Supporting Information for

Total Synthesis and Stereochemical Revision of Relgro and 10′-Oxorelgro

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Table 2. ^{1}H chemical shifts* and coupling constants ($J_{H\text{-}H}$) for Natural product, Synthetic compounds 1, 1b, 2, and 2a (400 MHz) in $CDCl_3$

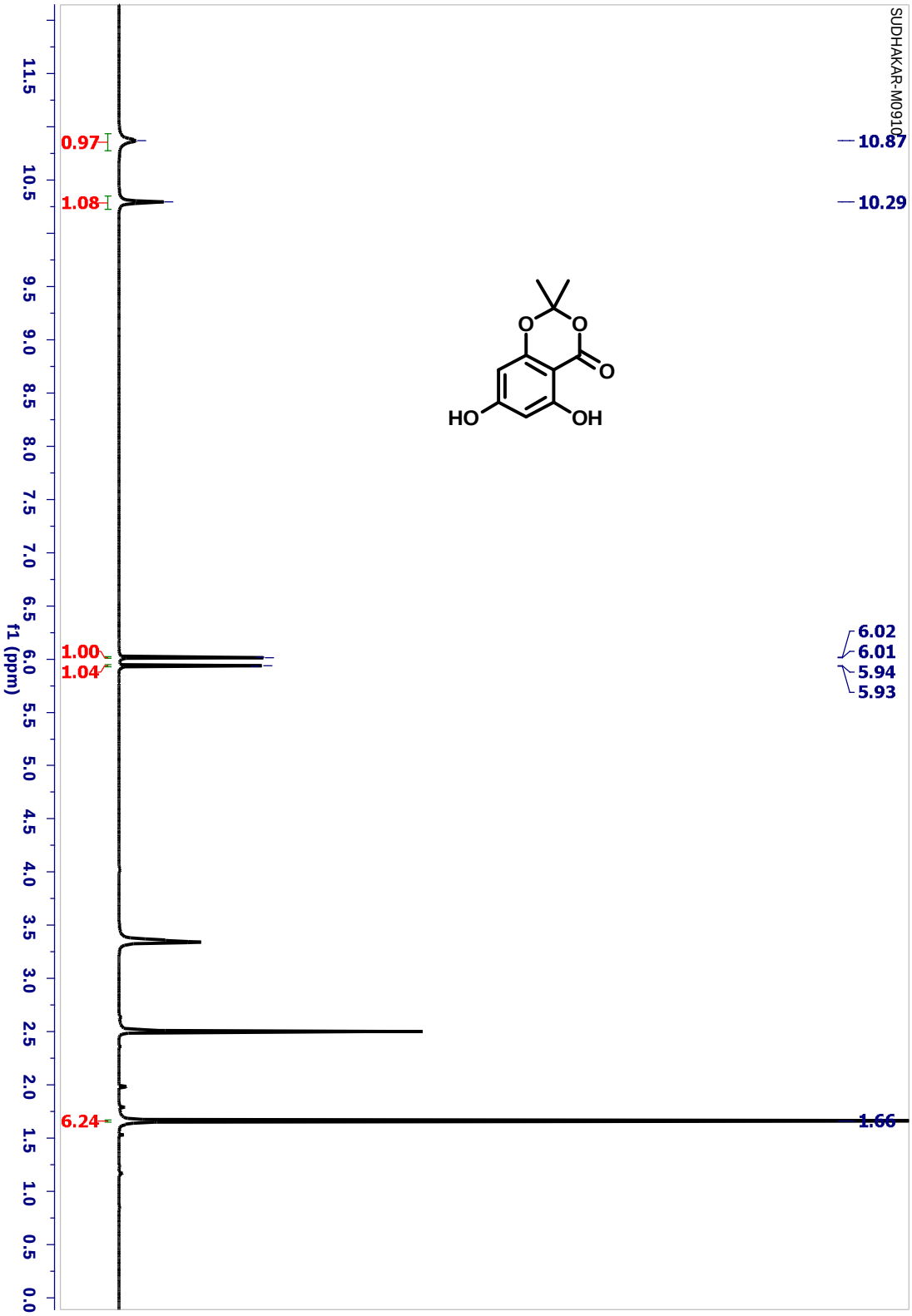
Position	10′-Oxorelgro Natural product	10′-Oxorelgro Proposed (2)	10′-Oxorelgro Revised (2a)	(6′*R*,10′*S*)-Relgro Proposed (1)	(6′*S*,10′*S*)-Relgro Revised (1b)
2 -OH	11.50, s	11.47, s	11.46, s	11.52, s	11.50, s
3	6.27 (d, *J* =2.5)	6.27 (d, *J* =2.7)	6.26 (d , *J* = 2.7)	6.26 (d, *J* = 2.5)	6.26 (d, *J* = 2.5)
4 -OH	5.42, br s	5.58, br s	5.36, br s	6.39, br s	5.87, br s
5	6.23 (d, *J* =2.5)	6.23 (d, *J* =2.7)	6.22 (d , *J* = 2.7)	6.22 (d, *J* = 2.5)	6.22 (d, *J* = 2.5)
1′-Ha 1′-Hb	3.41 (t, *J* = 12.5) 2.27 (dt, *J* = 12.5, 9.0)	3.40 (dt, *J* = 2.6, 9.6) 2.26 (ddd, *J* = 8.6, 9.6, 12.8)	3.41 (dt, *J* = 2.6, 9.5) 2.26 (ddd, *J* = 8.5, 9.5, 12.9)	3.40 (ddd, *J* = 2.4, 9.8, 12.5) 2.25 (dt, *J*= 9.0, 12.7)	3.41 (ddd, *J*= 2.6, 9.6, 12.5) 2.25 (dt, *J*= 8.6, 12.5)
2′- Ha 2′- Hb	1.33-1.45, m	1.33-1.45, m	1.32-1.43, m	1.33-1.44, m	1.35-1.46, m
3′-Ha 3′-Hb	1.47-1.58, m 1.38-1.43, m	1.52, m 1.40, m	1.53, m 1.40, m	1.52, m 1.40, m	1.52, m 1.40, m
4′-Ha 4′-Hb	1.73-1.83, m 1.66-1.70, m	1.77, m 1.70, m	1.77, m 1.70, m	1.80, m 1.67, m	1.80, m 1.67, m
5′-Ha 5′-Hb	1.75-1.81, m 1.66-1.72, m	1.80, m 1.66, m	1.79, m 1.66, m	1.74, m	1.73, m
6′	5.25-5.28, m	5.25, m	5.25, m	5.26, m	5.26, m
7′-Ha 7′-Hb	1.81-1.84, m 1.60-1.68, m	1.81, m 1.62, m	1.81, m 1.62, m	1.84, m 1.58, m	1.84, m 1.58, m
8′-Ha 8′-Hb	1.58-1.65, m 0.81-0.85, m	1.63, m 0.84, m	1.63, m 0.83, m	1.47, m 1.39, m	1.47, m 1.39, m
9′	2.45-2.54, m	2.50, m	2.50, m	1.50, m	1.50, m
10′	-	-	-	3.84, m	3.82, m
11′	2.14, s	2.14, s	2.14, s	1.20 (d , *J* =6.1)	1.20 (d , *J* =6.2)

Multiplicities: s = singlet, br s = broad singlet, d = doublet, dd = doublet of a doublet, ddd = doublet of doublets of doublets, dt = doublet of triplets, t = triplet, m = multiplet. *The chemical shifts are in δ values (ppm) with reference to TMS. #couplings have been obtained with the help of extensive decoupling experiments.

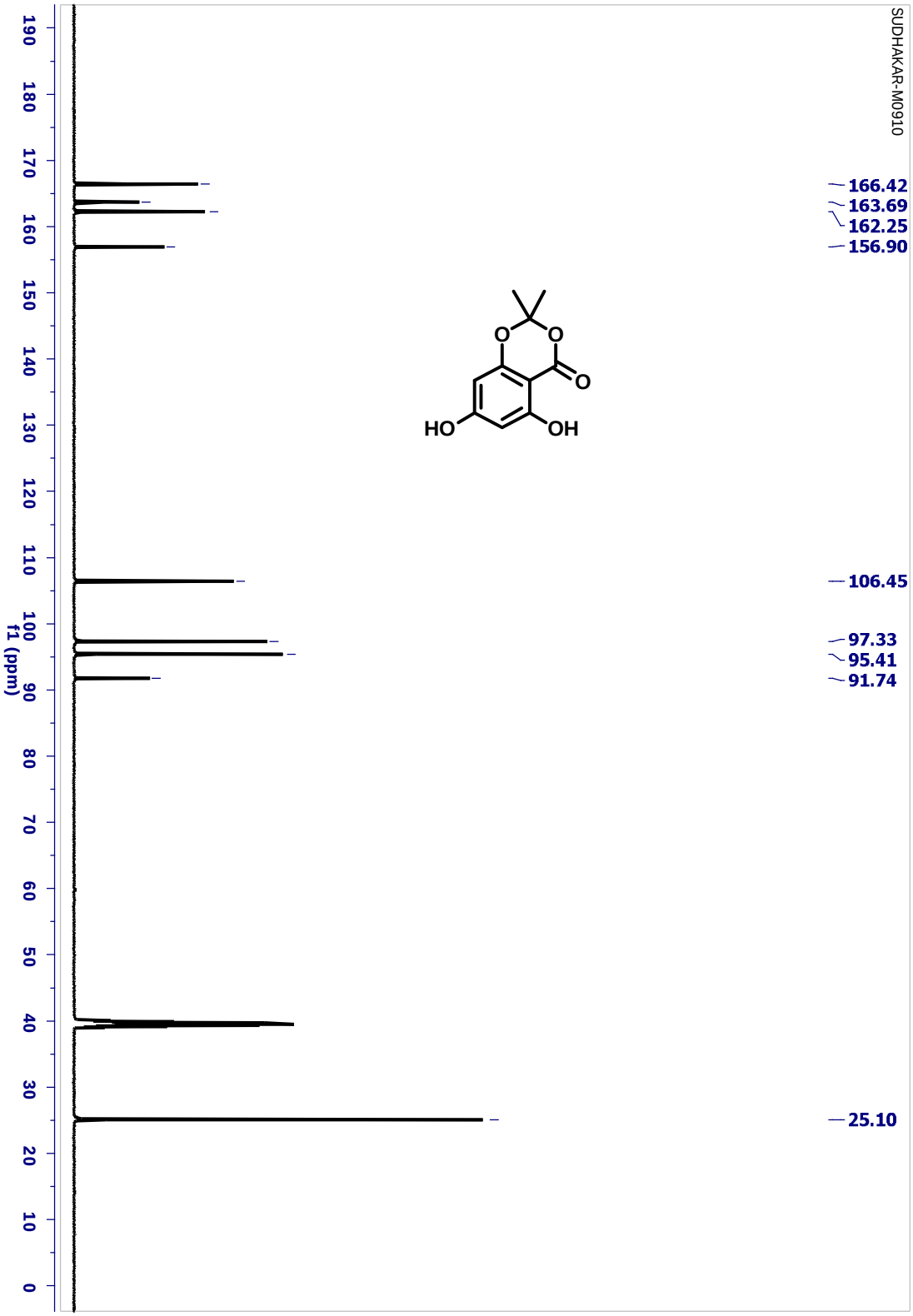
Table 3. ^{13}C chemical shifts* for Natural product, Synthetic compounds 1, 1b, 2, and 2a (400 MHz) in $CDCl_3$

Position	10′-Oxorelgro Natural product	10′-Oxorelgro Proposed (2)	10′-Oxorelgro Revised (2a)	(6′*R*,10′*S*)-Relgro Proposed (1)	(6′S,10′*S*)-Relgro Revised (1b)
1	105.8	105.8	105.8	105.4	105.5
2	165.6	165.5	165.6	165.2	165.3
3	101.6	101.6	101.6	101.3	101.3
4	160.4	160.6	160.5	160.7	160.5
5	111.0	111.1	111.1	111.0	111.0
6	149.9	149.9	149.9	149.6	149.7
1′	34.8	34.7	34.7	34.5	34.5
2′	29.5	29.4	29.4	29.2	29.2
3′	27.8	27.8	27.8	27.6	27.6
4′	19.4	19.3	19.3	19.0	19.0
5′	30.5	30.5	30.5	30.3	30.3
6′′	74.9	74.9	74.9	75.0	75.1
7′	33.2	33.2	33.2	33.6	33.6
8′	20.0	20.0	20.0	21.8	21.9
9′	43.3	43.3	43.3	38.8	38.9
10′	208.5	209.0	208.8	68.2	68.1
11′	30.1	30.2	30.2	23.4	23.5
12′	171.1	171.1	171.1	171.0	171.0

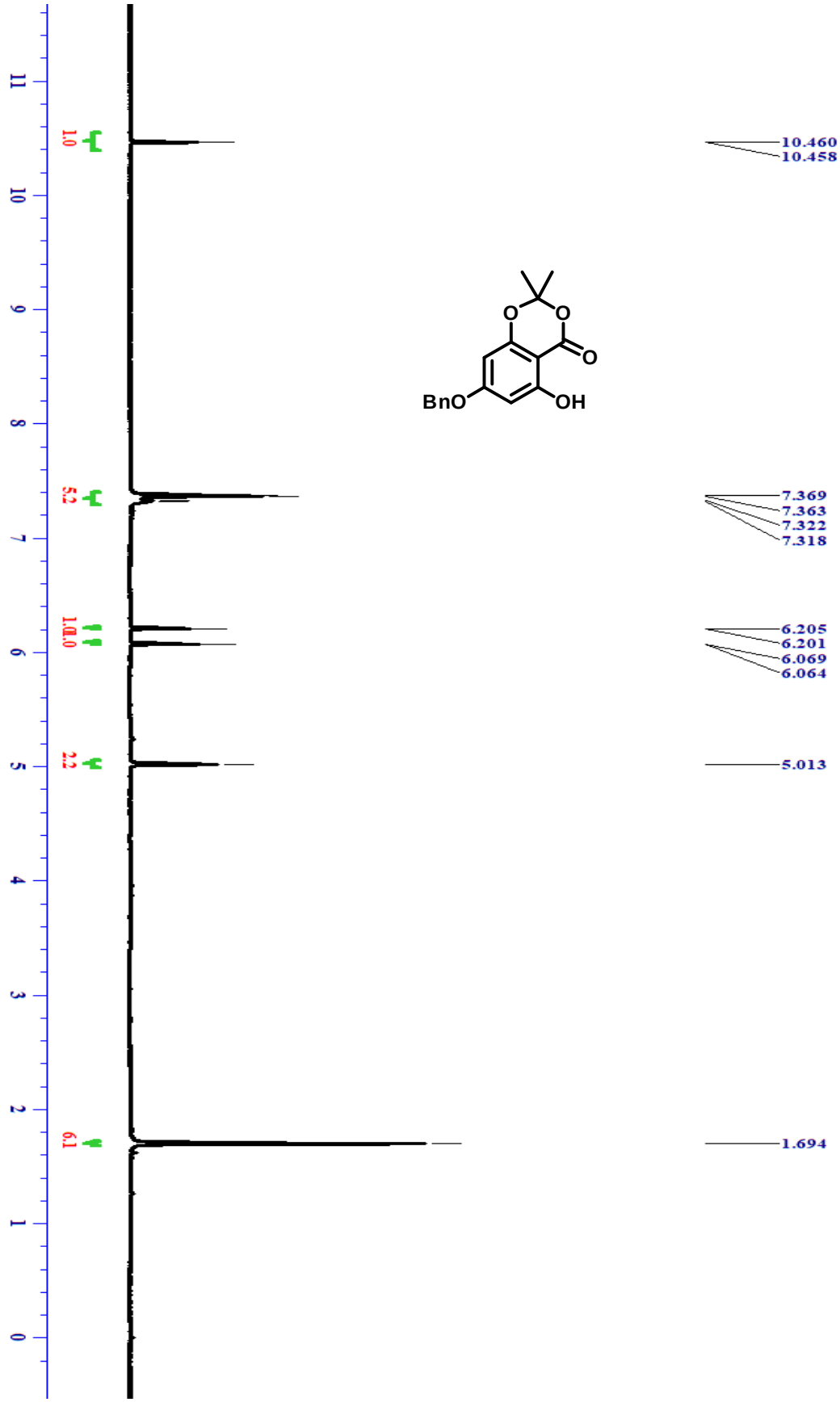
*The chemical shifts are in δ values (ppm)



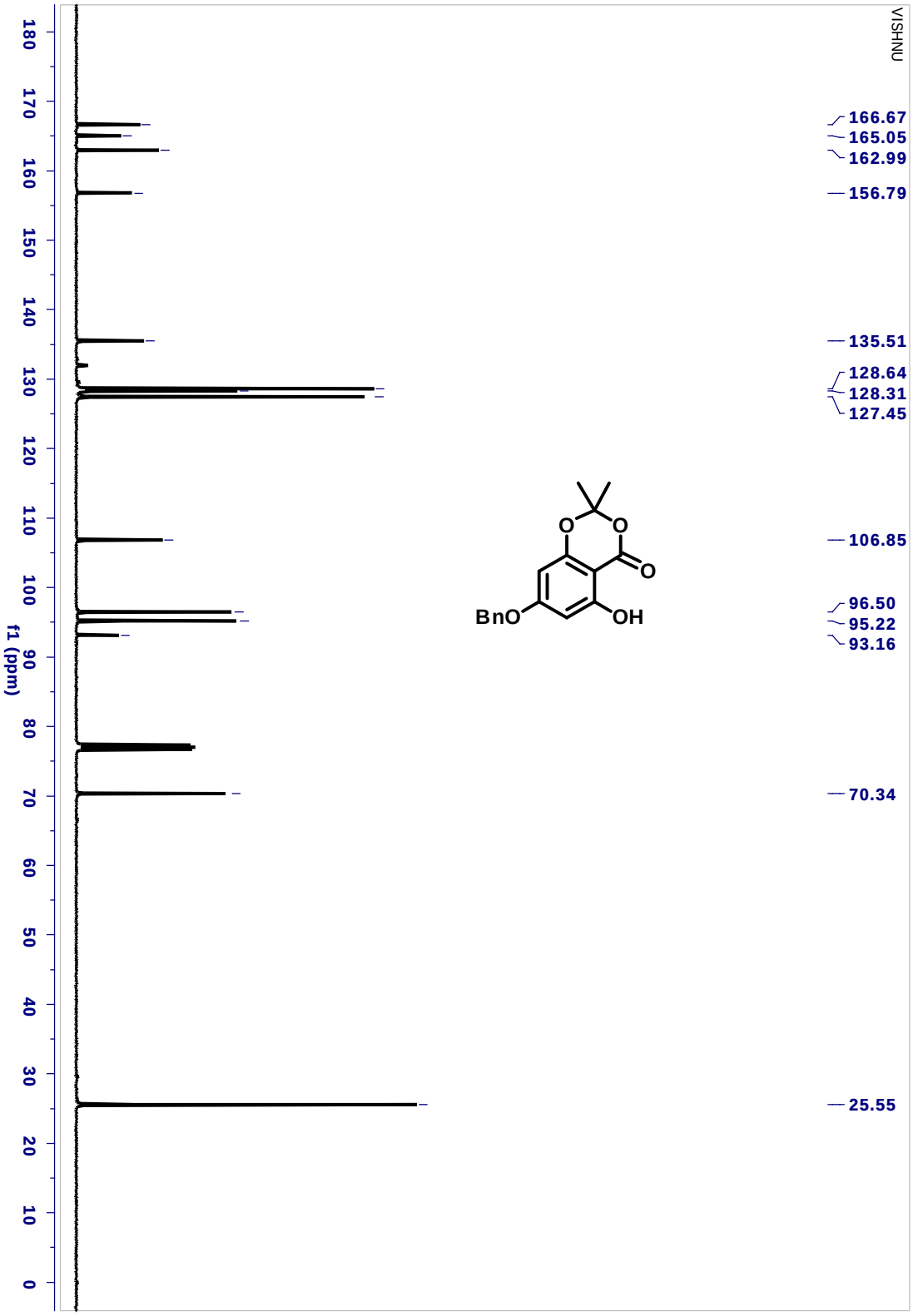
^{1}H NMR spectrum of 9 (500 MHz, DMSO-d_6)



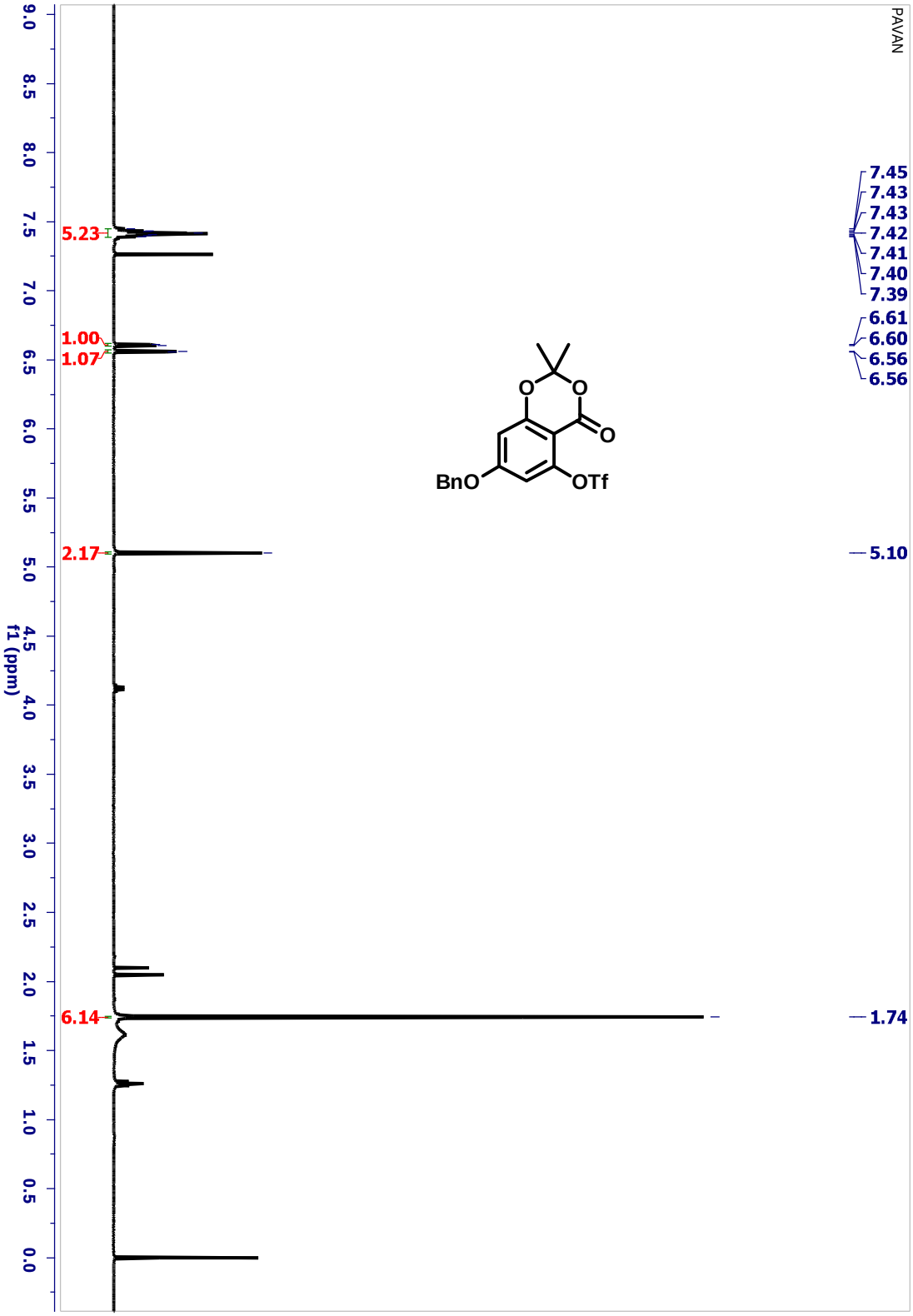
^{13}C NMR spectrum of 9 (125 MHz, DMSO-d_6)



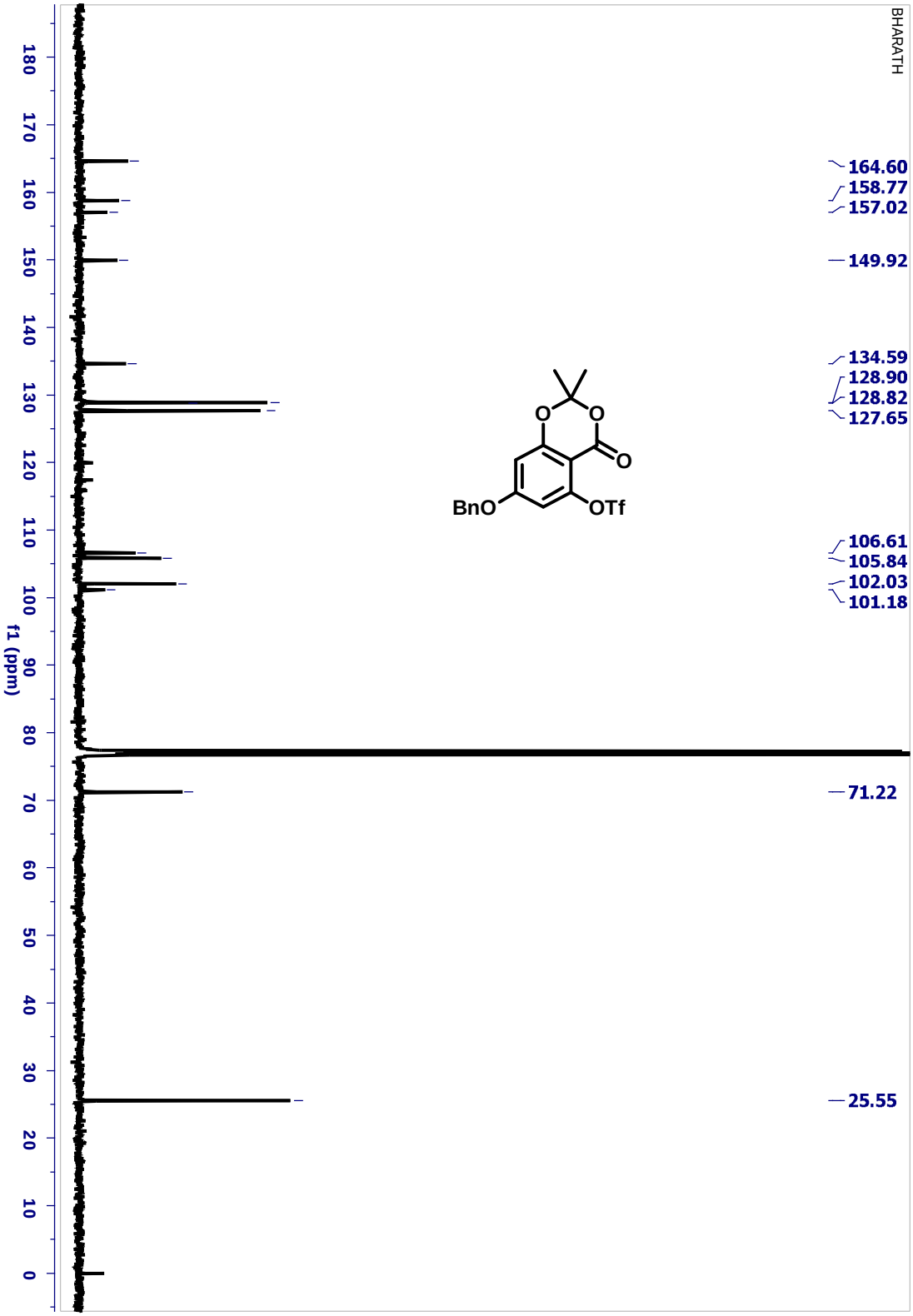
^{1}H NMR spectrum of 10 (300 MHz, $CDCl_3$)



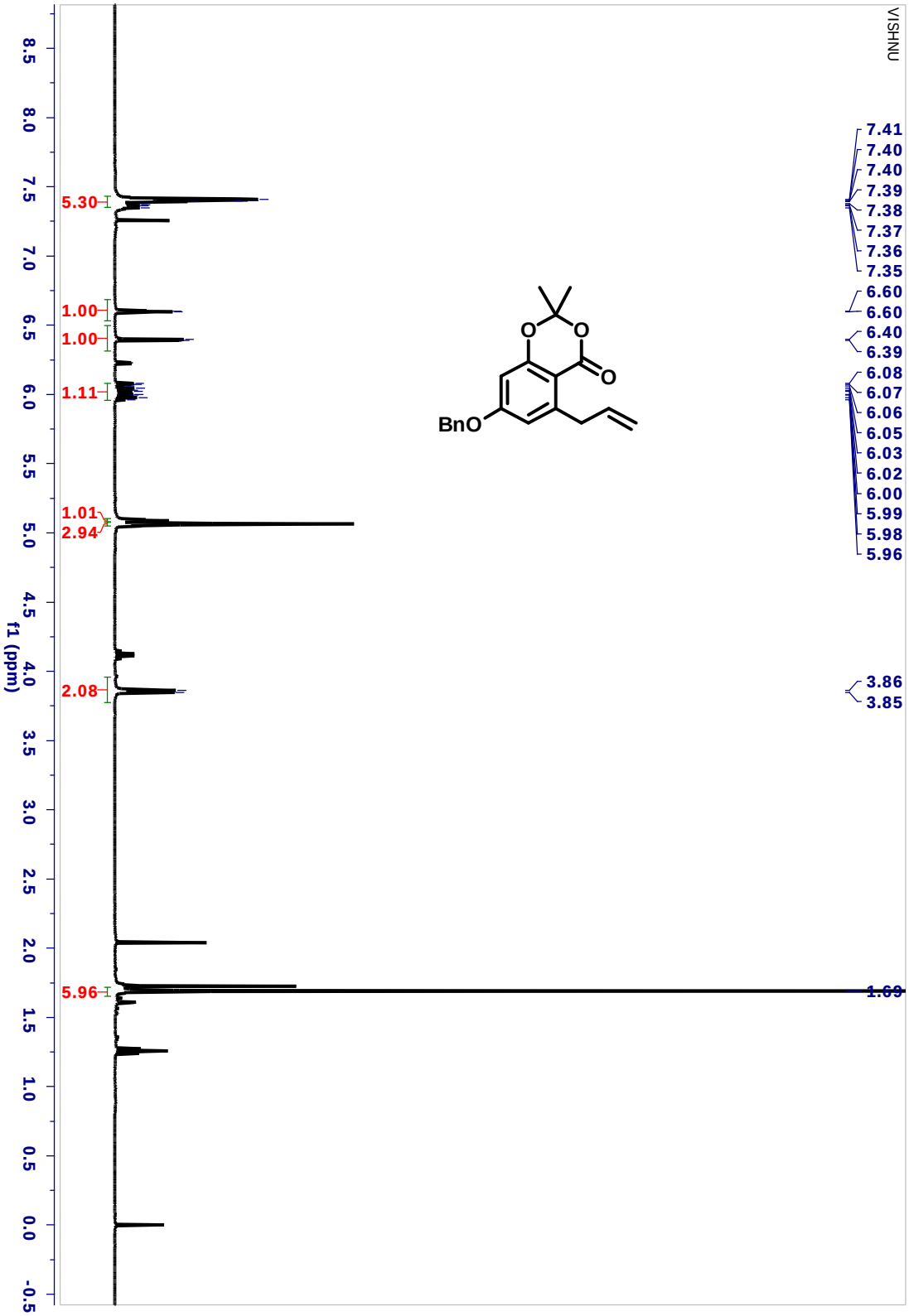
^{13}C NMR spectrum of 10 (125 MHz, $CDCl_3$)



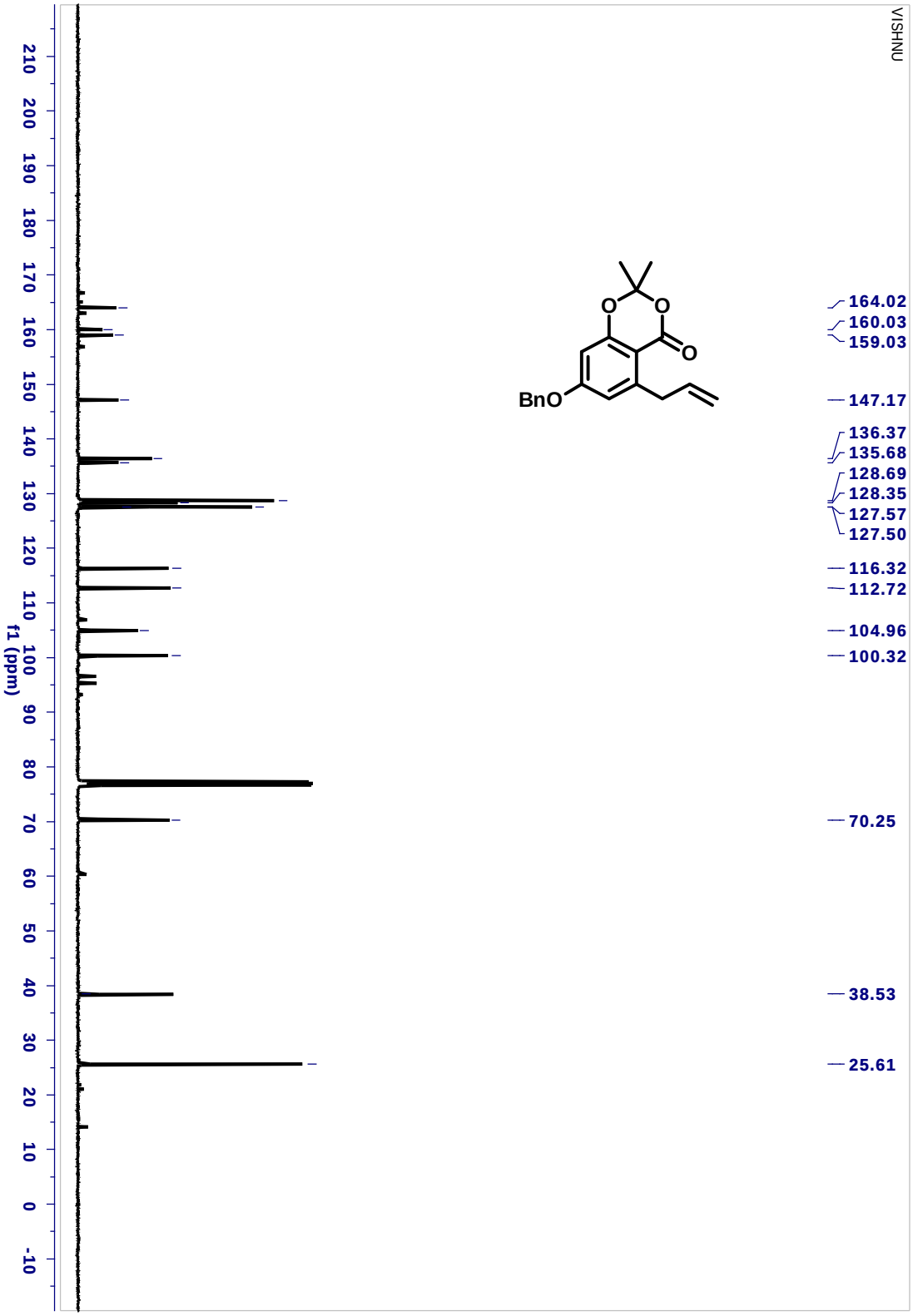
^{1}H NMR spectrum of 11 (300 MHz, $CDCl_3$)



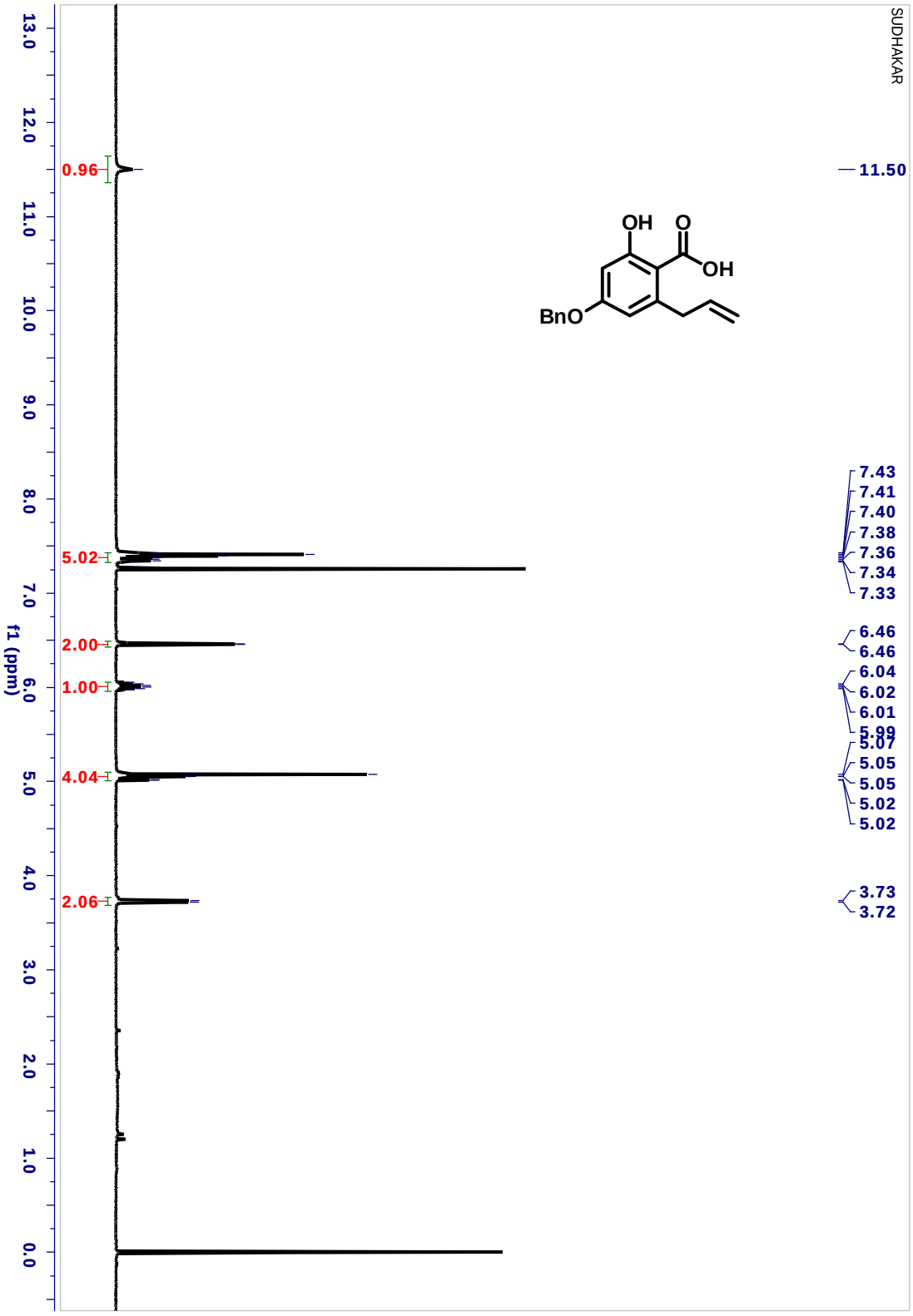
^{13}C NMR spectrum of 11 (125 MHz, $CDCl_3$)



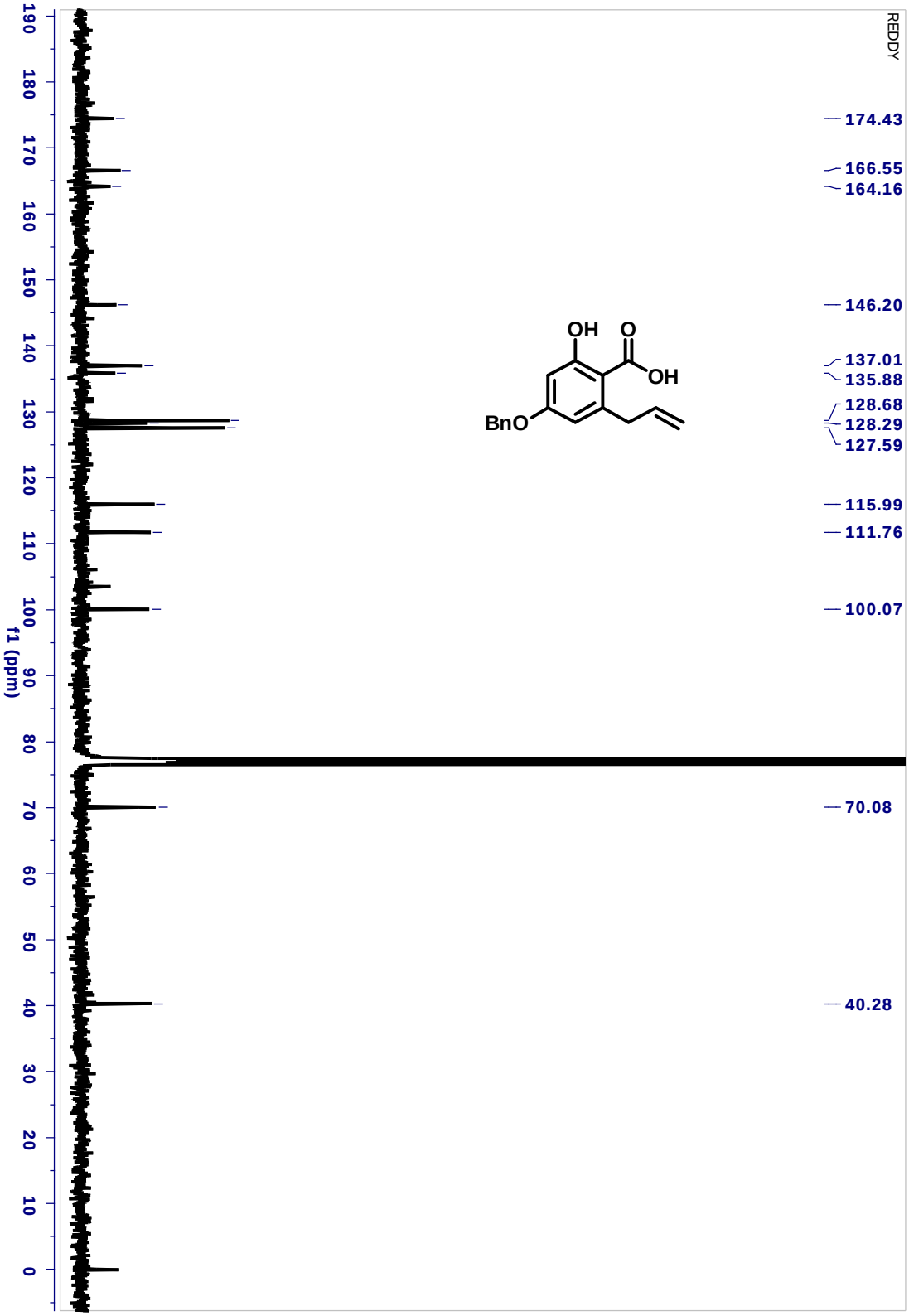
^{1}H NMR spectrum of 12 (400 MHz, $CDCl_3$)



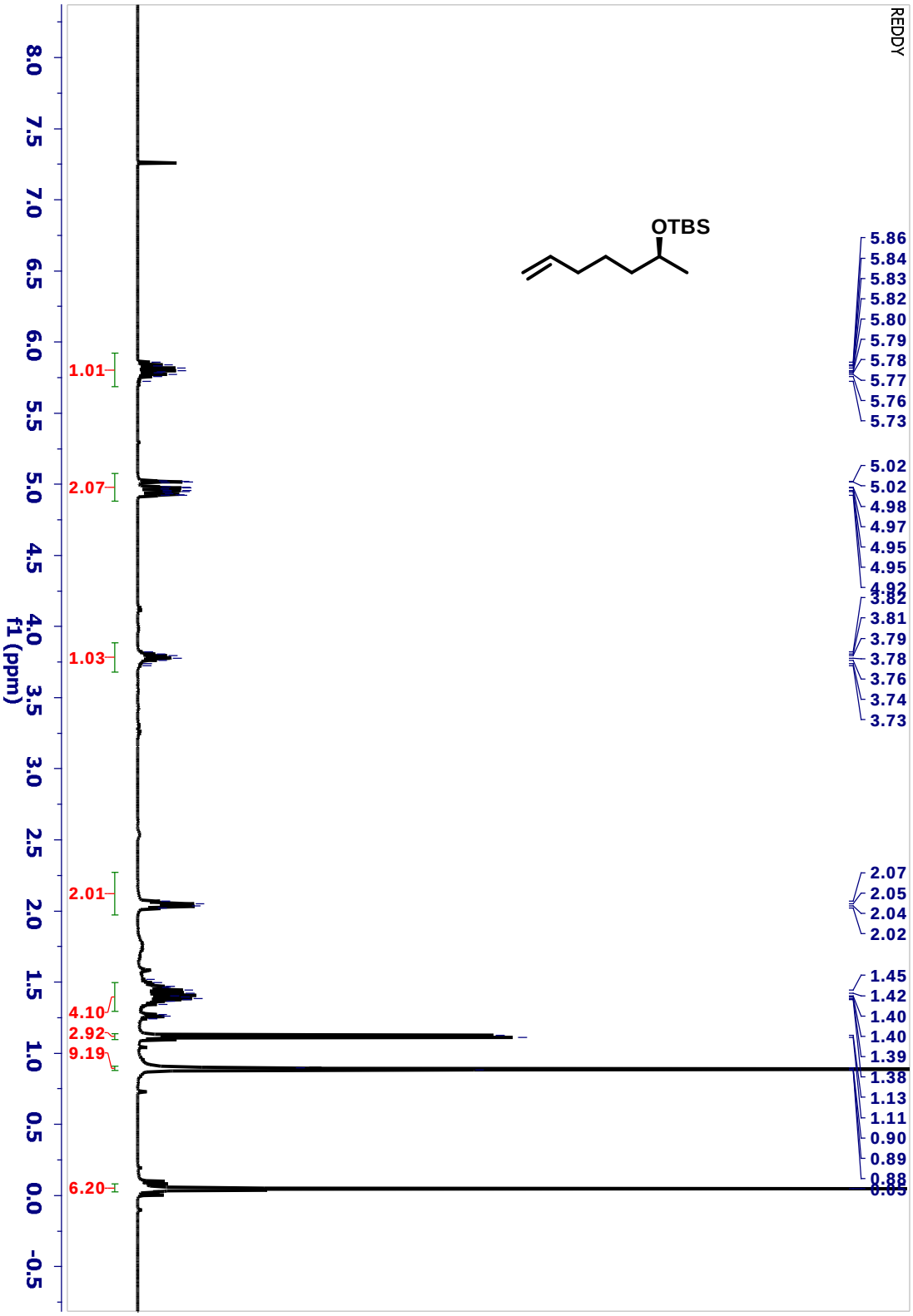
^{13}C NMR spectrum of 12 (100 MHz, $CDCl_3$)



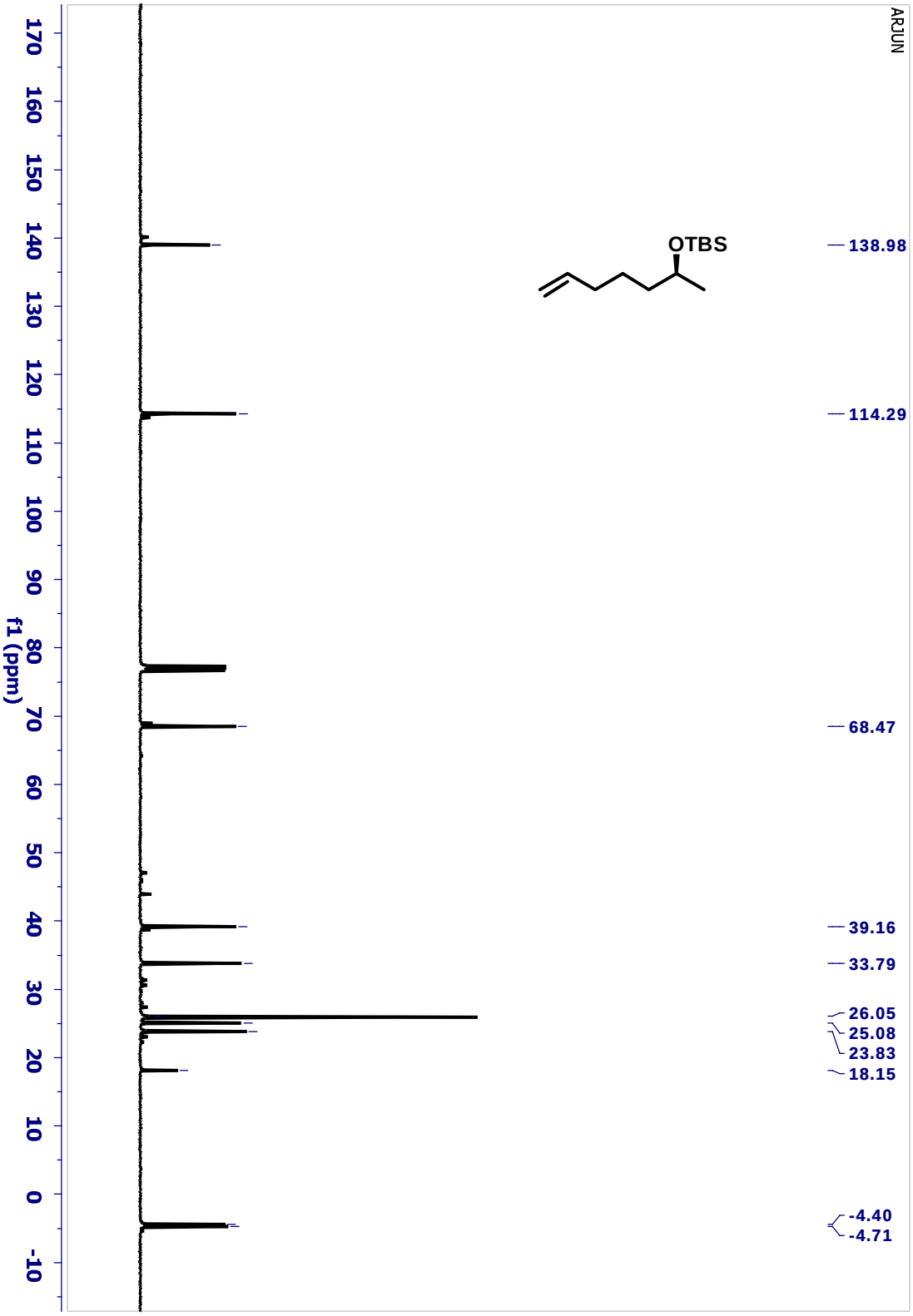
^{1}H NMR spectrum of 5 (500 MHz, $CDCl_3$)



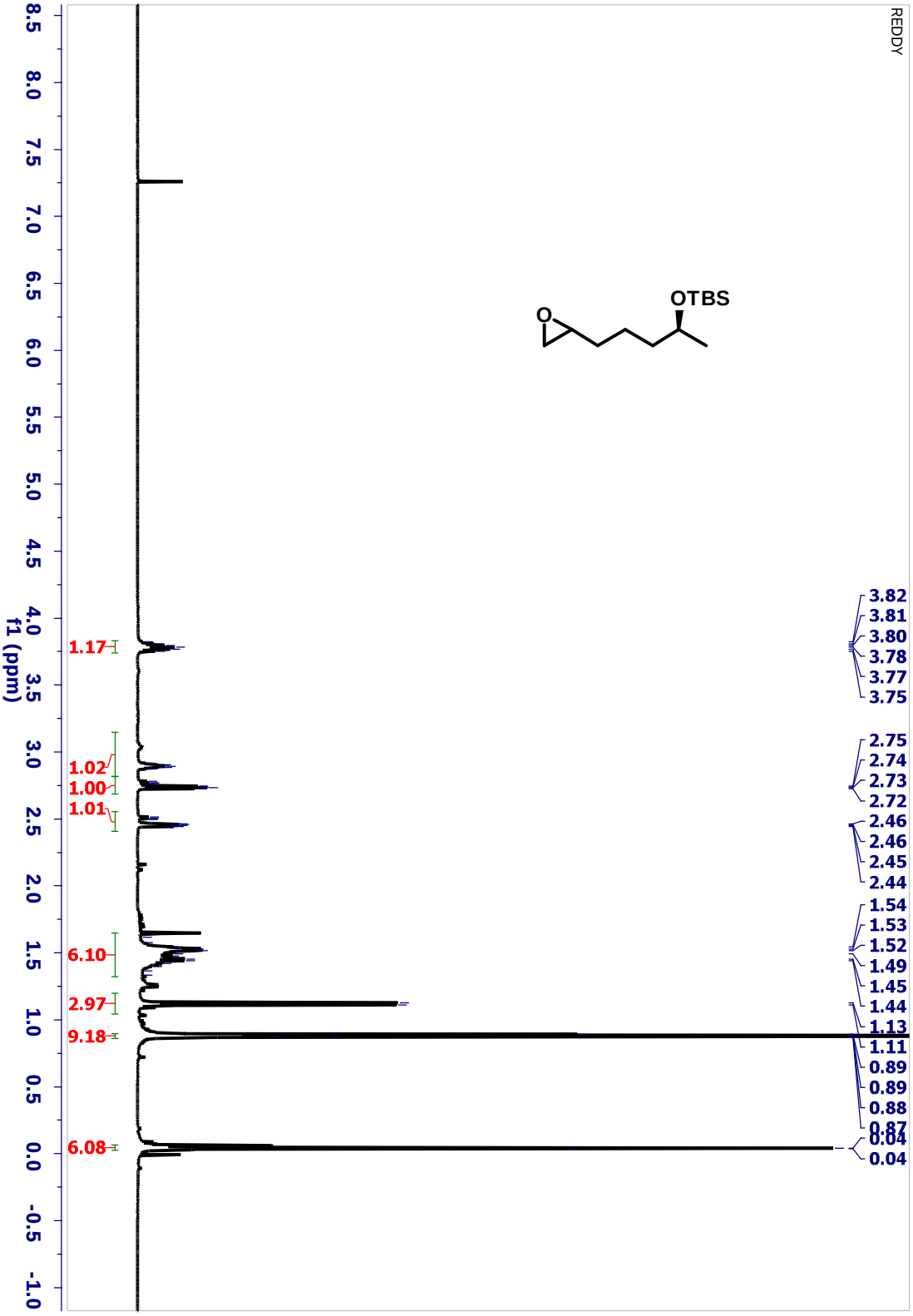
^{13}C NMR spectrum of 5 (100 MHz, $CDCl_3$)



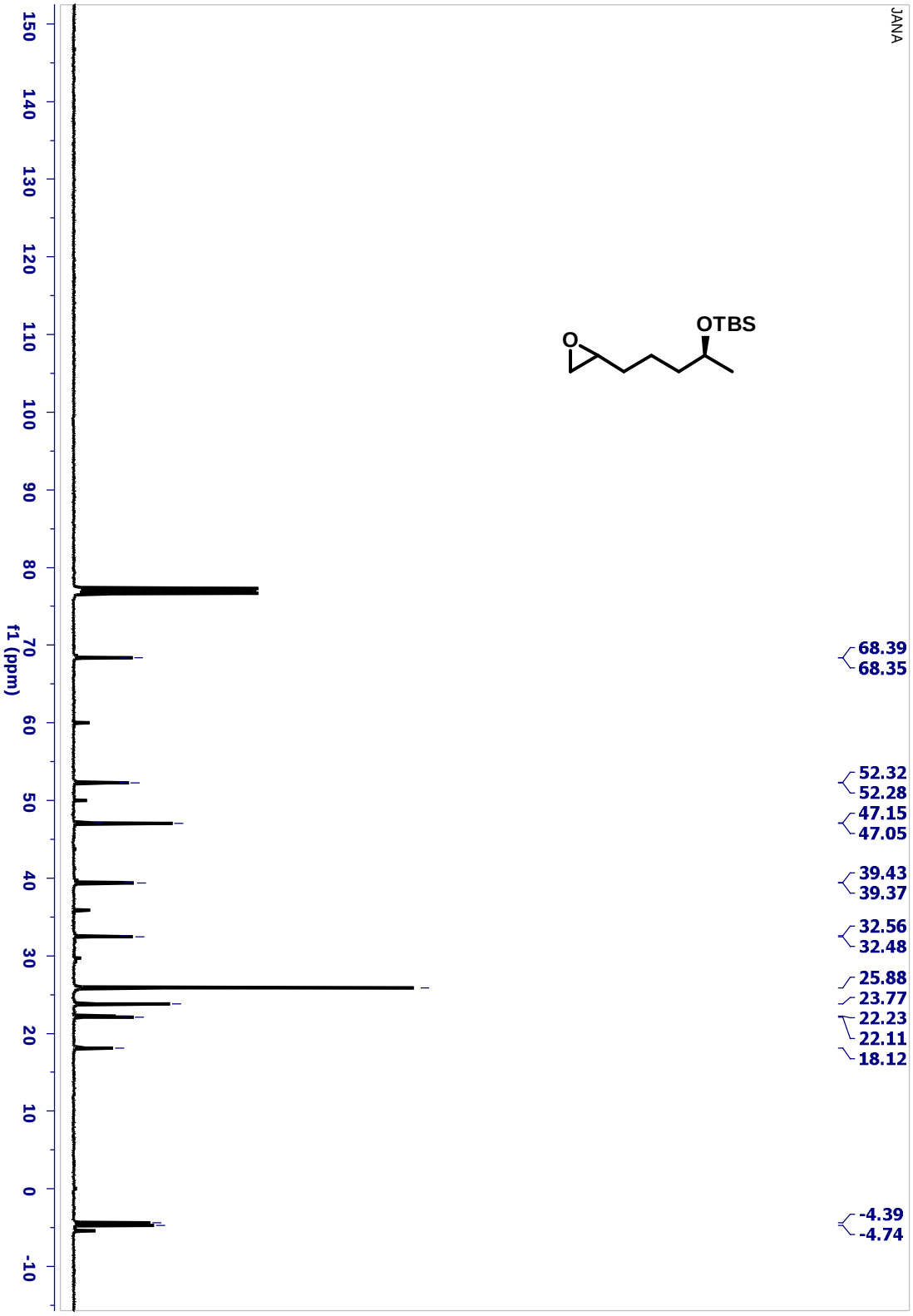
^{1}H NMR spectrum of 13 (400 MHz, $CDCl_3$)



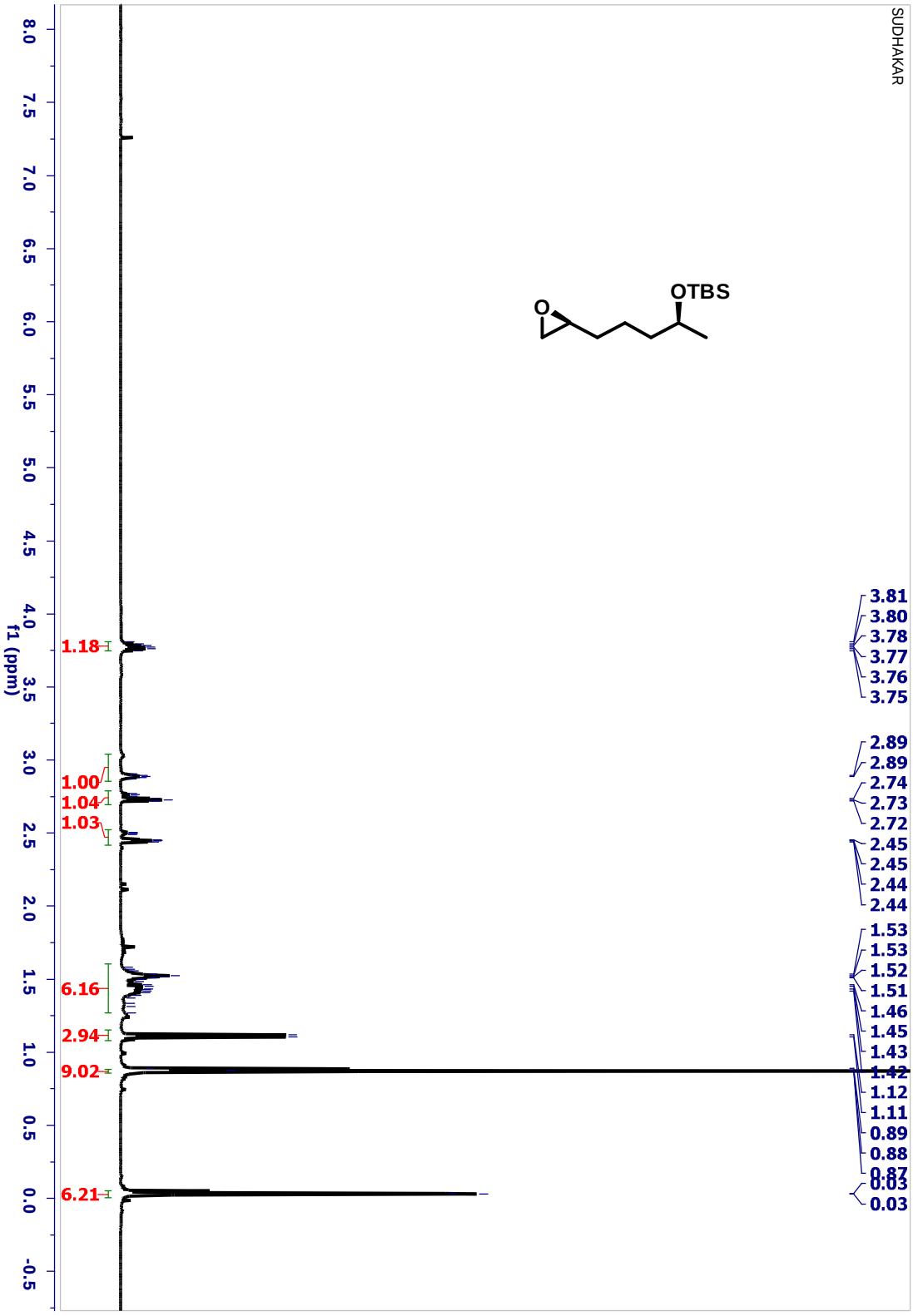
^{13}C NMR spectrum of 13 (100 MHz, $CDCl_3$)



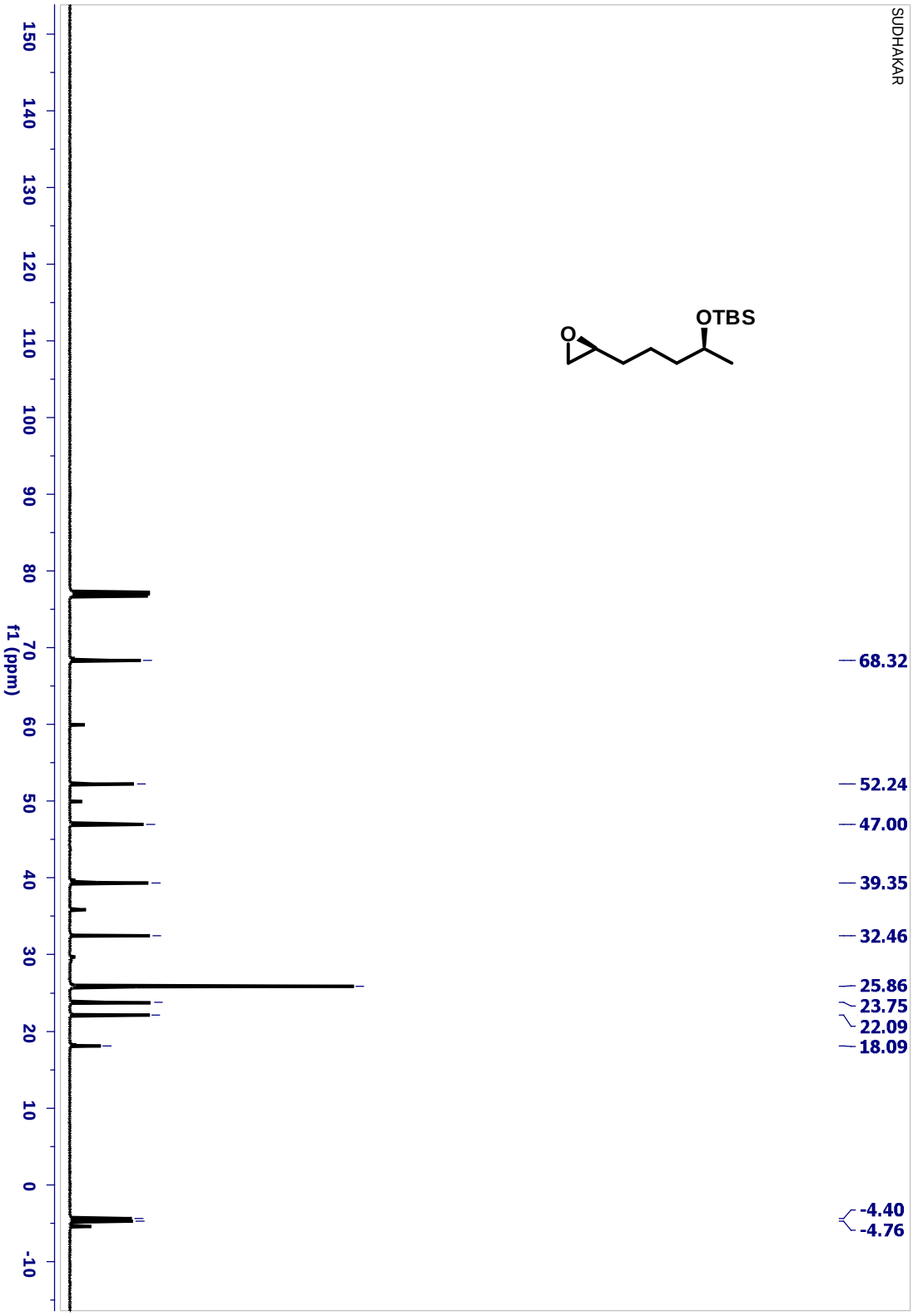
^{1}H NMR spectrum of 14 (400 MHz, $CDCl_3$)



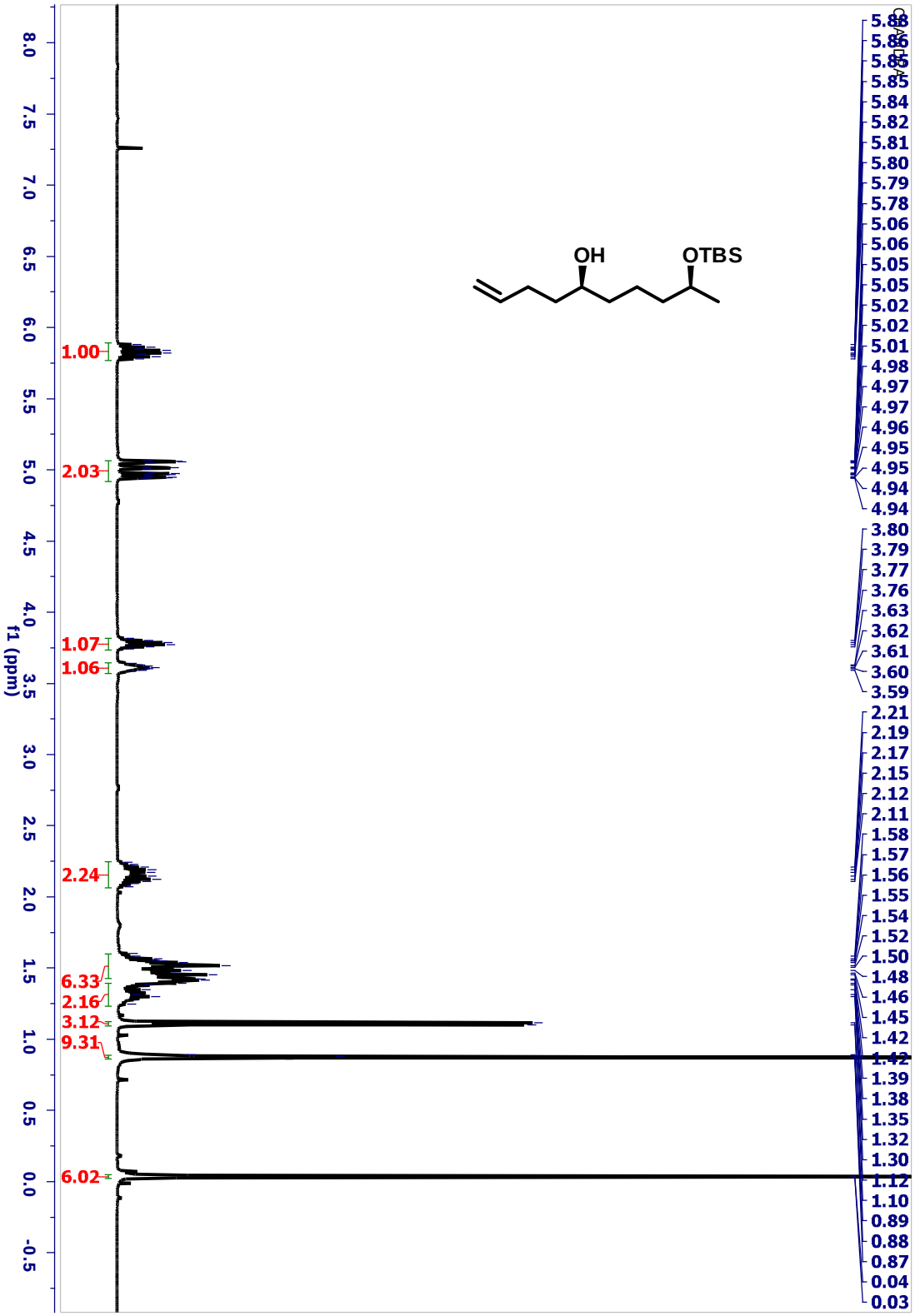
^{13}C NMR spectrum of 14 (125 MHz, $CDCl_3$)



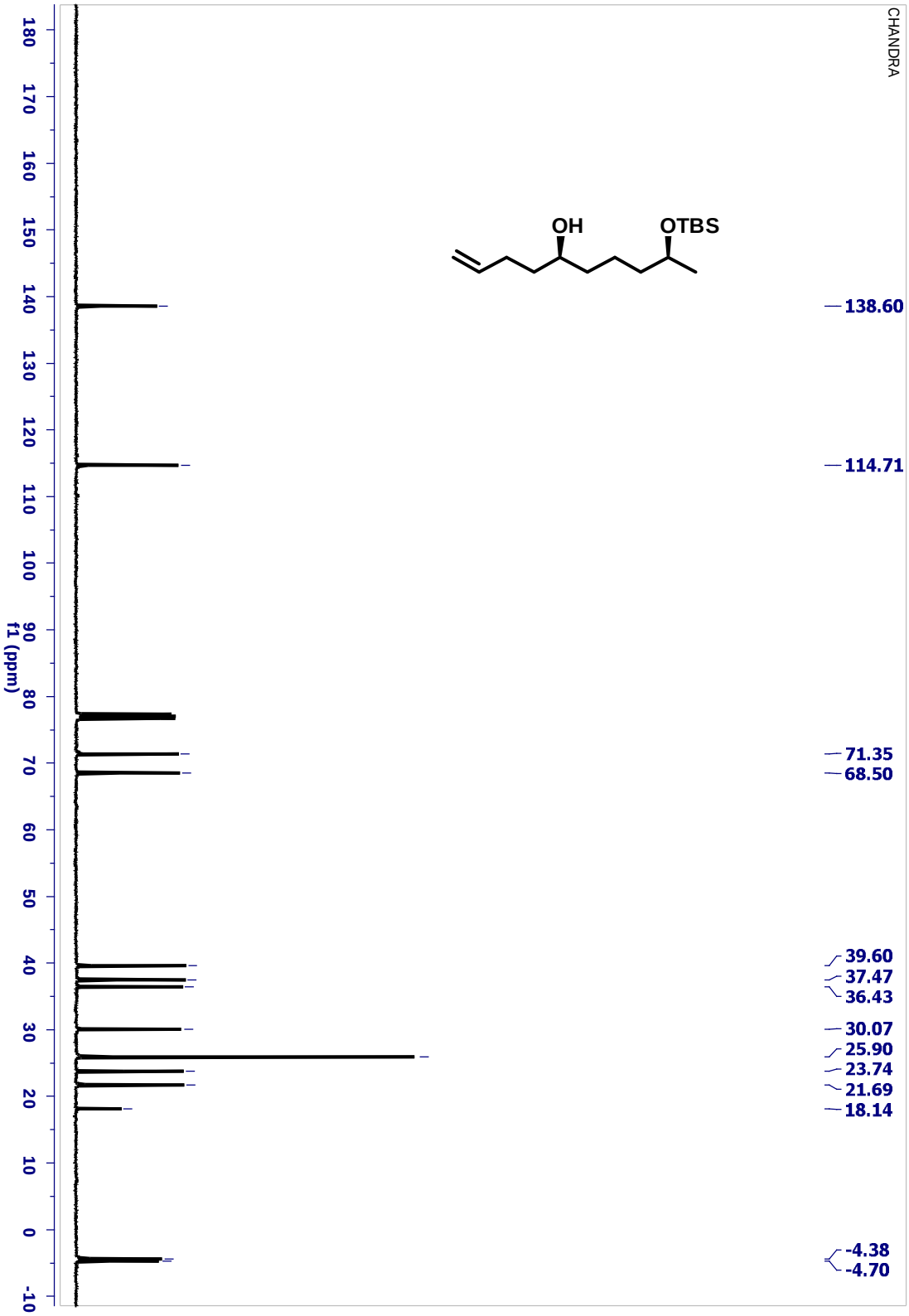
^{1}H NMR spectrum of 15 (400 MHz, $CDCl_3$)



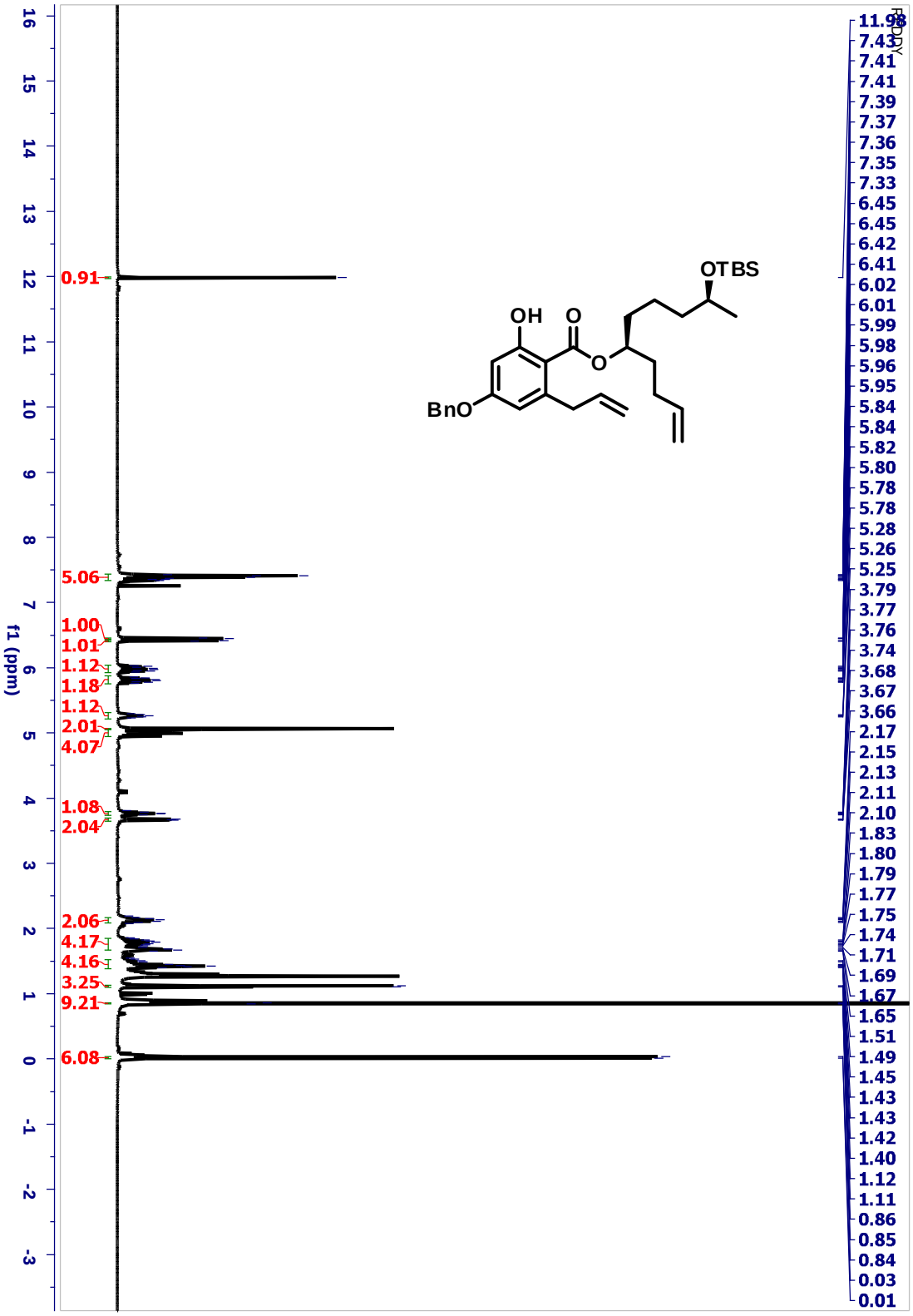
^{13}C NMR spectrum of 15 (125 MHz, $CDCl_3$)



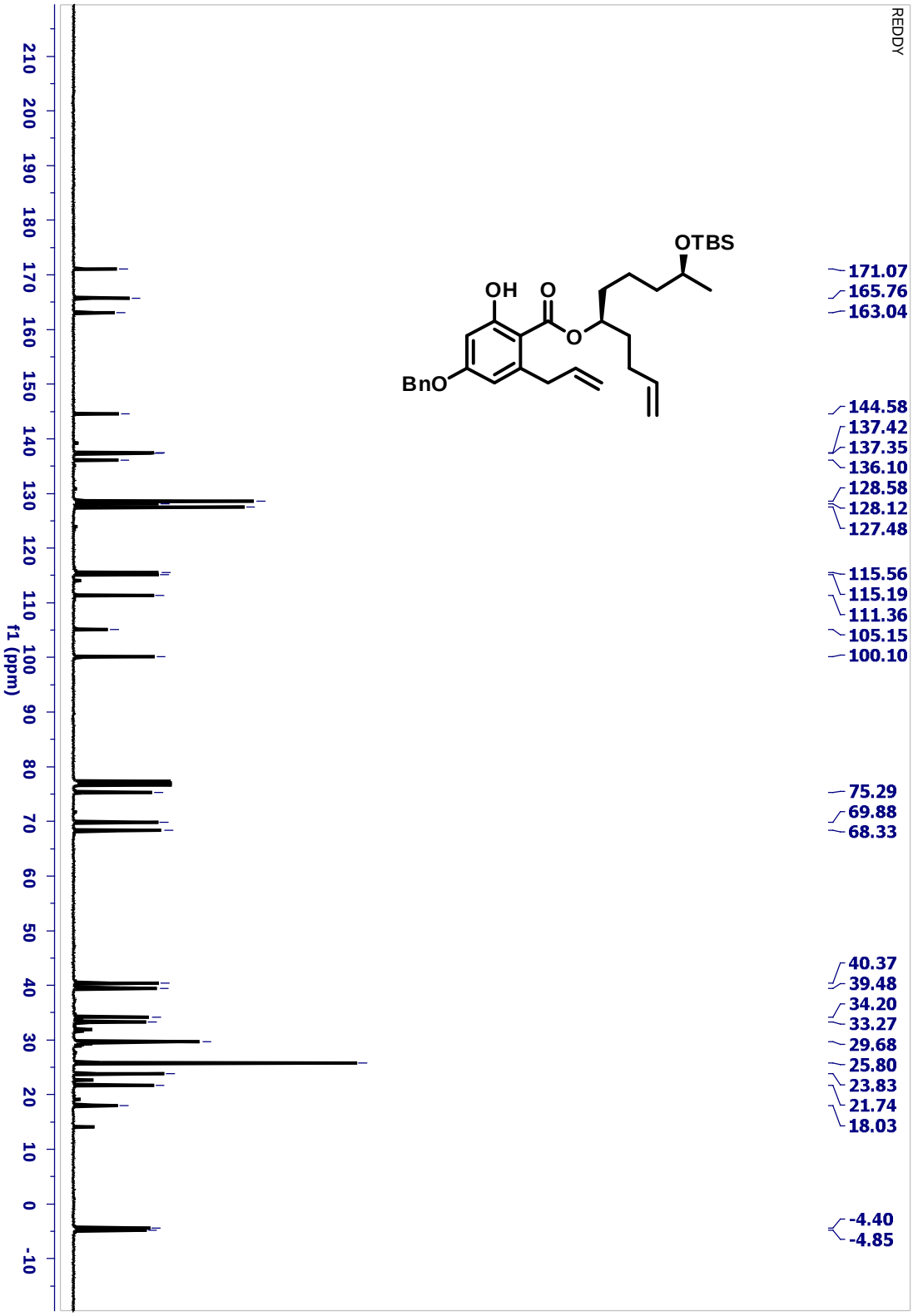
^{1}H NMR spectrum of 6 (400 MHz, $CDCl_3$)



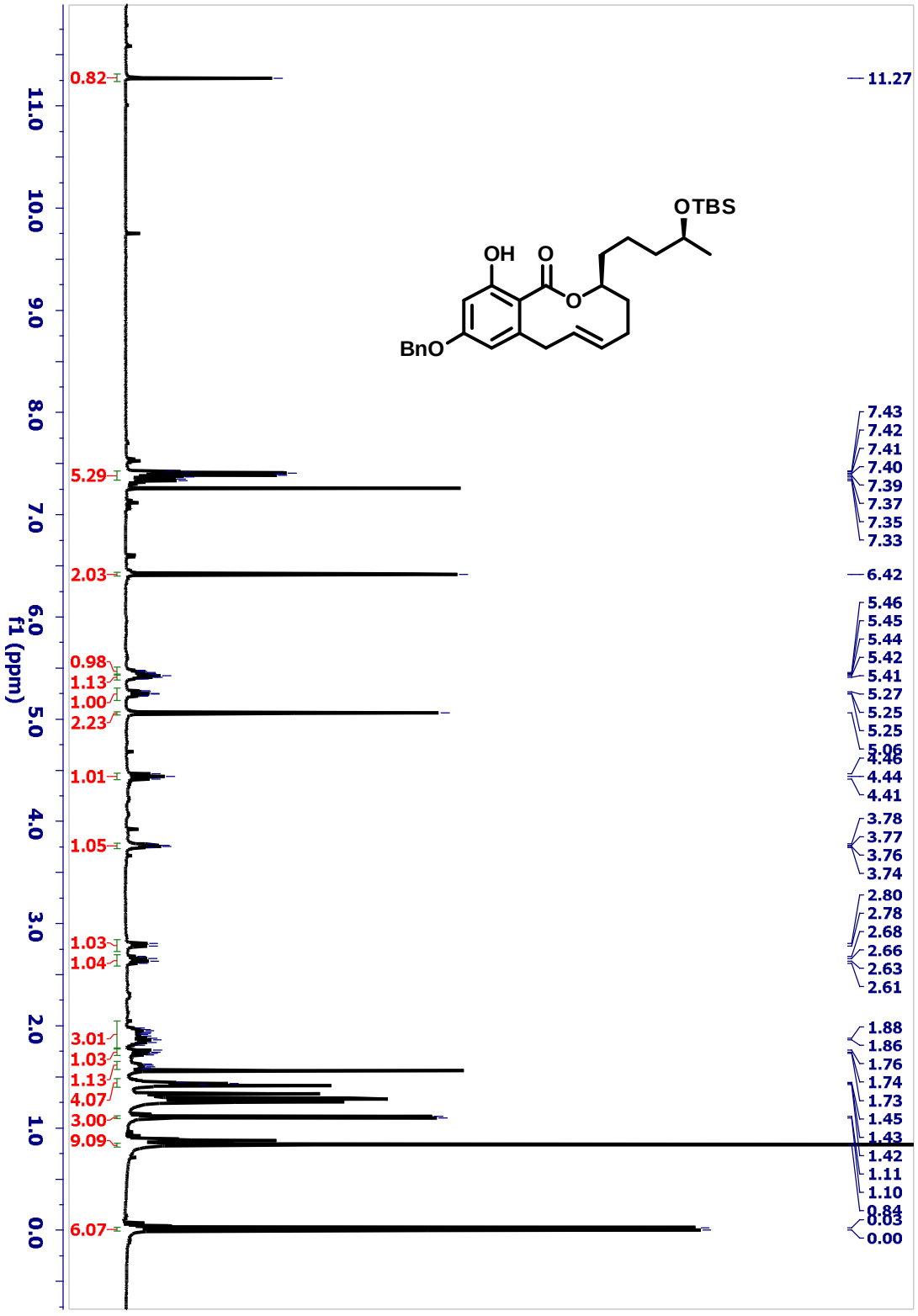
^{13}C NMR spectrum of 6 (125 MHz, $CDCl_3$)



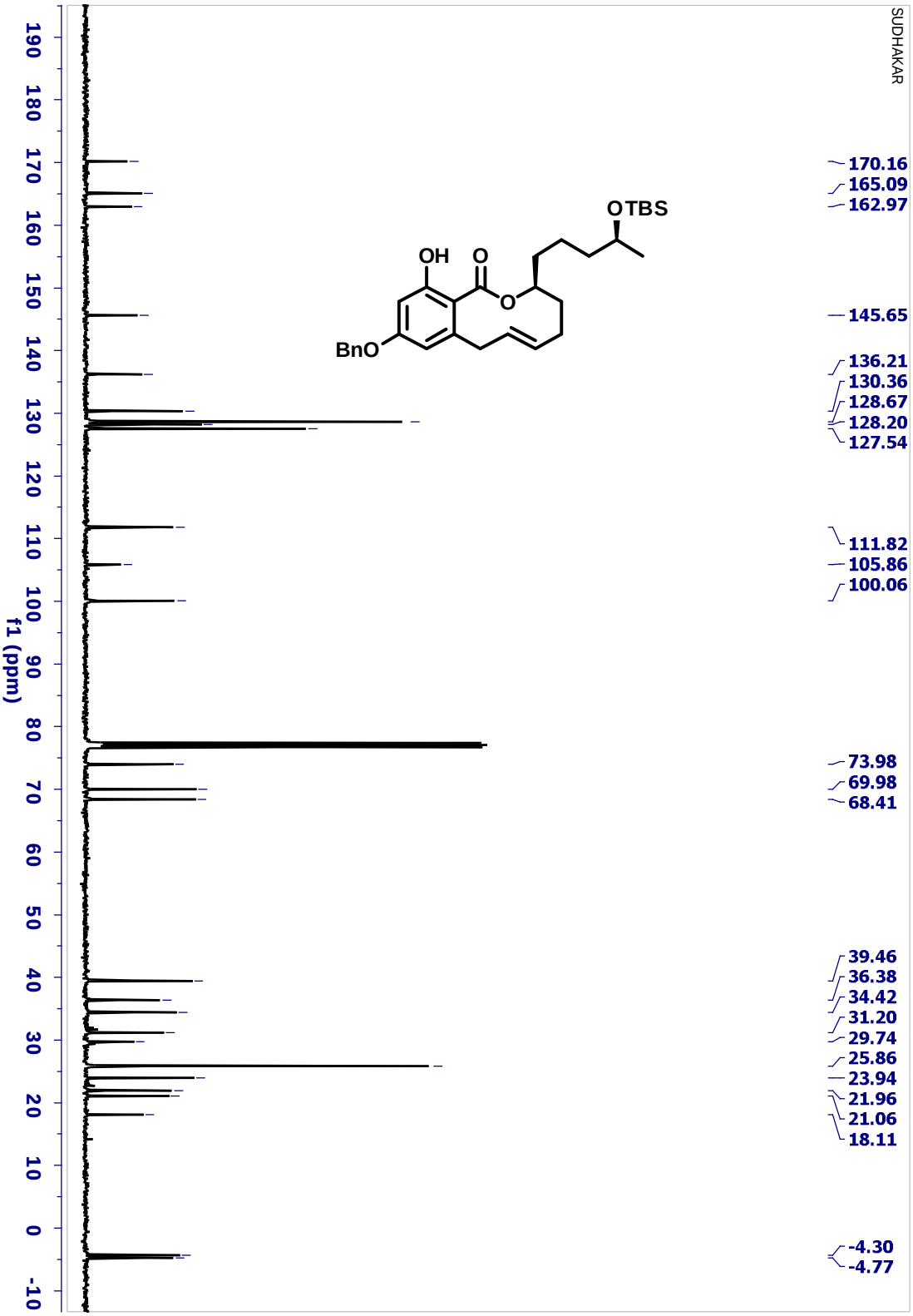
^{1}H NMR spectrum of 4 (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 4 (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of 16 (500 MHz, $CDCl_3$)



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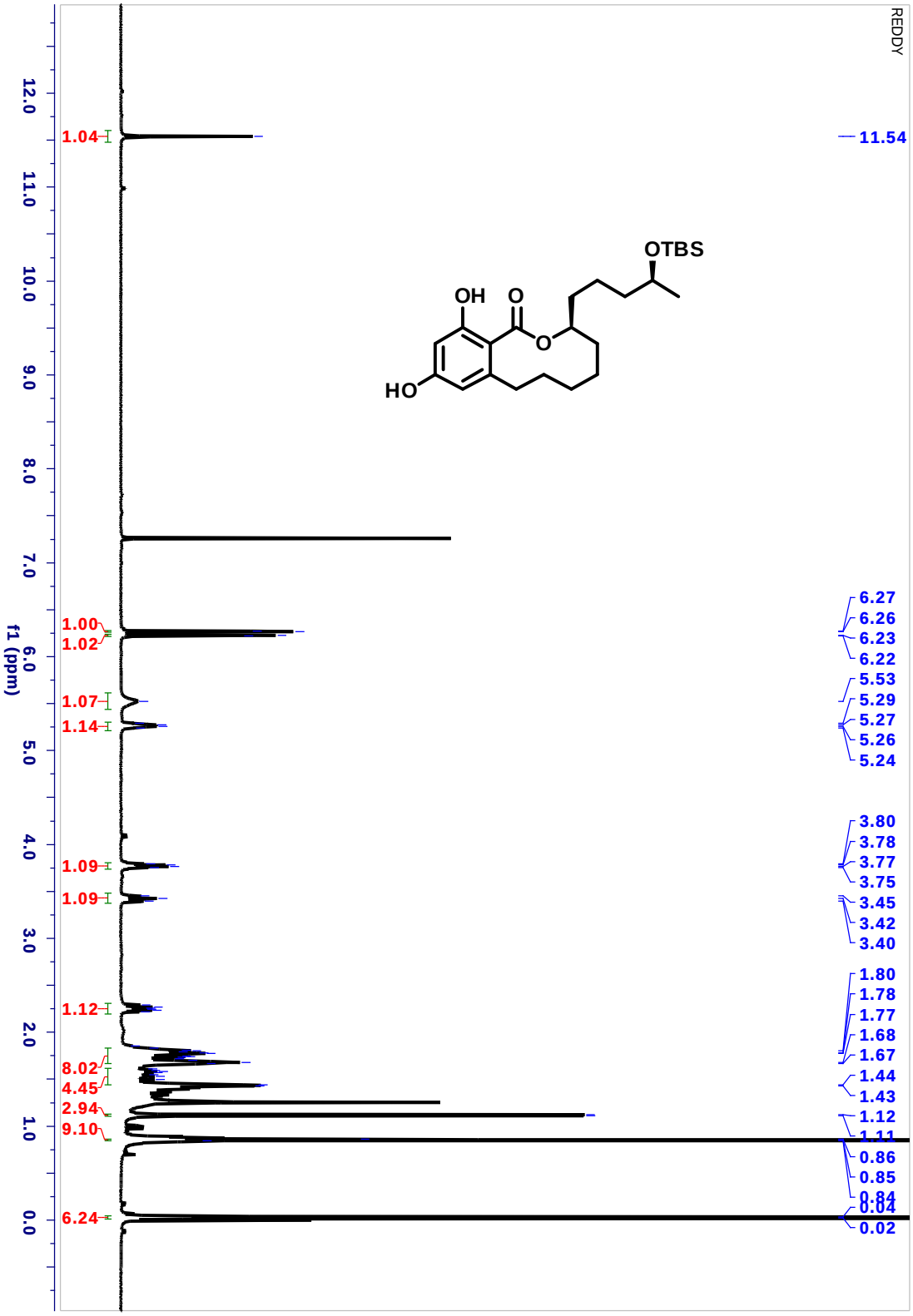
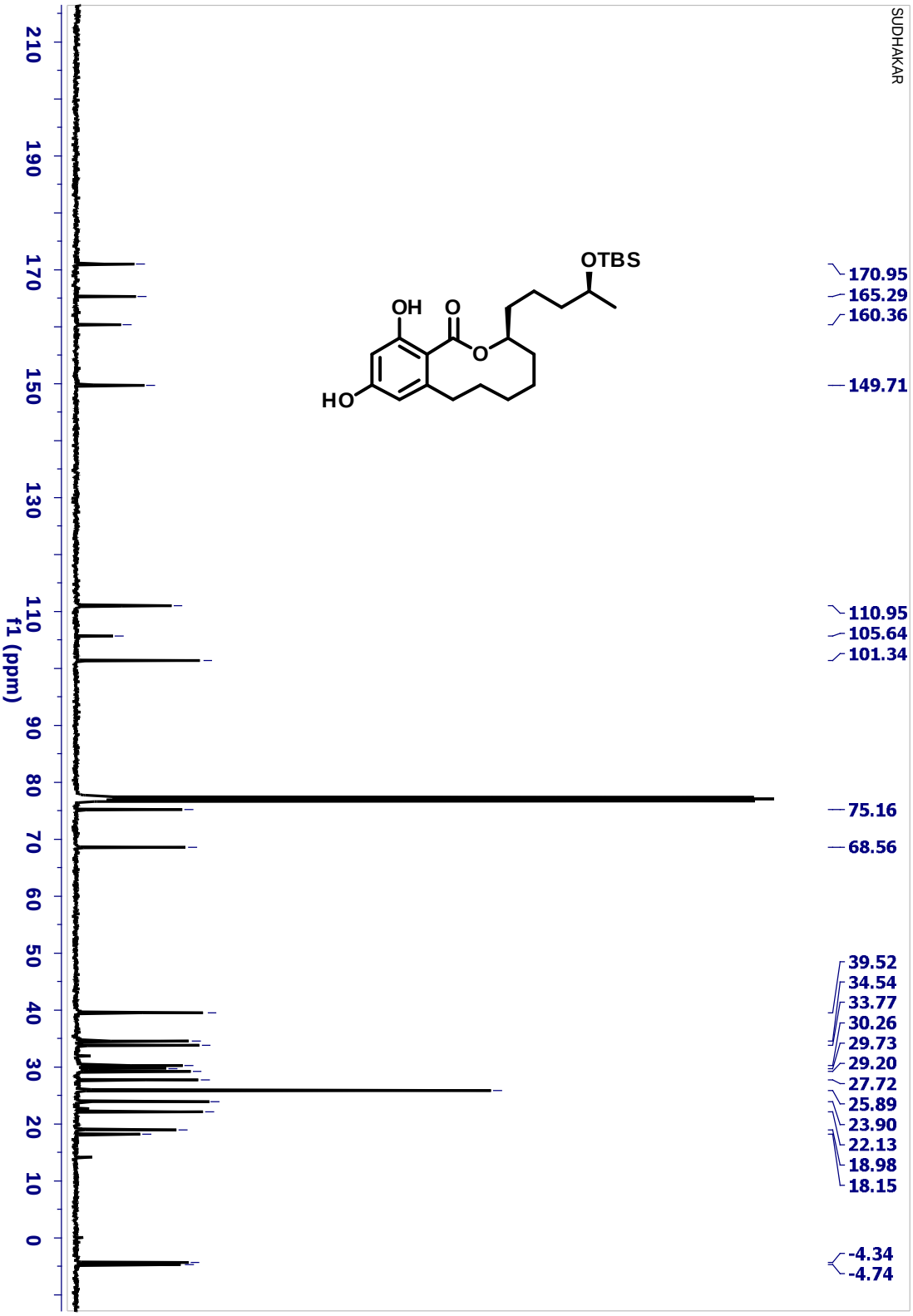
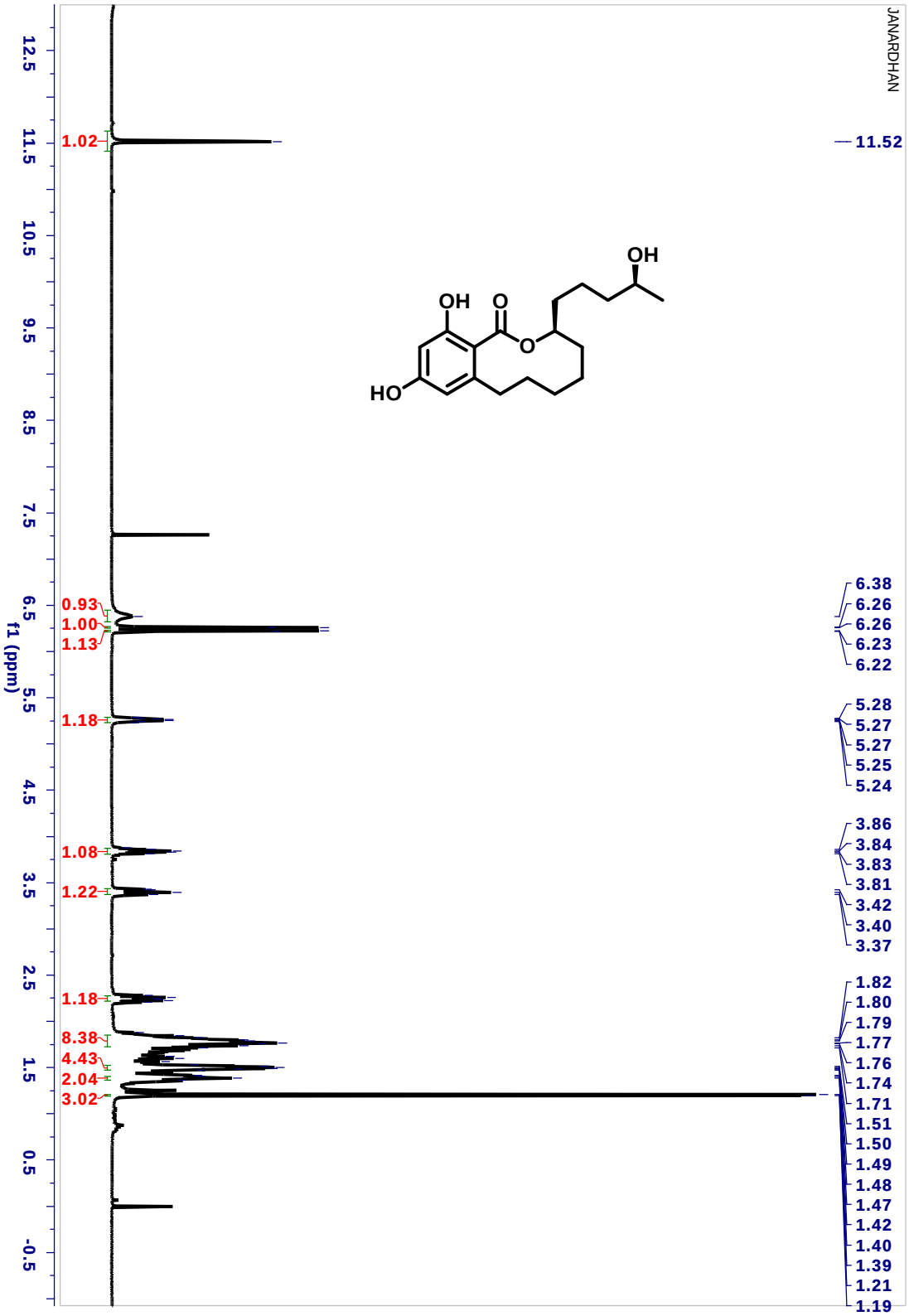


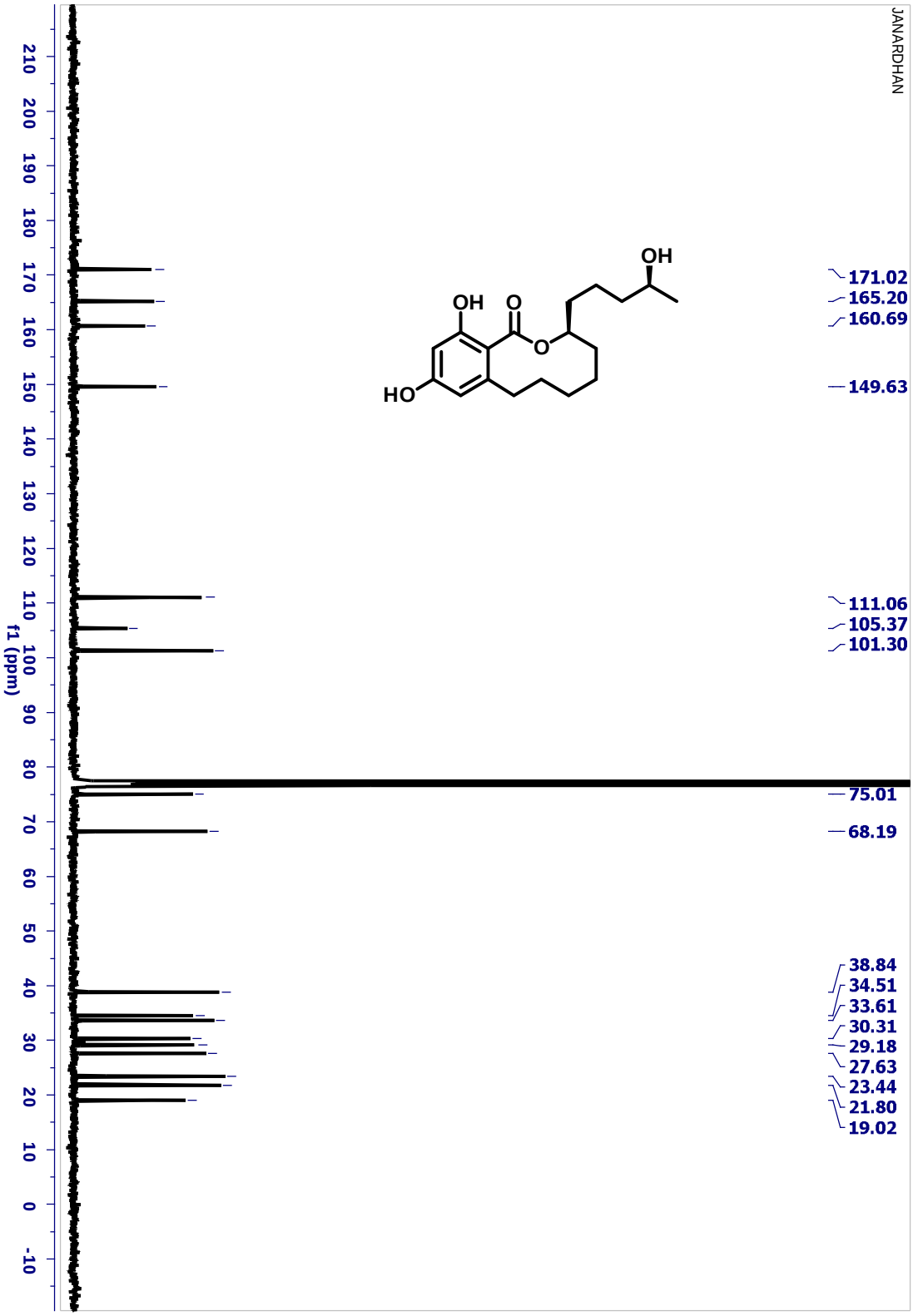
^{1}H NMR spectrum of 17 (400 MHz, $CDCl_3$)



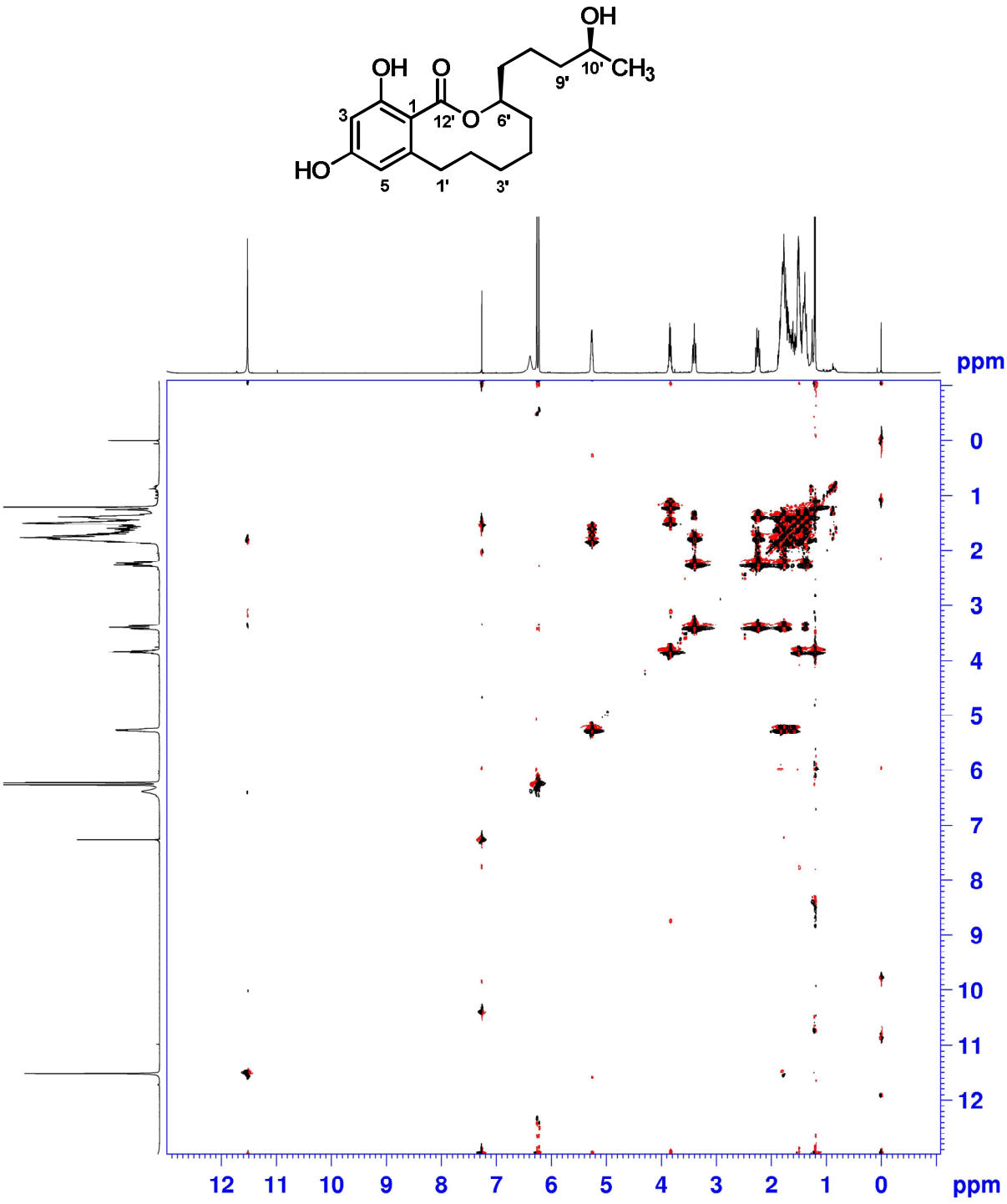
^{13}C NMR spectrum of 17 (100 MHz, $CDCl_3$)



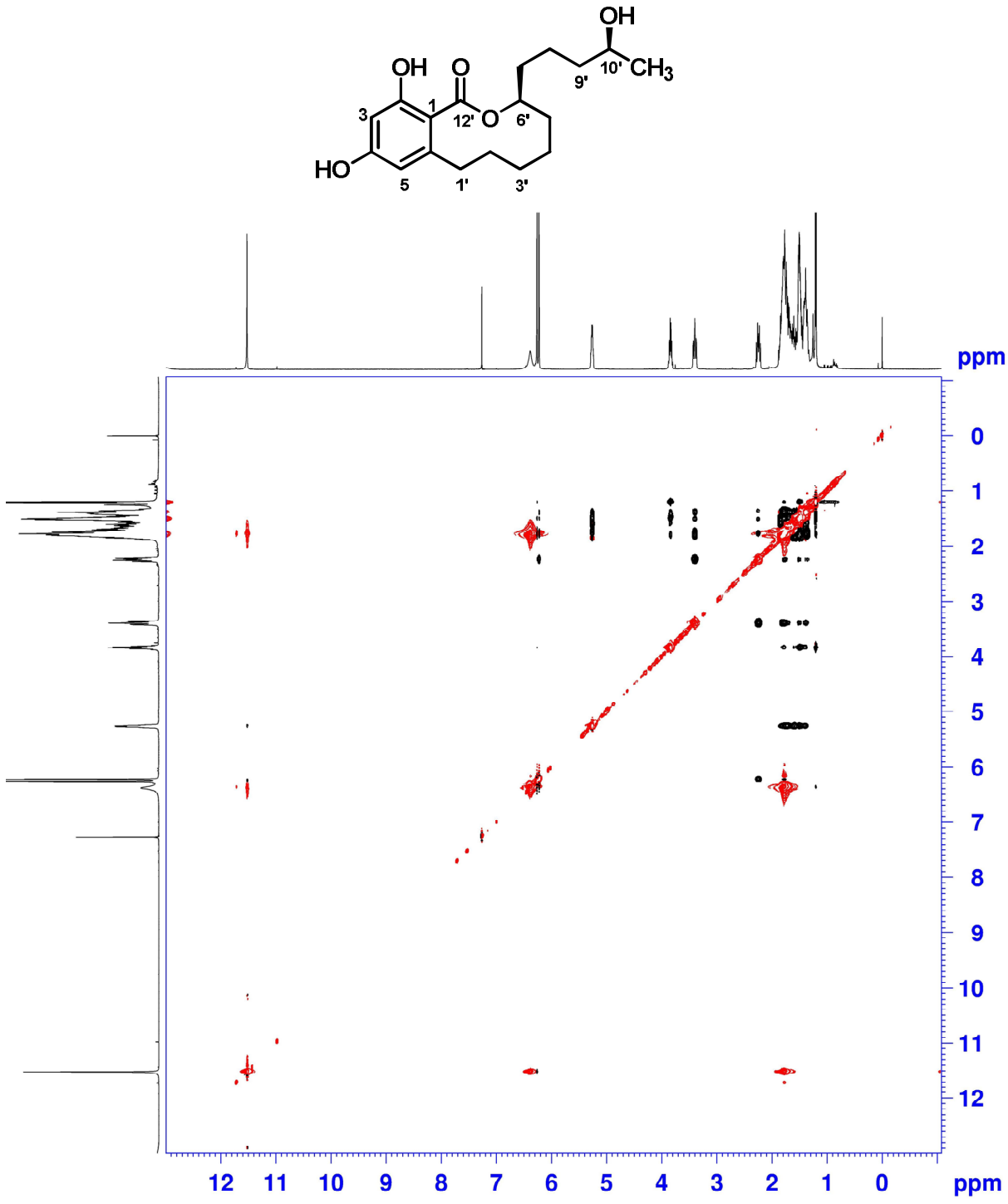
^{1}H NMR spectrum of 1 (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 1 (100 MHz, $CDCl_3$)



DQFCOSY spectrum of 1 ($CDCl_3$, 295 K, 400 MHz)



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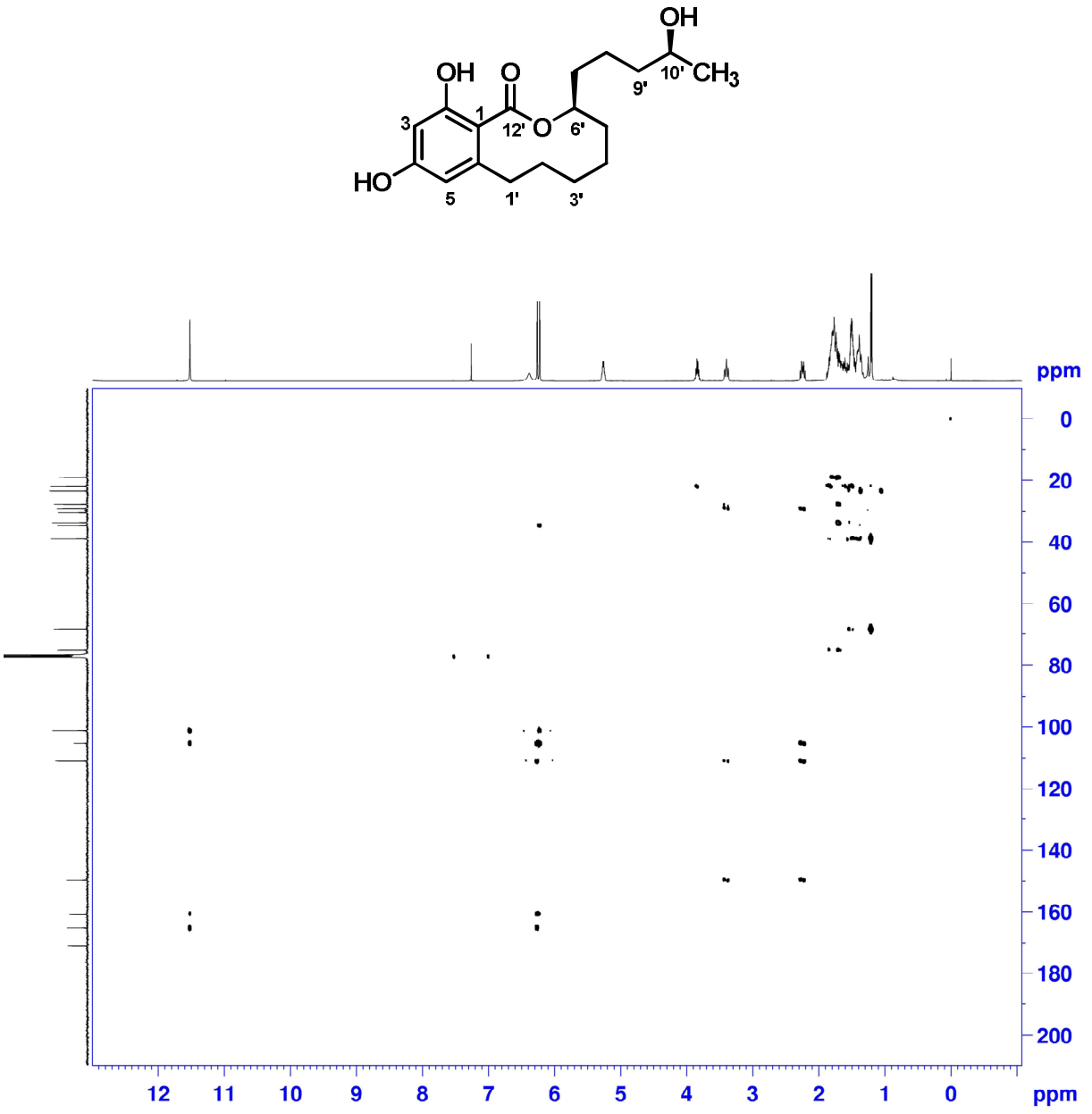
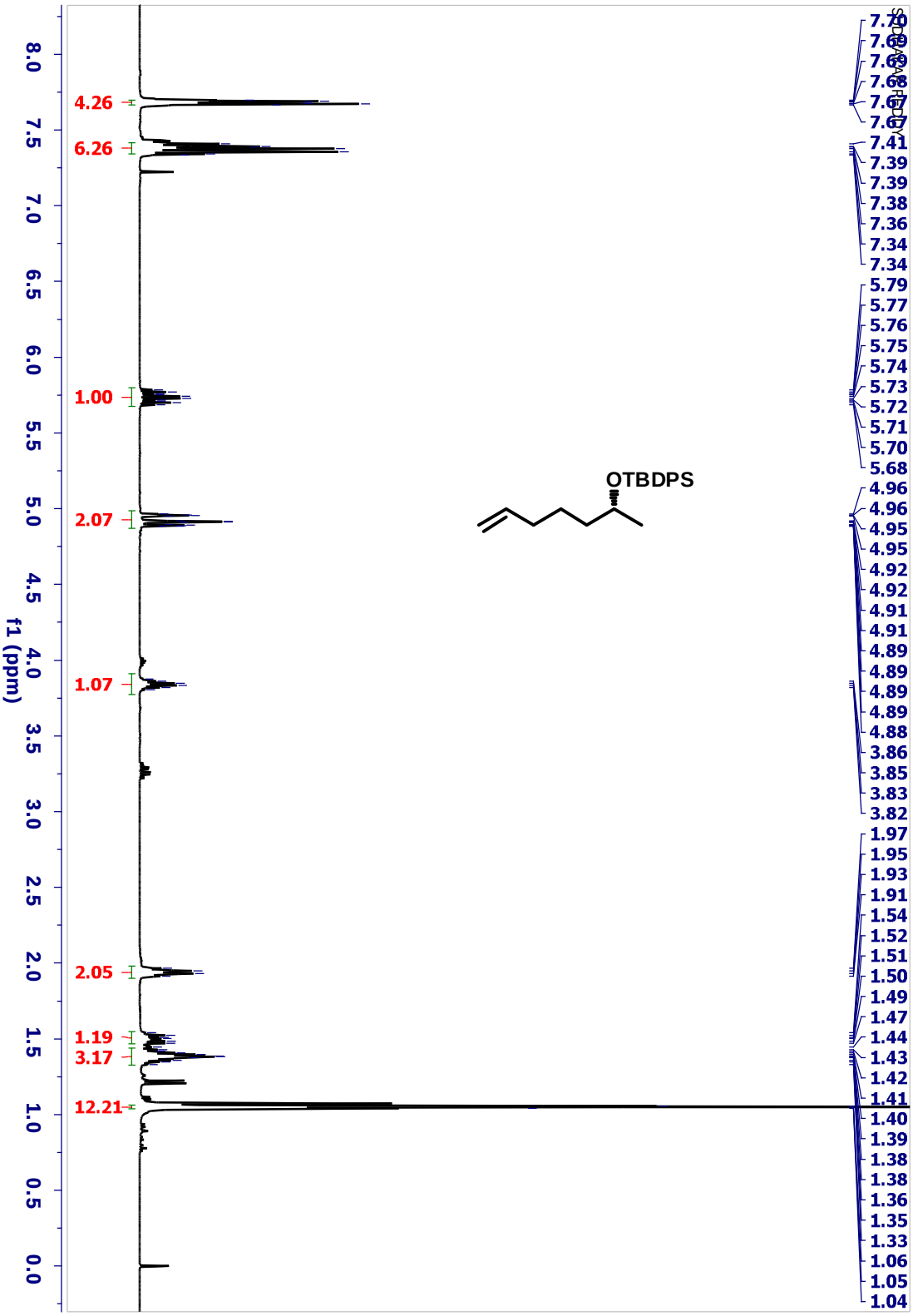
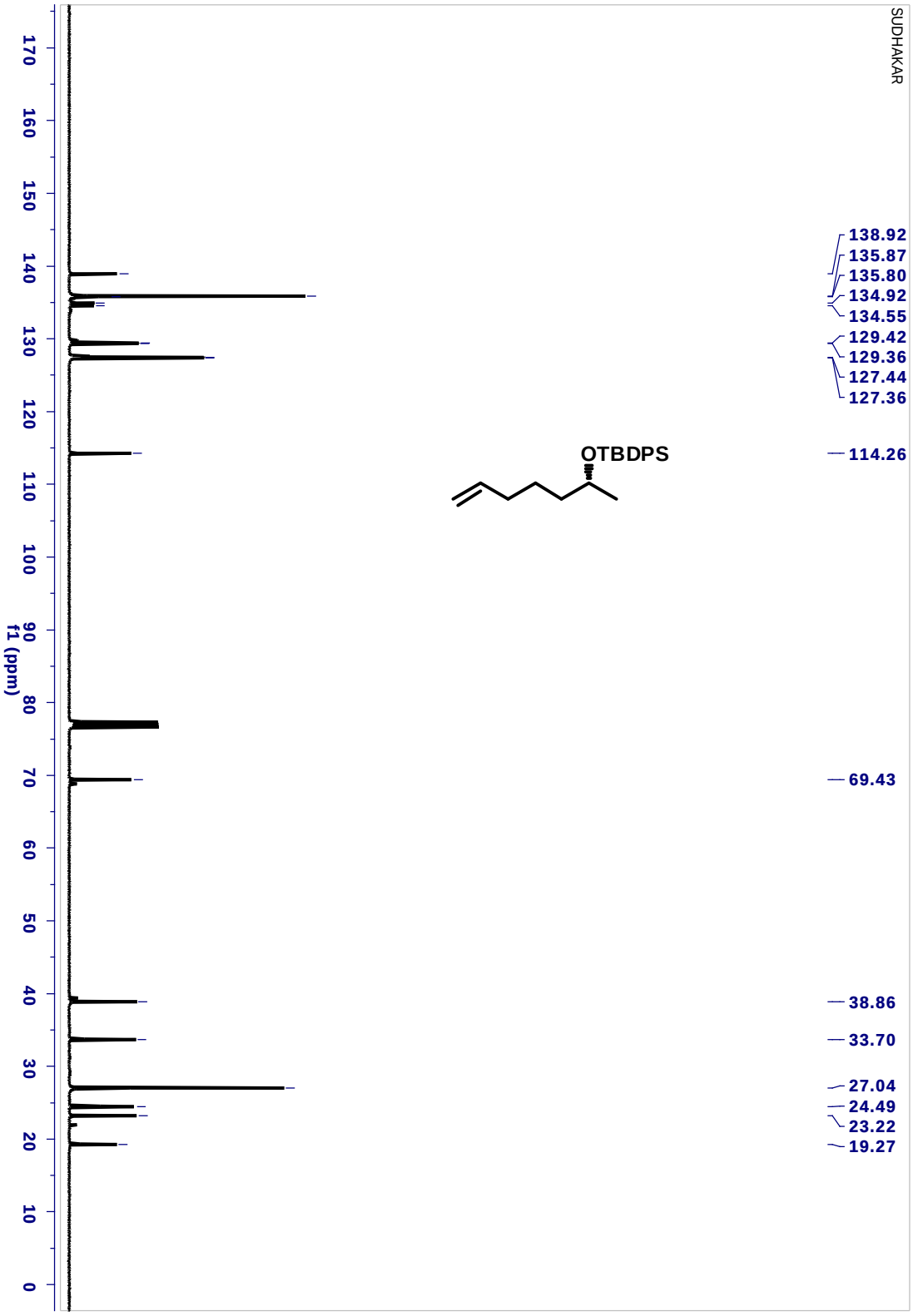


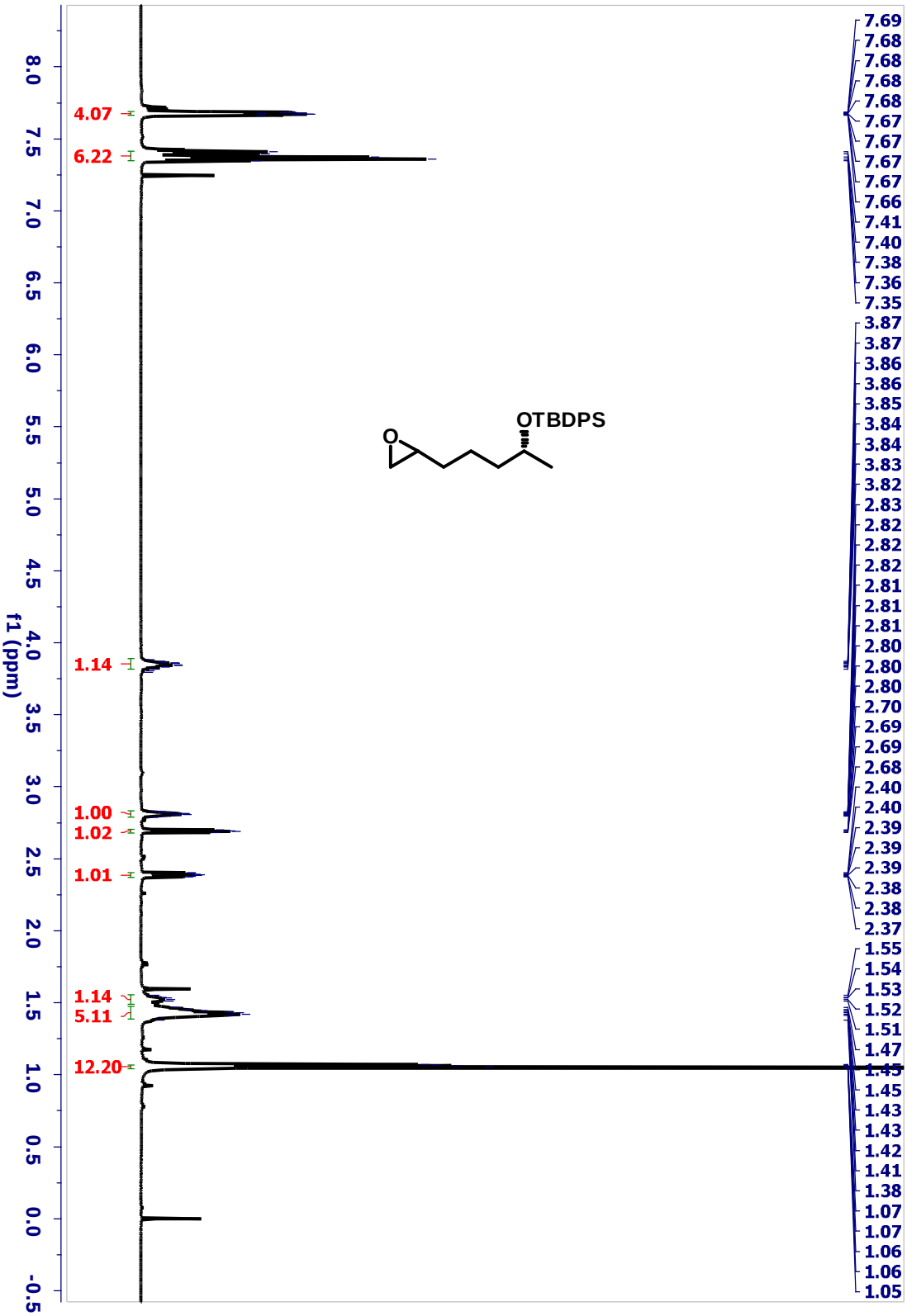
HMBC spectrum of 1 ($CDCl_3$, 295 K, 400 MHz)



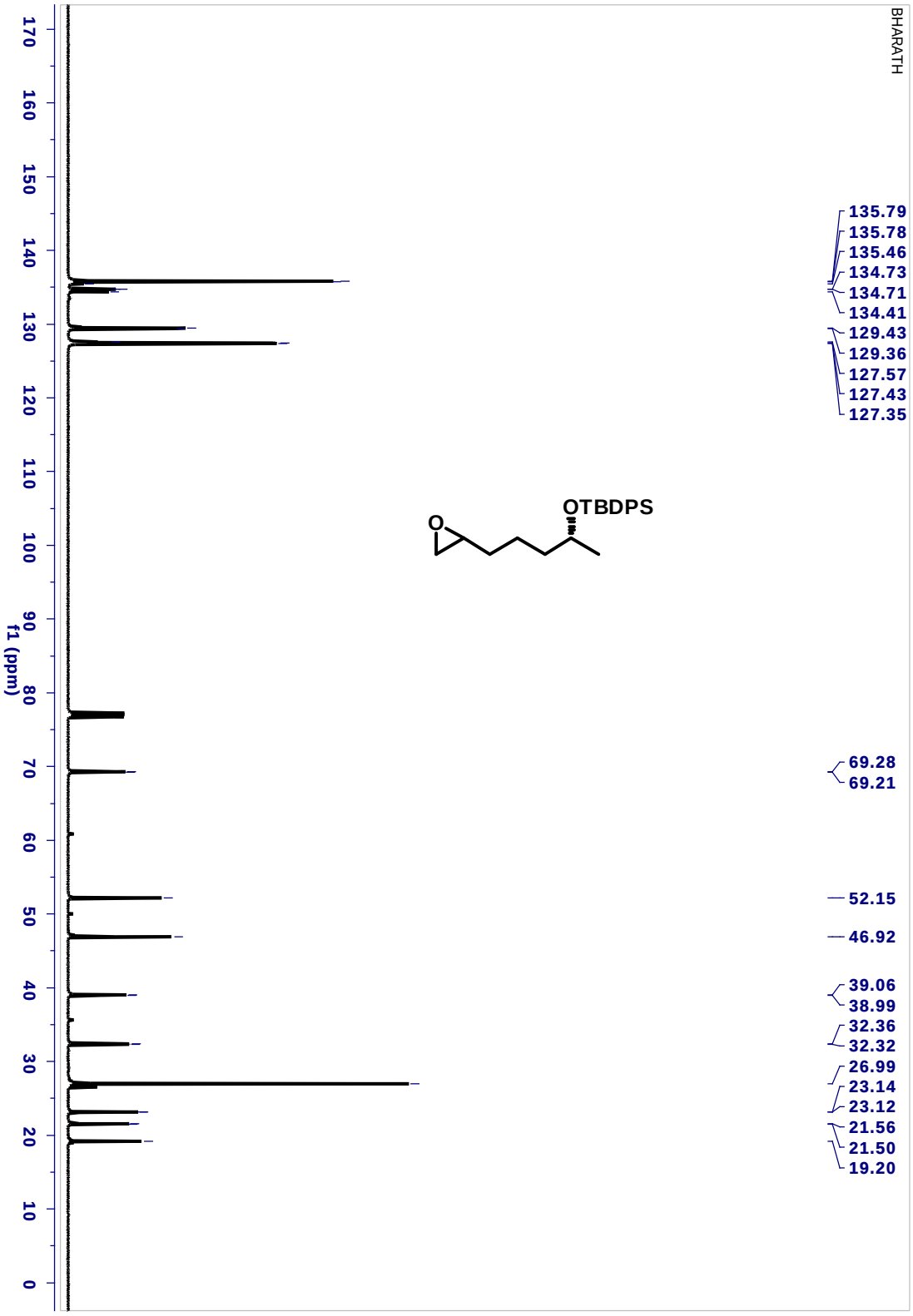
^{1}H NMR spectrum of 13a (400 MHz, $CDCl_3$)



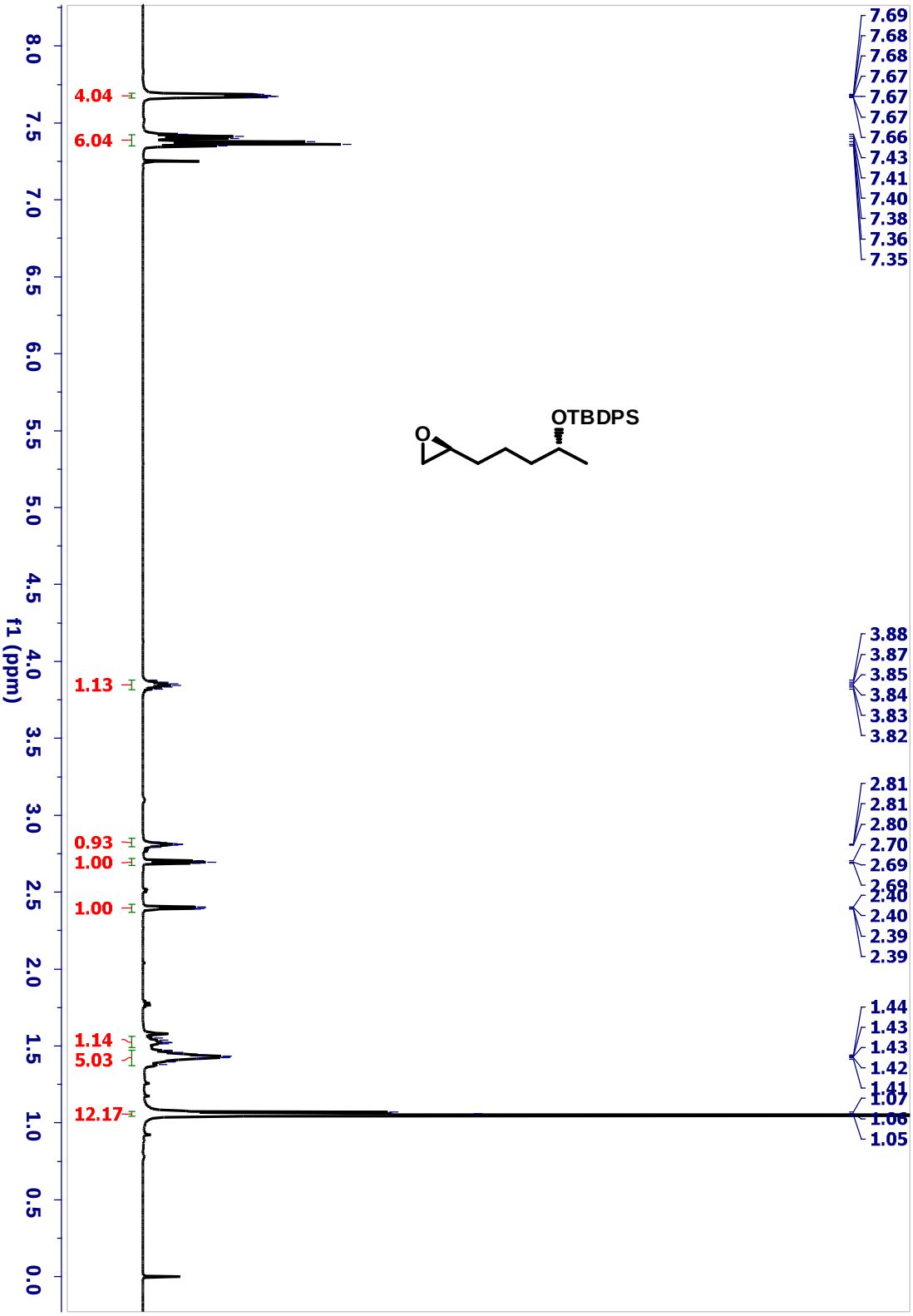
^{13}C NMR spectrum of 13a (100 MHz, $CDCl_3$)



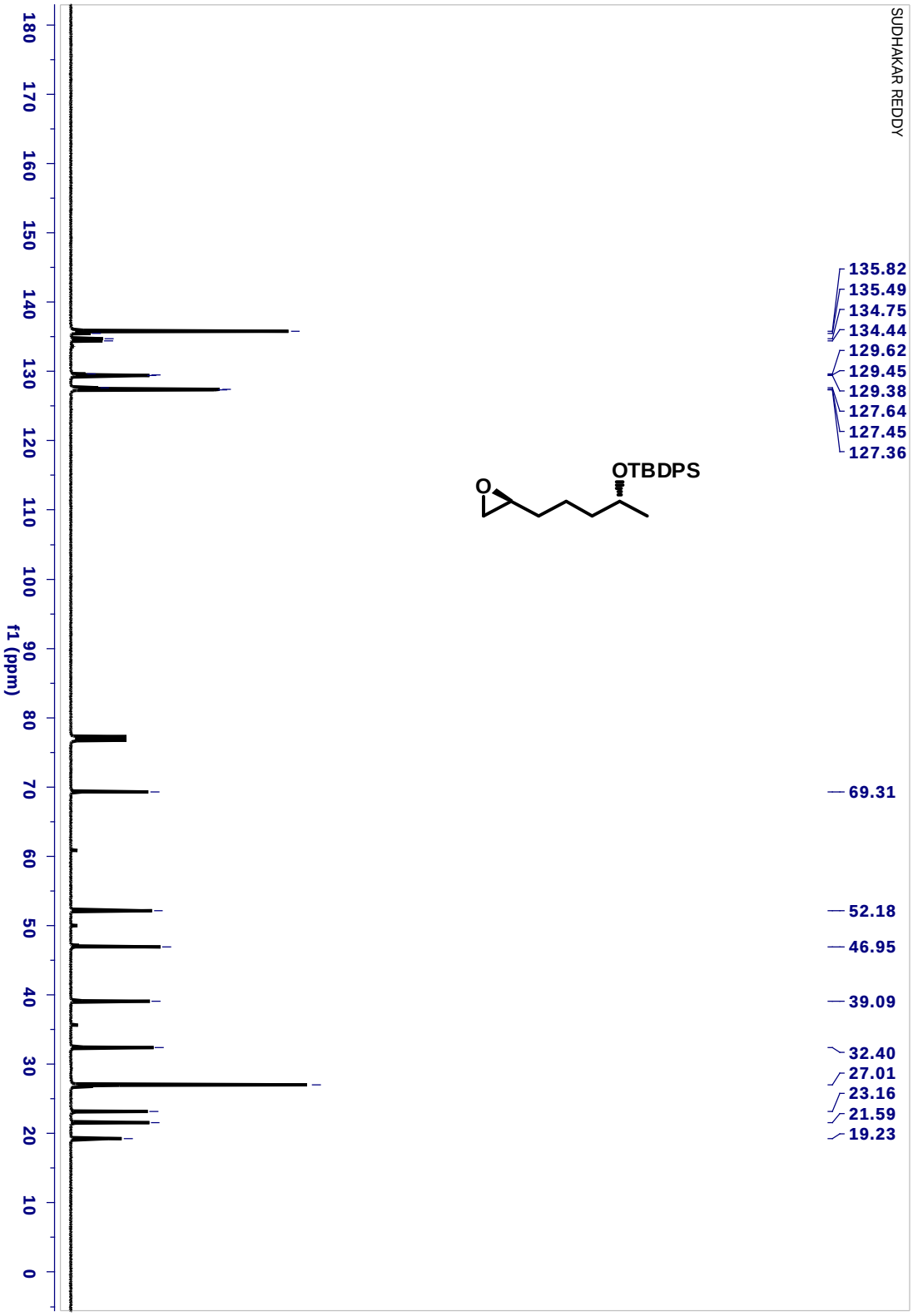
^{1}H NMR spectrum of 14a (500 MHz, $CDCl_3$)



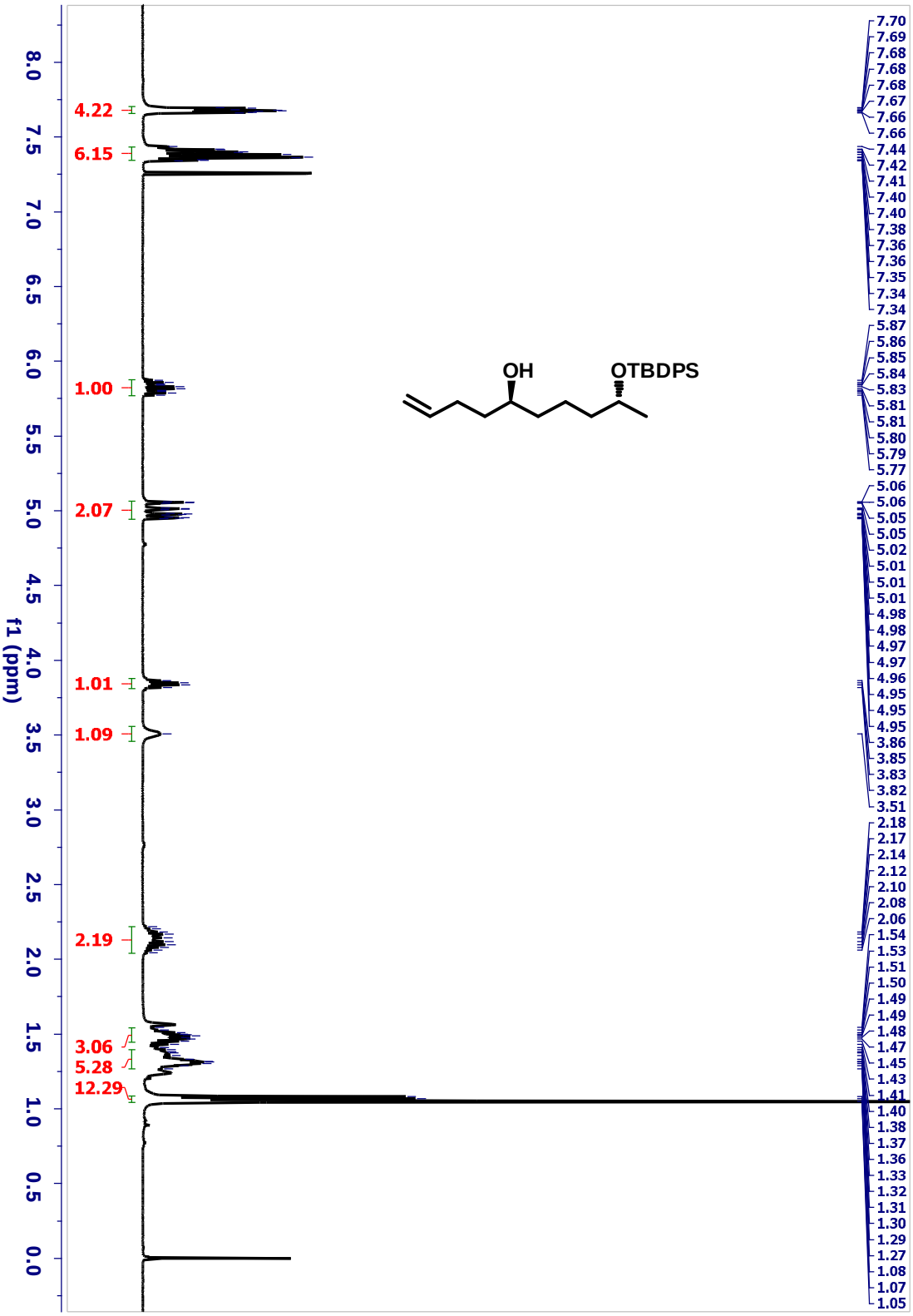
^{13}C NMR spectrum of 14a (125 MHz, $CDCl_3$)



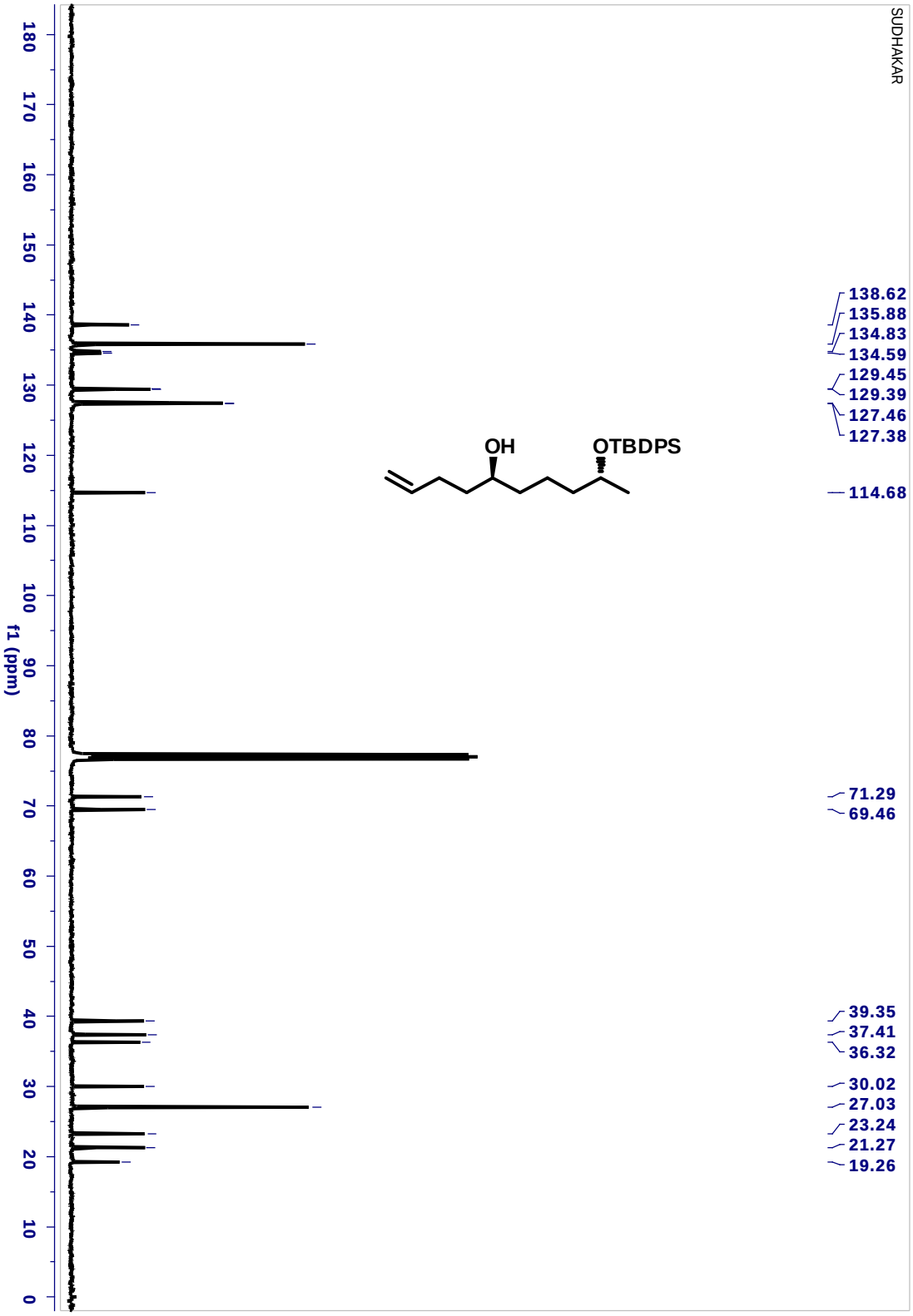
^{1}H NMR spectrum of 15a (500 MHz, $CDCl_3$)



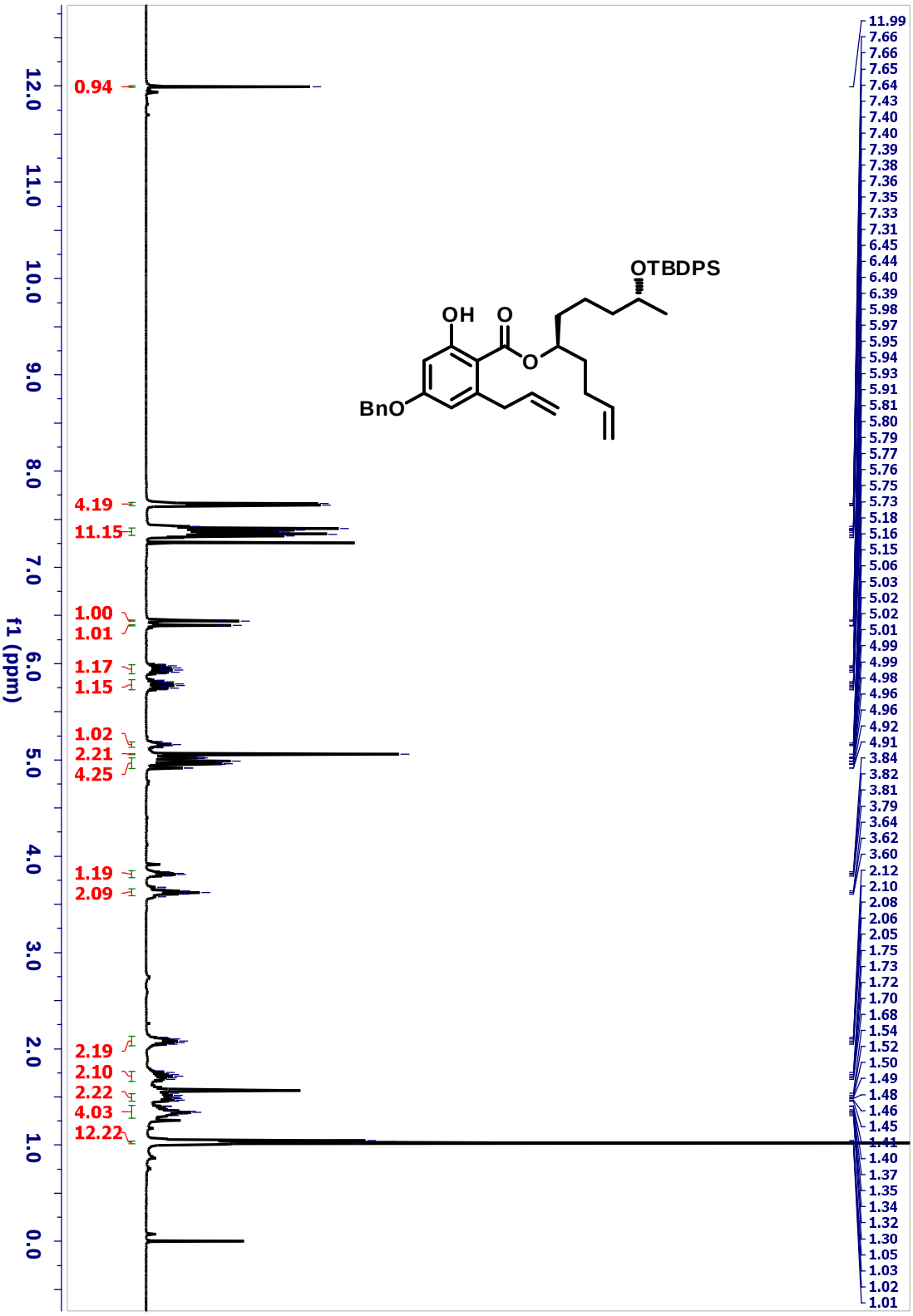
^{13}C NMR spectrum of 15a (125 MHz, $CDCl_3$)



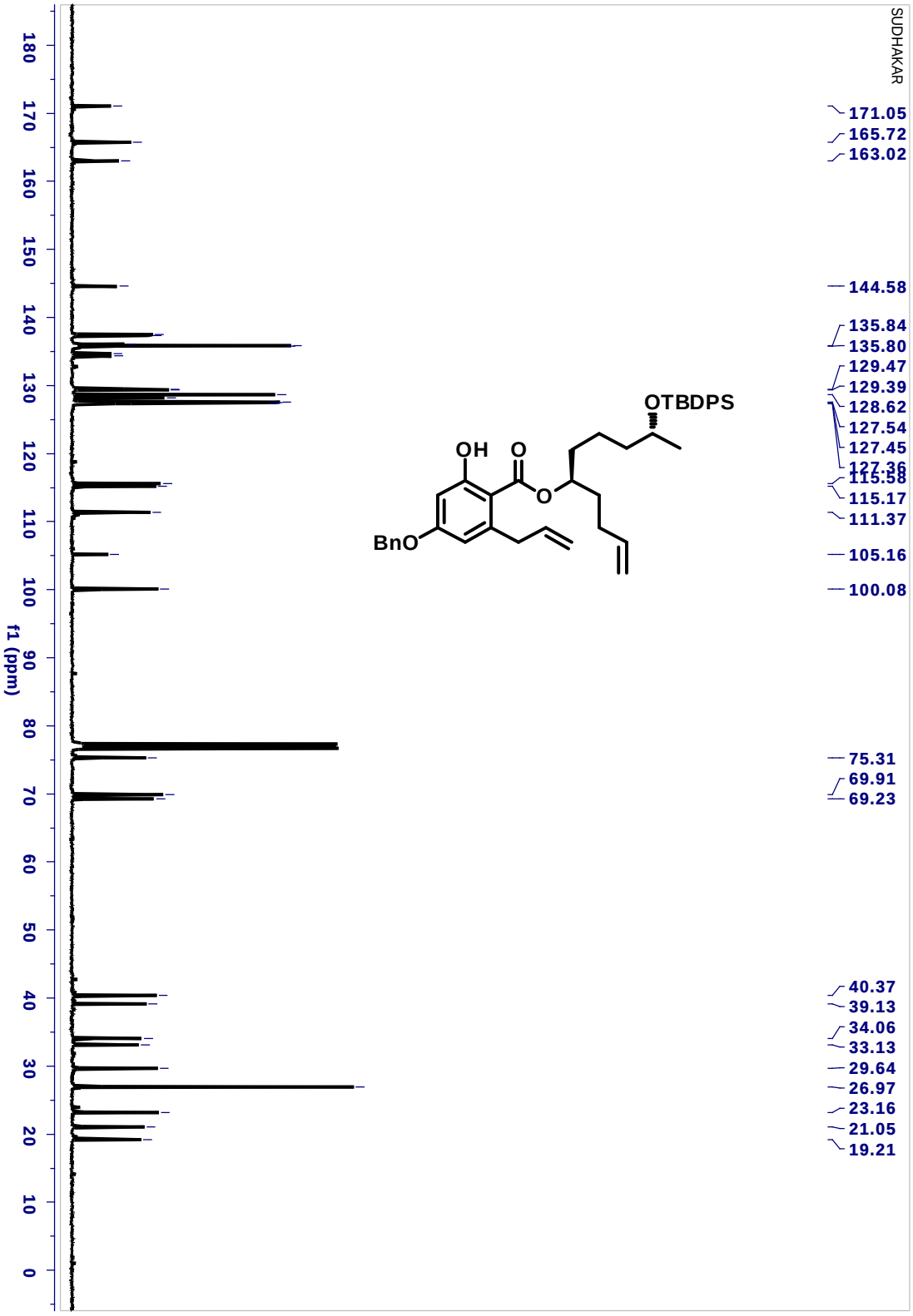
^{1}H NMR spectrum of 6a (400 MHz, $CDCl_3$)



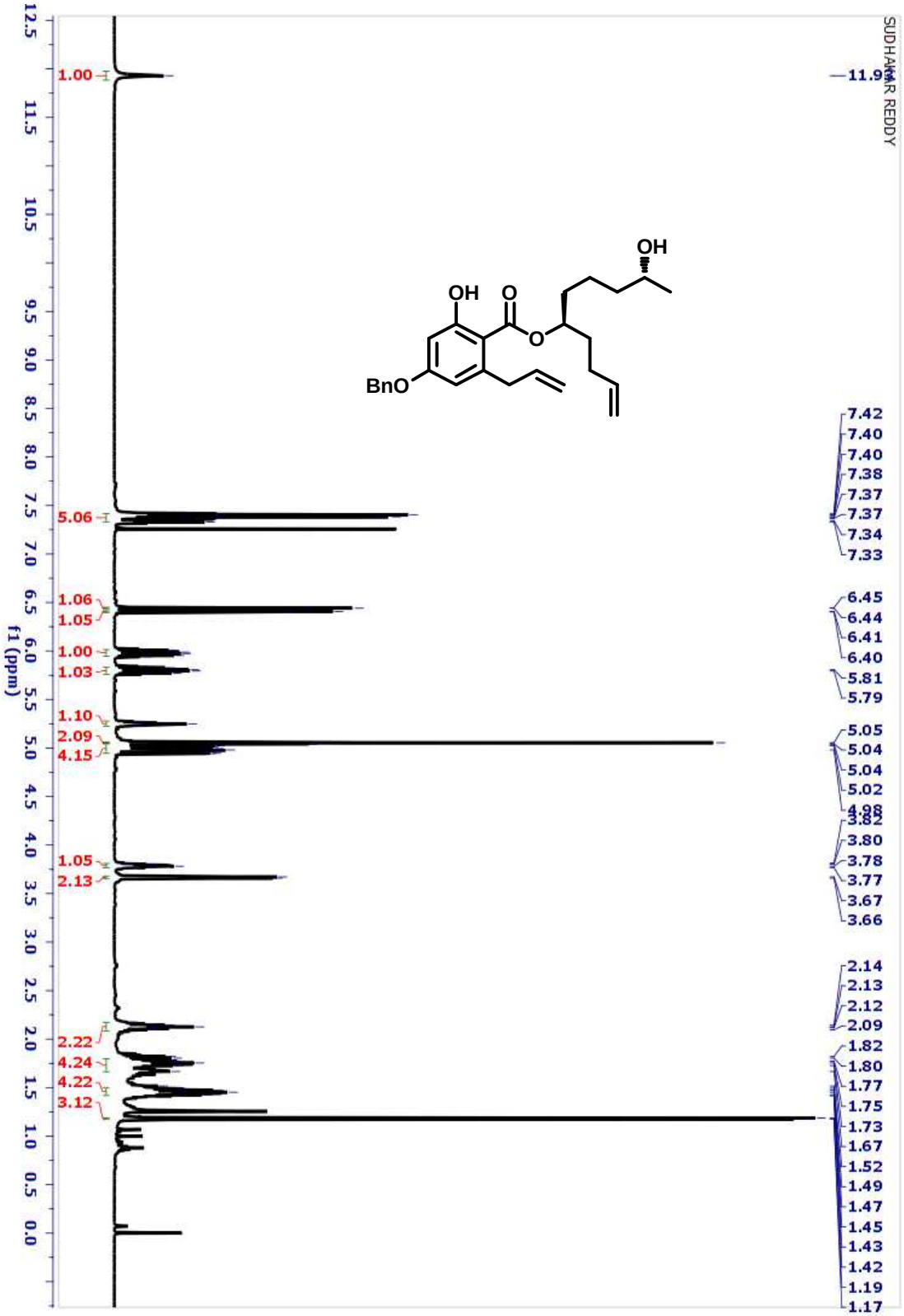
^{13}C NMR spectrum of 6a (100 MHz, $CDCl_3$)



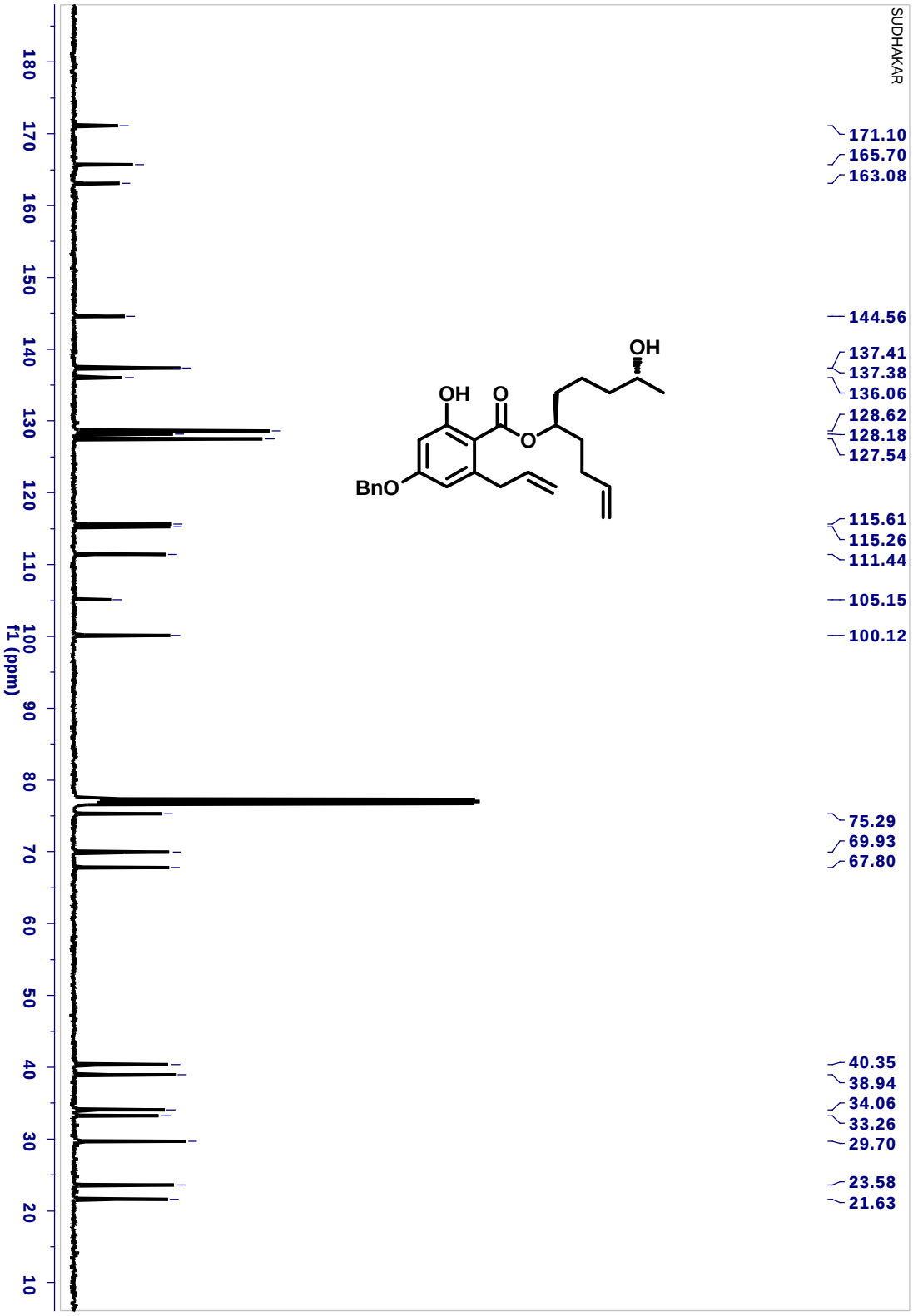
^{1}H NMR spectrum of 18 (400 MHz, $CDCl_3$)



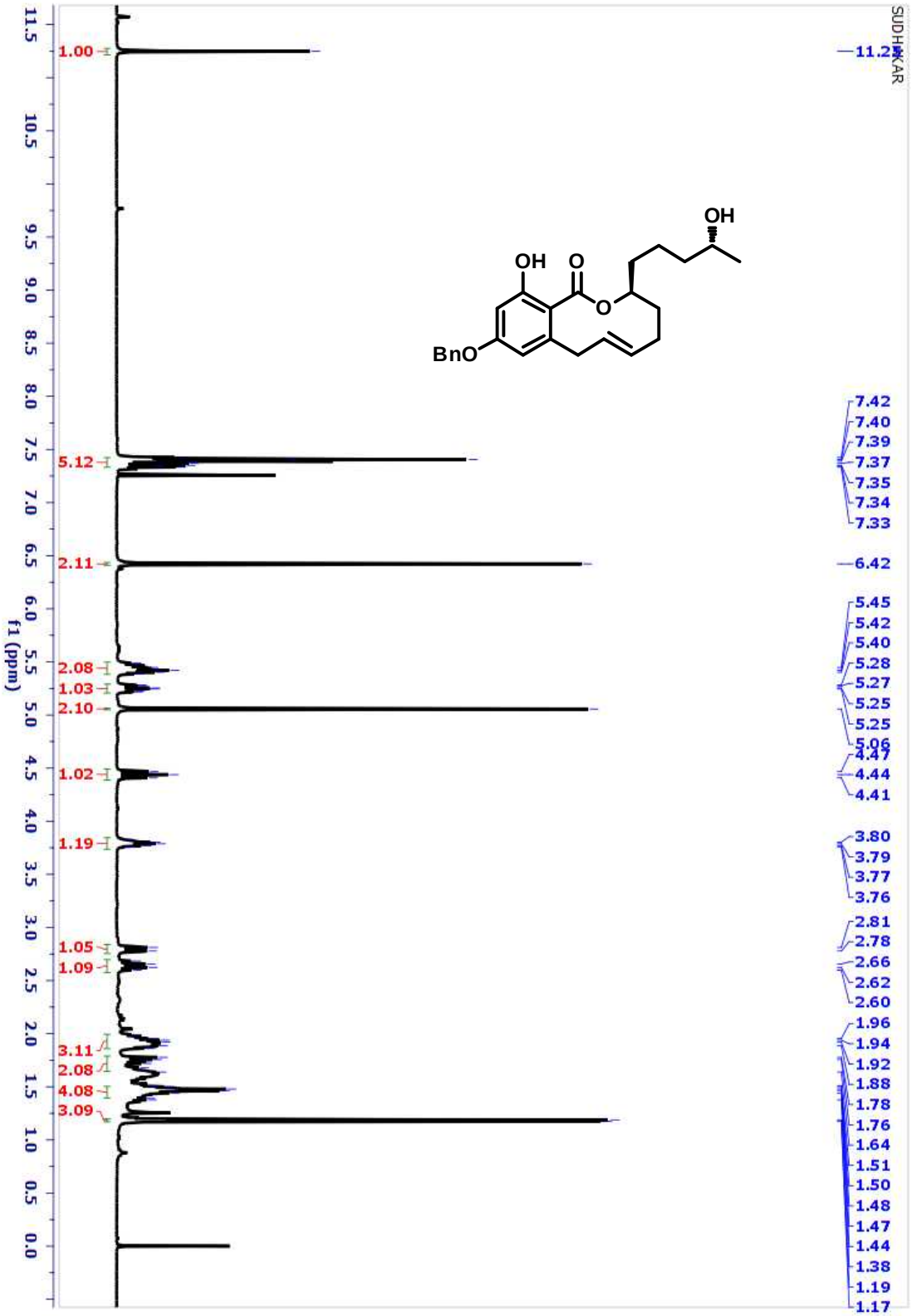
^{13}C NMR spectrum of 18 (100 MHz, $CDCl_3$)



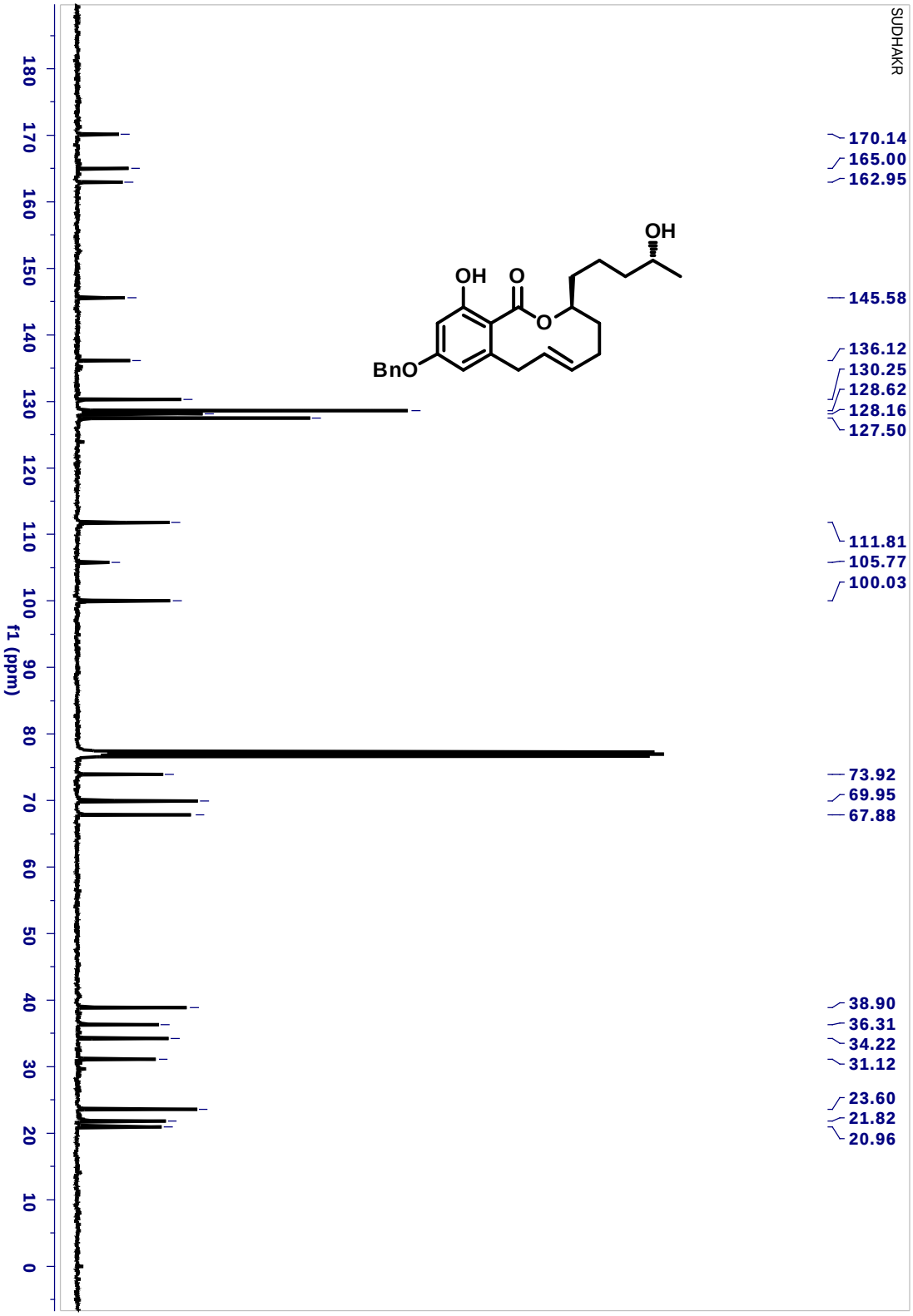
^{1}H NMR spectrum of 19 (500 MHz, $CDCl_3$)



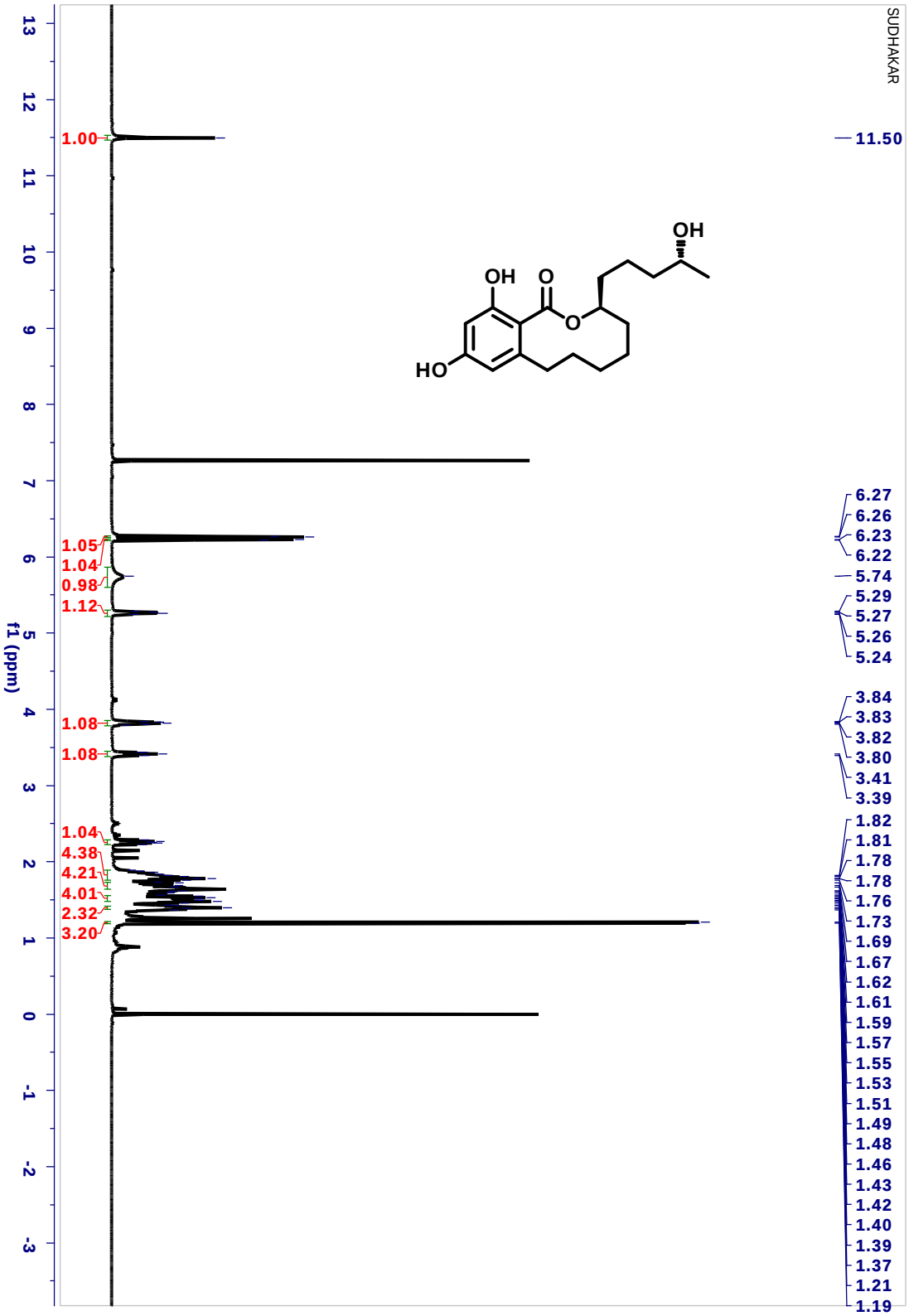
^{13}C NMR spectrum of 19 (100 MHz, $CDCl_3$)



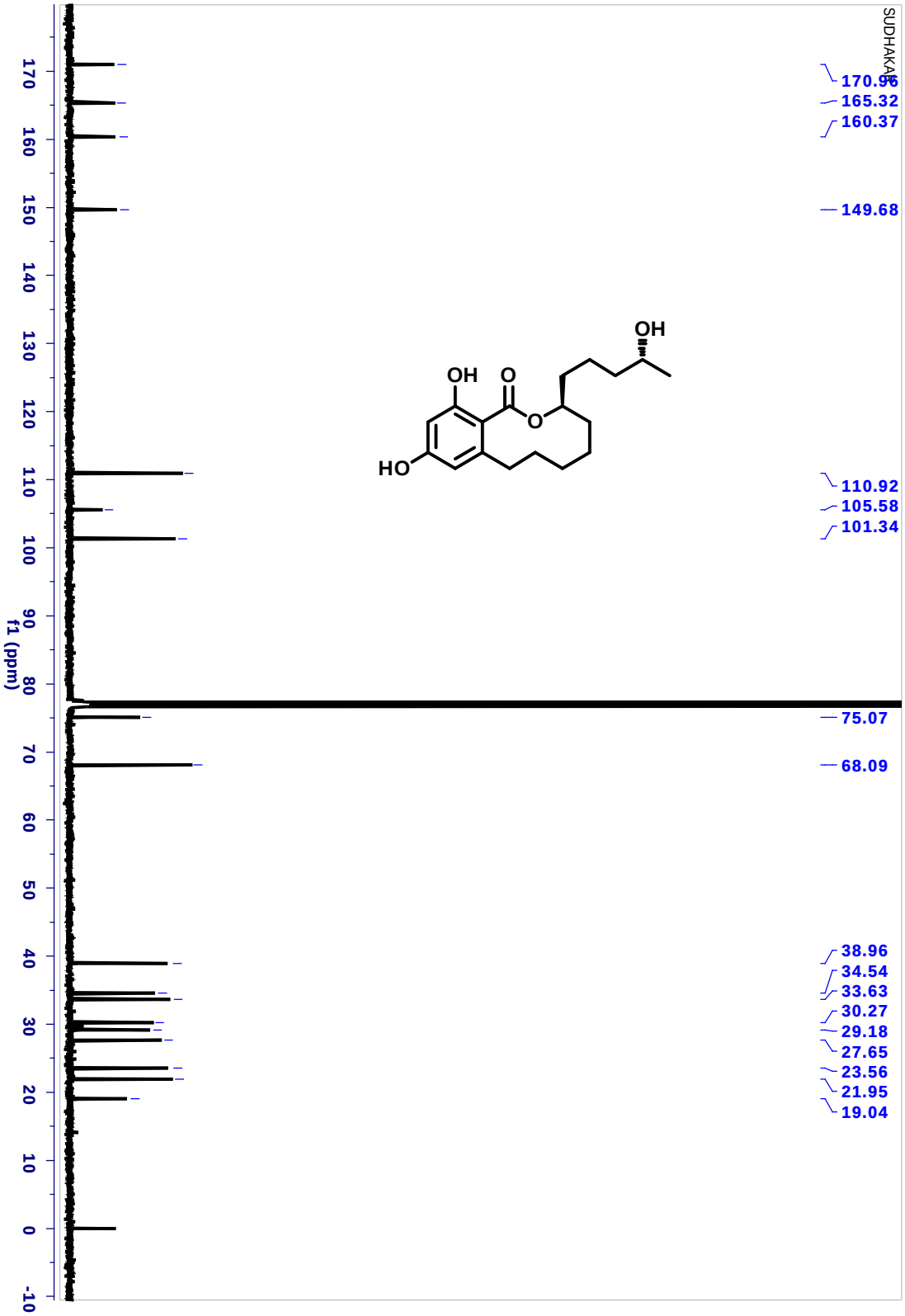
^{1}H NMR spectrum of 20 (500 MHz, $CDCl_3$)



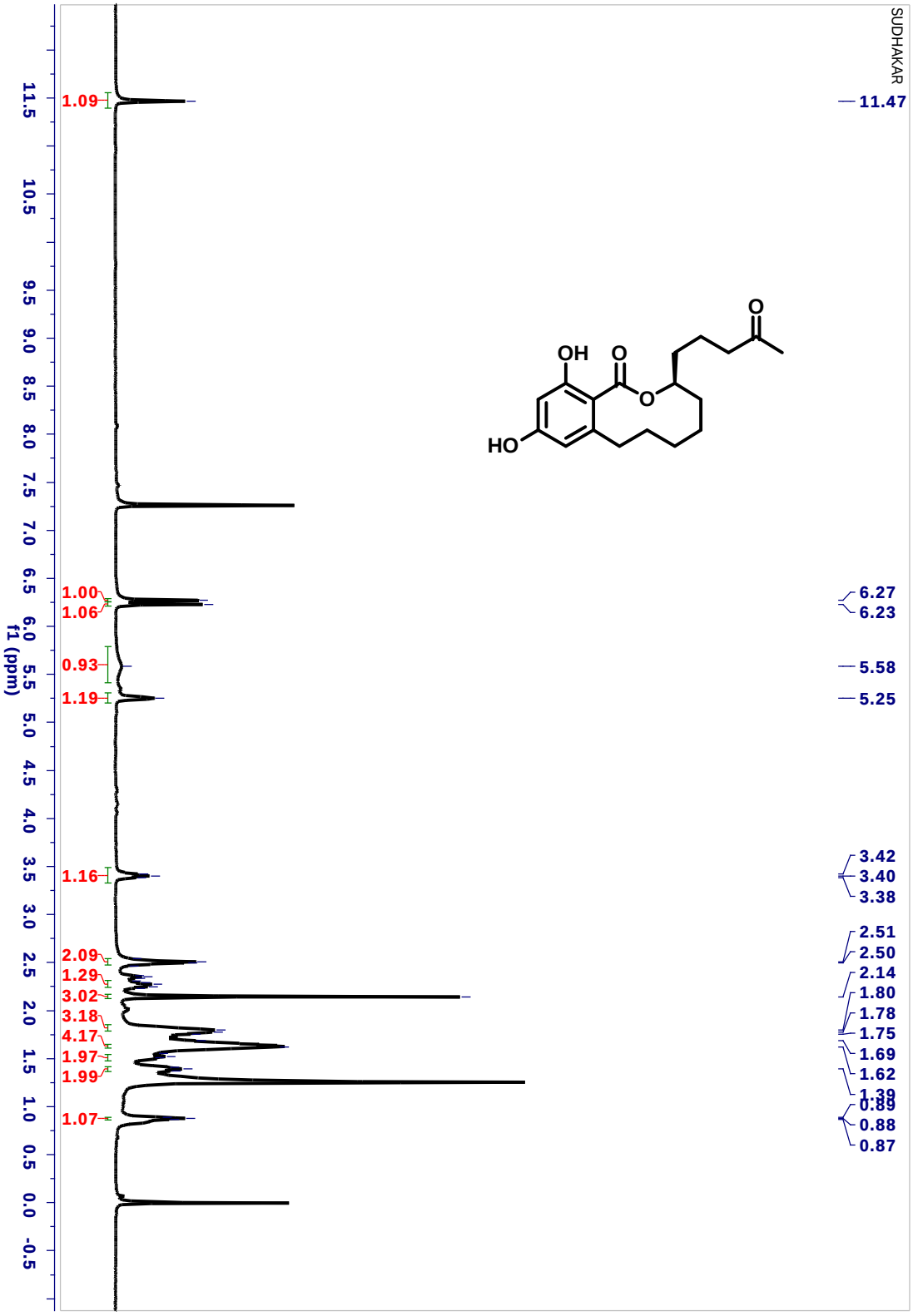
^{13}C NMR spectrum of 20 (100 MHz, $CDCl_3$)



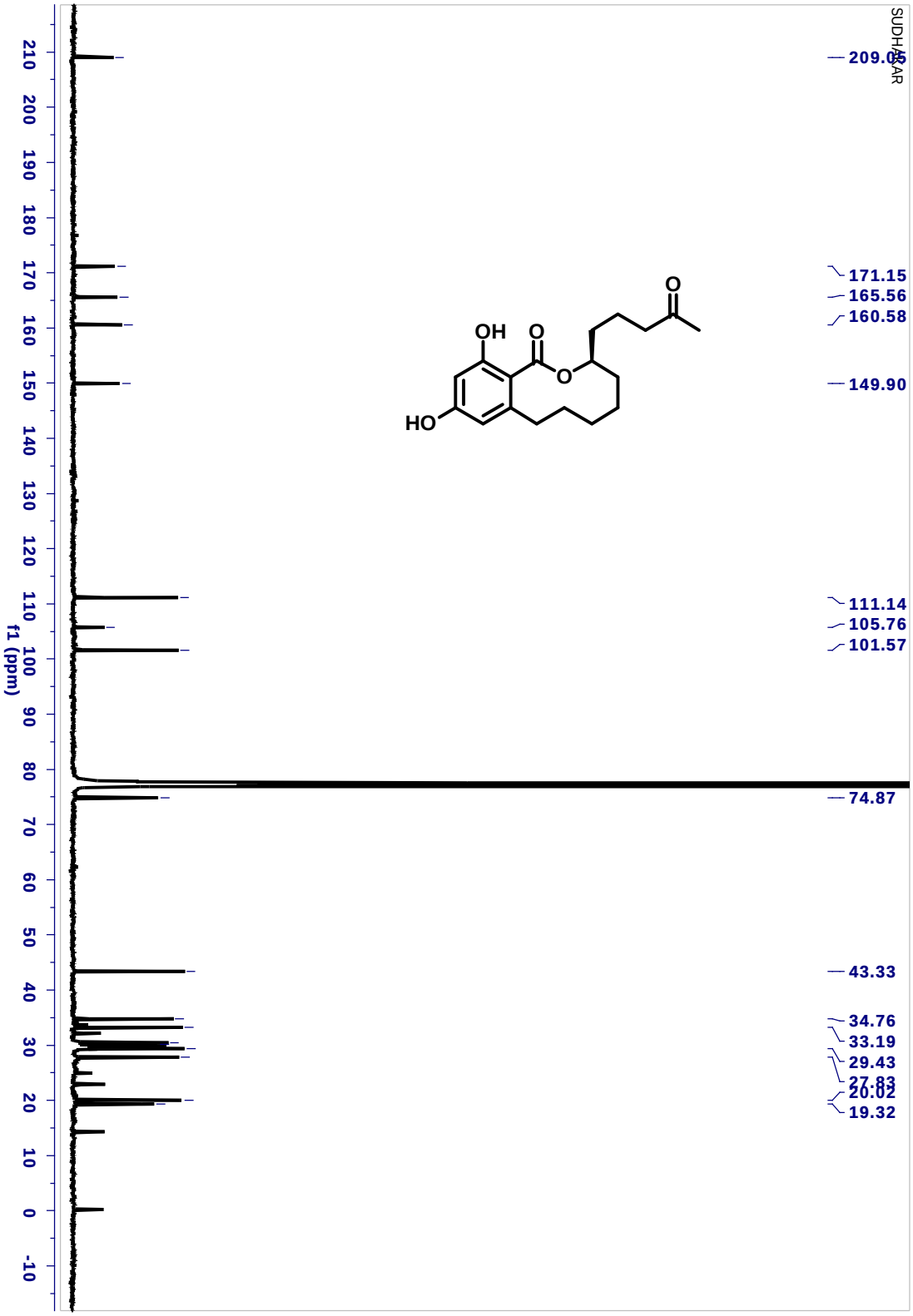
^{1}H NMR spectrum of 1a (500 MHz, $CDCl_3$)



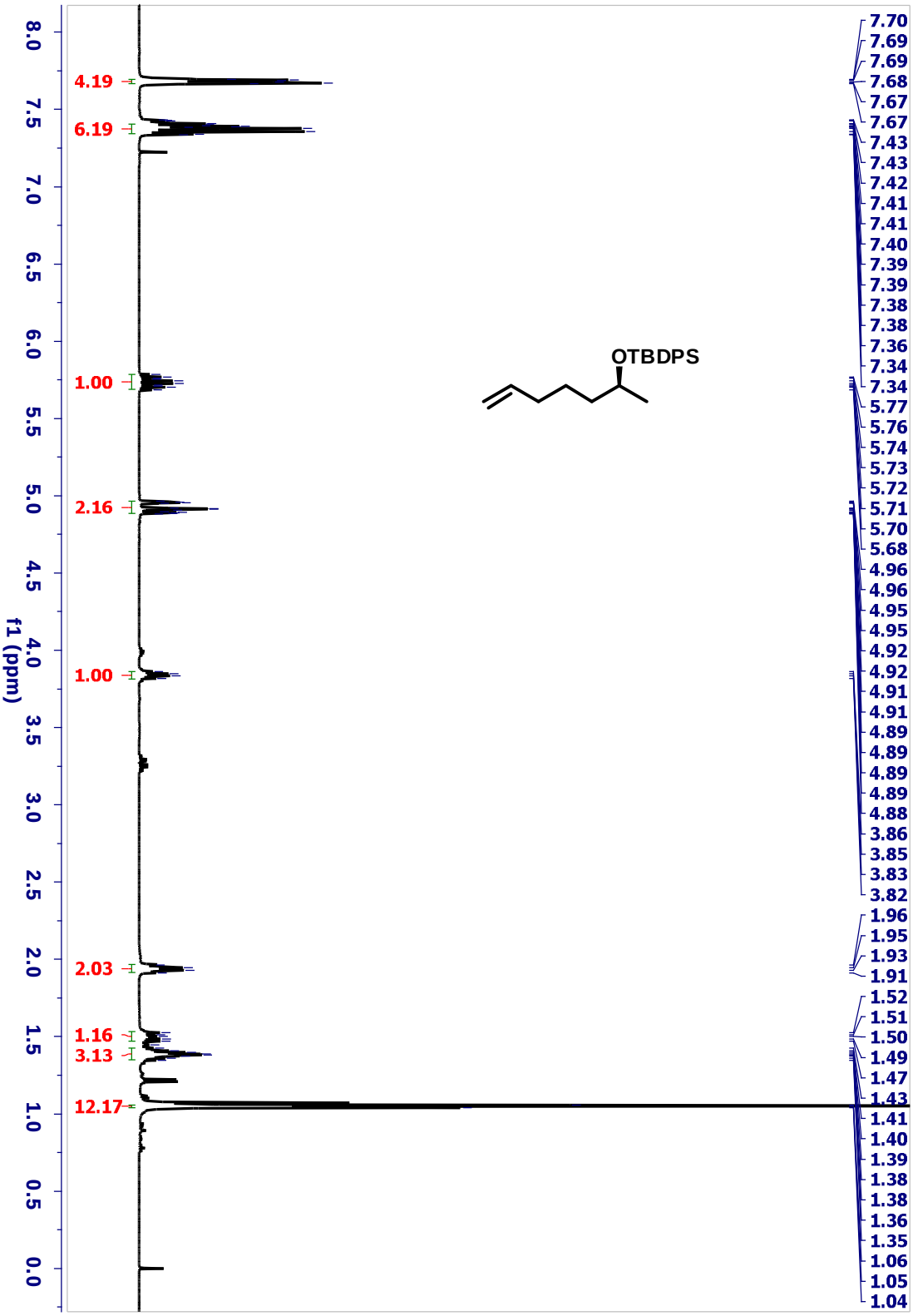
^{13}C NMR spectrum of 1a (125 MHz, $CDCl_3$)



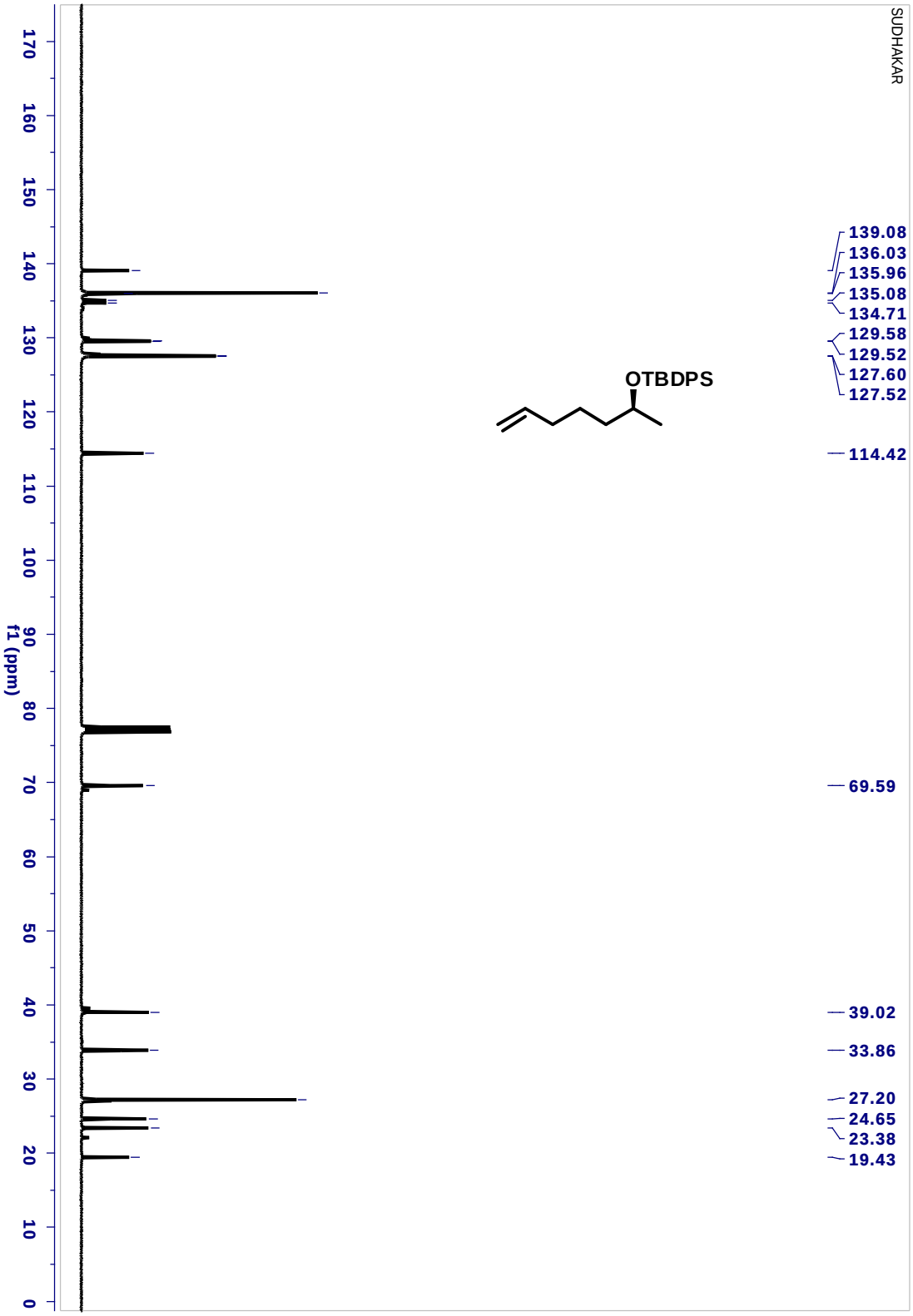
^{1}H NMR spectrum of 2 (400 MHz, $CDCl_3$)



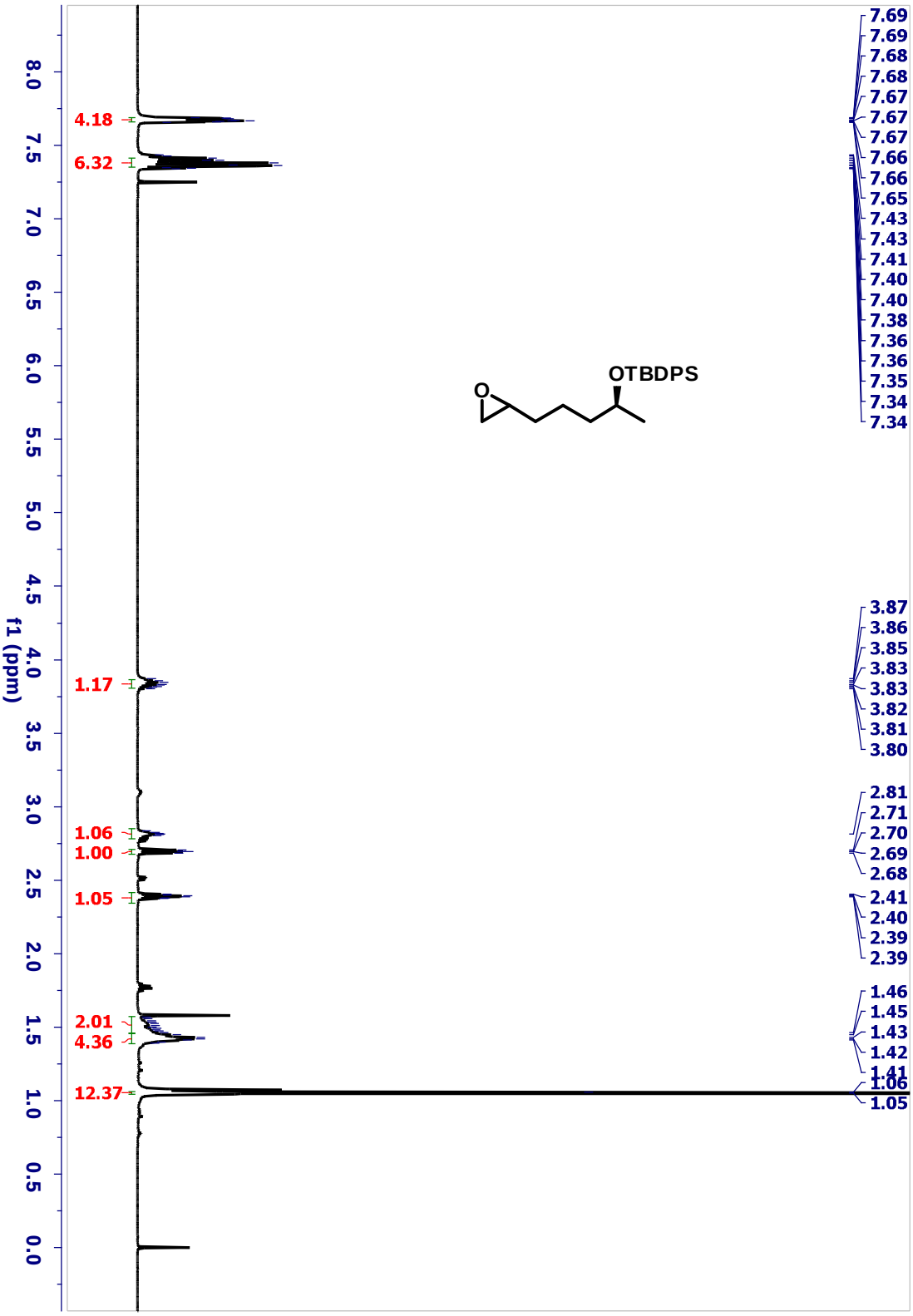
^{13}C NMR spectrum of 2 (100 MHz, $CDCl_3$)



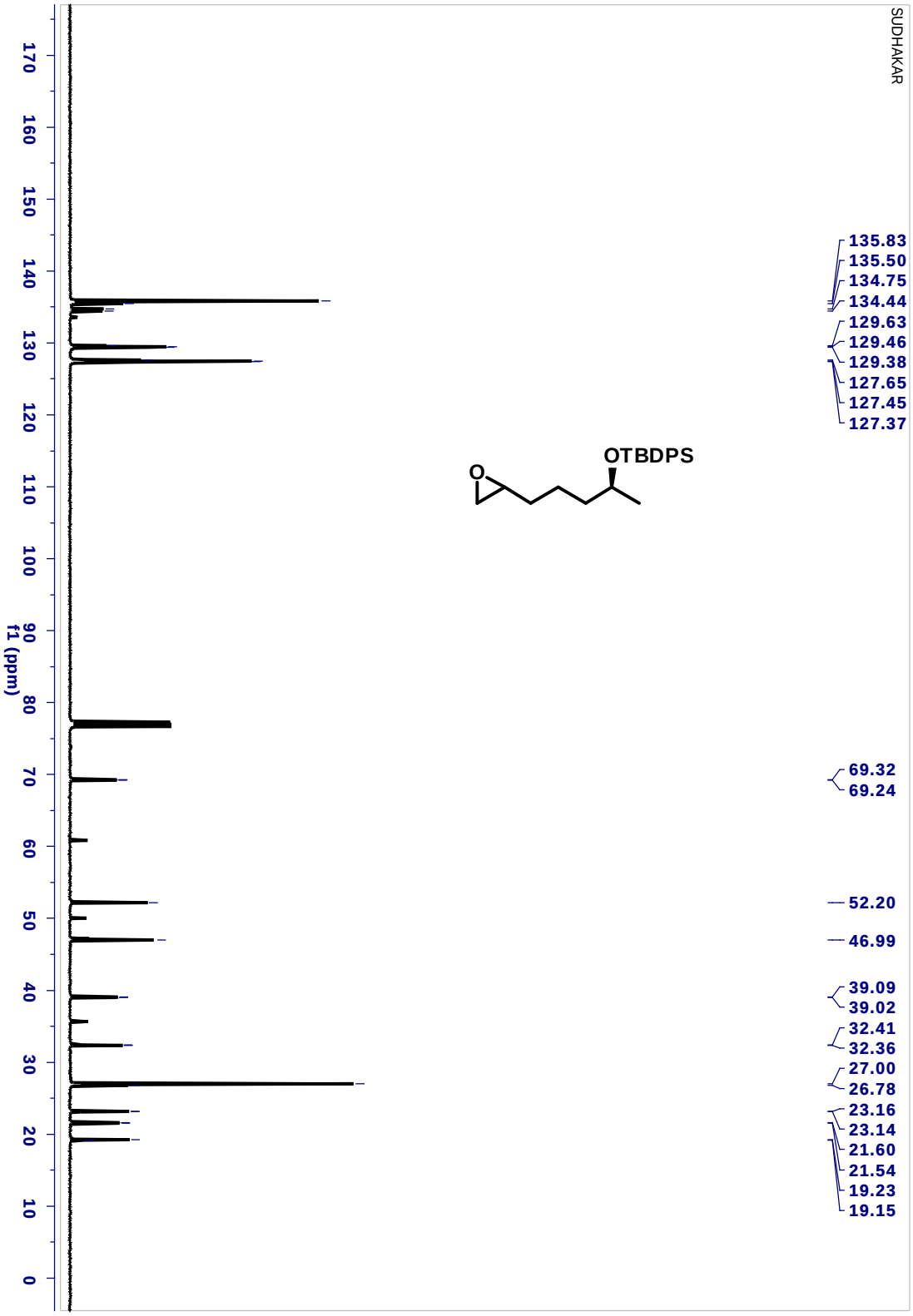
^{1}H NMR spectrum of 13b (400 MHz, $CDCl_3$)



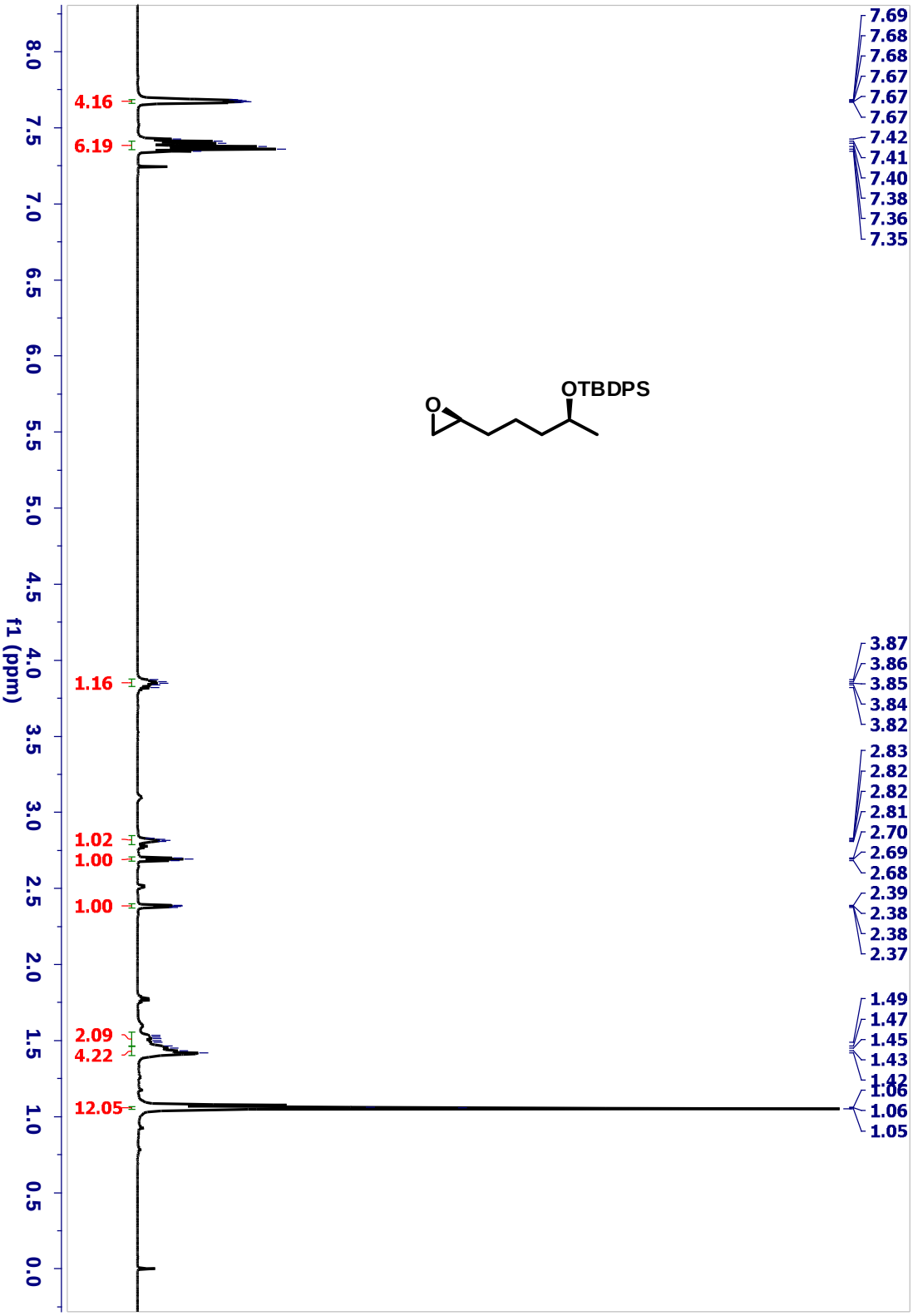
^{13}C NMR spectrum of 13b (100 MHz, $CDCl_3$)



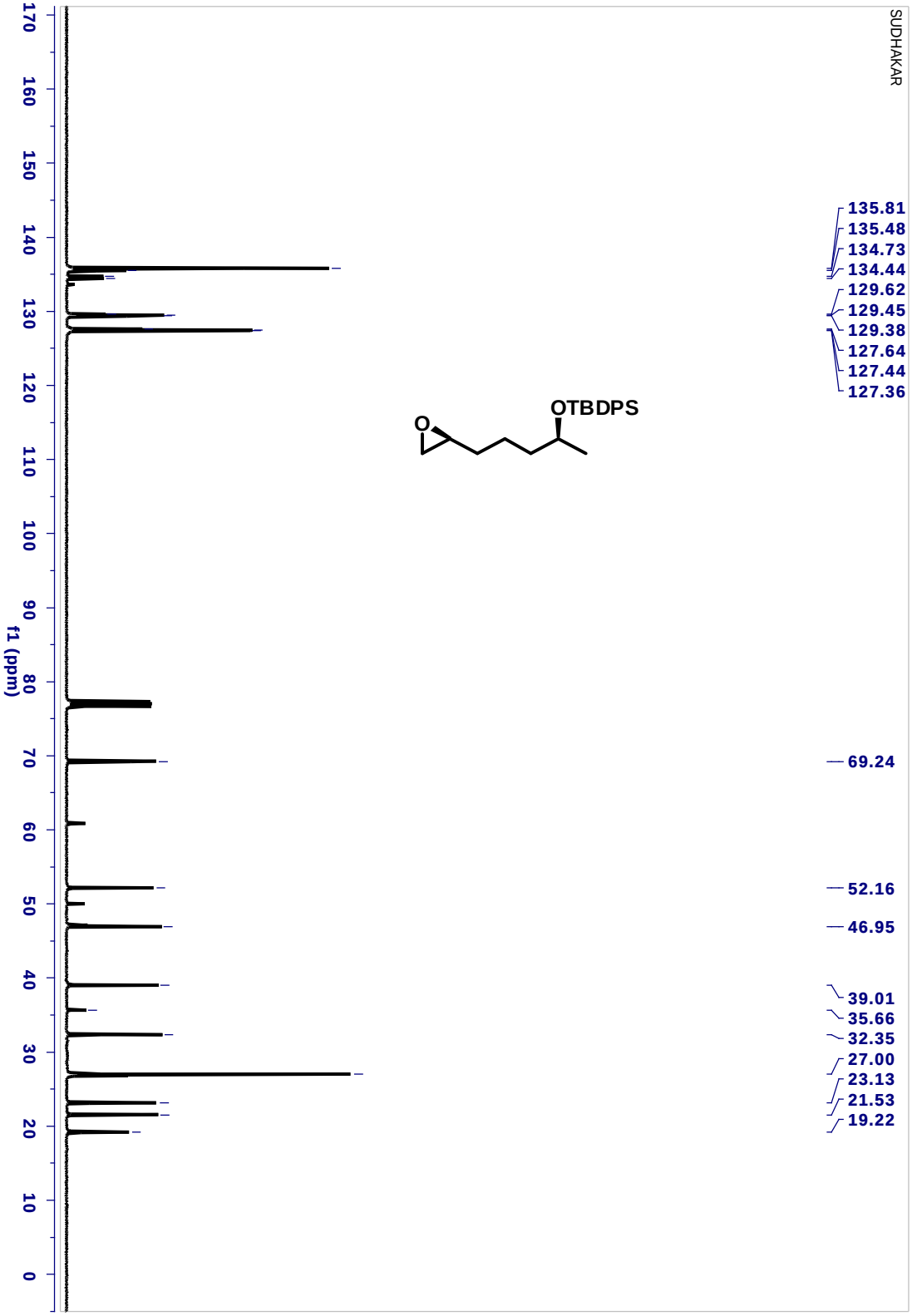
^{1}H NMR spectrum of 14b (400 MHz, $CDCl_3$)



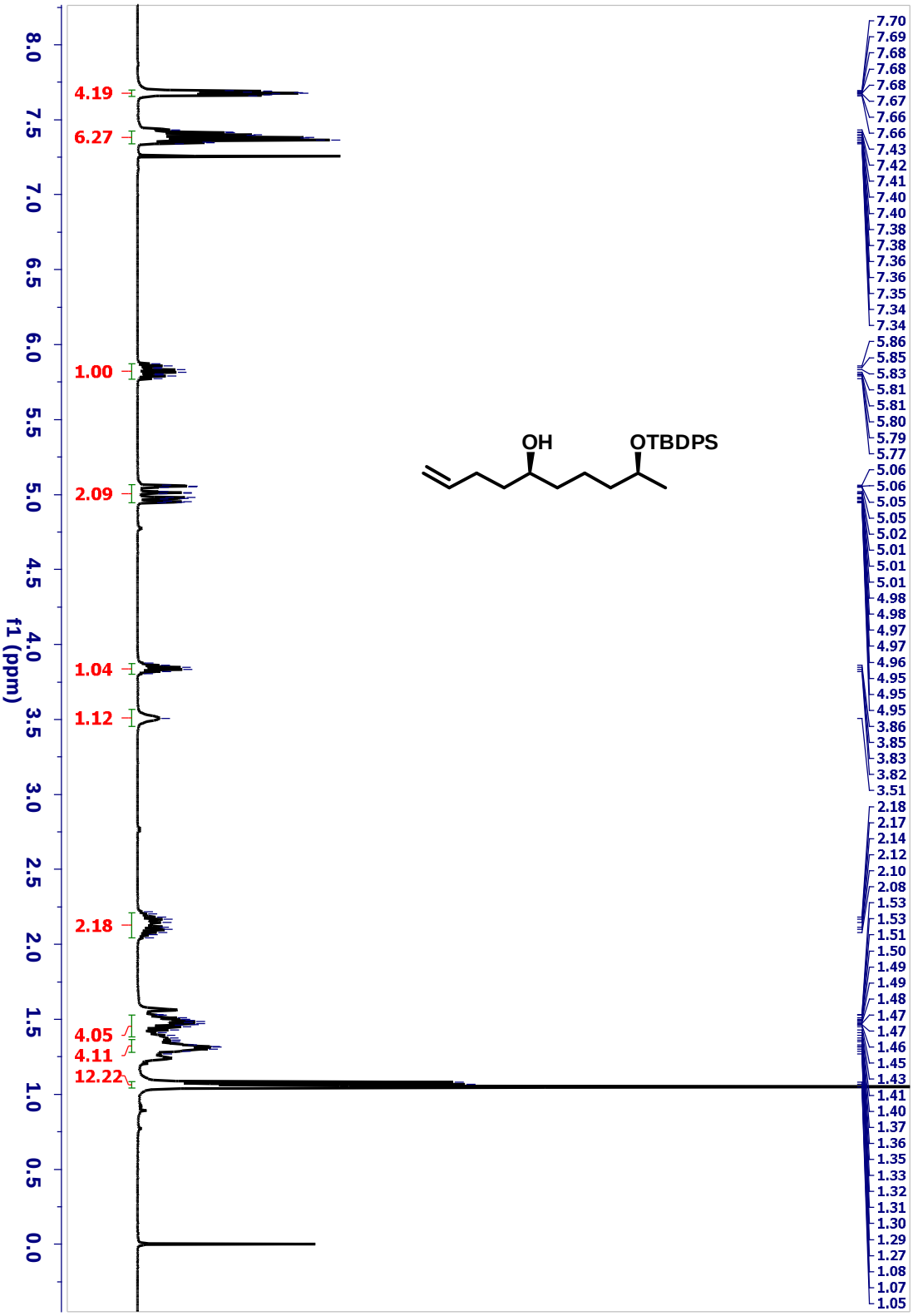
^{13}C NMR spectrum of 14b (100 MHz, $CDCl_3$)



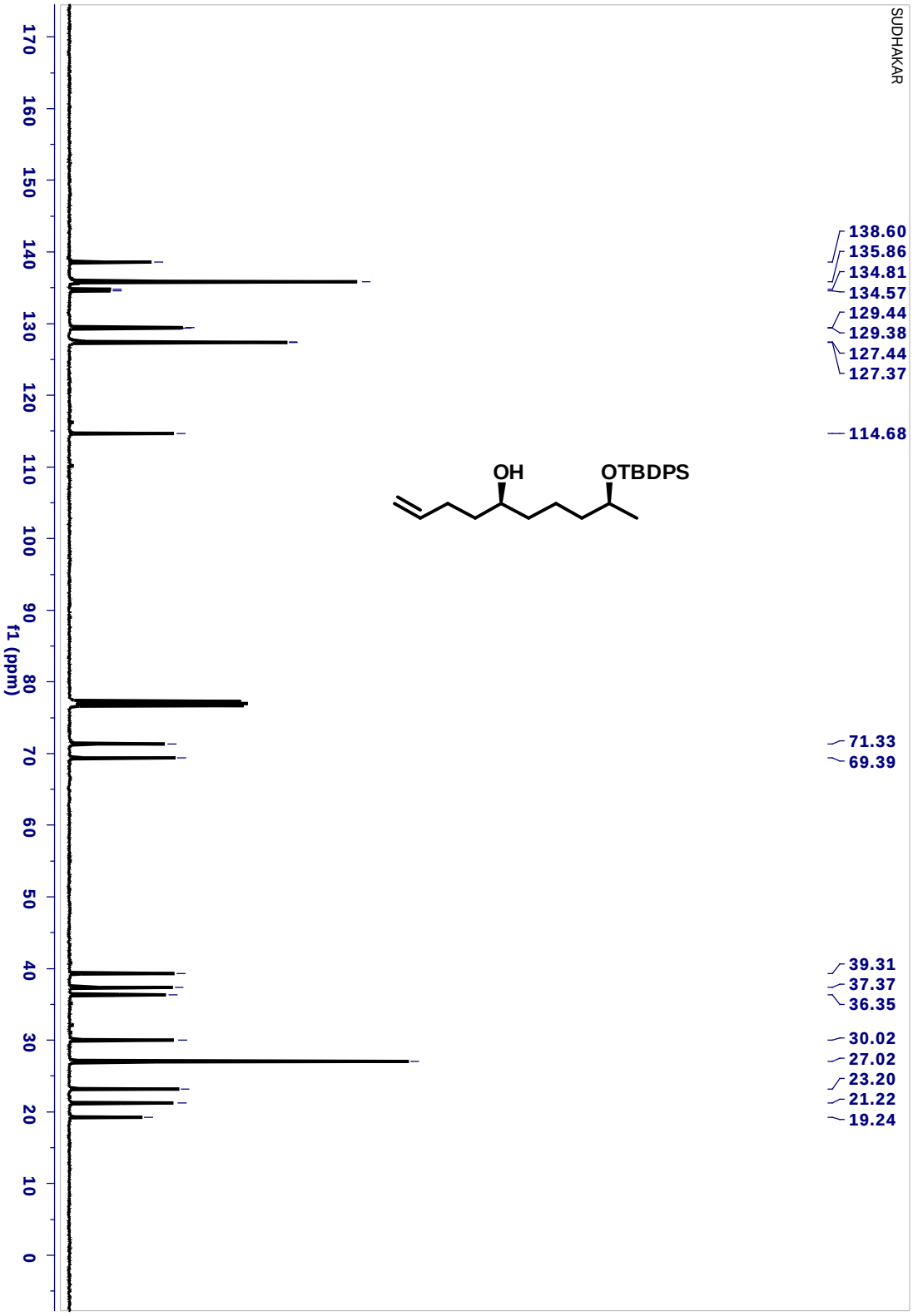
^{1}H NMR spectrum of 15b (500 MHz, $CDCl_3$)



^{13}C NMR spectrum of 15b (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of 6b (400 MHz, $CDCl_3$)

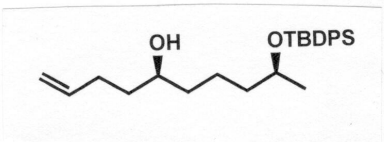


^{13}C NMR spectrum of 6b (100 MHz, $CDCl_3$)

SHIMADZU LabSolutions

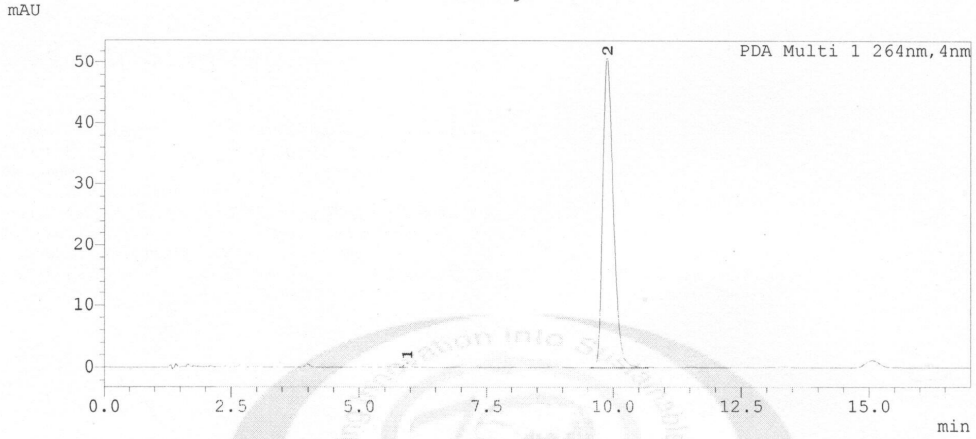
LC-MS DATA REPORT

IICT-DNPC



Sample Code : DKM-GSR-ALLYOP-410
Data File : 080518.4.lcd
Method : HPLC_ISO.lcm
Injection Volume : 5
Date Acquired : 5/8/2018 5:39:09 PM
Report File : Mass Data Report.lsr
Chromatographic Conditions : olumn: ECLIPSE XDB-C18 (150 X 4.6mm, 5u)
Mobile Phase: 90%ACN in 0.1% Formic Acid
Flow Rate: 1.0 mL/min

Chromatogram

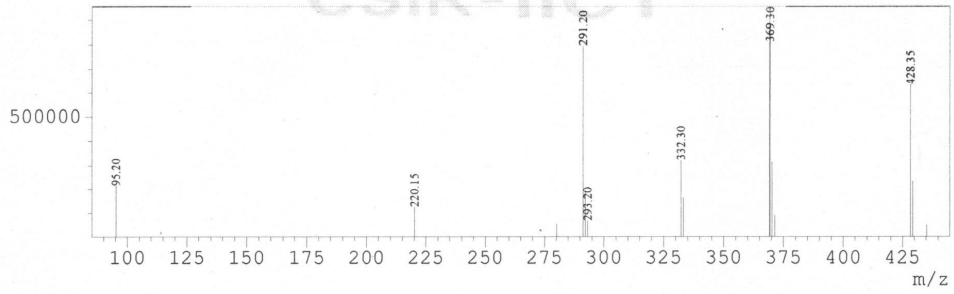


Peak Table

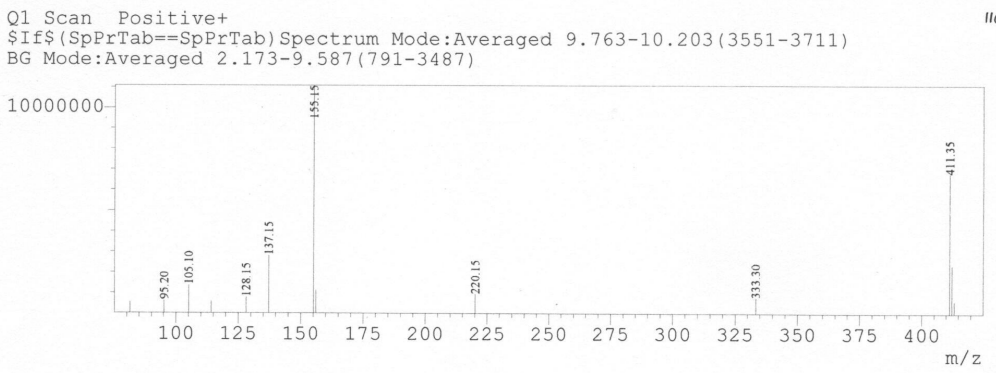
PDA Ch1 264nm

Peak#	Ret. Time	Peak Start	Peak End	Area	Area%
1	5.936	5.760	6.165	5682	0.771
2	9.872	9.536	10.688	731102	99.229
Total				736784	100.000

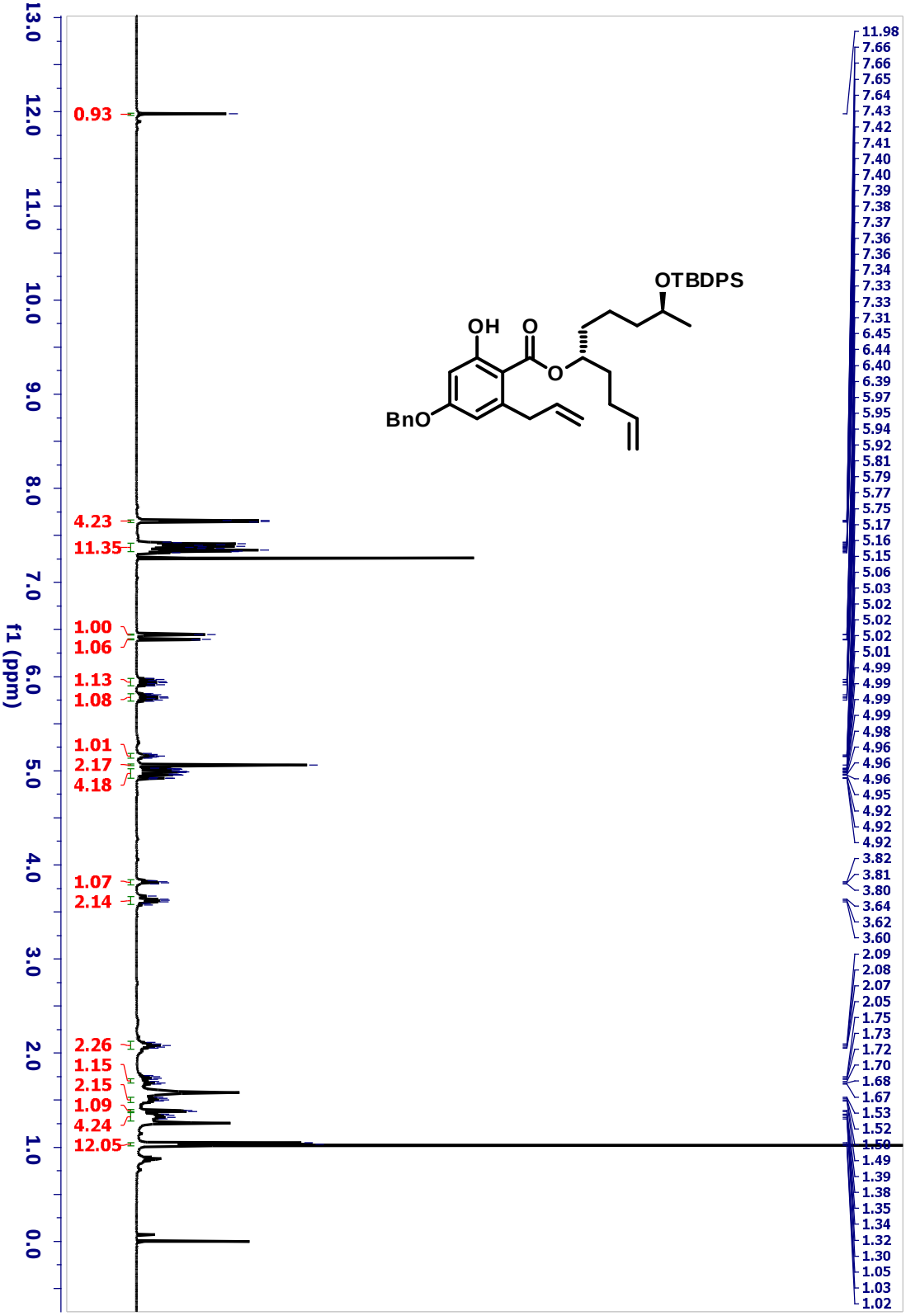
Q1 Scan Positive+
If(SpPrTab==SpPrTab)Spectrum Mode:Averaged 5.880-6.094(2139-2217)
BG Mode:Averaged 0.930-5.654(339-2057)



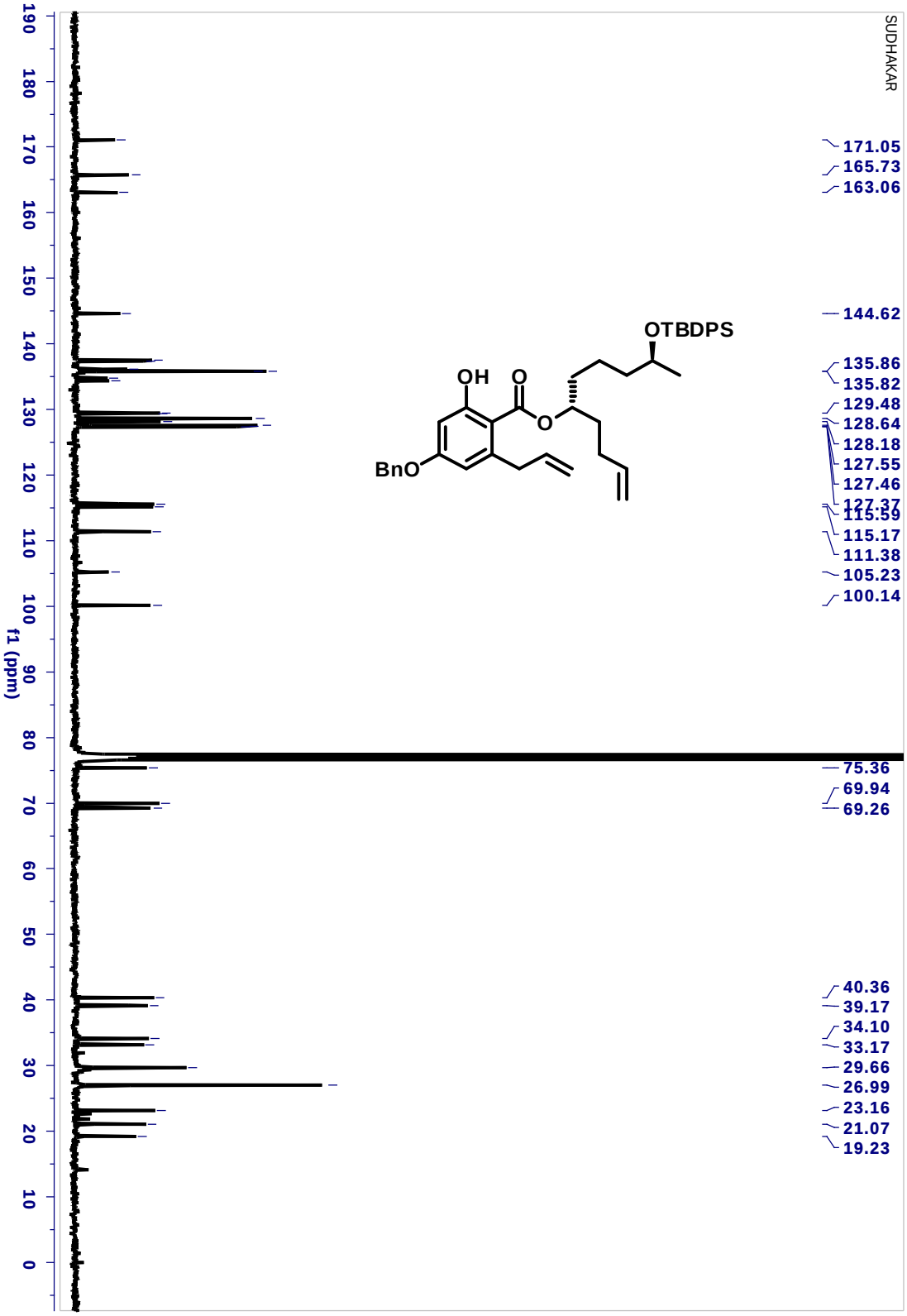
LC-LCMS Chromatogram of 6b



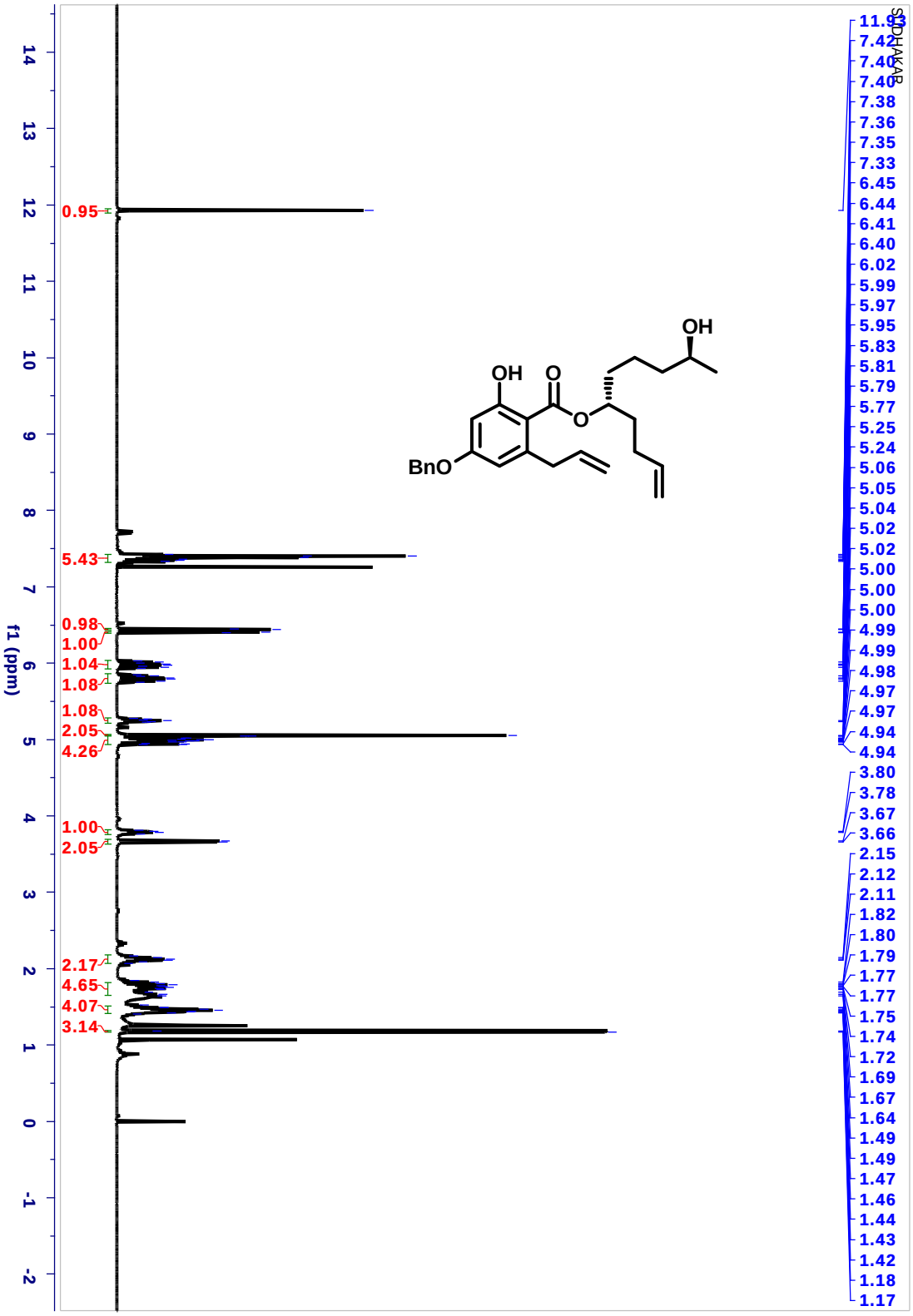
LC-LCMS Chromatogram of 6b



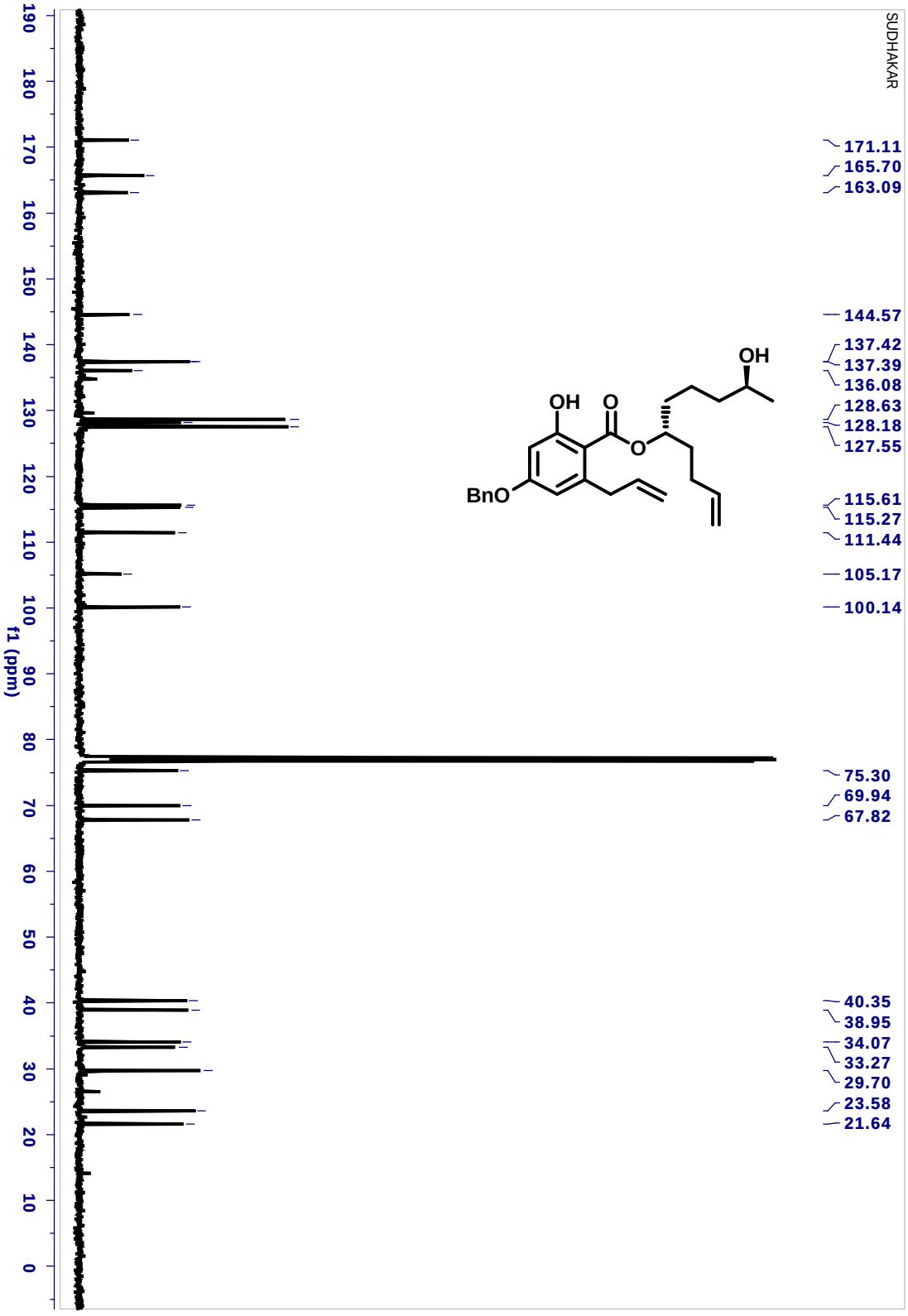
^{1}H NMR spectrum of 18a (500 MHz, $CDCl_3$)



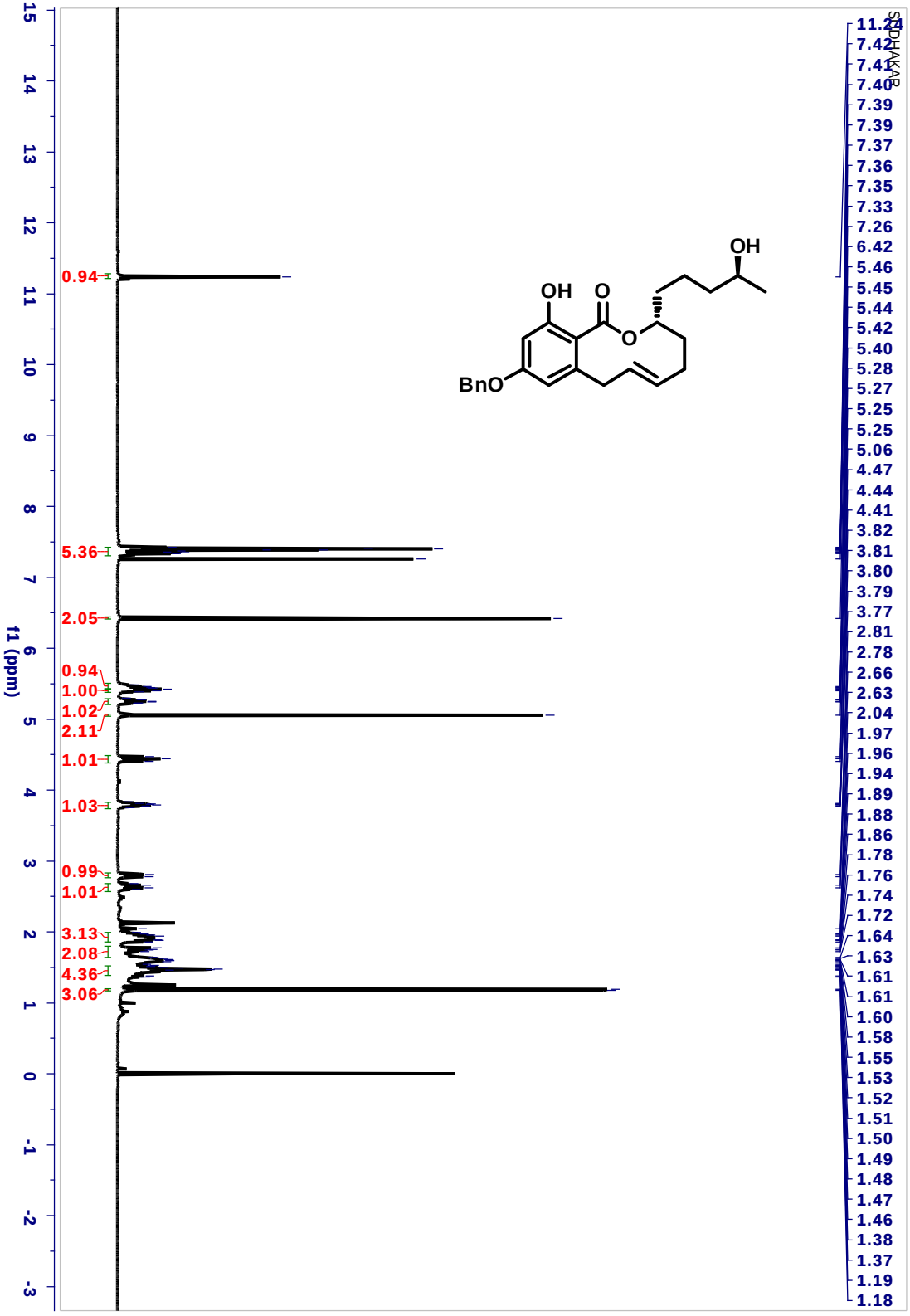
^{13}C NMR spectrum of 18a (100 MHz, $CDCl_3$)



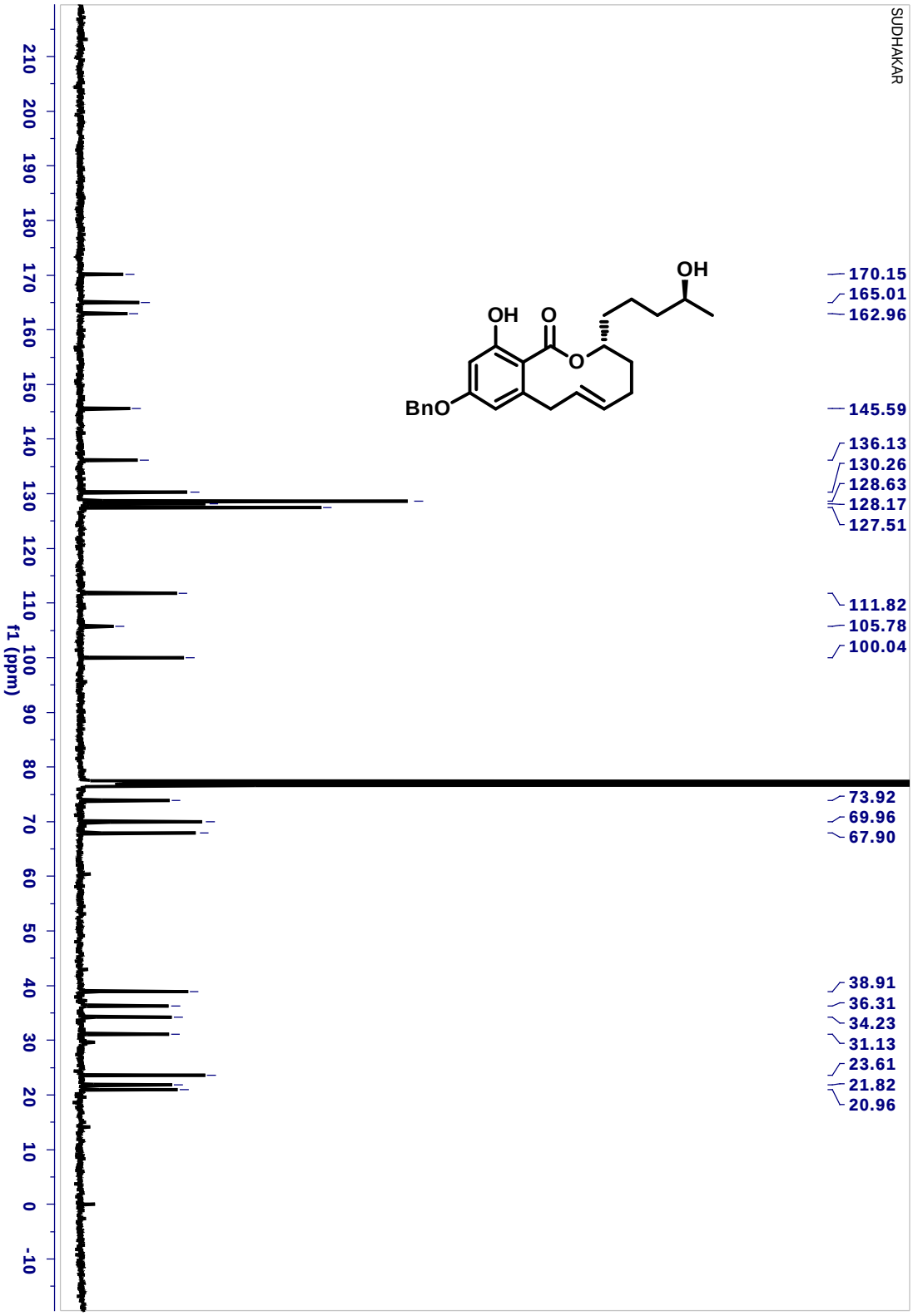
^{1}H NMR spectrum of 19a (500 MHz, $CDCl_3$)



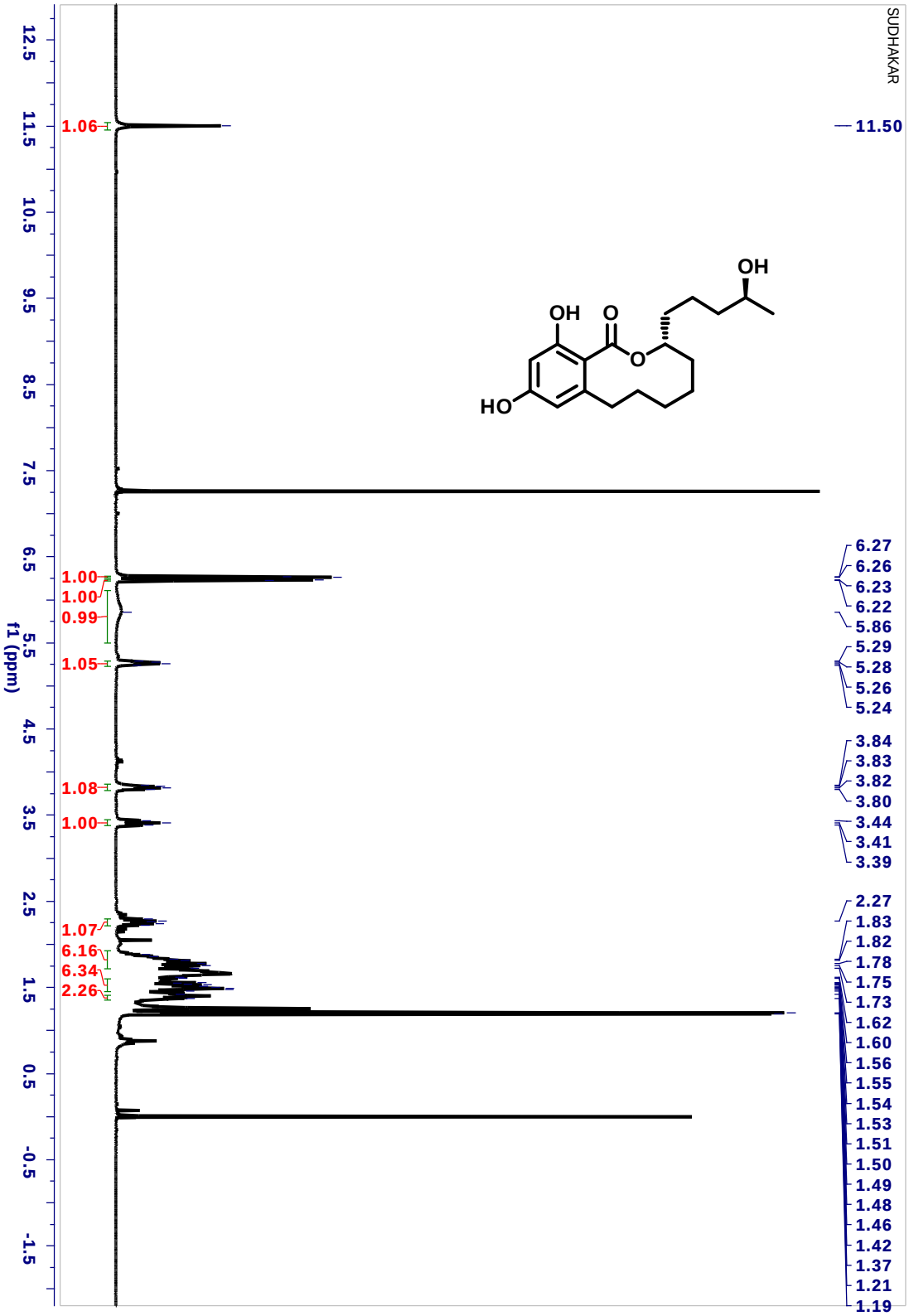
^{13}C NMR spectrum of 19a (100 MHz, $CDCl_3$)



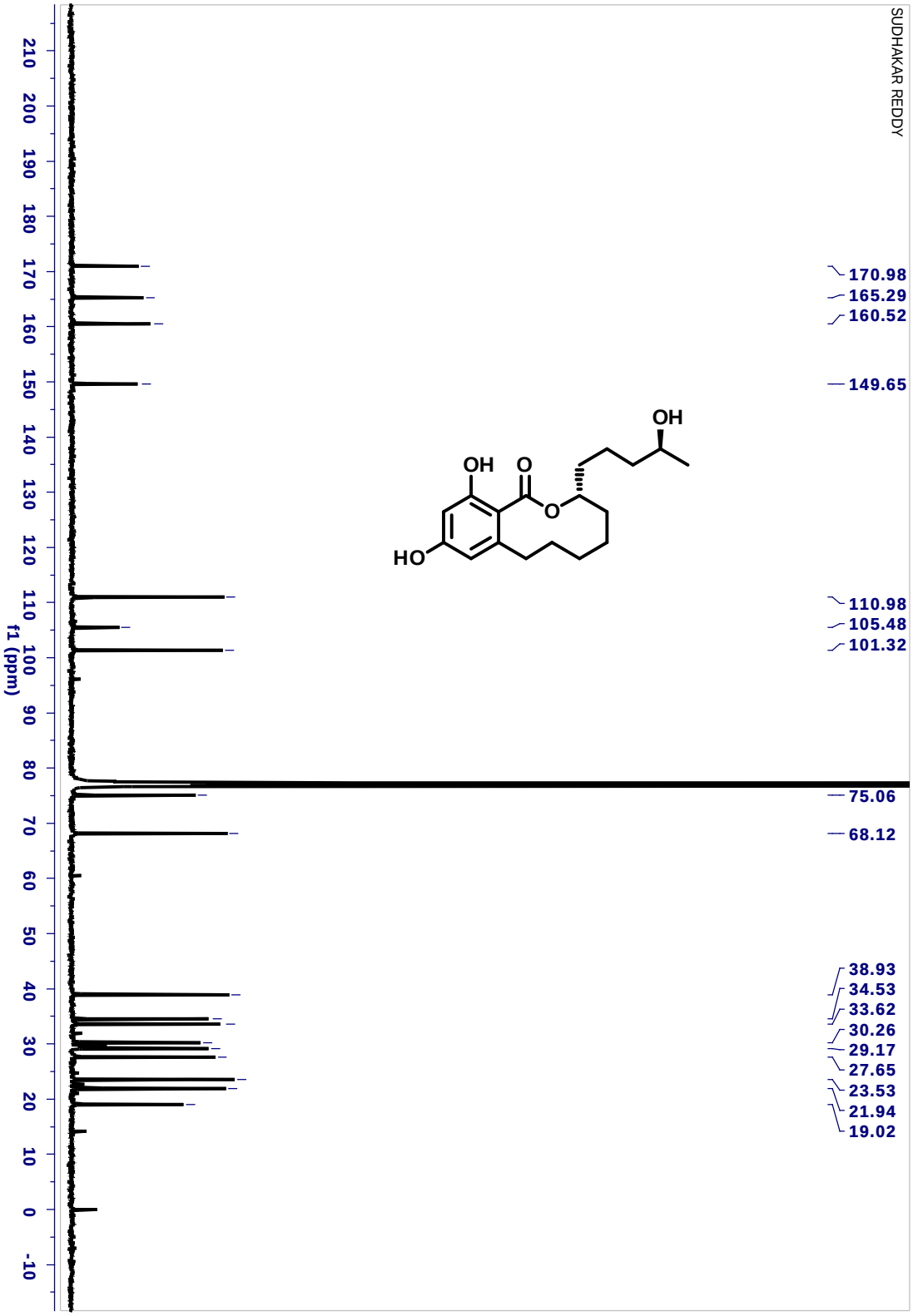
^{1}H NMR spectrum of 20a (500 MHz, $CDCl_3$)



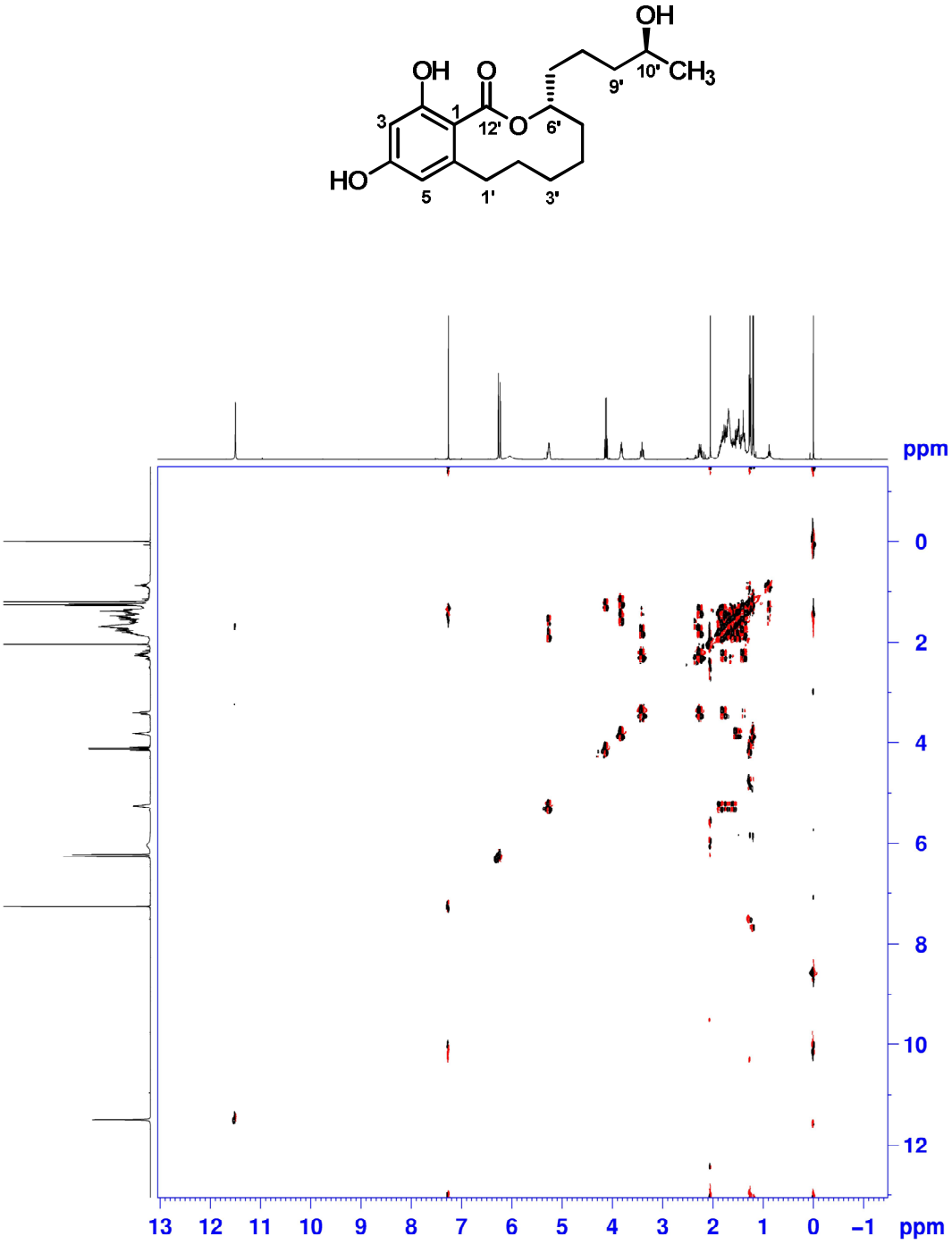
^{13}C NMR spectrum of 20a (100 MHz, $CDCl_3$)



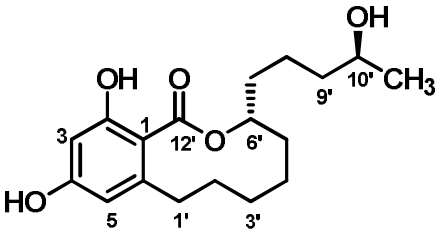
^{1}H NMR spectrum of 1b (400 MHz, $CDCl_3$)

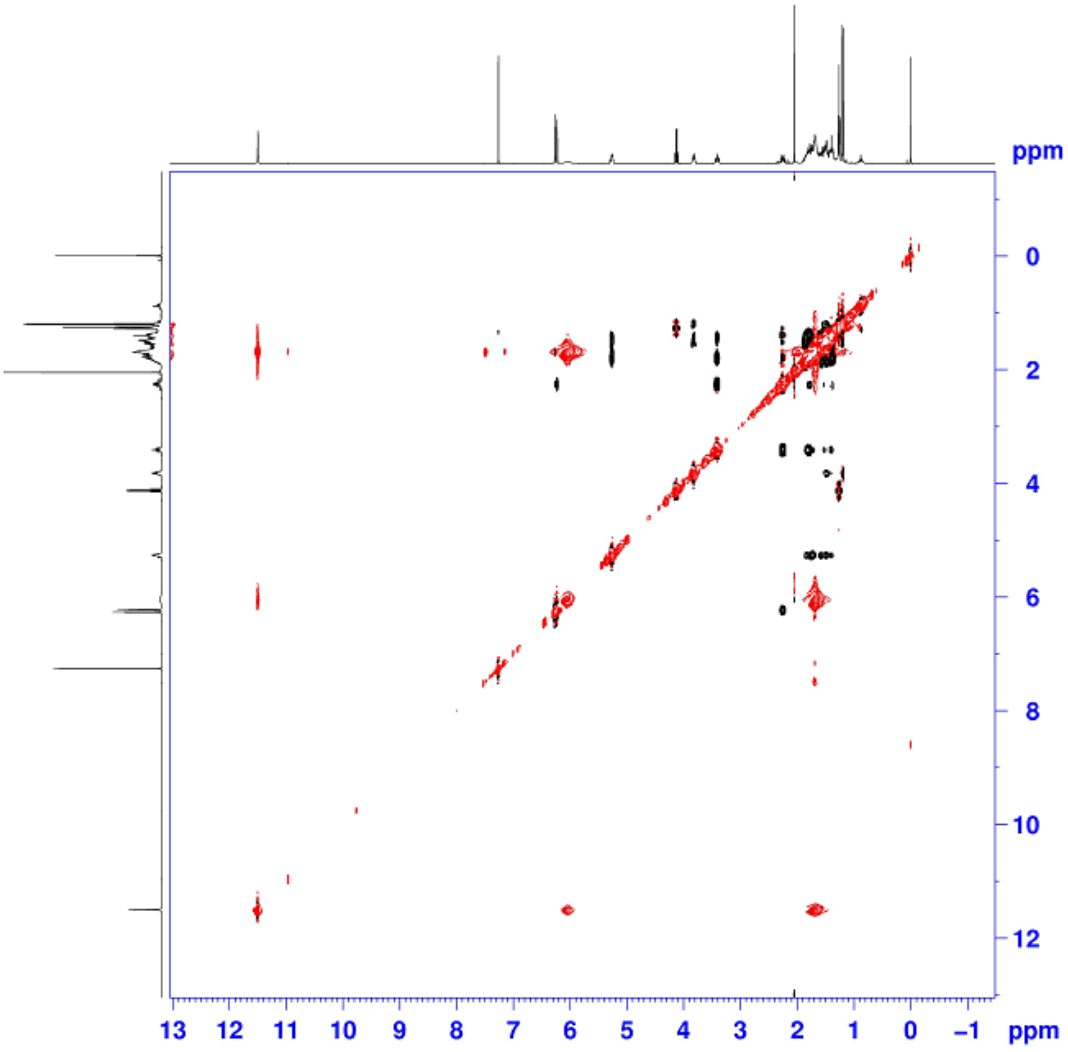


^{13}C NMR spectrum of 1b (400 MHz, $CDCl_3$)

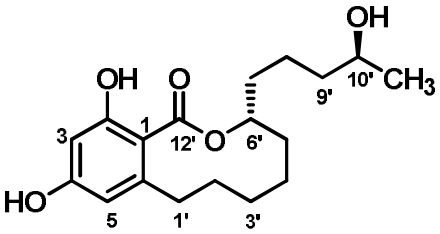


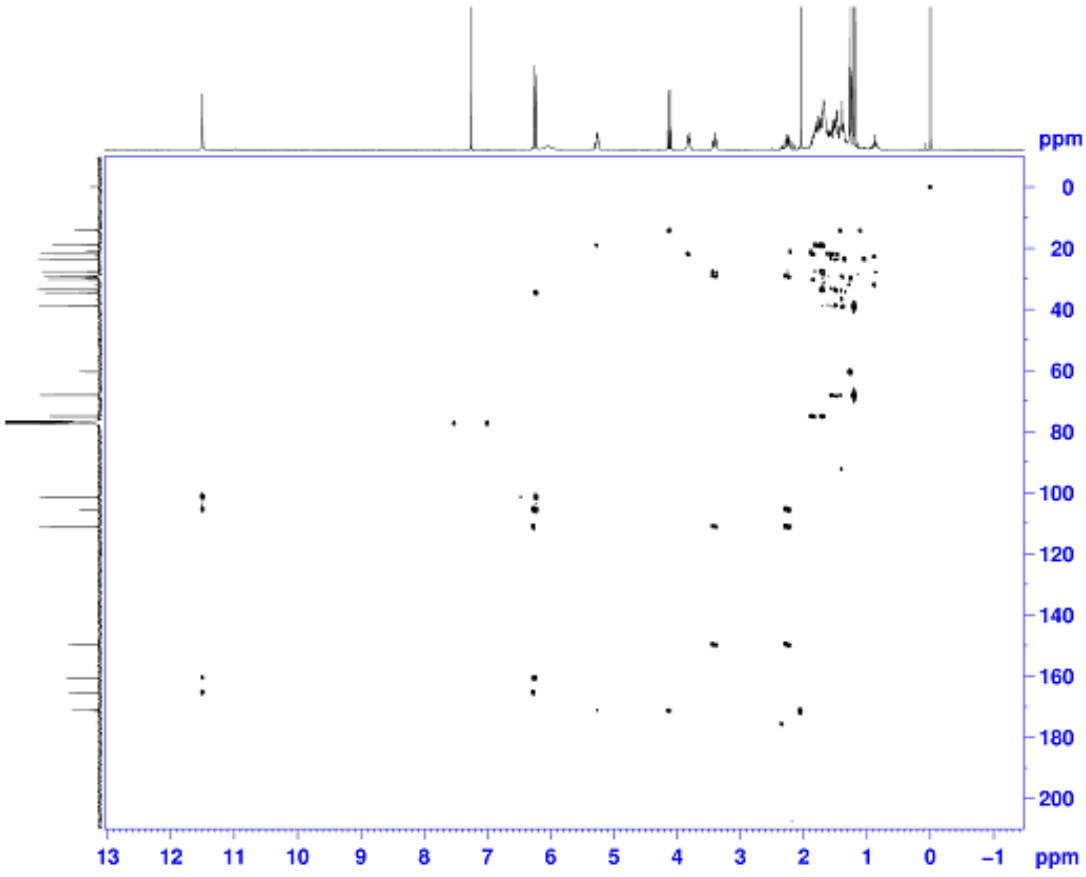
DQFCOSY spectrum of 1b ($CDCl_3$, 295 K, 400 MHz)



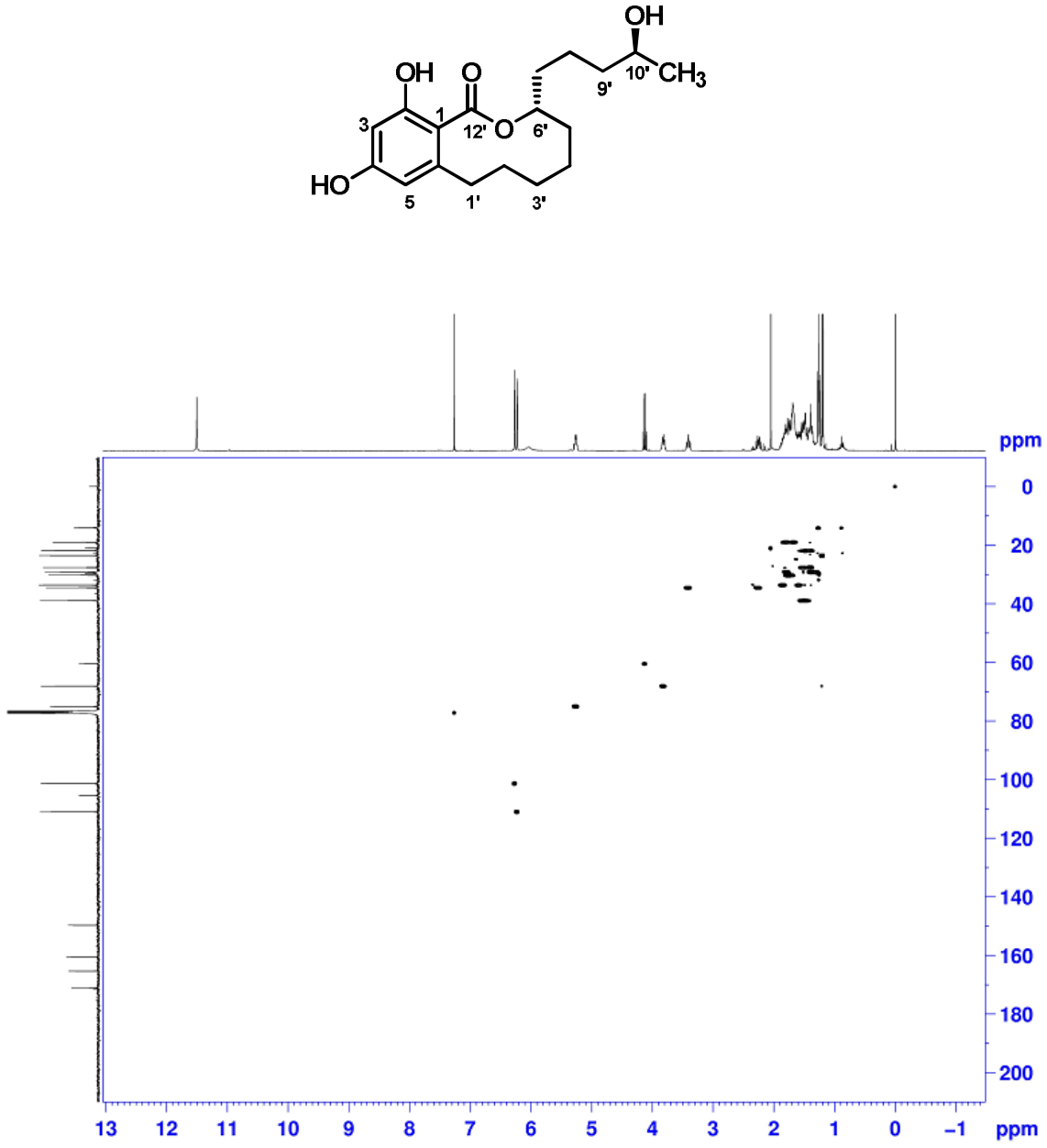


NOESY spectrum of 1b ($CDCl_3$, 295 K, 400 MHz)

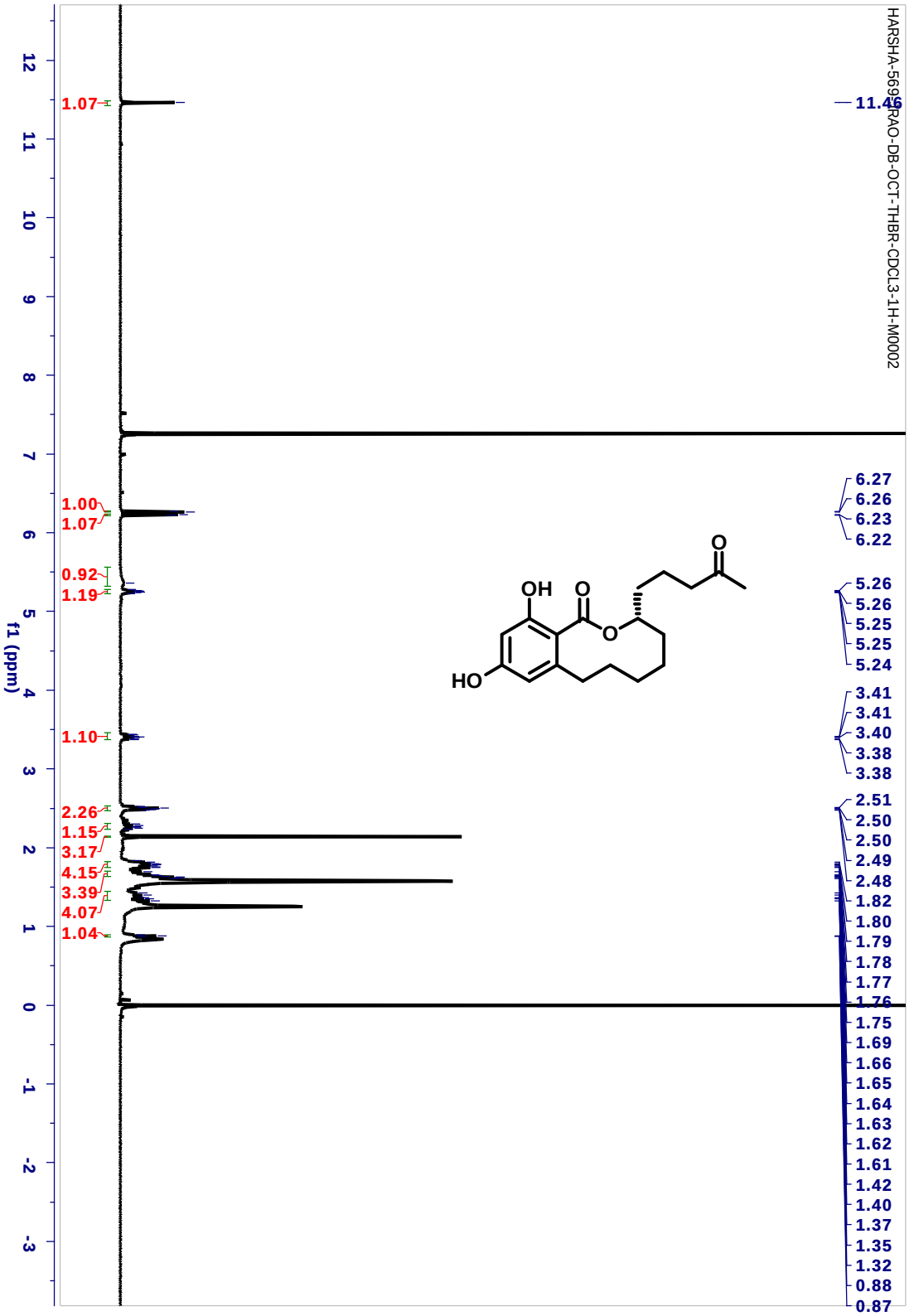




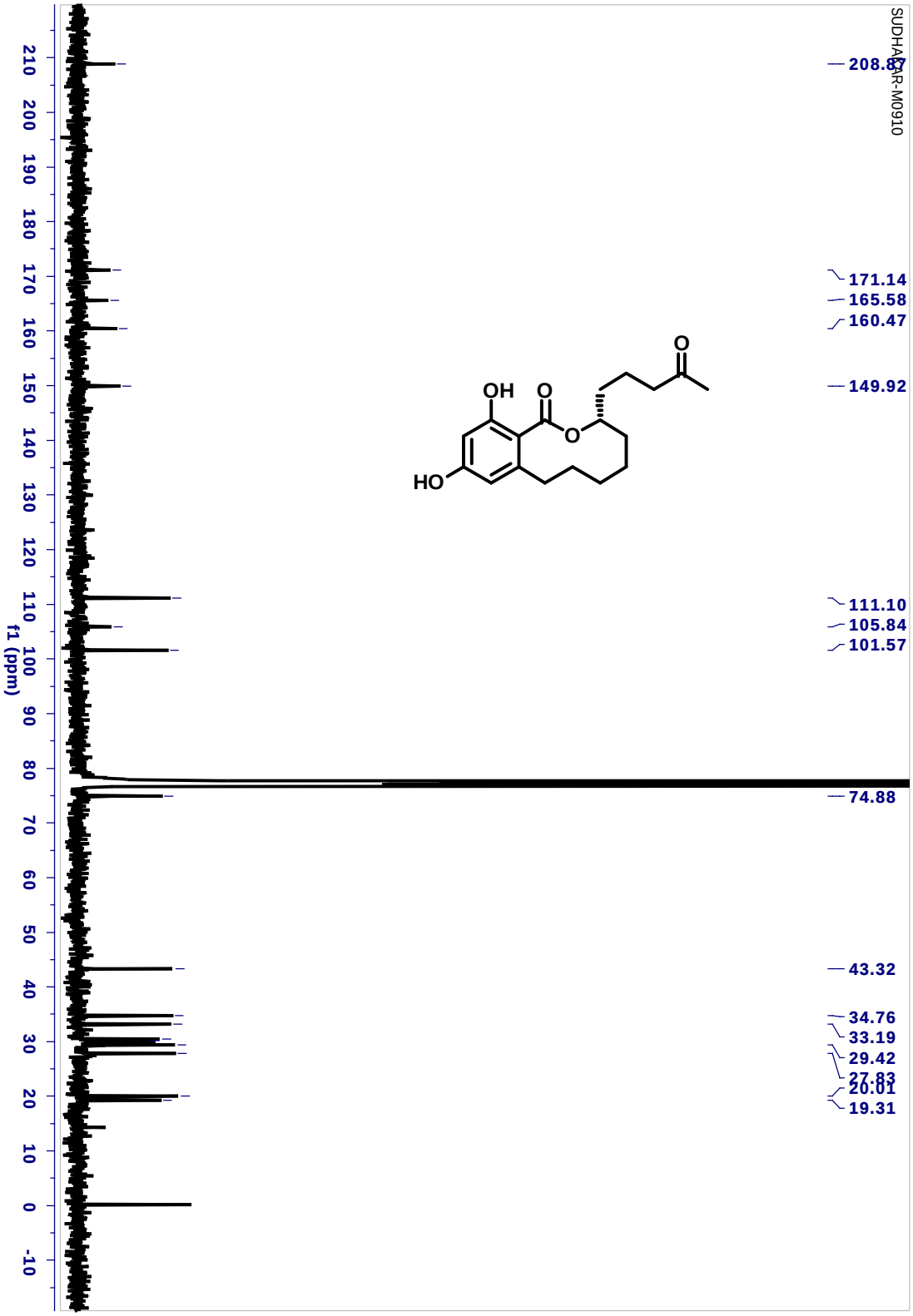
HMBC spectrum of 1b ($CDCl_3$, 295 K, 400 MHz)



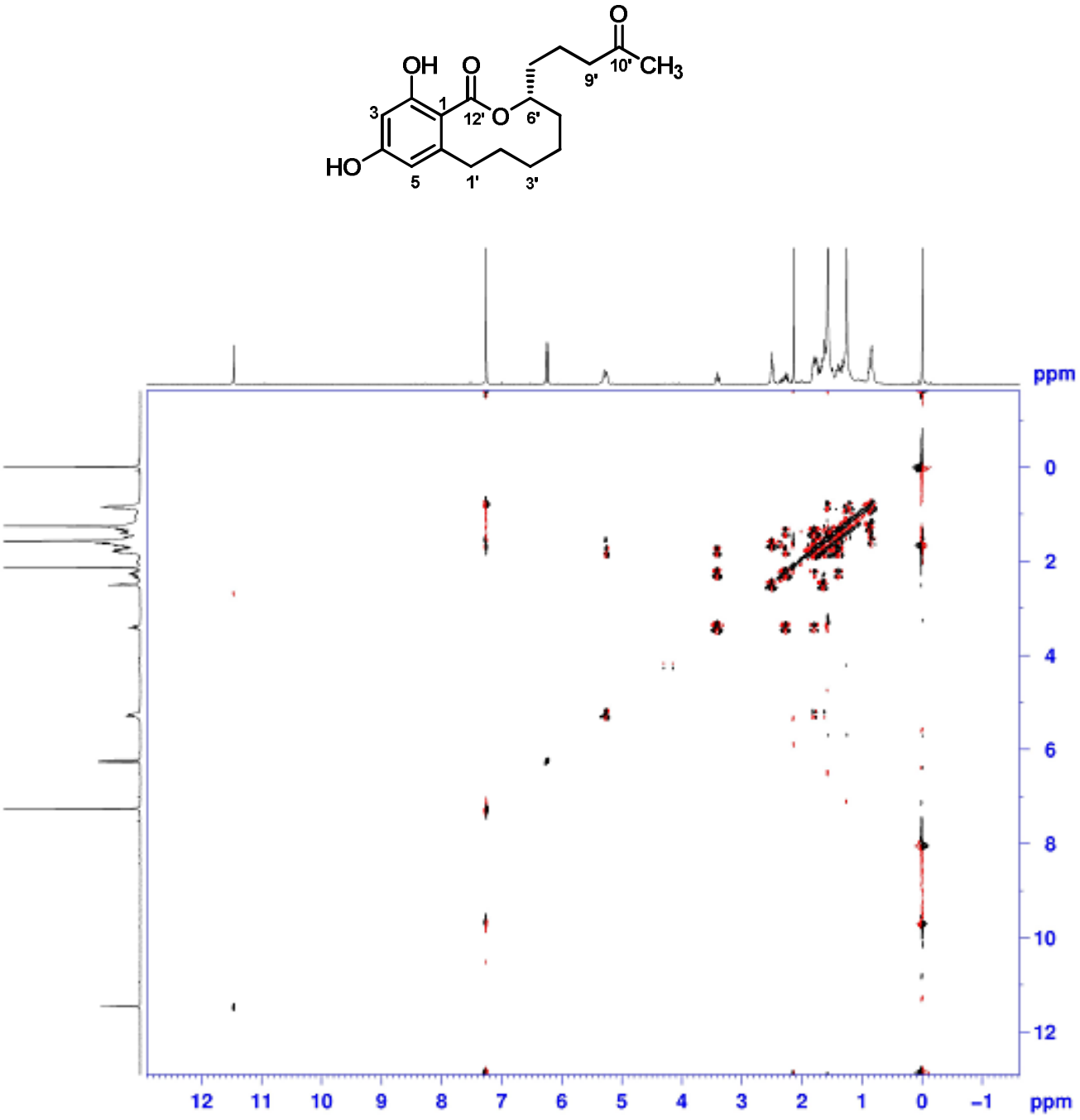
HSQC spectrum of 1b ($CDCl_3$, 295 K, 400 MHz)



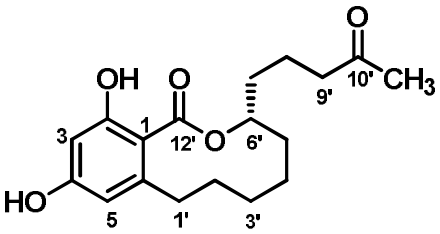
^{1}H NMR spectrum of 2a (400 MHz, $CDCl_3$)

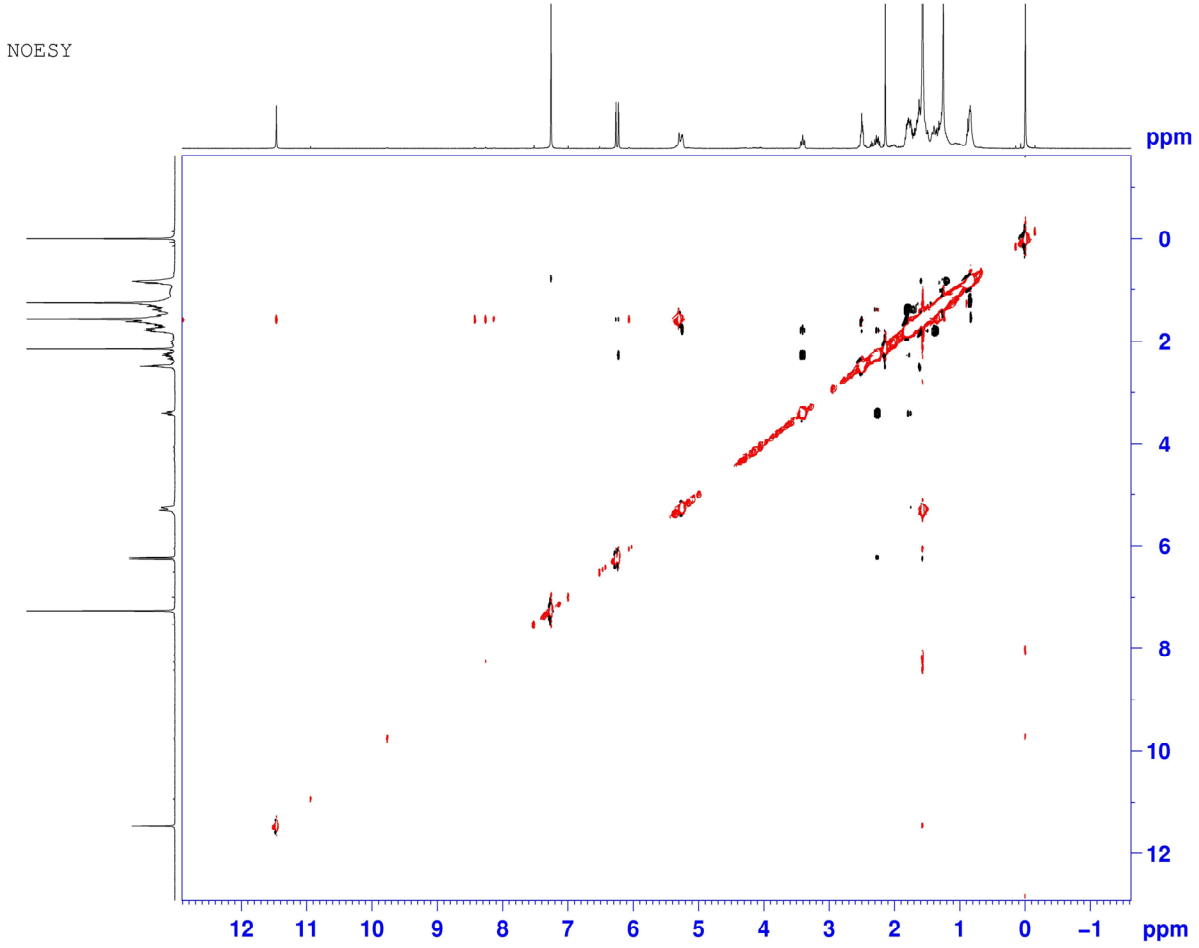


^{13}C NMR spectrum of 2a (100 MHz, $CDCl_3$)

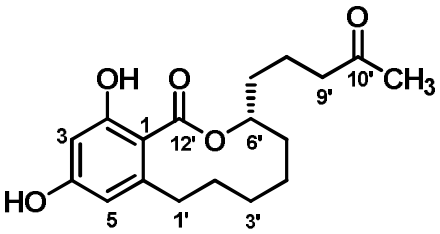


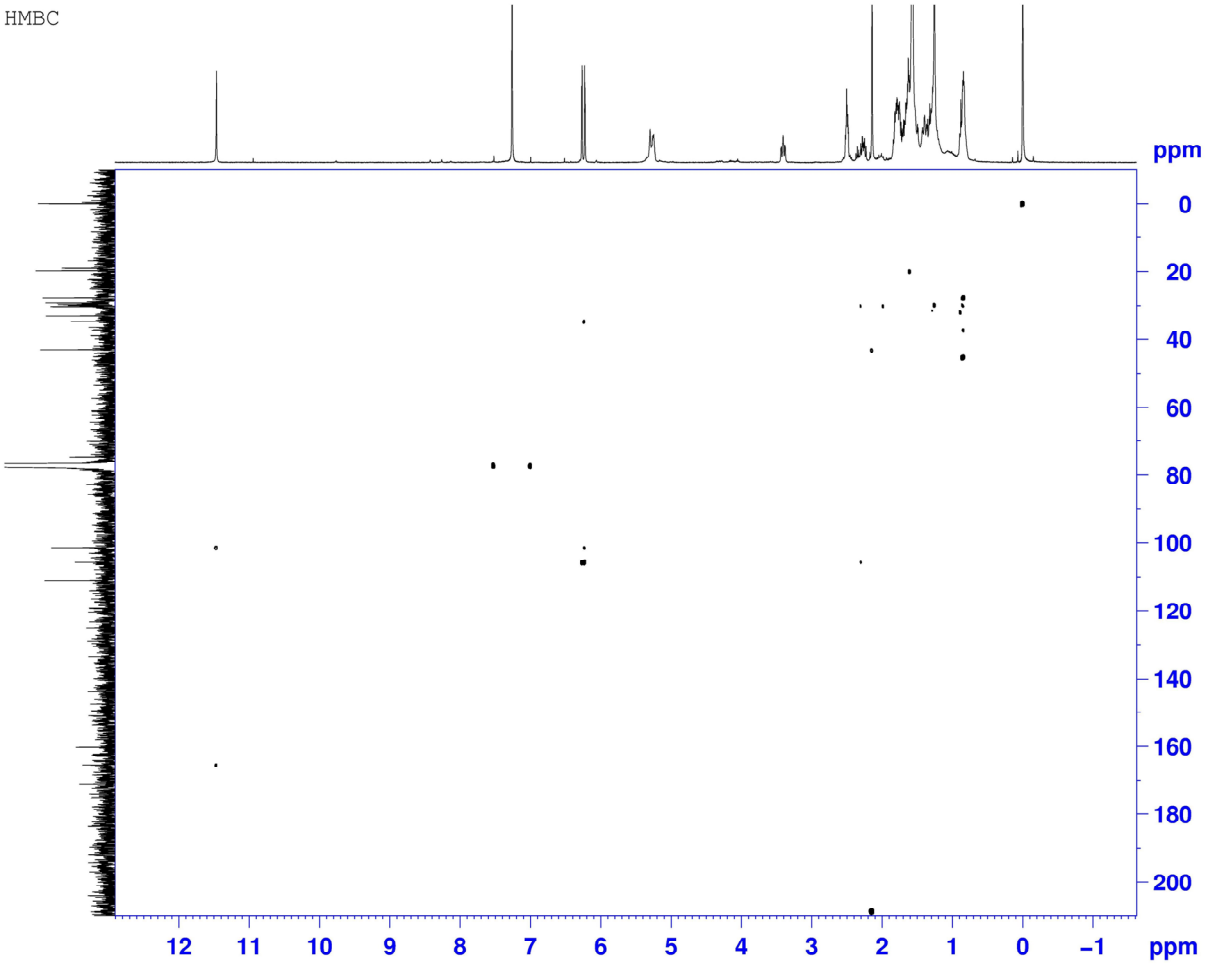
DQFCOSY spectrum of 2a ($CDCl_3$, 295 K, 400 MHz)



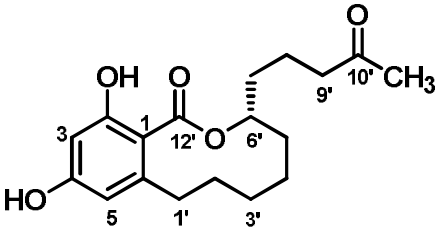


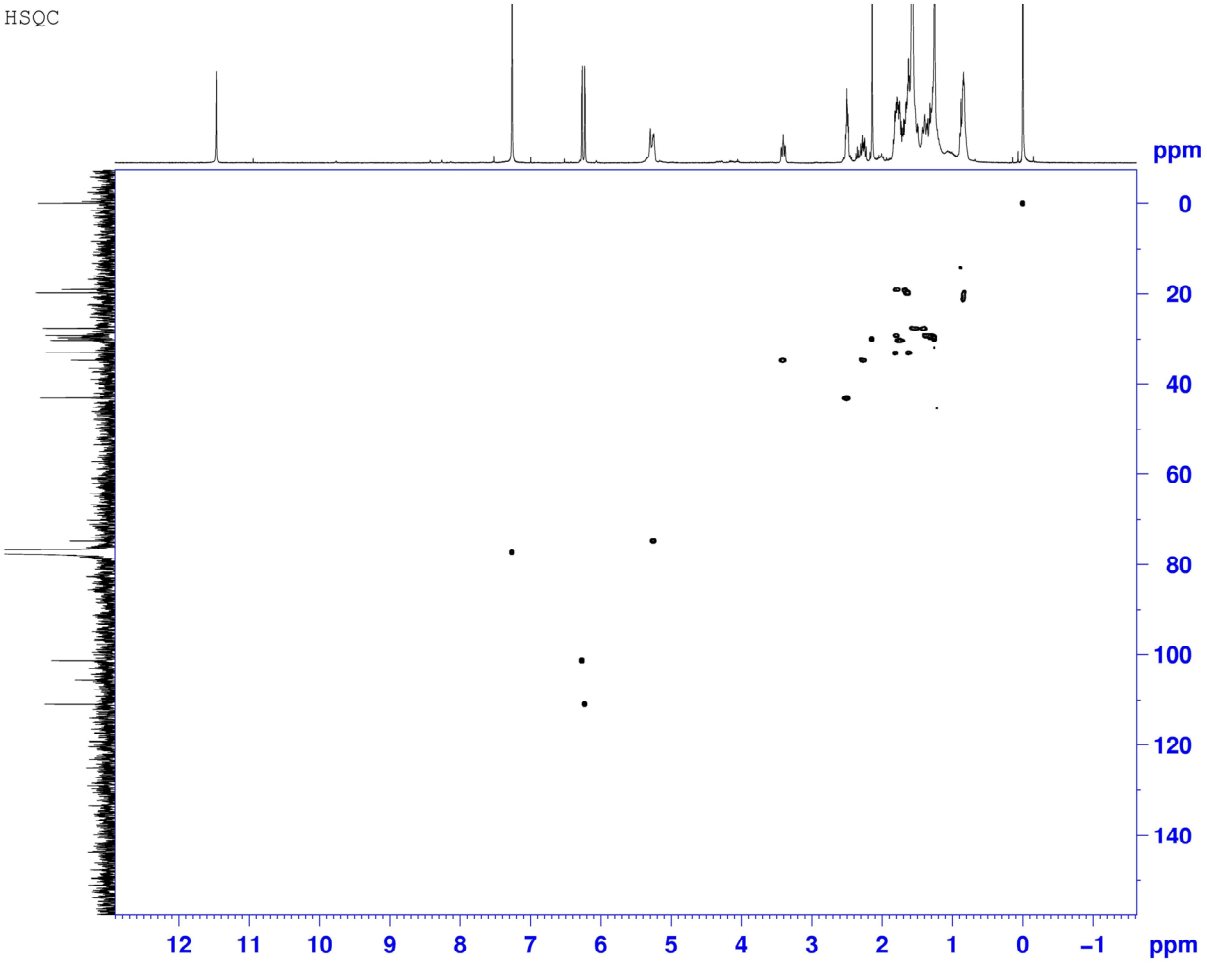
NOESY spectrum of 2a ($CDCl_3$, 295 K, 400 MHz)





HMBC spectrum of 2a ($CDCl_3$, 295 K, 400 MHz)





HSQC spectrum of 2a ($CDCl_3$, 295 K, 400 MHz)