

Taste-Active Maillard Reaction Products in Roasted Garlic (*Allium Sativum*)

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(2*R*)-3-(allylthio)-2-((4*S*)-4-(allylthiomethyl)-6-formyl-3-oxo-3,4-dihydropyrrolo[1,2-*a*]pyrazin-2(1*H*)-yl)propanoic acid (compound **9**)

Figure S58. HRESIMS (negative) spectrum

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Figure S71. CD spectra of Maillard reaction product **7** (green) and synthesized references **10** (blue) and **11** (red)

3. Analytical conditions for quantitative analysis on identified compounds in garlic preparations

Table S2. UPLC-MS/MS (ESI) parameters for quantitative analysis on identified compounds.

1. Analytical conditions for purification of crude fractions (GS-1, 2, 3, 4, 5 and 6)

	Gradient conditions	Collected peaks
GS-1	12.5%B → 12.5%B → 18%B → 95%B 0 min 3 min 15 min 17.5 min	10.3 min (Compound.1)
GS-2	12.5%B → 12.5%B → 18%B → 95%B 0 min 3 min 15 min 17.5 min	11.4 min (Compound.2), 12.4 min (Compound.3), 13.3 min (Compound.4), 14.8 min (Compound.5)
GS-3	30%B → 30%B → 80%B 0 min 3 min 18 min	7.6 min (Compound.6)
GS-4	30%B → 30%B → 80%B 0 min 3 min 18 min	12.8 min (Compound.7)
GS-5	40%B → 40%B → 80%B 0 min 3 min 20 min	11.4 min (Compound.8)
GS-6	30%B → 30%B → 80%B 0 min 3 min 20 min	14.9 min (Compound.9)

Table S1. Analytical conditions for HPLC purifications and retention times for collected peaks.

2. MS and NMR data of compound **1-9**

Acortatarin A (**1**)

Jun

30052015_MRGS X1a 470 (1.848) Cm (468:471)

1: TOF MS ES+
9.11e5

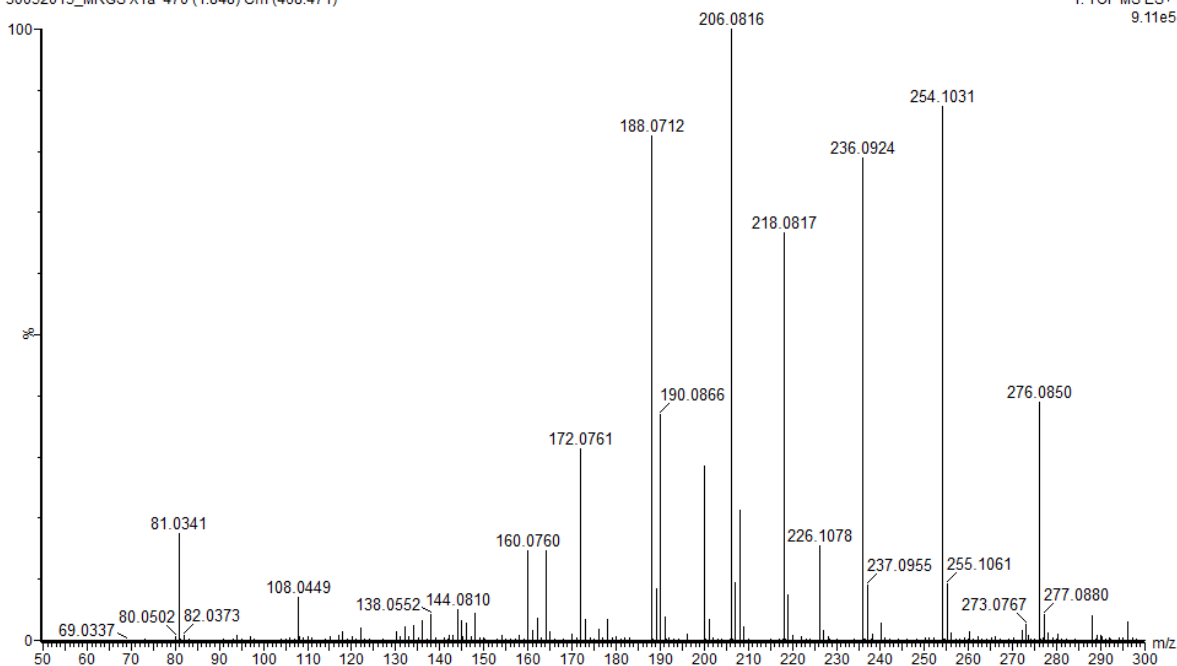


Figure S1. HRESIMS (positive) spectra

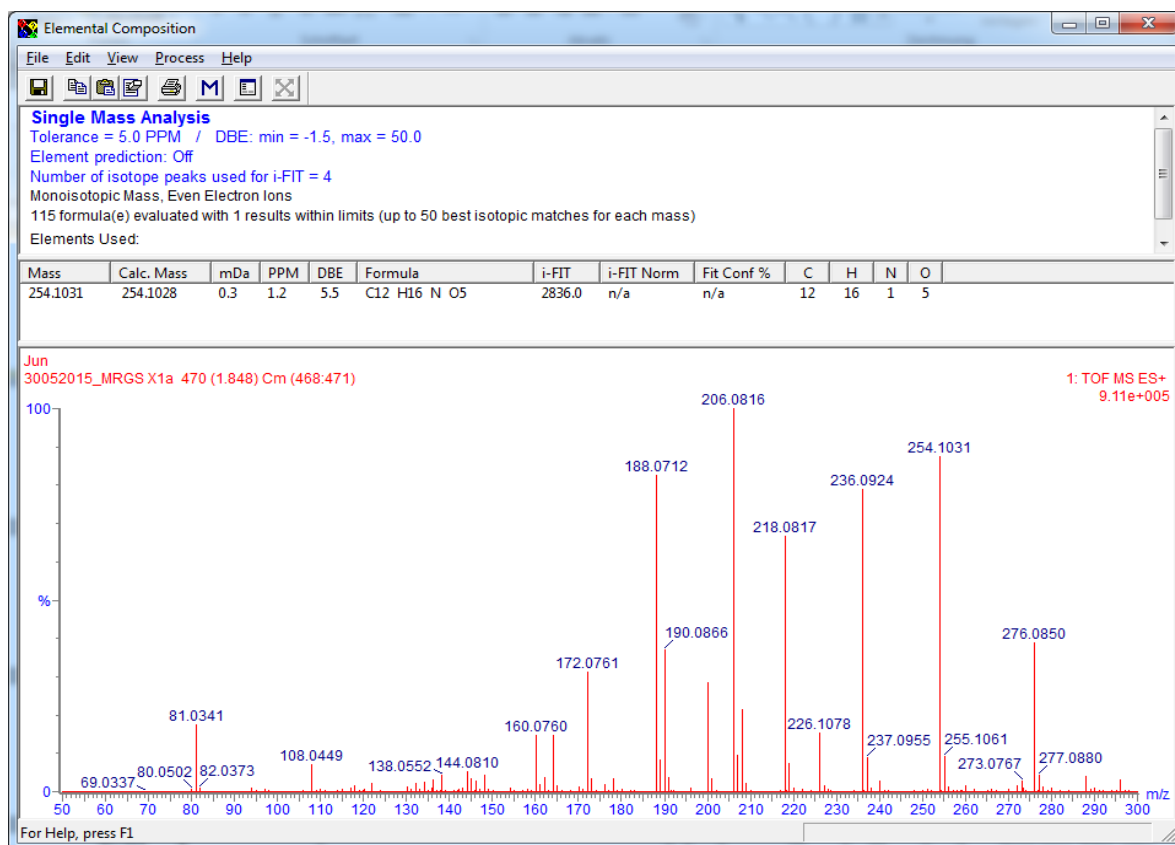


Figure S2. Elemental composition report of the precursor ion

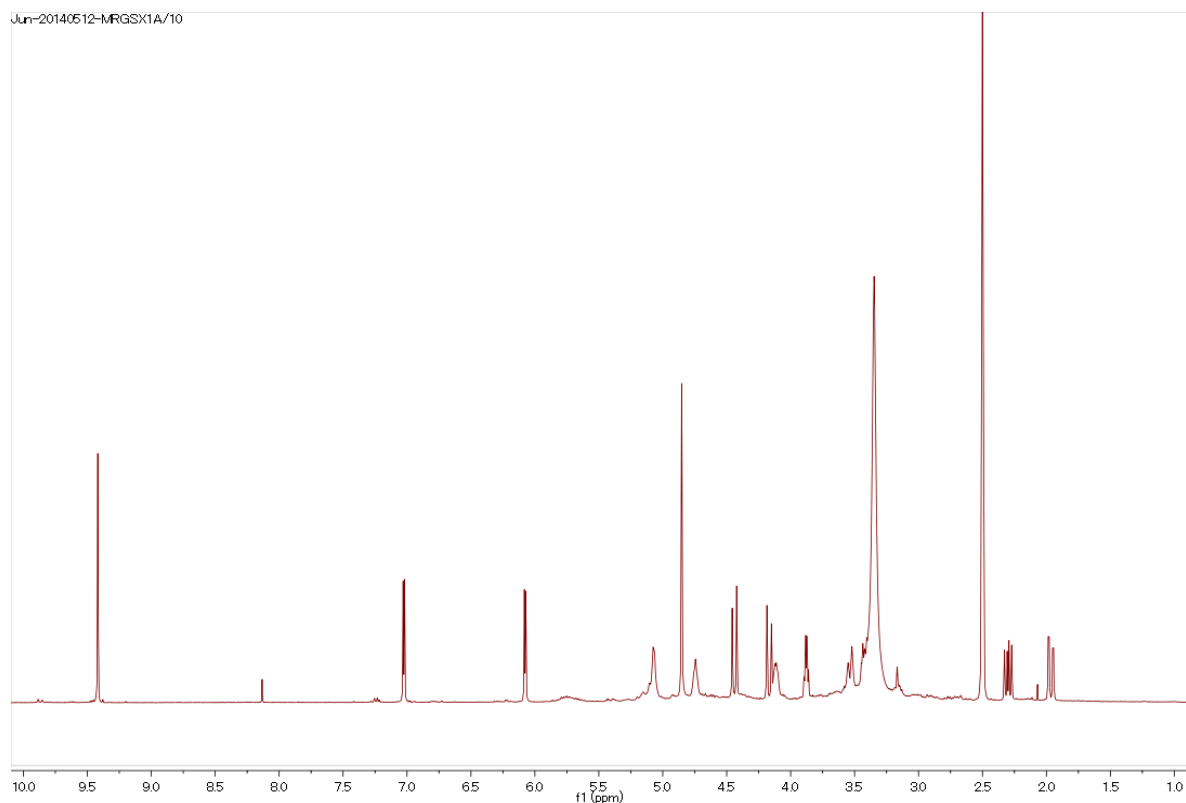


Figure S3. ^1H NMR spectrum (DMSO- d_6 , 400 MHz)

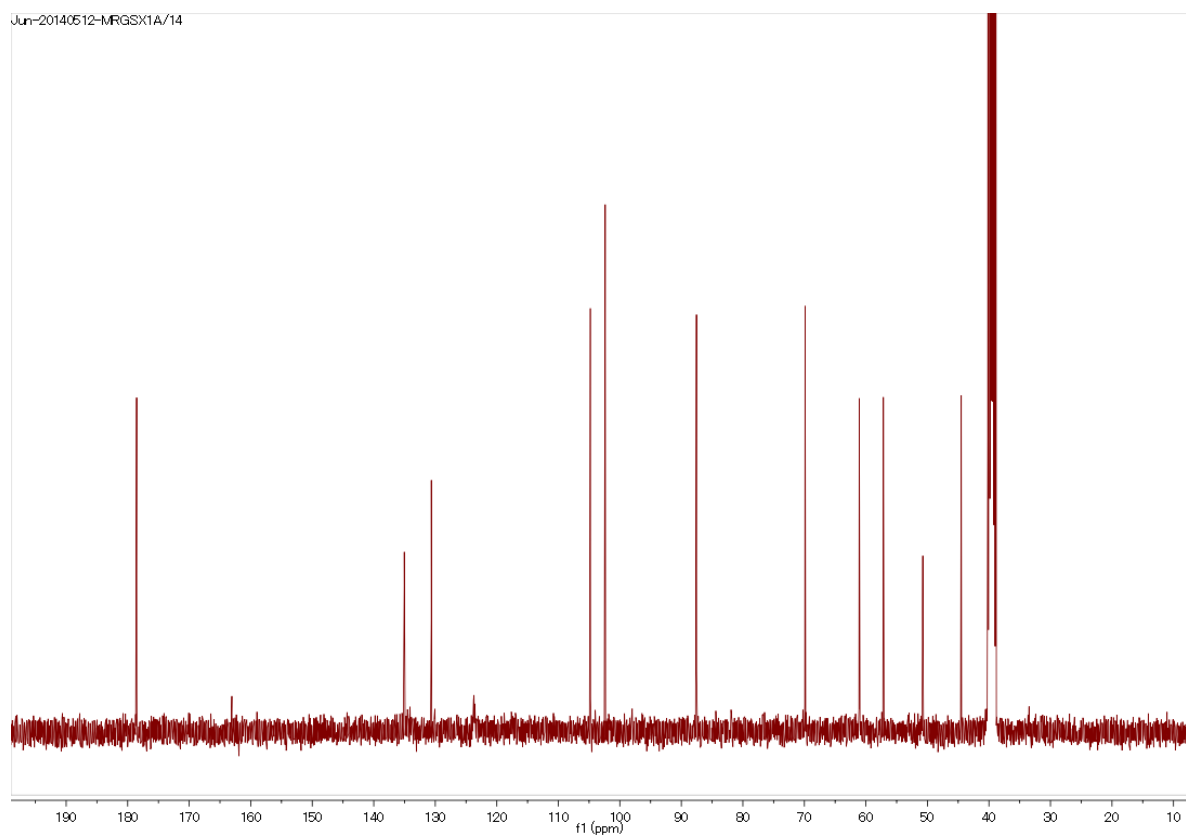


Figure S4. ^{13}C NMR spectrum (DMSO- d_6 , 100 MHz)

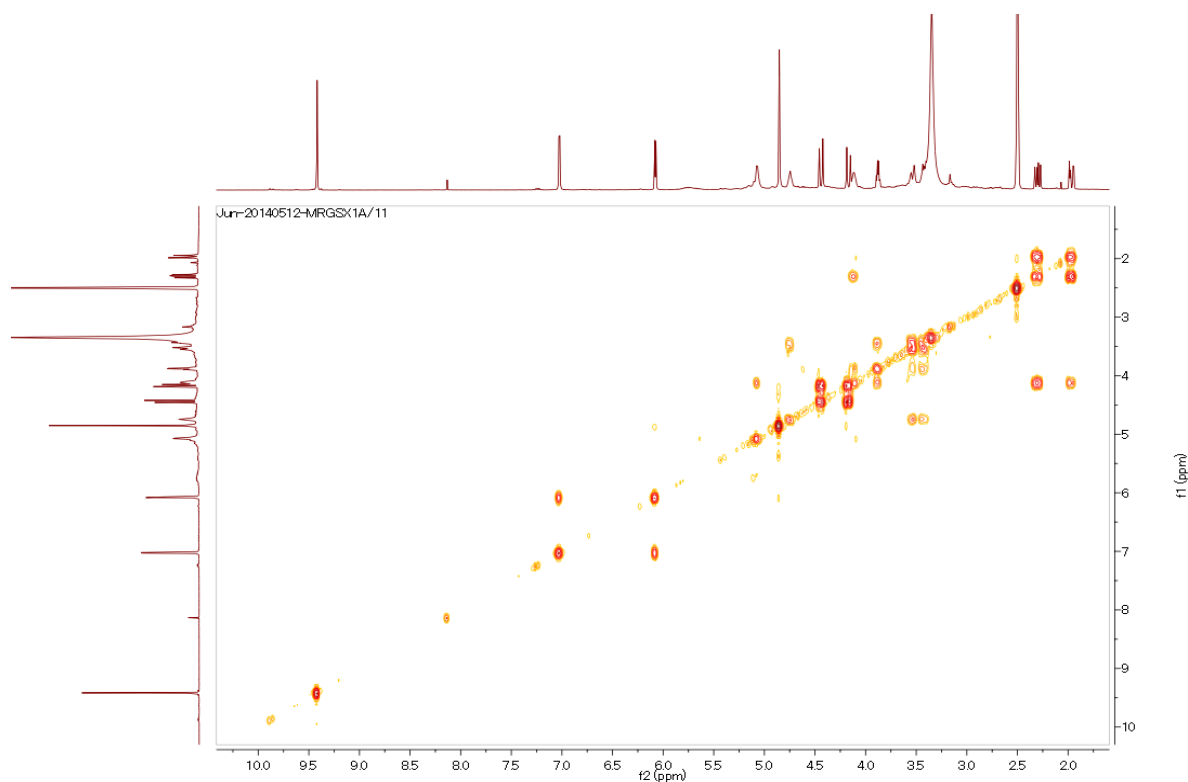


Figure S5. COSY correlations

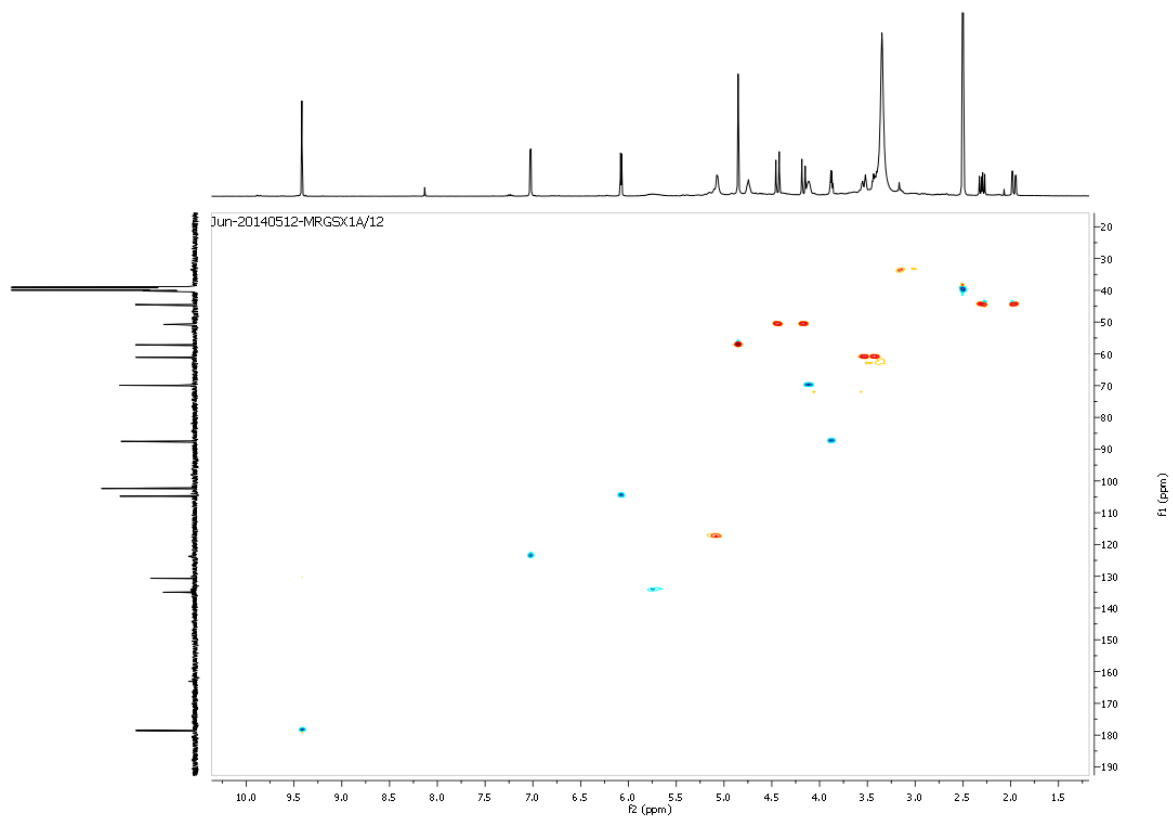


Figure S6. HSQC correlations

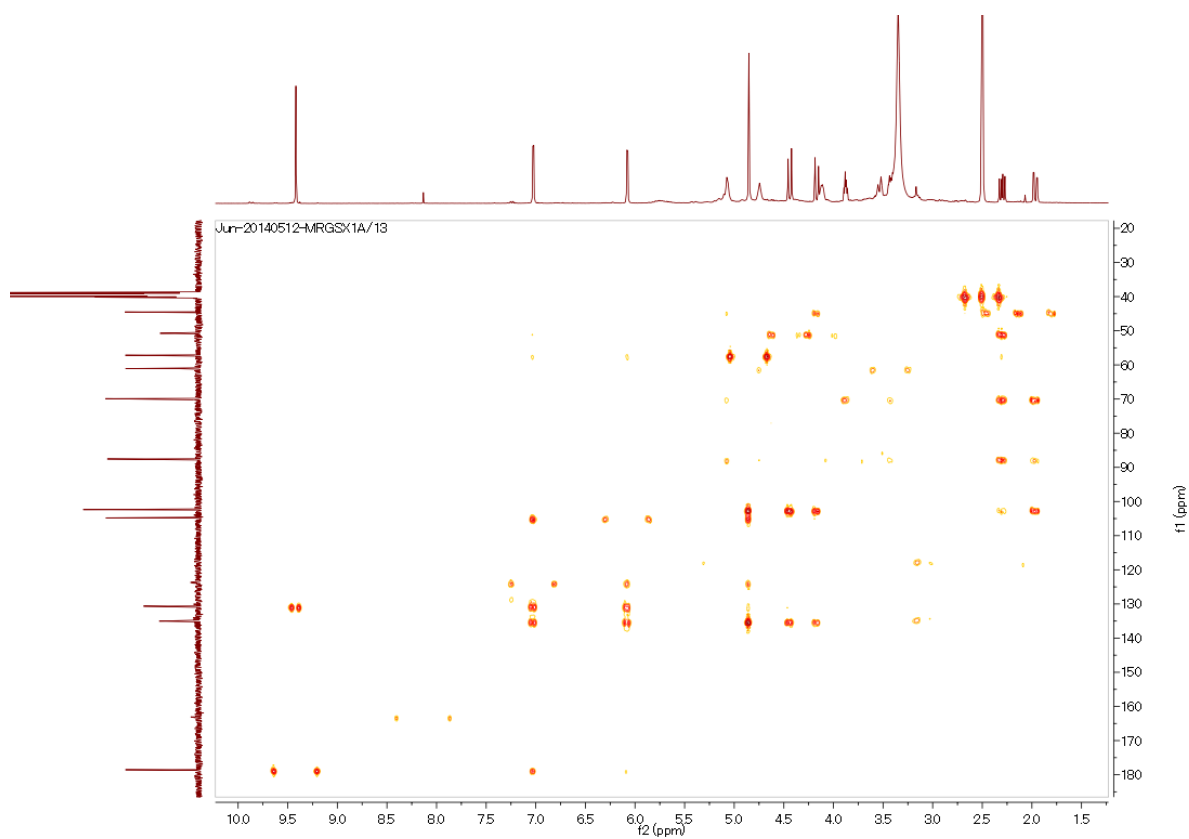


Figure S7. HMBC correlations

Pollenopyrroside A (2)

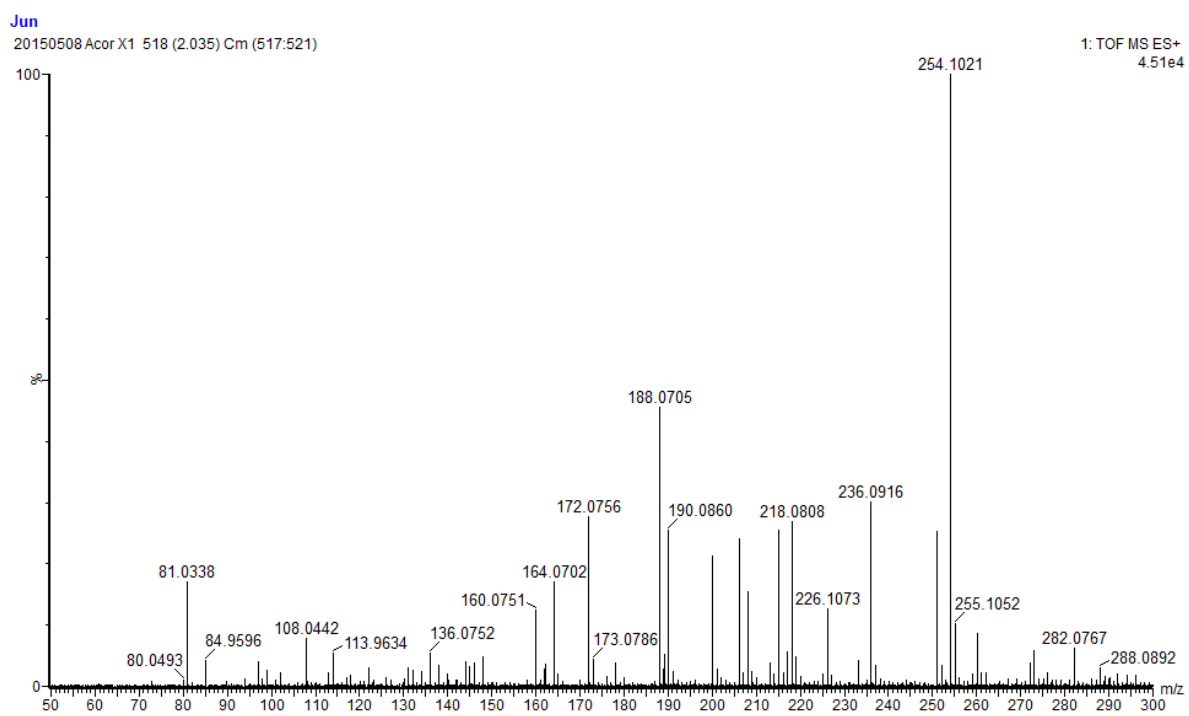


Figure S8. HRESIMS (positive) spectra

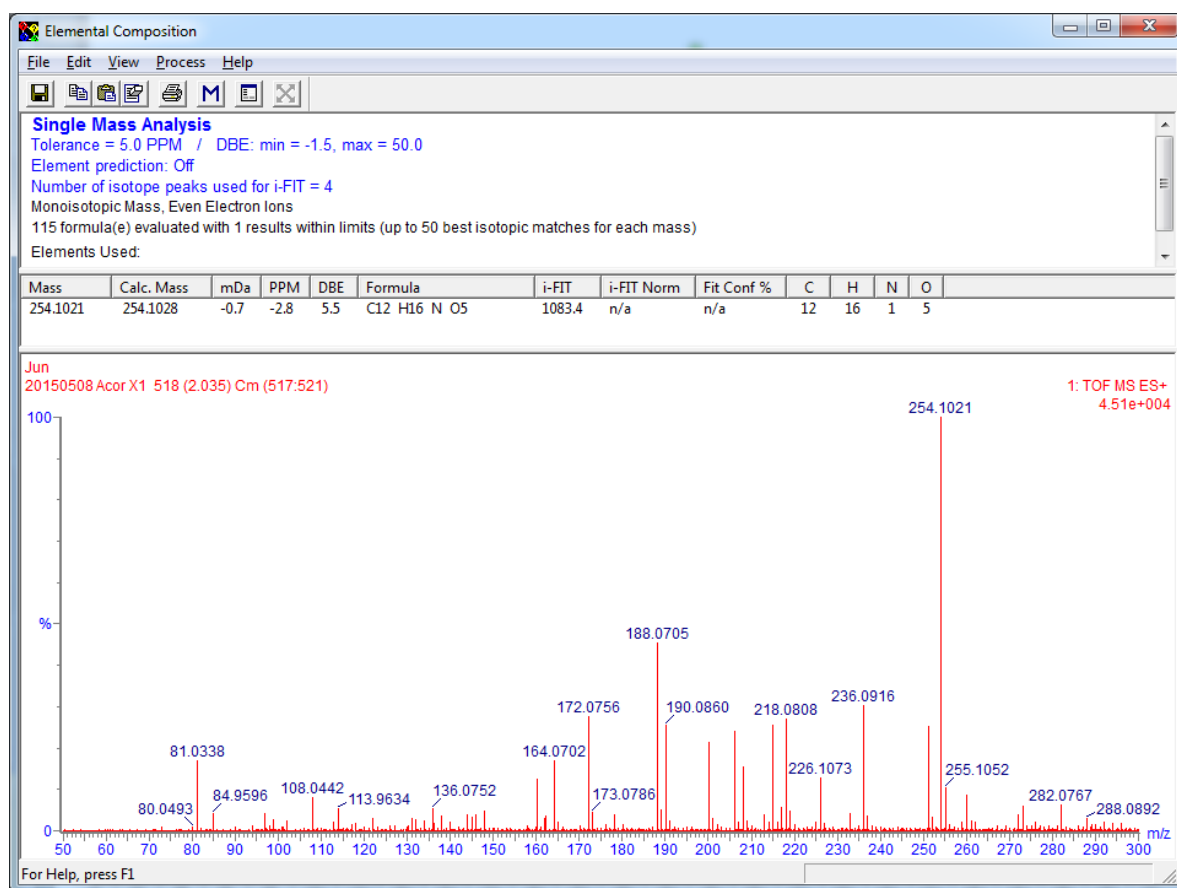


Figure S9. Elemental composition report of the precursor ion

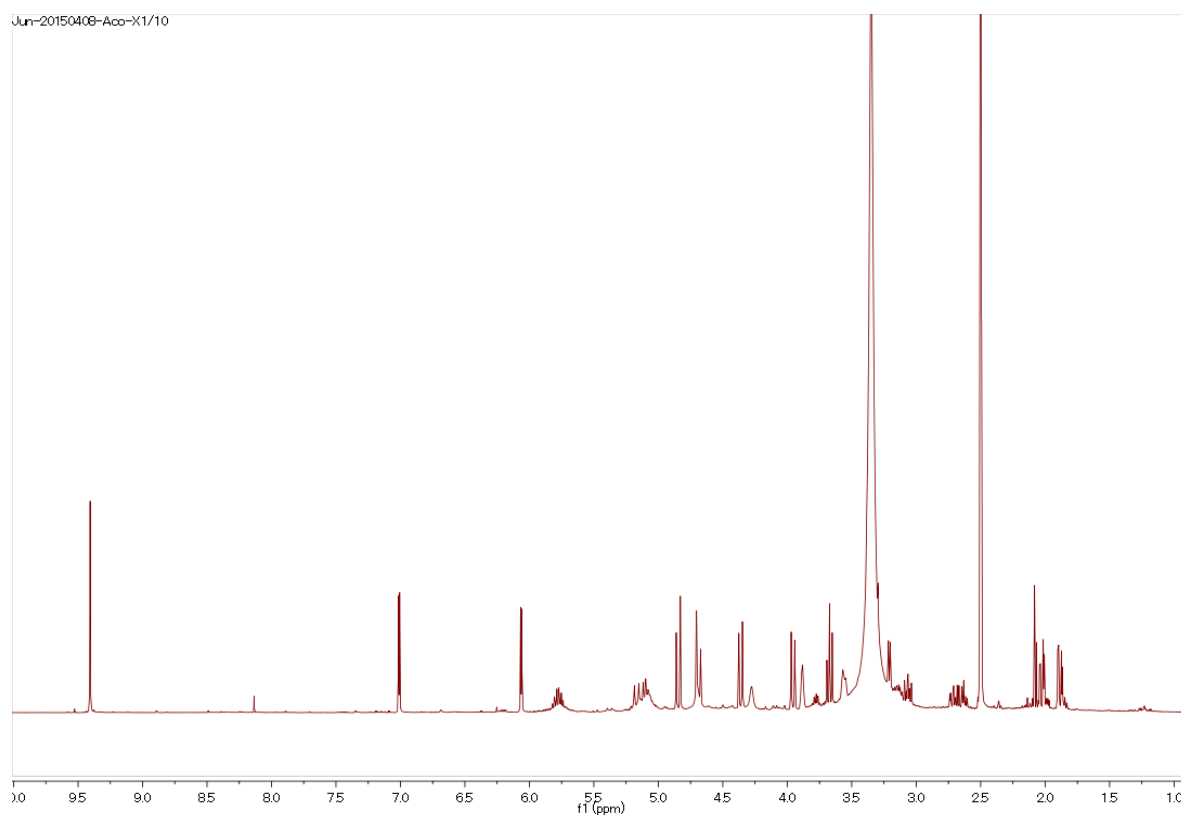


Figure S10. ^1H NMR spectrum (DMSO- d_6 , 500 MHz)

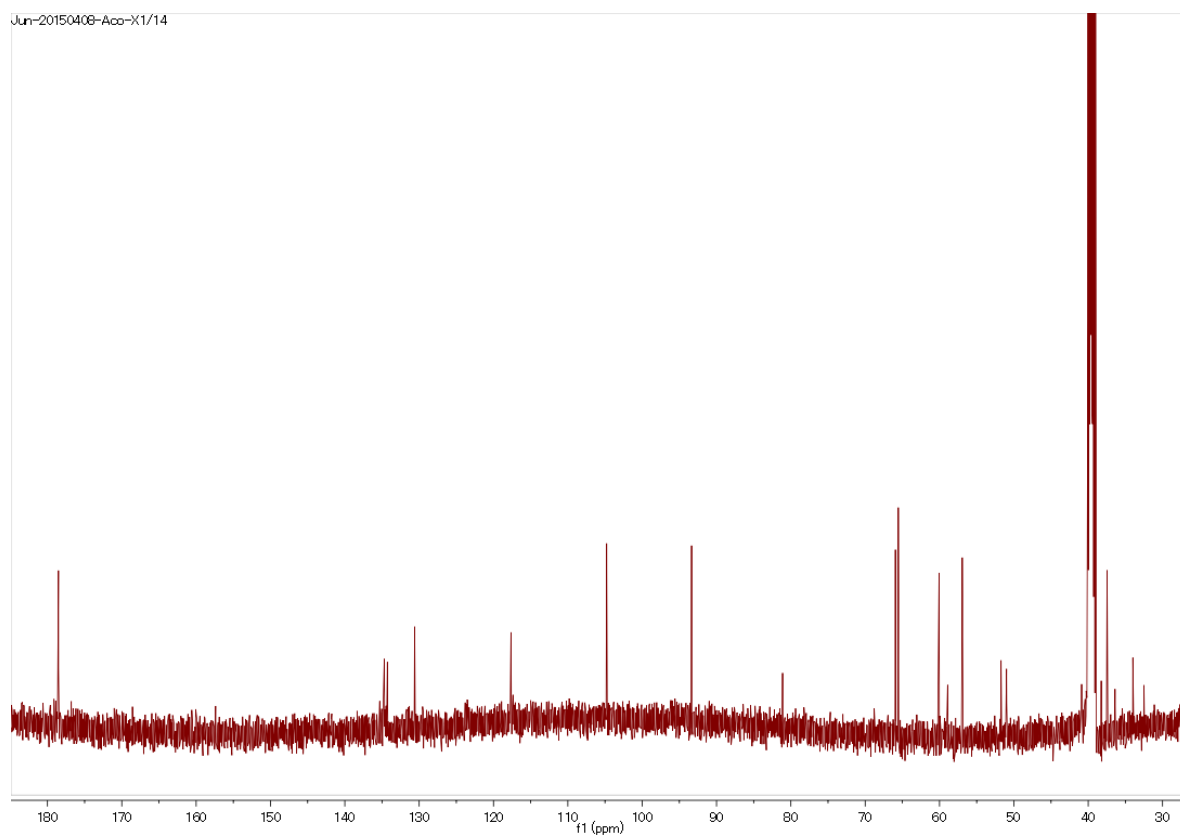


Figure S11. ^{13}C NMR spectrum (DMSO- d_6 , 125 MHz)

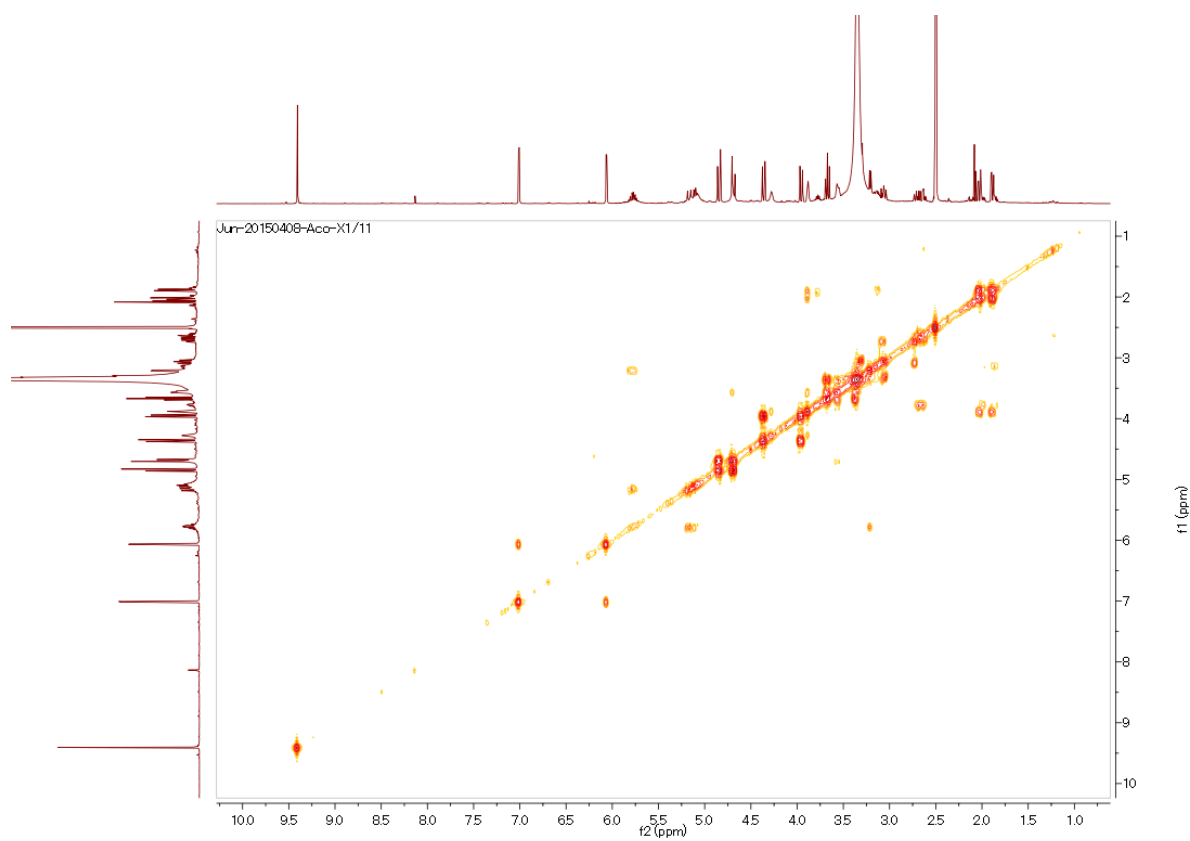


Figure S12. COSY correlations

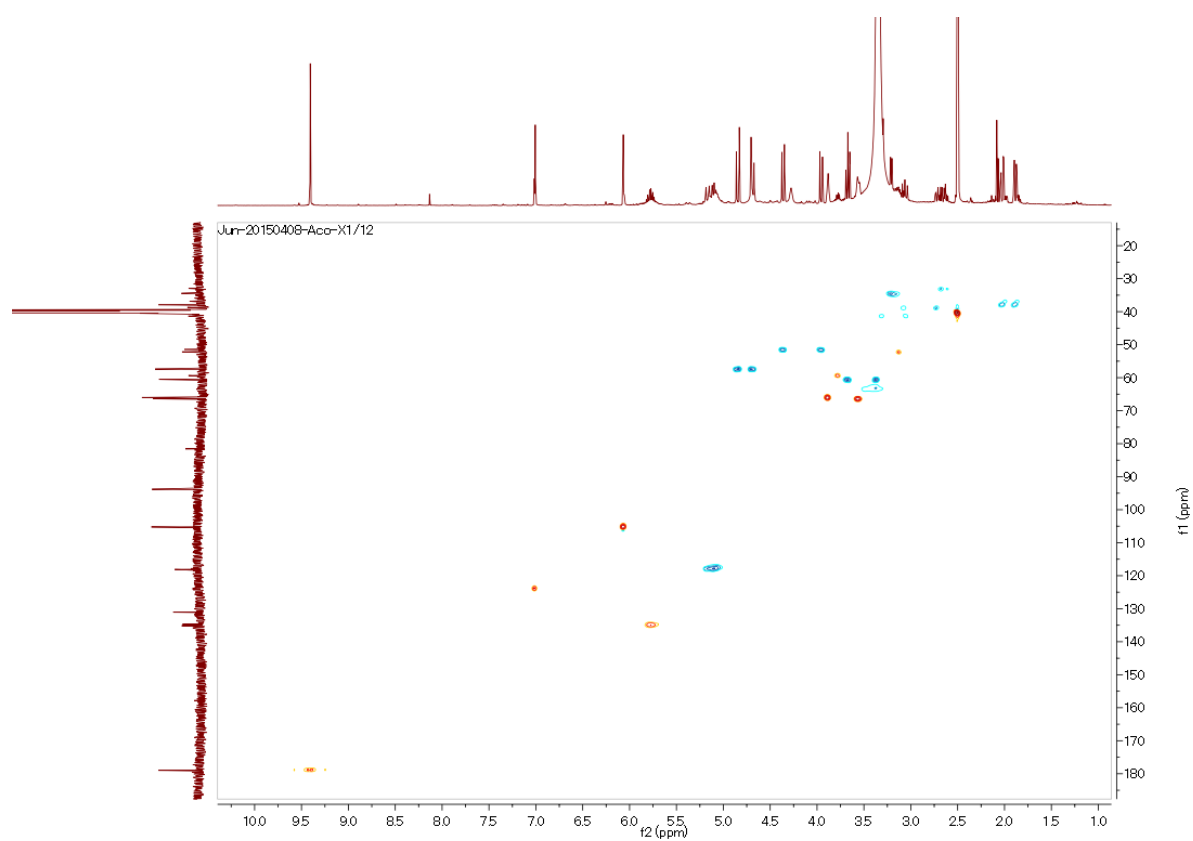


Figure S13. HSQC correlations

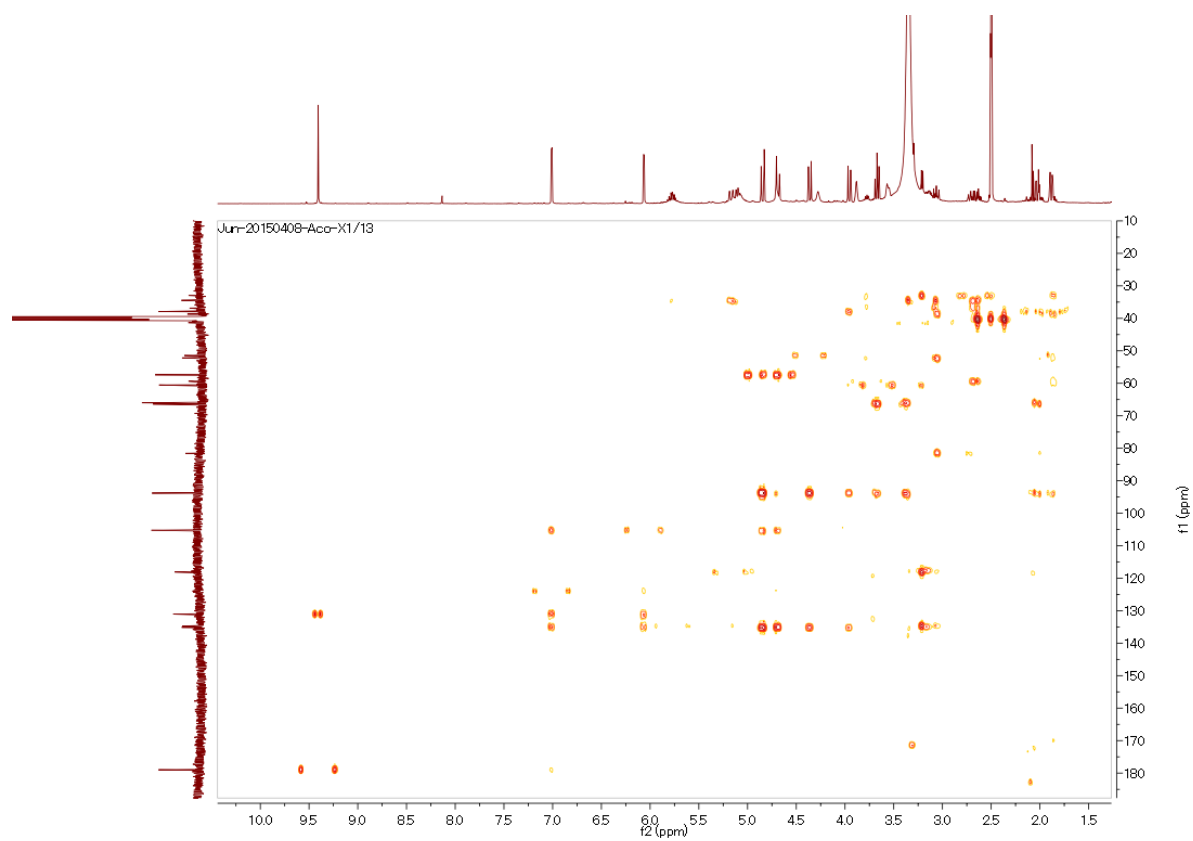


Figure S14. HMBC correlations

epi-Acortatarin A (3)

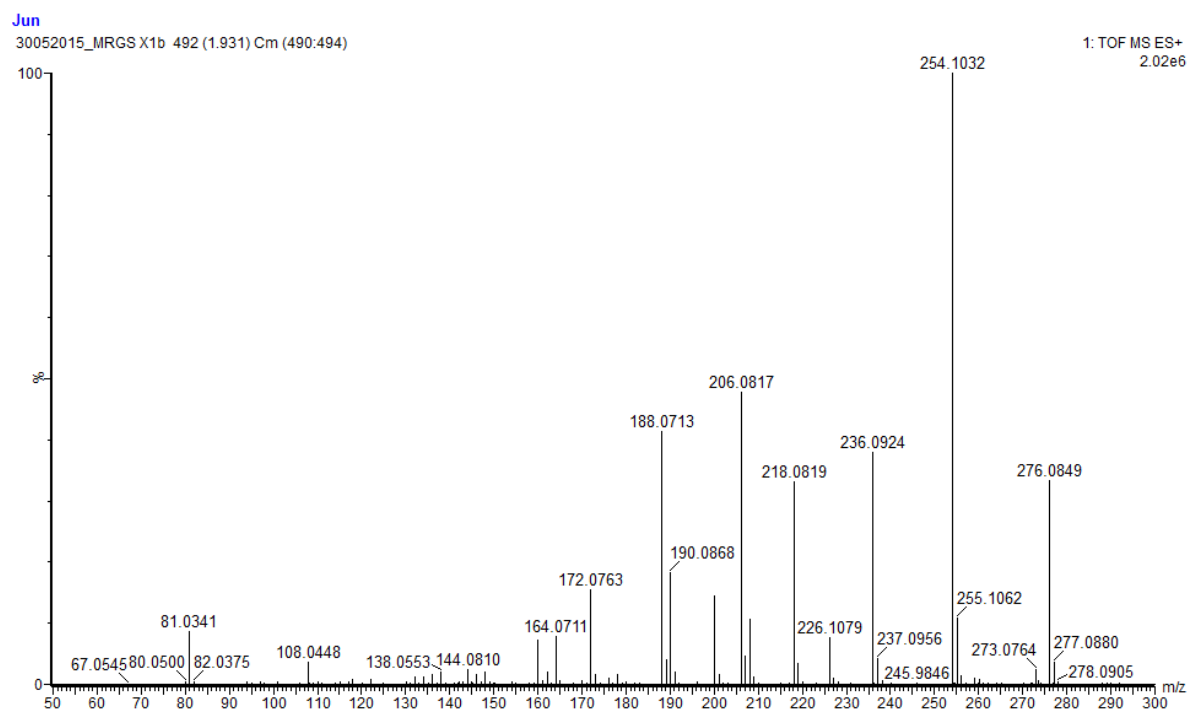


Figure S15. HRESIMS (positive) spectrum

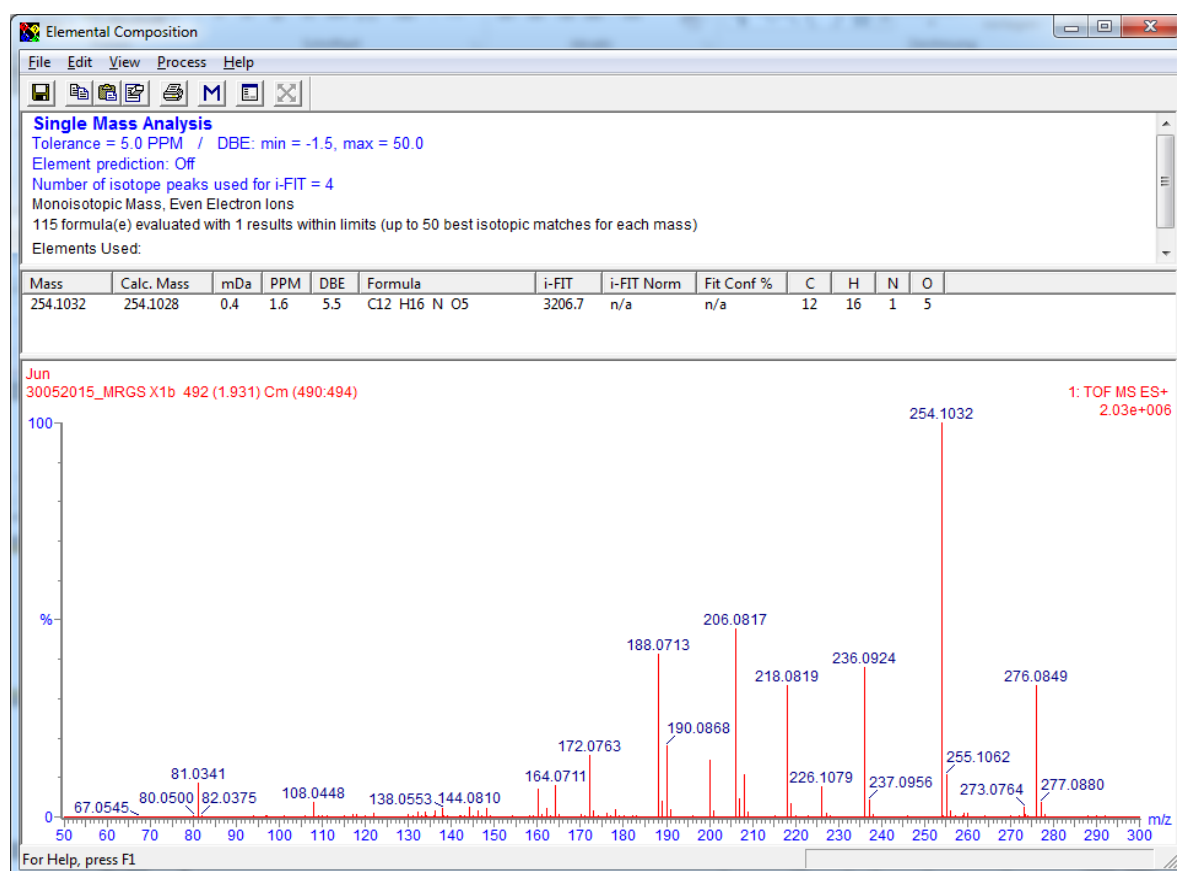


Figure S16. Elemental composition report of the precursor ion

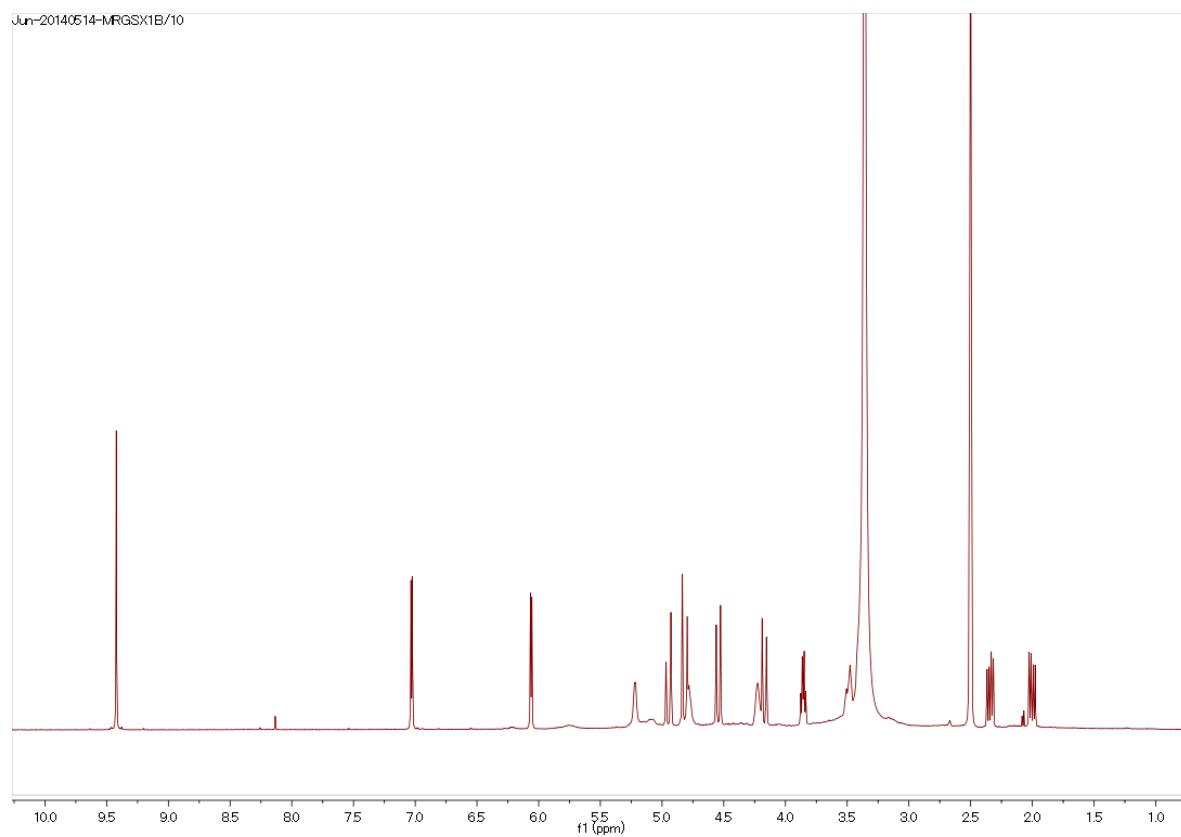


Figure S17. ^1H NMR spectrum (DMSO- d_6 , 400 MHz)

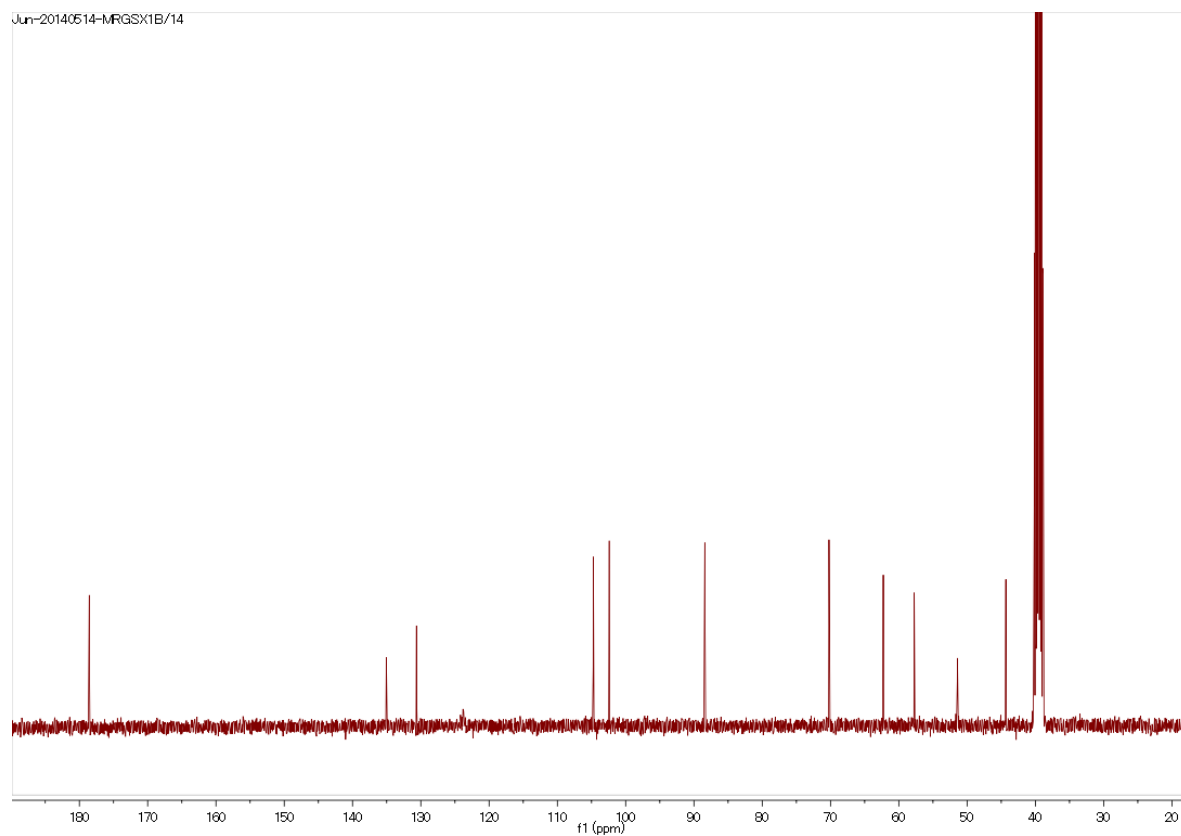


Figure S18. ^{13}C NMR spectrum (DMSO- d_6 , 100 MHz)

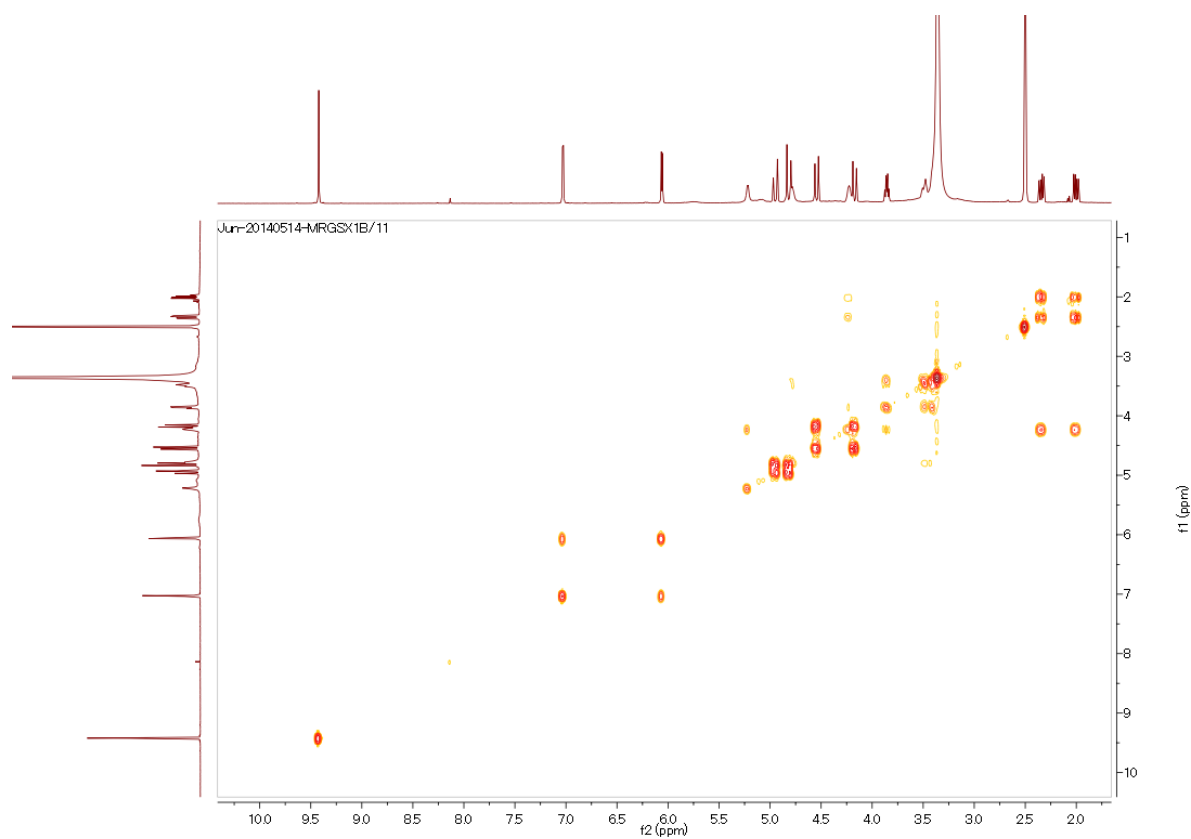


Figure S19. COSY correlations

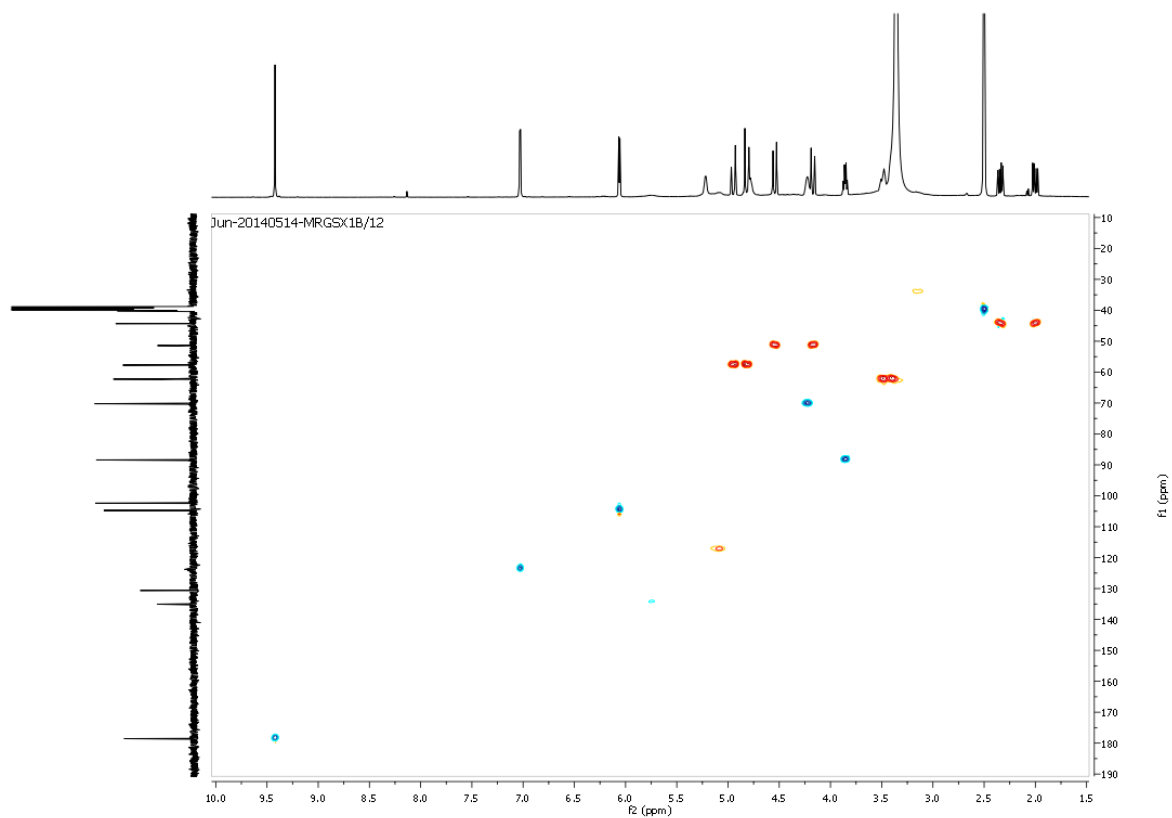


Figure S20. HSQC correlations

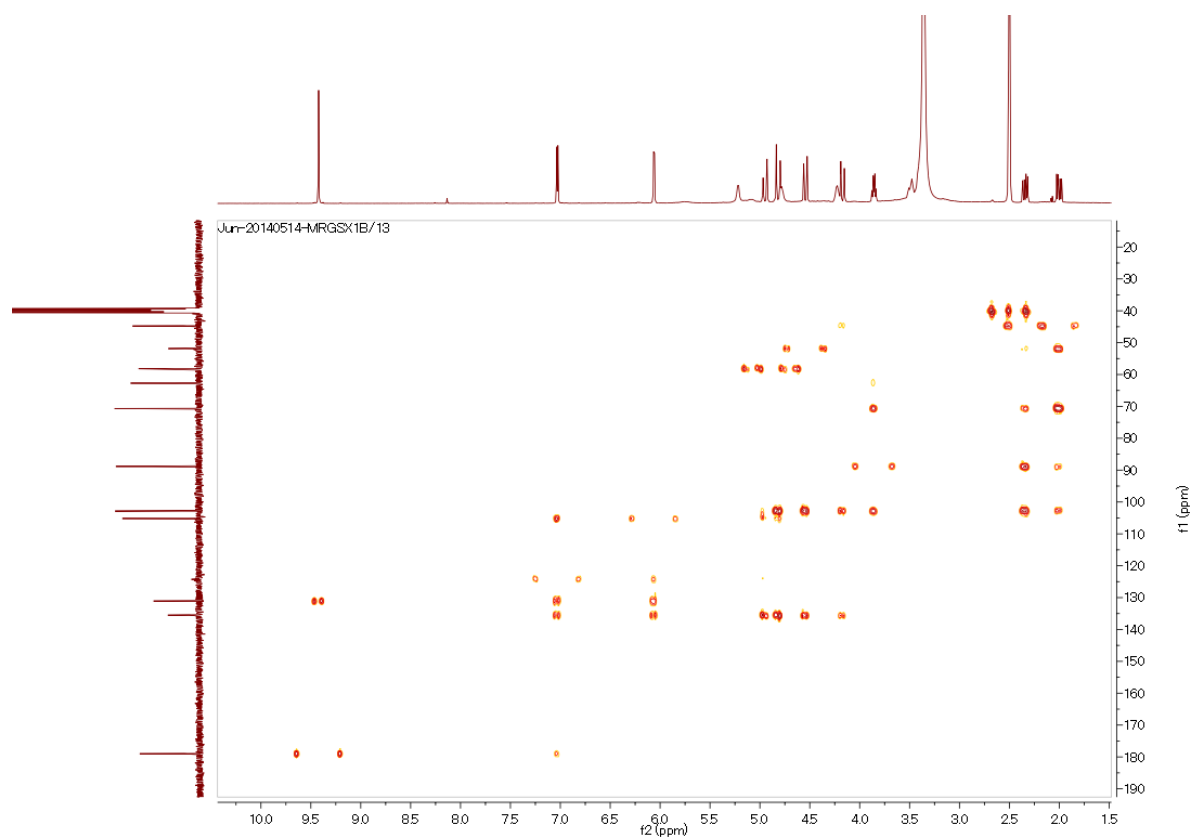


Figure S21. HMBC correlations

Xylapyrroside A (4)

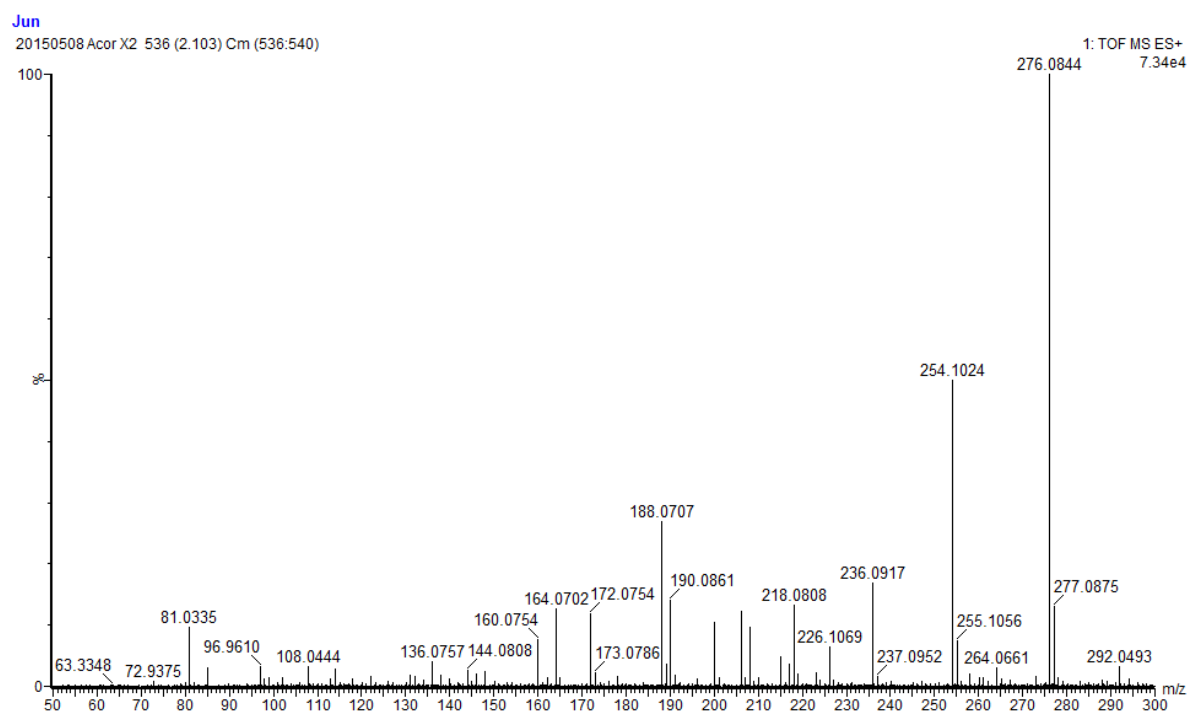


Figure S22. HRESIMS (positive) spectrum

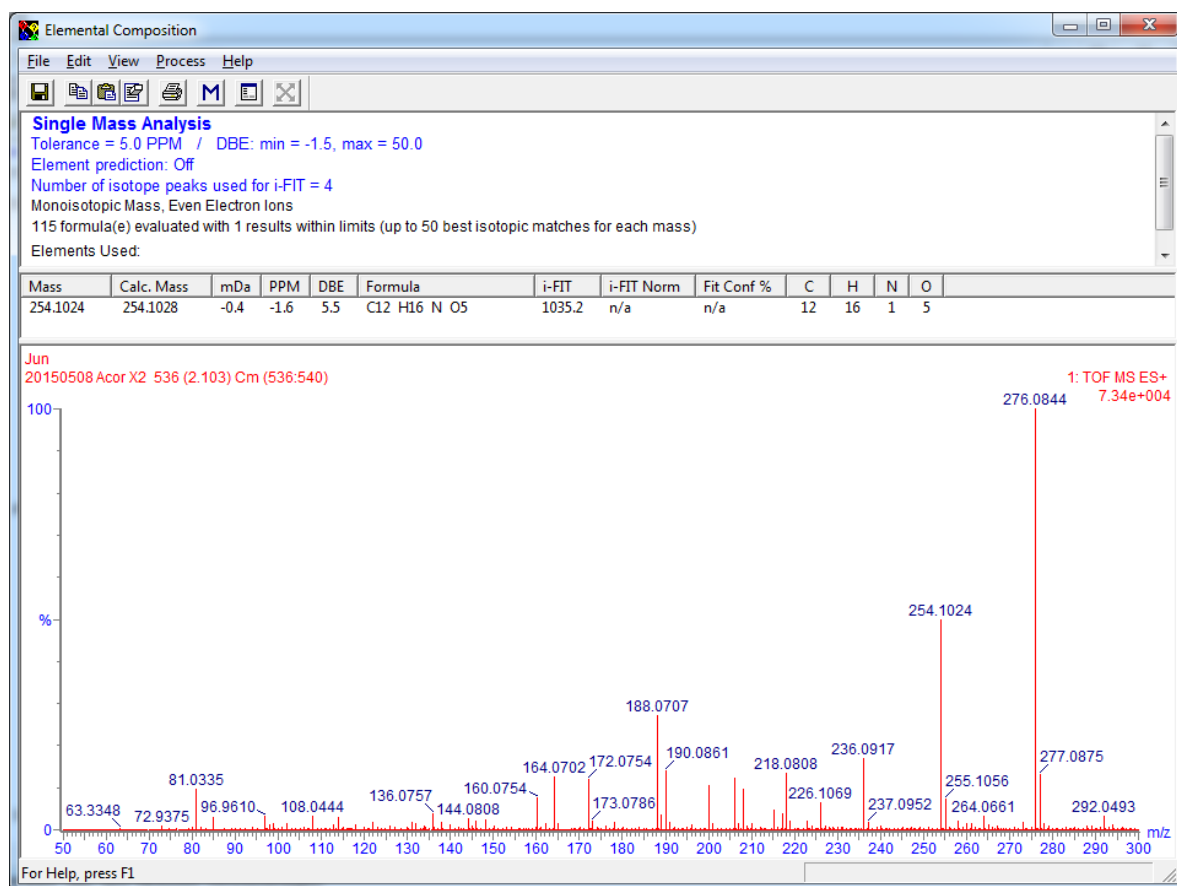


Figure S23. Elemental composition report of the precursor ion

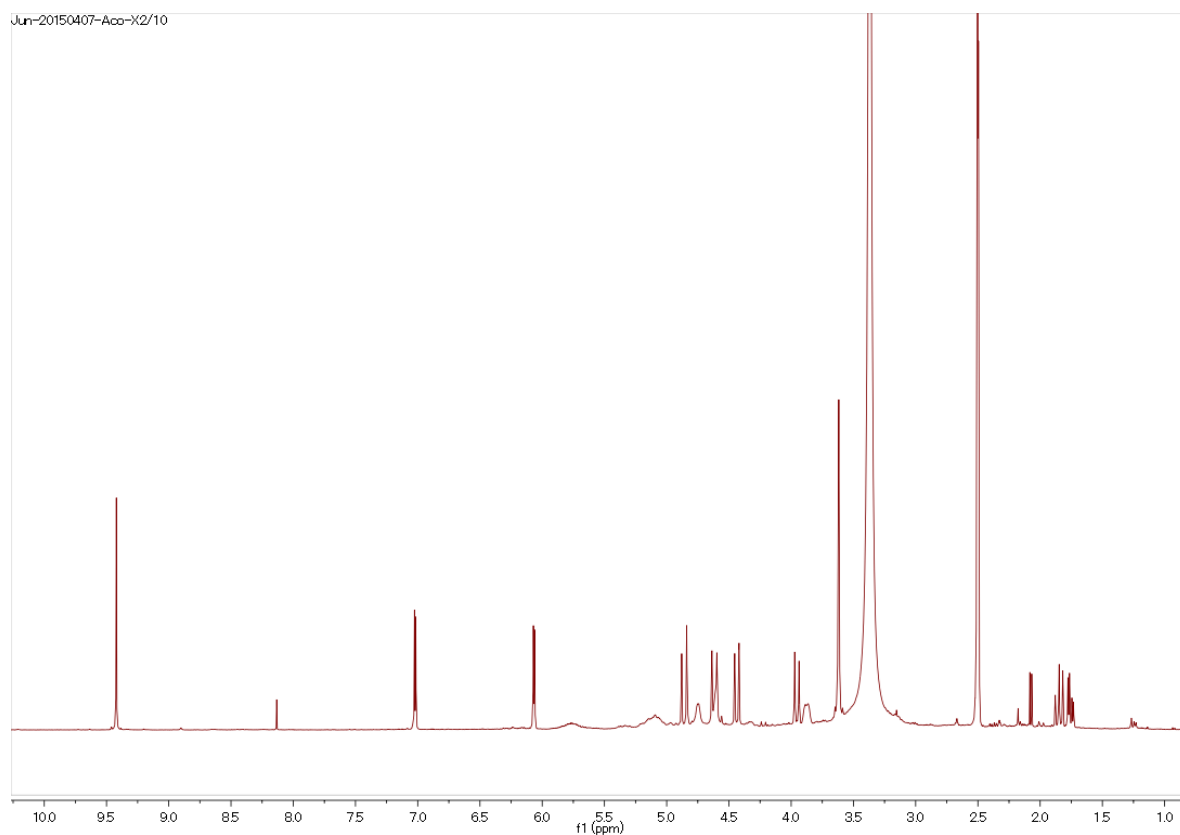


Figure S24. ^1H NMR spectrum (DMSO- d_6 , 400 MHz)

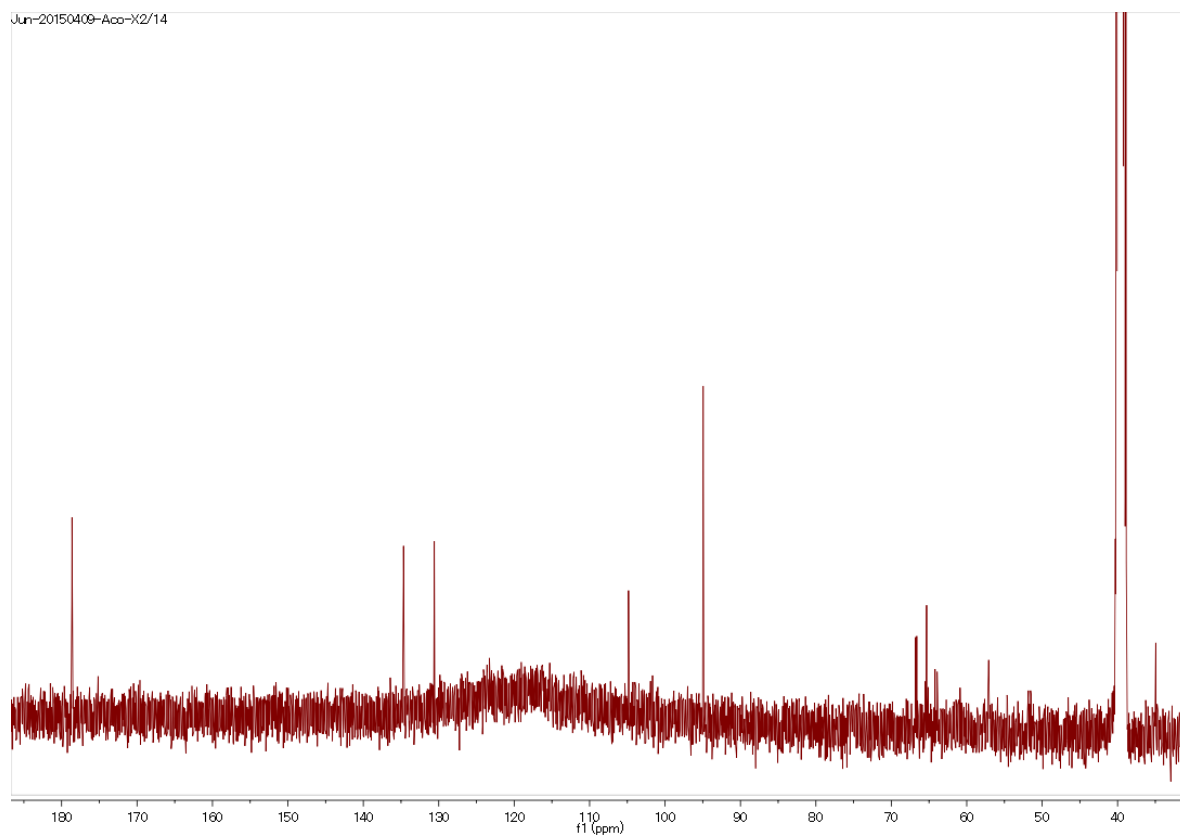


Figure S25. ^{13}C NMR spectrum (DMSO- d_6 , 100 MHz)

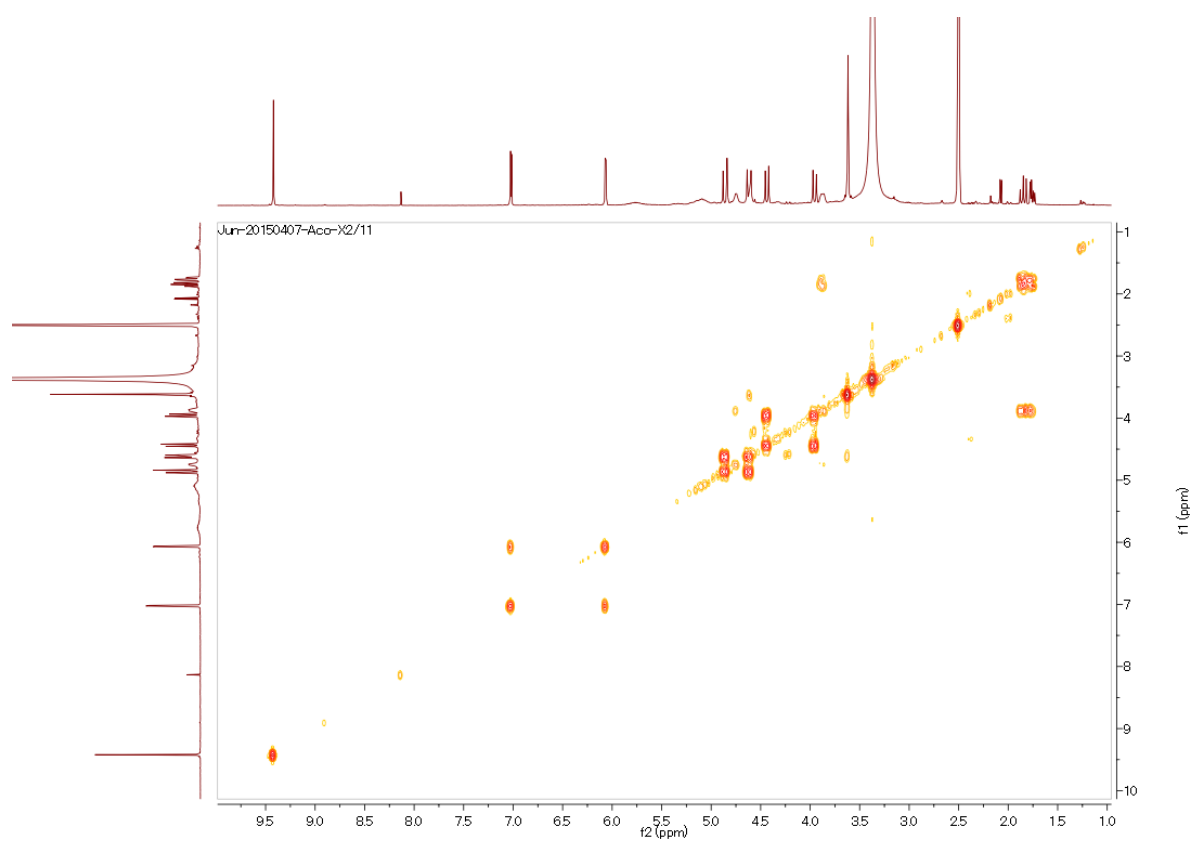


Figure S26. COSY correlations

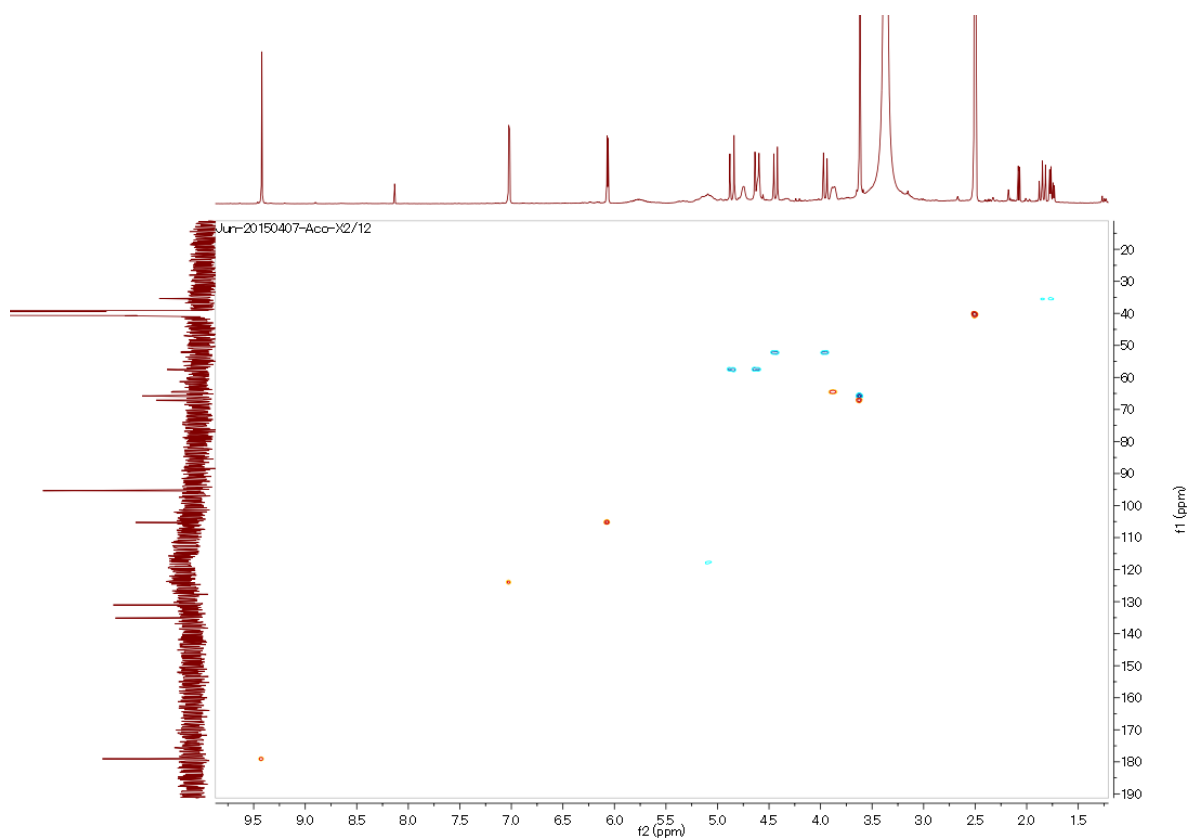


Figure S27. HSQC correlations

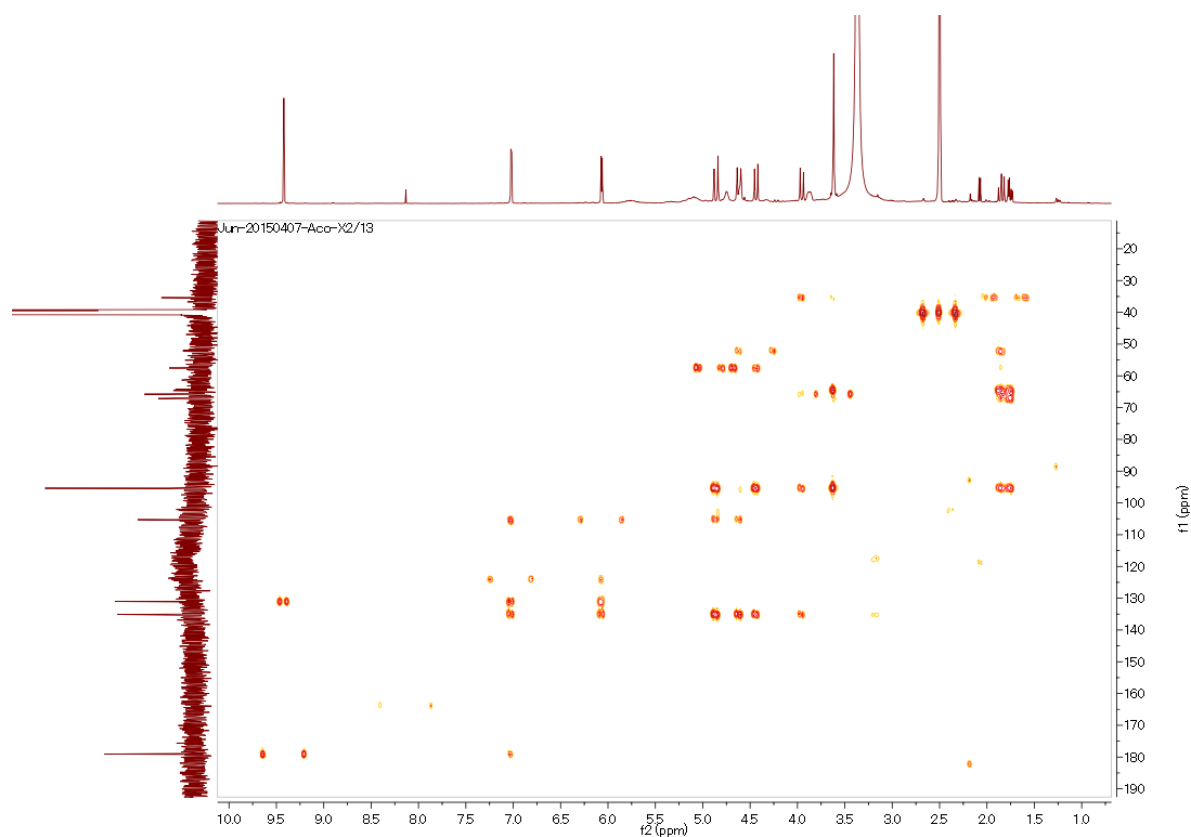


Figure S28. HMBC correlations

5-hydroxymethyl-1-[(5-hydroxymethyl-2-furanyl)methyl]-1H-pyrrole-2-carbaldehyde (5)

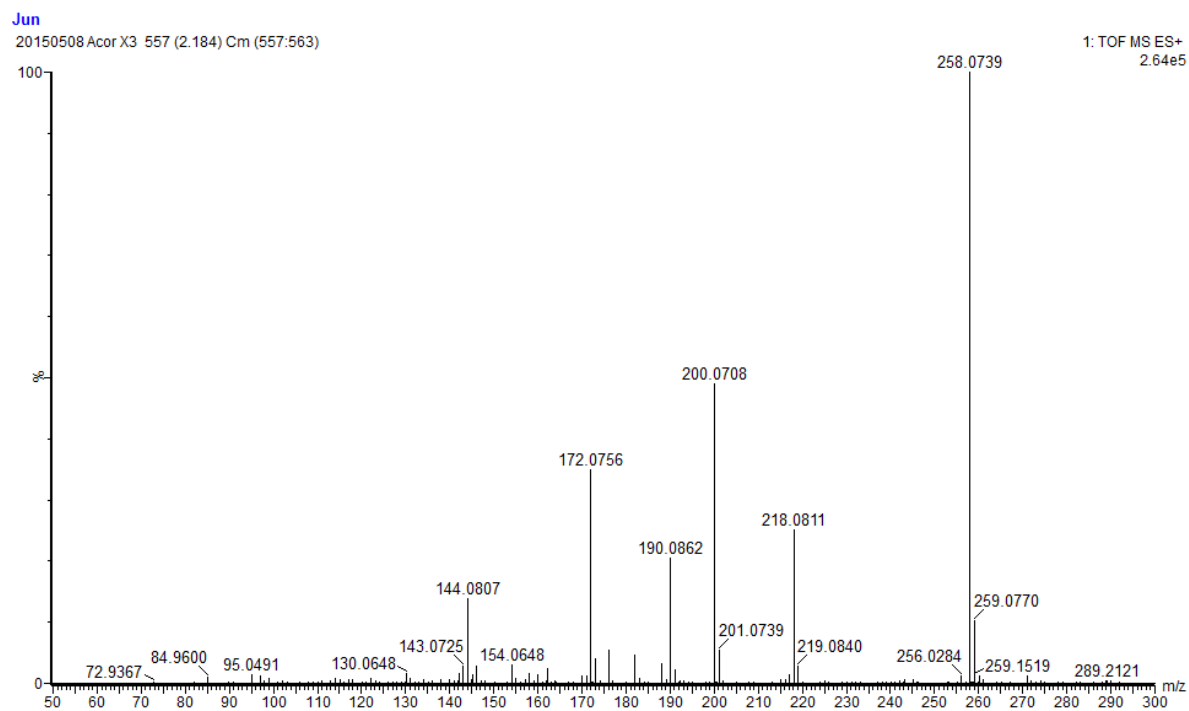


Figure S29. HRESIMS (positive) spectrum

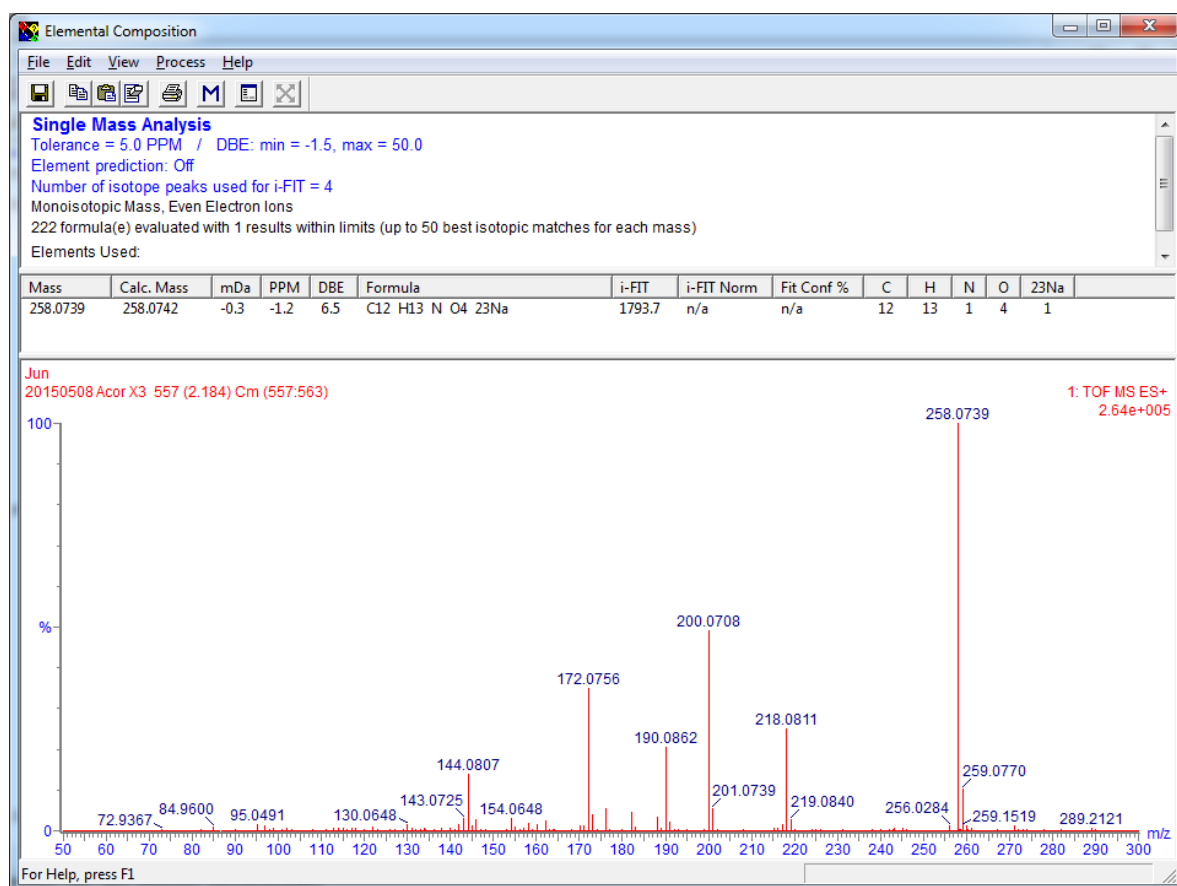


Figure S30. Elemental composition report of the precursor ion

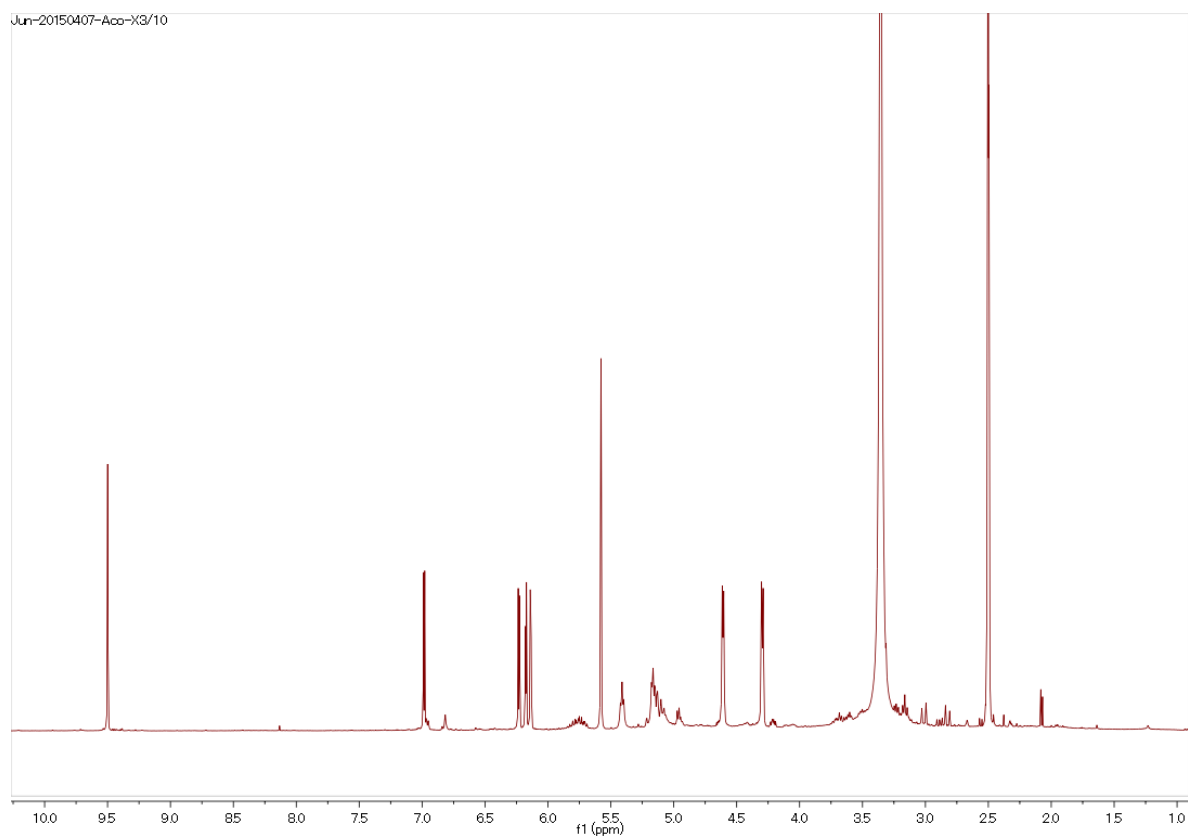


Figure S31. ^1H NMR spectrum (DMSO- d_6 , 400 MHz)

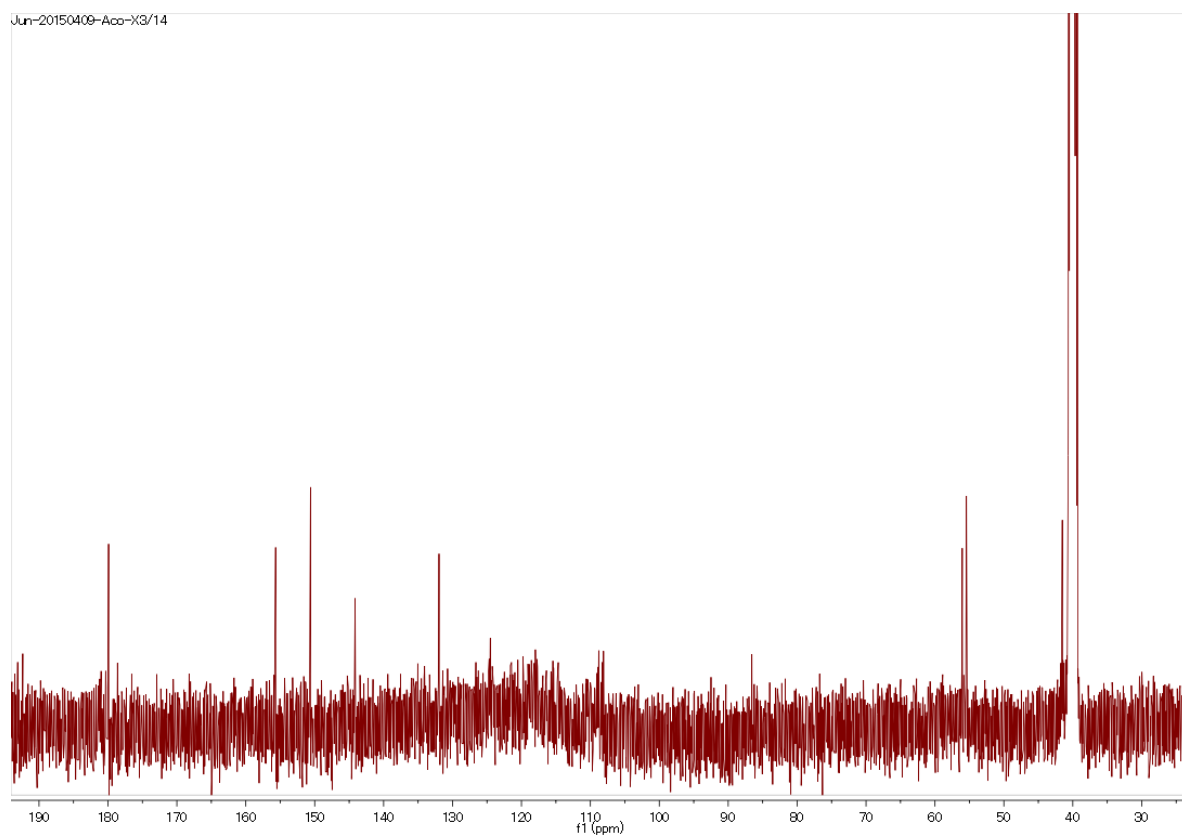


Figure S32. ^{13}C NMR spectrum (DMSO- d_6 , 100 MHz)

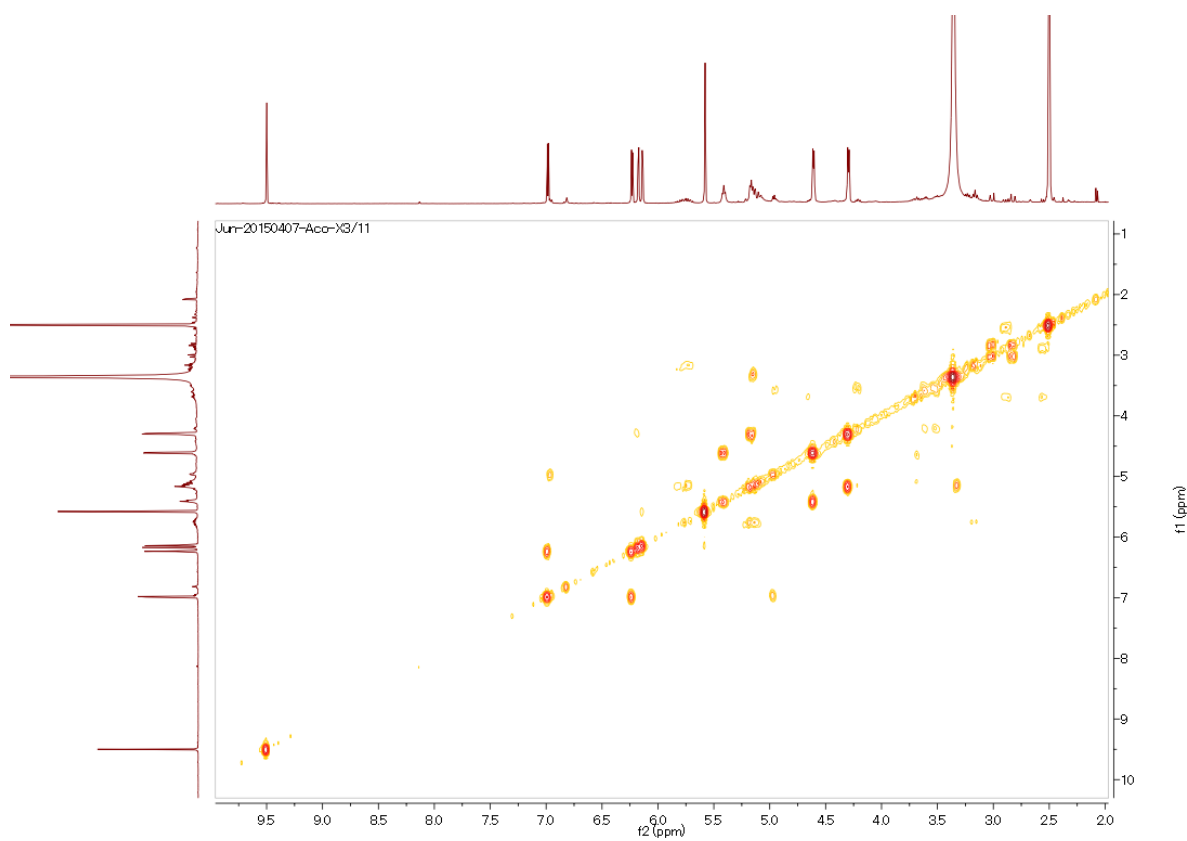


Figure S33. COSY correlations

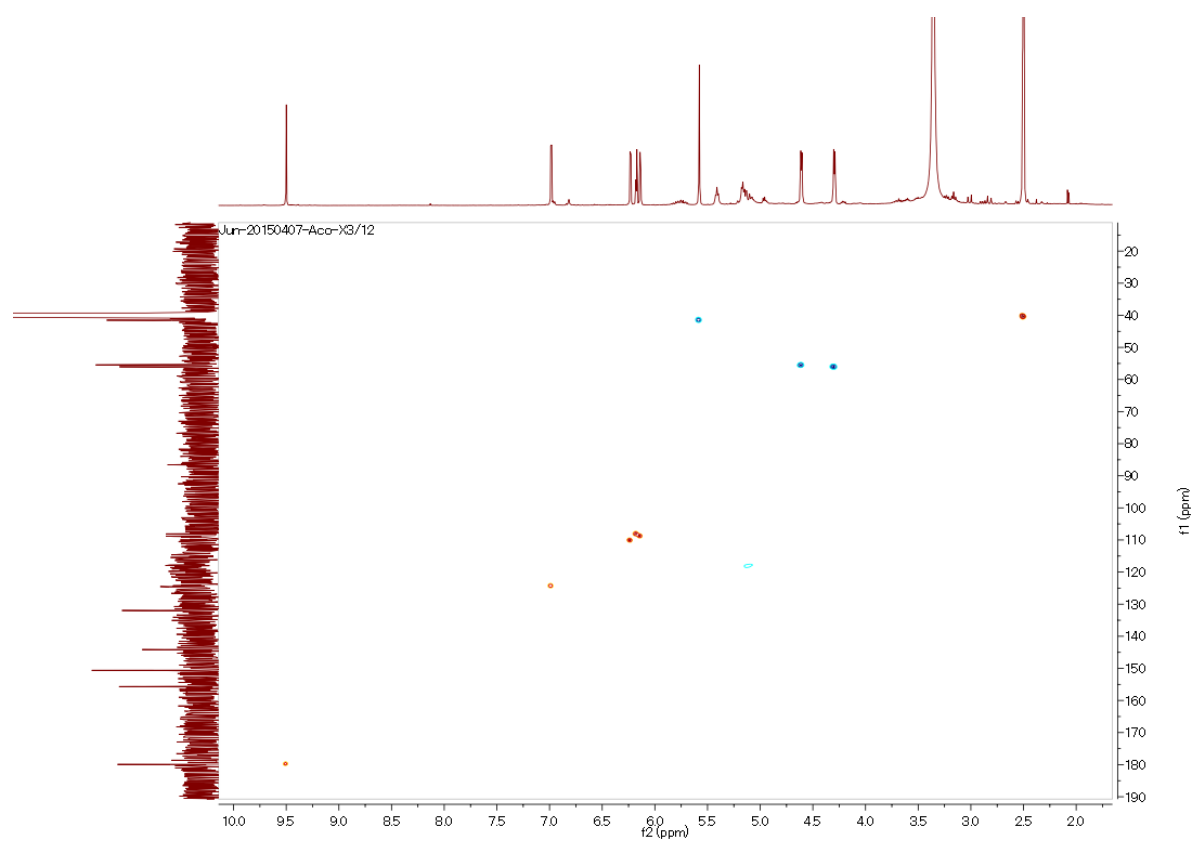


Figure S34. HSQC correlations

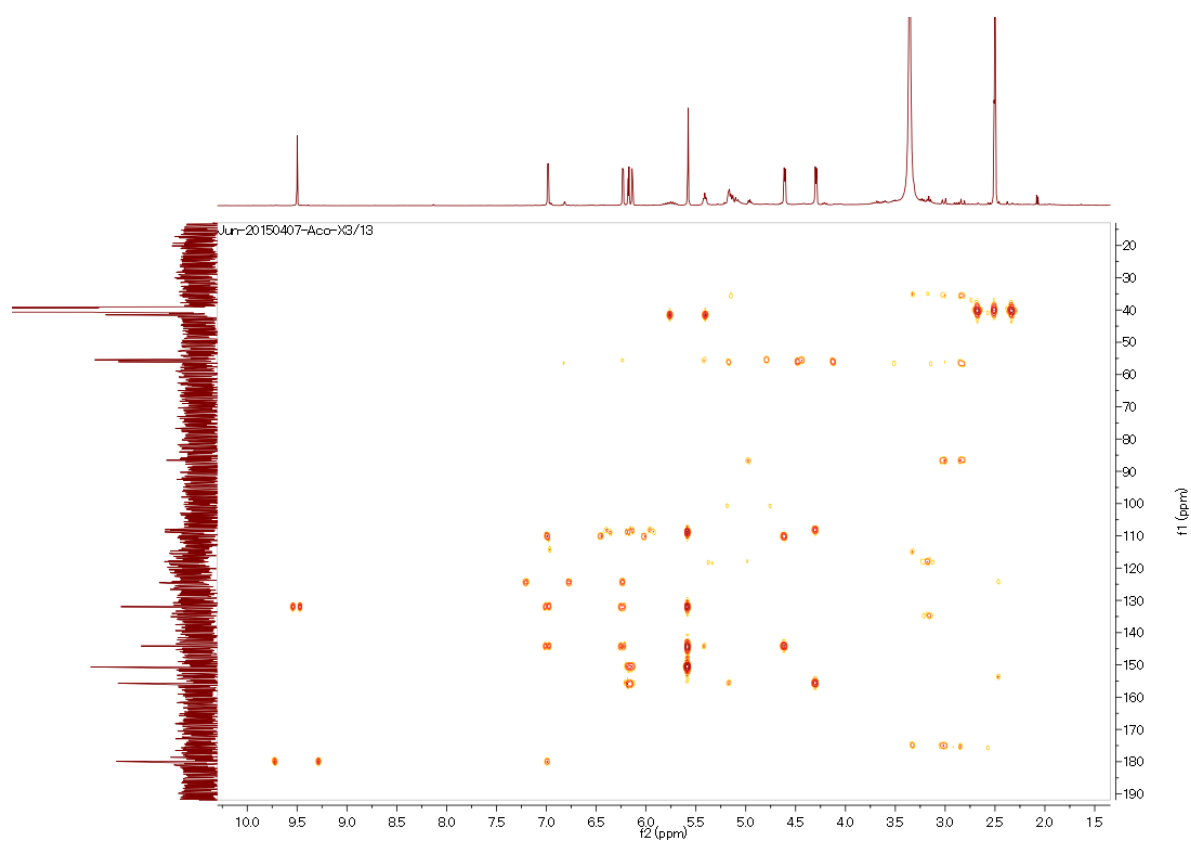


Figure S35. HMBC correlations

3-(allylthio)-2-(2-formyl-5-hydroxymethyl-1*H*-pyrrol-1-yl)propanoic acid (**6**)

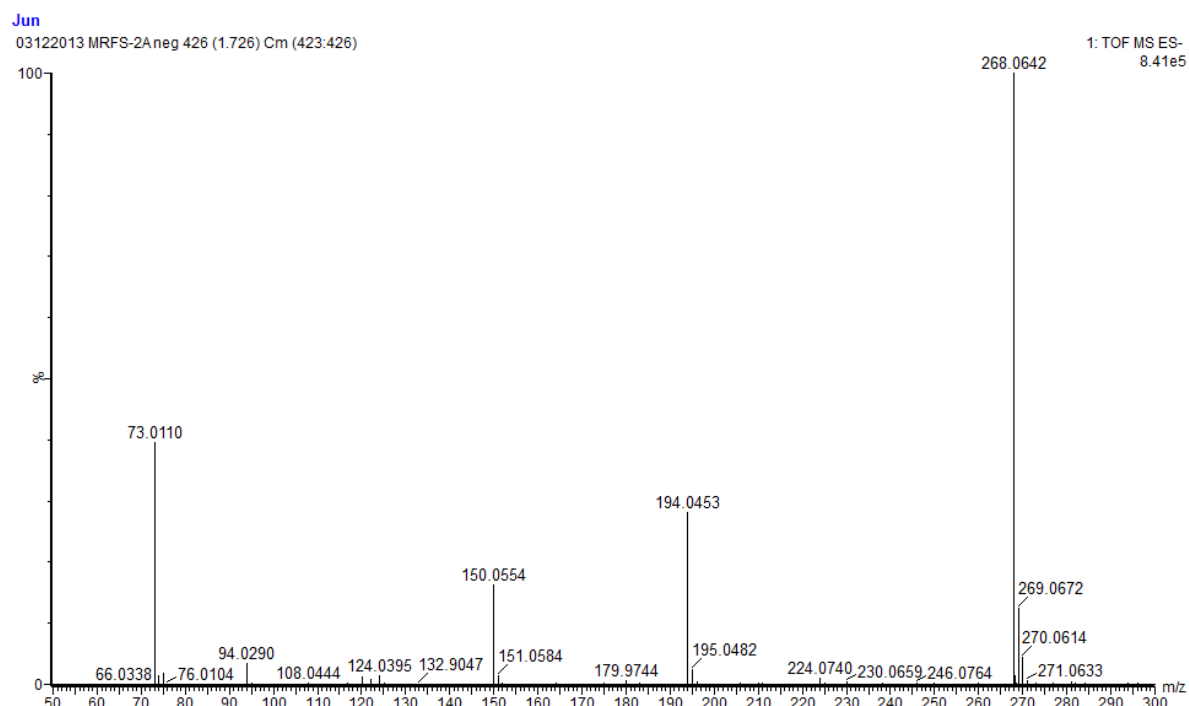


Figure S36. HRESIMS (positive) spectrum

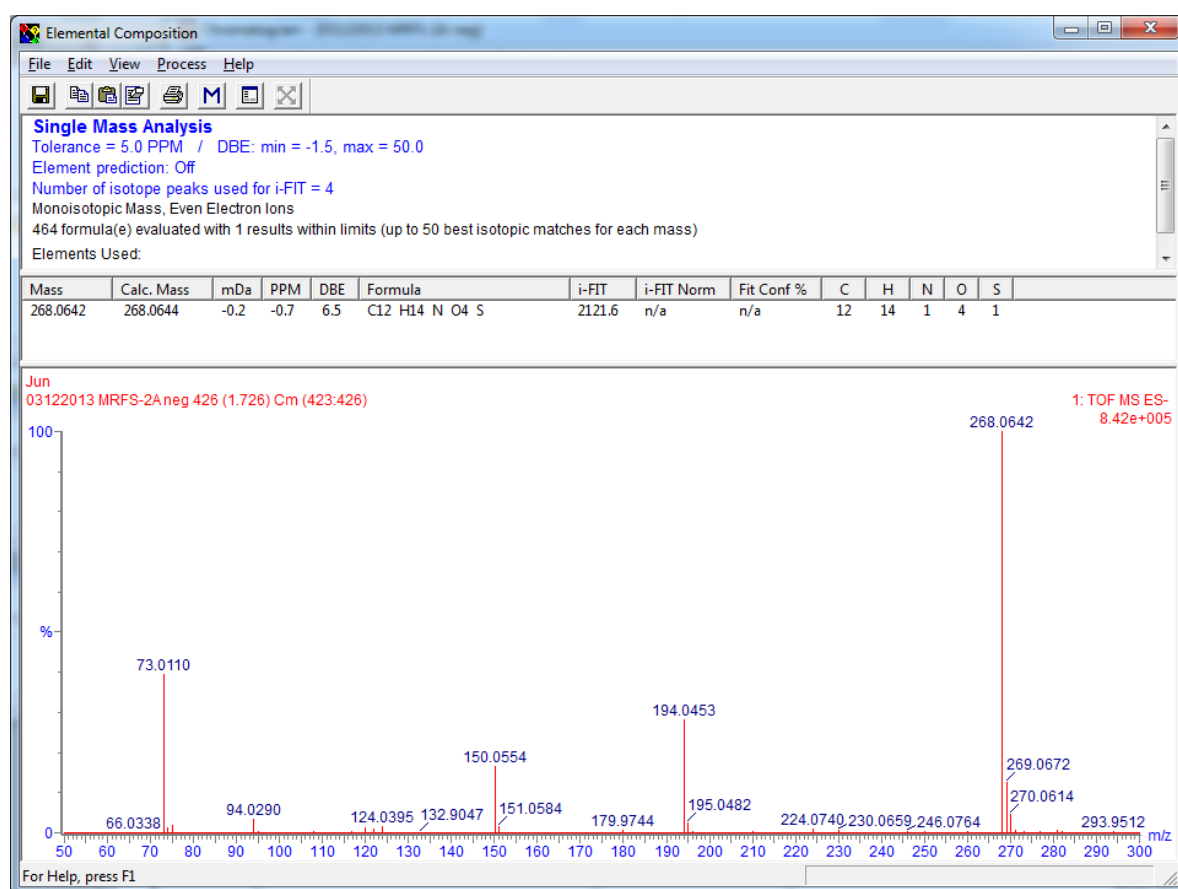


Figure S37. Elemental composition report of the precursor ion

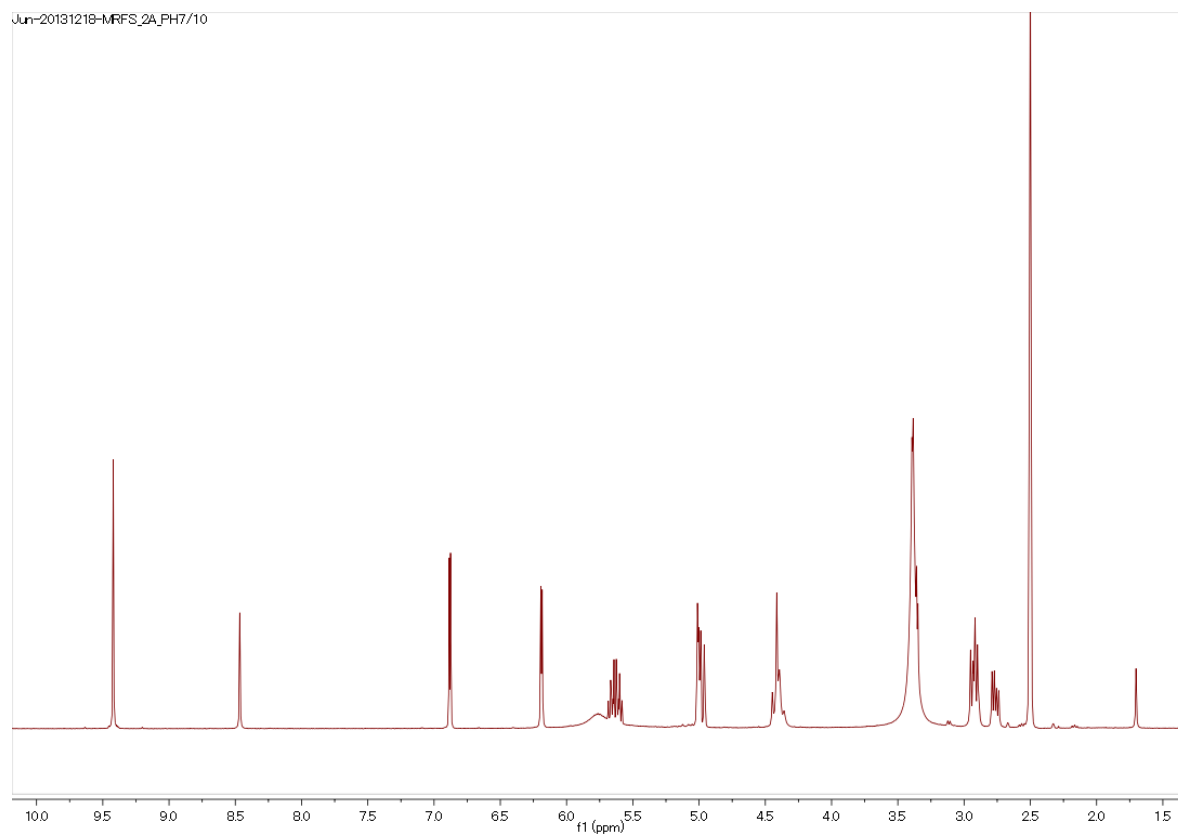


Figure S38. ^1H NMR spectrum (DMSO- d_6 , 400 MHz)

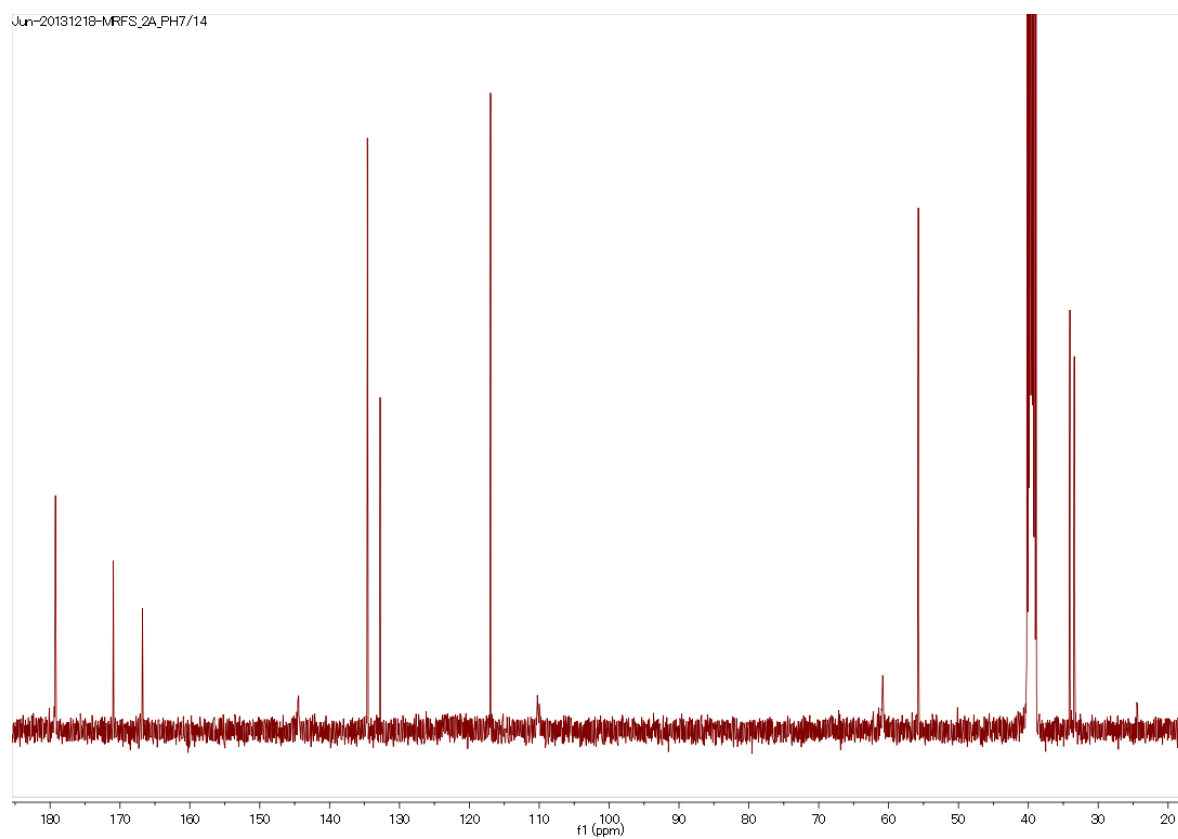


Figure S39. ^{13}C NMR spectrum (DMSO- d_6 , 100 MHz)

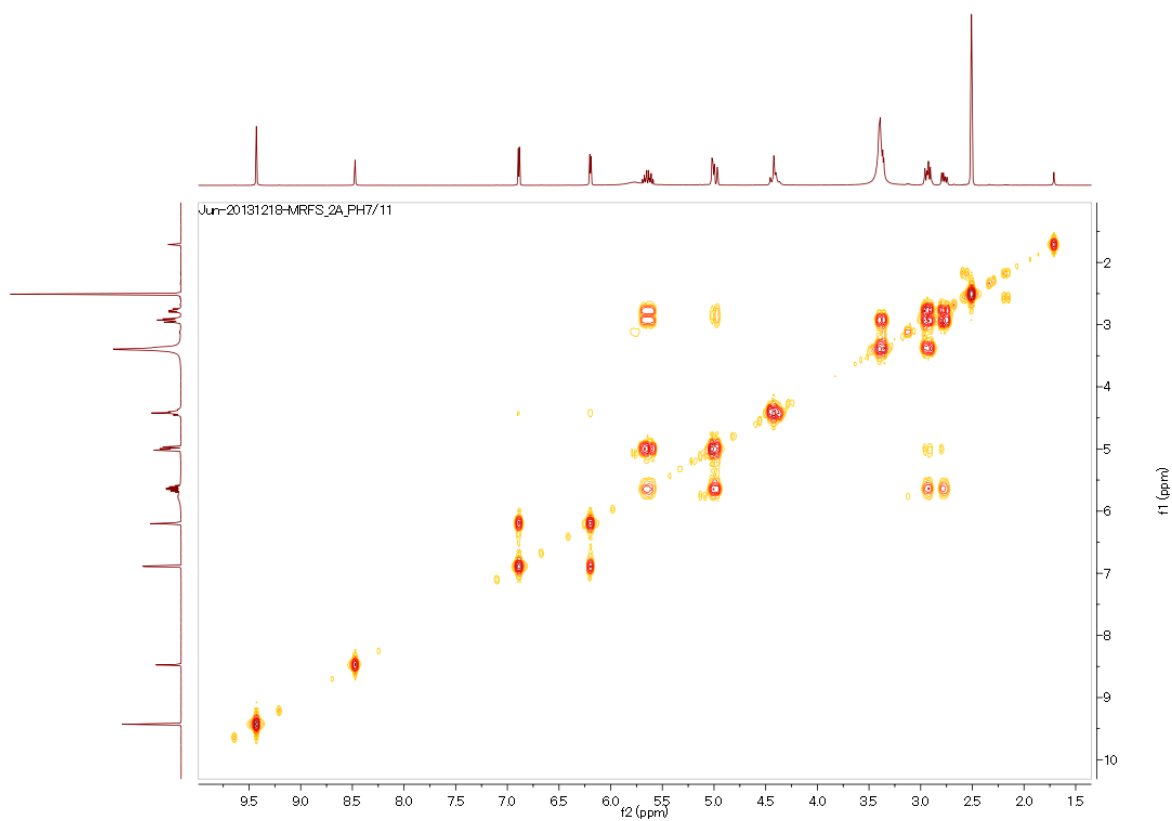


Figure S40. COSY correlations

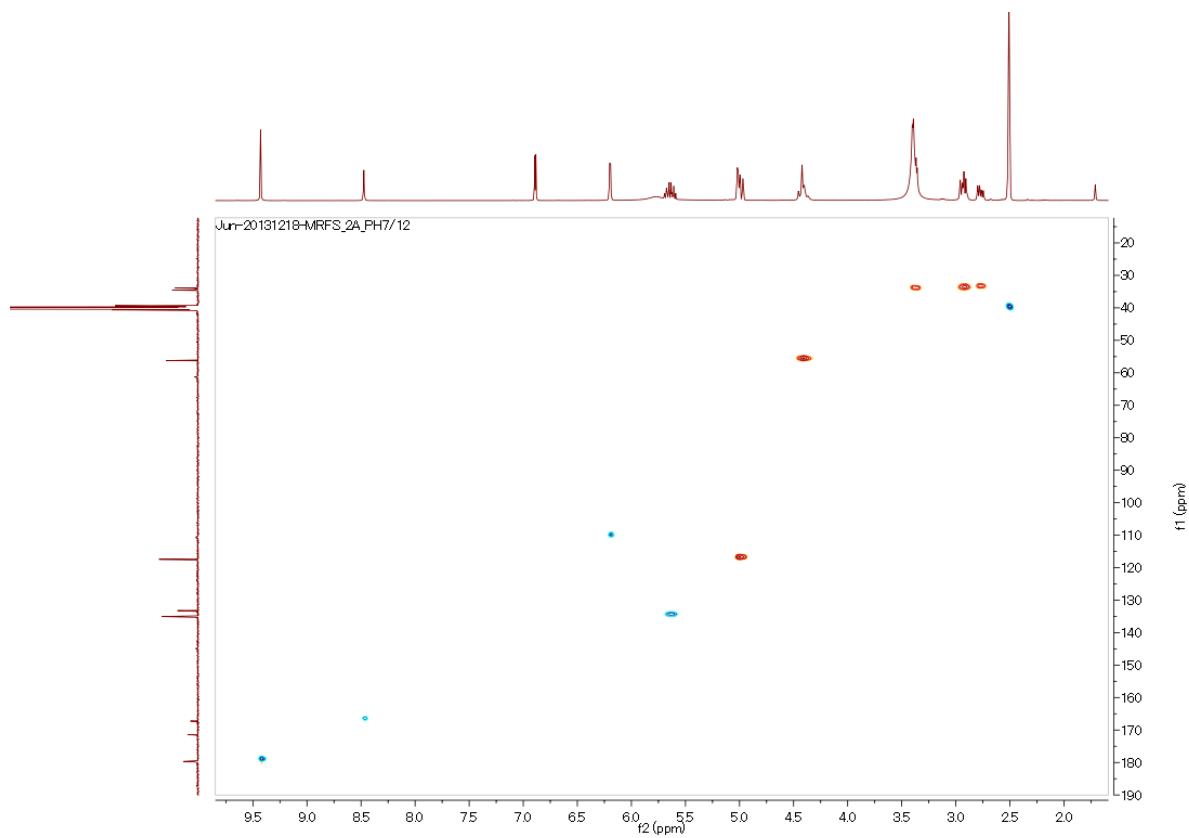


Figure S41. HSQC correlations

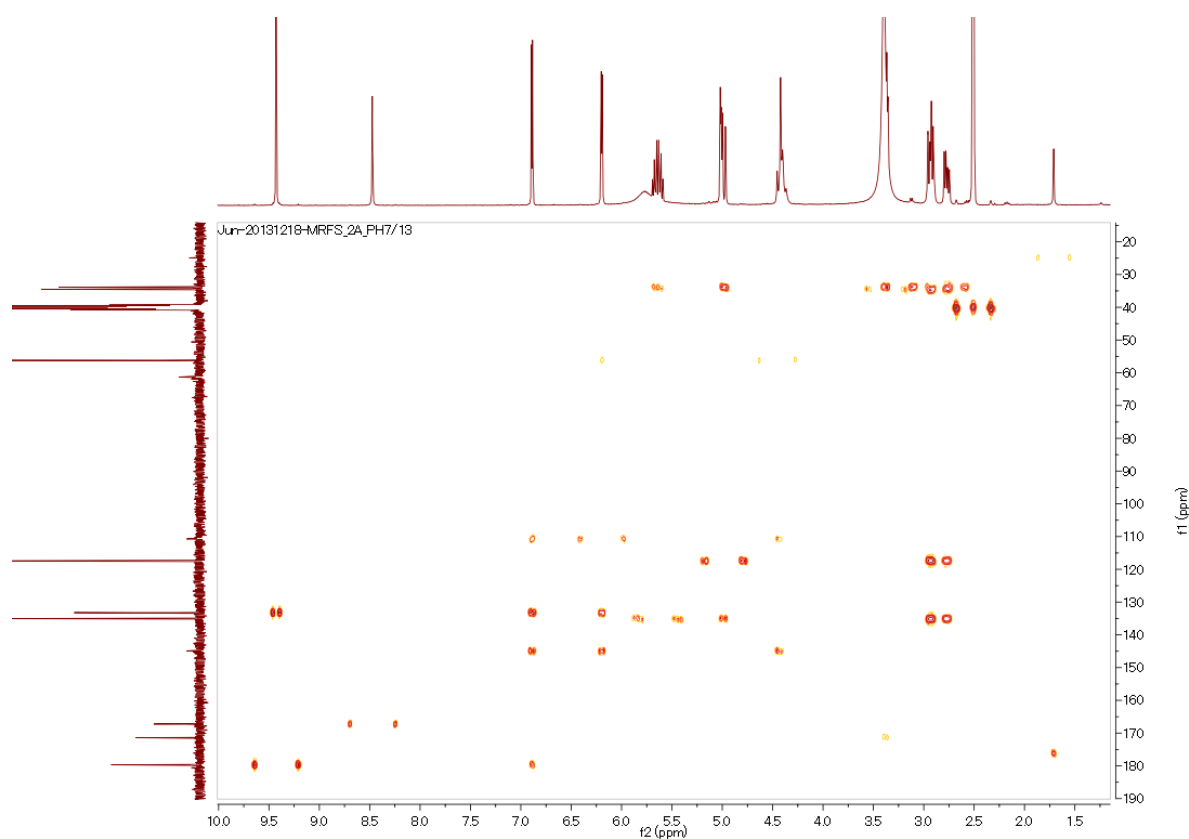


Figure S42. HMBC correlations

(4S)-4-allylthiomethyl-3,4-dihydro-3-oxo-1H-pyrrolo[2,1-c][1,4]oxazine-6-carbaldehyde (**7**)

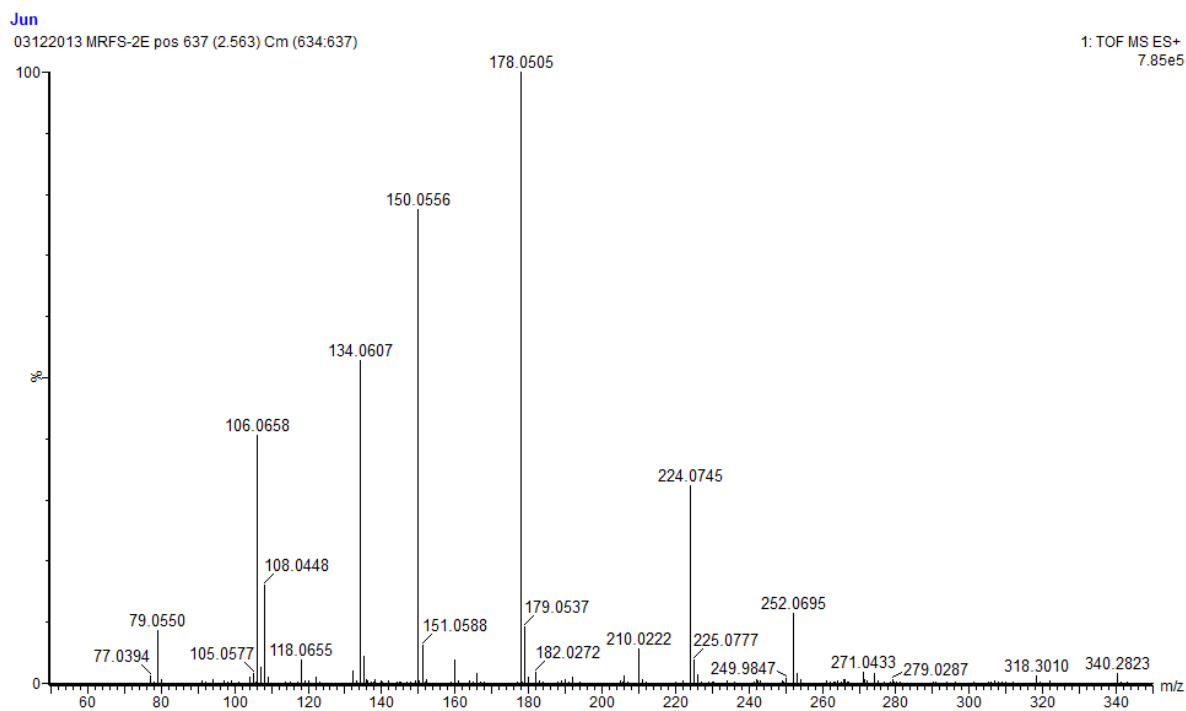


Figure S43. HRESIMS (positive) spectrum

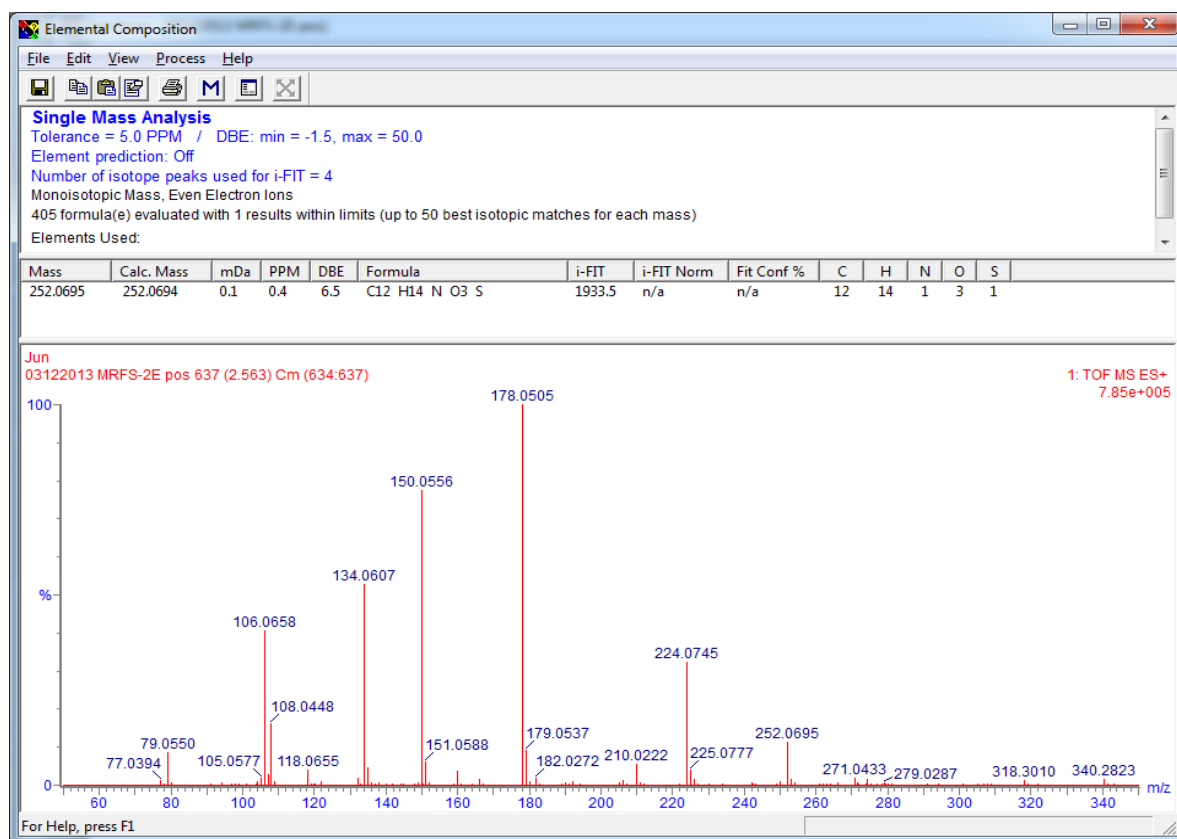


Figure S44. Elemental composition report of the precursor ion

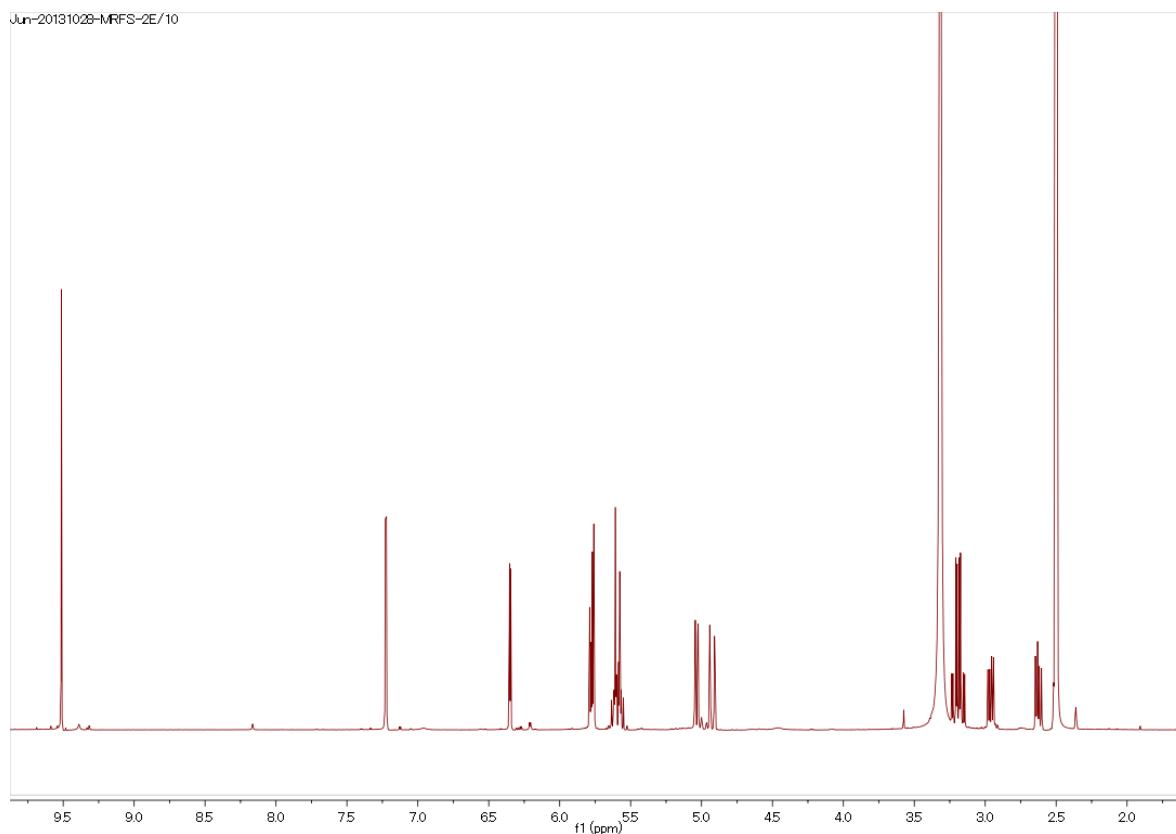


Figure S45. ^1H NMR spectrum (DMSO- d_6 , 500 MHz)

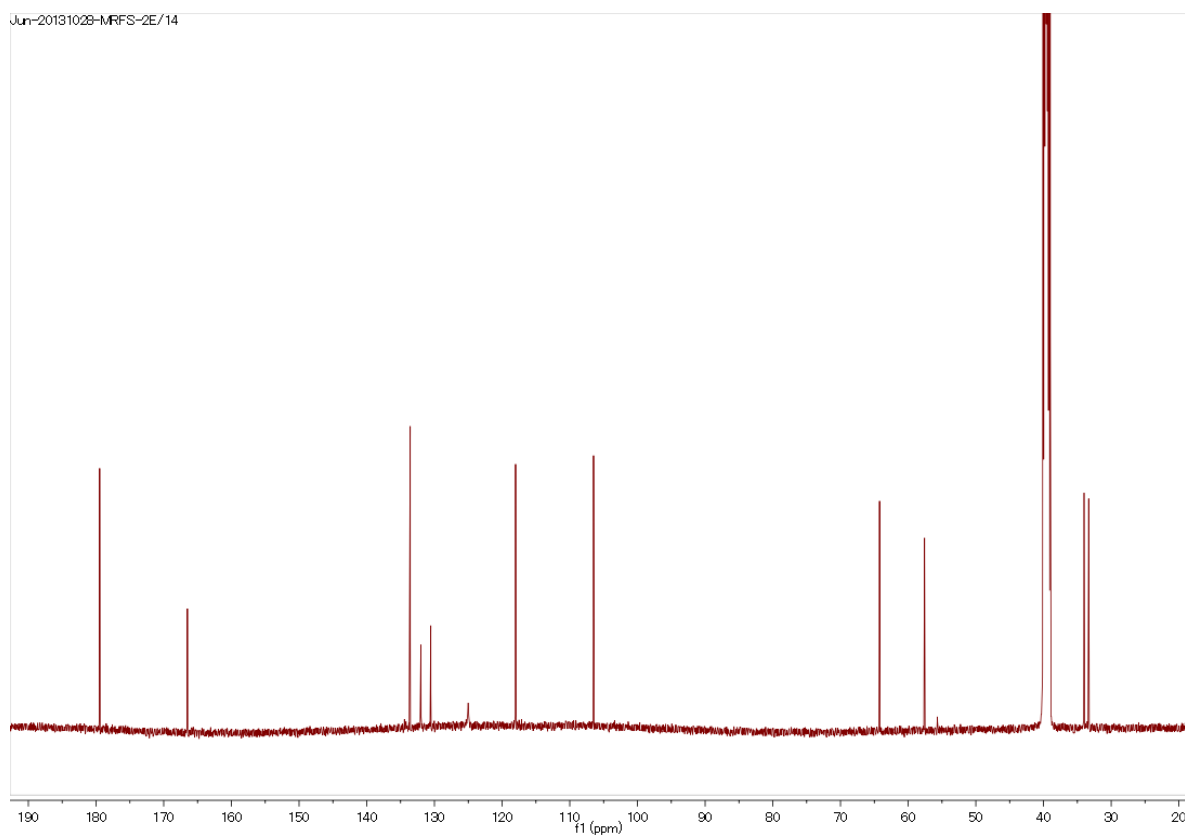


Figure S46. ^{13}C NMR spectrum (DMSO- d_6 , 125 MHz)

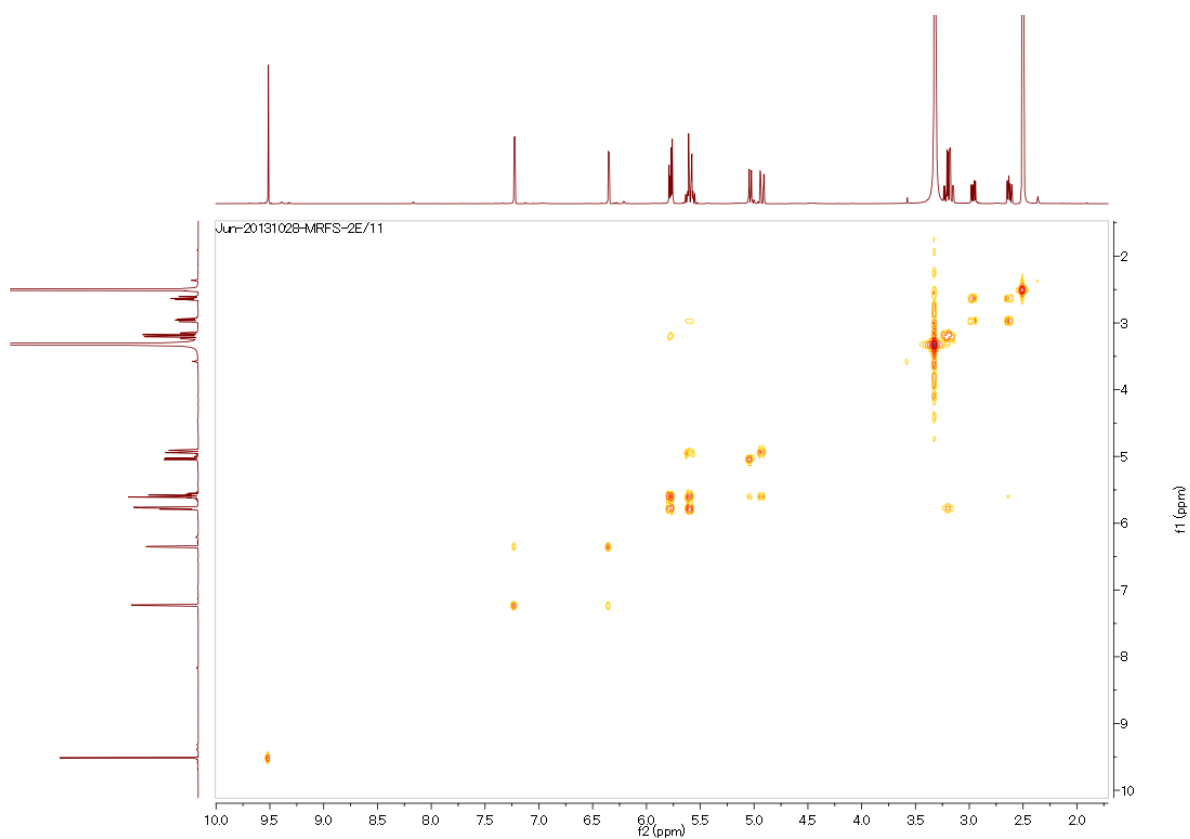


Figure S47. COSY correlations

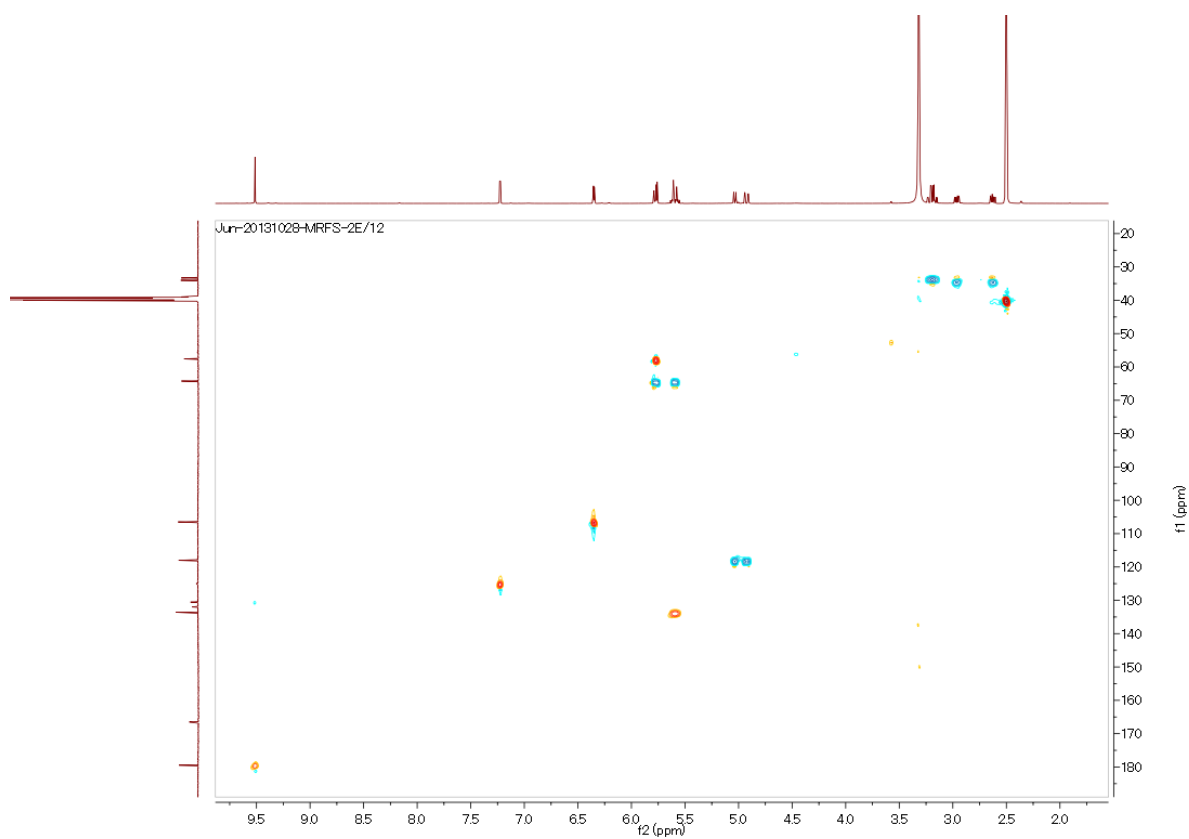


Figure S48. HSQC correlations

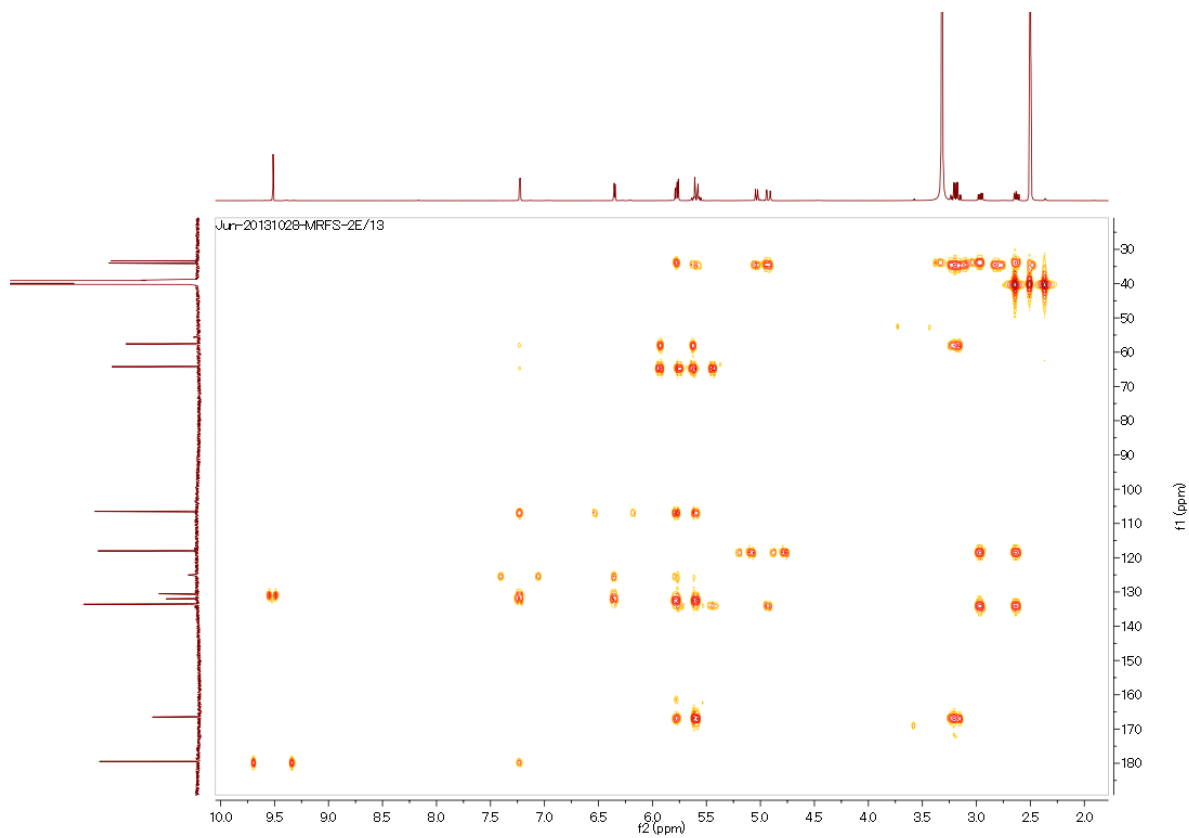


Figure S49. HMBC correlations

(2*R*)-3-(allylthio)-2-((4*R*)-4-(allylthiomethyl)-6-formyl-3-oxo-3,4-dihydropyrrolo[1,2-*a*]-pyrazin-2(1*H*)-yl)propanoic acid (**8**)

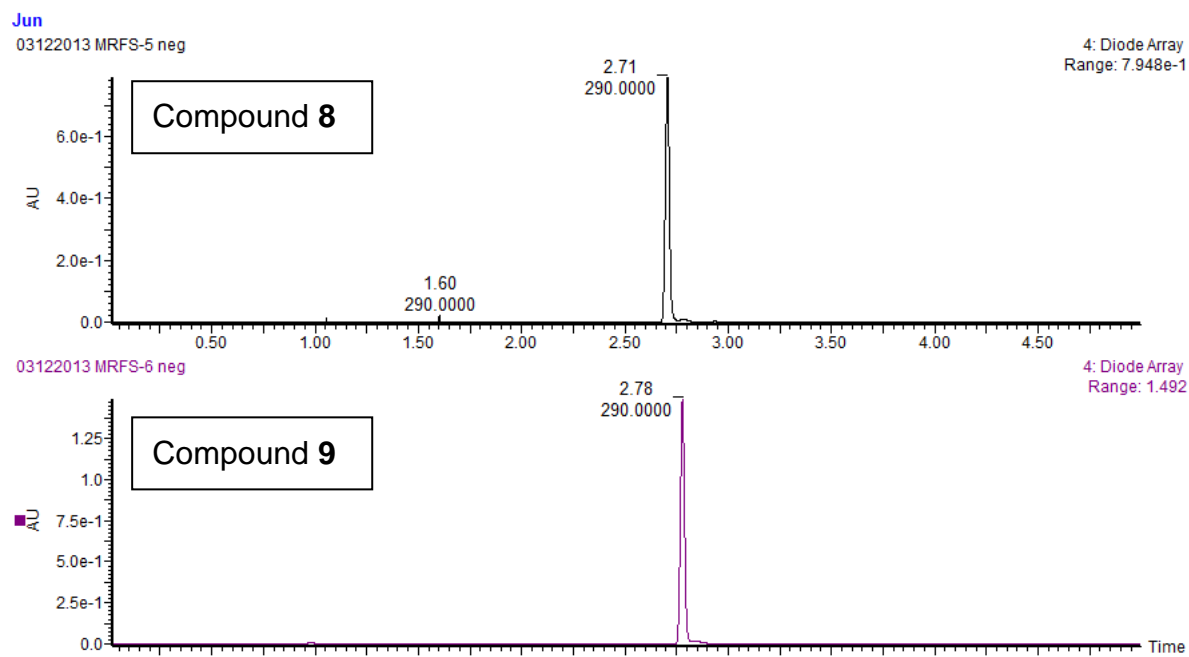


Figure S50. Chromatograms of compounds **8** and **9** recorded by UV detection (290 nm) using UPLC-TOF-MS

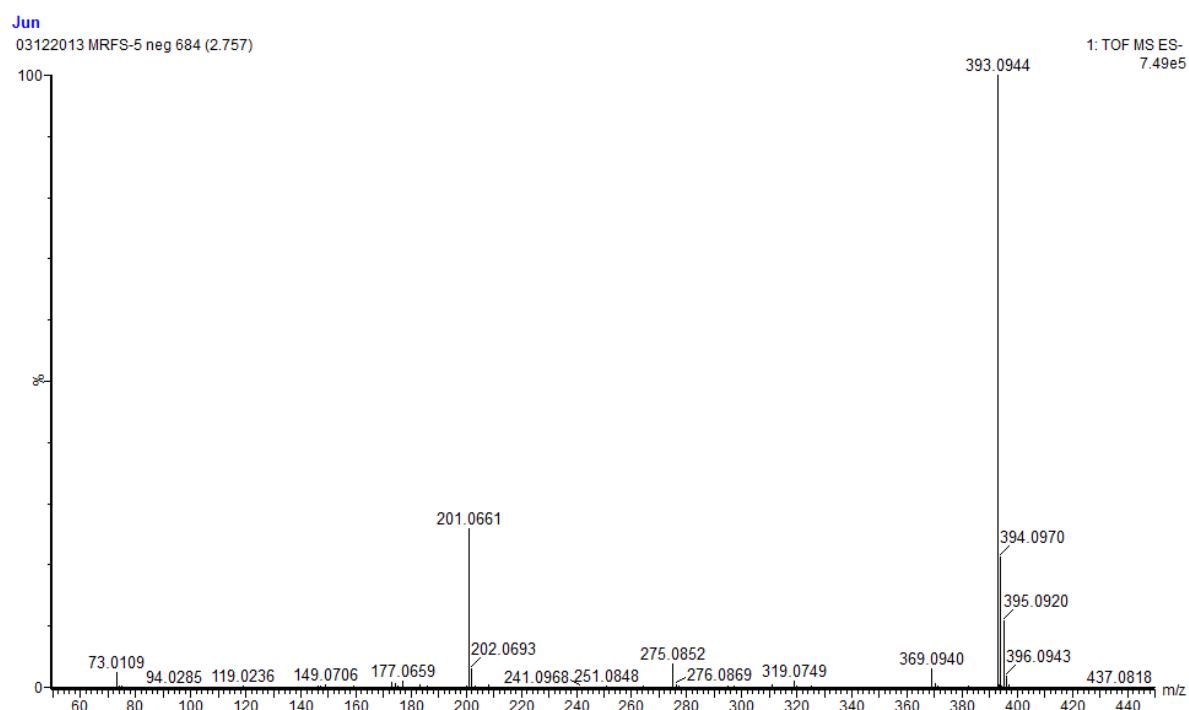


Figure S51. HRESIMS (negative) spectrum

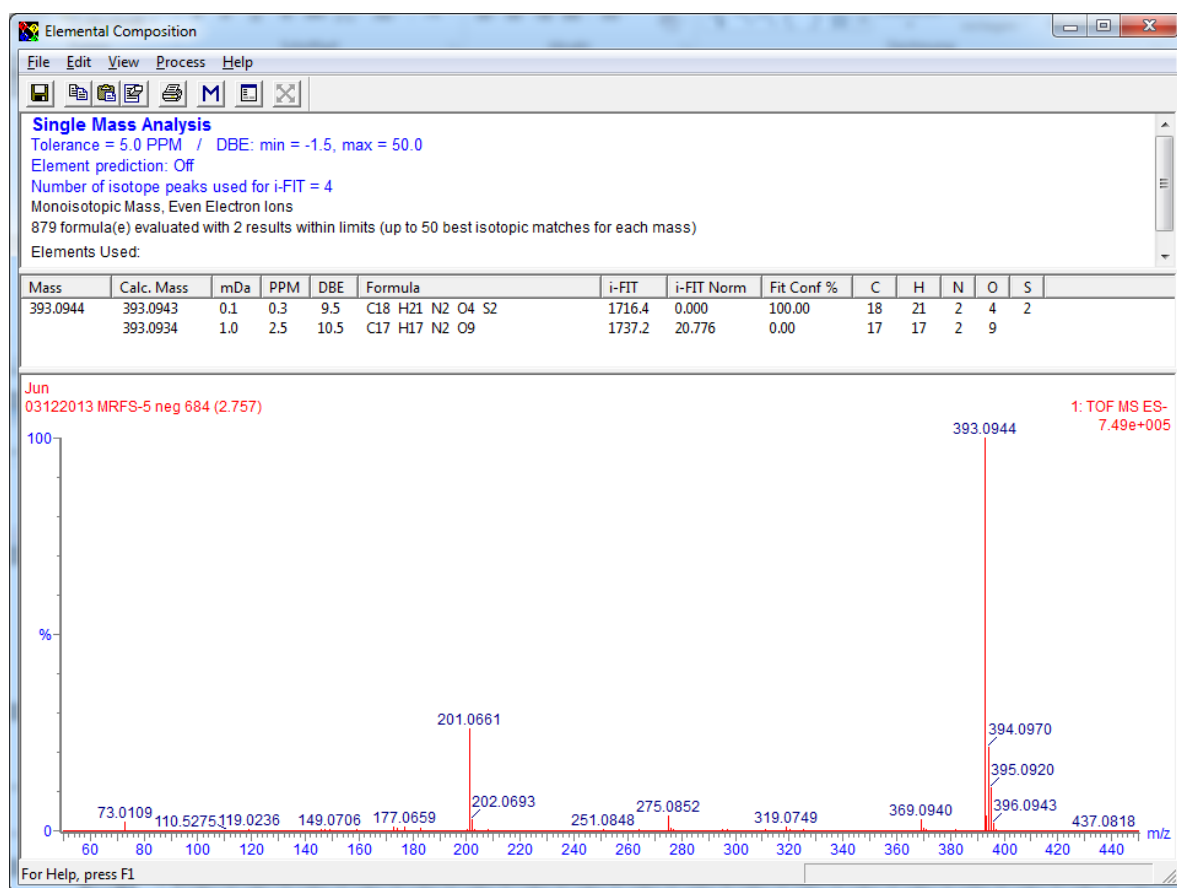


Figure S52. Elemental composition report of the precursor ion

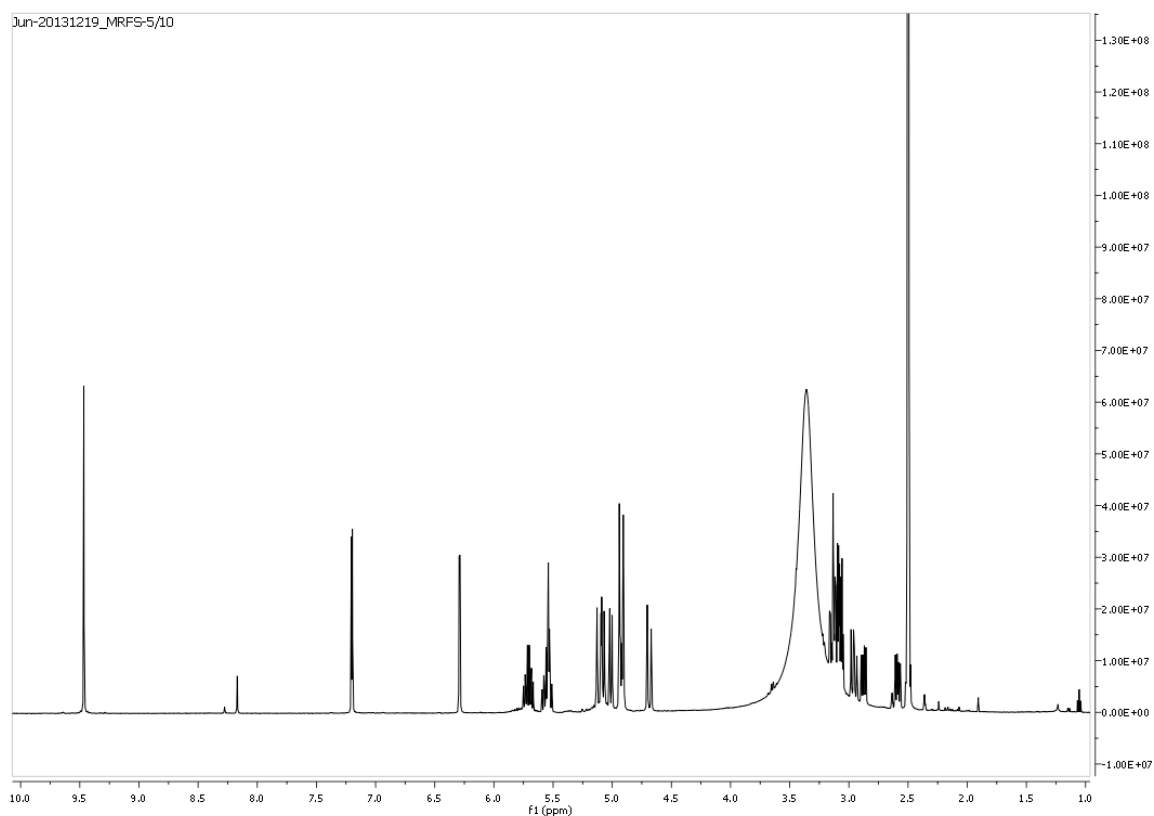


Figure S53. ^1H NMR spectrum (DMSO- d_6 , 500 MHz)

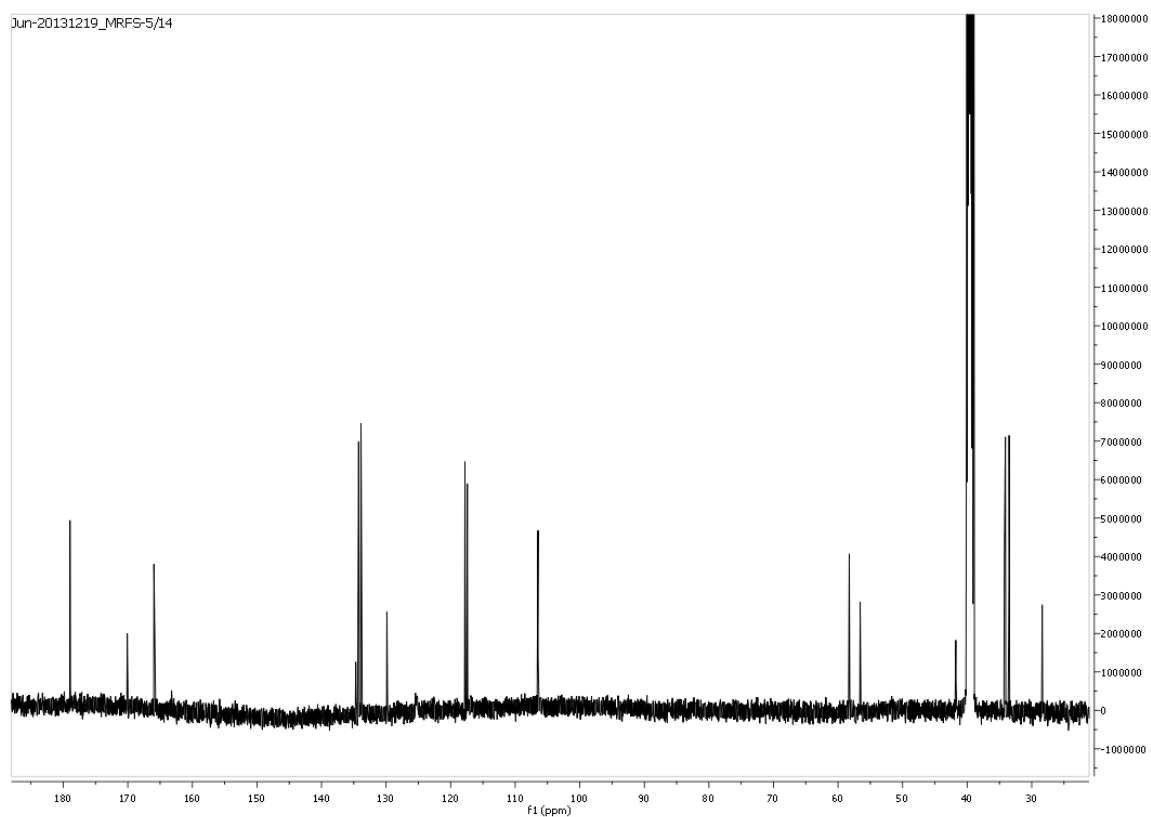


Figure S54. ^{13}C NMR spectrum (DMSO- d_6 , 125 MHz)

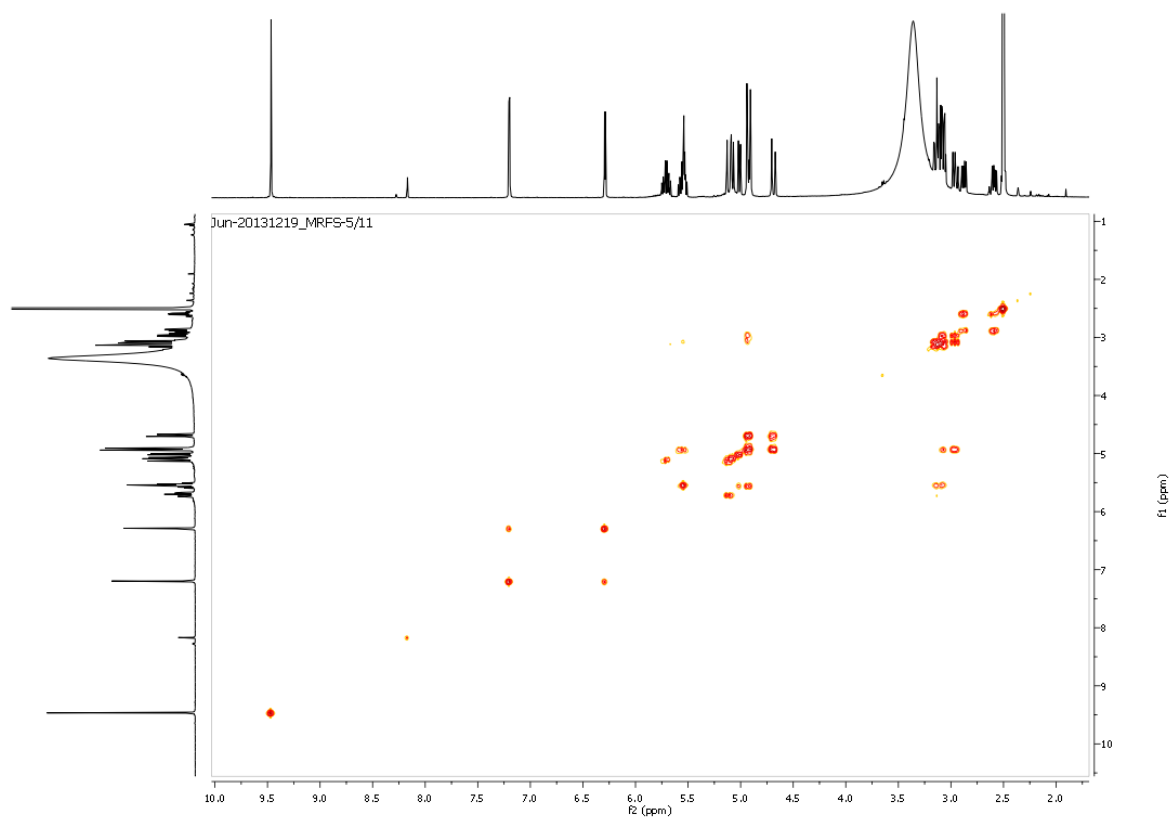


Figure S55. COSY correlations

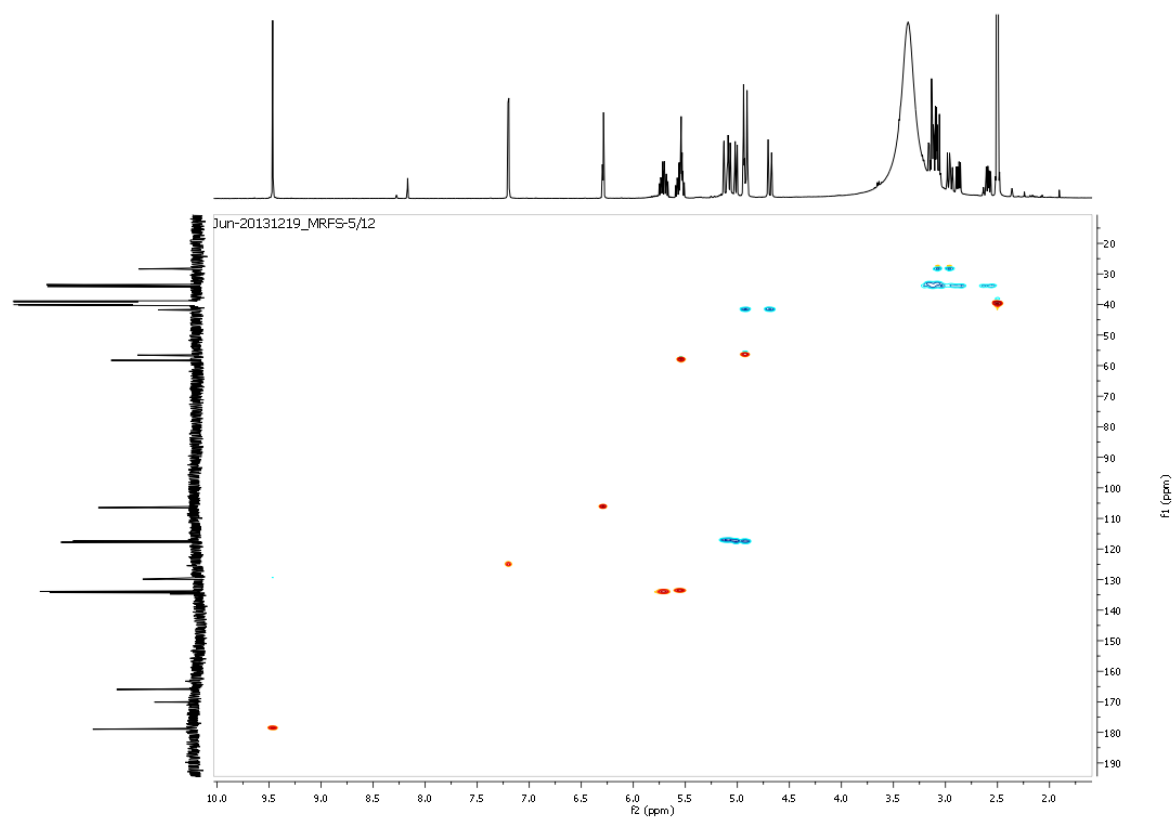


Figure S56. HSQC correlations

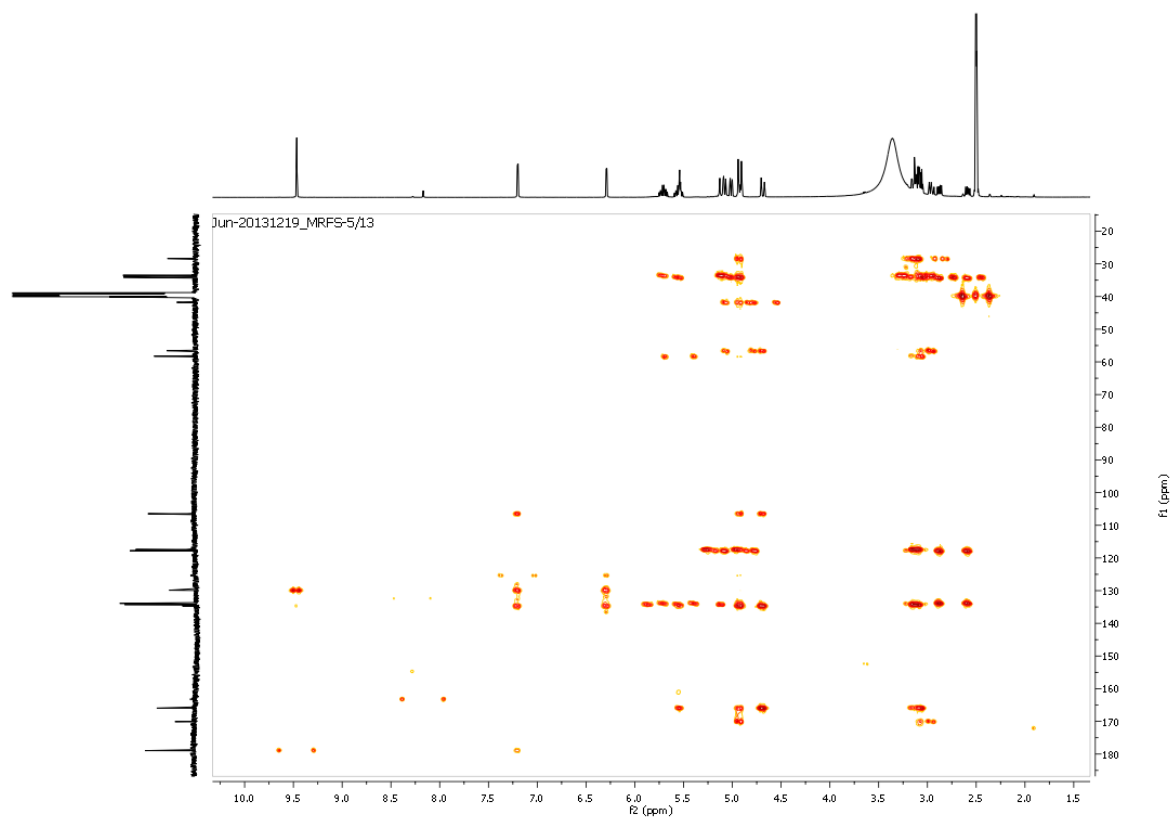


Figure S57. HMBC correlations

(2*R*)-3-(allylthio)-2-((4*S*)-4-(allylthiomethyl)-6-formyl-3-oxo-3,4-dihydropyrrolo[1,2-*a*]-pyrazin-2(1*H*)-yl)propanoic acid (**9**)

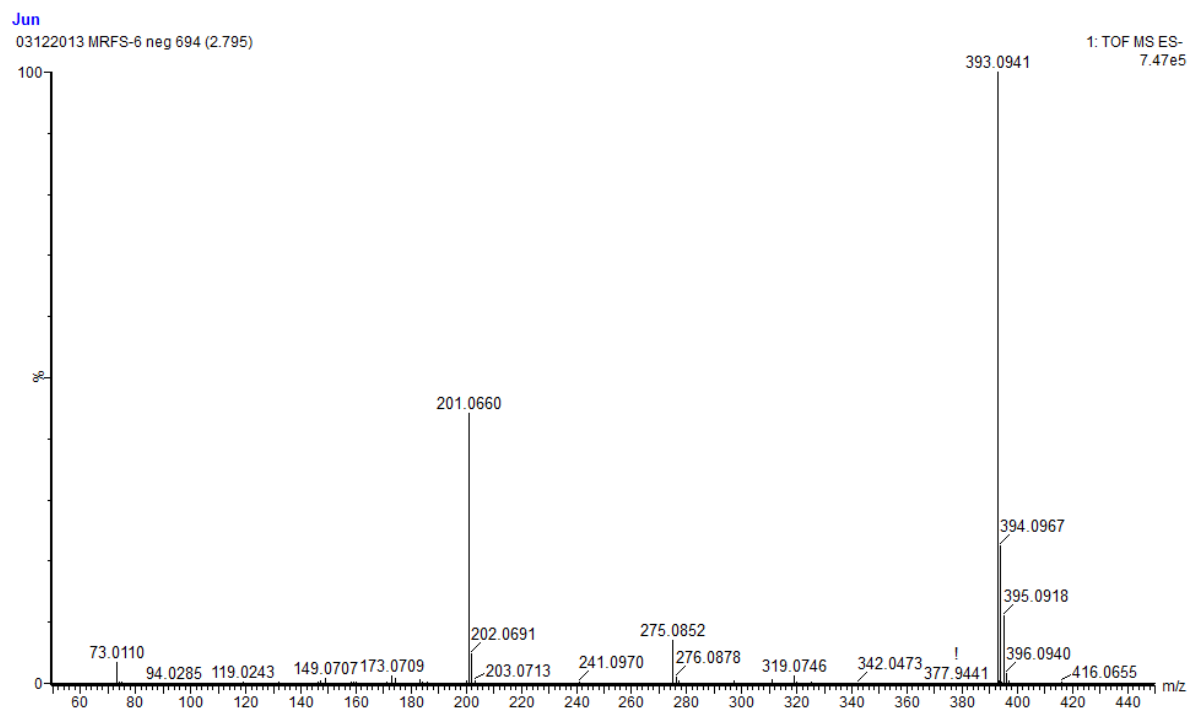


Figure S58. HRESIMS (negative) spectrum

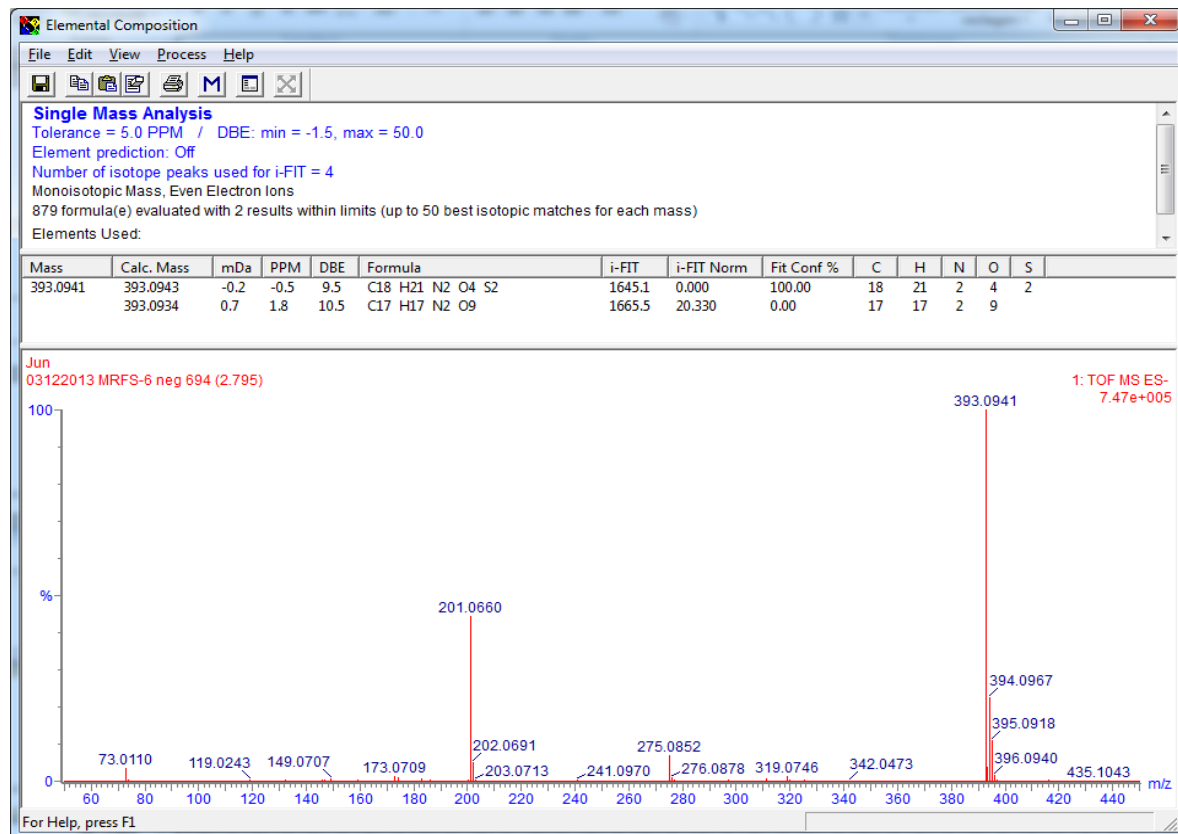


Figure S59. Elemental composition report of the precursor ion

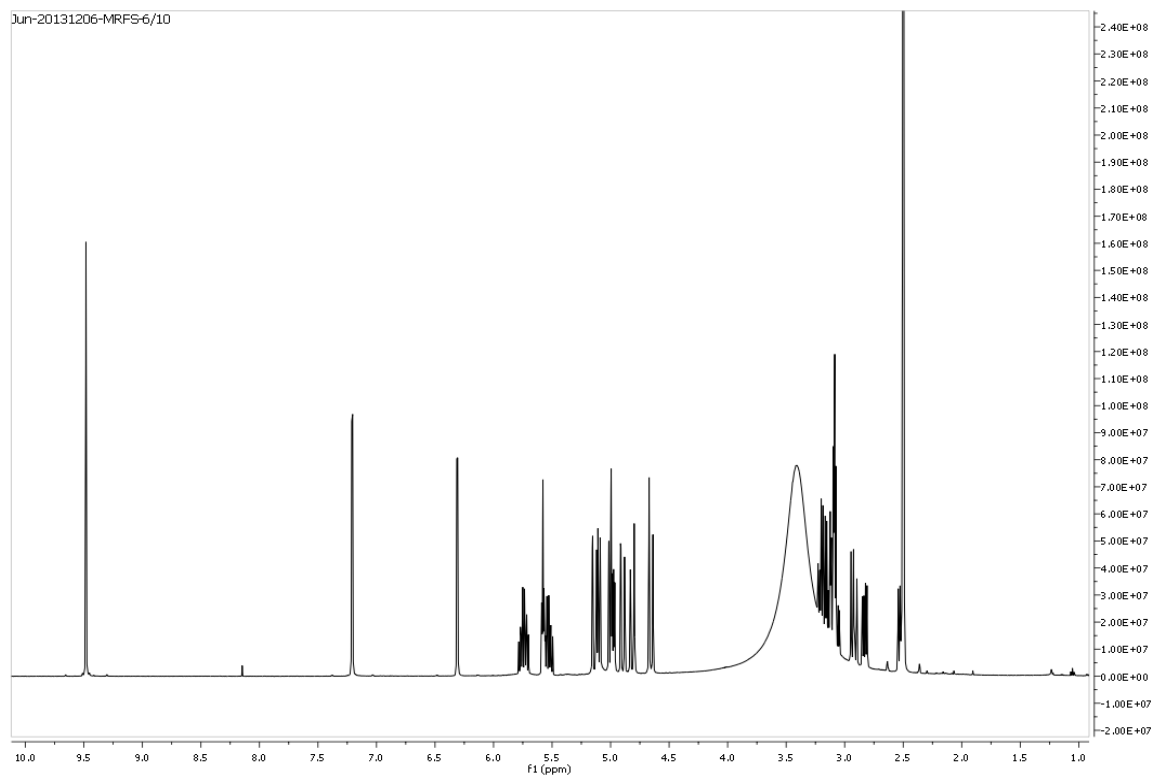


Figure S60. ^1H NMR spectrum (DMSO- d_6 , 500 MHz)

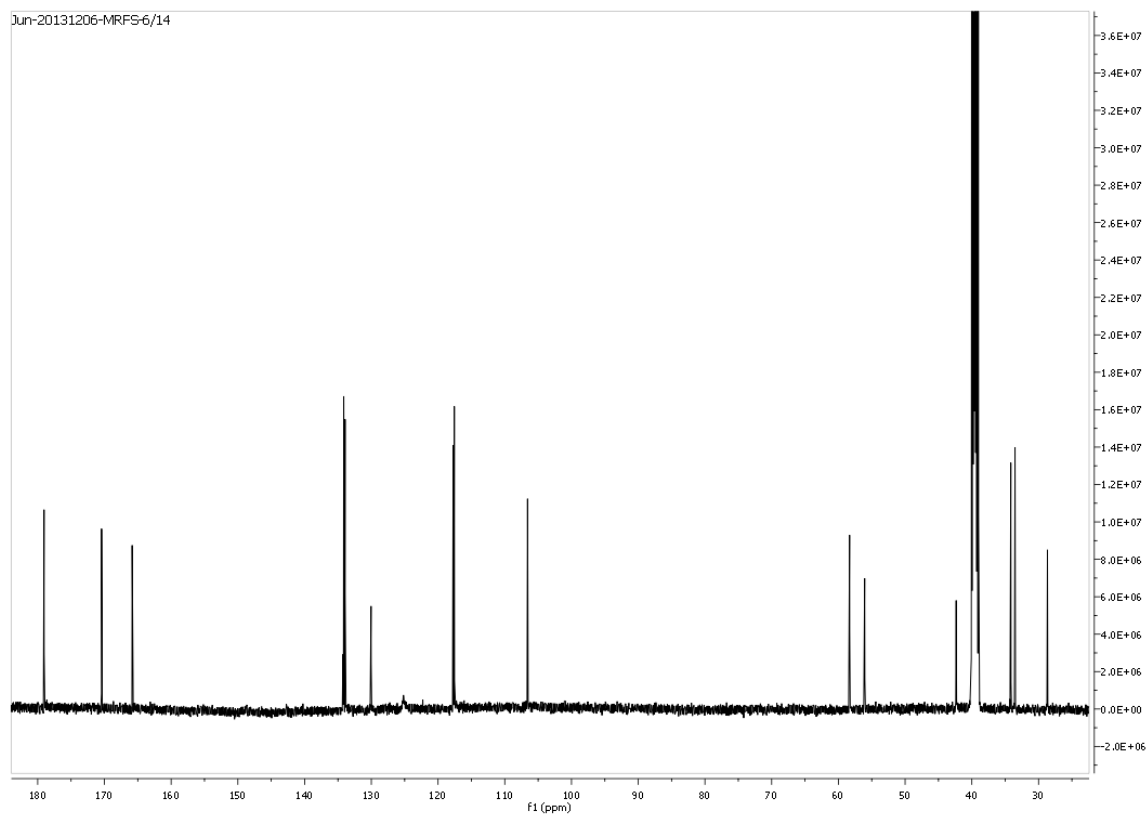


Figure S61. ^{13}C NMR spectrum (DMSO- d_6 , 125 MHz)

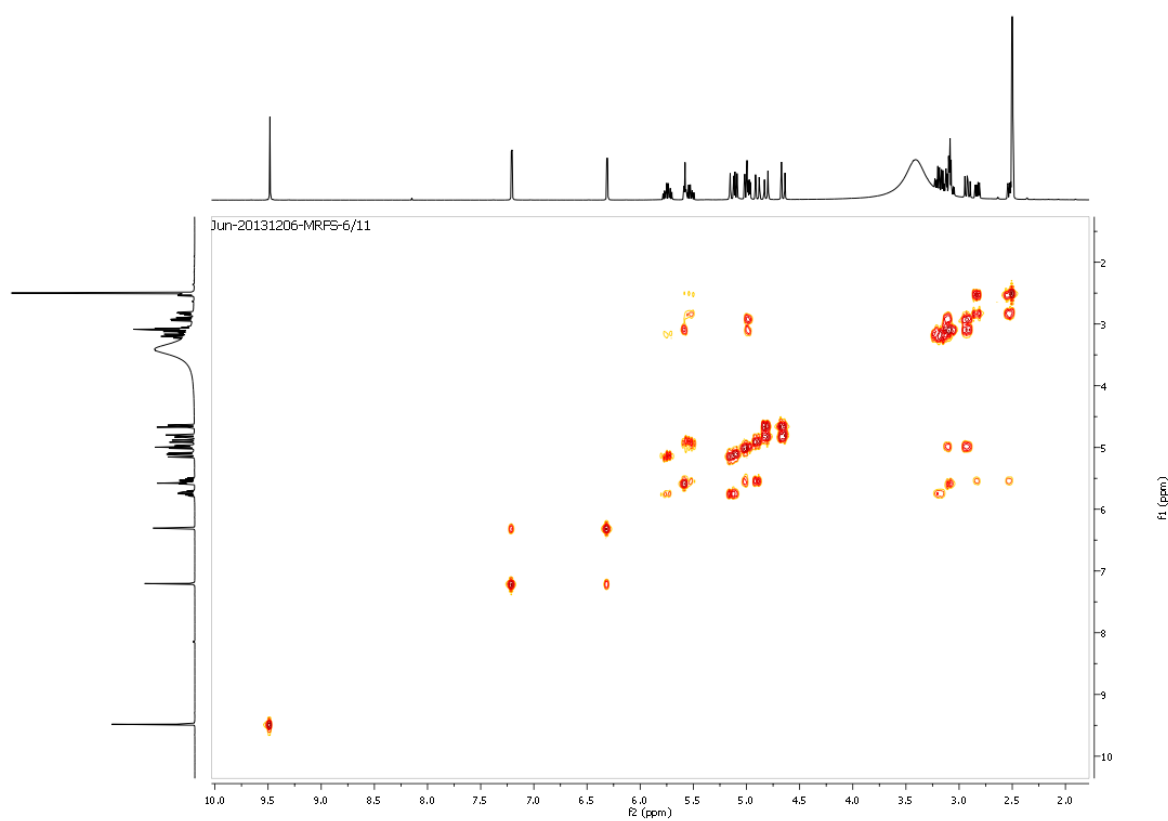


Figure S62. COSY correlations

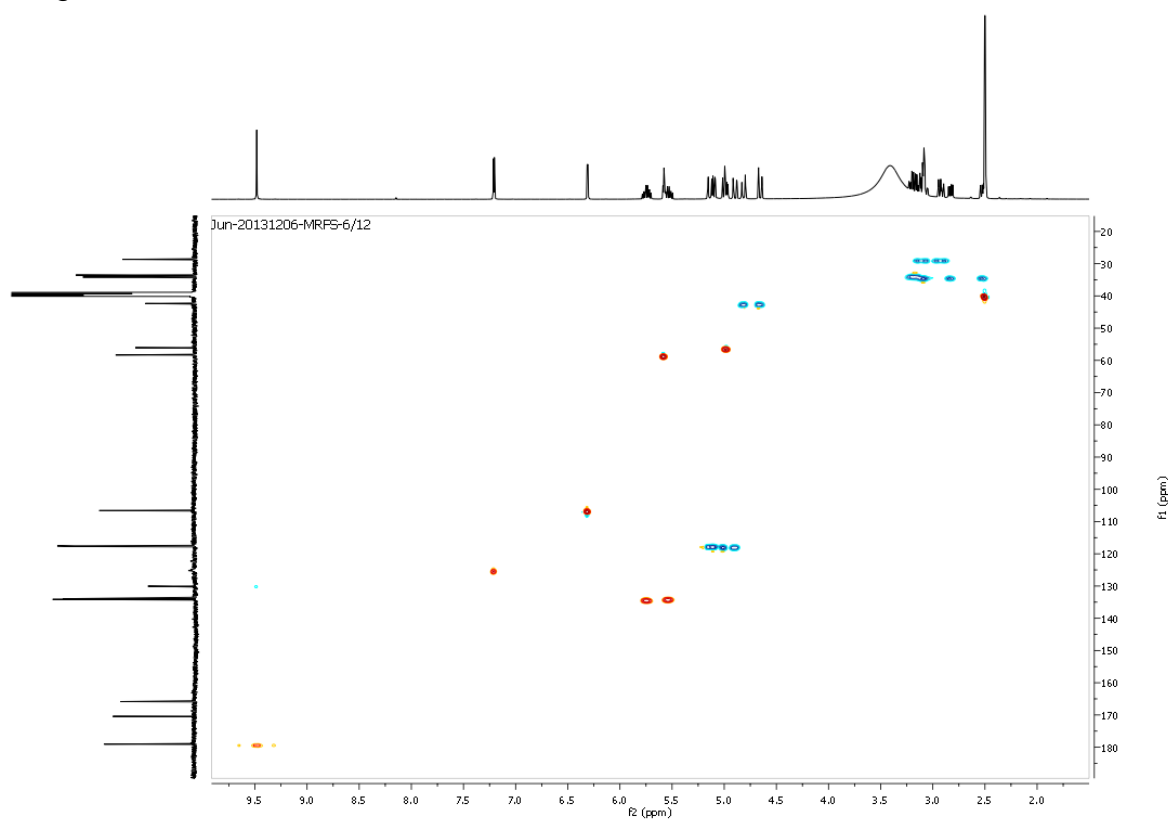


Figure S63. HSQC correlations

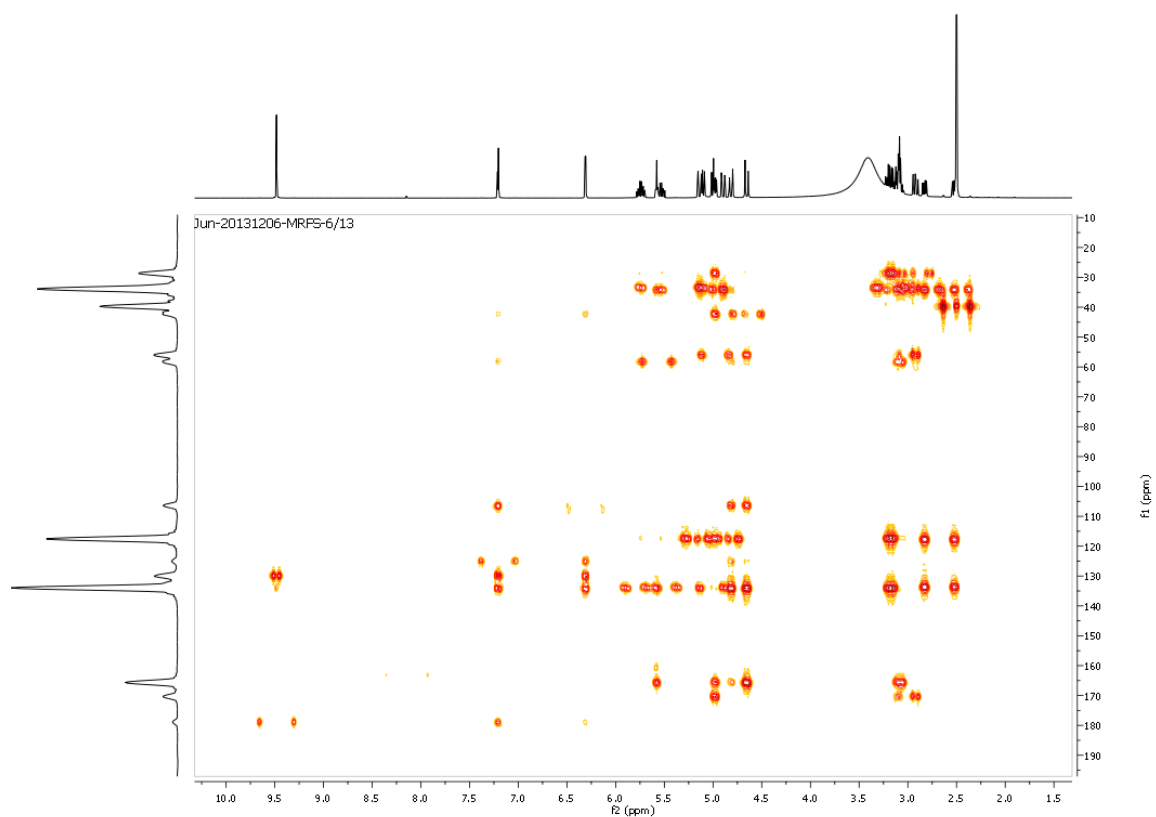


Figure S64. HMBC correlations

2-(allylthioethyl)-4-(allylthiomethyl)-3-oxo-3,4-dihydropyrrolo[1,2a]pyrazin-2(1*H*)-6-carbaldehyde (racemate of compound **10** and **11**)

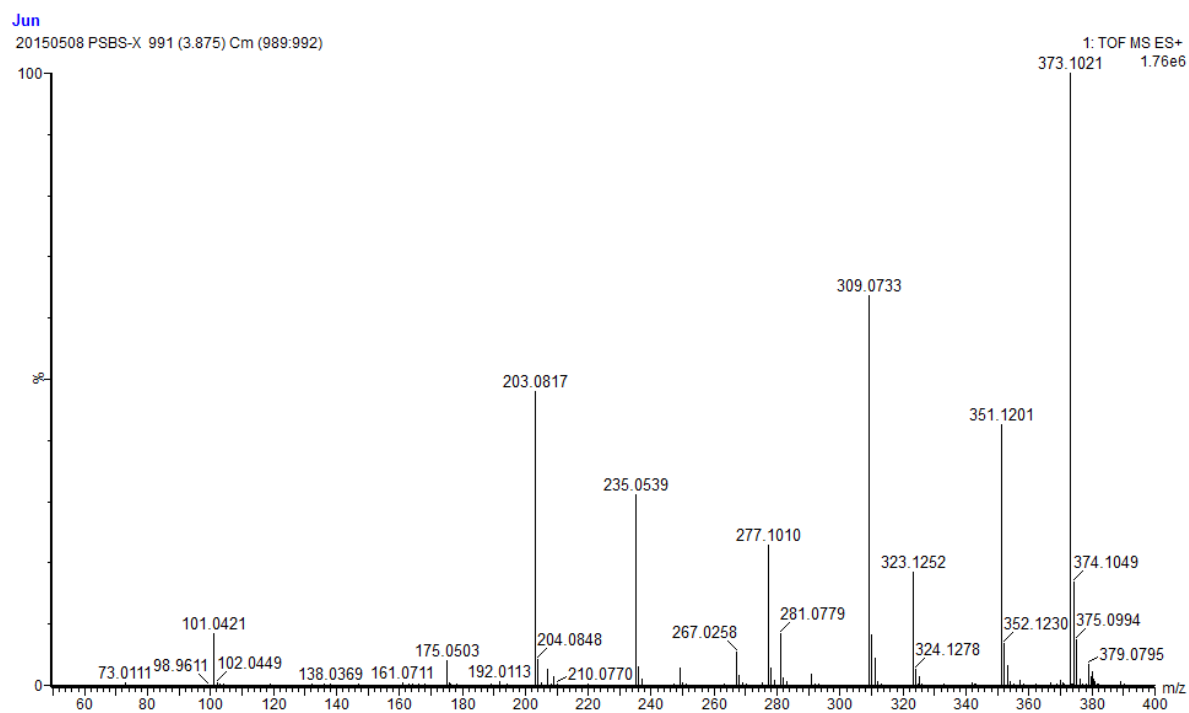


Figure S64. HRESIMS (negative) spectrum

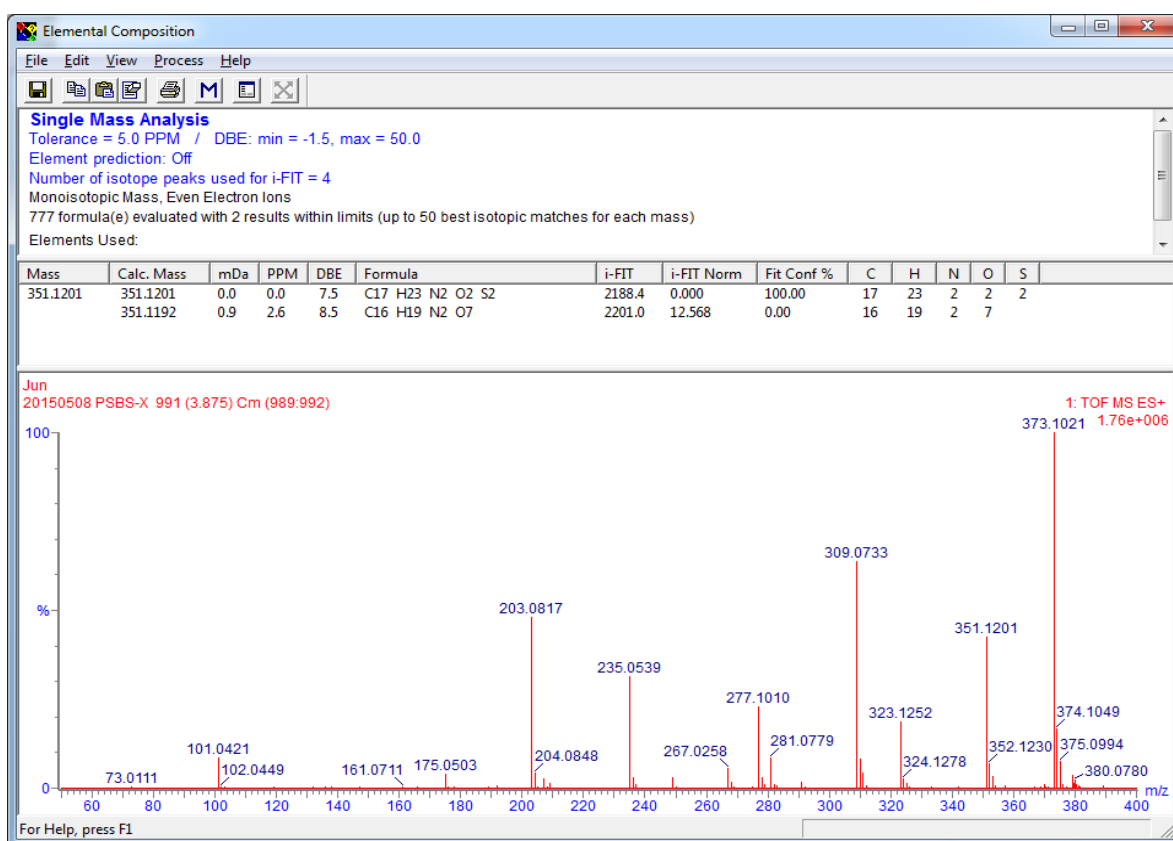
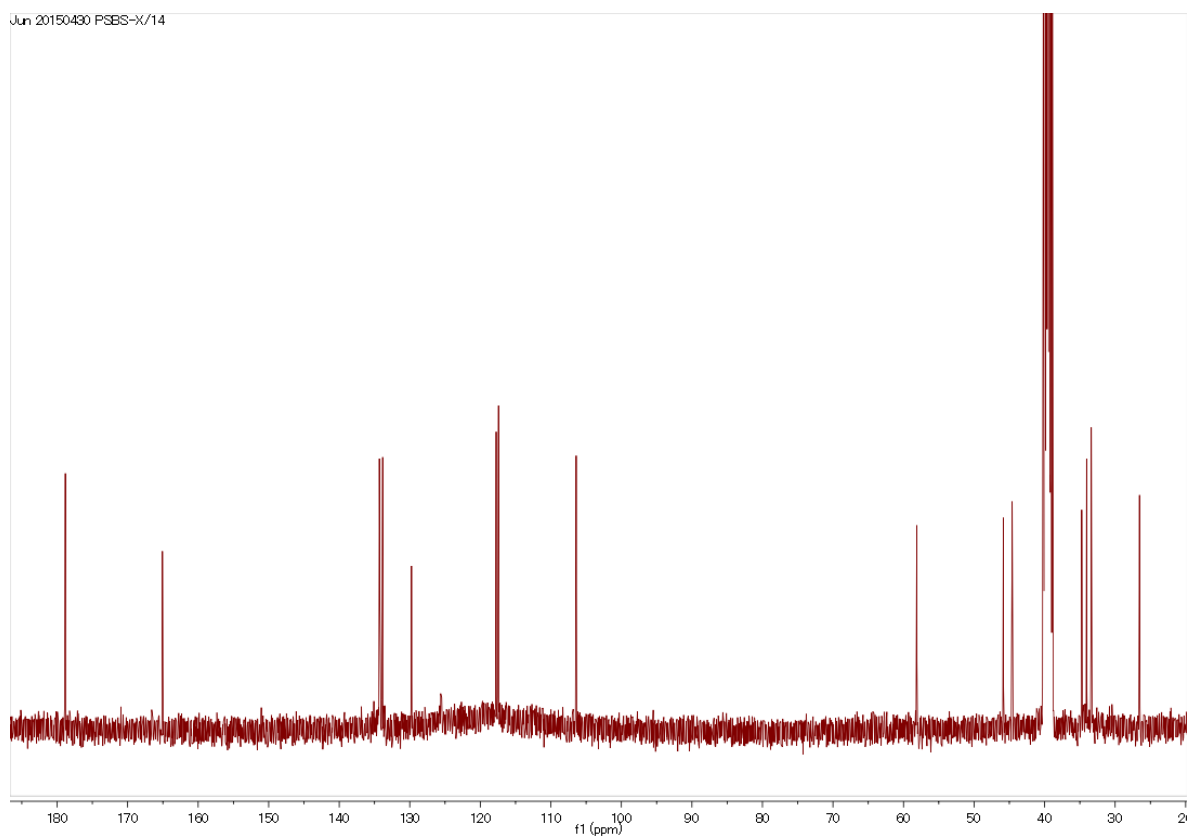
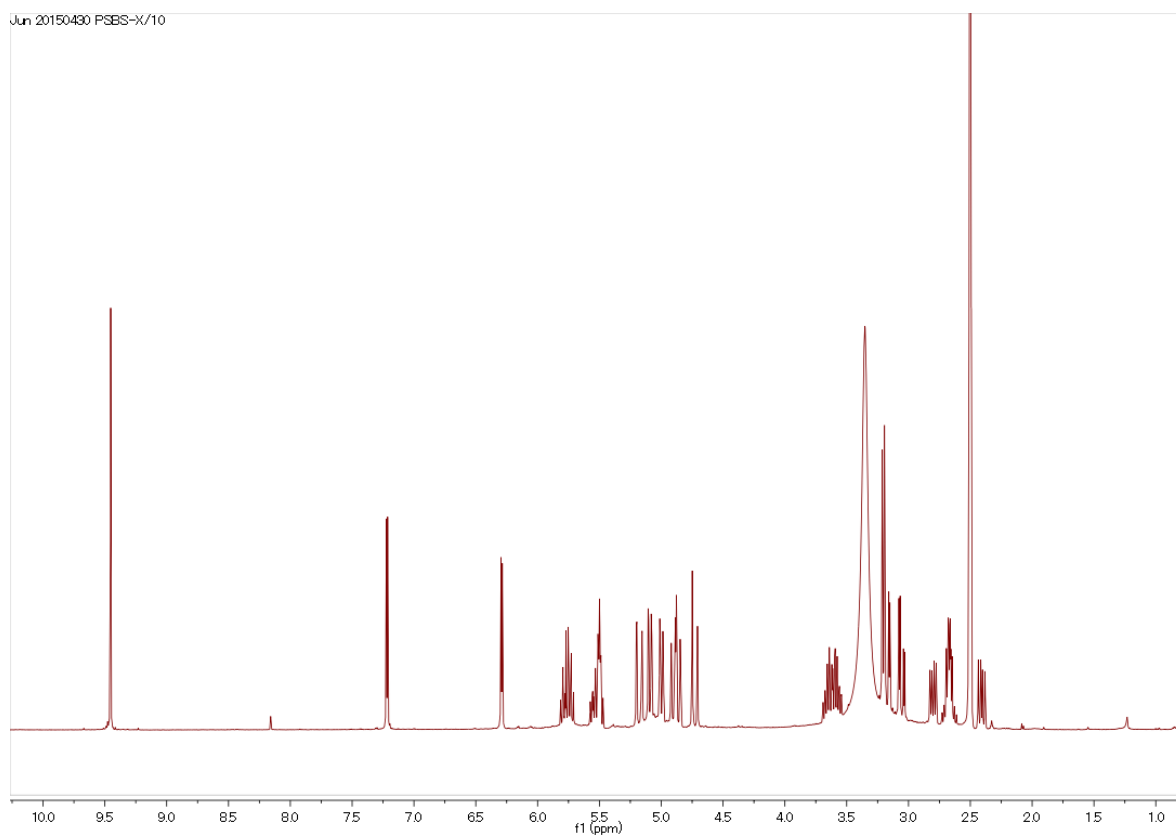


Figure S65. Elemental composition report of the precursor ion



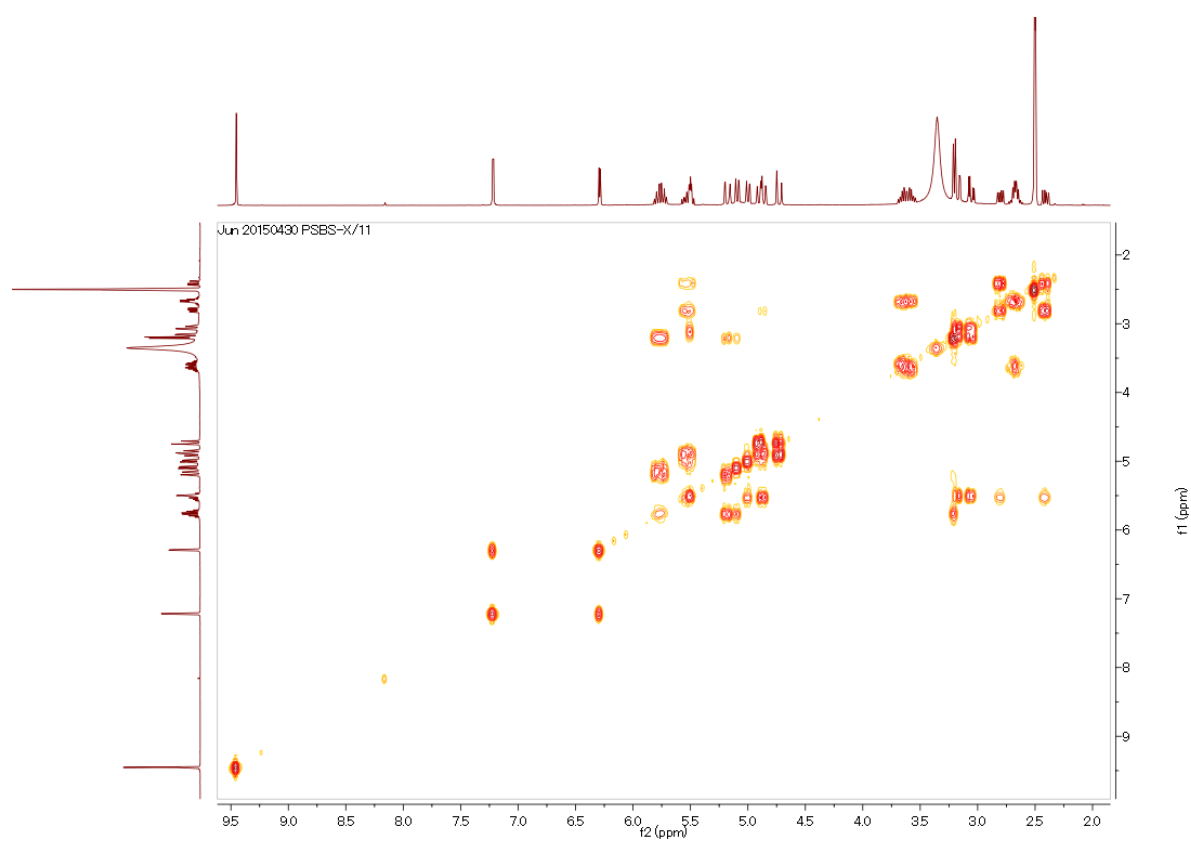


Figure S68. COSY correlations

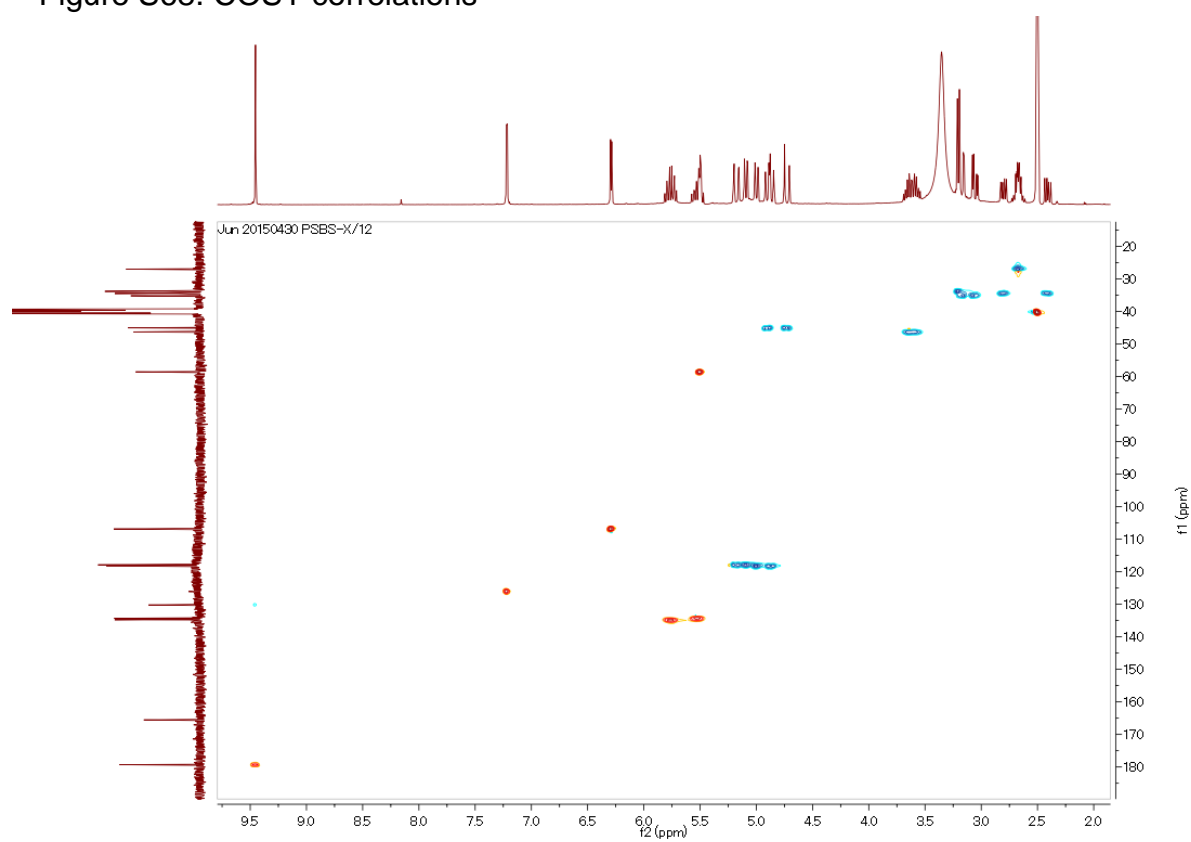


Figure S69. HSQC correlations

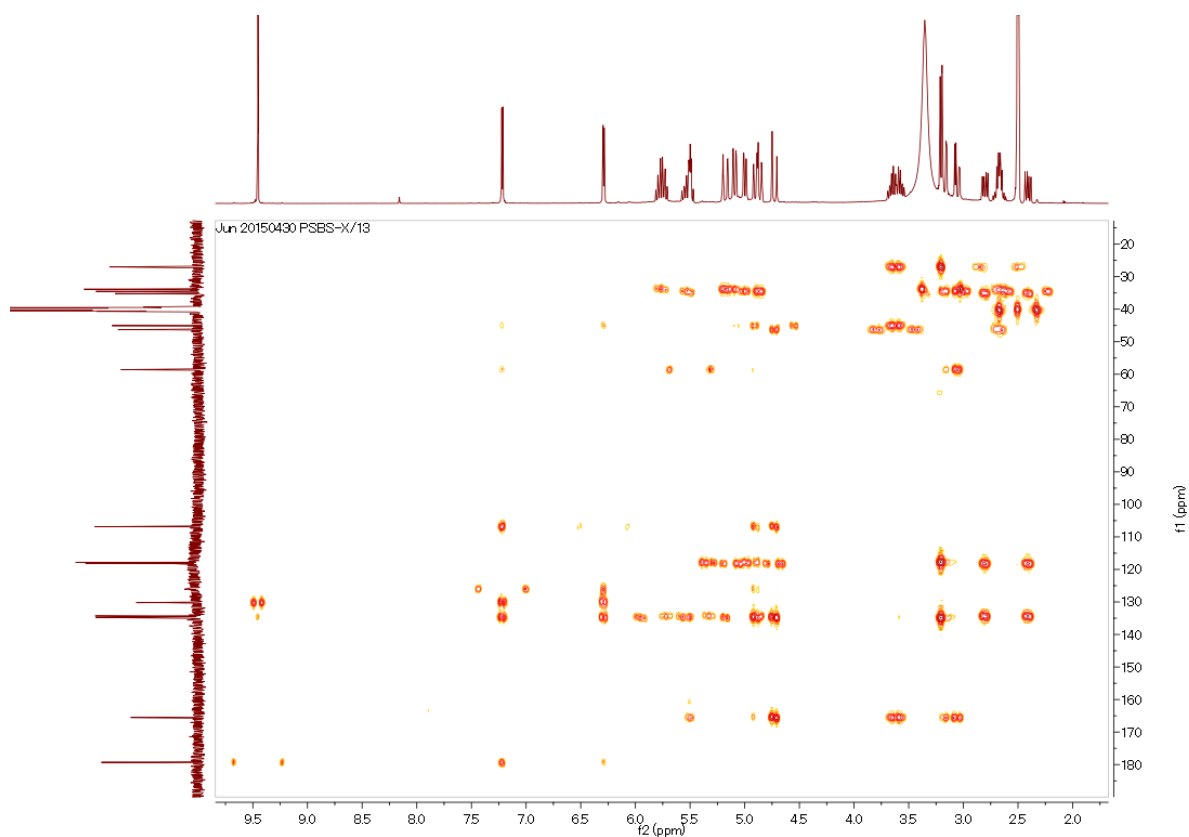


Figure S70. HMBC correlations

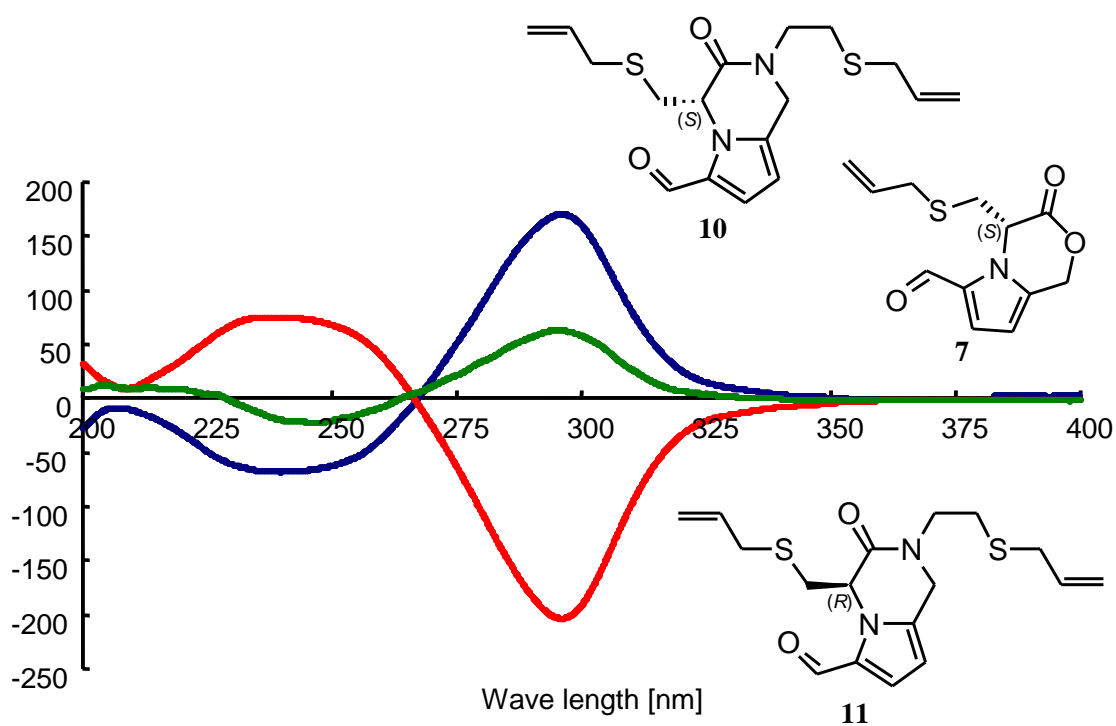


Figure S71. CD spectra of Maillard reaction product **7** (green) and synthesized references **10** (blue) and **11** (red)

3. Analytical conditions for quantitative analysis on identified compounds in garlic preparations

Compounds	MW	Gradient conditions	Mass transition (<i>m/z</i>)	Retention time (min)	Cone voltage (V)	Collision energy (eV)
1	253	10%B → 20%B → 99%B 0 min 7 min 8 min	254.2 → 206.1	4.47	4.0	10.0
2	253		254.2 → 206.1	4.92	4.0	10.0
3	253		254.2 → 206.1	5.22	4.0	10.0
4	253		254.2 → 206.1	5.71	4.0	10.0
5	235		258.3 → 200.1	5.99	35.0	11.0
6	269	30%B → 60%B → 99%B	270.2 → 228.1	2.00	26.0	8.0
7	251	0 min 4 min 4.2 min	252.2 → 178.0	3.24	22.0	16.0
8	394		395.2 → 99.1	3.79	30.0	20.0
9	394		395.2 → 99.1	3.91	30.0	20.0

Table S2. UPLC-MS/MS (ESI) parameters for quantitative analysis on identified compounds.