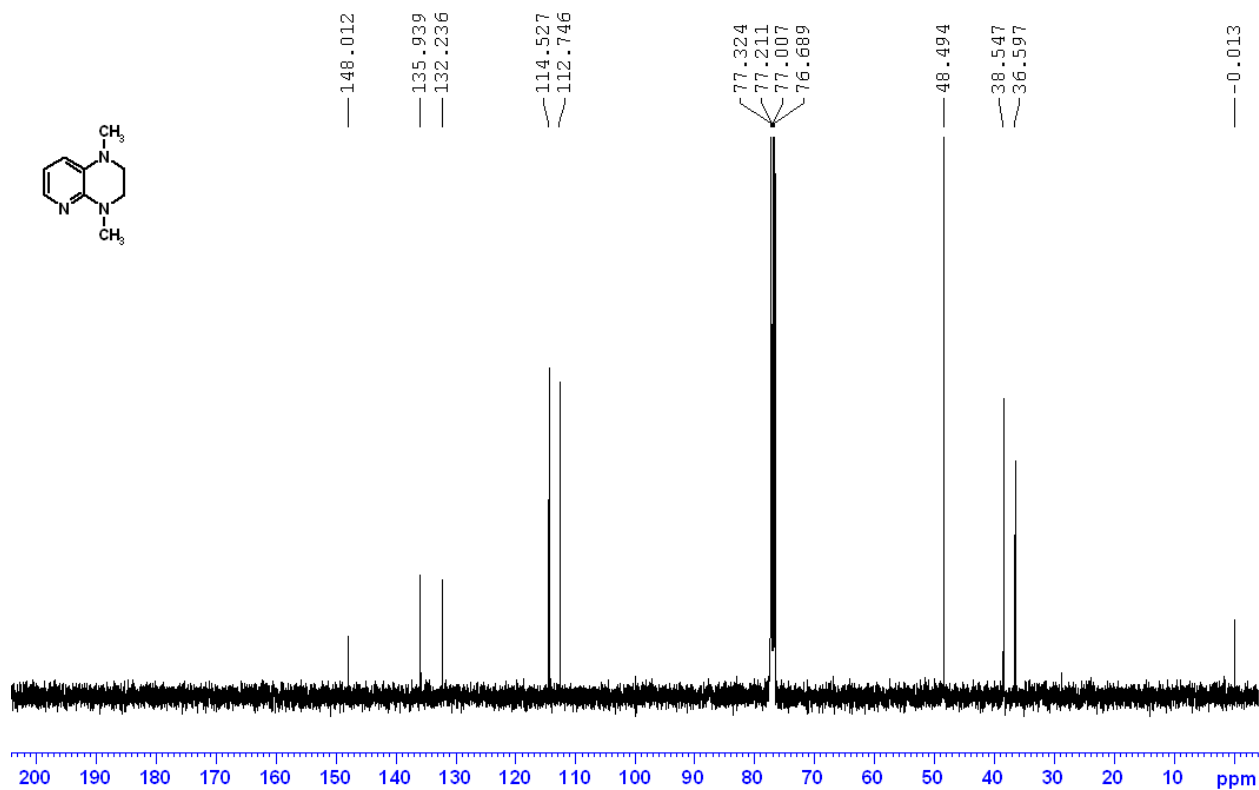
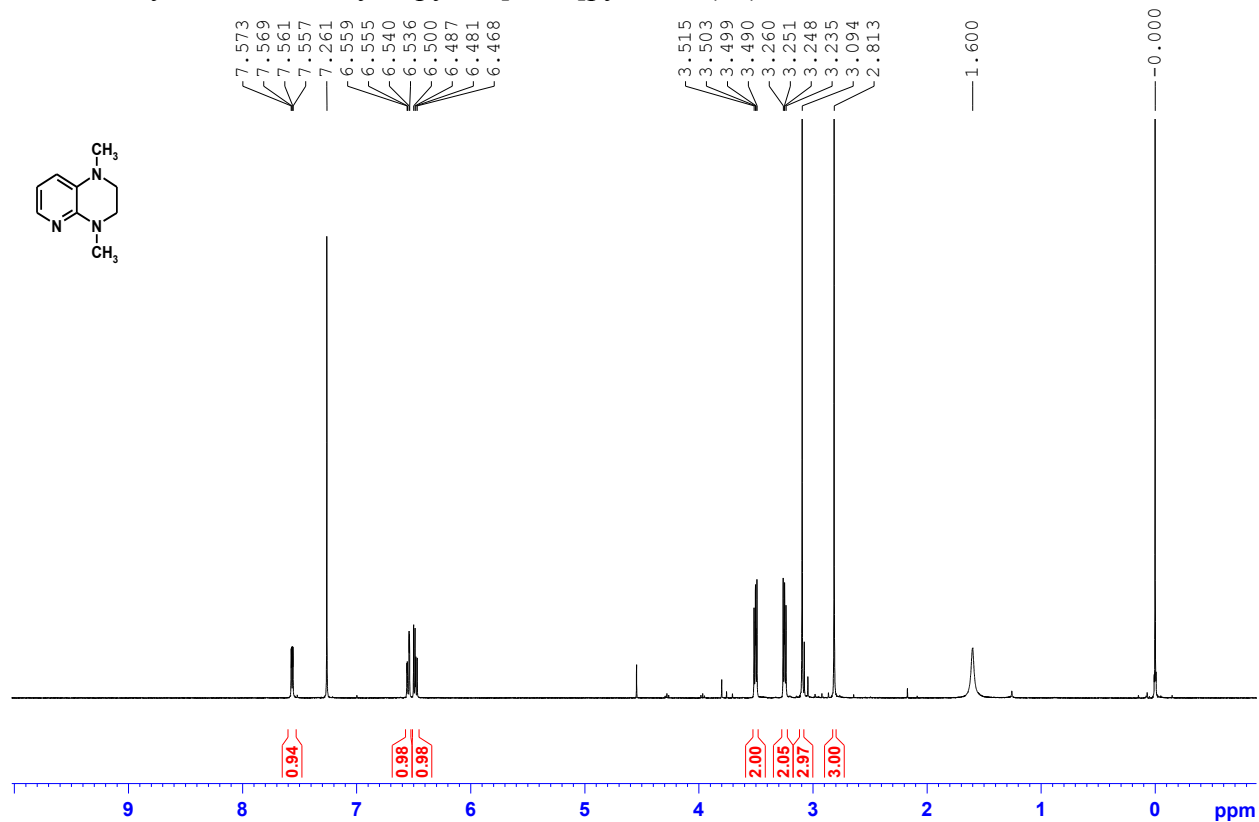


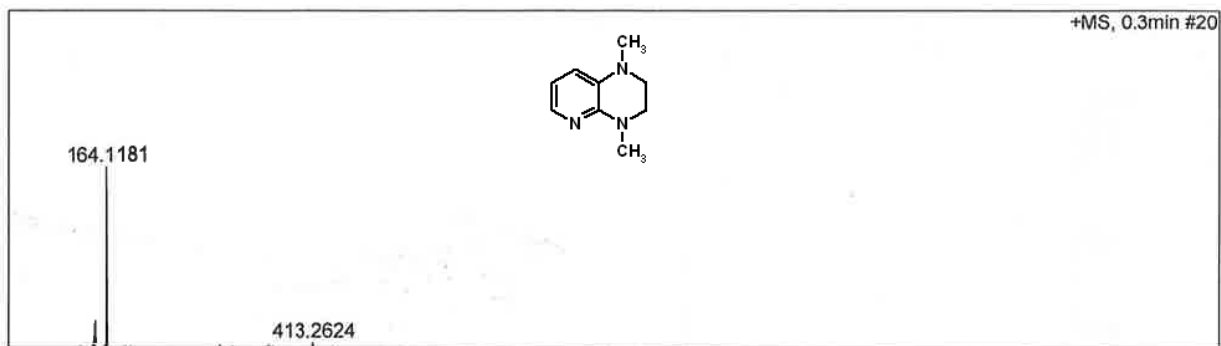
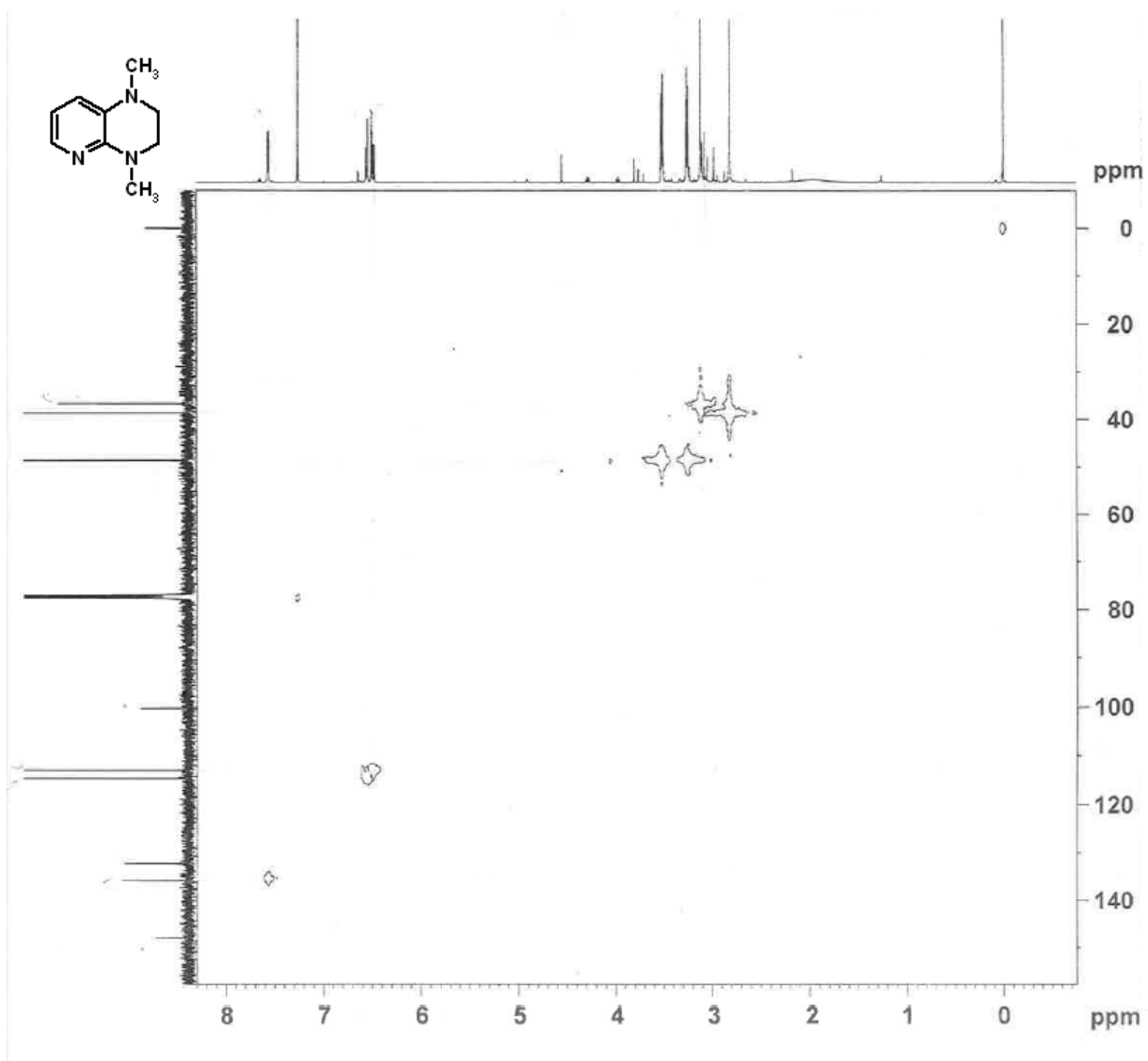




Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
206.1286	1	C 11 H 16 N 3 O	100.00	206.1288	1.0	1.5	7.2	5.5	even	ok

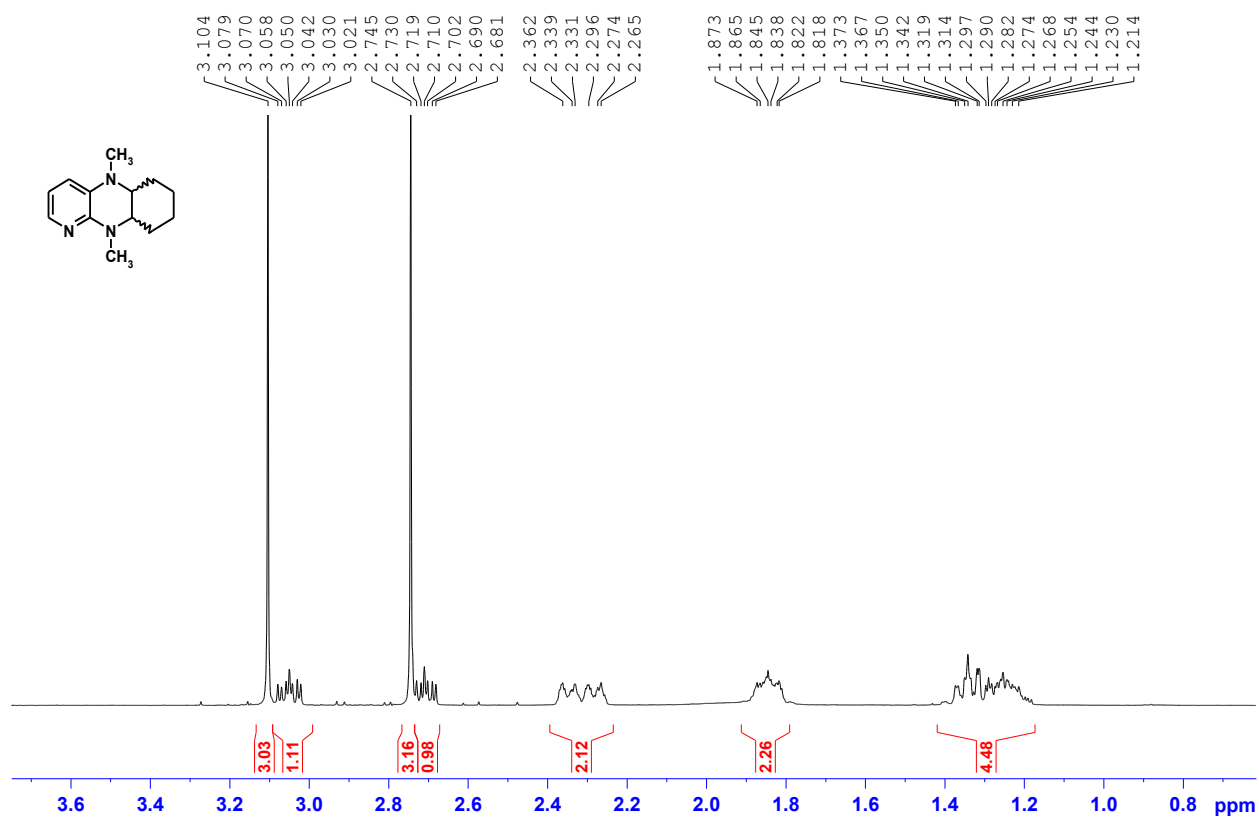
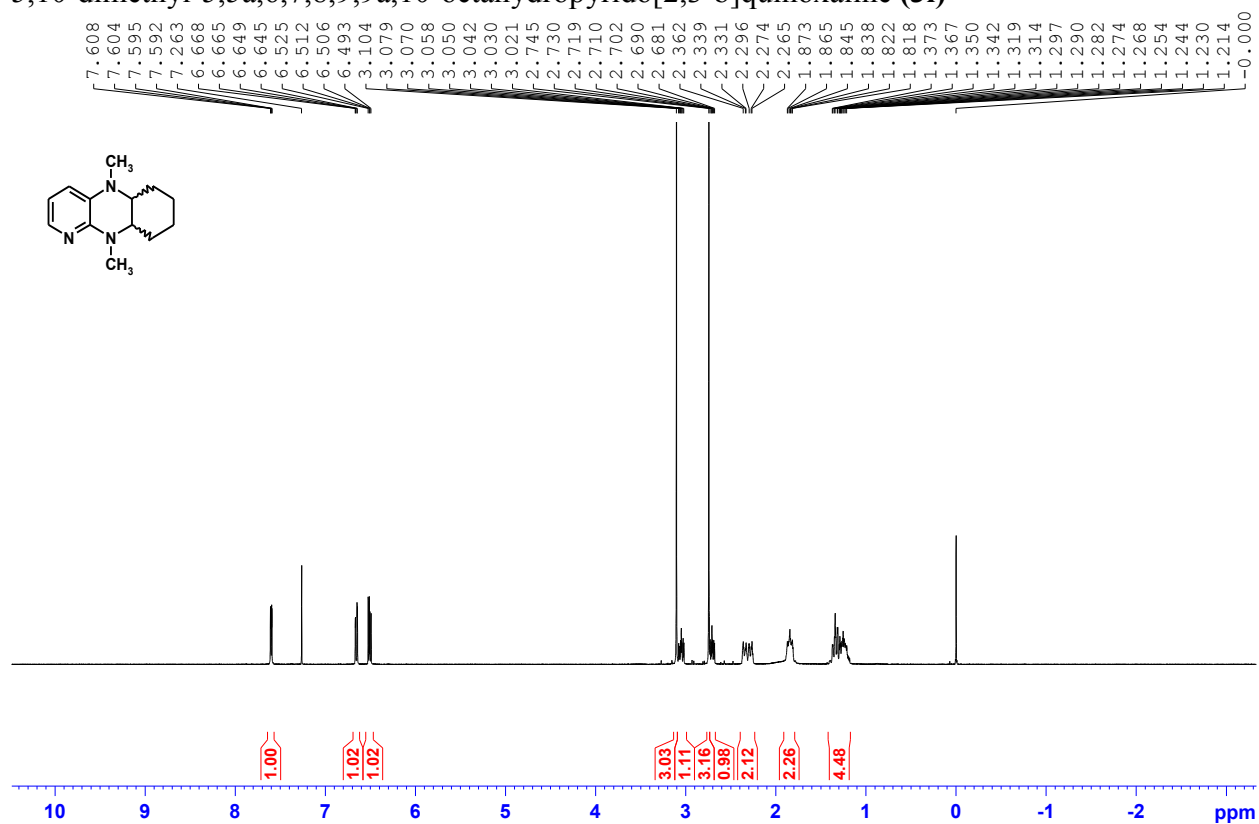
### 1,4-dimethyl-1,2,3,4-tetrahydropyrido[2,3-b]pyrazine (**3k**)

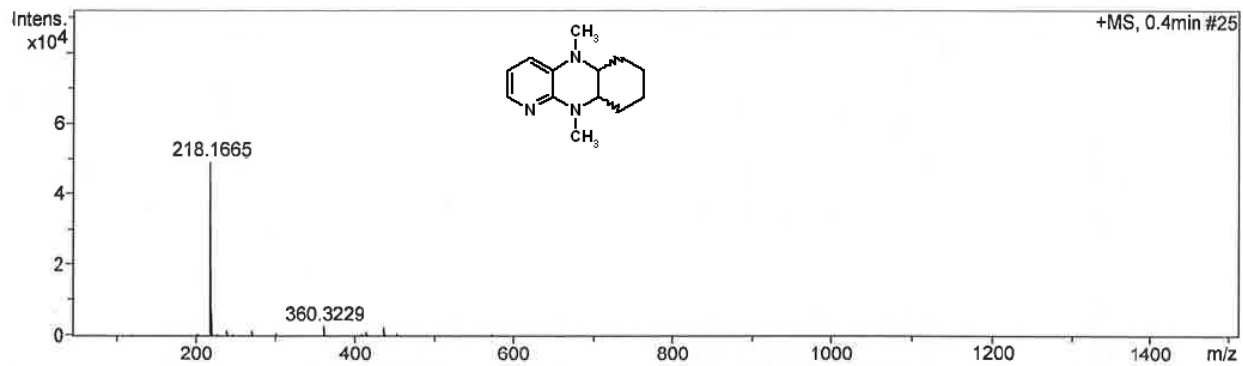
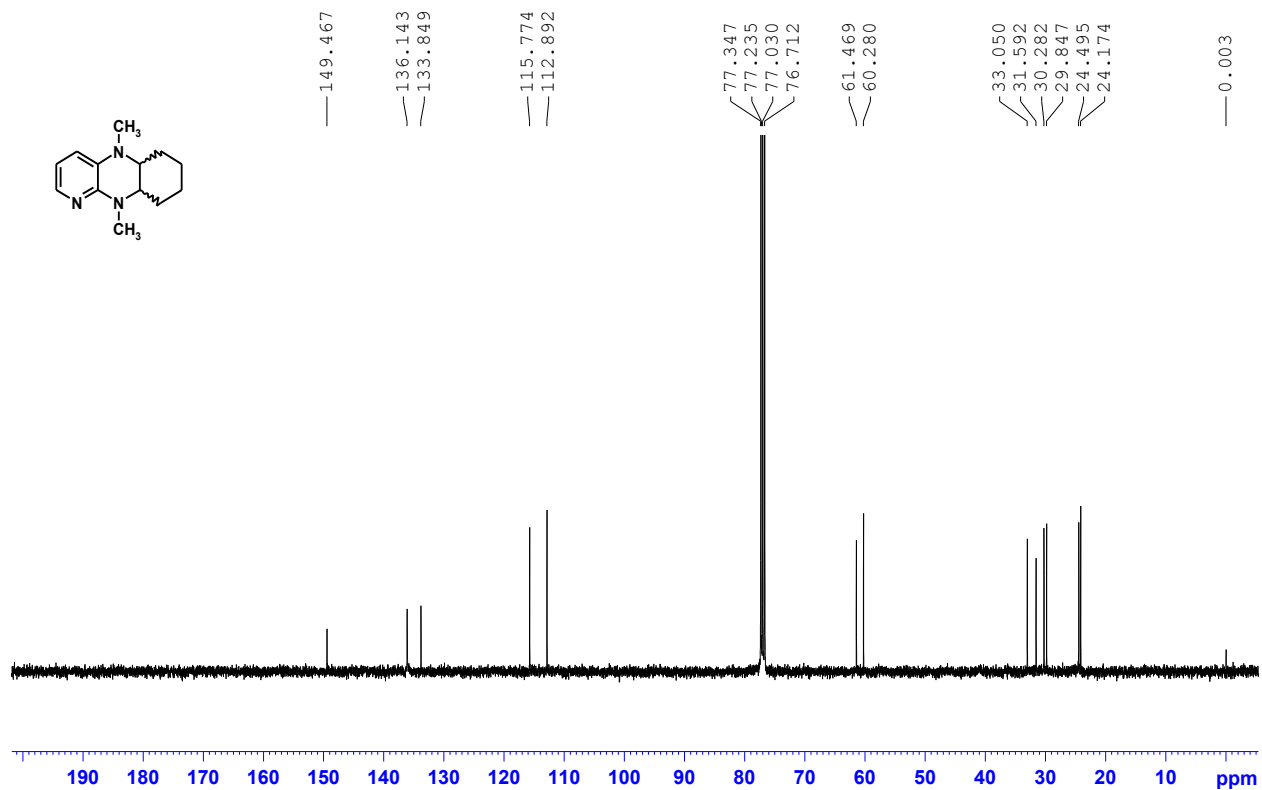




Meas. $m/z$	#	Formula	Score	$m/z$	err [ppm]	Mean err [ppm]	mSigma	rdb	$e^-$ Conf	N-Rule
164.1181	1	$\text{C}_9\text{H}_{14}\text{N}_3$	100.00	164.1182	0.8	1.2	4.7	4.5	even	ok

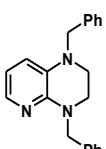
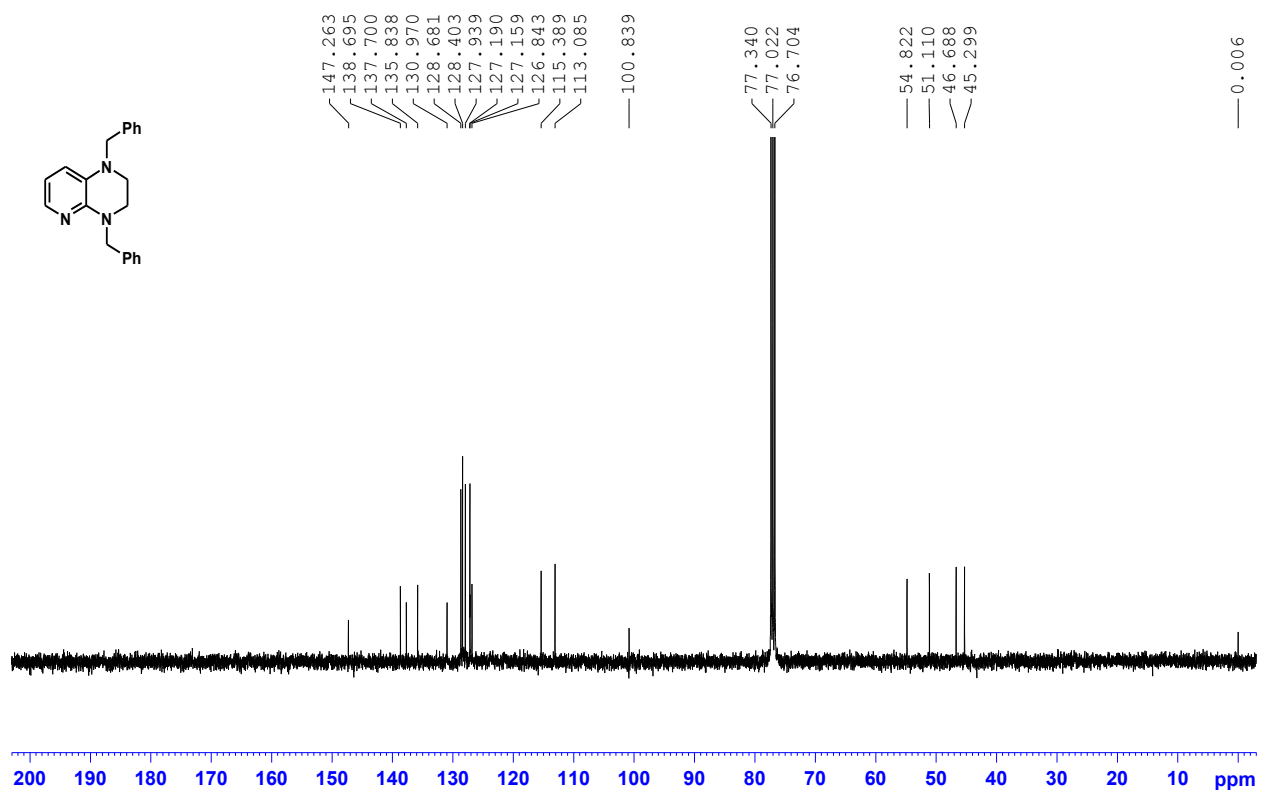
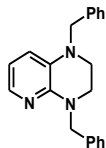
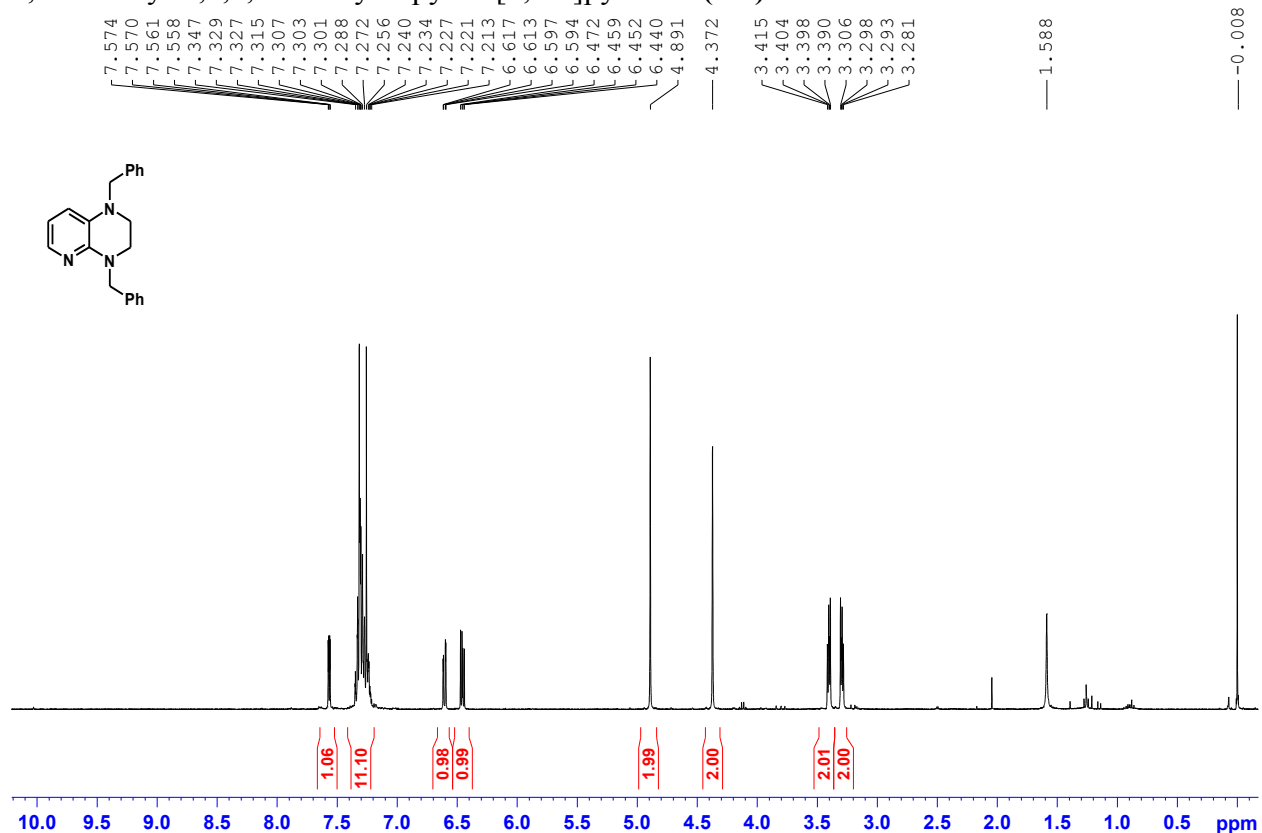
### 5,10-dimethyl-5,5a,6,7,8,9,9a,10-octahydropyrido[2,3-b]quinoxaline (31)

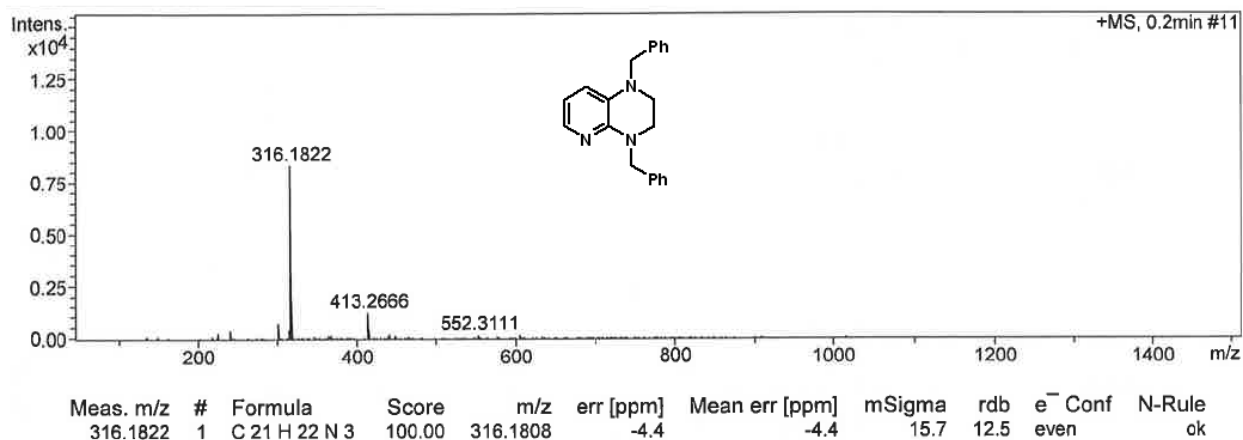




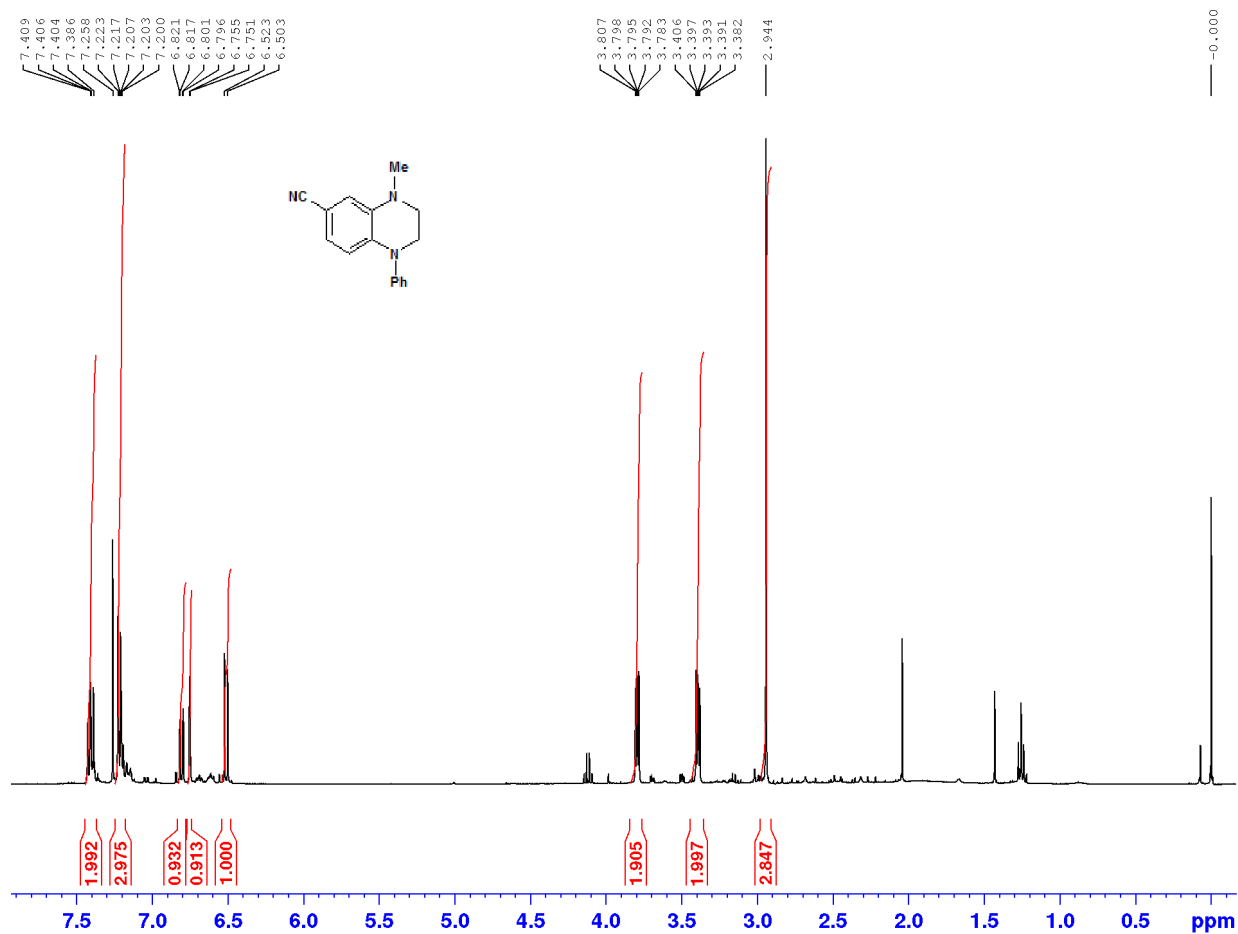
Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
218.1665	1	C <sub>13</sub> H <sub>20</sub> N <sub>3</sub>	100.00	218.1652	-5.9	-5.7	6.2	5.5	even	ok

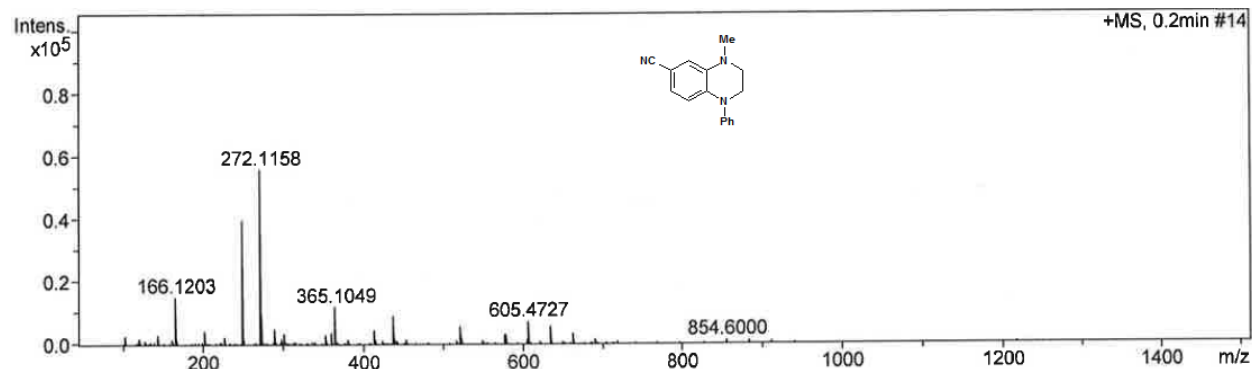
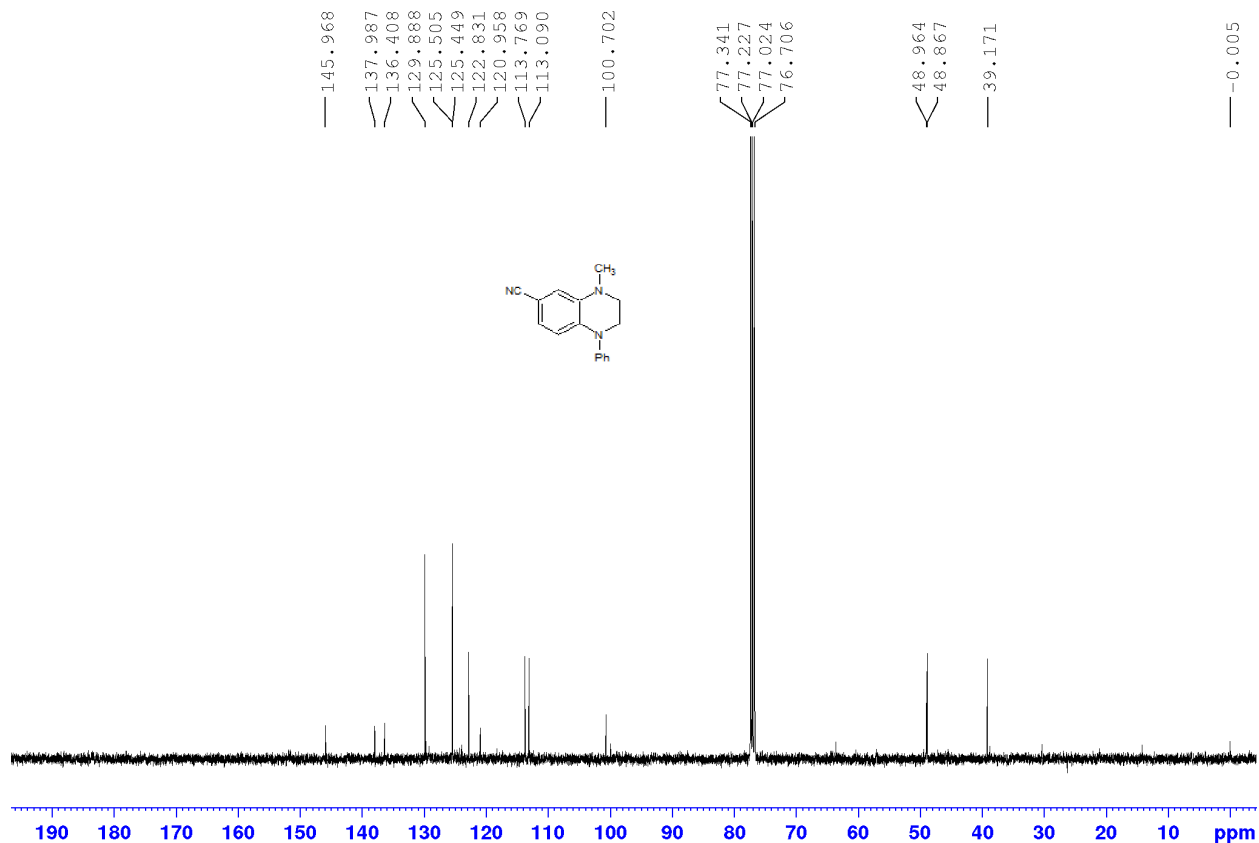
### 1,4-dibenzyl-1,2,3,4-tetrahydropyrido[2,3-b]pyrazine (**3m**)





### 4-methyl-1-phenyl-1,2,3,4-tetrahydroquinoline-6-carbonitrile (3n)

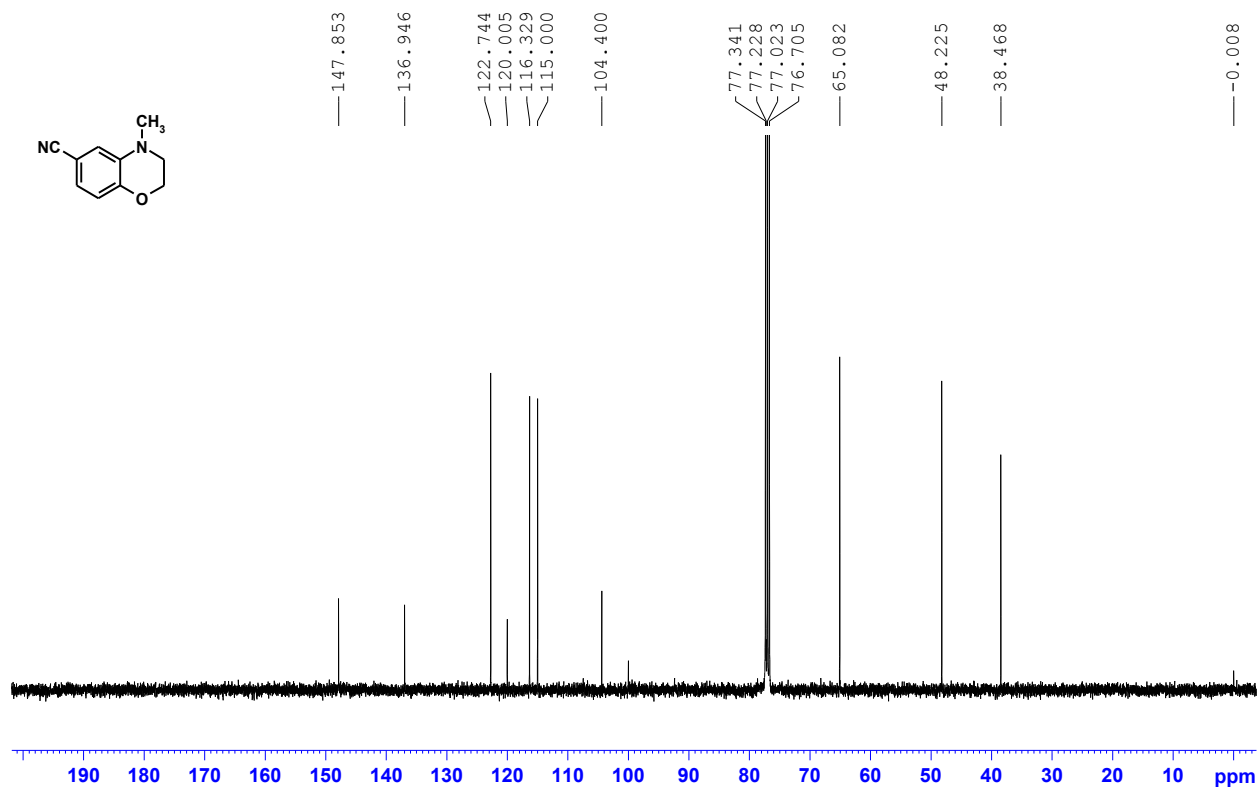
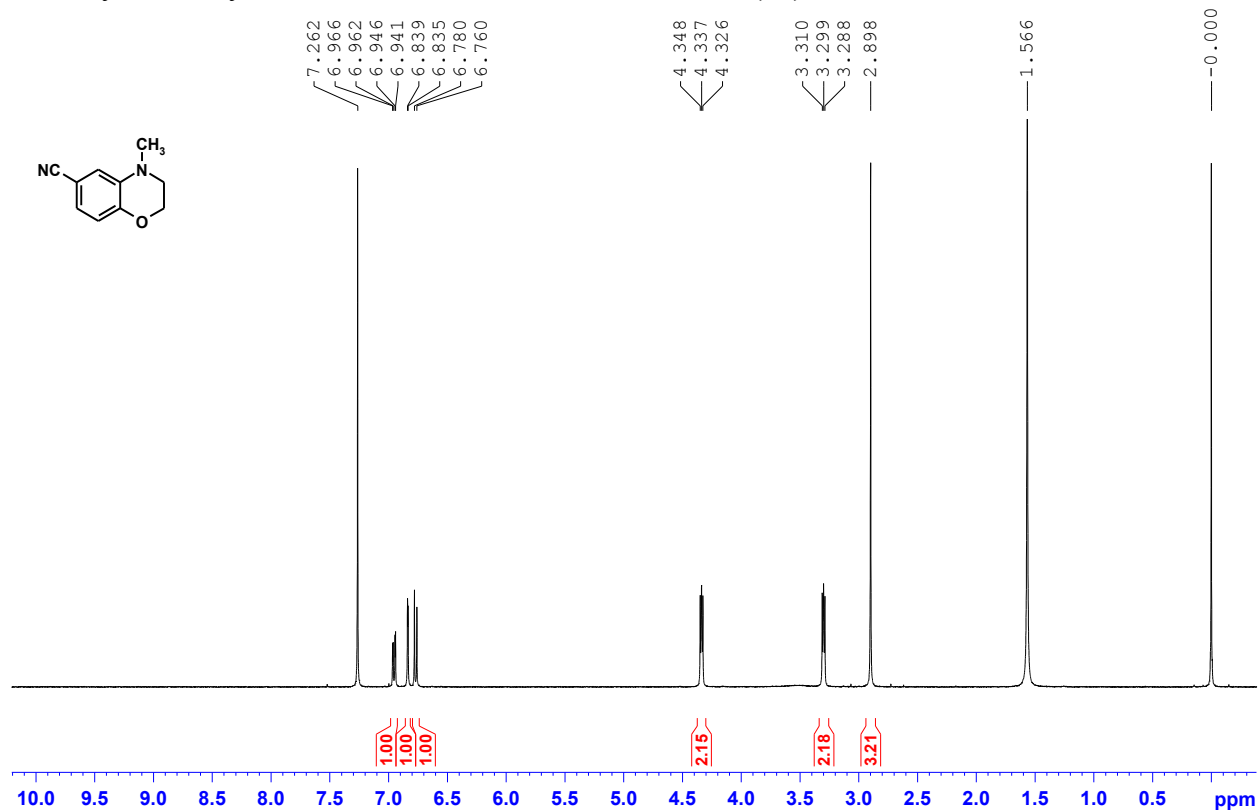


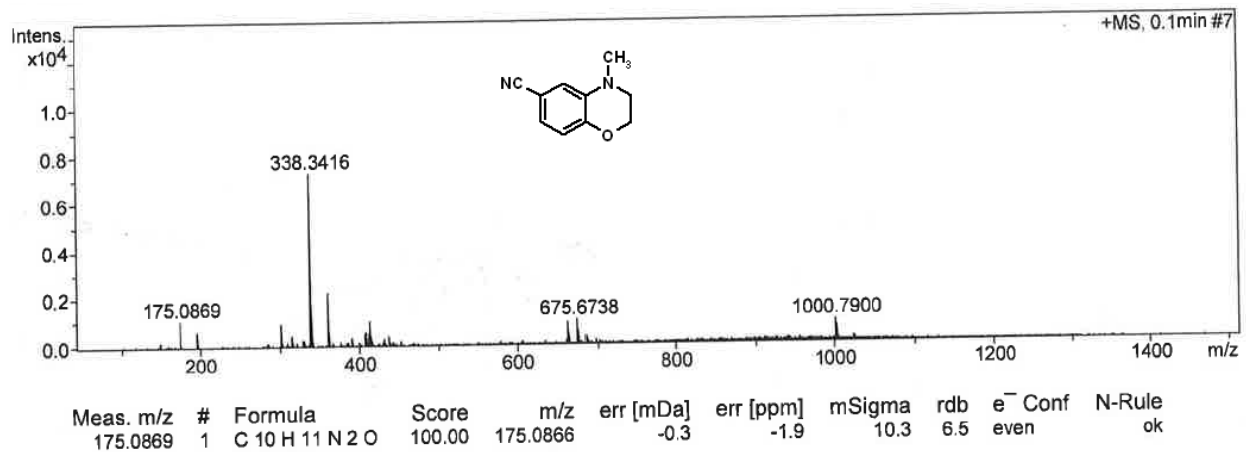


Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
272.1158	1	C 16 H 15 N 3 Na	100.00	272.1158	0.1	0.6	10.6	10.5	even	ok

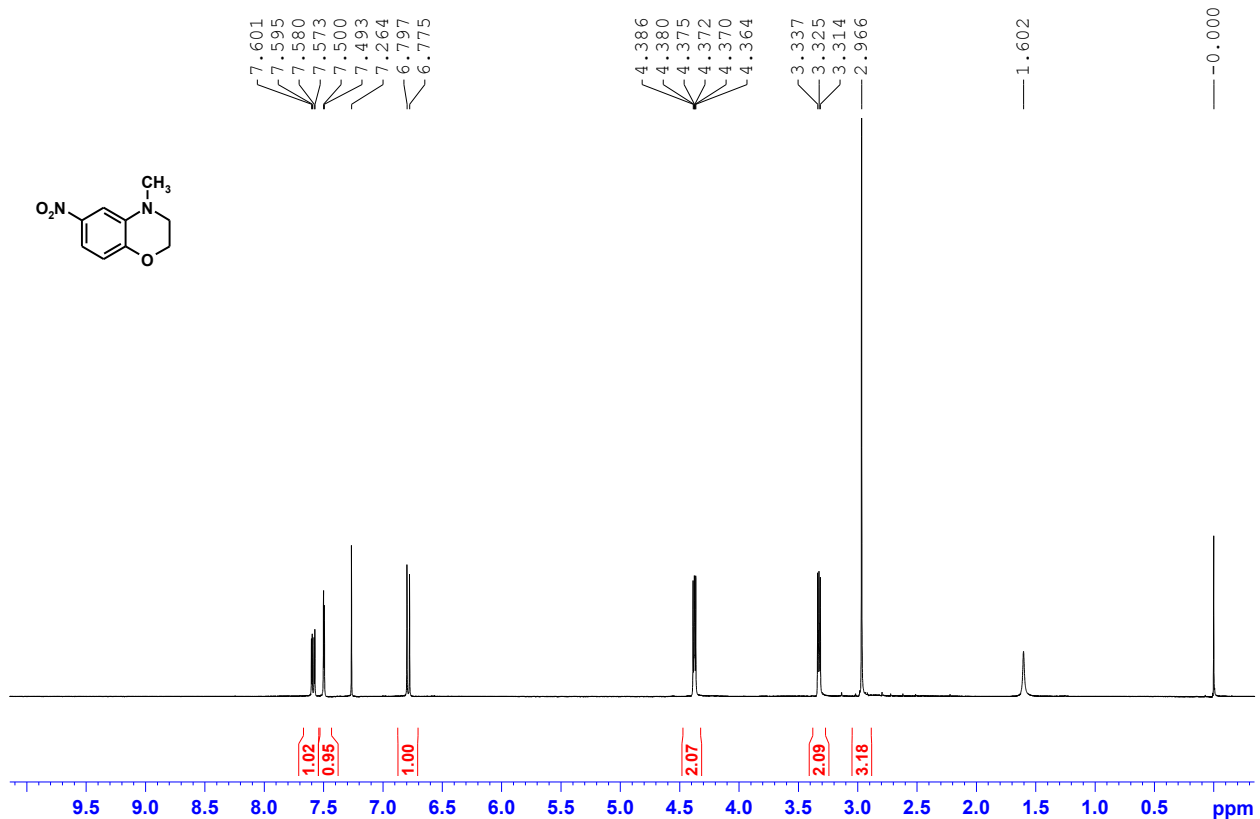


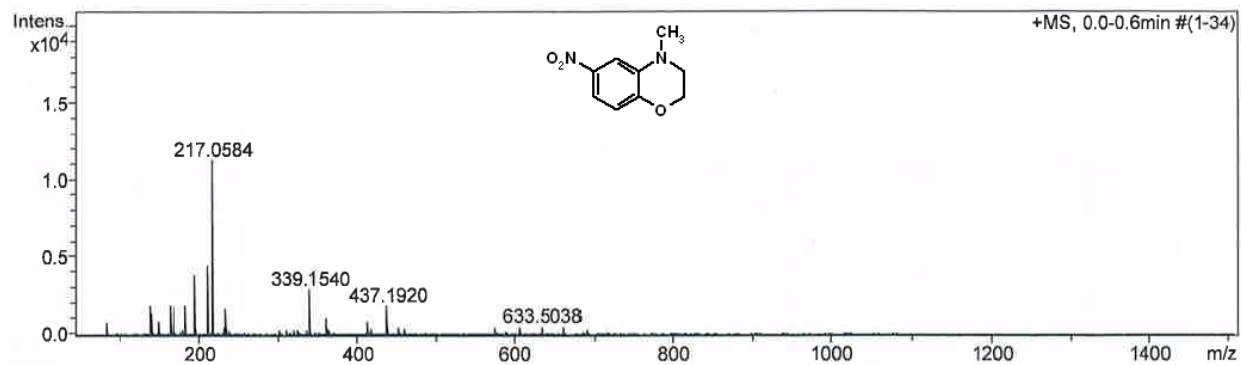
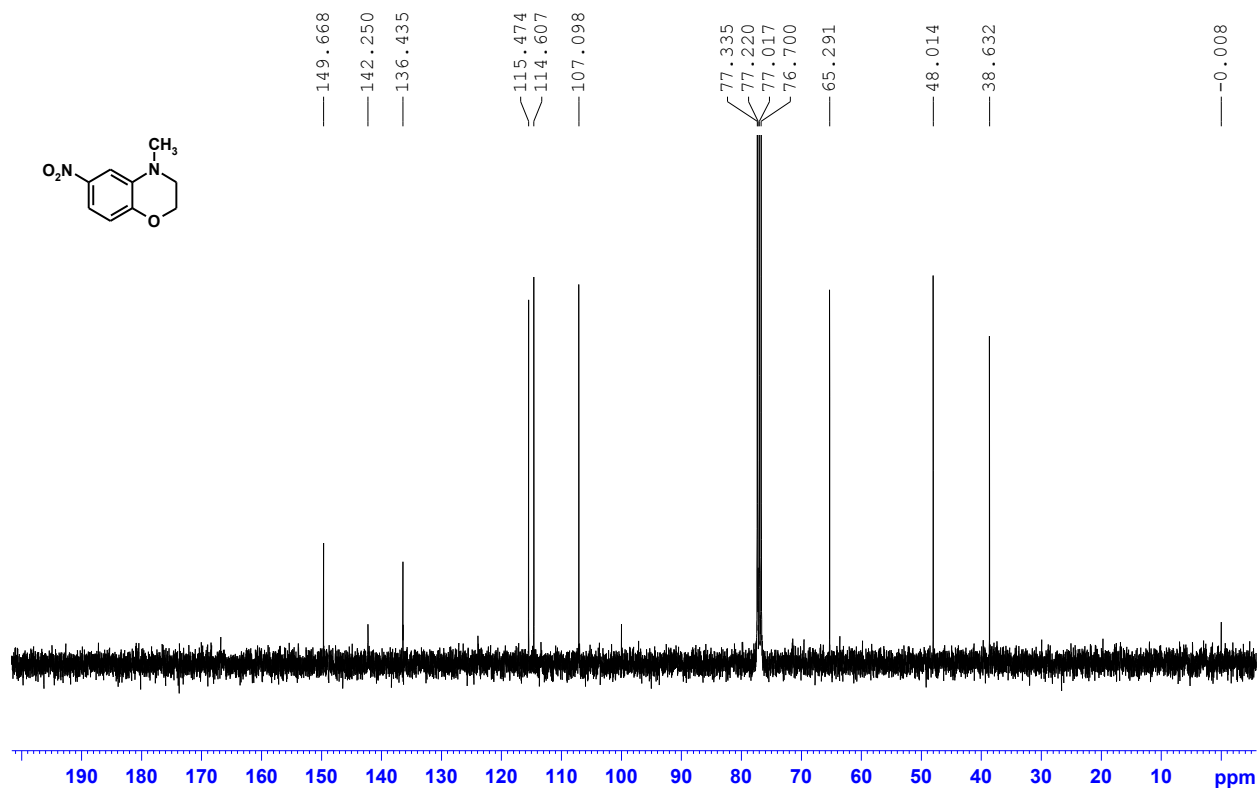
### 4-methyl-3,4-dihydro-2H-1,4-benzoxazine-6-carbonitrile (**6a**)





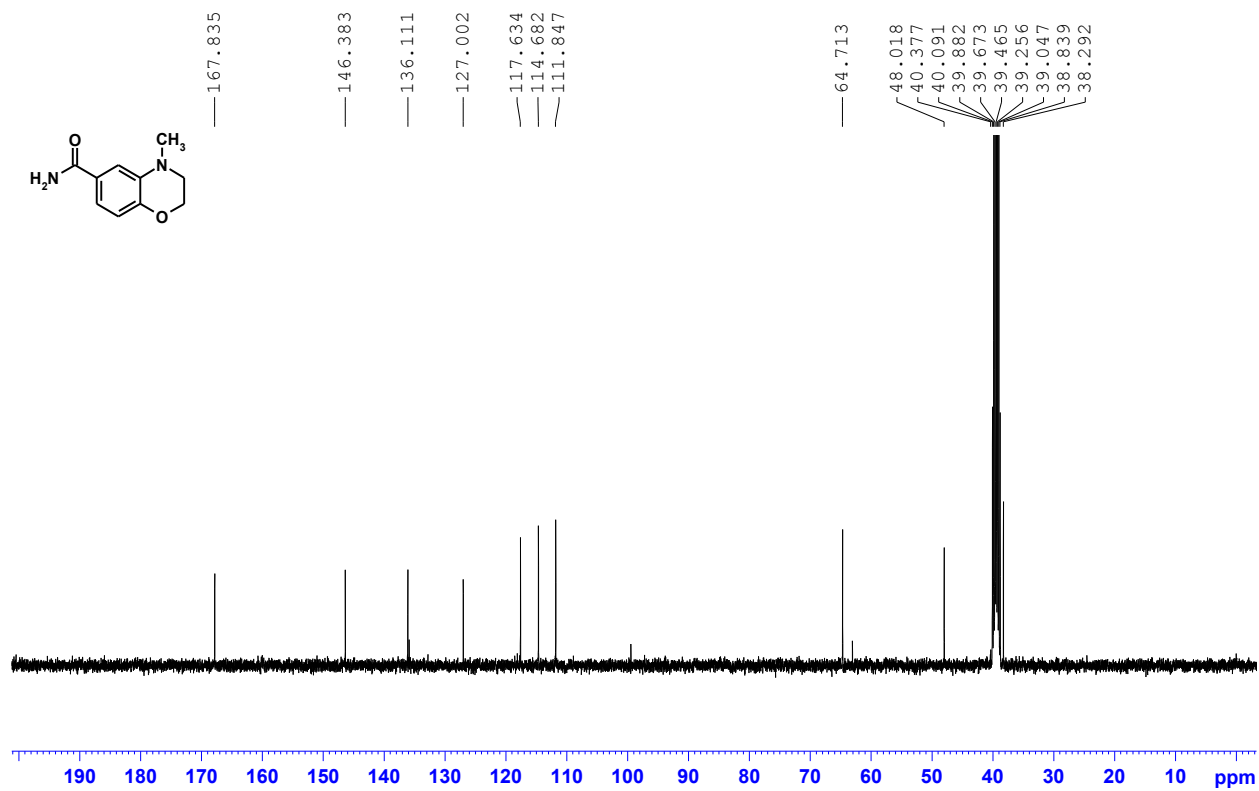
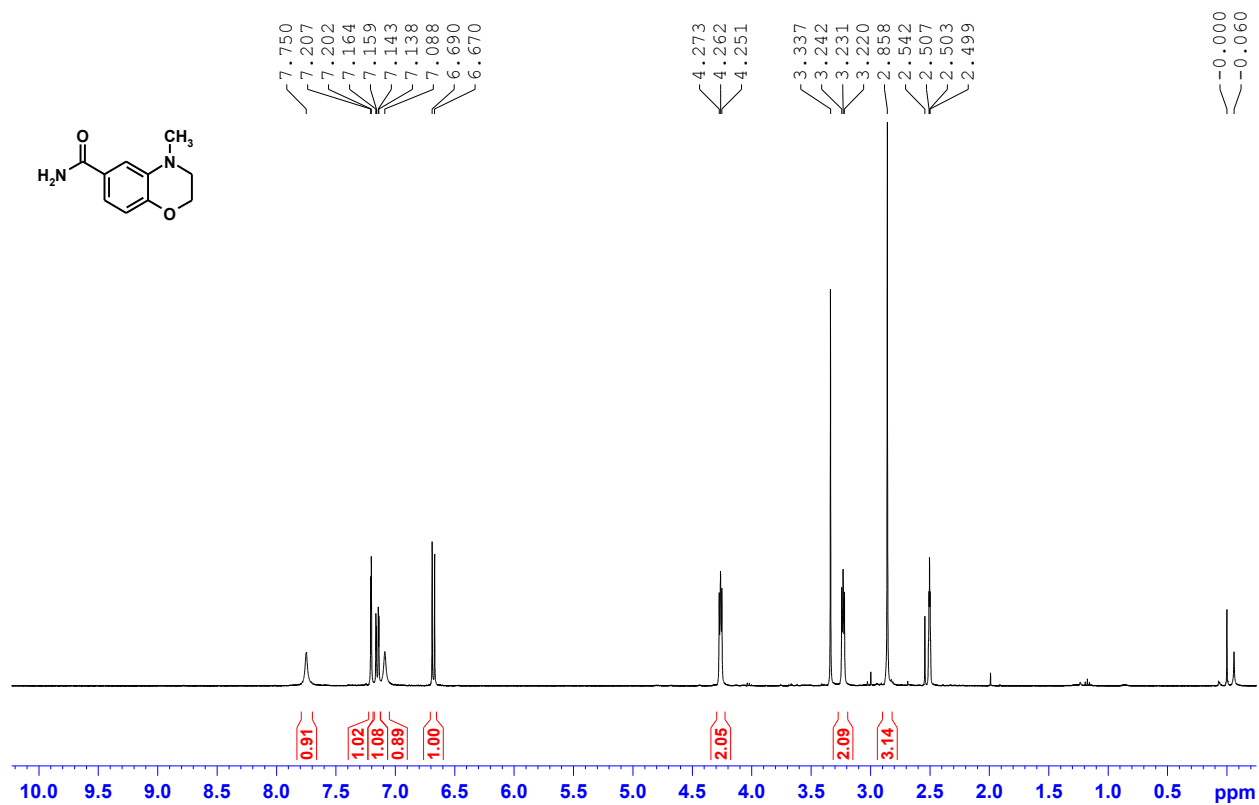
4-methyl-6-nitro-3,4-dihydro-2H-1,4-benzoxazine (**6b**)

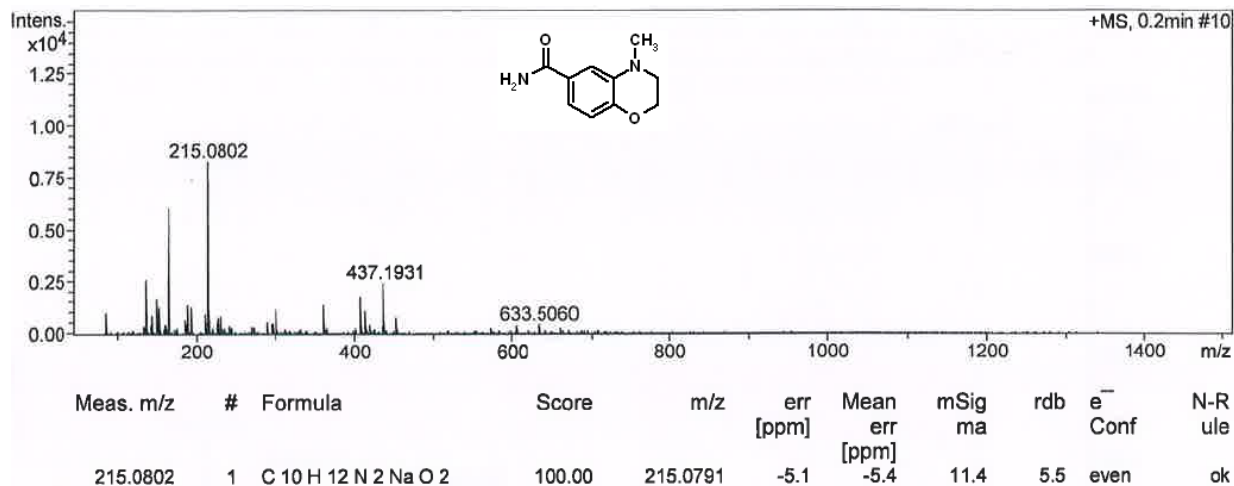




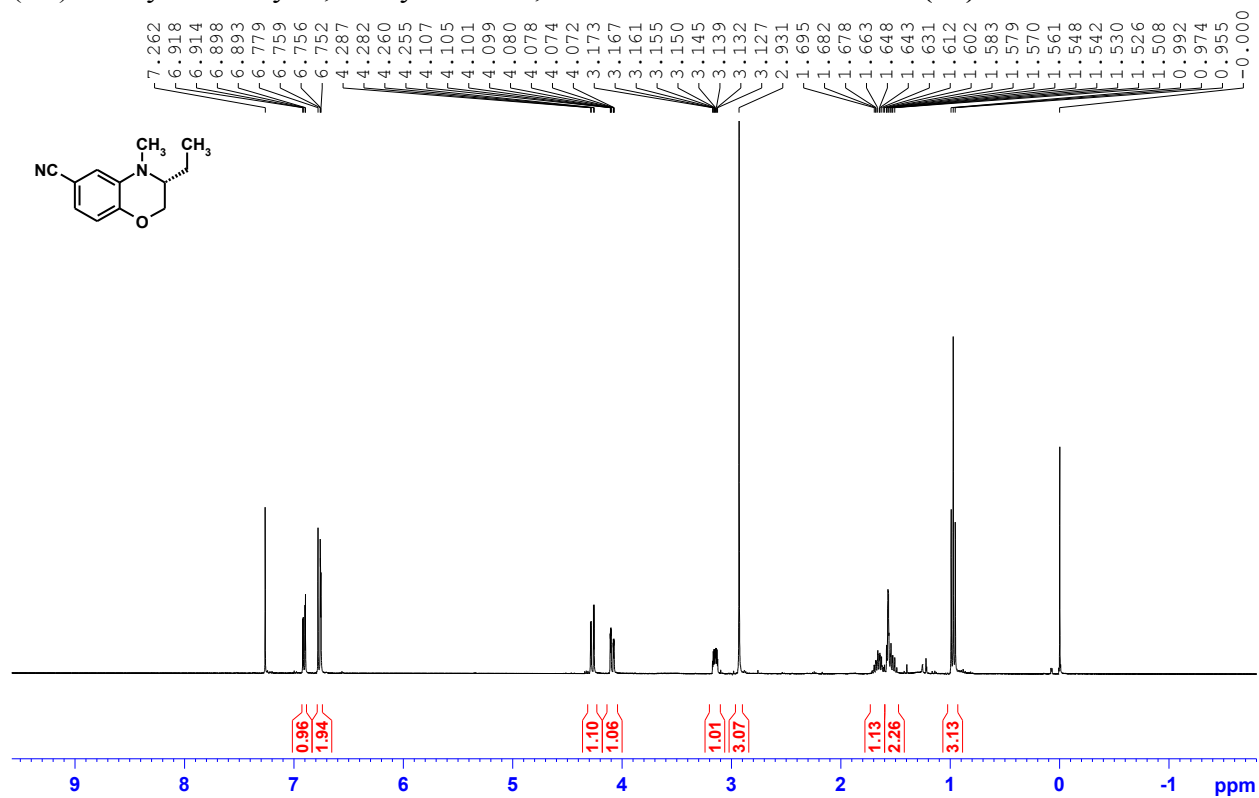
Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSig ma	rdb	e <sup>-</sup> Conf	N-R ule
217.0584	1	C <sub>9</sub> H <sub>10</sub> N <sub>2</sub> NaO <sub>3</sub>	100.00	217.0584	-0.2	-0.4	2.3	5.5	even	ok

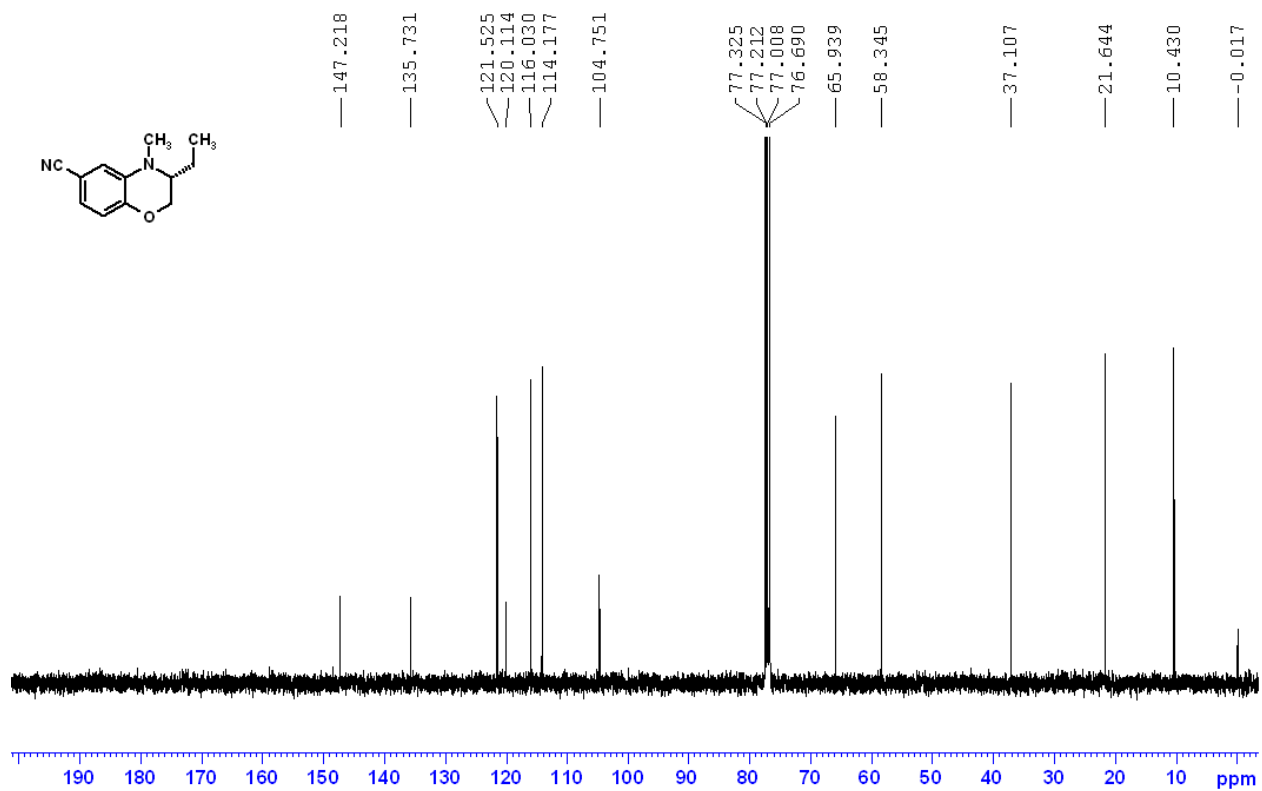
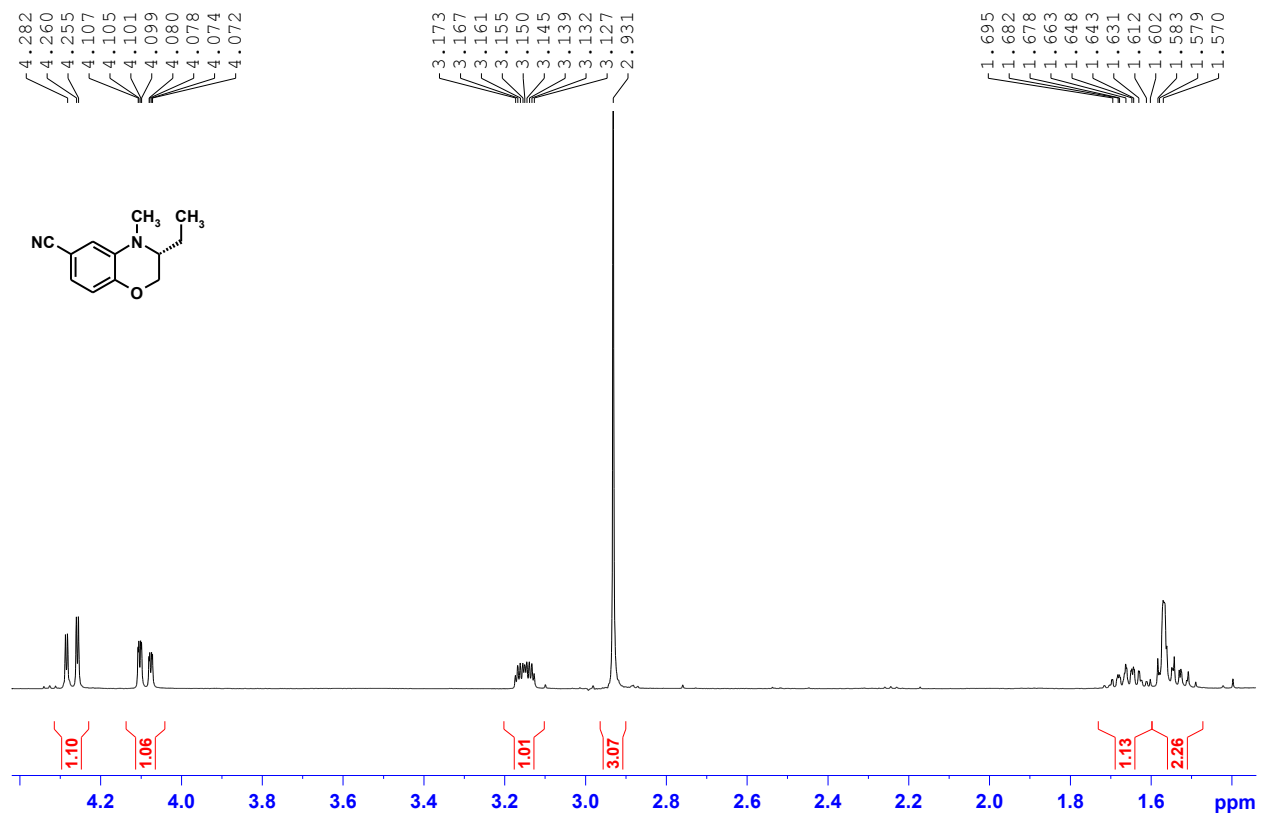
### 4-methyl-3,4-dihydro-2H-1,4-benzoxazine-6-carboxamide (**6c**)

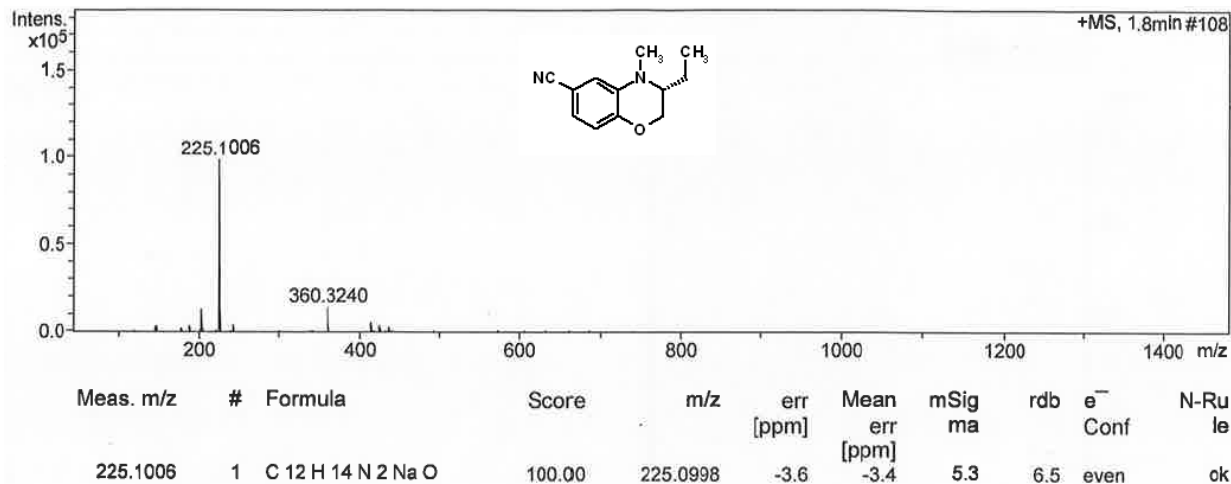




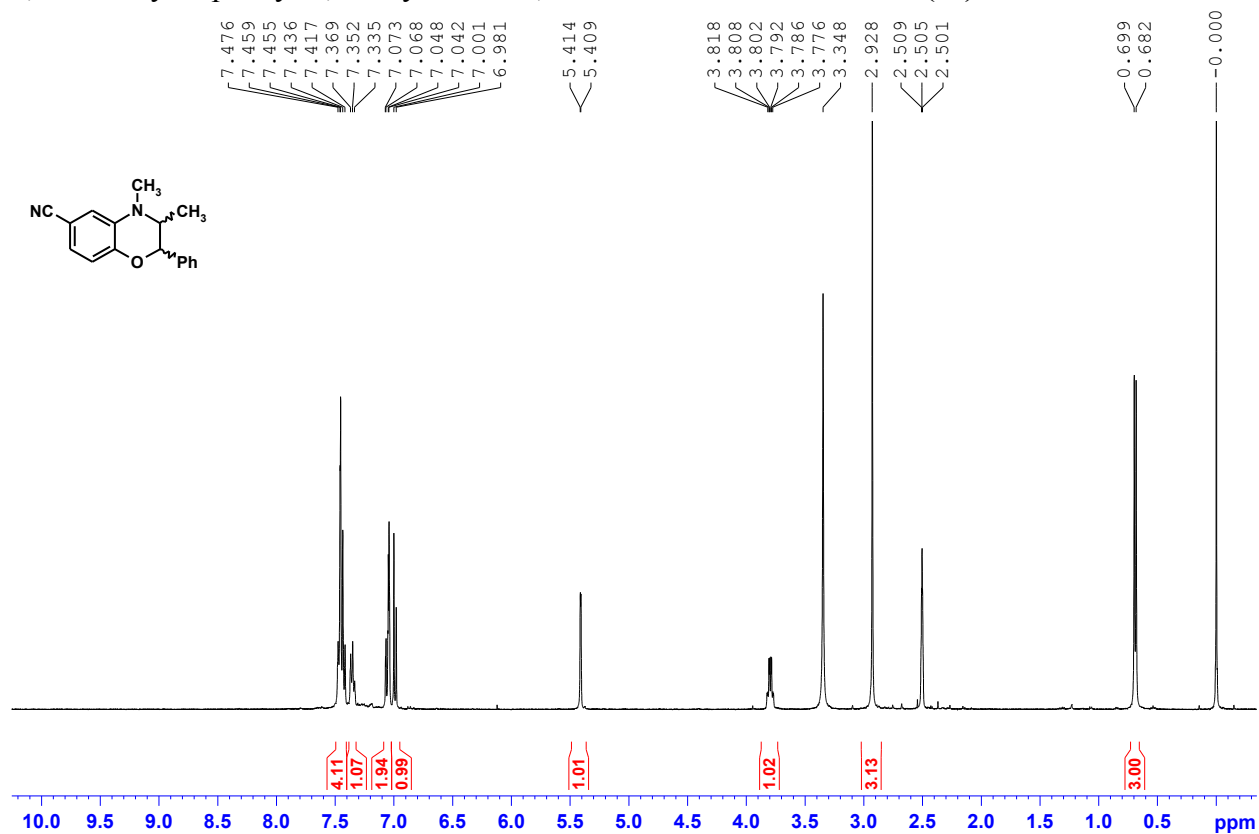
(3R)-3-ethyl-4-methyl-3,4-dihydro-2H-1,4-benzoxazine-6-carbonitrile (**6d**)

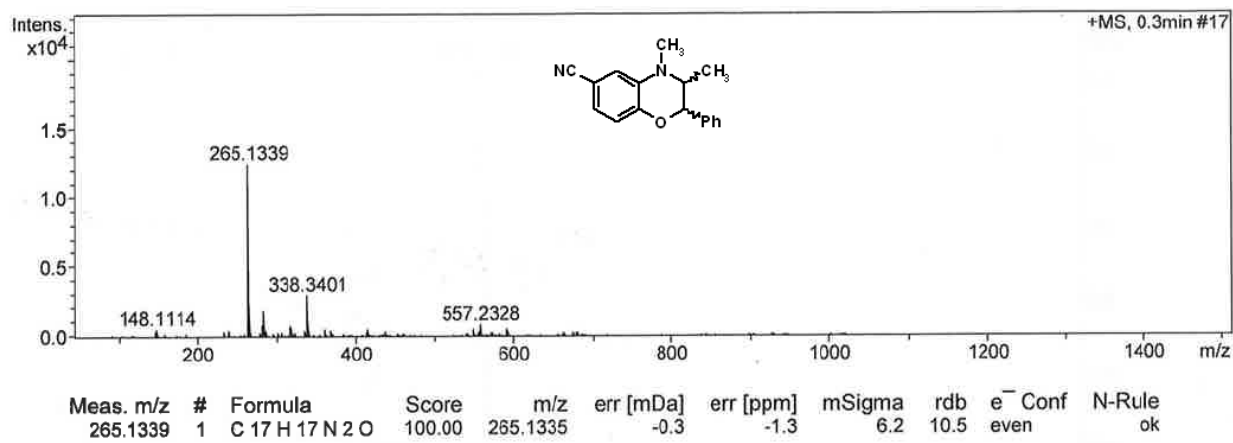
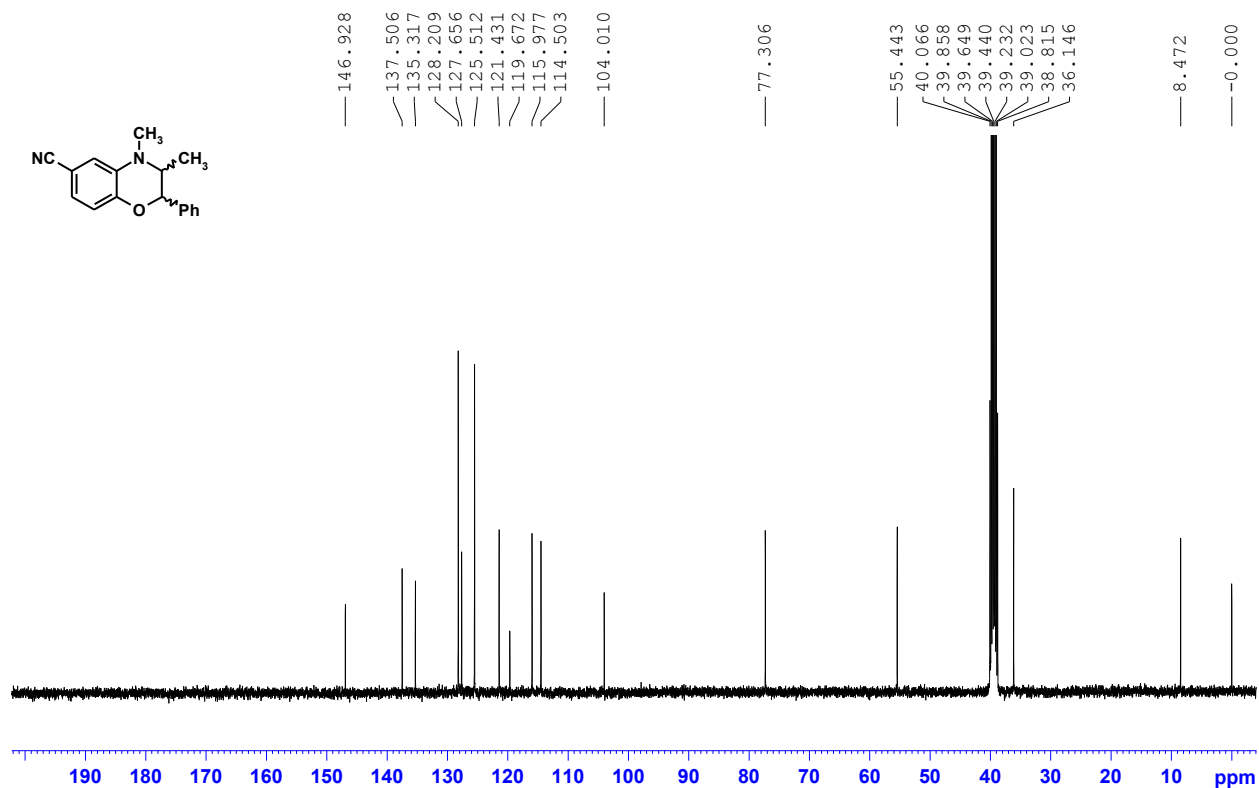






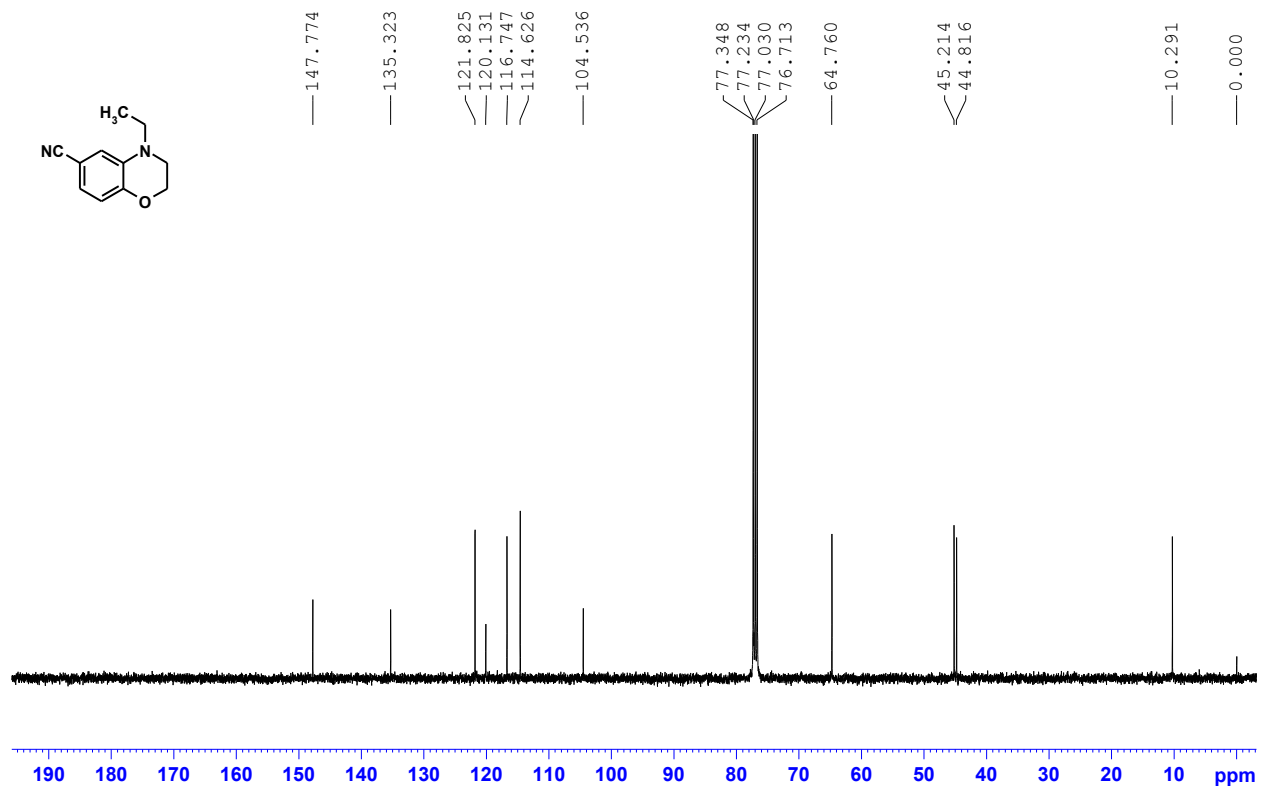
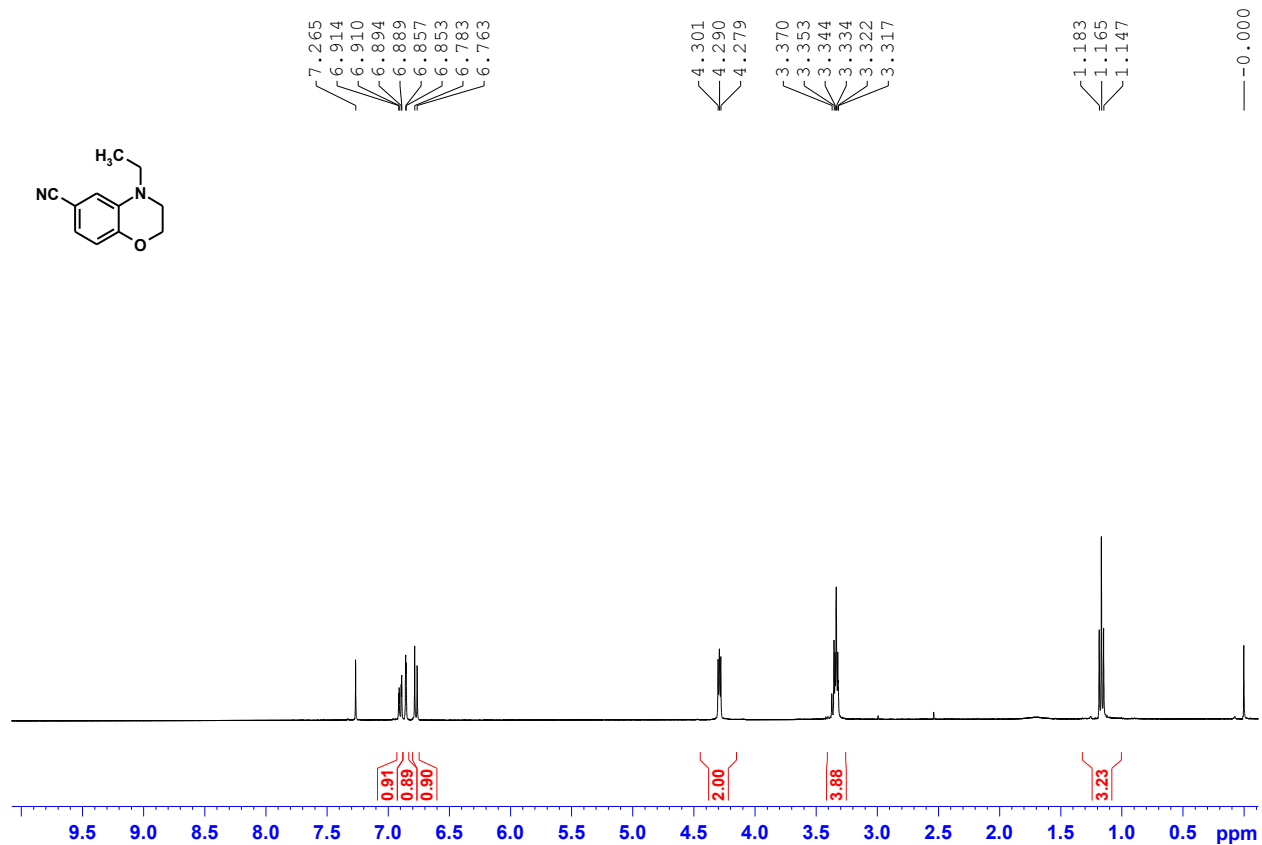
3,4-dimethyl-2-phenyl-3,4-dihydro-2H-1,4-benzoxazine-6-carbonitrile (**6e**)

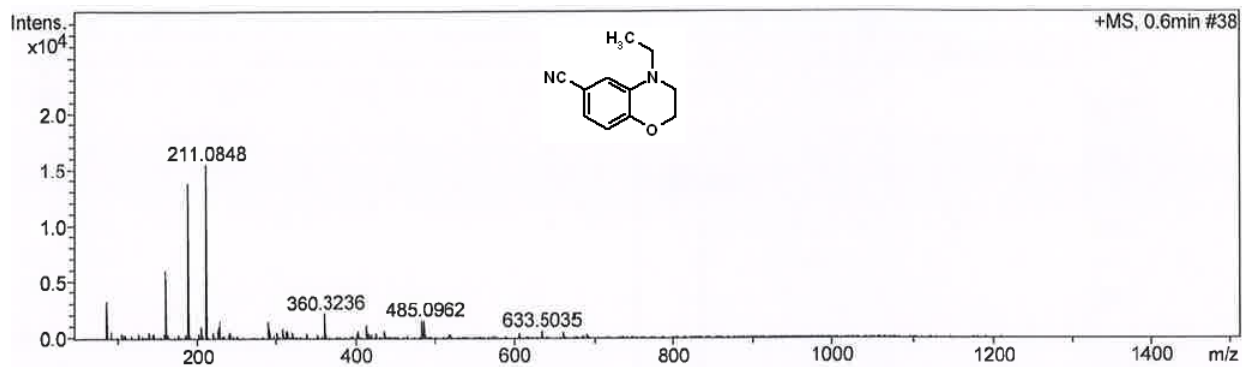




4-ethyl-3,4-dihydro-2H-1,4-benzoxazine-6-carbonitrile (**6f**)

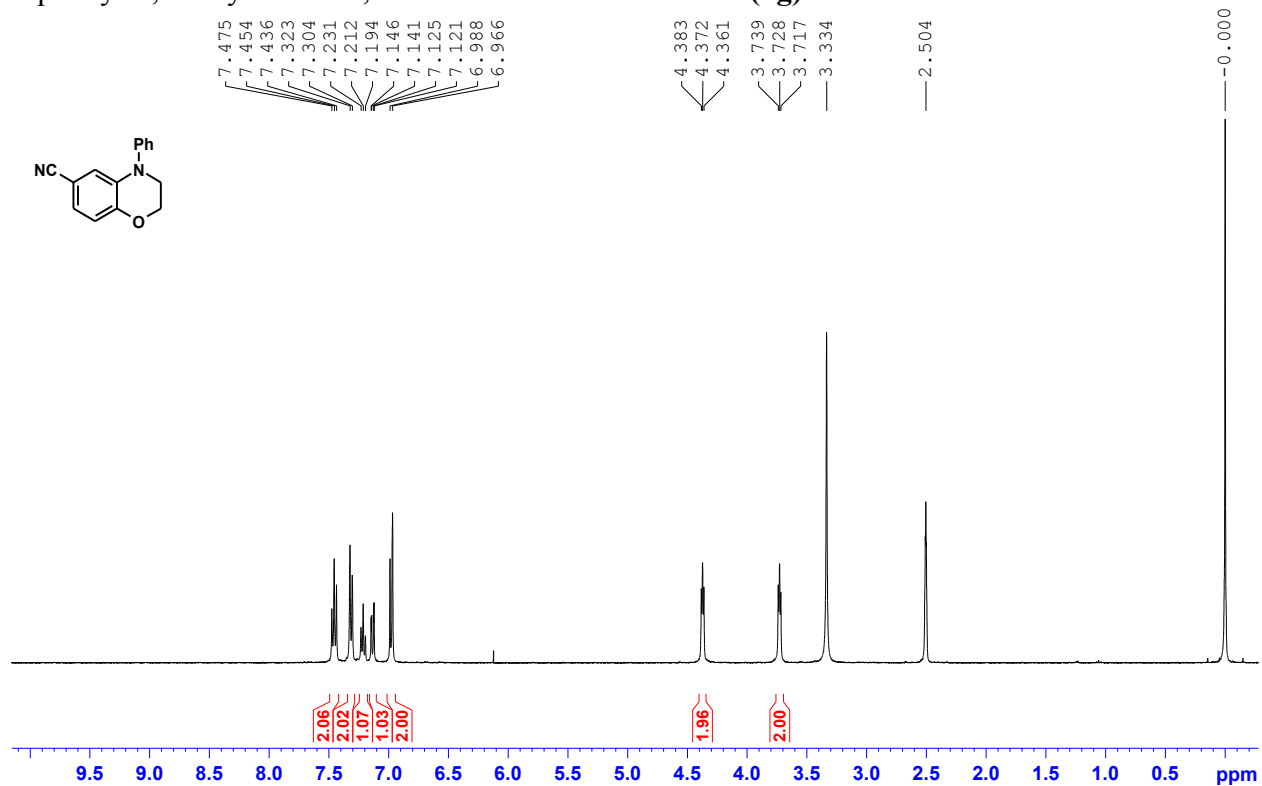


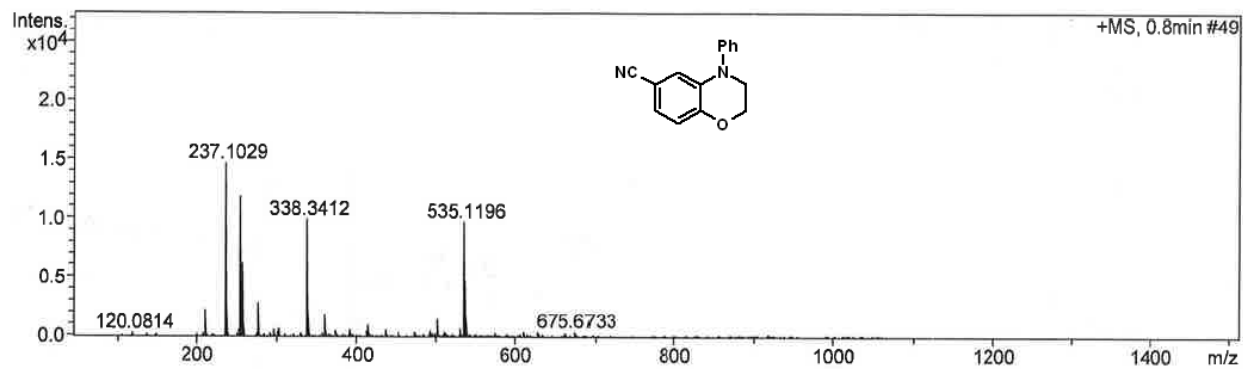
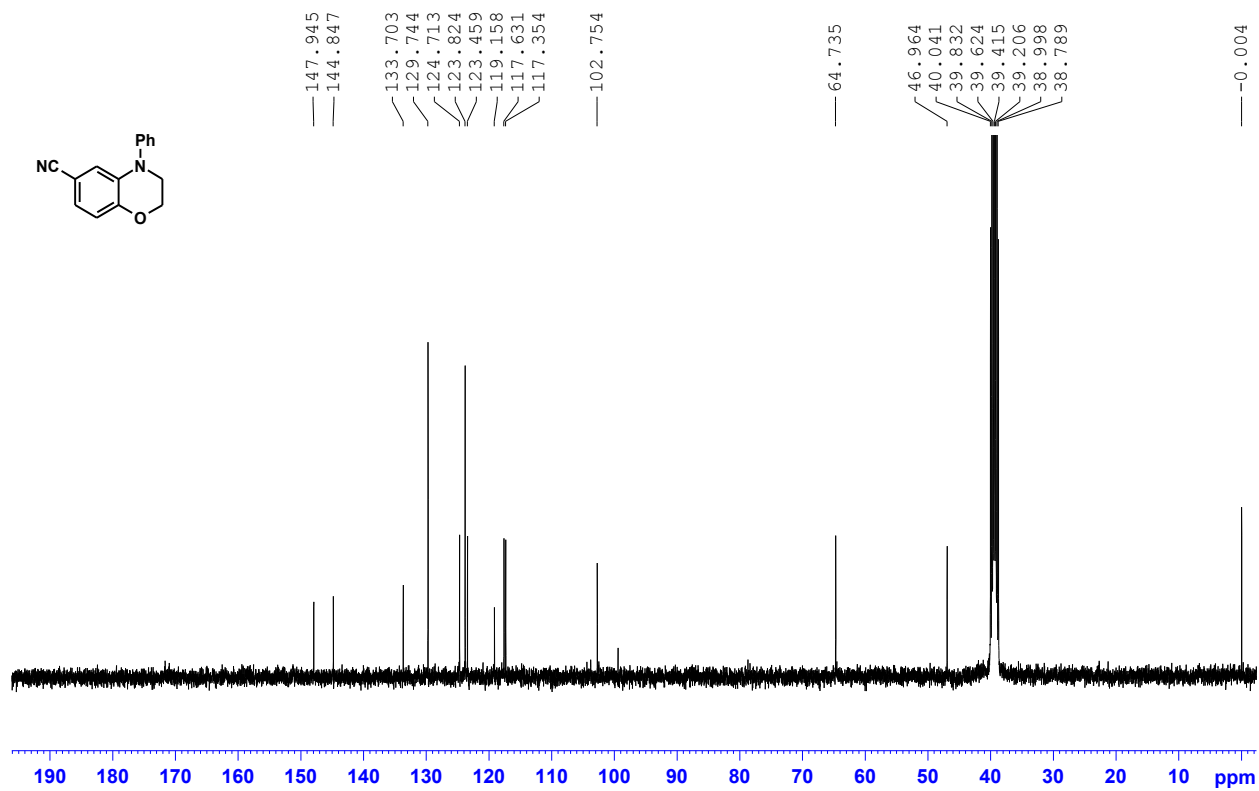




Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSig ma	rdb	e <sup>-</sup> Conf	N-Rule
211.0848	1	C 11 H 12 N 2 Na O	100.00	211.0842	-2.9	-2.5	5.2	6.5	even	ok

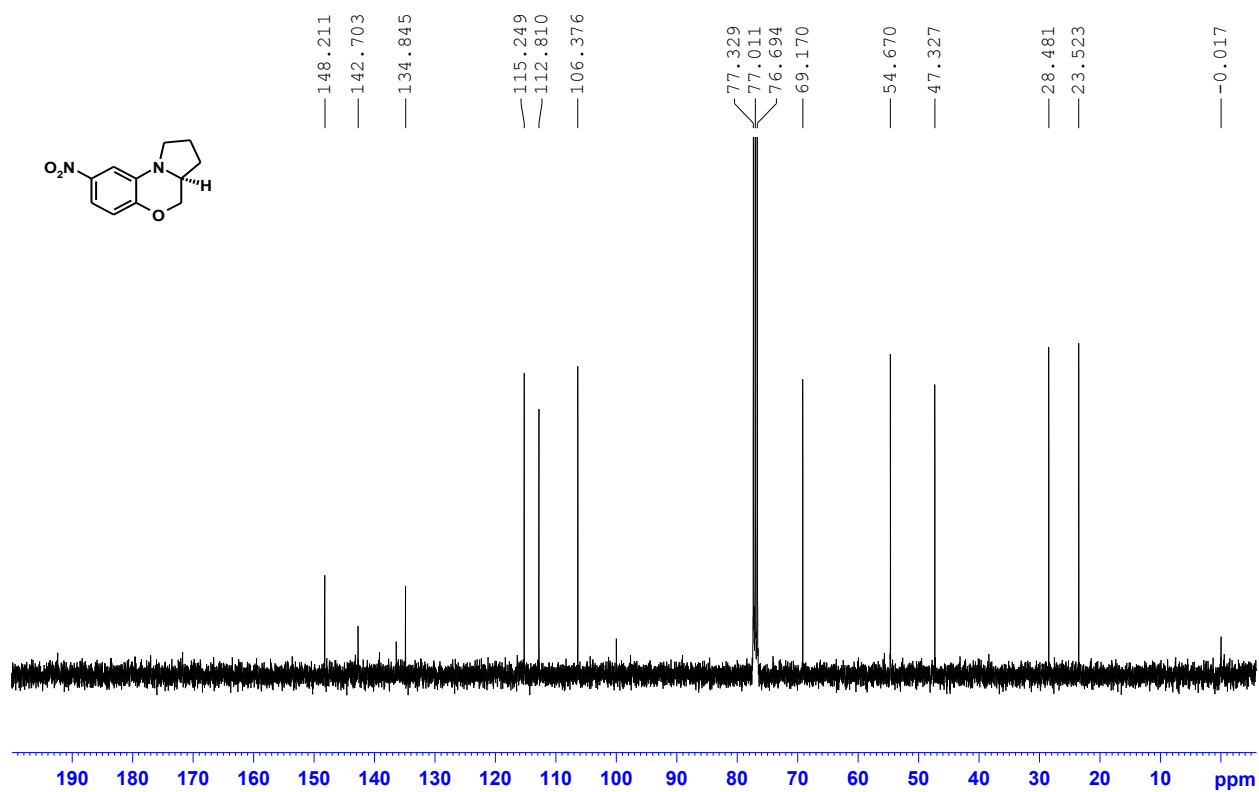
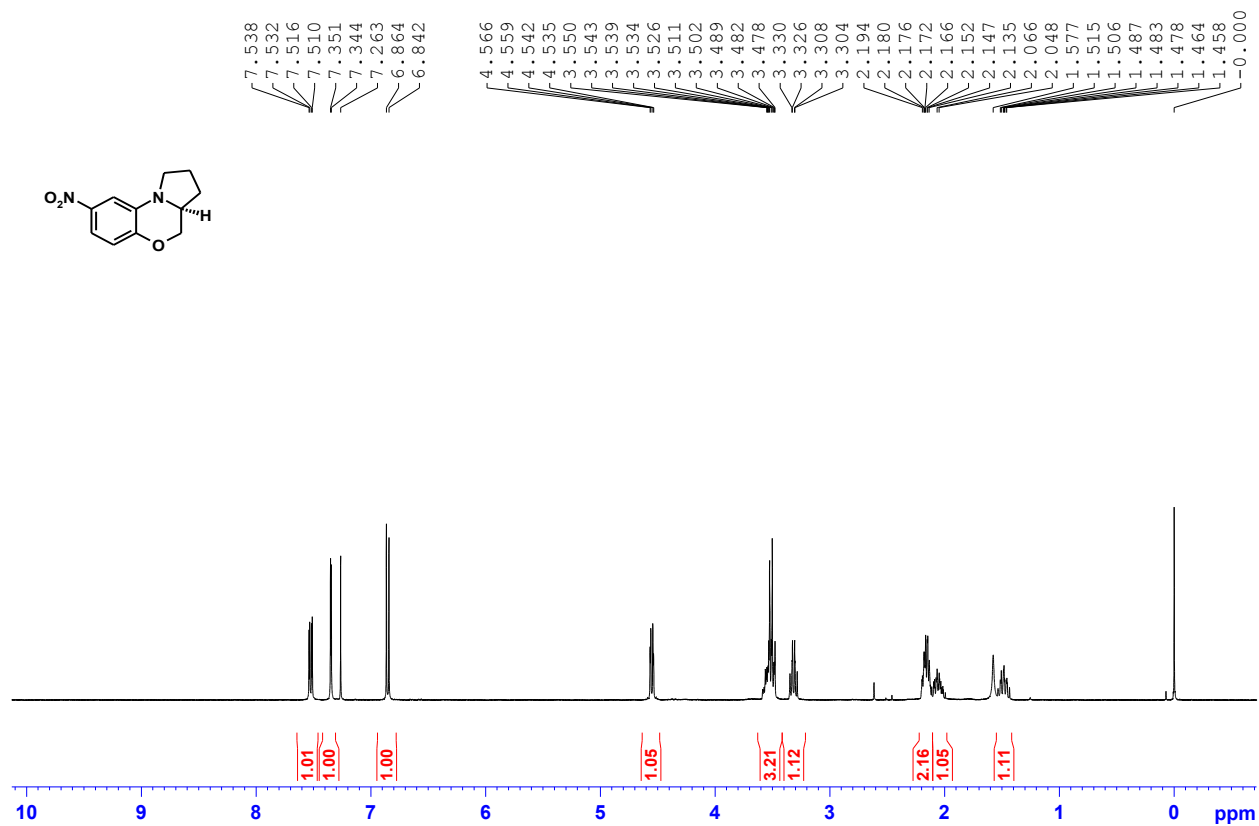
### 4-phenyl-3,4-dihydro-2H-1,4-benzoxazine-6-carbonitrile (**6g**)

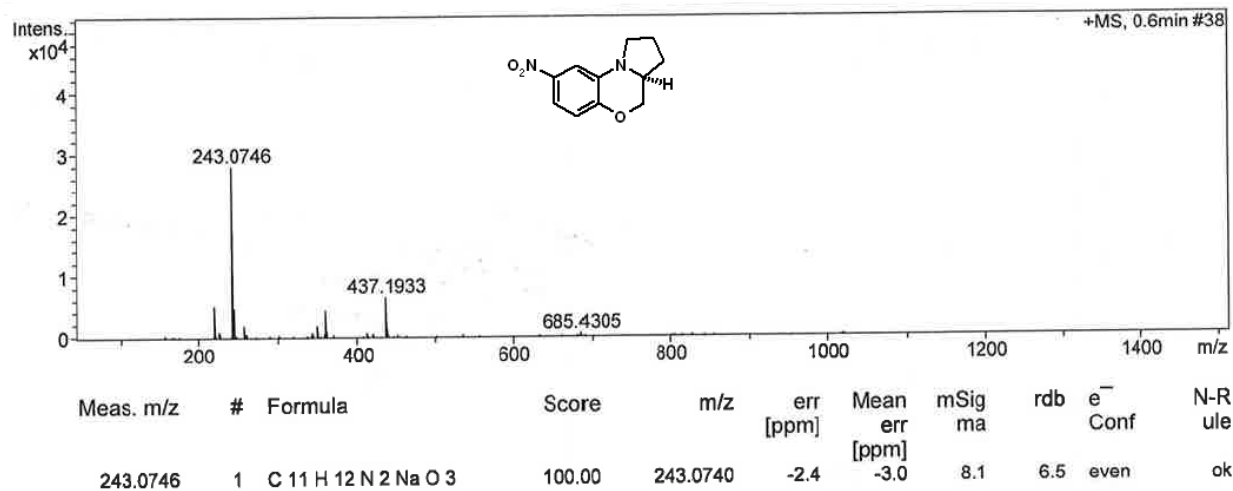




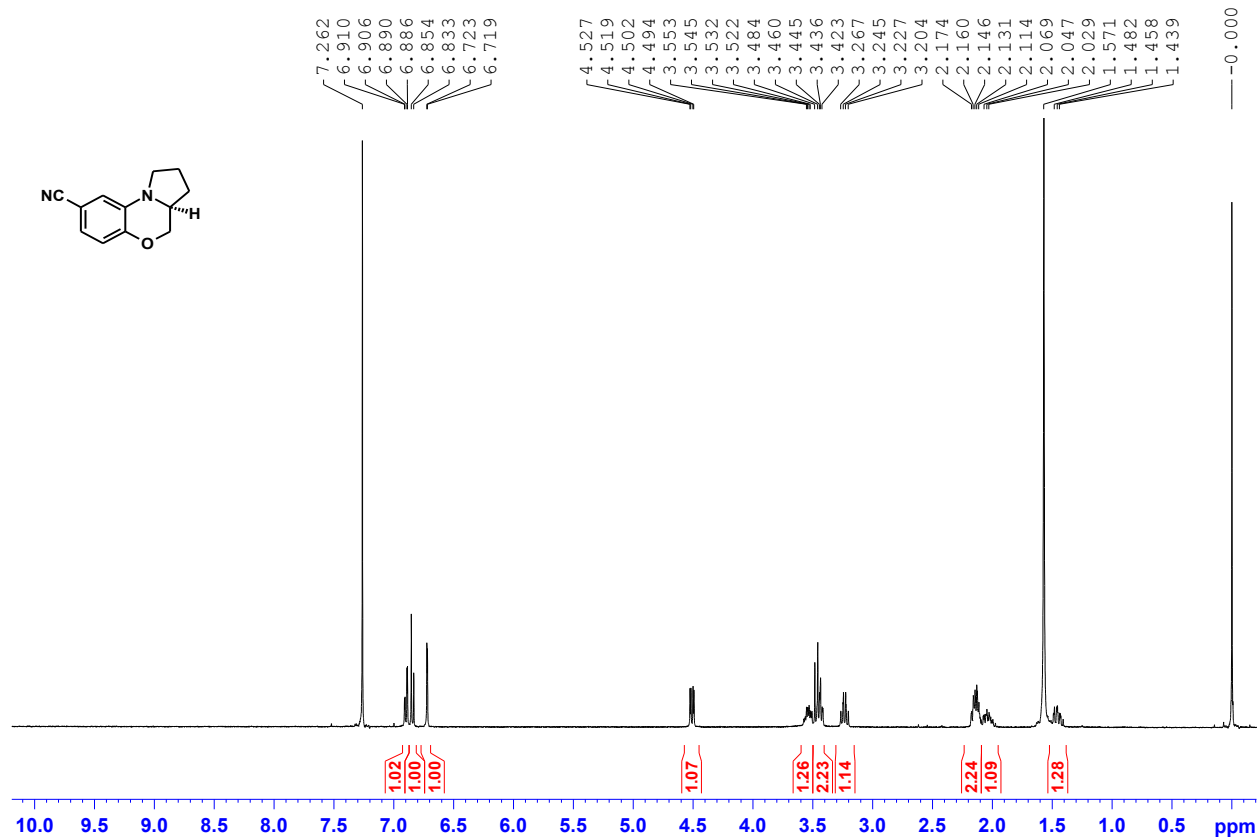
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
237.1029	1	C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O	100.00	237.1022	-0.7	-2.9	5.9	10.5	even	ok

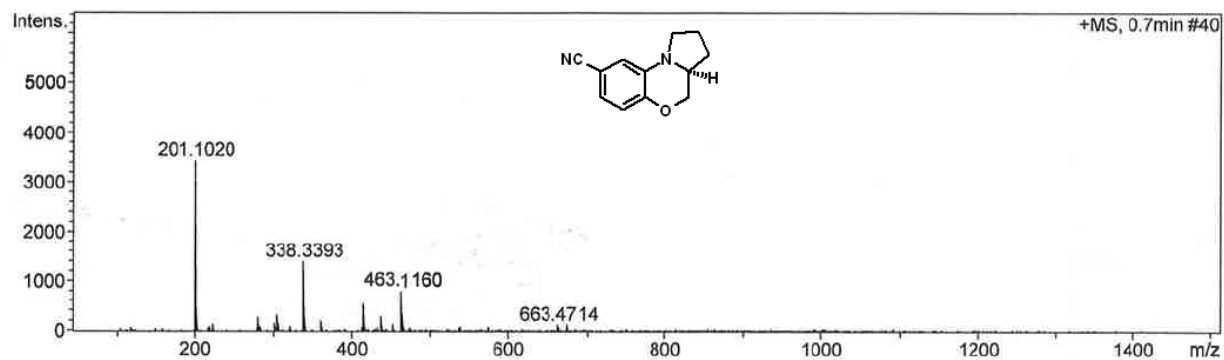
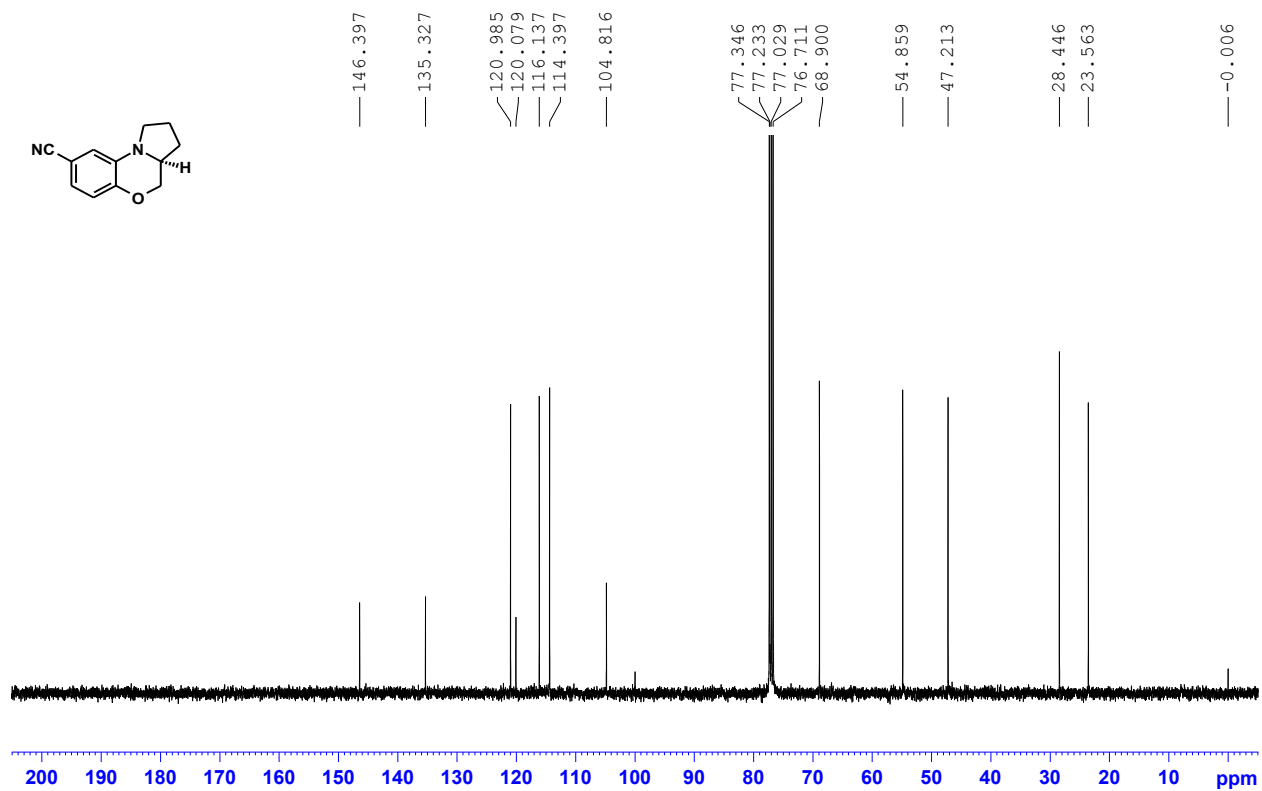
(3aS)-8-nitro-2,3,3a,4-tetrahydro-1H-pyrrolo[2,1-c][1,4]benzoxazine (**6h**)



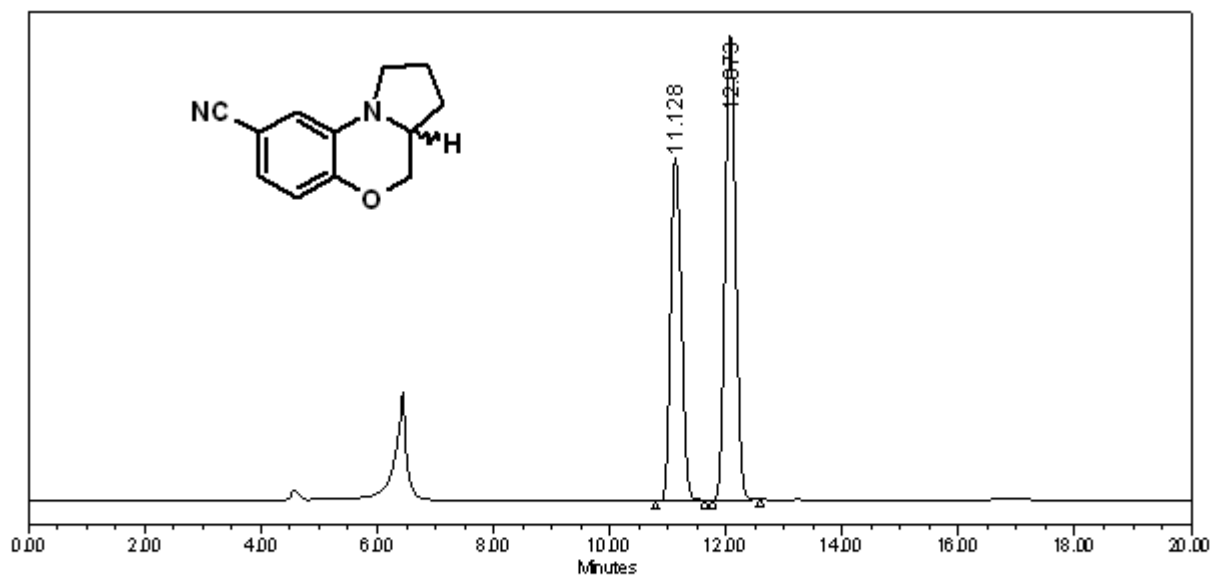


(3aS)-2,3,3a,4-tetrahydro-1H-pyrrolo[2,1-c][1,4]benzoxazine-8-carbonitrile (**6i**)

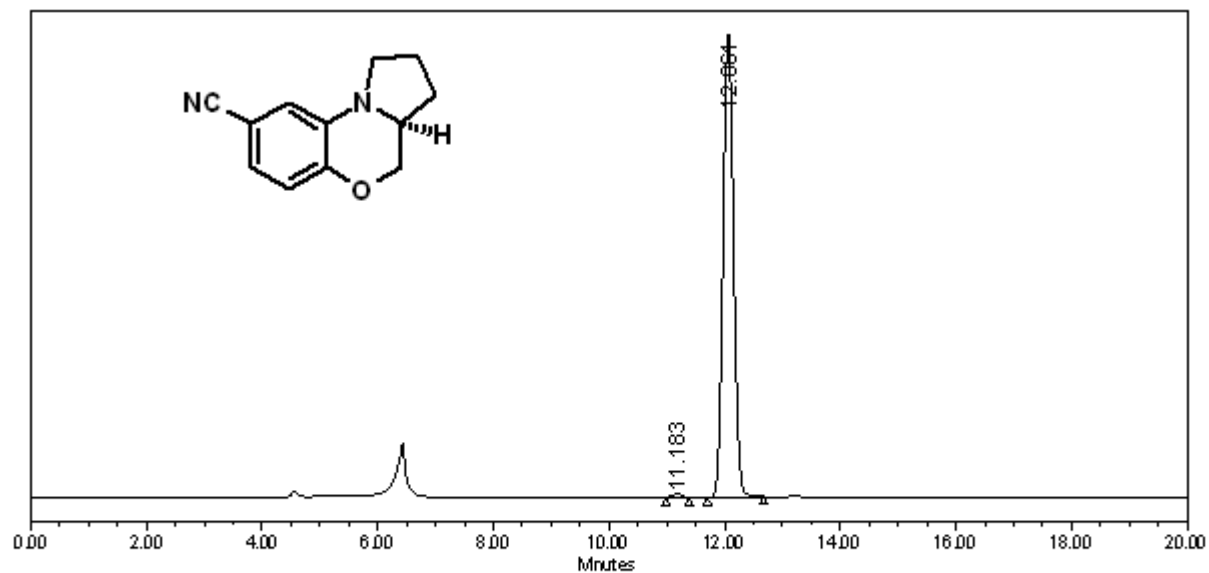




Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
201.1020	1	C <sub>12</sub> H <sub>13</sub> N <sub>2</sub> O	100.00	201.1022	0.3	1.3	5.6	7.5	even	ok

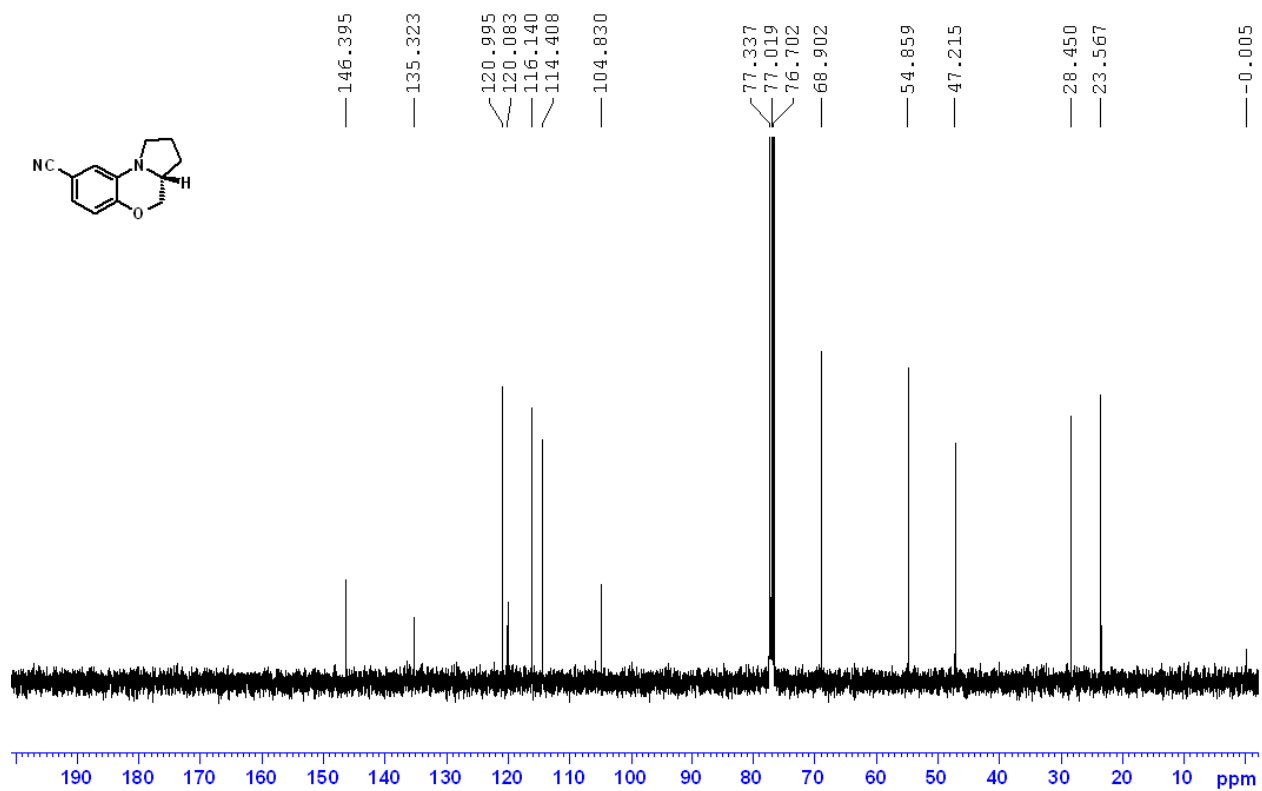
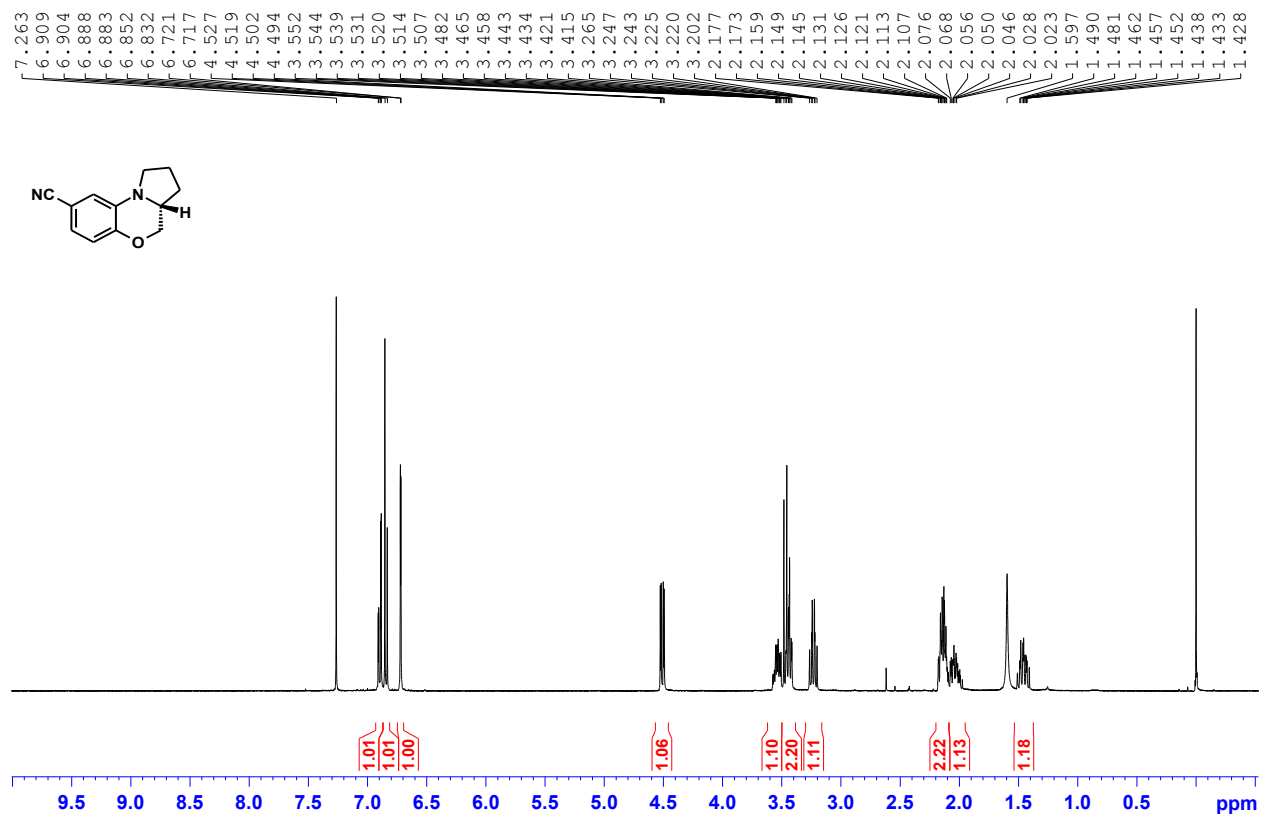


Peak	RT	% Area
1	11.128	43.26
2	12.073	56.74

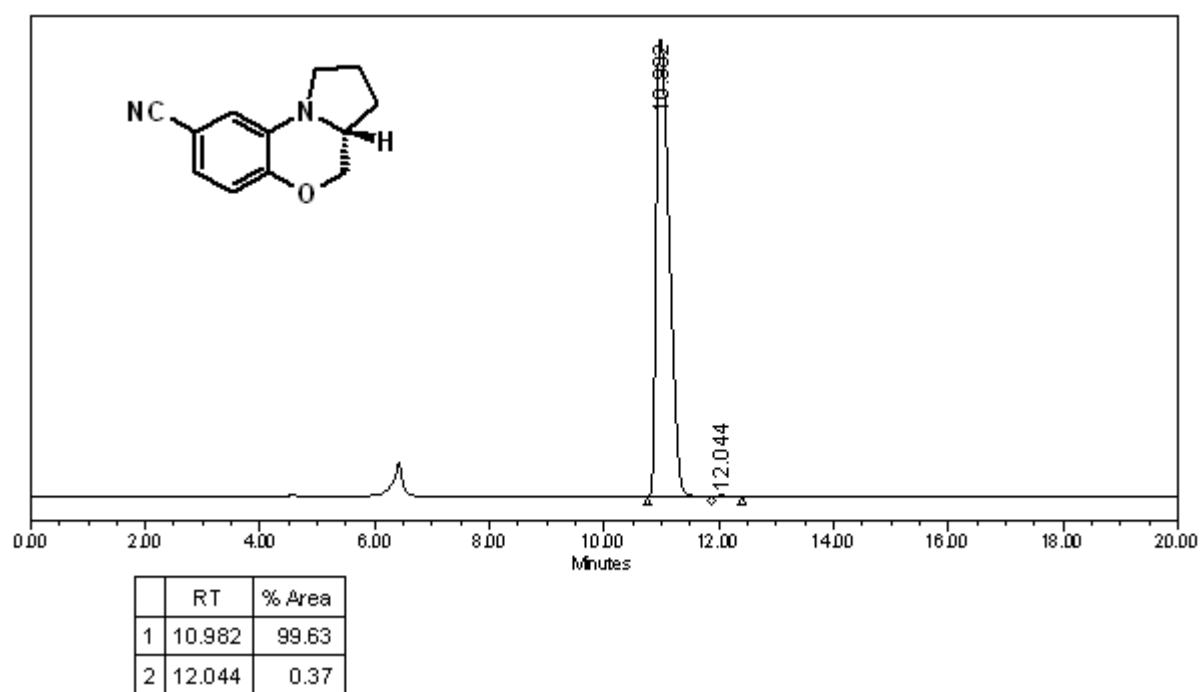
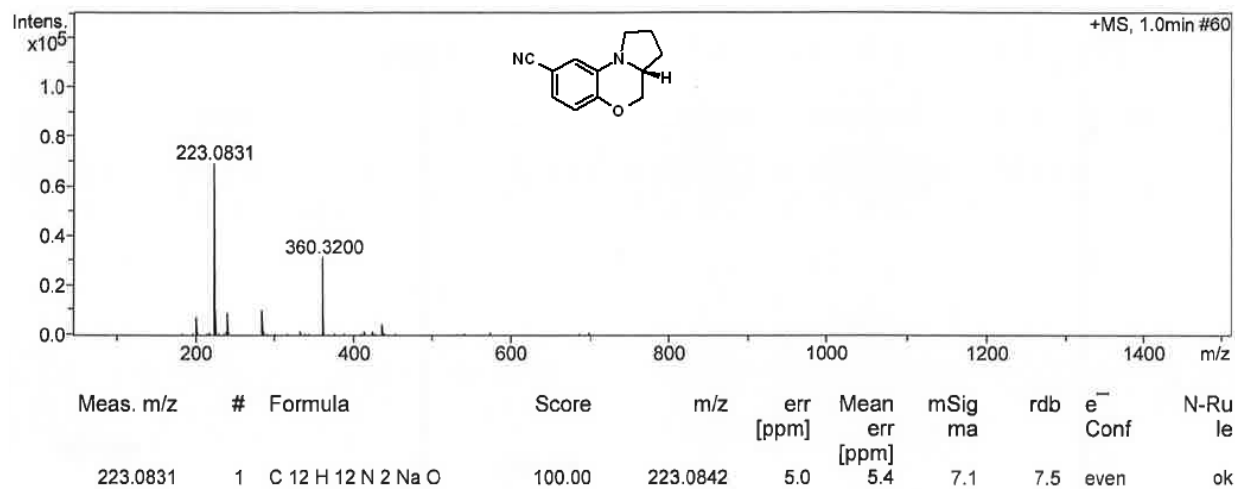


Peak	RT	% Area
1	11.183	0.61
2	12.061	99.39

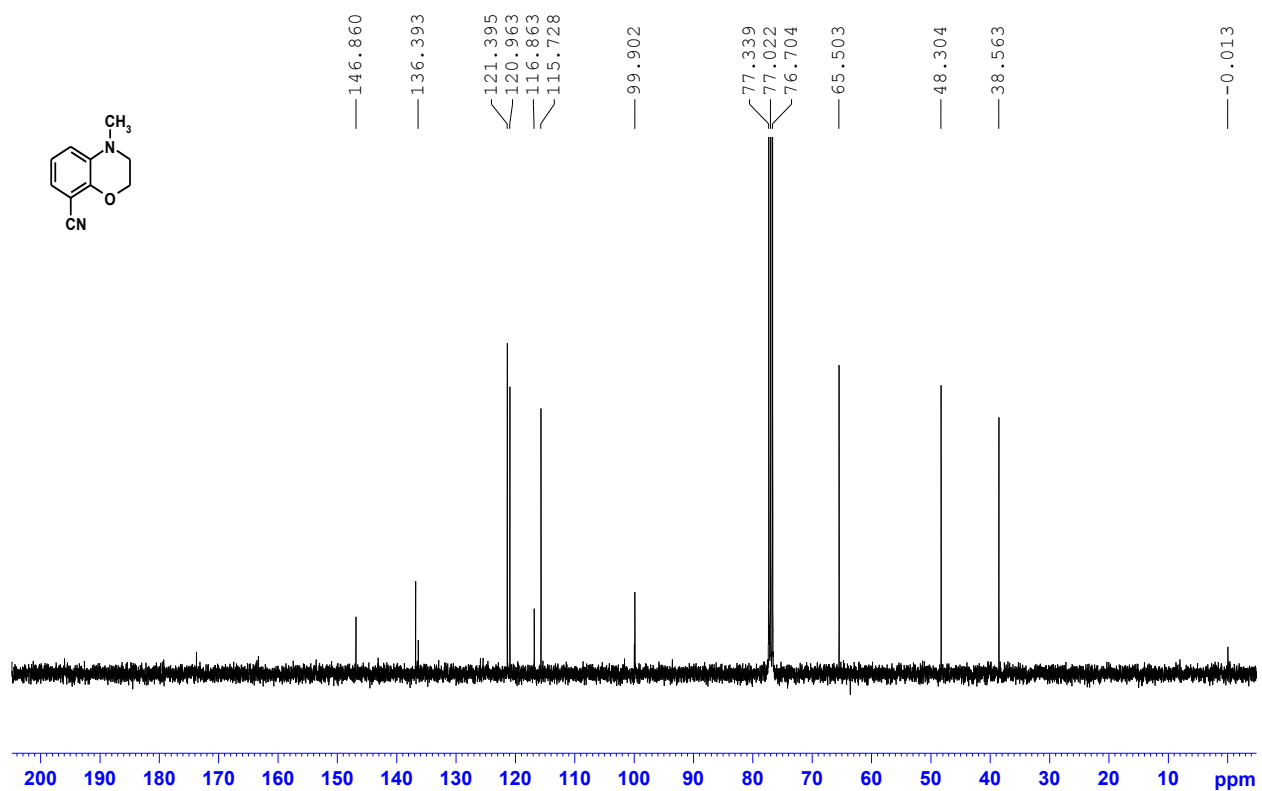
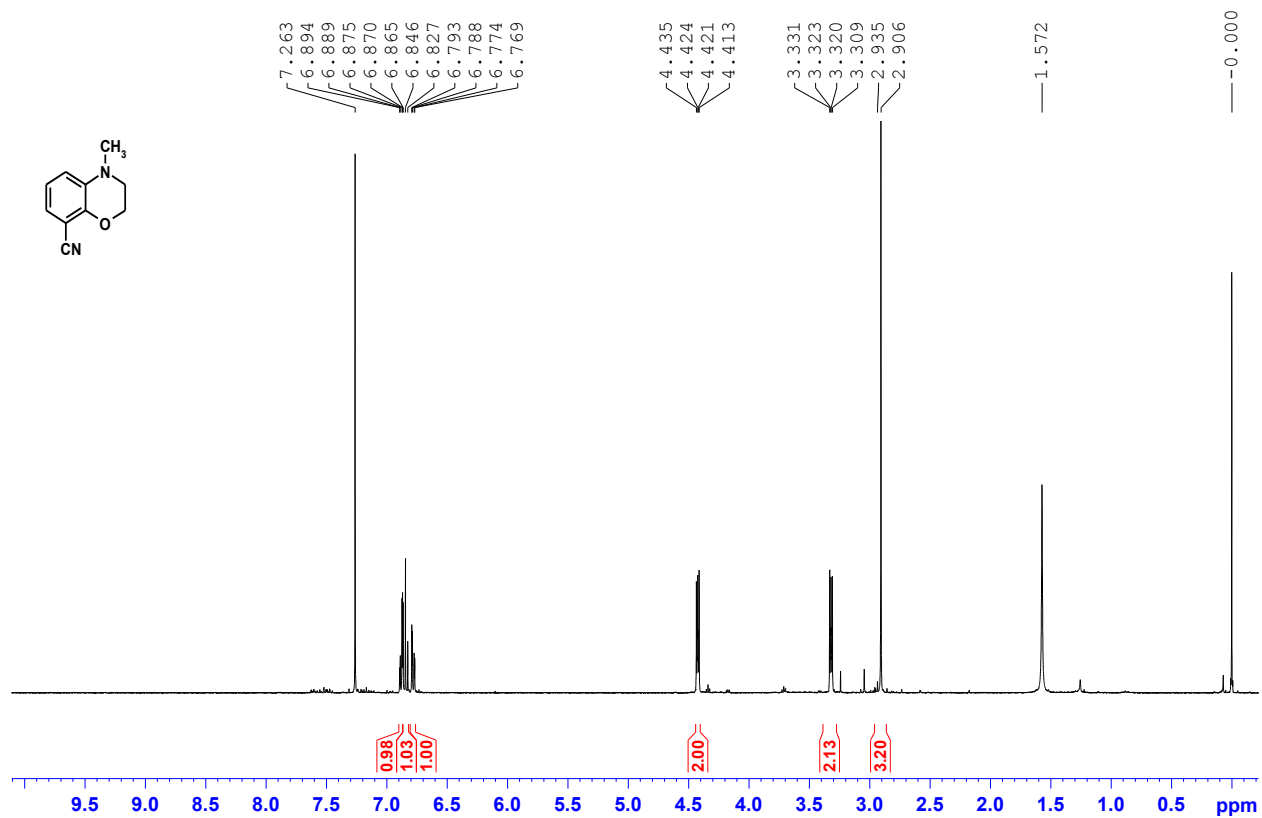
(3aR)-2,3,3a,4-tetrahydro-1H-pyrrolo[2,1-c][1,4]benzoxazine-8-carbonitrile (**6j**)

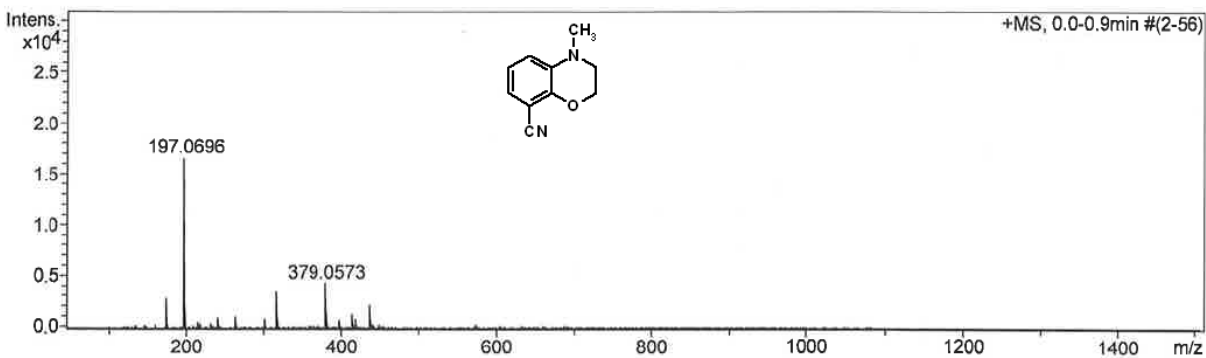






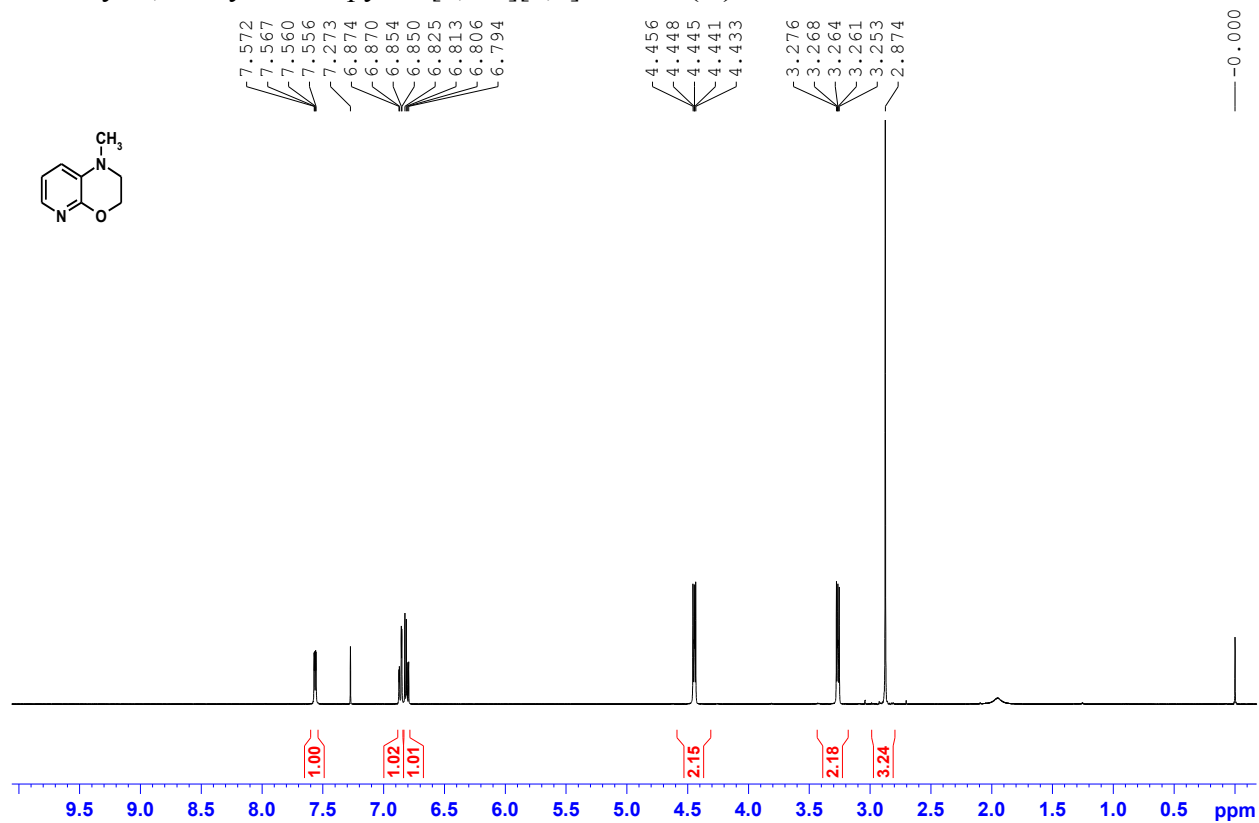
4-methyl-3,4-dihydro-2H-1,4-benzoxazine-8-carbonitrile (**6k**)

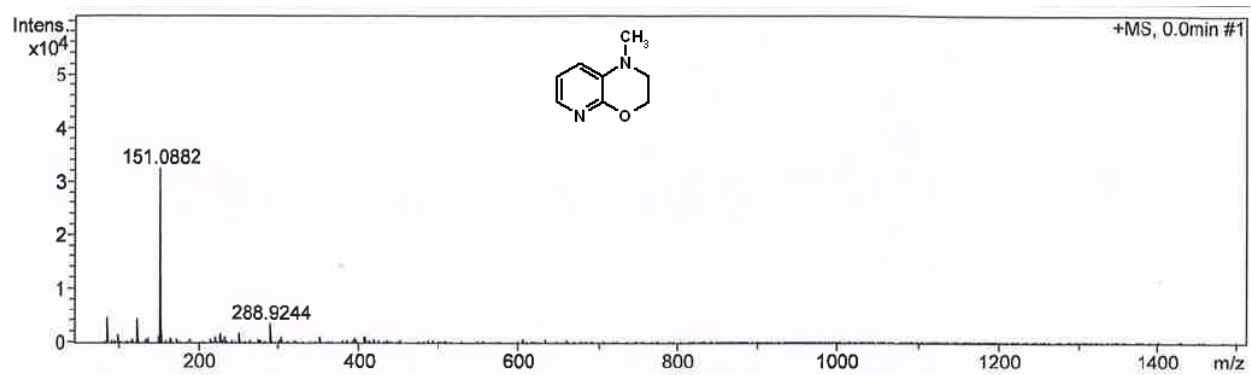
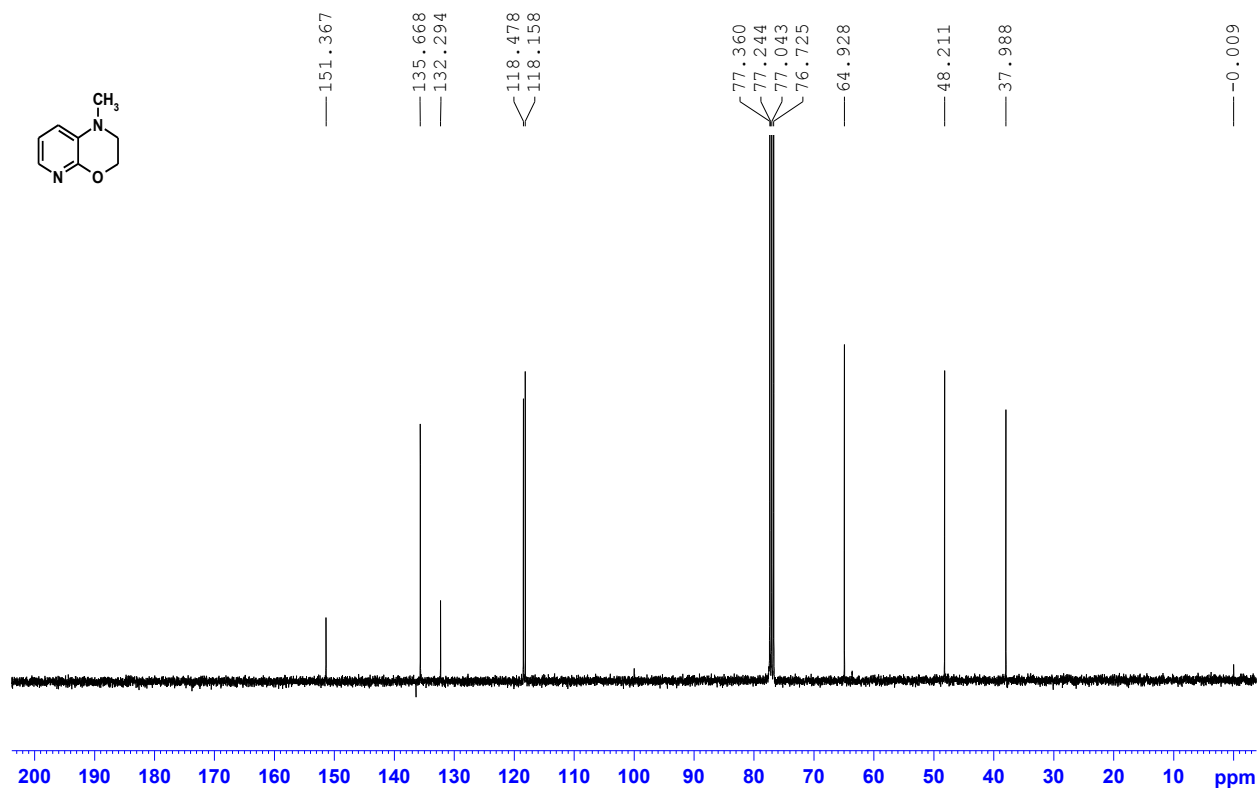




Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSig ma	rdb	e <sup>-</sup> Conf	N-Ru le
197.0696	1	C 10 H 10 N 2 Na O	100.00	197.0685	-5.6	-5.4	5.4	6.5	even	ok

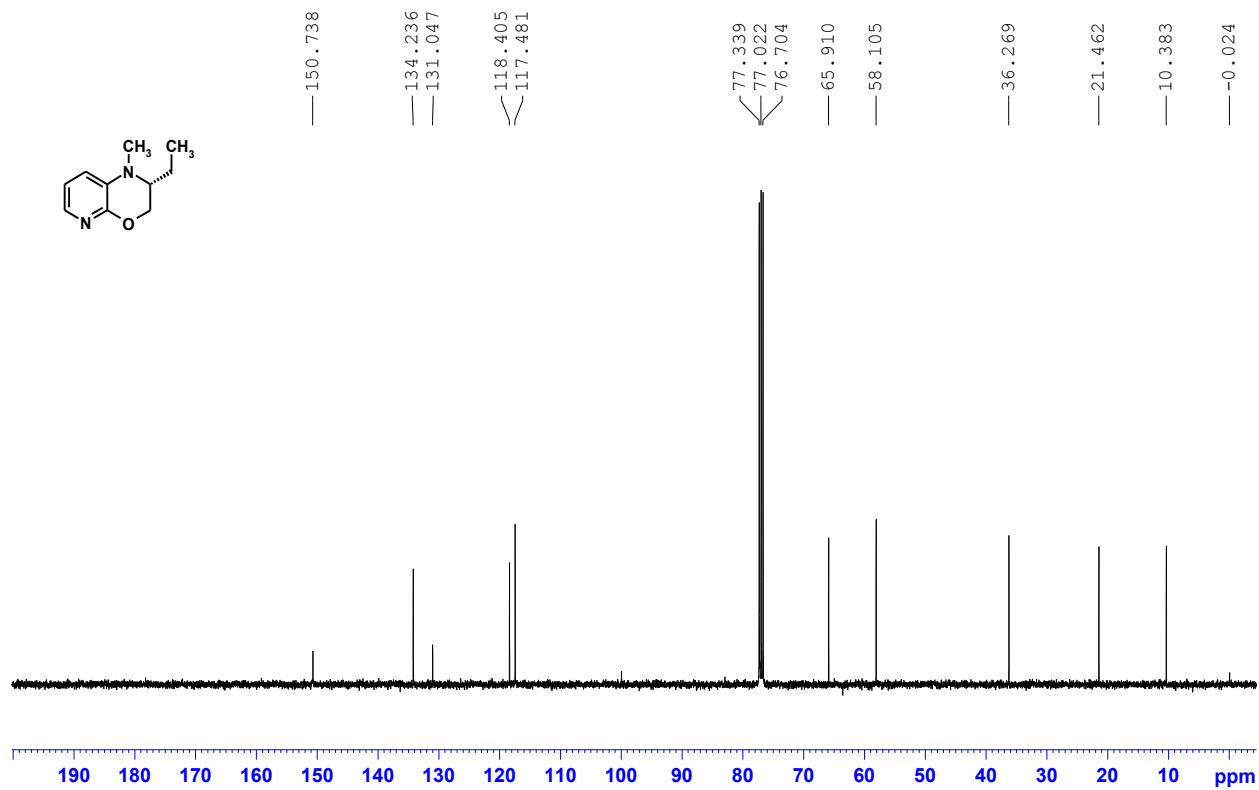
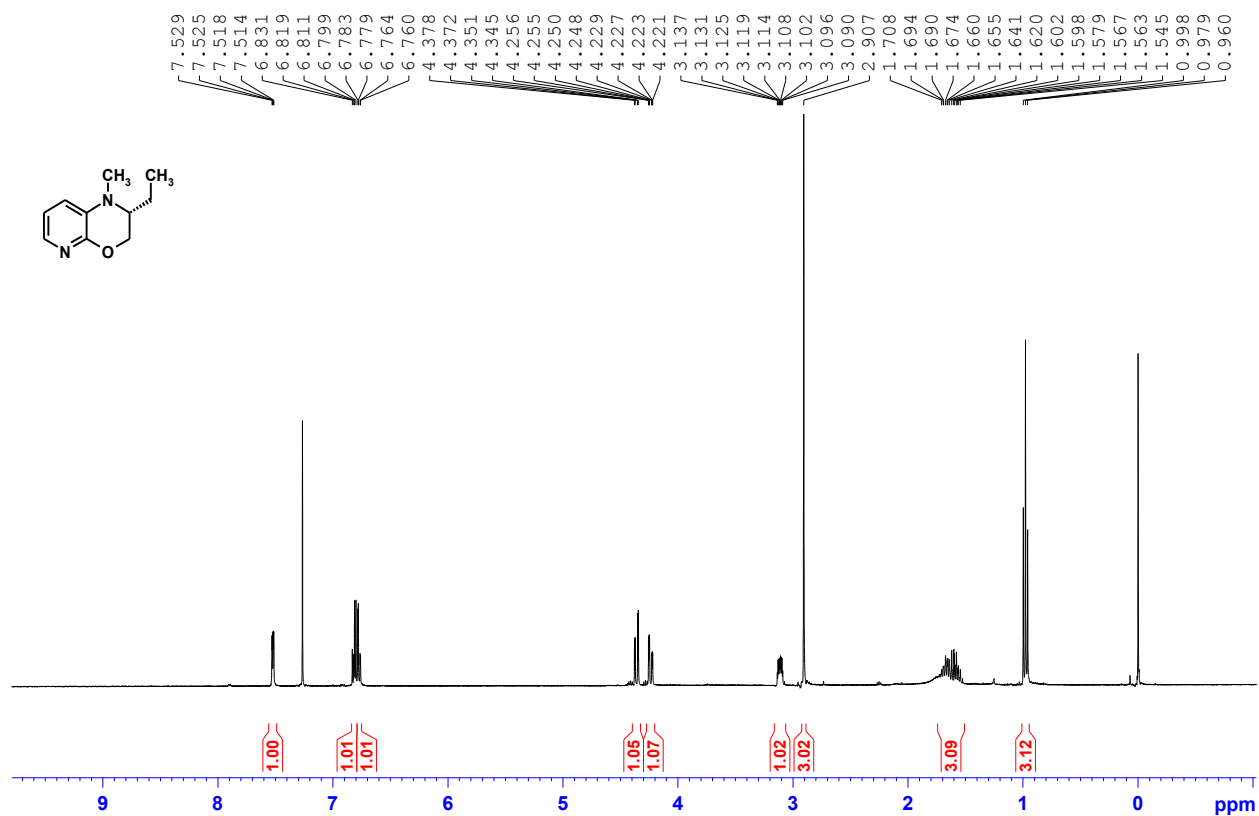
1-methyl-2,3-dihydro-1H-pyrido[2,3-b][1,4]oxazine (6l)

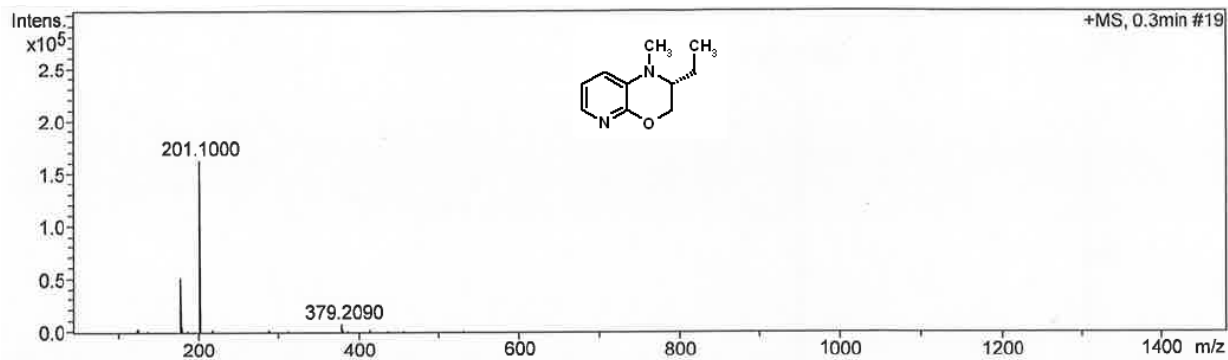




Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
151.0882	1	C <sub>8</sub> H <sub>11</sub> N <sub>2</sub> O	100.00	151.0866	-10.8	-9.3	9.5	4.5	even	ok

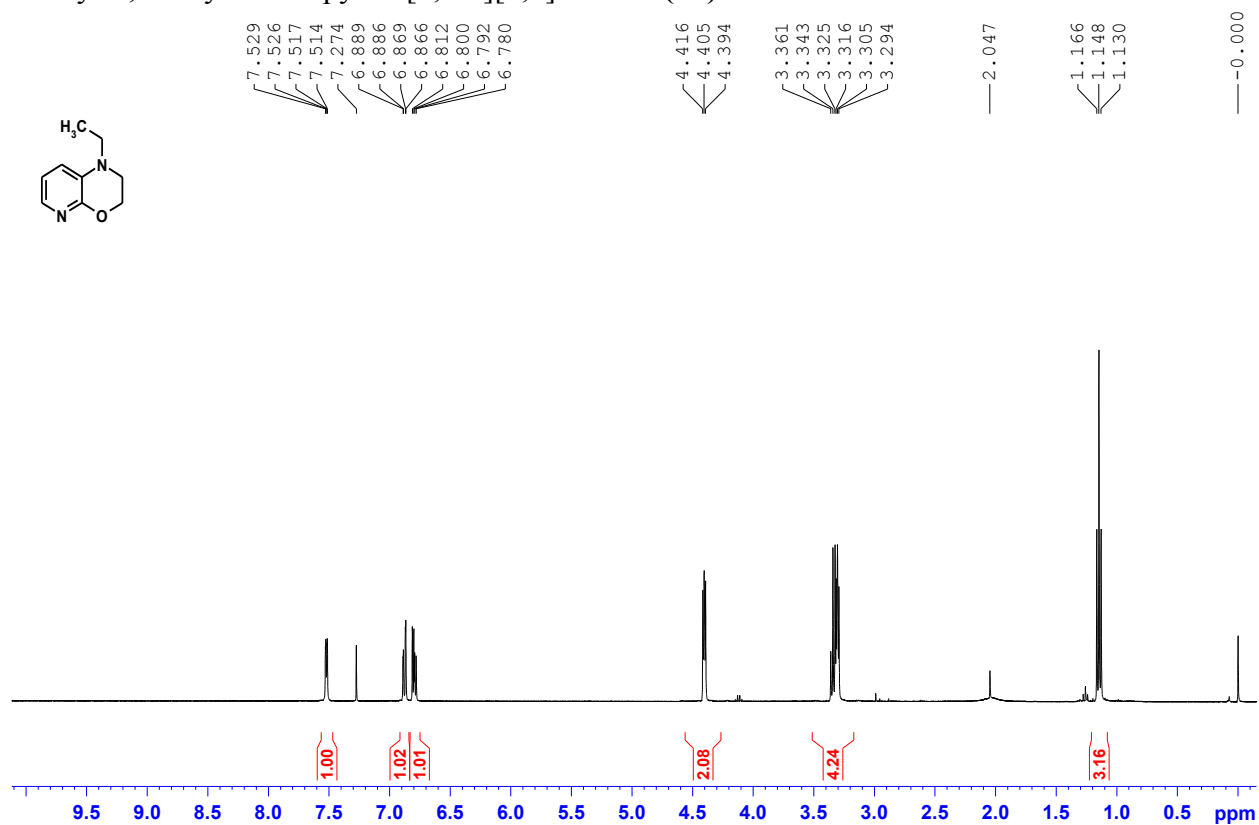
(2R)-2-ethyl-1-methyl-2,3-dihydro-1H-pyrido[2,3-b][1,4]oxazine (**6m**)

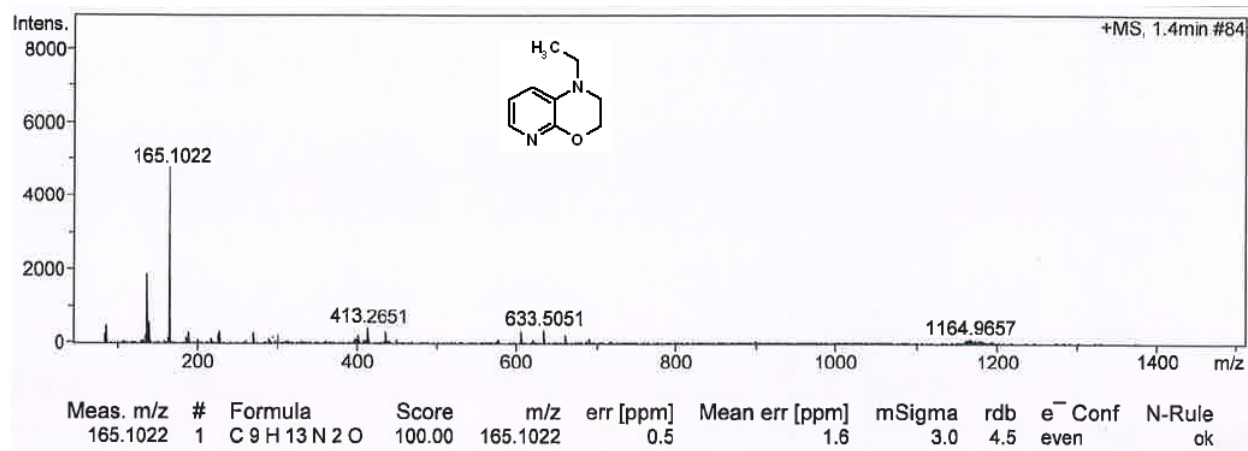
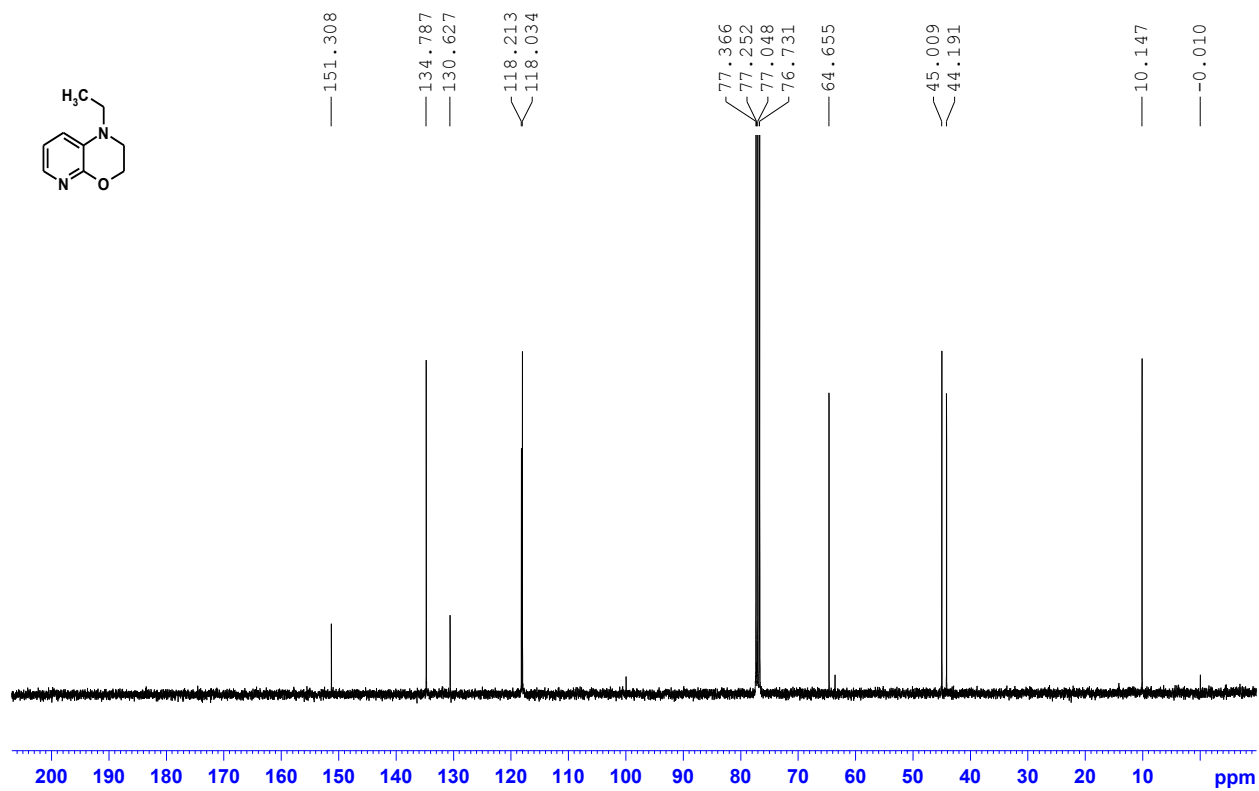




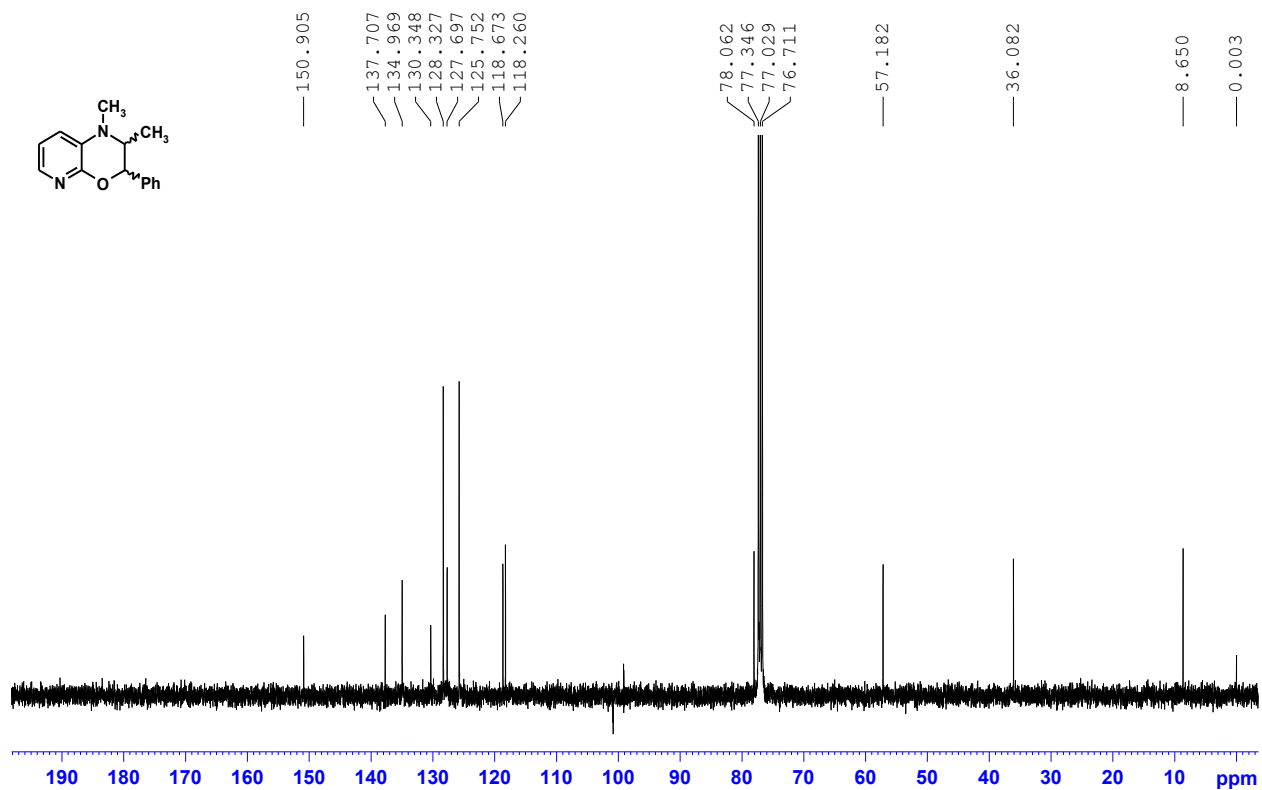
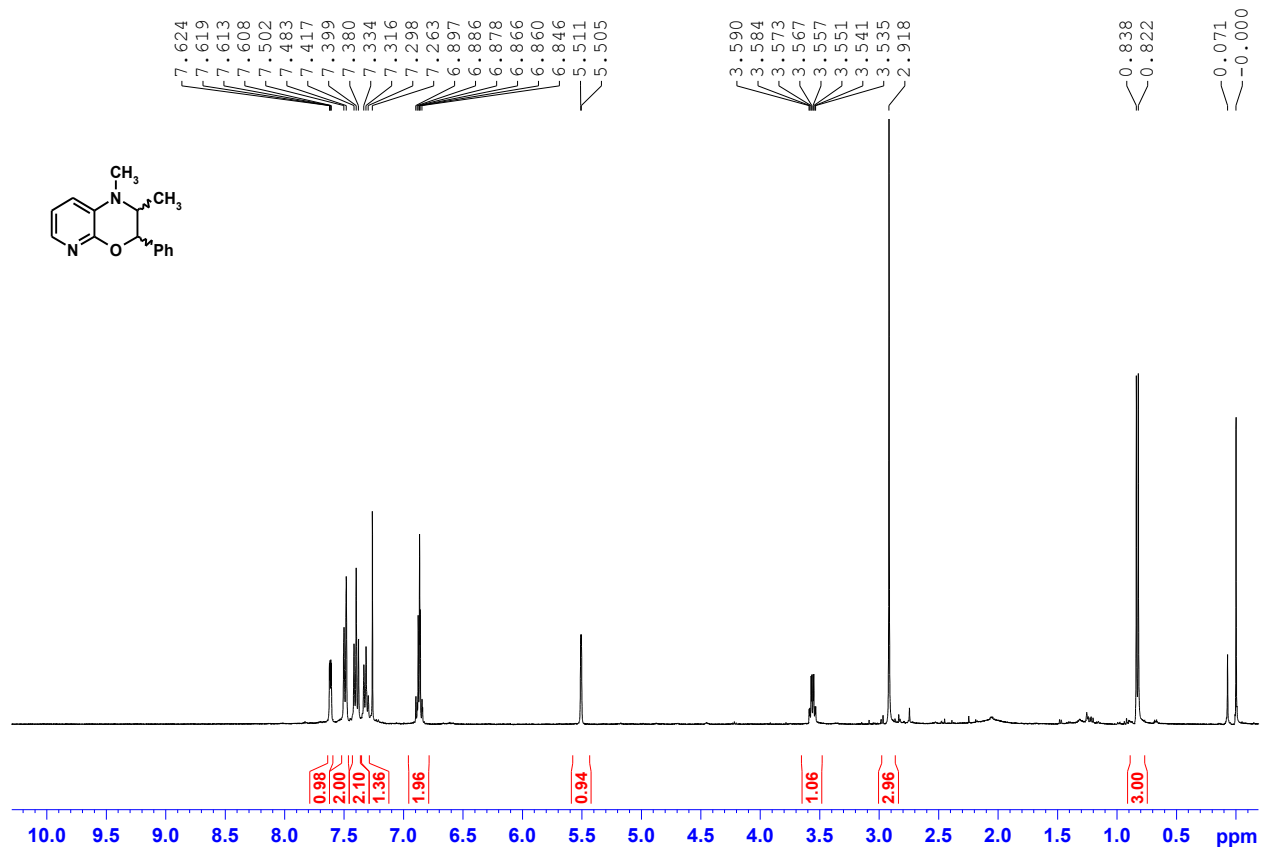
Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
201.1000	1	C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> NaO	100.00	201.0998	-1.0	-0.7	4.3	4.5	even	ok

1-ethyl-2,3-dihydro-1H-pyrido[2,3-b][1,4]oxazine (**6n**)

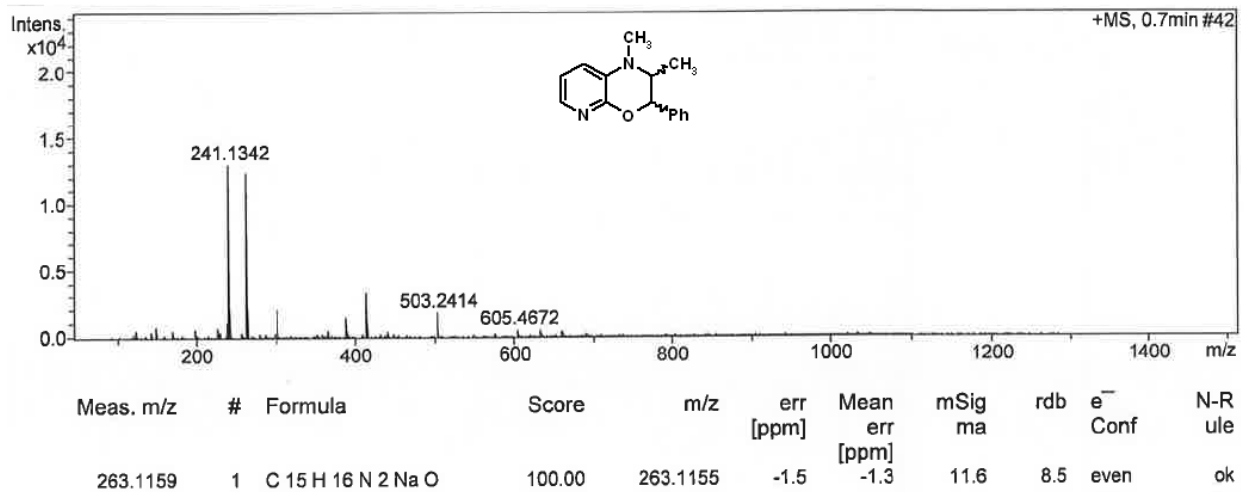




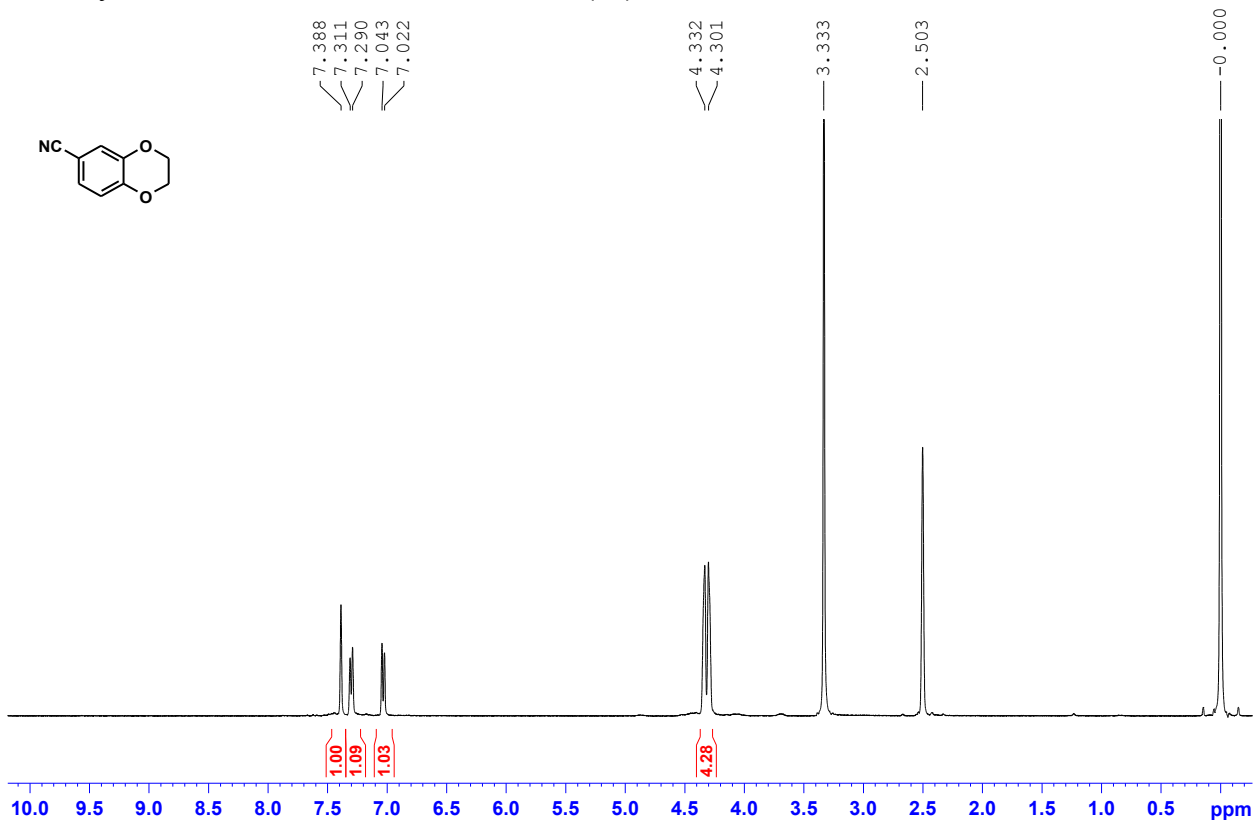
1,2-dimethyl-3-phenyl-2,3-dihydro-1H-pyrido[2,3-b][1,4]oxazine (**60**)

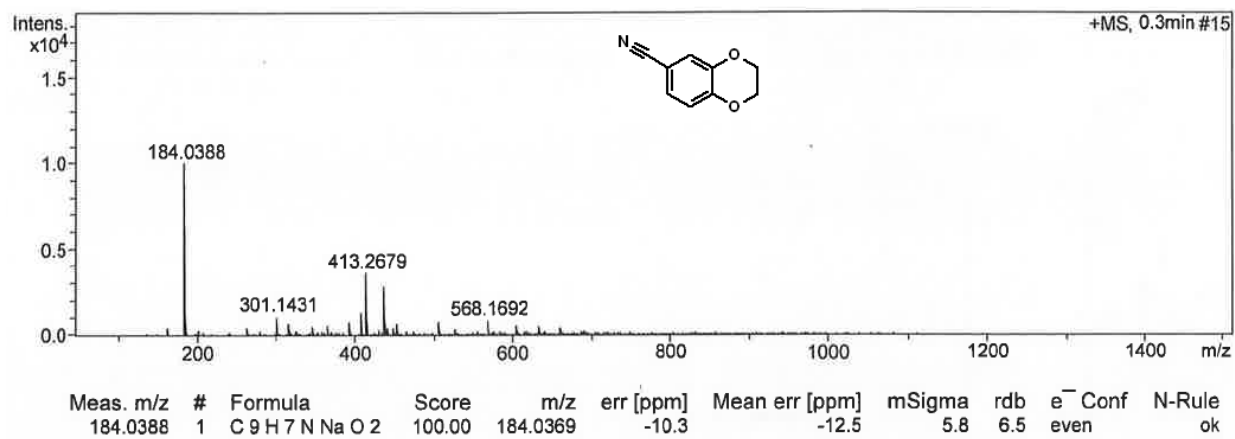
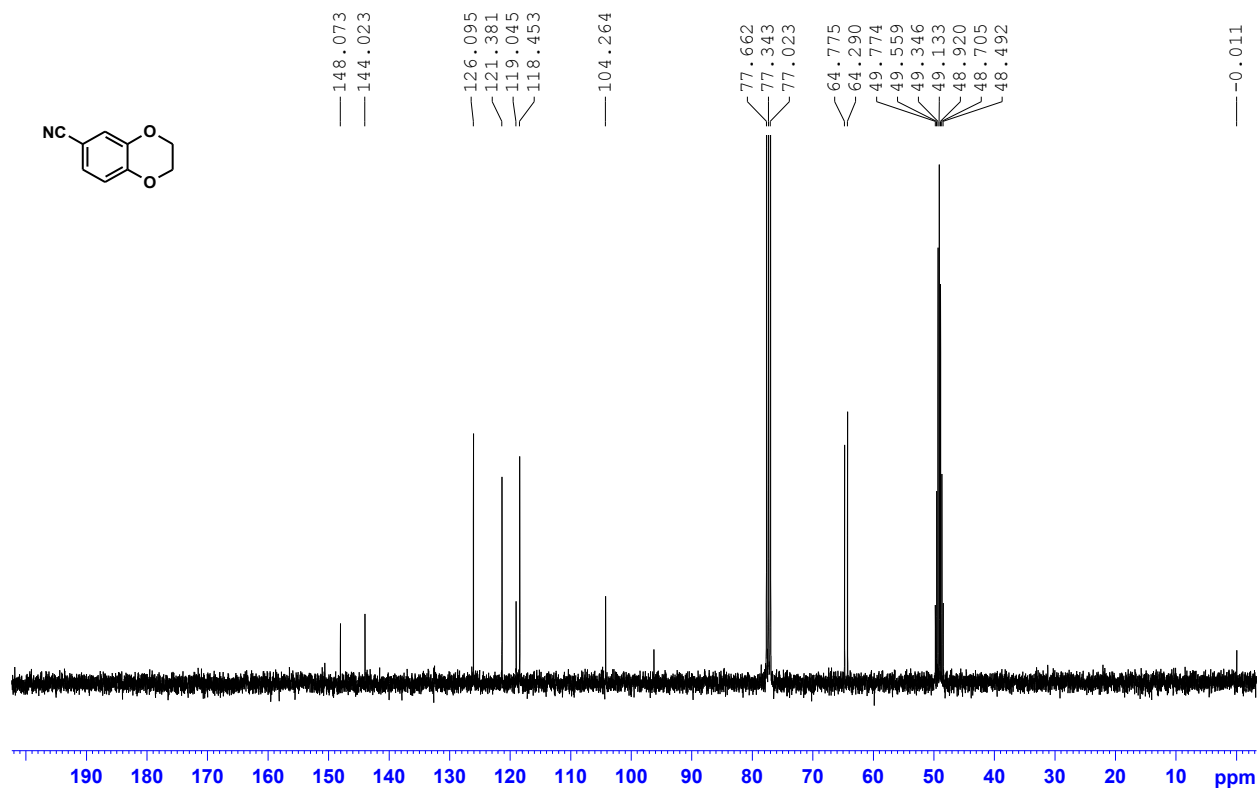




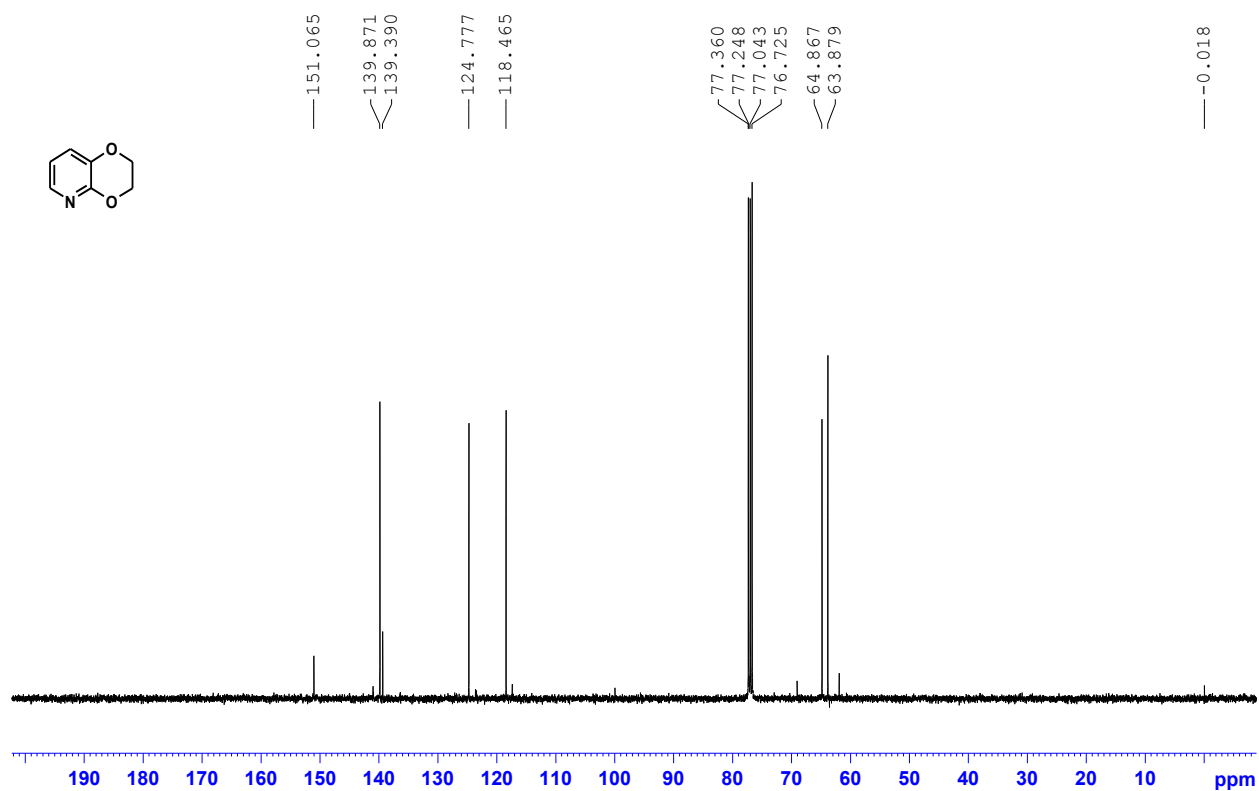
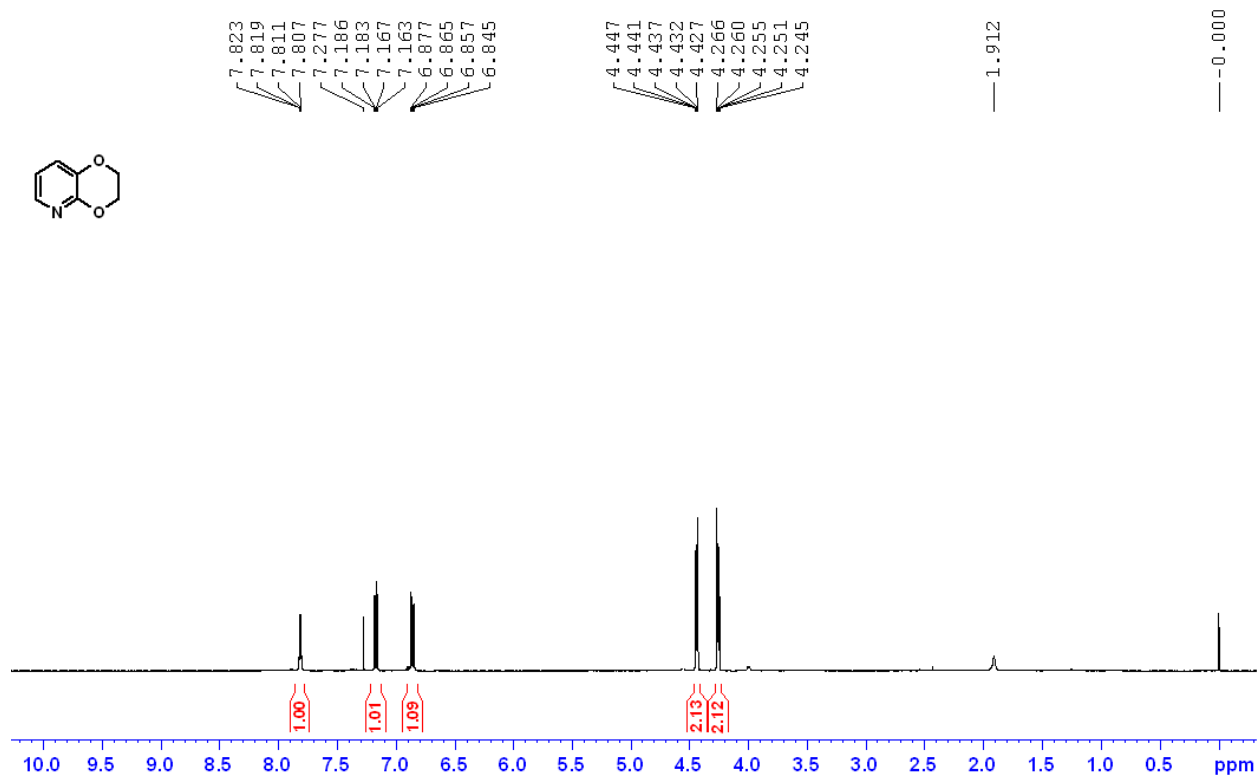


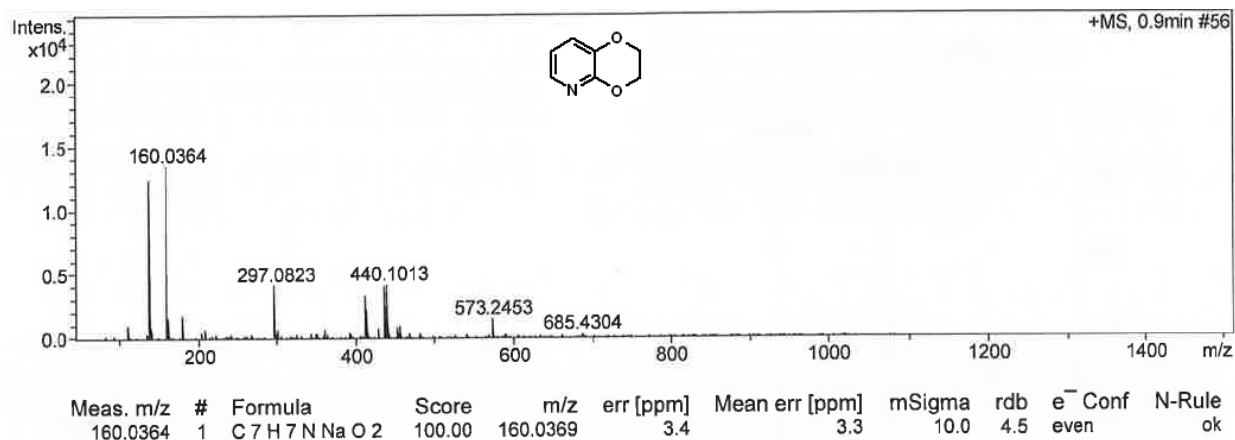
### 2,3-dihydro-1,4-benzodioxine-6-carbonitrile (7a)



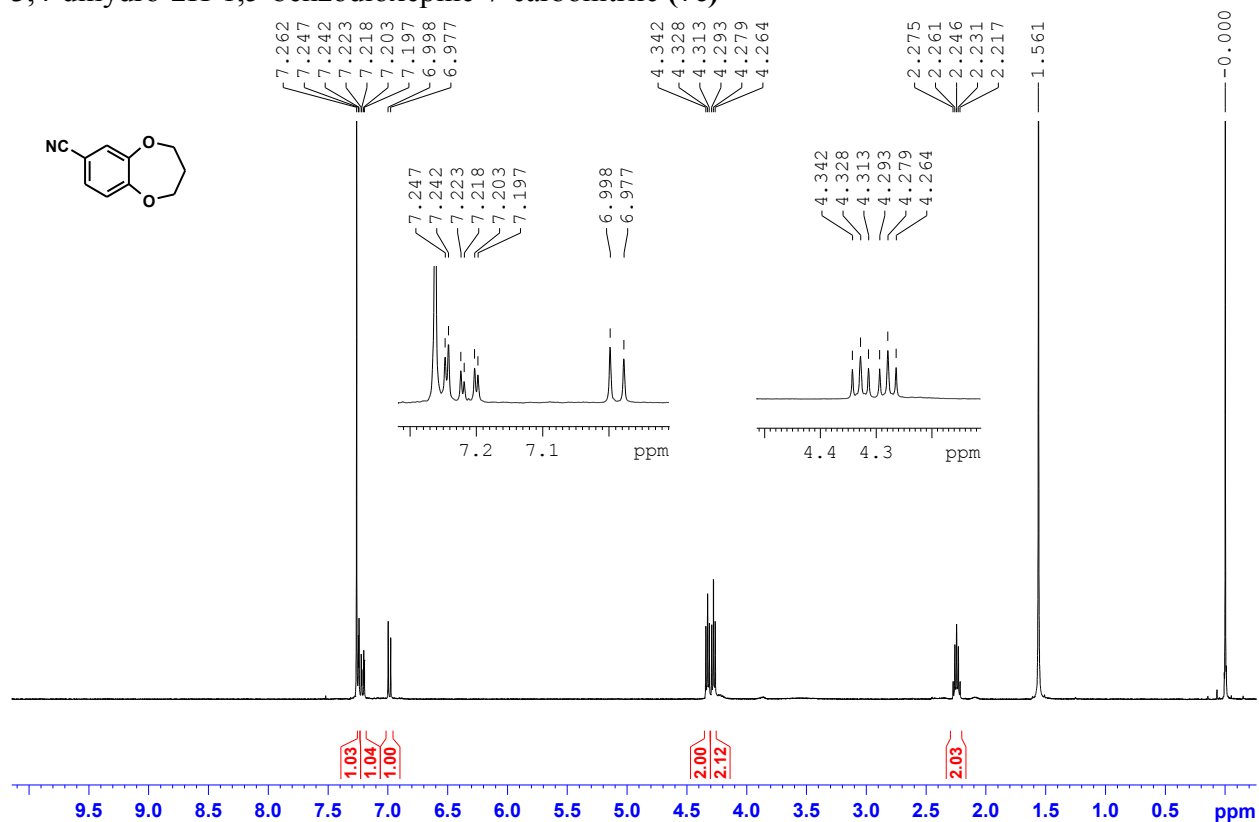


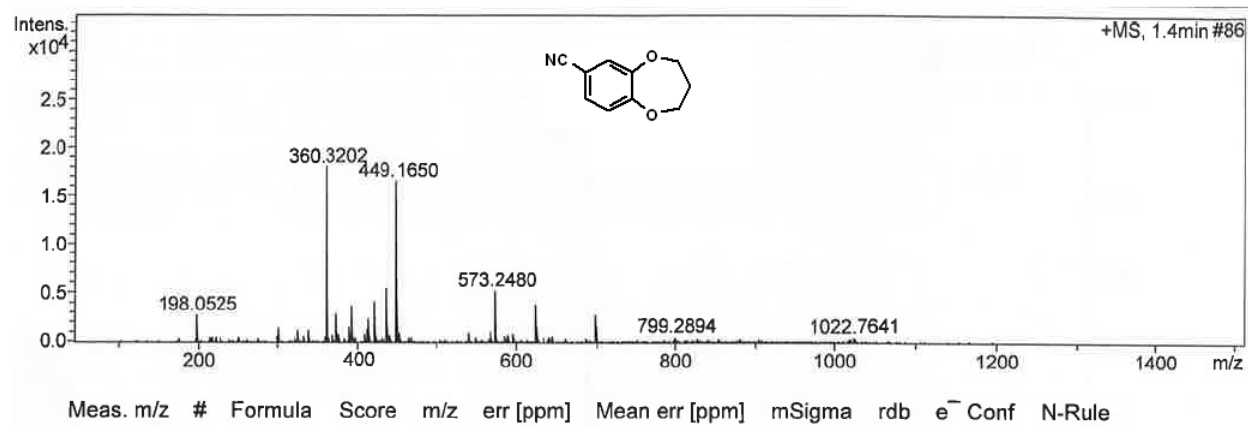
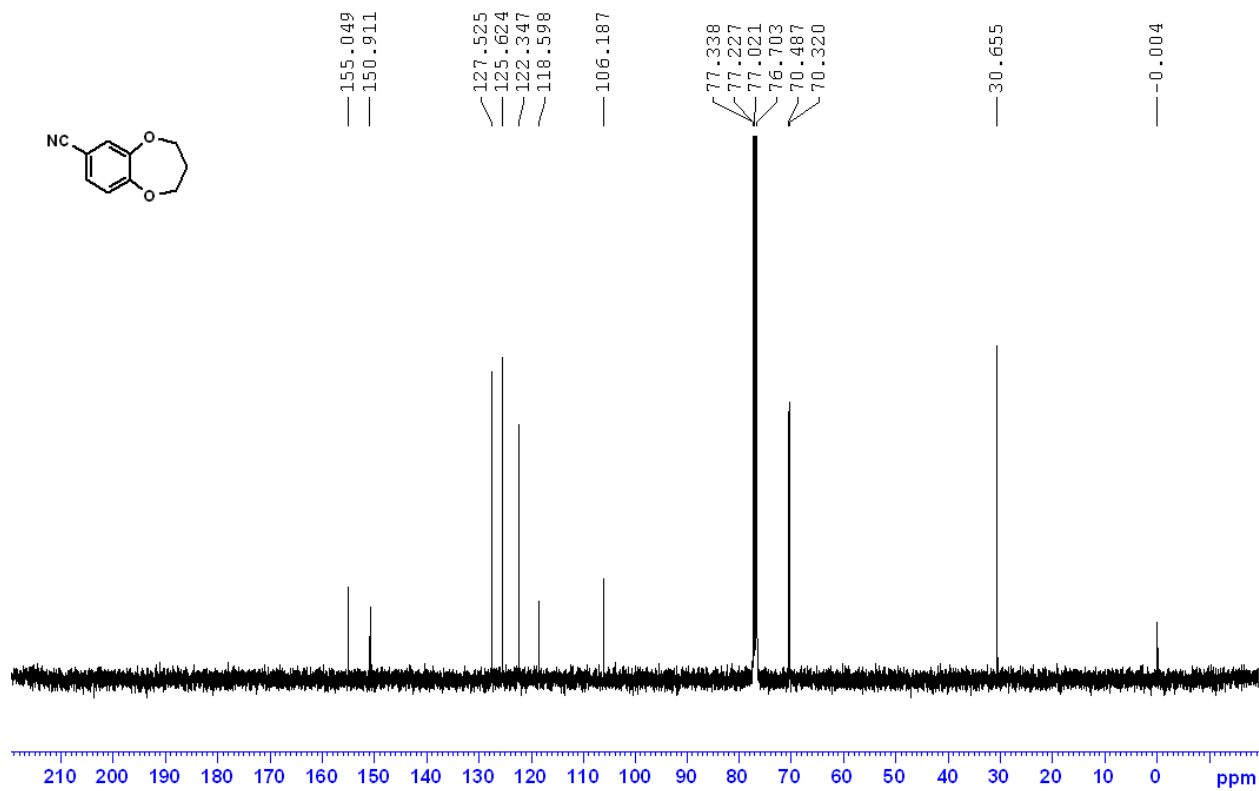
2,3-dihydro[1,4]dioxino[2,3-b]pyridine (**7b**)



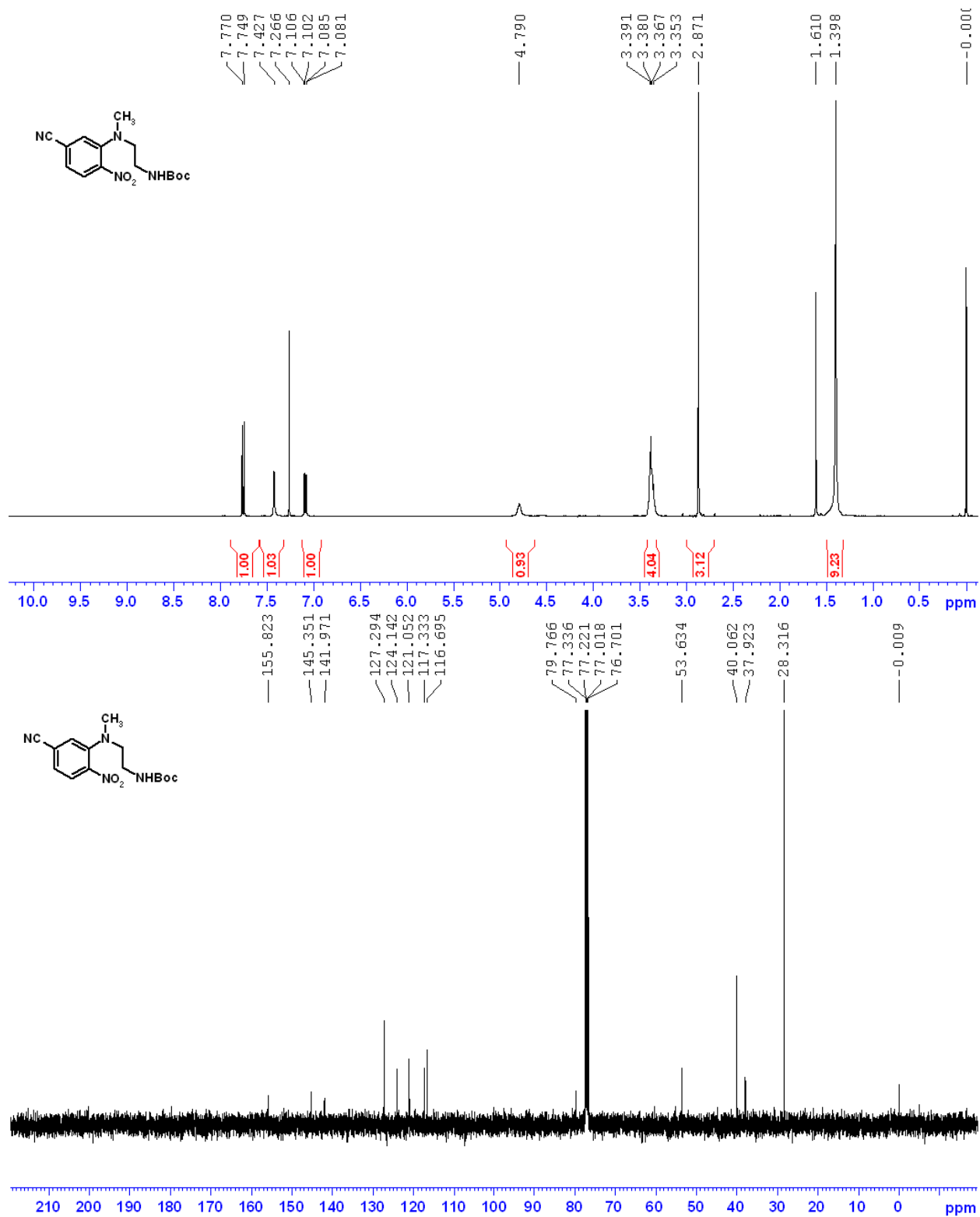


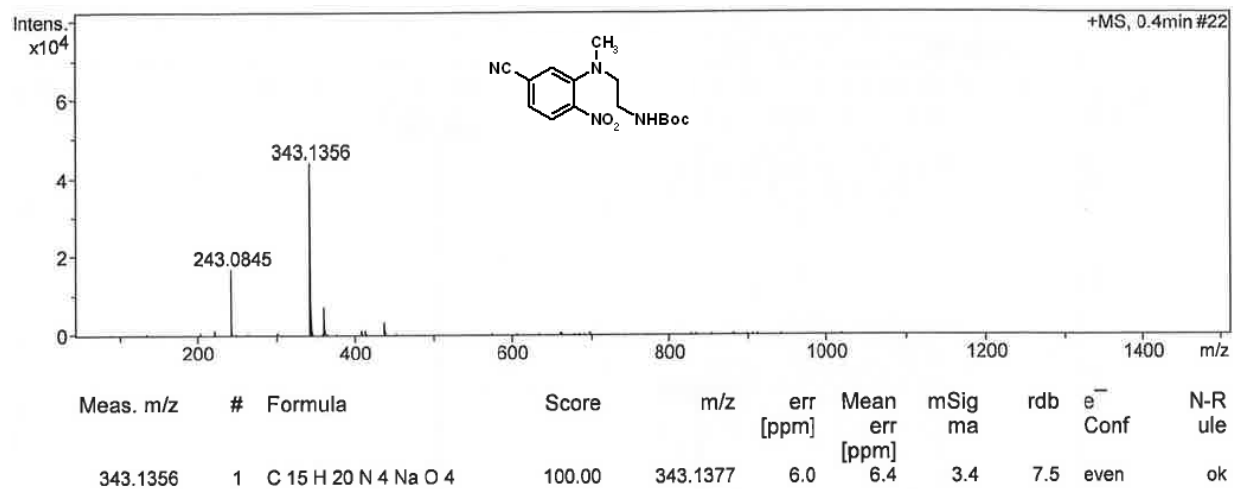
3,4-dihydro-2H-1,5-benzodioxepine-7-carbonitrile (7c)



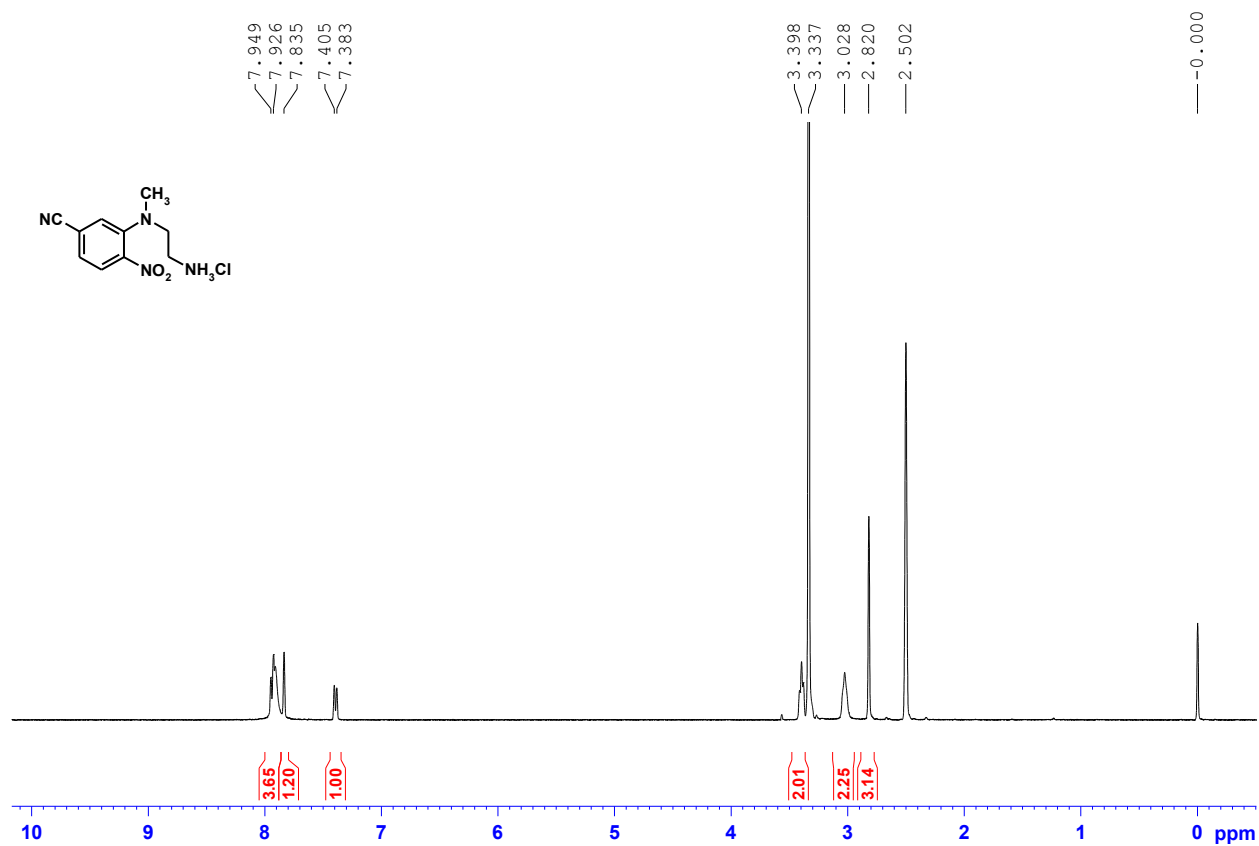


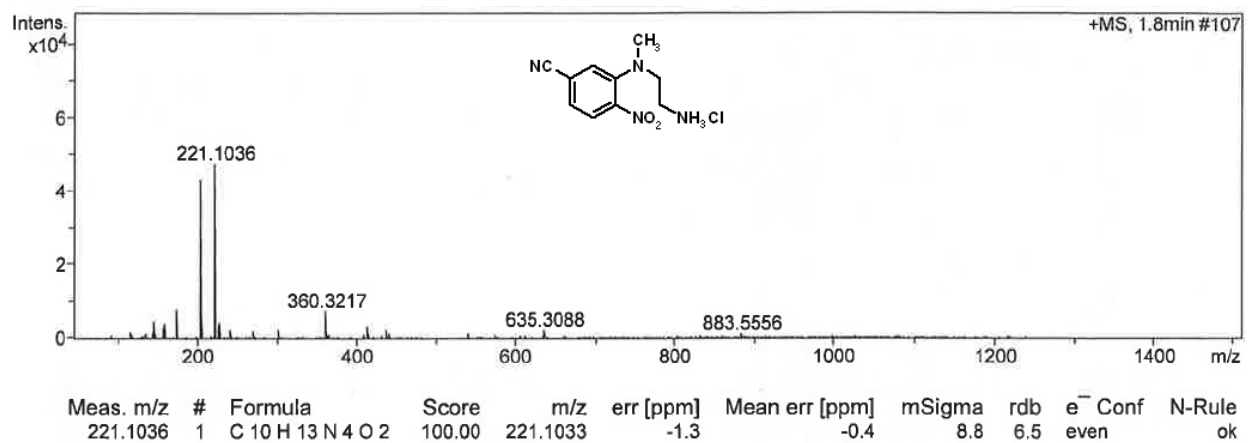
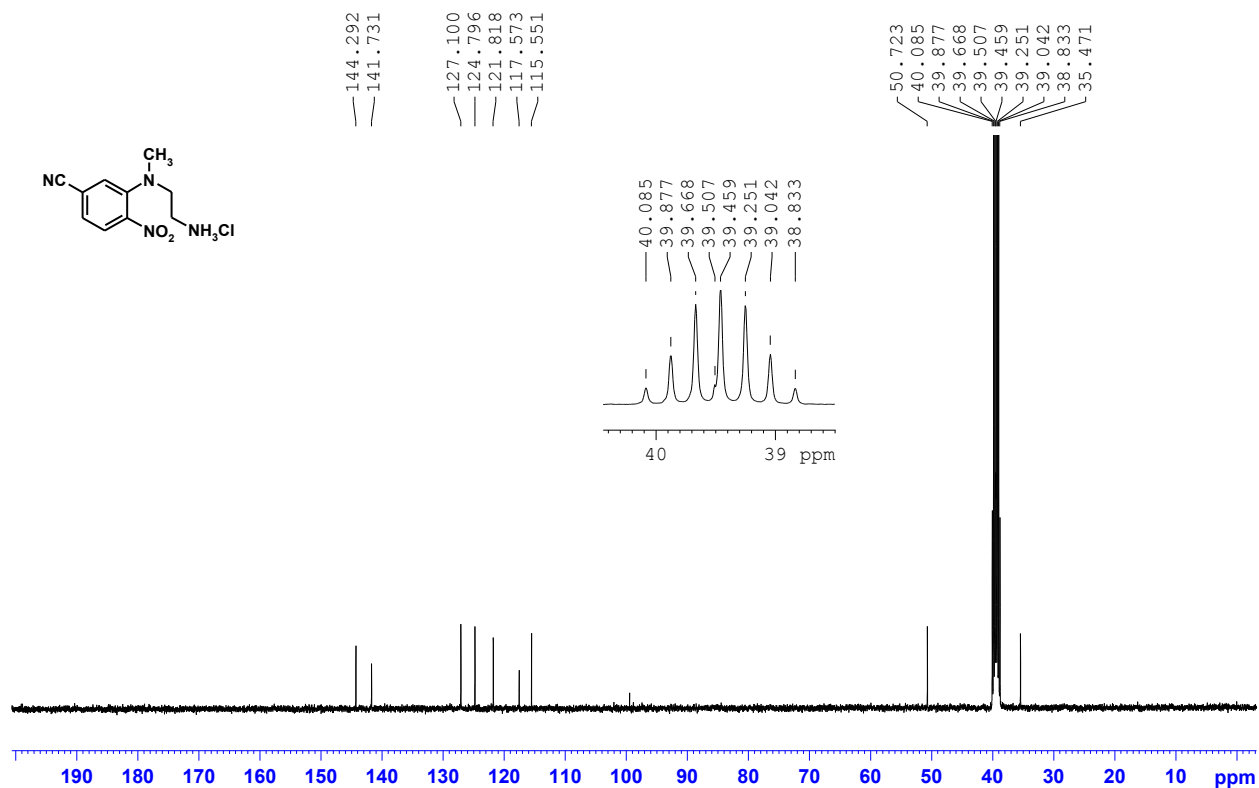
**tert-butyl {2-[(5-cyano-2-nitrophenyl)(methyl)amino]ethyl}carbamate (11)**





**3-[(2-aminoethyl)(methyl)amino]-4-nitrobenzonitrile hydrochloride (12)**





**4-methyl-1,2,3,4-tetrahydroquinoxaline-6-carbonitrile (13)**



