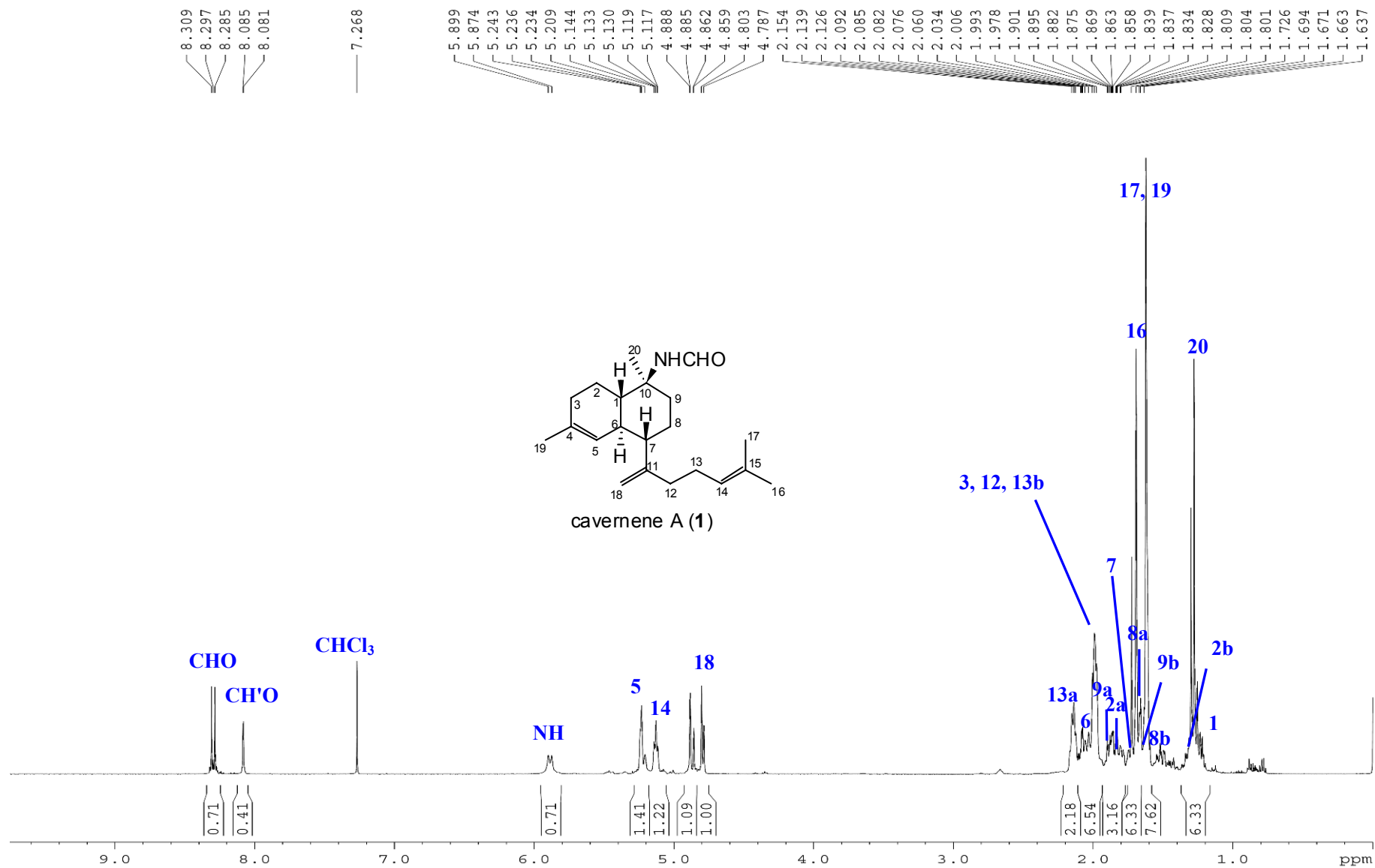


## Supporting Information

- Figure S1.**  $^1\text{H}$  NMR spectrum of cavernene A (**1**) in  $\text{CDCl}_3$ .
- Figure S2.**  $^{13}\text{C}$  NMR spectrum of cavernene A (**1**) in  $\text{CDCl}_3$ .
- Figure S3.** HSQC spectrum of cavernene A (**1**) in  $\text{CDCl}_3$ .
- Figure S4.** HMBC spectrum of cavernene A (**1**) in  $\text{CDCl}_3$ .
- Figure S5.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of cavernene A (**1**) in  $\text{CDCl}_3$ .
- Figure S6.** NOESY spectrum of cavernene A (**1**) in  $\text{CDCl}_3$ .
- Figure S7.** IR spectrum of cavernene A (**1**).
- Figure S8.** HRESIMS of cavernene A (**1**).
- Figure S9.** UV spectrum of cavernene A (**1**).
- Figure S10.**  $^1\text{H}$  NMR spectrum of cavernene B (**2**) in  $\text{CDCl}_3$ .
- Figure S11.**  $^{13}\text{C}$  NMR spectrum of cavernene B (**2**) in  $\text{CDCl}_3$ .
- Figure S12.** HSQC spectrum of cavernene B (**2**) in  $\text{CDCl}_3$ .
- Figure S13.** HMBC spectrum of cavernene B (**2**) in  $\text{CDCl}_3$ .
- Figure S14.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of cavernene B (**2**) in  $\text{CDCl}_3$ .
- Figure S15.** NOESY spectrum of cavernene B (**2**) in  $\text{CDCl}_3$ .
- Figure S16.** IR spectrum of cavernene B (**2**).
- Figure S17.** HRESIMS of cavernene B (**2**).
- Figure S18.** UV spectrum of cavernene B (**2**).
- Figure S19.**  $^1\text{H}$  NMR spectrum of cavernene C (**3**) in  $\text{CDCl}_3$ .
- Figure S20.**  $^{13}\text{C}$  NMR spectrum of cavernene C (**3**) in  $\text{CDCl}_3$ .
- Figure S21.** HSQC spectrum of cavernene C (**3**) in  $\text{CDCl}_3$ .
- Figure S22.** HMBC spectrum of cavernene C (**3**) in  $\text{CDCl}_3$ .
- Figure S23.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of cavernene C (**3**) in  $\text{CDCl}_3$ .
- Figure S24.** NOESY spectrum of cavernene C (**3**) in  $\text{CDCl}_3$ .
- Figure S25.** IR spectrum of cavernene C (**3**).
- Figure S26.** HRESIMS of cavernene C (**3**).
- Figure S27.** UV spectrum of cavernene C (**3**).
- Figure S28.**  $^1\text{H}$  NMR spectrum of cavernene D (**4**) in  $\text{CDCl}_3$ .
- Figure S29.**  $^{13}\text{C}$  NMR spectrum of cavernene D (**4**) in  $\text{CDCl}_3$ .
- Figure S30.** HSQC spectrum of cavernene D (**4**) in  $\text{CDCl}_3$ .
- Figure S31.** HMBC spectrum of cavernene D (**4**) in  $\text{CDCl}_3$ .
- Figure S32.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of cavernene D (**4**) in  $\text{CDCl}_3$ .
- Figure S33.** NOESY spectrum of cavernene D (**4**) in  $\text{CDCl}_3$ .
- Figure S34.** IR spectrum of cavernene D (**4**).
- Figure S35.** HRESIMS of cavernene D (**4**).
- Figure S36.** UV spectrum of cavernene D (**4**).
- Figure S37.**  $^1\text{H}$  NMR spectrum of kalihinene E (**5**) in  $\text{CDCl}_3$ .
- Figure S38.**  $^{13}\text{C}$  NMR spectrum of kalihinene E (**5**) in  $\text{CDCl}_3$ .
- Figure S39.** HSQC spectrum of kalihinene E (**5**) in  $\text{CDCl}_3$ .
- Figure S40.** HMBC spectrum of kalihinene E (**5**) in  $\text{CDCl}_3$ .
- Figure S41.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of kalihinene E (**5**) in  $\text{CDCl}_3$ .

- Figure S42.** NOESY spectrum of kalihinene E (5) in CDCl<sub>3</sub>.
- Figure S43.** IR spectrum of kalihinene E (5).
- Figure S44.** HRESIMS of kalihinene E (5).
- Figure S45.** UV spectrum of kalihinene E (5).
- Figure S46.** <sup>1</sup>H NMR spectrum of kalihinene F (6) in CDCl<sub>3</sub>.
- Figure S47.** <sup>13</sup>C NMR spectrum of kalihinene F (6) in CDCl<sub>3</sub>.
- Figure S48.** HSQC spectrum of kalihinene F (6) in CDCl<sub>3</sub>.
- Figure S49.** HMBC spectrum of kalihinene F (6) in CDCl<sub>3</sub>.
- Figure S50.** <sup>1</sup>H-<sup>1</sup>H COSY spectrum of kalihinene F (6) in CDCl<sub>3</sub>.
- Figure S51.** NOESY spectrum of kalihinene F (6) in CDCl<sub>3</sub>.
- Figure S52.** IR spectrum of kalihinene F (6).
- Figure S53.** HRESIMS of kalihinene F (6).
- Figure S54.** UV spectrum of kalihinene F (6).
- Figure S55.** <sup>1</sup>H NMR spectrum of kalihipyran C (7) in CDCl<sub>3</sub>.
- Figure S56.** <sup>13</sup>C NMR spectrum of kalihipyran C (7) in CDCl<sub>3</sub>.
- Figure S57.** HSQC spectrum of kalihipyran C (7) in CDCl<sub>3</sub>.
- Figure S58.** HMBC spectrum of kalihipyran C (7) in CDCl<sub>3</sub>.
- Figure S59.** <sup>1</sup>H-<sup>1</sup>H COSY spectrum of kalihipyran C (7) in CDCl<sub>3</sub>.
- Figure S60.** NOESY spectrum of kalihipyran C (7) in CDCl<sub>3</sub>.
- Figure S61.** IR spectrum of kalihipyran C (7).
- Figure S62.** HRESIMS of kalihipyran C (7).
- Figure S63.** UV spectrum kalihipyran C (7).

Figure S1.  $^1\text{H}$  NMR spectrum of cavernene A (1) in  $\text{CDCl}_3$ .

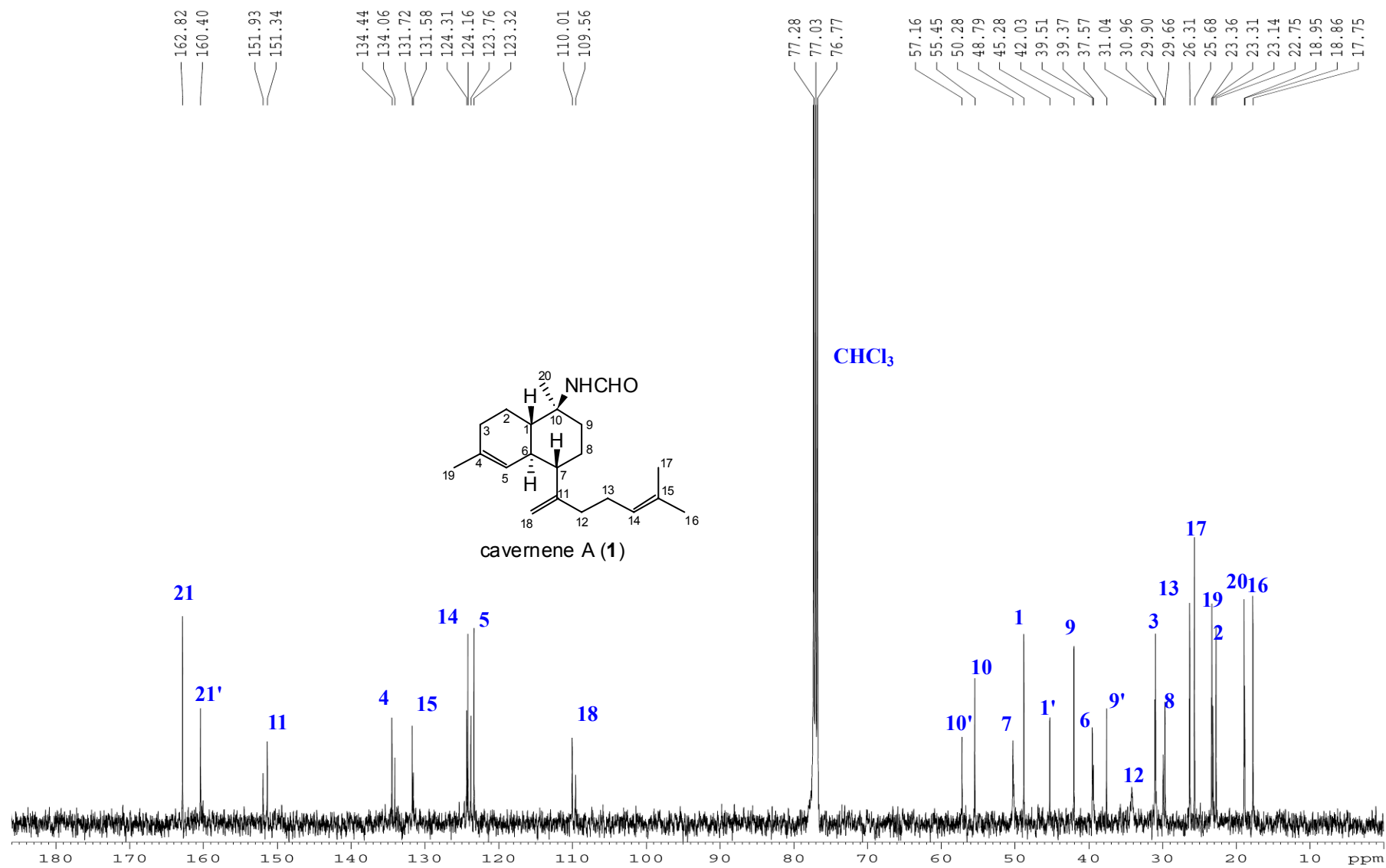
**Figure S2.**  $^{13}\text{C}$  NMR spectrum of cavernene A (**1**) in  $\text{CDCl}_3$ .



Figure S3. HSQC spectrum of cavernene A (1) in CDCl<sub>3</sub>.

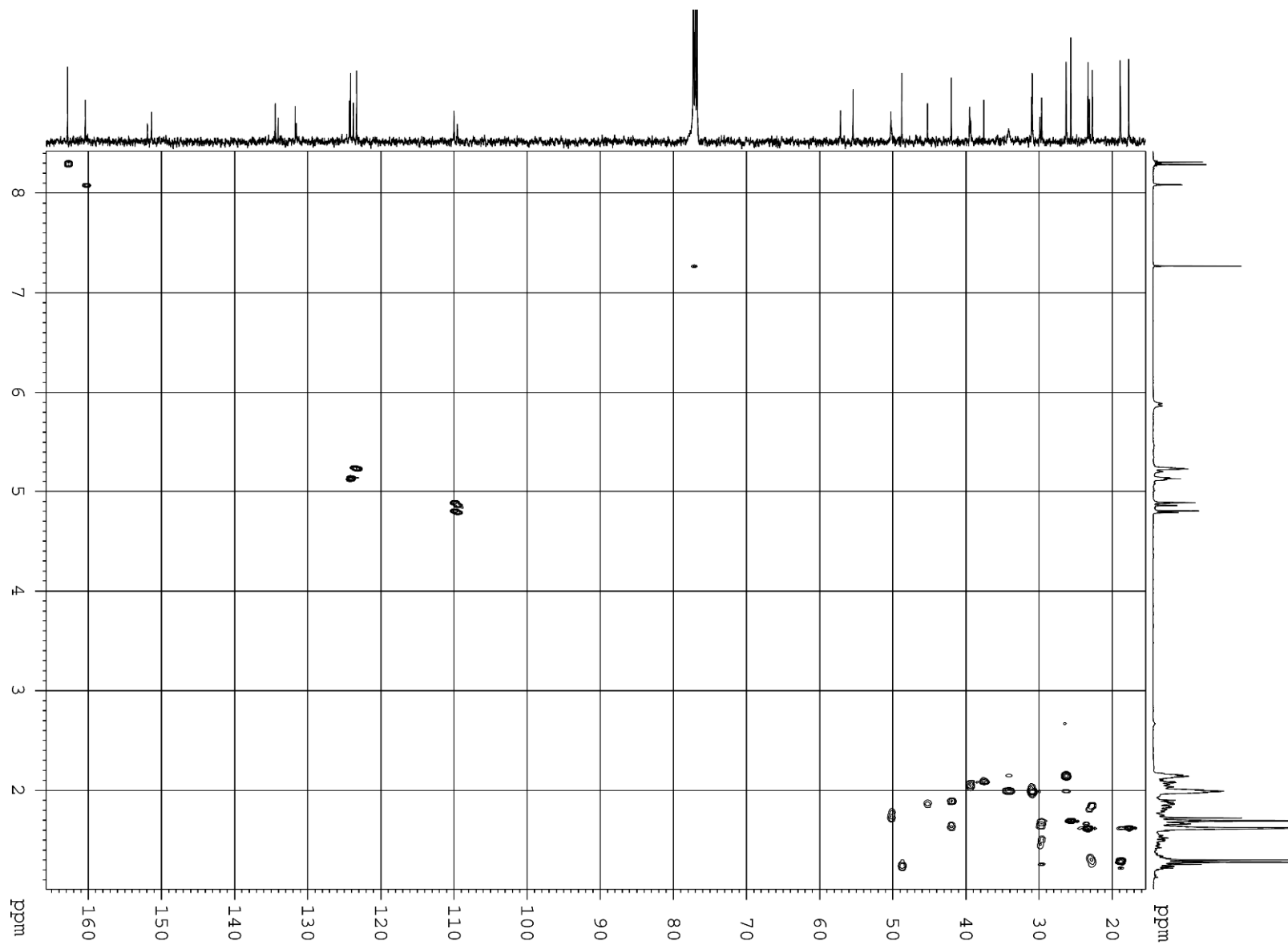
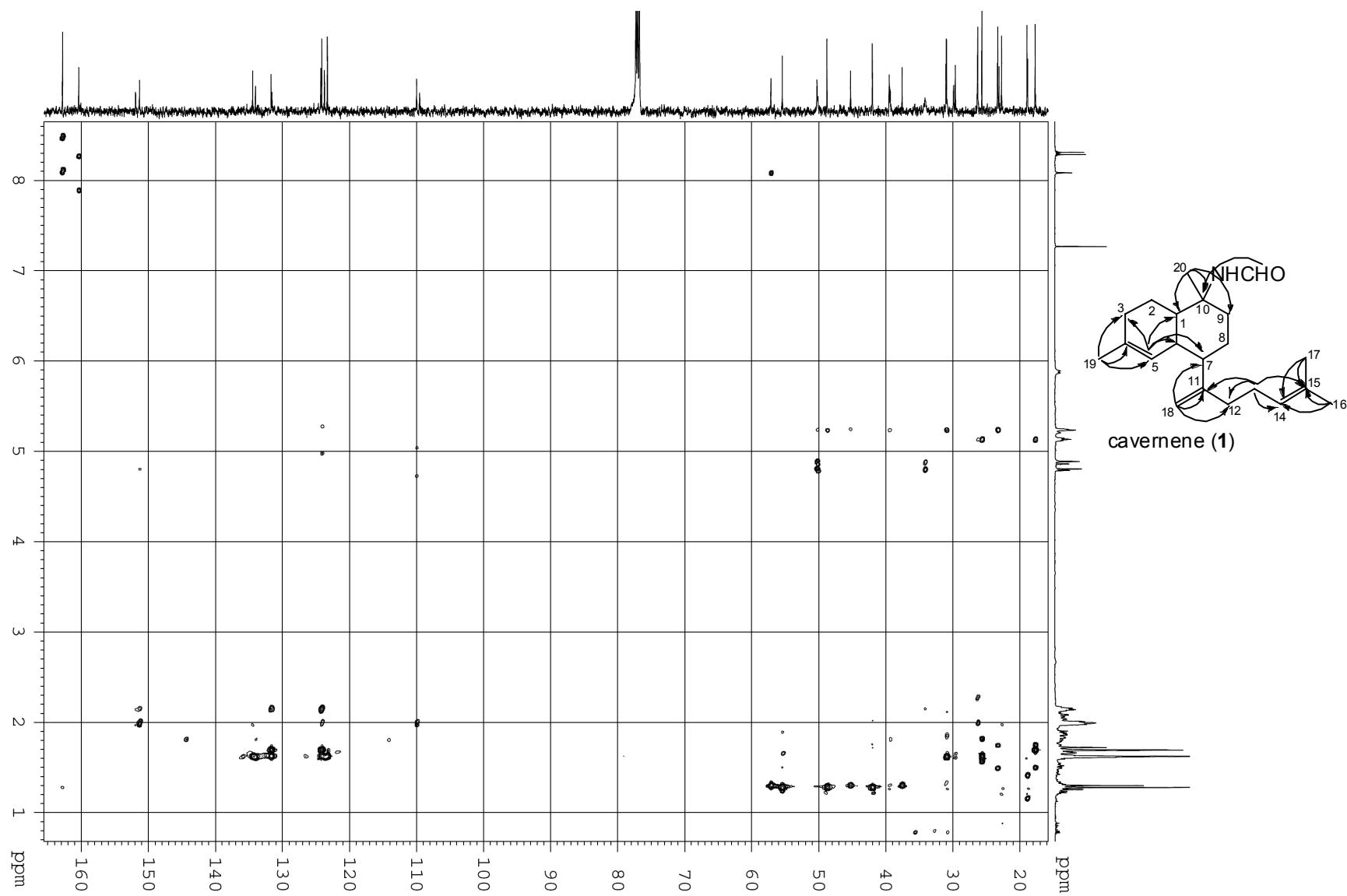


Figure S4. HMBC spectrum of cavernene A (1) in CDCl<sub>3</sub>.

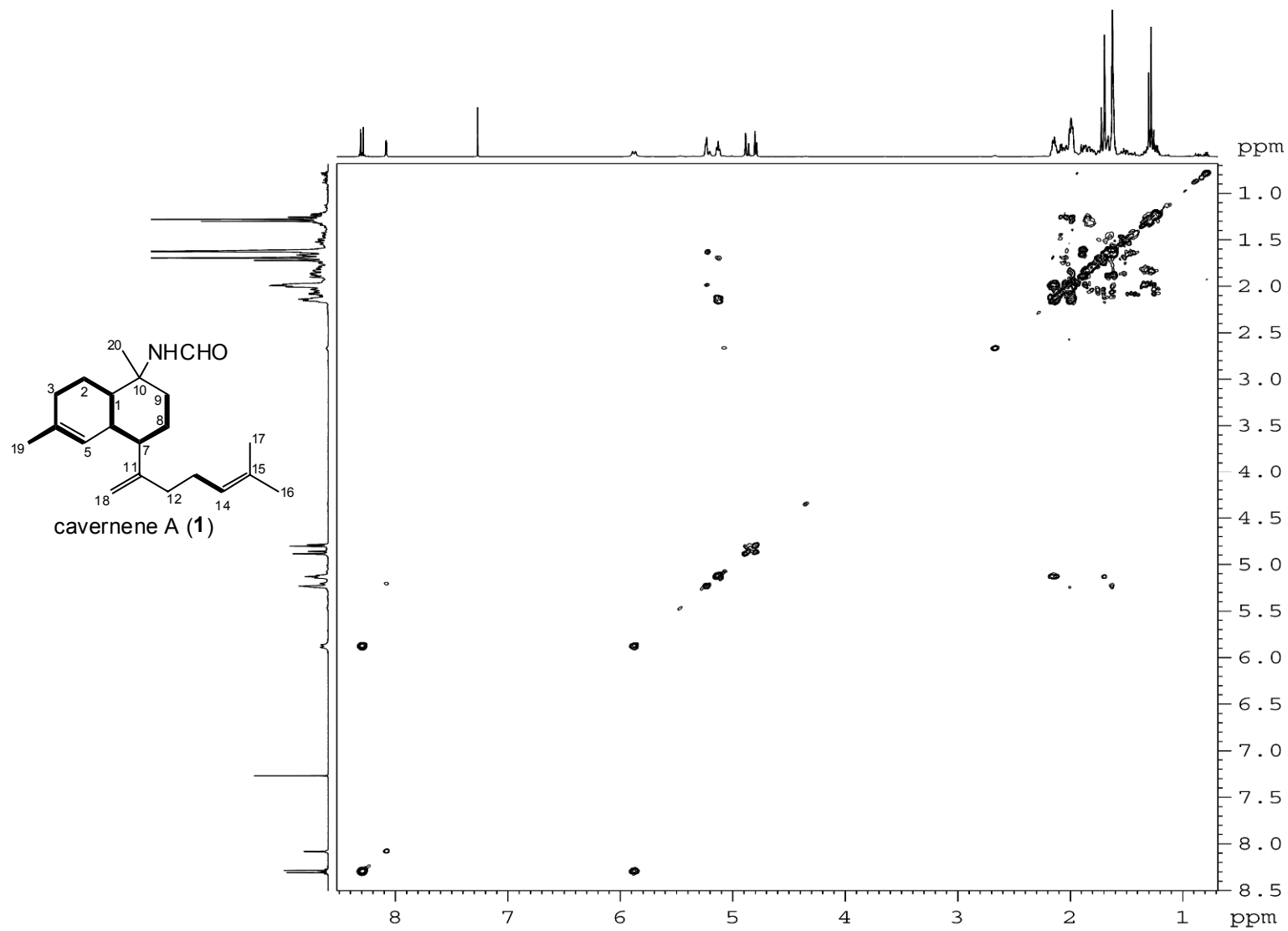
**Figure S5.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of cavernene A (**1**) in  $\text{CDCl}_3$ .

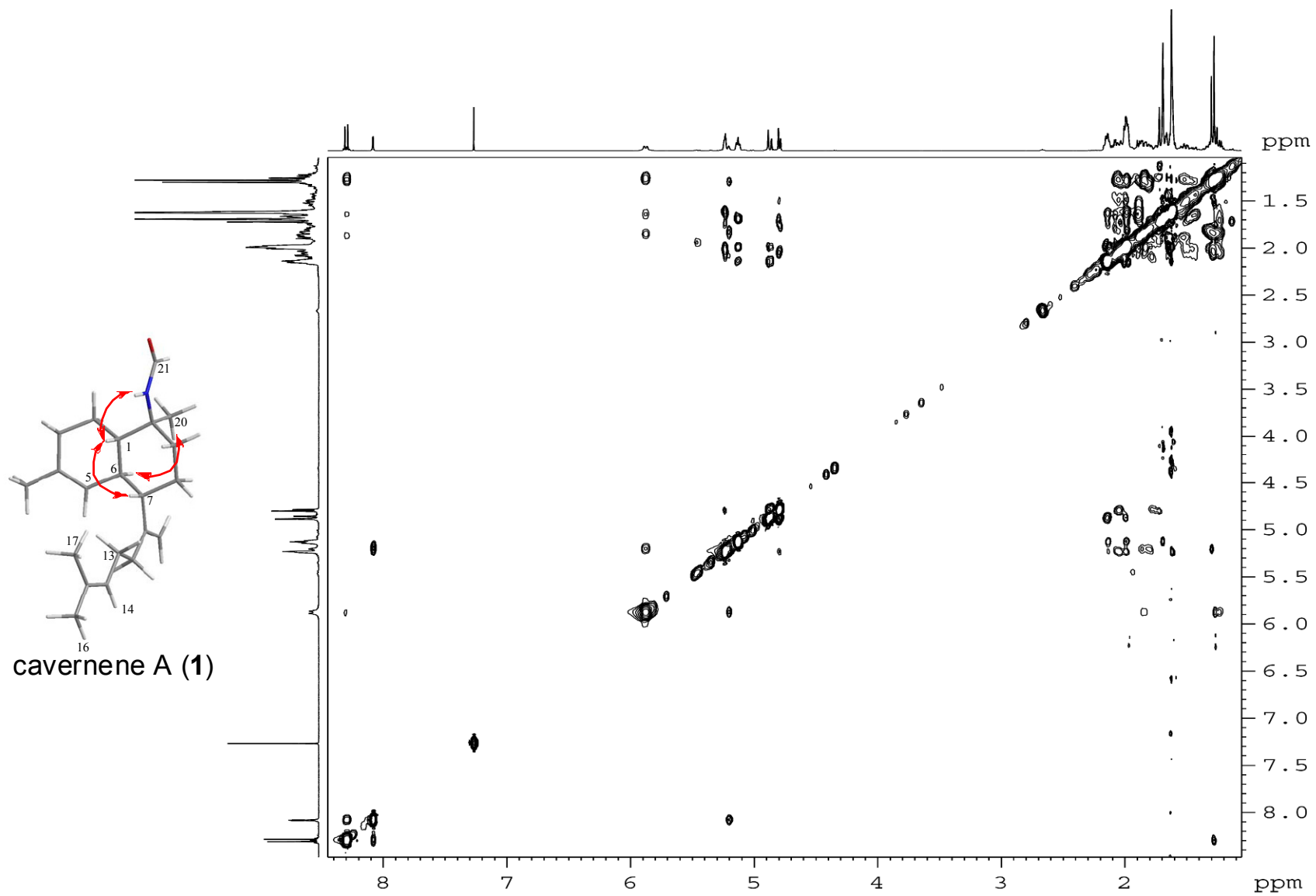
Figure S6. NOESY spectrum of cavernene A (1) in CDCl<sub>3</sub>.

Figure S7. IR spectrum of cavernene A (1).

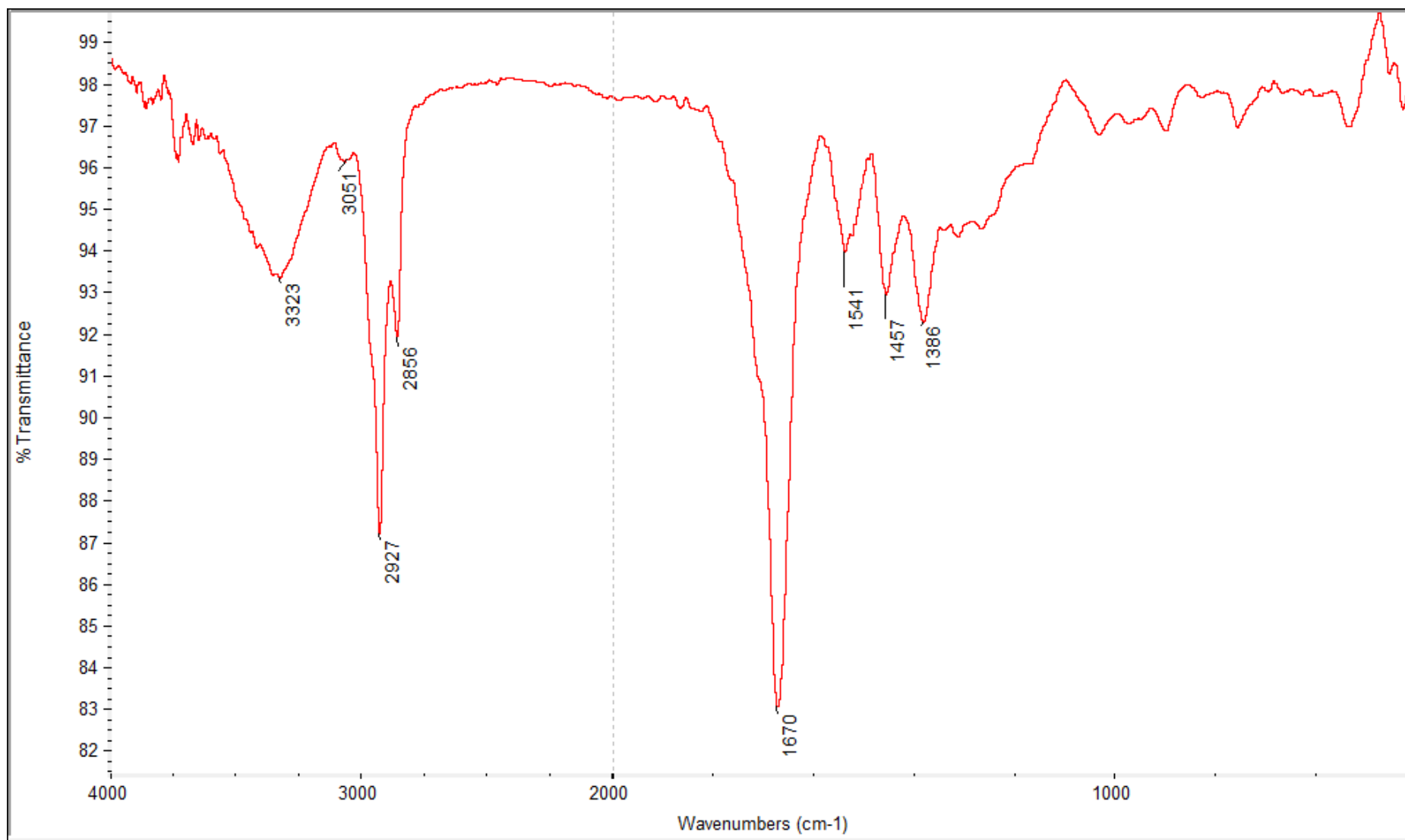


Figure S8. HRESIMS of cavernene A (1).

Elemental Composition Report

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

Selected filters: None

Monoisotopic Mass, Even Electron Ions

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

Elements Used:

C: 5-25 H: 10-40 N: 1-1 O: 1-2 Na: 1-1

SIPI

Q-ToF micro  
YA019

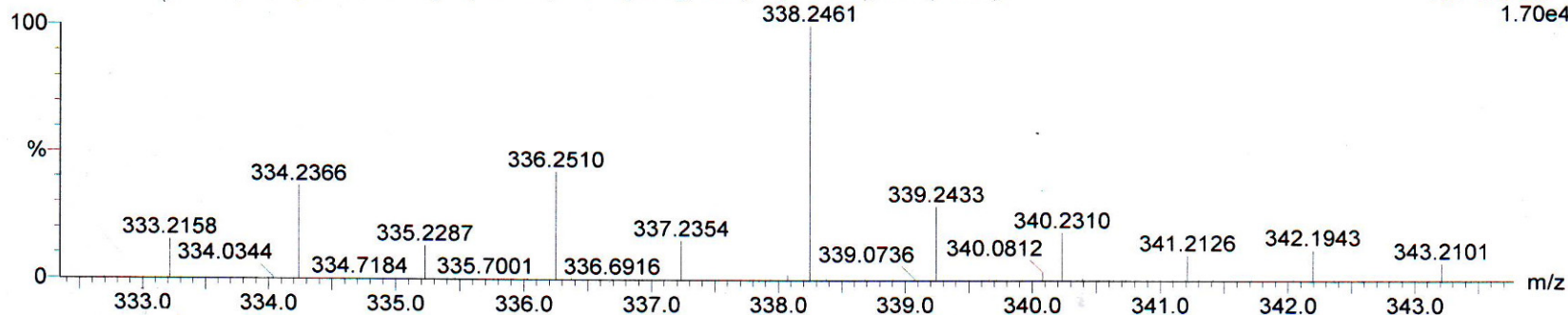
20-May-2011,12:59:41

0.00000000

WQ11-310H 21 (0.740) AM (Cen,6, 80.00, Ar,5000.0,325.16,0.70); Sm (SG, 2x3.00); Cm (15:36)

TOF MS ES+

1.70e4



Minimum: 45.00 -1.5  
Maximum: 100.00 5.0 10.0 50.0

Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
338.2461	100.00	338.2460	0.1	0.3	5.5	1181.0	C21 H33 N O Na

Figure S9. UV spectrum of cavernene A (1).

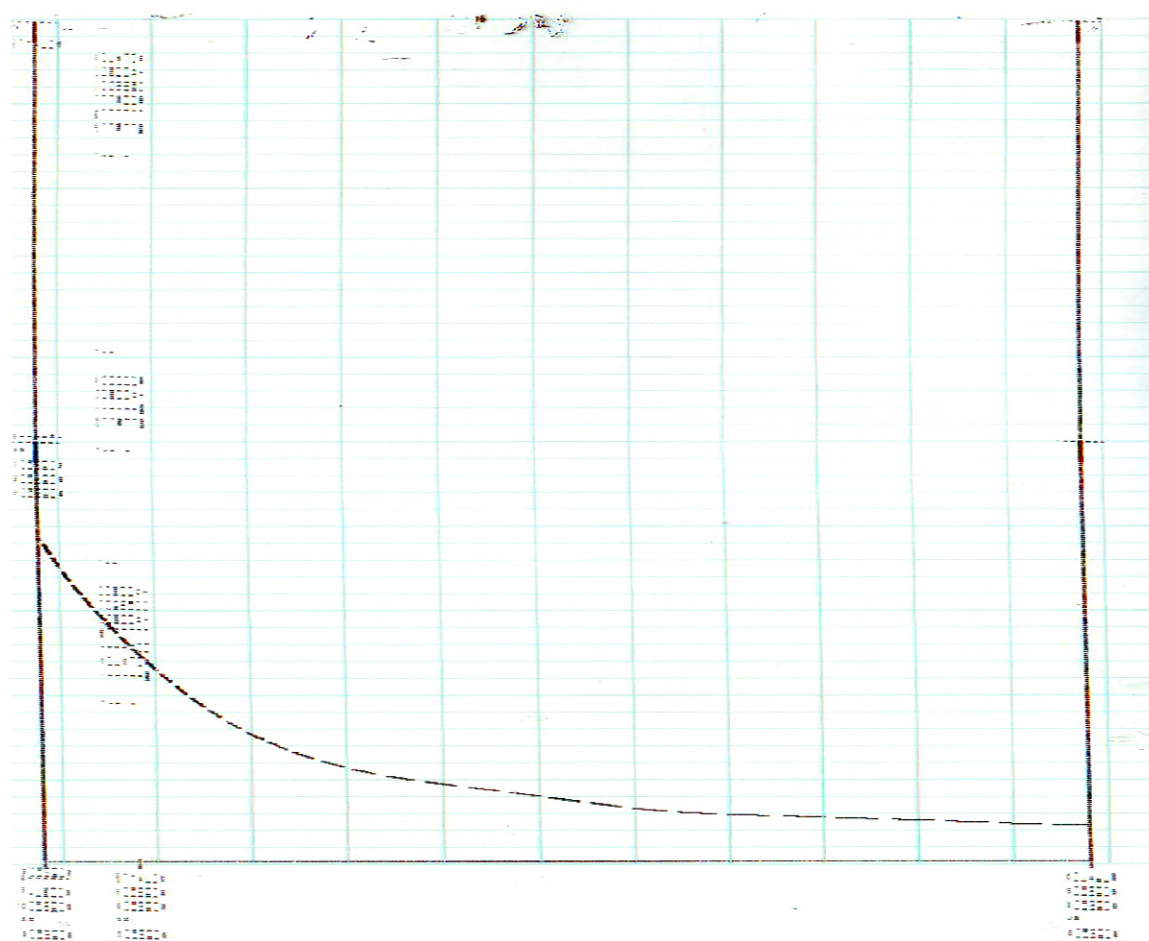
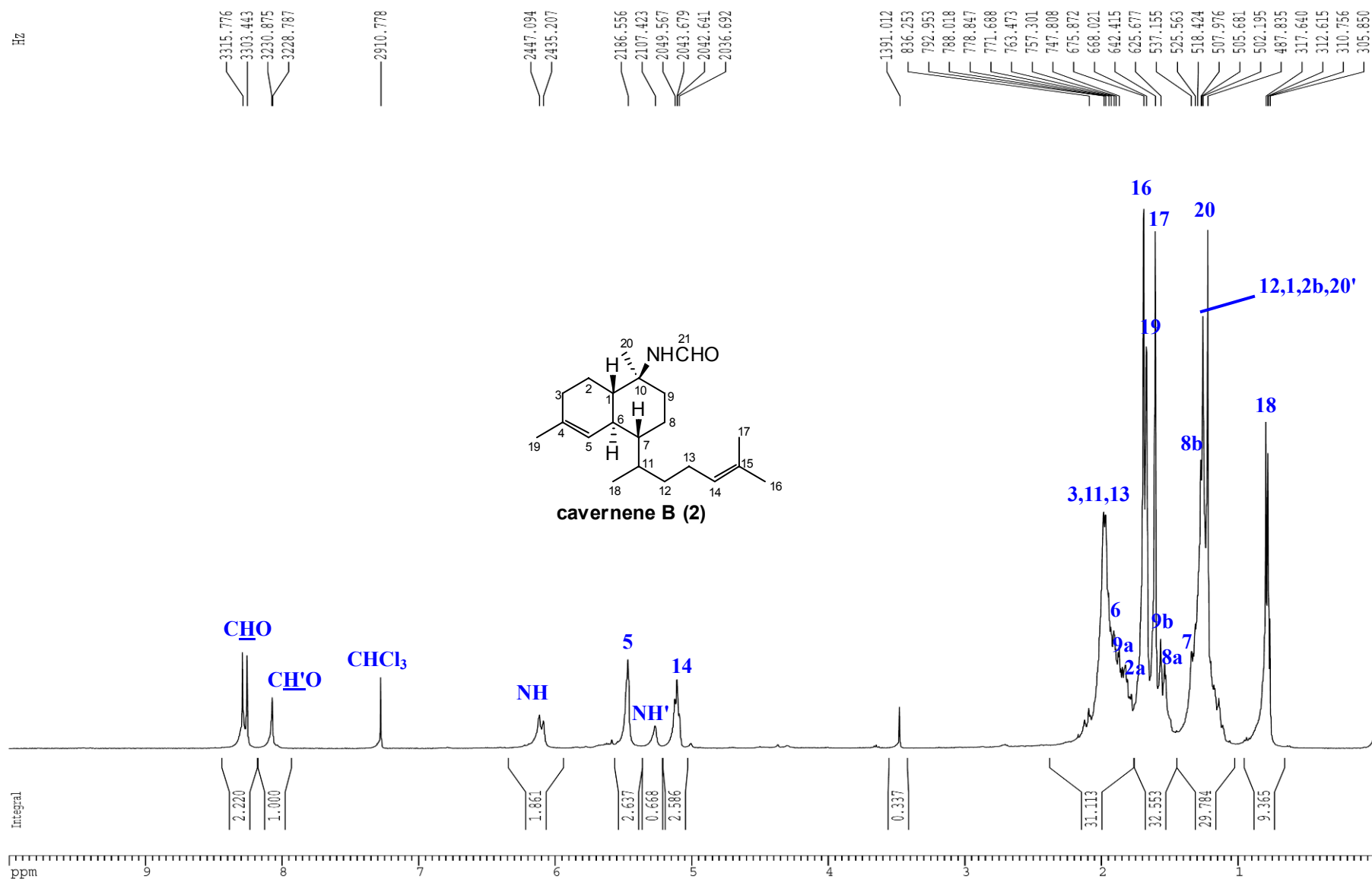


Figure S10.  $^1\text{H}$  NMR spectrum of cavernene B (2) in  $\text{CDCl}_3$ .



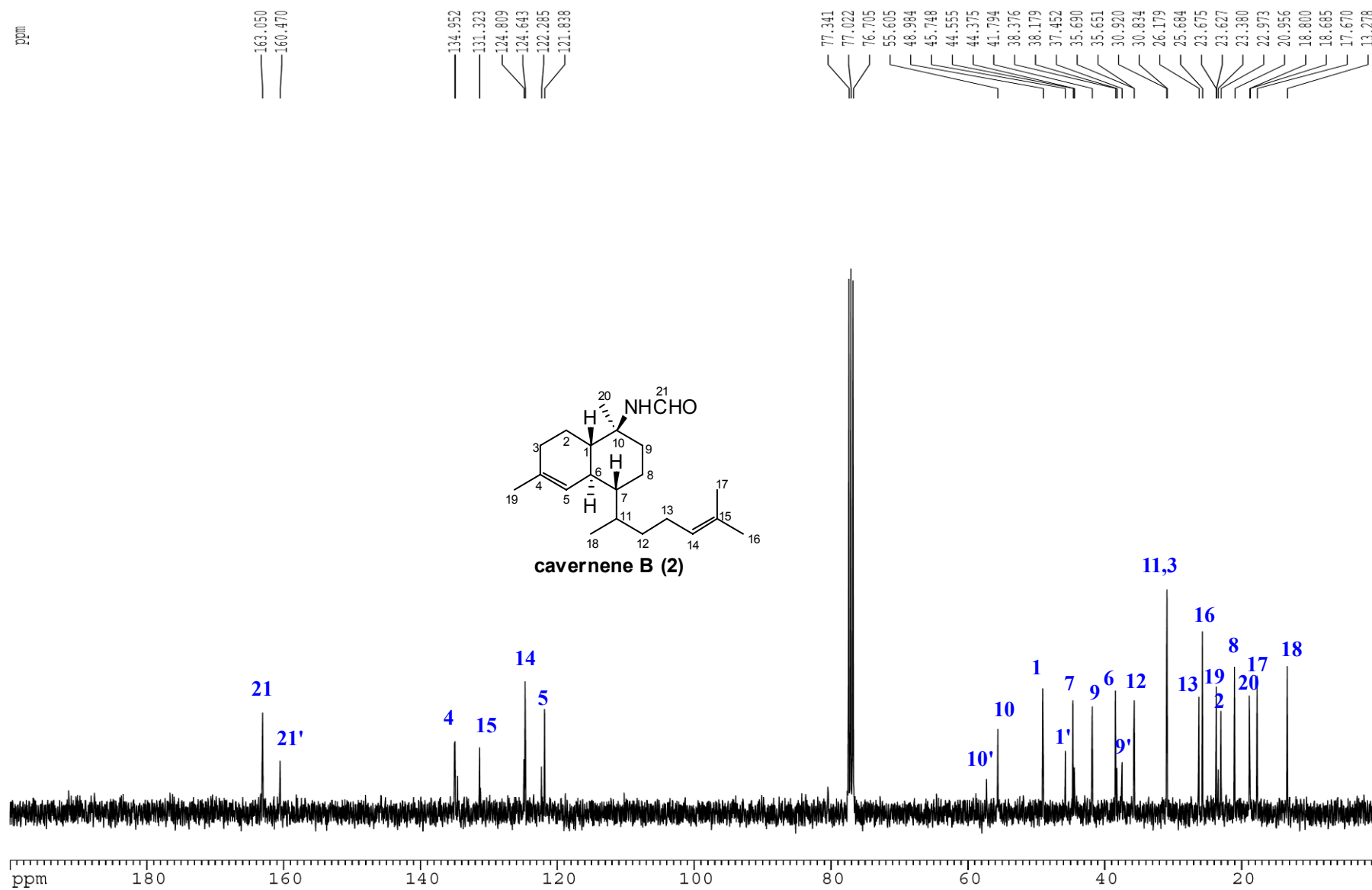
**Figure S11.**  $^{13}\text{C}$  NMR spectrum of cavernene B (2) in  $\text{CDCl}_3$ .

Figure S12. HSQC spectrum of cavernene B (2) in CDCl<sub>3</sub>.

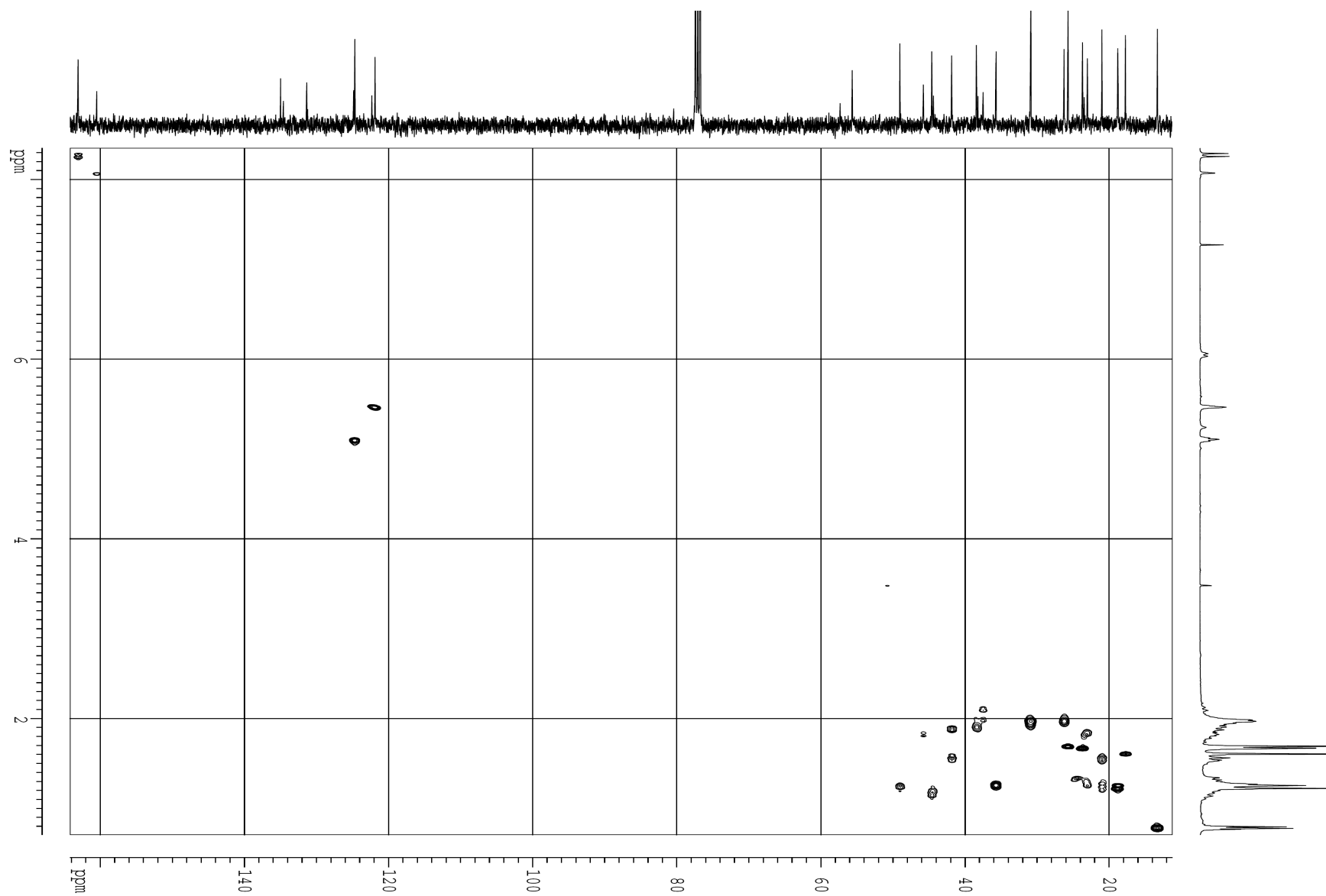
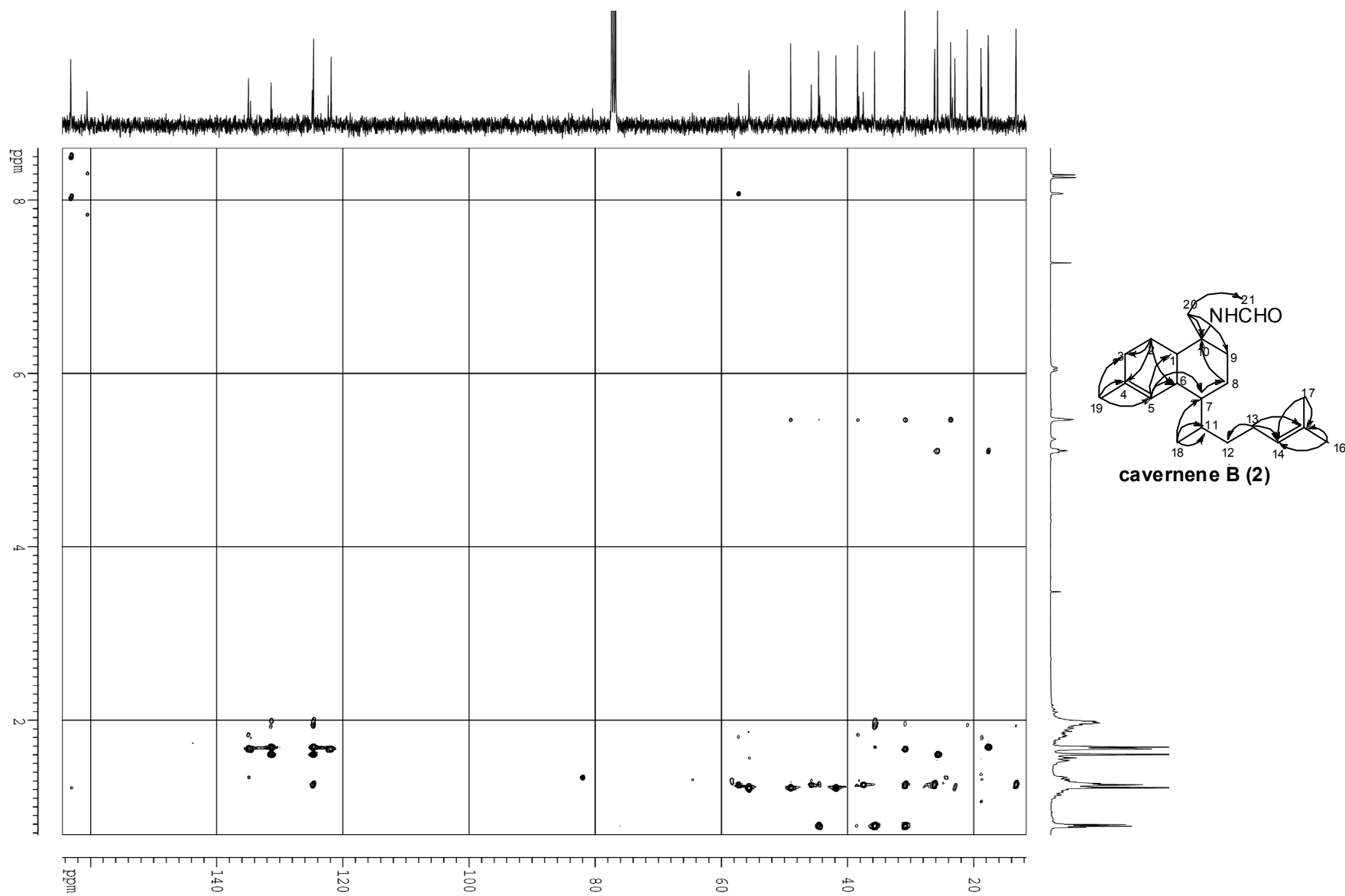


Figure S13. HMBC spectrum of cavernene B (2) in CDCl<sub>3</sub>.

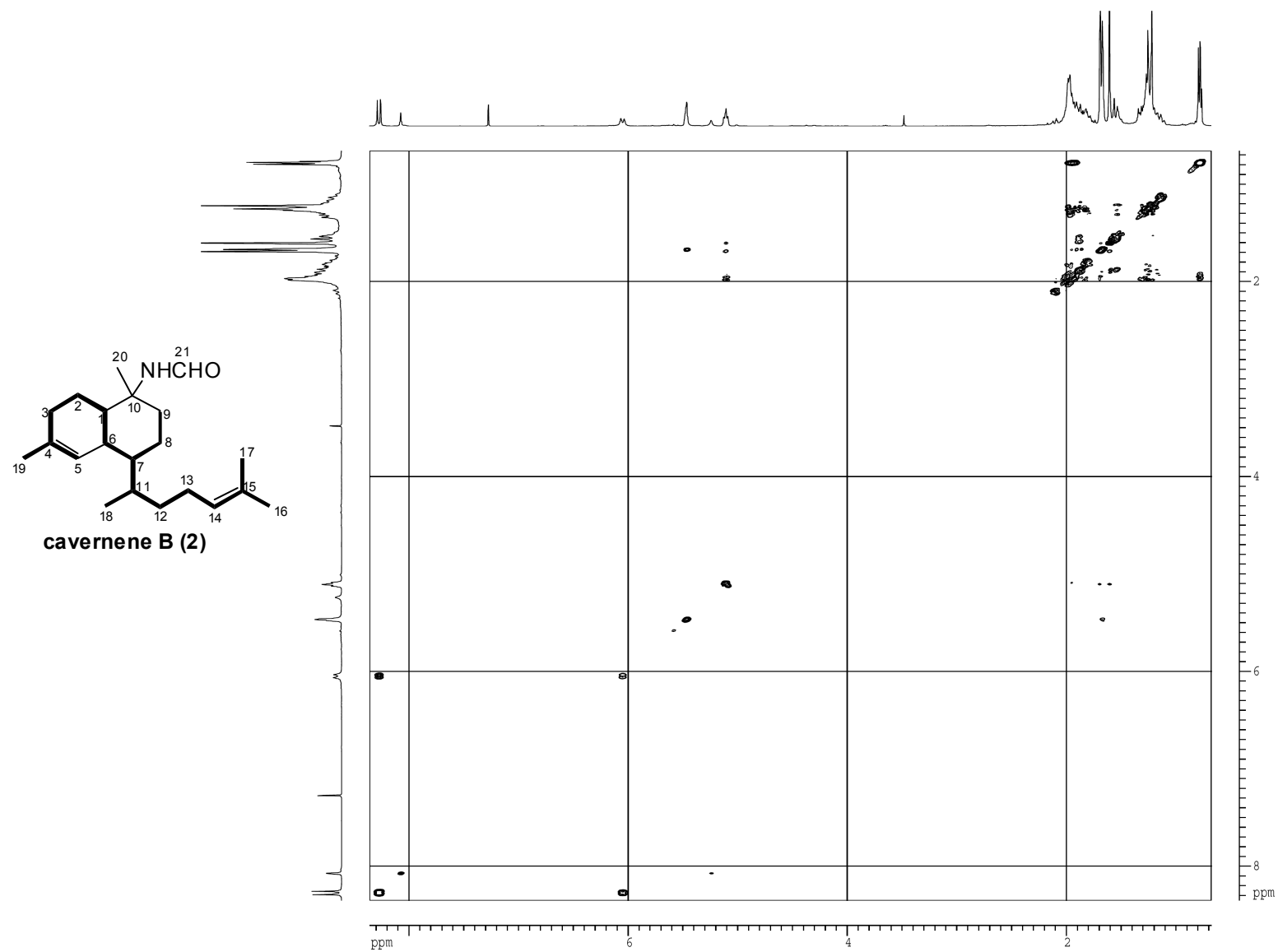
**Figure S14.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of cavernene B (**2**) in  $\text{CDCl}_3$ .

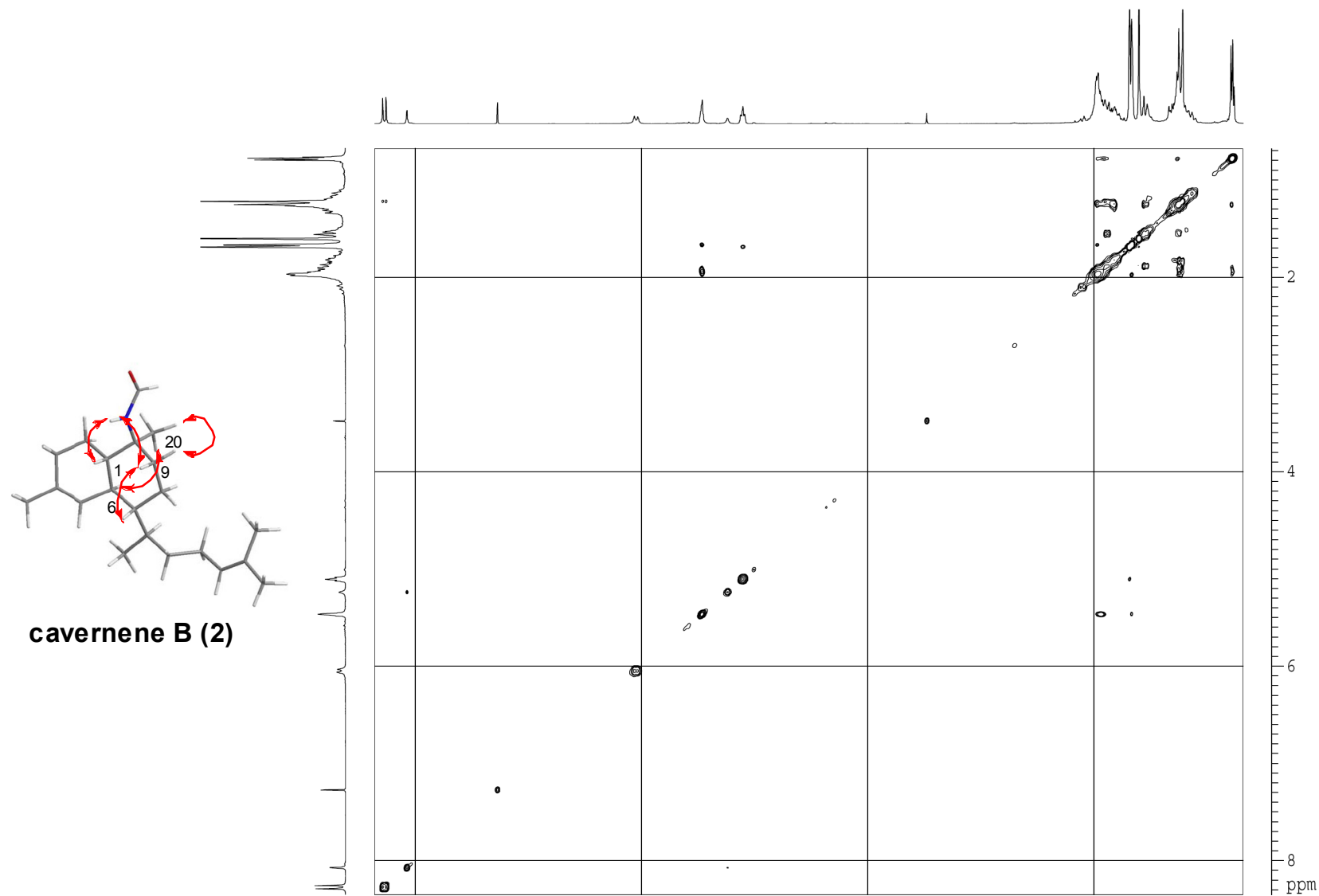
Figure S15. NOESY spectrum of cavernene B (2) in CDCl<sub>3</sub>.

Figure S16. IR spectrum of cavernene B (2).

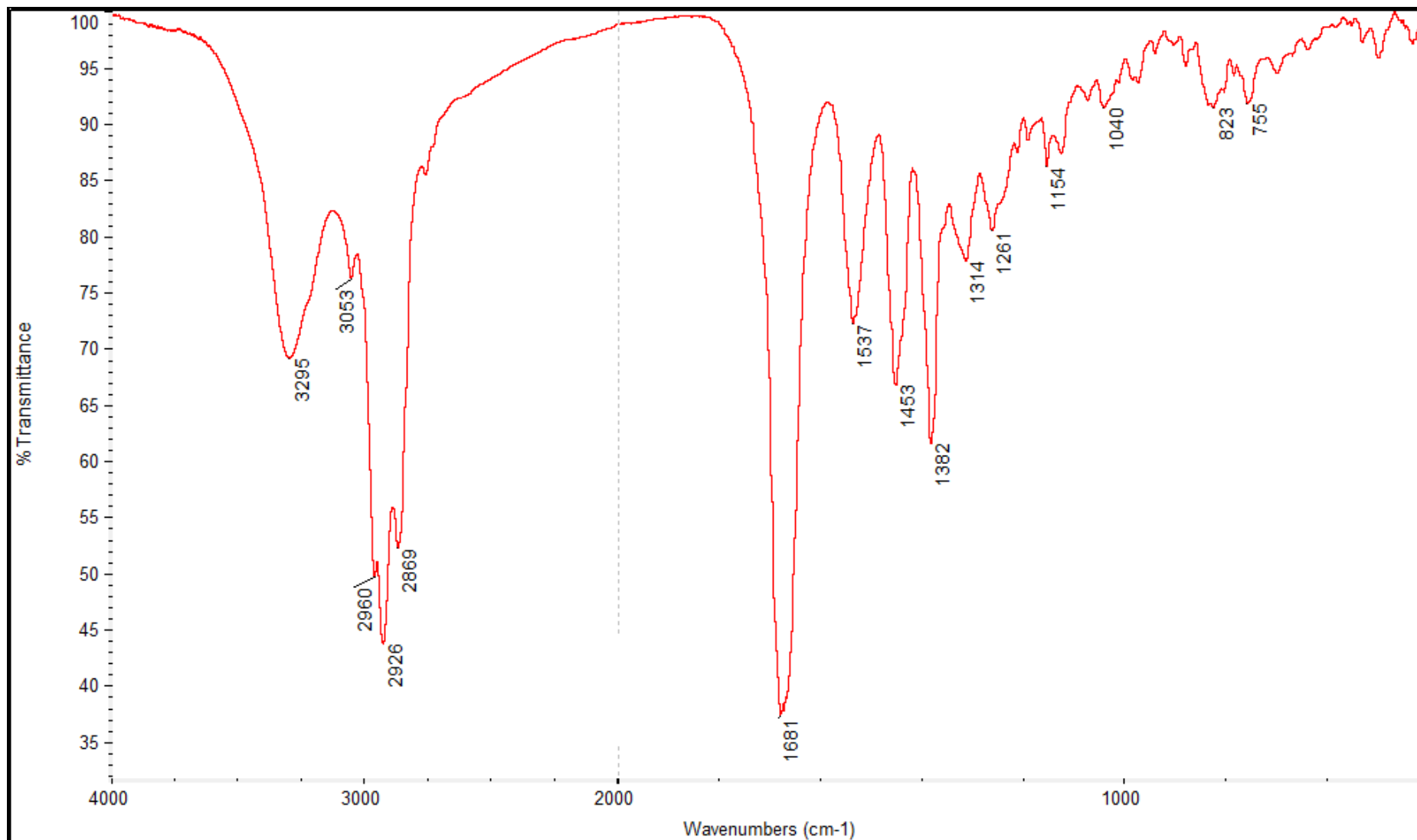


Figure S17. HRESIMS of cavernene B (2).

### Elemental Composition Report

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

Monoisotopic Mass, Even Electron Ions

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

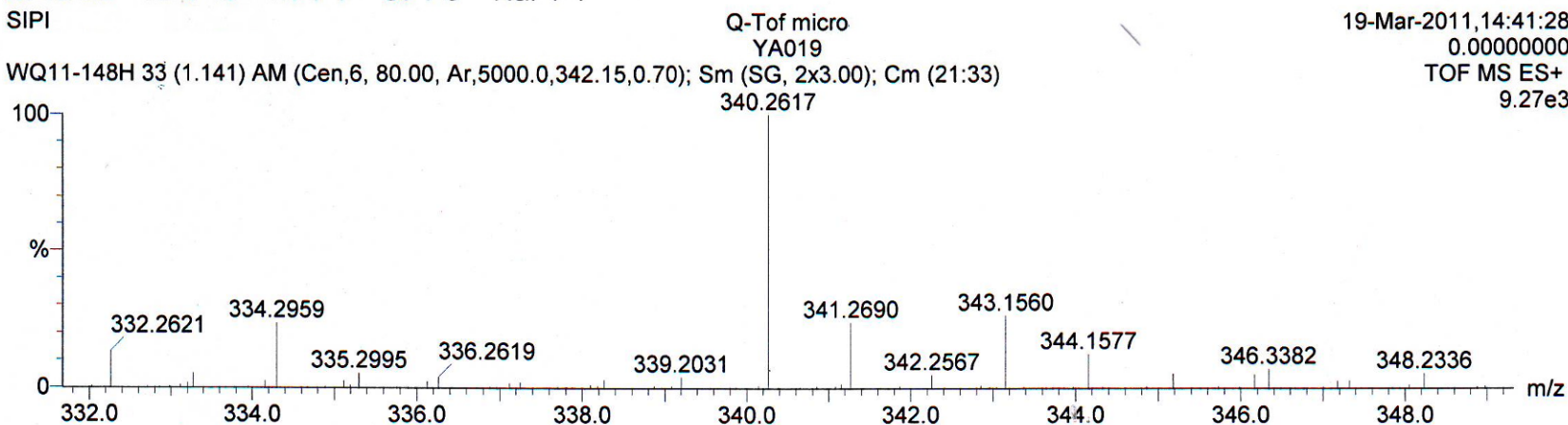
Elements Used:

C: 10-23 H: 5-40 N: 1-1 O: 1-3 Na: 1-1

SIPI

WQ11-148H 33 (1.141) AM (Cen,6, 80.00, Ar,5000.0,342.15,0.70); Sm (SG, 2x3.00); Cm (21:33)

19-Mar-2011,14:41:28  
 0.00000000  
 TOF MS ES+  
 9.27e3



Minimum: 30.00 -1.5  
 Maximum: 100.00 5.0 10.0 50.0

Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
340.2617	100.00	340.2616	0.1	0.3	4.5	27.4	C21 H35 N O Na

Figure S18. UV spectrum of cavernene B (2).

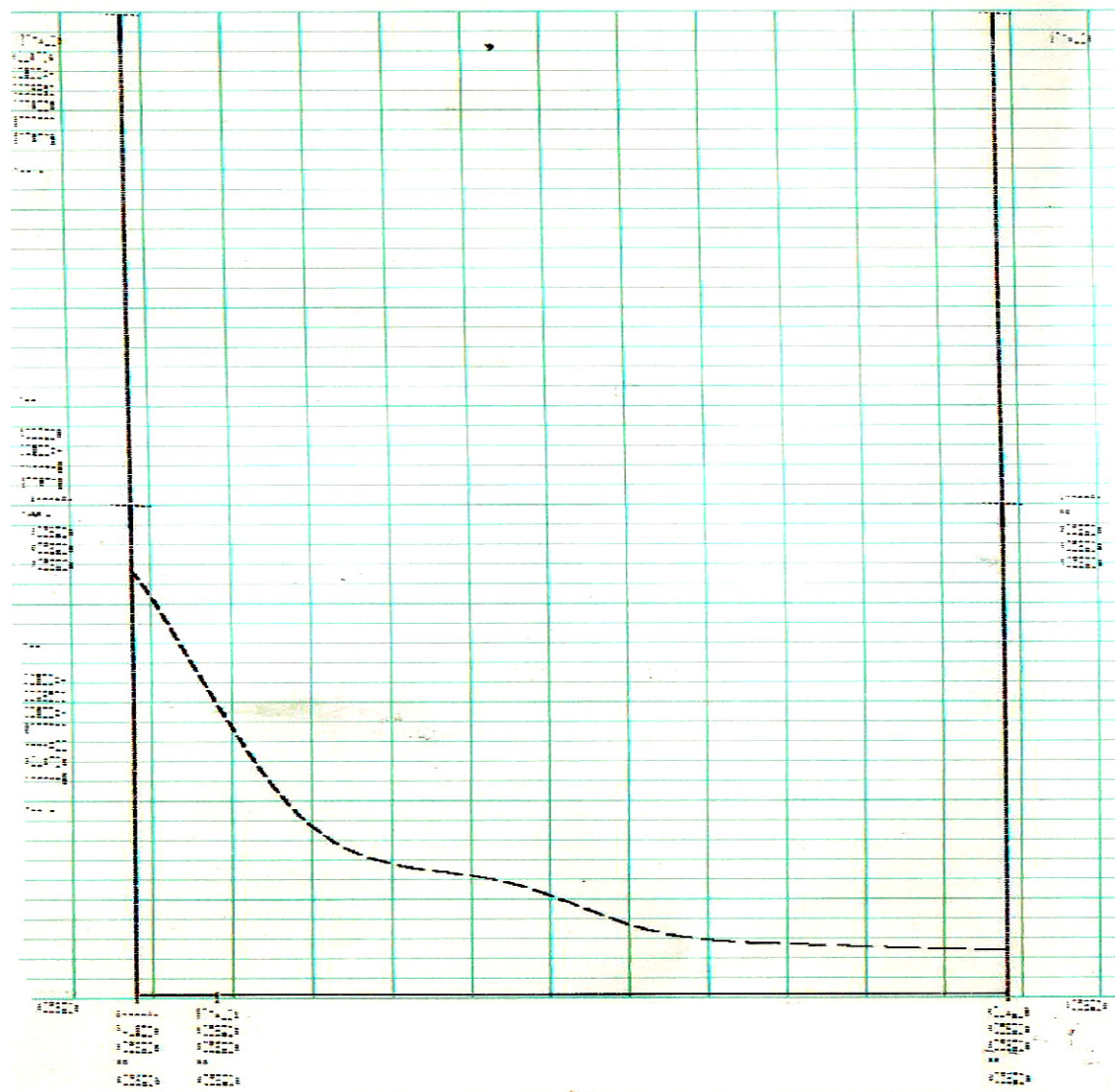
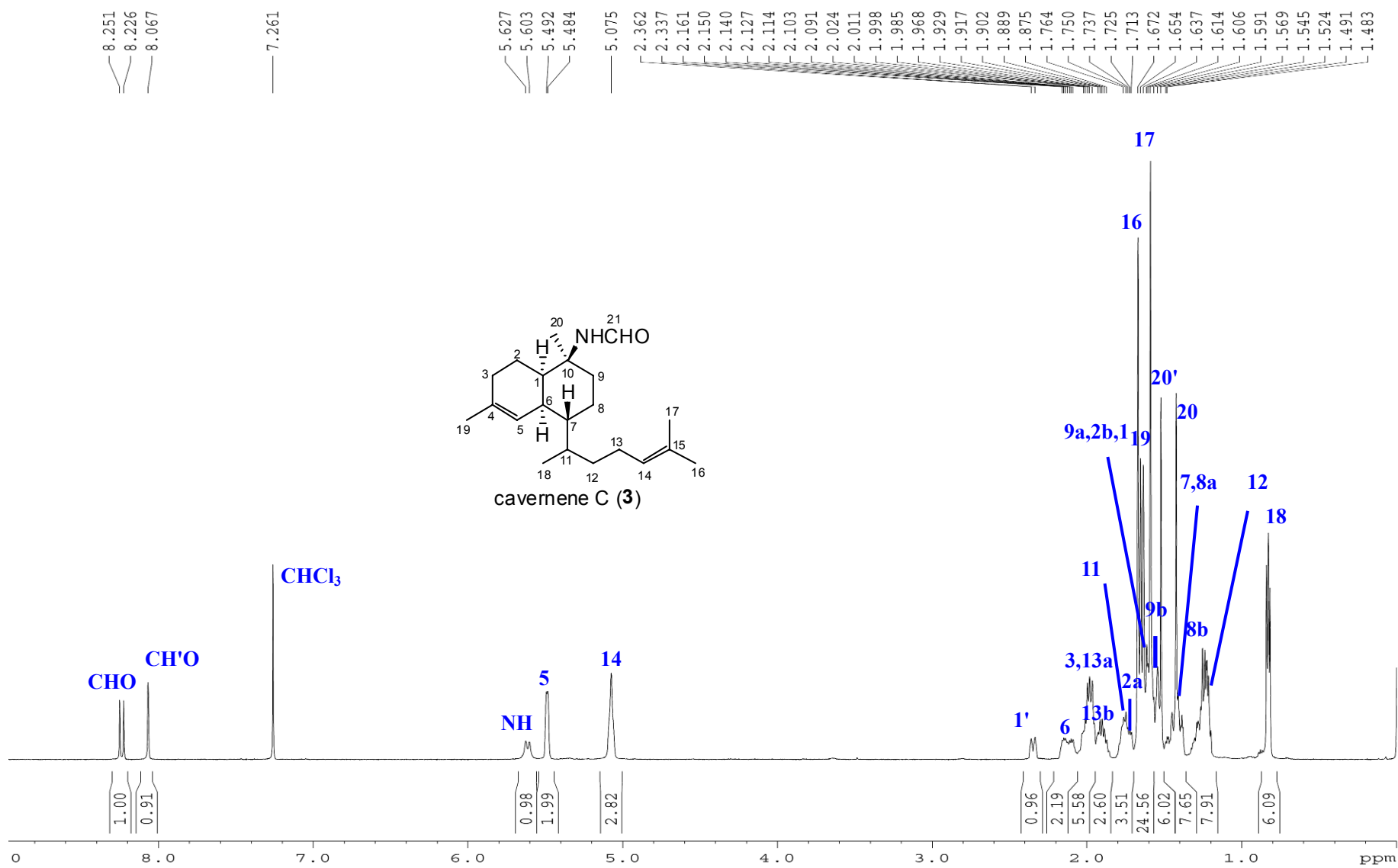




Figure S19.  $^1\text{H}$  NMR spectrum of cavernene C (3) in  $\text{CDCl}_3$ .

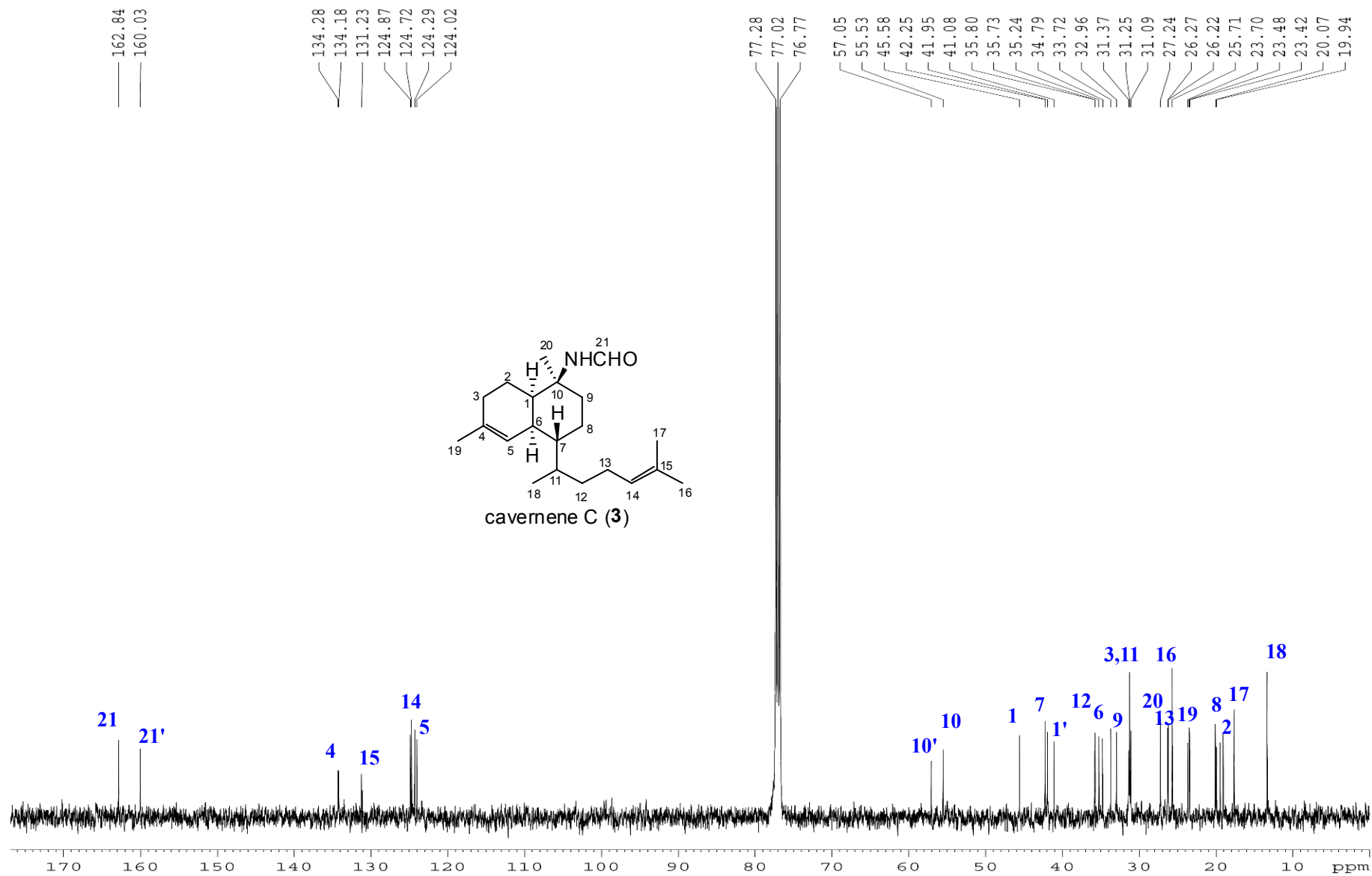
**Figure S20.**  $^{13}\text{C}$  NMR spectrum of cavernene C (**3**) in  $\text{CDCl}_3$ .

Figure S21. HSQC spectrum of cavernene C (3) in CDCl<sub>3</sub>.

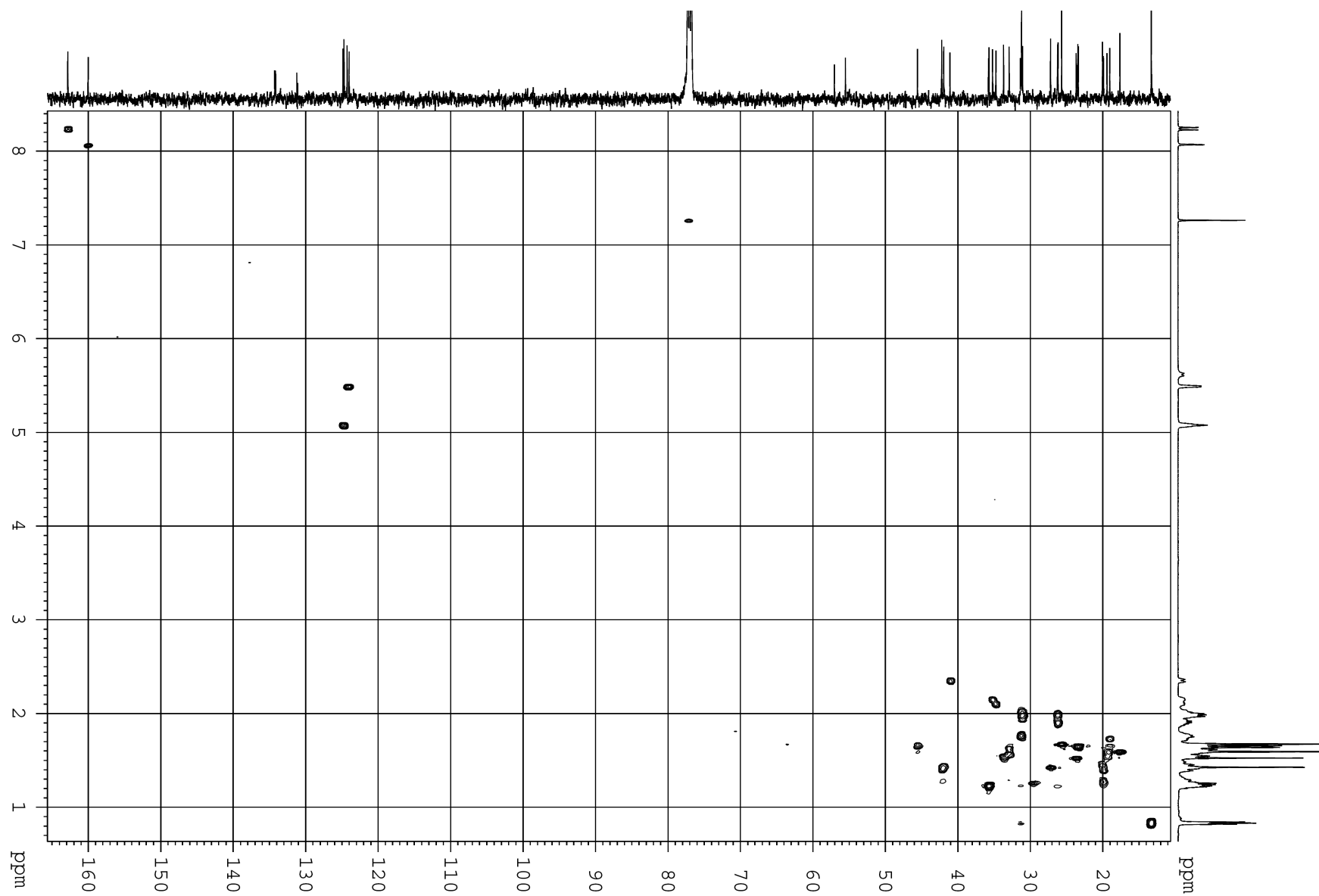
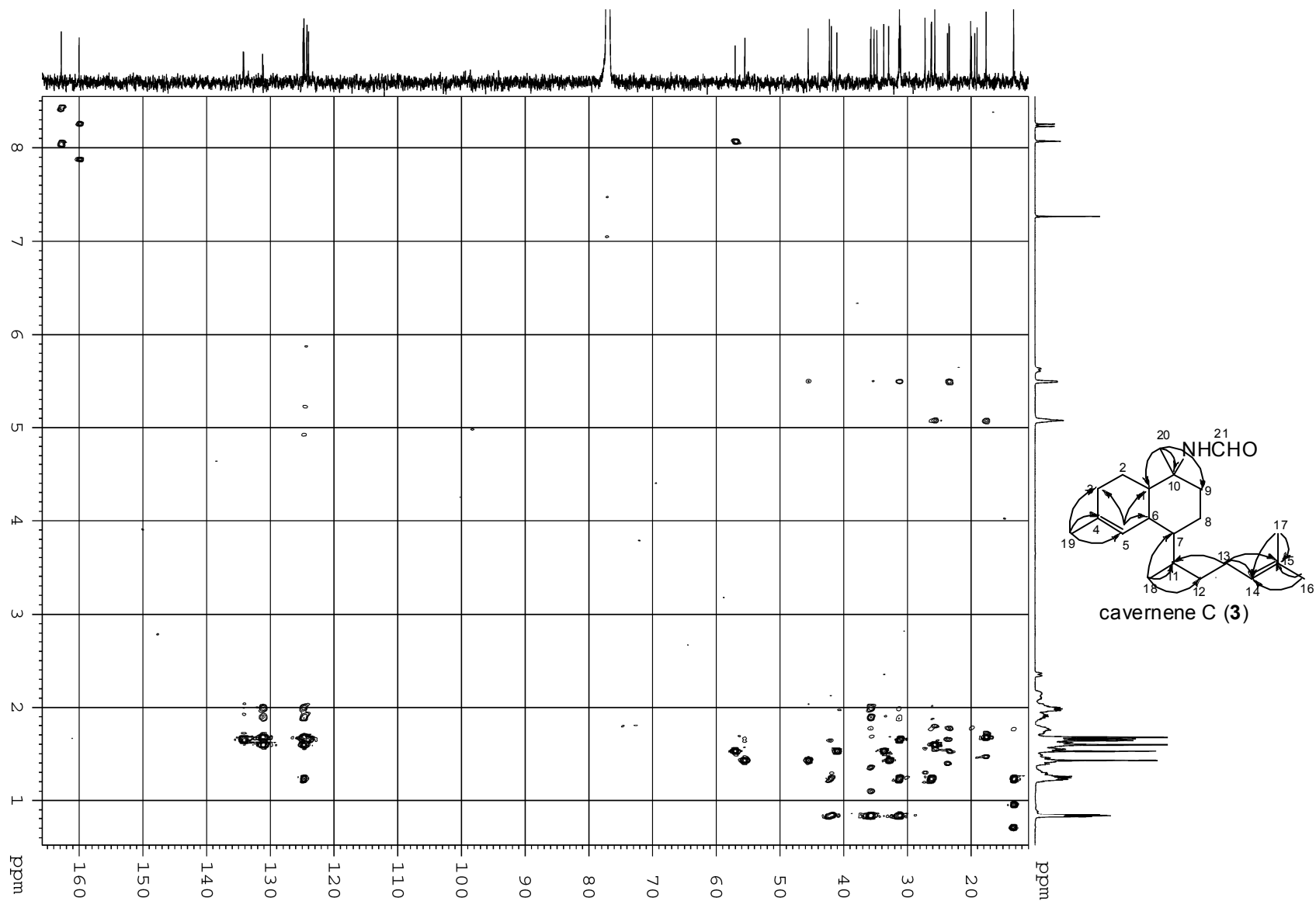


Figure S22. HMBC spectrum of cavernene C (3) in CDCl<sub>3</sub>.

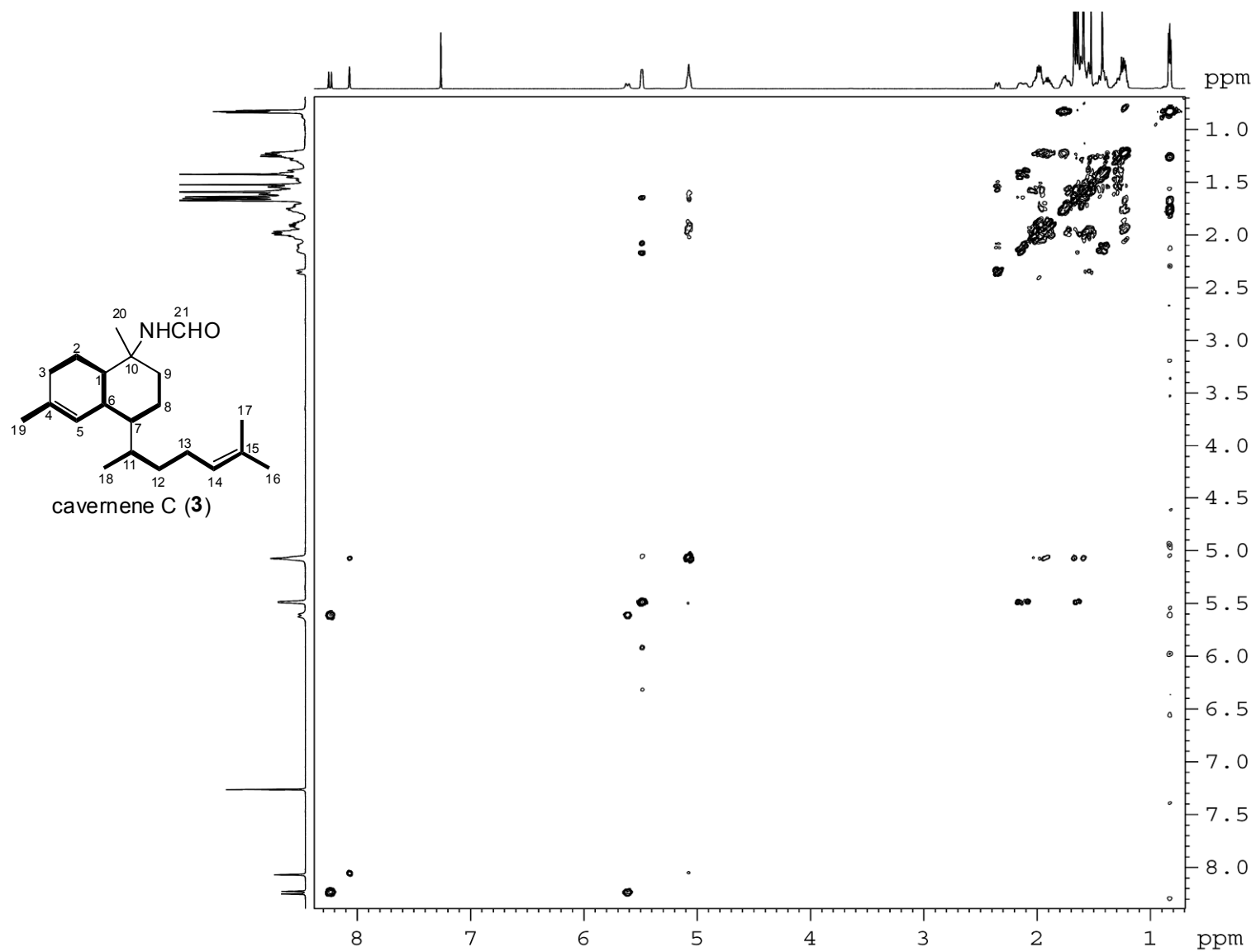
**Figure S23.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of cavernene C (**3**) in  $\text{CDCl}_3$ .

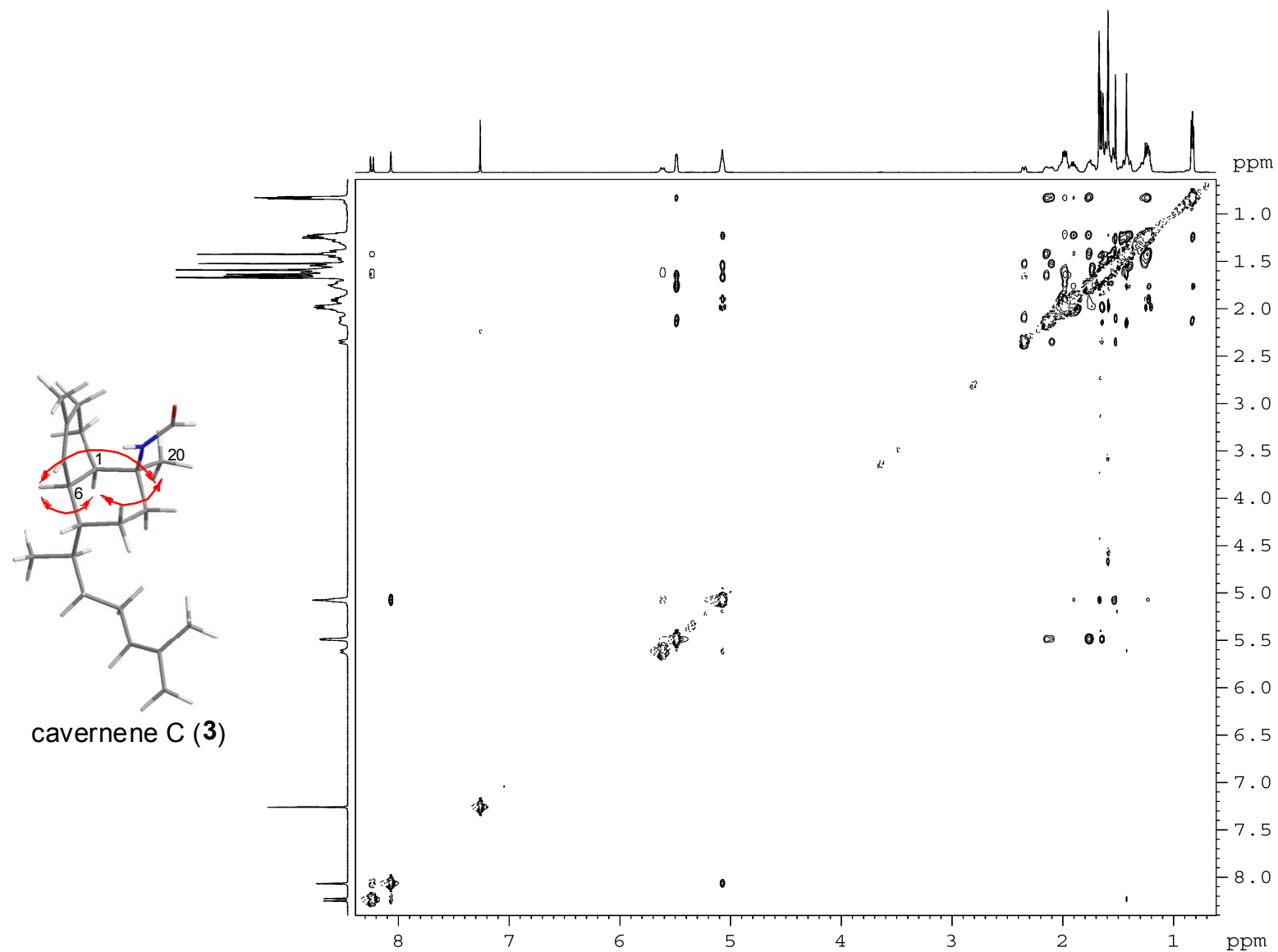
Figure S24. NOESY spectrum of cavernene C (3) in CDCl<sub>3</sub>.

Figure S25. IR spectrum of cavernene C (3).

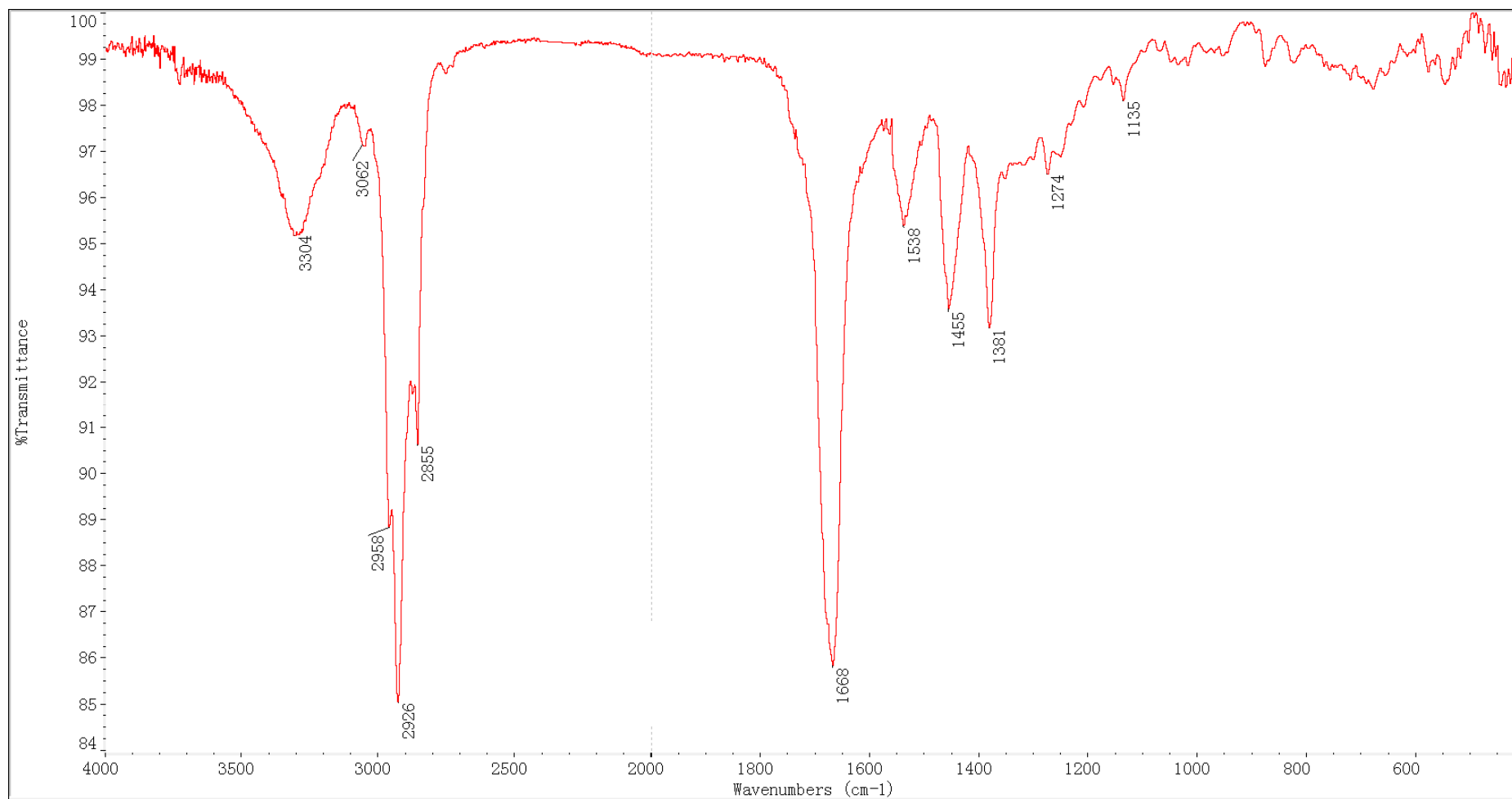


Figure S26. HRESIMS of cavernene C (3).

### Elemental Composition Report

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

Monoisotopic Mass, Even Electron Ions

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

Elements Used:

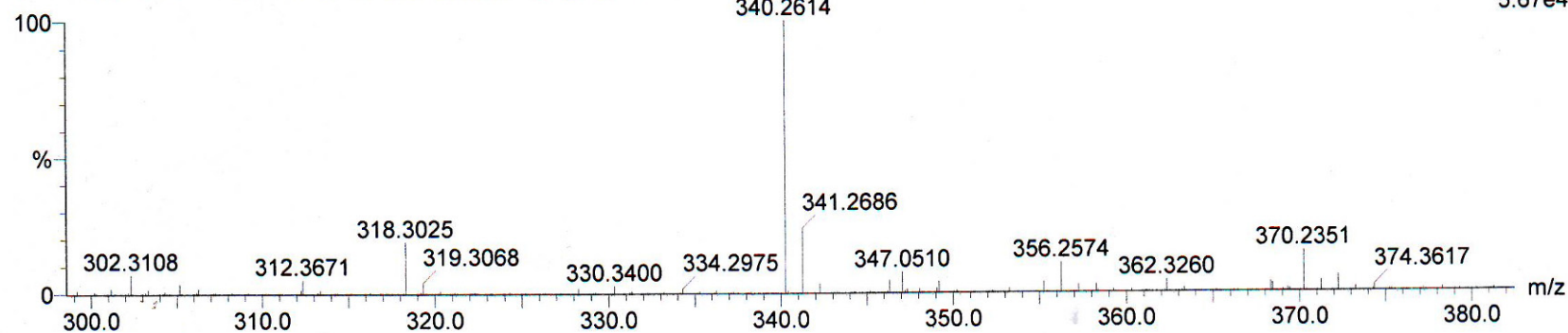
C: 10-25 H: 5-40 N: 1-1 O: 1-3 Na: 1-1

SIPI

WQ11-233H 32 (1.126) AM (Med,6, Ar,5000.0,354.24,0.70); Sm (SG, 2x3.00); Cm (20:32)

Q-ToF micro  
 YA019

09-Apr-2011,14:55:03  
 0.00000000  
 TOF MS ES+  
 5.67e4



Minimum: 30.00 -1.5  
 Maximum: 100.00 5.0 50.0 50.0

Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
340.2614	100.00	340.2616	-0.2	-0.6	4.5	25.4	C21 H35 N O Na



Figure S27. UV spectrum of cavernene C (3).

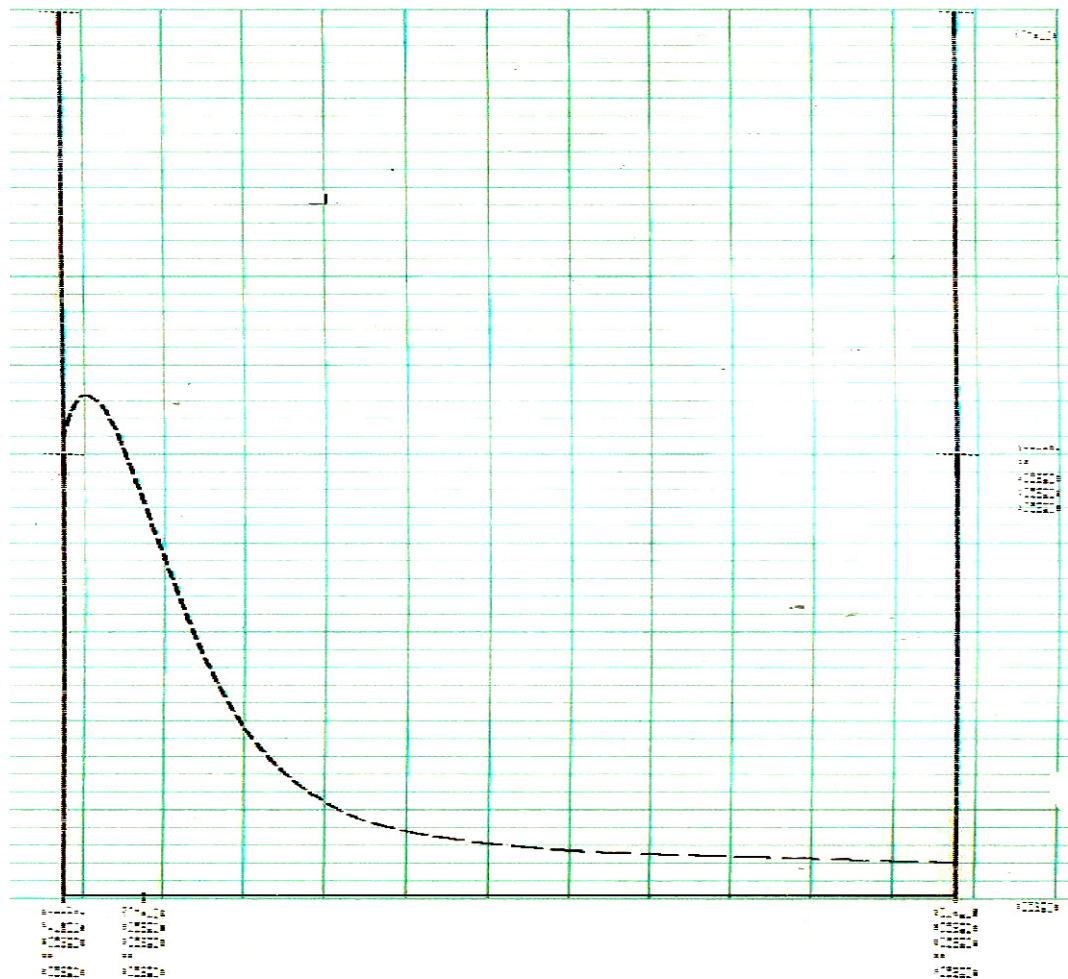
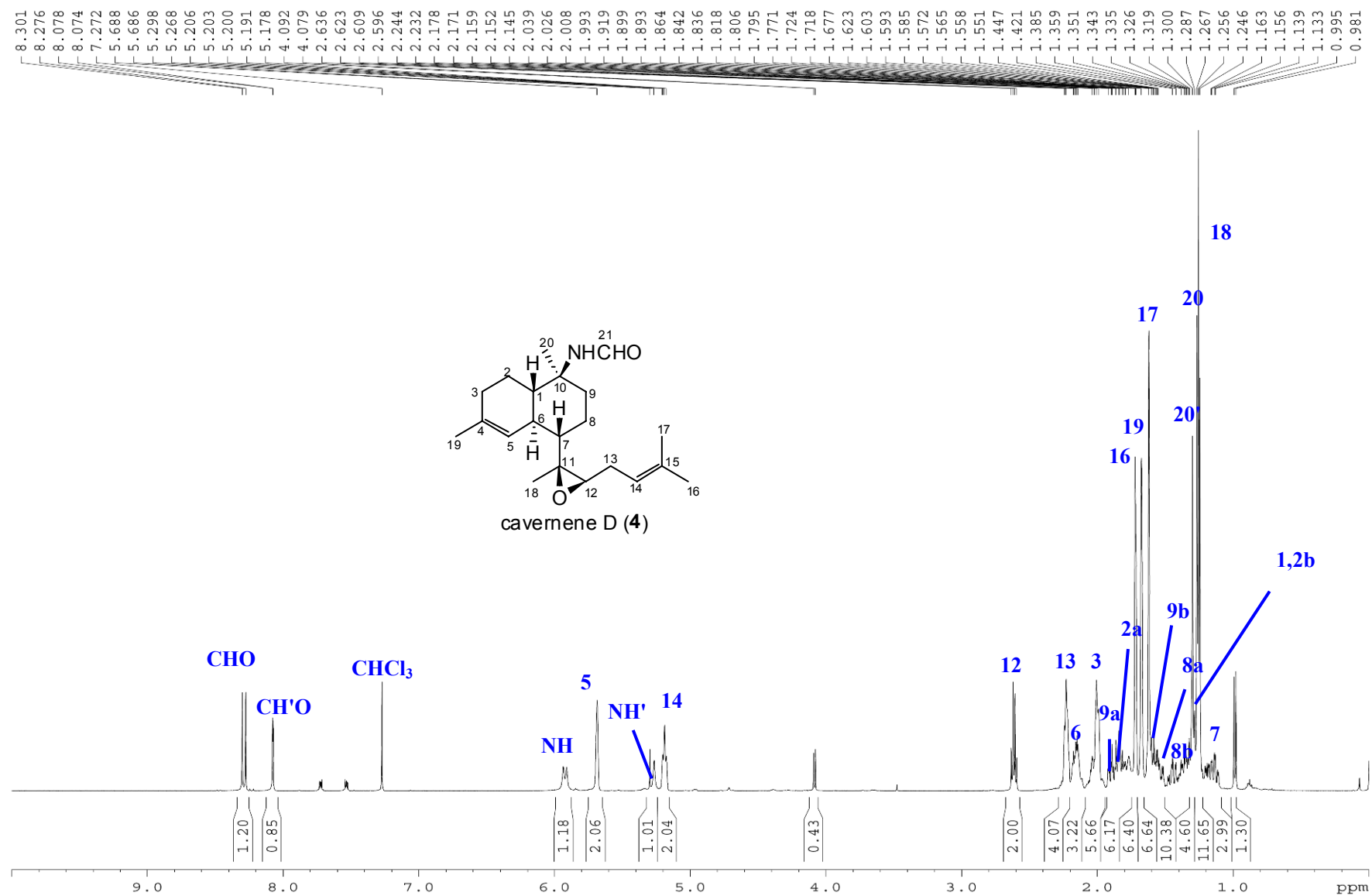


Figure S28.  $^1\text{H}$  NMR spectrum of cavernene D (4) in  $\text{CDCl}_3$ .

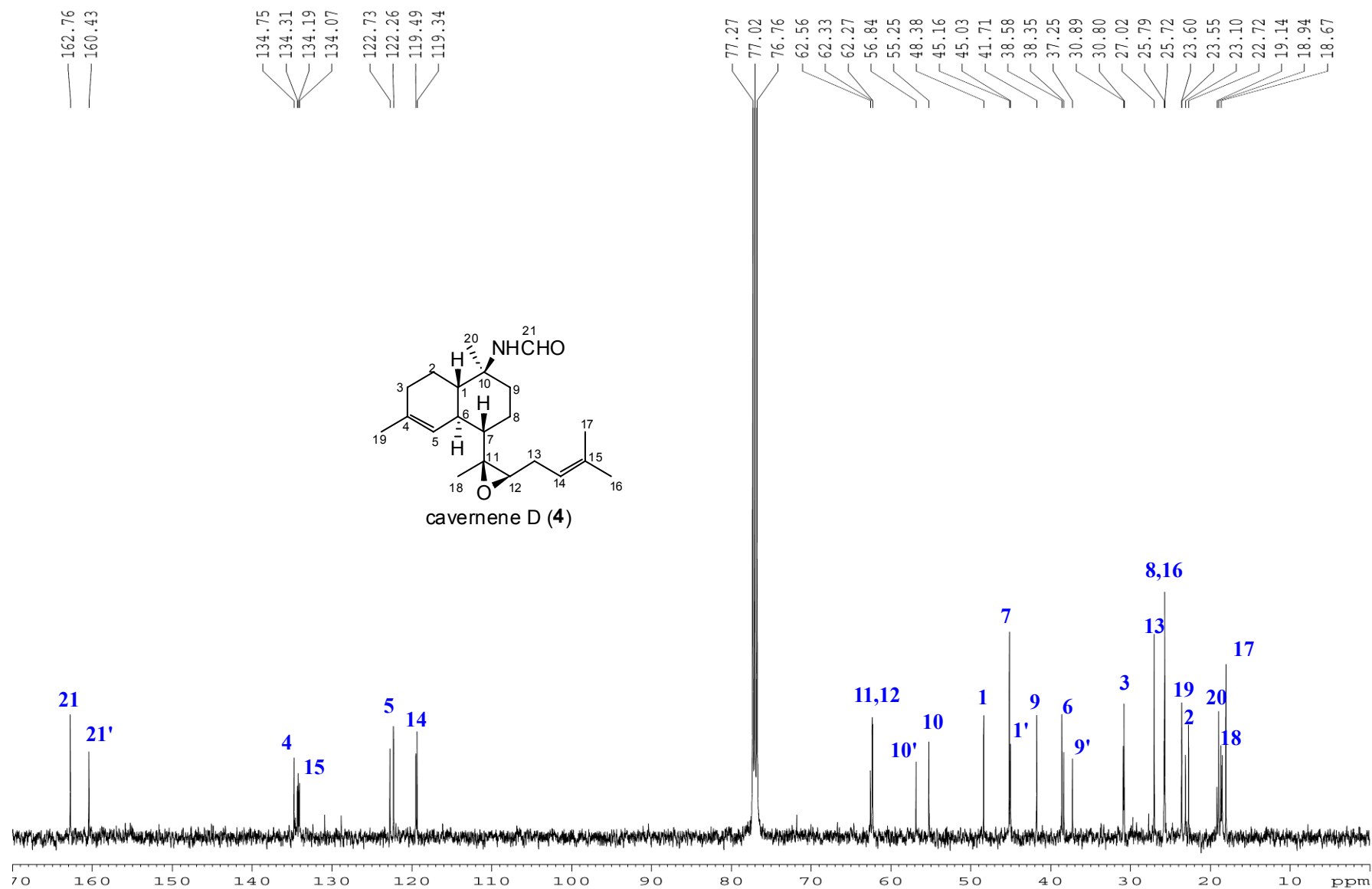
**Figure S29.**  $^{13}\text{C}$  NMR spectrum of cavernene D (**4**) in  $\text{CDCl}_3$ .

Figure S30. HSQC spectrum of cavernene D (4) in CDCl<sub>3</sub>.

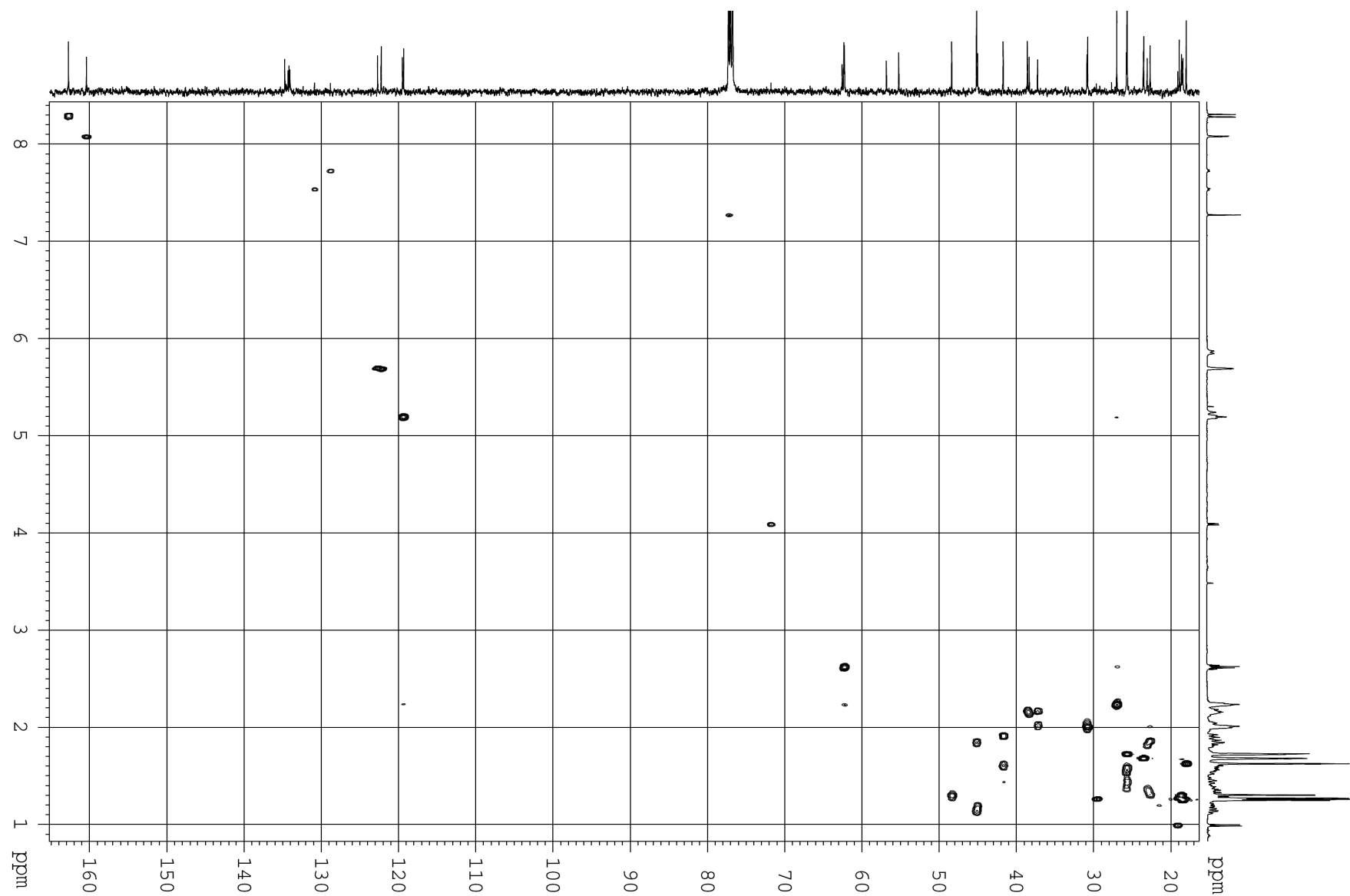
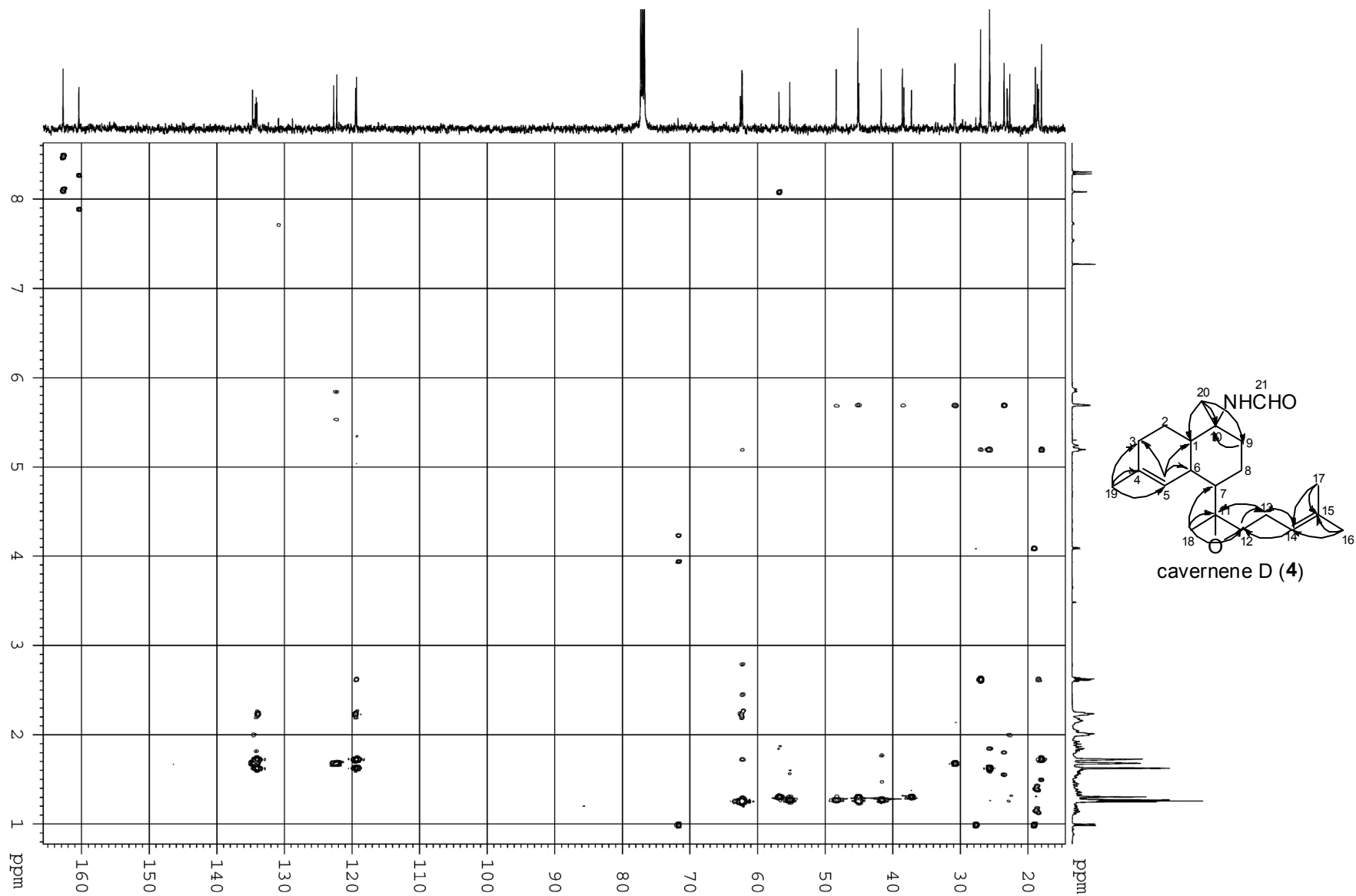


Figure S31. HMBC spectrum of cavernene D (4) in CDCl<sub>3</sub>.

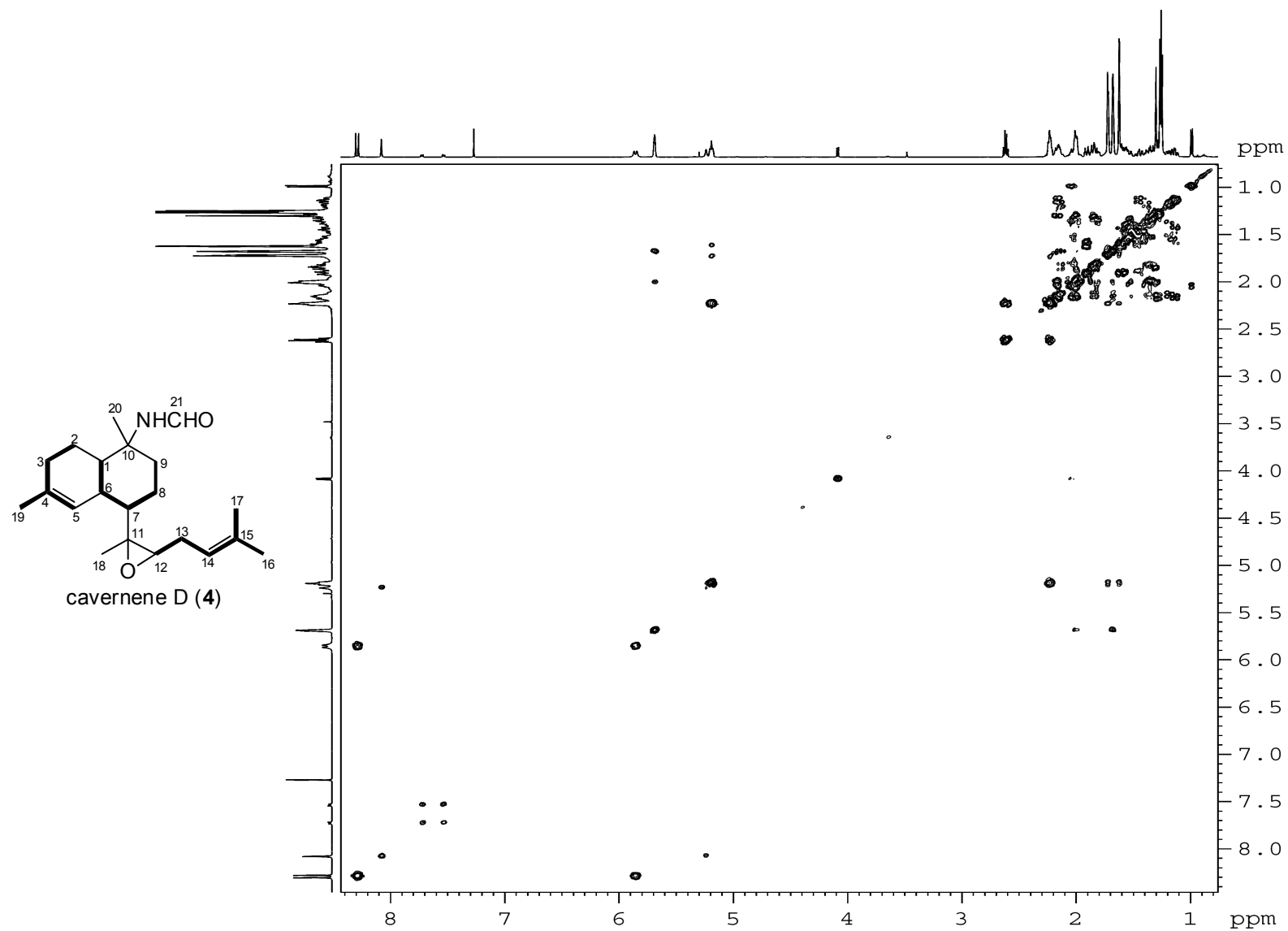
**Figure S32.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of cavernene D (**4**) in  $\text{CDCl}_3$ .

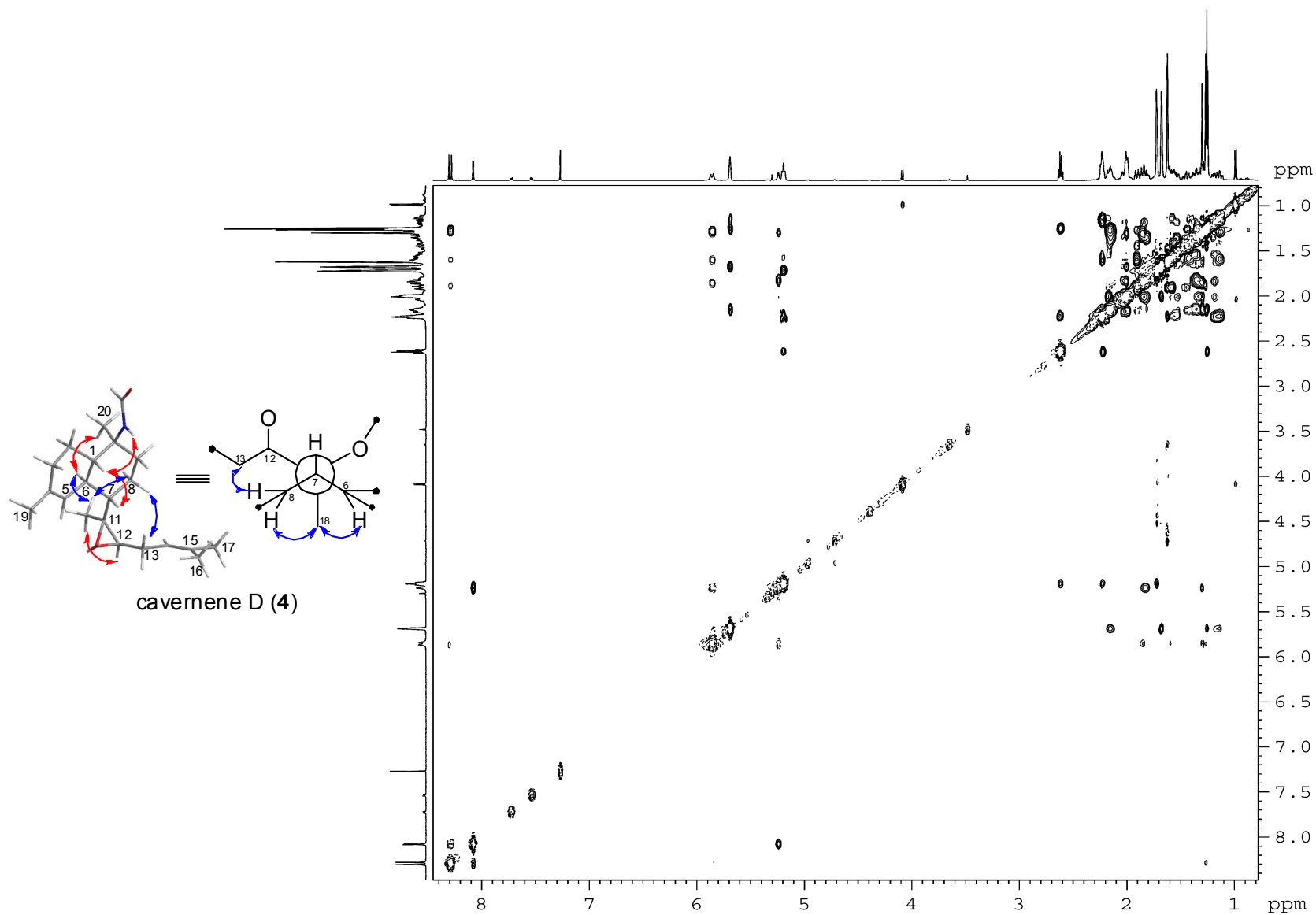
Figure S33. NOESY spectrum of cavernene D (4) in CDCl<sub>3</sub>.

Figure S34. IR spectrum of cavernene D (4).

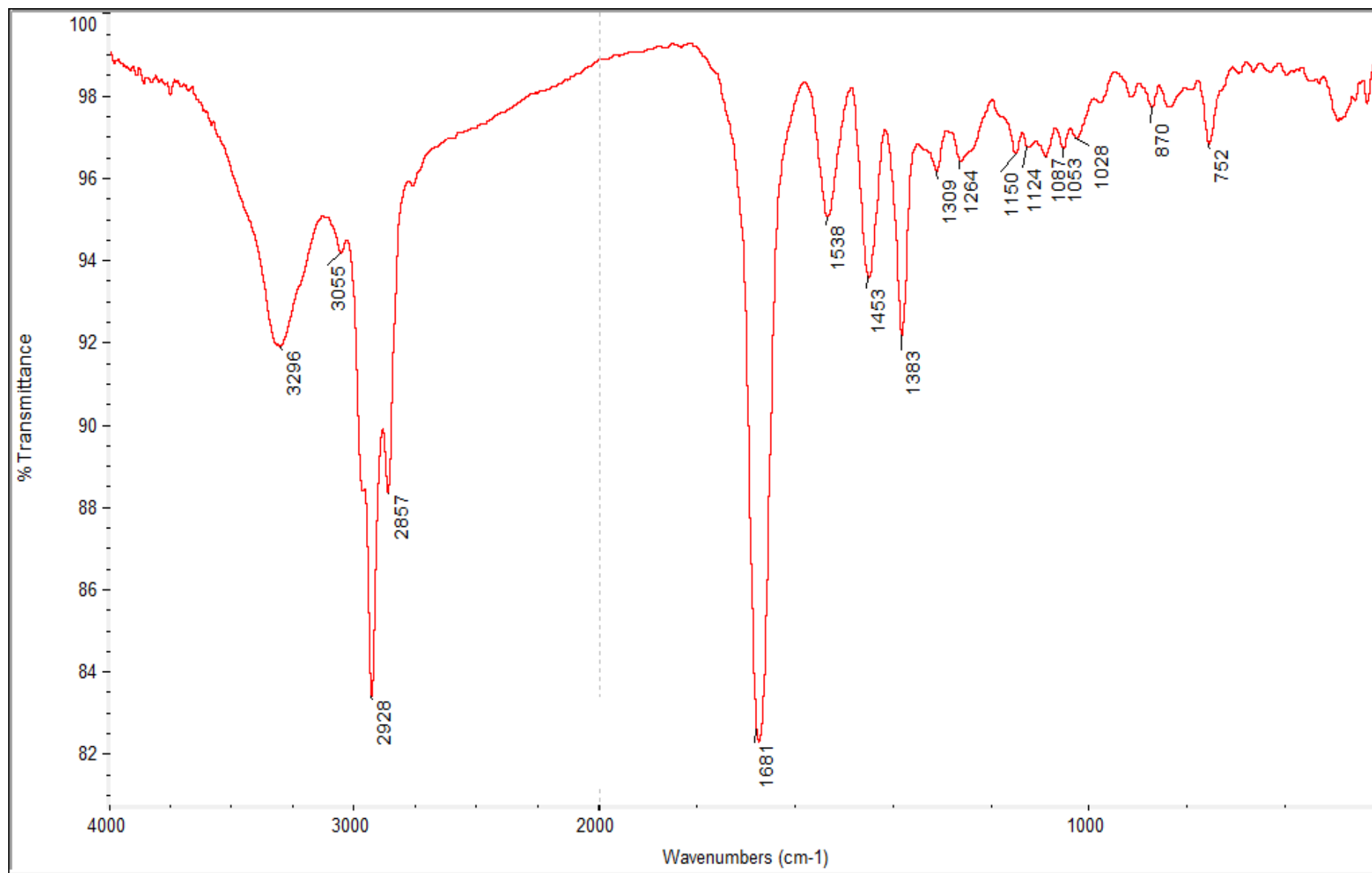




Figure S35. HRESIMS of cavernene D (4).

### Elemental Composition Report

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

Selected filters: None

Monoisotopic Mass, Even Electron Ions

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

Elements Used:

C: 10-23 H: 5-36 N: 1-1 O: 1-3 Na: 1-1

SIPI

Q-ToF micro  
YA019

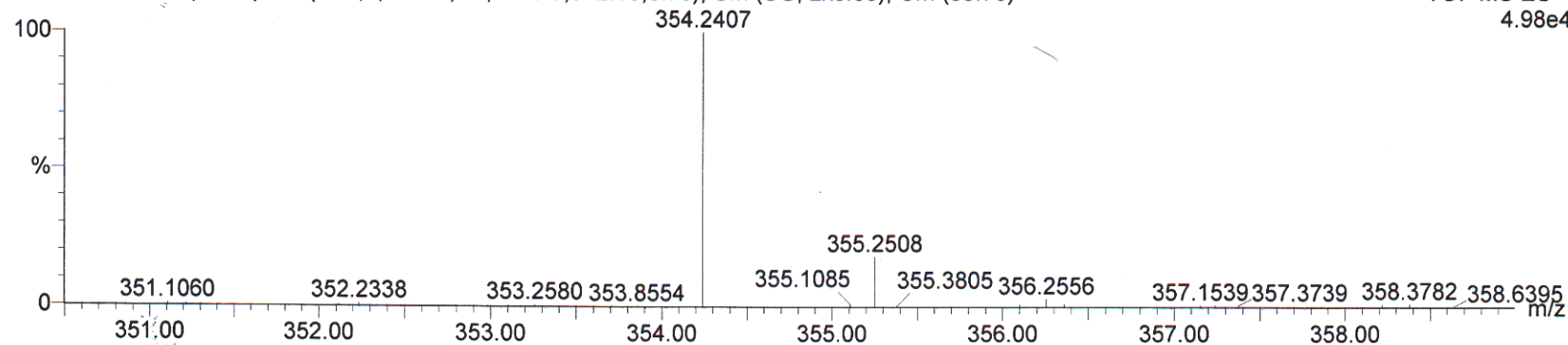
19-Mar-2011,14:31:46

0.00000000

WQ11-147H1 56 (1.934) AM (Cen,6, 80.00, Ar,5000.0,342.15,0.70); Sm (SG, 2x3.00); Cm (55:70)

TOF MS ES+

4.98e4



Minimum: 30.00  
Maximum: 100.00

Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
354.2407	100.00	354.2409	-0.2	-0.6	5.5	424.7	C21 H33 N O2 Na

Figure S36. UV spectrum of cavernene D (4).

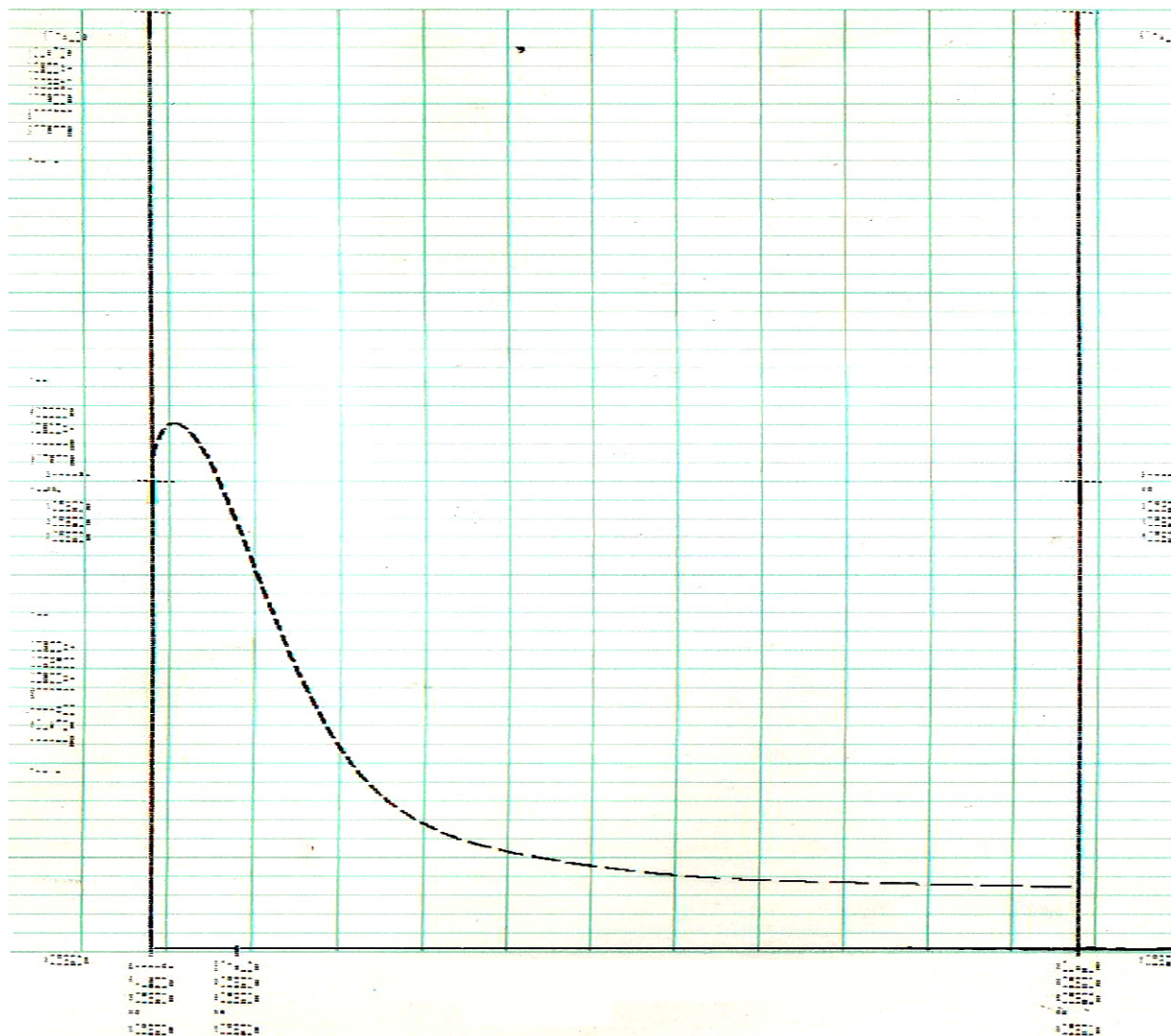


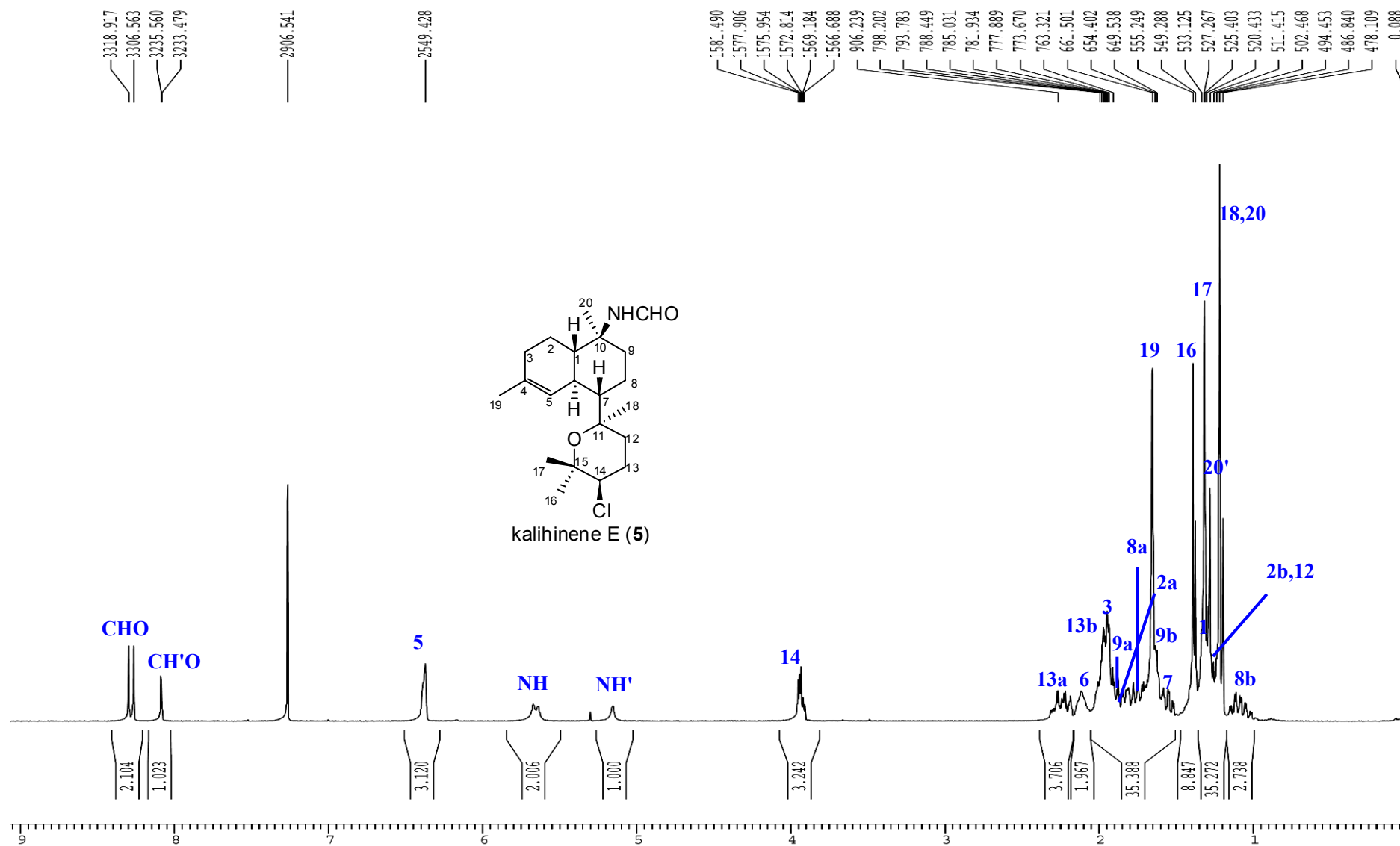
Figure S37.  $^1\text{H}$  NMR spectrum of kalihinene E (**5**) in  $\text{CDCl}_3$ .

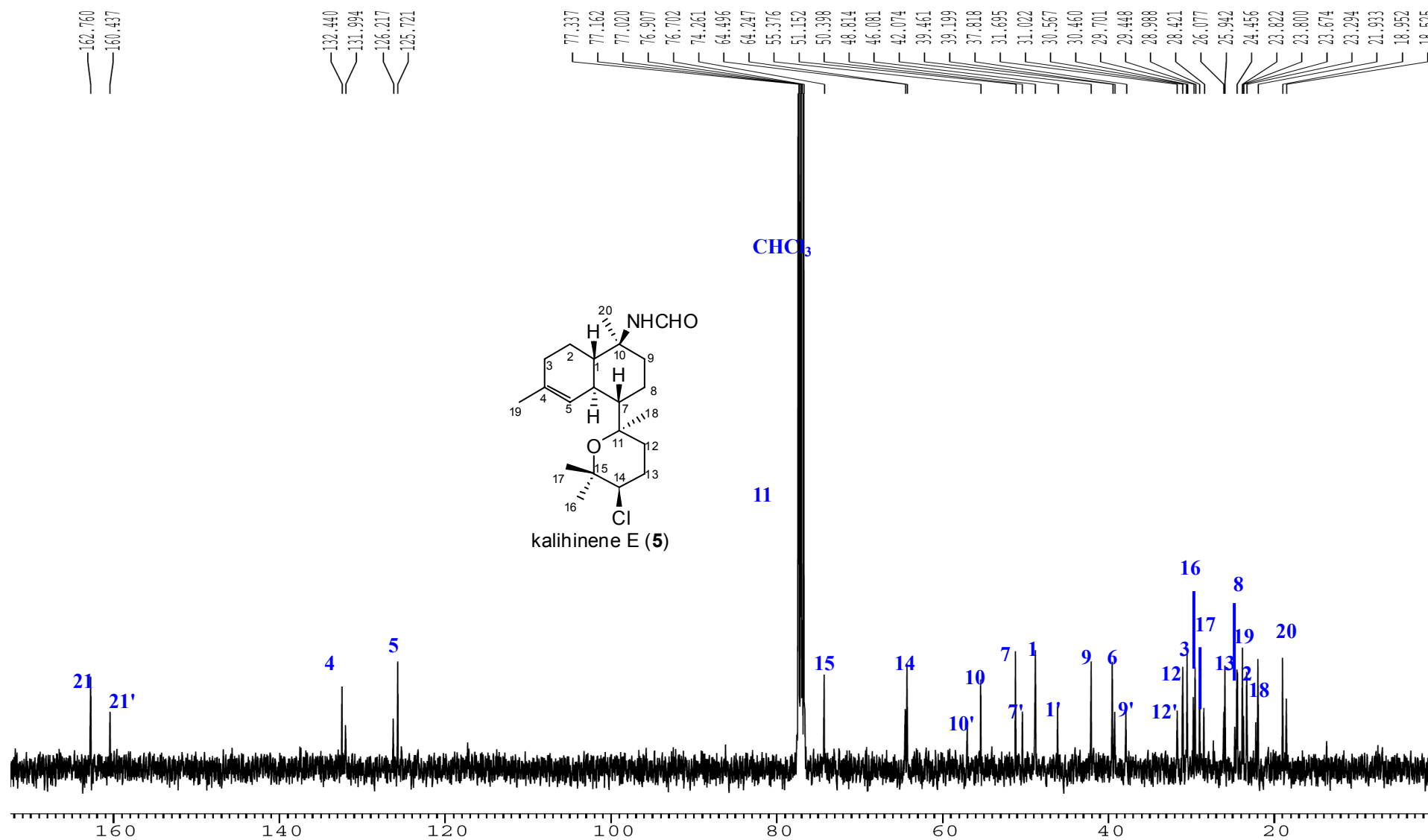
Figure S38.  $^{13}\text{C}$  NMR spectrum of kalihinene E (5) in  $\text{CDCl}_3$ .

Figure S39. HSQC spectrum of kalihinene E (5) in CDCl<sub>3</sub>.

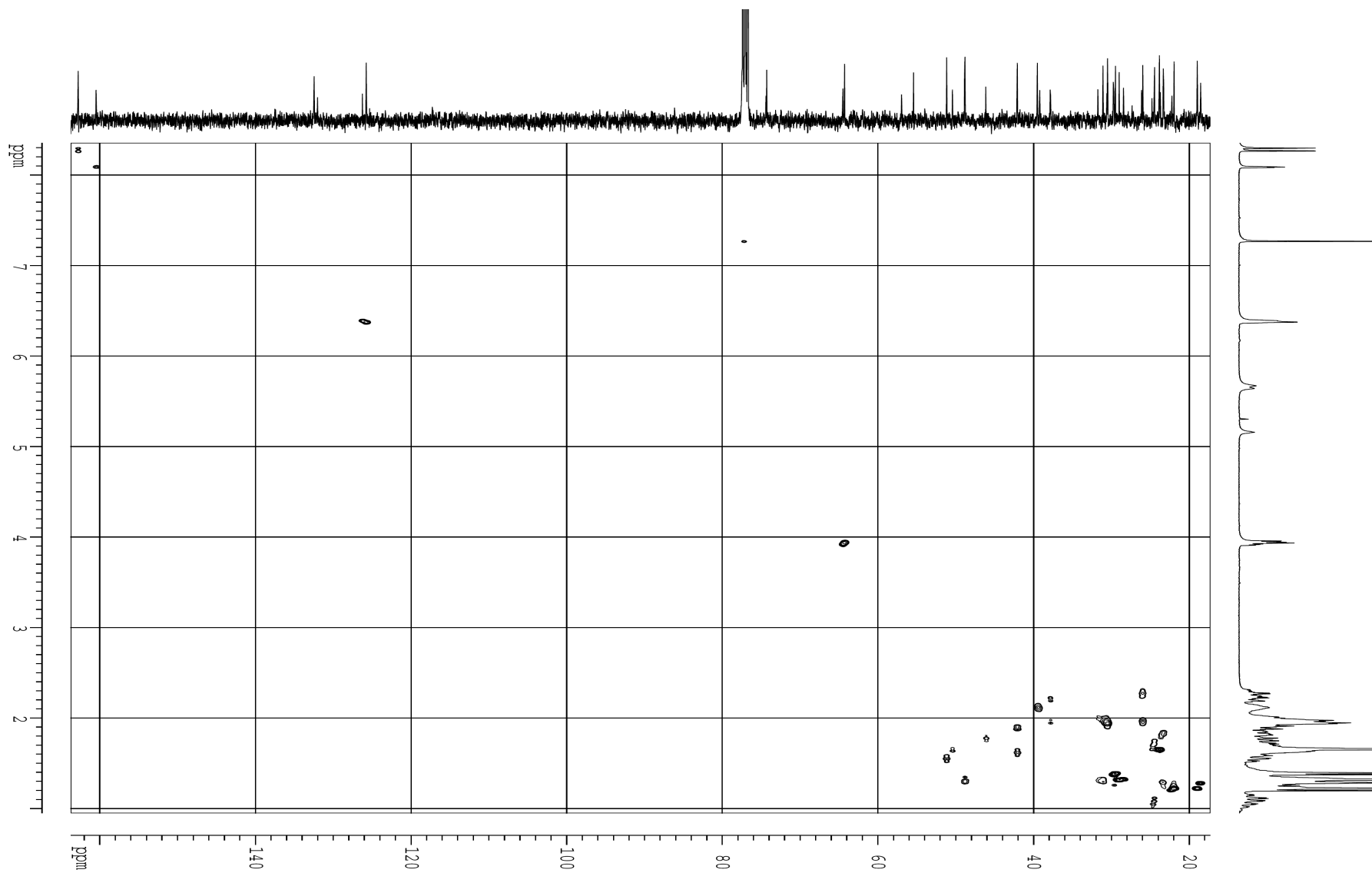
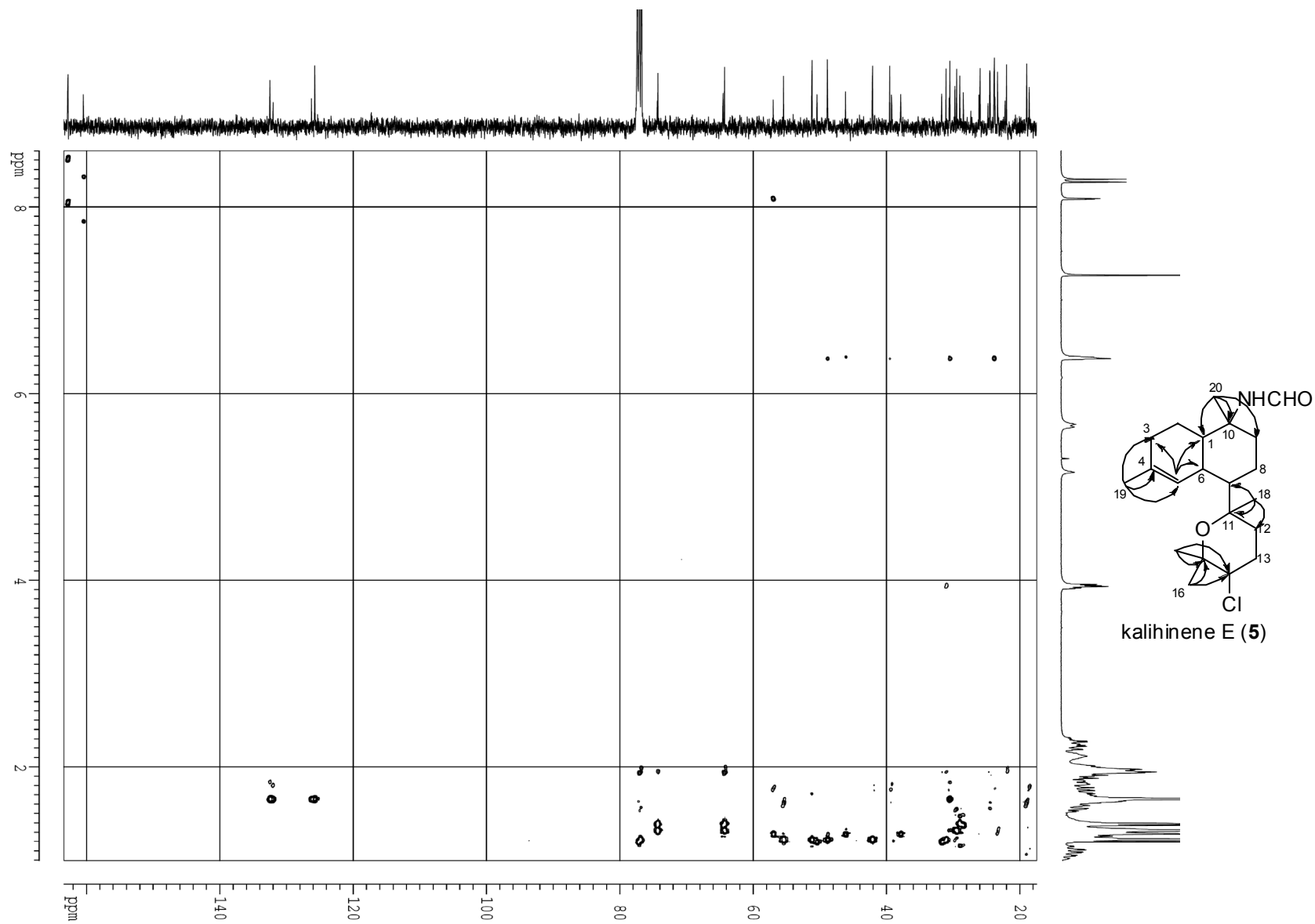
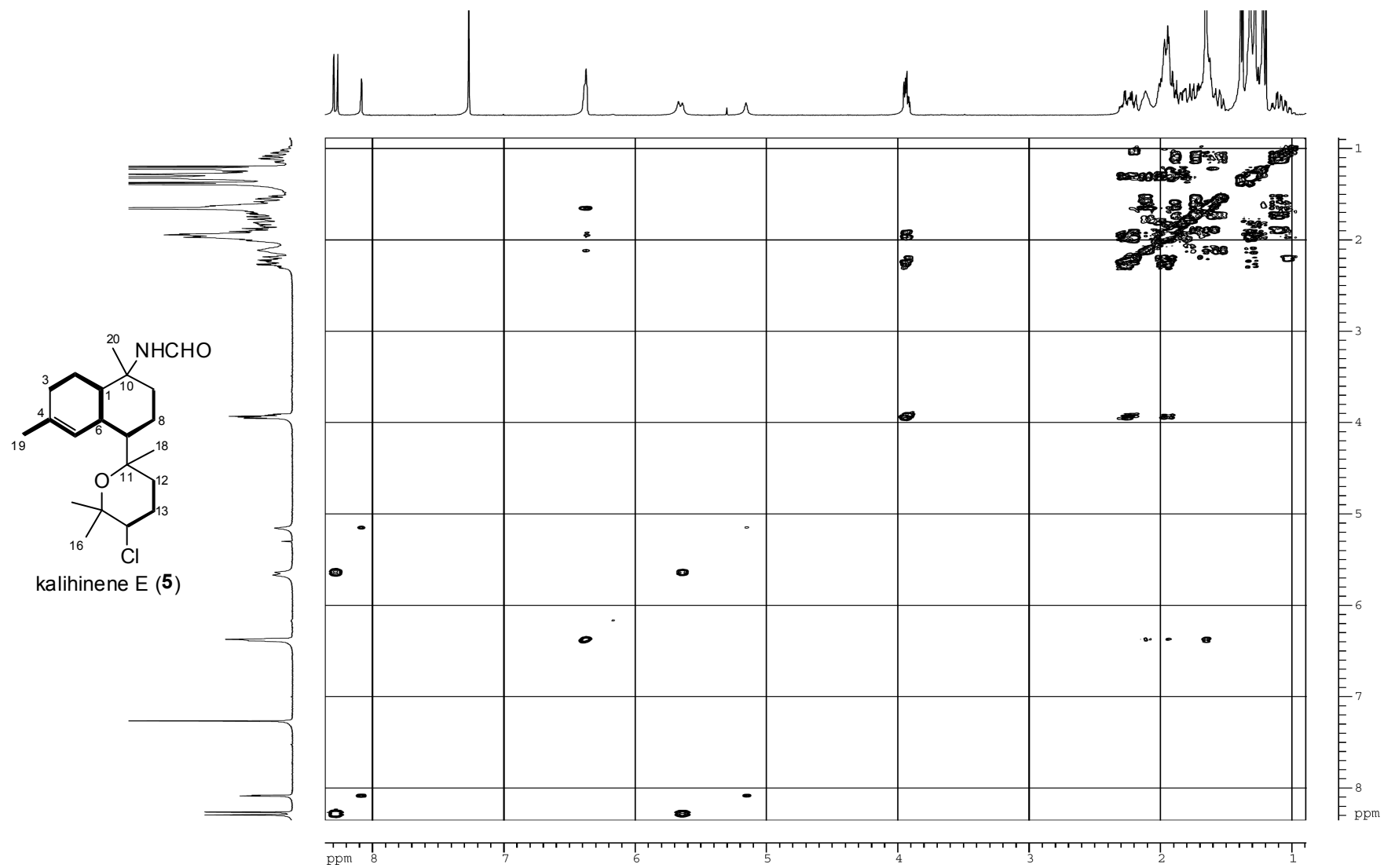


Figure S40. HMBC spectrum of kalihinene E (5) in CDCl<sub>3</sub>.

**Figure S41.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of kalihinene E (**5**) in  $\text{CDCl}_3$ .

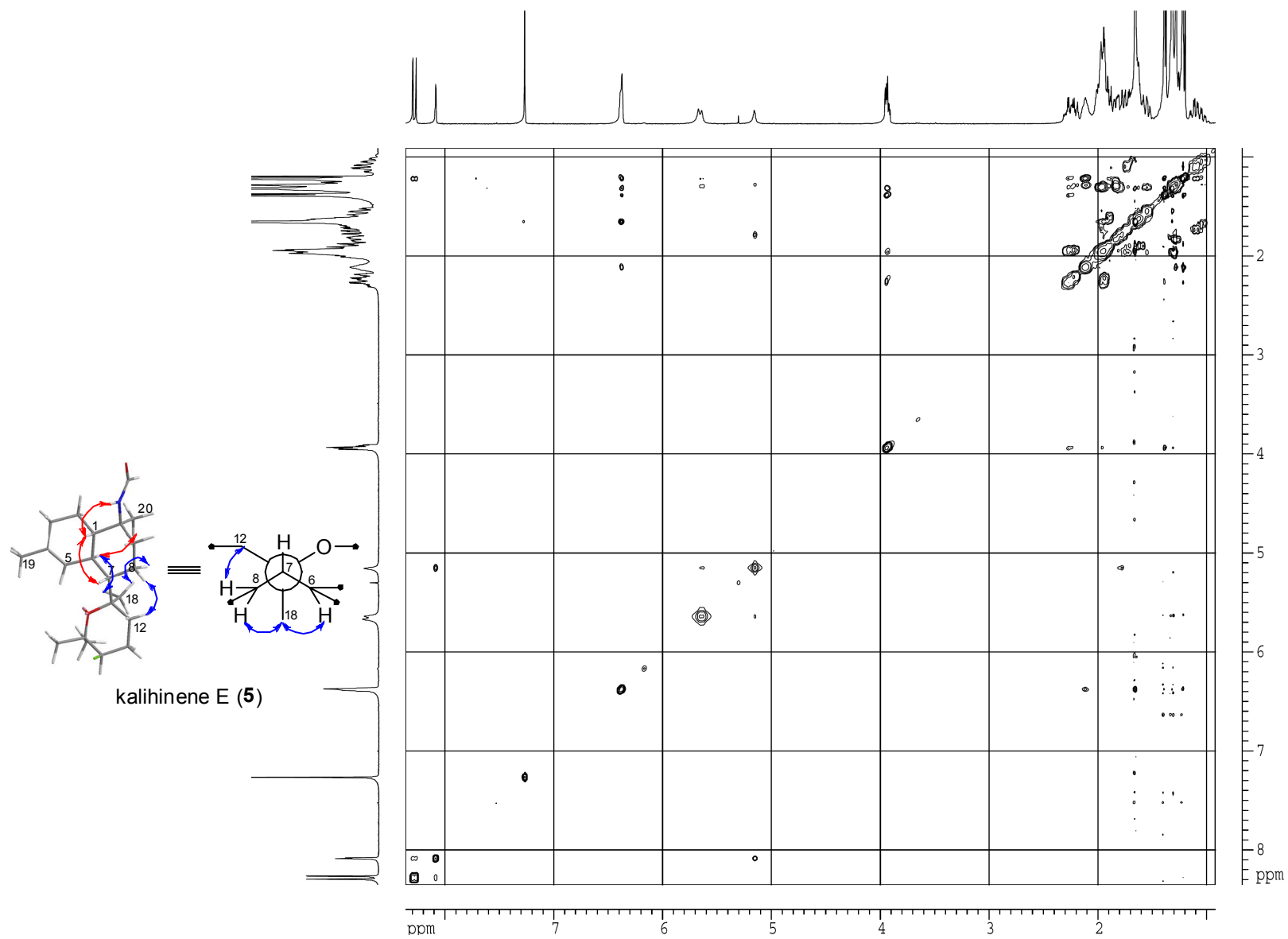
**Figure S42.** NOESY spectrum of kalihinene E (**5**) in CDCl<sub>3</sub>.



Figure S43. IR spectrum of kalihinene E (5).

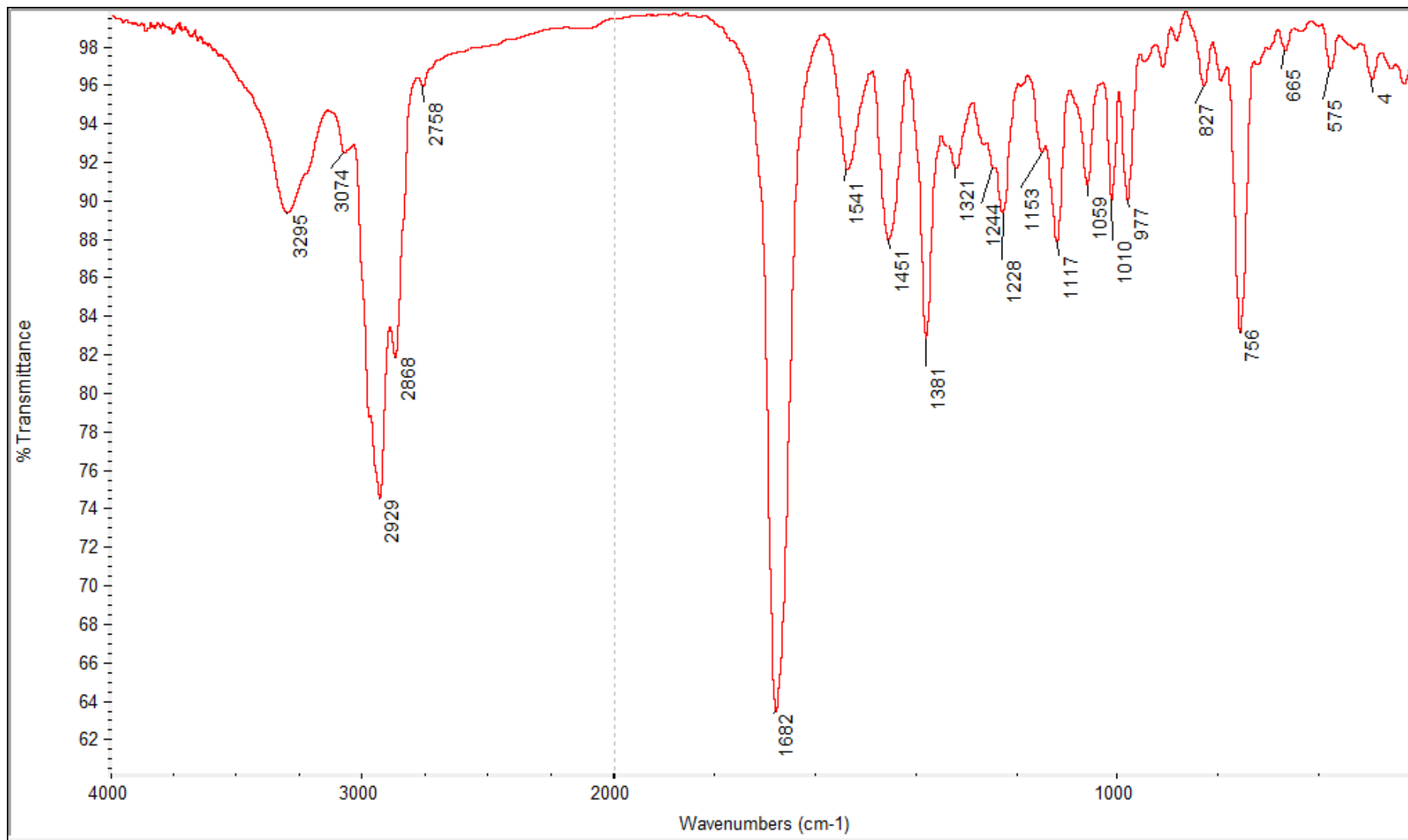


Figure S44. HRESIMS of kalihinene E (5).

## Elemental Composition Report

## Multiple Mass Analysis: 2 mass(es) processed

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

Selected filters: None

## Monoisotopic Mass, Even Electron Ions

53 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 10-23 H: 5-40 N: 1-1 O: 1-3 35Cl: 0-1 37Cl: 0-1

SIPI

Q-ToF micro  
YA019

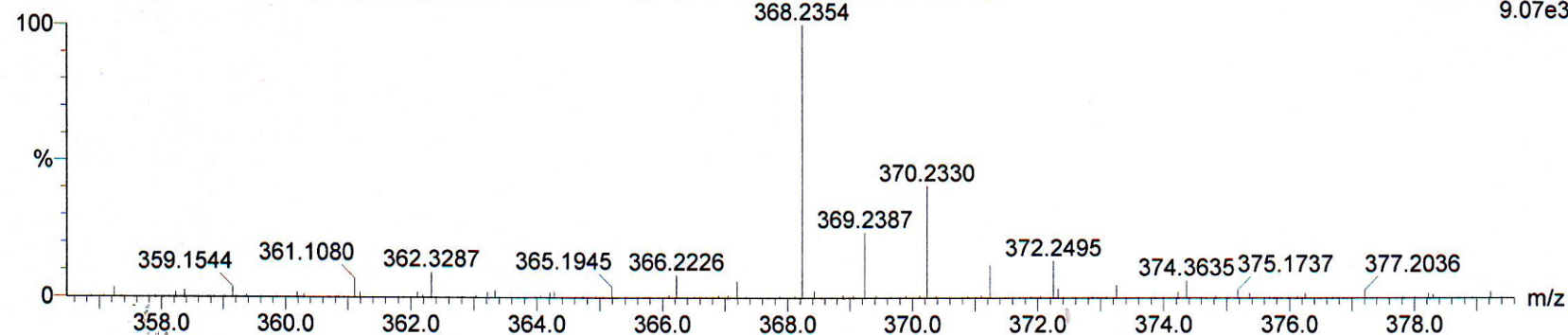
19-Mar-2011,14:51:28

0.00000000

WQ11-149H 50 (1.728) AM (Cen,6, 80.00, Ar,5000.0,354.24,0.70); Sm (SG, 2x3.00); Cm (48:65)

TOF MS ES+

9.07e3



Minimum: 25.00  
Maximum: 100.00

Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
368.2354	100.00	368.2356	-0.2	-0.5	4.5	28.9	C21 H35 N O2 35Cl
370.2330	40.56	370.2327	0.3	0.8	4.5	502.6	C21 H35 N O2 37Cl

Figure S45. UV spectrum of kalihinene E (5).

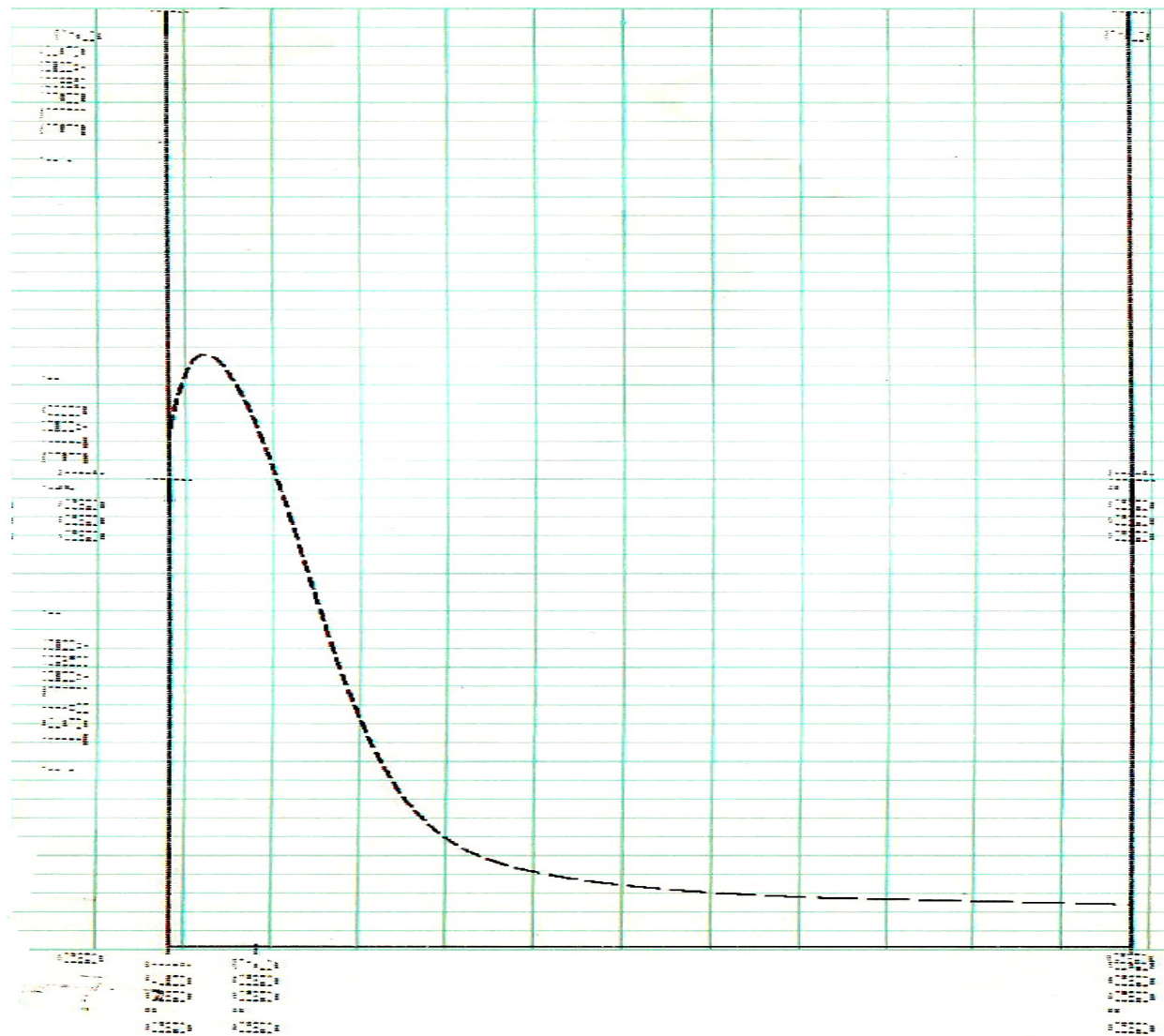


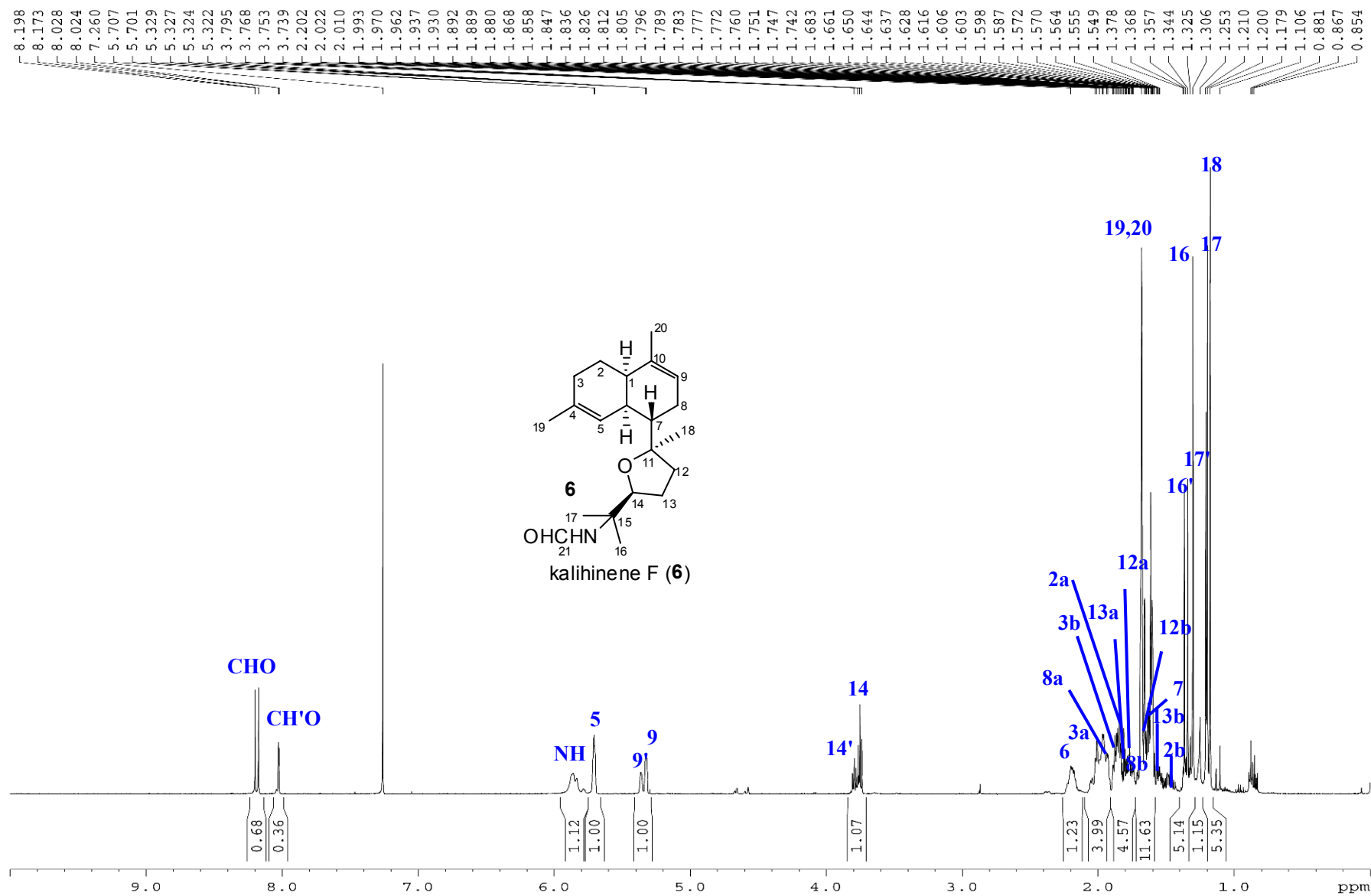
Figure S46.  $^1\text{H}$  NMR spectrum of kalihinene F (6) in  $\text{CDCl}_3$ .

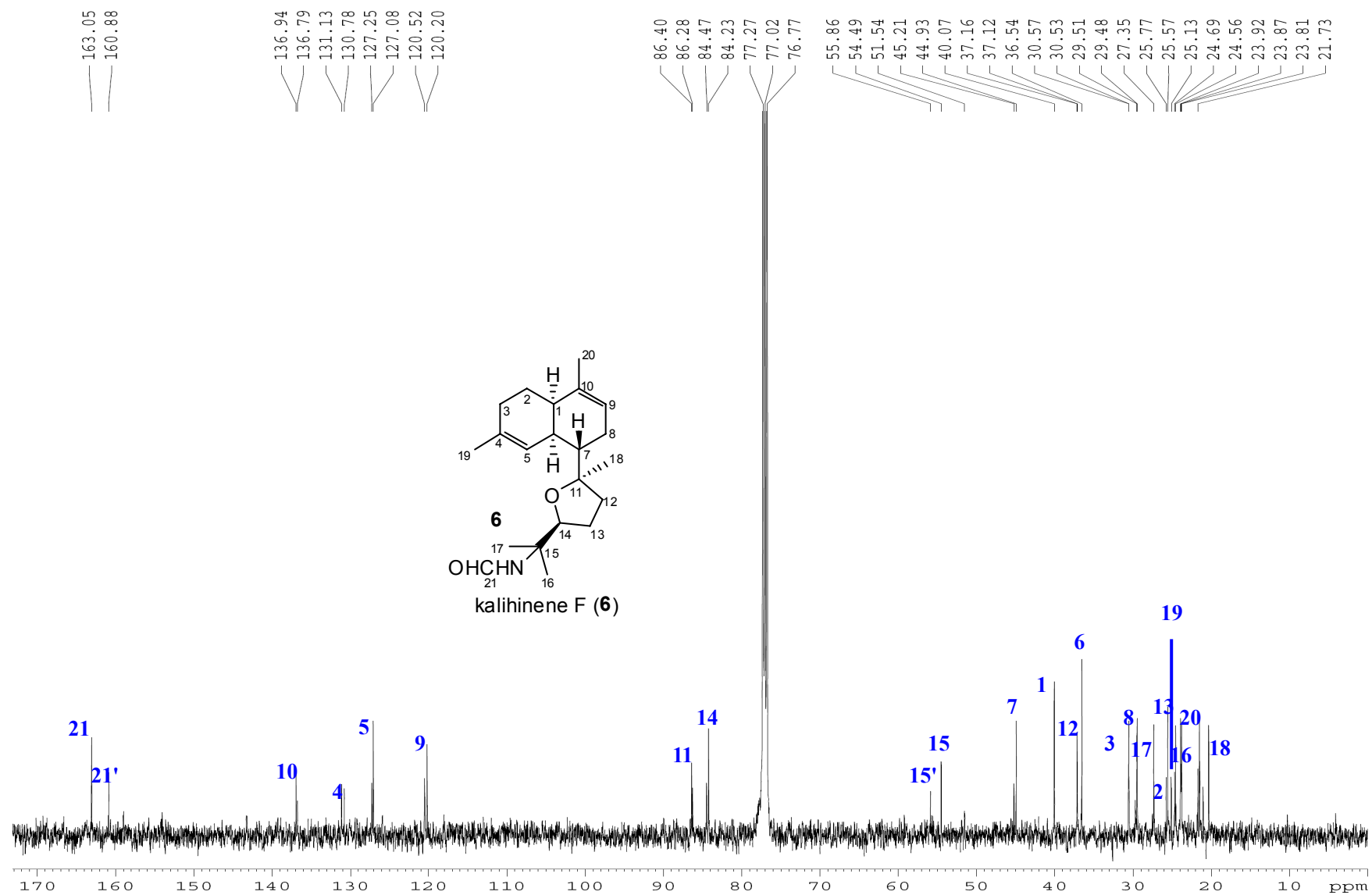
Figure S47.  $^{13}\text{C}$  NMR spectrum of kalihinene F (6) in  $\text{CDCl}_3$ .

Figure S48. HSQC spectrum of kalihinene F(6) in CDCl<sub>3</sub>.

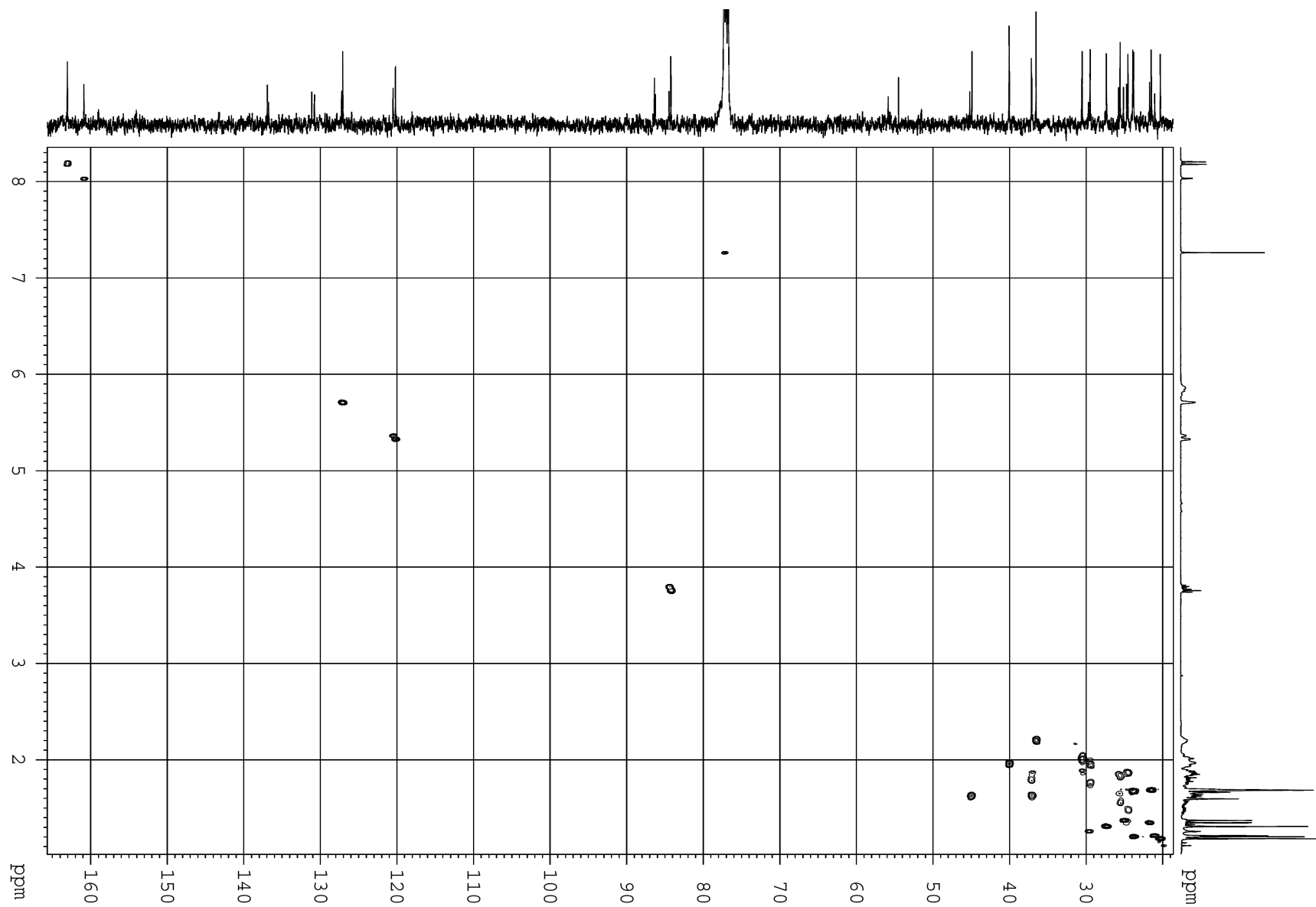
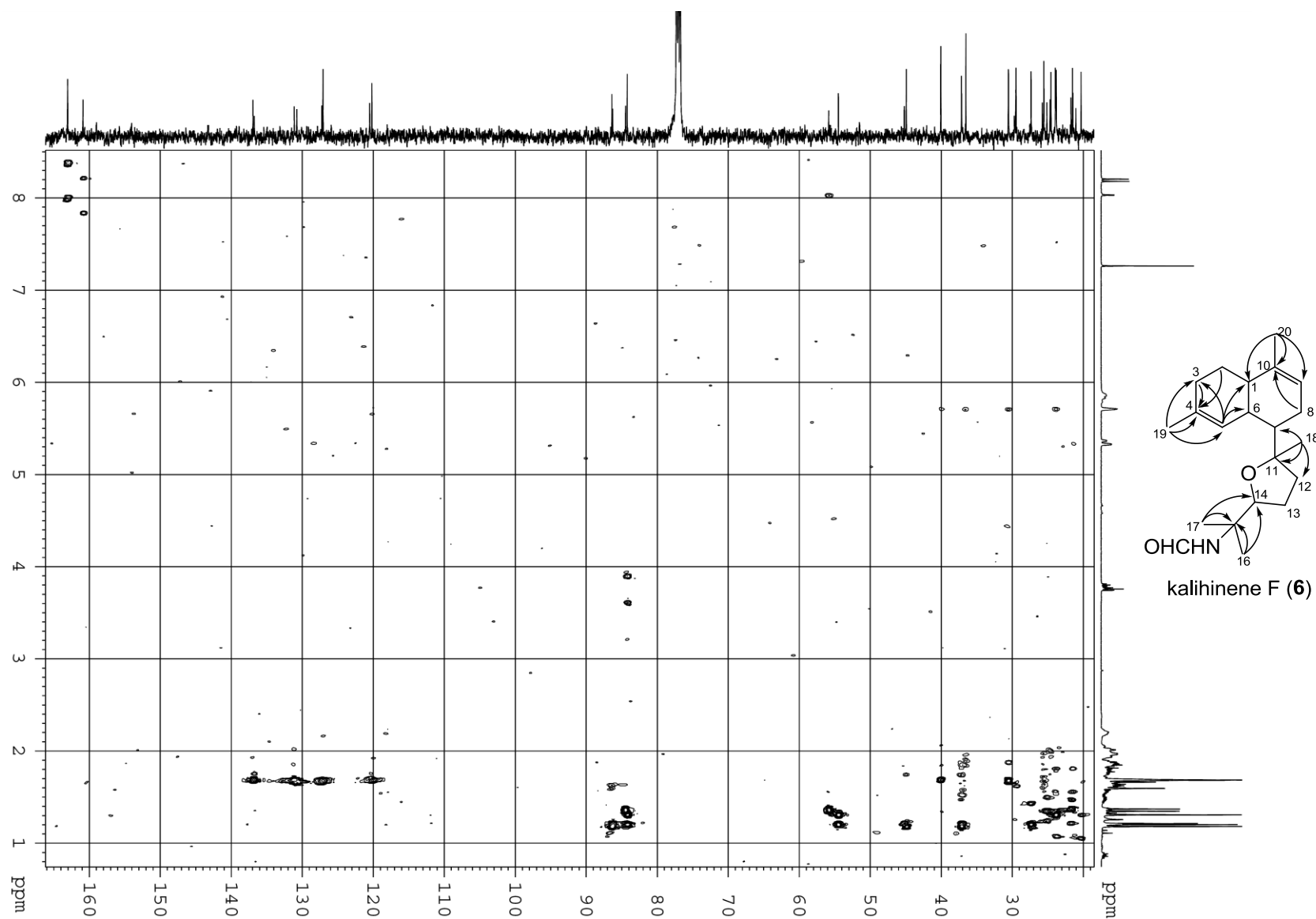


Figure S49. HMBC spectrum of kalihinene F (6) in CDCl<sub>3</sub>.

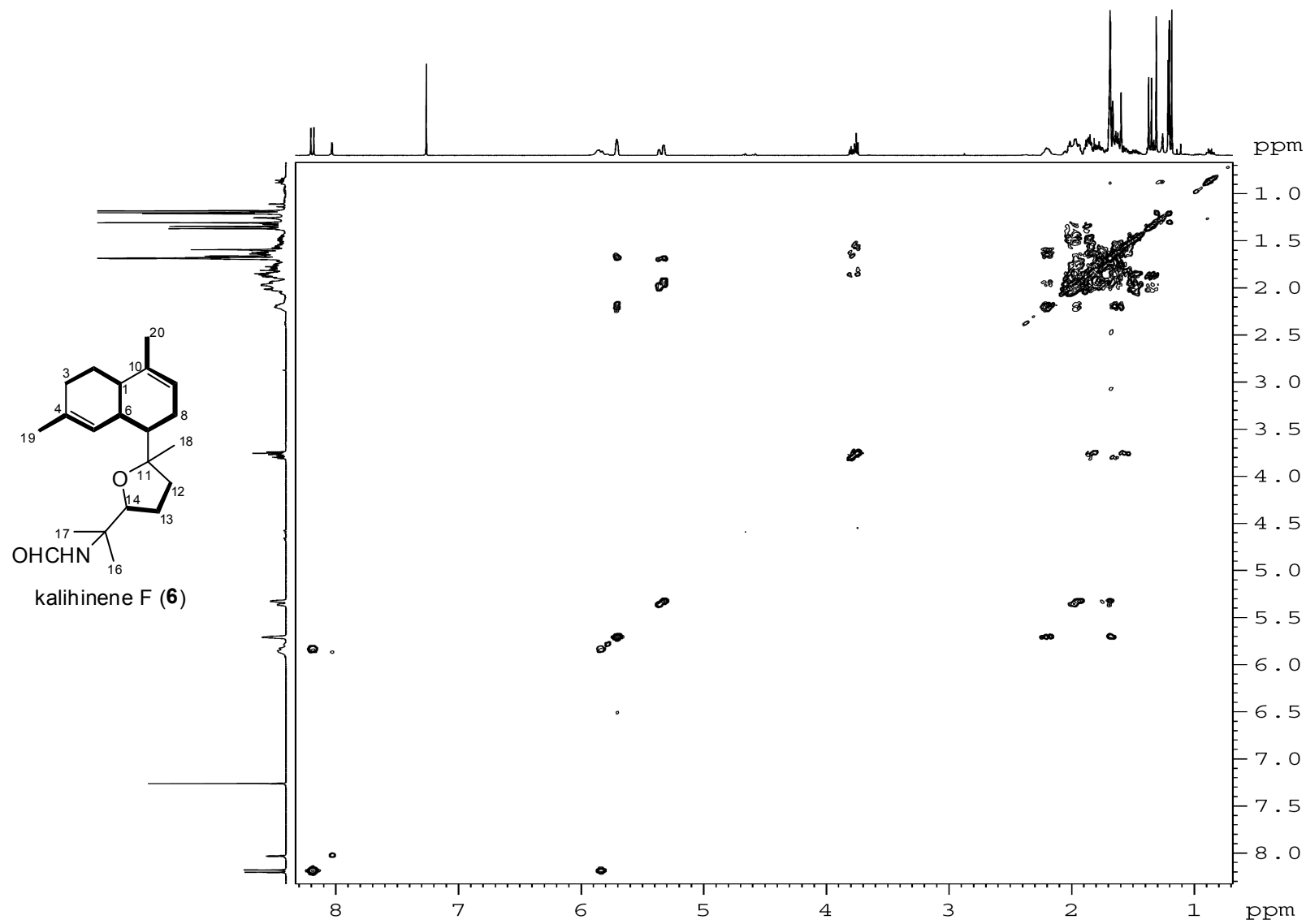
**Figure S50.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of kalihinene F (**6**) in  $\text{CDCl}_3$ .



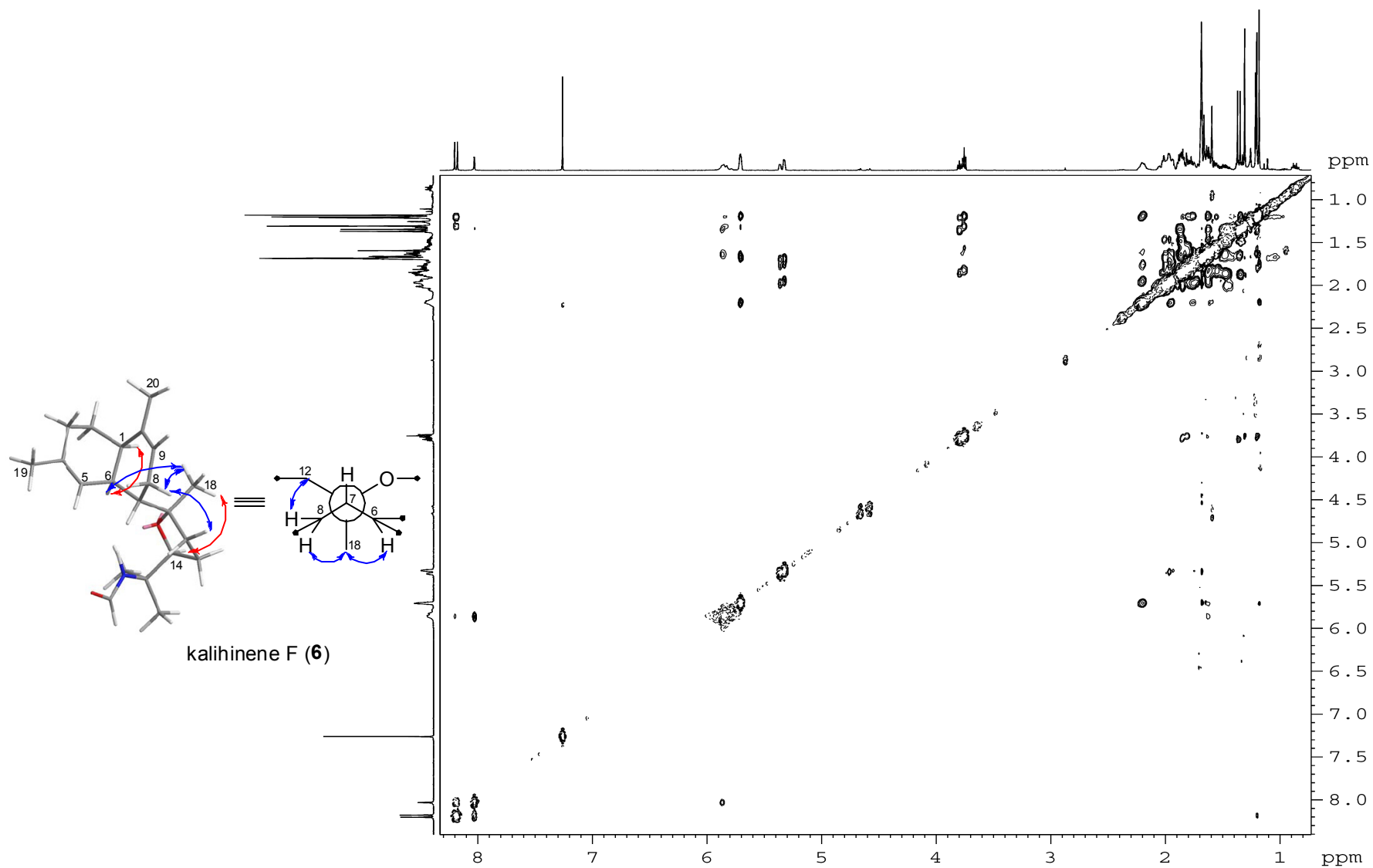
Figure S51. NOESY spectrum of kalihinene F (6) in CDCl<sub>3</sub>.

Figure S52. IR spectrum of kalihinene F (6).

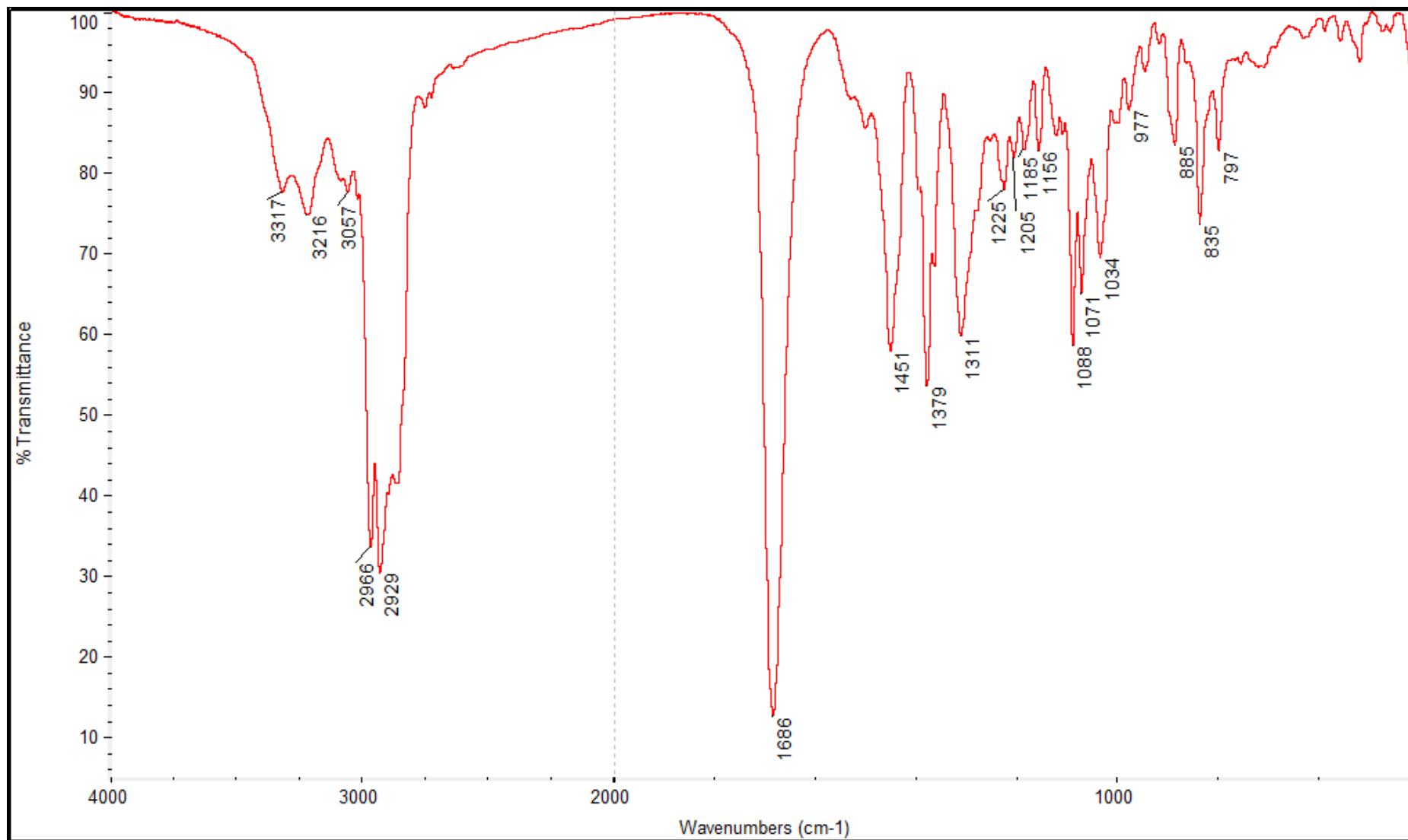


Figure S53. HRESIMS of kalihinene F (6).

### Elemental Composition Report

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

Selected filters: None

Monoisotopic Mass, Even Electron Ions

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

Elements Used:

C: 10-23 H: 5-40 N: 1-1 O: 1-2 Na: 1-1

SIPI

Q-ToF micro  
YA019

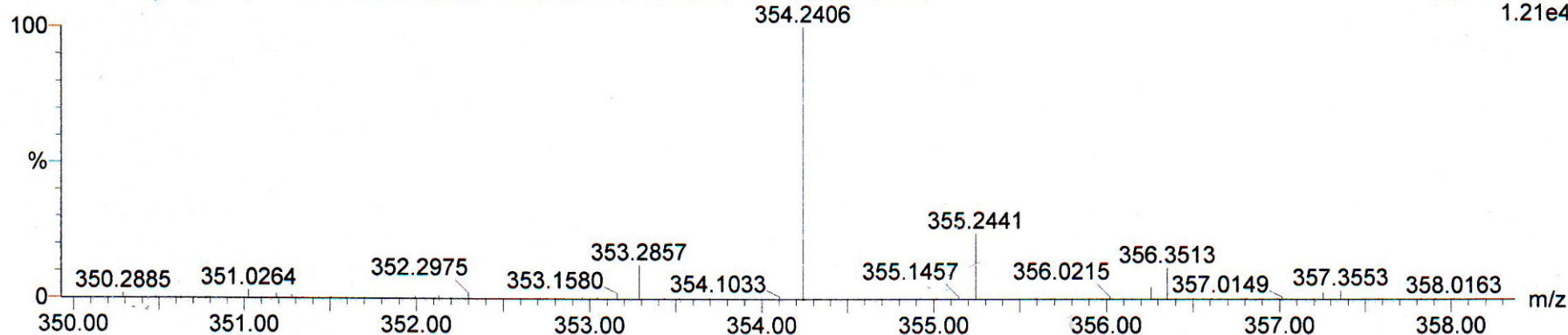
09-Apr-2011,13:56:04

0.00000000

WQ11-230H1 11 (0.387) AM (Med,6, Ar,5000.0,345.00,0.70); Sm (SG, 2x3.00); Cm (4:18)

TOF MS ES+

1.21e4



Minimum: 30.00 -1.5  
Maximum: 100.00 5.0 50.0 50.0

Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
354.2406	100.00	354.2409	-0.3	-0.8	5.5	18.9	C21 H33 N O2 Na

Figure S54. UV spectrum of kalihinene F (6).

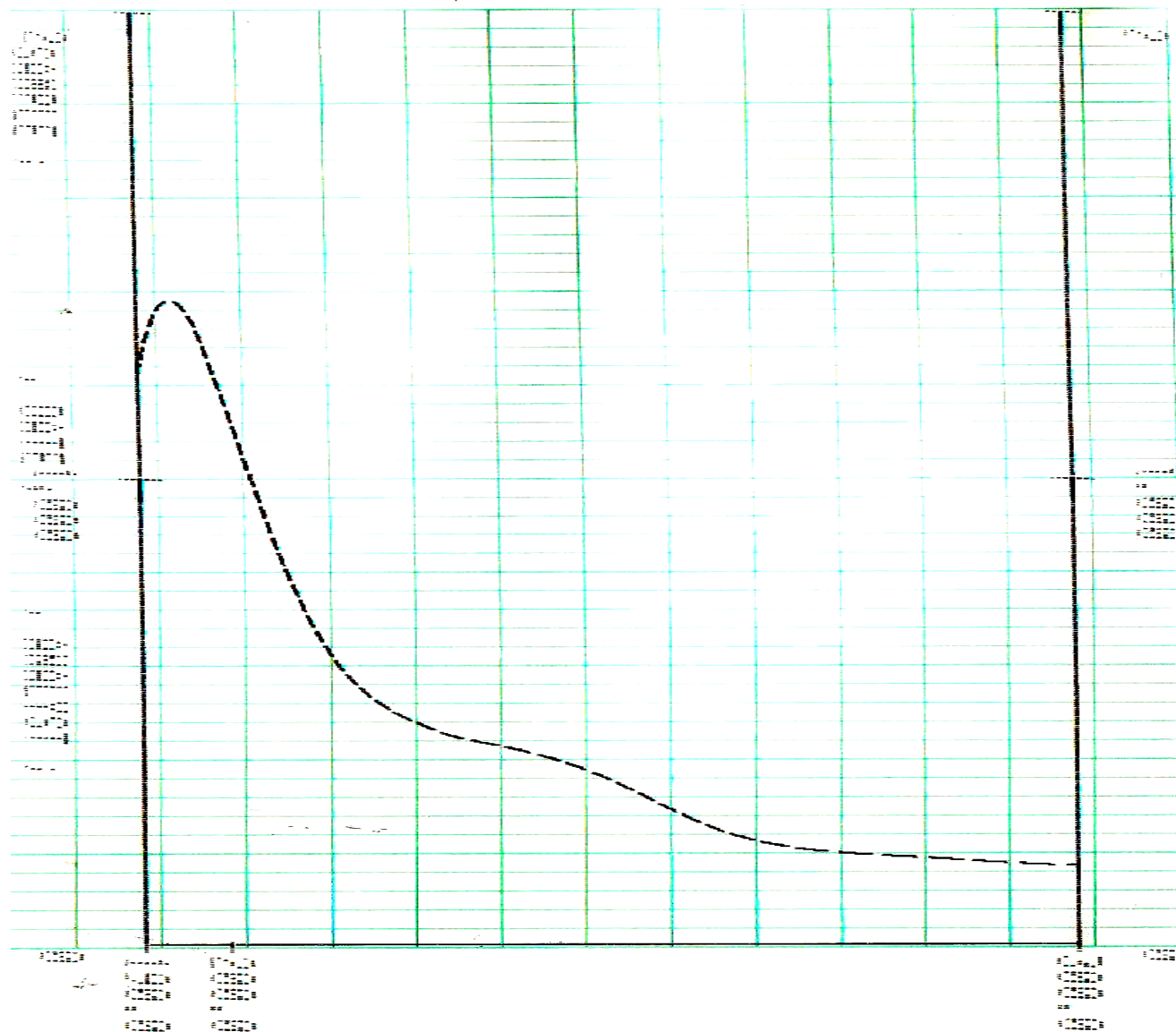
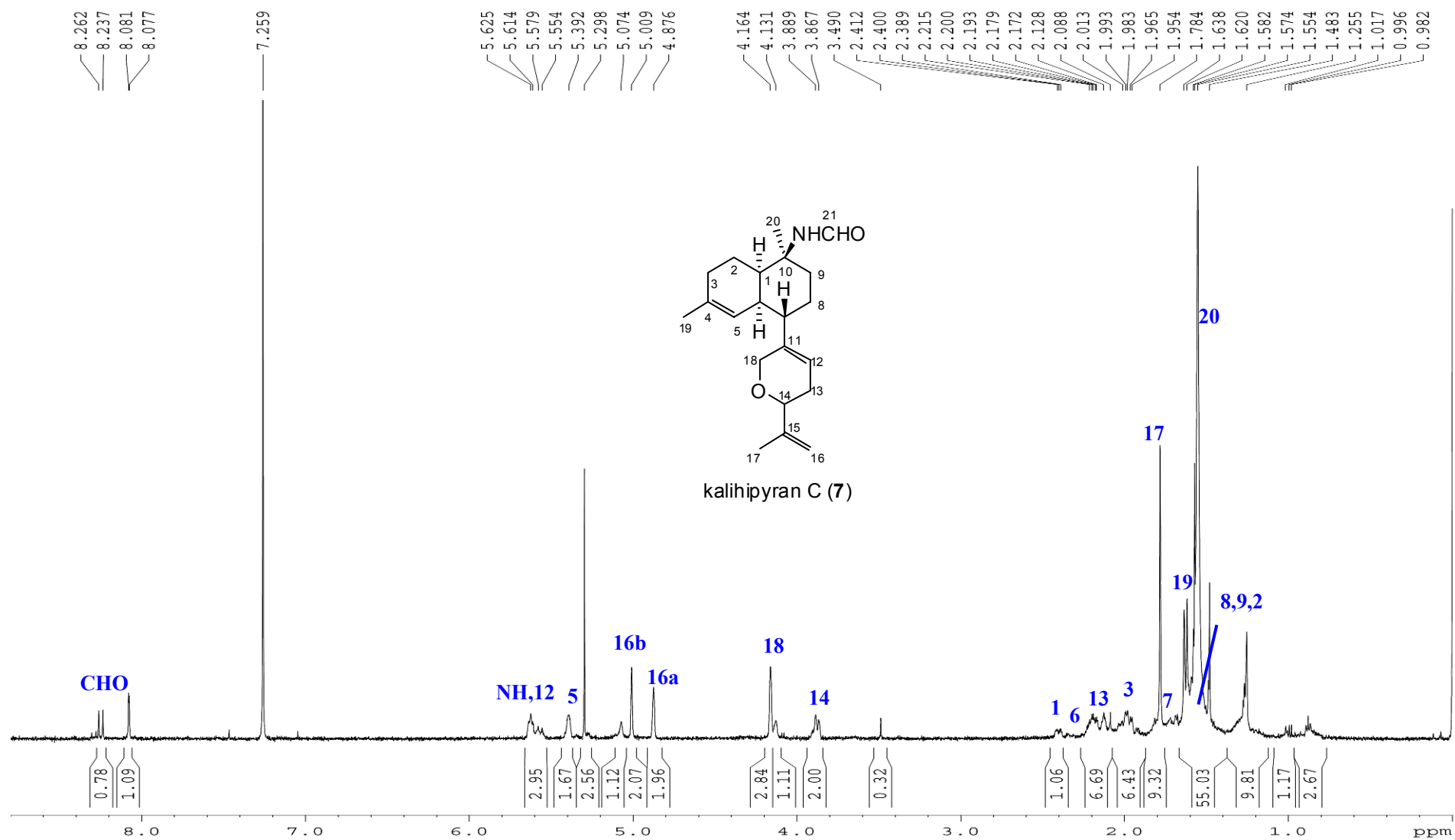


Figure S55.  $^1\text{H}$  NMR spectrum of kalihipyran C (7) in  $\text{CDCl}_3$ .

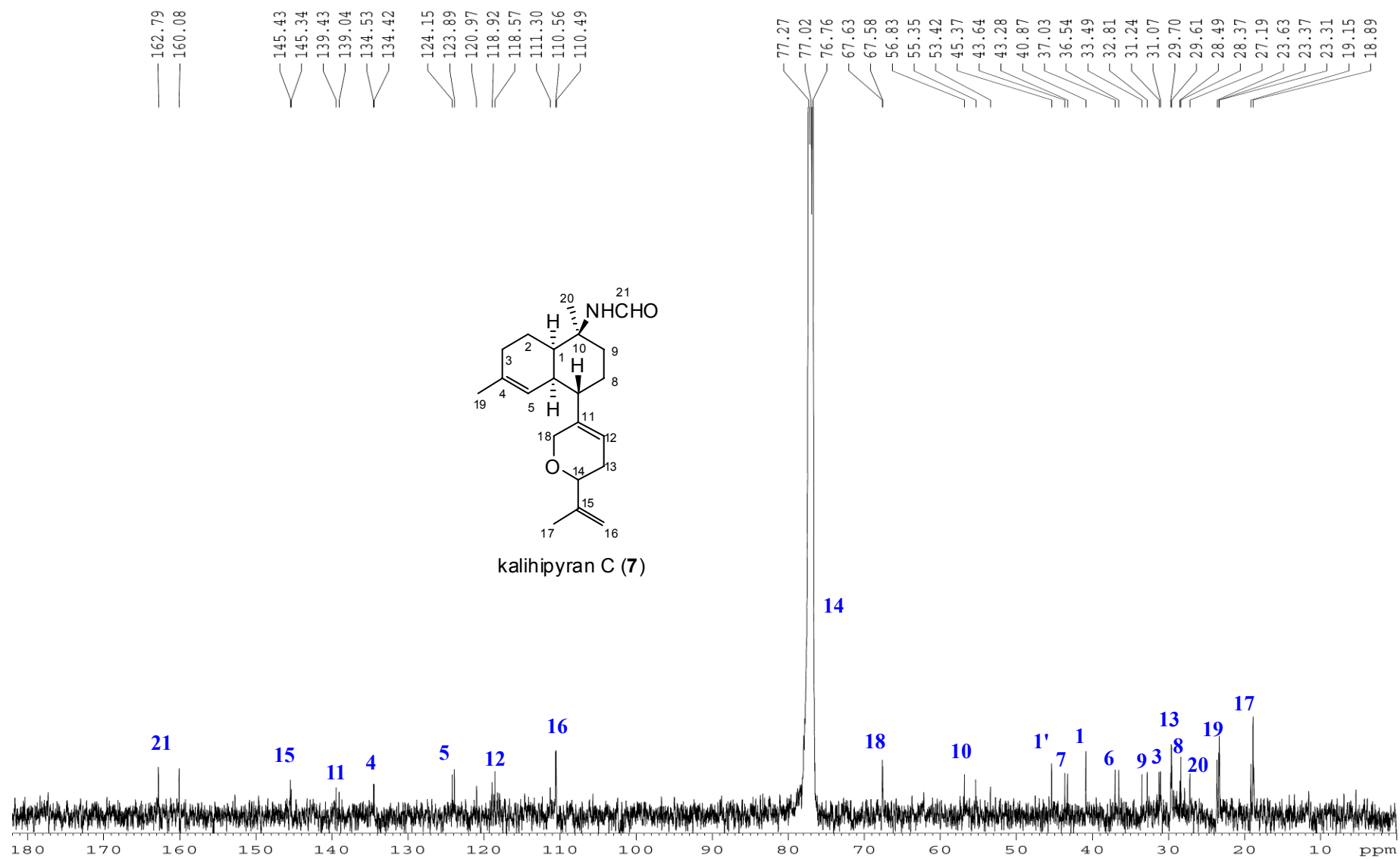
**Figure S56.**  $^{13}\text{C}$  NMR spectrum of kalihipyran C (7) in  $\text{CDCl}_3$ .

Figure S57. HSQC spectrum of kalihipyran C (7) in CDCl<sub>3</sub>.

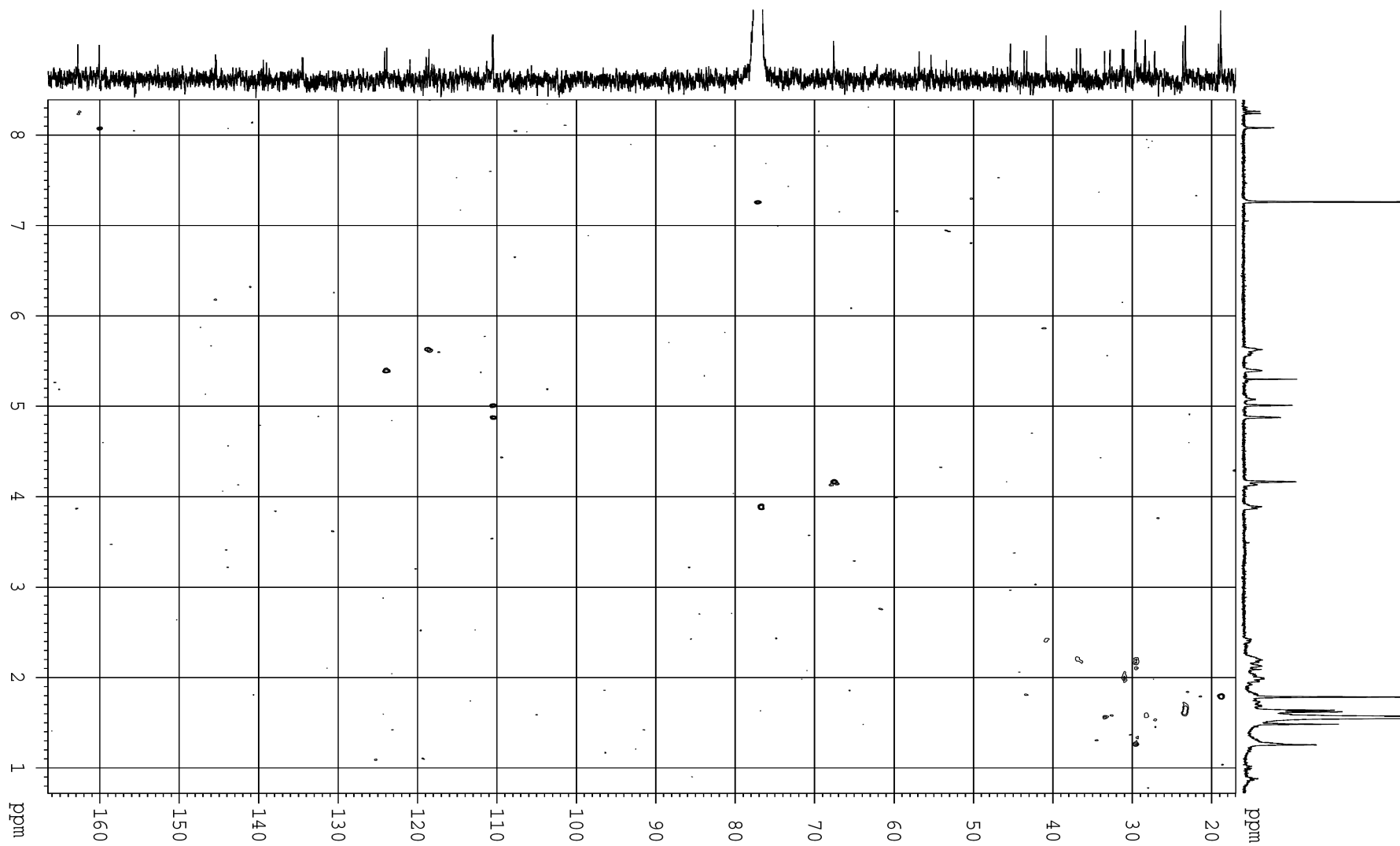


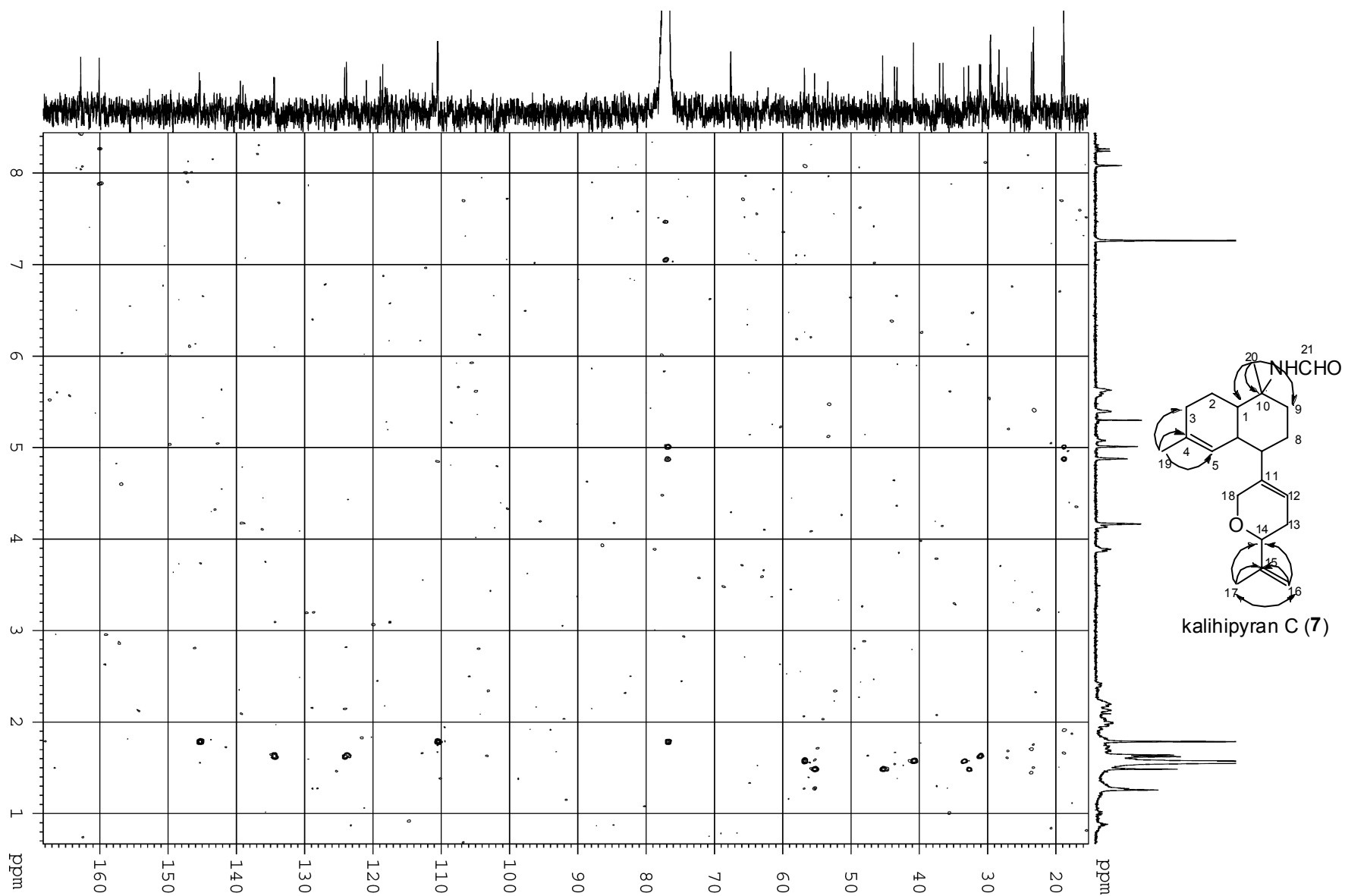
Figure S58. HMBC spectrum of kalihipyran C (7) in CDCl<sub>3</sub>.



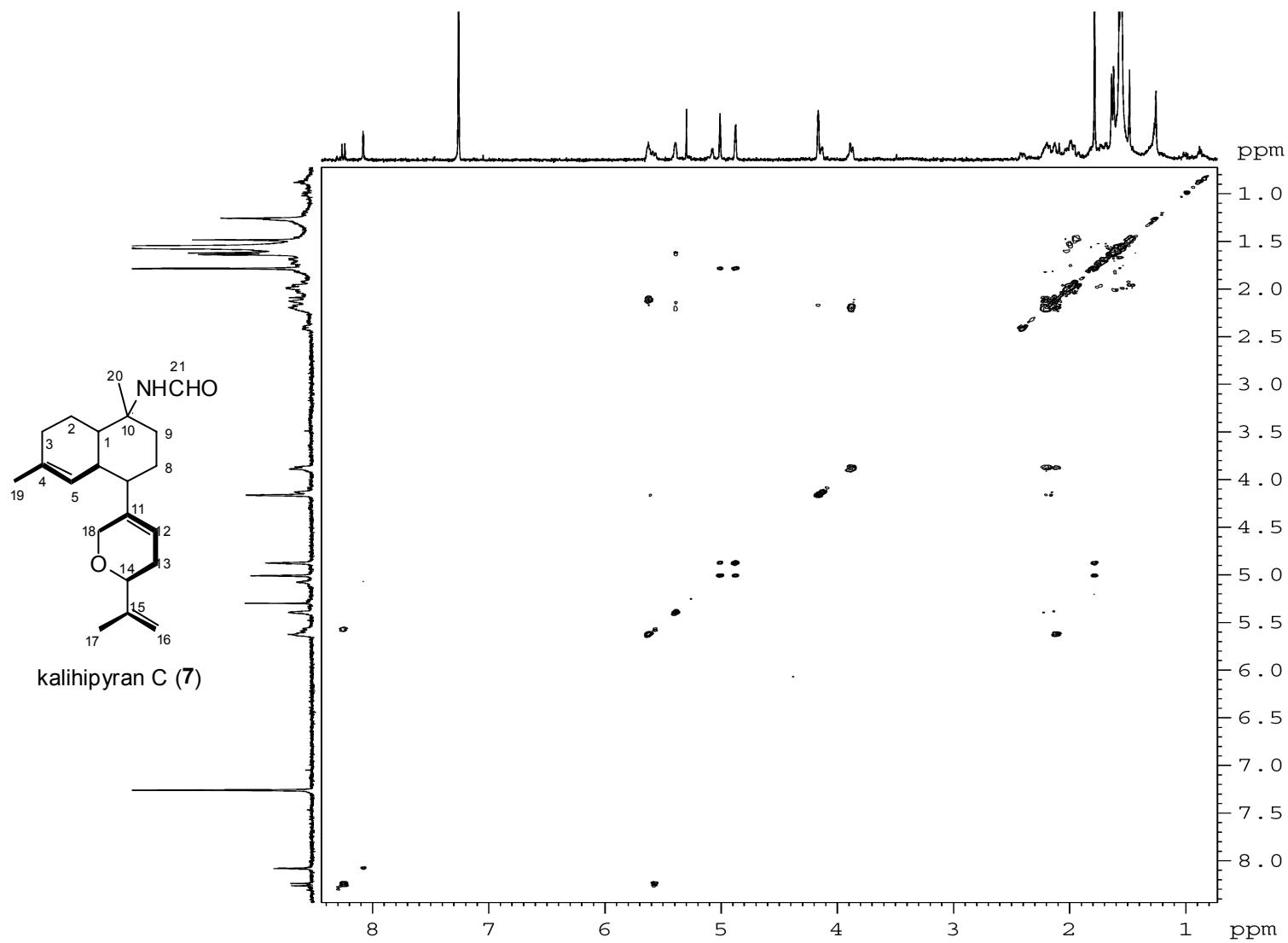
Figure S59.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of kalihipyran C (7) in  $\text{CDCl}_3$ .

Figure S60. NOESY spectrum of kalihipyran C (7) in CDCl<sub>3</sub>.

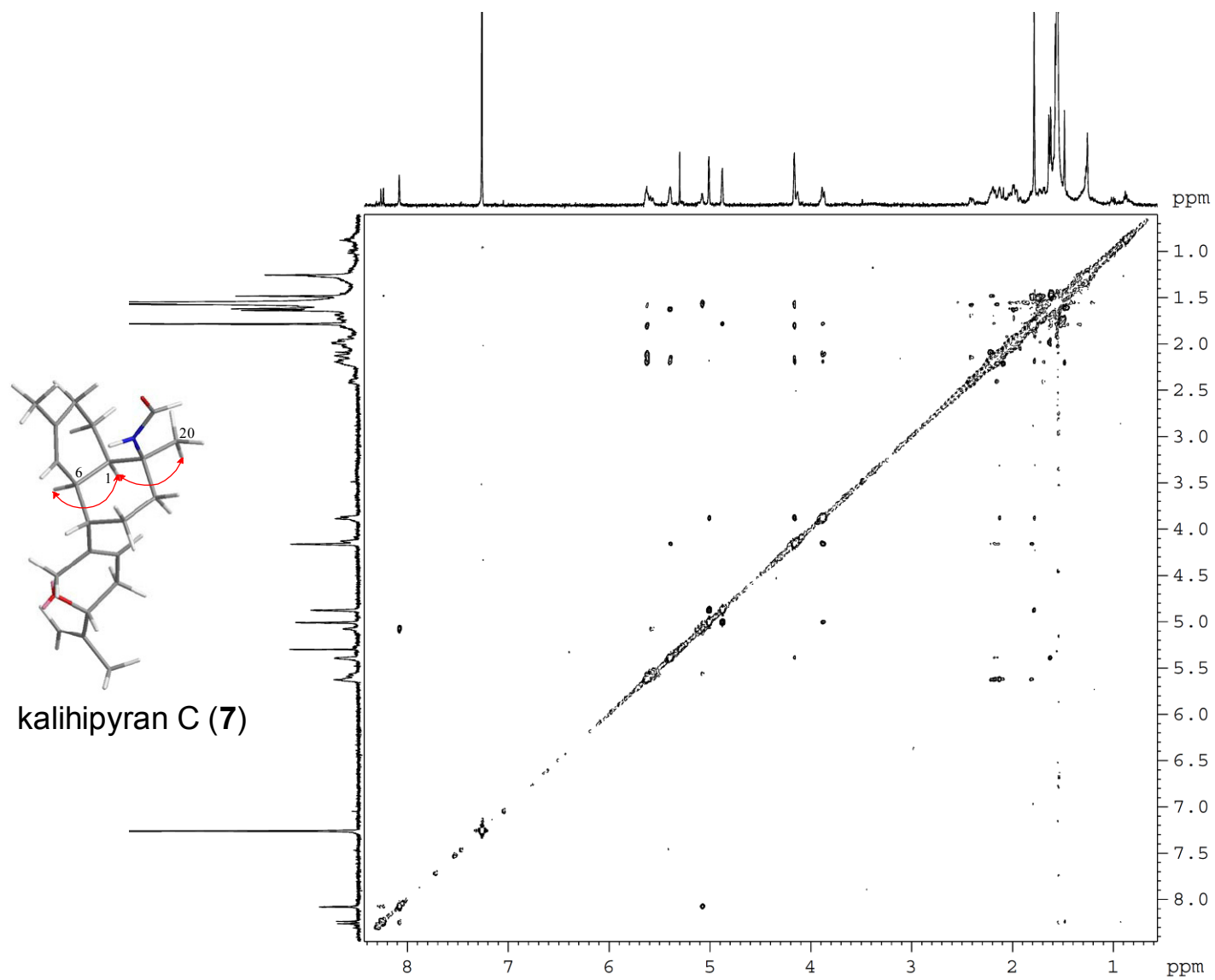


Figure S61. IR spectrum of kalihipyran C (7).

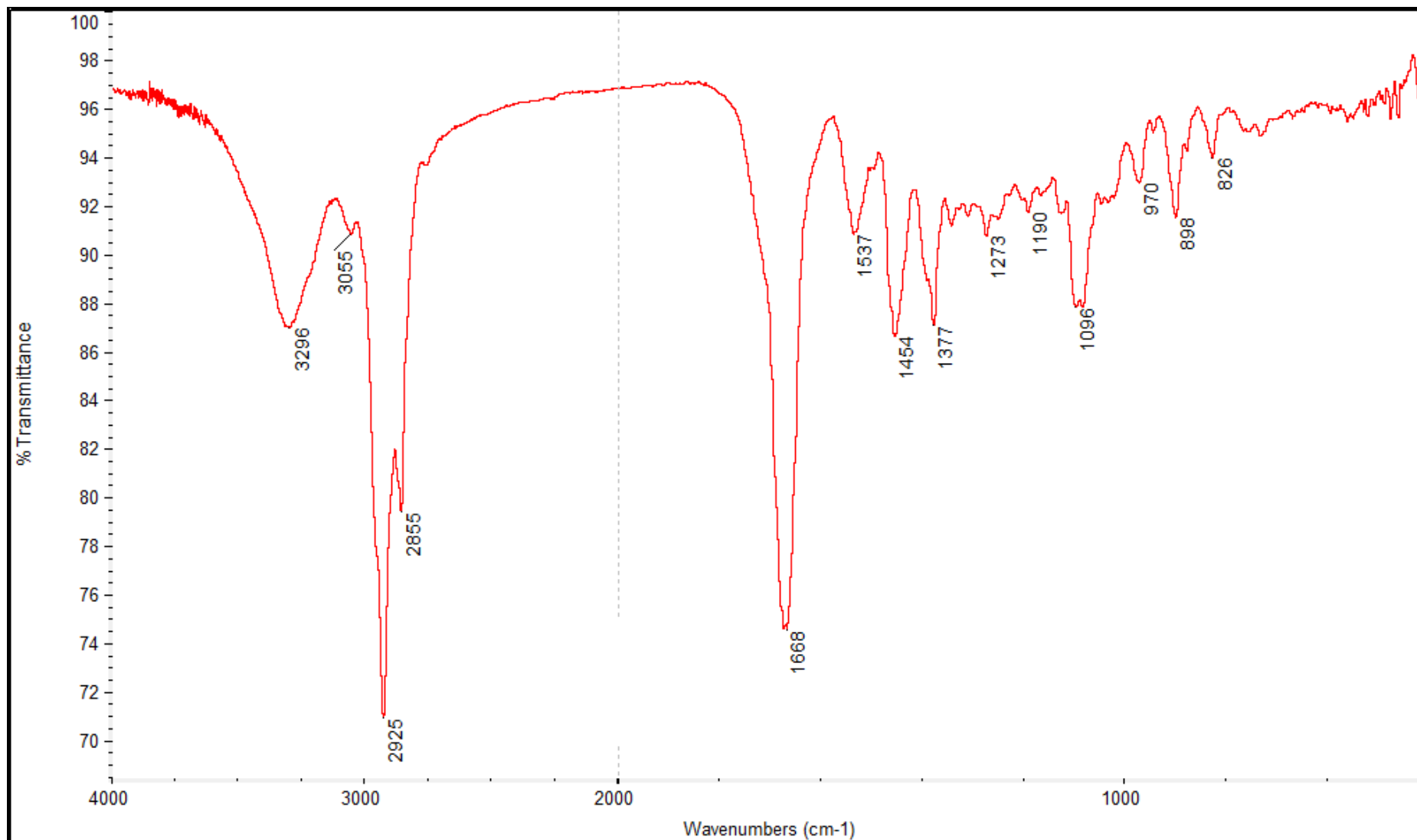


Figure S62. HRESIMS of kalihipyran C (7).

### Elemental Composition Report

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

Selected filters: None

Monoisotopic Mass, Even Electron Ions

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

Elements Used:

C: 5-25 H: 10-40 N: 1-1 O: 1-2 Na: 1-1

SIPI

Q-ToF micro  
YA019

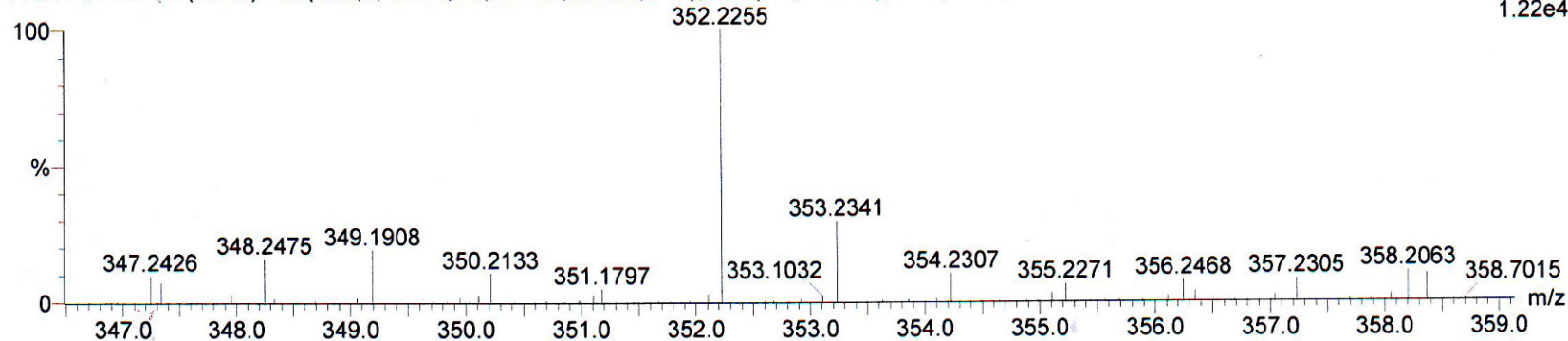
20-May-2011,13:23:30

0.00000000

TOF MS ES+

1.22e4

WQ11-311H1 63 (2.218) AM (Cen,6, 80.00, Ar,5000.0,360.05,0.70); Sm (SG, 2x3.00); Cm (62:72)



Minimum: 45.00  
Maximum: 100.00

Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
352.2255	100.00	352.2252	0.3	0.9	6.5	331.8	C21 H31 N O2 Na

Figure S63. UV spectrum of kalihipyran C (7).

