Electronic Supplementary Material (ESI) for RSC Advances.

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Electronic supplementary information for

The Stereochemistry of Cleistanthane Diterpenoids from *Phyllanthus emblica*

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[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China..

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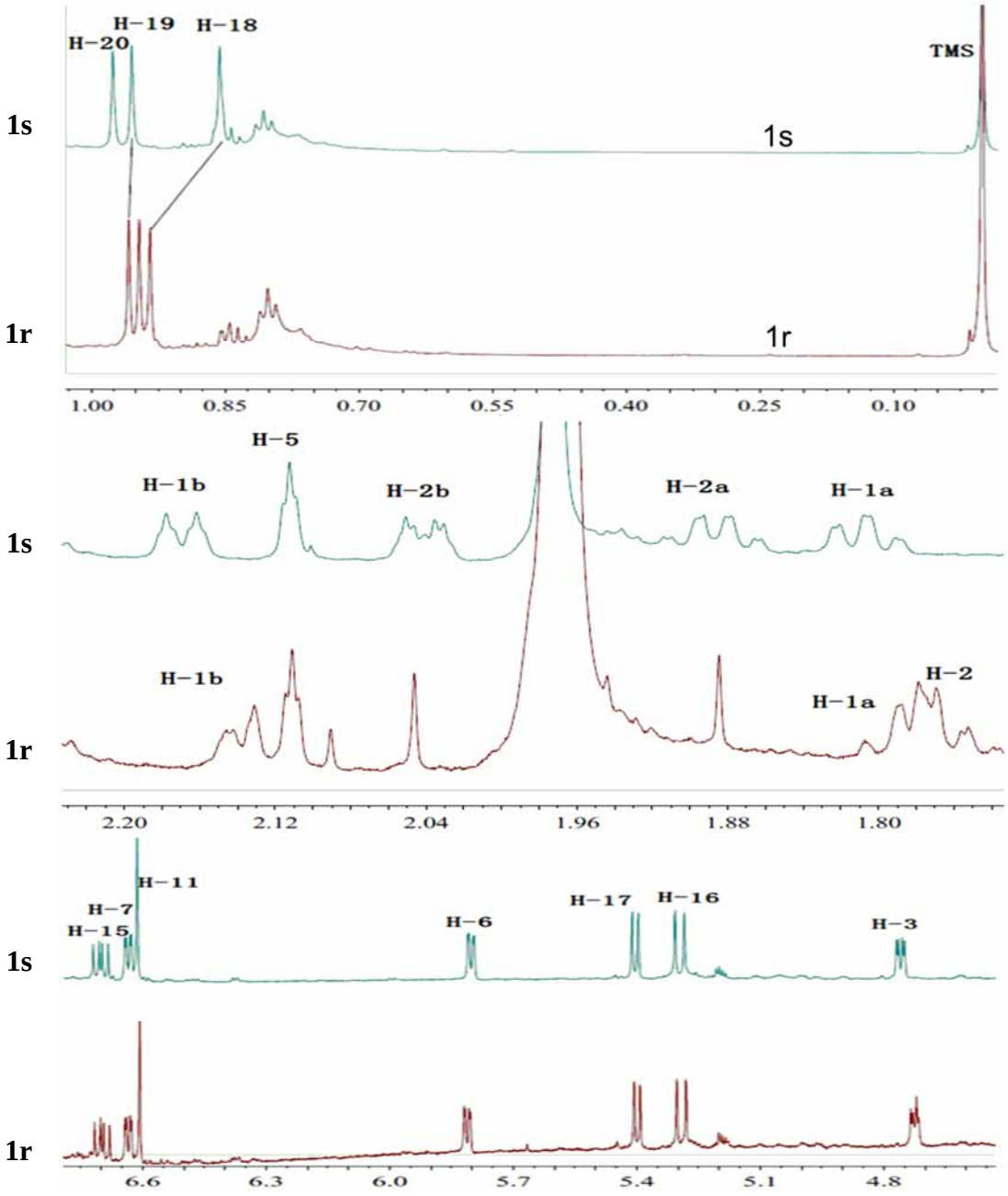
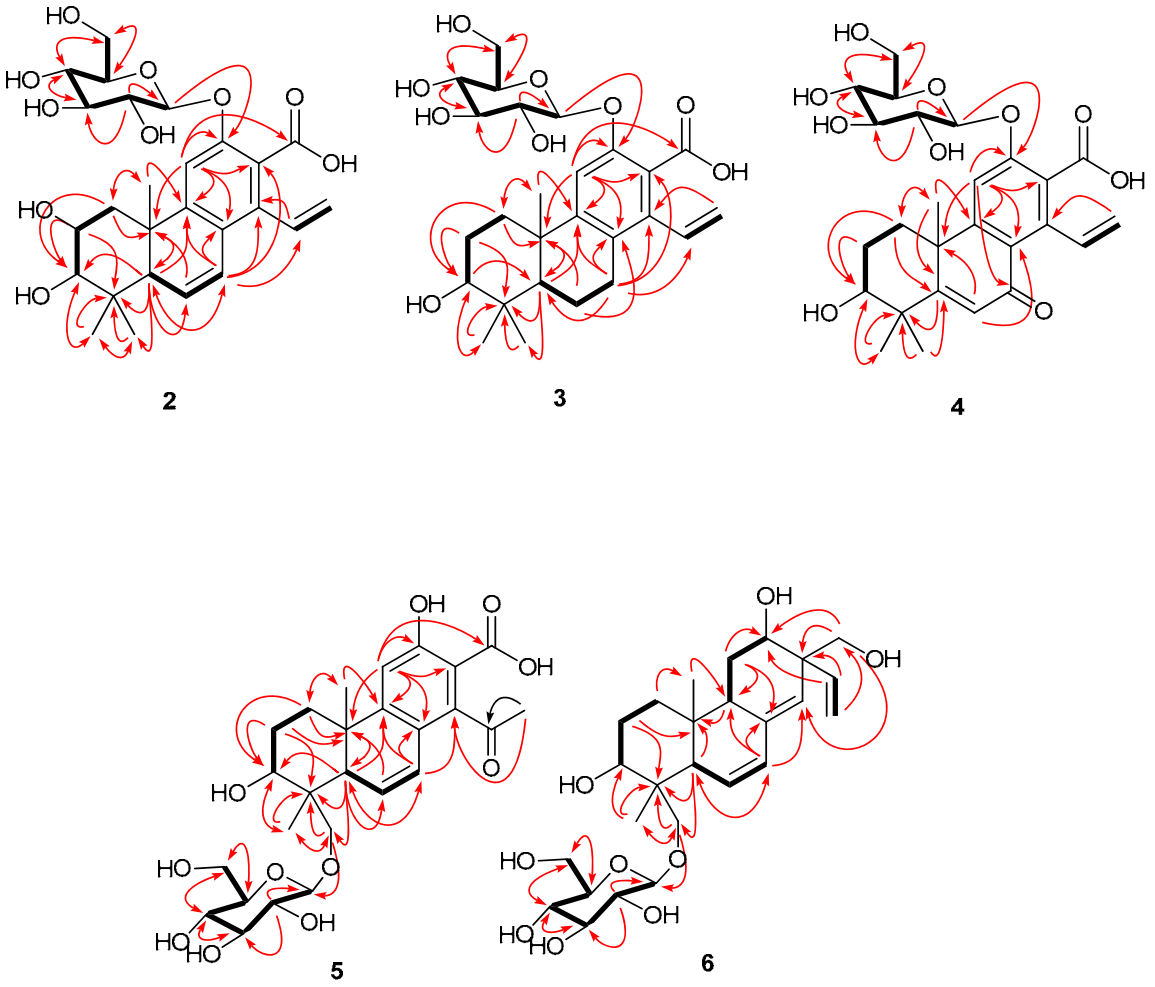
1. S1 Figure 1. Partial ^{1}H NMR spectra of (*S*)- and (*R*)-MTPA esters **1s** and **1r** of **1B**



2. S2 Figure 2. Key ^{1}H-^{1}H COSY (—) and HMBC (→) correlations of compounds **2-6**



3. S3 HRESIMS of compound **1**

Data File: D:\分子量测定\2013-01-24\gca40_TLJ1751_24.lcd

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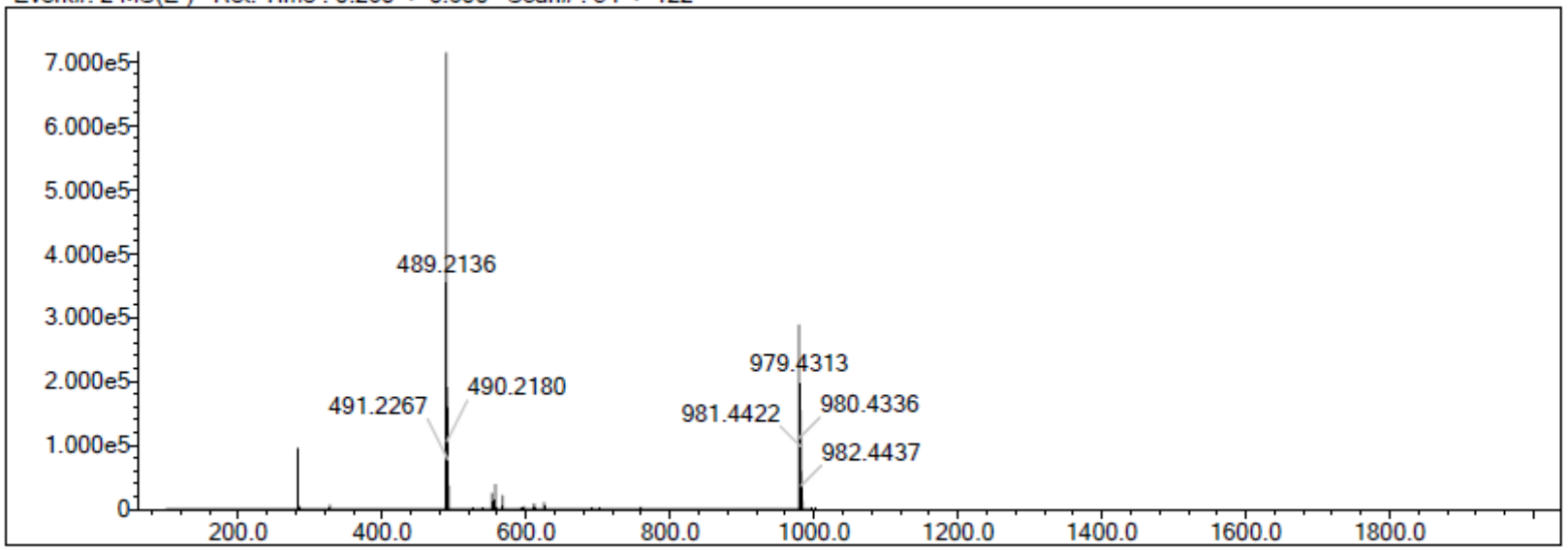
H	1	0	100	N	3	0	0	P	3	0	0	Br	1	0	0	H
B	3	0	0	O	2	0	30	S	2	0	0	I	3	0	0	
C	4	0	50	F	1	0	0	Cl	1	0	0					

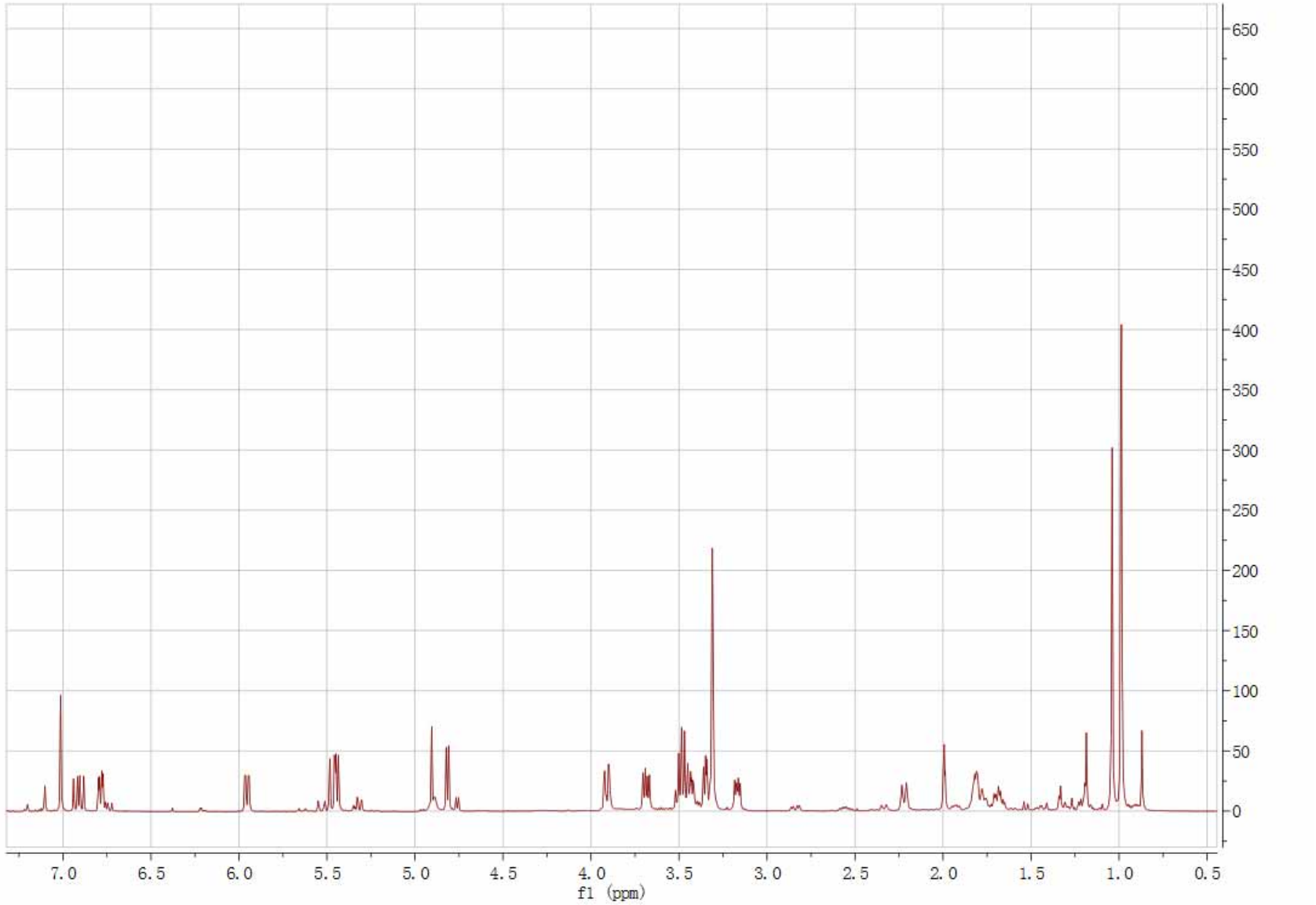
Error Margin (mDa): 20.0
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

DBE Range: 0.0 - 30.0
Apply N Rule: no
Isotope RI (%): 1.00
MSn Logic Mode: OR

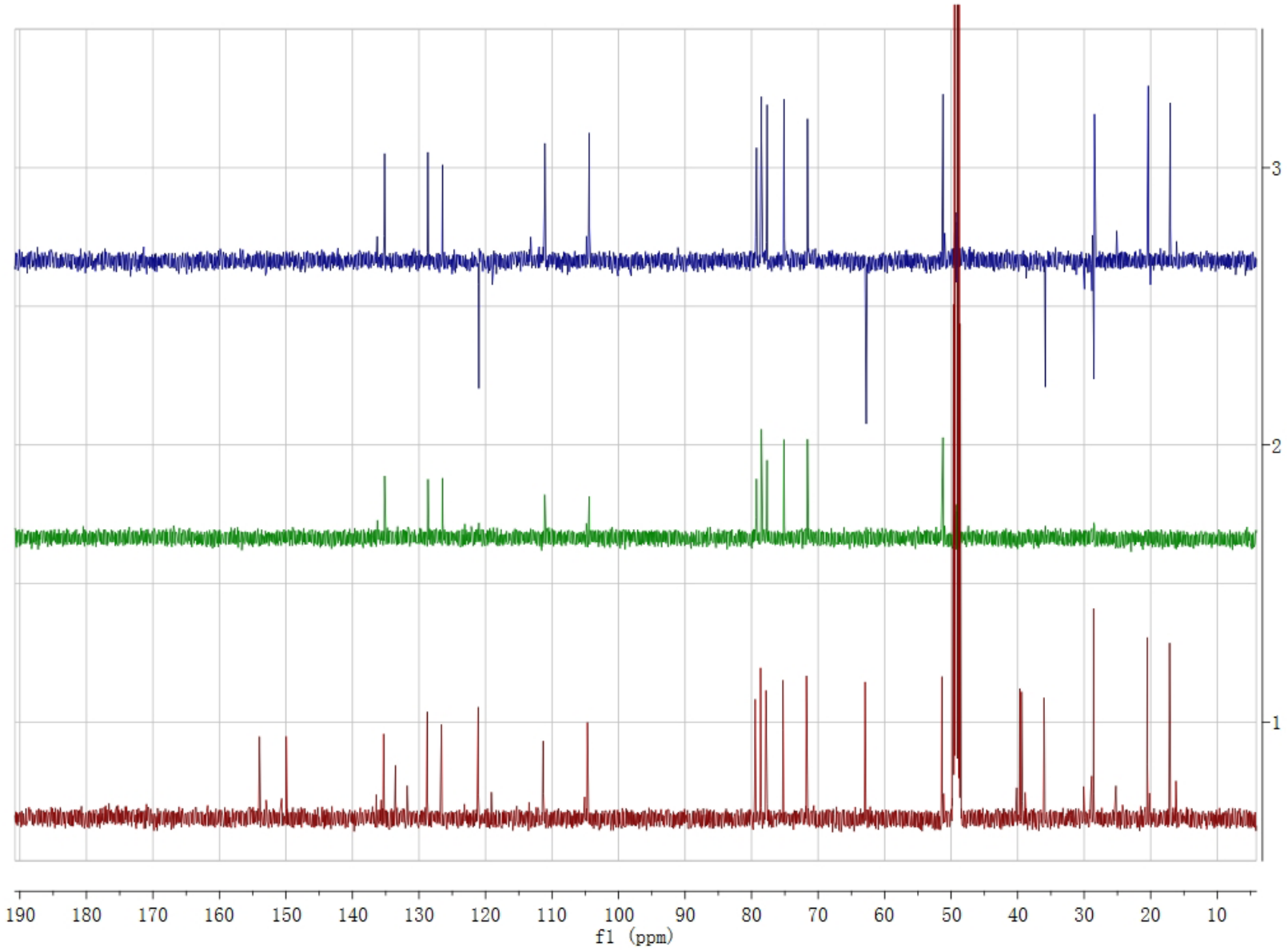
Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 800

Event#: 2 MS(E-) Ret. Time : 0.260 -> 0.600 Scan# : 54 -> 122

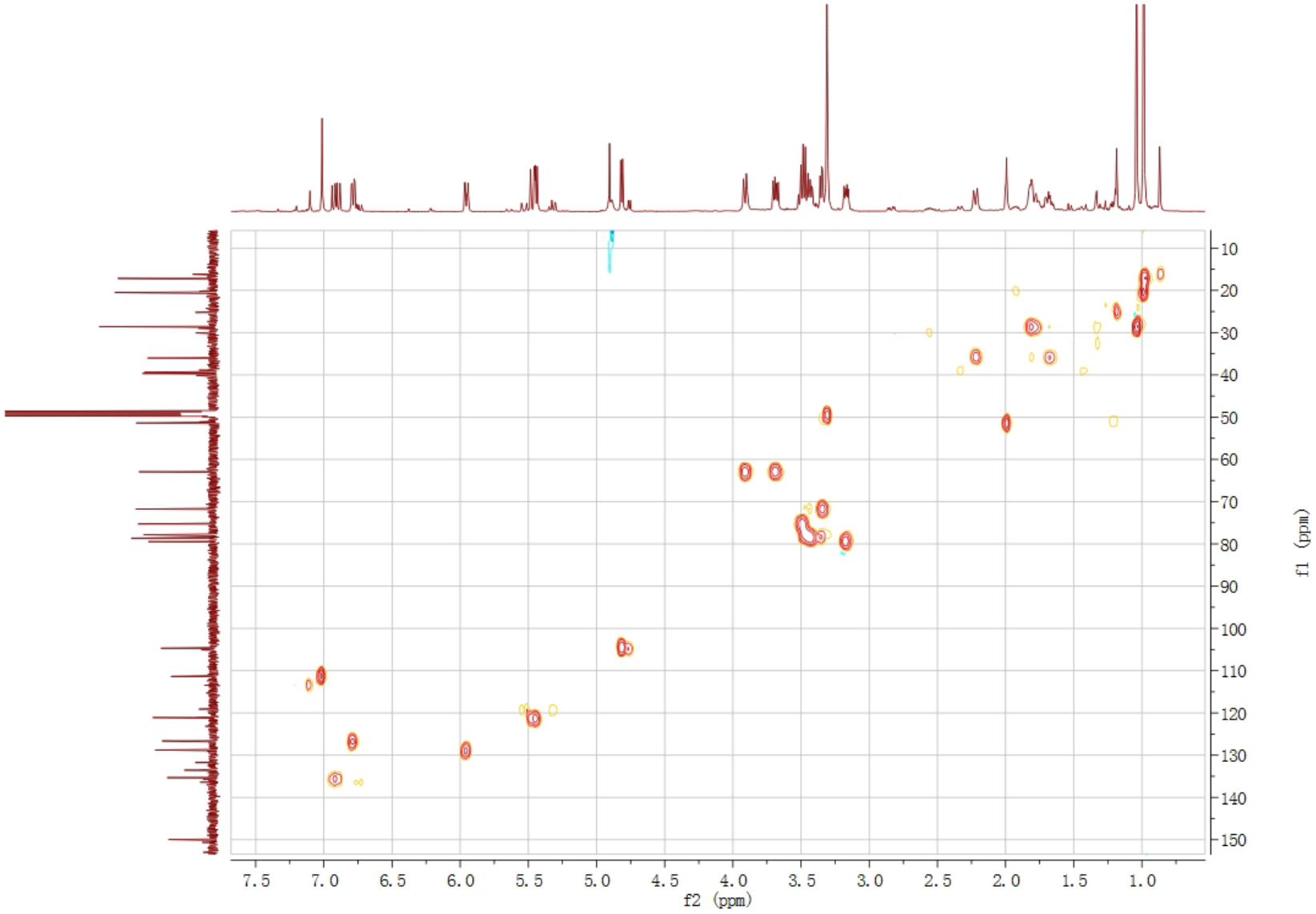




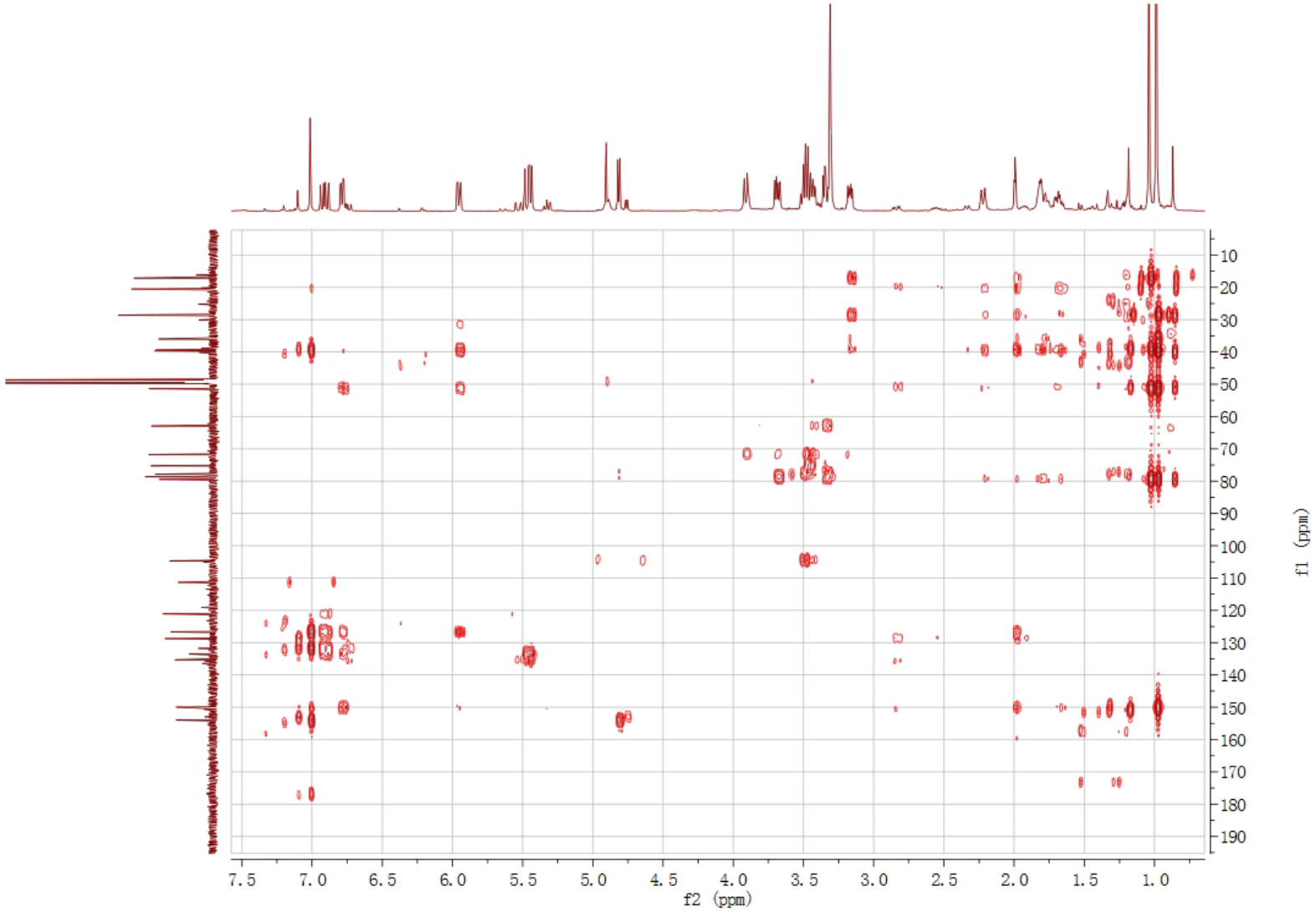
5. S5 ^{13}C NMR (125 MHz) spectrum of compound **1** in CD_3OD



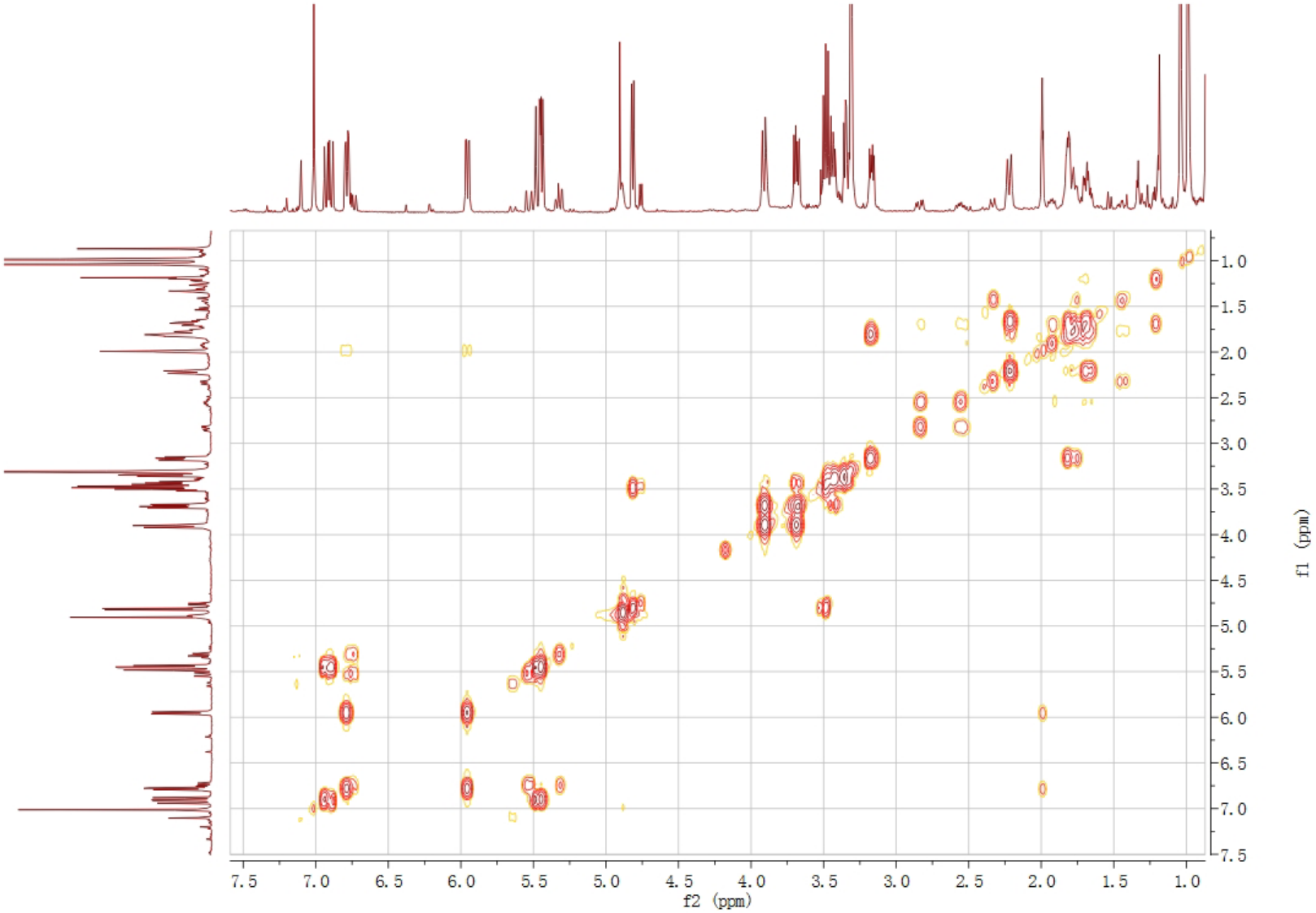
6. S6 HSQC spectrum of compound **1** in CD_3OD



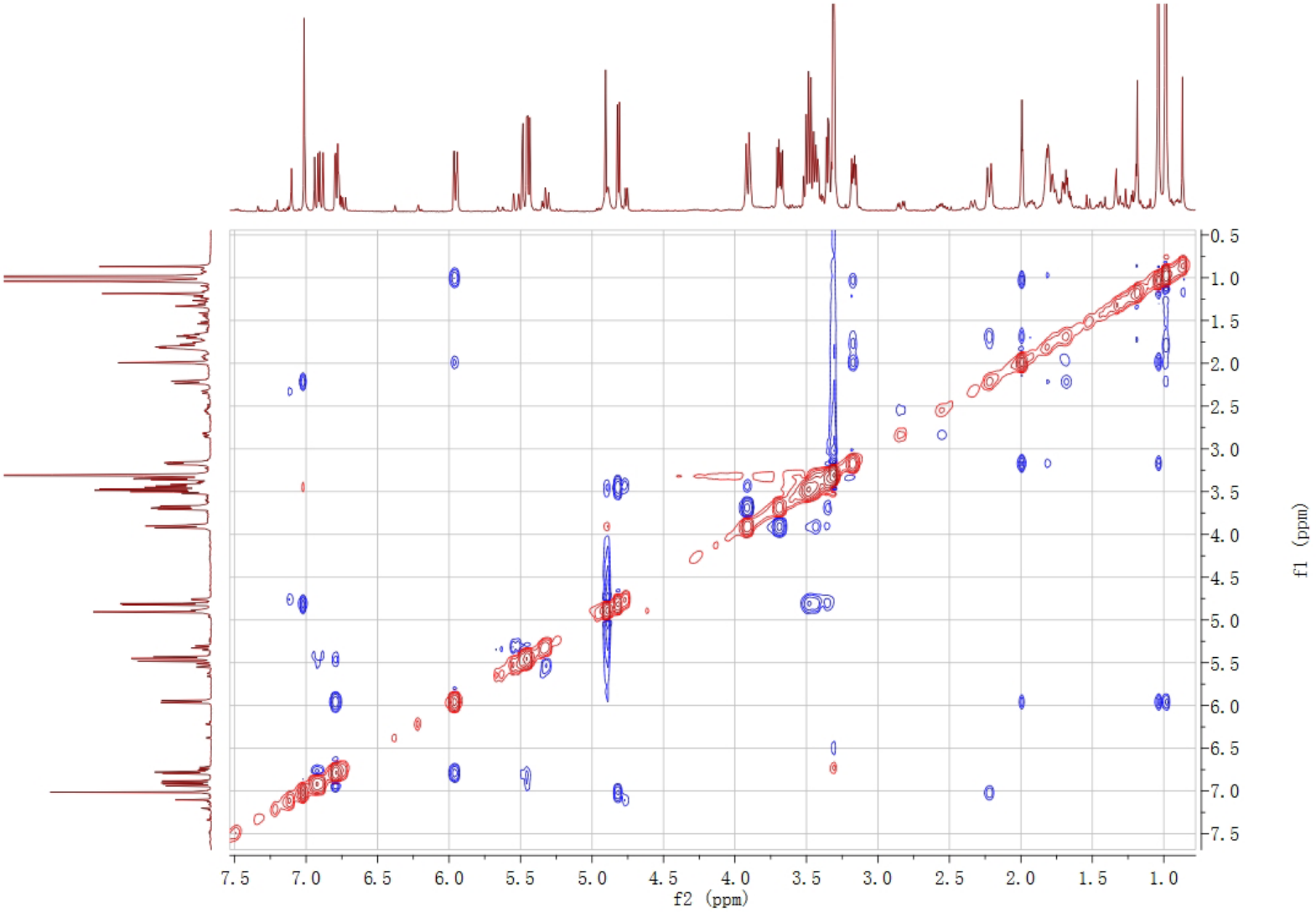
7. S7 HMBC spectrum of compound **1** in CD_3OD



8. S8 ^{1}H-^{1}H COSY spectrum of compound **1** in CD_3OD



9. S9 ROESY spectrum of compound **1** in CD_3OD



10. S10 HRESIMS of compound **1A**

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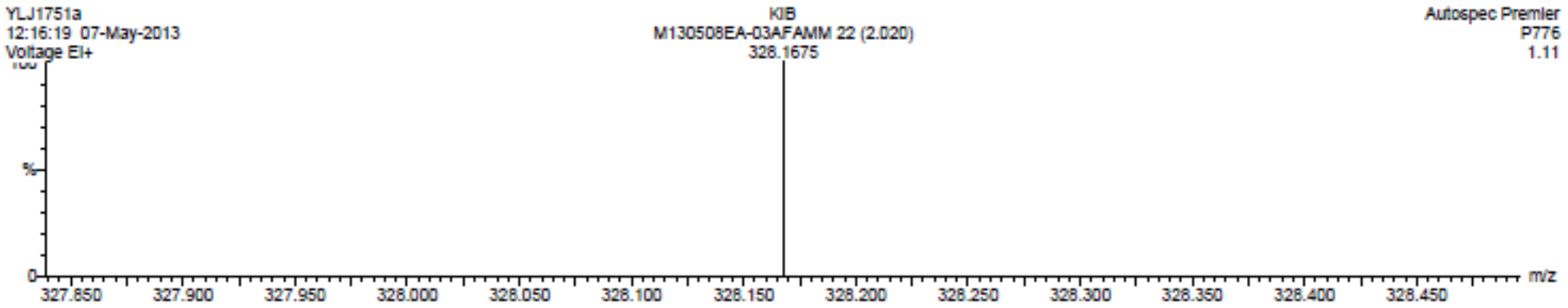
17 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 O: 3-5



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Maximum:		200.0	10.0	120.0		
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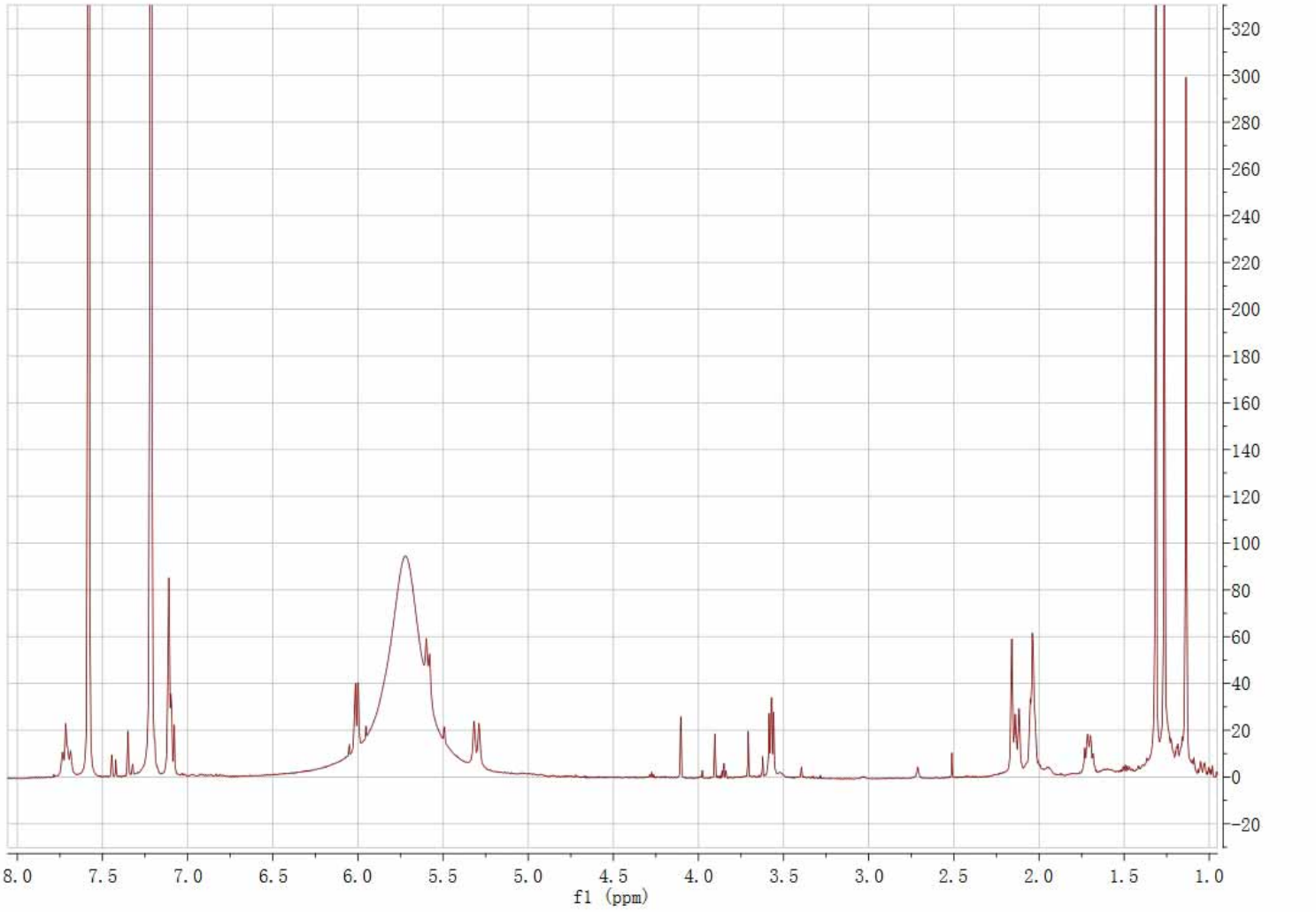
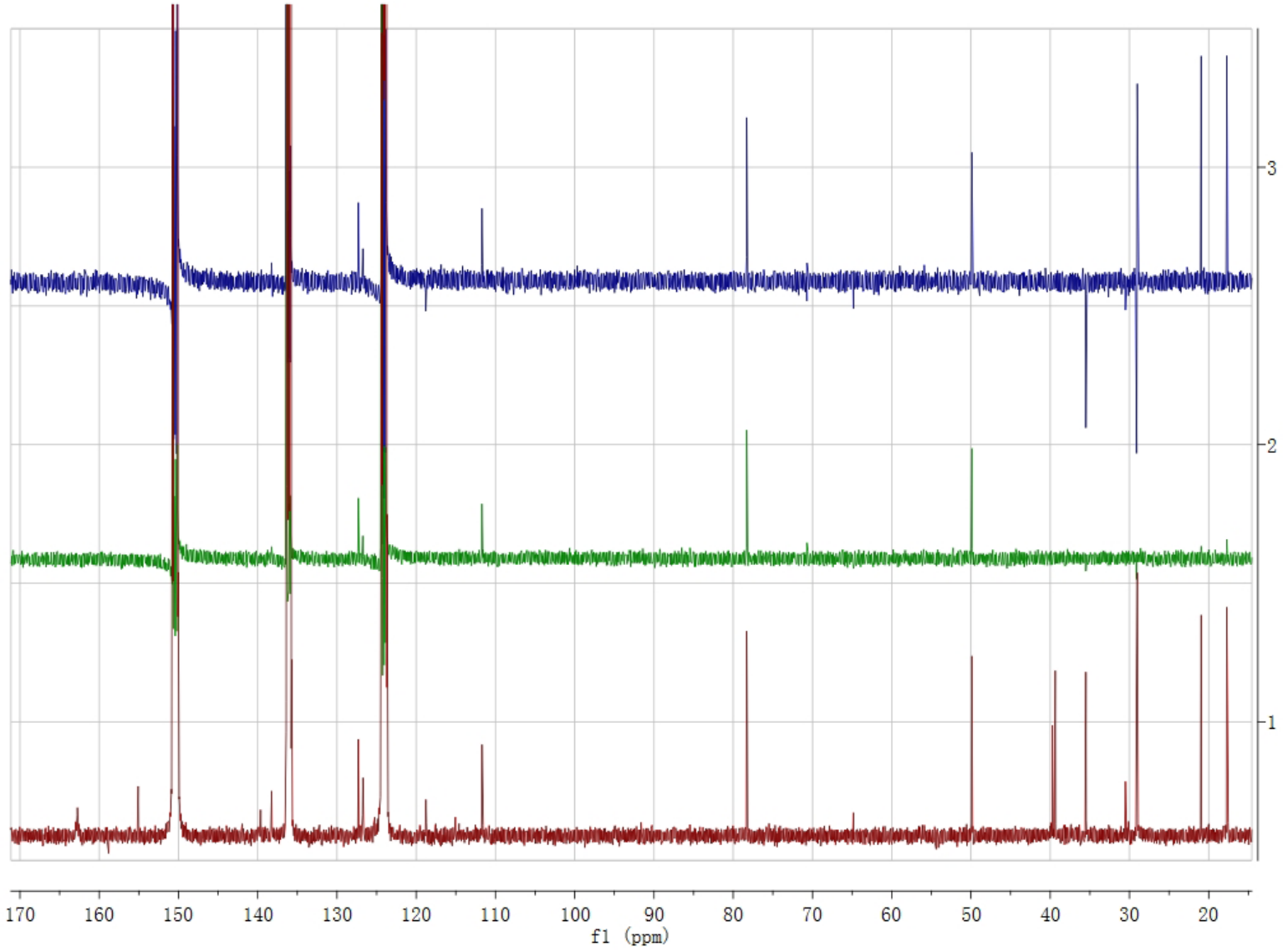
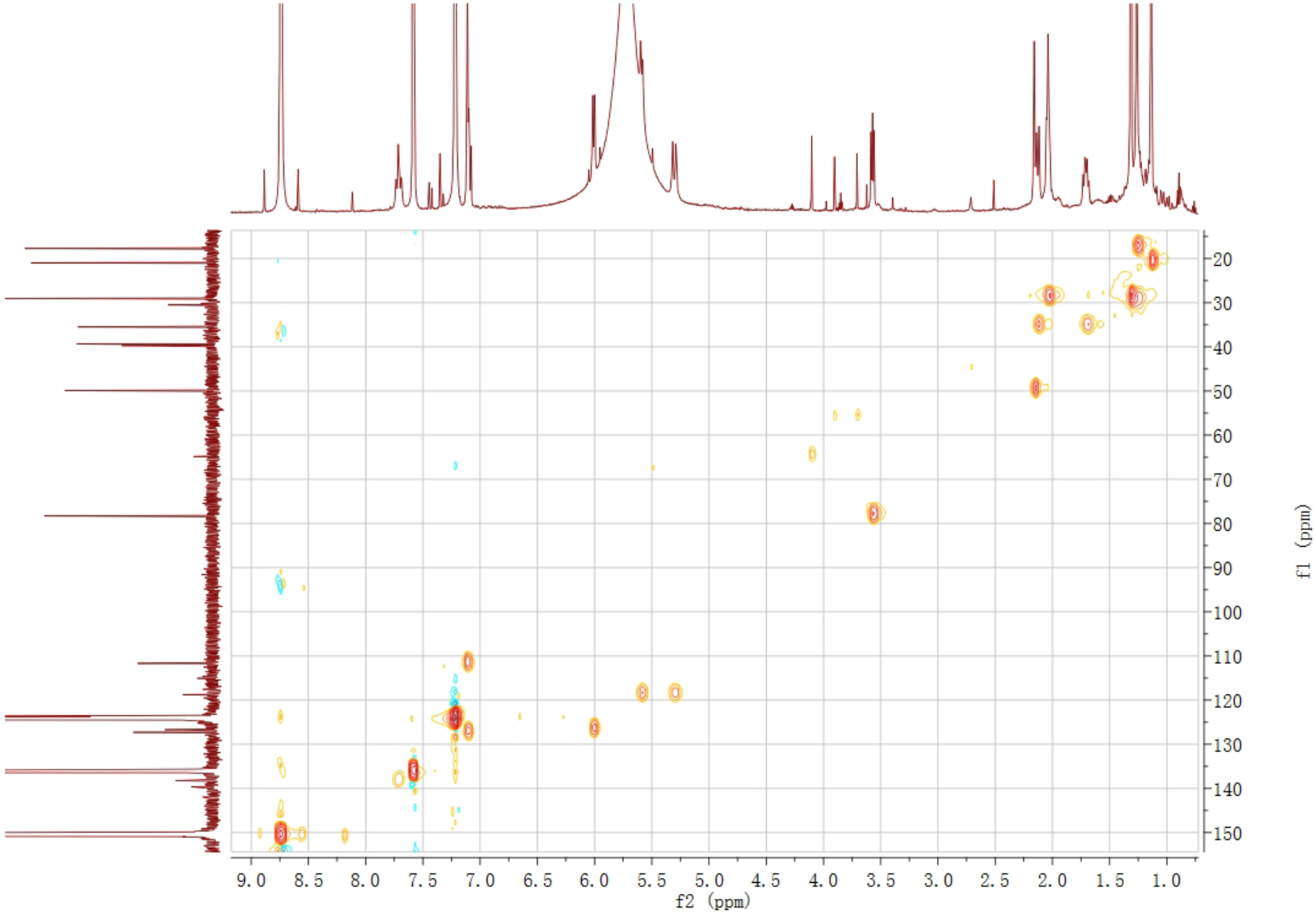
11.S11 ^{1}H NMR (600 MHz) spectrum of compound **1A** in C_5D_5N



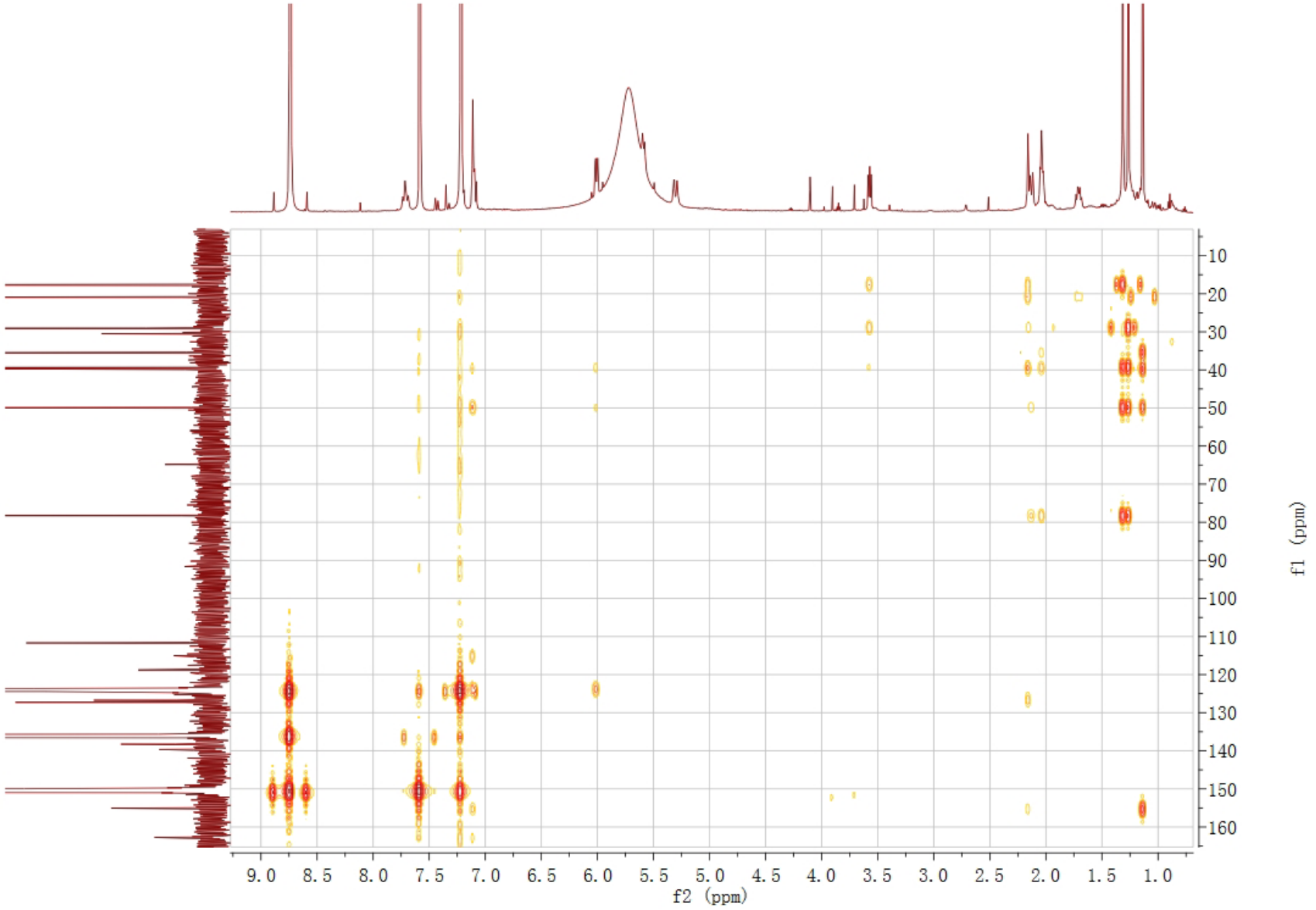
12.S12 ^{13}C NMR (150 MHz) spectrum of compound **1A** in C_5D_5N



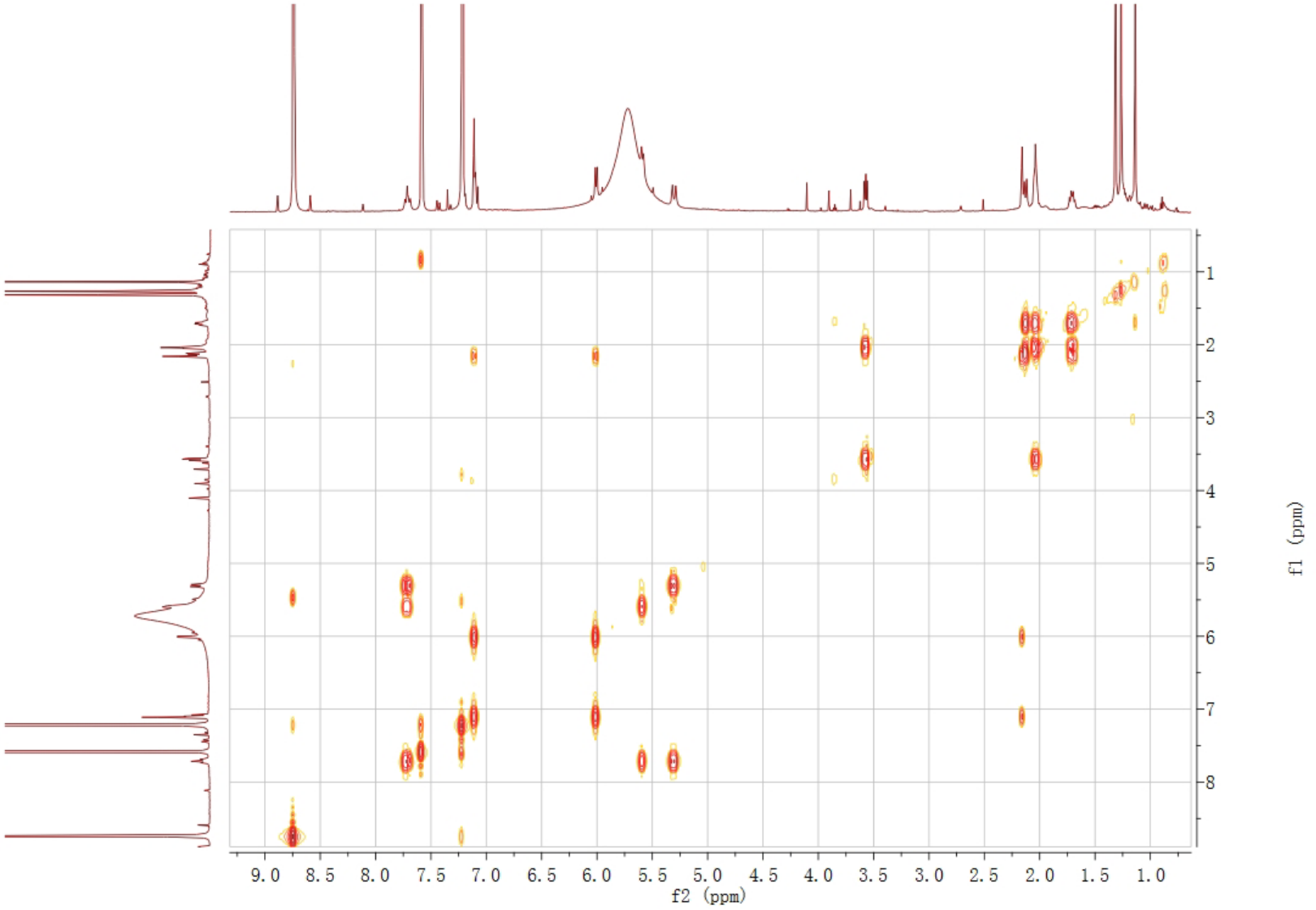
13. S13 HSQC spectrum of compound **1A** in C_5D_5N



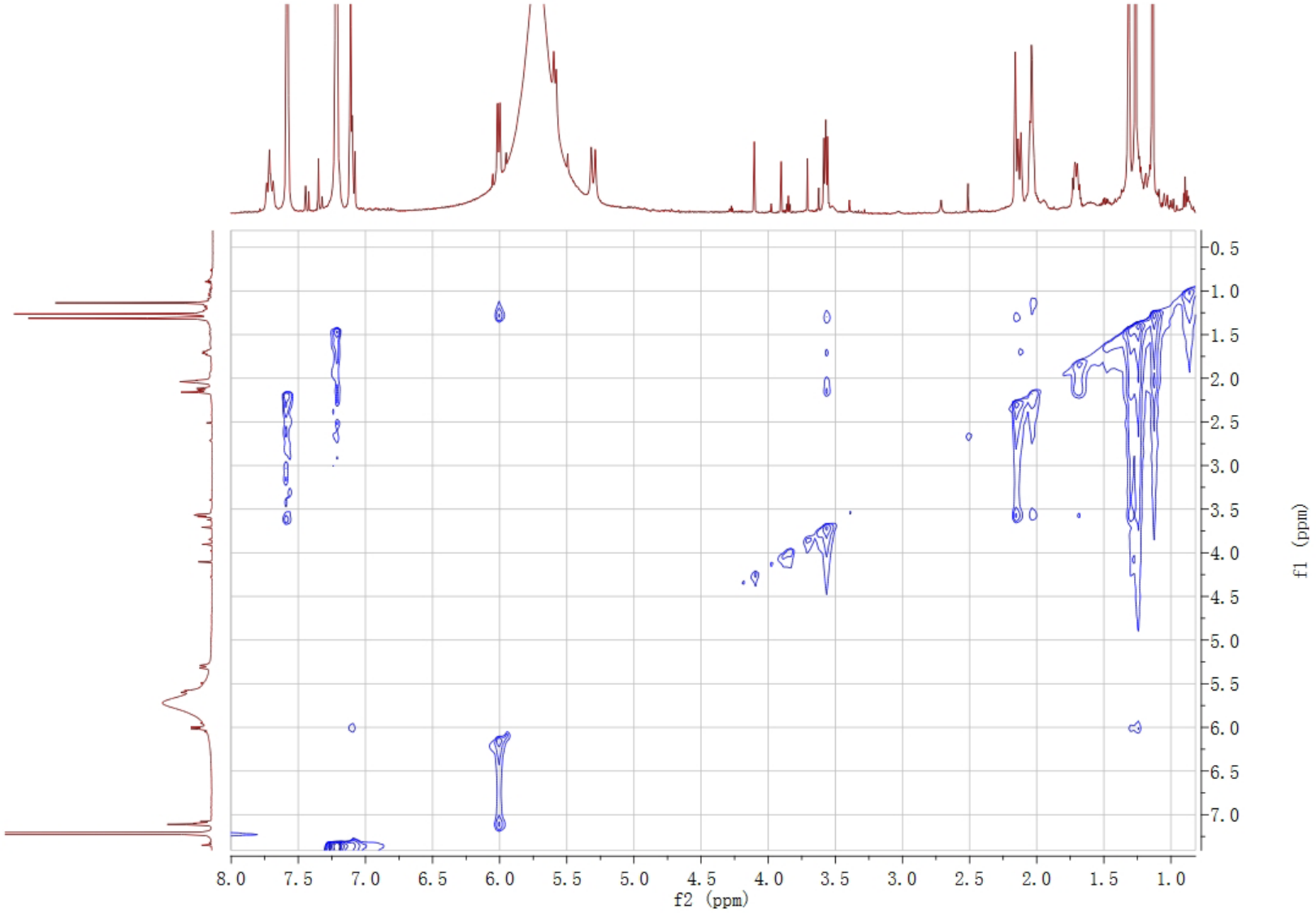
14. S14 HMBC spectrum of compound **1A** in C_5D_5N



15. S15 ^{1}H-^{1}H COSY spectrum of compound **1A** in C_5D_5N



16. S16 ROESY spectrum of compound **1A** in C_5D_5N



17. S17 HRESIMS of compound **2**

Single Mass Analysis
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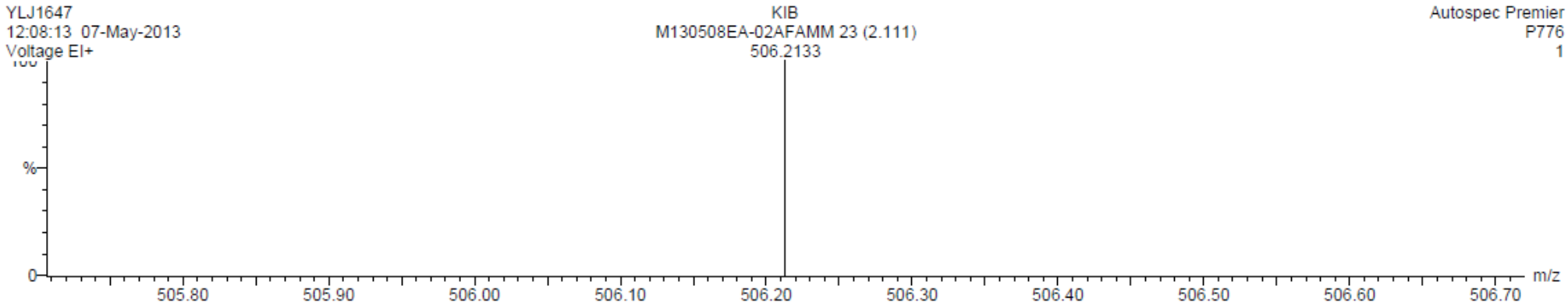
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 O: 9-11



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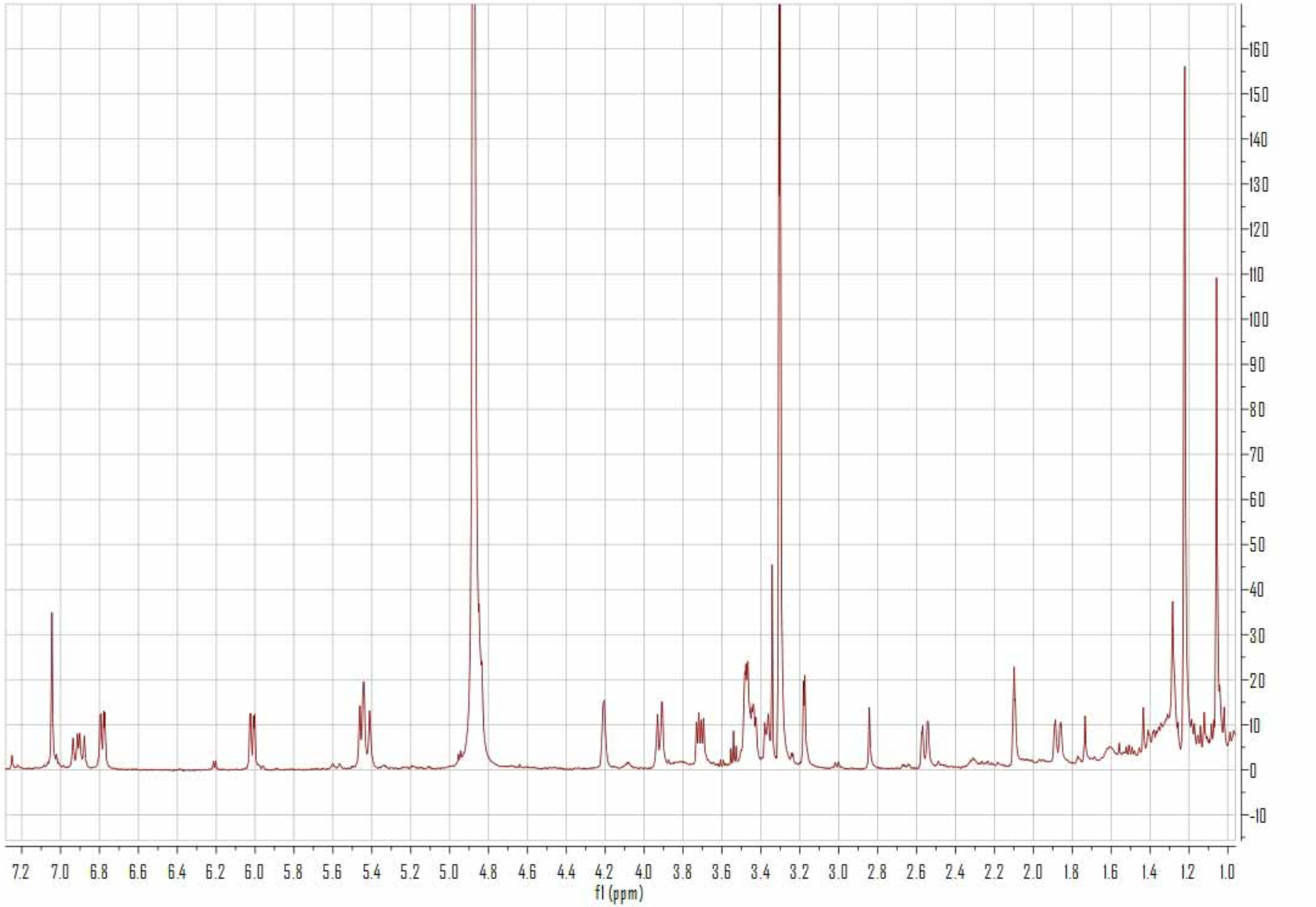
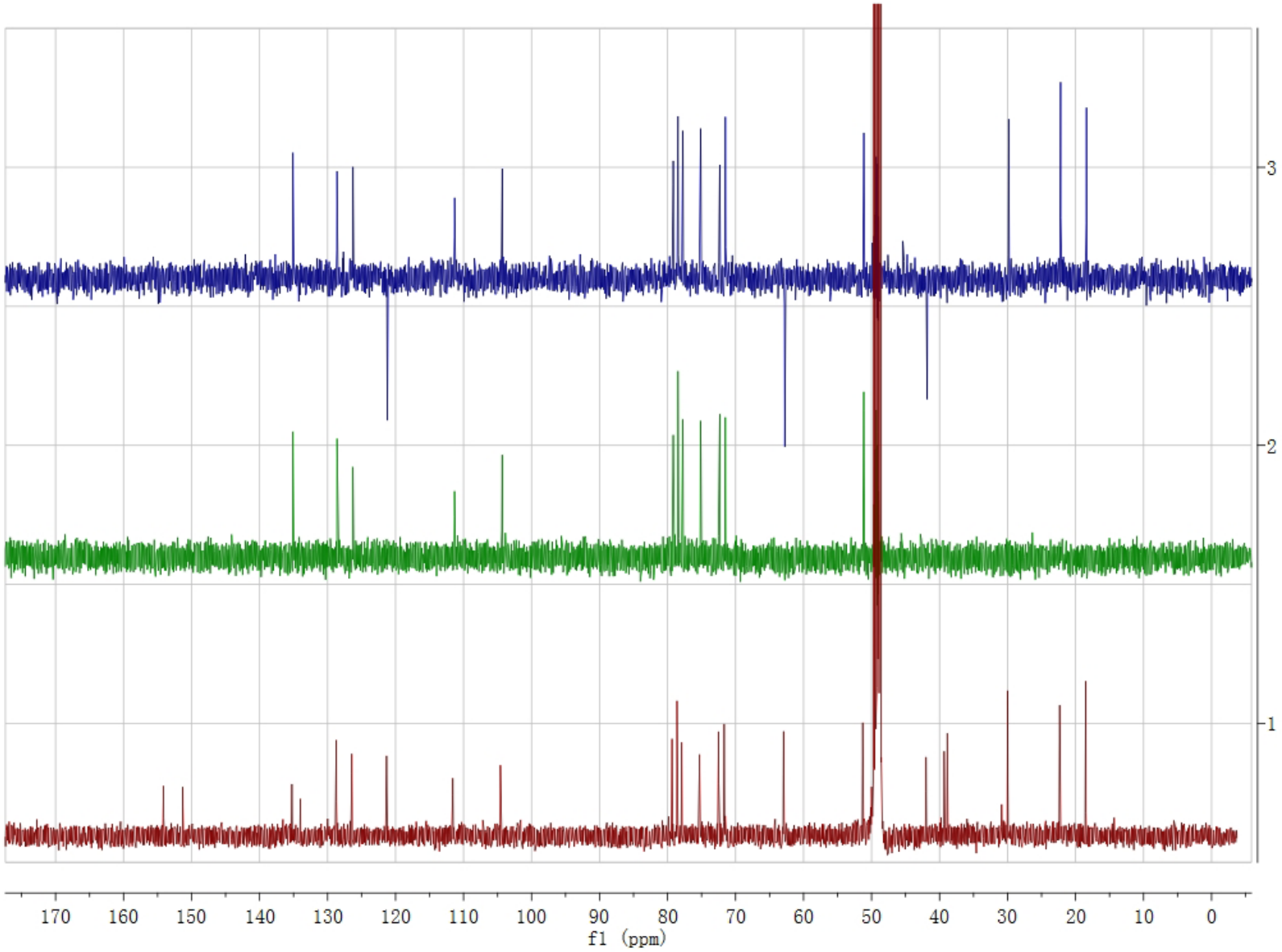
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
506.2133	506.2152	-1.9	-3.8	10.0	5546026.0	C26 H34 O10

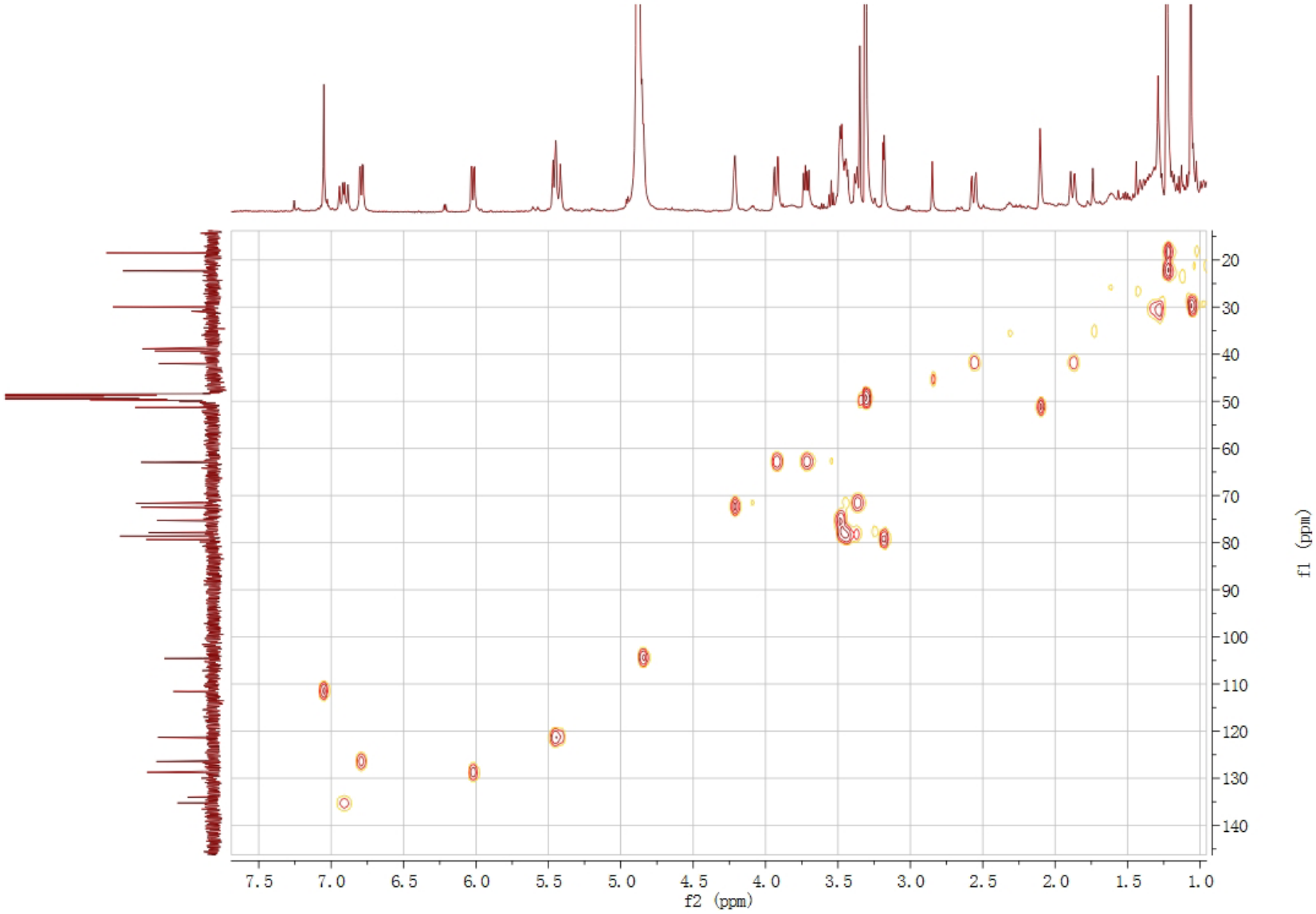
18. S18 ^{1}H NMR (500 MHz) spectrum of compound **2** in CD_3OD



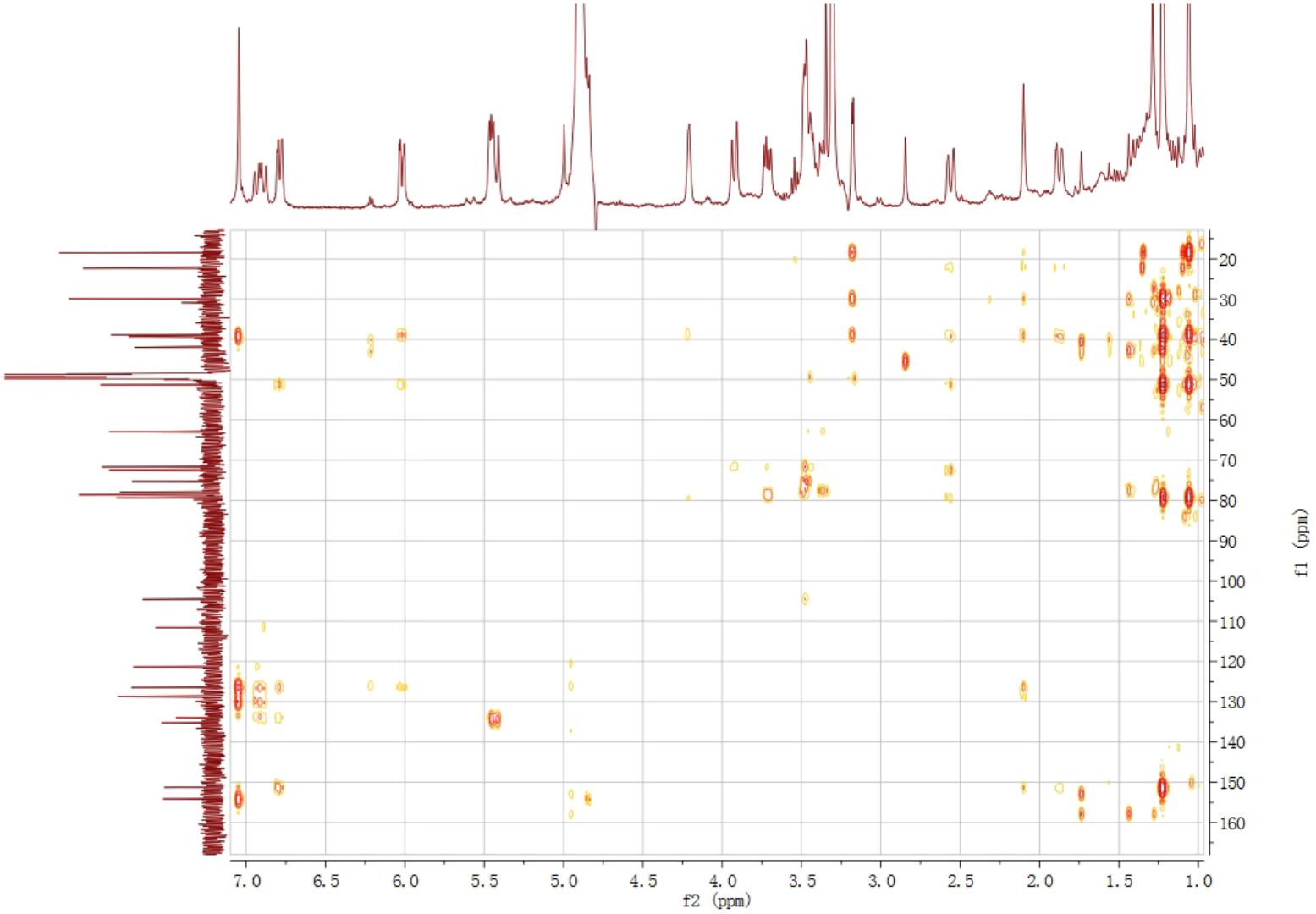
19. S19 ^{13}C NMR (125 MHz) spectrum of compound **2** in CD_3OD



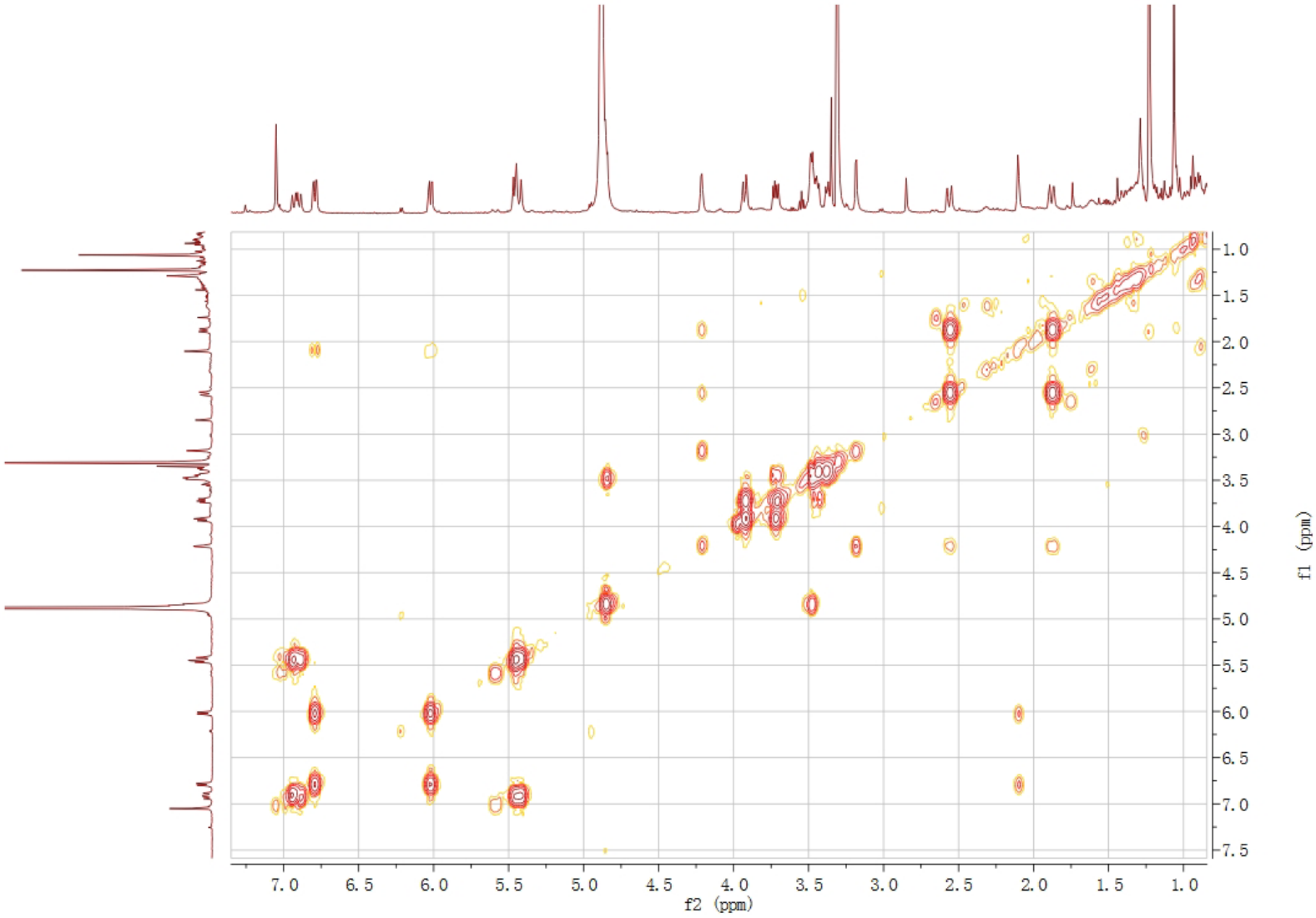
20. S20 HSQC spectrum of compound **2** in CD_3OD



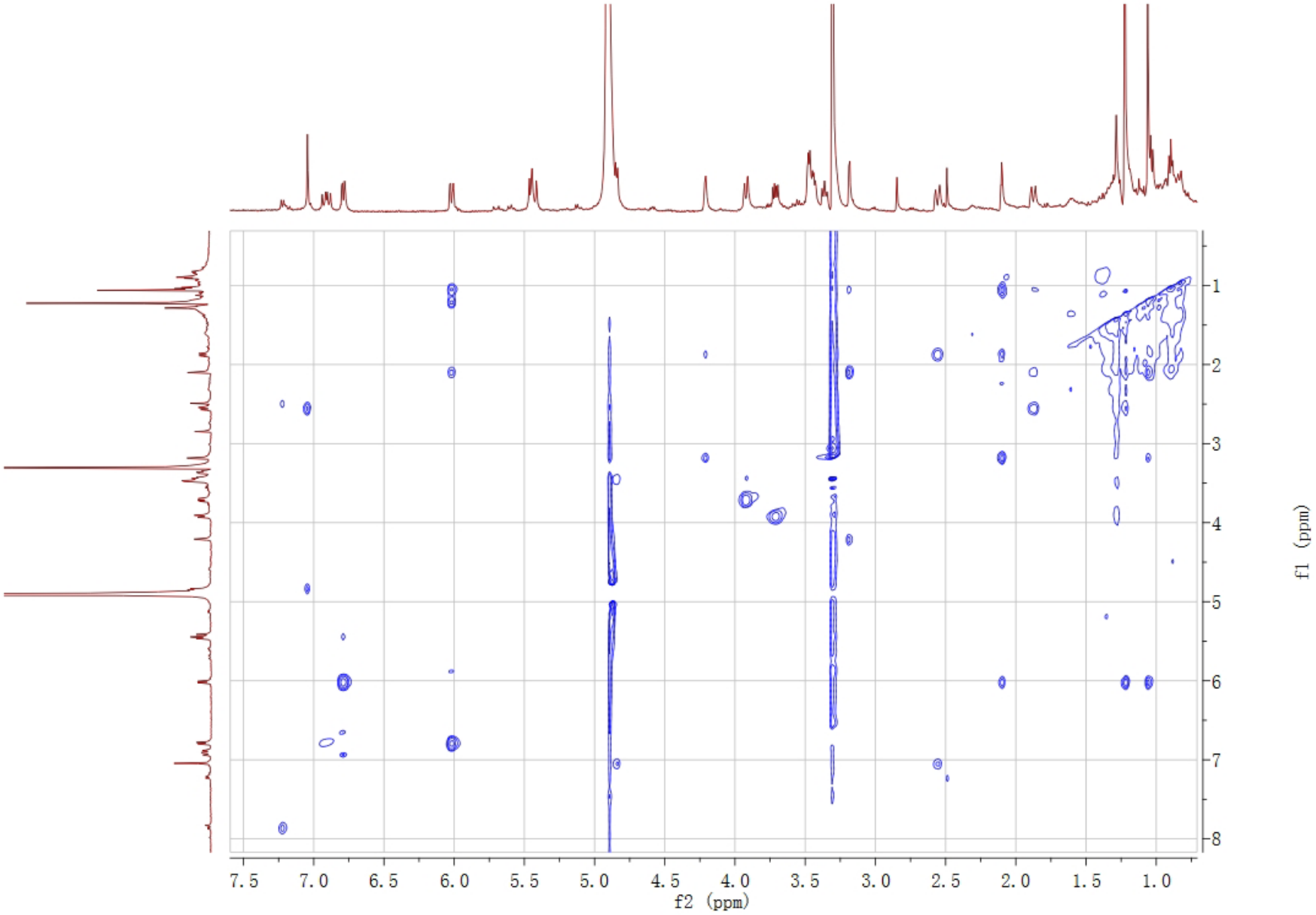
21. S21 HMBC spectrum of compound **2** in CD_3OD



22. S22 ^{1}H-^{1}H COSY spectrum of compound **2** in CD_3OD



23. S23 ROESY spectrum of compound **2** in CD_3OD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6.0
5.5
5.0
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3.5
3.0
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2.0
1.5
1.0
f2 (ppm)
1
2
3
4
5
6
7
8
f1 (ppm)

24. S24 HRESIMS of compound **3**

Data File: D:\分子量测定\2013-01-24\gca40_TLJ1752A_25.lcd

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C	4	0	50	F	1	0	0	Cl	1	0	0					

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Max Isotopes:	all	Isotope RI (%):	1.00	Isotope Res:	10000
MSn Iso RI (%):	75.00	MSn Logic Mode:	OR	Max Results:	800

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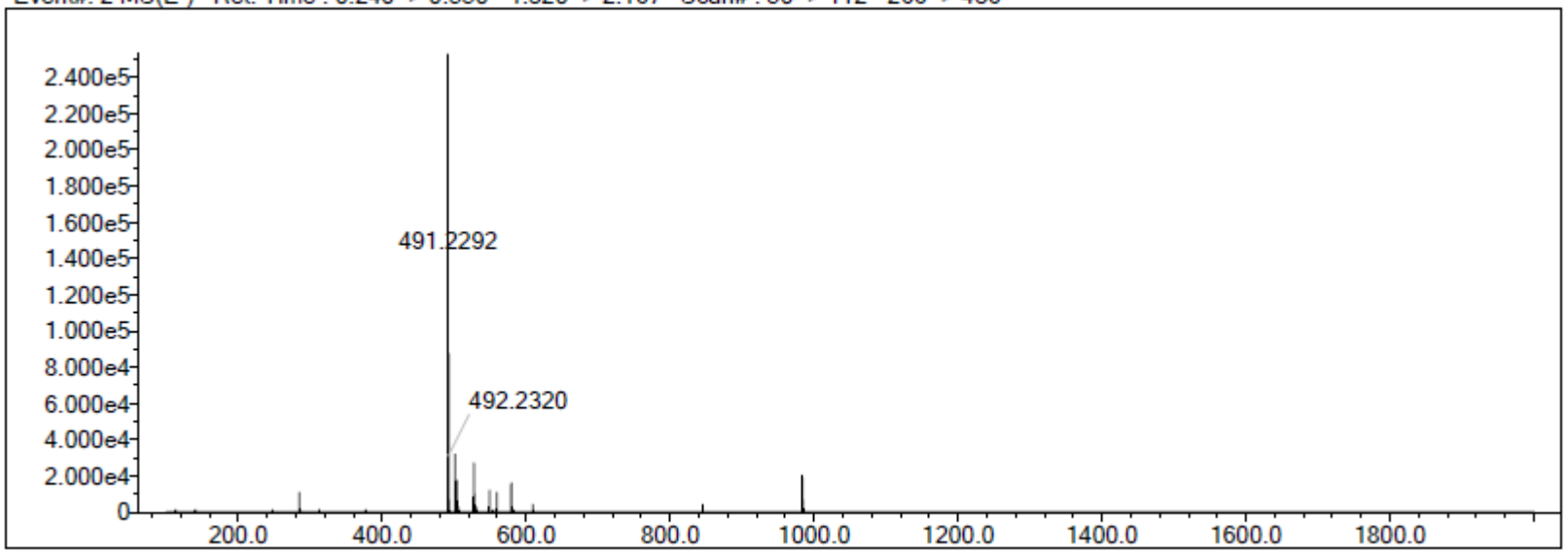
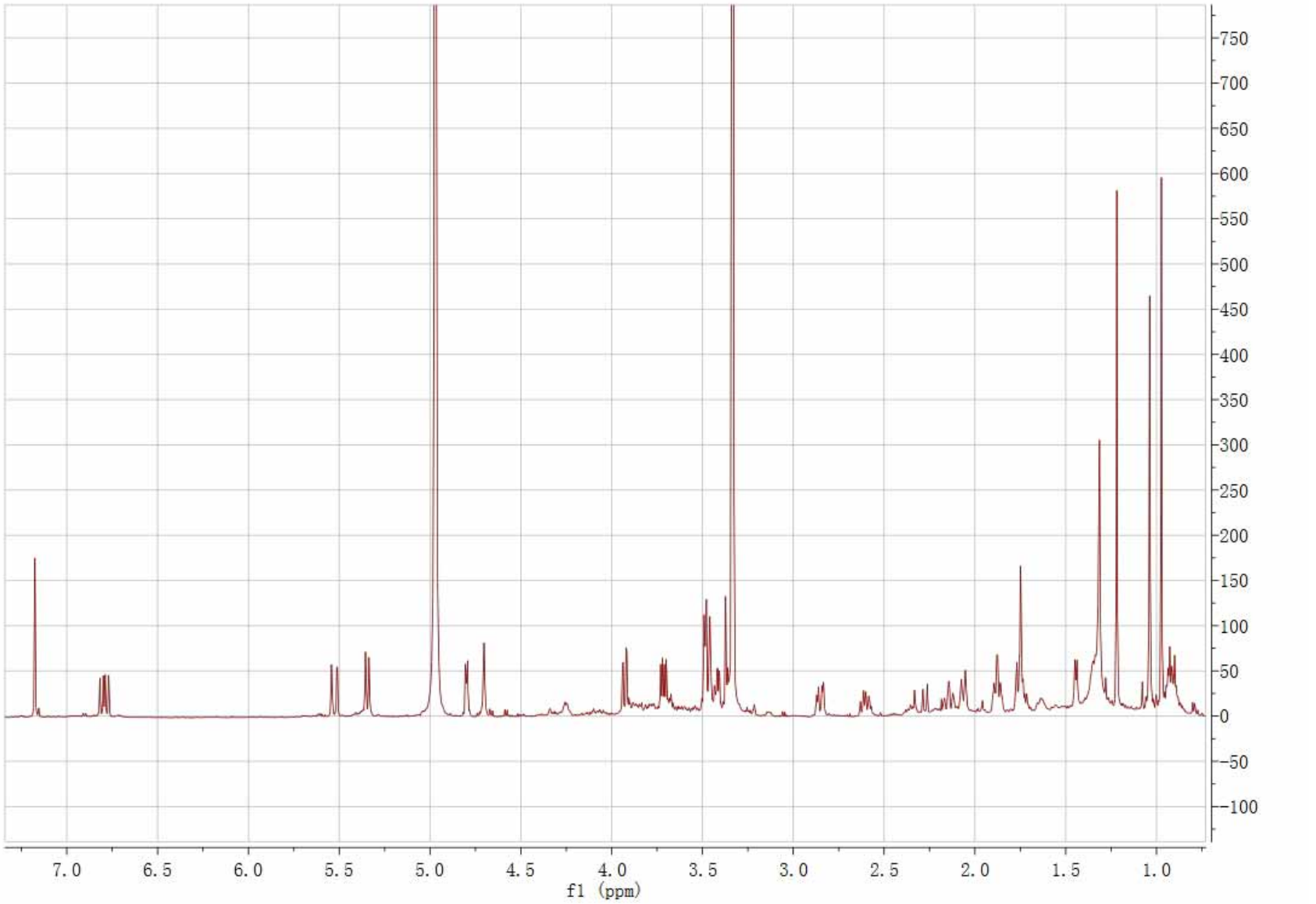
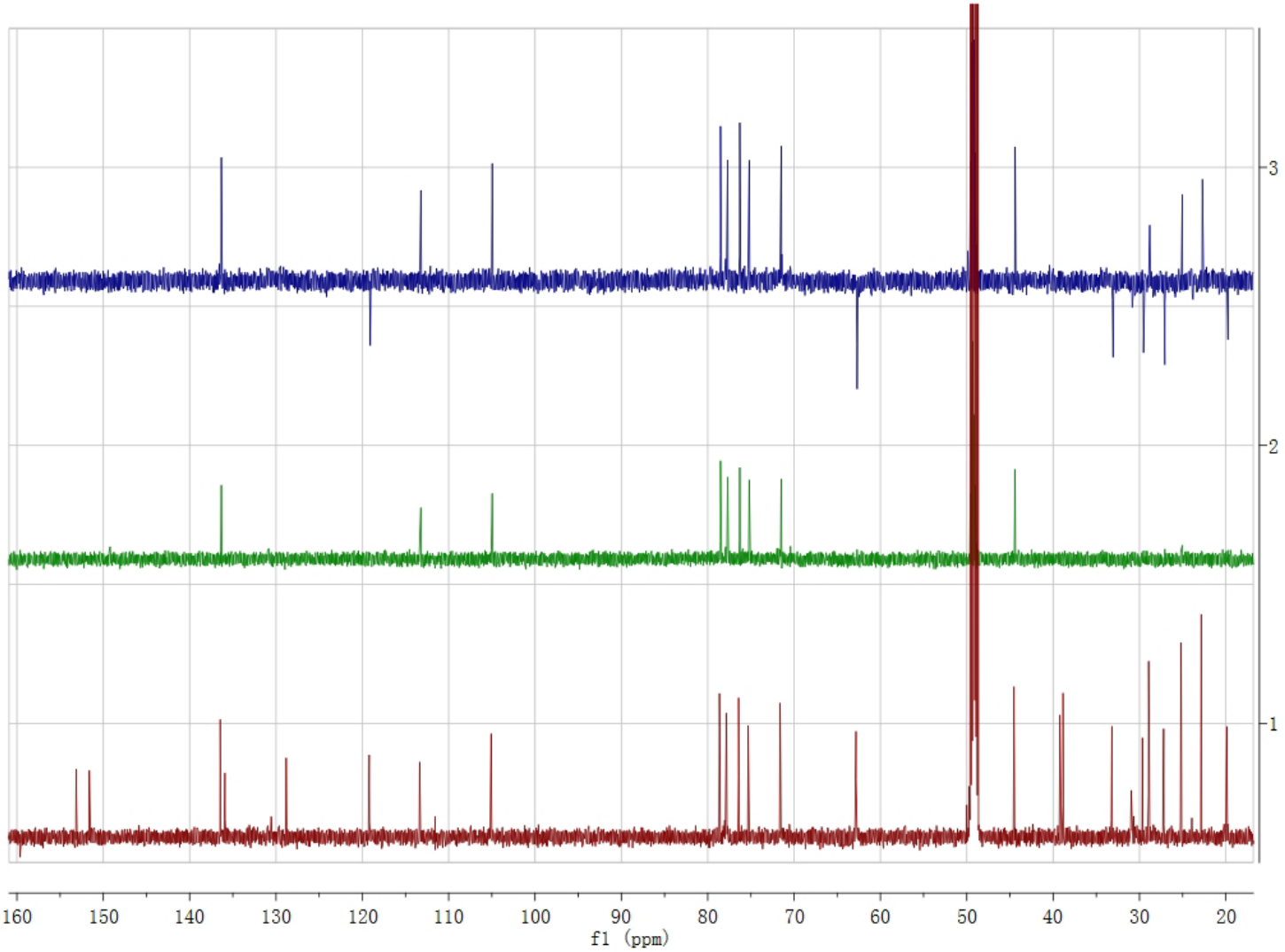


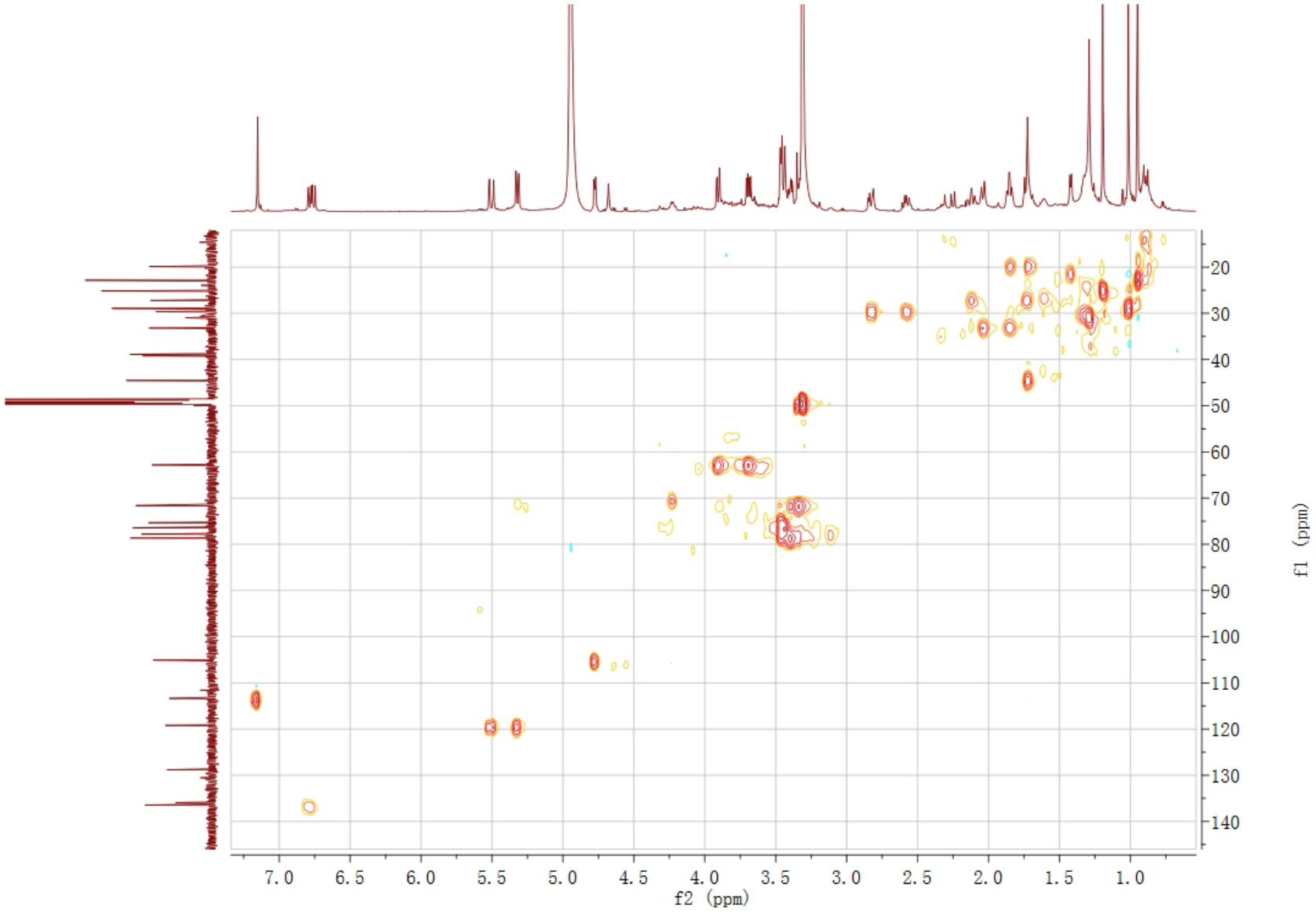
25. S25 ^{1}H NMR (600 MHz) spectrum of compound **3** in CD_3OD



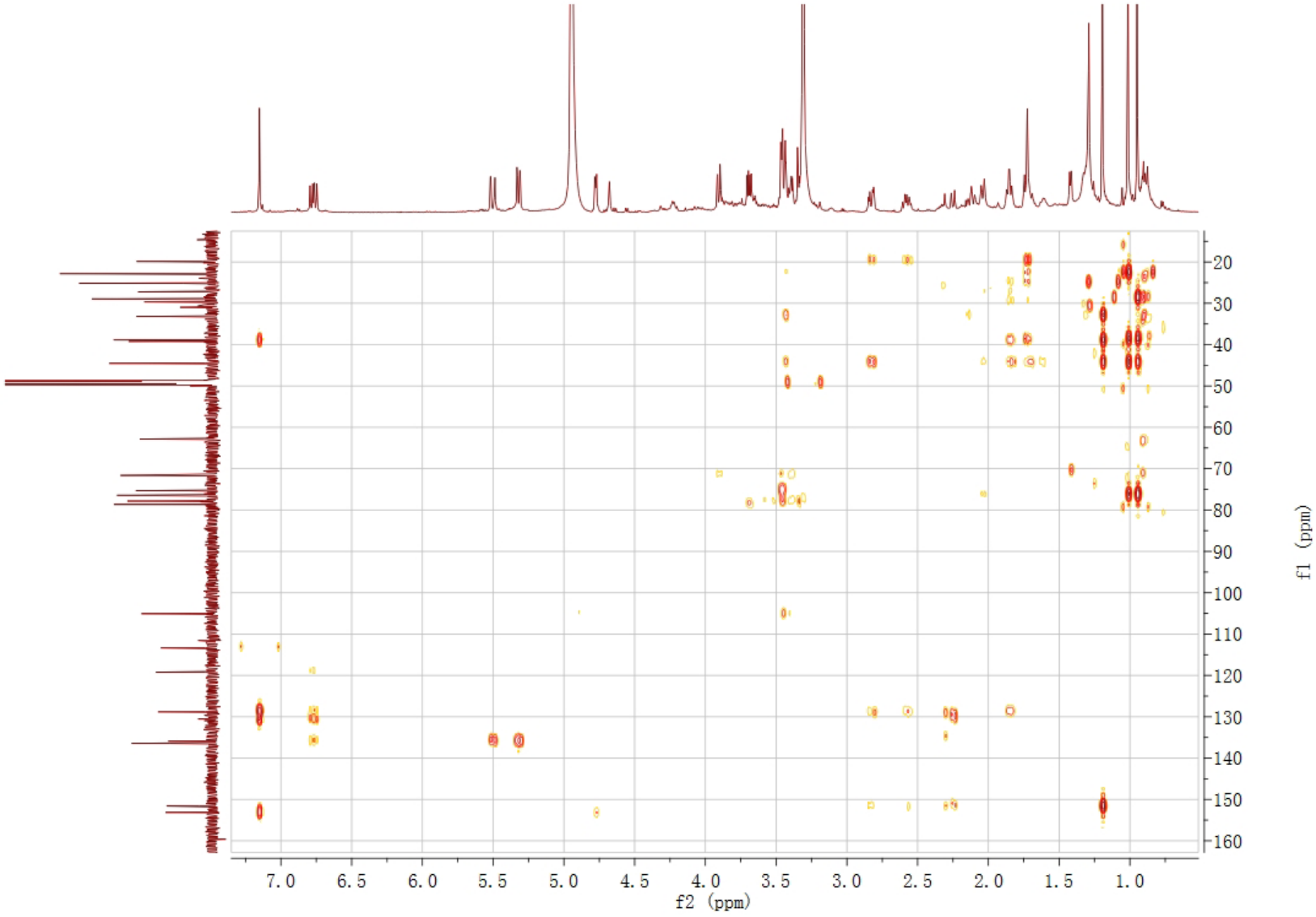
26. S26 ^{13}C NMR (150 MHz) spectrum of compound **3** in CD_3OD

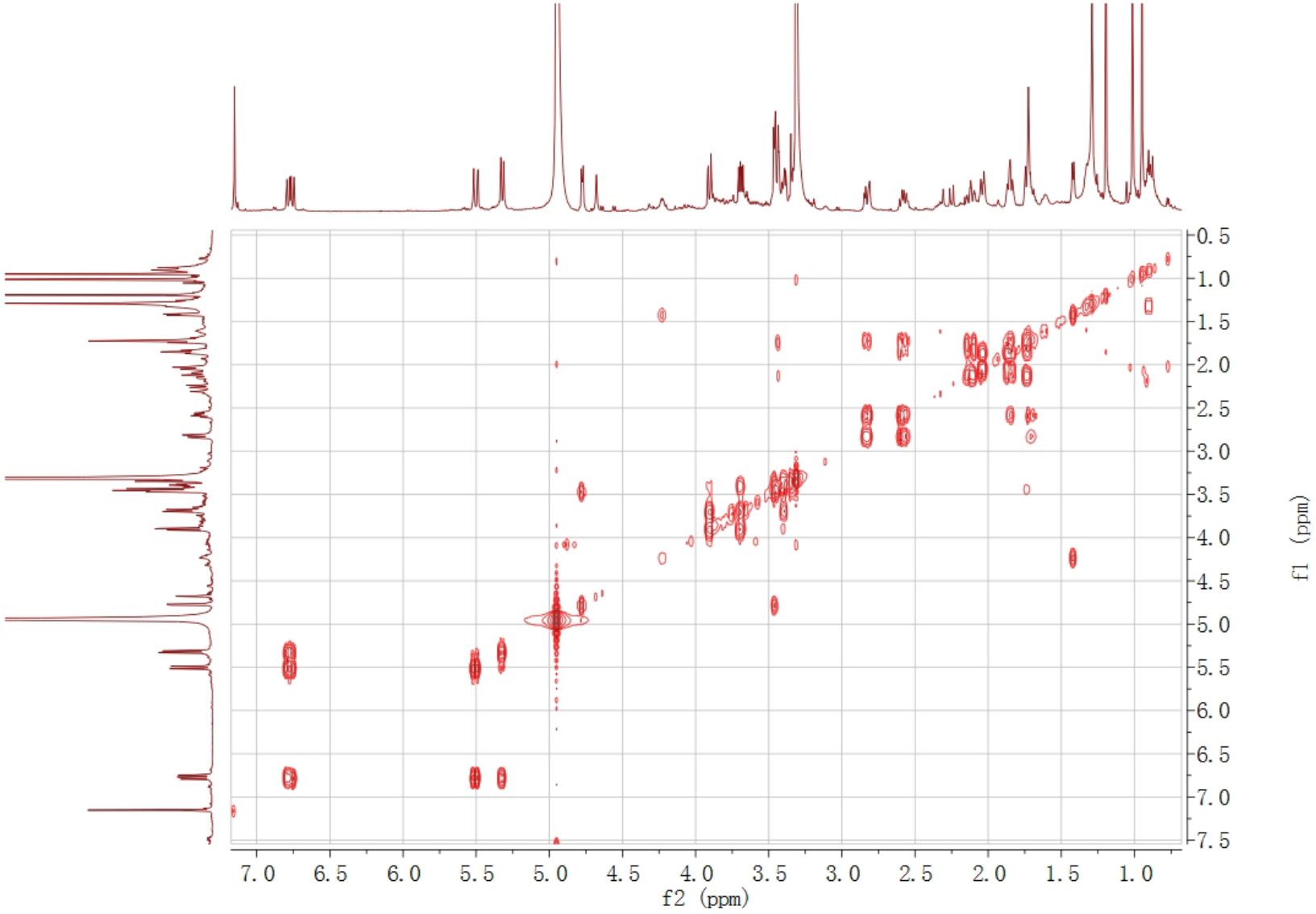


27. S27 HSQC spectrum of compound **3** in CD_3OD



28. S28 HMBC spectrum of compound **3** in CD_3OD

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6.0
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5.0
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4.0
3.5
3.0
2.5
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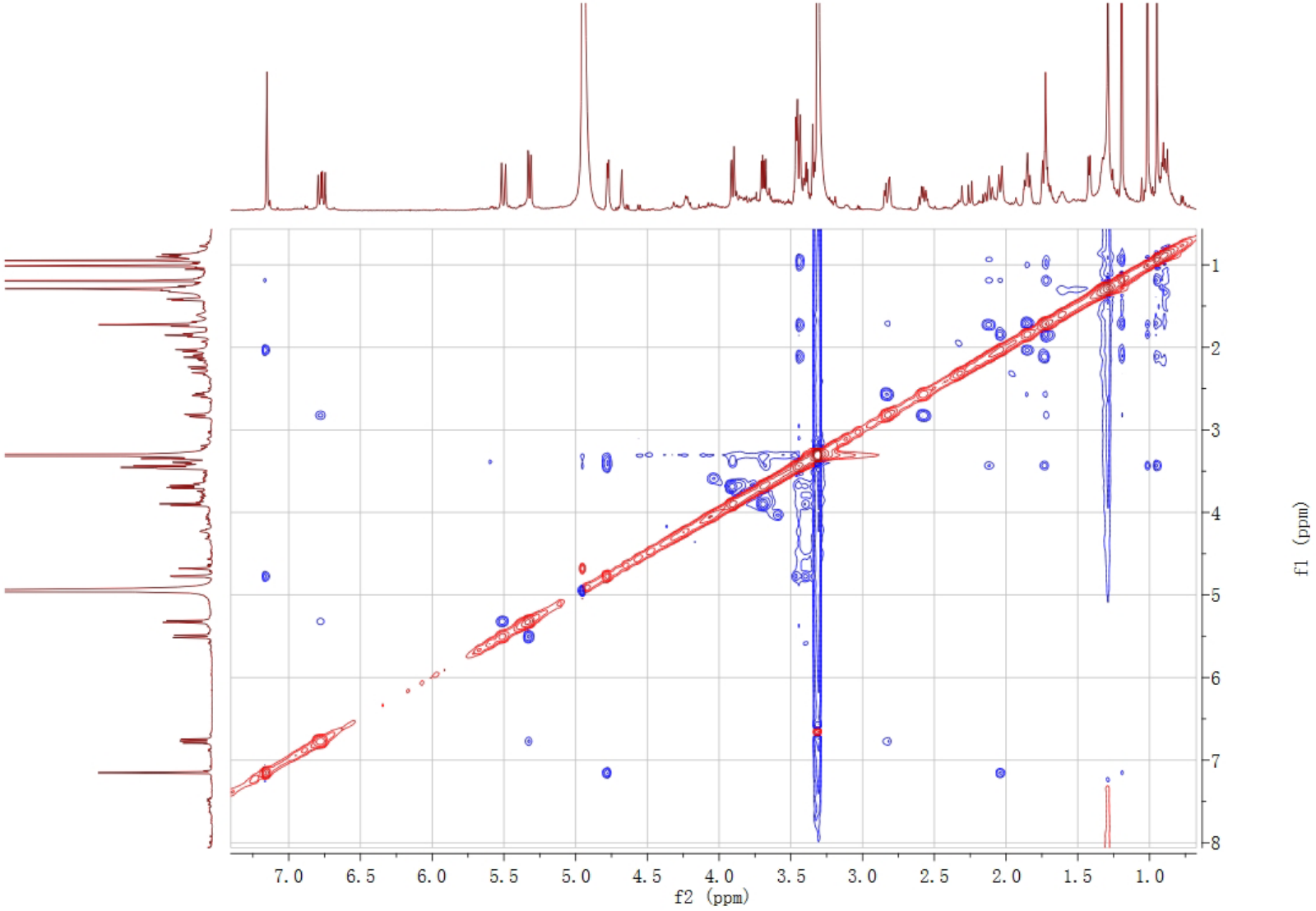
1.0
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)

30. S30 ROESY spectrum of compound **3** in CD_3OD



31. S31 HRESIMS of compound **4**

Elemental Composition Report **Page 1**

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Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
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YLJ112201
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Voltage EI+

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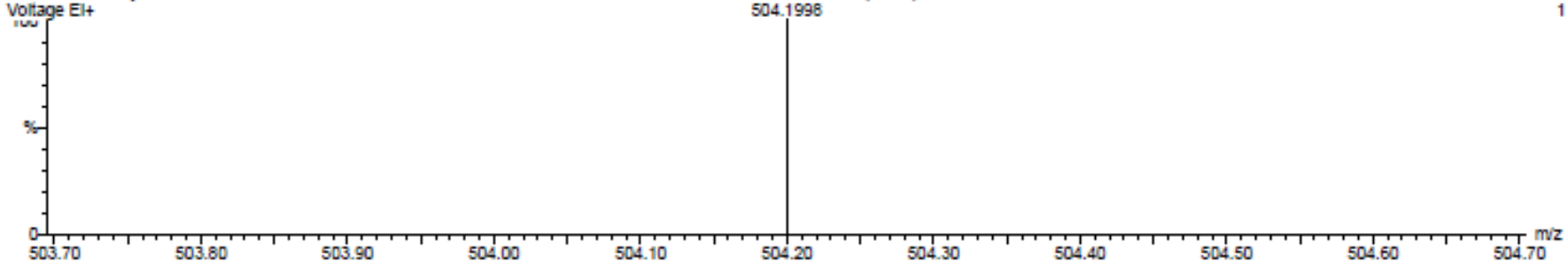
504.1998

Autospec Premier
P776
1



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Maximum:		200.0	10.0	120.0		
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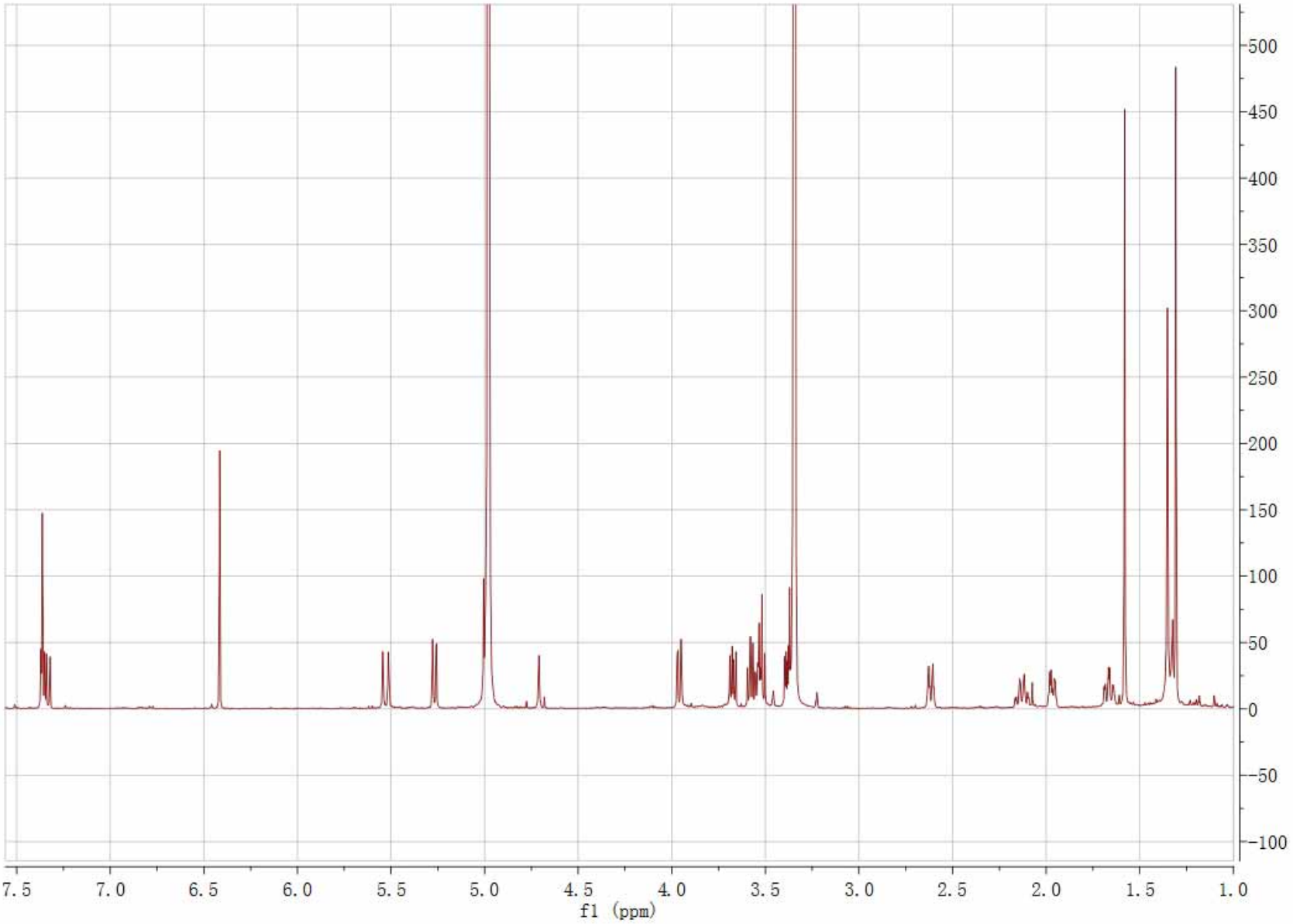
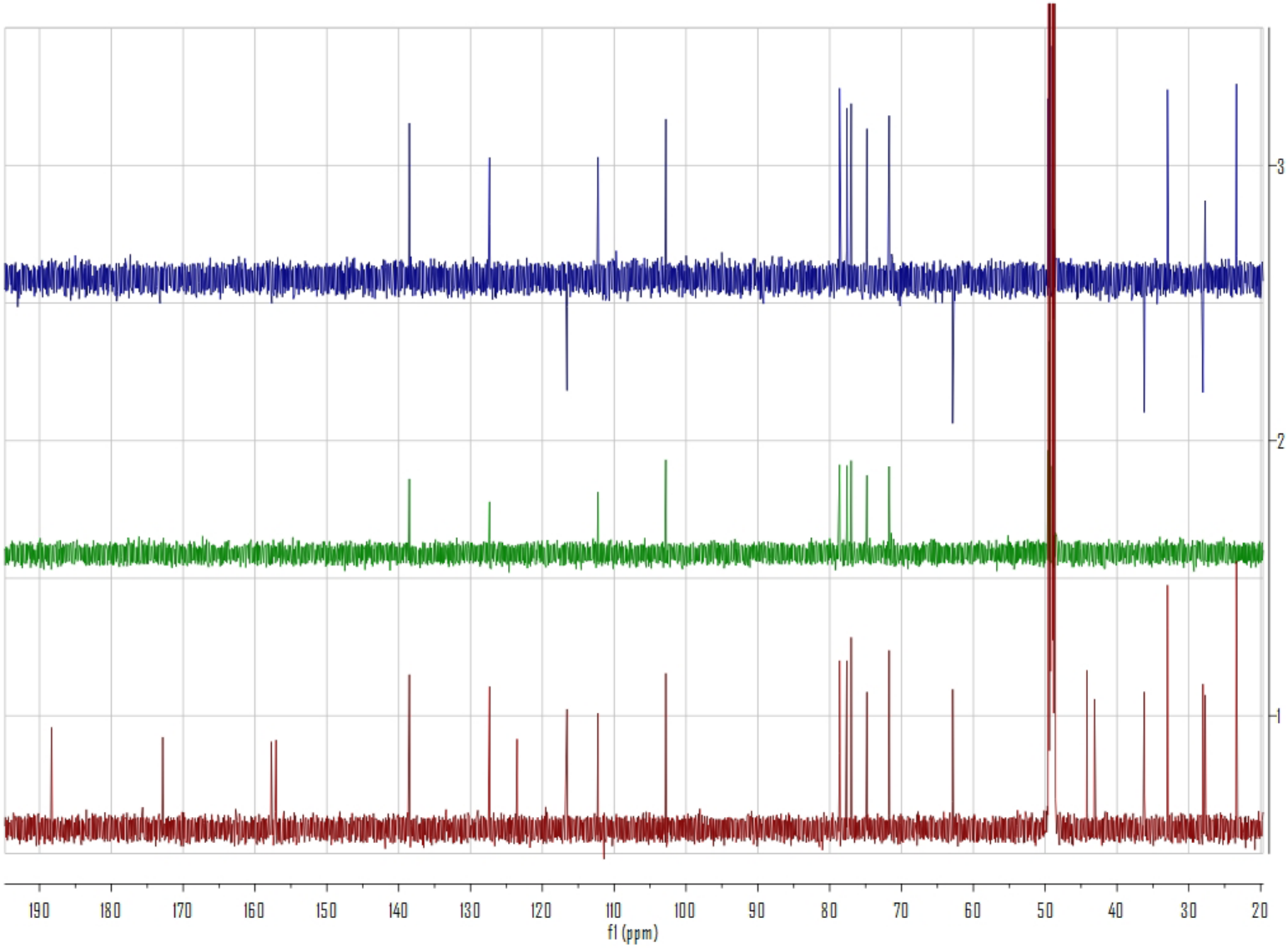
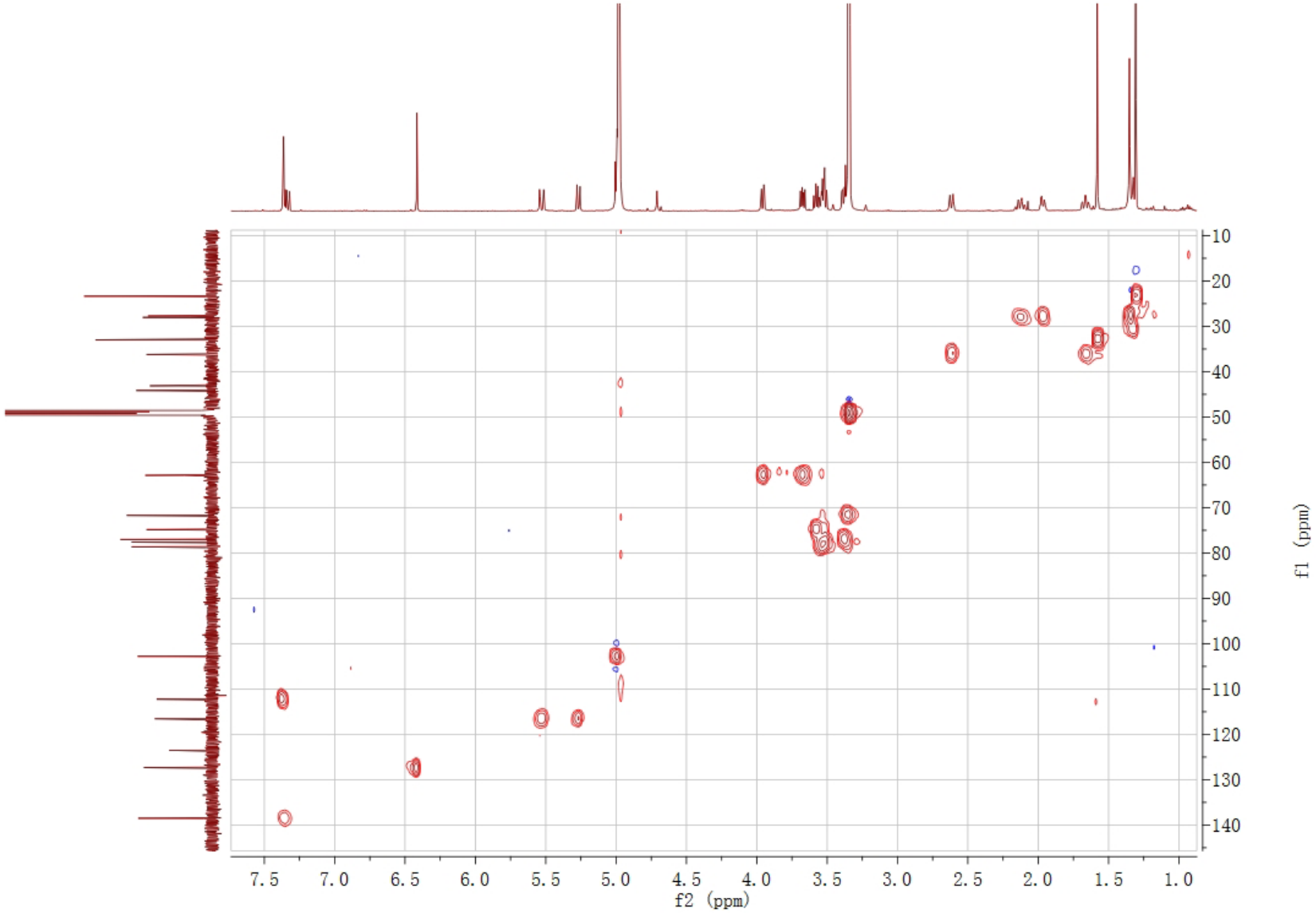
32. S32 ^{1}H NMR (600 MHz) spectrum of compound **4** in CD_3OD



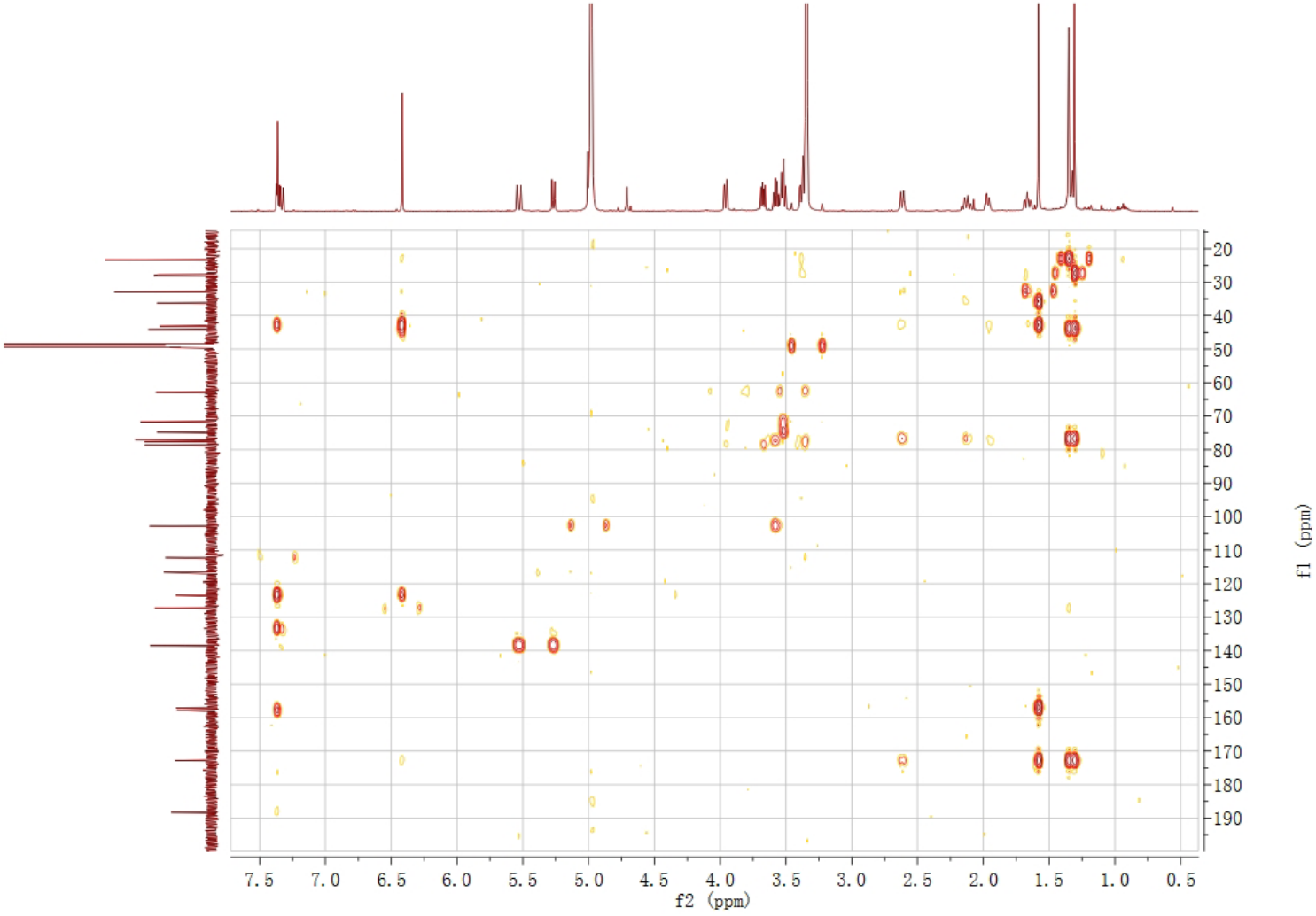
33. S33 ^{13}C NMR (150 MHz) spectrum of compound **4** in CD_3OD



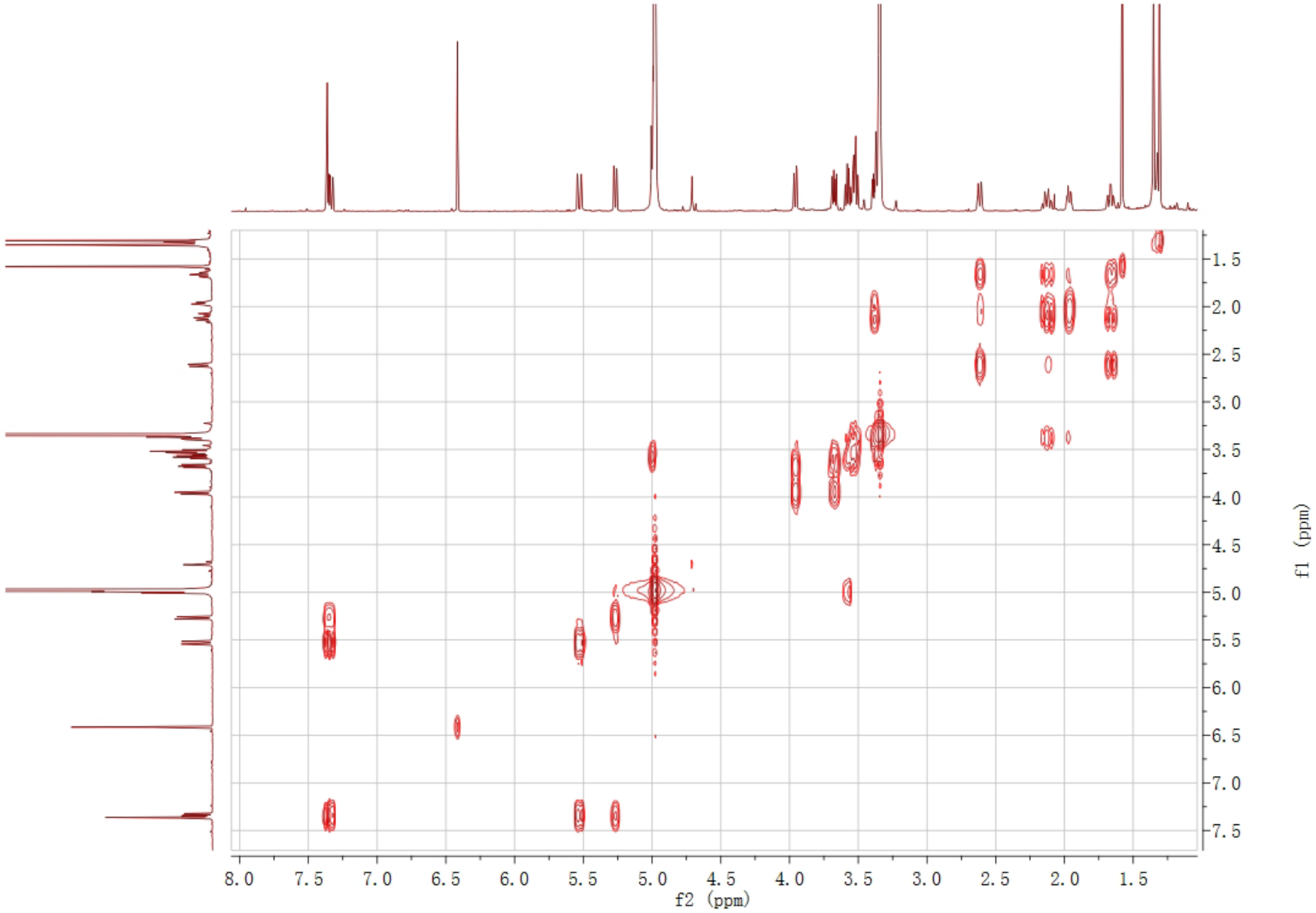
34. S34 HSQC spectrum of compound **4** in CD_3OD



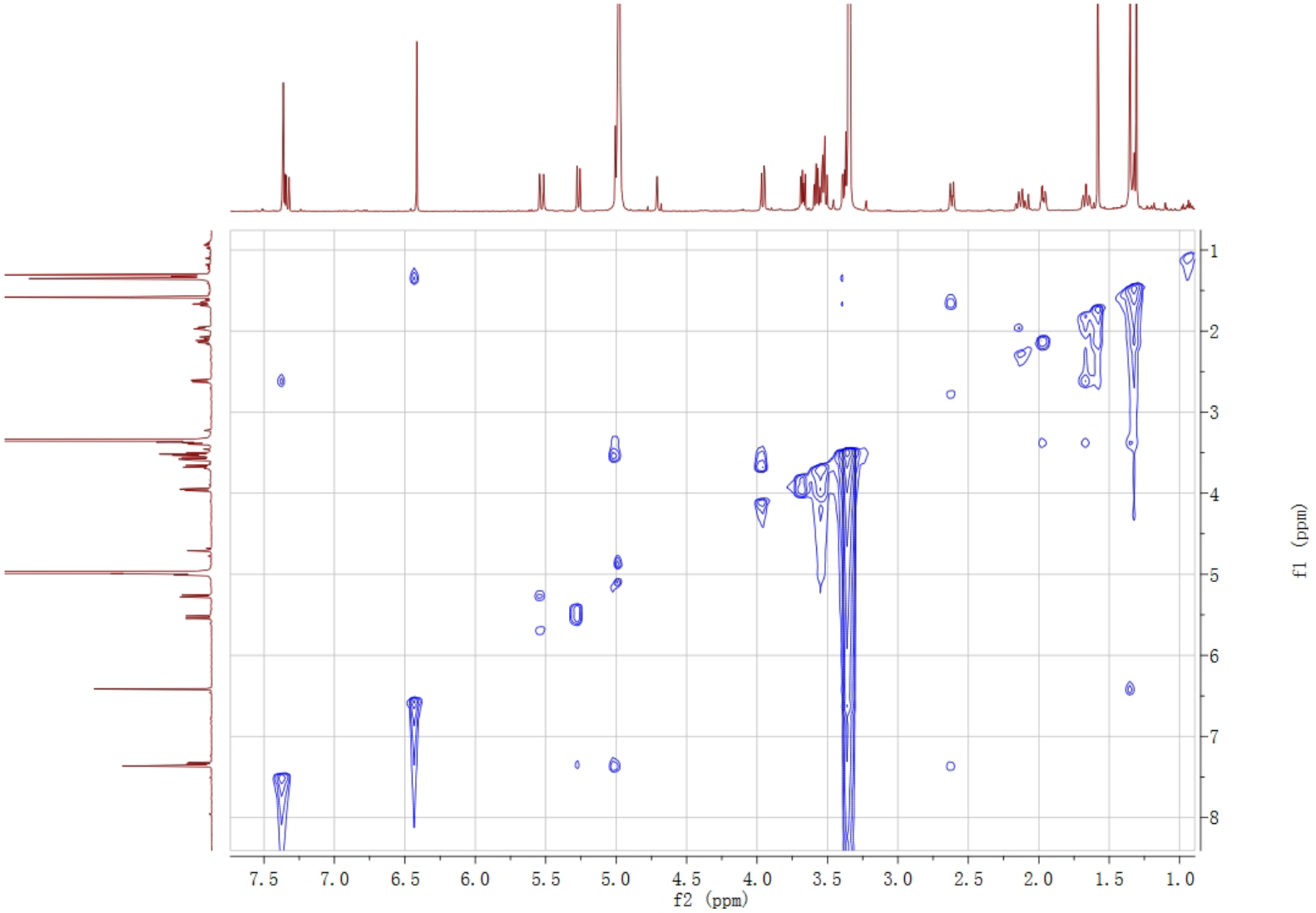
35. S35 HMBC spectrum of compound **4** in CD_3OD



36. S36 ^{1}H-^{1}H COSY spectrum of compound **4** in CD_3OD



37. S37 ROESY spectrum of compound **4** in CD_3OD



38. S38 HRESIMS of compound **5**

Formula Predictor Report - gca40_TLJ1728_23.lcd

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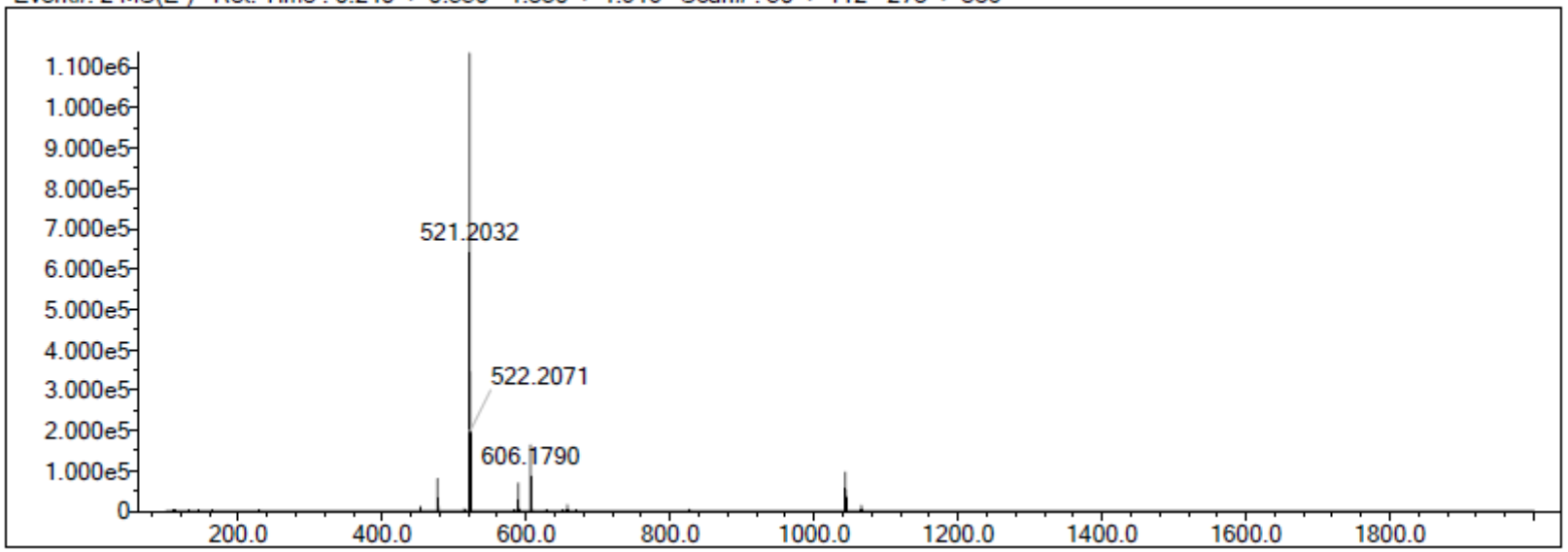
B	3	0	0	O	2	0	30	S	2	0	0	I	3	0	0	
C	4	0	50	F	1	0	0	Cl	1	0	0					

Error Margin (mDa): 20.0
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

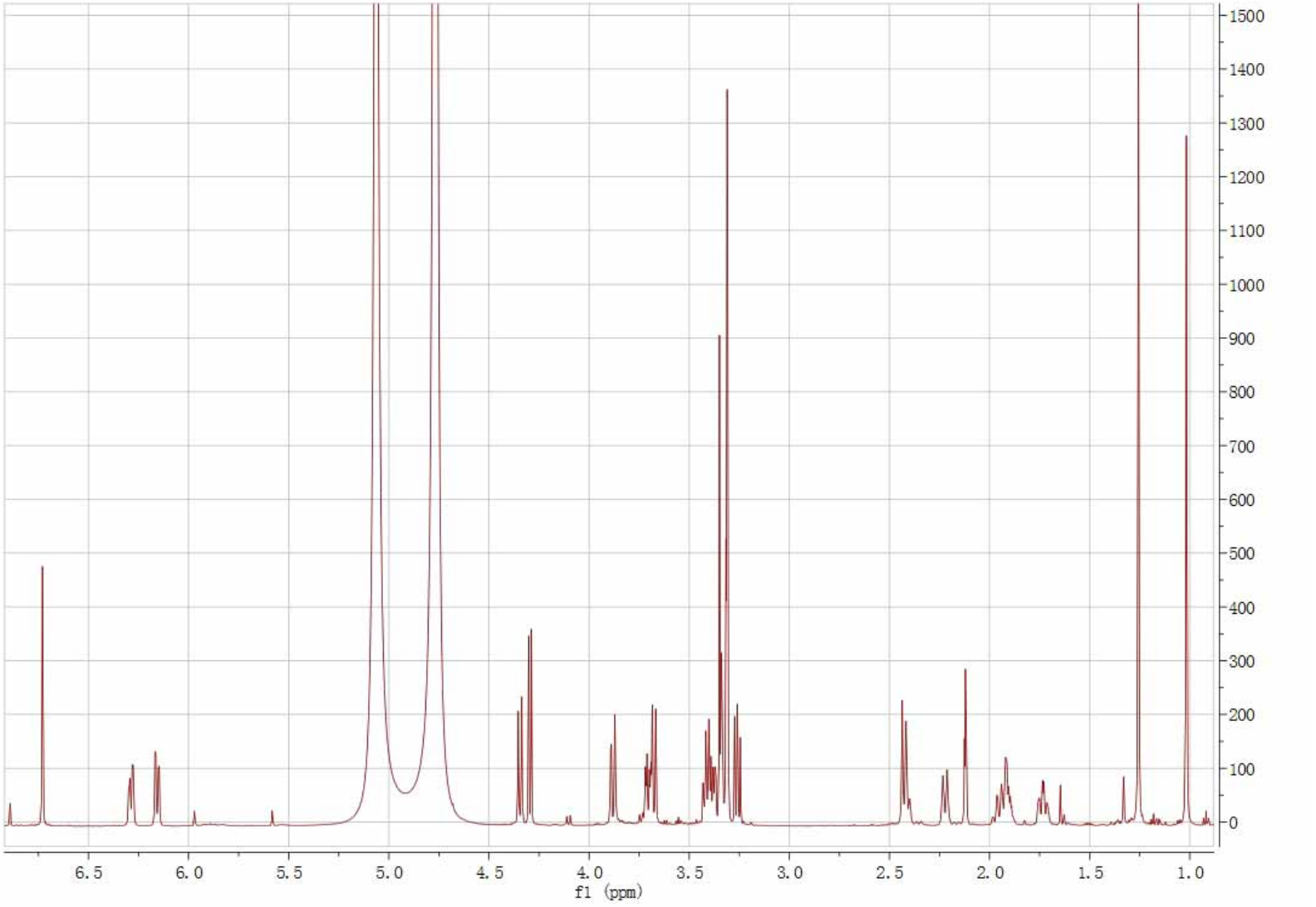
DBE Range: 0.0 - 30.0
Apply N Rule: no
Isotope RI (%): 1.00
MSn Logic Mode: OR

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 800

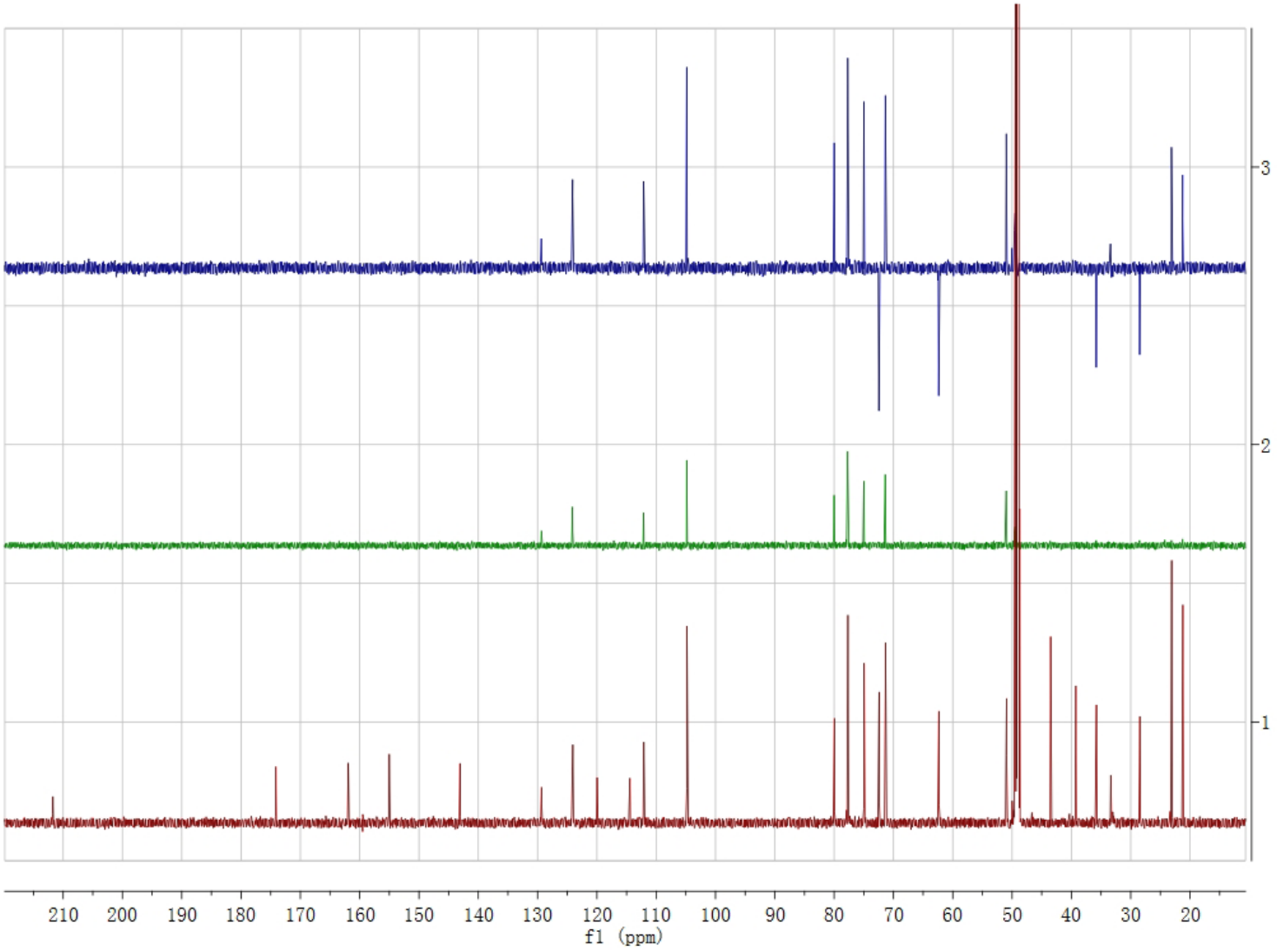
Event#: 2 MS(E-) Ret. Time : 0.240 -> 0.550 - 1.380 -> 1.916 Scan# : 50 -> 112 - 278 -> 386



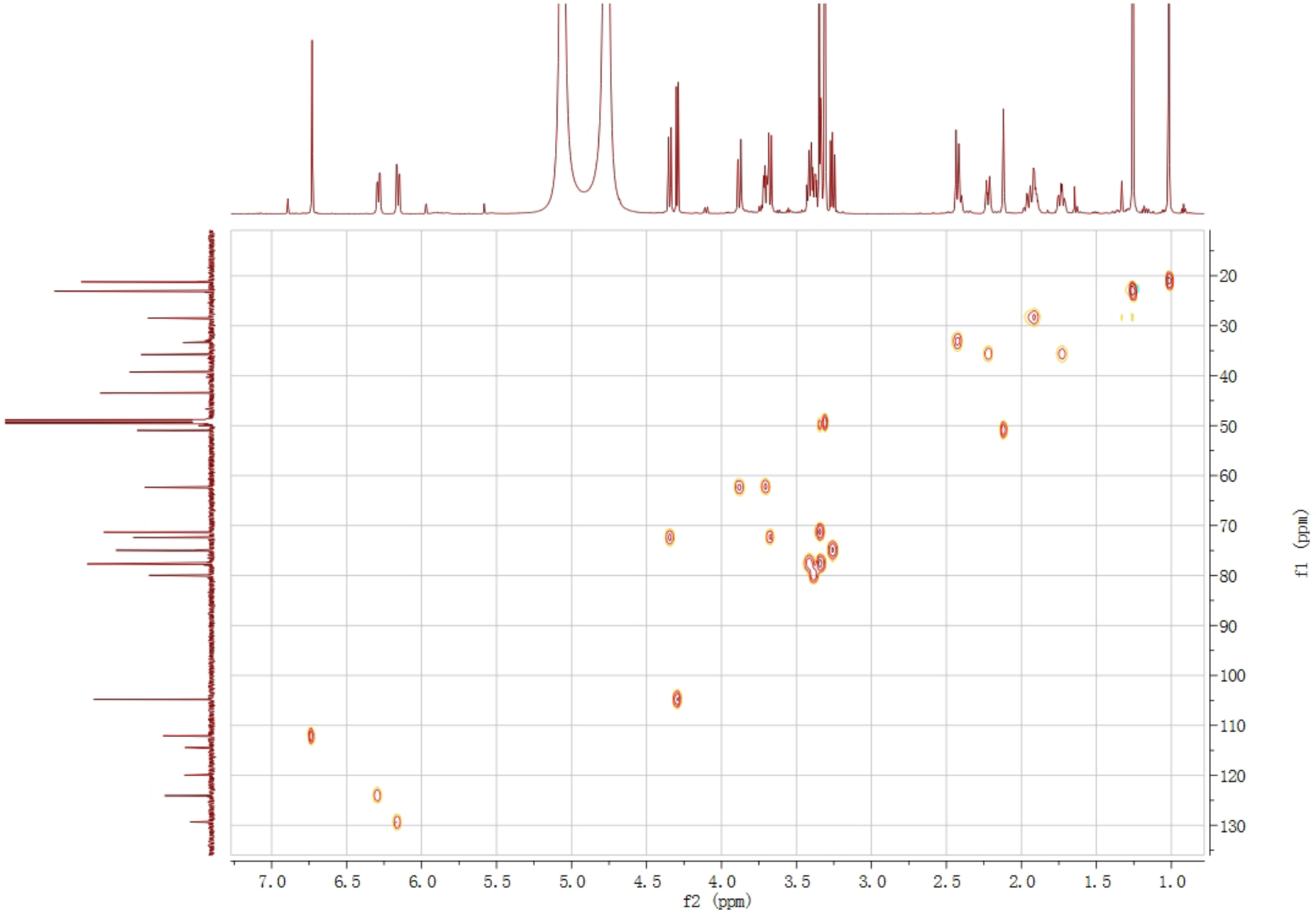
39. S39 ^{1}H NMR (600 MHz) spectrum of compound **5** in CD_3OD



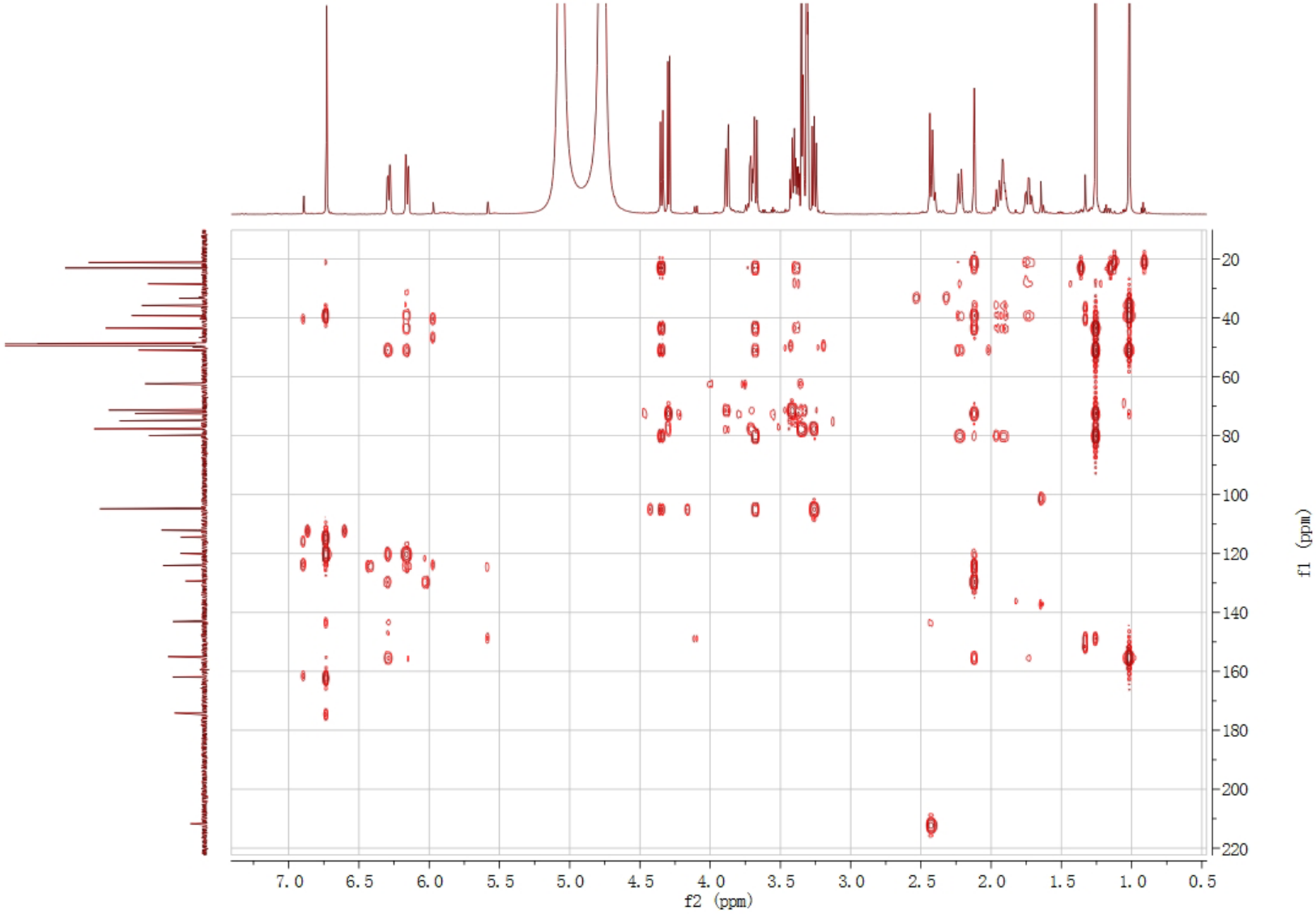
40. S40 ^{13}C NMR (150 MHz) spectrum of compound **5** in CD_3OD



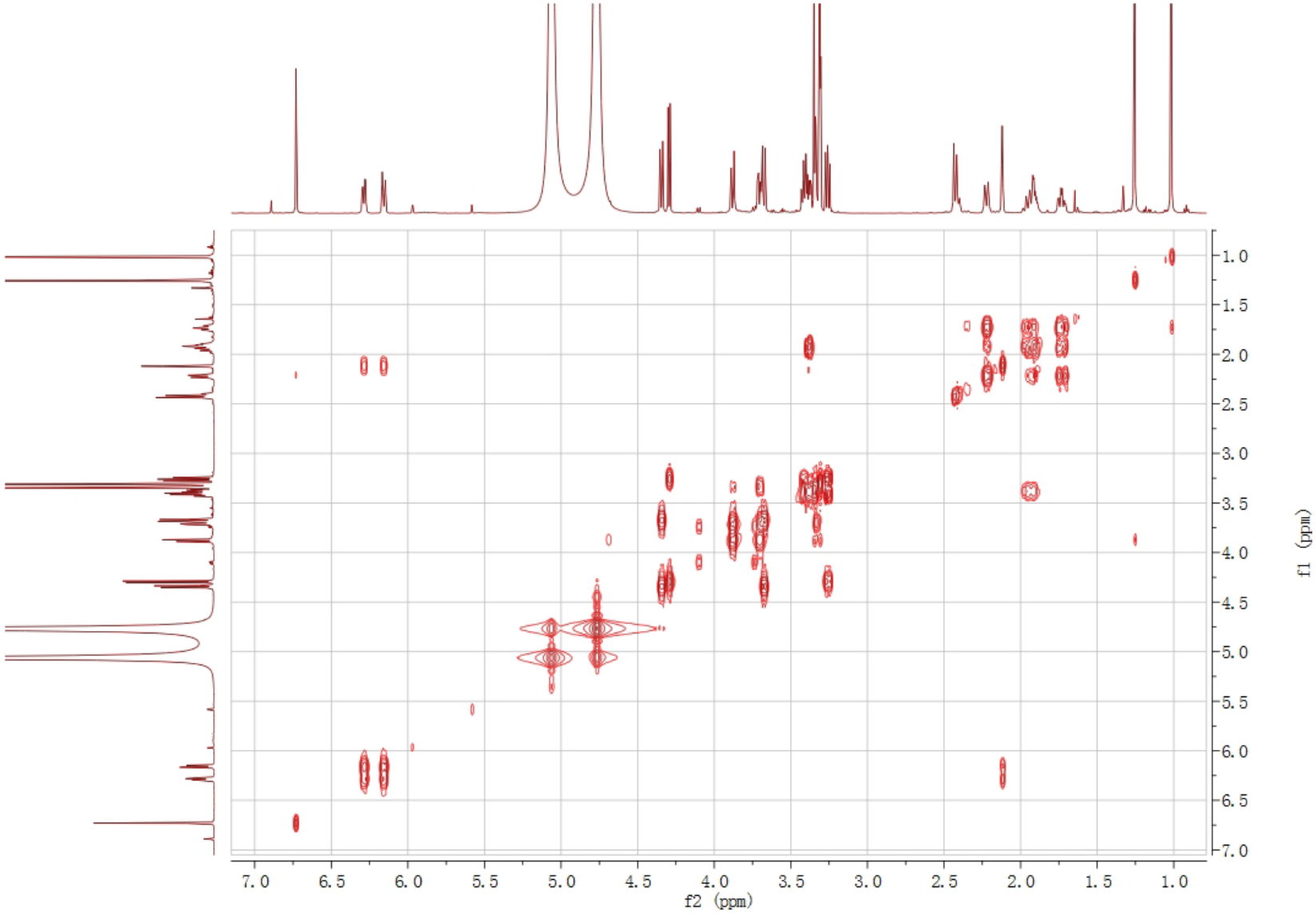
41. S41 HSQC spectrum of compound **5** in CD_3OD



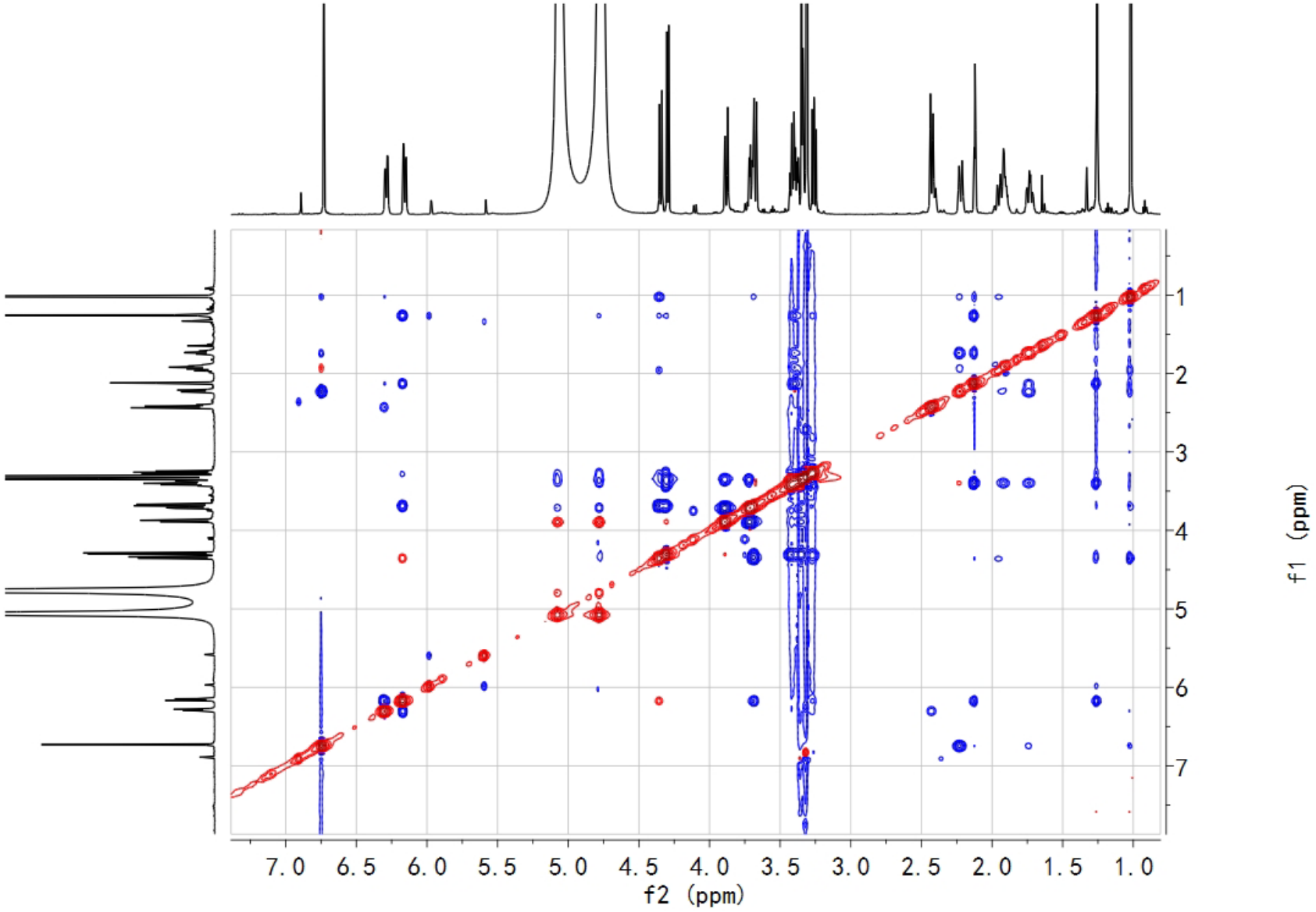
42. S42 HMBC spectrum of compound **5** in CD_3OD



43. S43 ^{1}H-^{1}H COSY spectrum of compound **5** in CD_3OD



44. S44 ROESY spectrum of compound **5** in CD_3OD



45. S45 HRESIMS of compound **6**

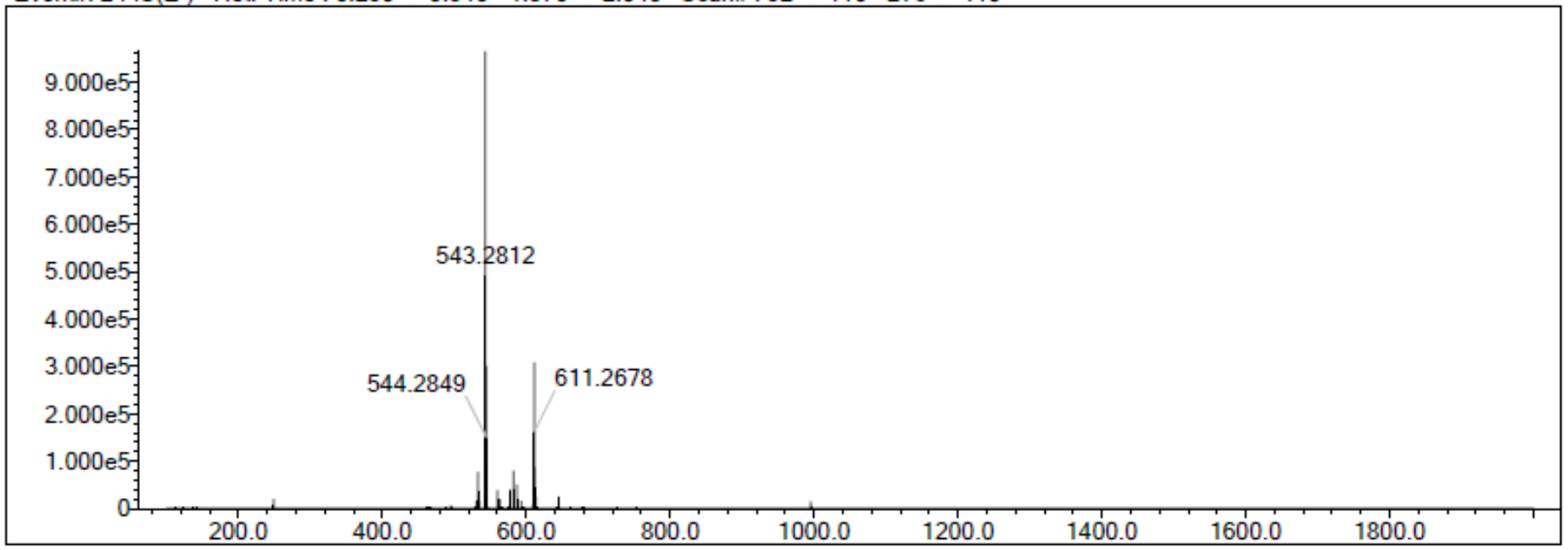
Formula Predictor Report - gca40_TLJ192113_22.lcd

Data File: D:\分子量测定\2013-01-24\gca40_TLJ192113_22.lcd

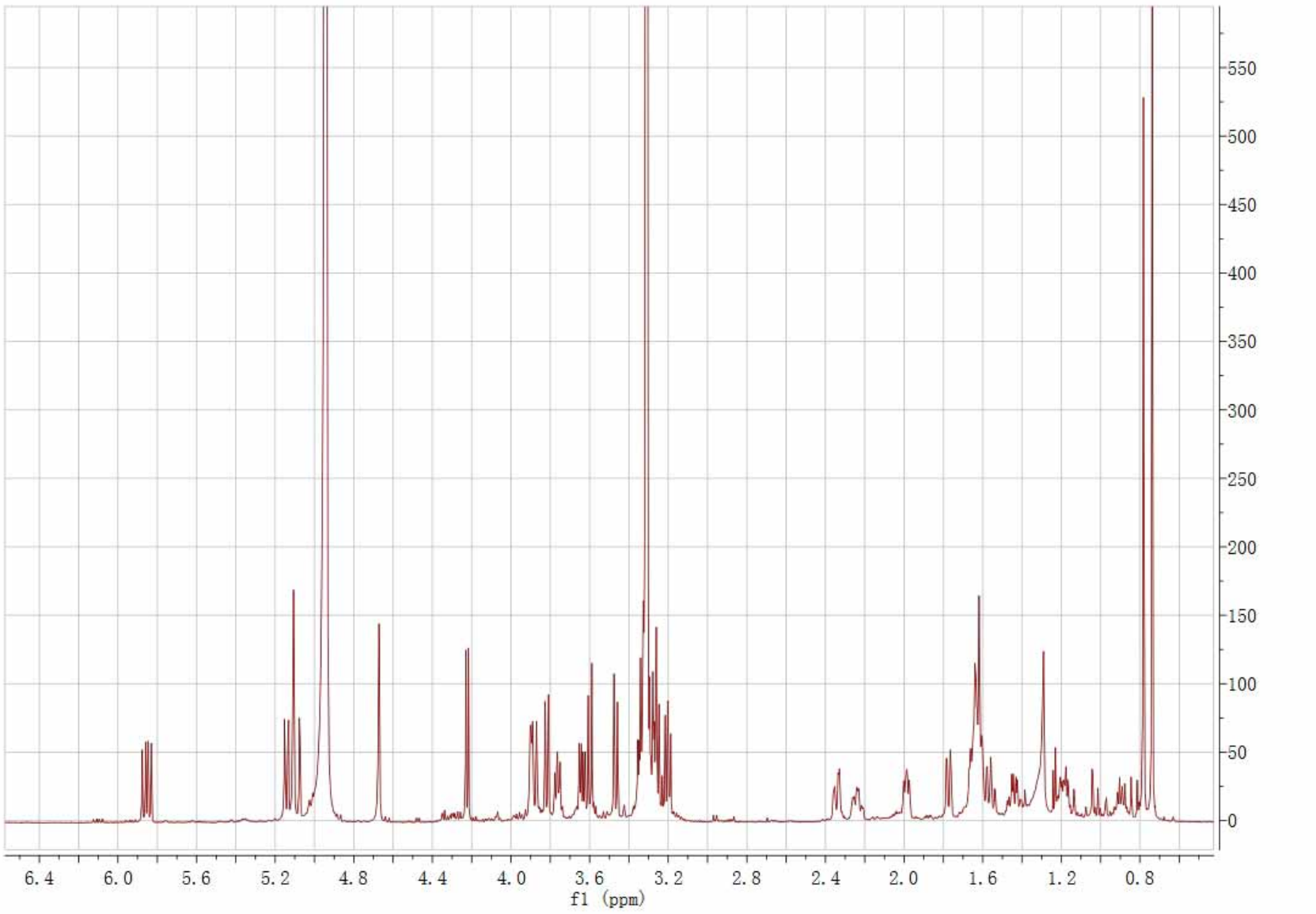
Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Use Adduct
H	1	0	100	N	3	0	0	P	3	0	0	Br	1	0	0	H
B	3	0	0	O	2	0	30	S	2	0	0	I	3	0	0	HCOO
C	4	0	50	F	1	0	0	Cl	1	0	0					

Error Margin (mDa):	20.0	DBE Range:	0.0 - 30.0	Electron Ions:	both
HC Ratio:	unlimited	Apply N Rule:	no	Use MSn Info:	yes
Max Isotopes:	all	Isotope RI (%):	1.00	Isotope Res:	10000
MSn Iso RI (%):	75.00	MSn Logic Mode:	OR	Max Results:	800

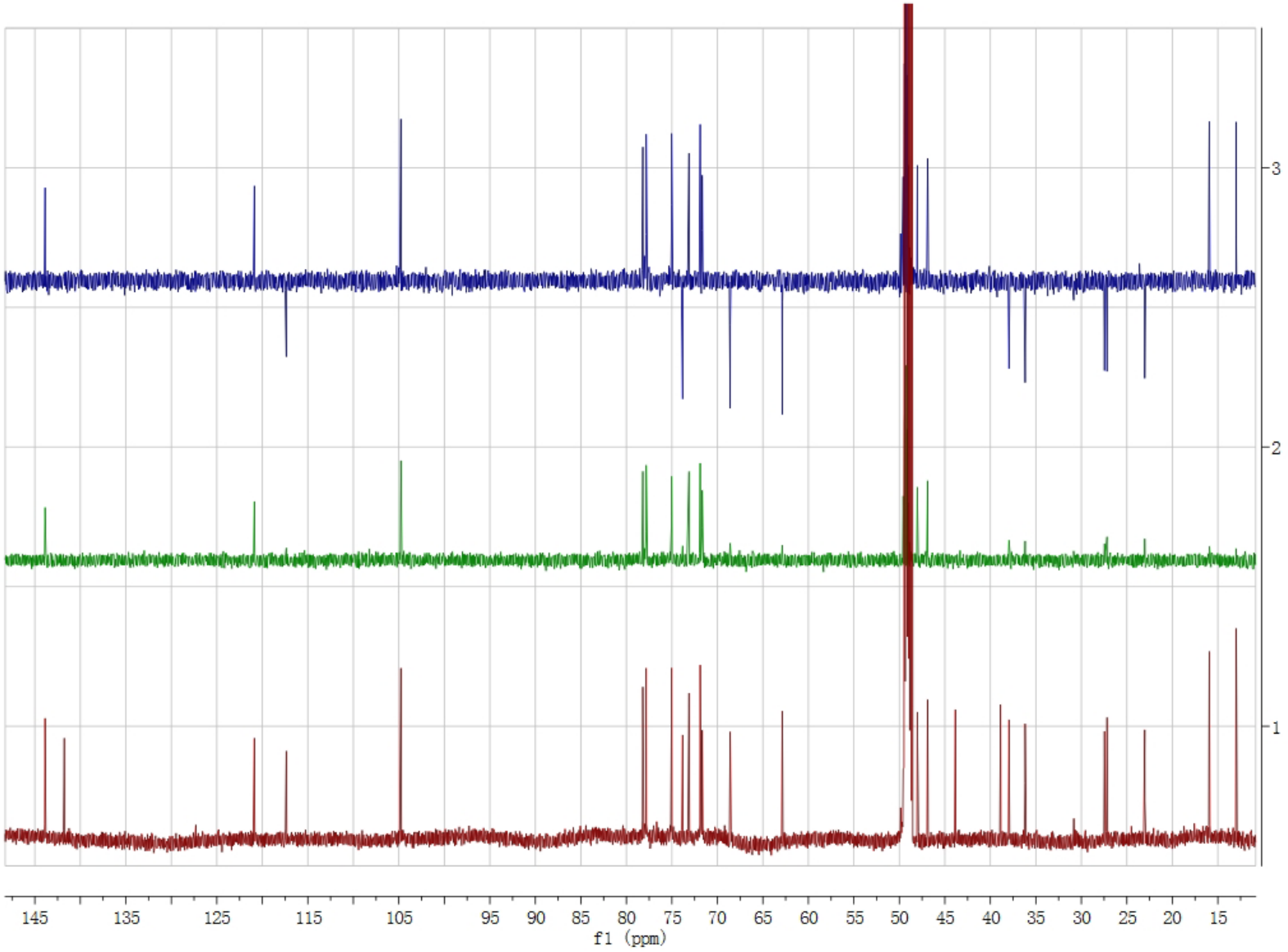
Event#: 2 MS(E-) Ret. Time : 0.250 -> 0.540 - 1.370 -> 2.040 Scan# : 52 -> 110 - 276 -> 410



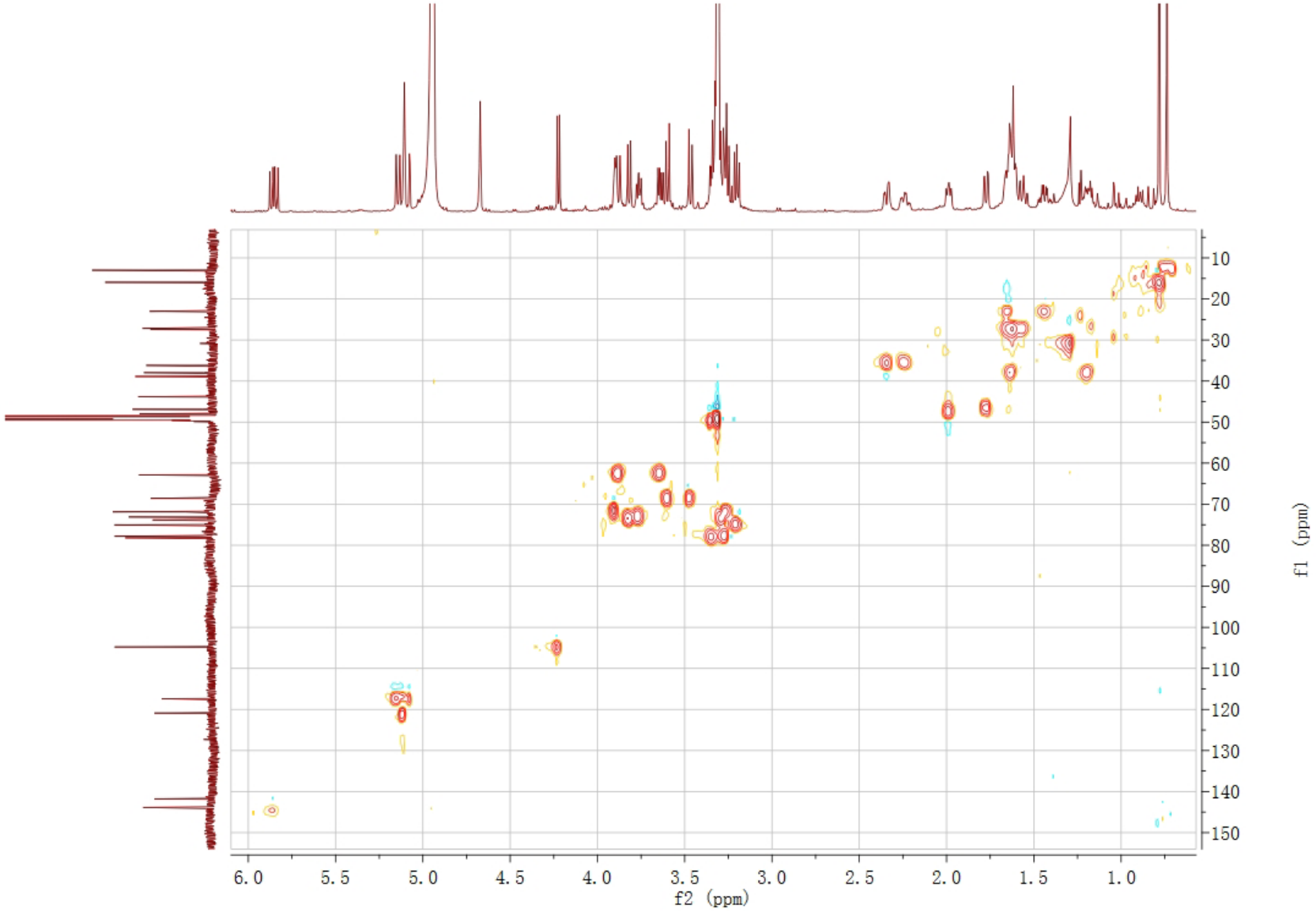
46. S46 ^{1}H NMR (600 MHz) spectrum of compound **6** in CD_3OD



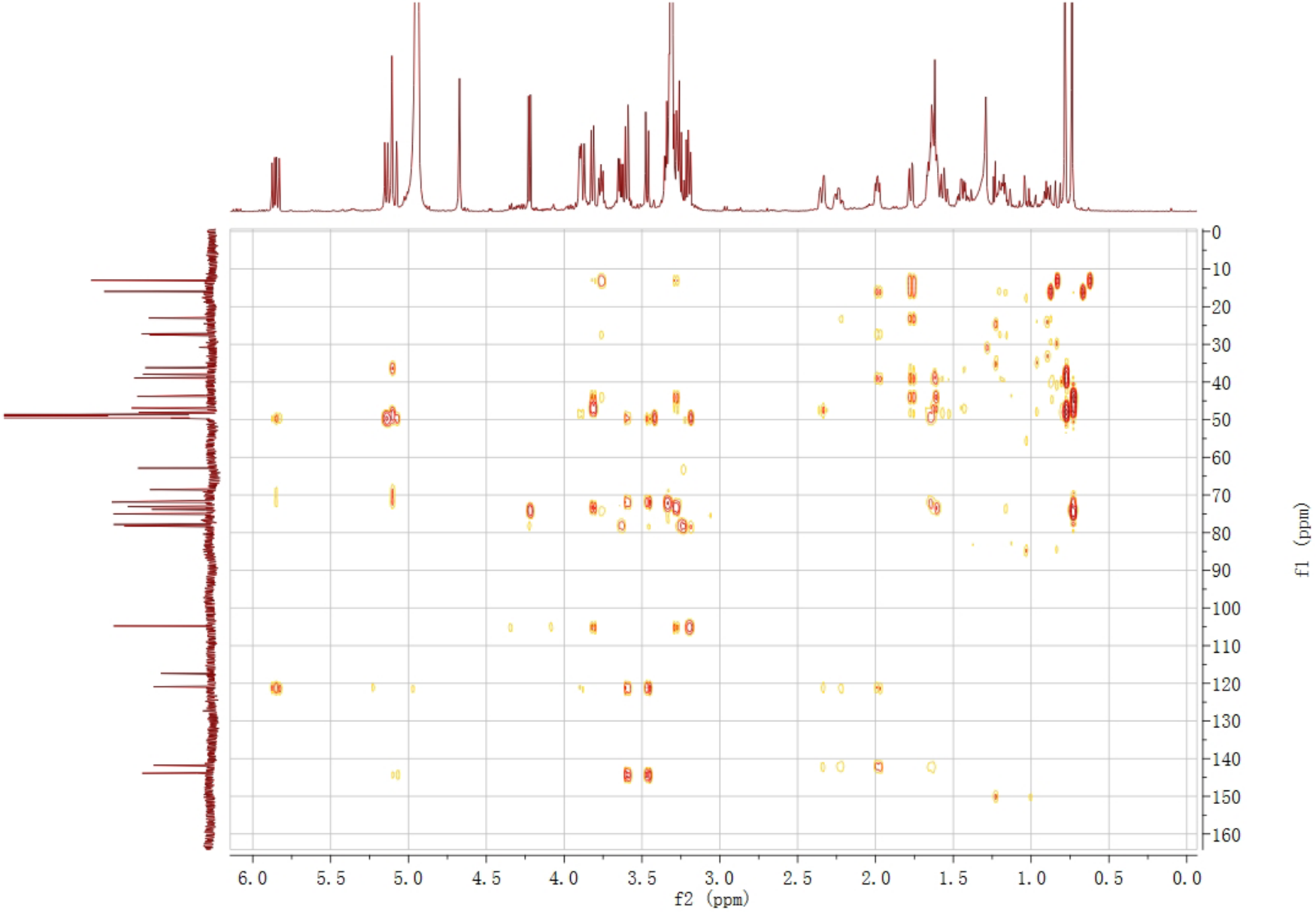
47. S47 ^{13}C NMR (150 MHz) spectrum of compound **6** in CD_3OD



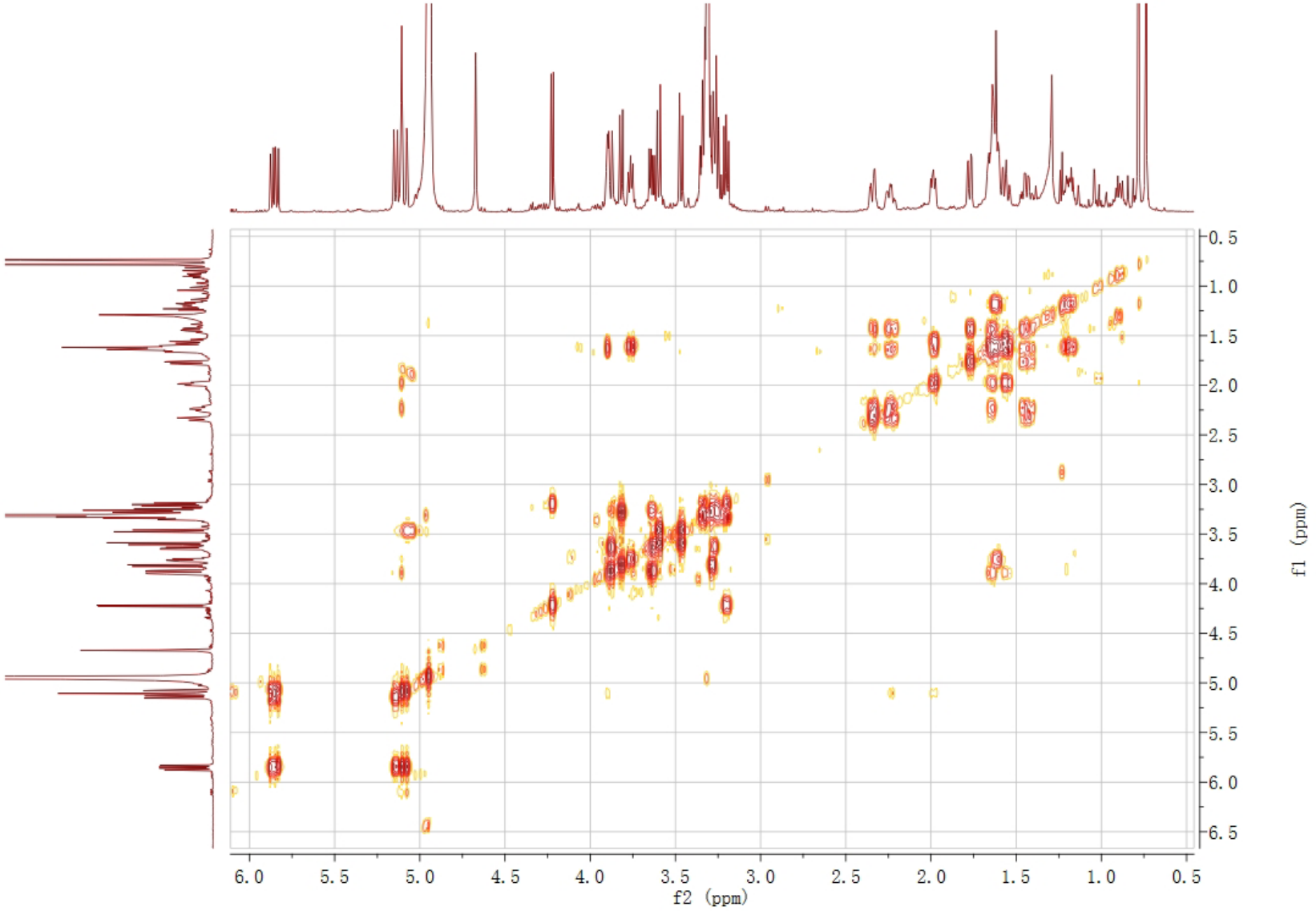
48. S48 HSQC spectrum of compound **6** in CD_3OD



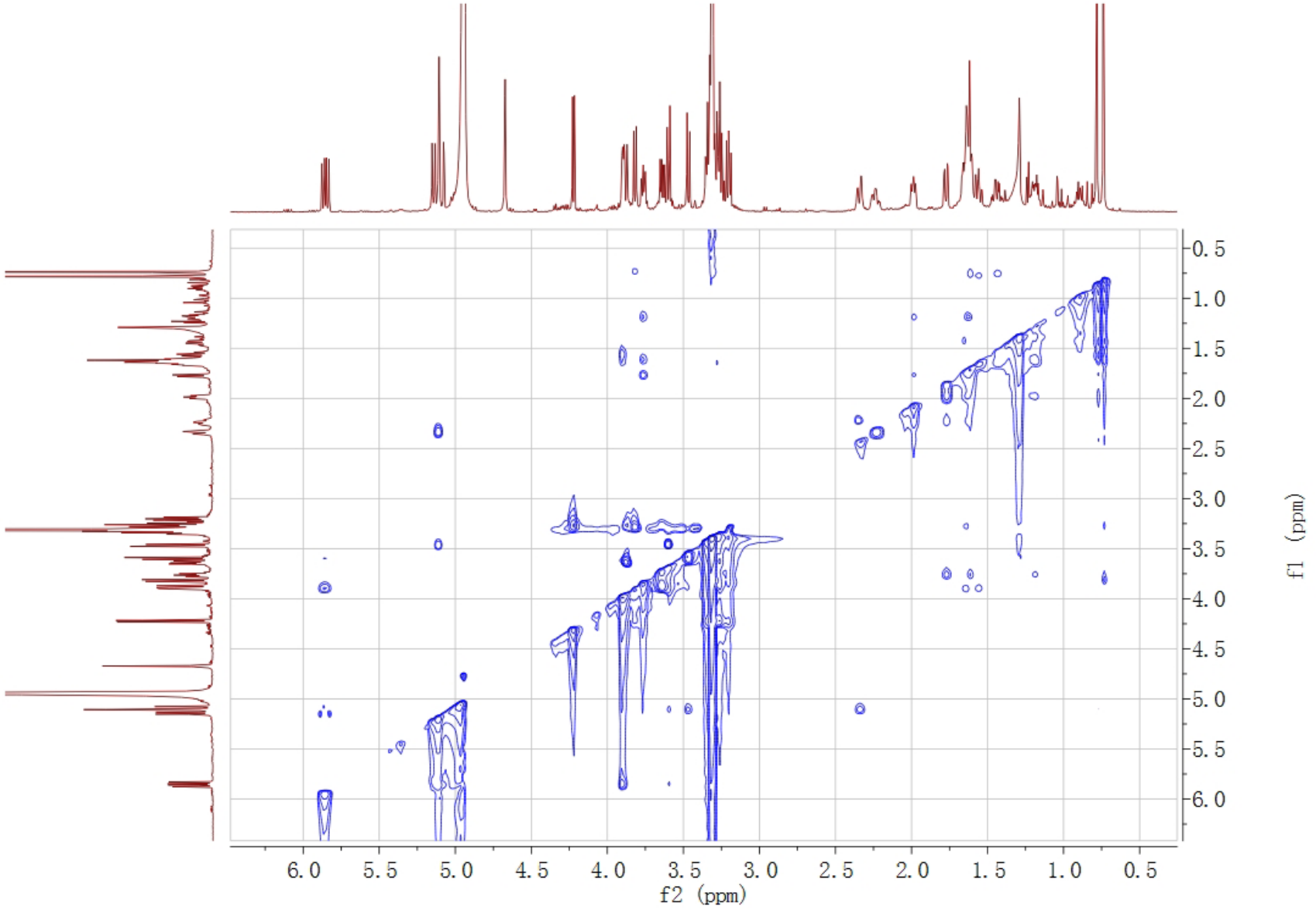
49. S49 HMBC spectrum of compound **6** in CD_3OD



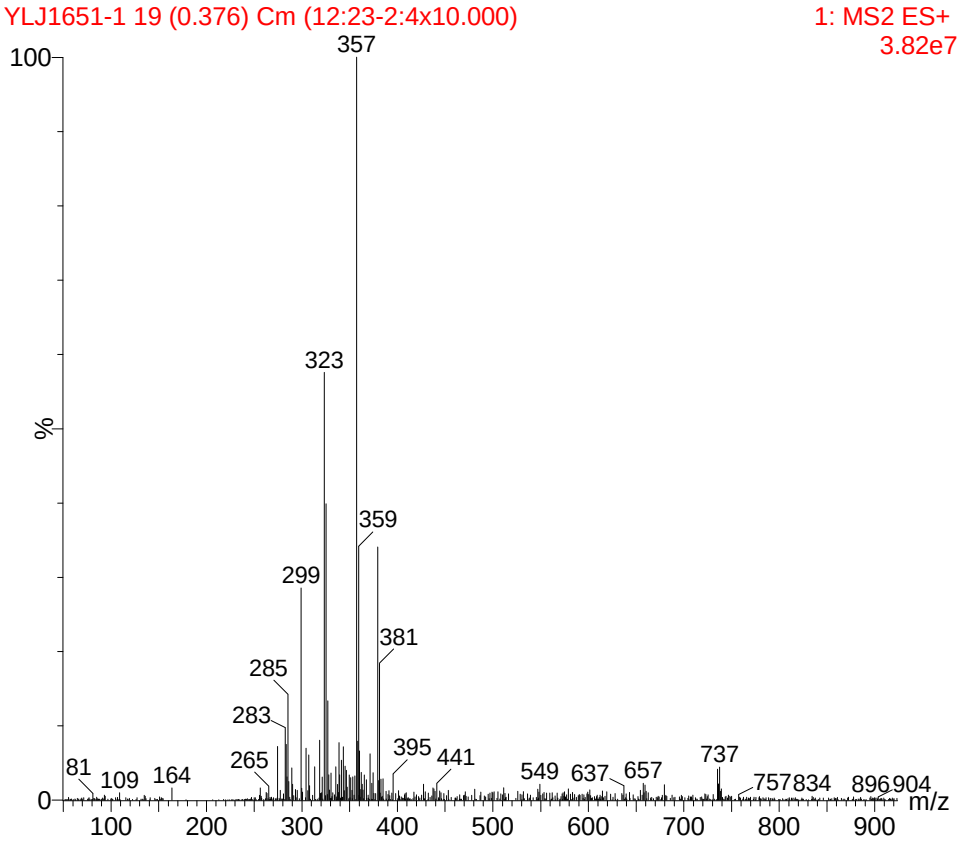
50. S50 ^{1}H-^{1}H COSY spectrum of compound **6** in CD_3OD



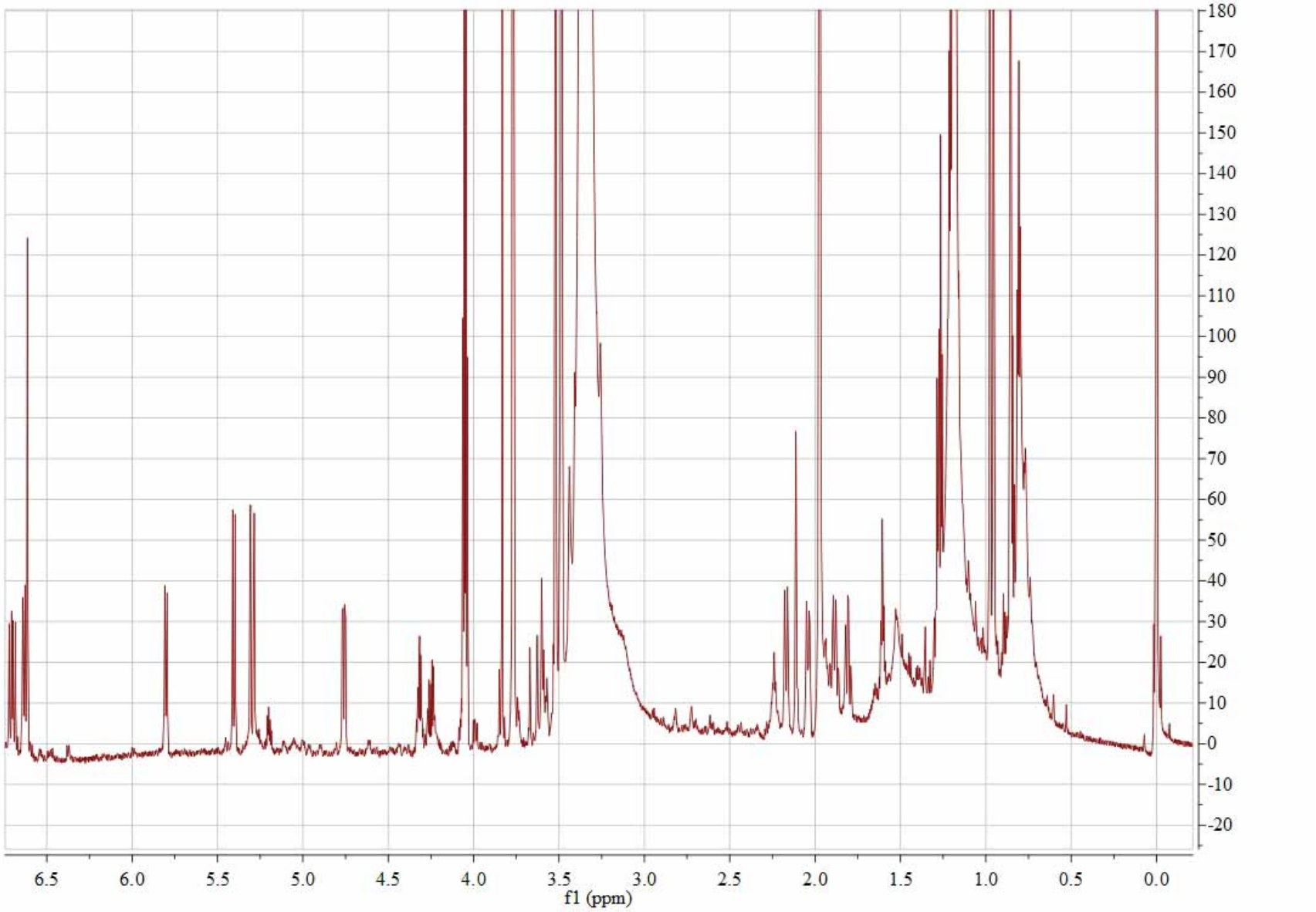
51. S51 ROESY spectrum of compound **6** in CD_3OD



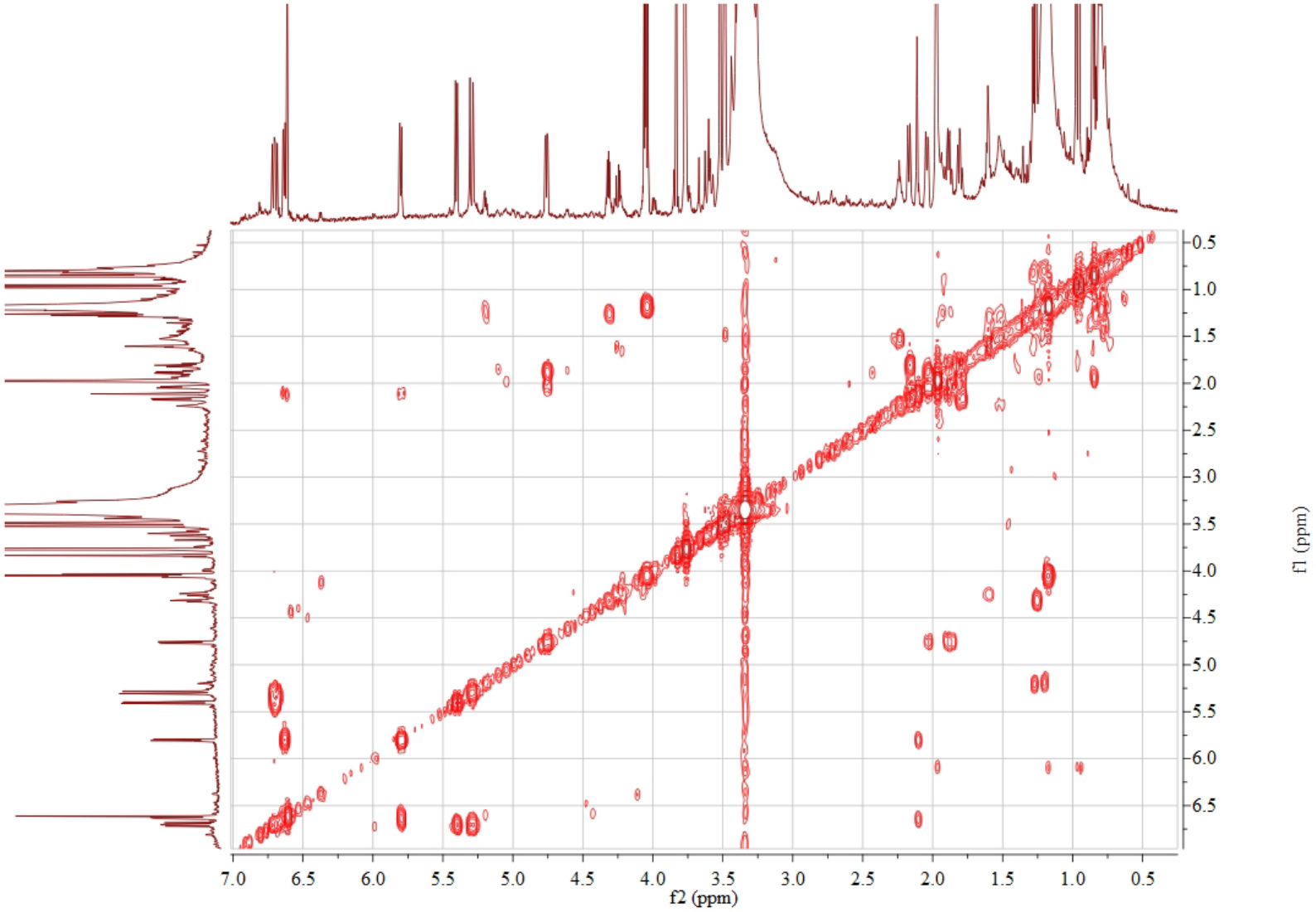
52. S52 ESI MS spectrum of **1B**



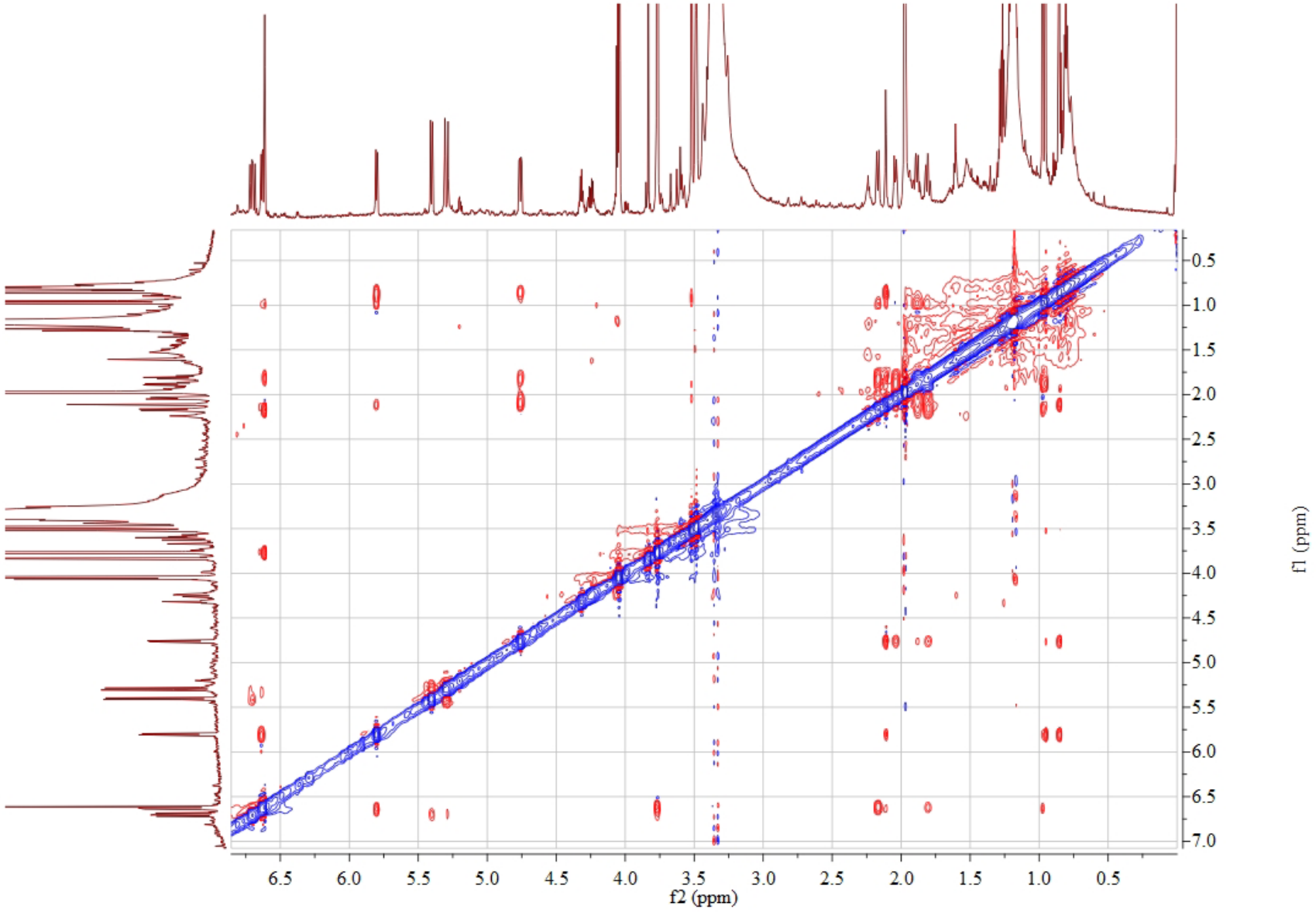
53. S53 ^{1}H NMR spectrum of (*S*)-MTPA ester derivative **1s** of **1B** (800 MHz, $CDCl_3$)



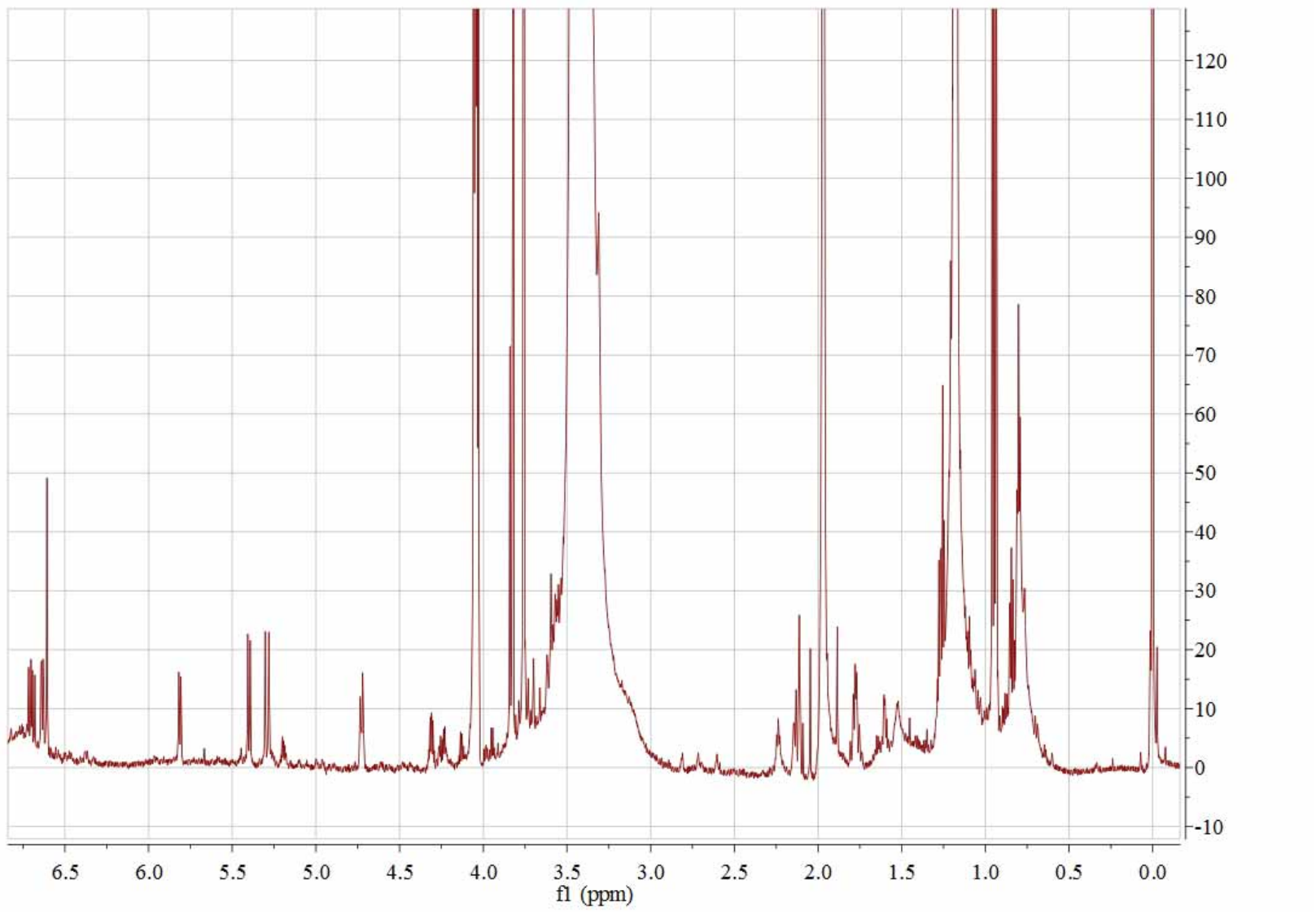
54. S54 ^{1}H-^{1}H COSY spectrum of (*S*)-MTPA ester derivative **1s** of **1B** (800 MHz, $CDCl_3$)



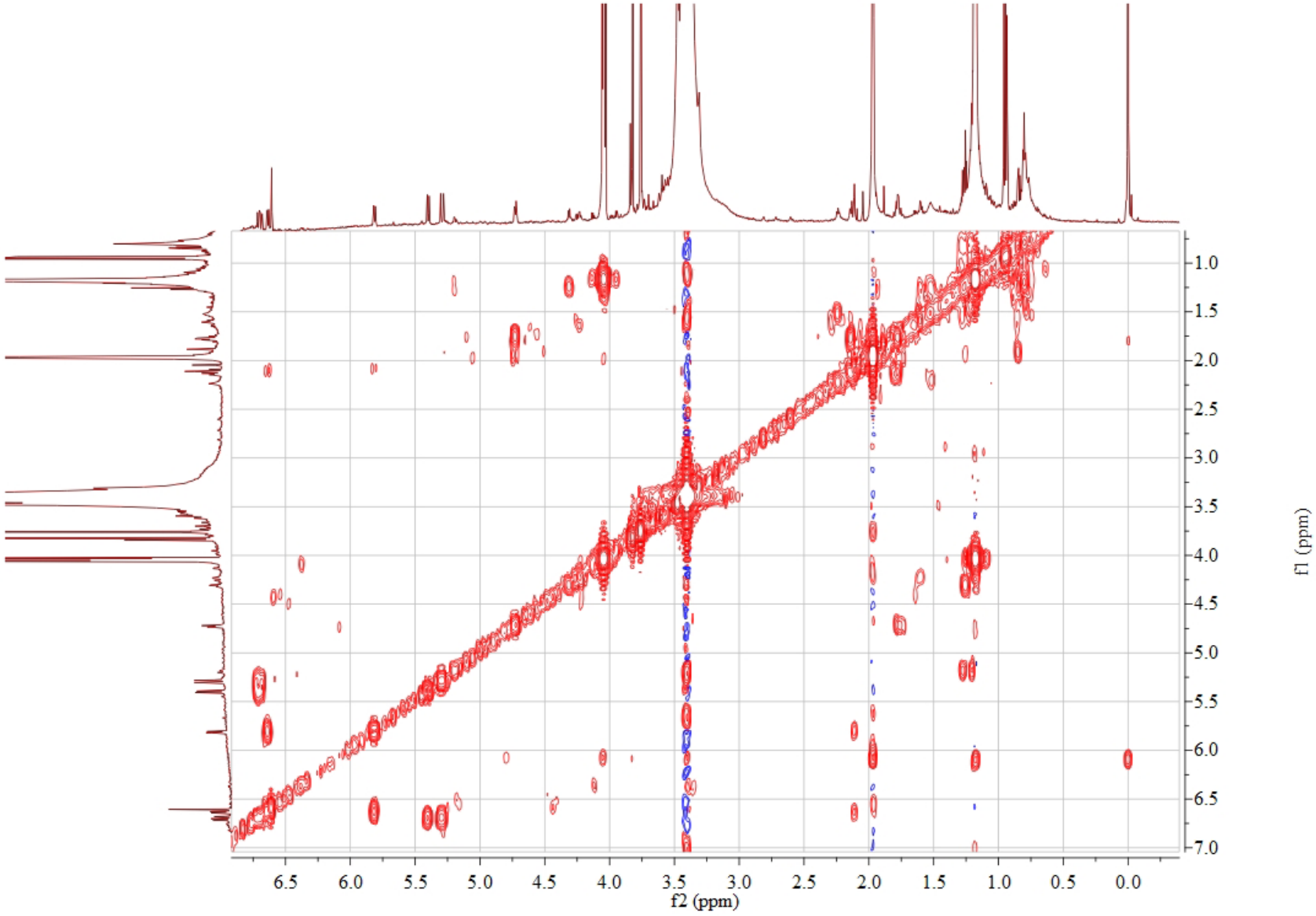
55. S55 ROESY spectrum of (*S*)-MTPA ester derivative **1s** of **1B** (800 MHz, $CDCl_3$)



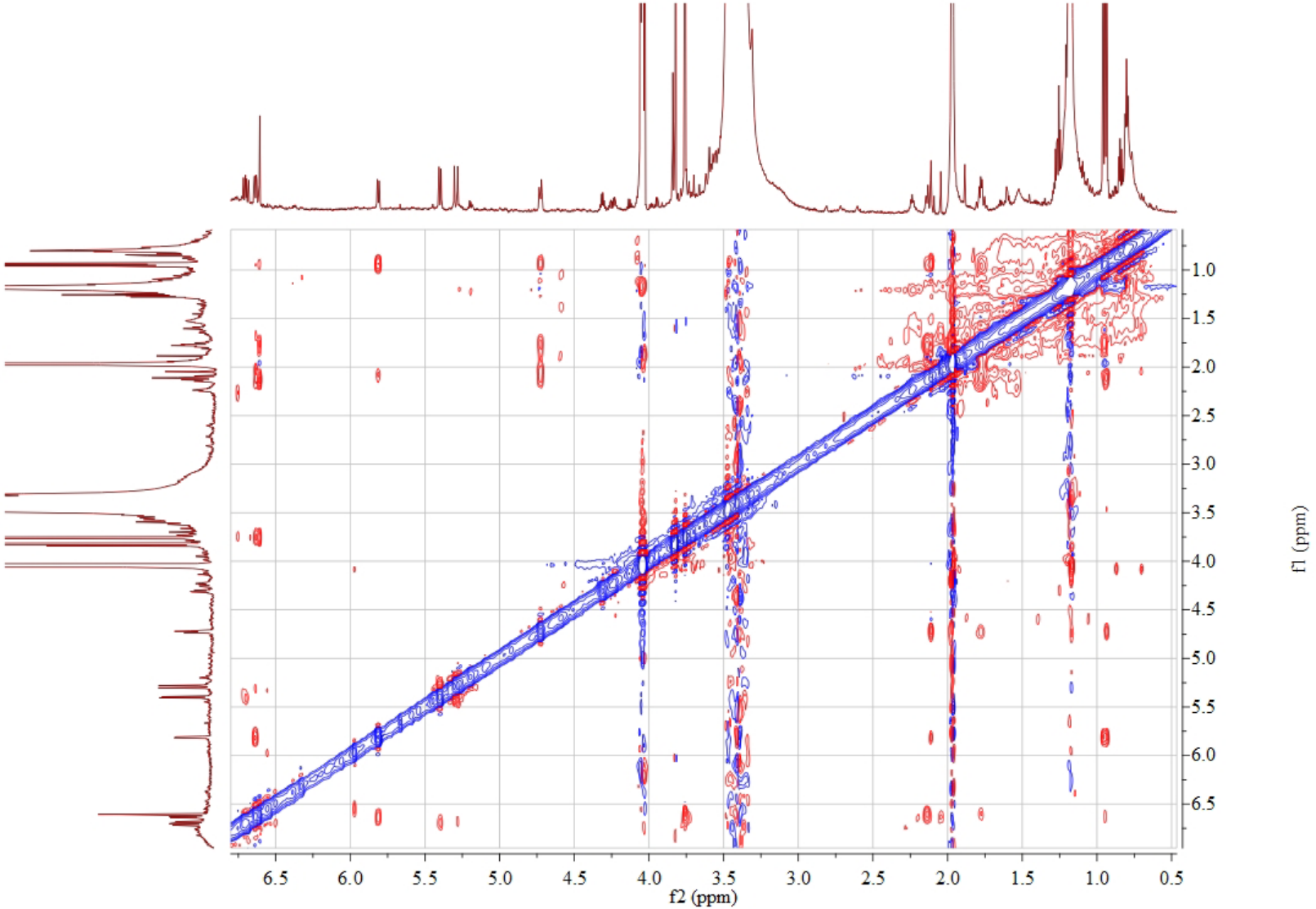
56. S56 ^{1}H NMR spectrum of (*R*)-MTPA ester derivative **1r** of **1B** (800 MHz, $CDCl_3$)



57. S57 ^{1}H-^{1}H COSY spectrum of (*R*)-MTPA ester derivative **1r** of **1B** (800 MHz, $CDCl_3$)



58. S58 ROESY spectrum of (*R*)-MTPA ester derivative **1r** of **1B** (800 MHz, $CDCl_3$)



59. S59 ECD calculations of compound **1A**

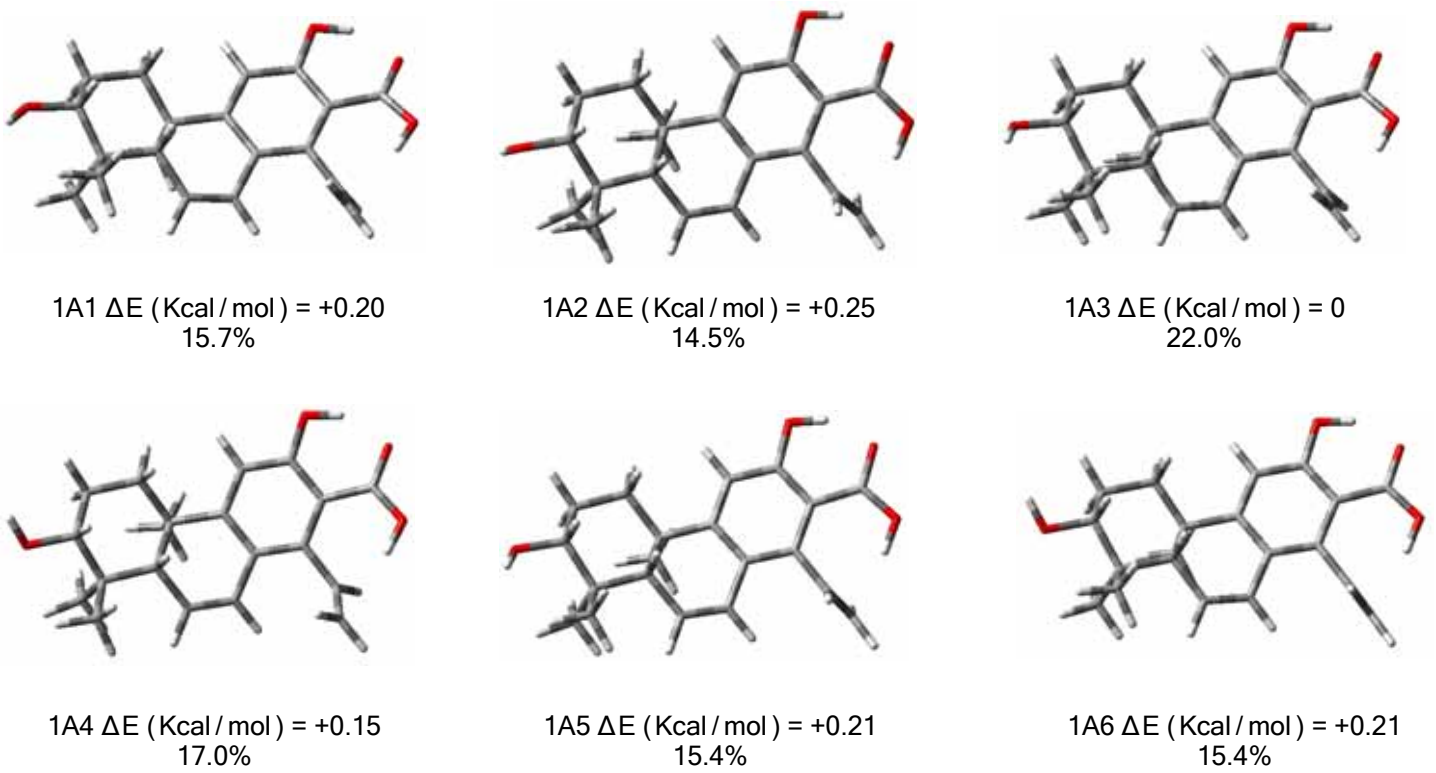


Figure 3. DFT optimized conformers of the aglycon of 3*R*,5*S*,10*R*-phyllanembloid A (**1A**) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.

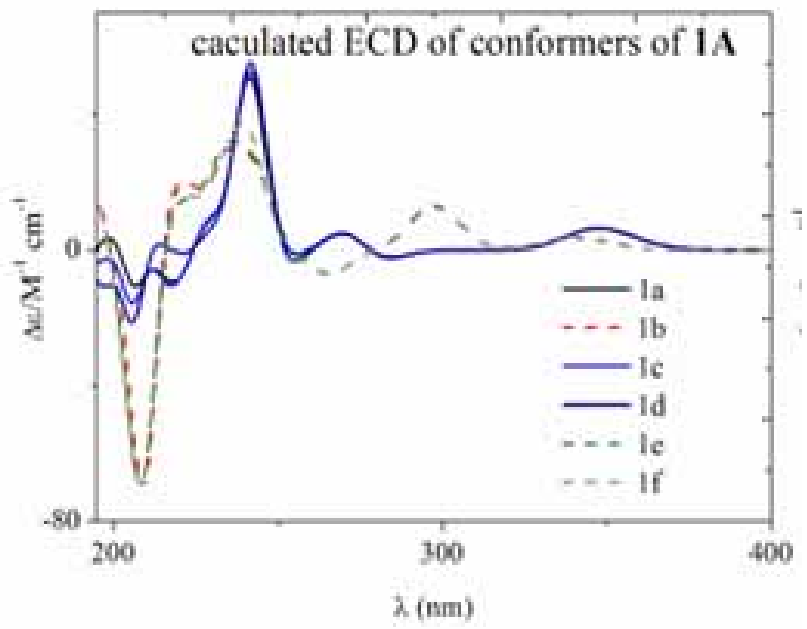


Figure 4. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon of 3*R*,5*S*,10*R*- phyllanembloid A (**1A**), with Gaussian band shape 0.3ev.

60. S60 ECD calculations of compound **1**

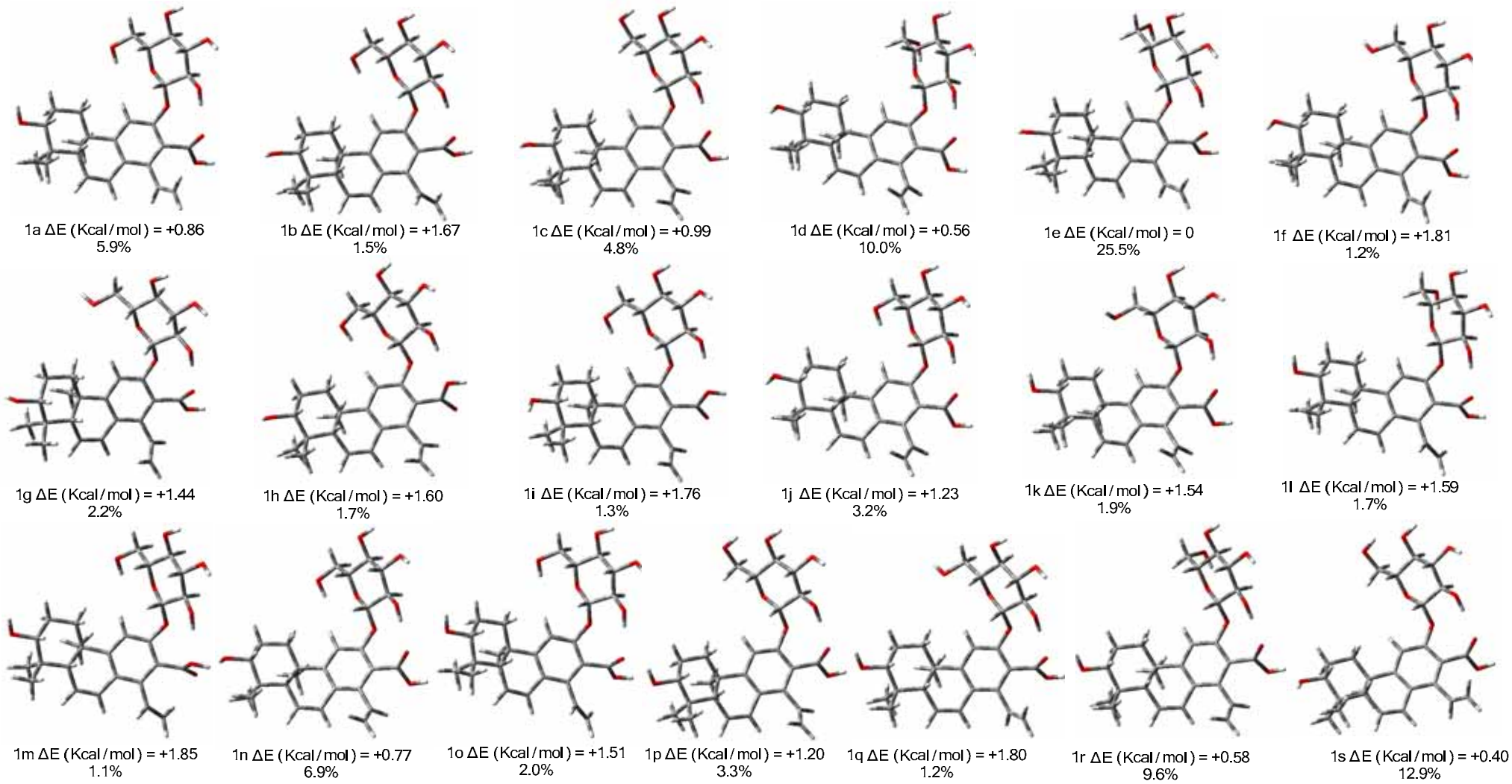


Figure 5. DFT optimized conformers of 3*R*,5*S*,10*R*- phyllanembloid A (**1**) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.

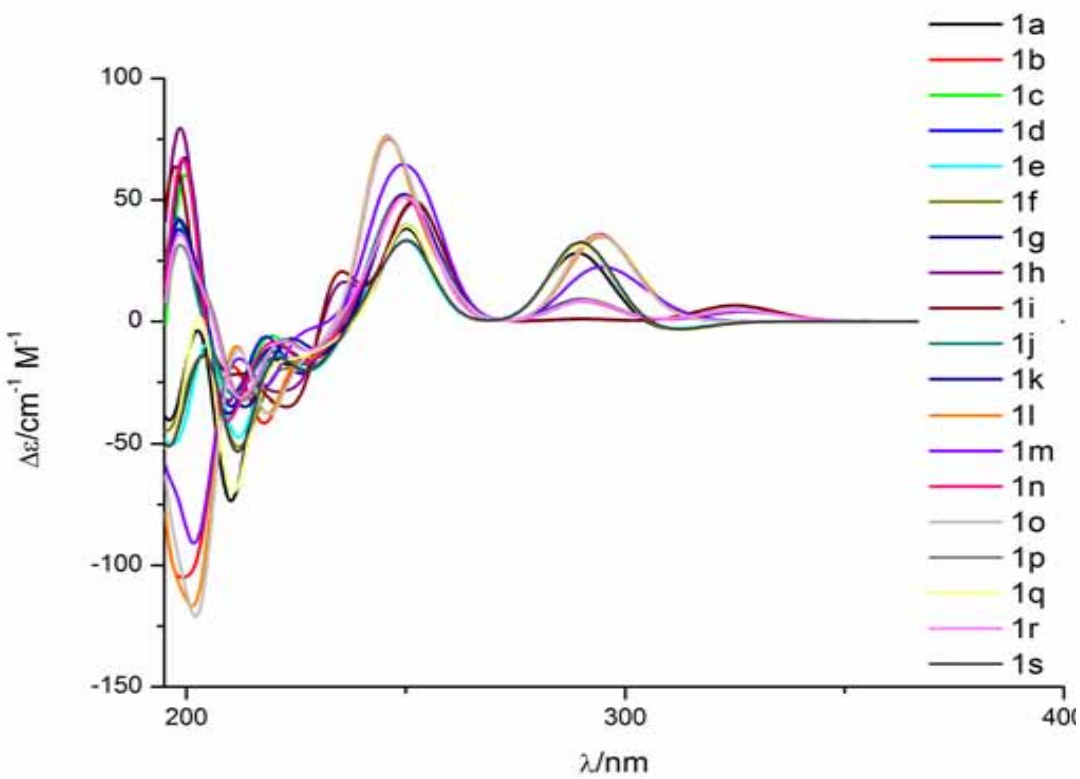


Figure 6. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of 3*R*,5*S*,10*R*-phyllanembloid A (**1**), with Gaussian band shape 0.3ev.

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61. S61 ECD calculations of compound **3**

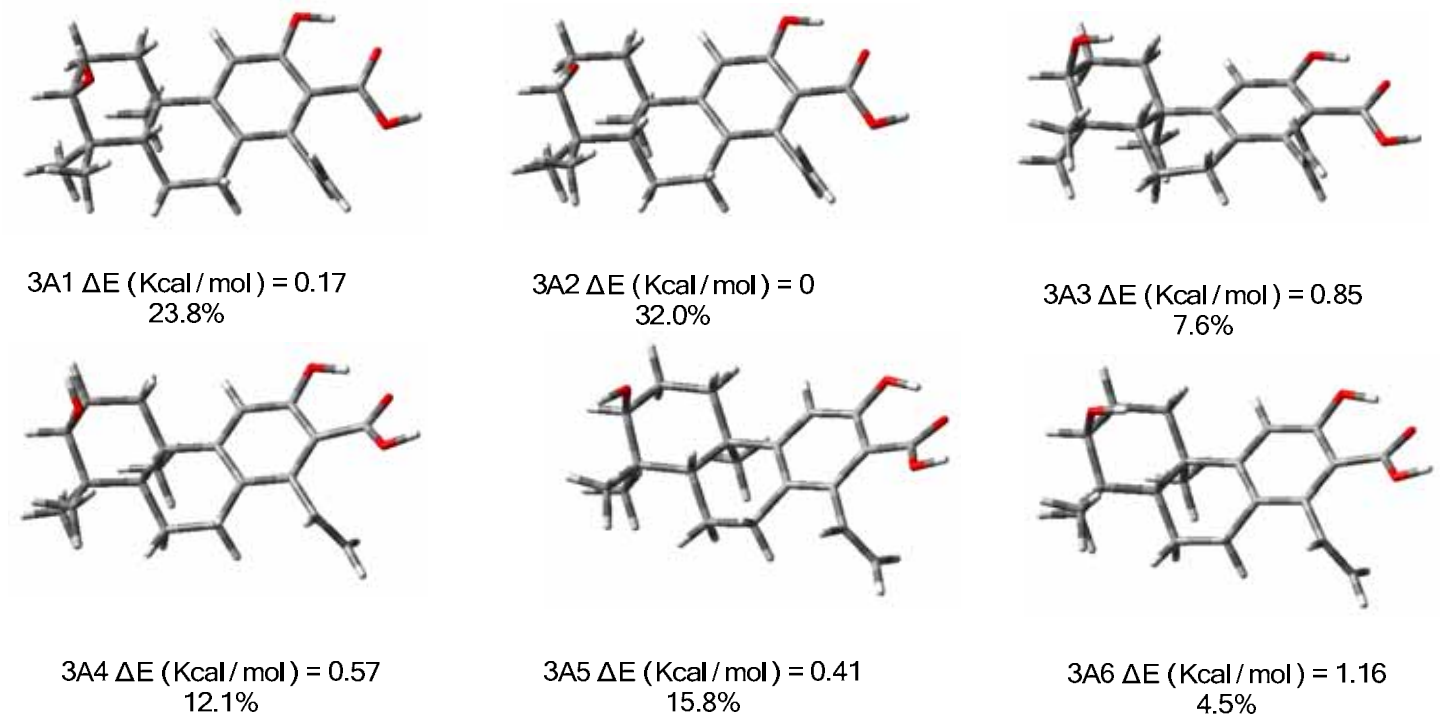

Figure 7. DFT optimized conformers of the aglycon of 3*S*,5*S*,10*R*- phyllanembloid C (**3**) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.

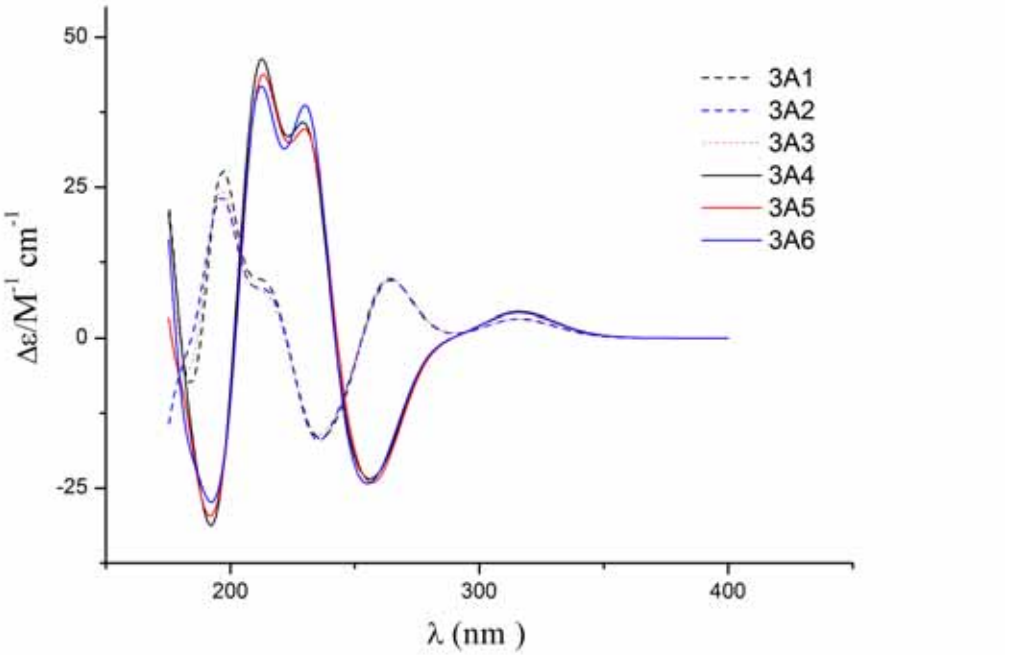

Figure 8. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon of 3*S*,5*S*,10*R*- phyllanembloid C (**3**), with Gaussian band shape 0.5ev.

62. S62 ECD calculations of compound **4**

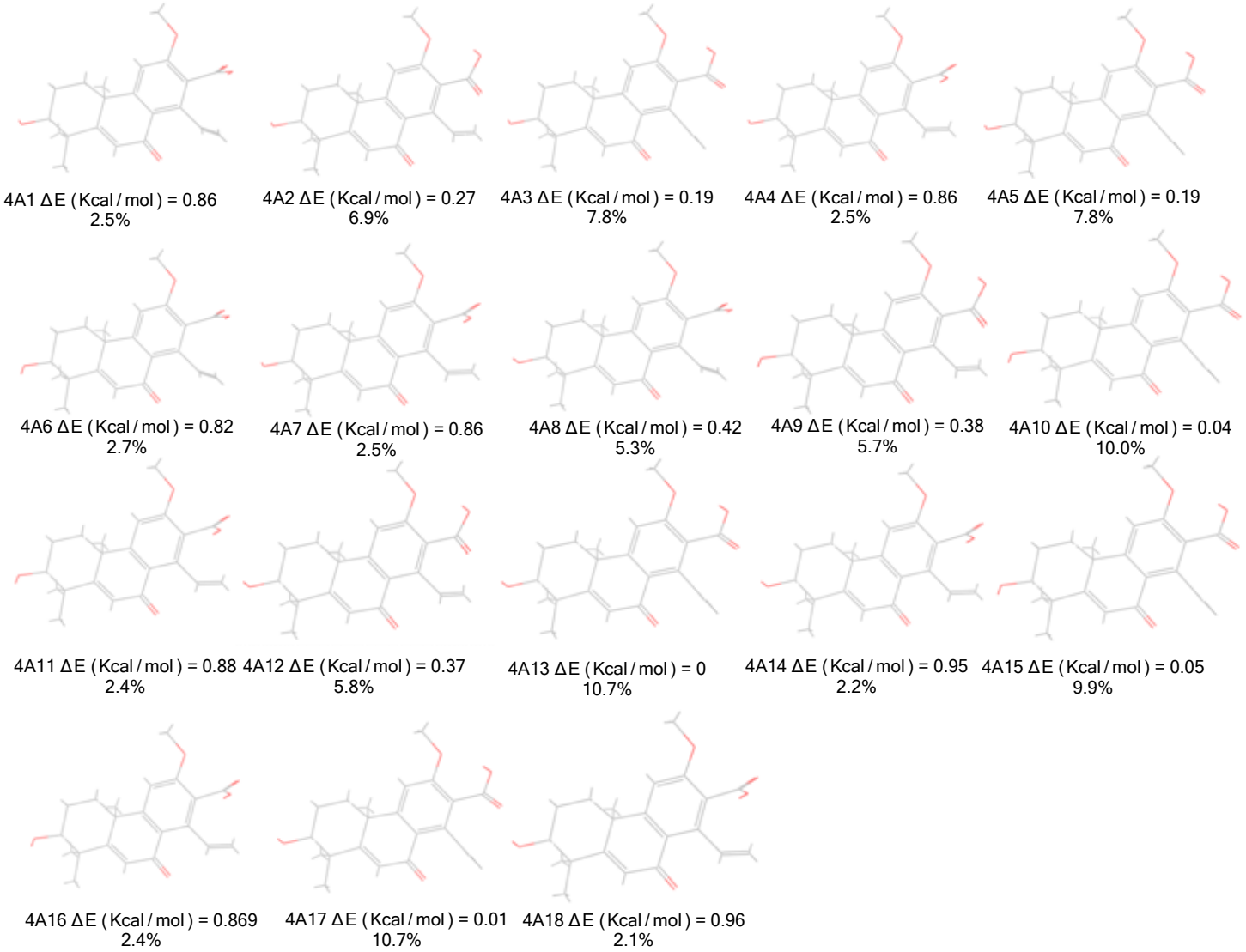

Figure 9. DFT optimized conformers of the aglycon of 3*R*,10*R*- phyllanembloid D (**4**) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.

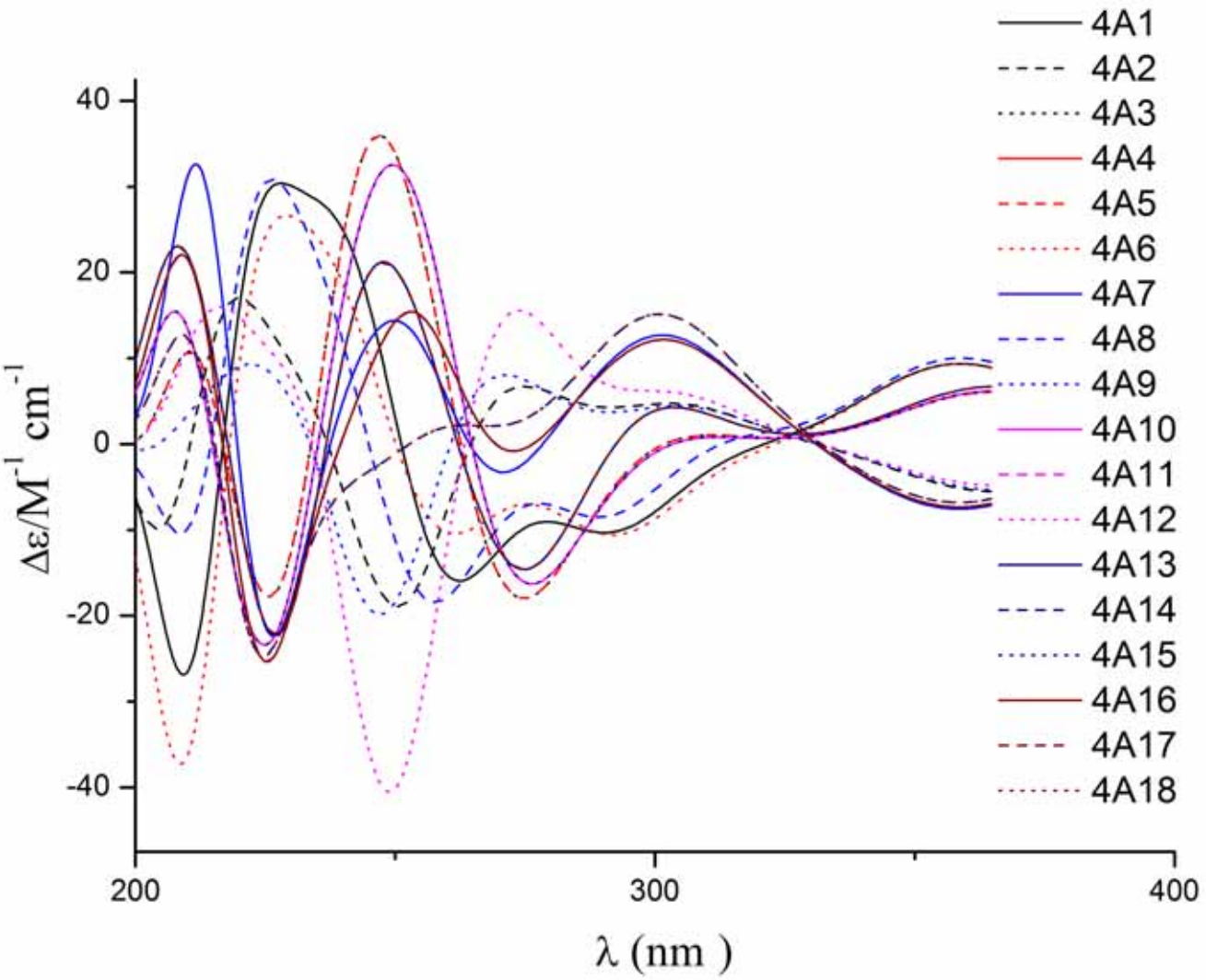

Figure 10. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon of 3*R*, 10*R*- phyllanembloid D (**4**), with Gaussian band shape 0.3ev.

63. S63 ECD calculations of compound **5**

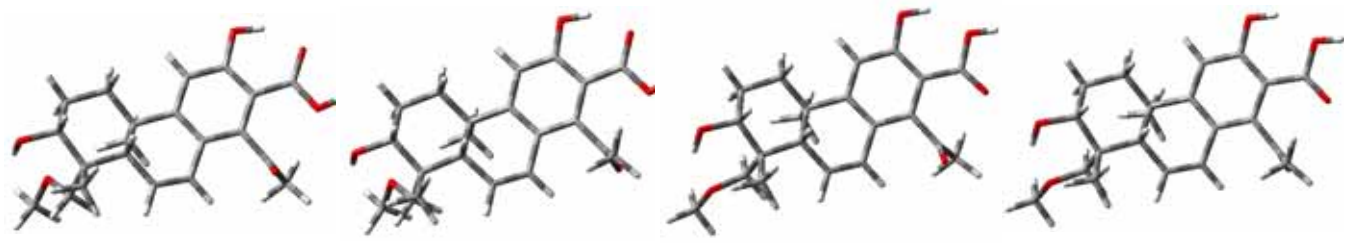

Figure 11. DFT optimized conformers of the aglycon of 3*R*,4*R*,5*S*,10*R*- phyllanembloid E (**5**) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.

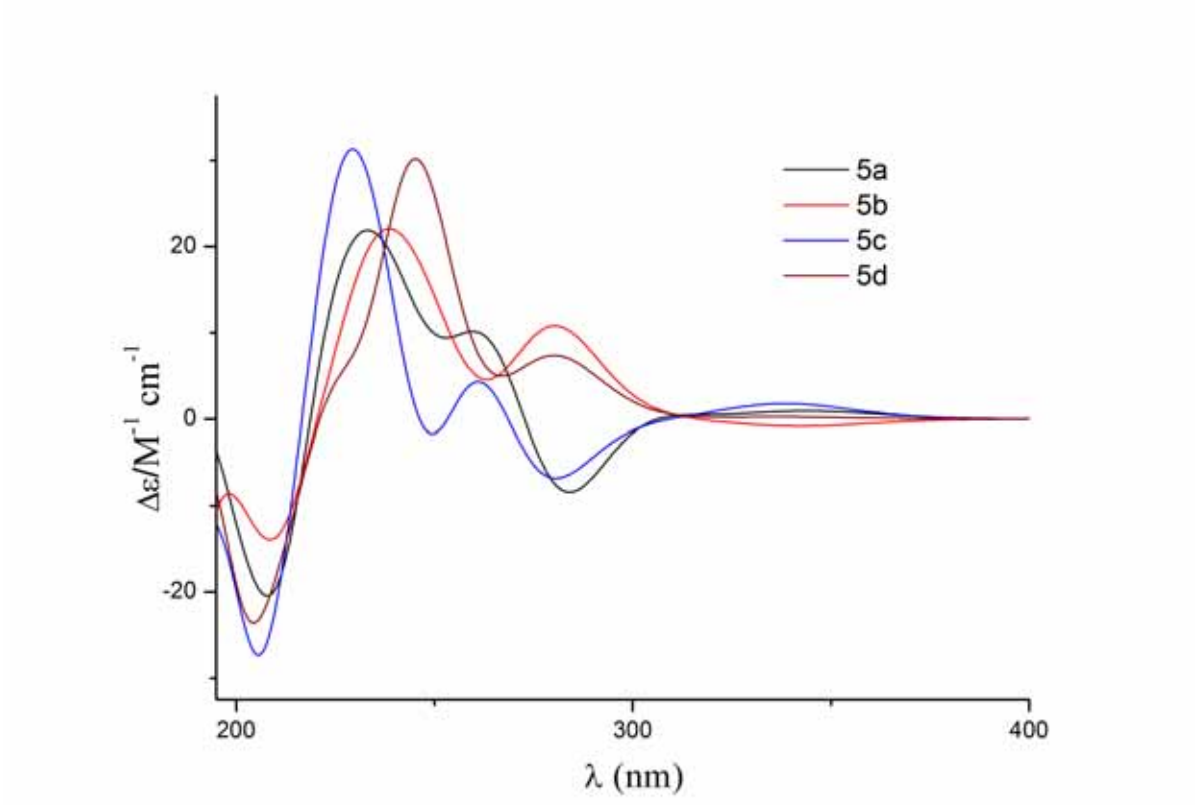

Figure 12. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon of 3*R*,4*R*,5*S*,10*R*- phyllanembloid E (**5**), with Gaussian band shape 0.5ev.

64. S64 OR calculations of compound **6**

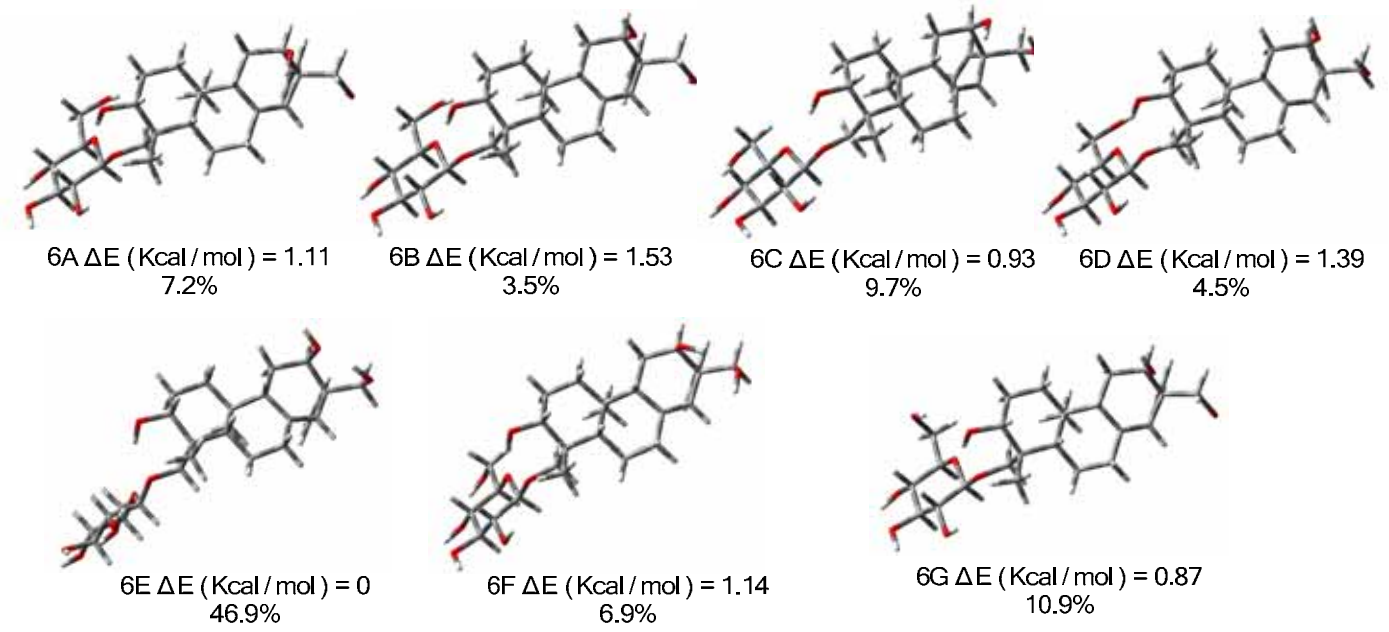

Figure 13. DFT optimized conformers of 3*R*,4*R*,5*S*,9*R*,10*S*,12*R*,13*R*- phyllanembloid F (**6**) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.

Table 1. Calculated optical rotations of conformers of 3*R*,4*R*,5*S*,9*R*,10*S*,12*R*,13*R*- phyllanembloid F (**6**)

conformers	6A	6B	6C	6D	6E	6F	6G
rotations	-64.8	-78.7	-88.7	-11.7	-110.5	-112.5	-97.6

Optical rotations were calculated with the basis set B3LYP 6-311G (++2d, p) at gas phase using the optimized conformers at B3LYP 6-311G (2d, p).