

Supporting Information:

The mass spectrometric fragmentation mechanisms of catenulane and isocatenulane diterpenes

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Table S1. NMR data of catenul-14-en-6-one (**4**) in C₆D₆ recorded at 298 K.

C ^[a]	type	¹ H ^[b]	¹³ C ^[b]
1	CH	2.93 (ddd, <i>J</i> = 11.8, 4.2, 1.3)	38.60
2	CH	1.94 (dd, <i>J</i> = 11.8, 4.2)	44.83
3	CH	1.53 (m)	28.21
4	CH ₂	1.43 (m, H _β) 1.57 (m, H _α)	33.61
5	CH ₂	2.13 (dddd, <i>J</i> = 14.3, 4.6, 2.7, 0.9, H _β) 2.58 (td, <i>J</i> = 14.3, 6.0, H _α)	33.82
6	C _q	–	213.88
7	C _q	–	49.94
8	CH ₂	1.81 (td, <i>J</i> = 14.4, 3.7, H _β) 1.61 (m, H _α)	30.69
9	CH ₂	1.43 (m, H _β) 1.70 (m, H _α)	23.46
10	CH	1.16 (m)	45.91
11	CH	1.59 (m)	27.87
12	CH ₂	1.58 (m, H _β) 0.87 (dd, <i>J</i> = 13.4, 3.9, H _α)	37.65
13	CH ₂	1.46 (m, H _β) 2.36 (m, H _α)	26.35
14	C _q	–	134.79
15	C _q	–	121.12
16	CH ₃	1.71 (d, <i>J</i> = 1.6)	20.78
17	CH ₃	1.62 (d, <i>J</i> = 0.9)	20.27
18	CH ₃	0.74 (d, <i>J</i> = 6.2)	20.08
19	CH ₃	1.09 (s)	19.84
20	CH ₃	0.84 (d, <i>J</i> = 7.3)	14.53

[a] Carbon numbering as shown in main text. [b] Chemical shifts δ in ppm, multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, coupling constants *J* are given in Hertz.

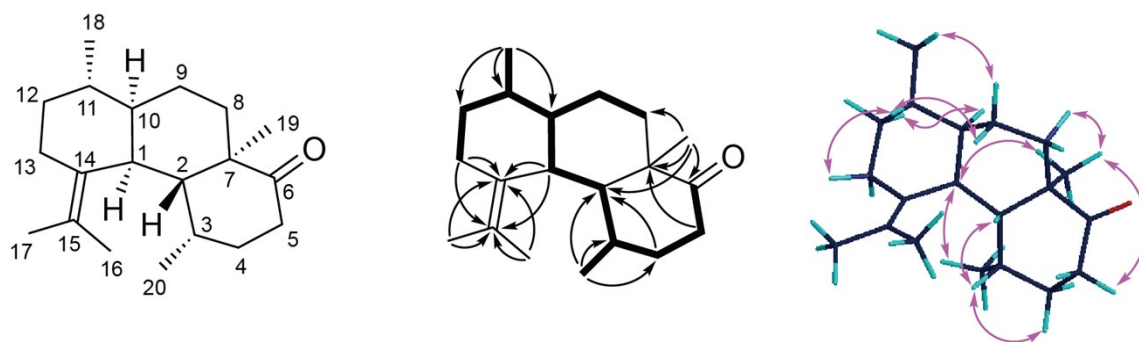


Figure S1. Carbon numbering and structure elucidation of **4**. Bold lines represent ^1H - ^1H COSY correlations, selected HMBC correlations are represented by single-headed arrows and key NOESY correlations are indicated by double headed arrows.

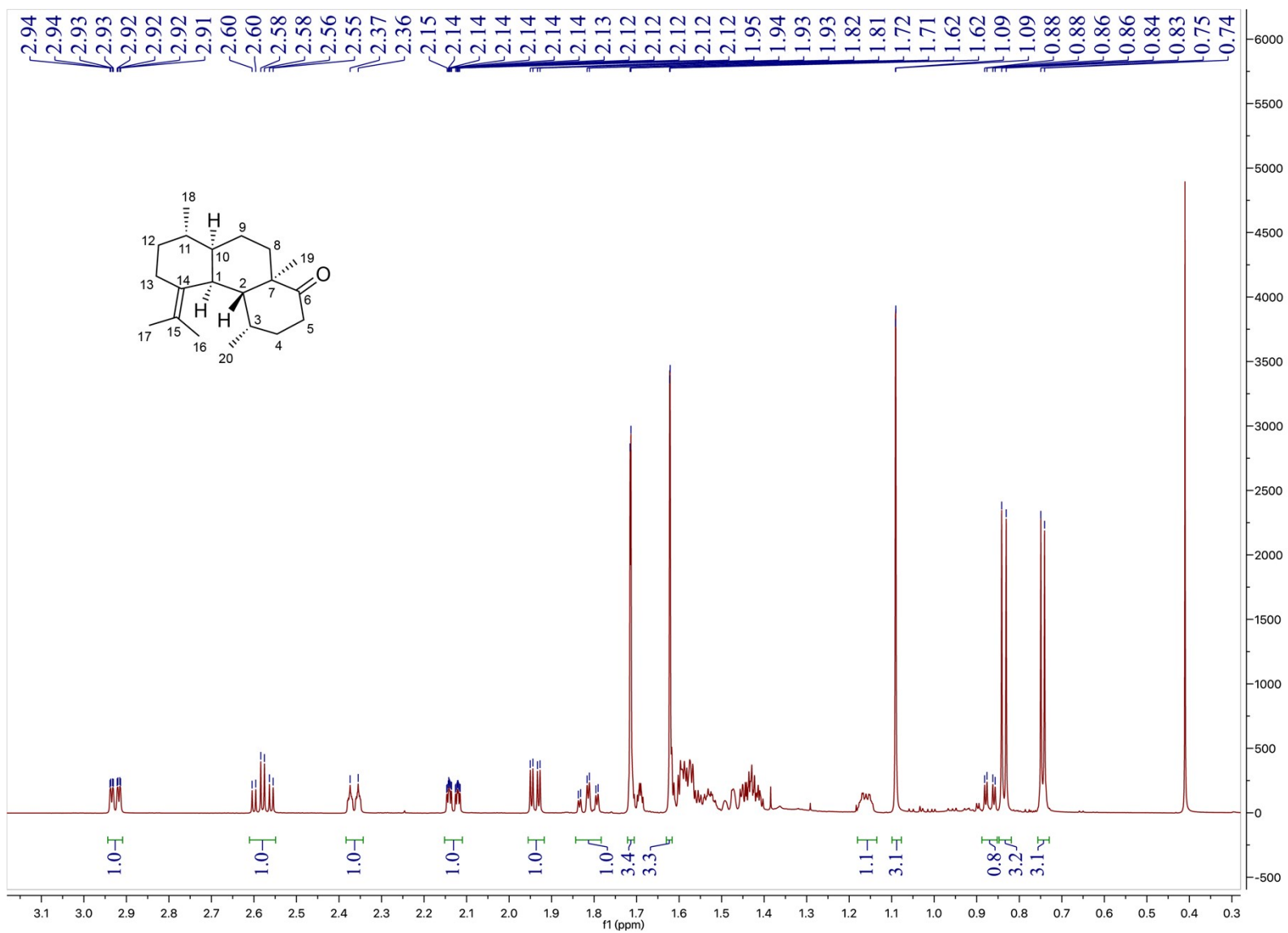


Figure S2. ¹H-NMR spectrum of **4** (700 MHz, C₆D₆).

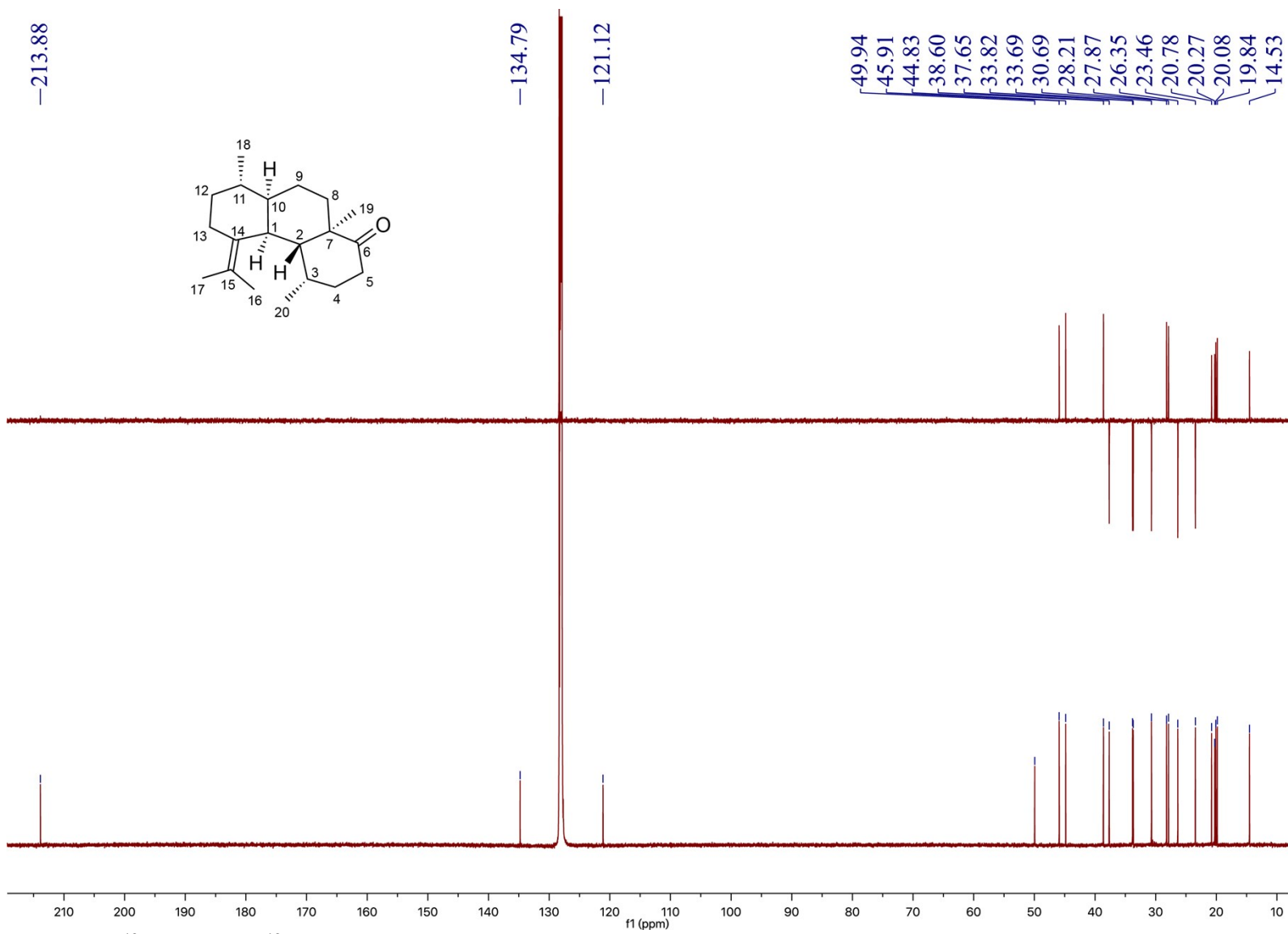


Figure S3. ^{13}C -NMR and ^{13}C -DEPT-135 spectra of **4** (175 MHz, C_6D_6).

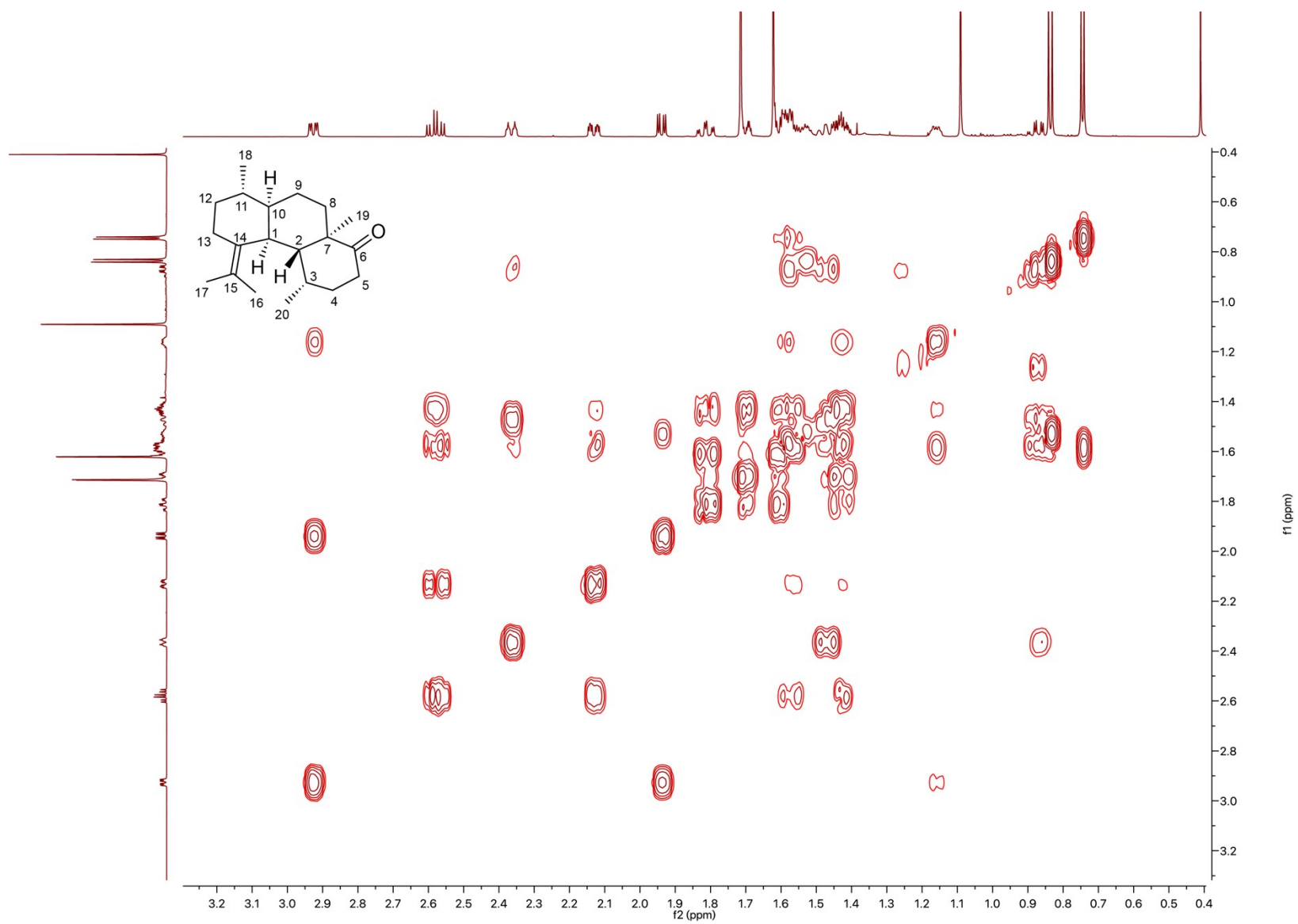
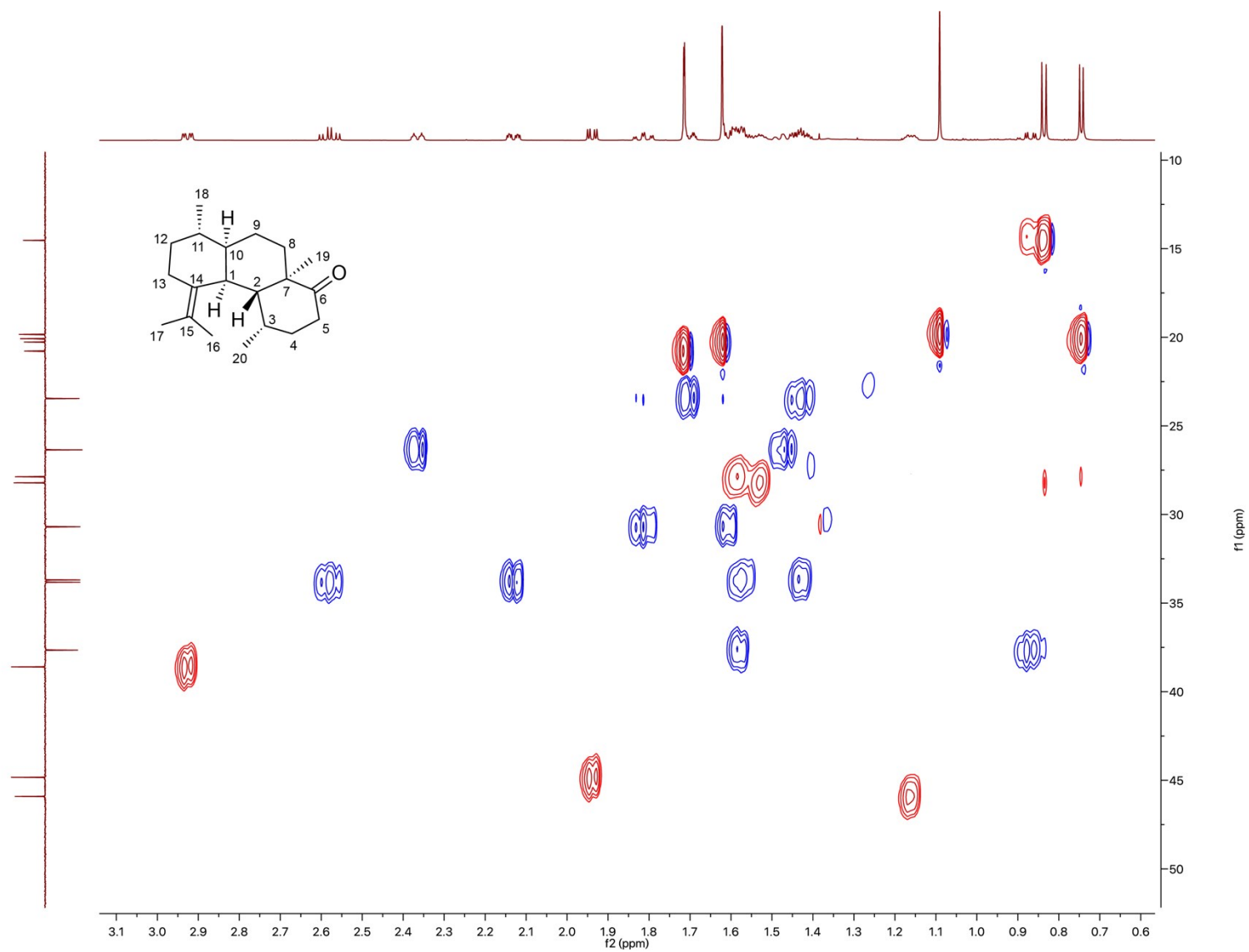


Figure S4. ^1H - ^1H COSY spectrum of **4** (C_6D_6).



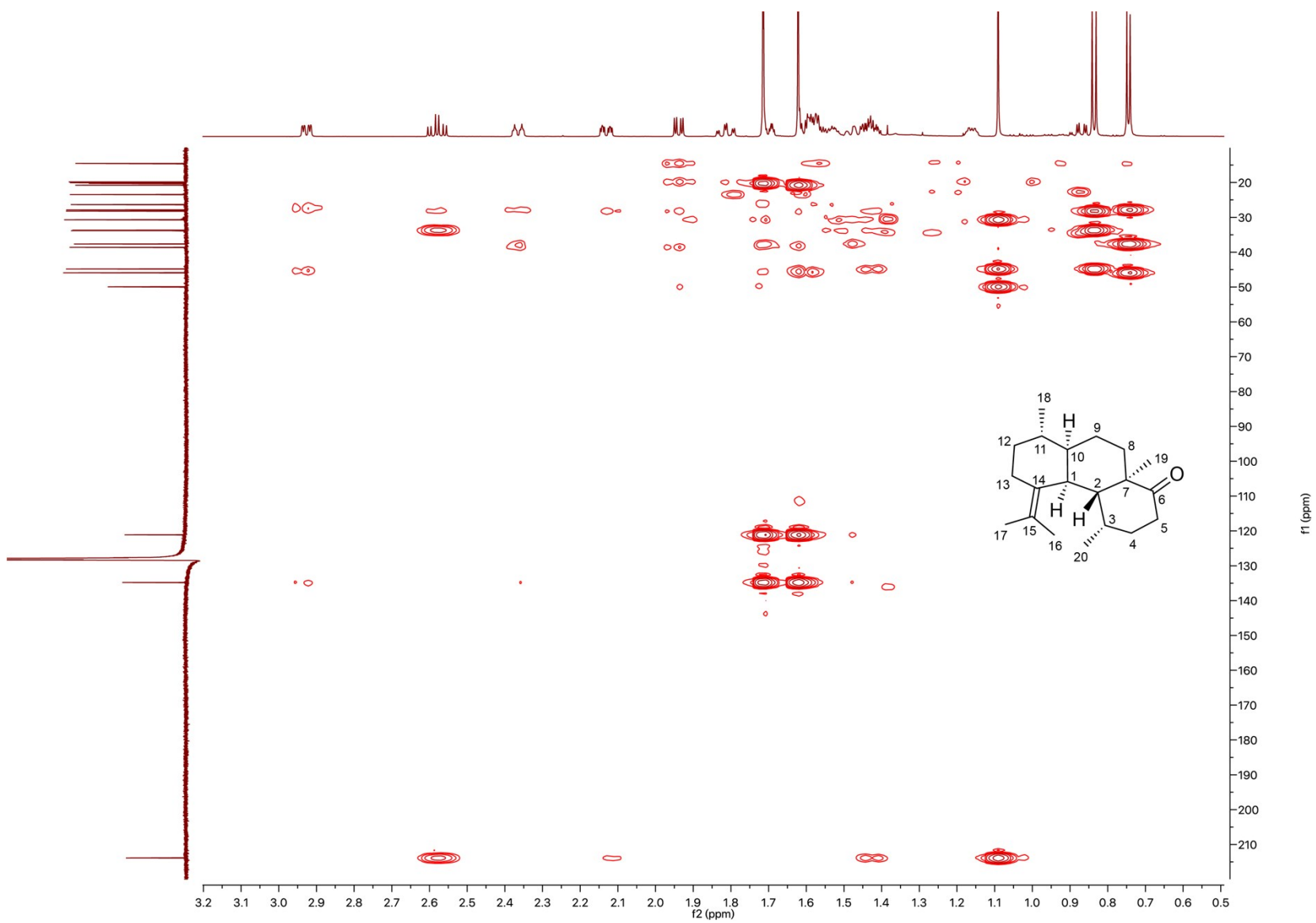


Figure S6. HMBC spectrum of **4** (C_6D_6).

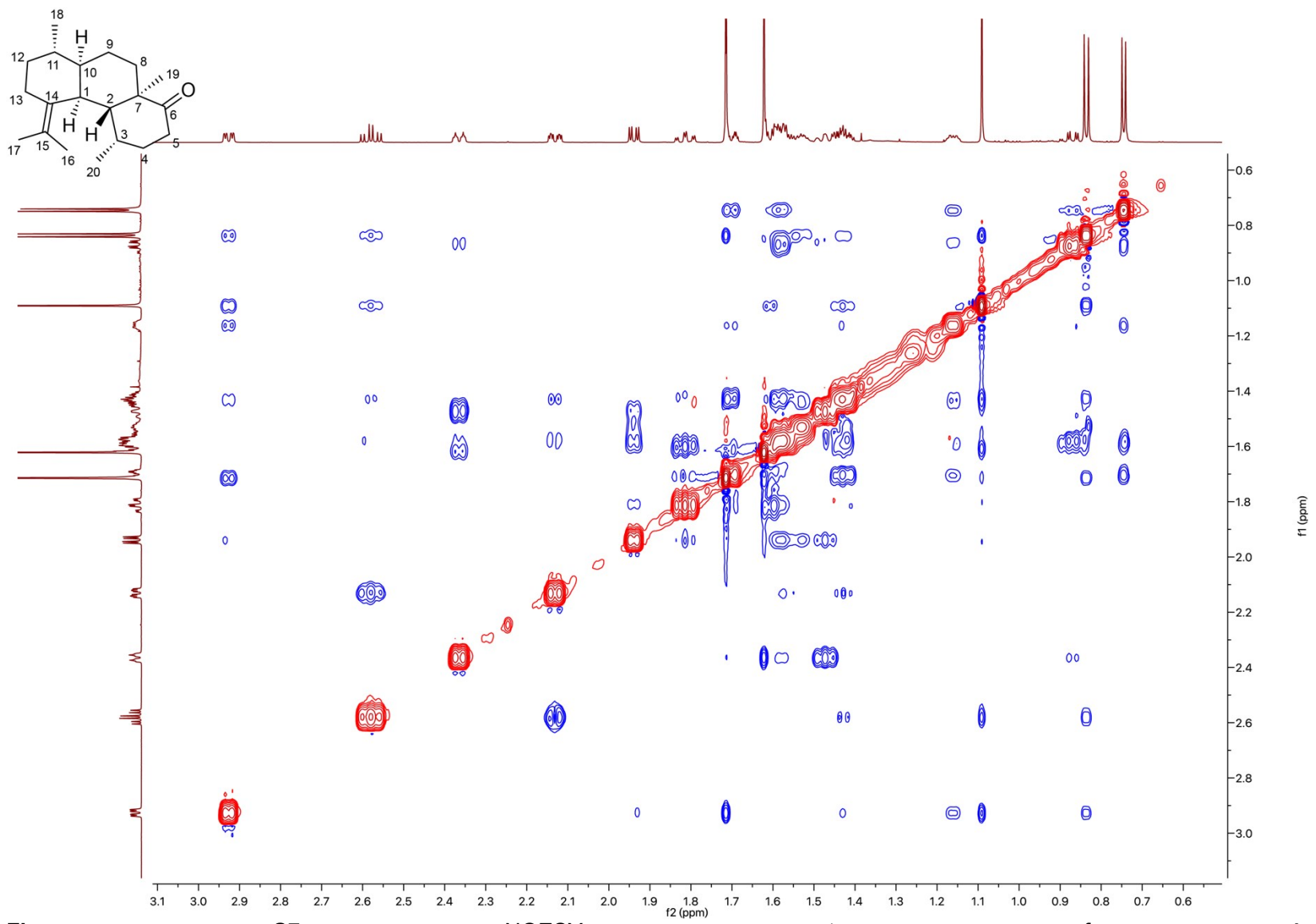


Figure 9

(C₆D₆).

Table S2. NMR data of catenul-14-en-6-yl acetate (**5**) in C₆D₆ recorded at 298 K.

C ^[a]	type	¹ H ^[b]	¹³ C ^[b]
1	CH	2.91 (dd, <i>J</i> = 11.8, 3.8)	38.38
2	CH	1.64 (m)	42.96
3	CH	1.45 (m)	28.32
4	CH ₂	1.45 (m, H _β) 1.35 (m, H _α)	31.80
5	CH ₂	1.74 (m, H _β) 1.74 (m, H _α)	23.54
6	CH	4.82 (m)	82.33
7	C _q	–	39.89
8	CH ₂	1.32 (m, H _β) 1.32 (m, H _α)	35.17
9	CH ₂	1.50 (m, H _β) 1.63 (m, H _α)	23.59
10	CH	1.23 (m)	46.05
11	CH	1.66 (m)	27.84
12	CH ₂	1.64 (m, H _β) 0.92 (dd, <i>J</i> = 13.4, 3.8, H _α)	37.80
13	CH ₂	1.55 (m, H _β) 2.40 (dt, <i>J</i> = 13.3, 2.6, H _α)	26.33
14	C _q	–	135.11
15	C _q	–	120.89
16	CH ₃	1.75 (d, <i>J</i> = 1.5)	20.82
17	CH ₃	1.65 (s)	20.30
18	CH ₃	0.78 (d, <i>J</i> = 6.1)	20.18
19	CH ₃	1.14 (s)	16.08
20	CH ₃	0.79 (d, <i>J</i> = 7.8)	15.26
21	C _q	–	170.03
22	CH ₃	1.78 (s)	20.91

[a] Carbon numbering as shown in main text. [b] Chemical shifts δ in ppm, multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, coupling constants *J* are given in Hertz.

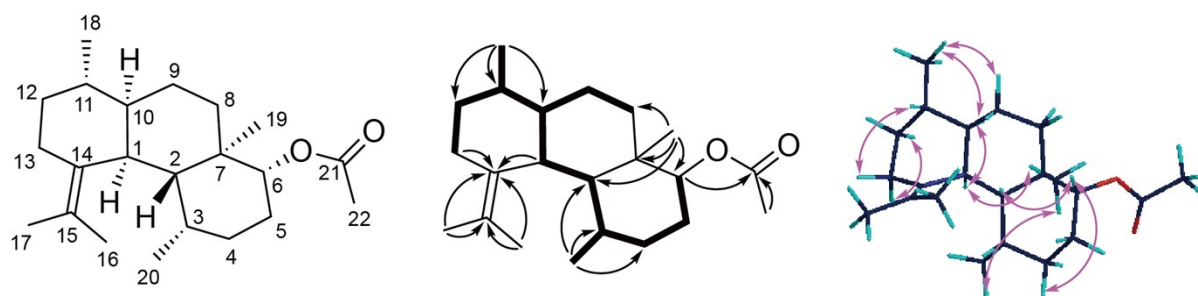


Figure S8. Carbon numbering and structure elucidation of **5**. Bold lines represent ^1H - ^1H COSY correlations, selected HMBC correlations are represented by single-headed arrows and key NOESY correlations are indicated by double headed arrows.

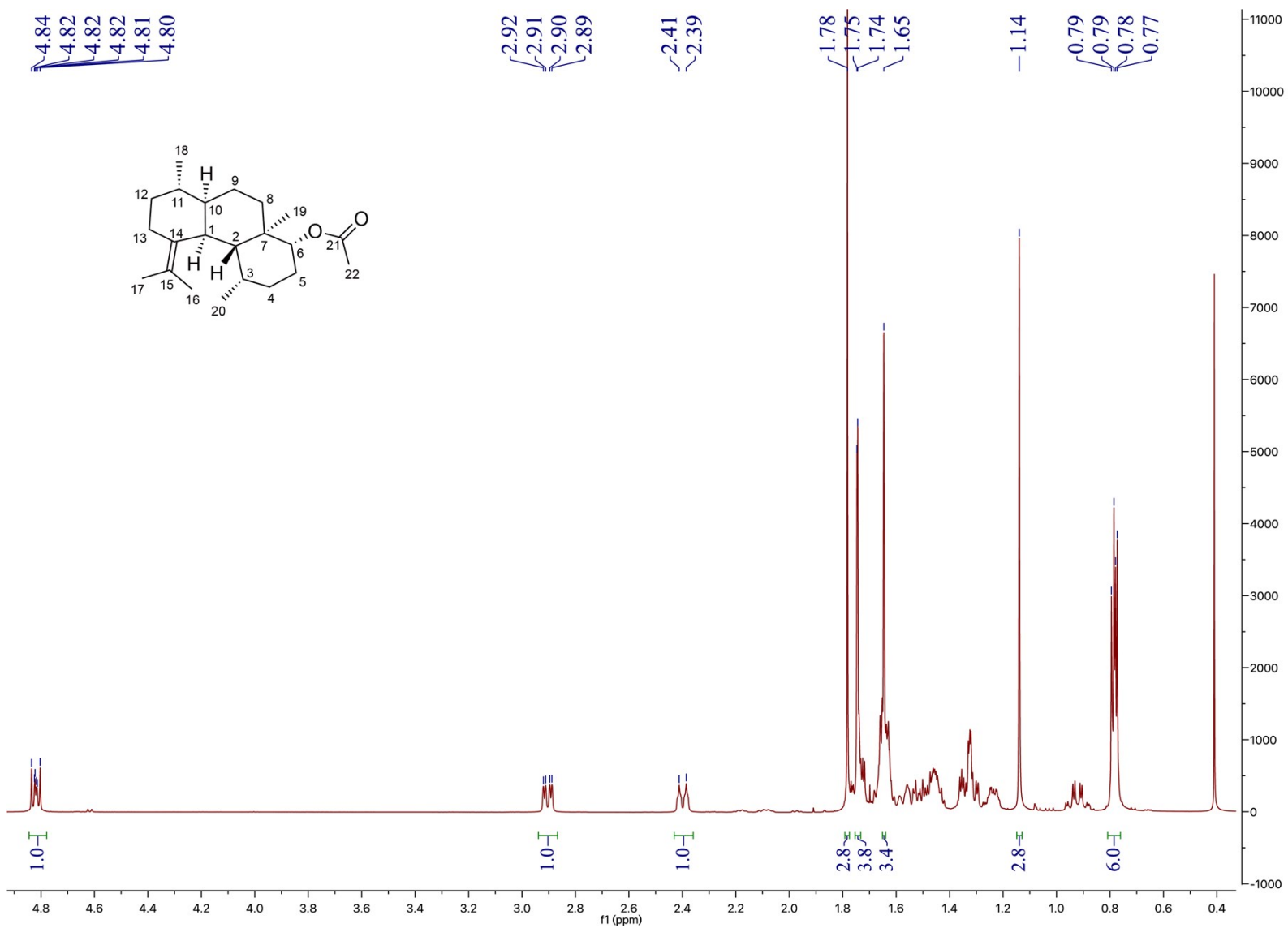


Figure S9. ¹H-NMR spectrum of **5** (500 MHz, C₆D₆).

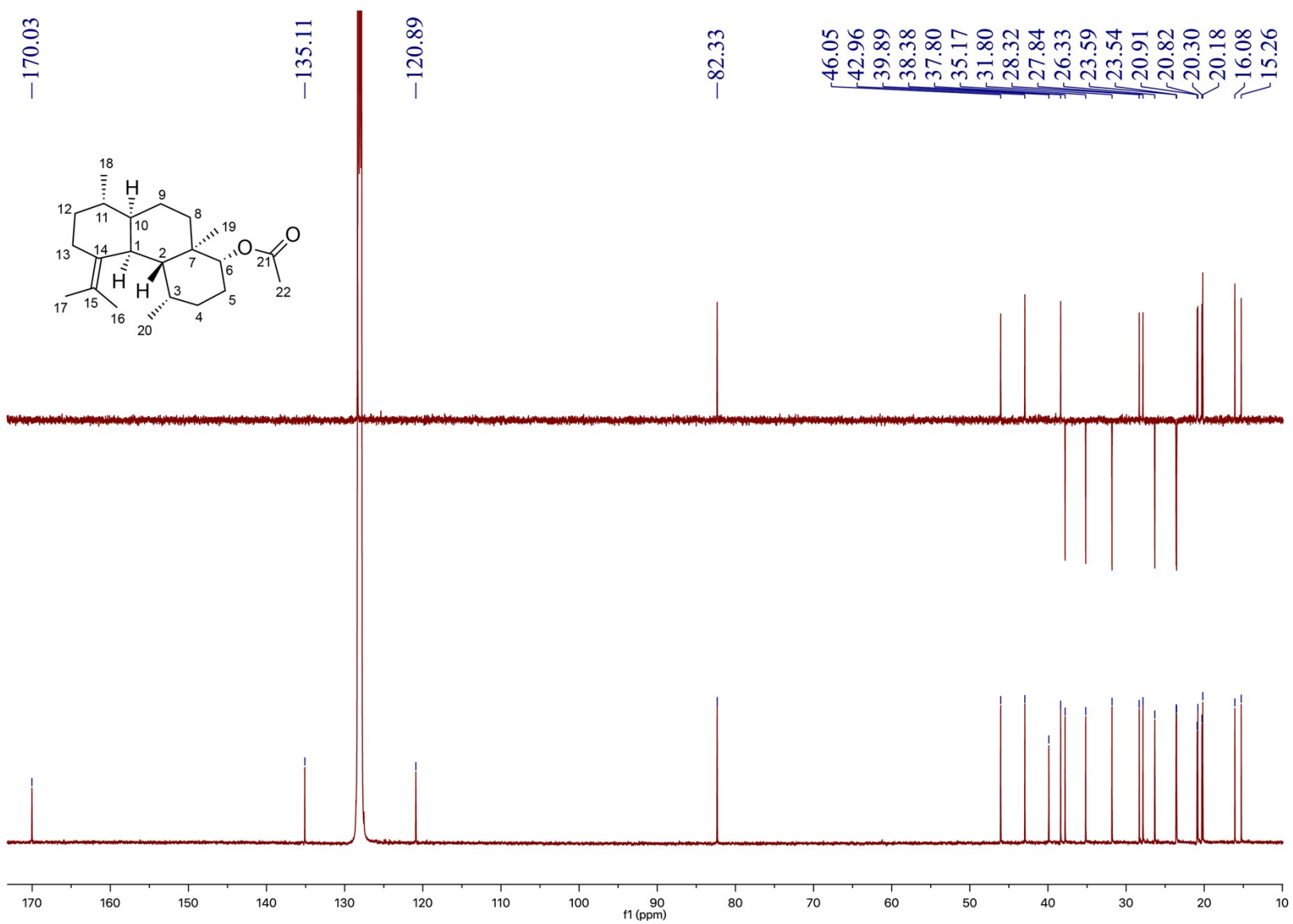


Figure S10. ^{13}C -NMR and ^{13}C -DEPT-135 spectra of **5** (125 MHz, C_6D_6).

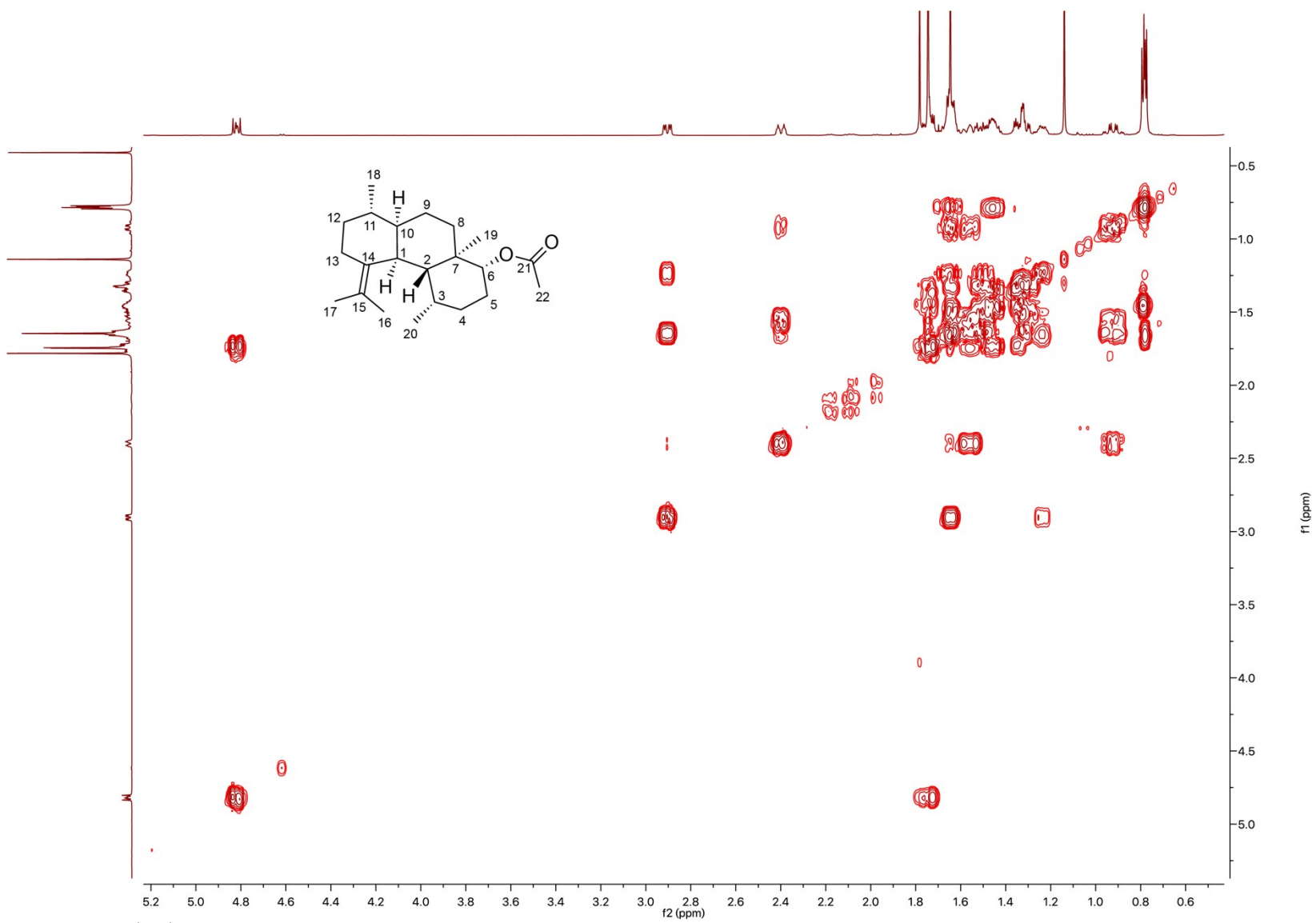


Figure S11. ^1H - ^1H COSY spectrum of **5** (C_6D_6).

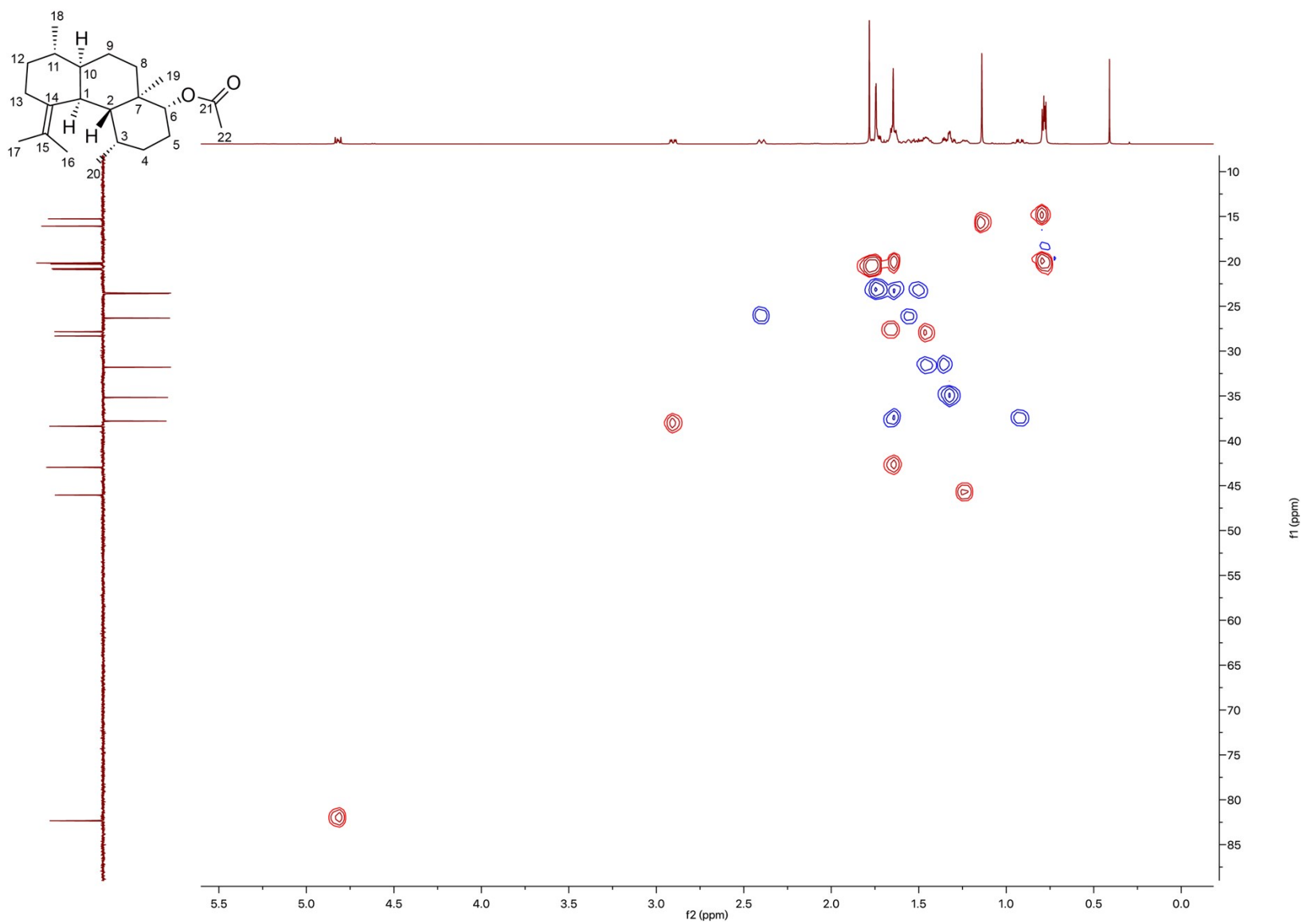


Figure S12. HSQC spectrum of **5** (C₆D₆).

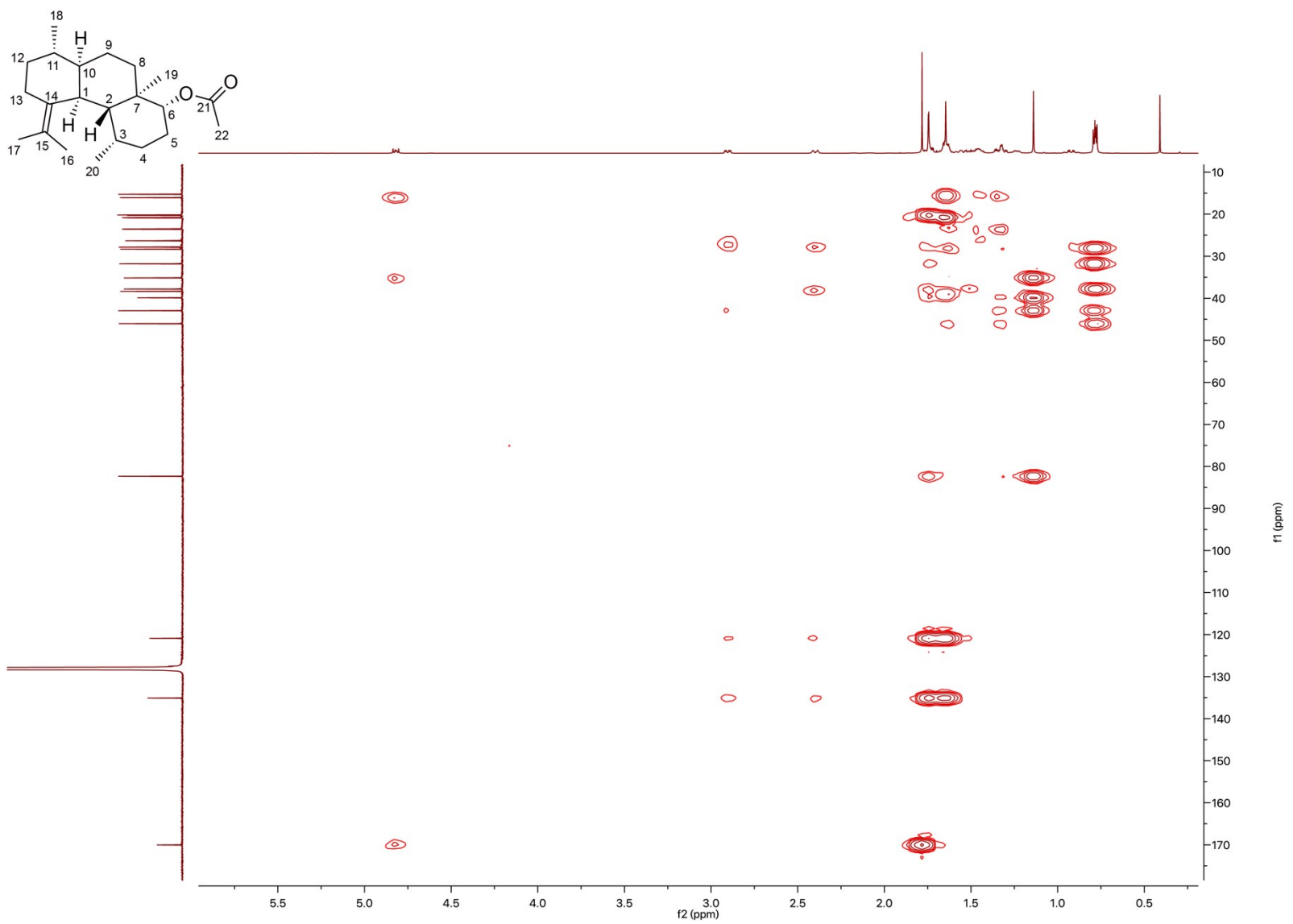
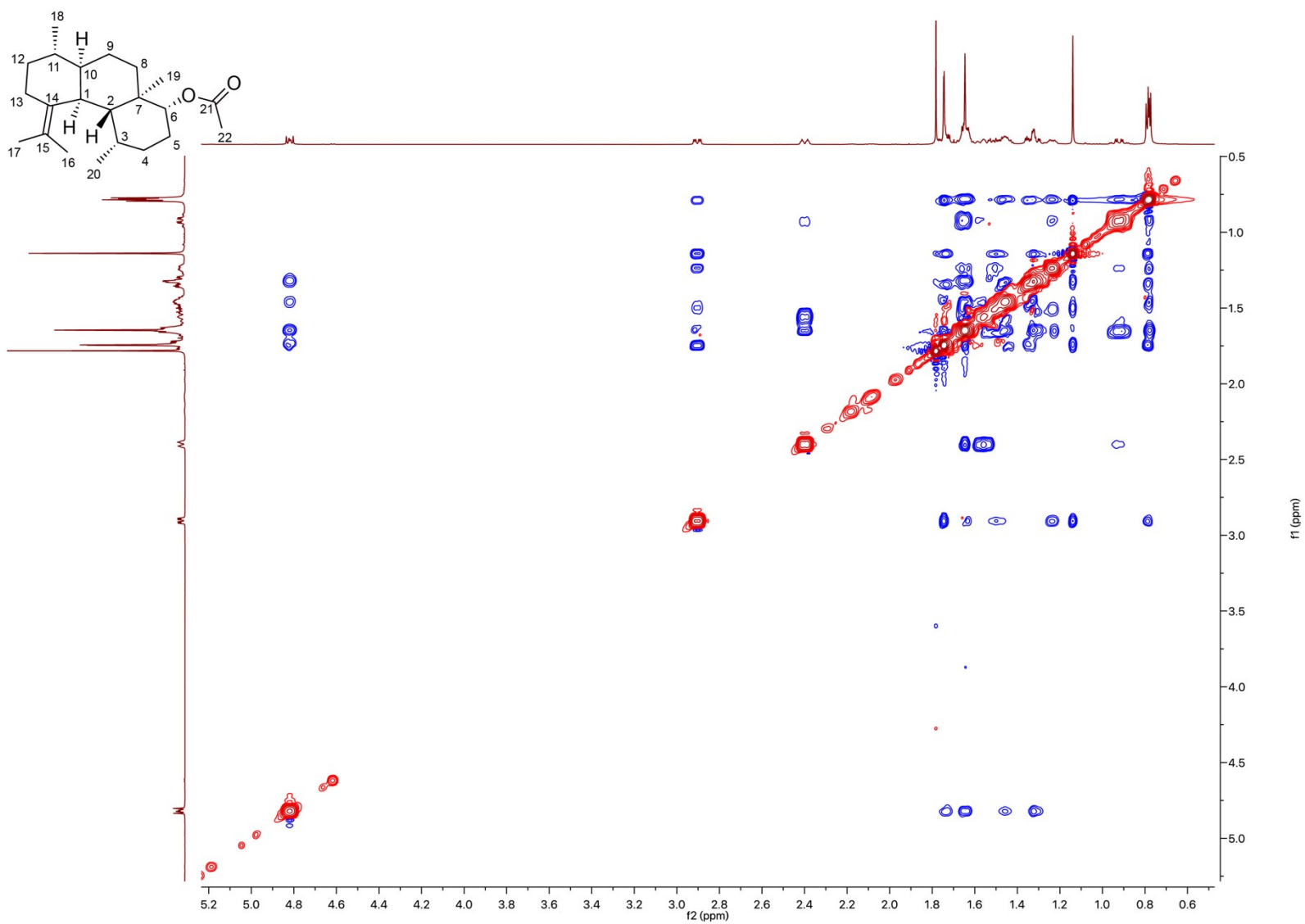


Figure S13. HMBC spectrum of 5 (C_6D_6).



Figure

S14.

NOESY

spectrum

of

5

(C₆D₆)

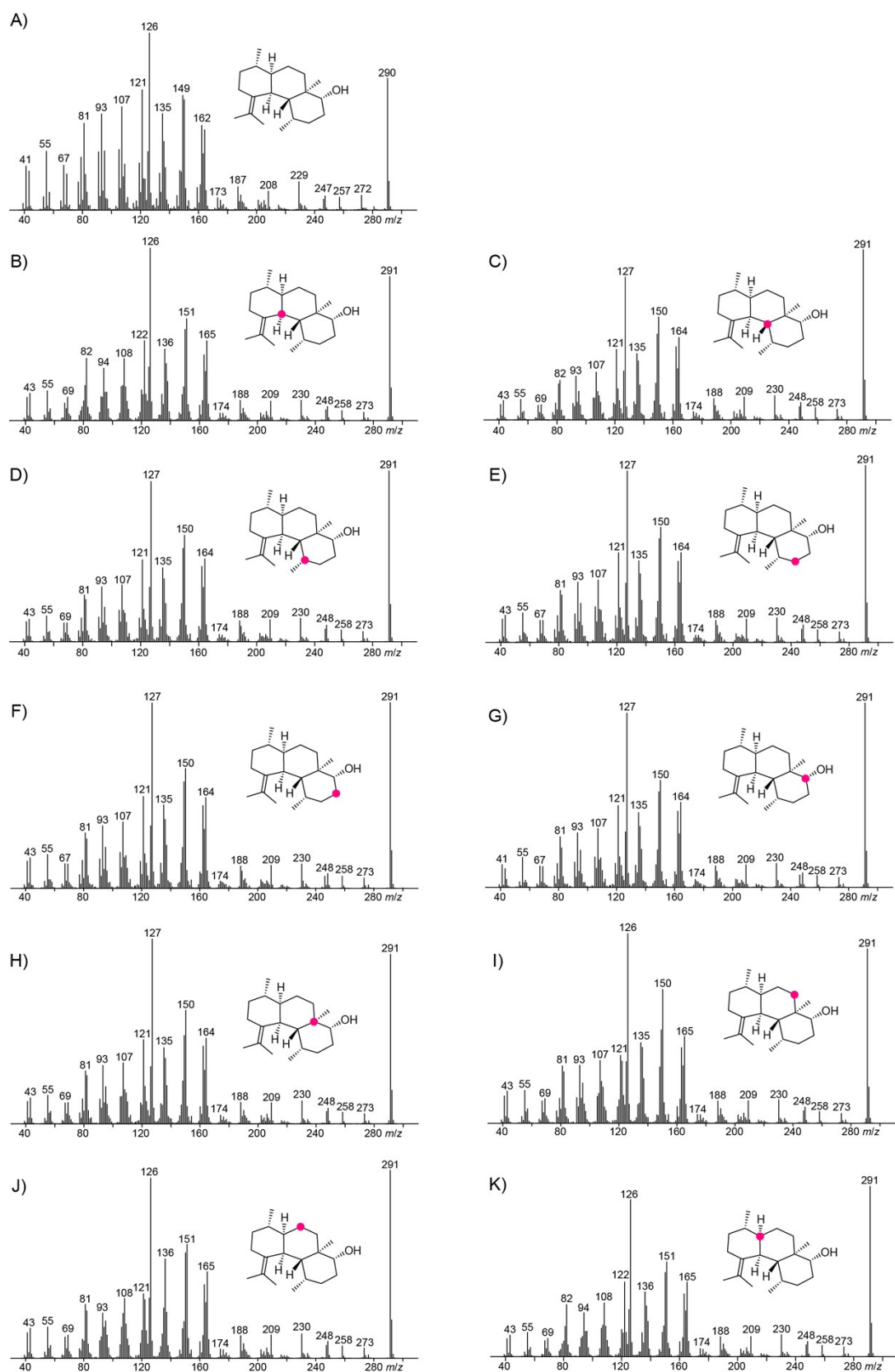


Figure S15. EI mass spectra of A) unlabelled **1** and of B) – K) ^{13}C -**1** with labellings at carbons C1 – C10. Pink dots indicate ^{13}C -labelled carbons.

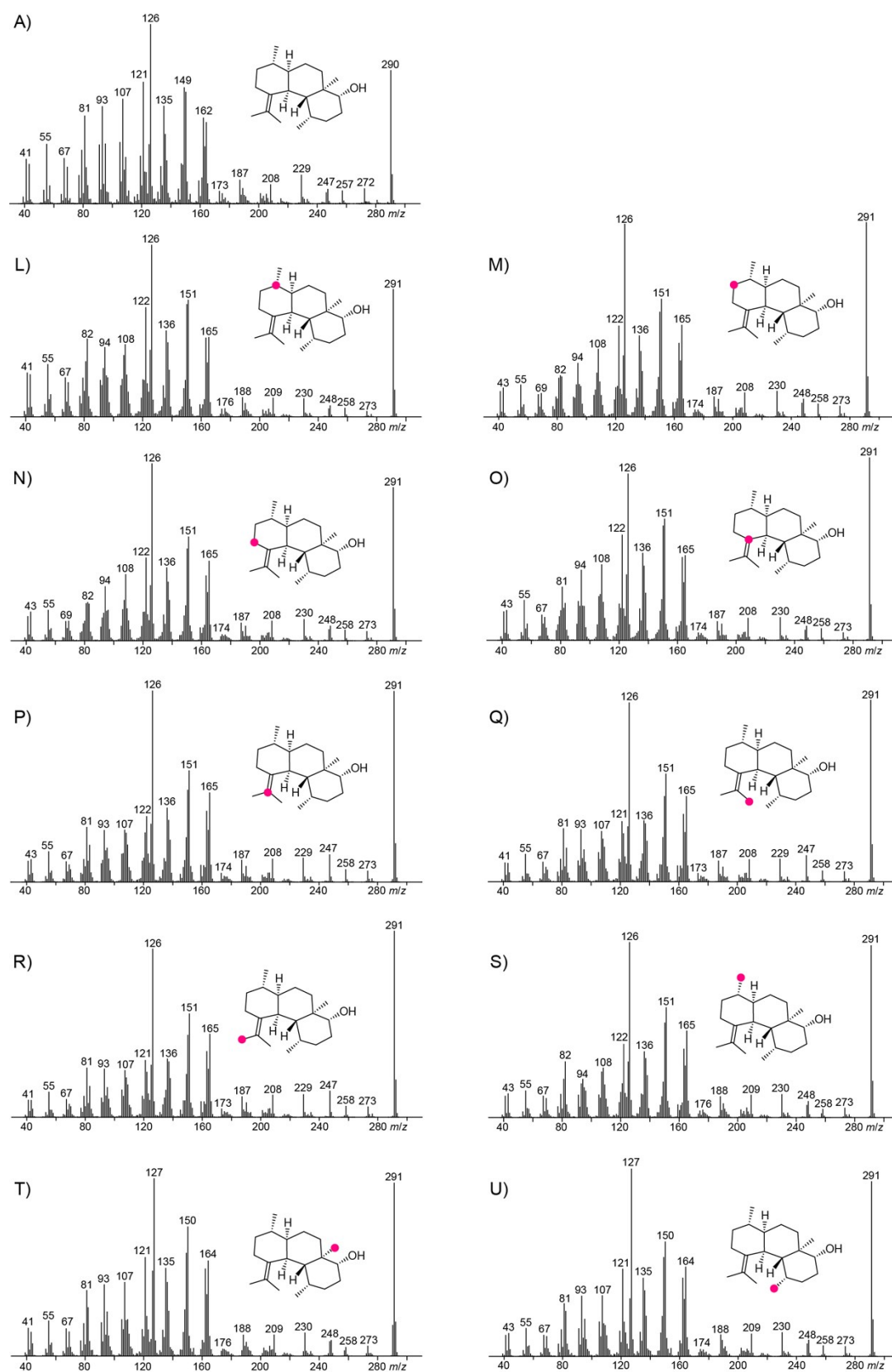


Figure S15 (continued). EI mass spectra of A) unlabelled **1** and of L) – U) (^{13}C)-**1** with labellings at carbons C11 – C20. Pink dots indicate ^{13}C -labelled carbons.

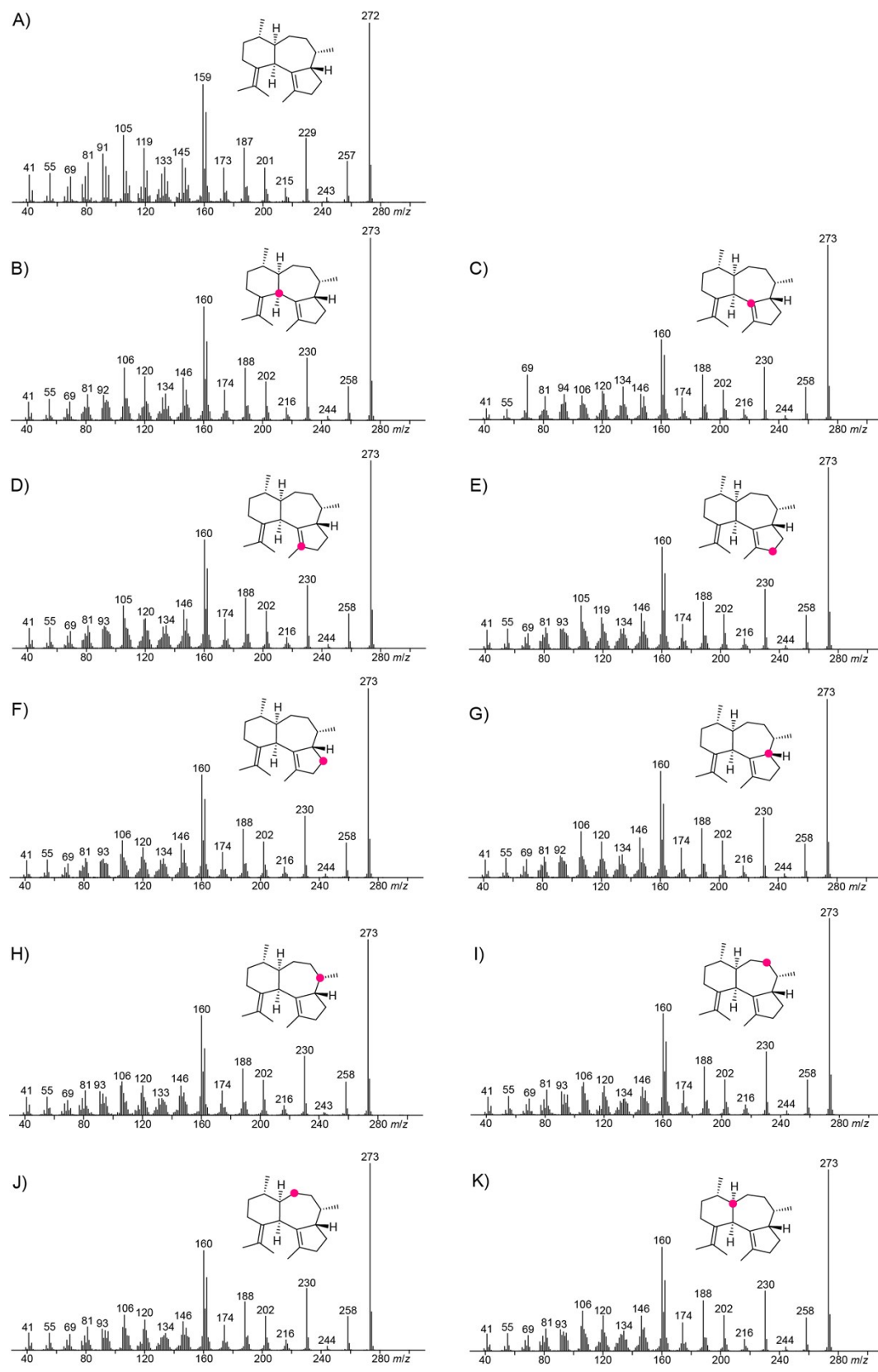


Figure S16. EI mass spectra of A) unlabelled **2** and of B) – K) ^{13}C -**2** with labellings at carbons C1 – C10. Pink dots indicate ^{13}C -labelled carbons.

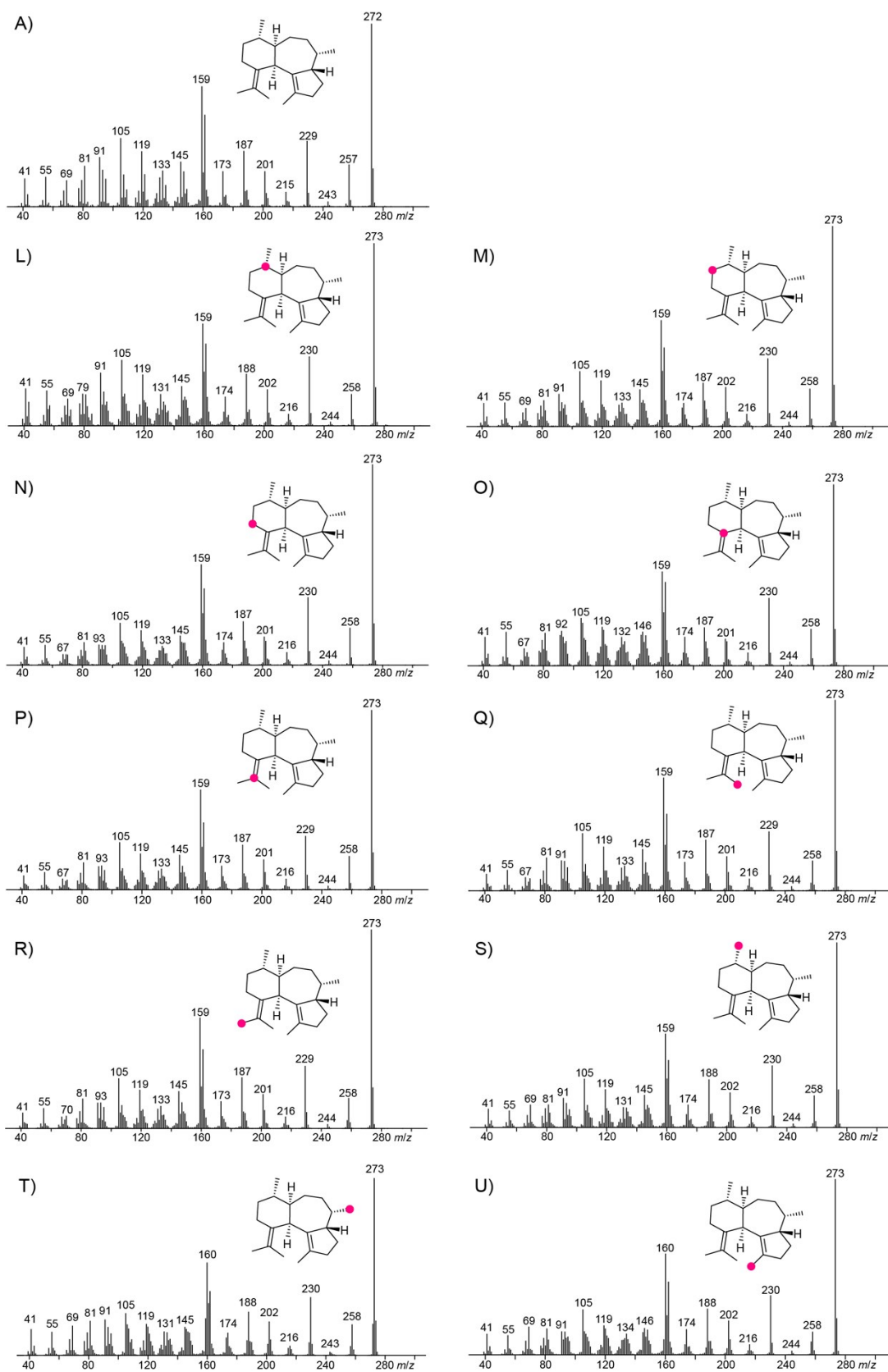


Figure S16 (continued). EI mass spectra of A) unlabelled **2** and of L) – U) (^{13}C)-**2** with labellings at carbons C11 – C20. Pink dots indicate ^{13}C -labelled carbons.

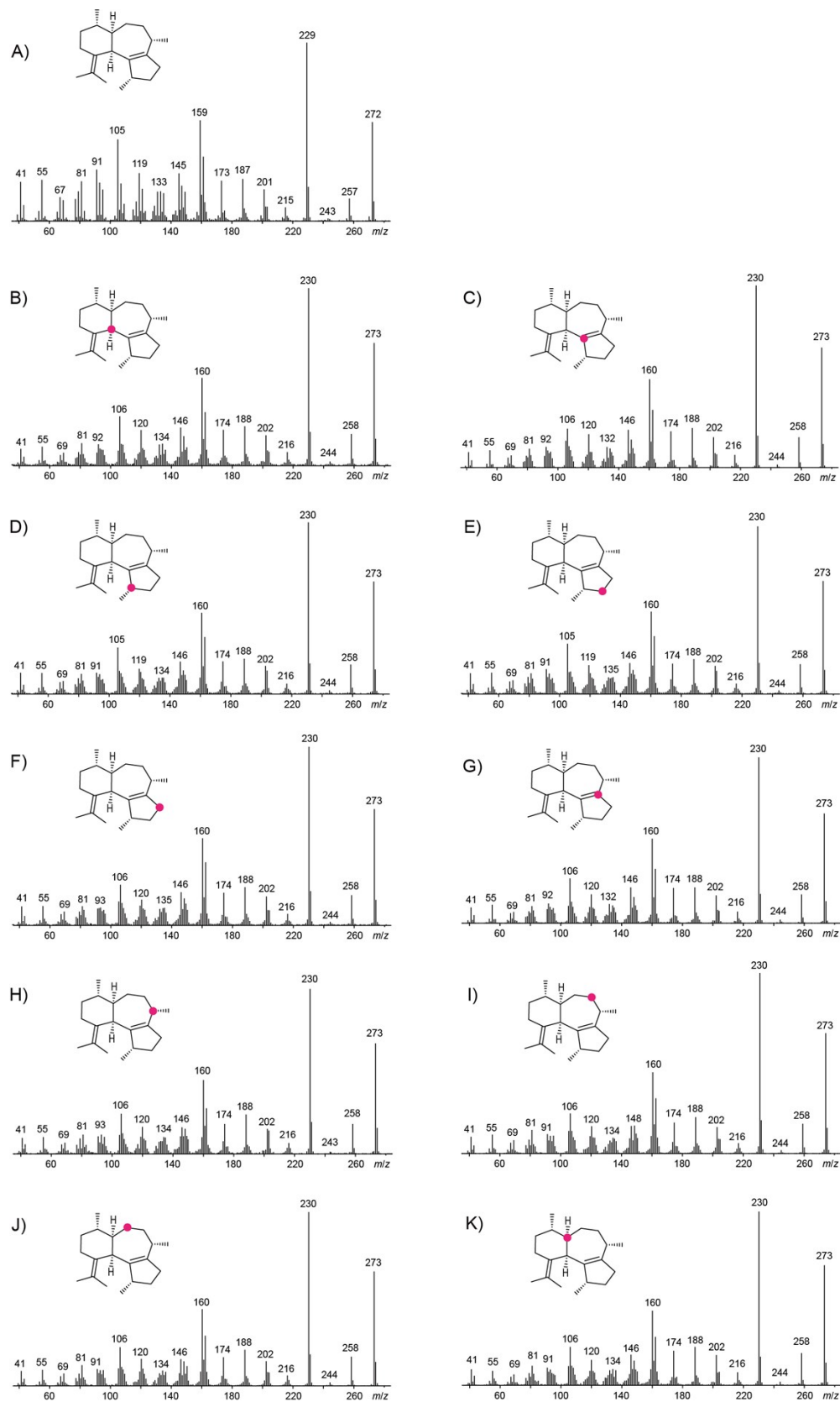


Figure S17. EI mass spectra of A) unlabelled **3** and of B) – K) ^{13}C -**3** with labellings at carbons C1 – C10. Pink dots indicate ^{13}C -labelled carbons.

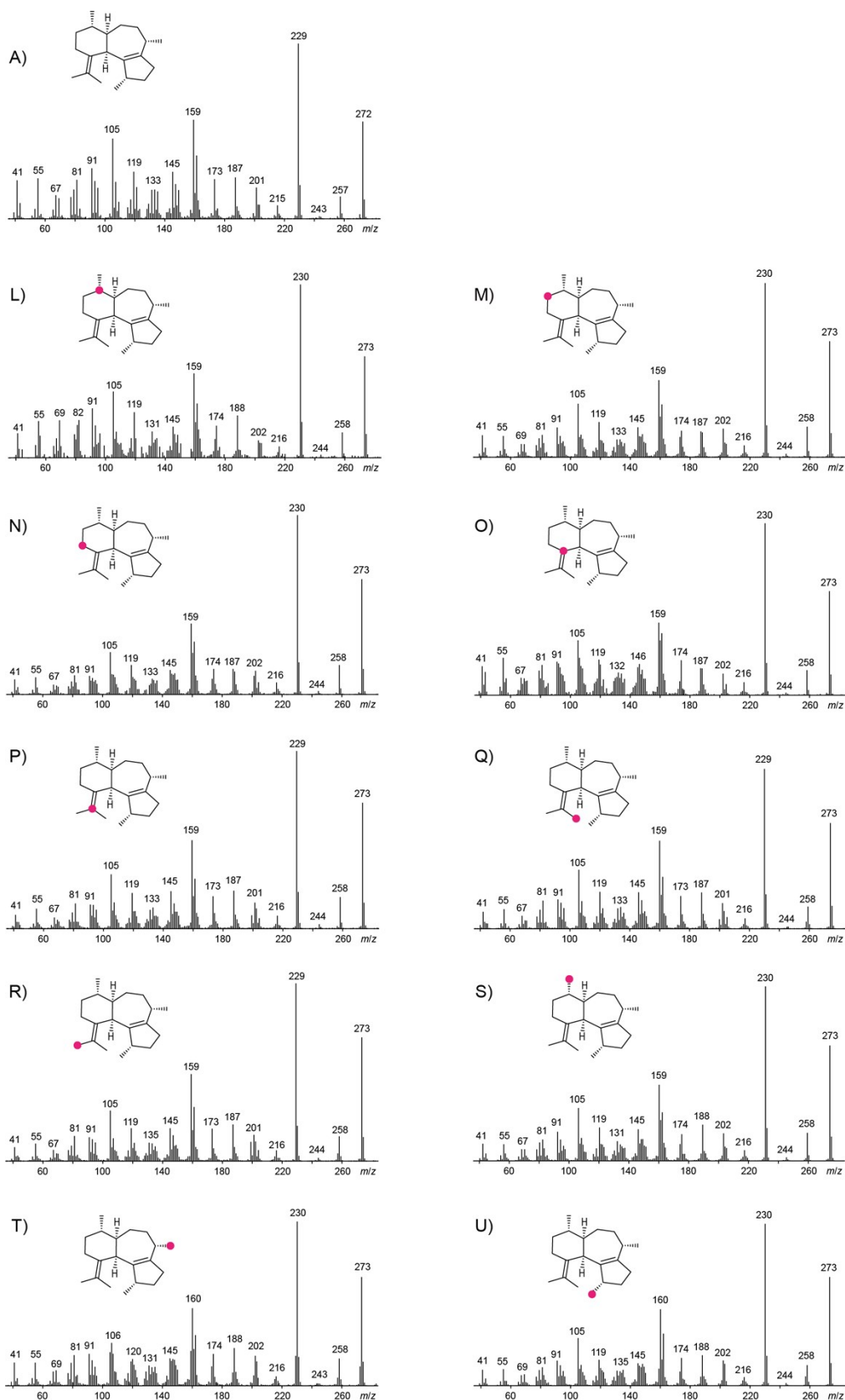


Figure S17 (continued). EI mass spectra of A) unlabelled **3** and of L) – U) (^{13}C)-**3** with labellings at carbons C11 – C20. Pink dots indicate ^{13}C -labelled carbons.

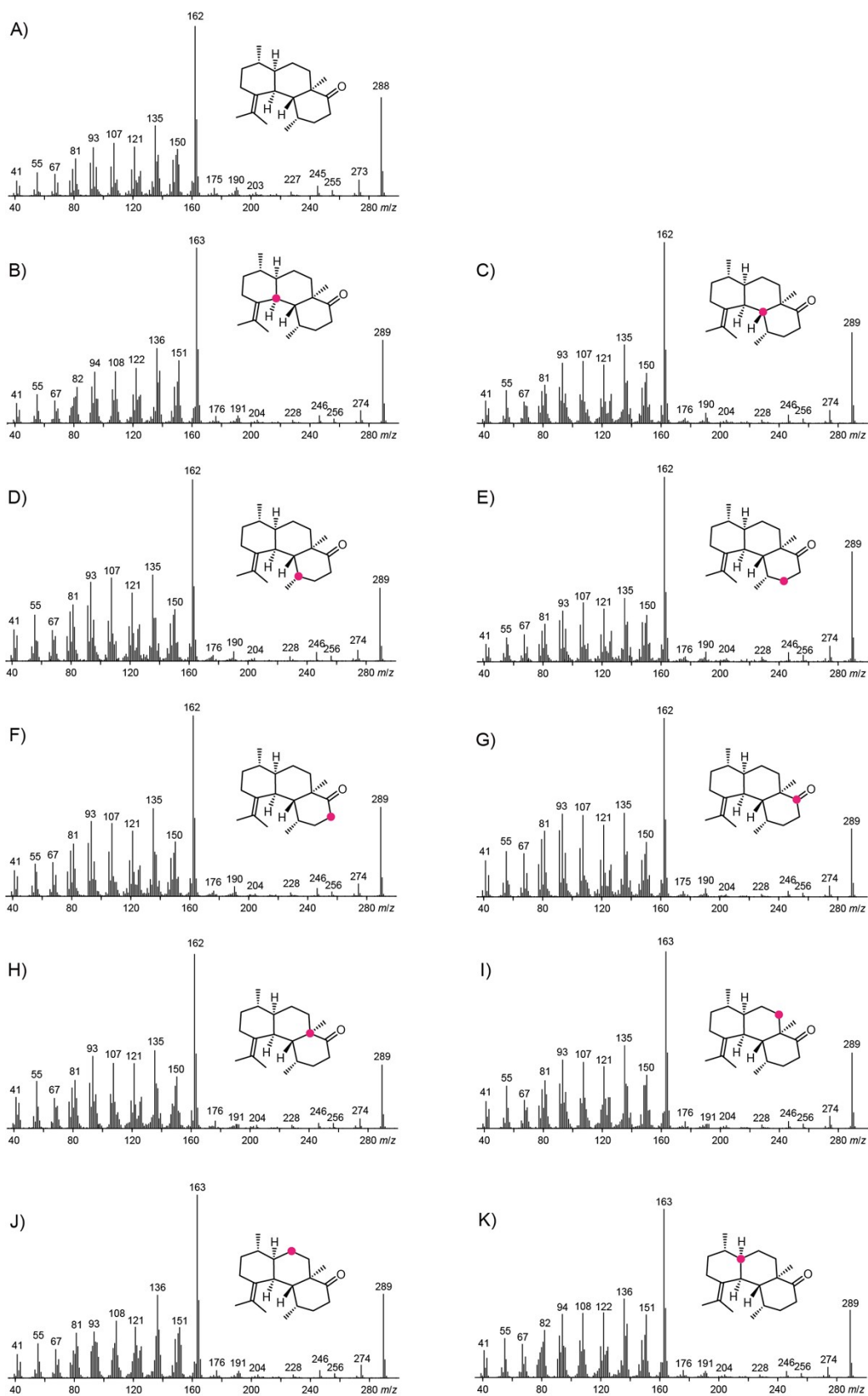


Figure S18. EI mass spectra of A) unlabelled **4** and of B) – K) (^{13}C)-**4** with labellings at carbons C1 – C10. Pink dots indicate ^{13}C -labelled carbons.

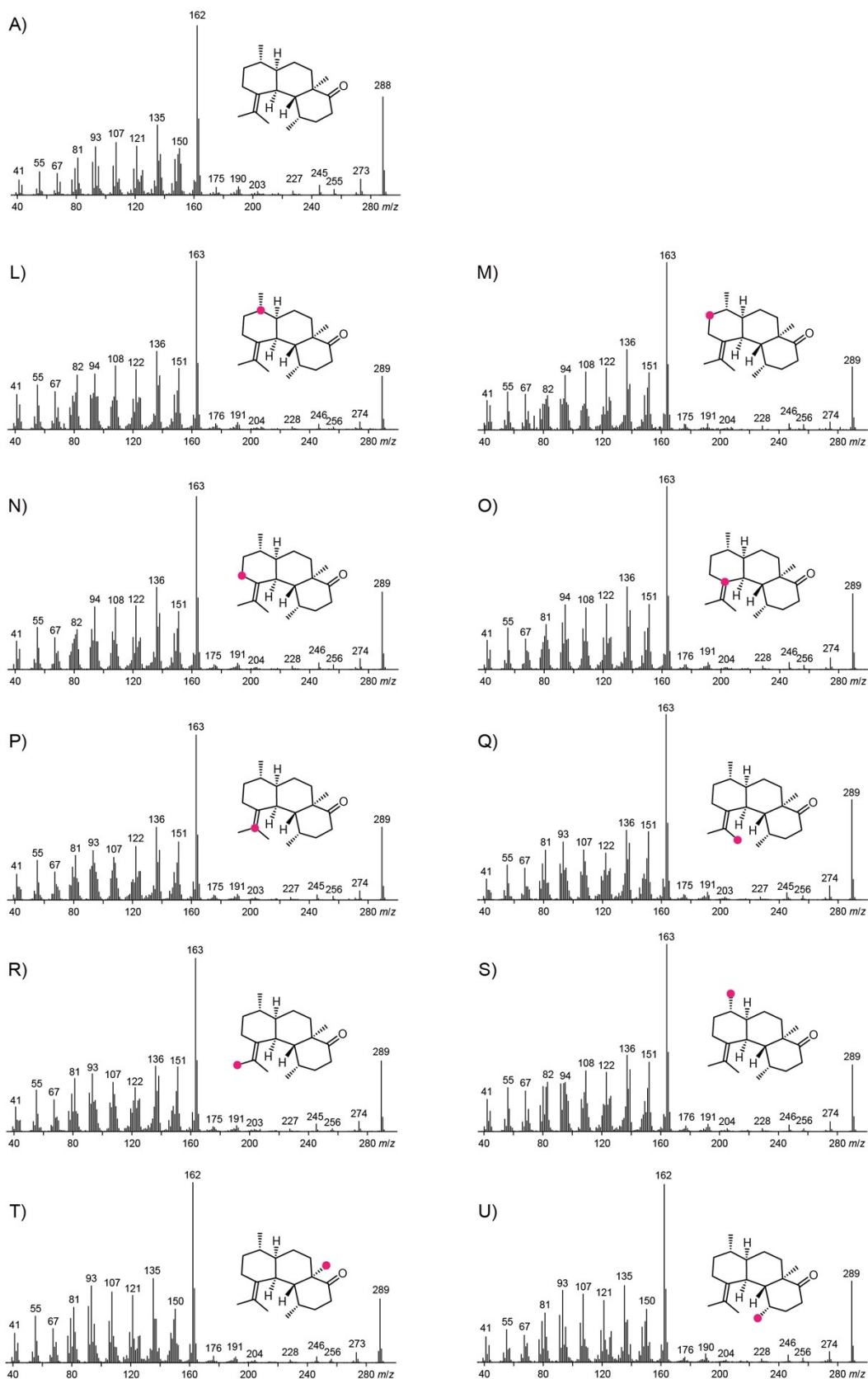


Figure S18 (continued). EI mass spectra of A) unlabelled **4** and of L) – U) (^{13}C)-**4** with labellings at carbons C11 – C20. Pink dots indicate ^{13}C -labelled carbons.

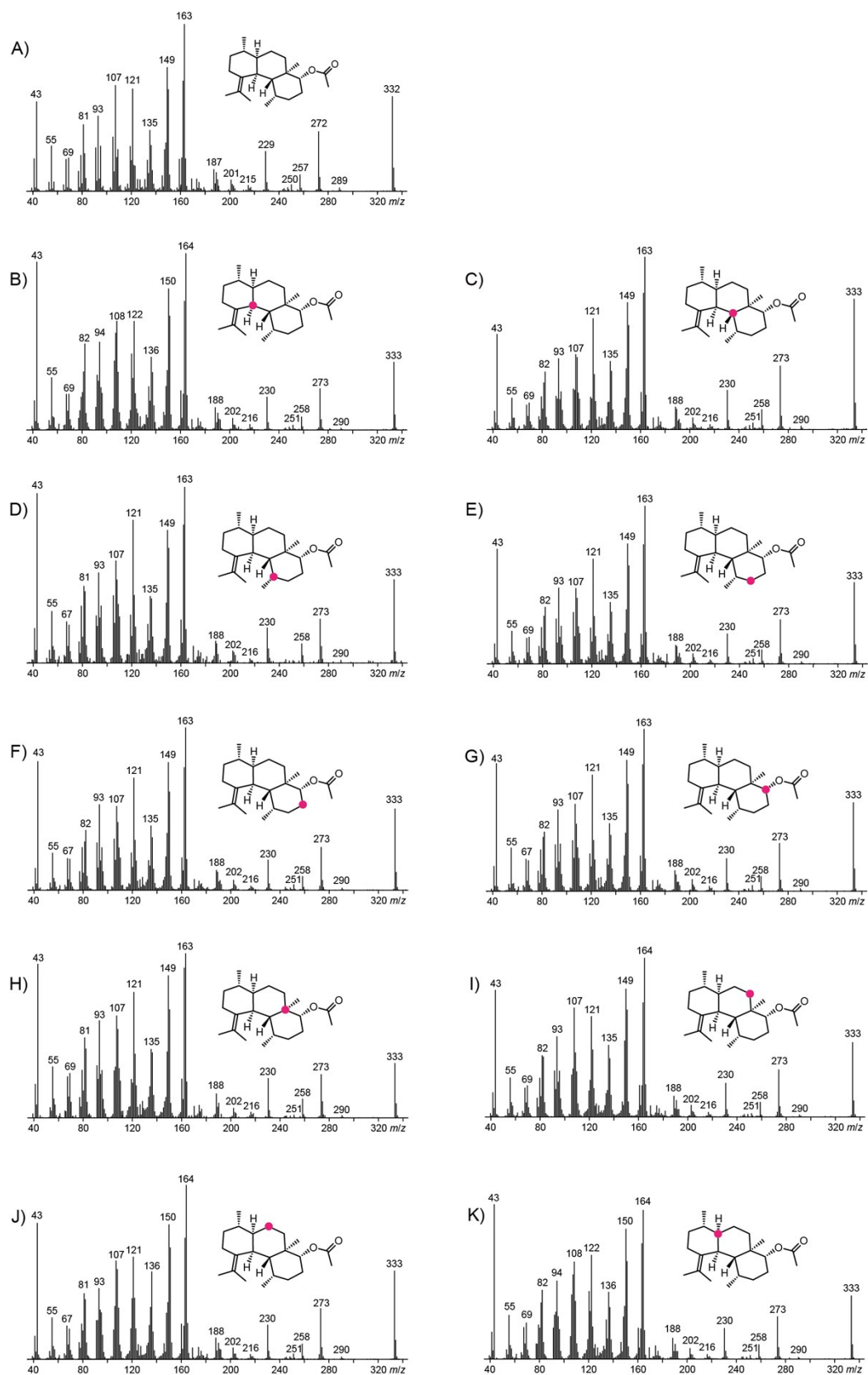


Figure S19. EI mass spectra of A) unlabelled **5** and of B) – K) ^{13}C -**5** with labellings at carbons C1 – C10. Pink dots indicate ^{13}C -labelled carbons.

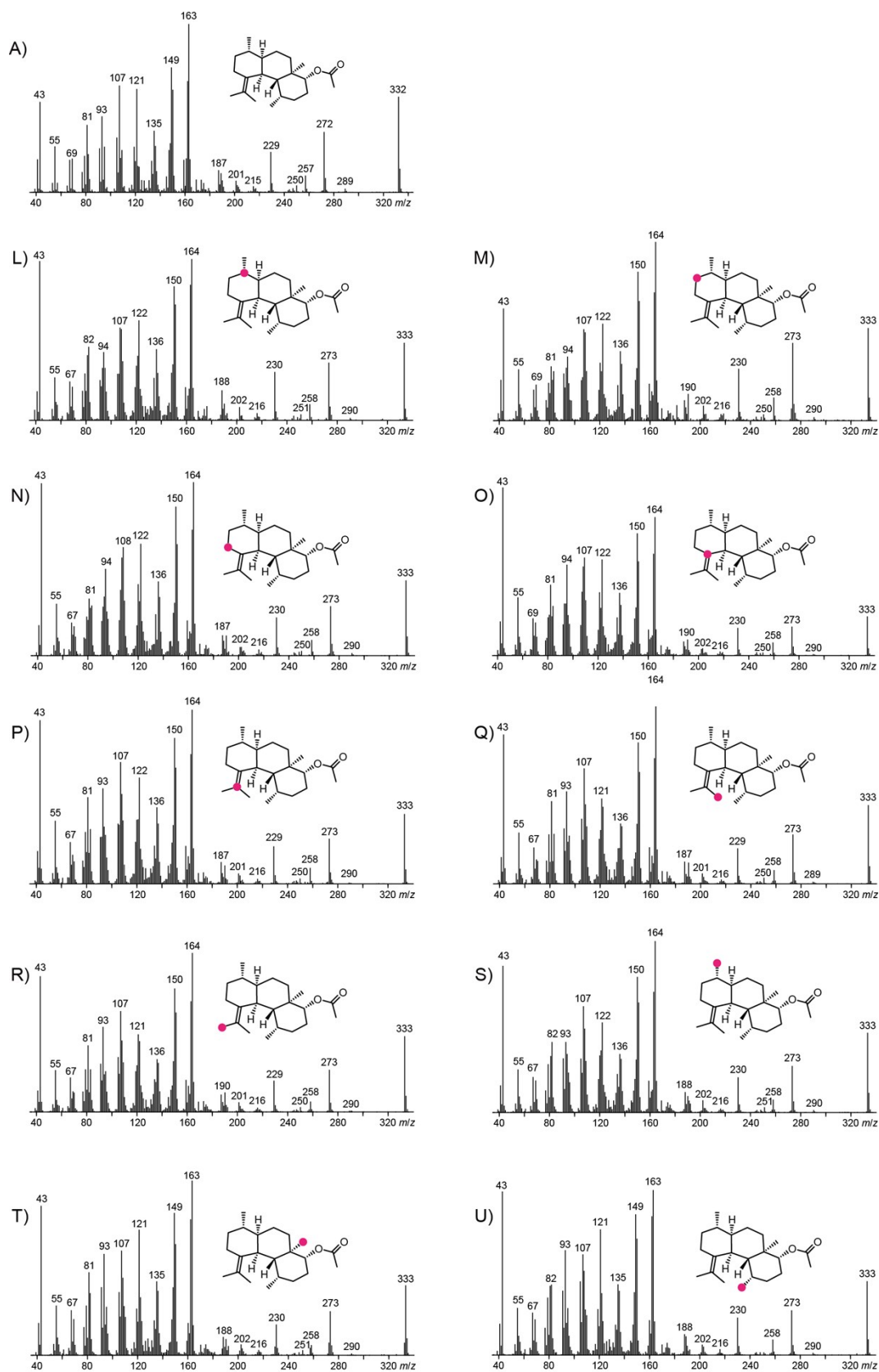


Figure S19 (continued). EI mass spectra of A) unlabelled **5** and of L) – U) (^{13}C)-**5** with labellings at carbons C11 – C20. Pink dots indicate ^{13}C -labelled carbons.

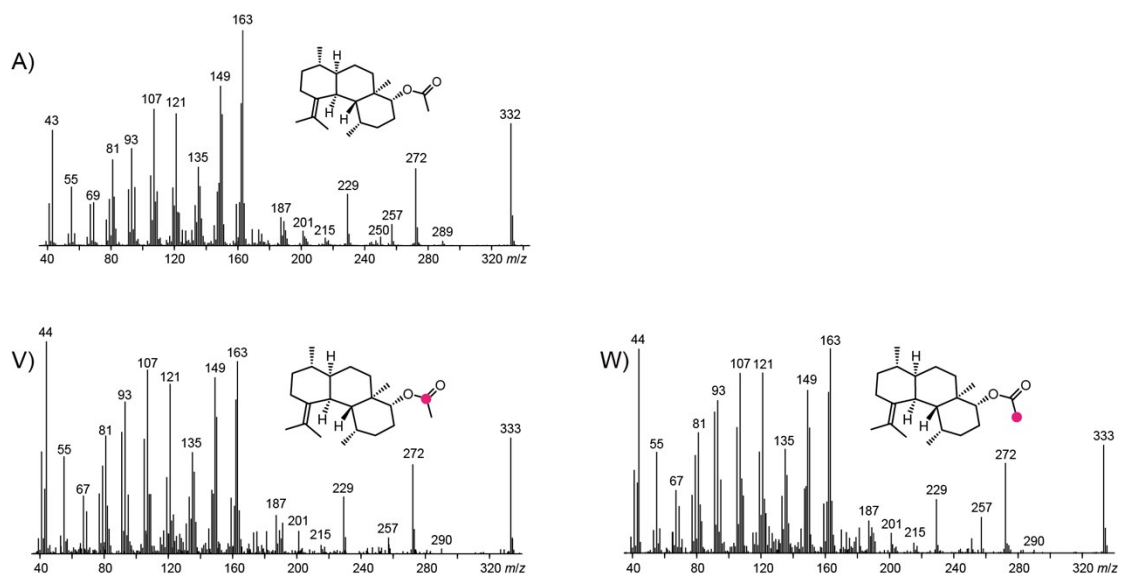


Figure S19 (continued). EI mass spectra of A) unlabelled **5** and of V) and W) (^{13}C)-**5** with labellings at carbons C21 and C22. Pink dots indicate ^{13}C -labelled carbons.