

Supporting Information

Stereoselective synthesis and structural confirmation of all four 8-hydroxyhexahydrocannabinol stereoisomers

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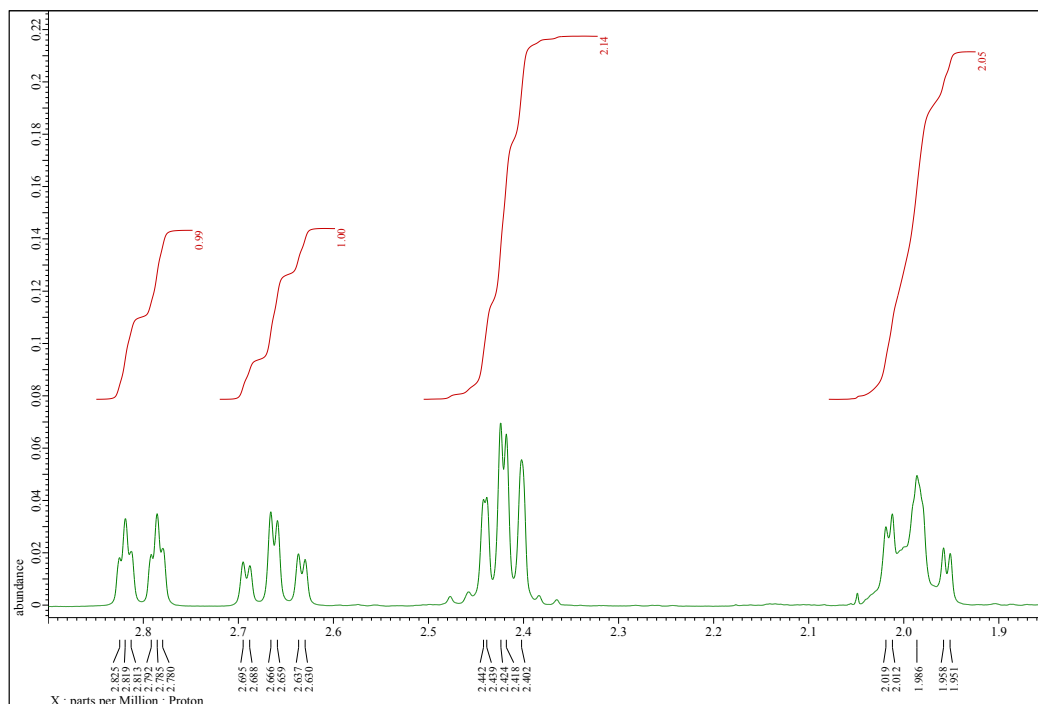
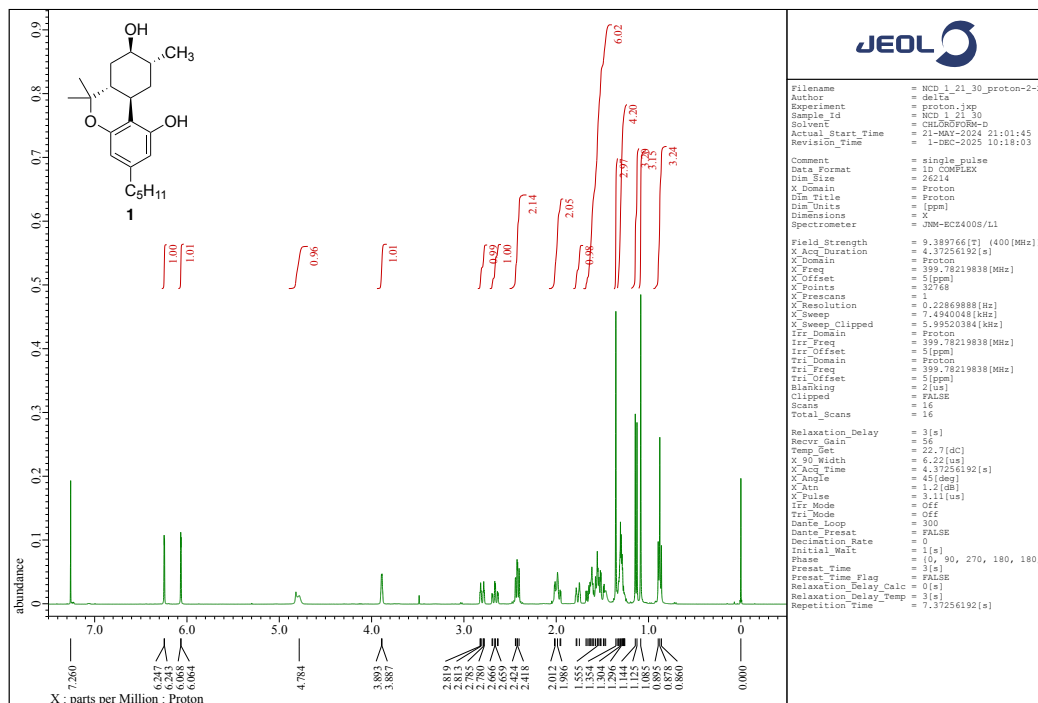
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1. NMR Spectra of 1

Figure S1. ¹H NMR (400 MHz, CDCl₃, ppm) of 1



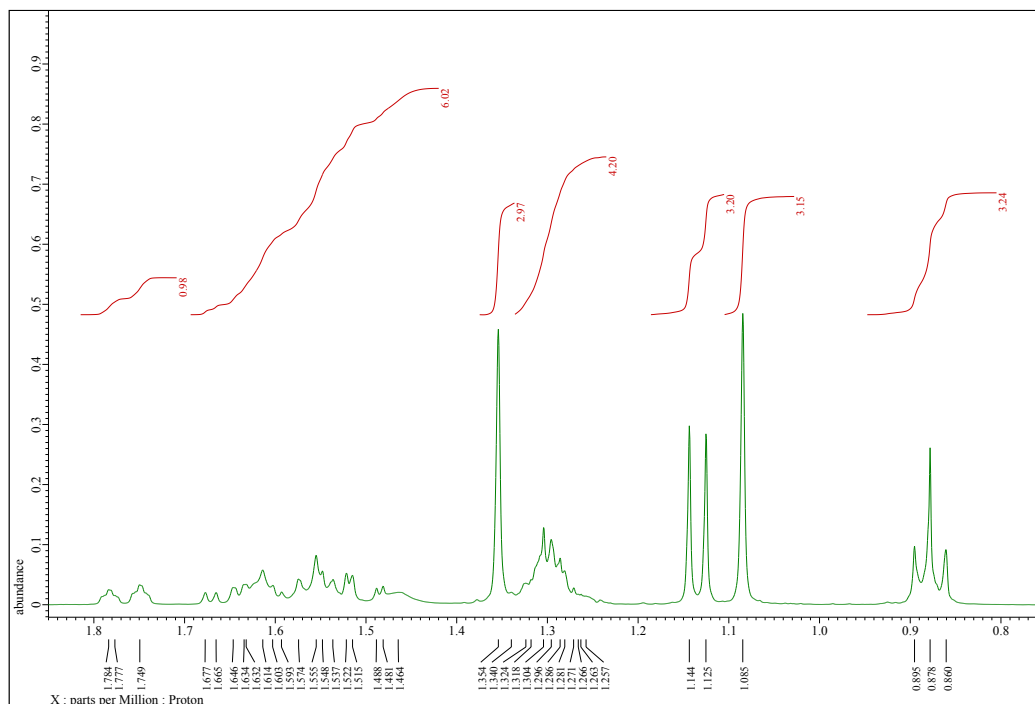
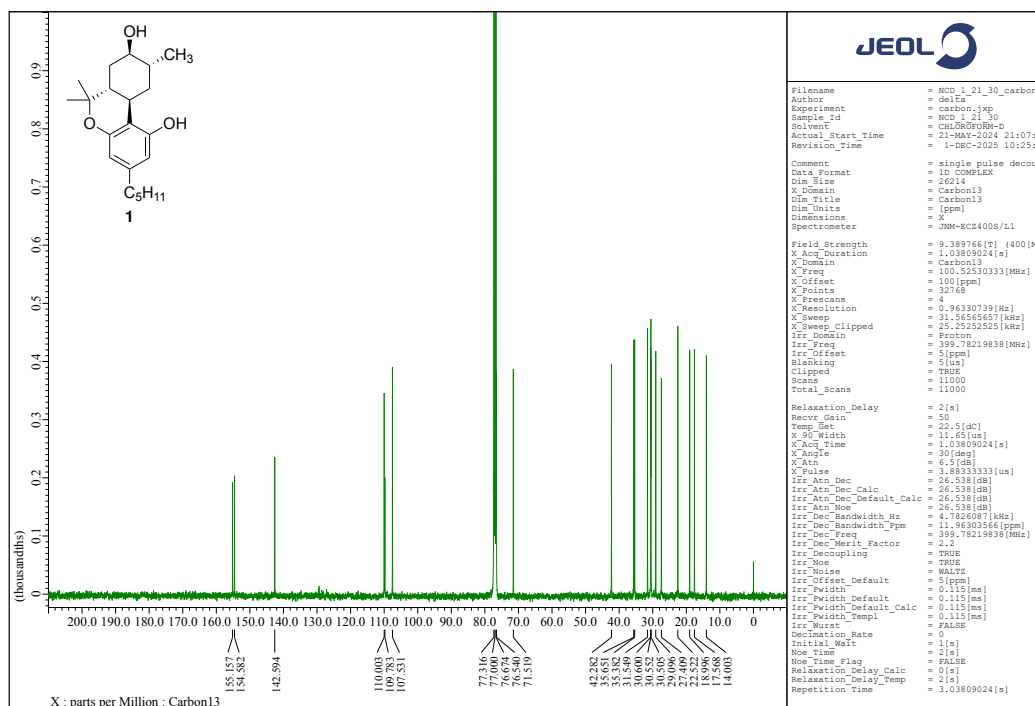


Figure S2. ^{13}C NMR (100 MHz, CDCl_3 , ppm) of **1**



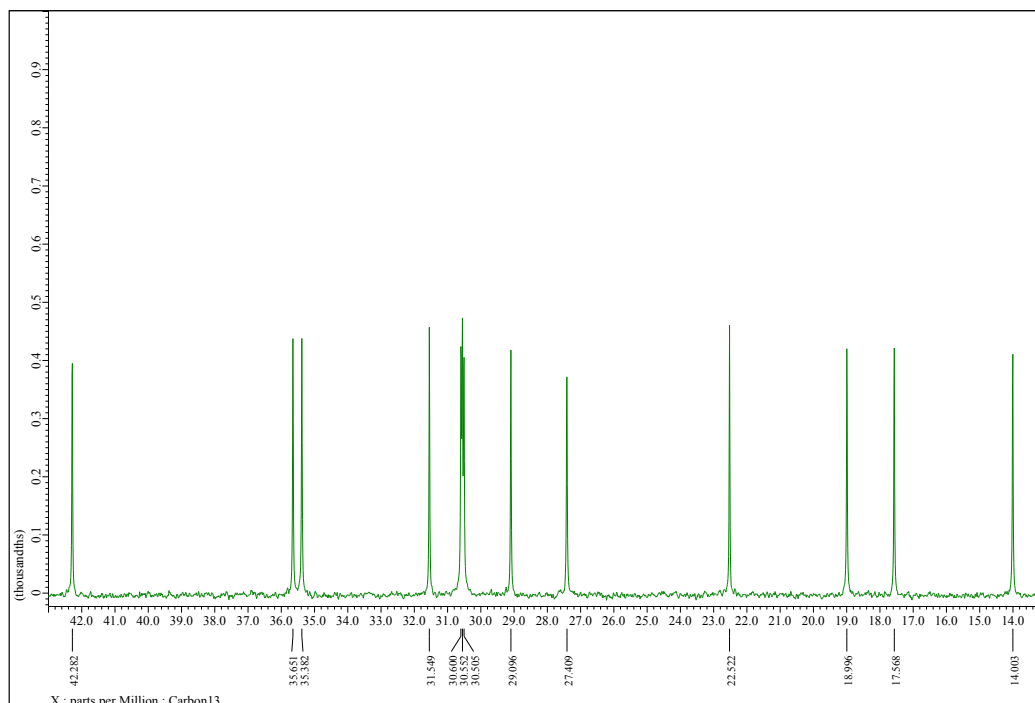
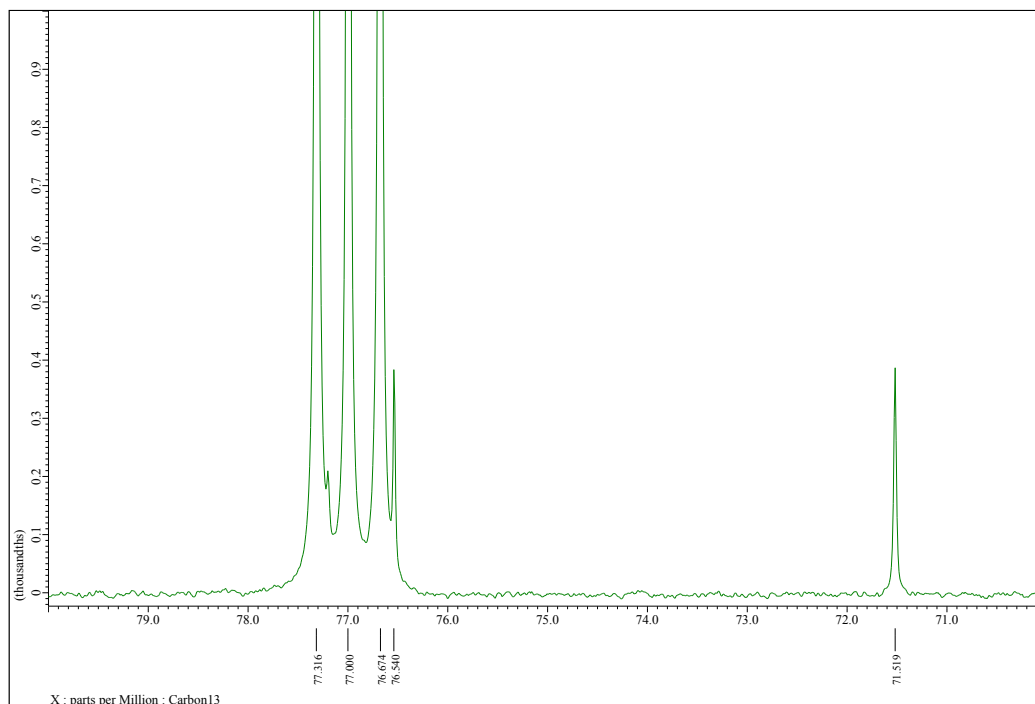


Figure S3. NOESY spectrum of **1**

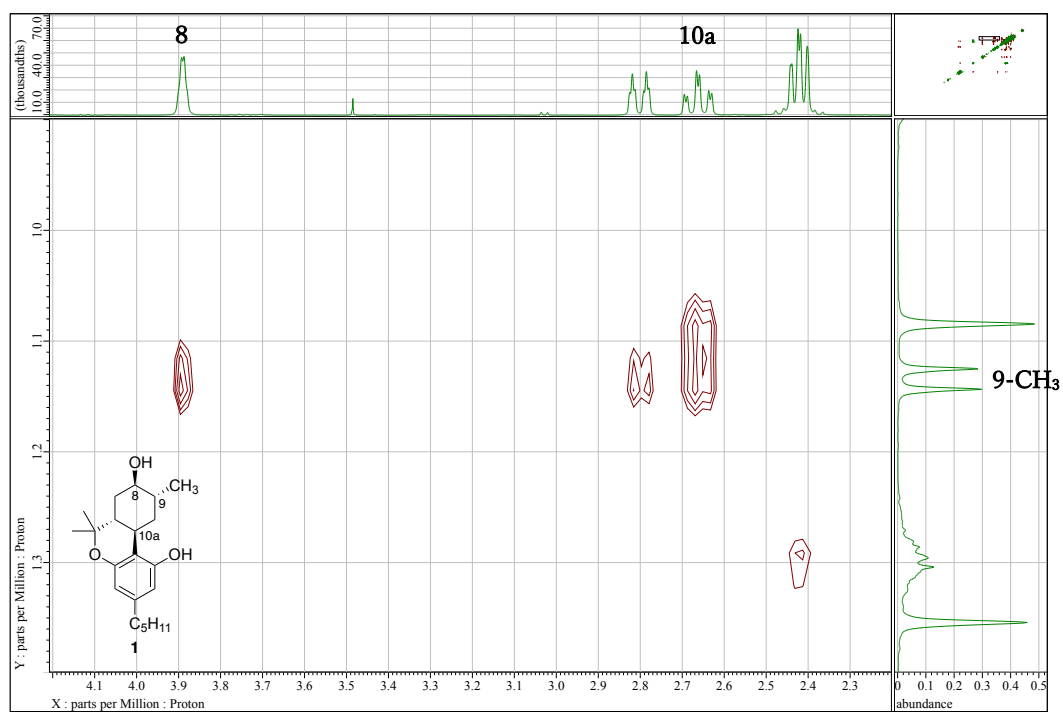
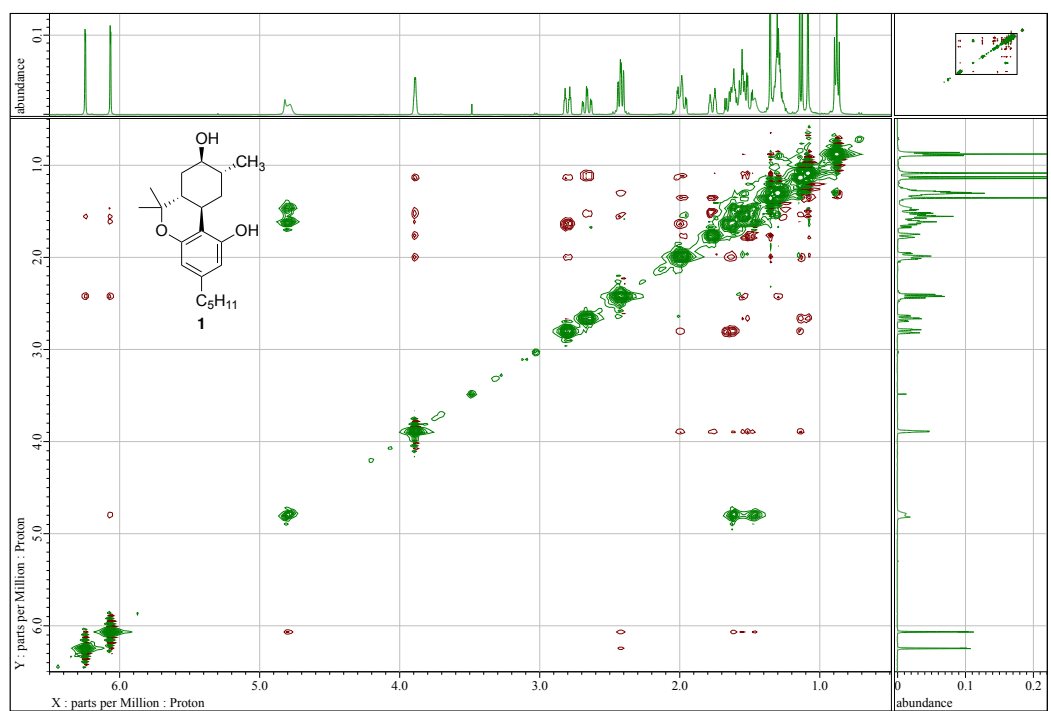


Figure S4. COSY spectrum of **1**

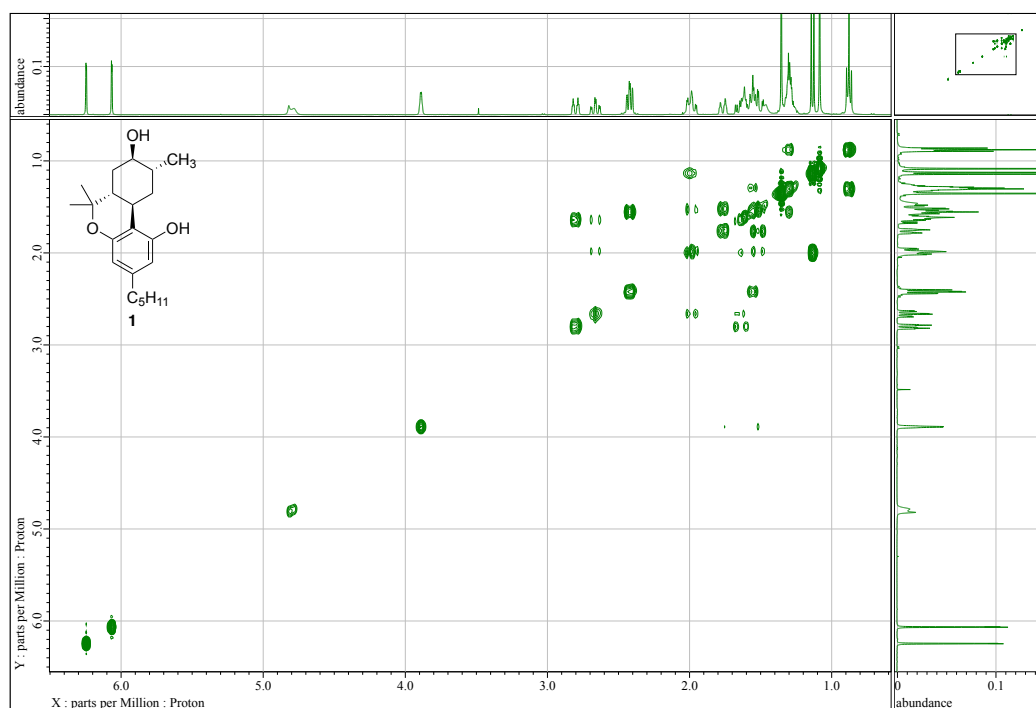


Figure S5. HSQC spectrum of **1**

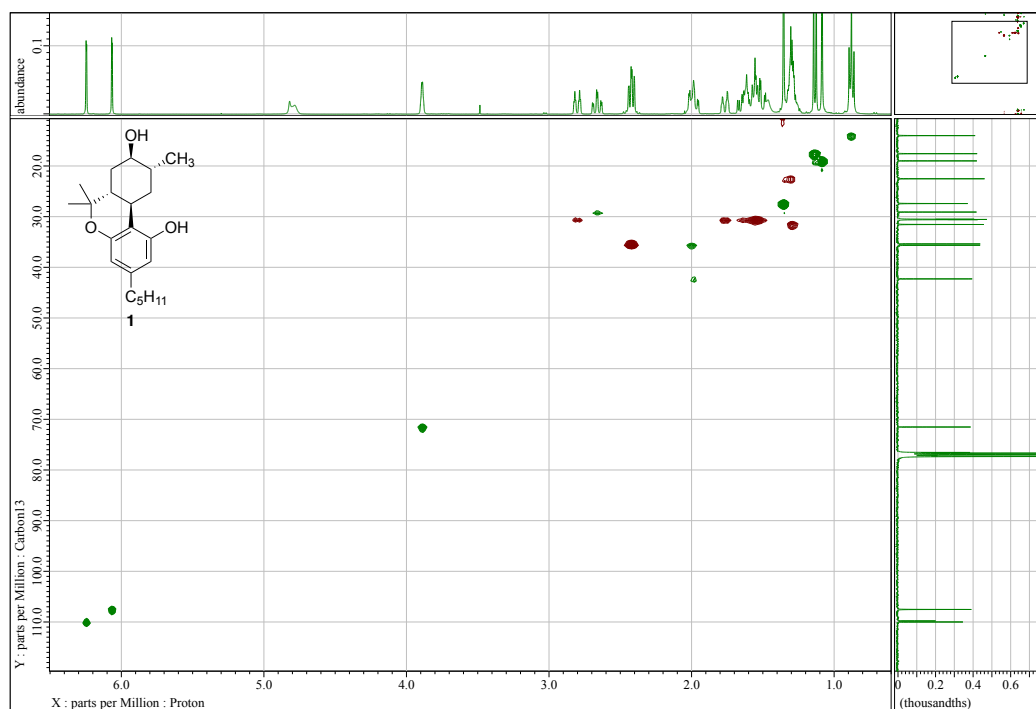


Figure S6. HMBC spectrum of **1**

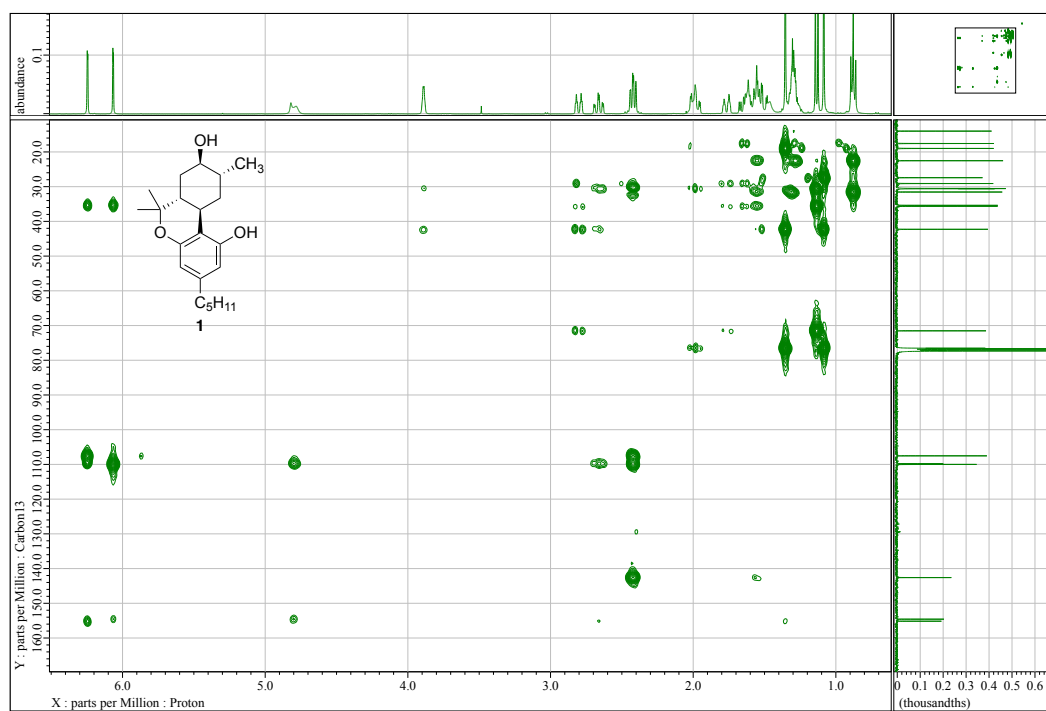
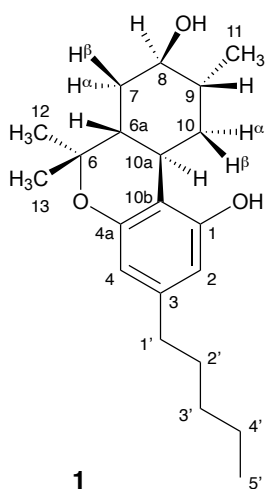


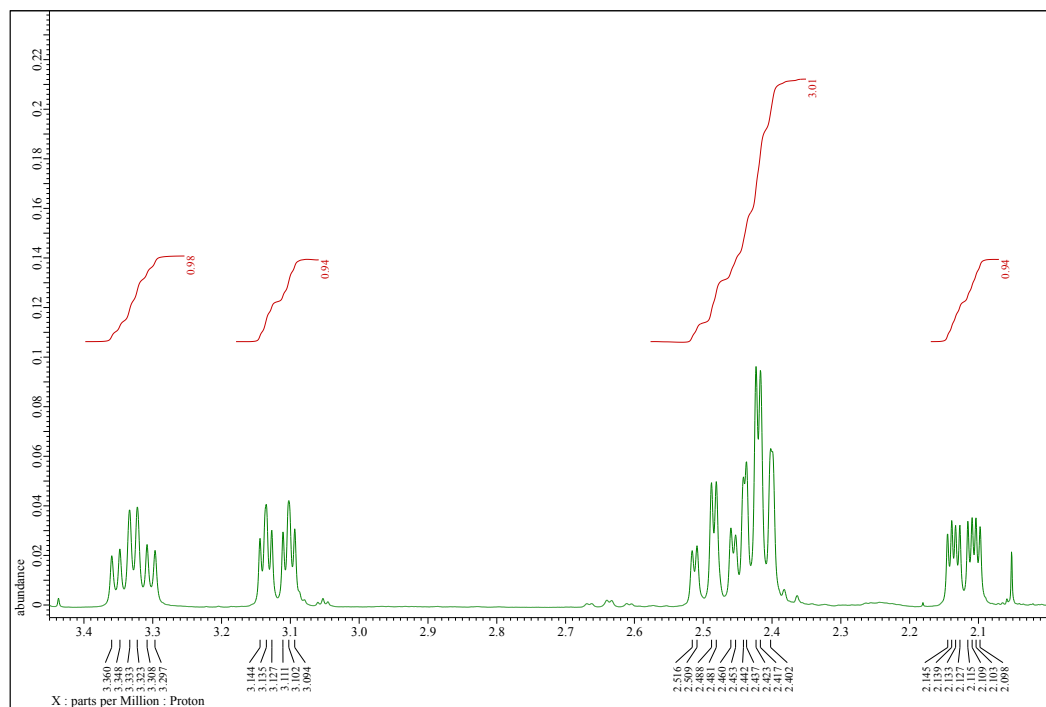
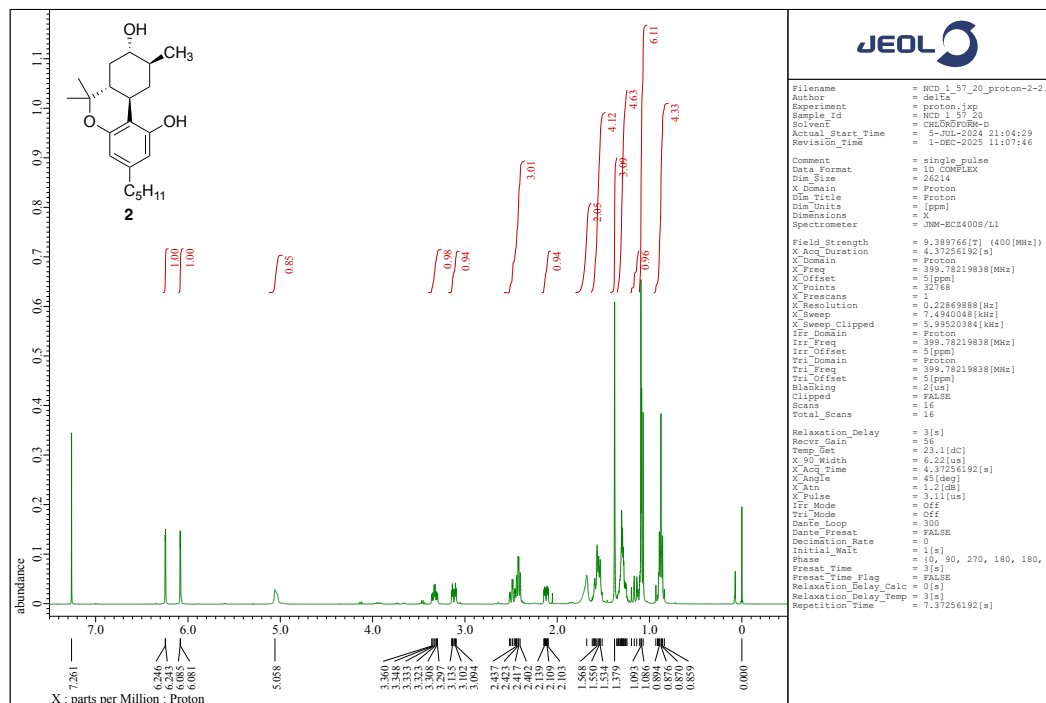
Table S1. Assignment of the peaks in the ^1H and ^{13}C NMR spectra of **1**.

	^1H	^{13}C		^1H	^{13}C
1		154.6	10	2.80 (td, 1H, 10 α)	30
				1.68–1.44 (m, 1H, 10 β)	
1-OH	4.80 (brs, 1H)		10a	2.66 (dt, 1H)	29.1
2	6.07 (d, 1H)	107.5	10b		109.8
3		142.6	11	1.14 (d, 3H)	17.6
4	6.25 (d, 1H)	110.0	12	1.09 (s, 3H)	19.0
4a		155.2	13	1.35 (s, 3H)	27.4
6		76.5	1'	2.48–2.36 (m, 2H)	35.4
6a	2.04–1.95 (m, 1H)	42.3	2'	1.68–1.44 (m, 2H)	30
7	1.68–1.44 (m, 1H, 7 α)	30	3'	1.34–1.24 (m, 2H)	31.5
	1.77 (dtd, 1H, 7 β)				
8	3.89 (q, 1H)	71.5	4'	1.34–1.24 (m, 2H)	22.5
8-OH	1.68–1.44 (m, 1H)		5'	0.88 (t, 3H)	14.0
9	2.04–1.95 (m, 1H)	35.7			



2. NMR Spectra of 2

Figure S7. ^1H NMR (400 MHz, CDCl_3 , ppm) of **2**



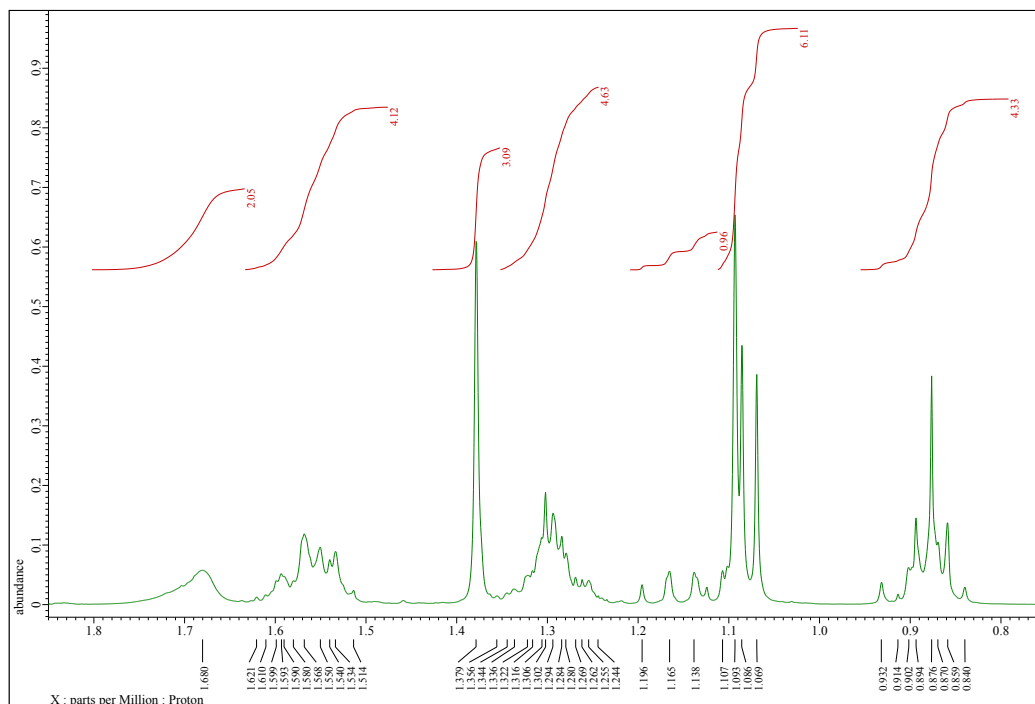
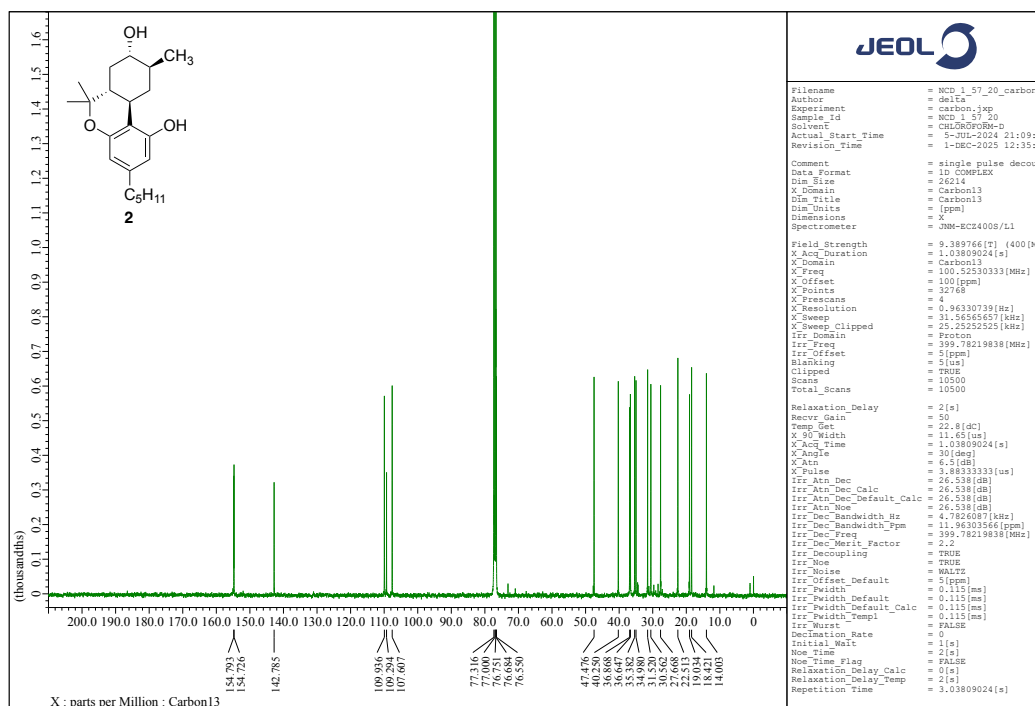


Figure S8. ^{13}C NMR (100 MHz, CDCl_3 , ppm) of **2**



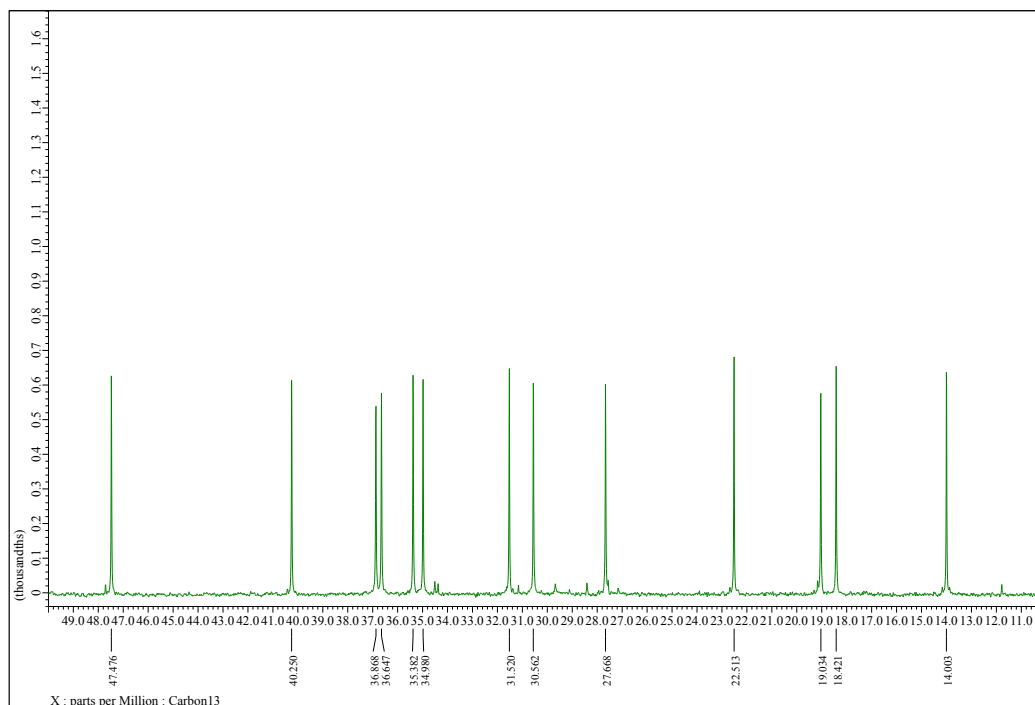
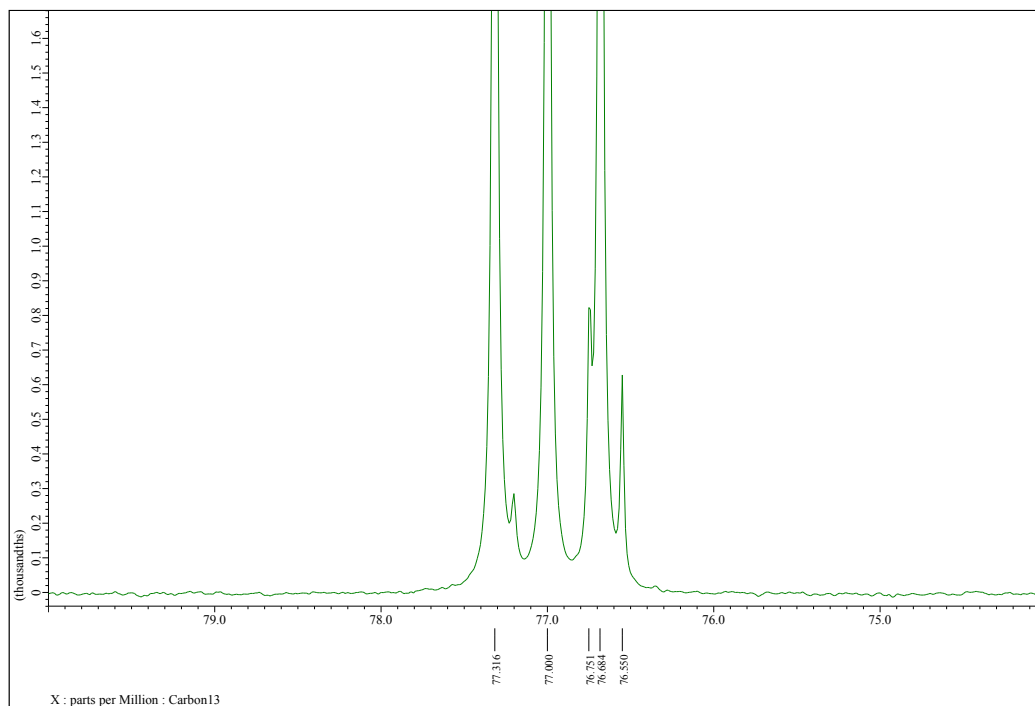
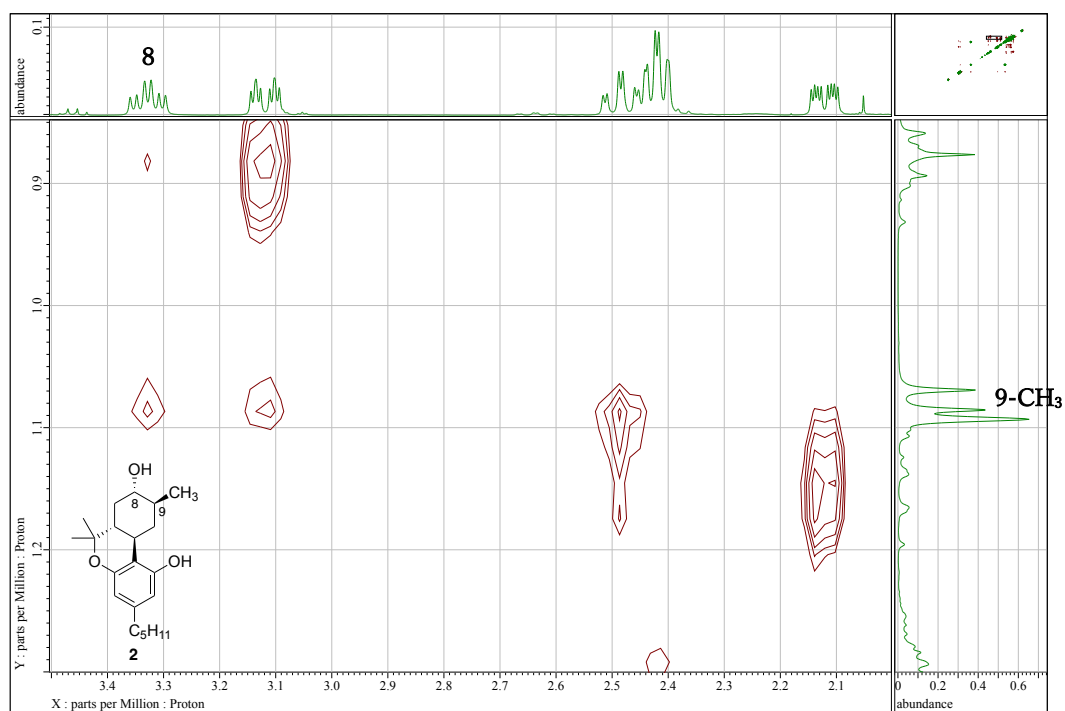
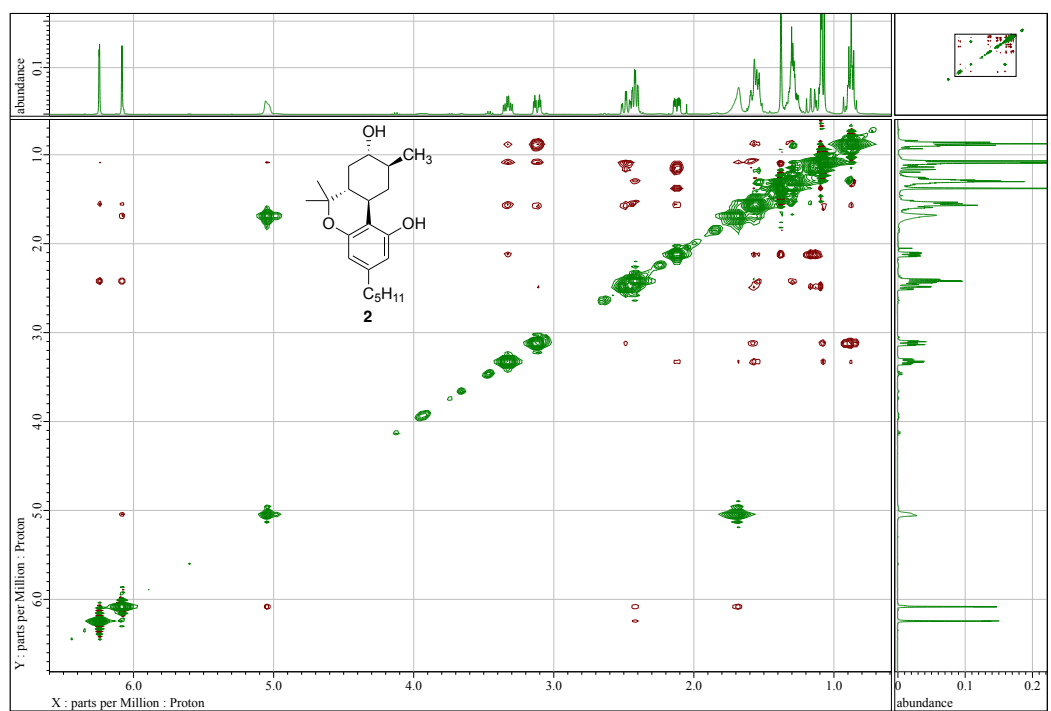


Figure S9. NOESY spectrum of **2**



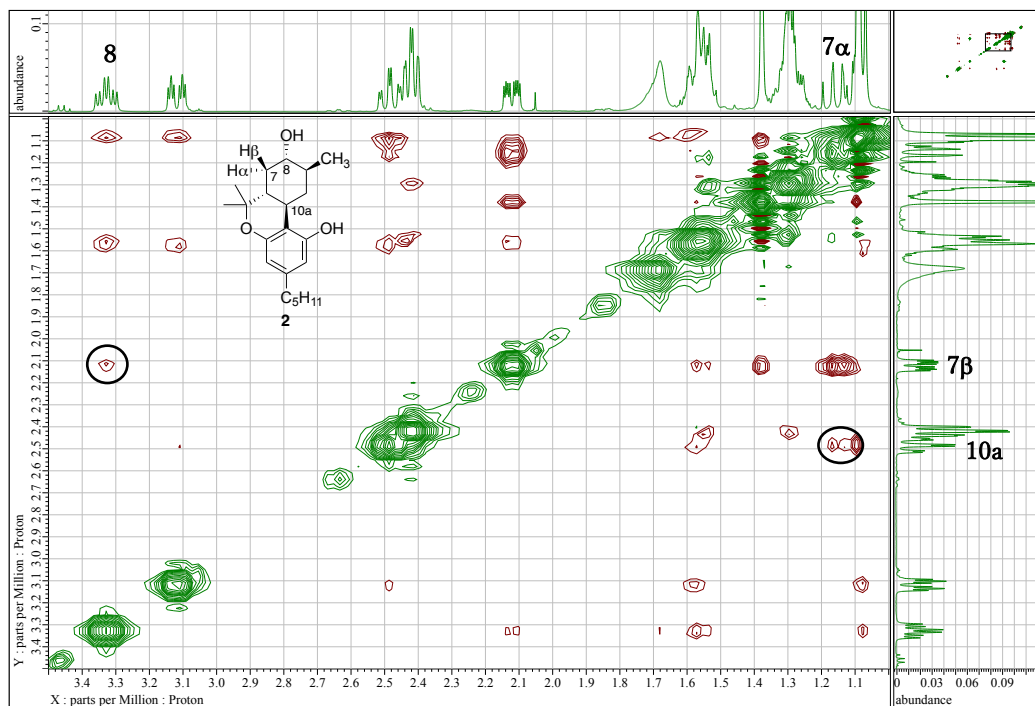


Figure S10. COSY spectrum of **2**

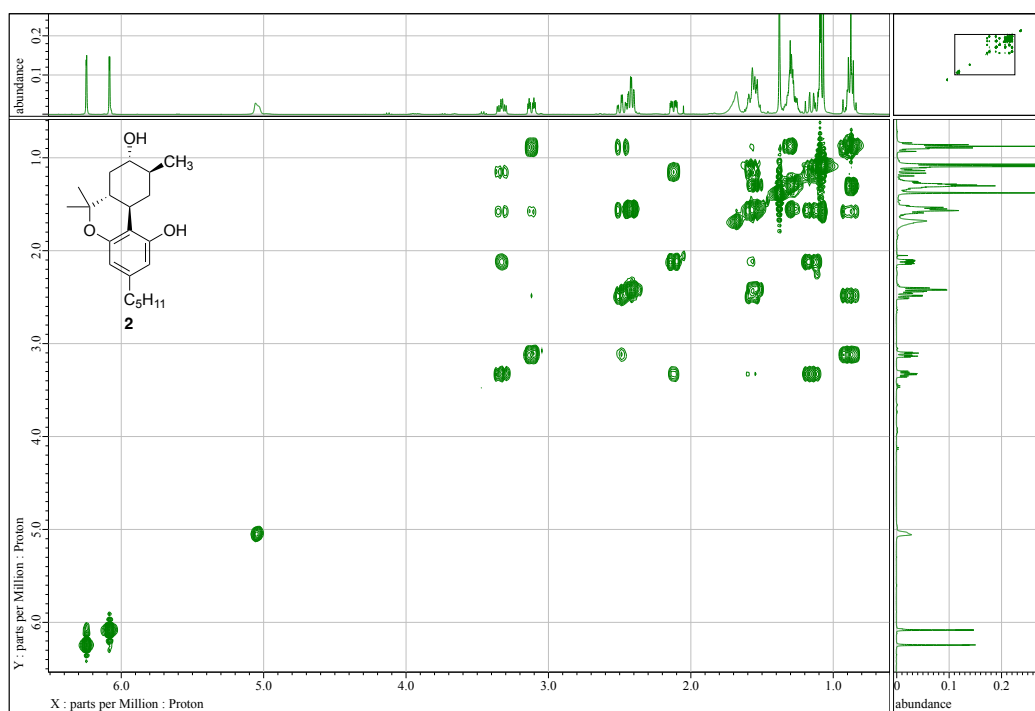


Figure S11. HSQC spectrum of **2**

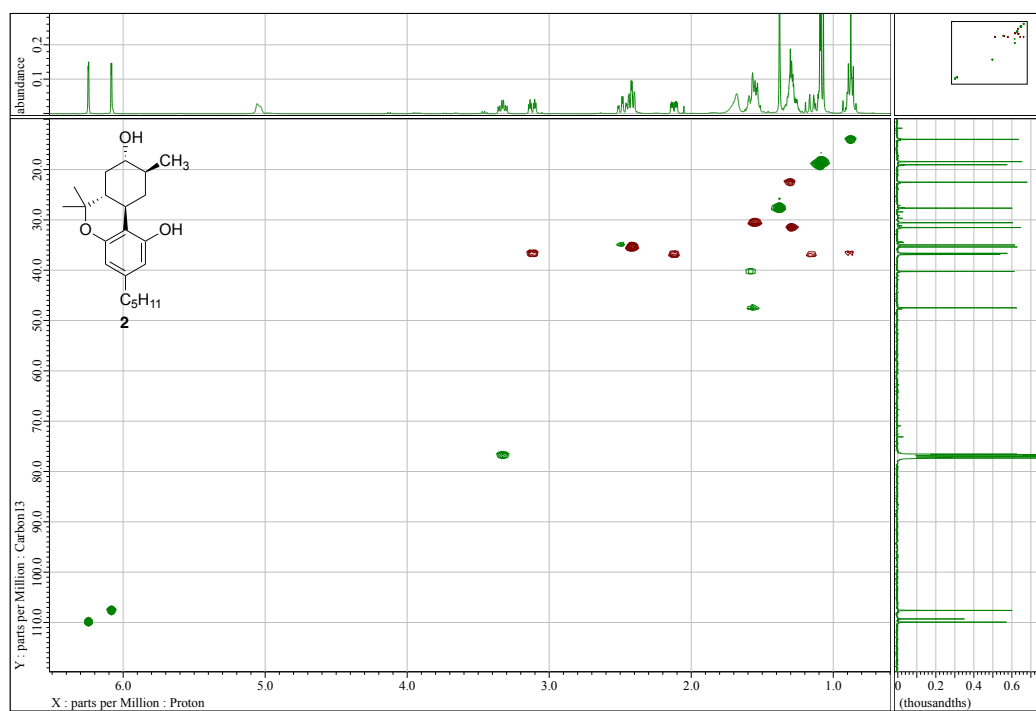


Figure S12. HMBC spectrum of **2**

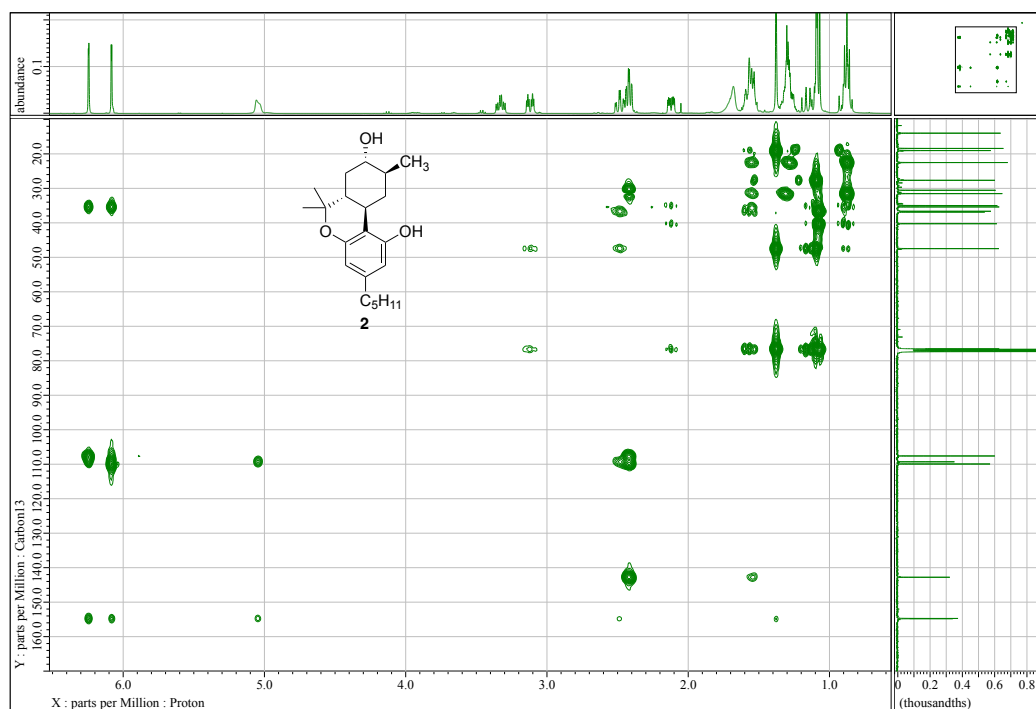
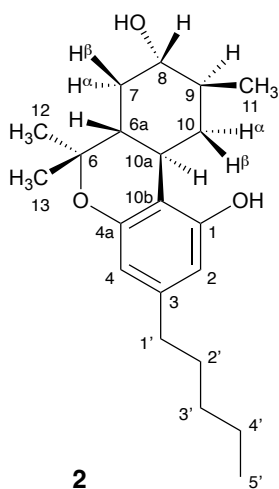


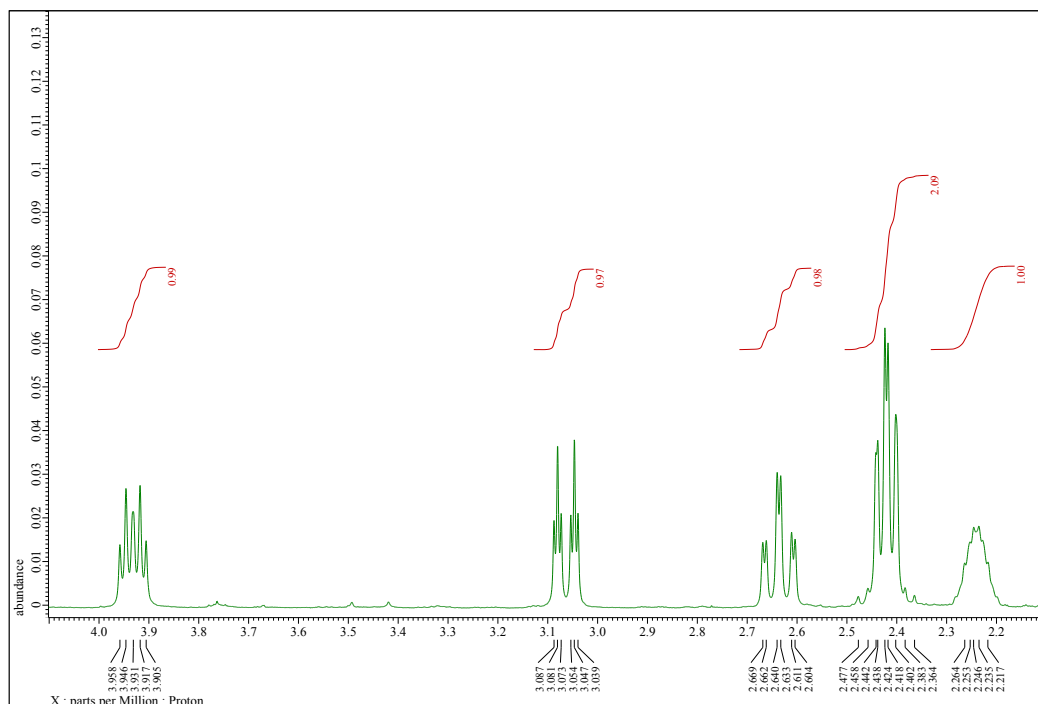
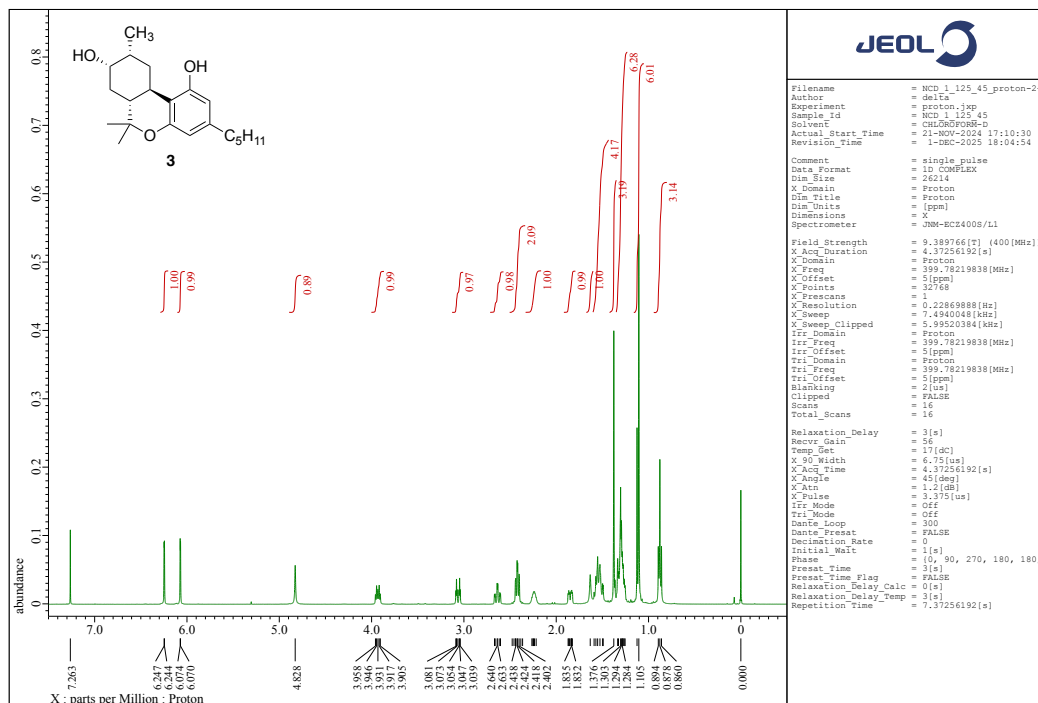
Table S2. Assignment of the peaks in the ^1H and ^{13}C NMR spectra of **2**.

	^1H	^{13}C		^1H	^{13}C
1		154	10	3.12 (td, 1H, 10 α) 1.77 (dtd, 1H, 10 β)	36.6
1-OH	5.06 (brs, 1H)		10a	2.48 (dt, 1H)	35.0
2	6.08 (d, 1H)	107.6	10b		109.3
3		142.8	11	1.08 (d, 3H)	19
4	6.24 (d, 1H)	109.9	12	1.09 (s, 3H)	19
4a		154	13	1.38 (s, 3H)	27.7
6		76	1'	2.44–2.40 (m, 2H)	35.4
6a	1.61–1.51 (m, 1H)	47.5	2'	1.61–1.51 (m, 2H)	30.6
7	1.20–1.10 (m, 1H, 7 α) 2.12 (ddd, 1H, 7 β)	36.9	3'	1.35–1.25 (m, 2H)	31.5
8	3.33 (dt, 1H)	76	4'	1.35–1.25 (m, 2H)	22.5
8-OH	1.68 (brs, 1H)		5'	0.88 (t, 3H)	14.0
9	1.61–1.51 (m, 1H)	40.3			



3. NMR Spectra of 3

Figure S13. ^1H NMR (400 MHz, CDCl_3 , ppm) of 3



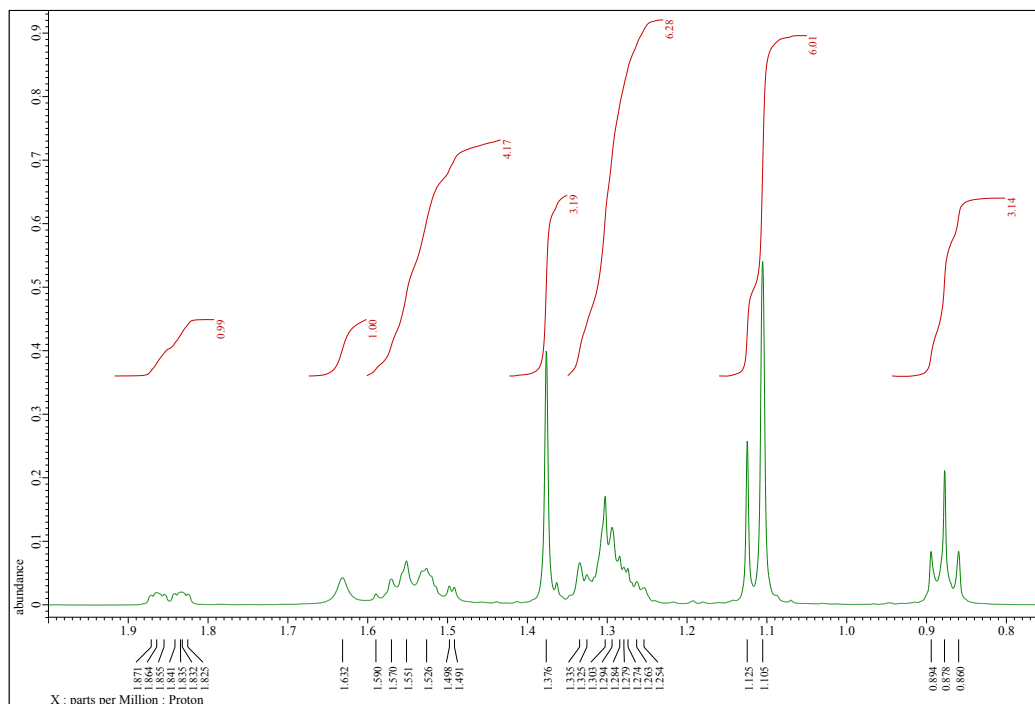
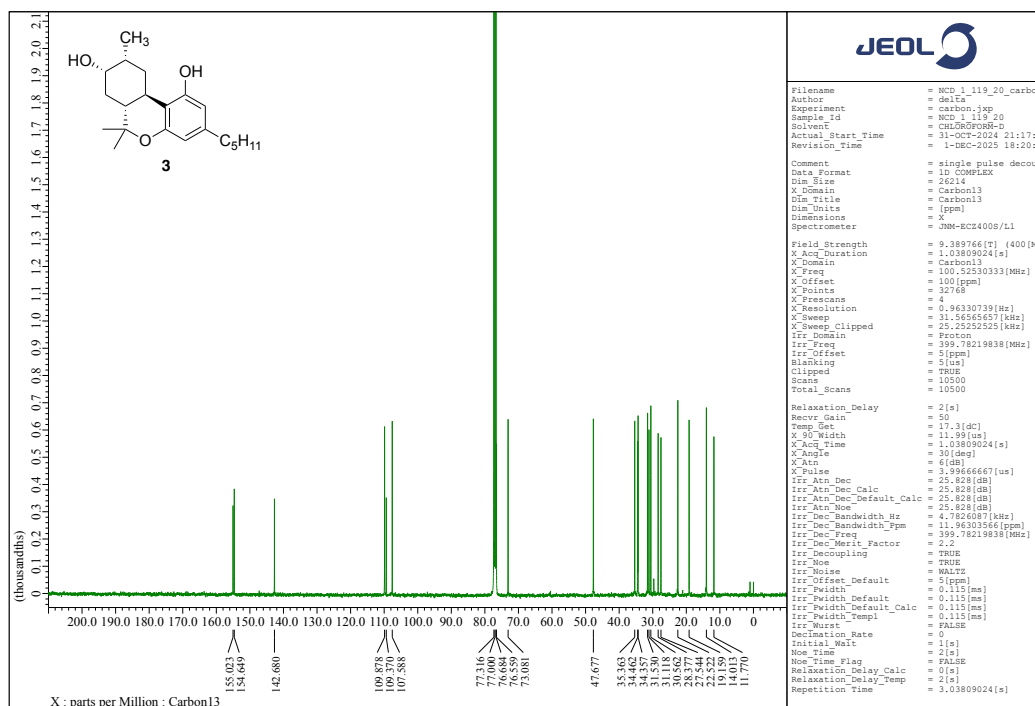


Figure S14. ^{13}C NMR (100 MHz, CDCl_3 , ppm) of **3**



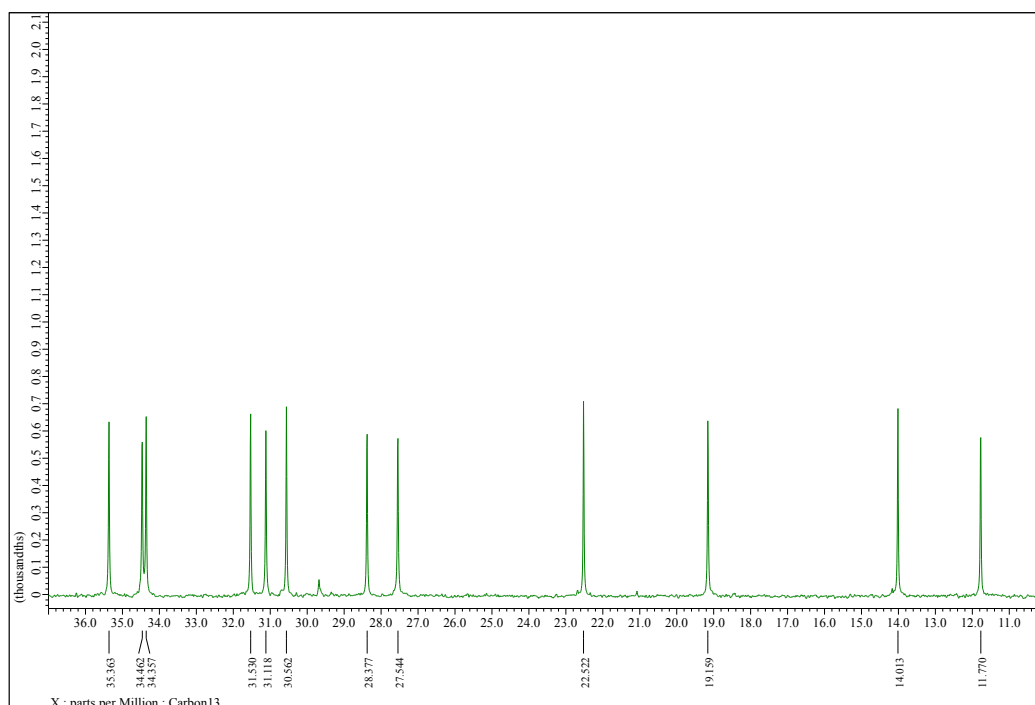
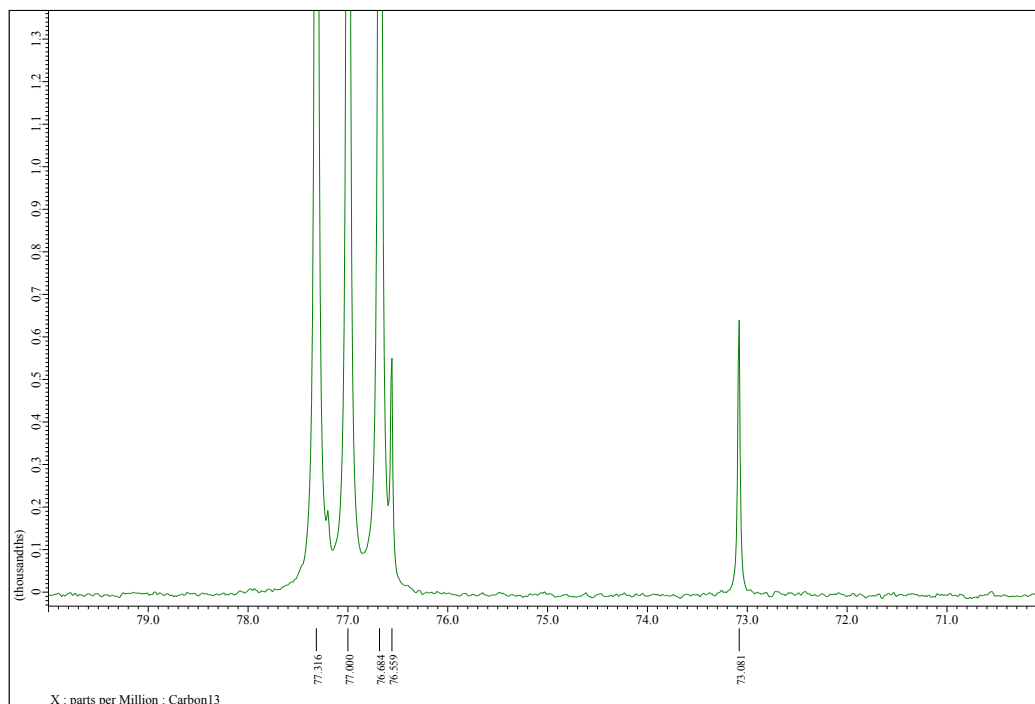
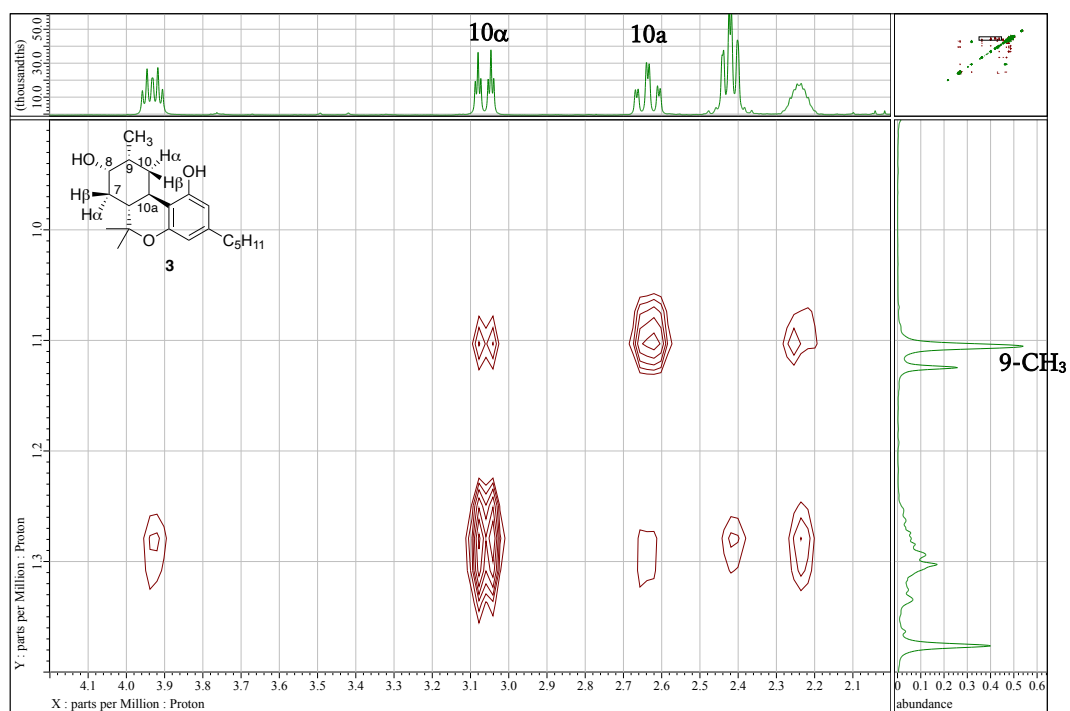
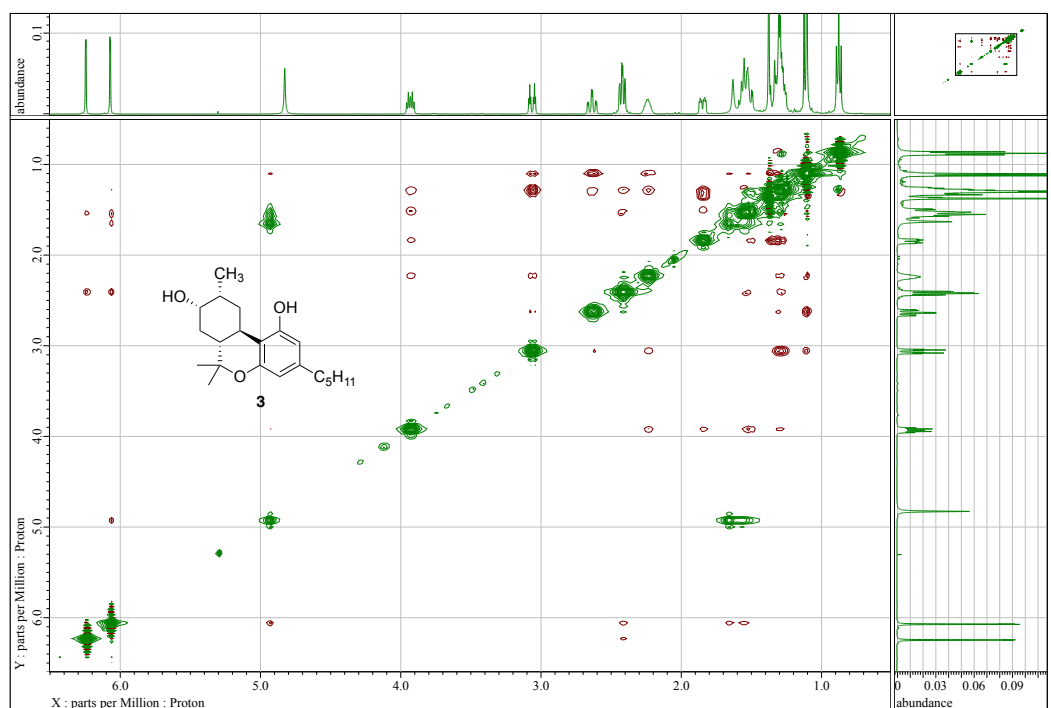


Figure S15. NOESY spectrum of **3**



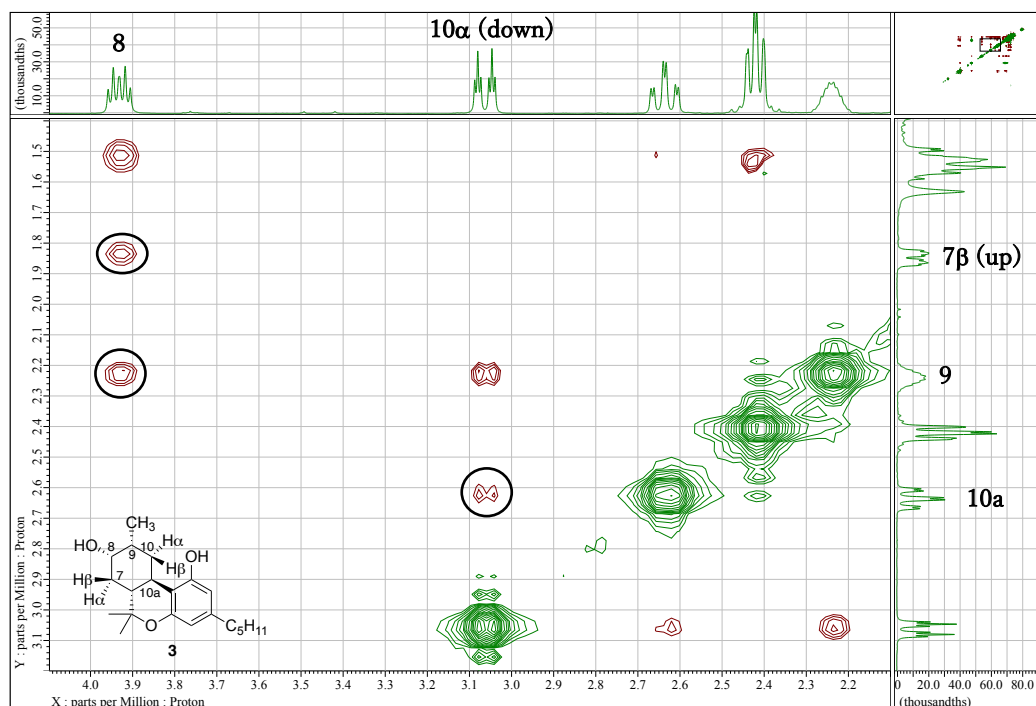


Figure S16. COSY spectrum of **3**

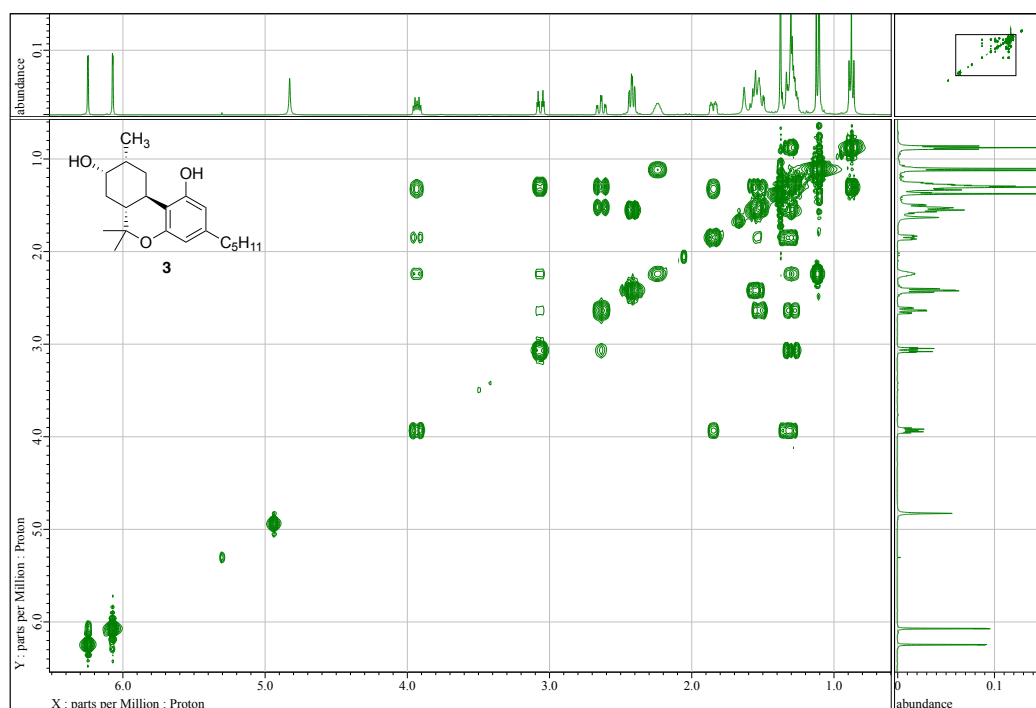


Figure S17. HSQC spectrum of **3**

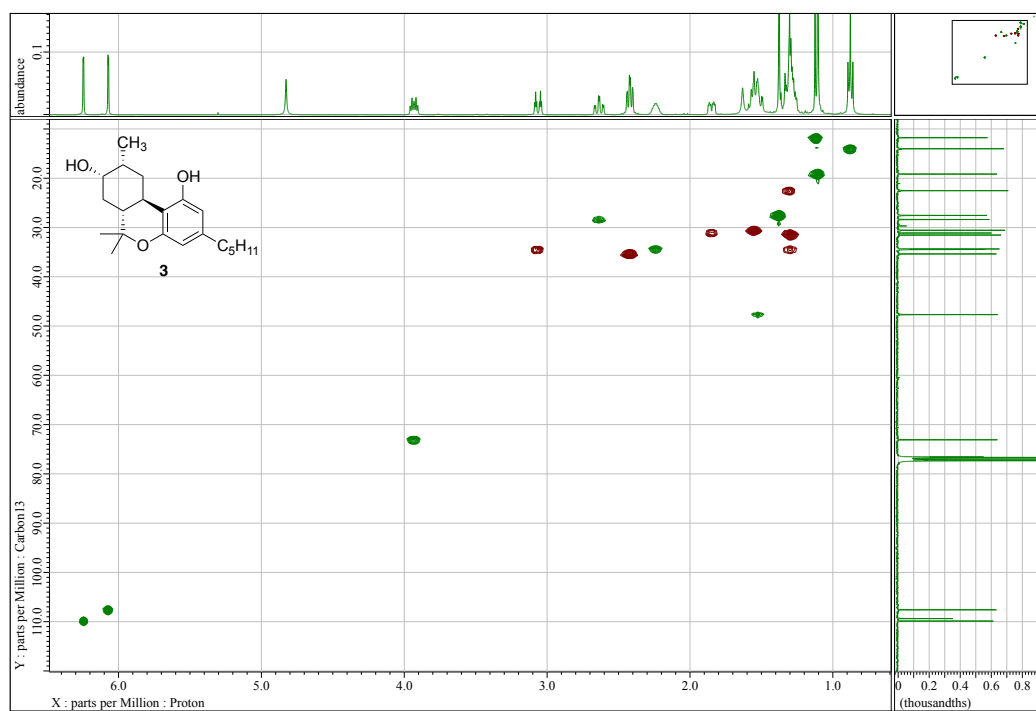


Figure S18. HMBC spectrum of **3**

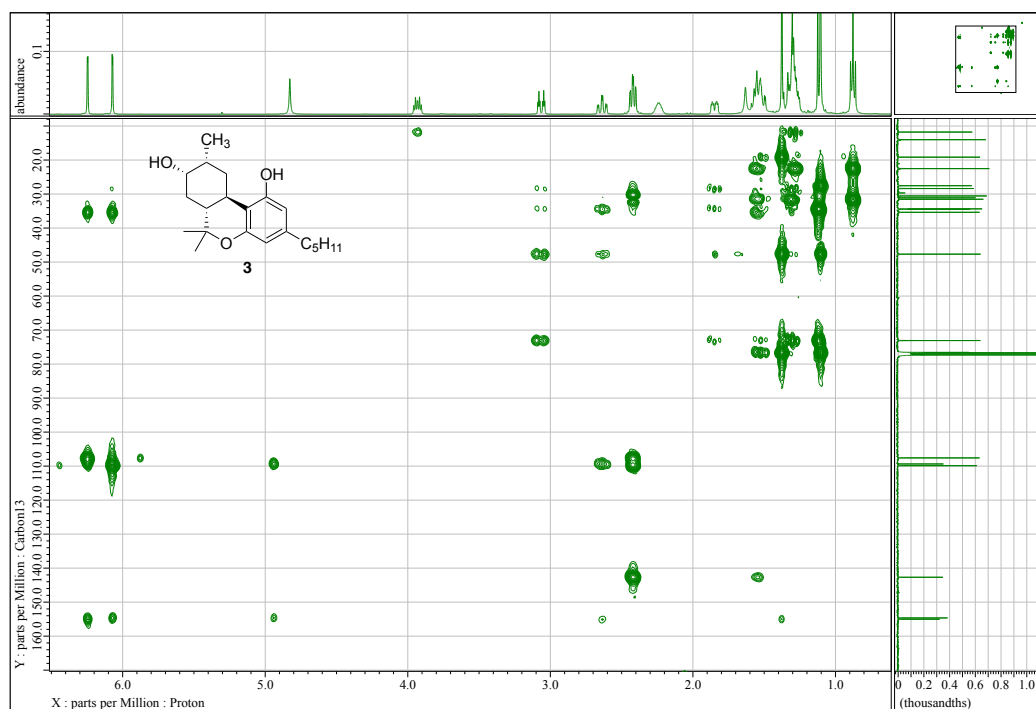
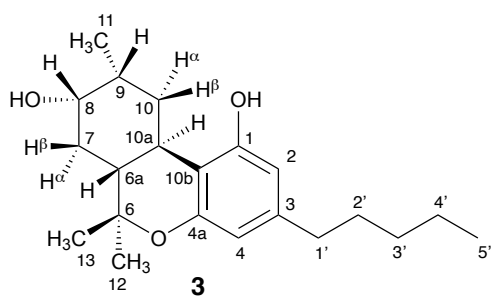


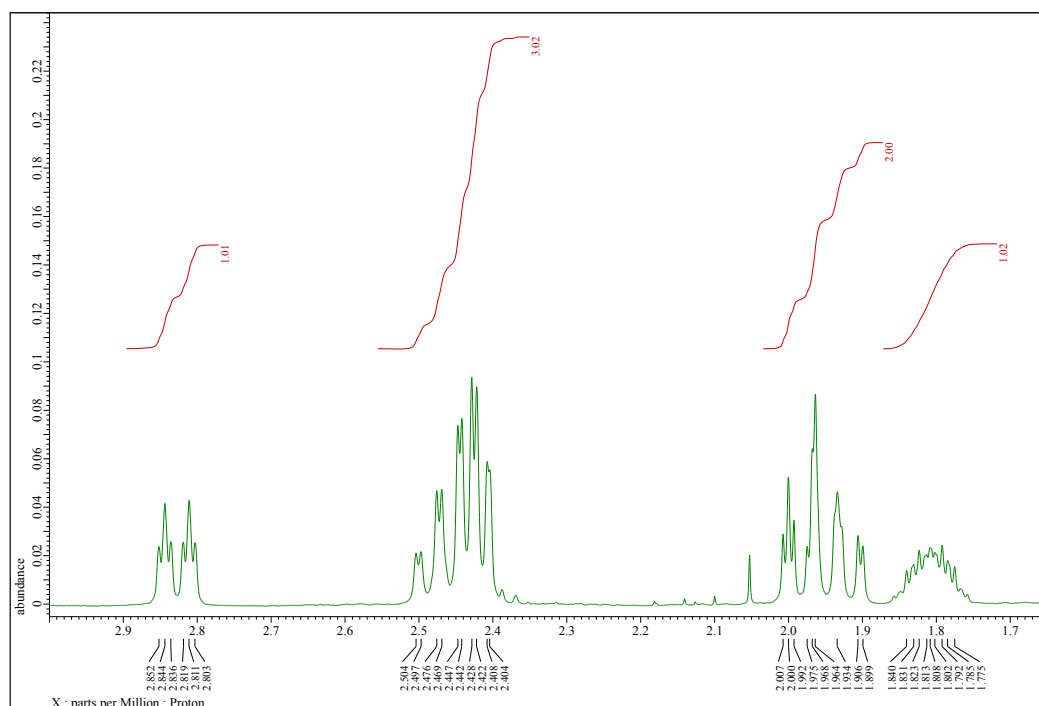
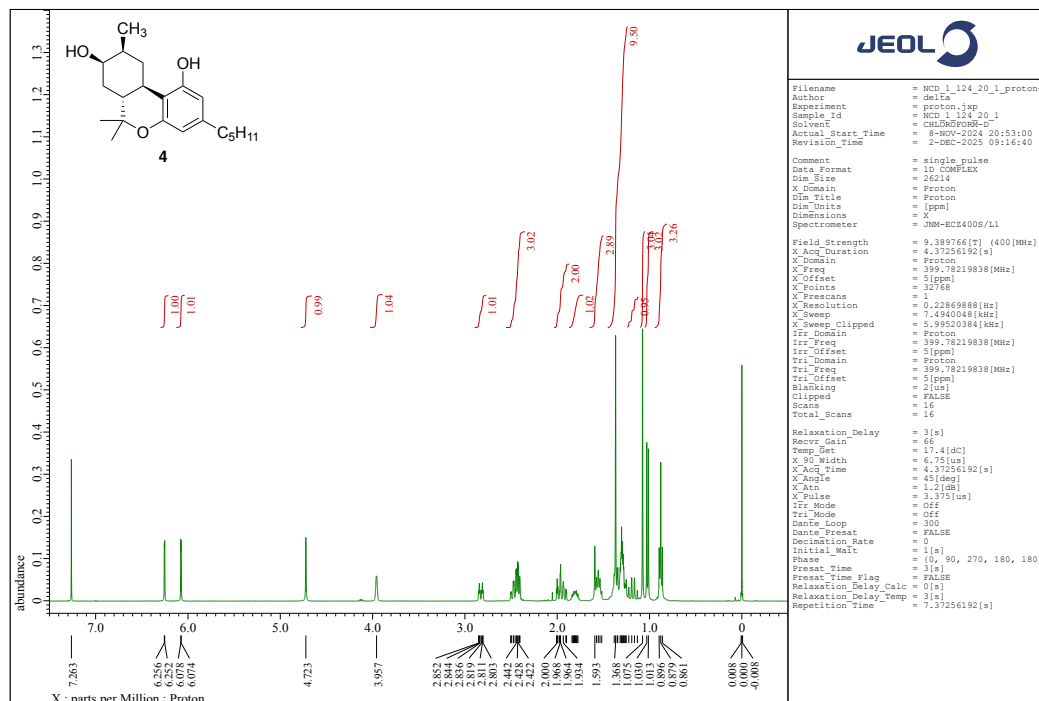
Table S3. Assignment of the peaks in the ^1H and ^{13}C NMR spectra of **3**.

	^1H	^{13}C		^1H	^{13}C
1		154.6	10	3.06 (td, 1H, 10 α)	34
				1.34–1.25 (m, 1H, 10 β)	
1-OH	4.83 (brs, 1H)		10a	2.64 (dt, 1H)	28.4
2	6.07 (d, 1H)	107.5	10b		107.6
3		142.7	11	1.12 (d, 3H)	11.8
4	6.25 (d, 1H)	109.9	12	1.11 (s, 3H)	19.2
4a		155.0	13	1.38 (s, 3H)	27.5
6		76.6	1'	2.44–2.40 (m, 2H)	35.4
6a	1.59–1.49 (m, 1H)	47.7	2'	1.59–1.49 (m, 2H)	30.6
7	1.34–1.25 (m, 1H, 7 α)	31	3'	1.34–1.25 (m, 2H)	31
	1.88–1.82 (m, 1H, 7 β)				
8	3.93 (td, 1H)	73.1	4'	1.34–1.25 (m, 2H)	22.5
8-OH	1.63 (brs, 1H)		5'	0.88 (t, 3H)	14.0
9	2.29–2.20 (m, 1H)	34			



4. NMR Spectra of 4

Figure S19. ^1H NMR (400 MHz, CDCl_3 , ppm) of 4



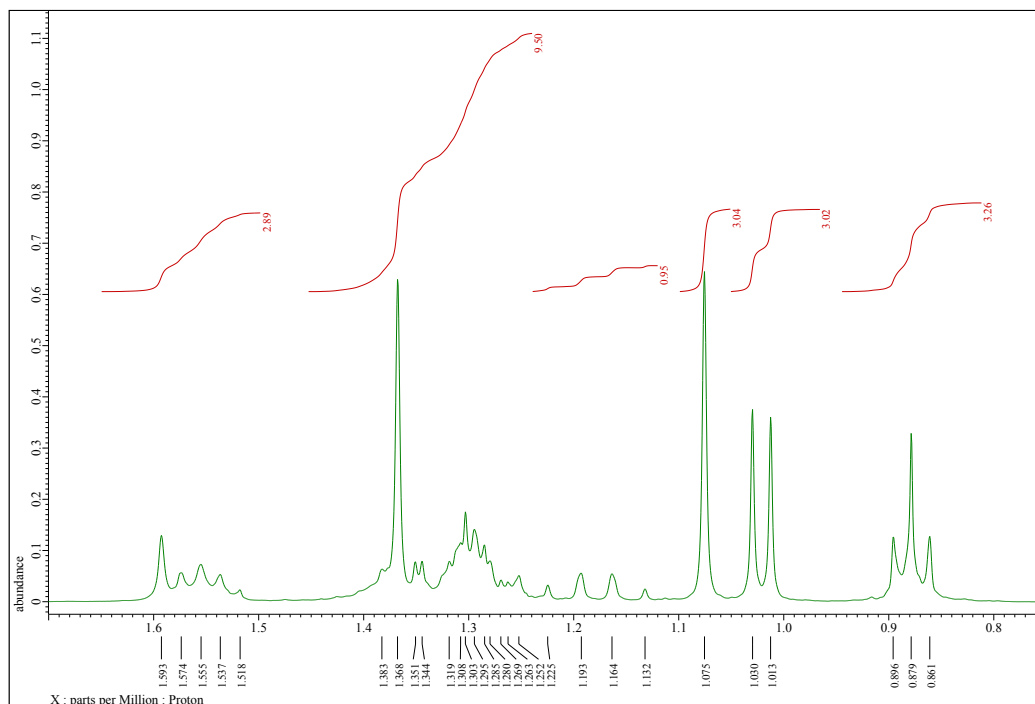
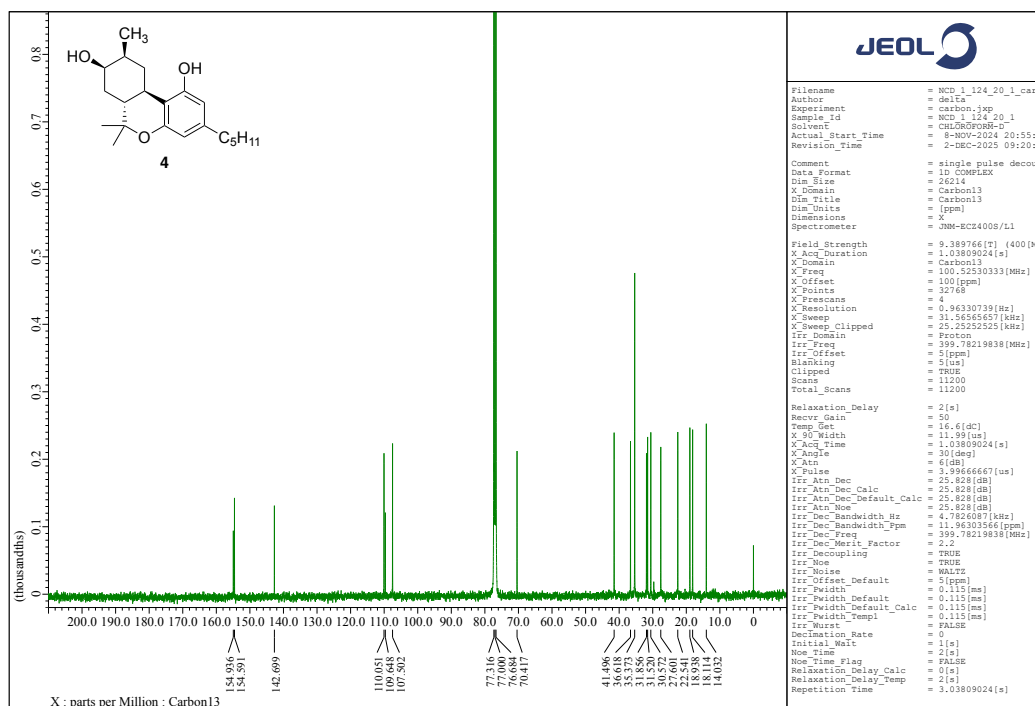


Figure S20. ^{13}C NMR (100 MHz, CDCl_3 , ppm) of **4**



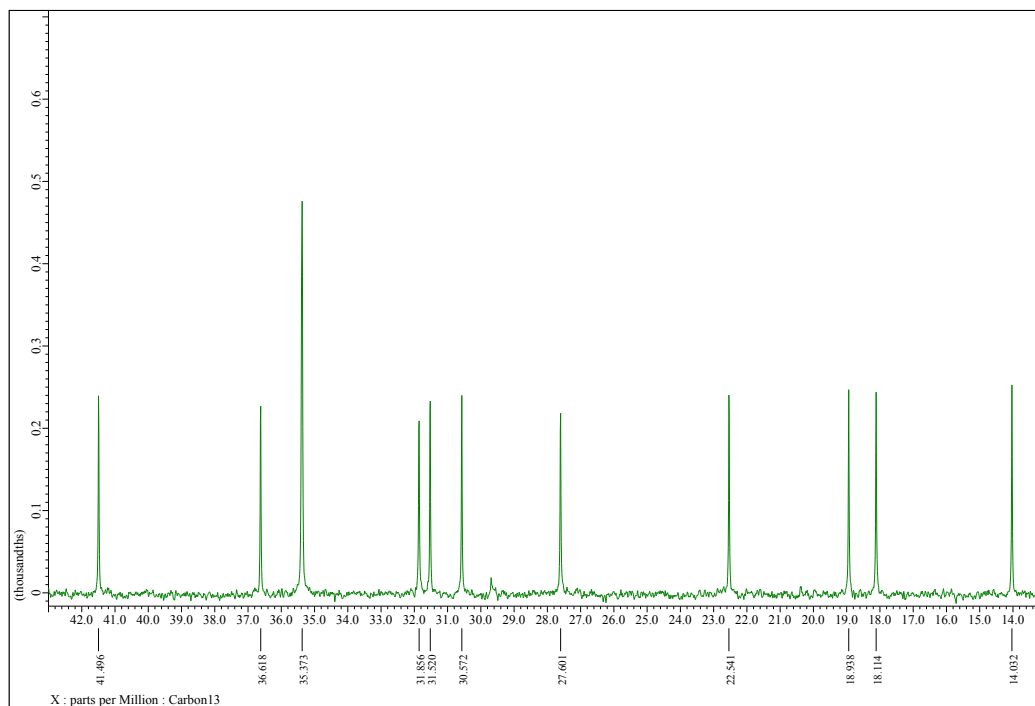
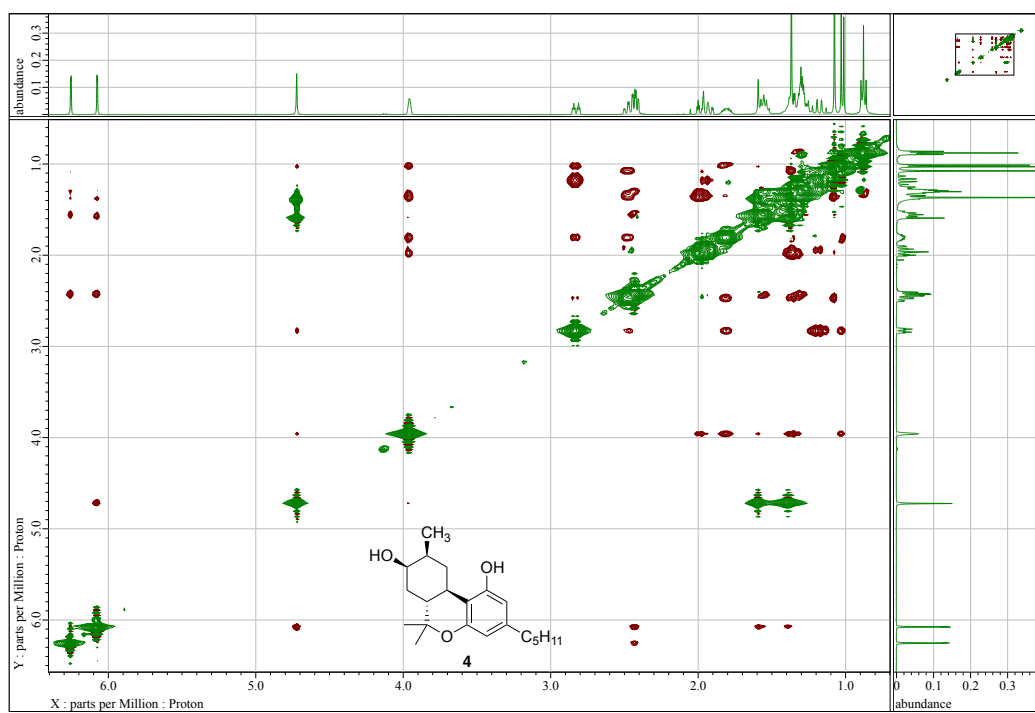


Figure S21. NOESY spectrum of **4**



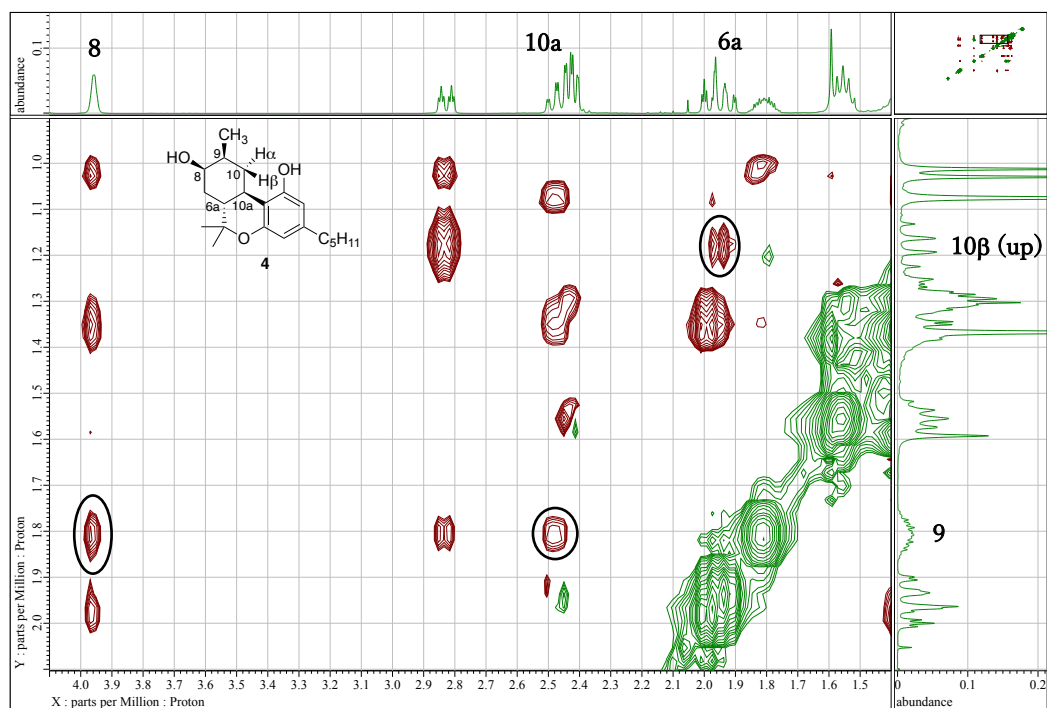


Figure S22. COSY spectrum of **4**

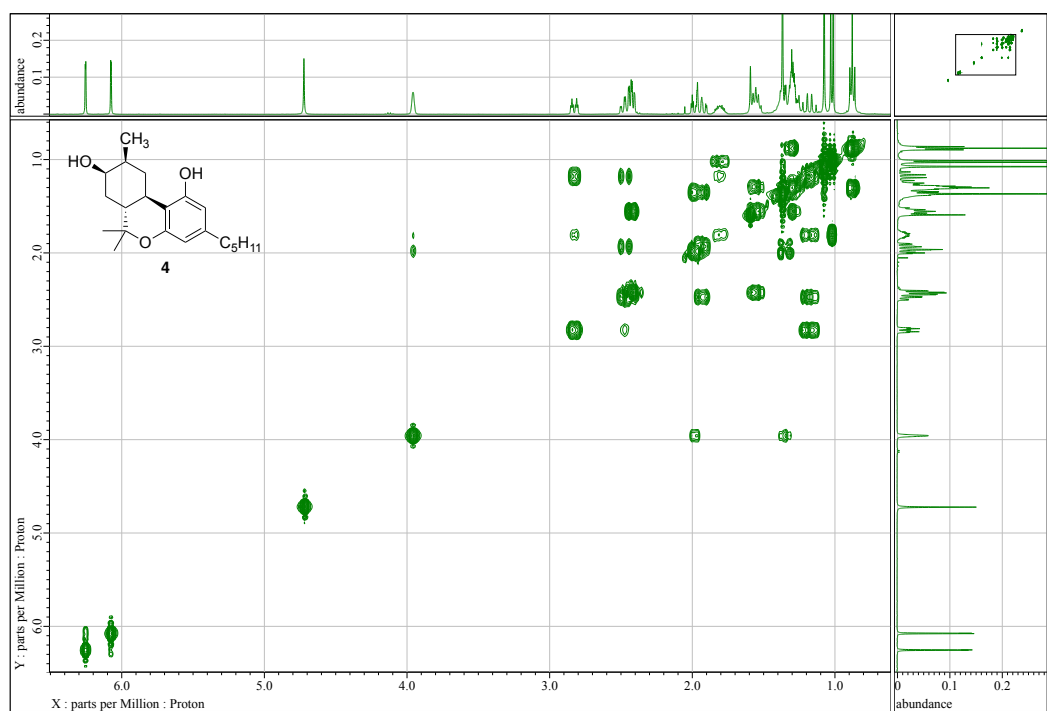


Figure S23. HSQC spectrum of **4**

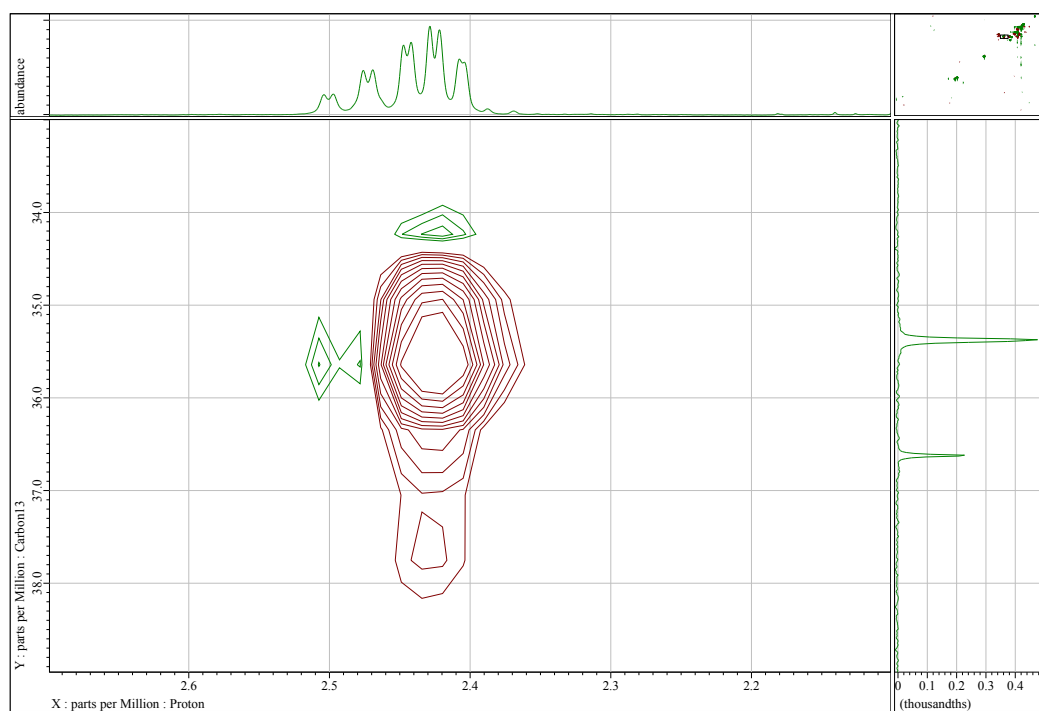
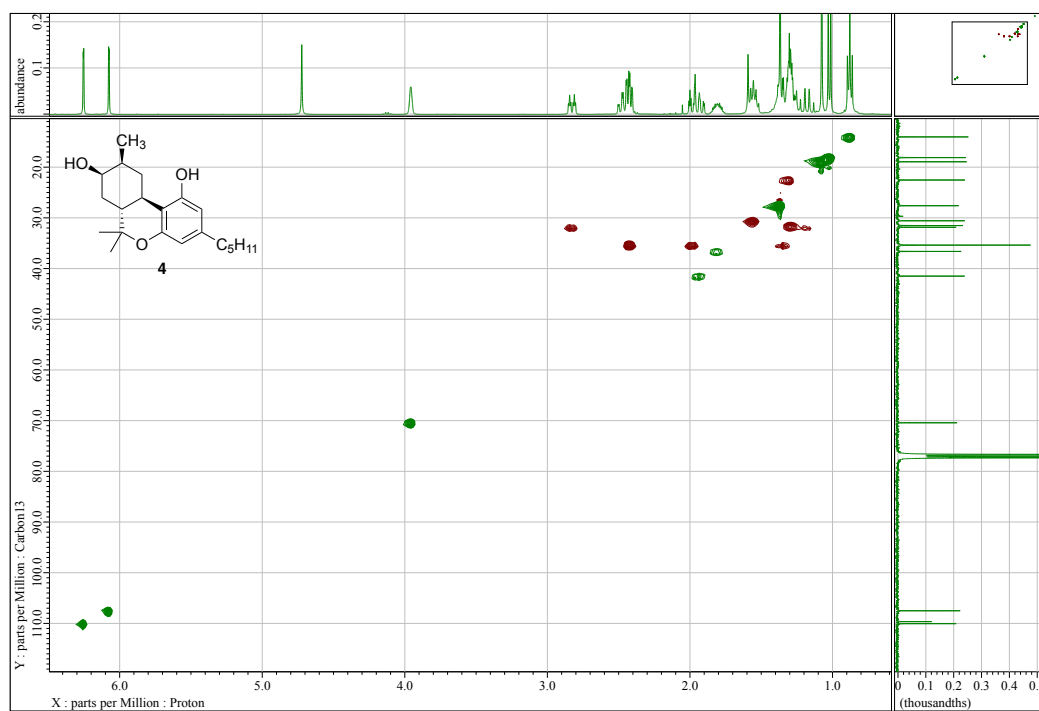


Figure S24. HMBC spectrum of **4**

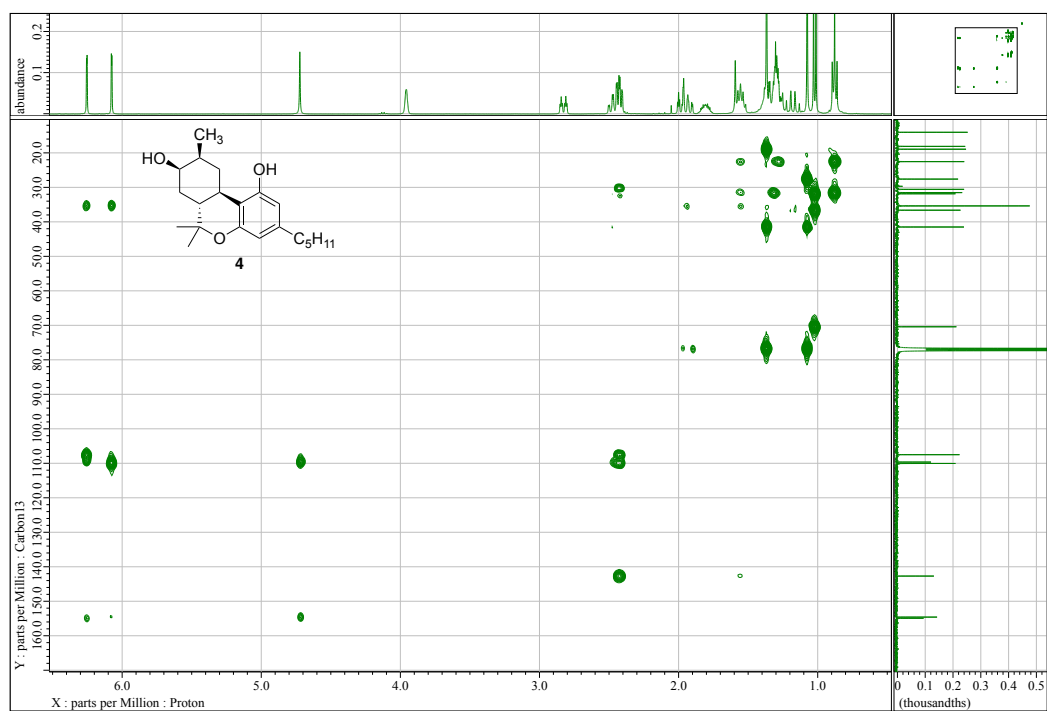
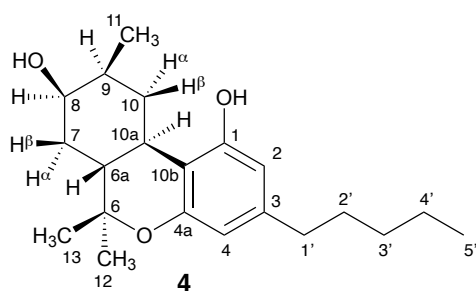


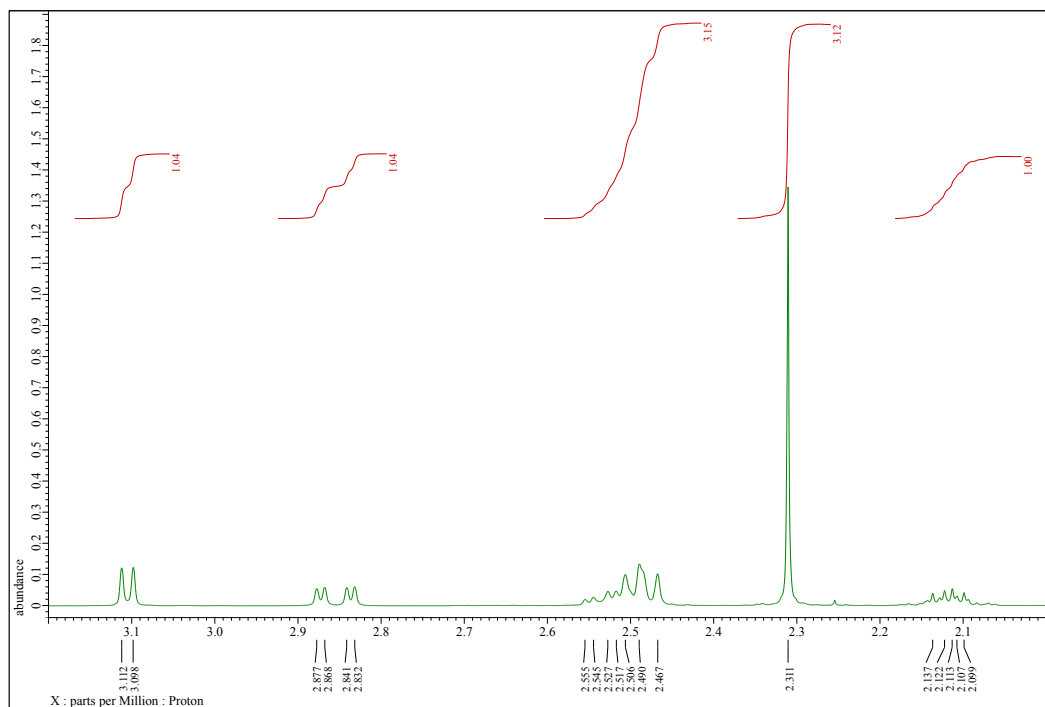
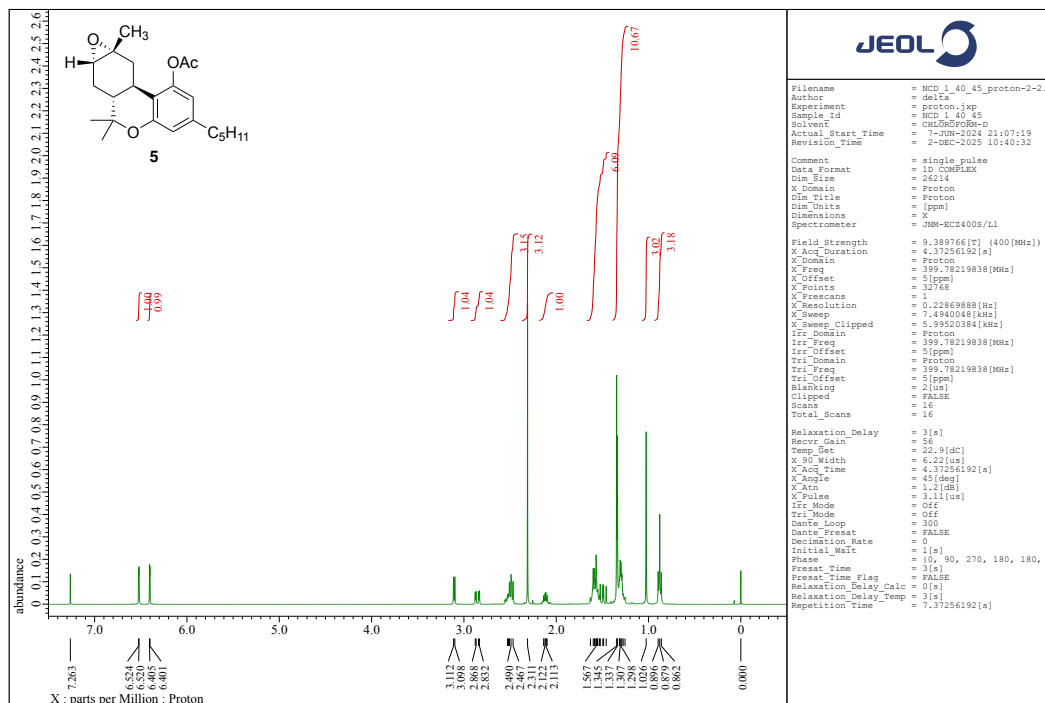
Table S4. Assignment of the peaks in the ^1H and ^{13}C NMR spectra of **4**.

	^1H	^{13}C		^1H	^{13}C
1		154.6	10	2.83 (td, 1H, 10 α)	31.9
				1.23–1.13 (m, 1H, 10 β)	
1-OH	4.72 (brs, 1H)		10a	2.50–2.40 (m, 1H)	35.4
2	6.08 (d, 1H)	107.5	10b		109.6
3		142.7	11	1.02 (d, 3H)	18.1
4	6.25 (d, 1H)	110.1	12	1.08 (s, 3H)	18.9
4a		154.9	13	1.37 (s, 3H)	27.6
6		77.2	1'	2.50–2.40 (m, 2H)	35.4
6a	2.01–1.90 (m, 1H)	41.5	2'	1.59–1.52 (m, 2H)	30.6
7	1.41–1.25 (m, 1H, 7 α)	35.4	3'	1.41–1.25 (m, 2H)	31.5
	2.01–1.90 (m, 1H, 7 β)				
8	3.98–3.94 (m, 1H)	70.4	4'	1.41–1.25 (m, 2H)	22.5
8-OH	1.59–1.52 (m, 1H)		5'	0.88 (t, 3H)	14.0
9	1.86–1.76 (m, 1H)	36.6			



5. NMR Spectra of **5**

Figure S25. ^1H NMR (400 MHz, CDCl_3 , ppm) of **5**



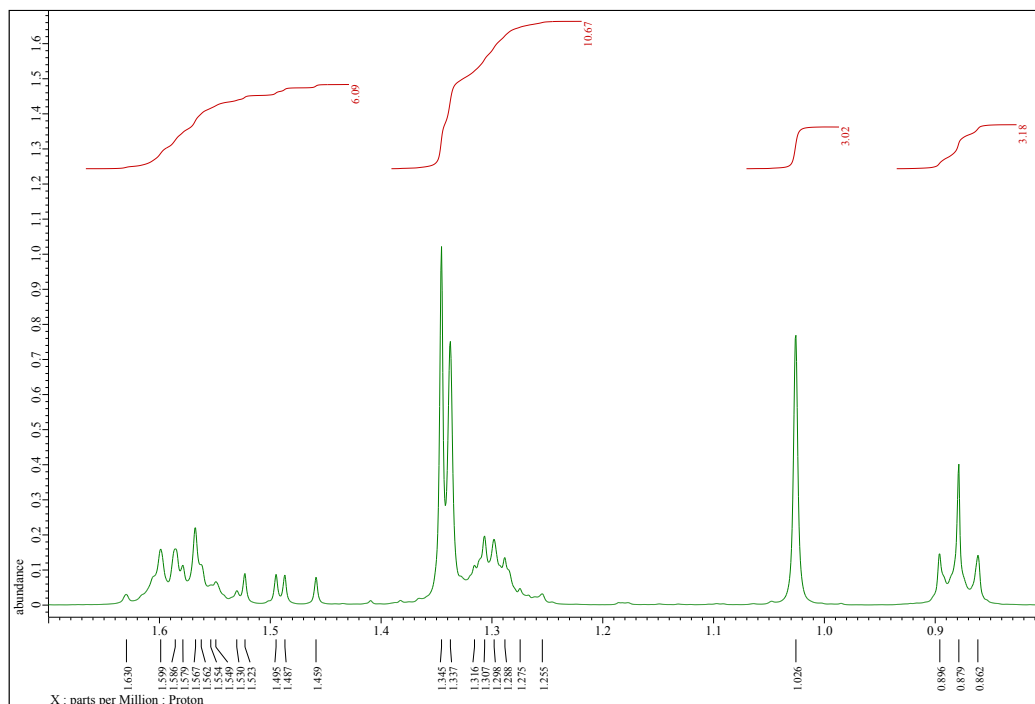
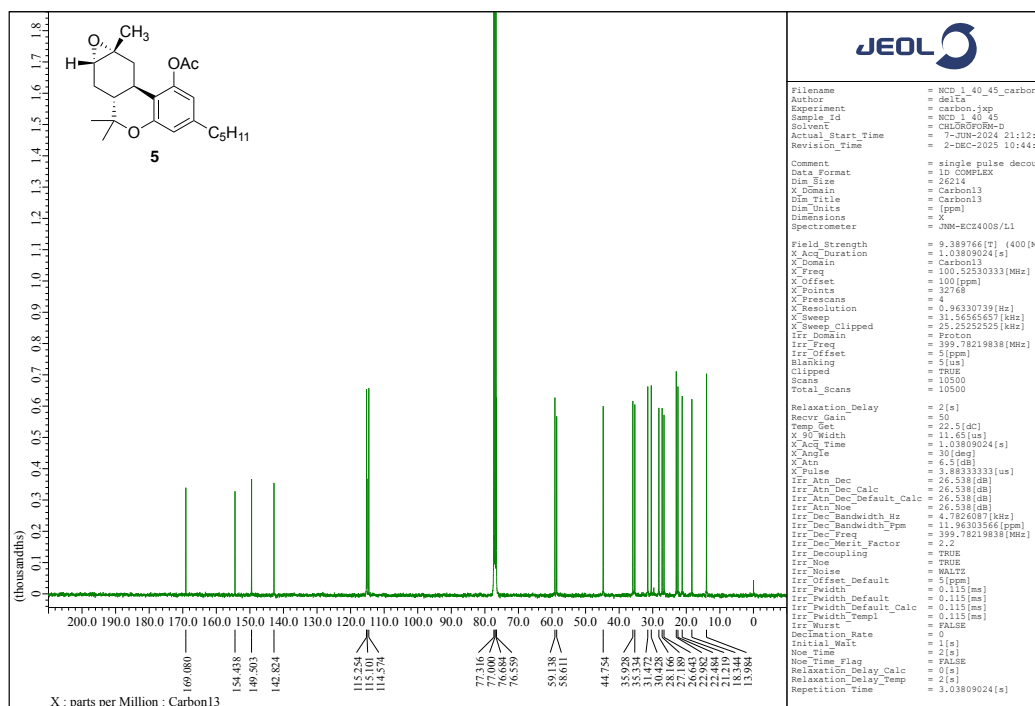
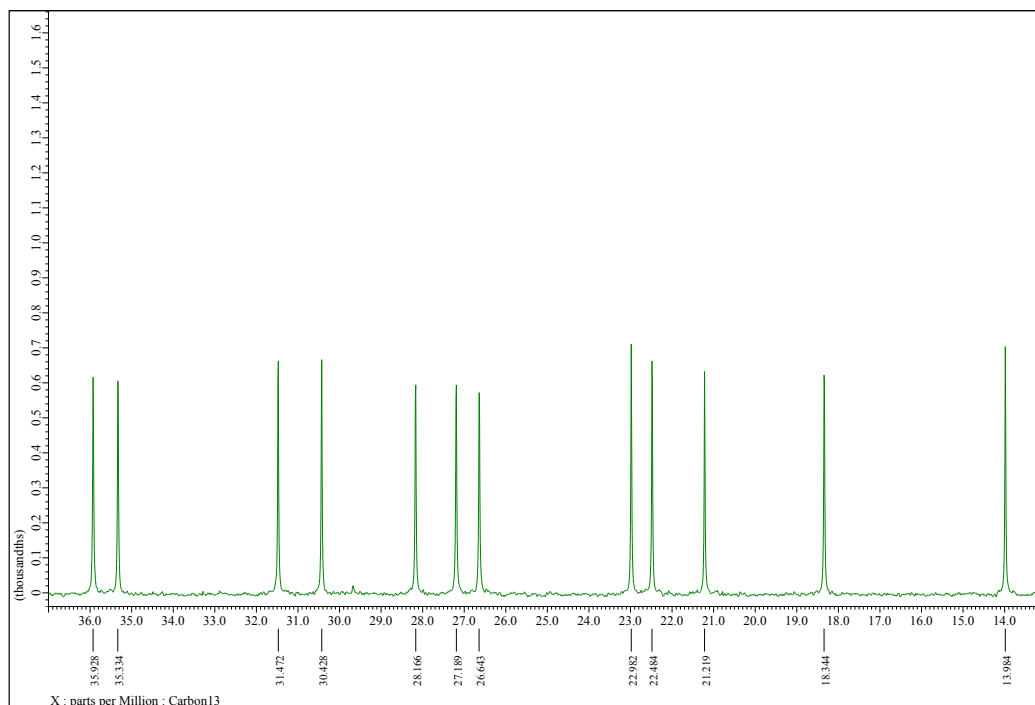
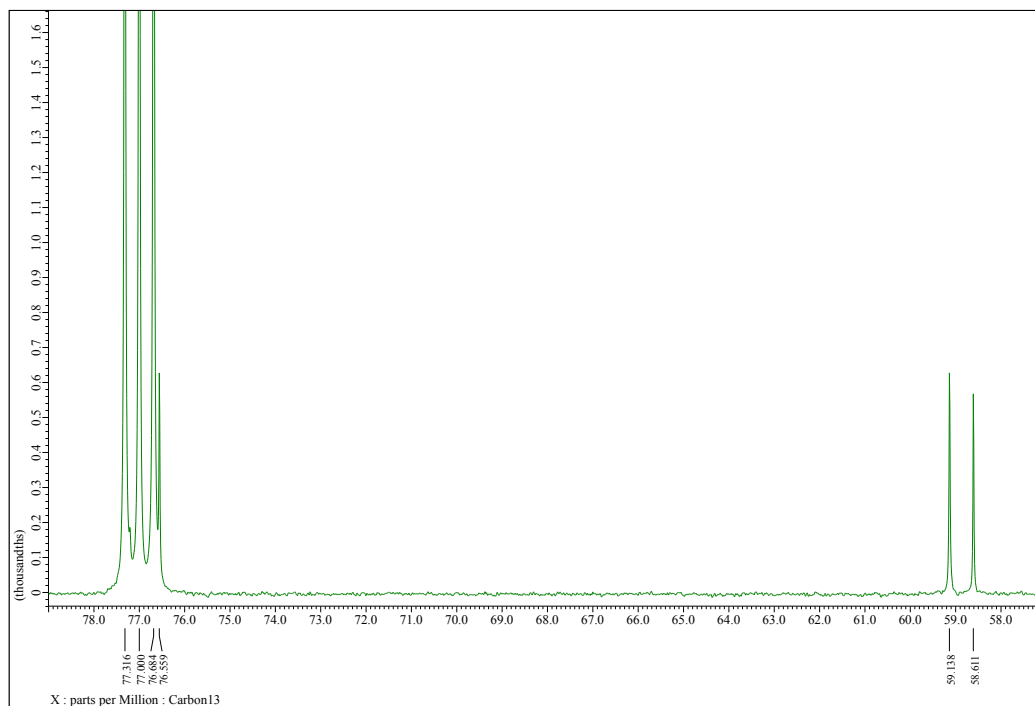


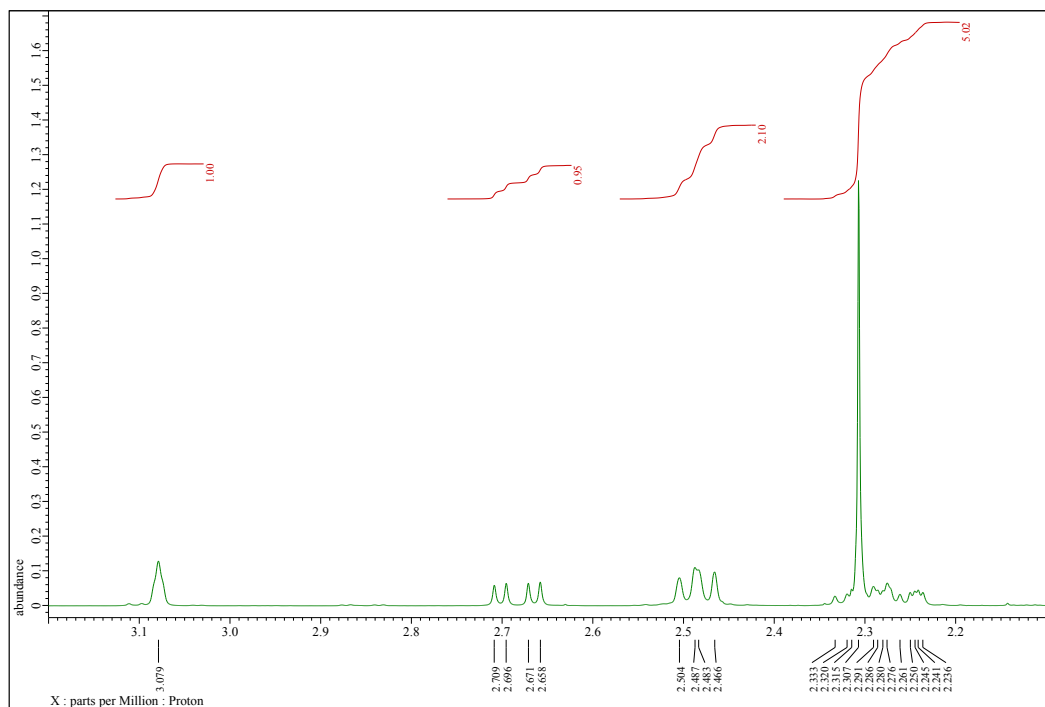
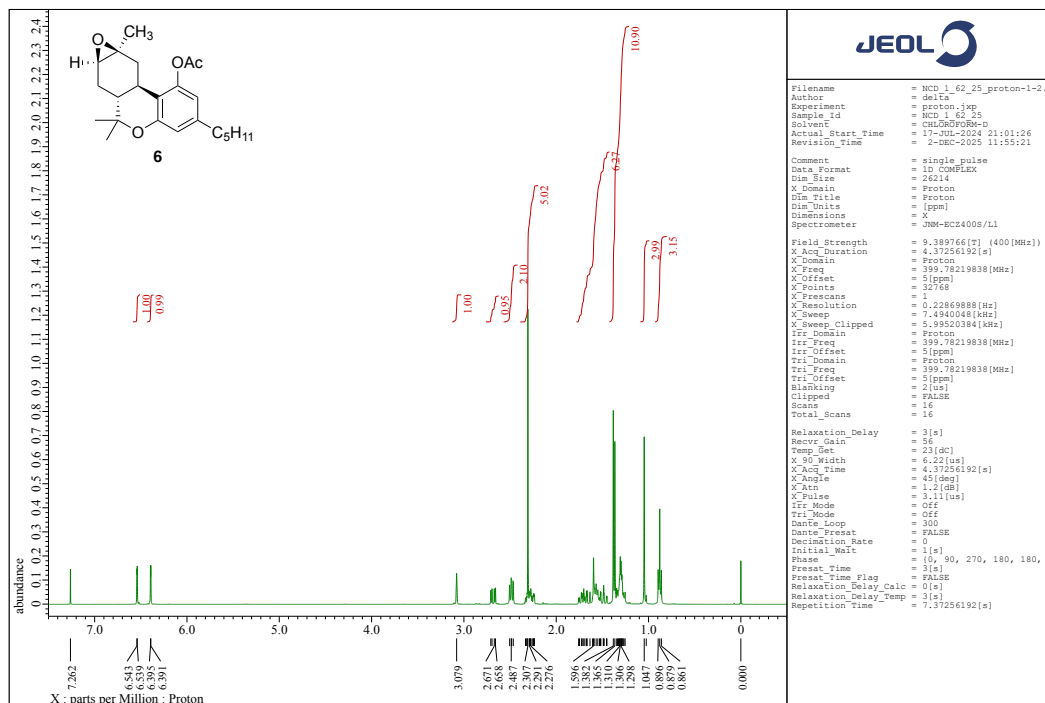
Figure S26. ^{13}C NMR (100 MHz, CDCl_3 , ppm) of **5**





6. NMR Spectra of 6

Figure S27. ^1H NMR (400 MHz, CDCl_3 , ppm) of **6**



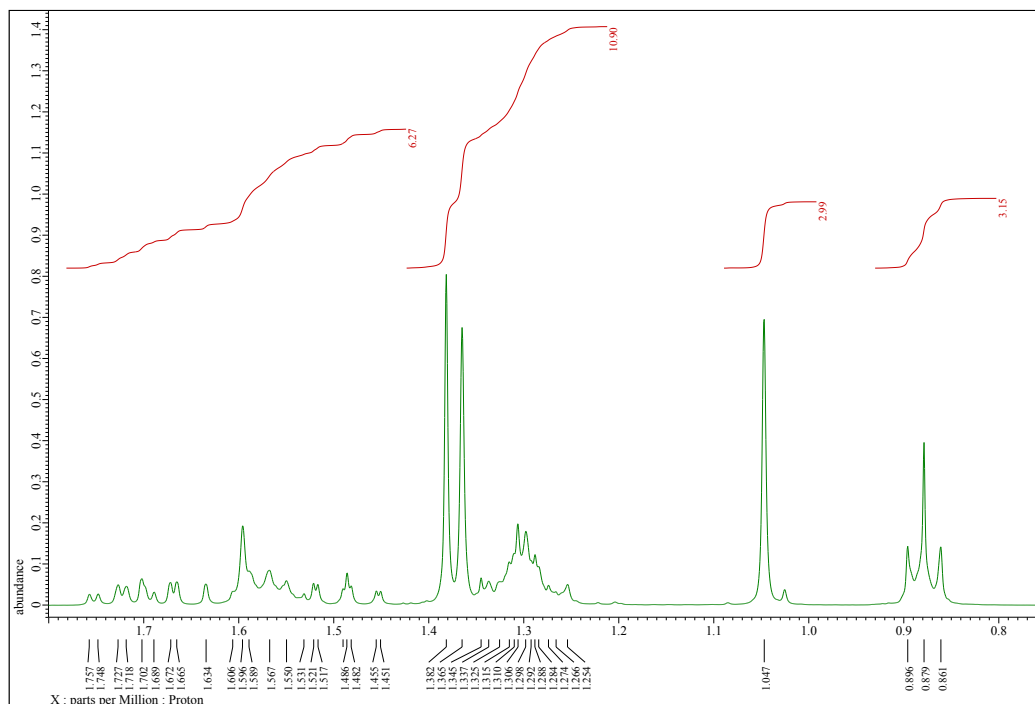
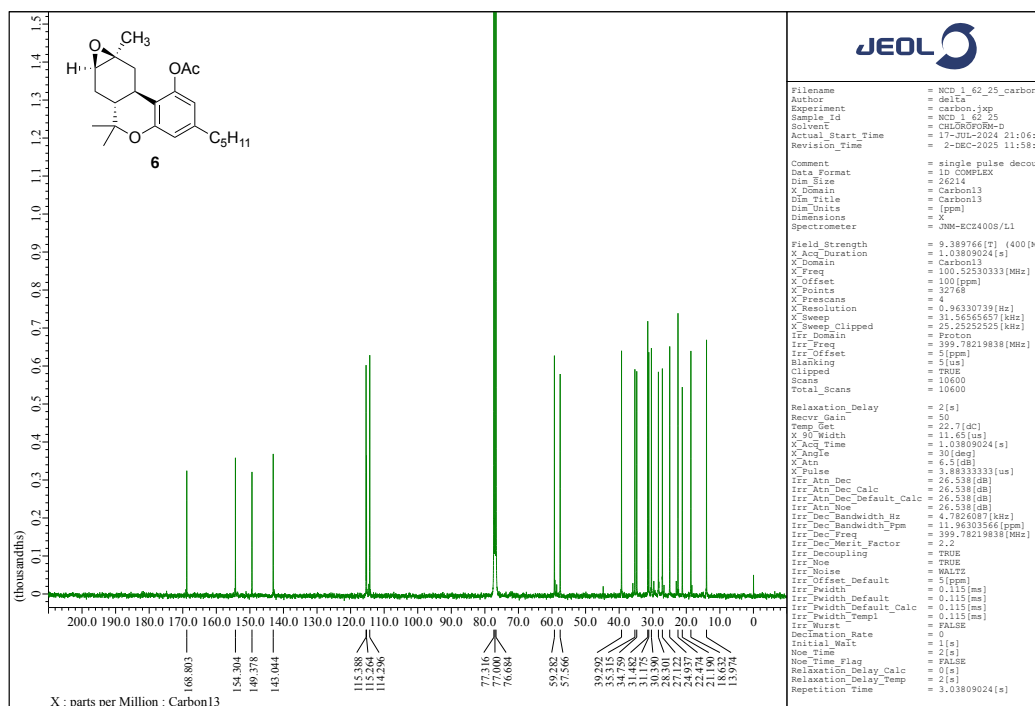
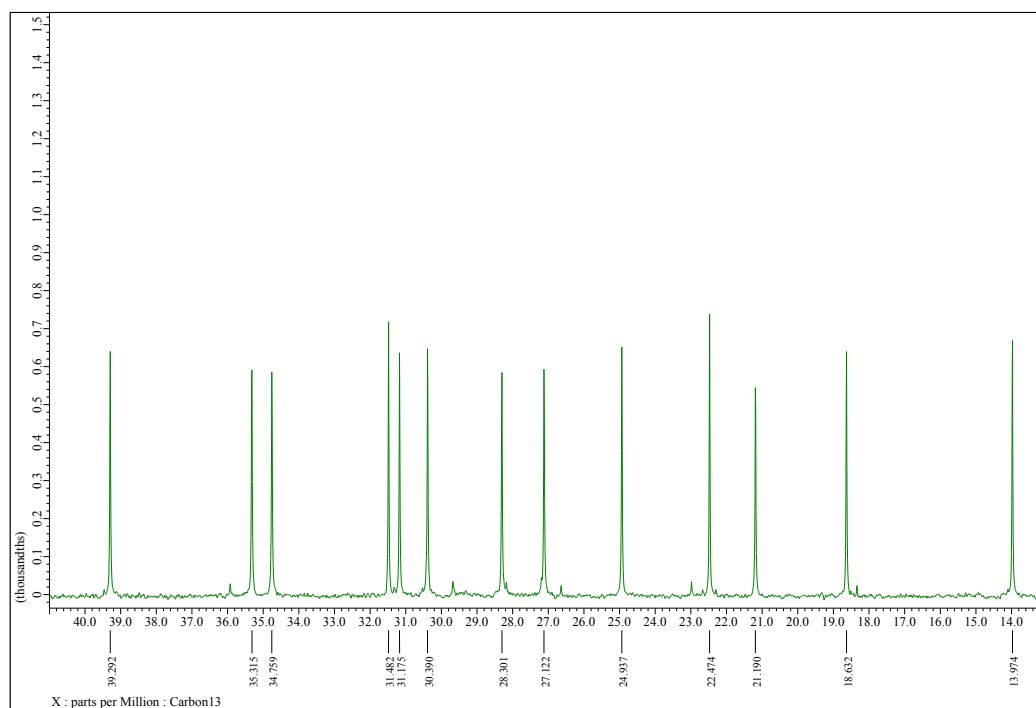


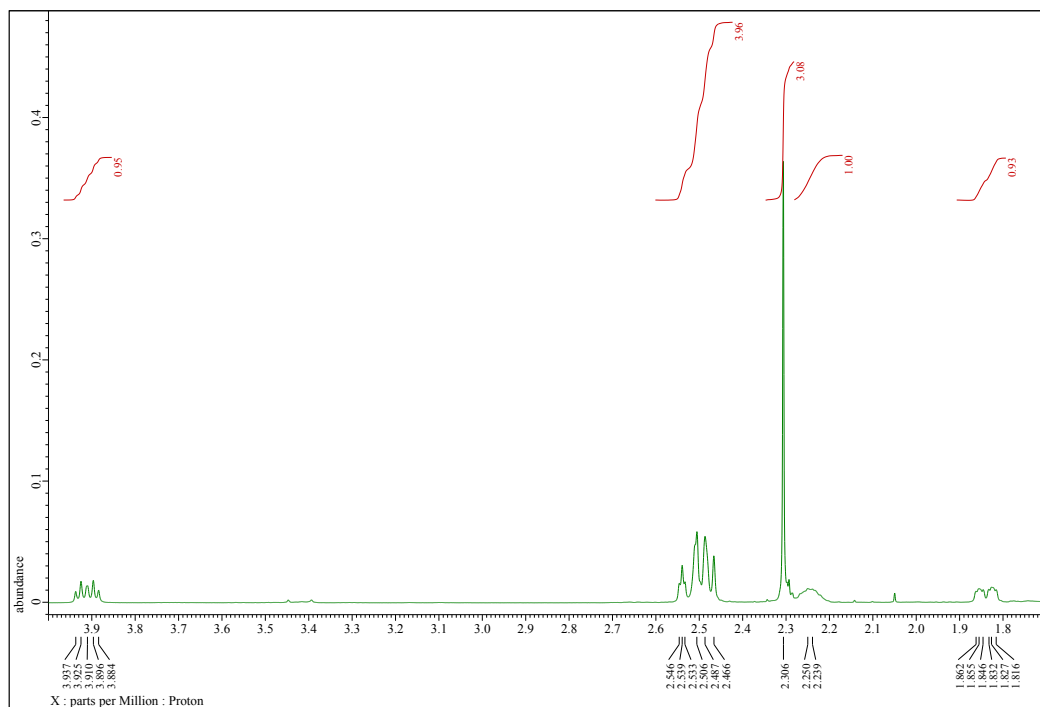
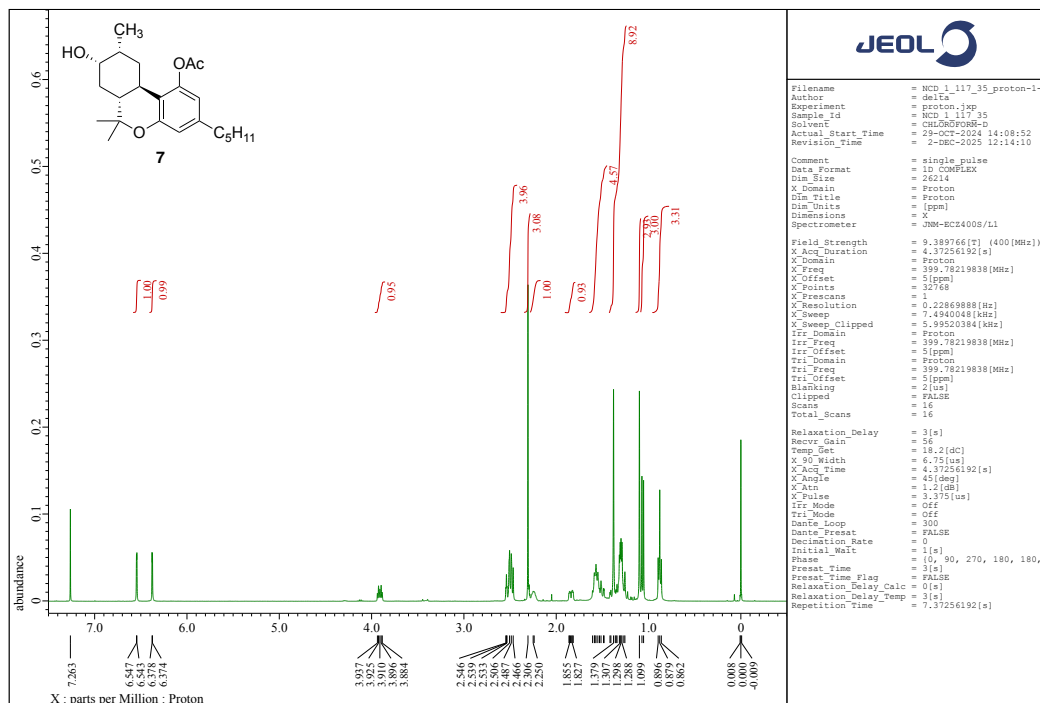
Figure S28. ^{13}C NMR (100 MHz, CDCl_3 , ppm) of **6**





7. NMR Spectra of 7

Figure S29. ^1H NMR (400 MHz, CDCl_3 , ppm) of 7



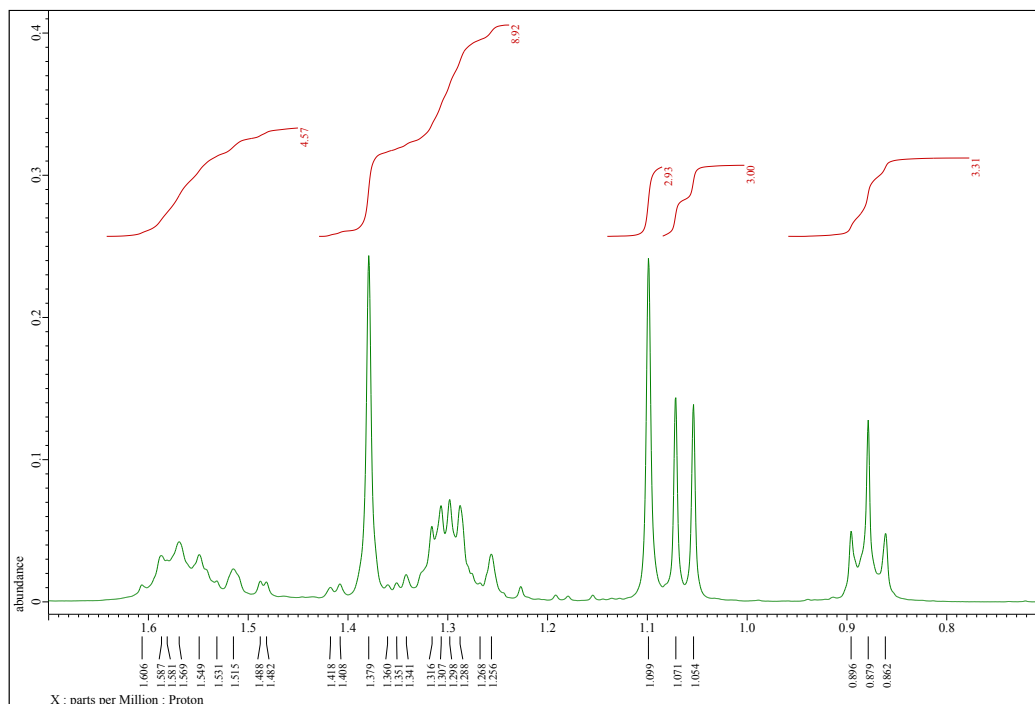
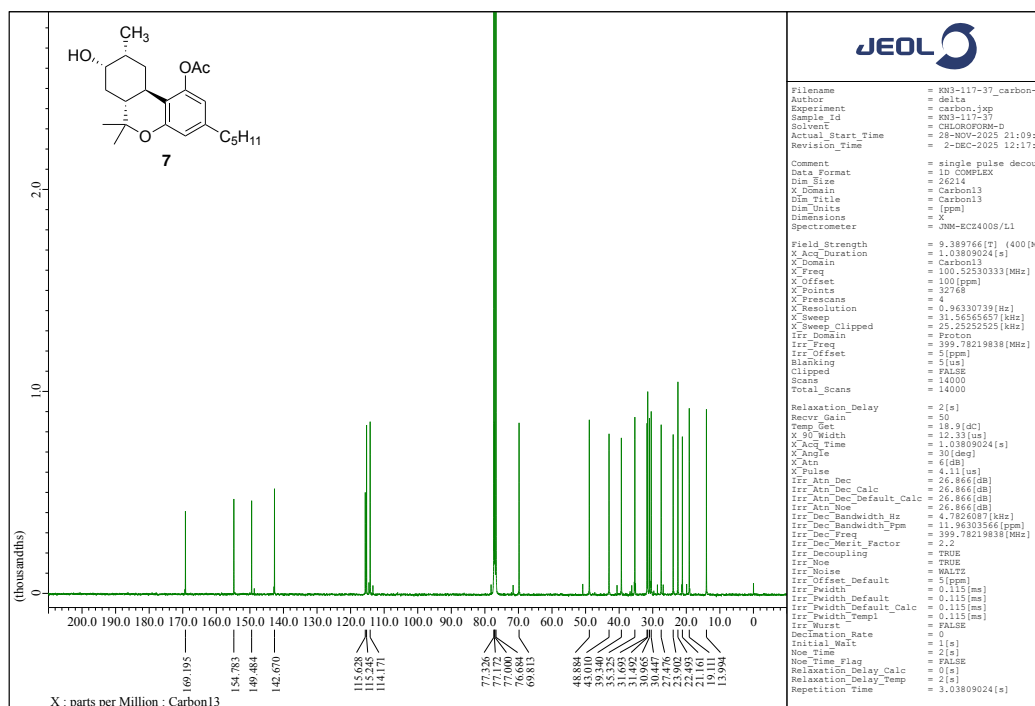
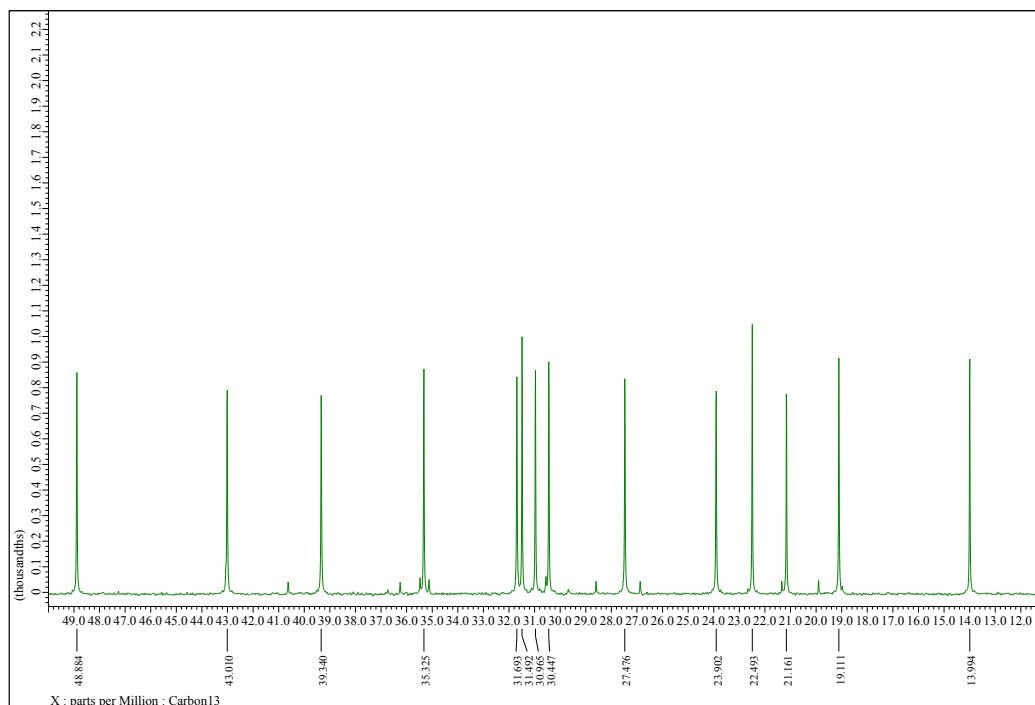
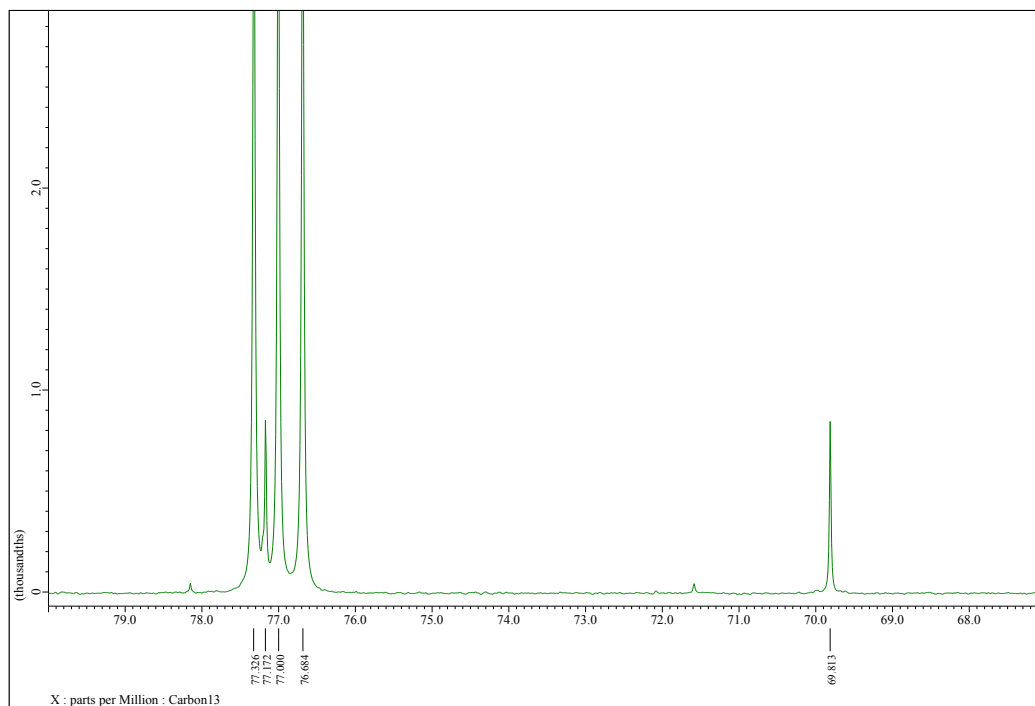


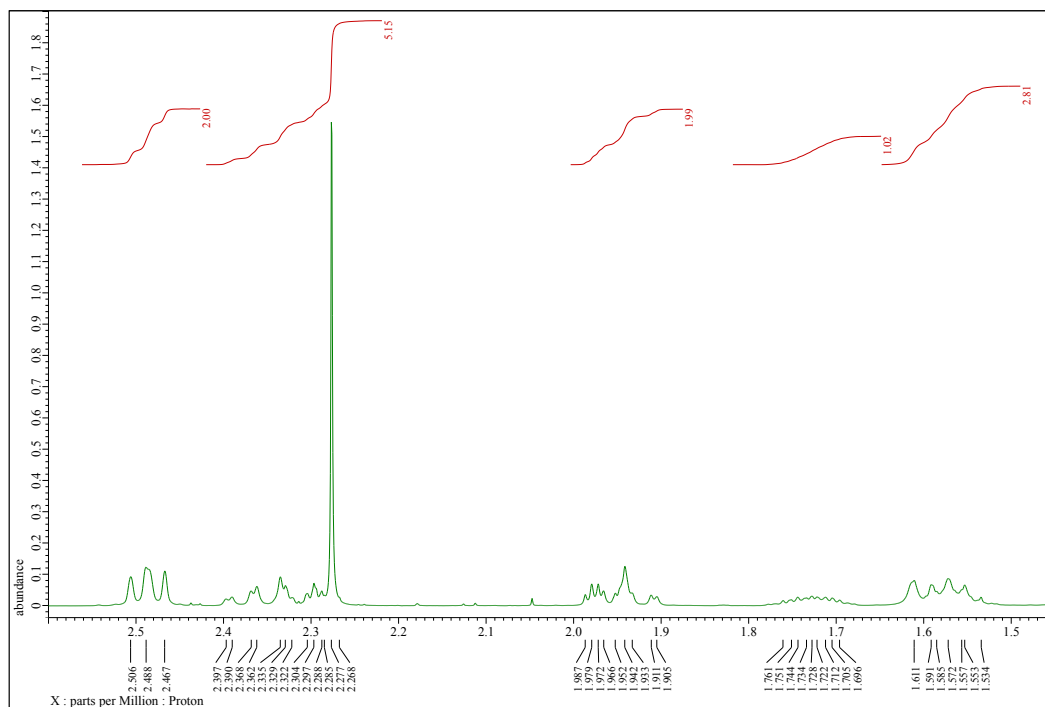
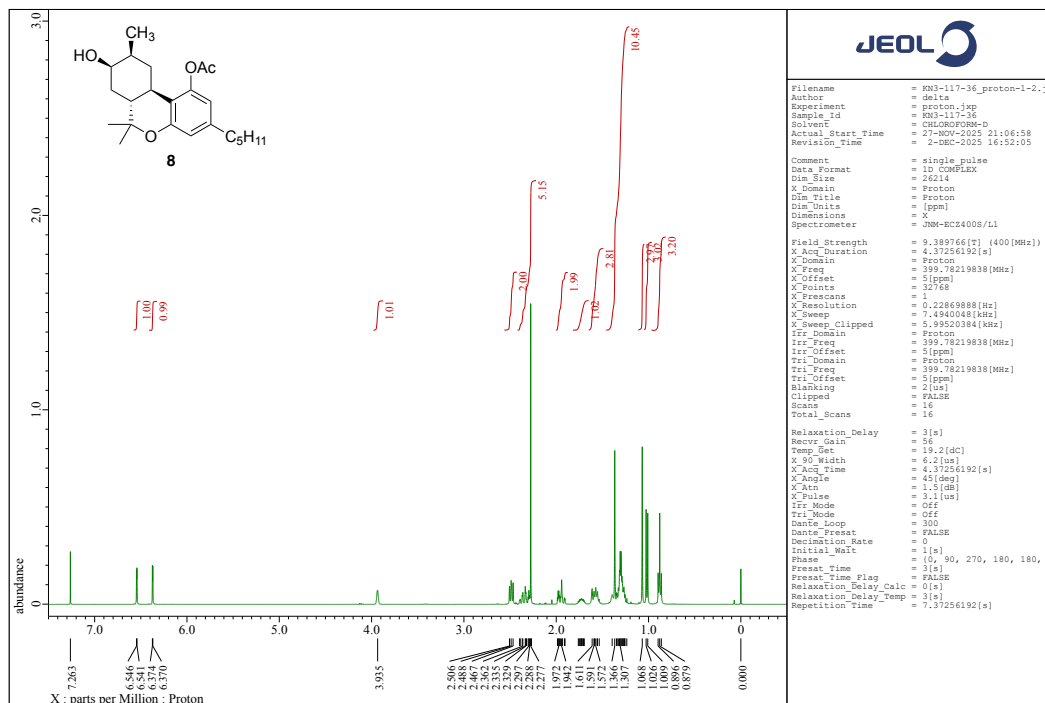
Figure S30. ^{13}C NMR (100 MHz, CDCl_3 , ppm) of **7**





8. NMR Spectra of **8**

Figure S31. ^1H NMR (400 MHz, CDCl_3 , ppm) of **8**



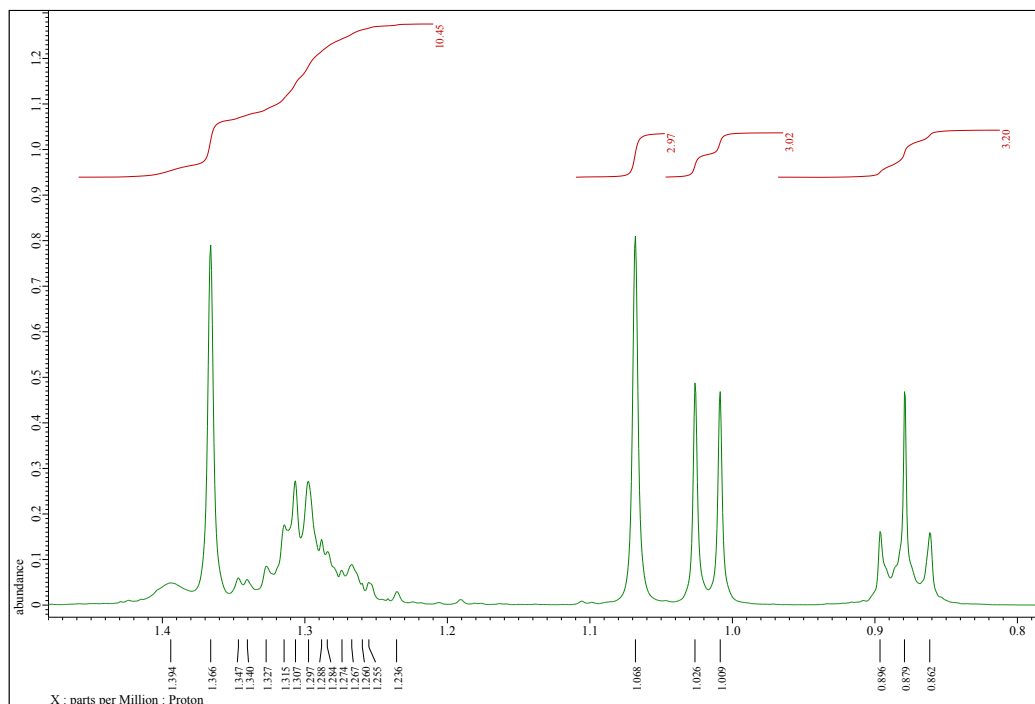
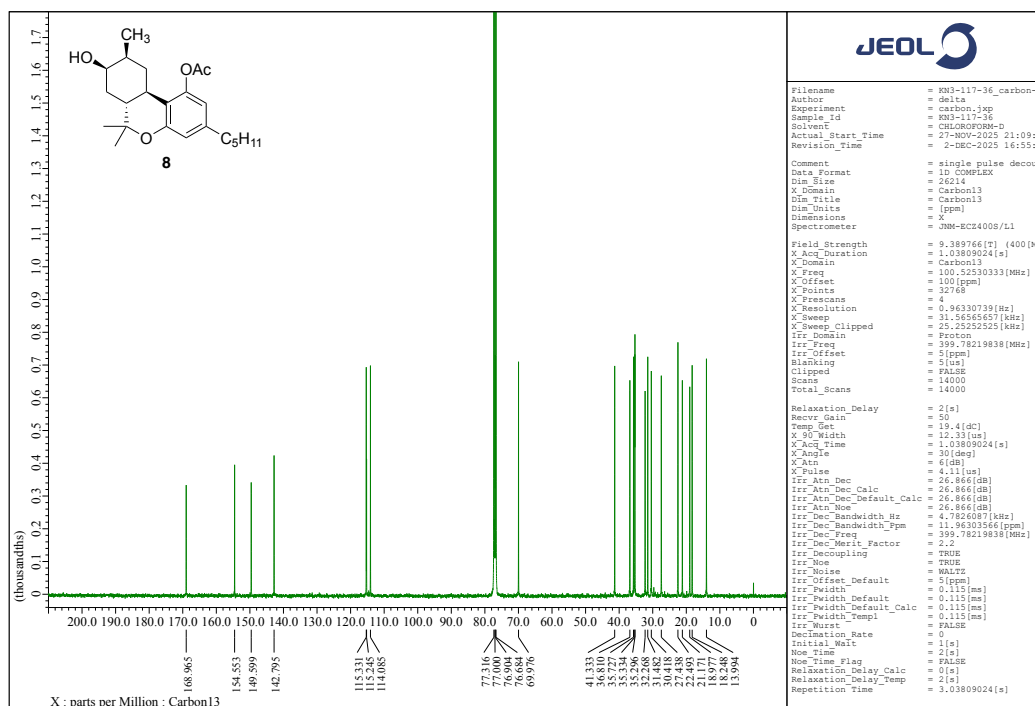
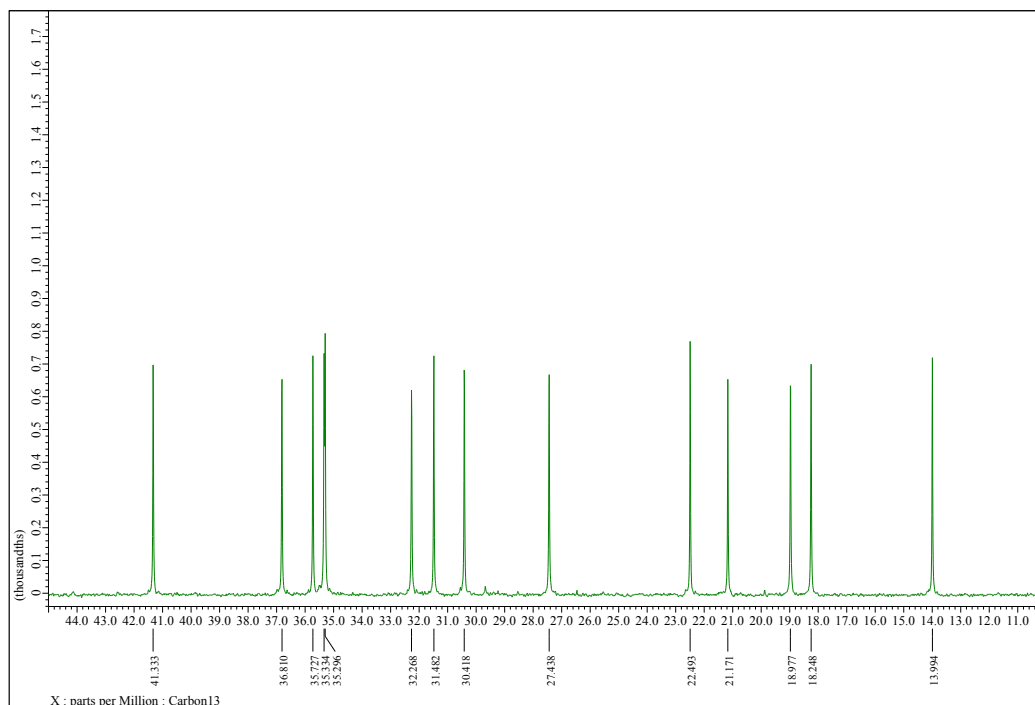
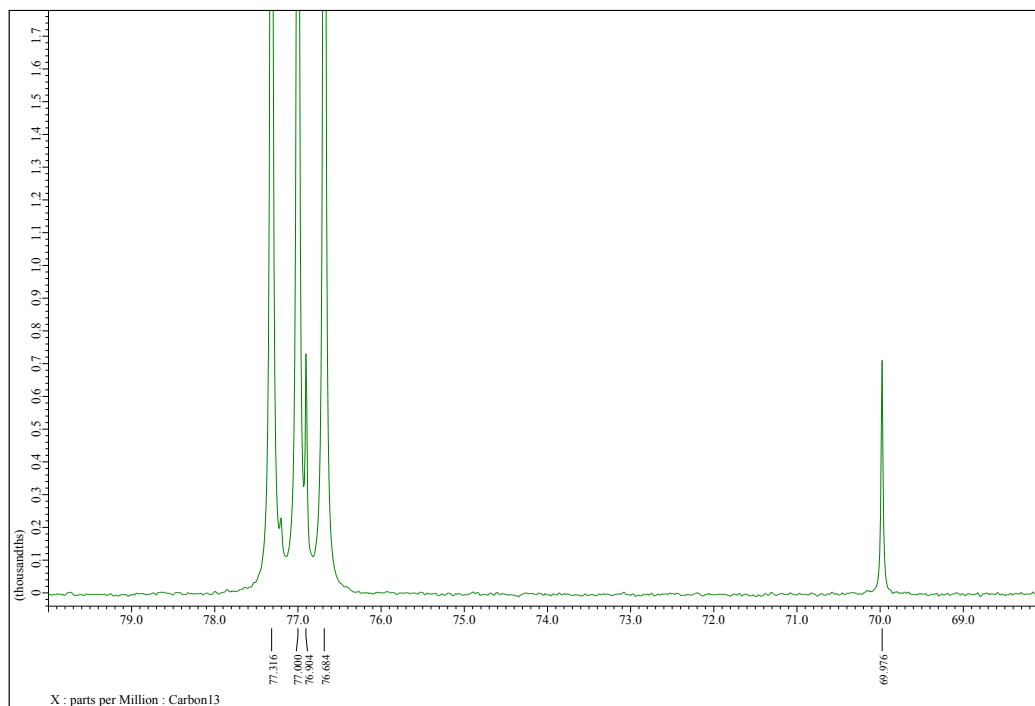


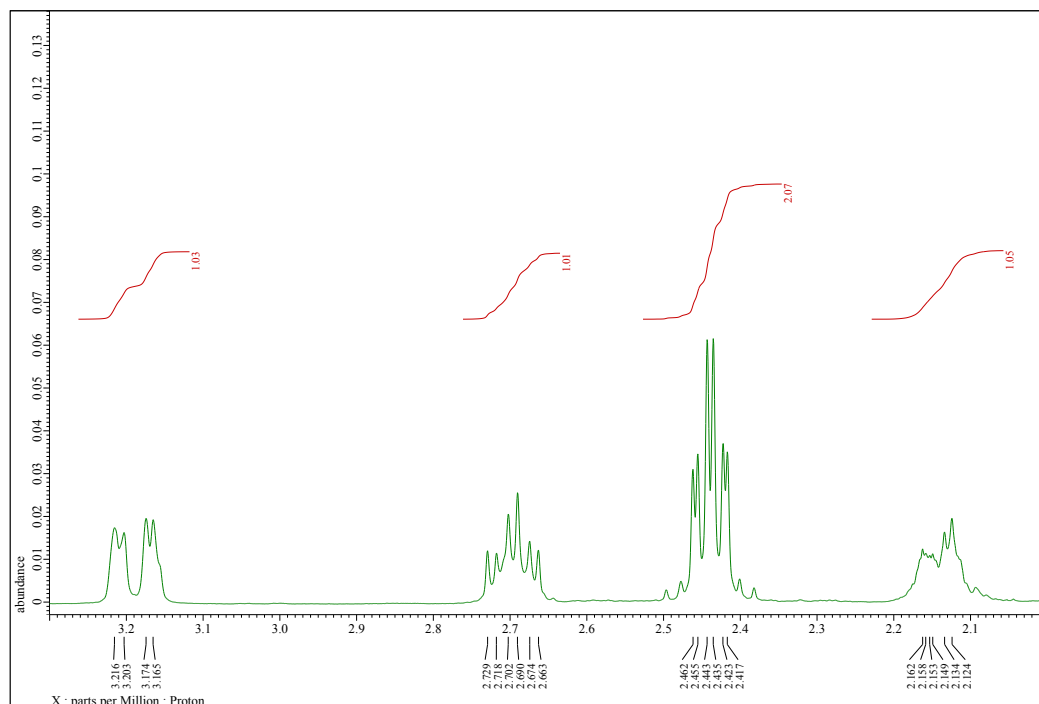
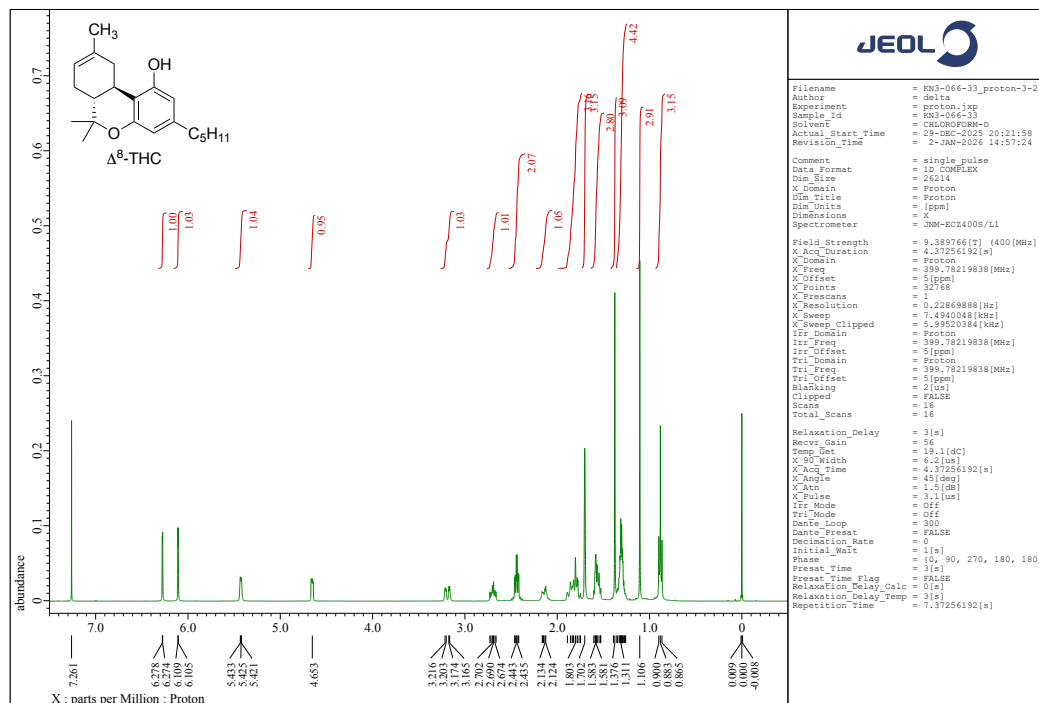
Figure S32. ¹³C NMR (100 MHz, CDCl₃, ppm) of **8**





9. NMR Spectra of Δ^8 -THC

Figure S33. ^1H NMR (400 MHz, CDCl_3 , ppm) of Δ^8 -THC



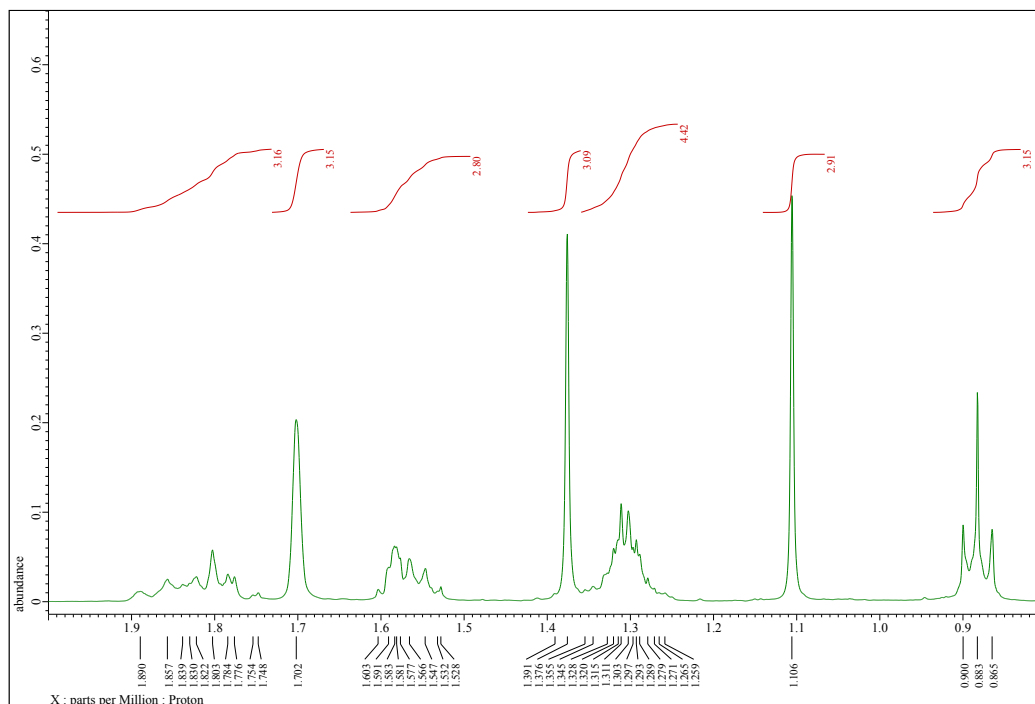
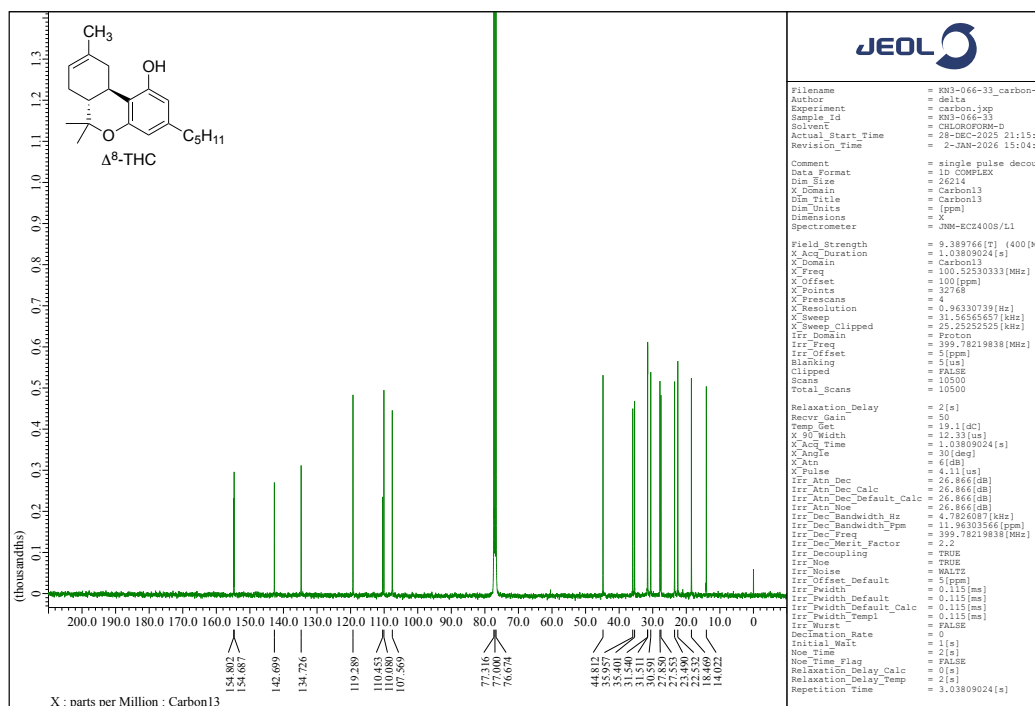


Figure S34. ^{13}C NMR (100 MHz, CDCl_3 , ppm) of Δ^8 -THC



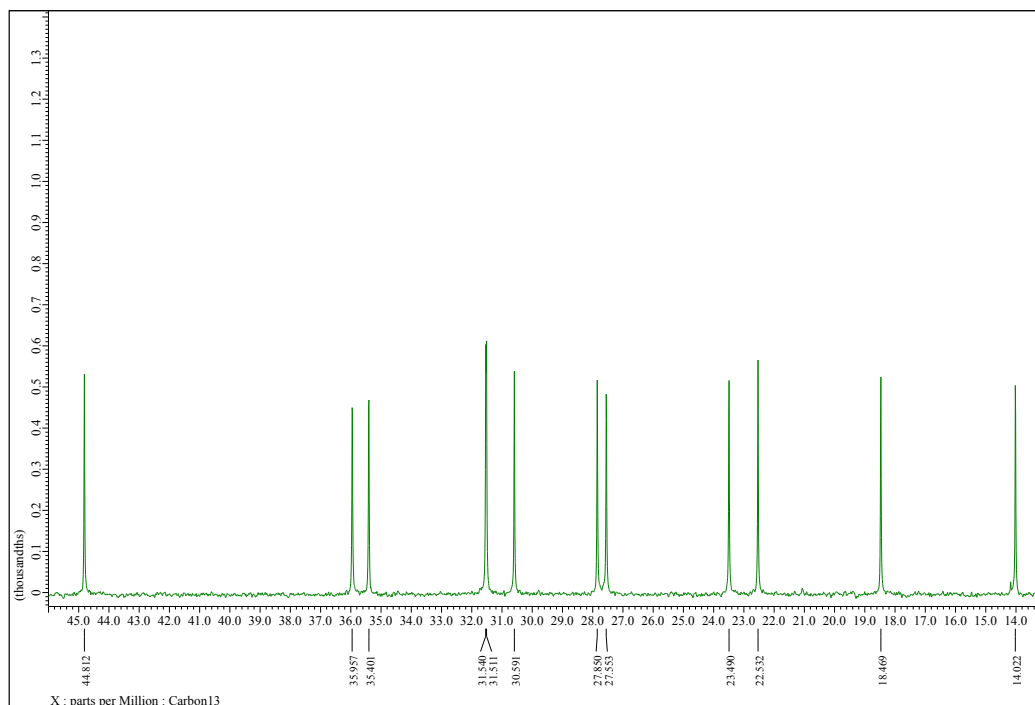
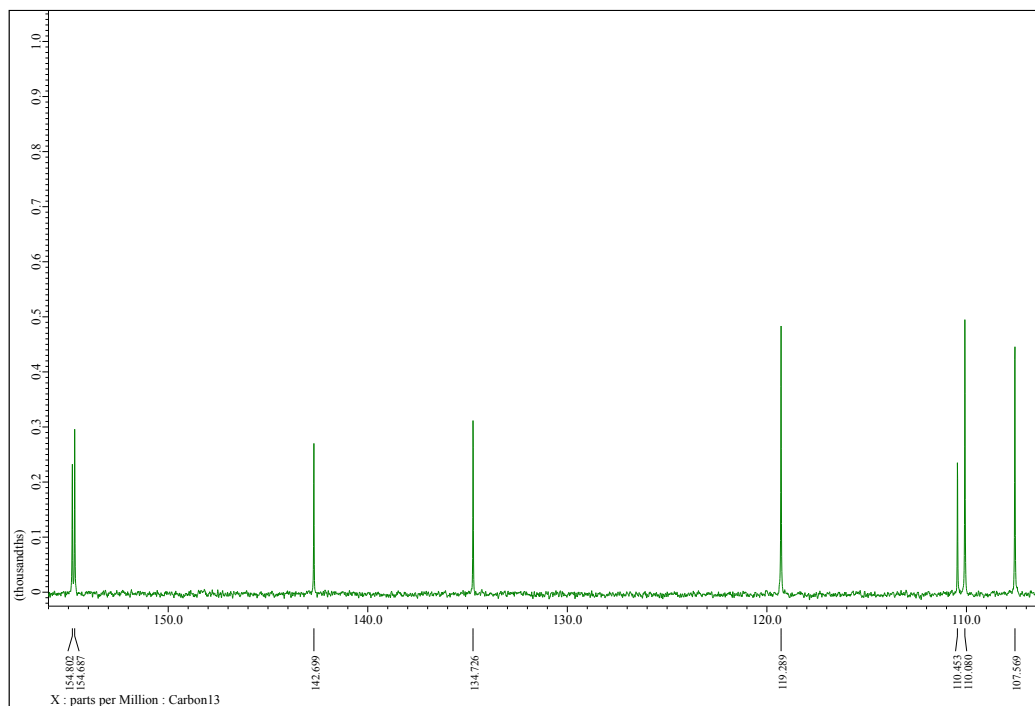


Figure S35. NOESY spectrum of Δ^8 -THC

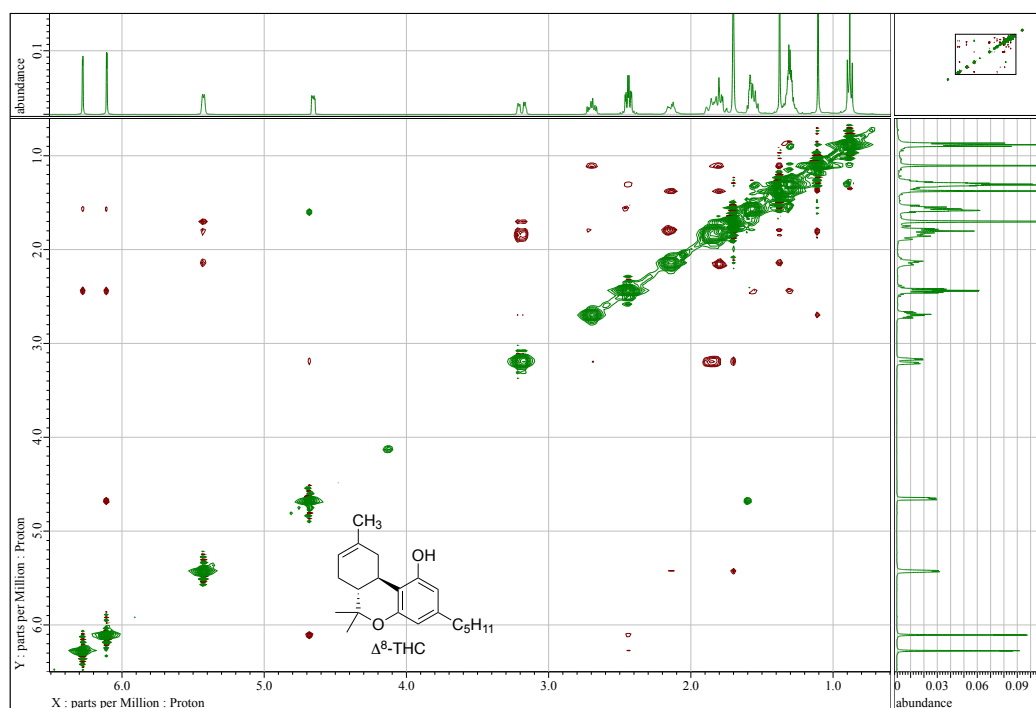


Figure S36. COSY spectrum of Δ^8 -THC

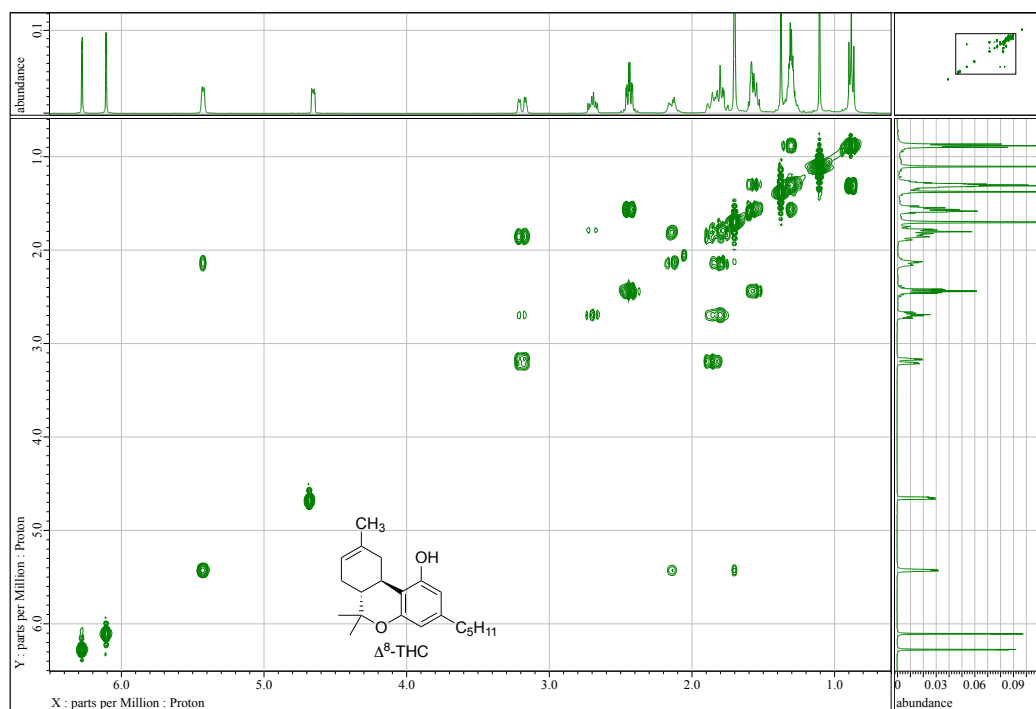


Figure S37. HSQC spectrum of Δ^8 -THC

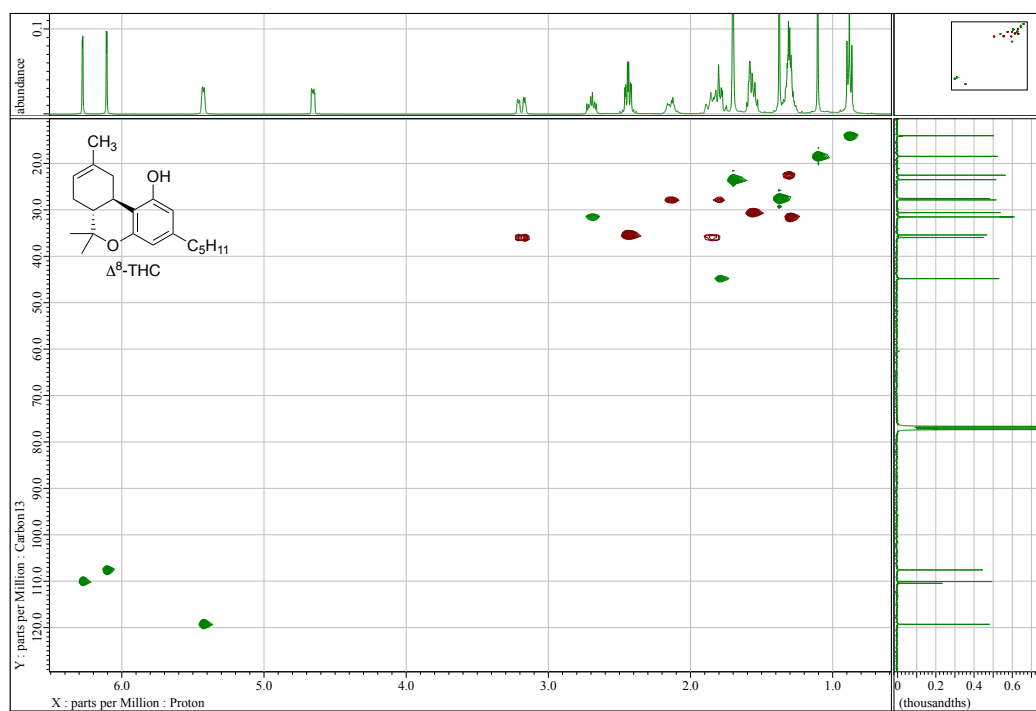


Figure S38. HMBC spectrum of Δ^8 -THC

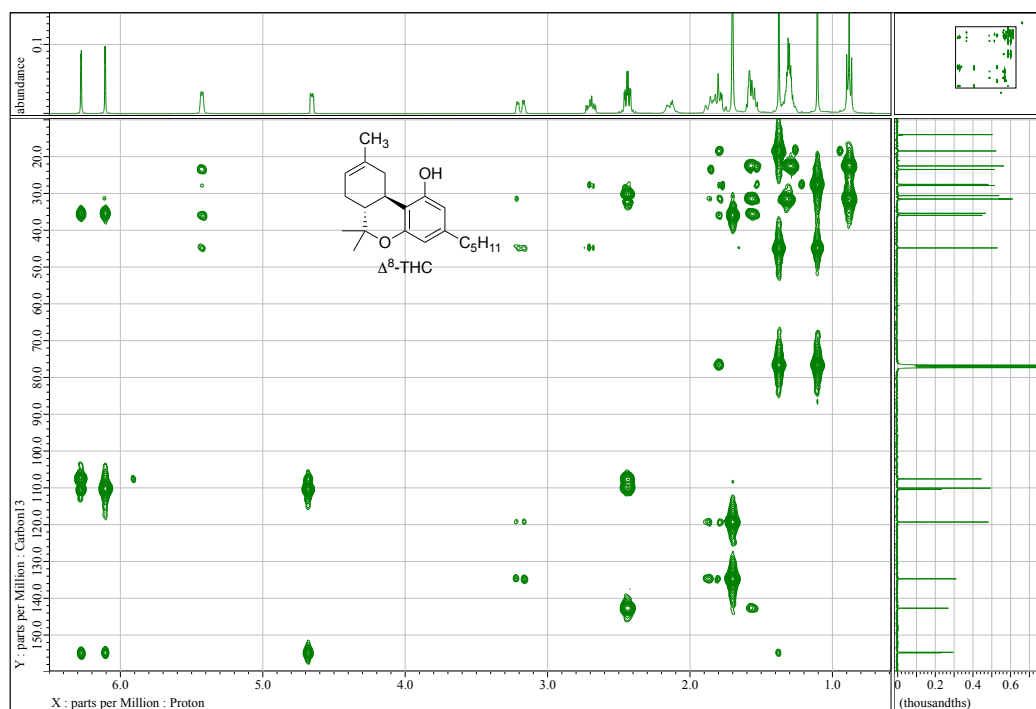
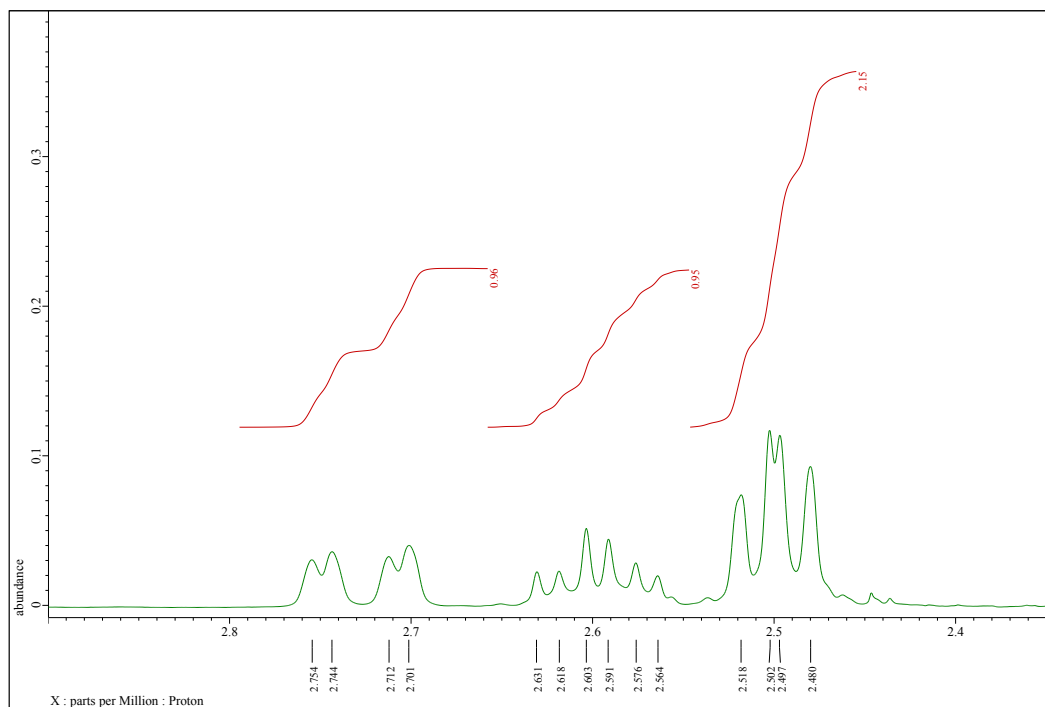


Figure S39. ^1H NMR (400 MHz, CDCl_3 , ppm) of Δ^8 -THC acetate



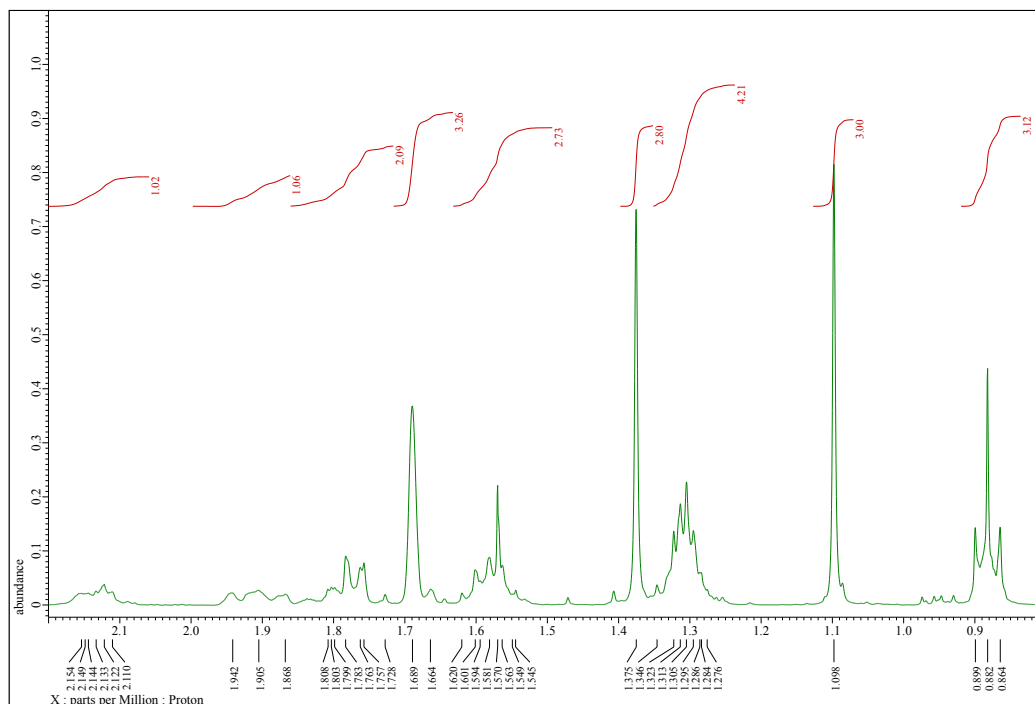
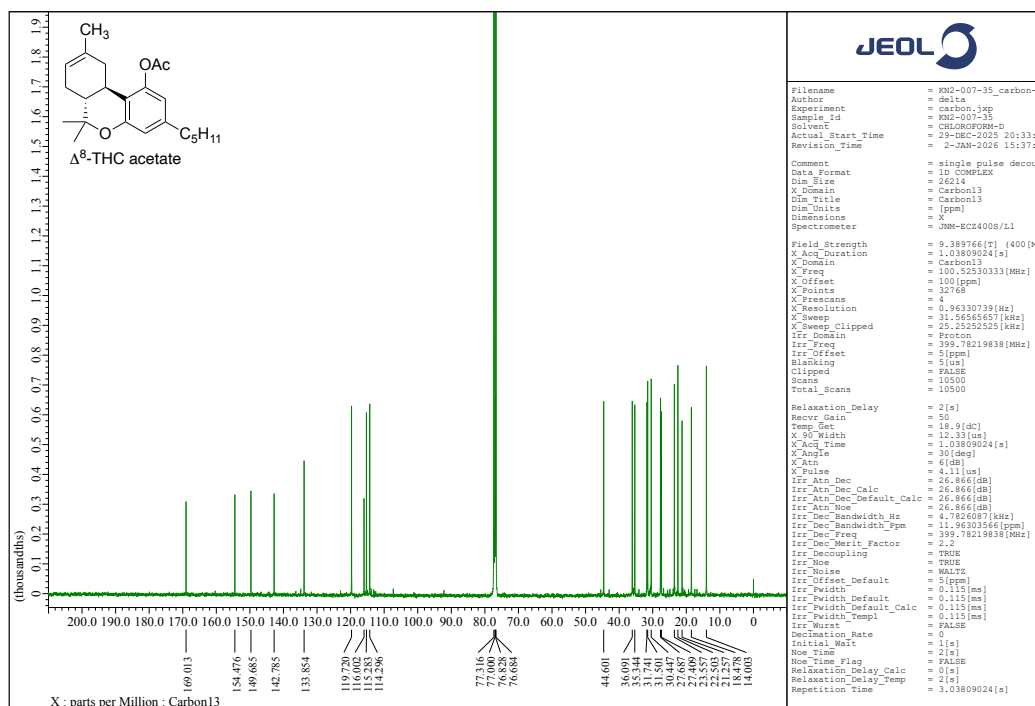


Figure S40. ^{13}C NMR (100 MHz, CDCl_3 , ppm) of Δ^8 -THC acetate



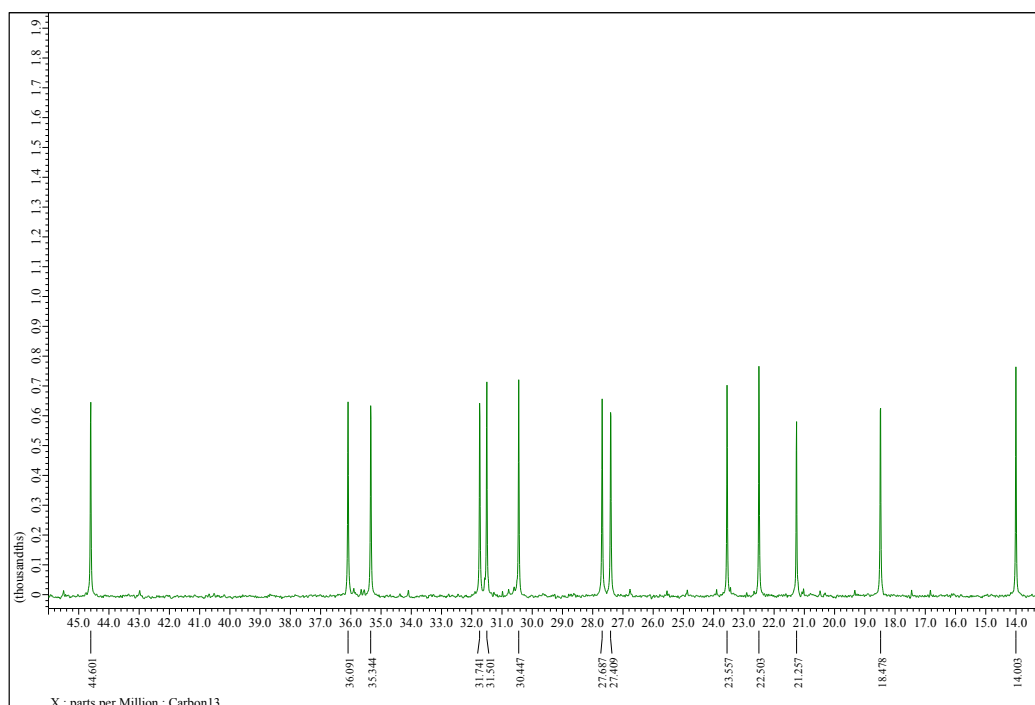
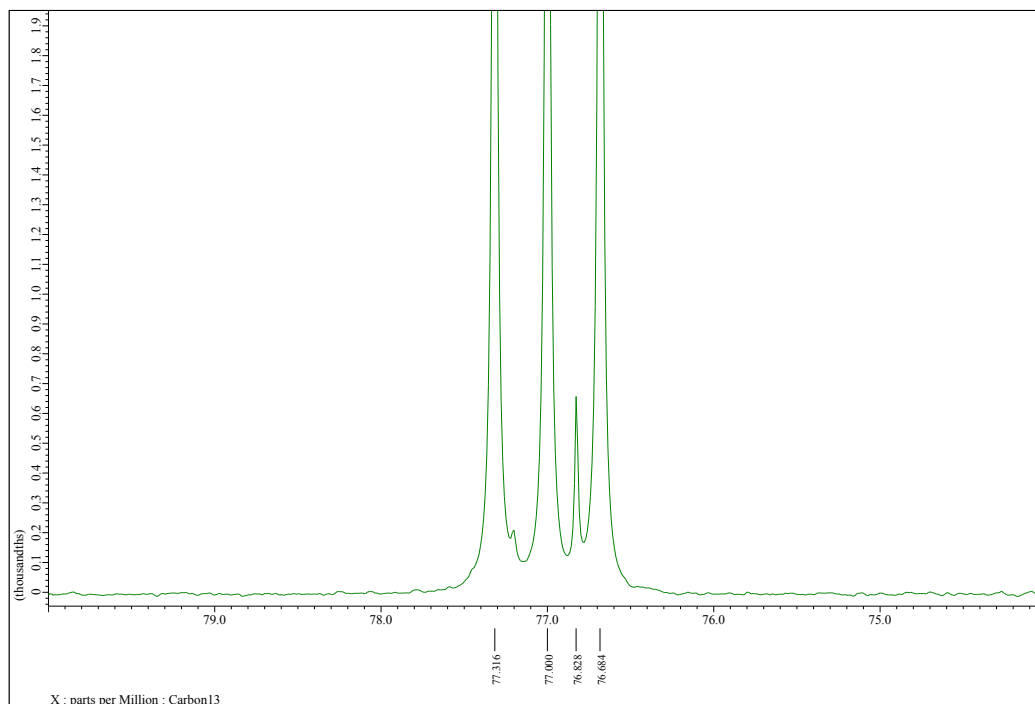


Figure S41. NOESY spectrum of Δ^8 -THC acetate

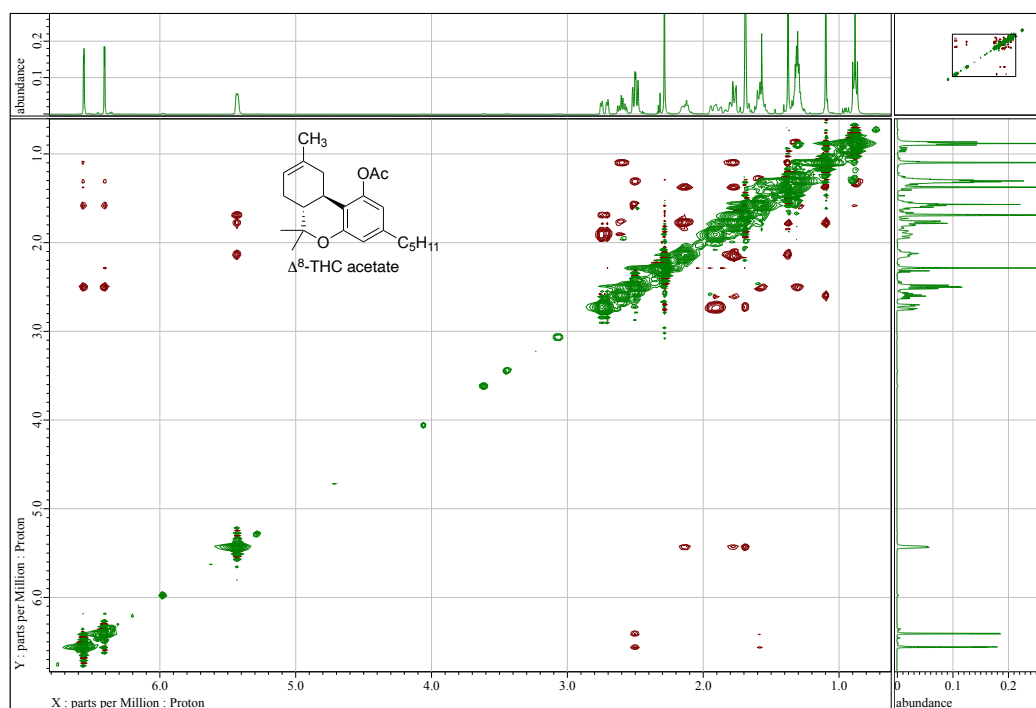


Figure S42. COSY spectrum of Δ^8 -THC acetate

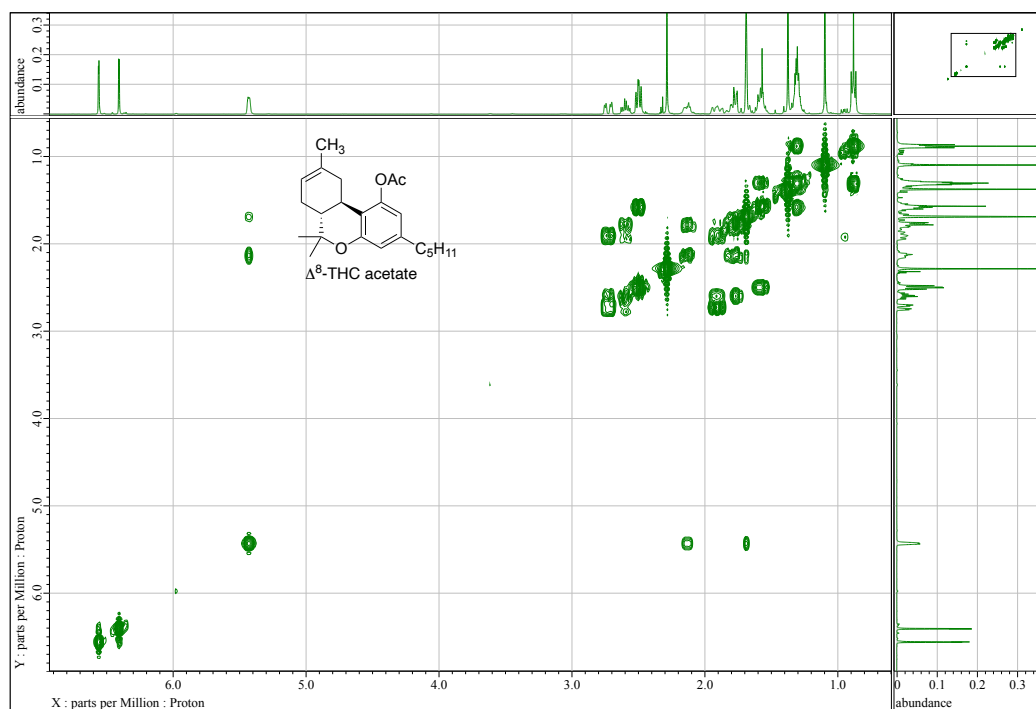


Figure S43. HSQC spectrum of Δ^8 -THC acetate

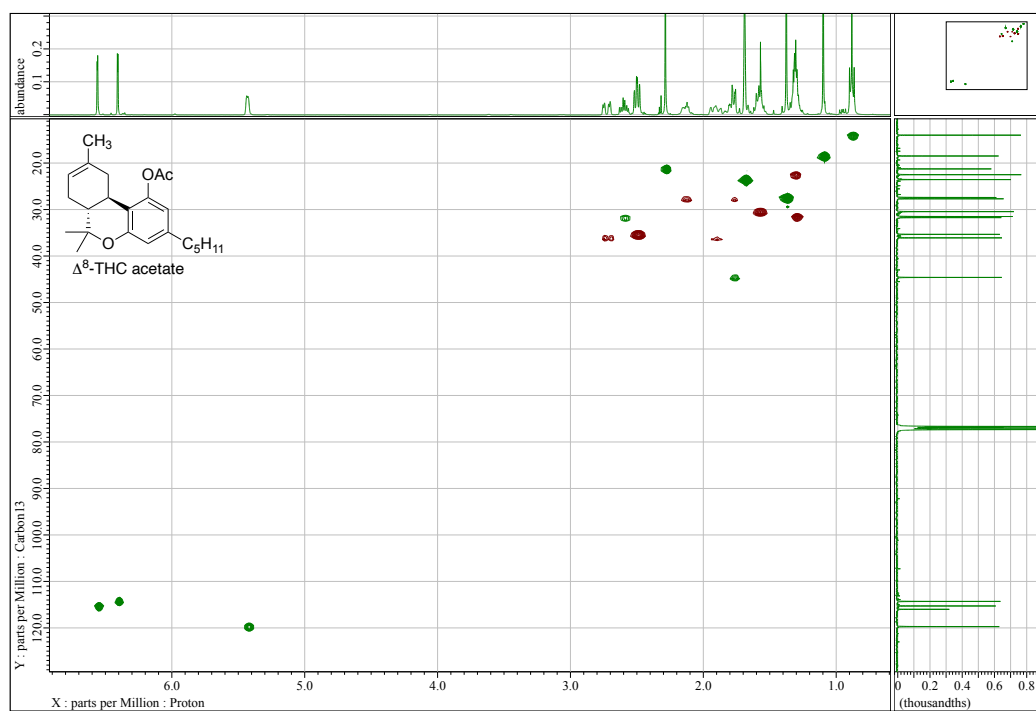


Figure S44. HMBC spectrum of Δ^8 -THC acetate

