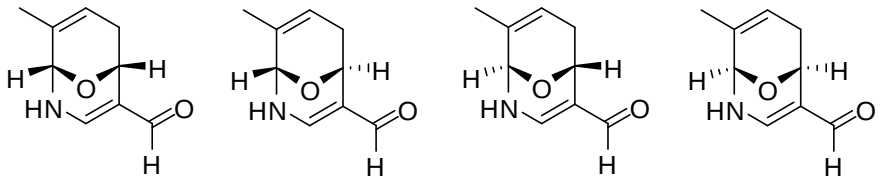
Supplementary Information

S1. Energy Minimization and ECD Calculations.

S1. Energy Minimization and ECD Calculations

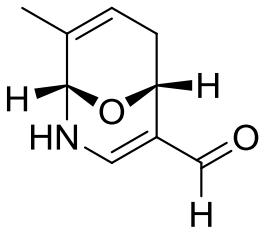
The initial conformational distribution search was performed using MMFF94 method overlaid with key correlations observed in the NOESY spectra of **1**. The corresponding minimum geometries were preoptimized at HF/6-31G level in Gaussian 03 program package [1,2], which was further checked by frequency calculation and resulted in no imaginary frequencies. And their minimum geometries were further optimized by DFT calculation B3LYP at 6-31 + g(d) level in the gas phase. The stable conformers obtained were submitted to ECD calculation by TDDFT [b3lyp/aug-cc-pvdz] method under Self-Consistent Reaction Field model of solvent (MeOH). The overall predicted ECD spectra of **1** were subsequently compared with the experimental one.

*S1.1. Energy Minimization of Four Possible Relative Structures of **1** (**1A**–**1D**)*



Formula: $\Delta E = (E - E_{1A}) \times 627.51$ kcal/mol [2]

1A

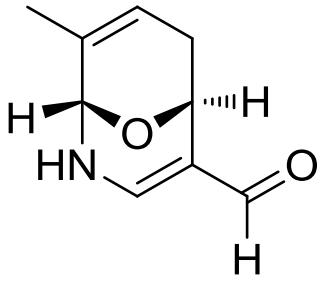


E(RHF/6-31G(d)) = −551.3563 a.u.
ΔE = 0 kcal/mol

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.102171	-0.099256	-0.930399
2	6	0	-1.798273	-0.426787	-0.255432
3	6	0	-1.277377	0.601481	0.733570
4	8	0	-0.319261	0.057862	1.582865
5	6	0	0.741647	-0.526112	0.850402
6	6	0	0.227165	-1.795318	0.176444
7	6	0	-1.099086	-1.523185	-0.483627
8	7	0	-0.733857	1.744730	0.013558
9	6	0	1.291673	0.513891	-0.102040
10	6	0	2.637915	0.374606	-0.644413
11	6	0	0.573753	1.606699	-0.376782
12	8	0	3.356972	-0.558984	-0.440264
13	1	0	2.976650	1.204636	-1.275062
14	1	0	1.504967	-0.769485	1.574830
15	1	0	-2.083543	0.956218	1.360713
16	1	0	-3.029737	0.834941	-1.479812
17	1	0	-3.903737	0.013643	-0.203414
18	1	0	-3.388959	-0.878972	-1.625918
19	1	0	0.953011	-2.147325	-0.548555
20	1	0	0.116056	-2.581577	0.920072
21	1	0	-1.473031	-2.264134	-1.171138
22	1	0	-0.988967	2.647504	0.353125
23	1	0	0.981117	2.424296	-0.946894

1B



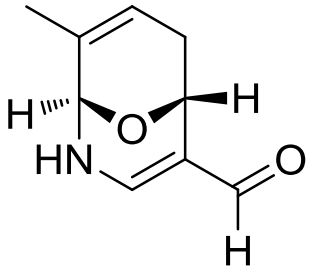
E(RHF/6-31G(d)) = −551.2413 a.u.

ΔE = 72.2 kcal/mol

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.473705	−0.218837	−0.438751
2	6	0	2.084722	0.233903	−0.080757
3	6	0	1.135059	−0.792785	0.600811
4	8	0	0.189380	−0.016980	1.182020
5	6	0	−0.450188	0.544816	0.013426
6	6	0	0.173358	1.929571	−0.012140
7	6	0	1.657201	1.497217	−0.198855
8	7	0	0.327975	−1.765557	−0.230878
9	6	0	−1.625824	−0.380148	−0.157152
10	6	0	−3.057186	−0.151050	−0.195651
11	6	0	−1.054412	−1.604168	−0.268576
12	8	0	−3.583063	0.918178	−0.104642
13	1	0	−3.660977	−1.056224	−0.332393
14	1	0	0.066627	0.187292	−0.854753
15	1	0	1.679276	−1.364427	1.344142
16	1	0	3.440492	−0.992517	−1.202957
17	1	0	3.988639	−0.640250	0.421801
18	1	0	4.073142	0.598762	−0.820566
19	1	0	−0.134072	2.527461	−0.863597
20	1	0	0.018954	2.501589	0.894354
21	1	0	2.345761	2.252628	−0.539983
22	1	0	0.641932	−2.710380	−0.215747
23	1	0	−1.624747	−2.505729	−0.407308

1C



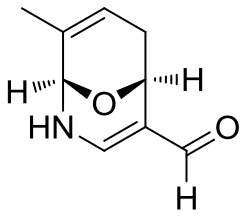
E(RHF/6-31G(d)) = −551.2345 a.u.

ΔE = 70.9 kcal/mol

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	−3.589795	0.245618	−0.204881
2	6	0	−2.165260	−0.210188	−0.202053
3	6	0	−0.907013	0.619393	−0.007103
4	8	0	−0.348234	0.090703	1.187403
5	6	0	0.651525	−0.691763	0.626756
6	6	0	−0.164112	−1.771791	−0.219065
7	6	0	−1.690721	−1.453934	−0.301720
8	7	0	−0.351136	1.936015	−0.158793
9	6	0	1.537007	0.401717	−0.038906
10	6	0	2.956043	0.153922	−0.299352
11	6	0	1.039860	1.650345	−0.195034
12	8	0	3.478952	−0.912519	−0.172552
13	1	0	3.537994	1.020699	−0.630466
14	1	0	1.226537	−1.174355	1.404237
15	1	0	−0.397099	0.208240	−0.848281
16	1	0	−3.764042	0.978754	−0.987595
17	1	0	−3.846337	0.715106	0.741247
18	1	0	−4.263334	−0.588229	−0.364557
19	1	0	0.245380	−1.878972	−1.220162
20	1	0	−0.051057	−2.739291	0.257694
21	1	0	−2.352507	−2.299270	−0.385857
22	1	0	−0.605149	2.636377	0.511627
23	1	0	1.676621	2.483443	−0.436992

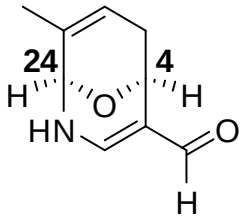
1D



Energetically could not exist

*S1.2. Standard Orientation of Two Enantiomers of **1A** for ECD Calculation*

Optimized structure of **1a**

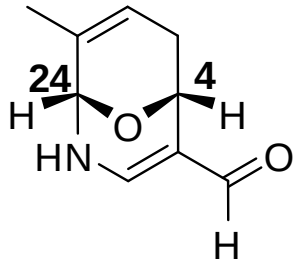


1a (4*S*, 24*R*)

Cartesian coordinate of **1a** optimized:
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.149957	−0.092595	0.900662
2	6	0	1.831941	−0.418435	0.251470
3	6	0	1.289853	0.607391	−0.737823
4	8	0	0.318826	0.053978	−1.602059
5	6	0	−0.750079	−0.544368	−0.830420
6	6	0	−0.213168	−1.805750	−0.140902
7	6	0	1.123753	−1.528448	0.495959
8	7	0	0.709516	1.752775	−0.012310
9	6	0	−1.317427	0.503220	0.107874
10	6	0	−2.661483	0.379048	0.629509
11	6	0	−0.589665	1.626778	0.376800
12	8	0	−3.413888	−0.569962	0.421567
13	1	0	−3.002564	1.229117	1.262961
14	1	0	−1.514927	−0.811558	−1.563754
15	1	0	2.091837	0.989067	−1.377028
16	1	0	3.092828	0.845144	1.470528
17	1	0	3.946859	0.032966	0.153304
18	1	0	3.457226	−0.885290	1.590639
19	1	0	−0.938695	−2.149436	0.606426
20	1	0	−0.117369	−2.616906	−0.878655
21	1	0	1.520930	−2.277754	1.180550
22	1	0	1.090493	2.678056	−0.160992
23	1	0	−1.014826	2.463982	0.927344

Optimized structure of the enantiomer **1b**



1b (4*R*, 24*S*)

Cartesian coordinate of the enantiomer **1b** optimized:
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	−3.149957	−0.092595	−0.900662
2	6	0	−1.831941	−0.418435	−0.251470
3	6	0	−1.289853	0.607391	0.737823
4	8	0	−0.318826	0.053978	1.602059
5	6	0	0.750079	−0.544368	0.830420
6	6	0	0.21316	−1.805750	0.140902
7	6	0	−1.123753	−1.528448	−0.495959
8	7	0	−0.709516	1.752775	0.012310
9	6	0	1.317427	0.503220	−0.107874
10	6	0	2.661483	0.379048	−0.629509
11	6	0	0.589665	1.626778	−0.376800
12	8	0	3.413888	−0.569962	−0.421567
13	1	0	3.002564	1.229117	−1.262961
14	1	0	1.514927	−0.811558	1.563754
15	1	0	−2.091837	0.989067	1.377028
16	1	0	−3.092828	0.845144	−1.470528
17	1	0	−3.946859	0.032966	−0.153304
18	1	0	−3.457226	−0.885290	−1.590639
19	1	0	0.938695	−2.149436	−0.606426
20	1	0	0.117369	−2.616906	0.878655
21	1	0	−1.520930	−2.277754	−1.180550
22	1	0	−1.090493	2.678056	0.160992
23	1	0	1.014826	2.463982	−0.927344

Figure S1. HRESIMS spectrum of compound **1**.

Elemental Composition Report **Page 1**

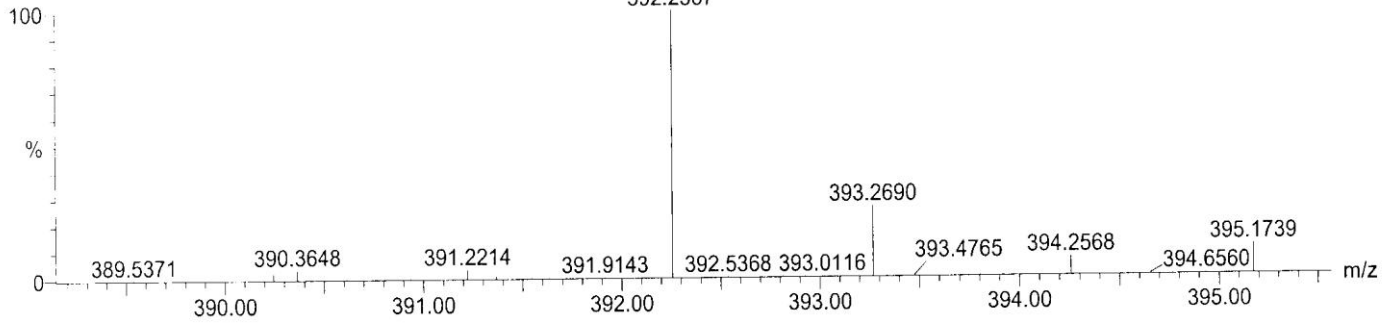
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
50 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 5-50 H: 5-100 N: 1-1 O: 1-18 Na: 1-1

SIPI
PSJ-B6 M.W=369
WQ10180H3 25 (0.880) AM (Med,6, Ar,5000.0,403.13,0.70); Sm (SG, 2x3.00); Cm (23:64)

Q-Tof micro
YA019

12-May-2010,14:30:05
0.00000000
TOF MS ES+
7.70e4



Minimum:	30.00				-1.5		
Maximum:	100.00		5.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
392.2567	100.00	392.2565	0.2	0.5	7.5	451.4	C24 H35 N O2 Na

Figure S2. IR spectrum of compound **1**.

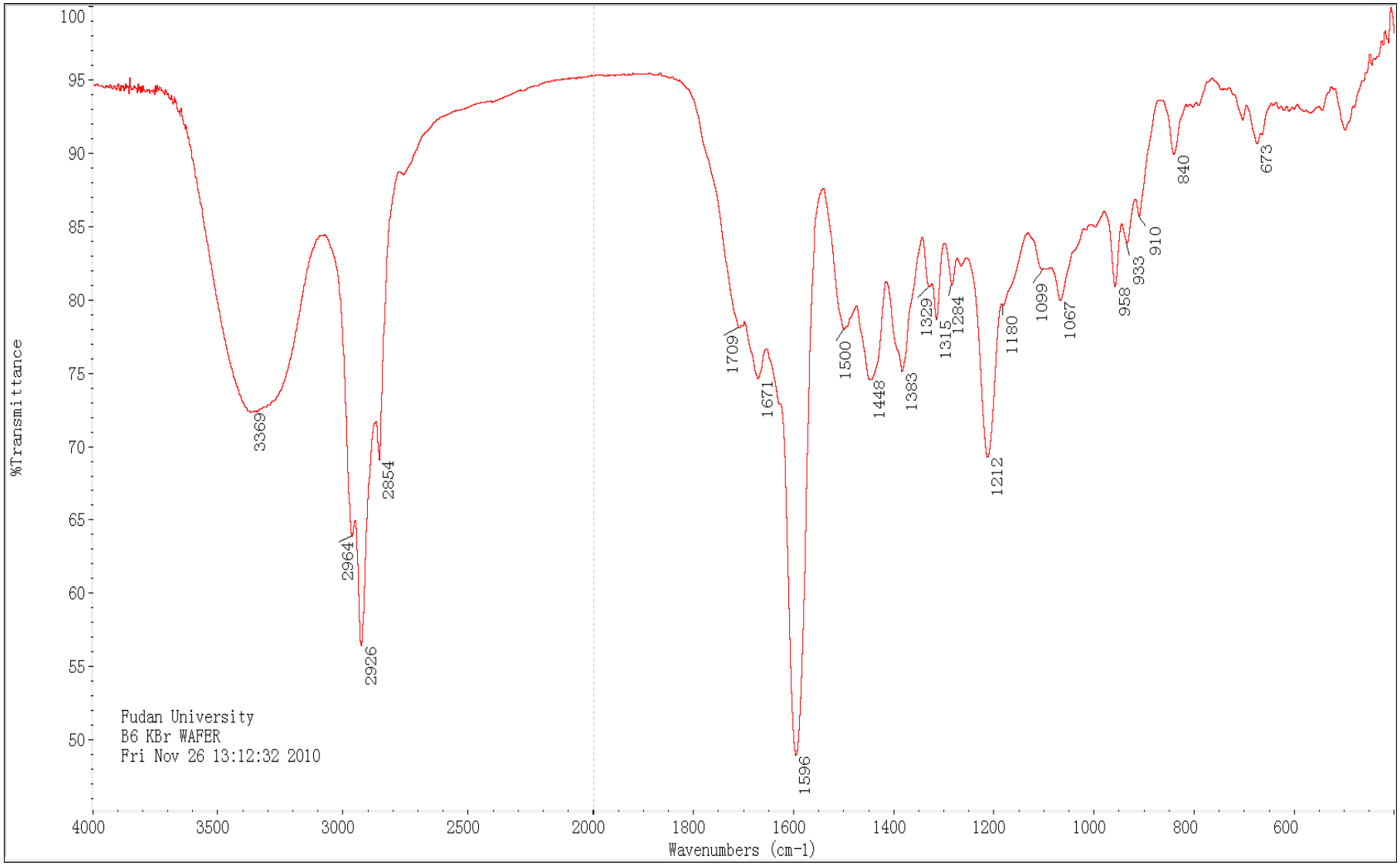


Figure S3. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

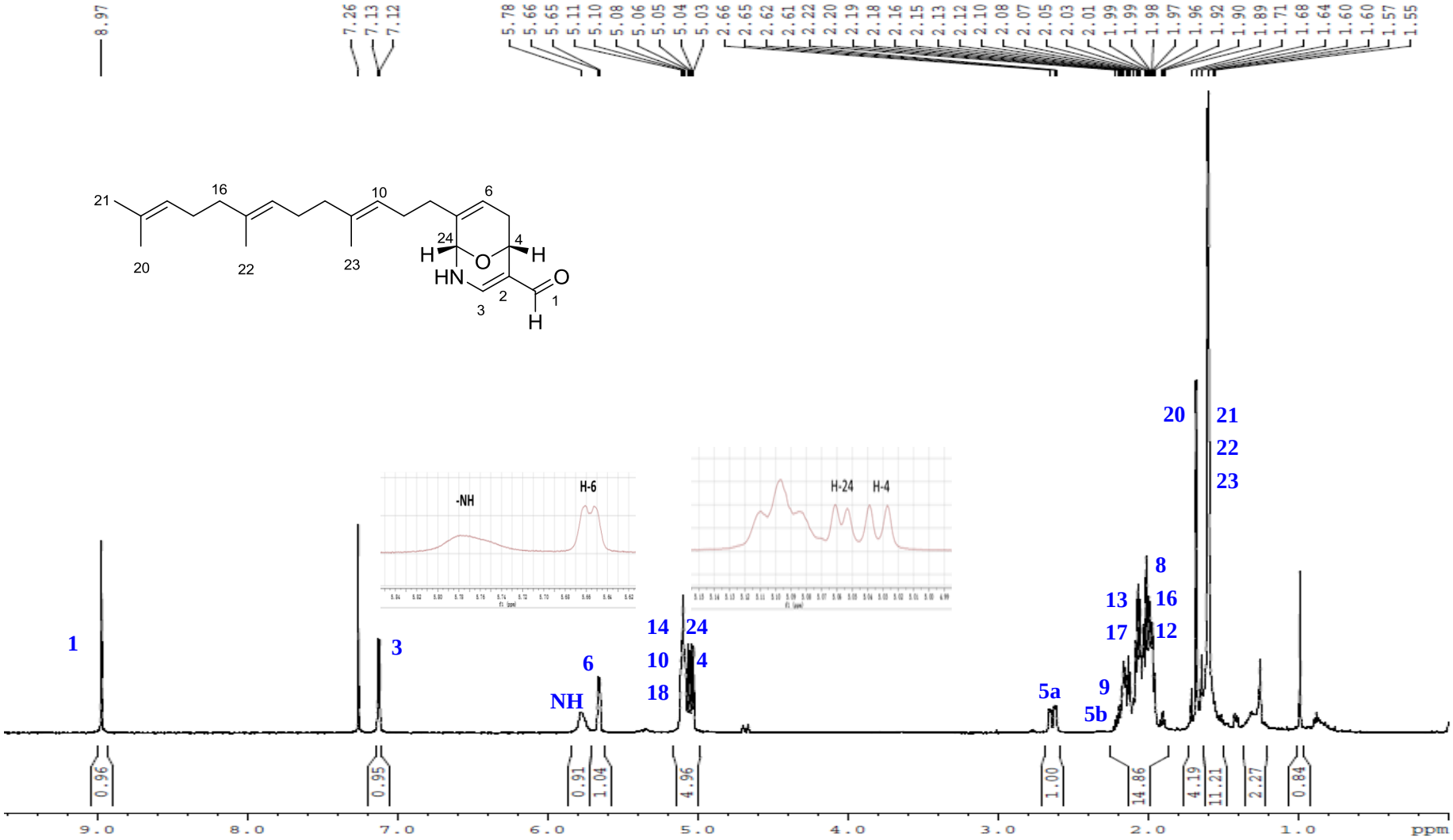


Figure S4. ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

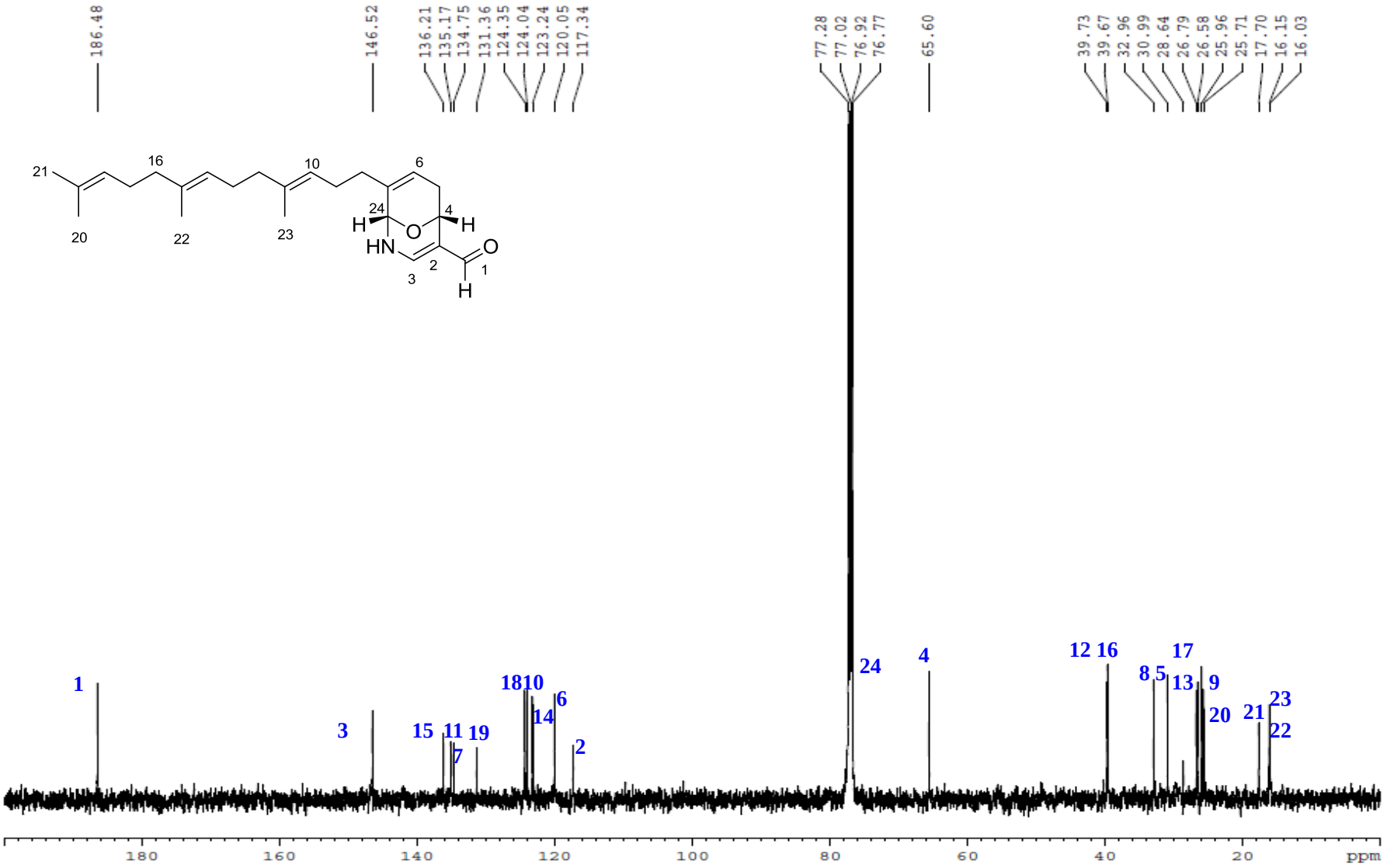


Figure S5. DEPT spectrum of compound **1** in $CDCl_3$.

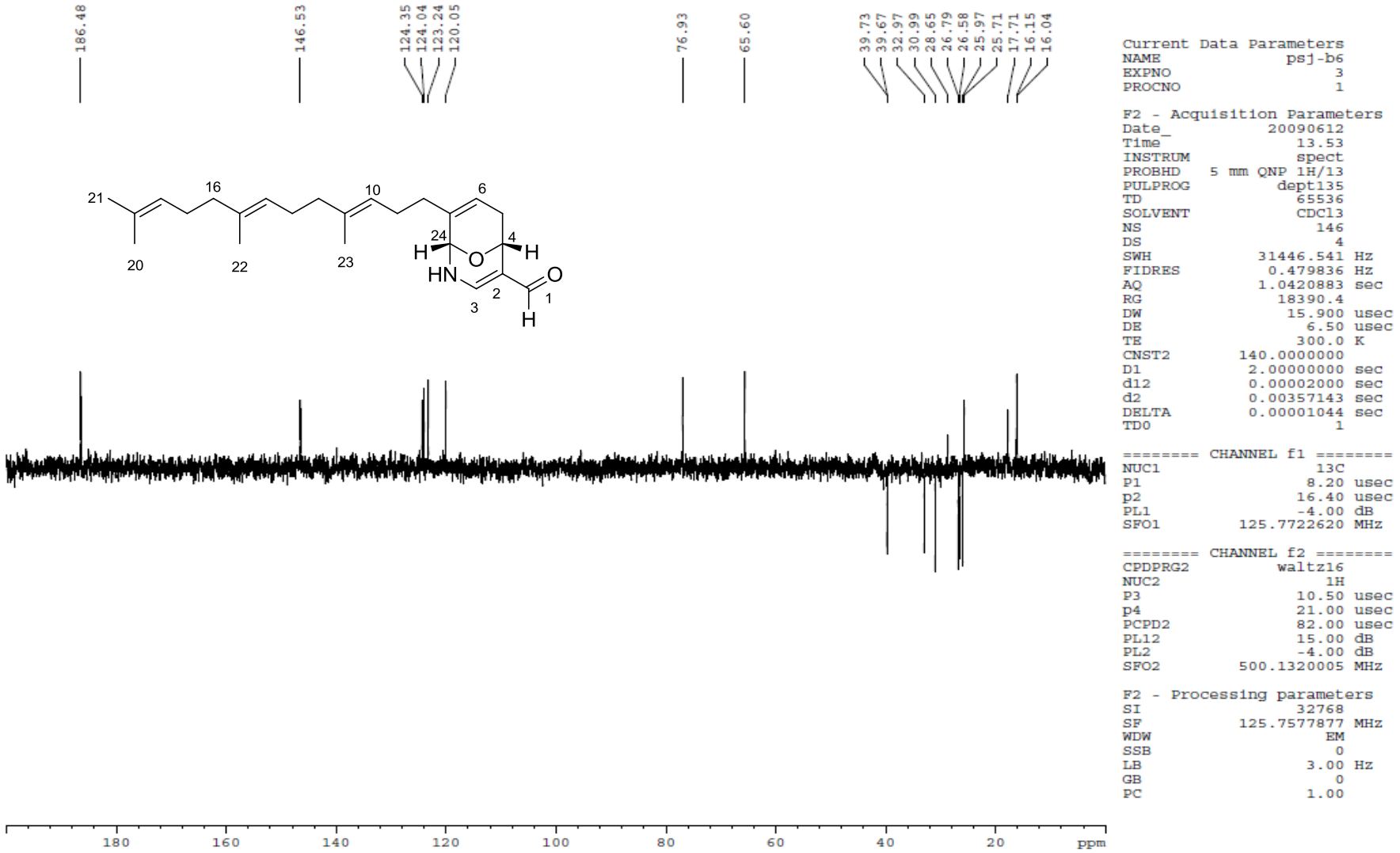


Figure S6. HSQC spectrum of compound **1** in $CDCl_3$.

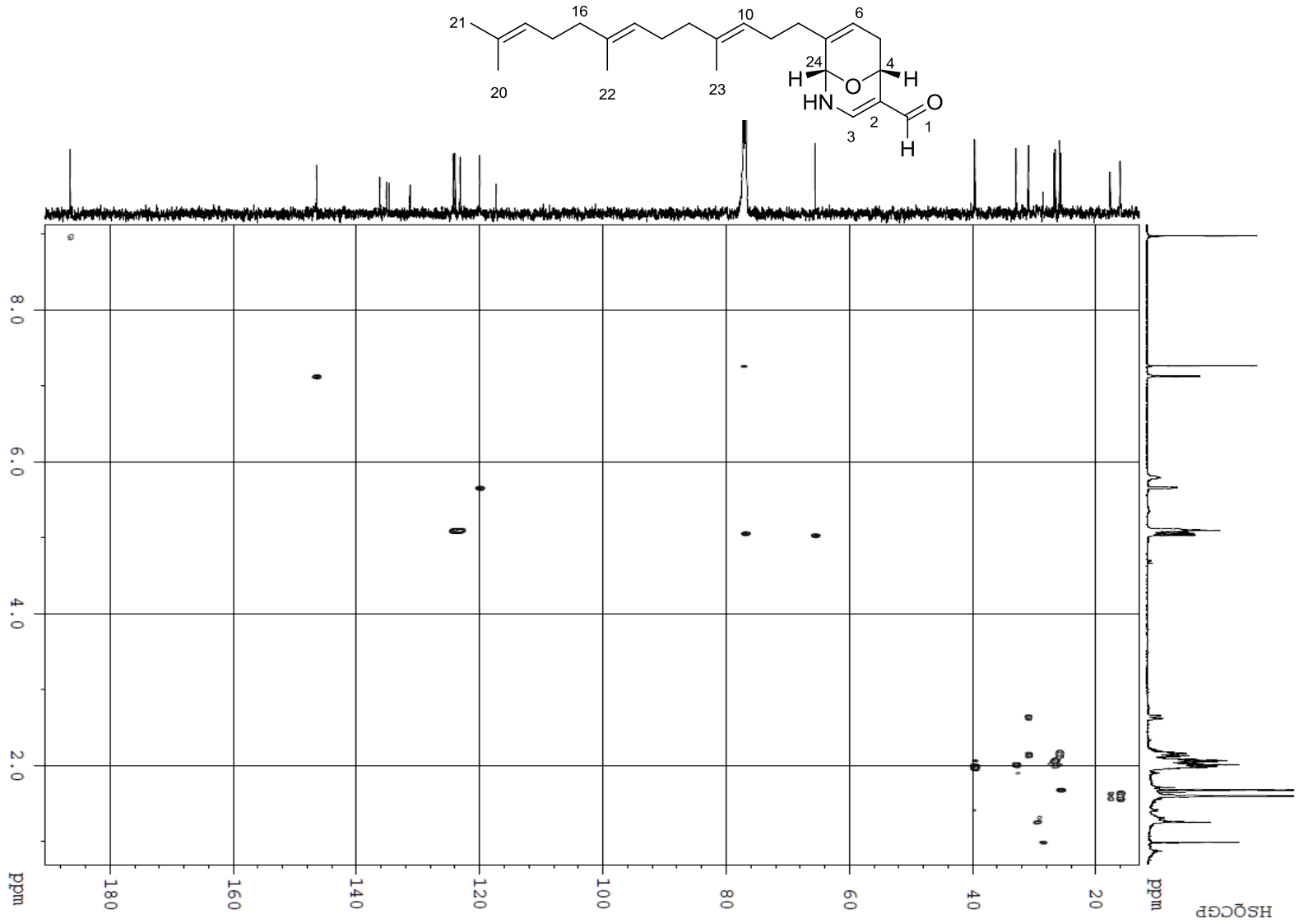


Figure S7. ^{1}H–^{1}H COSY spectrum of compound **1** in $CDCl_3$.

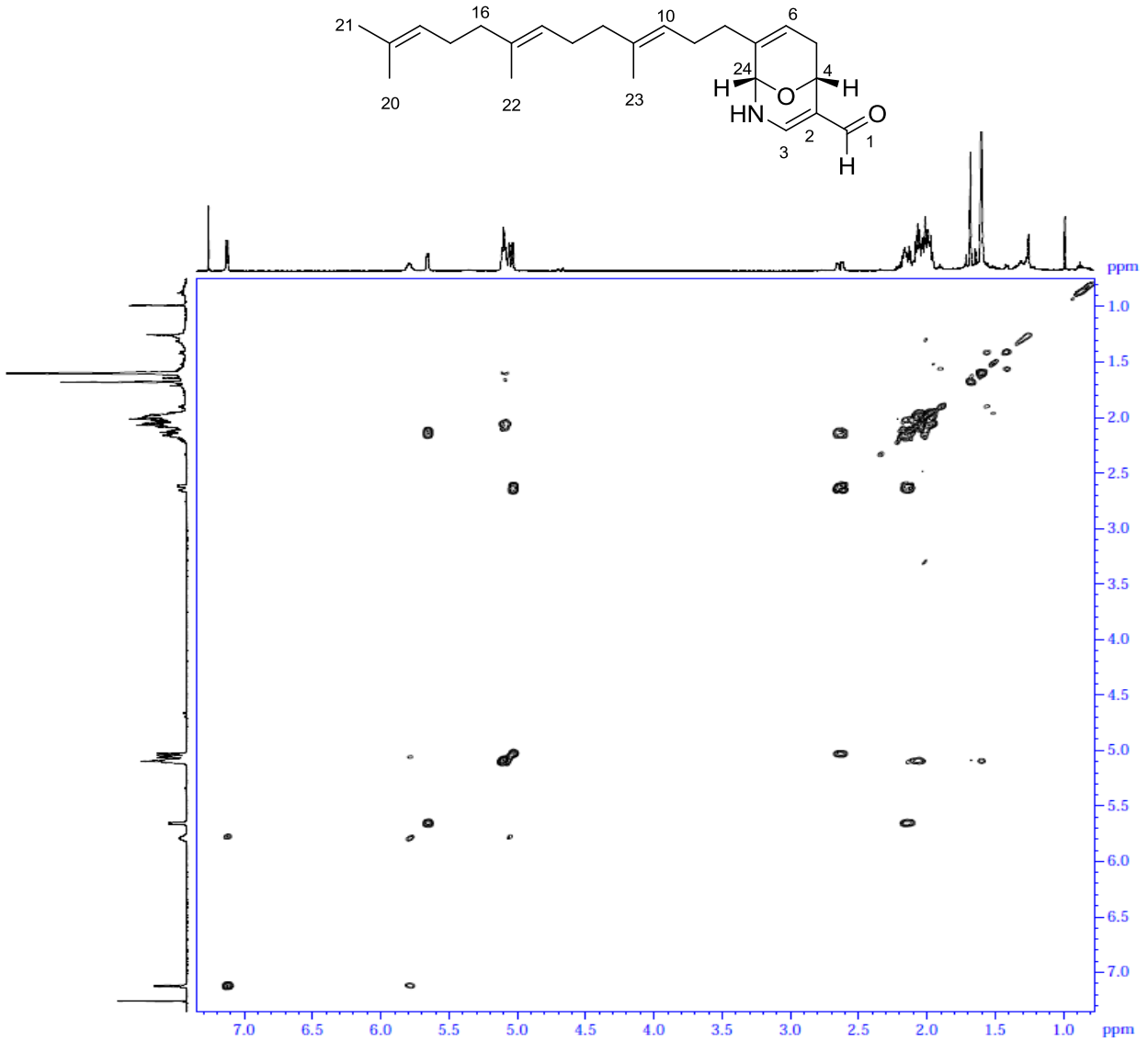


Figure S8. HMBC spectrum of compound **1** in $CDCl_3$.

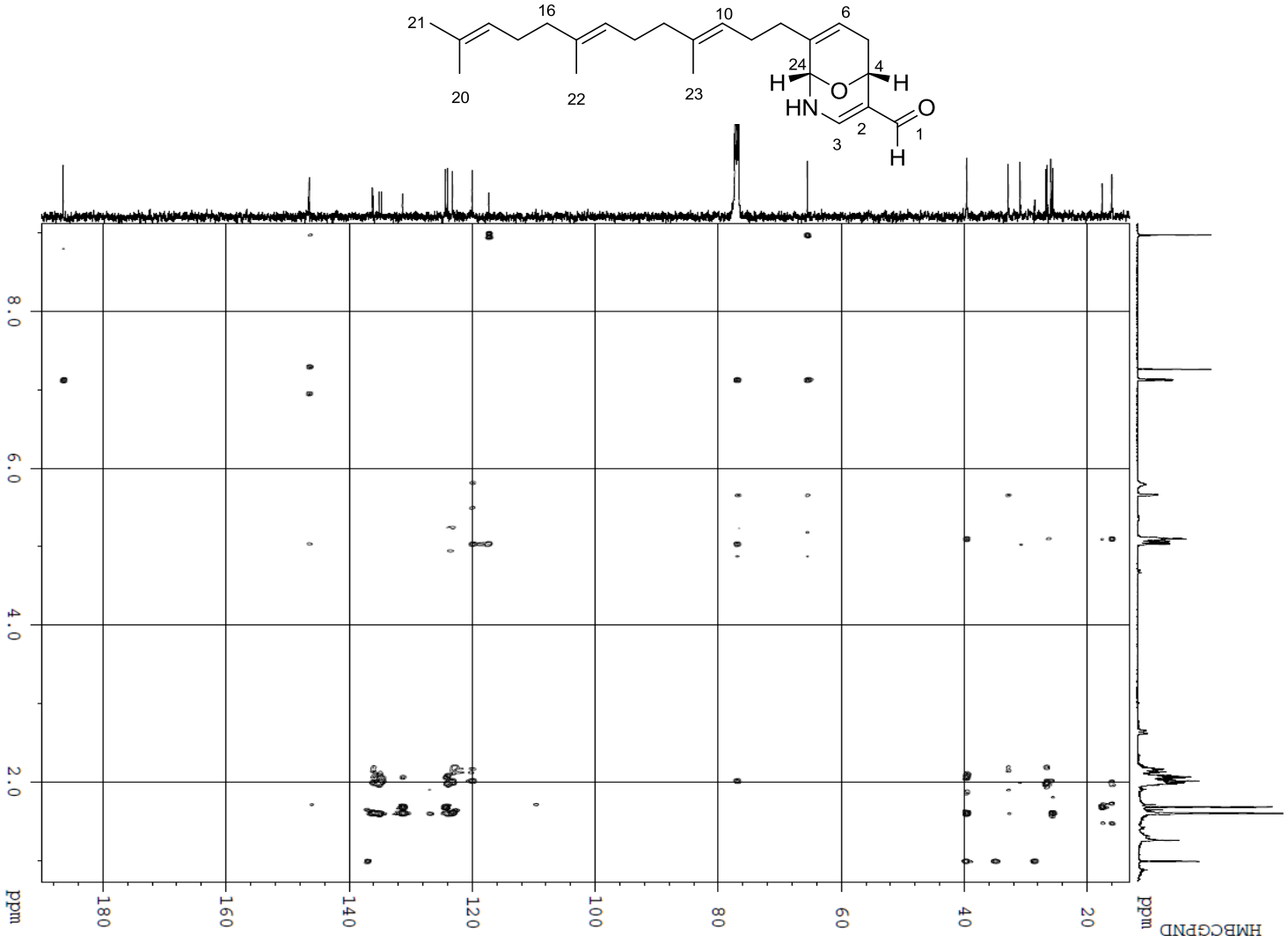


Figure S9. NOESY spectrum of compound **1** in $CDCl_3$.

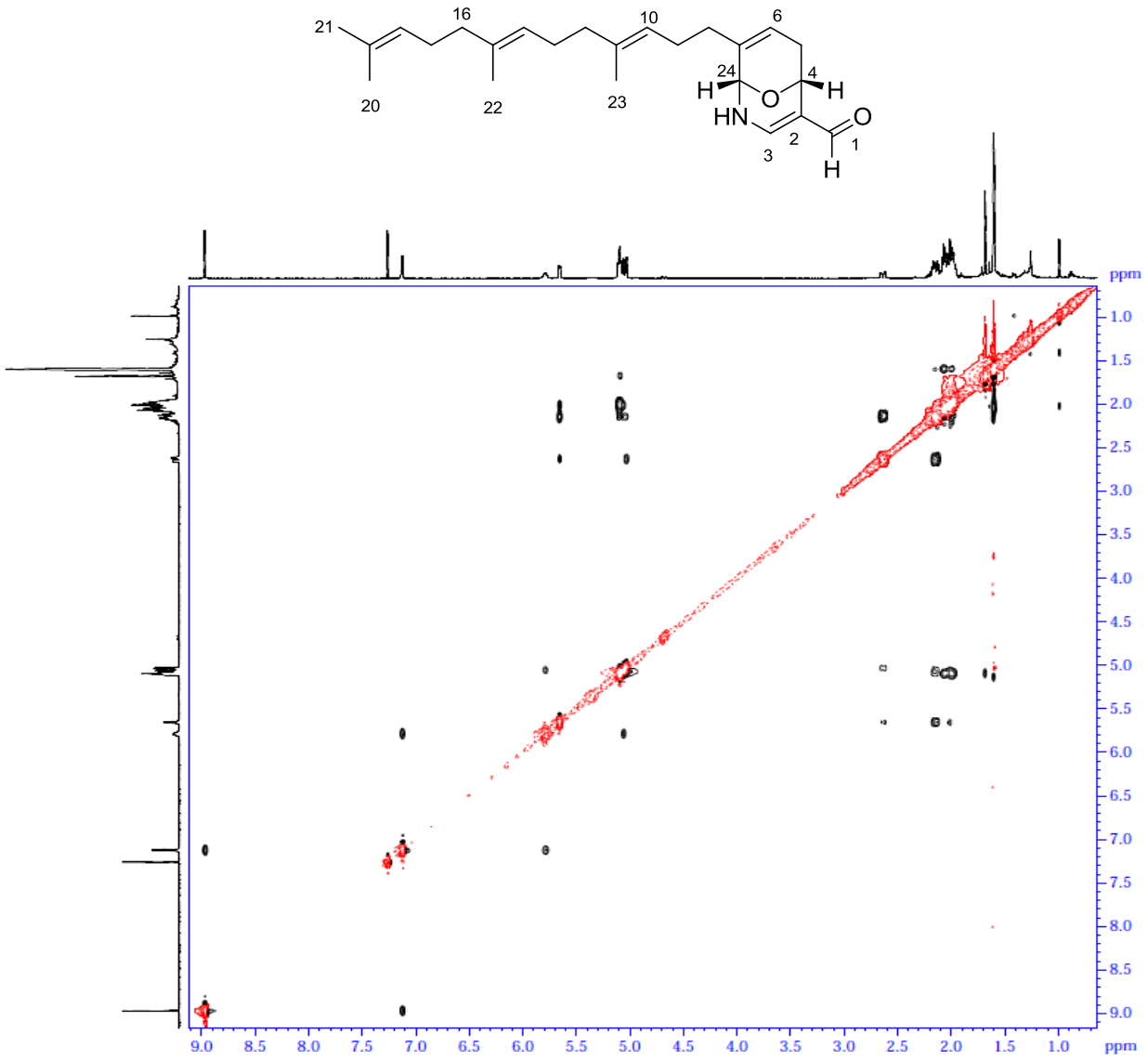


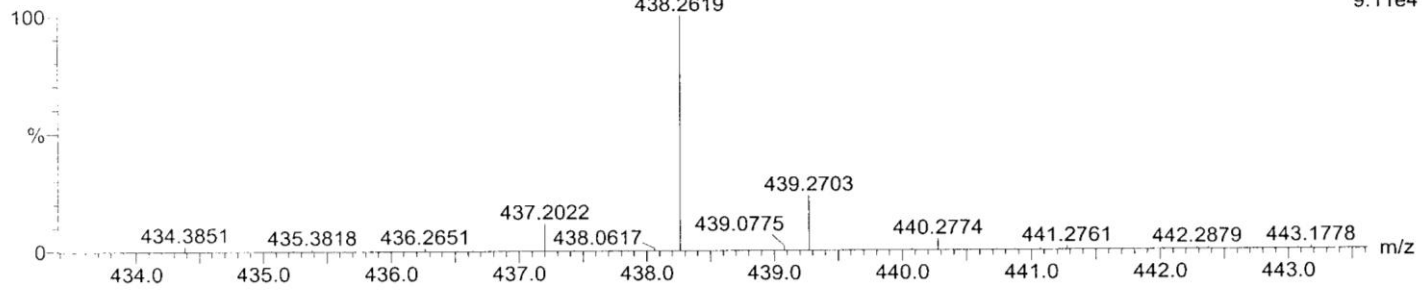
Figure S10. HRESIMS spectrum of compound **2**.

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: 5-30 H: 5-42 N: 0-1 O: 1-6 Na: 1-1

SIPI
PSJ-B84 M.W=415
WQ10172H 30 (1.057) AM (Cen,6, 80.00, Ar,5000.0,447.03,0.70); Sm (SG, 2x3.00); Cm (25:42)
Q-Tof micro
YA019
10-May-2010,15:32:08
0.00000000
TOF MS ES+
9.11e4



Minimum:	25.00				-1.5		
Maximum:	100.00		5.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
438.2619	100.00	438.2620	-0.1	-0.2	7.5	487.0	C25 H37 N O4 Na

Figure S11. IR spectrum of compound **2**.

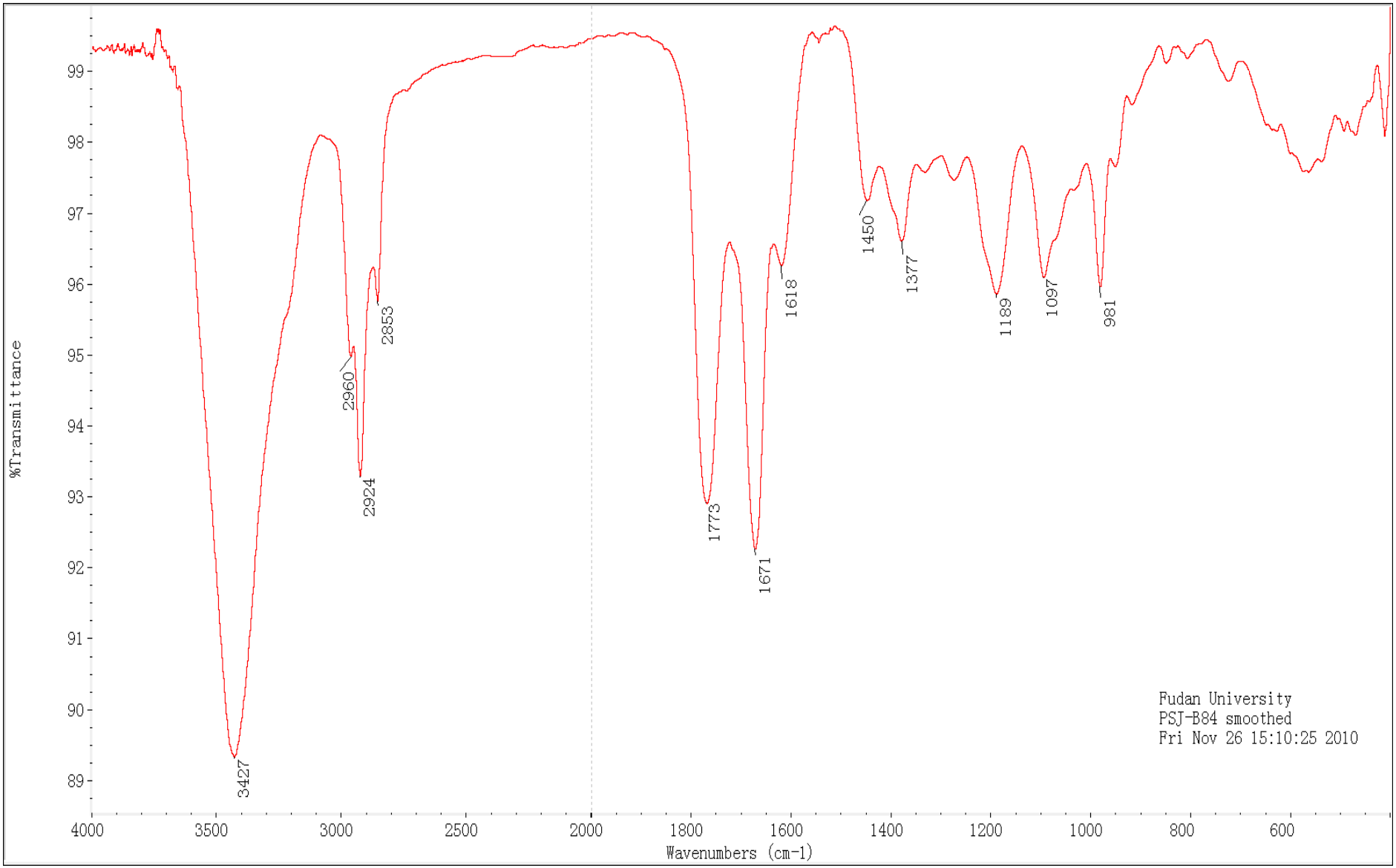


Figure S12. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

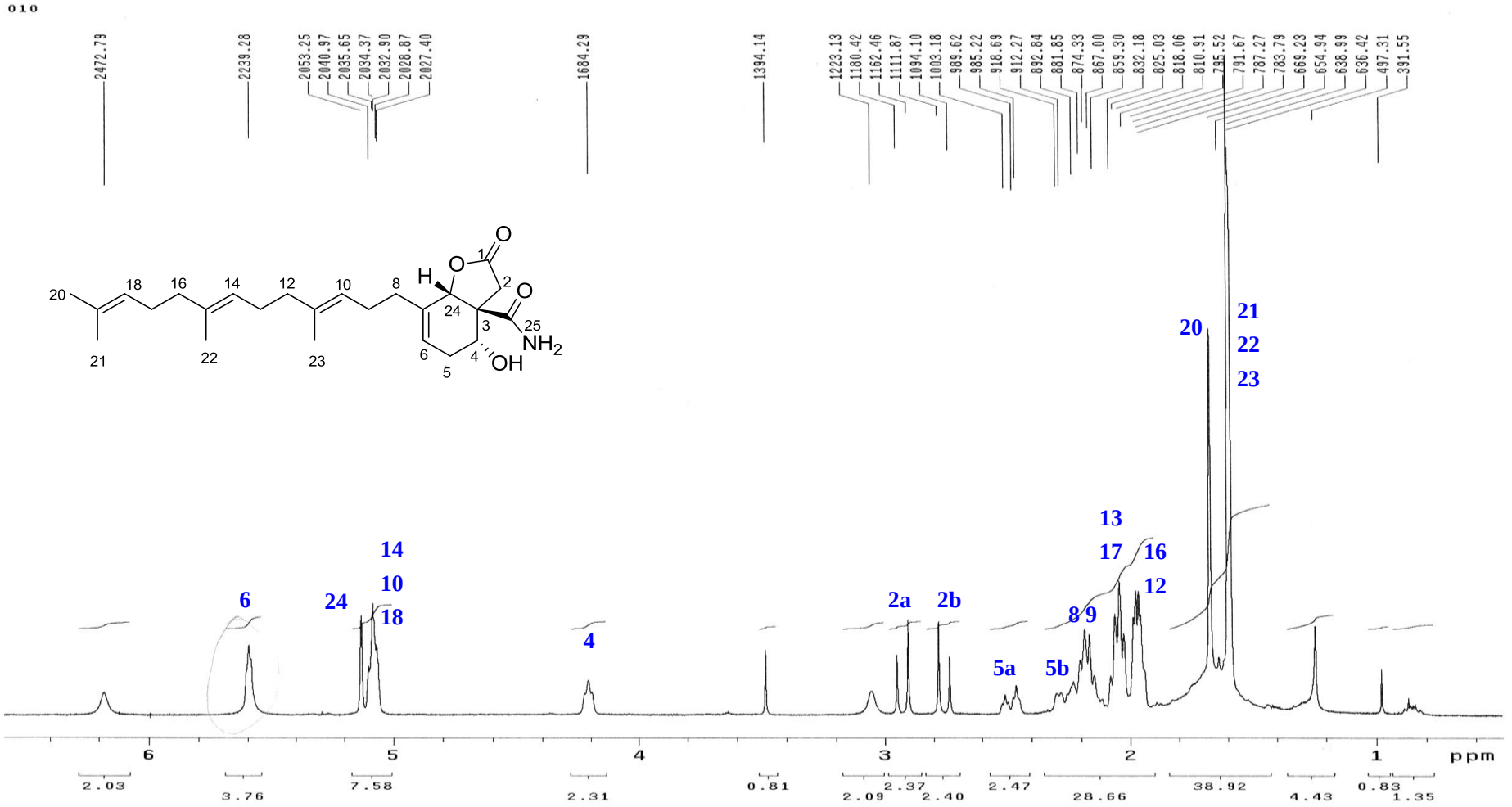


Figure S13. ^{1}H NMR spectrum of compound **2** in DMSO.

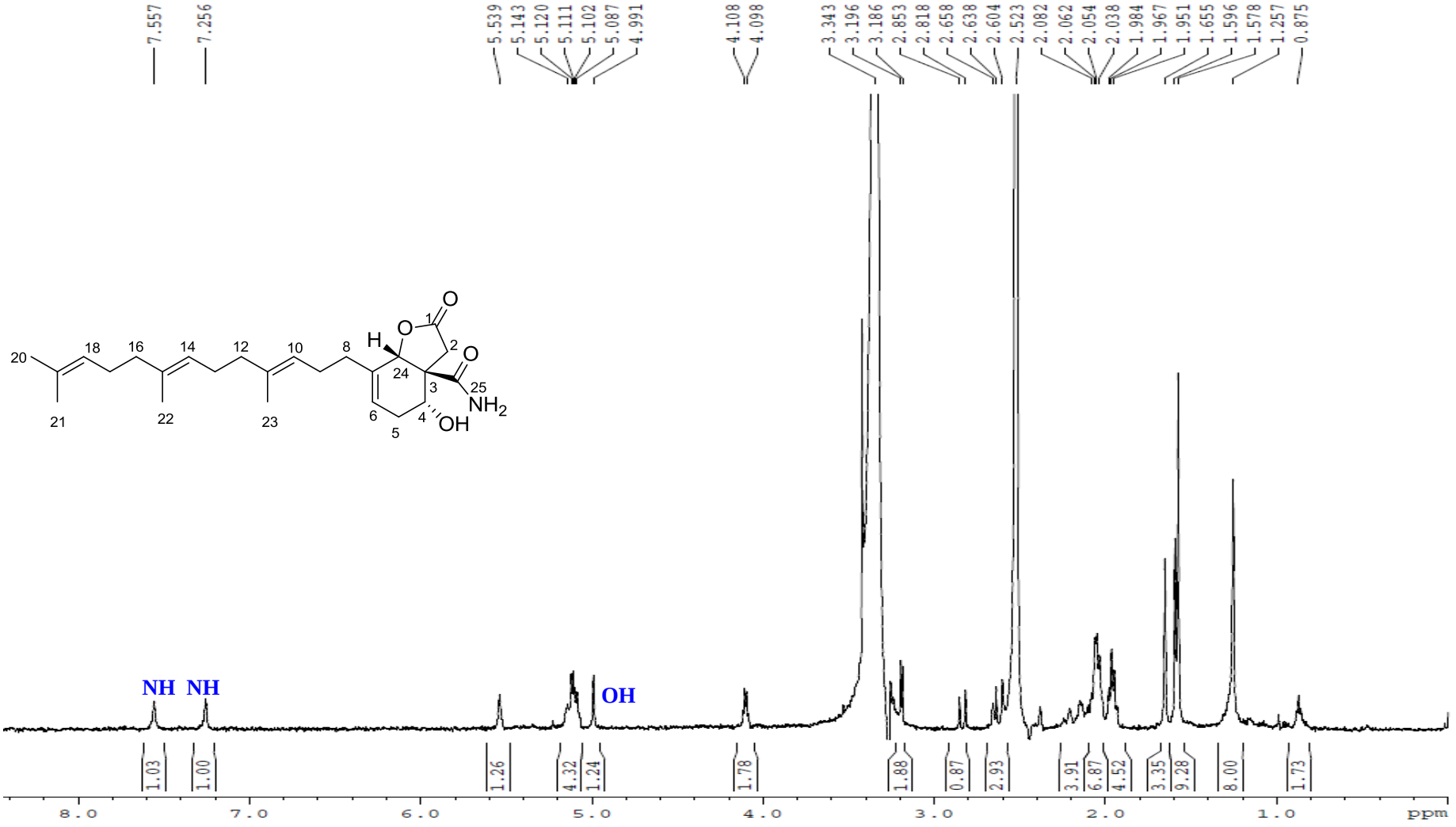


Figure S14. ^{13}C NMR and DEPT spectrum of compound **2** in $CDCl_3$.

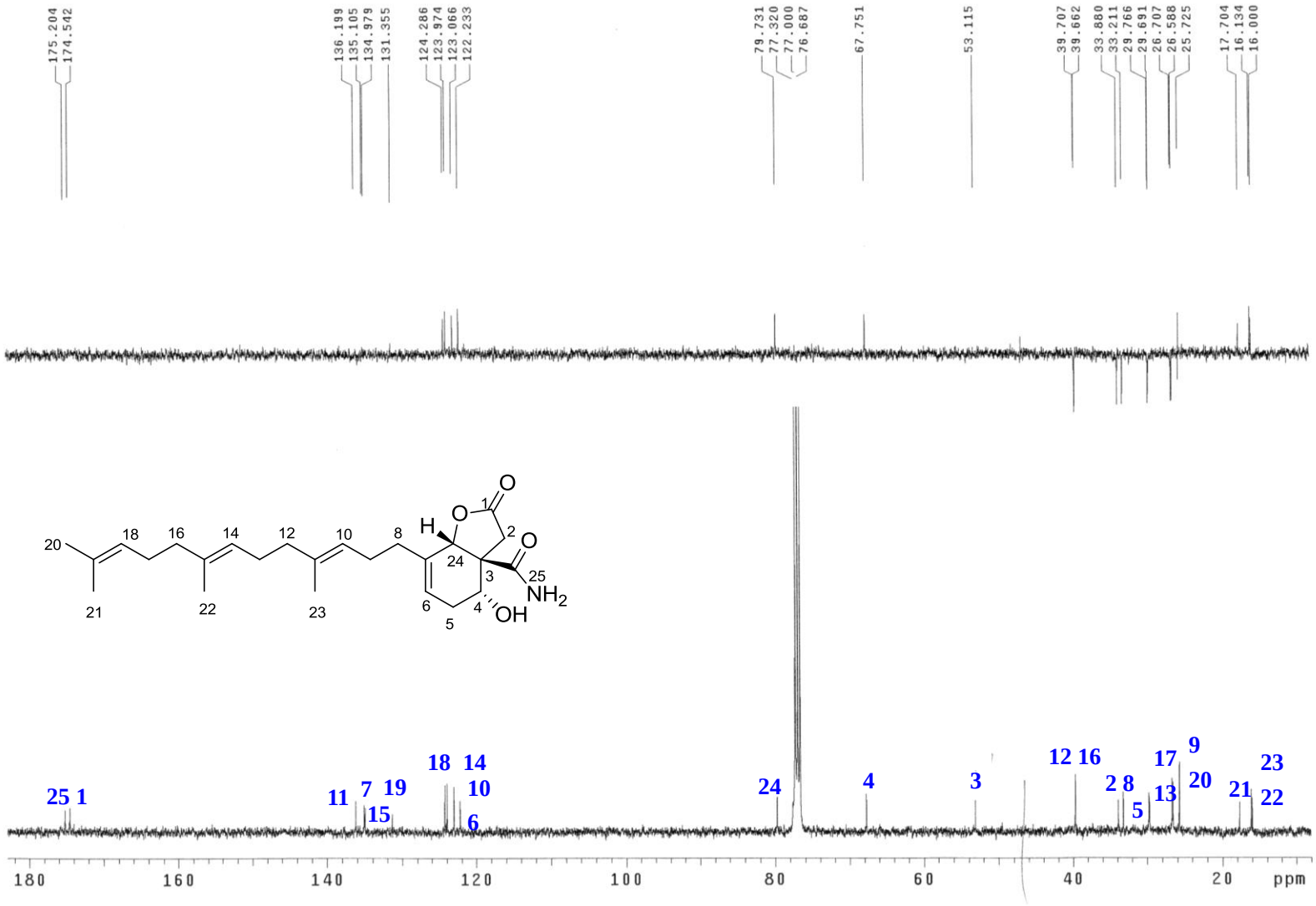


Figure S15. HSQC spectrum of compound **2** in $CDCl_3$.

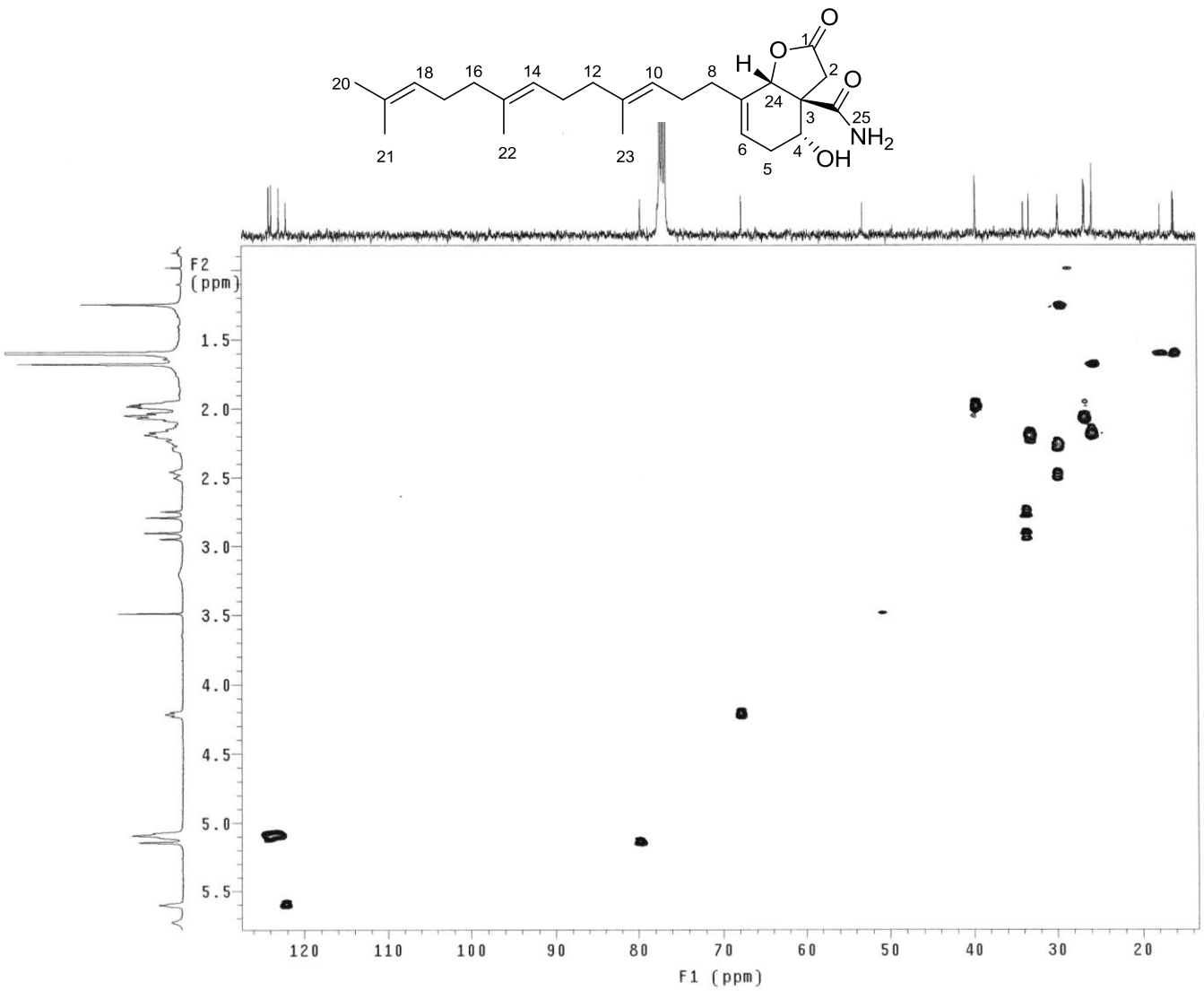


Figure S16. $^{1}H–^{1}H$ COSY spectrum of compound **2** in $CDCl_3$.

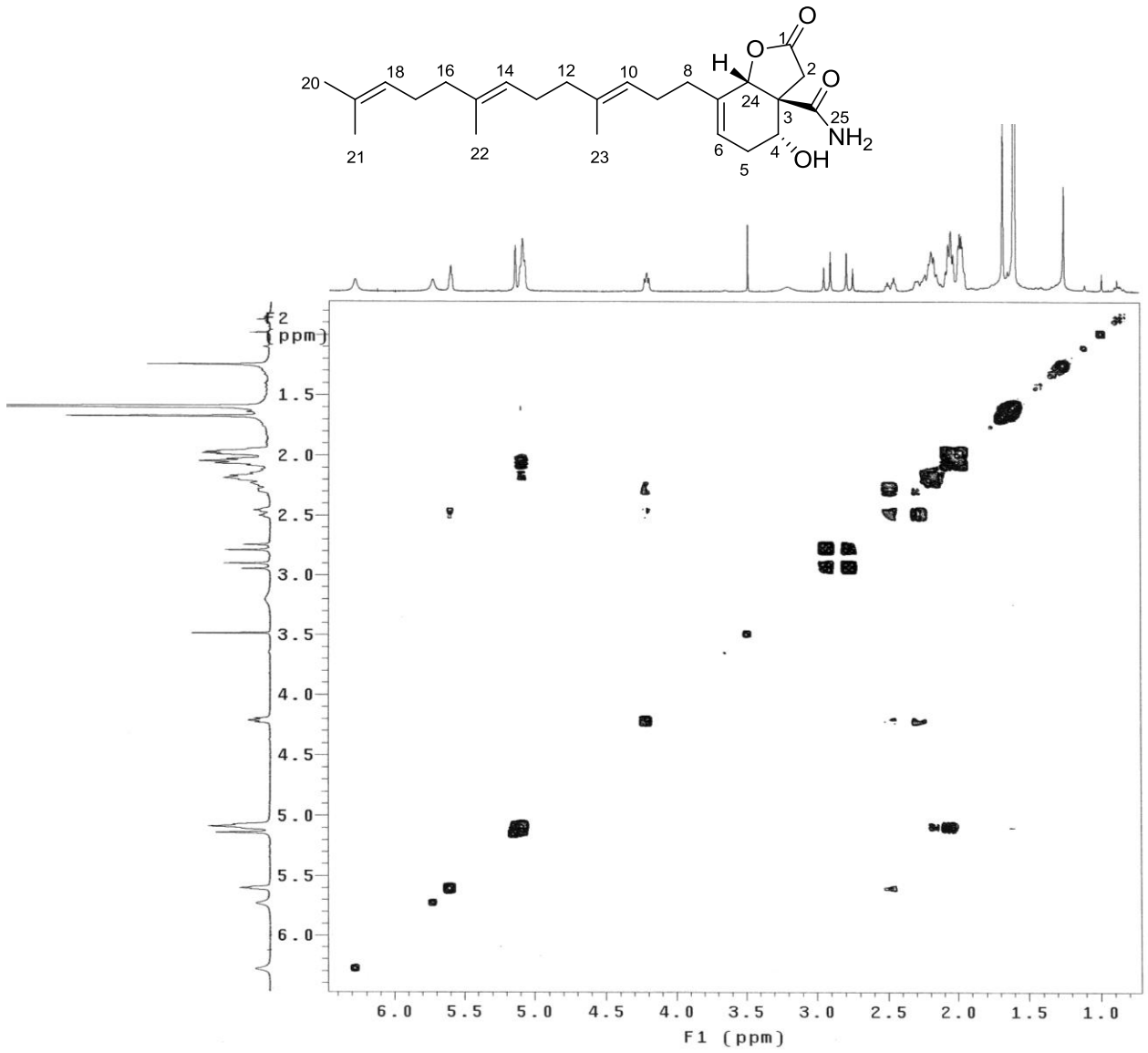


Figure S17. HMBC spectrum of compound **2** in $CDCl_3$.

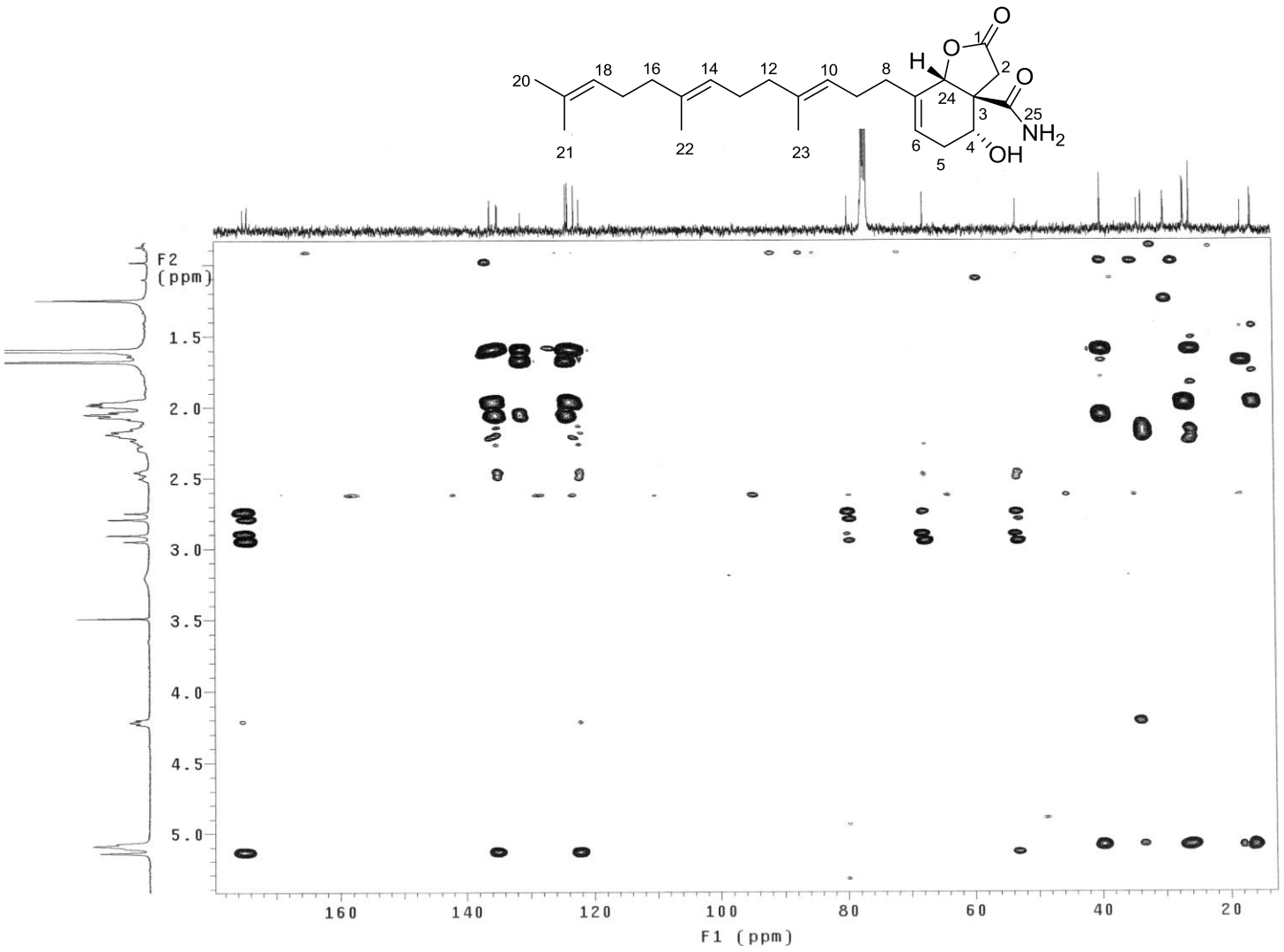


Figure S18. NOESY spectrum of compound **2** in $CDCl_3$.

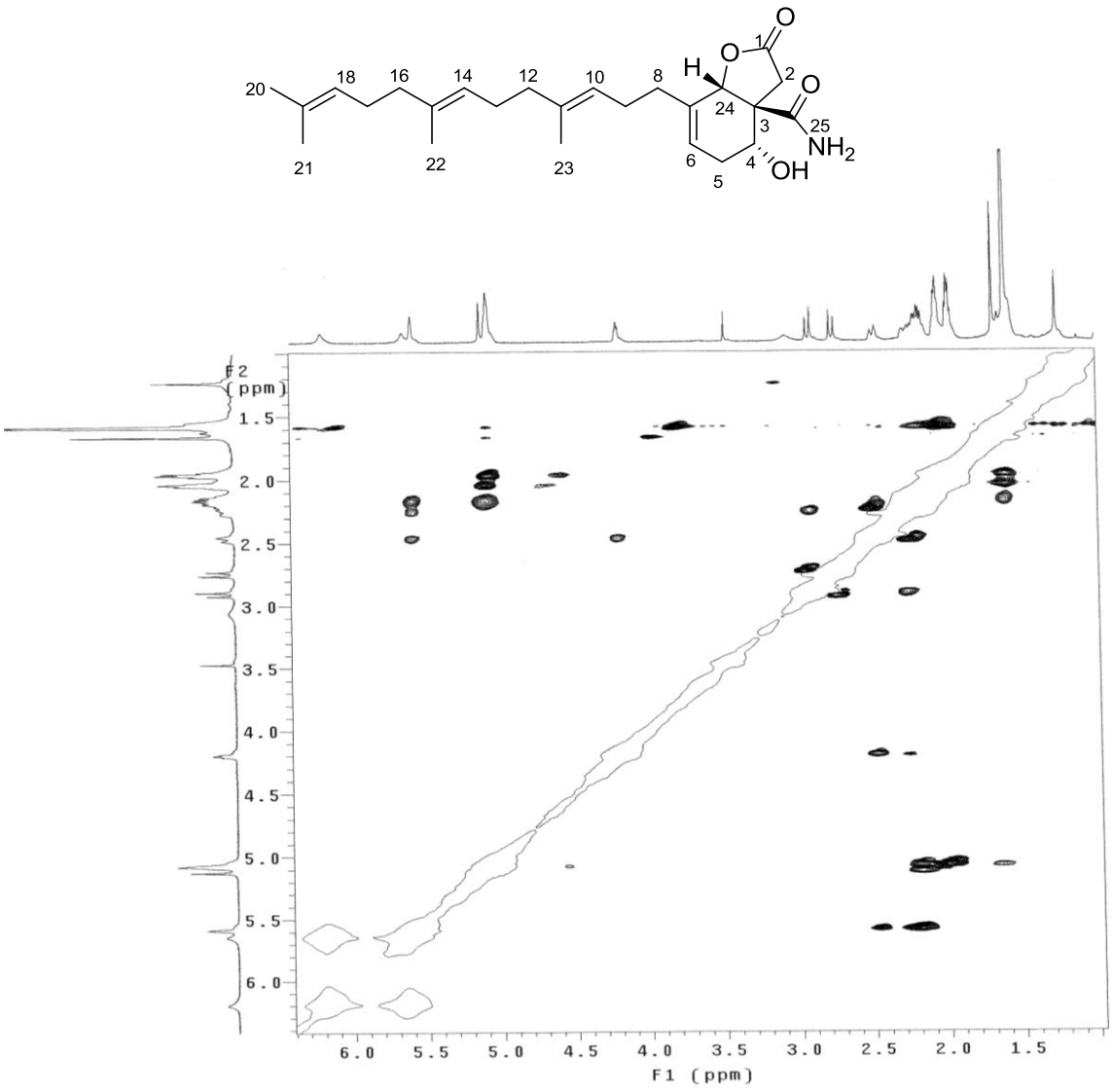


Figure S19. Partial NOESY spectrum of compound **2** in $CDCl_3$.

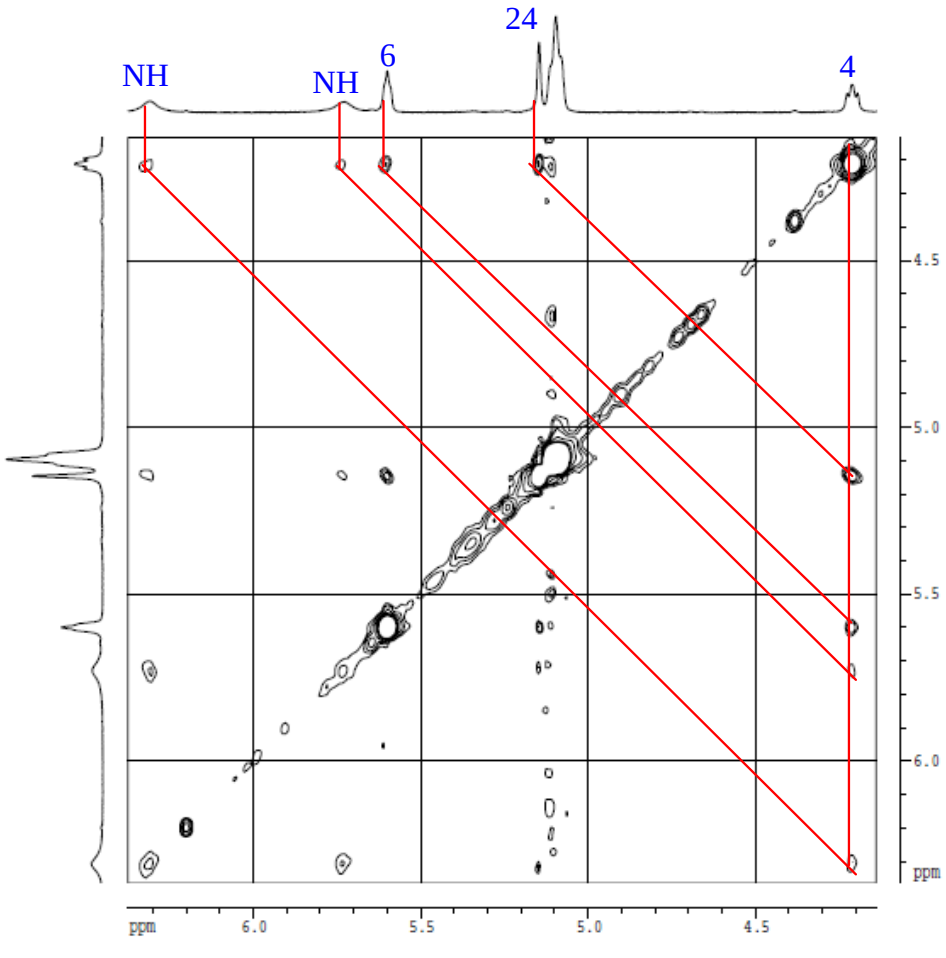


Figure S20. HRESIMS spectrum of compound **3**.

Elemental Composition Report **Page 1**

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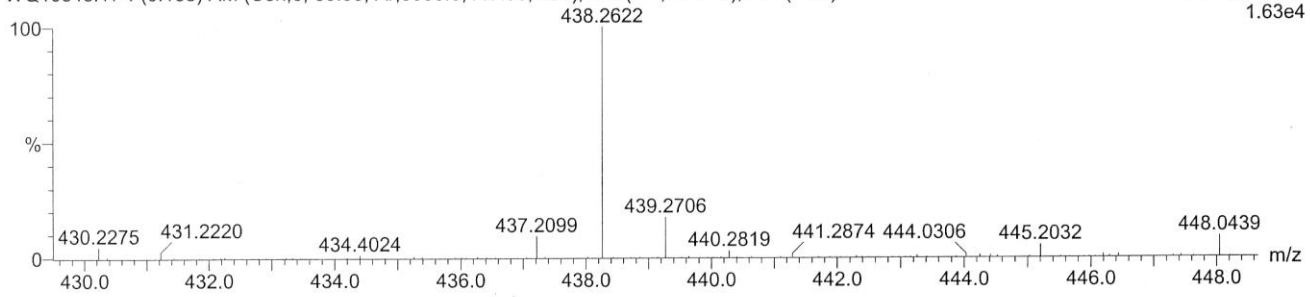
Selected filters: None

Monoisotopic Mass, Even Electron Ions
20 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 5-27 H: 10-50 N: 1-3 O: 3-4 Na: 1-1

SIPI
PSJ-B10 M.W=415
WQ10348H1 4 (0.138) AM (Cen,6, 80.00, Ar,5000.0,447.03,1.00); Sm (SG, 2x3.00); Cm (1:22)

Q-Tof micro
YA019

04-Oct-2010,11:47:44
0.00000000
TOF MS ES+
1.63e4



Minimum:	50.00				-1.5		
Maximum:	100.00		5.0	20.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
438.2622	100.00	438.2620	0.2	0.5	7.5	464.9	C25 H37 N O4 Na

Figure S21. IR spectrum of compound **3**.

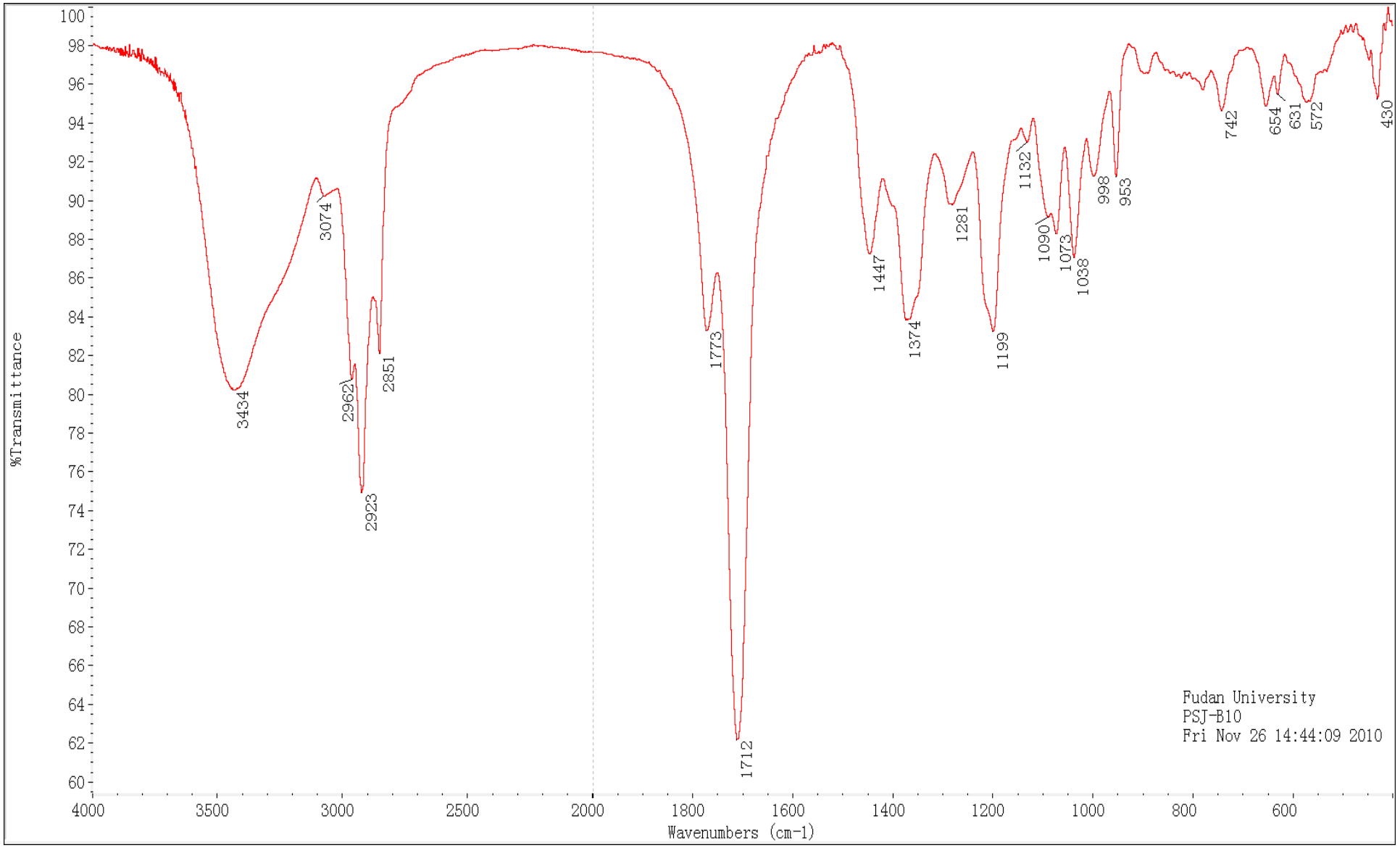


Figure S22. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

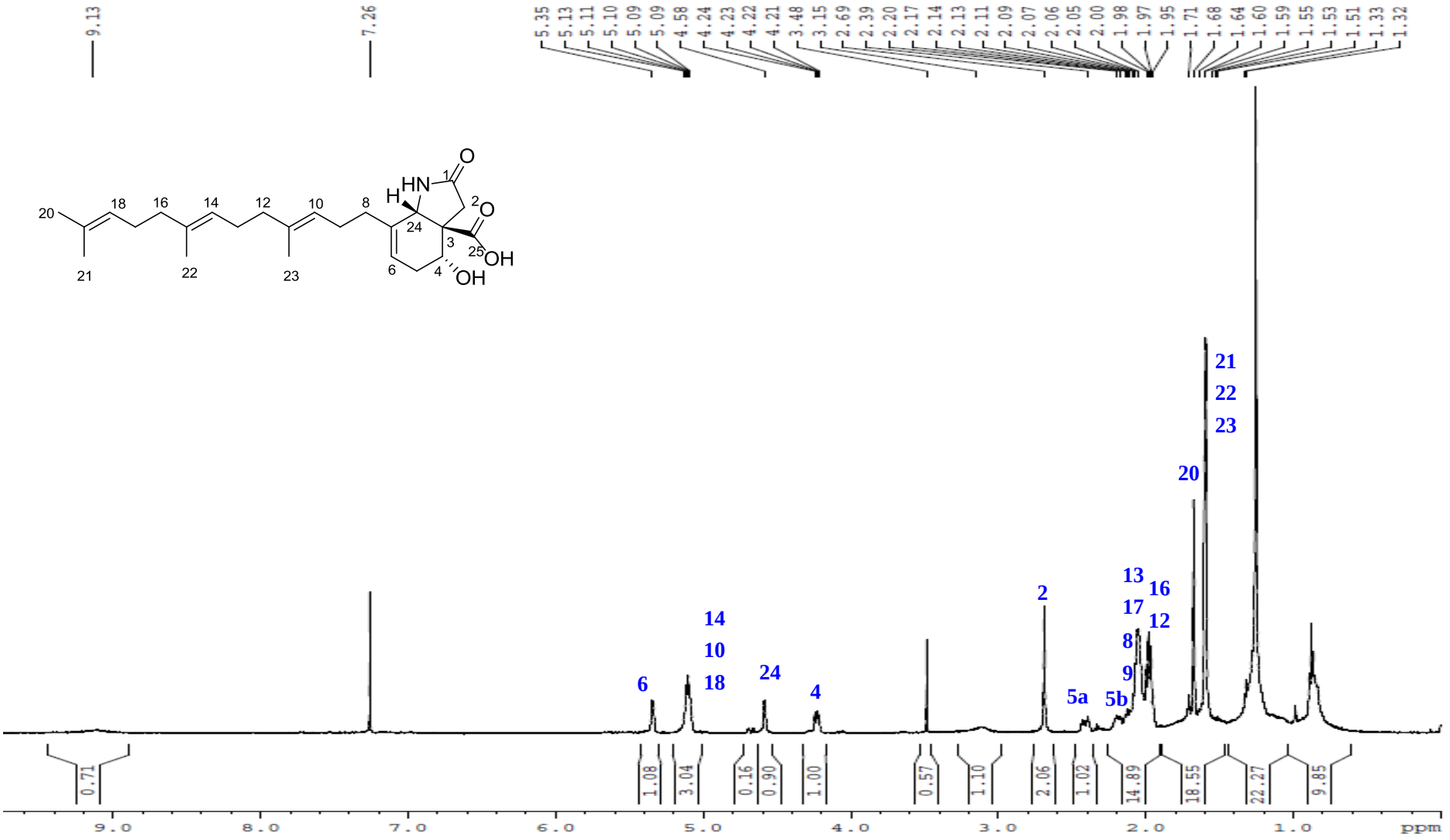


Figure S23. ^{1}H NMR spectrum of compound **3** in DMSO.

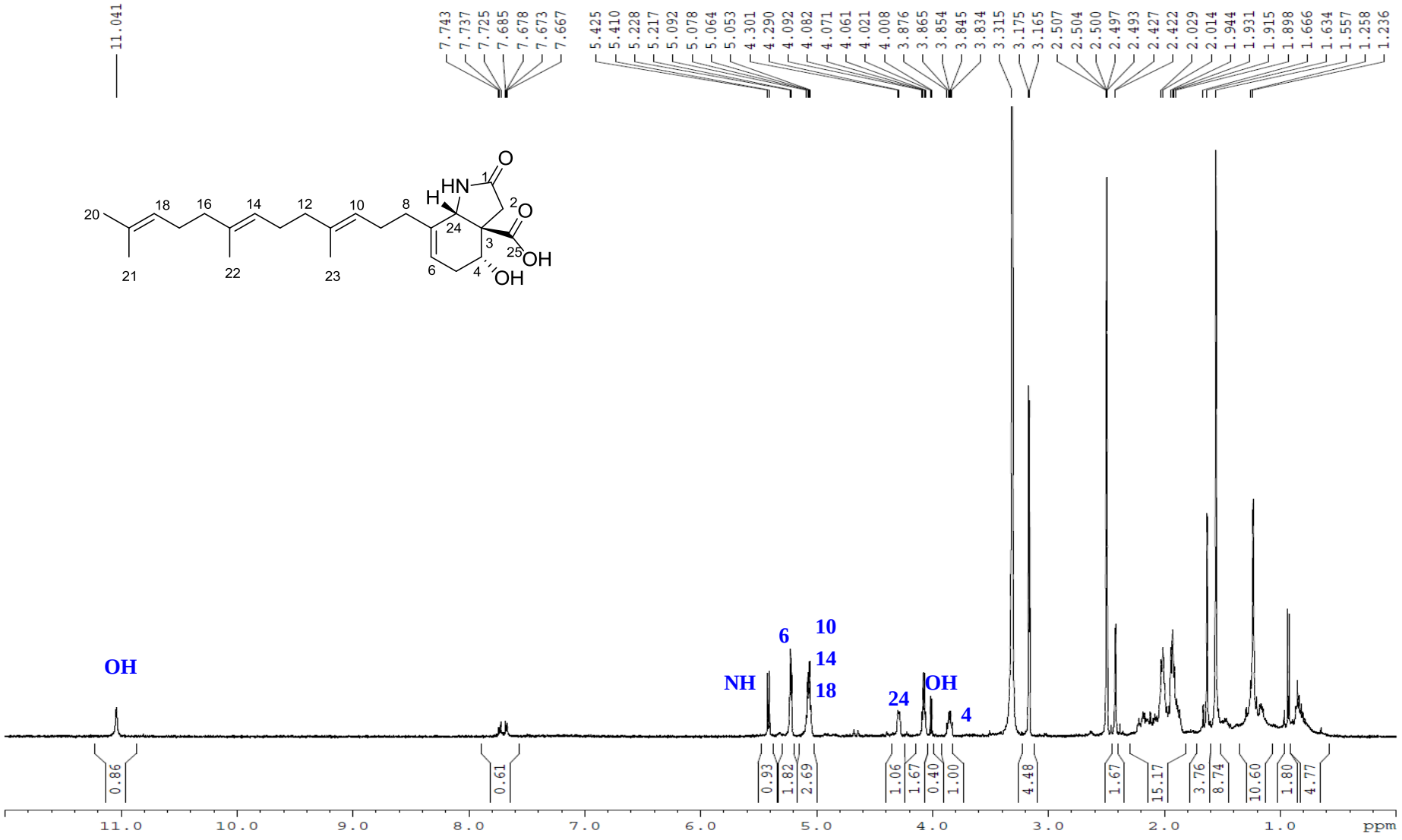


Figure S24. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

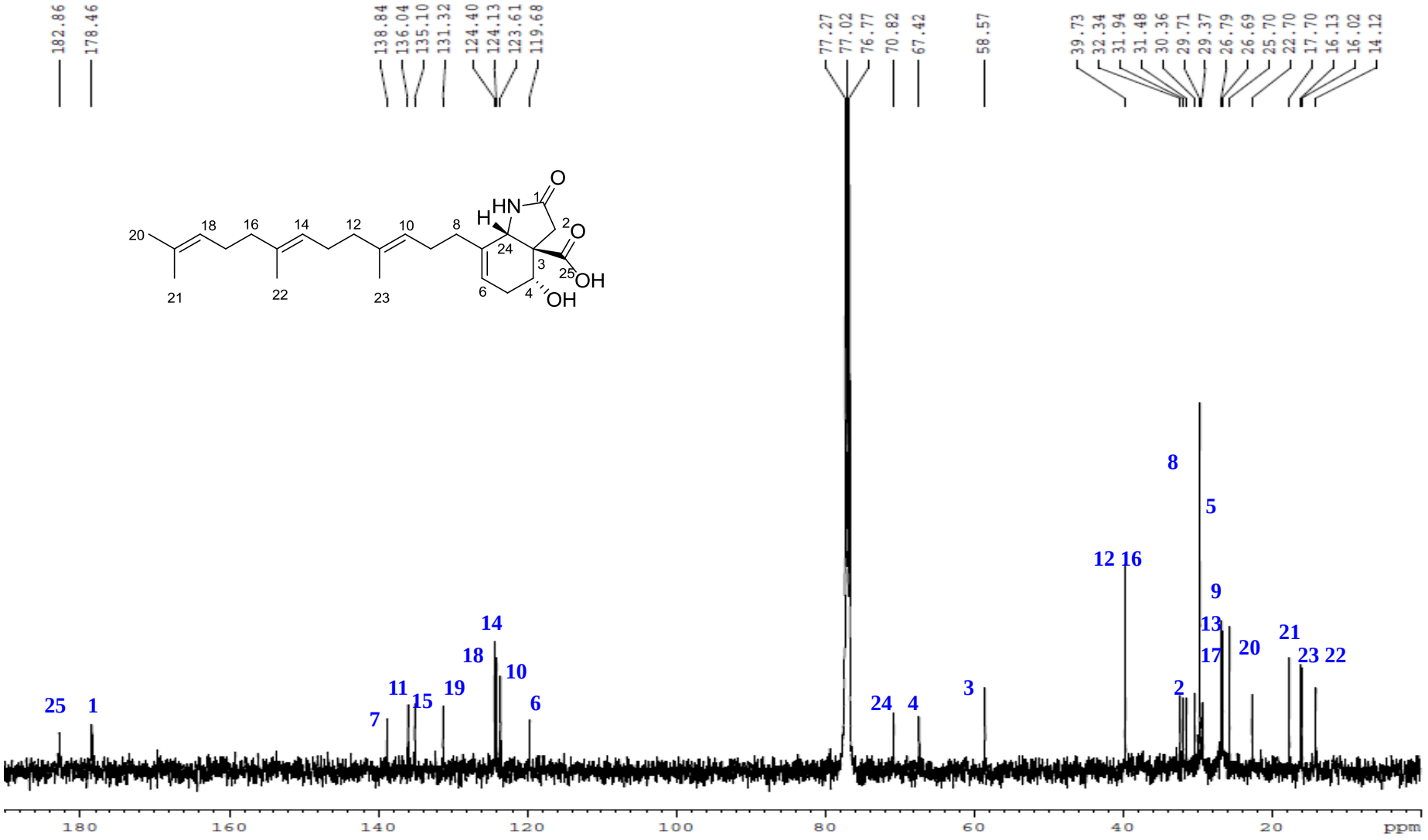


Figure S25. DEPT spectrum of compound **3** in $CDCl_3$.

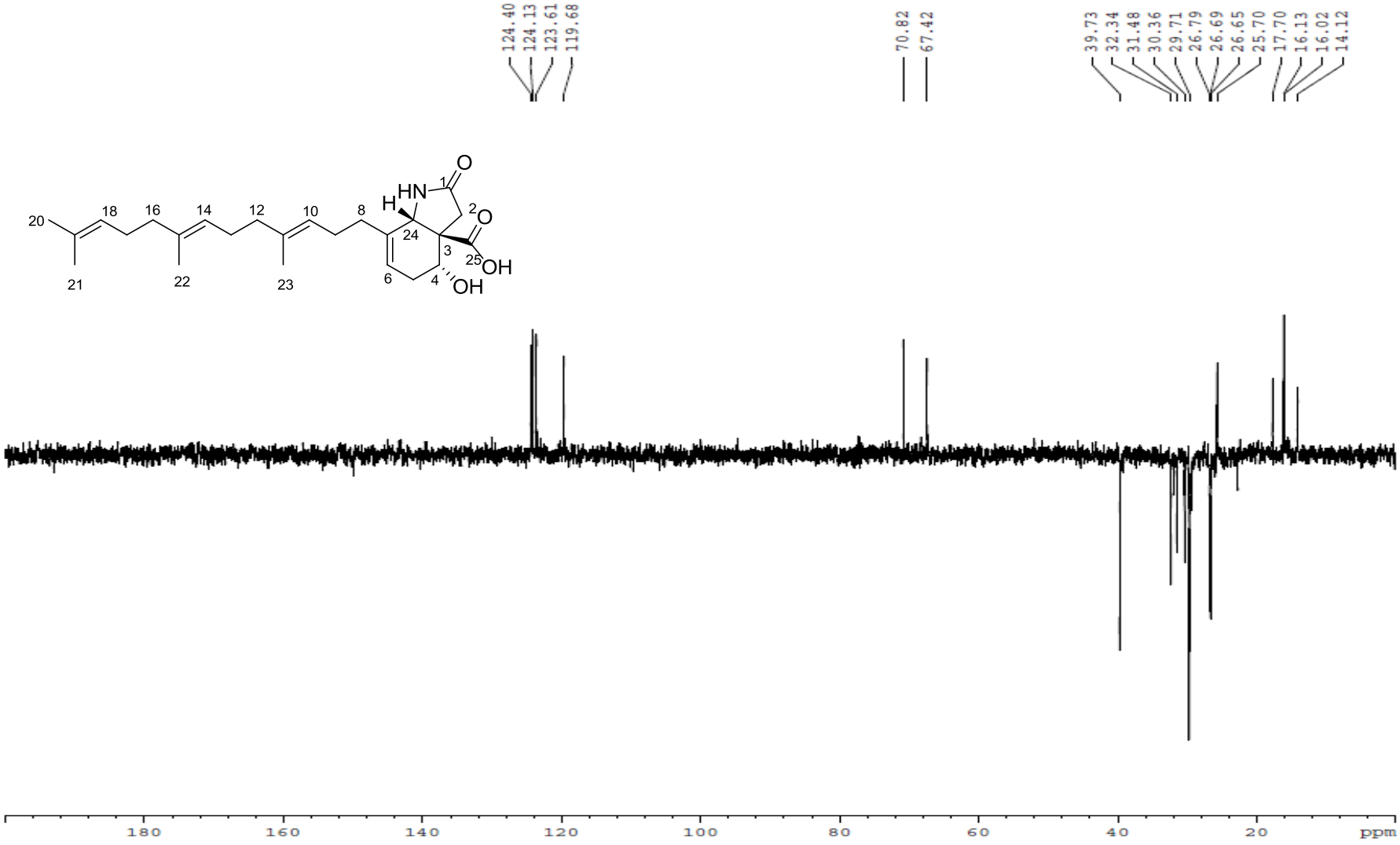


Figure S26. HSQC spectrum of compound **3** in $CDCl_3$.

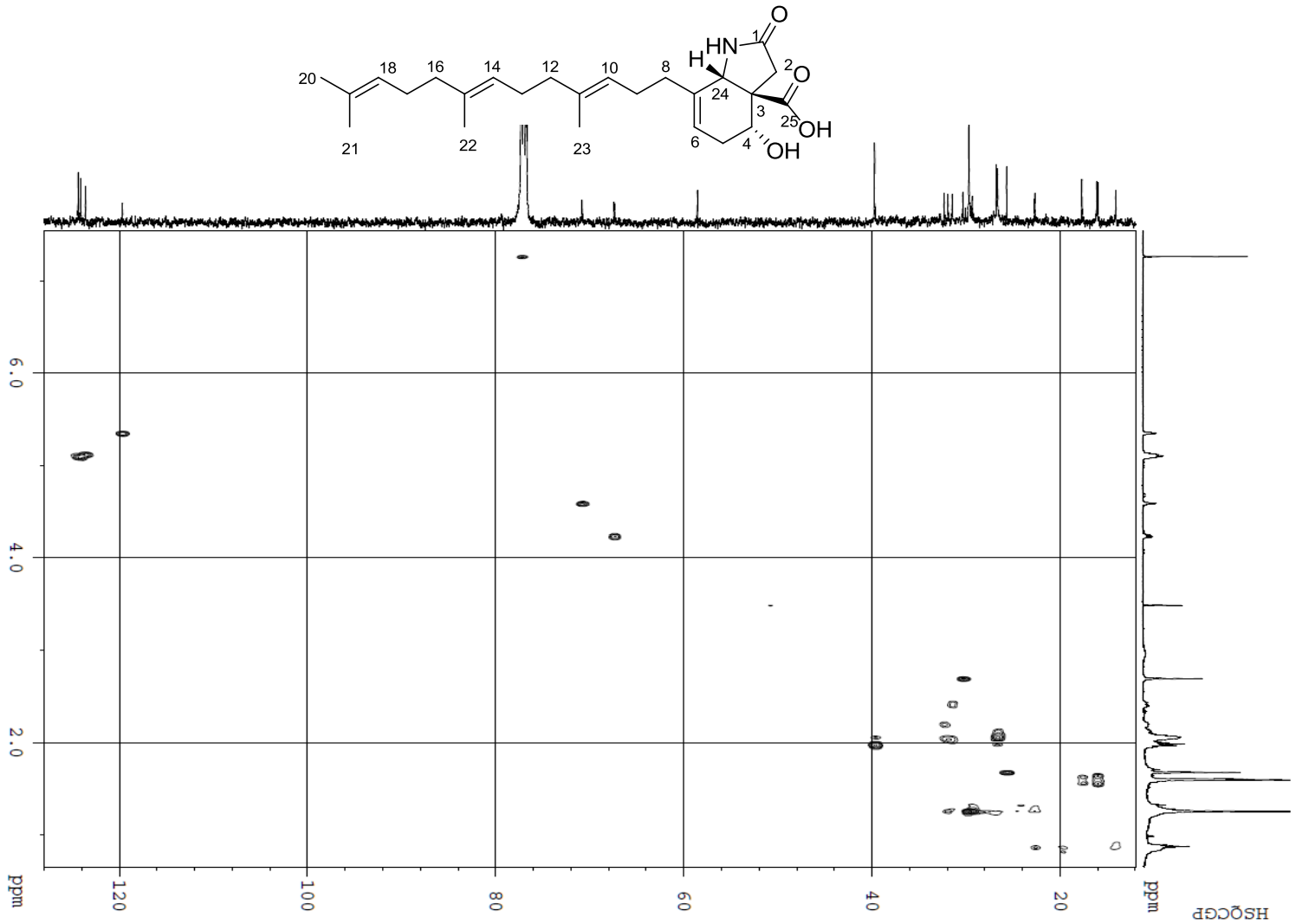


Figure S27. $^{1}H–^{1}H$ COSY spectrum of compound **3** in $CDCl_3$.

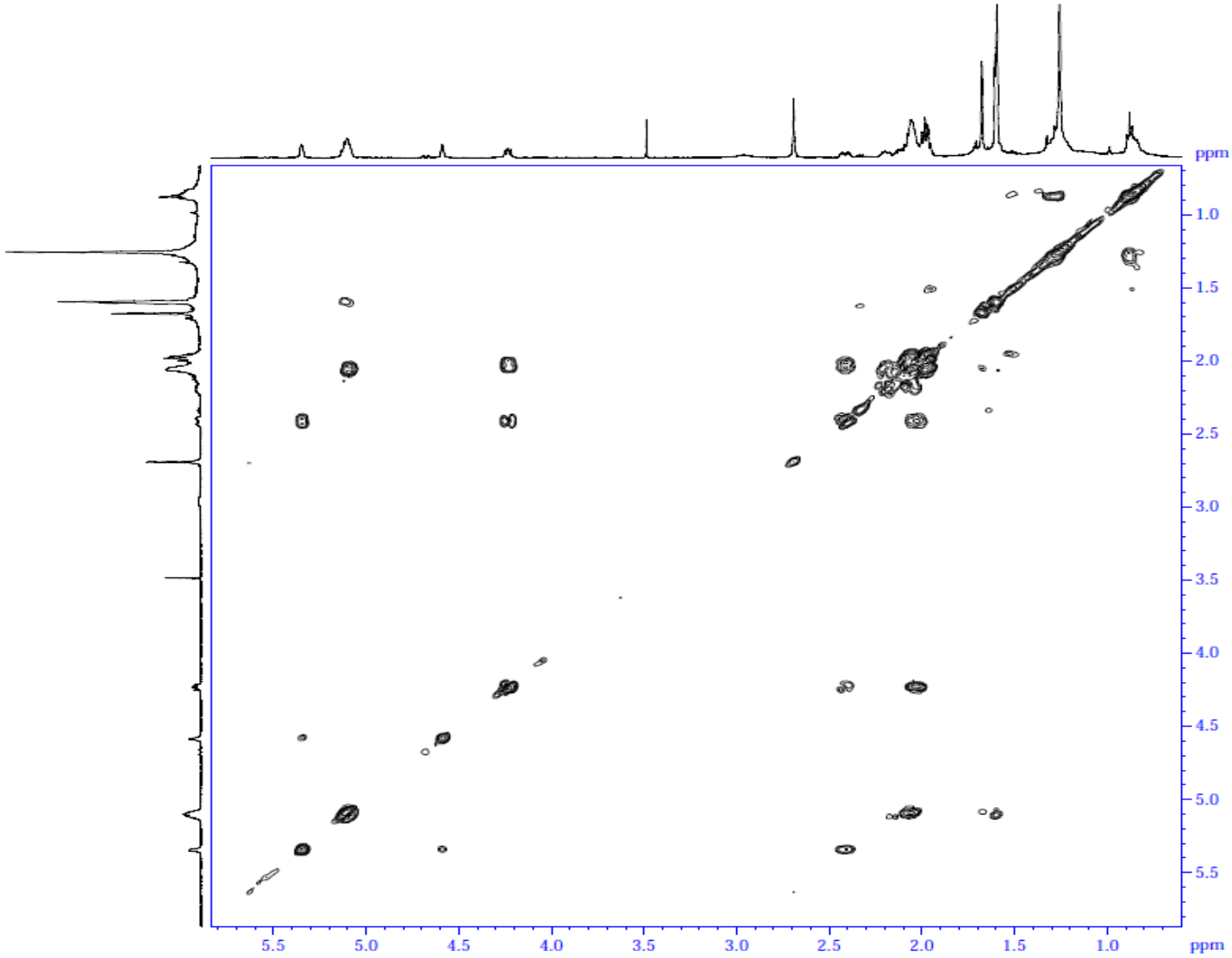


Figure S28. HMBC spectrum of compound **3** in $CDCl_3$.

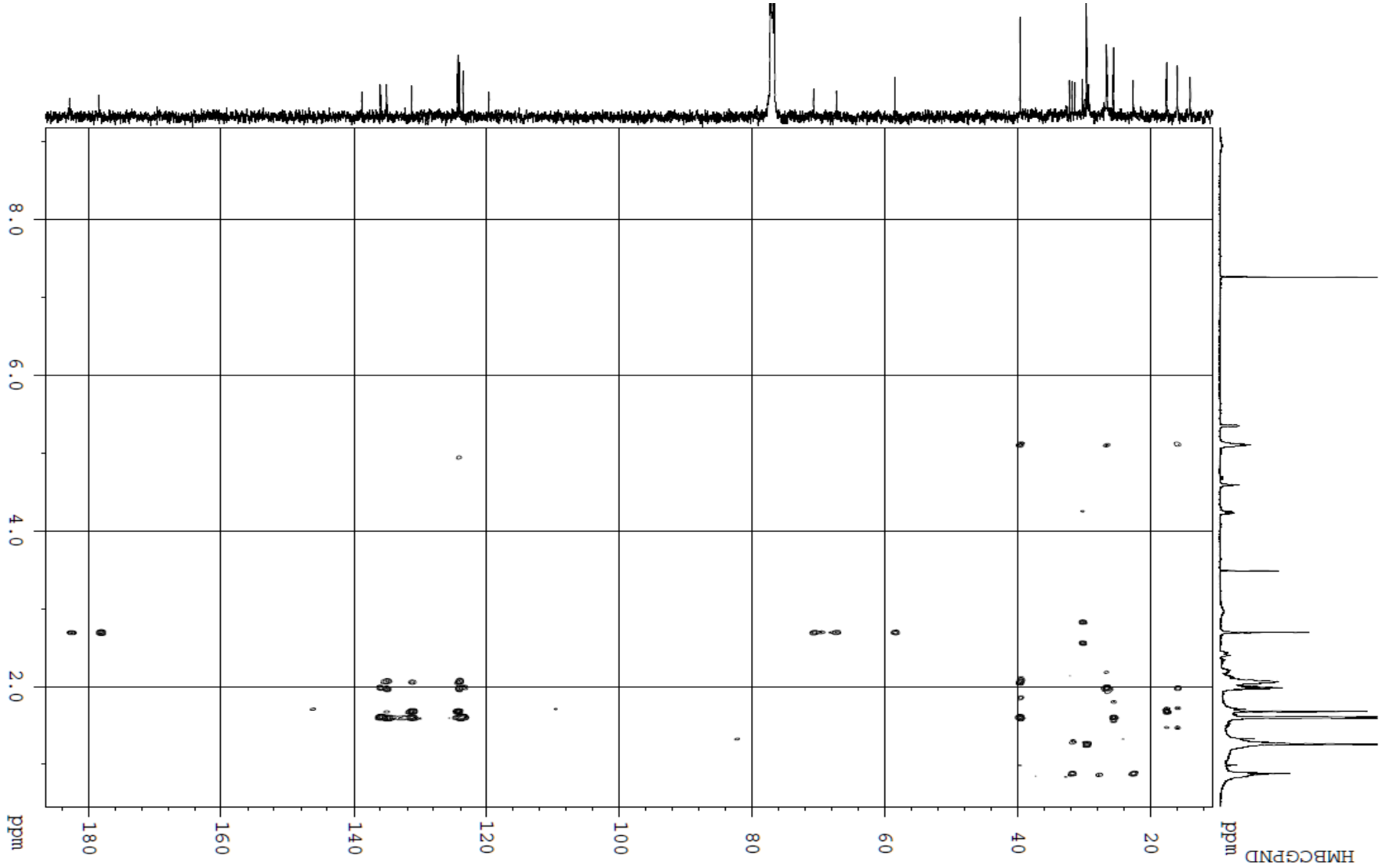


Figure S29. NOESY spectrum of compound **3** in $CDCl_3$.

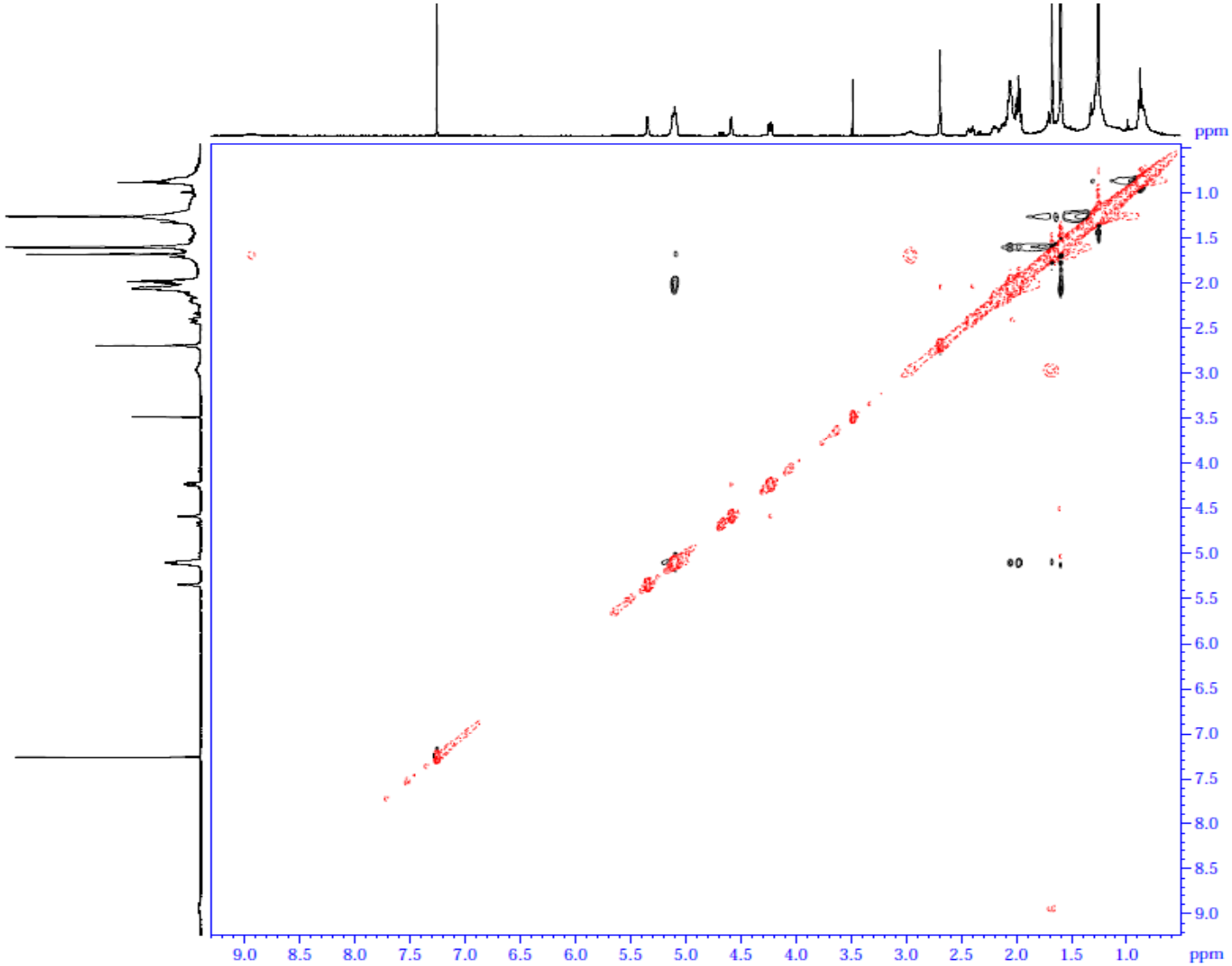


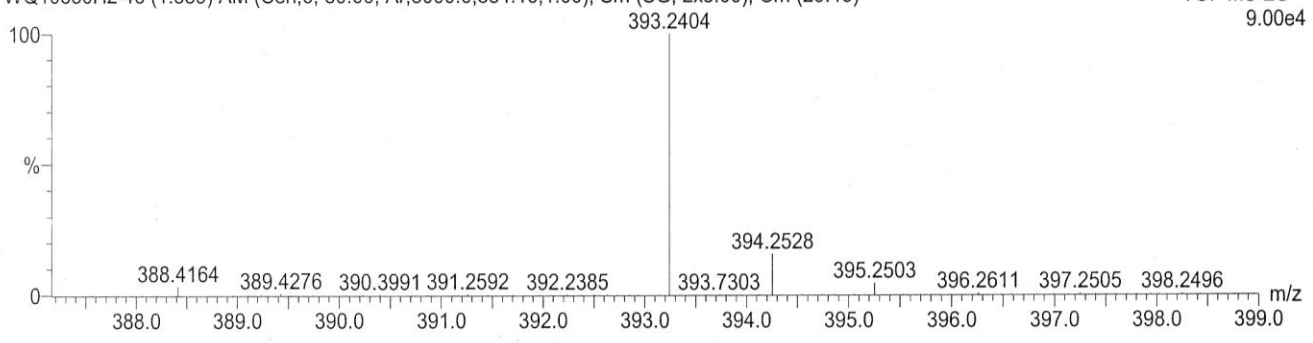
Figure S30. HRESIMS spectrum of compound **4**.

Elemental Composition Report **Page 1**

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

Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 5-27 H: 10-50 O: 3-4 Na: 1-1

SIPI
PSJ-B11 M.W=370
WQ10350H2 46 (1.589) AM (Cen,6, 80.00, Ar,5000.0,384.16,1.00); Sm (SG, 2x3.00); Cm (29:46)
Q-Tof micro
YA019
04-Oct-2010,13:56:02
0.00000000
TOF MS ES+
9.00e4



Minimum:	50.00				-1.5		
Maximum:	100.00		5.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
393.2404	100.00	393.2406	-0.2	-0.5	7.5	2754.3	C24 H34 O3 Na

Figure S31. IR spectrum of compound **4**.

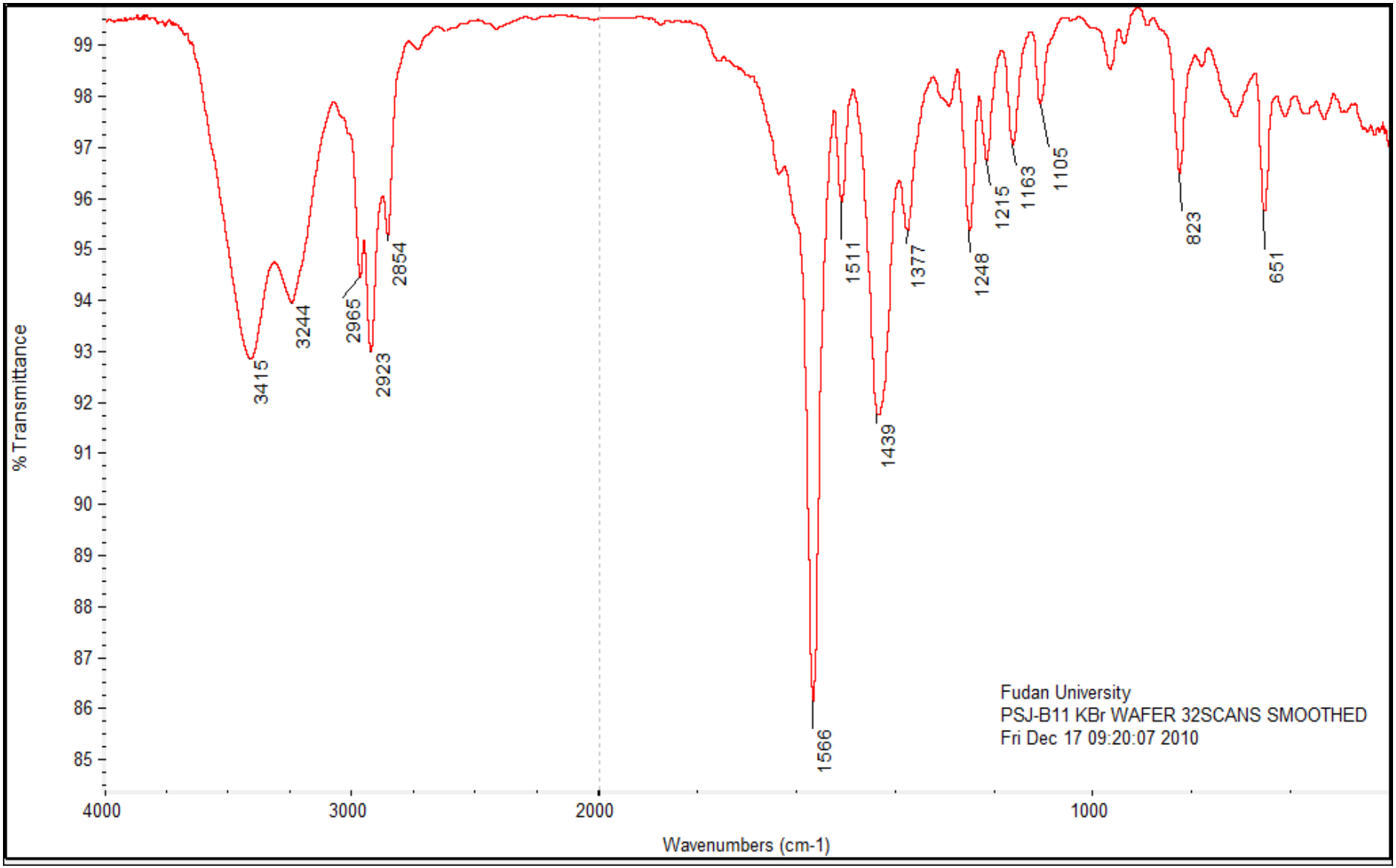


Figure S32. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

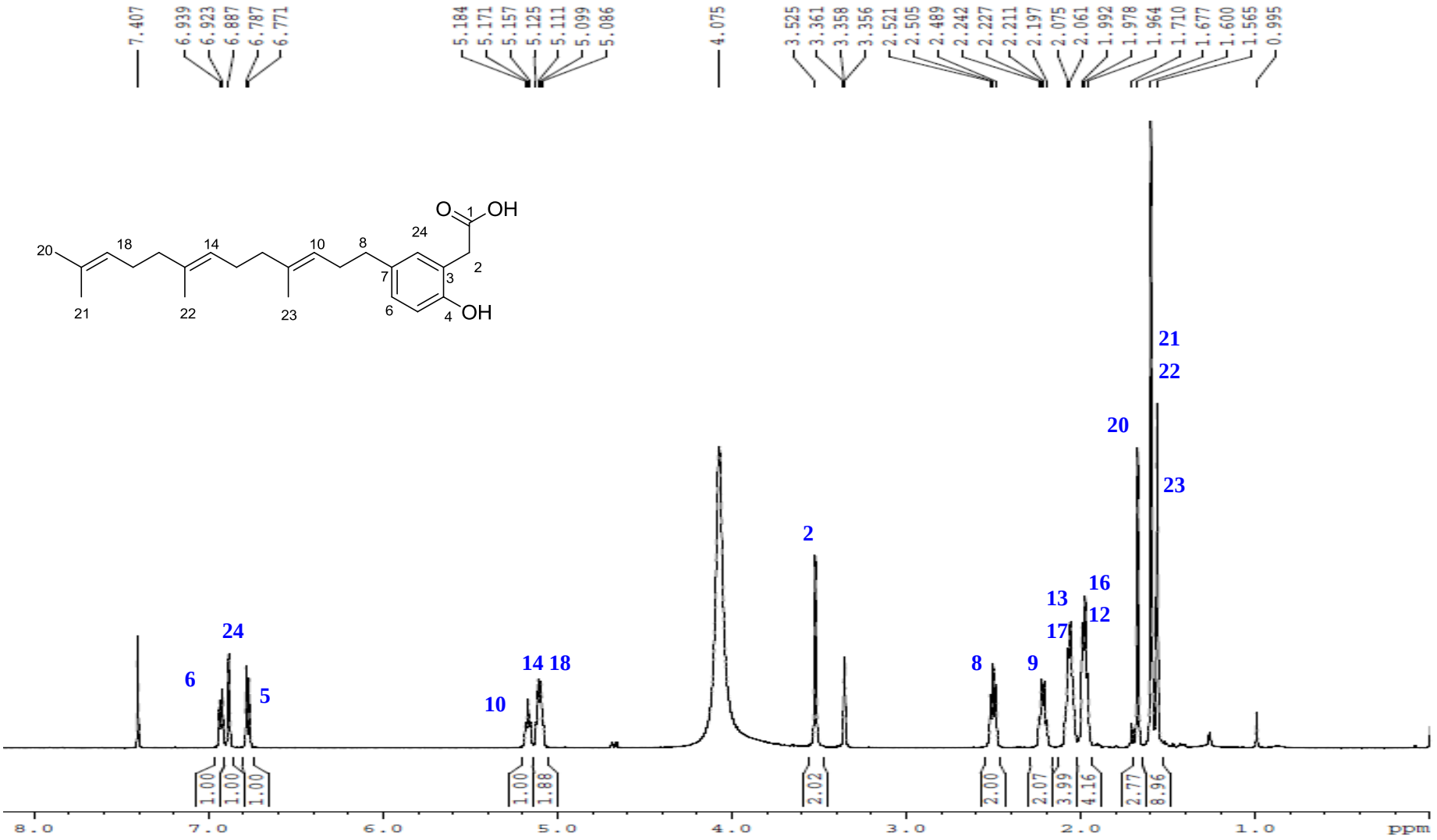


Figure S33. ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

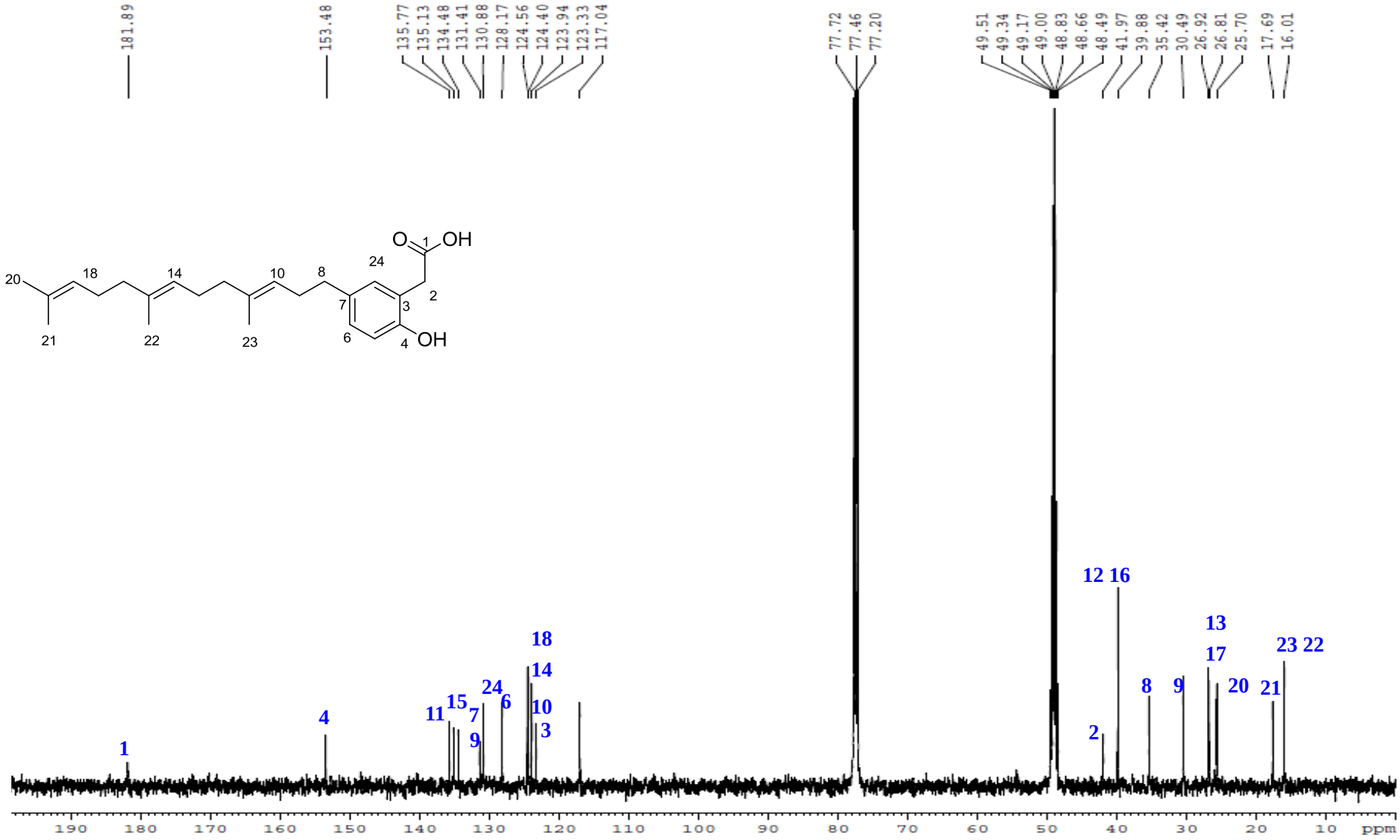


Figure S34. DEPT spectrum of compound **4** in $CDCl_3$.

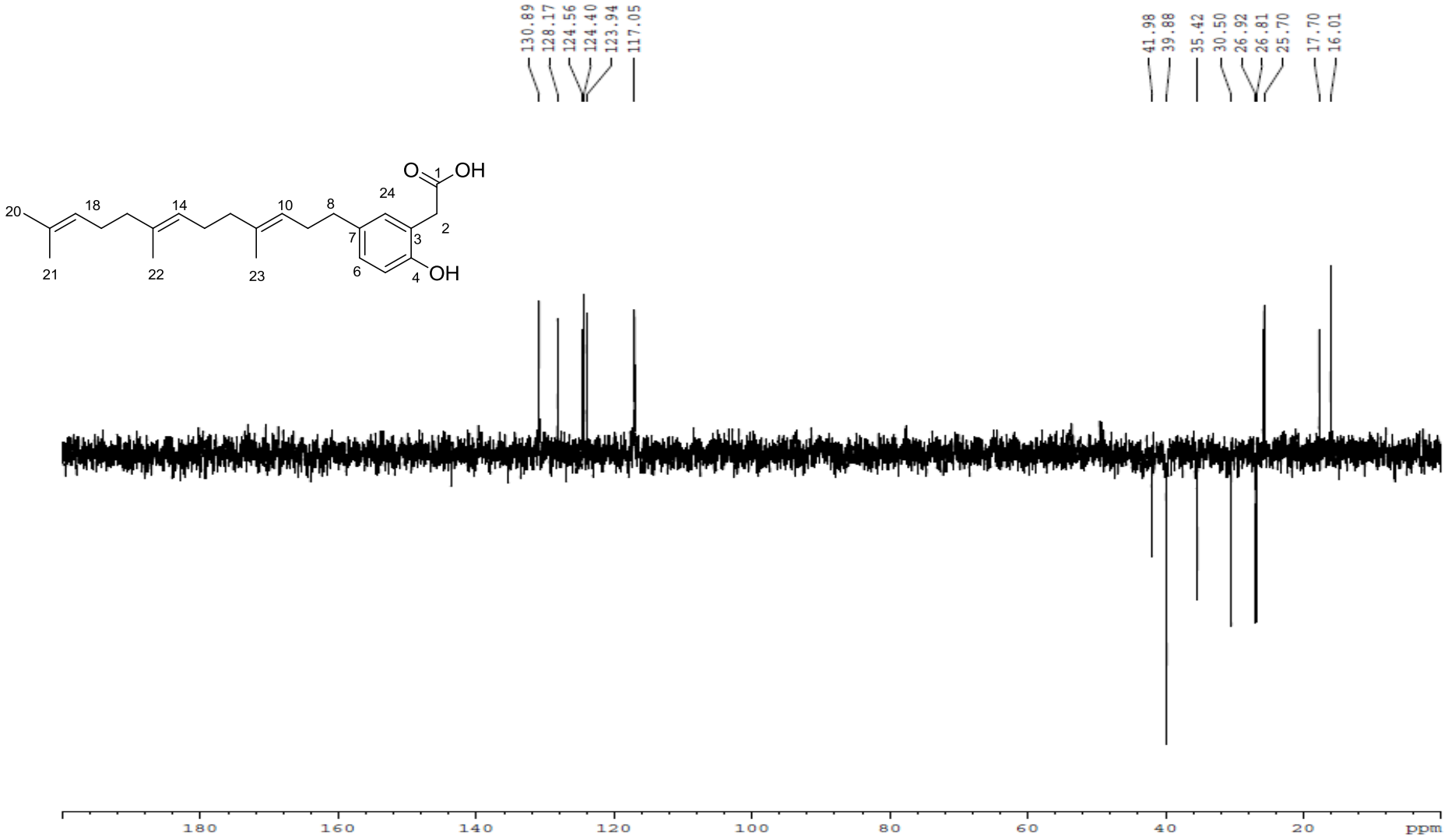


Figure S35. HSQC spectrum of compound **4** in $CDCl_3$.

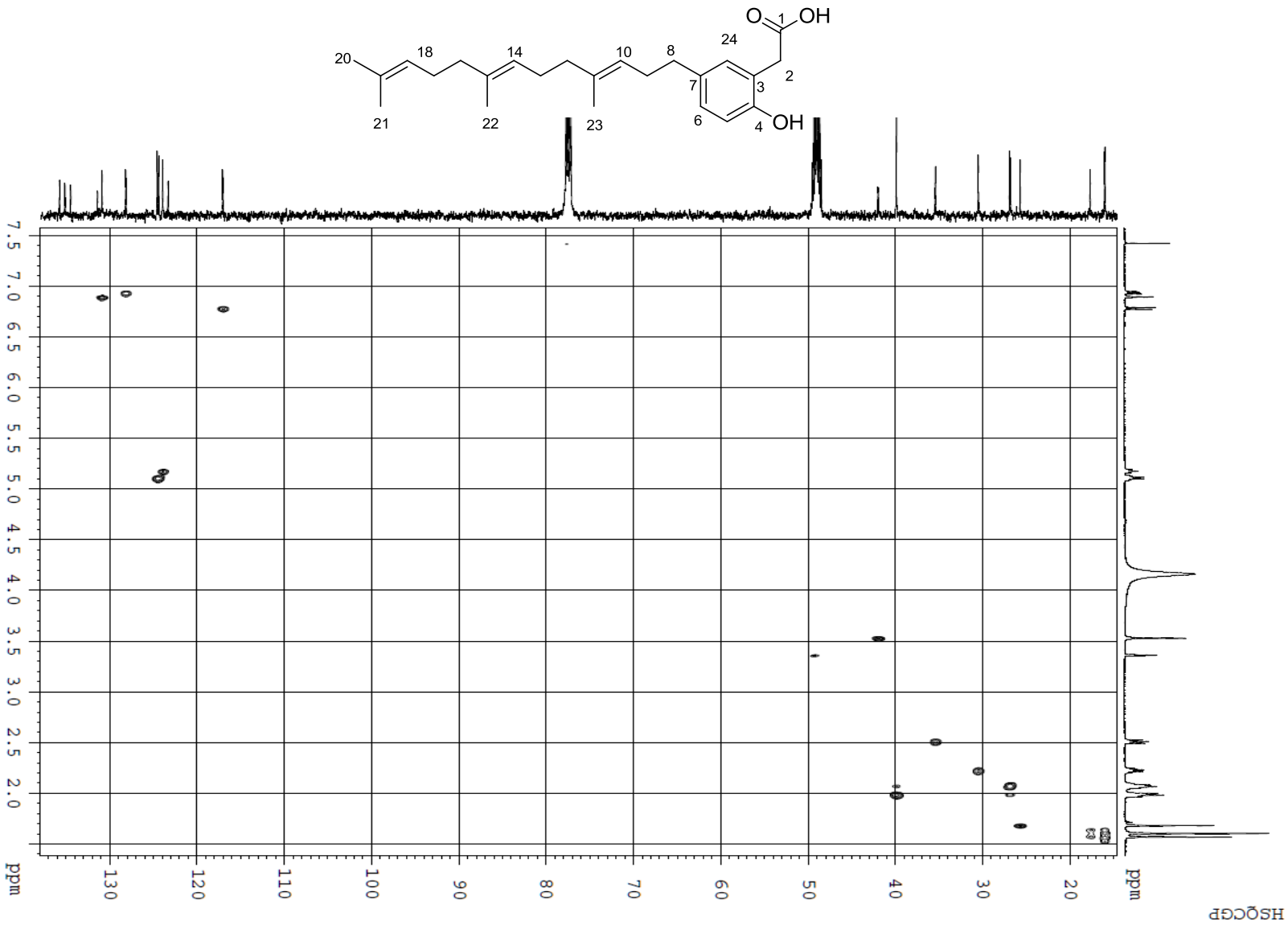


Figure S36. $^{1}H–^{1}H$ COSY spectrum of compound **4** in $CDCl_3$.

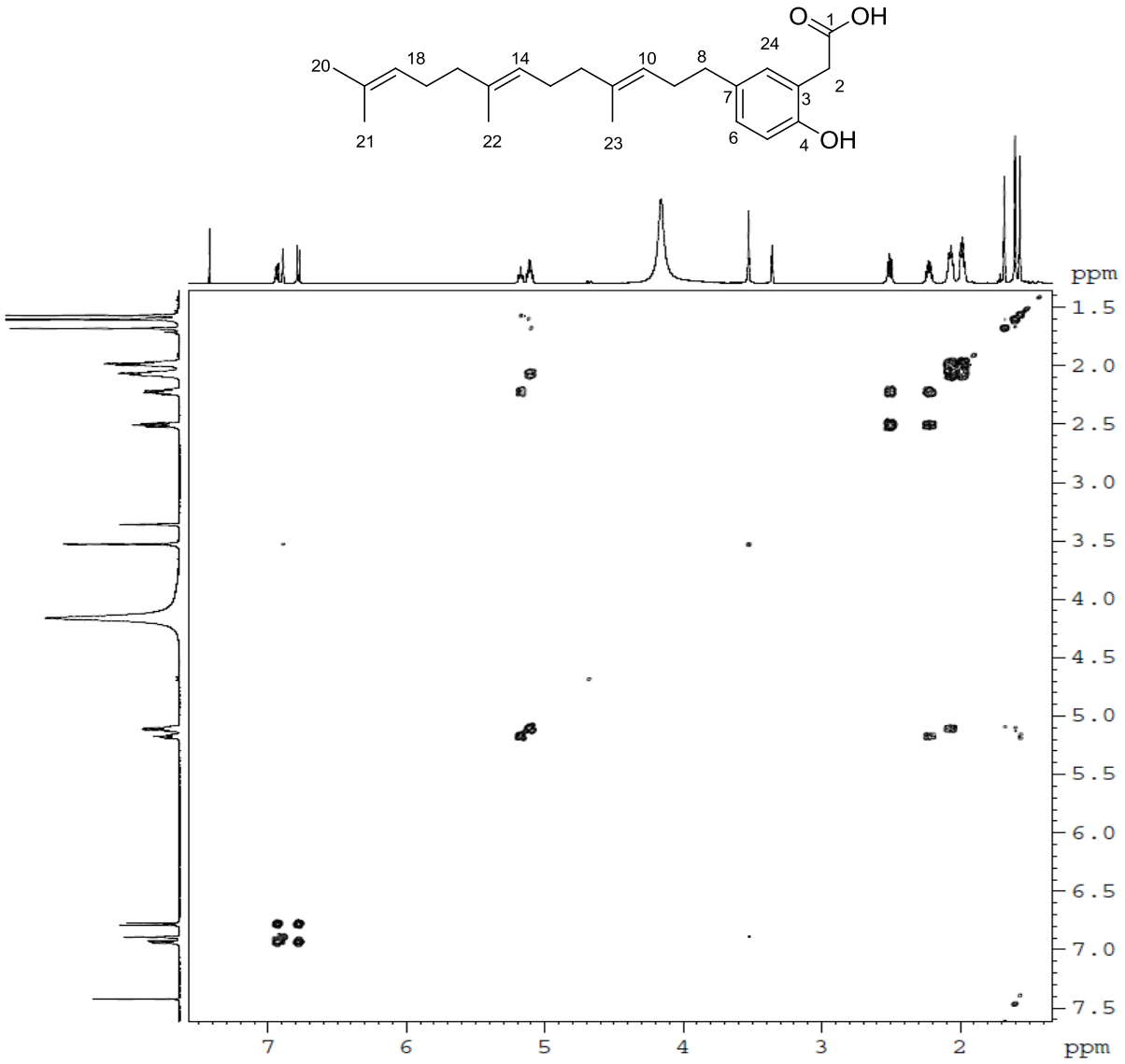


Figure S37. HMBC spectrum of compound **4** in $CDCl_3$.

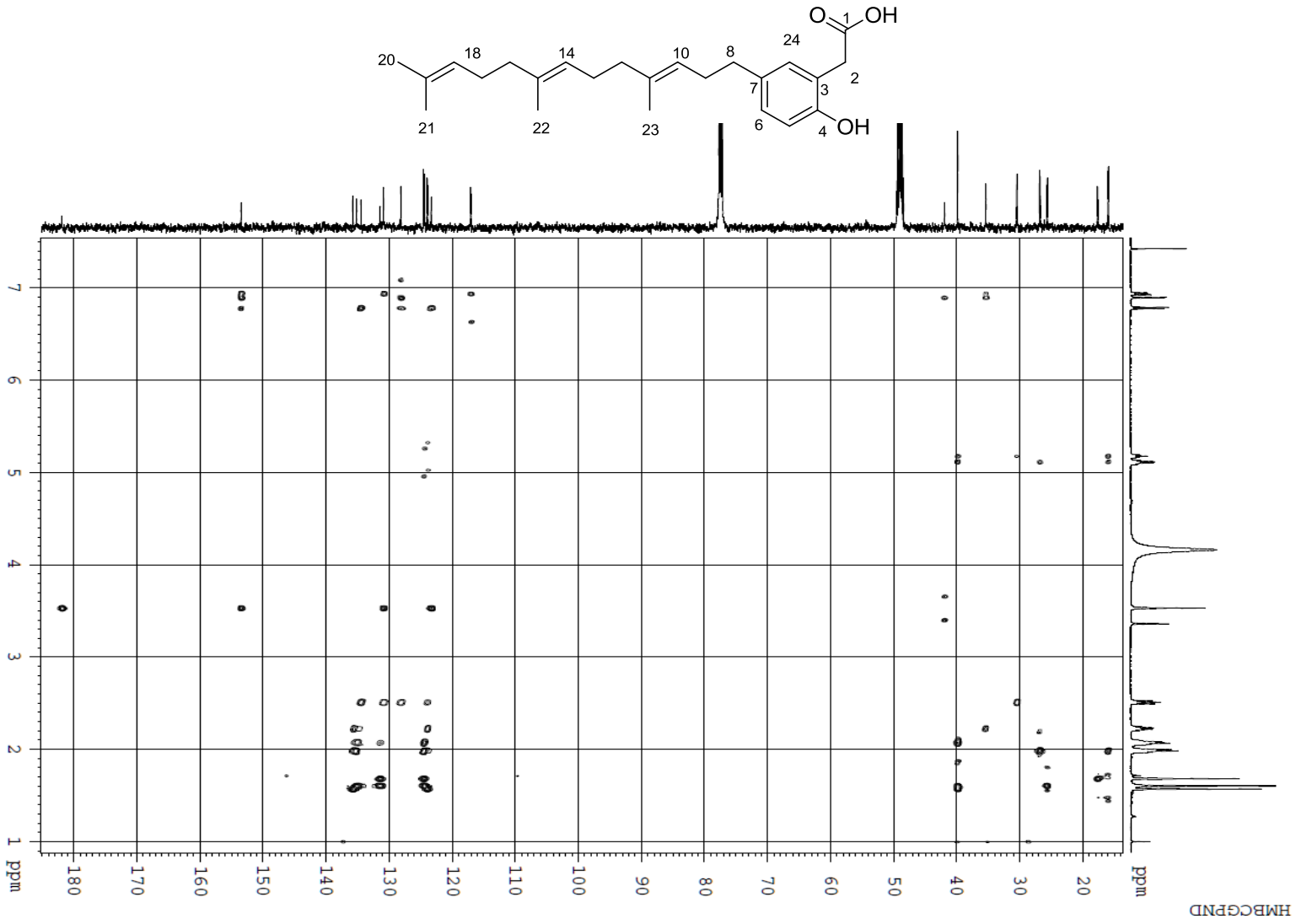


Figure S38. NOESY spectrum of compound **4** in $CDCl_3$.

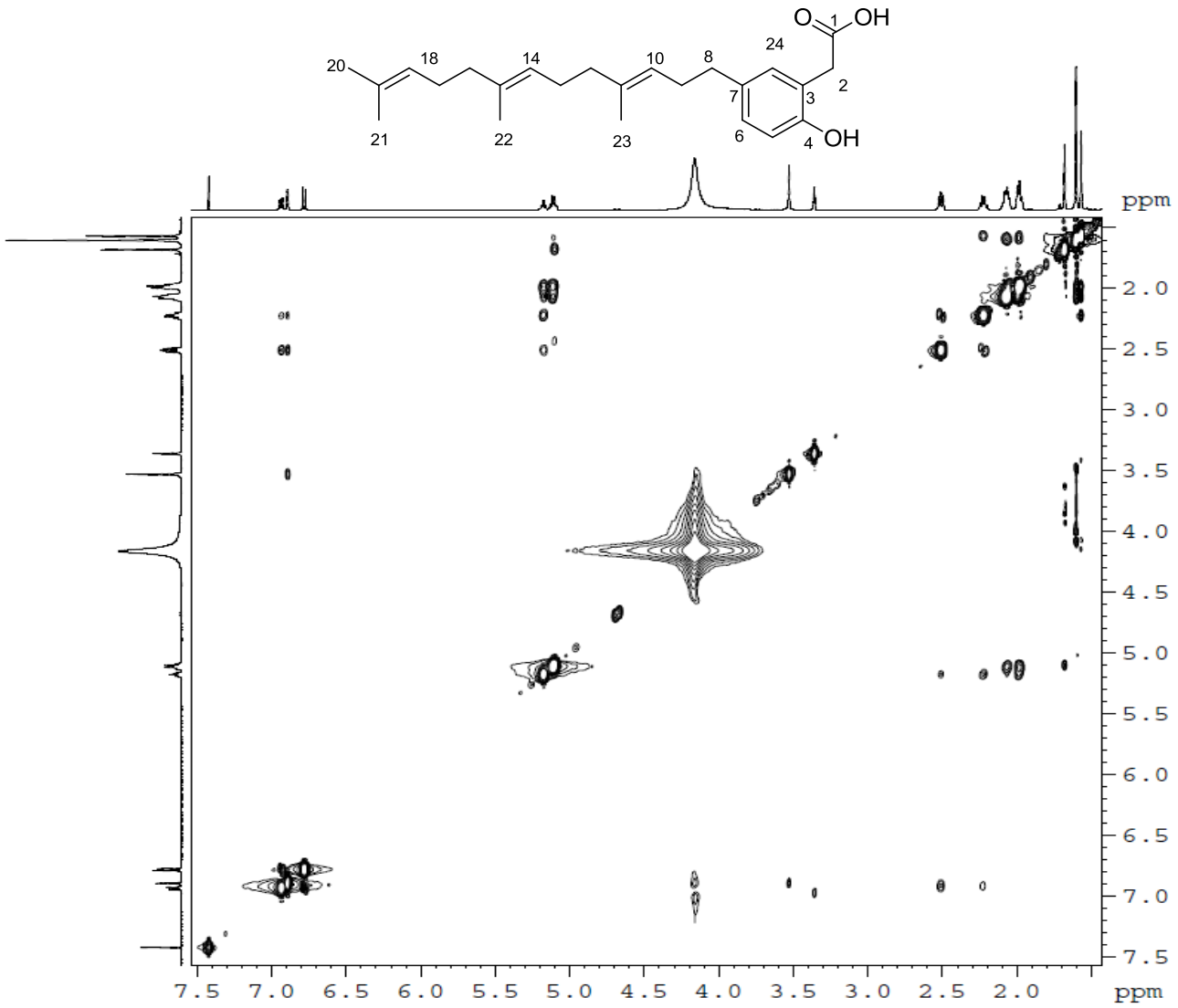


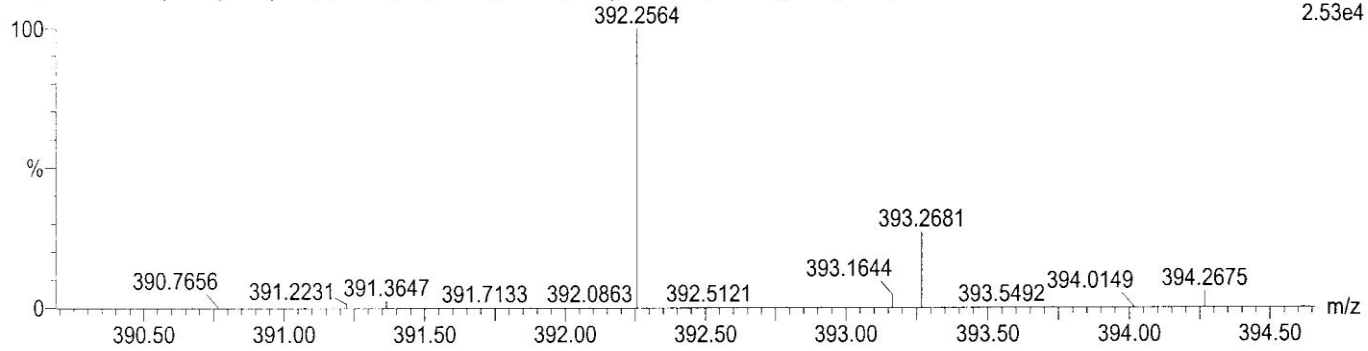
Figure S39. HRESIMS spectrum of compound **5**.

Elemental Composition Report **Page 1**

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

Monoisotopic Mass, Even Electron Ions
42 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 5-30 H: 5-45 N: 0-1 O: 1-6 Na: 1-1

SIPI Q-Tof micro 13-May-2010,13:10:28
PSJ-B8 M.W=369 YA019 0.00000000
WQ10182H1 63 (2.176) AM (Cen,6, 80.00, Ar,5000.0,385.24,0.70); Sm (SG, 2x3.00); Cm (49:66) TOF MS ES+
2.53e4



Minimum:	30.00				-1.5		
Maximum:	100.00		5.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
392.2564	100.00	392.2565	-0.1	-0.3	7.5	57.9	C24 H35 N O2 Na

Figure S40. IR spectrum of compound **5**.

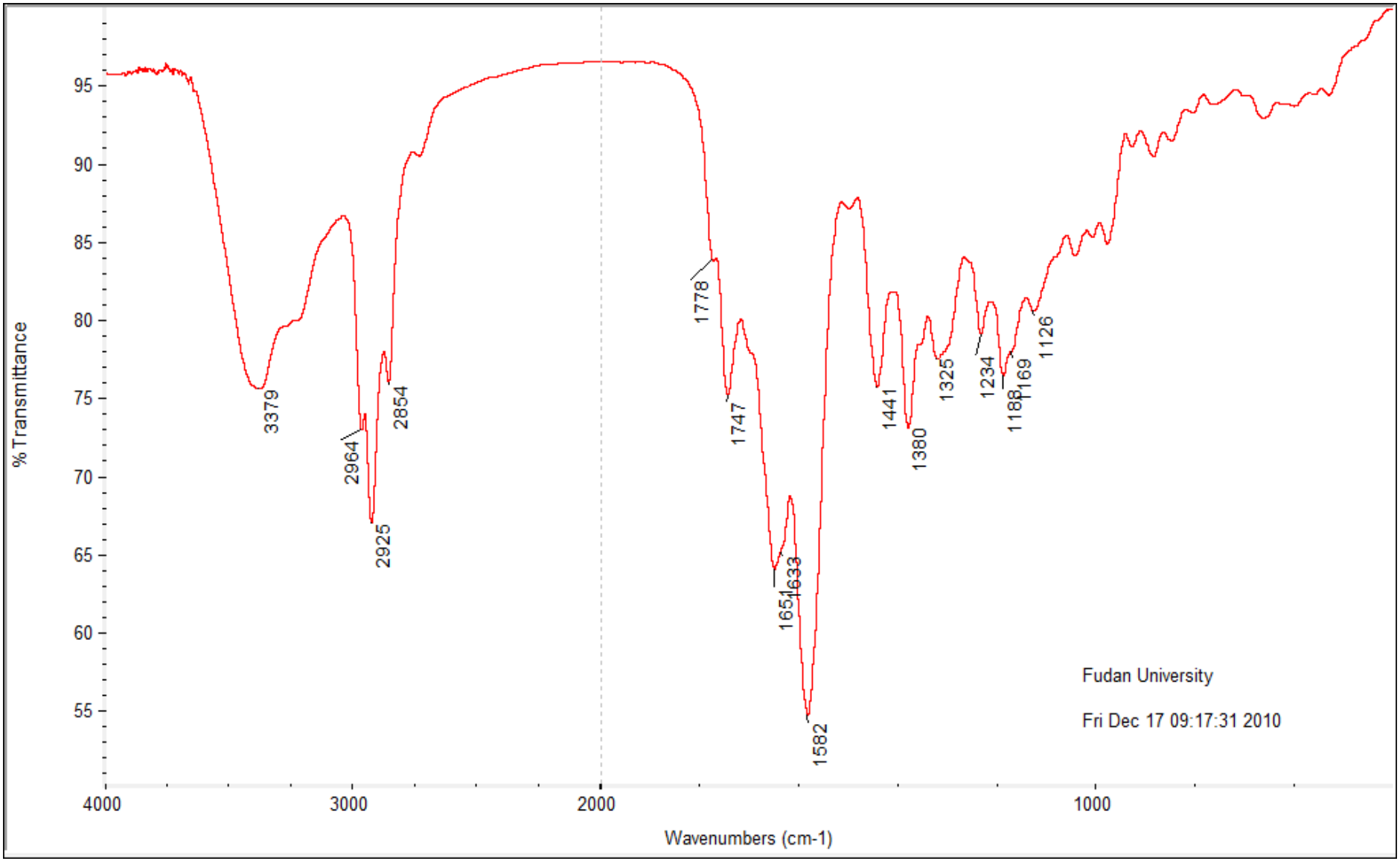


Figure S41. ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

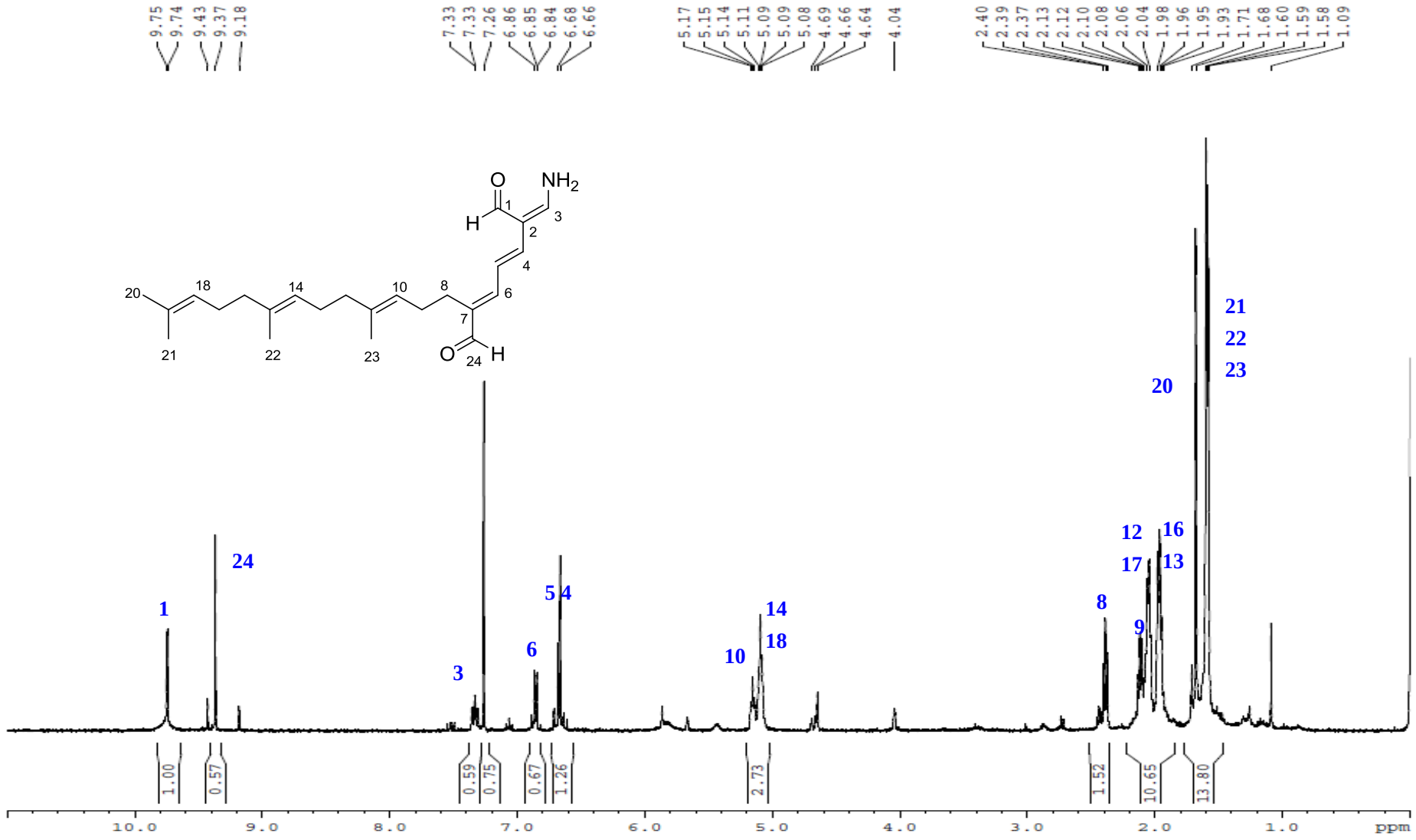


Figure S42. ^{1}H NMR spectrum of compound **5** in DMSO-d_6.

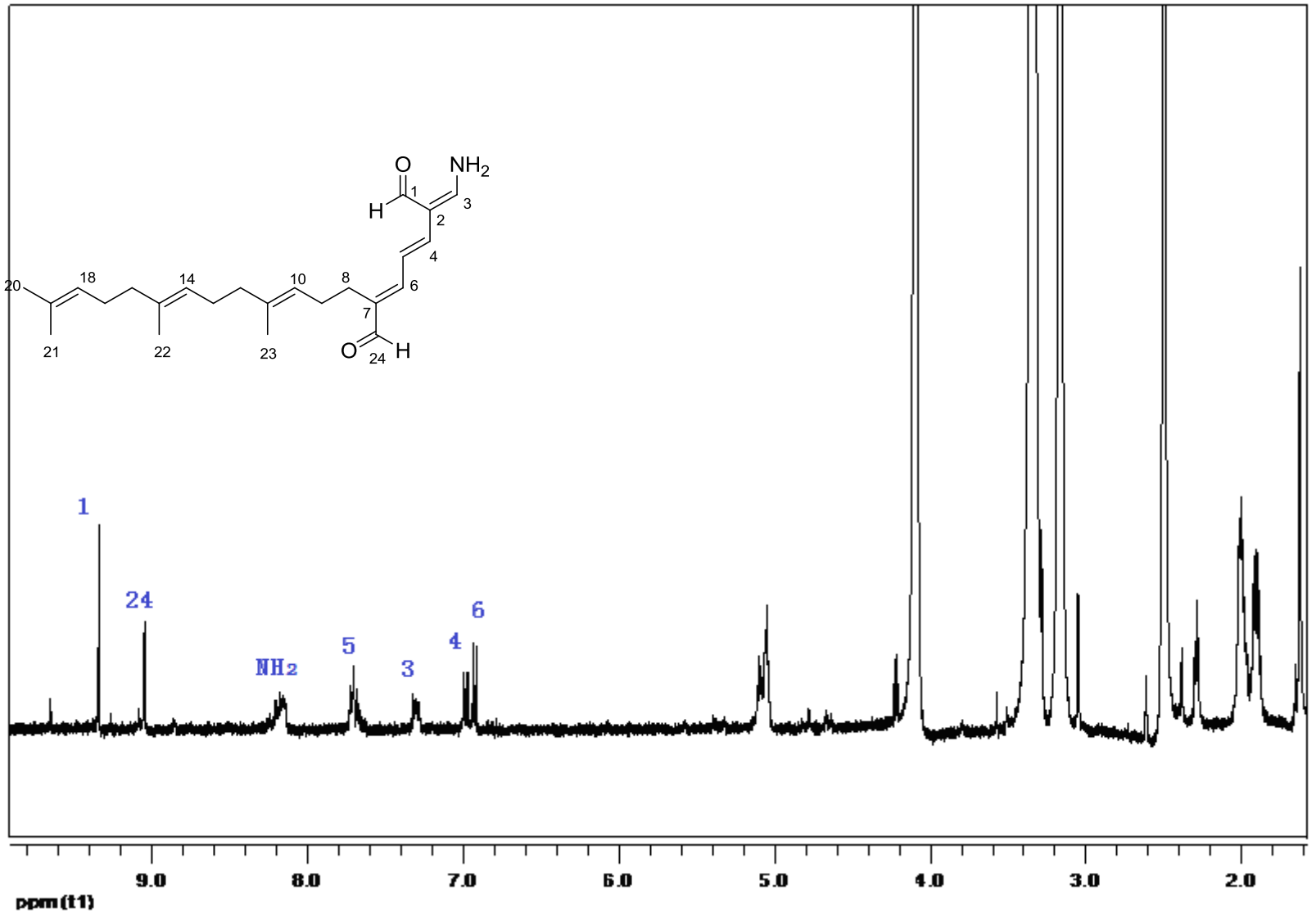


Figure S43. ^{13}C NMR spectrum of compound **5** in $CDCl_3$.

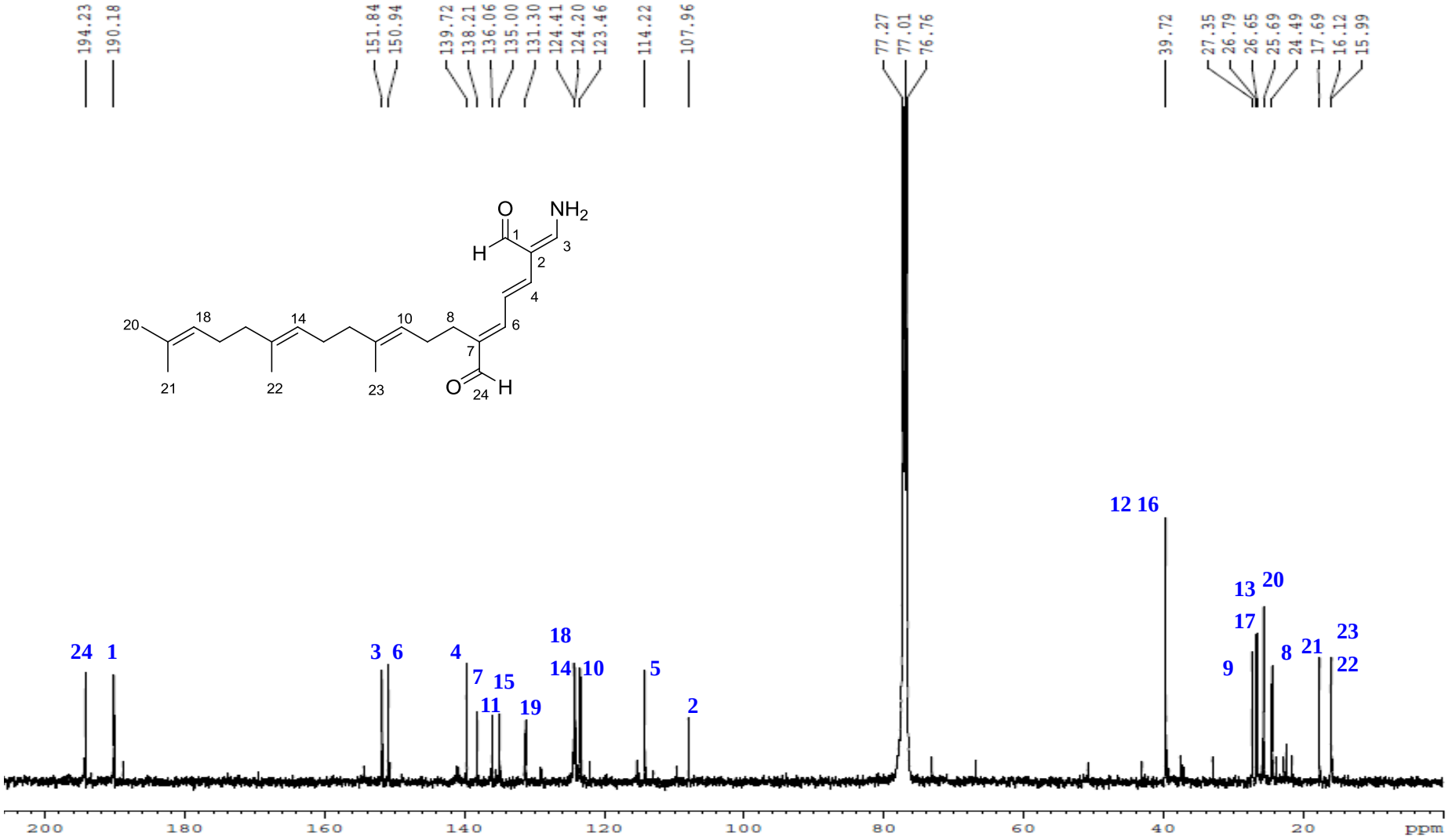


Figure S44. DEPT spectrum of compound **5** in $CDCl_3$.

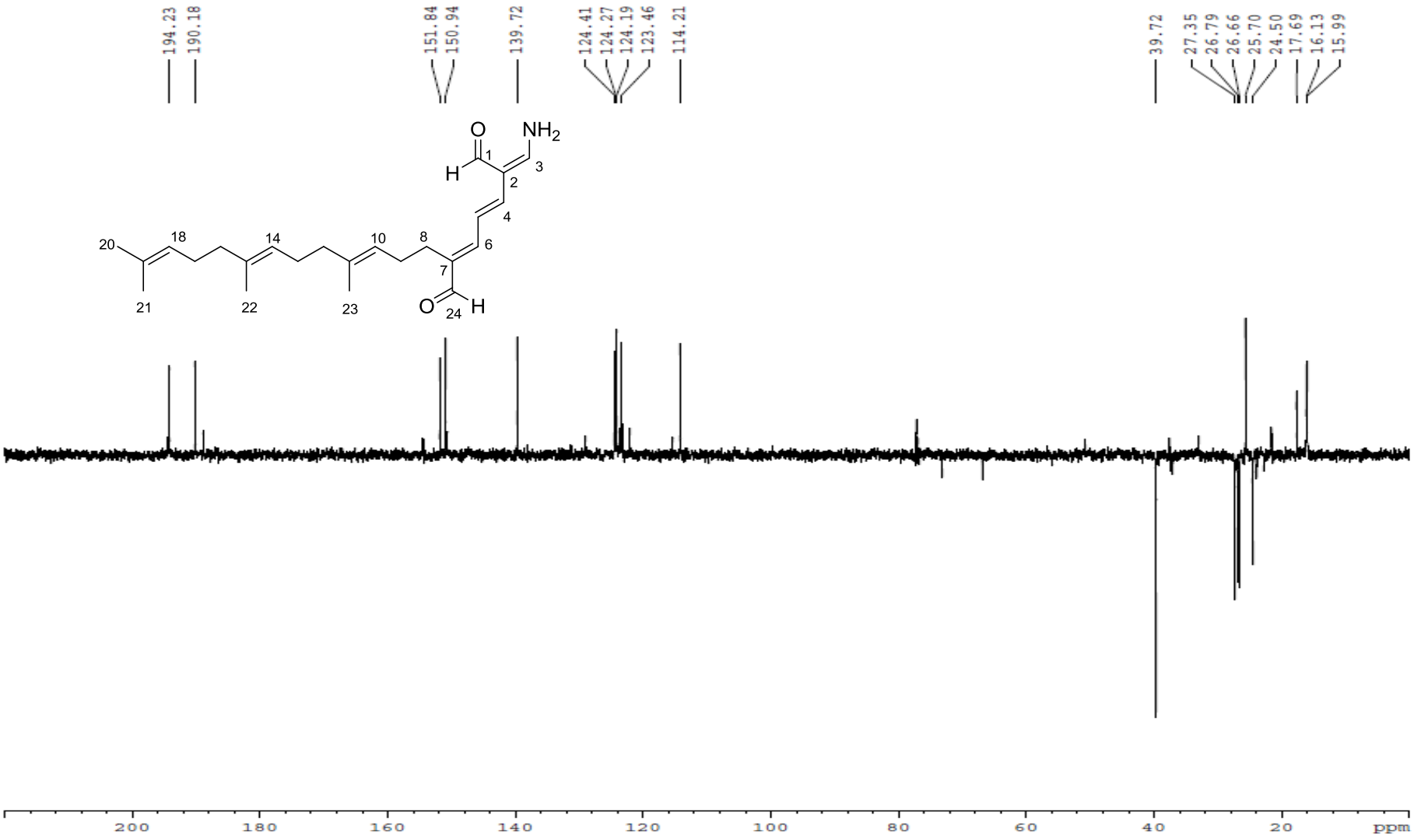


Figure S45. HSQC spectrum of compound **5** in $CDCl_3$.

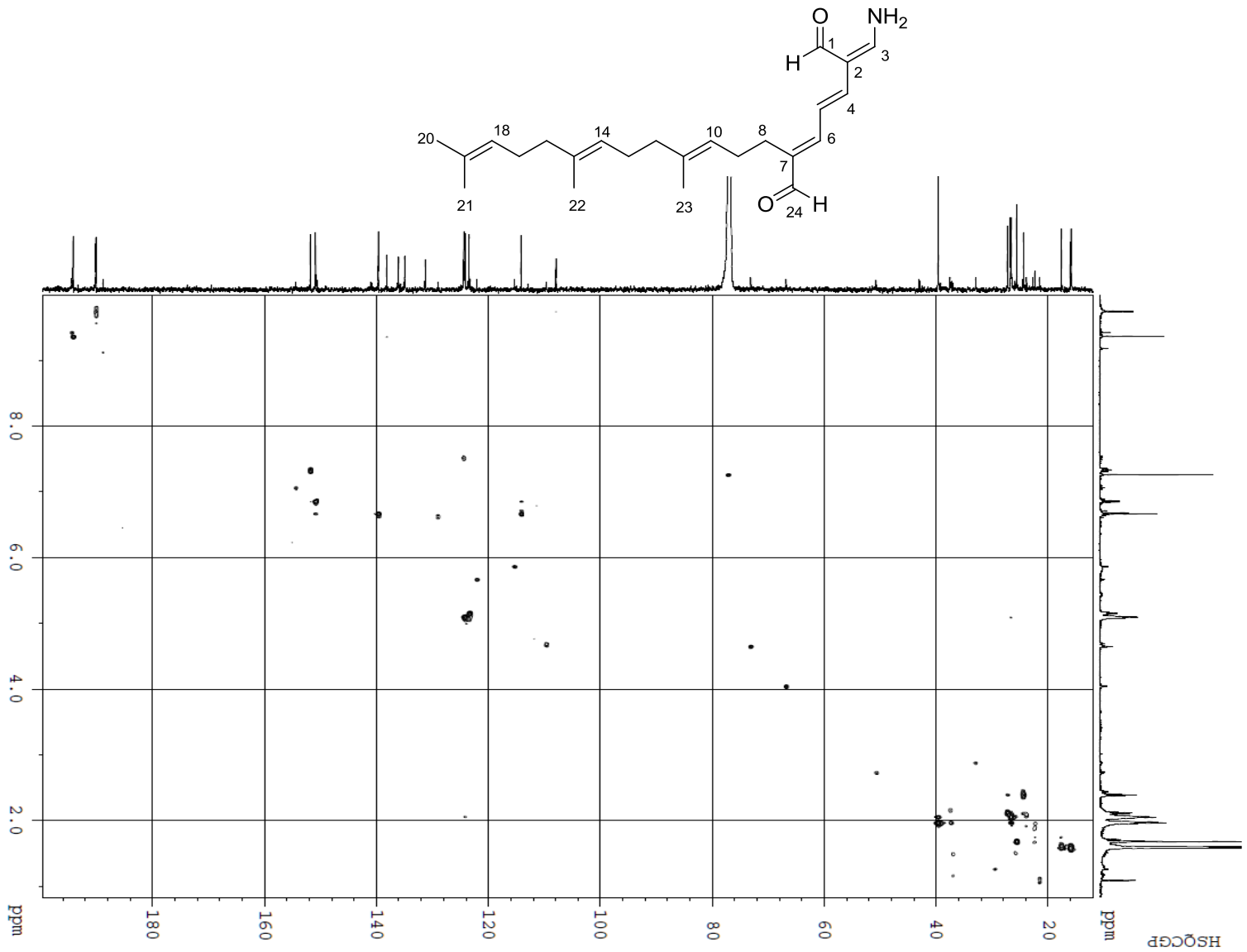


Figure S46. $^{1}H–^{1}H$ COSY spectrum of compound **5** in $CDCl_3$.

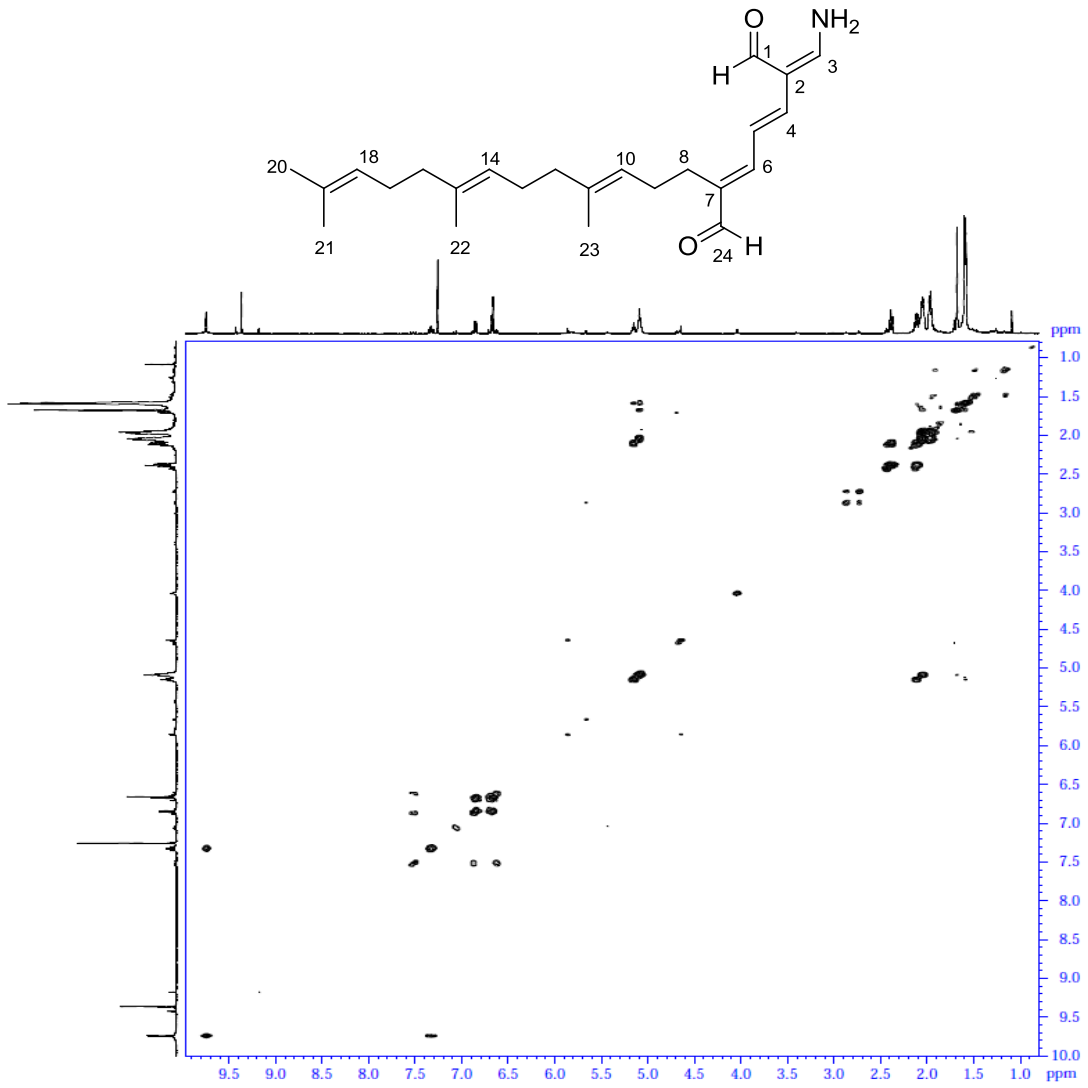


Figure S47. HMBC spectrum of compound **5** in $CDCl_3$.

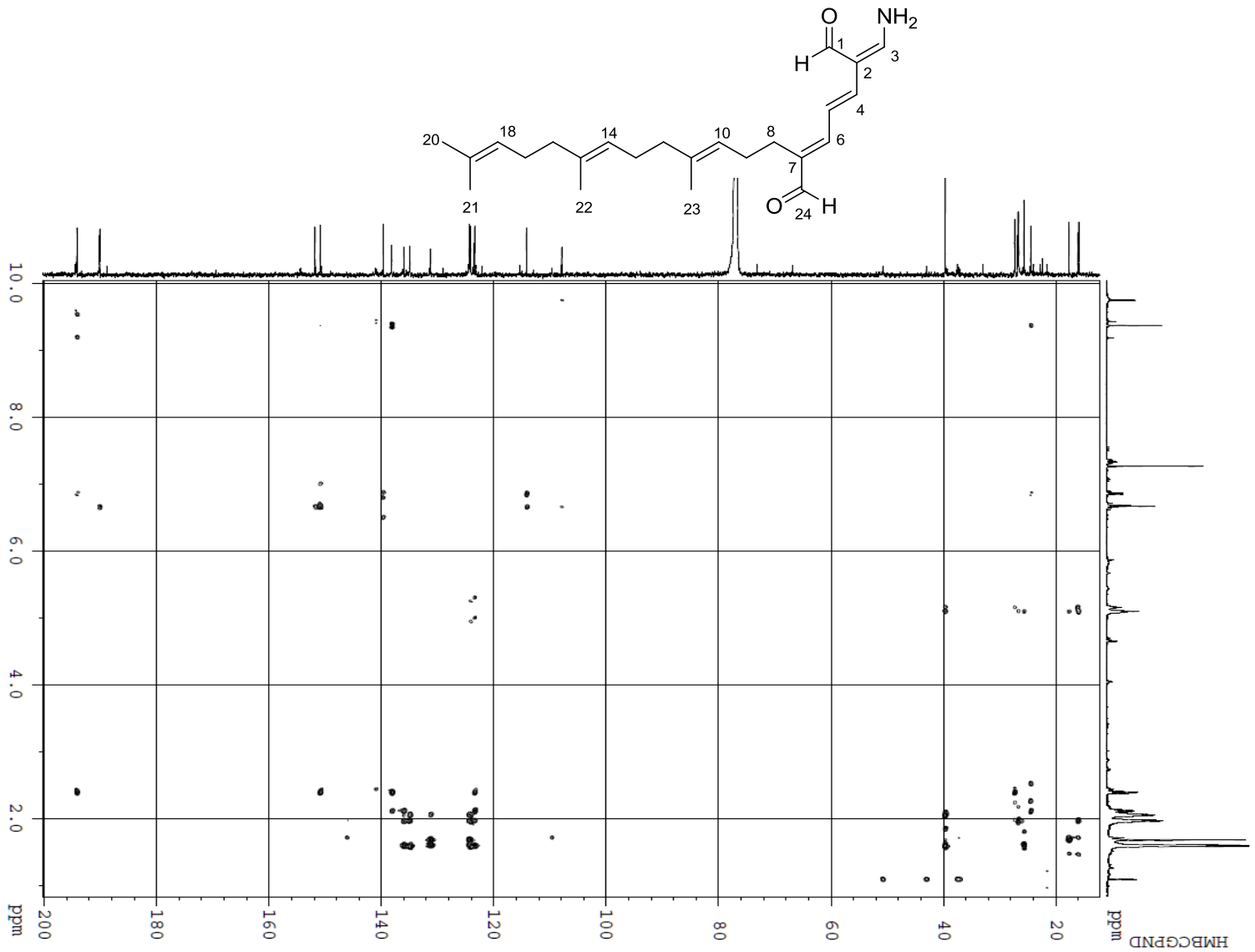


Figure S48. NOESY spectrum of compound **5** in $CDCl_3$.

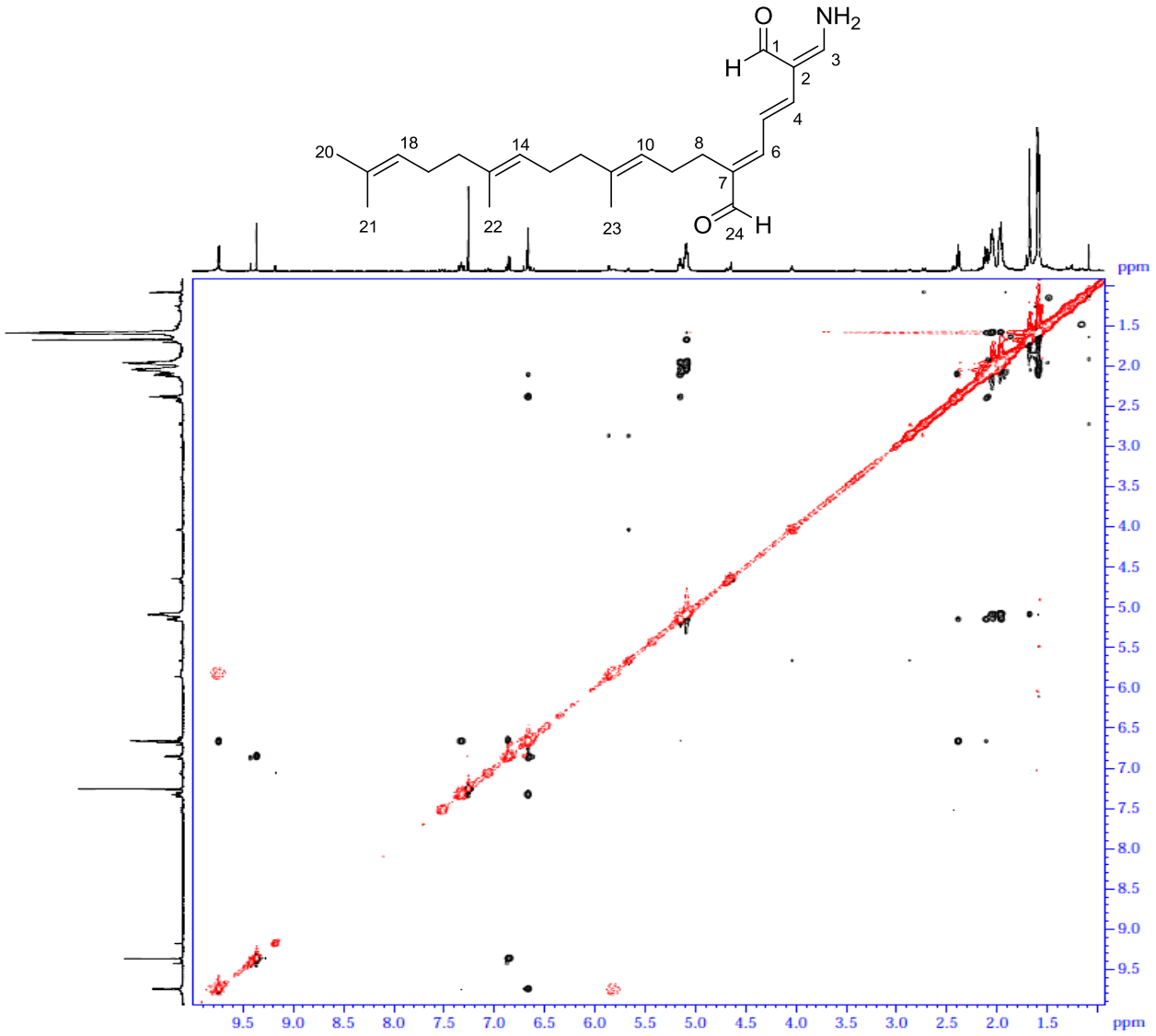


Figure S49. ^{1}H NMR data of MTPA esters (**2*S***, **2*R***, **3*S***, **3*R***).

^{1}H NMR data of **2*S*** (500 MHz, $CDCl_3$): δ 2.893 (1H, m, H-2a), 2.769 (1H, m, H-2b), 3.858 (1H, m, H-4), 2.313 (1H, m, H-5a), 2.163 (1H, m, H-5b), 5.462 (1H, br s, H-6).
^{1}H NMR data of **2*R*** (500 MHz, $CDCl_3$): δ 2.901 (1H, m, H-2a), 2.782 (1H, m, H-2b), 3.860 (1H, m, H-4), 2.231 (1H, m, H-5a), 2.143 (1H, m, H-5b), 5.457 (1H, br s, H-6).
^{1}H NMR data of **3*S*** (500 MHz, $CDCl_3$): δ 2.733 (1H, m, H-2), 4.141 (1H, m, H-4), 2.419 (1H, m, H-5a), 2.208 (1H, m, H-5b), 5.381 (1H, br s, H-6).
^{1}H NMR data of **3*R*** (500 MHz, $CDCl_3$): δ 2.735 (1H, m, H-2), 4.145 (1H, m, H-4), 2.385 (1H, m, H-5a), 2.194 (1H, m, H-5b), 5.363 (1H, br s, H-6).

References

1. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A., Jr.; Vreven, T.; Kudin, K.N.; Burant, J.C.; *et al. Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, USA, 2013.
2. Available online: http://www.gaussian.com (accessed on 11 December 2013).