

Supporting Information

Halogenated and Nonhalogenated Metabolites from the Marine-Alga-Endophytic Fungus *Trichoderma asperellum* cf44-2

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Figure S60. Energy-minimized conformers with populations of
(3*S*,7*S*)-1-hydroxy-3-*p*-menthen-9-oic acid.

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Figure S64. Energy-minimized conformers with populations of
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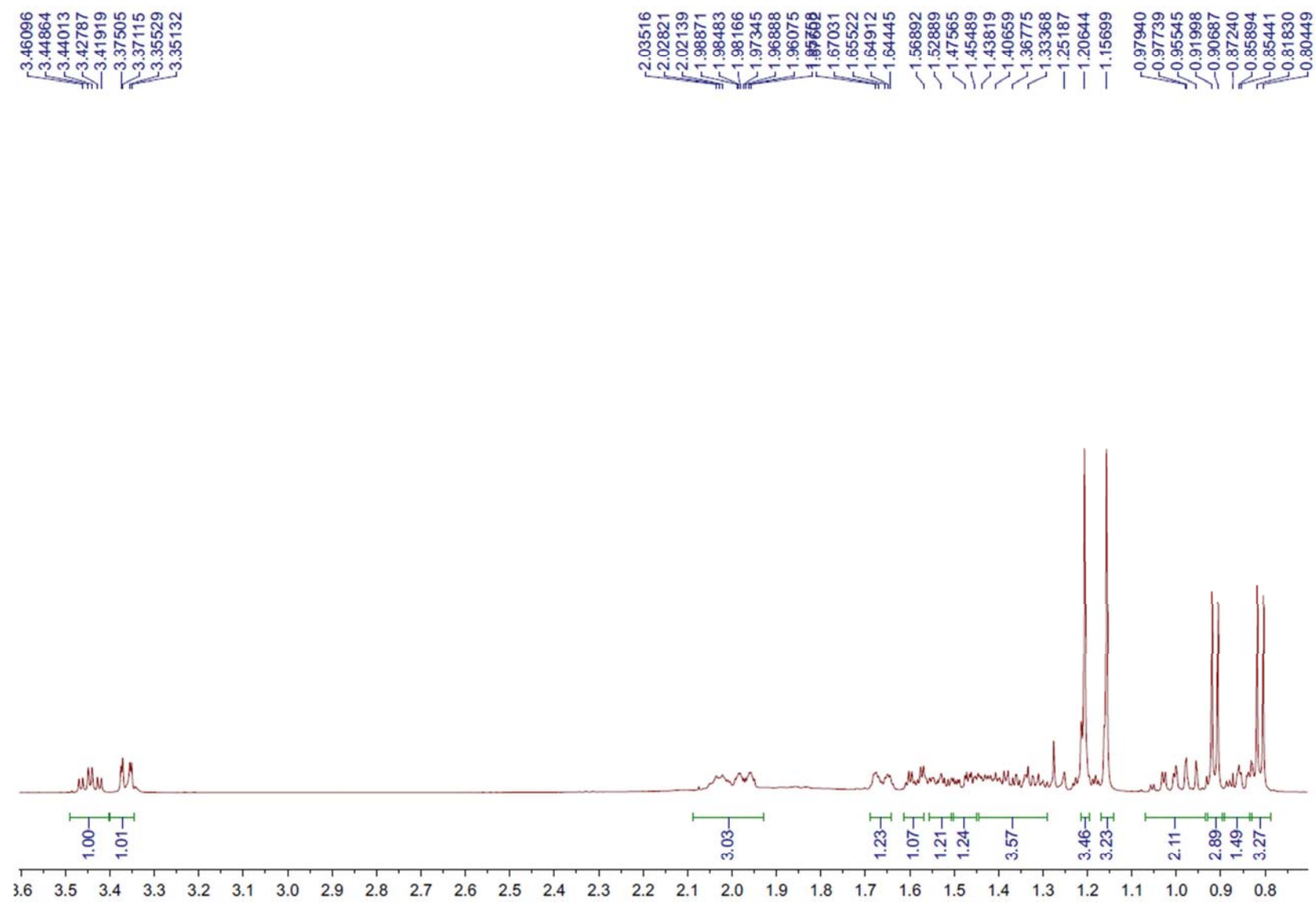


Figure S1. ^1H NMR spectrum of compound **1** in CDCl_3 .

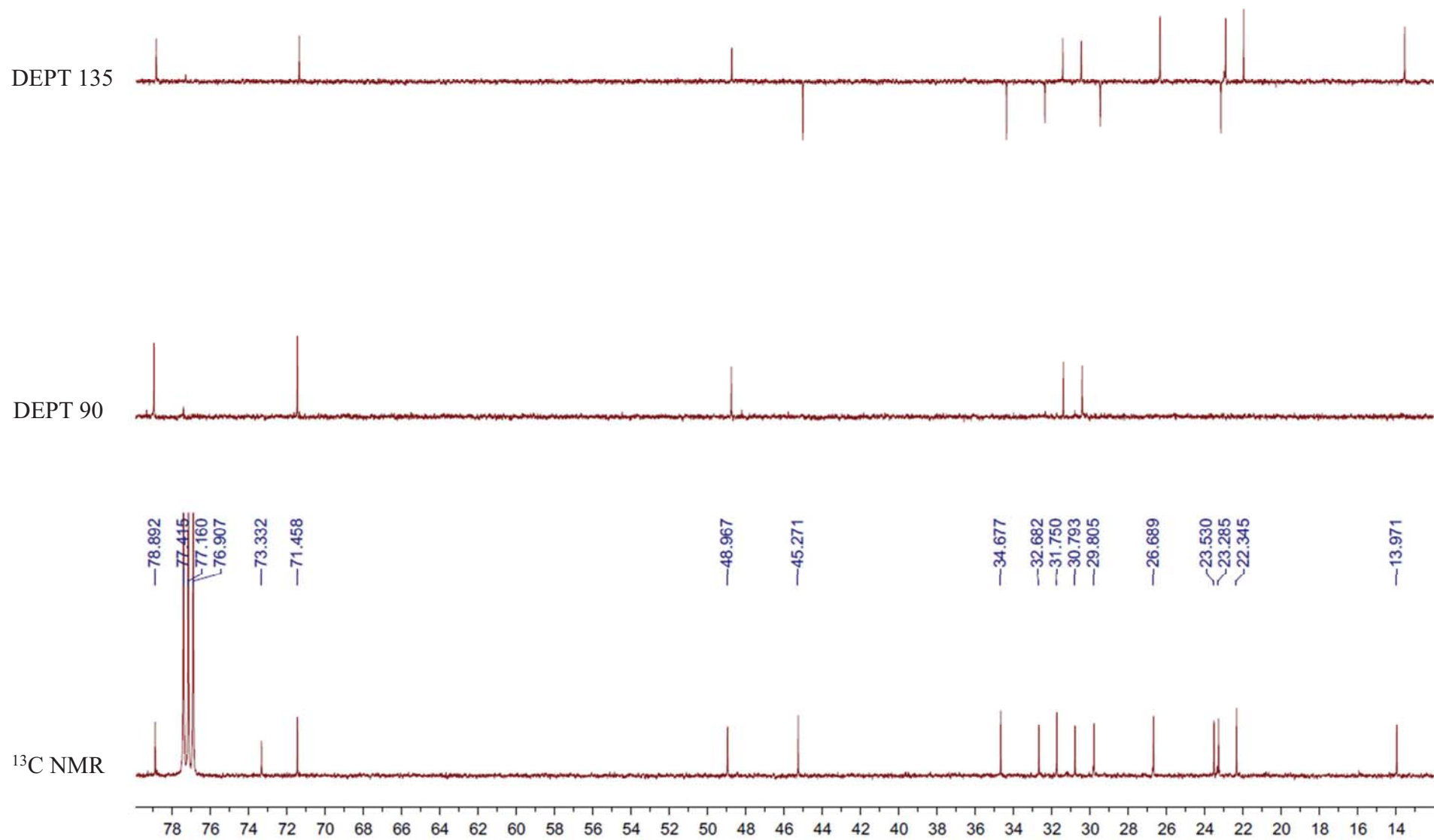


Figure S2. ^{13}C NMR and DEPT spectra of compound **1** in CDCl_3 .

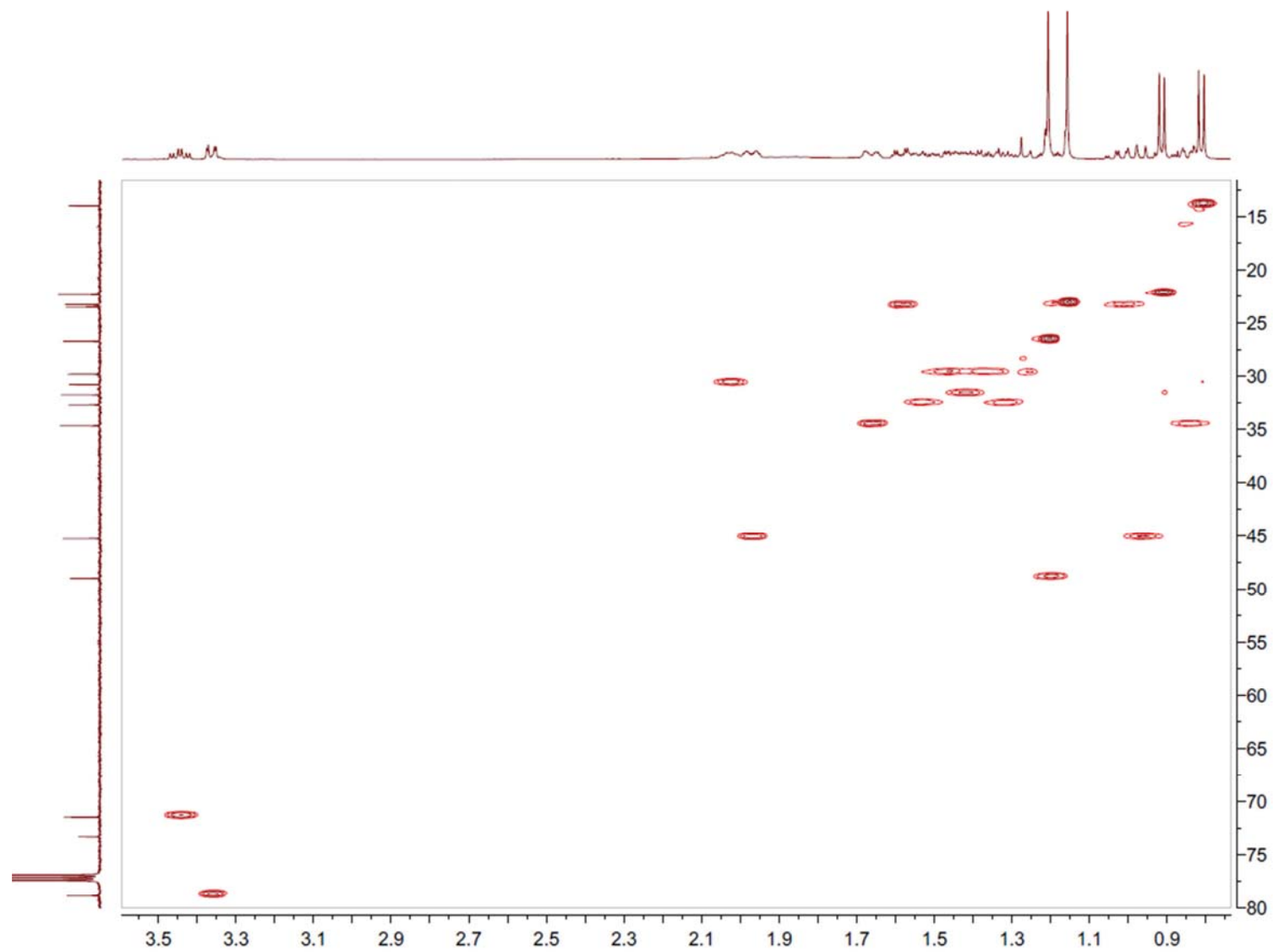


Figure S3. HSQC spectrum of compound **1** in CDCl_3 .

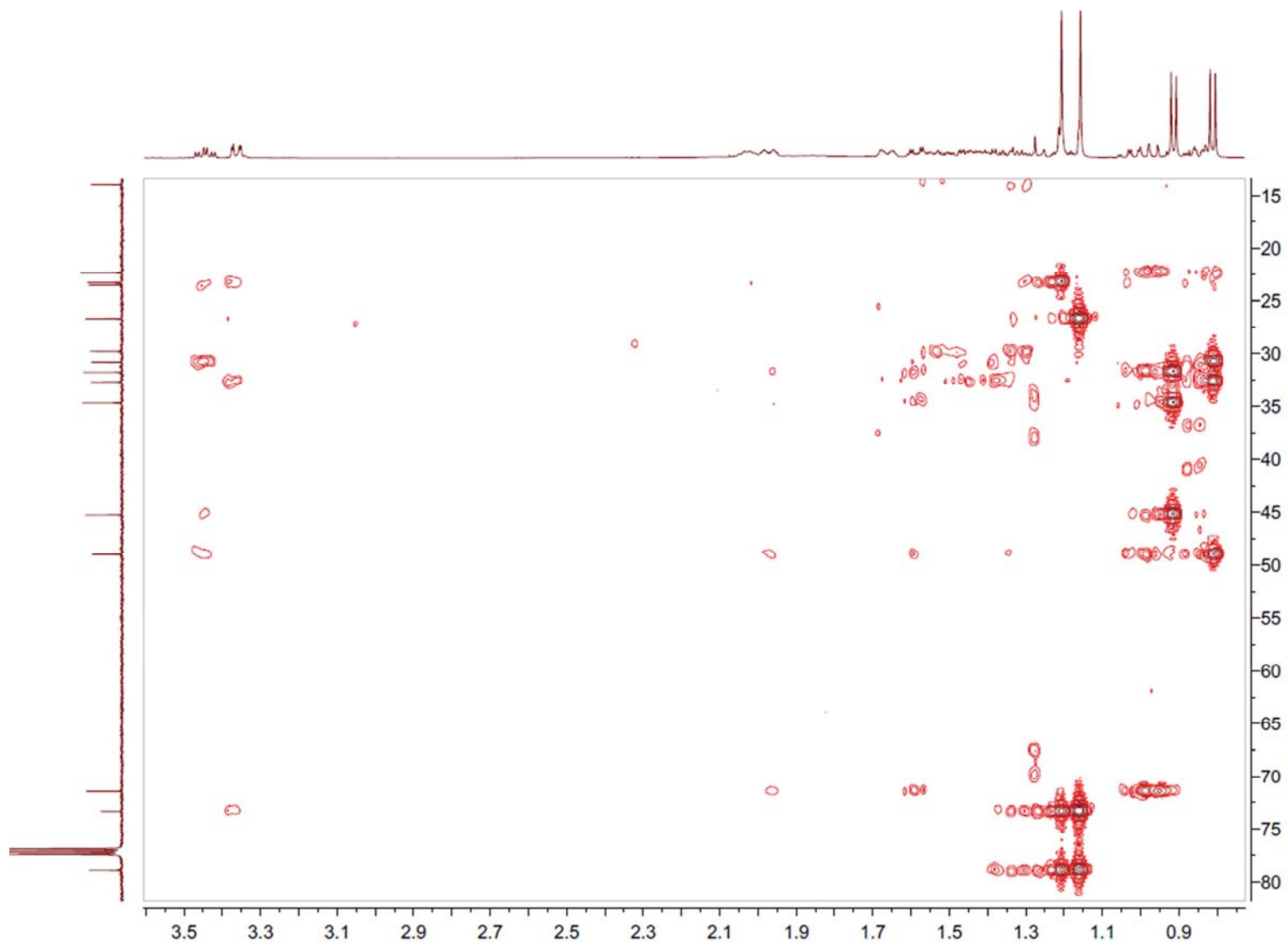


Figure S4. HMBC spectrum of compound 1 in CDCl₃.

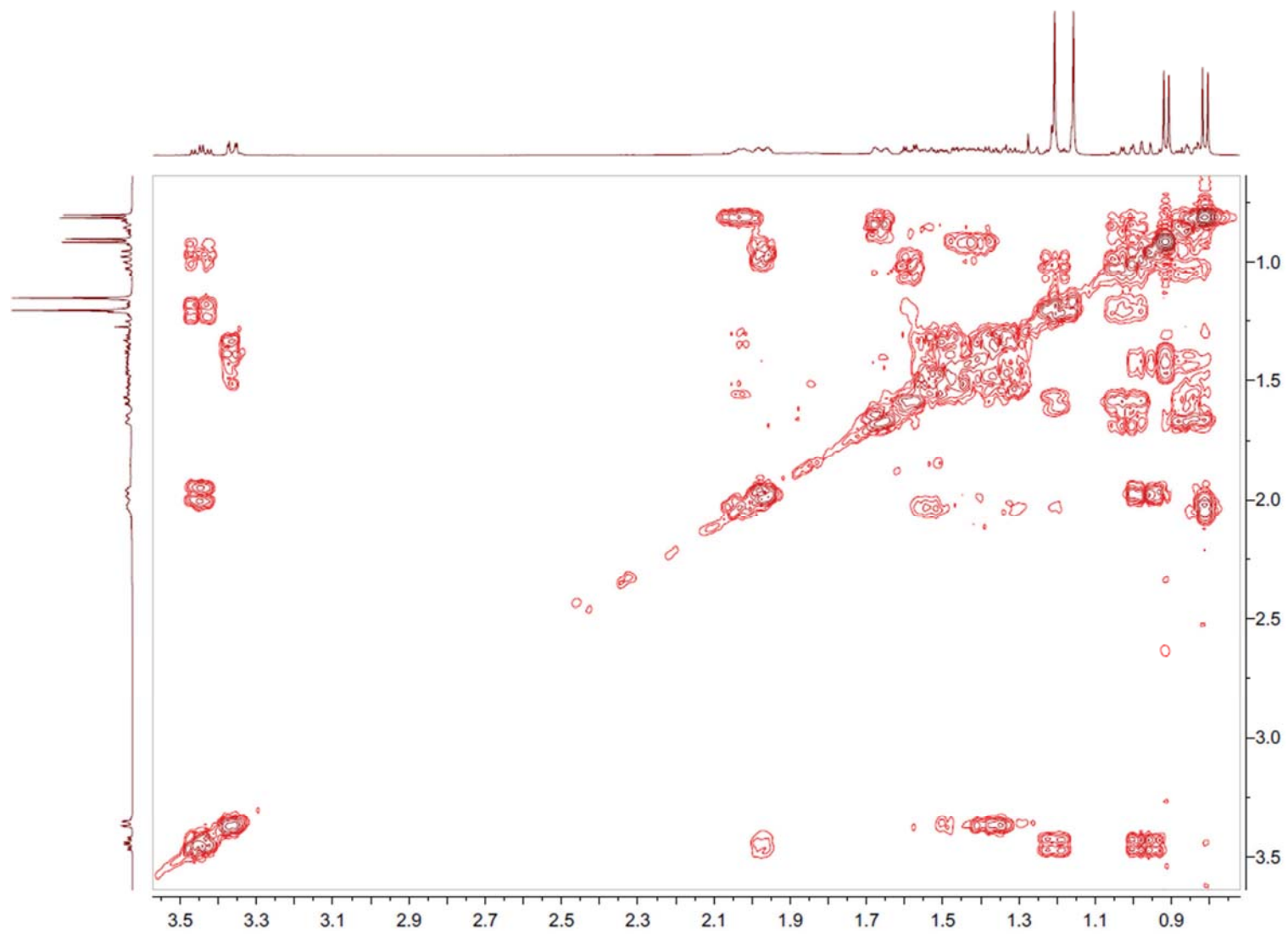


Figure S5. COSY spectrum of compound 1 in CDCl_3 .

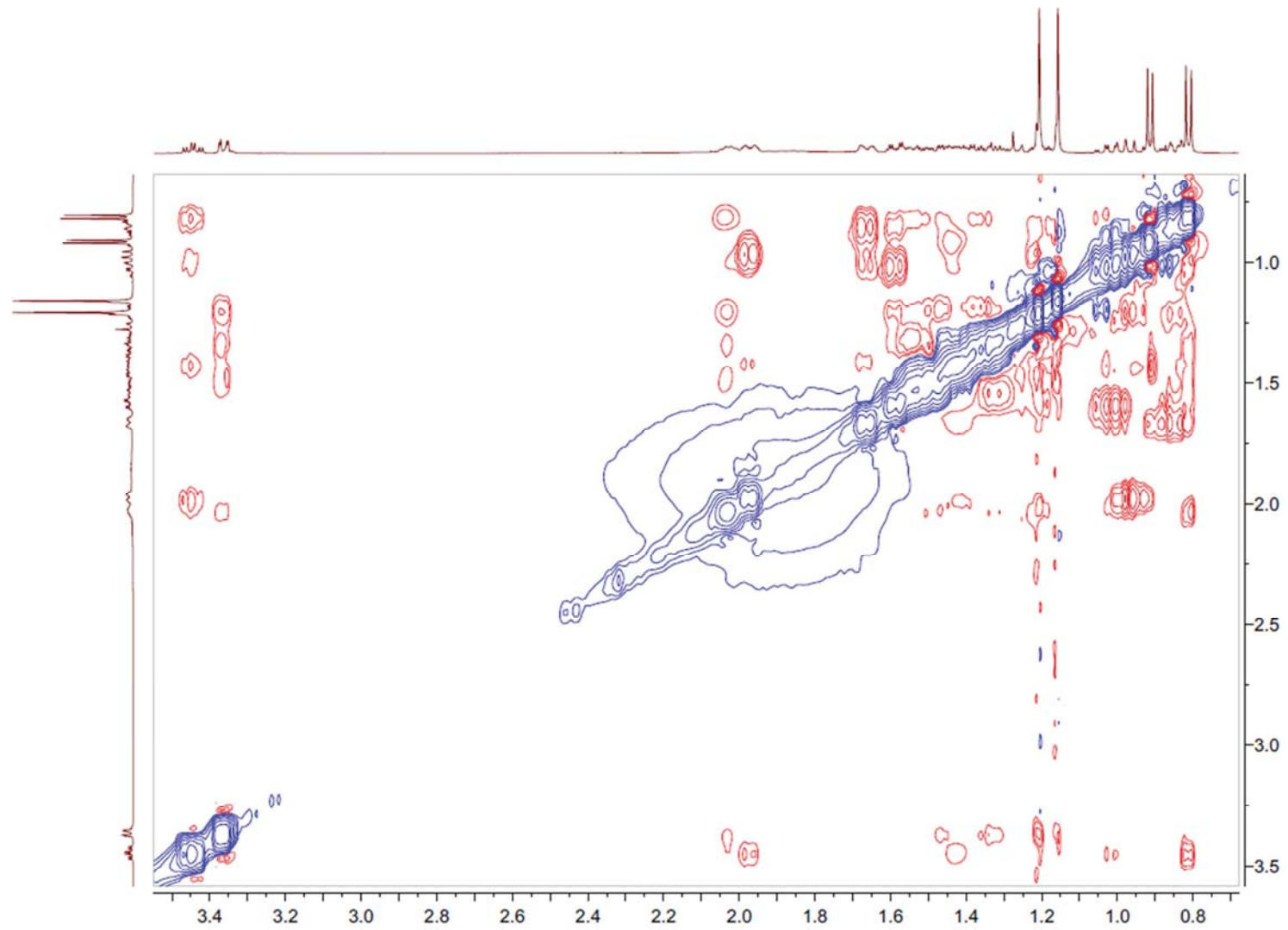


Figure S6. NOESY spectrum of compound **1** in CDCl_3 .

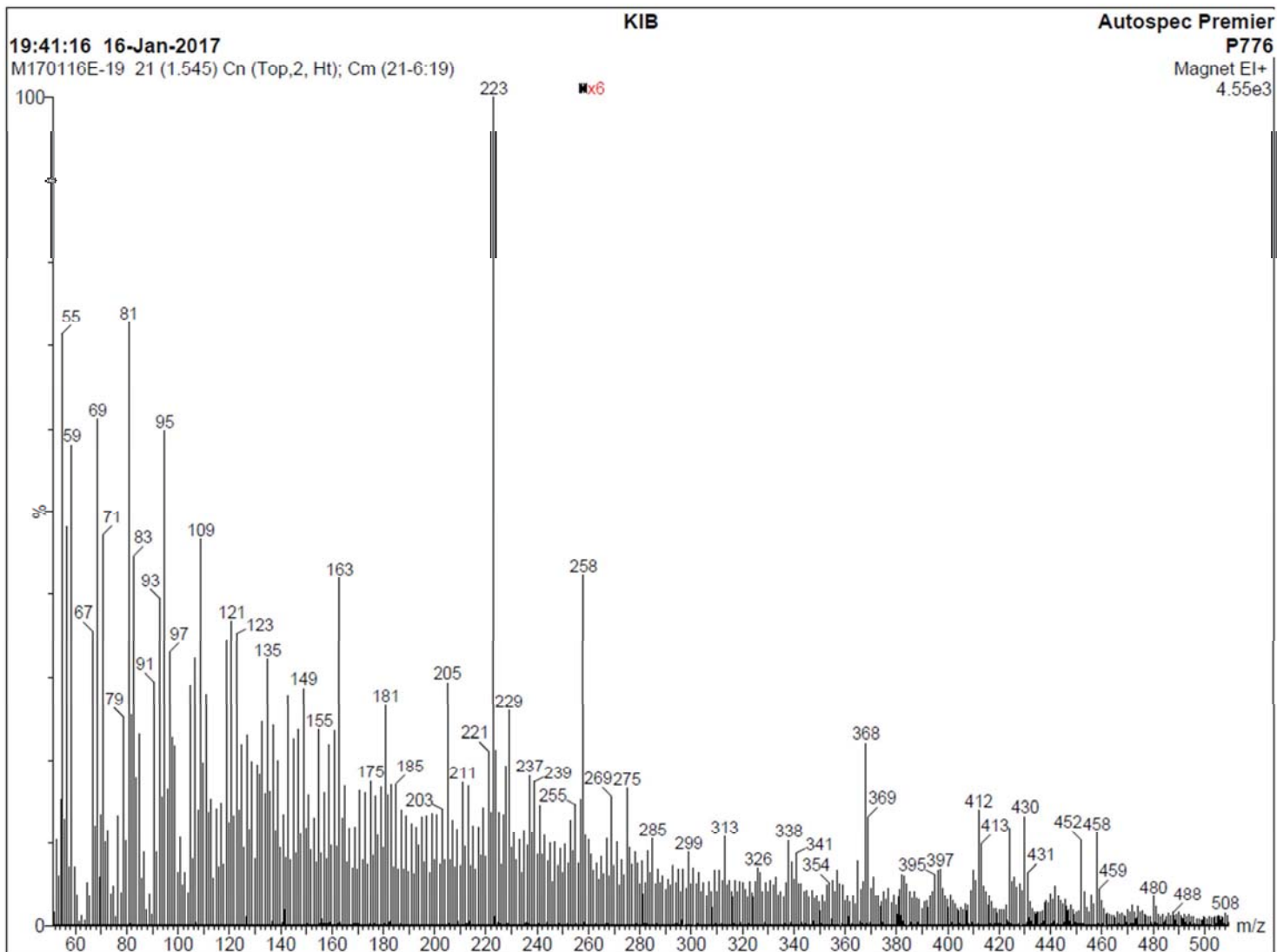


Figure S7. EIMS spectrum of compound 1.

Single Mass Analysis

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Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

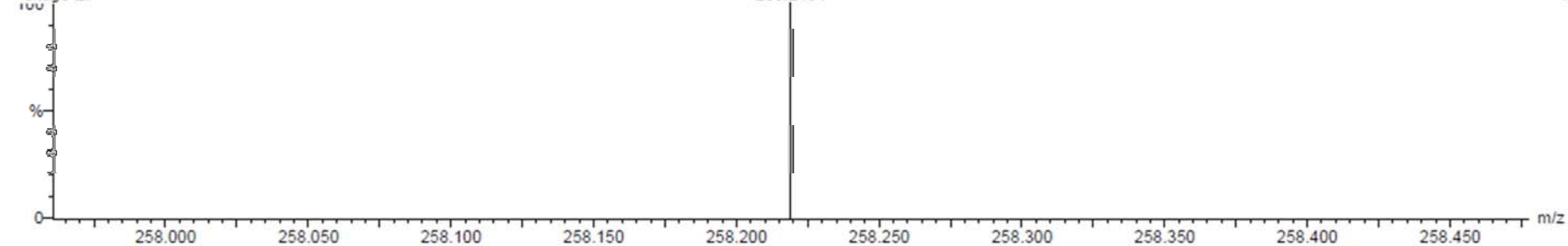
28 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)

Elements Used:

C: 0-200 H: 0-400 O: 0-5

19:36:21 16-Jan-2017

Voltage EI+



Minimum:				-10.0		
Maximum:	200.0	10.0		120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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Figure S8. HREIMS spectrum of compound 1.

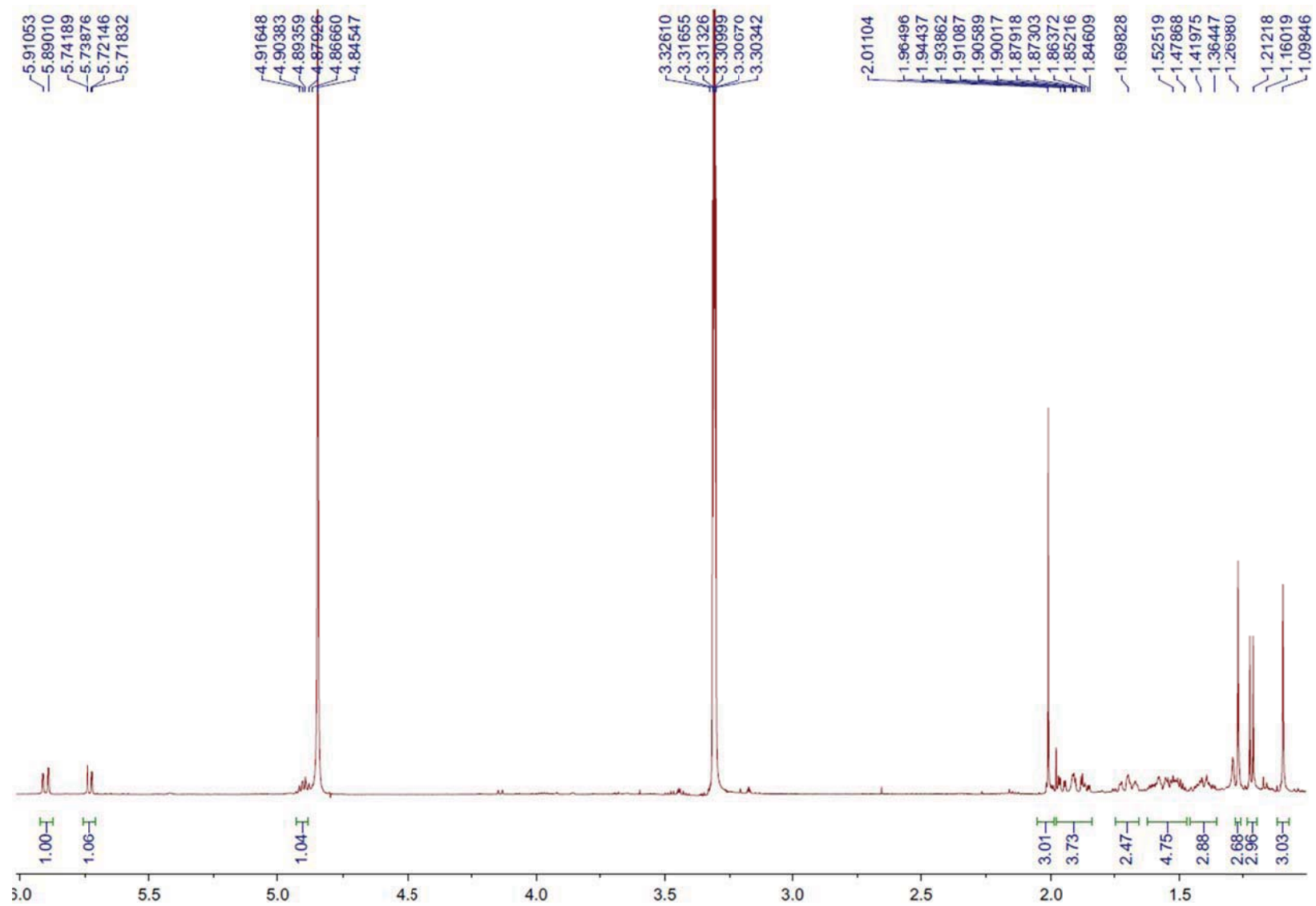


Figure S8. ^1H NMR spectrum of compound **2** in CD_3OD .

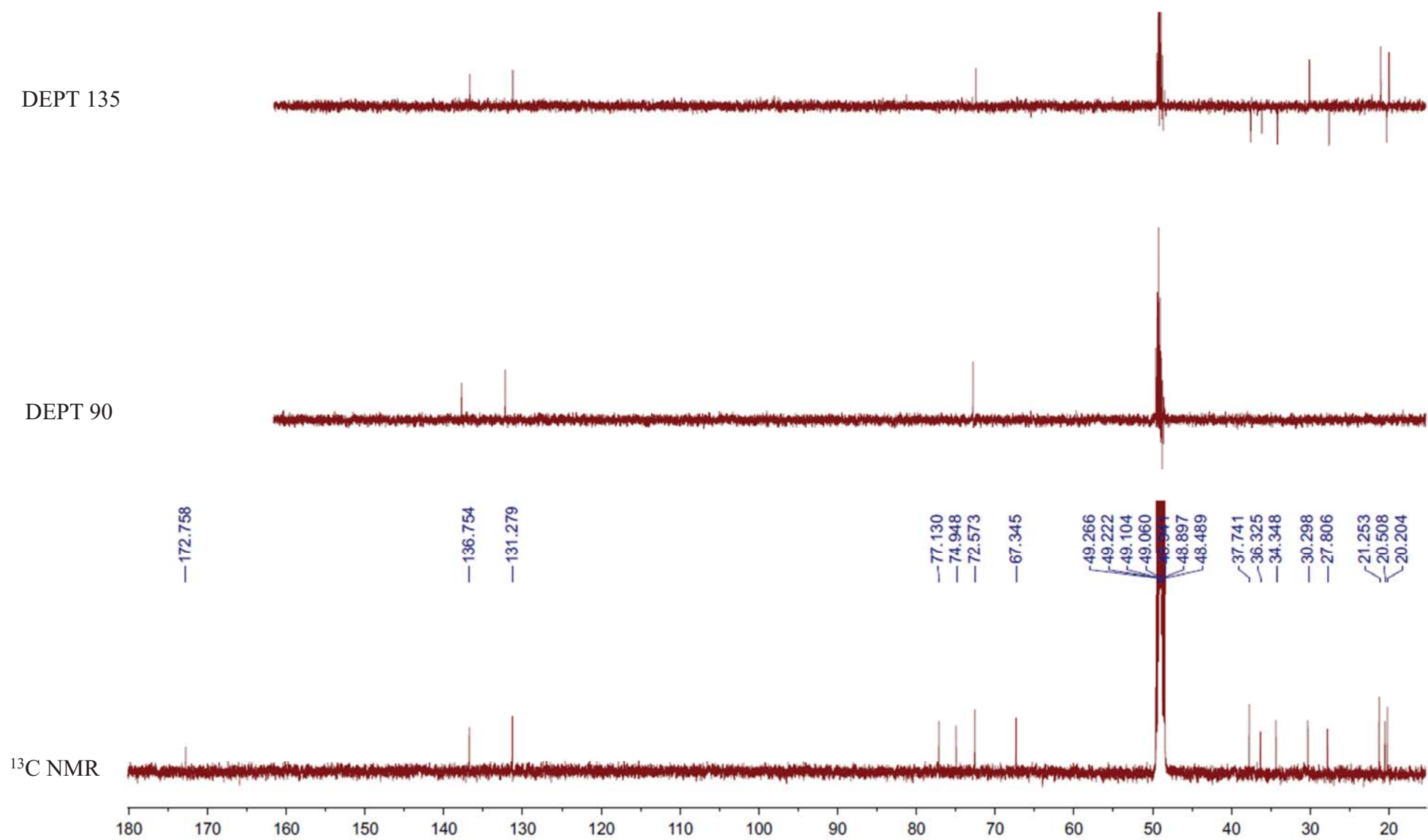


Figure S10. ^{13}C NMR and DEPT spectra of compound **2** in CD_3OD .

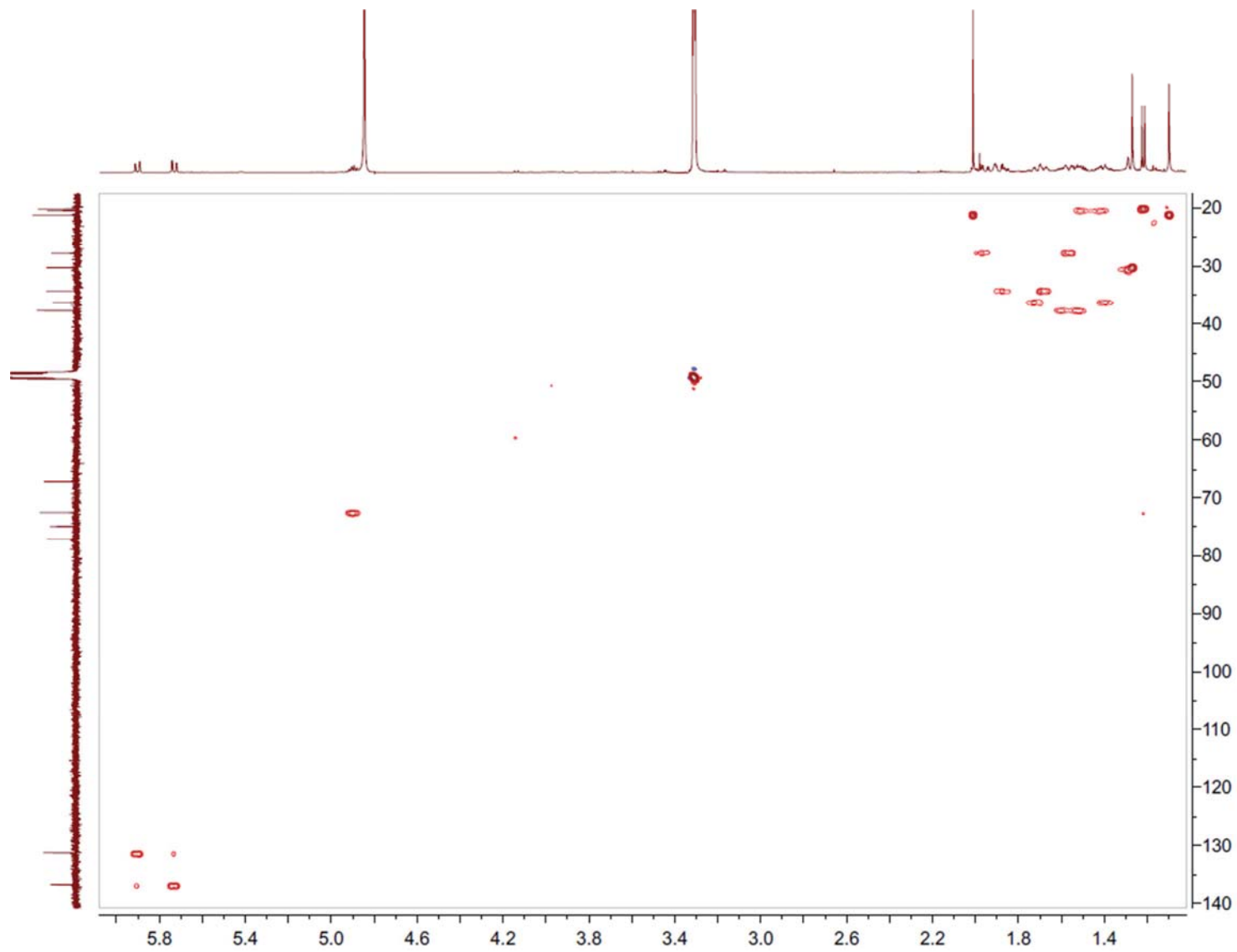


Figure S11. HSQC spectrum of compound **2** in CD₃OD.

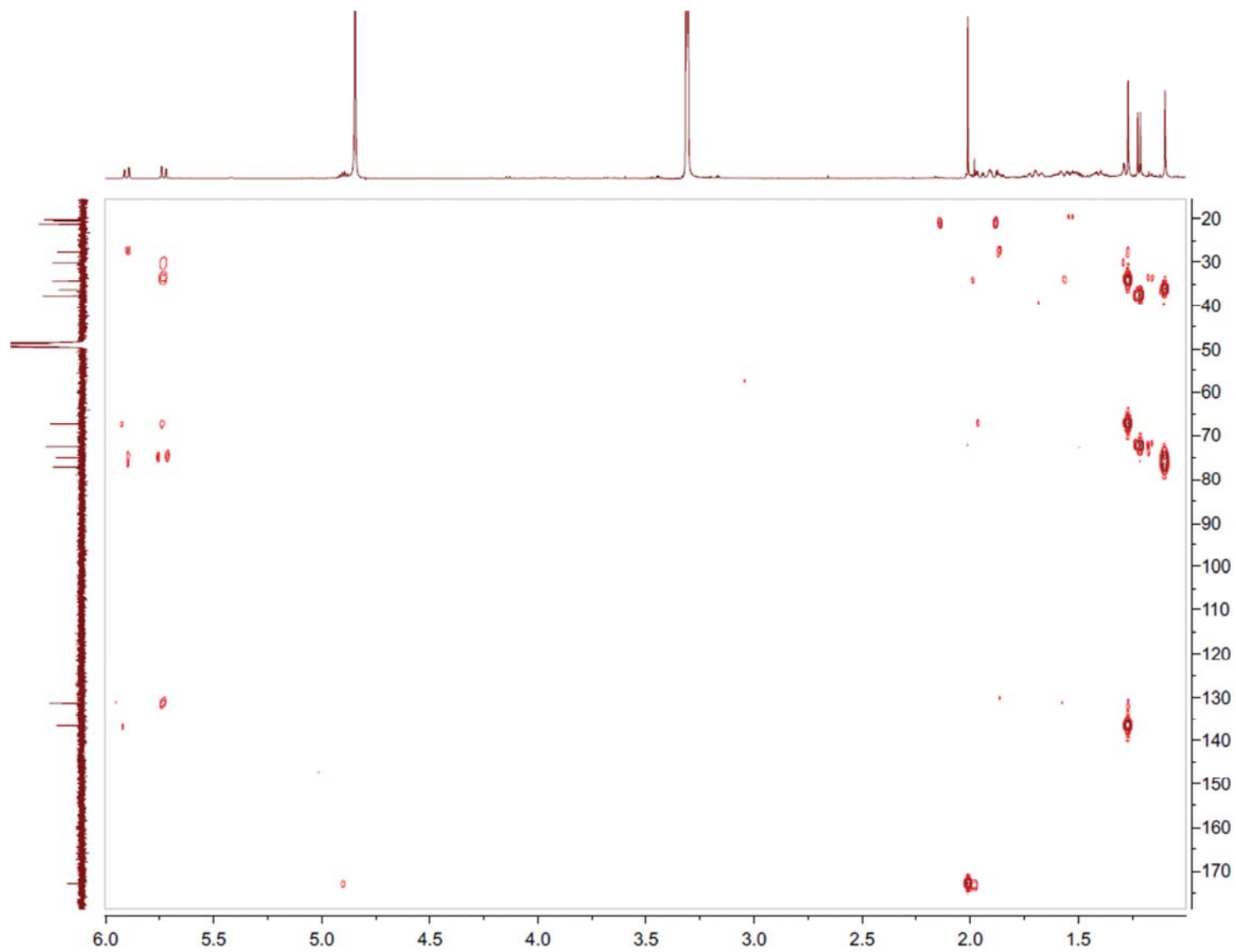


Figure S12. HMBC spectrum of compound **2** in CD₃OD.

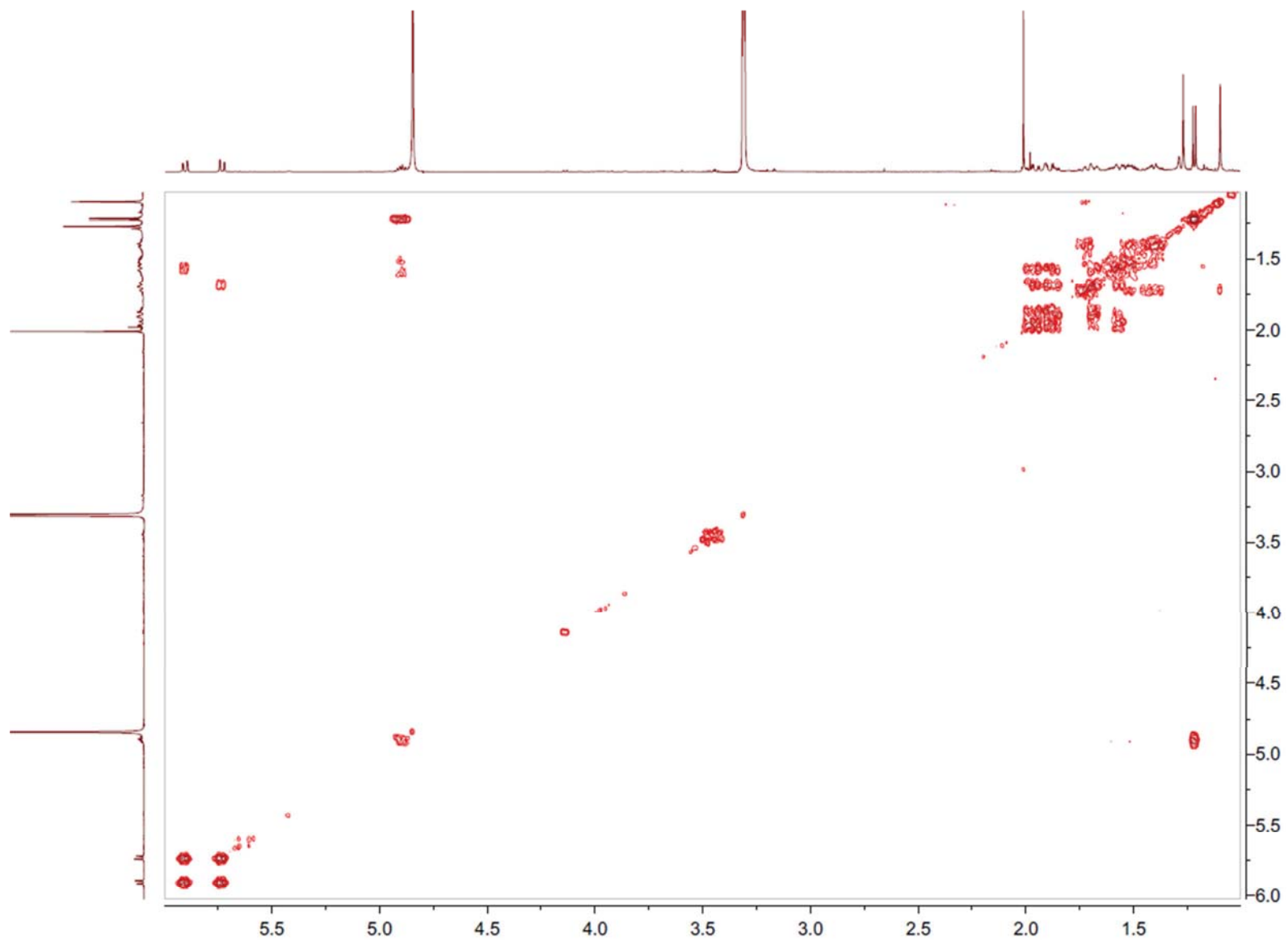


Figure S13. COSY spectrum of compound **2** in CD₃OD.

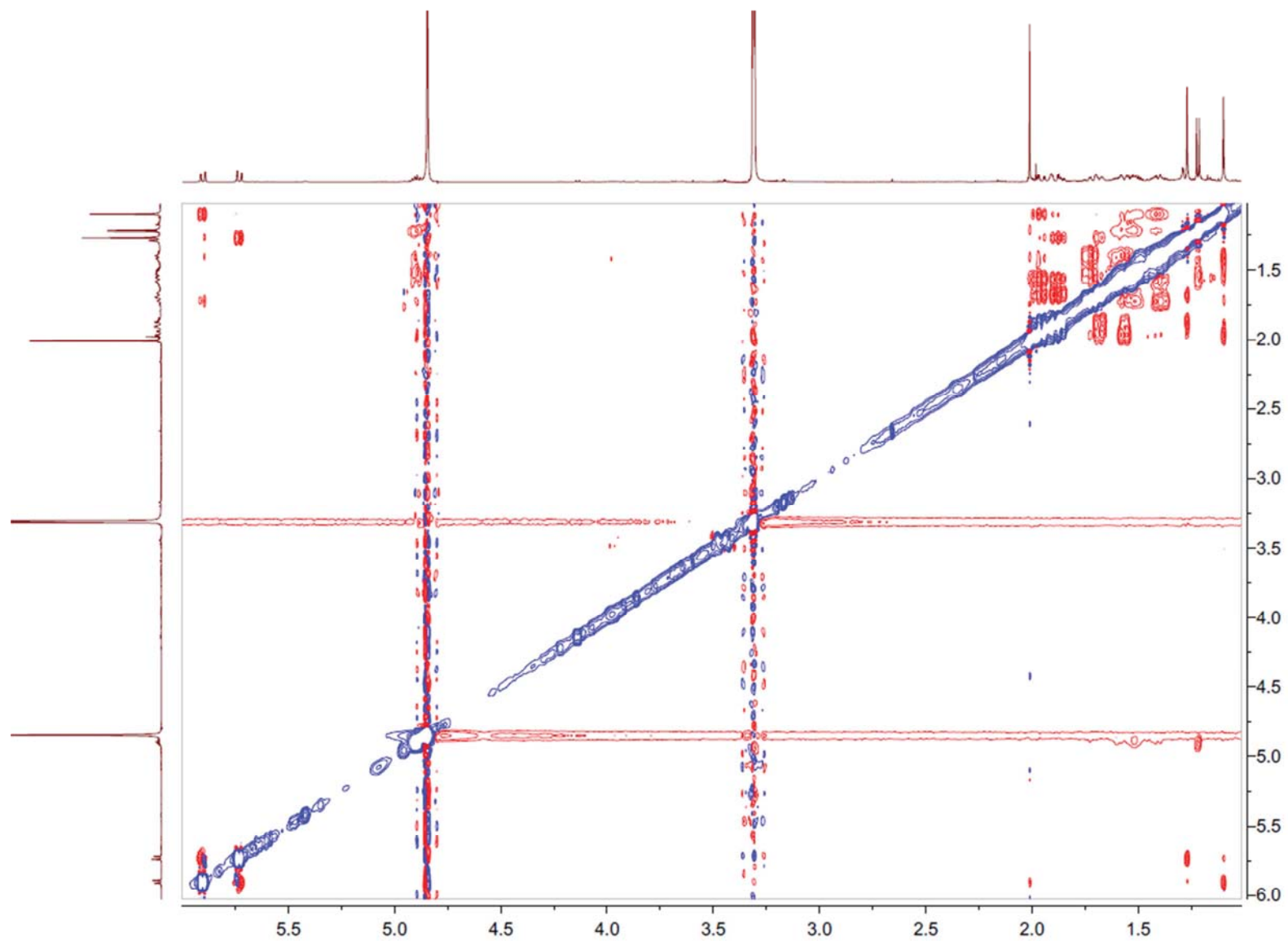


Figure S14. NOESY spectrum of compound 2 in CD₃OD.

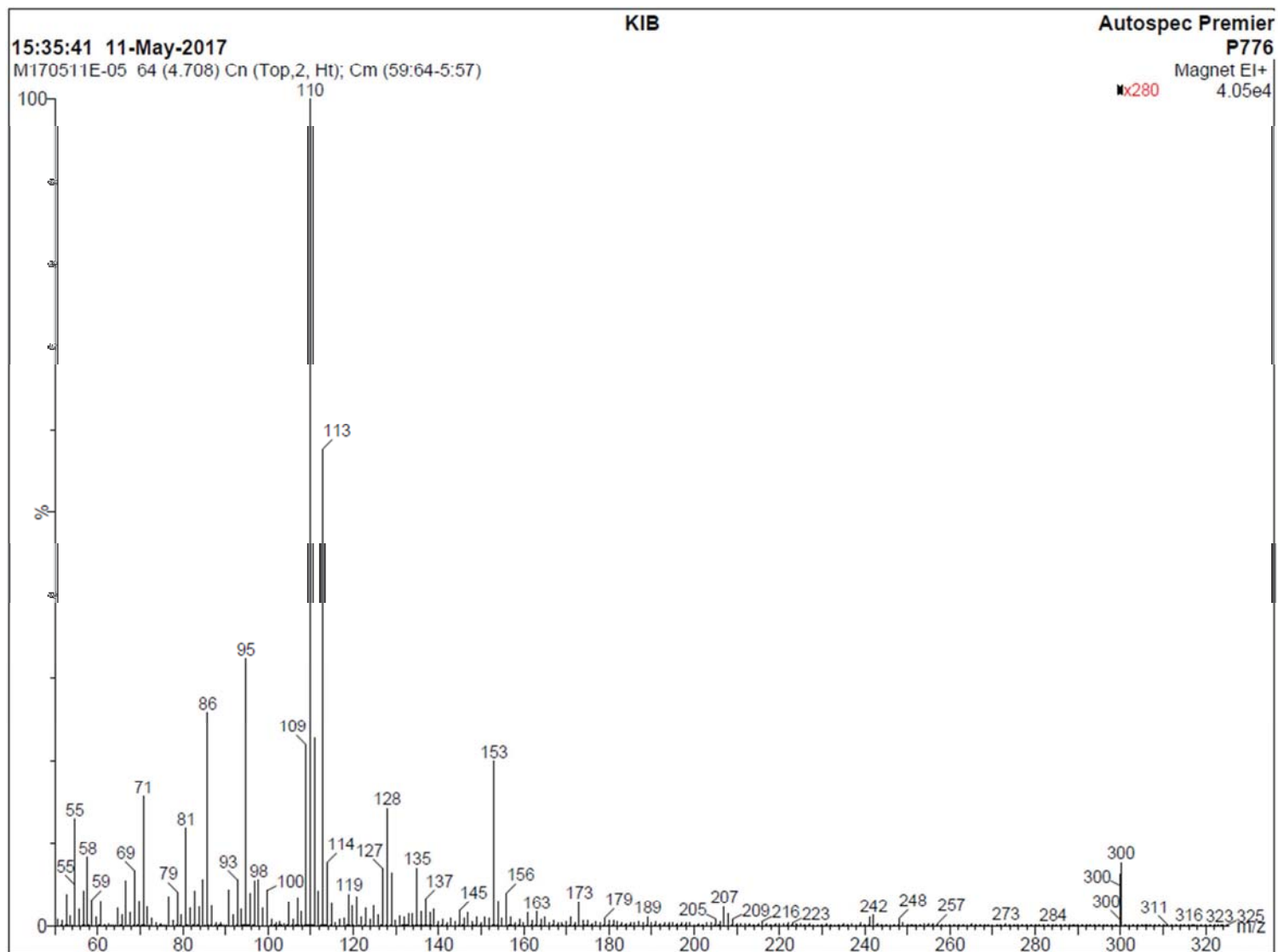


Figure S15. EIMS spectrum of compound 2.

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

15 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)

Elements Used:

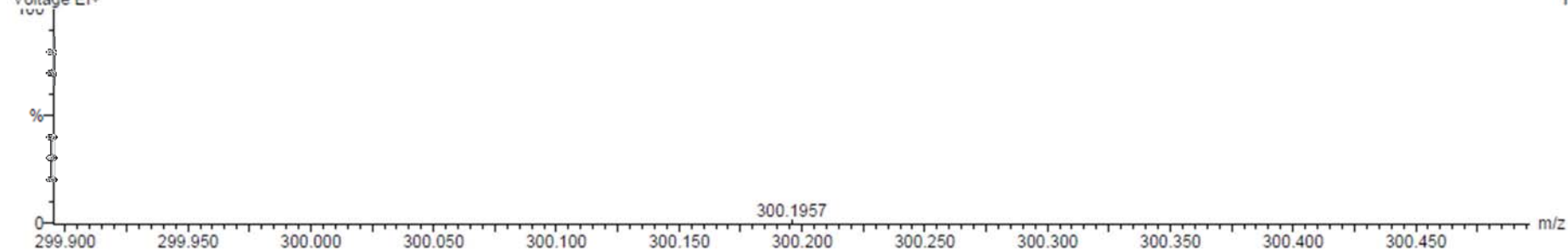
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17:38:53 11-May-2017

Voltage EI+

KIB
M170511EA-05AFAMMA 25 (2.296)

Autospec Premier
P776
1



Minimum:				-10.0		
Maximum:	10.0	10.0		120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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Figure S16. HREIMS spectrum of compound 2.

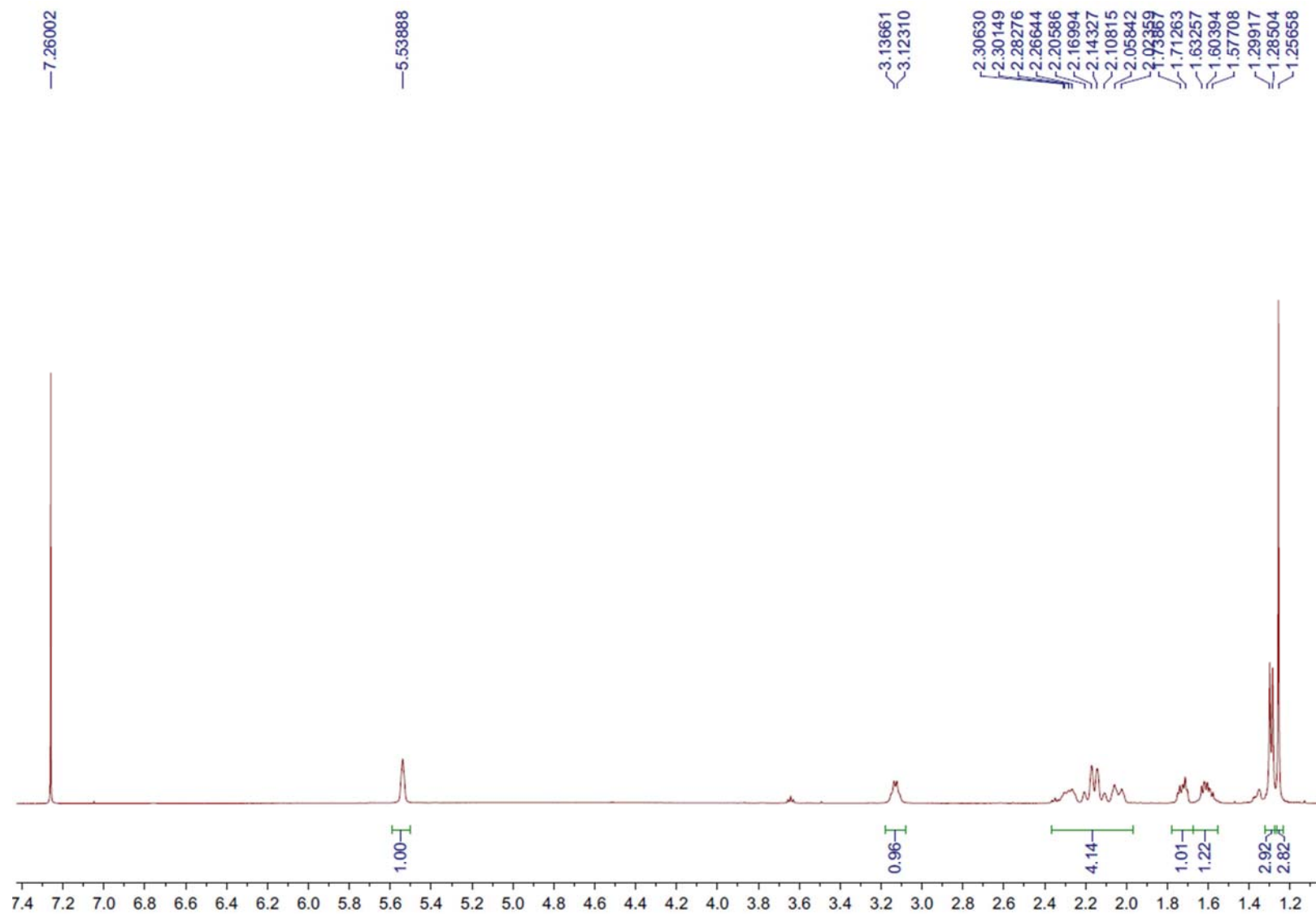


Figure S17. ^1H NMR spectrum of compound **3** in CDCl_3 .

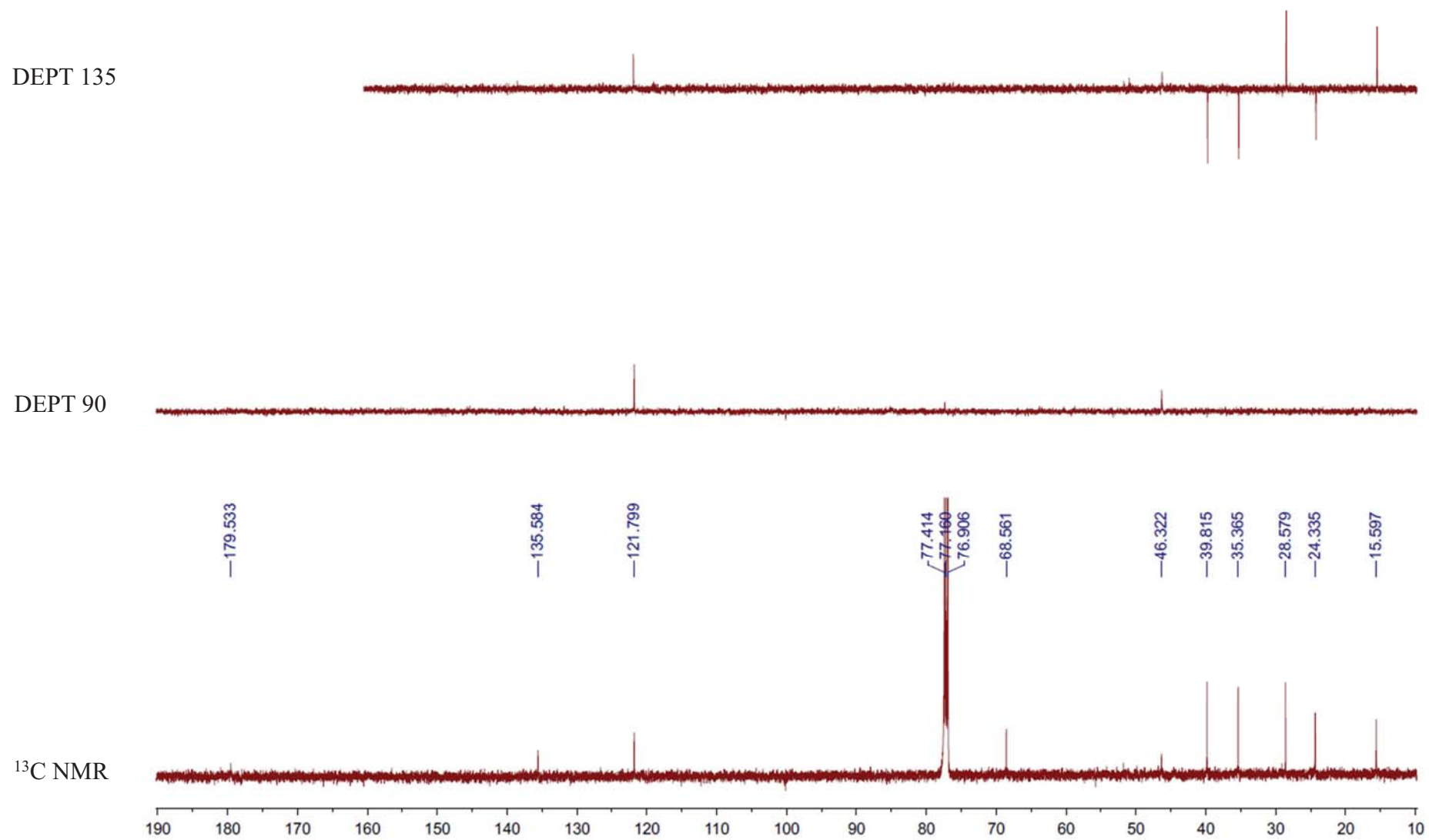


Figure S18. ^{13}C NMR and DEPT spectra of compound **3** in CDCl_3 .

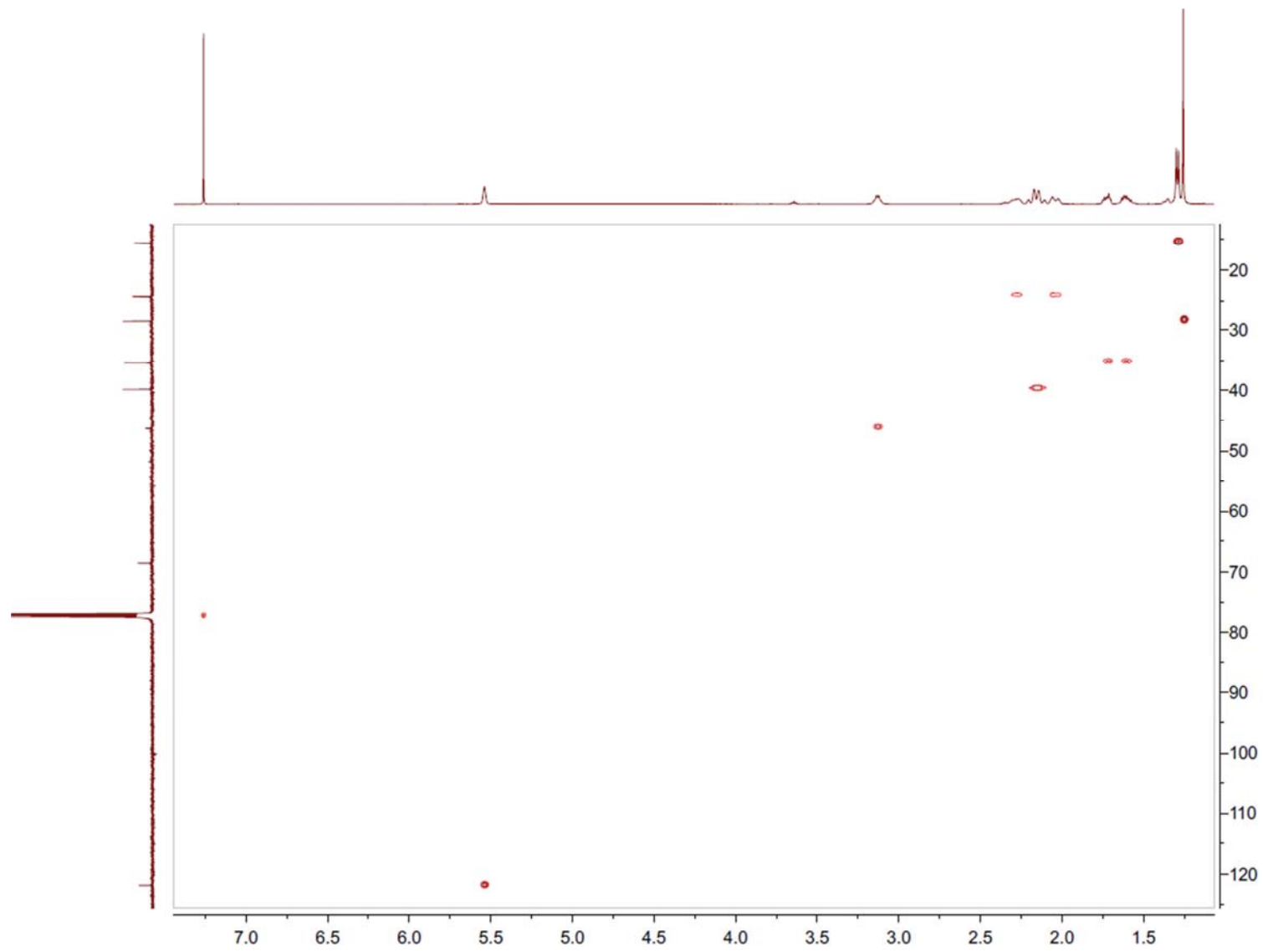


Figure S19. HSQC spectrum of compound **3** in CDCl₃.

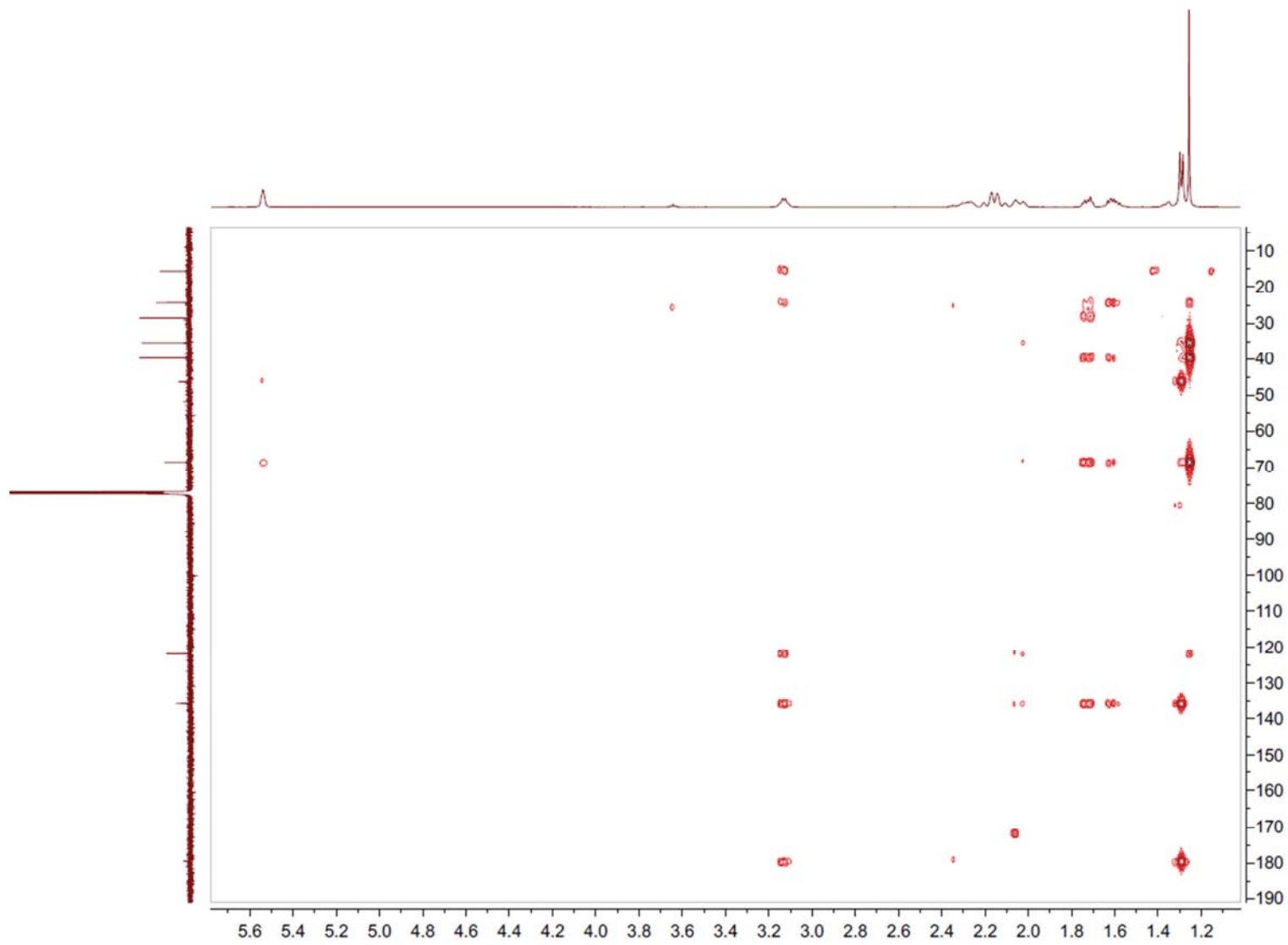


Figure S20. HMBC spectrum of compound **3** in CDCl₃.

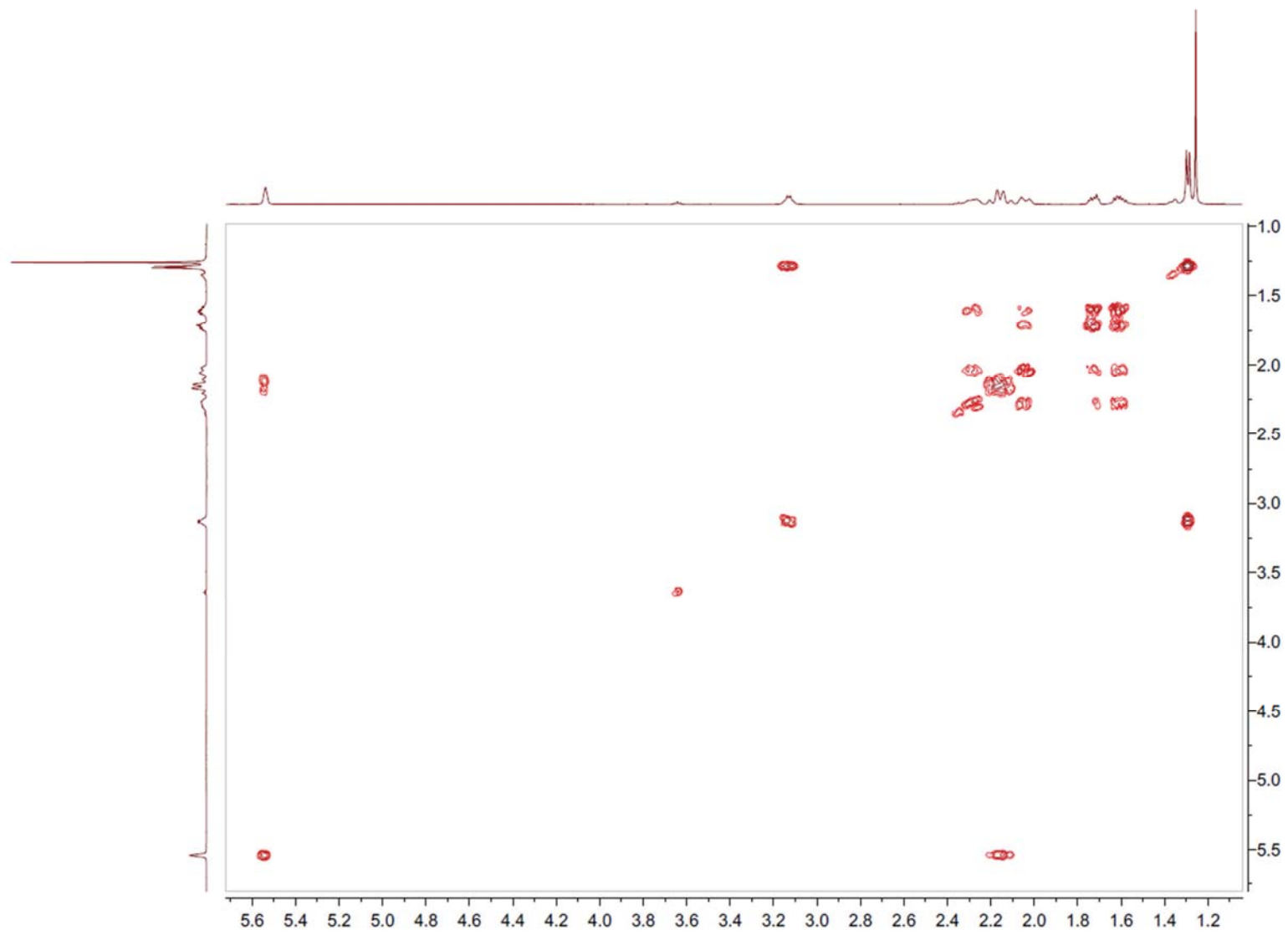


Figure S21. COSY spectrum of compound **3** in CDCl₃.

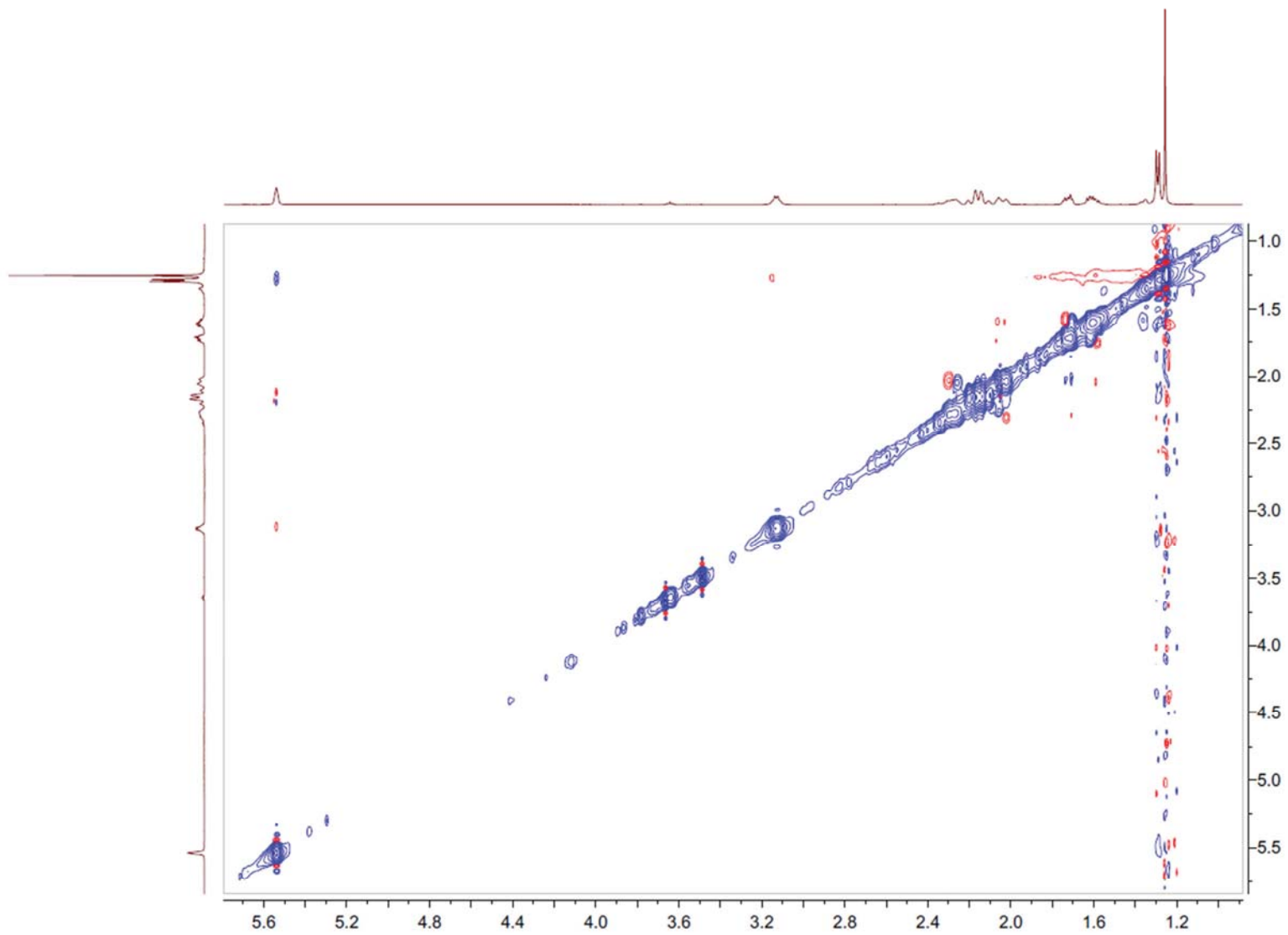


Figure S22. NOESY spectrum of compound **3** in CDCl₃.

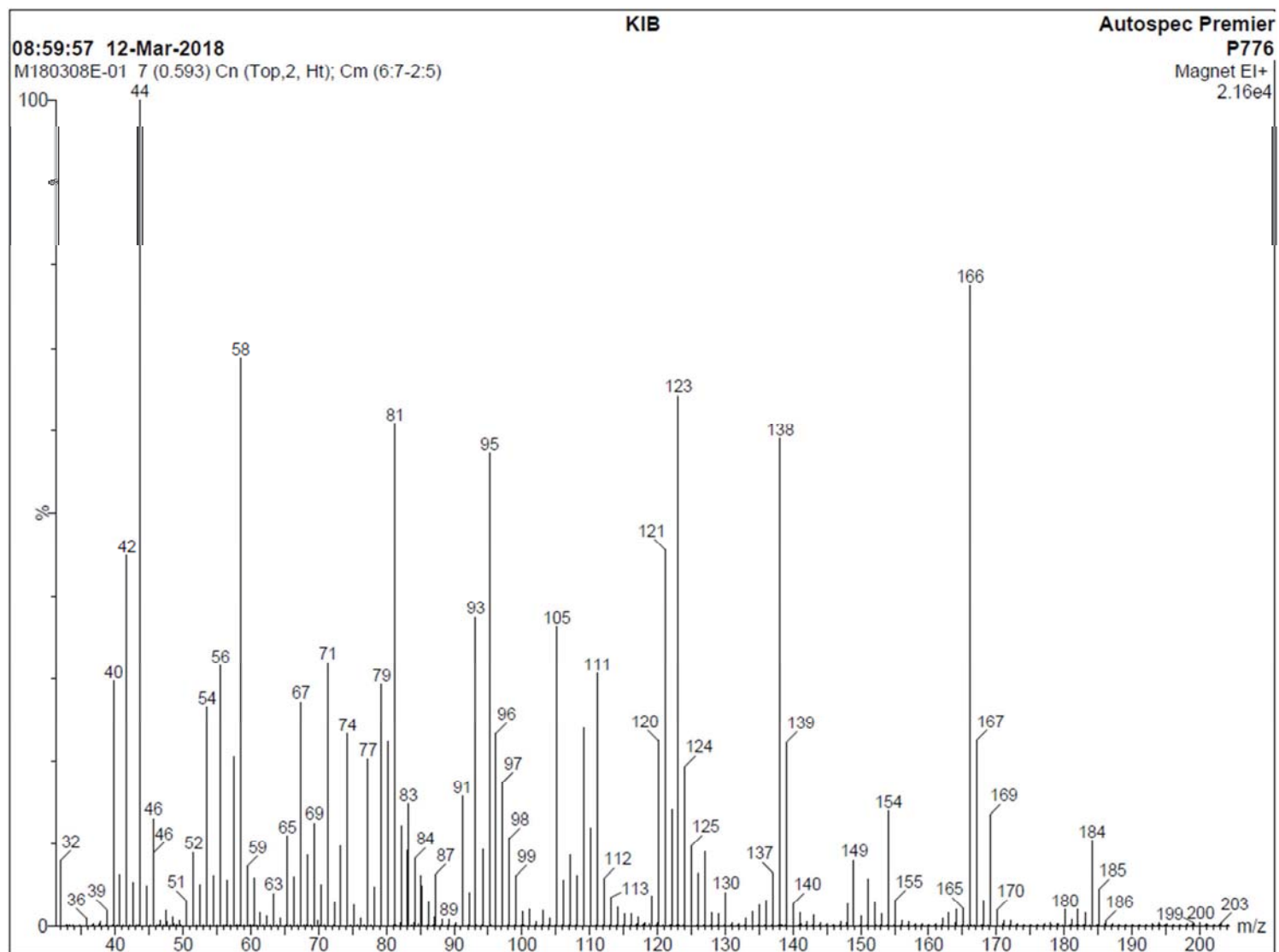


Figure S23. EIMS spectrum of compound 3.

Single Mass Analysis

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Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

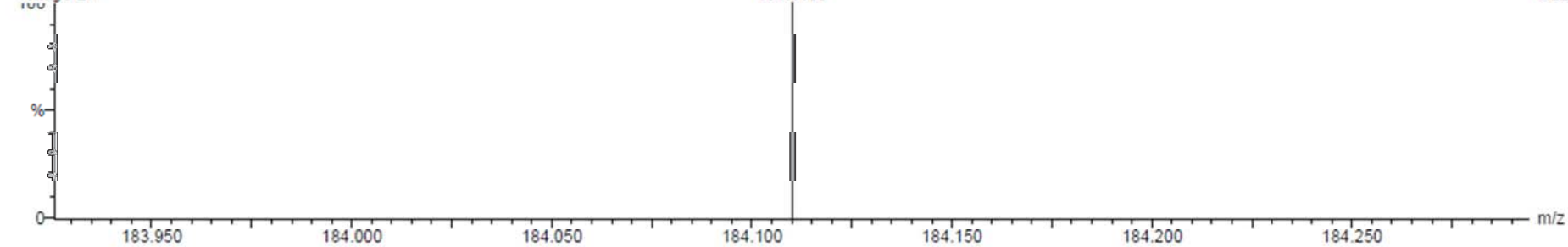
12 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)

Elements Used:

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10:43:27 12-Mar-2018

Voltage EI+



Autospec Premier
P776
4.22

Minimum:				-10.0		
Maximum:	200.0	10.0		120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
184.1100	184.1099	0.1	0.5	3.0	5546025.5	C10 H16 O3

Figure S24. HREIMS spectrum of compound 3.

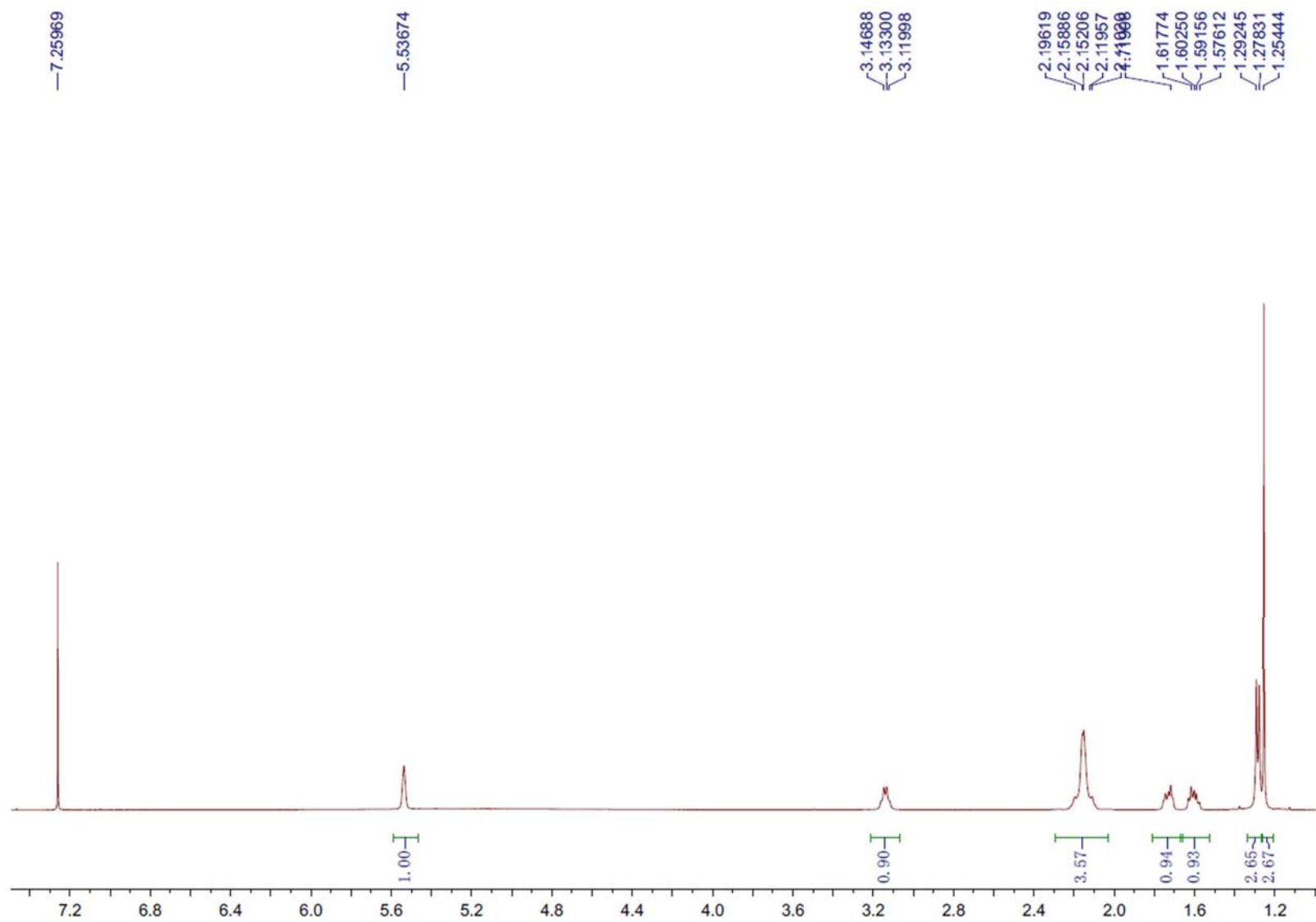


Figure S25. ^1H NMR spectrum of compound 4 in CDCl_3 .

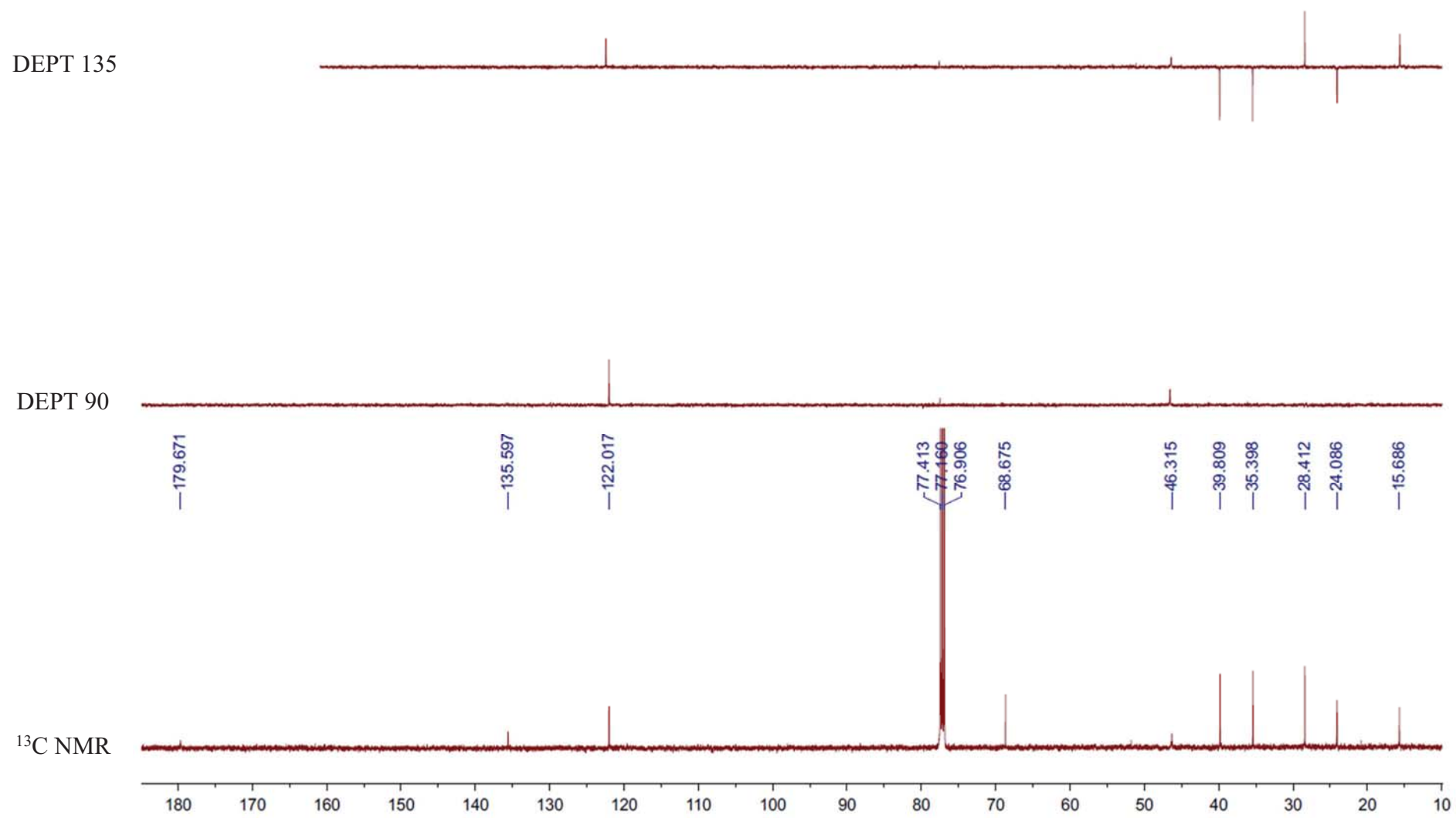


Figure S26. ^{13}C NMR and DEPT spectra of compound 4 in CDCl_3 .

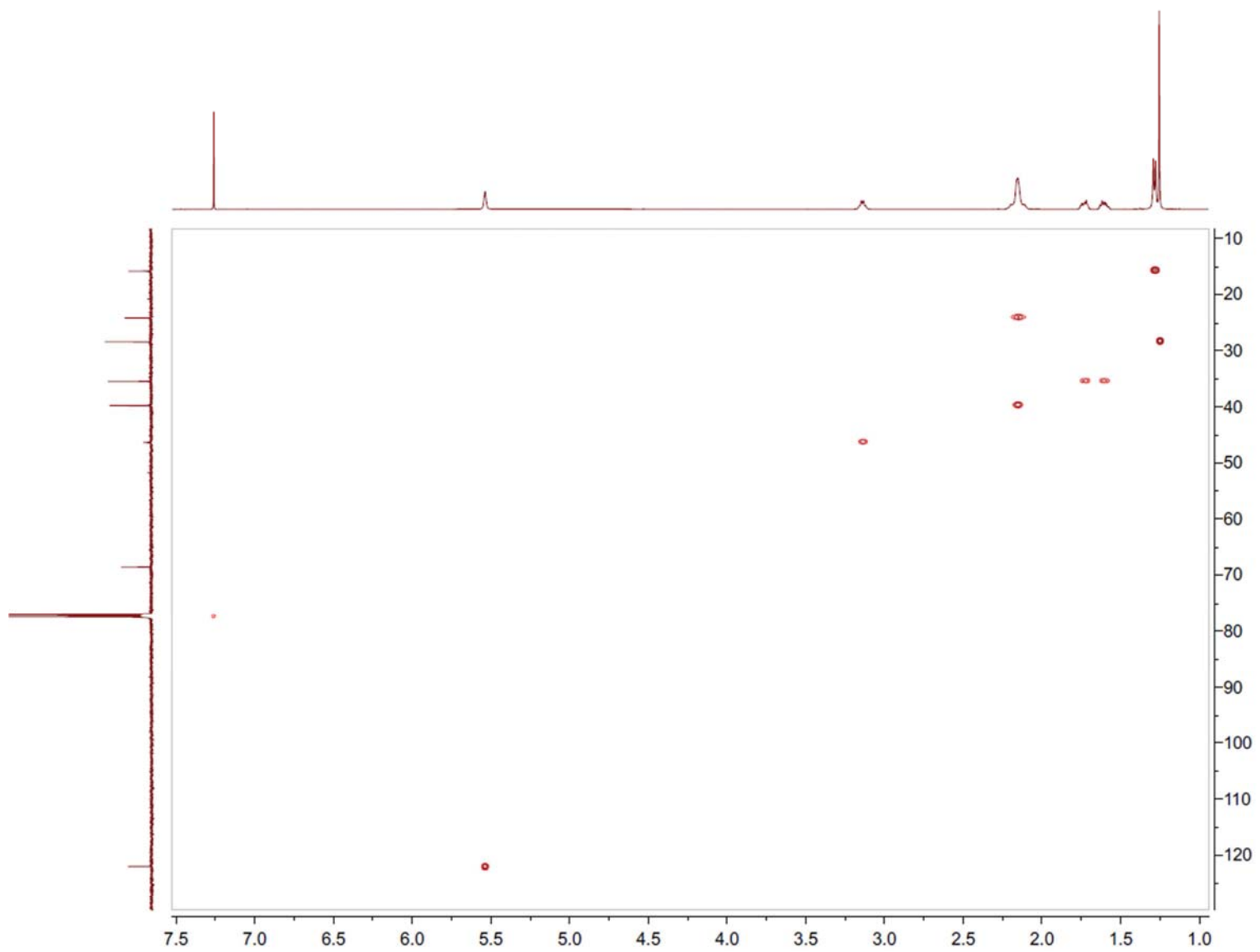


Figure S27. HSQC spectrum of compound **4** in CDCl_3 .

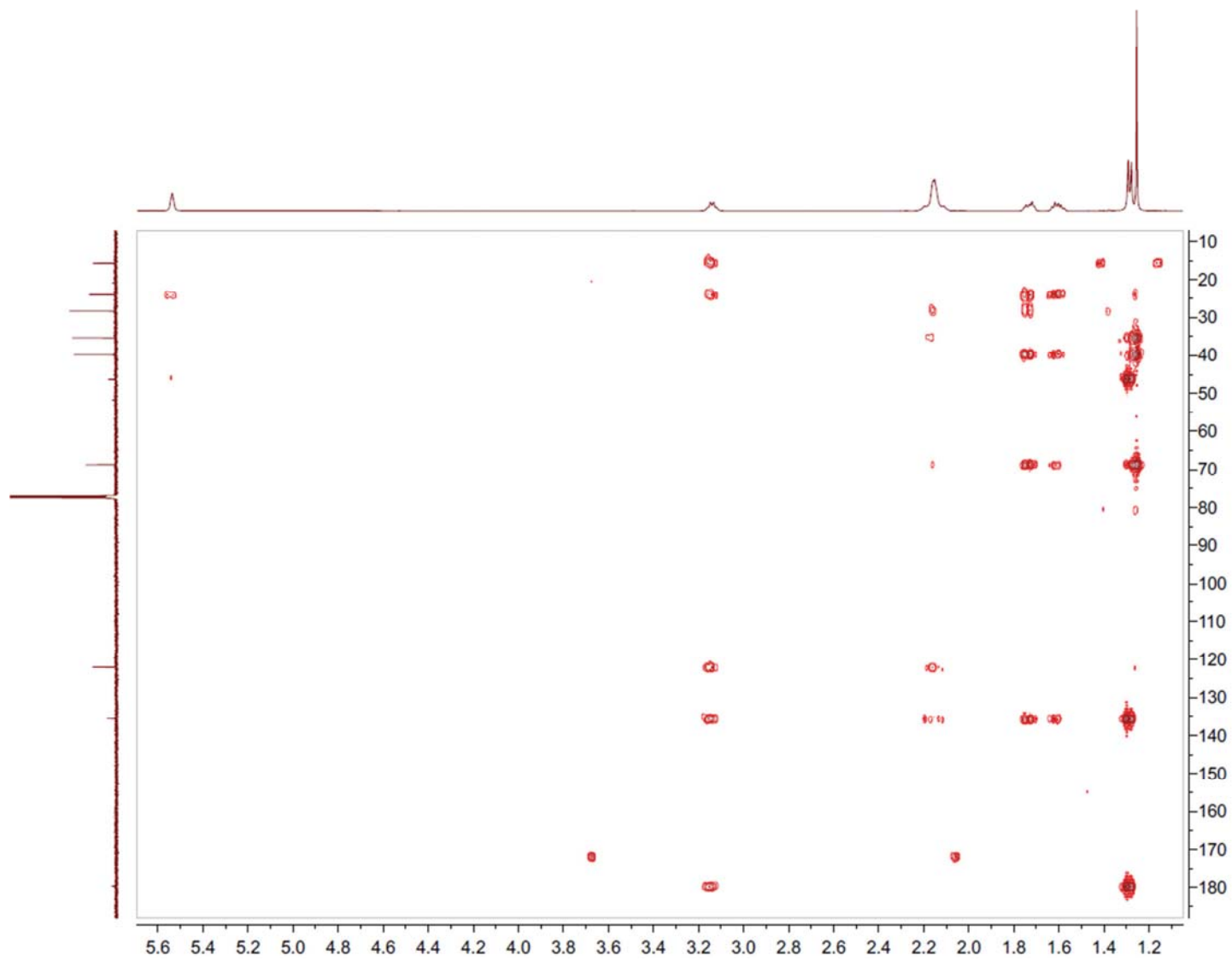


Figure S28. HMBC spectrum of compound **4** in CDCl_3 .

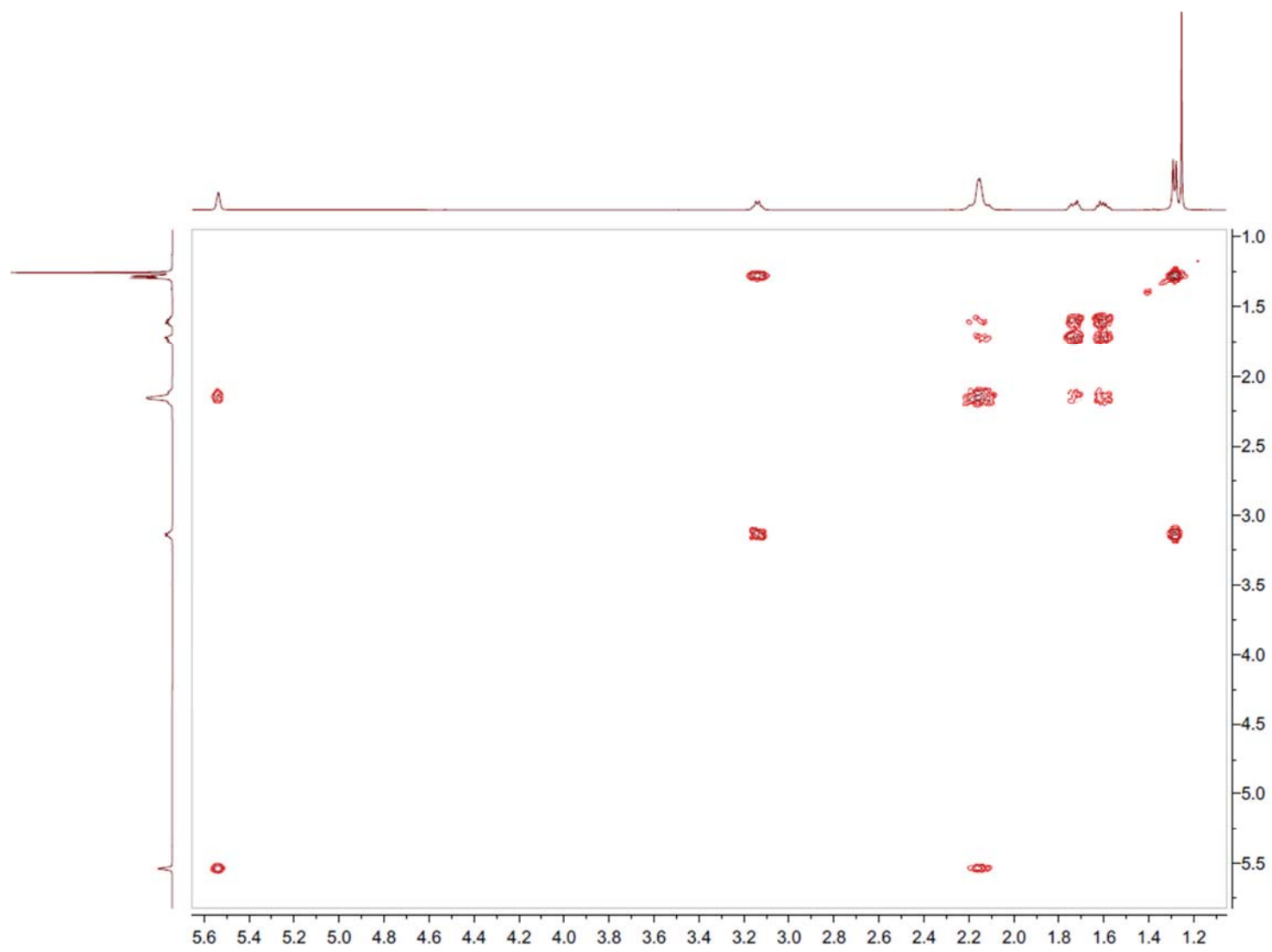


Figure S29. COSY spectrum of compound 4 in CDCl₃.

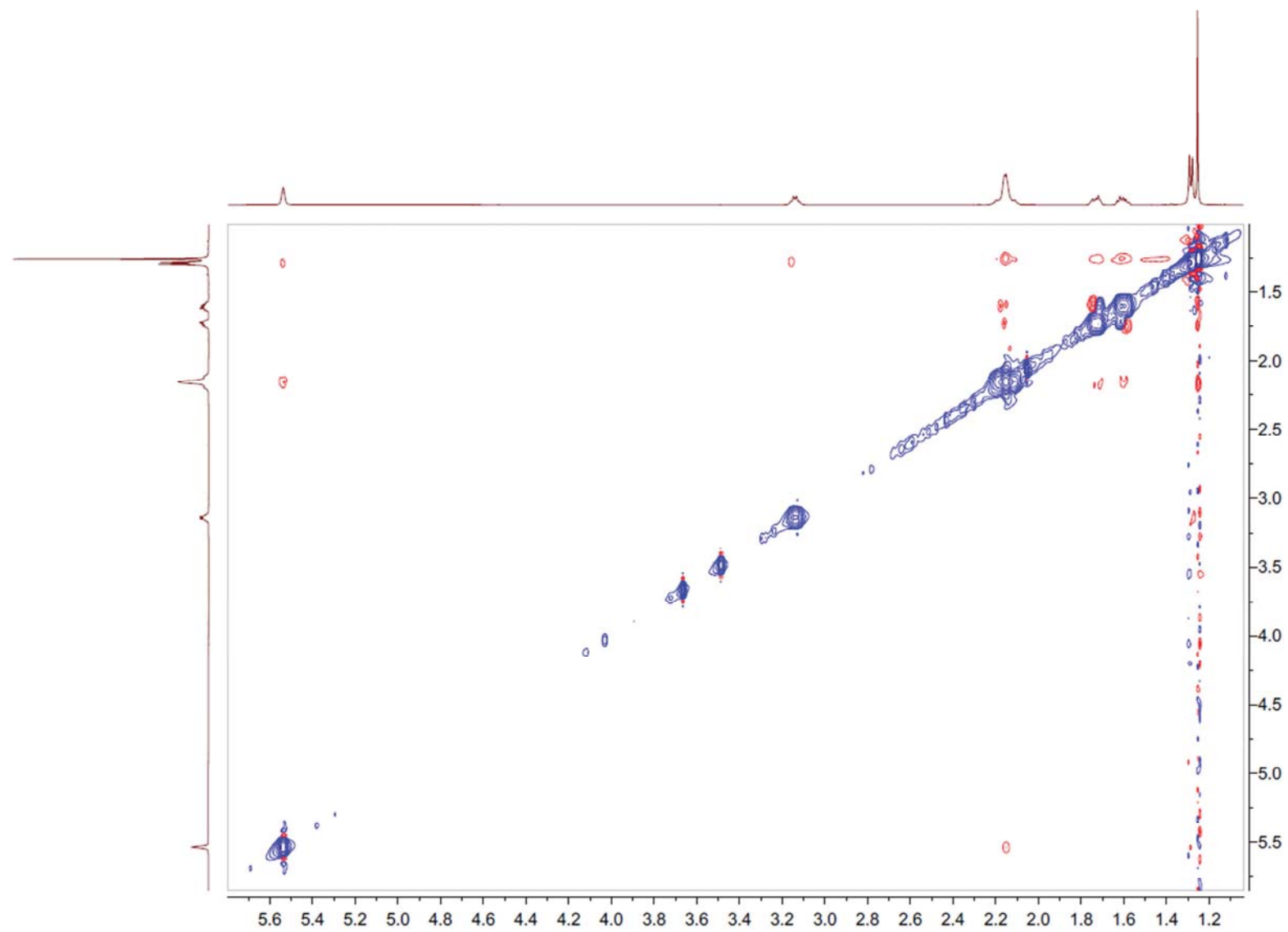


Figure S30. NOESY spectrum of compound **4** in CDCl₃.

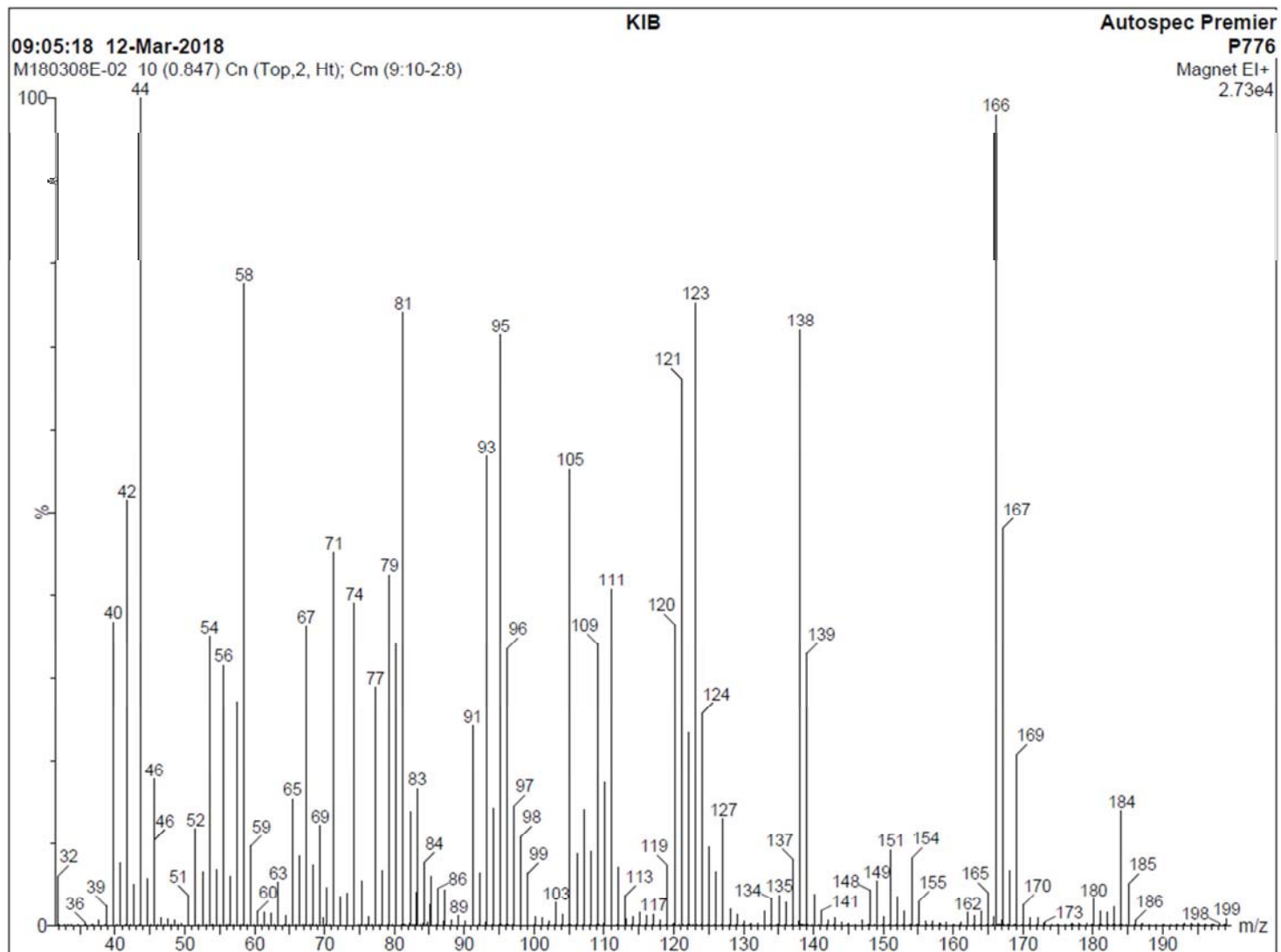


Figure S31. EIMS spectrum of compound 4.

Single Mass Analysis

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Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

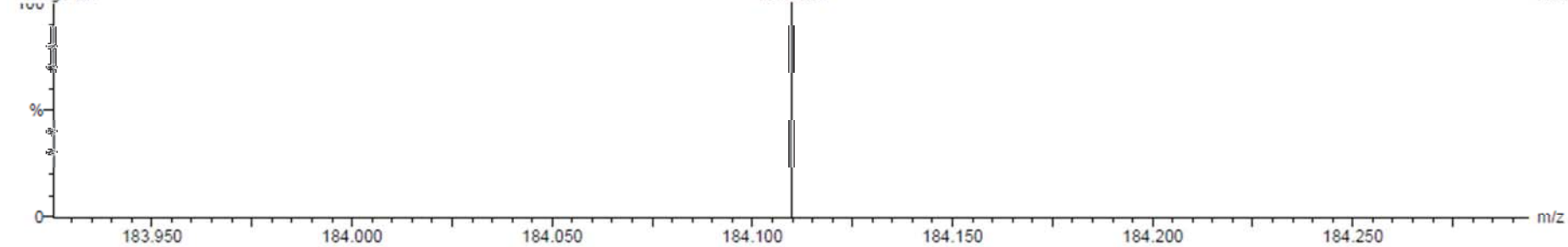
12 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)

Elements Used:

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10:32:47 12-Mar-2018

Voltage EI+



Autospec Premier
P776
7.22

Minimum: -10.0
Maximum: 200.0 10.0 120.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
184.1097	184.1099	-0.2	-1.1	3.0	5546025.5	C10 H16 O3

Figure S32. HREIMS spectrum of compound 4.

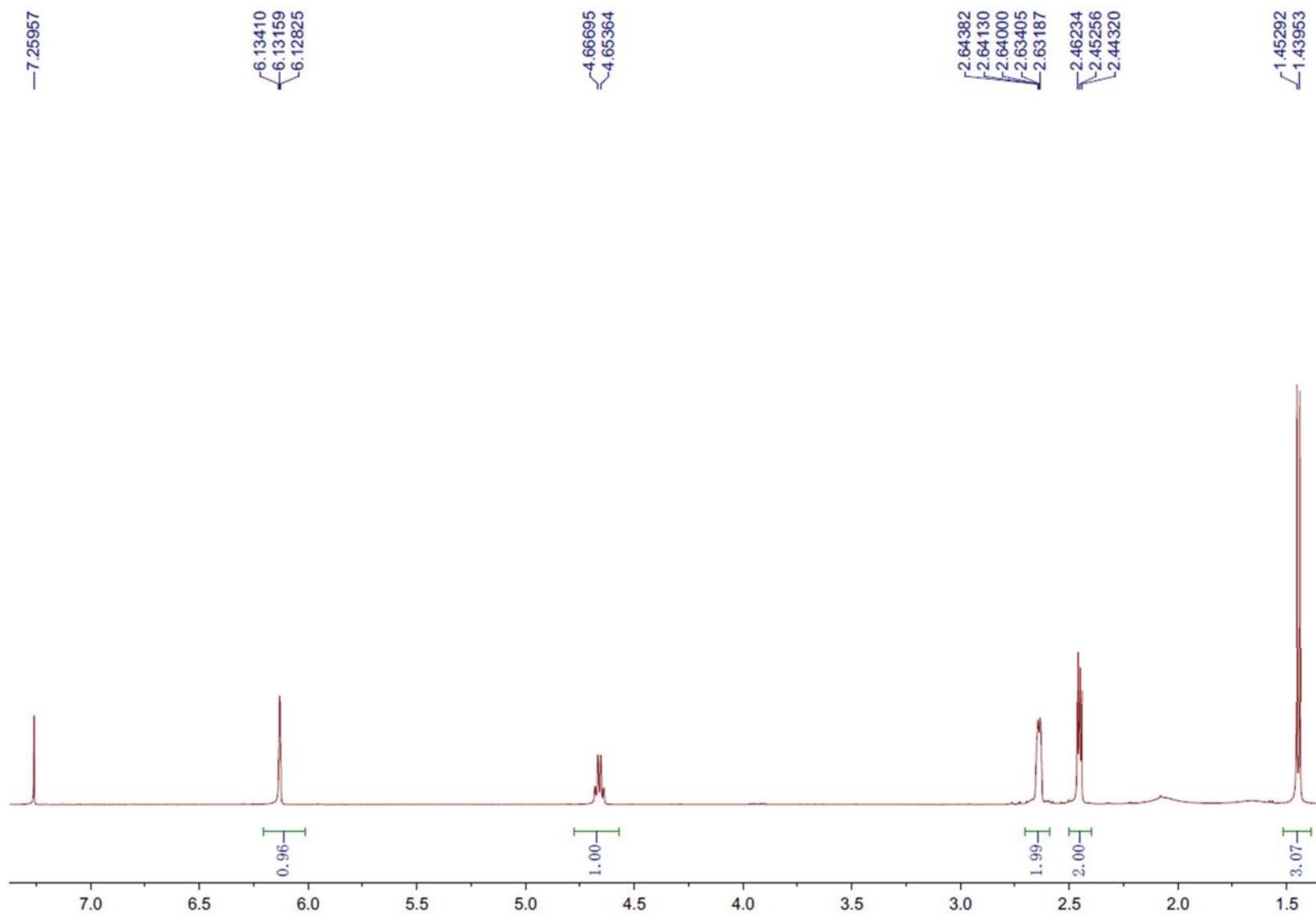


Figure S33. ^1H NMR spectrum of compound **5** in CDCl_3 .

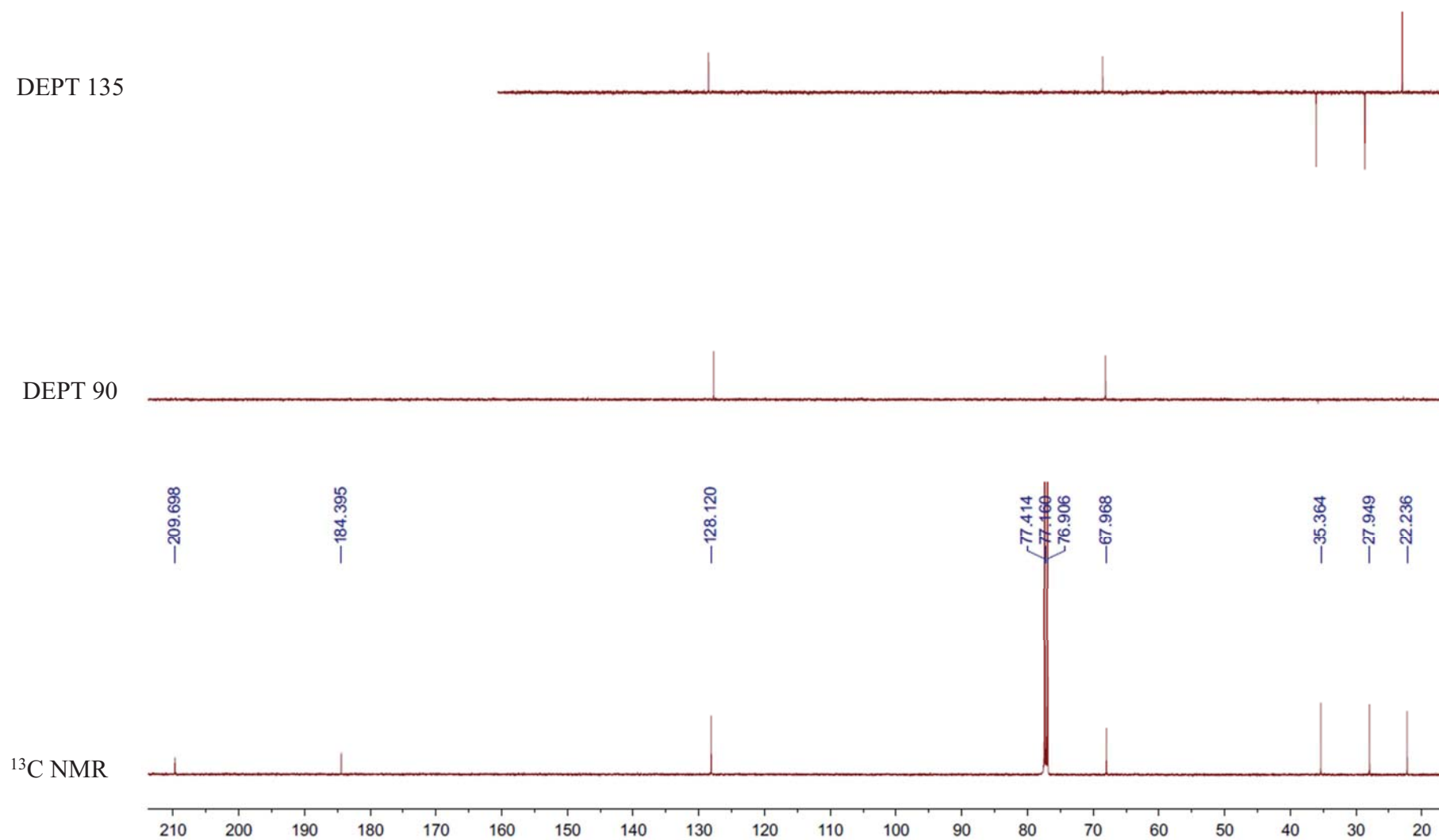


Figure S34. ^{13}C NMR and DEPT spectra of compound **5** in CDCl_3 .

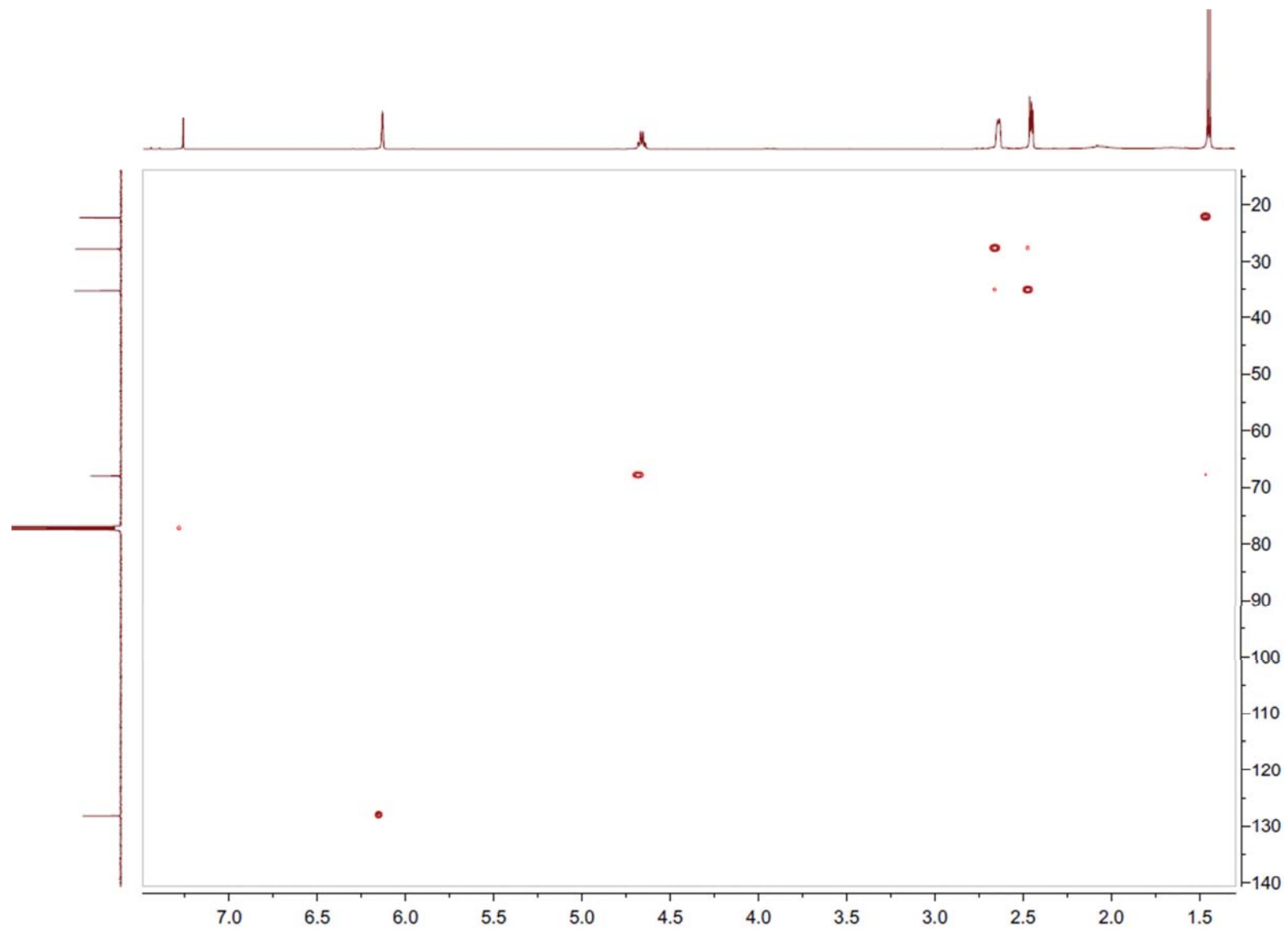


Figure S35. HSQC spectrum of compound **5** in CDCl₃.

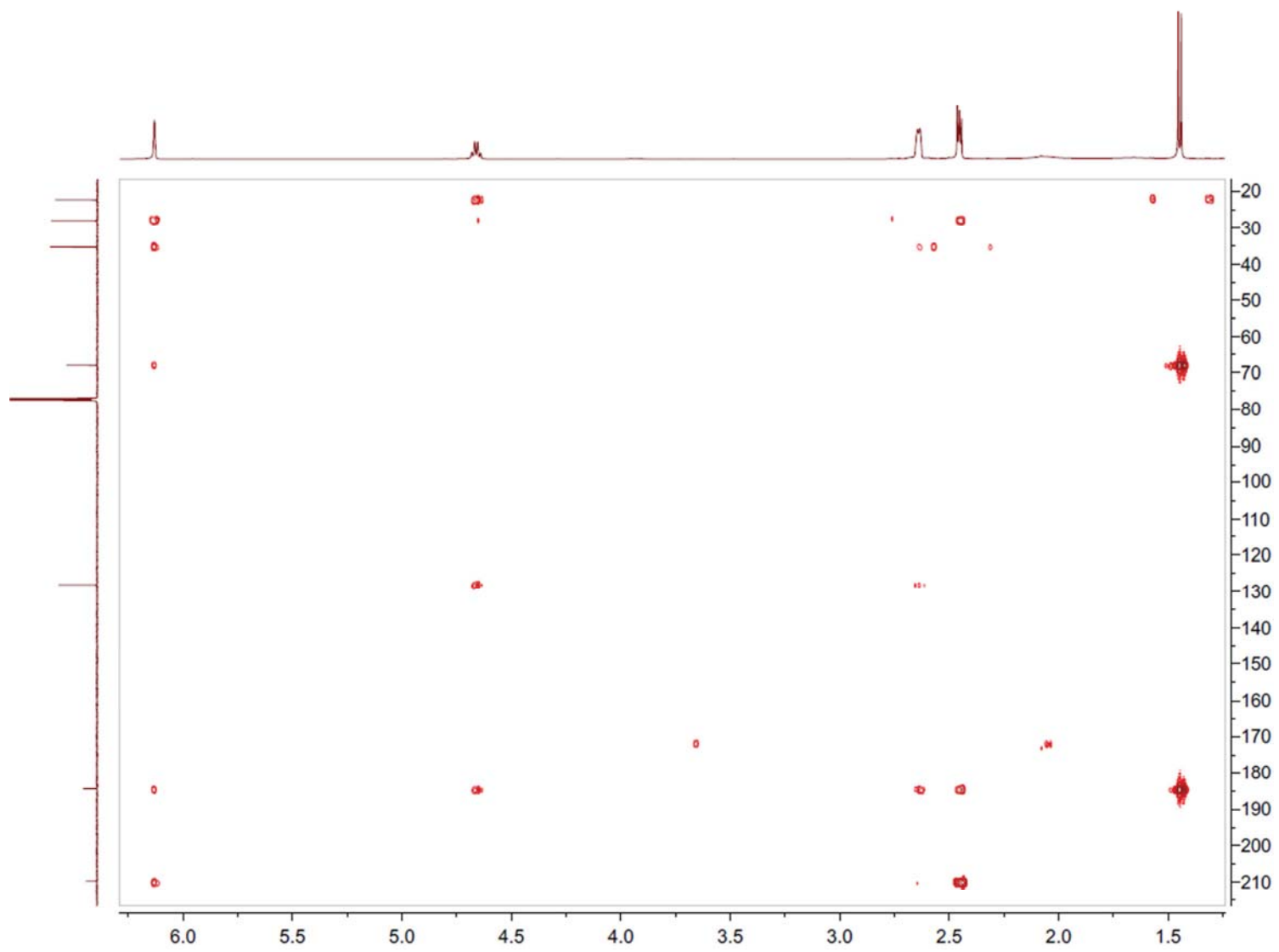


Figure S36. HMBC spectrum of compound 5 in CDCl₃.

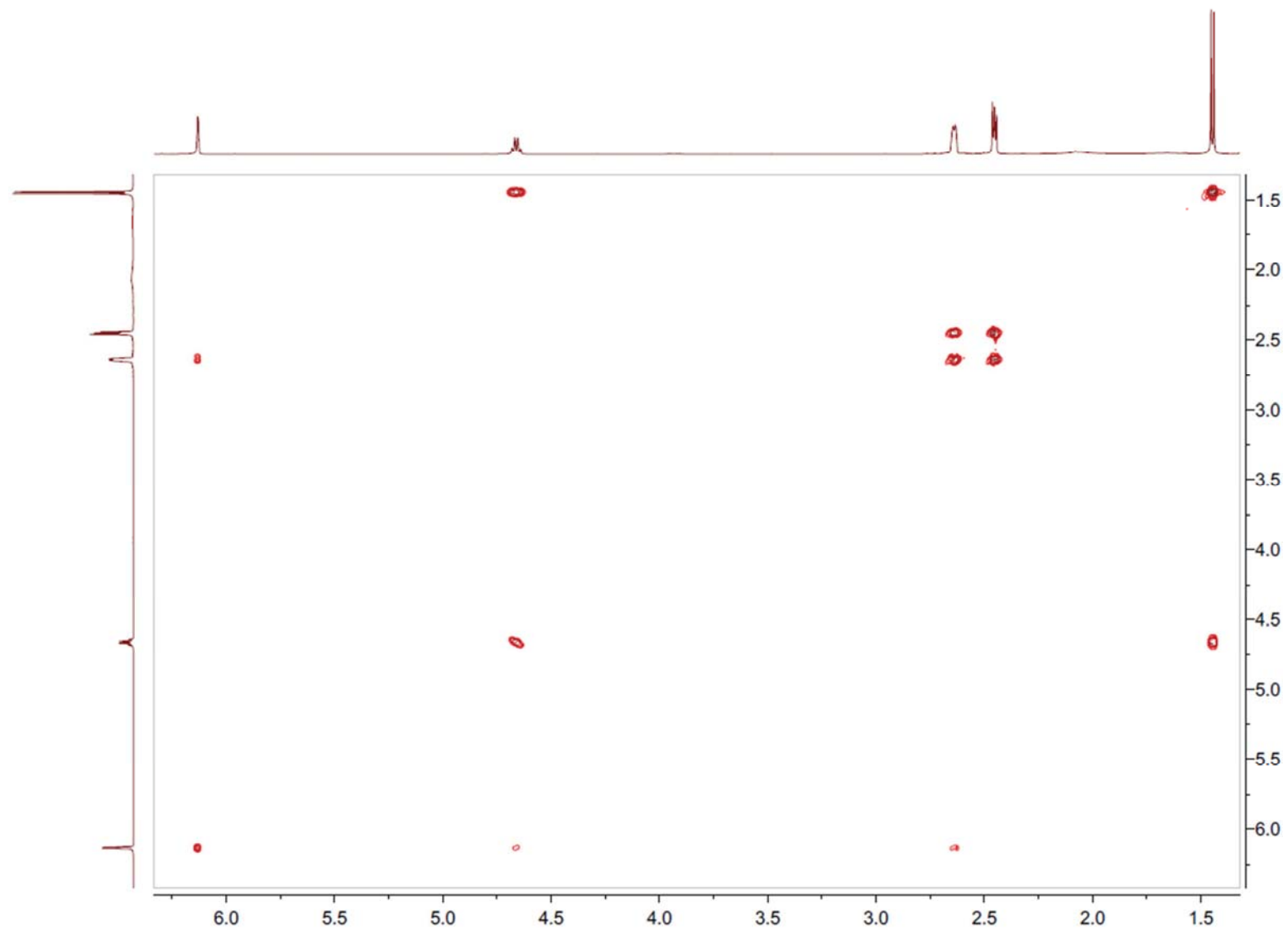


Figure S37. COSY spectrum of compound **5** in CDCl₃.

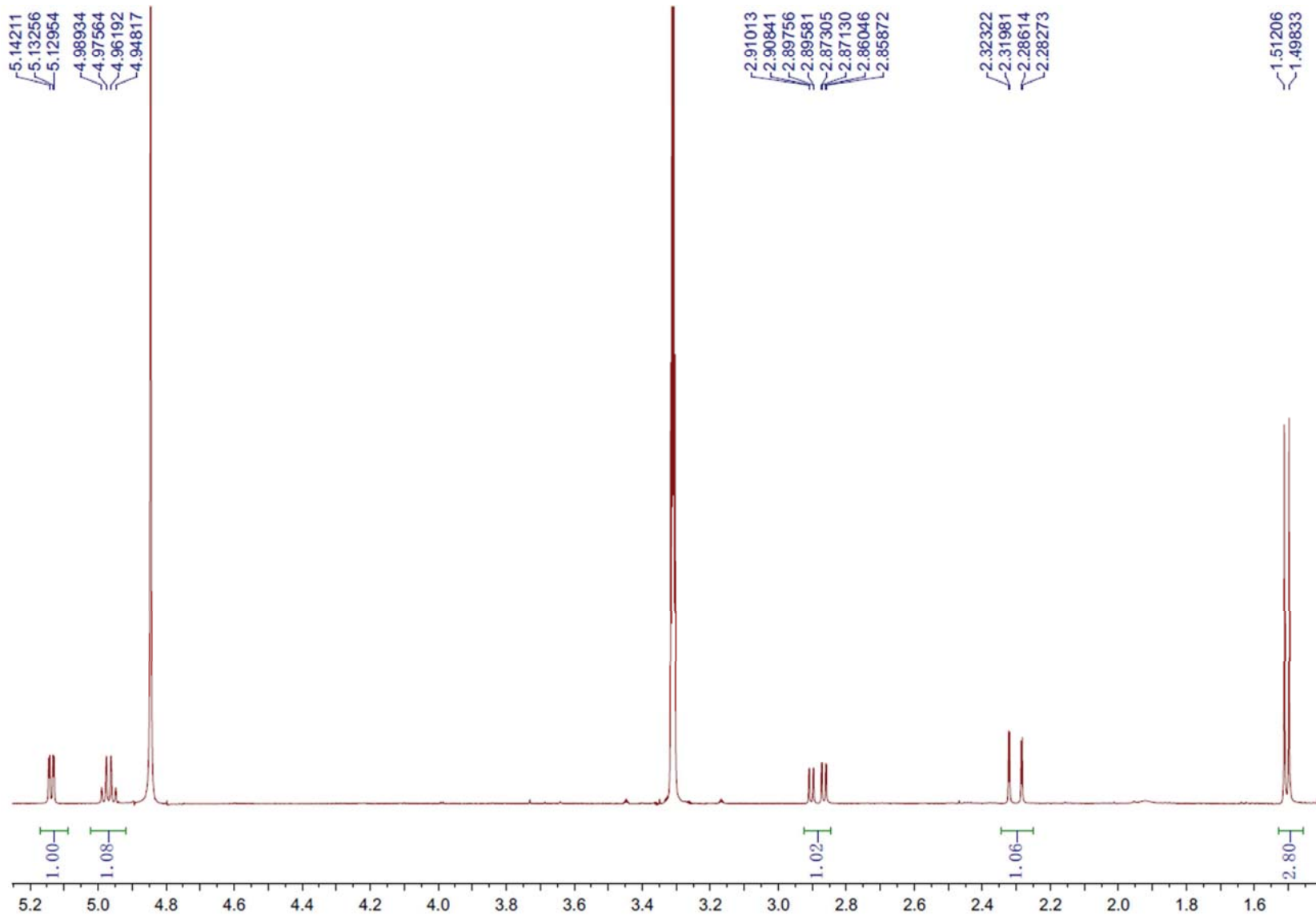


Figure S38. ^1H NMR spectrum of compound **6** in CD_3OD .

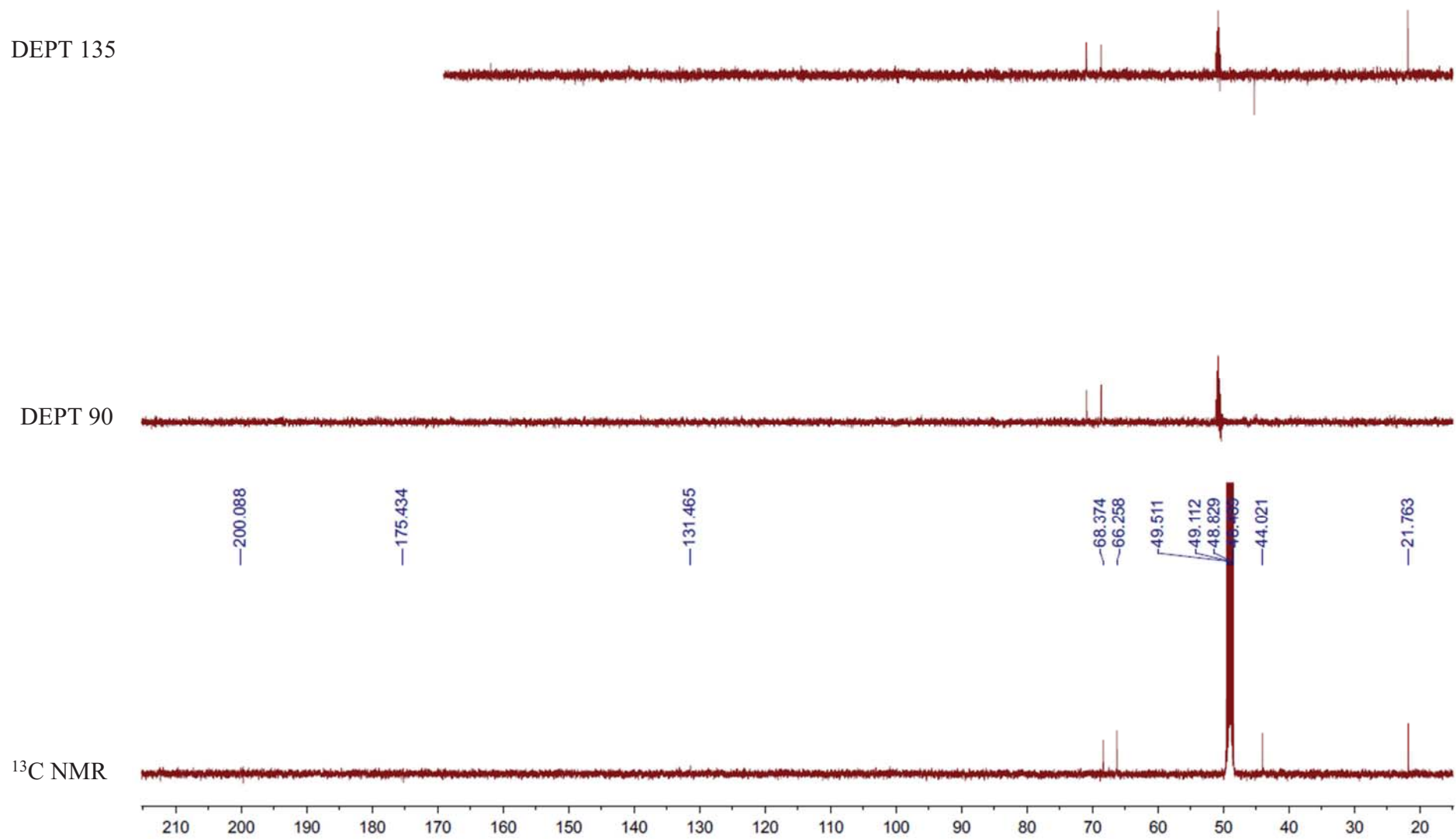


Figure S39. ^{13}C NMR and DEPT spectra of compound **6** in CD_3OD .

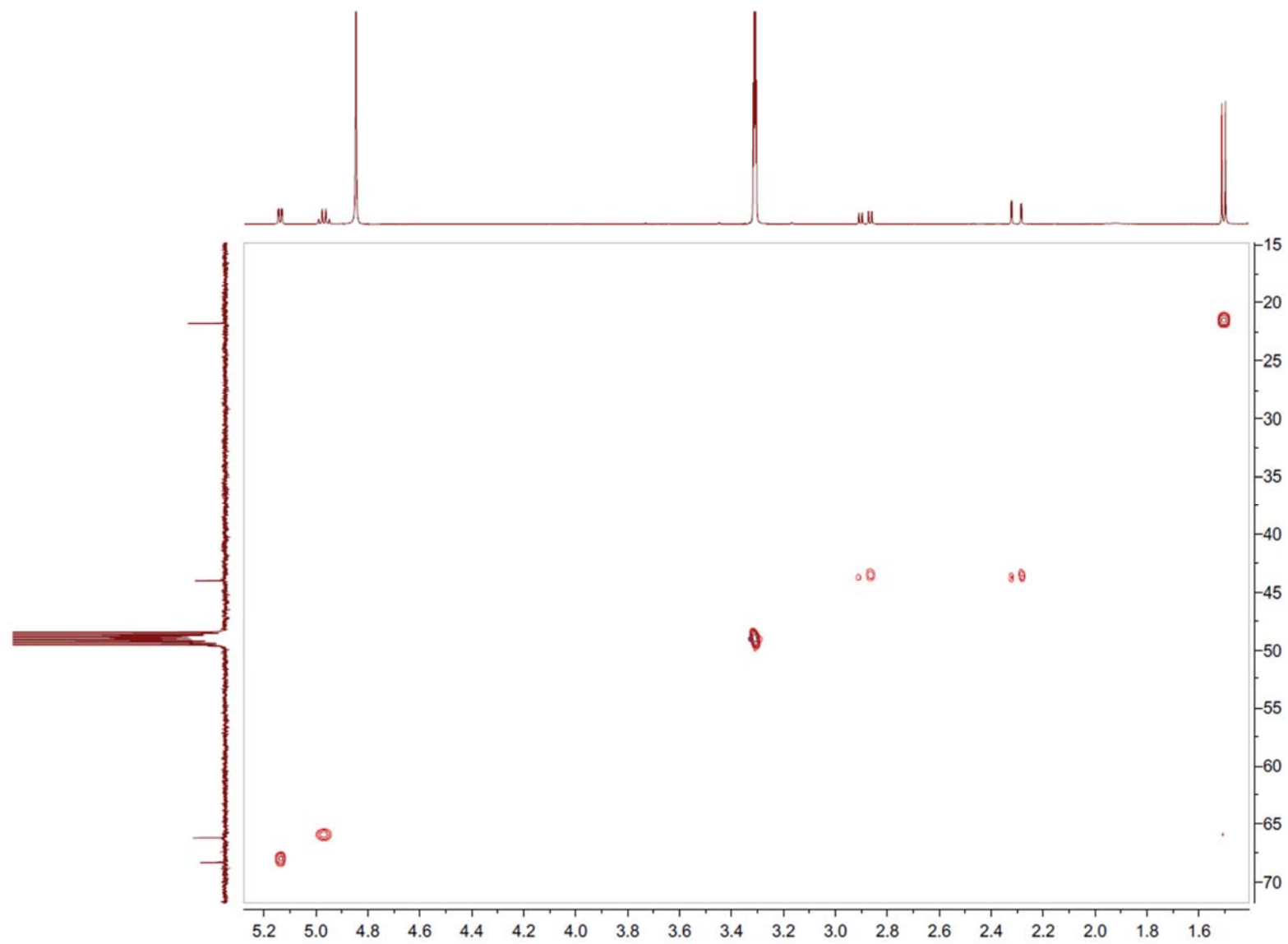


Figure S40. HSQC spectrum of compound **6** in CD₃OD.

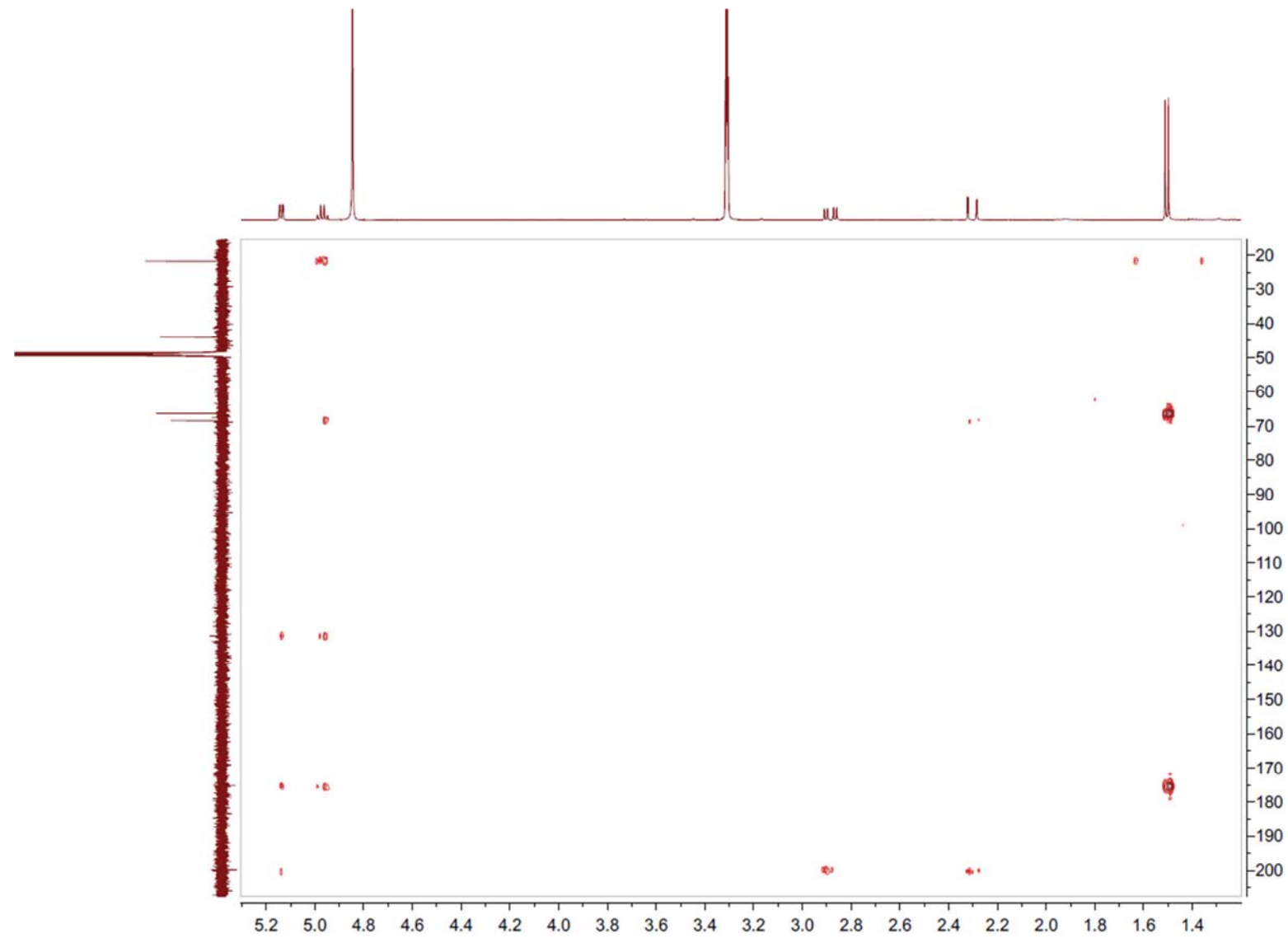


Figure S41. HMBC spectrum of compound 6 in CD₃OD.

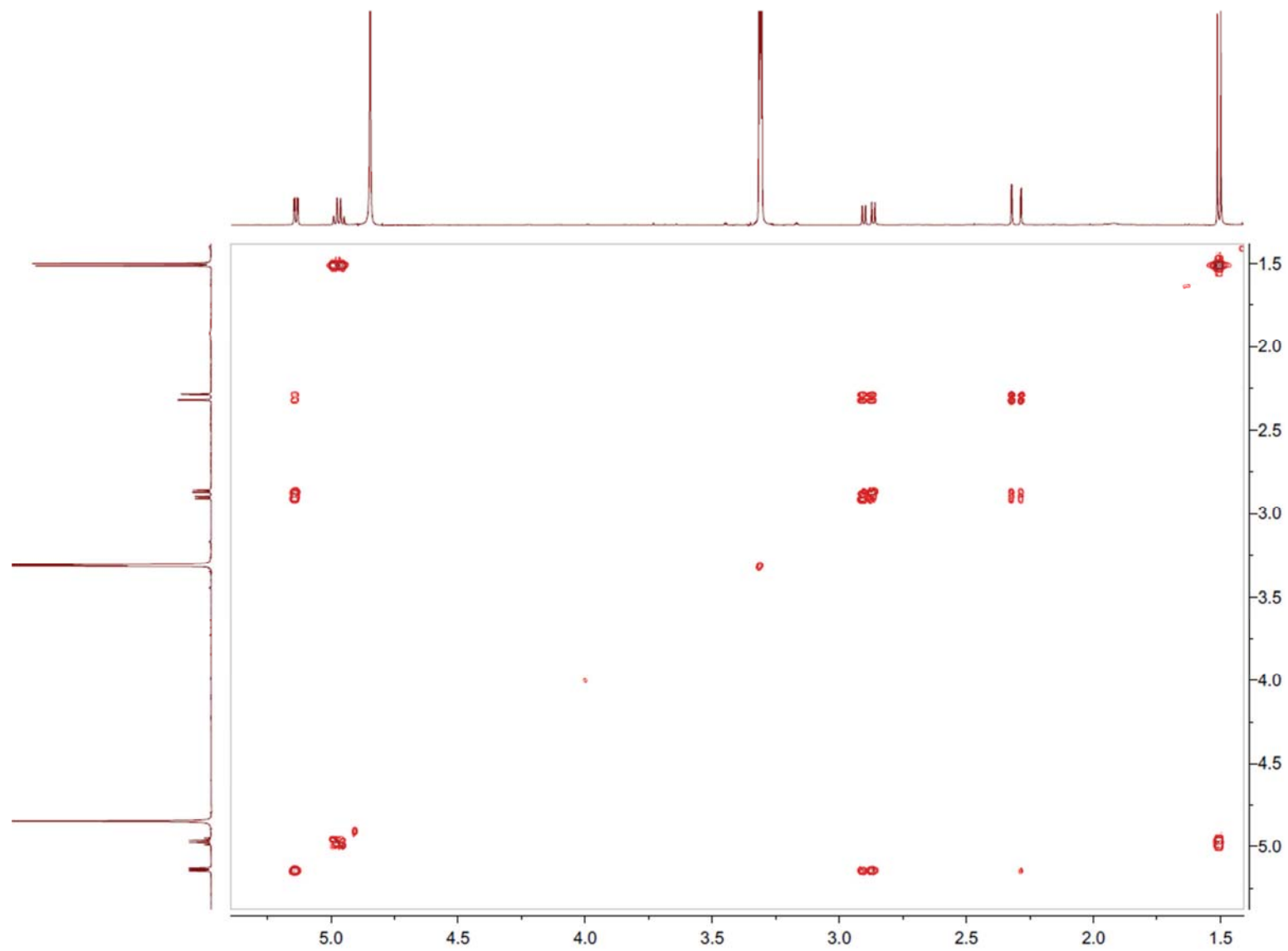


Figure S42. COSY spectrum of compound 6 in CD₃OD.

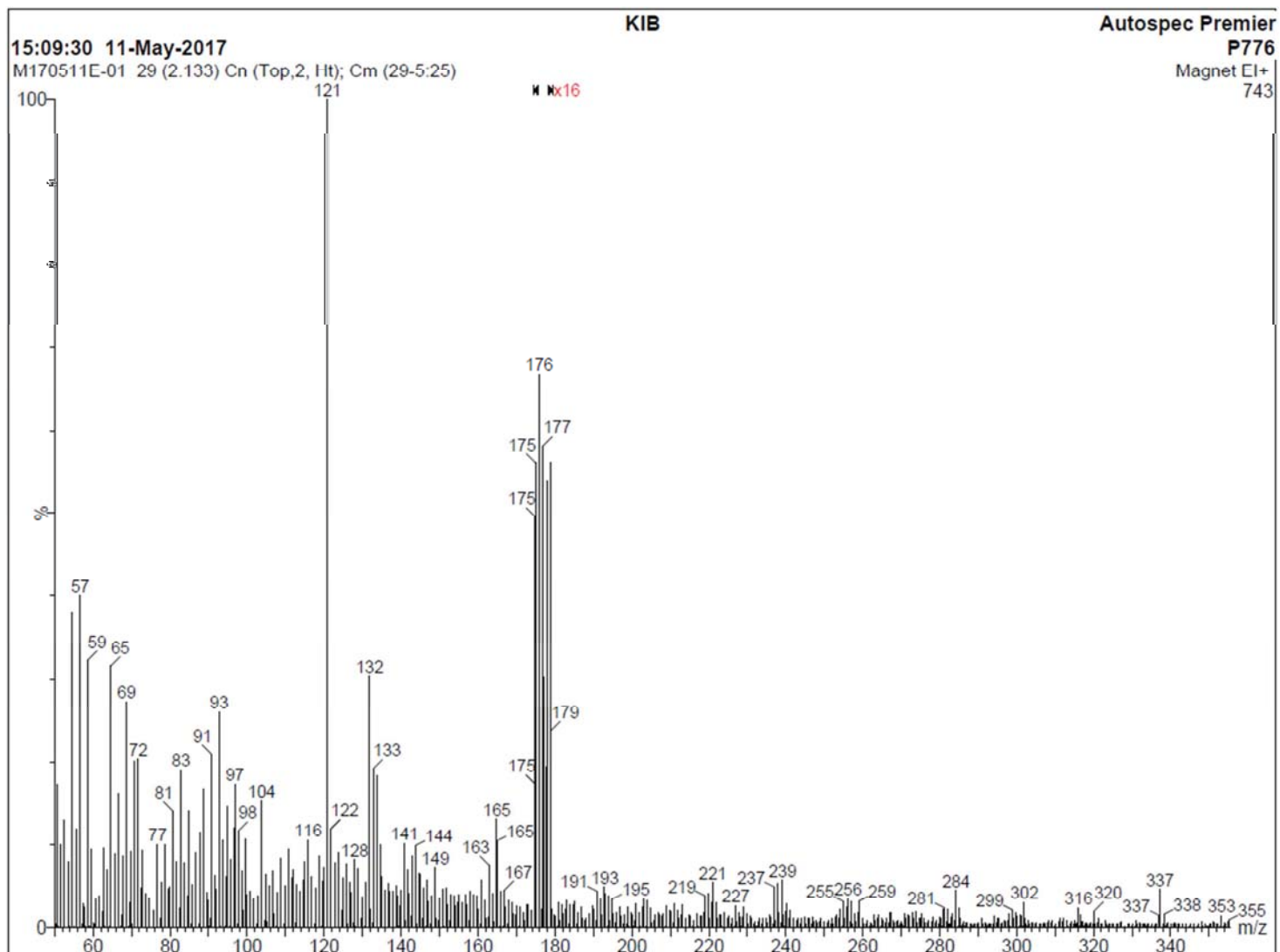


Figure S43. EIMS spectrum of compound 6.

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

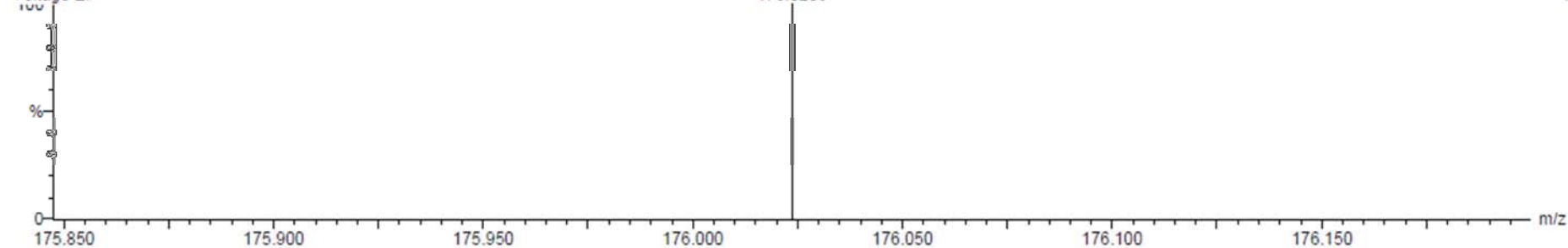
10 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)

Elements Used:

C: 0-200 H: 0-400 O: 2-4 Cl: 1-1

16:48:13 11-May-2017

Voltage EI+



Minimum: -10.0
Maximum: 200.0 10.0 120.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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Figure S44. HREIMS spectrum of compound 6.

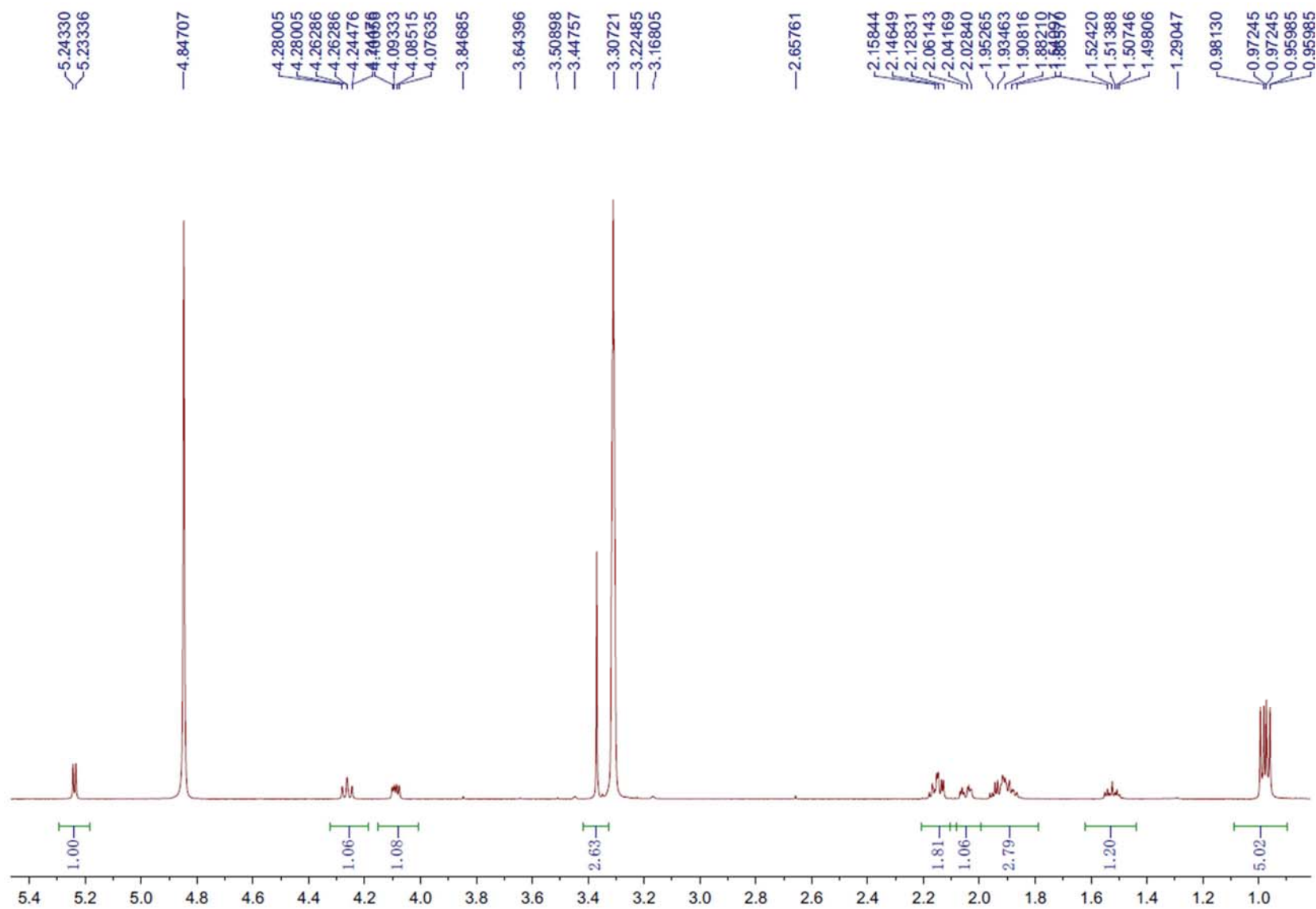


Figure S45. ^1H NMR spectrum of compound **7** in CD_3OD .

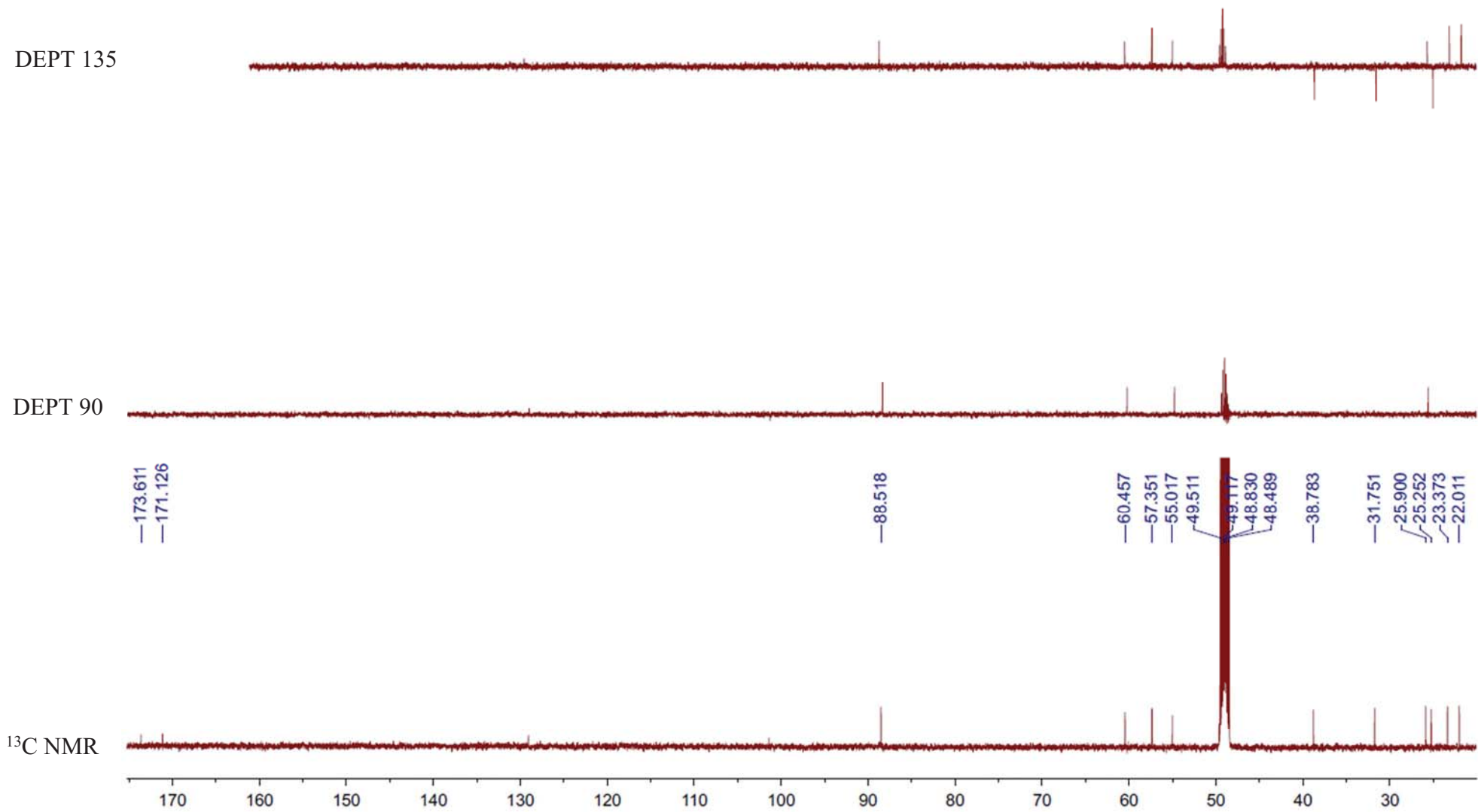


Figure S46. ^{13}C NMR and DEPT spectra of compound 7 in CD_3OD .

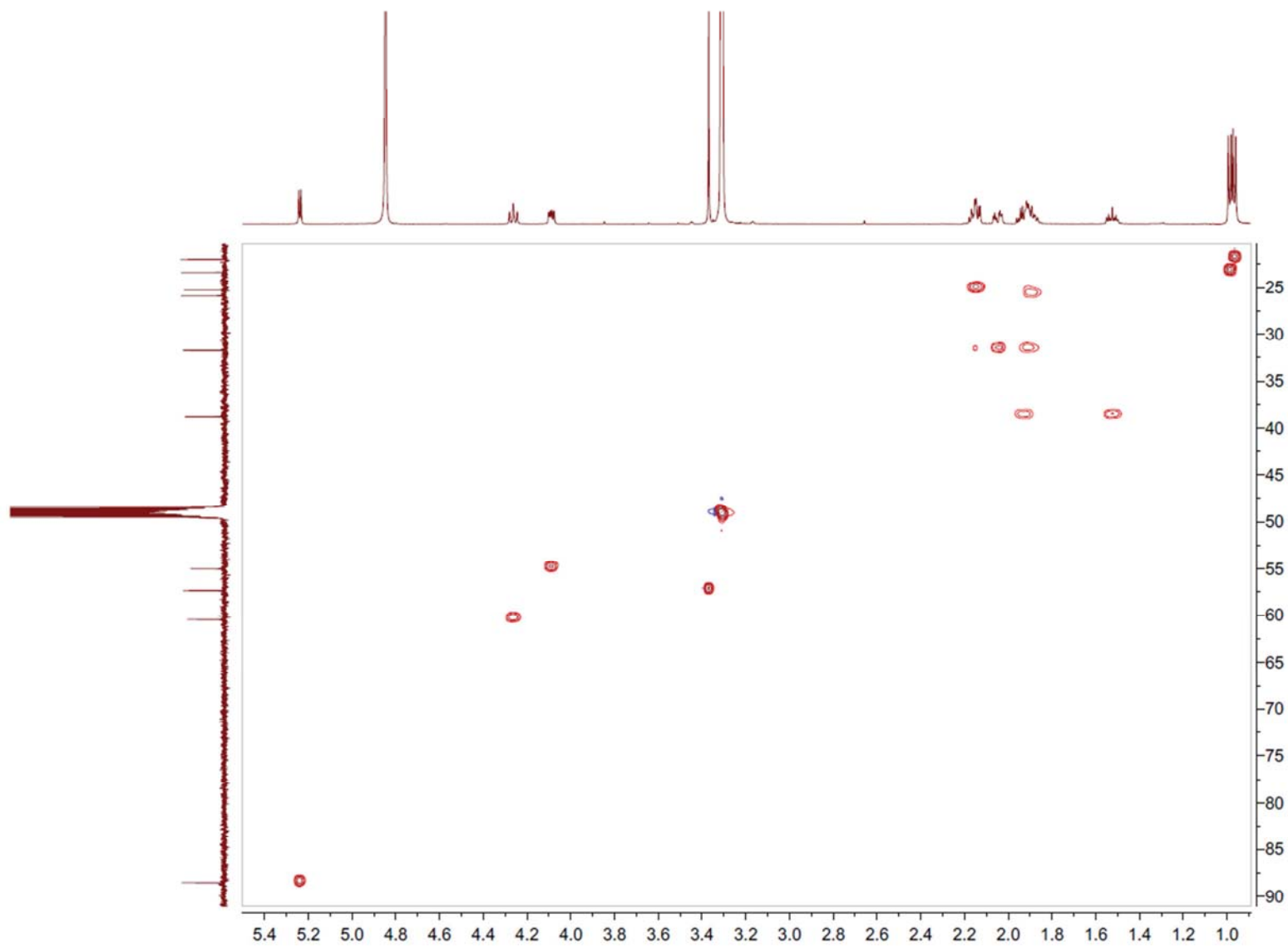


Figure S47. HSQC spectrum of compound 7 in CD₃OD.

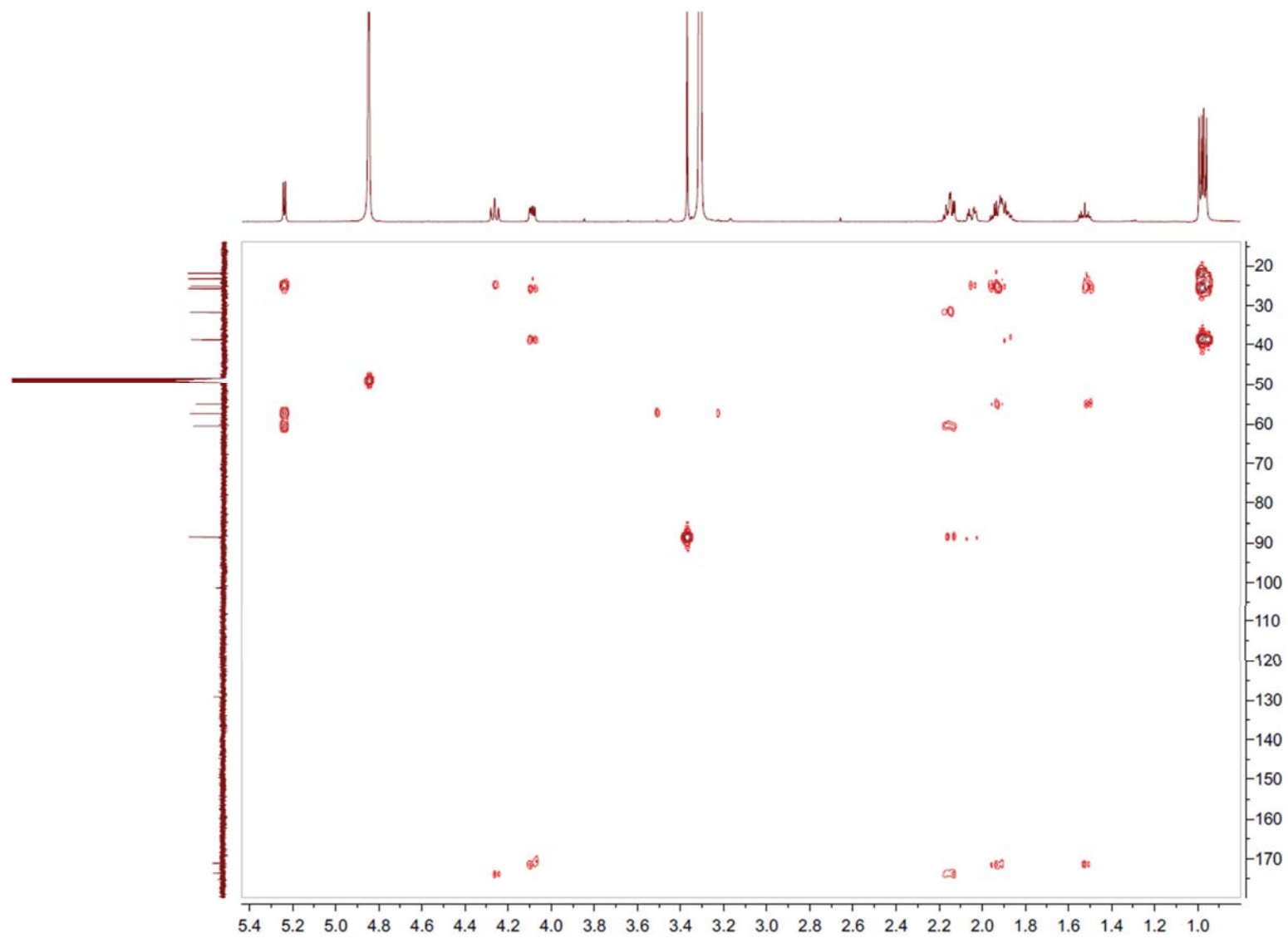


Figure S48. HMBC spectrum of compound 7 in CD₃OD.

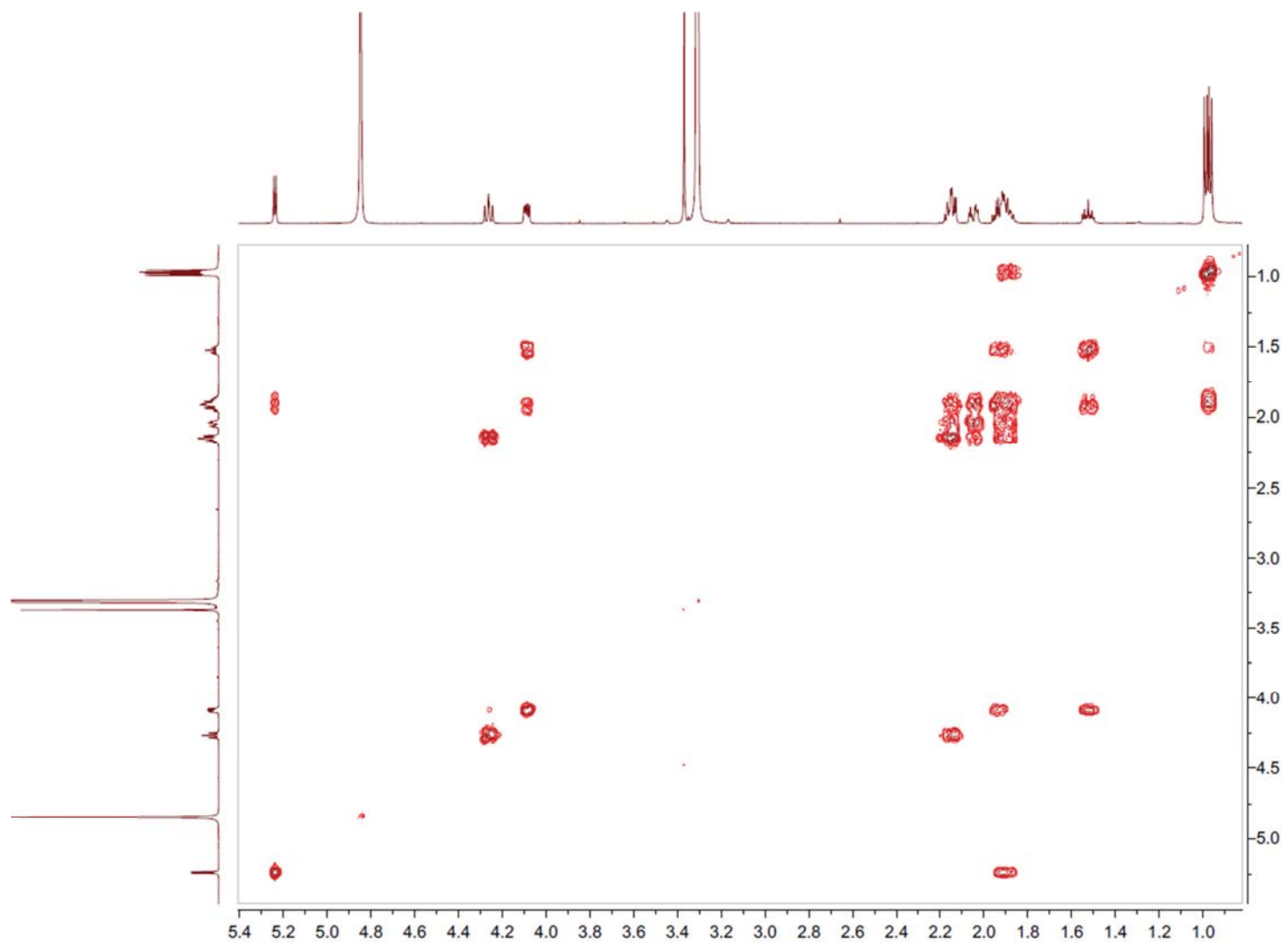


Figure S49. COSY spectrum of compound **7** in CD_3OD .

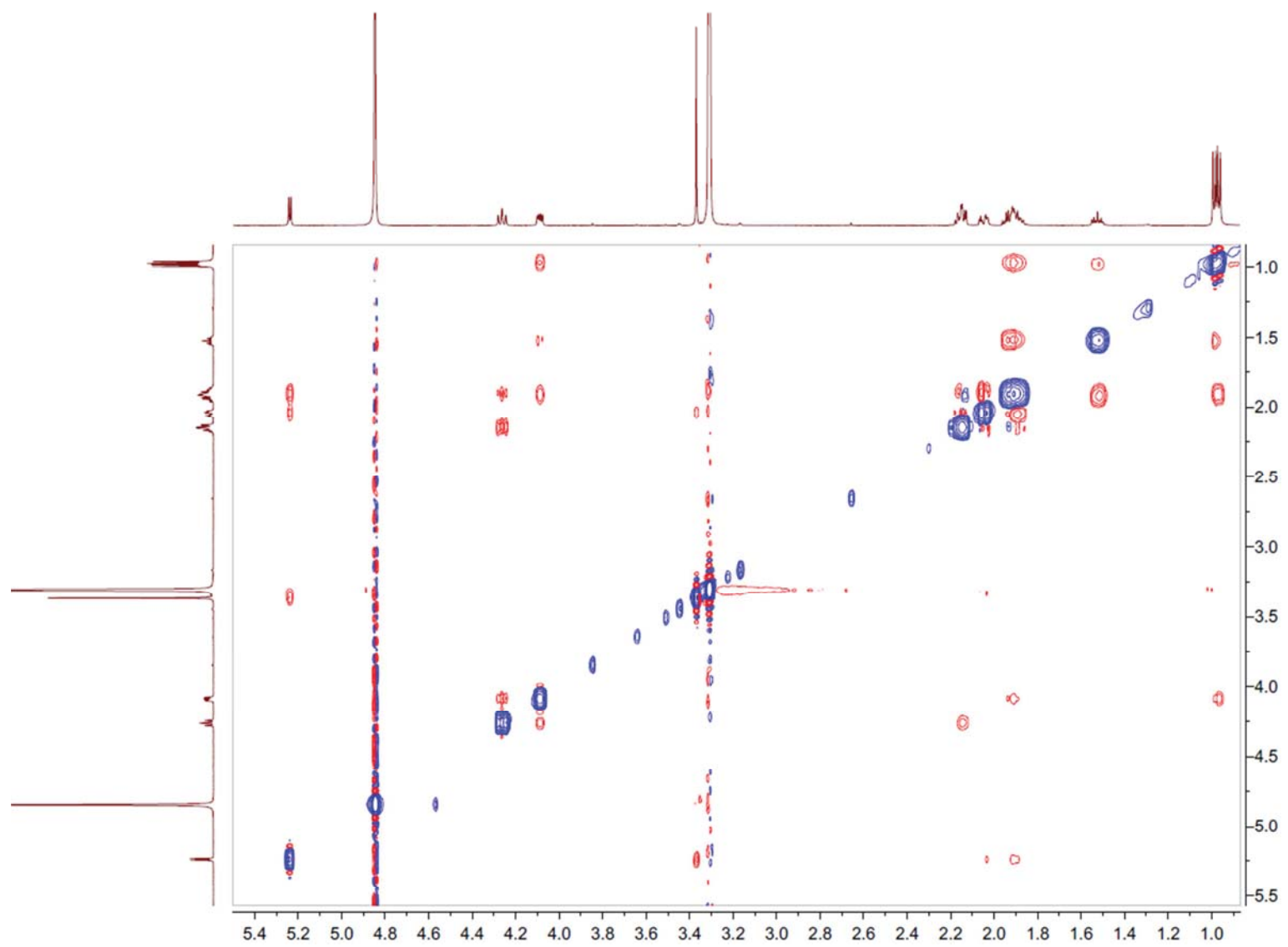


Figure S50. NOESY spectrum of compound **7** in CD₃OD.

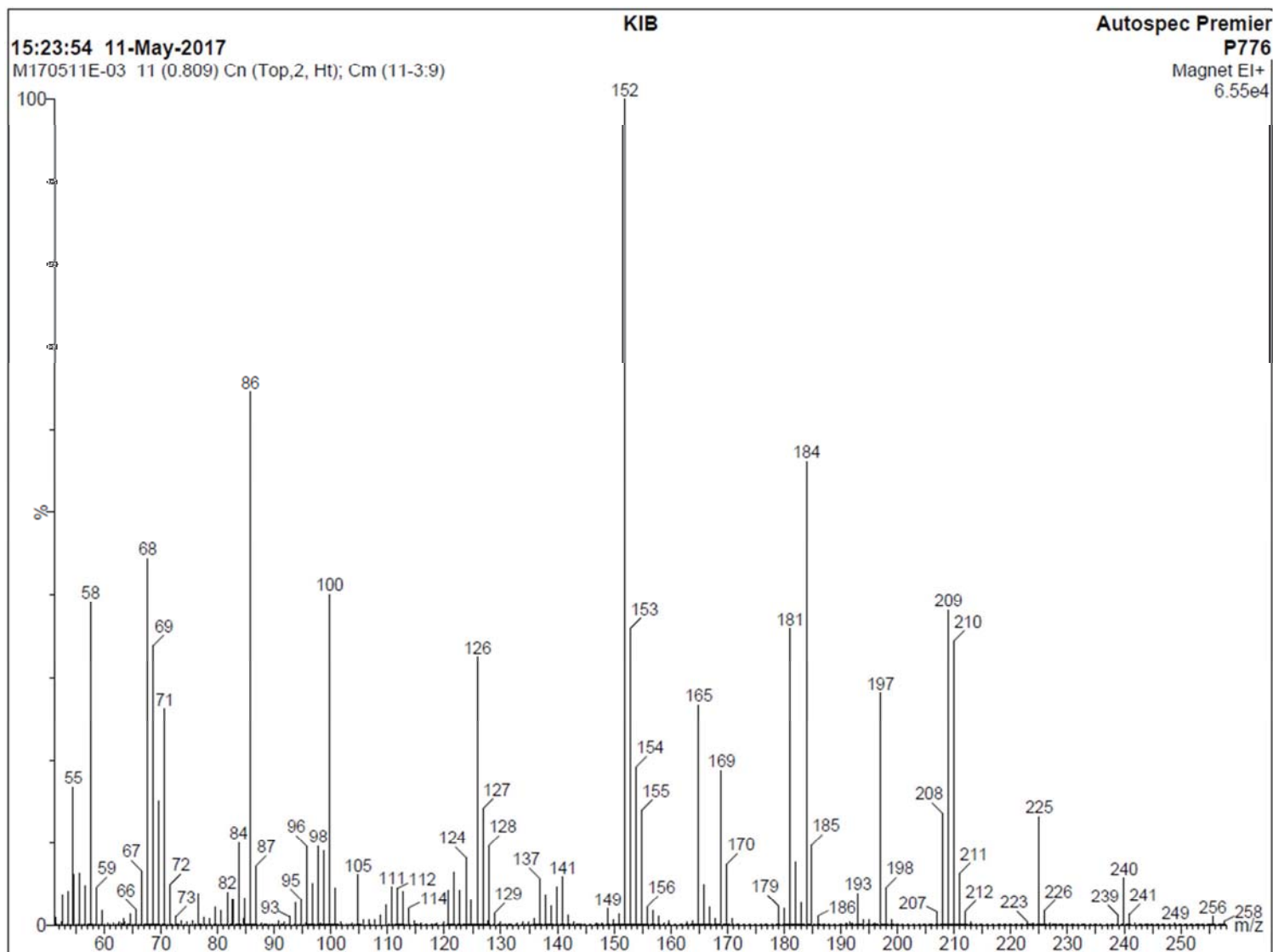


Figure S51. EIMS spectrum of compound 7.

Single Mass Analysis

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Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

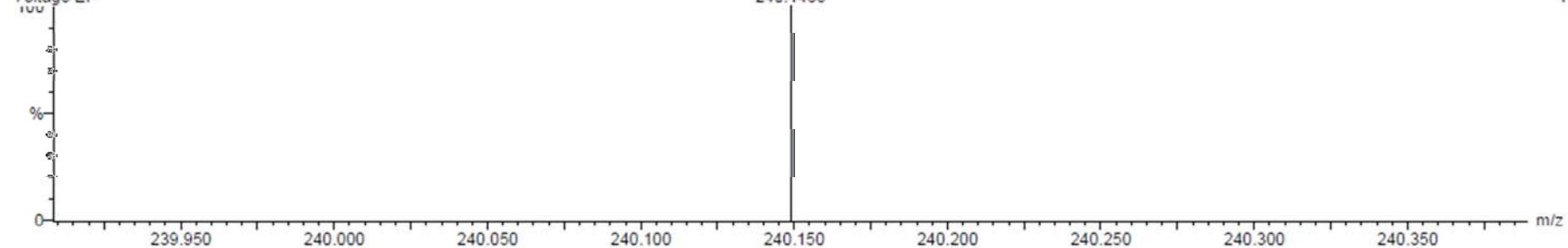
13 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)

Elements Used:

C: 0-200 H: 0-400 N: 2-2 O: 2-4

17:19:27 11-May-2017

Voltage EI+



Minimum:				-10.0		
Maximum:	200.0	10.0		120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
240.1488	240.1474	1.4	5.8	4.0	5546026.0	C12 H20 N2 O3

Figure S52. HREIMS spectrum of compound 7.

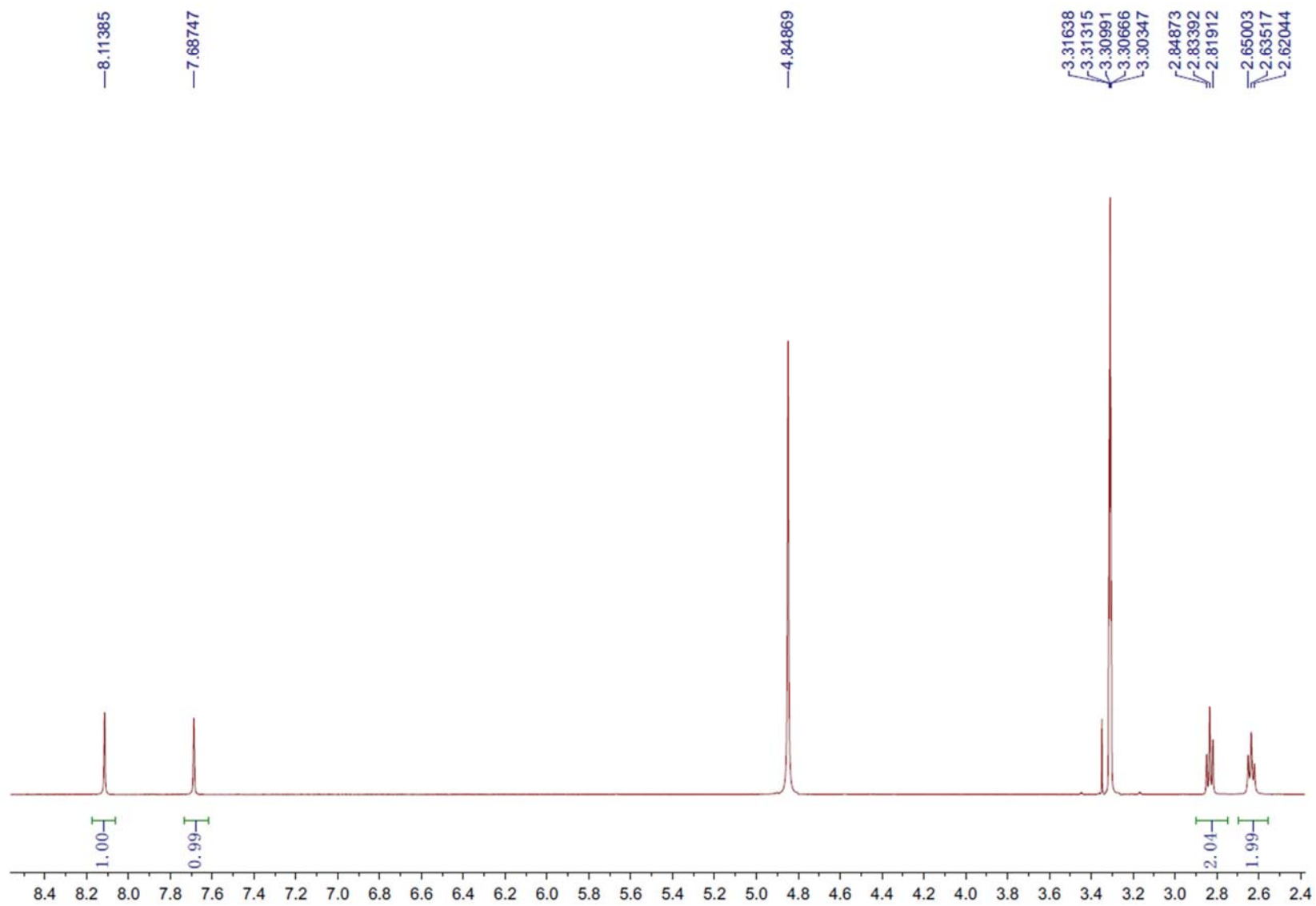


Figure S53. ^1H NMR spectrum of compound **8** in CD_3OD .

DEPT 135



DEPT 90



—176.154

—153.360

—140.094

—136.541

49.511

49.455

49.341

49.284

49.170

49.000

48.830

48.660

48.489

—33.673

—22.357

^{13}C NMR

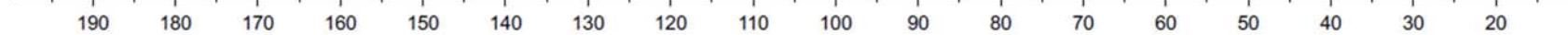


Figure S54. ^{13}C NMR and DEPT spectra of compound **8** in CD_3OD .

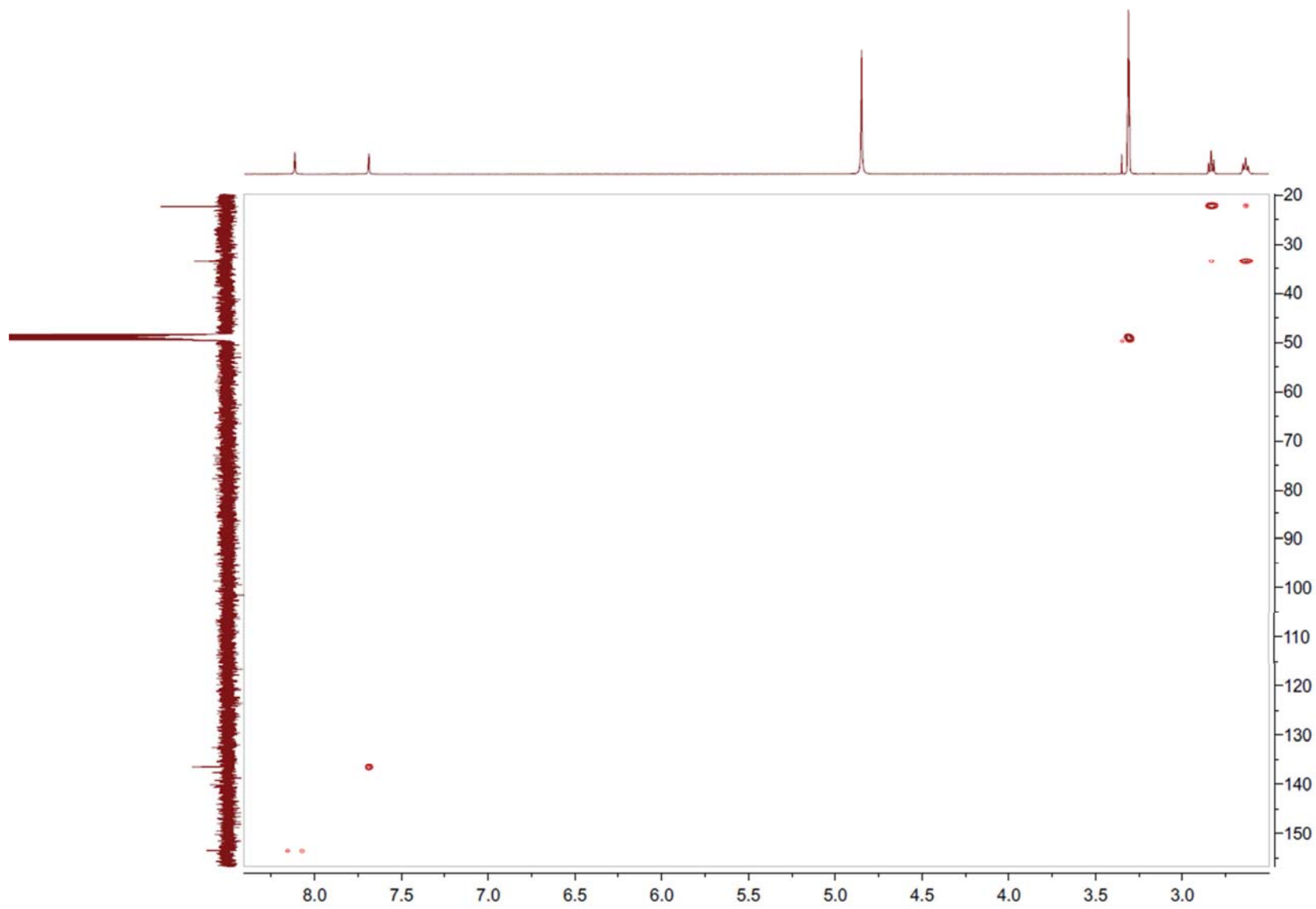


Figure S55. HSQC spectrum of compound **8** in CD₃OD.

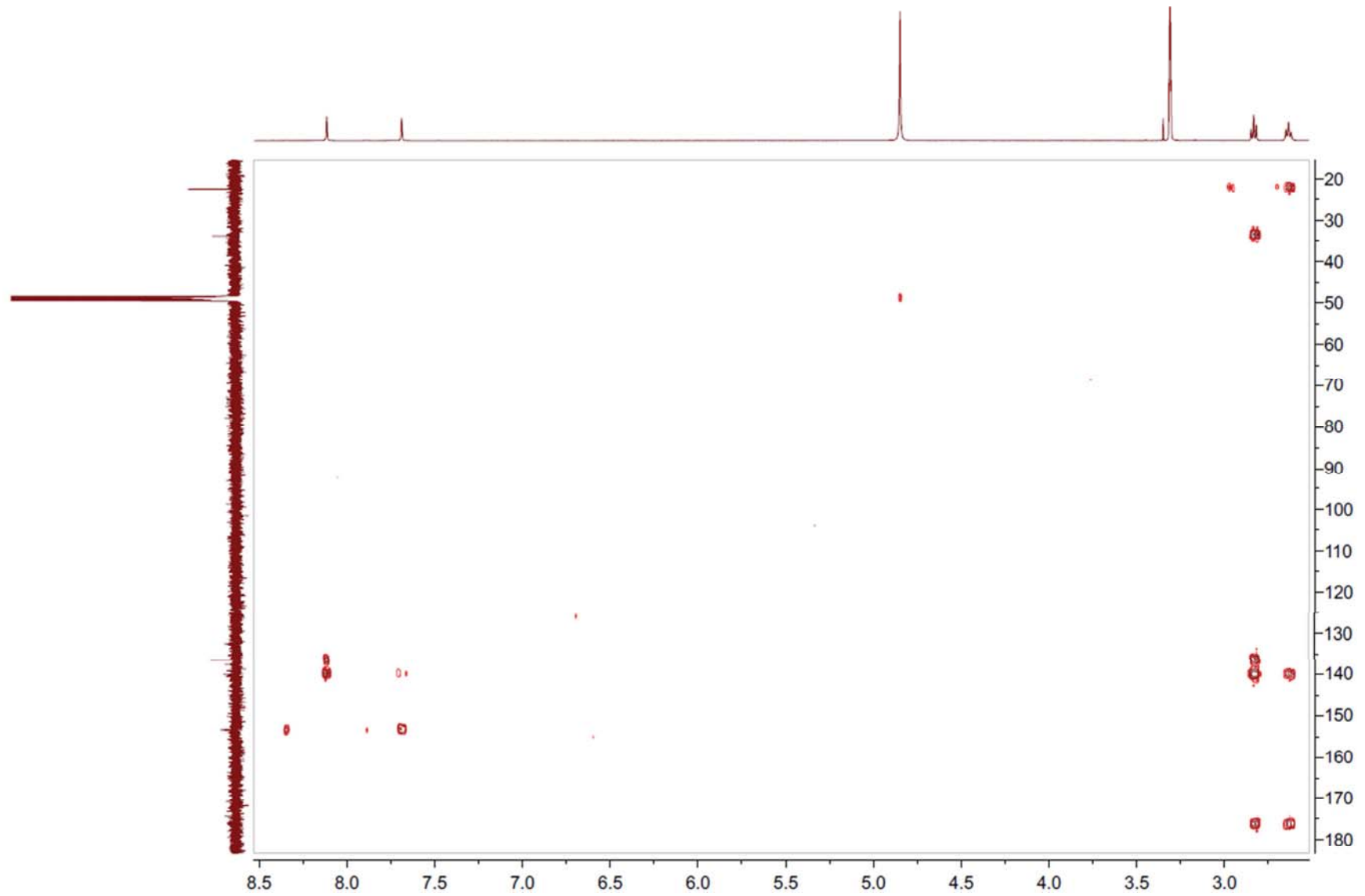


Figure S56. HMBC spectrum of compound 8 in CD₃OD.

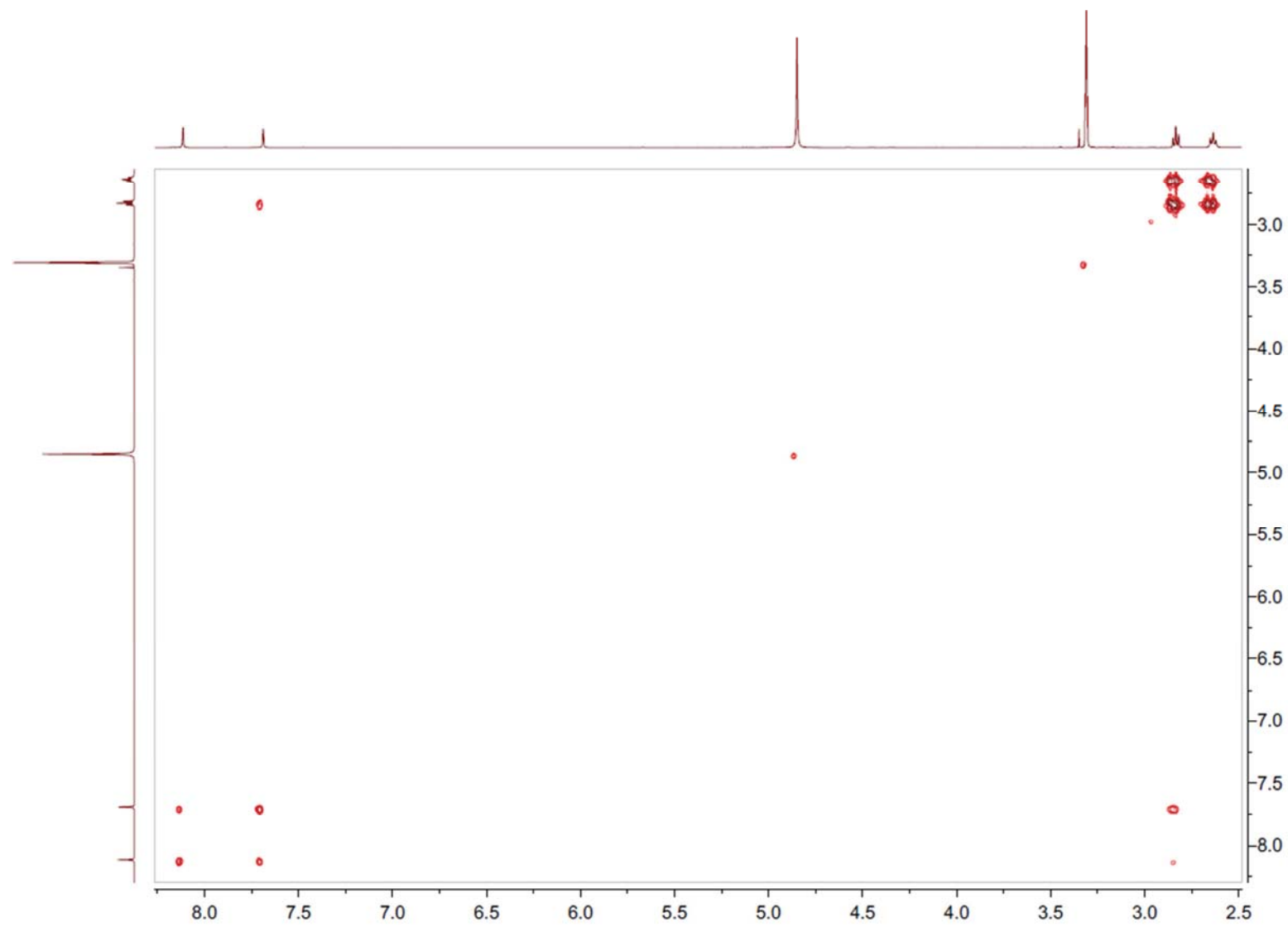


Figure S57. COSY spectrum of compound **8** in CD₃OD.

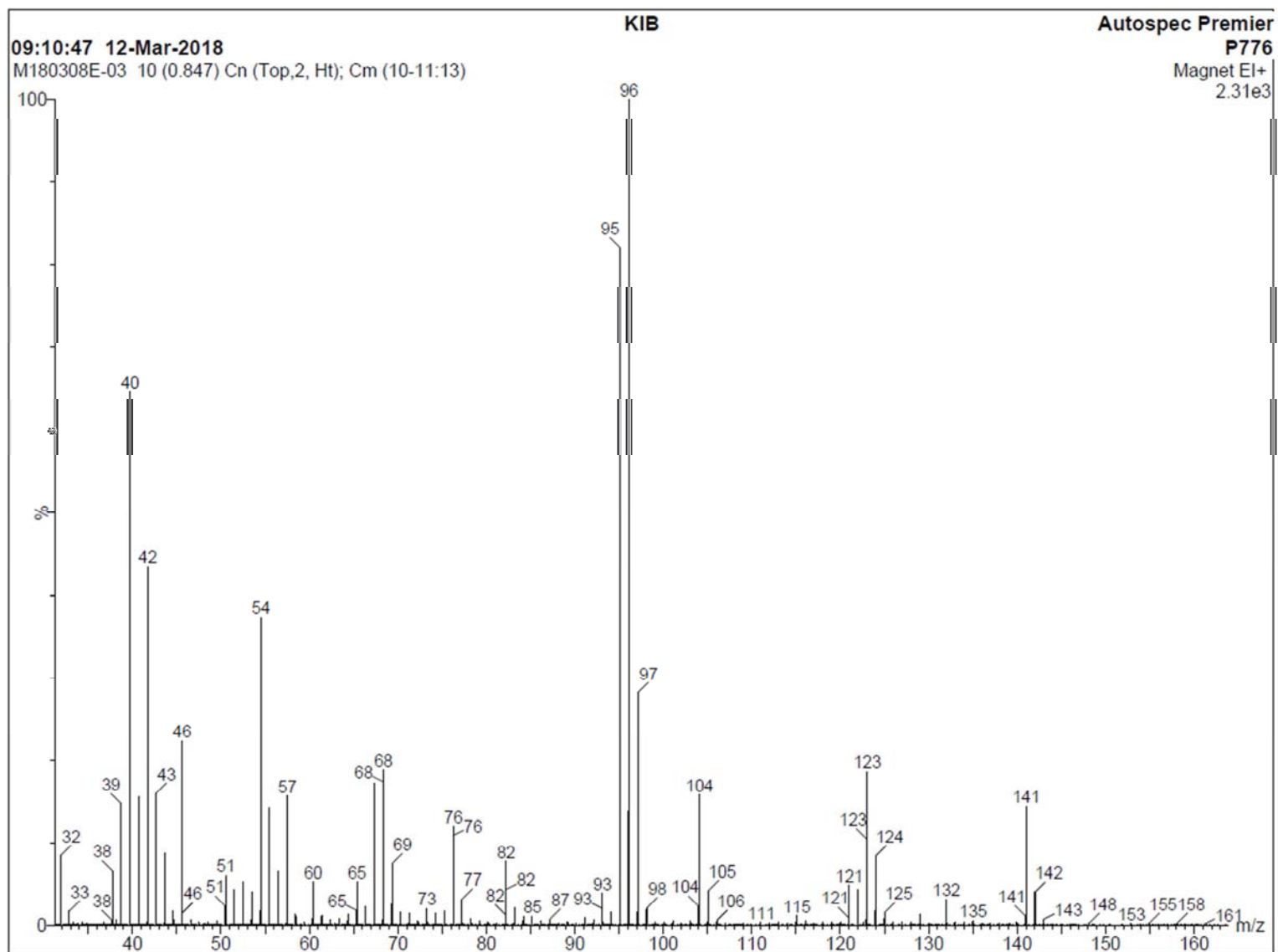


Figure S58. EIMS spectrum of compound 8.

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

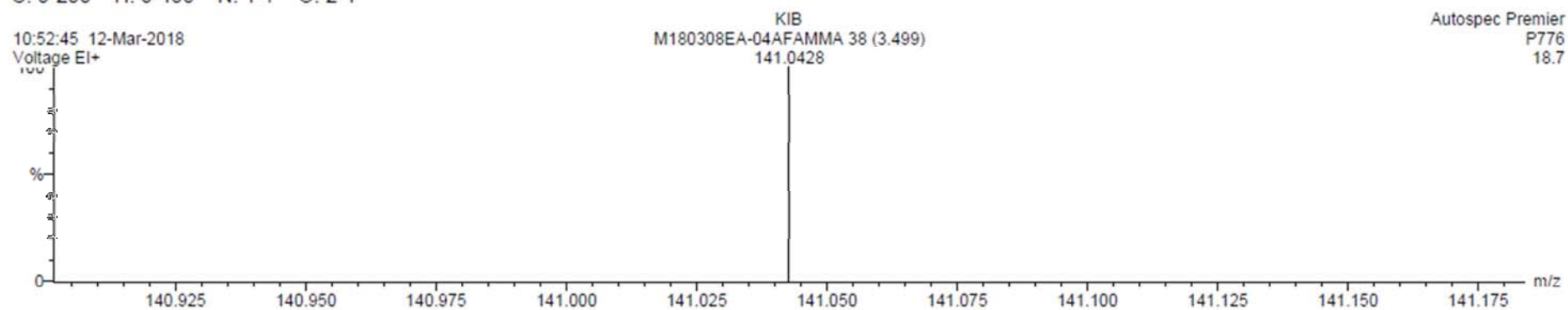
10 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)

Elements Used:

C: 0-200 H: 0-400 N: 1-1 O: 2-4

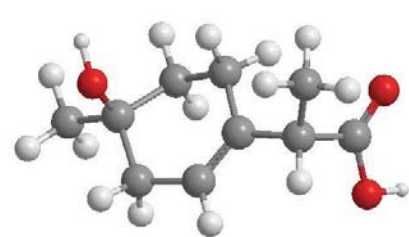
10:52:45 12-Mar-2018

Voltage EI+

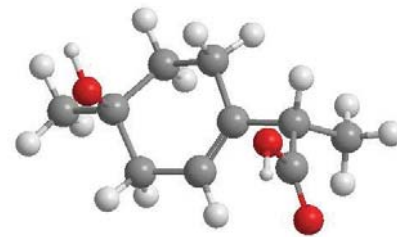


Minimum:				-10.0		
Maximum:	200.0	10.0		120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
141.0428	141.0426	0.2	1.4	4.0	5546025.5	C6 H7 N O3

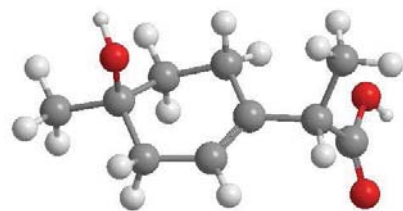
Figure S59. HREIMS spectrum of compound 8.



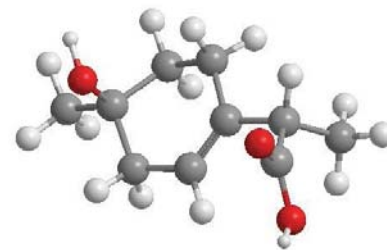
a (67.4%)



b (19.3%)



c (9.8%)



d (3.5%)

Figure S60. Energy-minimized conformers with populations of (3*S*,7*S*)-1-hydroxy-3-*p*-menthen-9-oic acid.
(Regardless of rotations of methyl and hydroxy groups)

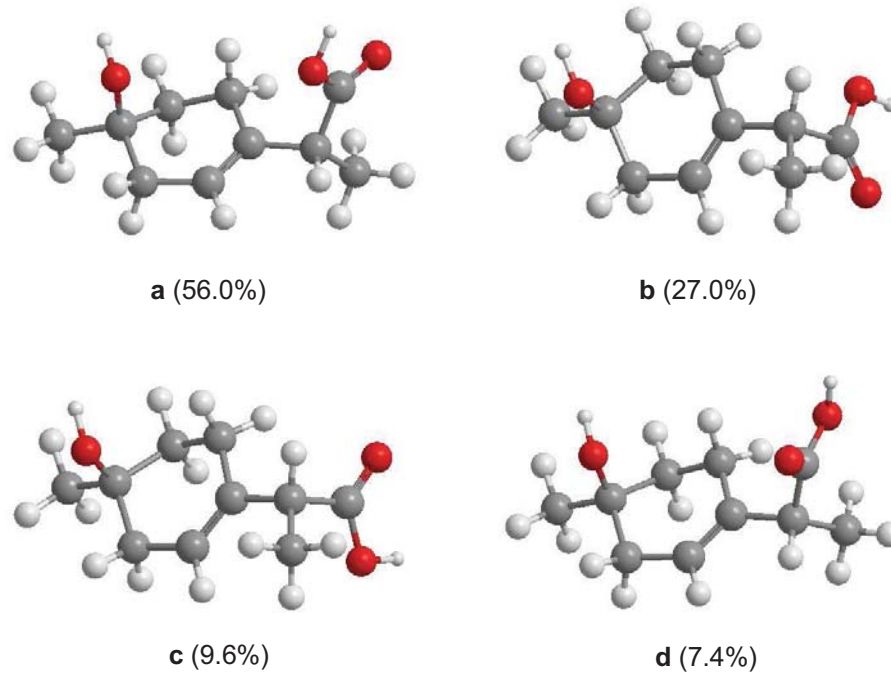


Figure S61. Energy-minimized conformers with populations of (3*S*,7*R*)-1-hydroxy-3-*p*-menthen-9-oic acid.
(Regardless of rotations of methyl and hydroxy groups)

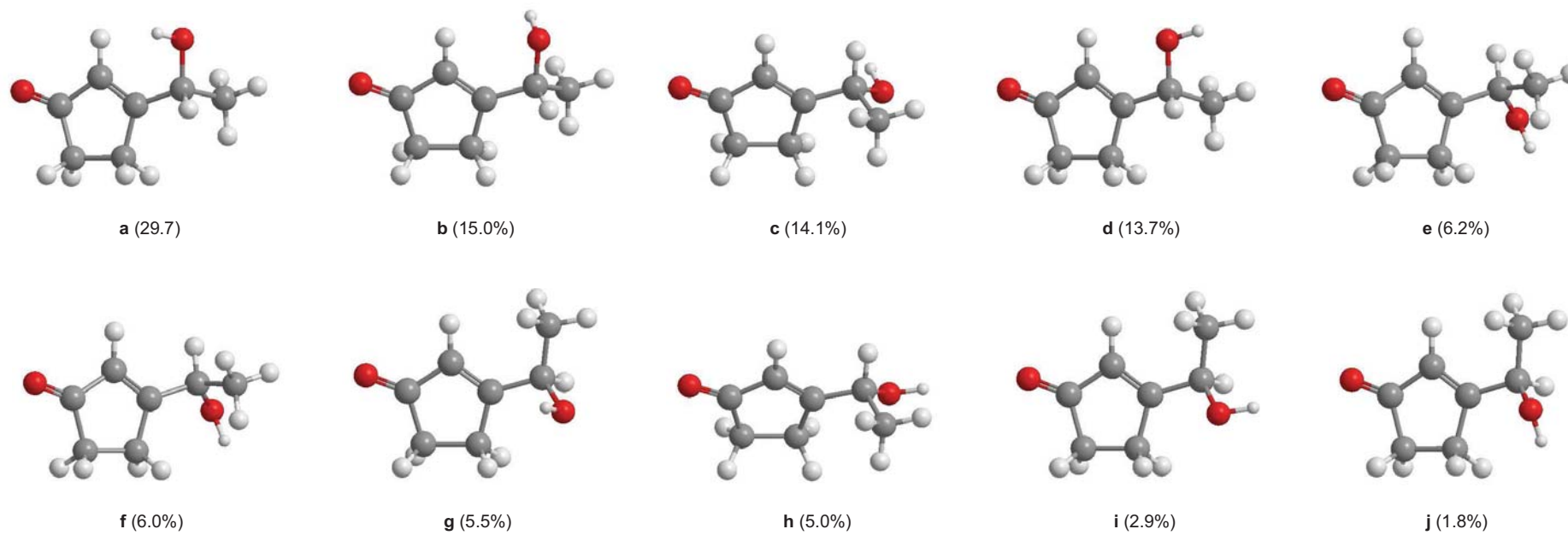


Figure S62. Energy-minimized conformers with populations of compound 5.

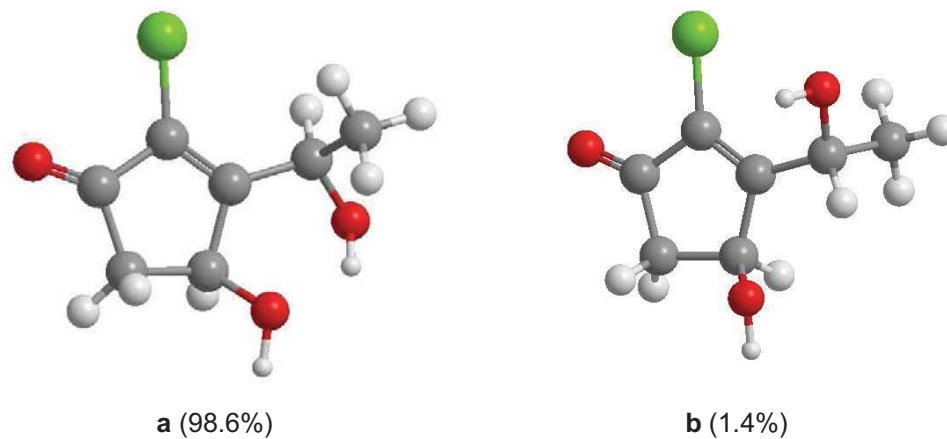


Figure S63. Energy-minimized conformers with populations of (3*S*,6*R*)-3-hydroxytrichodenone C.
(Regardless of rotations of methyl and hydroxy groups)

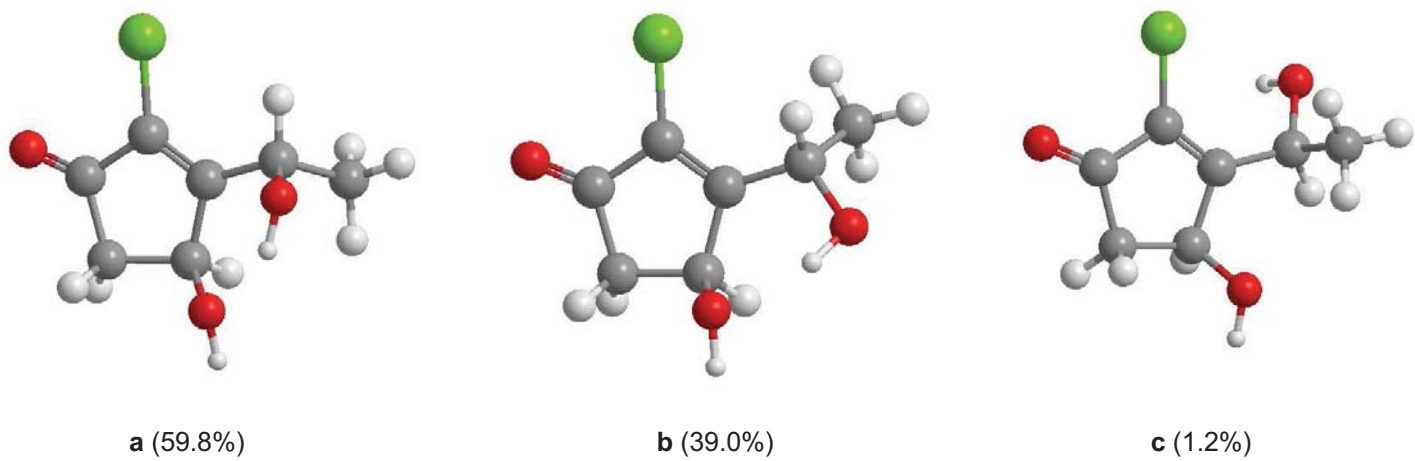


Figure S64. Energy-minimized conformers with populations of (3*S*,6*S*)-3-hydroxytrichodenone C.
(Regardless of rotations of methyl and hydroxy groups)