# Supporting Information

**Figure S1.** $^{1}$H NMR spectrum of cavernene A (**1**) in $CDCl_3$.

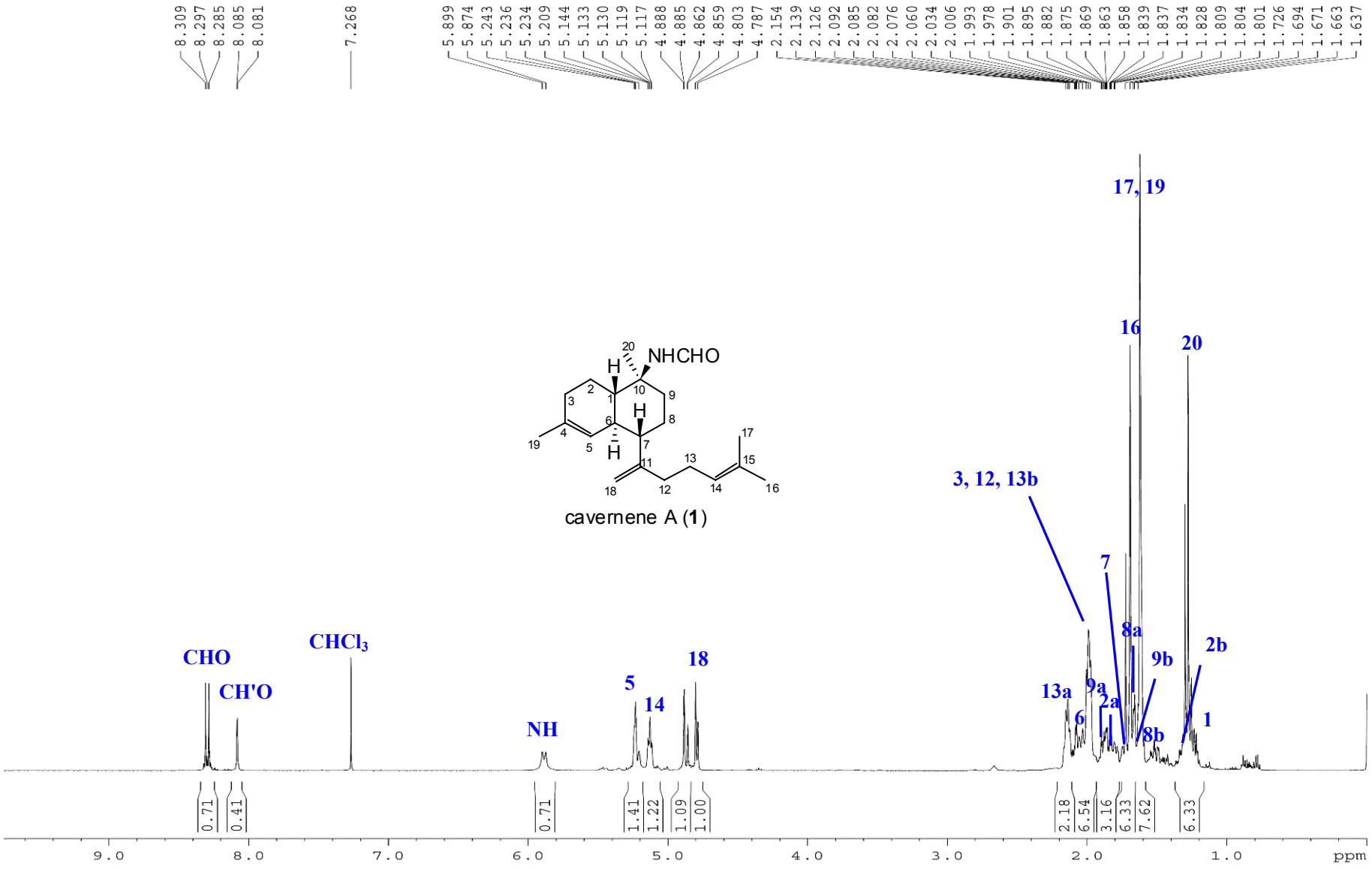


**Figure S2.** $^{13}C$ NMR spectrum of cavernene A (**1**) in $CDCl_3$.

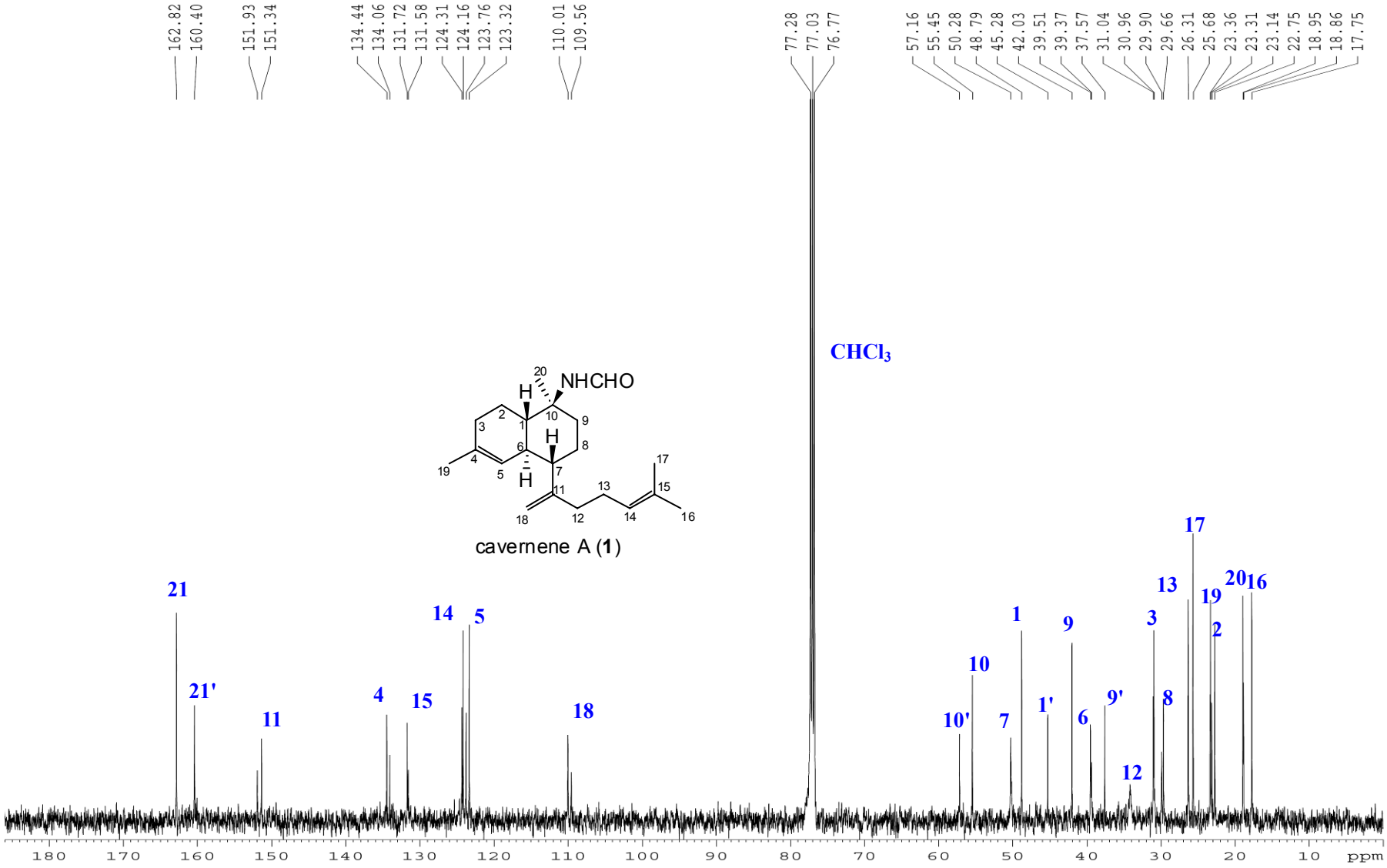


**Figure S3.** HSQC spectrum of cavernene A (**1**) in $CDCl_3$.

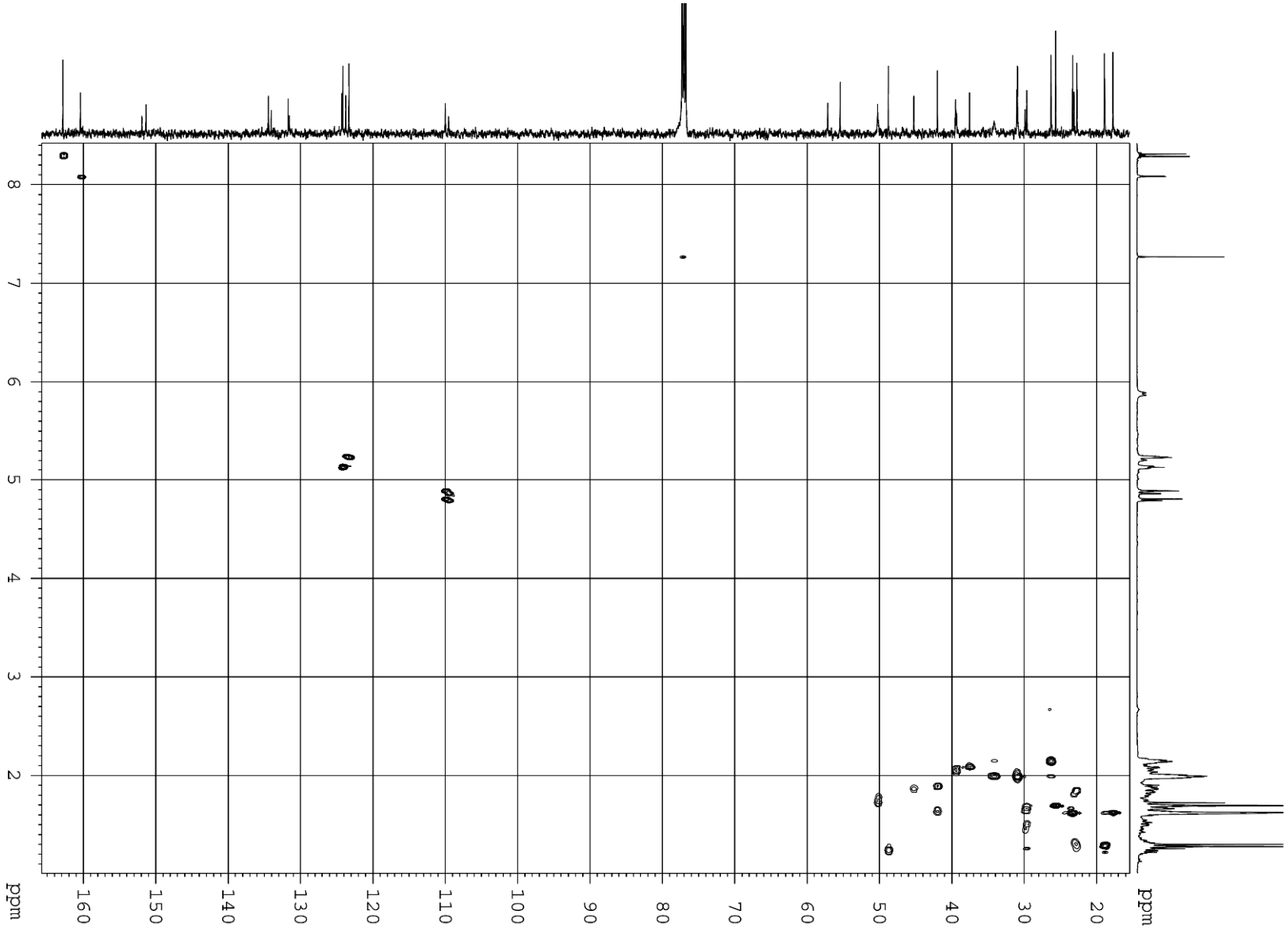


**Figure S4.** HMBC spectrum of cavernene A (**1**) in $CDCl_3$.

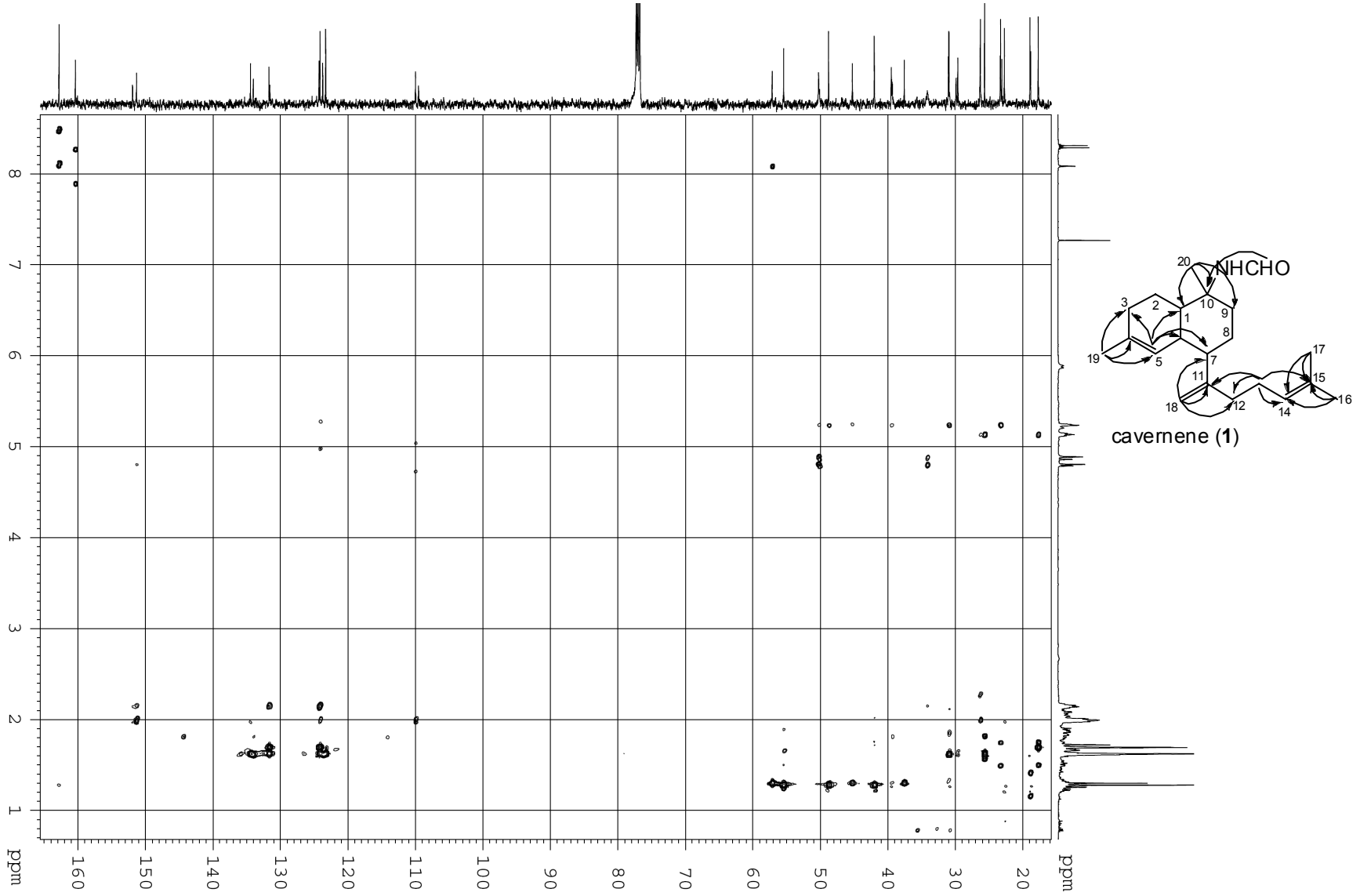


**Figure S5.** $^{1}$H-$^{1}$H COSY spectrum of cavernene A (**1**) in $CDCl_3$.

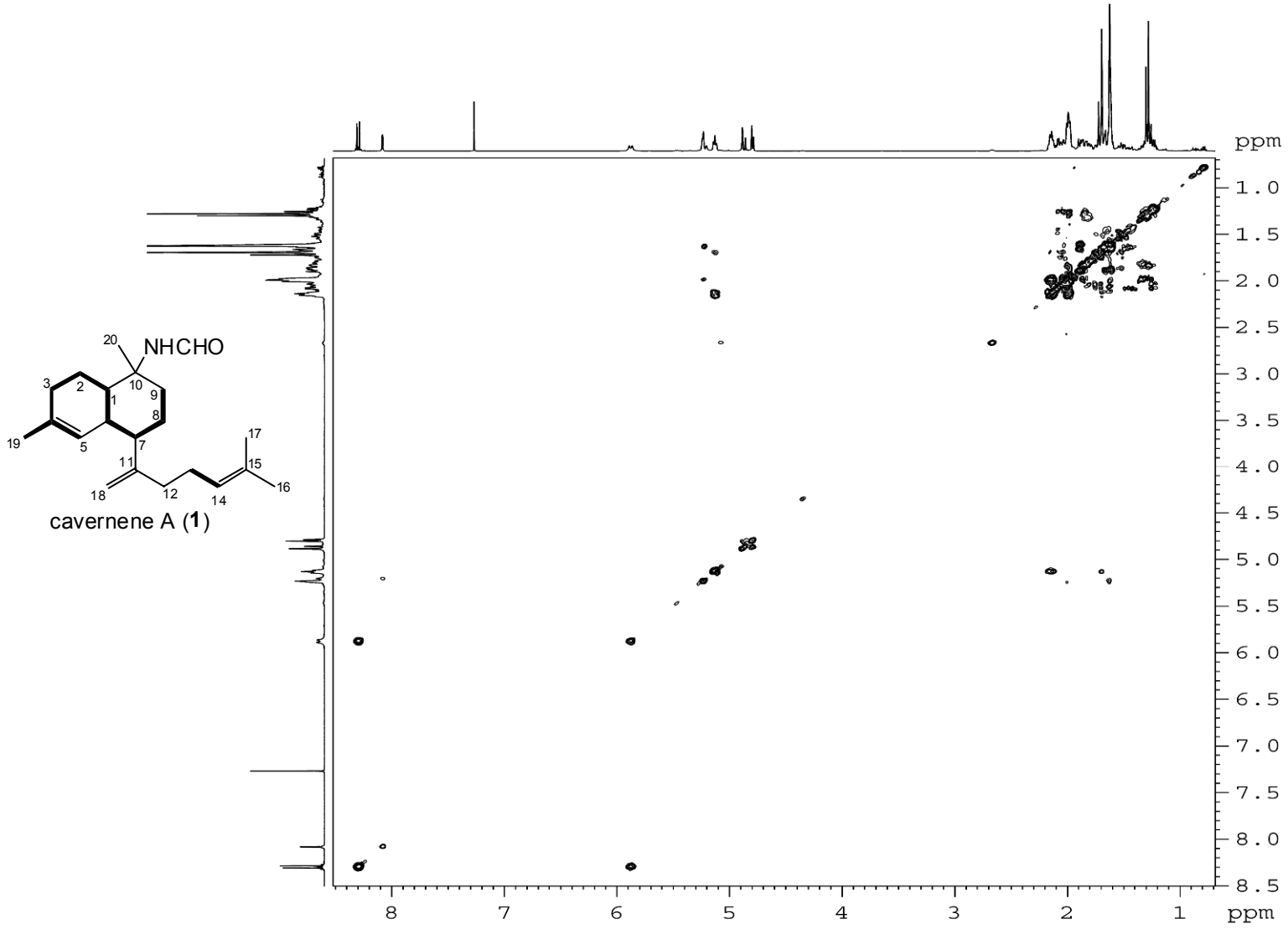


**Figure S6.** NOESY spectrum of cavernene A (**1**) in $CDCl_3$.

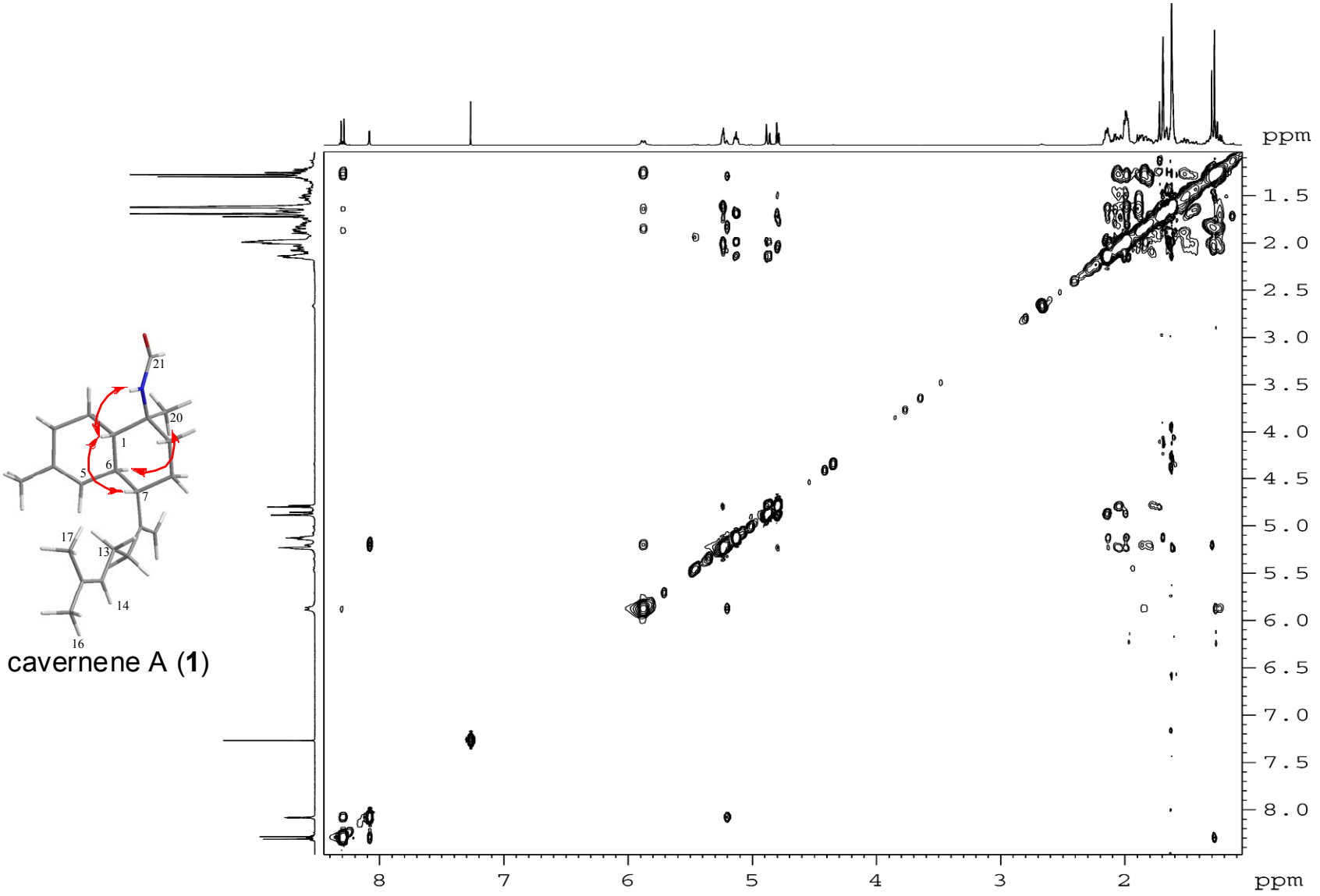


**Figure S7.** IR spectrum of cavernene A (**1**).

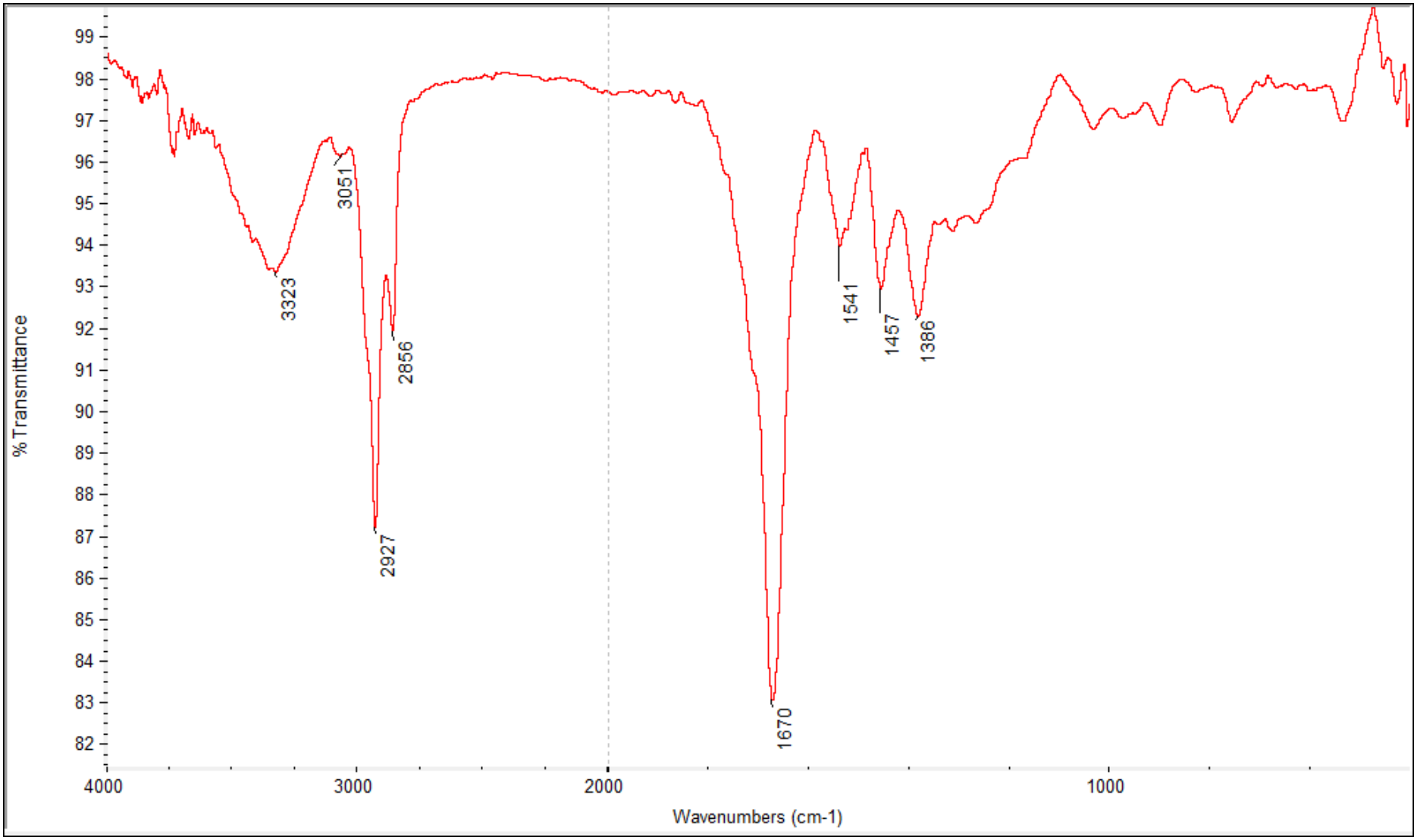
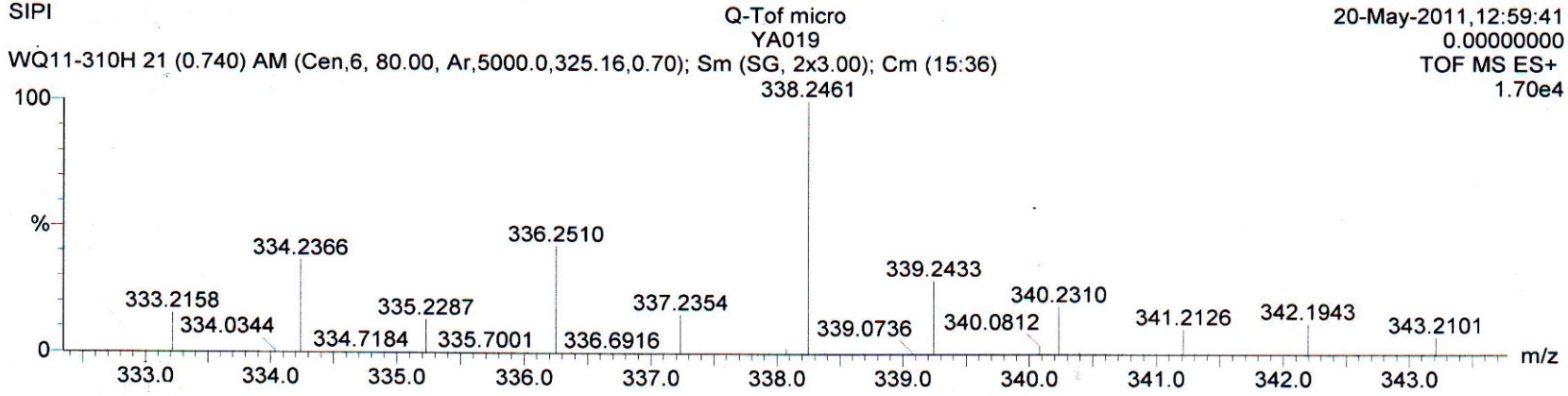


**Figure S8.** HRESIMS of cavernene A (**1**).

**Elemental Composition Report** **Page 1**

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

Monoisotopic Mass, Even Electron Ions
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




| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 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**).

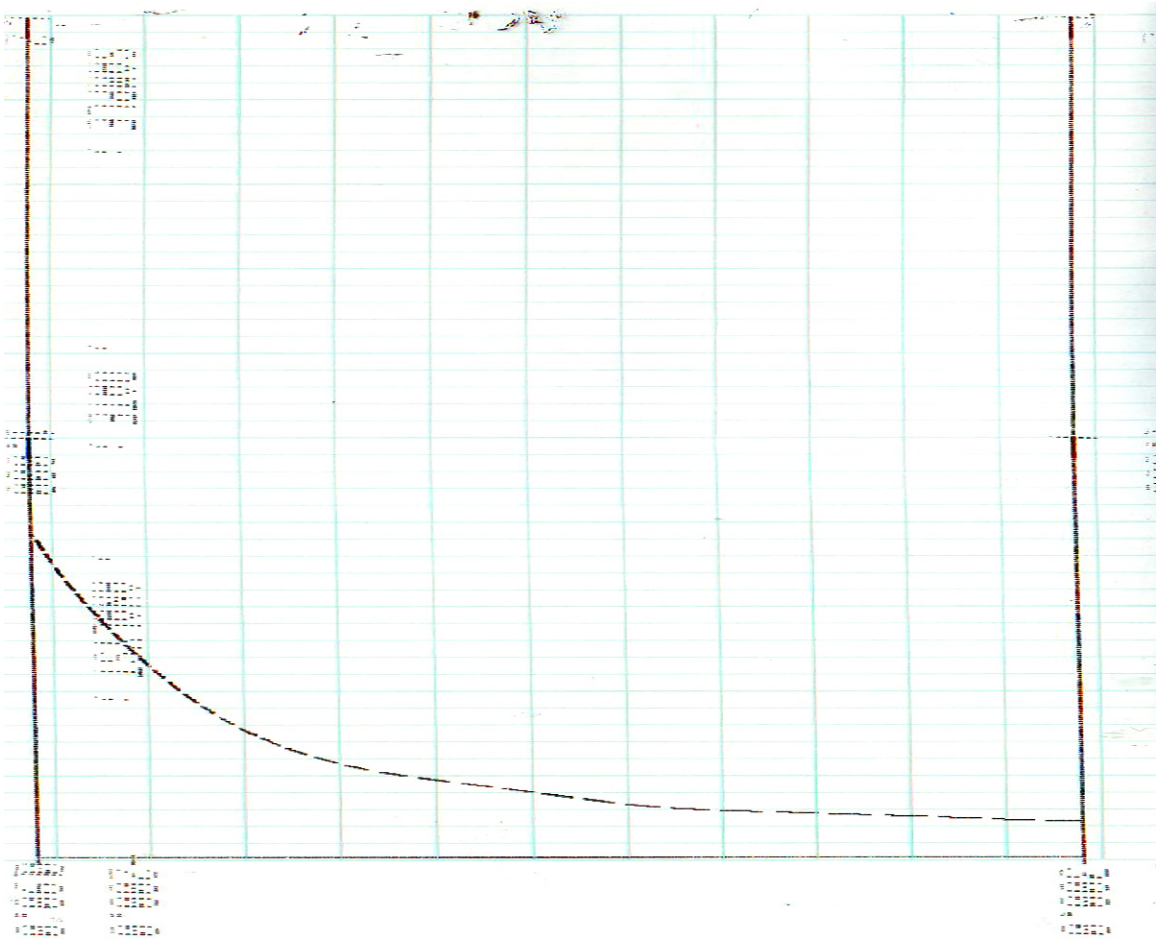


**Figure S10.** $^{1}$H NMR spectrum of cavernene B (**2**) in $CDCl_3$.

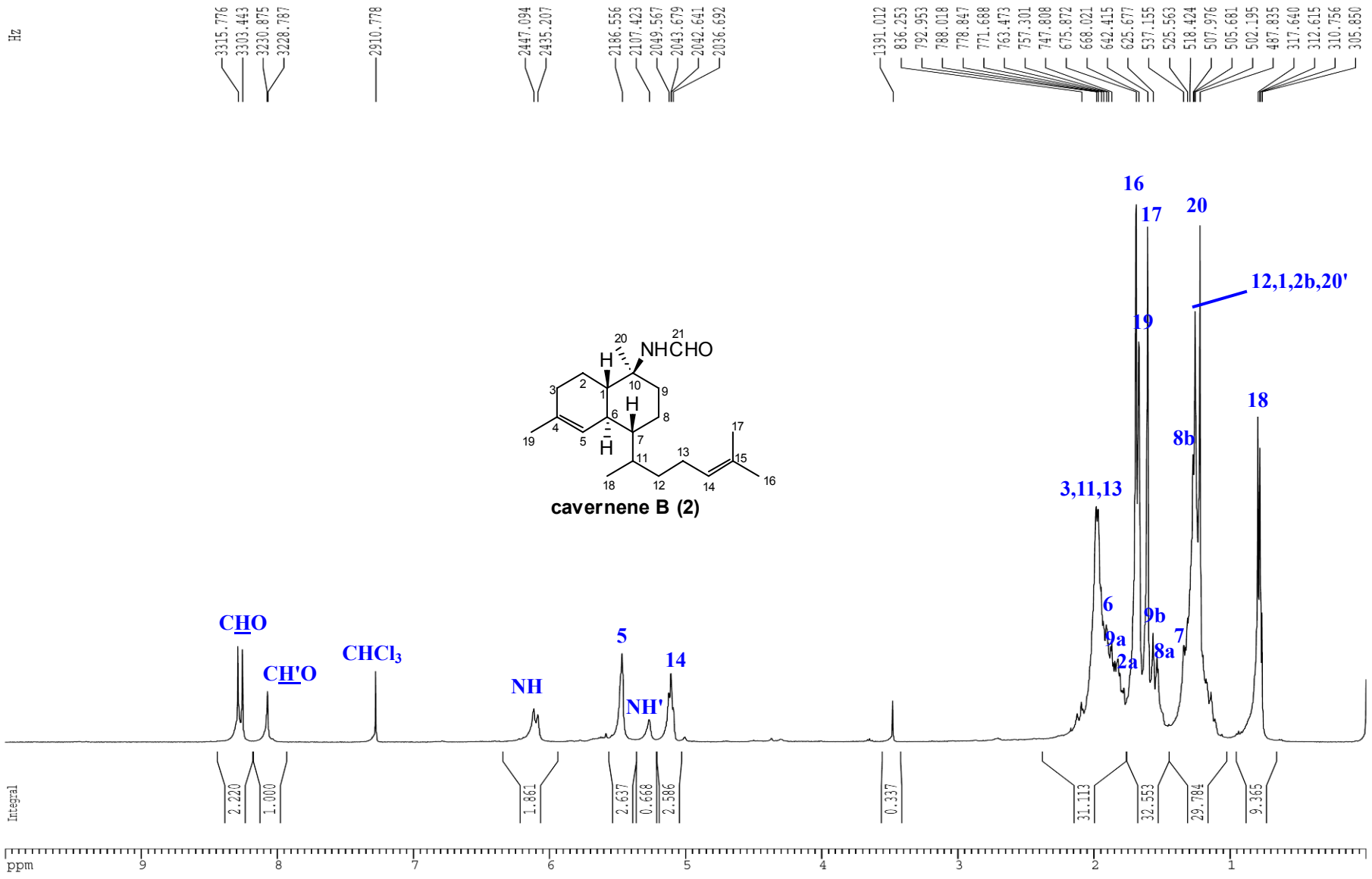


**Figure S11.** $^{13}C$ NMR spectrum of cavernene B (**2**) in $CDCl_3$.

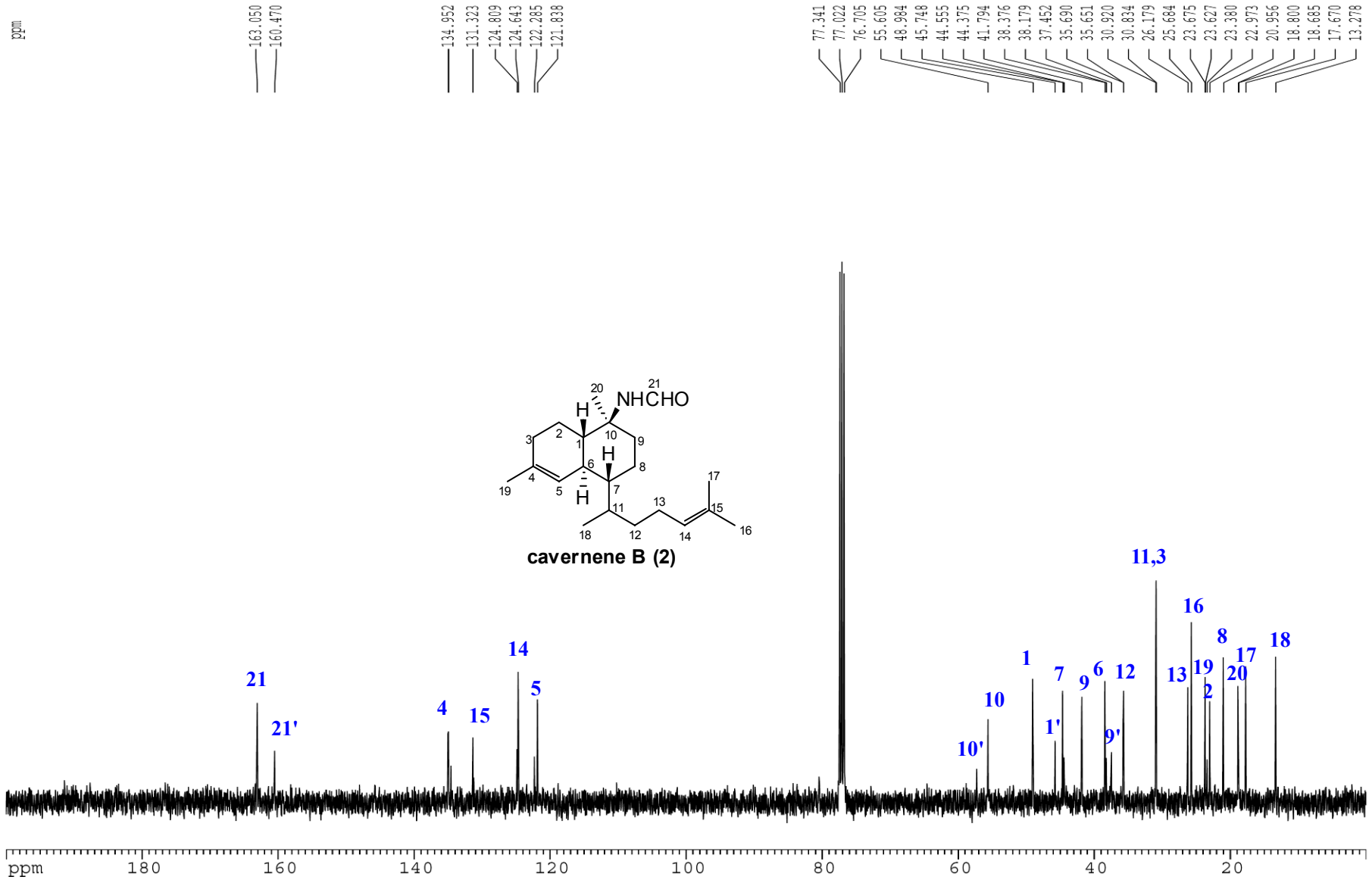


**Figure S12.** HSQC spectrum of cavernene B (**2**) in $CDCl_3$.

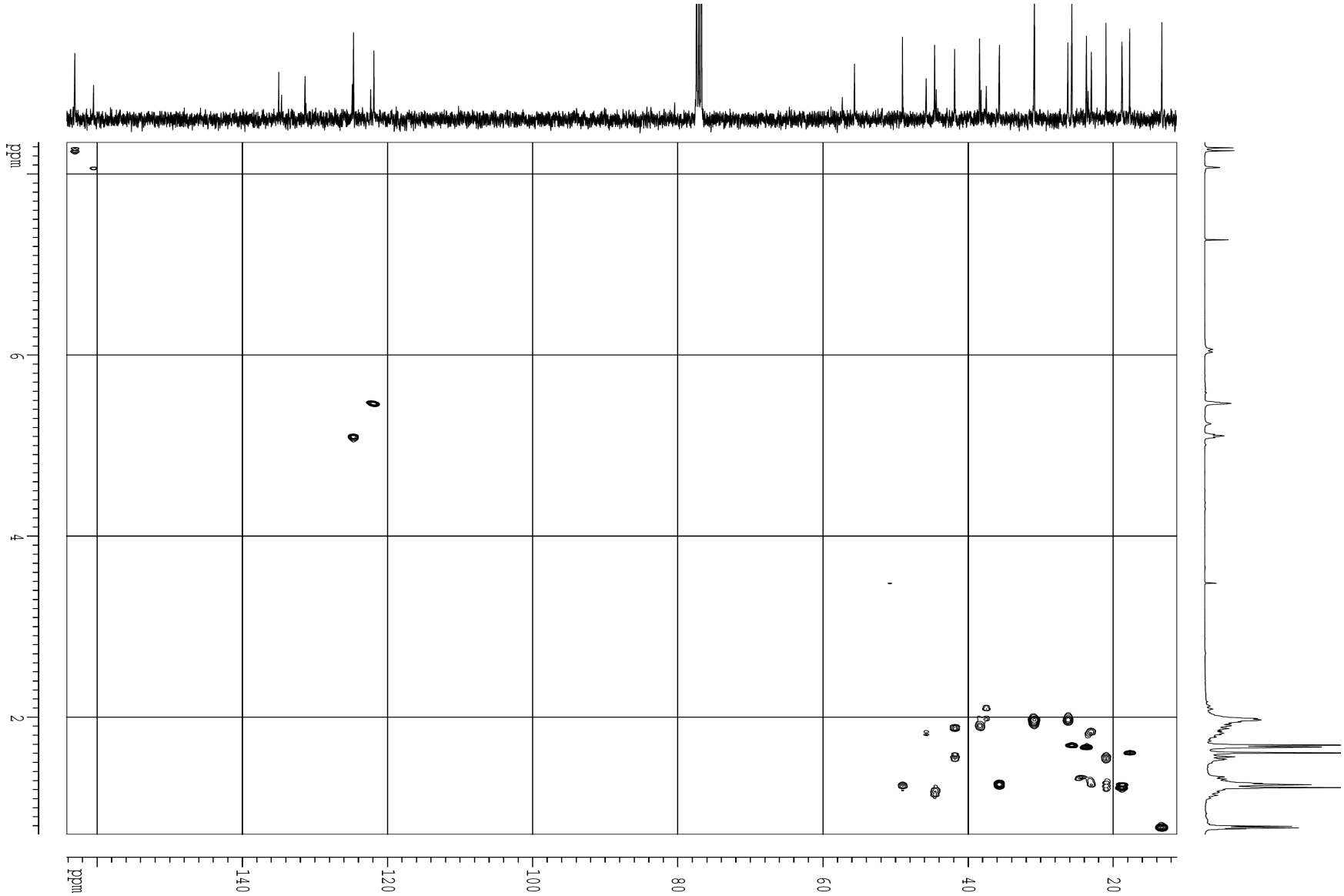


**Figure S13.** HMBC spectrum of cavernene B (**2**) in $CDCl_3$.

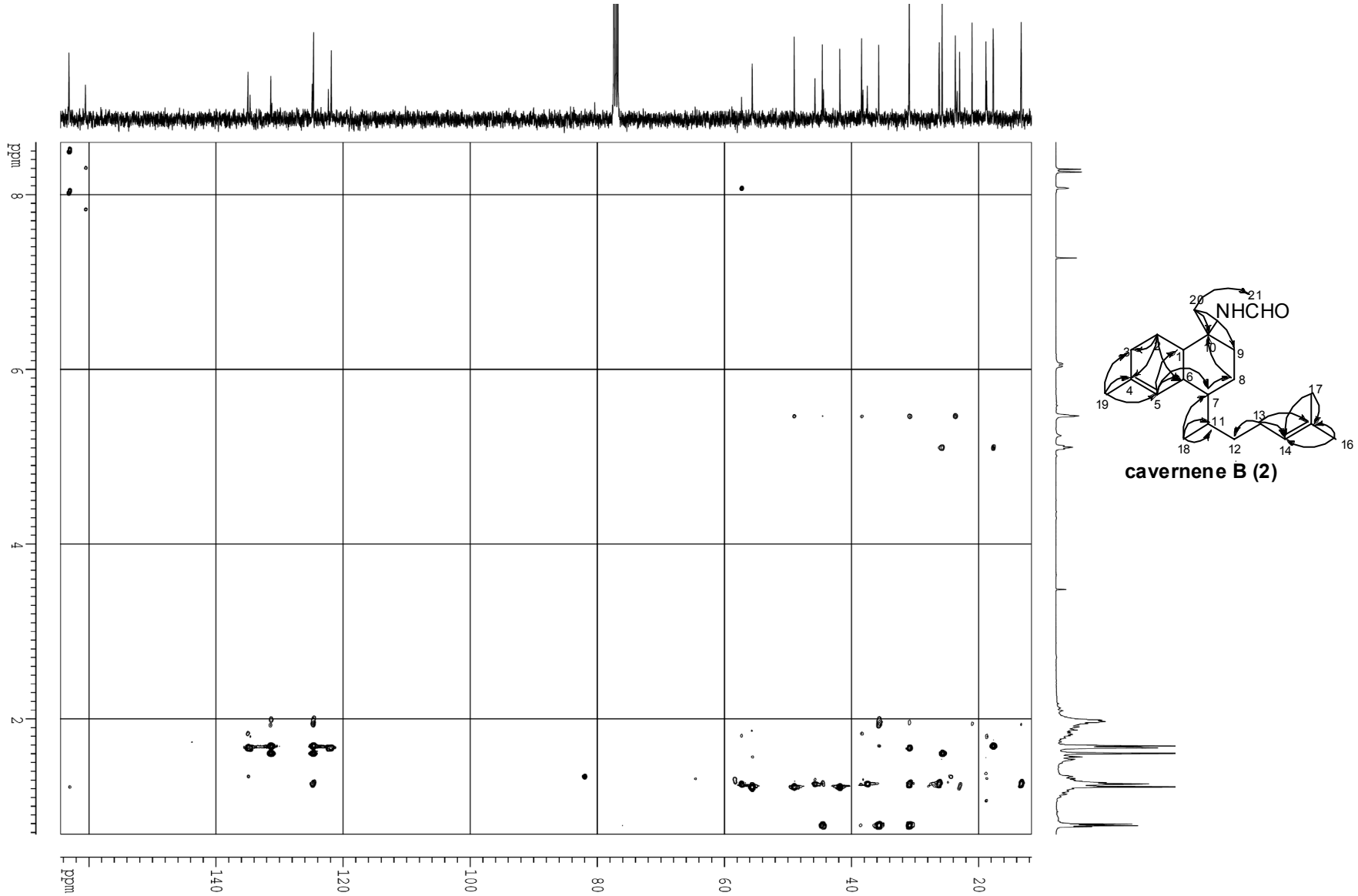


**Figure S14.** $^{1}H$-$^{1}H$ COSY spectrum of cavernene B (**2**) in $CDCl_3$.

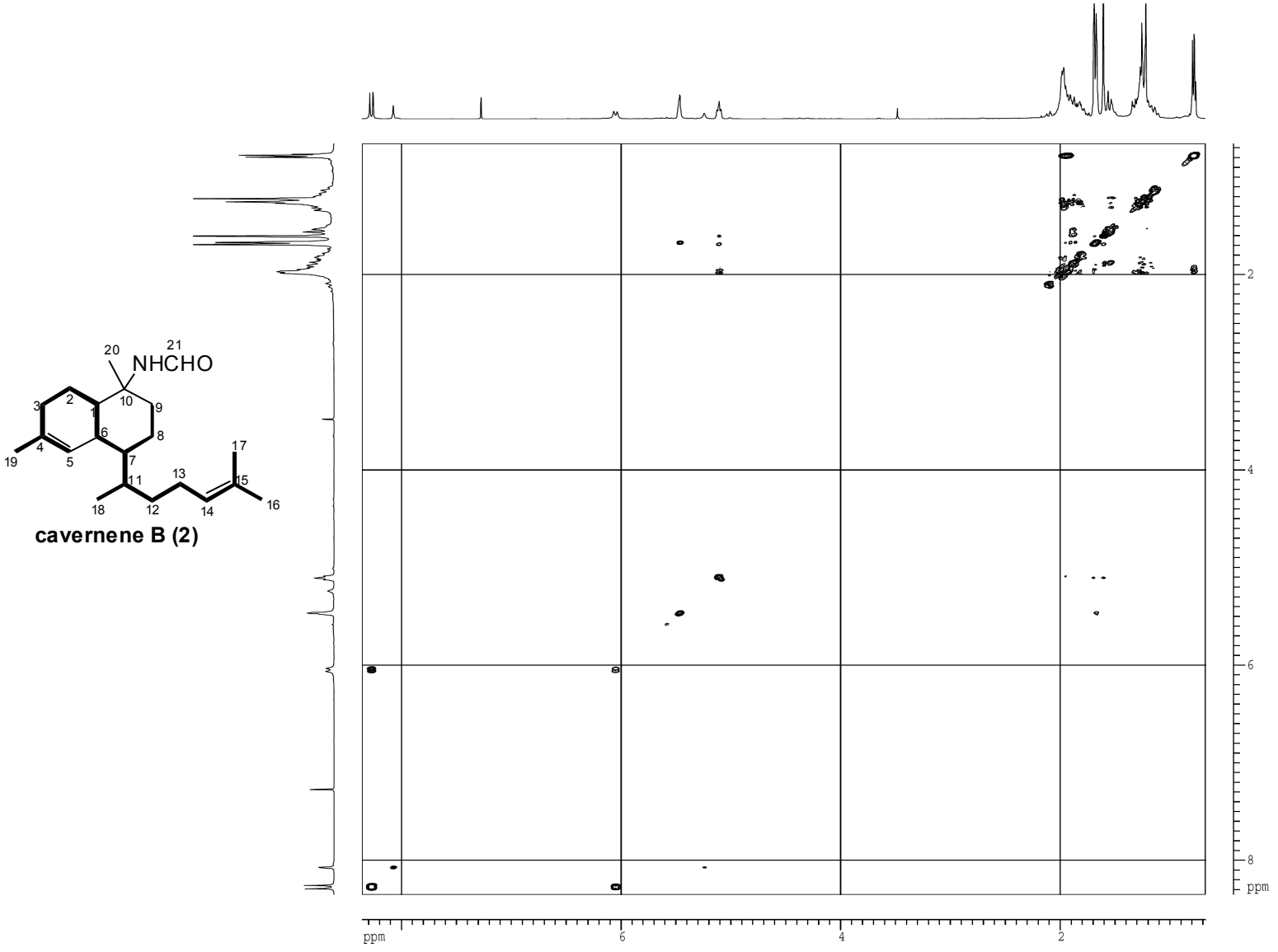


**Figure S15.** NOESY spectrum of cavernene B (**2**) in $CDCl_3$.

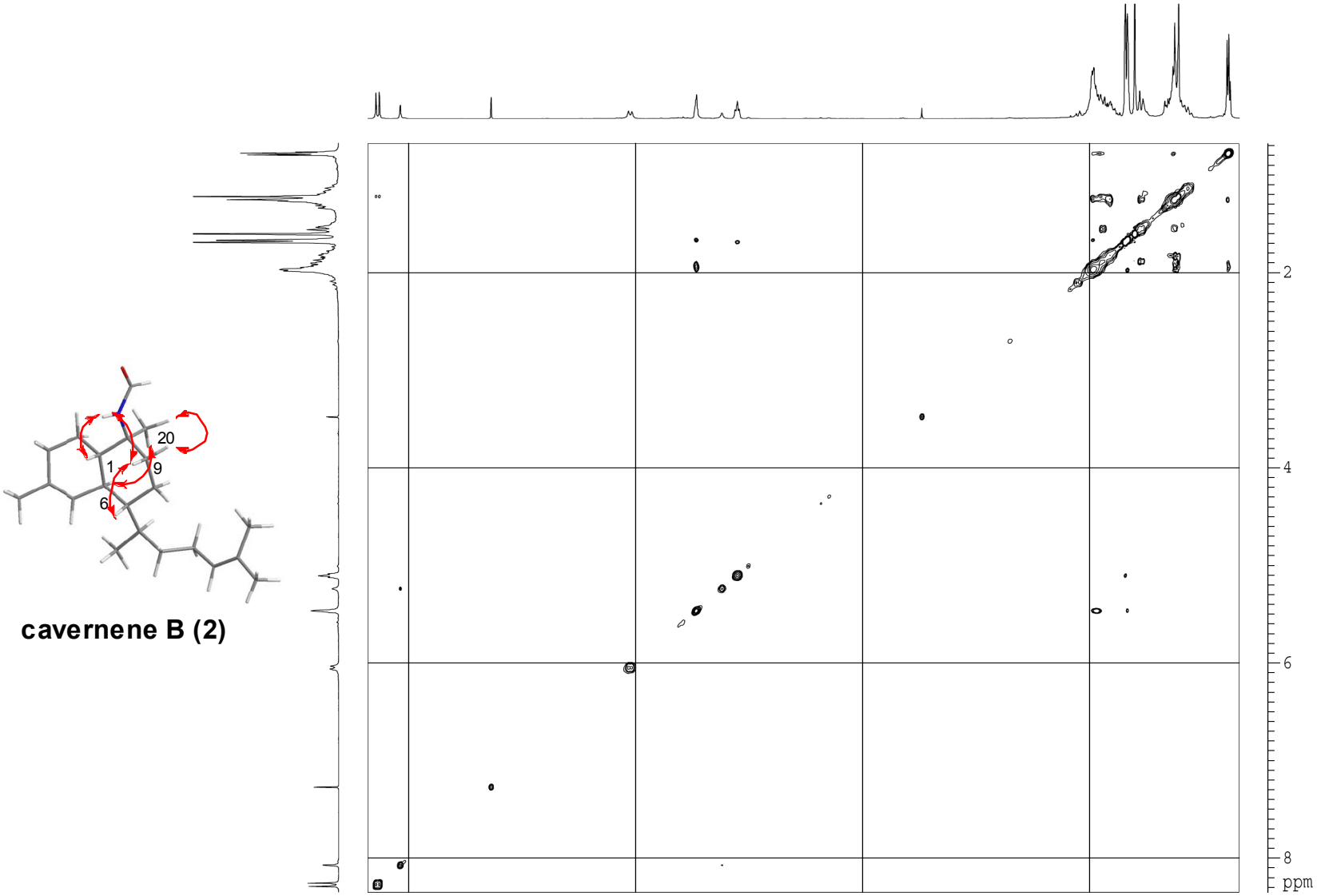


**Figure S16.** IR spectrum of cavernene B (**2**).

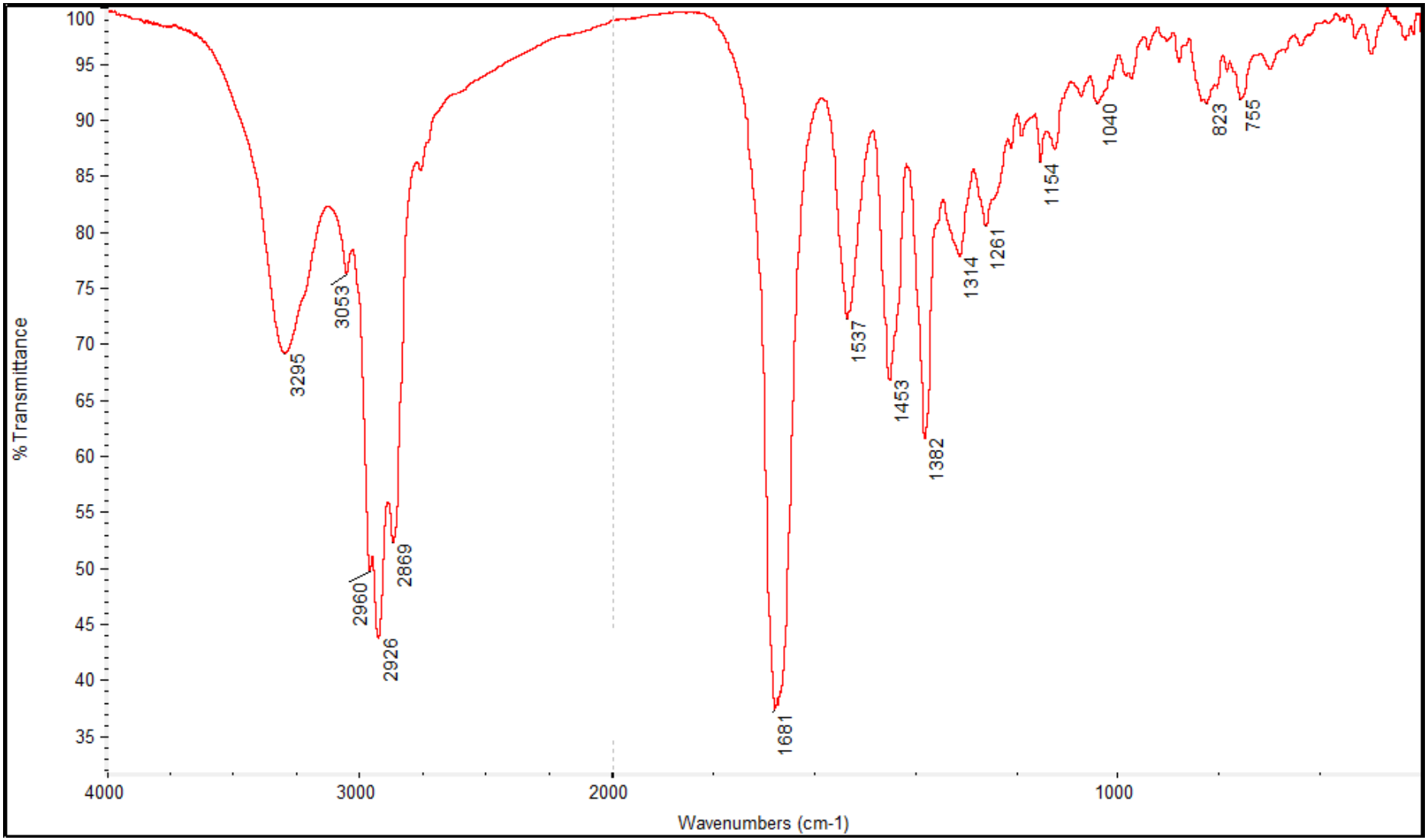
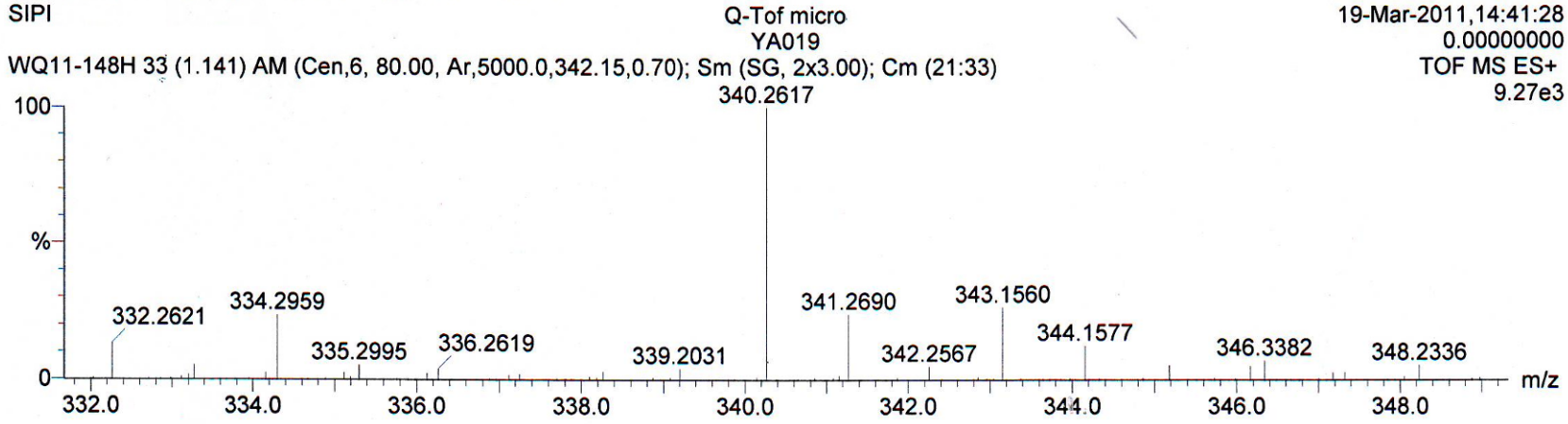


**Figure S17.** HRESIMS of cavernene B (**2**).

## 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




| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 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**).

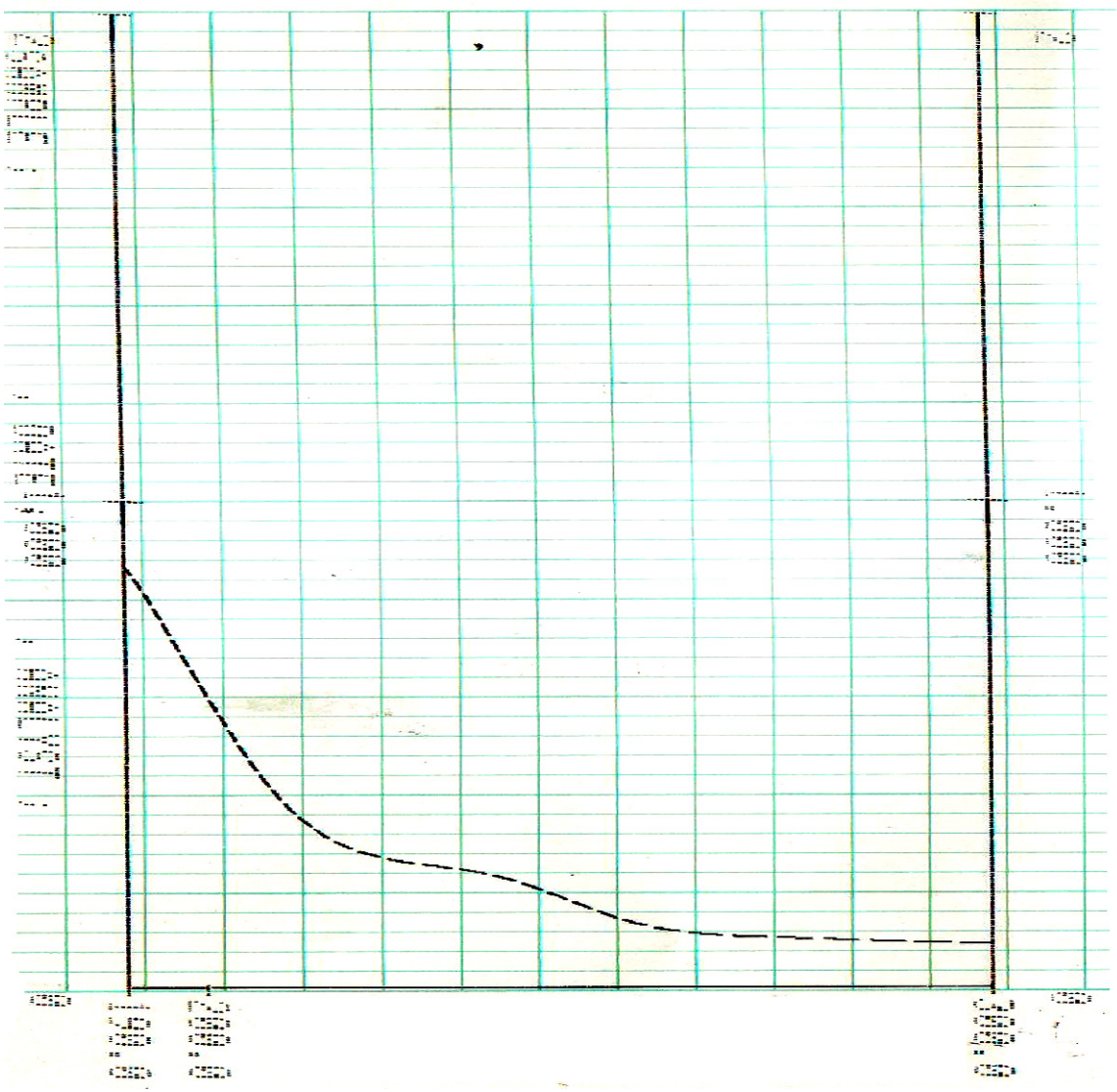


**Figure S19.** $^{1}$H NMR spectrum of cavernene C (**3**) in $CDCl_3$.

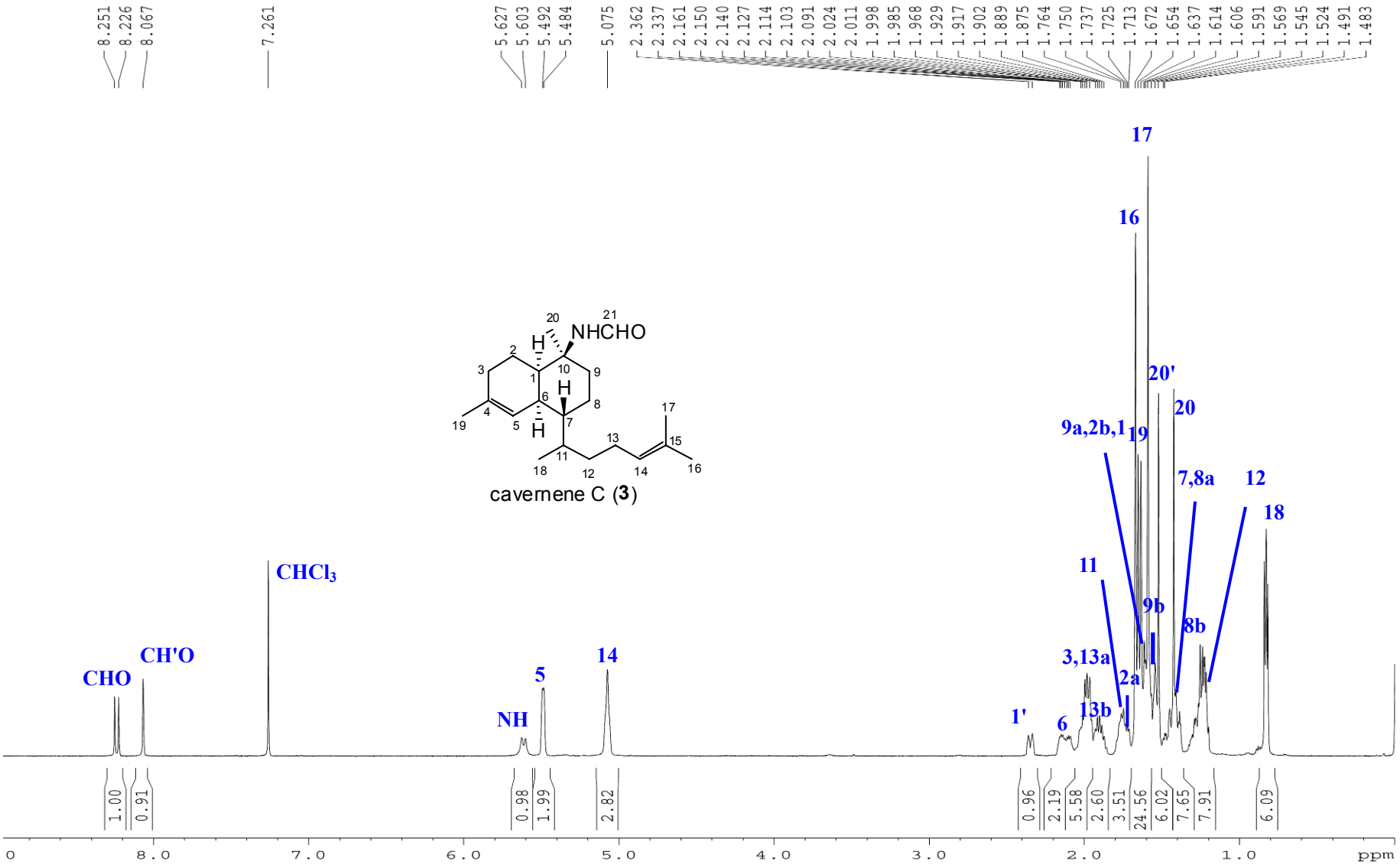


**Figure S20.** $^{13}C$ NMR spectrum of cavernene C (**3**) in $CDCl_3$.

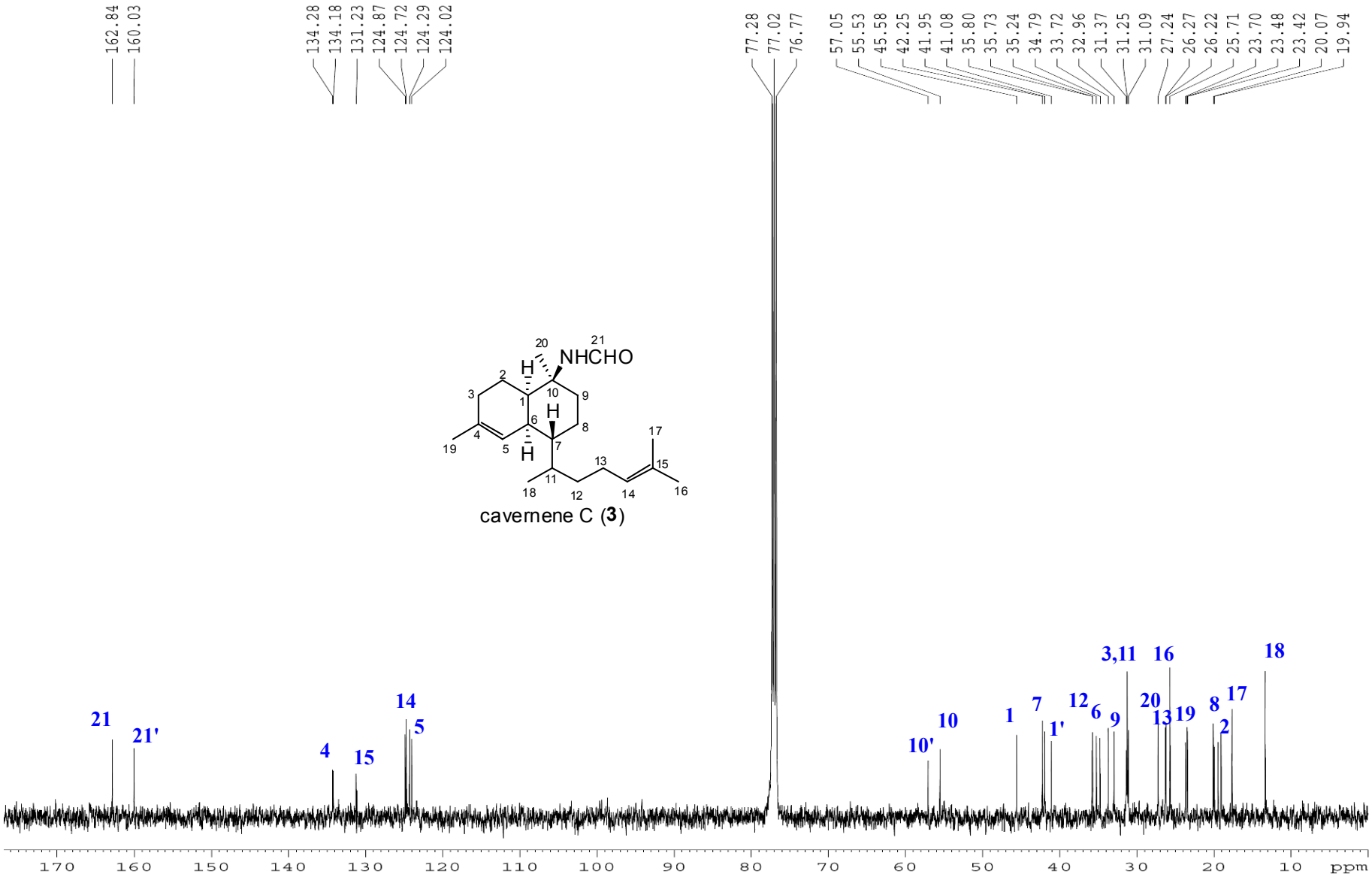


**Figure S21.** HSQC spectrum of cavernene C (**3**) in $CDCl_3$.

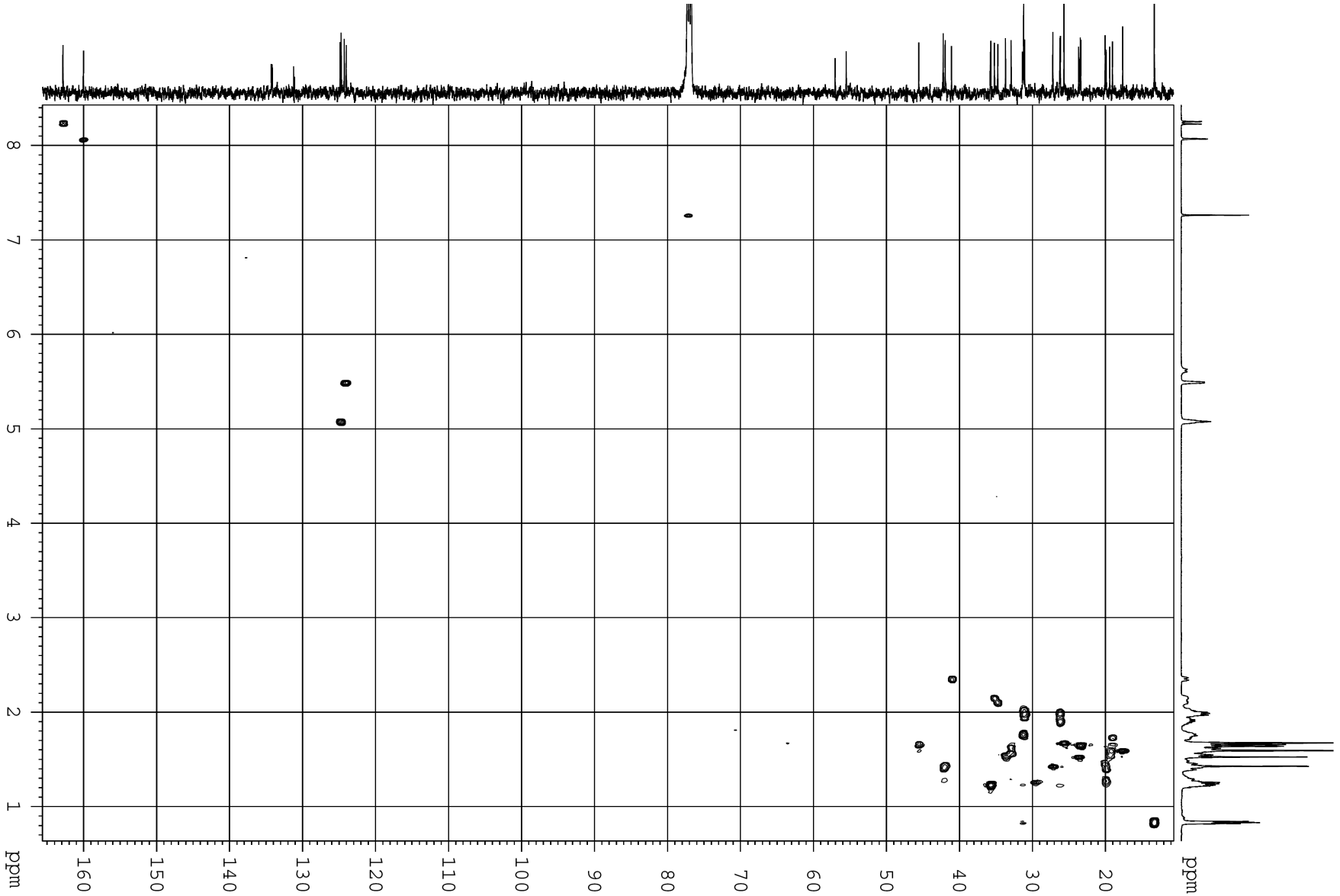


**Figure S22.** HMBC spectrum of cavernene C (**3**) in $CDCl_3$.

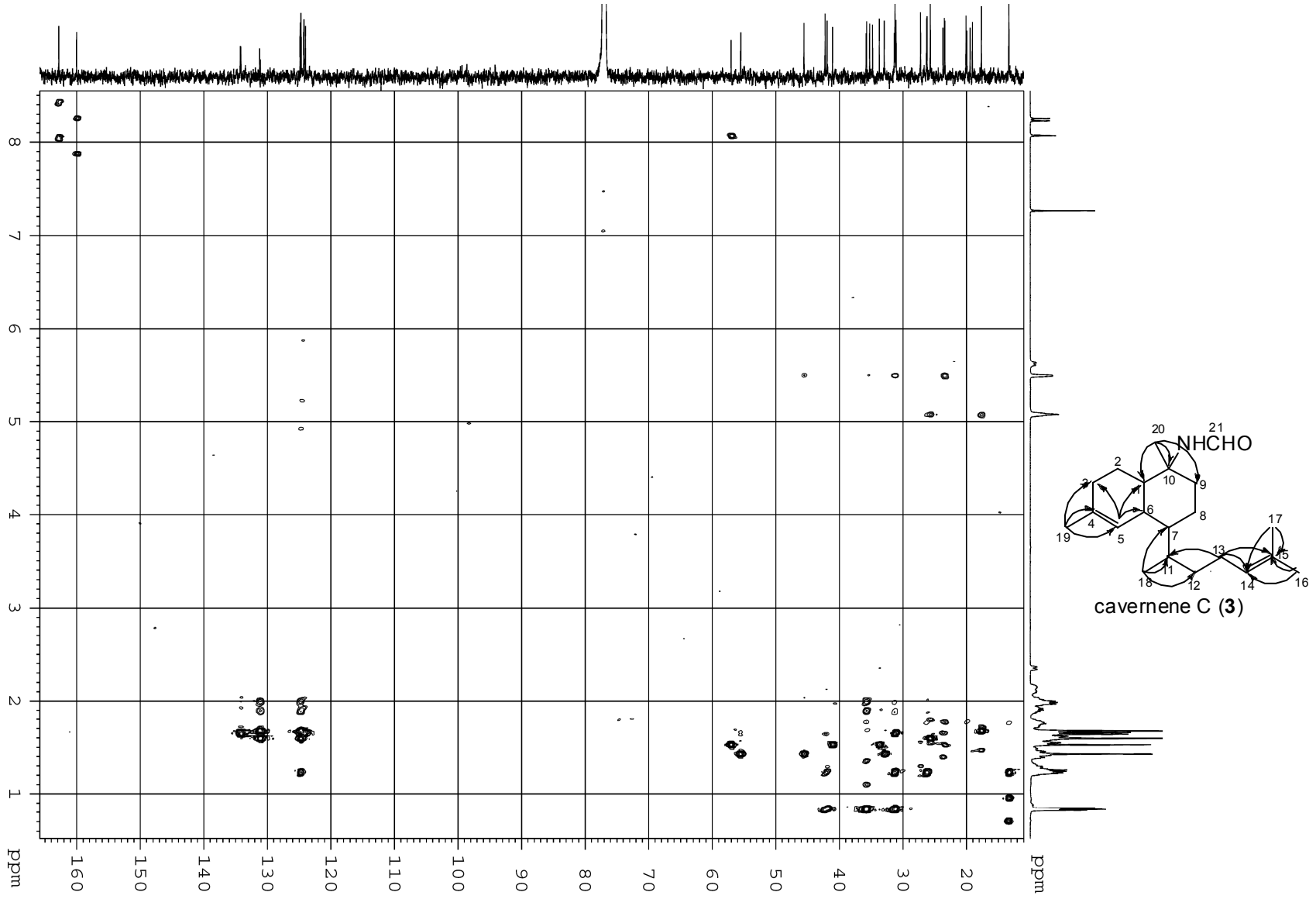


**Figure S23.** $^{1}H$-$^{1}H$ COSY spectrum of cavernene C (**3**) in $CDCl_3$.

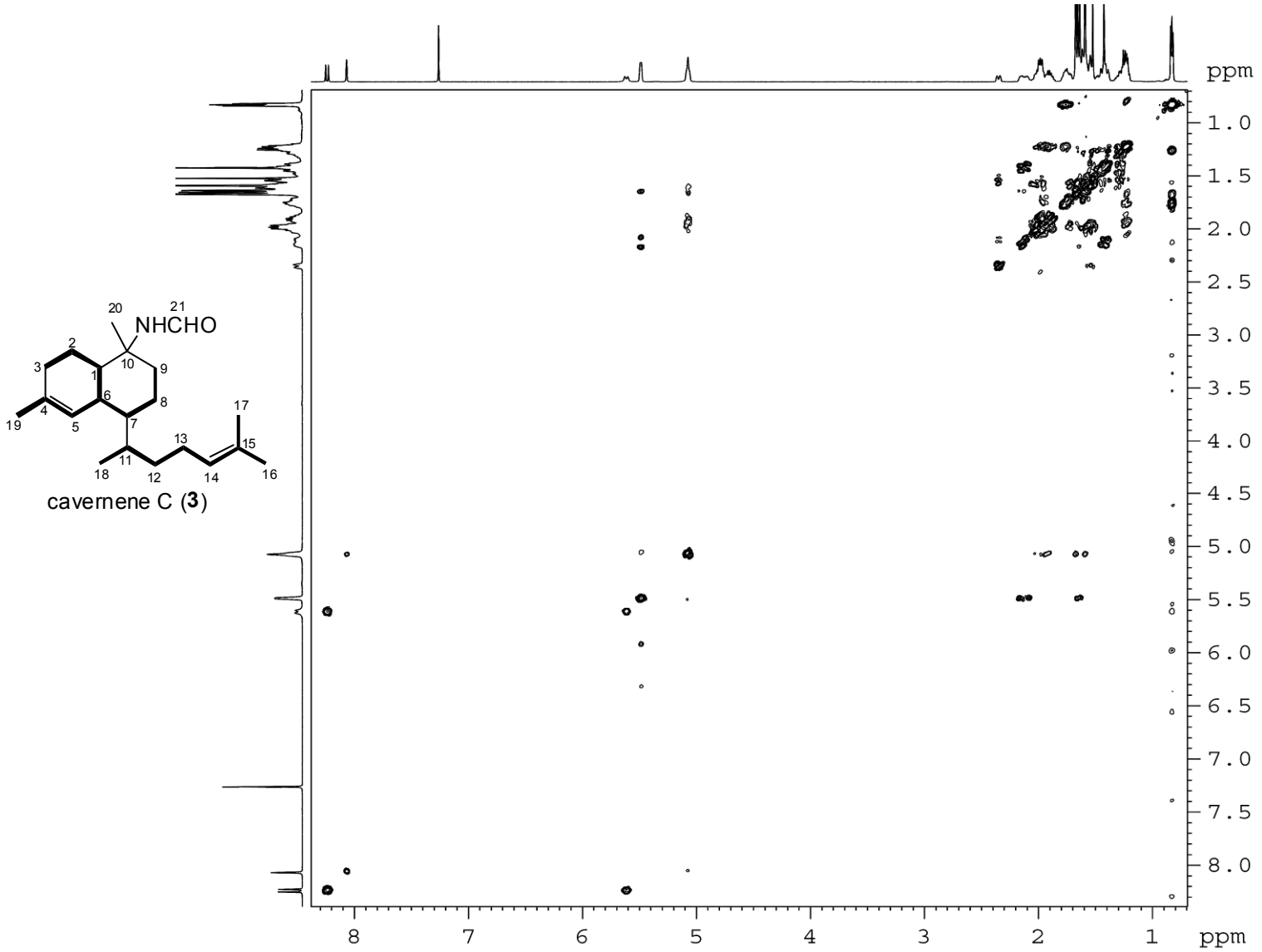


**Figure S24.** NOESY spectrum of cavernene C (**3**) in $CDCl_3$.

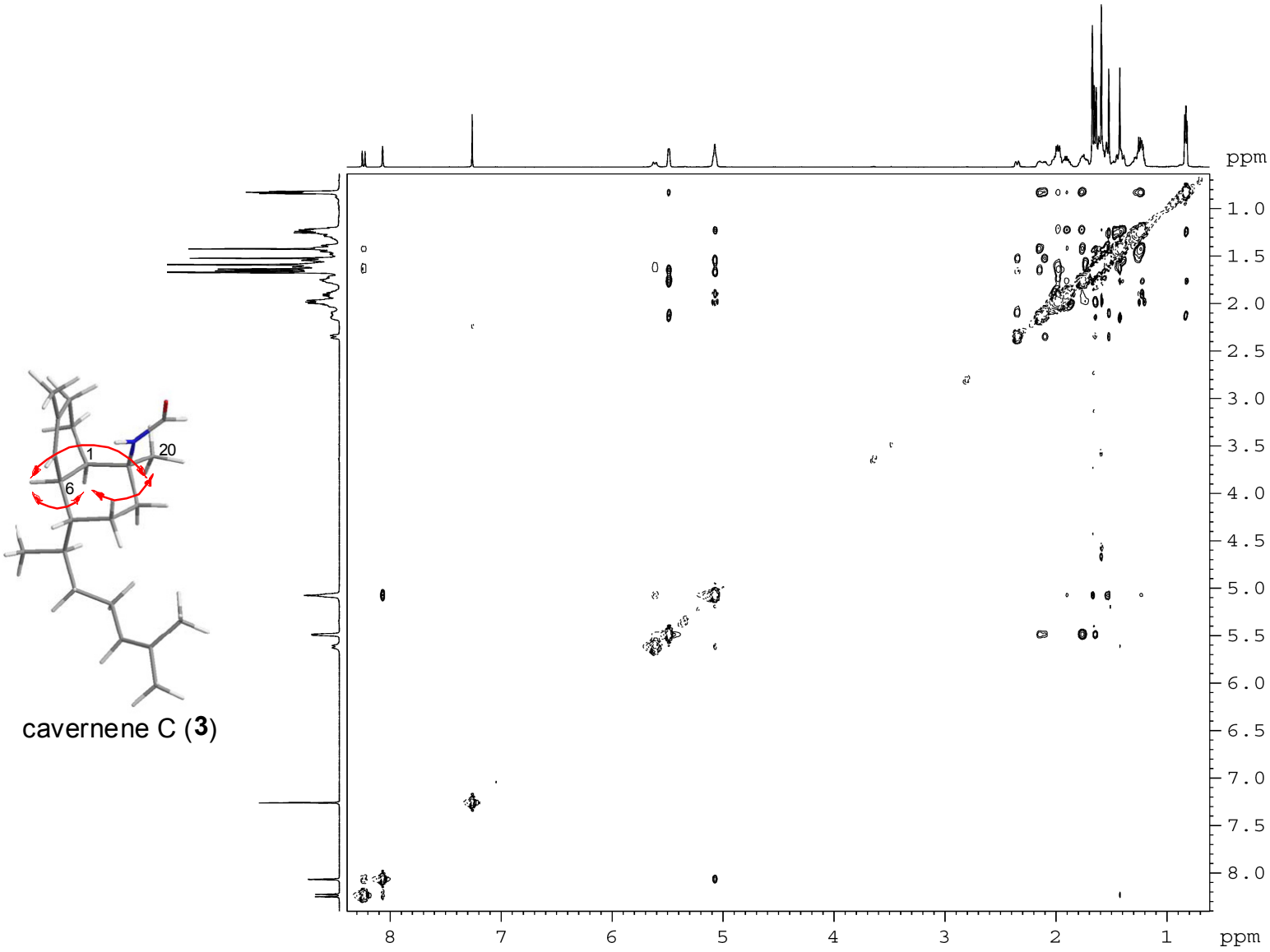


**Figure S25.** IR spectrum of cavernene C (**3**).

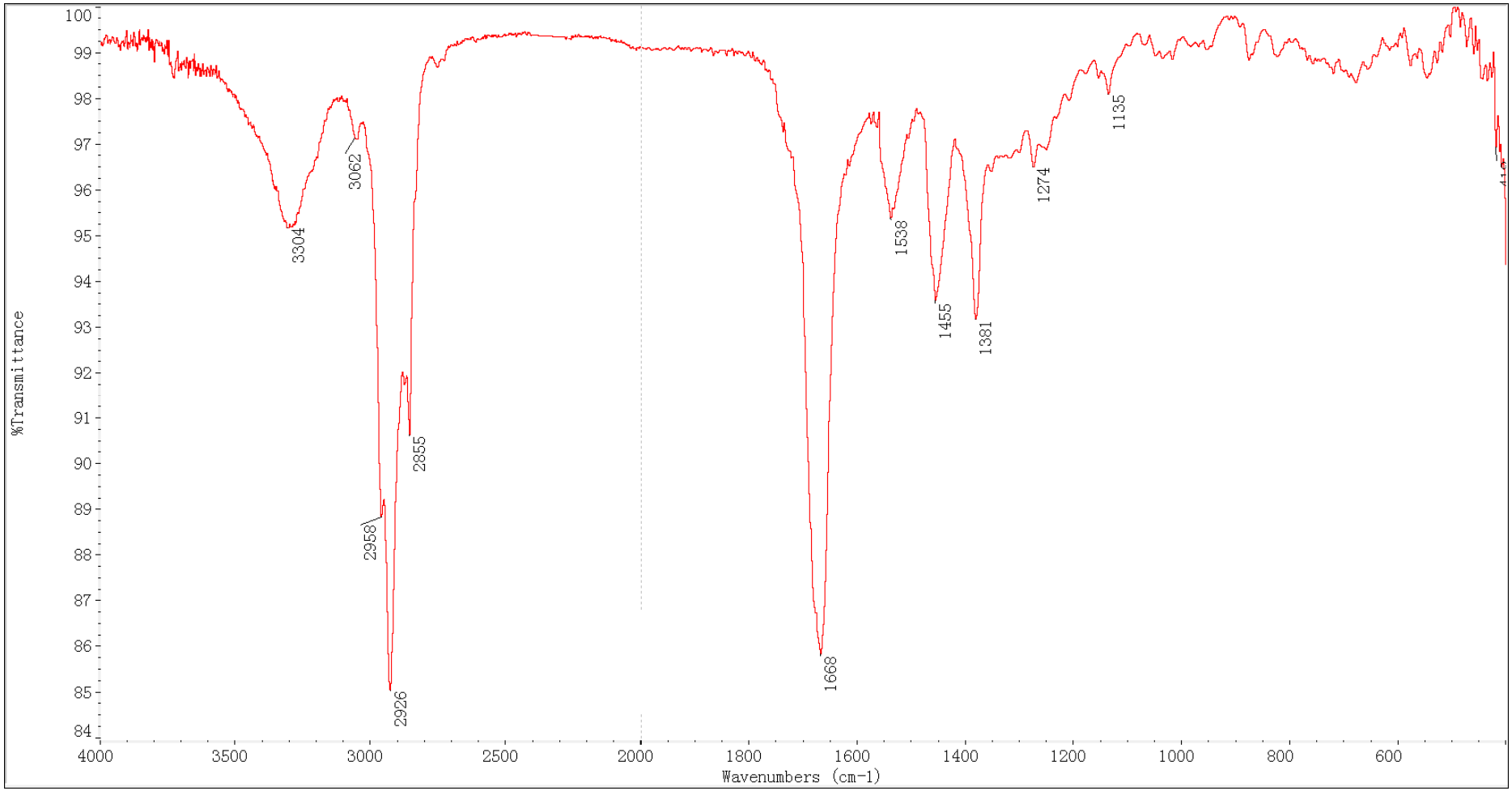
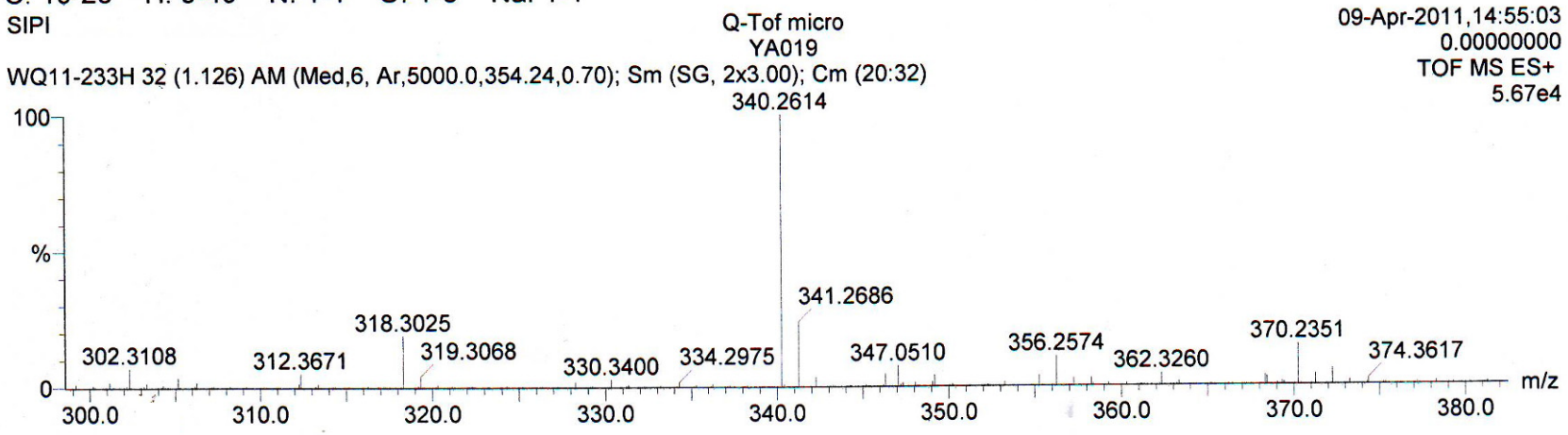


**Figure S26.** HRESIMS of cavernene C (**3**).

## 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




| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 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**).

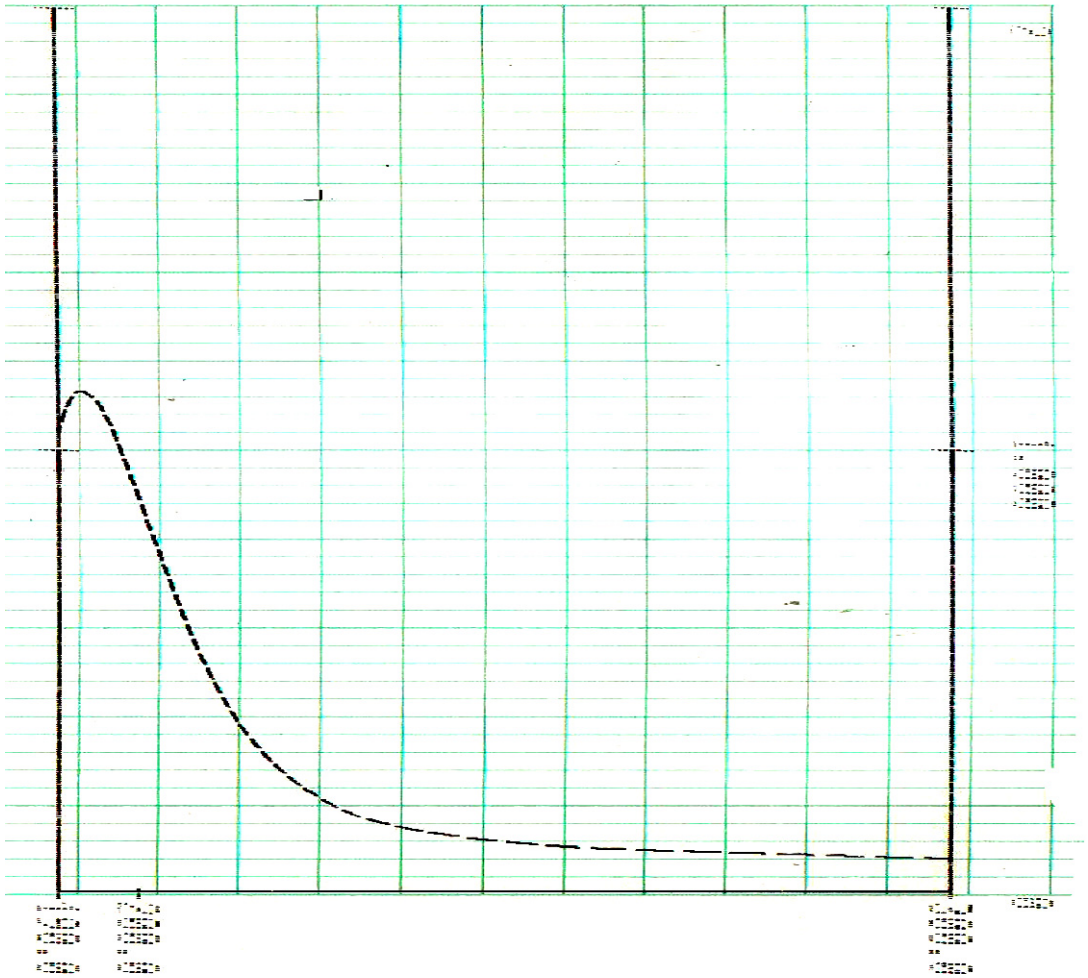


**Figure S28.** $^{1}$H NMR spectrum of cavernene D (**4**) in $CDCl_3$.

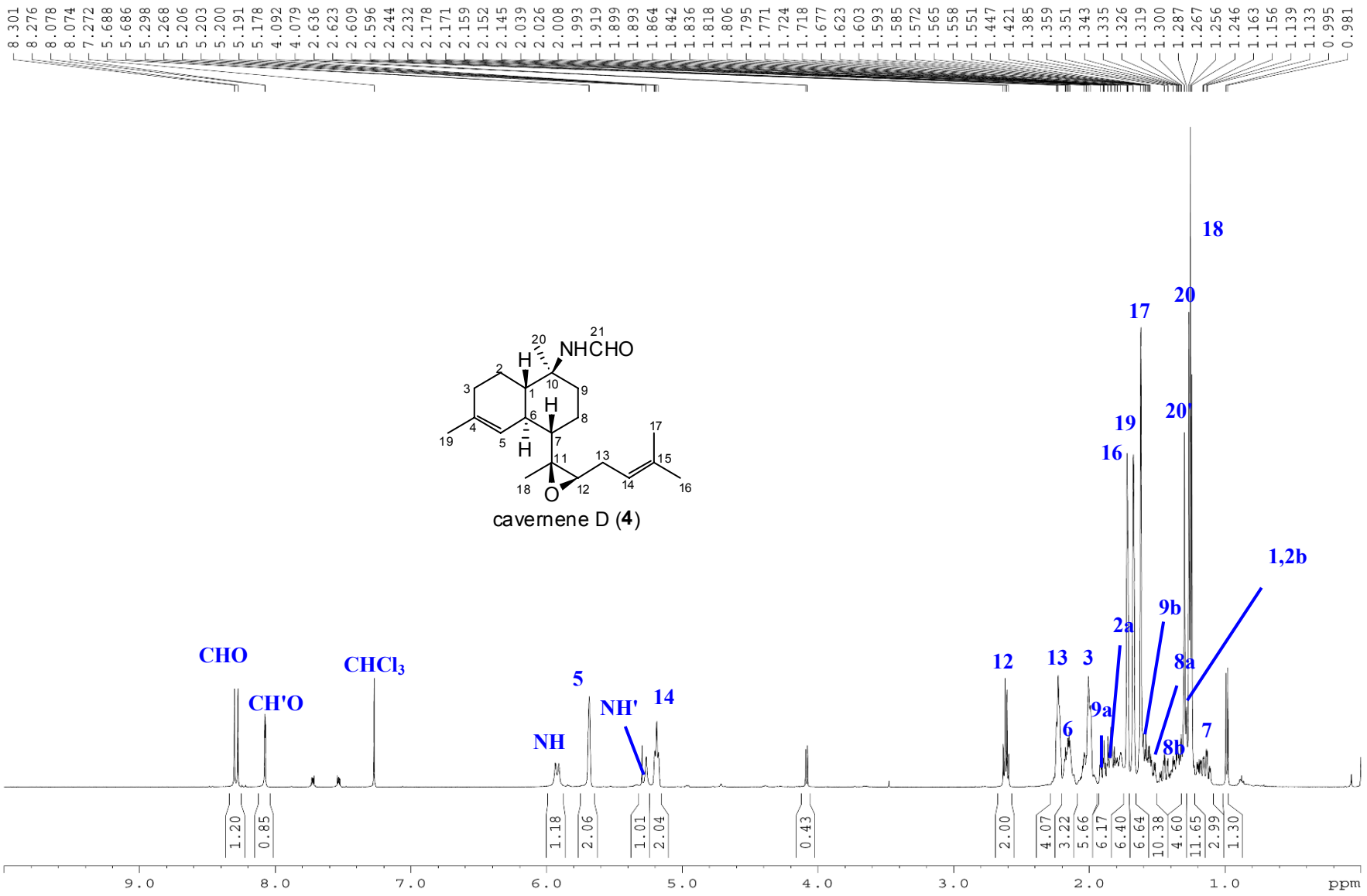


**Figure S29.** $^{13}C$ NMR spectrum of cavernene D (**4**) in $CDCl_3$.

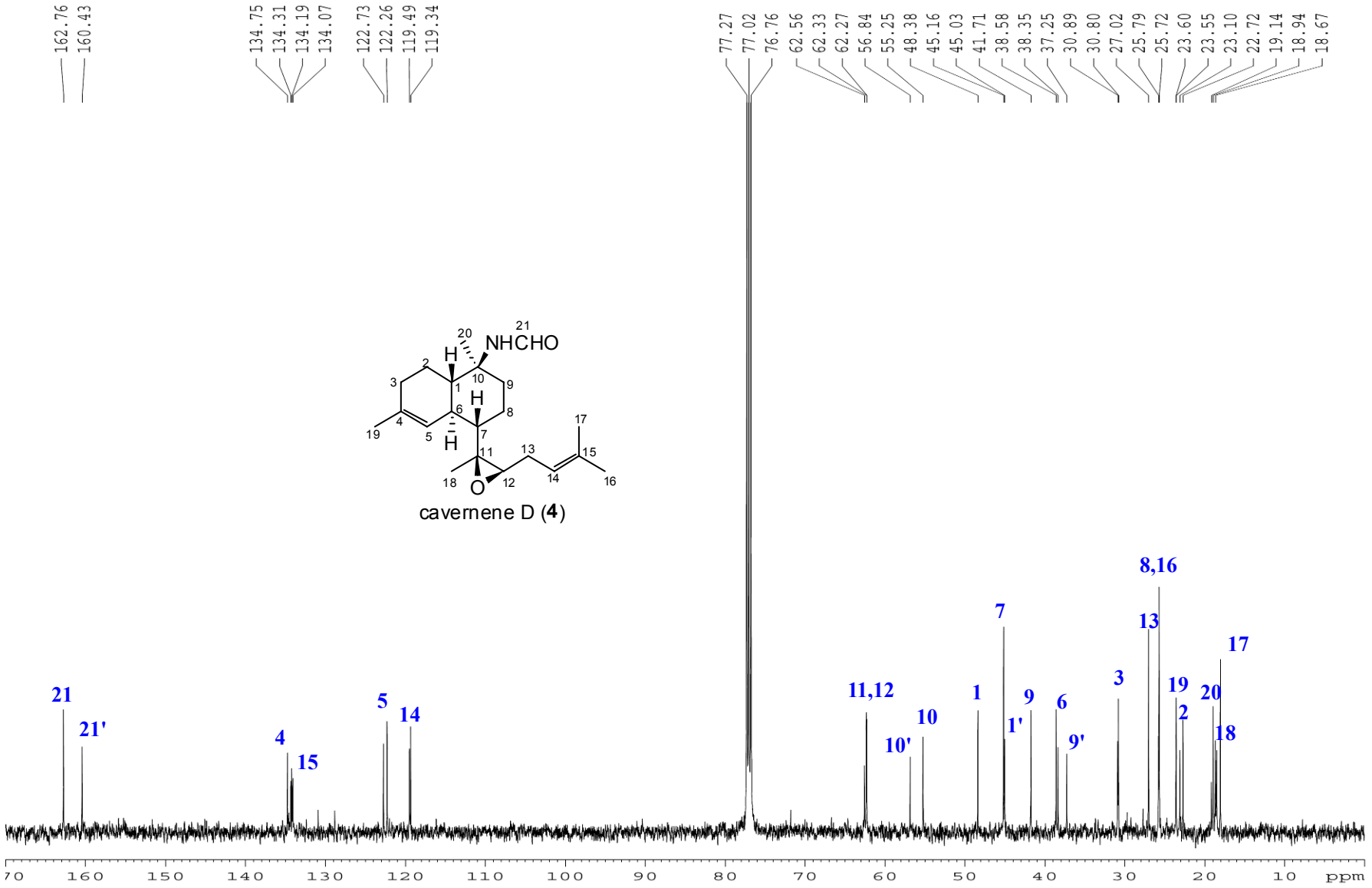


**Figure S30.** HSQC spectrum of cavernene D (**4**) in $CDCl_3$.

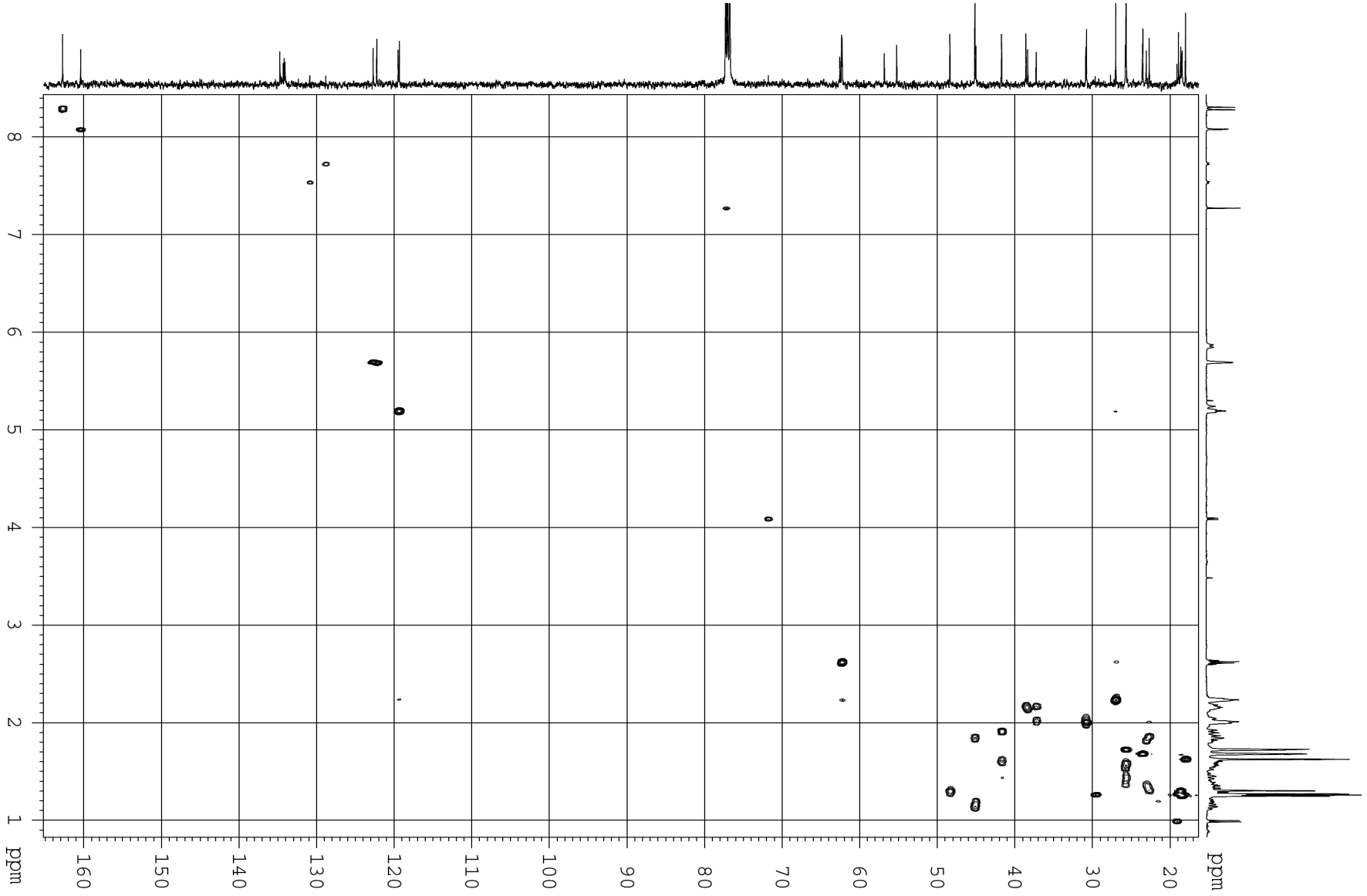


**Figure S31.** HMBC spectrum of cavernene D (**4**) in $CDCl_3$.

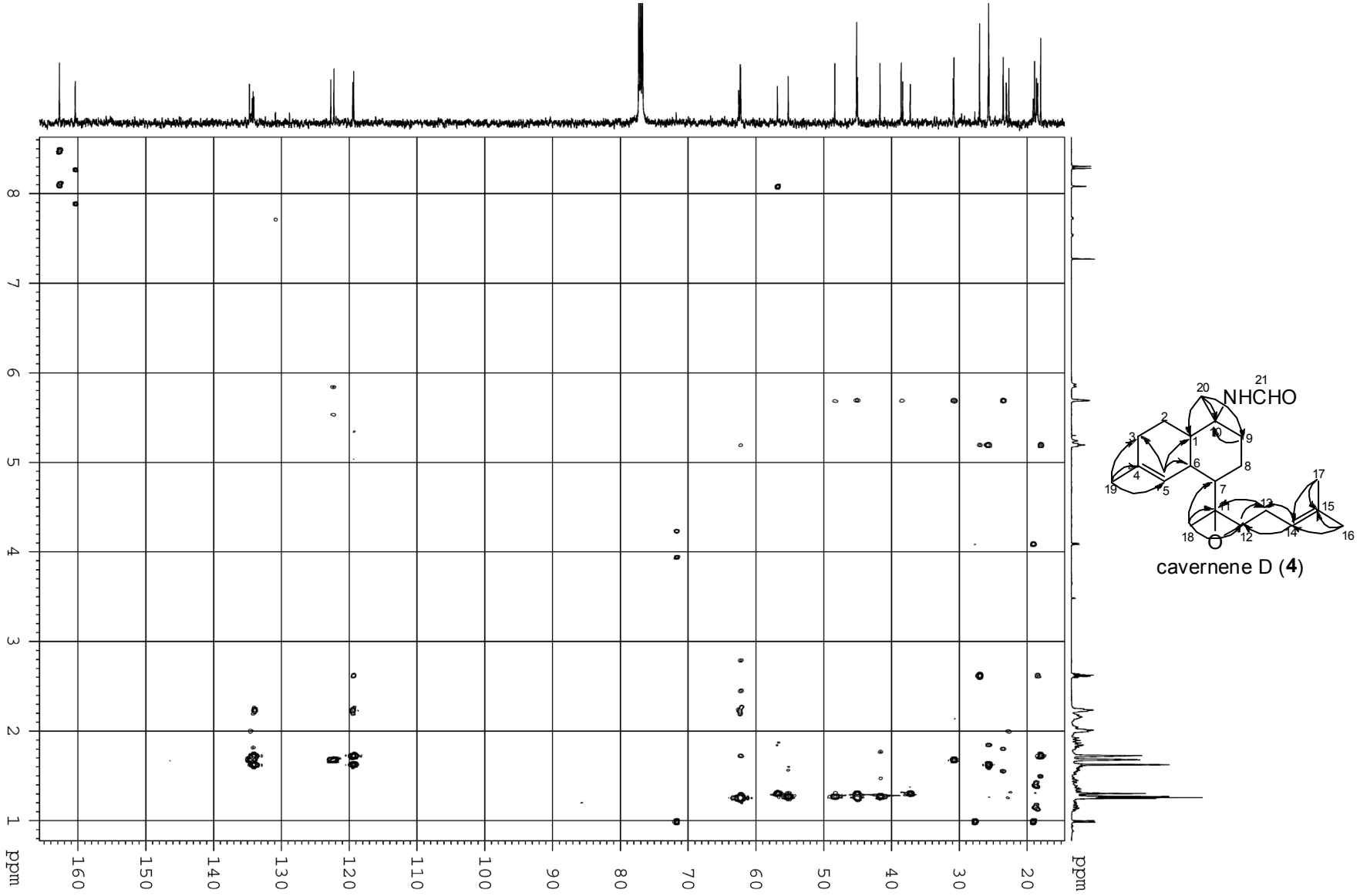


**Figure S32.** $^{1}H$-$^{1}H$ COSY spectrum of cavernene D (**4**) in $CDCl_3$.

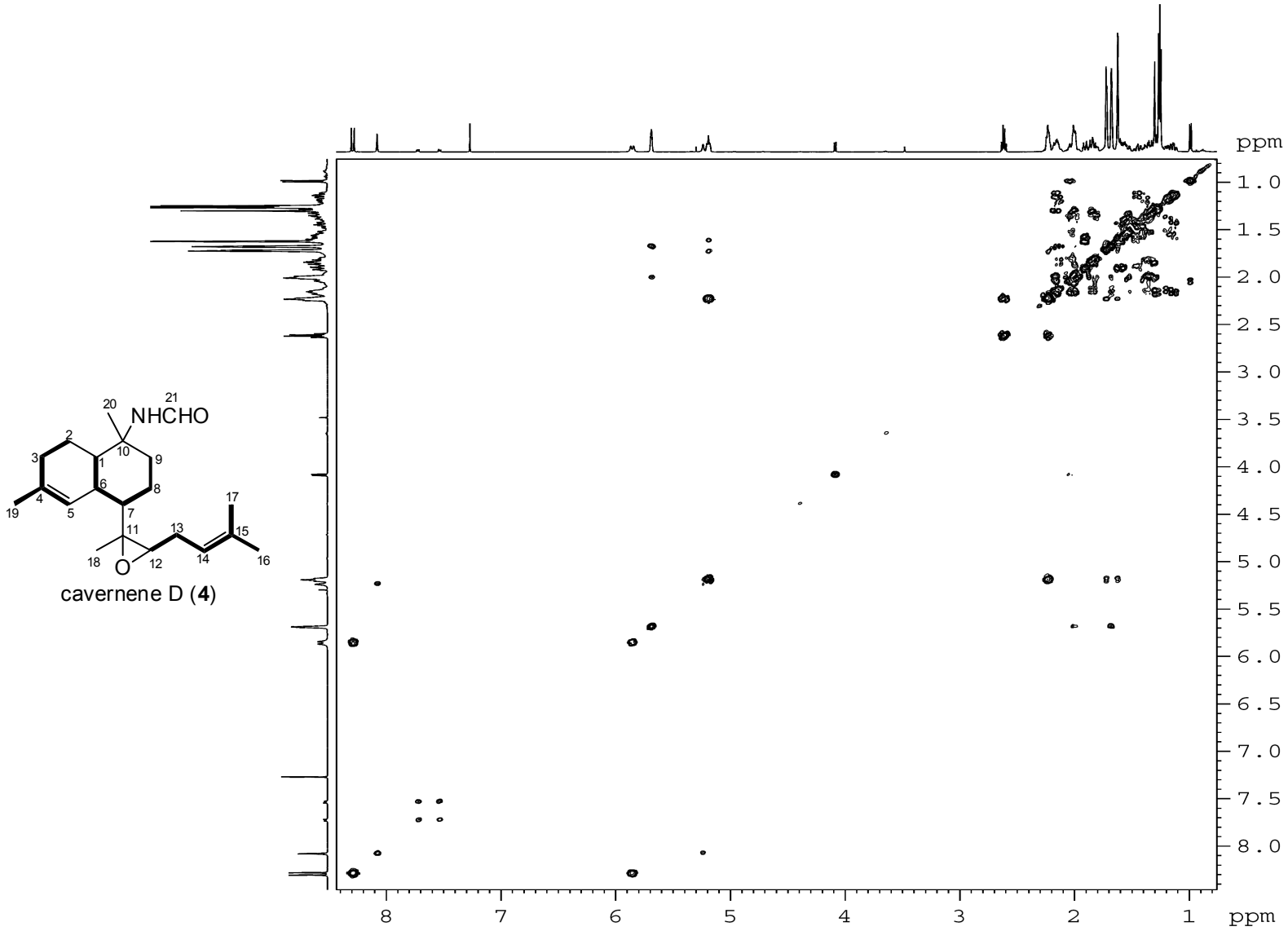


**Figure S33.** NOESY spectrum of cavernene D (**4**) in $CDCl_3$.

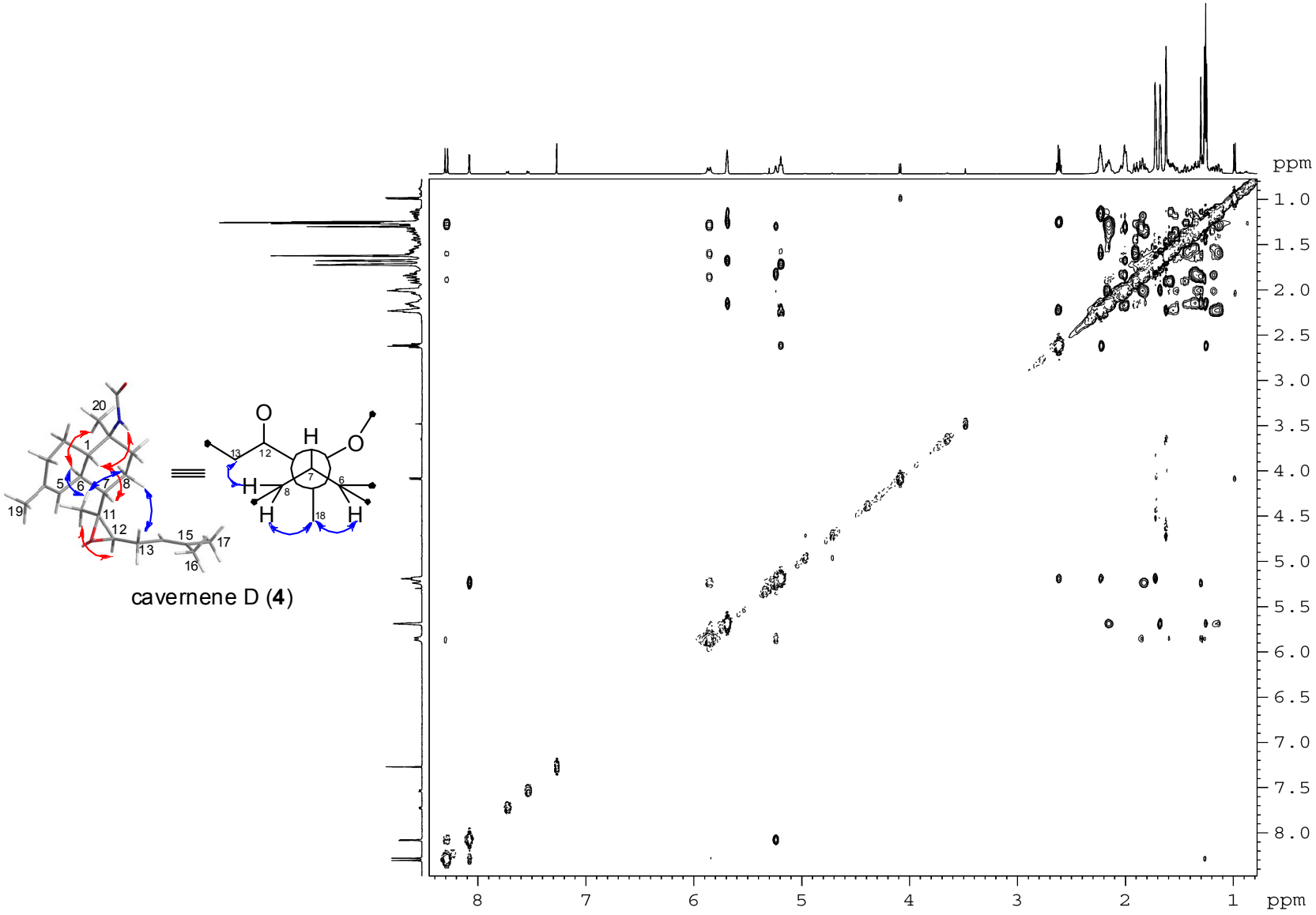


**Figure S34.** IR spectrum of cavernene D (**4**).

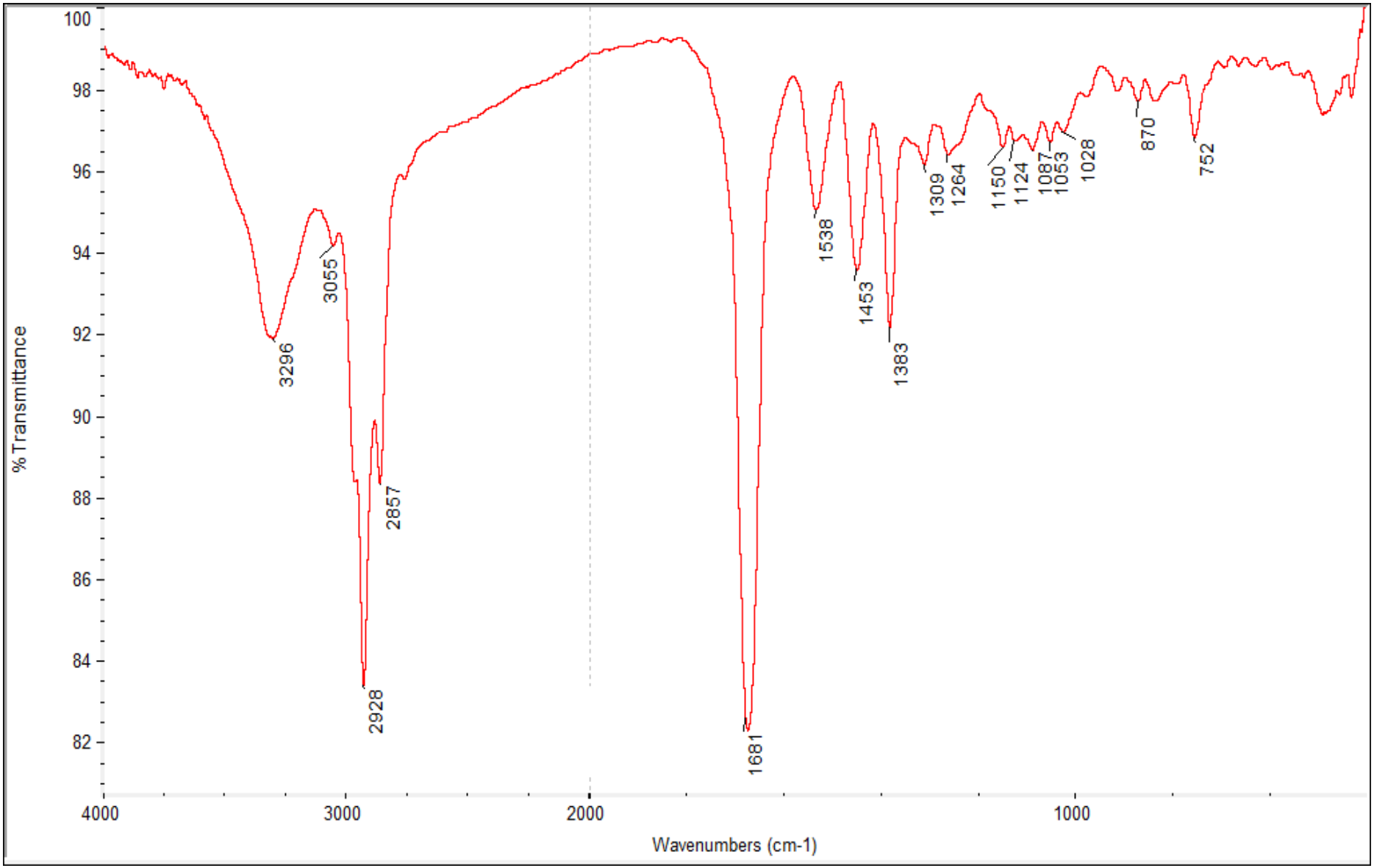
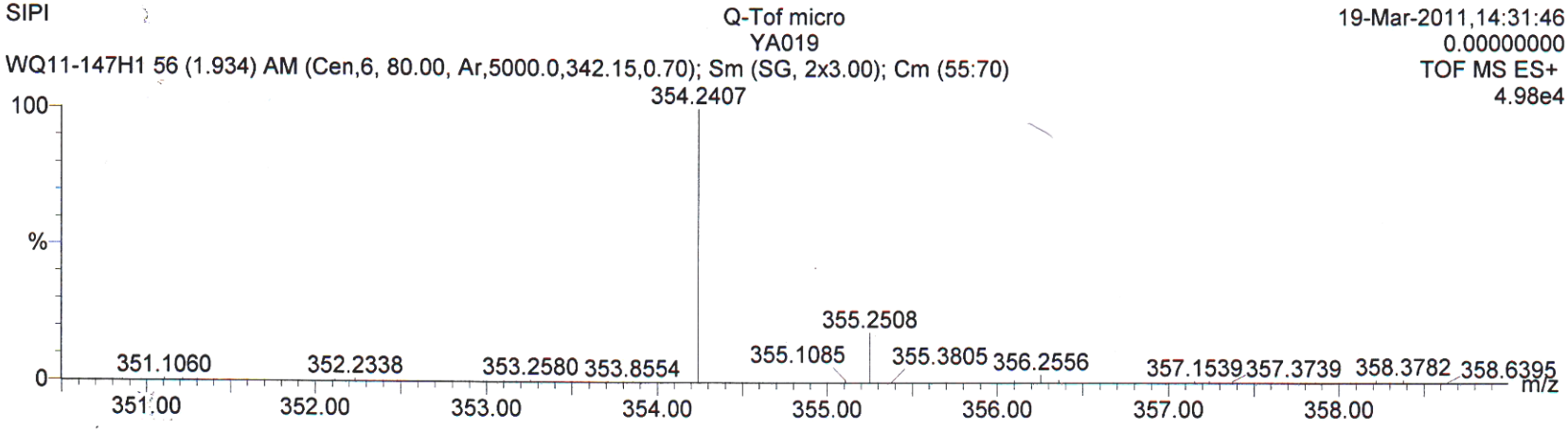


**Figure S35.** HRESIMS of cavernene D (**4**).

## 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




| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 30.00 | | | | -1.5 | | |
| Maximum: | 100.00 | | 5.0 | 10.0 | 50.0 | | |
| 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**).

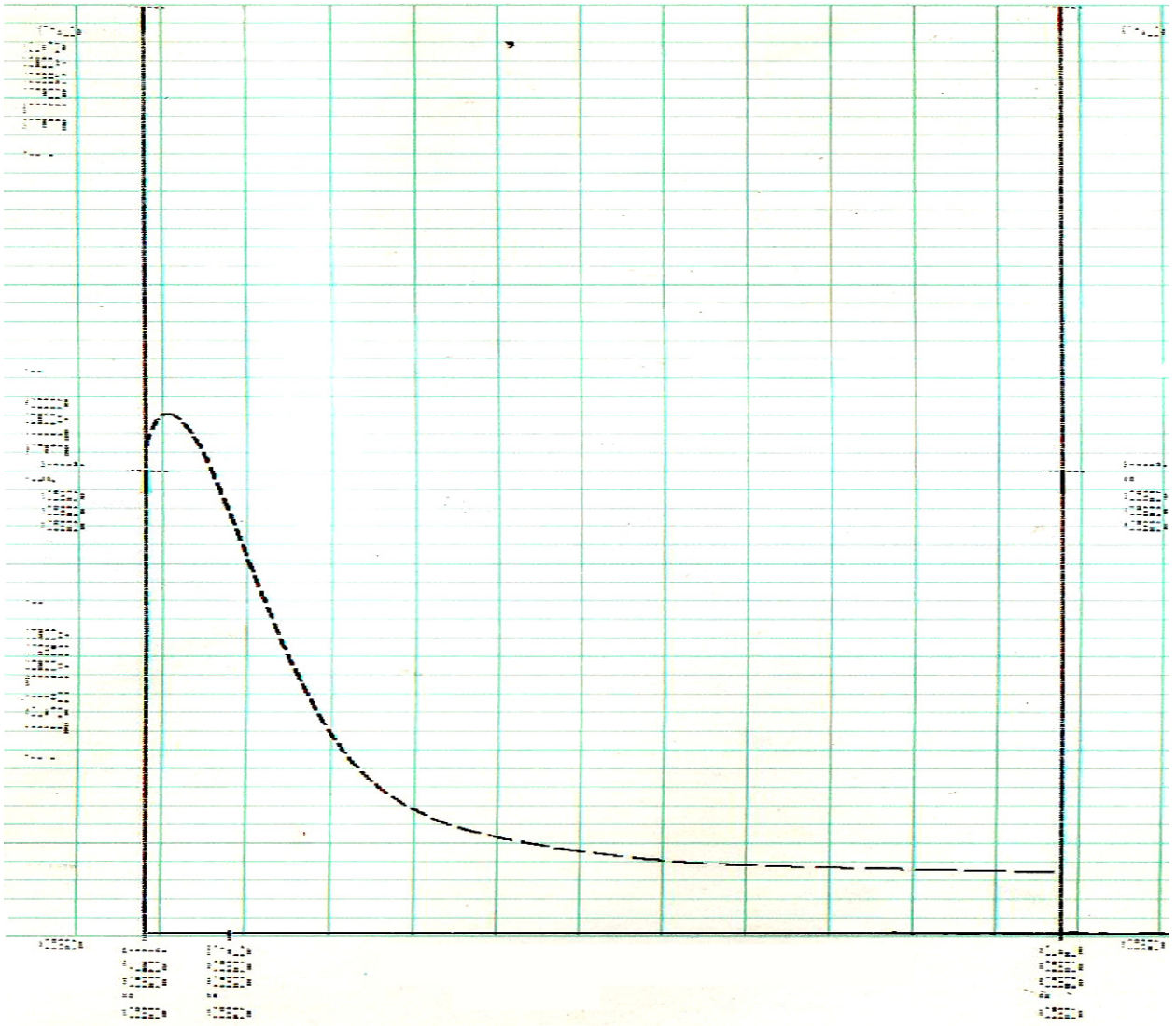


**Figure S37.** $^{1}$H NMR spectrum of kalihinene E (**5**) in $CDCl_3$.

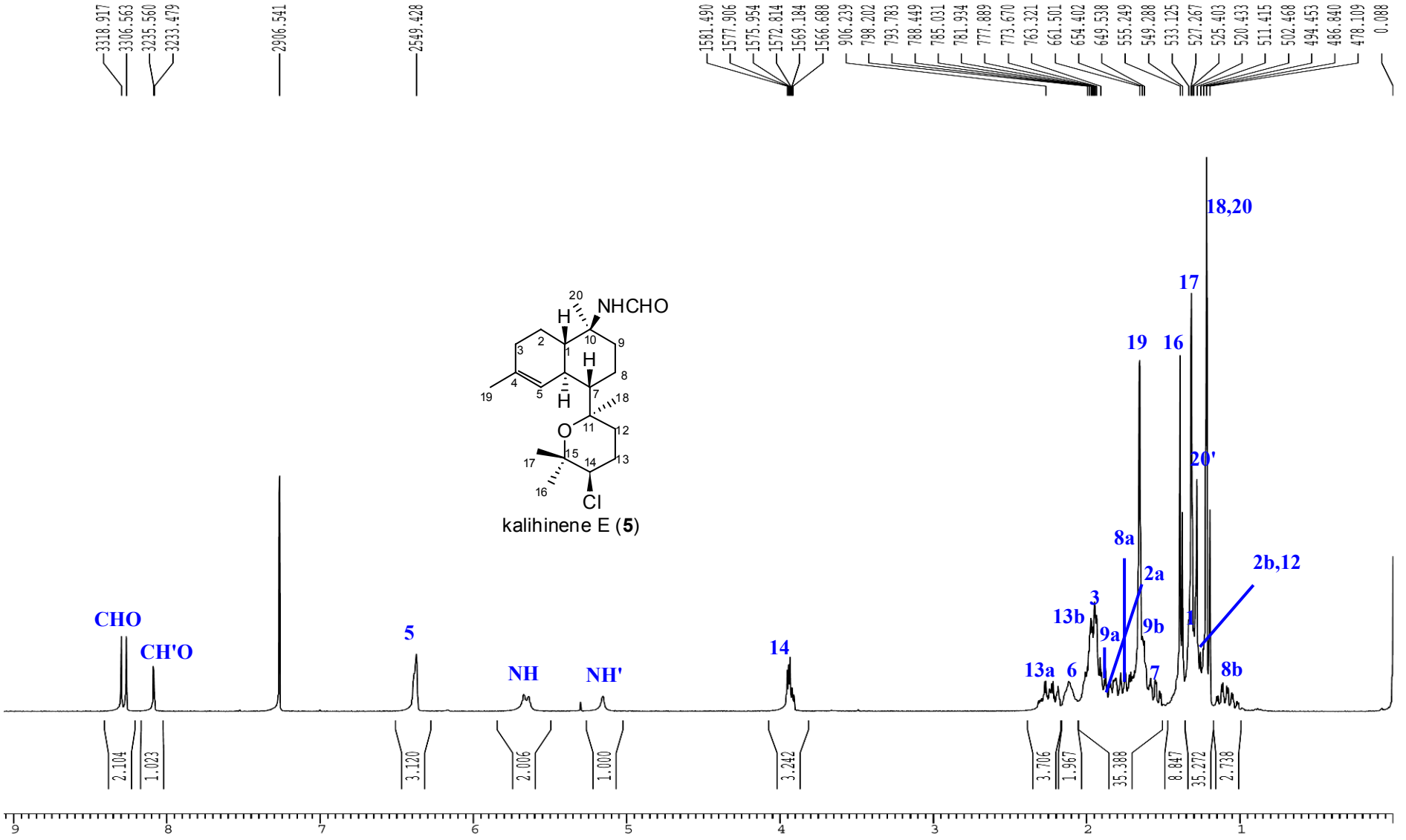


**Figure S38.** $^{13}C$ NMR spectrum of kalihinene E (**5**) in $CDCl_3$.

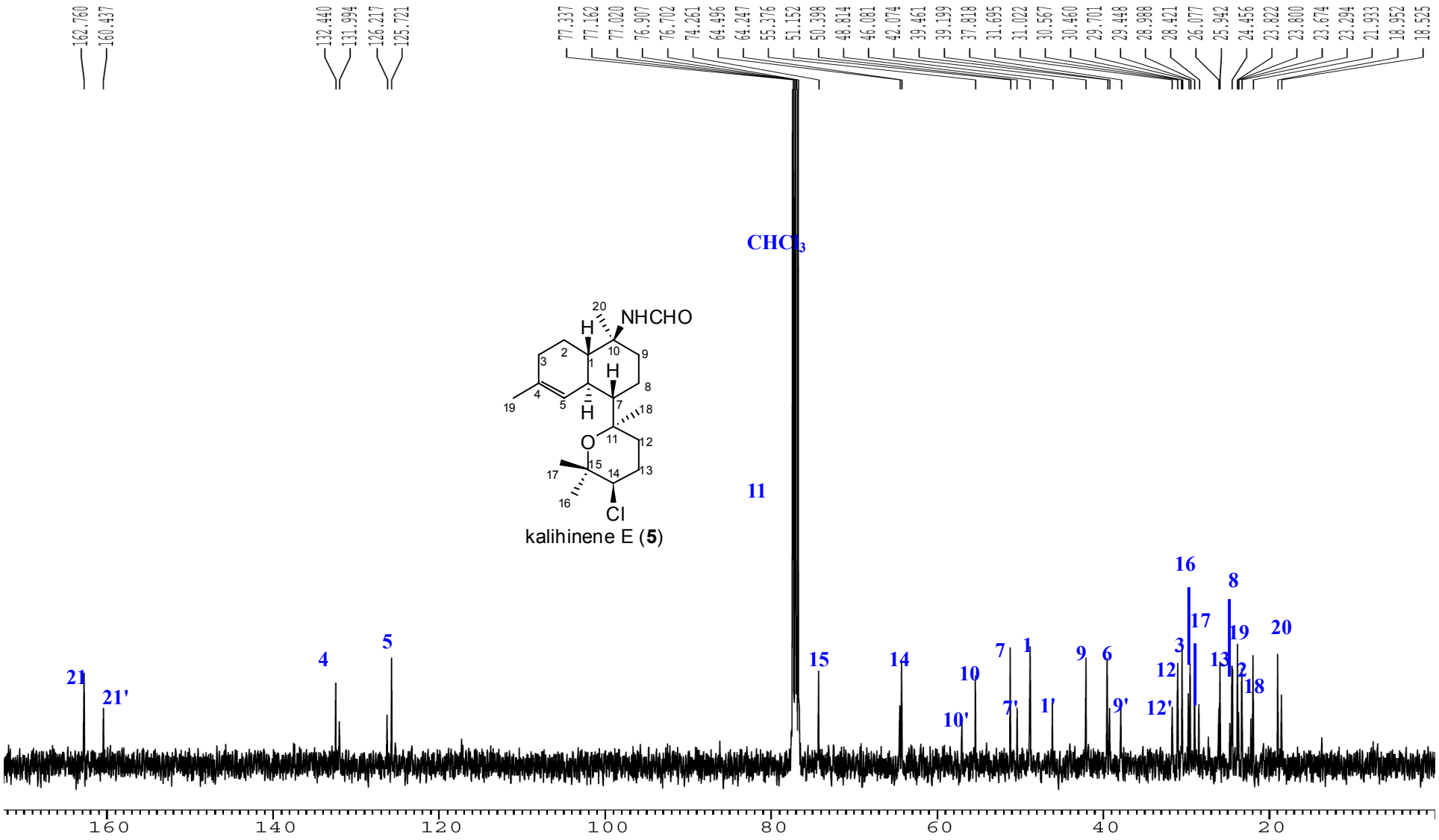


**Figure S39.** HSQC spectrum of kalihinene E (**5**) in $CDCl_3$.

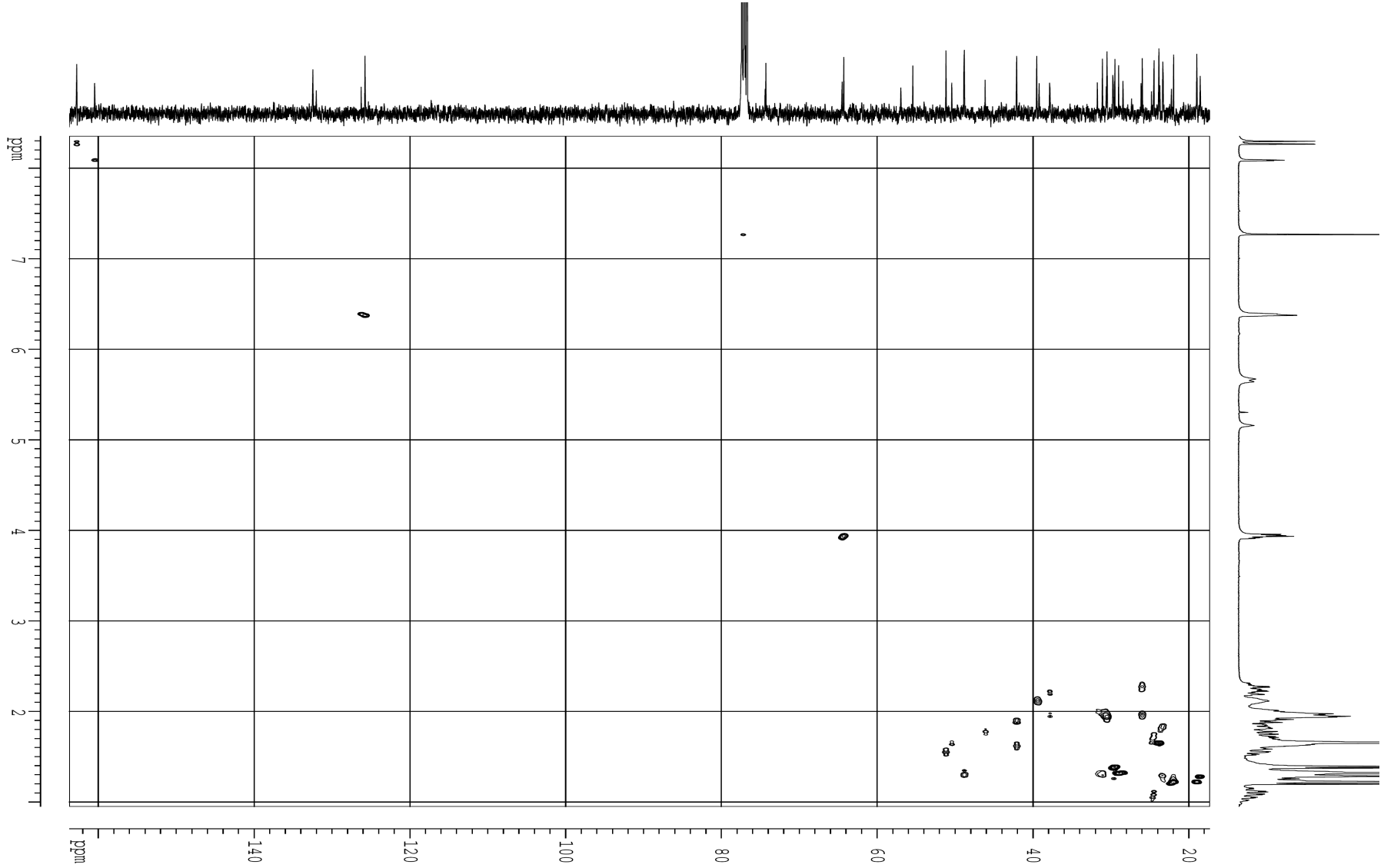


**Figure S40.** HMBC spectrum of kalihinene E (**5**) in $CDCl_3$.

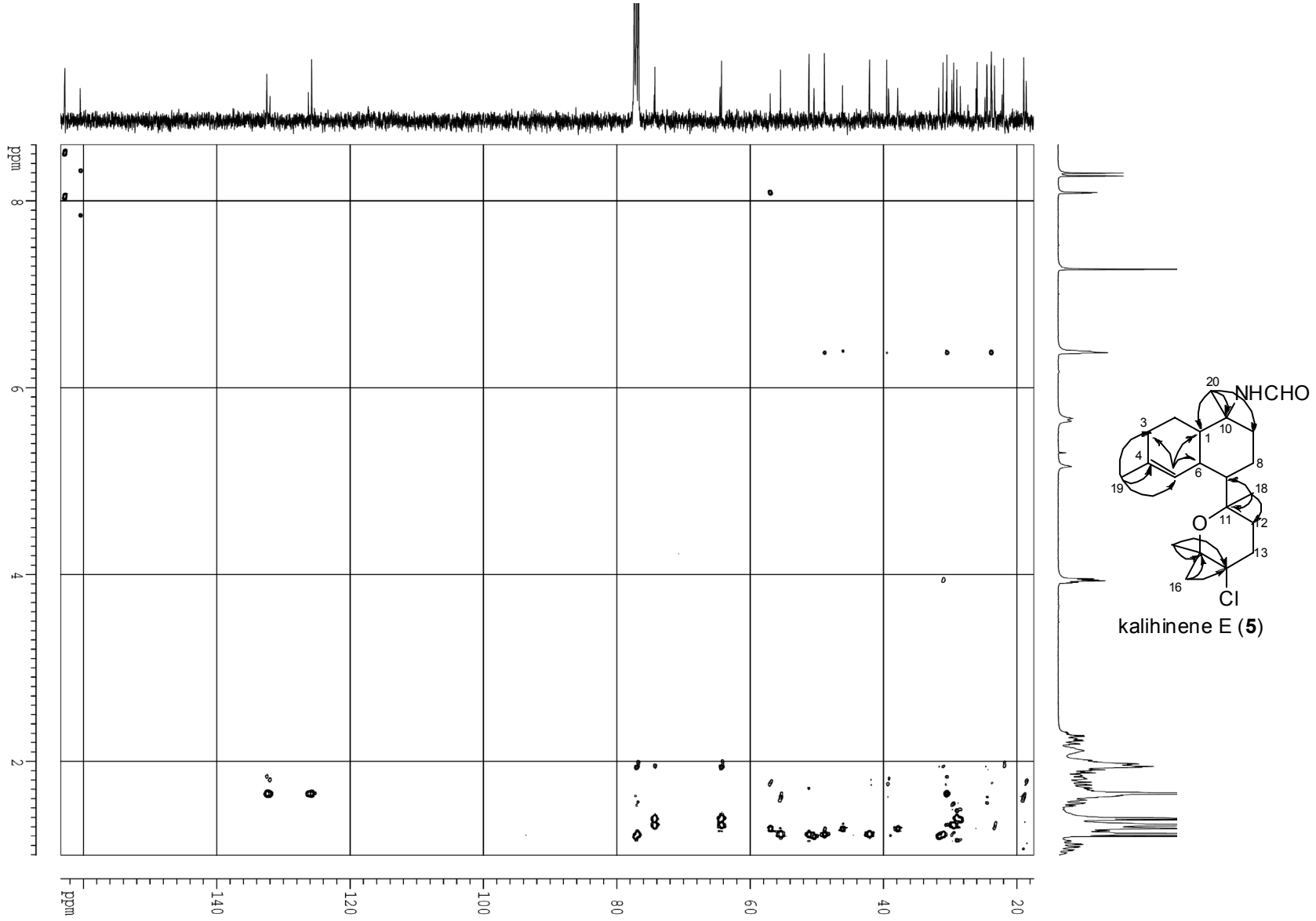


**Figure S41.** $^{1}H$-$^{1}H$ COSY spectrum of kalihinene E (**5**) in $CDCl_3$.

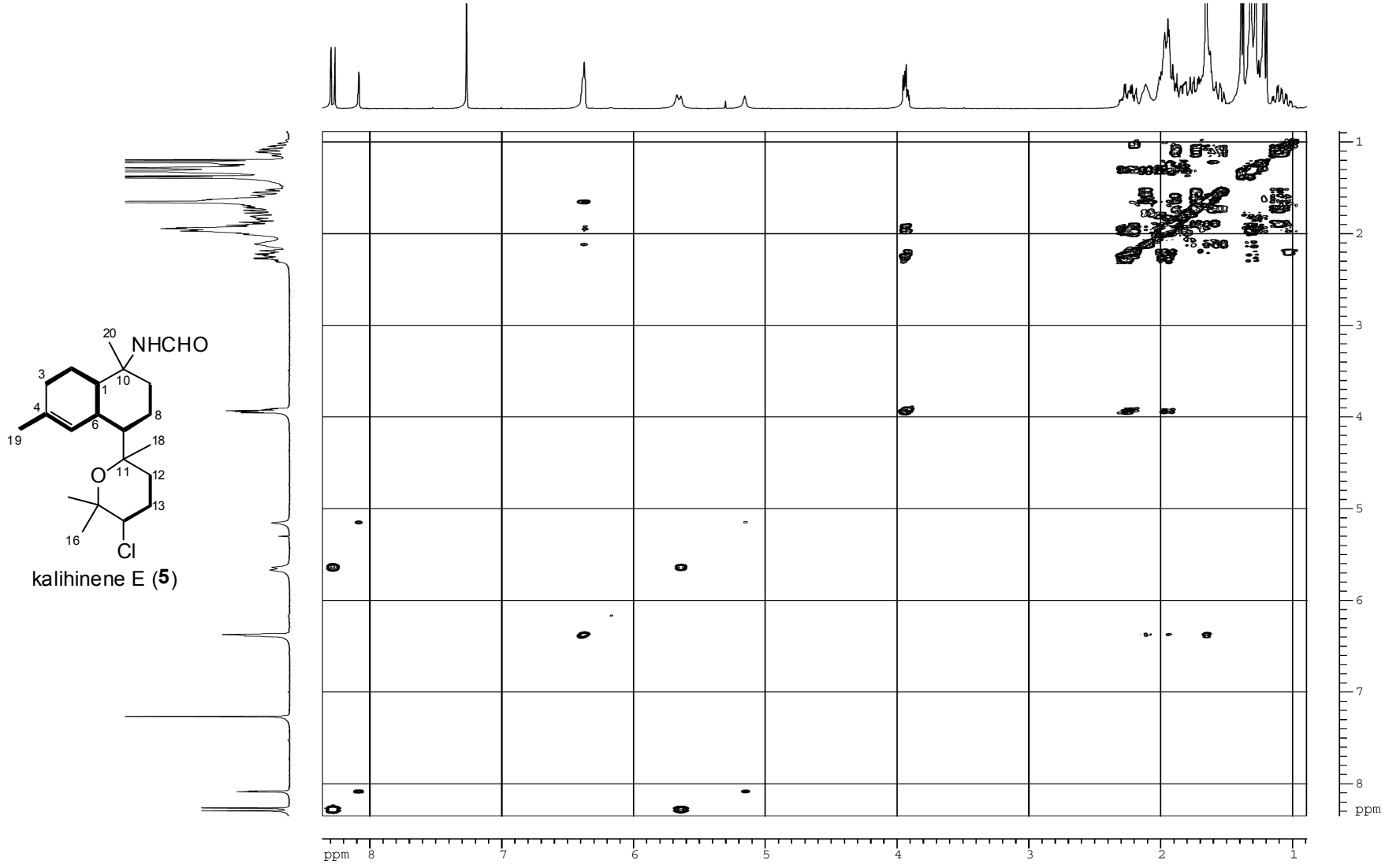


**Figure S42.** NOESY spectrum of kalihinene E (**5**) in $CDCl_3$.

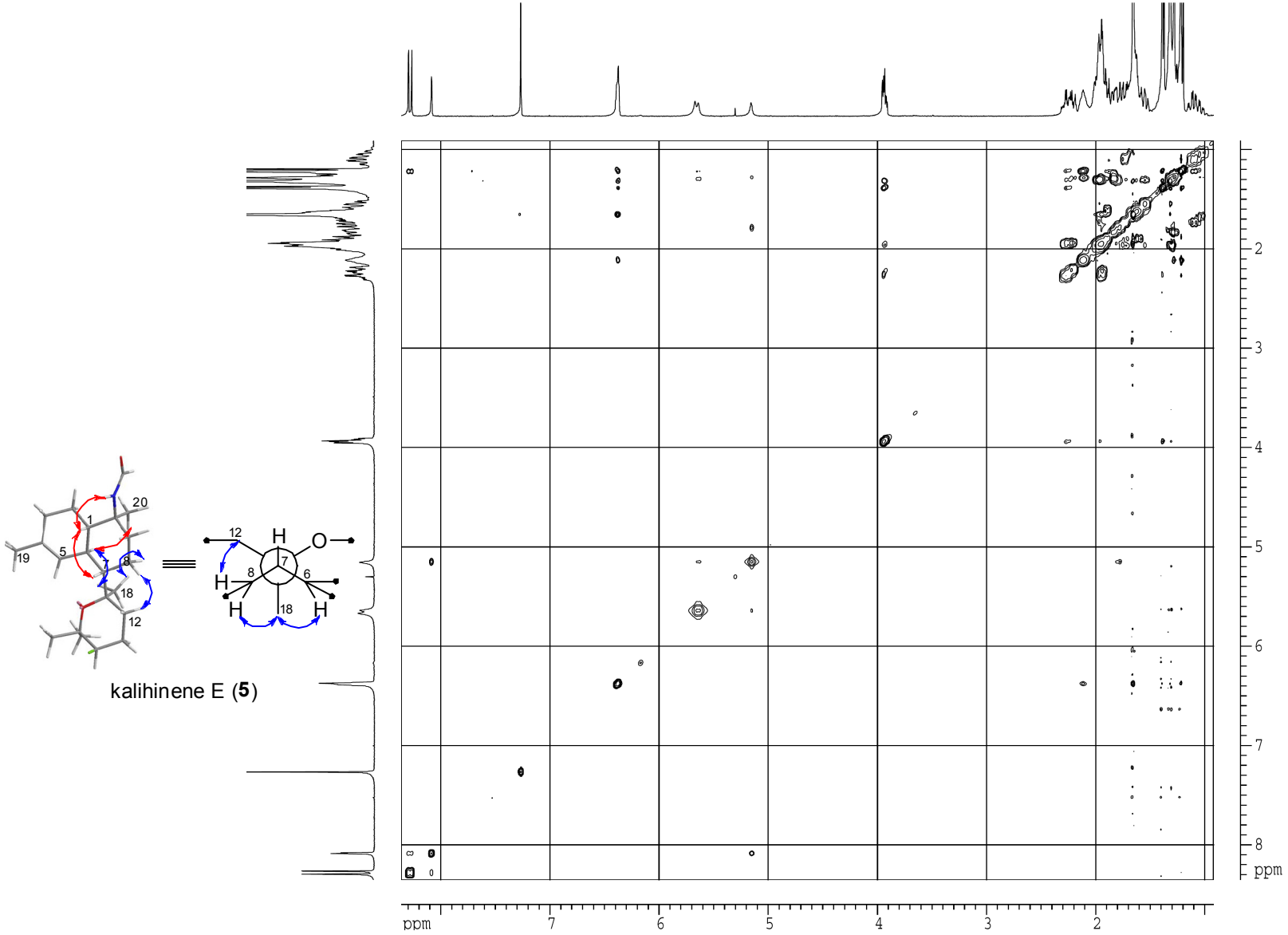


**Figure S43.** IR spectrum of kalihinene E (**5**).

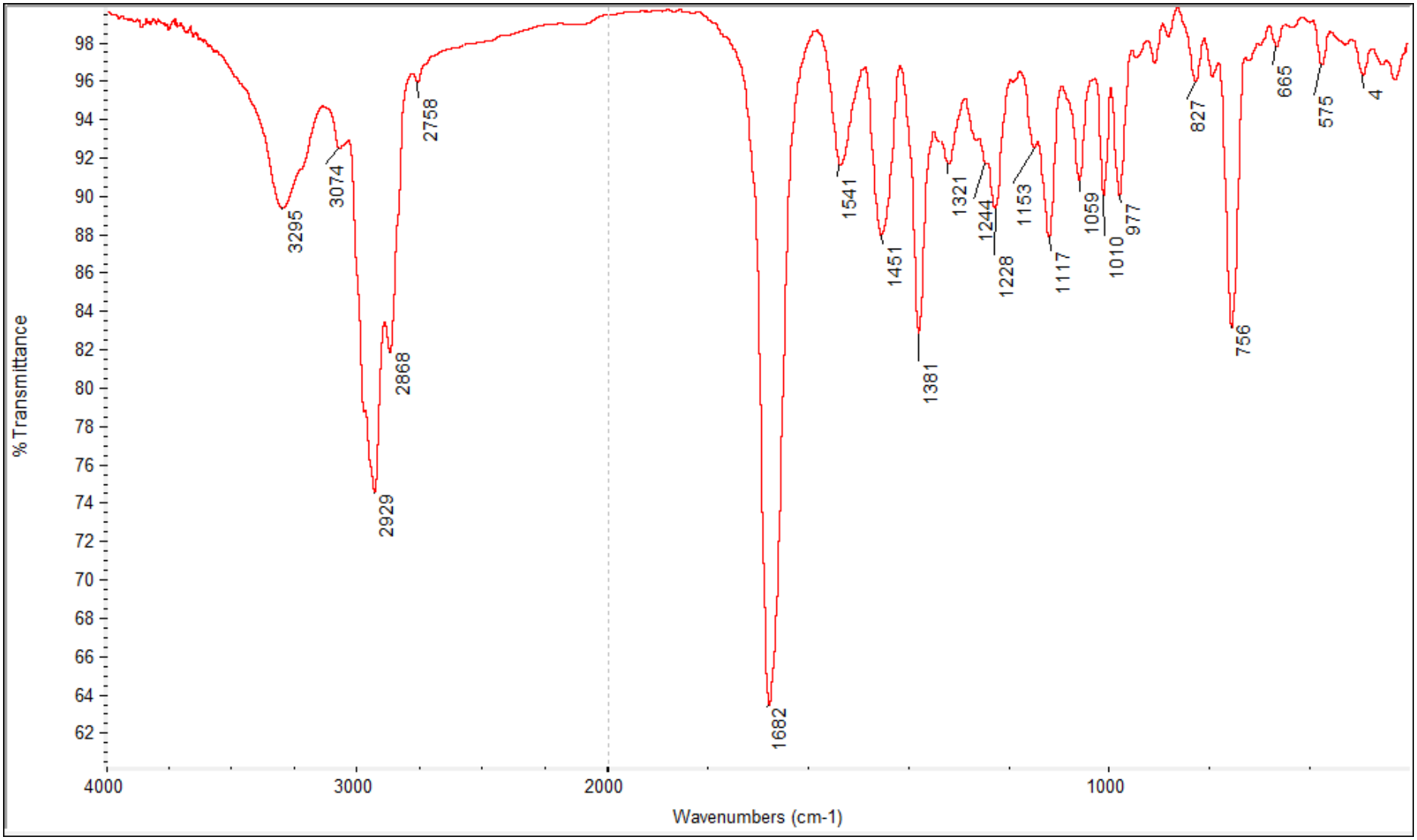


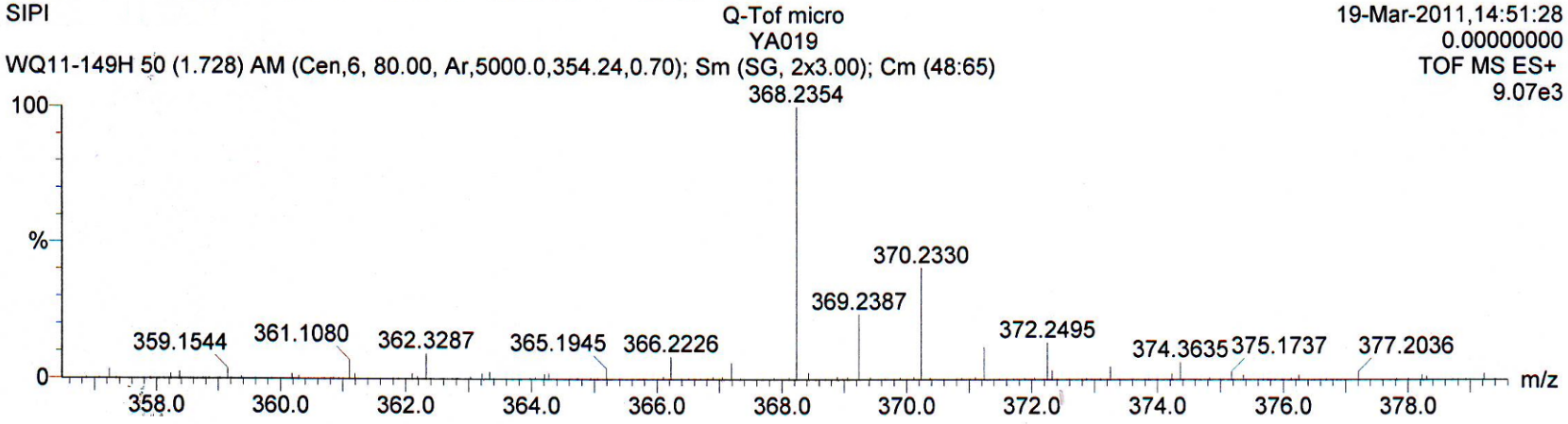
**Figure S44.** HRESIMS of kalihinene E (**5**).

## 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




| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 25.00 | | | | -1.5 | | |
| Maximum: | 100.00 | | 5.0 | 10.0 | 50.0 | | |
| 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**).

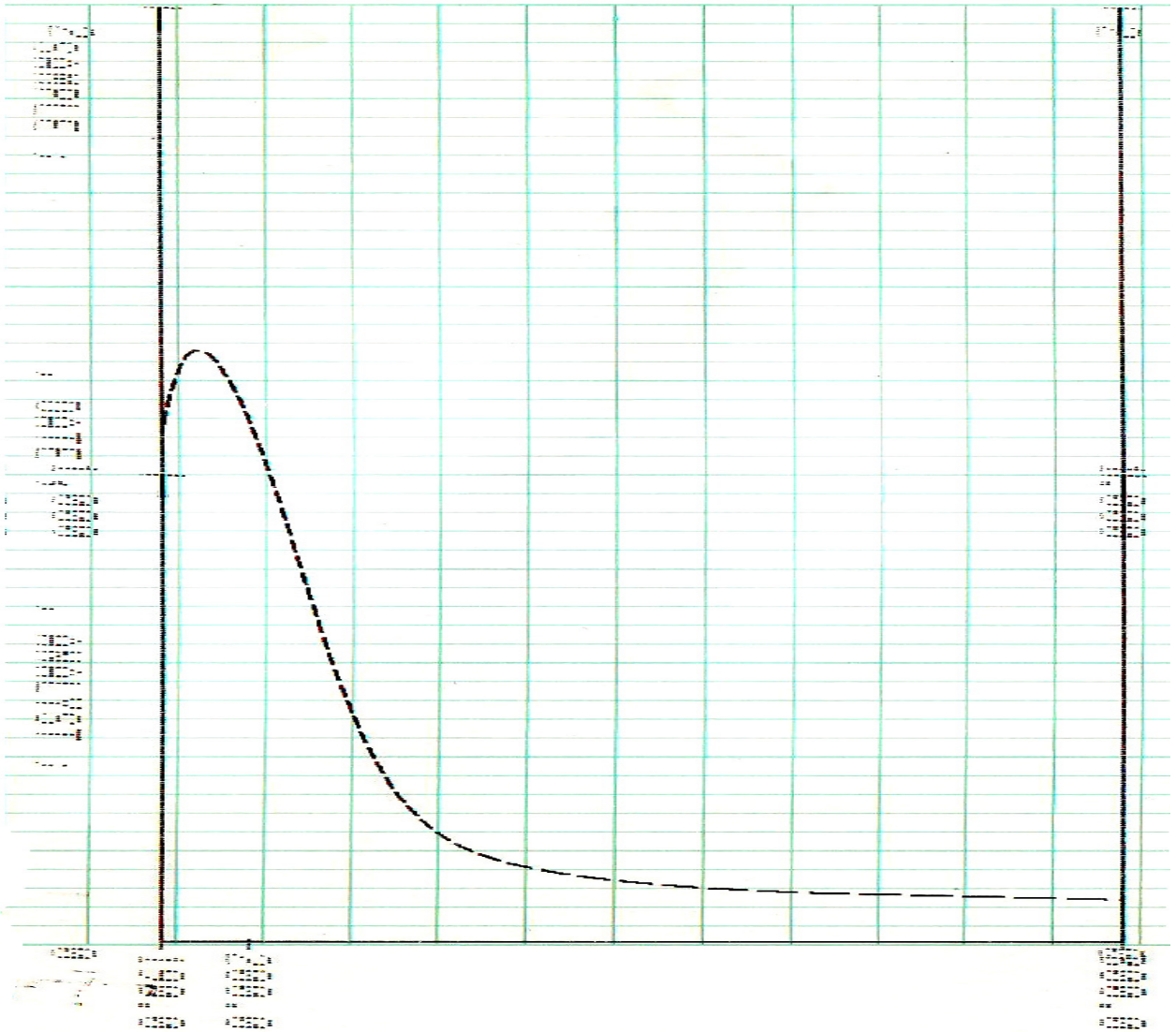


**Figure S46.** $^{1}$H NMR spectrum of kalihinene F (**6**) in $CDCl_3$.

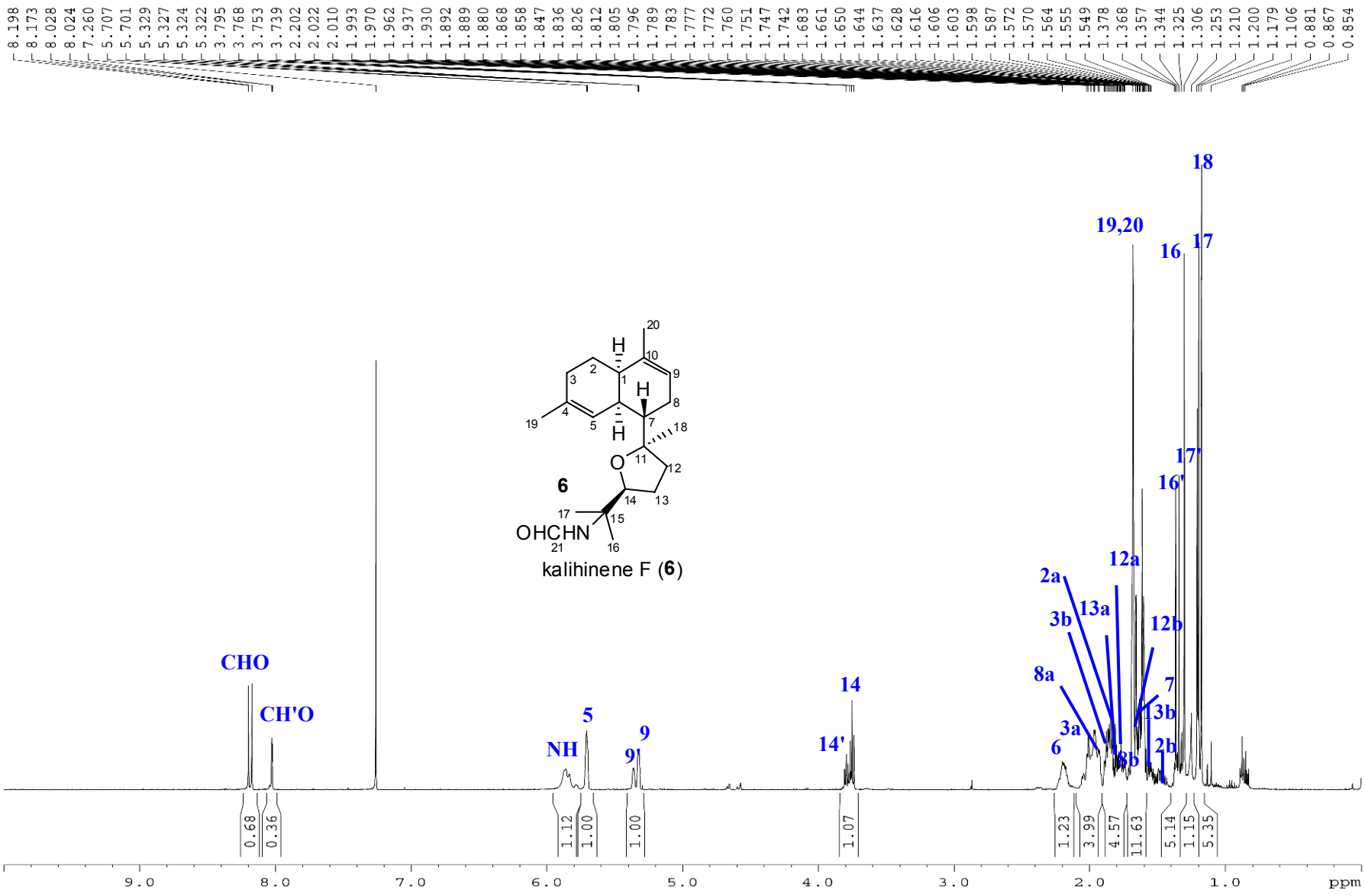


**Figure S47.** $^{13}C$ NMR spectrum of kalihinene F (**6**) in $CDCl_3$.

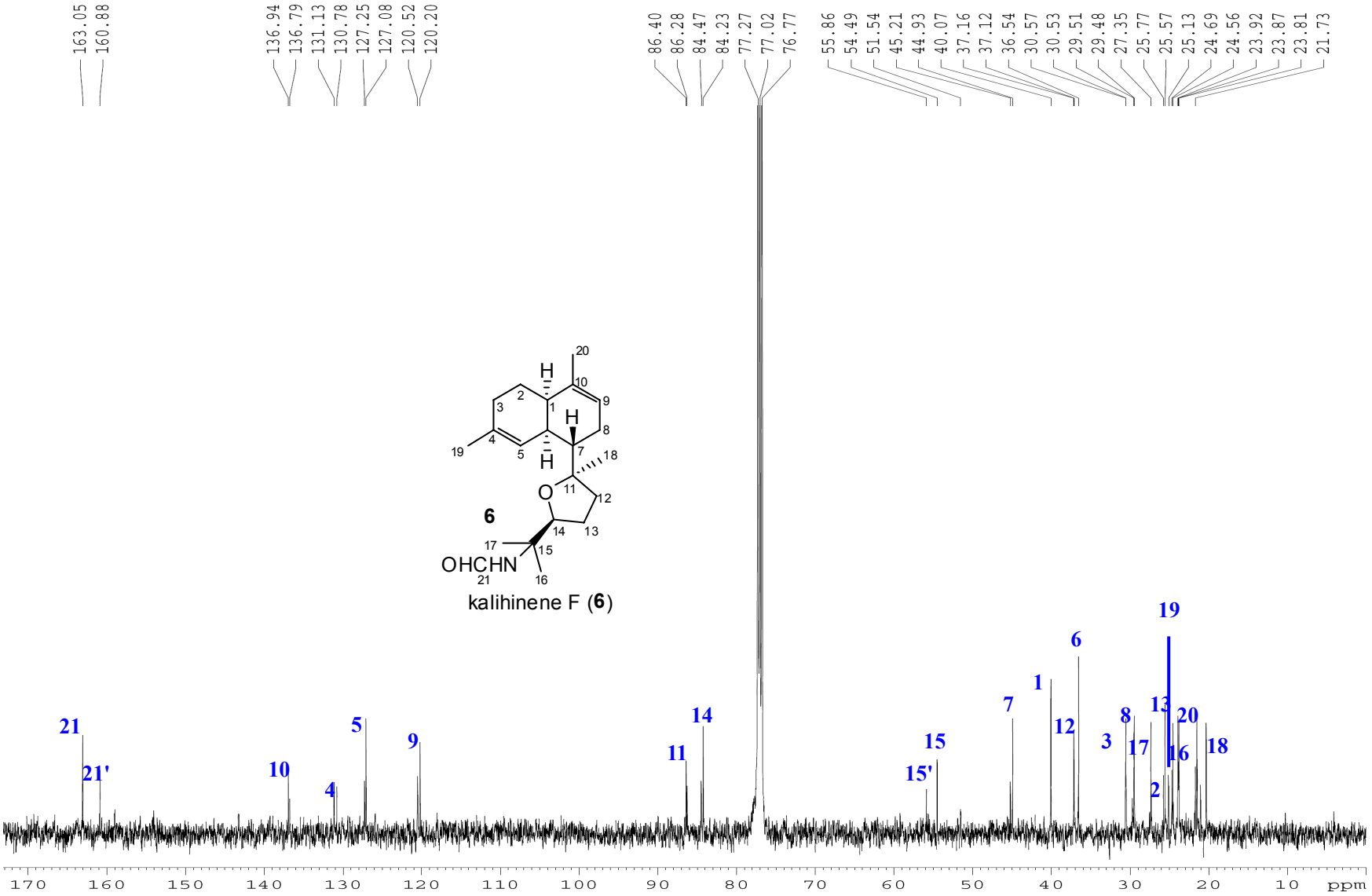


**Figure S48.** HSQC spectrum of kalihinene F(**6**) in $CDCl_3$.

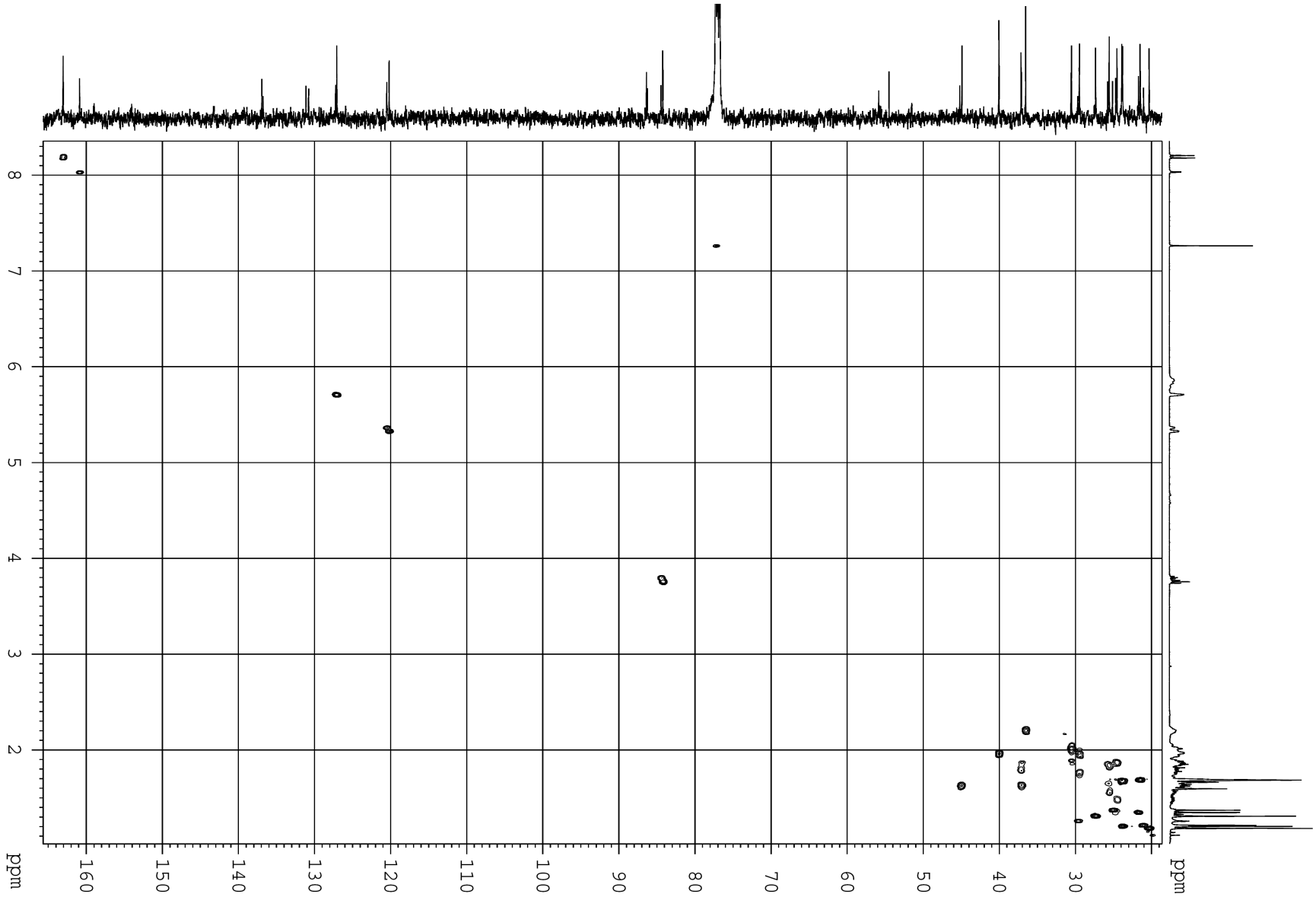


**Figure S49.** HMBC spectrum of kalihinene F (**6**) in $CDCl_3$.

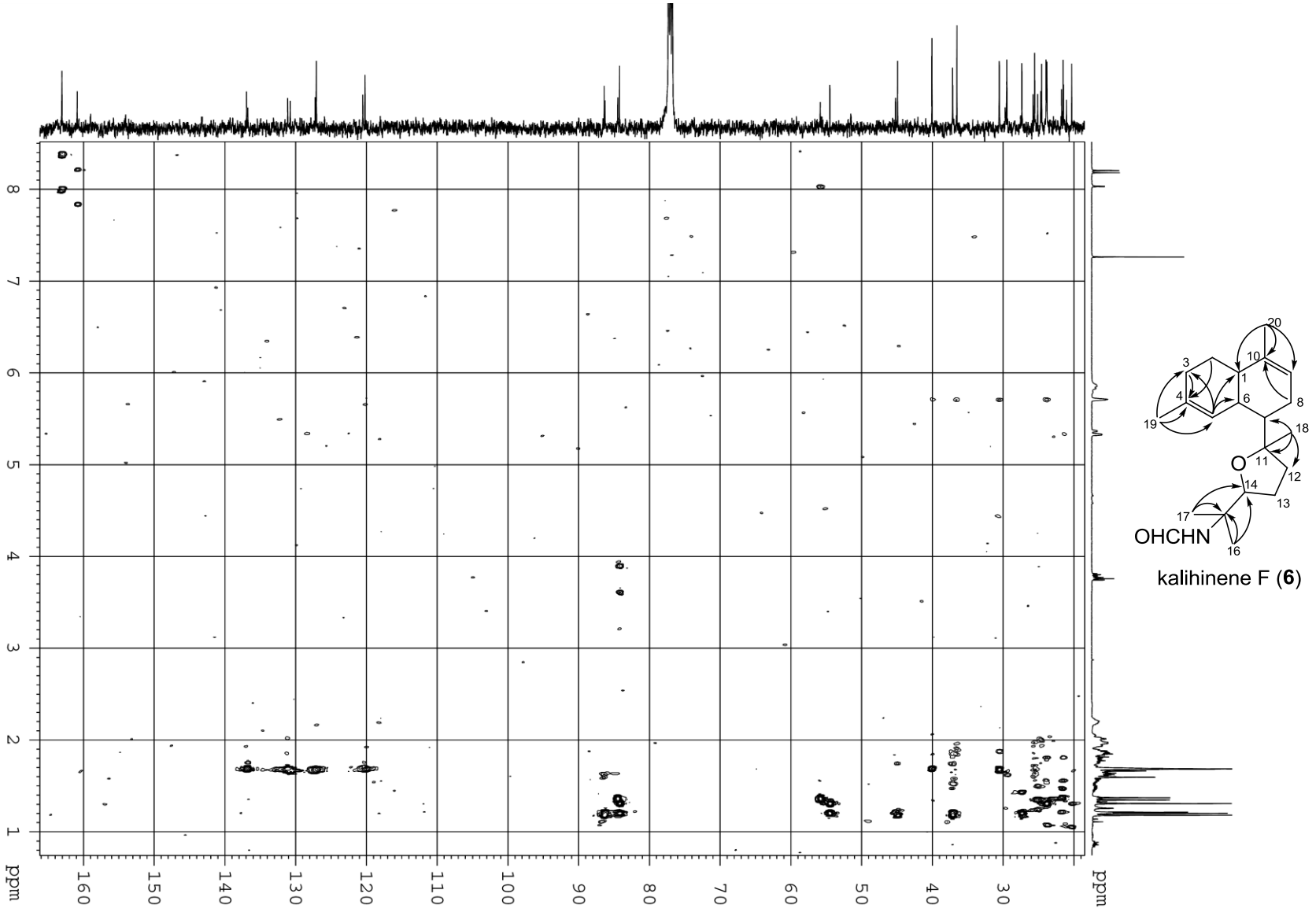


**Figure S50.** $^{1}H$-$^{1}H$ COSY spectrum of kalihinene F (**6**) in $CDCl_3$.

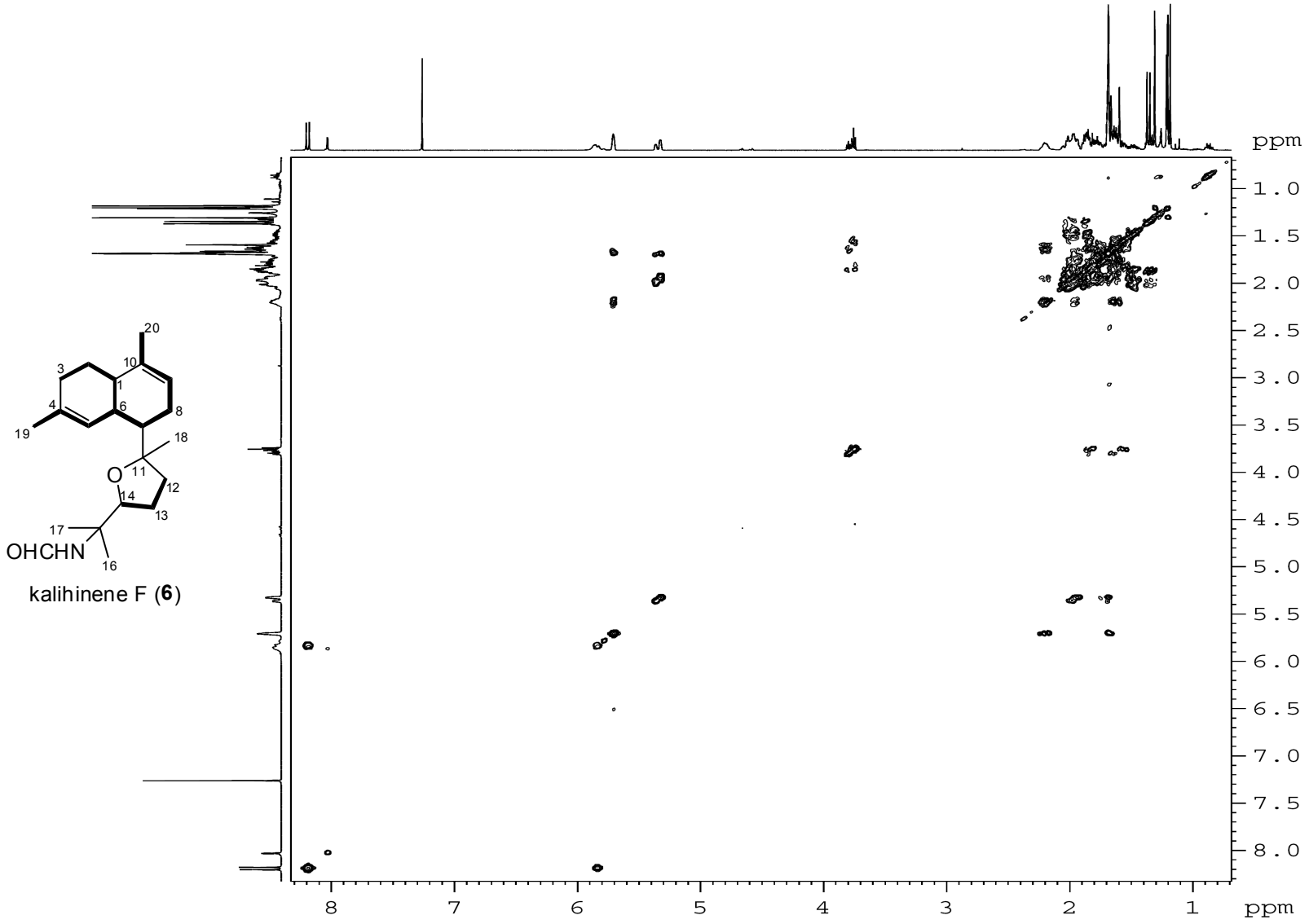


**Figure S51.** NOESY spectrum of kalihinene F (**6**) in $CDCl_3$.

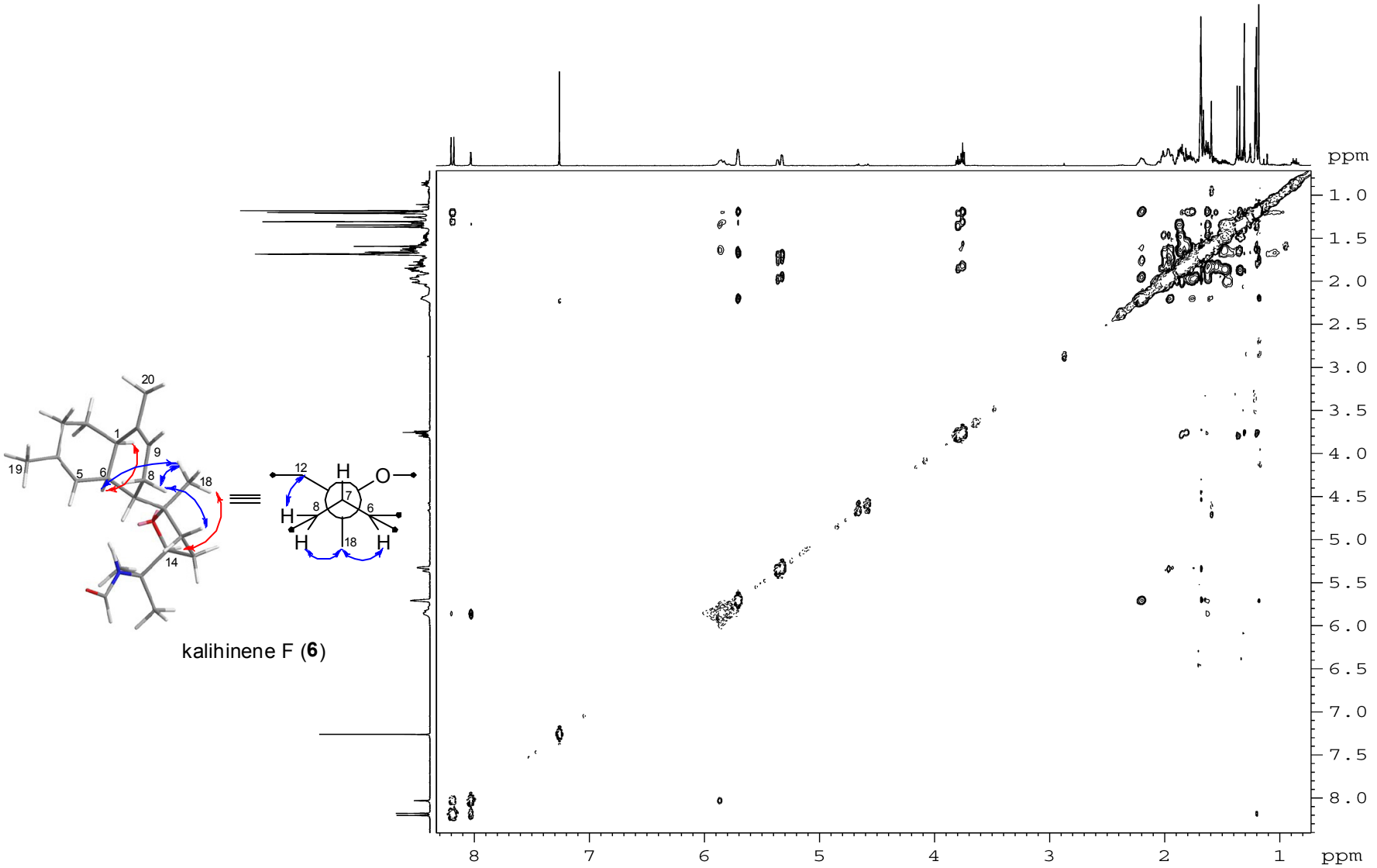


**Figure S52.** IR spectrum of kalihinene F (**6**).

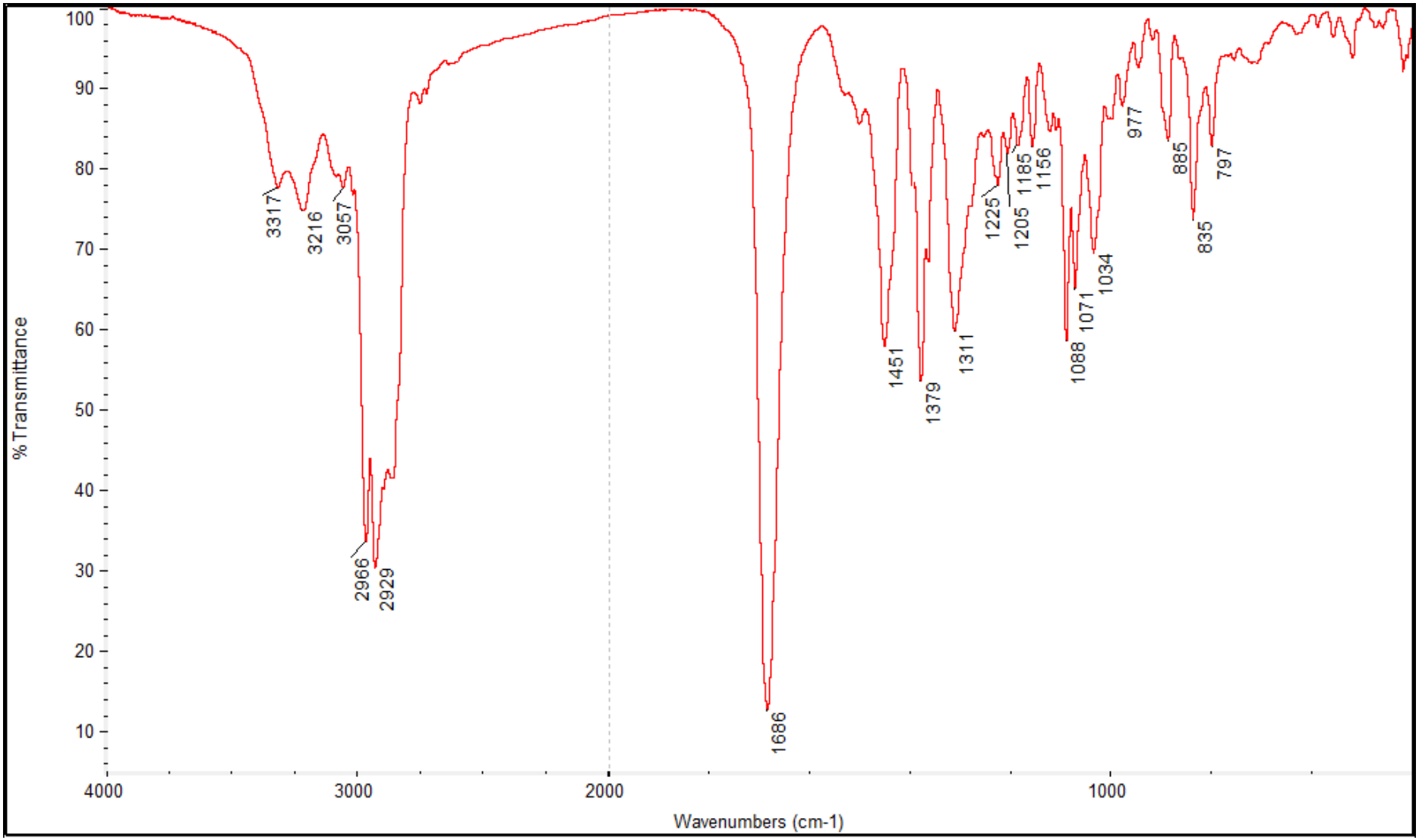
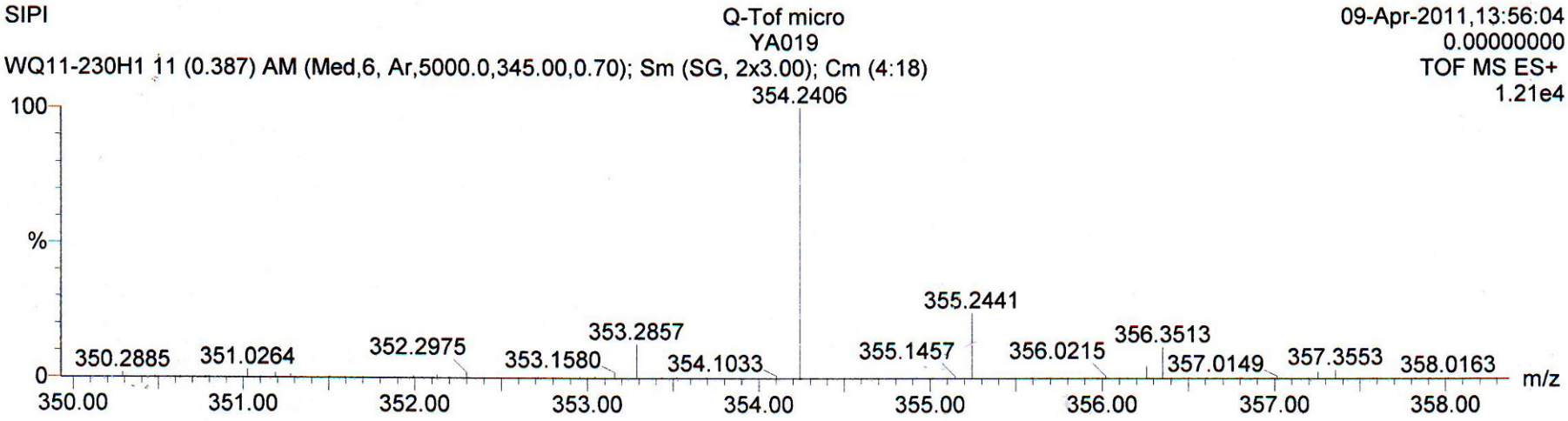


**Figure S53.** HRESIMS of kalihinene F (**6**).

## 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




| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 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**).

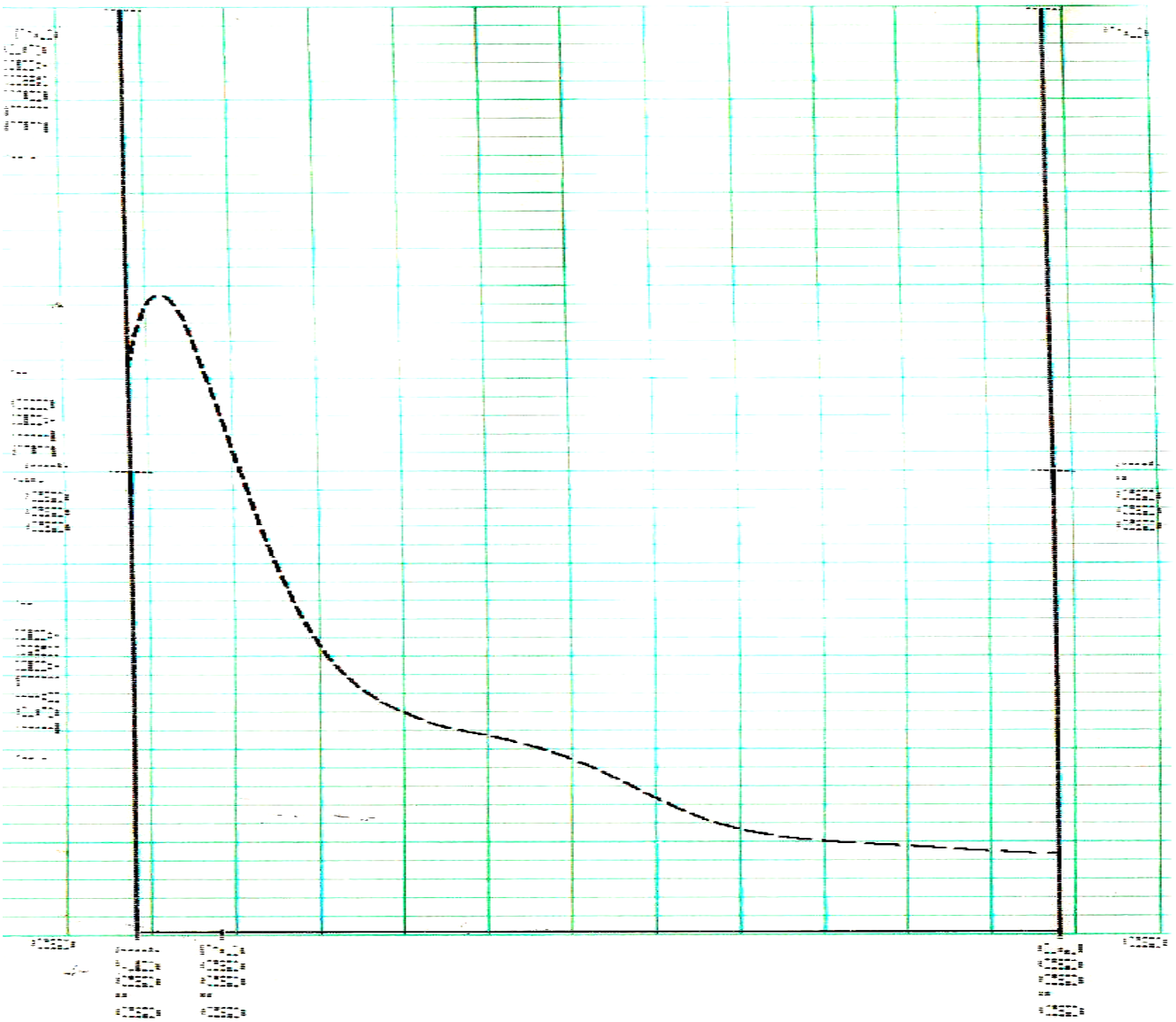


**Figure S55.** $^{1}$H NMR spectrum of kalihipyran C (**7**) in $CDCl_3$.

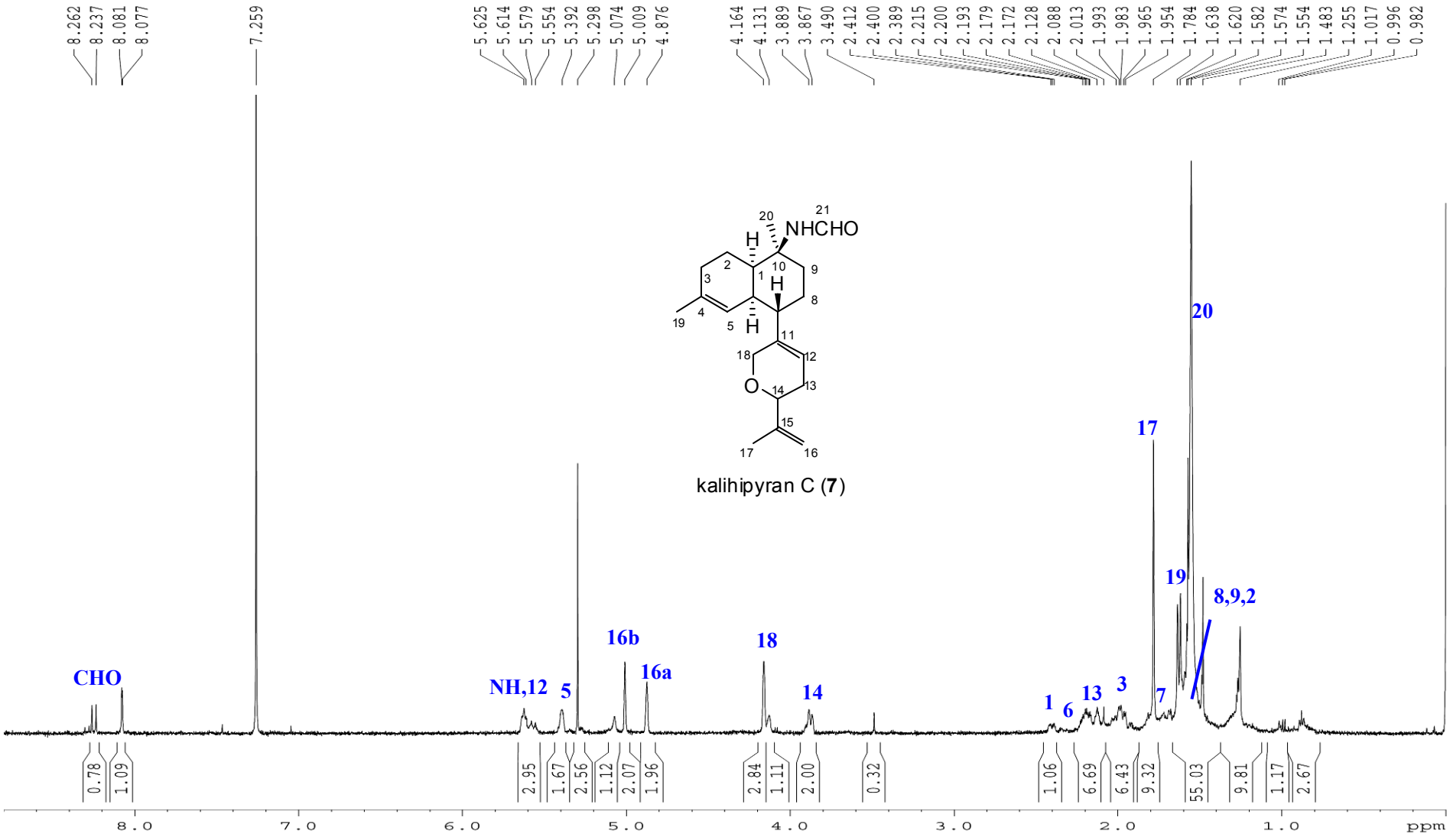


**Figure S56.** $^{13}$C NMR spectrum of kalihipyran C (**7**) in $CDCl_3$.

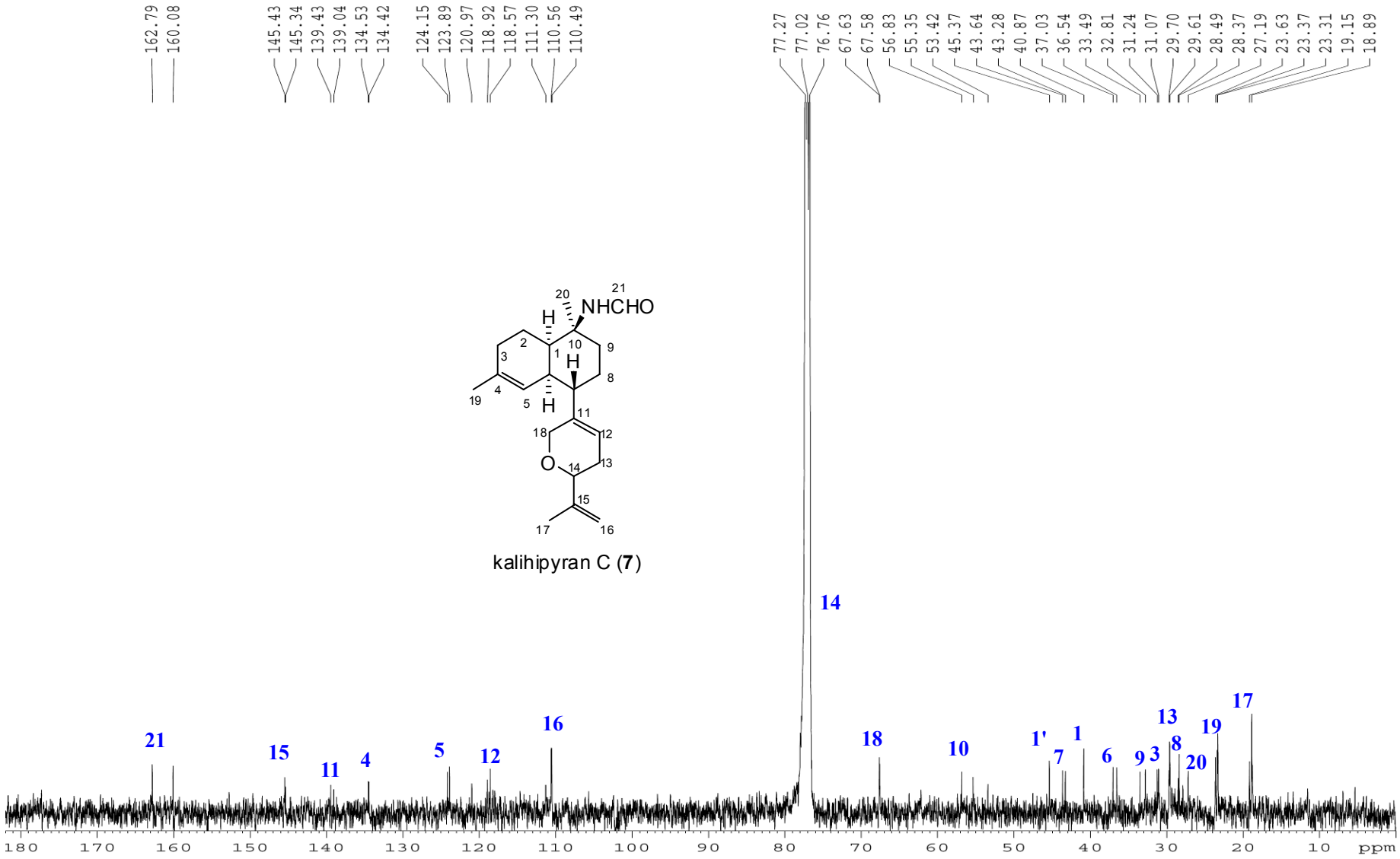


**Figure S57.** HSQC spectrum of kalihipyran C (**7**) in $CDCl_3$.

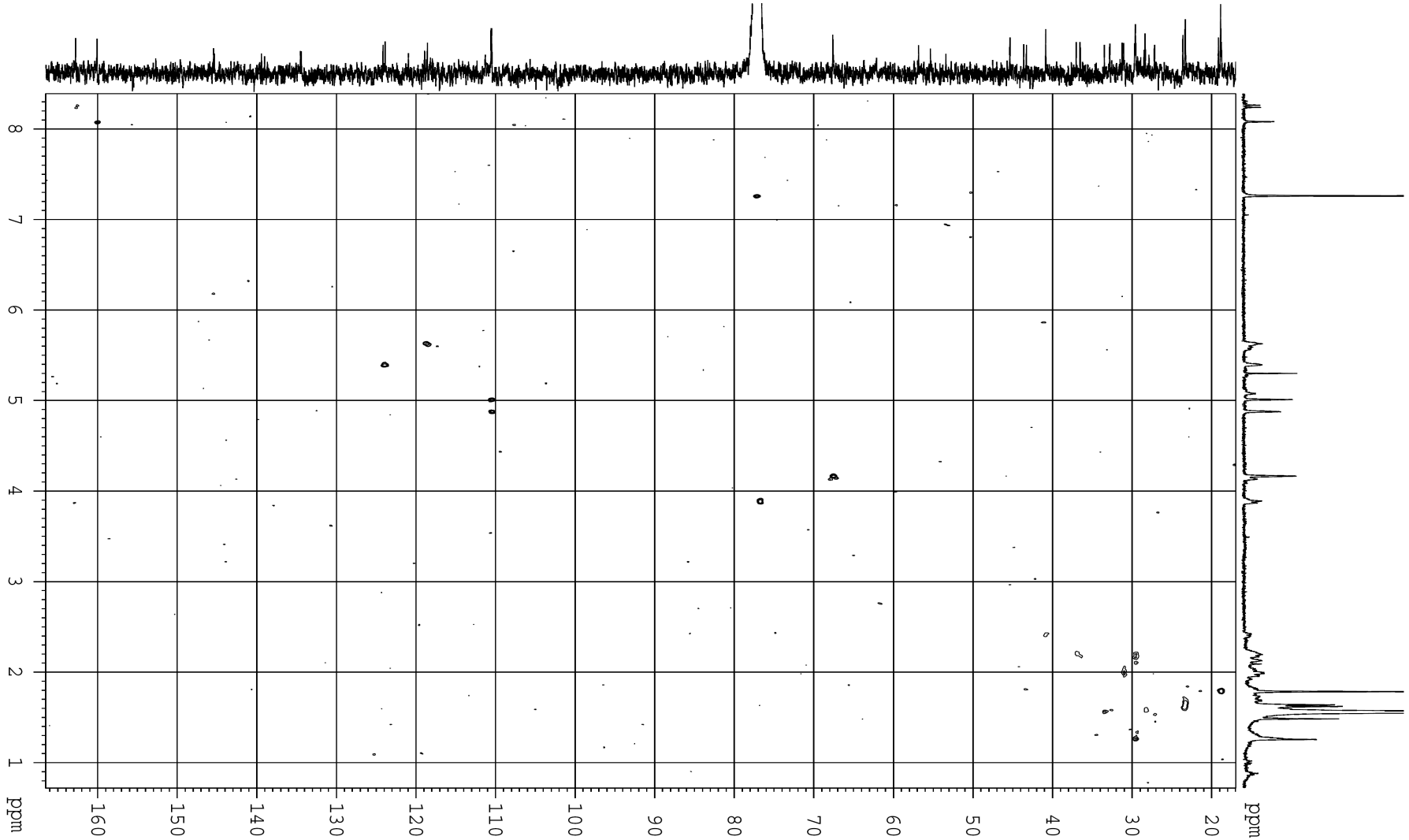


**Figure S58.** HMBC spectrum of kalihipyran C (**7**) in $CDCl_3$.

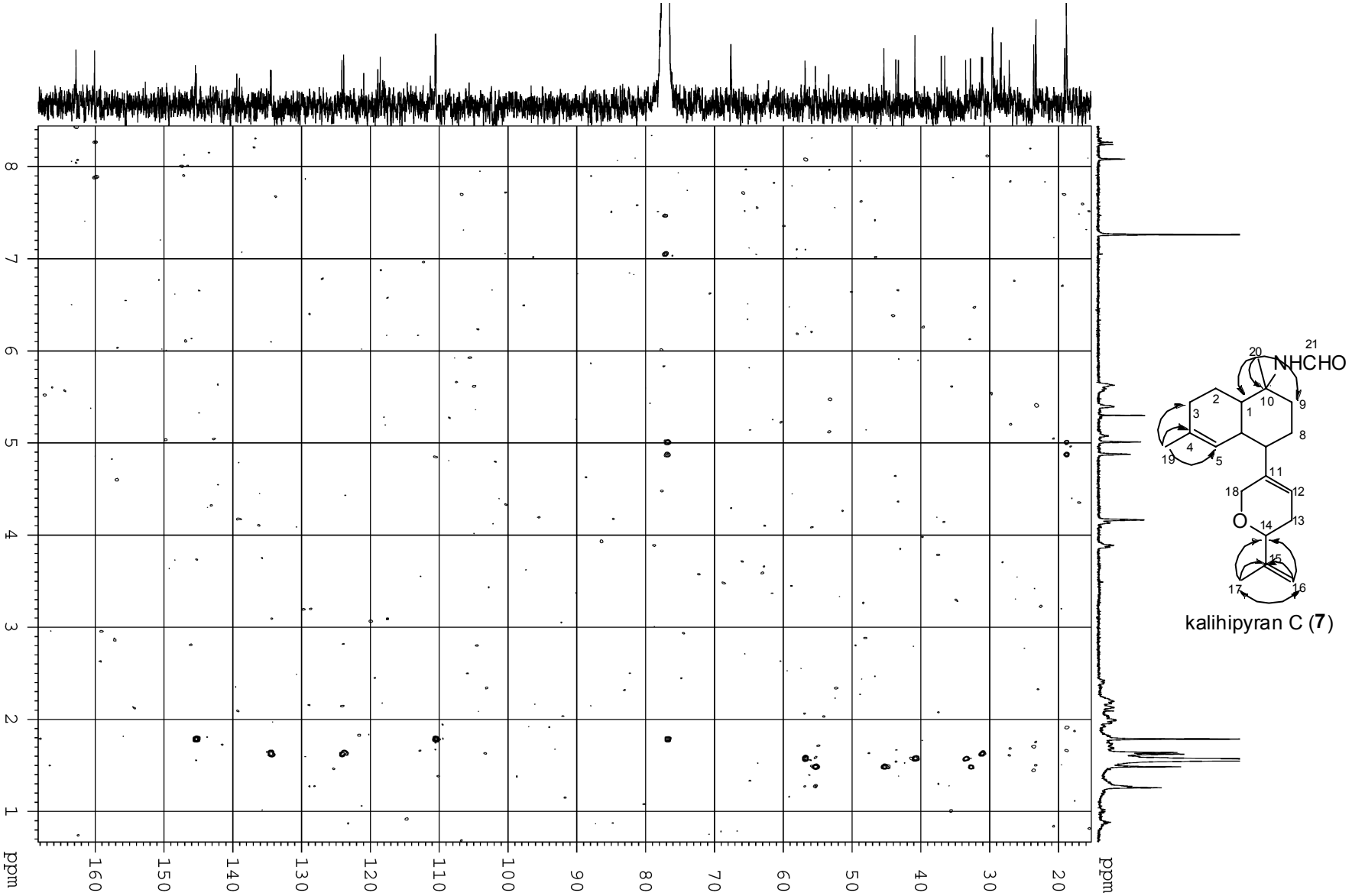


**Figure S59.** $^{1}$H-$^{1}$H COSY spectrum of kalihipyran C (**7**) in $CDCl_3$.

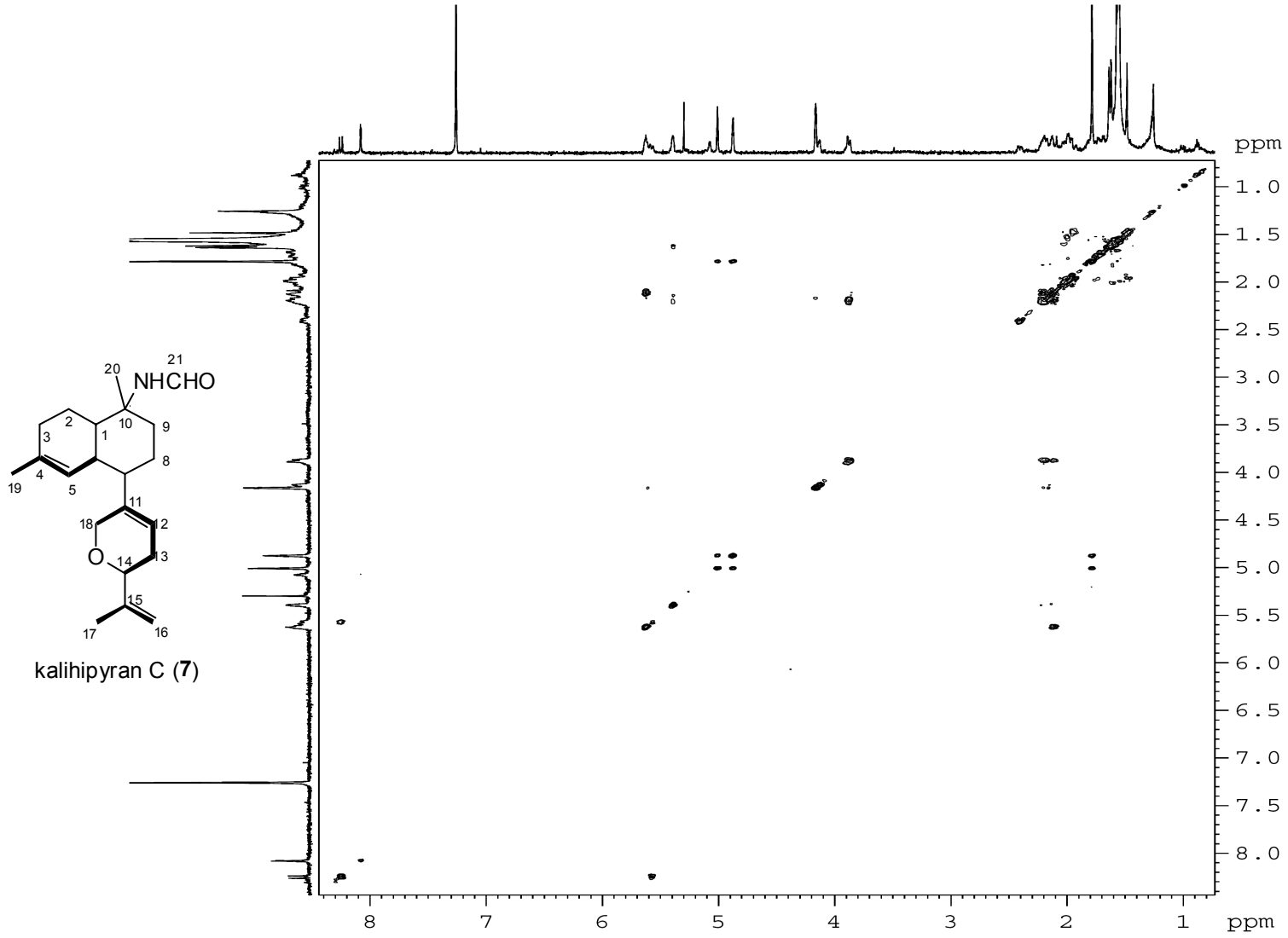


**Figure S60.** NOESY spectrum of kalihipyran C (**7**) in $CDCl_3$.

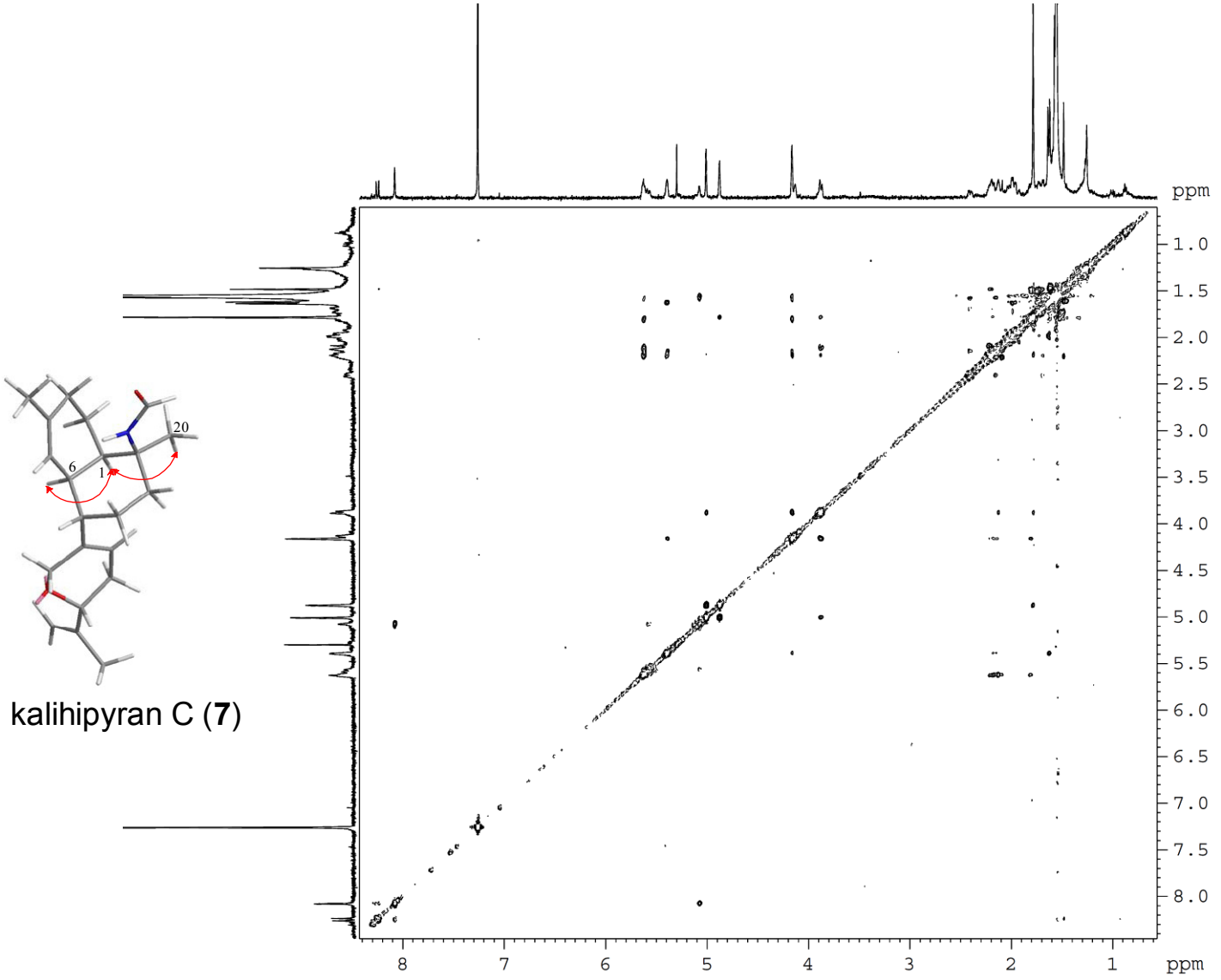


**Figure S61.** IR spectrum of kalihipyran C (**7**).

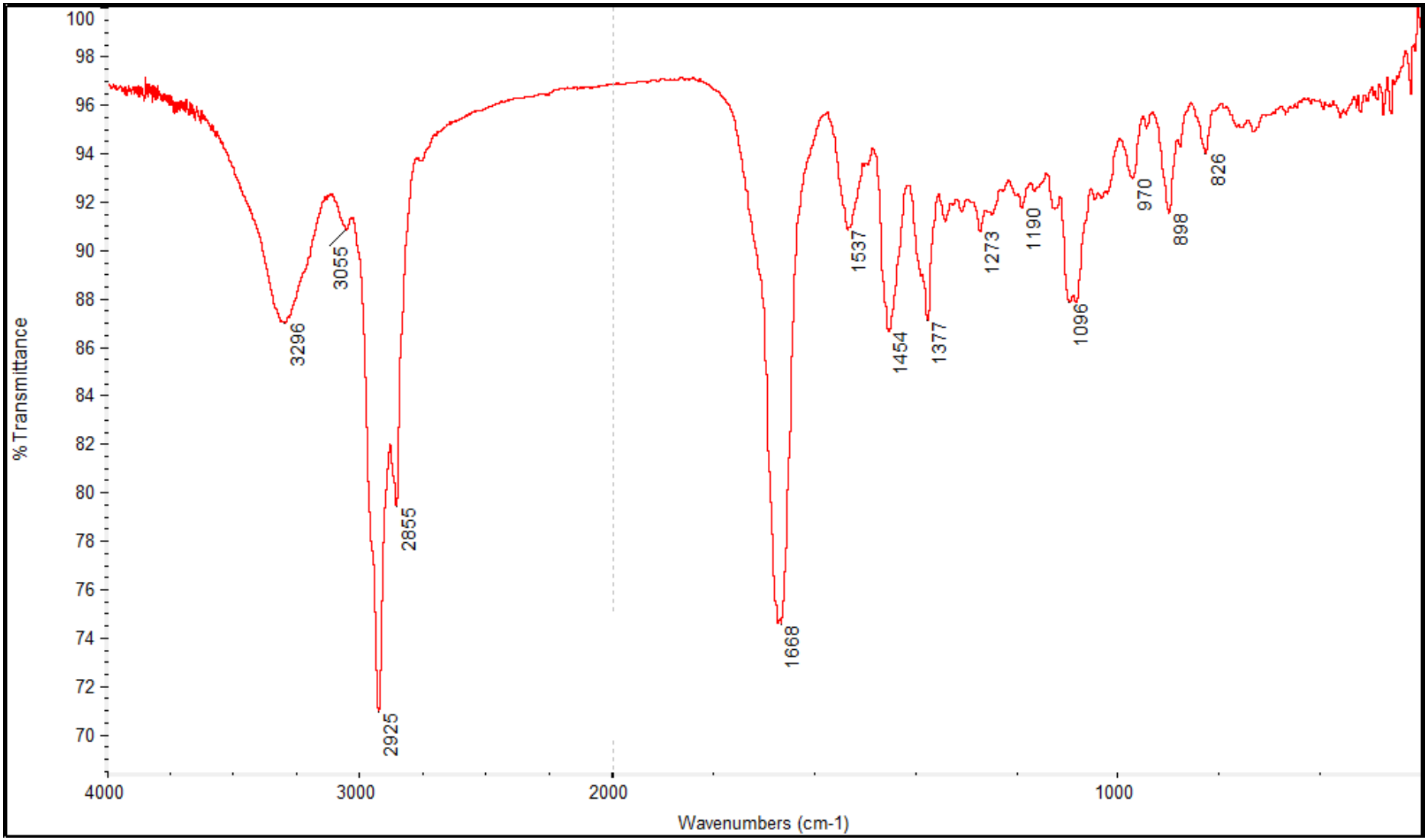
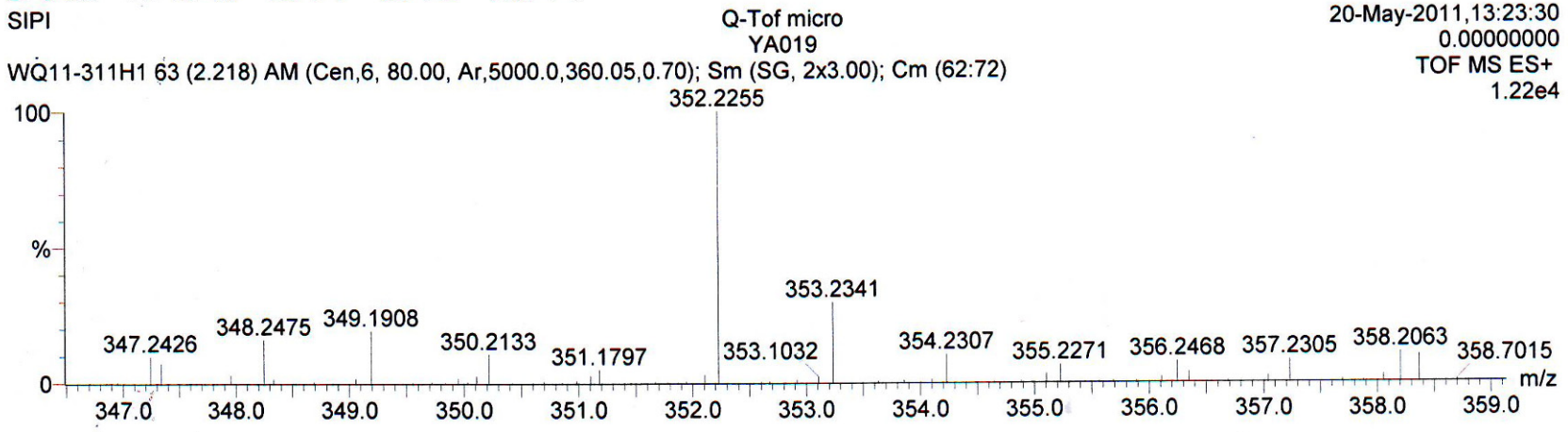


**Figure S62.** HRESIMS of kalihipyran C (**7**).

## 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




| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 45.00 | | | | -1.5 | | |
| Maximum: | 100.00 | | 5.0 | 10.0 | 50.0 | | |
| 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**).