

**Efficient synthesis of functionalized spiro[indoline-3,4'-pyridines] and
spiro[indene-2,4'-pyridines] via three-component reaction**

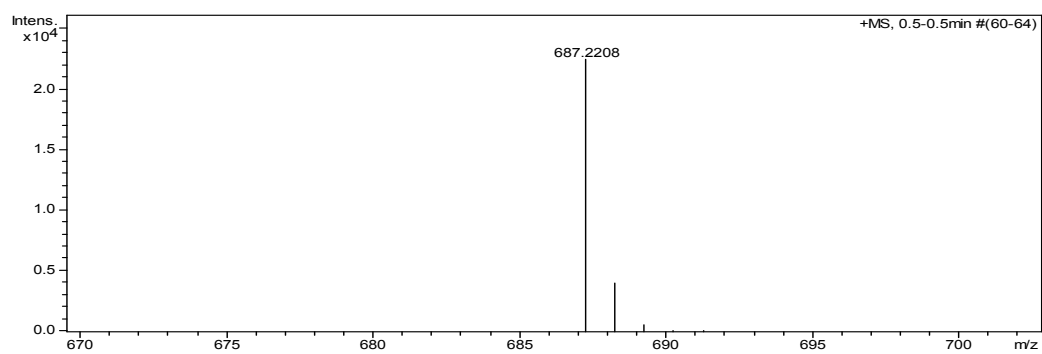
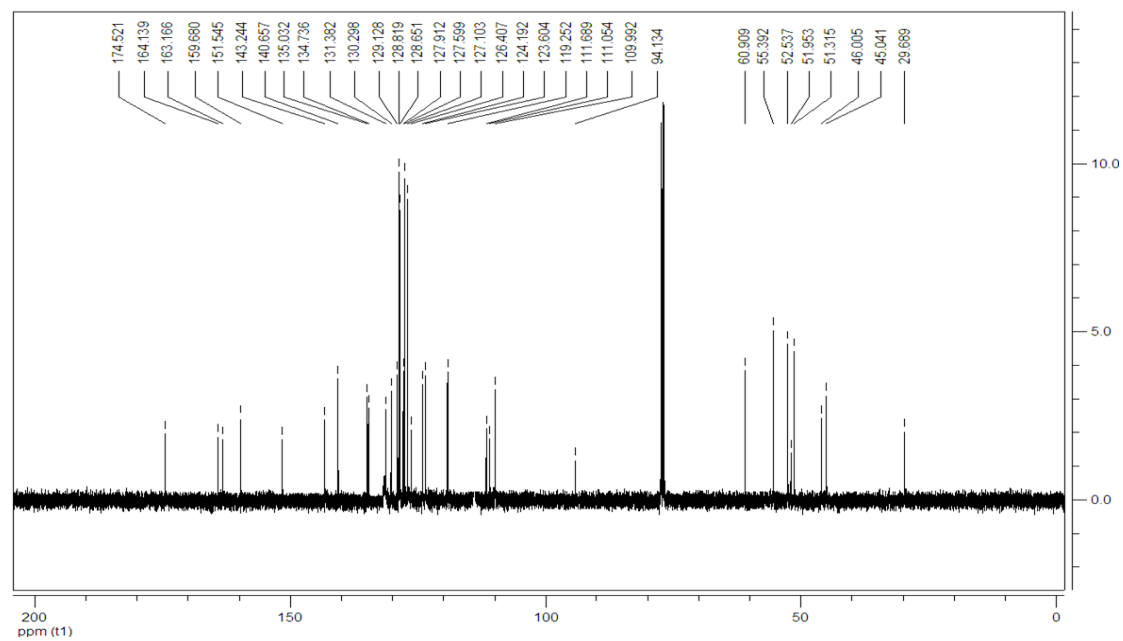
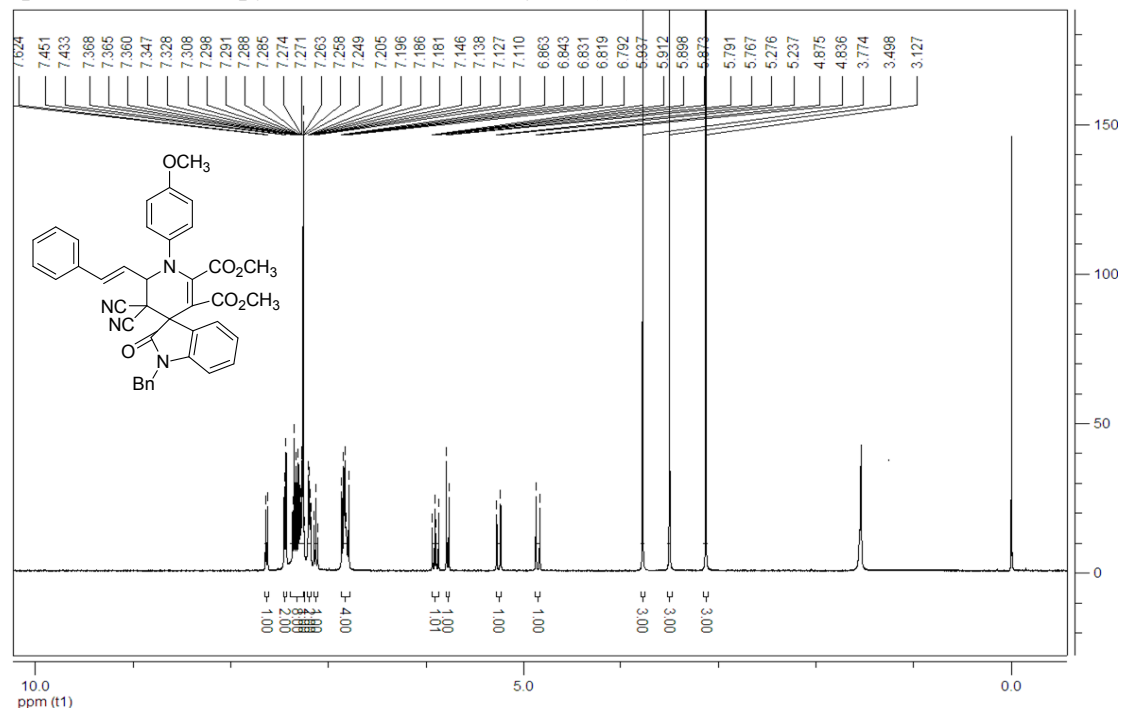
Jing Zhang, Jing Sun, Chao-Guo Yan*

Supporting Information

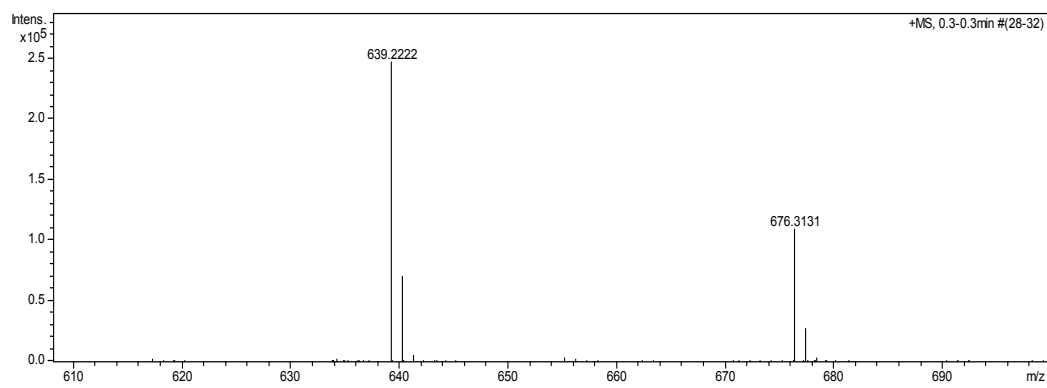
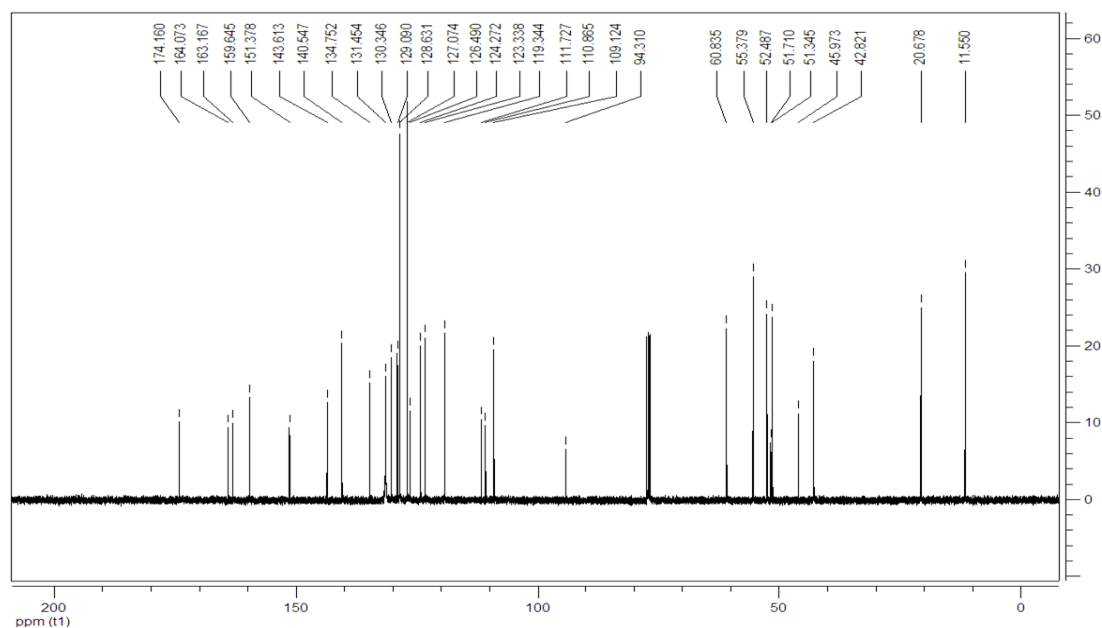
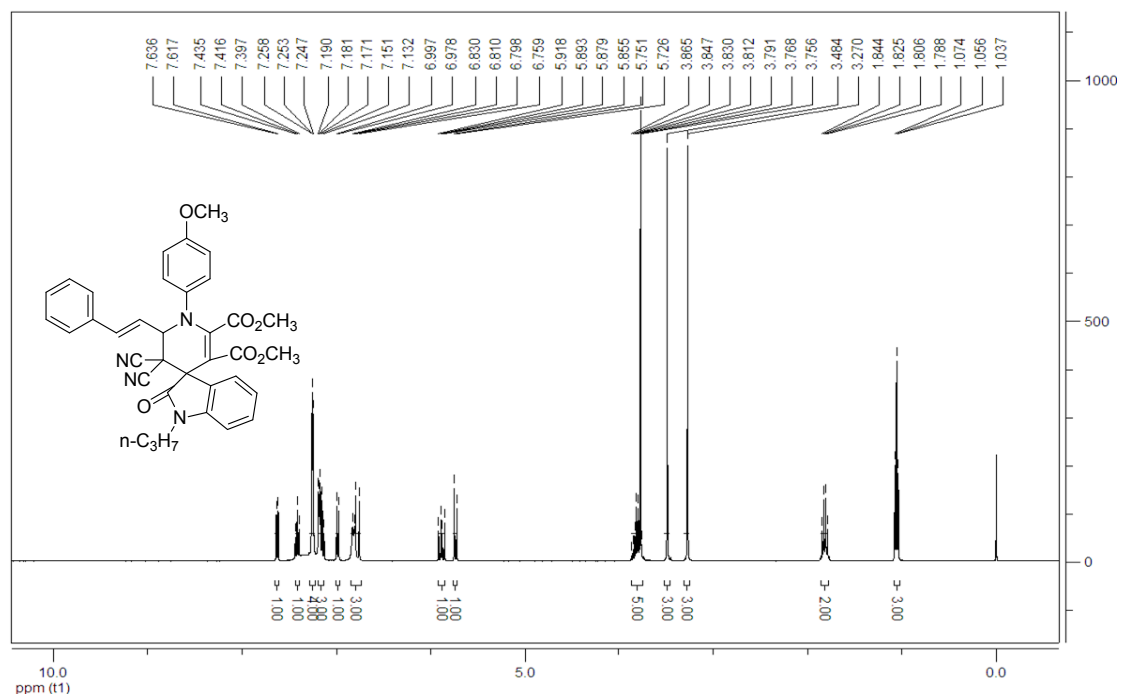
¹H, ¹³C NMR and HRMS spectra of the new compounds:

2-28

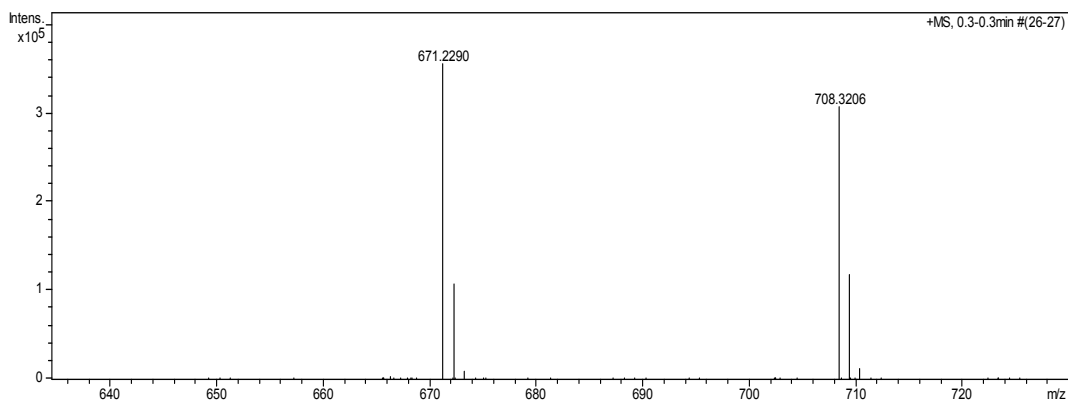
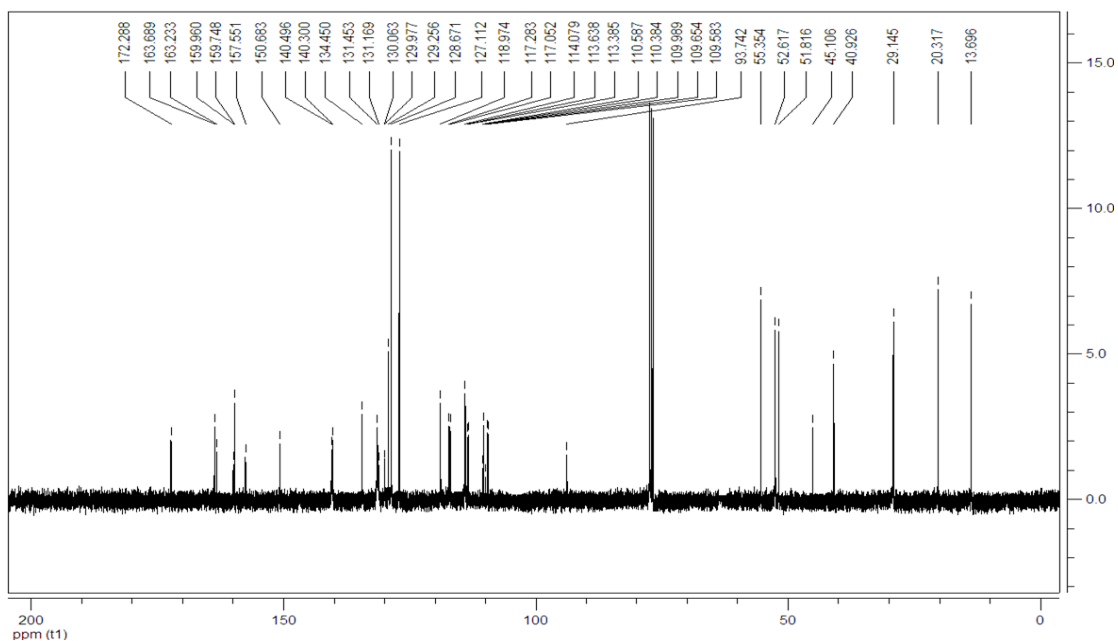
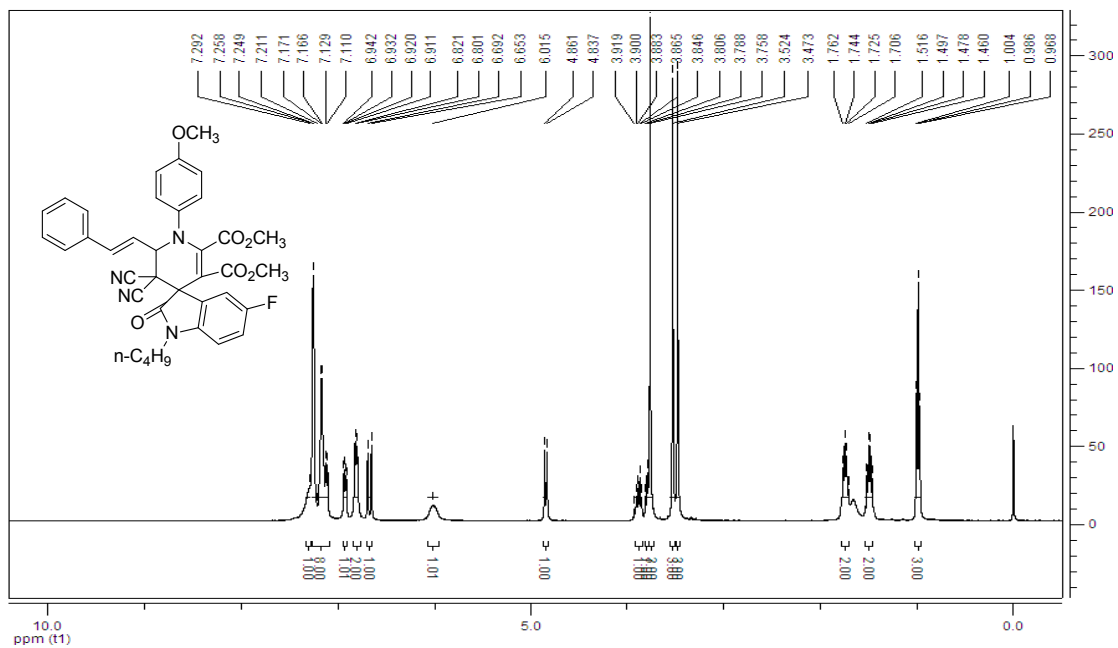
Dimethyl 1-benzyl-3',3'-dicyano-1'-(4-methoxyphenyl)-2-oxo-2'-styryl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (3a):



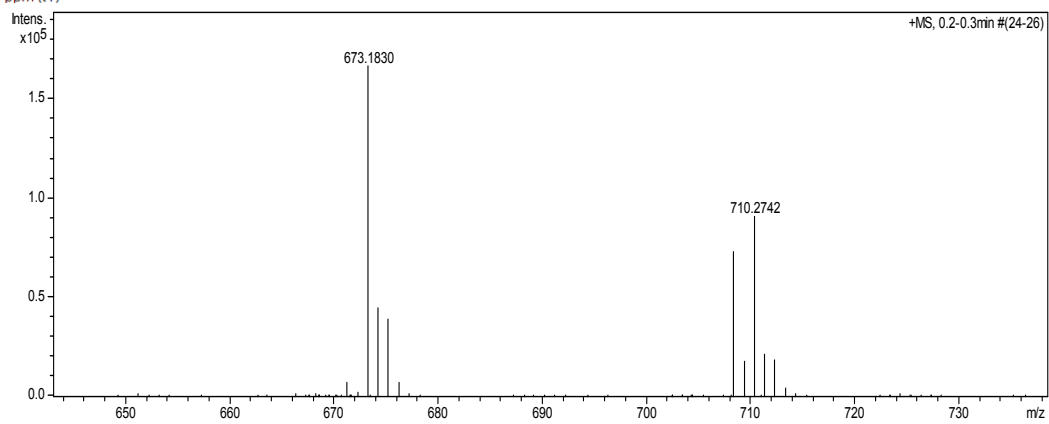
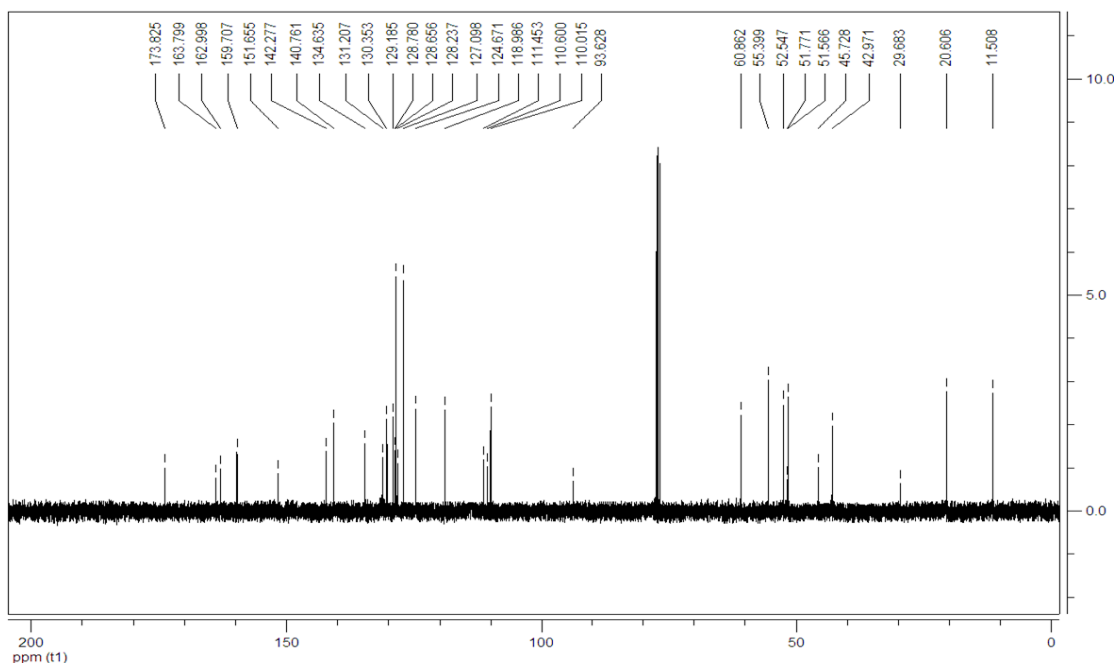
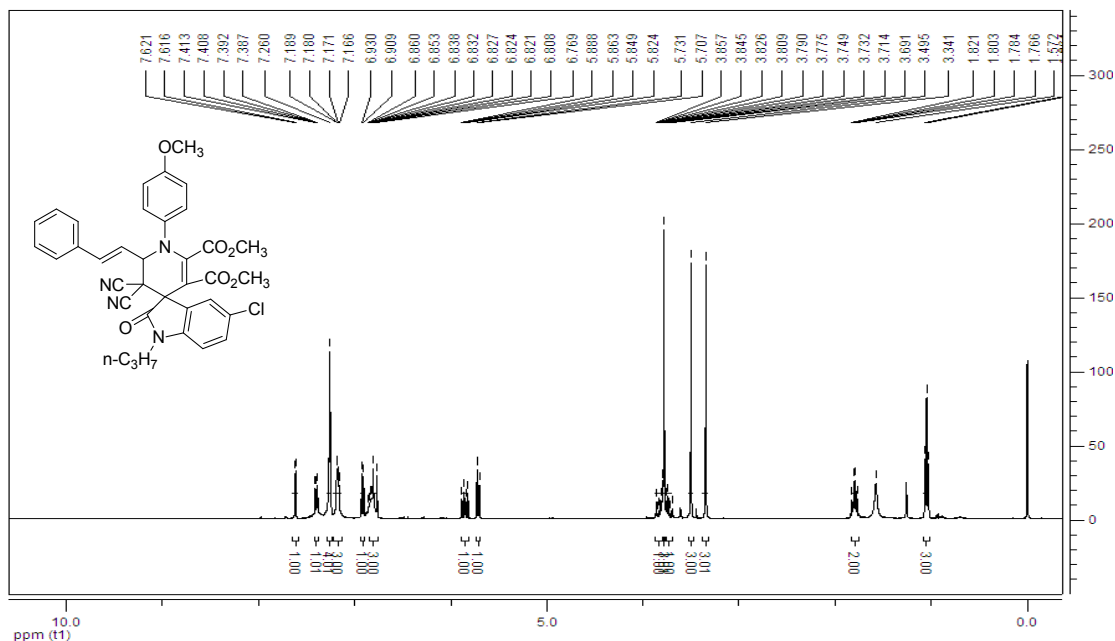
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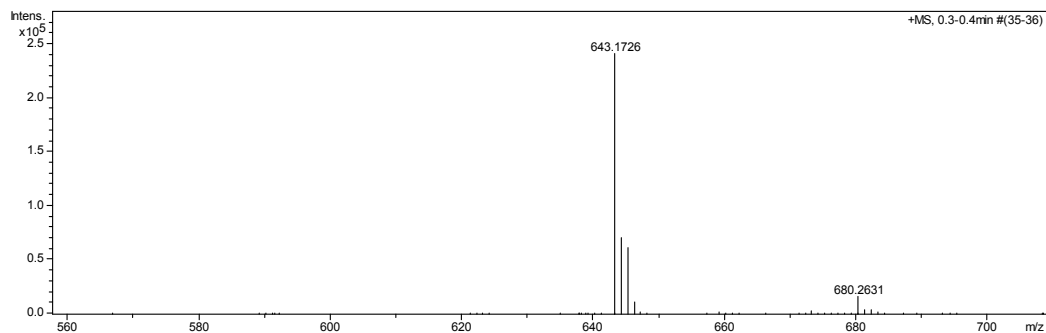
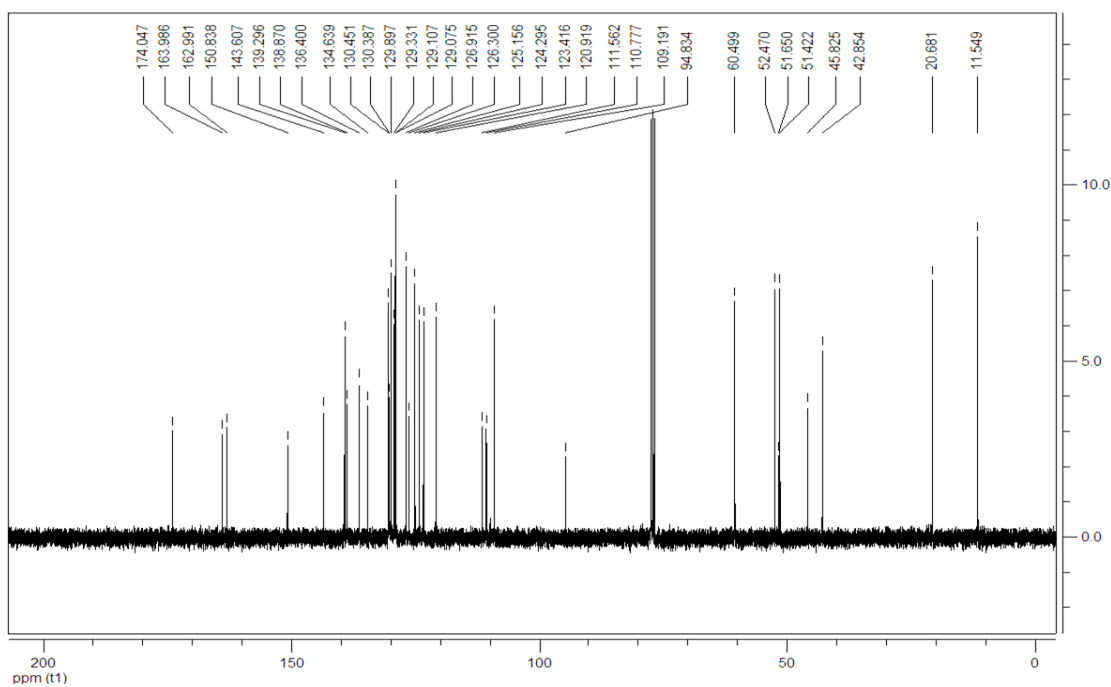
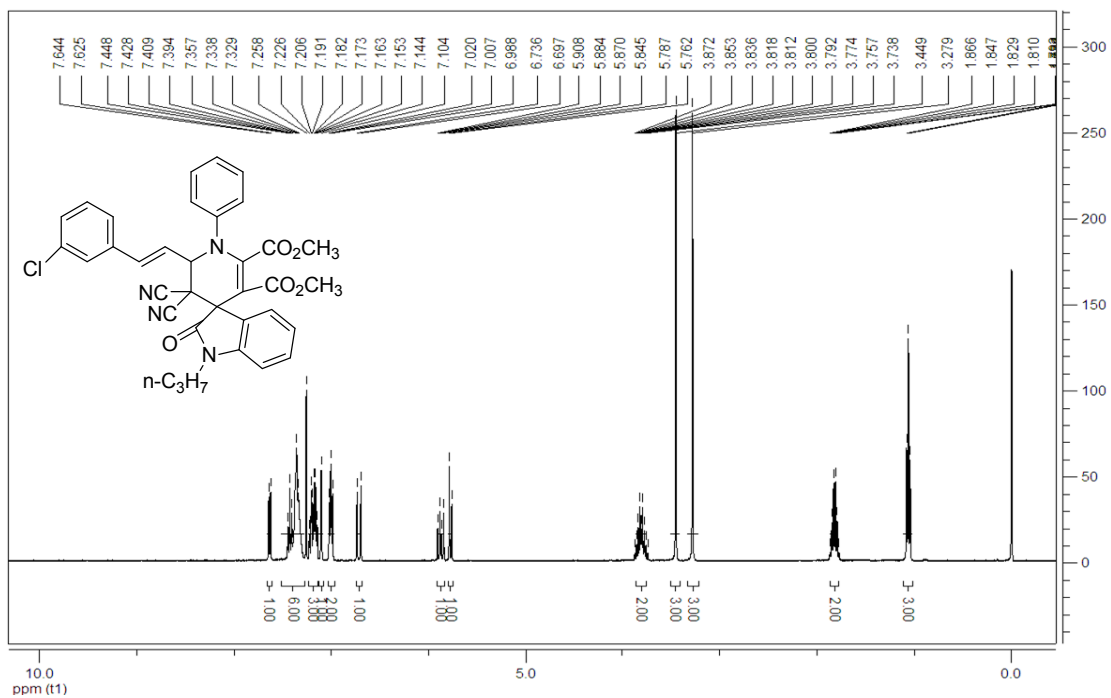
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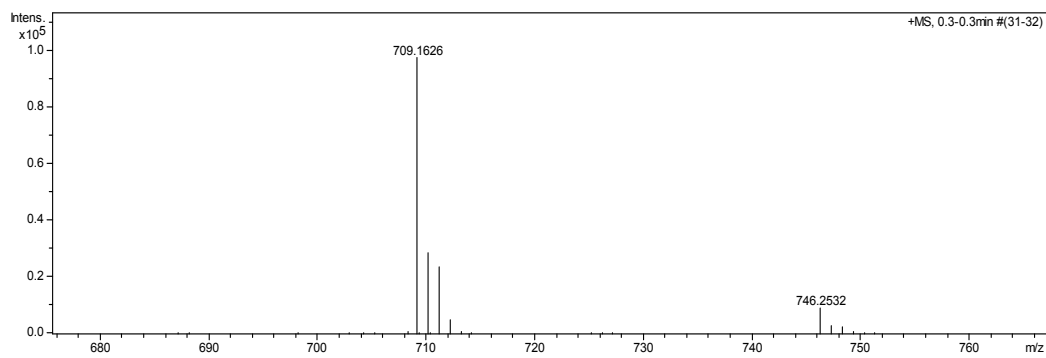
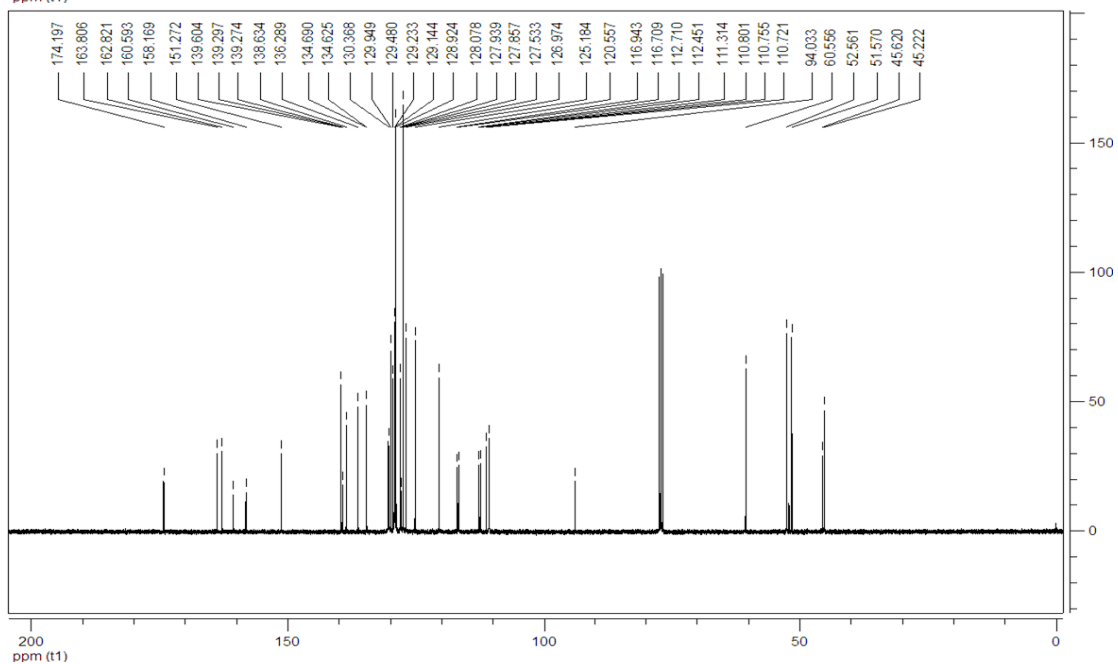
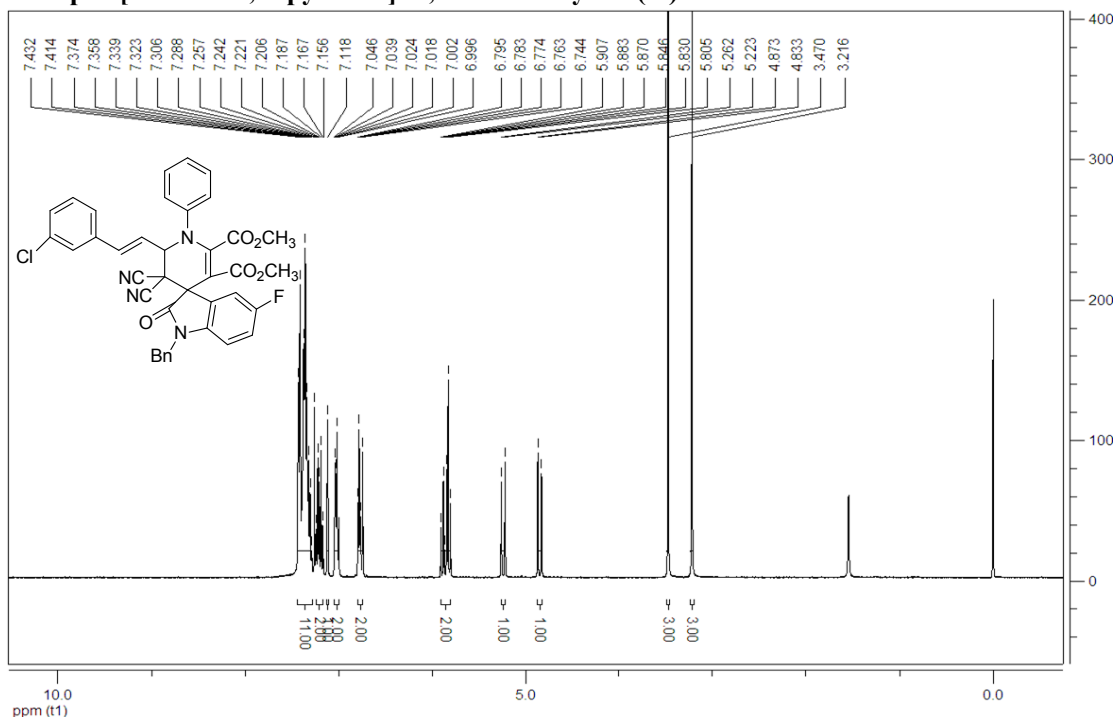
Dimethyl 5-chloro-3',3'-dicyano-1'-(4-methoxyphenyl)-2-oxo-1-propyl-2'-styryl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (3d):



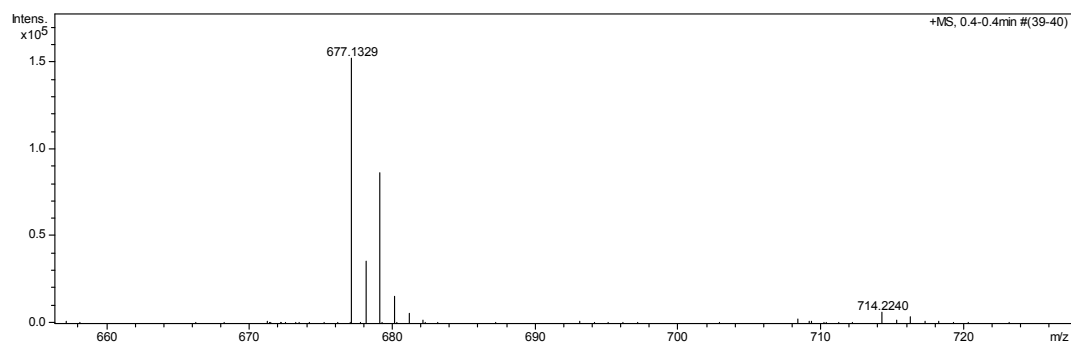
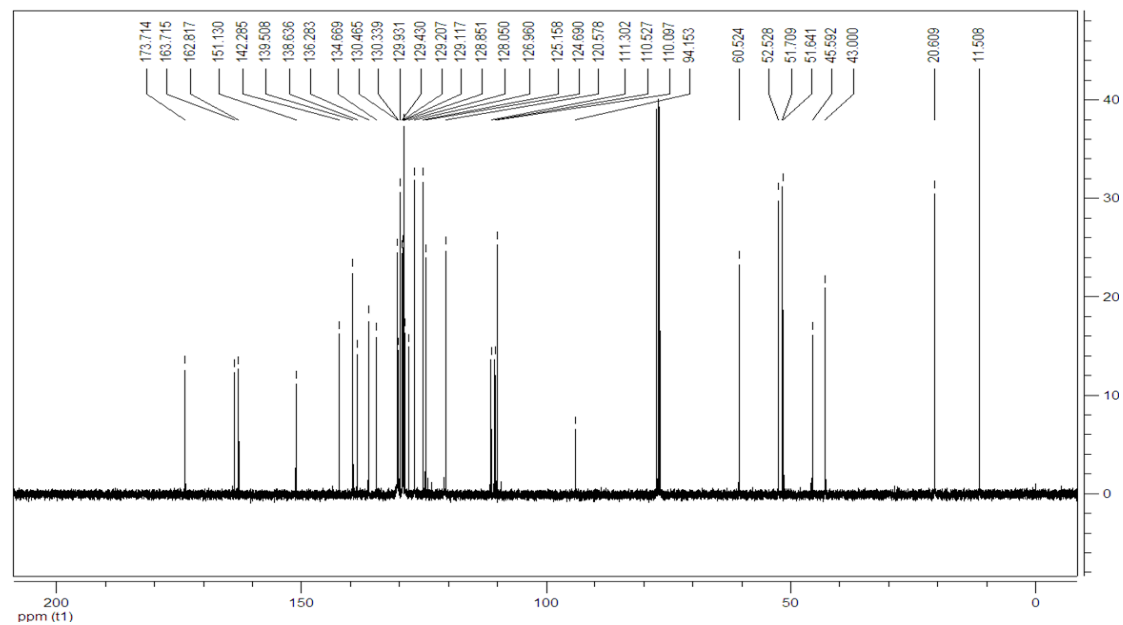
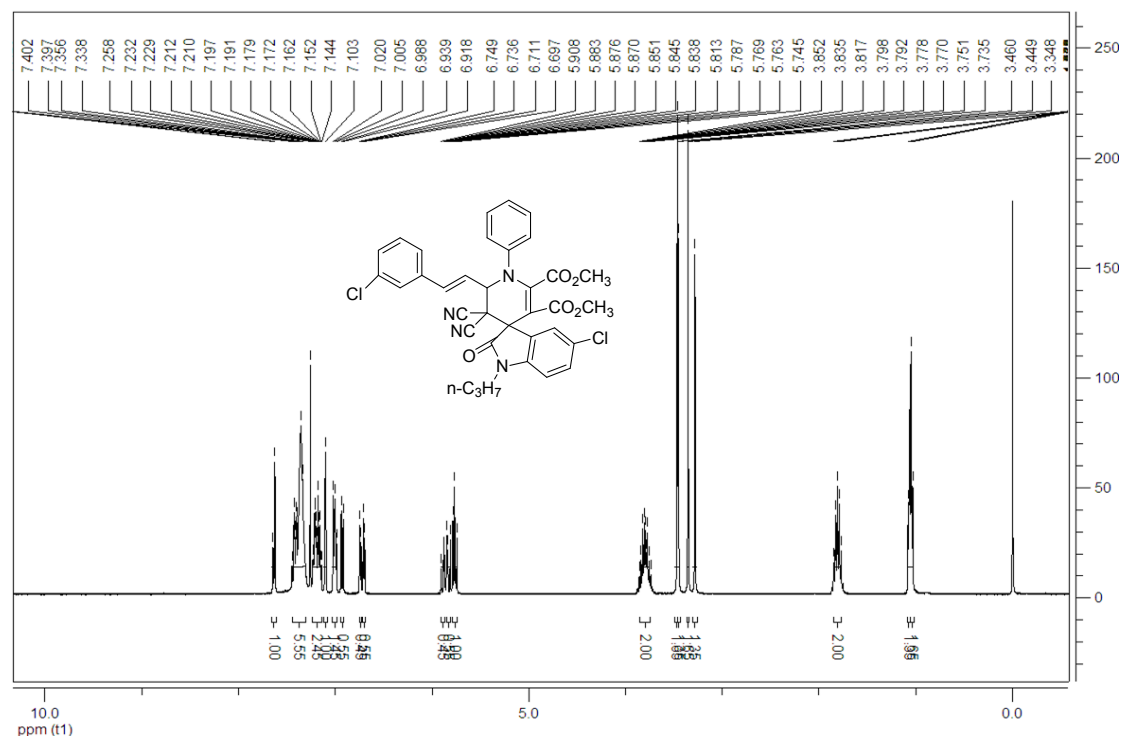
Dimethyl 2'-(3-chlorostyryl)-3,3'-dicyano-2-oxo-1'-phenyl-1-propyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (3e):



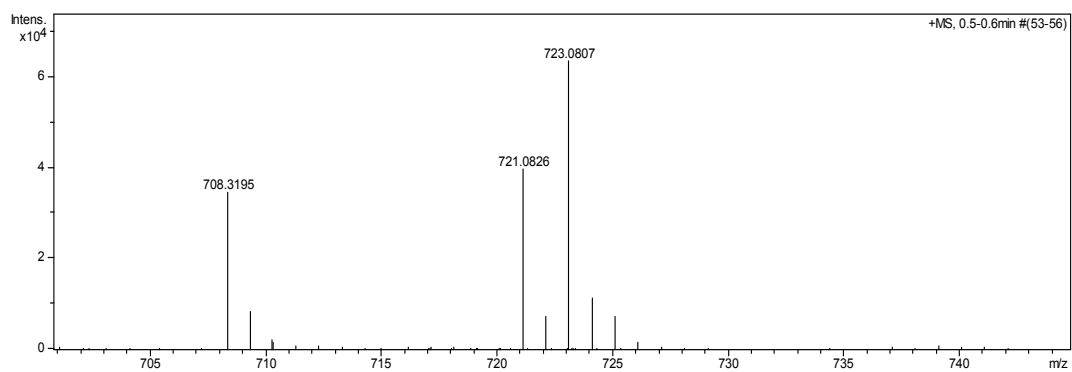
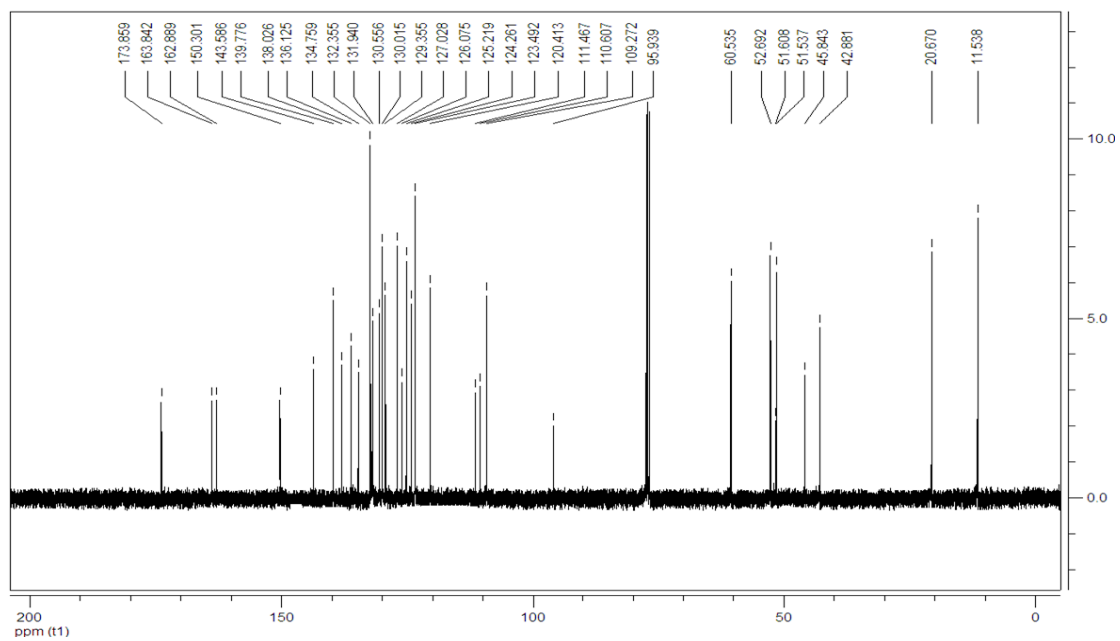
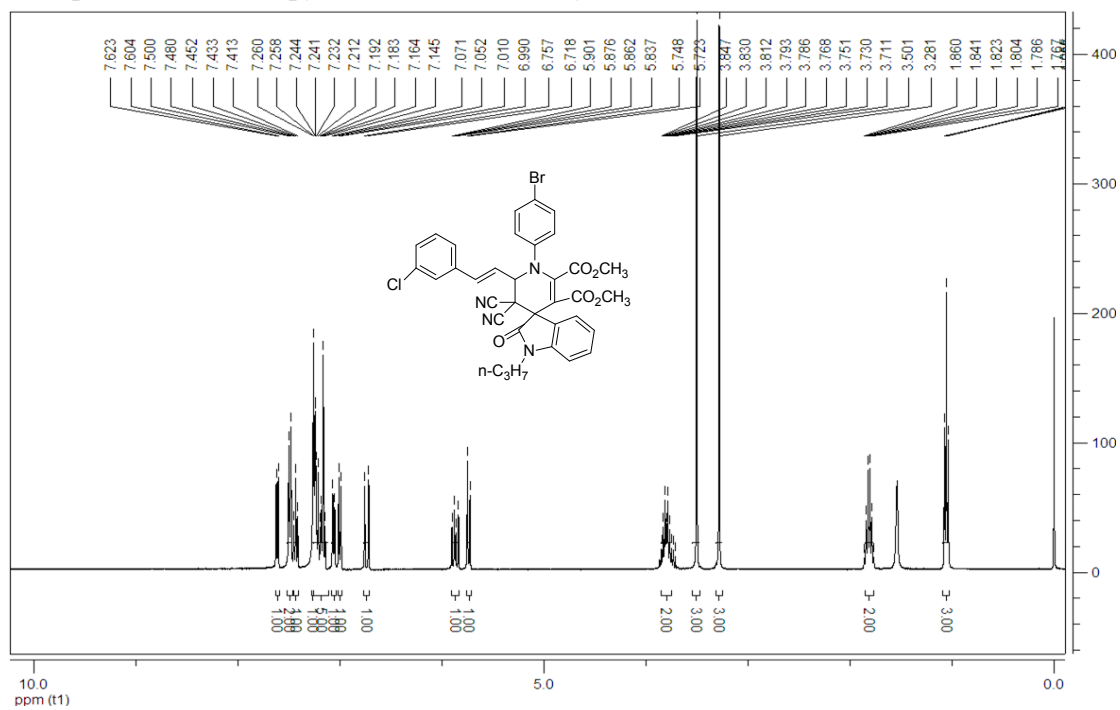
Dimethyl 1-benzyl-2'-(3-chlorostyryl)-3',3'-dicyano-5-fluoro-2-oxo-1'-phenyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (3f):



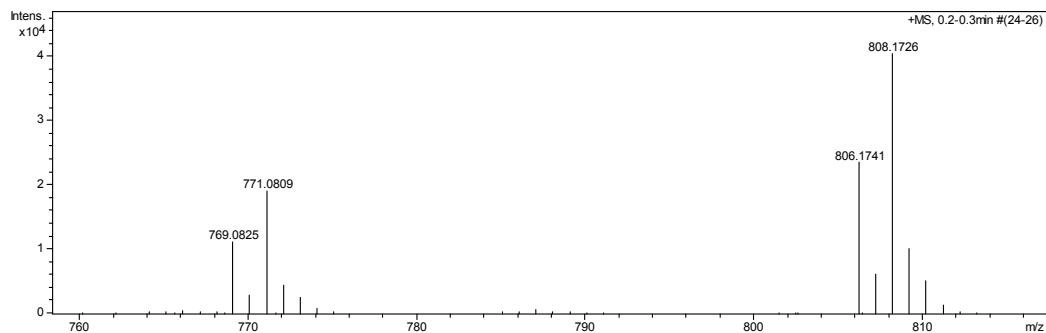
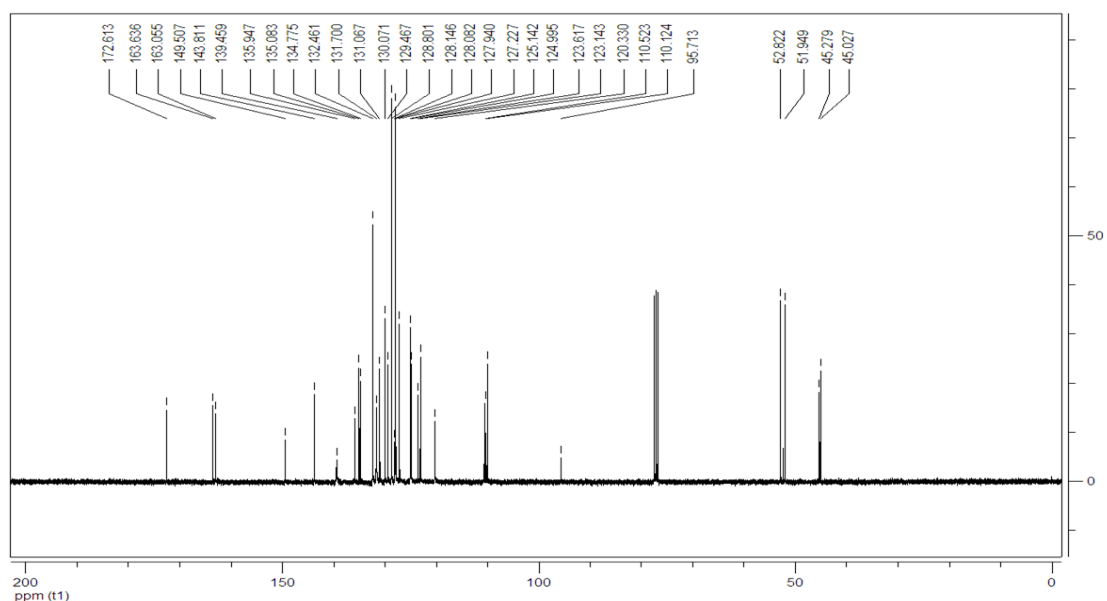
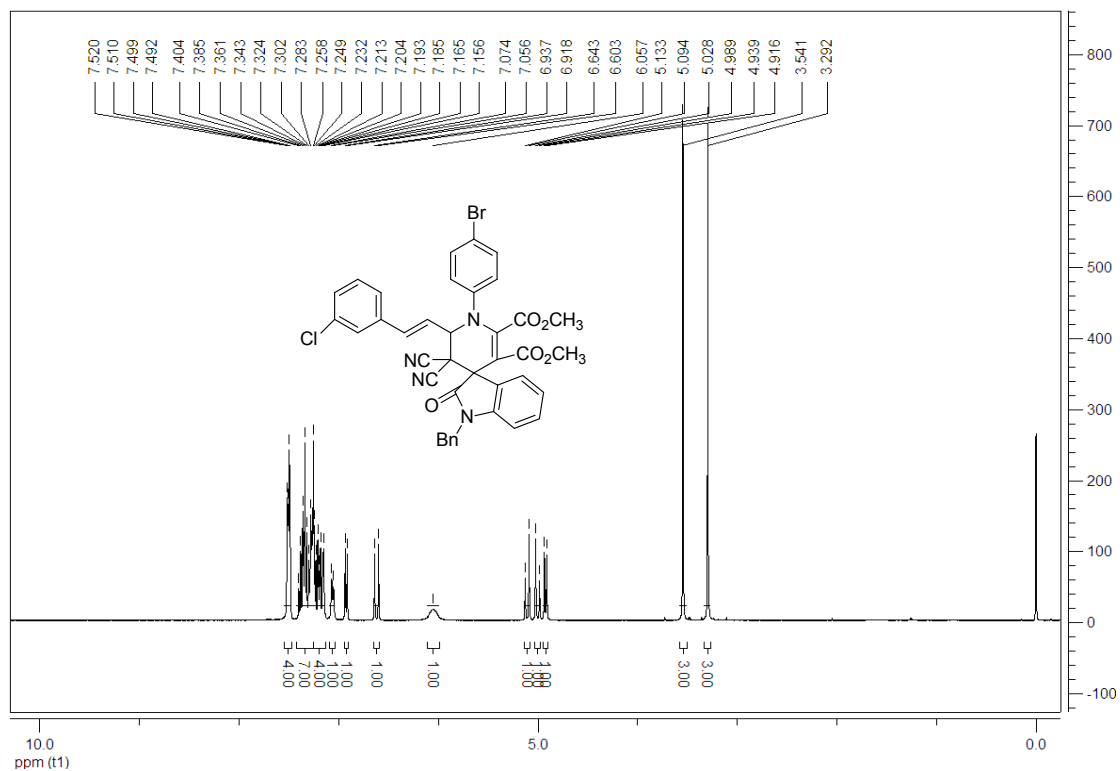
Dimethyl 5-chloro-2'-(3-chlorostyryl)-3,3'-dicyano-2-oxo-1'-phenyl-1-propyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (3g):



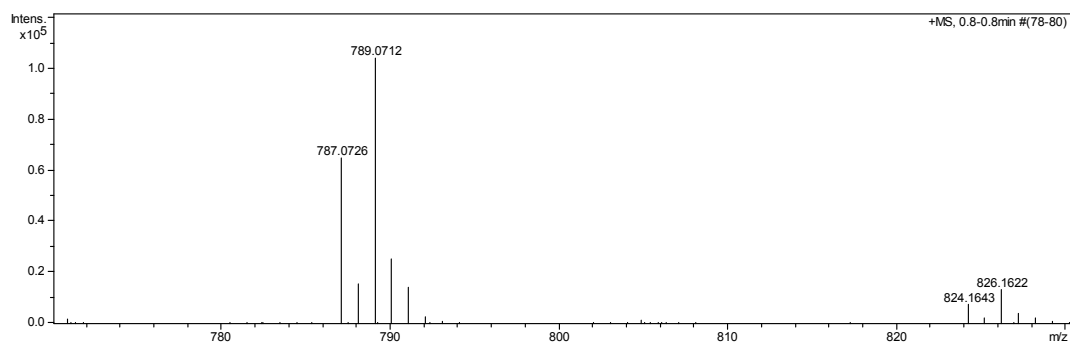
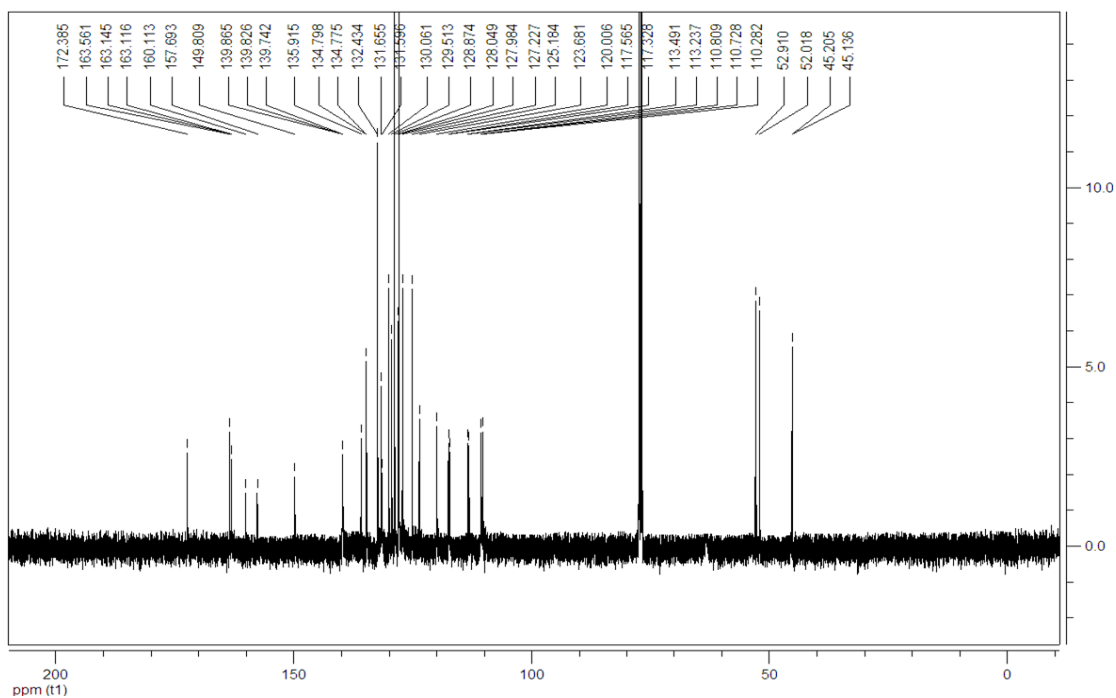
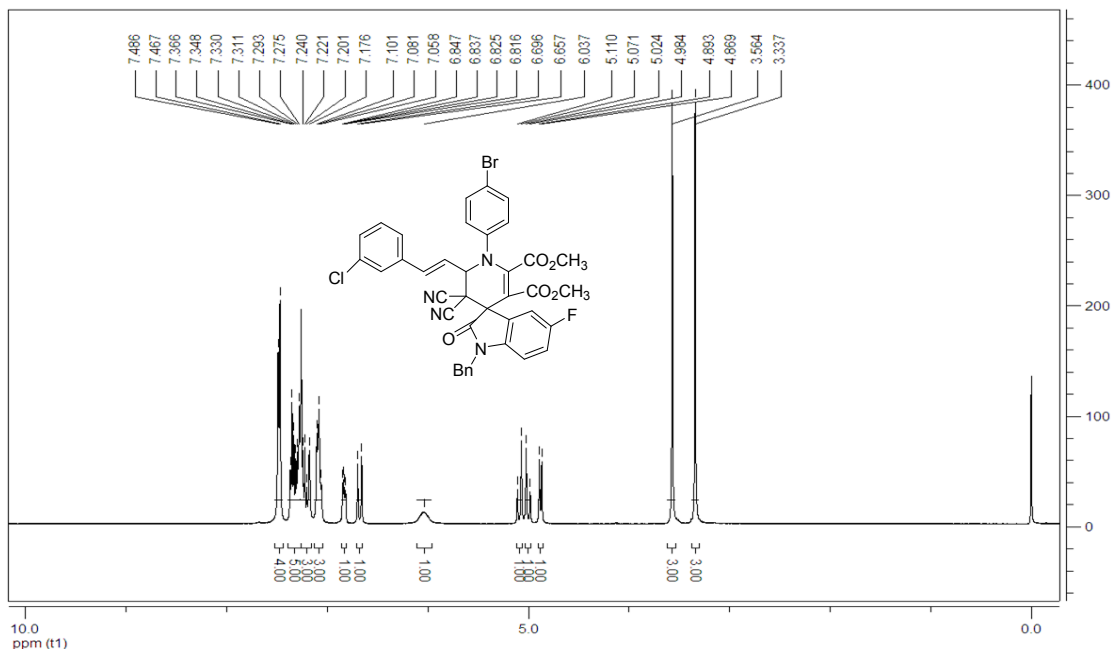
Dimethyl 1'-(4-bromophenyl)-2'-(3-chlorostyryl)-3',3'-dicyano-2-oxo-1-propyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (3h):



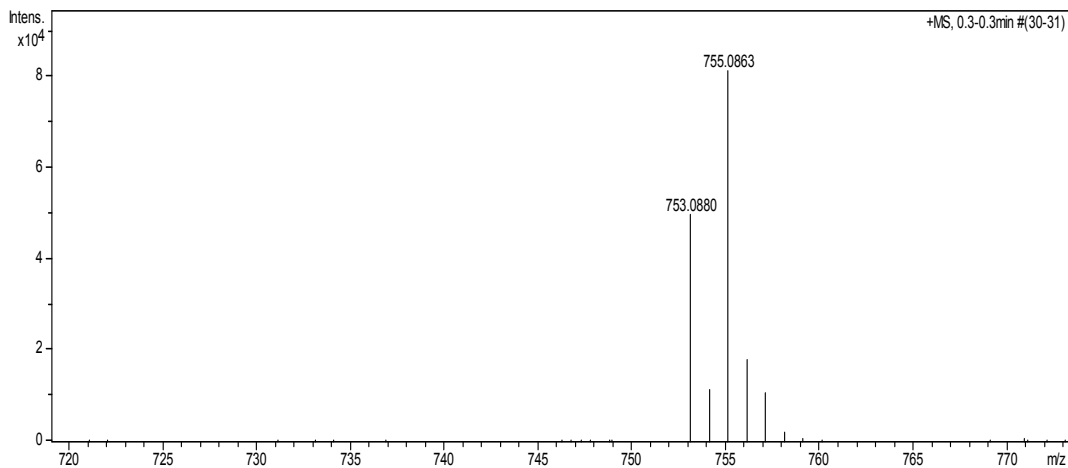
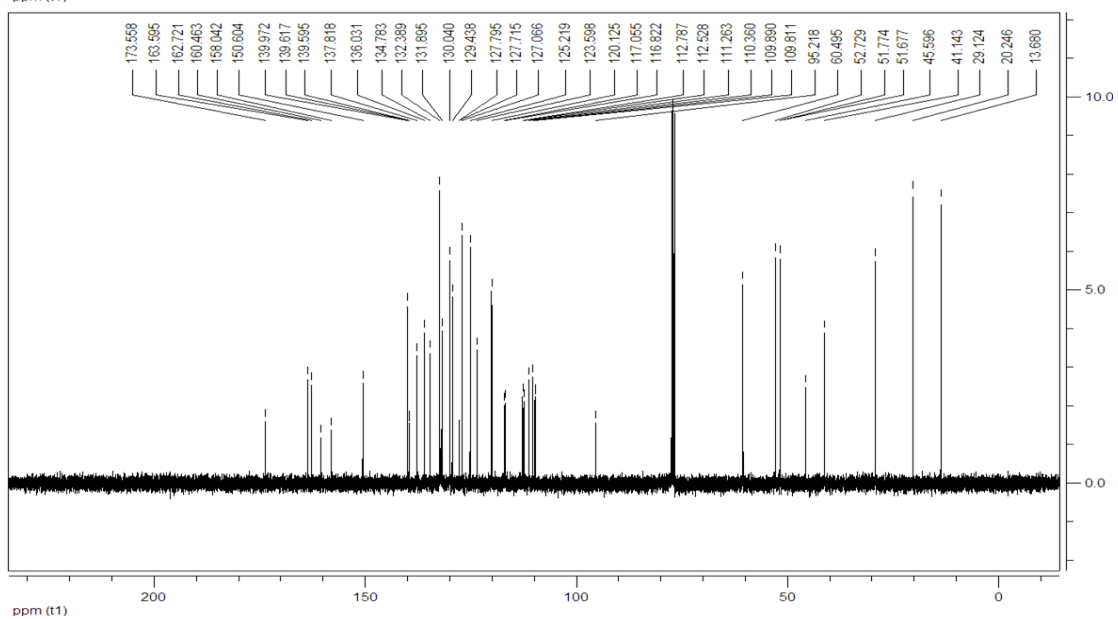
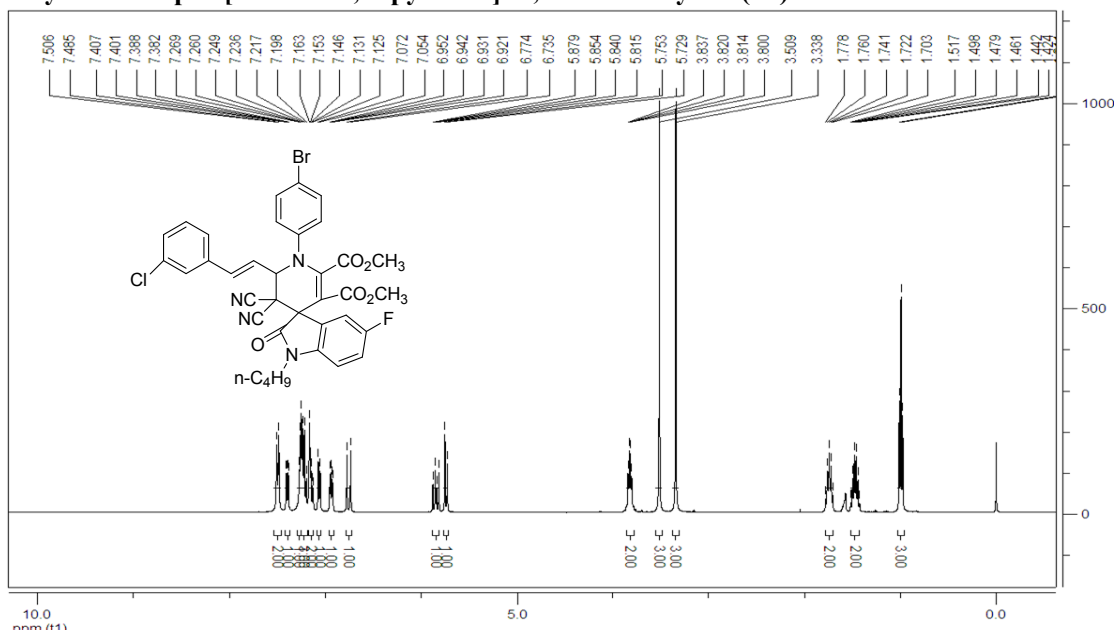
Dimethyl 1-benzyl-1'-(4-bromophenyl)-2'-(3-chlorostyryl)-3',3'-dicyano-2-oxo-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (3i):



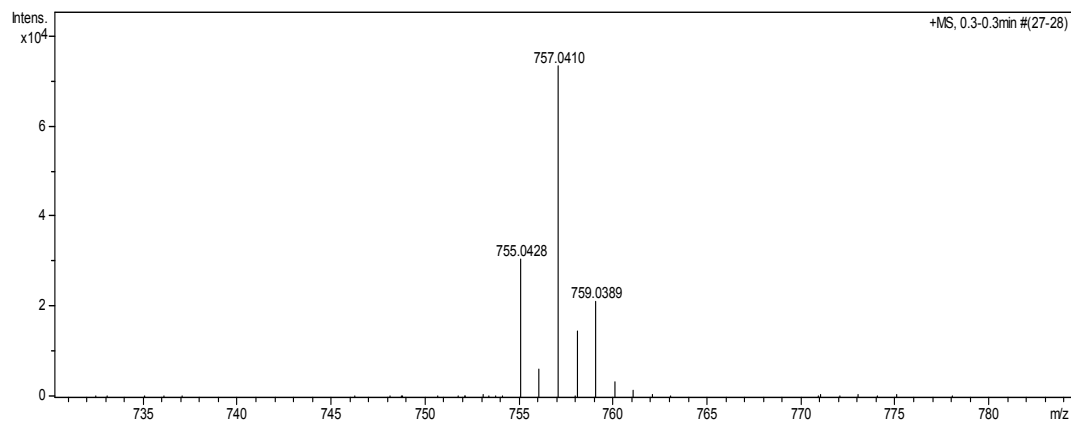
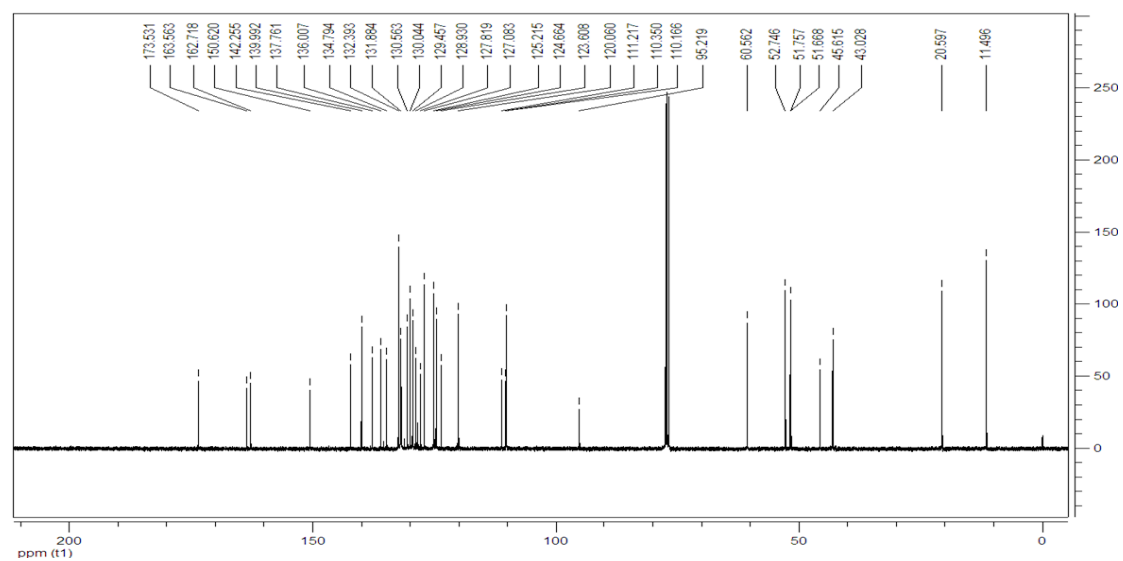
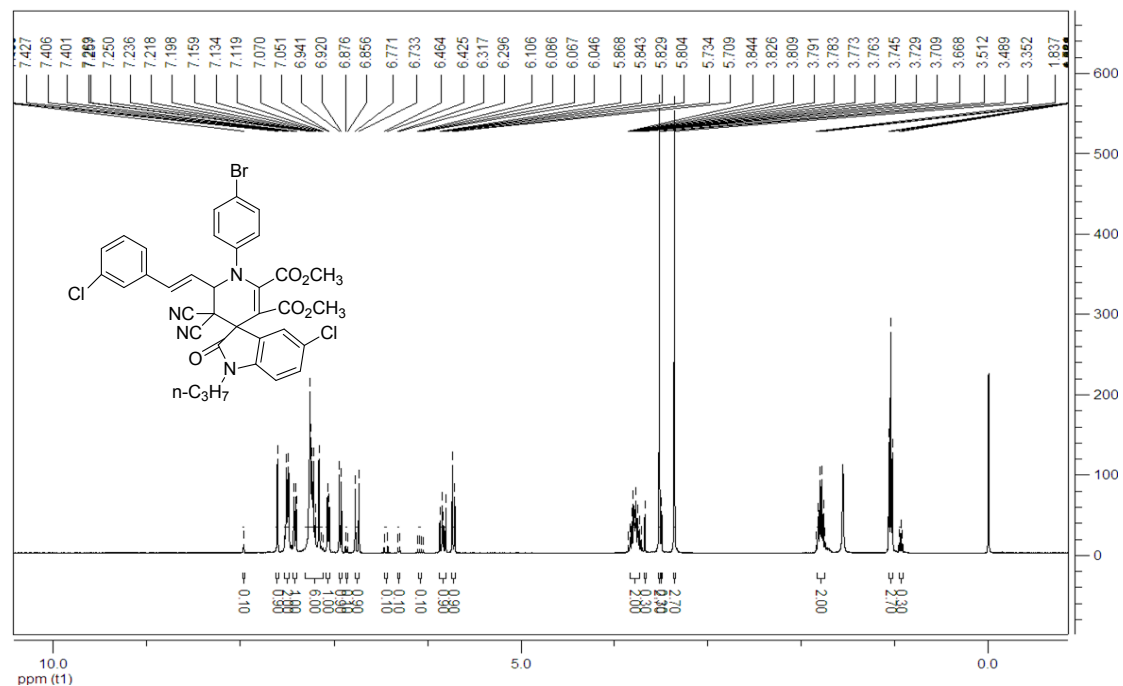
Dimethyl 1-benzyl-1'-(4-bromophenyl)-2'-(3-chlorostyryl)-3',3'-dicyano-5-fluoro-2-oxo- 2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (3j):



Dimethyl 1'-(4-bromophenyl)-1-butyl-2'-(3-chlorostyryl)-3',3'-dicyano-5-fluoro-2-oxo-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (3k):

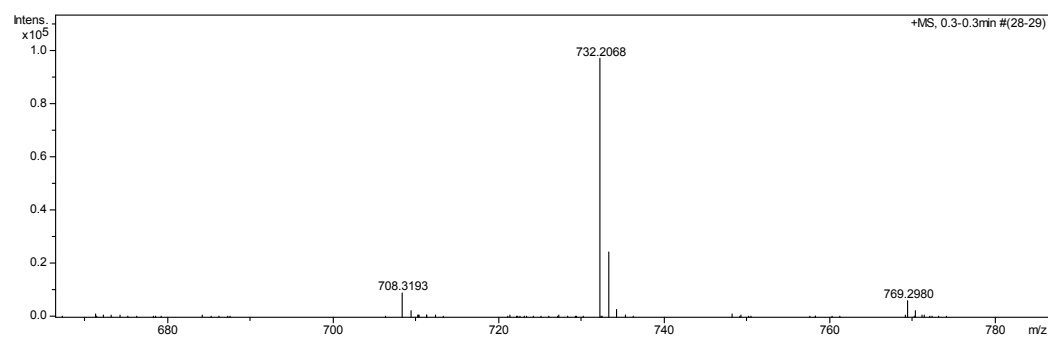
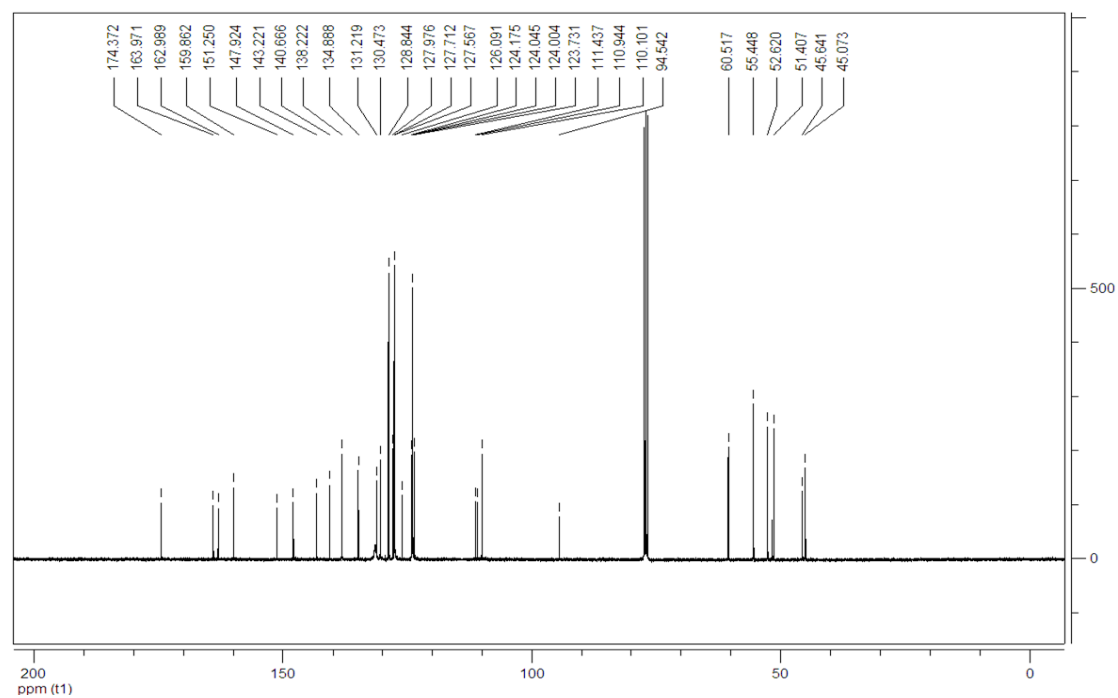
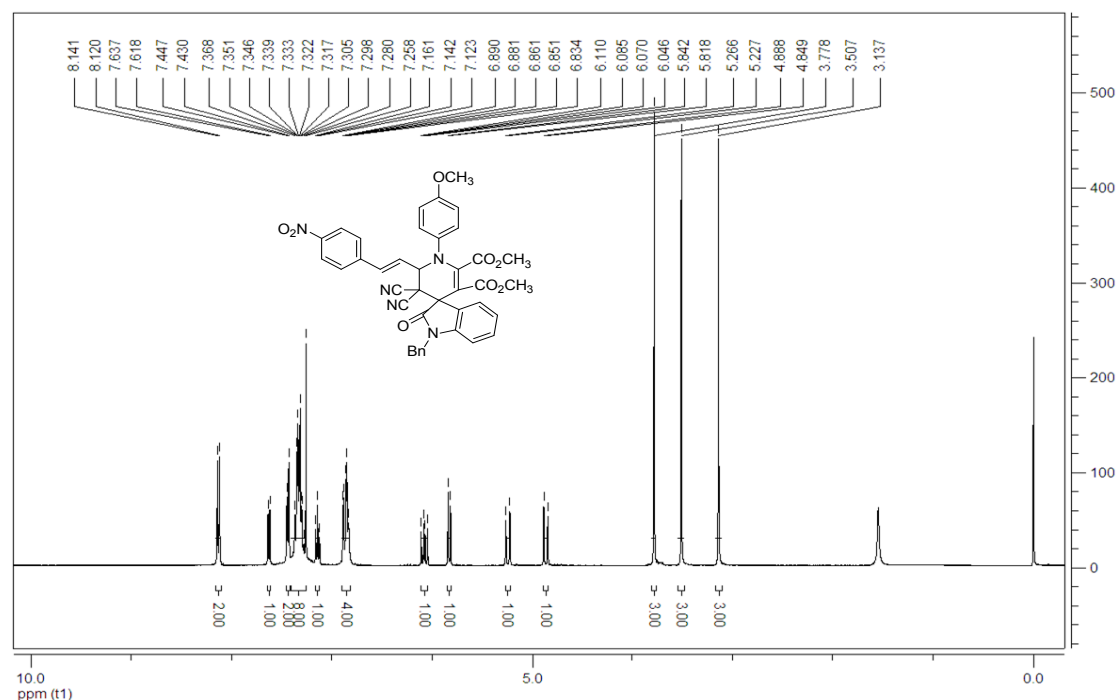


Dimethyl 1'-(4-bromophenyl)-5-chloro-2'-(3-chlorostyryl)-3',3'-dicyano-2-oxo-1-propyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (3l):



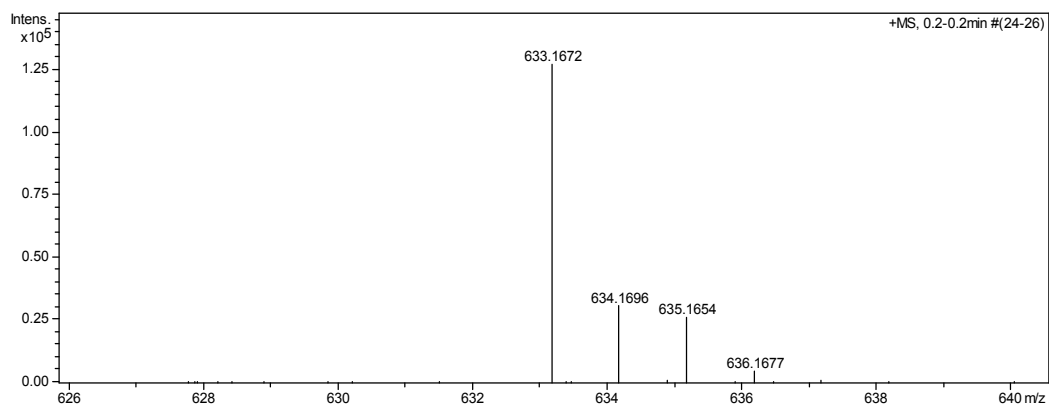
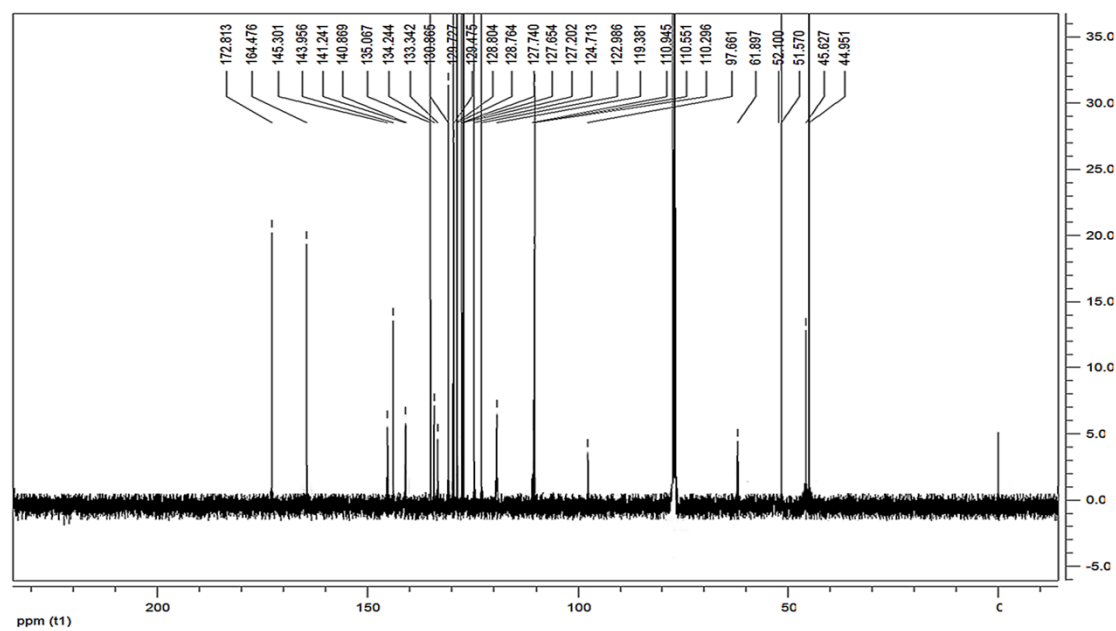
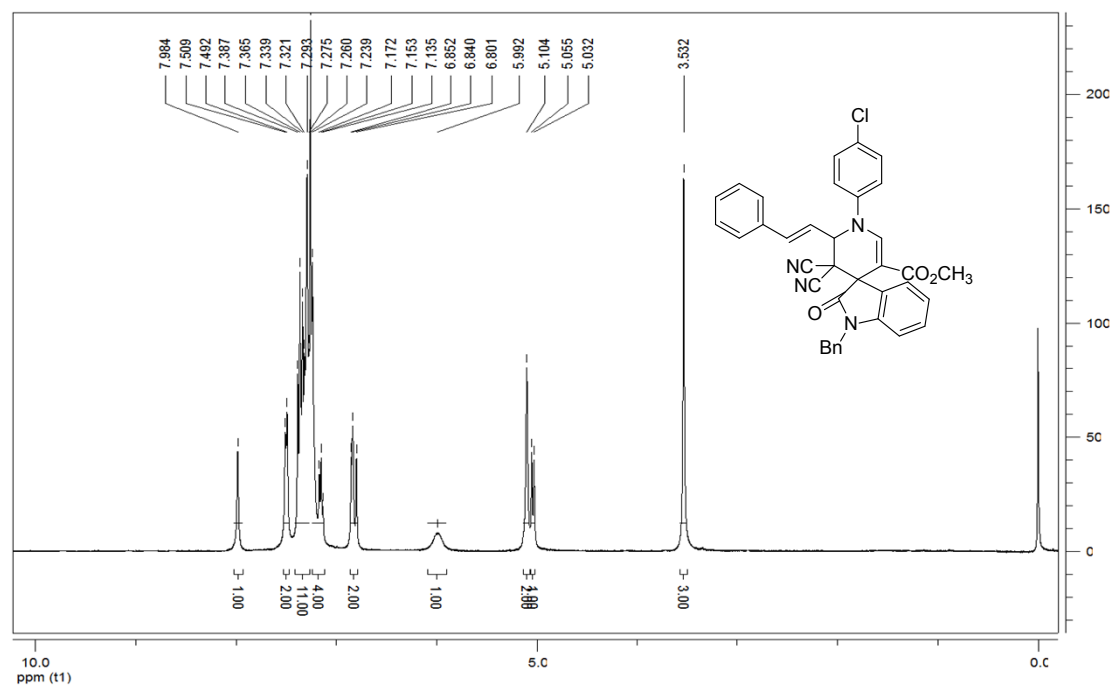
Dimethyl 1-benzyl-3',3'-dicyano-1'-(4-methoxyphenyl)-2'-(4-nitrostyryl)-2-oxo-2',3'-dihydro-

¹H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (3m):



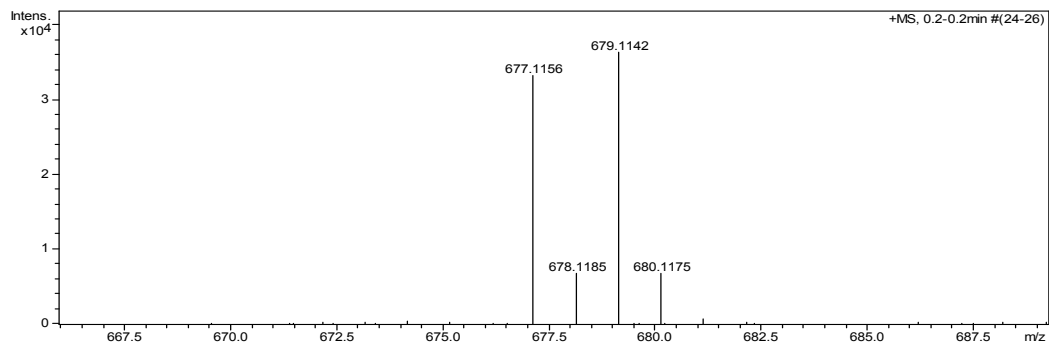
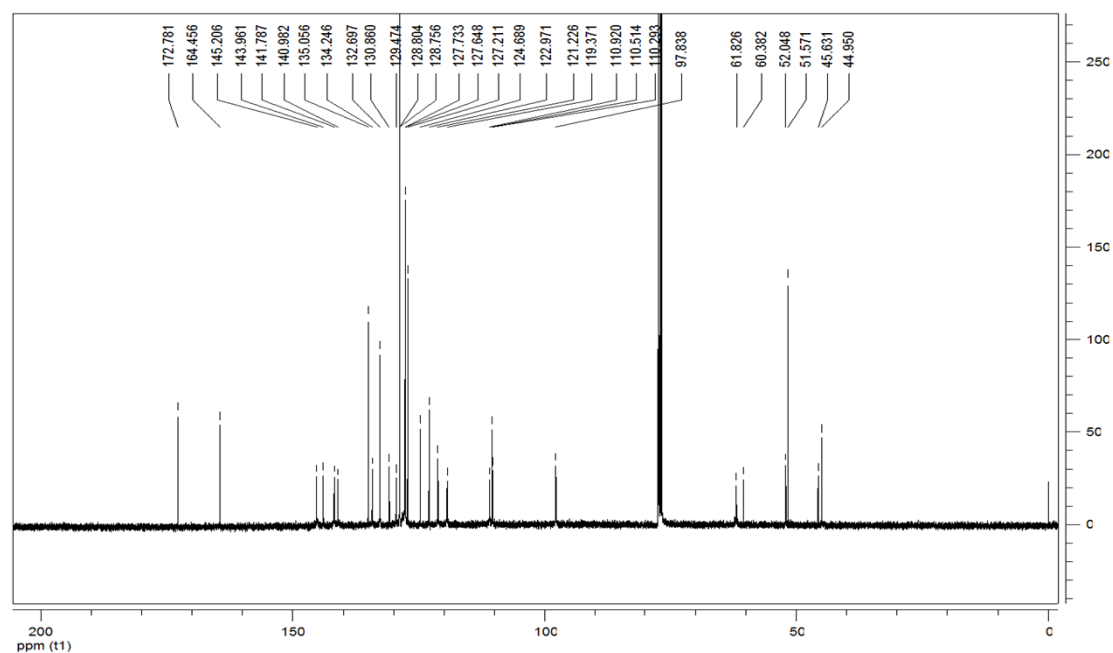
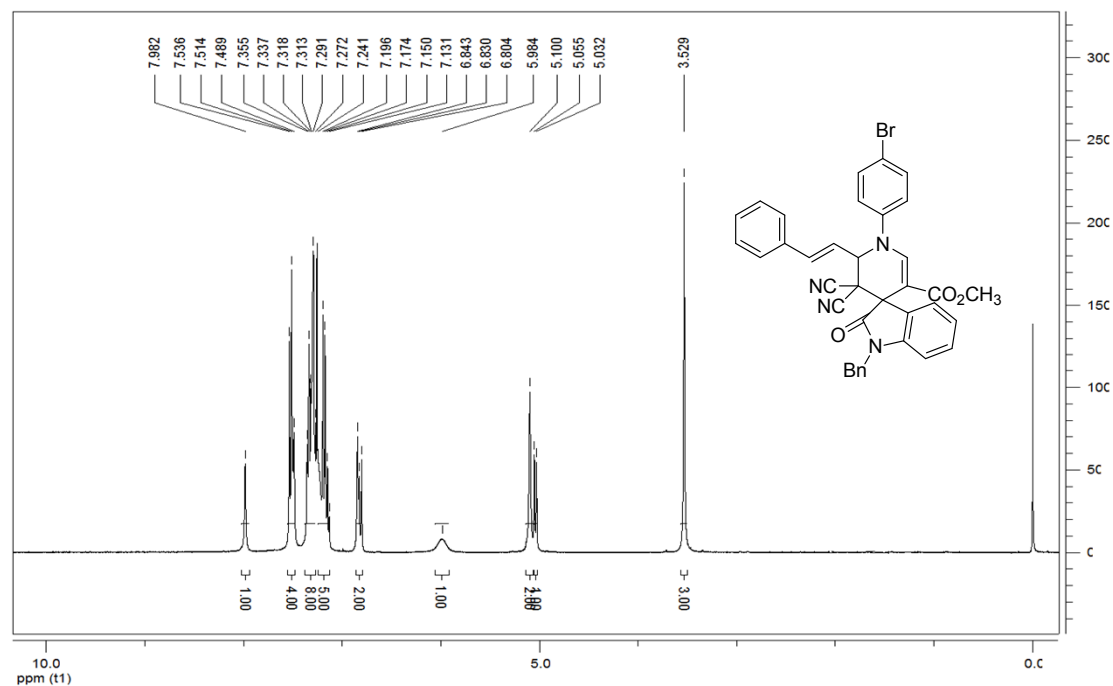
Methyl 1-benzyl-1'-(4-chlorophenyl)-3',3'-dicyano-2-oxo-2'-styryl-2',3'-dihydro-1'H-

spiro[indoline-3,4'-pyridine]-5'-carboxylate (4a):



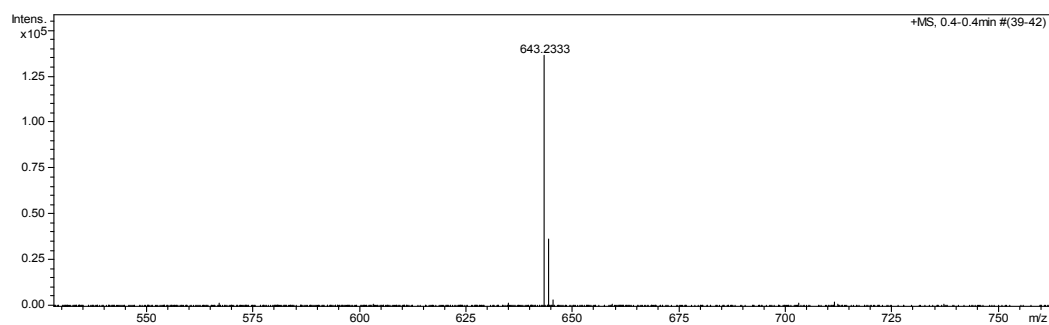
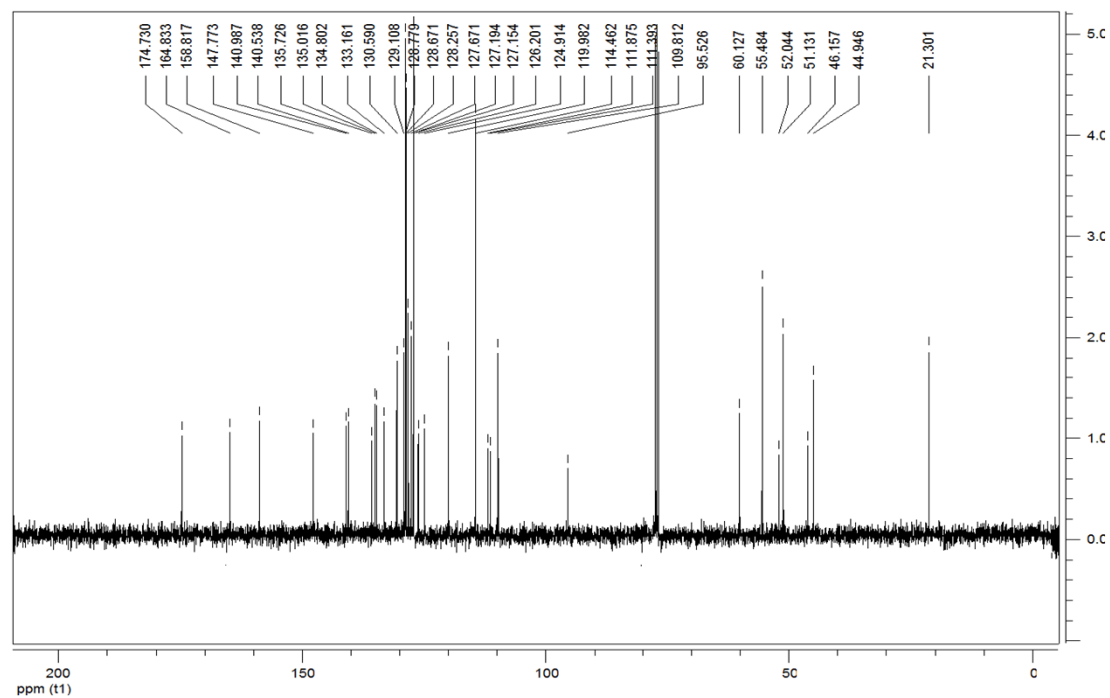
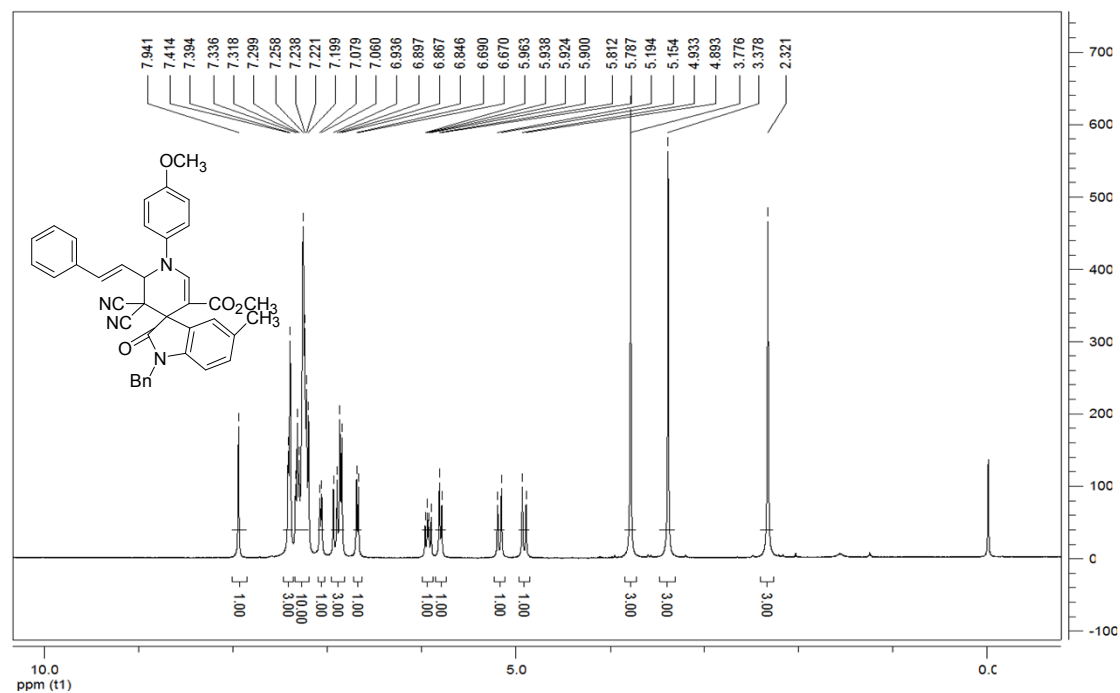
Methyl 1-benzyl-1'-(4-bromophenyl)-3',3'-dicyano-2-oxo-2'-styryl-2',3'-dihydro-1'H-spiro

[indoline-3,4'-pyridine]-5'-carboxylate (4b):



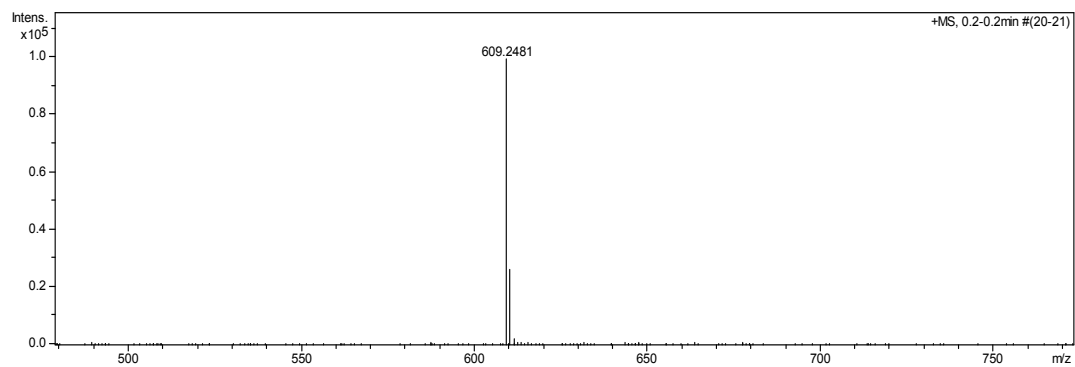
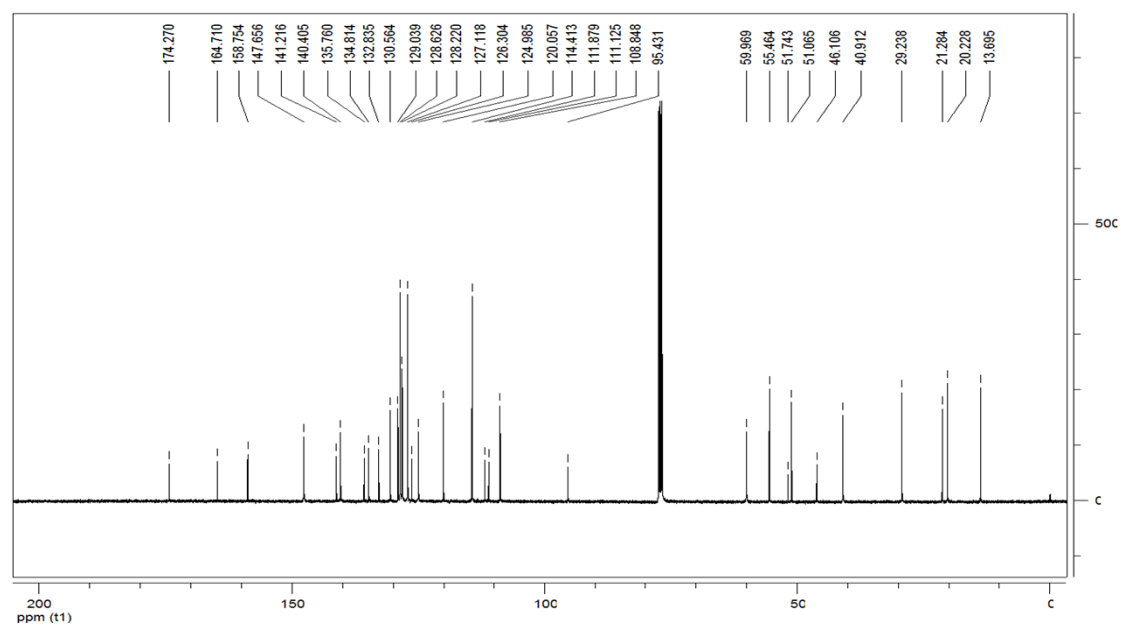
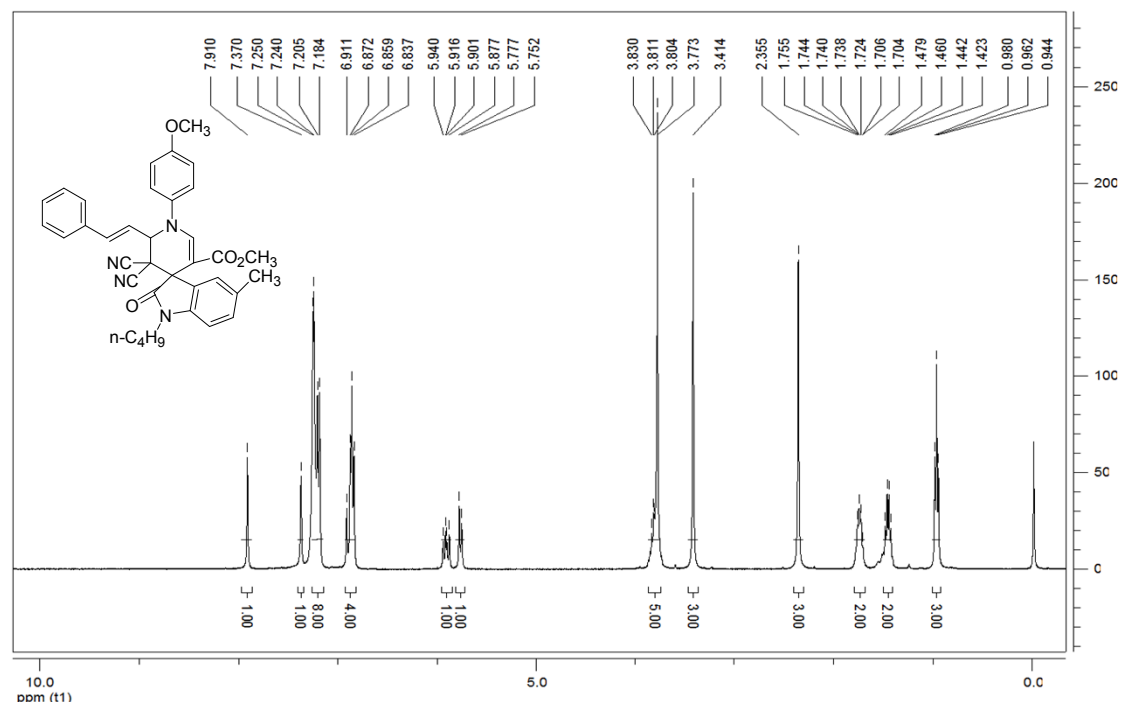
Methyl 1-benzyl-3',3'-dicyano-1'-(4-methoxyphenyl)-5-methyl-2-oxo-2'-styryl-2',3'-dihydro-

¹H-spiro[indoline-3,4'-pyridine]-5'-carboxylate (4c):



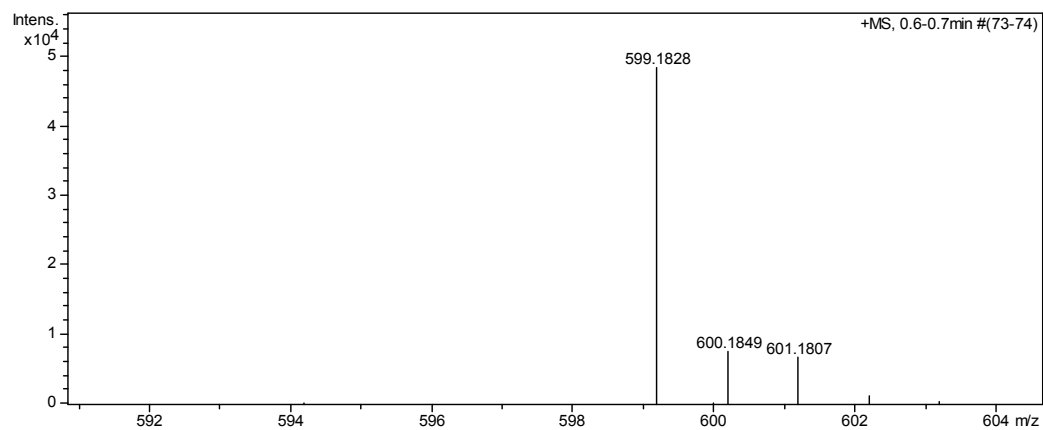
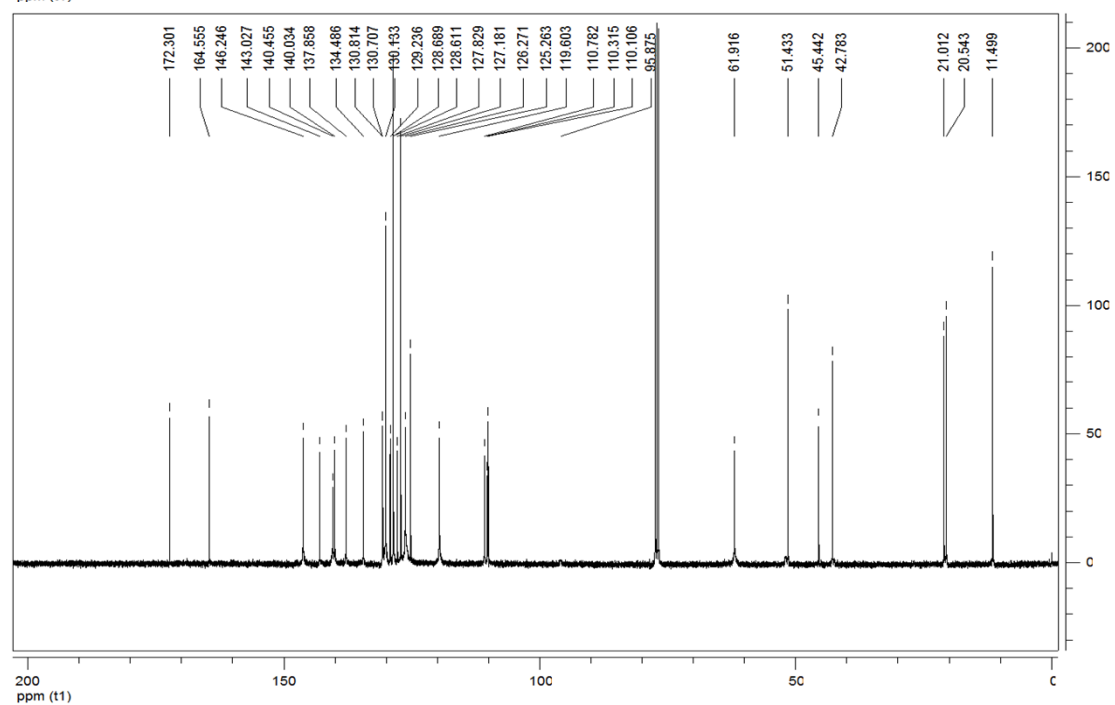
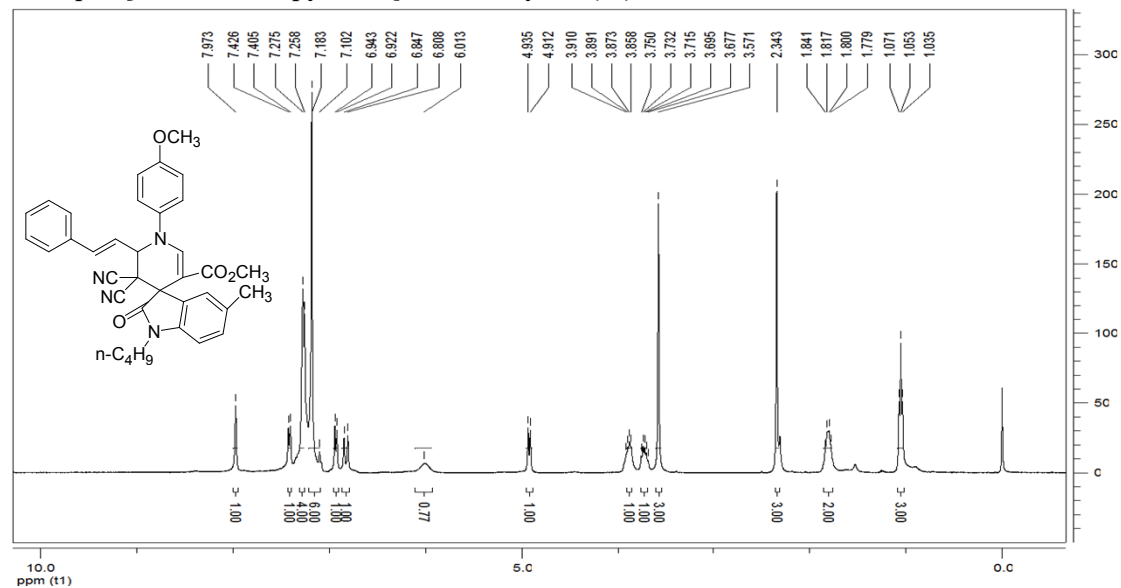
Methyl 1-butyl-3',3'-dicyano-1'-(4-methoxyphenyl)-5-methyl-2-oxo-2'-styryl-2',3'-dihydro-

¹H-spiro[indoline-3,4'-pyridine]-5'-carboxylate (4d):



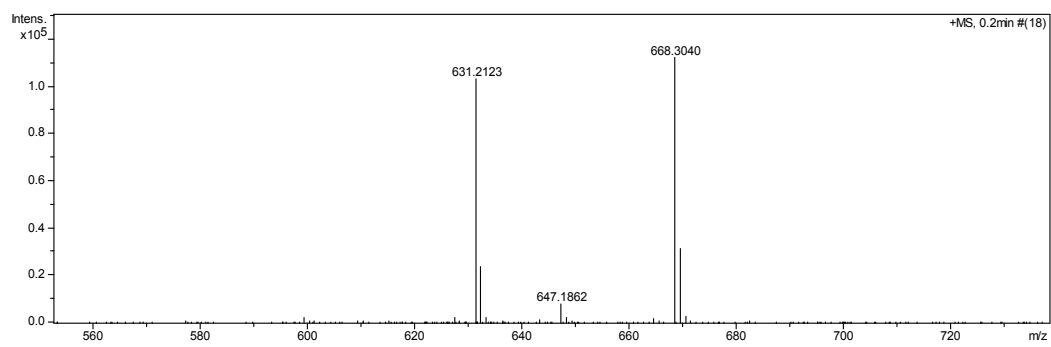
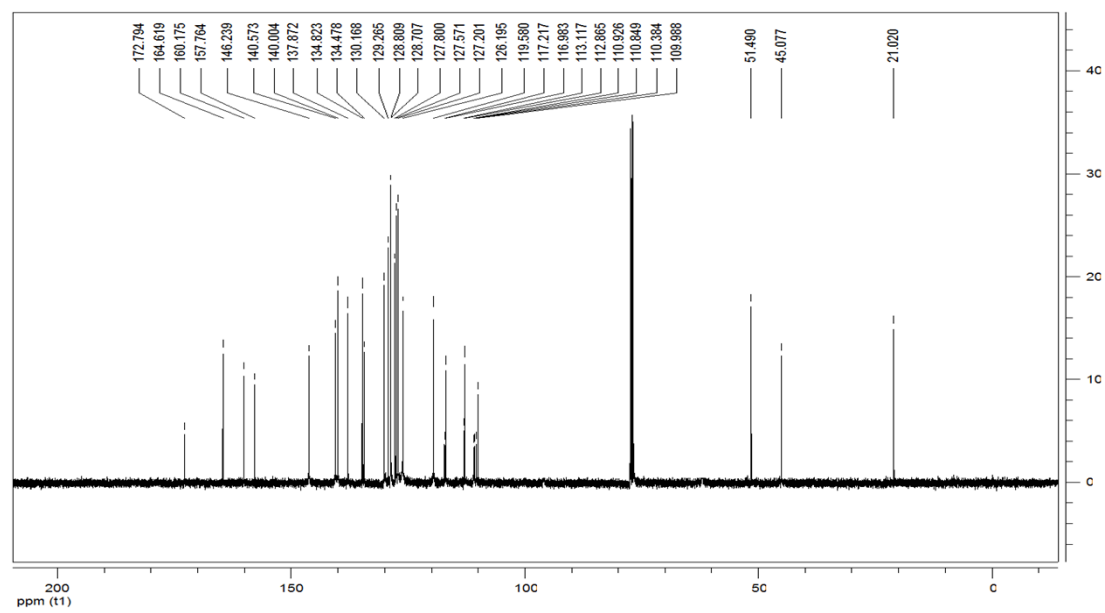
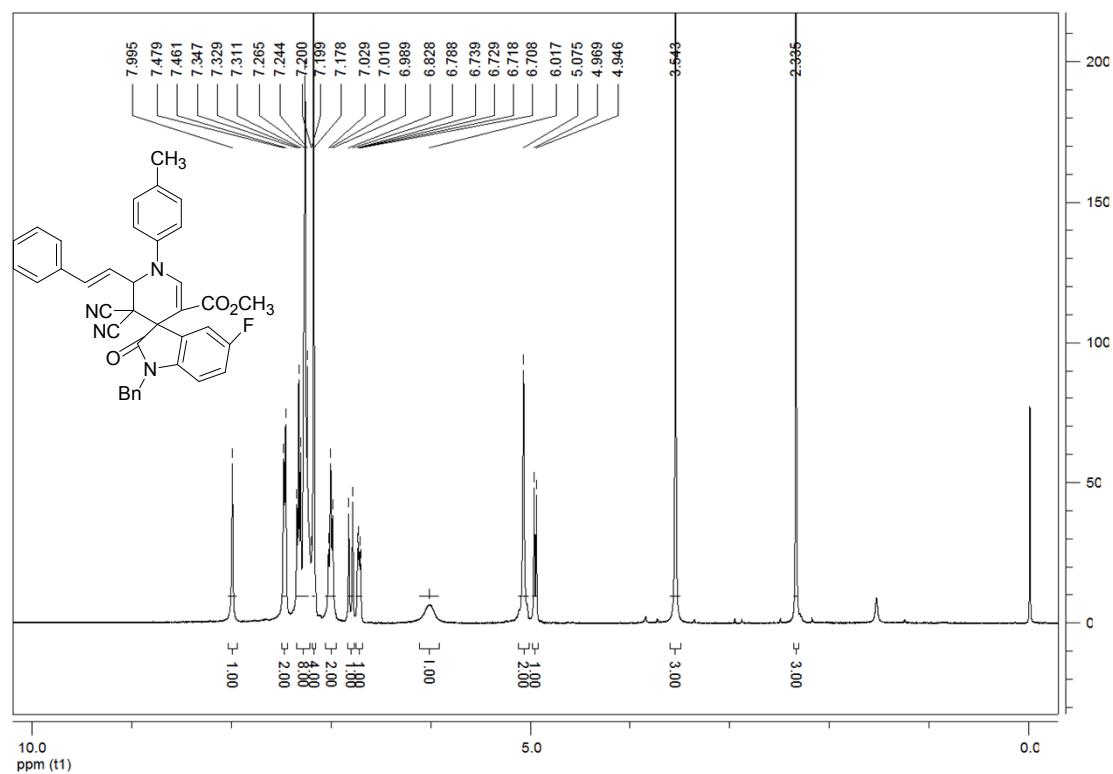
Methyl 1-butyl-3',3'-dicyano-1'-(4-methoxyphenyl)-5-methyl-2-oxo-2'-styryl-2',3'-dihydro-

¹H-spiro[indoline-3,4'-pyridine]-5'-carboxylate (4e):

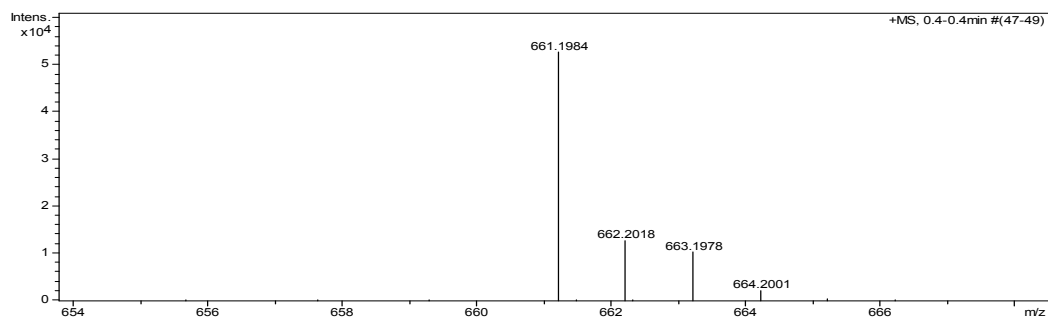
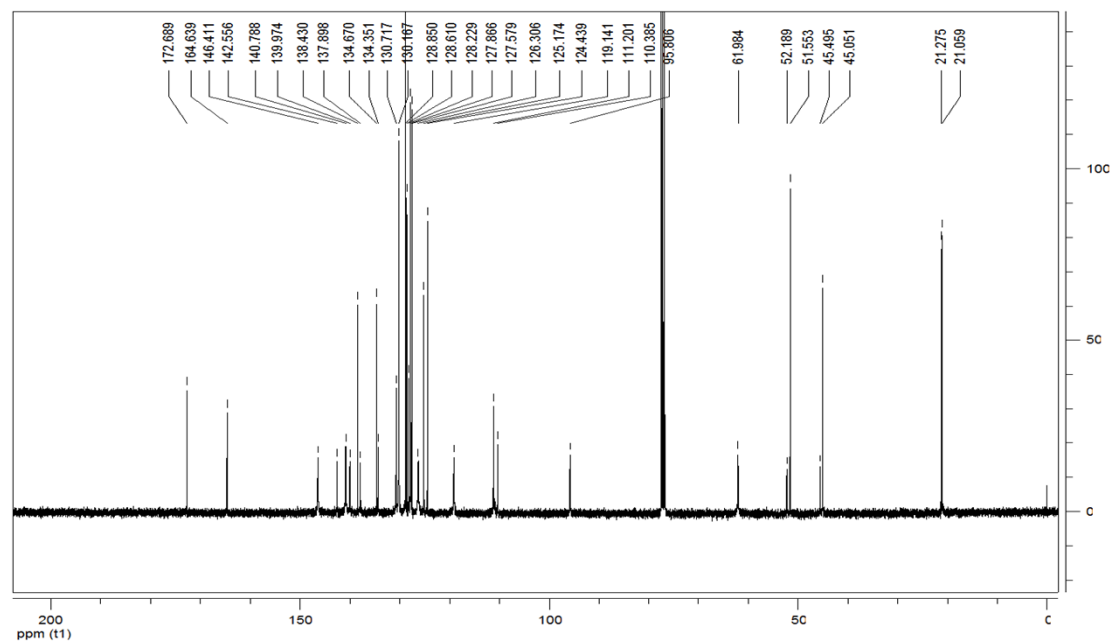
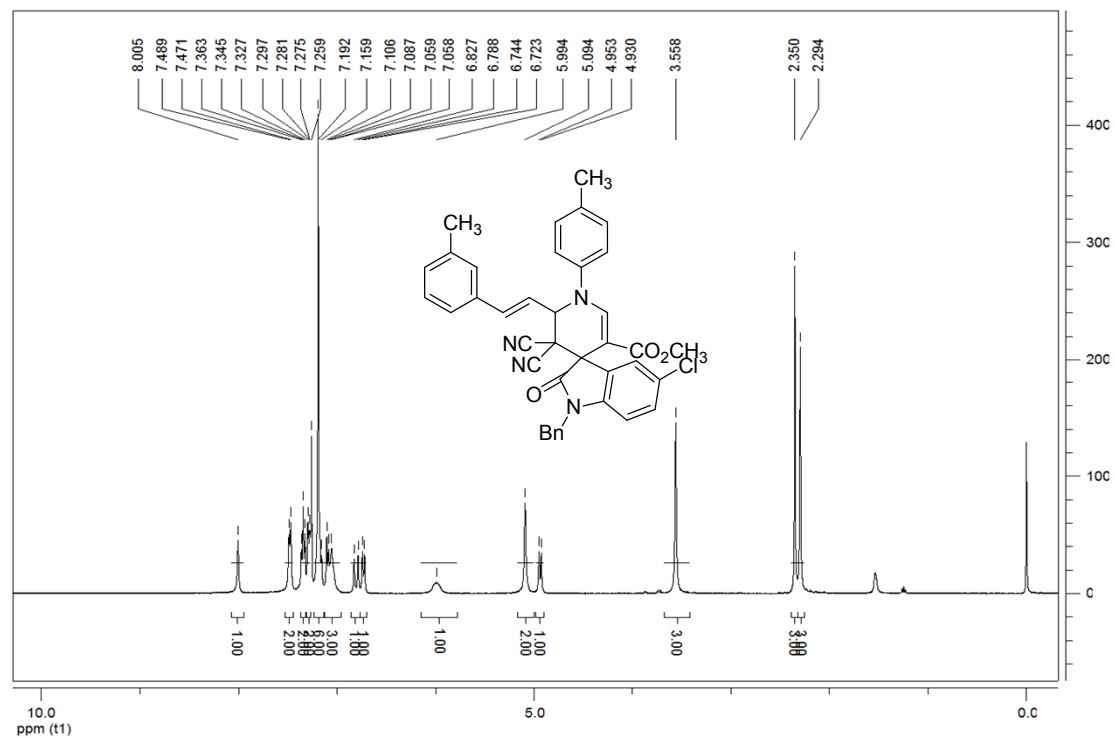


Methyl 1-benzyl-3,3'-dicyano-5-fluoro-2-oxo-2'-styryl-1'-p-tolyl-2',3'-dihydro-1'H-

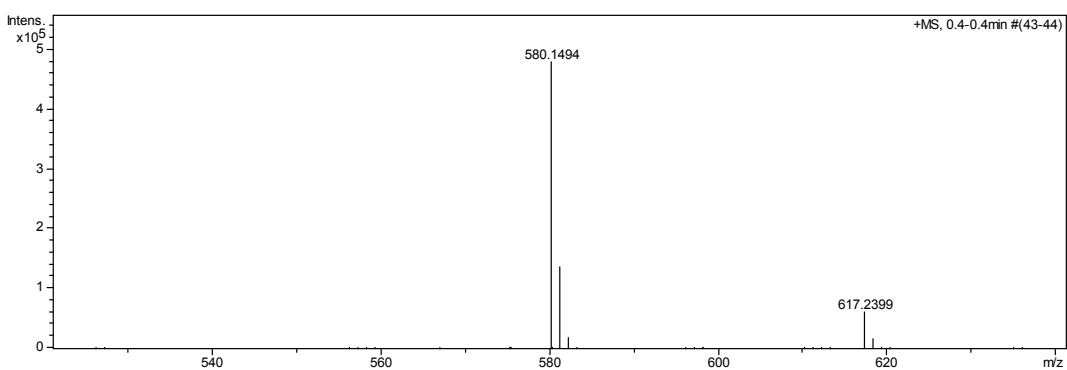
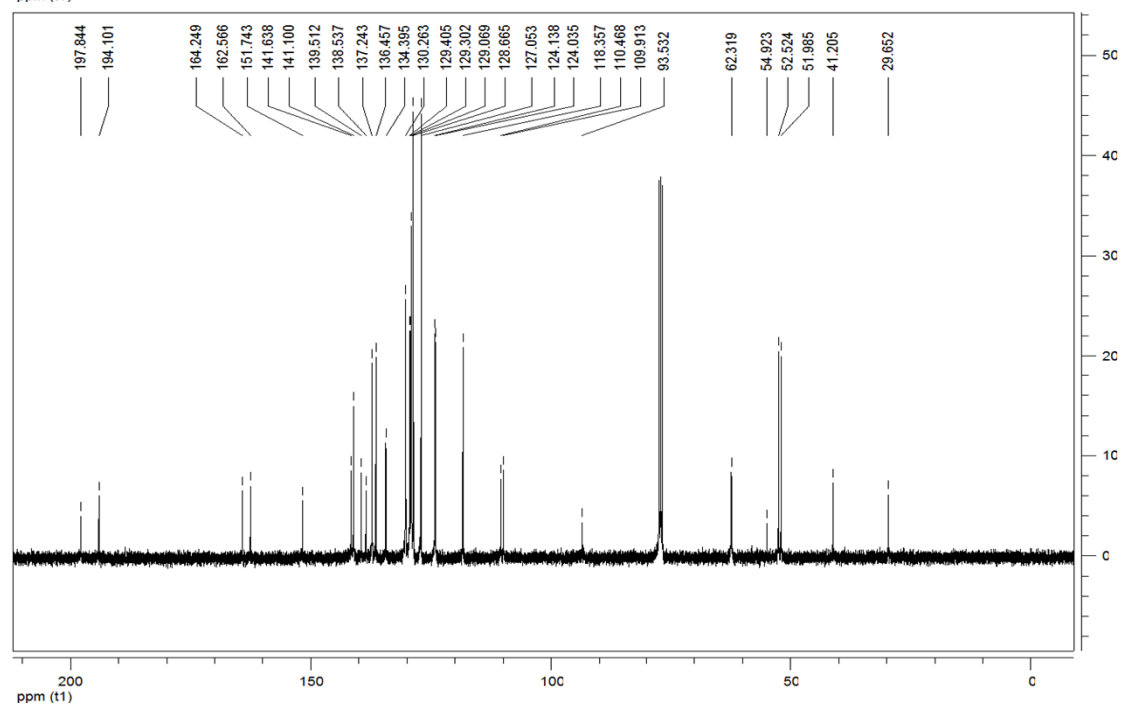
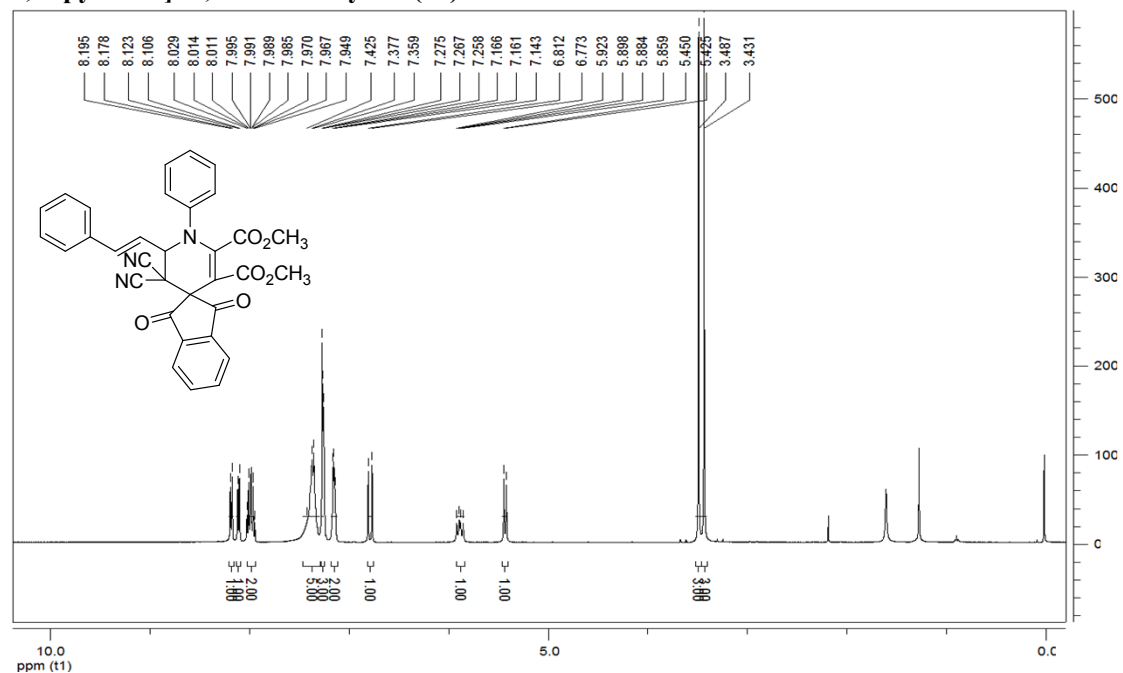
spiro[indoline-3,4'-pyridine]-5'-carboxylate (4f):



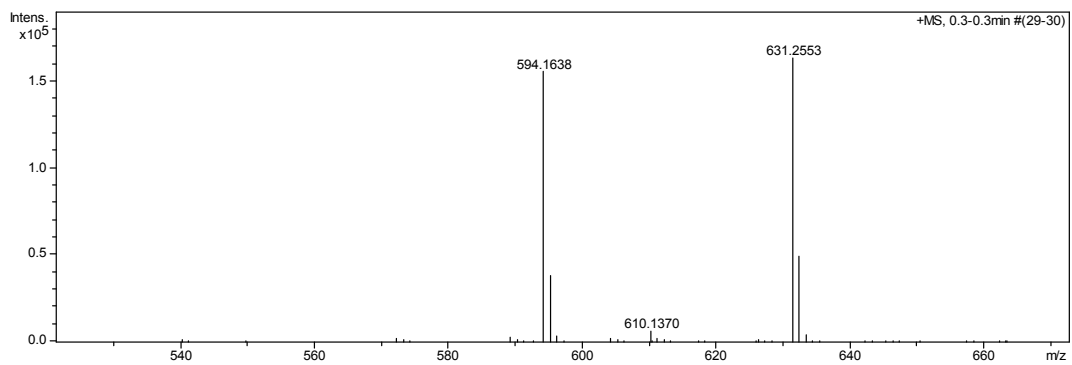
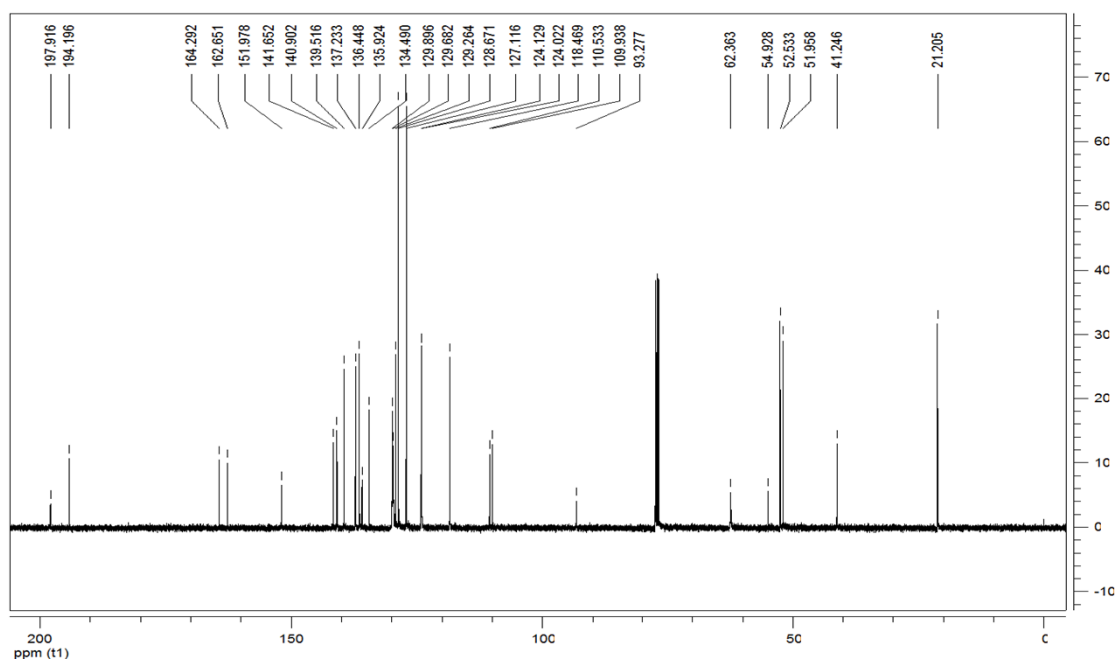
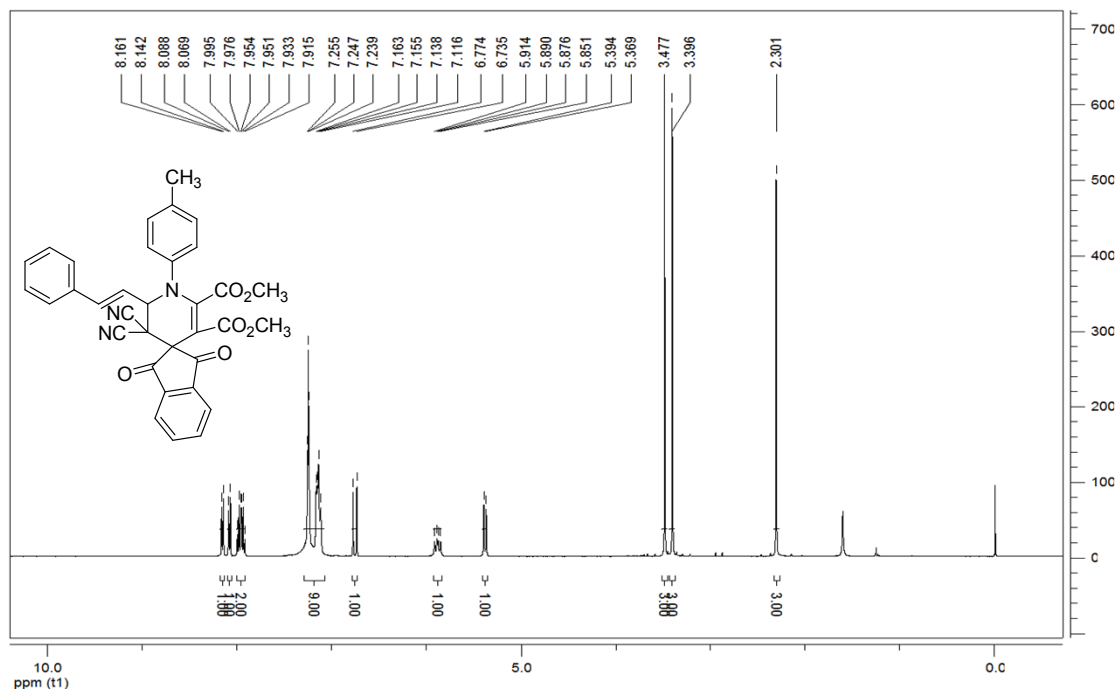
Methyl 1-benzyl-5-chloro-3',3'-dicyano-1'-(4-methylphenyl)-2'-(3-methylstyryl)-2-oxo-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-5'-carboxylate (4g):



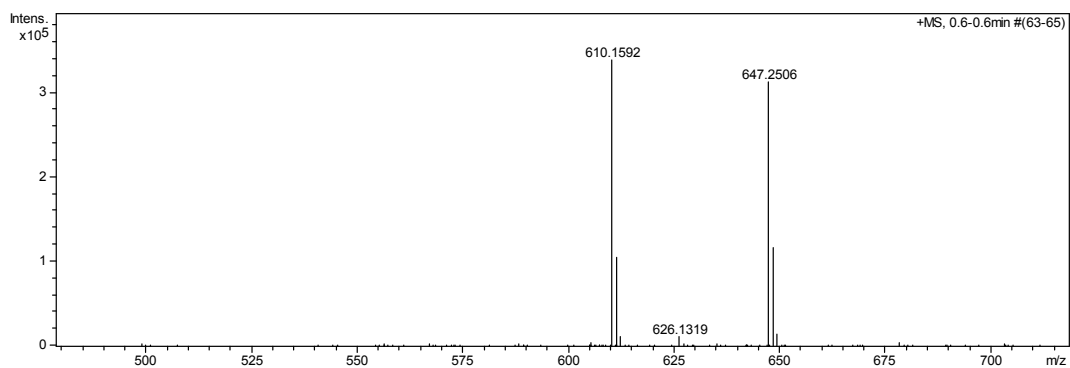
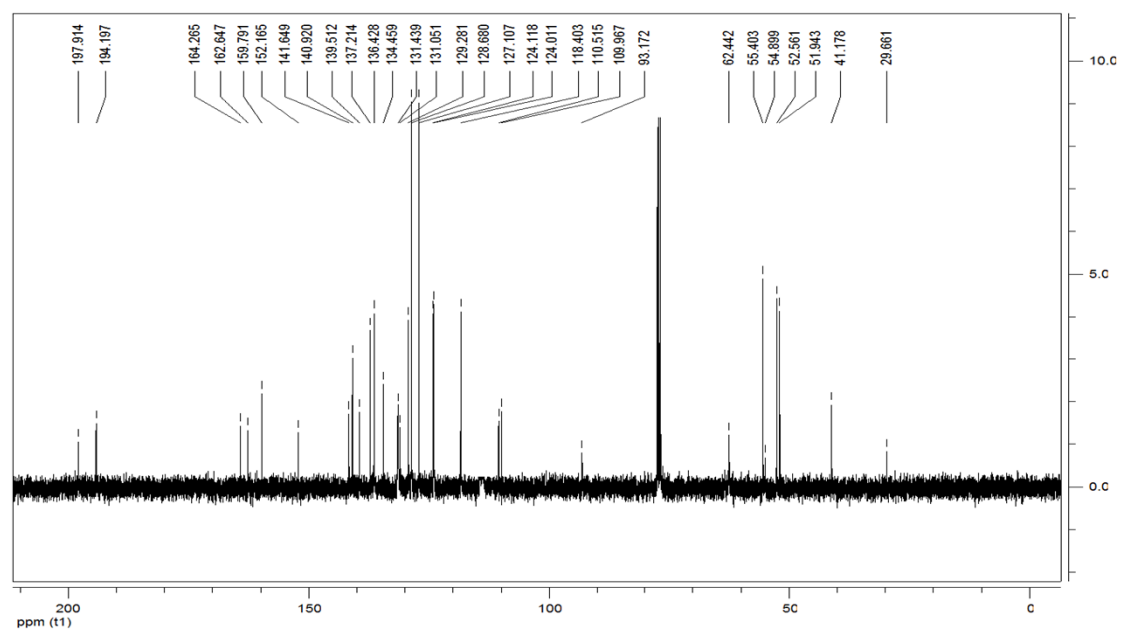
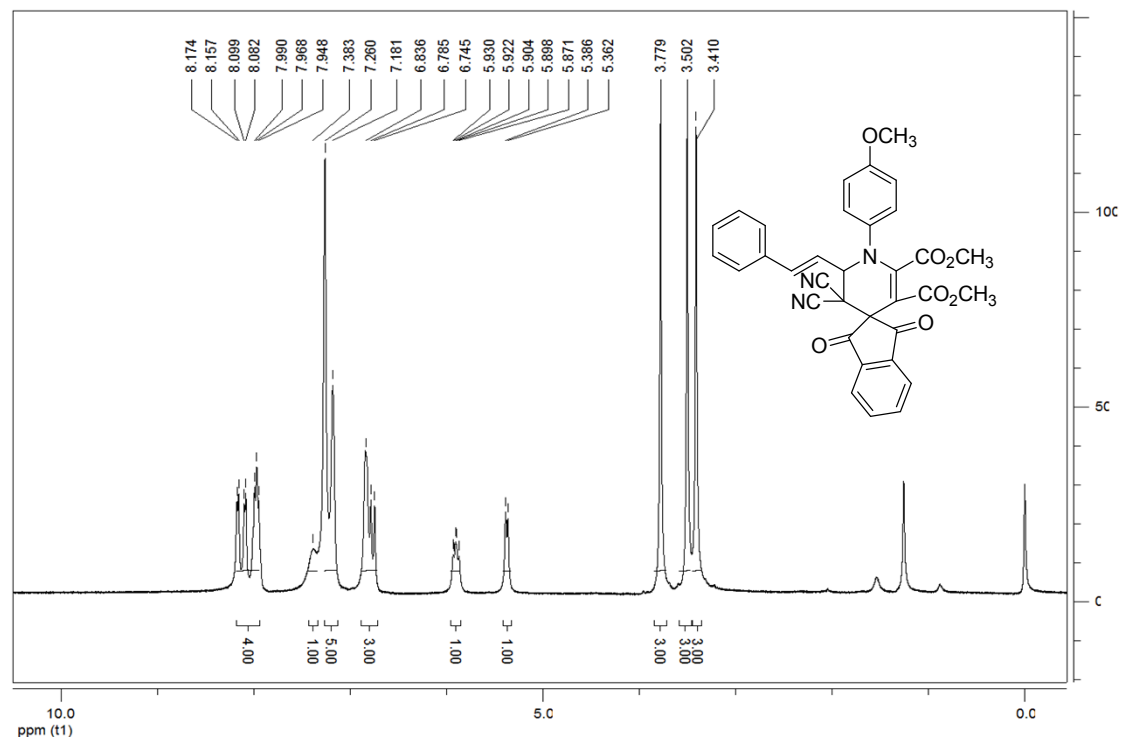
Dimethyl 3',3'-dicyano-1,3-dioxo-1'-phenyl-2'-styryl-1,2',3,3'-tetrahydro-1'H-spiro[indene-2,4'-pyridine]-5',6'-dicarboxylate (5a):



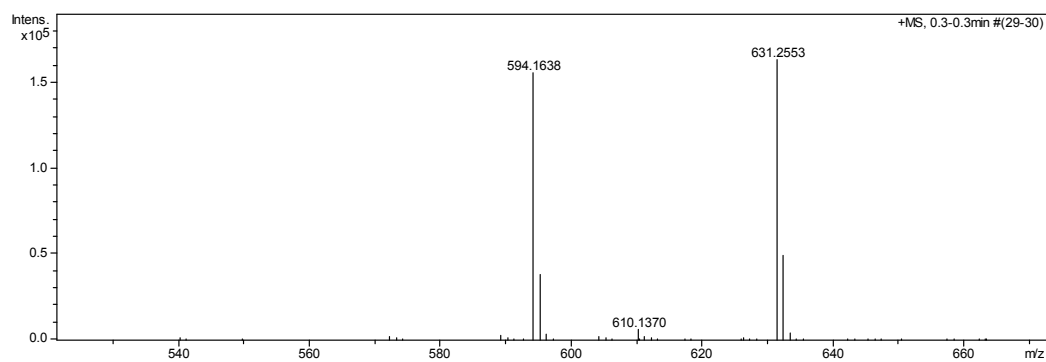
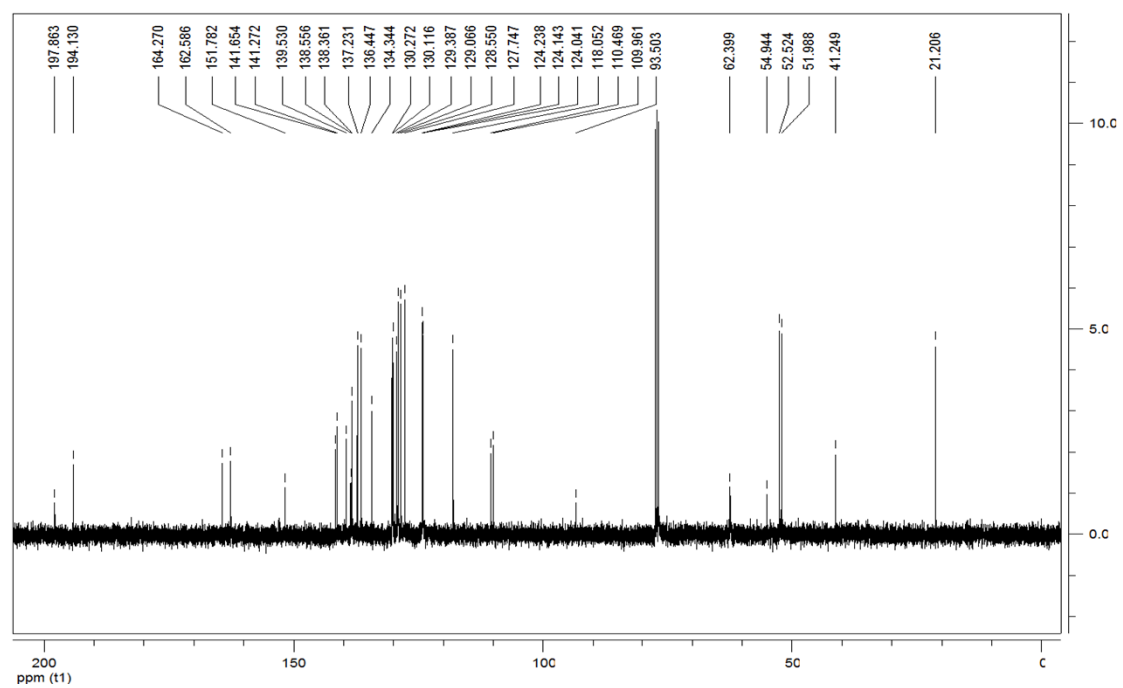
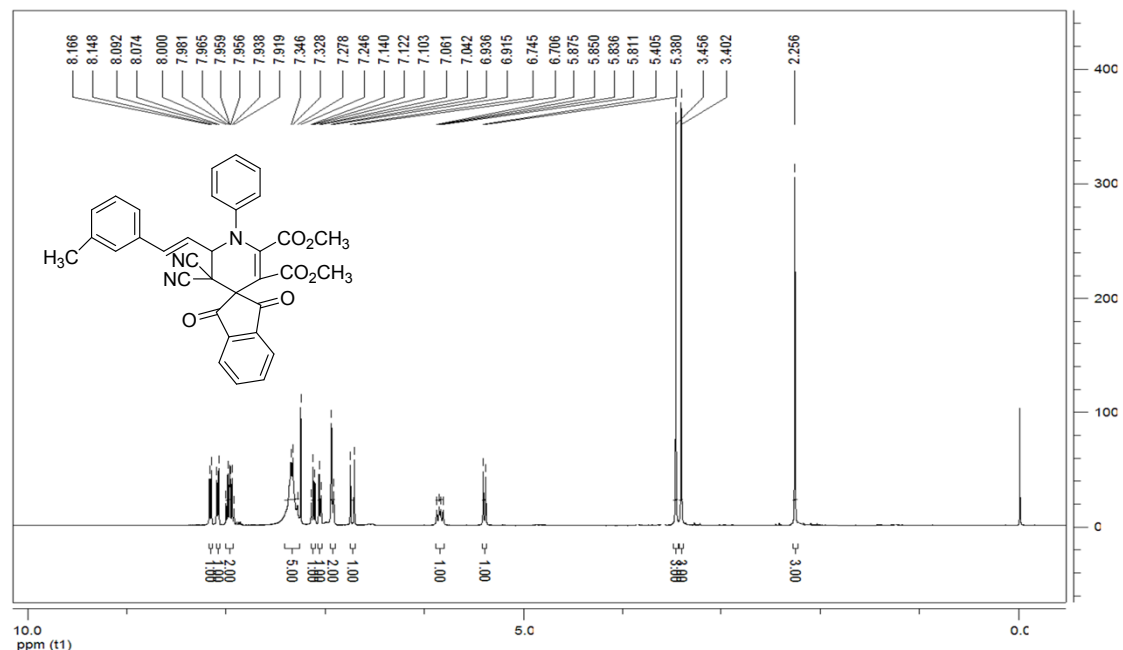
Dimethyl 3',3'-dicyano-1,3-dioxo-2'-styryl-1'-p-tolyl-1,2',3,3'-tetrahydro-1'H-spiro[indene-2,4'-pyridine]-5',6'-dicarboxylate (5b):



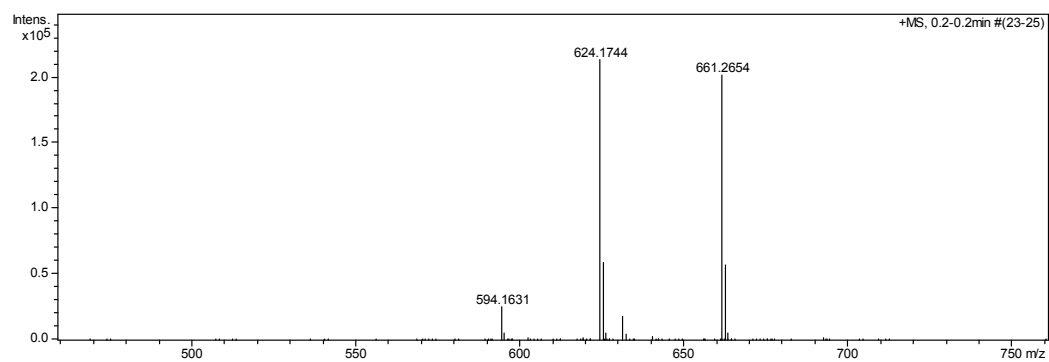
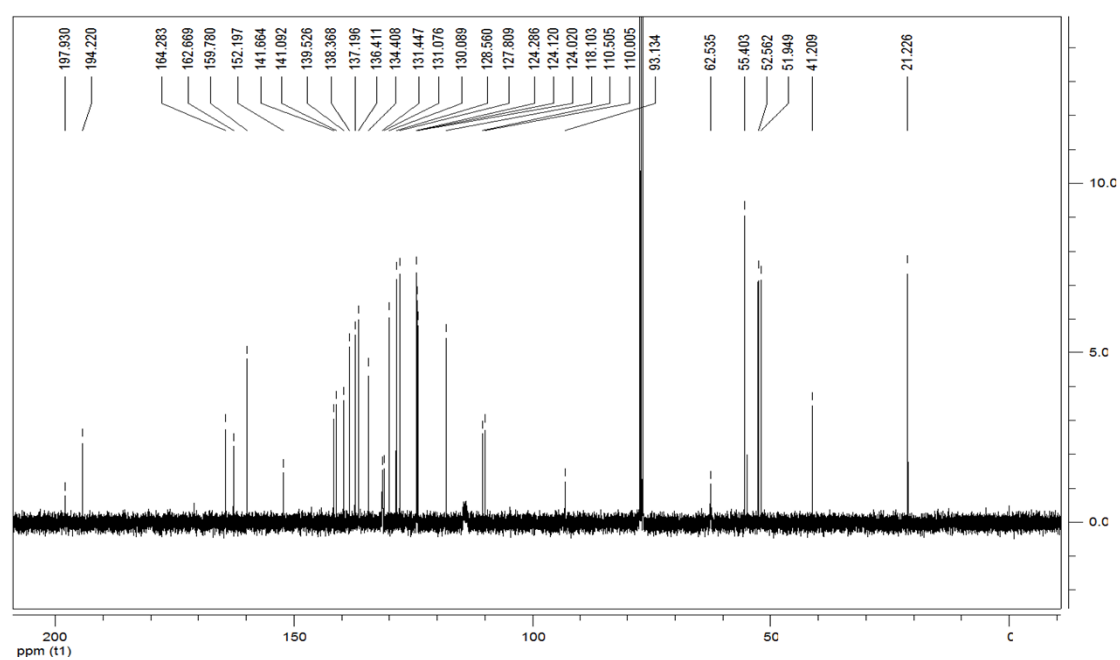
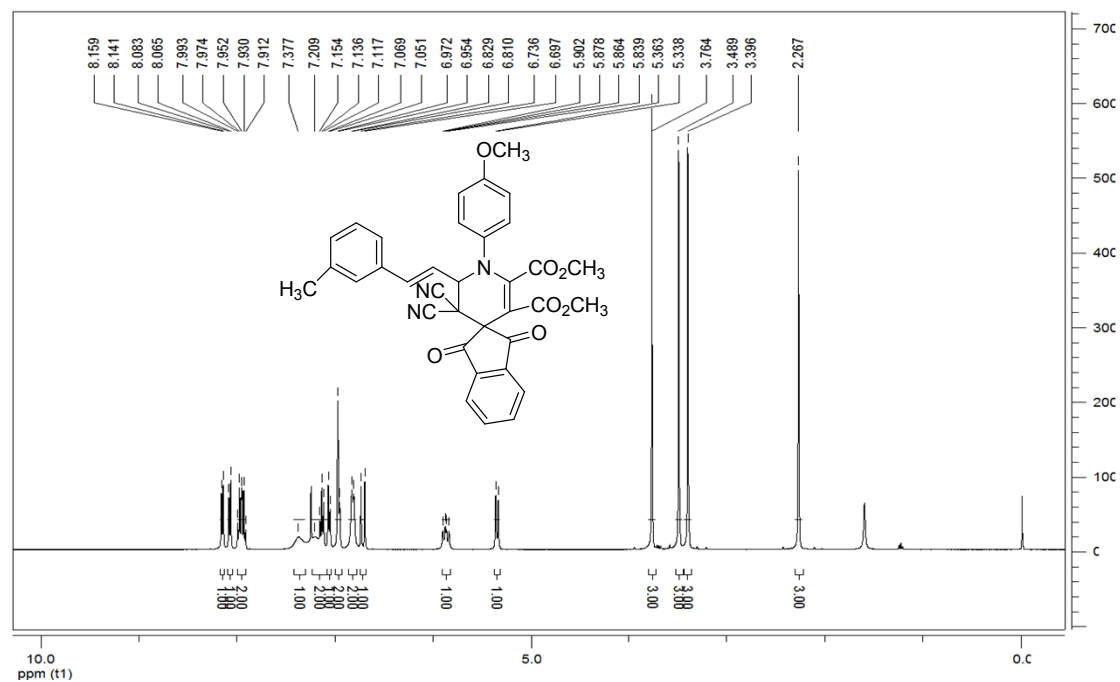
Dimethyl 3',3'-dicyano-1'-(4-methoxyphenyl)-1,3-dioxo-2'-styryl-1,2',3,3'-tetrahydro-1'H-spiro[indene-2,4'-pyridine]-5',6'-dicarboxylate (5c):



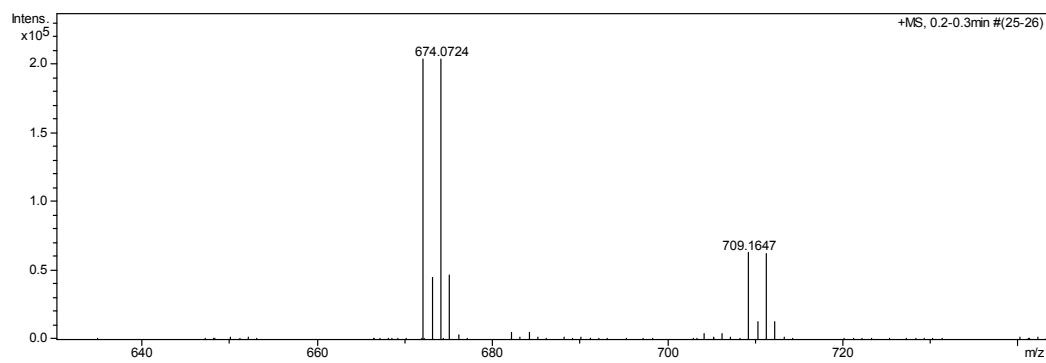
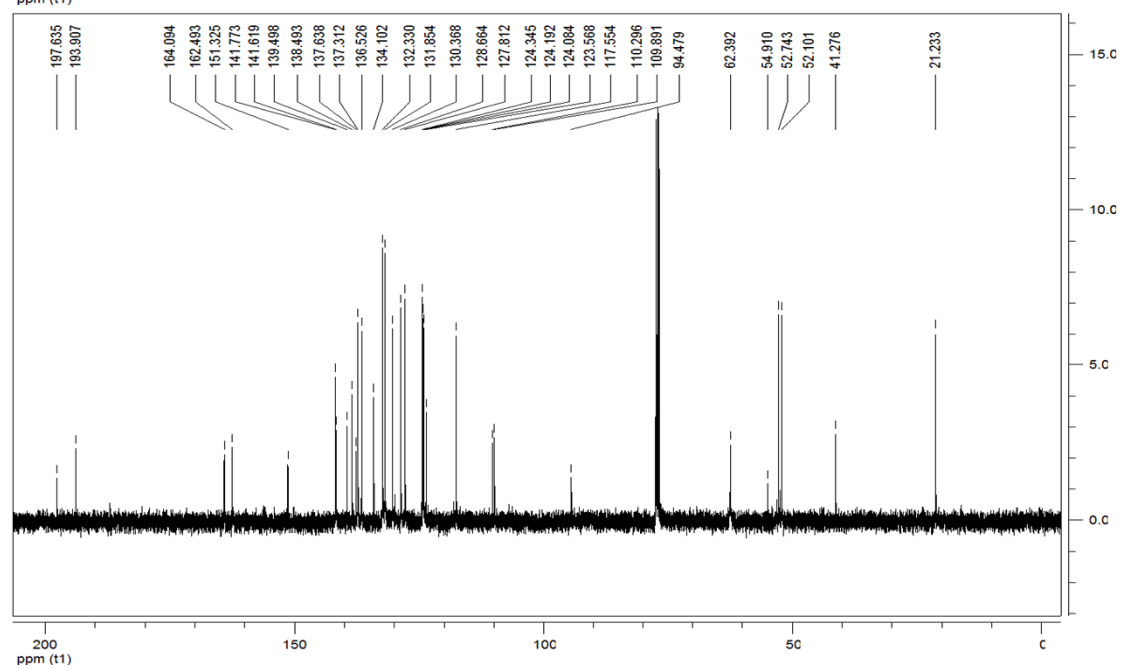
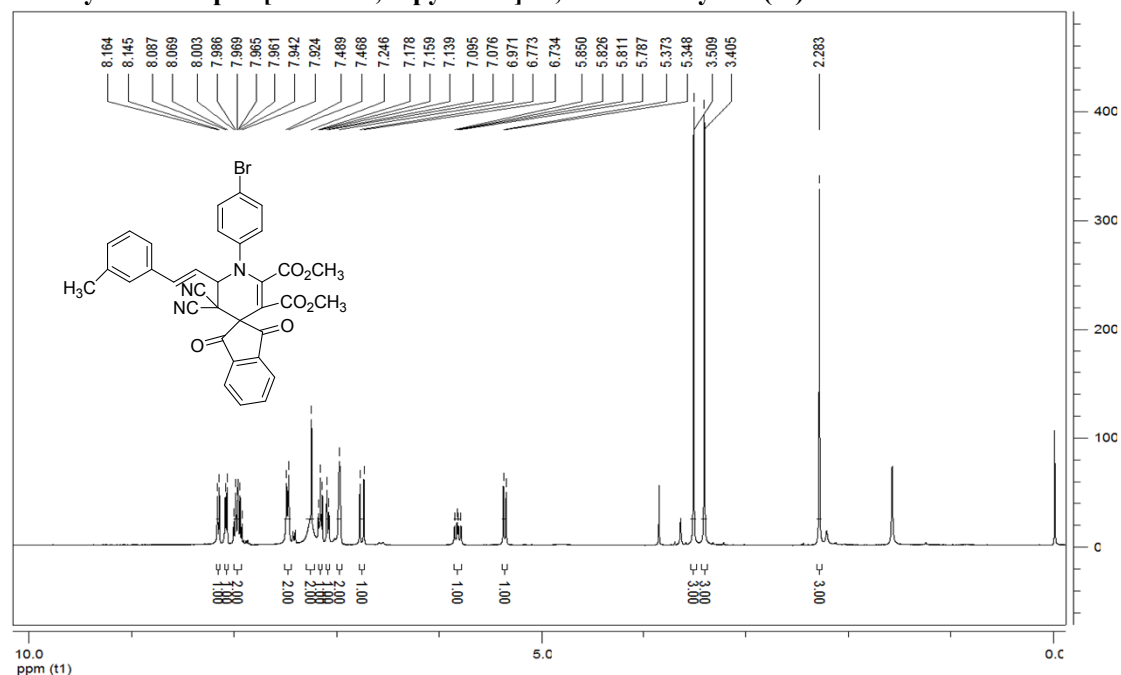
Dimethyl 3',3'-dicyano-2'-(3-methylstyryl)-1,3-dioxo-1'-phenyl-1,2',3,3'-tetrahydro-1'H-spiro[indene-2,4'-pyridine]-5',6'-dicarboxylate (5d):

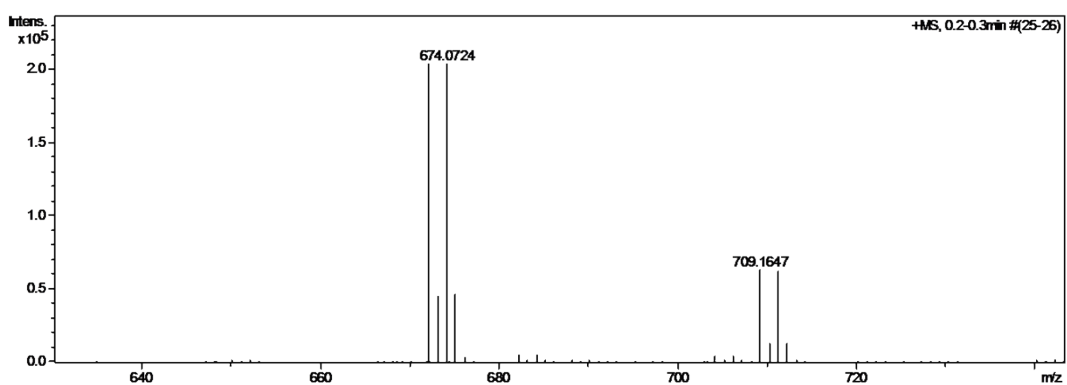
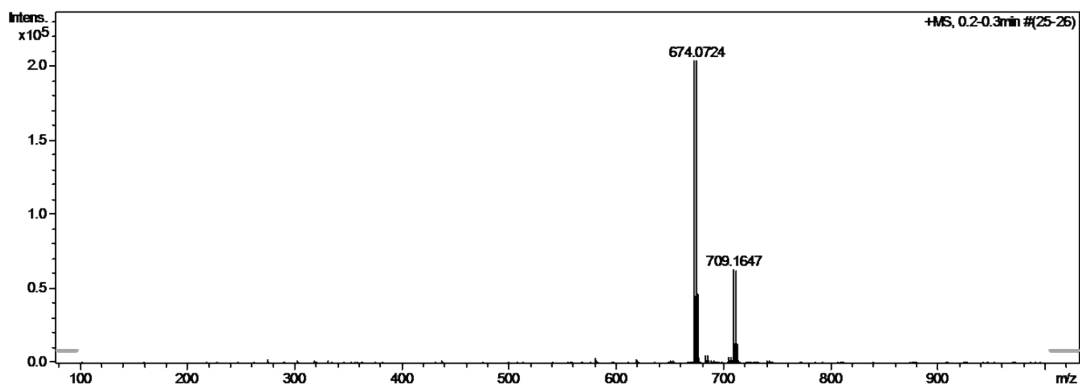


Dimethyl 3',3'-dicyano-1'-(4-methoxyphenyl)-2'-(3-methylstyryl)-1,3-dioxo-1,2',3,3'-tetrahydro-1'H-spiro[indene-2,4'-pyridine]-5',6'-dicarboxylate (5e):



Dimethyl 1'-(4-bromophenyl)-3',3'-dicyano-2'-(3-methylstyryl)-1,3-dioxo-1,2',3,3'-tetrahydro-1'H-spiro[indene-2,4'-pyridine]-5',6'-dicarboxylate (5f):





Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
672.0738	1	C 15 H 16 Br N 21 Na O 5	46.96	672.0719	-1.9	-2.9	14.3	17.5	even	ok
	2	C 18 H 24 Br N 11 Na O 11	100	672.0732	-0.6	-0.9	18.2	11.5	even	ok
	3	C 17 H 28 Br N 7 Na O 15	42.93	672.0719	-1.9	-2.9	19.1	6.5	even	ok
	4	C 21 H 32 Br N Na O 17	79.66	672.0746	0.8	1.1	24.6	5.5	even	ok
	5	C 19 H 20 Br N 15 Na O 7	75.83	672.0746	0.7	1.1	27	16.5	even	ok
	6	C 16 H 12 Br N 25 Na O	81.2	672.0732	-0.6	-0.9	27.4	22.5	even	ok
	7	C ₃₄ H ₂₄ Br ₃ Na ₆ O ₆	13.23	672.0741	0.2	0.4	87.3	23.5	even	ok
	8	C 31 H 16 Br N 13 Na	8.13	672.0727	-1.1	-1.6	88.5	29.5	even	ok
	9	C 35 H 20 Br N 7 Na O 2	3.57	672.0754	1.6	2.4	99.8	28.5	even	ok

