

## Supporting information

### Unexpected regiospecific Michael addition Product: 5,6-dihydrobenzo[1,7]phenanthroline synthesis

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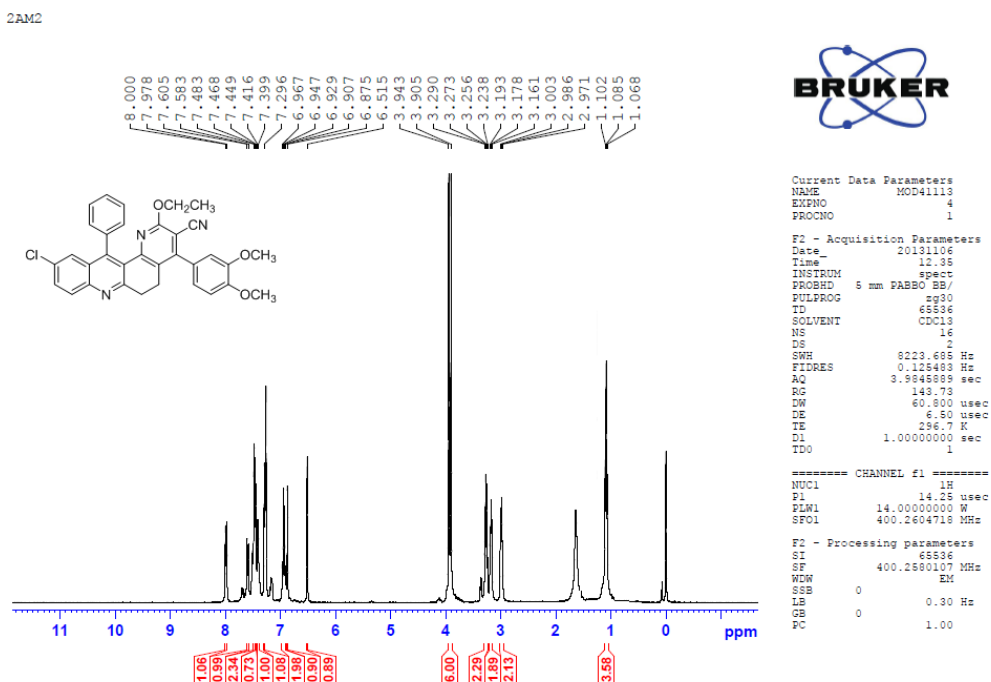
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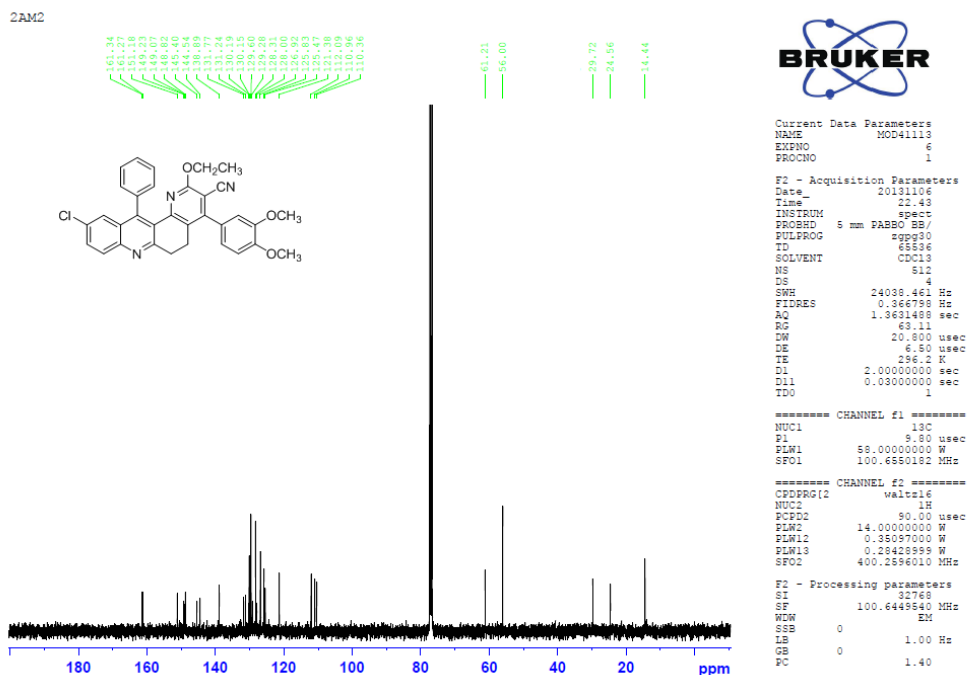
**Table S1.** Crystallographic data of 10-chloro-4-(4-chlorophenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5**):

Empirical formula	C <sub>30</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>2</sub> O
Formula weight	497.40
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 11.3697(2) Å    α = 90 ° b = 28.8078(5) Å    β = 98.4130(10) ° c = 15.2132(3) Å    γ = 90 °
Volume	4929.25(16) Å <sup>3</sup>
Z, Calculated density	8, 1.340 Mg/m <sup>3</sup>
Absorption coefficient	0.290 mm <sup>-1</sup>
F(000)	2064
Crystal size	0.35 x 0.30 x 0.30 mm
Theta range for data collection	2.21- 25.00 °
Limiting indices	-13<=h<=13, -25<=k<=34, -18<=l<=18
Reflections collected / unique	45391 / 8675 [R(int) = 0.0351]
Completeness to theta = 25.00 °	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9568 and 0.9021
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	8675 / 0 / 632
Goodness-of-fit on F <sup>2</sup>	1.021
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0379, wR <sub>2</sub> = 0.0888
R indices (all data)	R <sub>1</sub> = 0.0599, wR <sub>2</sub> = 0.1025
Extinction coefficient	0.0024(2)
Largest diff. peak and hole	0.257 and -0.333 e.Å <sup>-3</sup>

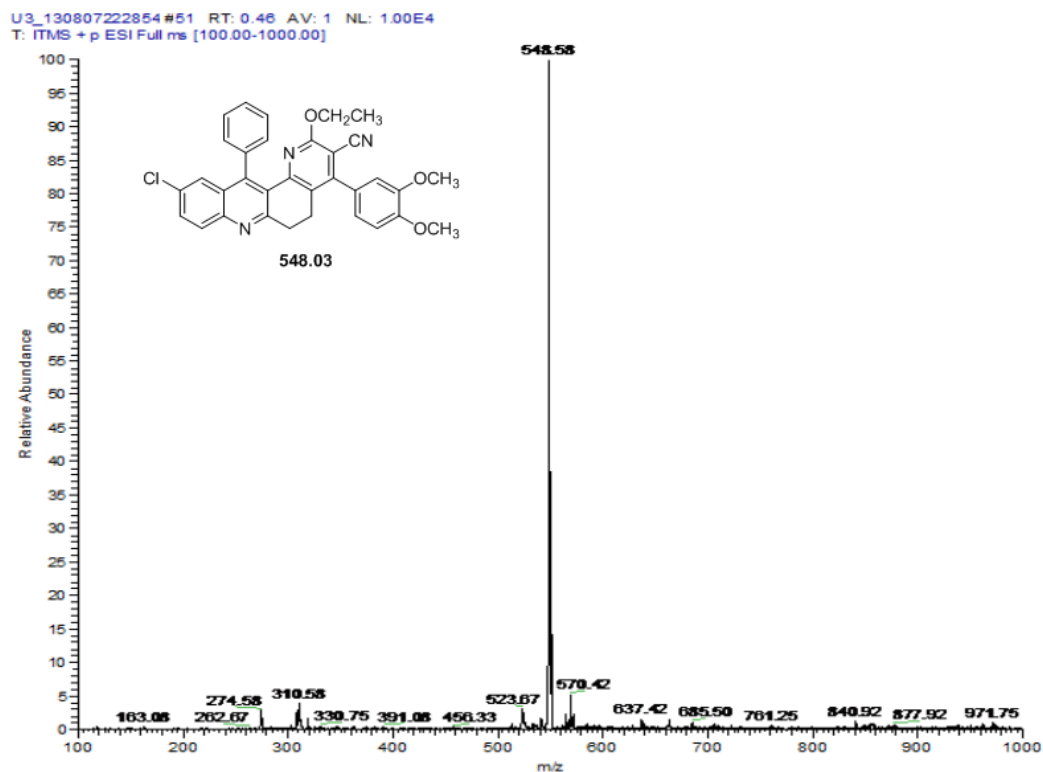
**Fig 1.**  $^1\text{H}$  NMR spectrum of 10-chloro-4-(3,4-dimethoxyphenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline-3-carbonitrile (**4a**)



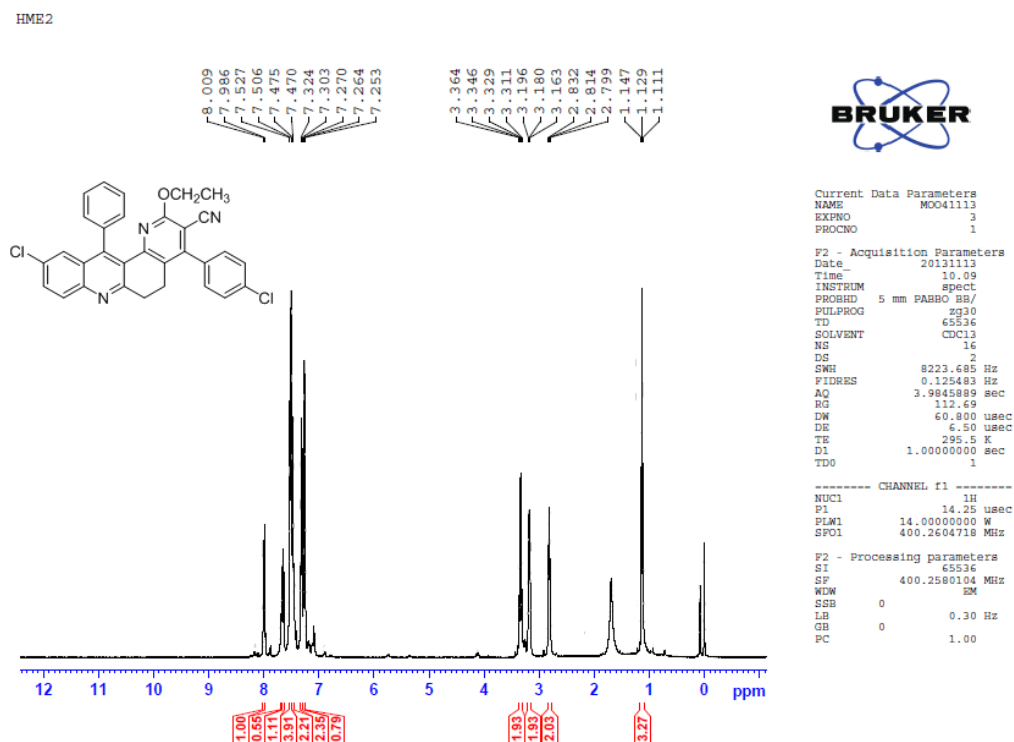
**Fig 2.**  $^{13}\text{C}$  NMR spectrum of 10-chloro-4-(3,4-dimethoxyphenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline-3-carbonitrile (**4a**)



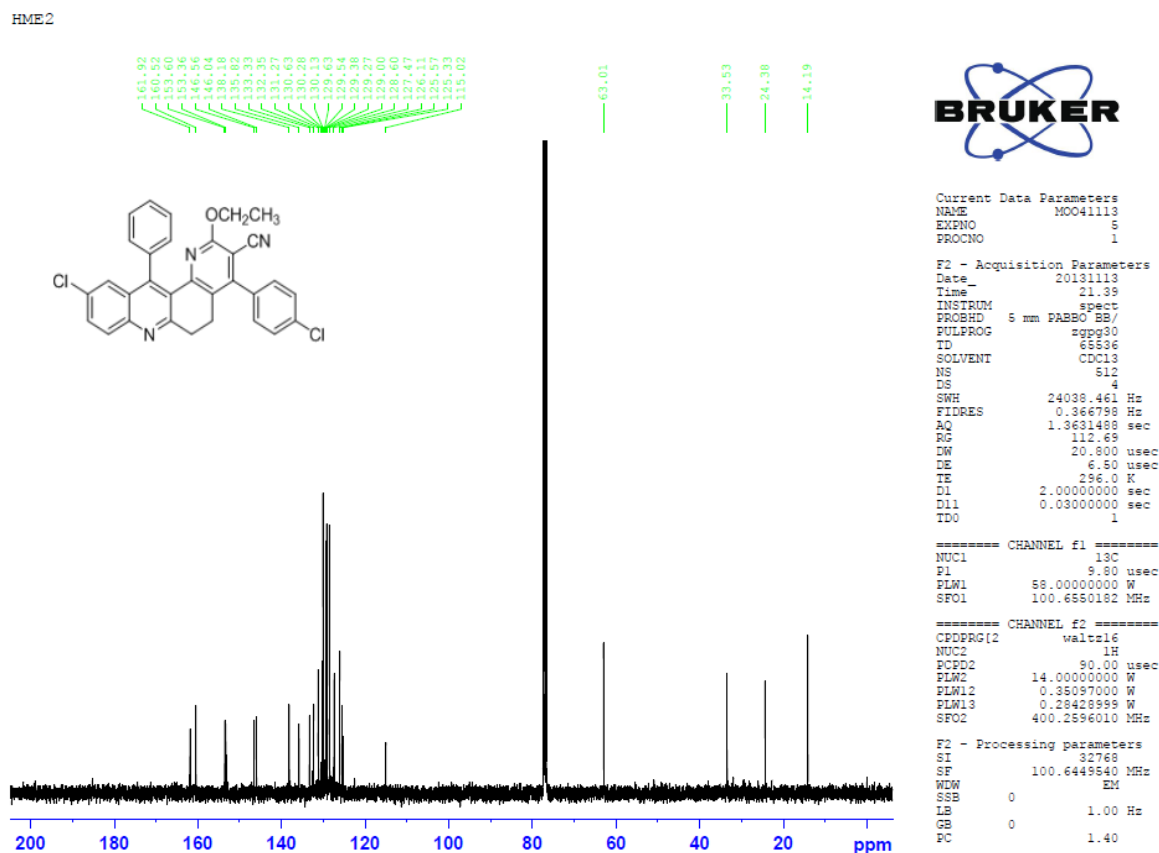
**Fig 3.** ESI-MS spectrum of 10-chloro-4-(3,4-dimethoxyphenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline-3-carbonitrile (**4a**)



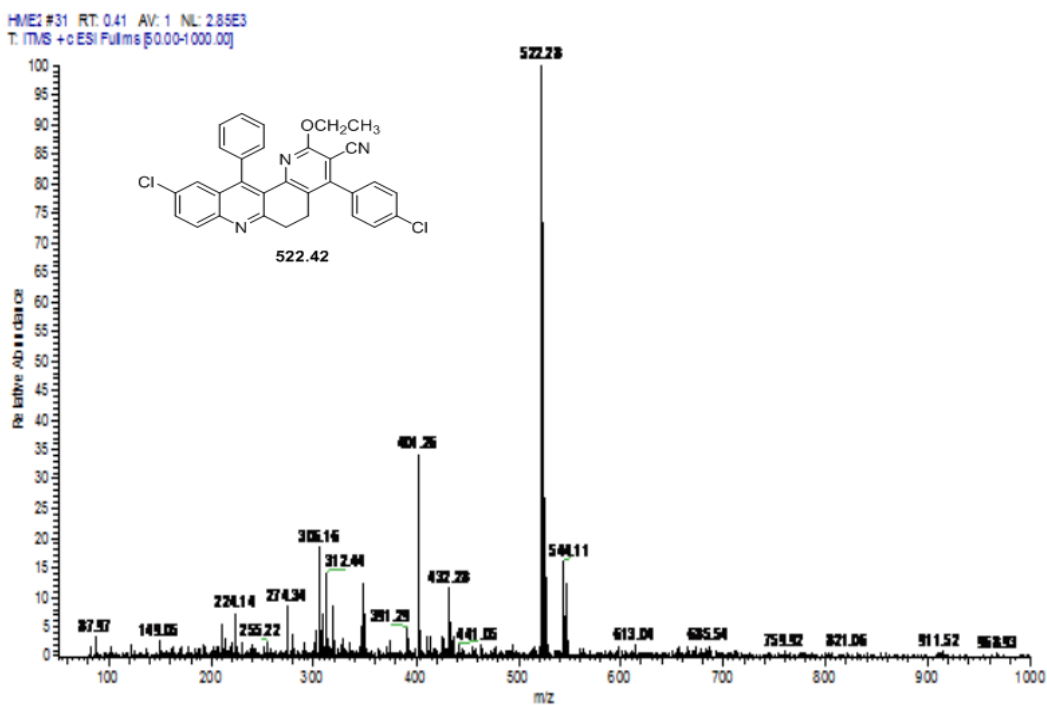
**Fig 4.** <sup>1</sup>H NMR spectrum of 10-chloro-4-(4-chlorophenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline-3-carbonitrile (**4b**)



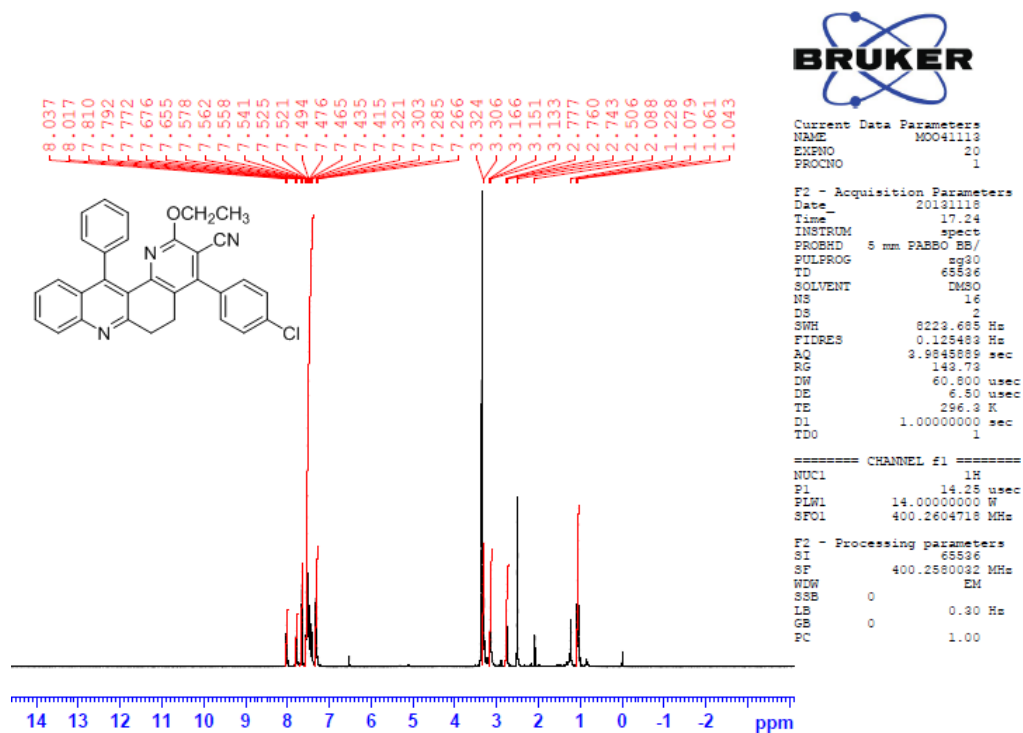
**Fig 5.**  $^{13}\text{C}$  NMR spectrum of 10-chloro-4-(4-chlorophenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline-3-carbonitrile (**4b**)



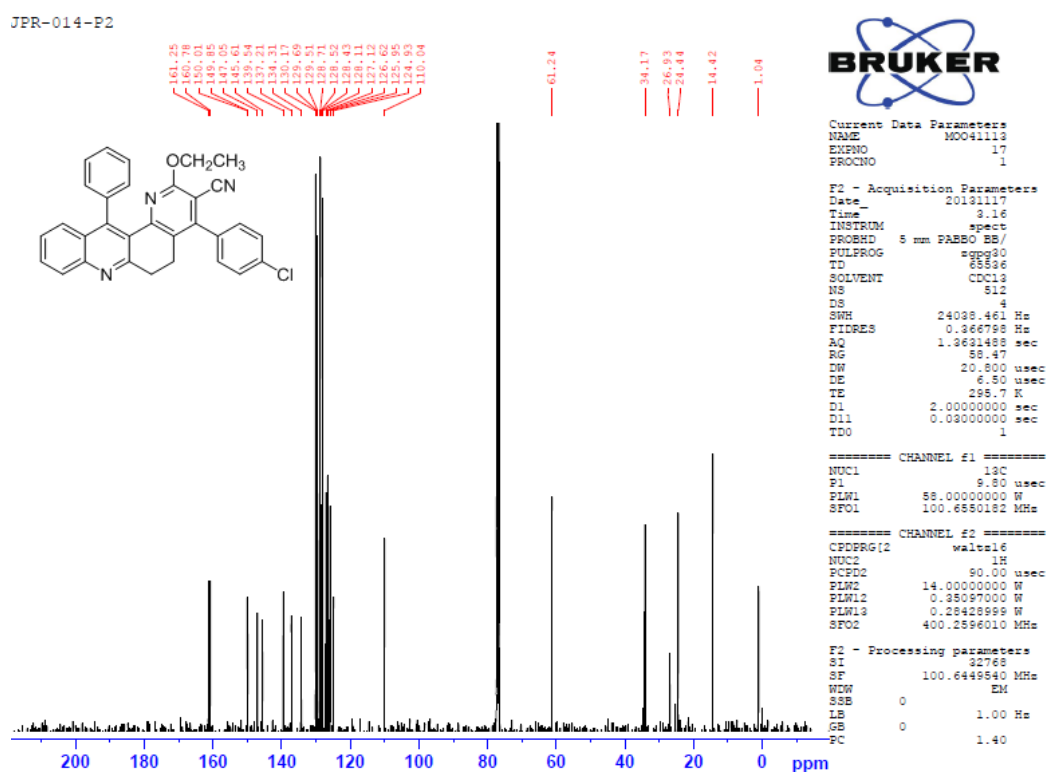
**Fig 6.** ESI-MS spectrum of 10-chloro-4-(4-chlorophenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline-3-carbonitrile (**4b**)



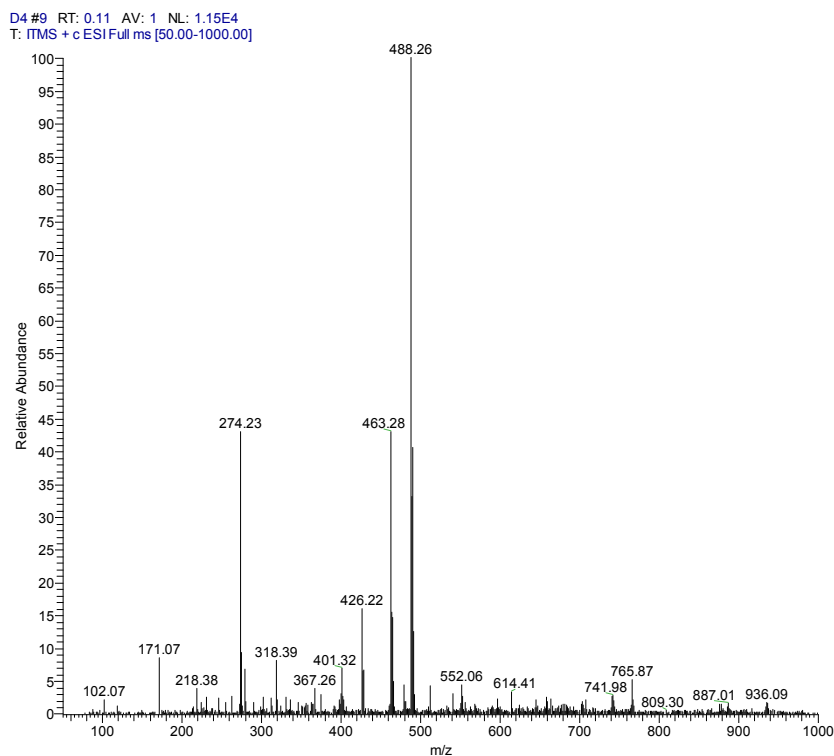
**Fig 7.**  $^1\text{H}$  NMR spectrum of 4-(4-Chloro-phenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline-3-carbonitrile (**4c**):



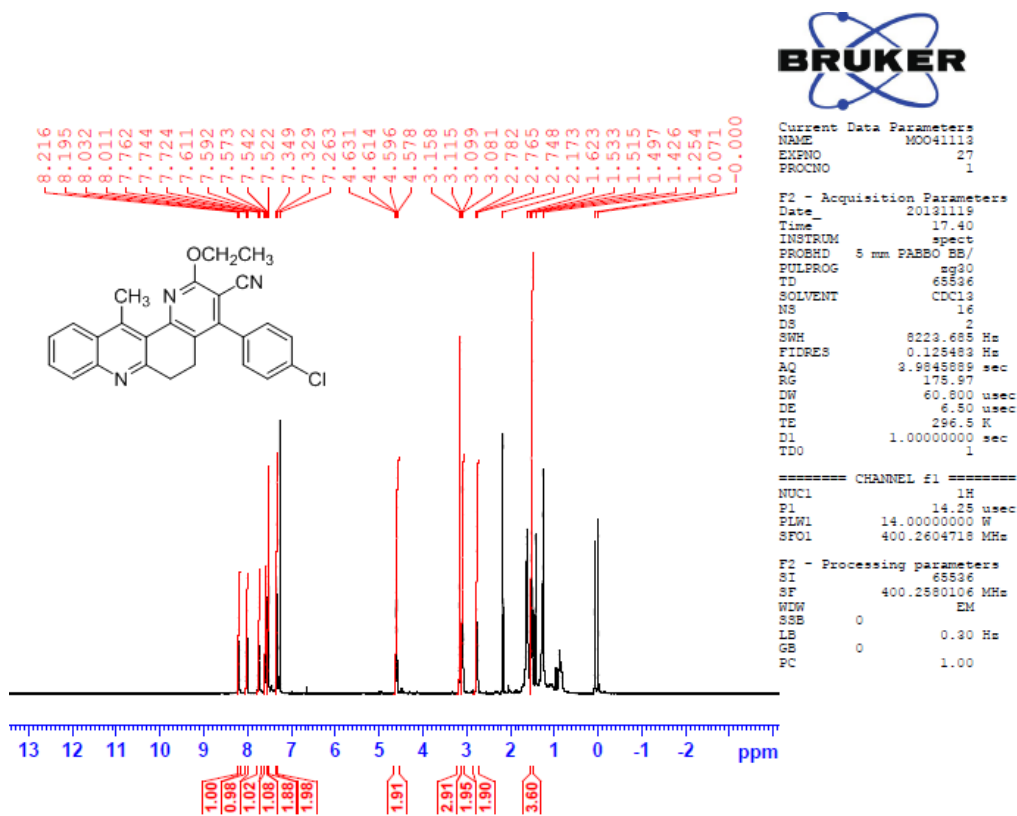
**Fig 8.**  $^{13}\text{C}$  NMR spectrum of 4-(4-Chloro-phenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7] phenanthroline-3-carbonitrile (**4c**):



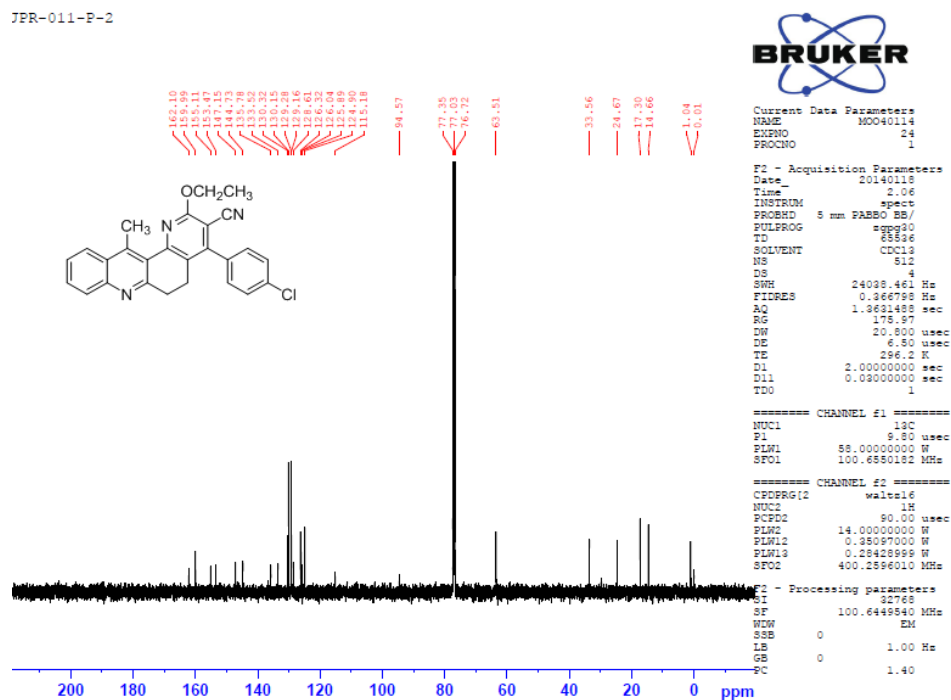
**Fig 9.** ESI-MS spectrum of 4-(4-Chloro-phenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7] phenanthroline-3-carbonitrile (**4c**):



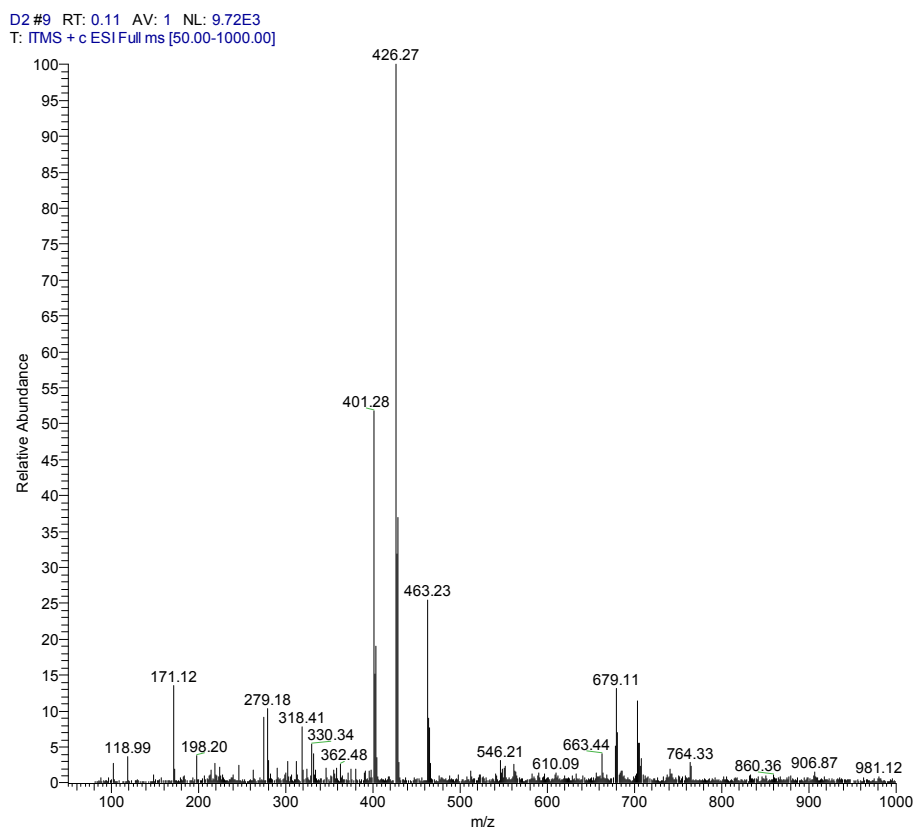
**Fig 10.** <sup>1</sup>H NMR spectrum of 4-(4-Chloro-phenyl)-2-ethoxy-12-methyl-5,6-dihydrobenzo[*j*][1,7] phenanthroline-3-carbonitrile (**4d**):



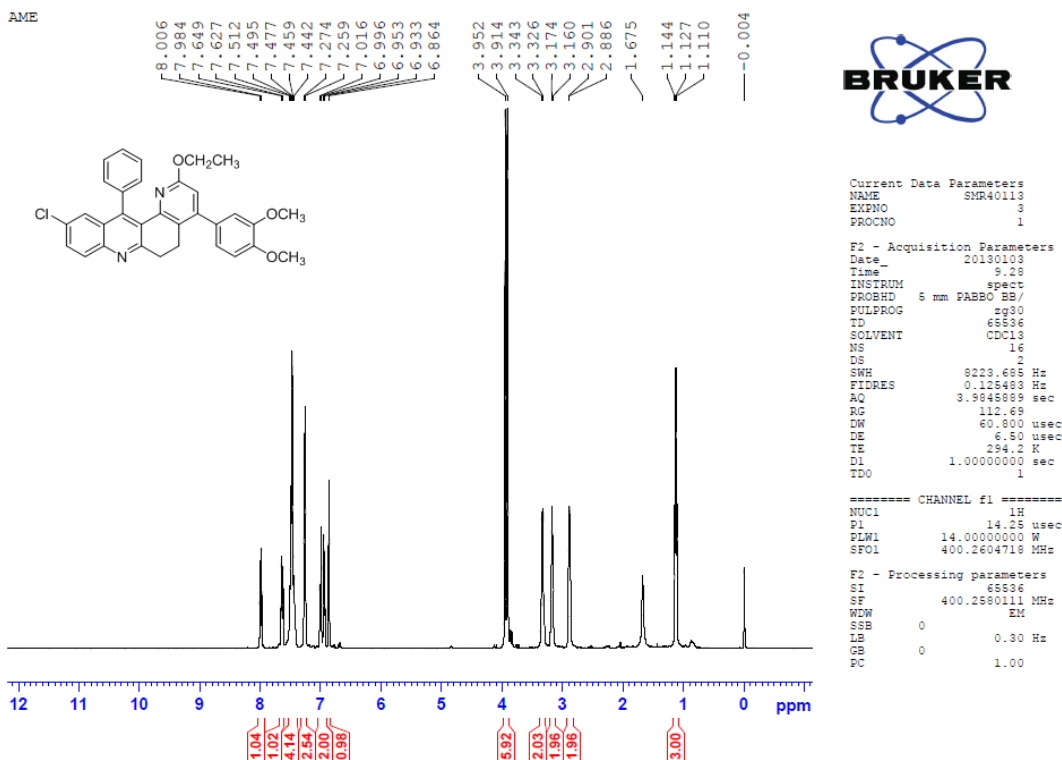
**Fig 11.**  $^{13}\text{C}$  NMR spectrum of 4-(4-Chloro-phenyl)-2-ethoxy-12-methyl-5,6-dihydrobenzo[*j*][1,7] phenanthroline-3-carbonitrile (**4d**):



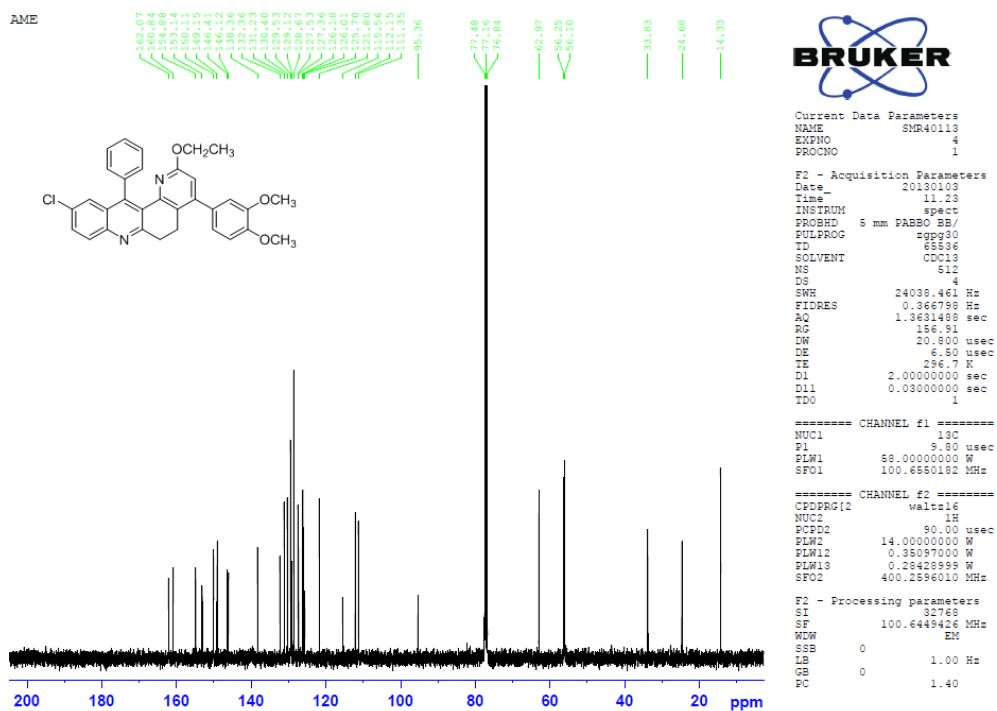
**Fig 12.** ESI-MS spectrum of 4-(4-Chloro-phenyl)-2-ethoxy-12-methyl-5,6-dihydrobenzo[*j*][1,7] phenanthroline-3-carbonitrile (**4d**):



**Fig 13.**  $^1\text{H}$  NMR spectrum of 10-chloro-4-(3,4-dimethoxyphenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5a**)

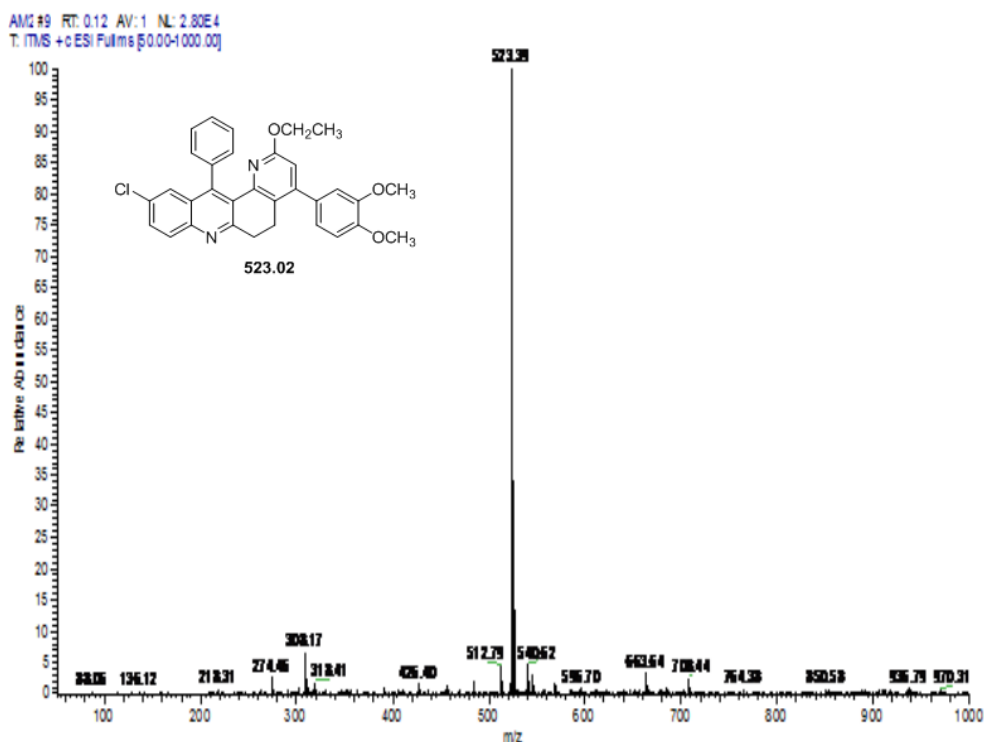


**Fig 14.**  $^{13}\text{C}$  NMR spectrum of 10-chloro-4-(3,4-dimethoxyphenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5a**)

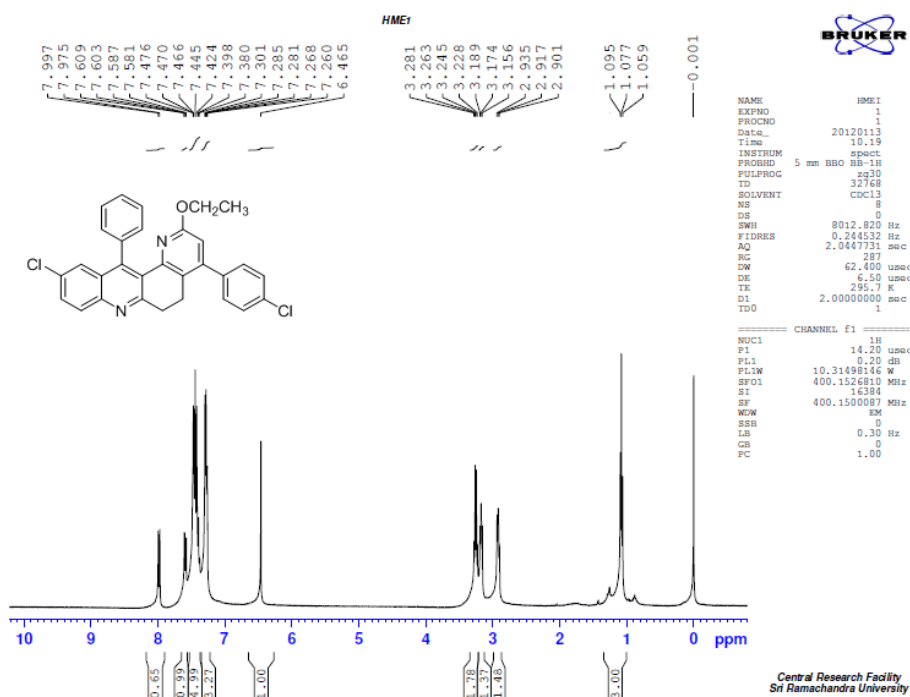




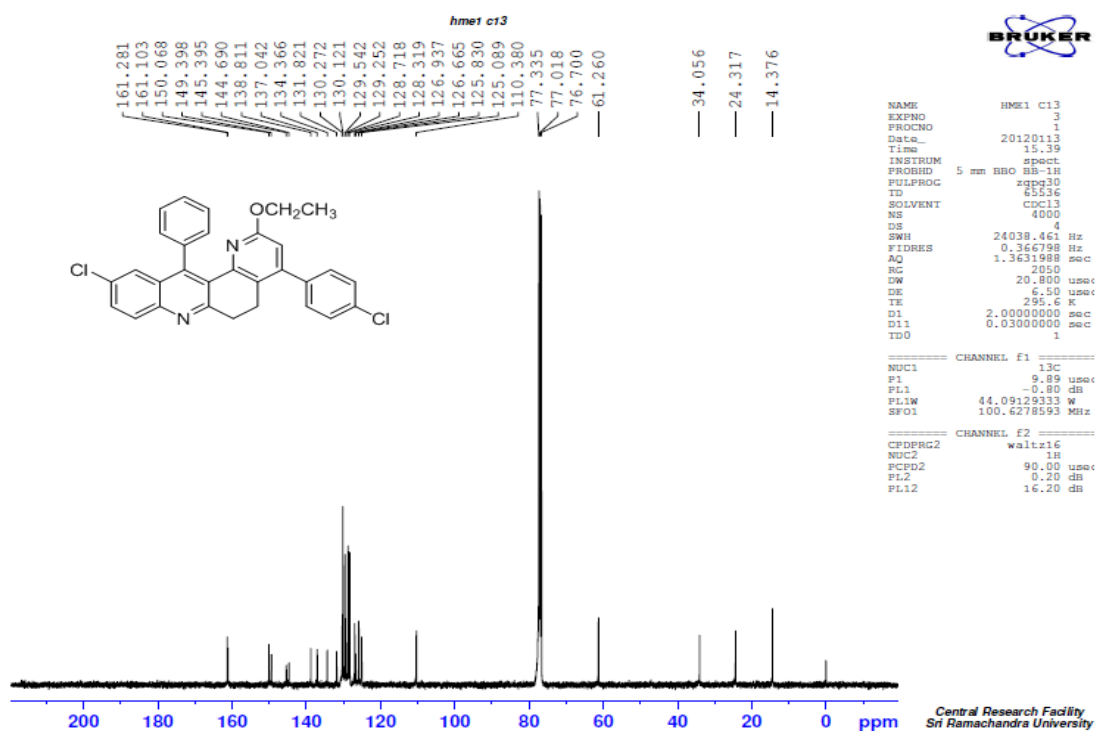
**Fig 15.** ESI-MS spectrum of 10-chloro-4-(3,4-dimethoxyphenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5a**)



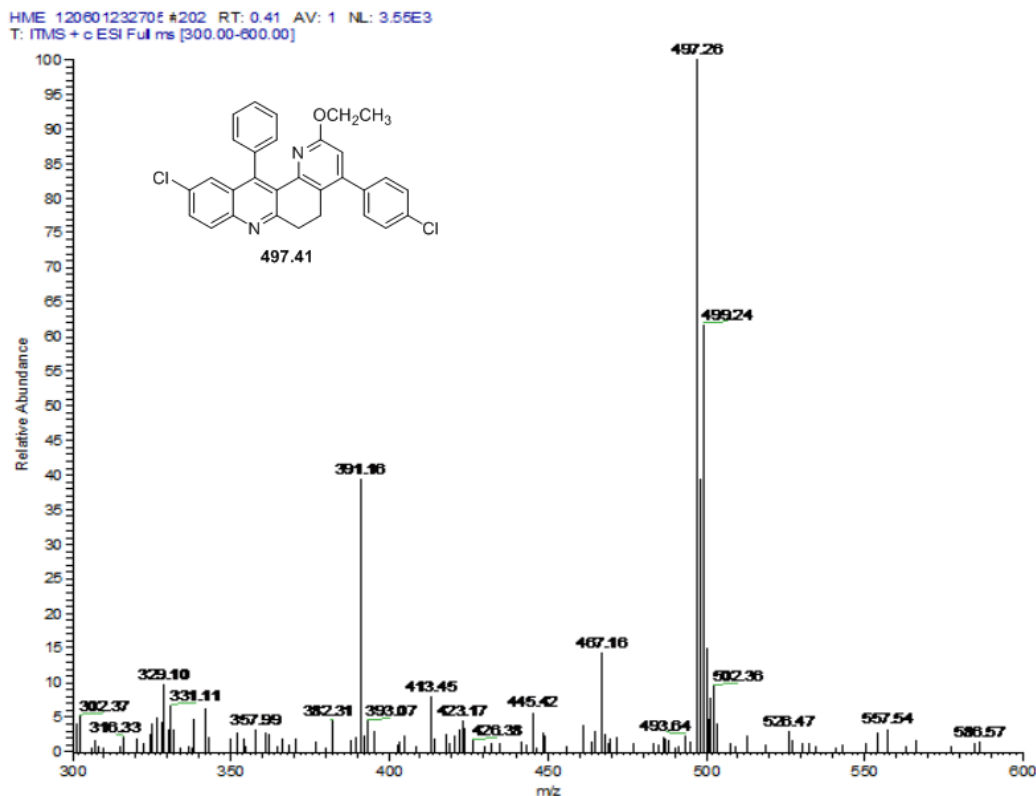
**Fig 16.** <sup>1</sup>H NMR spectrum of 10-chloro-4-(4-chlorophenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5b**)



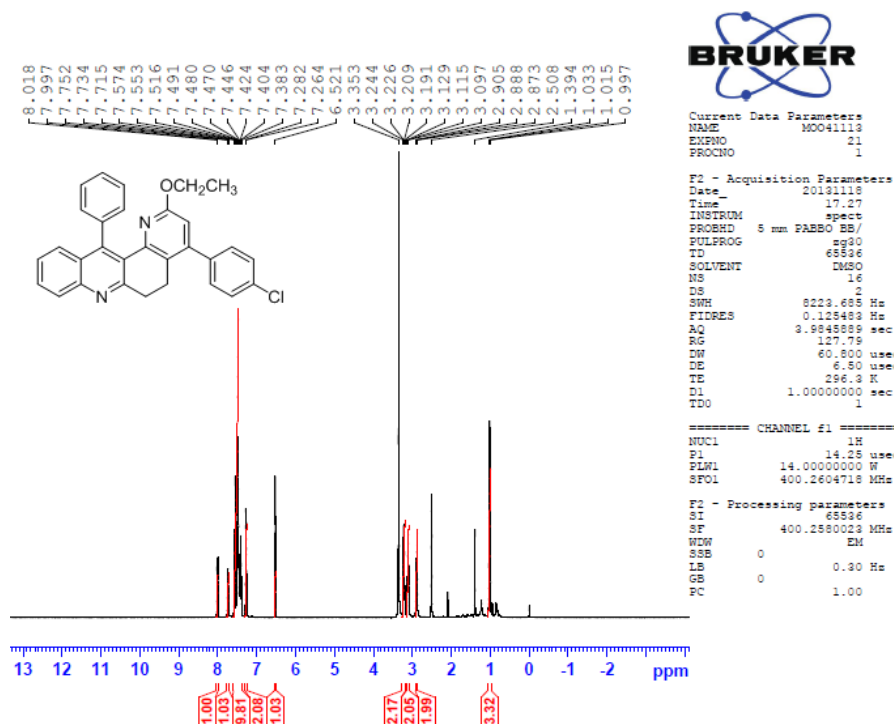
**Fig 17.**  $^1\text{H}$  NMR spectrum of 10-chloro-4-(4-chlorophenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5b**)



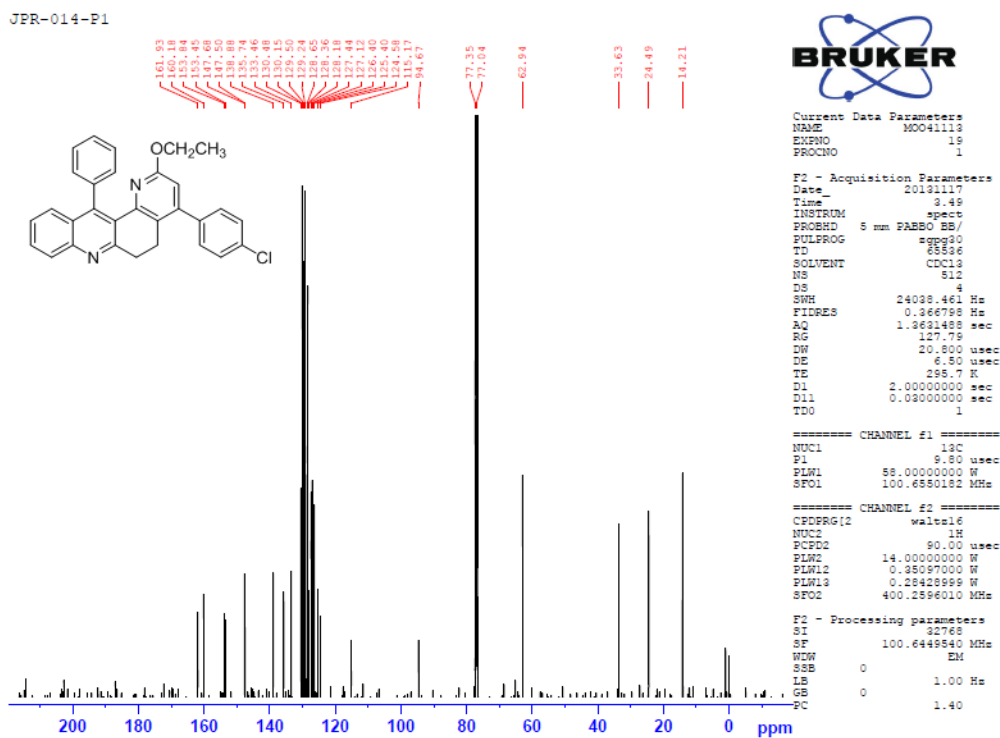
**Fig 18.** ESI-MS spectrum of 10-chloro-4-(4-chlorophenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5b**)



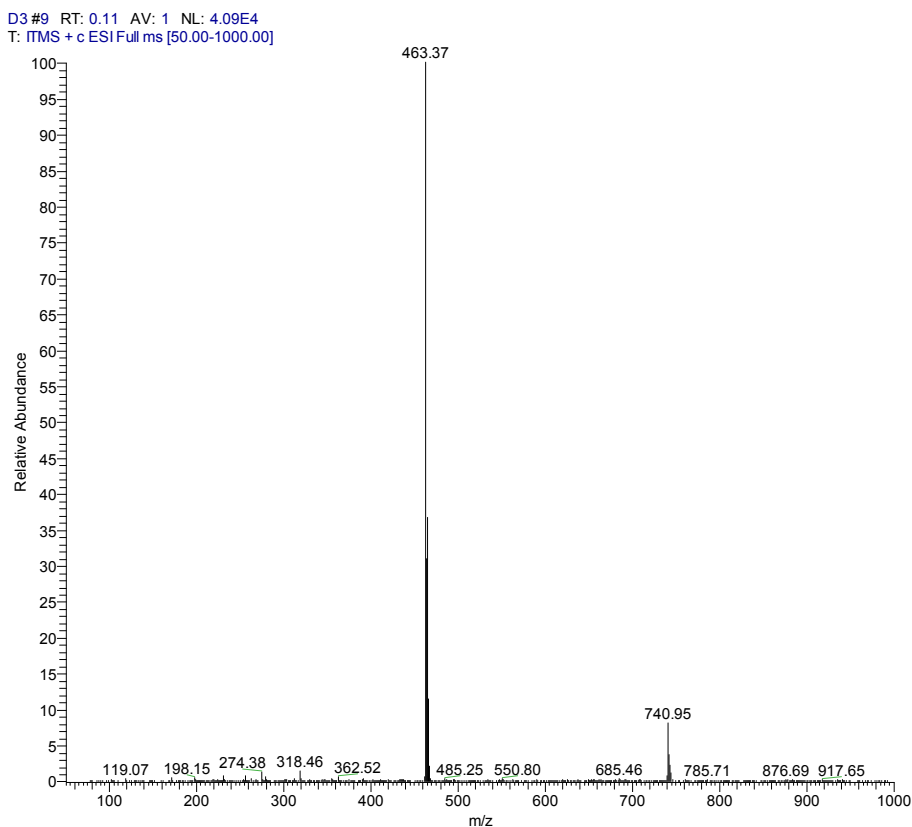
**Fig 19.**  $^1\text{H}$  NMR spectrum of 4-(4-Chloro-phenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5c**):



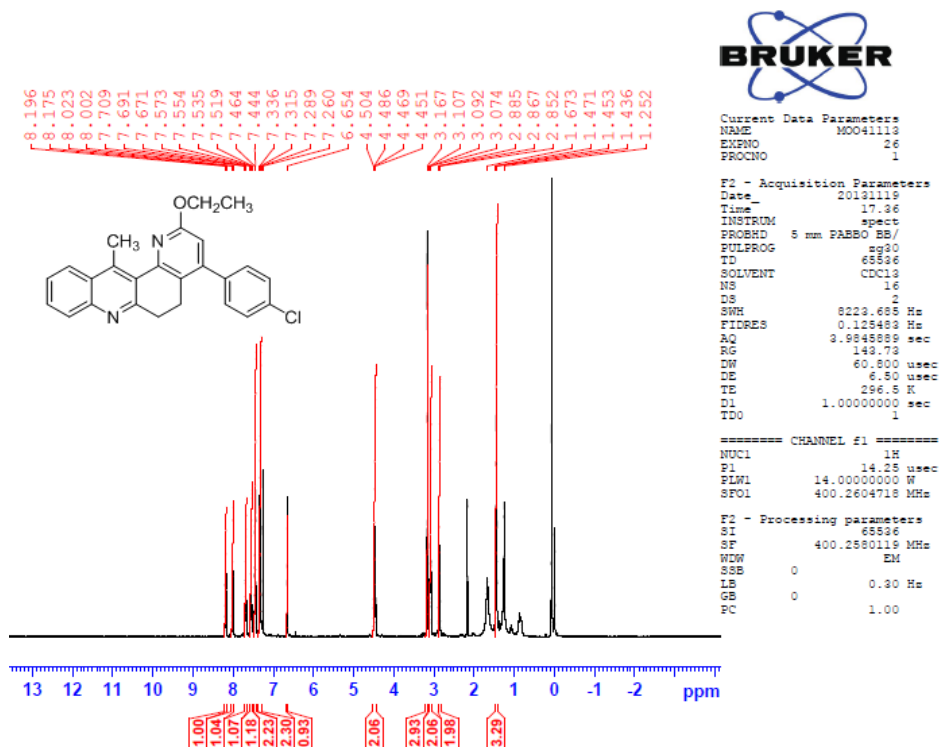
**Fig 20.**  $^{13}\text{C}$  NMR spectrum of 4-(4-Chloro-phenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5c**):



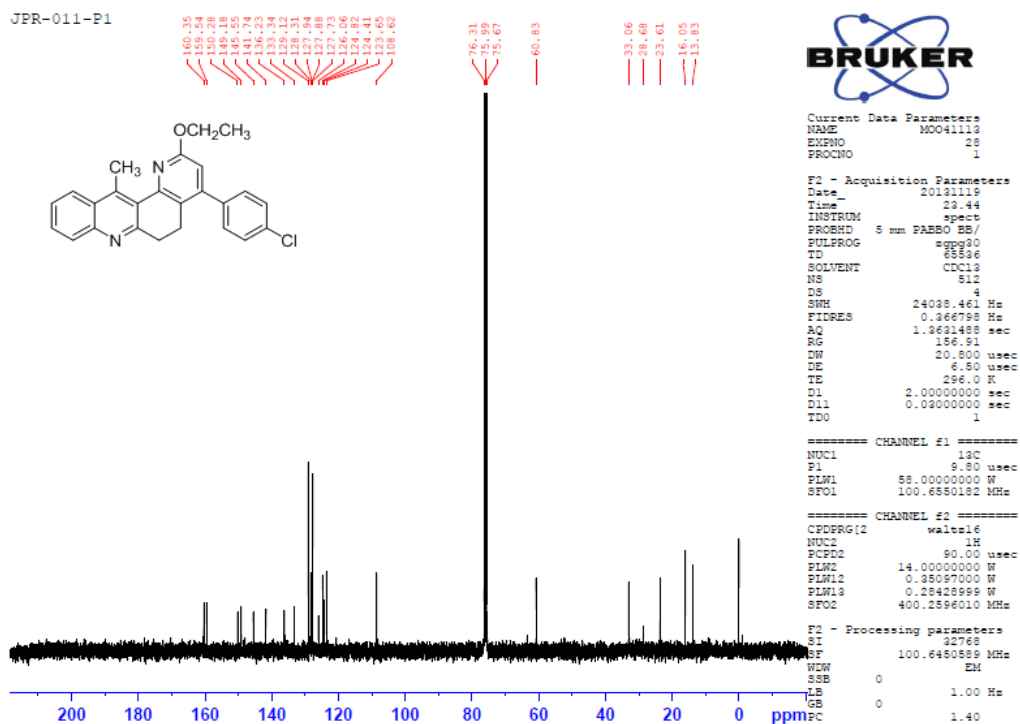
**Fig 21.** ESI-MS spectrum of 4-(4-Chloro-phenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5c**):



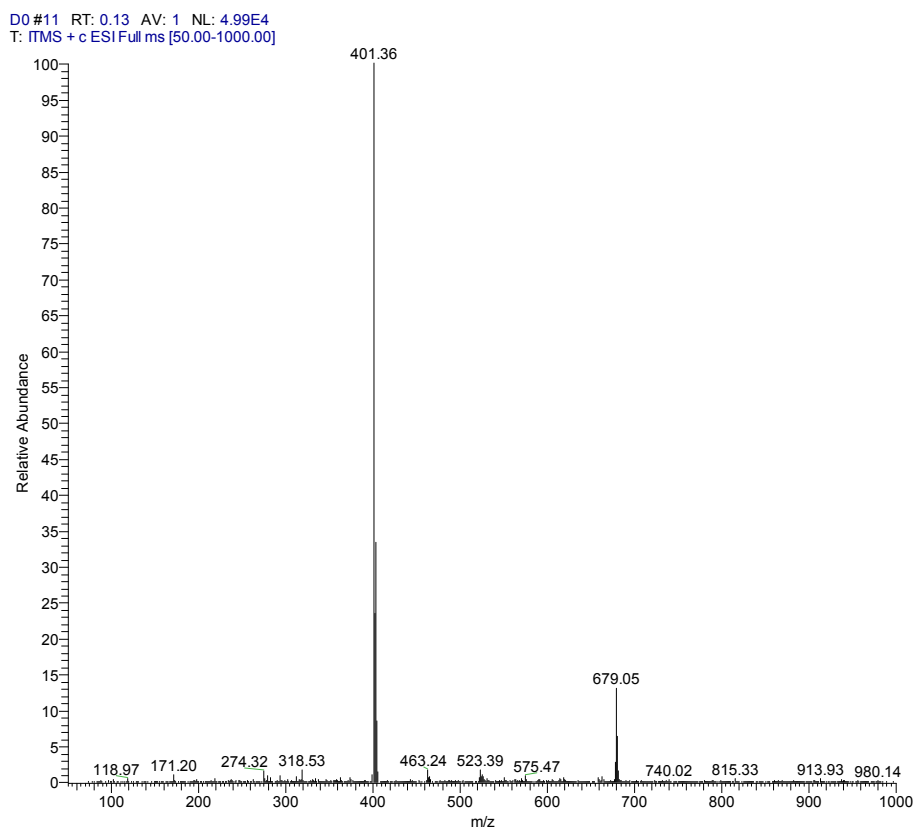
**Fig 22.** <sup>1</sup>H NMR spectrum of 4-(4-Chloro-phenyl)-2-ethoxy-12-methyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5d**):



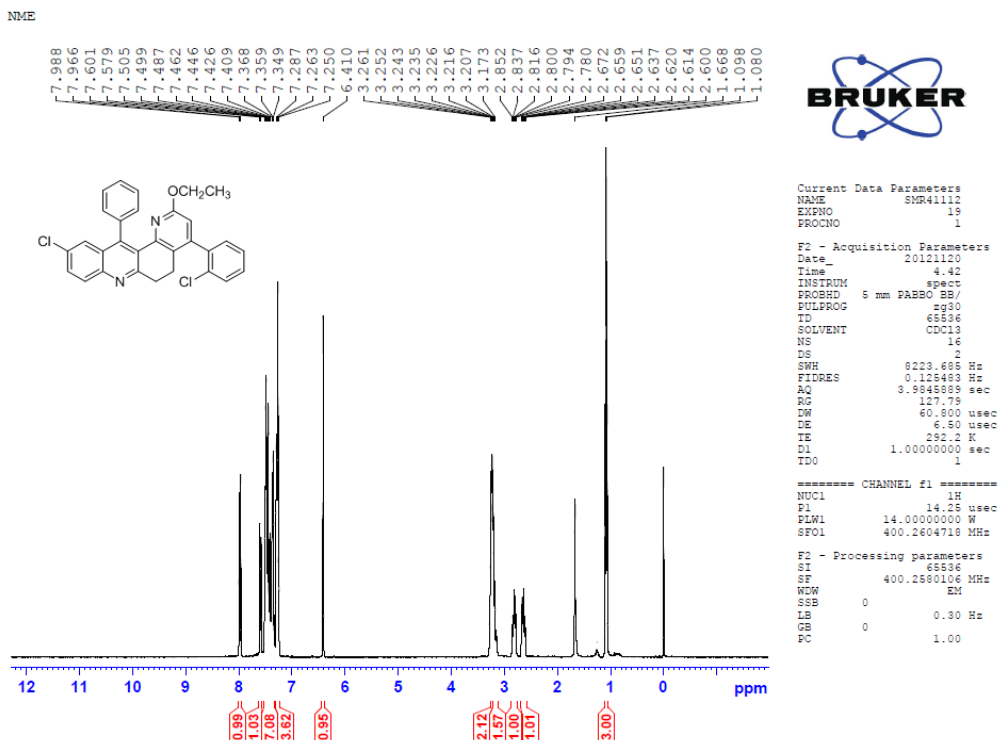
**Fig 23.**  $^{13}\text{C}$  NMR spectrum of 4-(4-Chloro-phenyl)-2-ethoxy-12-methyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5d**):



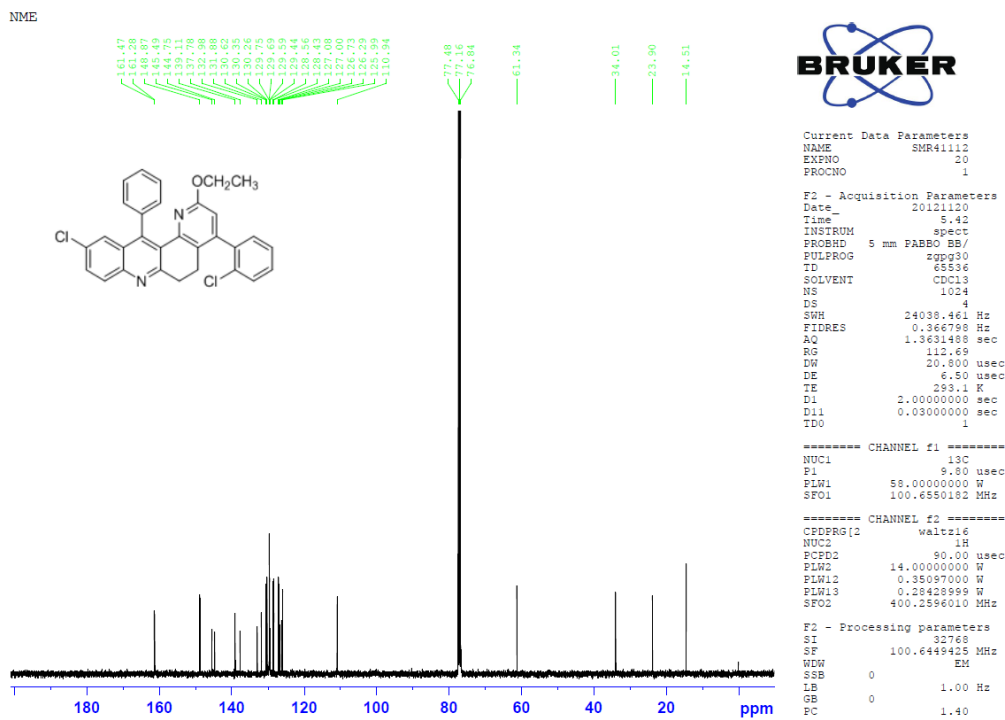
**Fig 24.** ESI-MS spectrum of 4-(4-Chloro-phenyl)-2-ethoxy-12-methyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5d**):



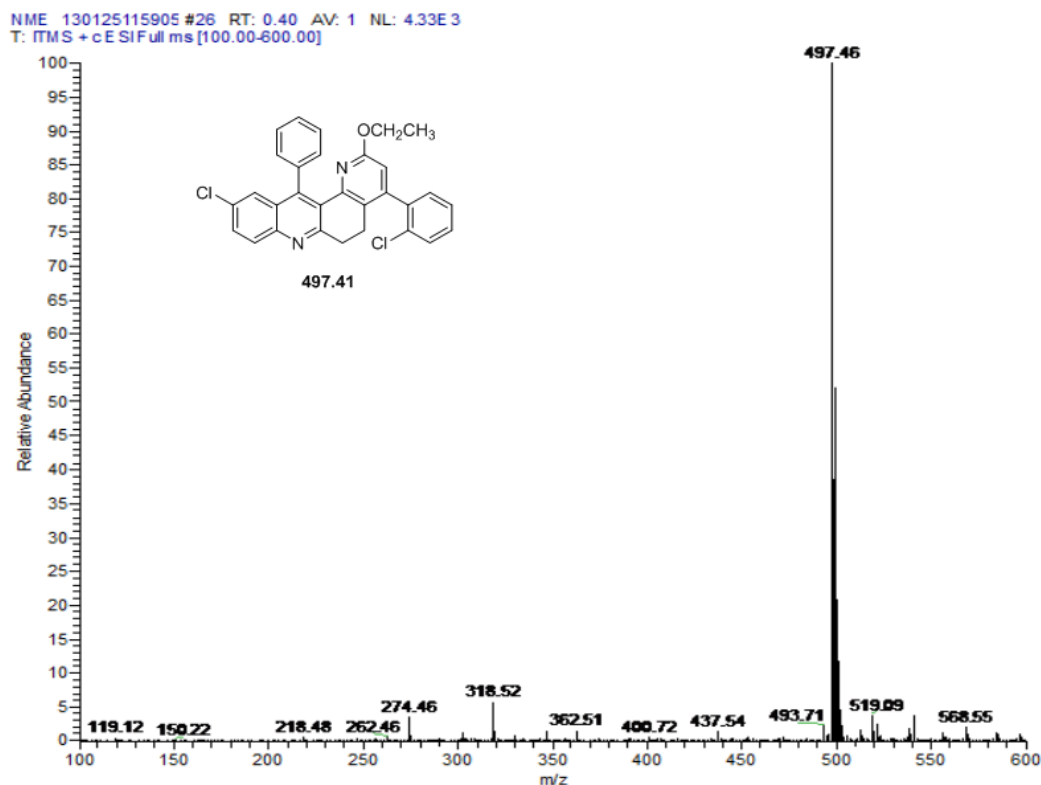
**Fig 25.**  $^1\text{H}$  NMR spectrum of 10-chloro-4-(2-chlorophenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5e**)



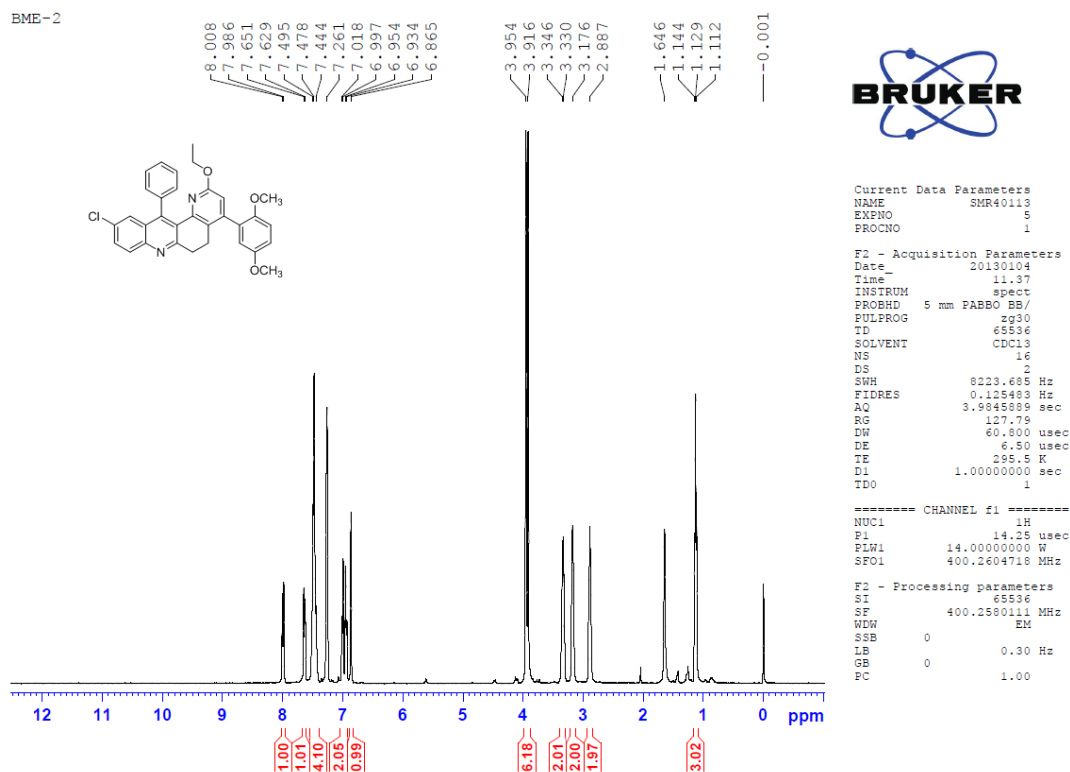
**Fig 26.**  $^{13}\text{C}$  NMR spectrum of 10-chloro-4-(2-chlorophenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5e**)



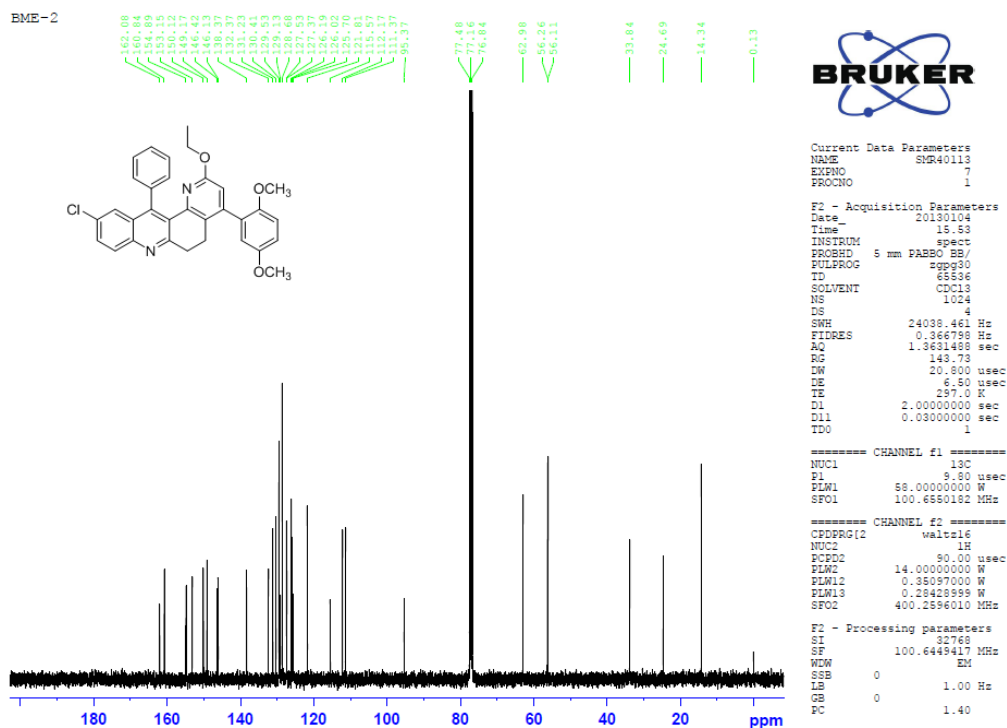
**Fig 27.** ESI-MS spectrum of 10-chloro-4-(2-chlorophenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5e**)



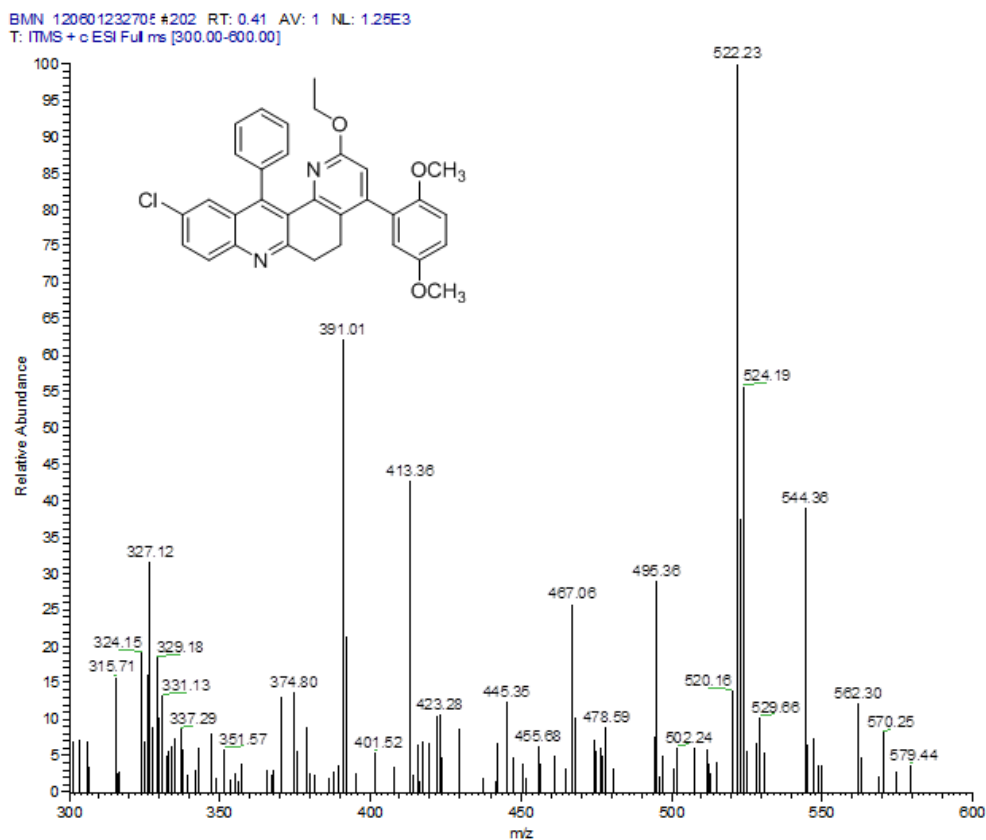
**Fig 28.** <sup>1</sup>H NMR spectrum of 10-chloro-4-(2,5-dimethoxyphenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5f**)



**Fig 29.**  $^{13}\text{C}$  NMR spectrum of 10-chloro-4-(2,5-dimethoxyphenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5f**)

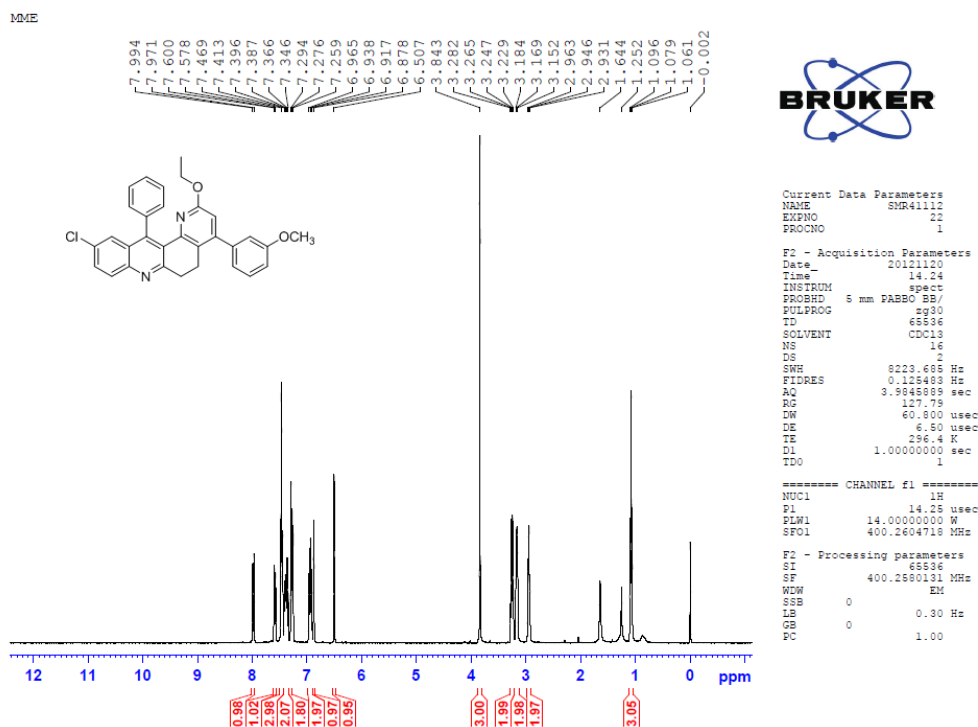


**Fig 30.** ESI-MS spectrum of 10-chloro-4-(2,5-dimethoxyphenyl)-2-ethoxy-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5f**)

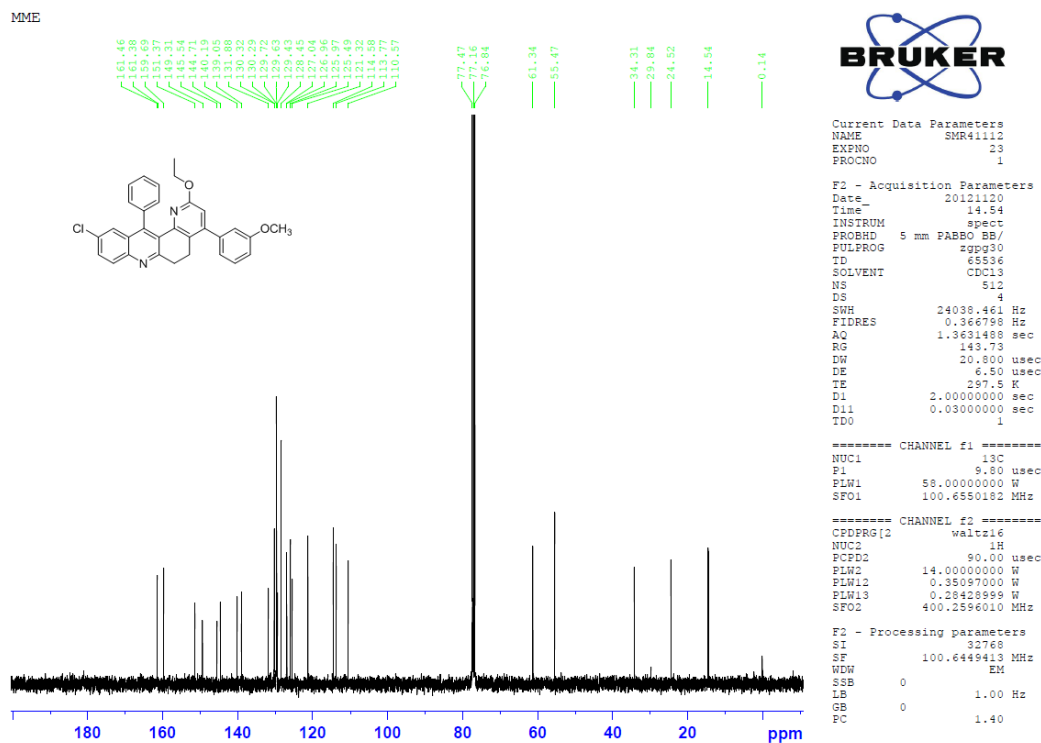




**Fig 31.**  $^1\text{H}$  NMR spectrum of 10-chloro-2-ethoxy-4-(3-methoxyphenyl)-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5g**)

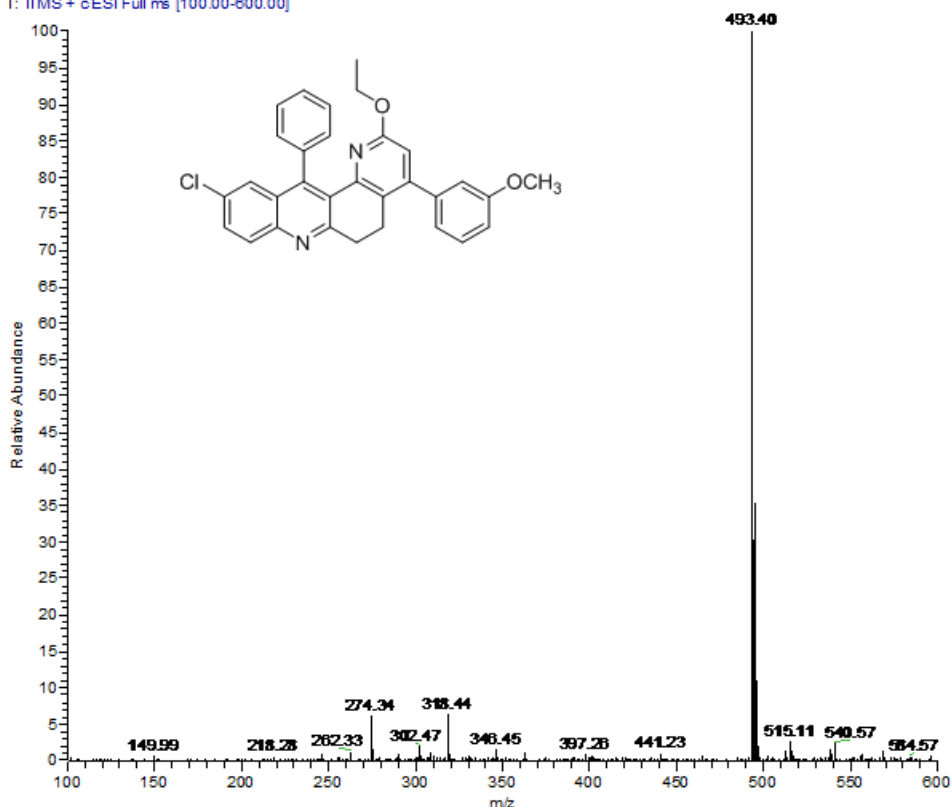


**Fig 32.**  $^{13}\text{C}$  NMR spectrum of 10-chloro-2-ethoxy-4-(3-methoxyphenyl)-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5g**)

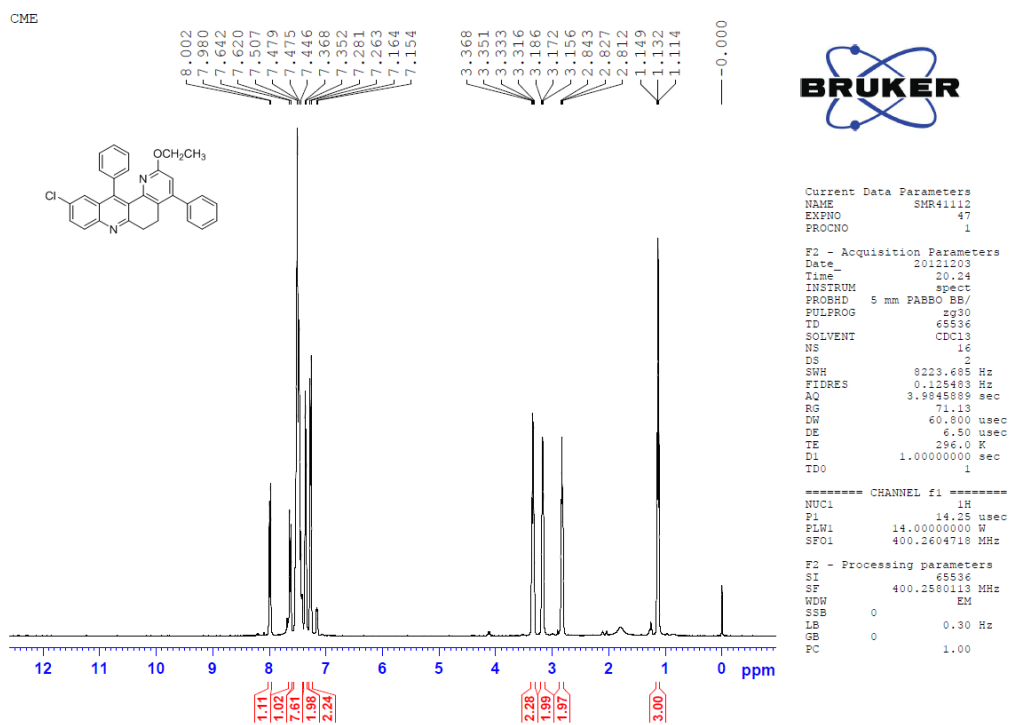


**Fig 33.** ESI-MS spectrum of 10-chloro-2-ethoxy-4-(3-methoxyphenyl)-12-phenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5g**)

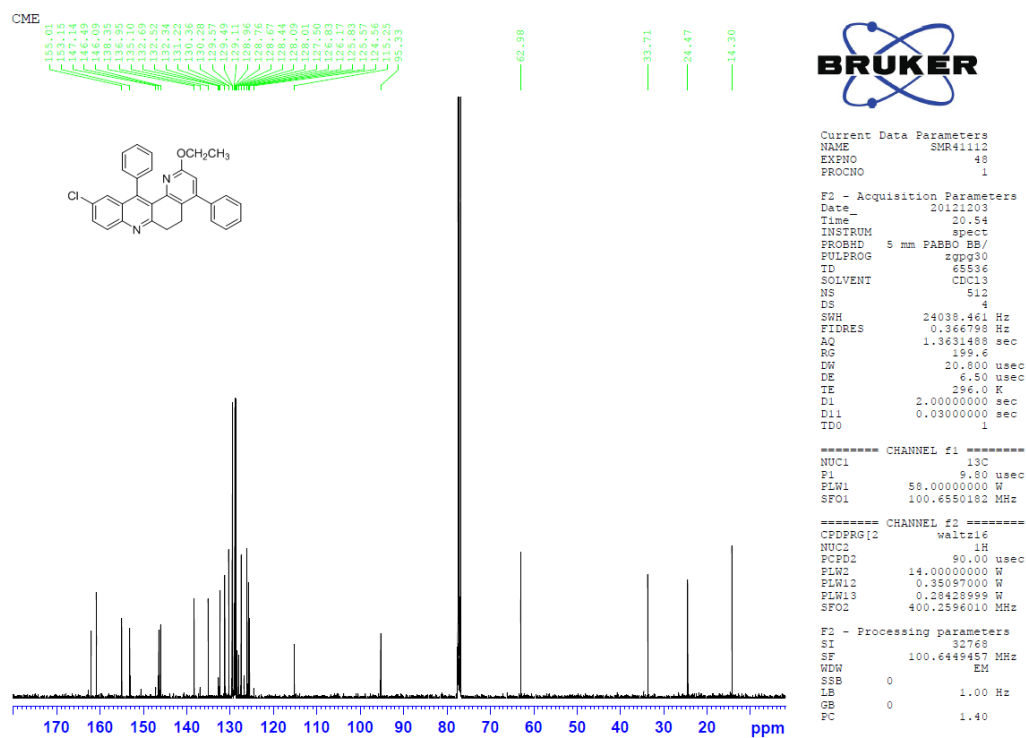
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T: TMS + cESI Full ms [100.00-600.00]



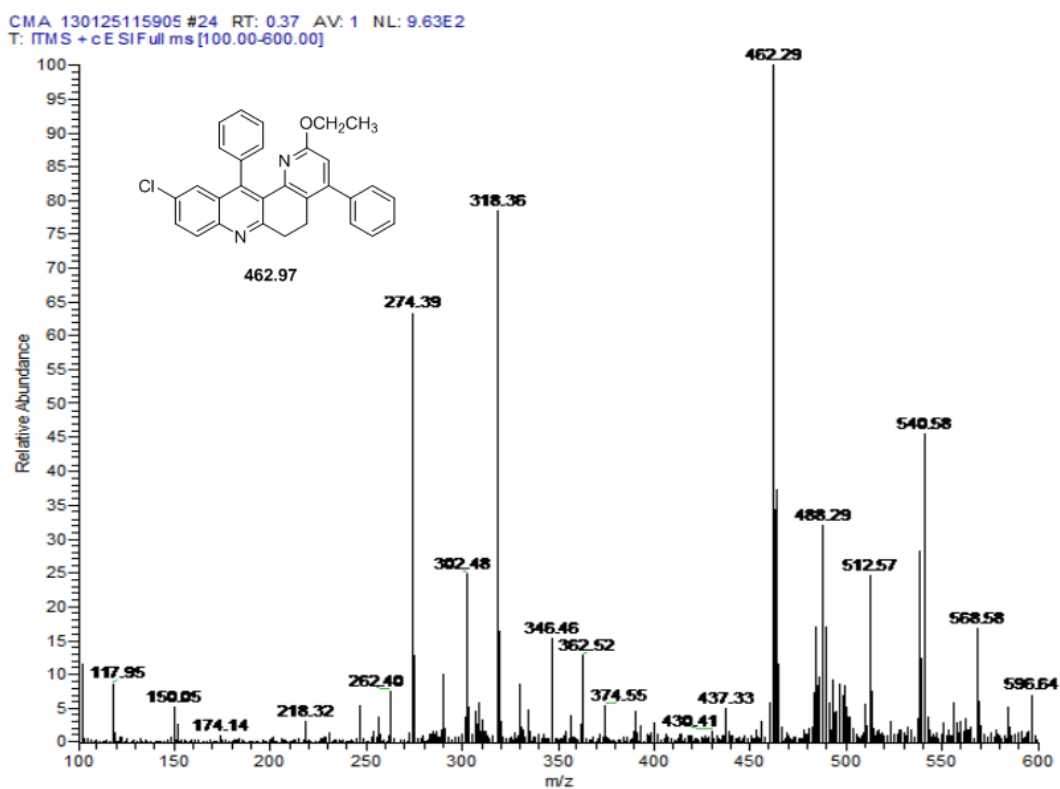
**Fig 34.** <sup>1</sup>H NMR spectrum of 10-chloro-2-ethoxy-4,12-diphenyl-5,6-dihydrobenzo[*j*][1,7]phenanthroline (**5h**)



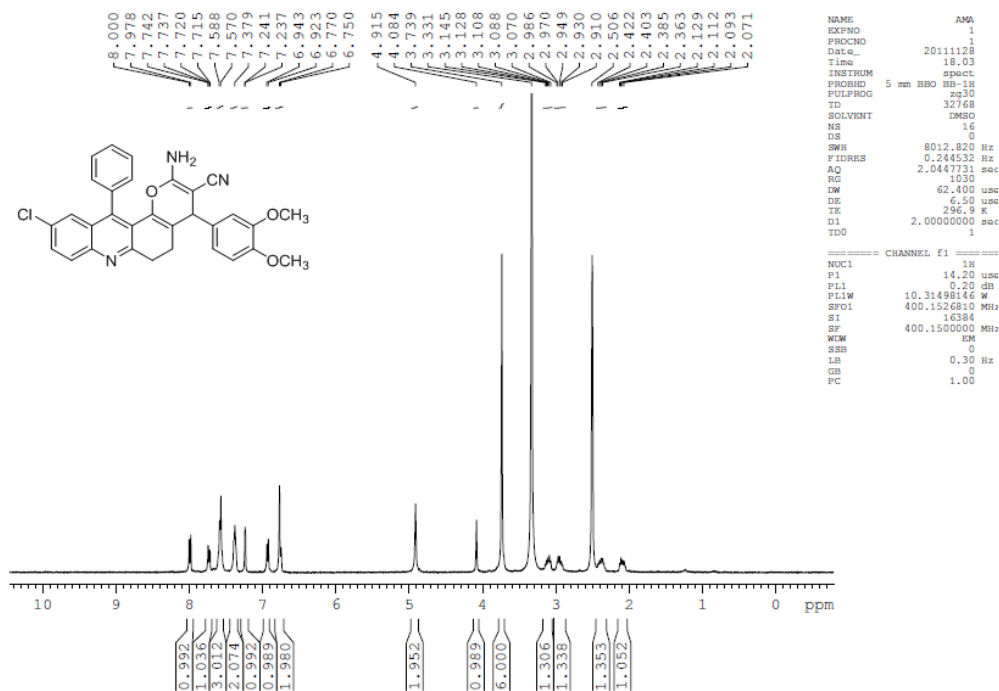
**Fig 35.**  $^{13}\text{C}$  NMR spectrum of 10-chloro-2-ethoxy-4,12-diphenyl-5,6-dihydrobenzo[*j*] [1,7] phenanthroline (**5h**)



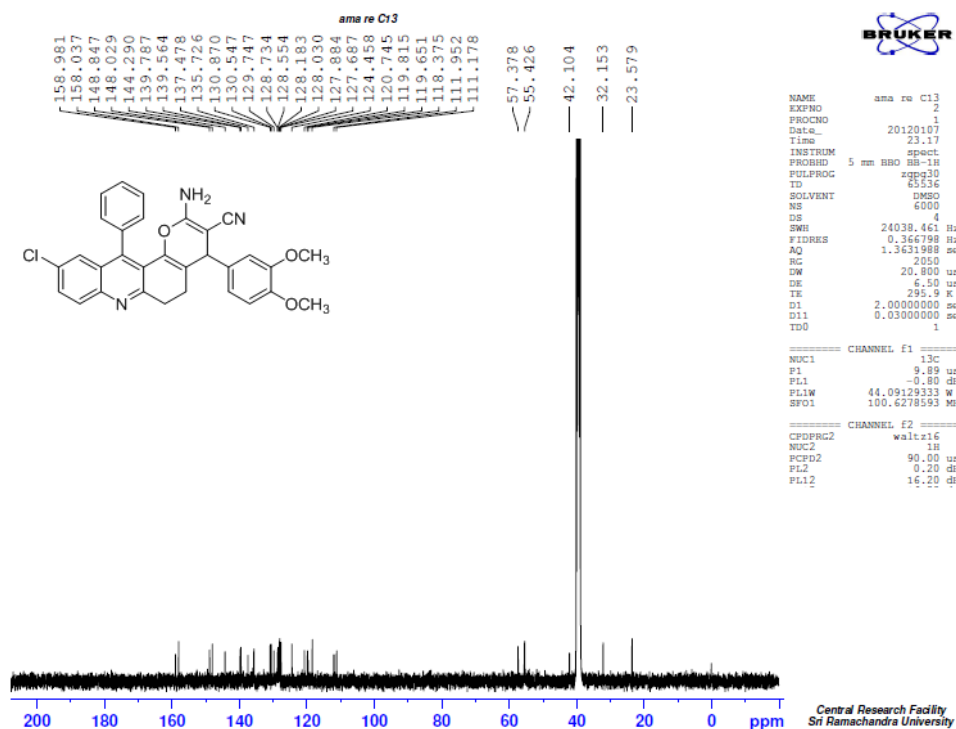
**Fig 36.** ESI-MS spectrum of 10-chloro-2-ethoxy-4,12-diphenyl-5,6-dihydrobenzo[*j*][1,7] phenanthroline (**5h**)



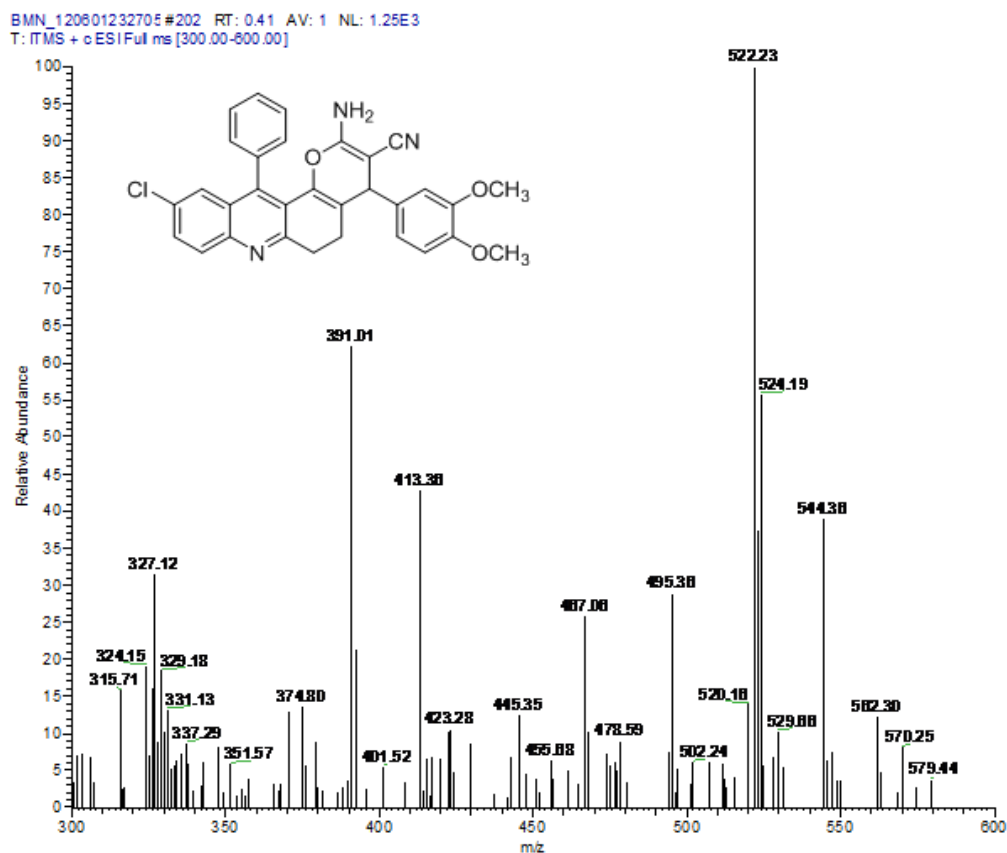
**Fig 37.**  $^1\text{H}$  NMR spectrum of 2-amino-10-chloro-4-(3,4-dimethoxyphenyl)-12-phenyl-5,6-dihydro-4*H*-pyrano[2,3-*a*]acridine-3-carbonitrile (**8a**)



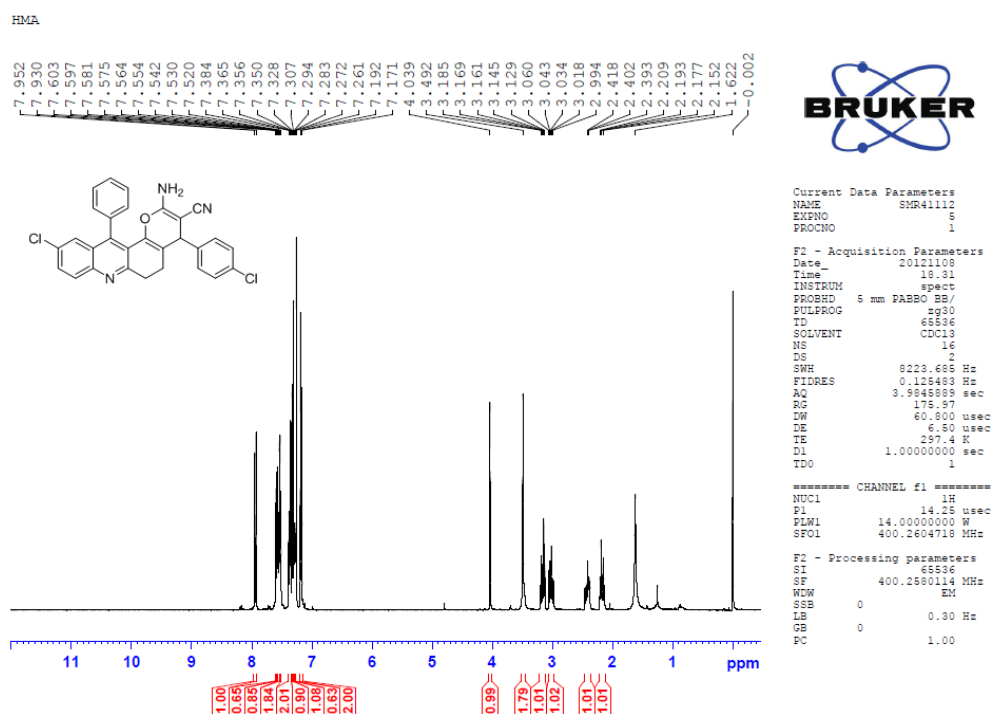
**Fig 38.**  $^{13}\text{C}$  NMR spectrum of 2-amino-10-chloro-4-(3,4-dimethoxyphenyl)-12-phenyl-5,6-dihydro-4*H*-pyrano[2,3-*a*]acridine-3-carbonitrile (**8a**)



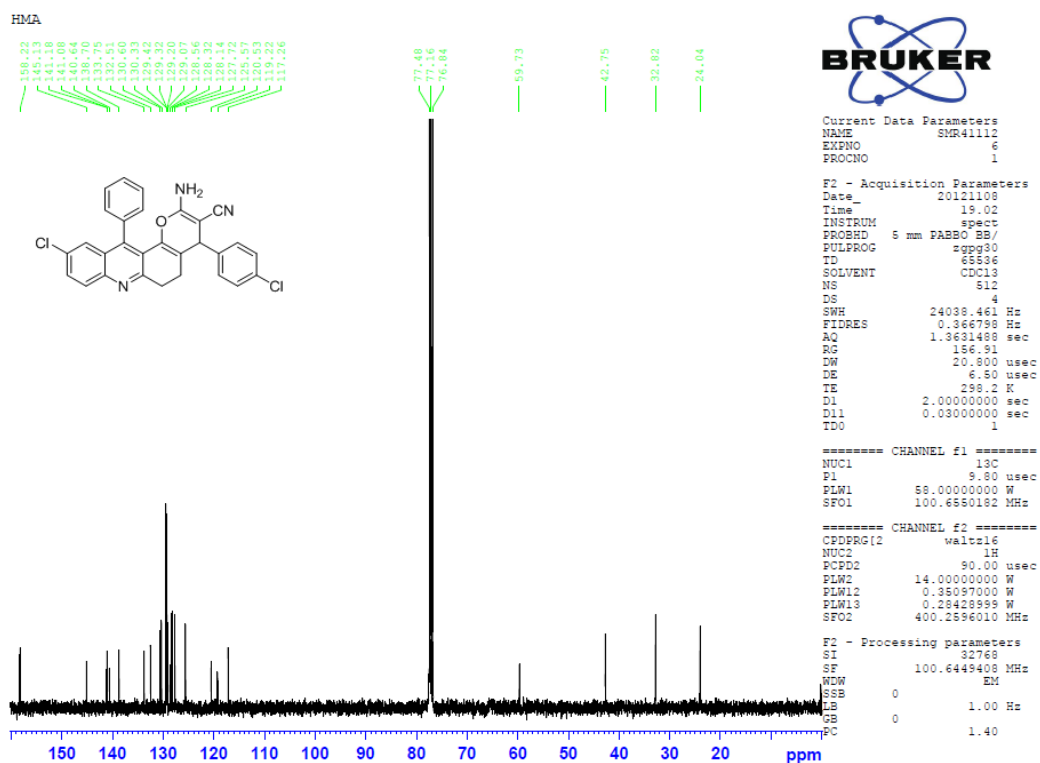
**Fig 39.** ESI-MS spectrum of 2-amino-10-chloro-4-(3,4-dimethoxyphenyl)-12-phenyl-5,6-dihydro-4*H*-pyrano[2,3-*a*]acridine-3-carbonitrile (**8a**)



**Fig 40.** <sup>1</sup>H NMR spectrum of 2-amino-10-chloro-4-(4-chlorophenyl)-12-phenyl-5,6-dihydro-4*H*-pyrano[2,3-*a*]acridine-3-carbonitrile (**8b**)



**Fig 41.**  $^{13}\text{C}$  NMR spectrum of 2-amino-10-chloro-4-(4-chlorophenyl)-12-phenyl-5,6-dihydro-4*H*-pyrano[2,3-*a*]acridine-3-carbonitrile (**8b**)



**Fig 42.** ESI-MS spectrum of 2-amino-10-chloro-4-(4-chlorophenyl)-12-phenyl-5,6-dihydro-4*H*-pyrano[2,3-*a*]acridine-3-carbonitrile (**8b**)

