

Supporting information

Cytotoxic Bryostatin Derivatives from the South China Sea Bryozoan

Bugula neritina

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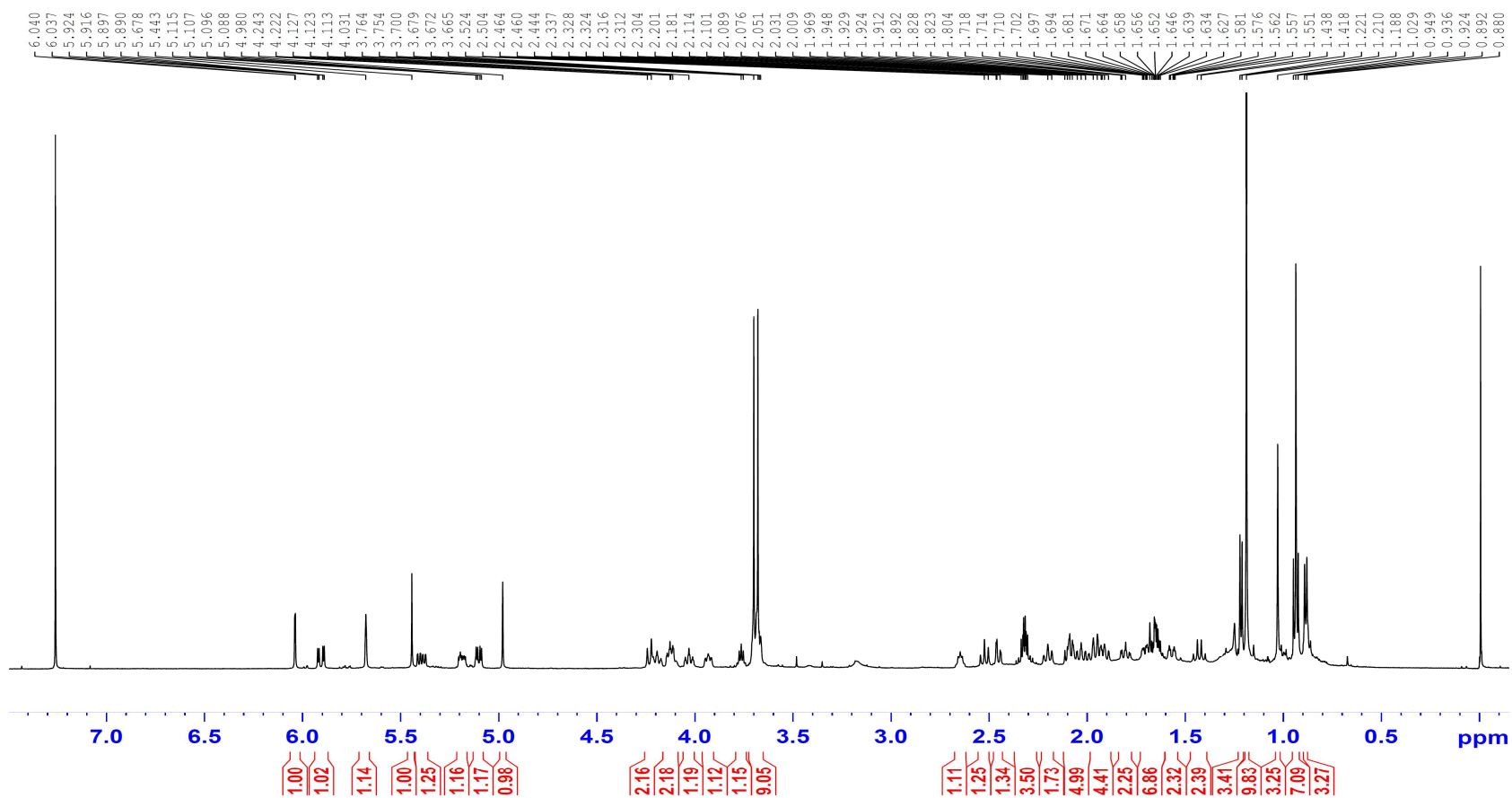
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Oncogenes and Related Genes, Renji Hospital, School of Medicine, Shanghai Jiao
Tong University, 160 Pujian Road, Shanghai 200127, China

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+86-21-58732594. E-mail: franklin67@126.com (H. W. Lin).

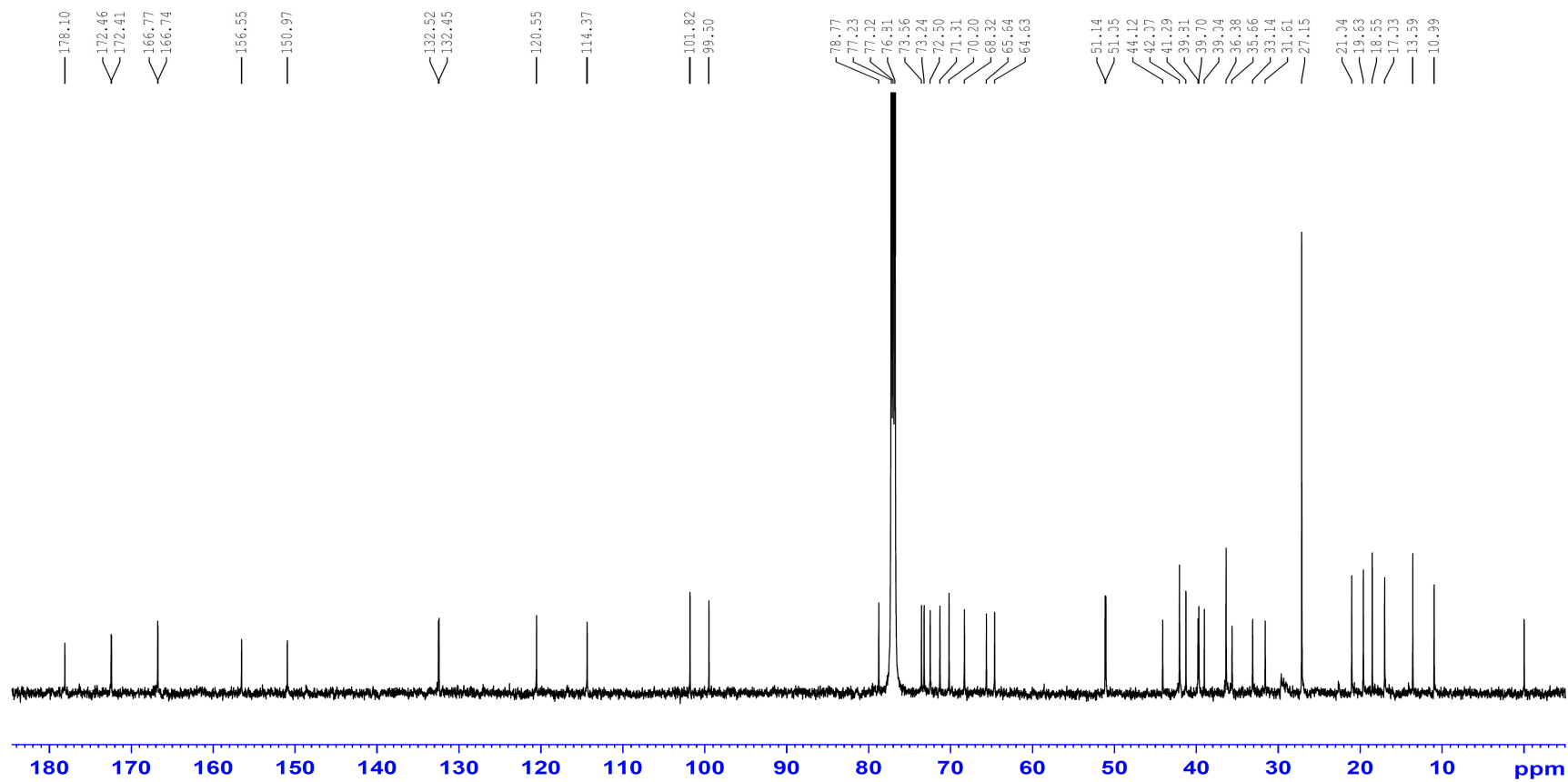
|| These authors contributed equally to this paper.

- S1.** ^1H NMR spectrum of compound **1** in CDCl_3 .
- S2.** ^{13}C NMR spectrum of compound **1** in CDCl_3 .
- S3.** DEPT135 Spectrum of compound **1** in CDCl_3 .
- S4.** HSQC spectrum of compound **1** in CDCl_3 .
- S5.** HMBC spectrum of compound **1** in CDCl_3 .
- S6.** ^1H - ^1H COSY spectrum of compound **1** in CDCl_3 .
- S7.** NOESY spectrum of compound **1** in CDCl_3 .
- S8.** IR spectrum of compound **1**.
- S9.** HRESIMS of compound **1**.
- S10.** UV spectrum of compound **1**.
- S11.** ^1H NMR spectrum of compound **2** in CDCl_3 .
- S12.** ^{13}C NMR spectrum of compound **2** in CDCl_3 .
- S13.** DEPT135 Spectrum of compound **2** in CDCl_3 .
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- S15.** HMBC spectrum of compound **2** in CDCl_3 .
- S16.** ^1H - ^1H COSY spectrum of compound **2** in CDCl_3 .
- S17.** NOESY spectrum of compound **2** in CDCl_3 .
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- S19.** HRESIMS of compound **2**.
- S20.** UV spectrum of compound **2**.
- S21.** ^1H NMR spectrum of the mixture of compound **3** and **4** in CDCl_3 .
- S22.** ^{13}C NMR spectrum of the mixture of compound **3** and **4** in CDCl_3 .
- S23.** DEPT135 Spectrum of the mixture of compound **3** and **4** in CDCl_3 .
- S24.** HSQC spectrum of the mixture of compound **3** and **4** in CDCl_3 .
- S25.** HMBC spectrum of the mixture of compound **3** and **4** in CDCl_3 .
- S26.** ^1H - ^1H COSY spectrum of the mixture of compound **3** and **4** in CDCl_3 .
- S27.** NOESY spectrum of the mixture of compound **3** and **4** in CDCl_3 .
- S28.** IR spectrum of the mixture of compound **3** and **4**.
- S29.** HRESIMS of the mixture of compound **3** and **4**.
- S30.** UV spectrum of the mixture of compound **3** and **4**.
- S31.** The pure form of compound **3** or **4** can be immediately interconvert into a mixture of the $\Delta^{21,34}$ *E* and $\Delta^{21,34}$ *Z* forms at room temperature.
- S32.** COSY, key HMBC, and selected NOESY correlations of compound **2**.

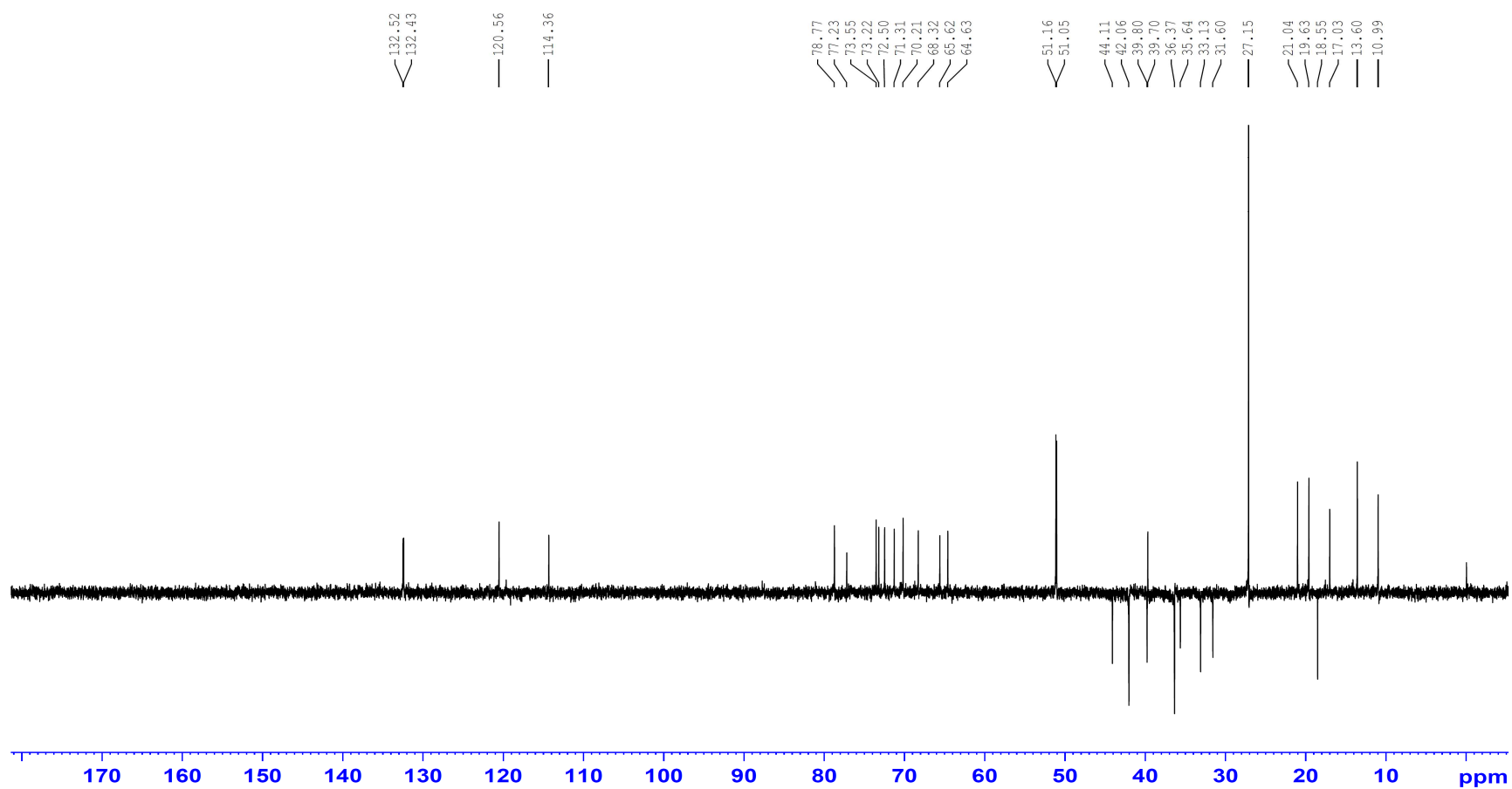
S1. ^1H NMR spectrum of compound **1** in CDCl_3 .



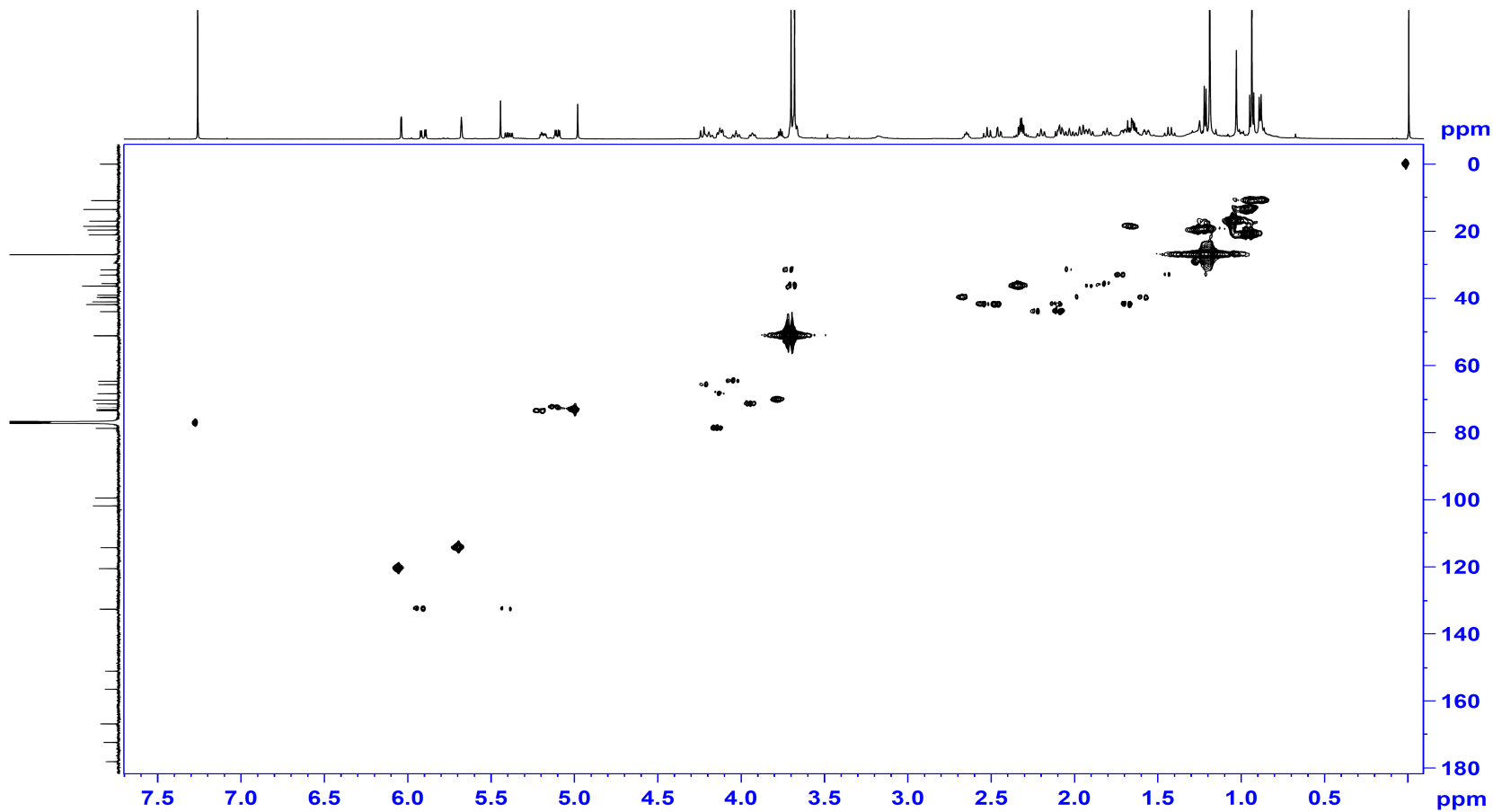
S2. ^{13}C NMR spectrum of compound **1** in CDCl_3 .



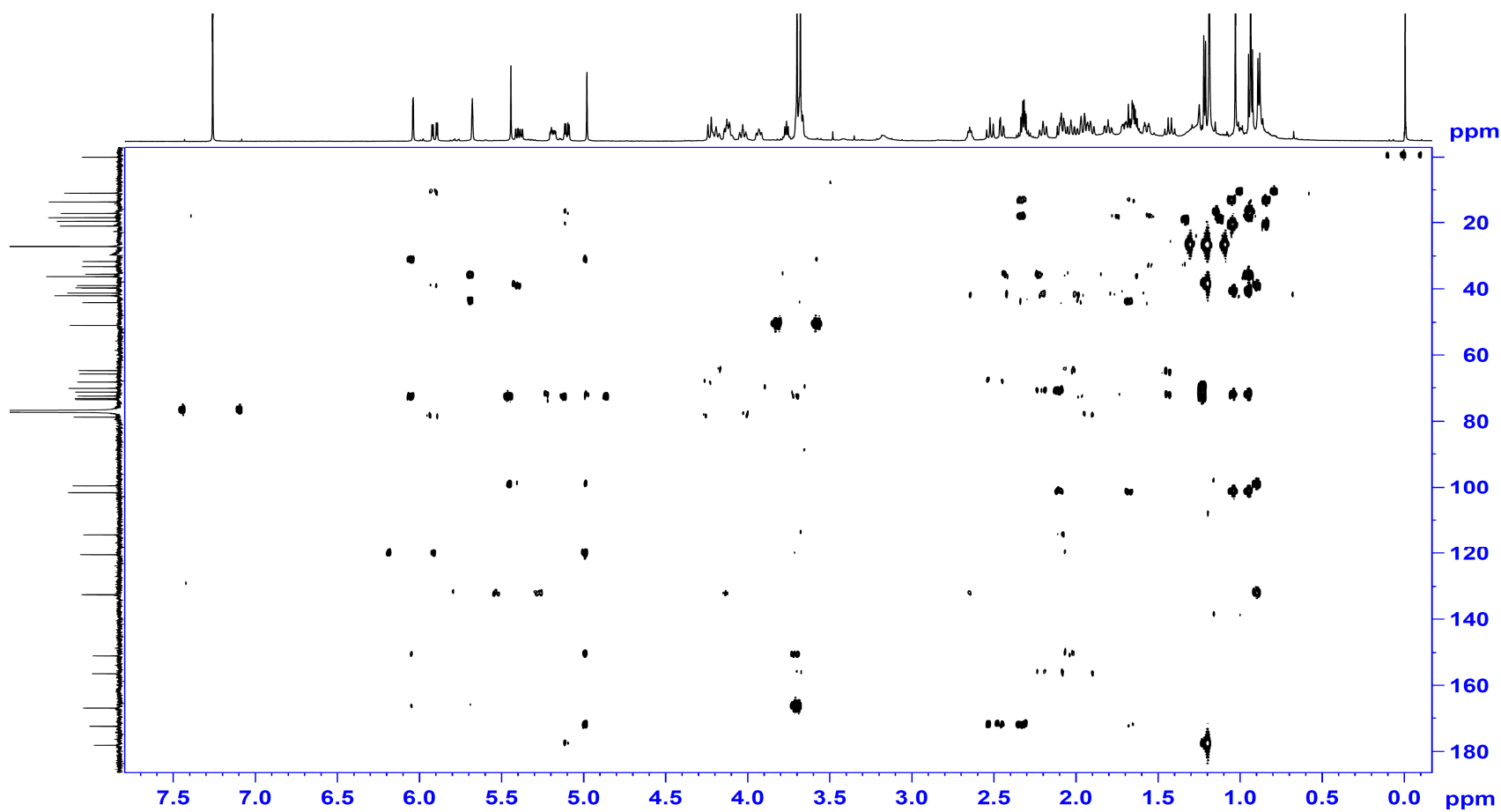
S3. DEPT135 Spectrum of compound **1** in CDCl₃.



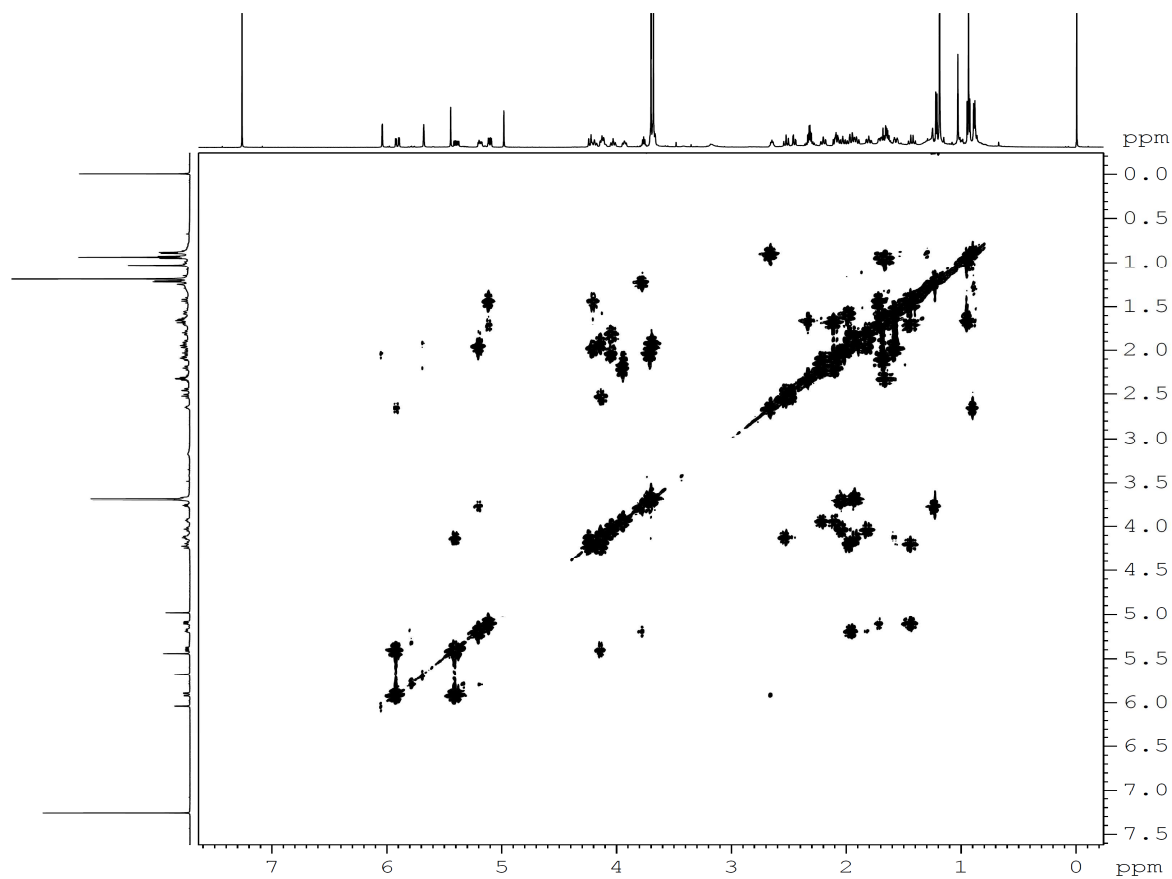
S4. HSQC spectrum of compound **1** in CDCl₃.



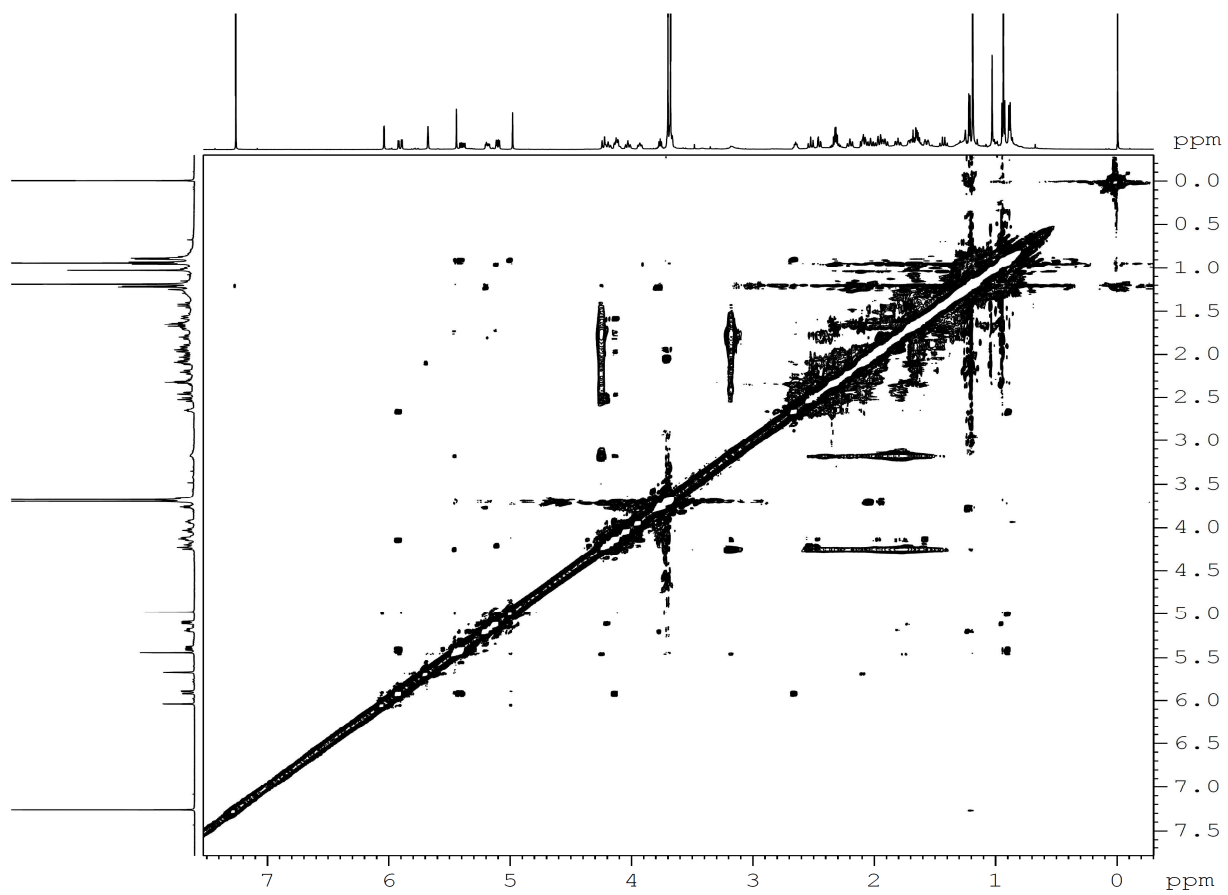
S5. HMBC spectrum of compound **1** in CDCl₃.



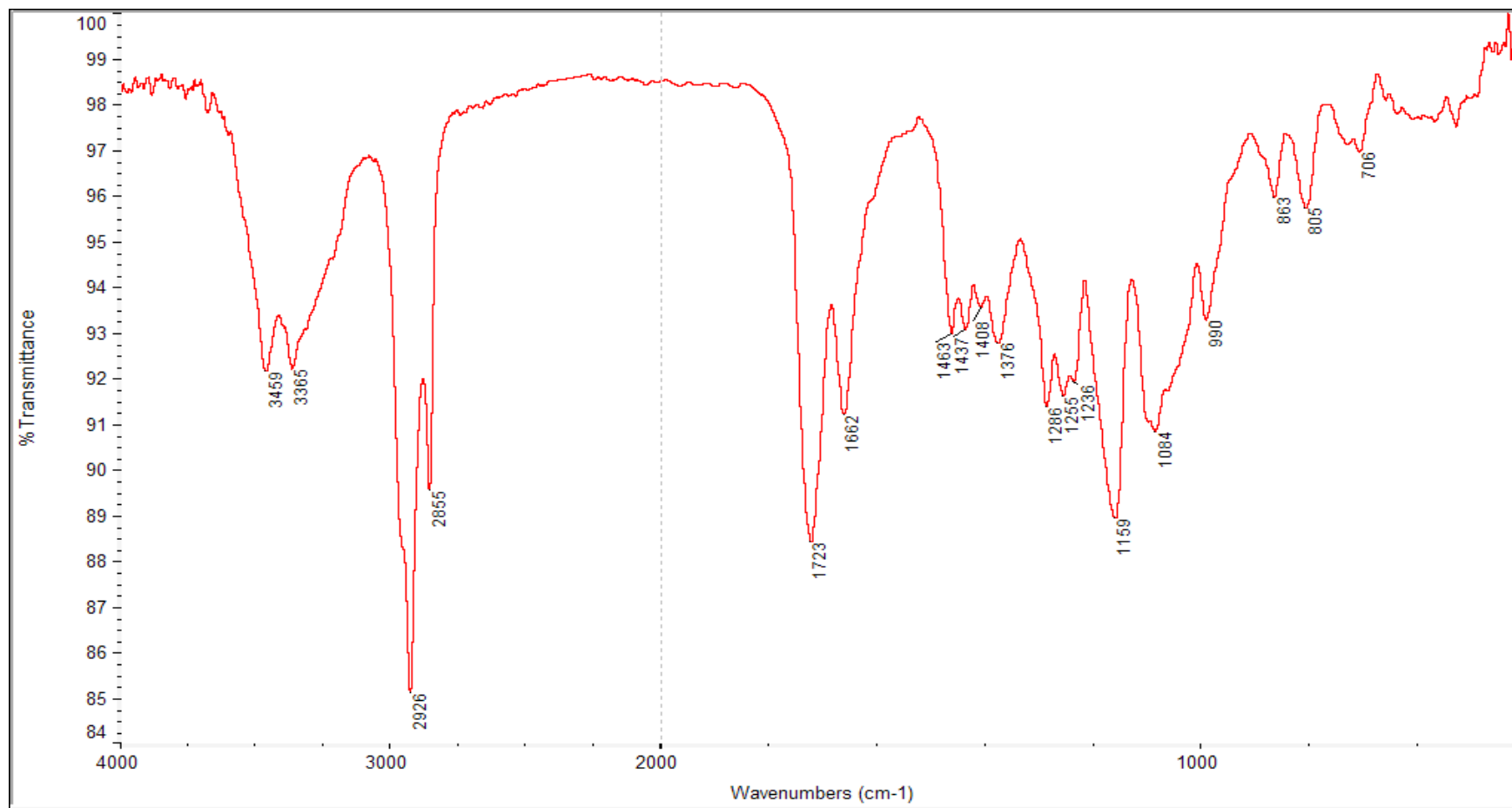
S6. ^1H - ^1H COSY spectrum of compound **1** in CDCl_3 .



S7. NOESY spectrum of compound **1** in CDCl₃.



S8. IR spectrum of compound **1**.



S9. HRESIMS of compound 1.

Elemental Composition Report

Page 1

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions

44 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 10-50 H: 10-90 O: 10-20 Na: 1-1

SIPI

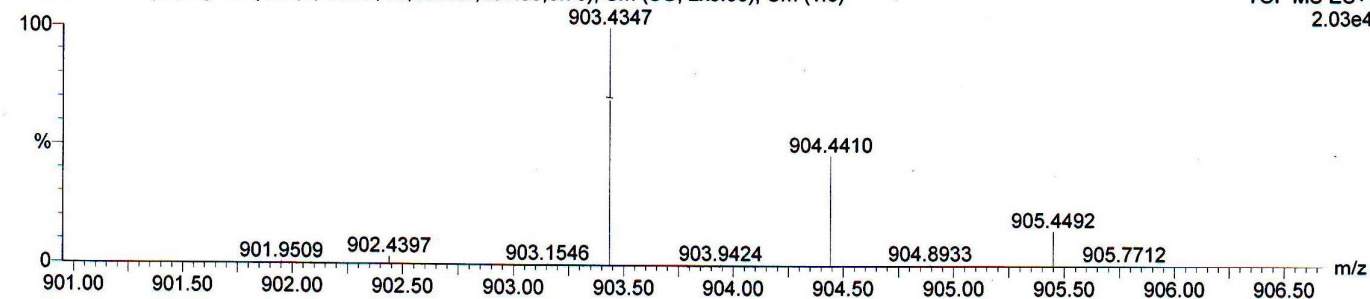
Q-ToF micro

21-May-2014, 14:34:21

YA019

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TOF MS ES+
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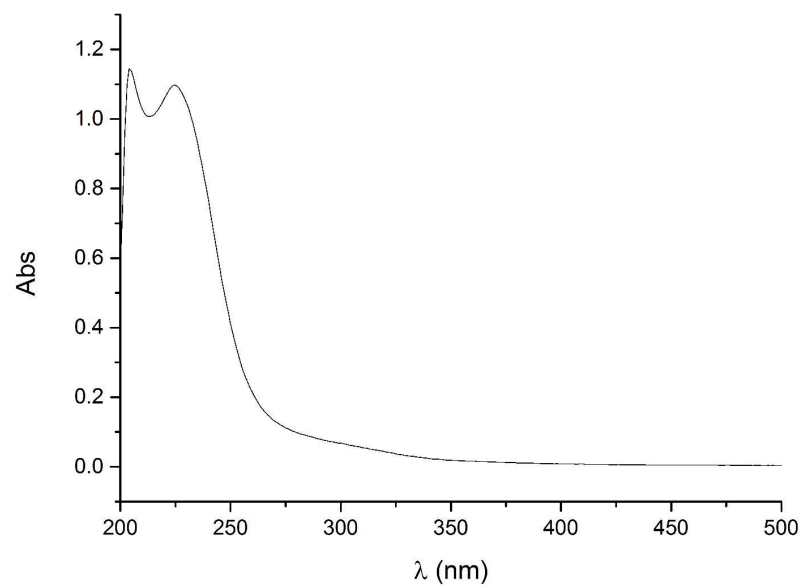


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Maximum: 100.00

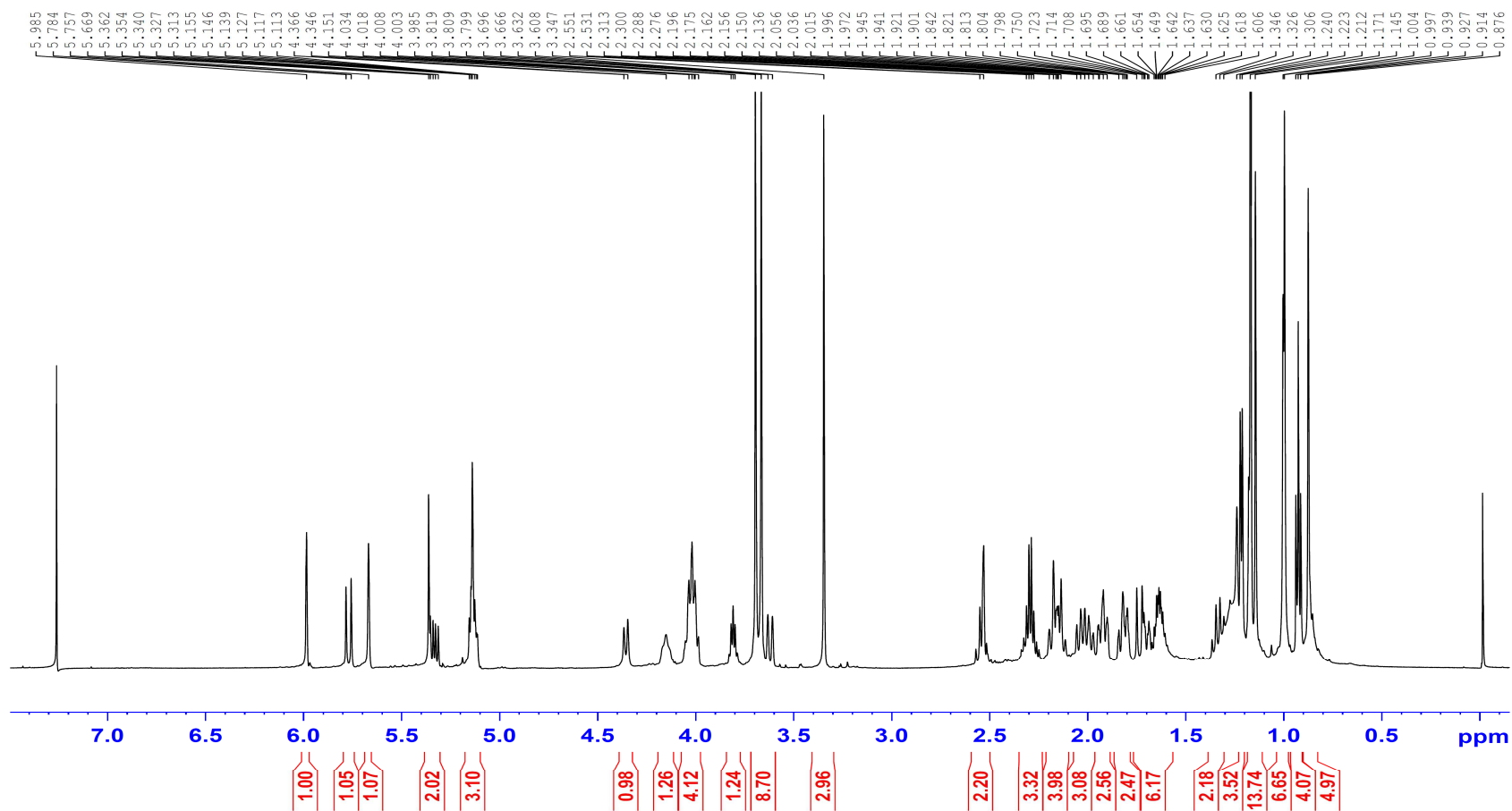
5.0 10.0 -1.5
50.0

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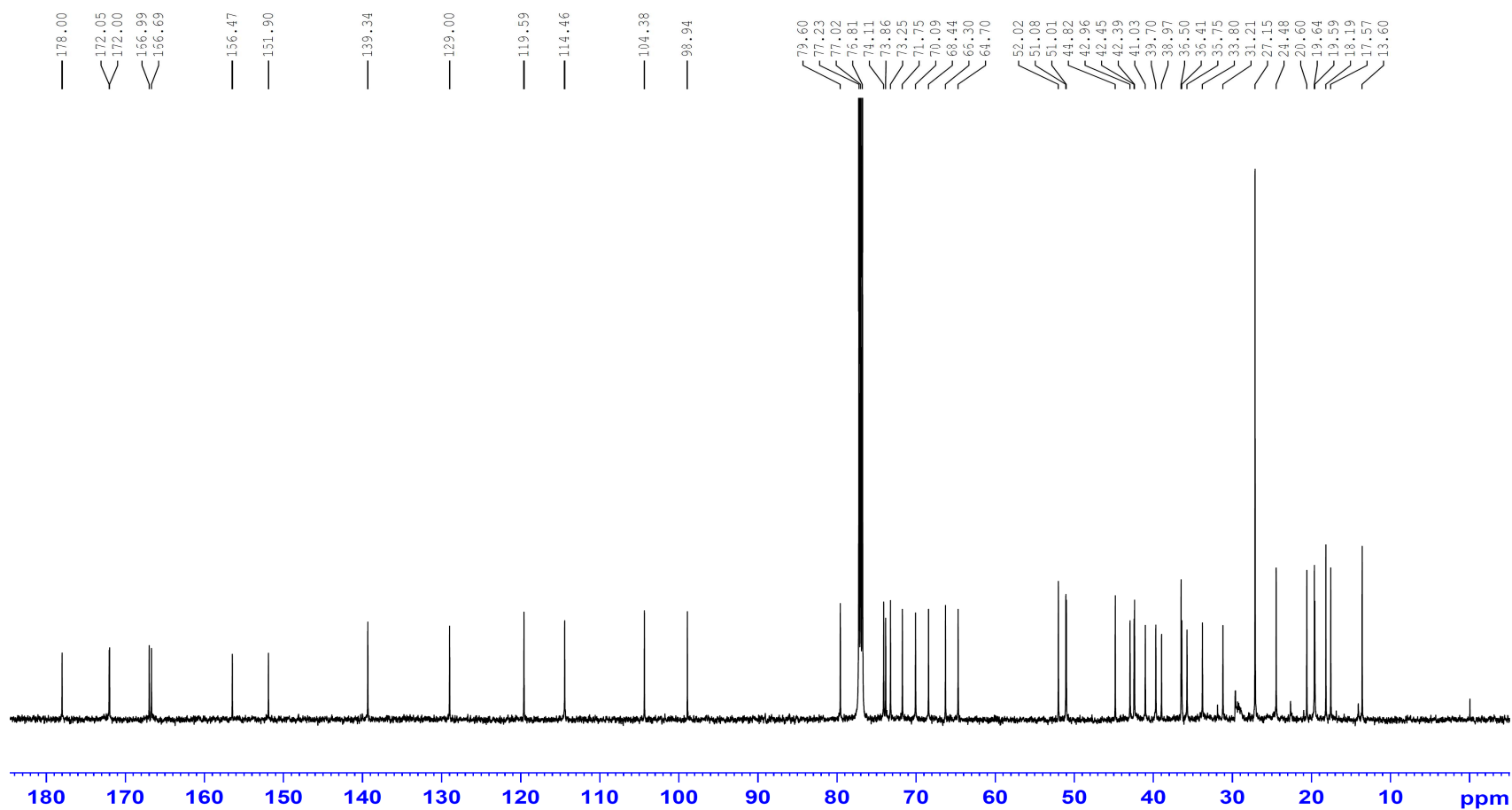
S10. UV spectrum of compound **1**.



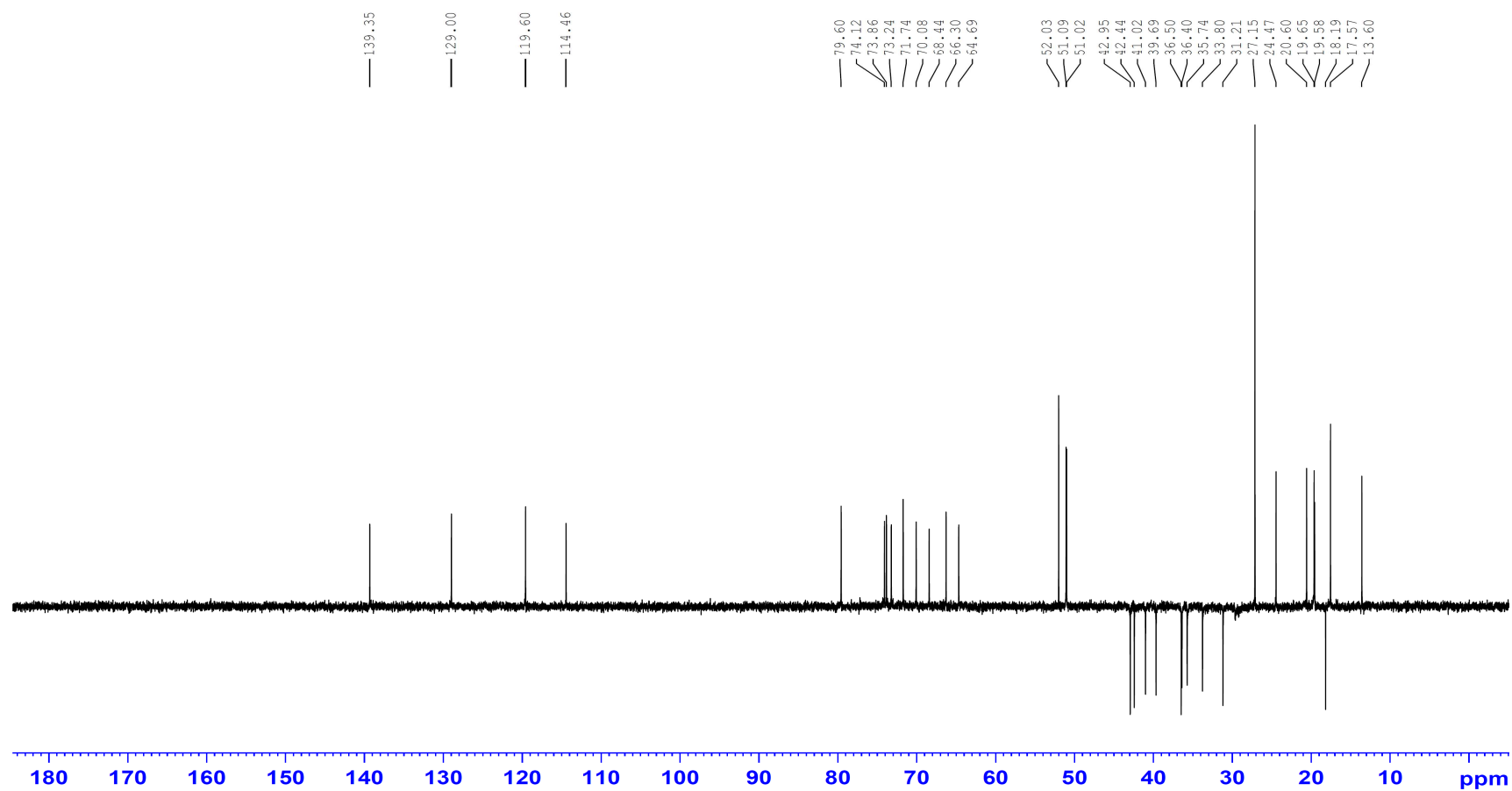
S11. ^1H NMR spectrum of compound **2** in CDCl_3 .



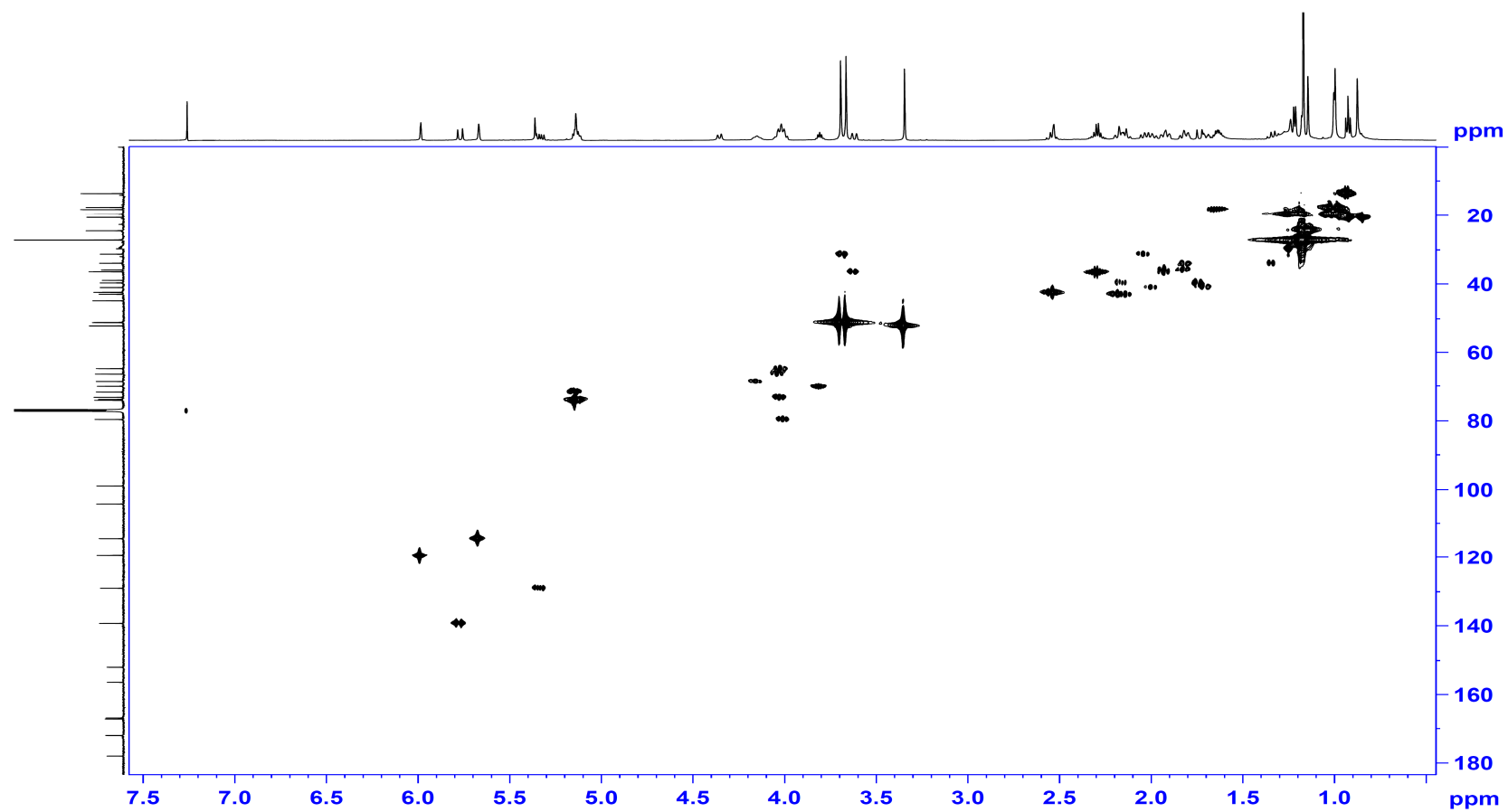
S12. ^{13}C NMR spectrum of compound **2** in CDCl_3 .



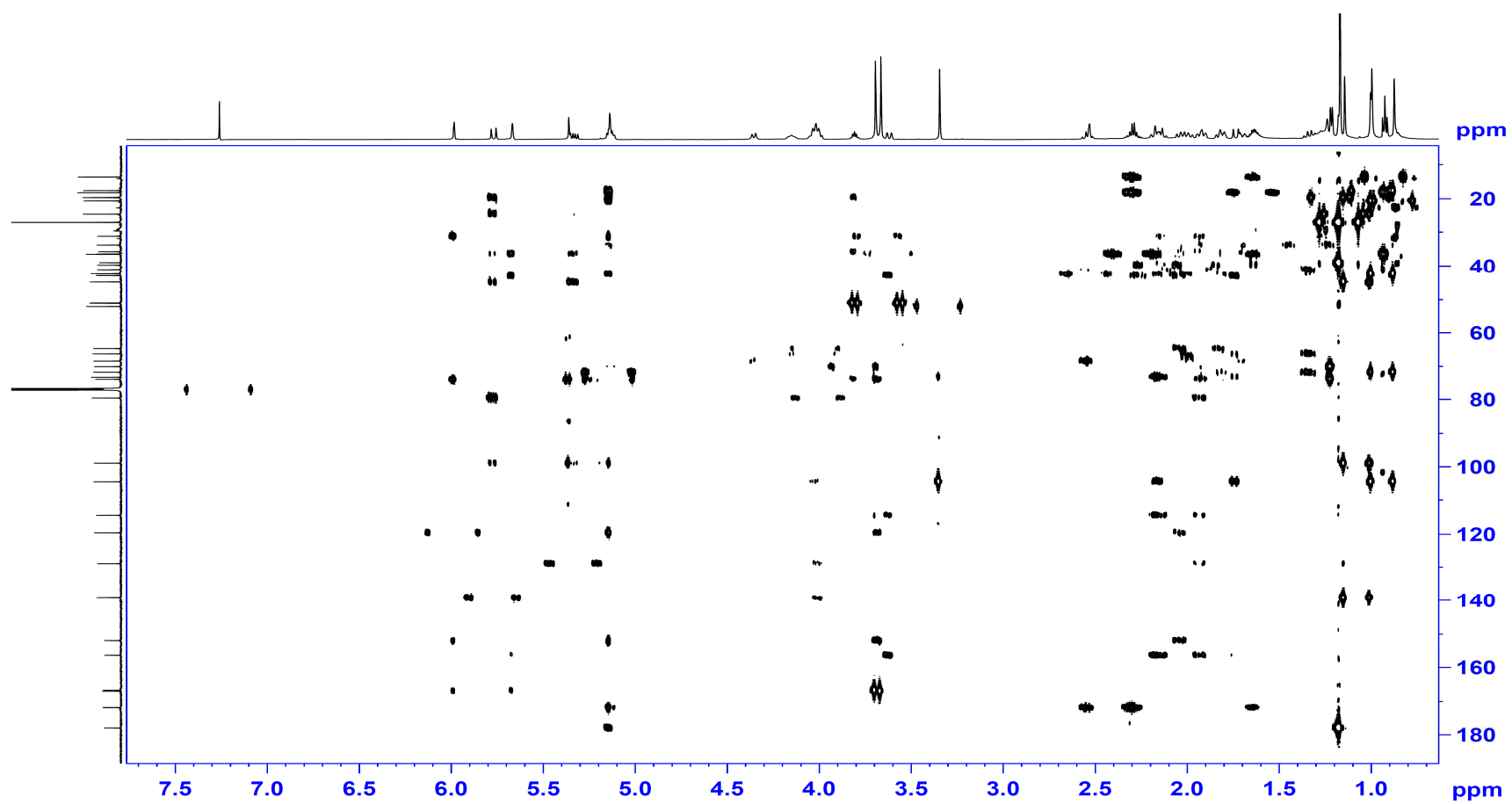
S13. DEPT135 Spectrum of compound **2** in CDCl₃.



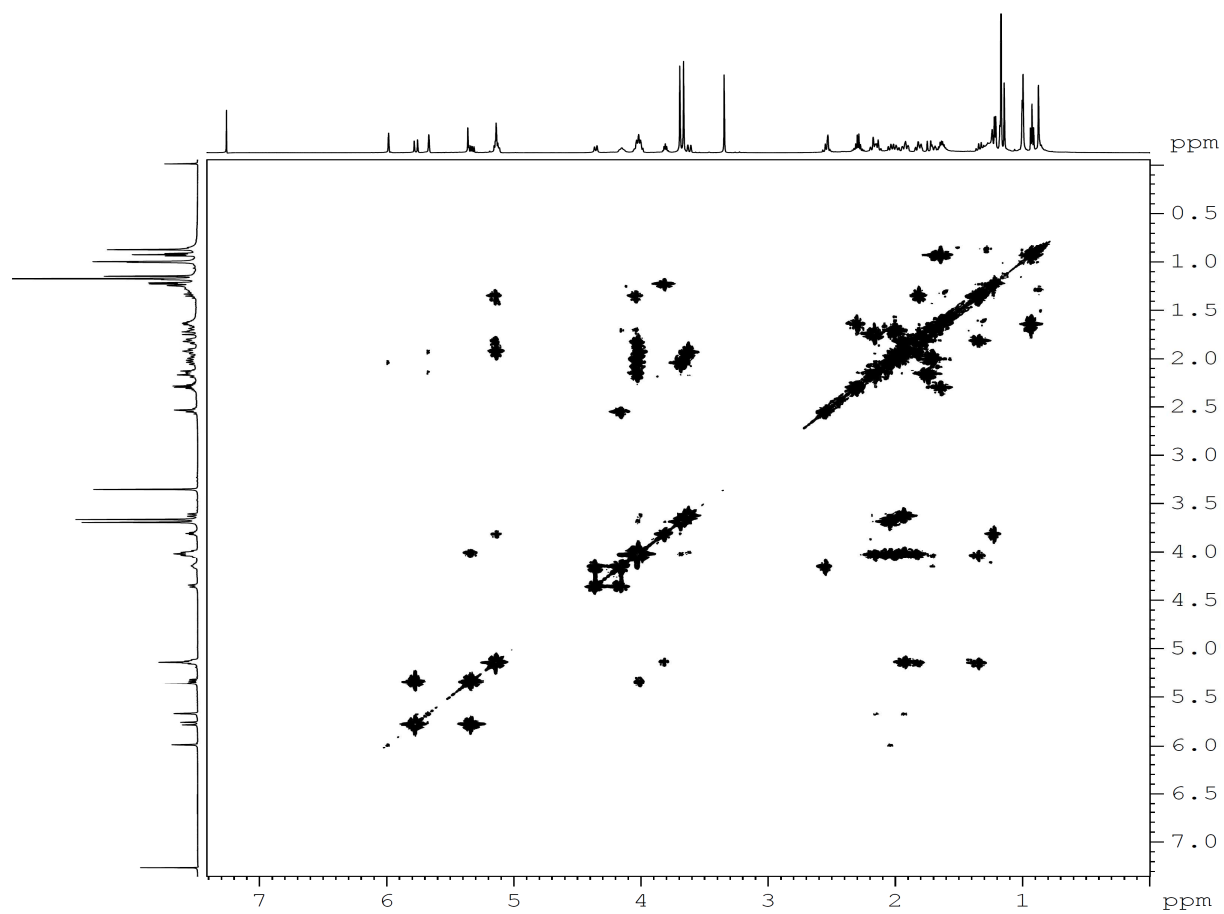
S14. HSQC spectrum of compound **2** in CDCl₃.



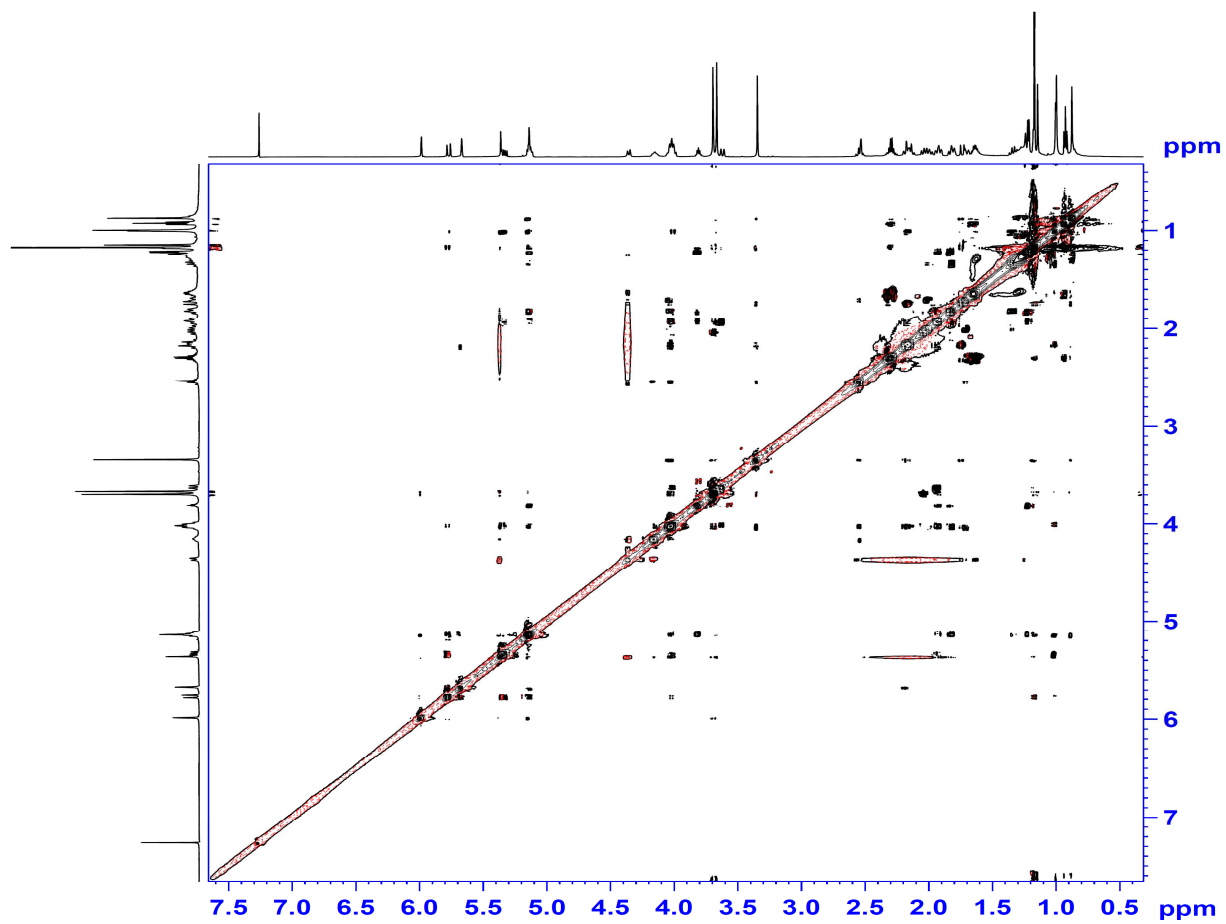
S15. HMBC spectrum of compound **2** in CDCl₃.



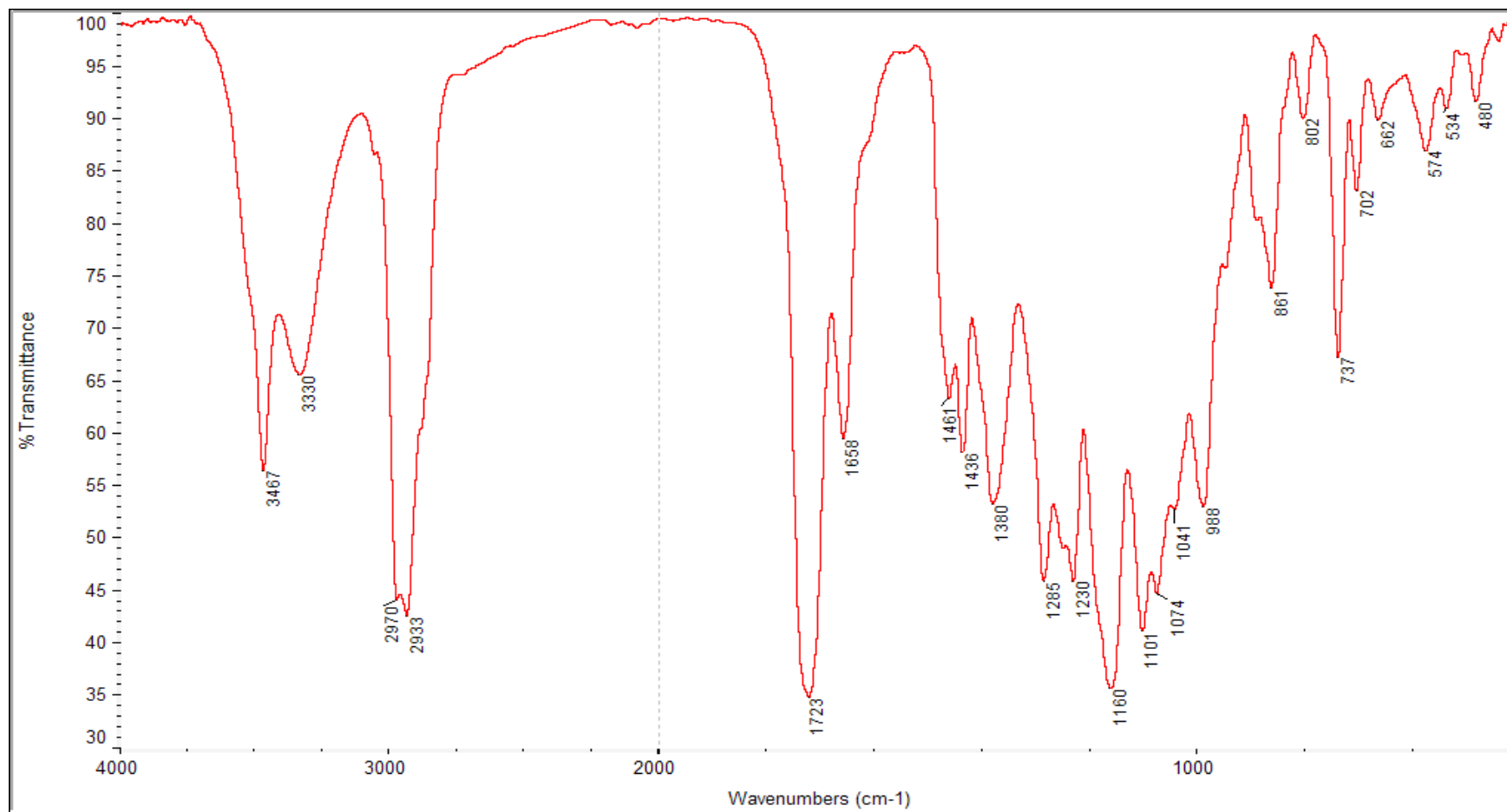
S16. ^1H - ^1H COSY spectrum of compound **2** in CDCl_3 .



S17. NOESY spectrum of compound **2** in CDCl_3 .



S18. IR spectrum of compound **2**.



S19. HRESIMS of compound 2.

Elemental Composition Report

Page 1

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

34 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 10-50 H: 10-90 O: 10-20 Na: 1-1

SIPI

M.W=908

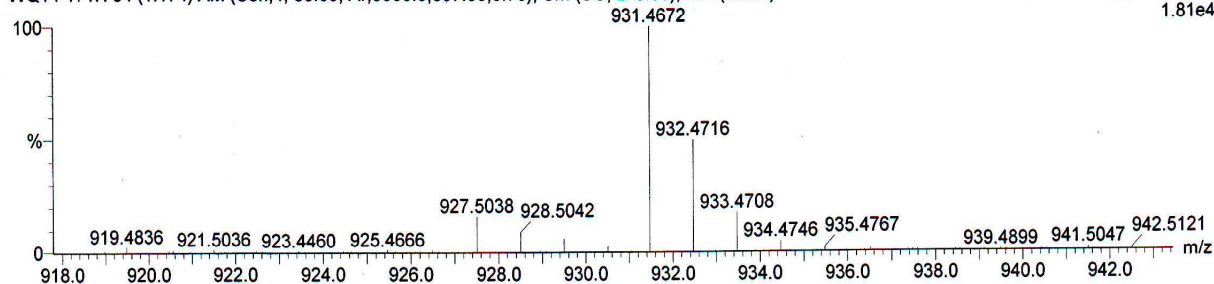
Q-ToF micro

YA019

21-May-2014,14:25:47

WQ14-171H 34 (1.174) AM (Cen,4, 80.00, Ar,5000.0,897.50,0.70); Sm (SG, 2x3.00); Cm (22:34)

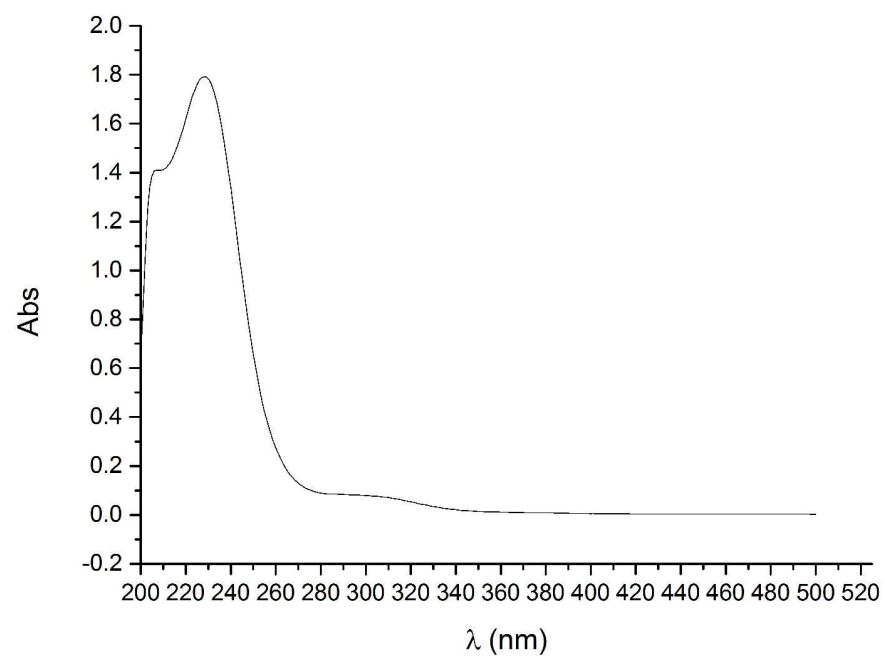
TOF MS ES+
1.81e4



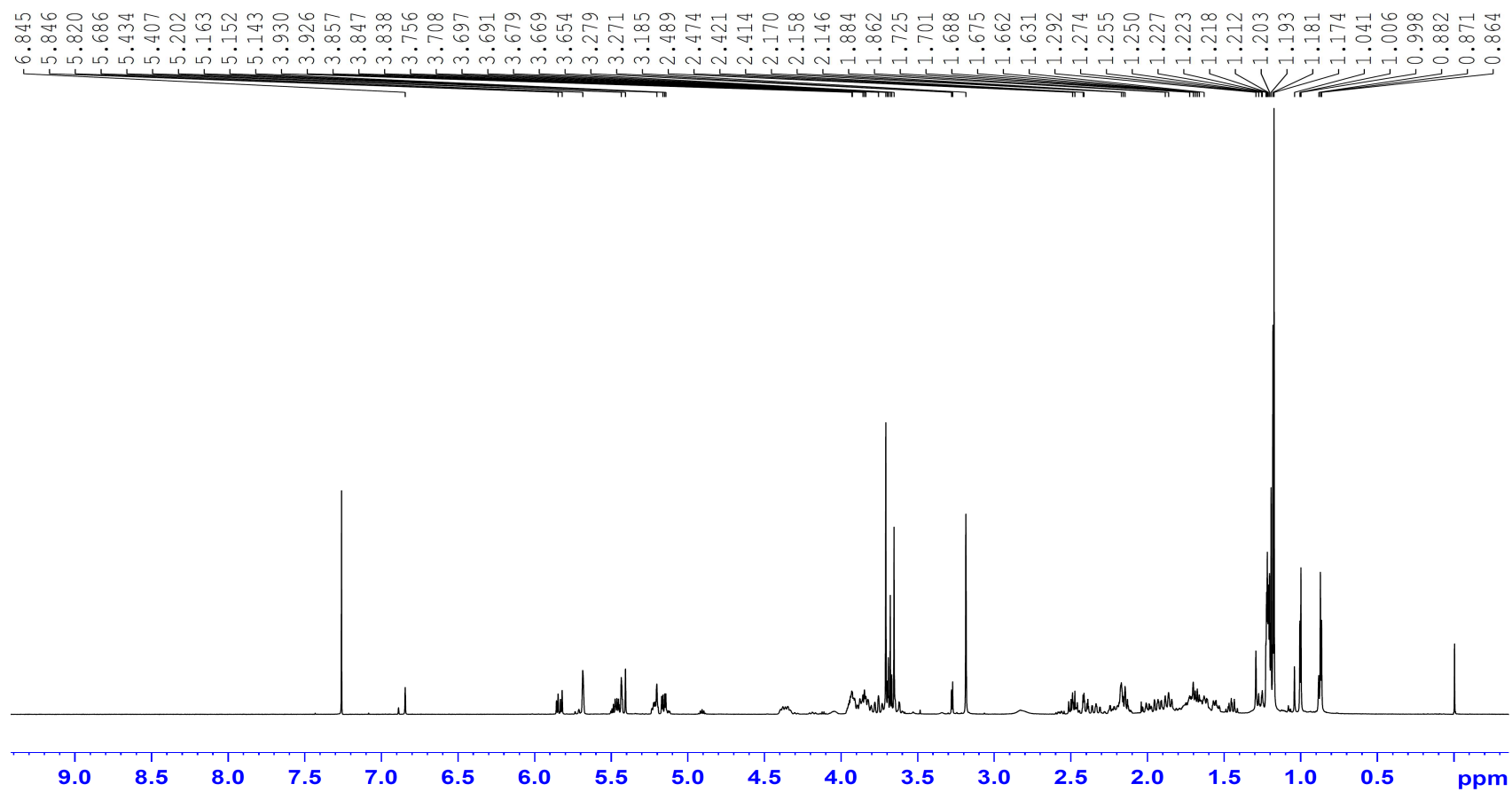
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Maximum: 100.00

Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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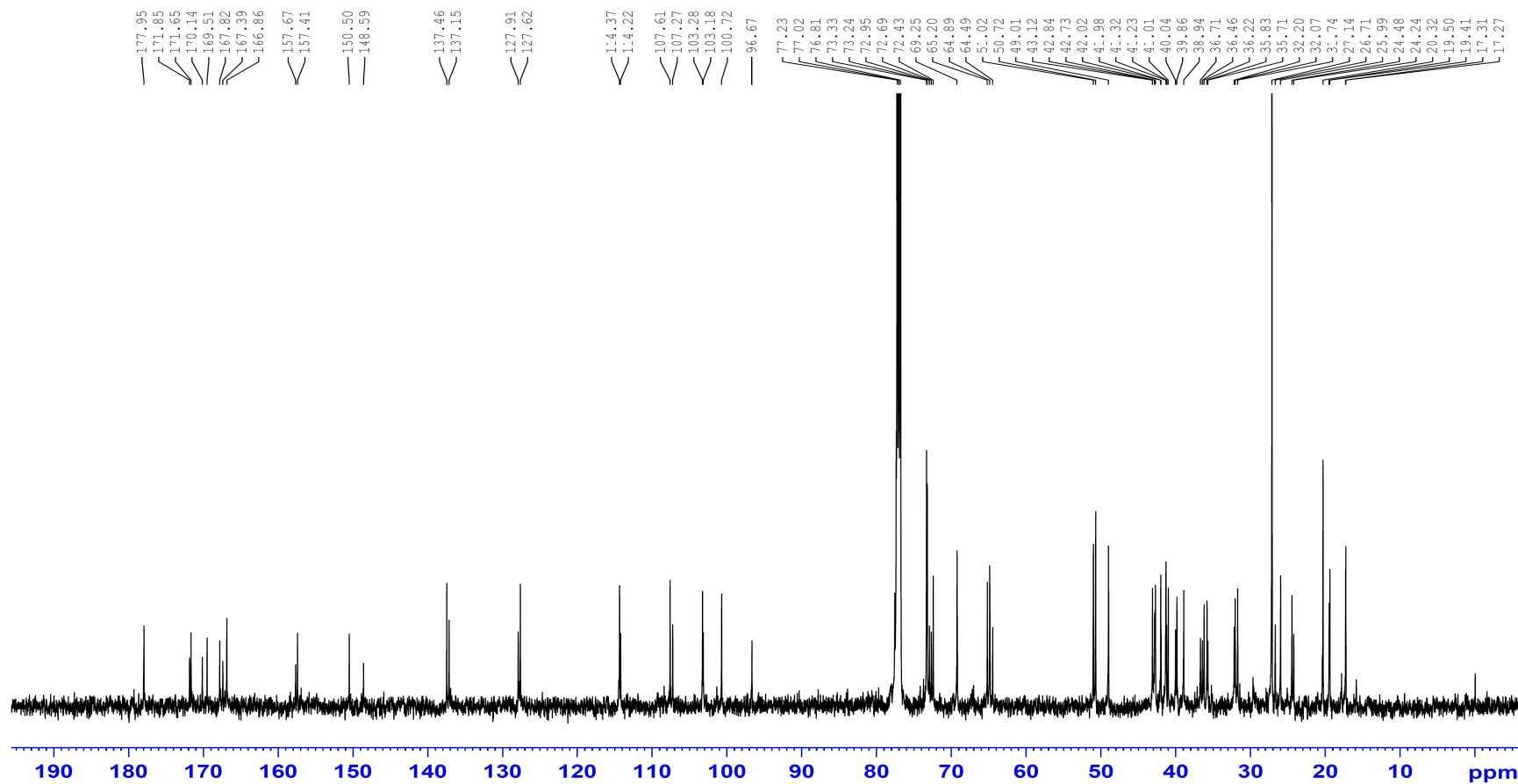
S20. UV spectrum of compound **2**.



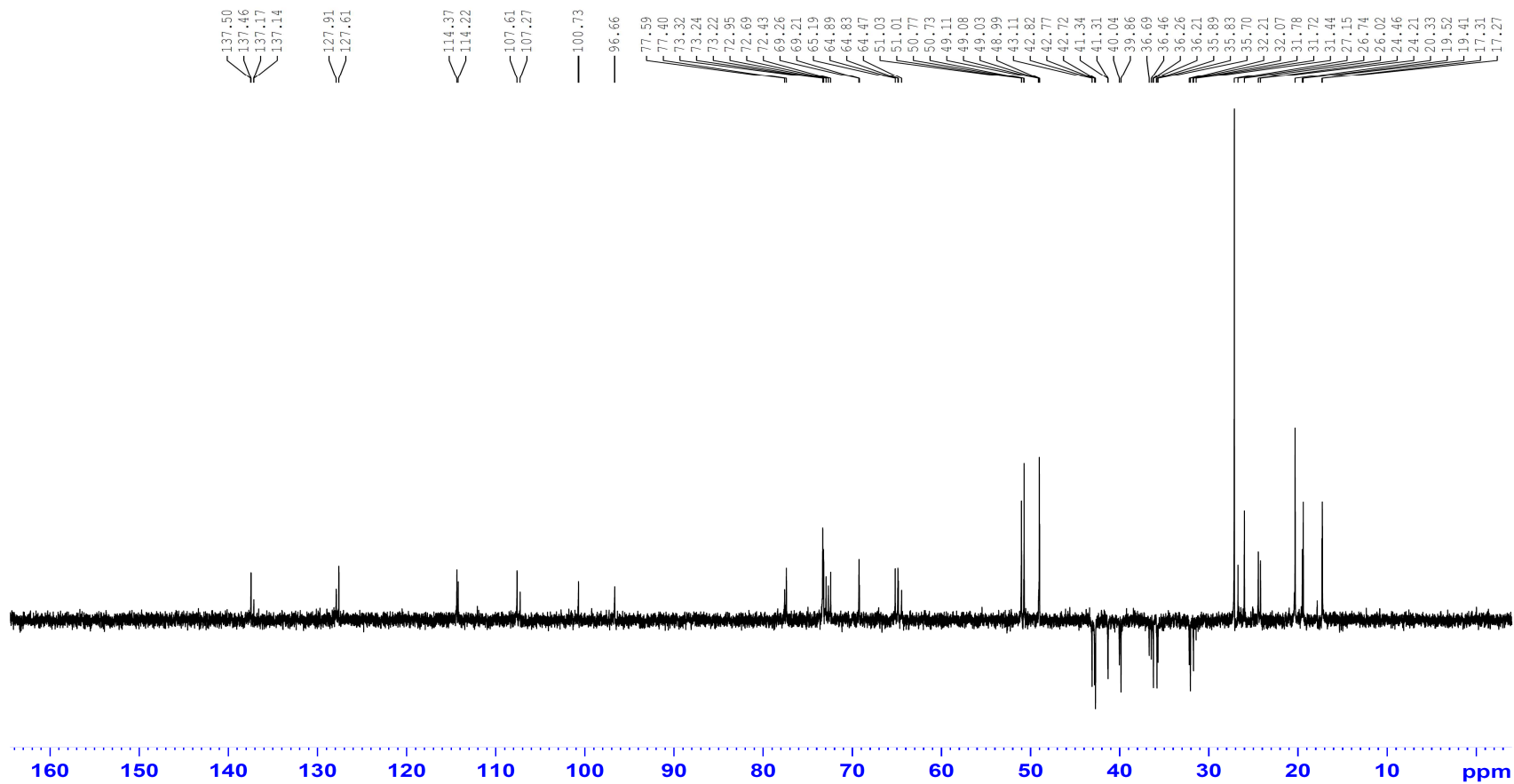
S21. ^1H NMR spectrum of the mixture of compound **3** and **4** in CDCl_3 .



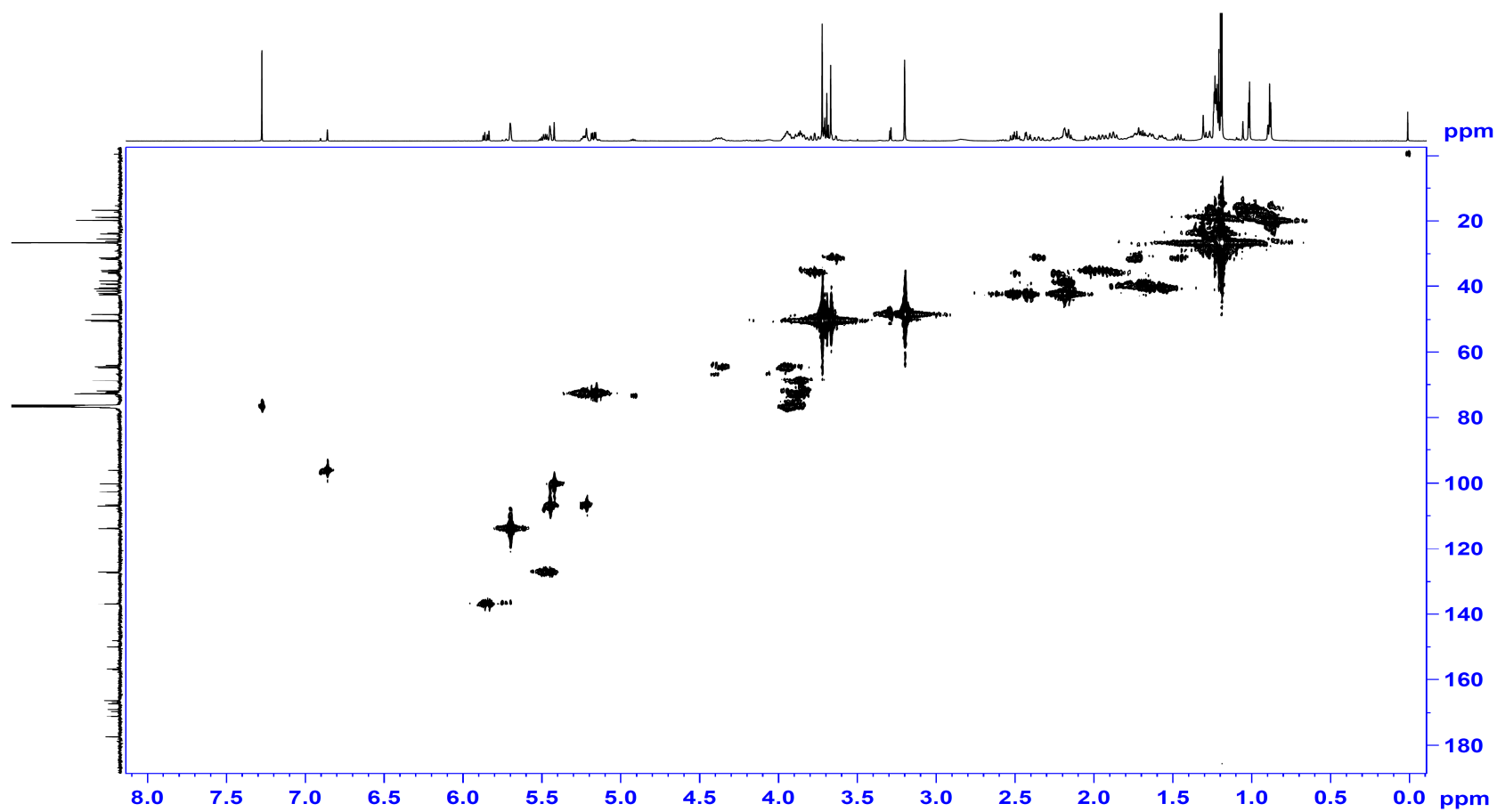
S22. ^{13}C NMR spectrum of the mixture of compound **3** and **4** in CDCl_3 .



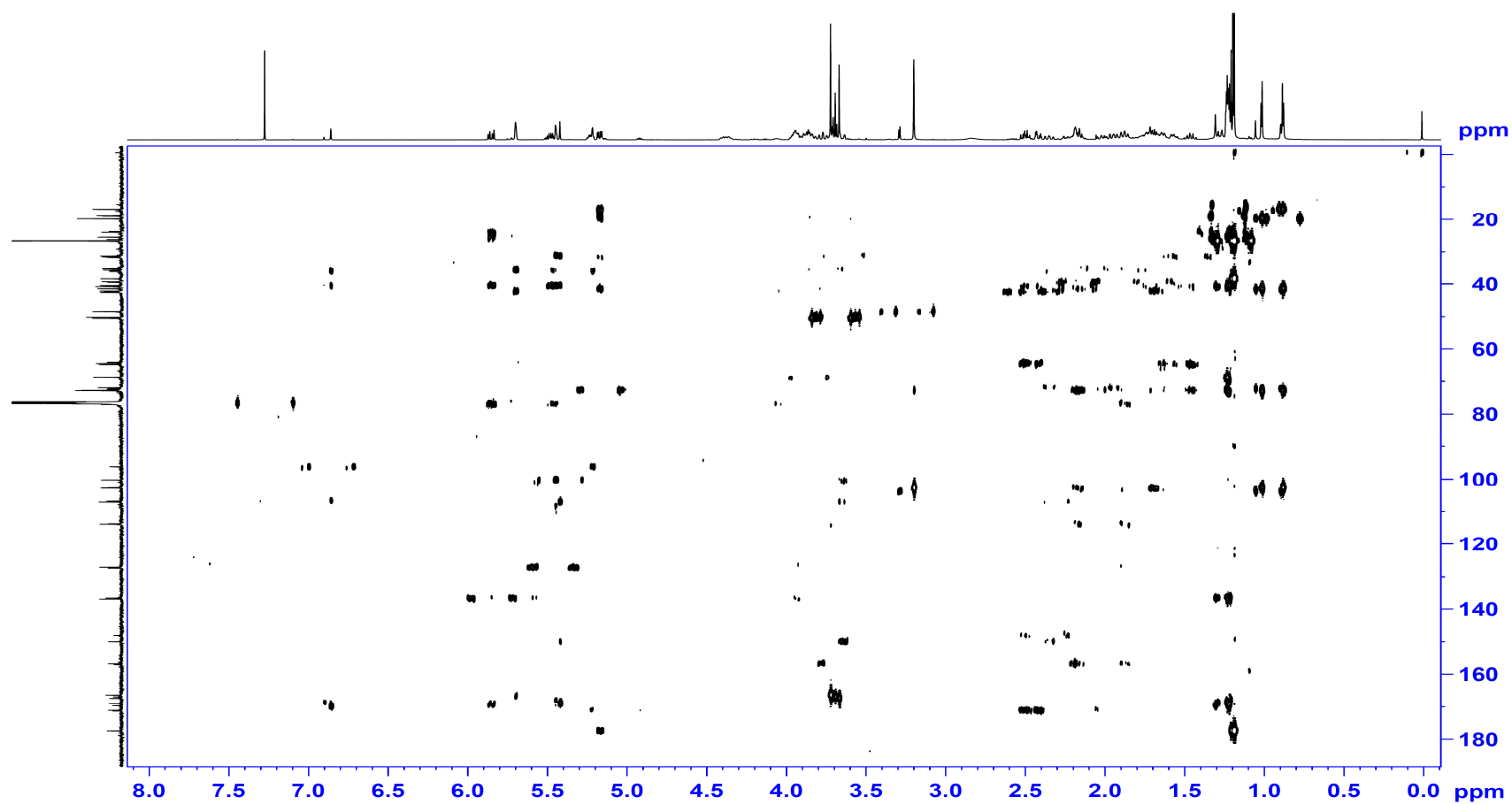
S23. DEPT135 Spectrum of the mixture of compound **3** and **4** in CDCl₃.



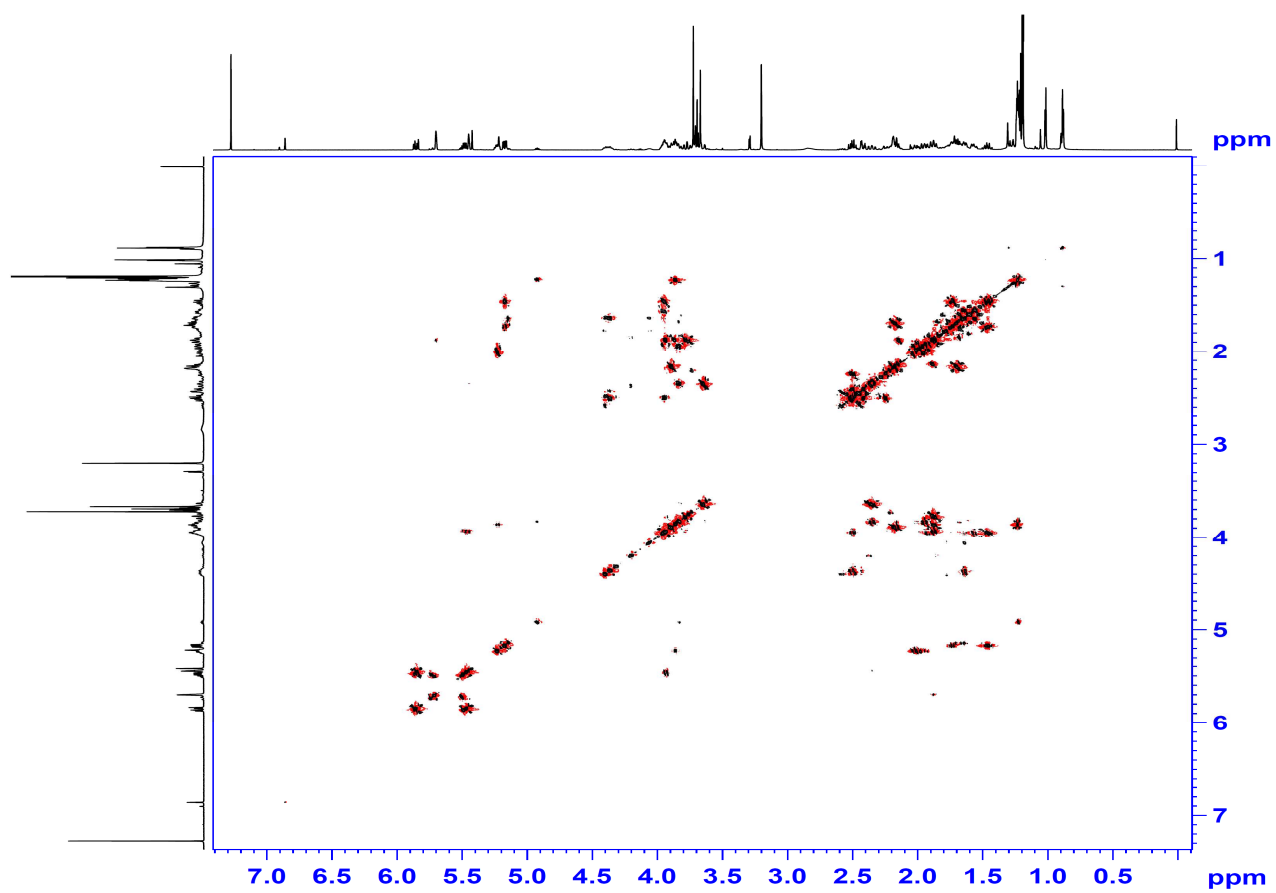
S24. HSQC spectrum of the mixture of compound **3** and **4** in CDCl₃.



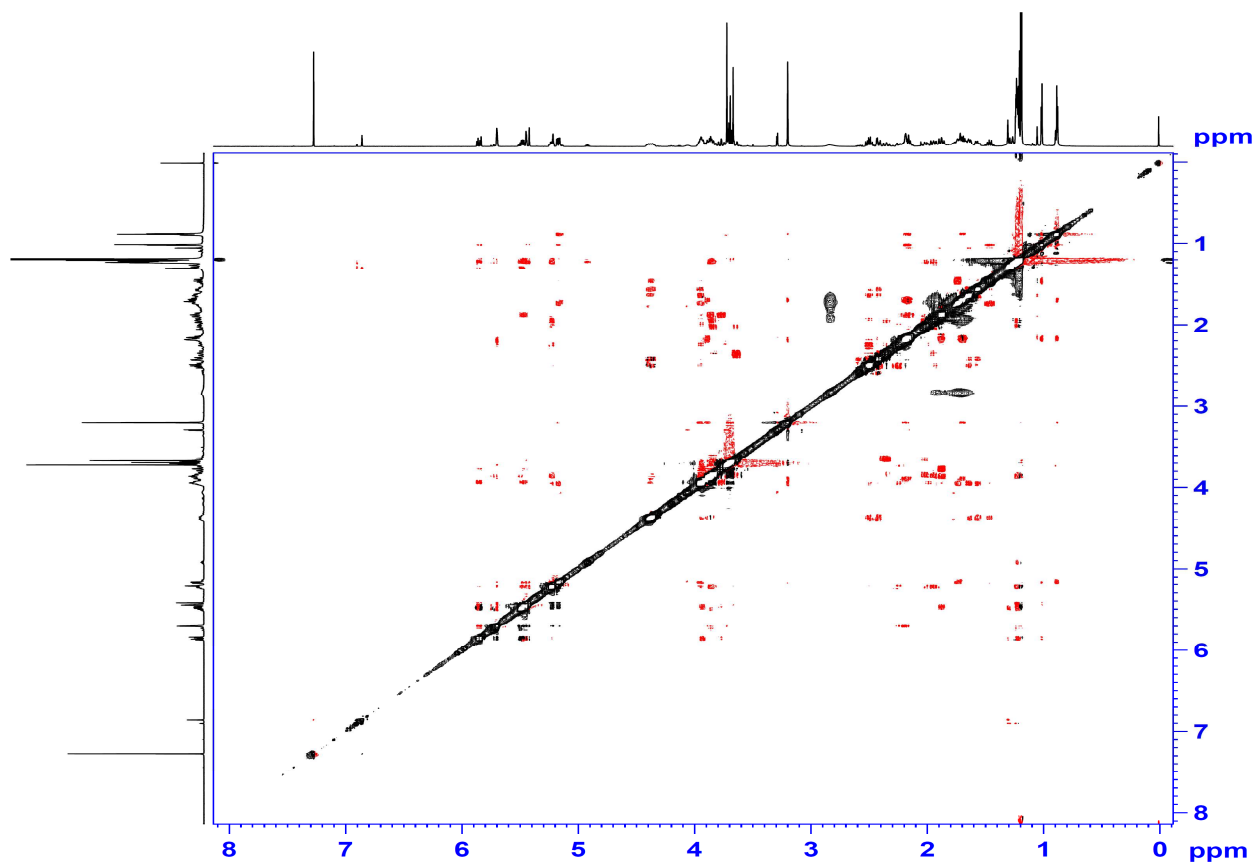
S25. HMBC spectrum of the mixture of compound **3** and **4** in CDCl₃.



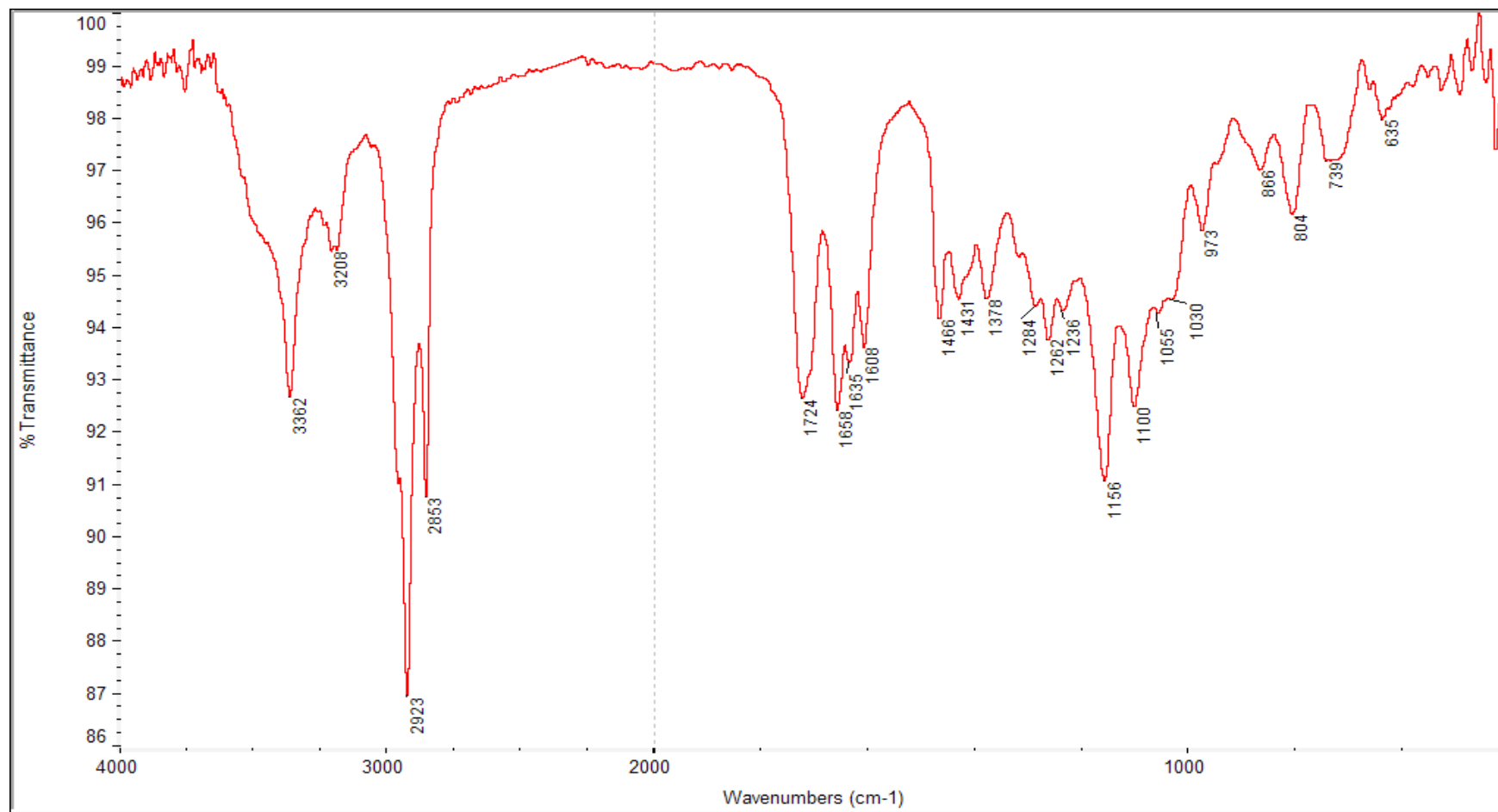
S26. ^1H - ^1H COSY spectrum of the mixture of compound **3** and **4** in CDCl_3 .



S27. NOESY spectrum of the mixture of compound **3** and **4** in CDCl₃.



S28. IR spectrum of the mixture of compound **3** and **4**.



S29. HRESIMS of the mixture of compound 3 and 4.

Elemental Composition Report

Page 1

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

43 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 10-50 H: 10-90 O: 10-16 Na: 1-1

SIPI

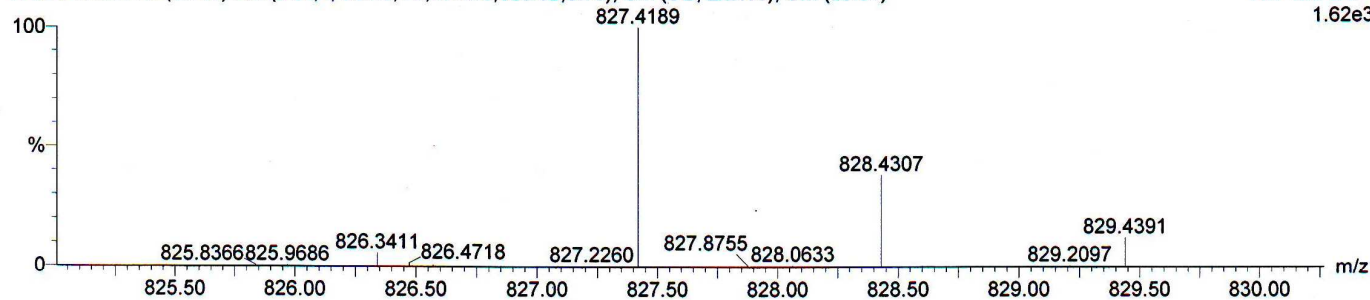
M.W.=804

Q-ToF micro
YA019

21-May-2014,14:58:41

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TOF MS ES+
1.62e3

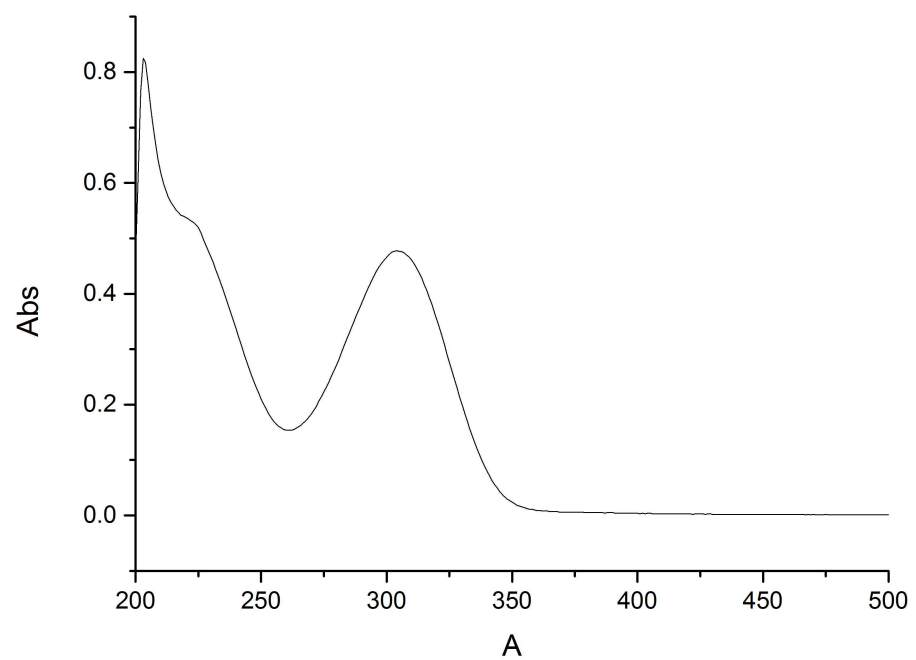


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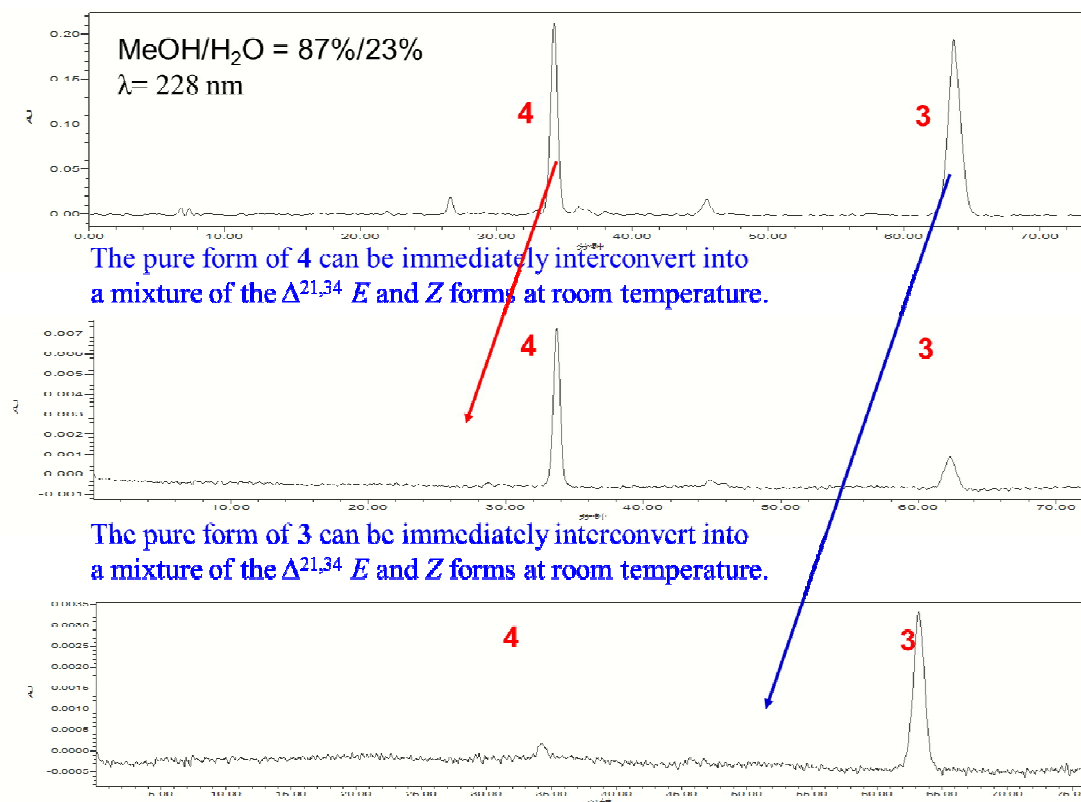
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50.0

Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
827.4189	100.00	827.4194	-0.5	-0.6	11.5	19.1	C43 H64 O14 Na

S30. UV spectrum of the mixture of compound **3** and **4**.



S31. The pure form of compounds **3** or **4** can be gradually interconvert into a mixture of the $\Delta^{21,34}$ *E* and *Z* forms at room temperature.



S32. COSY, key HMBC, and selected NOESY correlations of compound **2**.

