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APPENDICES

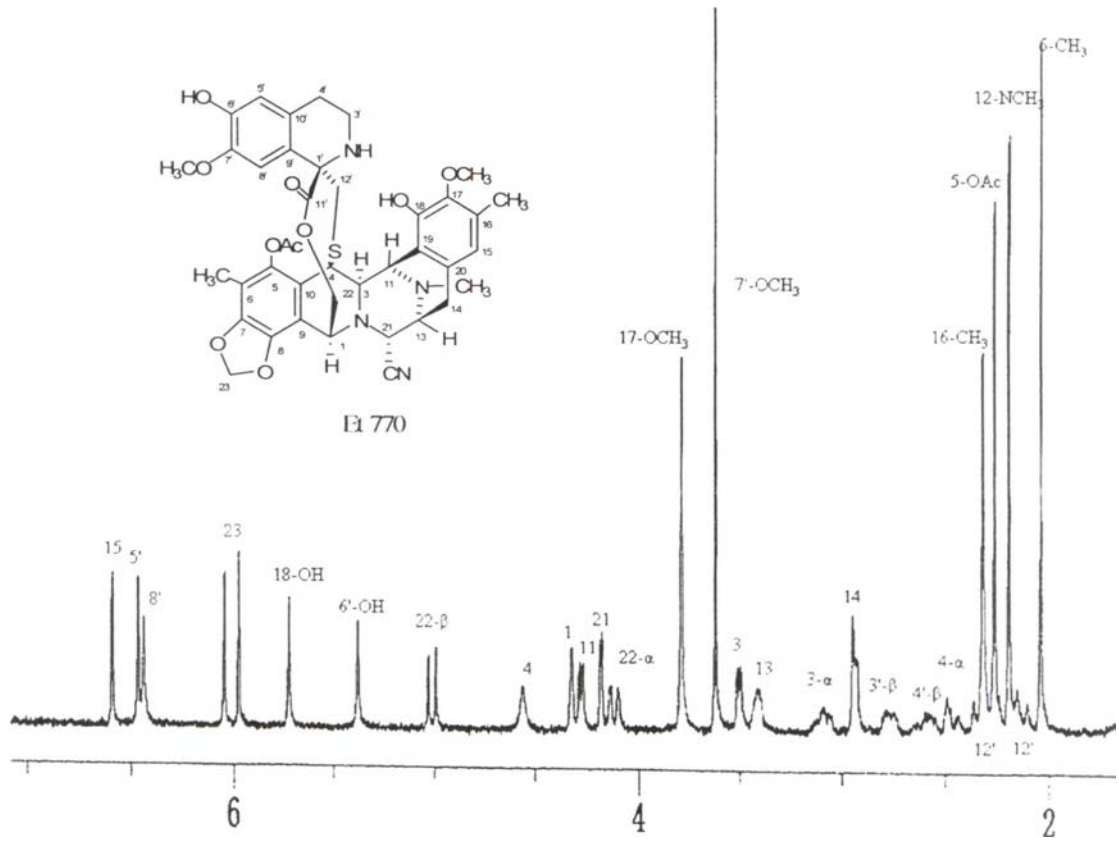


Figure 23. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Et 770 (**2**)

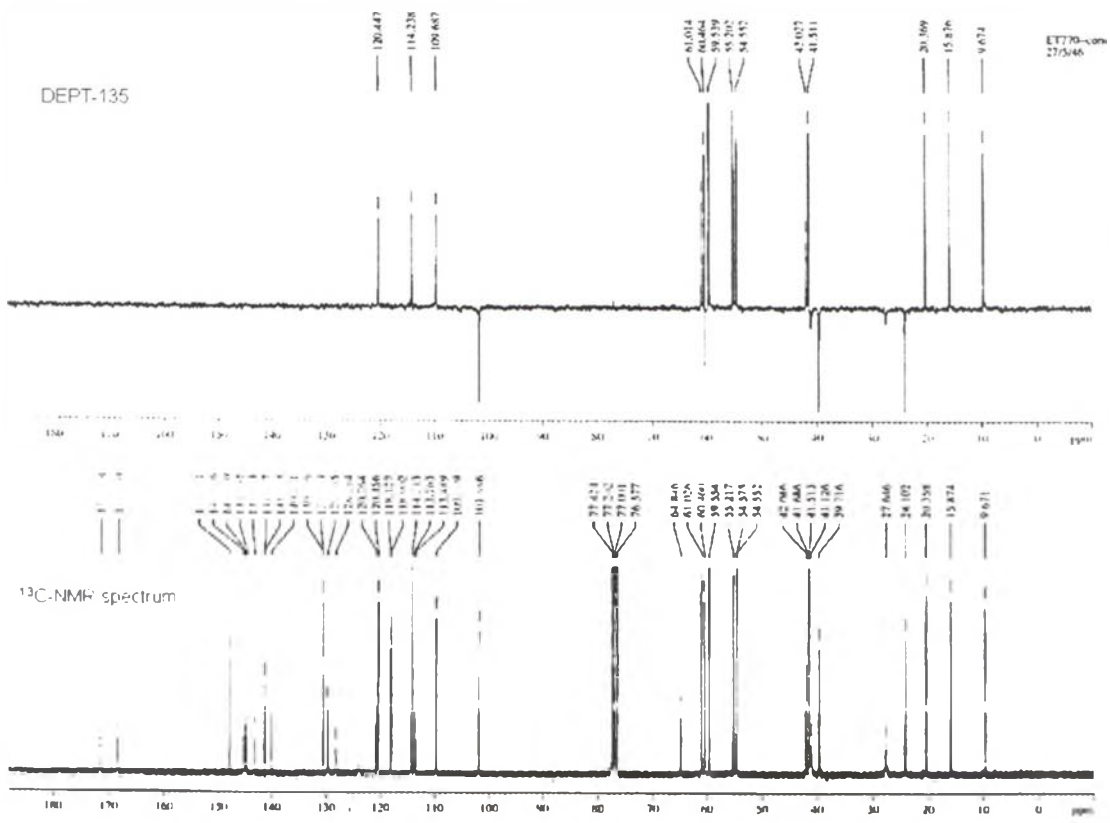


Figure 24. The 125 MHz ^{13}C-NMR, DEPT-135 spectra (in $CDCl_3$) of Et 770 (**2**)

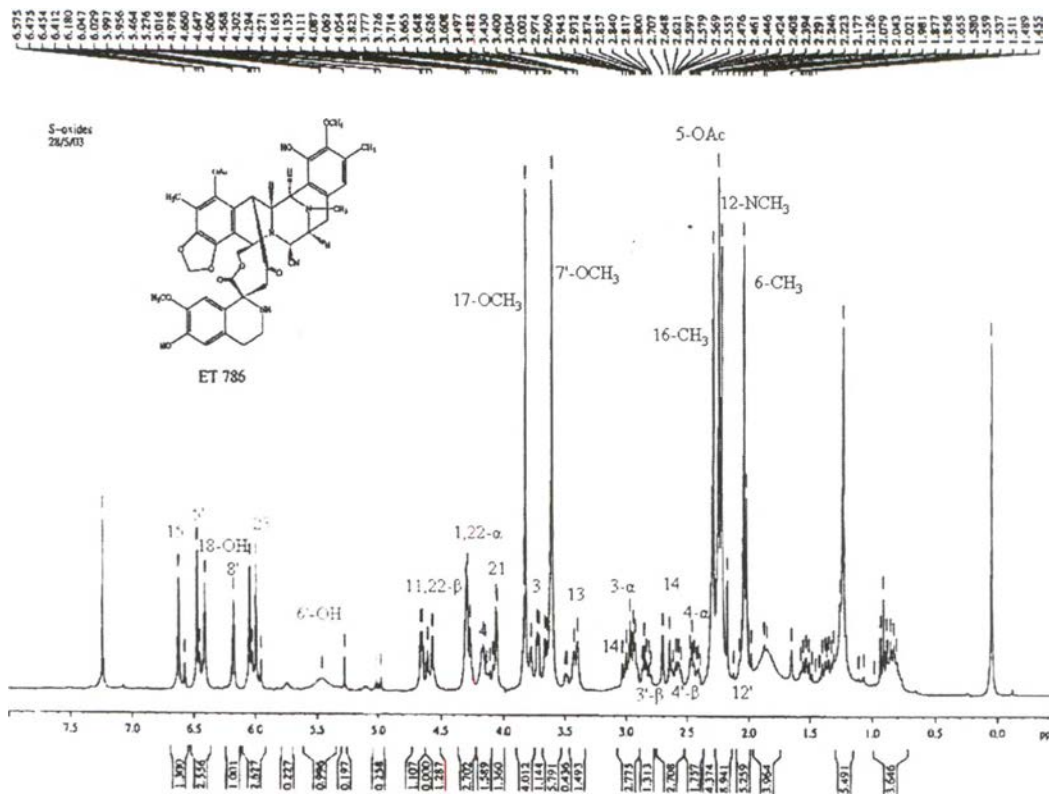


Figure 25. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Et 786 (**4**)

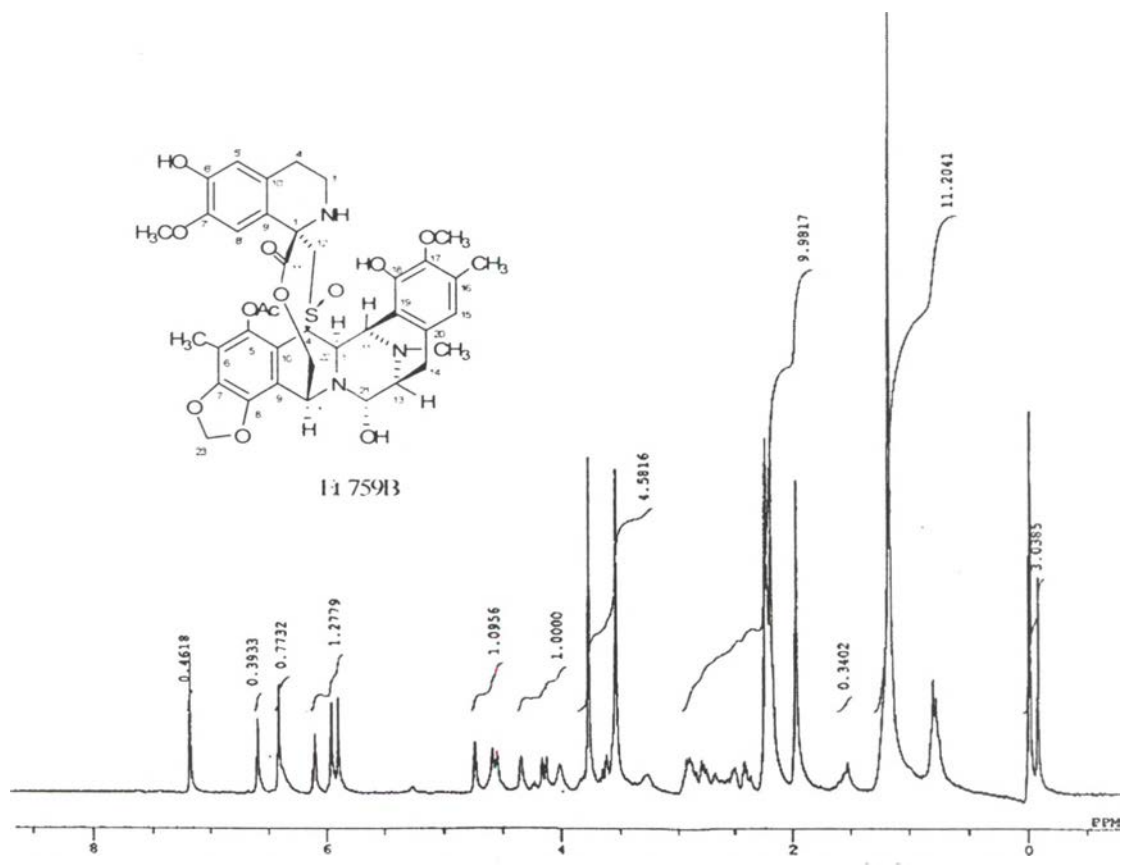


Figure 26. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Et 759B (**3**)

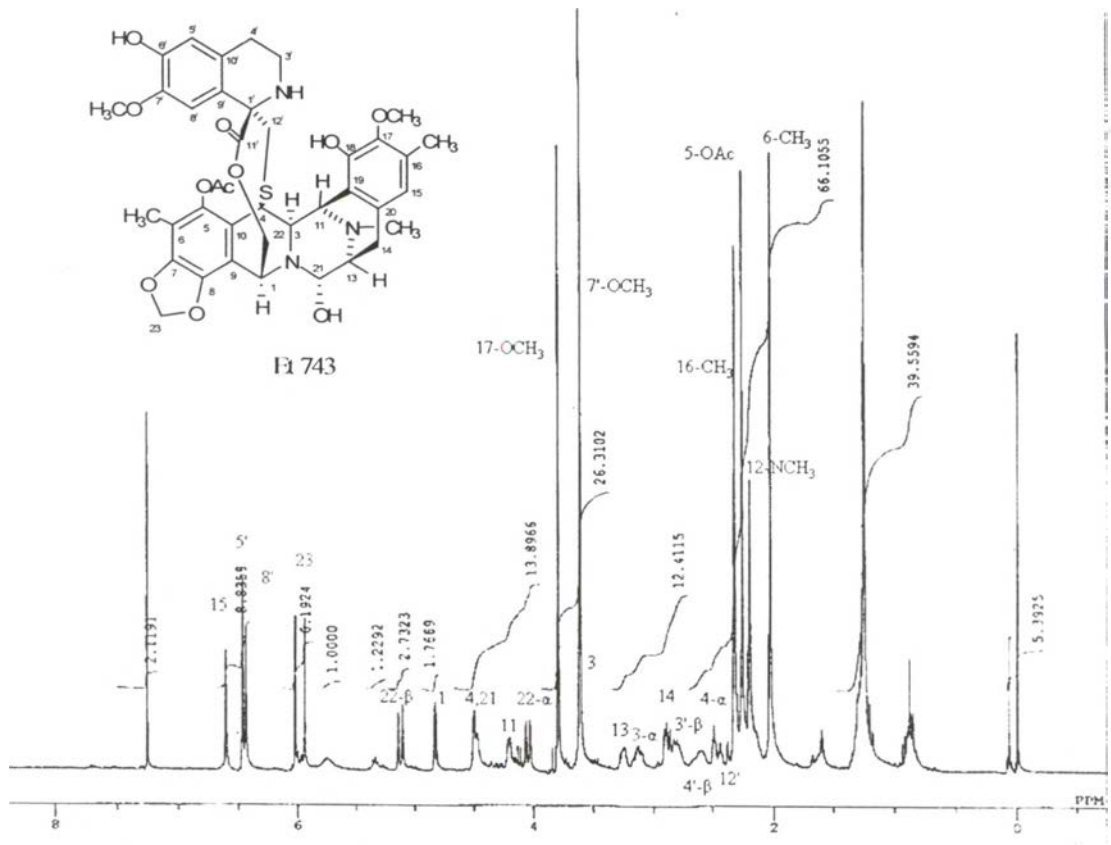


Figure 27. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Et 743 (**1**)

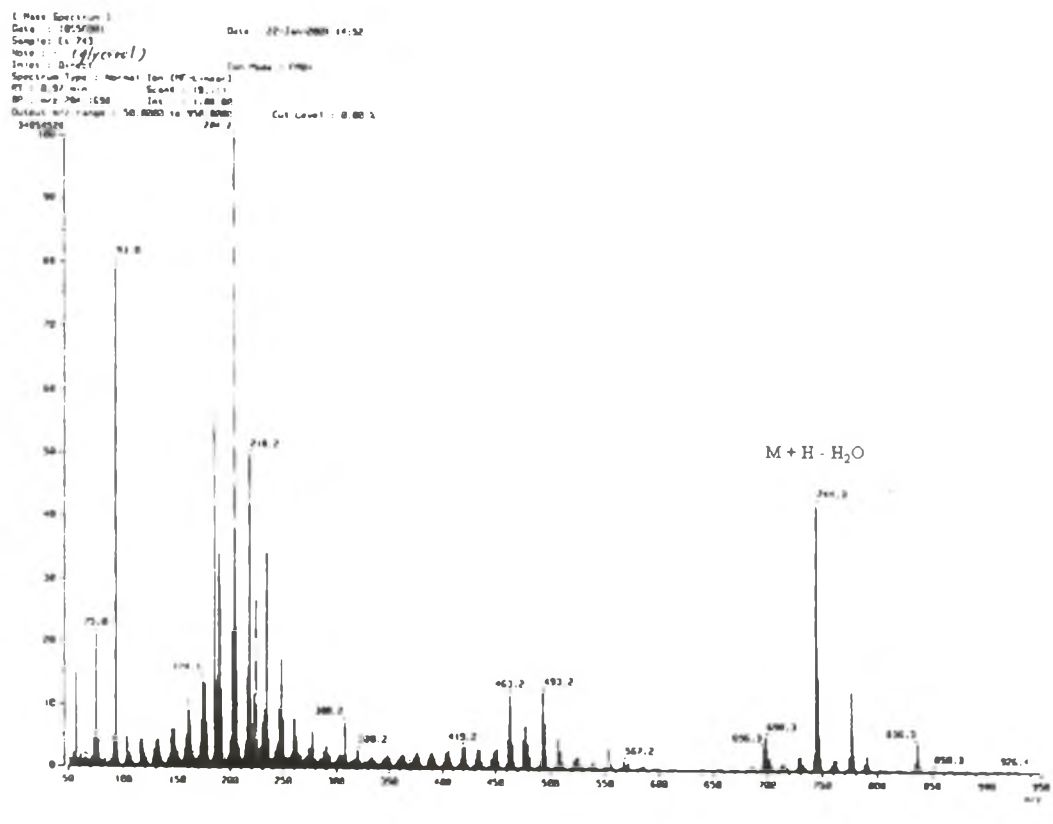


Figure 28. The FAB-mass spectrum of Et 743 (**1**)

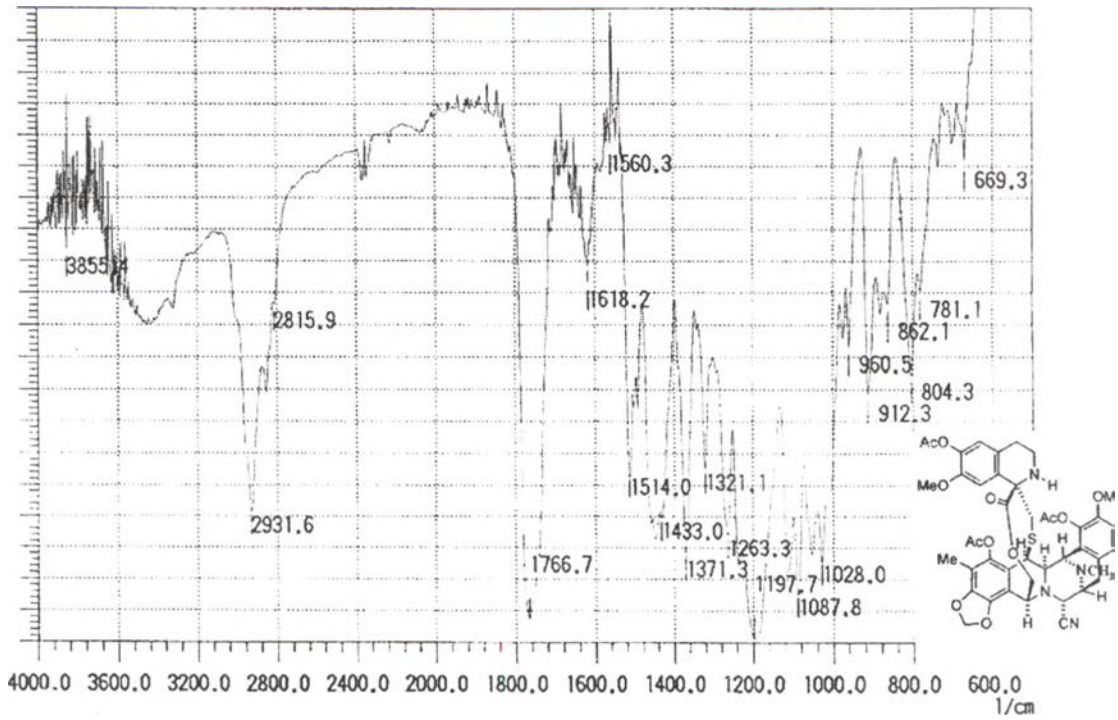
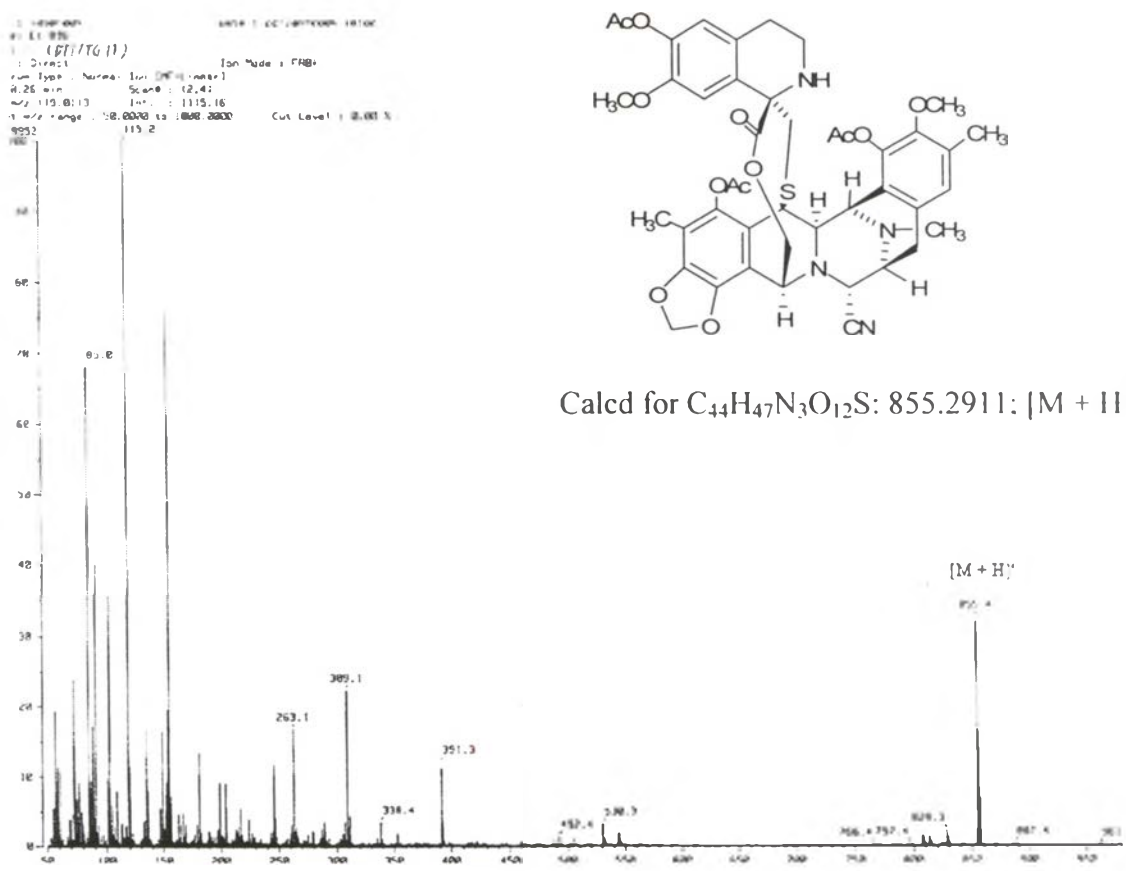


Figure 29. The IR spectrum 18,6'-diacetylecteinascidin 770 (**18**)



Calcd for $C_{44}H_{47}N_3O_{12}S$: 855.2911; [M + H]$^+$

Figure 30. The FAB-mass spectrum of 18,6'-diacetyl-ecteinascidin 770 (**18**)

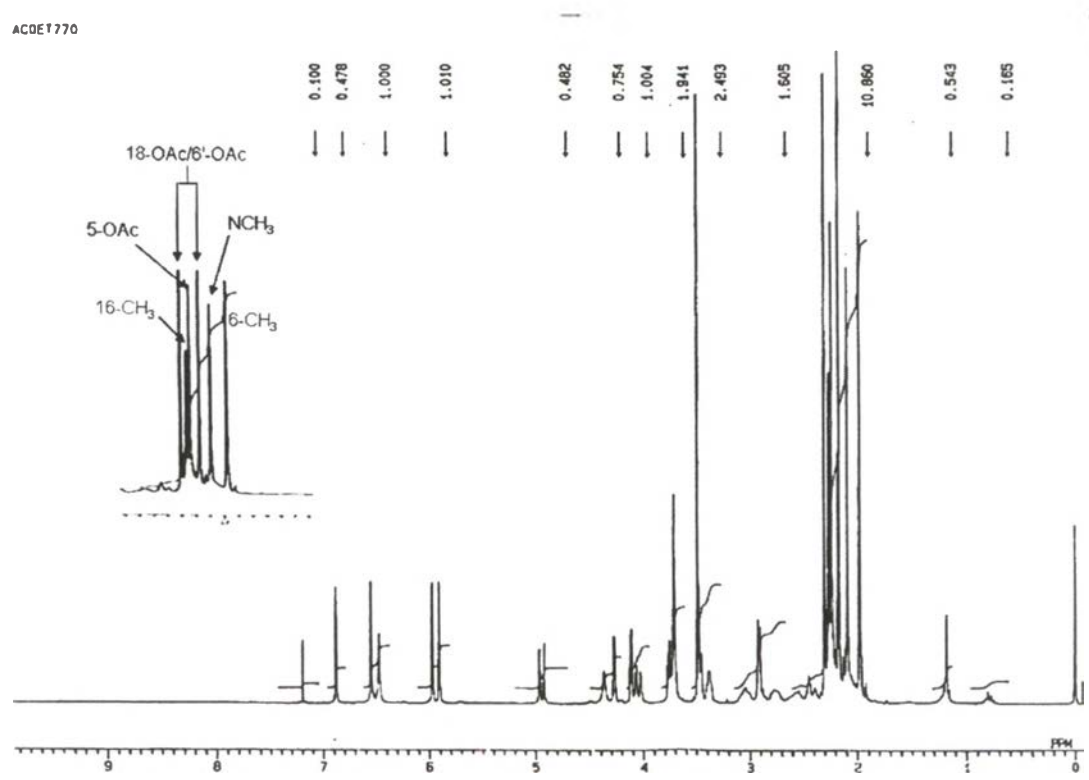


Figure 31. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 18,6'-diacetyl-ecteinascidin 770 (**18**)

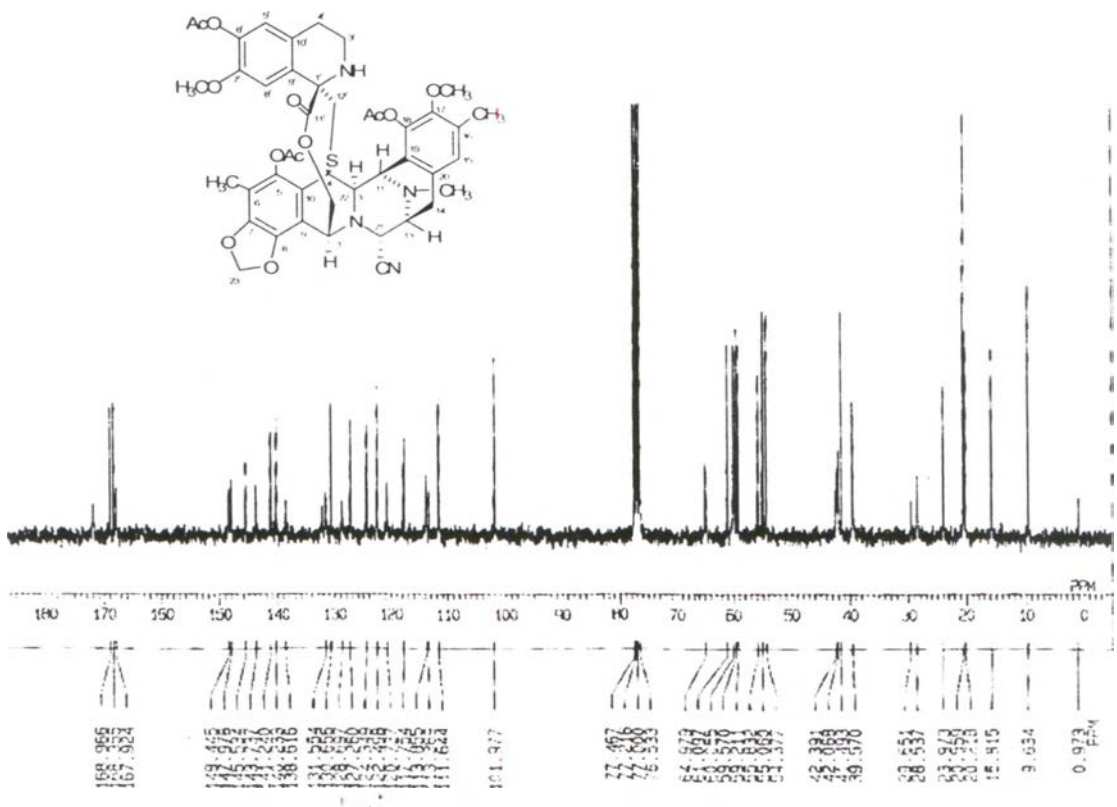


Figure 32. The 125 MHz ^{13}C-NMR spectrum (in $CDCl_3$) of 18,6'-diacetyl-ecteinascidin 770 (**18**)

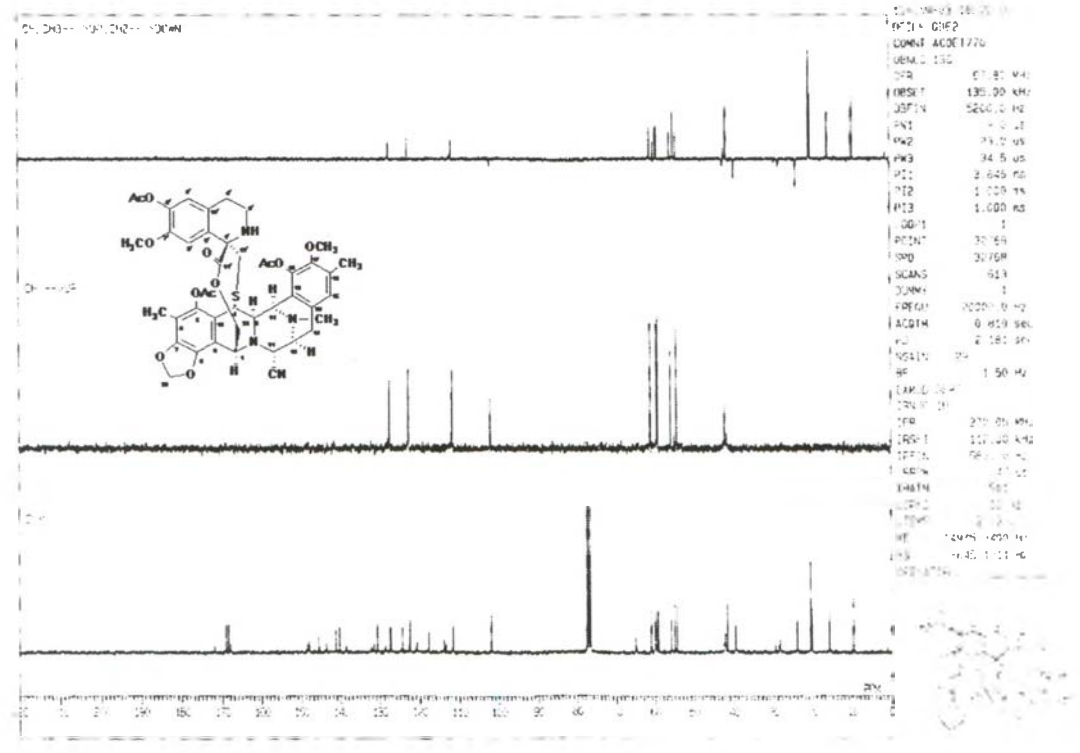


Figure 33. The 125 MHz ^{13}C-NMR and DEPT-135 spectra (in $CDCl_3$) of 18,6'-diacetylecteinascidin 770 (**18**)

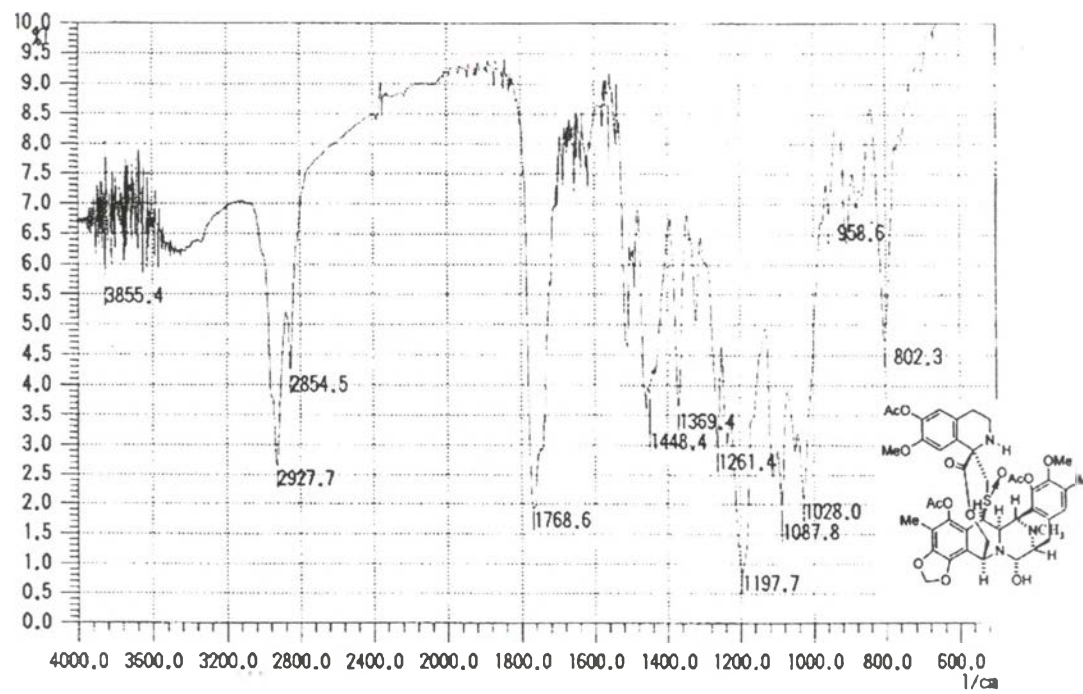
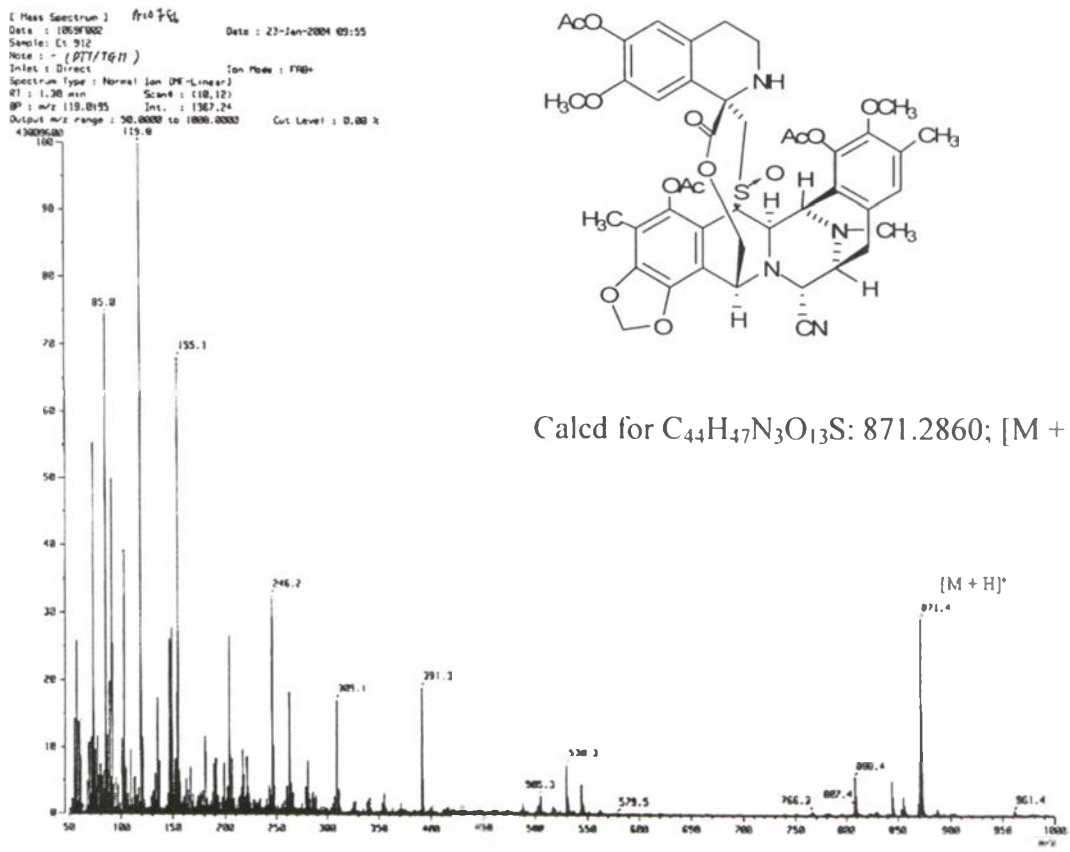


Figure 34. The IR spectrum 18,6'-diacetylecteinascidin 786 (**19**)



Calcd for $C_{44}H_{47}N_3O_{13}S$: 871.2860; $[M + H]^+$

Figure 35. The FAB-mass spectrum of 18,6'-diacetyl-ecteinascidin 786 (**19**)

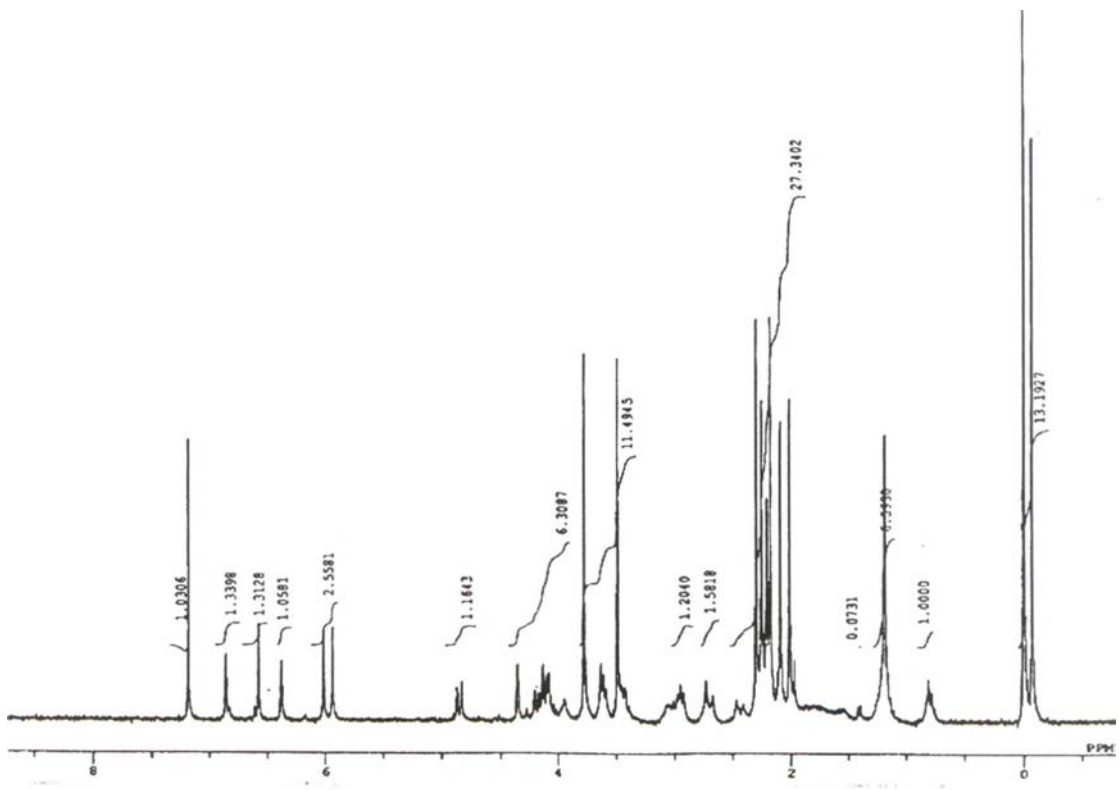


Figure 36. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 18,6'-diacetyl-ecteinascidin 786 (**19**)

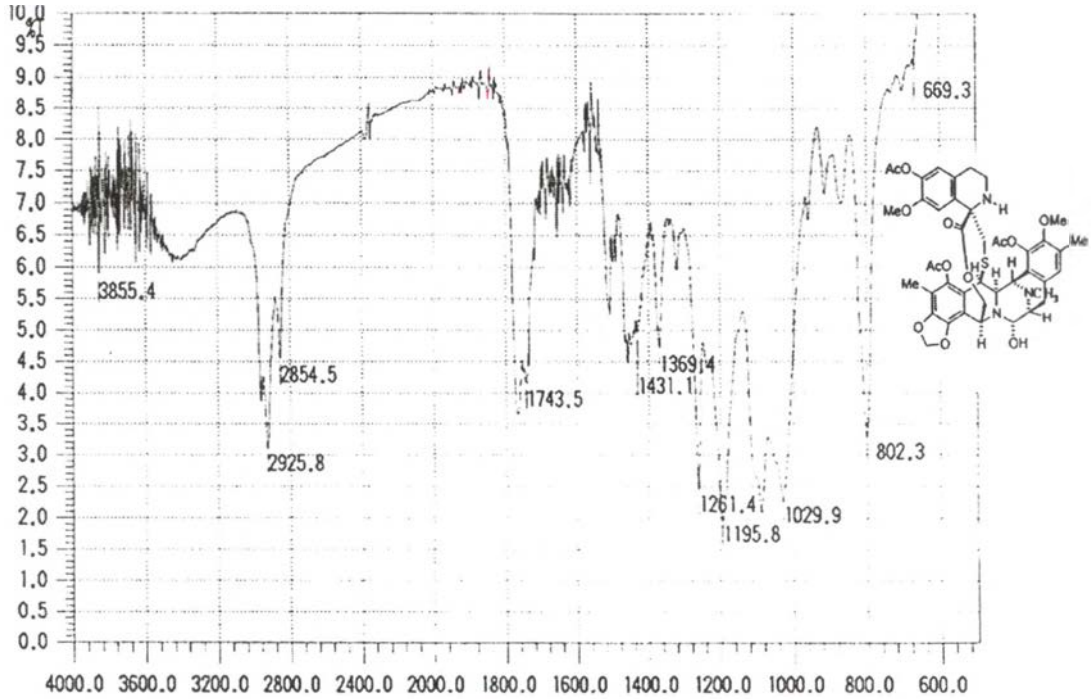


Figure 37. The IR spectrum 18,6'-diacetylecteinascidin 743 (**20**)

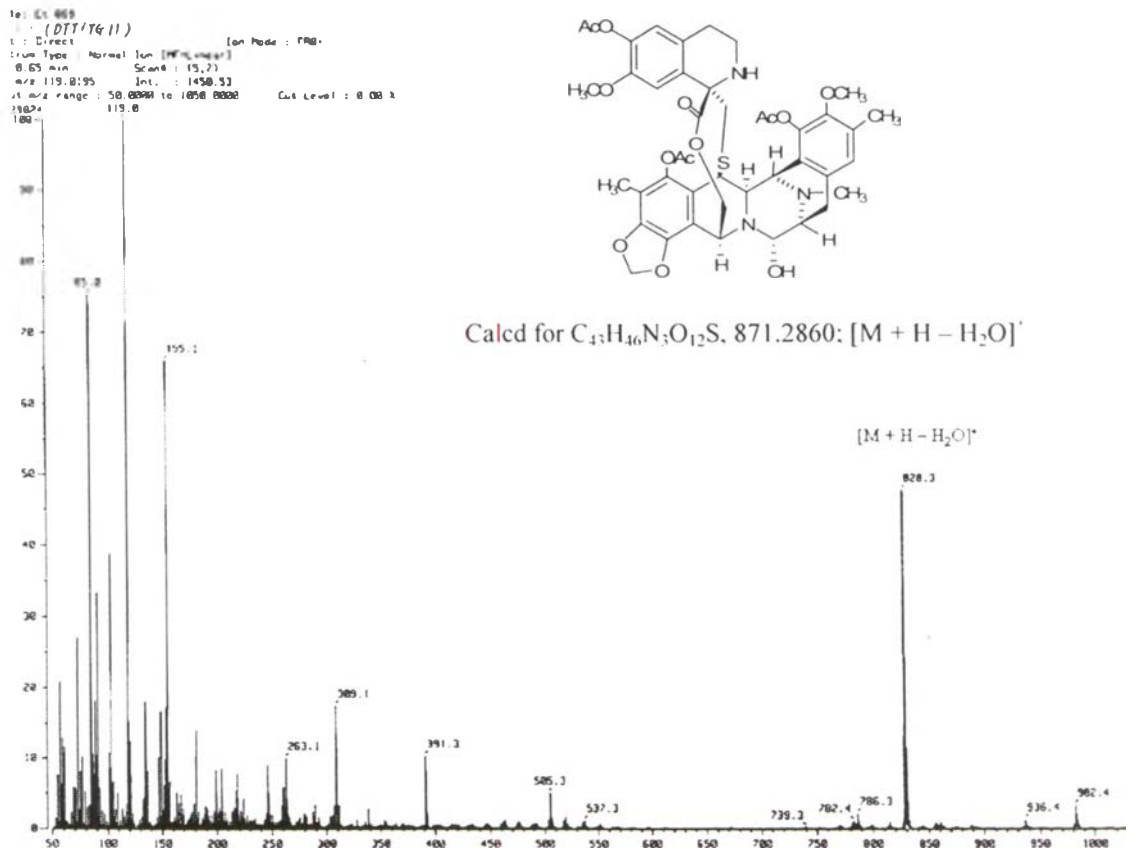


Figure 38. The FAB-mass spectrum of 18,6'-diacetyl-ecteinascidin 743 (**20**)

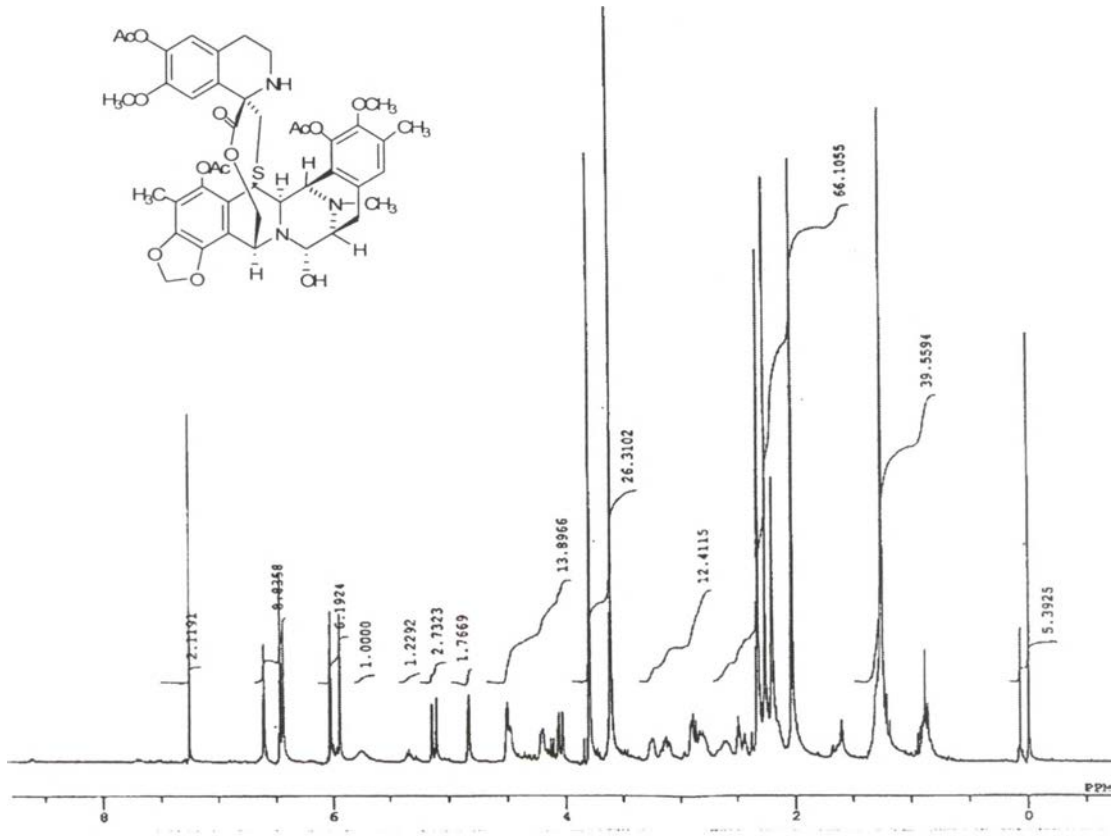


Figure 39. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 18,6'-diacetyl-ecteinascidin 7*43* (**20**)

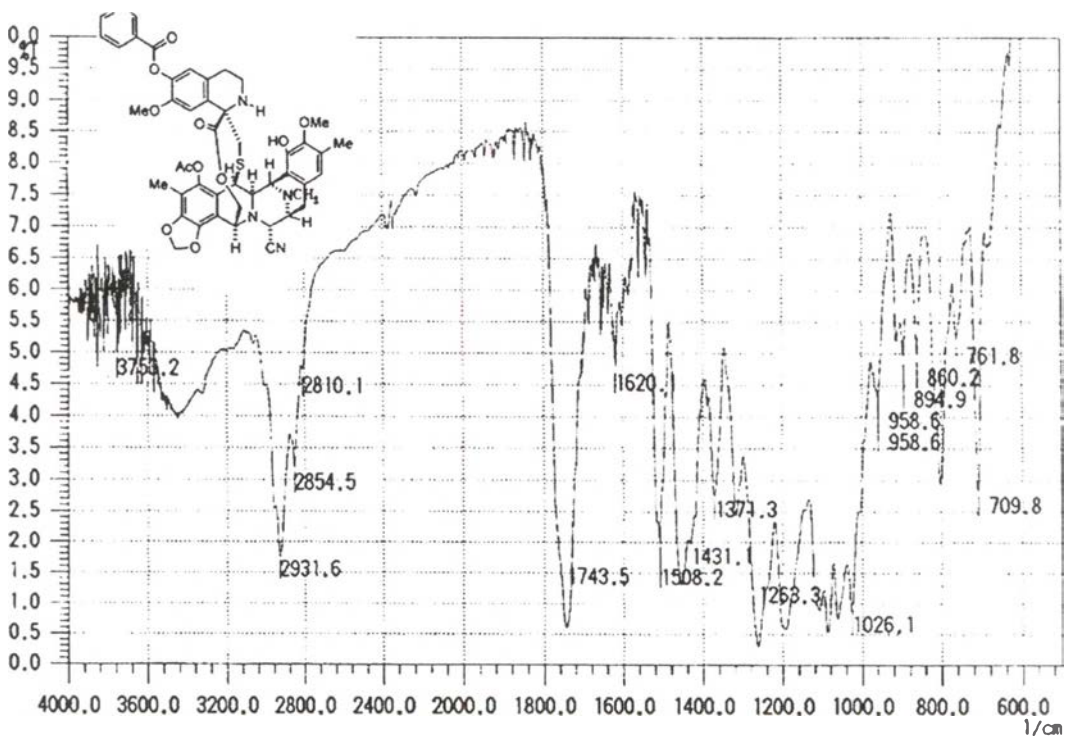


Figure 40. The IR spectrum of Ecteinascidin 770 6'-*O*-benzoate (**21**)

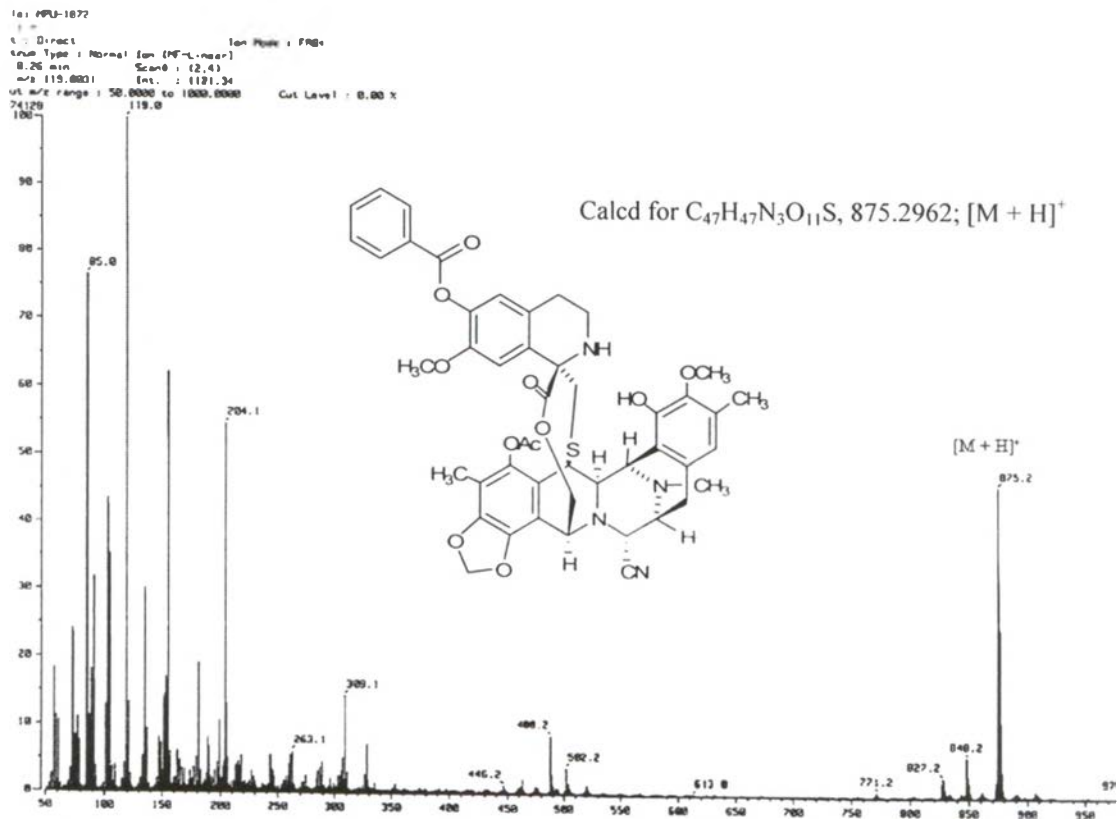


Figure 41. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-benzoate (**21**)

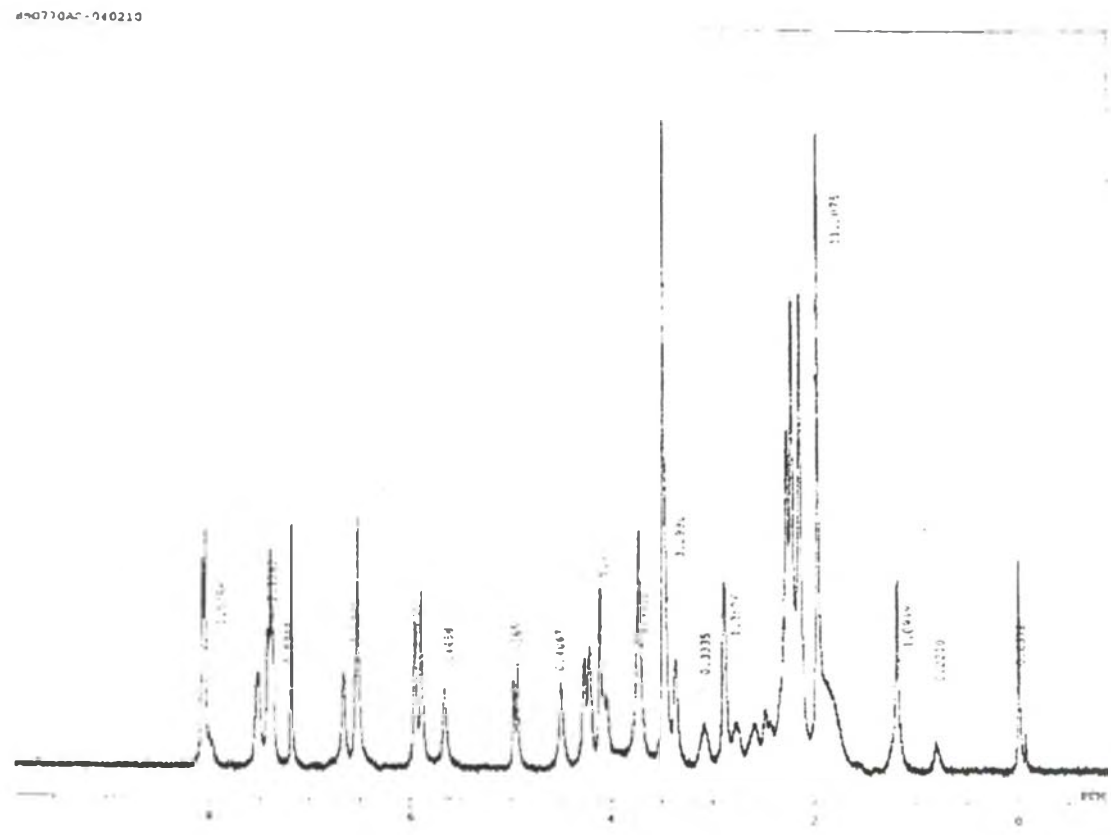


Figure 42. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-benzoate (**21**)

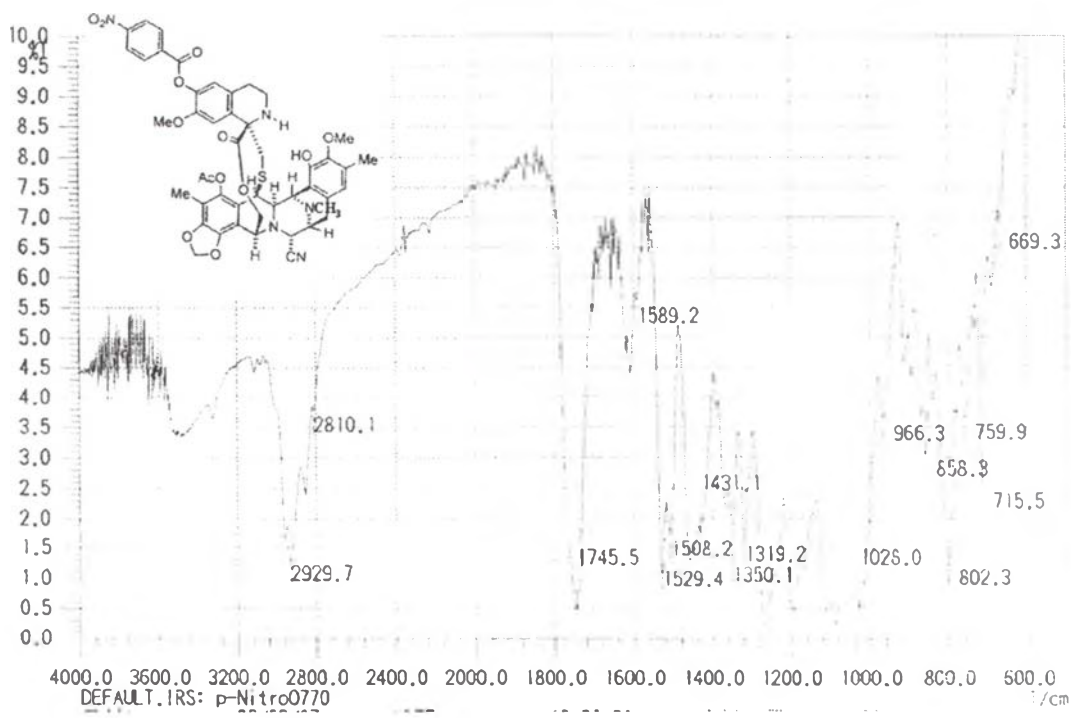


Figure 43. The IR spectrum of Ecteinascidin 770 6'-*O*-4"-nitrobenzoate (**22**)

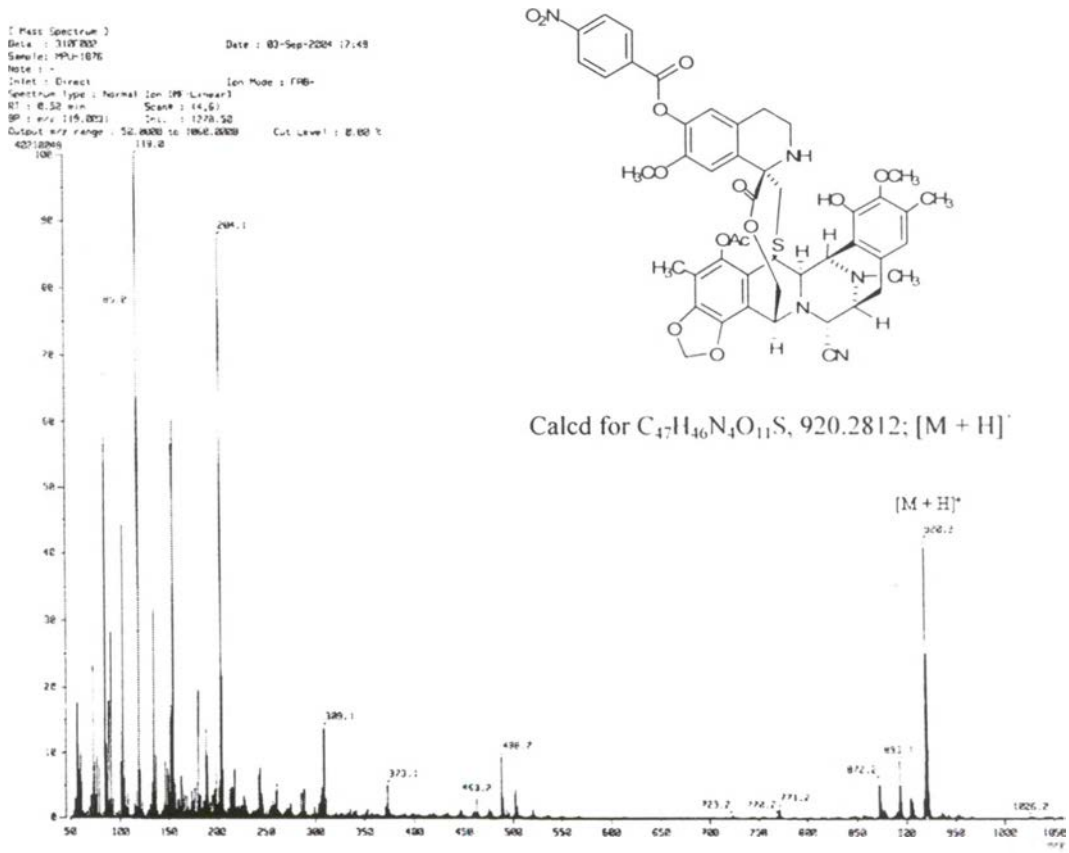


Figure 44. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-4"-nitrobenzoate (**22**)

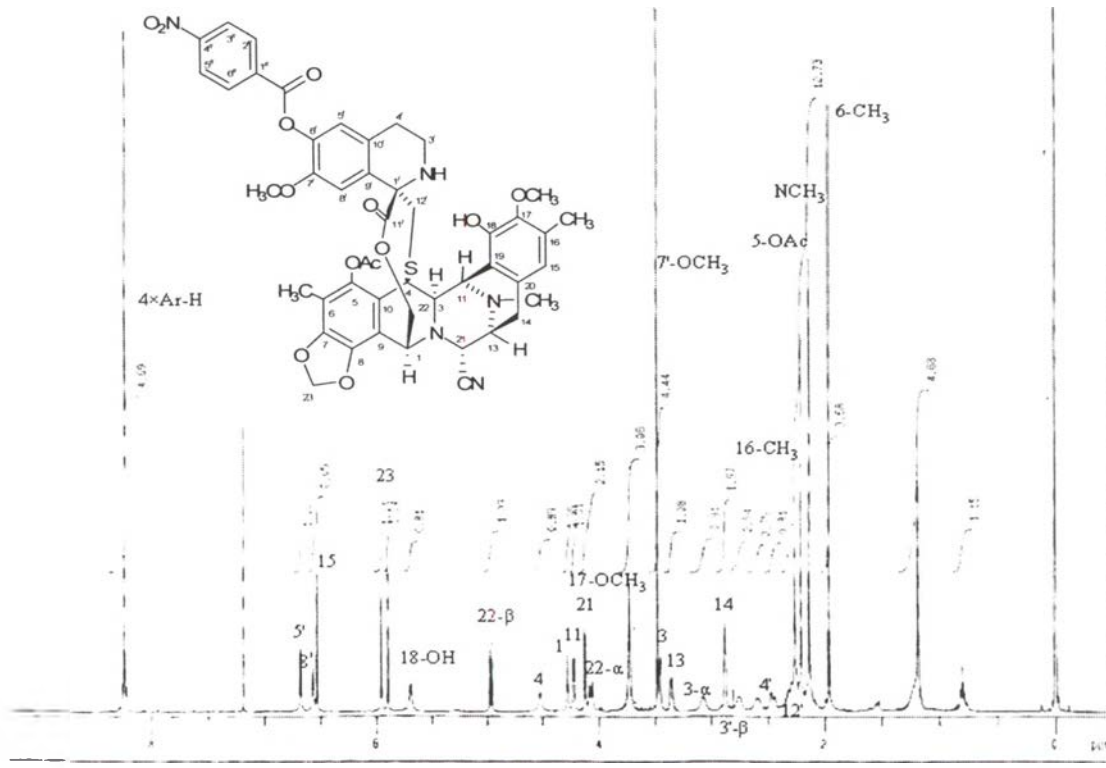


Figure 45. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-nitrobenzoate (**22**)

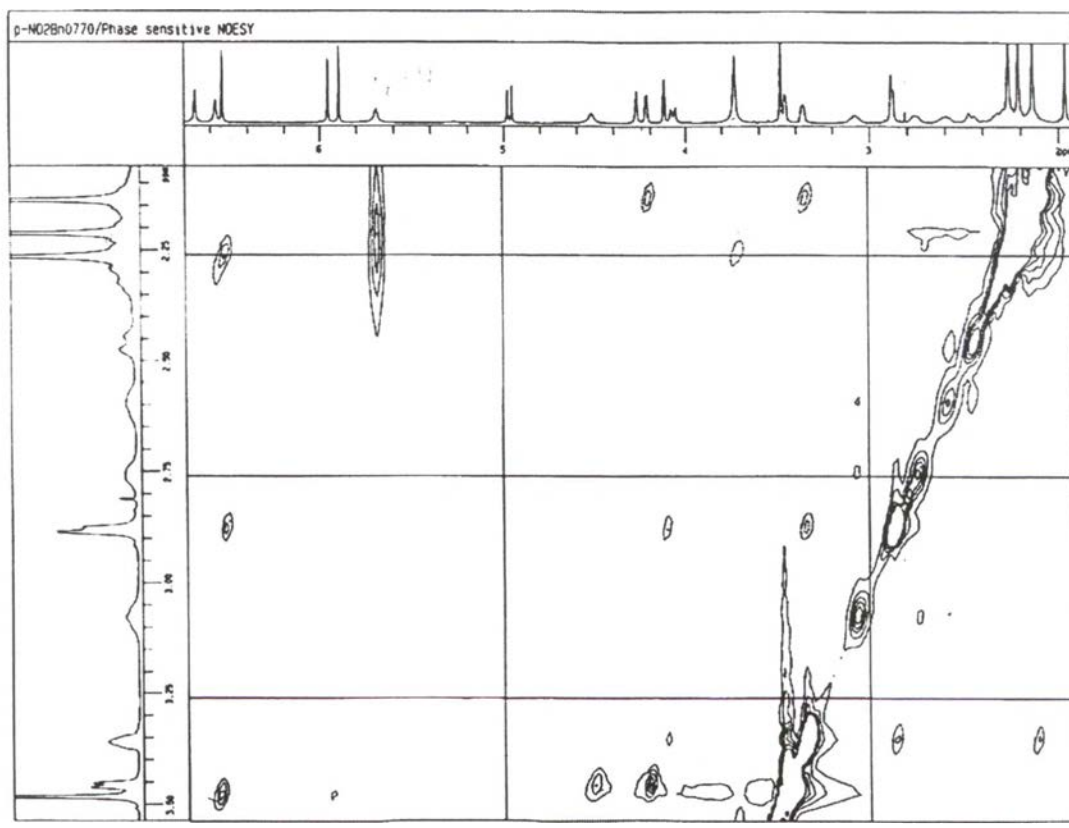


Figure 46. The 500 MHz NOESY spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-nitrobenzoate (**22**)

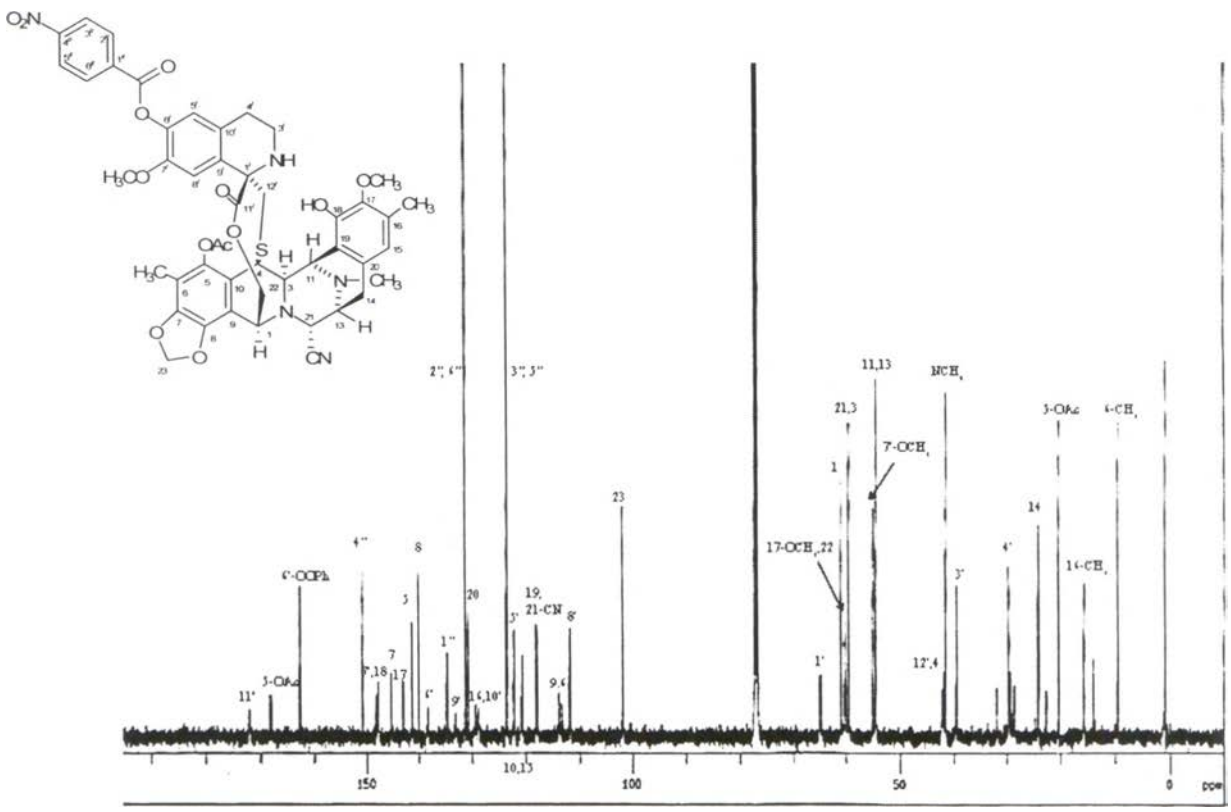


Figure 47. The 125 MHz ^{13}C-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-nitrobenzoate (**22**)

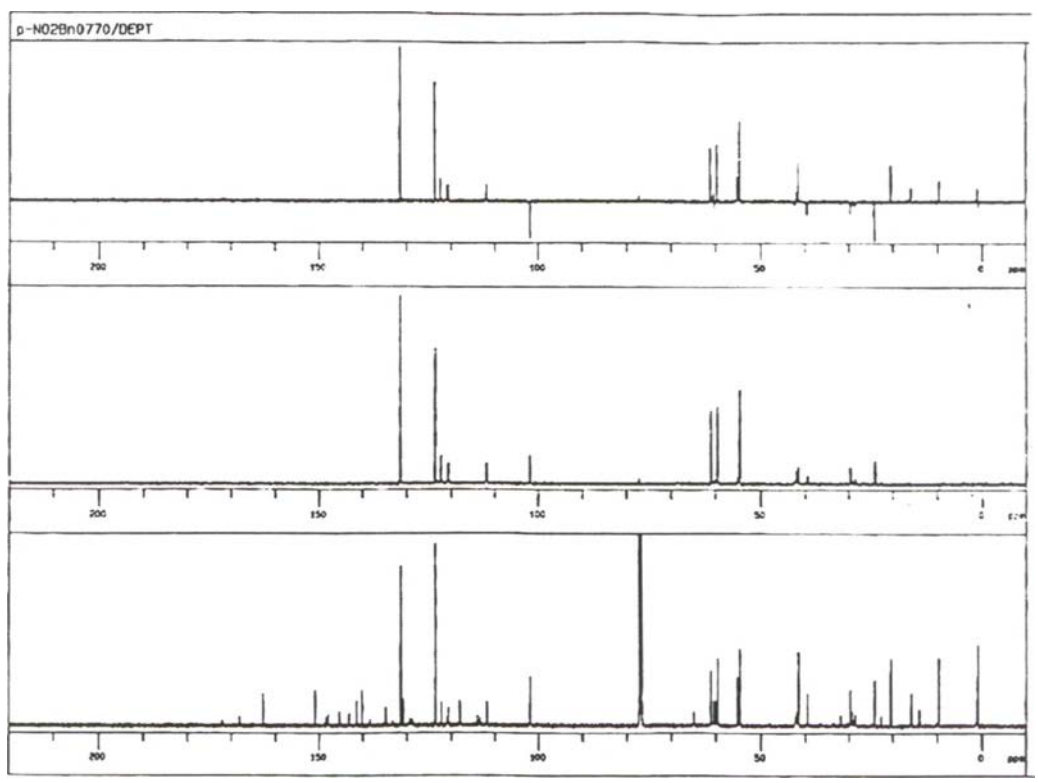


Figure 48. The 500 MHz ^{13}C-NMR and DEPTspectra (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-nitrobenzoate (**22**)

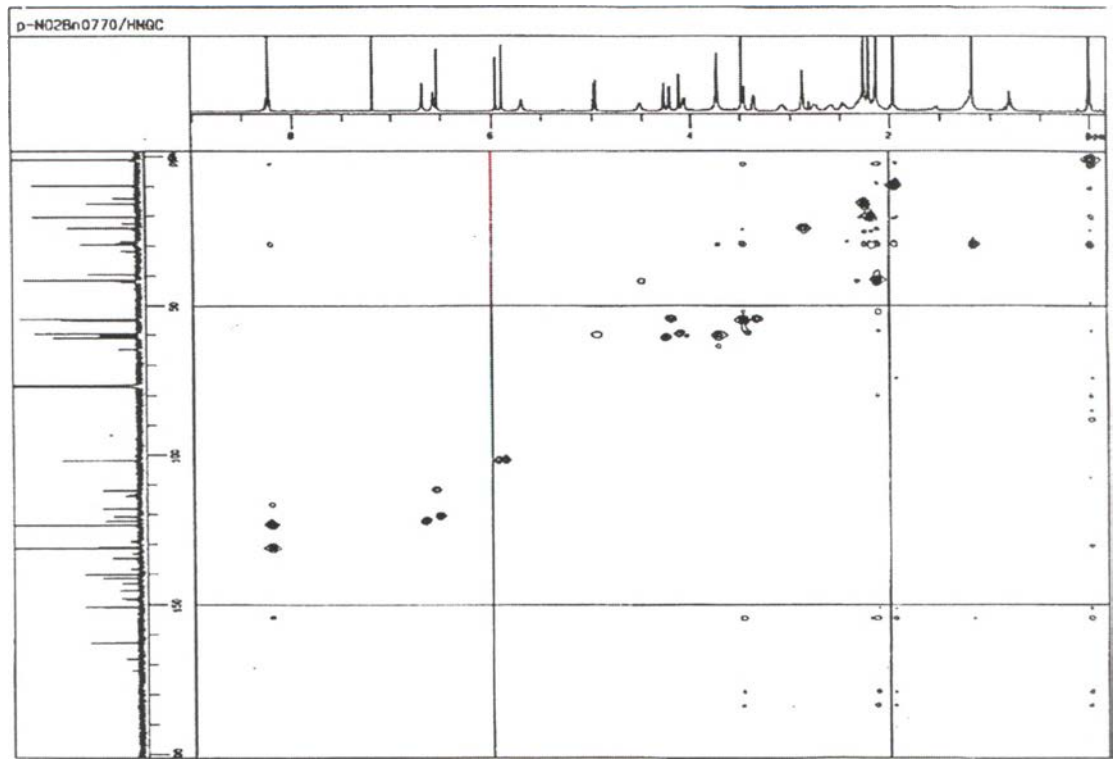


Figure 49 The 500 MHz HMQC spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-nitrobenzoate (**22**)

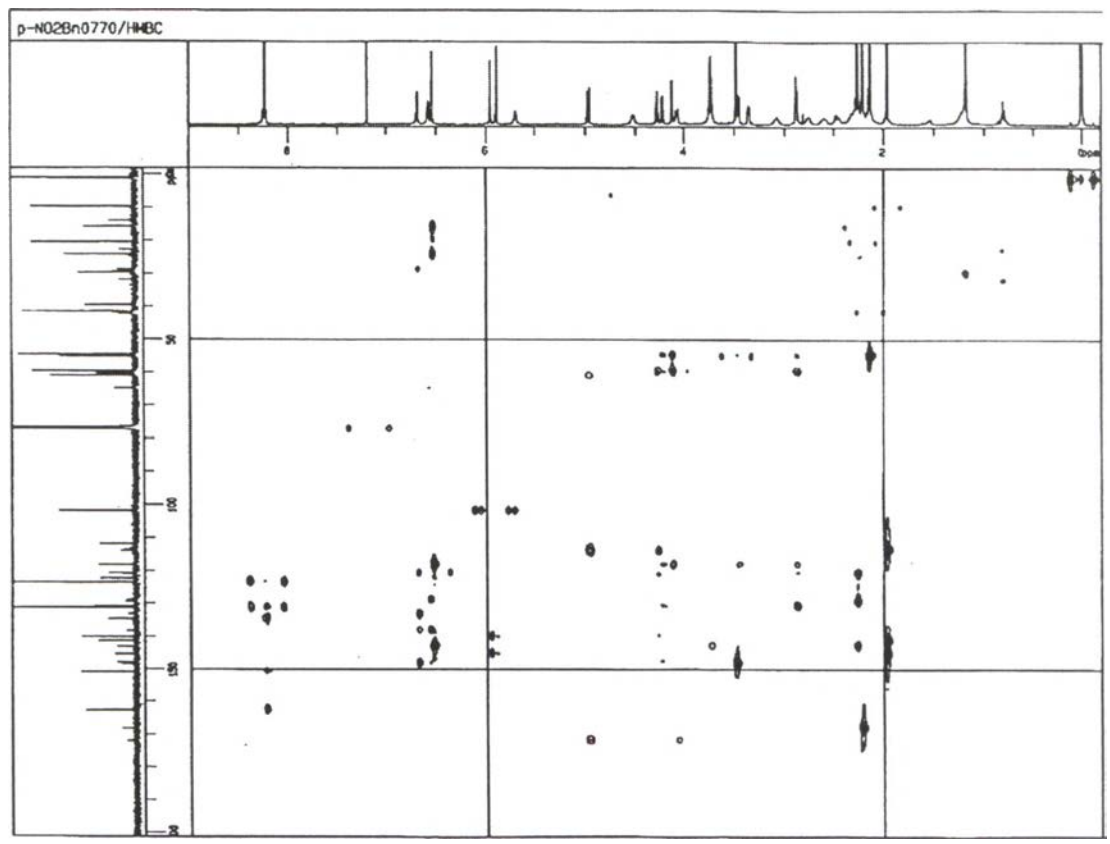


Figure 50. The 500 MHz HMBC spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-nitrobenzoate (**22**)

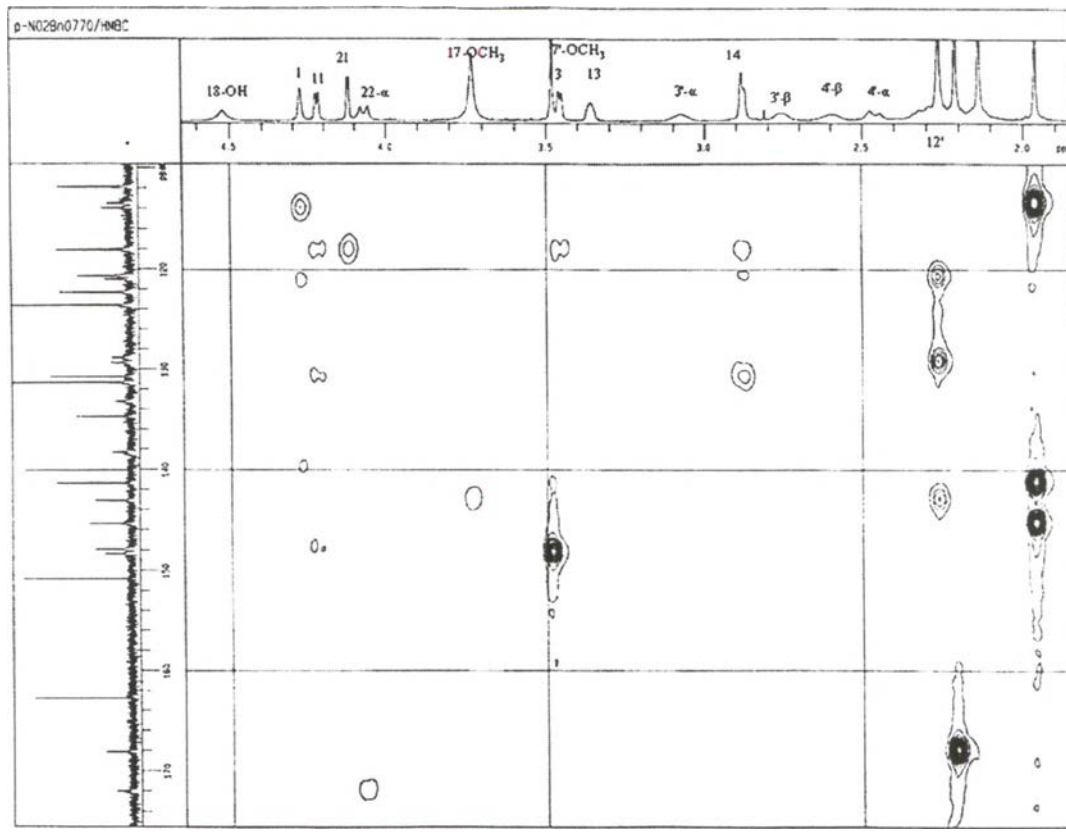


Figure 51. The 500 MHz HMBC spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-nitrobenzoate (**22**) (expanded from δ_H 1.8-4.7 ppm and δ_C 115-173 ppm)

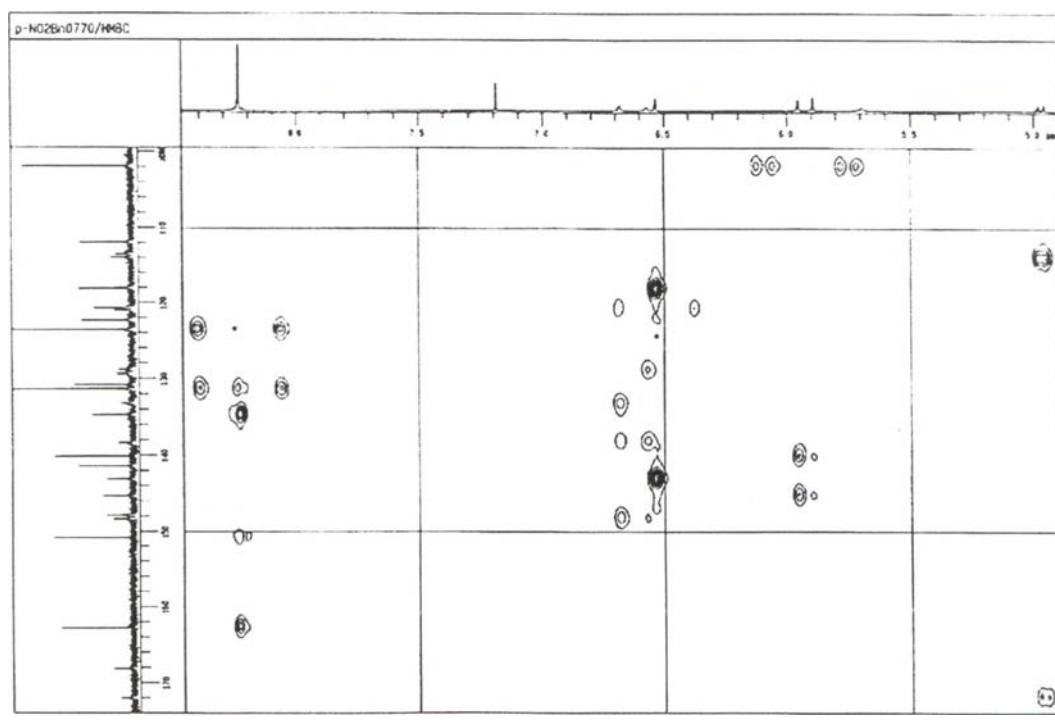


Figure 52. The 500 MHz HMBC spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-nitrobenzoate (**22**) (expanded from δ_H 4.9-8.5 ppm and δ_C 105-172 ppm)

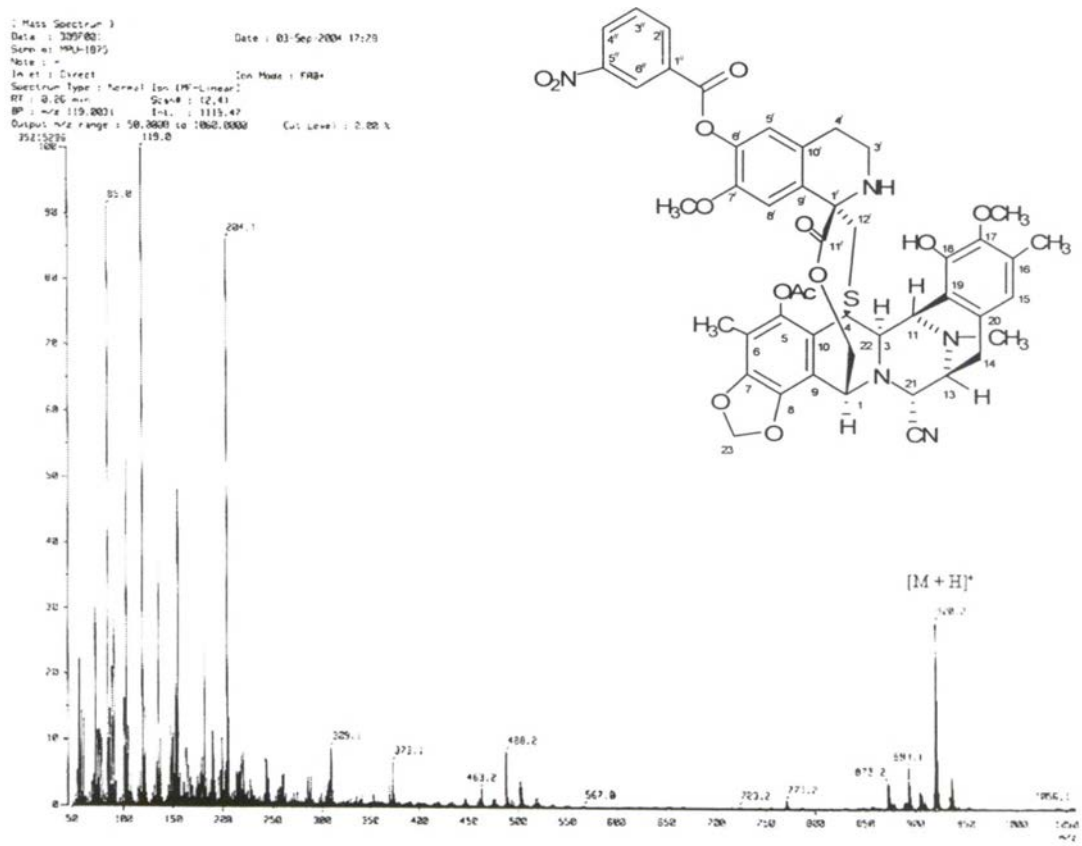


Figure 53. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-3"-nitrobenzoate (**23**)

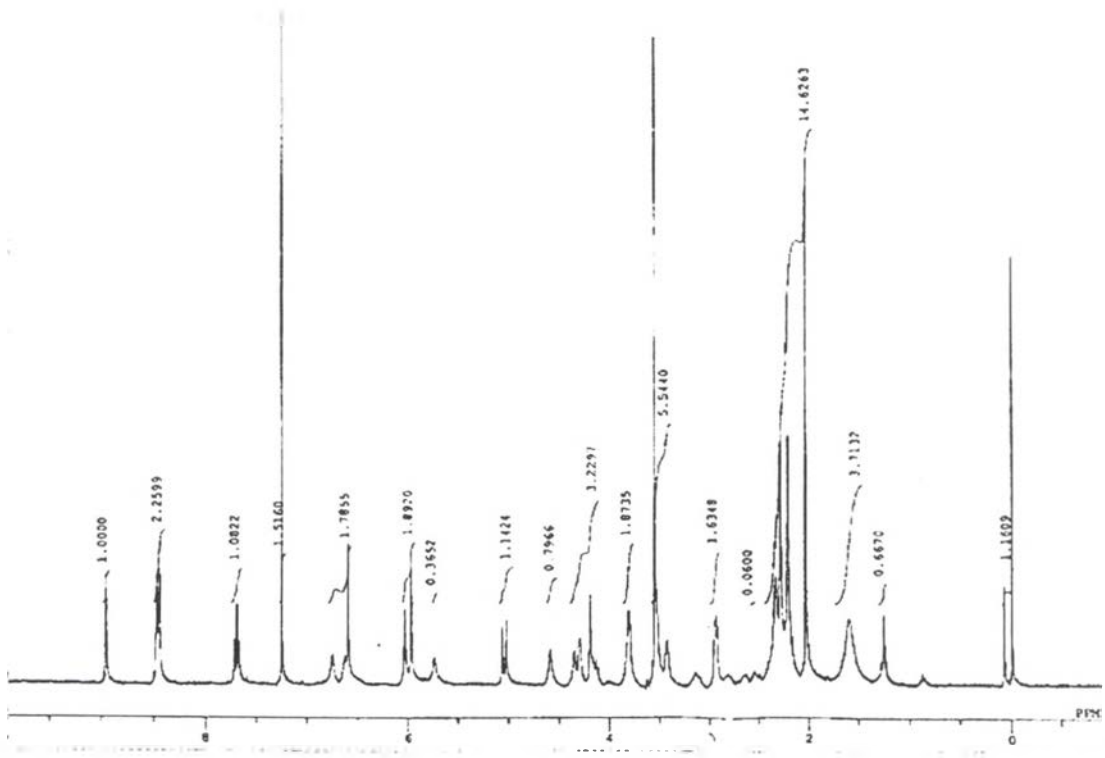


Figure 54. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-3"-nitrobenzoate (**23**)

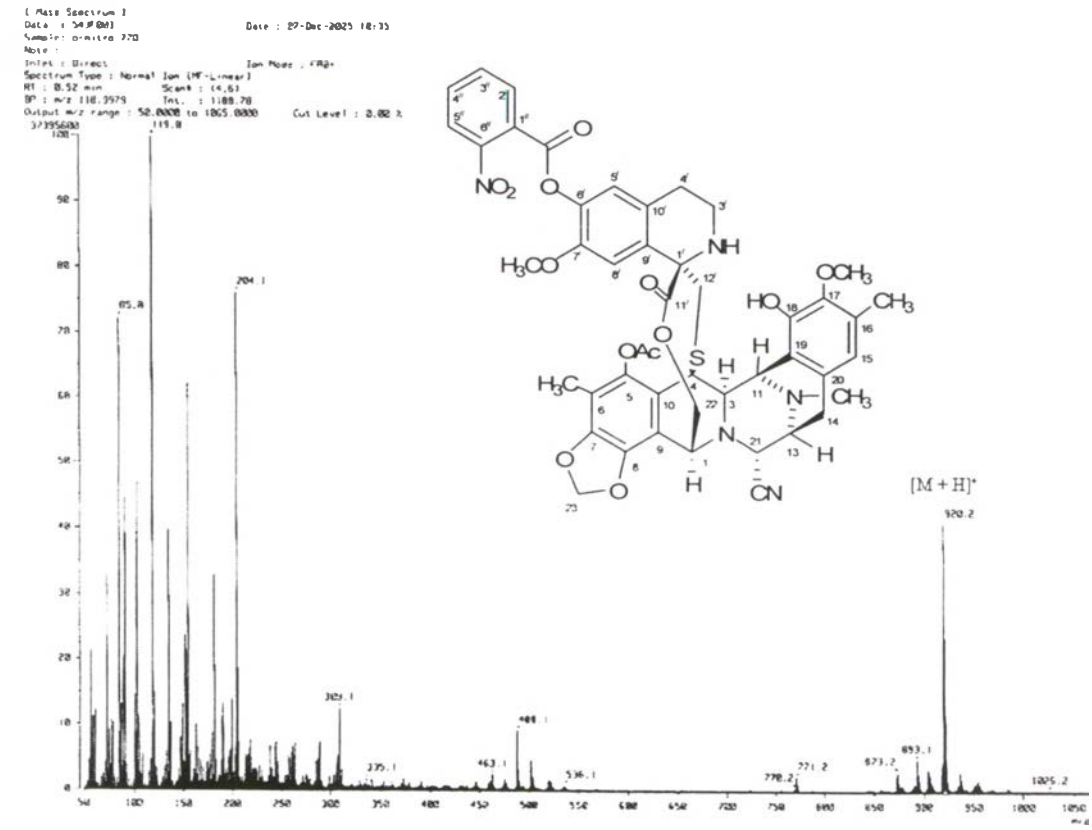


Figure 55. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-2"-nitrobenzoate (**24**)

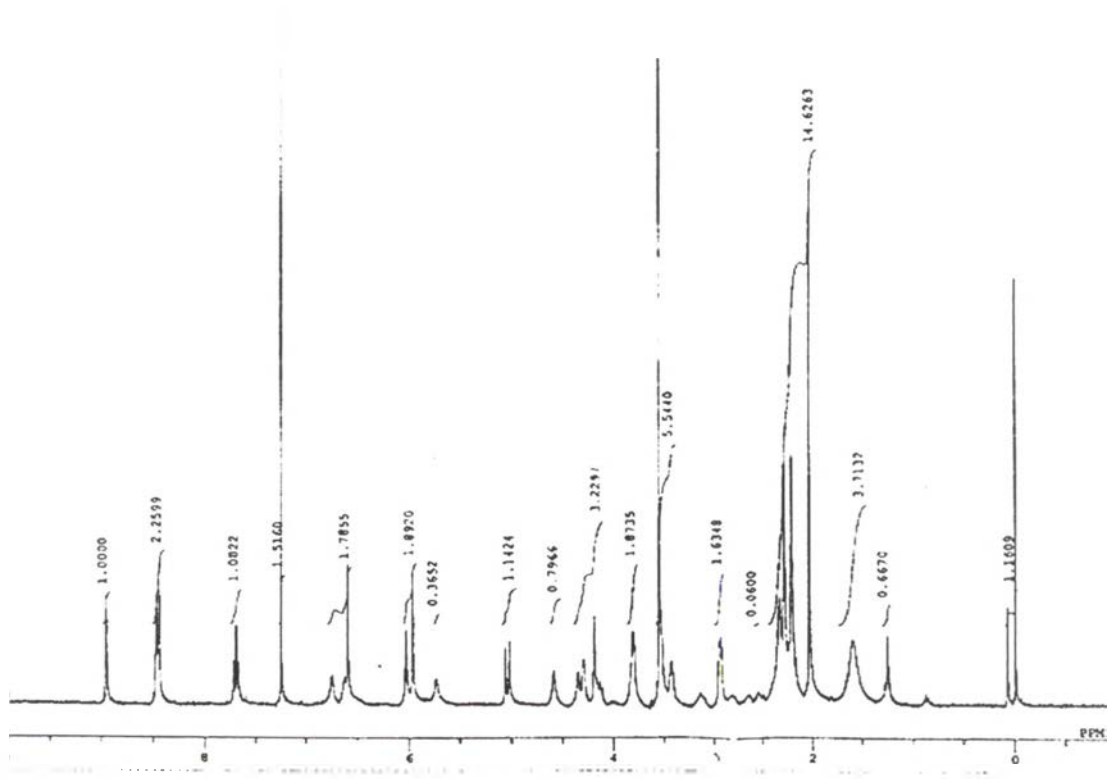


Figure 56. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-2"-nitrobenzoate (**24**)

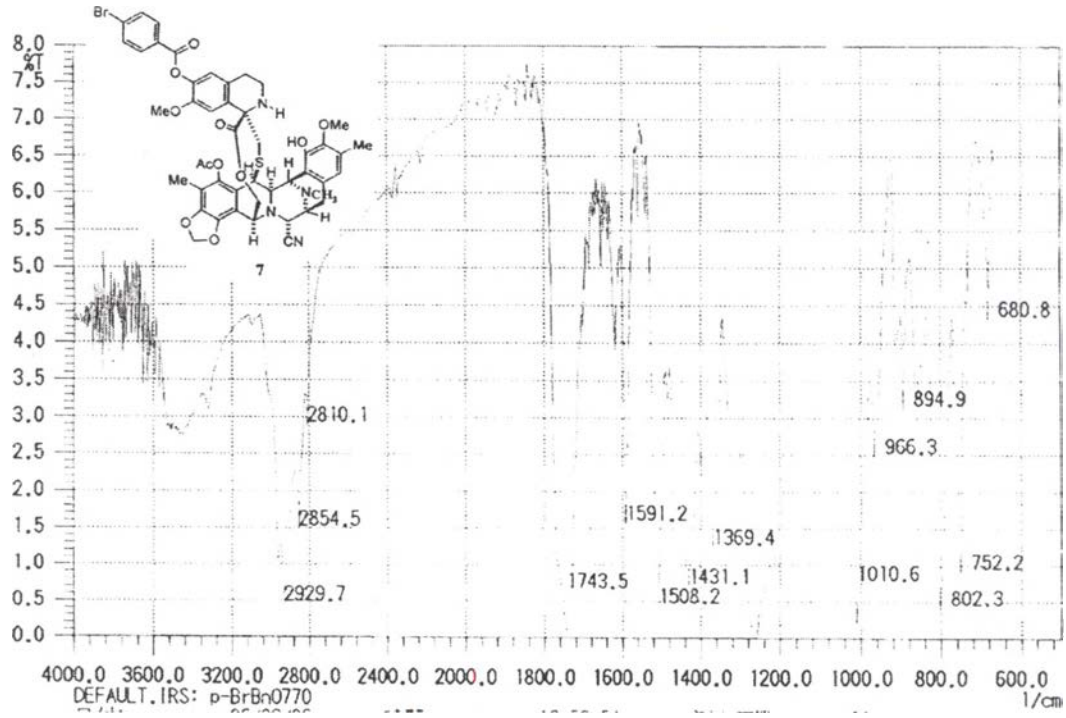


Figure 57. The IR spectrum of Ecteinascidin 770 6'-*O*-4"-bromobenzoate (**25**)

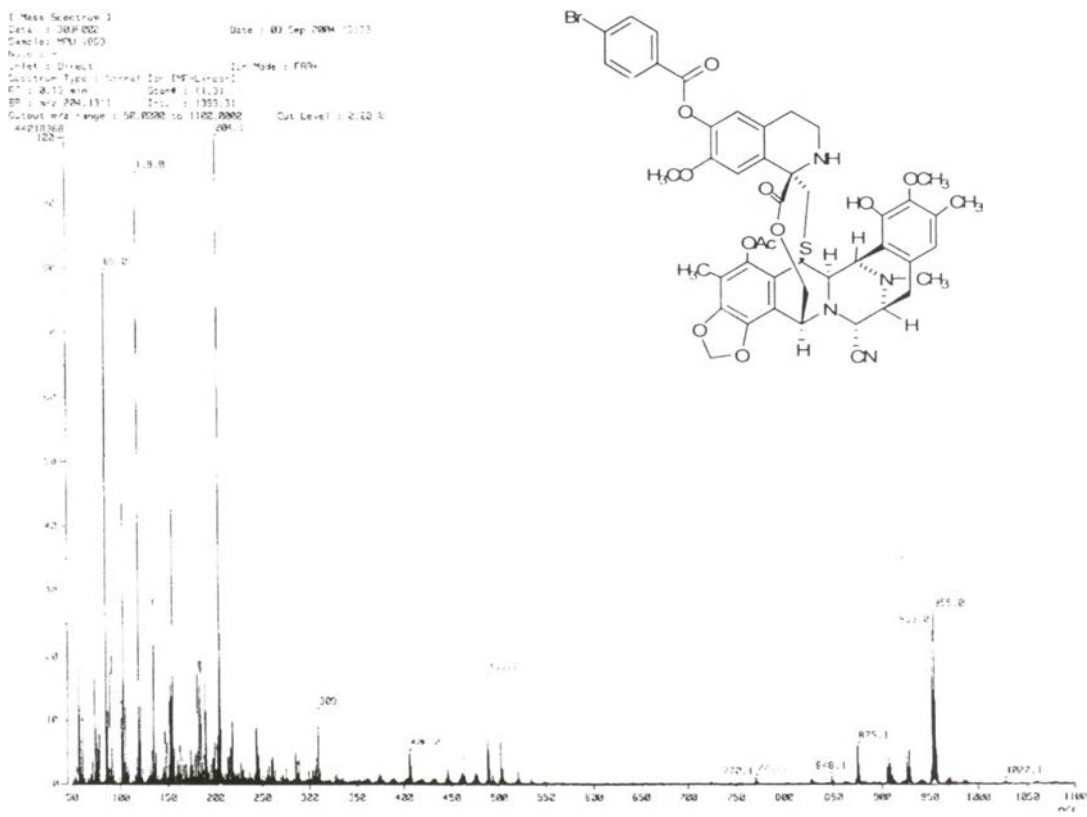


Figure 58. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-4"-bromobenzoate (**25**)

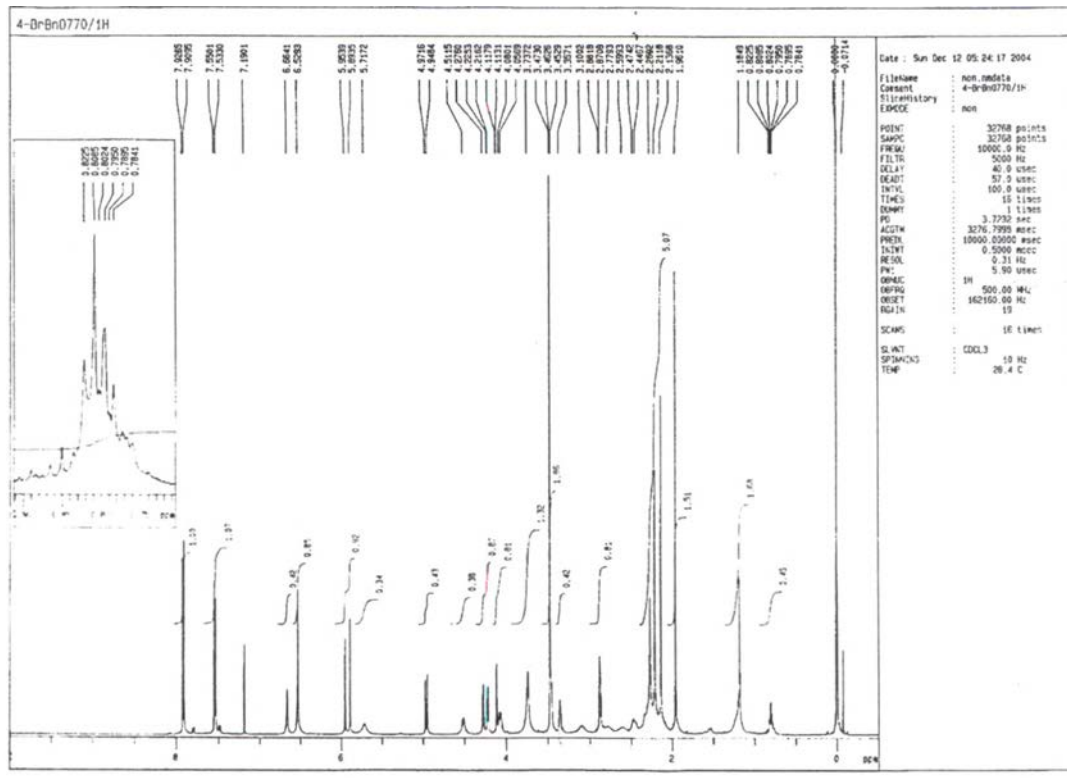


Figure 59. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-bromobenzoate (**25**)

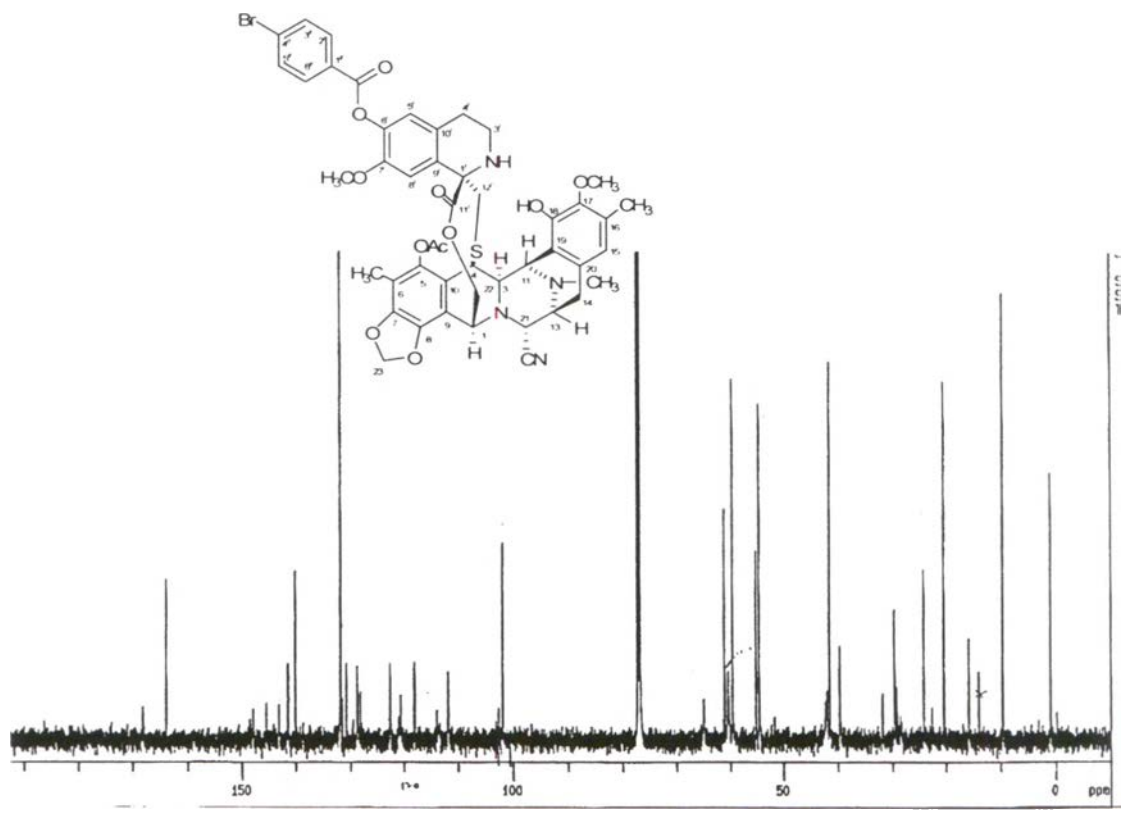


Figure 60. The 125 MHz ^{13}C-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-bromobenzoate (**25**)

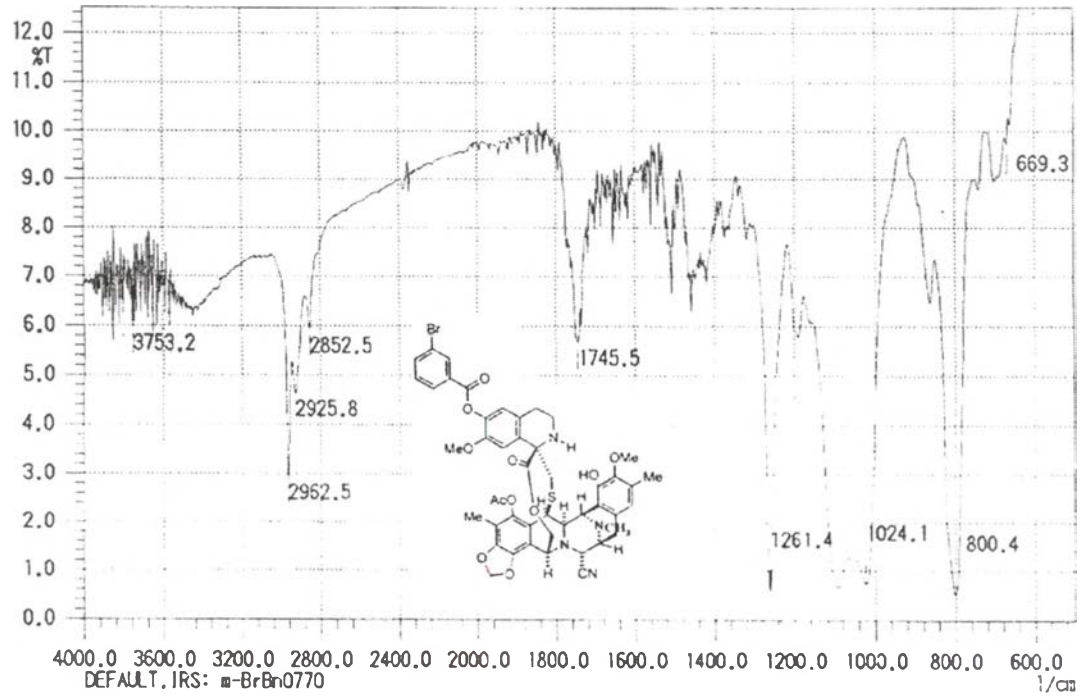


Figure 61. The IR spectrum of Ecteinascidin 770 6'-*O*-3"-bromobenzoate (**26**)

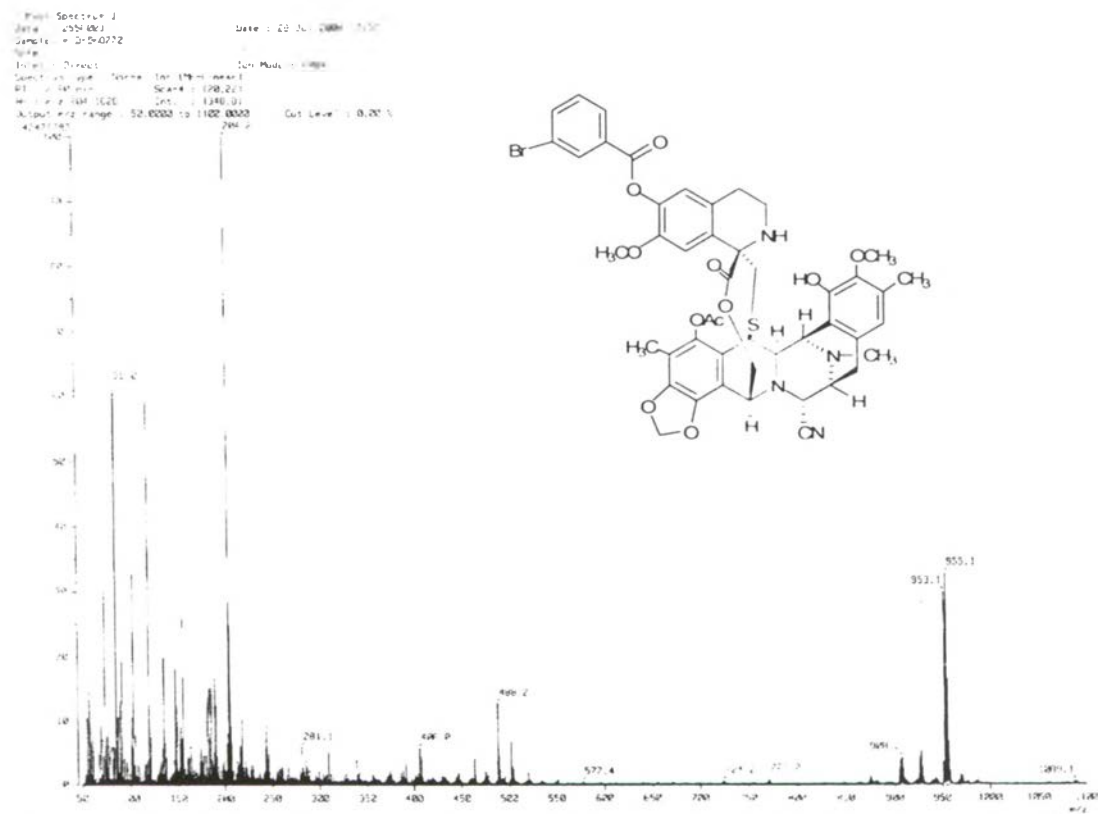


Figure 62. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-3"-bromobenzoate (**26**)

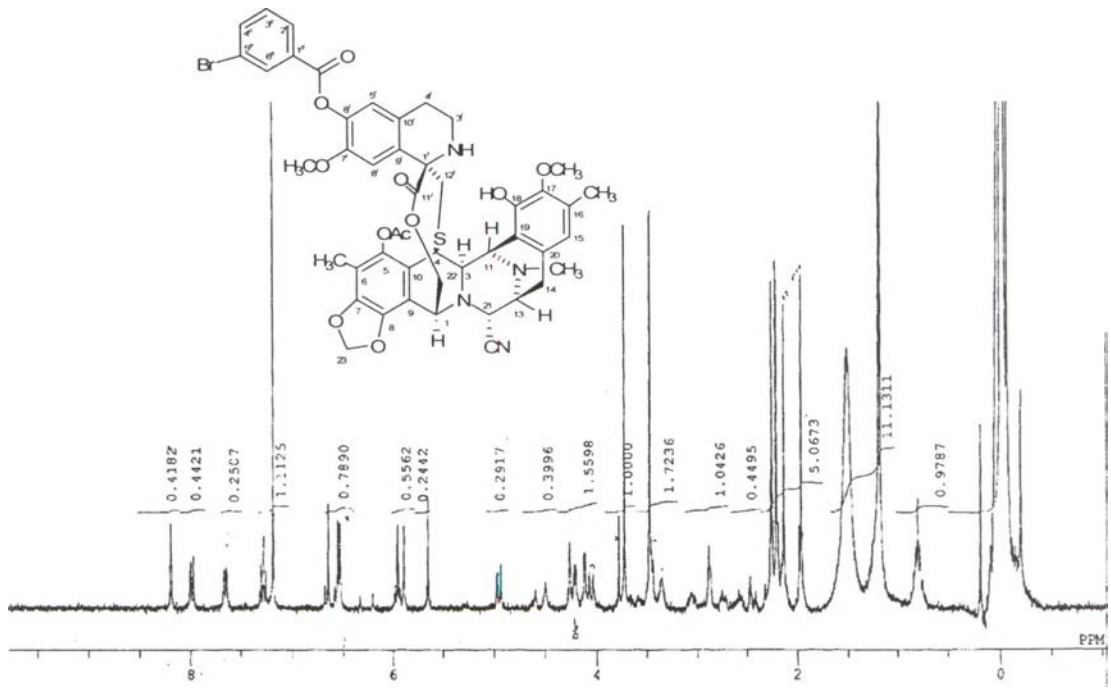


Figure 63. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-3"-bromobenzoate (**26**)

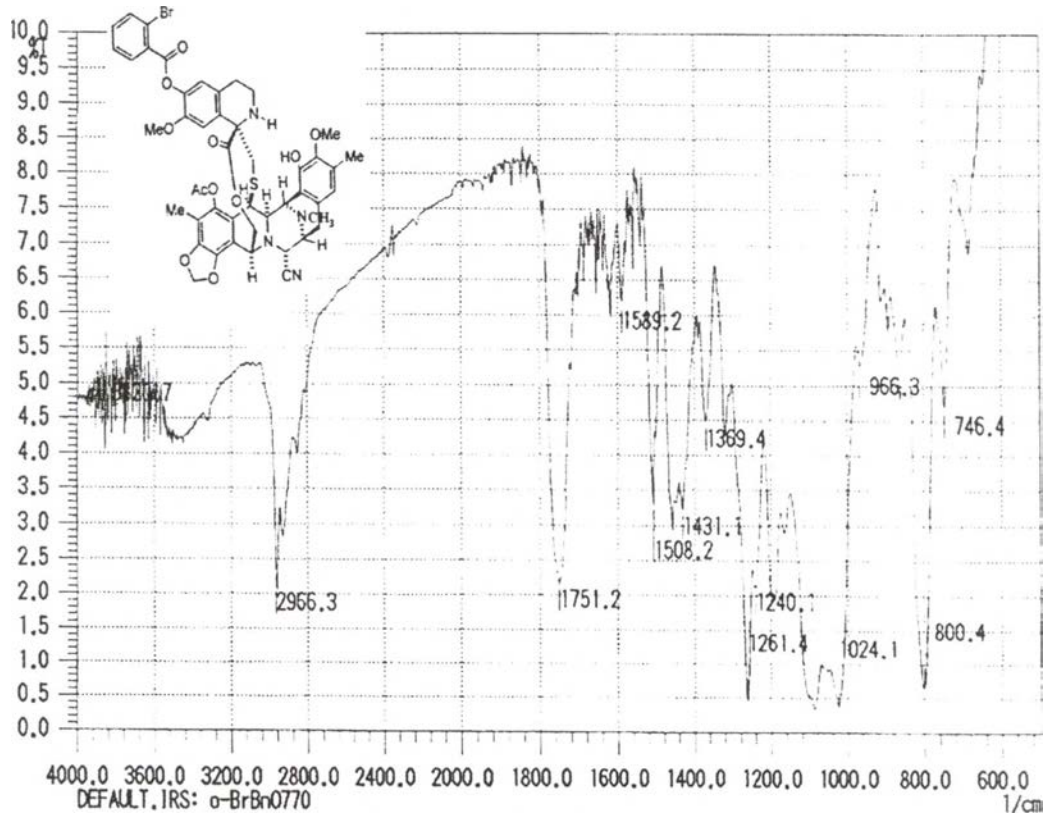


Figure 64. The IR spectrum of Ecteinascidin 770 6'-*O*-2"-bromobenzoate (**27**)

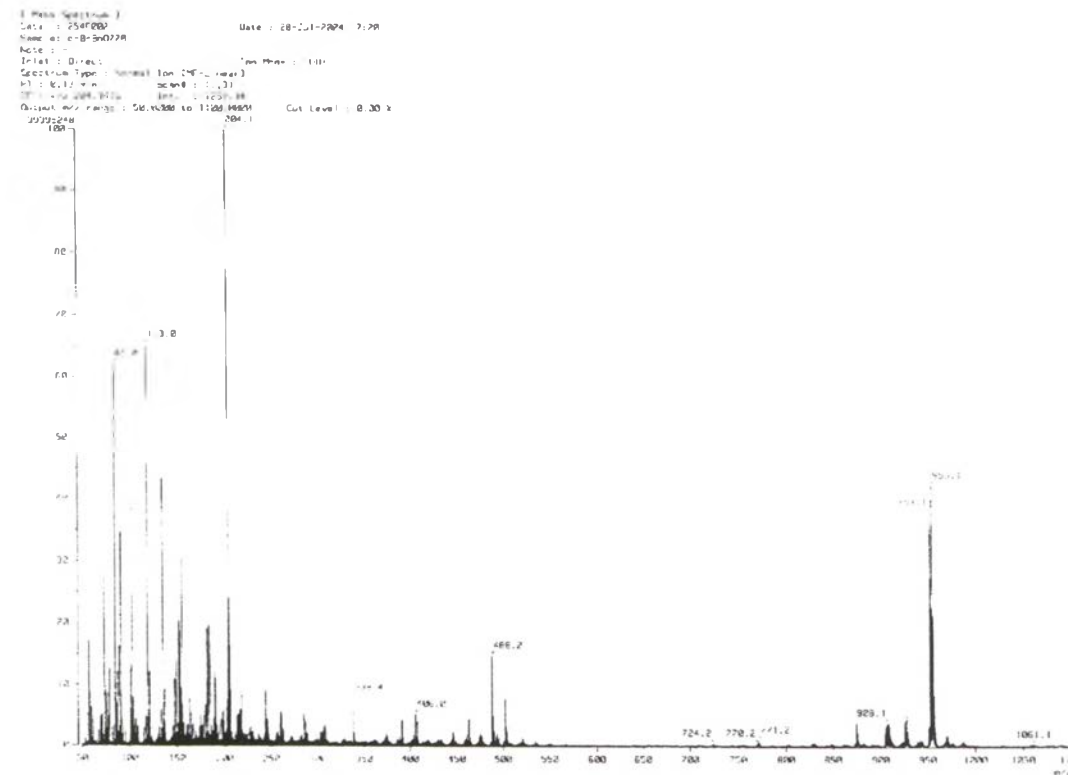


Figure 65. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-2"-bromobenzoate (**27**)

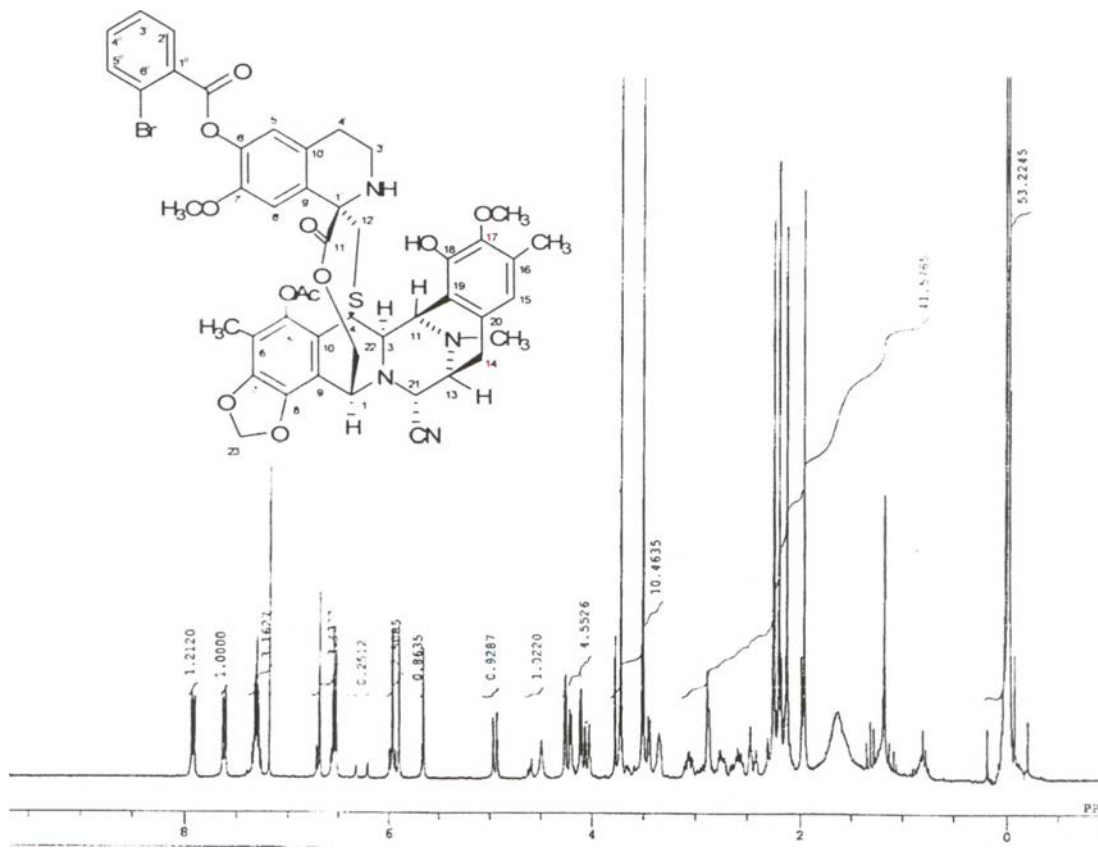


Figure 66. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-2"-bromobenzoate (**27**)

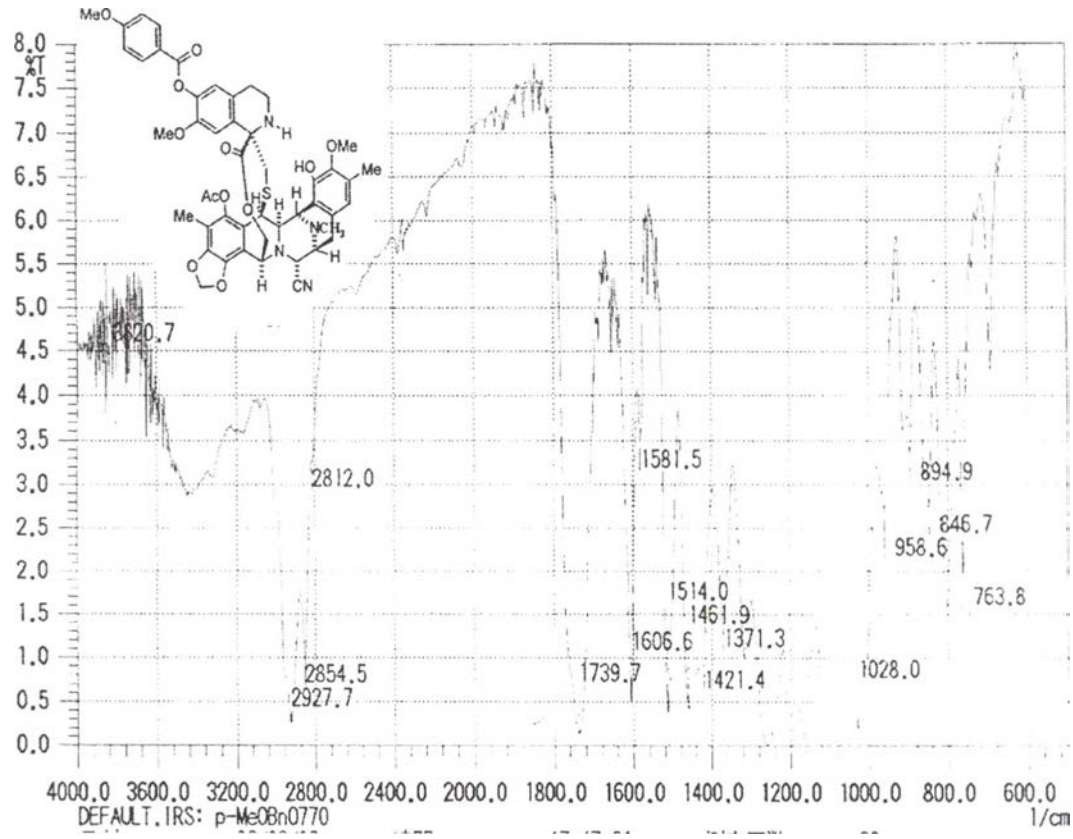


Figure 67. The IR spectrum of Ecteinascidin 770 6'-*O*-4"-methoxybenzoate (**28**)

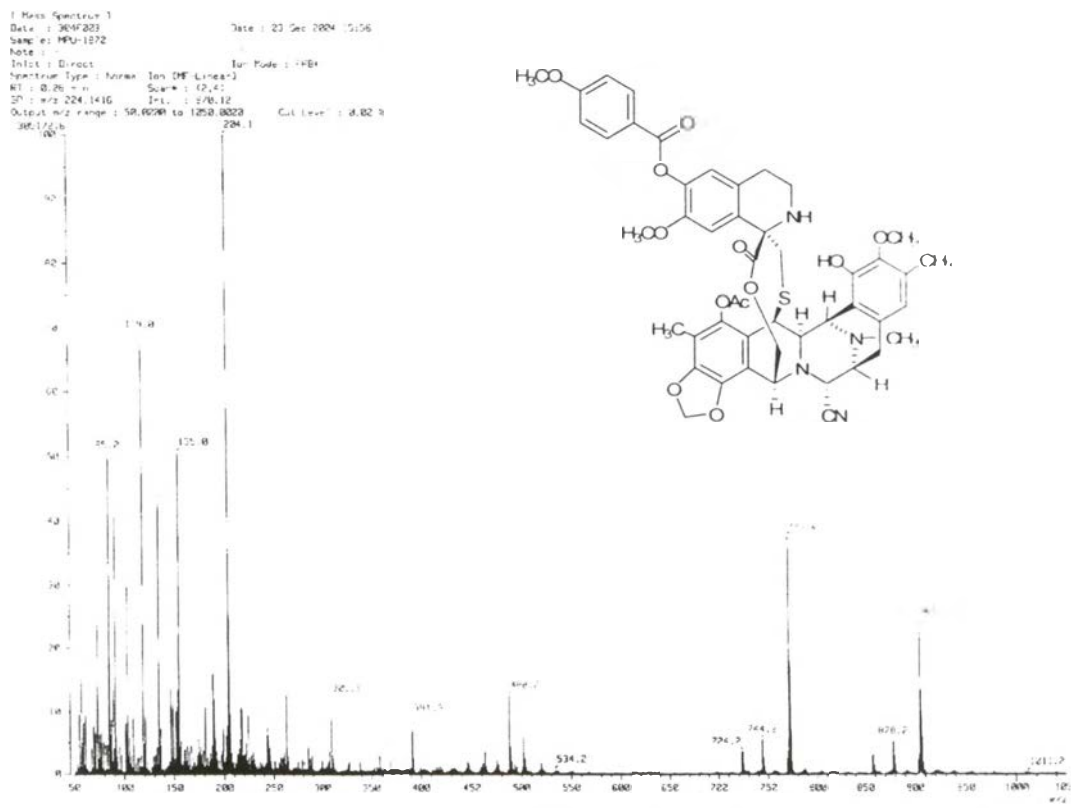


Figure 68. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-4"-methoxybenzoate (**28**)

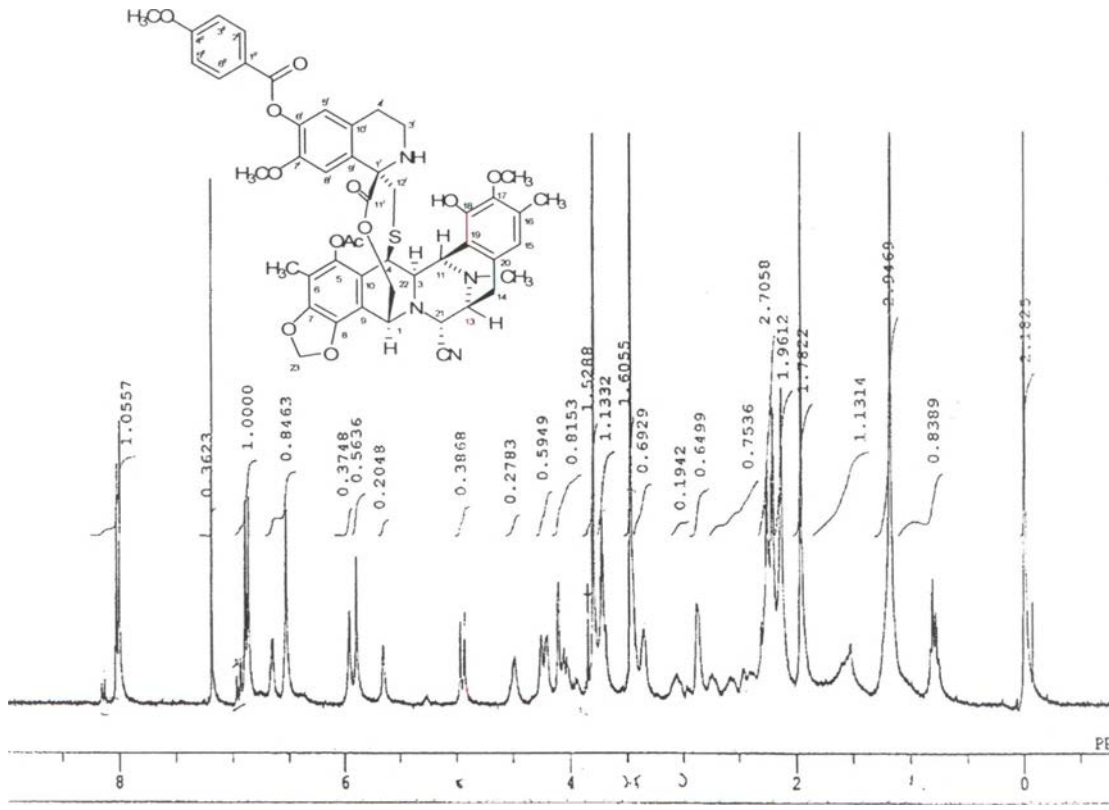


Figure 69. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-methoxybenzoate (**28**)

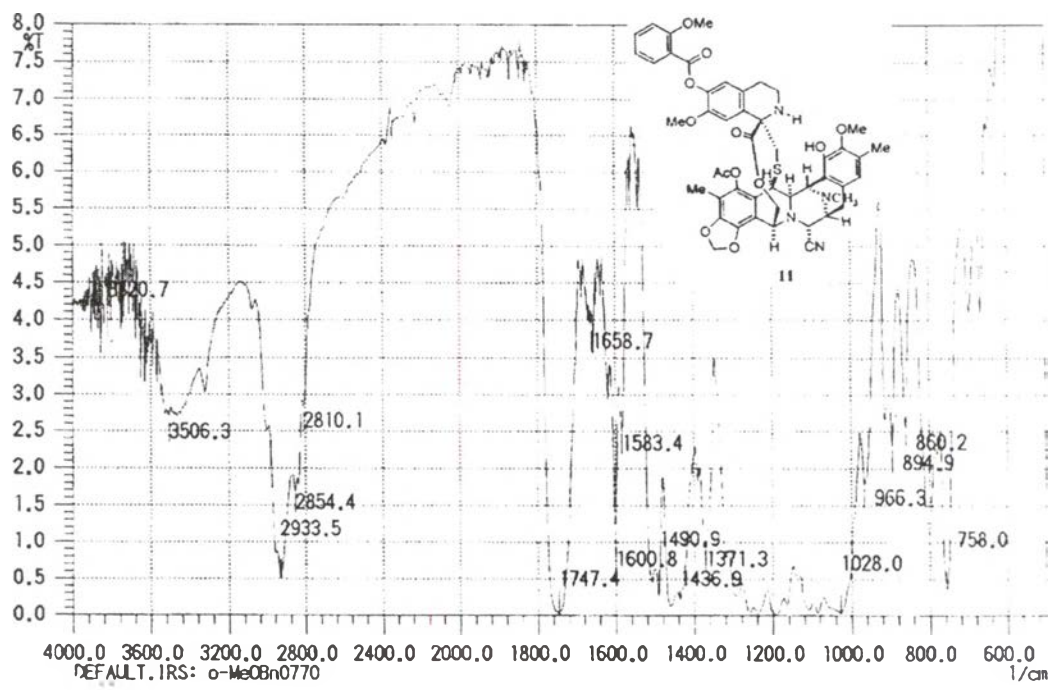


Figure 70. The IR spectrum of Ecteinascidin 770 6'-*O*-2"-methoxybenzoate (**29**)

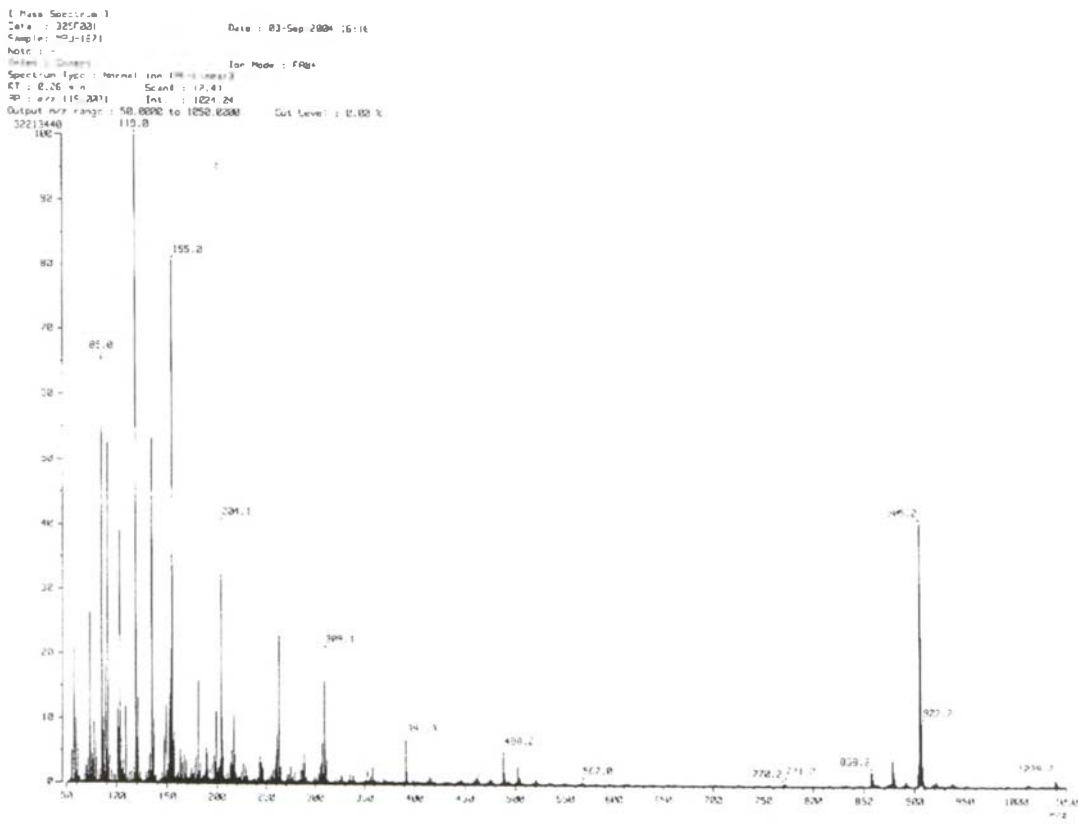


Figure 71. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-2"-methoxybenzoate (**29**)

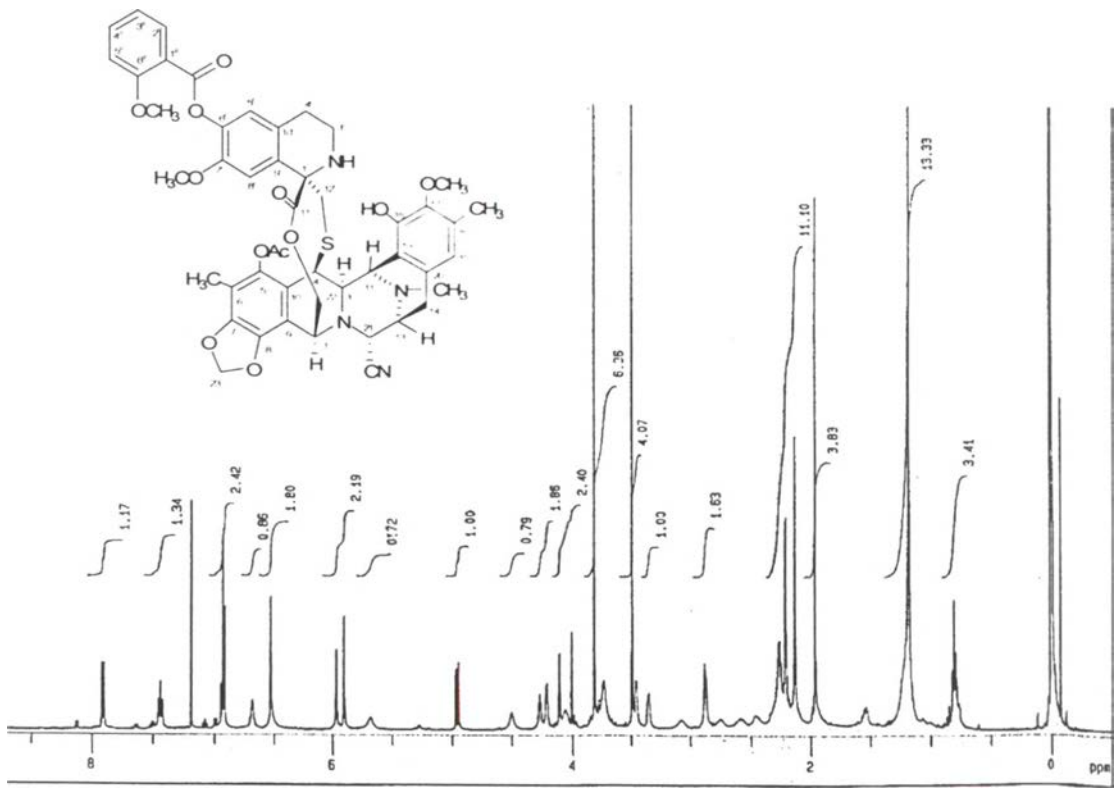


Figure 72. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-2"-methoxybenzoate (**29**)

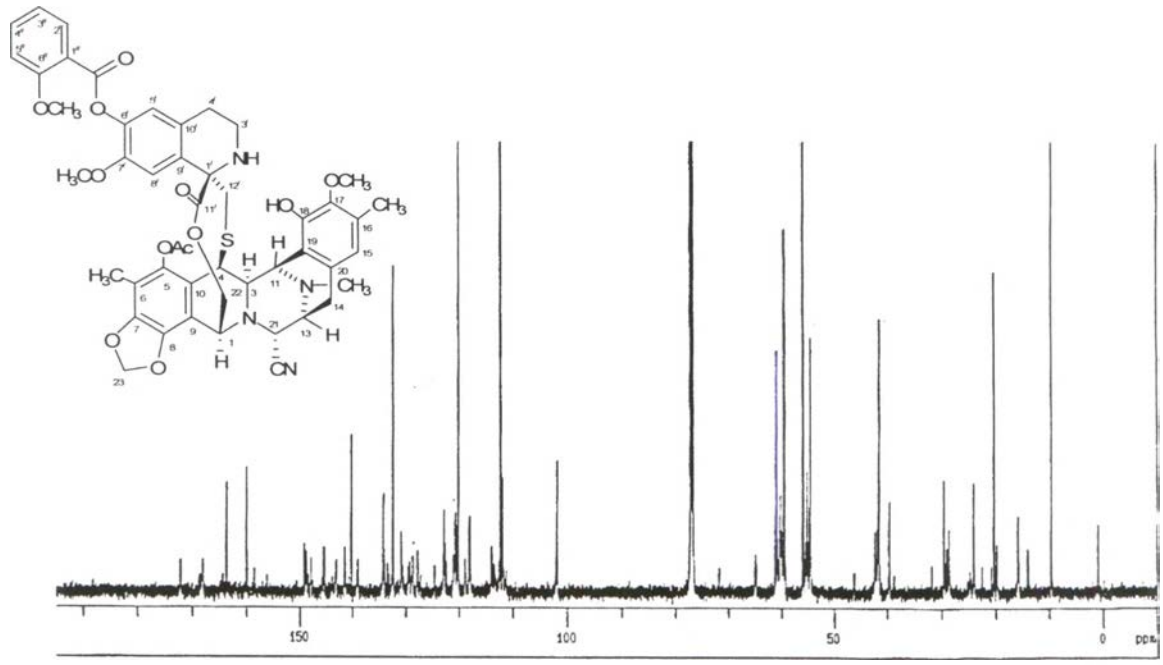


Figure 73. The 125 MHz ^{13}C-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-2"-methoxybenzoate (**29**)

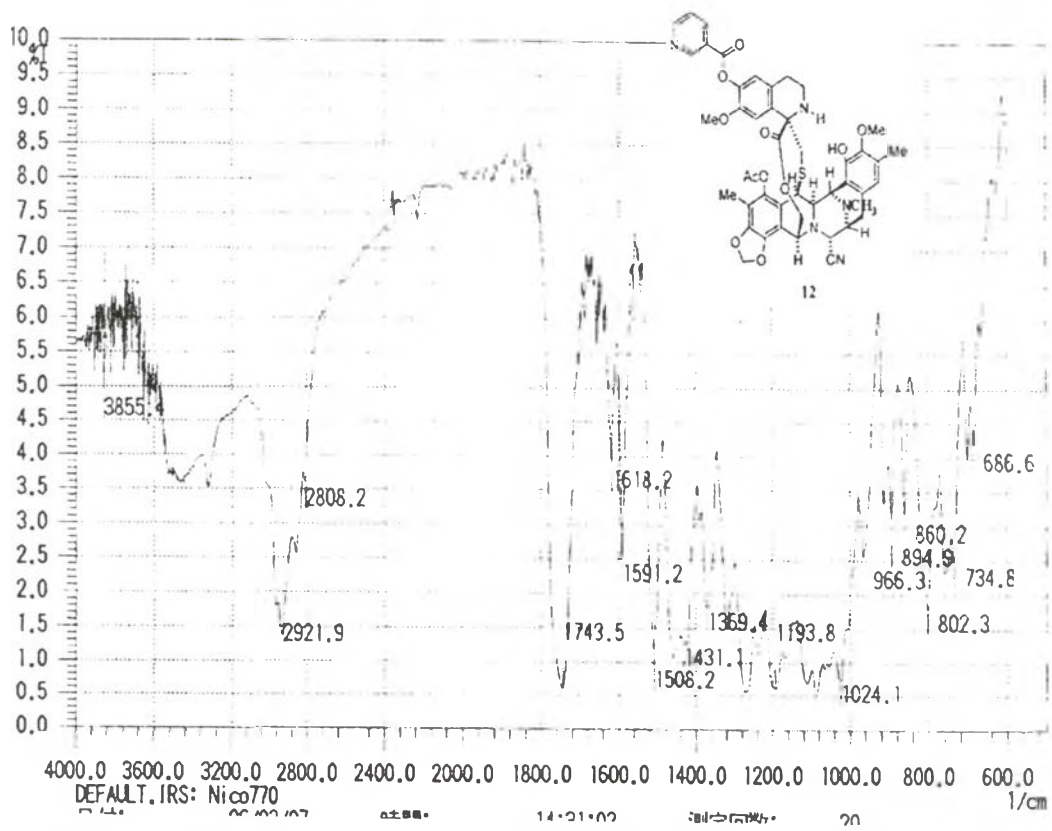


Figure 74. The IR spectrum of Ecteinascidin 770 6'-*O*-nicotinate (**30**)

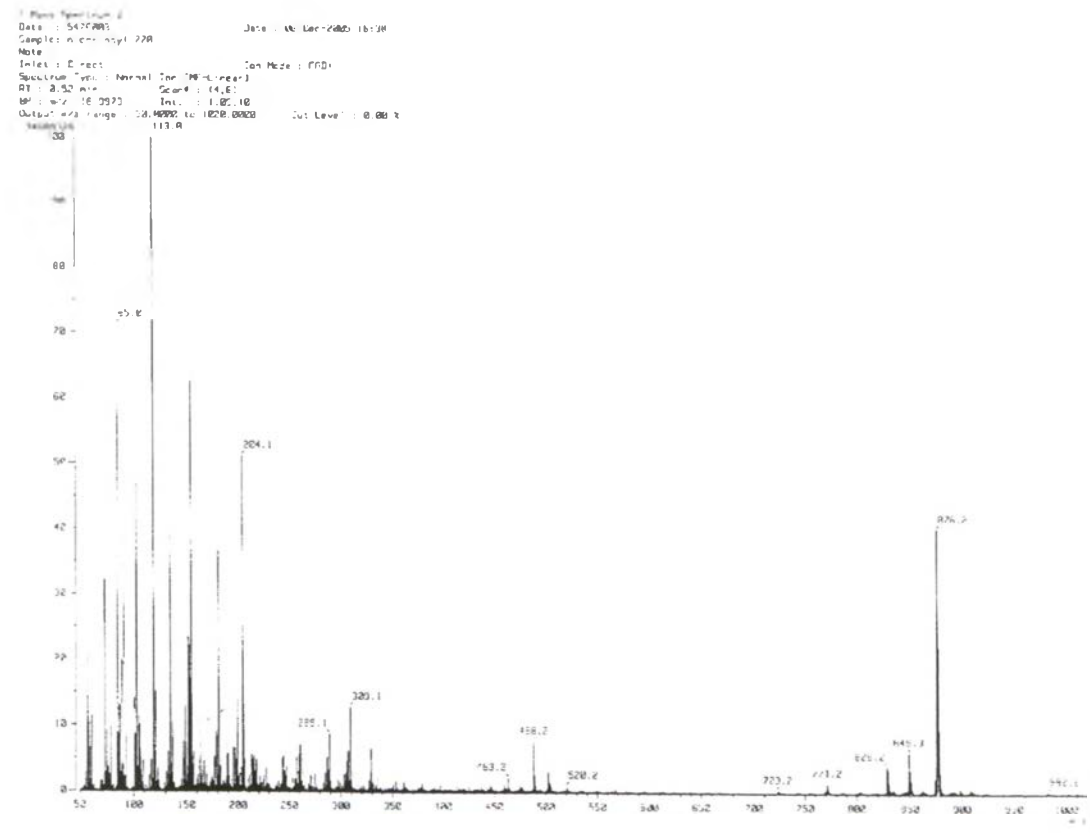


Figure 75. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-nicotinate (**30**)

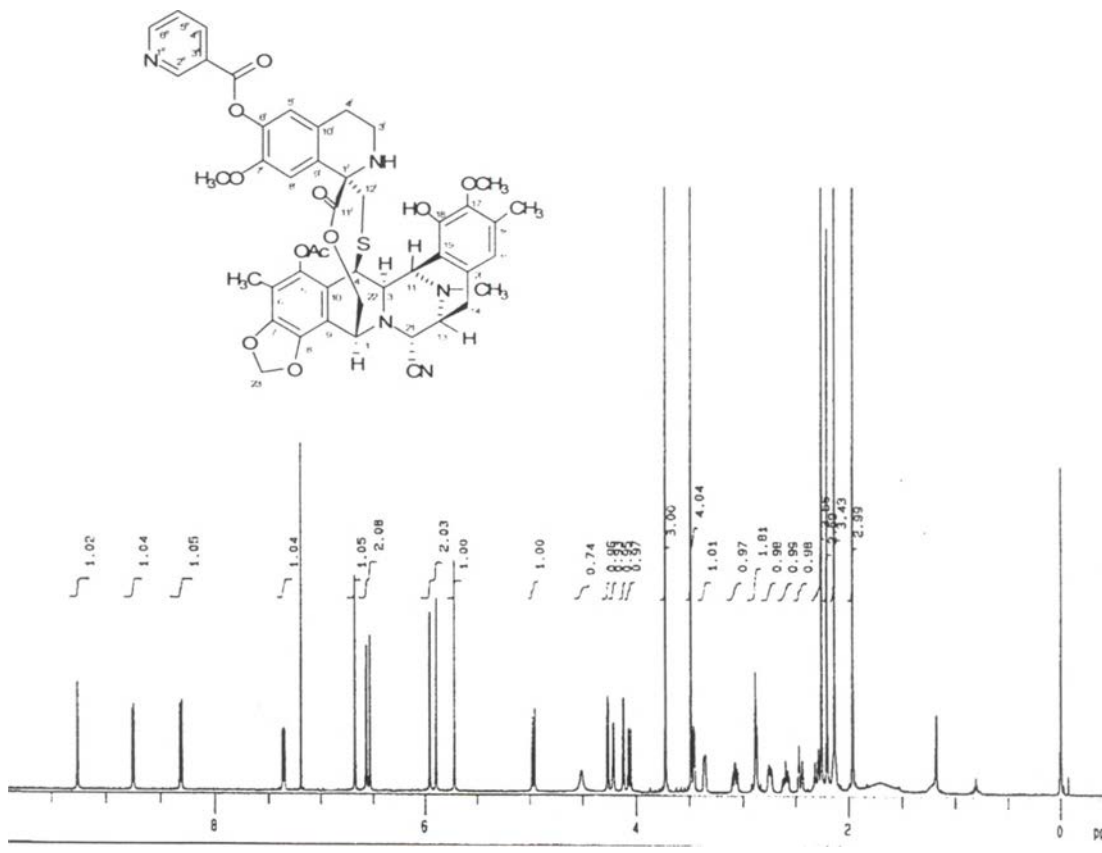


Figure 76. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-nicotinate (**30**)

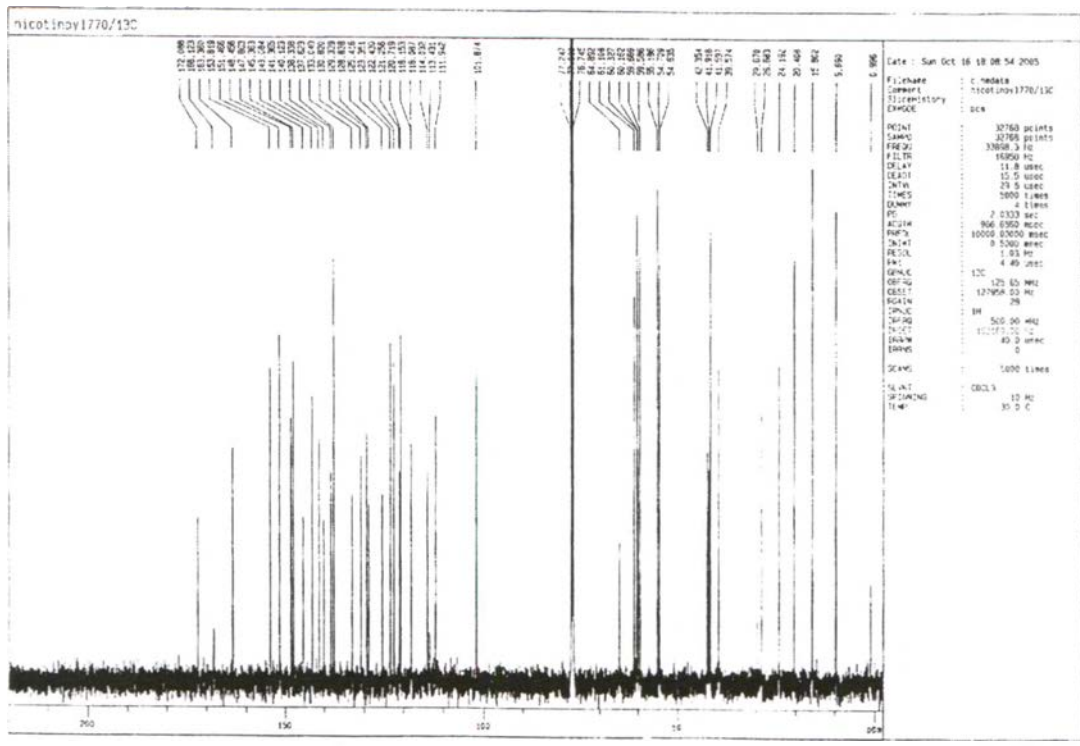


Figure 77. The 125 MHz ^{13}C-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-nicotinate (**30**)

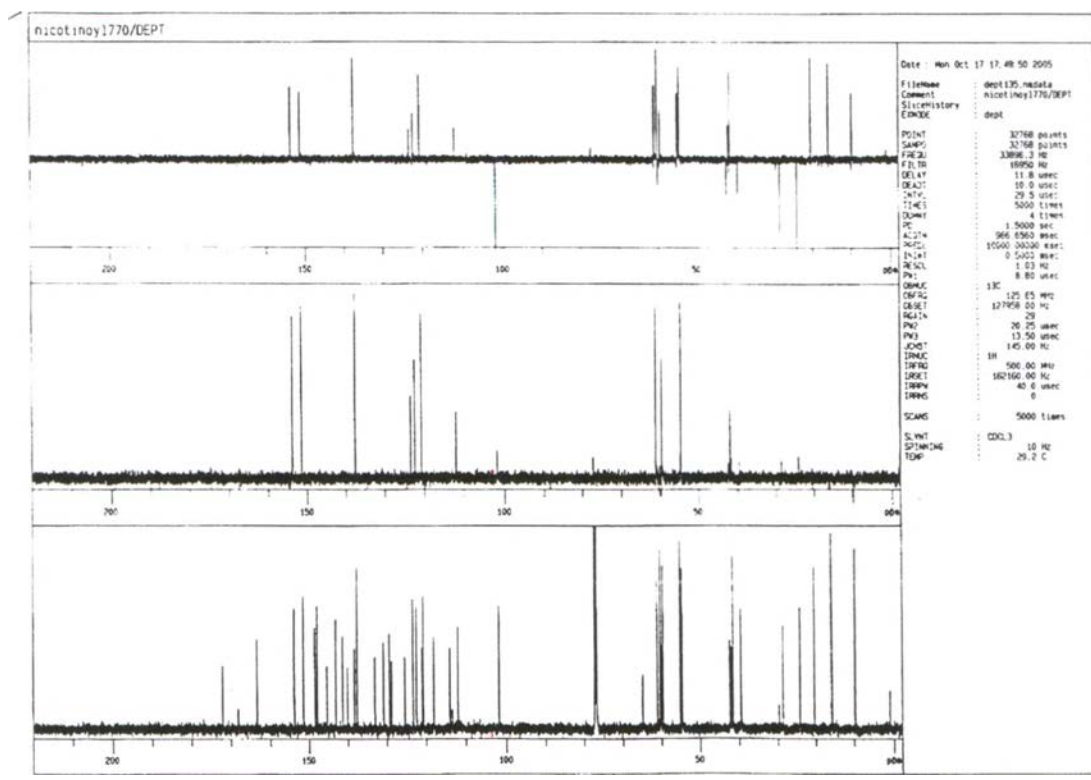


Figure 78. The 500 MHz ^{13}C-NMR and DEPTspectra (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-nicotinate (**30**)

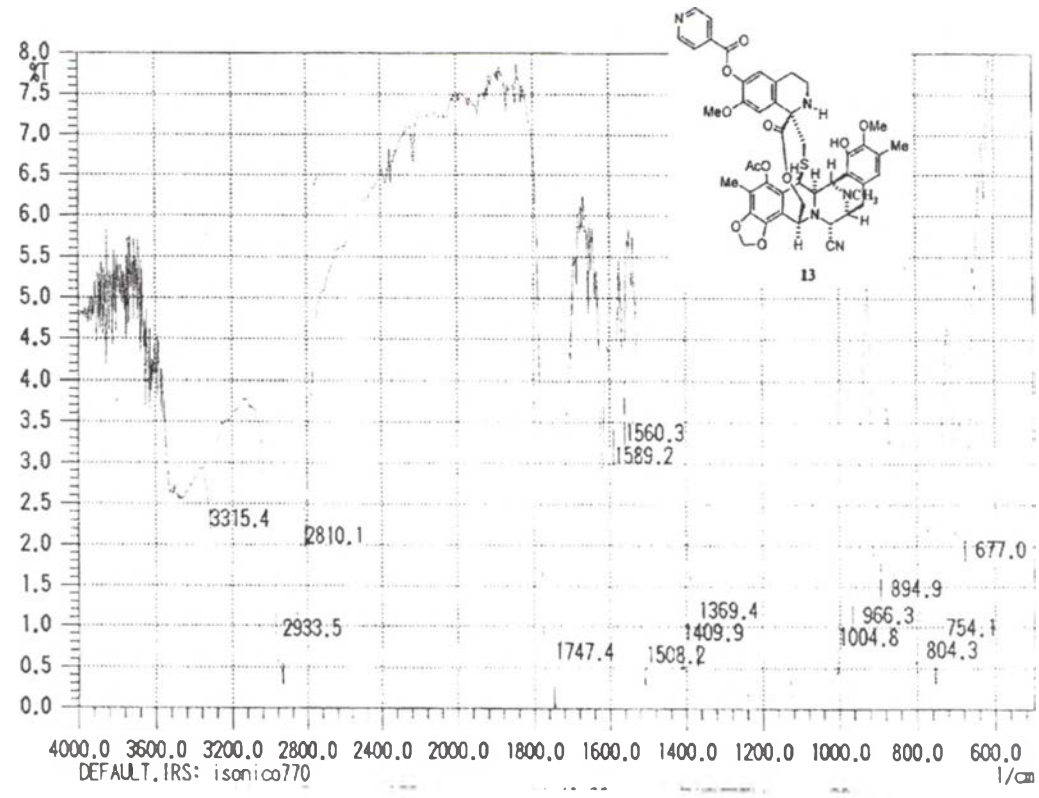


Figure 79. The IR spectrum of Ecteinascidin 770 6'-*O*-isonicotinate (**31**)

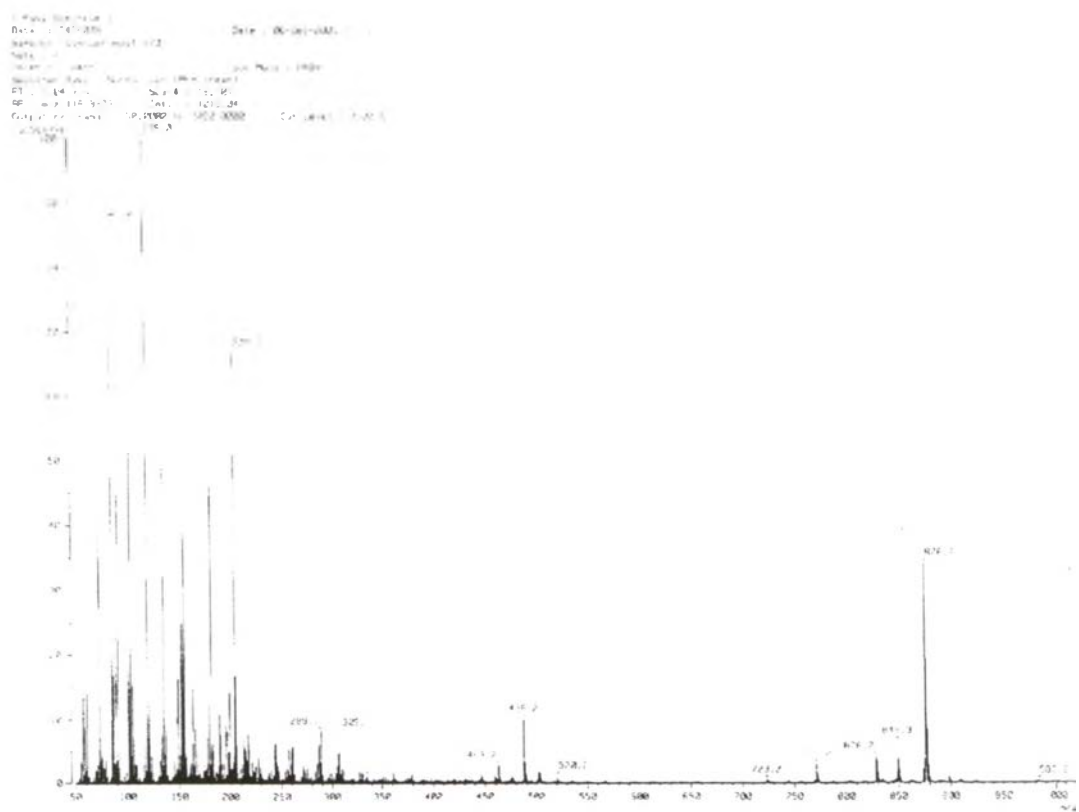


Figure 80. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-isonicotinate (**31**)

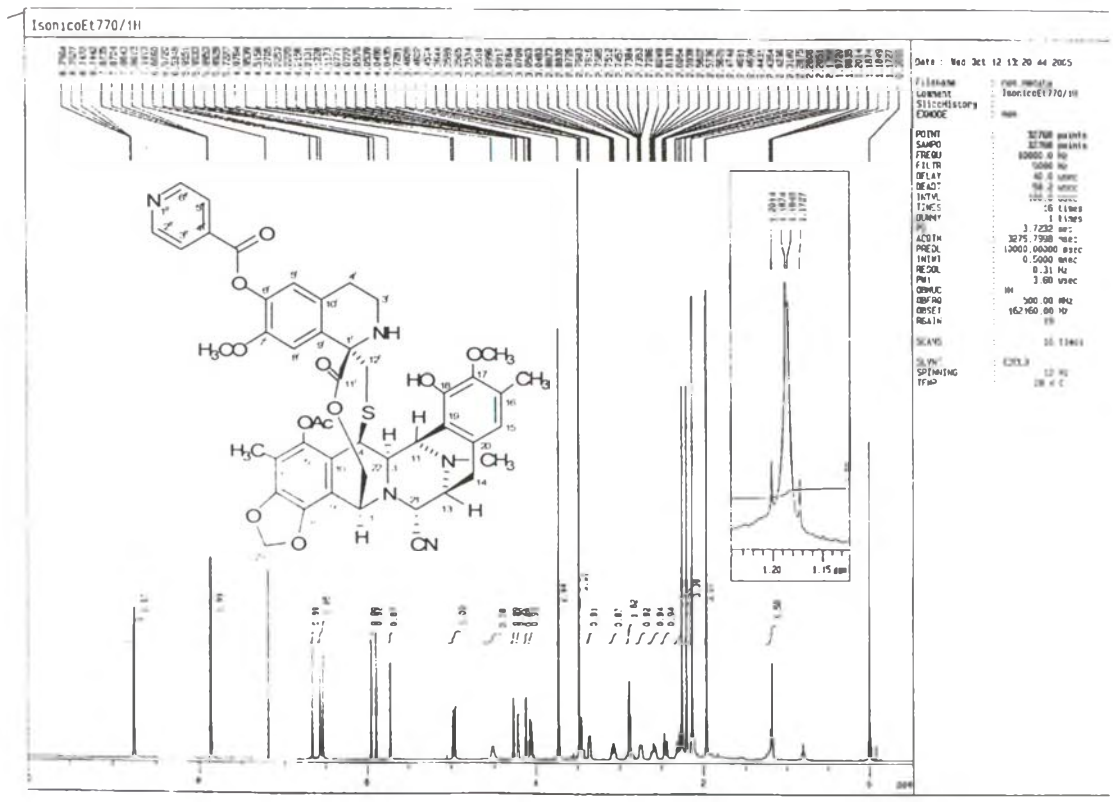


Figure 81. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-isonicotinate (**31**)

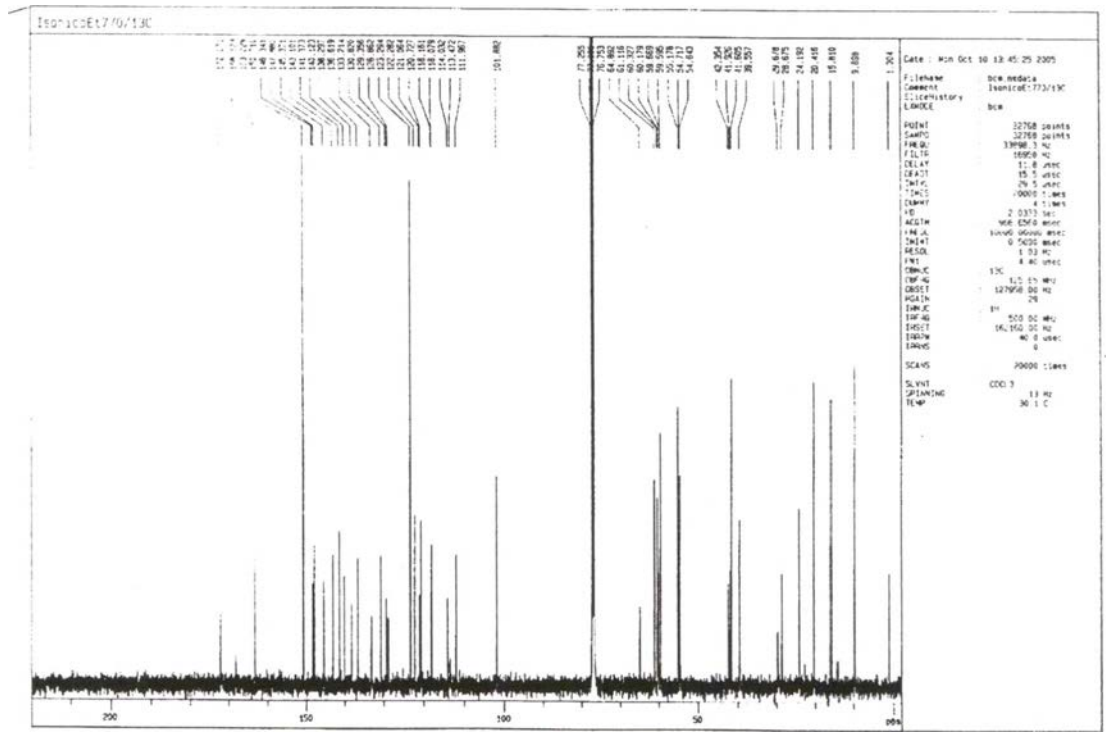


Figure 82. The 125 MHz ^{13}C-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-isonicotinate (**31**)

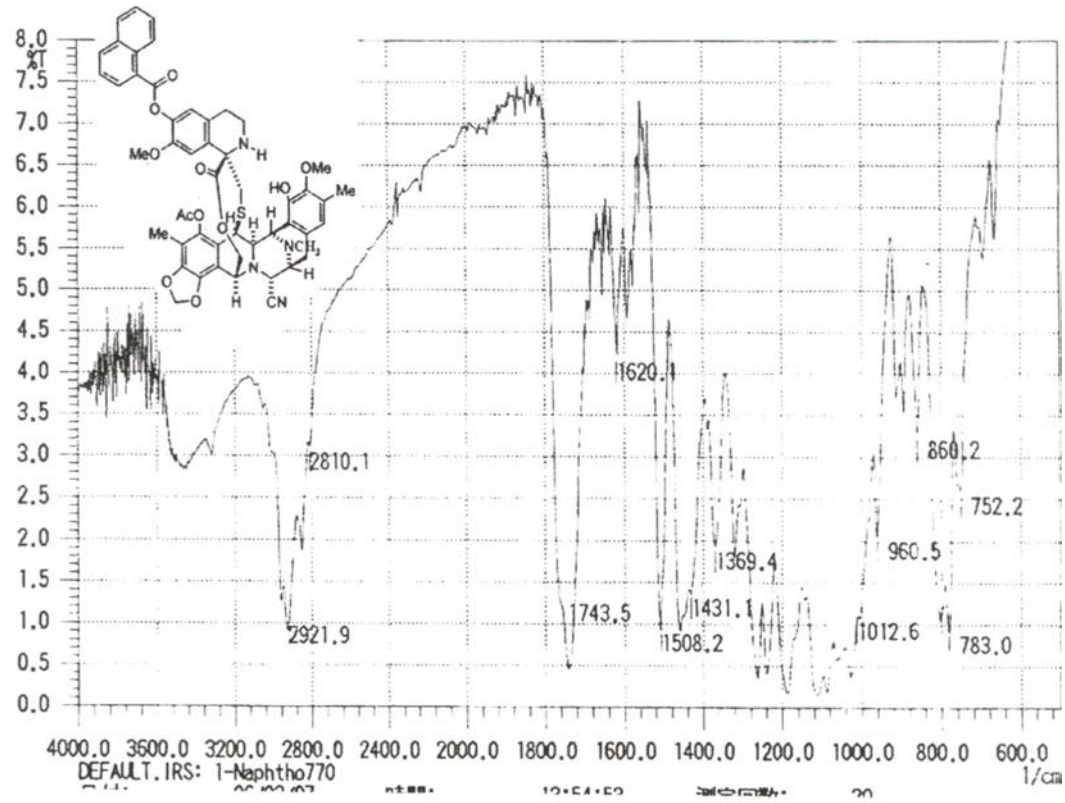


Figure 83. The IR spectrum of Ecteinascidin 770 6'-*O*-1"-naphthoate (**32**)

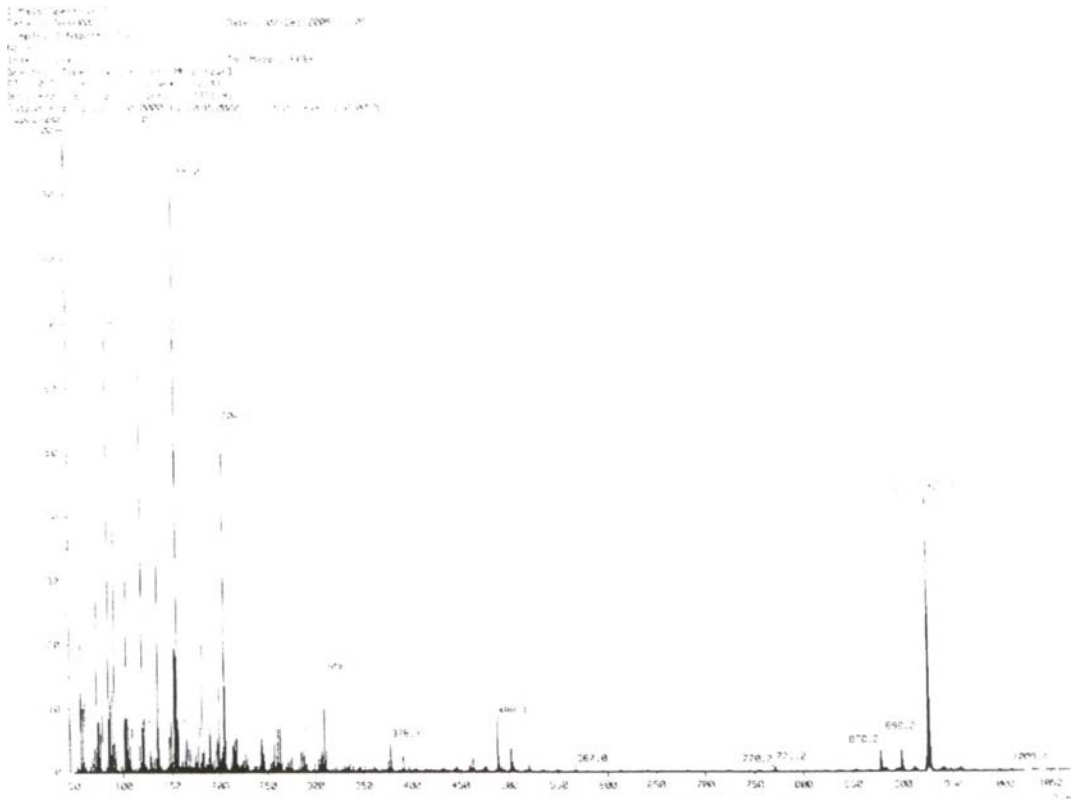


Figure 84. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-1"-naphthoate (**32**)

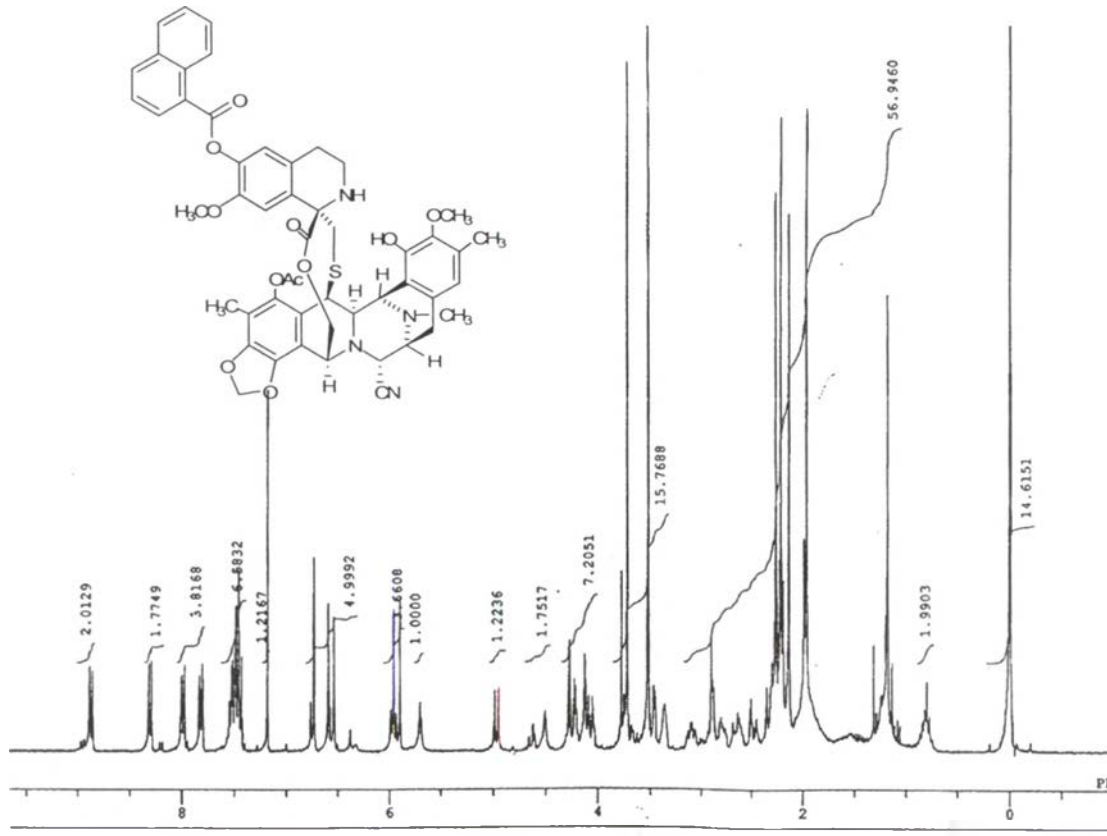


Figure 85. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-1"-naphthoate (**32**)

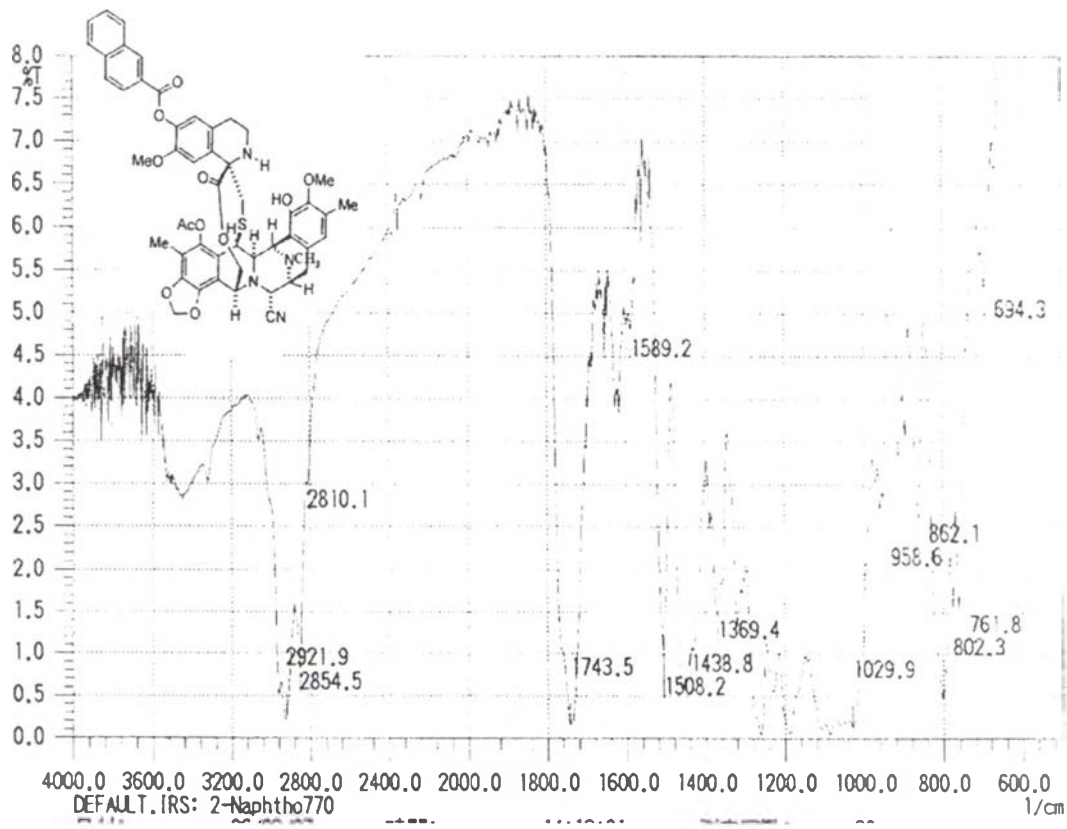


Figure 86. The IR spectrum of Ecteinascidin 770 6'-*O*-2"-naphthoate (**33**)

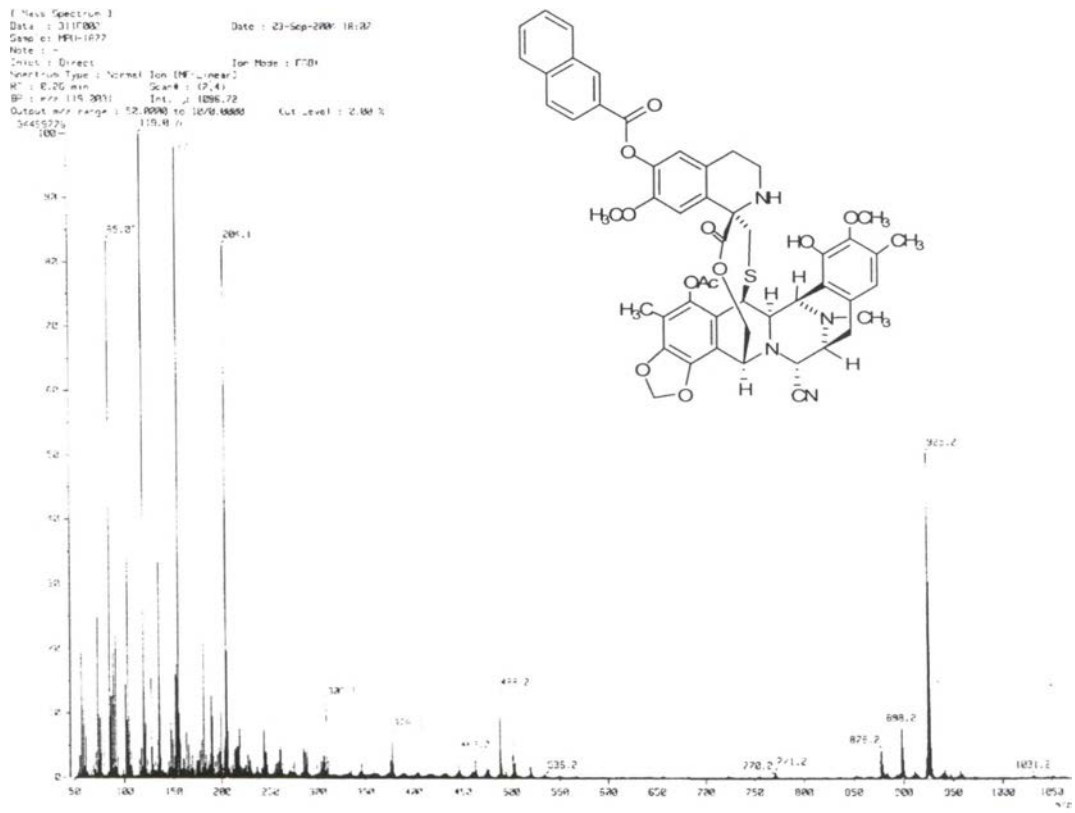


Figure 87. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-2"-naphthoate (**33**)

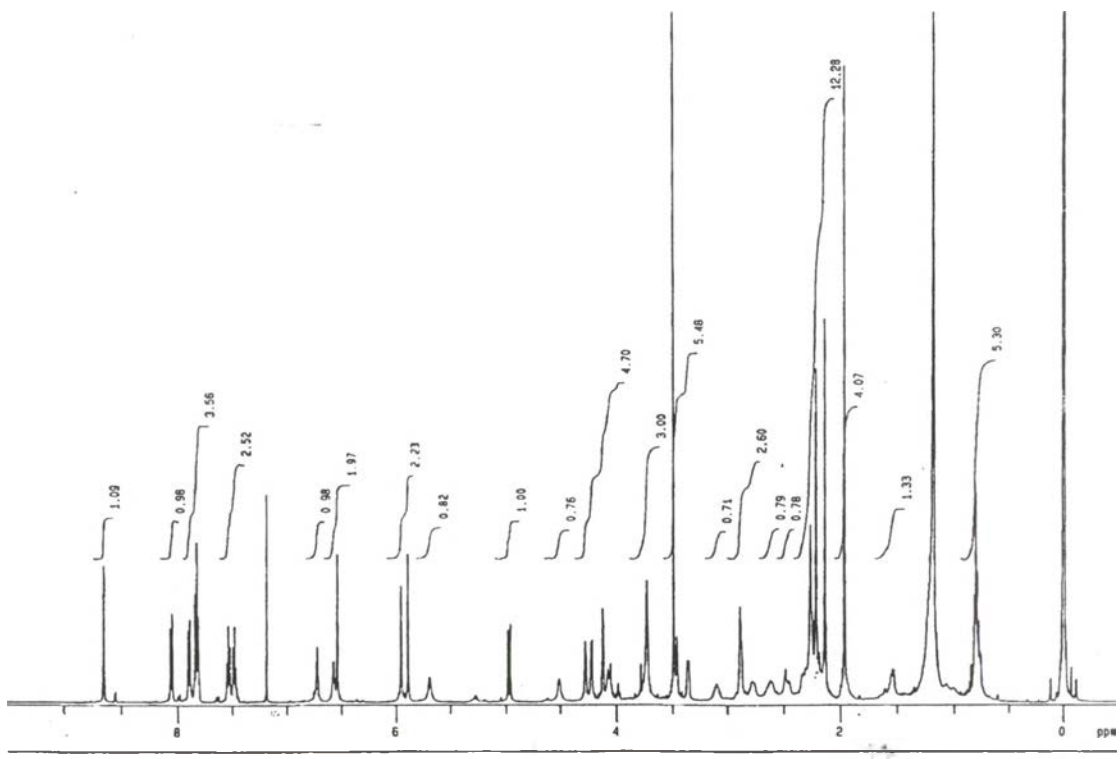


Figure 88. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-2"-naphthoate (**33**)

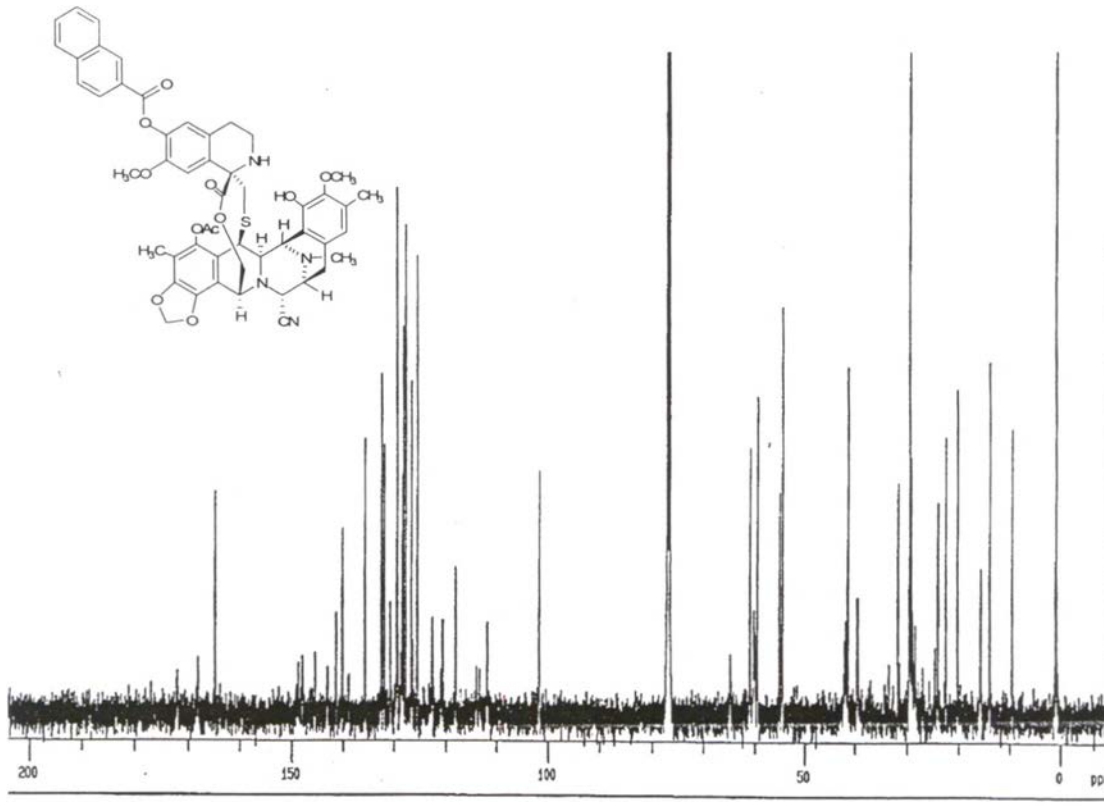


Figure 89. The 125 MHz ^{13}C-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-2"-naphthoate (**33**)

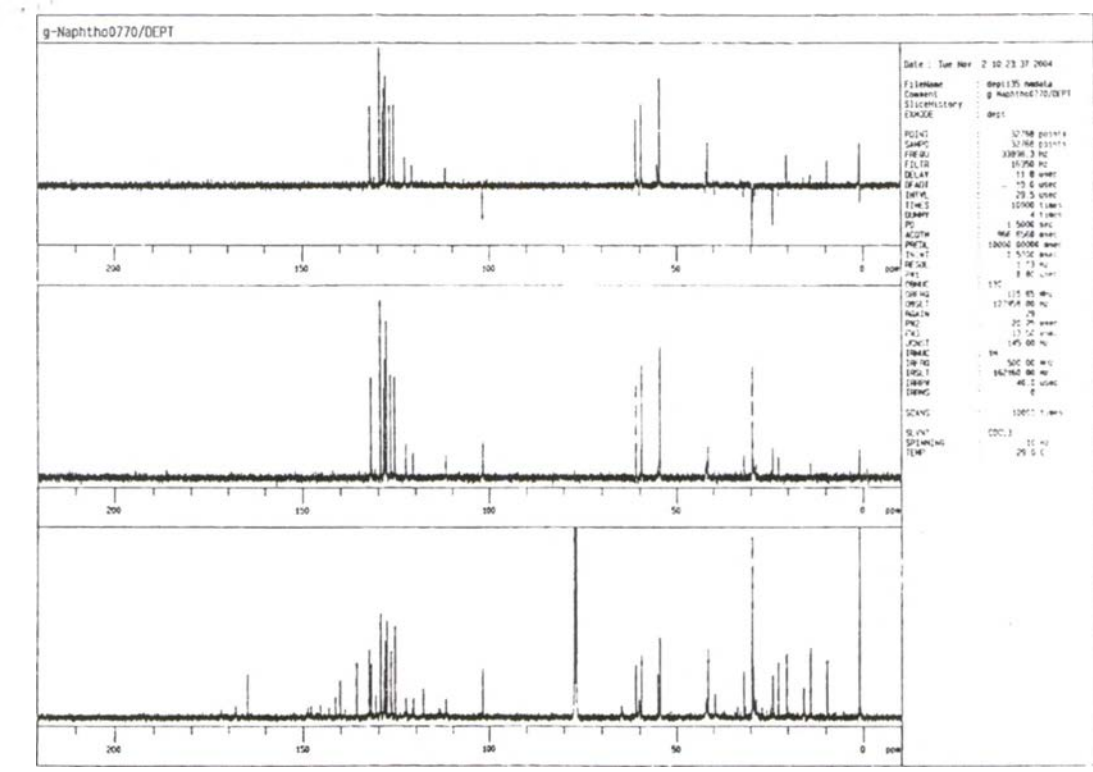


Figure 90. The 500 MHz ^{13}C-NMR and DEPTspectra (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-2"-naphthoate (**33**)

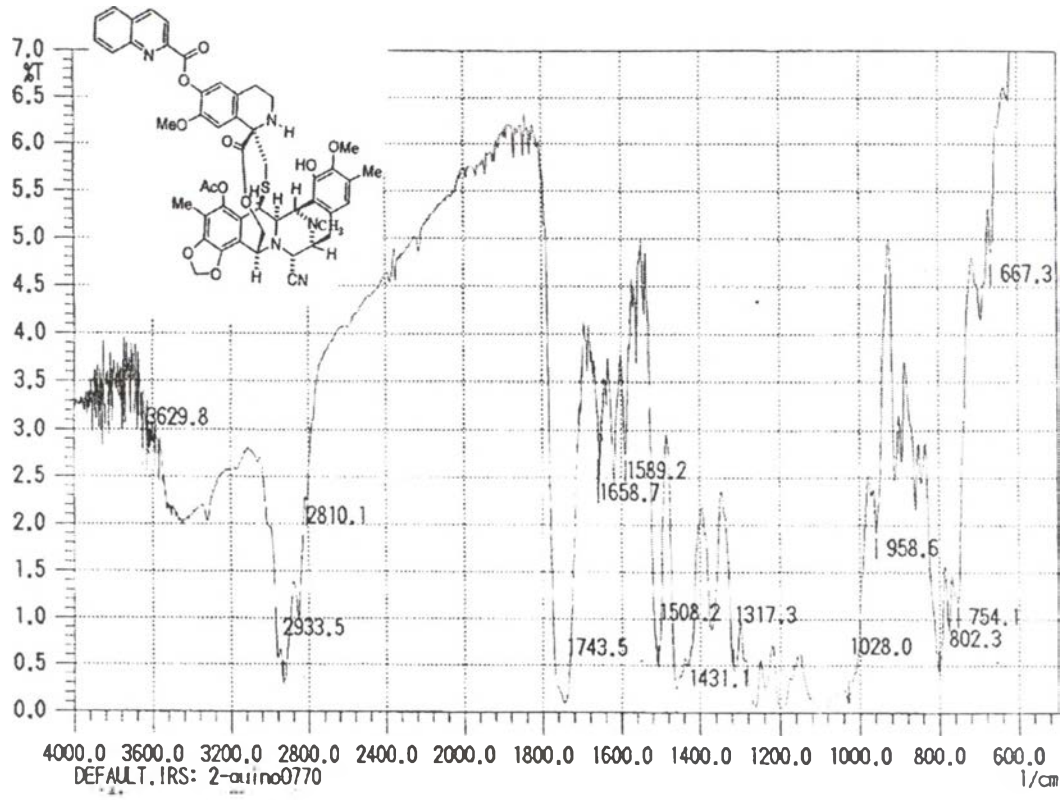


Figure 91. The IR spectrum of Ecteinascidin 770 6'-*O*-2"-quinolinecarboxylate (**34**)

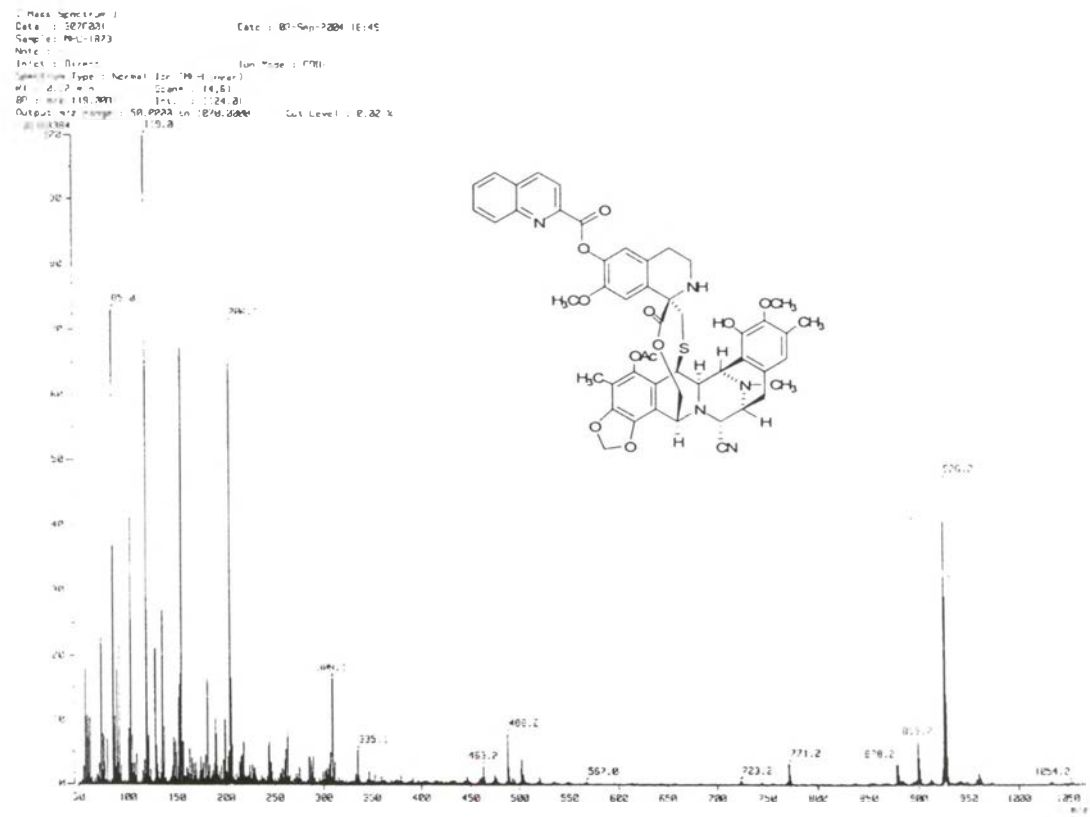


Figure 92. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-2"-quinoline-carboxylate (**34**)

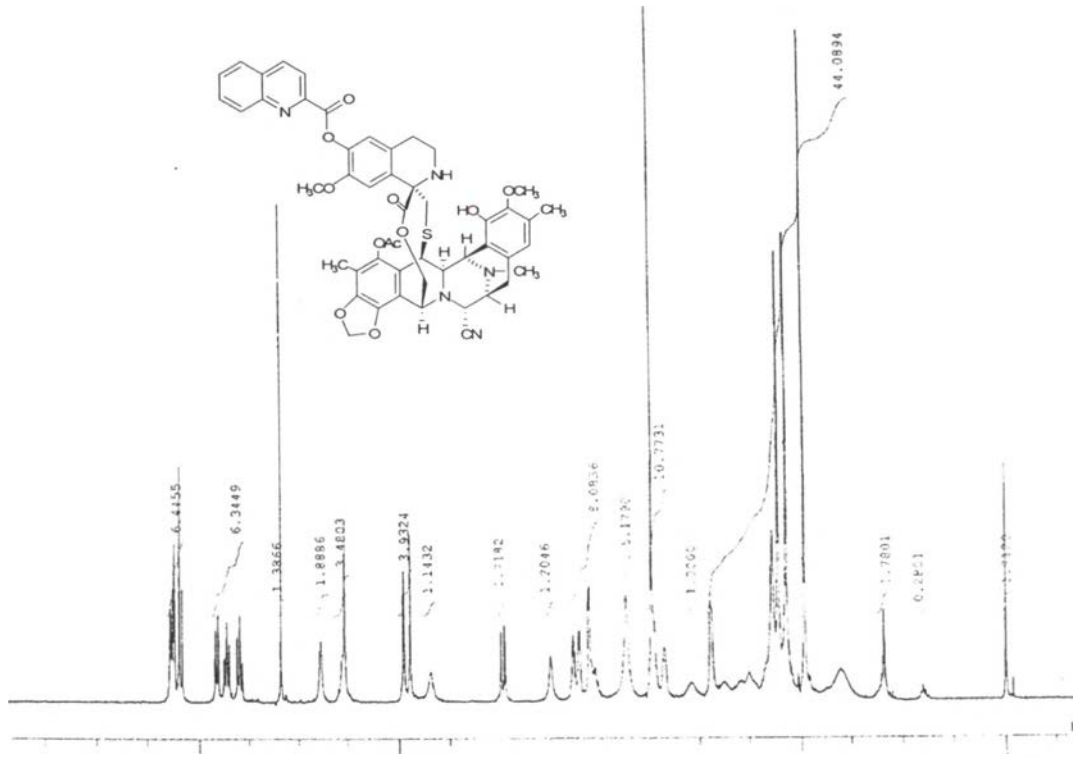


Figure 93. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-2"-quinolinecarboxylate (**34**)

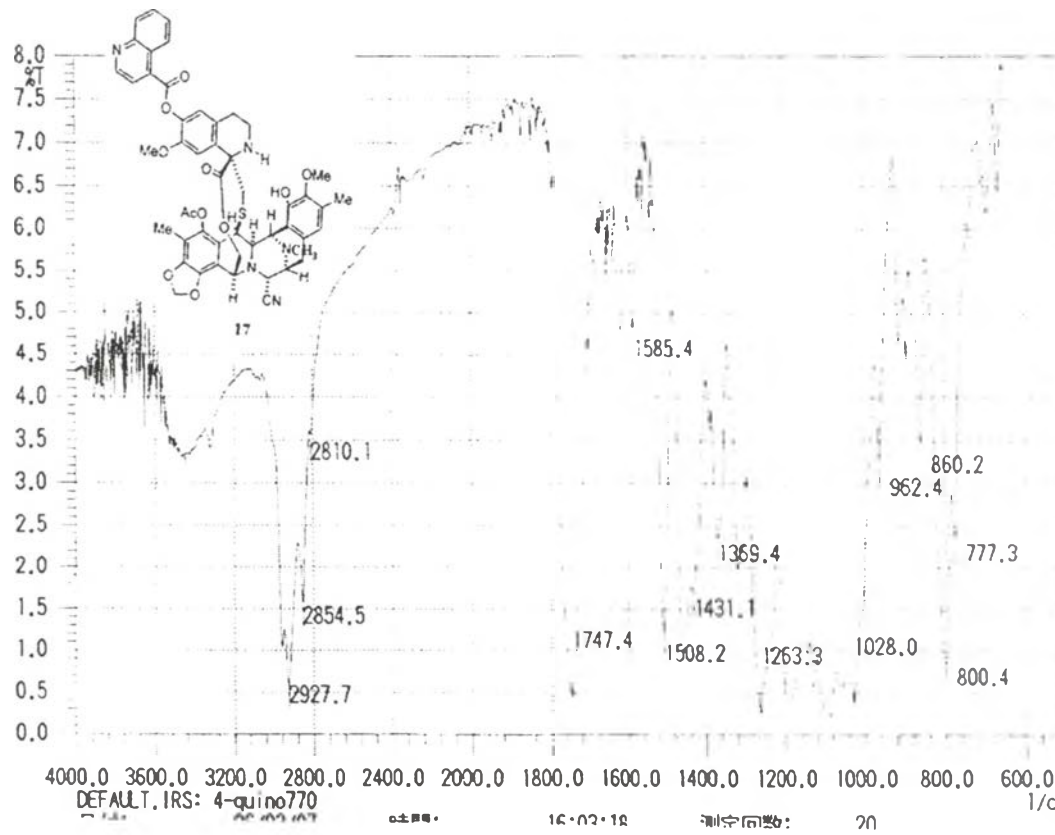


Figure 94. The IR spectrum of Ecteinascidin 770 6'-*O*-4"-quinolinecarboxylate (**35**)

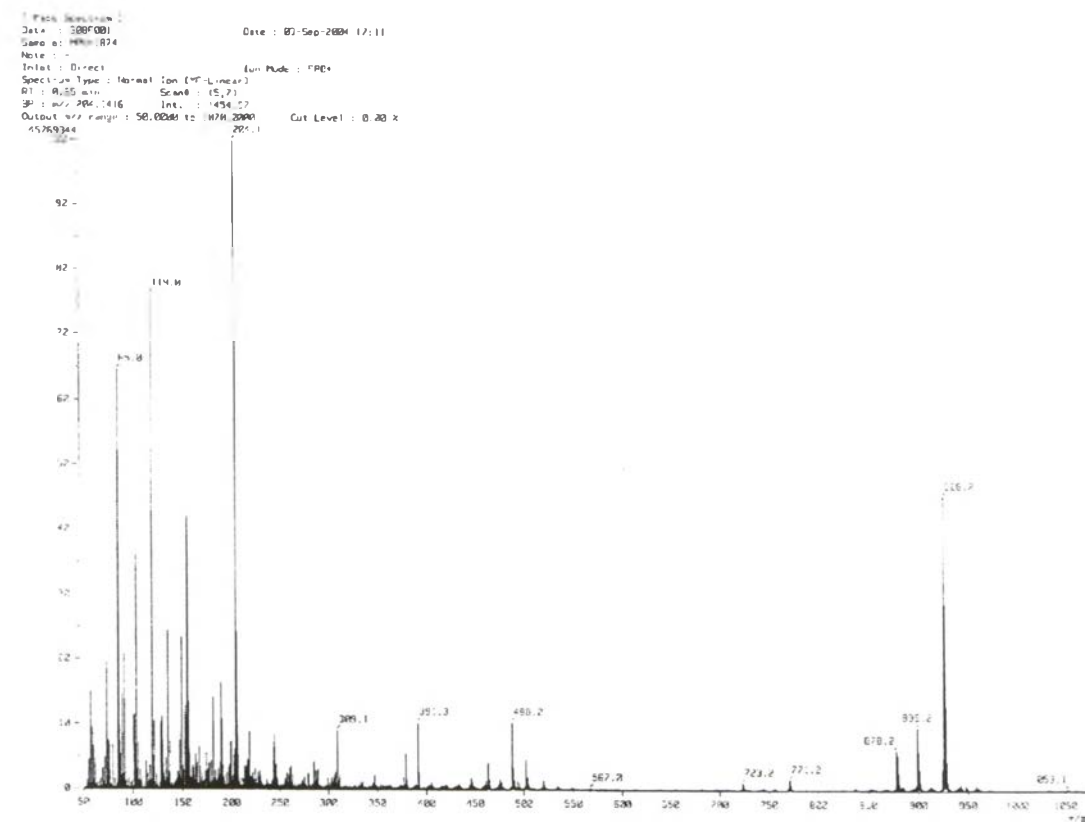


Figure 95. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-4"-quinoline-carboxylate (**35**)

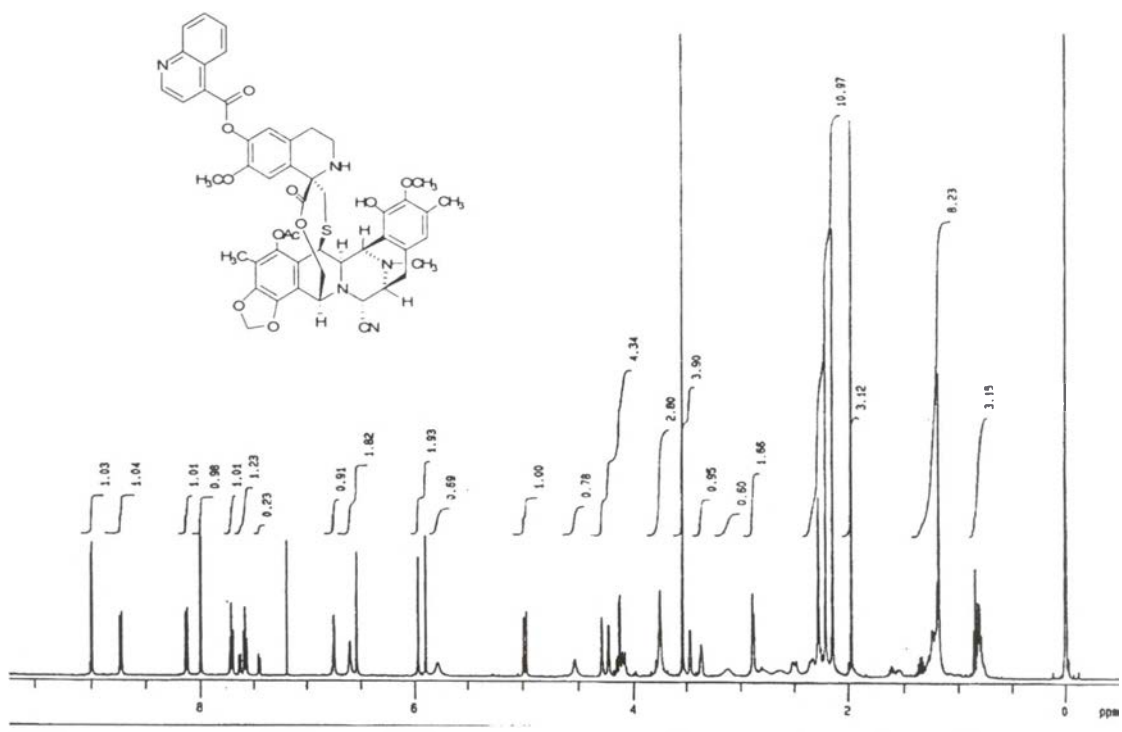


Figure 96. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) Ecteinascidin 770 6'-*O*-4"-quinolinecarboxylate (**35**)

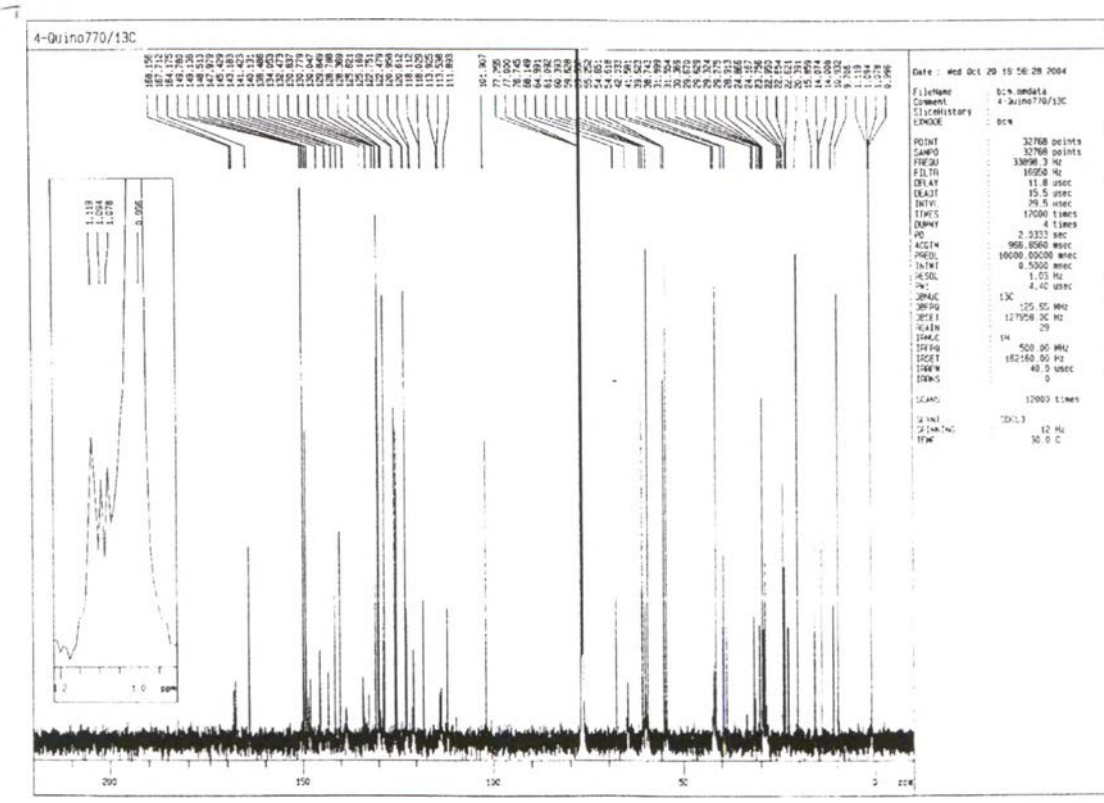


Figure 97. The 125 MHz ^{13}C-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-quinolinecarboxylate (**35**)

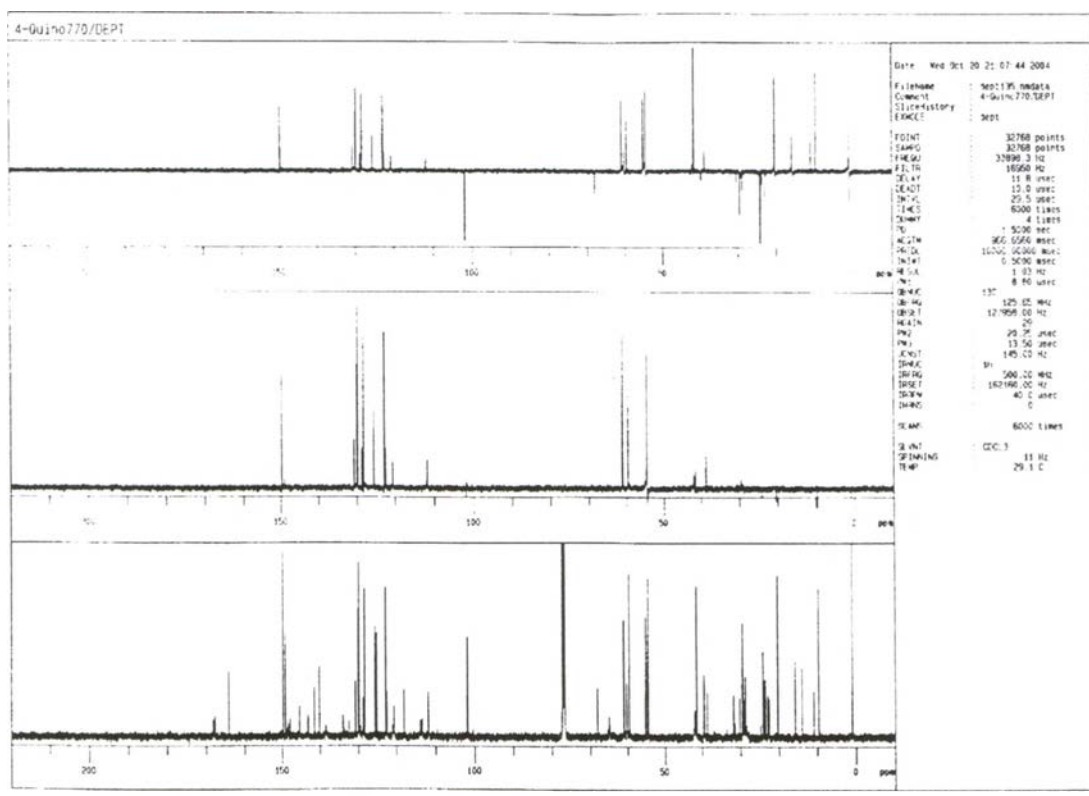


Figure 98. The 500 MHz ^{13}C-NMR and DEPTspectra (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-4"-quinolinecarboxylate (**35**)

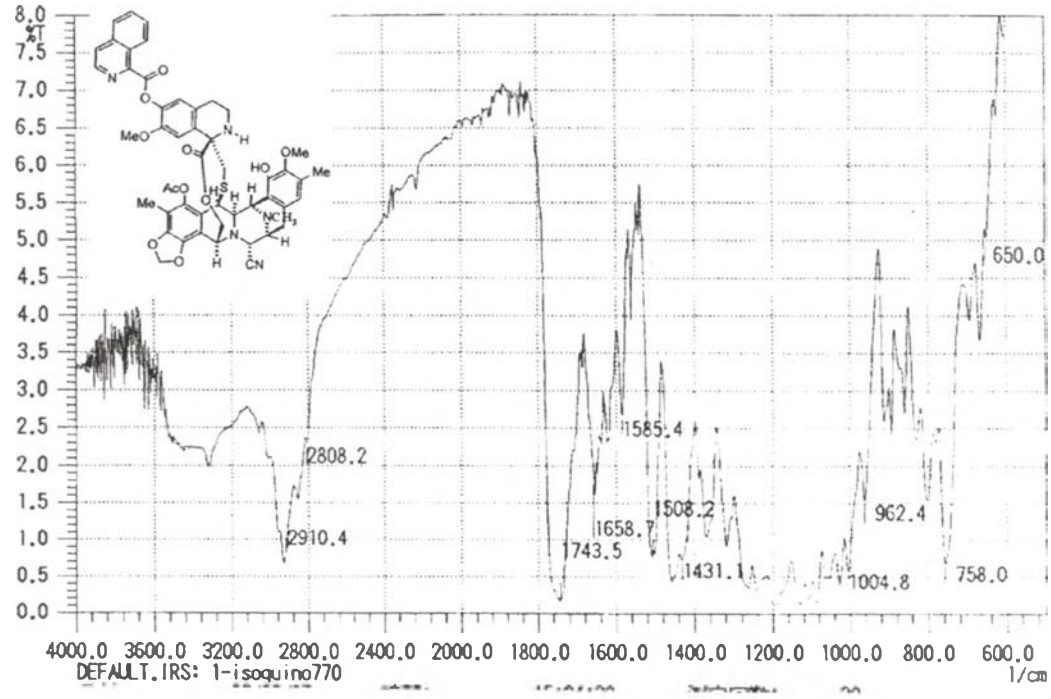


Figure 99. The IR spectrum of Ecteinascidin 770 6'-*O*-1"- isoquinolinecarboxylate (**36**)

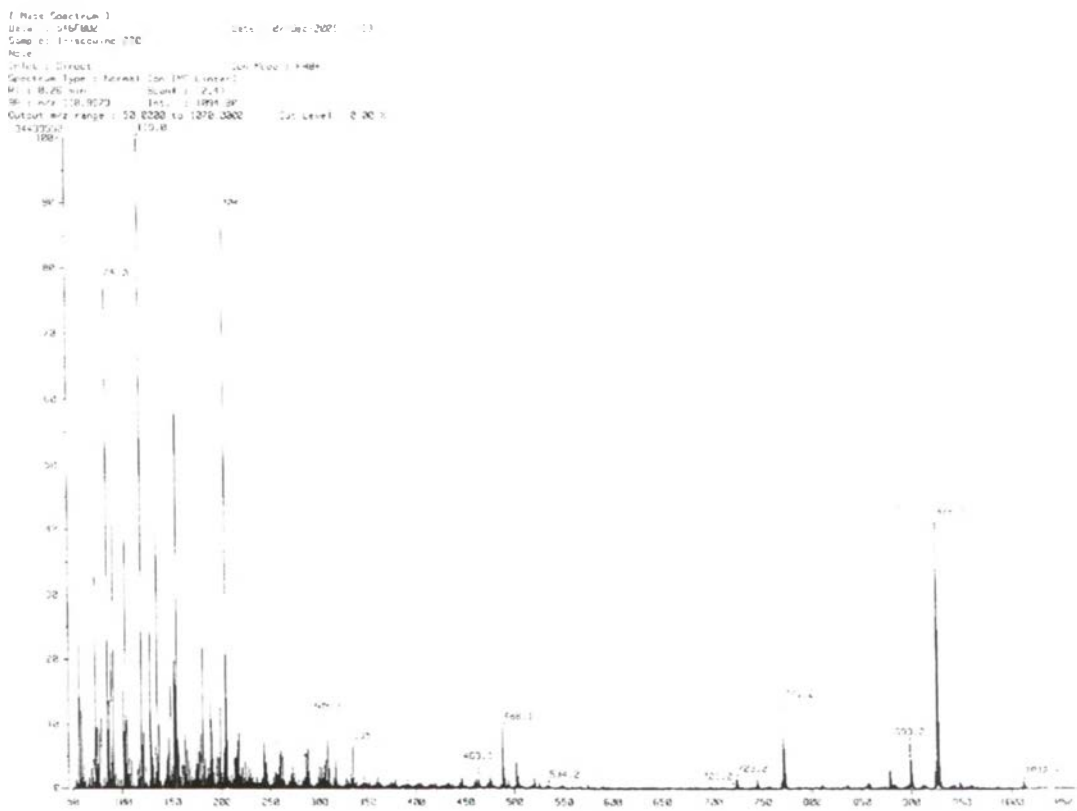


Figure 100. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-1"- isoquinoline-carboxylate (**36**)

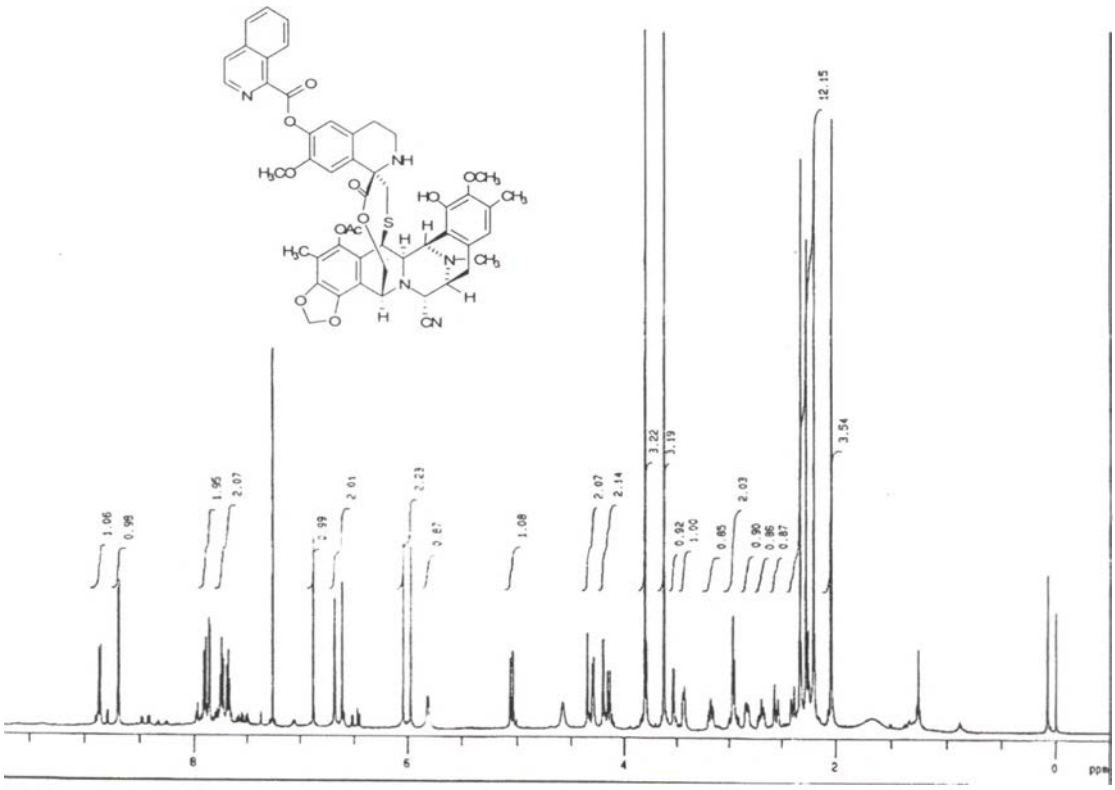


Figure 101. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-1"- isoquinolinecarboxylate (**36**)

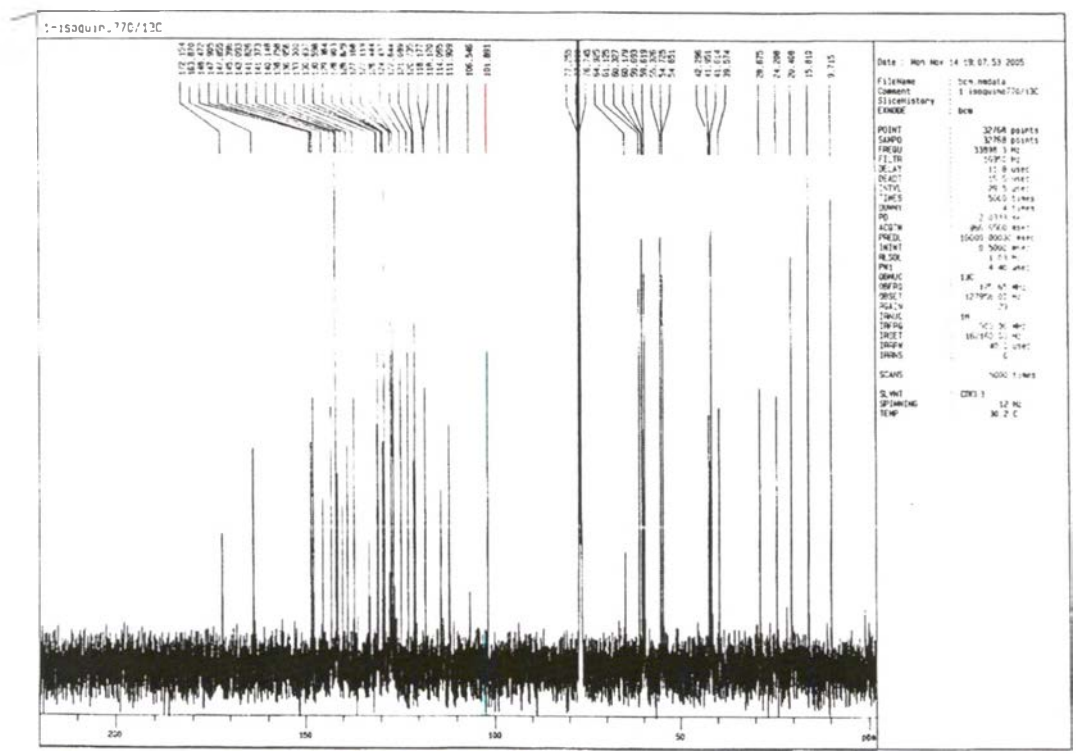


Figure 102. The 125 MHz ^{13}C-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-1"- isoquinolinecarboxylate (**36**)

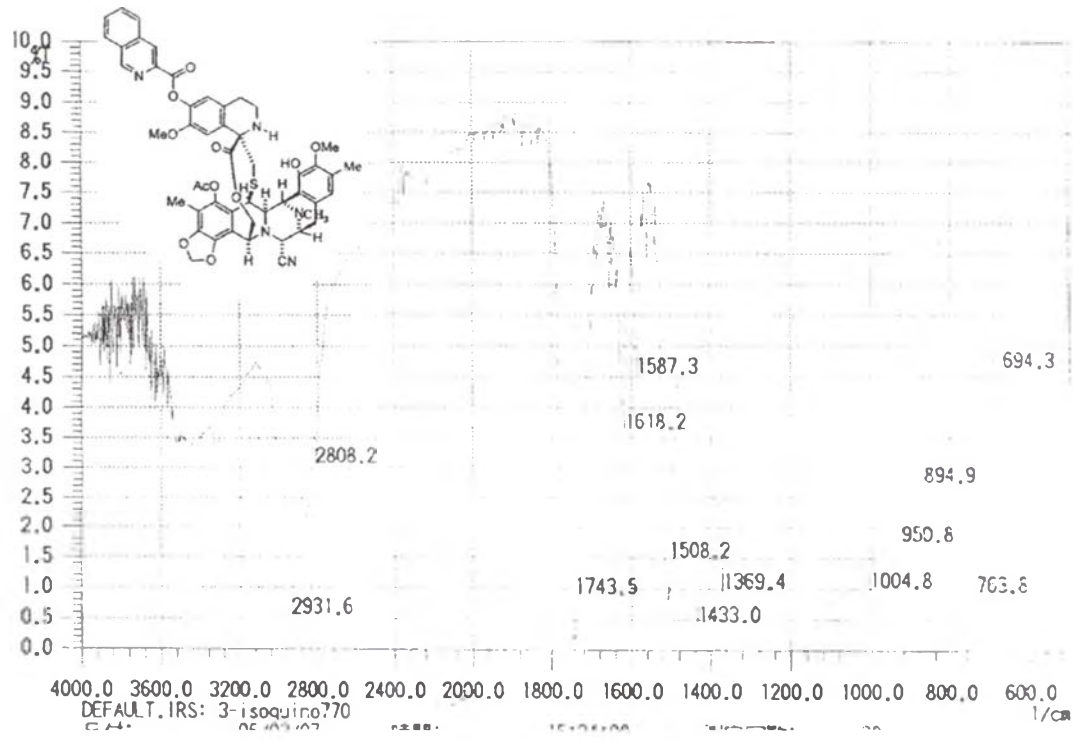


Figure 103. The IR spectrum of Ecteinascidin 770 6'-*O*-3"- isoquinolinecarboxylate (**37**)

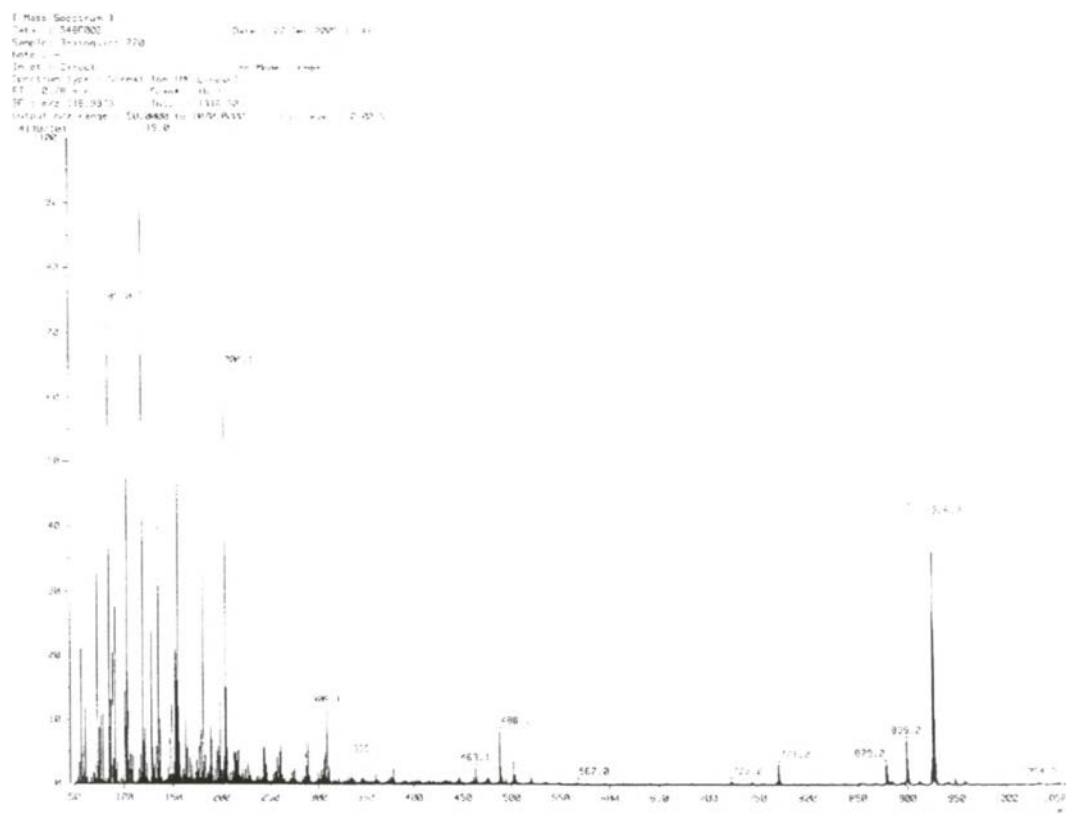


Figure 104. The FAB-mass spectrum of Ecteinascidin 770 6'-*O*-3"- isoquinoline-carboxylate (**37**)

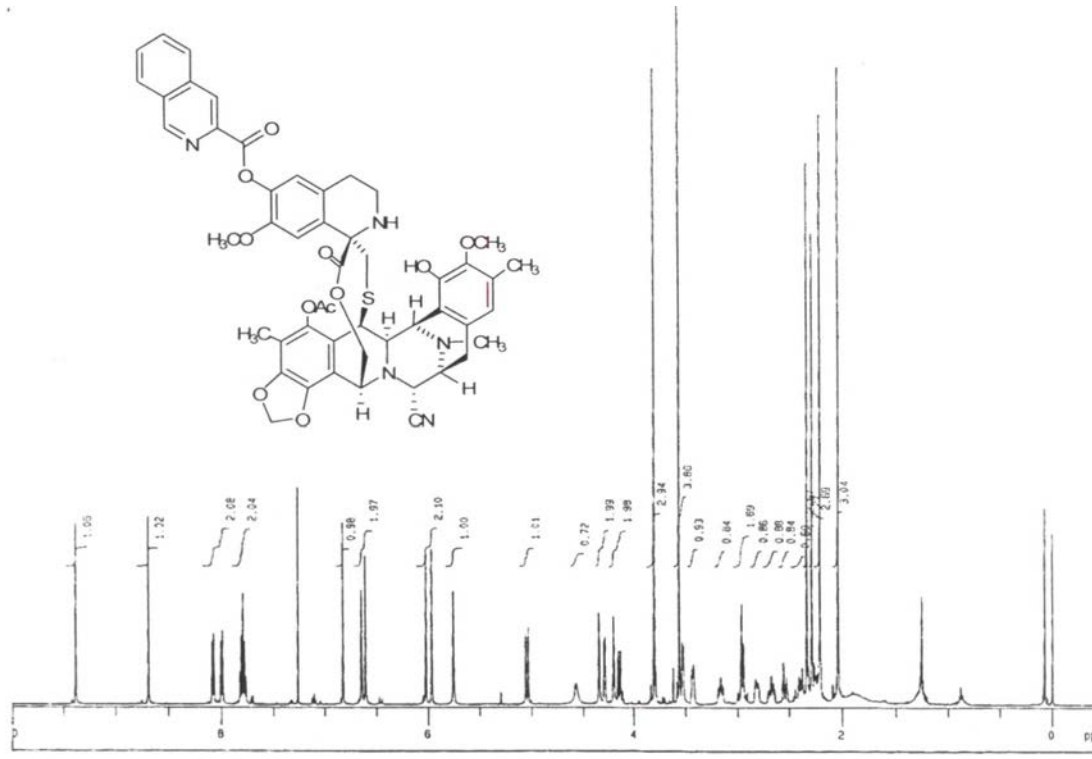


Figure 105. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-3"- isoquinolinecarboxylate (**37**)

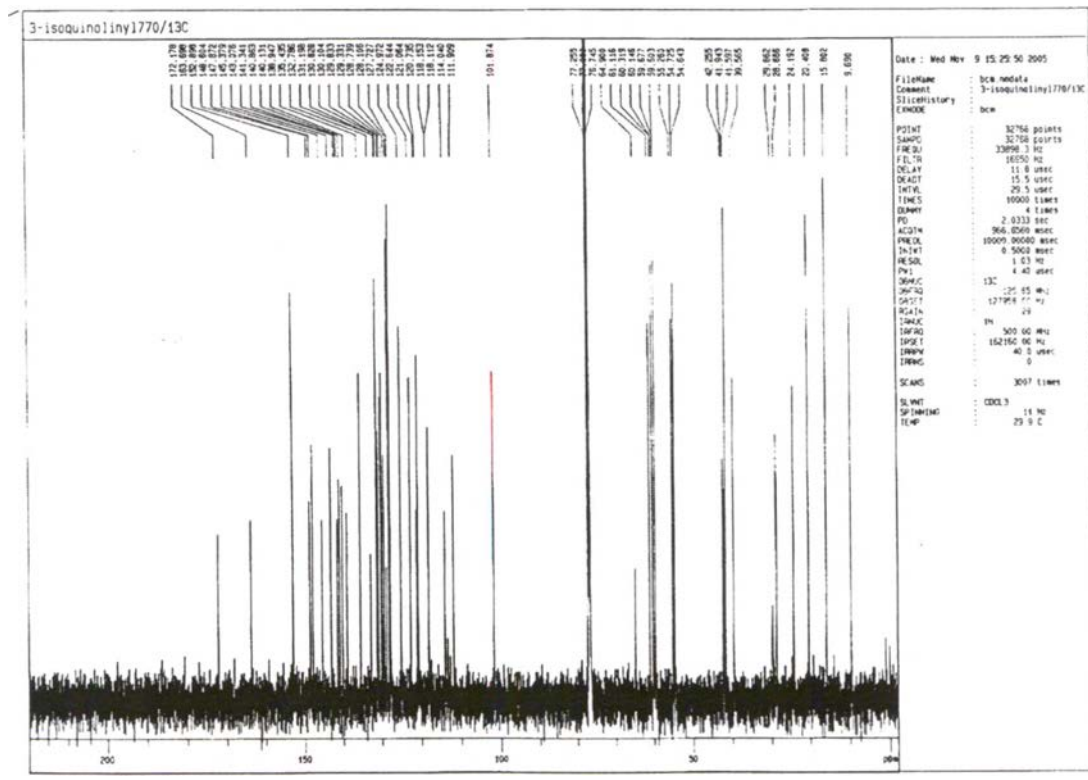


Figure 106. The 125 MHz ^{13}C-NMR spectrum (in $CDCl_3$) of Ecteinascidin 770 6'-*O*-3"- isoquinolinecarboxylate (**37**)

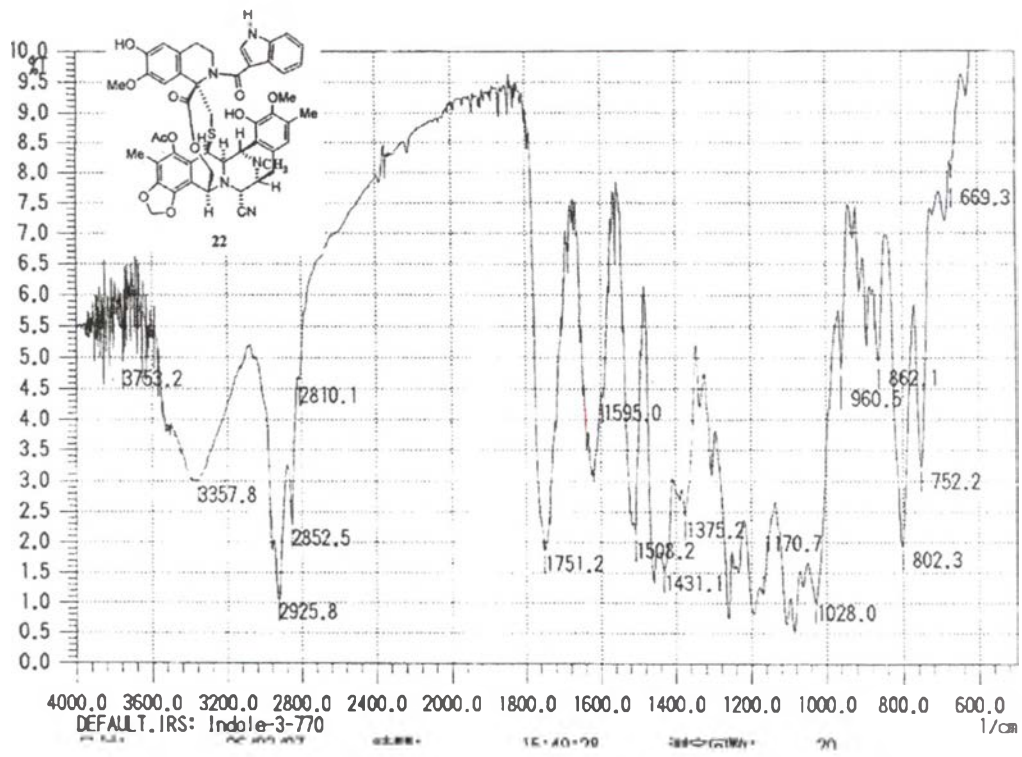


Figure 107. The IR spectrum of *2'-N*-3"-indolecarboxylecteinascidin 770 (**39**)

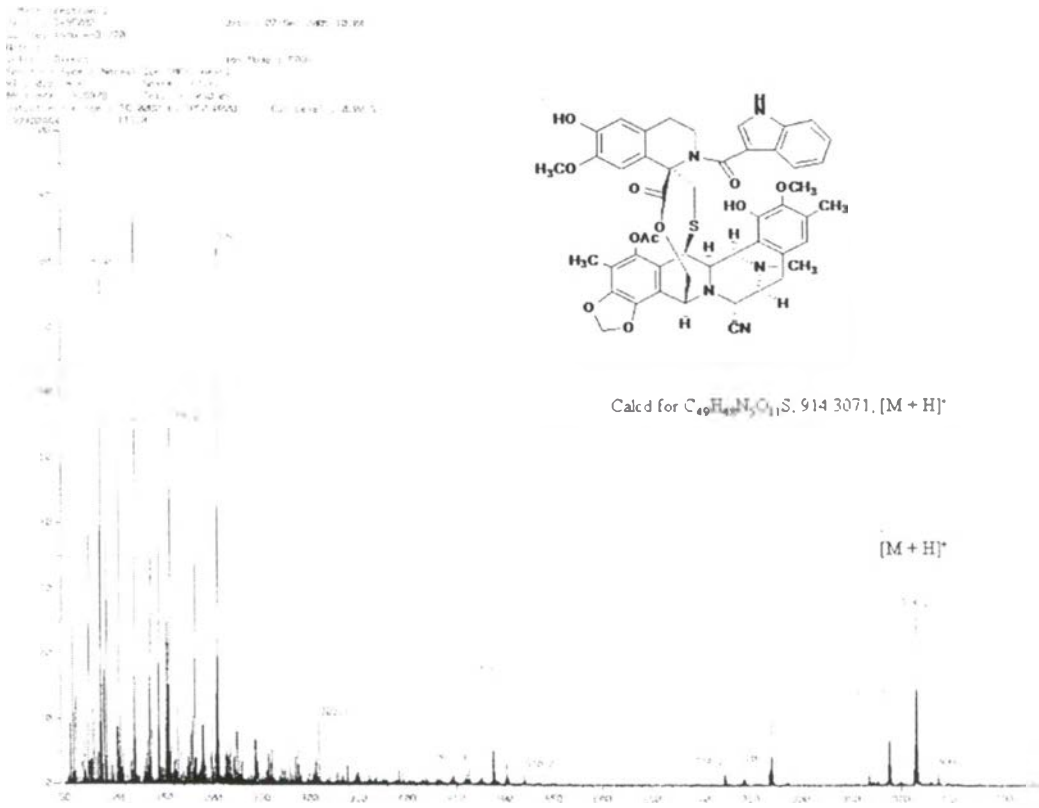


Figure 108. The FAB-mass spectrum of *2'-N*-3"-indolecarboxylecteinascidin 770 (**39**)

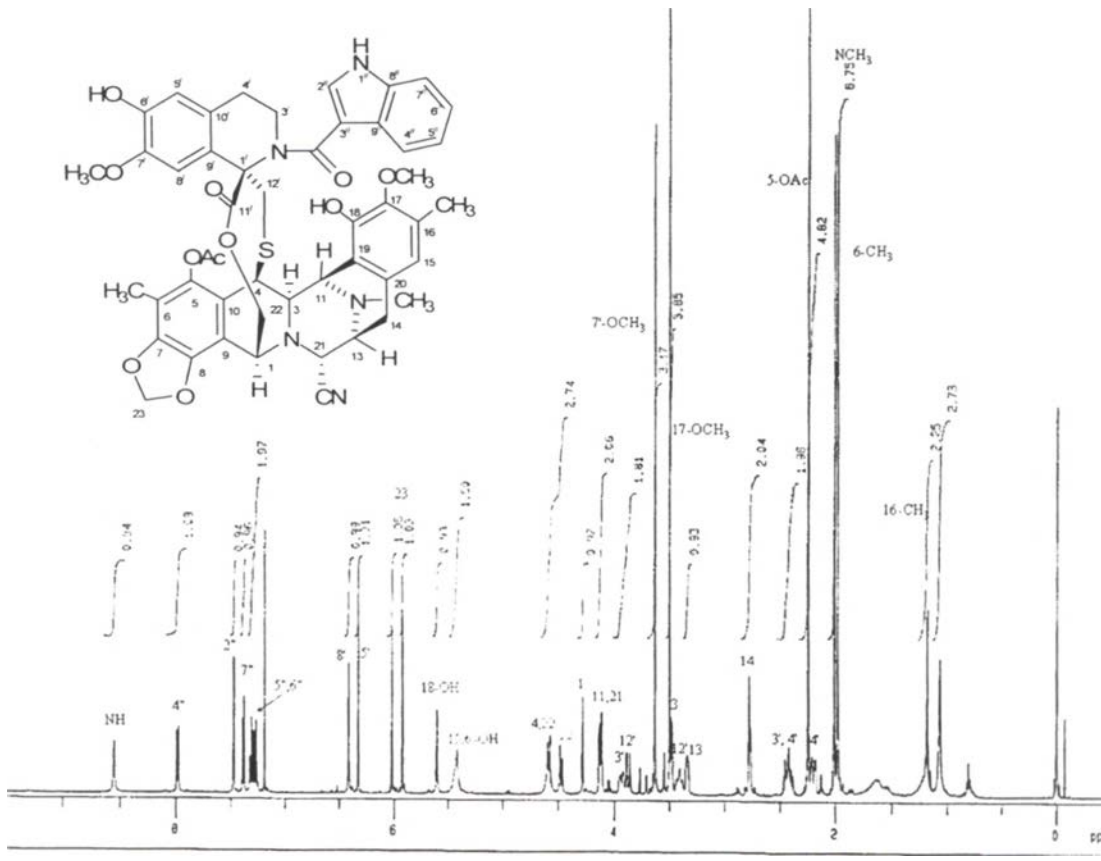


Figure 109. The 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of *2'-N*-3"-indolecarboxylecteinascidin 770 (**39**)

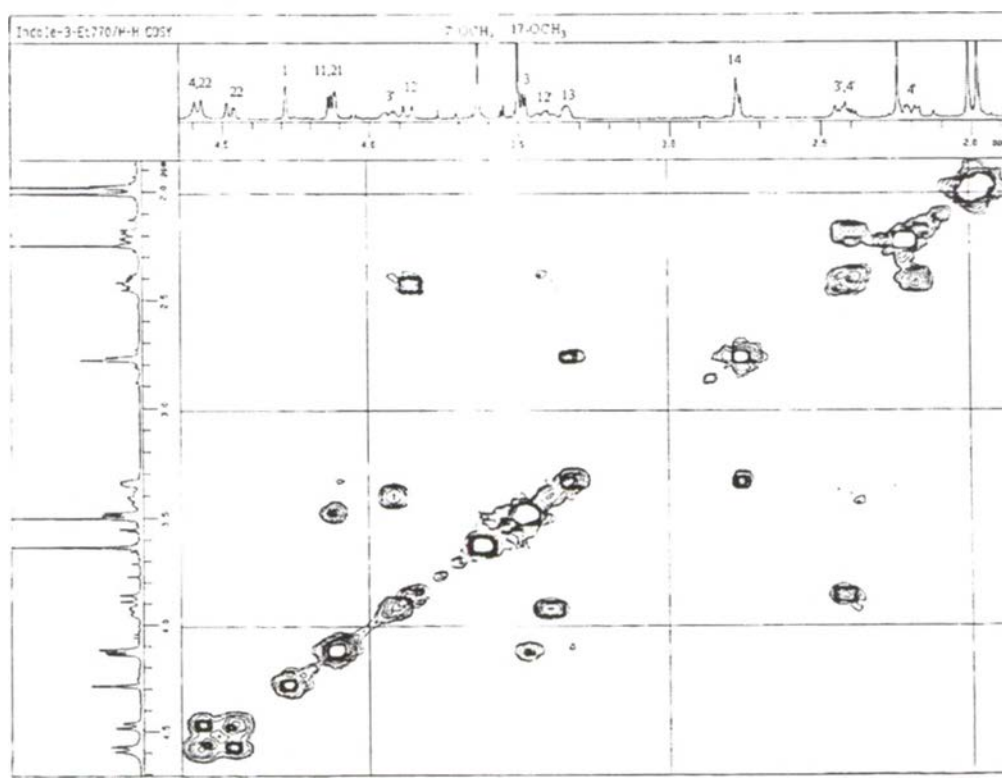


Figure 110. The 500 MHz ^{1}H-^{1}H COSY spectrum (in $CDCl_3$) of *2'-N*-3"-indolecarboxylecteinascidin 770 (**39**) (expanded from δ_H 1.9 to 4.7 ppm)

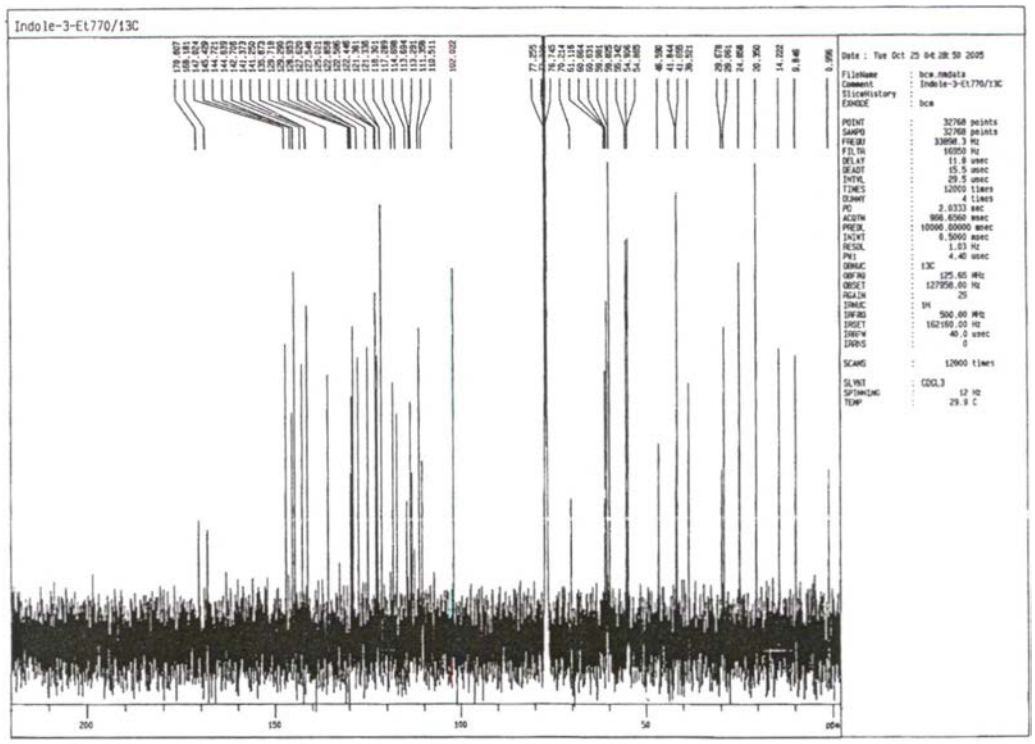


Figure 111. The 125 MHz ^{13}C-NMR spectrum (in $CDCl_3$) of *2'-N*-3"-indolecarboxyl ecteinascidin 770 (**39**)

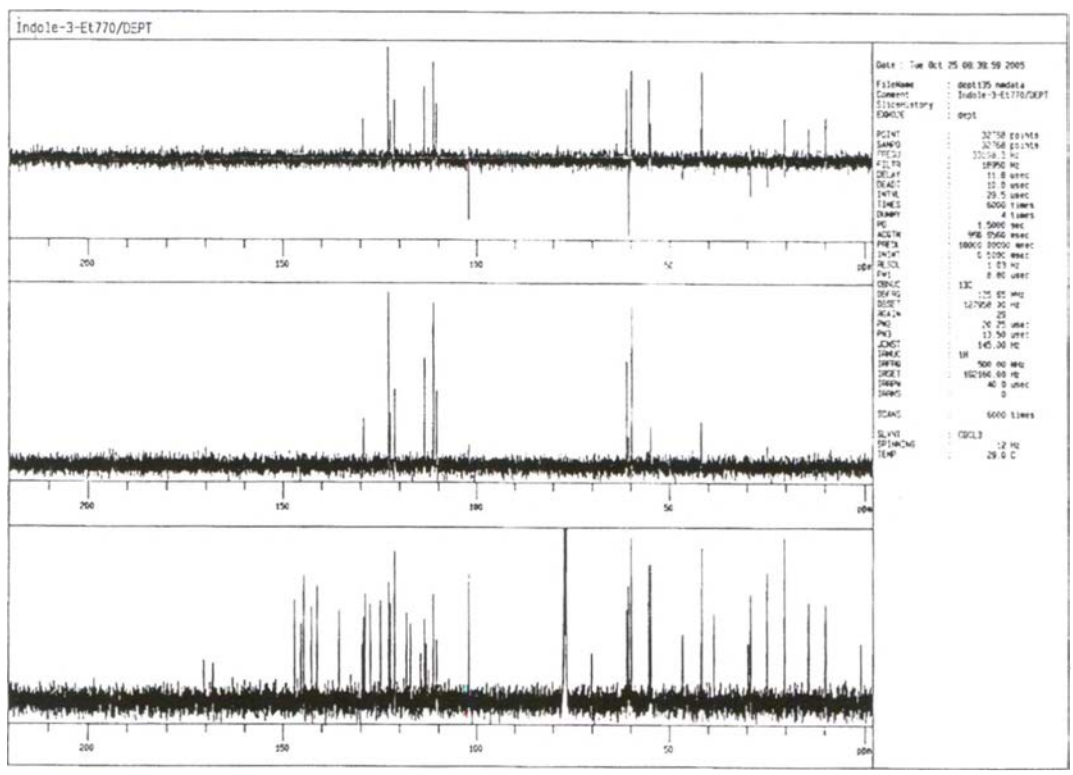


Figure 112. The 500 MHz ^{13}C-NMR and DEPT spectra (in $CDCl_3$) of *2'-N*-3"-indolecarboxylecteinascidin 770 (**39**)

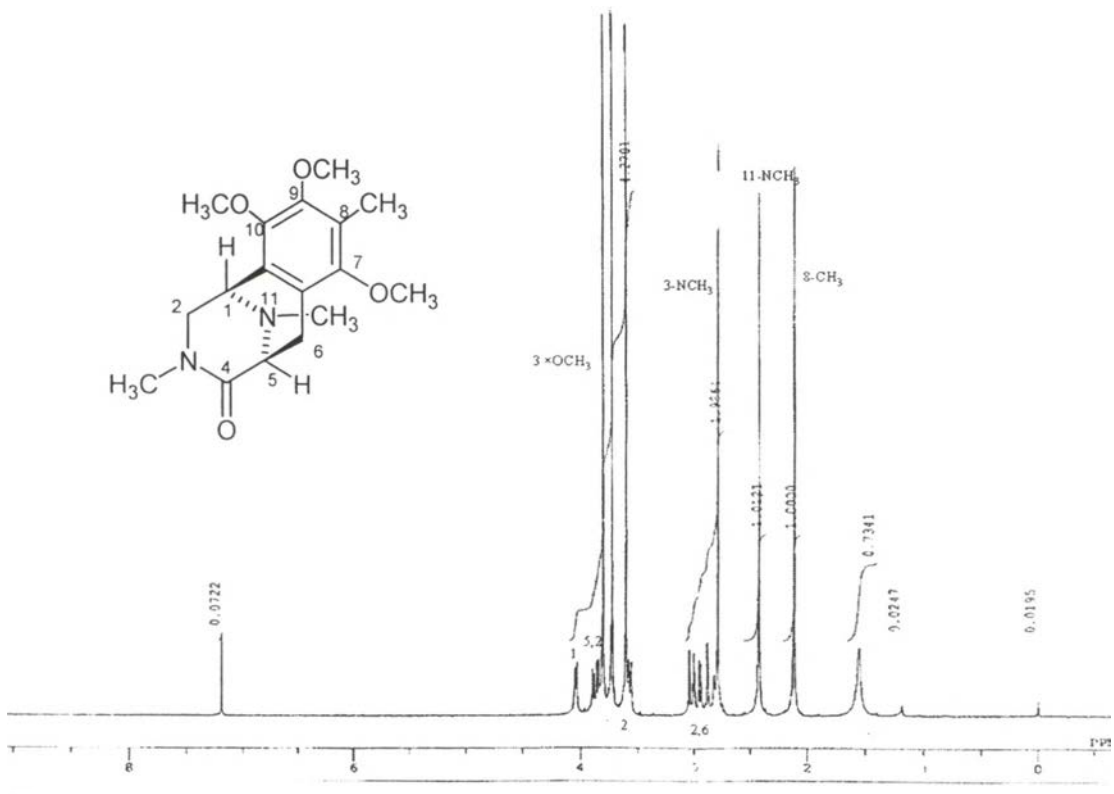


Figure 113. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 1,2,3,4,5,6-Hexahydro-7,9,10-trimethoxy-3,8,11-trimethyl-4-oxo-1,5-imino-3-benzazocin (**40**)

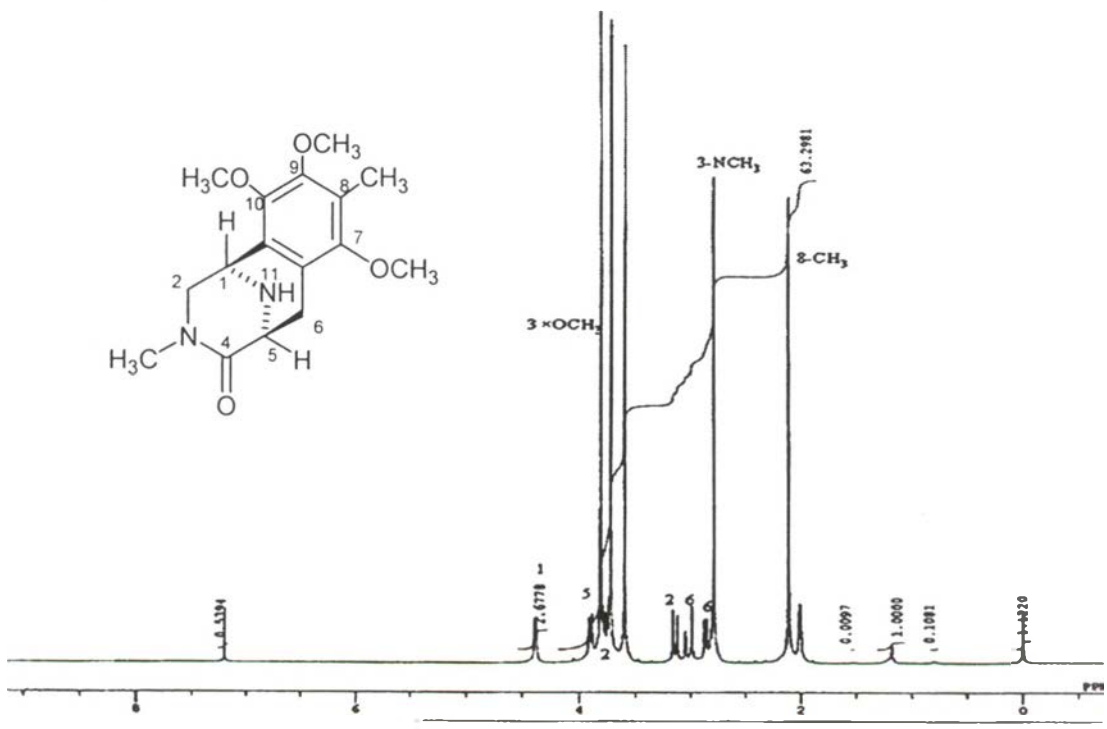


Figure 114. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 1,2,3,4,5,6-Hexahydro-7,9,10-trimethoxy-3,8-dimethyl-4-oxo-1,5-imino-3-benzazocin (**40a**)

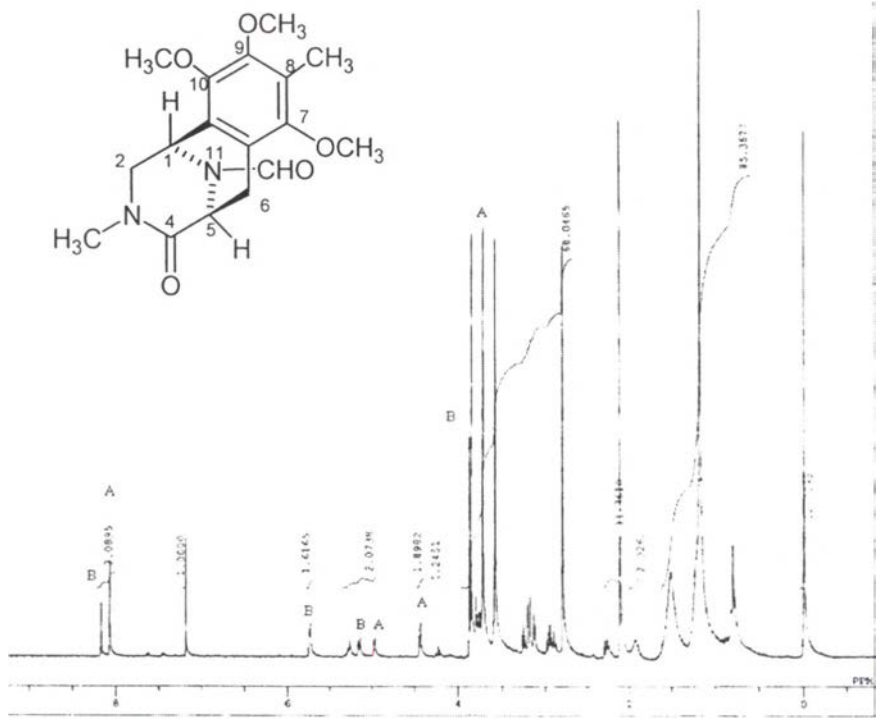


Figure 115. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) 1,2,3,4,5,6-Hexahydro-7,9,10-trimethoxy-3,8-dimethyl-4-oxo-1,5-imino-11-carbonyl-3-benzazocin (**40**b)

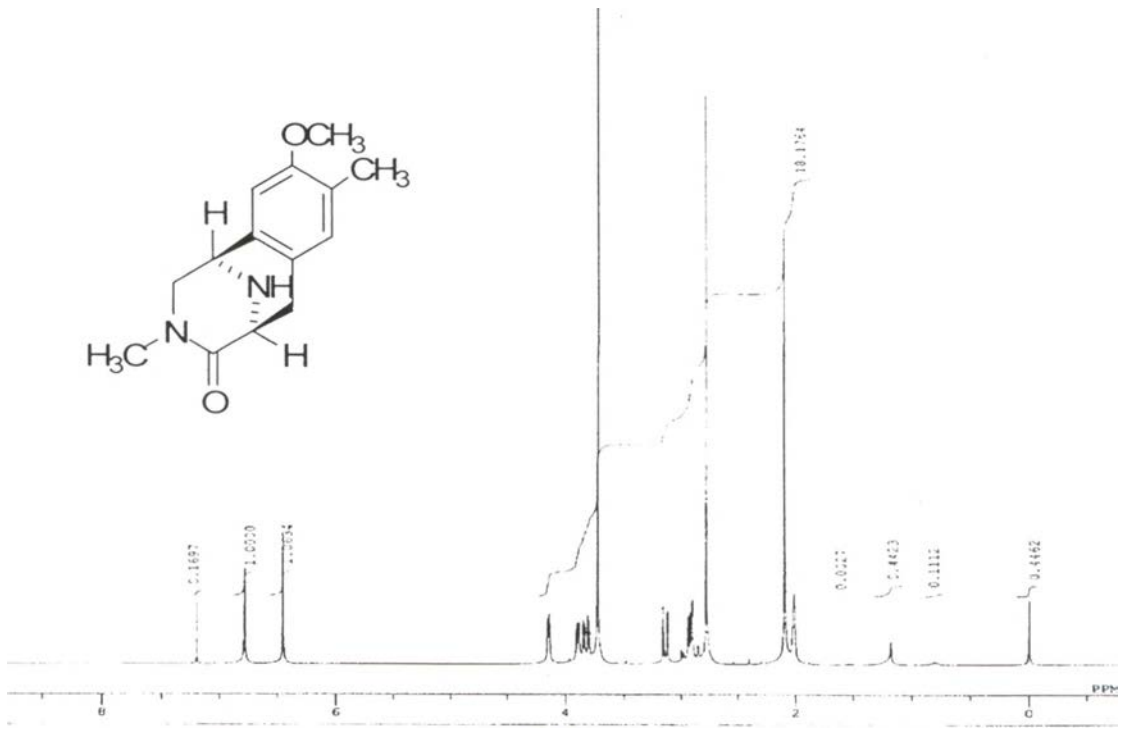


Figure 116. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 1,2,3,4,5,6-Hexahydro-9-methoxy-3,8-dimethyl-4-oxo-1,5-imino-3-benzazocin (**41**a)

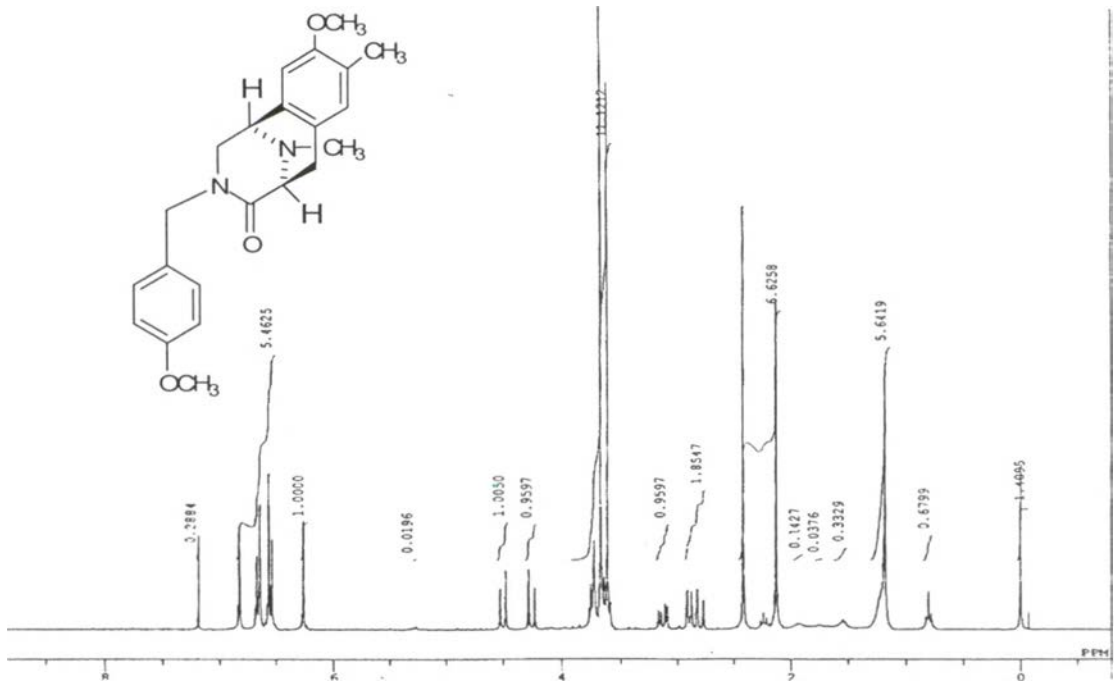


Figure 117. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 1,2,3,4,5,6-Hexahydro-9-methoxy-8,11-dimethyl-3-{4-methoxy-1-phenylmetyl}-4-oxo-1,5-imino-3-benzazocin (**42**)

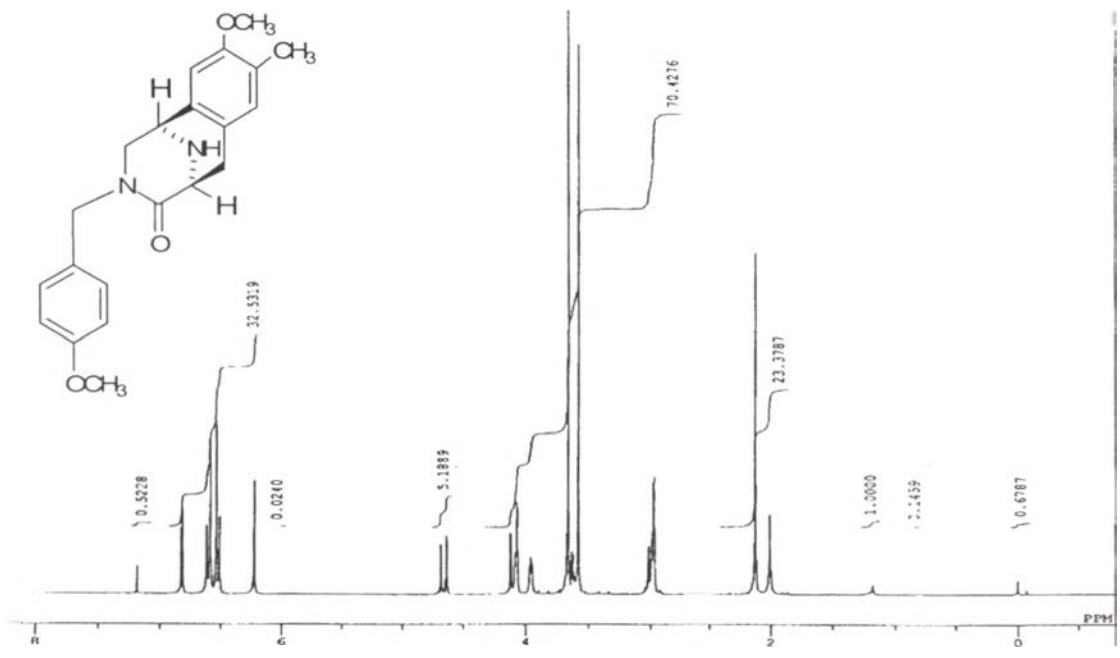


Figure 118. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 1,2,3,4,5,6-Hexahydro-9-methoxy-8-methyl-3-{4-methoxy-1-phenylmetyl}-4-oxo-1,5-imino-3-benzazocin (**42a**)

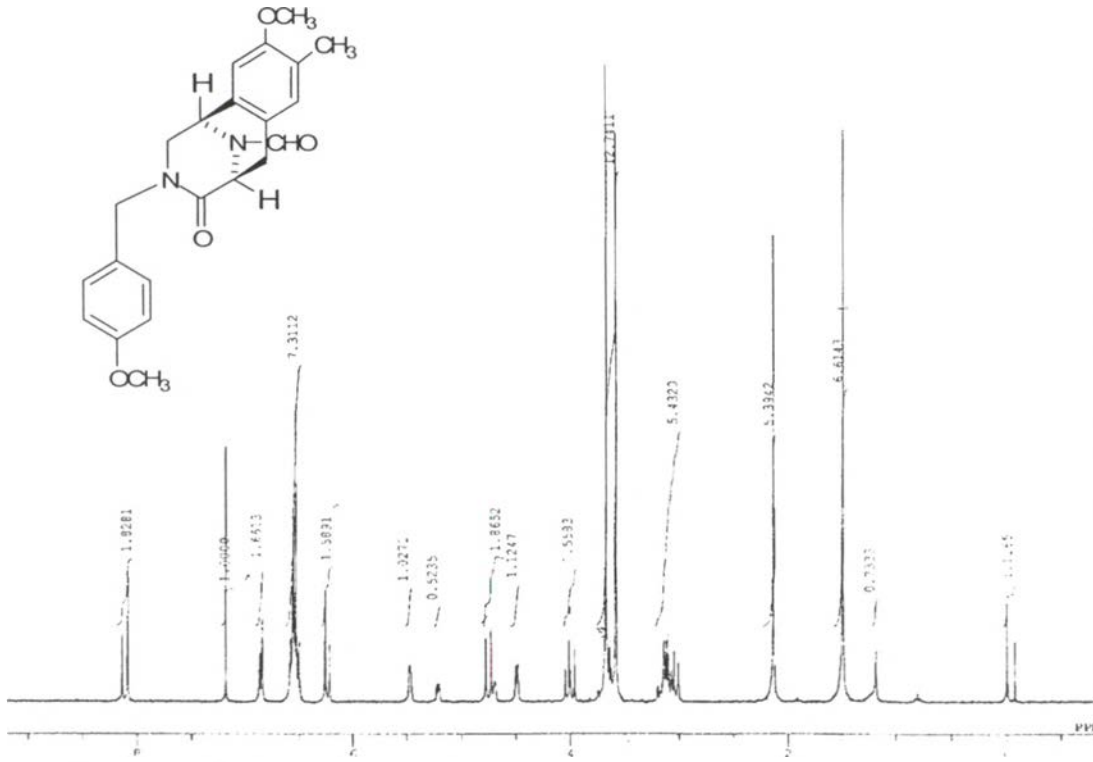


Figure 119. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 1,2,3,4,5,6-Hexahydro-9-methoxy-8-methyl-3-{4-methoxy-1-phenylmetyl}-4-oxo-1,5-imino-11-carbonyl-3-benzazocin (**42b**)

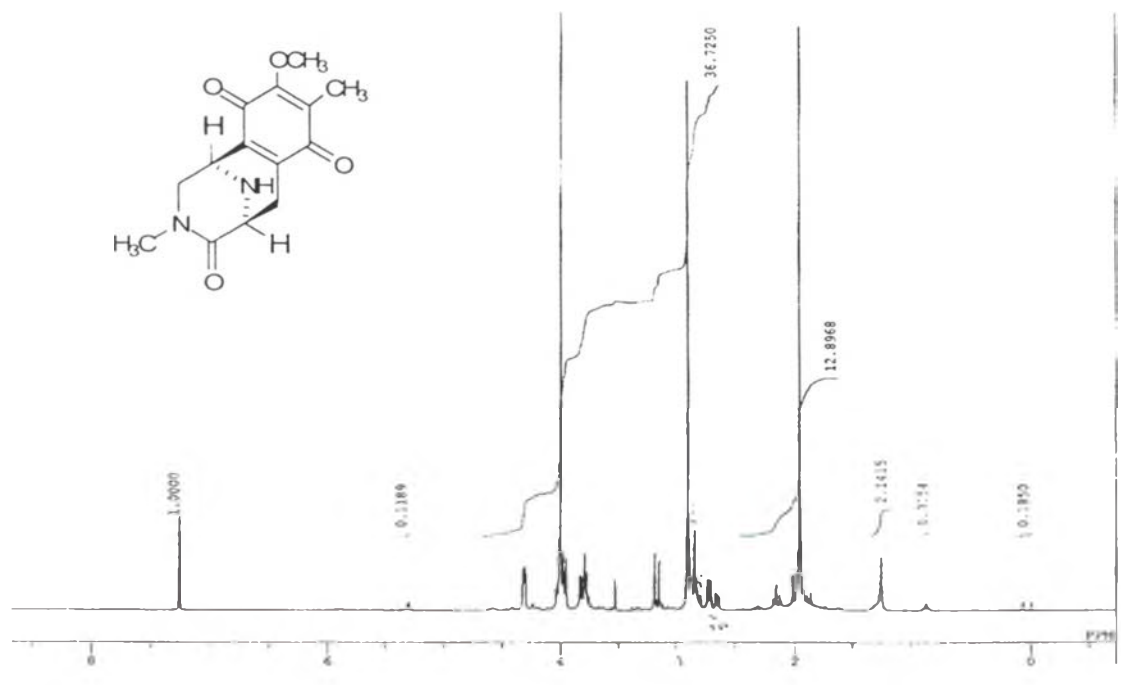


Figure 120. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 1,2,3,4,5,6-Hexahydro-9-methoxy3,-8-dimethyl-7,10-quinone-4-oxo-1,5-imino-3-benzazocin (**43a**)

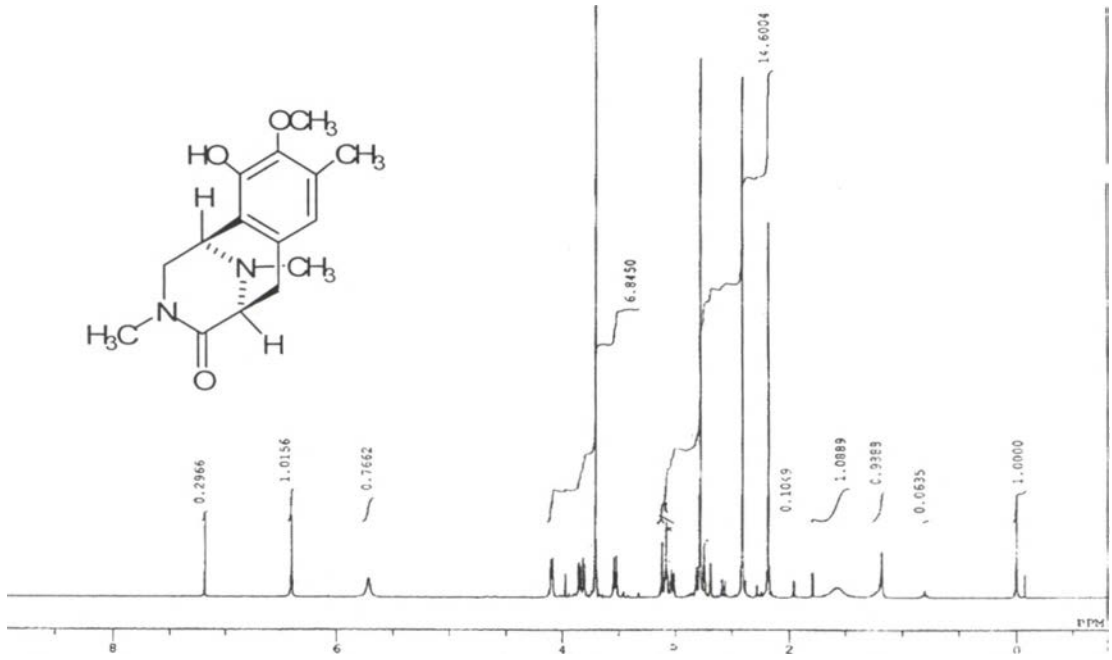


Figure 121. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 1,2,3,4,5,6-hexahydro-10-hydroxy-9-methoxy-3,8,11-trimethyl-4-oxo-1,5-imino-3-benzazocin (**44**)

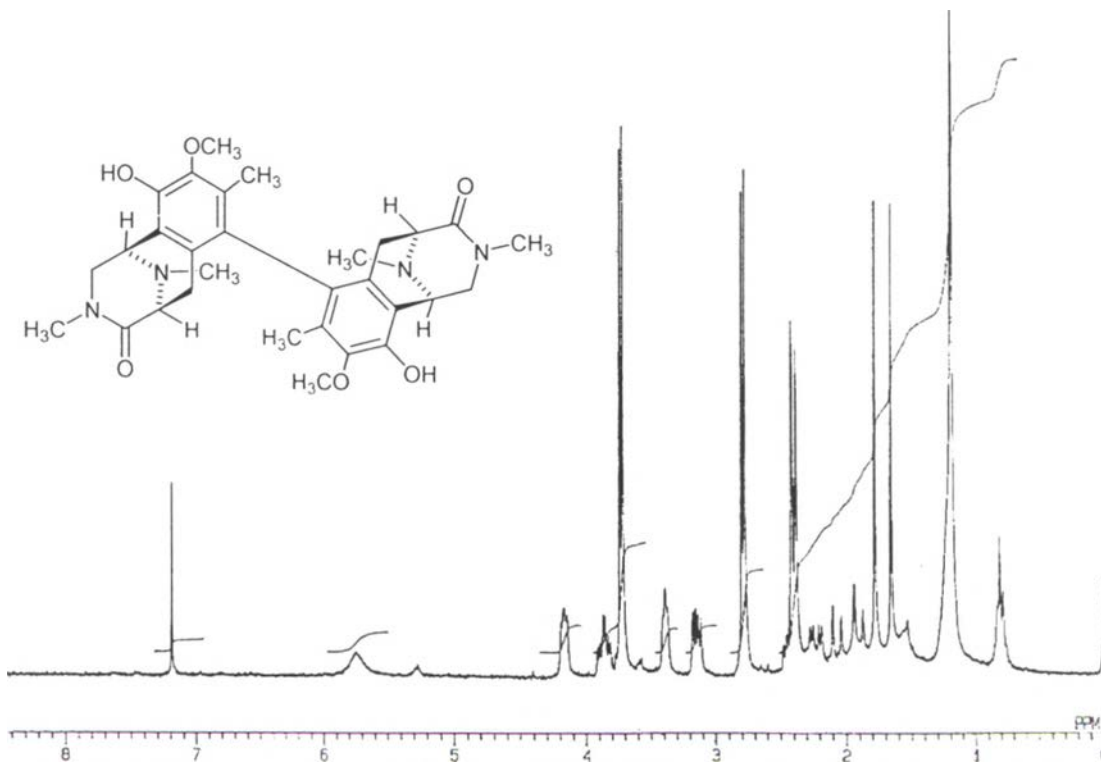


Figure 122. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of Bis-1,2,3,4,5,6-hexahydro-10-hydroxy-9-methoxy-3,8,11-trimethyl-4-oxo-1,5-imino-3-benzazocin (**44b**)

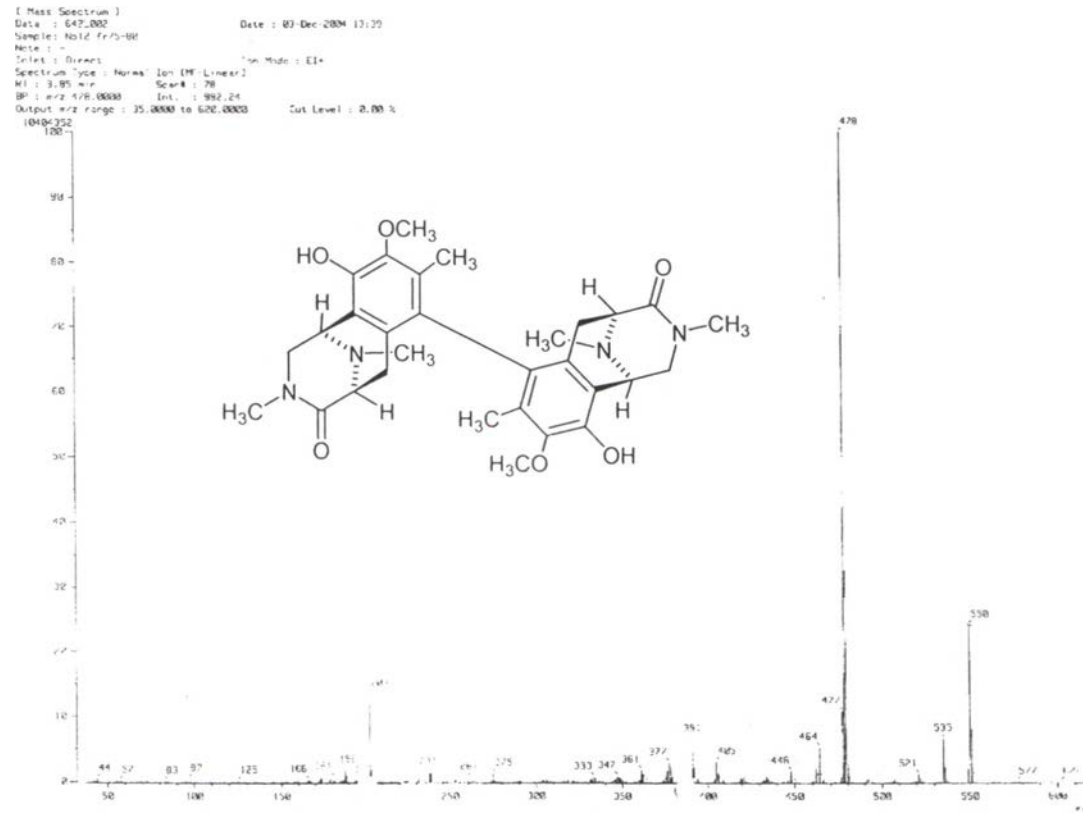


Figure 123. The FAB-mass spectrum of Bis-1,2,3,4,5,6-hexahydro-10-hydroxy-9-methoxy-3,8,11-trimethyl-4-oxo-1,5-imino-3-benzazocin (**44b**)

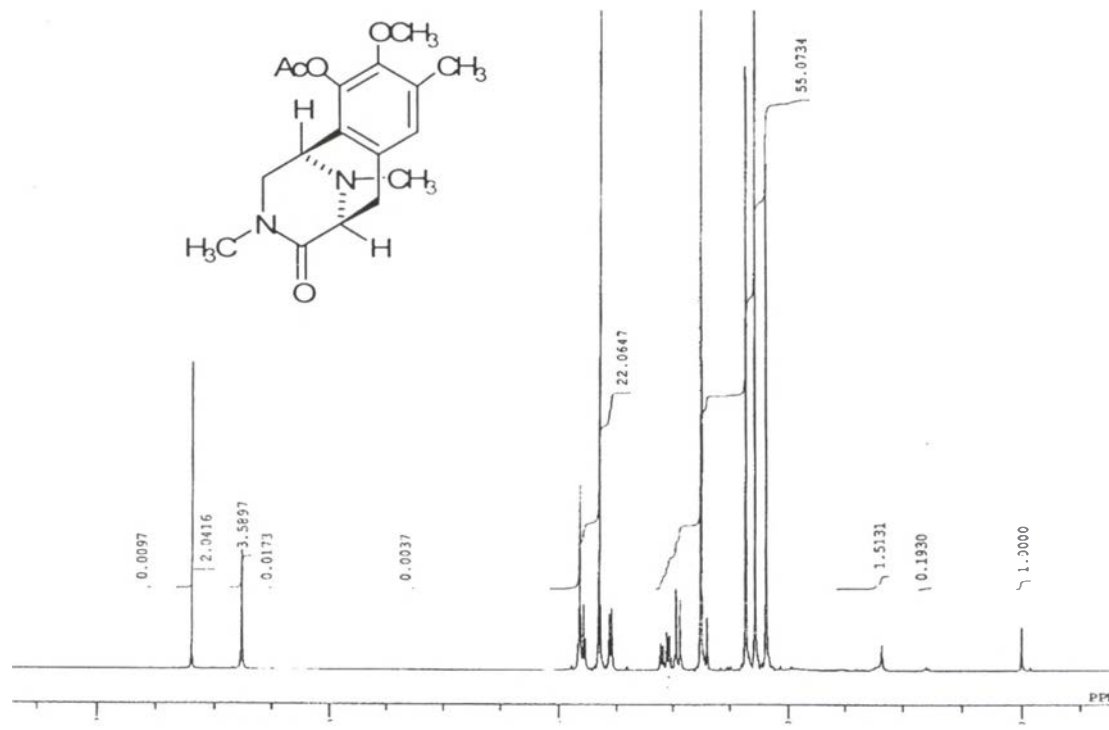


Figure 124. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 1,2,3,4,5,6-Hexahydro-10-acetate-9-methoxy-3,8,11-trimethyl-4-oxo-1,5-imino-3-benzazocin (**45**)

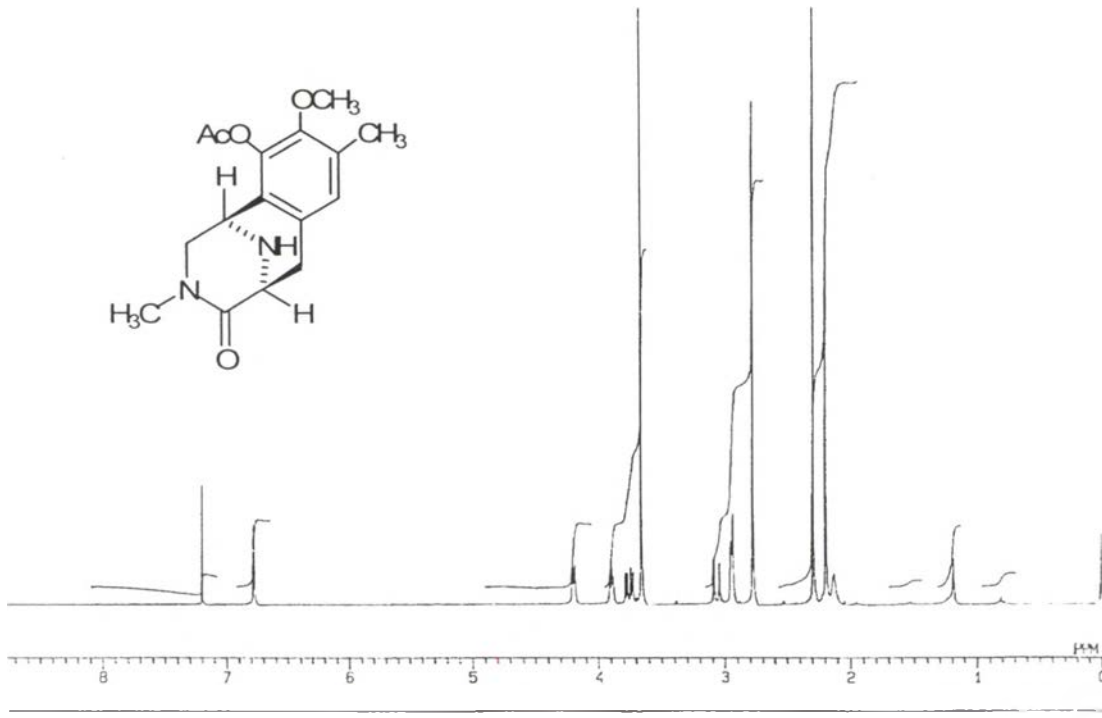


Figure 125. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 1,2,3,4,5,6-Hexahydro-10-acetate-9-methoxy-3,8-dimethyl-4-oxo-1,5-imino-3-benzazocin (**45a**)

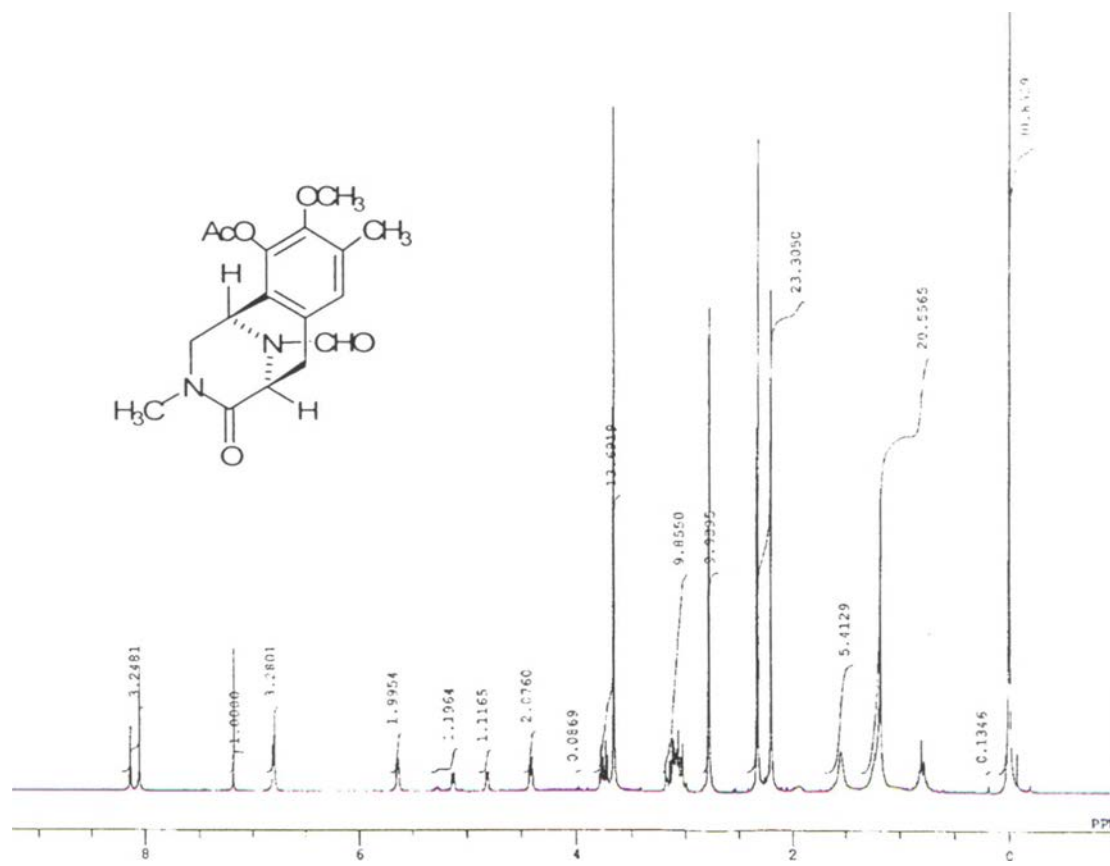


Figure 126. The 300 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of 1,2,3,4,5,6-Hexahydro-10-acetate-9-methoxy-3,8-dimethyl-4-oxo-1,5-imino-11-carbonyl-3-benzazocin (**45b**)

VITA

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Publication

Ploenthip Puthongking, Chamnan Patarapanich, Surattana Amnuoypol, Khanit Suwanborirux, Akinori Kubo, and Naoki Saito. 2006. Chemistry of Ecteinascidins. Part 2.1 Preparation of 6'-*O*-Acyl Derivatives of stable Ecteinascidin and Evaluation of Antitumor Activity. Chem. Pharm. Bull. (in press)

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