

Supporting Information Available

**Bioactive metabolites from Cultures of the Entomopathogenic
Fungus *Pleurocordyceps ophiocordycipiticola* TBRC-BCC 9612**

Siriporn Saepua,^a Karoon Sadorn,^b Jittra Kornsakulkarn,^a Patchanee Auncharoen,^a Suchada Mongkolsamrit,^a Donnaya Thanakitpipattana,^a and Chawanee Thongpanchang^{*,a}

^a National Center for Genetic Engineering and Biotechnology (BIOTEC), National Science and Technology Development Agency (NSTDA), 111 Thailand Science Park, Phahonyothin Road, Khlong Nueng, Khlong Luang, Pathum Thani 12120 Thailand

^b Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Chalongkrung Road, Ladkrabang, Bangkok 10520 Thailand

* Corresponding author. Tel: +66 2 5646700 ext. 3559. Fax: +66 2 5646707. E-mail: chawanee@biotec.or.th

Table of contents

Figure S1. HRESIMS spectrum of compound 1	1
Figure S2. ¹ H NMR spectrum of compound 1 in Pyridine- <i>d</i> ₅	1
Figure S3. ¹³ C NMR spectrum of compound 1 in Pyridine- <i>d</i> ₅	2
Figure S4. COSY spectrum of compound 1 in Pyridine- <i>d</i> ₅	2
Figure S5. HSQC spectrum of compound 1 in Pyridine- <i>d</i> ₅	3
Figure S6. HMBC spectrum of compound 1 in Pyridine- <i>d</i> ₅	3
Figure S7. NOESY spectrum of compound 1 in Pyridine- <i>d</i> ₅	4
Figure S8. HRESIMS spectrum of compound 2	4
Figure S9. ¹ H NMR spectrum of compound 2 in Pyridine- <i>d</i> ₅	5
Figure S10. ¹³ C NMR spectrum of compound 2 in Pyridine- <i>d</i> ₅	5
Figure S11. COSY spectrum of compound 2 in Pyridine- <i>d</i> ₅	6
Figure S12. HSQC spectrum of compound 2 in Pyridine- <i>d</i> ₅	6
Figure S13. HMBC spectrum of compound 2 in Pyridine- <i>d</i> ₅	7
Figure S14. NOESY spectrum of compound 2 in Pyridine- <i>d</i> ₅	7
Figure S15. HRESIMS spectrum of compound 3	8
Figure S16. ¹ H NMR spectrum of compound 3 in Acetone- <i>d</i> ₆	8
Figure S17. ¹³ C NMR spectrum of compound 3 in Acetone- <i>d</i> ₆	9
Figure S18. COSY spectrum of compound 3 in Acetone- <i>d</i> ₆	9
Figure S19. HSQC spectrum of compound 3 in Acetone- <i>d</i> ₆	10
Figure S20. HMBC spectrum of compound 3 in Acetone- <i>d</i> ₆	10
Figure S21. NOESY spectrum of compound 3 in Acetone- <i>d</i> ₆	11
Figure S22. HRESIMS spectrum of compound 4	11
Figure S23. ¹ H NMR spectrum of compound 4 in Acetone- <i>d</i> ₆	12
Figure S24. ¹³ C NMR spectrum of compound 4 in Acetone- <i>d</i> ₆	12
Figure S25. COSY spectrum of compound 4 in Acetone- <i>d</i> ₆	13
Figure S26. HSQC spectrum of compound 4 in Acetone- <i>d</i> ₆	13
Figure S27. HMBC spectrum of compound 4 in Acetone- <i>d</i> ₆	14
Figure S28. NOESY spectrum of compound 4 in Acetone- <i>d</i> ₆	14
Figure S29. HRESIMS spectrum of compound 5	15
Figure S30. ¹ H NMR spectrum of compound 5 in Acetone- <i>d</i> ₆	15
Figure S31. ¹³ C NMR spectrum of compound 5 in Acetone- <i>d</i> ₆	16

Figure S32. COSY spectrum of compound 5 in Acetone- <i>d</i> ₆	16
Figure S33. HSQC spectrum of compound 5 in Acetone- <i>d</i> ₆	17
Figure S34. HMBC spectrum of compound 5 in Acetone- <i>d</i> ₆	17
Figure S35. NOESY spectrum of compound 5 in Acetone- <i>d</i> ₆	18
Figure S36. HRESIMS spectrum of compound 6	18
Figure S37. ¹ H NMR spectrum of compound 6 in DMSO- <i>d</i> ₆	19
Figure S38. ¹³ C NMR spectrum of compound 6 in DMSO- <i>d</i> ₆	19
Figure S39. COSY spectrum of compound 6 in DMSO- <i>d</i> ₆	20
Figure S40. HSQC spectrum of compound 6 in DMSO- <i>d</i> ₆	20
Figure S41. HMBC spectrum of compound 6 in DMSO- <i>d</i> ₆	21
Figure S42. NOESY spectrum of compound 6 in DMSO- <i>d</i> ₆	21
Figure S43. HRESIMS spectrum of compound 7	22
Figure S44. ¹ H NMR spectrum of compound 7 in Acetone- <i>d</i> ₆	22
Figure S45. ¹³ C NMR spectrum of compound 7 in Acetone- <i>d</i> ₆	23
Figure S46. COSY spectrum of compound 7 in Acetone- <i>d</i> ₆	23
Figure S47. HSQC spectrum of compound 7 in Acetone- <i>d</i> ₆	24
Figure S48. HMBC spectrum of compound 7 in Acetone- <i>d</i> ₆	24
Figure S49. NOESY spectrum of compound 7 in Acetone- <i>d</i> ₆	25
Figure S50. HRESIMS spectrum of compound 8	25
Figure S51. ¹ H NMR spectrum of compound 8 in Acetone- <i>d</i> ₆	26
Figure S52. ¹³ C NMR spectrum of compound 8 in Acetone- <i>d</i> ₆	26
Figure S53. COSY spectrum of compound 8 in Acetone- <i>d</i> ₆	27
Figure S54. HSQC spectrum of compound 8 in Acetone- <i>d</i> ₆	27
Figure S55. HMBC spectrum of compound 8 in Acetone- <i>d</i> ₆	28
Figure S56. NOESY spectrum of compound 8 in Acetone- <i>d</i> ₆	28
Figure S57. HRESIMS spectrum of compound 9	29
Figure S58. ¹ H NMR spectrum of compound 9 in DMSO- <i>d</i> ₆	29
Figure S59. ¹³ C NMR spectrum of compound 9 in DMSO- <i>d</i> ₆	30
Figure S60. COSY spectrum of compound 9 in DMSO- <i>d</i> ₆	30
Figure S61. HSQC spectrum of compound 9 in DMSO- <i>d</i> ₆	31
Figure S62. HMBC spectrum of compound 9 in DMSO- <i>d</i> ₆	31
Figure S63. NOESY spectrum of compound 9 in DMSO- <i>d</i> ₆	32
Figure S64. HRESIMS spectrum of akanthomycin	32

Figure S65. ^1H NMR spectrum of akanthomycin in $\text{DMSO}-d_6$	33
Figure S66. ^{13}C NMR spectrum of akanthomycin in $\text{DMSO}-d_6$	33
Figure S67. HRESIMS spectrum of cordypyridone A.....	34
Figure S68. ^1H NMR spectrum of cordypyridone A in Acetone- d_6	34
Figure S69. ^{13}C NMR spectrum of cordypyridone A in Acetone- d_6	35
Figure S70. HRESIMS spectrum of cordypyridone B.....	35
Figure S71. ^1H NMR spectrum of cordypyridone B in Acetone- d_6	36
Figure S72. ^{13}C NMR spectrum of cordypyridone B in Acetone- d_6	36
Figure S73. HRESIMS spectrum of cordypyridone C.....	37
Figure S74. ^1H NMR spectrum of cordypyridone C in Acetone- d_6	37
Figure S75. ^{13}C NMR spectrum of cordypyridone C in Acetone- d_6	38
Figure S76. HRESIMS spectrum of cordytropolone	38
Figure S77. ^1H NMR spectrum of cordytropolone in $\text{DMSO}-d_6$	39
Figure S78. ^{13}C NMR spectrum of cordytropolone in $\text{DMSO}-d_6$	39
Figure S79. HRESIMS spectrum of stipitalide	40
Figure S80. ^1H NMR spectrum of stipitalide in $\text{DMSO}-d_6$	40
Figure S81. ^{13}C NMR spectrum of stipitalide in $\text{DMSO}-d_6$	41
Figure S82. HRESIMS spectrum of 4-hydroxy-3,6-dimethyl-2H-pyran-2-one	41
Figure S83. ^1H NMR spectrum of 4-hydroxy-3,6-dimethyl-2H-pyran-2-one in Acetone- d_6	42
Figure S84. ^{13}C NMR spectrum of 4-hydroxy-3,6-dimethyl-2H-pyran-2-one in Acetone- d_6	42
Figure S85. HRESIMS spectrum of indole-2-carboxylic acid, 3-methylorcinaldehyde.....	43
Figure S86. ^1H NMR spectrum of indole-2-carboxylic acid, 3-methylorcinaldehyde in $\text{DMSO}-d_6$	43
Figure S87. ^{13}C NMR spectrum of indole-2-carboxylic acid, 3-methylorcinaldehyde in $\text{DMSO}-d_6$...	44
Figure S88. HRESIMS spectrum of <i>trans-trans</i> -farnesol.....	44
Figure S89. ^1H NMR spectrum of <i>trans-trans</i> -farnesol in Acetone- d_6	45
Figure S90. ^{13}C NMR spectrum of <i>trans-trans</i> -farnesol in Acetone- d_6	45
Figure S91. RAxML tree of <i>Pleurocordyceps</i> and related species from a combined LSU, <i>TEF1</i> and <i>RPB1</i> dataset. Numbers at the major nodes represent Maximum Likelihood Bootstrap (MLB) support values.	46

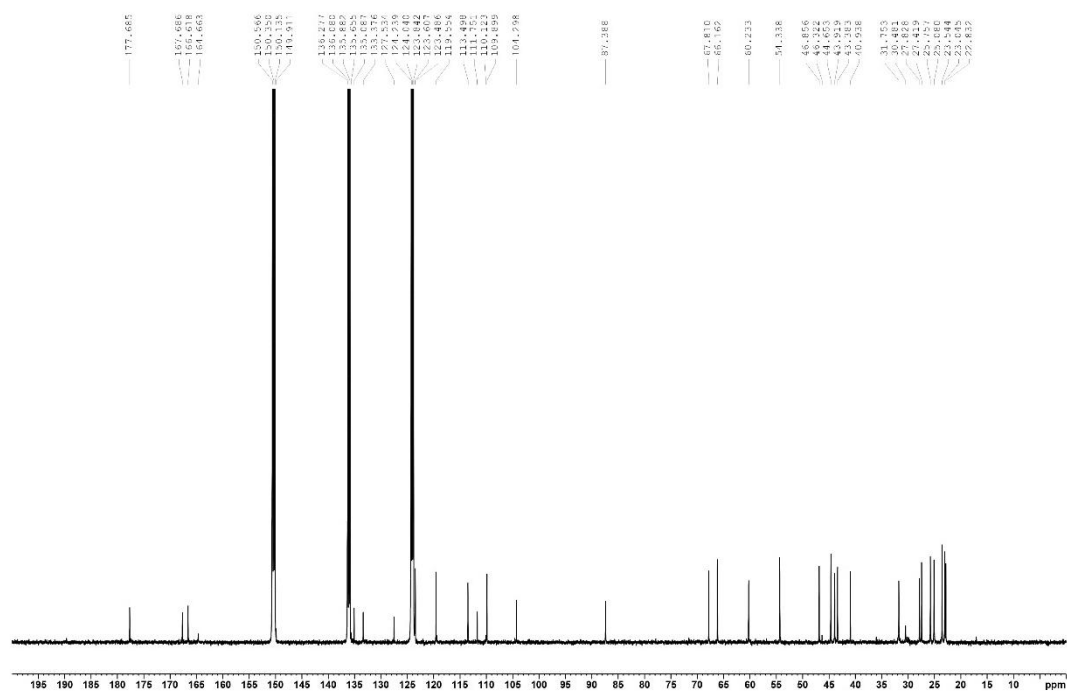


Figure S3. ^{13}C NMR spectrum of compound **1** in Pyridine- d_5

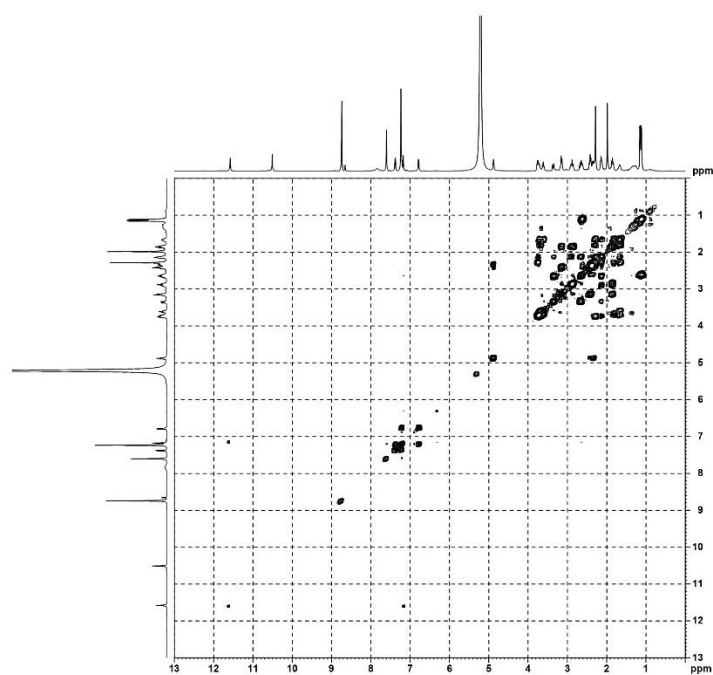


Figure S4. COSY spectrum of compound **1** in Pyridine- d_5

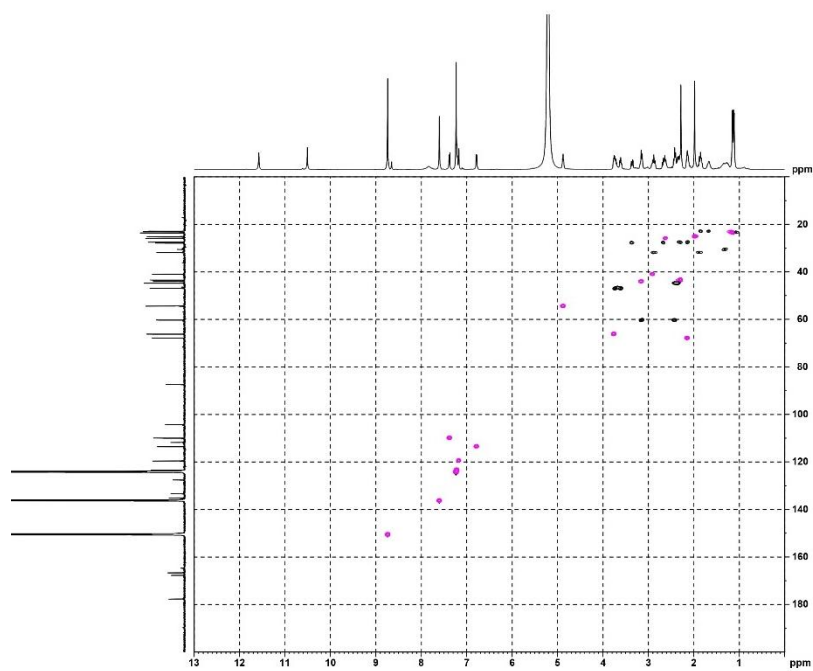


Figure S5. HSQC spectrum of compound **1** in Pyridine-*d*₅

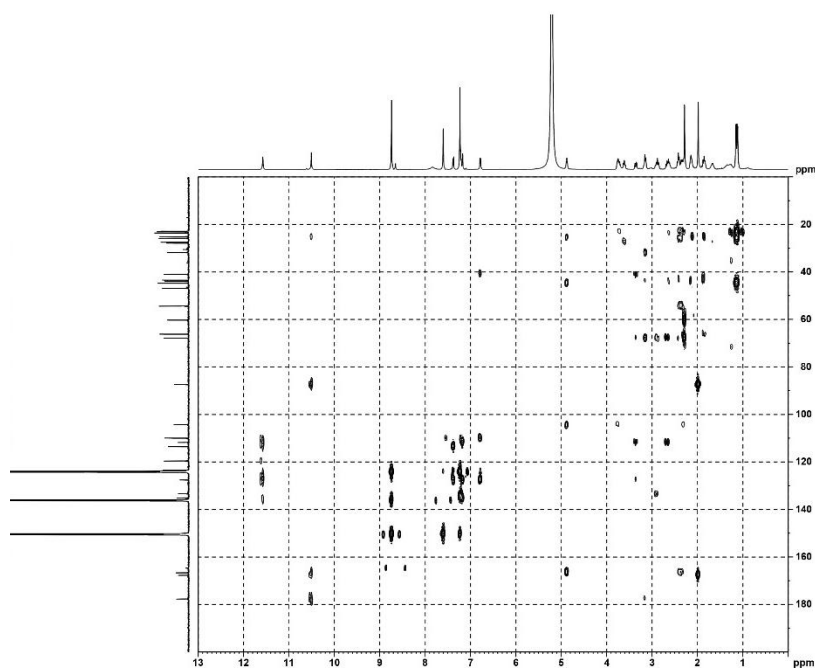


Figure S6. HMBC spectrum of compound **1** in Pyridine-*d*₅

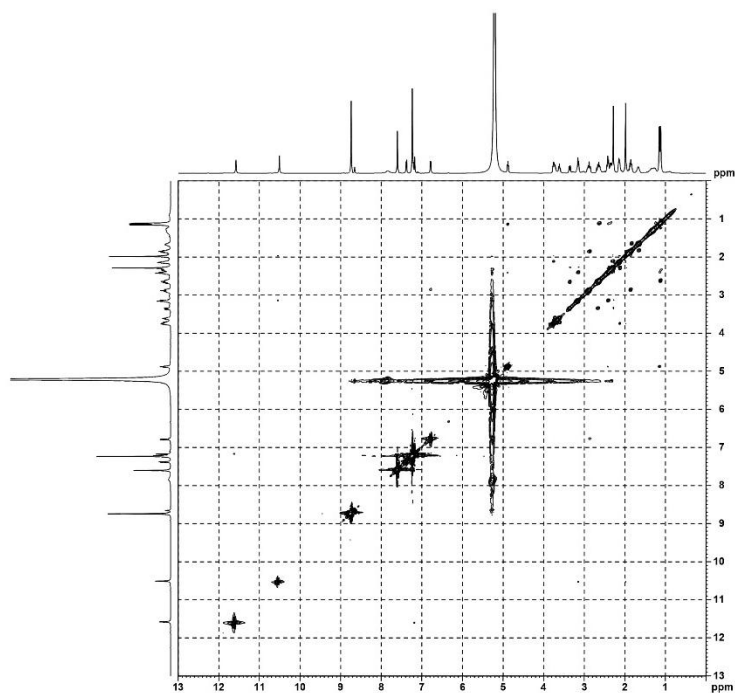


Figure S7. NOESY spectrum of compound **1** in Pyridine-*d*₅

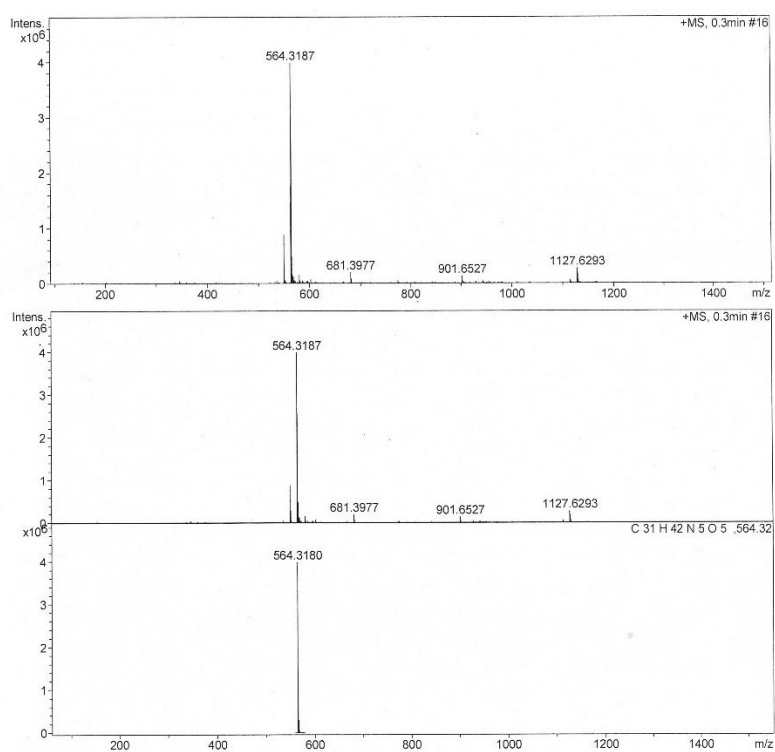


Figure S8. HRESIMS spectrum of compound **2**

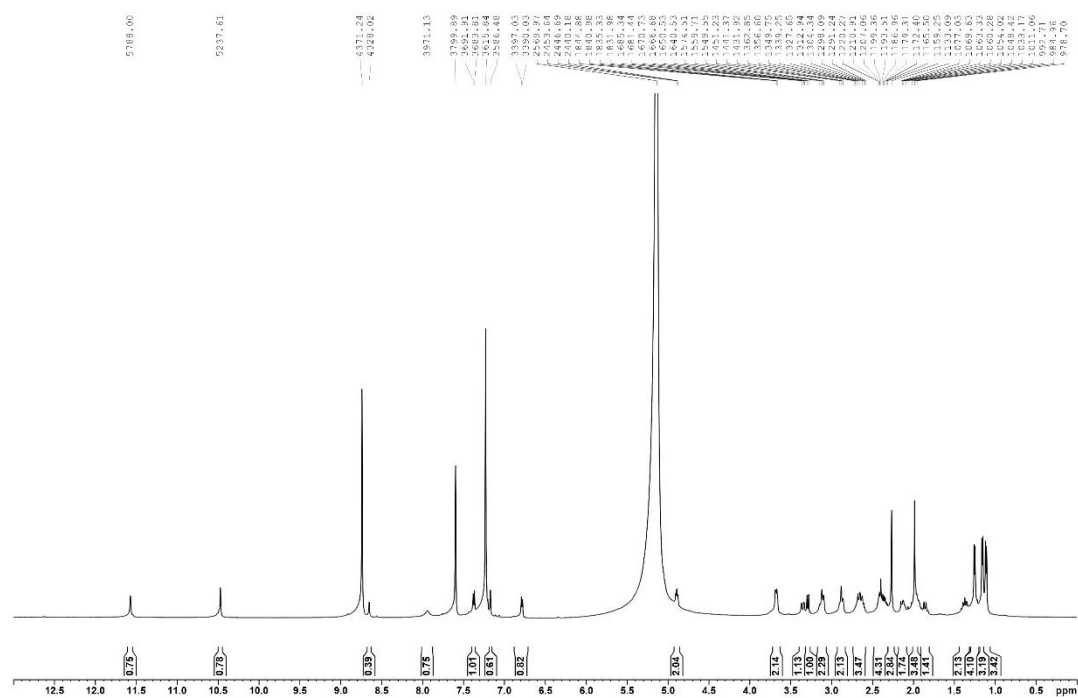
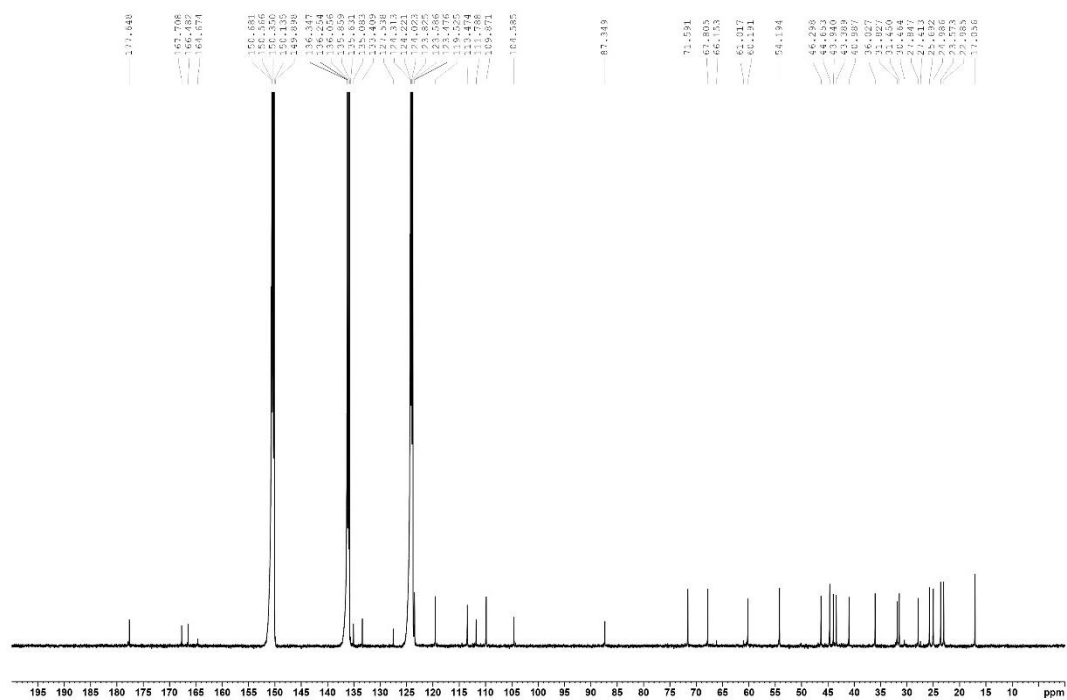


Figure S9. ^1H NMR spectrum of compound **2** in Pyridine- d_5



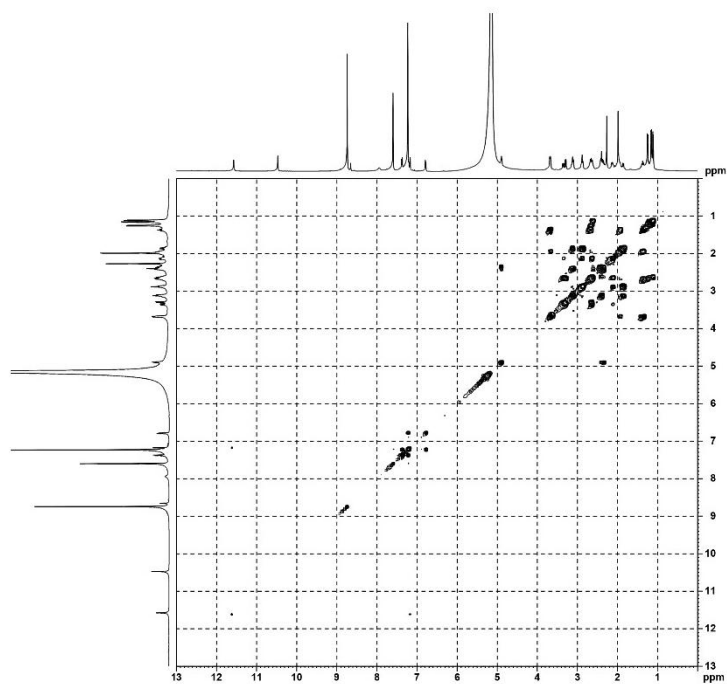


Figure S11. COSY spectrum of compound **2** in Pyridine-*d*₅

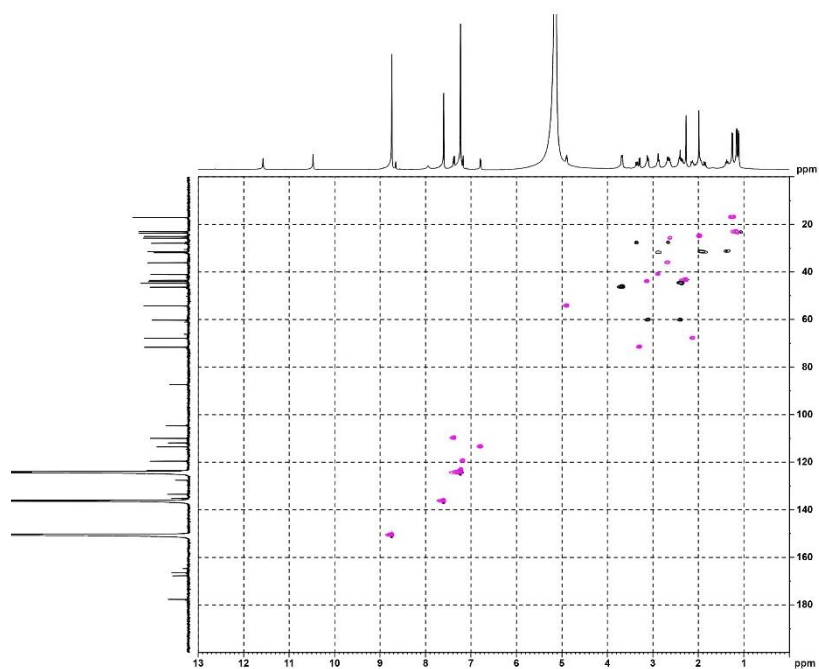


Figure S12. HSQC spectrum of compound **2** in Pyridine-*d*₅

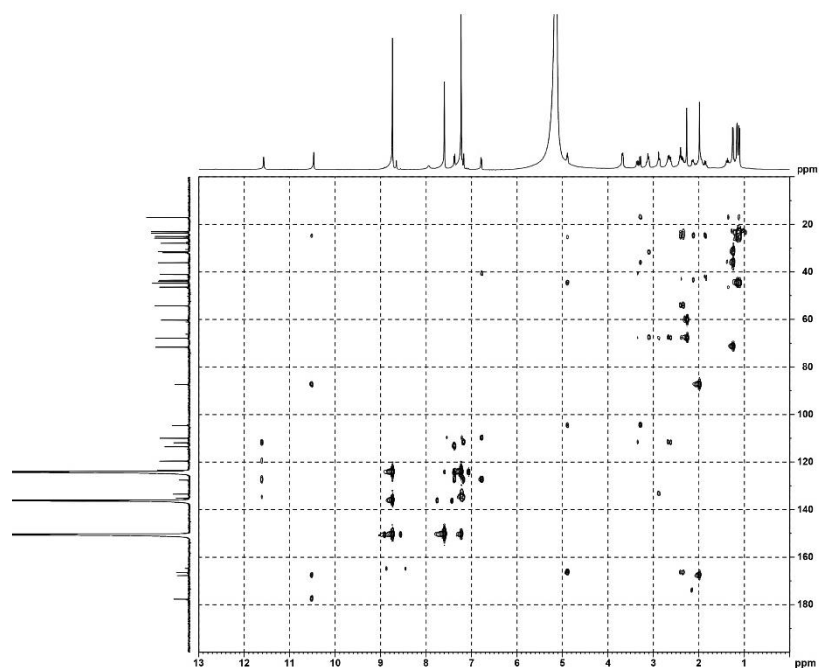


Figure S13. HMBC spectrum of compound **2** in Pyridine-*d*₅

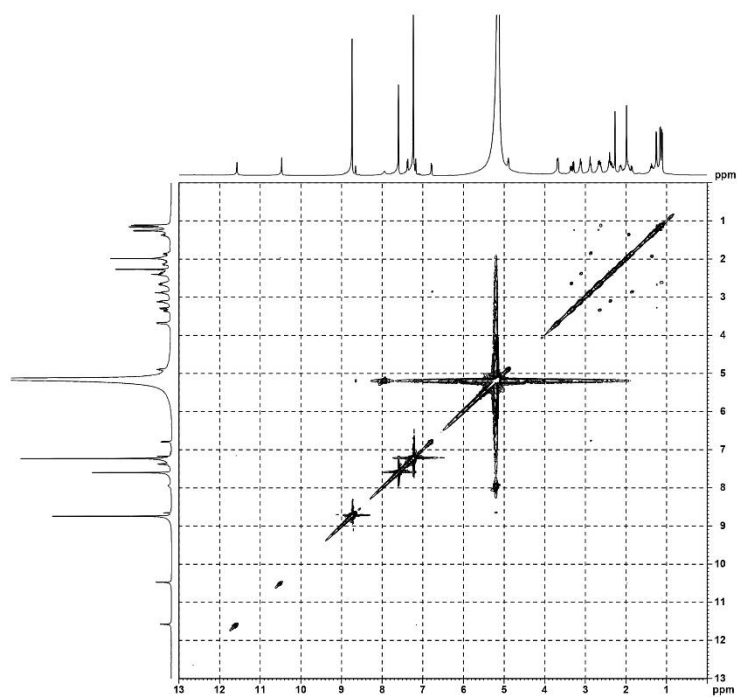


Figure S14. NOESY spectrum of compound **2** in Pyridine-*d*₅

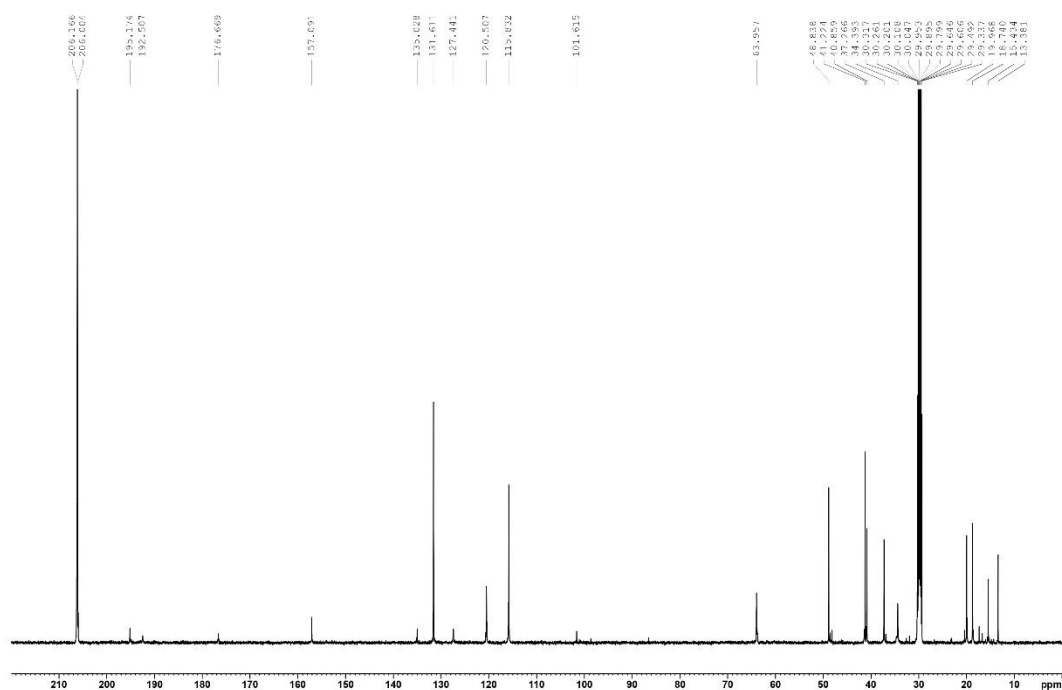


Figure S17. ^{13}C NMR spectrum of compound **3** in Acetone- d_6

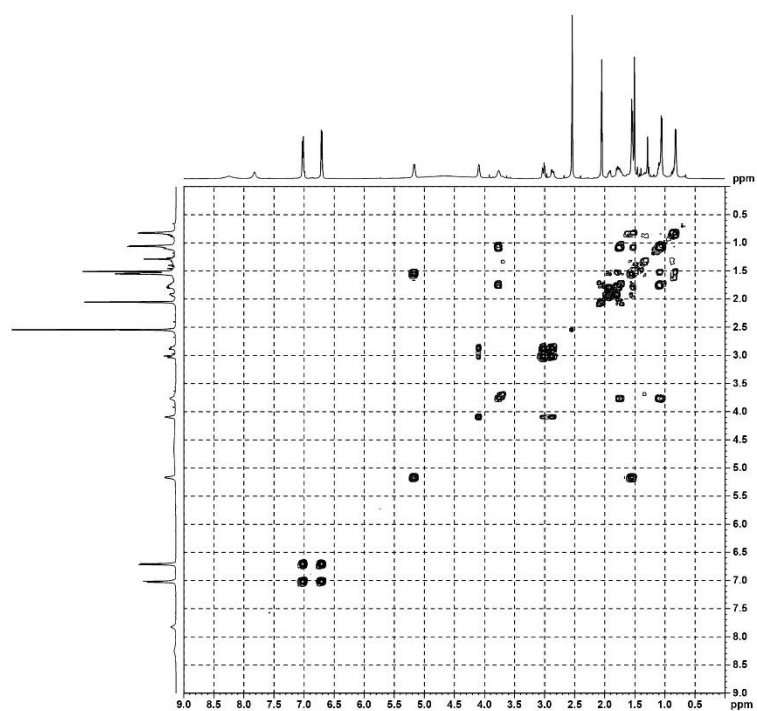


Figure S18. COSY spectrum of compound **3** in Acetone- d_6

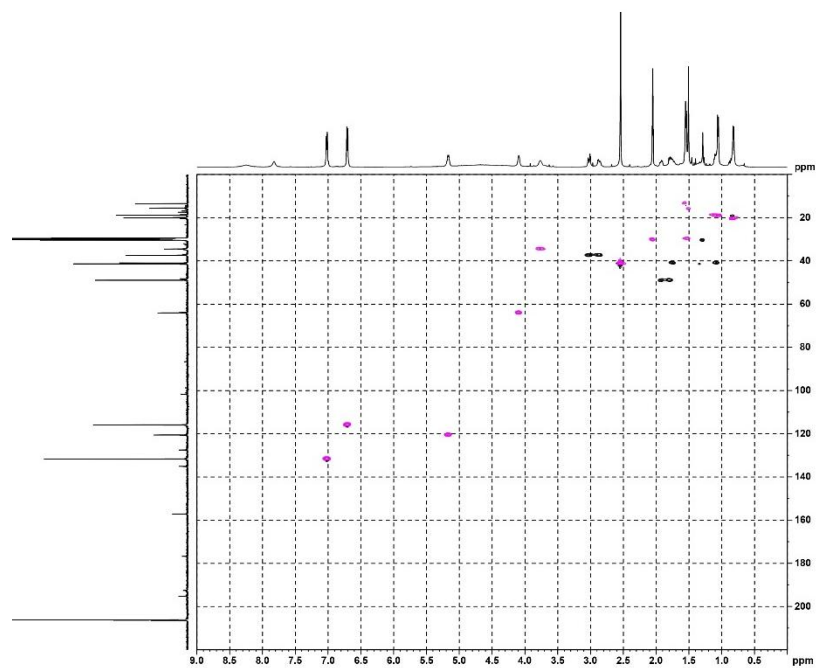


Figure S19. HSQC spectrum of compound **3** in Acetone- d_6

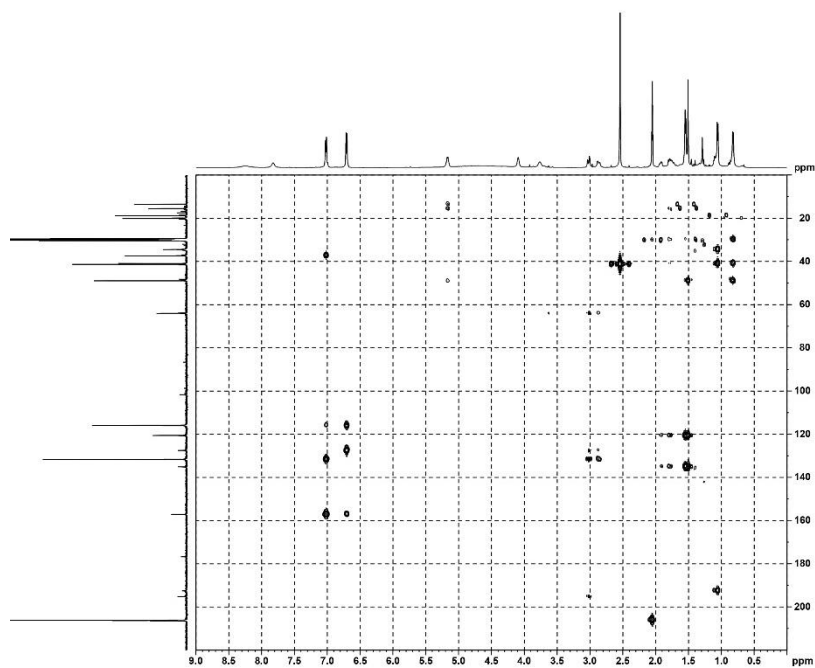


Figure S20. HMBC spectrum of compound **3** in Acetone- d_6

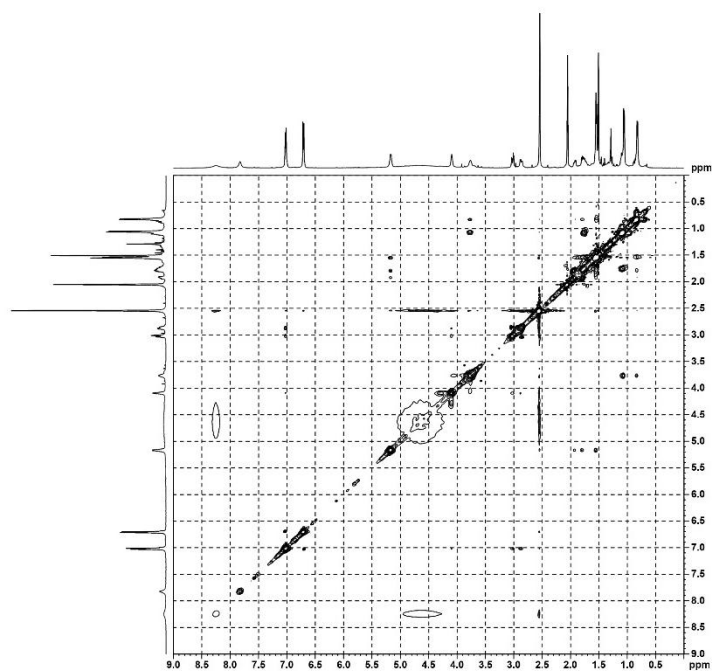


Figure S21. NOESY spectrum of compound **3** in Acetone- d_6

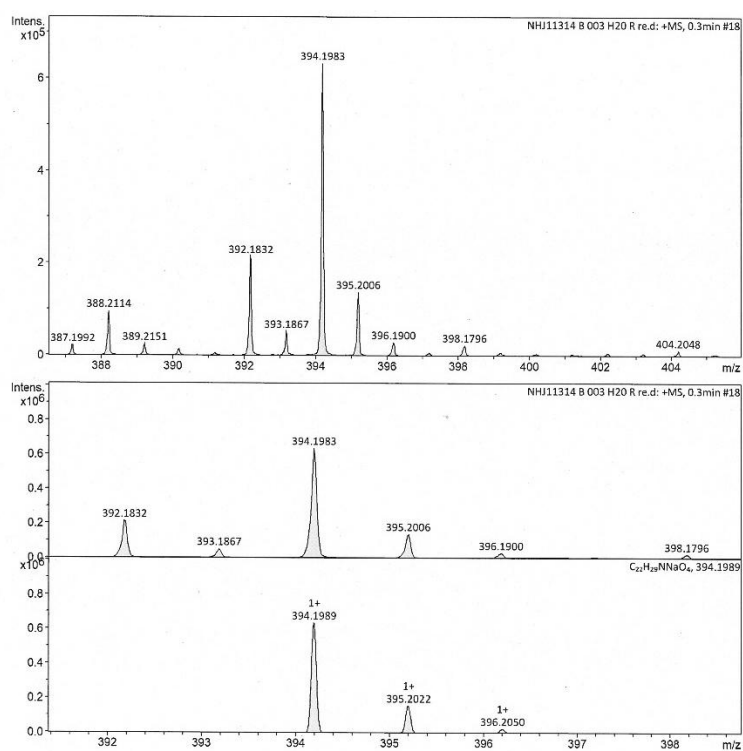


Figure S22. HRESIMS spectrum of compound **4**

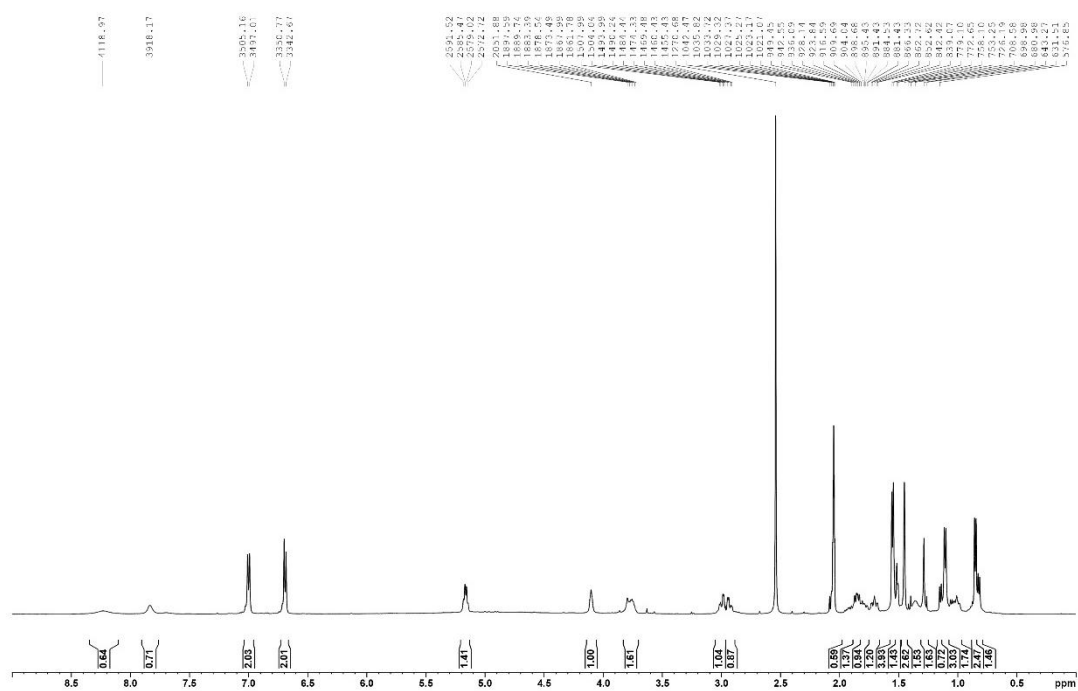


Figure S23. ^1H NMR spectrum of compound **4** in Acetone- d_6

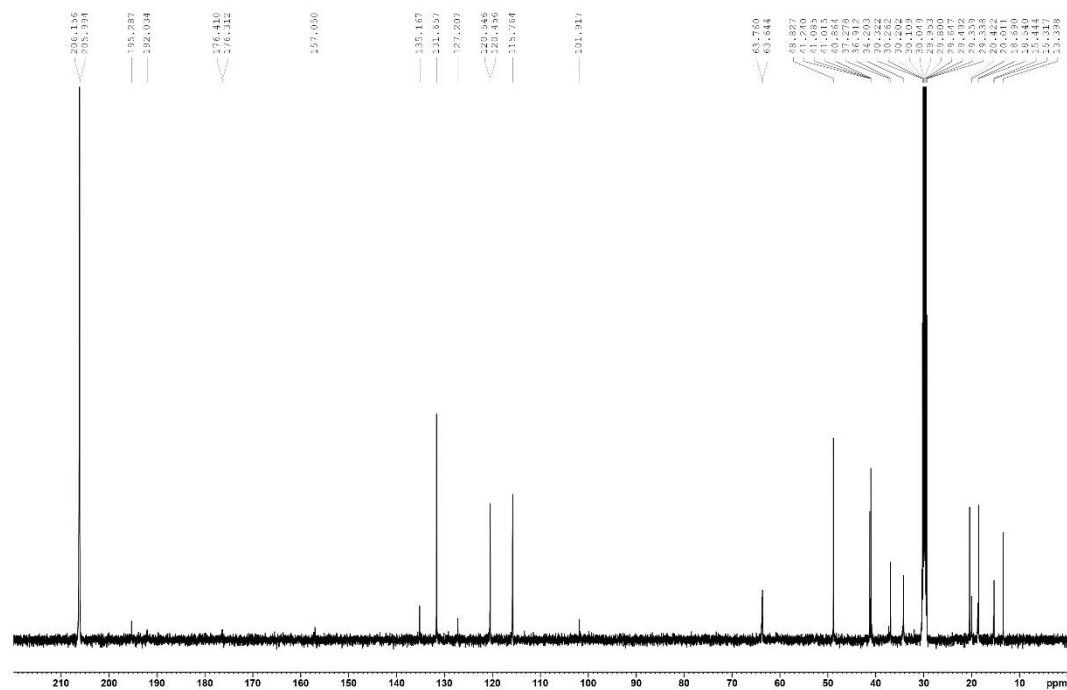


Figure S24. ^{13}C NMR spectrum of compound **4** in Acetone- d_6

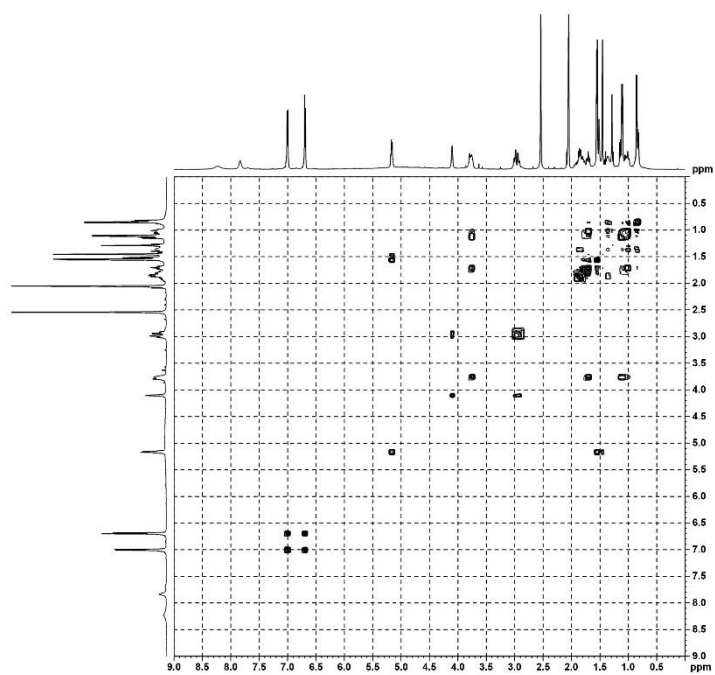


Figure S25. COSY spectrum of compound **4** in Acetone- d_6

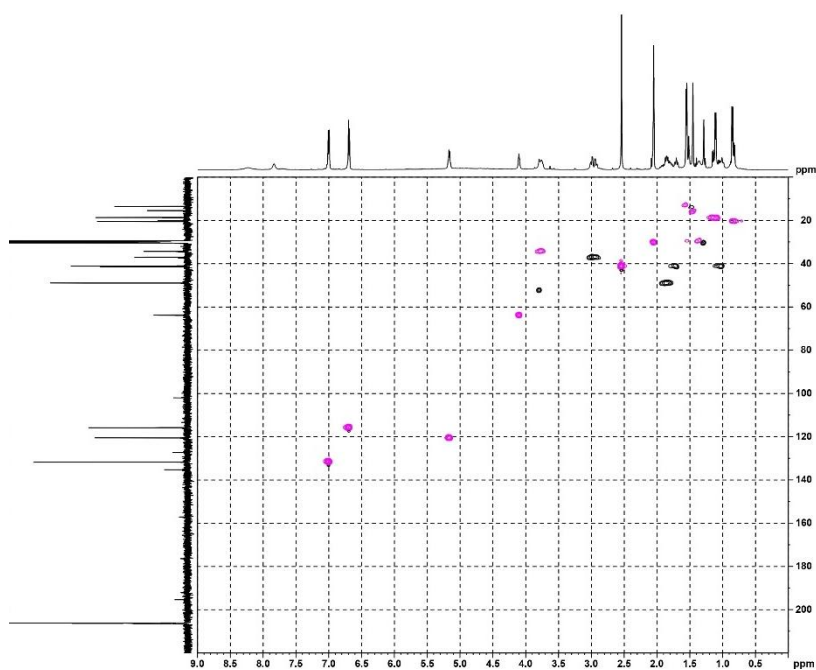


Figure S26. HSQC spectrum of compound **4** in Acetone- d_6

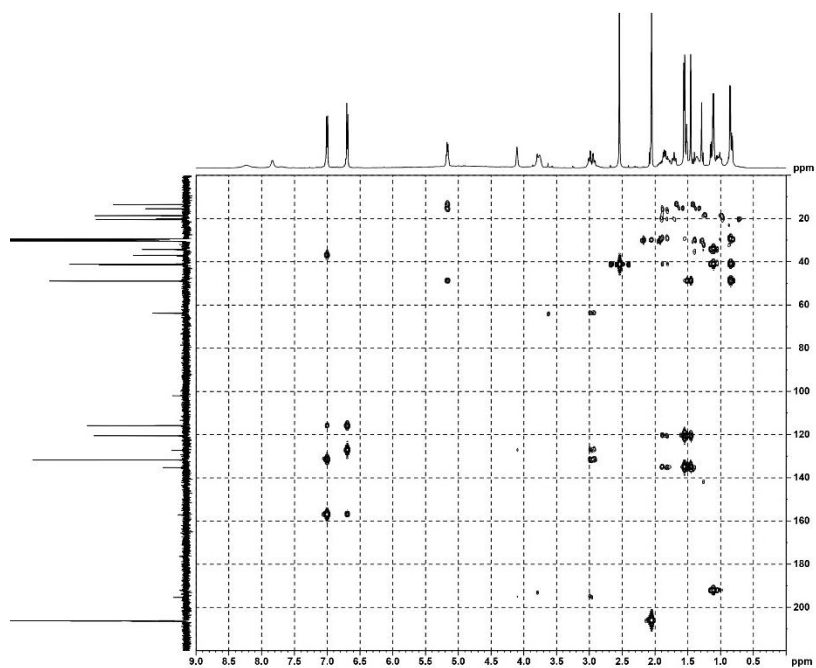


Figure S27. HMBC spectrum of compound **4** in Acetone- d_6

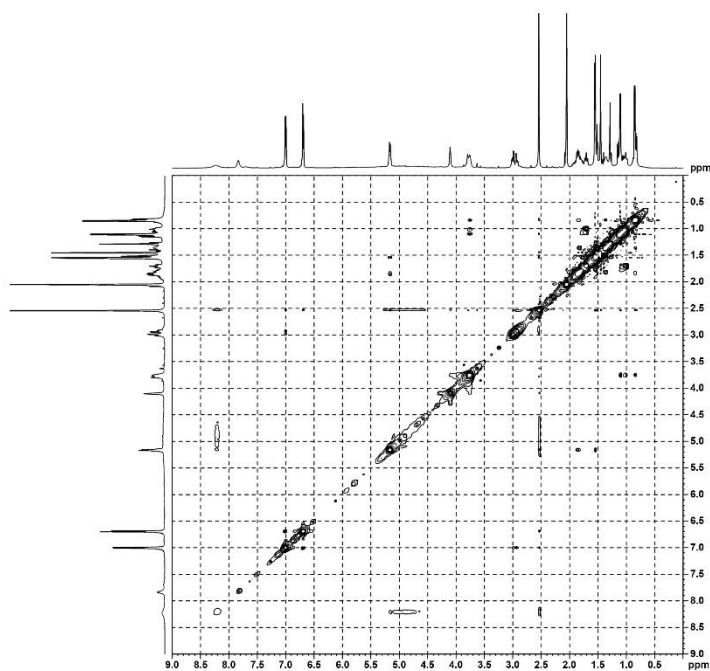


Figure S28. NOESY spectrum of compound **4** in Acetone- d_6

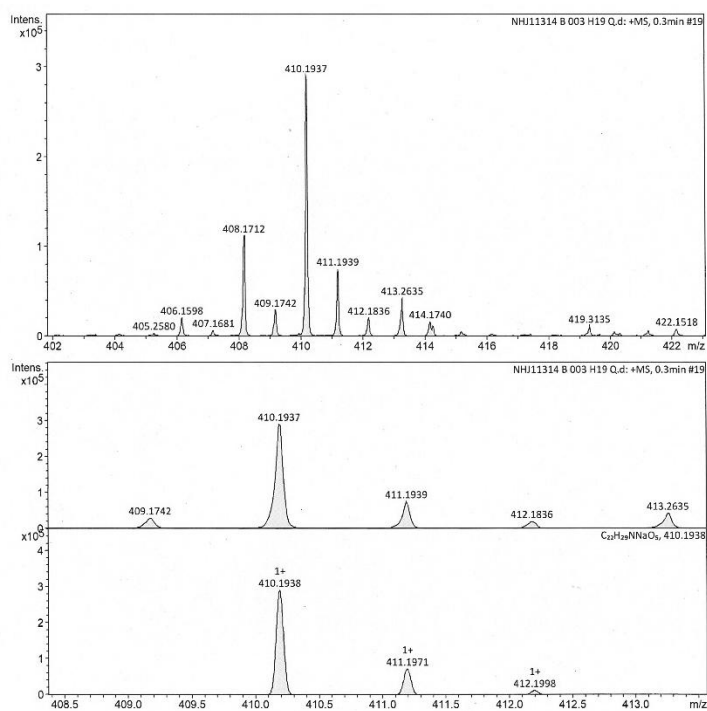


Figure S29. HRESIMS spectrum of compound **5**

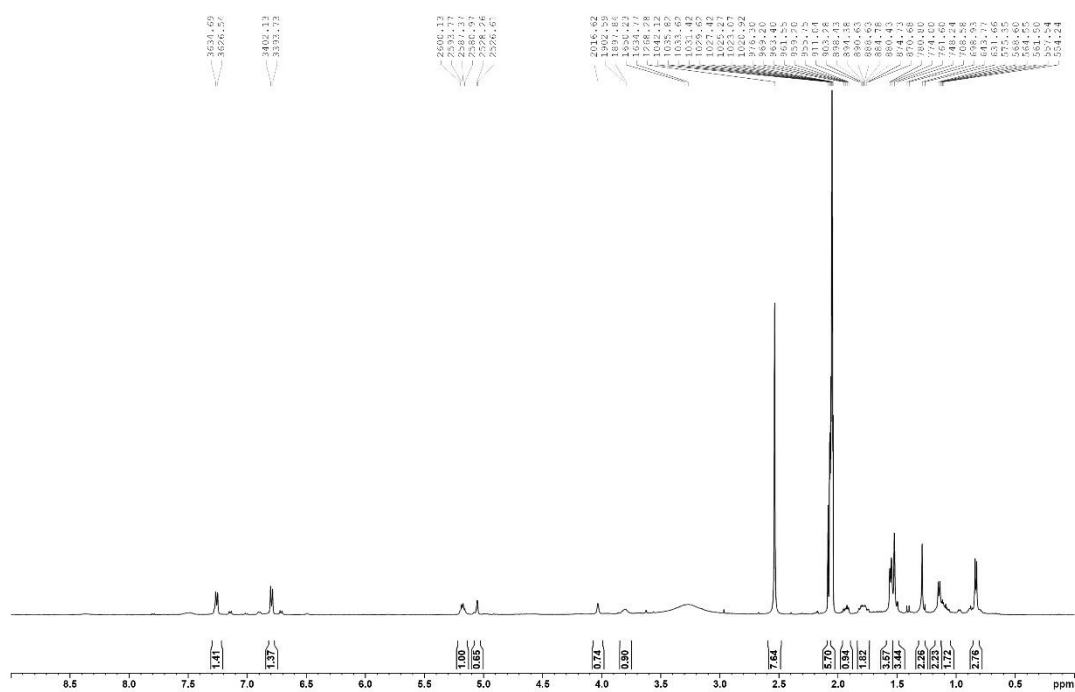


Figure S30. ¹H NMR spectrum of compound **5** in Acetone-*d*₆

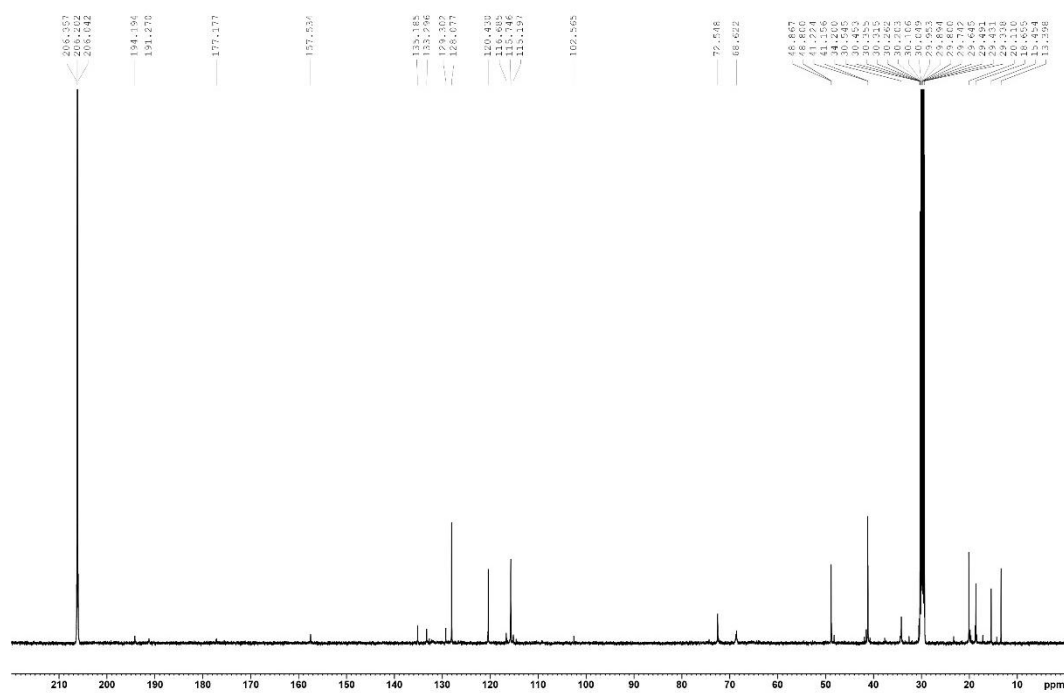


Figure S31. ^{13}C NMR spectrum of compound **5** in Acetone- d_6

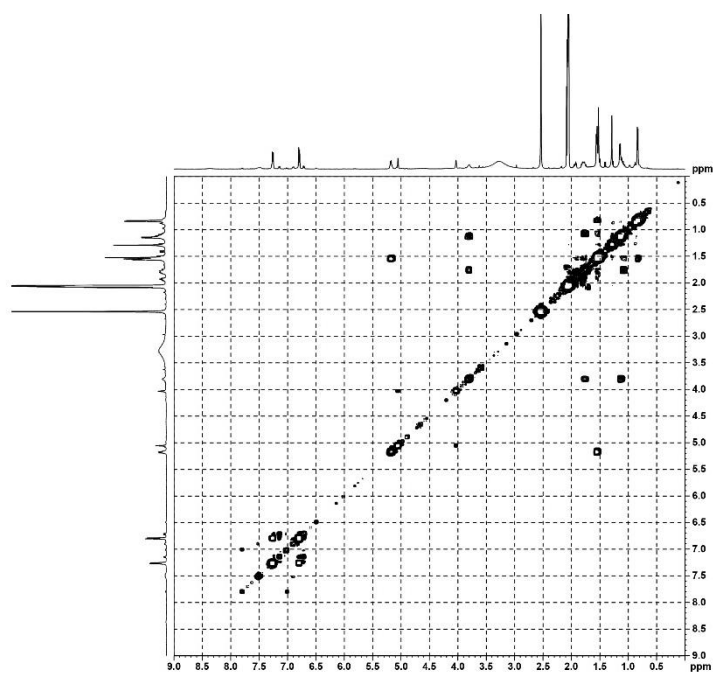


Figure S32. COSY spectrum of compound **5** in Acetone- d_6

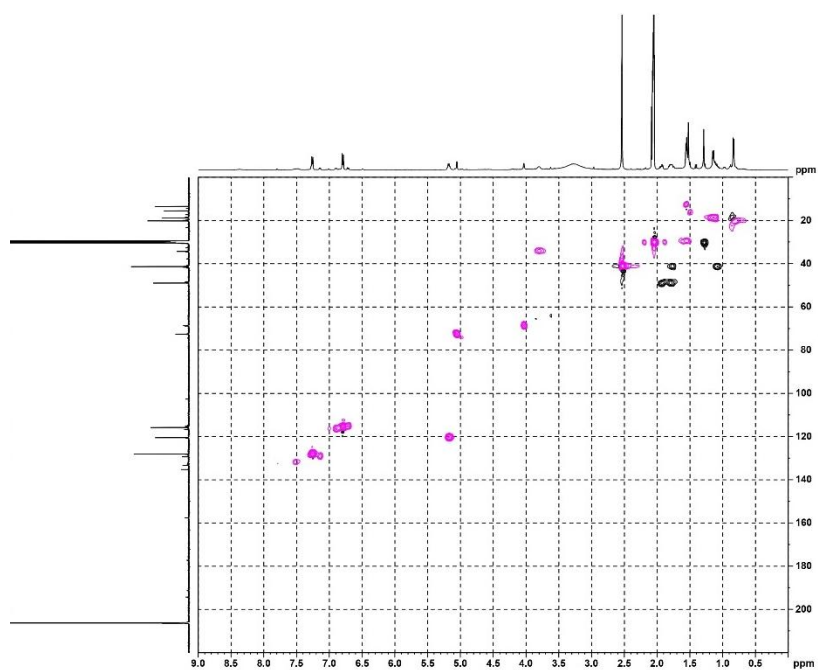


Figure S33. HSQC spectrum of compound **5** in Acetone- d_6

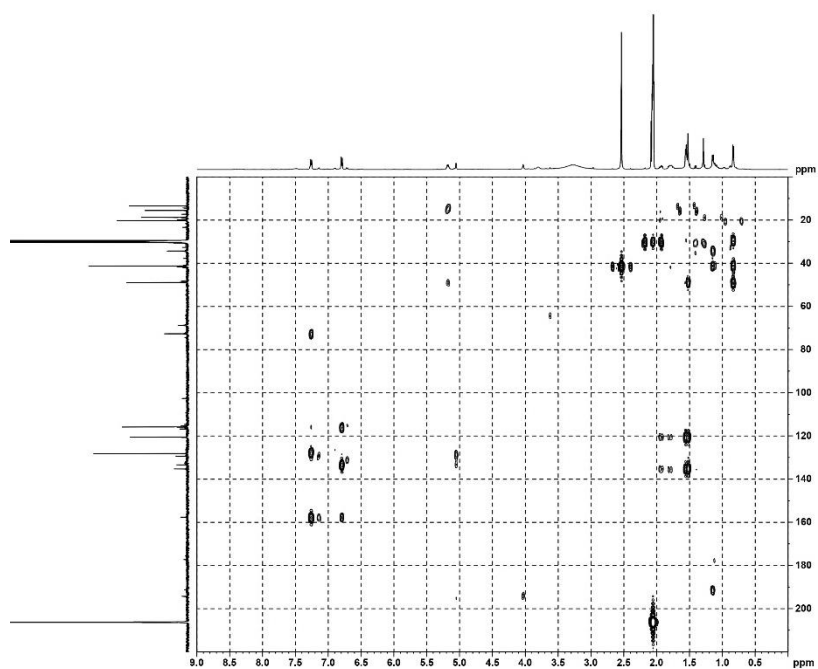


Figure S34. HMBC spectrum of compound **5** in Acetone- d_6

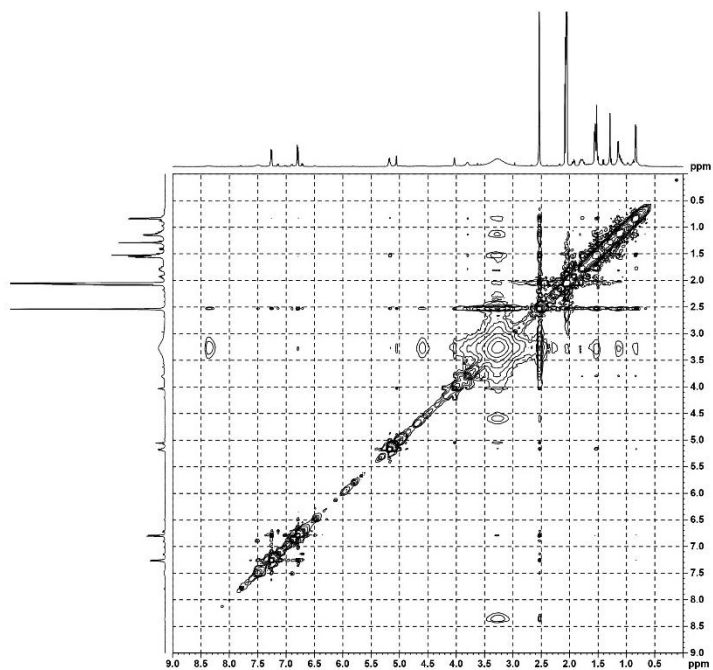


Figure S35. NOESY spectrum of compound **5** in Acetone- d_6

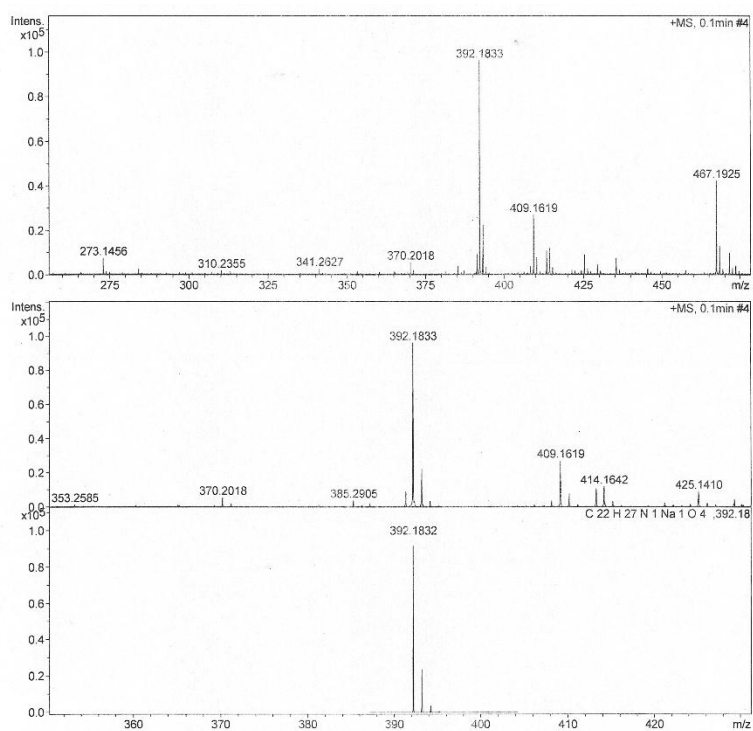


Figure S36. HRESIMS spectrum of compound **6**

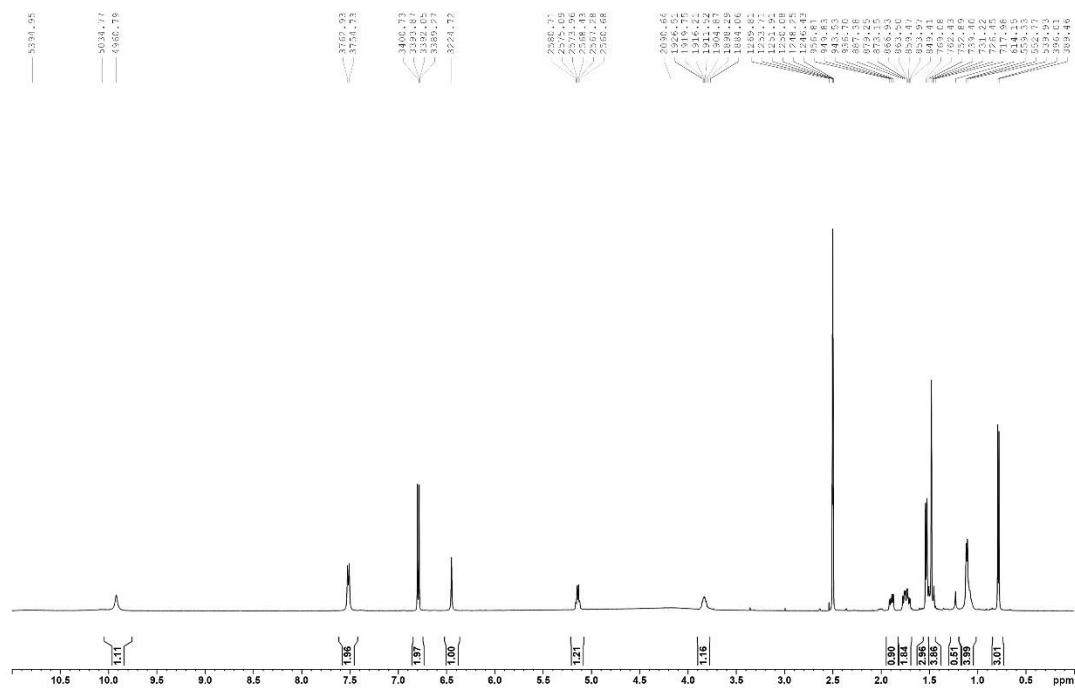


Figure S37. ¹H NMR spectrum of compound **6** in DMSO-*d*₆

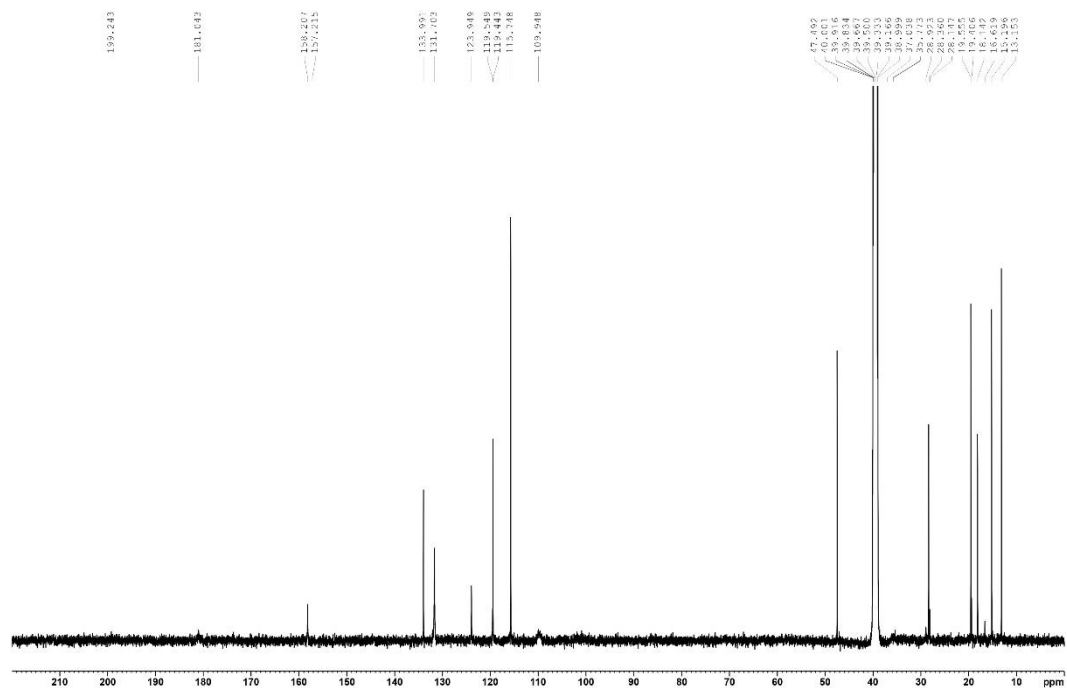


Figure S38. ¹³C NMR spectrum of compound **6** in DMSO-*d*₆

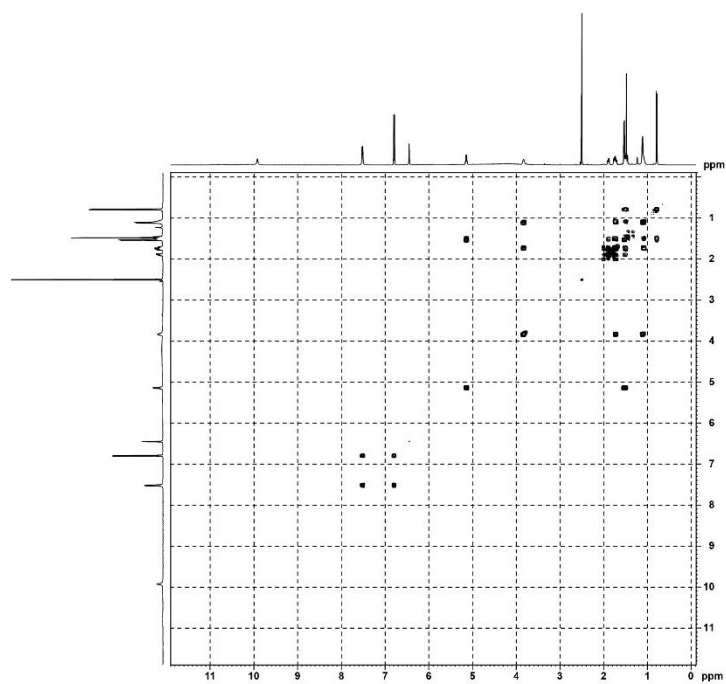


Figure S39. COSY spectrum of compound **6** in DMSO- d_6

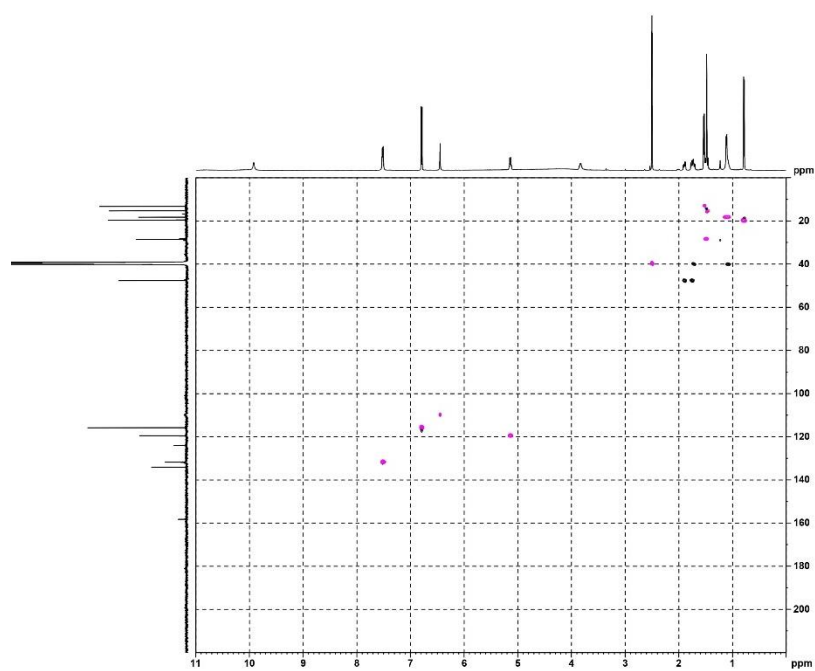


Figure S40. HSQC spectrum of compound **6** in DMSO- d_6

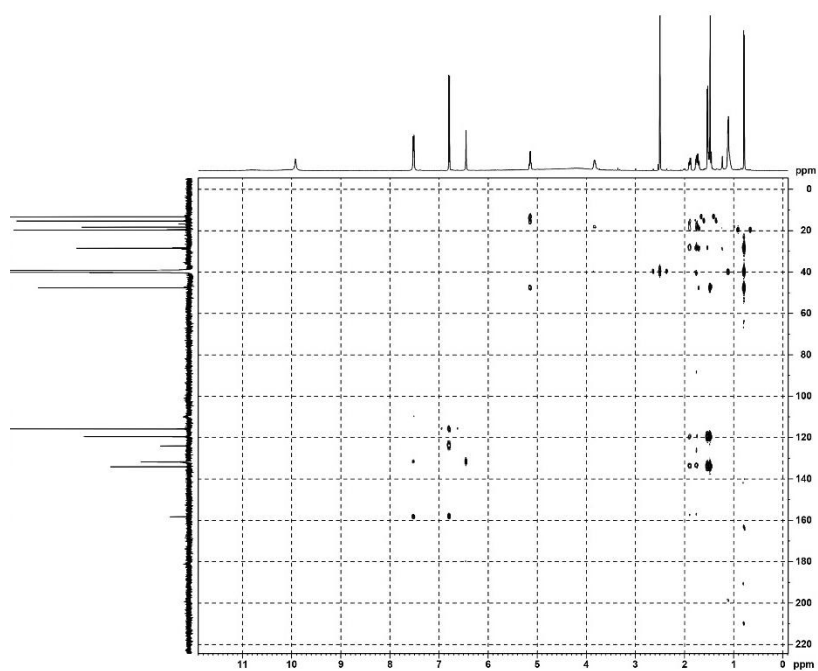


Figure S41. HMBC spectrum of compound **6** in DMSO- d_6

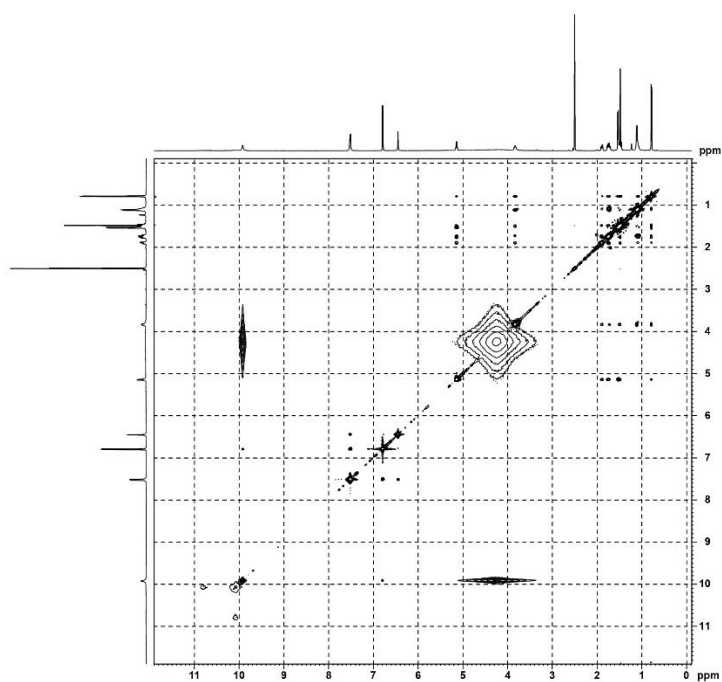


Figure S42. NOESY spectrum of compound **6** in DMSO- d_6

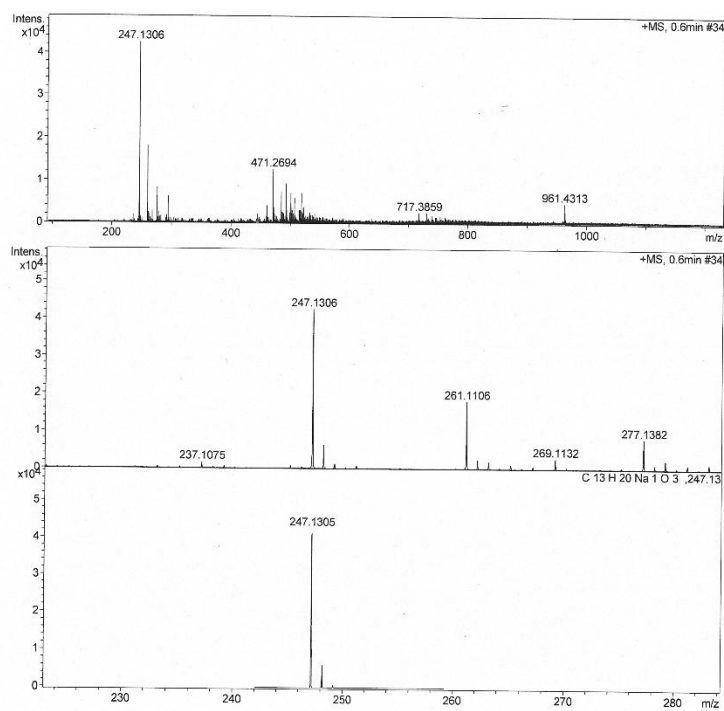


Figure S43. HRESIMS spectrum of compound **7**

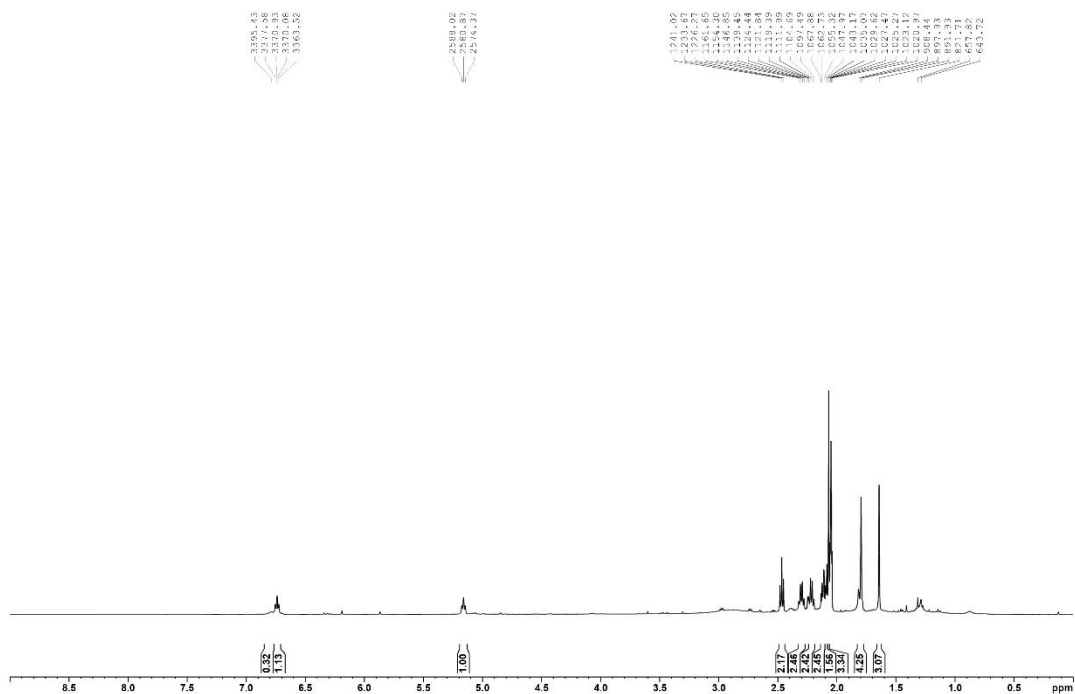


Figure S44. ^1H NMR spectrum of compound **7** in Acetone- d_6

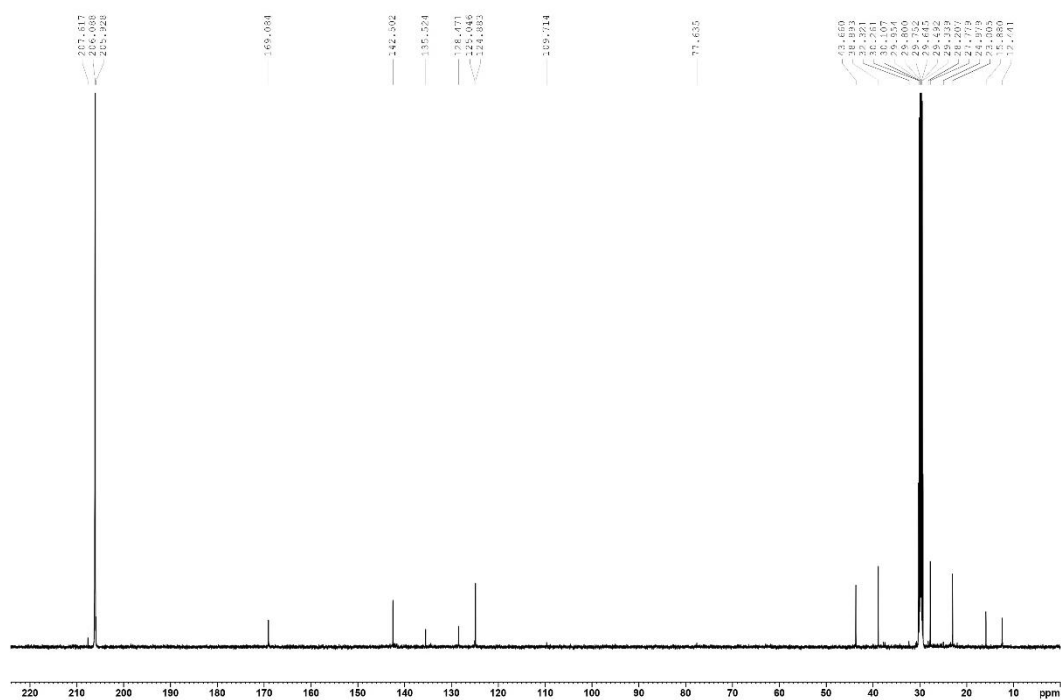


Figure S45. ^{13}C NMR spectrum of compound **7** in Acetone- d_6

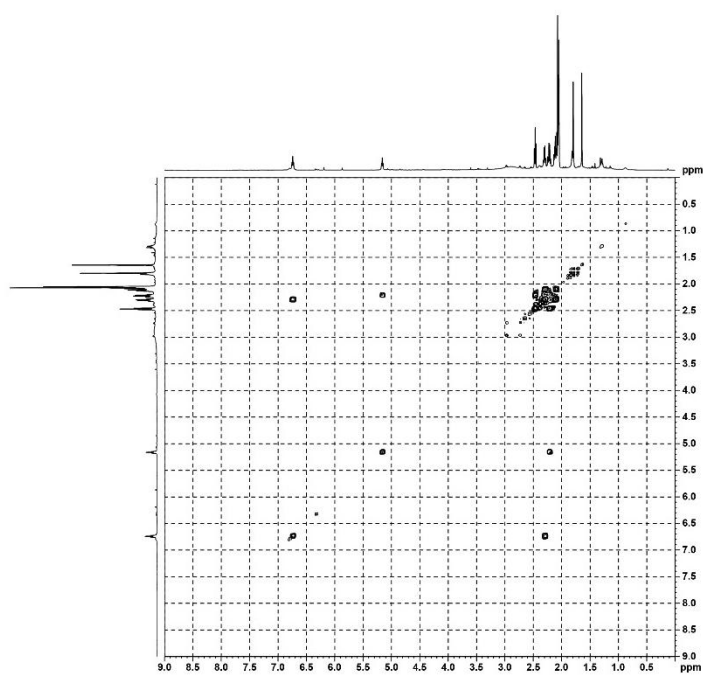


Figure S46. COSY spectrum of compound **7** in Acetone- d_6

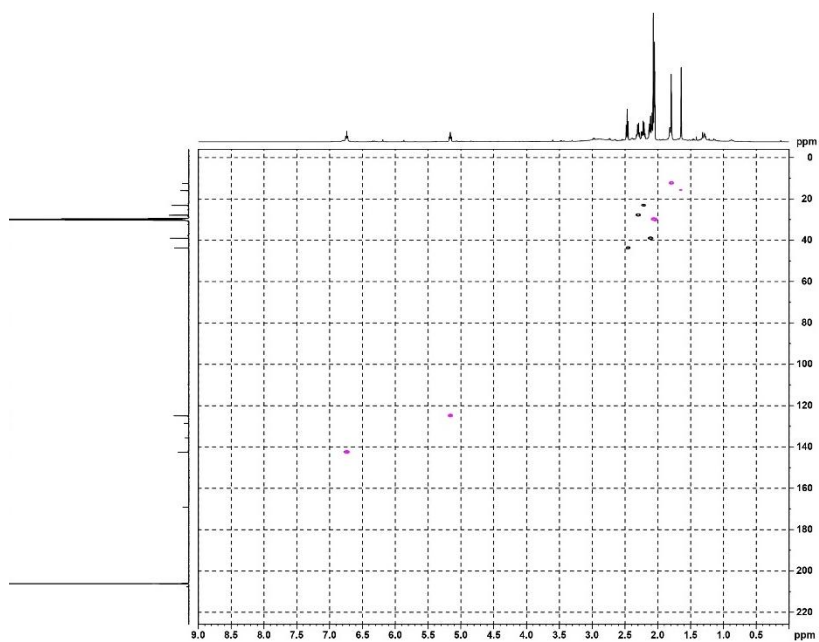


Figure S47. HSQC spectrum of compound **7** in Acetone- d_6

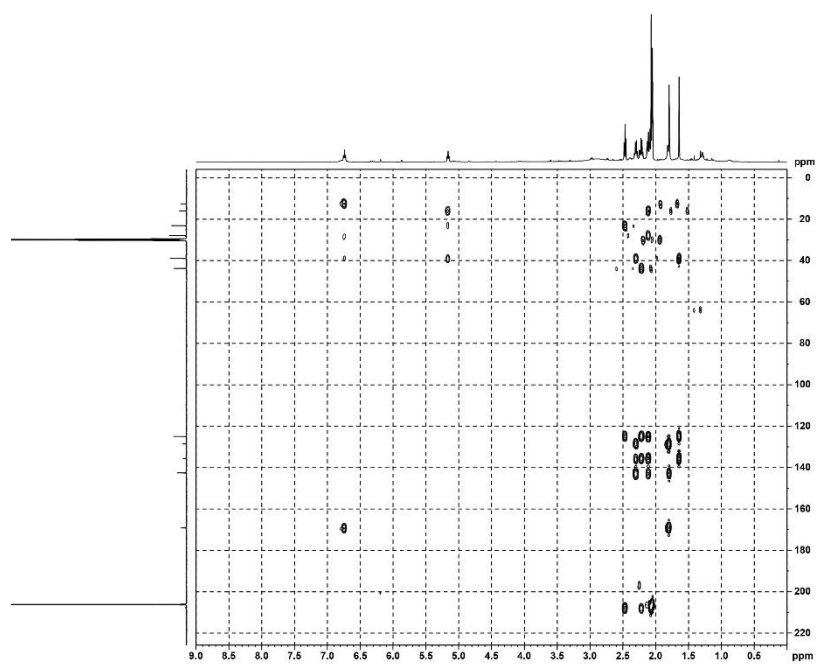


Figure S48. HMBC spectrum of compound **7** in Acetone- d_6

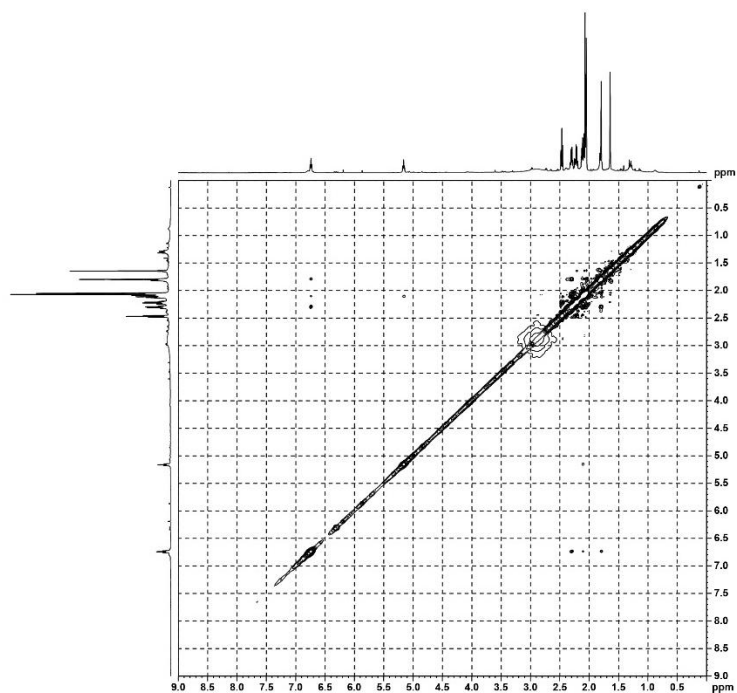


Figure S49. NOESY spectrum of compound **7** in Acetone- d_6

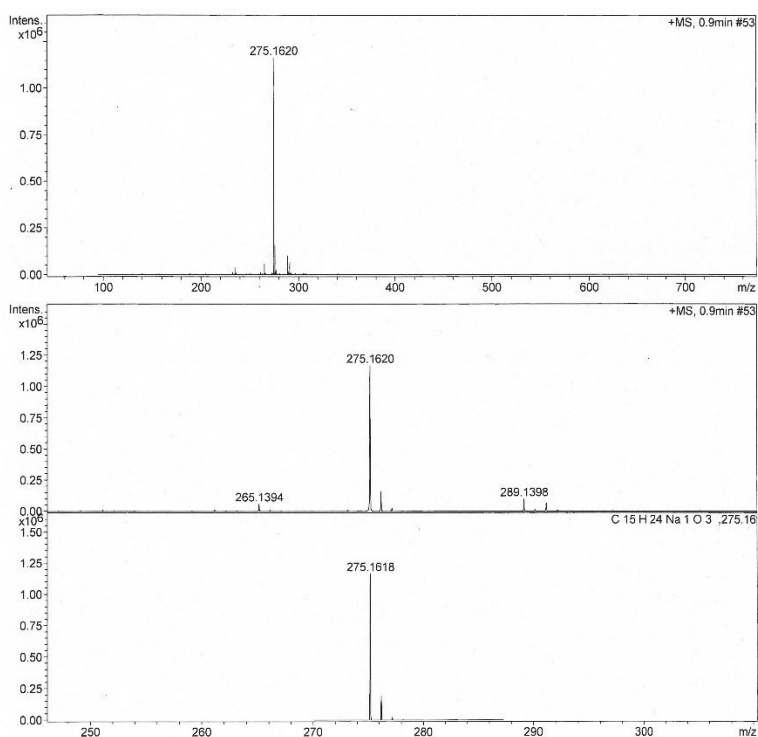
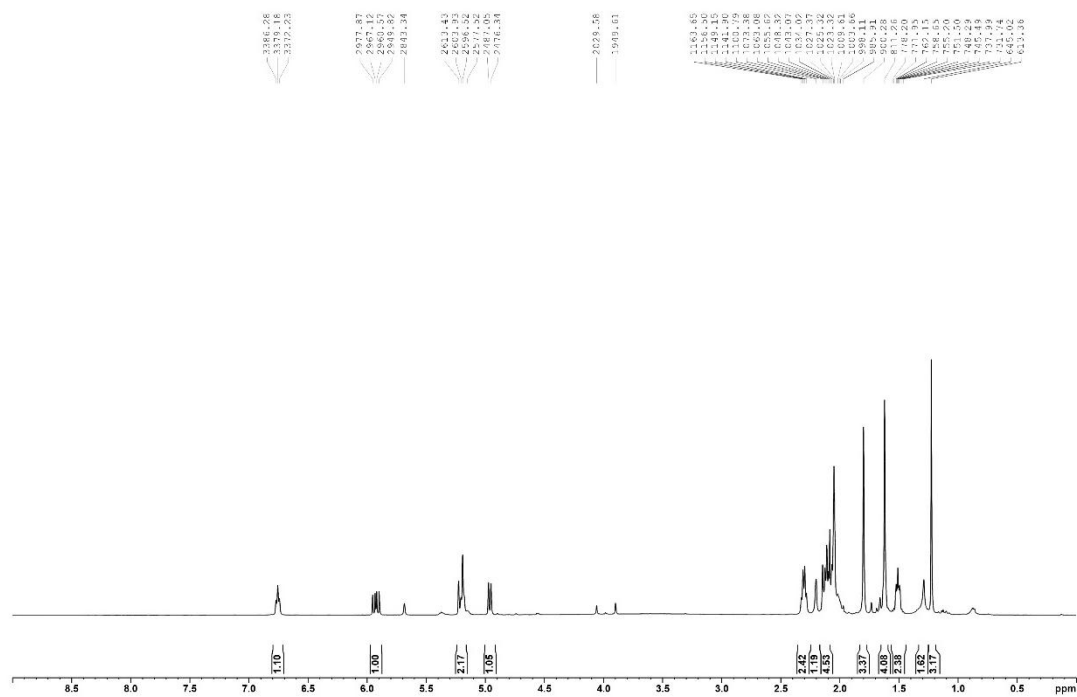


Figure S50. HRESIMS spectrum of compound **8**



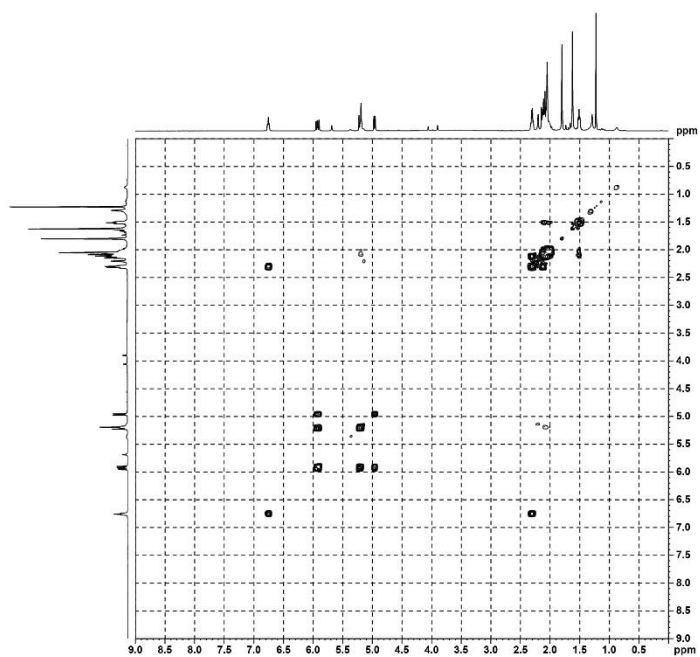


Figure S53. COSY spectrum of compound **8** in Acetone- d_6

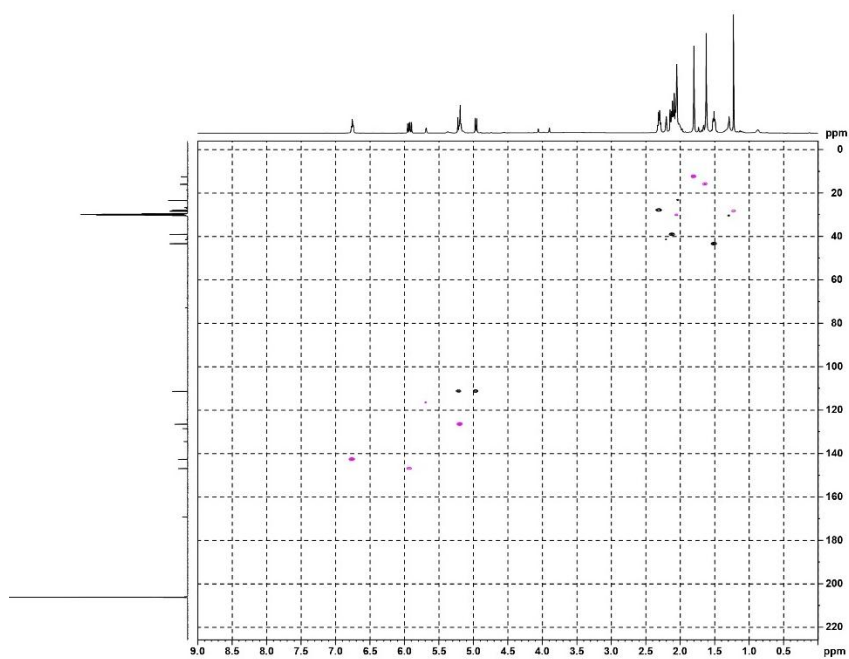


Figure S54. HSQC spectrum of compound **8** in Acetone- d_6

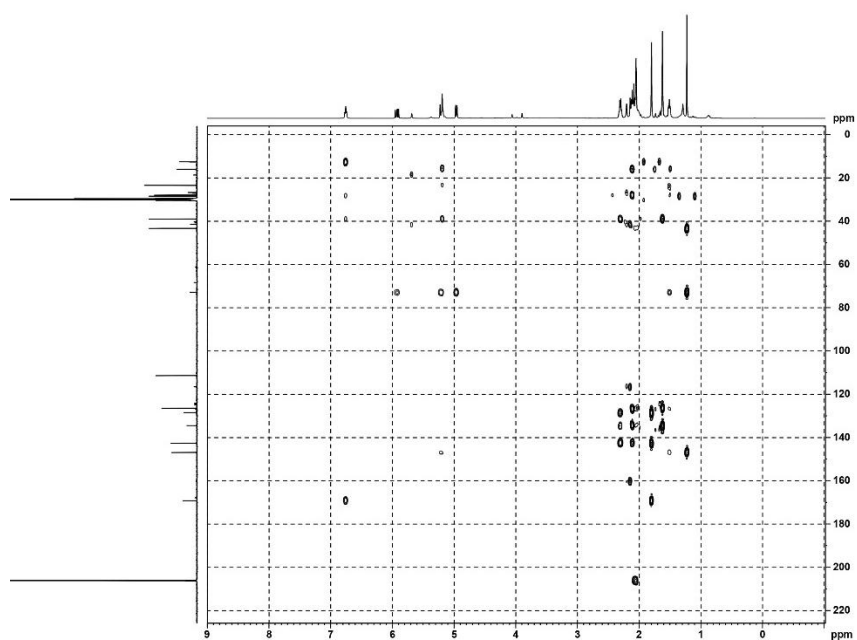


Figure S55. HMBC spectrum of compound **8** in Acetone- d_6

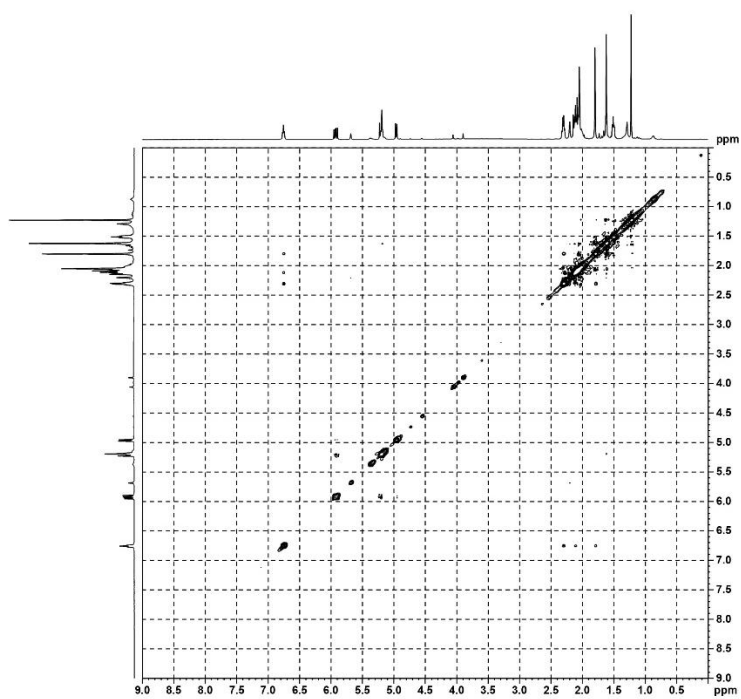


Figure S56. NOESY spectrum of compound **8** in Acetone- d_6

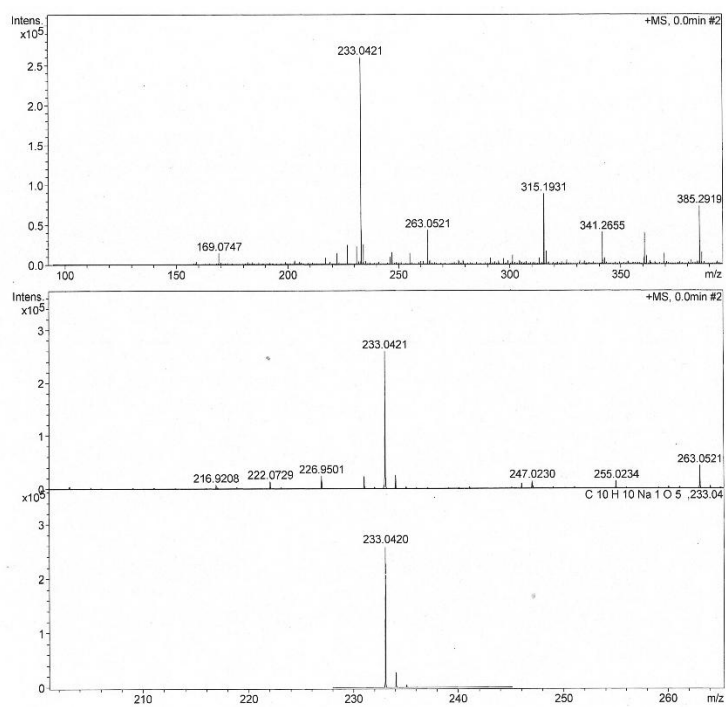


Figure S57. HRESIMS spectrum of compound **9**

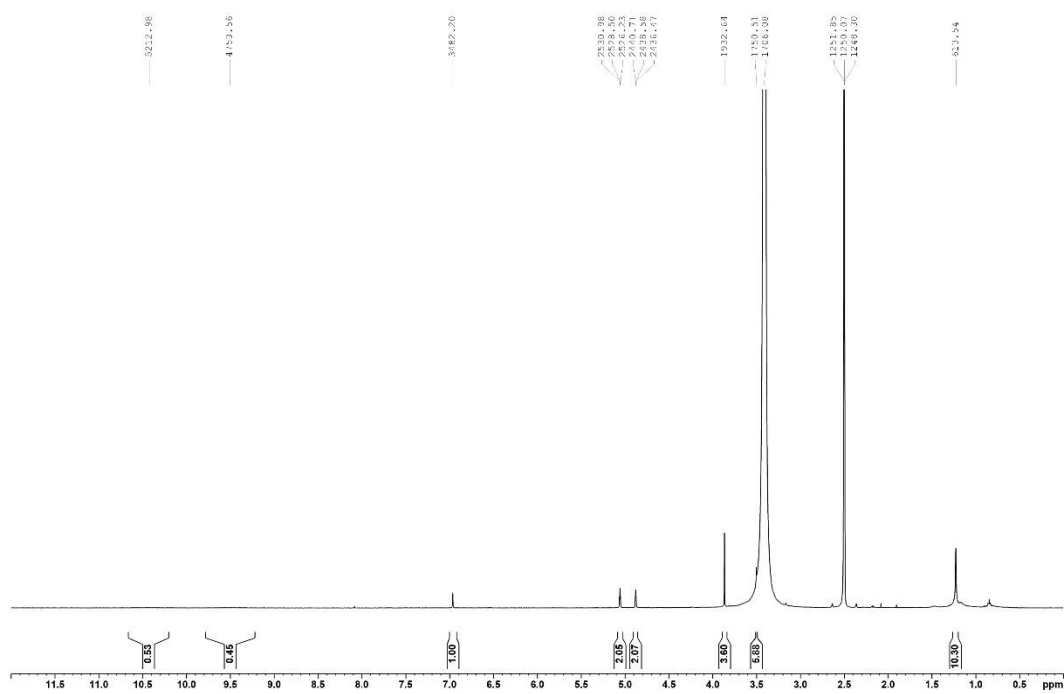


Figure S58. ^1H NMR spectrum of compound **9** in $\text{DMSO-}d_6$

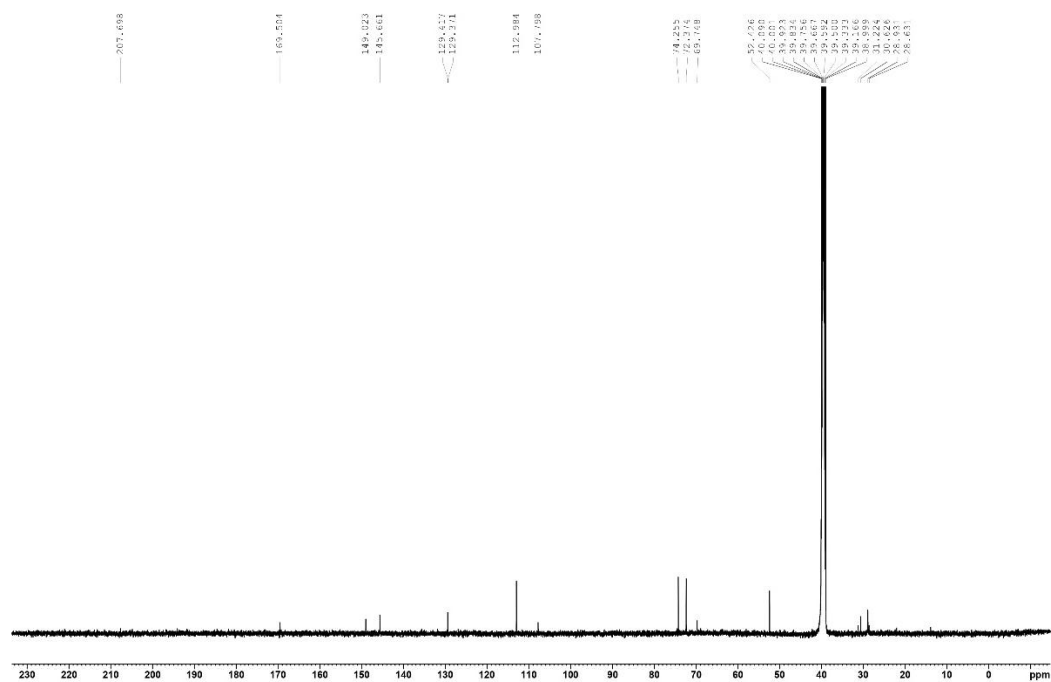


Figure S59. ^{13}C NMR spectrum of compound **9** in $\text{DMSO-}d_6$

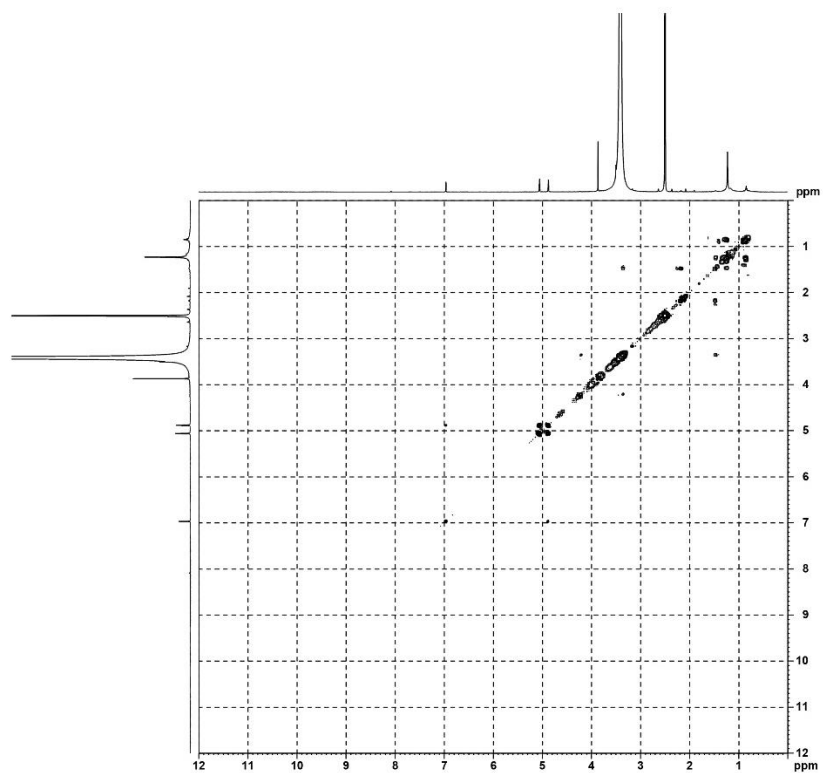
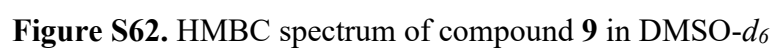
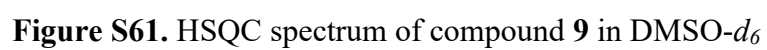


Figure S60. COSY spectrum of compound **9** in $\text{DMSO-}d_6$



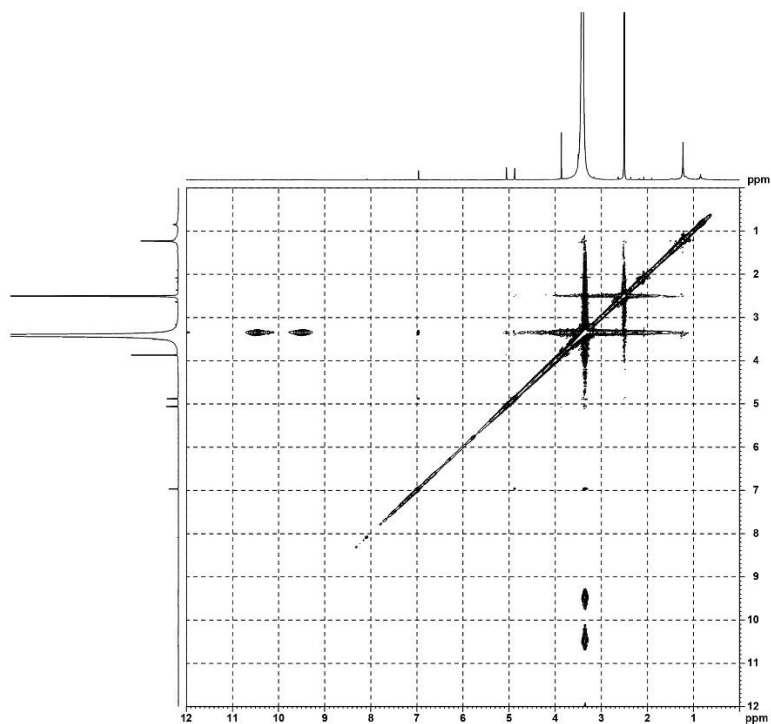


Figure S63. NOESY spectrum of compound **9** in DMSO-*d*₆

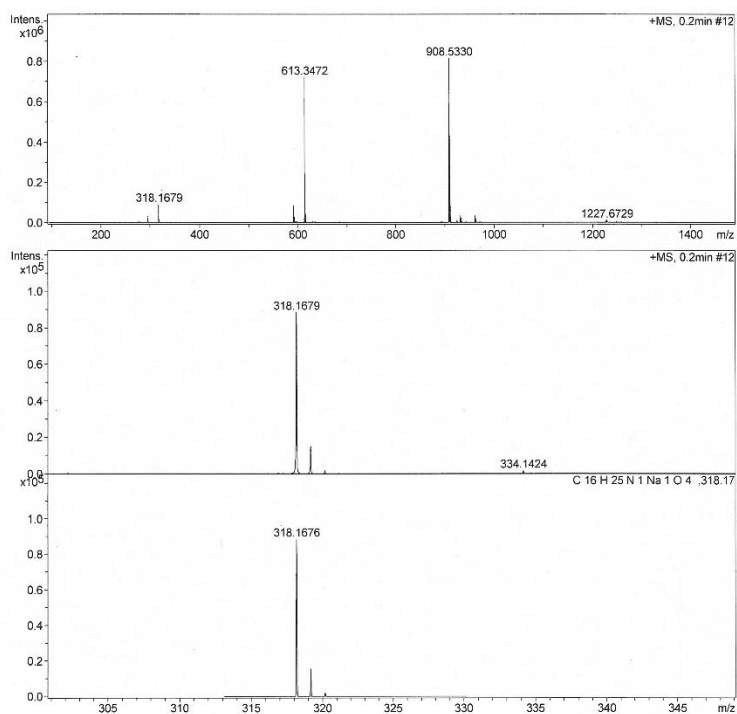


Figure S64. HRESIMS spectrum of akanthomycin

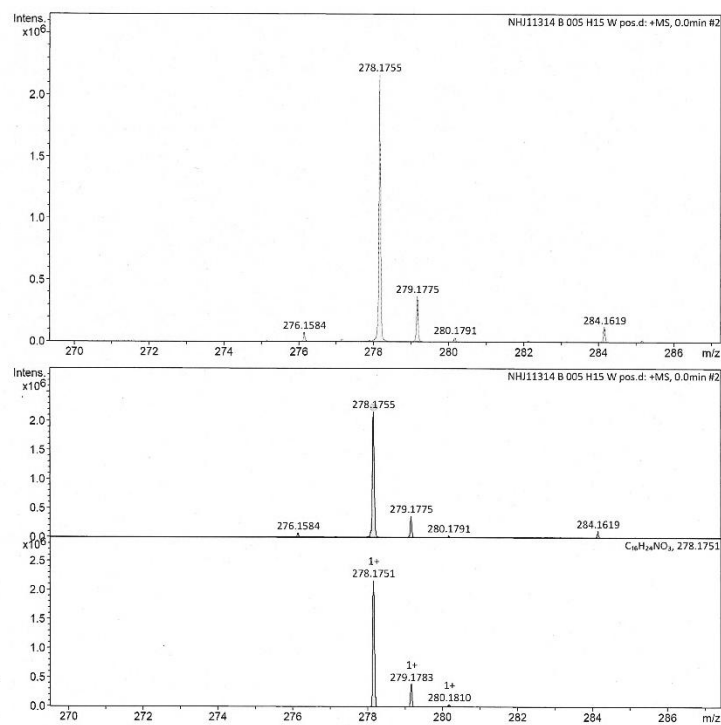


Figure S67. HRESIMS spectrum of cordypyridone A

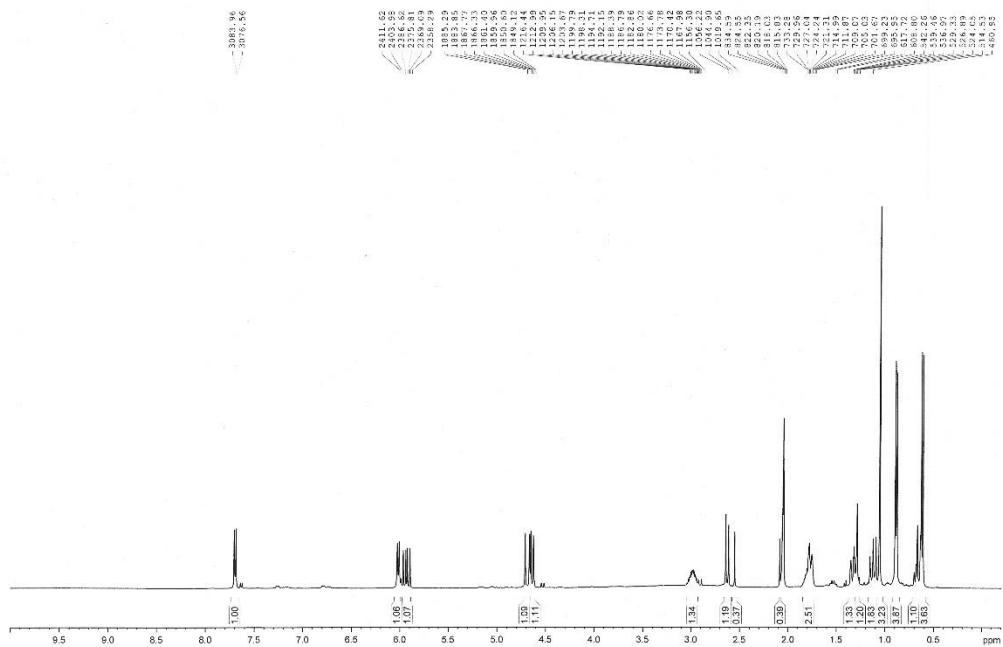


Figure S68. 1H NMR spectrum of cordypyridone A in $Acetone-d_6$

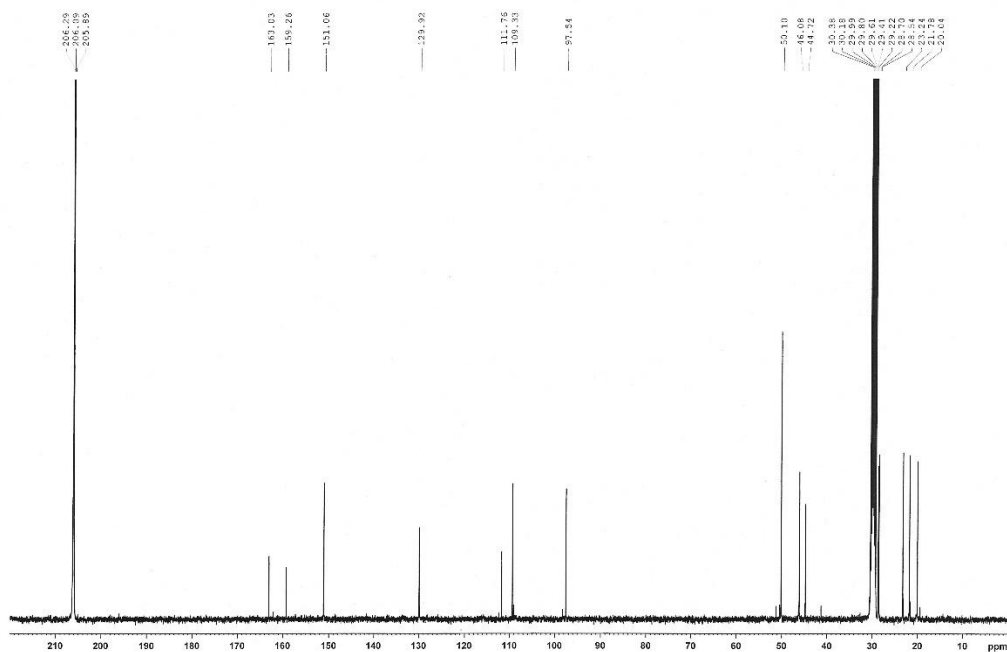


Figure S69. ^{13}C NMR spectrum of cordypyridone A in Acetone- d_6

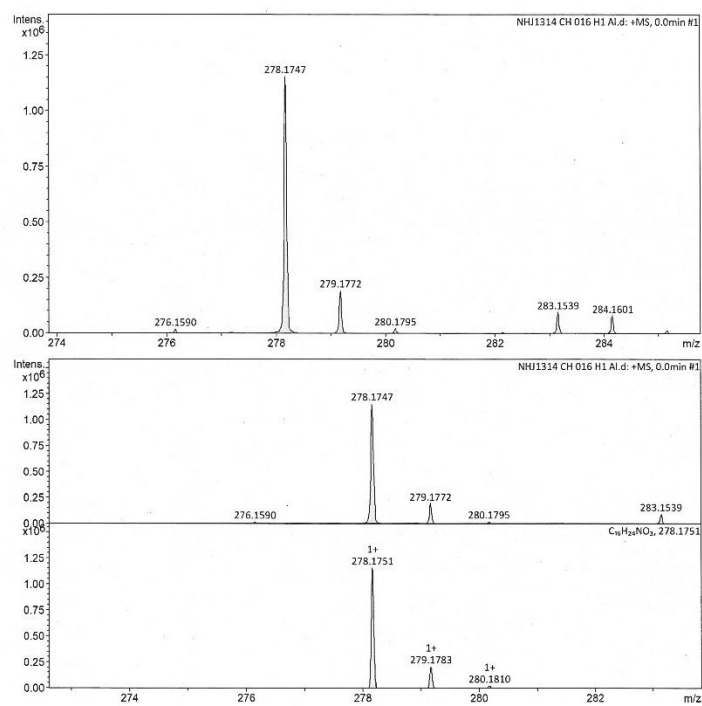
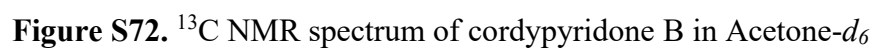
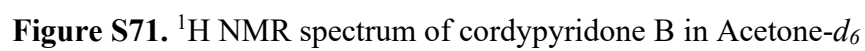


Figure S70. HRESIMS spectrum of cordypyridone B



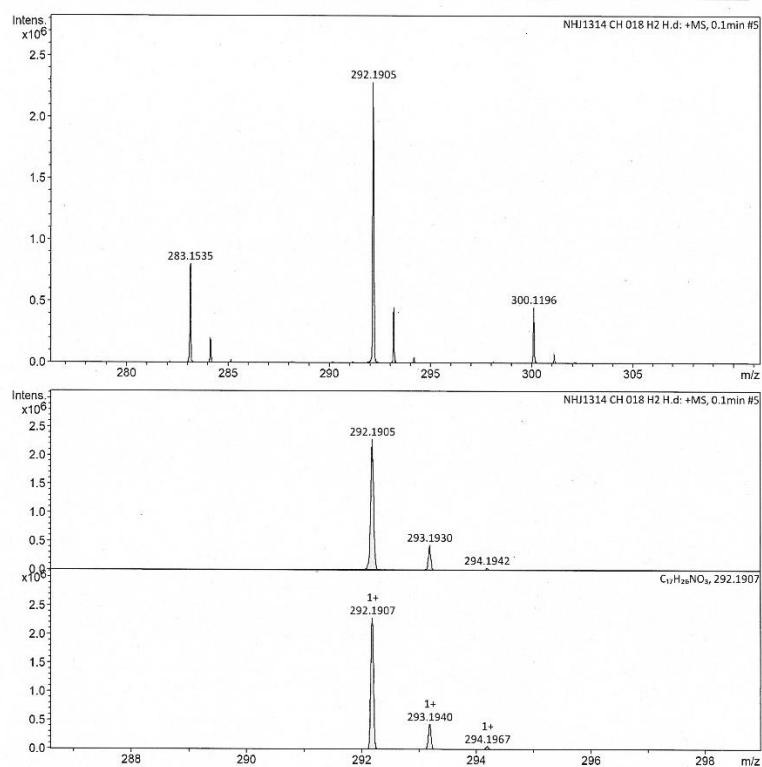


Figure S73. HRESIMS spectrum of cordypyridone C

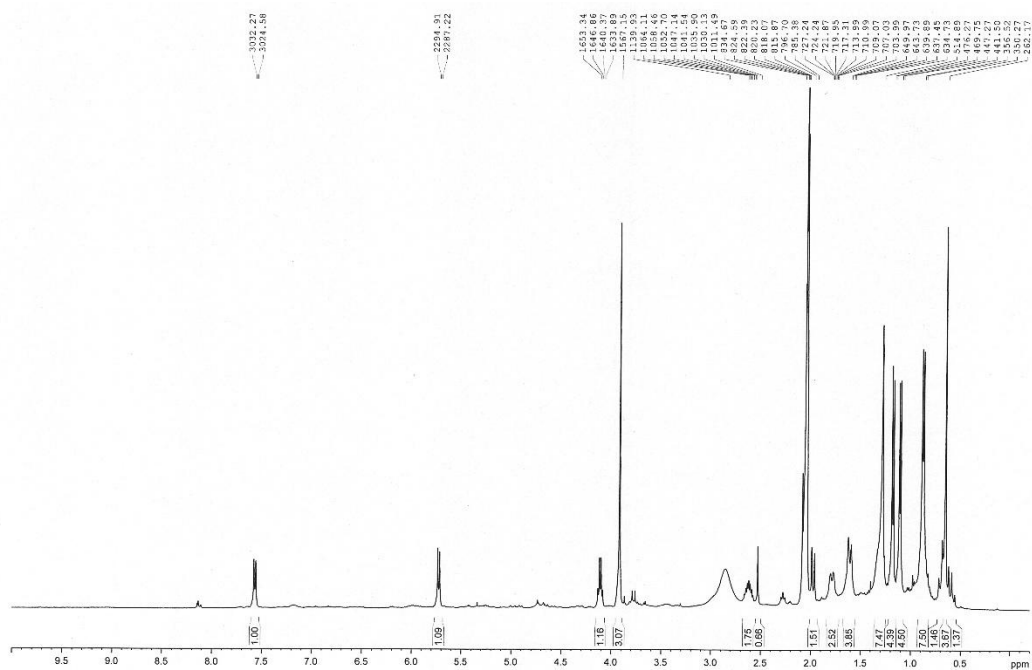


Figure S74. ¹H NMR spectrum of cordypyridone C in Acetone-*d*₆

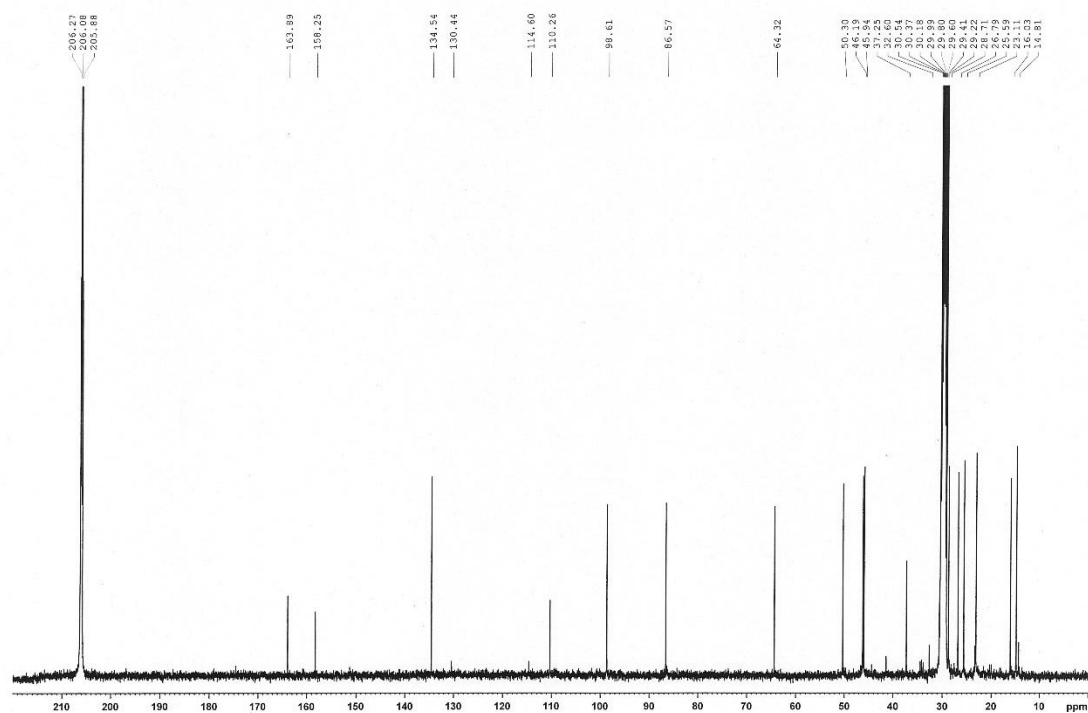


Figure S75. ^{13}C NMR spectrum of cordypiridone C in Acetone- d_6

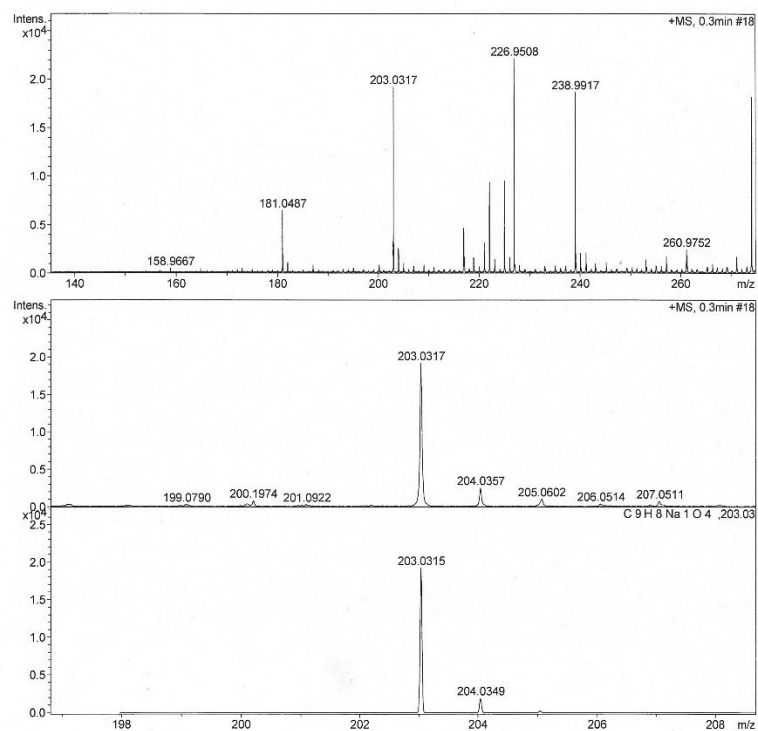
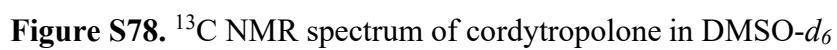
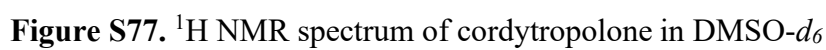


Figure S76. HRESIMS spectrum of cordytropolone



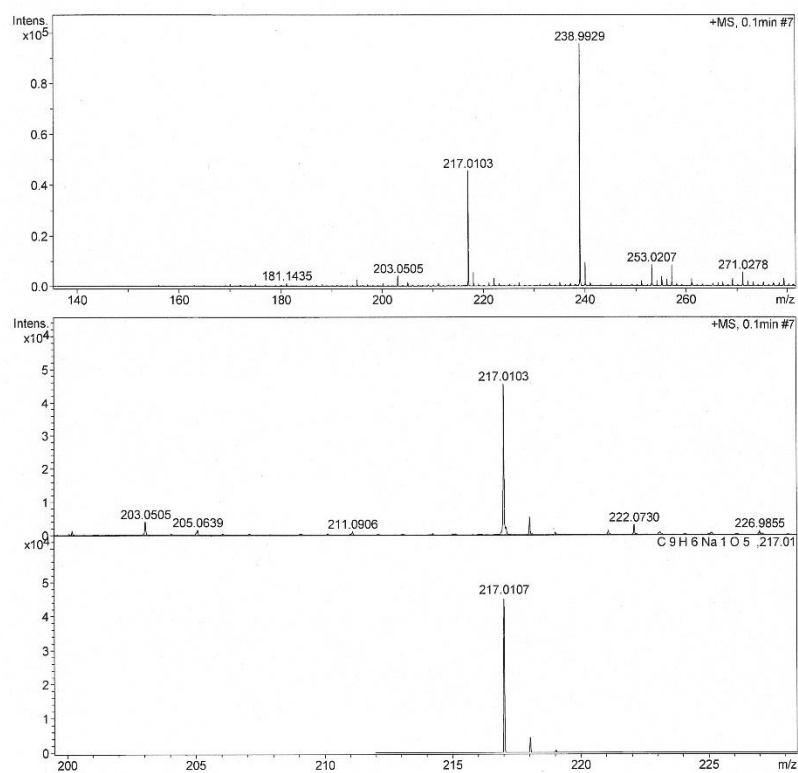


Figure S79. HRESIMS spectrum of stipitalide

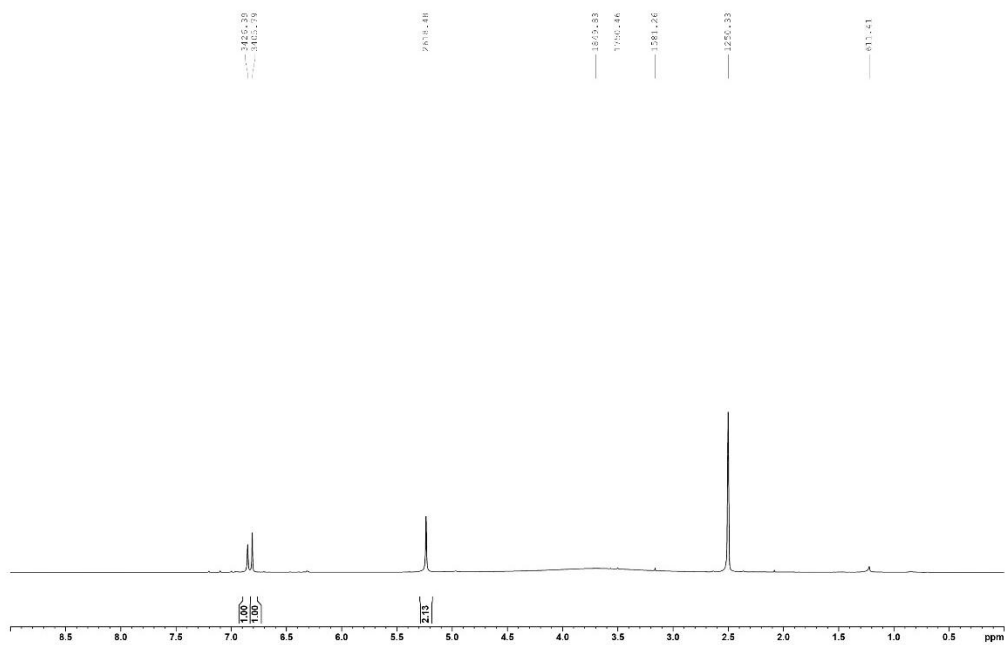


Figure S80. ^1H NMR spectrum of stipitalide in $\text{DMSO}-d_6$

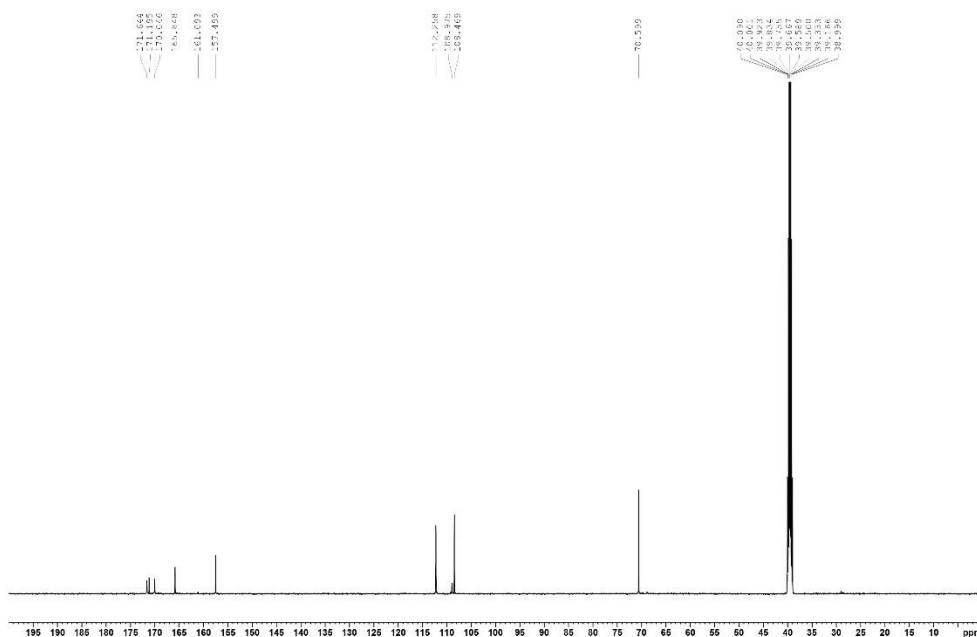


Figure S81. ^{13}C NMR spectrum of stipitalide in $\text{DMSO-}d_6$

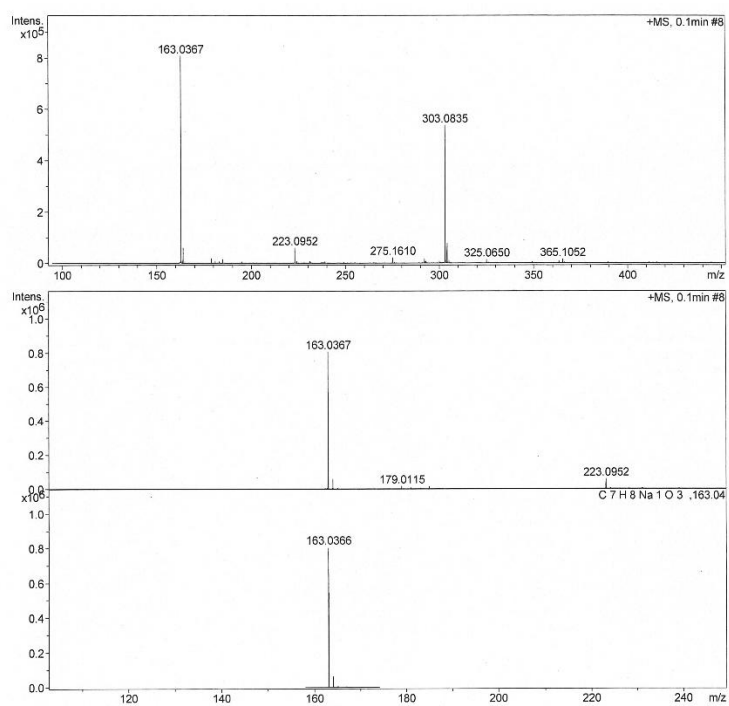


Figure S82. HRESIMS spectrum of 4-hydroxy-3,6-dimethyl-2*H*-pyran-2-one

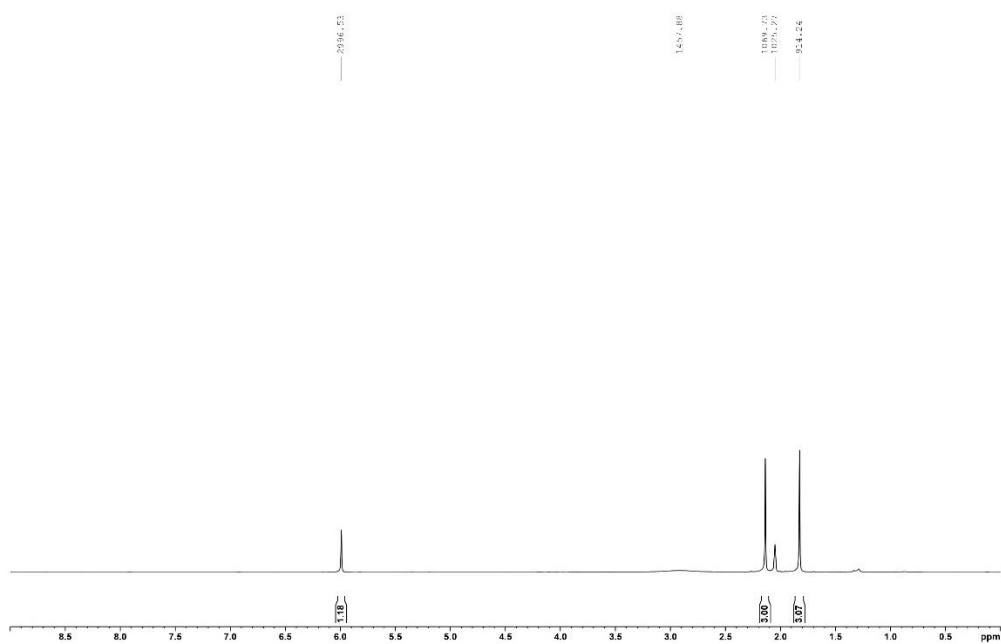


Figure S83. ¹H NMR spectrum of 4-hydroxy-3,6-dimethyl-2*H*-pyran-2-one in Acetone-*d*₆

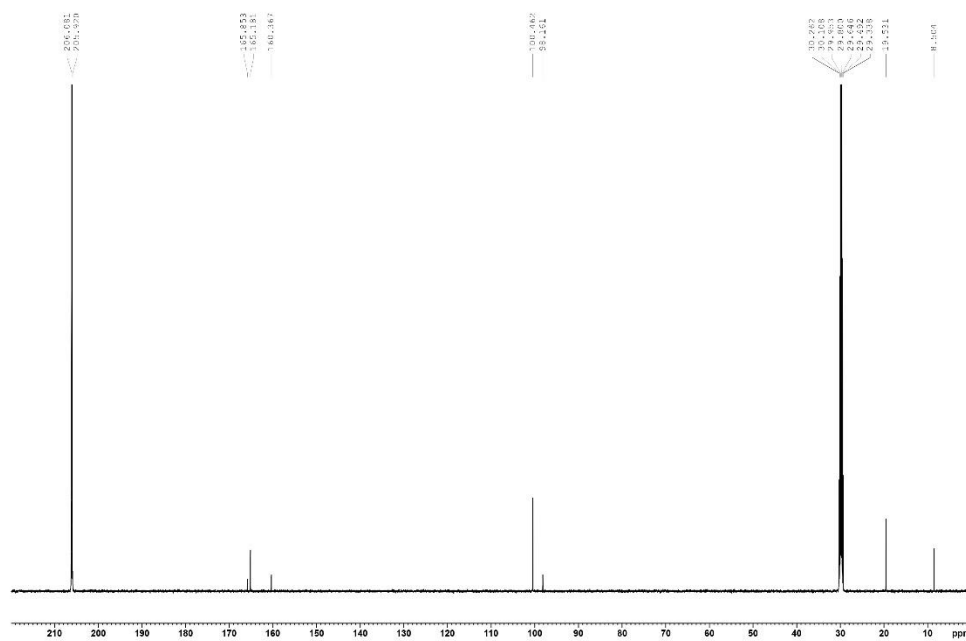


Figure S84. ¹³C NMR spectrum of 4-hydroxy-3,6-dimethyl-2*H*-pyran-2-one in Acetone-*d*₆

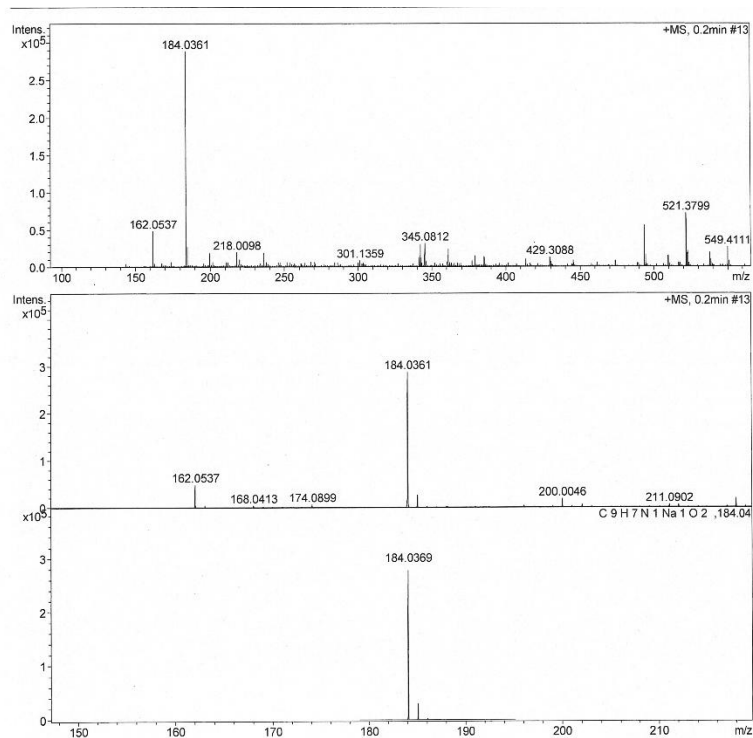


Figure S85. HRESIMS spectrum of indole-2-carboxylic acid, 3-methylorcinolaldehyde

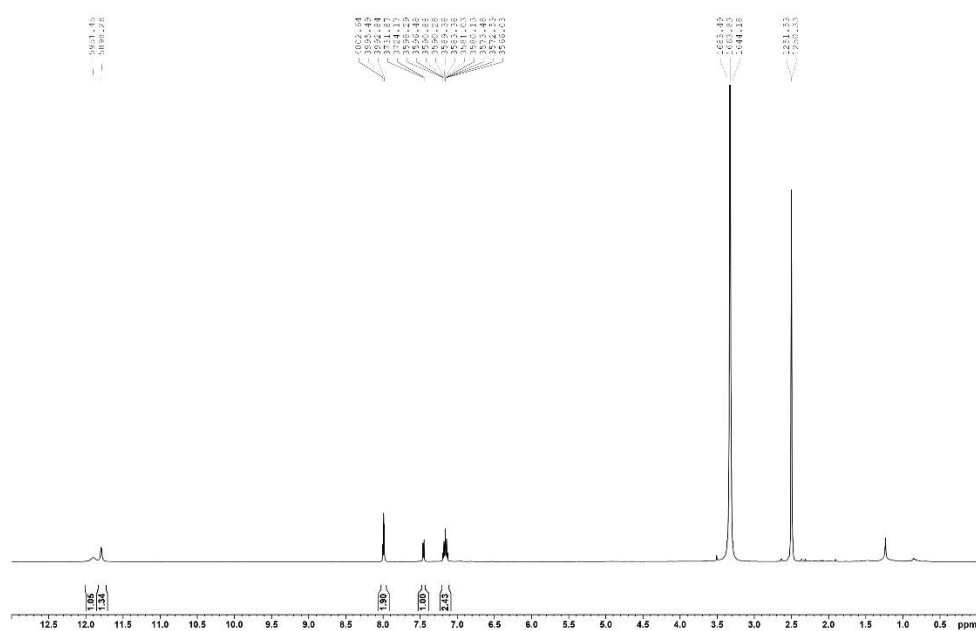


Figure S86. ^1H NMR spectrum of indole-2-carboxylic acid, 3-methylorcinolaldehyde in $\text{DMSO}-d_6$

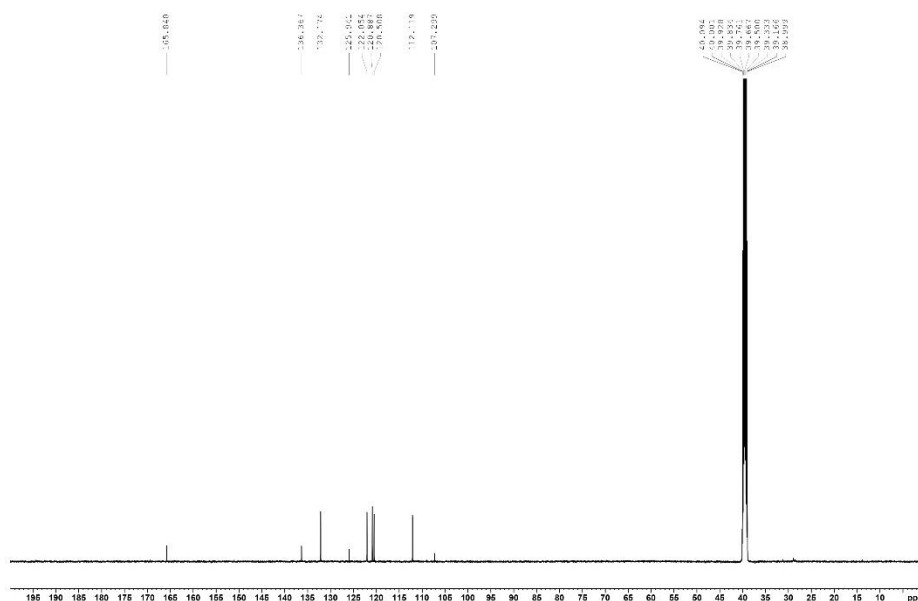


Figure S87. ¹³C NMR spectrum of indole-2-carboxylic acid, 3-methylorcinol in DMSO-*d*₆

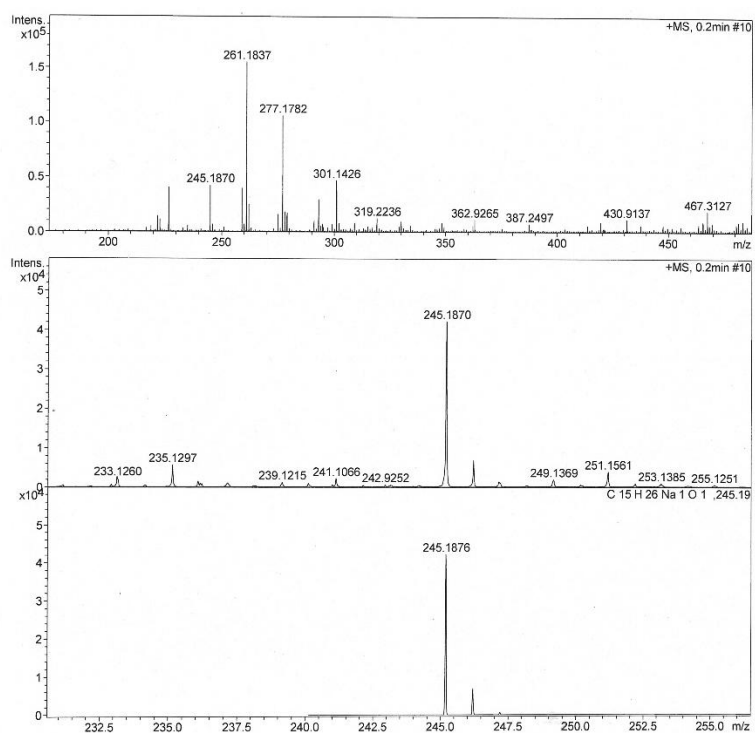
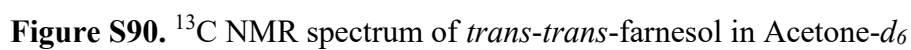
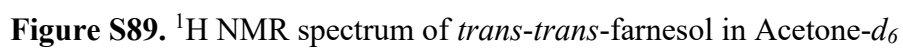


Figure S88. HRESIMS spectrum of *trans-trans*-farnesol



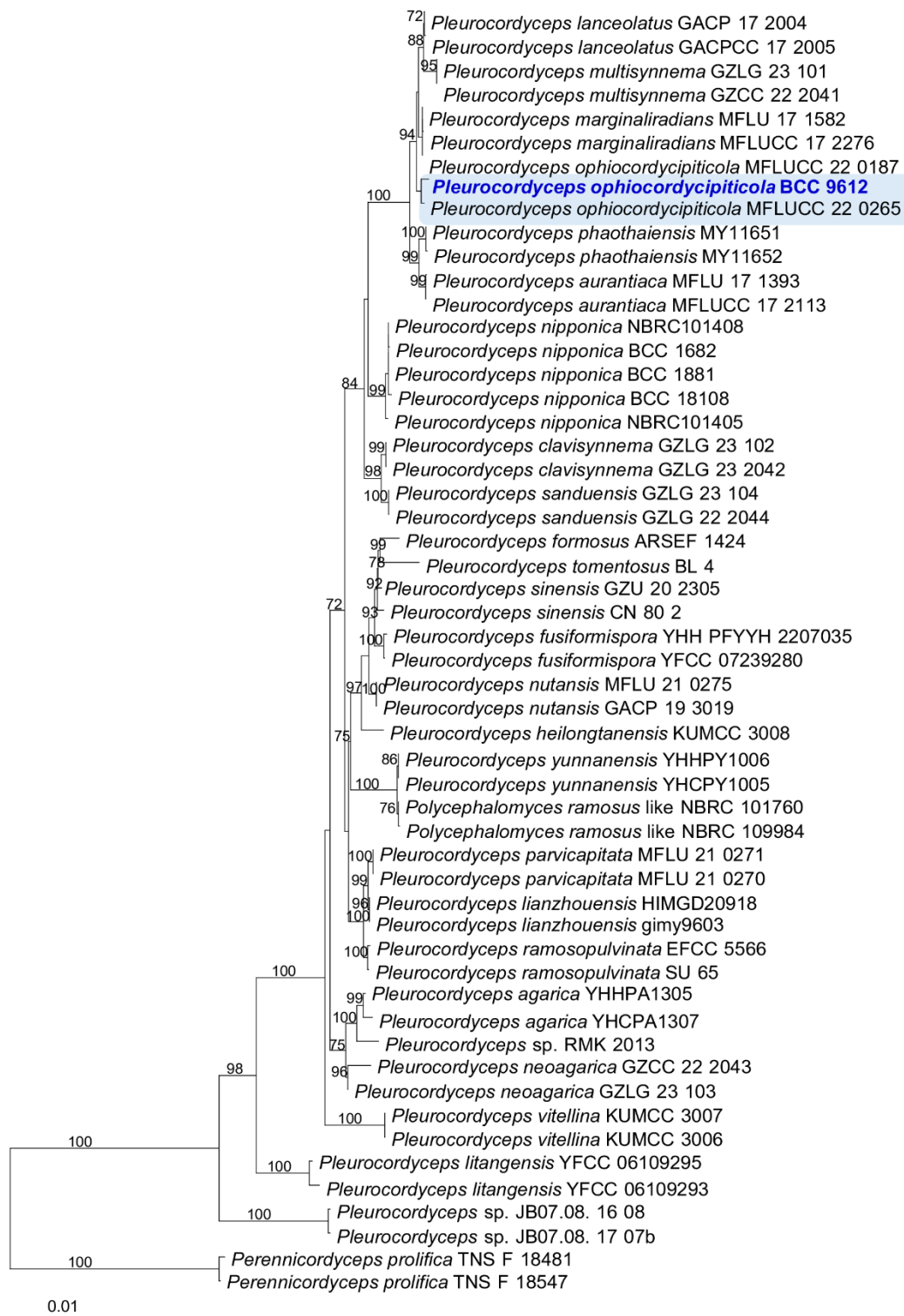


Figure S91. RAxML tree of *Pleurocordyceps* and related species from a combined LSU, *TEF1* and *RPB1* dataset. Numbers at the major nodes represent Maximum Likelihood Bootstrap (MLB) support values.