

Iron/acetic acid mediated synthesis of 6,7-dihydrodibenzo [b,j] [1,7] phenanthroline derivatives *via* intramolecular reductive cyclization

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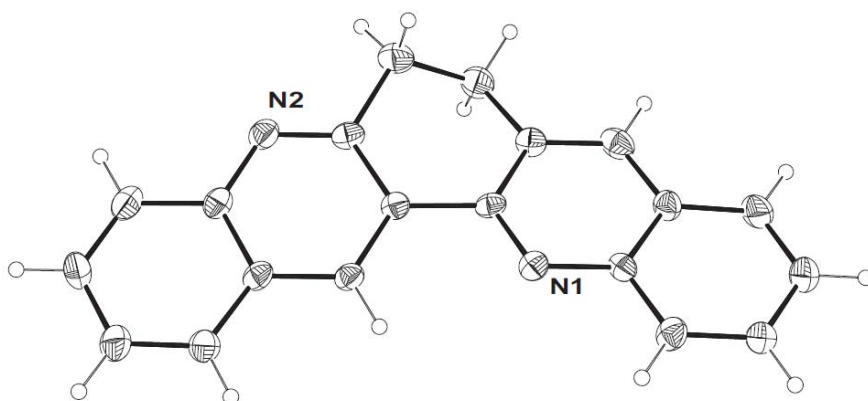
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Table of Contents

1. X-ray Crystallographic Structures	2-5
2. ¹H and ¹³C NMR & HRMS Spectra	6-61

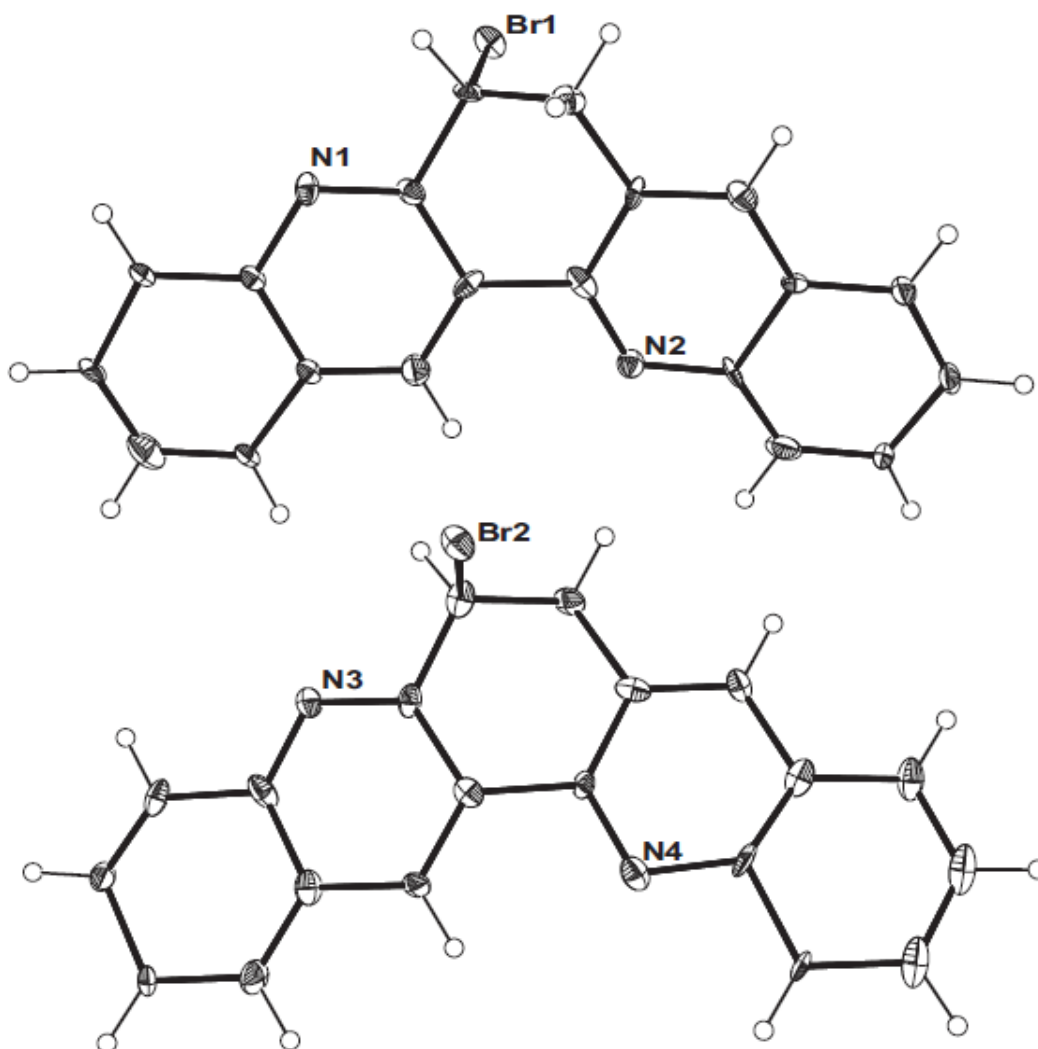
1. Crystal structure of compound **1a** (CCDC No: 1050602)



Identification code	ch16265
Empirical formula	C ₂₀ H ₁₄ N ₂
Formula weight	282.33
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 4.5670(10) Å α = 90°. b = 11.716(3) Å β = 90°. c = 26.496(7) Å γ = 90°.
Volume	1417.7(6) Å ³
Z	4
Density (calculated)	1.323 Mg/m ³
Absorption coefficient	0.078 mm ⁻¹
F(000)	592
Crystal size	0.66 x 0.08 x 0.03 mm ³
Theta range for data collection	1.54 to 25.03°.

Index ranges	-2<=h<=5, -13<=k<=13, -31<=l<=31
Reflections collected	8126
Independent reflections	2515 [R(int) = 0.0965]
Completeness to theta = 25.03°	99.9 %
Absorption correction	multi-scan
Max. and min. transmission	0.9977 and 0.9501
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2515 / 0 / 199
Goodness-of-fit on F ²	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0701, wR2 = 0.1596
R indices (all data)	R1 = 0.1344, wR2 = 0.2262
Absolute structure parameter	-1(9)
Largest diff. peak and hole	0.345 and -0.461 e.Å ⁻³

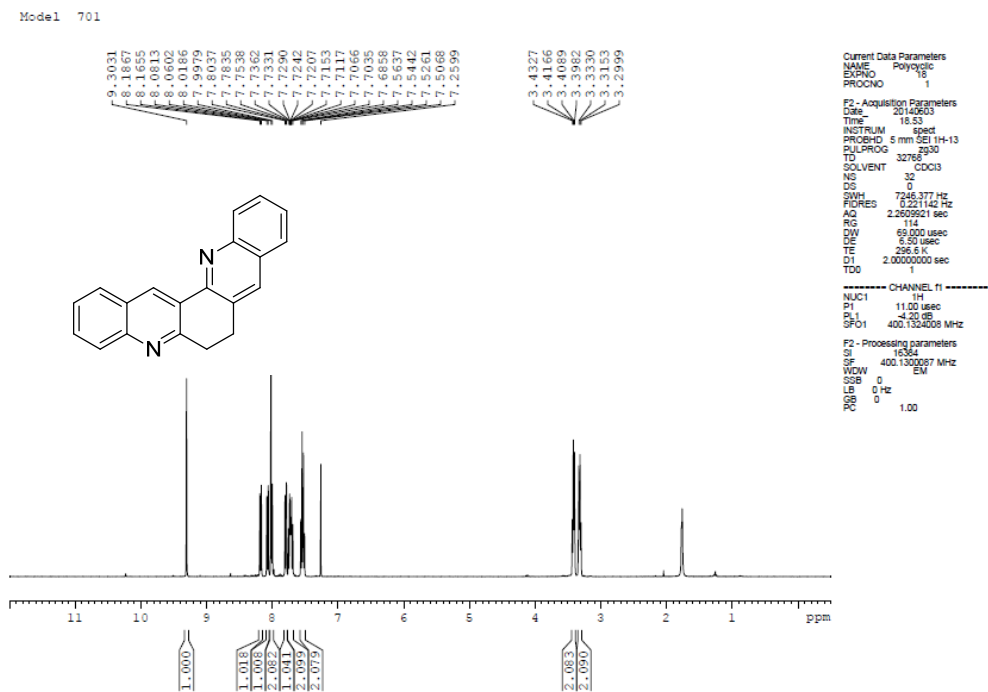
1. Crystal structure of compound **5f** (CCDC No:1052475)



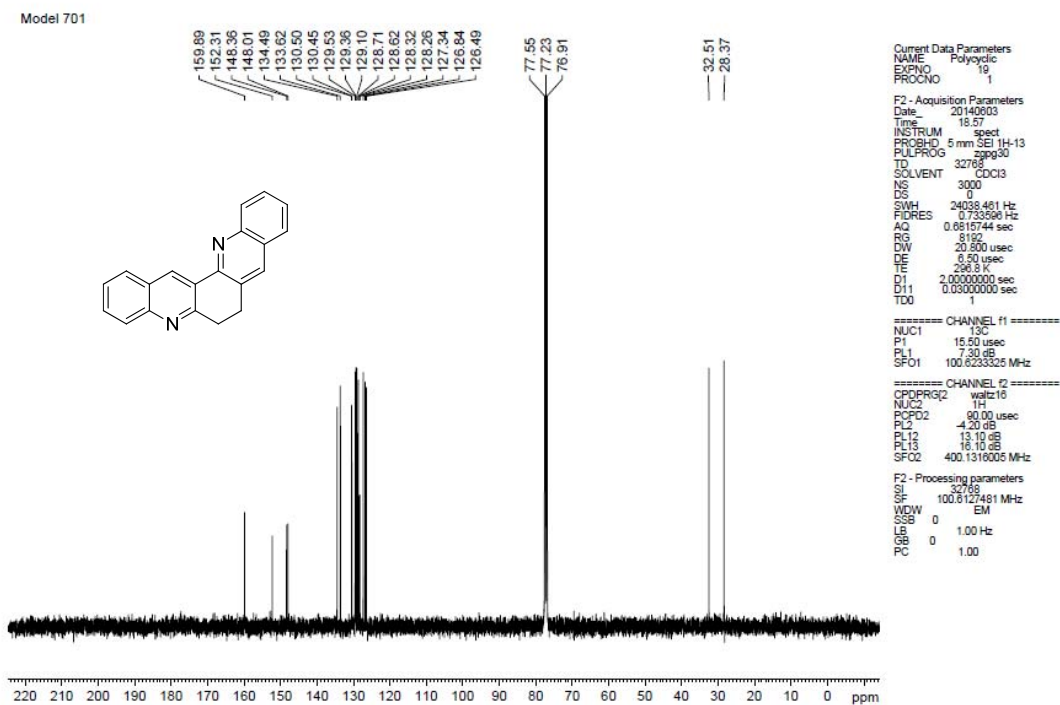
Identification code	a16933
Empirical formula	C ₂₀ H ₁₃ Br N ₂
Formula weight	361.23
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P n
Unit cell dimensions	a = 6.4502(5) Å α = 90°.

	$b = 10.8097(8) \text{ \AA}$	$\beta = 95.457(4)^\circ$
	$c = 22.0781(17) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$1532.4(2) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.566 Mg/m^3	
Absorption coefficient	2.683 mm^{-1}	
F(000)	728	
Crystal size	$0.23 \times 0.08 \times 0.03 \text{ mm}^3$	
Theta range for data collection	$1.85 \text{ to } 25.18^\circ$	
Index ranges	$-7 \leq h \leq 6, -12 \leq k \leq 12, -23 \leq l \leq 26$	
Reflections collected	6473	
Independent reflections	3831 [R(int) = 0.0456]	
Completeness to theta = 25.18°	99.0 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9239 and 0.5774	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3831 / 2 / 391	
Goodness-of-fit on F^2	1.024	
Final R indices [I > 2sigma(I)]	R1 = 0.0747, wR2 = 0.1724	
R indices (all data)	R1 = 0.0901, wR2 = 0.1856	
Absolute structure parameter	0.19(3)	
Largest diff. peak and hole	5.225 and $-0.714 \text{ e.\AA}^{-3}$	

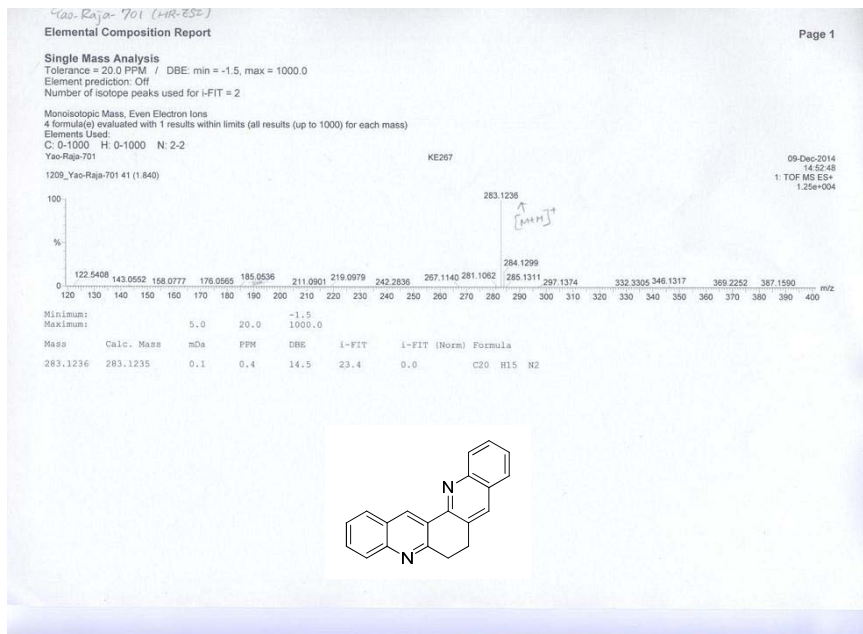
1. 6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4a) : ^1H NMR (400 MHz, CDCl_3)



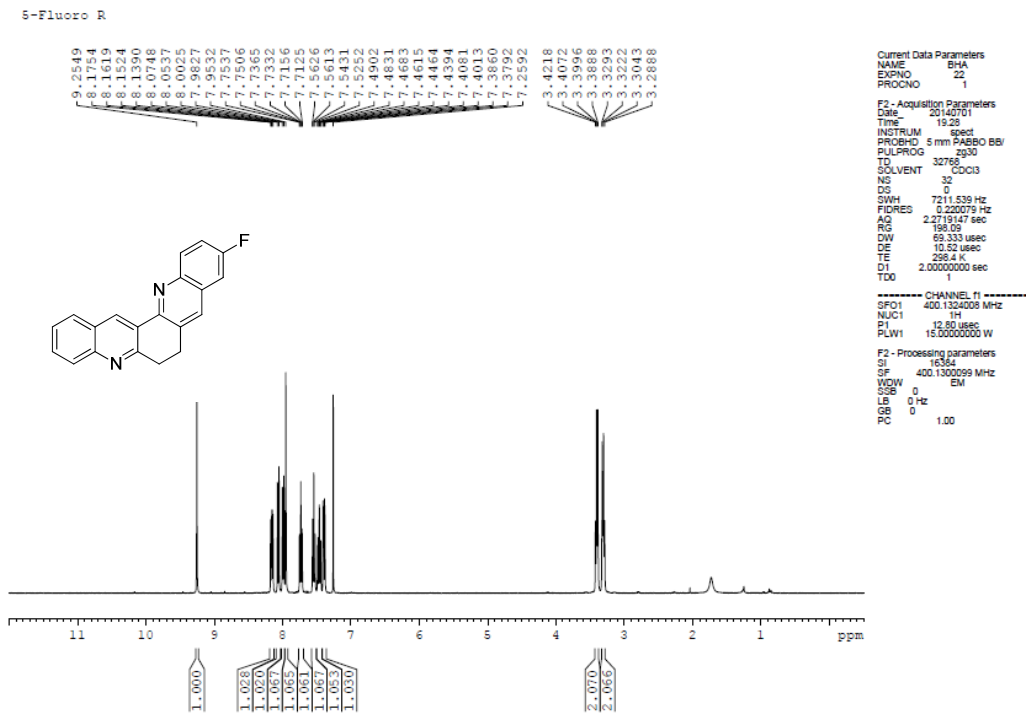
6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4a) : ^{13}C NMR (100 MHz, CDCl_3)



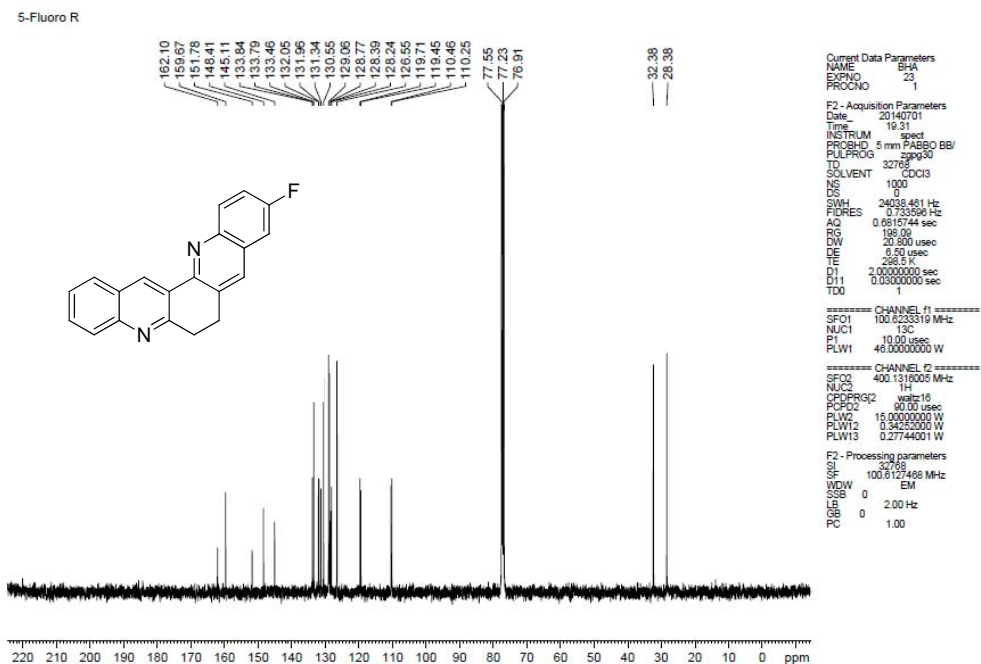
6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4a) : HRMS



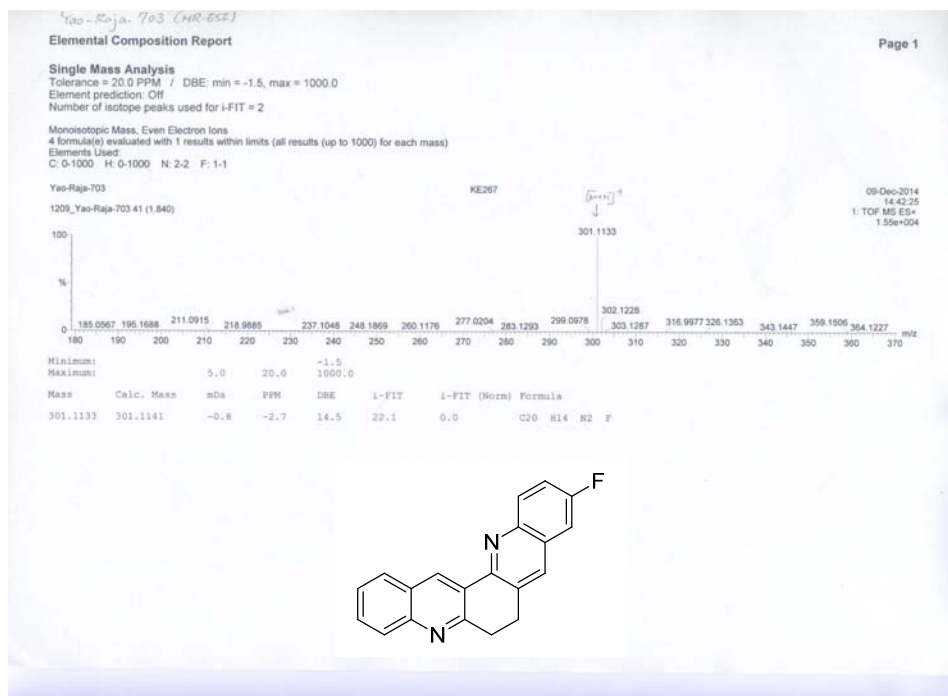
2. 10-fluoro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4b) : ¹H NMR (400 MHz, CDCl₃)



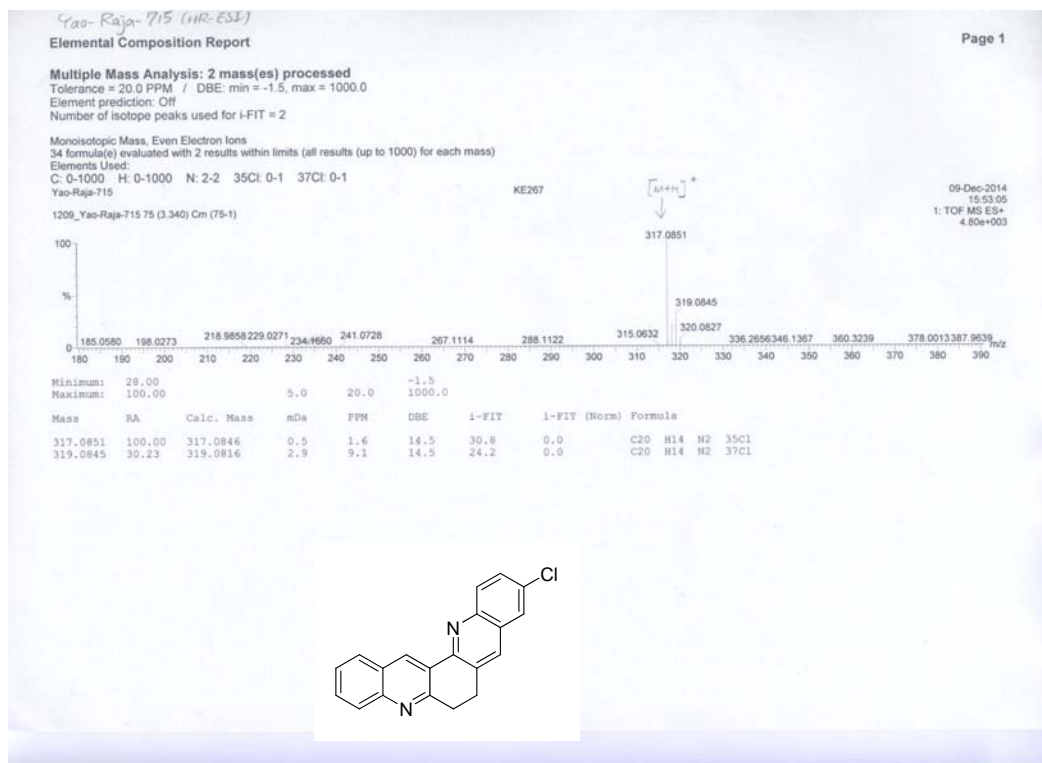
10-fluoro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4b) : ^{13}C NMR (100 MHz, CDCl_3)



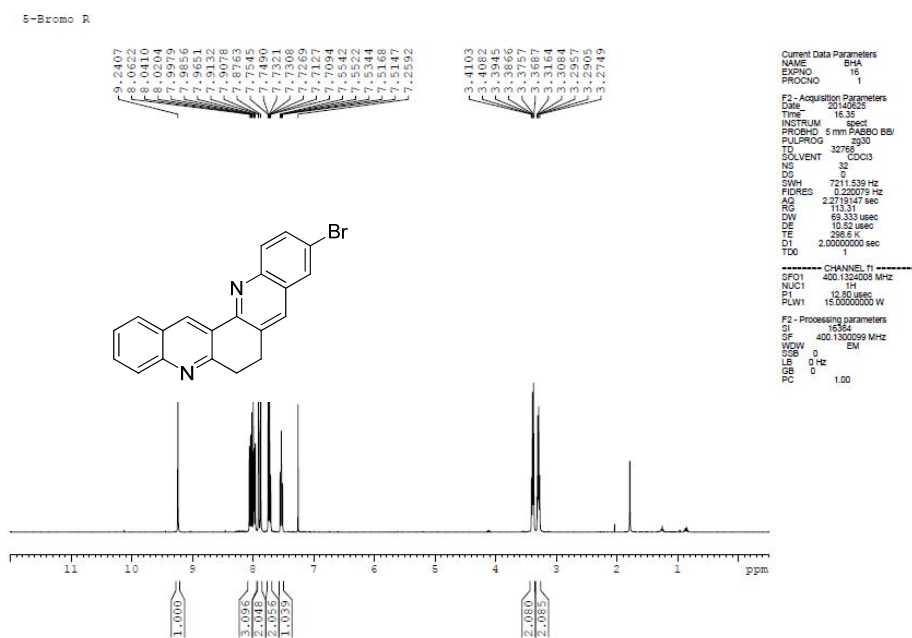
10-fluoro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4b) : HRMS



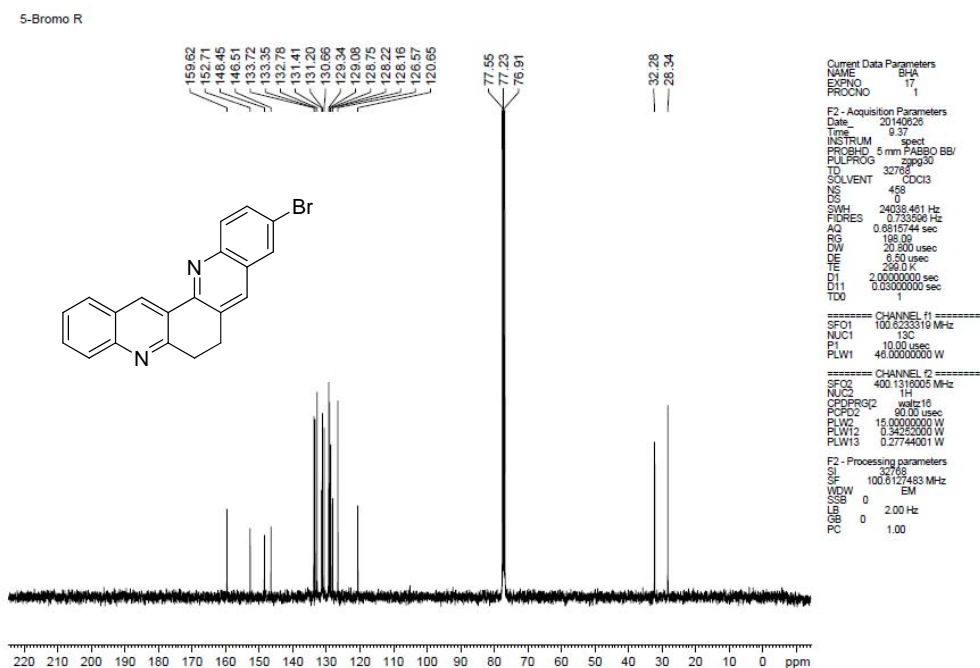
10-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4c) : HRMS



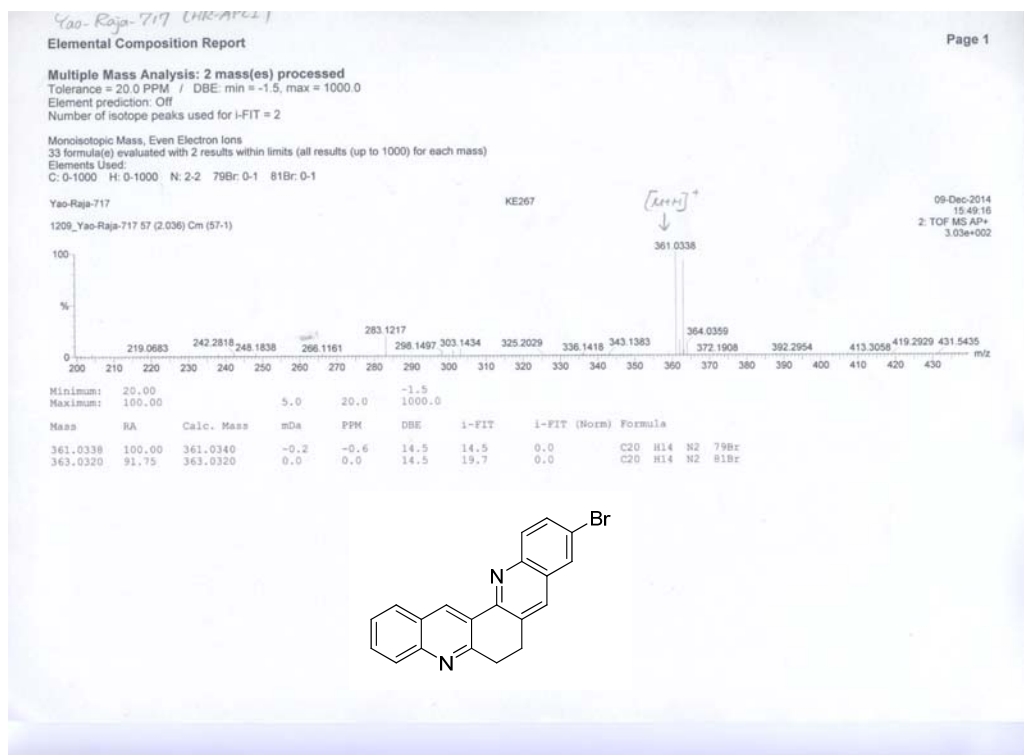
4. 10-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4d) : ¹H NMR (400 MHz, CDCl₃)



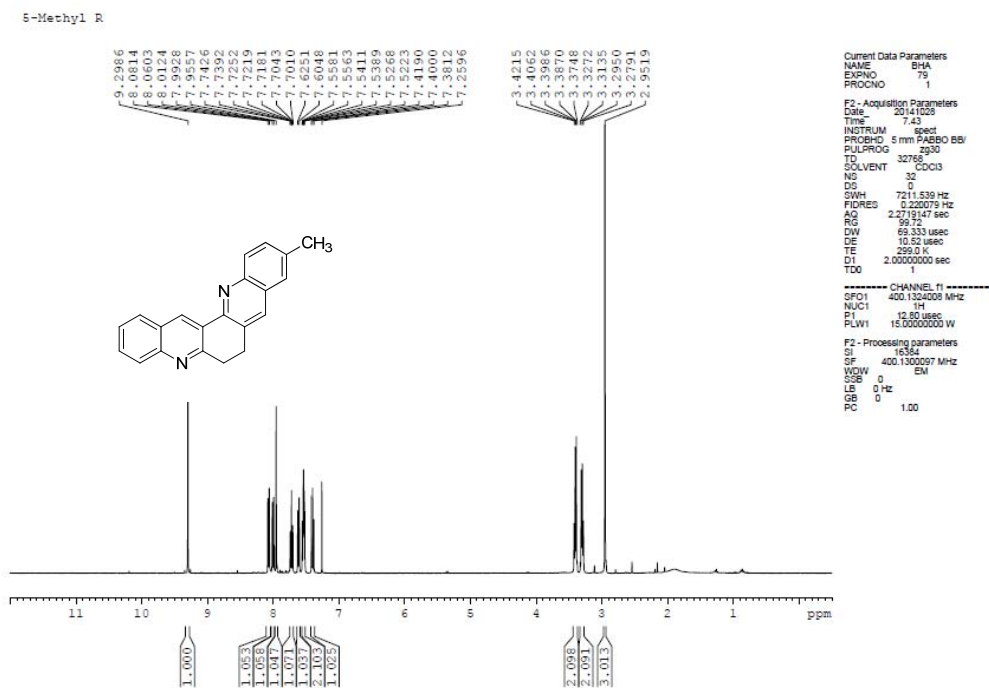
10-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4d) : ^{13}C NMR (100 MHz, CDCl_3)



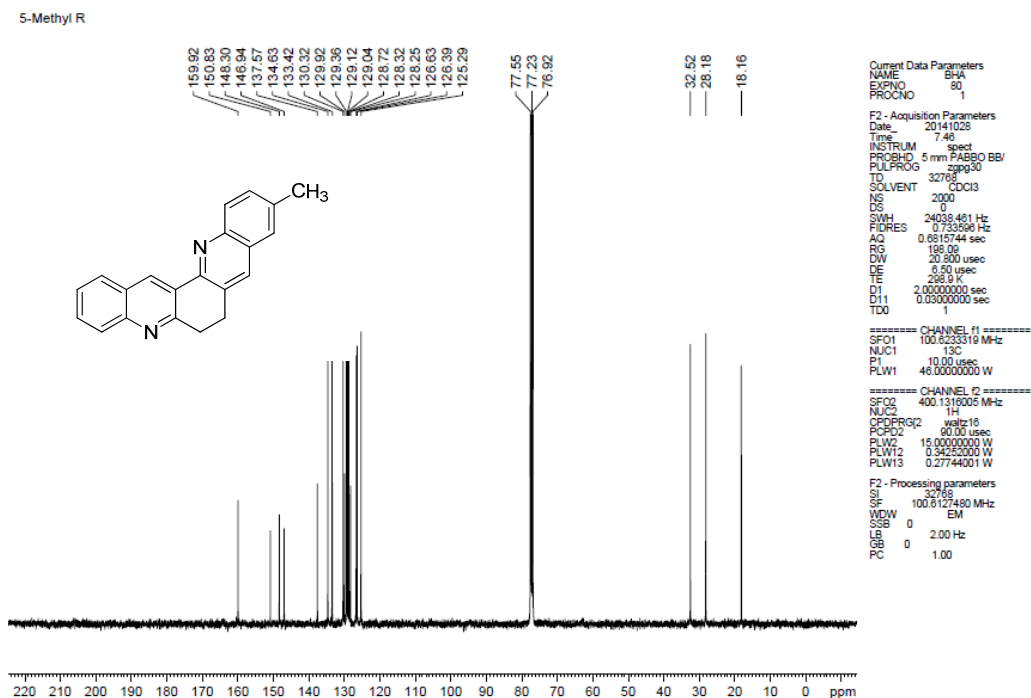
10-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4d) : HRMS



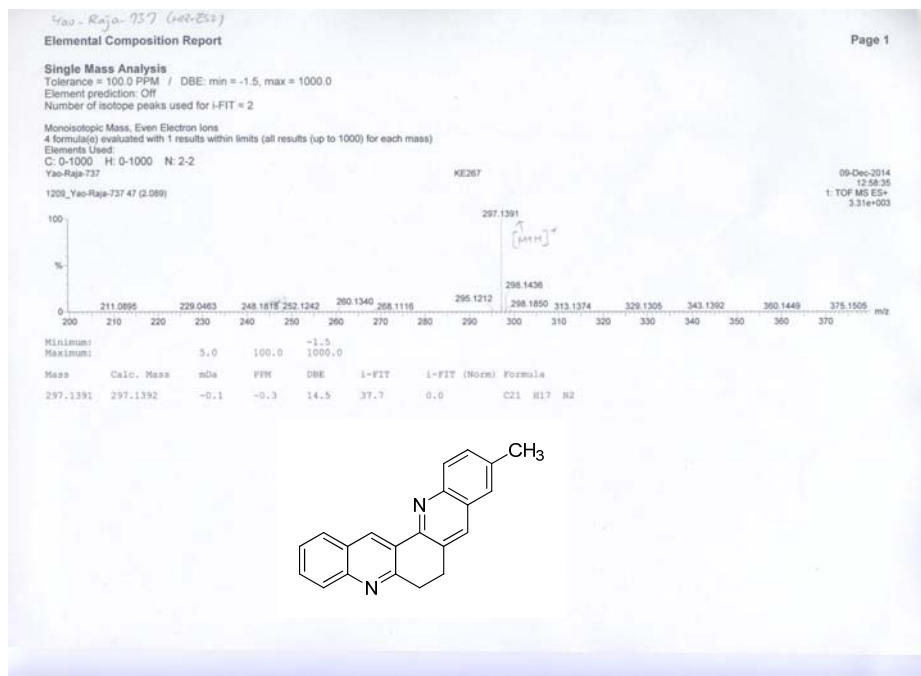
5.10-methyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4e) : ¹H NMR (400 MHz, CDCl₃)



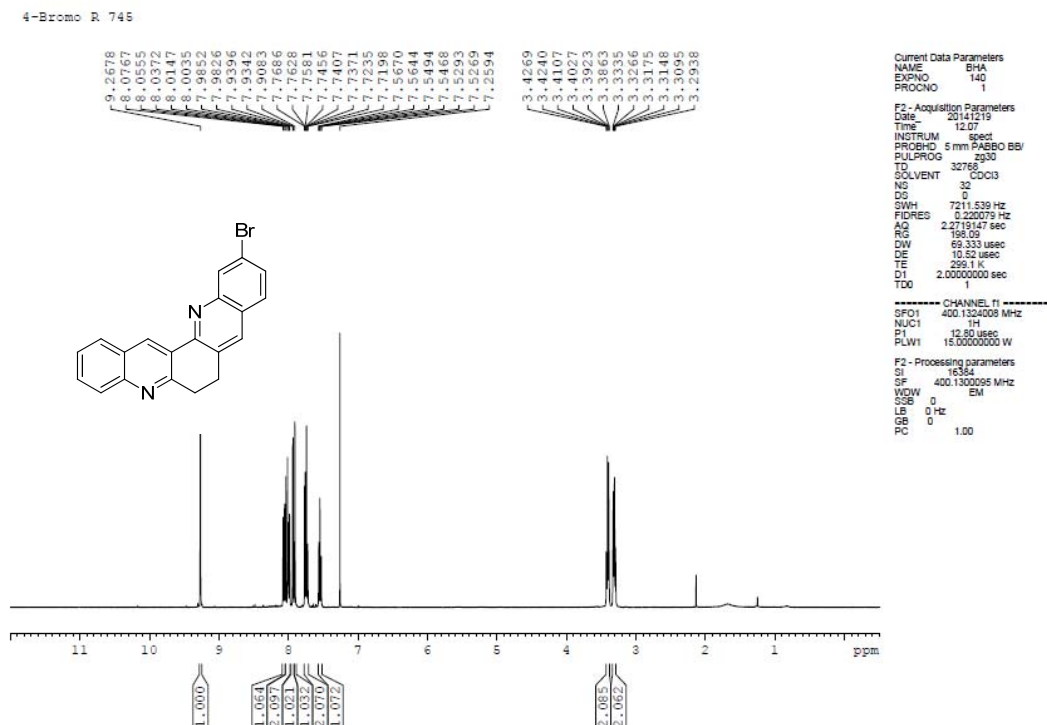
10-methyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4e) : ¹³C NMR (100 MHz, CDCl₃)



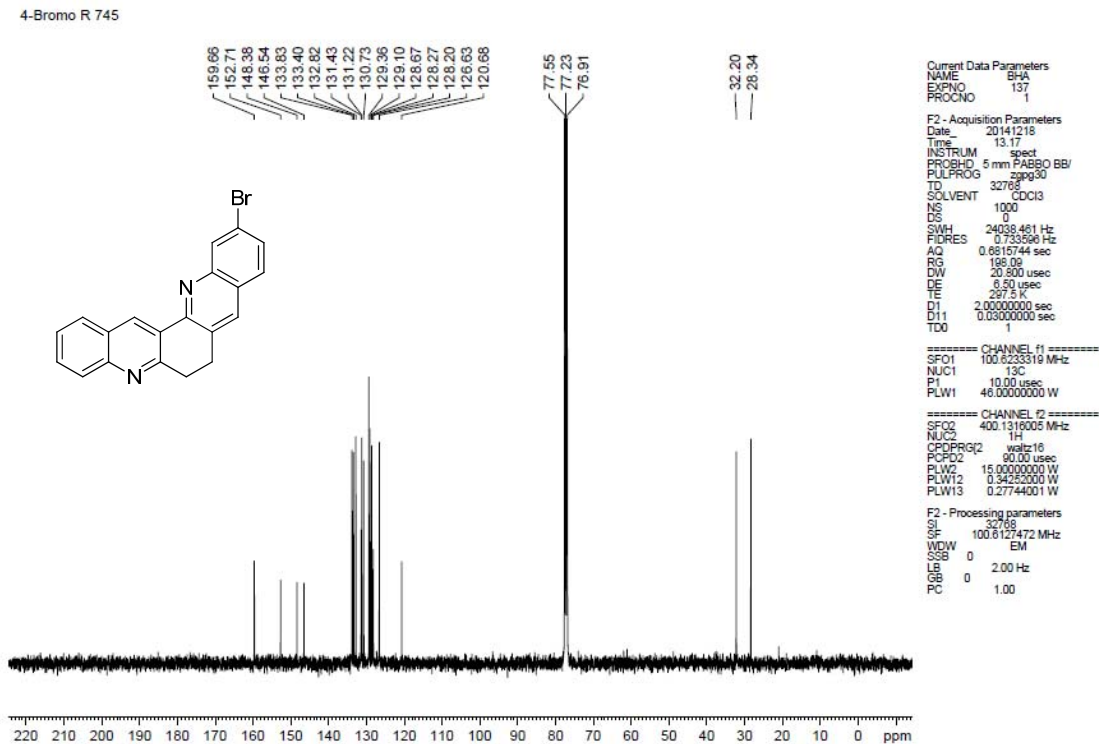
10-methyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4e) : HRMS



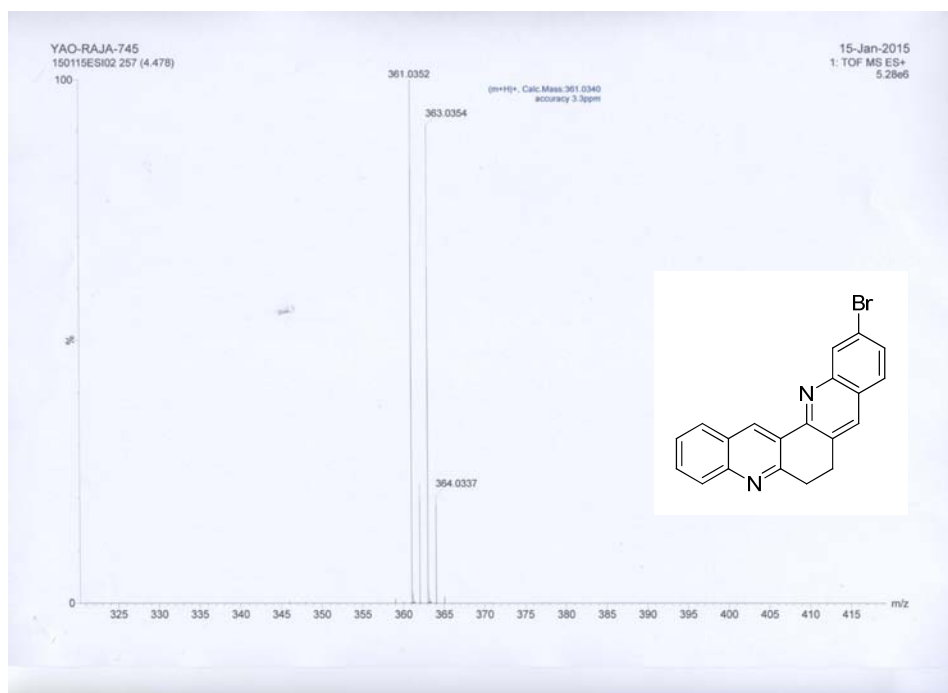
6. 11-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4f) : ¹H NMR (400 MHz, CDCl₃)



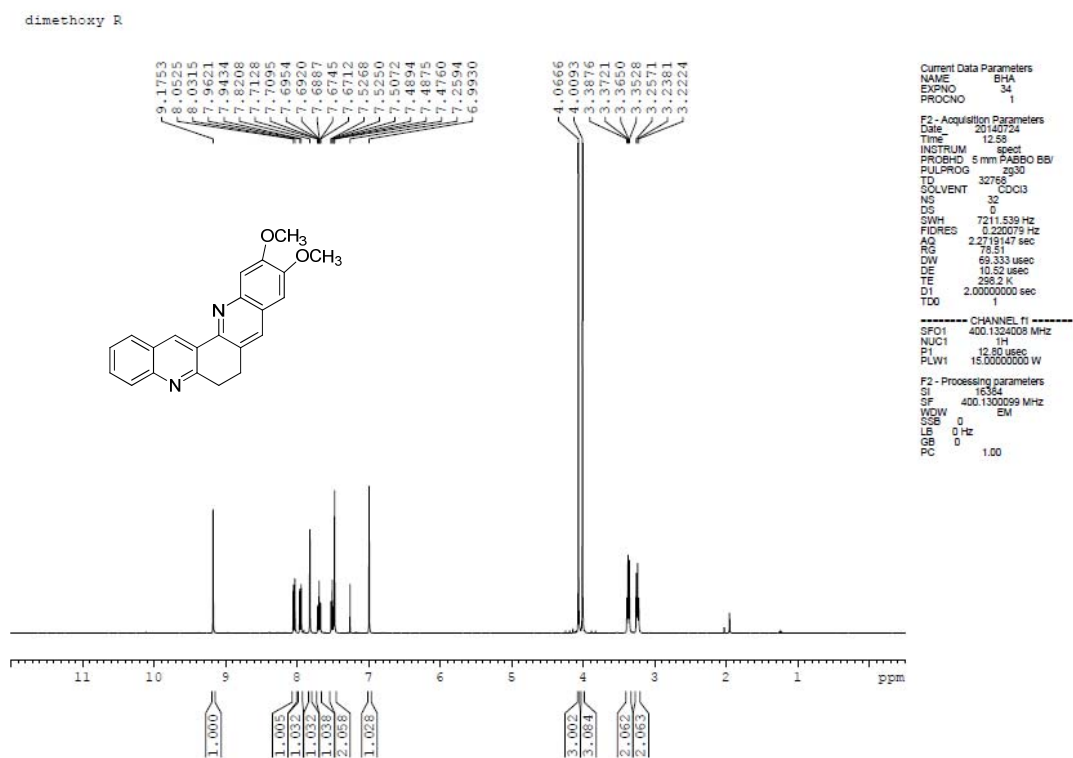
11-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4f) : ^{13}C NMR (100 MHz, CDCl_3)



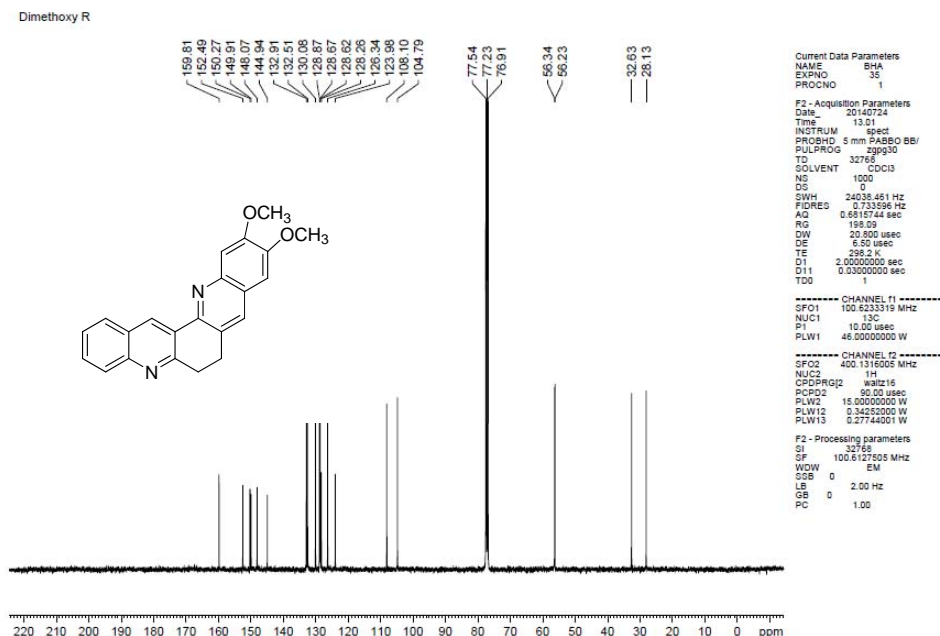
11-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4f) : HRMS



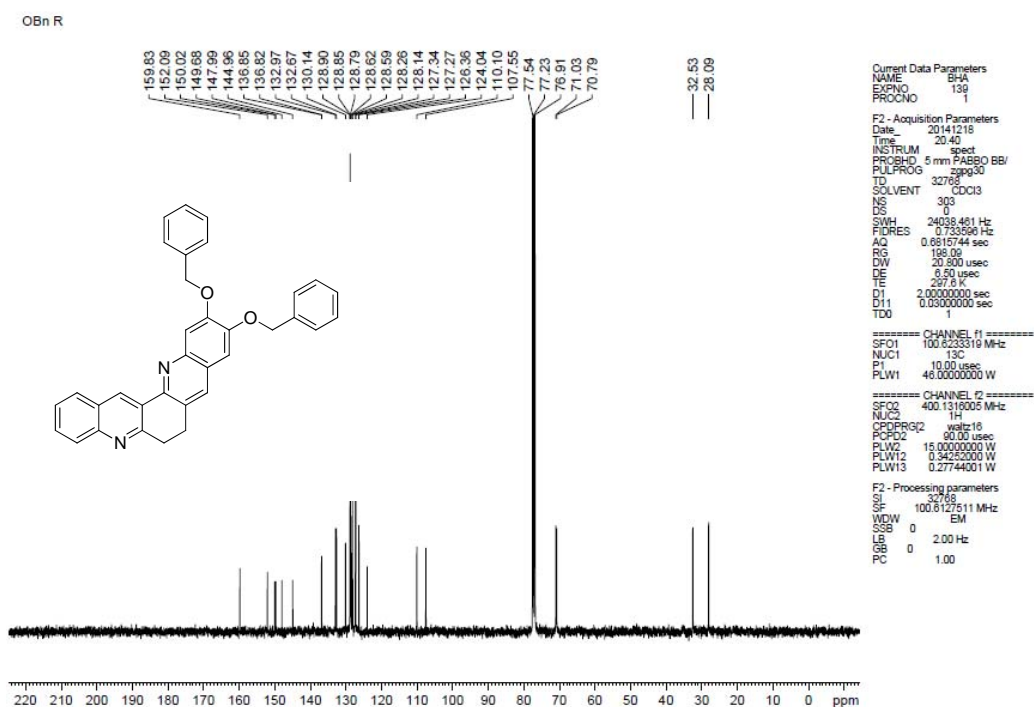
7. 10,11-dimethoxy-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4g) : ¹H NMR (400 MHz, CDCl₃)



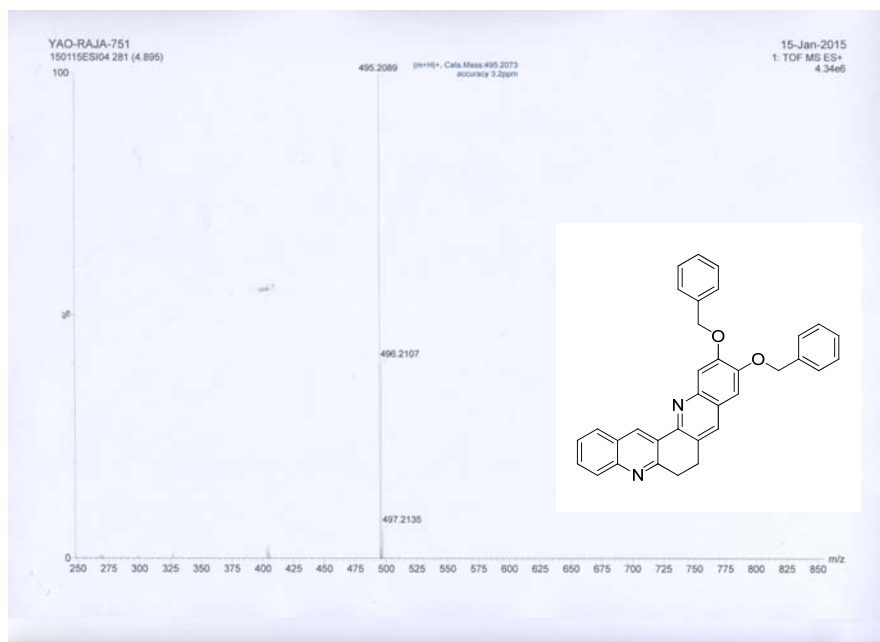
10,11-dimethoxy-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4g) : ¹³C NMR (100 MHz, CDCl₃)



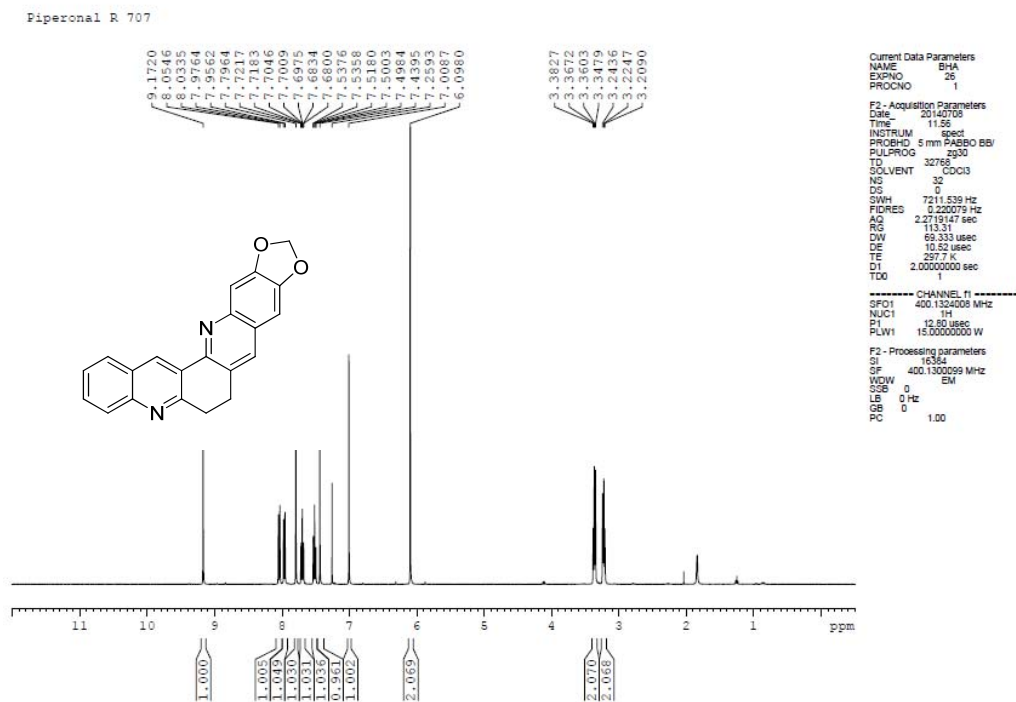
10,11-bis(benzyloxy)-6,7-dihydrodibenzo[b,j][1,7]phenanthroline(4h) : ¹³C NMR (100 MHz, CDCl₃)



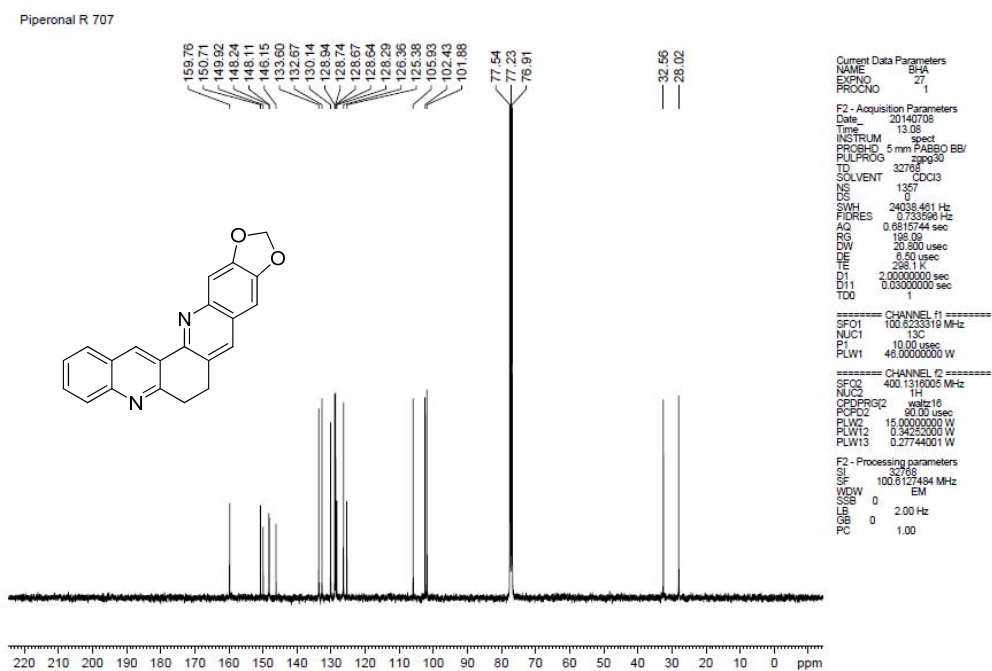
10,11-bis(benzyloxy)-6,7-dihydrodibenzo[b,j][1,7]phenanthroline(4h) : HRMS



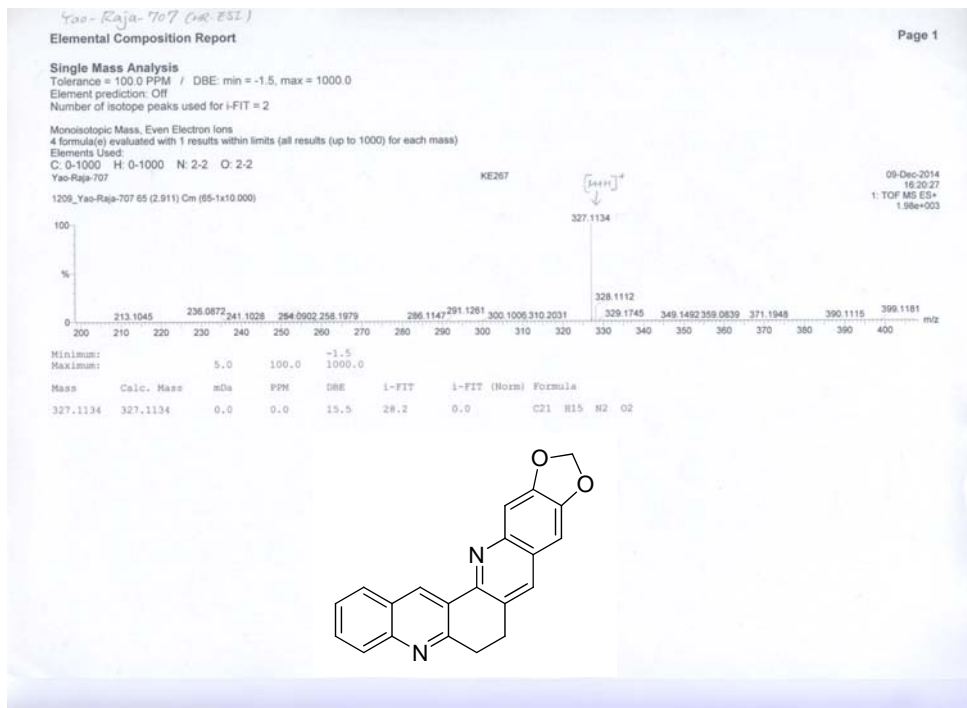
9. 6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[j][1,7]phenanthroline (4i) : ^1H NMR (400 MHz, CDCl_3)



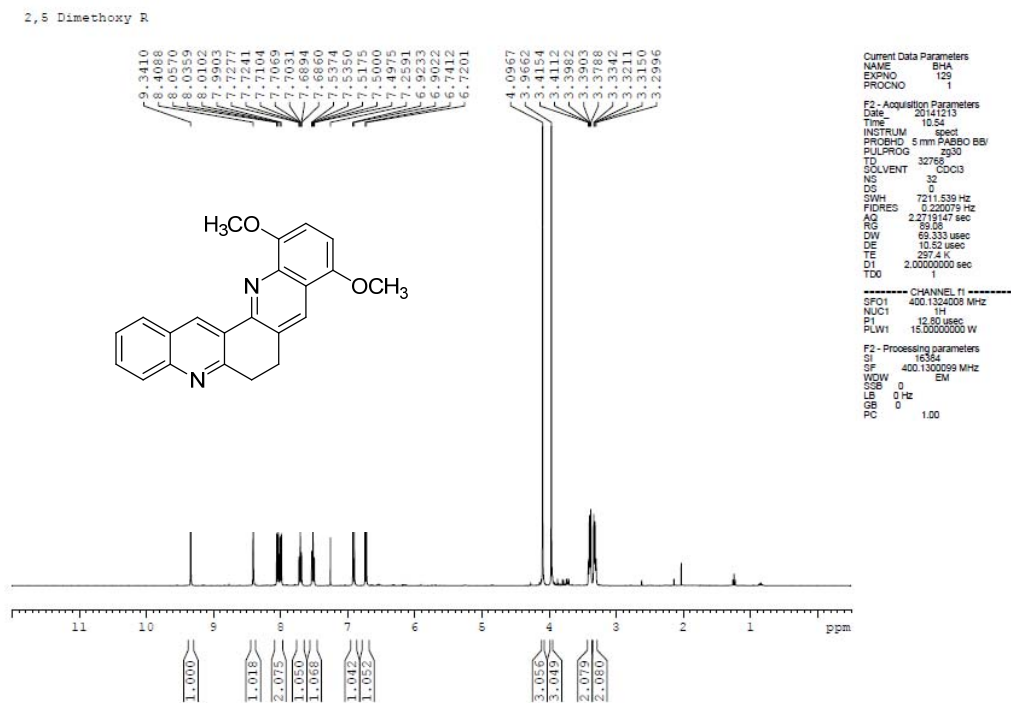
6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[j][1,7]phenanthroline (4i) : ^{13}C NMR (100 MHz, CDCl_3)



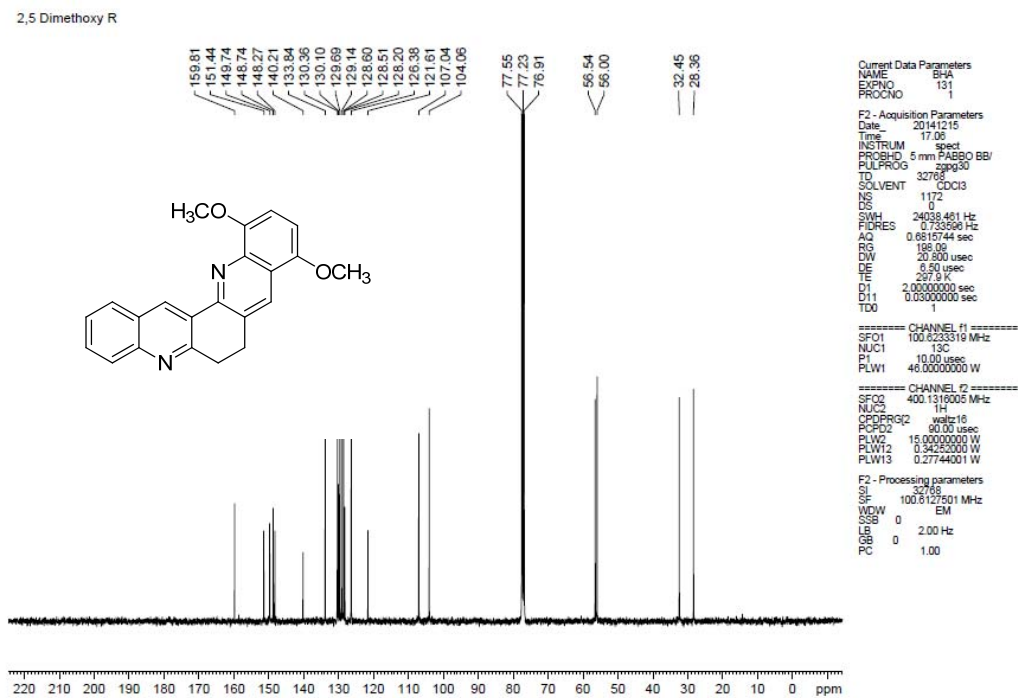
6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[j][1,7]phenanthroline (4i) : HRMS



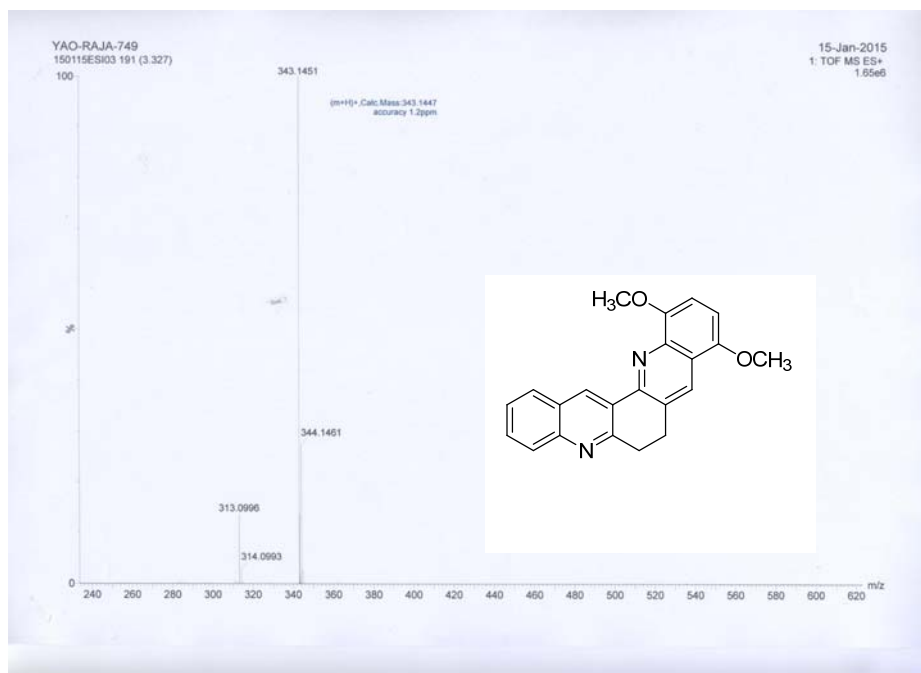
10. 9,12-dimethoxy-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4j) : ¹H NMR (400 MHz, CDCl₃)



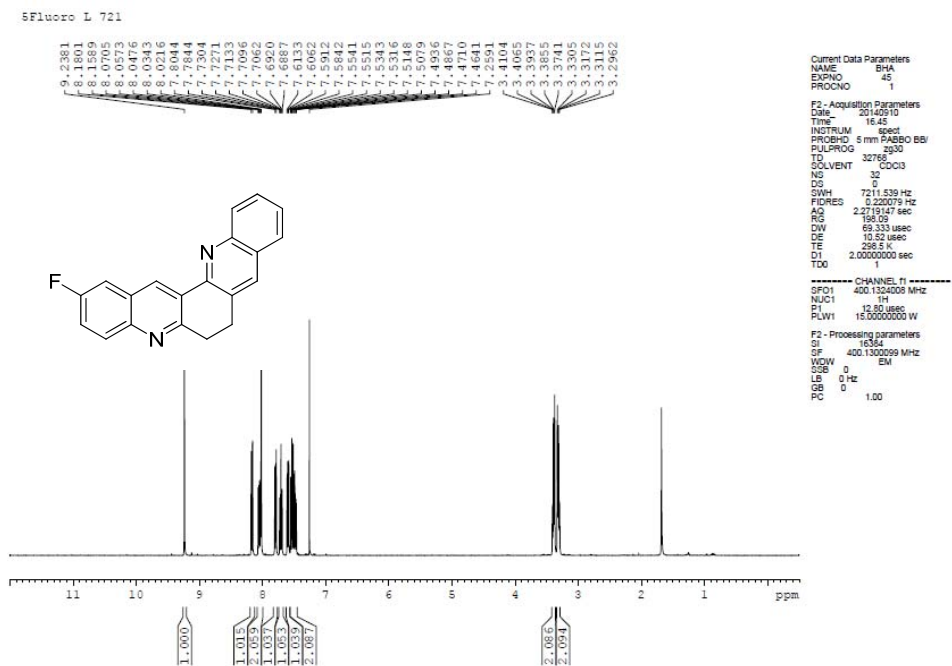
9,12-dimethoxy-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4j) : ¹³C NMR (100 MHz, CDCl₃)



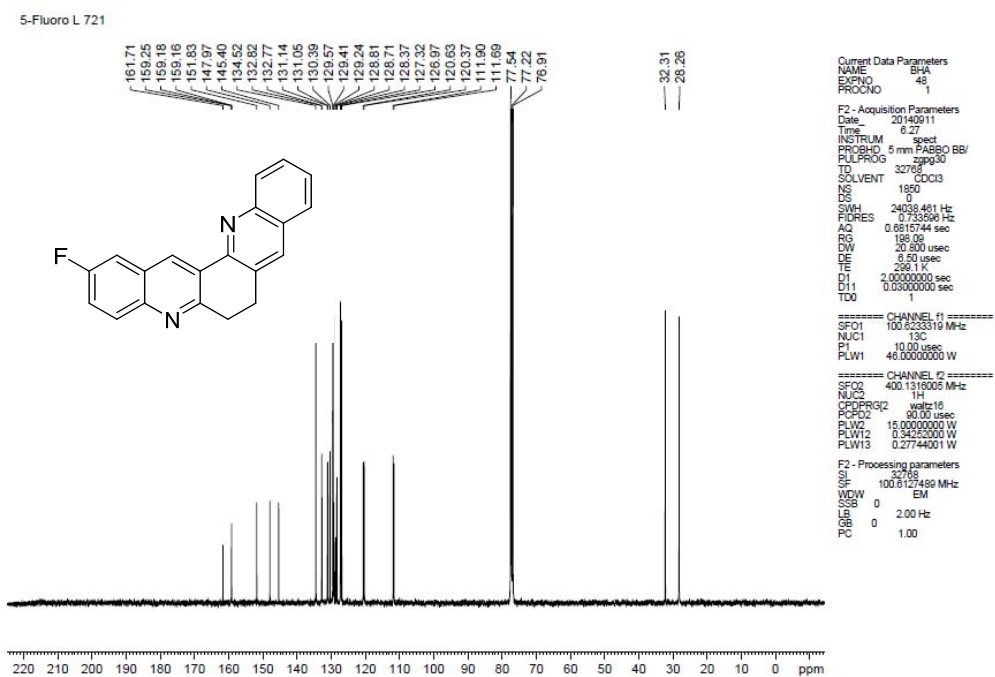
9,12-dimethoxy-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4j) : HRMS



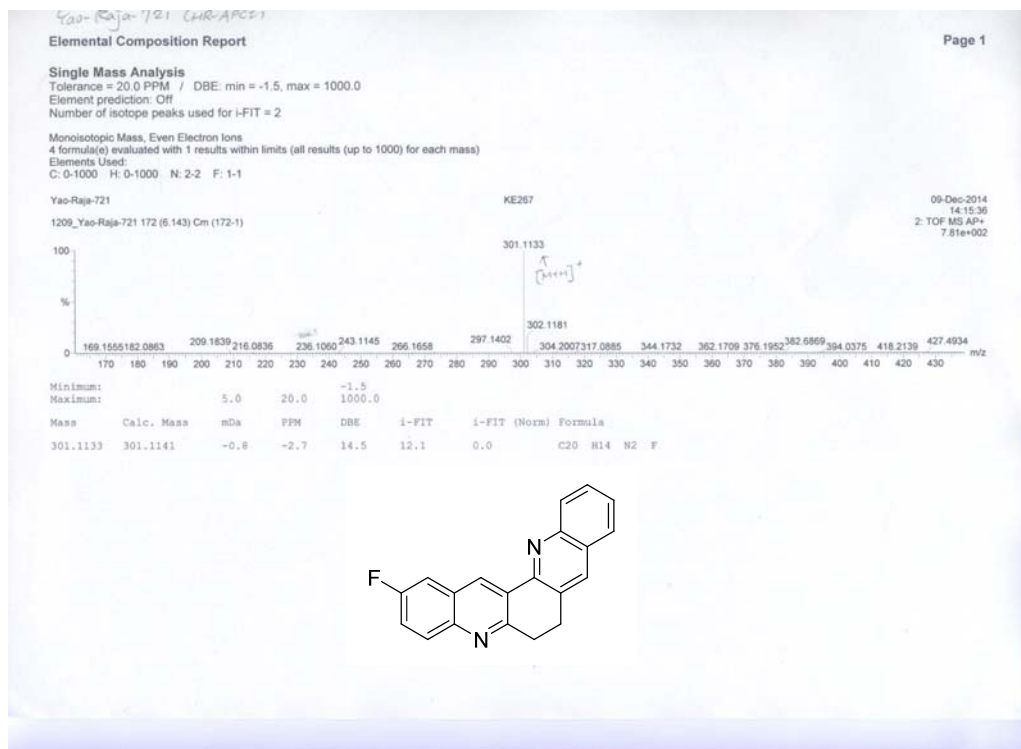
11. 2-fluoro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4k) : ¹H NMR (400 MHz, CDCl₃)



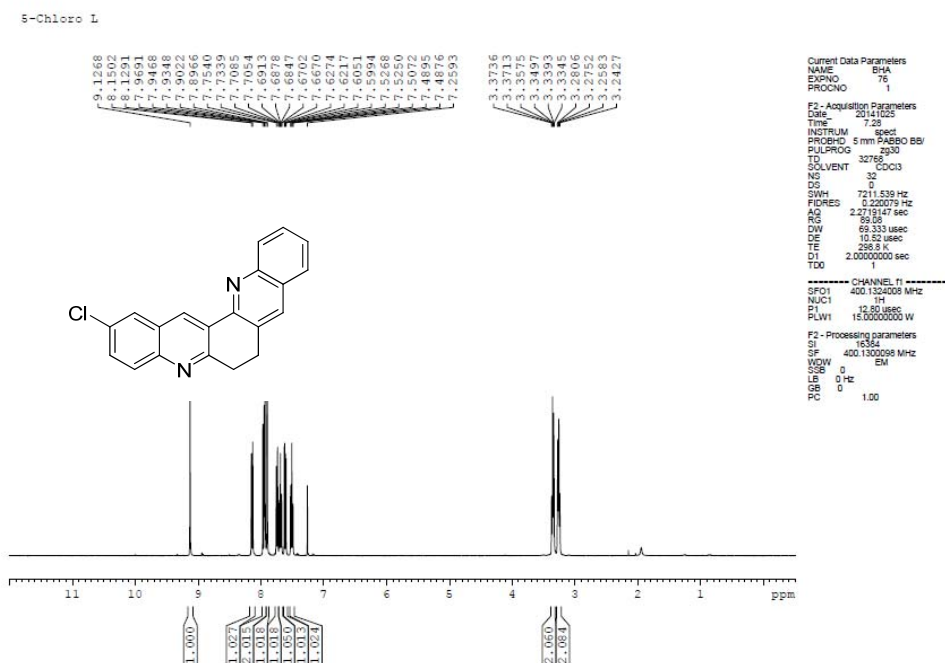
2-fluoro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4k) : ¹³C NMR (100 MHz, CDCl₃)



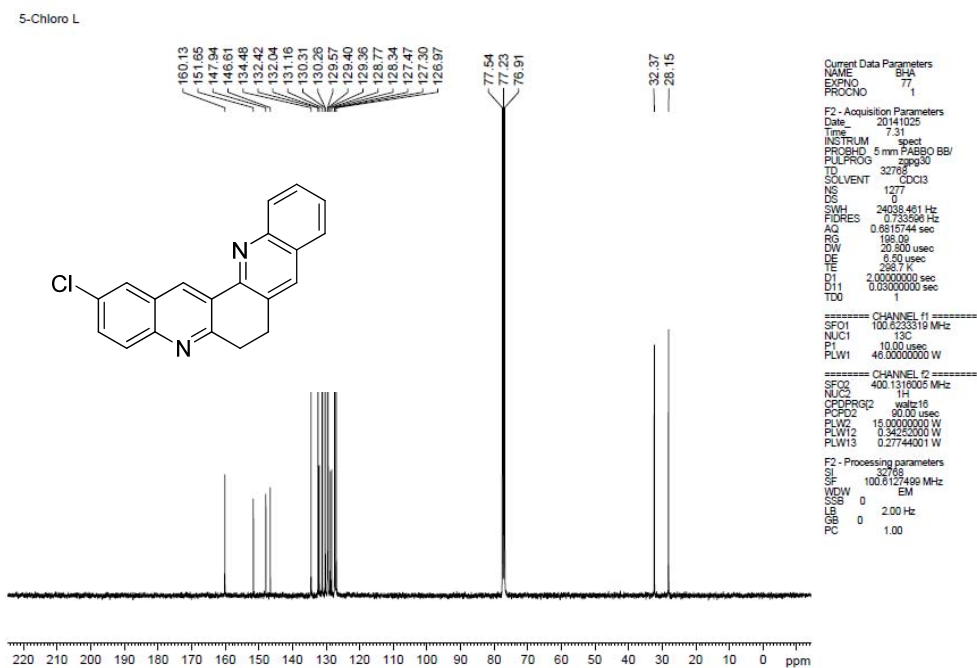
2-fluoro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4k) : HRMS



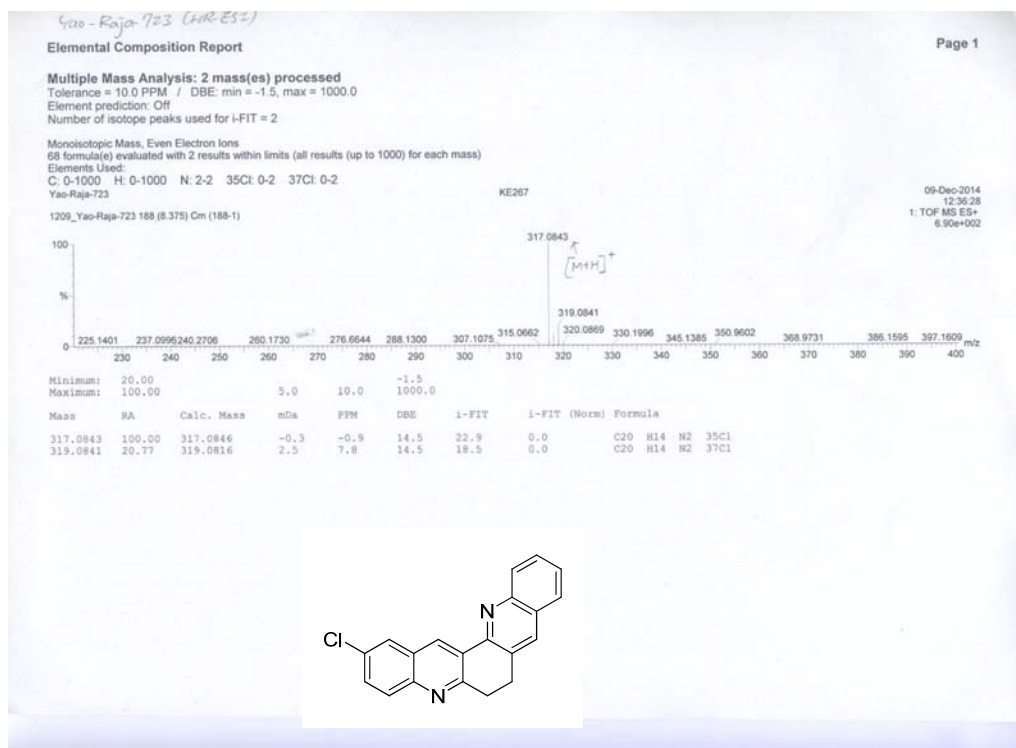
12. 2-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4l) : ¹H NMR (400 MHz, CDCl₃)



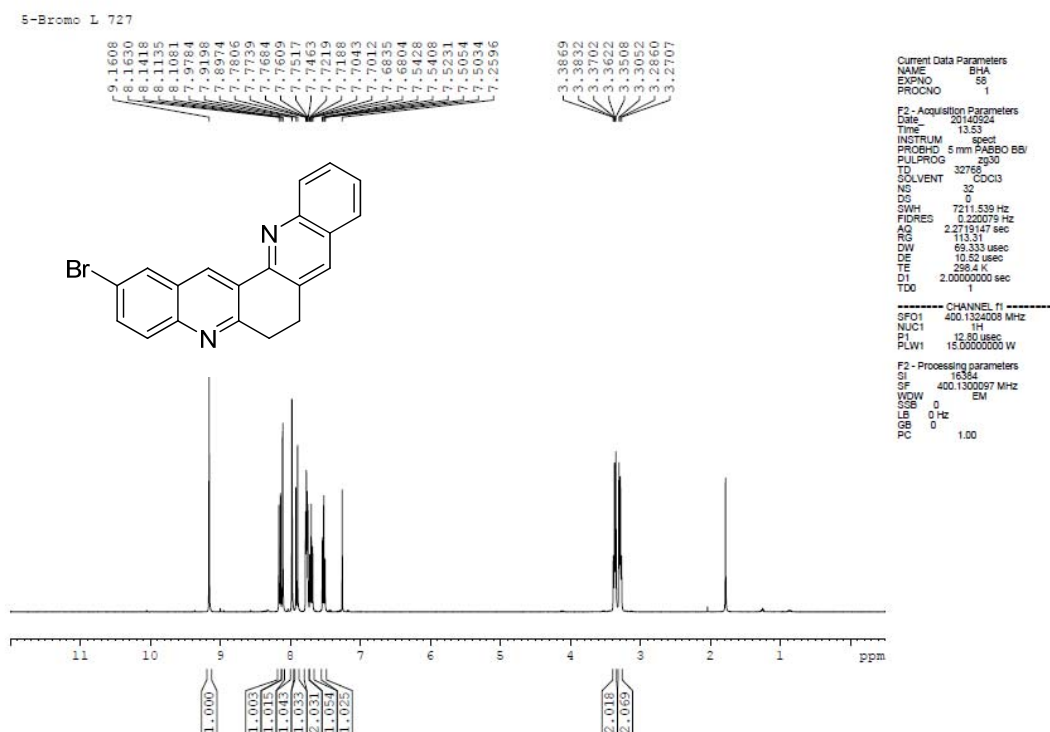
2-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4I) : ^{13}C NMR (100 MHz, CDCl_3)



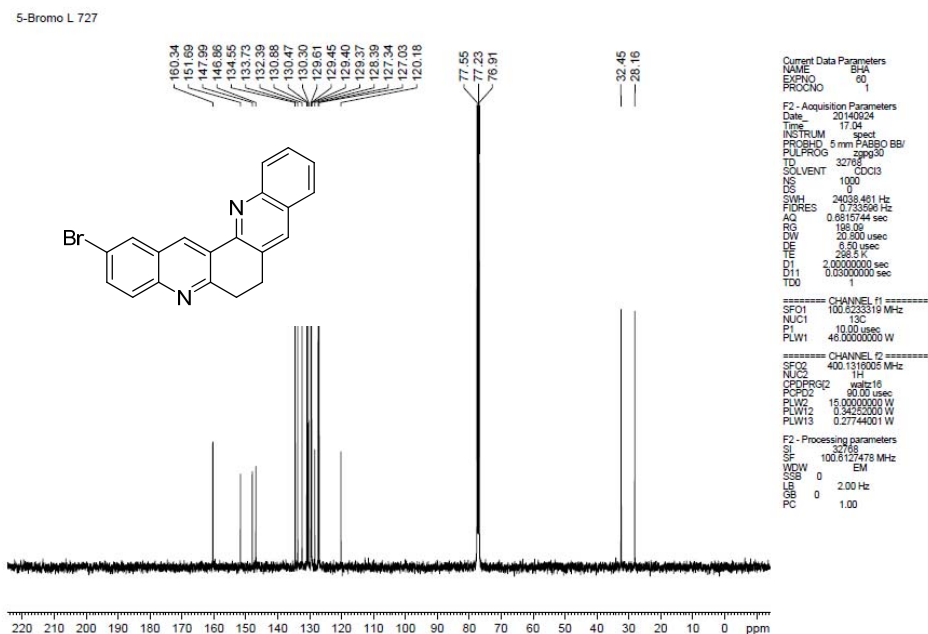
2-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4I) : HRMS



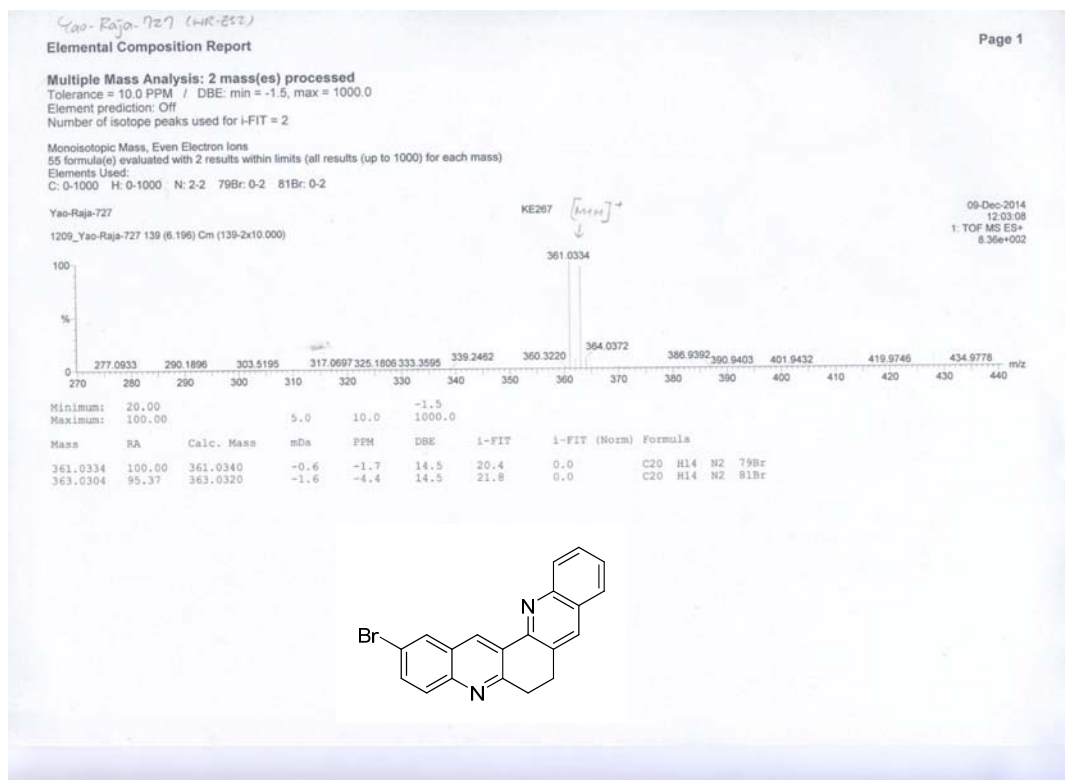
13. 2-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4m) : ^1H NMR (400 MHz, CDCl_3)



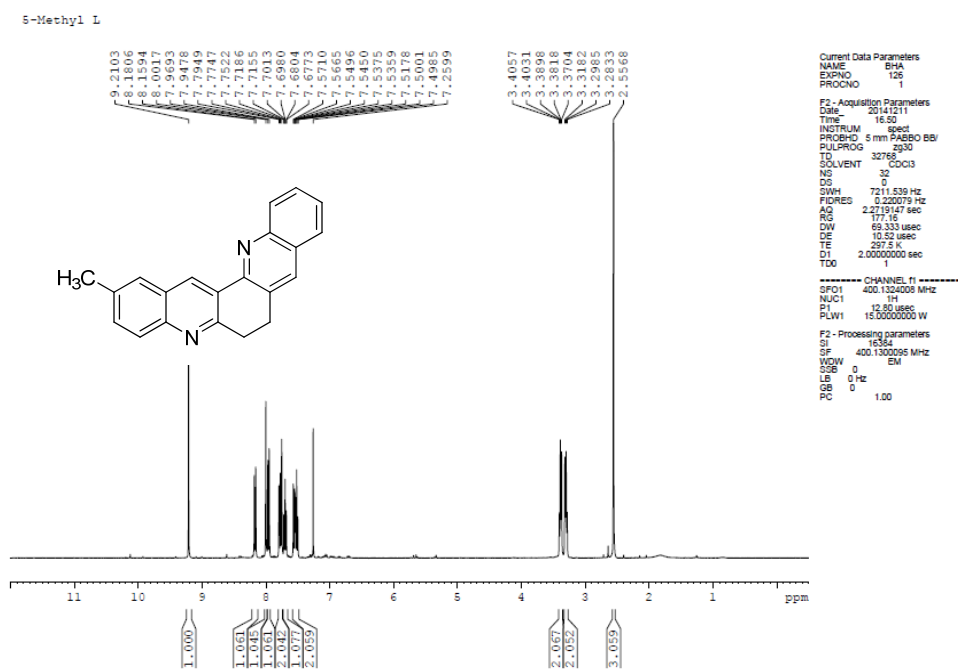
2-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4m) : ^{13}C NMR (100 MHz, CDCl_3)



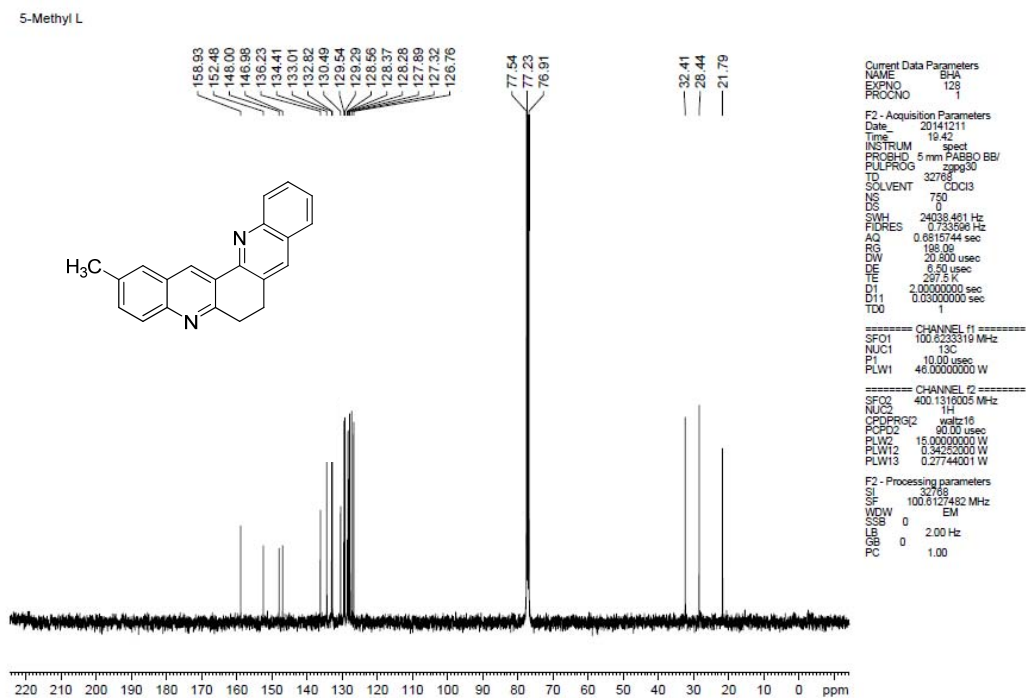
2-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4m) : HRMS



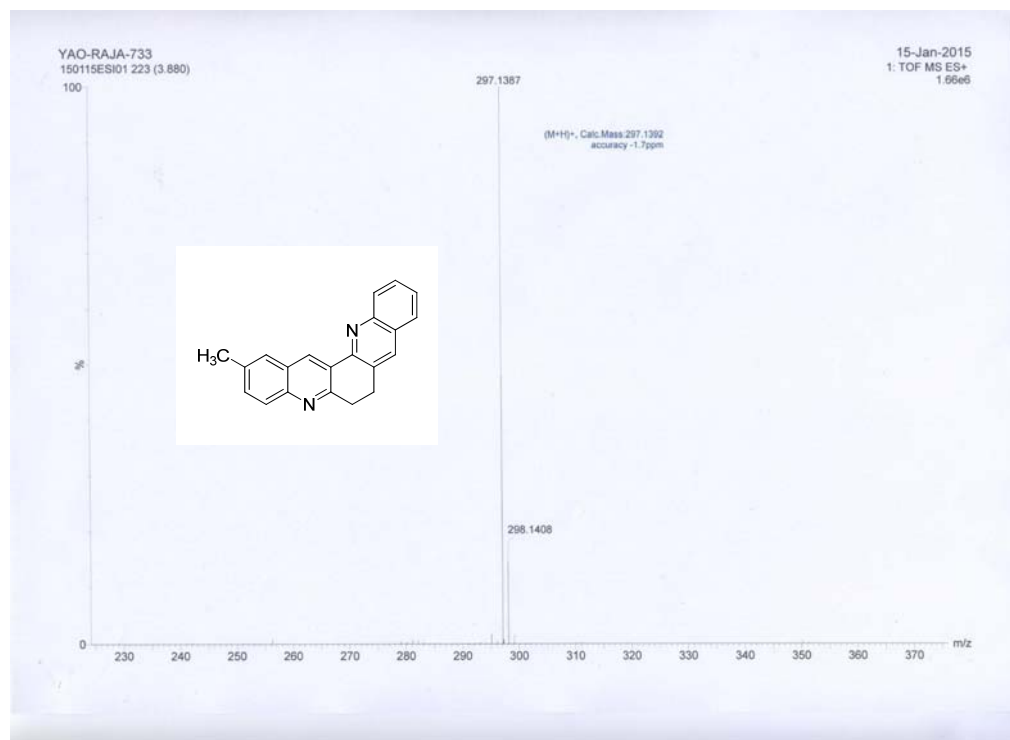
14. 2-methyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4n) : ¹H NMR (400 MHz, CDCl₃)



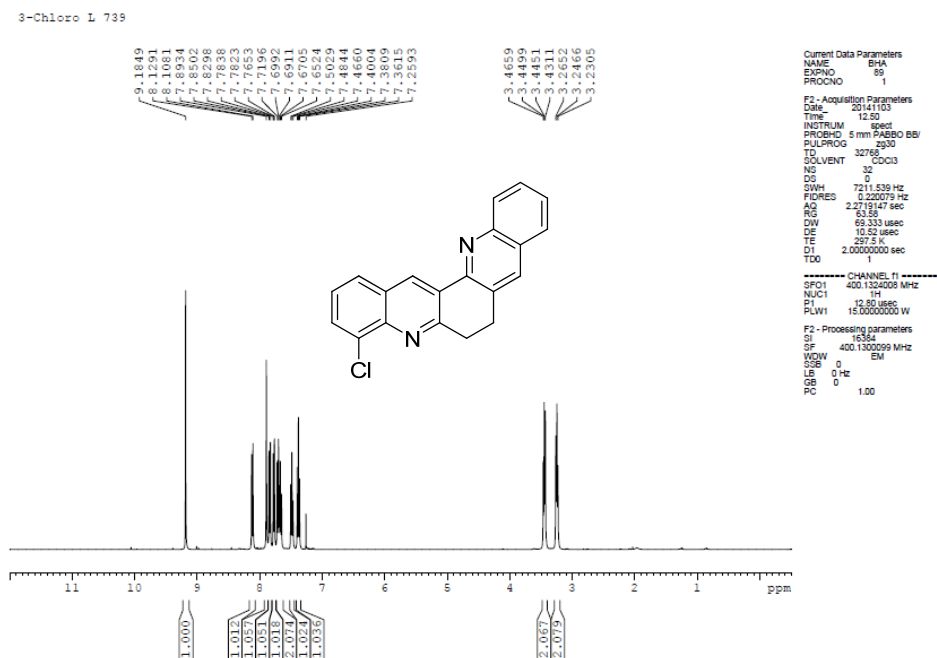
2-methyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4n) : ^{13}C NMR (100 MHz, CDCl_3)



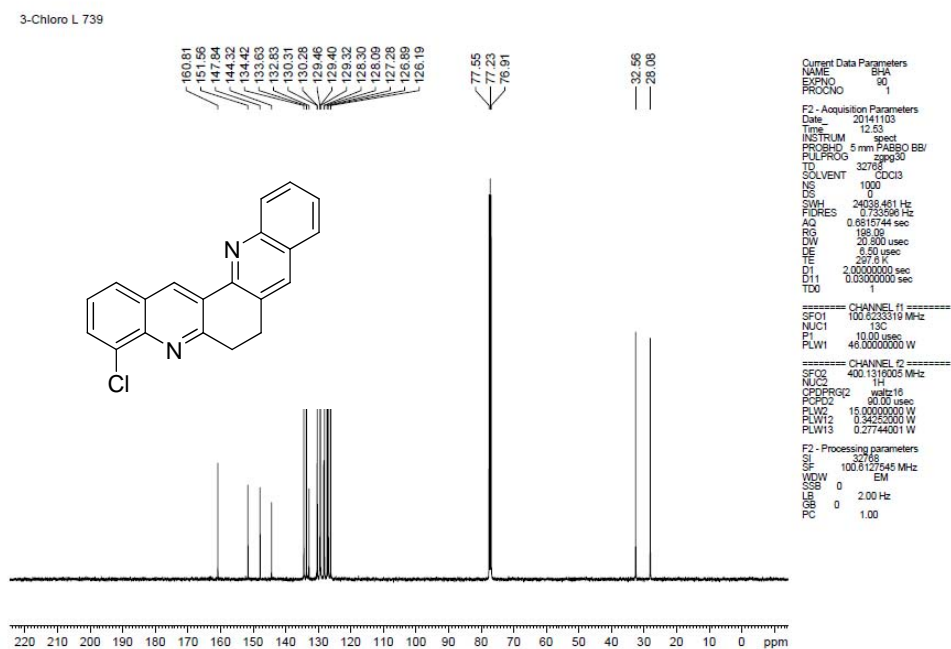
2-methyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4n) : HRMS



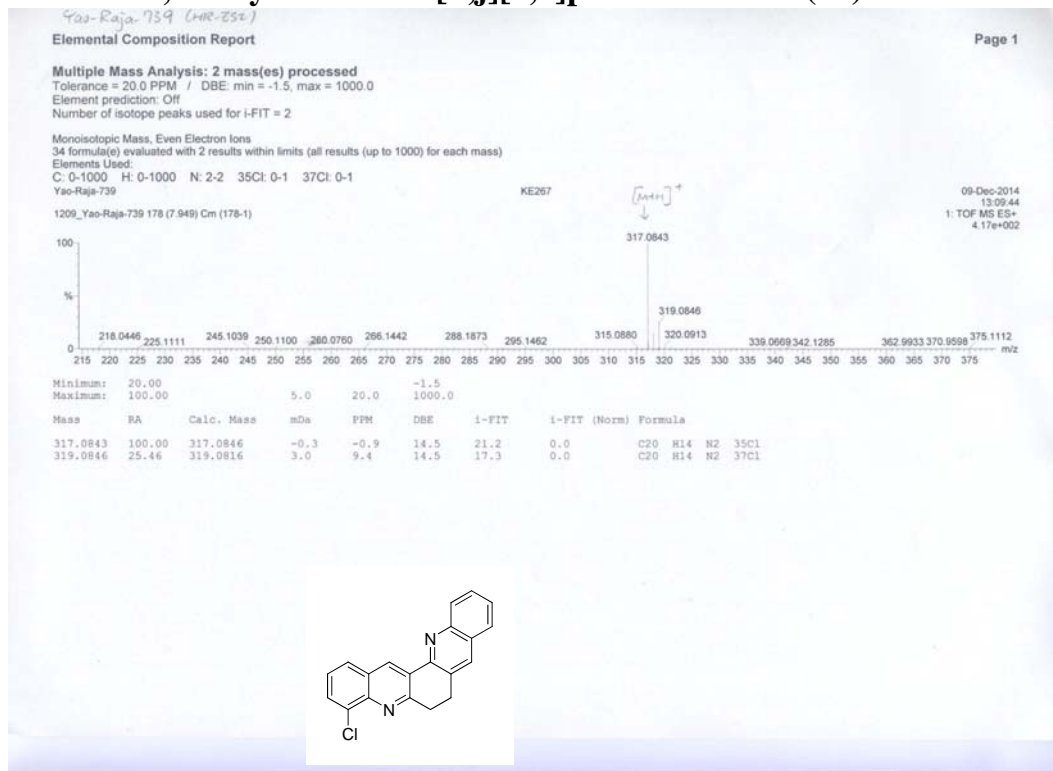
15. 4-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4o) : ¹H NMR (400 MHz, CDCl₃)



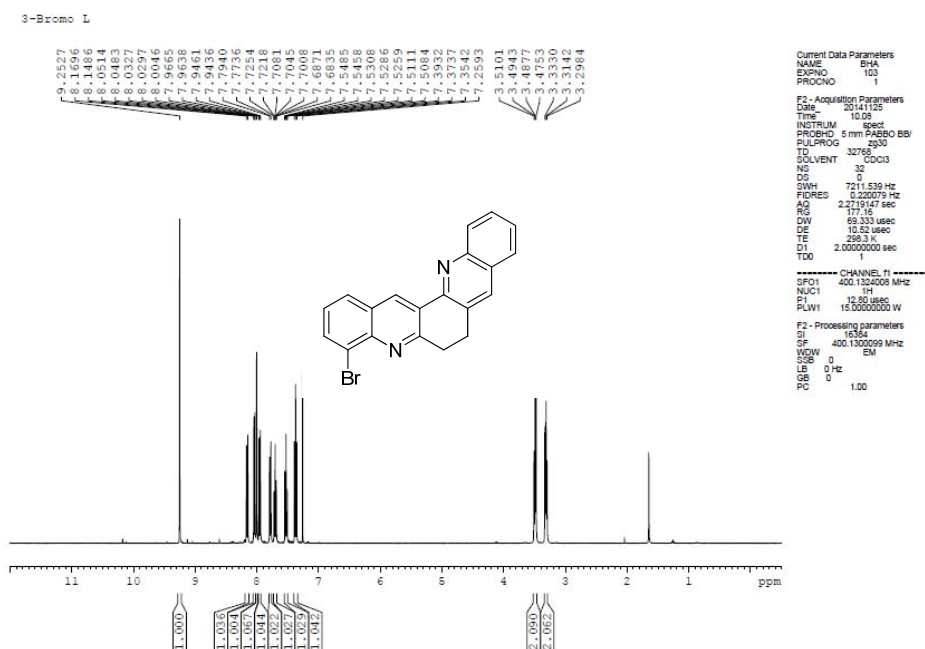
4-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4o) : ¹³C NMR (100 MHz, CDCl₃)



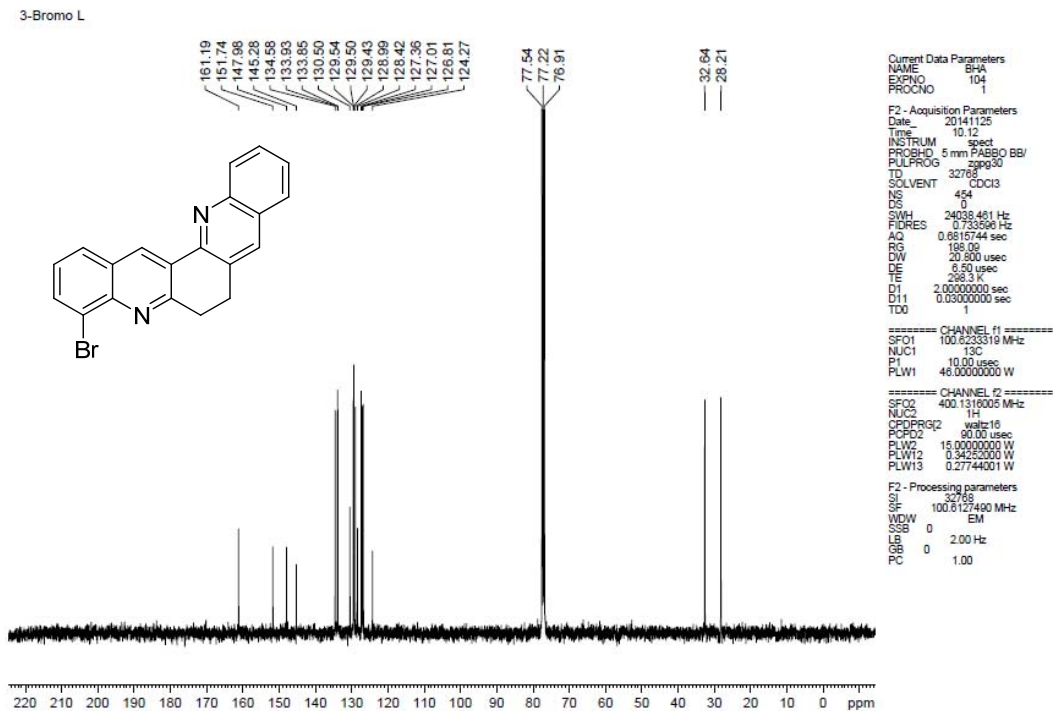
4-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4o) : HRMS



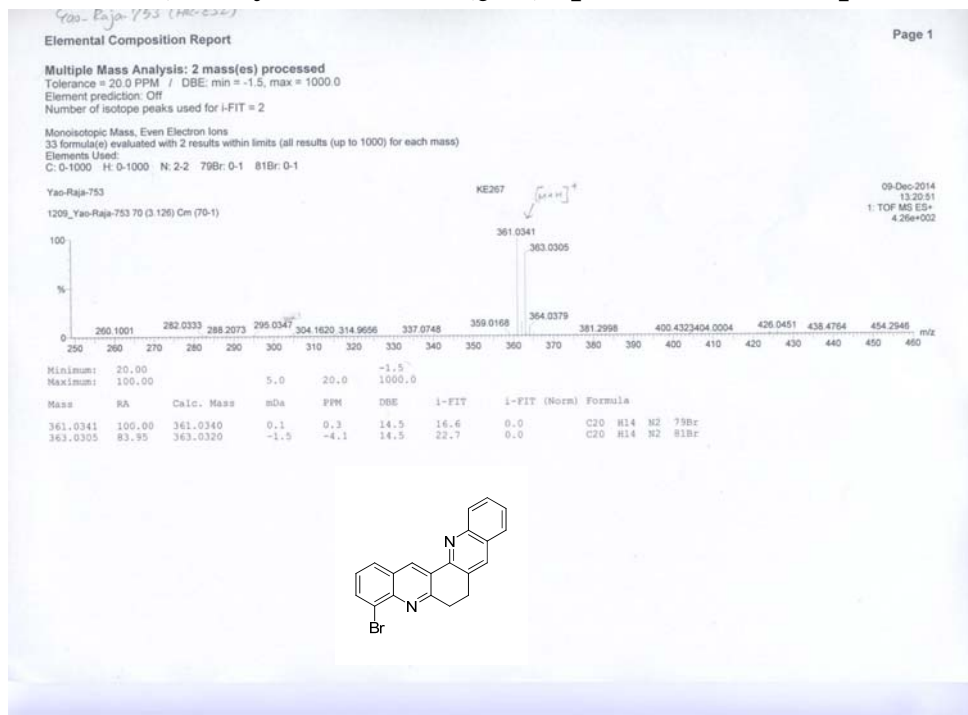
16. 4-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4p) : ¹H NMR (400 MHz, CDCl₃)



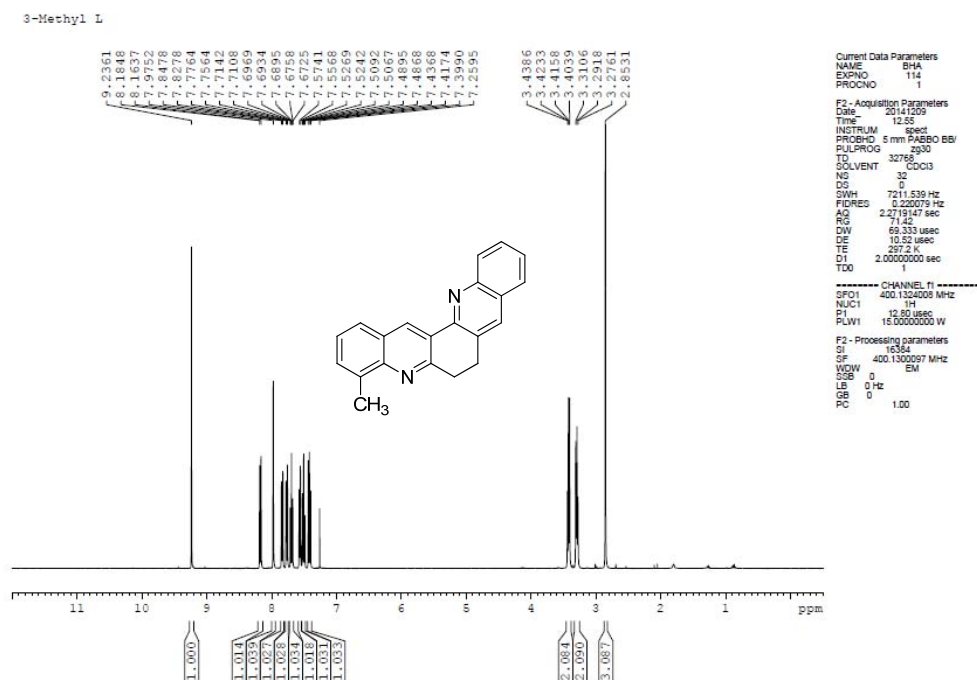
4-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4p) : ¹³C NMR (100 MHz, CDCl₃)



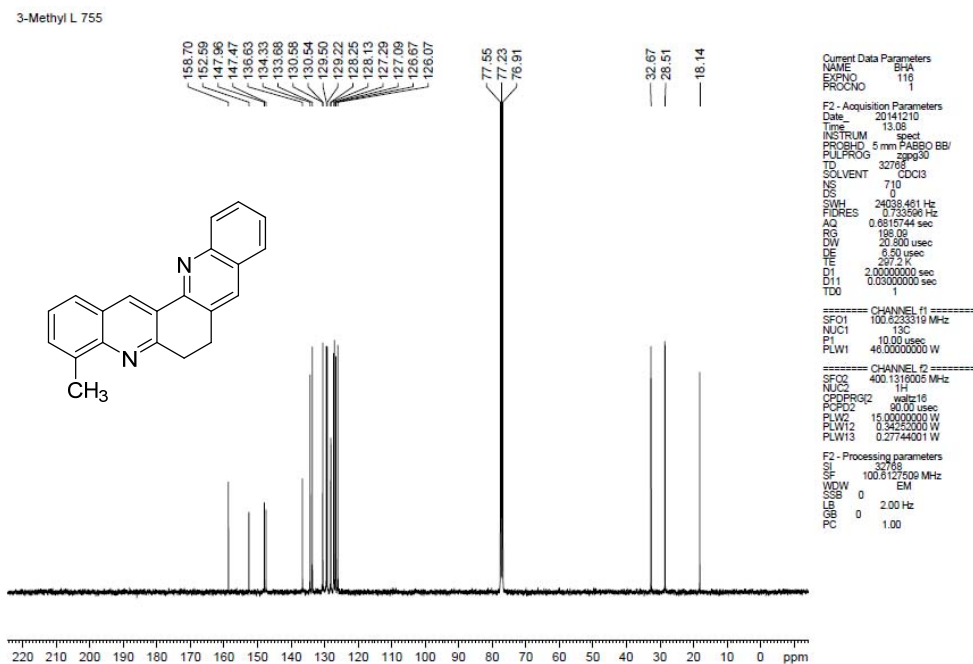
4-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4p) : HRMS



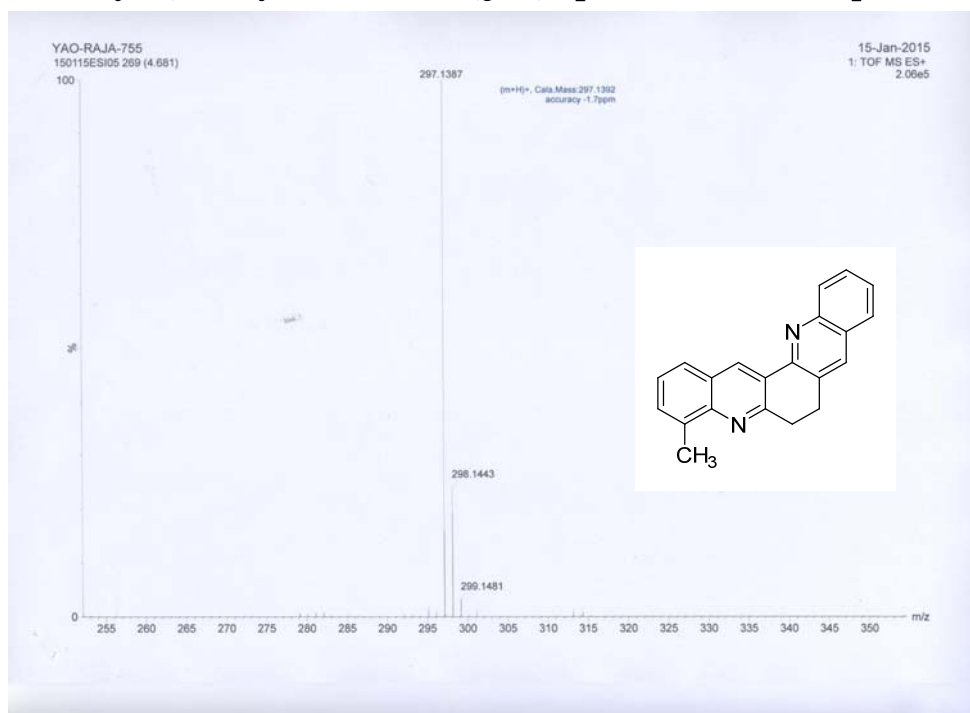
17. 4-methyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4q) : ¹H NMR (400 MHz, CDCl₃)



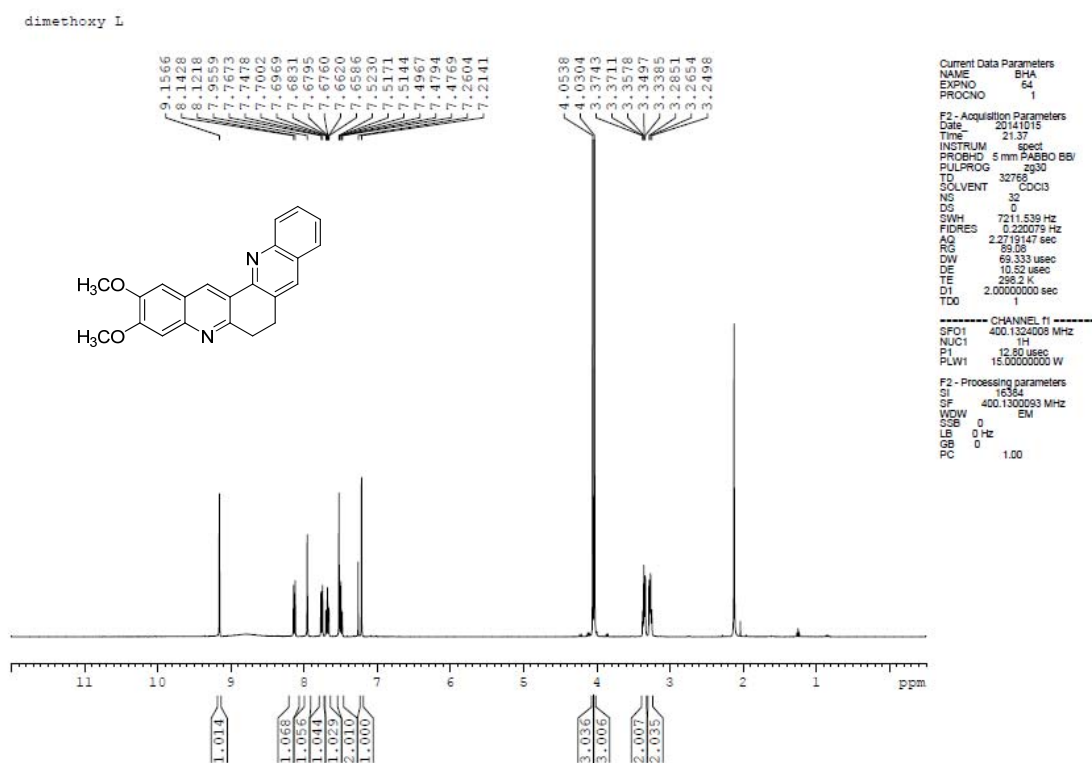
4-methyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4q) : ¹³C NMR (100 MHz, CDCl₃)



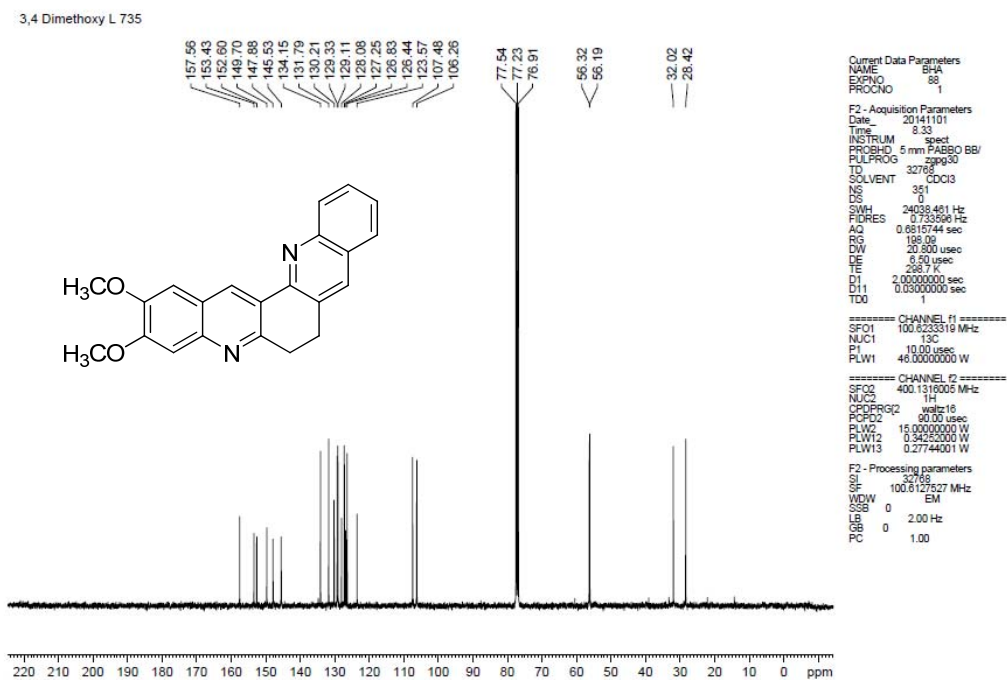
4-methyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4q) : HRMS



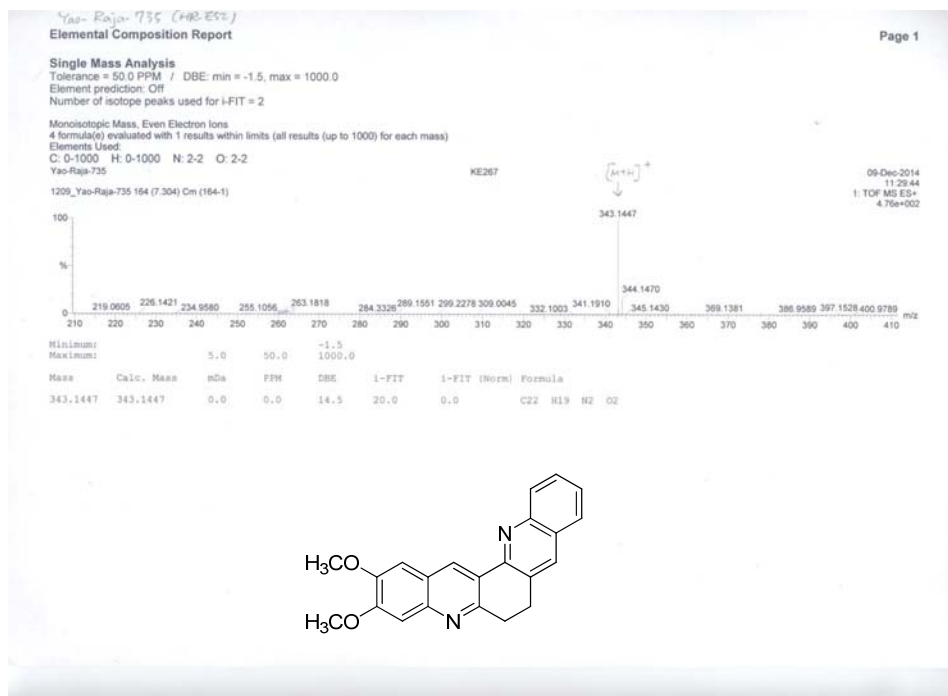
18. 2,3-dimethoxy-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4r) : ¹H NMR (400 MHz, CDCl₃)



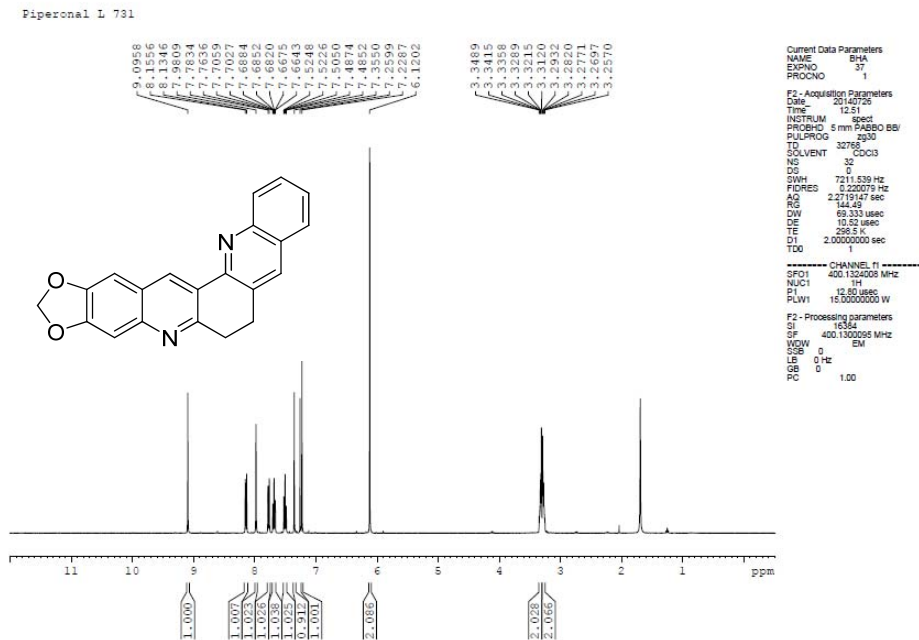
2,3-dimethoxy-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4r) : ¹³C NMR (100 MHz, CDCl₃)



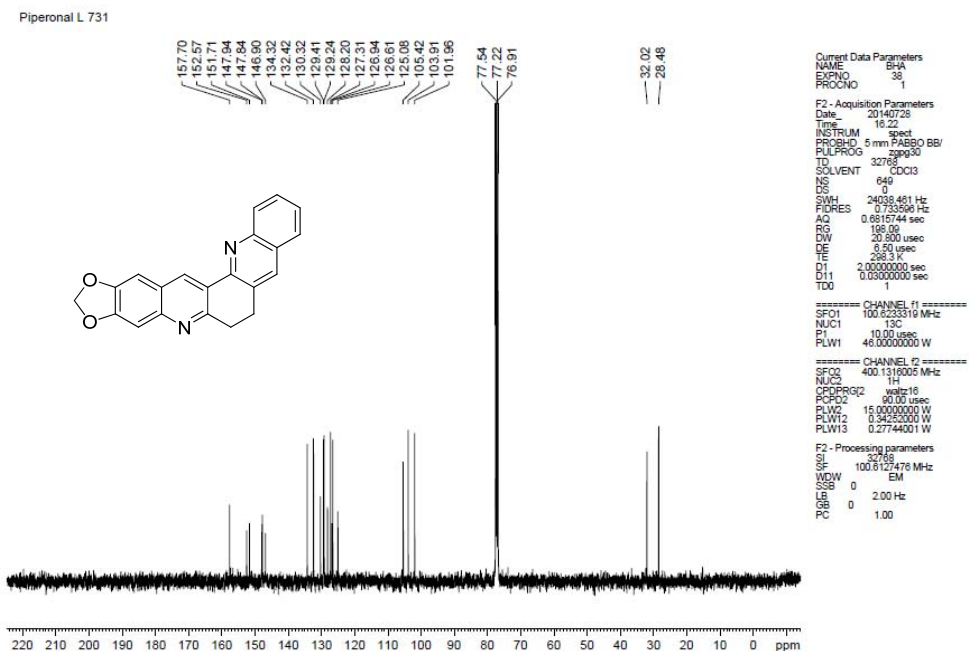
2,3-dimethoxy-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4r) : HRMS



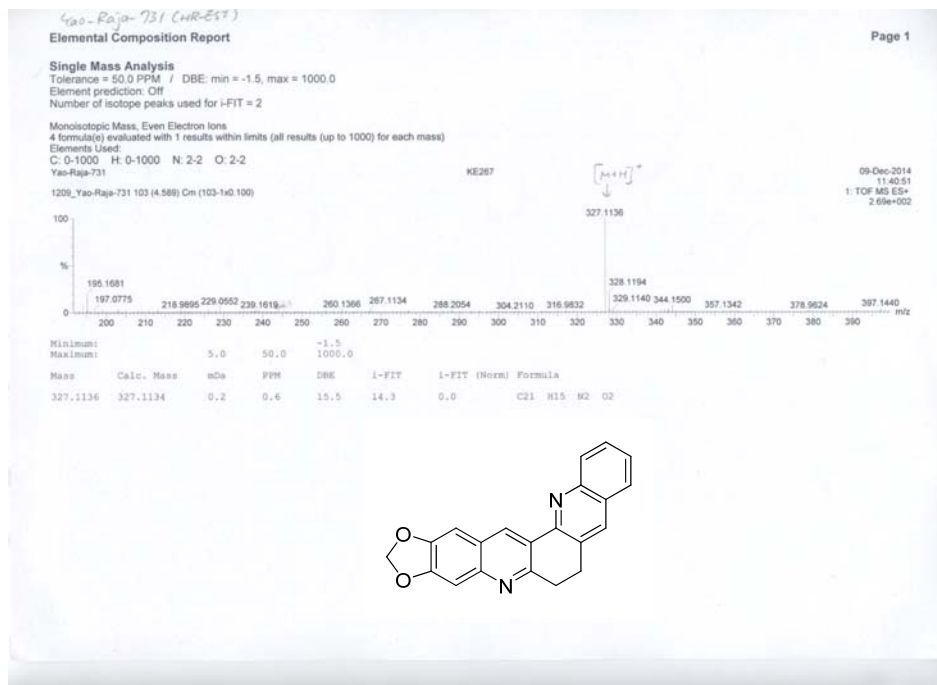
19. 6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-j]benzo[b][1,7]phenanthroline (4s) : ¹H NMR (400 MHz, CDCl₃)



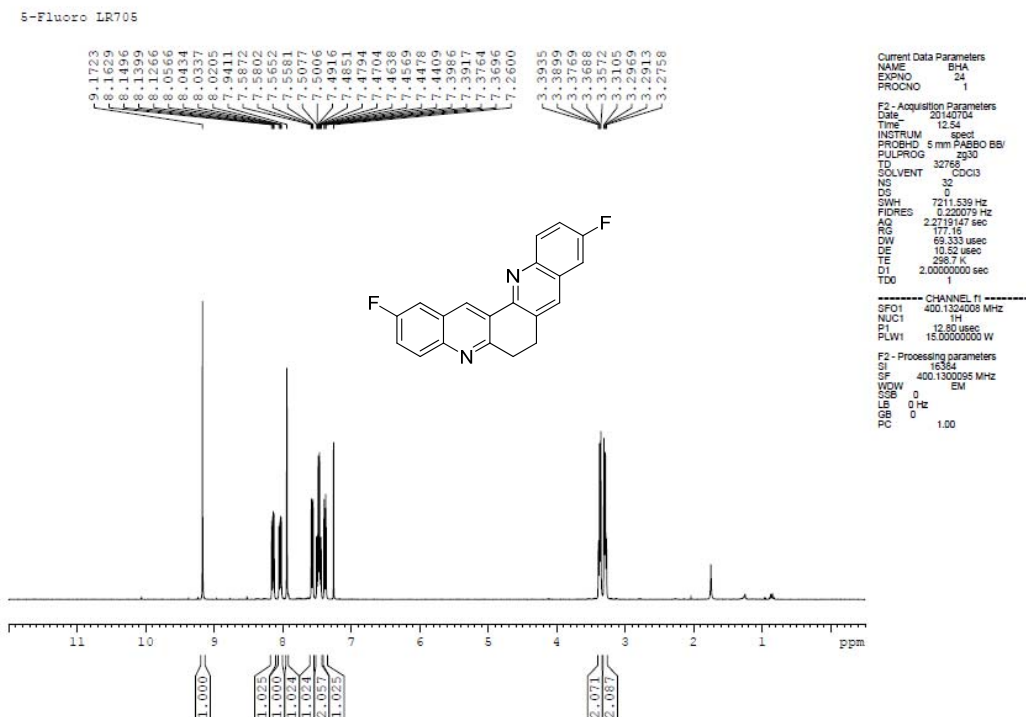
6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-j]benzo[b][1,7]phenanthroline (4s) : ¹³C NMR (100 MHz, CDCl₃)



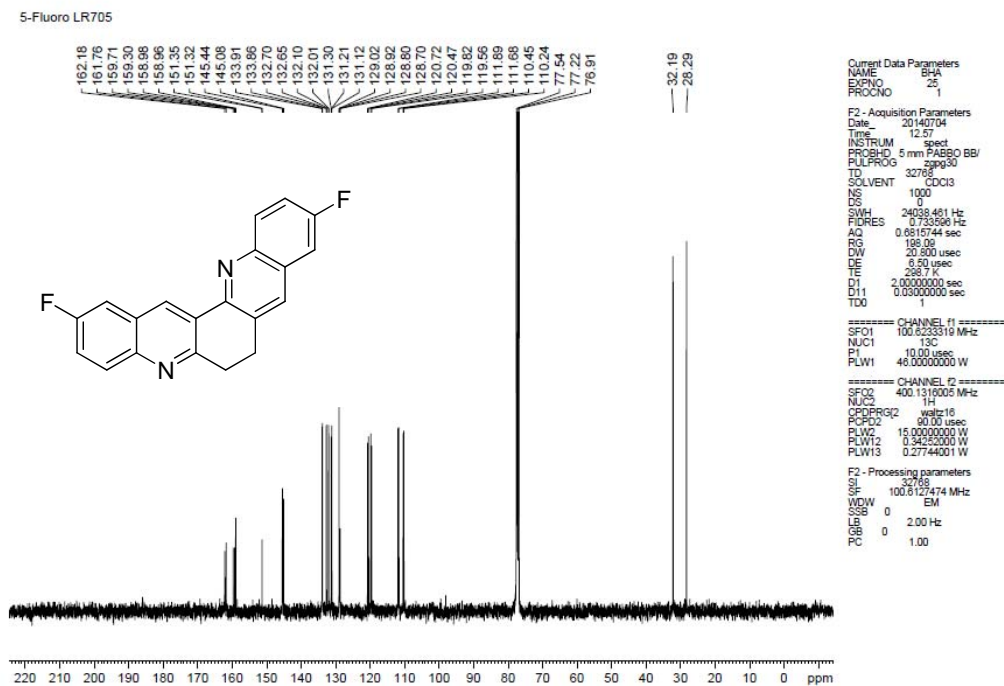
6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-j]benzo[b][1,7]phenanthroline (4s) : HRMS



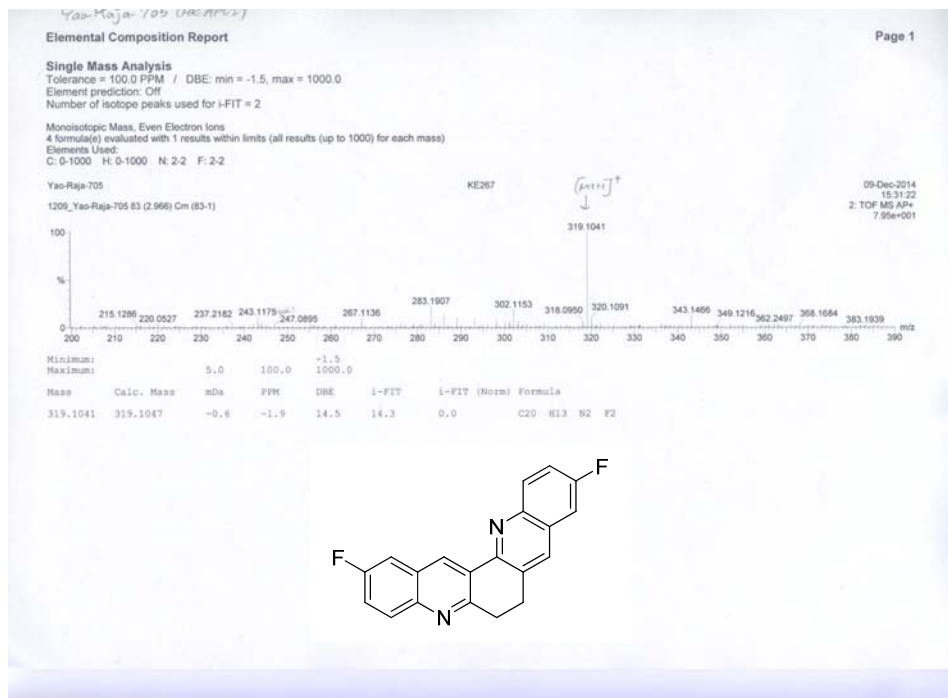
20. 2,10-difluoro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4t) : ¹H NMR (400 MHz, CDCl₃)



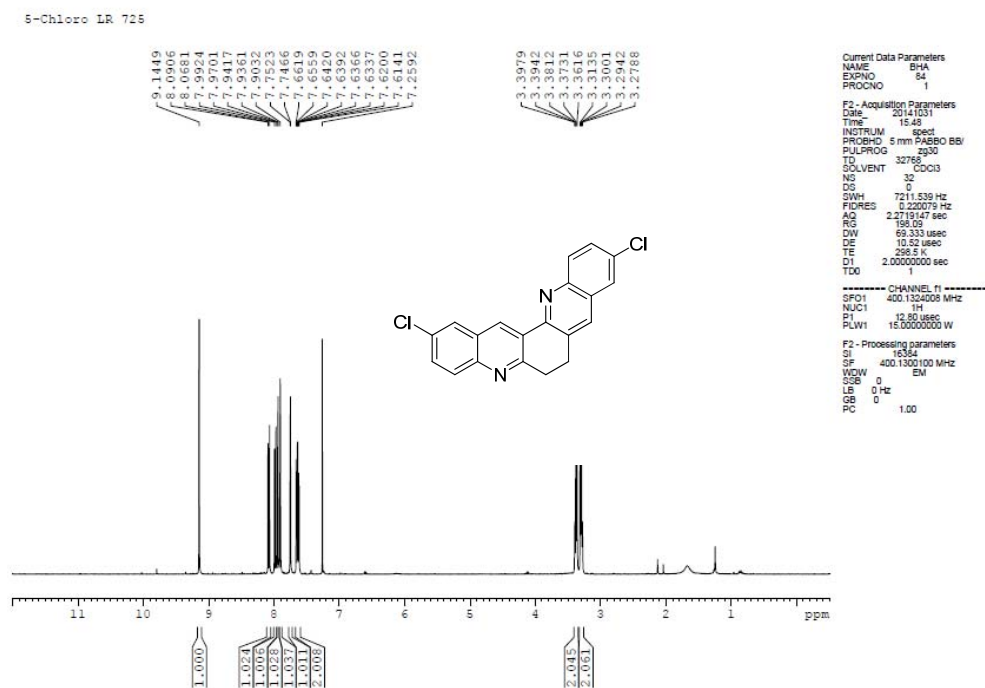
2,10-difluoro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4t) : ¹³C NMR (100 MHz, CDCl₃)



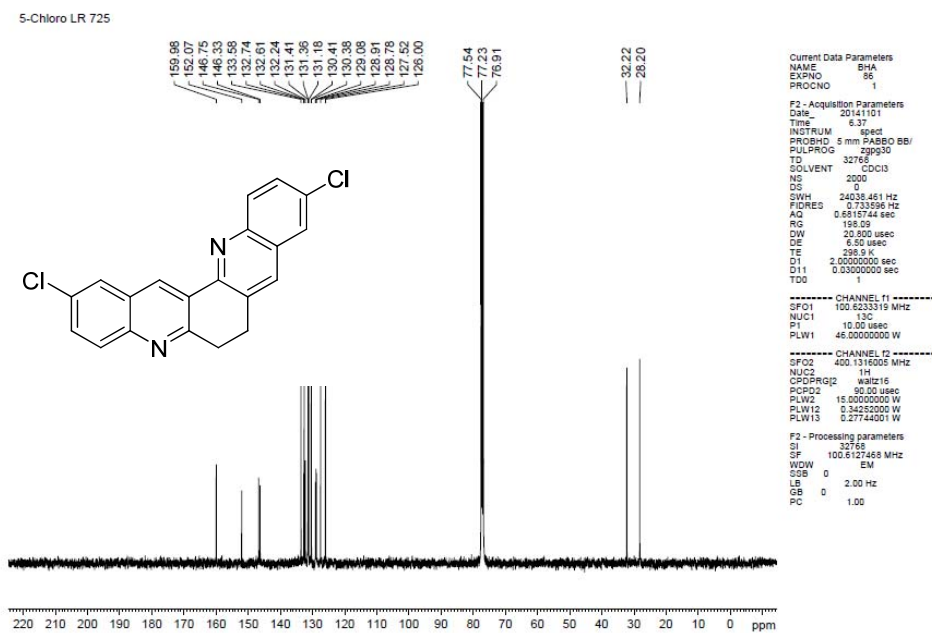
2,10-difluoro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4t) : HRMS



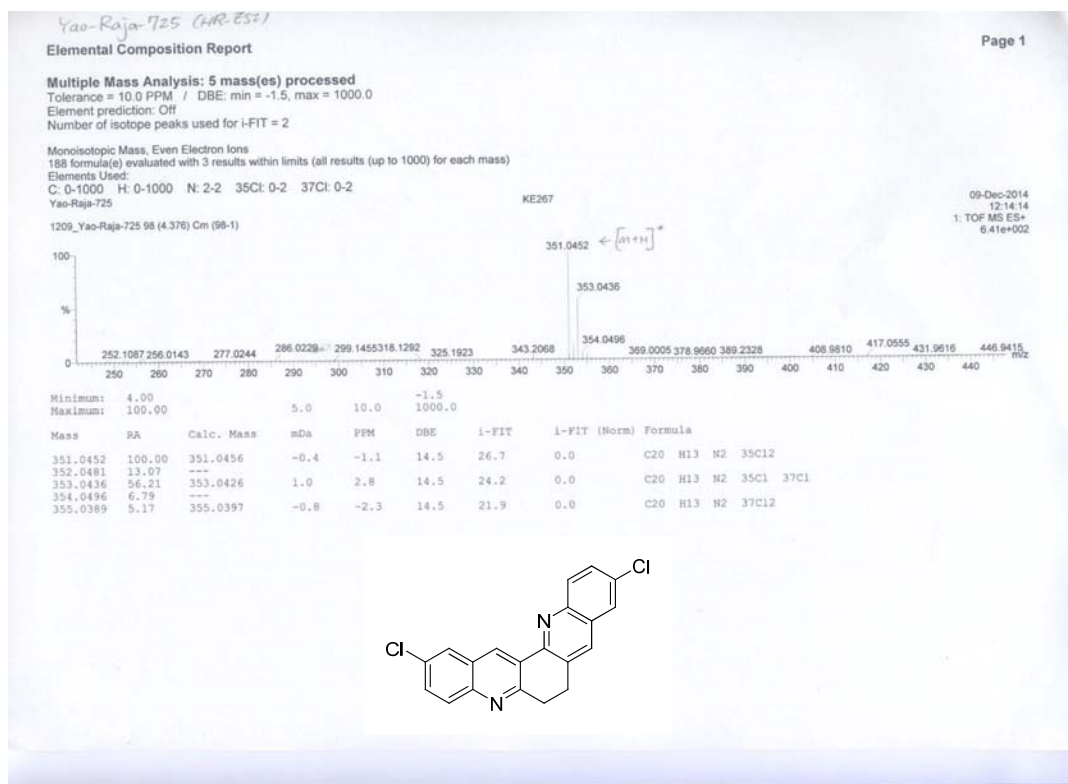
21. 2,10-dichloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4u) : ¹H NMR (400 MHz, CDCl₃)



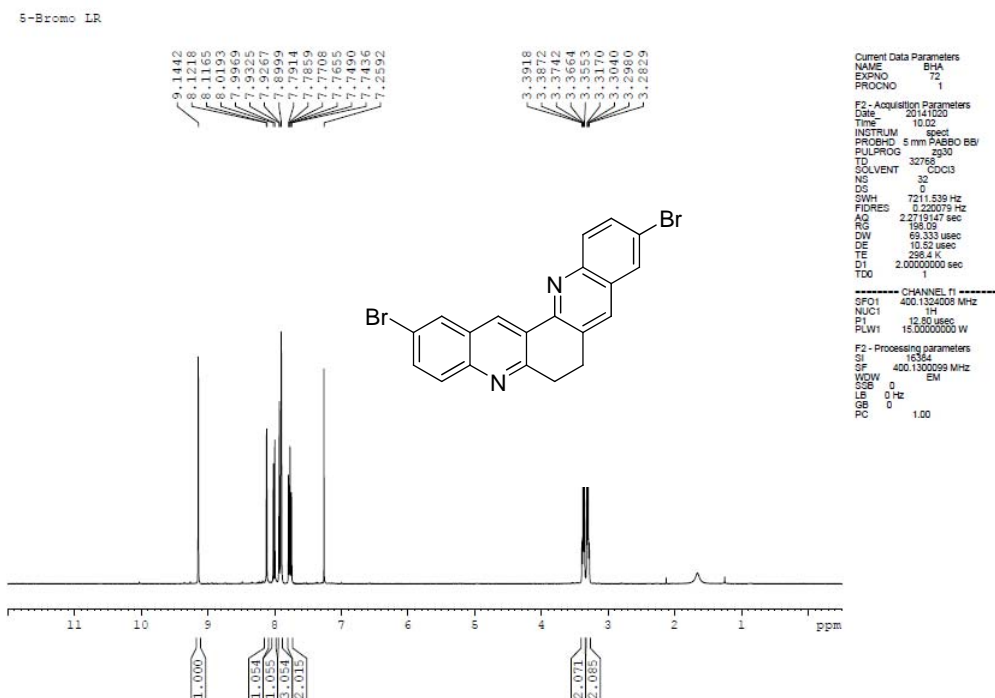
2,10-dichloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4u) : ¹³C NMR (100 MHz, CDCl₃)



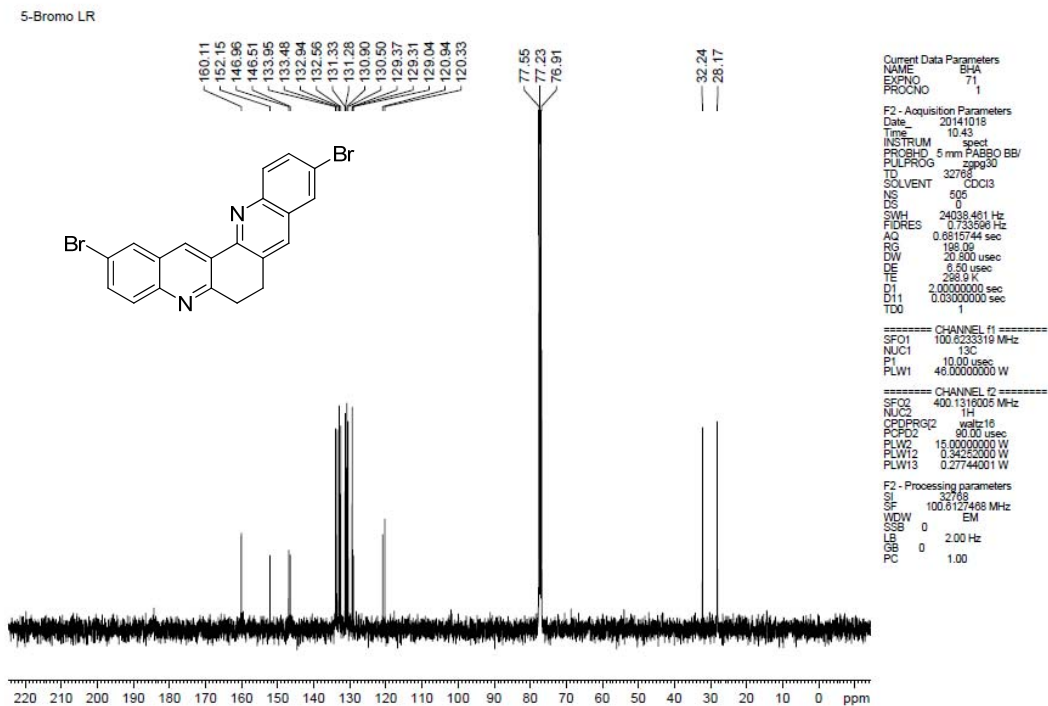
2,10-dichloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4u) : HRMS



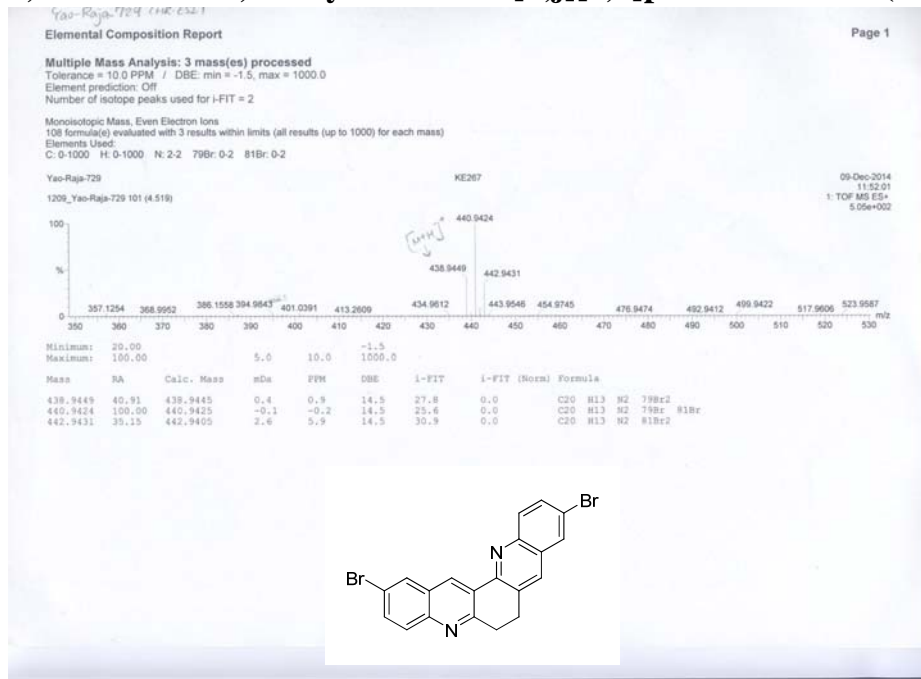
22. 2,10-dibromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4v) : ¹H NMR (400 MHz, CDCl₃)



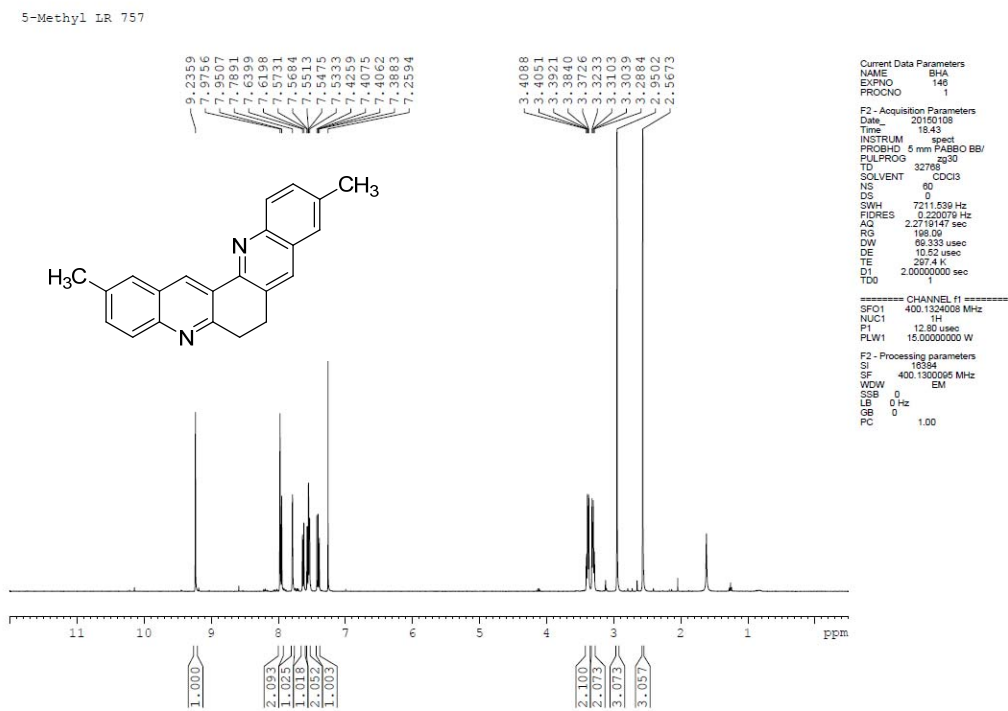
2,10-dibromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4v) : ^{13}C NMR (100 MHz, CDCl_3)



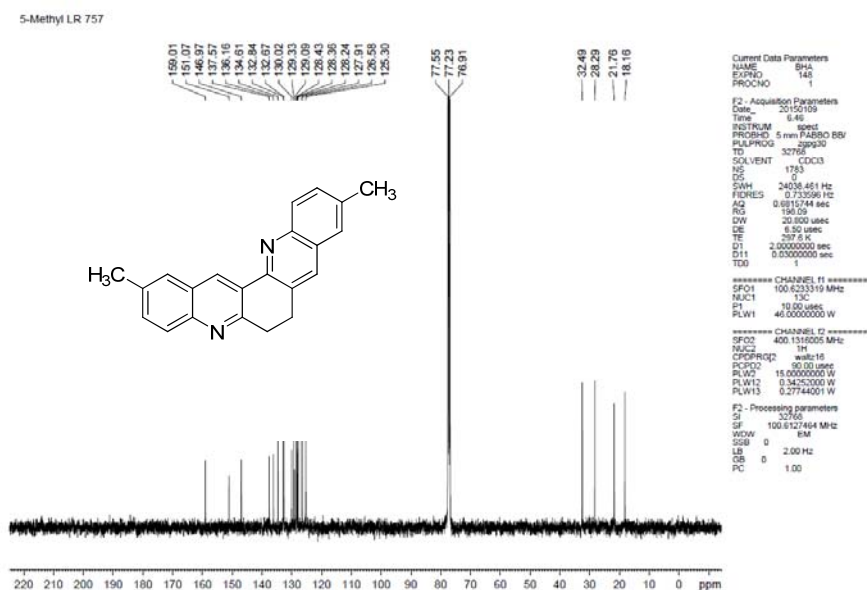
2,10-dibromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4v) : HRMS



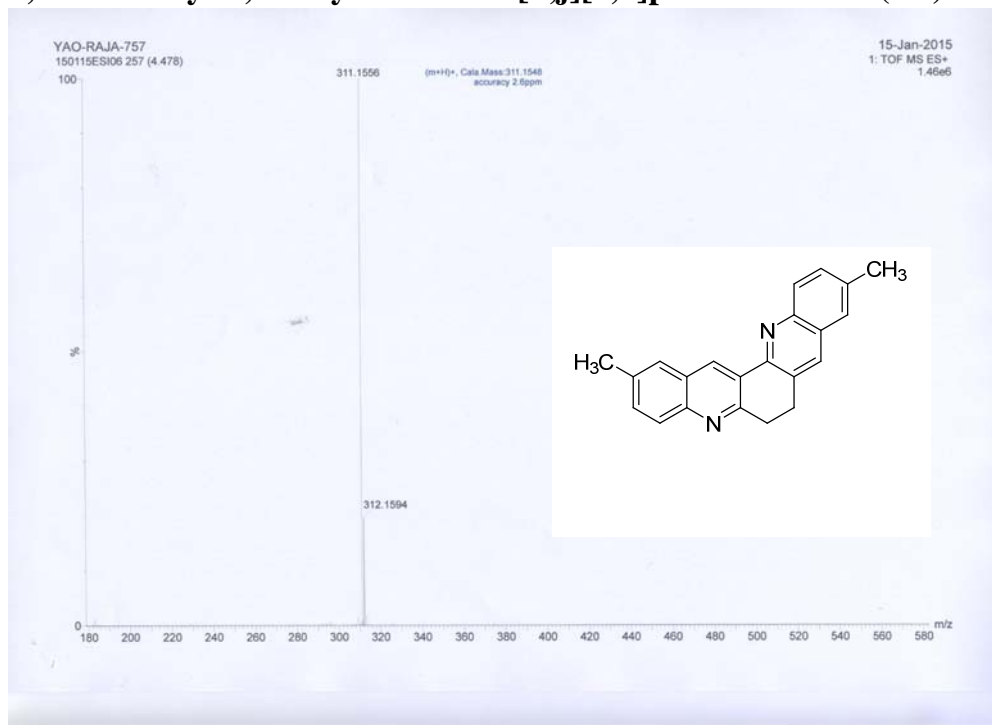
23. 2,10-dimethyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline(4w) : ¹H NMR (400 MHz, CDCl₃)



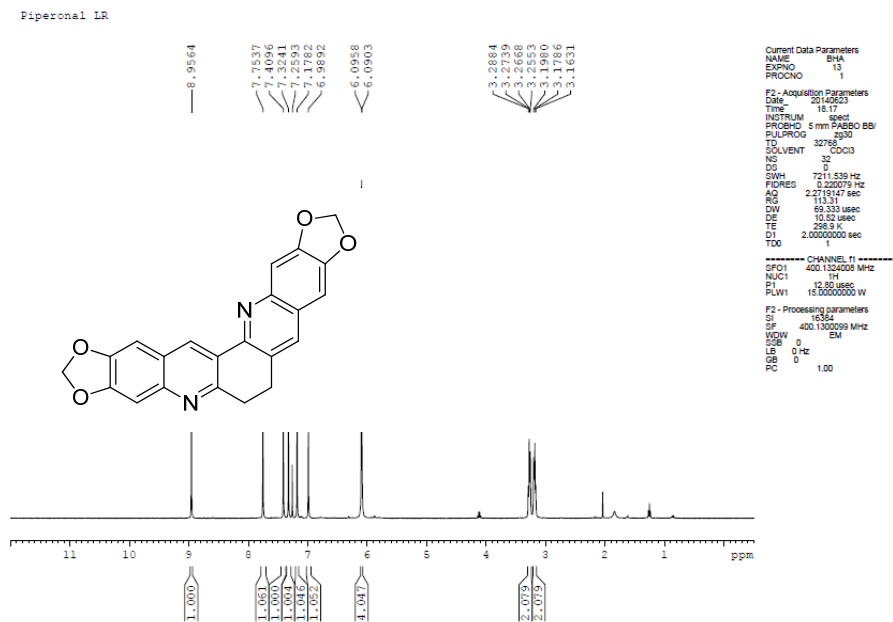
2,10-dimethyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline(4w) : ¹³C NMR (100 MHz, CDCl₃)



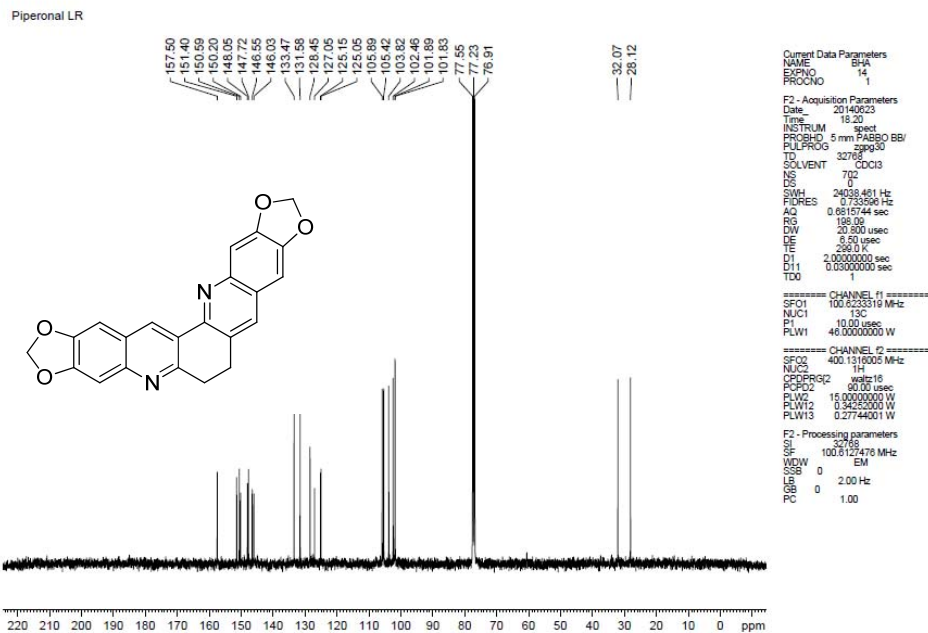
2,10-dimethyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline(4w) : HRMS



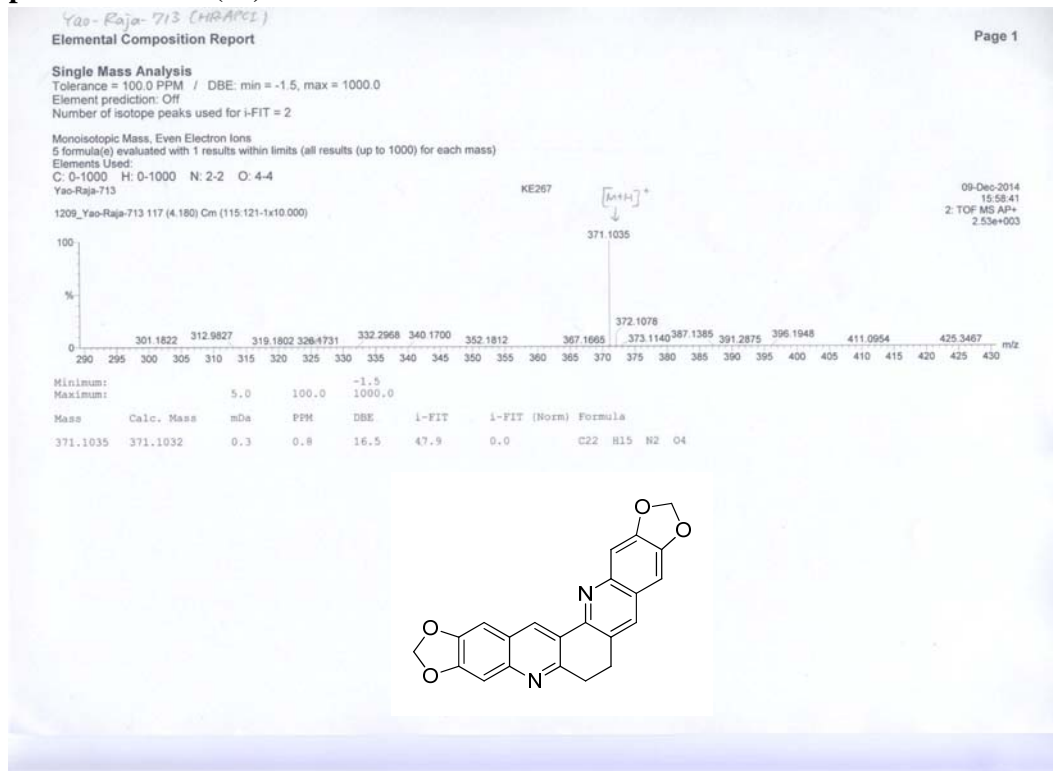
24. 6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-b][1,3]dioxolo[4',5':4,5]benzo[1,2-j][1,7]phenanthroline (4x) : ¹H NMR (400 MHz, CDCl₃)



6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-b][1,3]dioxolo[4',5':4,5]benzo[1,2-j][1,7]phenanthroline (4x) : ¹³C NMR (100 MHz, CDCl₃)



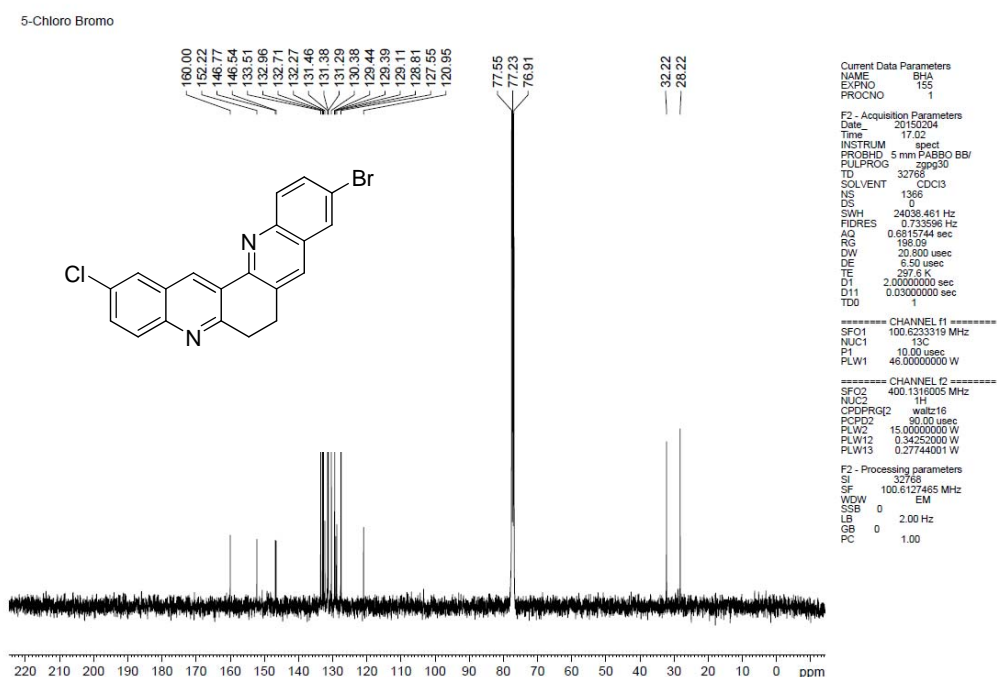
6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-b][1,3]dioxolo[4',5':4,5]benzo[1,2-j][1,7]phenanthroline (4x) : HRMS



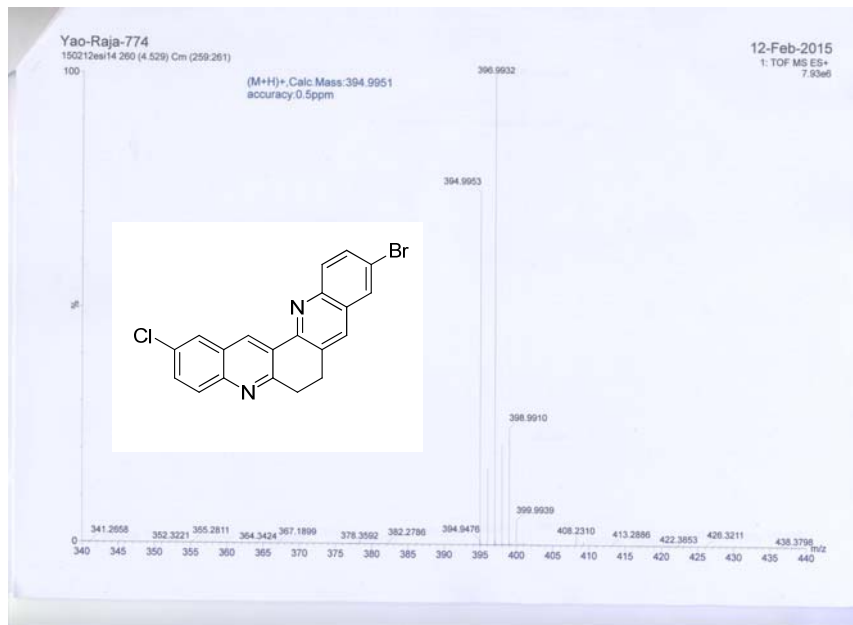
25. 10-bromo-2-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4y) : ¹H NMR (400 MHz, CDCl₃)



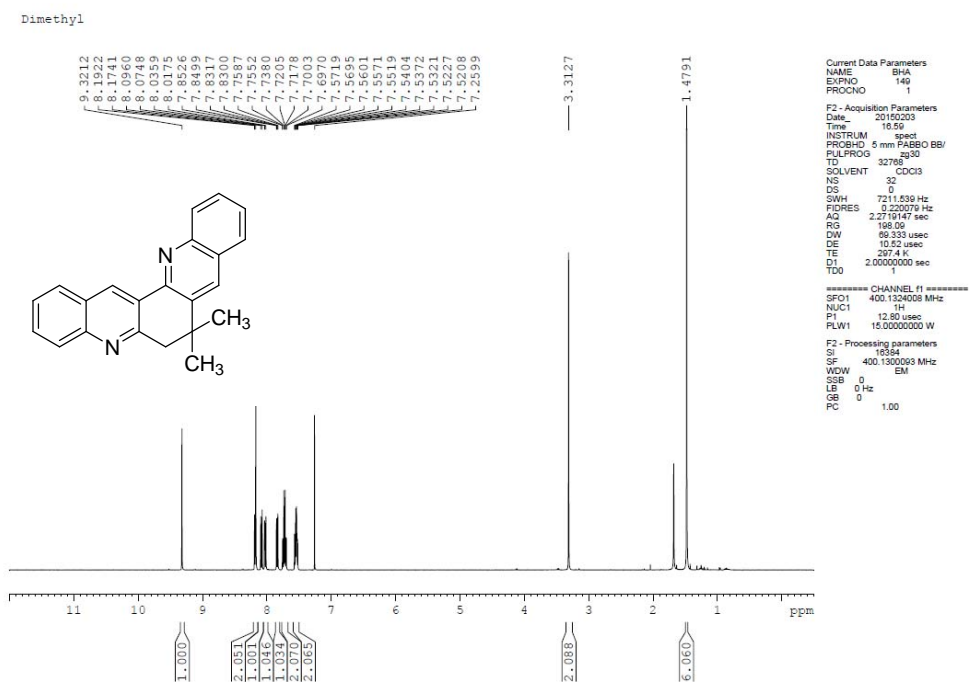
10-bromo-2-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4y) : ¹³C NMR (100 MHz, CDCl₃)



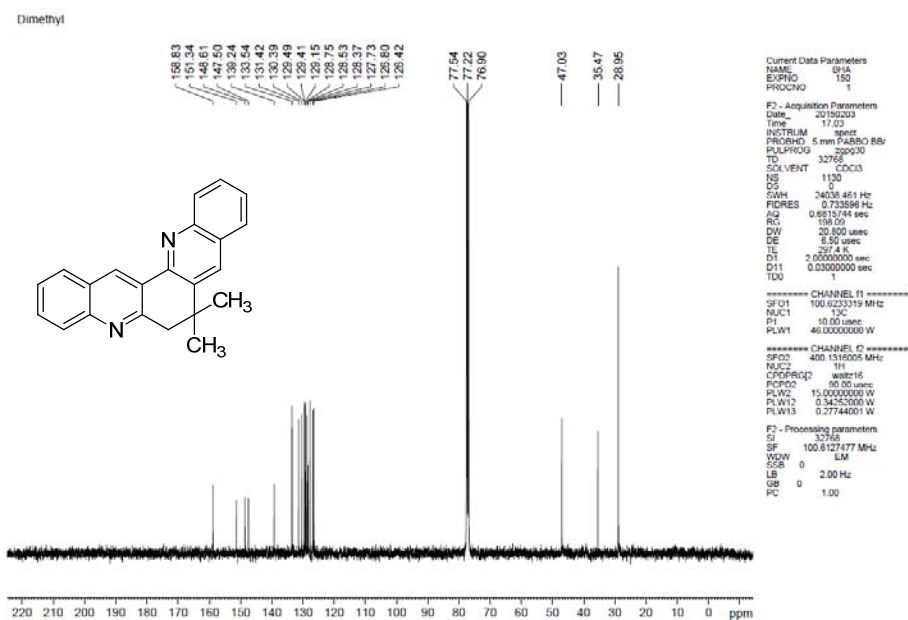
10-bromo-2-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4y) : HRMS



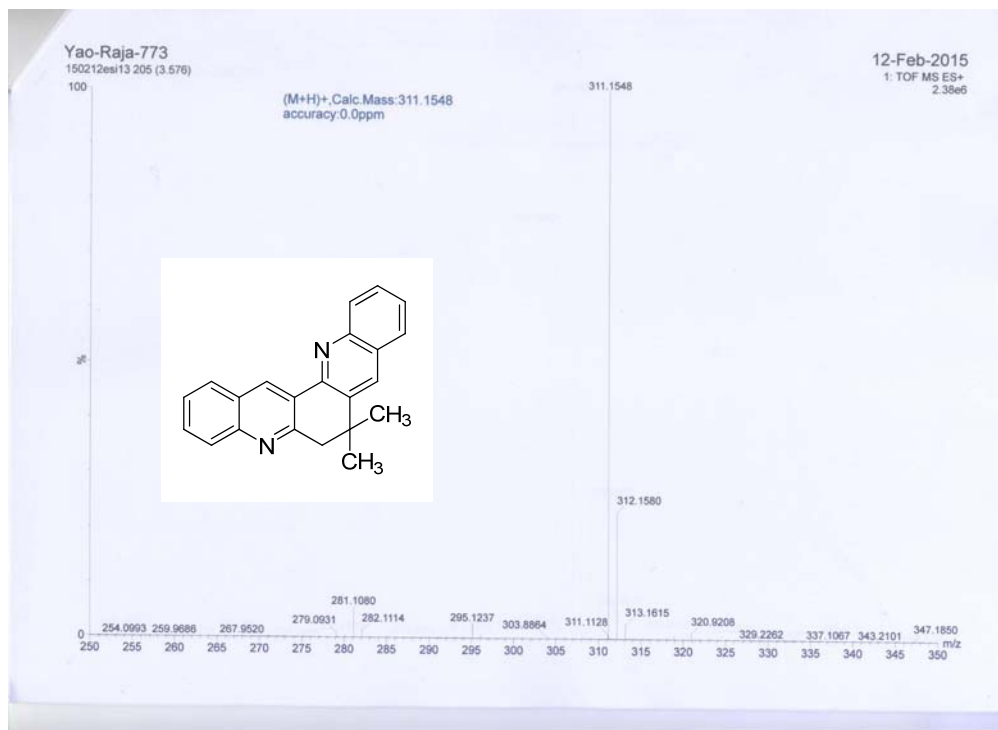
26. 7,7-dimethyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4z) : ¹H NMR (400 MHz, CDCl₃)



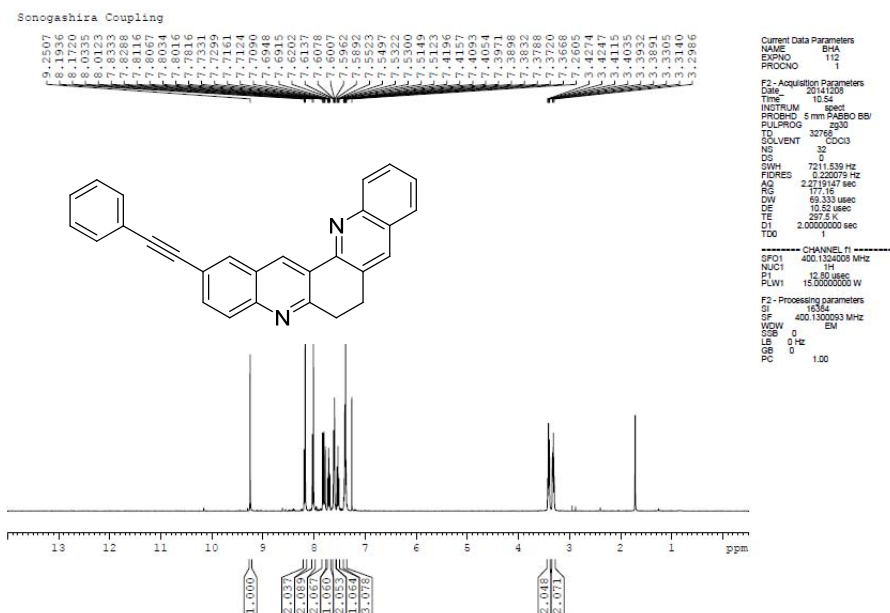
7,7-dimethyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4z) : ^{13}C NMR (100 MHz, CDCl_3)



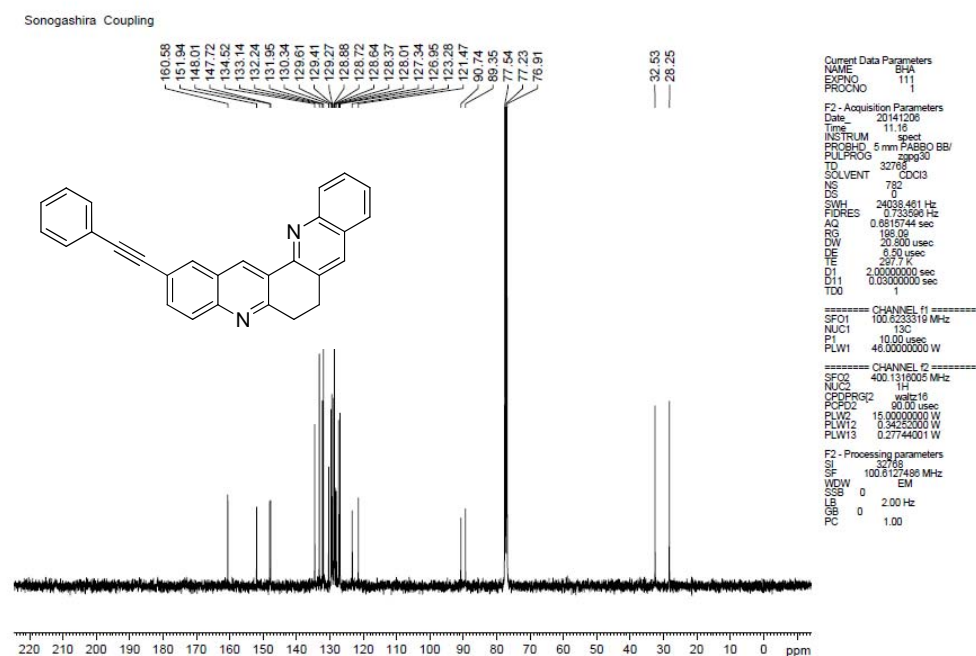
7,7-dimethyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (4z) : HRMS



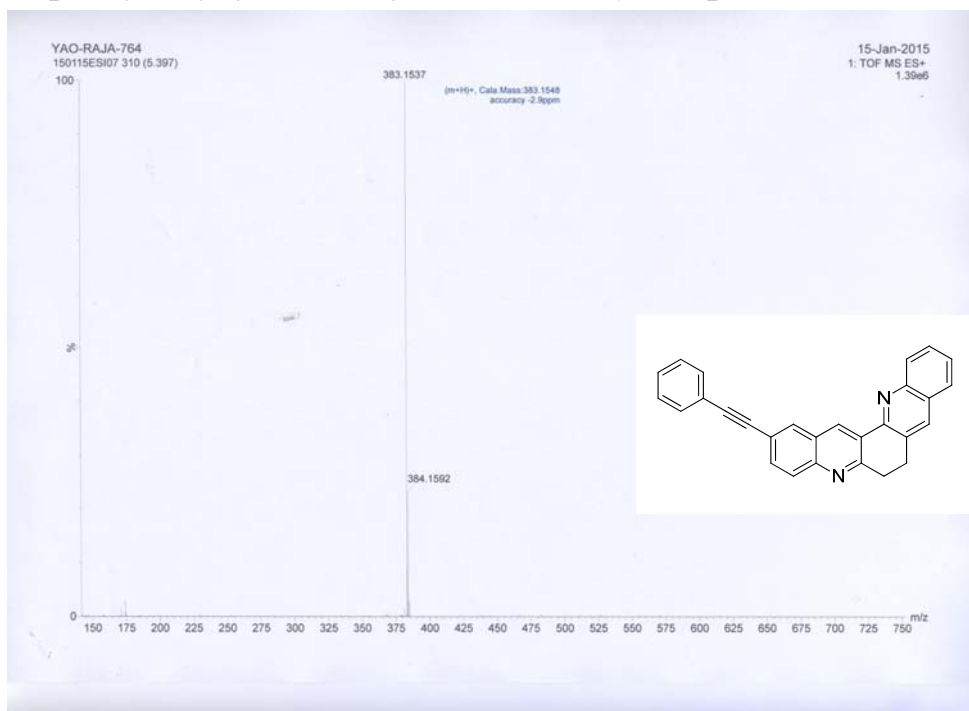
27. 2-(phenylethynyl)-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5a) : ¹H NMR (400 MHz, CDCl₃)



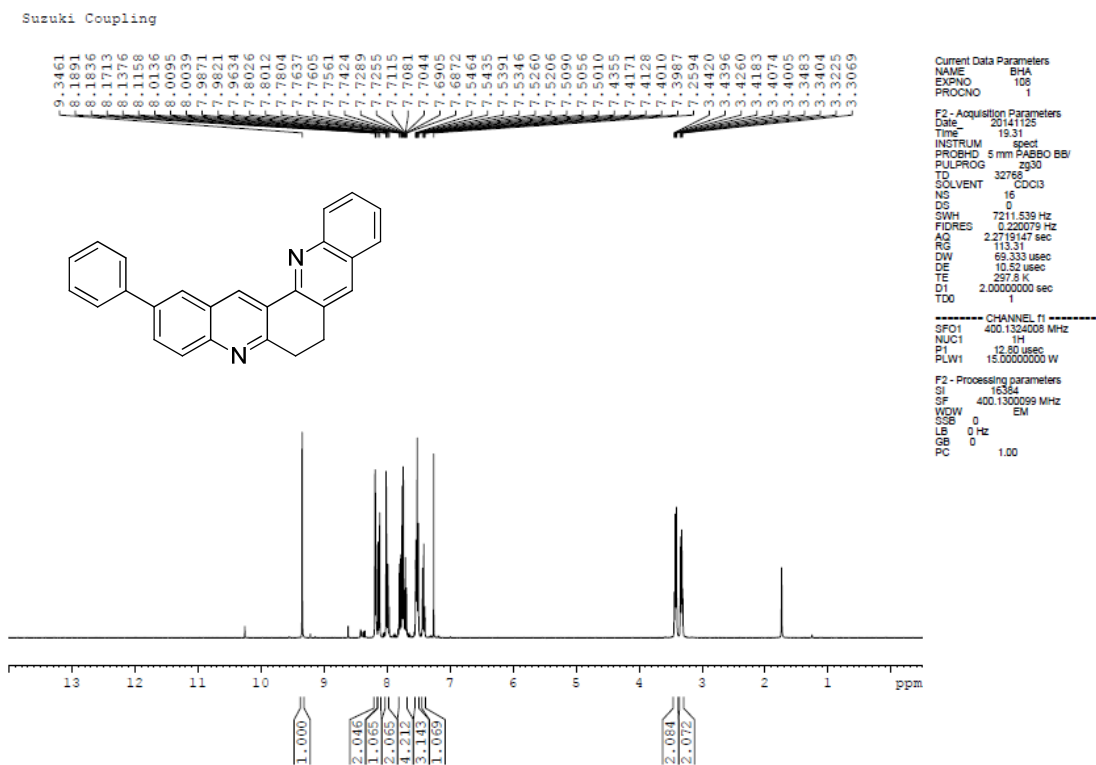
2-(phenylethynyl)-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5a) : ¹³C NMR (100 MHz, CDCl₃)



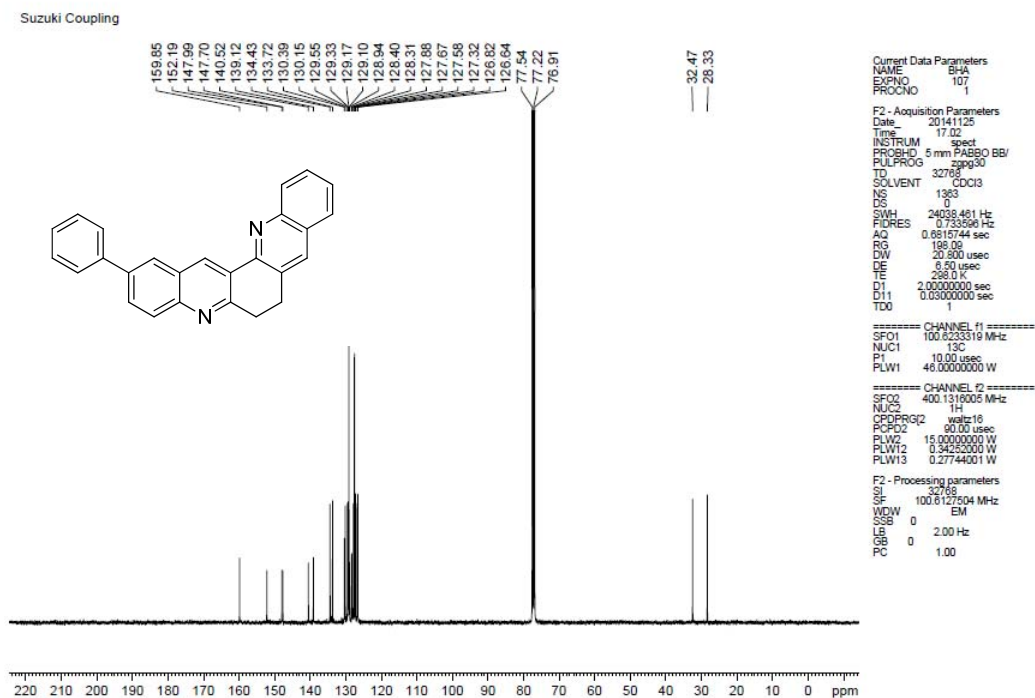
2-(phenylethynyl)-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5a) : HRMS



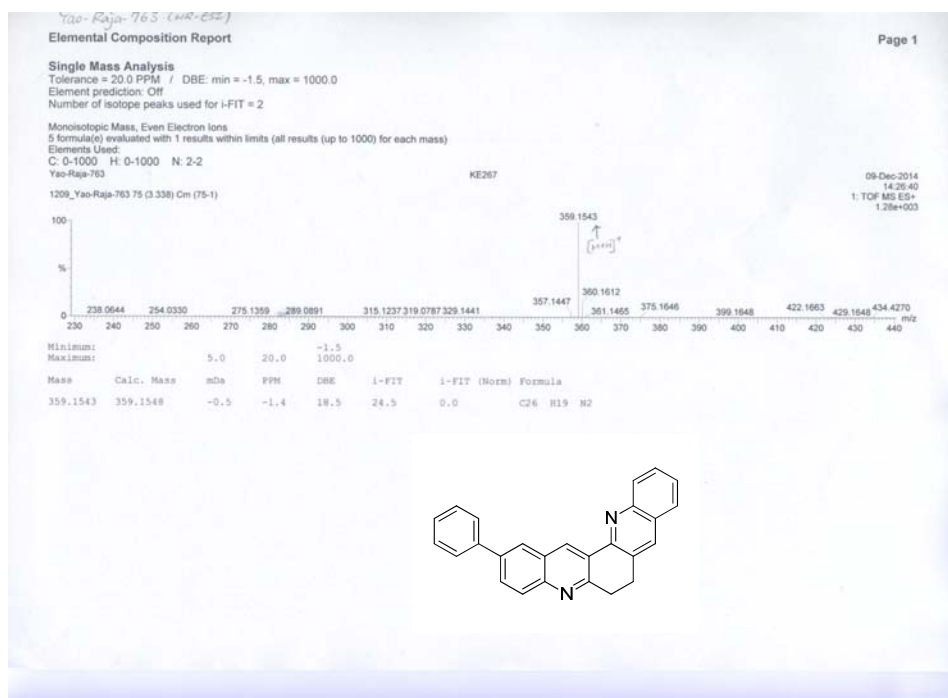
28. 2-phenyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5b) : ¹H NMR (400 MHz, CDCl₃)



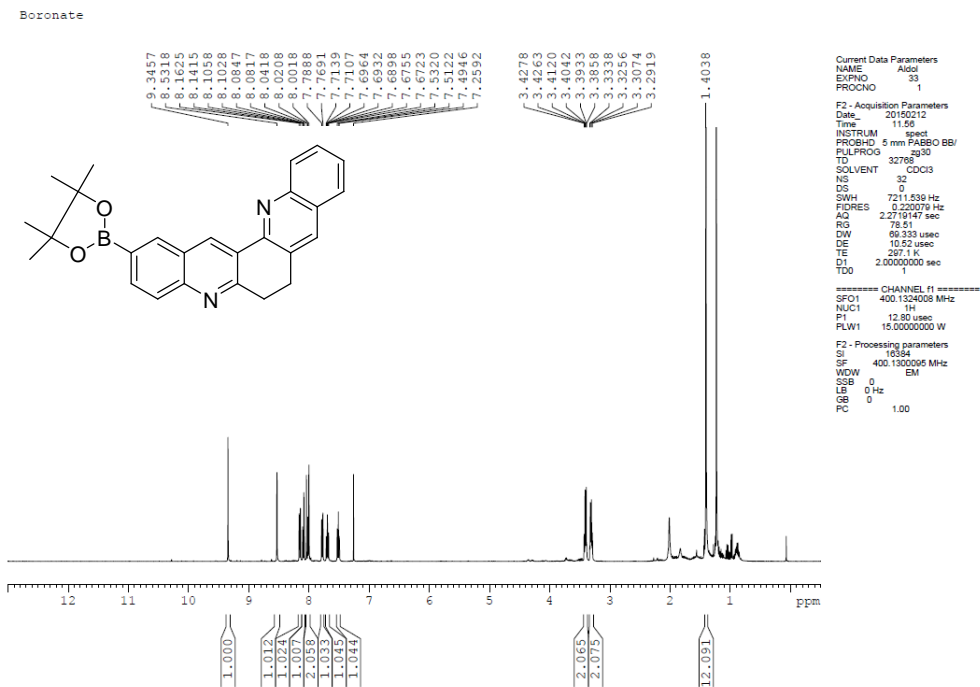
2-phenyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5b) : ^{13}C NMR (100 MHz, CDCl_3)



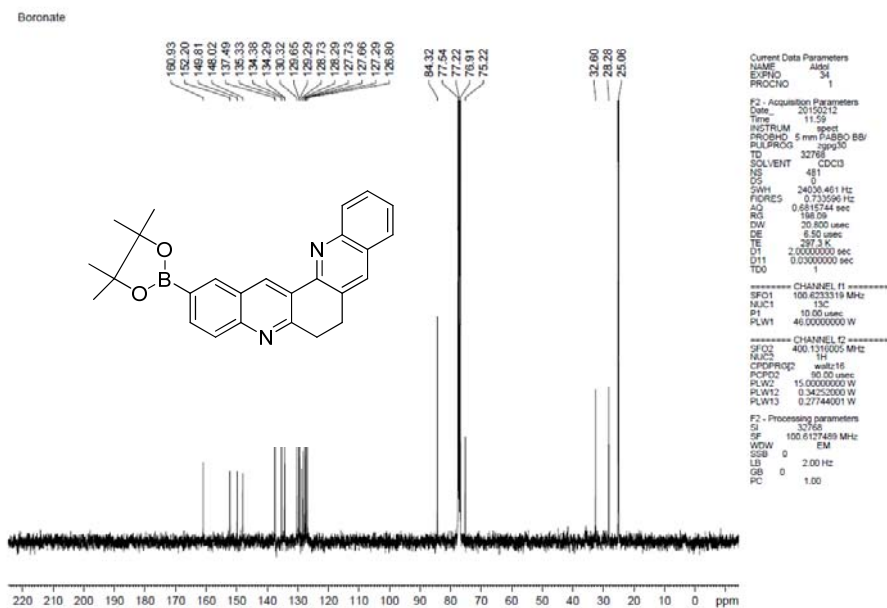
2-phenyl-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5b) : HRMS



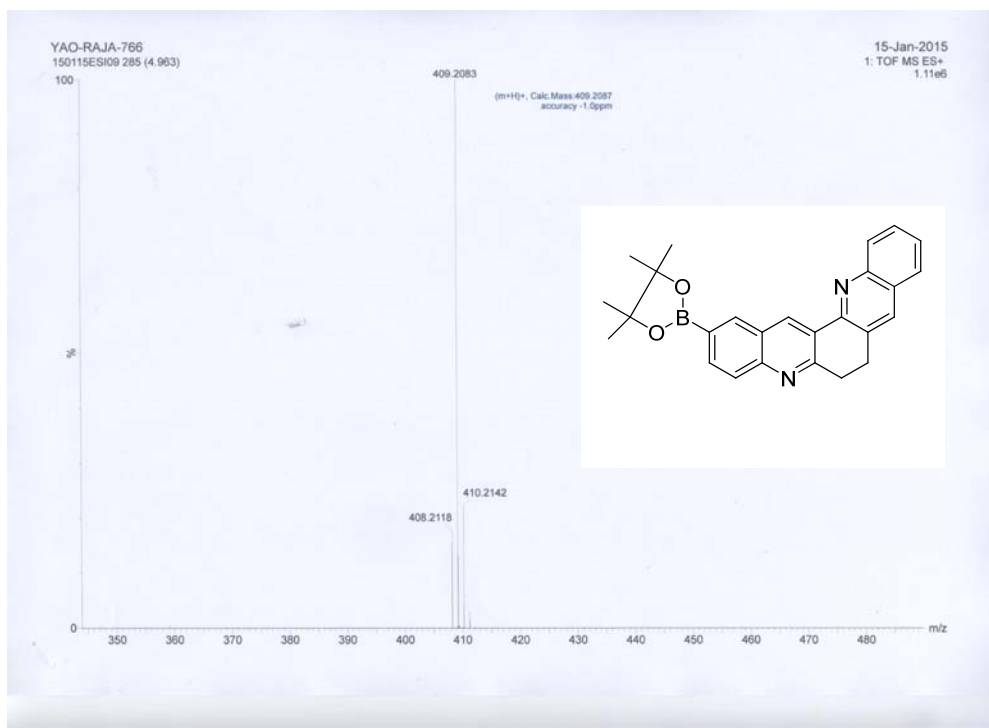
29. 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5c) : ¹H NMR (400 MHz, CDCl₃)



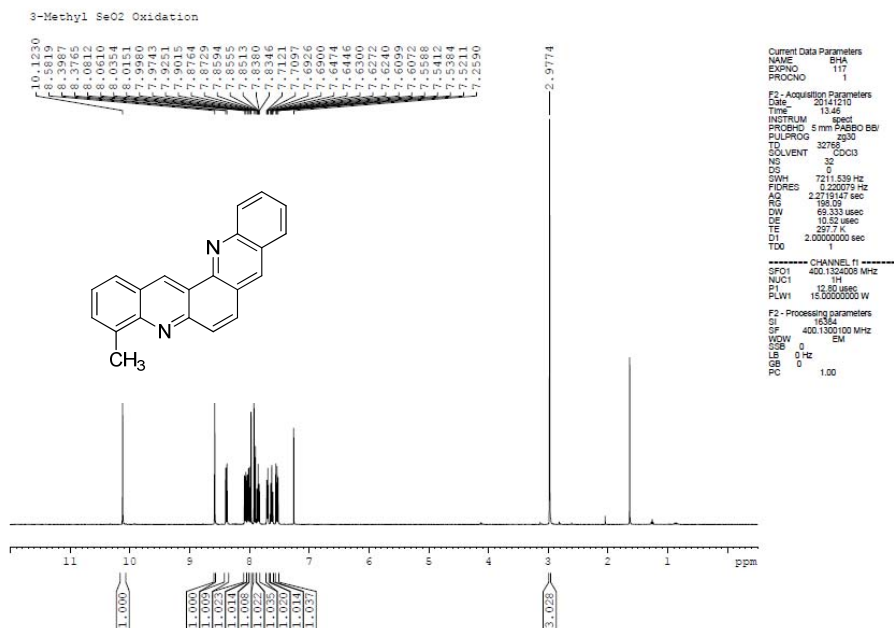
2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5c) : ¹³C NMR (100 MHz, CDCl₃)



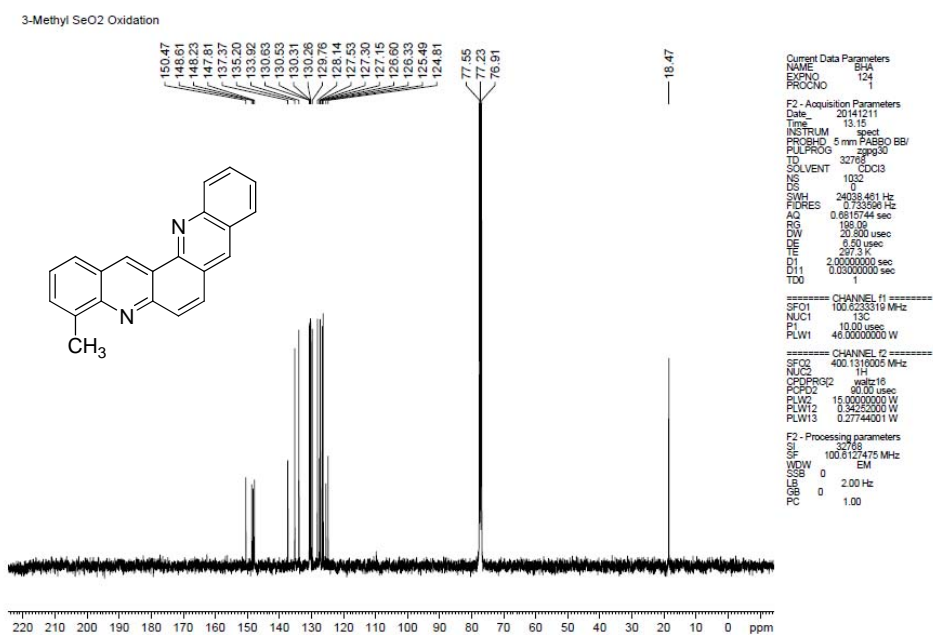
2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5c) : HRMS



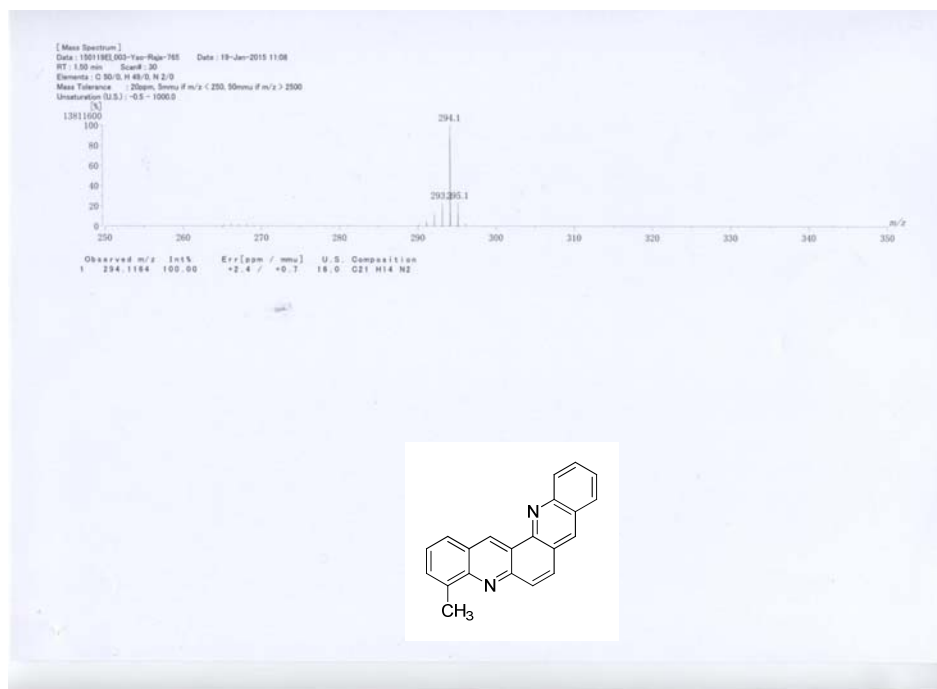
30. 4-methyldibenzo[b,j][1,7]phenanthroline (5d) : ¹H NMR (400 MHz, CDCl₃)



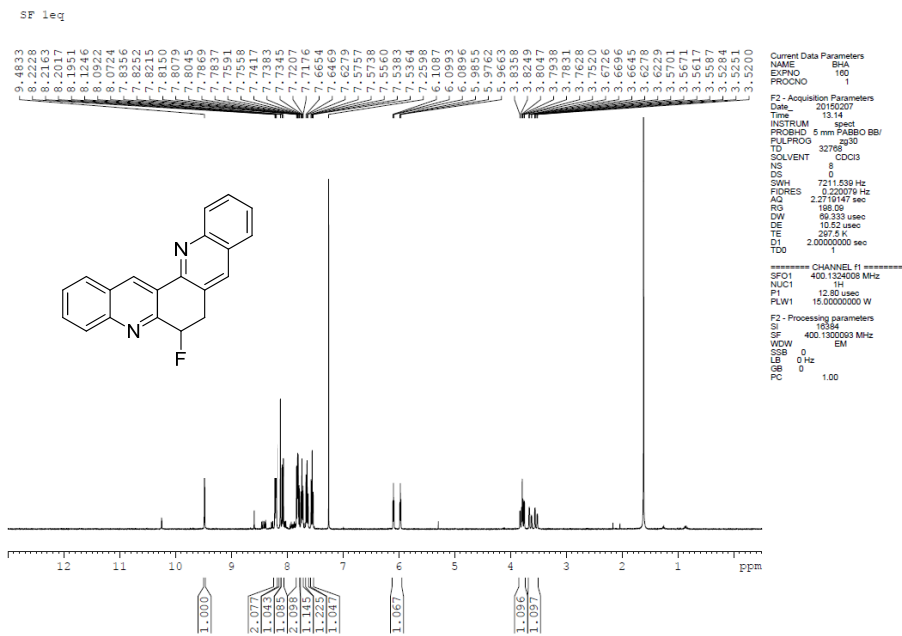
4-methyldibenzo[b,j][1,7]phenanthroline (5d) : ^{13}C NMR (100 MHz, CDCl_3)



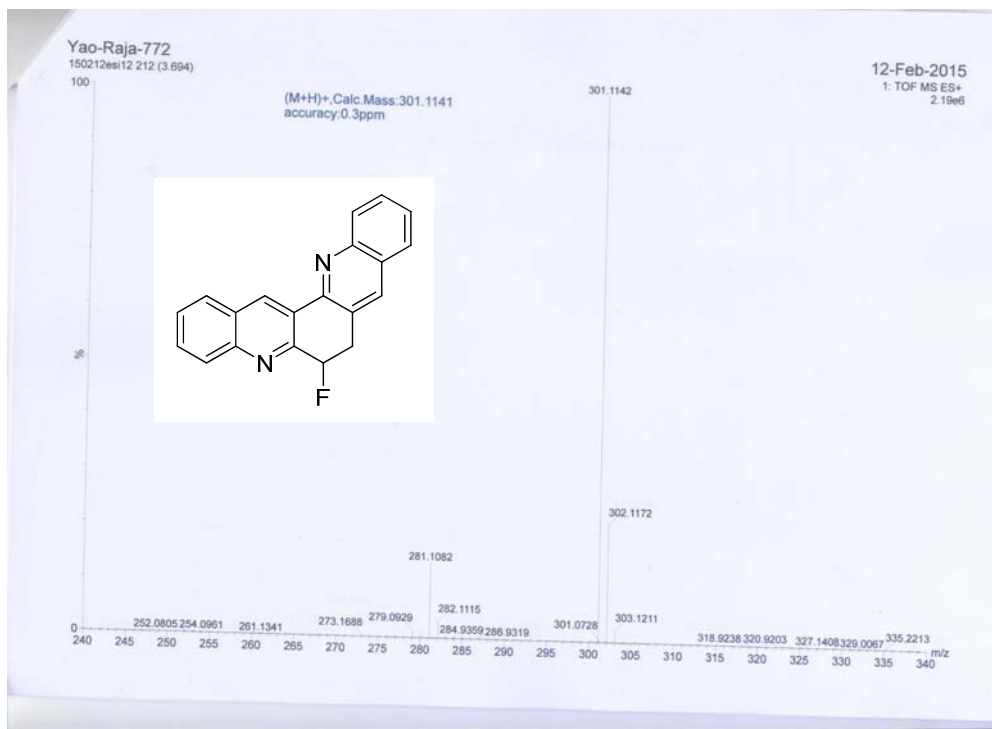
4-methyldibenzo[b,j][1,7]phenanthroline (5d) : HRMS



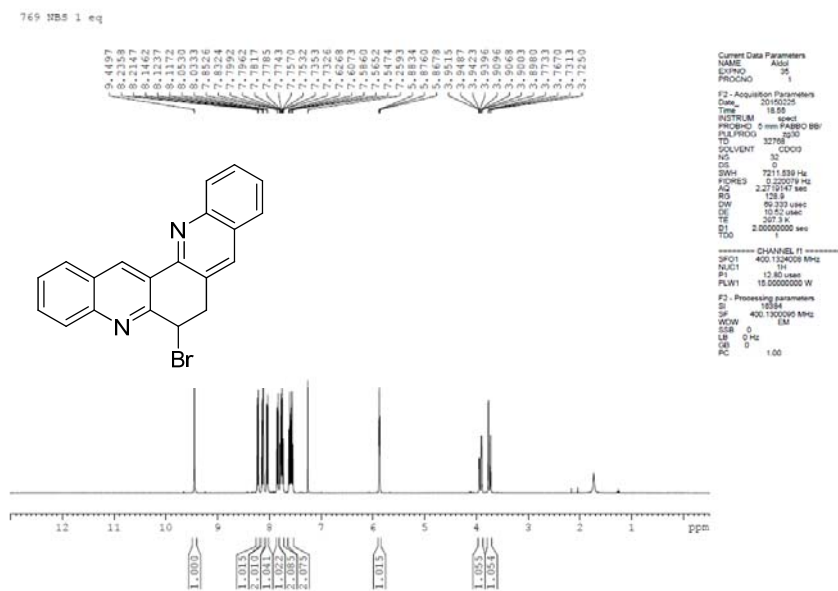
31. 6-fluoro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5e) : ^1H NMR (400 MHz, CDCl_3)



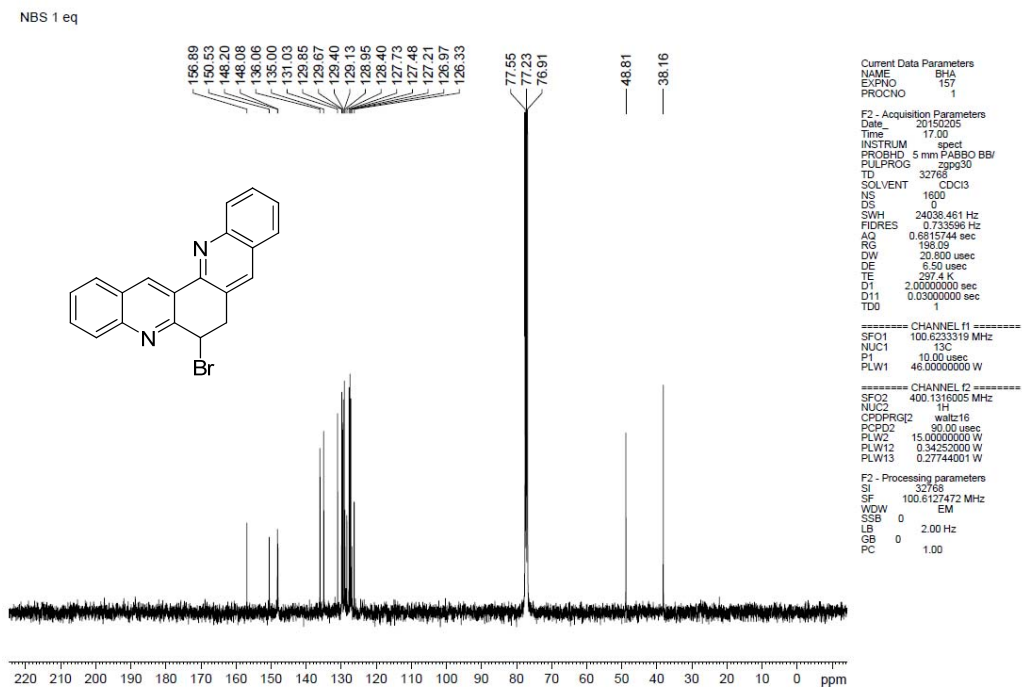
6-fluoro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5e) : HRMS



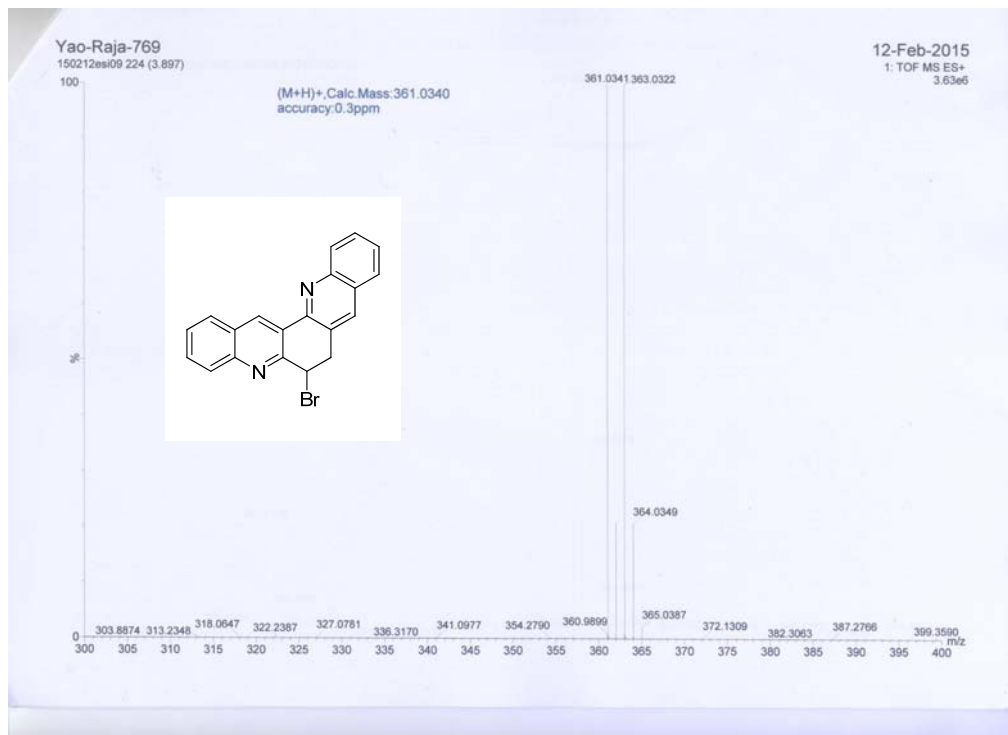
32. 6-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5f) : ¹H NMR (400 MHz, CDCl₃)



6-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5f) : ^{13}C NMR (100 MHz, CDCl_3)

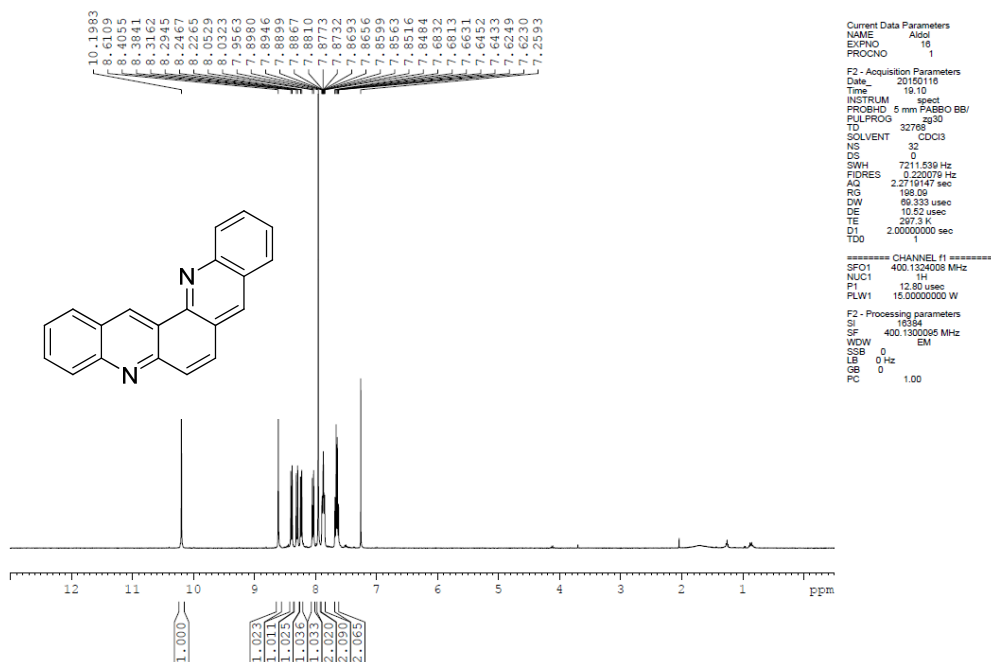


6-bromo-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5f) : HRMS



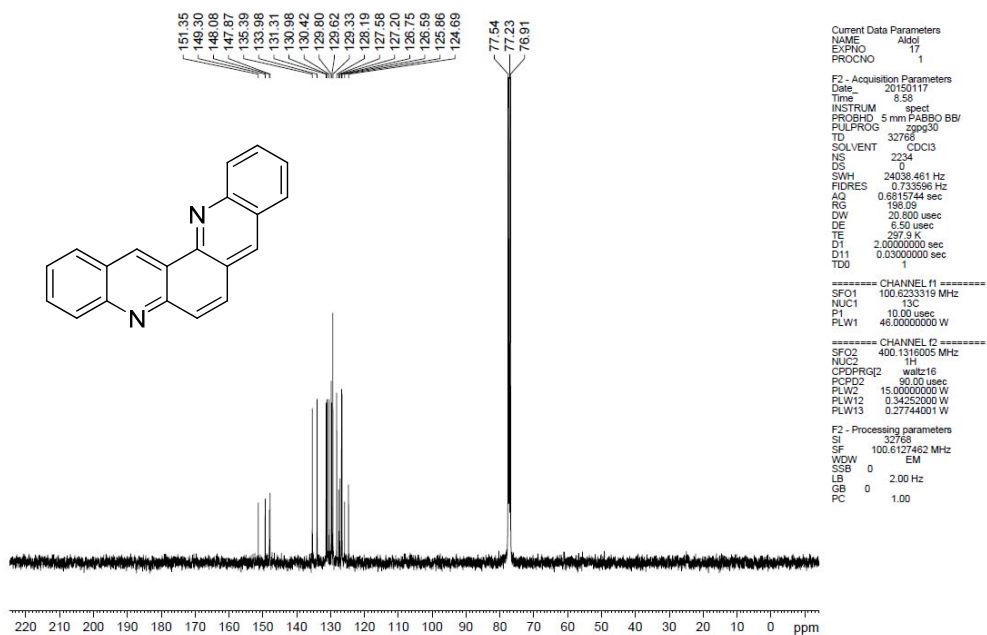
33. dibenzo[b,j][1,7]phenanthroline (5g) : ¹H NMR (400 MHz, CDCl₃)

701 with NBS 2eq lower spot

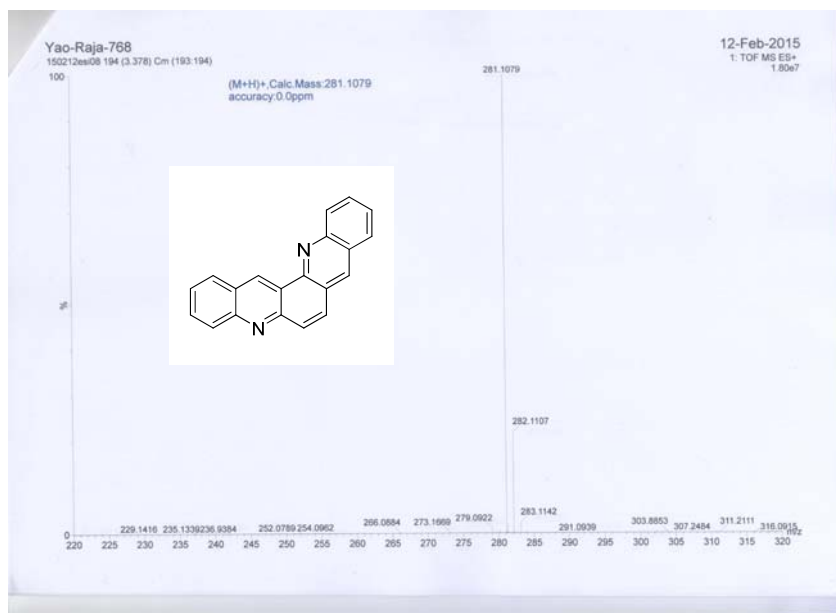


dibenzo[b,j][1,7]phenanthroline (5g) : ¹³C NMR (100 MHz, CDCl₃)

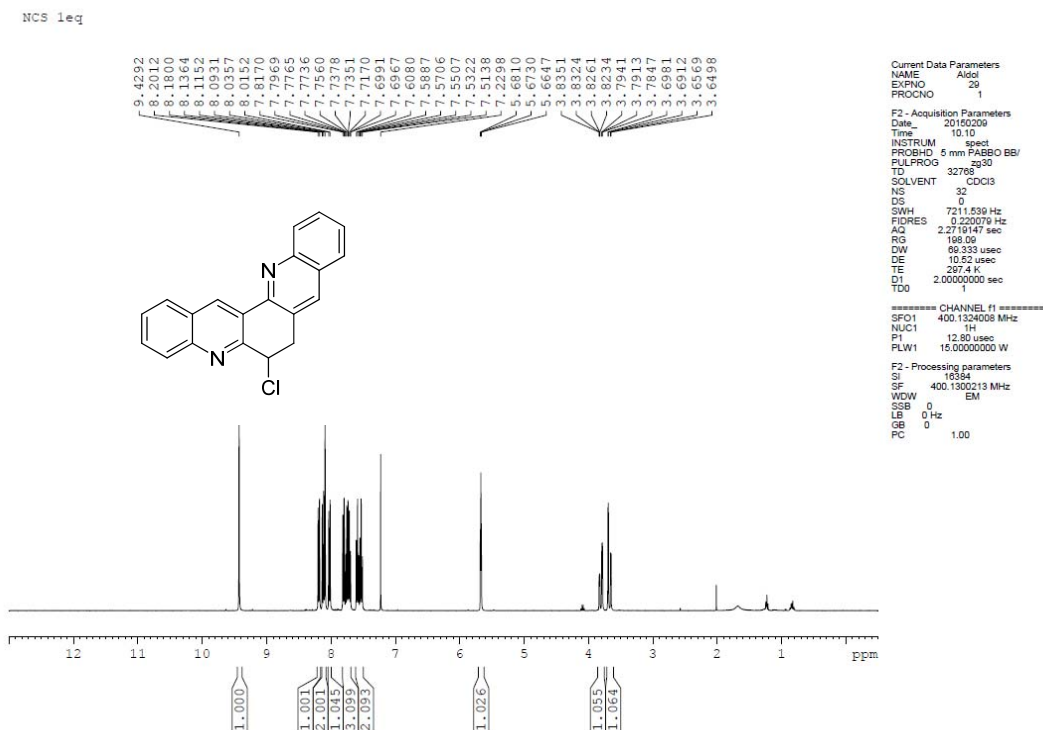
701 with NBS 2eq lower spot



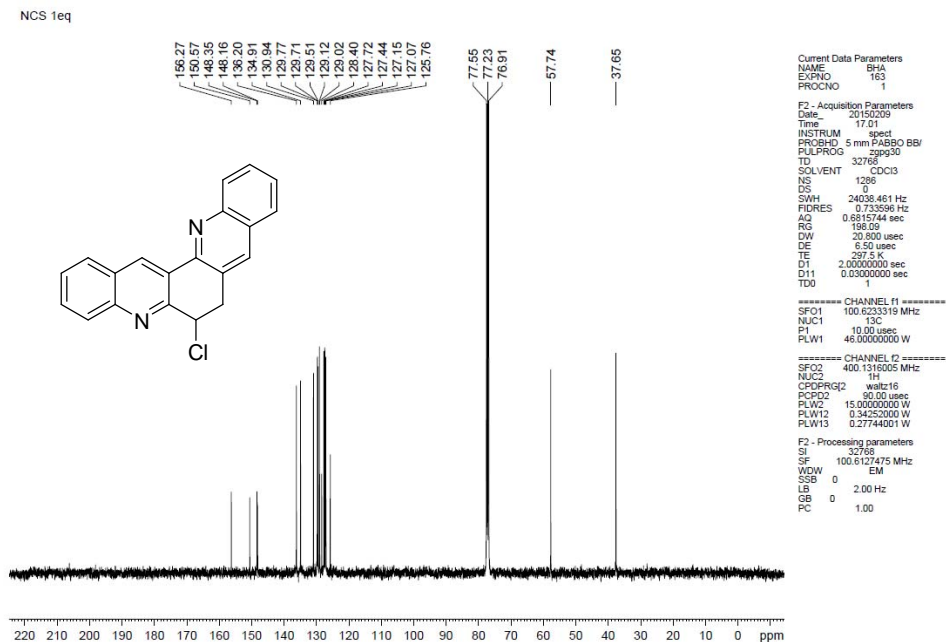
dibenzo[b,j][1,7]phenanthroline (5g) : HRMS



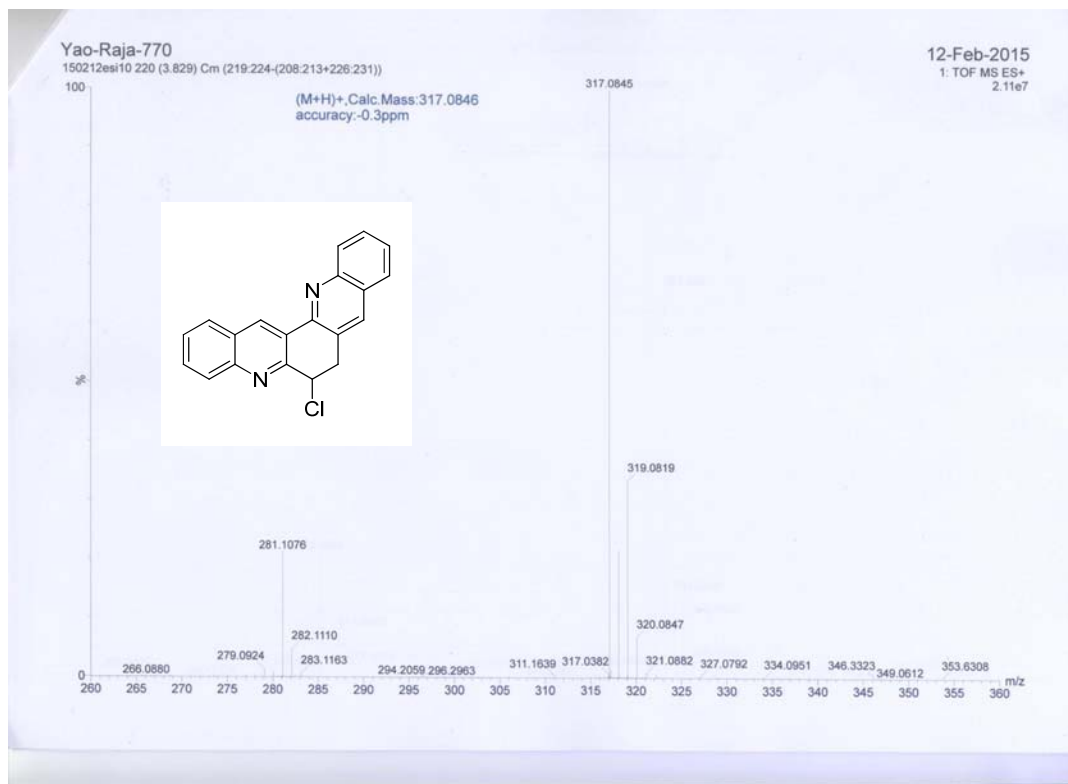
34. 6-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5h) : ¹H NMR (400 MHz, CDCl₃)



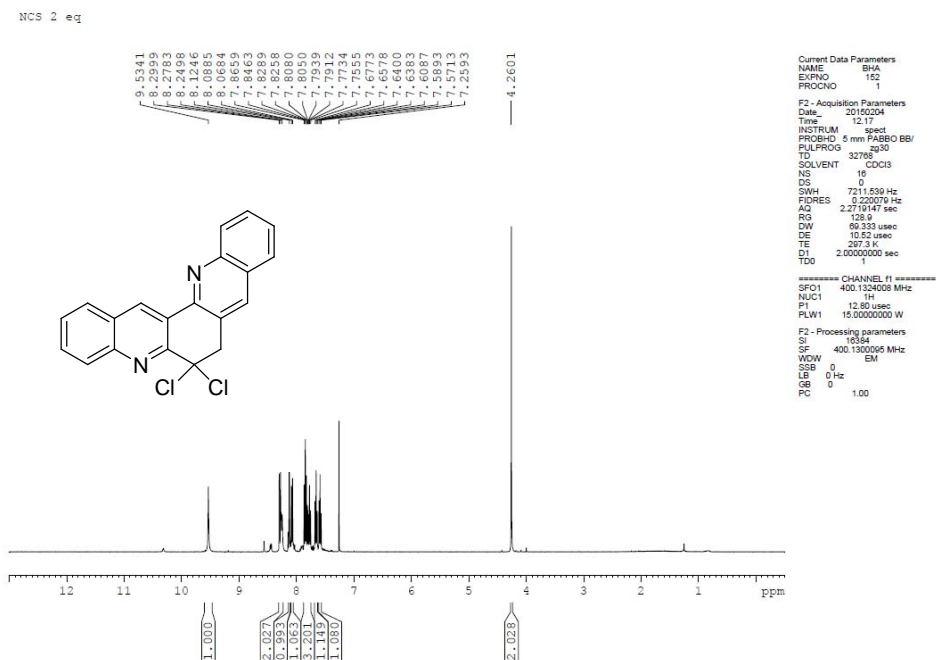
6-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5h) : ¹³C NMR (100 MHz, CDCl₃)



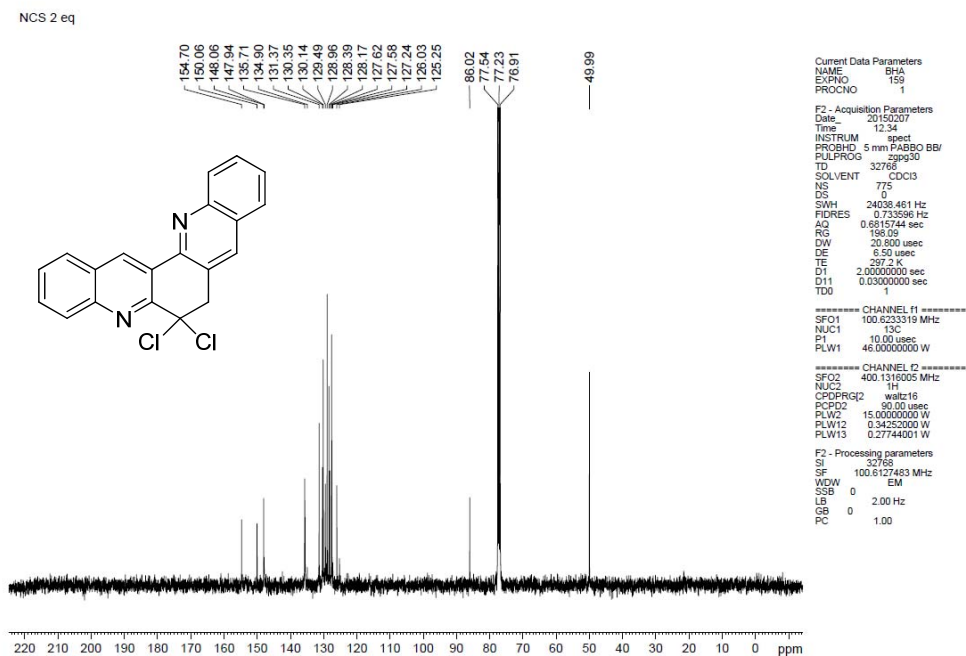
6-chloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5h) : HRMS



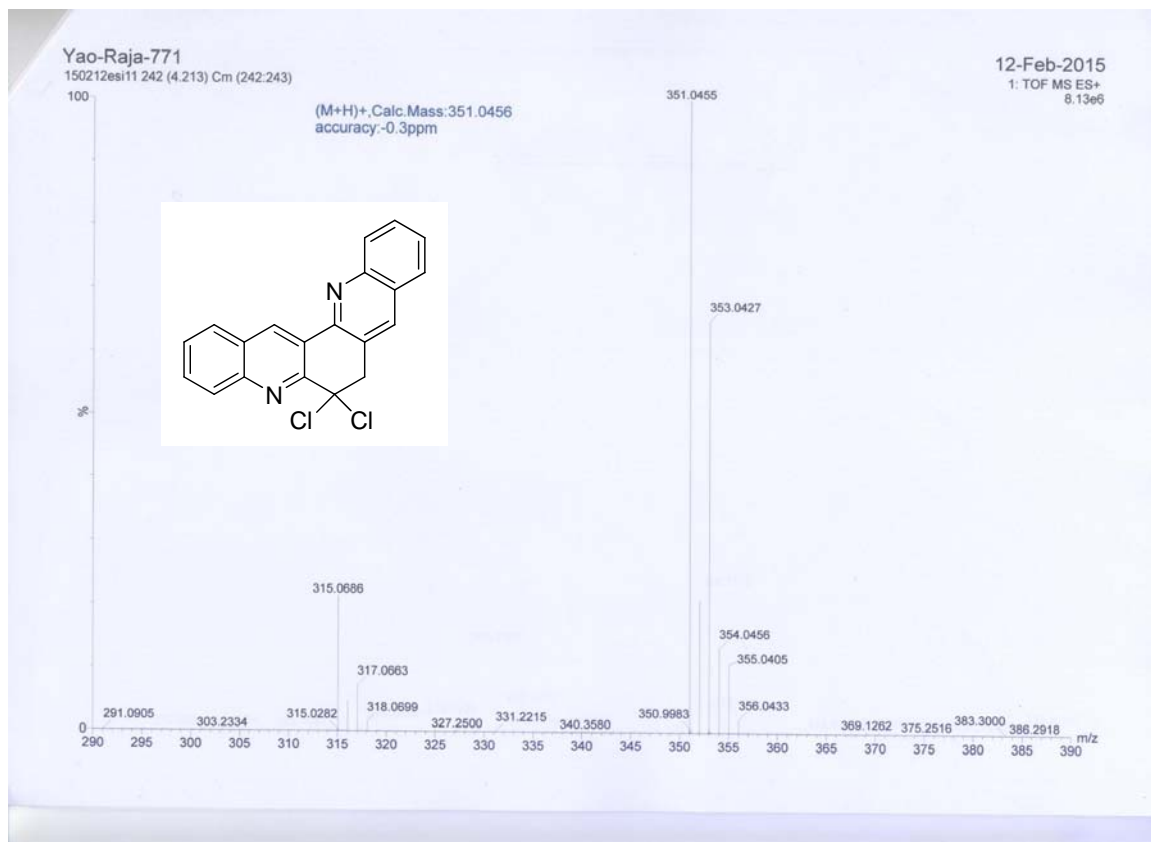
35. 6,6-dichloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5i) : ¹H NMR (400 MHz, CDCl₃)



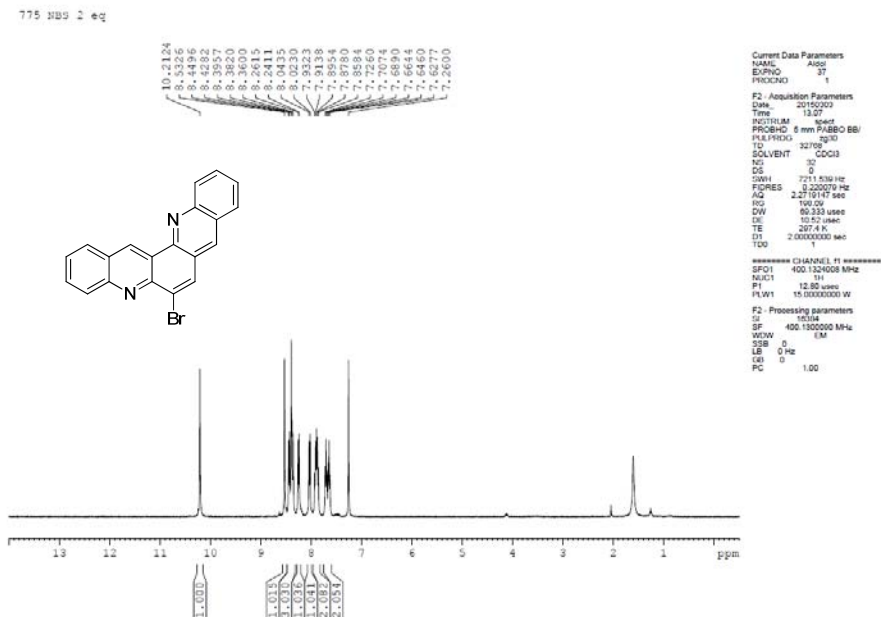
6,6-dichloro-6,7-dihydrodibenzo[b,j][1,7]phenanthroline (5i) : ¹³C NMR (100 MHz, CDCl₃)



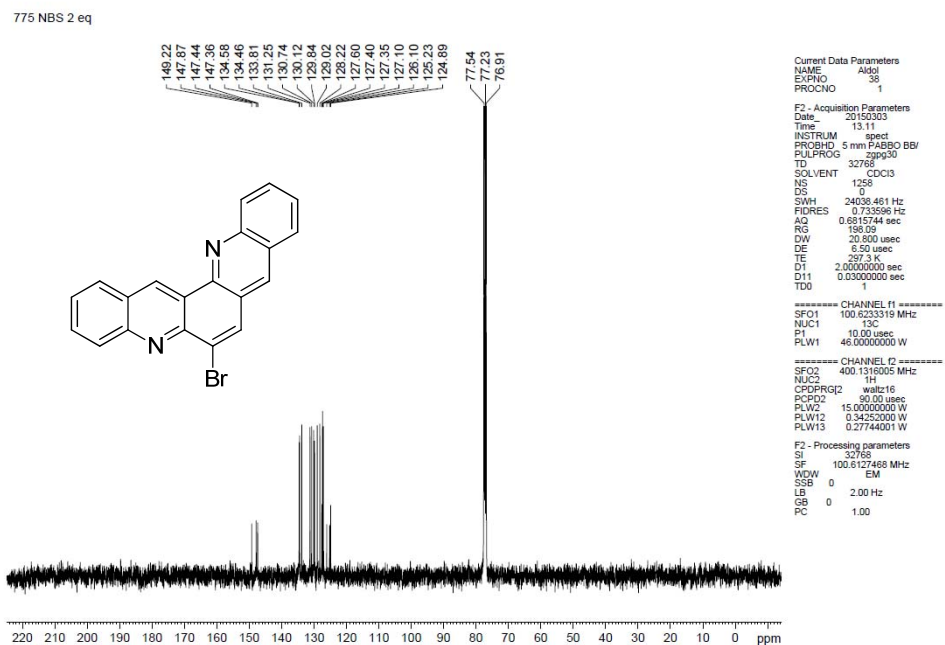
6,6-dichloro-6,7-dihydrobenzo[b,j][1,7]phenanthroline (5i) : HRMS



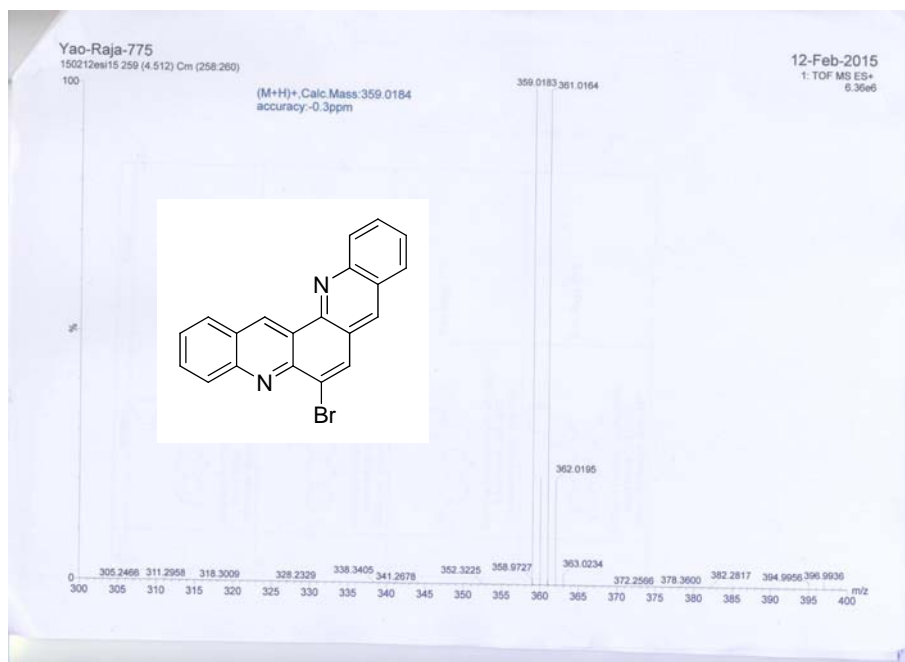
36. 6-bromodibenzo[b,j][1,7]phenanthroline (5j) : ¹H NMR (400 MHz, CDCl₃)



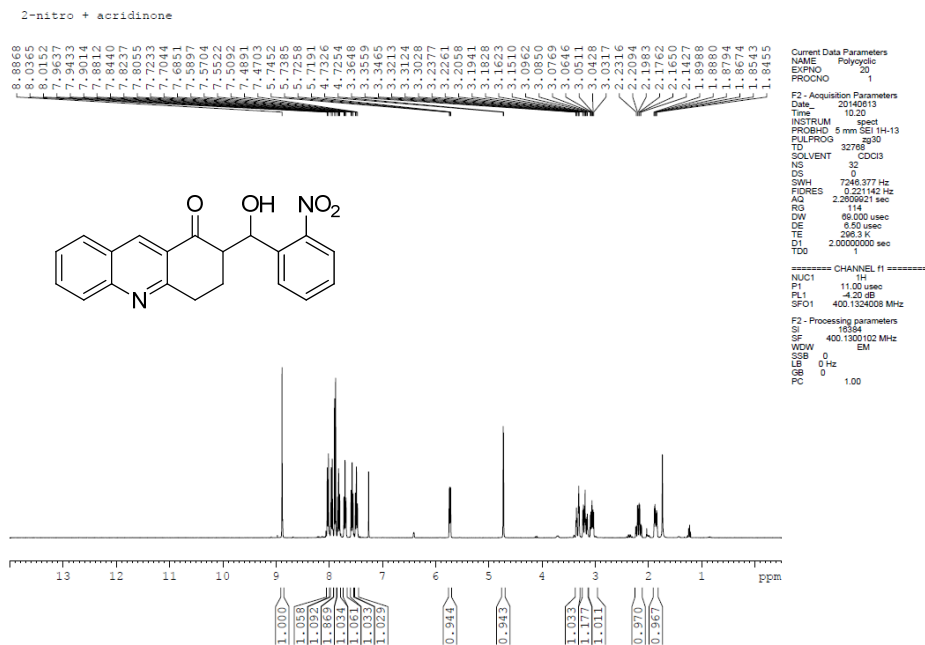
6-bromodibenzo[b,j][1,7]phenanthroline (5j) : ^{13}C NMR (100 MHz, CDCl_3)



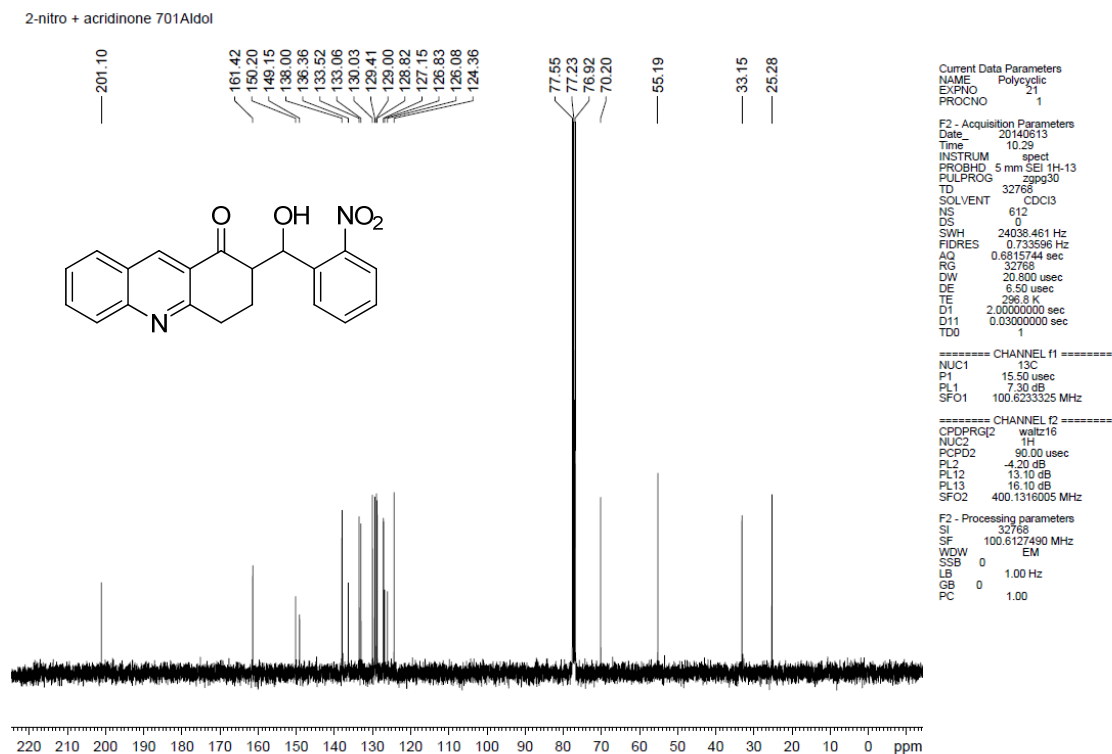
6-bromodibenzo[b,j][1,7]phenanthroline (5j) : HRMS



37. 2-(hydroxy(2-nitrophenyl)methyl)-3,4-dihydroacridin-1(2H)-one (3a) :
¹H NMR (400 MHz, CDCl₃)



2-(hydroxy(2-nitrophenyl)methyl)-3,4-dihydroacridin-1(2H)-one (3a) :
¹³C NMR (100 MHz, CDCl₃)



2-(hydroxy(2-nitrophenyl)methyl)-3,4-dihydroacridin-1(2H)-one (3a) : HRMS

