

Electronic Supplementary Information of

**Total synthesis of (12*R*)- and (12*S*)-12-hydroxymonocerins: stereoselective
oxylactonization using a chiral hypervalent iodine(III) species**

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Tables S1 and S2	S1–S2
¹H and ¹³C NMR spectra	S3–S37
NOESY spectra	S38–S45

Table S1 Comparison of ^1H NMR data δ_{H} (CDCl_3) for natural and synthetic 12-hydroxymonocerinins.^a

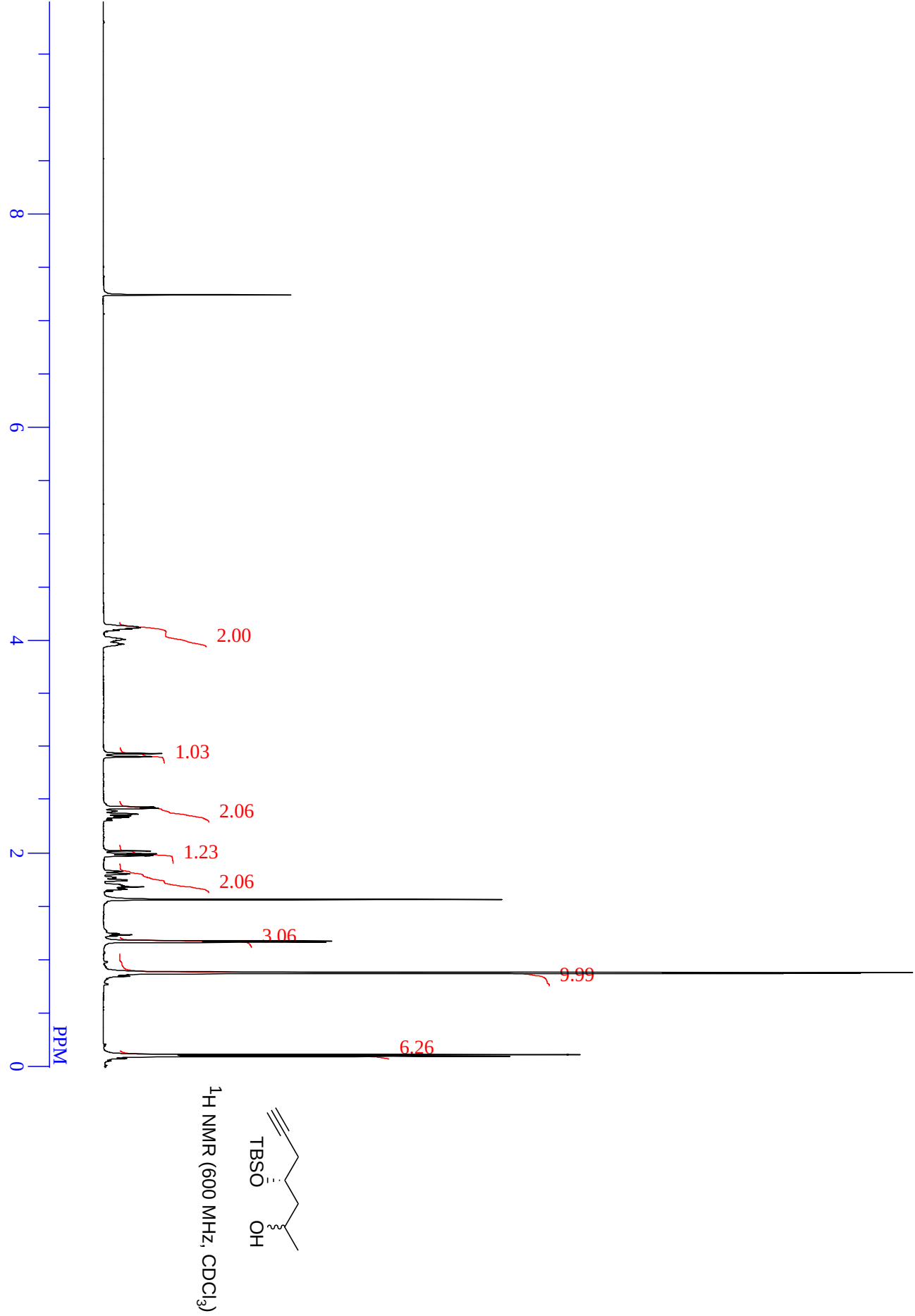
δ_{H} (ppm) (J in Hz)			
natural 1	synthetic 1	natural 2	synthetic 2
11.23(1H, s)	11.21 (1H, s)	11.24 (1H, s)	11.24 (1H, s)
6.57 (1H, s)	6.55 (1H, s)	6.58 (1H, s)	6.57 (1H, s)
5.06 (1H, dd, J 6.0, 3.0)	5.04 (1H, dd, J 5.5, 2.7)	5.05 (1H, ddd, J 6.0, 3.0, 1.0)	5.05 (1H, dd, J 5.5, 2.7)
4.60 (1H, d, J 3.0)	4.58 (1H, d, J 2.7)	4.56 (1H, d, J 3.0)	4.55 (1H, d, J 2.7)
4.35 (1H, m)	4.33 (1H, m)	4.41 (1H, m)	4.40 (1H, m)
3.98 (1H, m)	3.95 (1H, m)	4.01 (1H, m)	4.00 (1H, m)
3.95 (3H, s)	3.93 (3H, s)	3.94 (3H, s)	3.93 (3H, s)
3.91 (3H, s)	3.88 (3H, s)	3.90 (3H, s)	3.88 (3H, s)
2.67 (1H, ddd, J 14.5, 8.5, 6.0)	2.65 (1H, ddd, J 14.4, 8.9, 6.2)	2.65 (1H, ddd, J 14.5, 8.5, 6.0)	2.65 (1H, ddd, J 14.4, 8.9, 6.2)
2.22 (1H, dd, J 14.5, 5.5)	2.20 (1H, dd, J 14.4, 5.5)	2.20 (1H, ddd, J 14.5, 5.5, 1.0)	2.19 (1H, dd, J 14.4, 6.2)
1.84 (1H, ddd, J 14.0, 9.0, 6.0)	1.81 (1H, dt, J 14.4, 8.9)	1.82 (1H, ddd, J 14.0, 8.0, 3.5)	1.81 (1H, ddd, J 14.4, 8.9, 2.7)
1.75 (1H, dt, J 14.0, 4.0)	1.72 (1H, dt, J 14.4, 2.7)	1.73 (1H, ddd, J 14.0, 9.0, 4.0)	1.72 (1H, ddd, J 14.4, 8.9, 4.1)
1.18 (3H, d, J 6.0)	1.16 (3H, d, J 6.2)	1.19 (3H, d, J 6.0)	1.18 (3H, d, J 6.2)

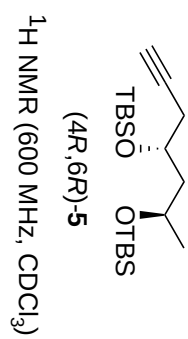
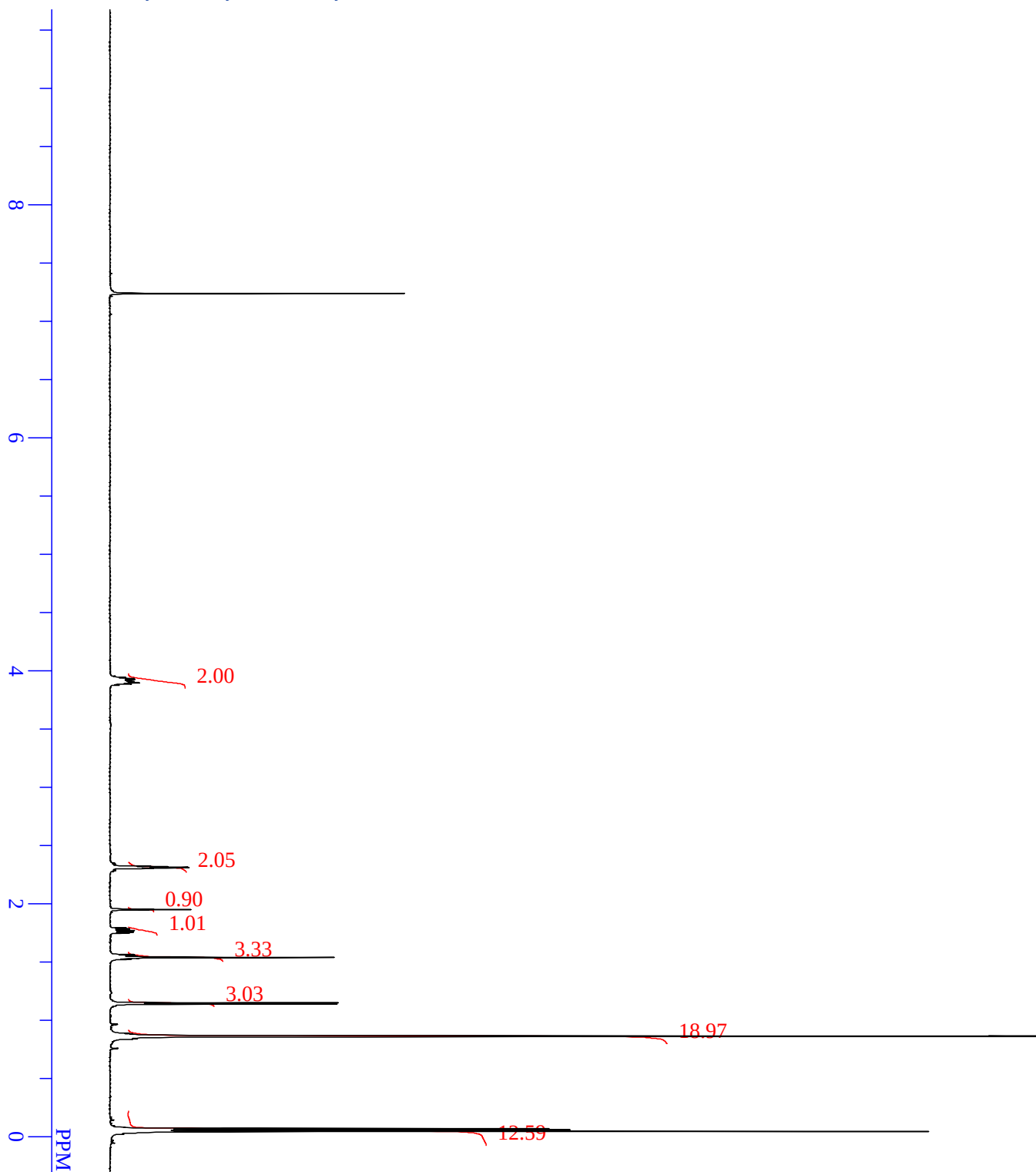
^aData for natural **1** and **2** are from ref. 2a (500 MHz). Data for synthetic **1** and **2** were recorded with 600 MHz operating frequency.

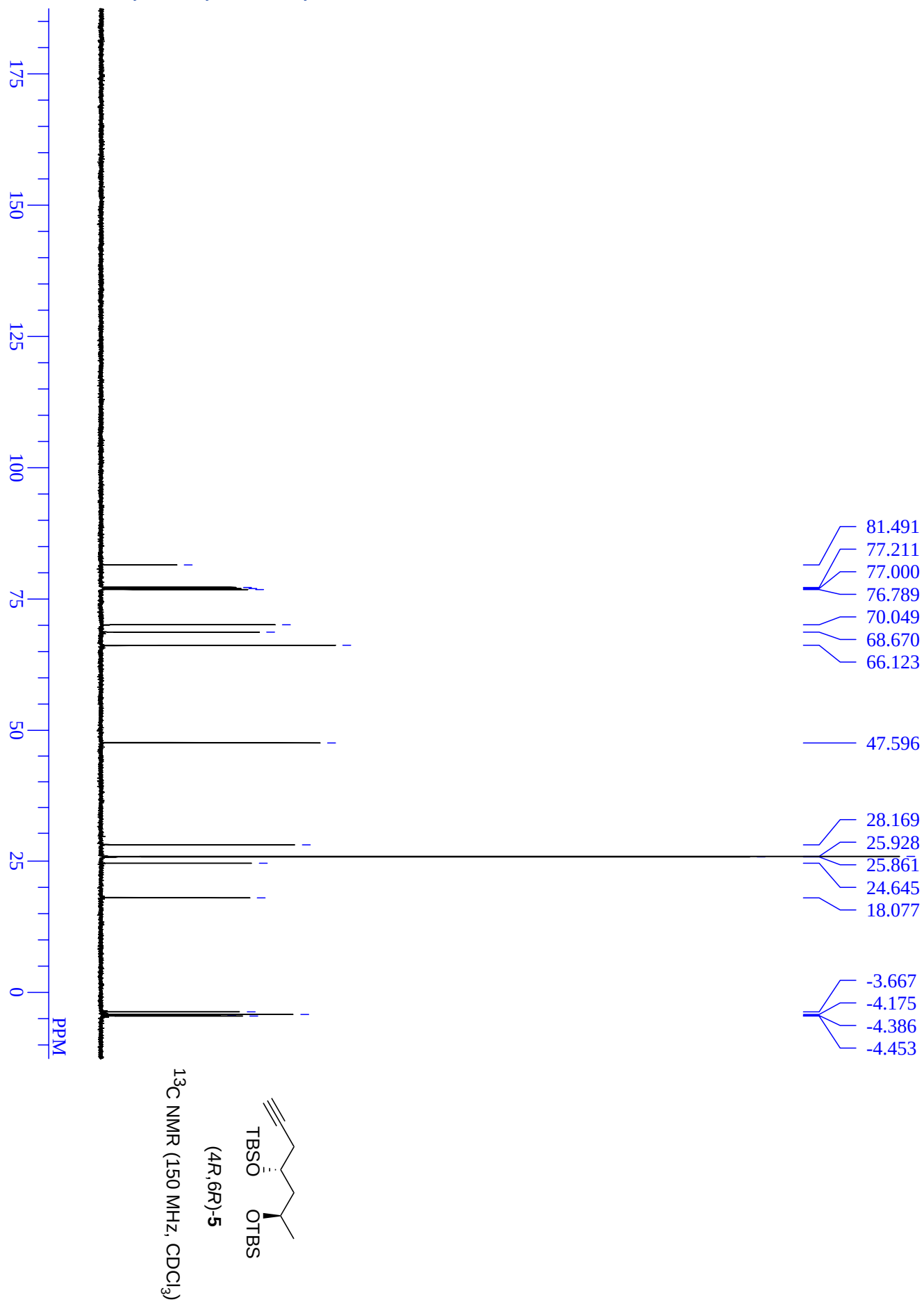
Table S2 Comparison of ^{13}C NMR data δ_{C} (CDCl_3) for natural and synthetic 12-hydroxymonocerinins.^a

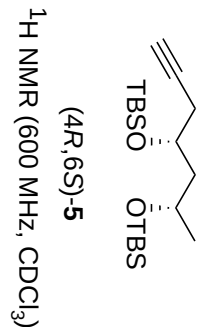
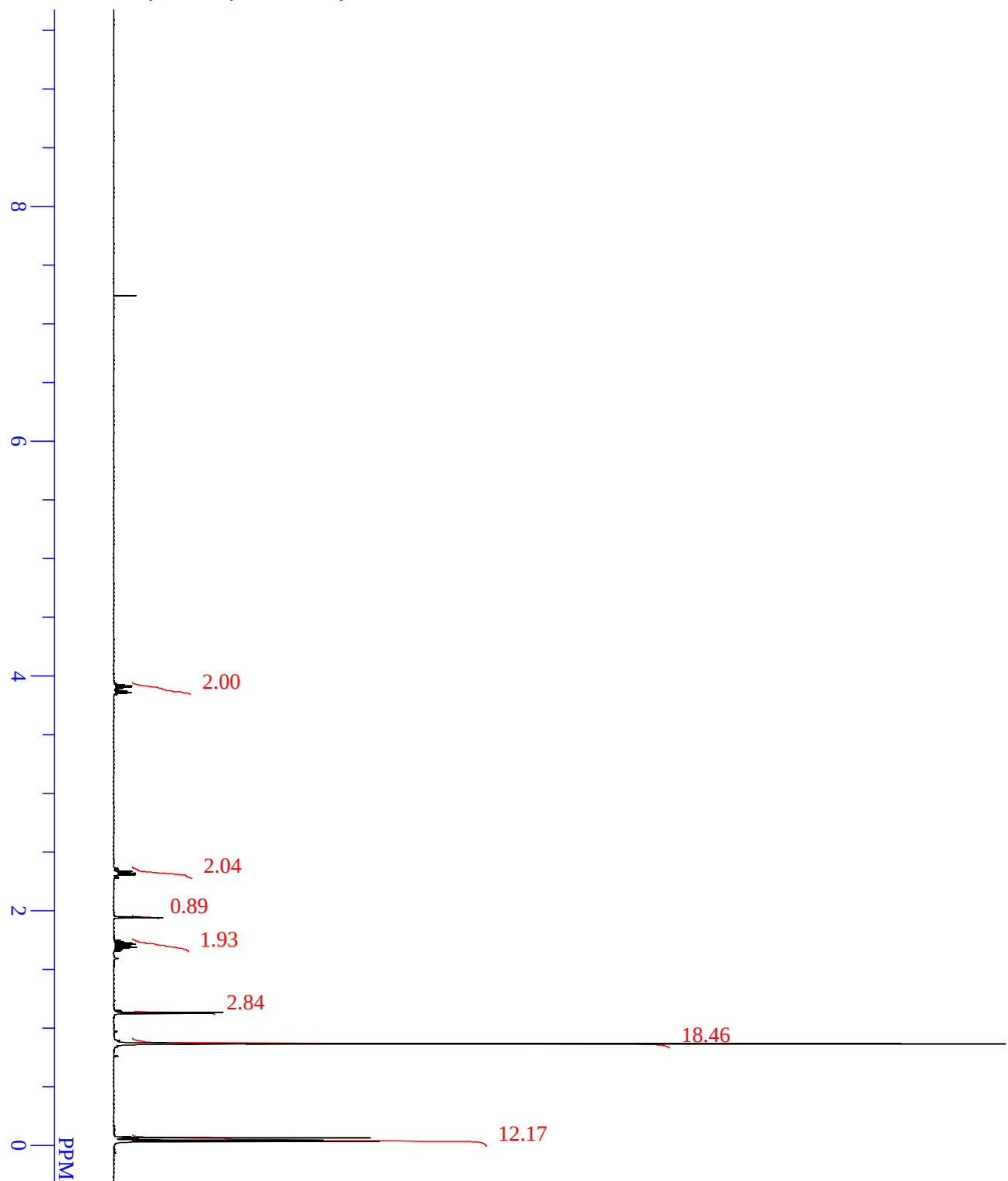
natural 1	synthetic 1	δ_{C} (ppm)	
		natural 2	synthetic 2
167.6	167.6	167.7	167.7
158.7	158.7	158.7	158.7
156.3	156.3	156.3	156.2
137.5	137.4	137.4	137.3
130.6	130.6	130.9	130.8
104.5	104.5	104.5	104.5
102.0	101.9	102.0	102.0
80.8	80.8	81.2	81.2
78.4	78.5	75.9	75.9
75.0	75.0	74.7	74.7
67.2	67.3	65.0	65.0
60.7	60.8	60.7	60.7
56.3	56.3	56.3	56.3
44.8	44.8	44.6	44.5
39.6	39.5	39.5	39.4
23.6	23.5	24.0	23.9

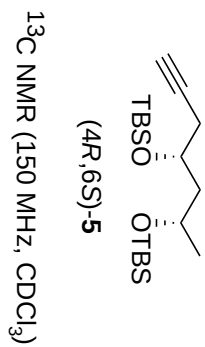
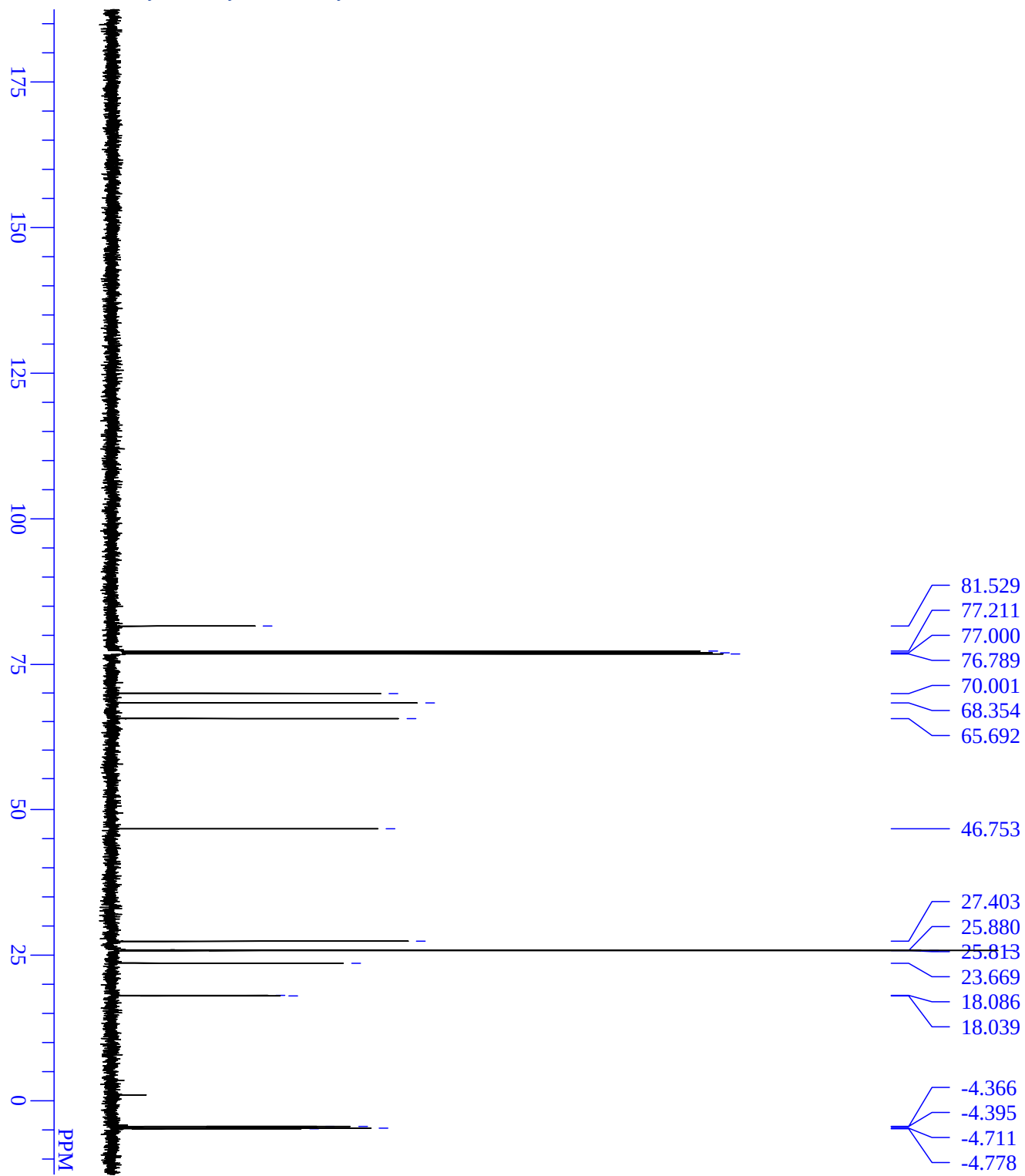
^aData for natural **1** and **2** are from ref. 2a (125 MHz). Data for synthetic **1** and **2** were recorded with 150 MHz operating frequency.

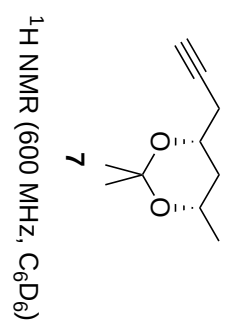
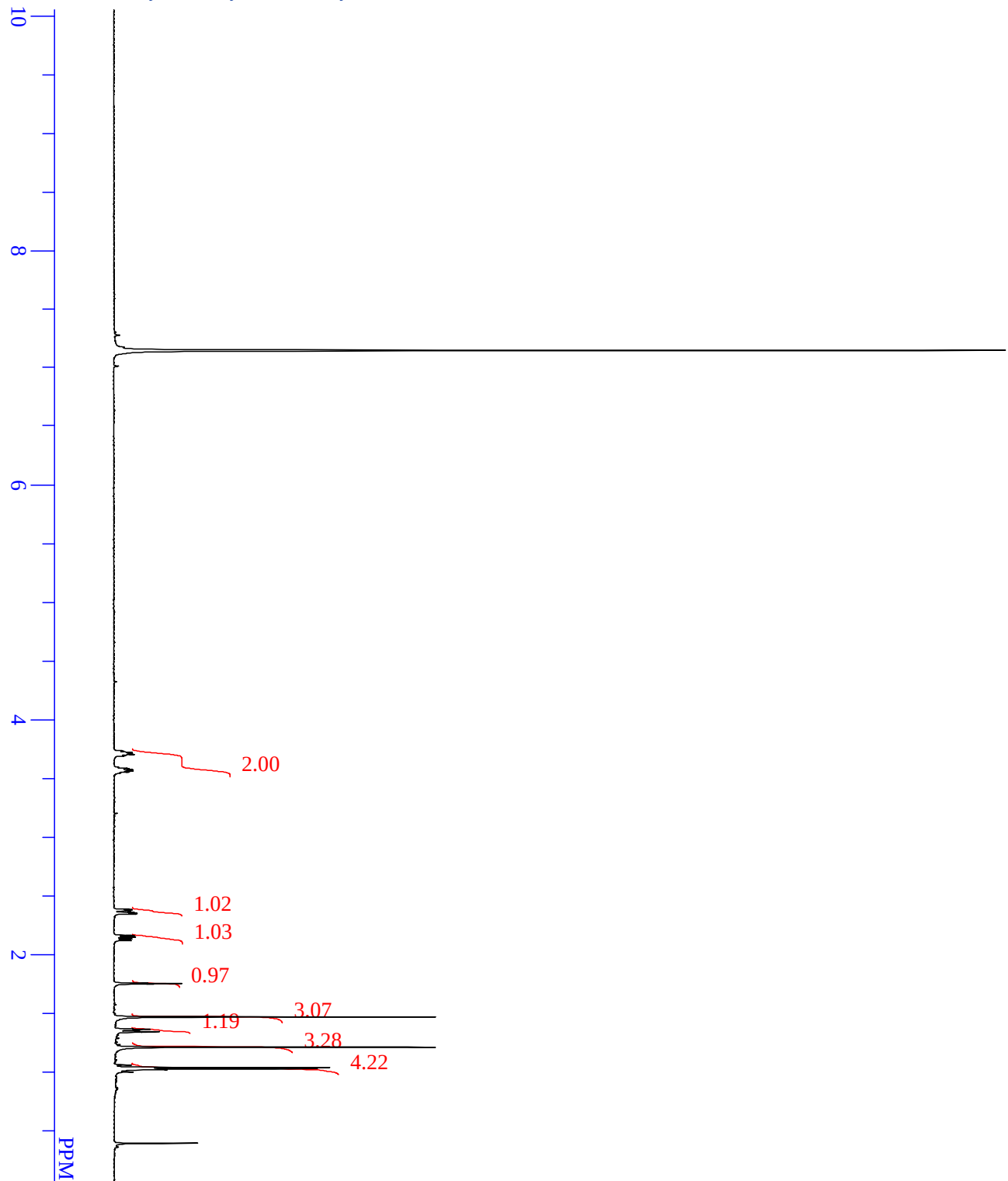


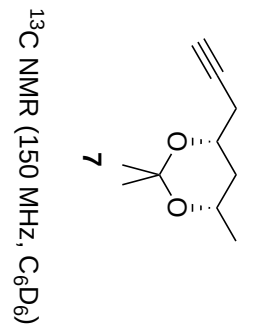
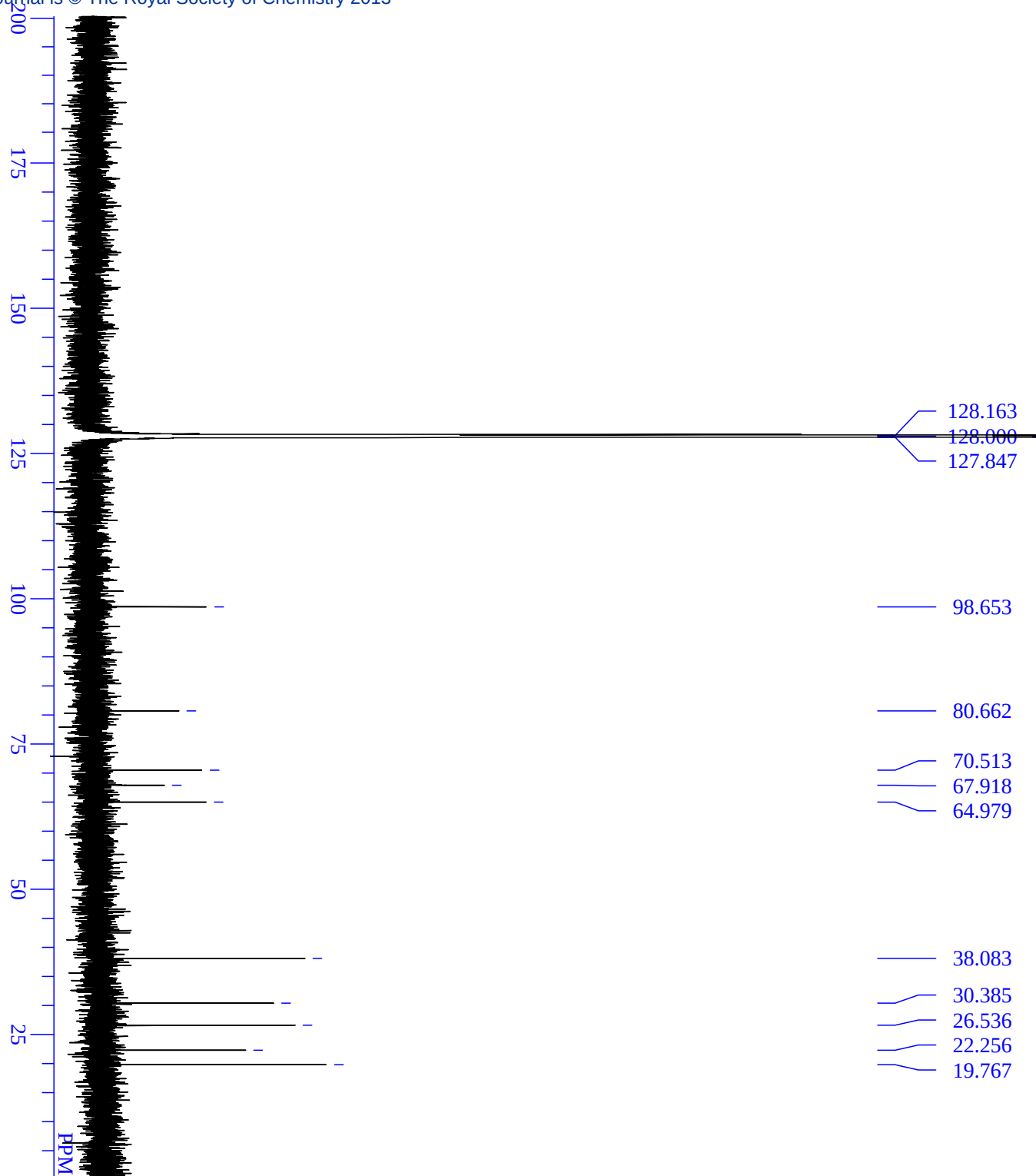


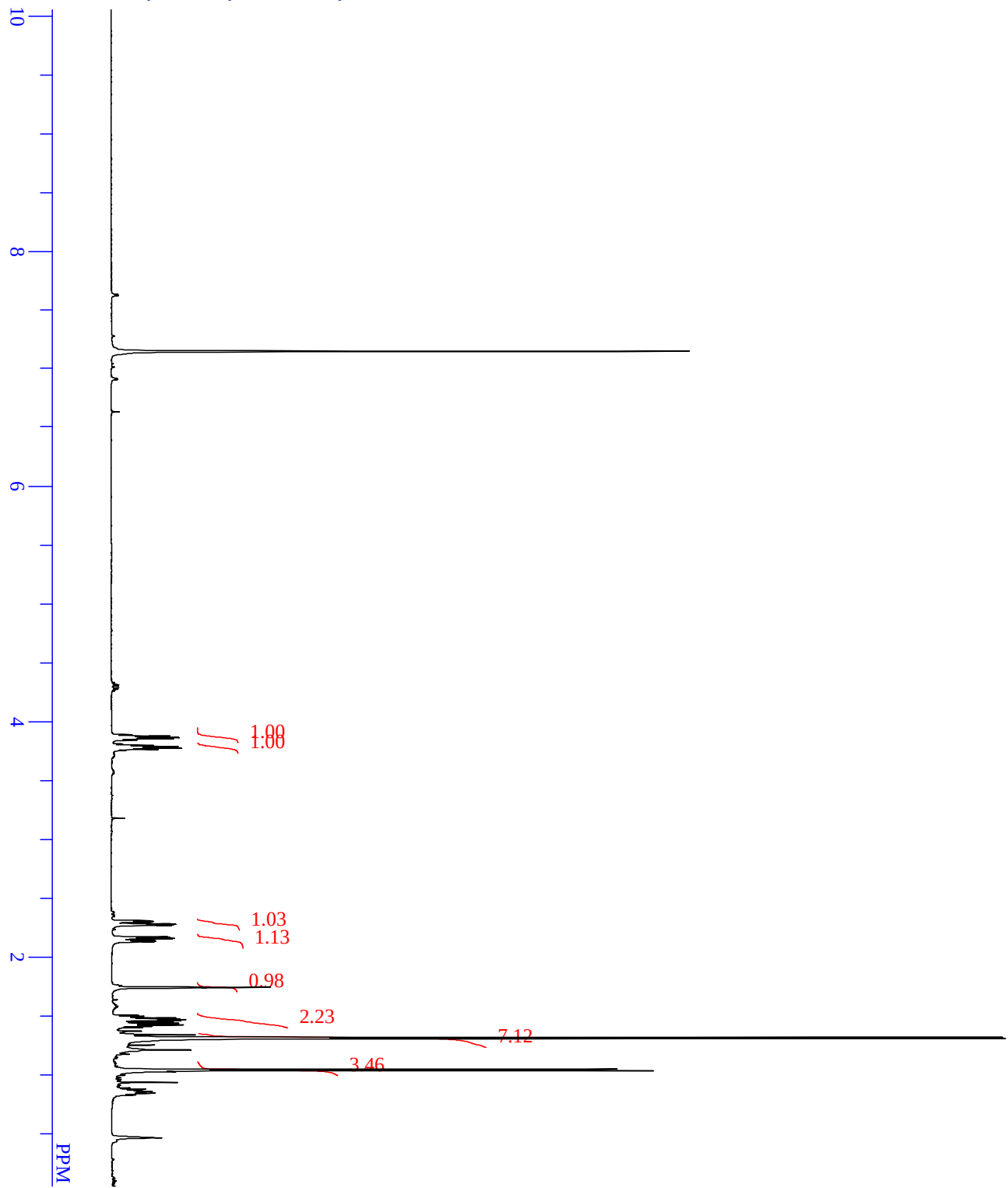




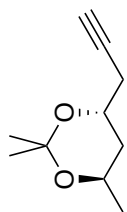


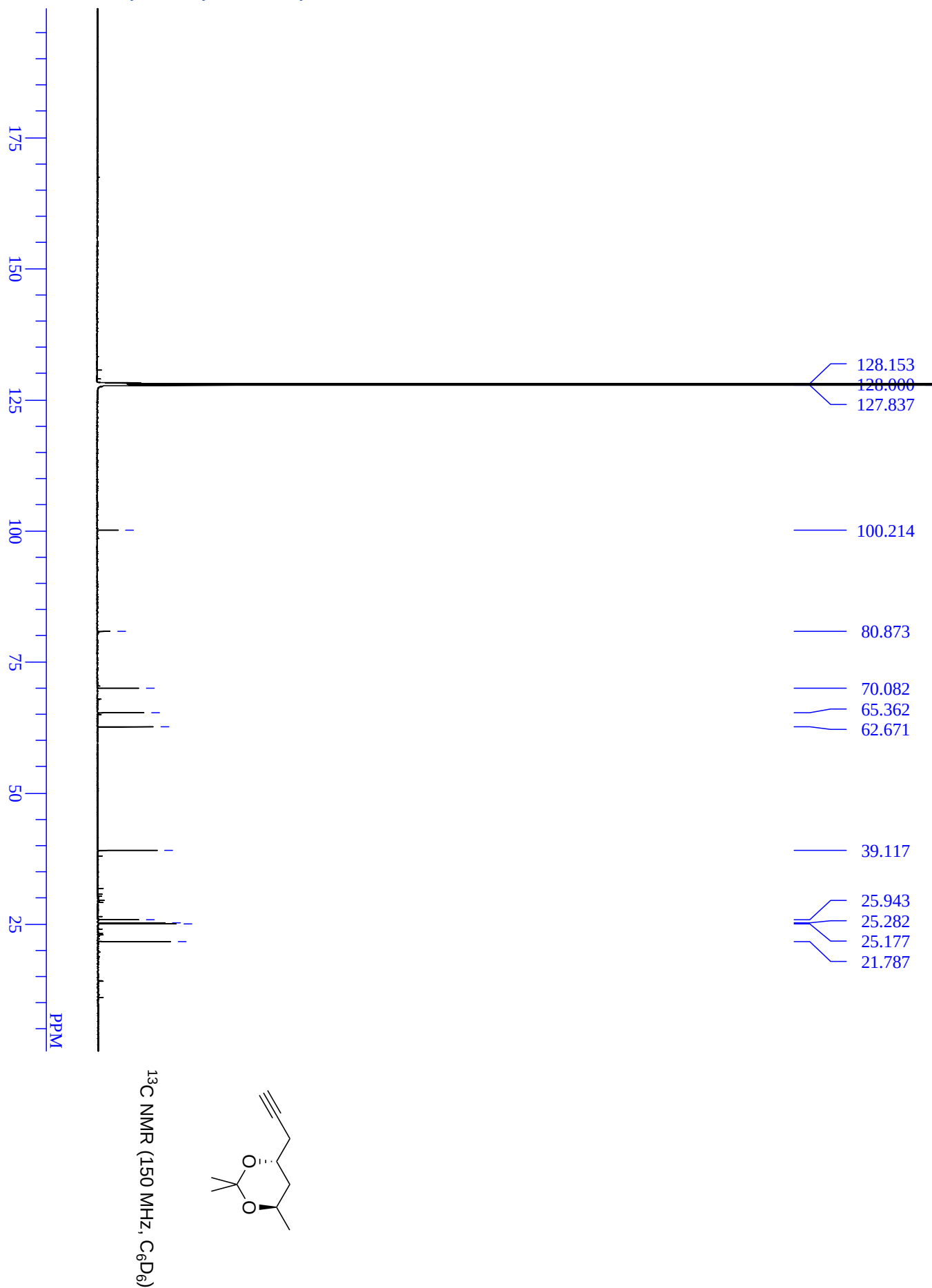


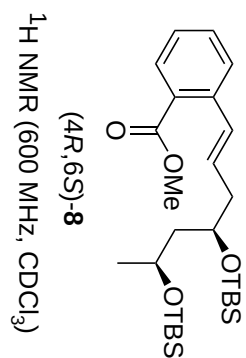
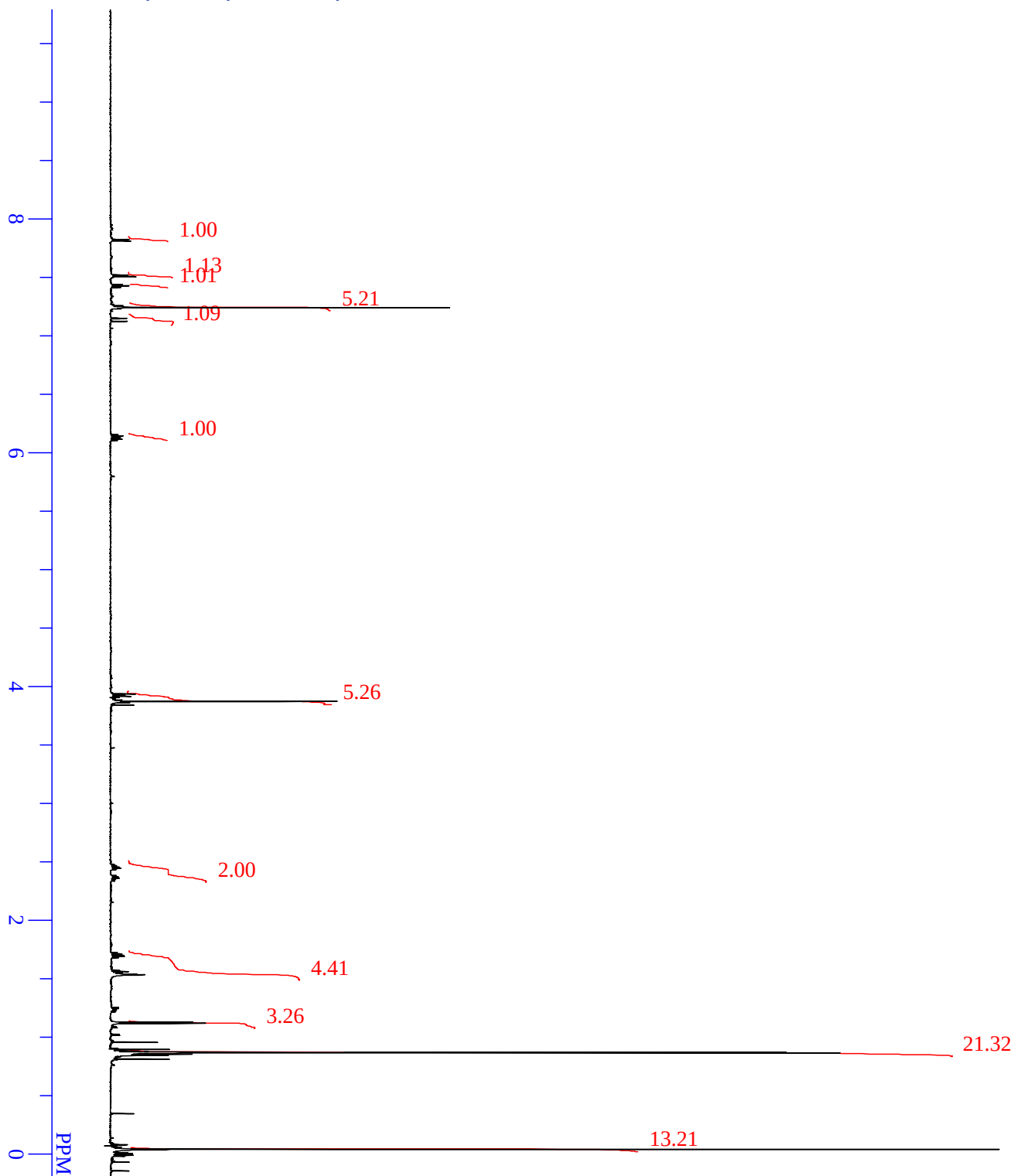


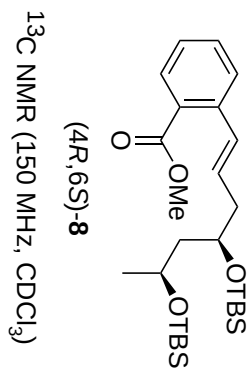
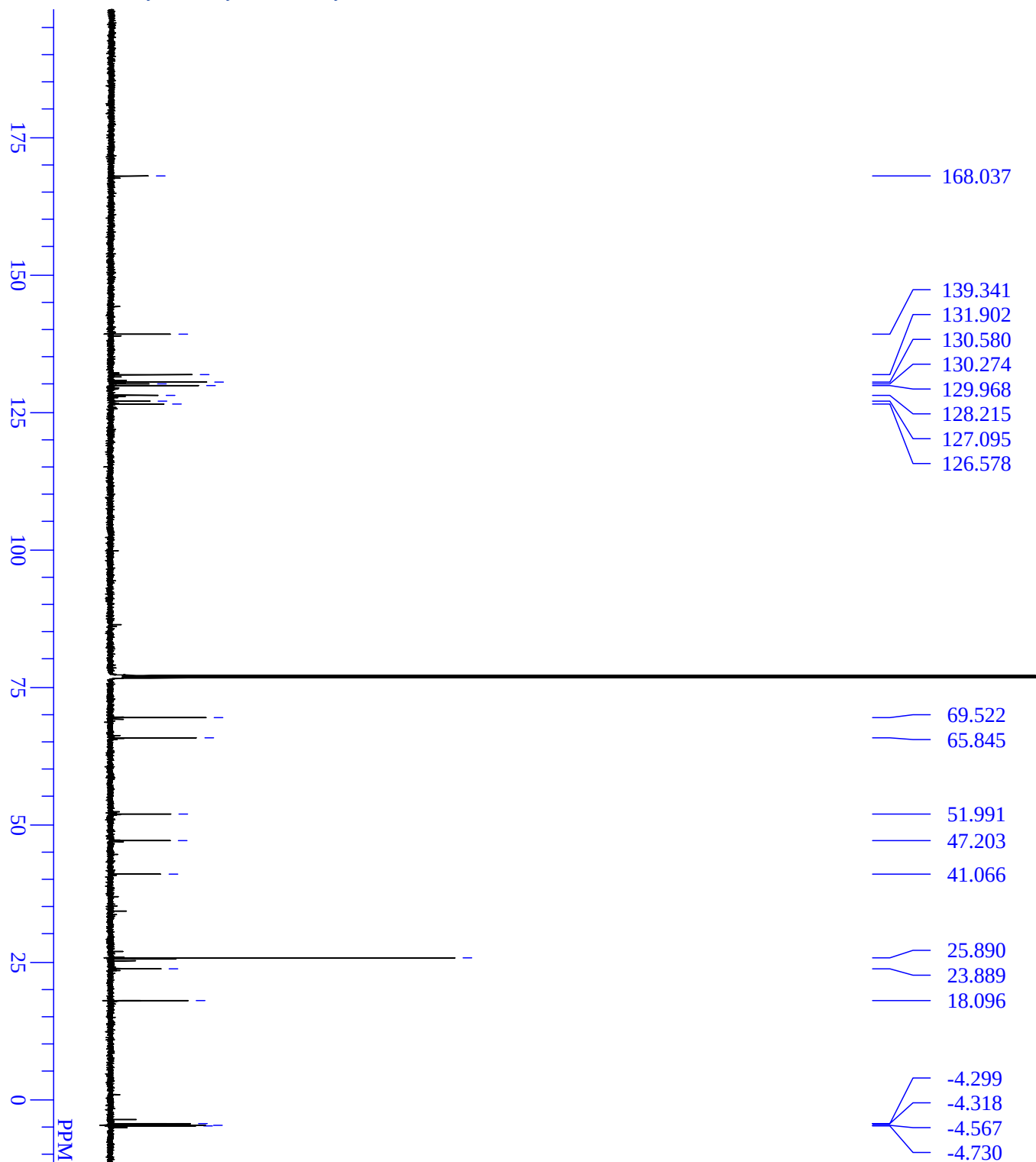


¹H NMR (600 MHz, C₆D₆)

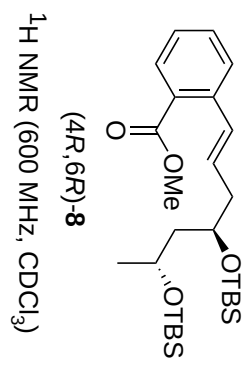
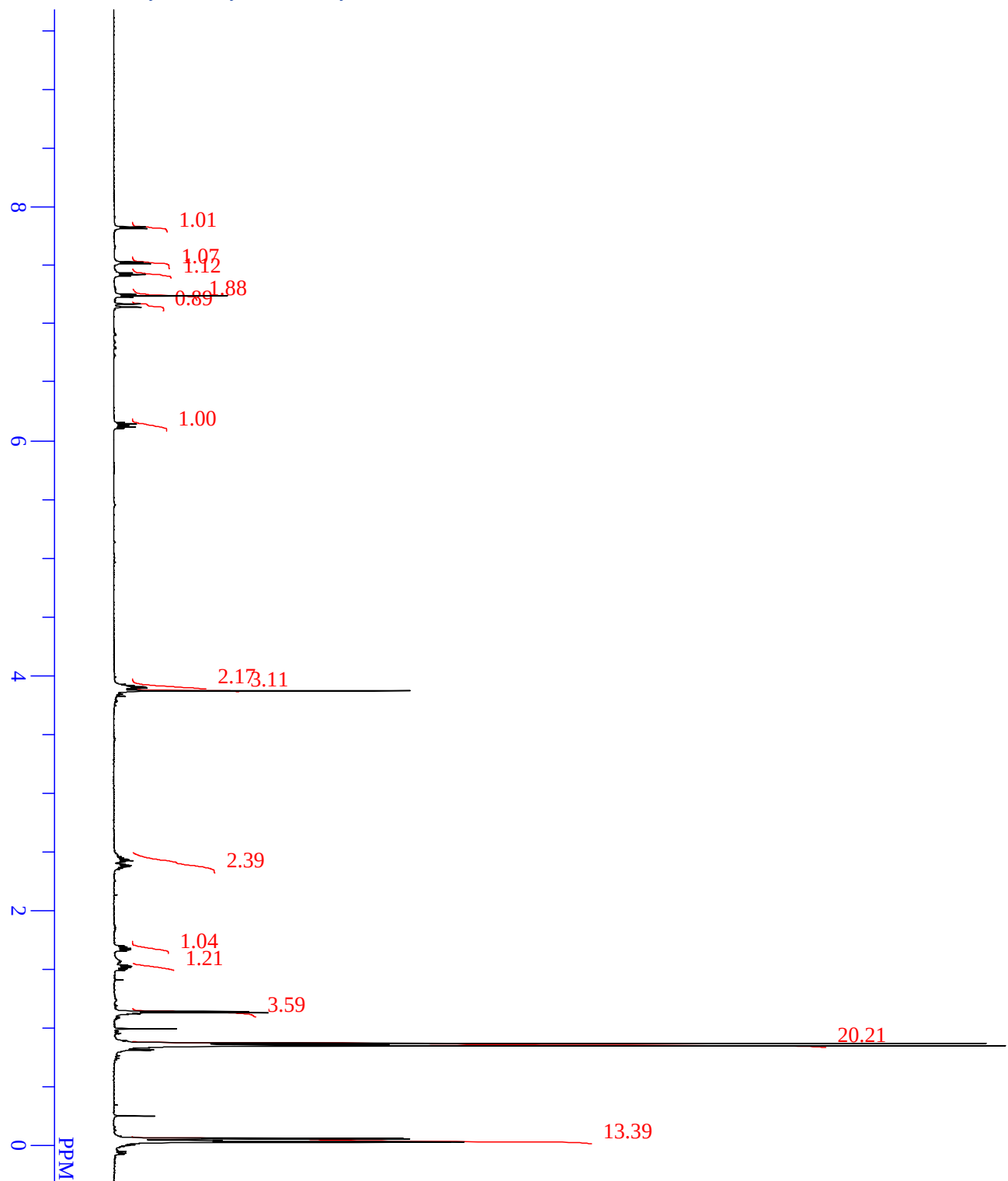


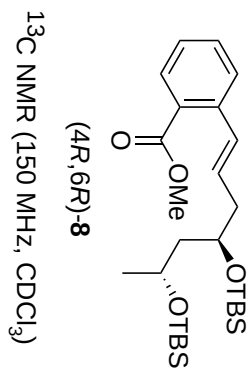
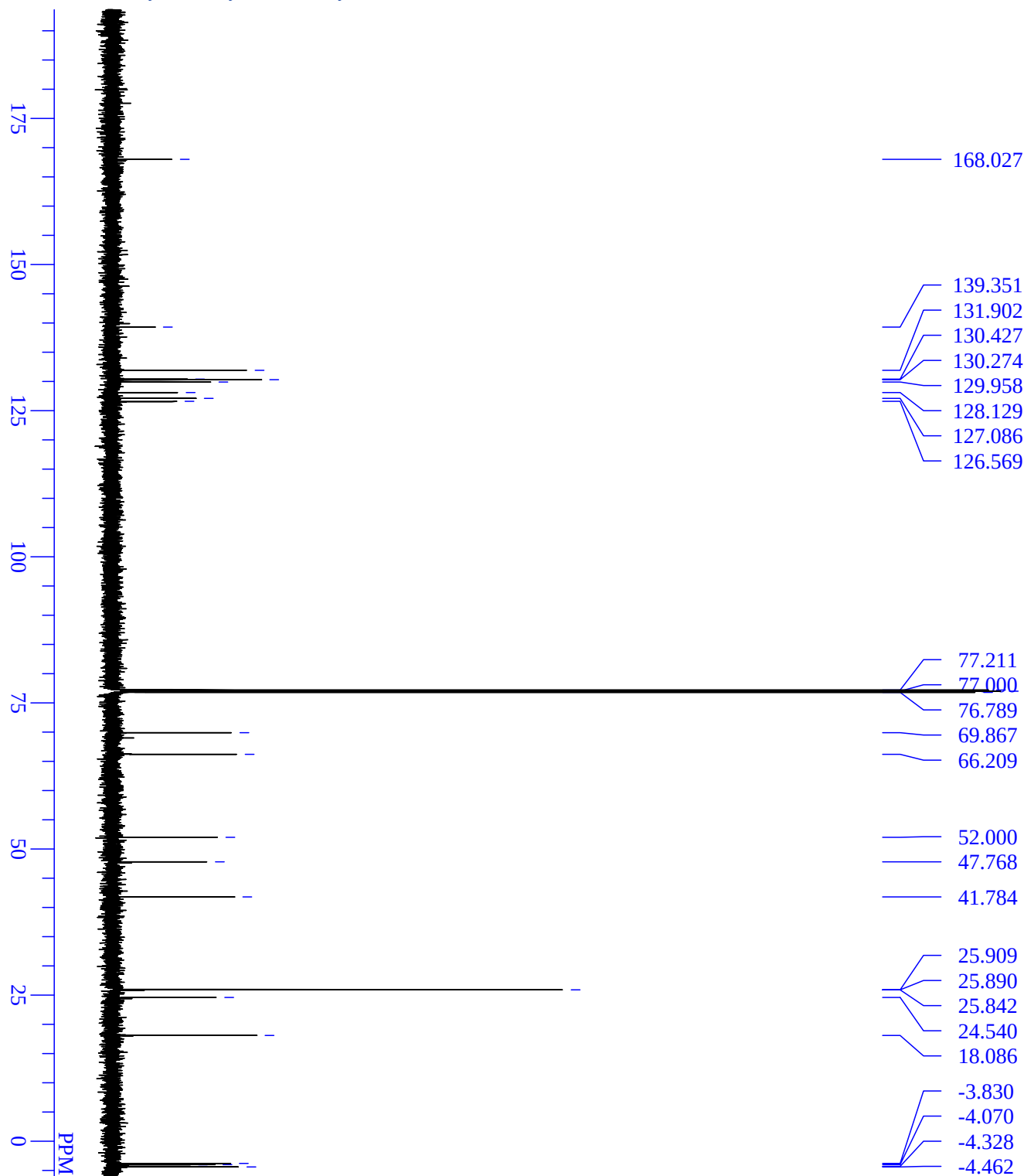


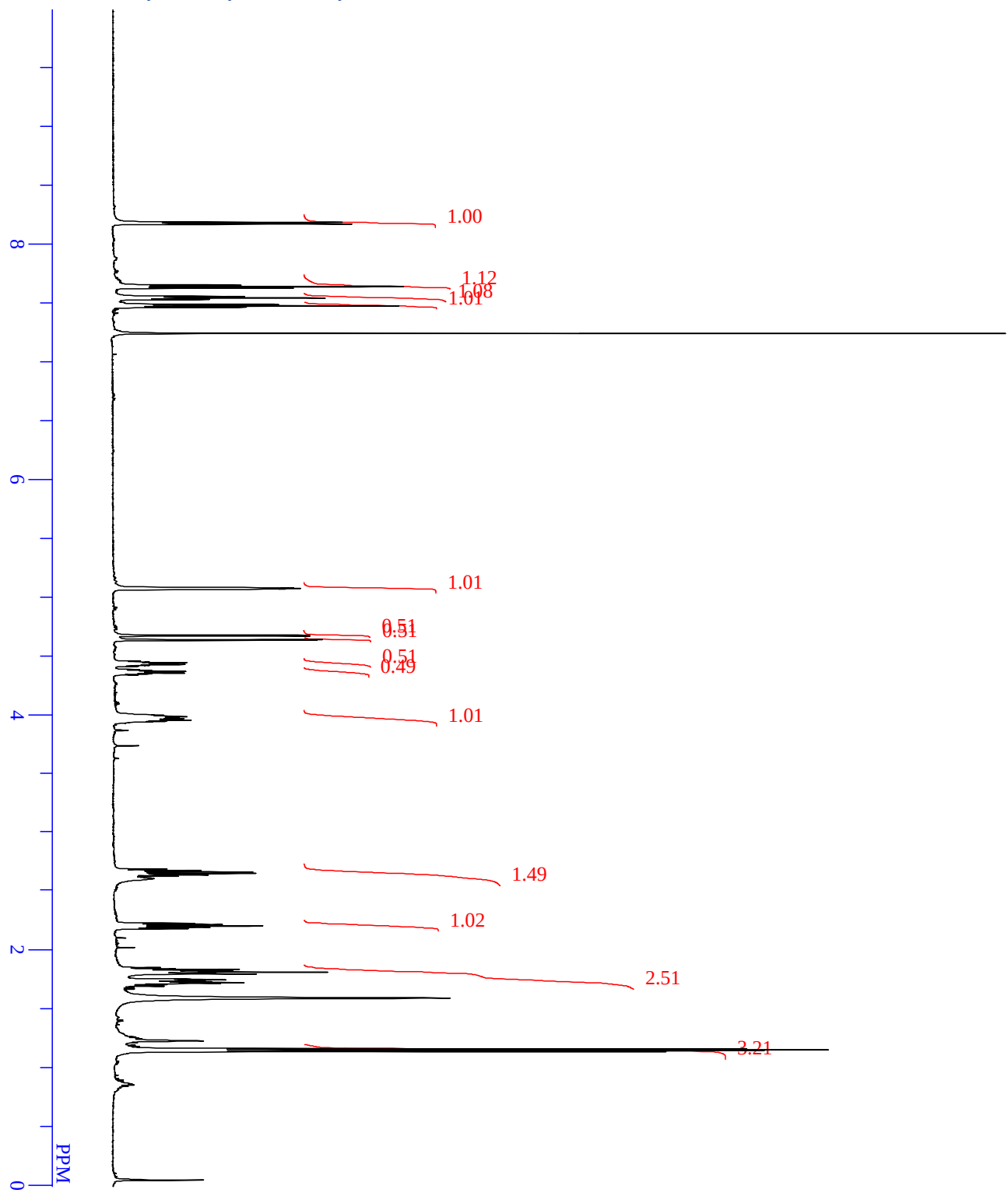




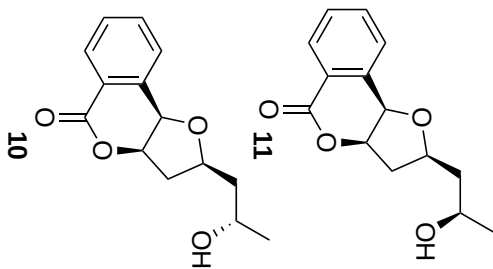
¹³C NMR (150 MHz, CDCl₃)

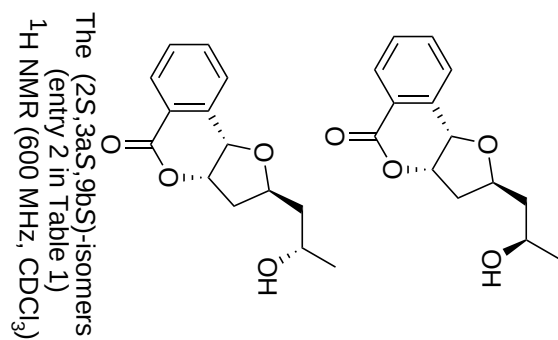
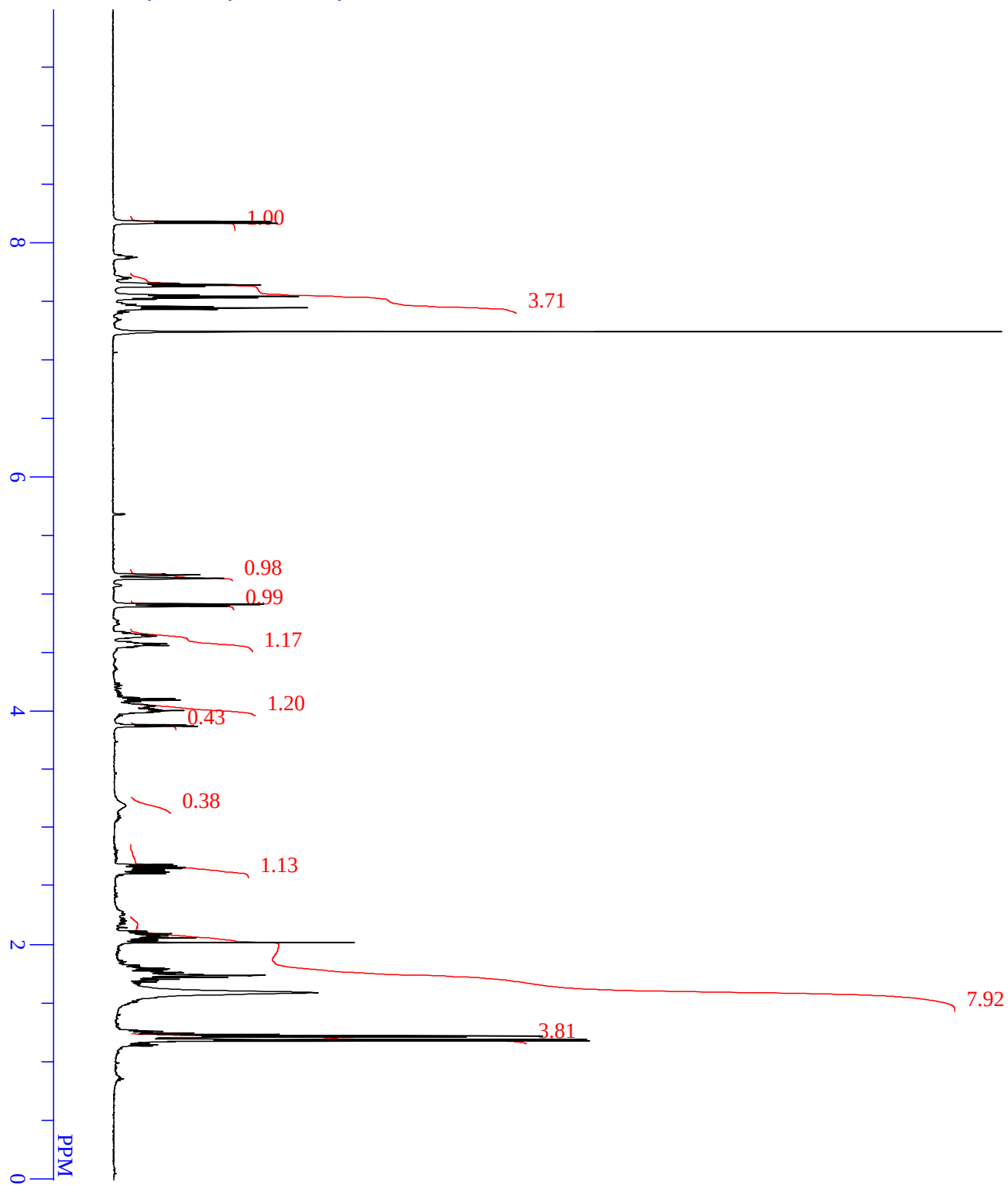


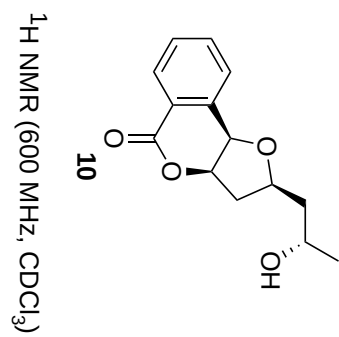
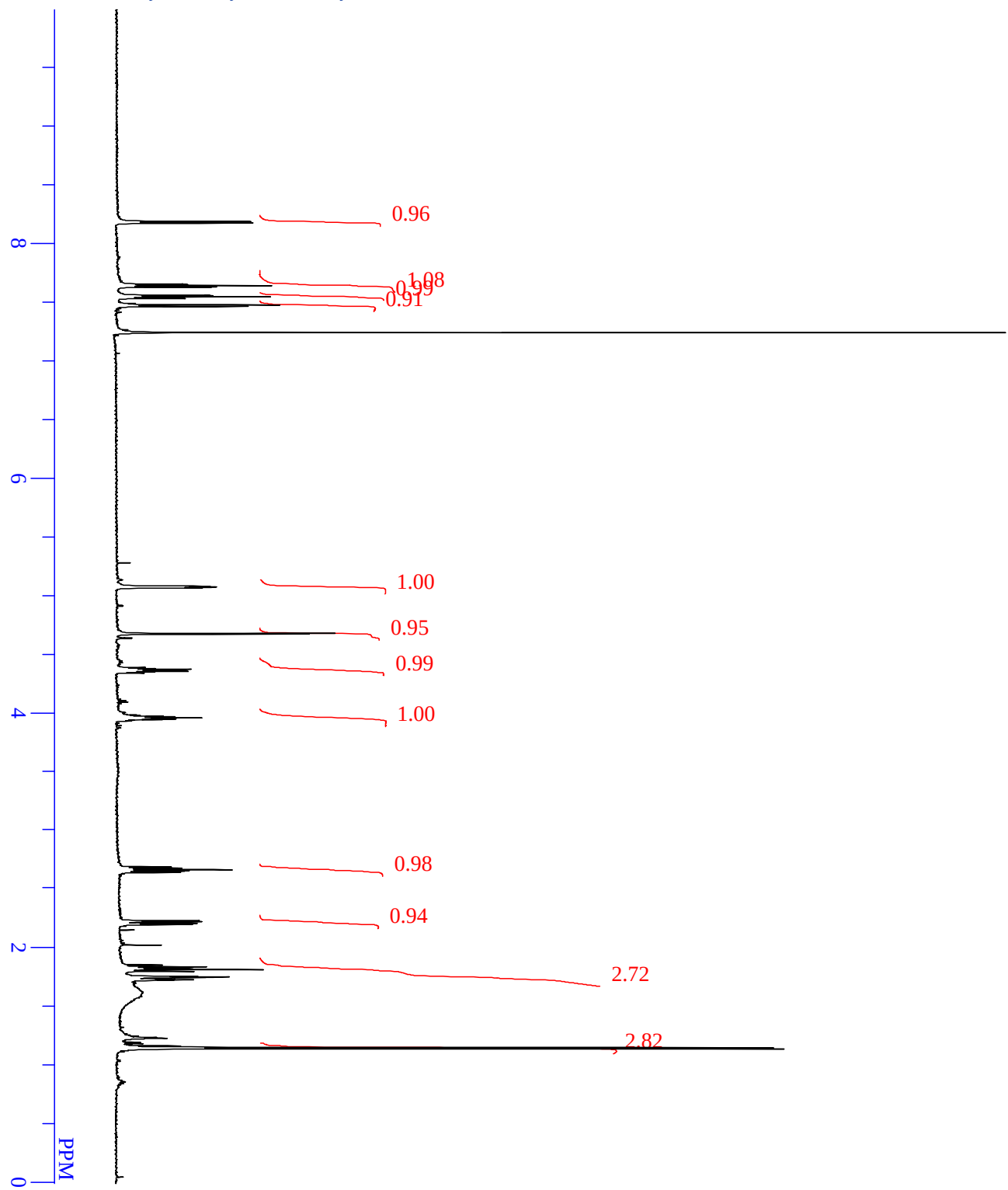


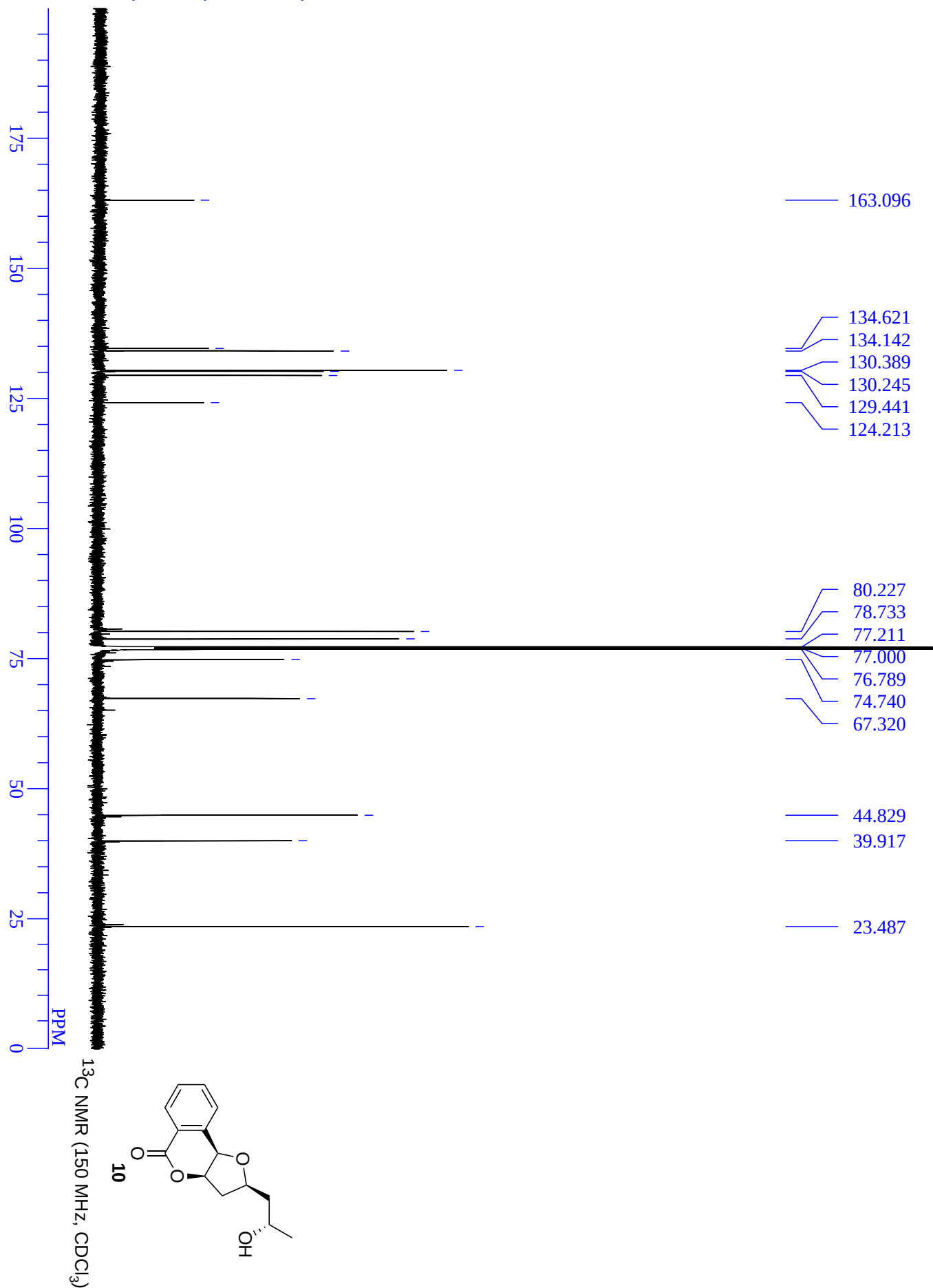


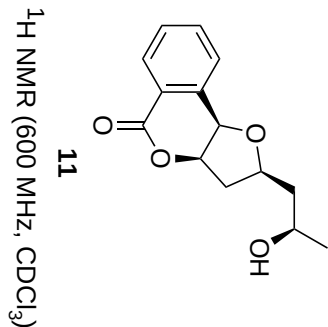
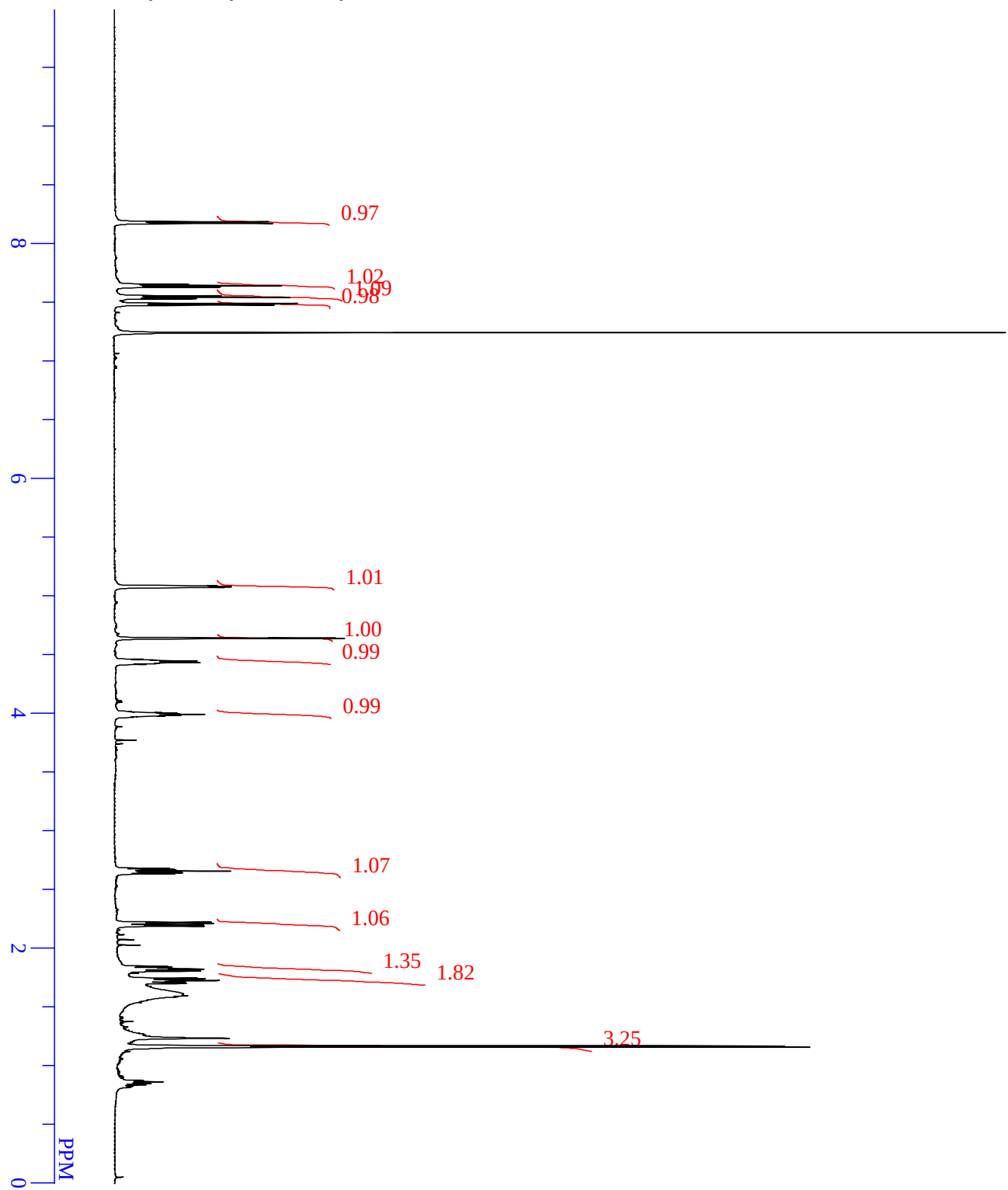
¹H NMR (600 MHz, CDCl₃)

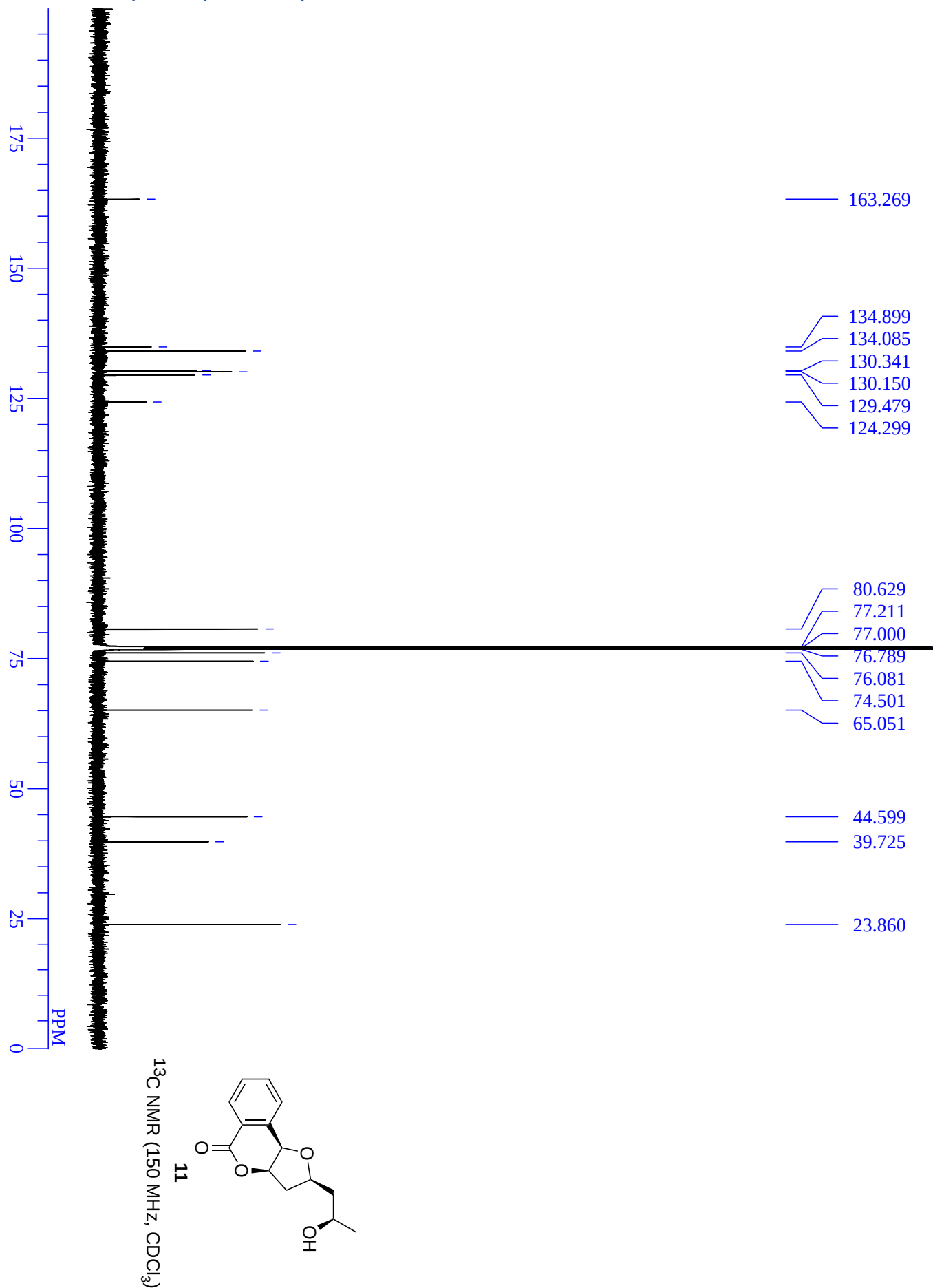


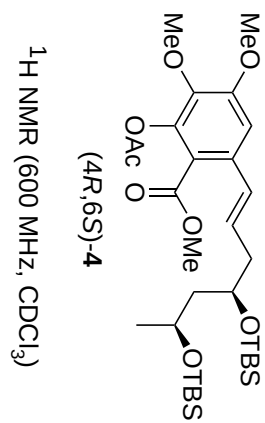
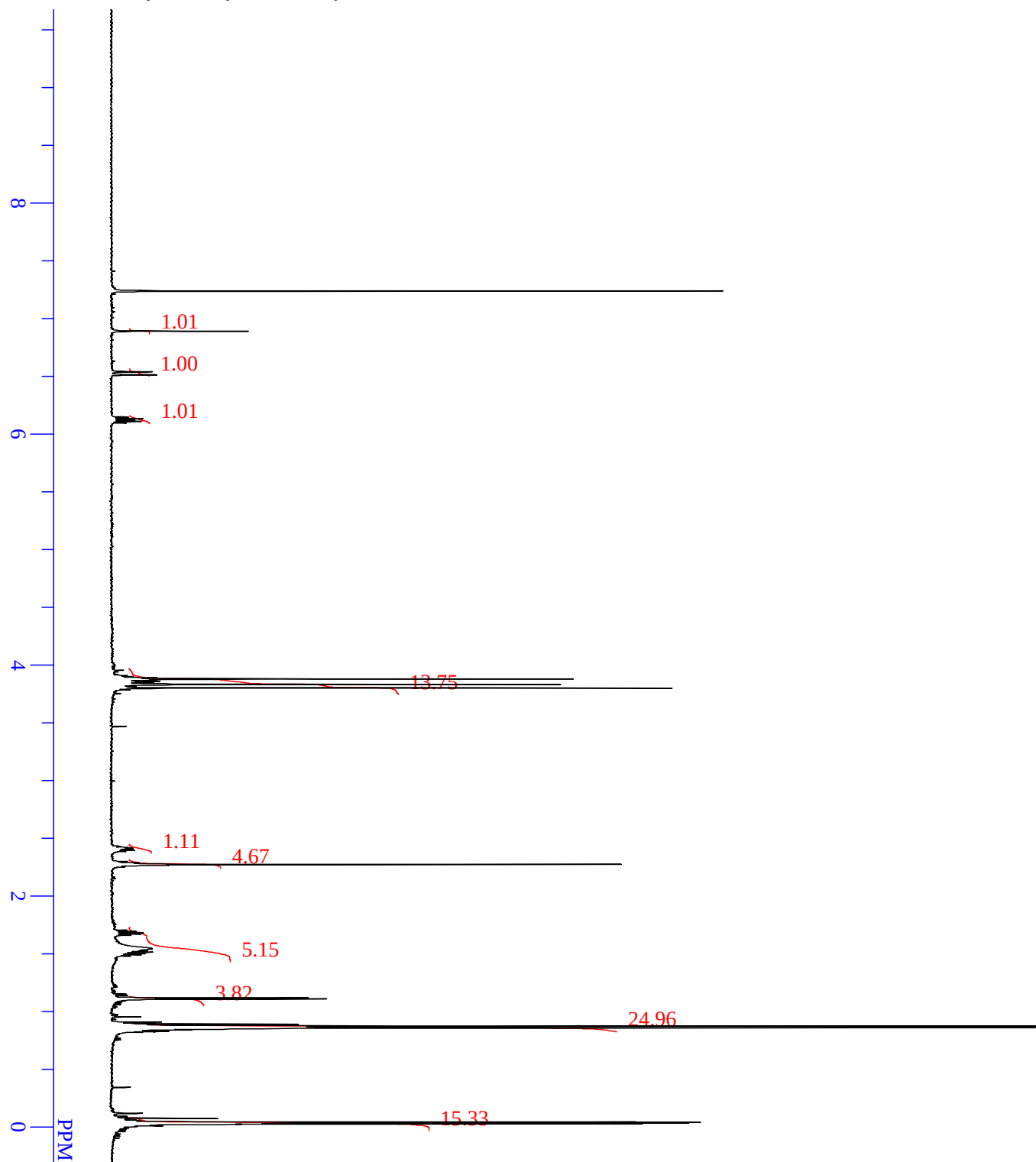


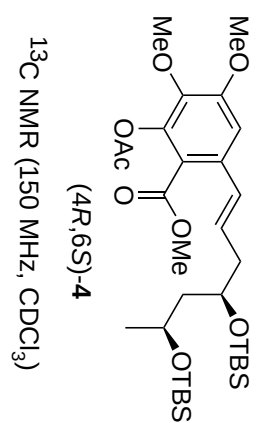
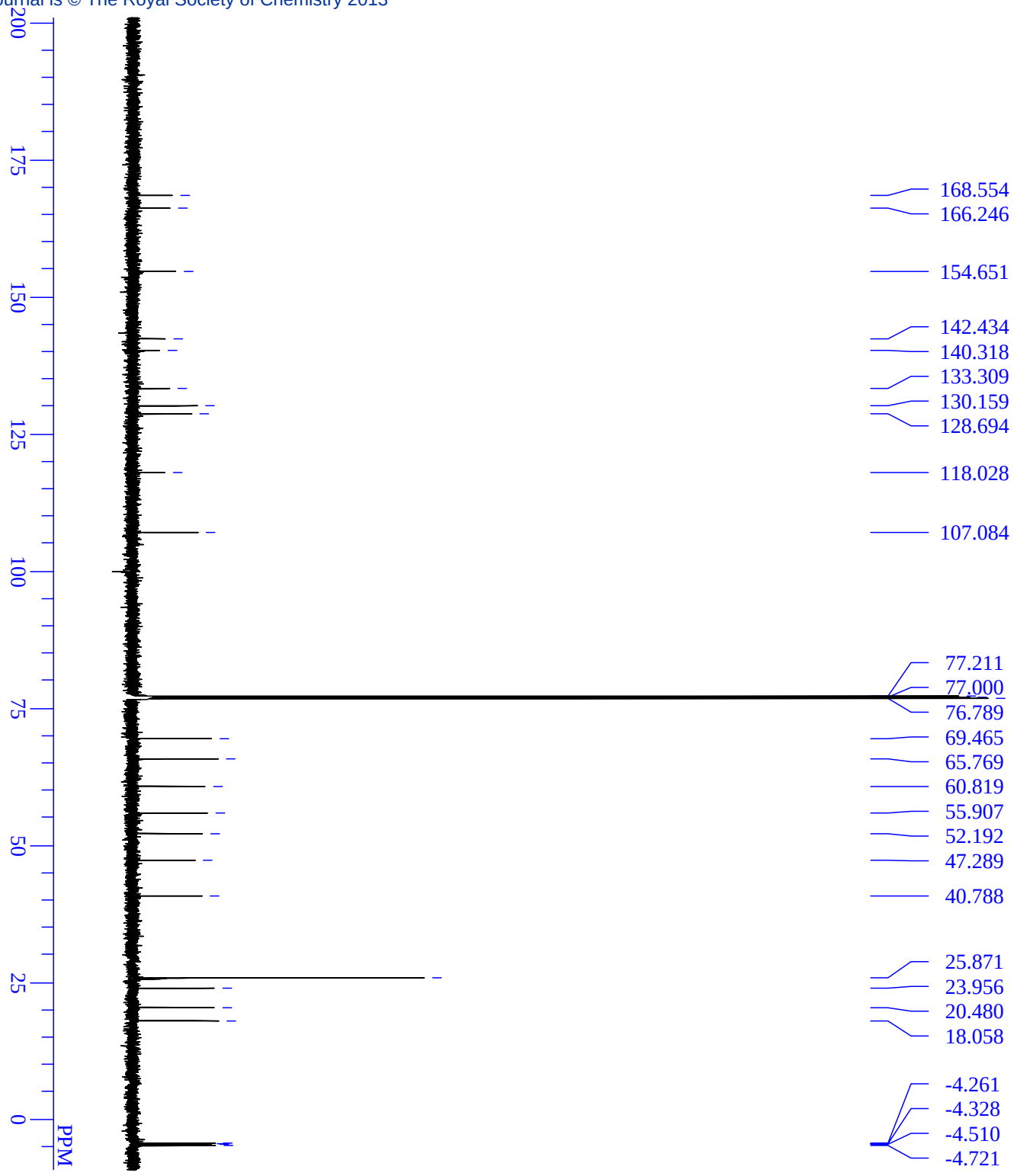


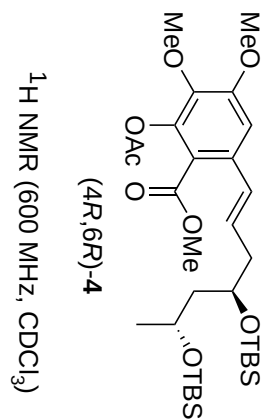
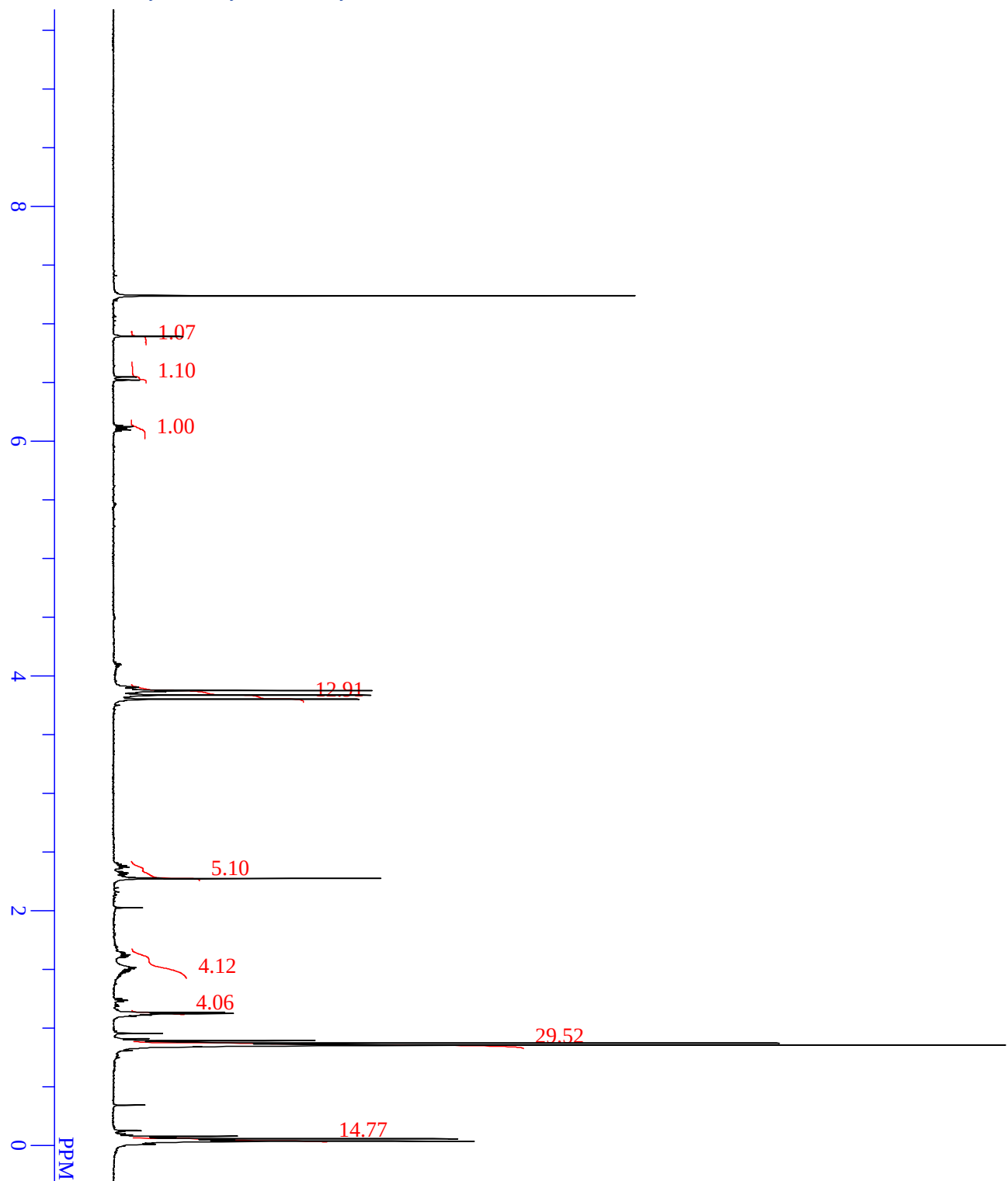


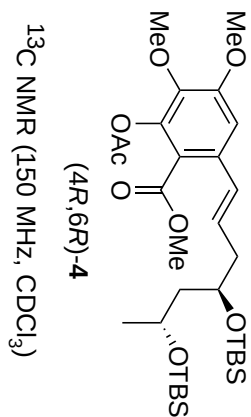
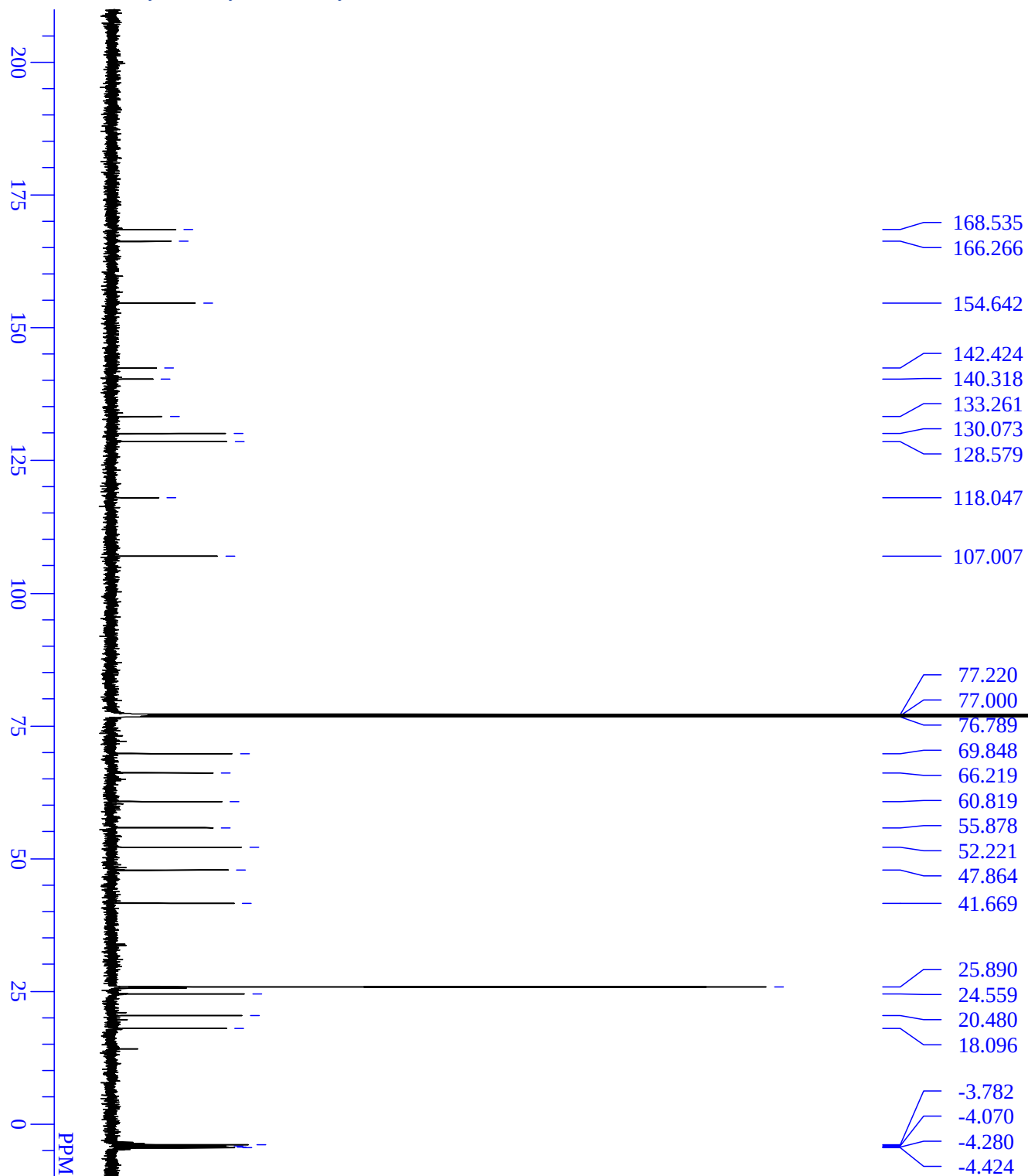


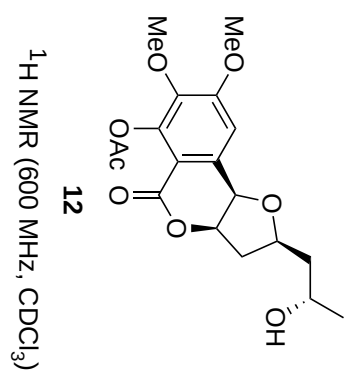
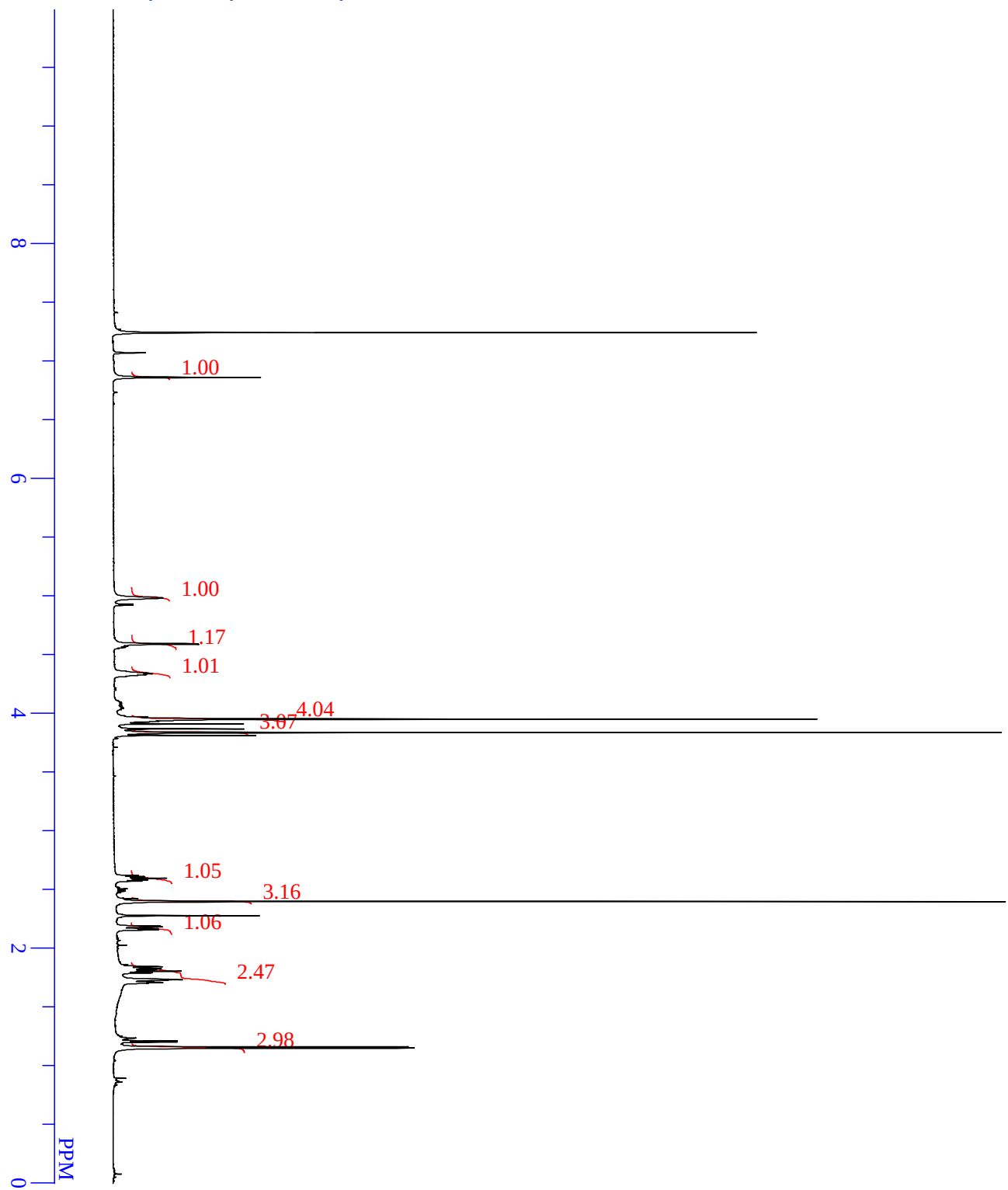


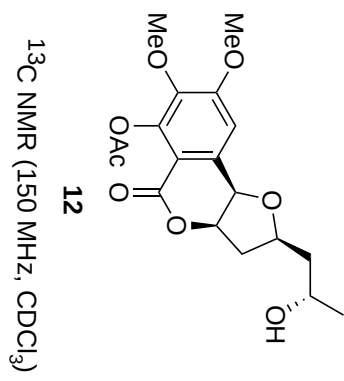
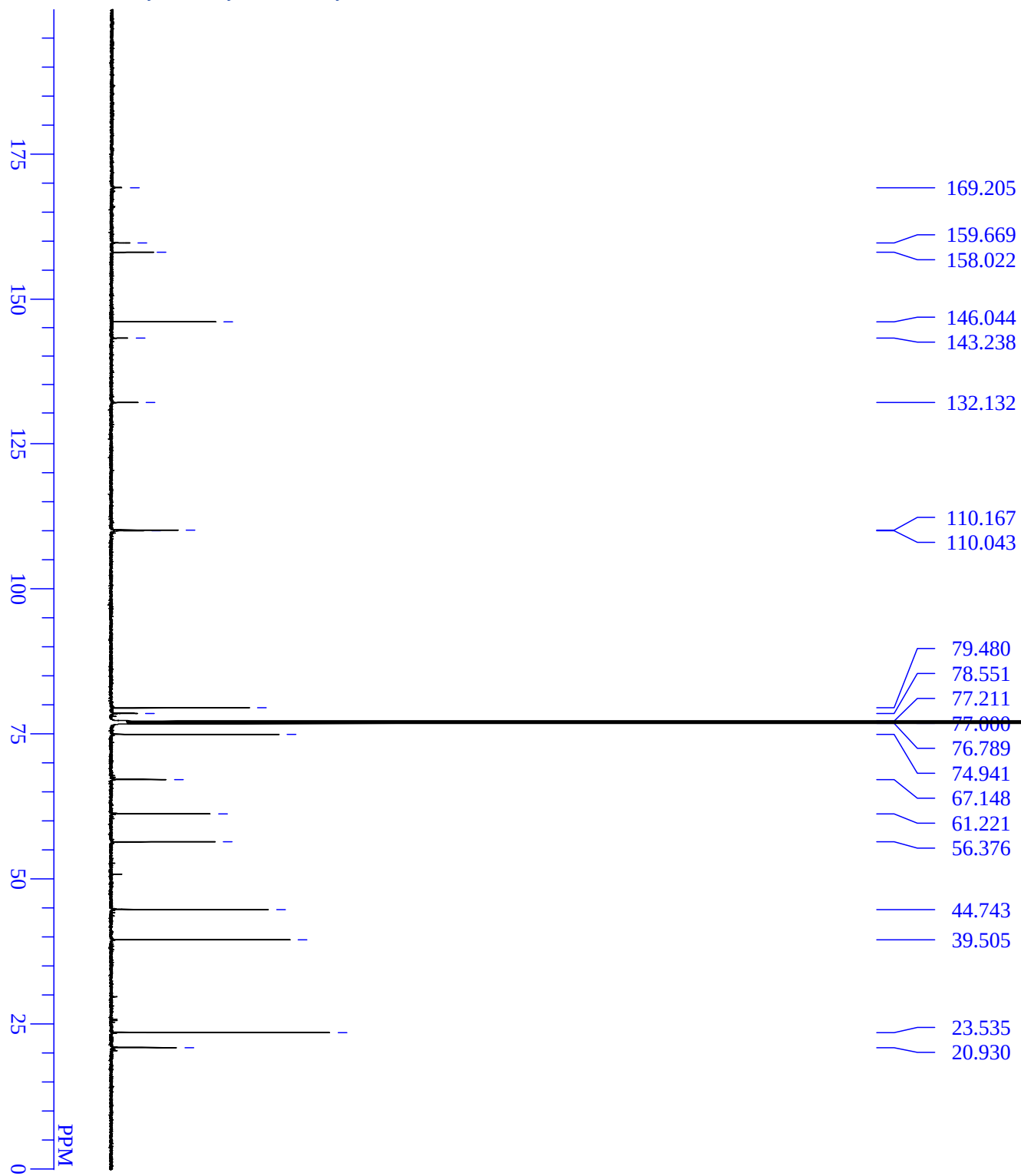


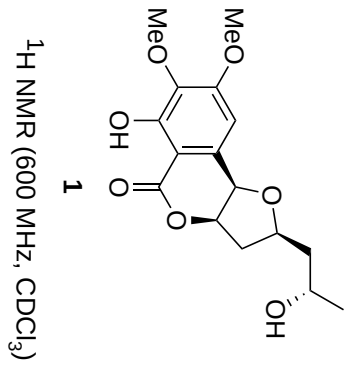
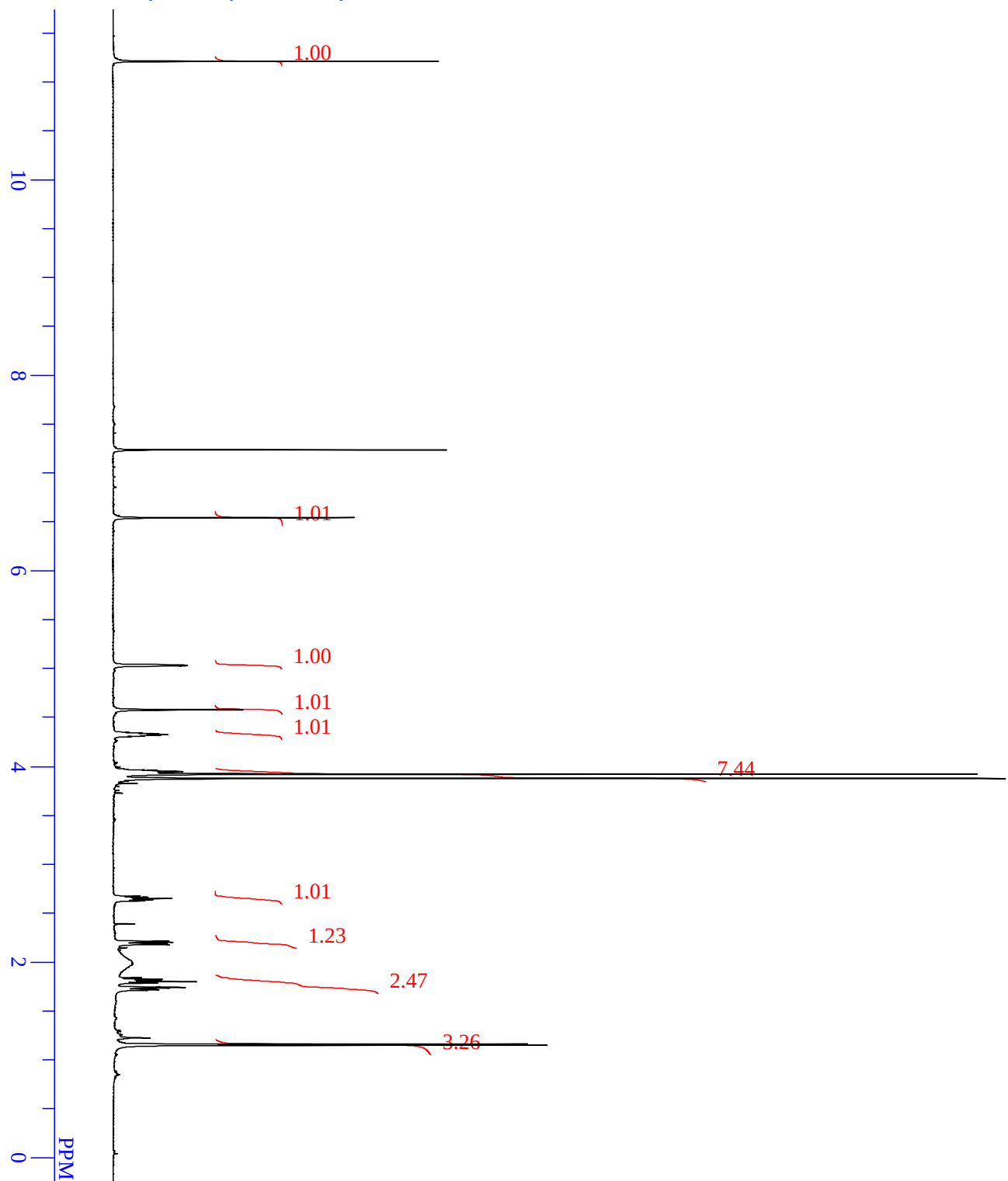


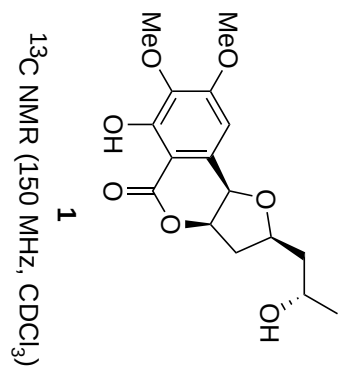
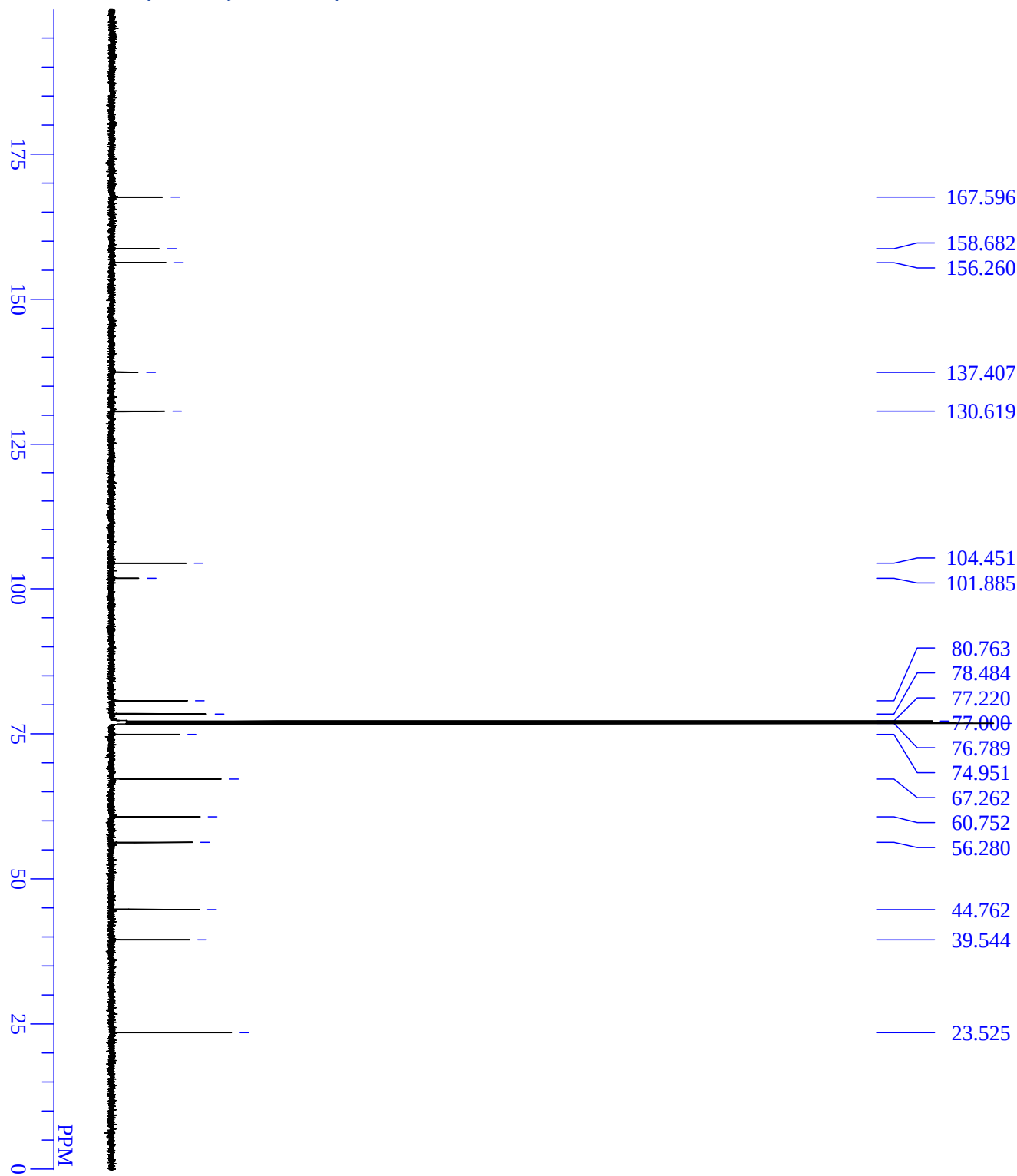


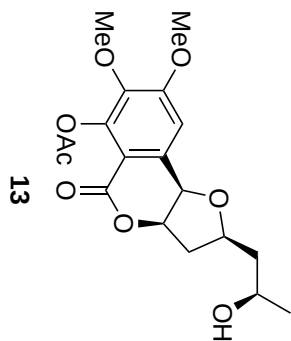
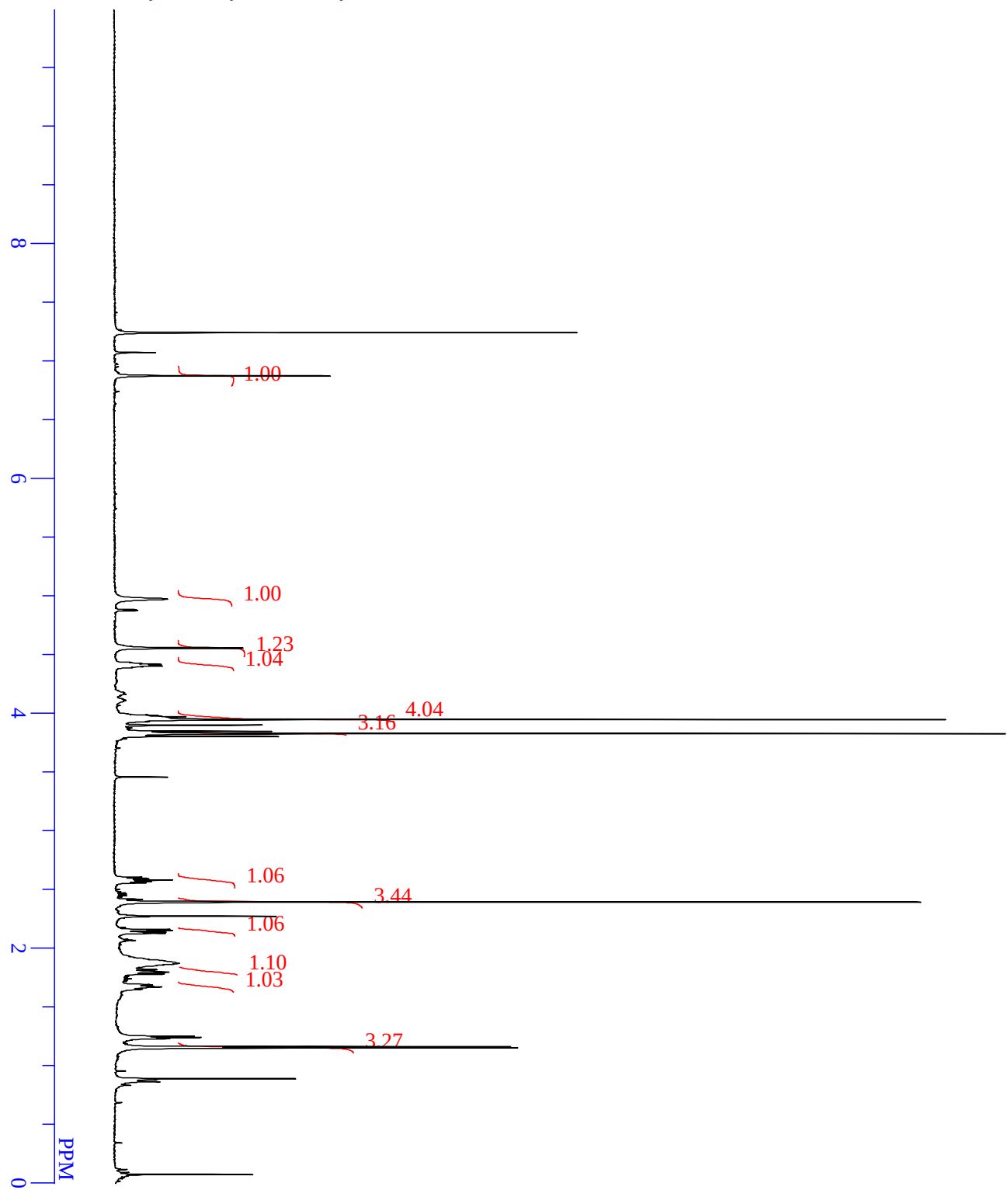




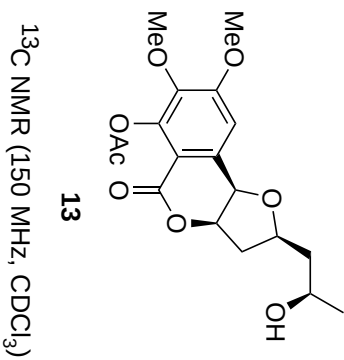
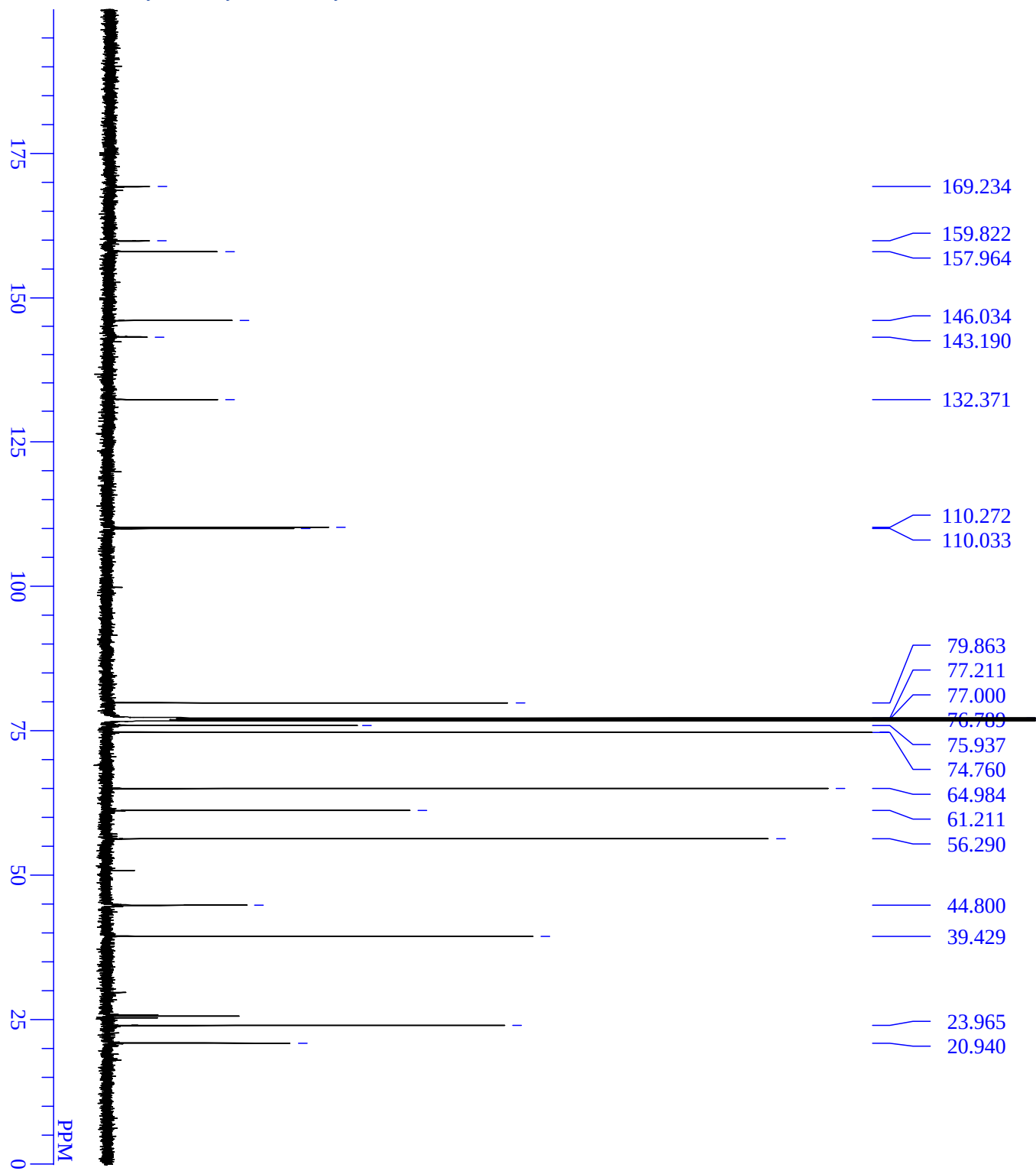


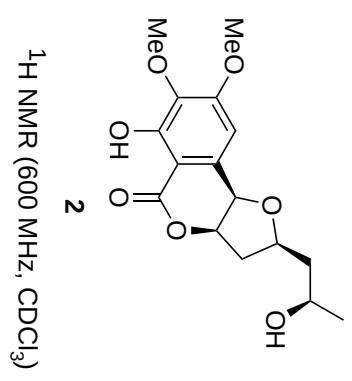
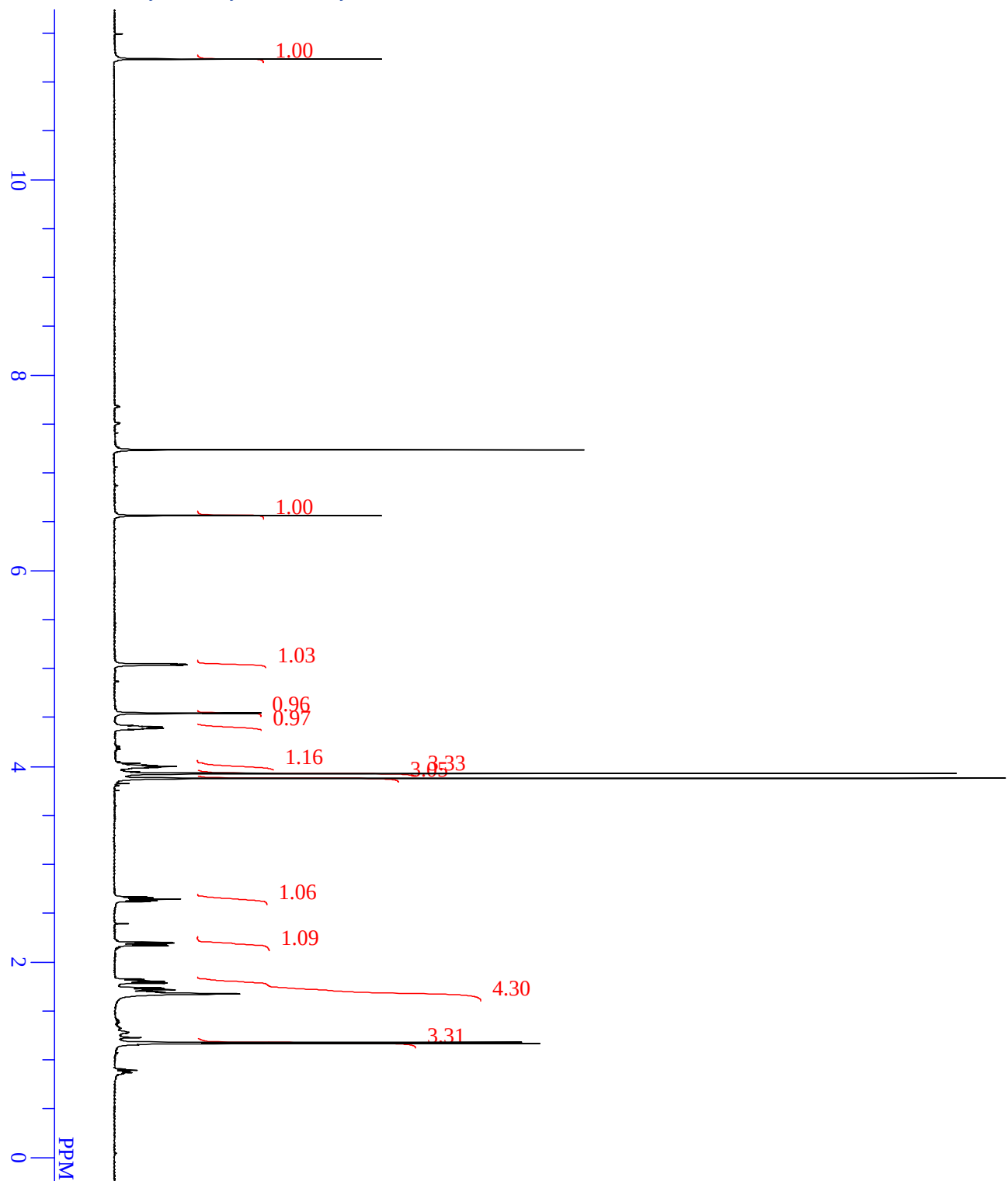


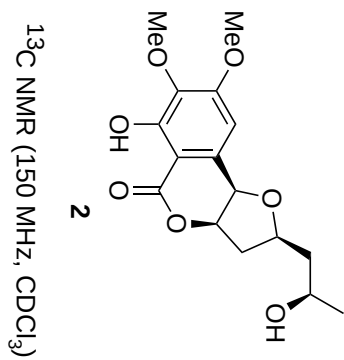
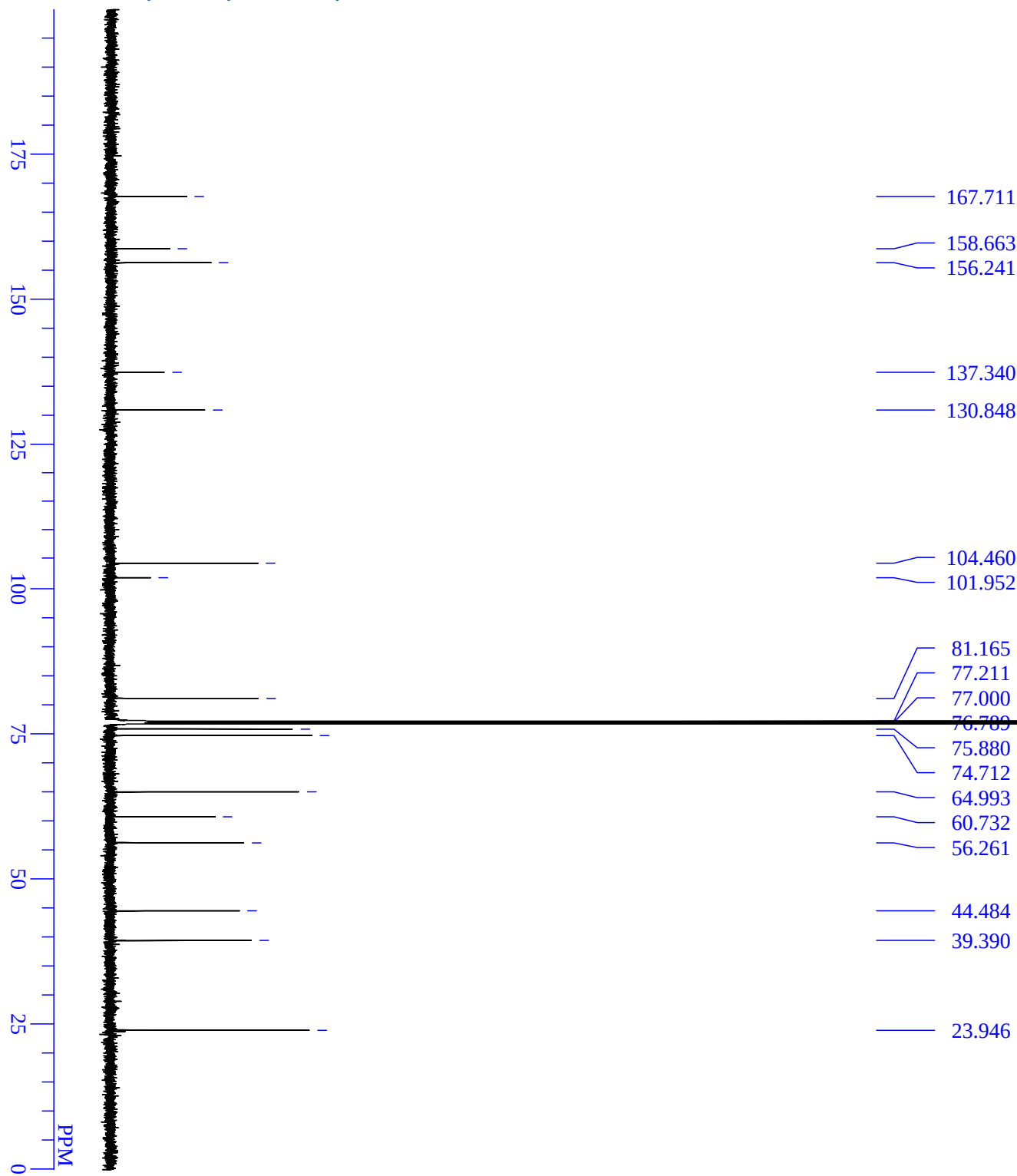


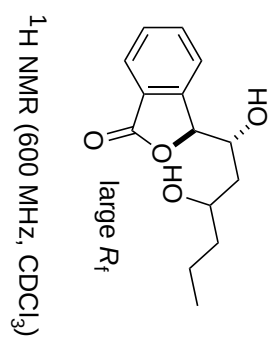
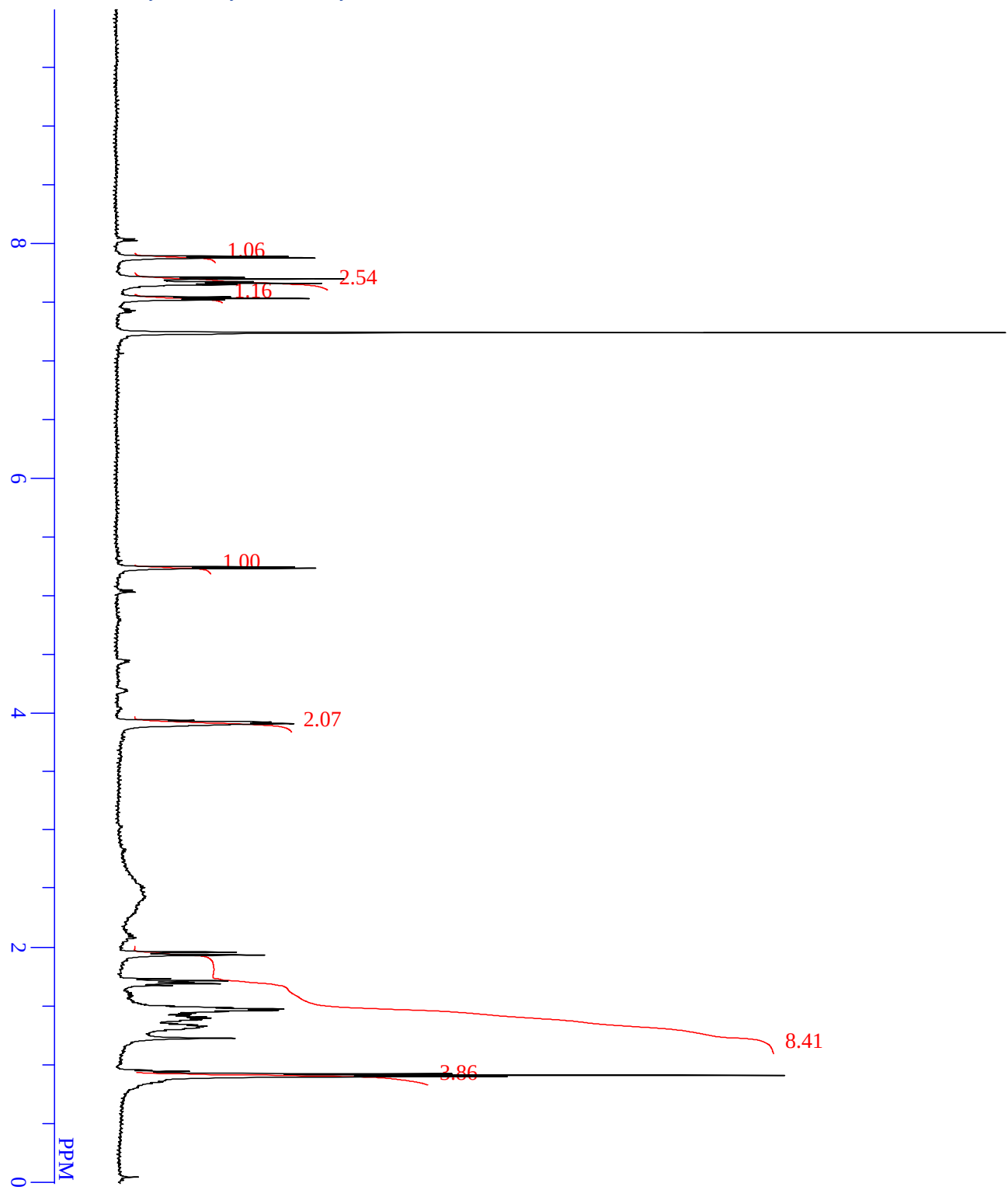


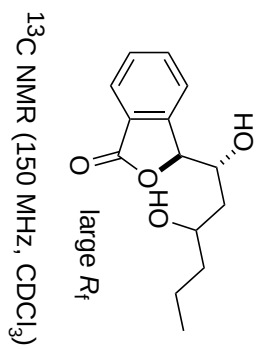
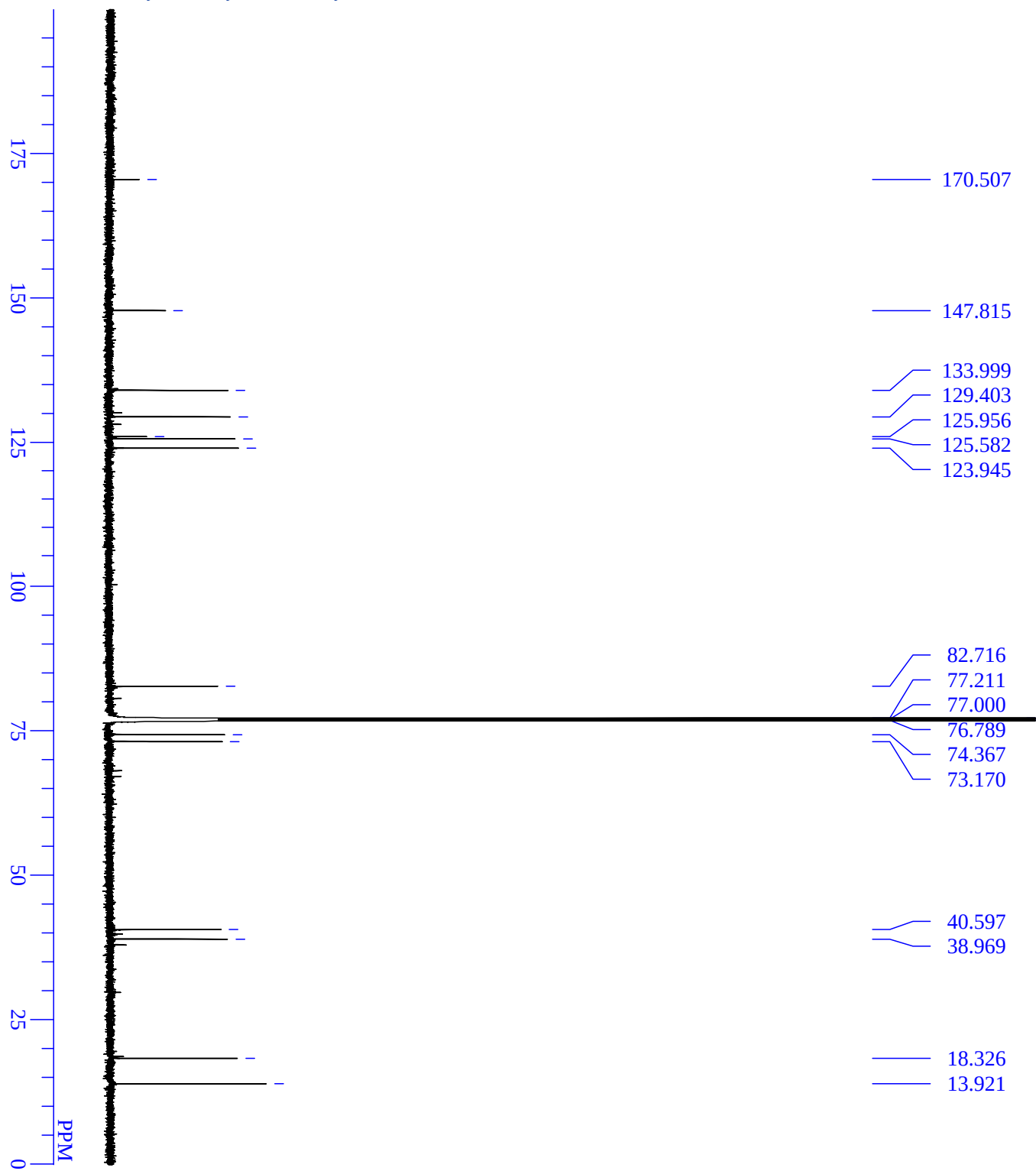
¹H NMR (600 MHz, CDCl₃)

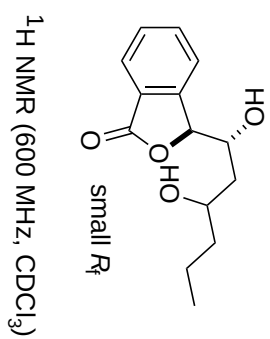
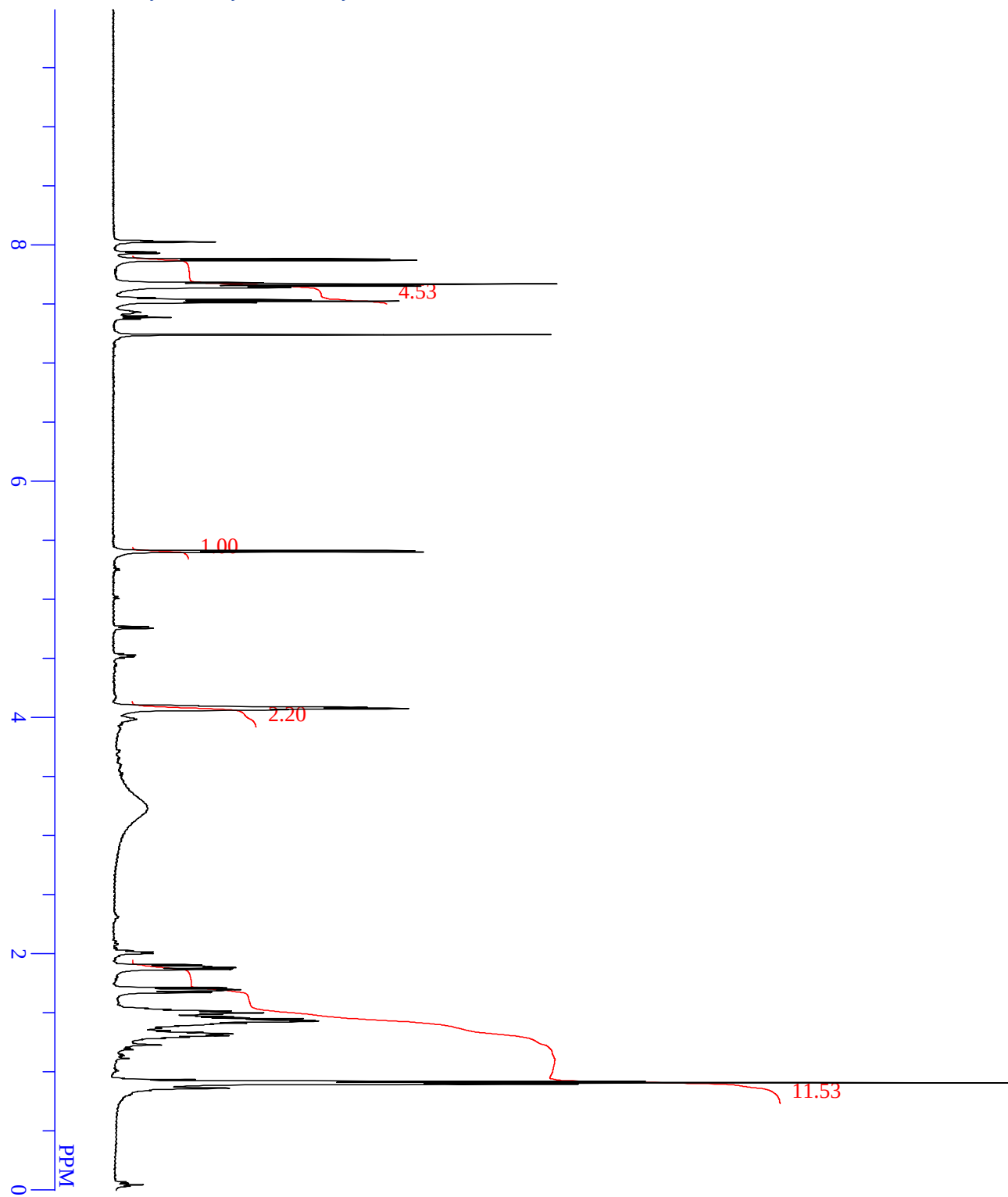


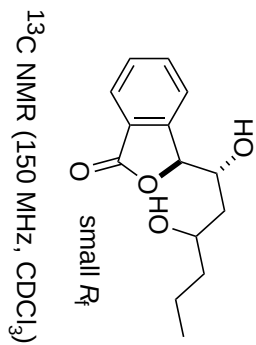
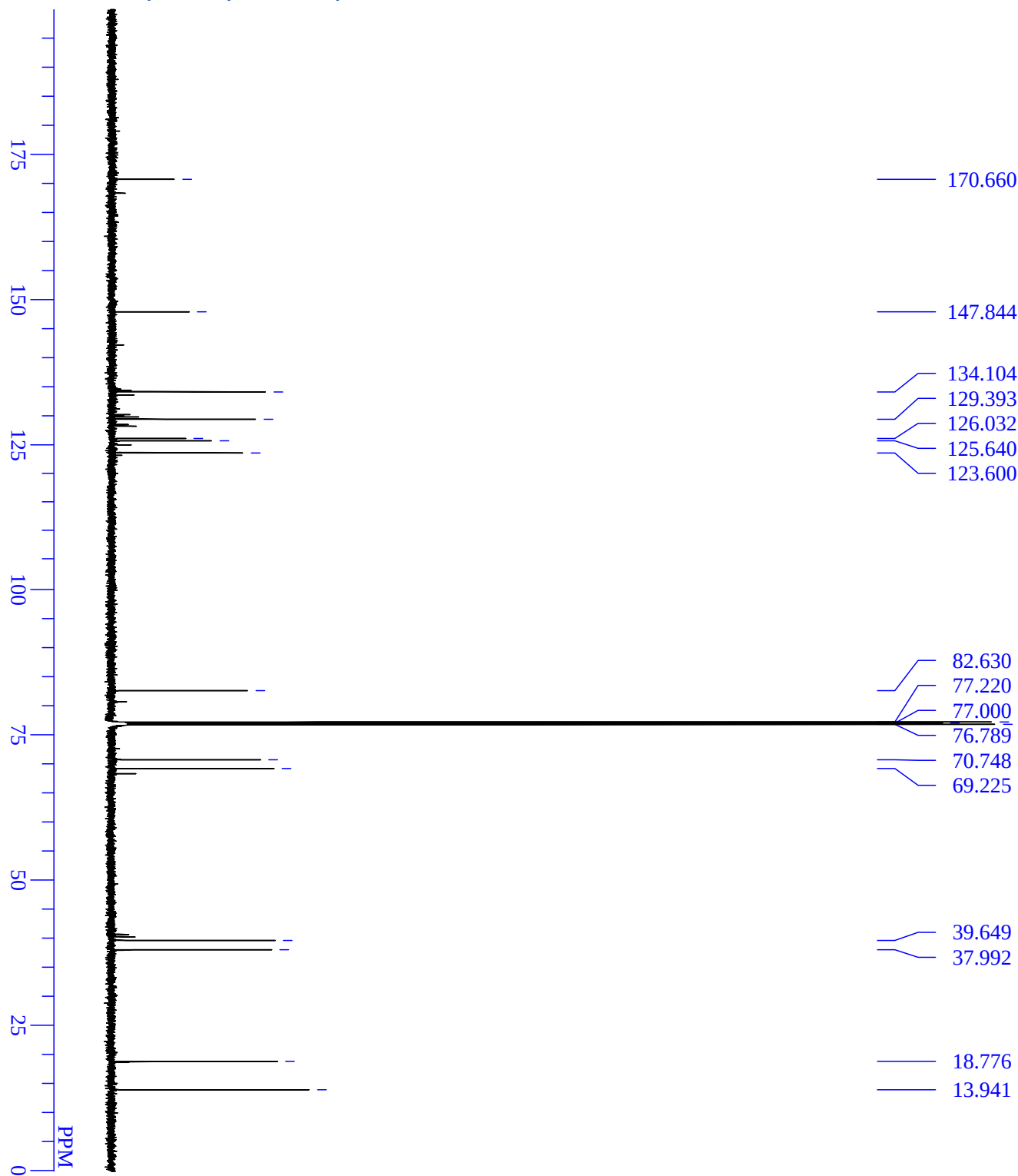


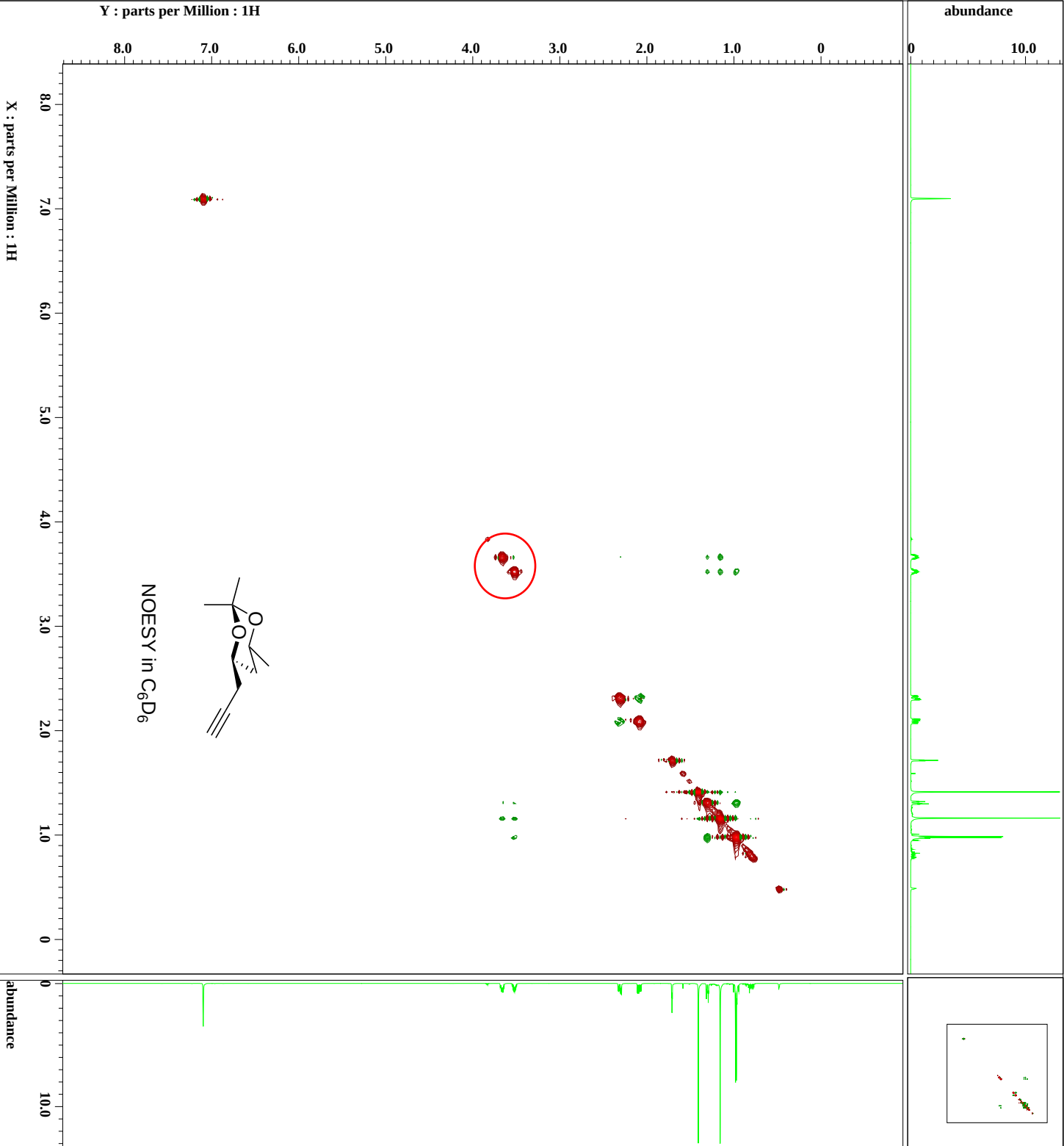






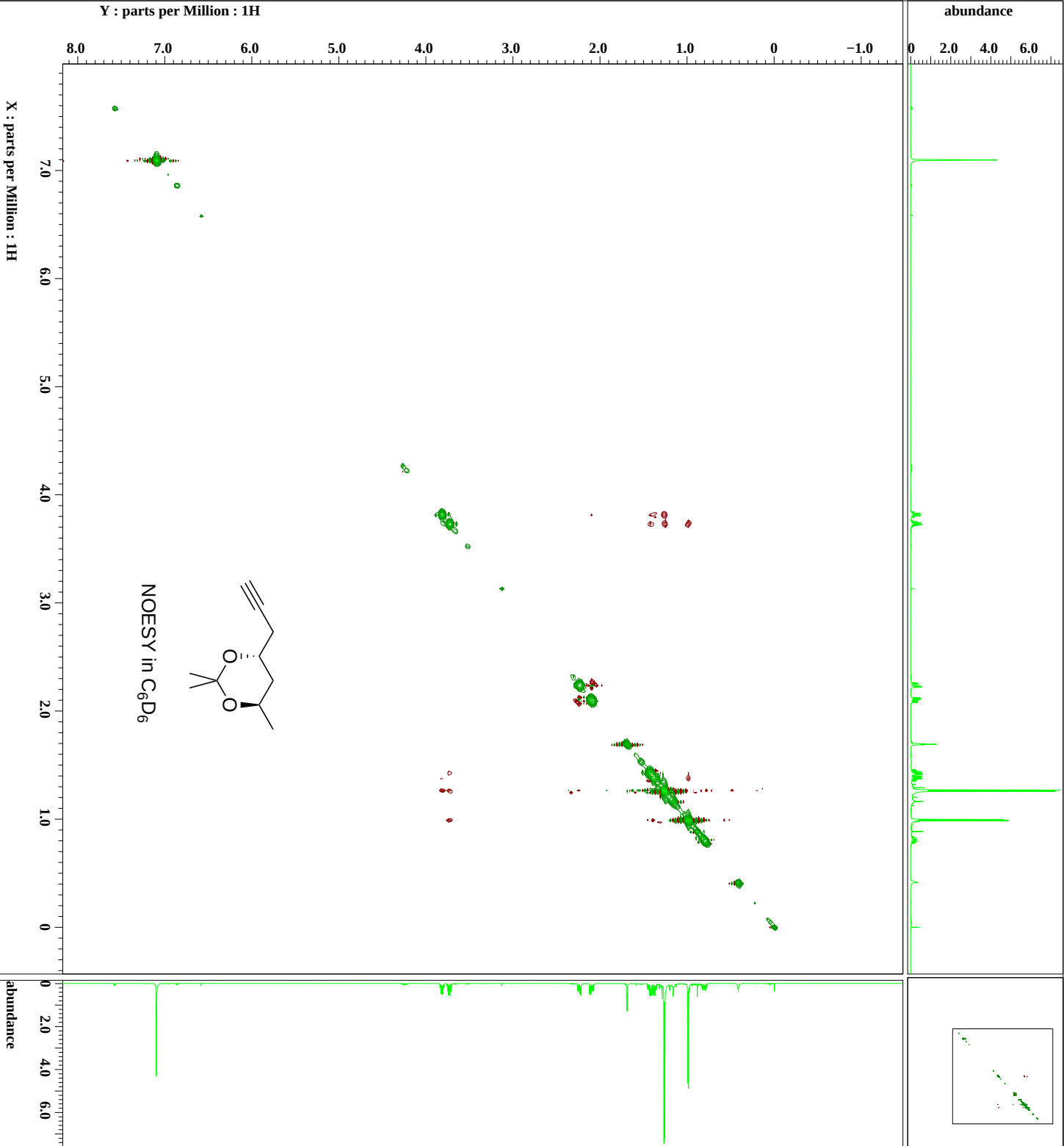




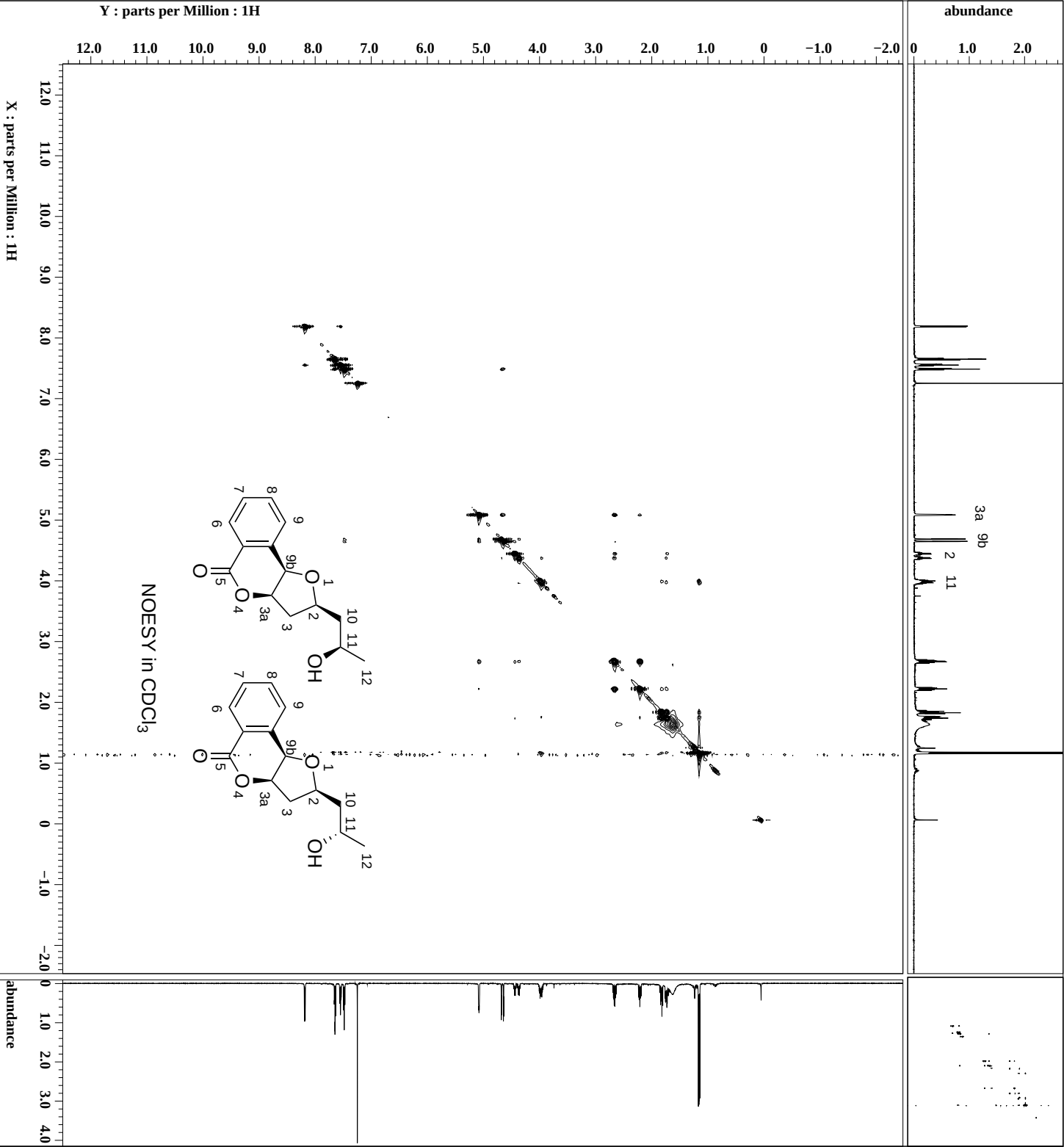


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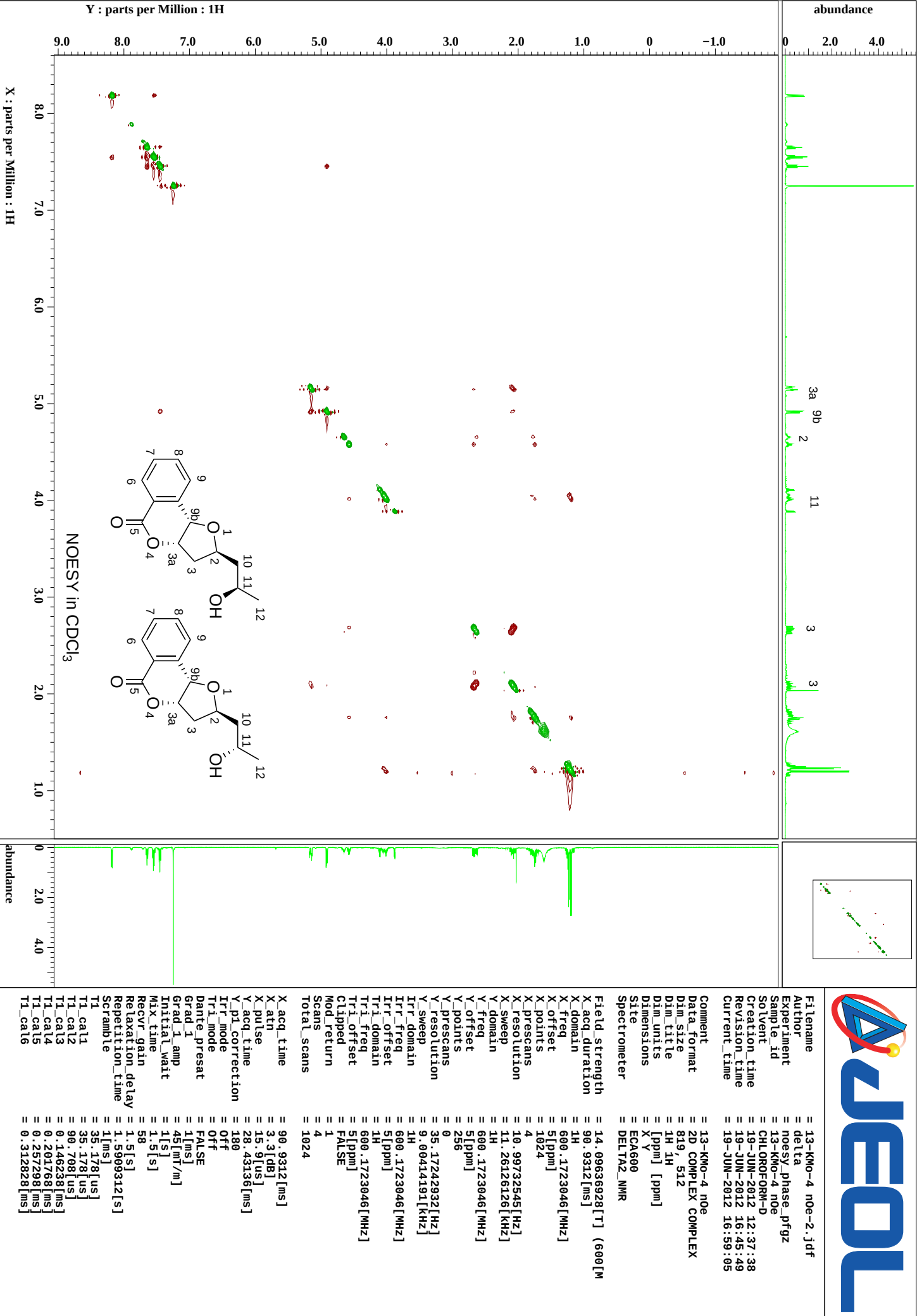


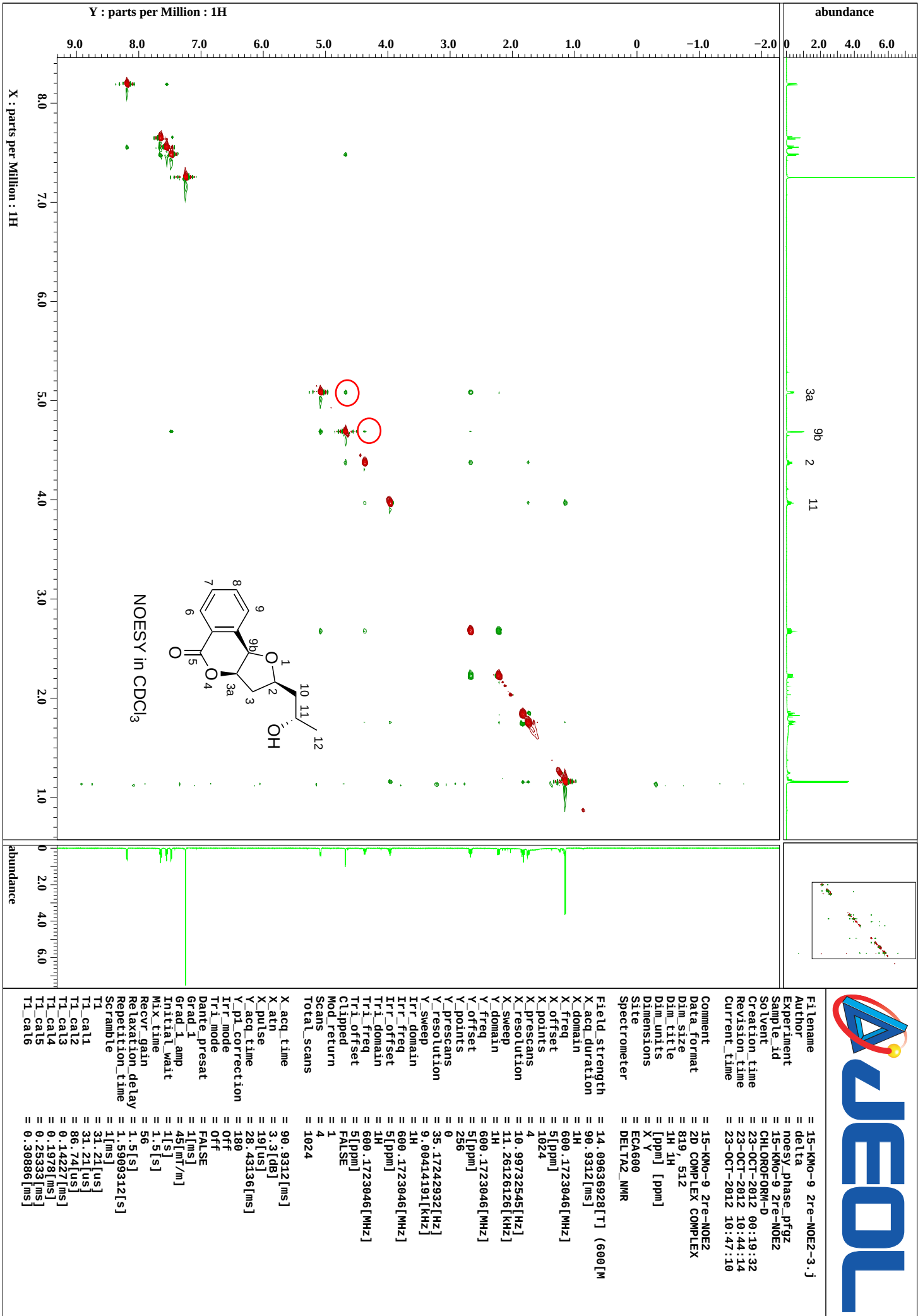
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Experiment	= noesy_phase_pfgz
Sample_id	= 18-MS-9_noesy
Solvent	= BENZENE-D6
Creation_time	= 23-MAY-2013 10:44:16
Revision_time	= 23-MAY-2013 11:51:17
Current_time	= 23-MAY-2013 11:56:57
Comment	= 18-MS-9 noesy
Data_format	= 2D COMPLEX COMPLEX
Dim_size	= 819, 512
Dim_title	= 1H 1H
Dim_units	= [ppm] [ppm]
Dimensions	= X Y
Site	= ECA600
Spectrometer	= DELTA2_NMR
Field_strength	= 14.09636928[T] (600[M
X_acq_duration	= 90.9312[ms]
X_domain	= 1H
X_freq	= 600.1723046[MHz]
X_offset	= 5[ppm]
X_points	= 1024
X_prescans	= 4
X_resolution	= 10.99732545[Hz]
X_sweep	= 11.26126126[kHz]
Y_domain	= 600.1723046[MHz]
Y_freq	= 5[ppm]
Y_offset	= 256
Y_points	= 0
Y_prescans	= 35.17242932[Hz]
Y_resolution	= 9.00414191[kHz]
Y_sweep	= 1H
Irr_domain	= 600.1723046[MHz]
Irr_freq	= 5[ppm]
Irr_offset	= 1H
Tri_domain	= 600.1723046[MHz]
Tri_freq	= 5[ppm]
Tri_offset	= FALSE
Clipped	= 1
Mod_return	= 4
Scans	= 1024
Total_scans	= 90.9312[ms]
X_acq_time	= 3.31[dB]
X_atn	= 12[us]
X_pulse	= 28.45136[ms]
Y_acq_time	= 180
Y_pi_correction	= Off
Irr_mode	= Off
Tri_mode	= FALSE
Dante.preset	= 1[ms]
Grad_1	= 45[mt/m]
Grad_1_amp	= 1[s]
Initial_wait	= 1.7[s]
Mix_time	= 50
Recvr_gain	= 1.5[s]
Relaxation_delay	= 1.5909312[s]
Repetition_time	= 1[ms]
Scramble	= 40.17[us]
T1	= 40.17[us]
T1_cal1	= 95.7[us]
T1_cal2	= 0.15123[ms]
T1_cal3	= 0.20676[ms]
T1_cal4	= 0.26229[ms]
T1_cal5	= 0.31782[ms]

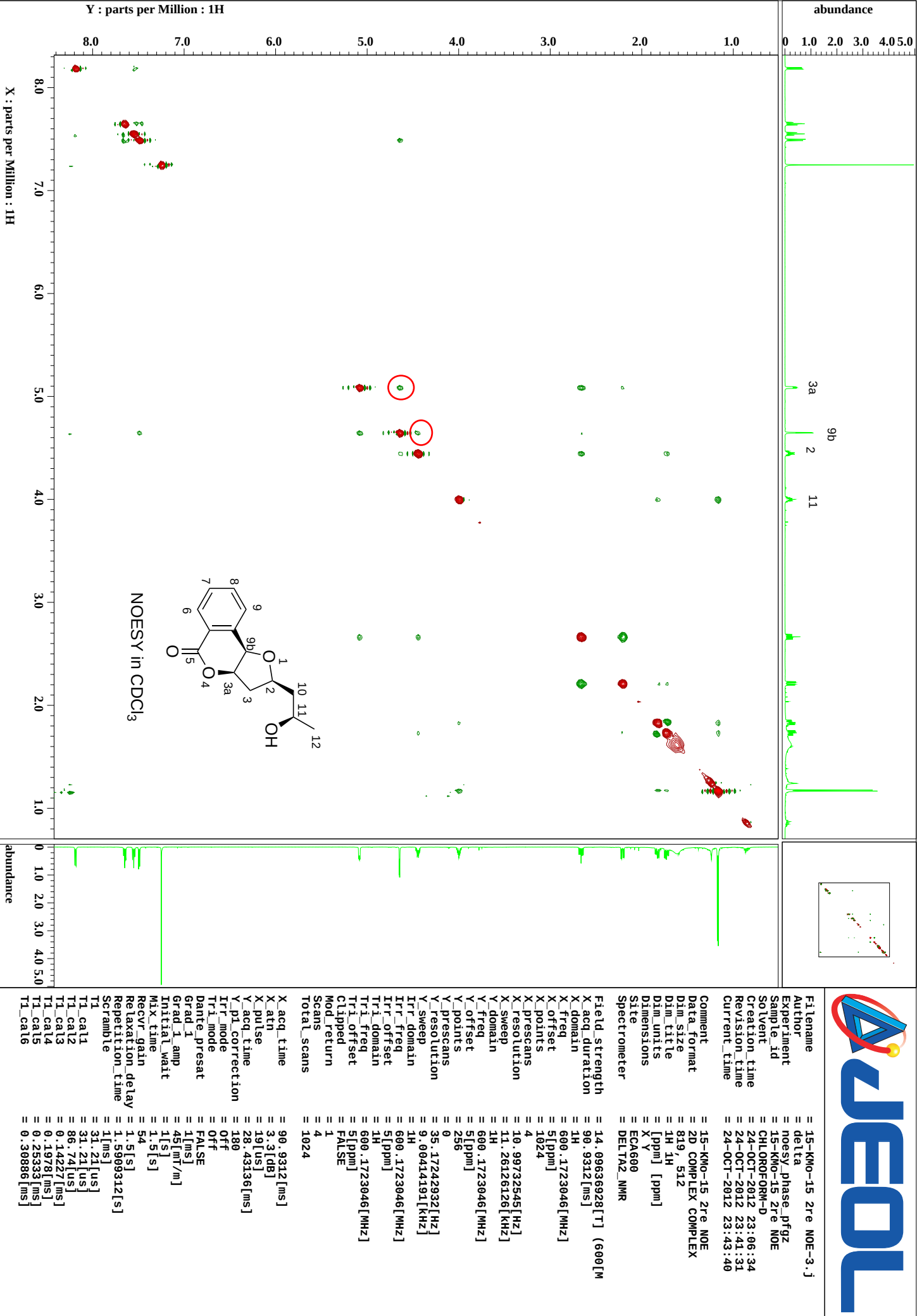


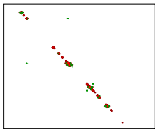
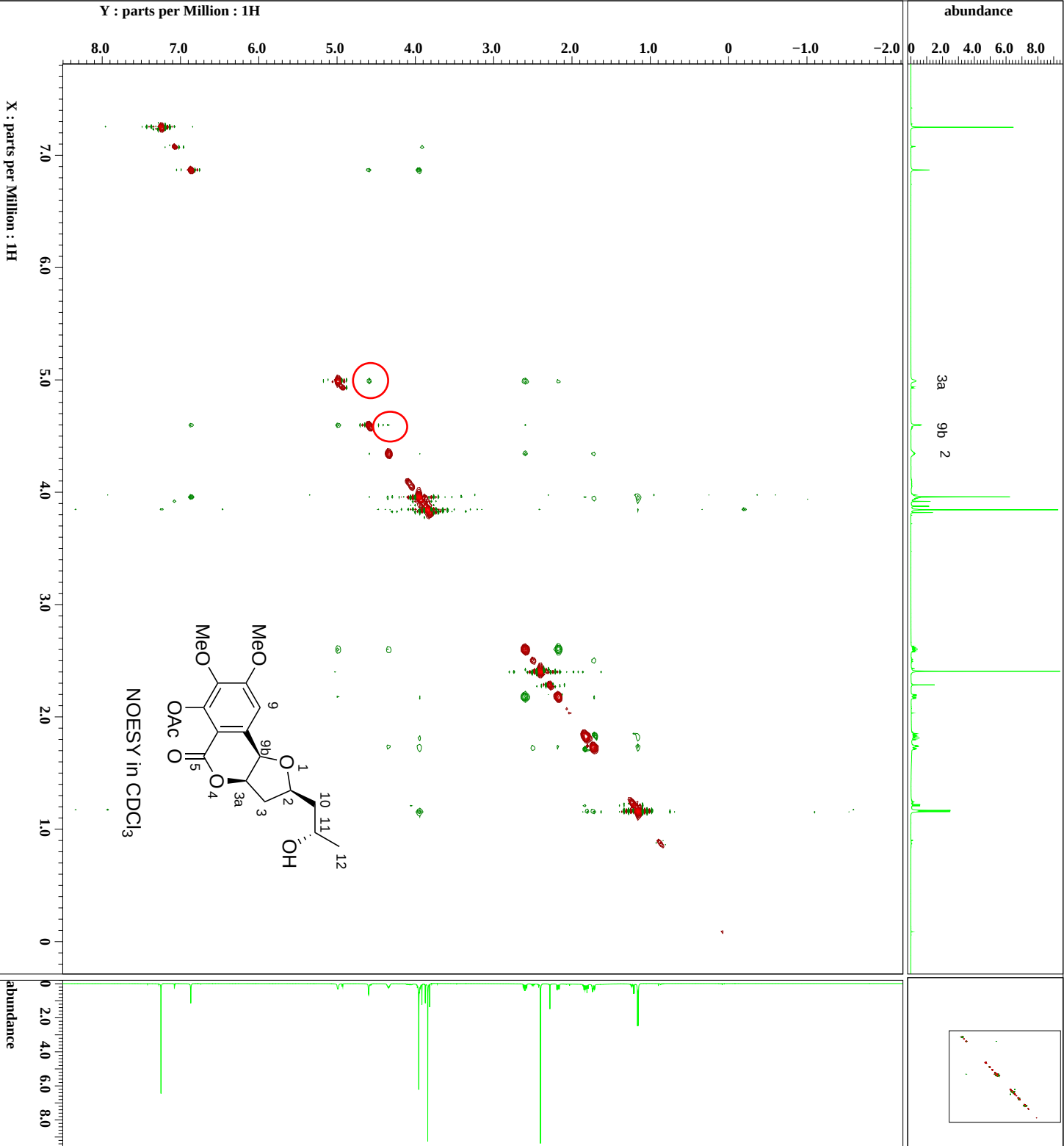
Filename	= 13-KMO-3 noesy-2.jdf
Author	= delta
Experiment	= noesy_phase_pfgz
Sample_id	= 13-KMO-3 noesy
Solvent	= CHLOROFORM-D
Creation_time	= 15-JUN-2012 12:39:43
Revision_time	= 15-JUN-2012 13:13:56
Current_time	= 15-JUN-2012 13:22:40
Comment	= 13-KMO-3 noesy
Data_format	= 2D COMPLEX COMPLEX
Dim_size	= 819, 512
Dim_title	= 1H 1H
Dim_units	= [ppm] [ppm]
Dimensions	= X Y
Site	= ECA600
Spectrometer	= DELTA2_NMR
Field_strength	= 14.09636928[T] (600[M
X_acq_duration	= 90.9312[ms]
X_domain	= 1H
X_freq	= 600.1723046[MHz]
X_offset	= 5[ppm]
X_points	= 1024
X_prescans	= 4
X_resolution	= 10.99732545[Hz]
X_sweep	= 11.26126126[kHz]
Y_domain	= 1H
Y_freq	= 600.1723046[MHz]
Y_offset	= 5[ppm]
Y_points	= 256
Y_prescans	= 0
Y_resolution	= 35.17242932[Hz]
Y_sweep	= 9.00414191[kHz]
Irr_domain	= 1H
Irr_freq	= 600.1723046[MHz]
Irr_offset	= 5[ppm]
Tri_domain	= 1H
Tri_freq	= 600.1723046[MHz]
Tri_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 4
Total_scans	= 1024
X_acq_time	= 90.9312[ms]
X_atn	= 3.3[dB]
X_pulse	= 15.9[us]
Y_acq_time	= 28.45136[ms]
Y_pi_correction	= 180
Irr_mode	= Off
Tri_mode	= Off
Dante_preset	= FALSE
Grad_1	= 1[ms]
Grad_1_amp	= 45[mr/m]
Initial_wait	= 1[s]
Mix_time	= 1.5[s]
Recvr_gain	= 56
Relaxation_delay	= 1.5[s]
Repetition_time	= 1.5909312[s]
Scramble	= 1[ms]
T1	= 35.178[us]
T1_cal1	= 35.178[us]
T1_cal2	= 90.708[us]
T1_cal3	= 0.146238[ms]
T1_cal4	= 0.201766[ms]
T1_cal5	= 0.257298[ms]
T1_cal6	= 0.312828[ms]











Filename	= 16-KMo-2 noesy-3.jdf
Author	= delta
Experiment	= noesy_phase_pfgz
Sample_id	= 16-KMo-2 noesy
Sovent	= CHLOROFORM-D
Creation_time	= 21-NOV-2012 19:28:58
Revision_time	= 21-NOV-2012 20:42:59
Current_time	= 21-NOV-2012 20:57:16
Comment	= 16-KMo-2 noesy
Data_format	= 2D COMPLEX COMPLEX
Dim_size	= 819, 512
Dim_title	= 1H 1H
Dim_units	= [ppm] [ppm]
Dimensions	= X Y
Site	= ECA600
Spectrometer	= DELTA2_NMR
Field_strength	= 14.09636928[T] (600[M
X_acq_duration	= 90.9312[ms]
X_domain	= 1H
X_freq	= 600.1723046[MHz]
X_offset	= 5[ppm]
X_points	= 1024
X_prescans	= 4
X_resolution	= 10.99732545[Hz]
X_sweep	= 11.26126126[kHz]
Y_domain	= 600.1723046[MHz]
Y_freq	= 600.1723046[MHz]
Y_offset	= 5[ppm]
Y_points	= 256
Y_prescans	= 0
Y_resolution	= 35.17242932[Hz]
Y_sweep	= 9.00414191[kHz]
Irr_domain	= 1H
Irr_freq	= 600.1723046[MHz]
Irr_offset	= 5[ppm]
Tri_domain	= 1H
Tri_freq	= 600.1723046[MHz]
Tri_offset	= 5[ppm]
Clipped	= TRUE
Mod_return	= 1
Scans	= 4
Total_scans	= 1024
X_acq_time	= 90.9312[ms]
X_atn	= 3.3[dB]
X_pulse	= 19[us]
Y_acq_time	= 28.43136[ms]
Y_pi_correction	= 180
Irr_mode	= Off
Tri_mode	= Off
Dante.preset	= FALSE
Grad_1	= 1[ms]
Grad_1_amp	= 45[mT/m]
Initial_wait	= 1[s]
Mix_time	= 0.5[s]
Recvr_gain	= 58
Relaxation_delay	= 1.5[s]
Repetition_time	= 1.5909312[s]
Scramble	= 1[ms]
T1	= 31.21[us]
T1_cal1	= 31.21[us]
T1_cal2	= 86.74[us]
T1_cal3	= 0.14227[ms]
T1_cal4	= 0.1978[ms]
T1_cal5	= 0.2533[ms]
T1_cal6	= 0.30886[ms]

