Supporting Information for

Stereoselective Synthesis of 1-Tuberculosinyl Adenosine; a virulence factor of *Mycobacterium tuberculosis*

Jeffrey Buter, Dorus Heijnen,[Δ] Ieng Chim Wan,[Δ] F. Matthias Bickelhaupt, David C. Young, Edwin Otten, D. Branch Moody and Adriaan J. Minnaard*

Table of contents

General remarks:

All reactions were performed using oven-dried glassware under an atmosphere of nitrogen (unless otherwise specified) by standard Schlenk techniques, using dry solvents. Reaction temperature refers to the temperature of the oil bath/cooling bath. Solvents were taken from a solvent purification system. All other reagents were purchased and used without further purification unless noted otherwise. The adenosine, fully ^{13}C labelled on the ribsose, was purchased from Omicron biochemicals.

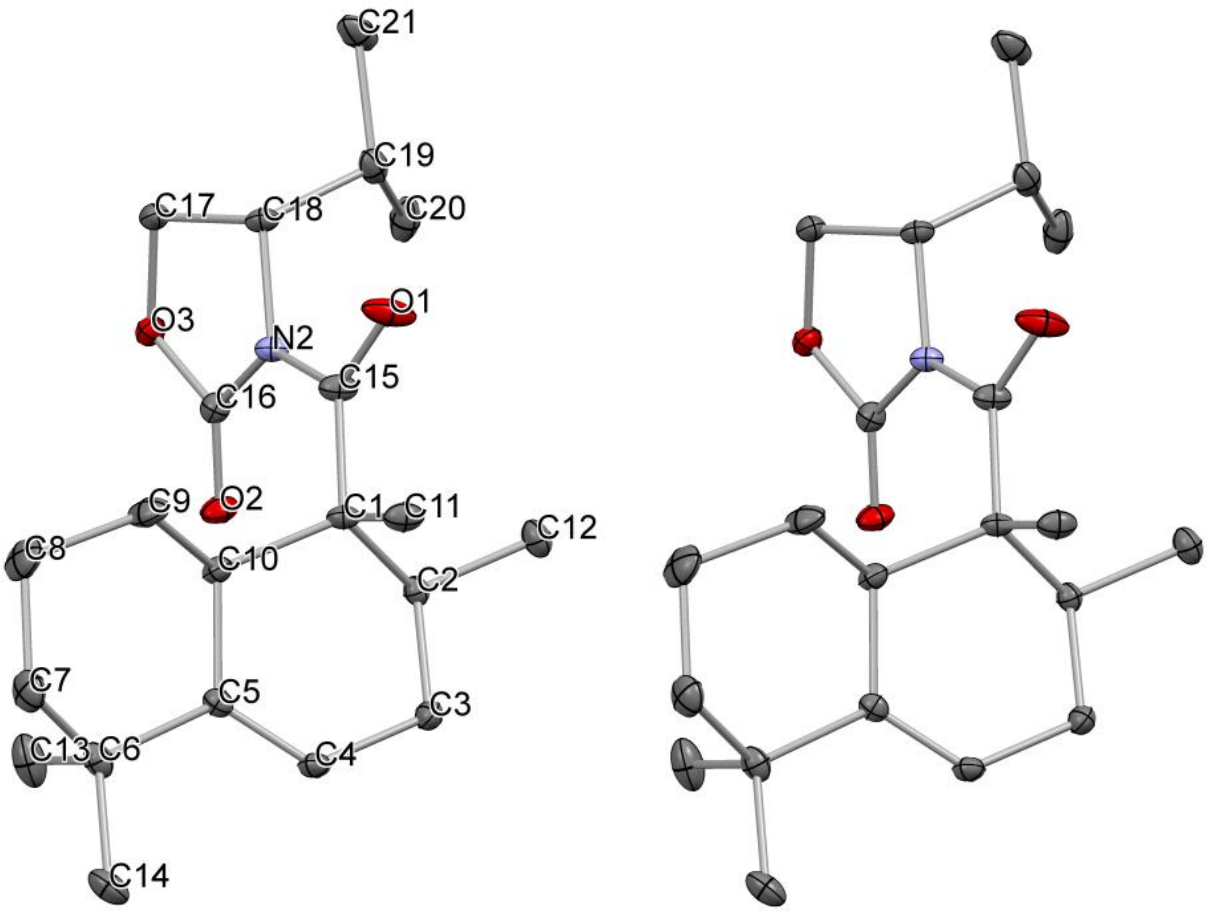
TLC analysis was performed on silica gel 60/Kieselguhr F254, 0.25 mm. Compounds were visualized using either Seebach's reagent (a mixture of phosphomolybdic acid (25 g), cerium (IV) sulfate (7.5 g), H_2O (500 mL) and H_2SO_4 (25 mL)), a $KMnO_4$ stain (K_2CO_3 (40 g), $KMnO_4$ (6 g), H_2O (600 mL) and 10% NaOH (5 mL)), or elemental iodine.
Flash chromatography was performed using silica gel type SiliaFlash P60 (230 – 400 mesh) or with automated column chromatography.

^1H- and ^{13}C-NMR spectra were recorded at 400 and 100.59 MHz, respectively, using $CDCl_3$ or CD_3OD as the solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 for ^1H, δ 77.2 for ^{13}C, MeOH-*d*4 δ 3.3 for ^1H, δ 49.0 for ^{13}C). Data are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, dd = double doublet, ddd = double double doublet, ddp = double double pentet, td = triple doublet, t = triplet, q = quartet, b = broad, m = multiplet), coupling constants *J* (Hz), and integration.
GC-MS measurements were performed with a gas chromatography system equipped with a mass sensitive detector. GC measurements were performed with a an AT5 column and FID detection
Enantiomeric excesses were determined by chiral HPLC analysis equipped with a diode-array detector. Integration at three different wavelengths (254, 225, 190 nm) was performed and the reported enantiomeric excess is an average of the three integrations. Retention times (tR) are given in min.

High resolution mass spectra (HRMS) were recorded on a Orbitrap XL. Optical rotations were measured on a polarimeter with a 10 cm cell (c given in g/mL) at ambient temperature (±23 °C). Melting points were recorded in °C.

X-ray crystallography:

A single crystal of Diels-Alder adduct **3** was mounted on top of a cryoloop and transferred into the cold nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX2.[1] The final unit cell was obtained from the xyz centroids of 8708 reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*). The structures were solved by direct methods using *SHELXS*.[2] The structure was solved in the chiral space group P2(1), and subsequent refinement allowed the location of all heavy atom positions. The hydrogen atoms were generated by geometrical considerations, constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. In the absence of significant anomalous scattering, the reflection data do not provide information on the stereochemistry of the molecule: the model chosen is based on the known configuration (*S* at C18) of the chiral auxiliary used in the synthesis. Crystal data and details on data collection and refinement are presented in Table 1.



X-ray structure of Diels-Alder adduct 3: *Ellipsoid contour percent probability level = 50% probability*

[1] Bruker, (2012). *APEX2* (v2012.4-3), *SAINT* (Version 8.18C) and *SADABS* (Version 2012/1). Bruker AXS Inc., Madison, Wisconsin, USA.[2] Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112-122

Table 1. Crystallographic dat for Diels-Alder adduct **3**

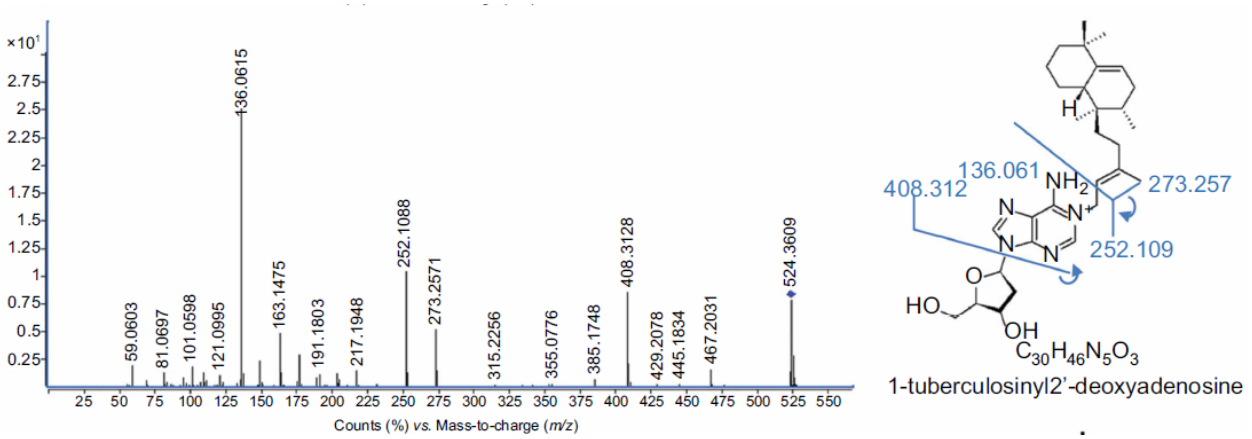
chemical formula	$C_{21}H_{33}NO_3$
M_r	347.48
cryst syst	monoclinic
color, habit	colorless, needle
size (mm)	0.45 x 0.21 x 0.13
space group	P2(1)
a (Å)	10.1677(6)
b (Å)	10.2037(5)
c (Å)	10.2235(6)
β, deg	111.168(2)
V ($Å^3$)	989.10(10)
Z	2
ρ_{calc}, $g.cm^{-3}$	1.167
μ(Mo $K\bar{\alpha}$), cm^{-1}	0.77

F(000)	380
temp (K)	100(2)
θ range (deg)	3.54 – 27.10
data collected (h,k,l)	-13:13, -12:13, -13:13
no. of rflns collected	10524
no. of indpndt reflns	4173
observed reflns	3845 ($F_o \geq 2\ \sigma(F_o)$)
R(F) (%)	4.04
$wR(F^2)$ (%)	10.07
GooF	1.051
Weighting a,b	0.0451, 0.2829
params refined	232
restraints	1
min, max resid dens	-0.176, 0.255

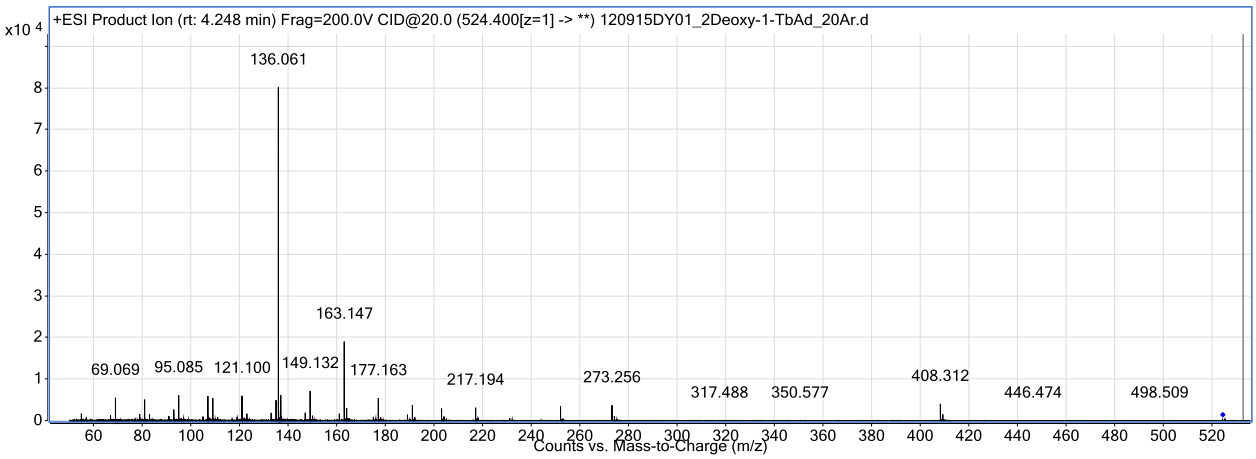
CID/MS analysis of 2’-deoxy 1-tuberculosinyl adenosine:

Reported MS spectrum of 2’-deoxy 1-TbAd:

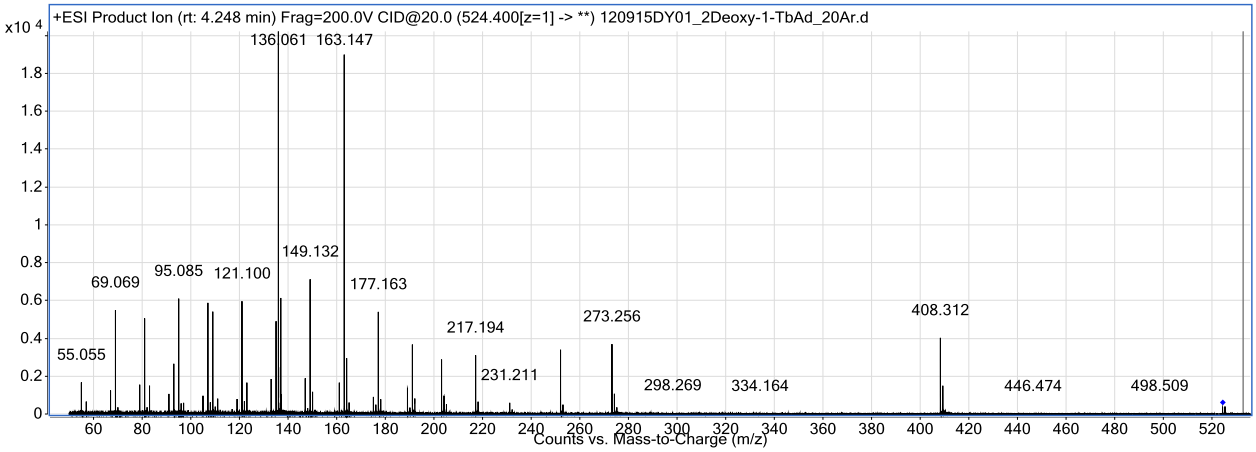
Reproduced from: Lau, S. K. P.; Lam, C-W.; Curreem, S. O. T.; Lee, K-C.; Lau, C. C. Y.; Chow, W-N.; Ngan, A. H. Y.; To, K. K. W.; Chan, J. F. W.; Hung, I. F. N.; Yam, W-C.; Yuen, K-Y.; Woo, P. C. Y. *Emerg. Microbes Infect*. 2015, *4*, e6 (doi: 10.1038/emi.2015.6)



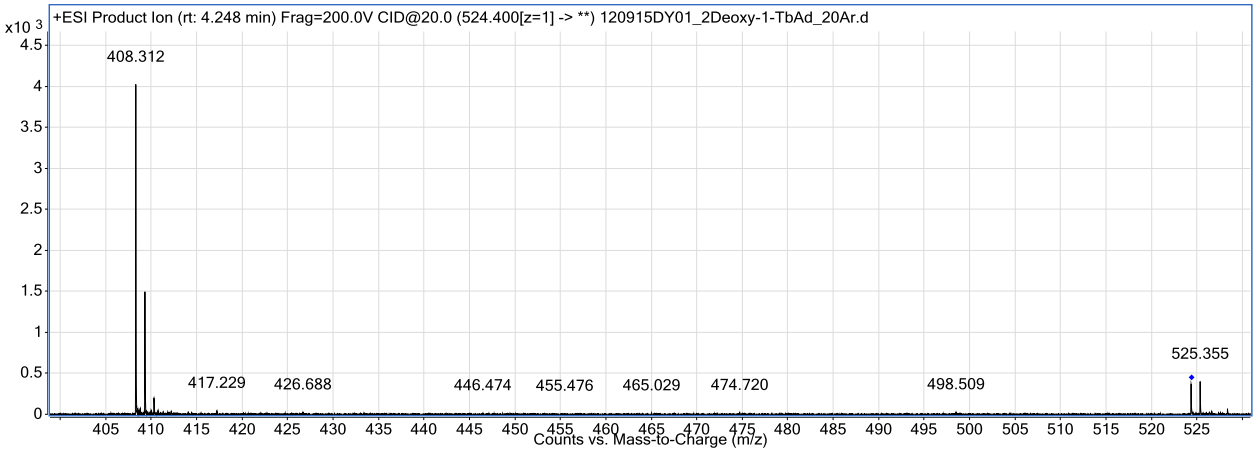
Complete MS spectrum of synthetic 2’-deoxy 1-TbAd:

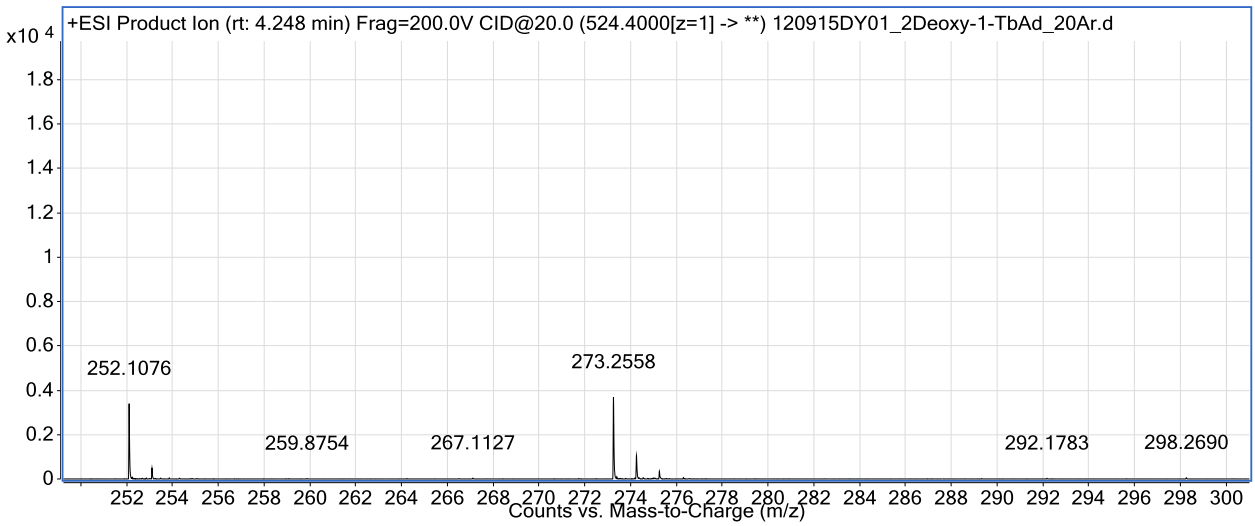


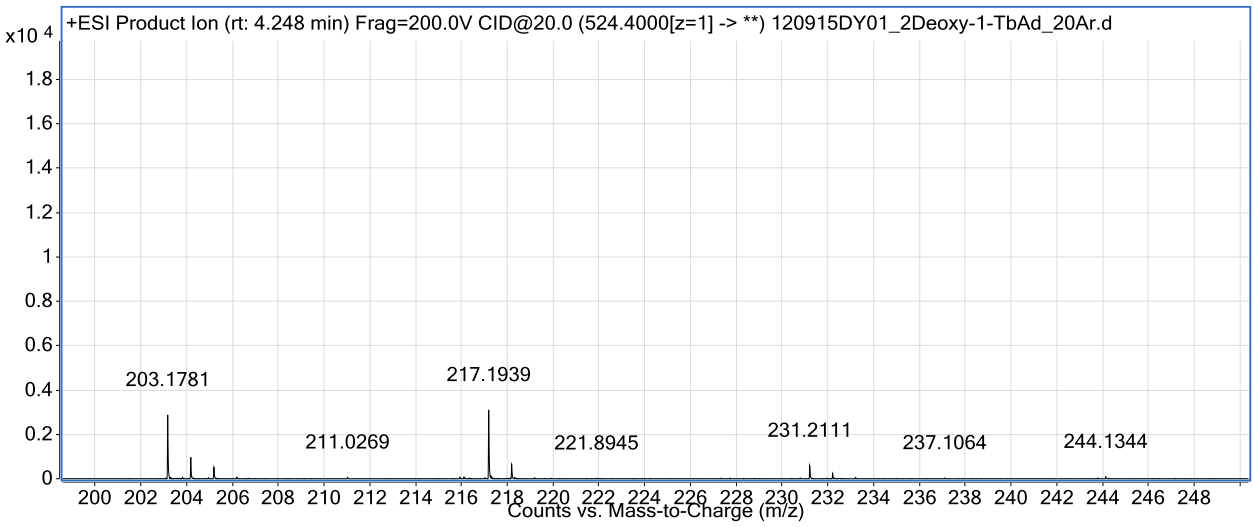
Zoom-in of complete MS spectrum of synthetic 2'-deoxy 1-TbAd:

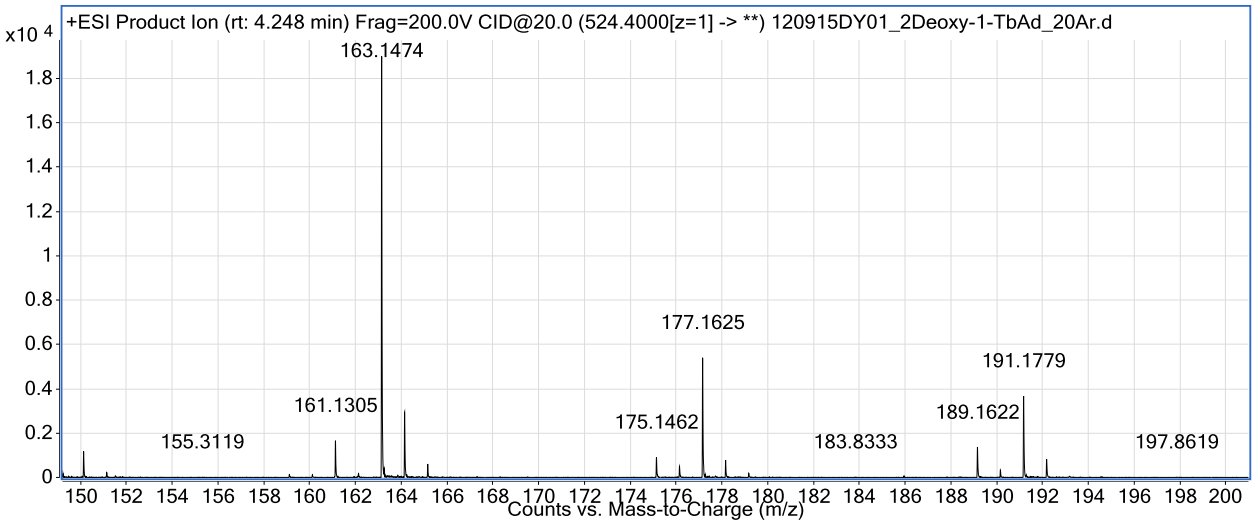


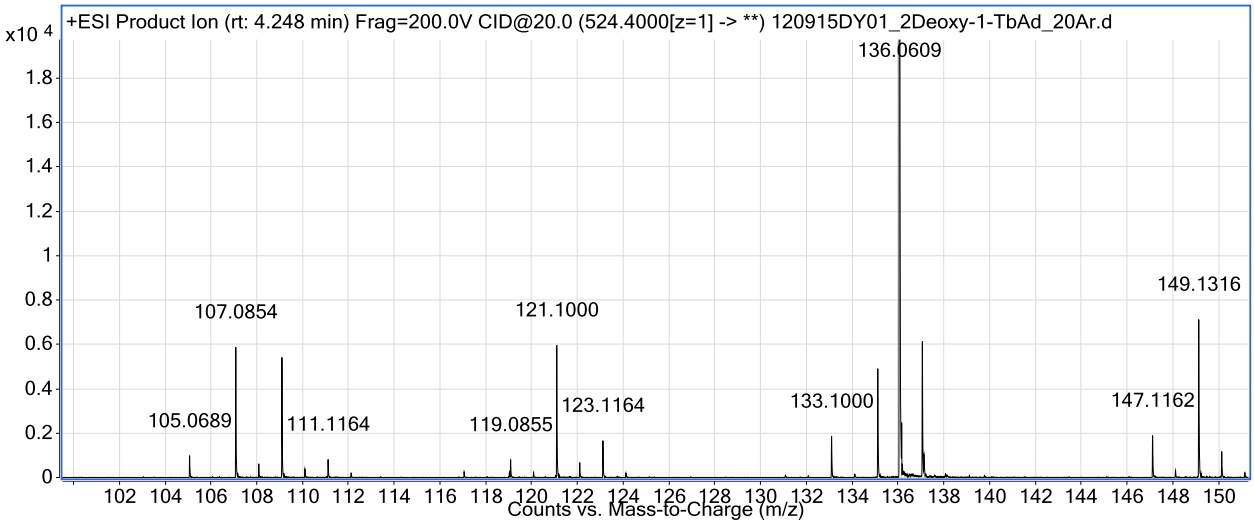
Detailed MS spectra of synthetic 2'-deoxy 1-TbAd:

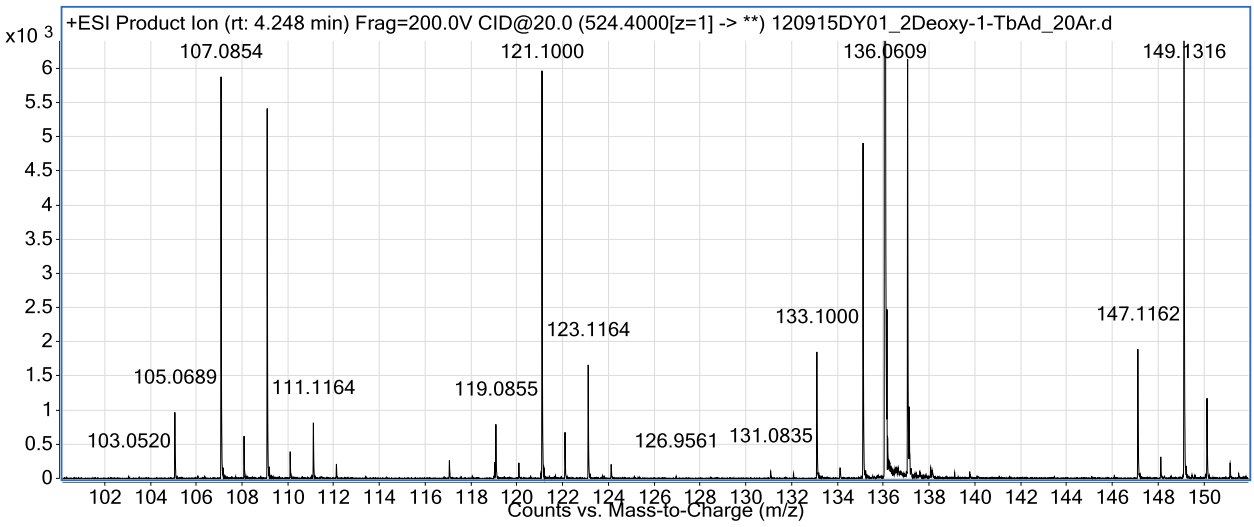


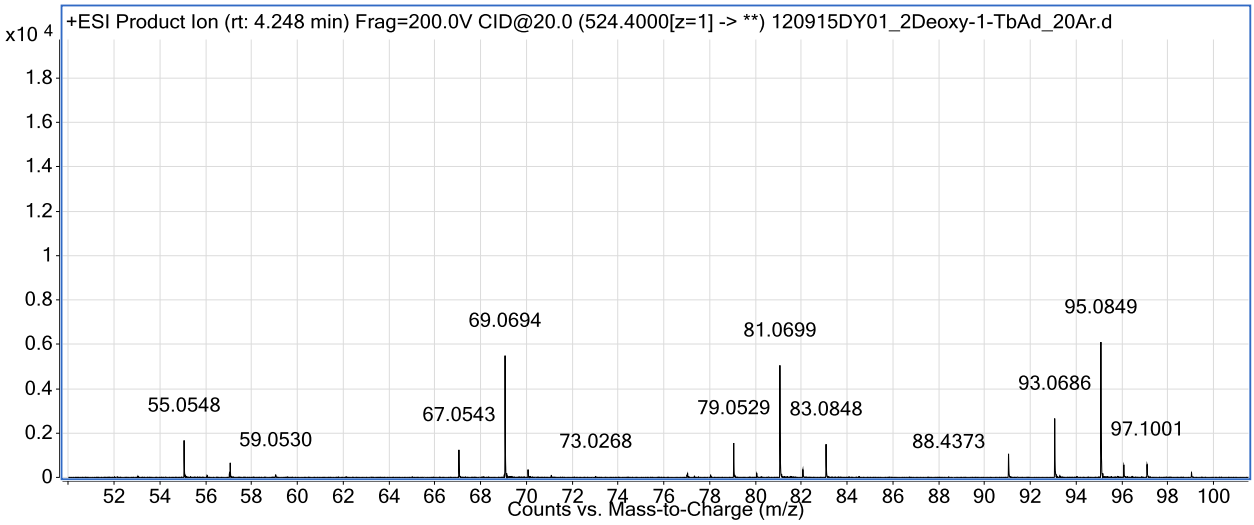


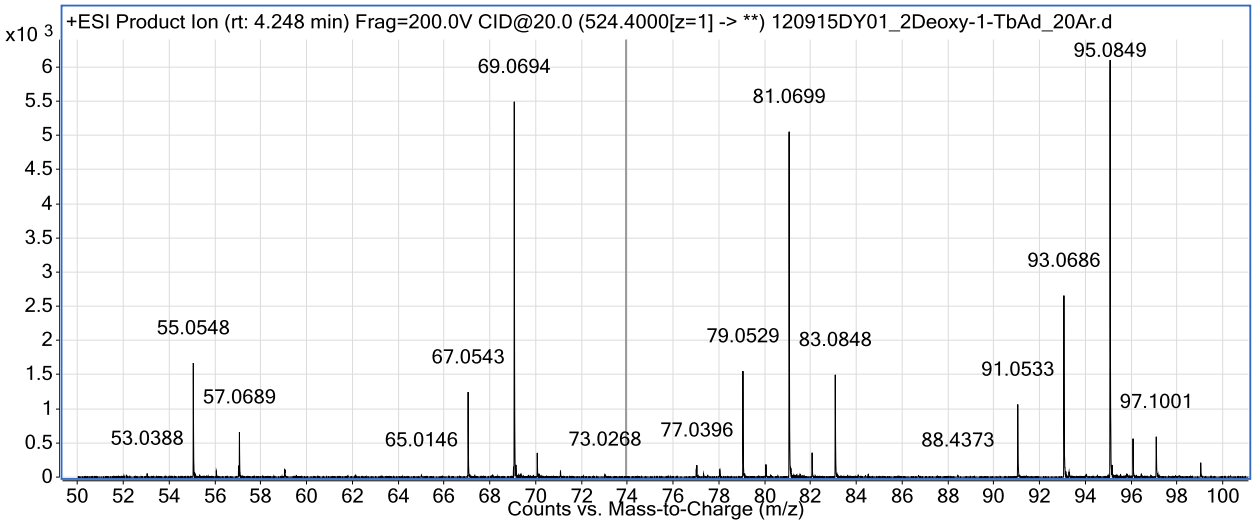

+ESI Product Ion (rt: 4.248 min) Frag=200.0V CID@20.0 (524.4000[z=1] -> **) 120915DY01_2Deoxy-1-TbAd_20Ar.d
x10 4
203.1781
211.0269
217.1939
221.8945
231.2111
237.1064
244.1344
Counts vs. Mass-to-Charge (m/z)


+ESI Product Ion (rt: 4.248 min) Frag=200.0V CID@20.0 (524.4000[z=1] -> **) 120915DY01_2Deoxy-1-TbAd_20Ar.d
x10 4
163.1474
177.1625
191.1779
161.1305
189.1622
175.1462
155.3119
183.8333
197.8619
Counts vs. Mass-to-Charge (m/z)


+ESI Product Ion (rt: 4.248 min) Frag=200.0V CID@20.0 (524.4000[z=1] -> **) 120915DY01_2Deoxy-1-TbAd_20Ar.d
x10 4
136.0609
149.1316
107.0854
121.1000
105.0689
111.1164
119.0855
123.1164
133.1000
147.1162
Counts vs. Mass-to-Charge (m/z)


+ESI Product Ion (rt: 4.248 min) Frag=200.0V CID@20.0 (524.4000[z=1] -> **) 120915DY01_2Deoxy-1-TbAd_20Ar.d
x10 3
107.0854
121.1000
136.0609
149.1316
123.1164
133.1000
147.1162
105.0689
111.1164
119.0855
103.0520
126.9561
131.0835
Counts vs. Mass-to-Charge (m/z)


+ESI Product Ion (rt: 4.248 min) Frag=200.0V CID@20.0 (524.4000[z=1] -> **) 120915DY01_2Deoxy-1-TbAd_20Ar.d
x10 4
69.0694
81.0699
95.0849
55.0548
67.0543
79.0529
83.0848
93.0686
59.0530
73.0268
88.4373
97.1001
Counts vs. Mass-to-Charge (m/z)


+ESI Product Ion (rt: 4.248 min) Frag=200.0V CID@20.0 (524.4000[z=1] -> **) 120915DY01_2Deoxy-1-TbAd_20Ar.d
x10 3
69.0694
95.0849
81.0699
93.0686
55.0548
79.0529
83.0848
67.0543
91.0533
57.0689
97.1001
53.0388
65.0146
73.0268
77.0396
88.4373
Counts vs. Mass-to-Charge (m/z)

Computational studies of the Diels-Alder cycloaddition:

Computational Details

All computations were performed using the ADF software suite. Geometry optimizations and vibrational analysis were performed using the BP86 DFT functional described by Becke and Perdew.[1] The numerical integration was performed using the procedure developed by Becke.[2] Geometry convergence is achieved by having an energy change of less than 10^{-5} Hartree and a gradient change of less than 10^{-5} Hartree/Å. The MOs were expanded in the Slater-type TZ2P basis set in combination with the small frozen core (FC) approximation. All calculations were performed with the corresponding charges and singlet ground state multiplicity in the gas phase. All reaction intermediates were confirmed local minima by vibrational analysis with zero imaginary frequencies, and all transition structures were confirmed to be a proper saddle point on the potential energy surface by the same analysis with only one imaginary frequency. The structures before and after the transition states **11a, 11b, 13a, 13b,15a** and **15b** were confirmed using IRC analysis restart from .t21 files containing the Hessian of the transition structures, using 6 points in either direction, and then fully optimizing to the next local minima from the 6th point. Electronic energies (ZPE corrected), internal energies and entropy (233.15K) were obtained from the output files, and free energies were calculated according to standard thermodynamic equations. The geometry of the dienes and the dienophiles at transition states **12a**, **12b**, **14a** and **14b** were isolated and are taking as the activated geometries. Single-point calculations were carried out on the activated geometries with at the same level of theory without further optimization.

[1] (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
[2] Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 2547.

Activation Strain Analyses

Table 2. Activation strain analysis of the transition states in the Diels-Alder reaction shown in figure 1.[a]

Transition states (TS)	$\Delta E^{\ddagger}$	$\Delta E^{\ddagger}_{int}$ [b]	$\Delta E^{\ddagger}_{strain}$ (diene)[c]	$\Delta E^{\ddagger}_{strain}$ (dienophile)[d]	$\Delta E^{\ddagger}_{strain}$ (total)[e]
12a	3.4	-13.1	5.6	10.9	16.5
12b	7.7	-15.7	8.0	15.4	23.4
14a	-0.2	-79.3	39.8	39.3	79.1
14b	3.9	-71.6	37.2	38.4	75.6

[a] Energy in kcal/mol. [b] $\Delta E^{\ddagger}_{int}$ = E(**TS**) - E(diene fragment in geom **TS**) - E(dienophile fragment in geom **TS**). [c] $\Delta E^{\ddagger}_{strain}$ (diene) = E(diene fragment in geom **TS**) - E(**1**). [d] $\Delta E^{\ddagger}_{strain}$ (dienophile) = E(dienophile fragment in geom **TS**) - E(**dienophile**). For **TS** = **12a** and **14a**, **dienophile** = **2a**; for **TS** = **12b** and **14b**, **dienophile** = **2b.** [e] $\Delta E^{\ddagger}_{strain}$ (total) **=** $\Delta E^{\ddagger}_{strain}$ (diene) **+** $\Delta E^{\ddagger}_{strain}$ (dienophile)

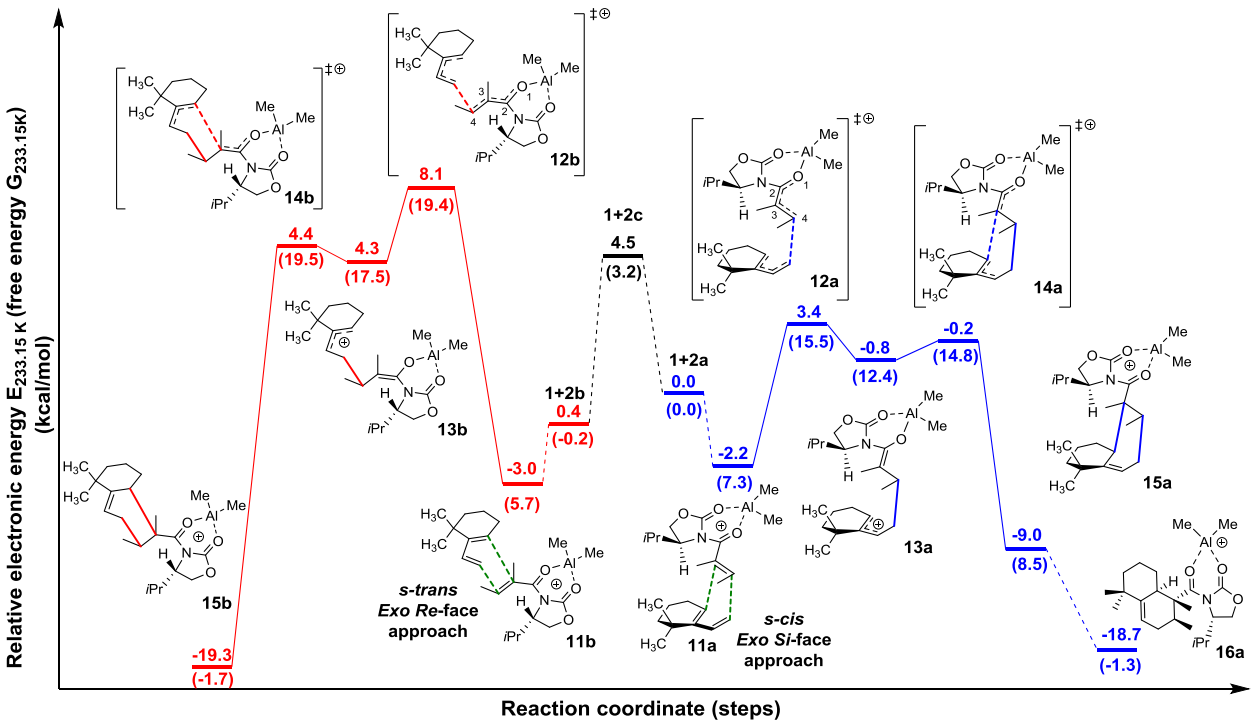


Figure 1. The geometry of diene **1**, aluminum-complexed *s-cis* conformer of the dienophile (**2a**) aluminum-complexed *s-cis* conformer of the dienophile (**2b**), and the transition state between **2a** and **2b** corresponding to the rotation along the C(2)-C(3) bond (**2c**) were optimized separately. The energies of the three states **1**+**2a**, **1**+**2b** and **1**+**2c** are the sum of the corresponding diene and aluminum-complexed dienophile fragments.

Table 3. Cartesian coordinates (in Å) and ADF total energies and thermodynamic corrections (in indicated units) of all stationary points computed at BP86/TZ2P in the gas phase.

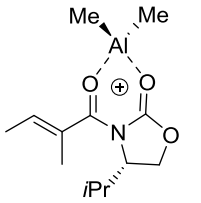
Diene (1)

ADF total bond energy: -3379.61 kcal/mol; Entropy: 88.894 cal/mole-K; Internal Energy: 146.884 kcal/mole

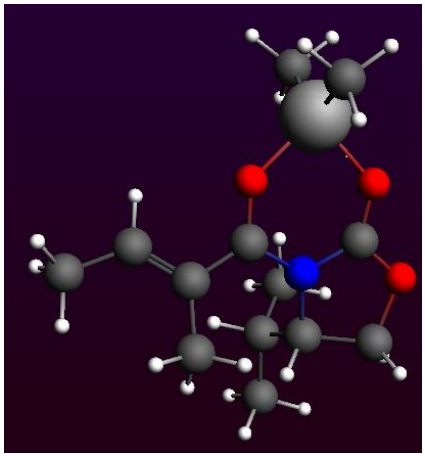
1.C	0.650551	-0.810000	-0.215214
2.C	2.161884	0.556609	1.290210
3.C	0.832843	0.066727	0.794508
4.C	1.829179	-1.490508	-0.929556
5.C	3.145711	-1.233193	-0.156207
6.C	3.296466	0.210936	0.322314
7.C	-0.712802	-1.143374	-0.666277
8.H	2.365286	0.120992	2.285918
9.H	2.108725	1.644563	1.458536
10.H	-0.054049	0.451410	1.304641
11.H	4.273434	0.356209	0.804696
12.H	-1.604213	0.784251	-0.560691
13.C	1.621381	-3.019377	-1.000801
14.H	3.992630	-1.524332	-0.796239
15.H	3.172018	-1.899402	0.722201
16.H	3.266419	0.896739	-0.538310
17.C	-1.731910	-0.278236	-0.771655
18.H	-0.896386	-2.183316	-0.949987
19.H	-2.723294	-0.608023	-1.080907
20.C	1.936567	-0.942292	-2.370490
21.H	2.732743	-1.464641	-2.920971

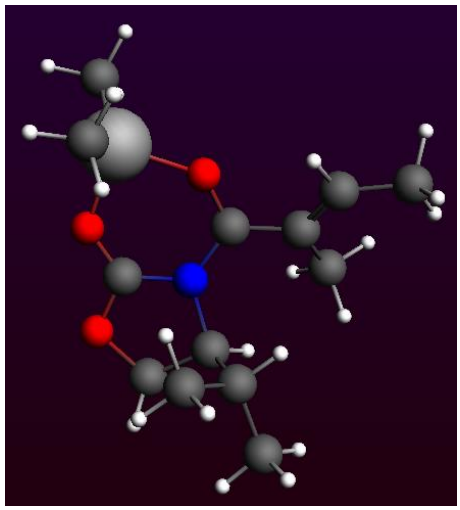
22.H	2.160726	0.132395	-2.376640
23.H	0.993866	-1.085507	-2.915472
24.H	2.529930	-3.495446	-1.396598
25.H	0.792556	-3.296851	-1.664460
26.H	1.423916	-3.440800	-0.005501

Aluminum complexed *s-cis* conformation of dienophile 2 (no diene 1 present!) (2a)



***s-cis* conformation**



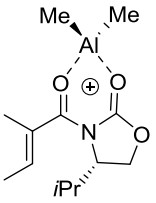


ADF total bond energy: -5229.85 kcal/mol; Entropy: 137.637 cal/mole-K; Internal Energy: 218.607 kcal/mole

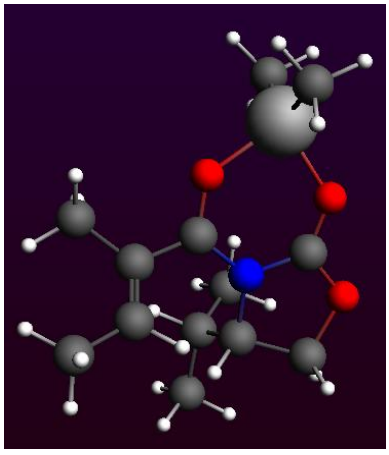
1.N	-0.315024	-2.991505	-0.794384
2.C	-0.180854	-4.303104	-1.505268
3.C	0.825176	-5.009363	-0.577981
4.O	1.470873	-3.934722	0.179058
5.C	0.773642	-2.822815	0.064653
6.C	0.264826	-4.139219	-2.975596
7.H	-1.137499	-4.830352	-1.475303
8.C	1.619102	-3.438869	-3.138182
9.C	0.244362	-5.509712	-3.668137
10.O	1.097990	-1.799415	0.677901
11.H	1.615331	-5.540954	-1.114175
12.H	0.353219	-5.675517	0.152534
13.H	-0.505701	-3.511743	-3.452914
14.H	2.441635	-4.022848	-2.702345
15.H	1.634934	-2.435945	-2.690822
16.H	1.845500	-3.315417	-4.203899
17.H	1.006312	-6.187733	-3.258566
18.H	0.461580	-5.392214	-4.736278
19.H	-0.732828	-6.003135	-3.578702
20.C	-1.209905	-1.955195	-1.077374
21.C	-2.460446	-2.217138	-1.800503
22.C	-2.929037	-1.171012	-2.532341

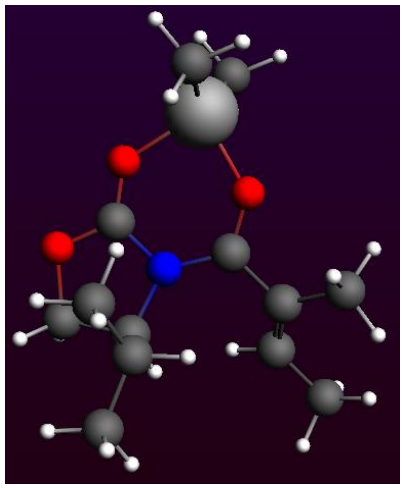
23.C	-4.162004	-1.132506	-3.352022
24.O	-0.936655	-0.791478	-0.681544
25.H	-4.809173	-0.312617	-2.999419
26.H	-4.735959	-2.063365	-3.351678
27.H	-3.909853	-0.871335	-4.391931
28.H	-2.328808	-0.258830	-2.535761
29.C	-3.200267	-3.527063	-1.653504
30.H	-2.987447	-4.009108	-0.692120
31.H	-2.985053	-4.241201	-2.460785
32.H	-4.279180	-3.337853	-1.675943
33.Al	0.402786	-0.008191	0.439223
34.C	-0.455074	0.531171	2.102738
35.C	1.651570	0.967702	-0.699152
36.H	1.962174	0.412974	-1.596155
37.H	2.567323	1.223638	-0.145868
38.H	1.217605	1.919183	-1.040534
39.H	0.294961	0.771831	2.870647
40.H	-1.113176	-0.242218	2.523481
41.H	-1.063534	1.436780	1.963742

Aluminum complexed *s-trans* conformation of dienophile 2 (no diene 1 present!) (2b)



***s-trans* conformation**



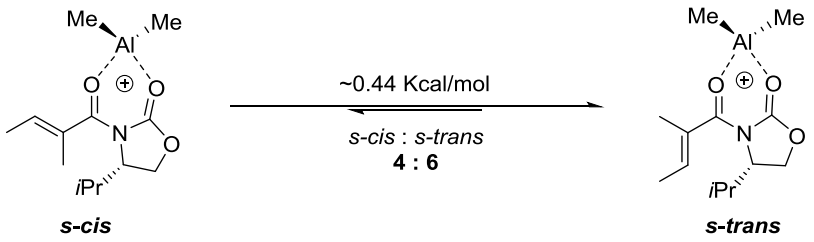


ADF total bond energy: -5229.42 kcal/mol; Entropy: 139.957 cal/mole-K; Internal Energy: 218.504 kcal/mole

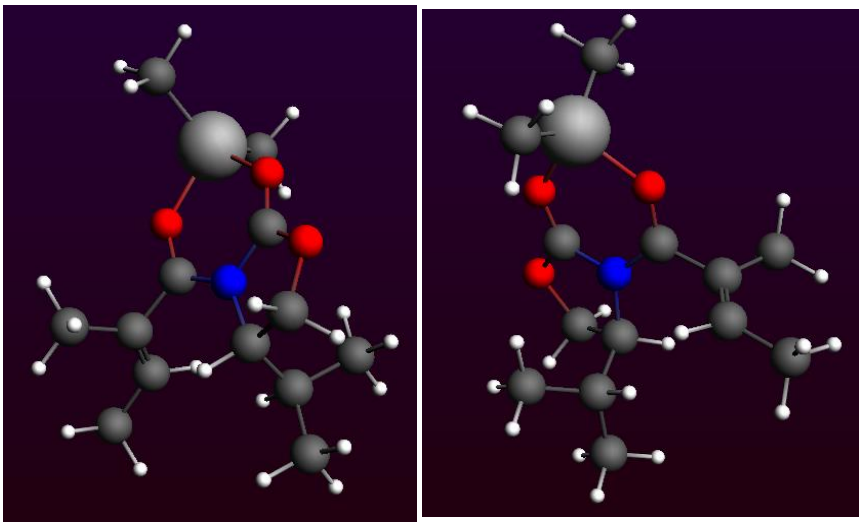
1.N	-0.198054	-2.951302	-0.981991
2.C	-0.101581	-4.378627	-1.437601
3.C	0.826031	-4.938109	-0.343570
4.O	1.514157	-3.768323	0.210827
5.C	0.876320	-2.669018	-0.137427
6.C	0.419872	-4.501230	-2.886412
7.H	-1.083337	-4.852923	-1.369360
8.C	1.816056	-3.903725	-3.098785
9.C	0.355504	-5.971692	-3.324418
10.O	1.234501	-1.559597	0.275670

11.H	1.597942	-5.610670	-0.725742
12.H	0.288362	-5.414153	0.483920
13.H	-0.296096	-3.938351	-3.507495
14.H	2.586113	-4.436223	-2.523491
15.H	1.867635	-2.838156	-2.837715
16.H	2.094393	-3.984856	-4.156208
17.H	1.055178	-6.600779	-2.756229
18.H	0.633175	-6.058730	-4.381390
19.H	-0.652541	-6.391692	-3.208530
20.C	-1.011960	-1.944616	-1.509144
21.C	-2.269929	-2.259412	-2.197120
22.C	-3.085566	-3.201882	-1.663252
23.C	-4.474027	-3.530165	-2.077695
24.O	-0.667014	-0.742420	-1.392044
25.H	-4.807611	-2.995766	-2.971083
26.H	-5.170481	-3.301224	-1.255367
27.H	-4.569970	-4.613264	-2.251417
28.H	-2.730755	-3.746729	-0.784448
29.C	-2.638231	-1.317838	-3.316360
30.H	-1.783271	-1.135297	-3.978942
31.H	-2.952929	-0.343065	-2.920073
32.H	-3.457117	-1.722593	-3.917307
33.Al	0.665576	0.182615	-0.357391
34.C	-0.256841	1.081780	1.103595
35.C	2.030903	0.842270	-1.583269
36.H	2.366371	0.096287	-2.317842
37.H	2.922580	1.175364	-1.031875
38.H	1.668320	1.713549	-2.148324
39.H	0.459790	1.434054	1.860314
40.H	-0.984572	0.440278	1.620476
41.H	-0.799307	1.969681	0.747445

Aluminum complexed *s-trans/s-cis* equilibrium transition state of dienophile 2 (no diene 1 present!) (2c)



s-cis ***s-trans***



ADF total bond energy: -5266.14 kcal/mol; Entropy: 161.488 cal/mole-K; Internal Energy: 222.564 kcal/mole

1.N	-0.217838	-2.848773	-0.976261
2.C	-0.183283	-4.156499	-1.701163
3.C	0.776501	-4.938303	-0.782736
4.O	1.523541	-3.907901	-0.045559
5.C	0.883919	-2.760944	-0.112401
6.C	0.288778	-4.033333	-3.166650
7.H	-1.189465	-4.590978	-1.676857
8.C	1.686798	-3.422618	-3.319354
9.C	0.183484	-5.405354	-3.848885
10.O	1.238147	-1.772037	0.535671
11.H	1.513339	-5.534620	-1.325295
12.H	0.268258	-5.555364	-0.033563
13.H	-0.436802	-3.365845	-3.654371
14.H	2.468056	-4.052651	-2.871730
15.H	1.761113	-2.418661	-2.879864
16.H	1.930211	-3.322794	-4.383806
17.H	0.893288	-6.132195	-3.429422
18.H	0.419194	-5.308986	-4.915236
19.H	-0.826719	-5.828226	-3.767269
20.C	-1.228193	-1.903479	-0.992544
21.C	-2.491436	-2.192607	-1.726371
22.C	-2.569422	-1.886484	-3.033470
23.C	-3.771138	-1.976547	-3.914328
24.O	-1.114409	-0.848212	-0.329168
25.H	-4.045304	-0.972418	-4.271337
26.H	-4.644809	-2.414334	-3.422260
27.H	-3.543172	-2.568428	-4.812667
28.H	-1.673655	-1.484582	-3.515915
29.C	-3.610537	-2.659865	-0.824652

30.H	-3.337027	-3.566753	-0.265561
31.H	-4.512219	-2.879891	-1.403363
32.H	-3.858176	-1.885215	-0.085093
33.Al	0.329543	-0.052394	0.682542
34.C	-0.264929	0.134588	2.525637
35.C	1.238953	1.196850	-0.505376
36.H	1.442013	0.789947	-1.506282
37.H	2.205487	1.505053	-0.079911
38.H	0.648883	2.114903	-0.641800
39.H	0.582740	0.349243	3.192846
40.H	-0.765219	-0.762739	2.916246
41.H	-0.968758	0.973011	2.631869

Aluminum complexed *s-cis* conformation of dienophile in presence of diene (11a)

ADF total bond energy: -8611.69 kcal/mol; Entropy: 187.115 cal/mole-K; Internal Energy: 366.327 kcal/mole

1.C	0.069226	-1.936119	-0.687088
2.C	1.731011	-1.164349	1.062029
3.C	0.535269	-1.002587	0.170472
4.C	0.750541	-3.302040	-0.862760
5.C	1.737385	-3.554414	0.303186
6.C	2.610428	-2.344908	0.637303
7.C	-1.117993	-1.670232	-1.516522
8.H	1.383527	-1.308637	2.101654
9.H	2.312001	-0.228405	1.082606
10.H	0.005409	-0.047284	0.230304
11.H	3.323819	-2.596273	1.433908
12.H	-2.283404	-0.483948	-0.183417
13.C	-0.303512	-4.429890	-0.846791
14.H	2.359613	-4.427234	0.055904
15.H	1.156827	-3.829100	1.198637
16.H	3.210956	-2.058938	-0.240110
17.C	-2.188326	-0.934285	-1.172292
18.H	-1.135859	-2.157198	-2.496710
19.H	-3.025266	-0.803422	-1.857430
20.C	1.501670	-3.340892	-2.213579
21.H	1.936581	-4.337338	-2.374535
22.H	2.314124	-2.603005	-2.244828
23.H	0.829463	-3.136403	-3.058068
24.H	0.195759	-5.407675	-0.894177
25.H	-0.991904	-4.367321	-1.699439
26.H	-0.901647	-4.397428	0.073439
27.N	2.344039	5.503612	-2.164703
28.C	3.091271	5.648194	-3.454380
29.C	4.167855	6.662809	-3.028128
30.O	3.638827	7.301092	-1.821279
31.C	2.634887	6.591675	-1.343469
32.C	2.180719	6.088166	-4.622697
33.H	3.565475	4.696746	-3.707186
34.C	1.483107	7.433906	-4.391449
35.C	2.989255	6.081288	-5.928257
36.O	2.075723	6.911330	-0.286768
37.H	4.335995	7.455841	-3.761171
38.H	5.120996	6.197923	-2.752883
39.H	1.405023	5.309408	-4.705957
40.H	2.199482	8.264098	-4.318800
41.H	0.859362	7.438178	-3.487666
42.H	0.820749	7.656883	-5.236421
43.H	3.773205	6.851770	-5.929758
44.H	2.329700	6.294138	-6.777825

45.H	3.467409	5.109741	-6.112463
46.C	1.311944	4.600498	-1.875522
47.C	1.177890	3.353200	-2.625963
48.C	-0.090962	2.862145	-2.709487
49.C	-0.524550	1.627209	-3.392122
50.O	0.509280	4.879164	-0.942591
51.H	-0.905265	0.903642	-2.641785
52.H	0.258507	1.135309	-3.976355
53.H	-1.385427	1.838190	-4.043967
54.H	-0.879884	3.446067	-2.230825
55.C	2.378606	2.627248	-3.188894
56.H	3.292386	2.855105	-2.627615
57.H	2.557047	2.838153	-4.252913
58.H	2.218818	1.547093	-3.099633
59.Al	0.405815	6.223277	0.406068
60.C	0.767263	5.384450	2.127801
61.C	-1.005369	7.479623	-0.085913
62.H	-0.976992	7.788219	-1.140904
63.H	-0.943066	8.396208	0.519237
64.H	-2.001618	7.051106	0.098939
65.H	1.638818	4.714782	2.110531
66.H	-0.092646	4.792092	2.473244
67.H	0.956530	6.143163	2.901593

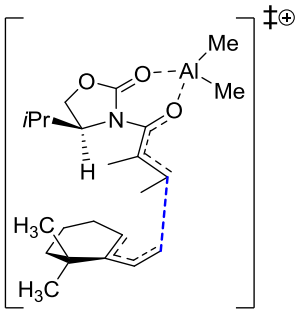
Aluminum complexed *s-trans* conformation of dienophile in presence of diene (11b)

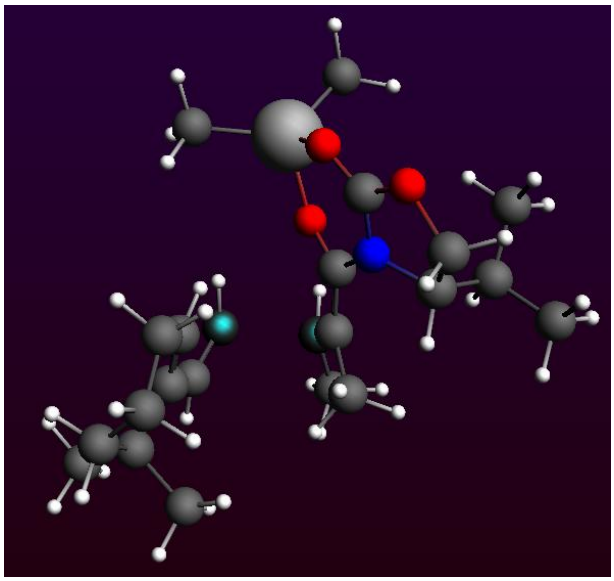
ADF total bond energy: -8612.44 kcal/mol; Entropy: 216.271 cal/mole-K; Internal Energy: 372.474 kcal/mole

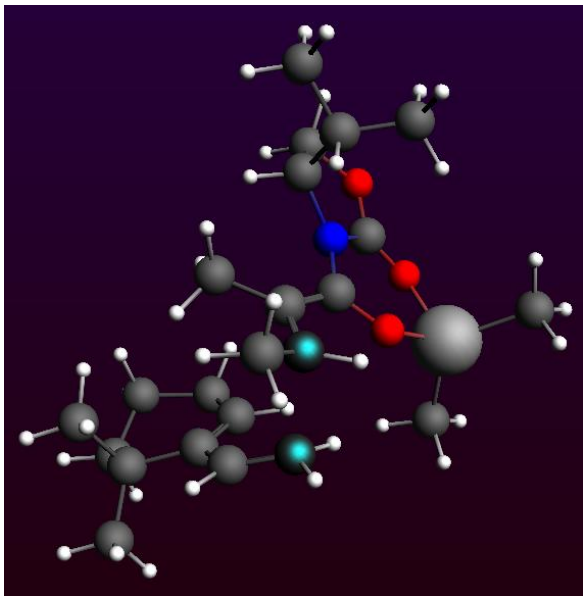
1.N	-0.634957	-1.667244	-0.678610
2.C	-1.647458	-2.769116	-0.806352
3.C	-1.725438	-3.226519	0.660903
4.O	-0.484019	-2.743748	1.280352
5.C	0.072687	-1.832554	0.513316
6.C	-1.217363	-3.846546	-1.826211
7.H	-2.609644	-2.348064	-1.107034
8.C	0.107609	-4.536980	-1.480782
9.C	-2.358335	-4.858759	-2.003753
10.O	1.094548	-1.229174	0.867605
11.H	-1.734816	-4.312802	0.780567
12.H	-2.559829	-2.773510	1.212462
13.H	-1.092145	-3.317005	-2.784822
14.H	0.045150	-5.105432	-0.542456
15.H	0.946063	-3.832177	-1.399763
16.H	0.368706	-5.251434	-2.270587
17.H	-2.538073	-5.439054	-1.087761
18.H	-2.102683	-5.575842	-2.792743
19.H	-3.299845	-4.370163	-2.287815
20.C	-0.222472	-0.775711	-1.669071
21.C	-1.078825	-0.455326	-2.817792
22.C	-2.398318	-0.225726	-2.608119
23.C	-3.383152	0.287313	-3.595795
24.O	0.909397	-0.233584	-1.587721
25.H	-3.764579	1.266357	-3.265760
26.H	-4.262192	-0.374789	-3.628353
27.H	-2.982859	0.396134	-4.607255
28.H	-2.793669	-0.358285	-1.596566
29.C	-0.338158	-0.187735	-4.104957
30.H	-1.022694	-0.175635	-4.957516
31.H	0.426502	-0.952209	-4.289599
32.H	0.177847	0.780959	-4.065828

33.Al	2.247533	-0.118821	-0.216417
34.C	2.199163	1.691076	0.504628
35.C	3.773496	-1.200984	-0.770060
36.H	3.498019	-2.196162	-1.147421
37.H	4.468639	-1.355522	0.068400
38.H	4.347106	-0.700646	-1.564209
39.H	2.768195	1.753627	1.444070
40.H	1.181545	2.047708	0.717760
41.H	2.658633	2.410304	-0.189056
42.C	-5.087557	-0.079344	1.126060
43.C	-3.780695	2.086218	0.938083
44.C	-3.939684	0.624566	1.243091
45.C	-6.372814	0.541472	0.556384
46.C	-6.065803	1.920043	-0.077389
47.C	-5.132709	2.784812	0.769684
48.C	-5.156159	-1.476592	1.592885
49.H	-3.168824	2.217054	0.025556
50.H	-3.194021	2.559019	1.741733
51.H	-3.057151	0.105065	1.630814
52.H	-5.000146	3.773742	0.310737
53.H	-3.996179	-1.321686	3.372526
54.C	-6.983070	-0.357543	-0.541135
55.H	-7.016371	2.440216	-0.264473
56.H	-5.601152	1.758314	-1.065502
57.H	-5.579010	2.958388	1.759875
58.C	-4.563259	-1.962416	2.695993
59.H	-5.786721	-2.157347	1.013635
60.H	-4.676410	-3.007782	2.983253
61.C	-7.406278	0.692257	1.696438
62.H	-8.352727	1.086299	1.300980
63.H	-7.048984	1.374600	2.477896
64.H	-7.614416	-0.274843	2.172643
65.H	-7.827940	0.162371	-1.012988
66.H	-7.368941	-1.304353	-0.143117
67.H	-6.249023	-0.584945	-1.327845

Aluminum complexed *s-cis* pathway, first transition state (12a)





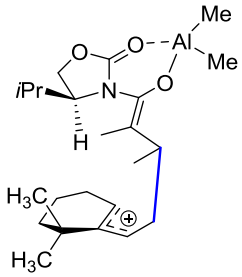


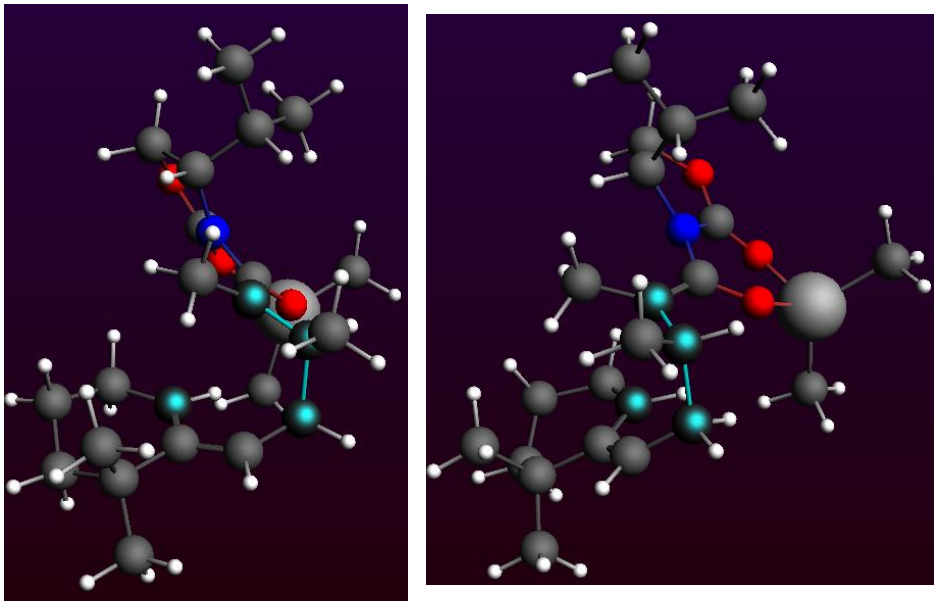
ADF total bond energy: -8606.04 kcal/mol; Entropy: 177.565 cal/mole-K; Internal Energy: 366.705 kcal/mole

1.C	0.433867	-0.547575	-0.732083
2.C	2.457255	0.172818	0.615797
3.C	1.134112	0.396342	-0.032228
4.C	0.931554	-1.998375	-0.859987
5.C	2.089099	-2.253453	0.137450
6.C	3.124811	-1.130434	0.171341
7.C	-0.802658	-0.196584	-1.380492
8.H	2.297510	0.167341	1.711447
9.H	3.106979	1.046475	0.442940
10.H	0.689258	1.384459	0.103213
11.H	3.947197	-1.385907	0.851797
12.H	-1.181396	1.791325	-0.644690
13.C	-0.206201	-2.986084	-0.517475
14.H	2.563126	-3.212327	-0.114956
15.H	1.663933	-2.373325	1.146885
16.H	3.574978	-0.996269	-0.823983
17.C	-1.443300	1.028379	-1.375854
18.H	-1.269755	-0.984646	-1.975387
19.H	-2.473604	1.056847	-1.727778
20.C	1.405404	-2.263644	-2.306042
21.H	1.698586	-3.316005	-2.419840
22.H	2.269069	-1.640433	-2.573506
23.H	0.606556	-2.065287	-3.034389

24.H	0.192287	-4.009455	-0.501278
25.H	-1.019853	-2.969704	-1.253904
26.H	-0.633308	-2.774338	0.471535
27.N	2.144131	4.251985	-1.964134
28.C	2.996386	4.513007	-3.166924
29.C	4.213520	5.166702	-2.488400
30.O	3.719686	5.648359	-1.199246
31.C	2.554130	5.072702	-0.937805
32.C	2.278748	5.369183	-4.234245
33.H	3.295201	3.564796	-3.620440
34.C	1.847651	6.753095	-3.734898
35.C	3.161123	5.465434	-5.487371
36.O	1.971035	5.297672	0.138146
37.H	4.603373	6.033566	-3.028483
38.H	5.025156	4.459715	-2.281526
39.H	1.371352	4.805226	-4.505910
40.H	2.708047	7.380066	-3.462156
41.H	1.174674	6.698002	-2.869161
42.H	1.305143	7.281332	-4.528252
43.H	4.082103	6.034700	-5.296941
44.H	2.622471	5.986478	-6.287799
45.H	3.446818	4.474949	-5.866852
46.C	0.882944	3.587915	-1.948661
47.C	0.614375	2.508740	-2.823038
48.C	-0.751316	2.185422	-3.017099
49.C	-1.206974	1.406959	-4.220500
50.O	-0.000173	4.025467	-1.123850
51.H	-2.264295	1.131827	-4.143840
52.H	-0.620991	0.499267	-4.399064
53.H	-1.103368	2.043958	-5.114036
54.H	-1.447053	2.954407	-2.679117
55.C	1.686484	1.698300	-3.504541
56.H	2.642086	1.738213	-2.972169
57.H	1.851762	1.989799	-4.553553
58.H	1.382446	0.643841	-3.520272
59.Al	0.081054	5.089601	0.420519
60.C	-0.175325	3.950012	1.992335
61.C	-0.783948	6.812885	0.091829
62.H	-0.477412	7.290444	-0.850070
63.H	-0.564923	7.526343	0.900065
64.H	-1.878807	6.707682	0.056459
65.H	0.495700	3.079101	2.021237
66.H	-1.206447	3.571799	2.059519
67.H	0.005076	4.518844	2.916985

Aluminum complexed *s-cis* intermediate (13a)



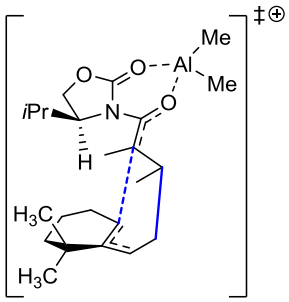


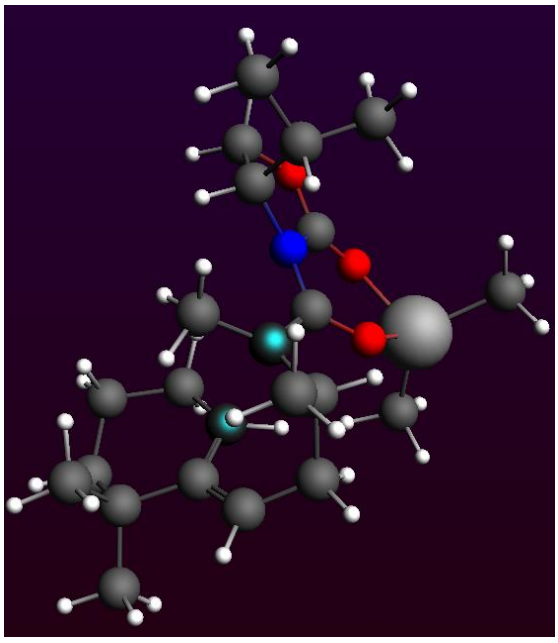
ADF total bond energy: -8610.21 kcal/mol; Entropy: 179.800 cal/mole-K; Internal Energy: 368.253 kcal/mole

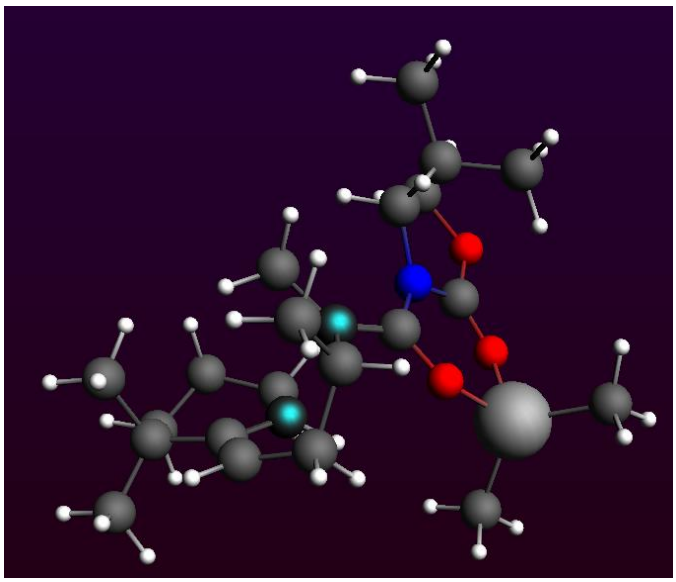
1.C	0.351259	-0.388783	-0.873689
2.C	2.384477	0.636988	0.255694
3.C	1.011448	0.698729	-0.299534
4.C	0.954579	-1.807243	-0.845679
5.C	2.166681	-1.847986	0.117801
6.C	3.120311	-0.666286	-0.060606
7.C	-0.867861	-0.155976	-1.515103
8.H	2.286786	0.770290	1.352223
9.H	2.951513	1.529398	-0.059945
10.H	0.451117	1.614444	-0.117215
11.H	3.993177	-0.771341	0.595910
12.H	-1.375259	1.797499	-0.817221
13.C	-0.103833	-2.805607	-0.328438
14.H	2.696572	-2.799268	-0.027253
15.H	1.797413	-1.853067	1.156102
16.H	3.507693	-0.639074	-1.089930
17.C	-1.483947	1.147842	-1.693718
18.H	-1.350976	-1.005647	-2.002669
19.H	-2.546710	1.050206	-1.942518
20.C	1.391462	-2.230469	-2.264770
21.H	1.763879	-3.263361	-2.249036
22.H	2.192131	-1.590818	-2.659174
23.H	0.551041	-2.192228	-2.971227

24.H	0.352385	-3.798706	-0.221395
25.H	-0.952183	-2.912308	-1.016536
26.H	-0.492315	-2.503976	0.653051
27.N	2.190115	4.053927	-1.904921
28.C	3.020736	4.360761	-3.111751
29.C	4.252373	4.981840	-2.427920
30.O	3.780501	5.419749	-1.115594
31.C	2.613020	4.838225	-0.862894
32.C	2.288655	5.260429	-4.132130
33.H	3.308113	3.430930	-3.609701
34.C	1.873752	6.626132	-3.572540
35.C	3.147398	5.400422	-5.397309
36.O	2.038978	5.032298	0.226786
37.H	4.641914	5.864349	-2.942505
38.H	5.061382	4.261355	-2.260014
39.H	1.372934	4.711610	-4.407483
40.H	2.742304	7.237170	-3.289672
41.H	1.214712	6.539677	-2.698882
42.H	1.321324	7.187733	-4.335616
43.H	4.075480	5.956574	-5.202324
44.H	2.597274	5.955239	-6.166687
45.H	3.419713	4.423777	-5.820198
46.C	0.893433	3.437417	-1.910850
47.C	0.601571	2.349223	-2.733236
48.C	-0.843985	2.030754	-2.921180
49.C	-1.201078	1.401118	-4.271173
50.O	0.000001	3.955397	-1.124859
51.H	-2.287567	1.271608	-4.349494
52.H	-0.735873	0.420094	-4.423838
53.H	-0.888070	2.052702	-5.097196
54.H	-1.410124	2.963497	-2.799077
55.C	1.626895	1.569507	-3.503827
56.H	2.619674	1.603363	-3.043093
57.H	1.714971	1.897634	-4.552568
58.H	1.328075	0.513612	-3.546489
59.Al	0.132709	4.931344	0.459113
60.C	-0.225865	3.753268	1.988405
61.C	-0.619371	6.723233	0.228703
62.H	-0.270646	7.236913	-0.678758
63.H	-0.368875	7.371126	1.081727
64.H	-1.717997	6.687827	0.174355
65.H	0.425172	2.867684	2.035393
66.H	-1.266607	3.394939	1.991174
67.H	-0.085564	4.295614	2.935680

Aluminum complexed *s-cis* pathway, second transition state (14a)





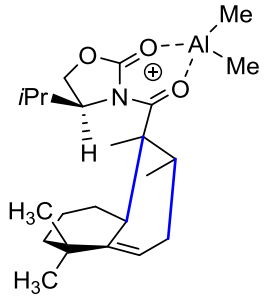


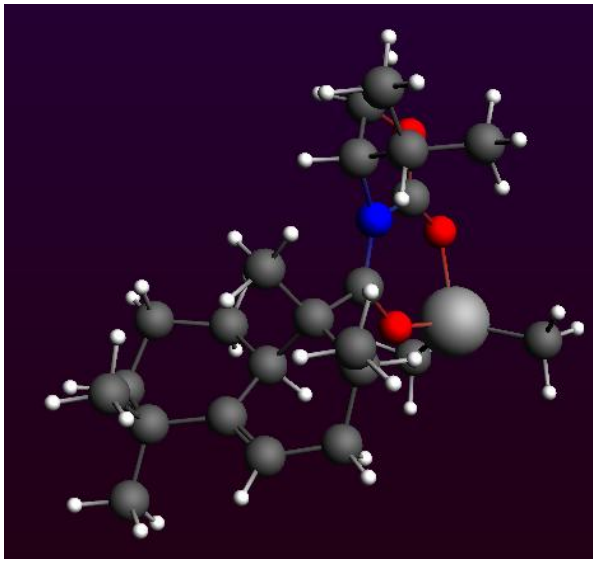
ADF total bond energy: -8609.63 kcal/mol; Entropy: 172.607 cal/mole-K; Internal Energy: 368.334 kcal/mole

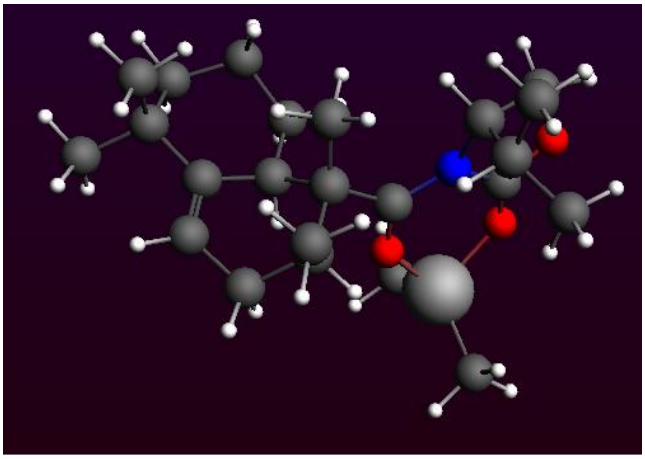
1.C	0.279625	-0.343308	-0.980985
2.C	2.352492	0.863488	-0.091088
3.C	0.929495	0.854282	-0.554810
4.C	0.974998	-1.720461	-0.921542
5.C	2.276661	-1.632141	-0.088638
6.C	3.127196	-0.411004	-0.434448
7.C	-0.996019	-0.211454	-1.477400
8.H	2.316194	0.987269	1.007990
9.H	2.874252	1.766906	-0.445014
10.H	0.288797	1.623845	-0.125063
11.H	4.072129	-0.428146	0.124020
12.H	-1.589995	1.712511	-0.775164
13.C	0.034754	-2.736390	-0.237647
14.H	2.848764	-2.558639	-0.234916
15.H	2.017584	-1.592382	0.981772
16.H	3.397266	-0.423360	-1.500861
17.C	-1.617181	1.104168	-1.691242
18.H	-1.525183	-1.098319	-1.829241
19.H	-2.663684	1.011250	-2.002407
20.C	1.298076	-2.226618	-2.344722
21.H	1.719380	-3.239610	-2.294168
22.H	2.029568	-1.588452	-2.857781
23.H	0.393740	-2.270524	-2.965939

24.H	0.558960	-3.693498	-0.113497
25.H	-0.867481	-2.934635	-0.829708
26.H	-0.275593	-2.387327	0.755731
27.N	2.174582	3.989388	-1.767158
28.C	3.045213	4.225611	-2.964540
29.C	4.247441	4.904536	-2.286284
30.O	3.727884	5.426602	-1.024027
31.C	2.560947	4.854876	-0.763252
32.C	2.336536	5.051040	-4.061545
33.H	3.358555	3.269588	-3.389074
34.C	1.894659	6.446182	-3.604353
35.C	3.230942	5.116620	-5.307903
36.O	1.958116	5.116853	0.292095
37.H	4.645775	5.753961	-2.847471
38.H	5.056658	4.207008	-2.041056
39.H	1.432713	4.477700	-4.327158
40.H	2.749659	7.083367	-3.338822
41.H	1.211402	6.412164	-2.745536
42.H	1.359701	6.950529	-4.418055
43.H	4.148284	5.693400	-5.123055
44.H	2.699159	5.614878	-6.127160
45.H	3.523354	4.117311	-5.658097
46.C	0.898094	3.351056	-1.759187
47.C	0.618750	2.184152	-2.512846
48.C	-0.858292	1.965824	-2.802536
49.C	-1.147739	1.398182	-4.199273
50.O	0.002559	3.851898	-0.984396
51.H	-2.231677	1.382732	-4.368185
52.H	-0.779732	0.372757	-4.326112
53.H	-0.703854	2.018179	-4.988217
54.H	-1.345276	2.947004	-2.725739
55.C	1.630568	1.500315	-3.393688
56.H	2.624564	1.453433	-2.936081
57.H	1.722523	1.974582	-4.383075
58.H	1.312906	0.468479	-3.578651
59.Al	0.060937	4.928997	0.552409
60.C	-0.225606	3.806657	2.131983
61.C	-0.784223	6.654658	0.191996
62.H	-0.458080	7.119570	-0.749556
63.H	-0.573450	7.374854	0.996343
64.H	-1.879038	6.556815	0.139198
65.H	0.438087	2.930964	2.183026
66.H	-1.260418	3.436188	2.184939
67.H	-0.057593	4.383902	3.053719

Product for the *s-cis* pathway before conformation change (15a)





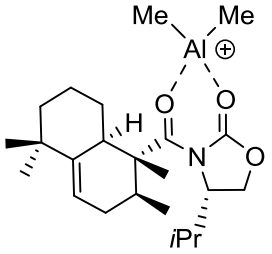


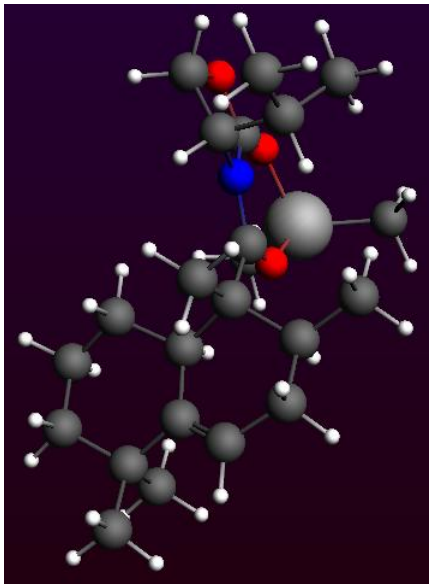
ADF total bond energy: -8618.42 kcal/mol: Entropy: 167.140 cal/mole-K: Internal Energy: 369.634 kcal/mole

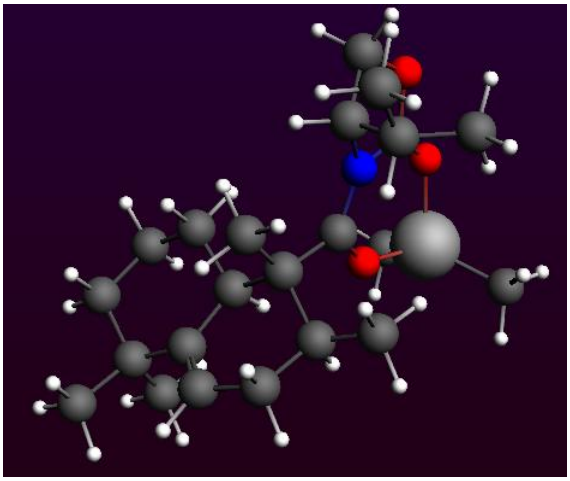
1.C	0.175537	-0.419841	-1.269325
2.C	2.159313	0.791080	-0.080673
3.C	0.799708	0.891185	-0.817254
4.C	0.863548	-1.786636	-1.108938
5.C	2.046428	-1.702322	-0.115032
6.C	2.946542	-0.493512	-0.354385
7.C	-1.048287	-0.286017	-1.814660
8.H	1.954228	0.828131	0.999270
9.H	2.786167	1.672691	-0.290855
10.H	0.084431	1.347690	-0.119148
11.H	3.819726	-0.530553	0.311668
12.H	-1.875054	1.488292	-0.955571
13.C	-0.139053	-2.827952	-0.567377
14.H	2.623089	-2.635837	-0.181290
15.H	1.653265	-1.652962	0.913642
16.H	3.341455	-0.510758	-1.381486
17.C	-1.641014	1.080307	-1.953474
18.H	-1.614003	-1.148283	-2.166476
19.H	-2.587818	1.056592	-2.506846
20.C	1.381131	-2.288603	-2.479332
21.H	1.806130	-3.296245	-2.372360
22.H	2.166569	-1.643663	-2.895215
23.H	0.563561	-2.340289	-3.209553

24.H	0.379434	-3.778550	-0.381184
25.H	-0.949245	-3.031547	-1.278268
26.H	-0.588106	-2.492121	0.376149
27.N	2.168158	4.130052	-1.678994
28.C	3.034562	4.219511	-2.902853
29.C	4.187190	5.072631	-2.356632
30.O	3.611995	5.793333	-1.220527
31.C	2.498562	5.203381	-0.835709
32.C	2.282167	4.827556	-4.108683
33.H	3.403668	3.227129	-3.161406
34.C	1.773015	6.255300	-3.875126
35.C	3.169039	4.736619	-5.358865
36.O	1.892331	5.602128	0.165478
37.H	4.550952	5.823460	-3.062385
38.H	5.025263	4.481118	-1.970802
39.H	1.405725	4.179109	-4.270686
40.H	2.594507	6.969311	-3.724786
41.H	1.092069	6.328516	-3.016589
42.H	1.212274	6.593889	-4.754421
43.H	4.059659	5.375415	-5.277116
44.H	2.611241	5.077066	-6.239152
45.H	3.504898	3.708971	-5.552510
46.C	1.091627	3.278194	-1.397396
47.C	0.812520	1.940636	-2.060926
48.C	-0.669051	2.062752	-2.669613
49.C	-0.747969	1.870221	-4.189573
50.O	0.313421	3.619134	-0.470788
51.H	-1.782974	2.043550	-4.510766
52.H	-0.474693	0.853047	-4.495841
53.H	-0.120323	2.577343	-4.746655
54.H	-1.034766	3.075577	-2.454325
55.C	1.831375	1.429479	-3.082818
56.H	2.831042	1.327171	-2.644481
57.H	1.892145	2.035467	-3.990920
58.H	1.517794	0.428096	-3.394253
59.Al	0.157760	5.038919	0.792606
60.C	0.365062	4.301682	2.583962
61.C	-1.168197	6.304226	0.120621
62.H	-1.060812	6.536236	-0.948805
63.H	-1.108585	7.258886	0.664193
64.H	-2.190442	5.925566	0.268178
65.H	1.218937	3.615961	2.676792
66.H	-0.533547	3.751042	2.898749
67.H	0.513561	5.103962	3.321893

Diels-Alder adduct 3, Me_2Al complexed (16a)





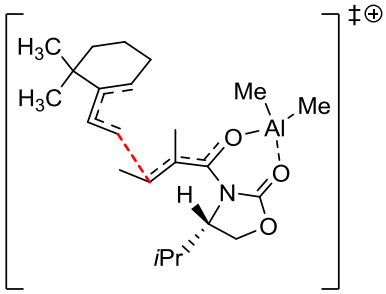


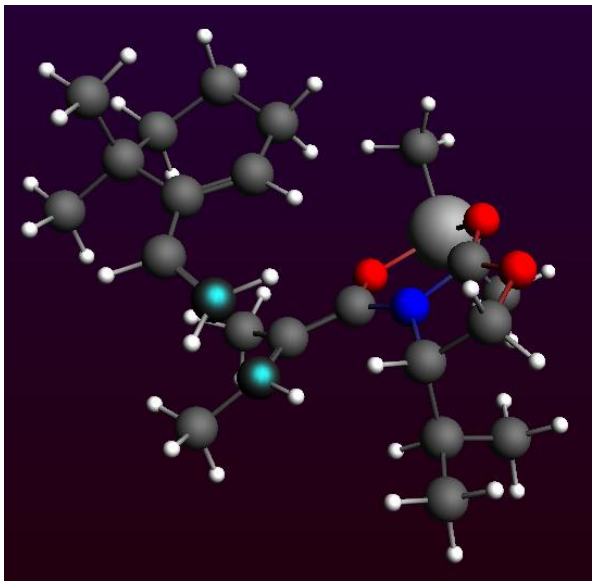
ADF total bond energy: -8628.15 kcal/mol; Entropy: 167.975 cal/mole-K; Internal Energy: 369.673 kcal/mole

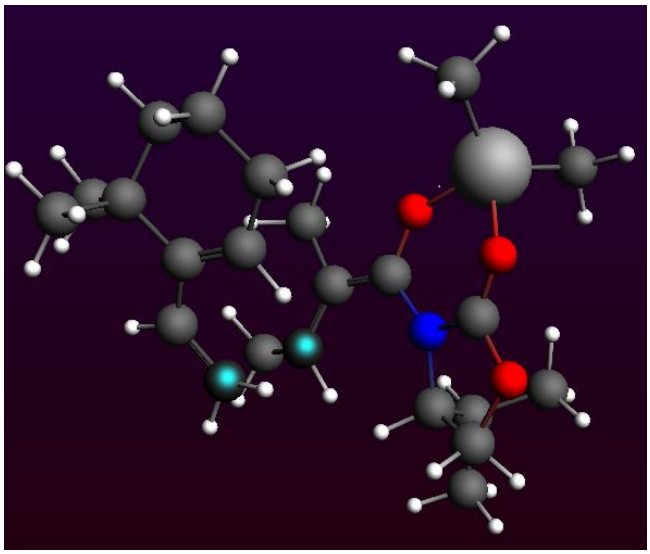
1.O	6.102669	4.978419	0.865728
2.O	6.618609	7.432118	0.146659
3.O	8.609315	7.628761	-0.806586
4.N	7.994375	5.534819	-0.256705
5.C	7.643059	3.183021	0.825331
6.C	6.497612	2.226851	0.304841
7.H	5.584658	2.552168	0.823474
8.C	6.799479	0.795910	0.753732
9.H	5.892710	0.192586	0.584769
10.H	7.565379	0.333044	0.105887
11.C	7.179405	0.697010	2.199187
12.H	7.136092	-0.301845	2.632174
13.C	7.494773	1.741401	2.980889
14.C	7.633795	1.596864	4.509282
15.C	8.773904	2.492327	5.055100
16.H	8.752916	2.452537	6.153743
17.H	9.740635	2.061812	4.745711
18.C	8.699570	3.939363	4.573124
19.H	7.785638	4.427636	4.943256
20.H	9.543974	4.515586	4.976288
21.C	8.736846	3.972486	3.045466
22.H	9.703989	3.557636	2.725061
23.H	8.697546	5.014131	2.684351
24.C	7.581296	3.160182	2.423118
25.H	6.645533	3.673373	2.694208
26.C	9.014917	2.689584	0.345860
27.H	9.066944	2.567869	-0.741587
28.H	9.197713	1.708235	0.796229

29.H	9.837254	3.329785	0.677361
30.C	6.242789	2.293336	-1.203070
31.H	5.959721	3.300210	-1.540755
32.H	5.411539	1.626644	-1.466317
33.H	7.113270	1.959103	-1.784229
34.C	6.285134	2.019058	5.149173
35.H	5.477215	1.360671	4.805502
36.H	6.002523	3.051154	4.906013
37.H	6.348457	1.941172	6.243457
38.C	7.928237	0.149279	4.936750
39.H	7.094064	-0.528922	4.716875
40.H	8.089859	0.117091	6.022420
41.H	8.831635	-0.240089	4.448687
42.C	7.225019	4.600824	0.448683
43.C	7.651000	6.898601	-0.275352
44.C	9.762159	6.781843	-1.117249
45.H	10.505091	6.948939	-0.328943
46.H	10.154255	7.115002	-2.081102
47.C	9.198930	5.355776	-1.140450
48.H	9.901398	4.672745	-0.664619
49.C	8.830324	4.824862	-2.544662
50.H	8.302667	3.873987	-2.375684
51.C	7.896344	5.744897	-3.340557
52.H	7.647602	5.274308	-4.299230
53.H	8.362272	6.713120	-3.570328
54.H	6.945593	5.935058	-2.824388
55.C	10.119304	4.514626	-3.320002
56.H	10.694914	5.424027	-3.542961
57.H	9.873490	4.048533	-4.281449
58.H	10.773739	3.823942	-2.771453
59.Al	5.037240	6.563348	0.826311
60.C	3.757703	6.400913	-0.638776
61.C	4.752163	7.159789	2.658327
62.H	5.665115	7.143670	3.269942
63.H	4.003010	6.538309	3.170398
64.H	4.368591	8.190721	2.678183
65.H	4.194810	6.024215	-1.574678
66.H	3.301618	7.375816	-0.866985
67.H	2.931416	5.725285	-0.372770

Aluminum complexed *s-trans* pathway, first transition state (12b)





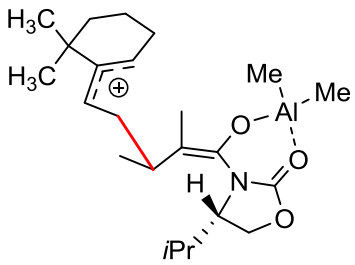


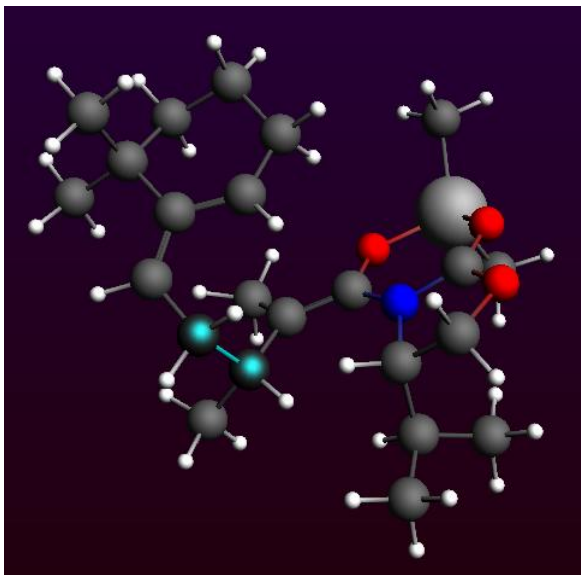
ADF total bond energy: -8601.32 kcal/mol; Entropy: 180.363 cal/mole-K; Internal Energy: 366.496 kcal/mole

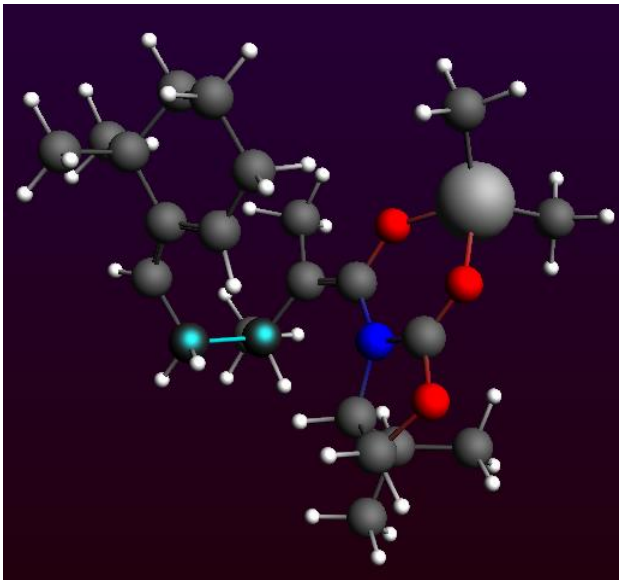
1.N	-0.590883	-2.588501	-0.535461
2.C	-0.641340	-3.898961	-1.262600
3.C	0.103155	-4.784505	-0.246872
4.O	0.903534	-3.857436	0.550914
5.C	0.448551	-2.624508	0.361861
6.C	-0.027432	-3.824730	-2.677843
7.H	-1.676904	-4.239830	-1.351720
8.C	1.452159	-3.423403	-2.695590
9.C	-0.264154	-5.156043	-3.405698
10.O	0.955676	-1.665279	0.973655
11.H	0.794554	-5.495270	-0.707385
12.H	-0.569497	-5.309931	0.441071
13.H	-0.600310	-3.046506	-3.208338
14.H	2.087831	-4.167110	-2.195147
15.H	1.628986	-2.446875	-2.226502
16.H	1.802181	-3.347198	-3.732137
17.H	0.290573	-5.982400	-2.938799
18.H	0.082046	-5.083752	-4.443588
19.H	-1.327674	-5.430340	-3.426920
20.C	-1.126009	-1.337219	-0.999289
21.C	-2.426640	-1.247834	-1.536486
22.C	-3.427343	-2.220442	-1.286000
23.C	-4.568499	-2.426150	-2.249924
24.O	-0.344026	-0.321037	-0.929429
25.H	-5.035544	-1.484889	-2.556253

26.H	-5.341114	-3.083131	-1.834805
27.H	-4.180954	-2.908343	-3.161678
28.H	-3.090684	-3.136213	-0.802266
29.C	-2.787245	-0.002674	-2.301292
30.H	-2.991214	-0.235231	-3.356847
31.H	-1.986958	0.739935	-2.261517
32.H	-3.703431	0.447564	-1.891505
33.Al	1.009808	0.133143	0.284951
34.C	0.265221	1.316710	1.659025
35.C	2.706666	0.391332	-0.651835
36.H	2.959326	-0.424212	-1.344544
37.H	3.541988	0.480281	0.058329
38.H	2.695303	1.320507	-1.241249
39.H	0.966002	1.431553	2.499428
40.H	-0.682343	0.949722	2.079518
41.H	0.082997	2.326338	1.261898
42.C	-5.099329	0.734949	0.692492
43.C	-3.792131	2.476467	1.997399
44.C	-4.042758	1.106950	1.479880
45.C	-6.189159	1.743817	0.285931
46.C	-5.671593	3.188674	0.494875
47.C	-4.996933	3.409574	1.847517
48.C	-5.264424	-0.639321	0.306072
49.H	-2.915903	2.882017	1.453395
50.H	-3.448371	2.411660	3.042252
51.H	-3.318884	0.344407	1.775888
52.H	-4.678954	4.454739	1.951191
53.H	-3.508161	-1.594660	1.105371
54.C	-6.570706	1.596673	-1.201914
55.H	-6.514443	3.882421	0.367106
56.H	-4.952064	3.423557	-0.306739
57.H	-5.708791	3.220435	2.663858
58.C	-4.391329	-1.708627	0.478232
59.H	-6.204760	-0.875649	-0.198027
60.H	-4.849743	-2.697115	0.516563
61.C	-7.446217	1.488176	1.149042
62.H	-8.250623	2.176294	0.855868
63.H	-7.243098	1.630060	2.217721
64.H	-7.821171	0.463566	1.018495
65.H	-7.295883	2.376474	-1.470059
66.H	-7.043089	0.631785	-1.427969
67.H	-5.697322	1.719582	-1.856736

Aluminum complexed *s-trans* intermediate (13b)





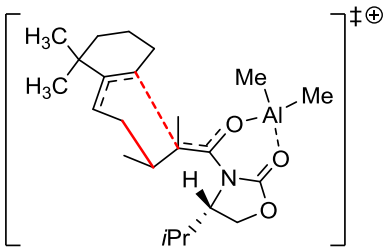


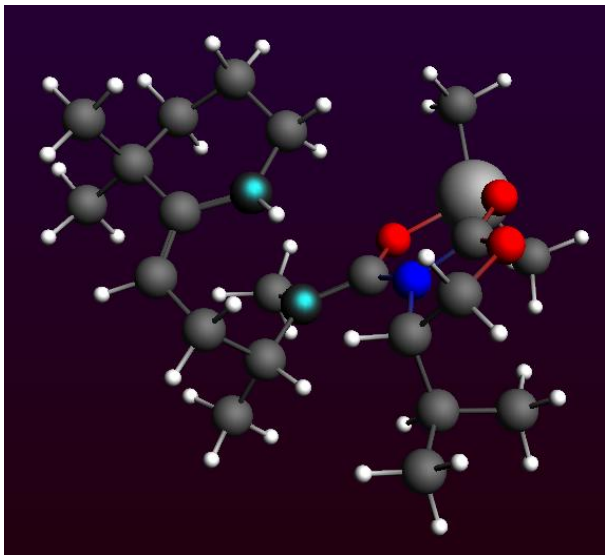
ADF total bond energy: -8605.14 kcal/mol; Entropy: 179.755 cal/mole-K; Internal Energy: 368.425 kcal/mole

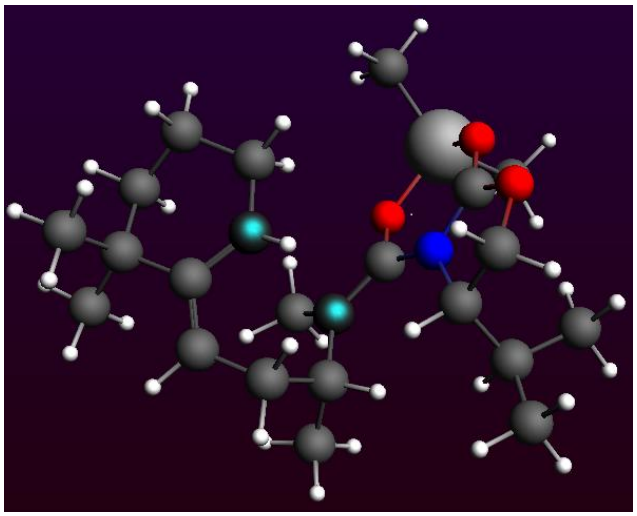
1.N	-0.827083	-2.063491	-0.244398
2.C	-1.092641	-3.498320	-0.575172
3.C	-0.468139	-4.182549	0.650823
4.O	0.488767	-3.214766	1.166516
5.C	0.212128	-2.015406	0.663170
6.C	-0.497852	-3.922586	-1.938594
7.H	-2.170576	-3.684106	-0.567207
8.C	1.029575	-3.802834	-2.010184
9.C	-0.973833	-5.340527	-2.285583
10.O	0.880416	-1.035702	1.038718
11.H	0.085390	-5.093761	0.409421
12.H	-1.193128	-4.387773	1.447763
13.H	-0.919780	-3.231561	-2.685820
14.H	1.532371	-4.486937	-1.312860
15.H	1.381147	-2.783290	-1.805973
16.H	1.372166	-4.063256	-3.018833
17.H	-0.572477	-6.089020	-1.587781
18.H	-0.629119	-5.619238	-3.288362
19.H	-2.069721	-5.423275	-2.275064
20.C	-1.355768	-0.877551	-0.870072
21.C	-2.551567	-0.807146	-1.612841
22.C	-3.452330	-1.932707	-2.022998
23.C	-4.042974	-1.782122	-3.436694
24.O	-0.674054	0.200755	-0.666163
25.H	-4.730096	-0.933386	-3.521323
26.H	-4.598978	-2.690258	-3.700872

27.H	-3.249506	-1.648927	-4.182399
28.H	-2.907037	-2.878582	-2.021686
29.C	-2.846915	0.528523	-2.239773
30.H	-2.534511	0.542071	-3.295625
31.H	-2.337906	1.350660	-1.733201
32.H	-3.930018	0.715658	-2.237902
33.Al	0.976862	0.626503	0.088176
34.C	0.776090	2.102726	1.356402
35.C	2.392771	0.467840	-1.257111
36.H	2.303580	-0.421416	-1.898322
37.H	3.385810	0.426200	-0.785142
38.H	2.401225	1.341892	-1.925662
39.H	1.740369	2.343788	1.828165
40.H	0.067664	1.895594	2.171101
41.H	0.440583	3.023239	0.854957
42.C	-4.975287	-0.016482	0.197947
43.C	-2.960001	0.874276	1.499779
44.C	-3.712743	-0.188866	0.803201
45.C	-5.774208	1.275302	0.443499
46.C	-4.785250	2.438235	0.706377
47.C	-3.770698	2.142766	1.808945
48.C	-5.442639	-1.027532	-0.623136
49.H	-2.096801	1.129816	0.843442
50.H	-2.480177	0.461246	2.400968
51.H	-3.335612	-1.204029	0.912953
52.H	-3.088263	2.991943	1.937595
53.H	-4.183534	-2.654792	-0.081424
54.C	-6.665375	1.659338	-0.750591
55.H	-5.365264	3.336347	0.961674
56.H	-4.255126	2.669876	-0.231788
57.H	-4.286635	2.014500	2.770540
58.C	-4.656626	-2.216381	-0.971649
59.H	-6.396633	-0.888016	-1.132007
60.H	-5.287944	-2.984523	-1.432828
61.C	-6.679522	1.036044	1.675778
62.H	-7.247509	1.947037	1.908182
63.H	-6.104856	0.753059	2.566597
64.H	-7.397981	0.229468	1.477674
65.H	-7.154215	2.620269	-0.544065
66.H	-7.465318	0.929843	-0.930833
67.H	-6.083901	1.775064	-1.675305

Aluminum complexed *s-trans* pathway, second transition state (14b)





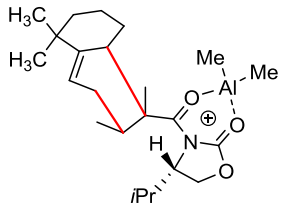


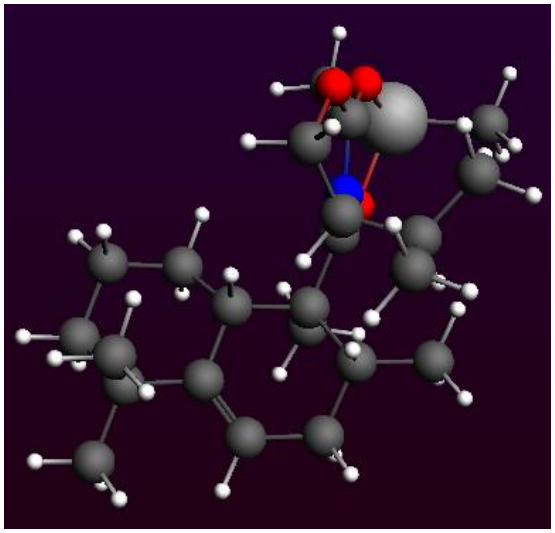
ADF total bond energy: -8605.10 kcal/mol; Entropy: 169.178 cal/mole-K; Internal Energy: 367.685 kcal/mol

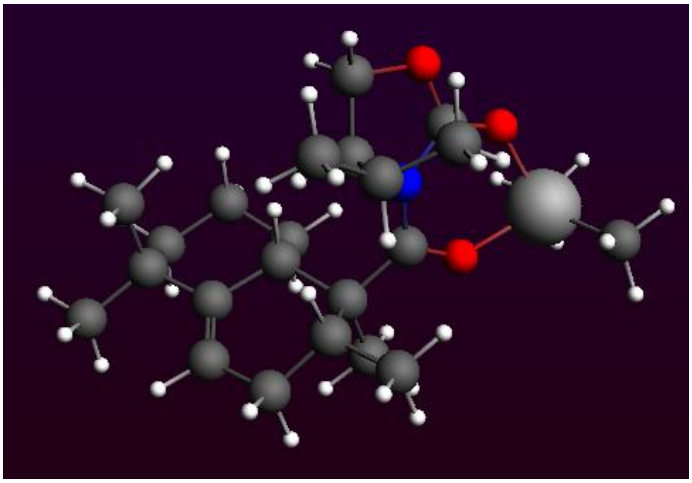
1.N	-0.821872	-2.014244	-0.255186
2.C	-1.110844	-3.453417	-0.546539
3.C	-0.495867	-4.111824	0.697840
4.O	0.483020	-3.147131	1.179718
5.C	0.223538	-1.957897	0.646429
6.C	-0.518922	-3.923164	-1.896620
7.H	-2.191539	-3.621272	-0.536223
8.C	1.010410	-3.829992	-1.968029
9.C	-1.017547	-5.341705	-2.207505
10.O	0.905232	-0.977341	0.992498
11.H	0.038732	-5.040788	0.483313
12.H	-1.221095	-4.276758	1.503858
13.H	-0.927658	-3.245520	-2.663406
14.H	1.501036	-4.503110	-1.251667
15.H	1.378538	-2.811182	-1.791046
16.H	1.350012	-4.123065	-2.968703
17.H	-0.630942	-6.077915	-1.488644
18.H	-0.674246	-5.652648	-3.201254
19.H	-2.114636	-5.405562	-2.198770
20.C	-1.345811	-0.835544	-0.891257
21.C	-2.583266	-0.750461	-1.574605
22.C	-3.454910	-1.892470	-2.029007
23.C	-4.016378	-1.716349	-3.452918
24.O	-0.641530	0.231556	-0.741891
25.H	-4.734820	-0.892592	-3.525219
26.H	-4.532033	-2.635751	-3.757106
27.H	-3.213977	-1.529825	-4.176982

28.H	-2.874489	-2.817253	-2.049657
29.C	-2.860941	0.587337	-2.210868
30.H	-2.466035	0.621557	-3.238073
31.H	-2.405834	1.413841	-1.660716
32.H	-3.942766	0.753659	-2.284400
33.Al	1.014171	0.666790	0.009929
34.C	0.814881	2.166904	1.248464
35.C	2.423581	0.470039	-1.335938
36.H	2.325126	-0.431360	-1.958540
37.H	3.417688	0.430016	-0.866111
38.H	2.436943	1.330411	-2.021874
39.H	1.775897	2.406707	1.727393
40.H	0.093998	1.981488	2.057307
41.H	0.494599	3.081004	0.725879
42.C	-4.962844	-0.046952	0.152461
43.C	-2.903652	0.835886	1.404567
44.C	-3.662738	-0.224698	0.695922
45.C	-5.765038	1.234185	0.445183
46.C	-4.790410	2.392025	0.770335
47.C	-3.758561	2.039380	1.838008
48.C	-5.463686	-1.057662	-0.638741
49.H	-2.102081	1.190397	0.722501
50.H	-2.357457	0.398510	2.253562
51.H	-3.328422	-1.248947	0.852153
52.H	-3.103615	2.897002	2.036395
53.H	-4.210902	-2.699936	-0.136226
54.C	-6.645491	1.663697	-0.742307
55.H	-5.380974	3.262562	1.089074
56.H	-4.273586	2.692936	-0.155589
57.H	-4.259442	1.805831	2.787634
58.C	-4.665987	-2.232695	-1.023064
59.H	-6.446265	-0.937123	-1.094927
60.H	-5.285678	-2.990318	-1.515957
61.C	-6.682920	0.939410	1.656355
62.H	-7.261914	1.835951	1.916280
63.H	-6.116232	0.627767	2.542679
64.H	-7.391400	0.134782	1.418732
65.H	-7.142875	2.612424	-0.501731
66.H	-7.437601	0.937326	-0.963810
67.H	-6.052895	1.821042	-1.653563

Product for the *s-trans* pathway before conformation change (15b)







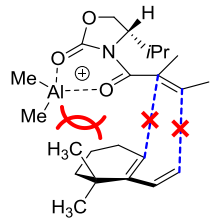
ADF total bond energy: -8628.73 kcal/mol; Entropy: 167.405 cal/mole-K; Internal Energy: 369.675 kcal/mole

1.N	-0.810979	-1.432528	-0.240454
2.C	-1.509183	-2.761749	-0.169669
3.C	-0.988866	-3.252376	1.186271
4.O	0.299536	-2.569144	1.347196
5.C	0.336858	-1.512324	0.560627
6.C	-1.160521	-3.689333	-1.359404
7.H	-2.590549	-2.605038	-0.131483
8.C	0.327260	-4.045577	-1.470918
9.C	-2.041571	-4.945806	-1.285393
10.O	1.288755	-0.723703	0.602704
11.H	-0.787683	-4.325498	1.219183
12.H	-1.617129	-2.957687	2.034914
13.H	-1.442164	-3.138748	-2.267645
14.H	0.685577	-4.623971	-0.608382
15.H	0.968603	-3.161028	-1.583131
16.H	0.487143	-4.666124	-2.360810
17.H	-1.807187	-5.564373	-0.407617
18.H	-1.873182	-5.570448	-2.170593
19.H	-3.110849	-4.697275	-1.250618
20.C	-1.167328	-0.231979	-0.874004
21.C	-2.594559	0.090848	-1.306078
22.C	-3.083297	-0.889693	-2.436098
23.C	-2.157823	-0.956107	-3.656676
24.O	-0.275620	0.635710	-1.008141
25.H	-2.144091	-0.009534	-4.210196
26.H	-2.513296	-1.728137	-4.351497
27.H	-1.117417	-1.200231	-3.398380
28.H	-3.155161	-1.893804	-1.994064
29.C	-2.603936	1.536139	-1.848452
30.H	-2.066699	1.611578	-2.799058

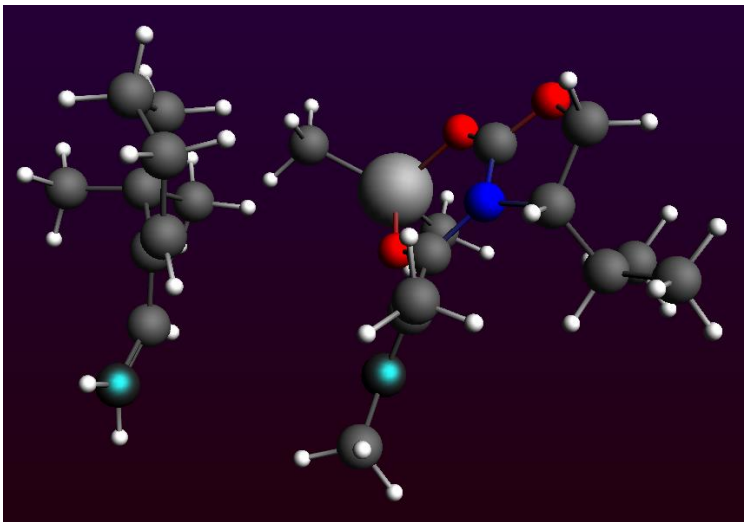
31.H	-2.136872	2.238729	-1.154829
32.H	-3.639958	1.852023	-2.005435
33.Al	1.581003	0.801615	-0.546698
34.C	1.788293	2.376250	0.578661
35.C	2.634146	0.211834	-2.080807
36.H	2.266556	-0.712985	-2.548296
37.H	3.679638	0.031843	-1.789348
38.H	2.657063	0.982775	-2.865098
39.H	2.770493	2.377315	1.073988
40.H	1.027907	2.449840	1.368804
41.H	1.735147	3.301095	-0.014072
42.C	-5.012246	-0.170885	-0.395253
43.C	-3.302582	1.122182	0.966711
44.C	-3.535243	-0.033664	-0.034515
45.C	-5.990151	-0.199783	0.794446
46.C	-5.652268	0.926094	1.806032
47.C	-4.179334	0.970576	2.209403
48.C	-5.421259	-0.333697	-1.662643
49.H	-3.547660	2.079437	0.486741
50.H	-2.237958	1.171445	1.247552
51.H	-3.255042	-0.950549	0.511328
52.H	-4.002198	1.814571	2.890218
53.H	-4.909123	-1.303580	-3.487359
54.C	-7.452224	-0.017451	0.356509
55.H	-6.290441	0.803961	2.693269
56.H	-5.925881	1.893511	1.354955
57.H	-3.900656	0.062547	2.767434
58.C	-4.510770	-0.506161	-2.840144
59.H	-6.488063	-0.390317	-1.876252
60.H	-4.503056	0.395925	-3.475191
61.C	-5.874818	-1.581987	1.487813
62.H	-6.563381	-1.632681	2.342409
63.H	-4.865698	-1.783775	1.871495
64.H	-6.141679	-2.385189	0.788449
65.H	-8.096317	0.020990	1.244899
66.H	-7.807605	-0.849746	-0.264695
67.H	-7.592604	0.917842	-0.201248

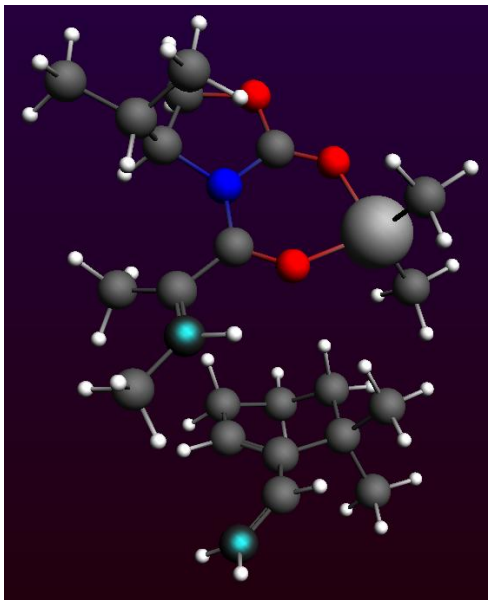
The disfavored approaches for the Diels-Alder reaction

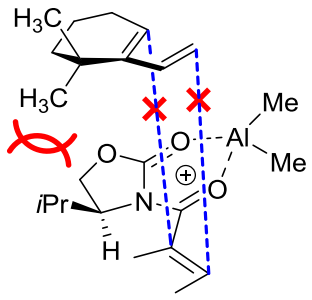
The reaction partners were brought together but not converged. From the different approaches the steric interactions are clearly visible. The carbons in the diene and dienophile involved in initial bond formation are highlighted.



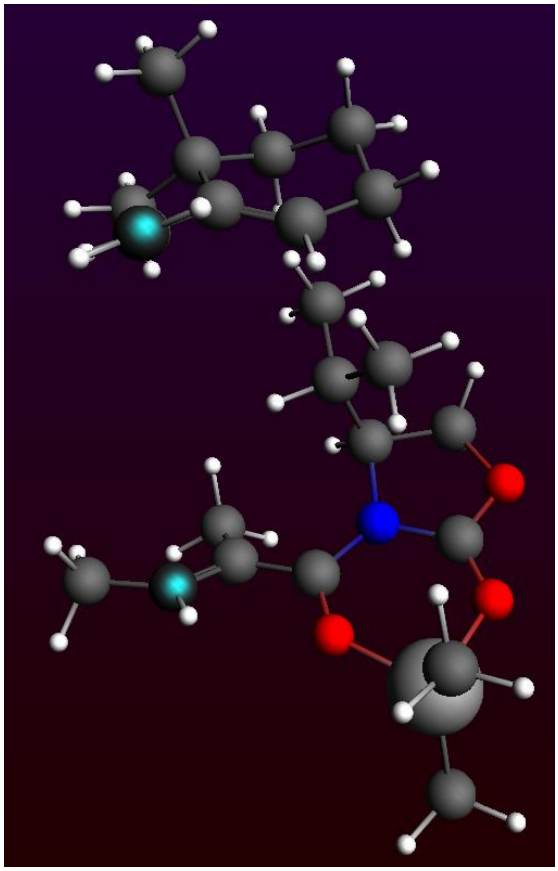
***Endo* approach**
Disfavored

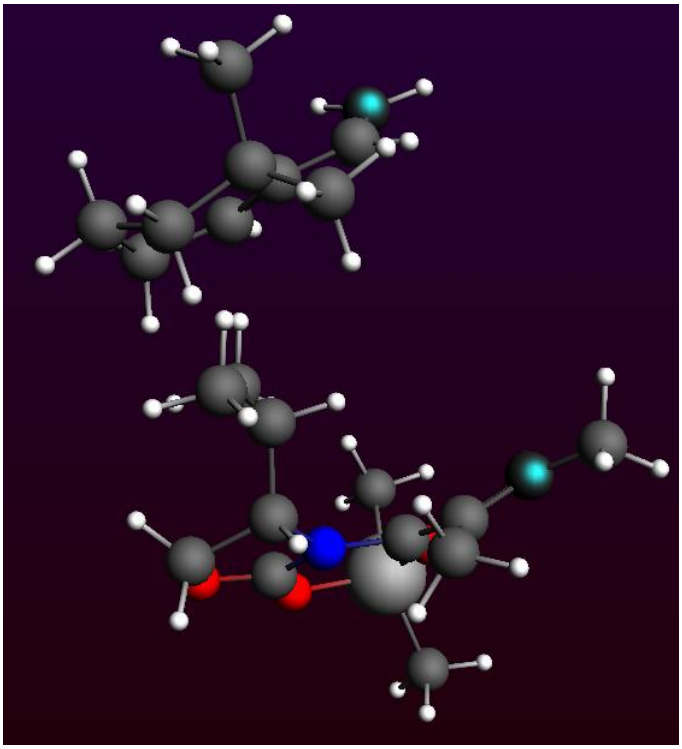


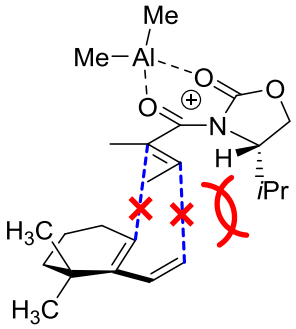




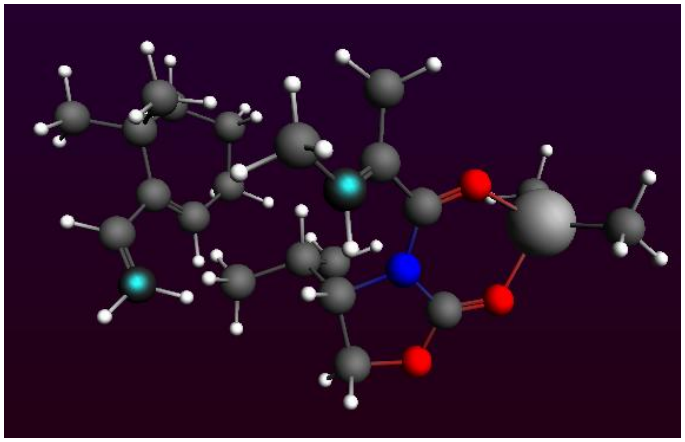
***Exo Re*-face approach**
Disfavored

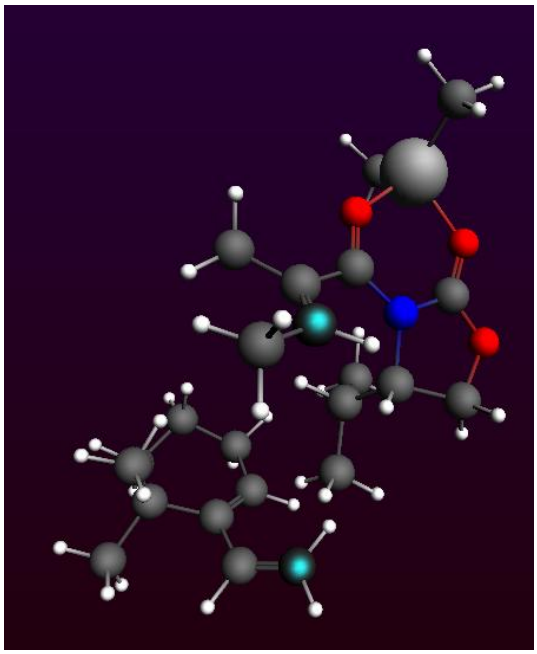


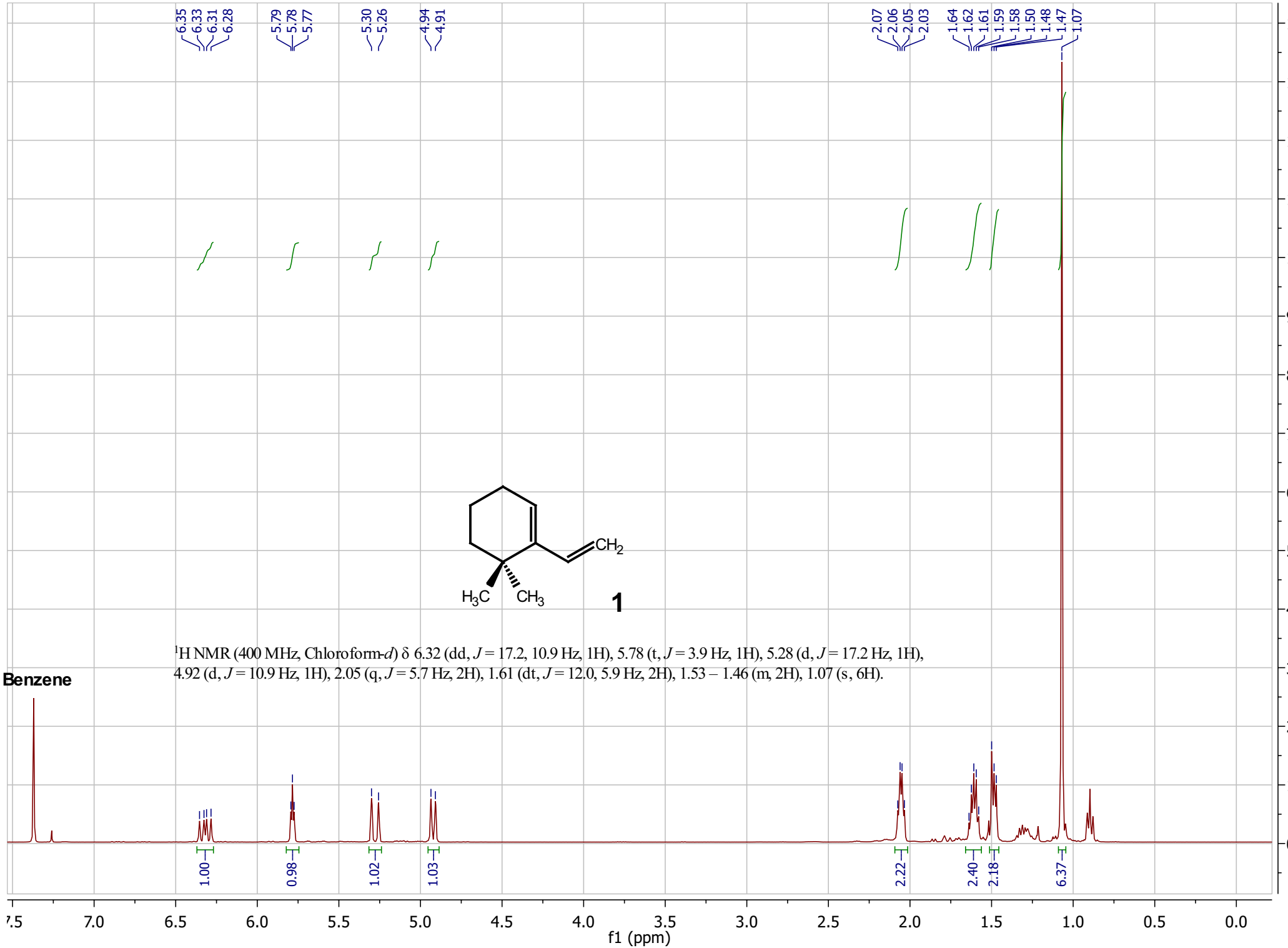




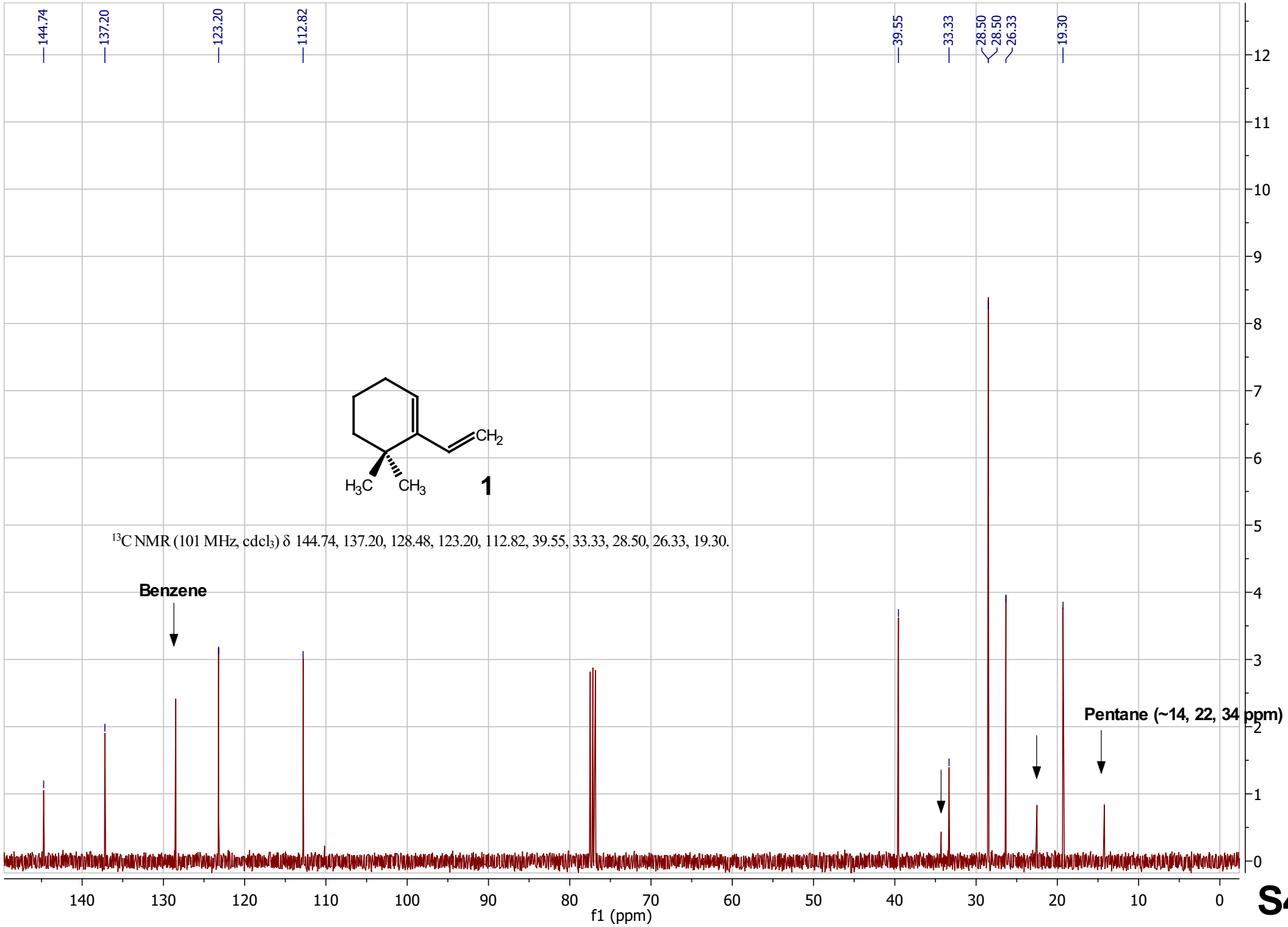
***Exo Si*-face approach**
Disfavored

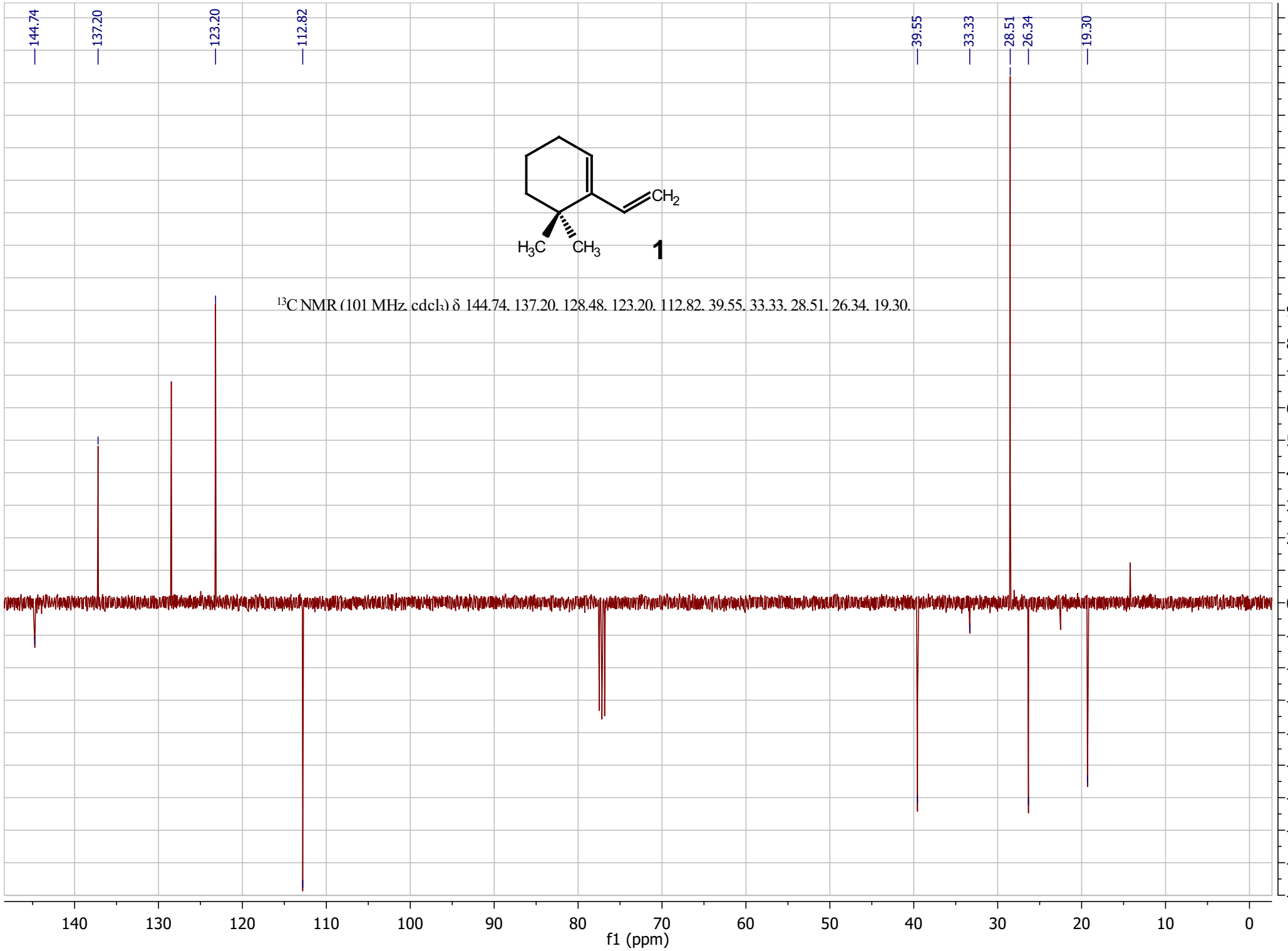


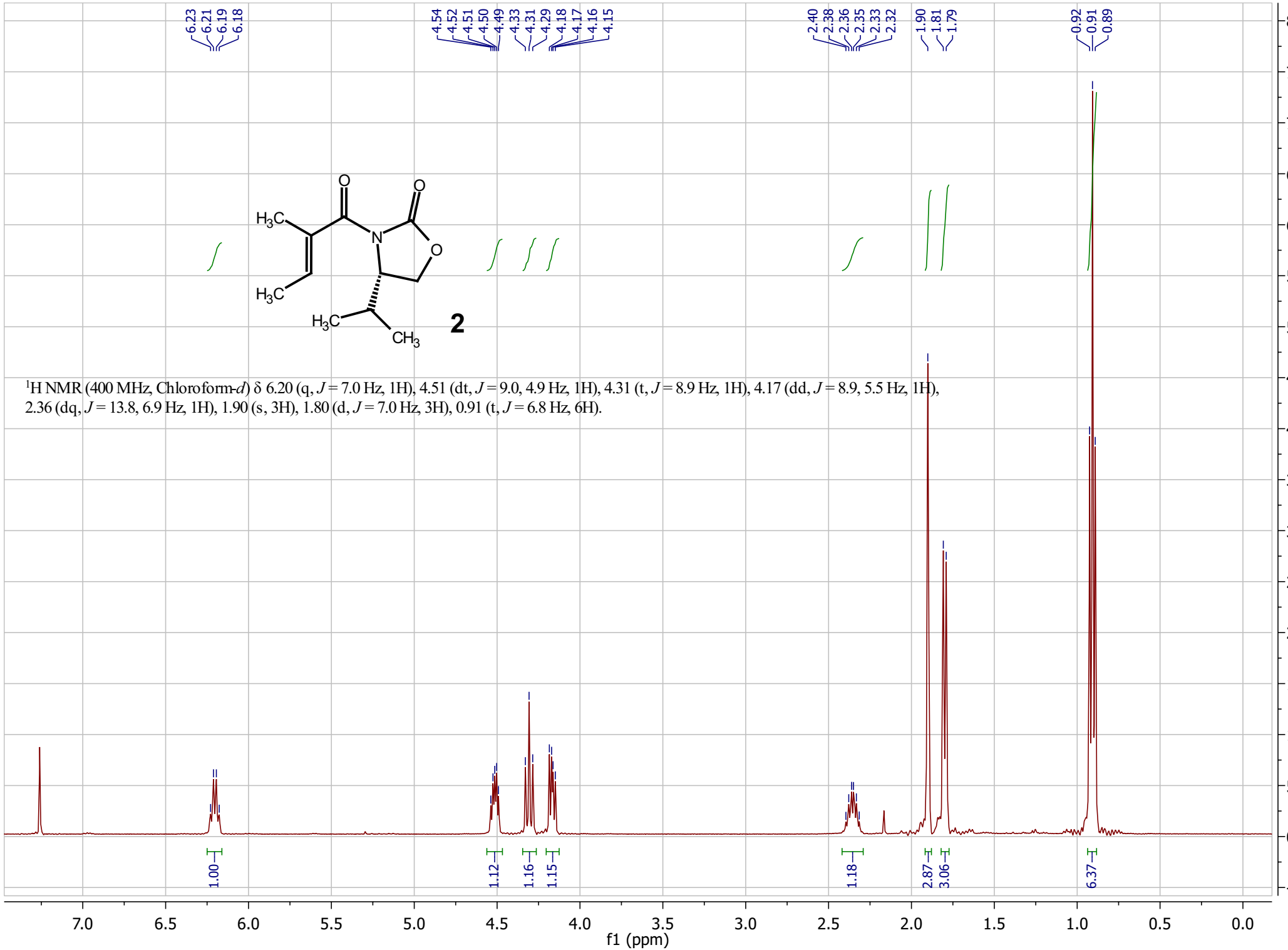




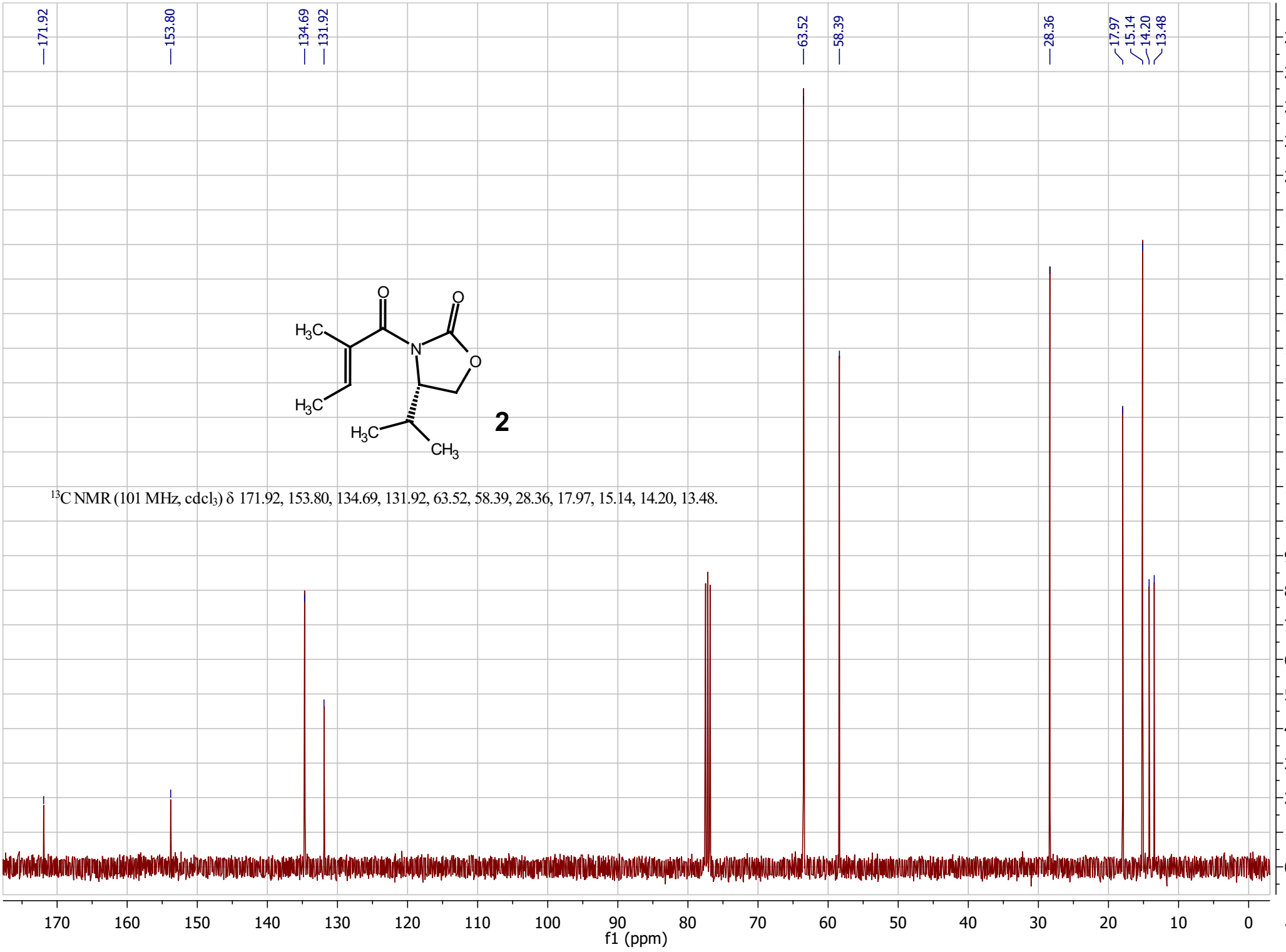
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.32 (dd, *J* = 17.2, 10.9 Hz, 1H), 5.78 (t, *J* = 3.9 Hz, 1H), 5.28 (d, *J* = 17.2 Hz, 1H), 4.92 (d, *J* = 10.9 Hz, 1H), 2.05 (q, *J* = 5.7 Hz, 2H), 1.61 (dt, *J* = 12.0, 5.9 Hz, 2H), 1.53 – 1.46 (m, 2H), 1.07 (s, 6H).


144.74
137.20
123.20
112.82
39.55
33.33
28.50
28.50
26.33
19.30
CH2
H3C
CH3
1
13C NMR (101 MHz, cdcl3) δ 144.74, 137.20, 128.48, 123.20, 112.82, 39.55, 33.33, 28.50, 26.33, 19.30.
Benzene
Pentane (~14, 22, 34 ppm)
f1 (ppm)


144.74
137.20
123.20
112.82
39.55
33.33
28.51
26.34
19.30
CH2
H3C
CH3
1
13C NMR (101 MHz, cdcl3) δ 144.74, 137.20, 128.48, 123.20, 112.82, 39.55, 33.33, 28.51, 26.34, 19.30.
f1 (ppm)

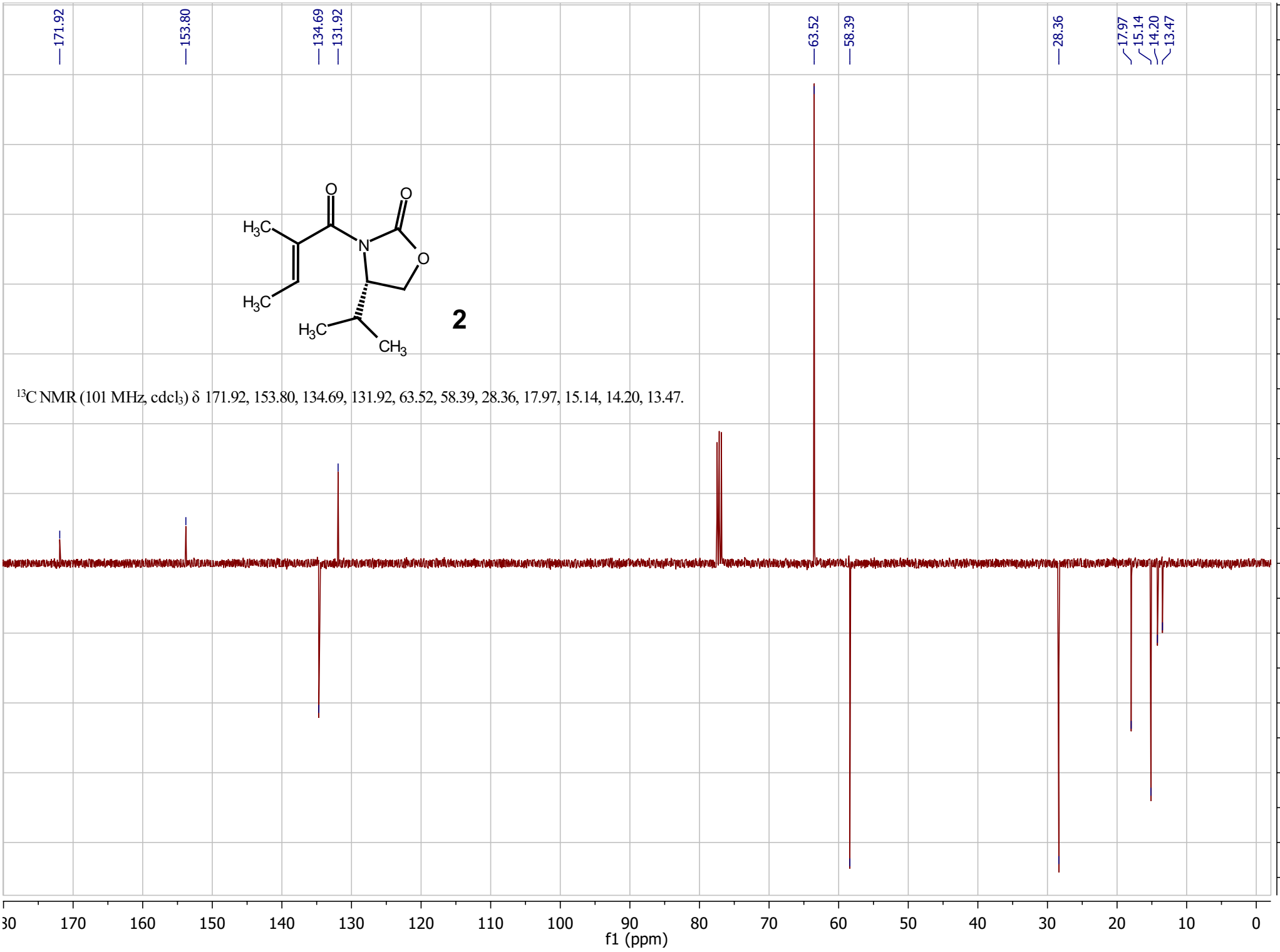


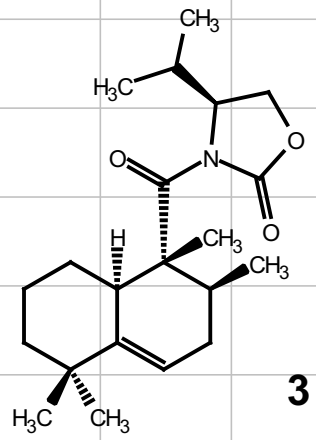
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.20 (q, *J* = 7.0 Hz, 1H), 4.51 (dt, *J* = 9.0, 4.9 Hz, 1H), 4.31 (t, *J* = 8.9 Hz, 1H), 4.17 (dd, *J* = 8.9, 5.5 Hz, 1H), 2.36 (dq, *J* = 13.8, 6.9 Hz, 1H), 1.90 (s, 3H), 1.80 (d, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 6.8 Hz, 6H).



2

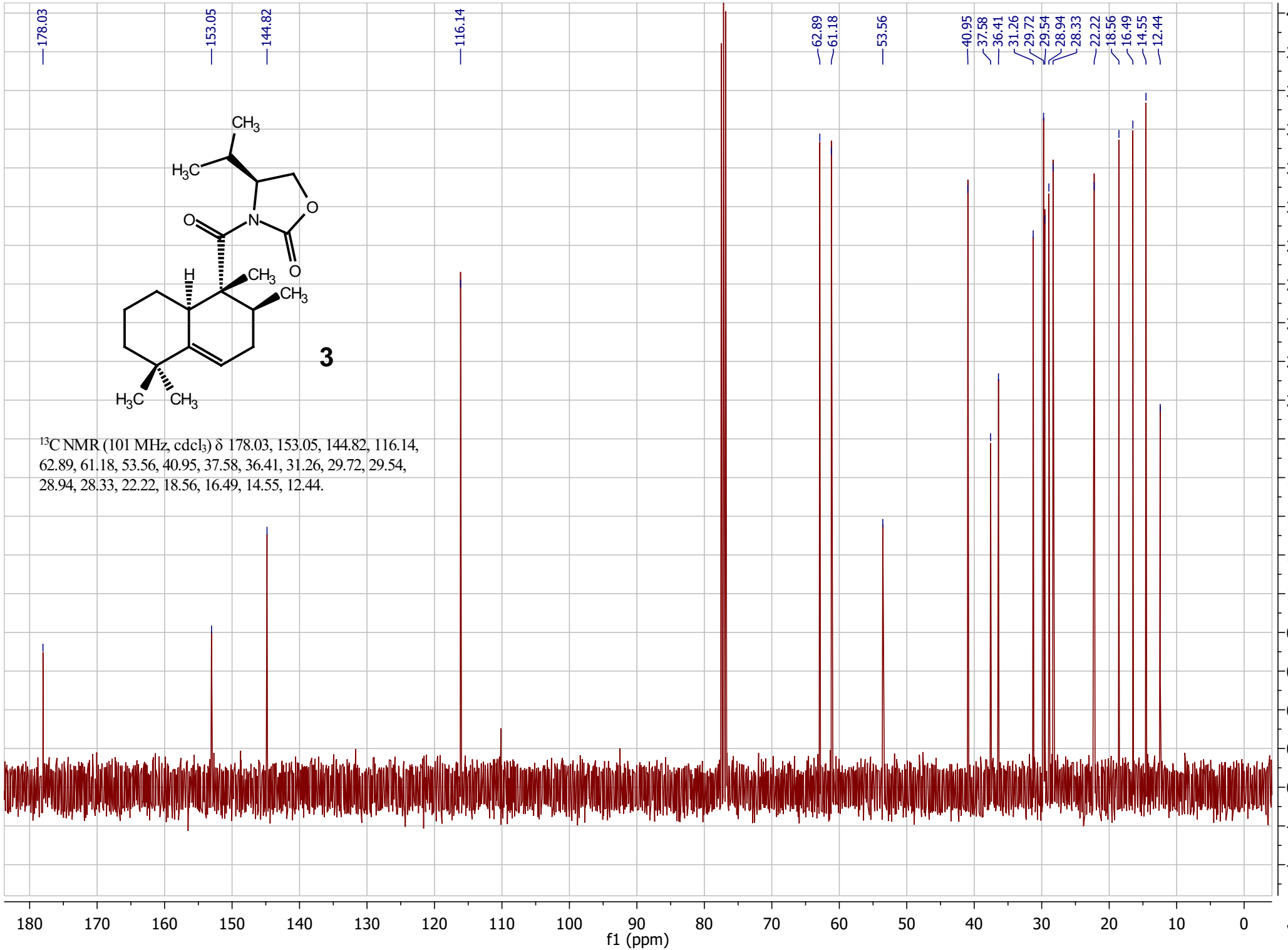
^{13}C NMR (101 MHz, cdcl$_3$) δ 171.92, 153.80, 134.69, 131.92, 63.52, 58.39, 28.36, 17.97, 15.14, 14.20, 13.48.

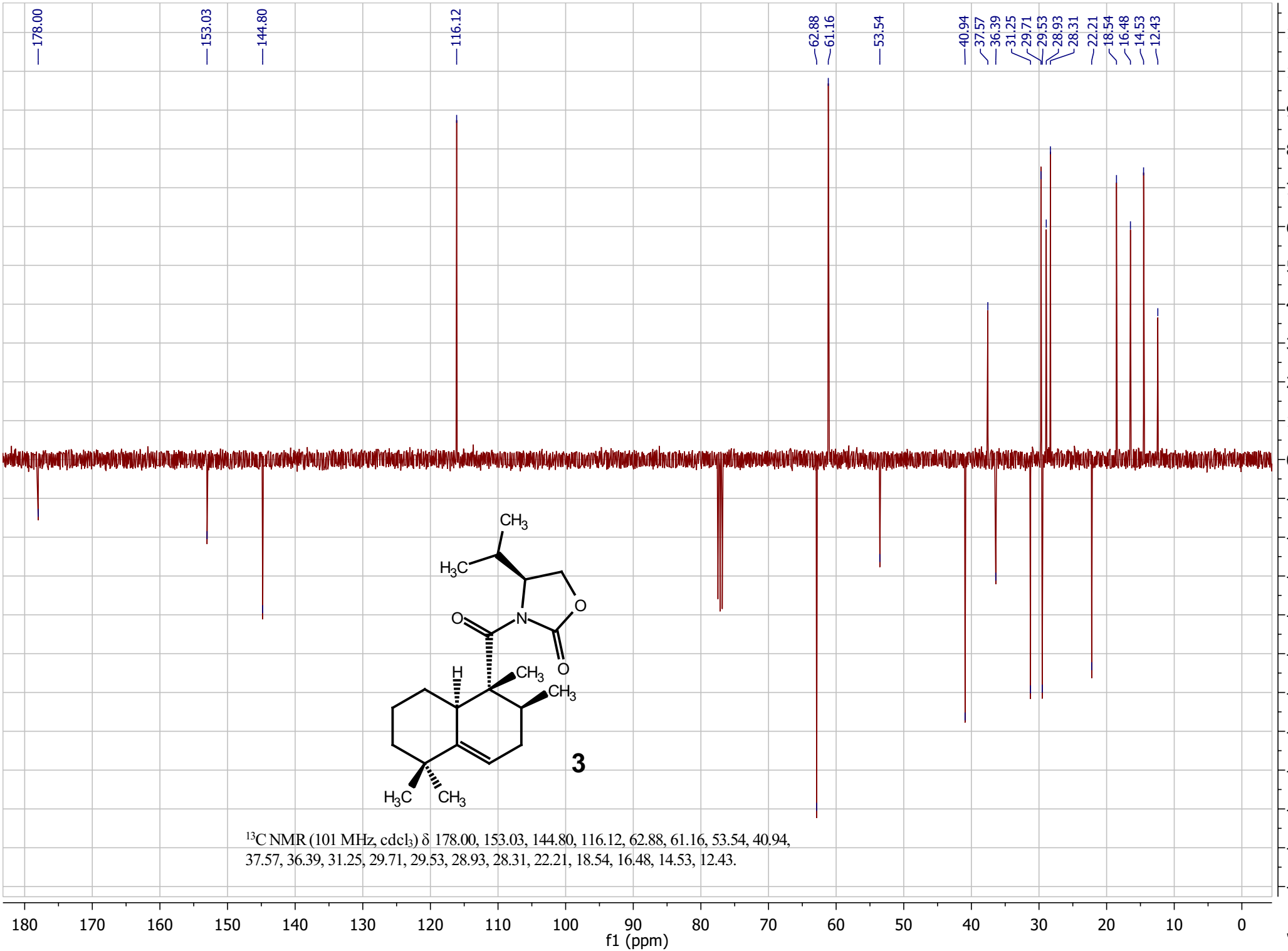

171.92
153.80
134.69
131.92
63.52
58.39
28.36
17.97
15.14
14.20
13.47
O
O
O
N
H_3C
H_3C
H_3C
CH_3
2
^{13}C NMR (101 MHz, cdcl$_3$) δ 171.92, 153.80, 134.69, 131.92, 63.52, 58.39, 28.36, 17.97, 15.14, 14.20, 13.47.
f1 (ppm)



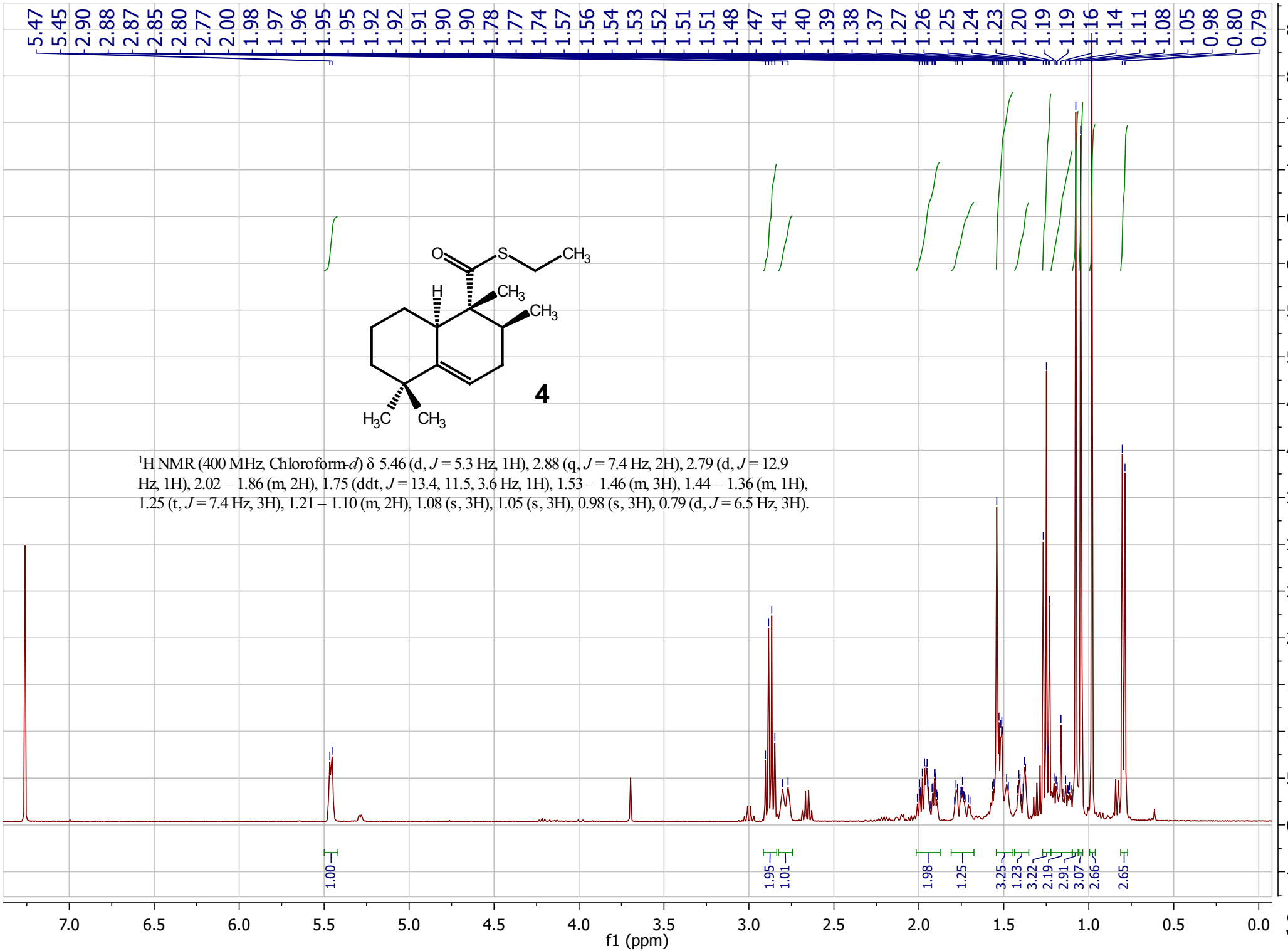
3

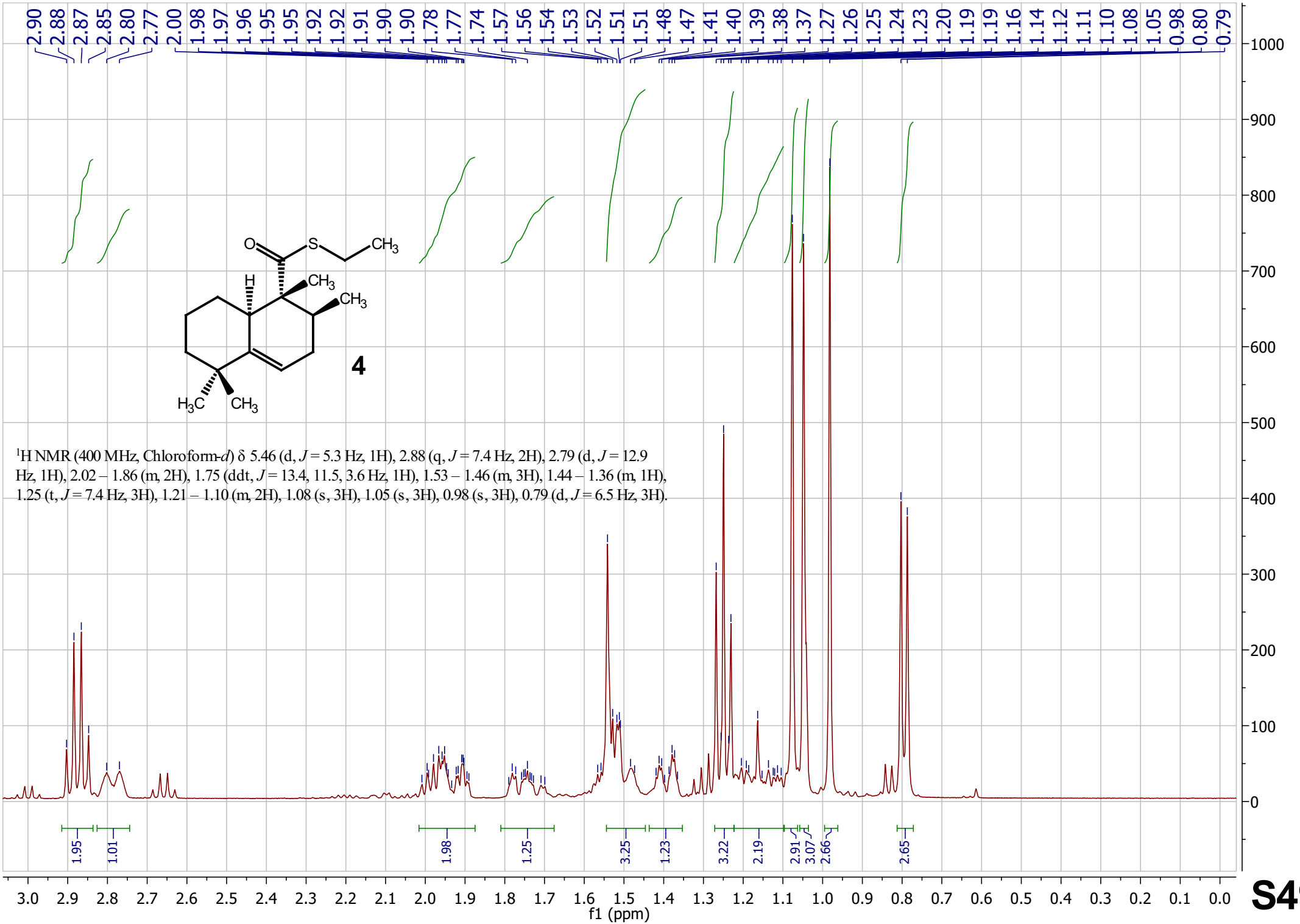
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.47 (d, *J* = 5.7 Hz, 1H), 4.54 (d, *J* = 8.2 Hz, 1H), 4.33 – 4.13 (m, 2H), 3.34 (d, *J* = 12.8 Hz, 1H), 3.15 (tt, *J* = 12.5, 6.5 Hz, 1H), 2.39 – 2.30 (m, 1H), 1.95 (dt, *J* = 17.5, 5.5 Hz, 1H), 1.79 – 1.63 (m, 2H), 1.54 (tt, *J* = 7.0, 3.1 Hz, 1H), 1.43 – 1.29 (m, 2H), 1.28 – 1.13 (m, 2H), 1.06 (s, 3H), 1.03 (s, 3H), 1.01 (s, 3H), 0.90 (t, *J* = 6.3 Hz, 6H), 0.78 (d, *J* = 6.8 Hz, 3H).

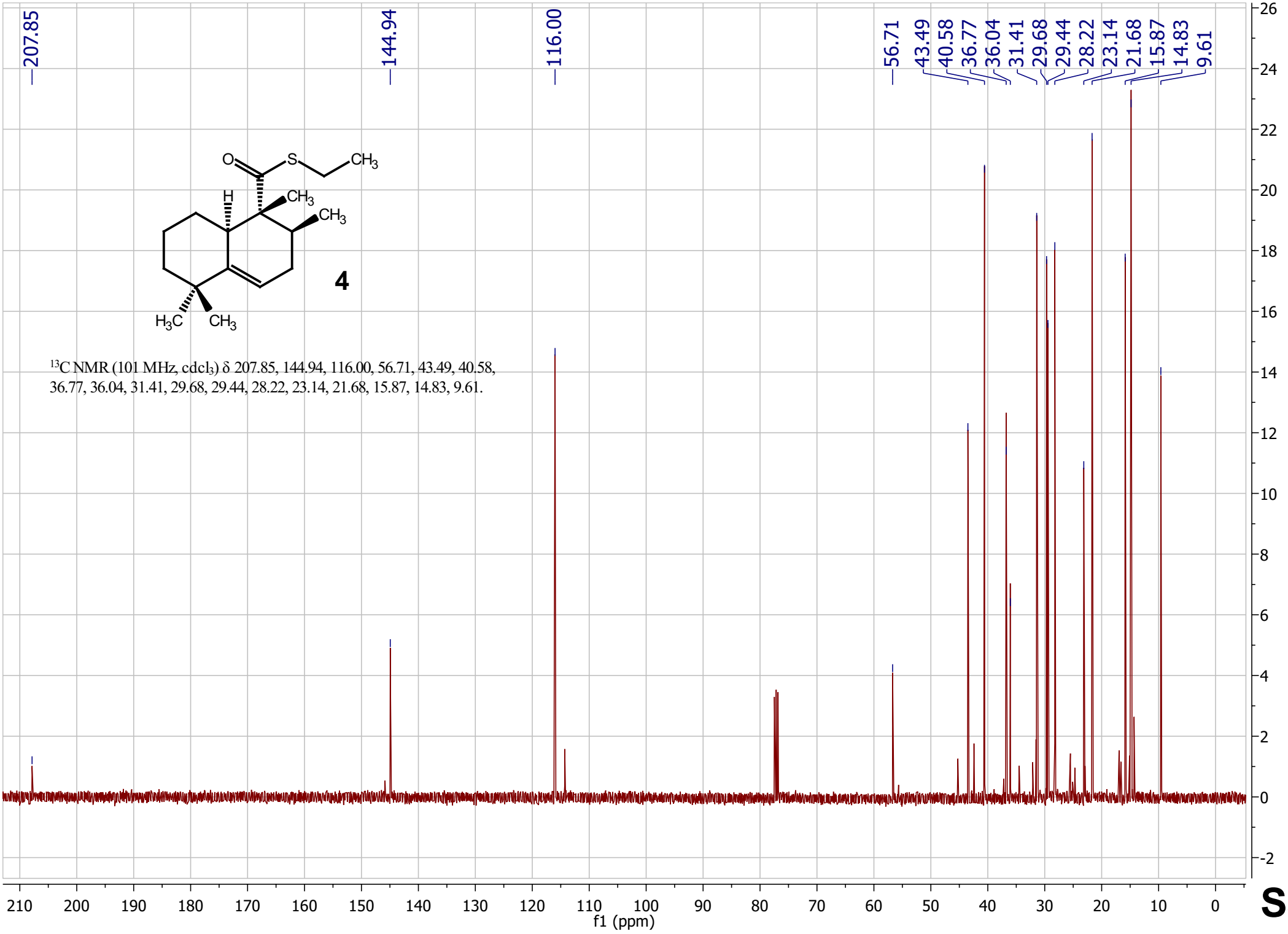

178.03
153.05
144.82
116.14
62.89
61.18
53.56
40.95
37.58
36.41
31.26
29.72
29.54
28.94
28.33
22.22
18.56
16.49
14.55
12.44
CH3
H3C
O
N
O
O
H
CH3
CH3
H3C
CH3
3
13C NMR (101 MHz, cdcl3) δ 178.03, 153.05, 144.82, 116.14, 62.89, 61.18, 53.56, 40.95, 37.58, 36.41, 31.26, 29.72, 29.54, 28.94, 28.33, 22.22, 18.56, 16.49, 14.55, 12.44.
f1 (ppm)

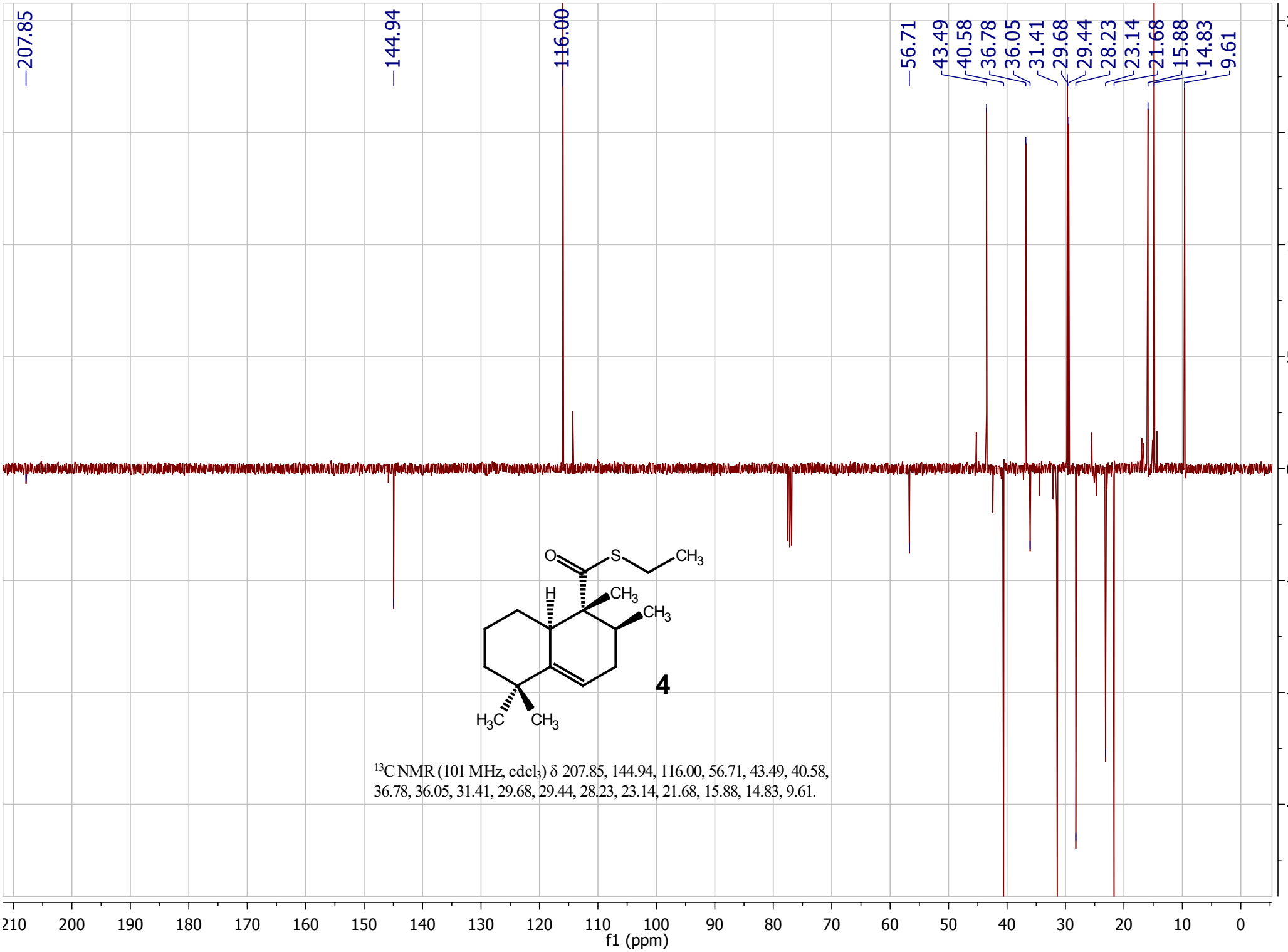


^{13}C NMR (101 MHz, cdcl$_3$) δ 178.00, 153.03, 144.80, 116.12, 62.88, 61.16, 53.54, 40.94, 37.57, 36.39, 31.25, 29.71, 29.53, 28.93, 28.31, 22.21, 18.54, 16.48, 14.53, 12.43.

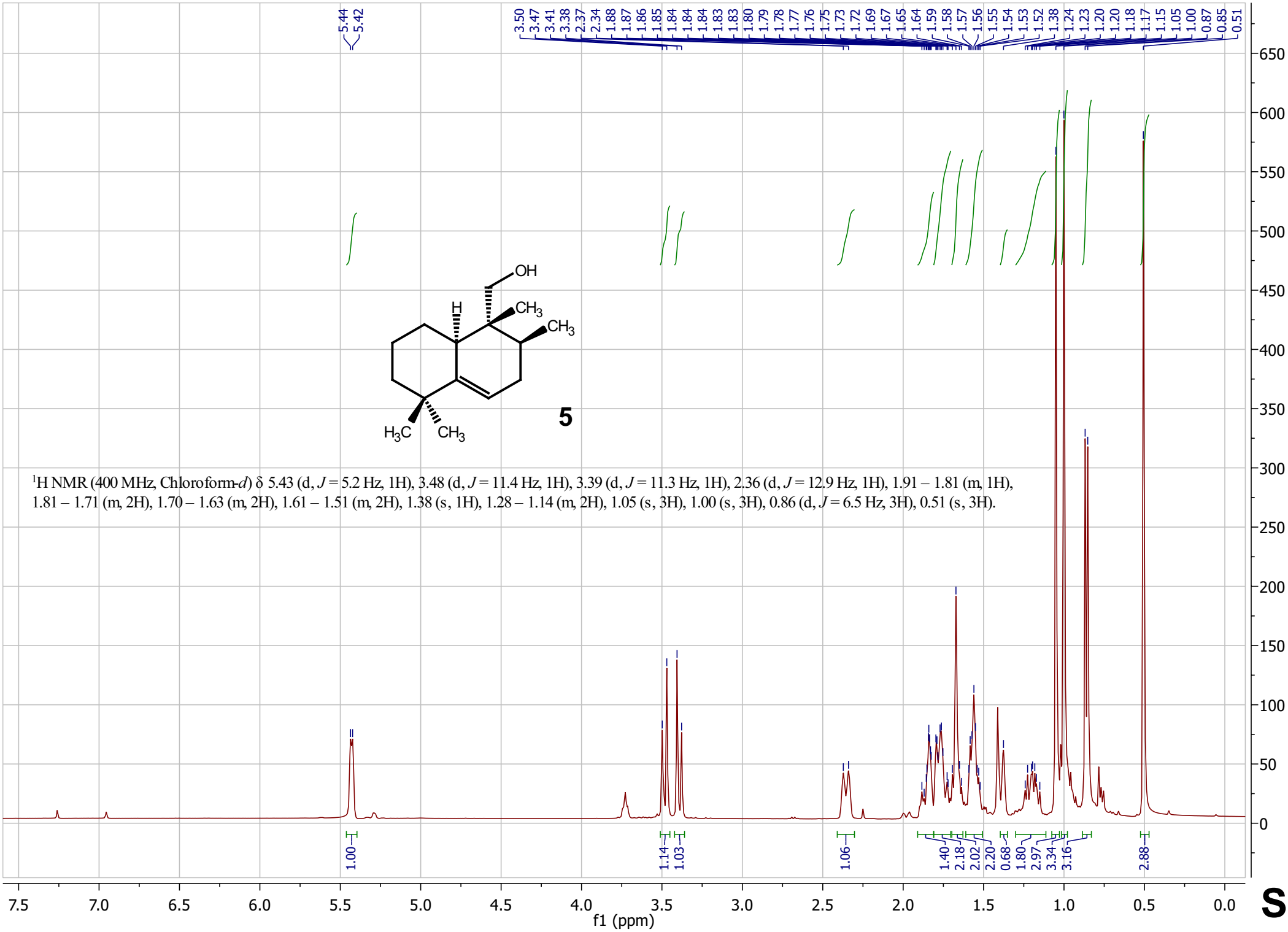

5.47 5.45 2.90 2.88 2.87 2.85 2.80 2.77 2.00 1.98 1.97 1.96 1.95 1.95 1.92 1.92 1.91 1.90 1.90 1.78 1.77 1.74 1.57 1.56 1.54 1.53 1.52 1.51 1.51 1.48 1.47 1.41 1.40 1.39 1.38 1.37 1.27 1.26 1.25 1.24 1.23 1.20 1.19 1.19 1.16 1.14 1.11 1.08 1.05 0.98 0.80 0.79
O
S
CH3
H
CH3
CH3
H3C
CH3
4
1H NMR (400 MHz, Chloroform-d) δ 5.46 (d, J = 5.3 Hz, 1H), 2.88 (q, J = 7.4 Hz, 2H), 2.79 (d, J = 12.9 Hz, 1H), 2.02 – 1.86 (m, 2H), 1.75 (ddt, J = 13.4, 11.5, 3.6 Hz, 1H), 1.53 – 1.46 (m, 3H), 1.44 – 1.36 (m, 1H), 1.25 (t, J = 7.4 Hz, 3H), 1.21 – 1.10 (m, 2H), 1.08 (s, 3H), 1.05 (s, 3H), 0.98 (s, 3H), 0.79 (d, J = 6.5 Hz, 3H).
1.00
1.95
1.01
1.98
1.25
3.25
1.23
3.22
2.19
2.91
3.07
2.66
2.65
f1 (ppm)


2.90 2.88 2.87 2.85 2.80 2.77 2.00 1.98 1.97 1.96 1.95 1.95 1.92 1.92 1.91 1.90 1.90 1.78 1.77 1.74 1.57 1.56 1.54 1.53 1.52 1.51 1.51 1.48 1.47 1.41 1.40 1.39 1.38 1.37 1.27 1.26 1.25 1.24 1.23 1.20 1.19 1.19 1.16 1.14 1.12 1.11 1.10 1.08 1.05 0.98 0.80 0.79
O
S
CH3
H
CH3
CH3
H3C
CH3
4
[1]H NMR (400 MHz, Chloroform-d) δ 5.46 (d, J = 5.3 Hz, 1H), 2.88 (q, J = 7.4 Hz, 2H), 2.79 (d, J = 12.9 Hz, 1H), 2.02 – 1.86 (m, 2H), 1.75 (ddt, J = 13.4, 11.5, 3.6 Hz, 1H), 1.53 – 1.46 (m, 3H), 1.44 – 1.36 (m, 1H), 1.25 (t, J = 7.4 Hz, 3H), 1.21 – 1.10 (m, 2H), 1.08 (s, 3H), 1.05 (s, 3H), 0.98 (s, 3H), 0.79 (d, J = 6.5 Hz, 3H).
1.95
1.01
1.98
1.25
3.25
1.23
3.22
2.19
2.91
3.07
2.66
2.65
f1 (ppm)

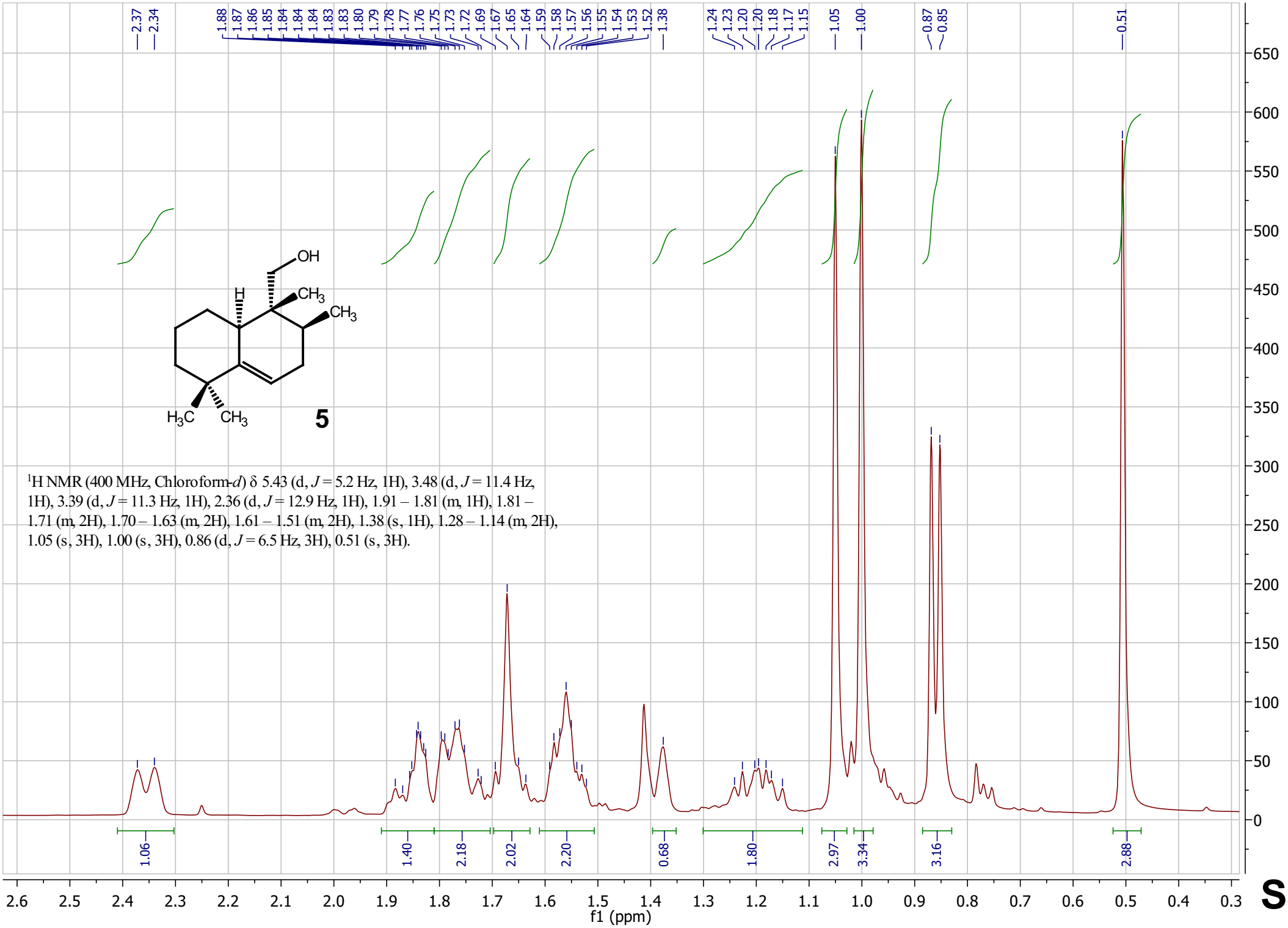

207.85
144.94
116.00
56.71
43.49
40.58
36.77
36.04
31.41
29.68
29.44
28.22
23.14
21.68
15.87
14.83
9.61
O
S
CH3
H
CH3
CH3
H3C
CH3
4
13C NMR (101 MHz, cdcl3) δ 207.85, 144.94, 116.00, 56.71, 43.49, 40.58,
36.77, 36.04, 31.41, 29.68, 29.44, 28.22, 23.14, 21.68, 15.87, 14.83, 9.61.
f1 (ppm)

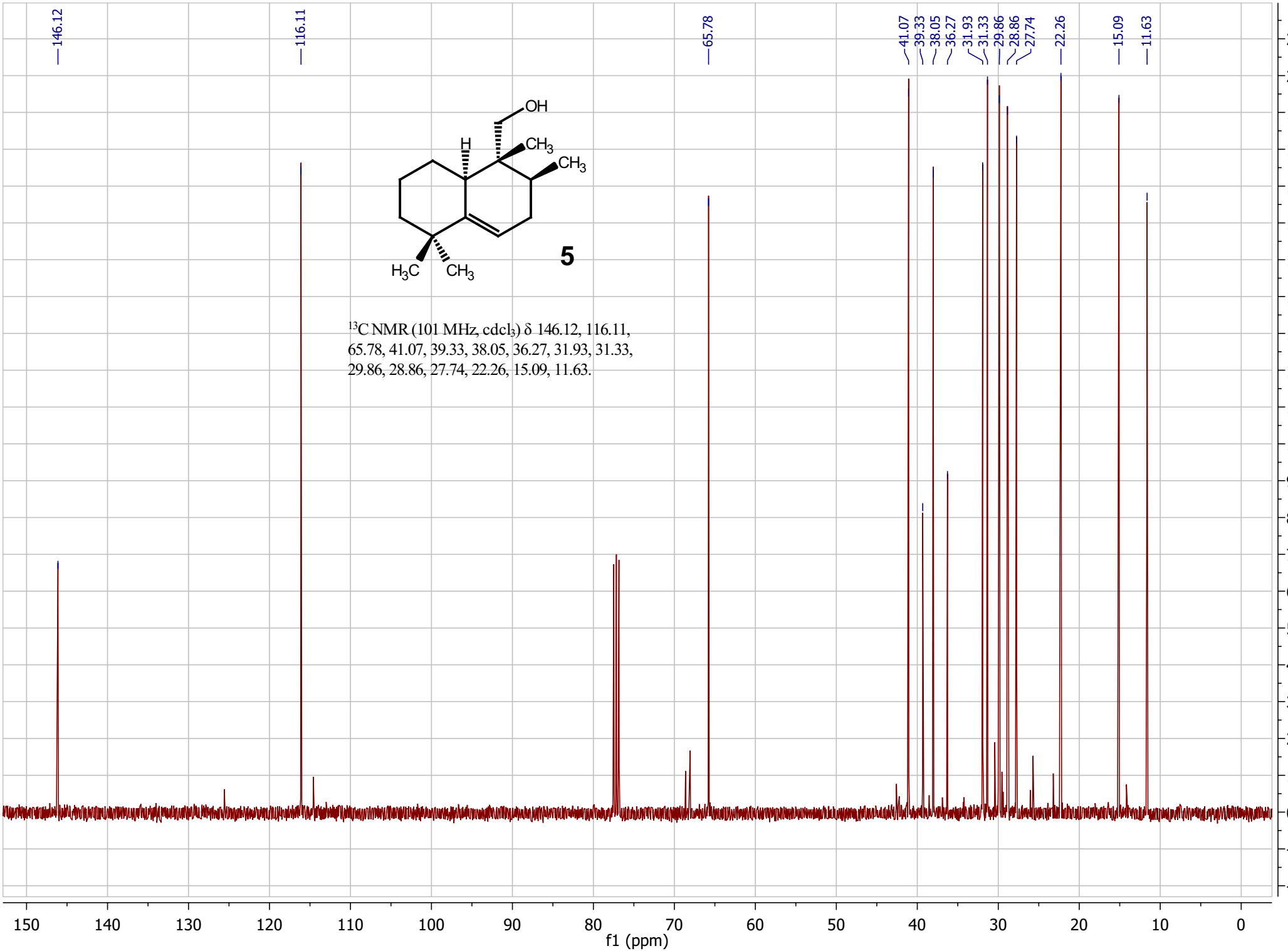


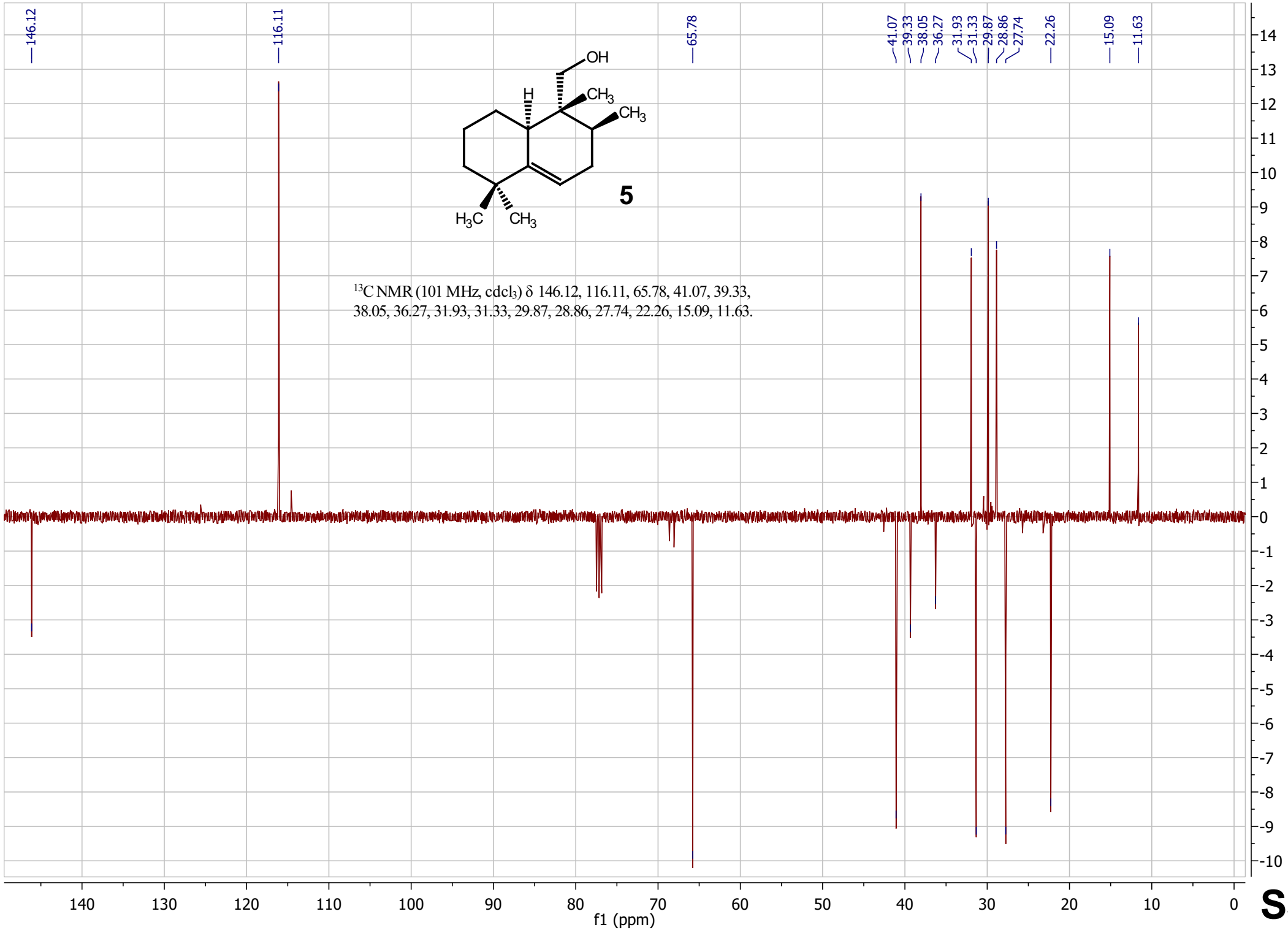
^{13}C NMR (101 MHz, cdcl$_3$) δ 207.85, 144.94, 116.00, 56.71, 43.49, 40.58, 36.78, 36.05, 31.41, 29.68, 29.44, 28.23, 23.14, 21.68, 15.88, 14.83, 9.61.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.43 (d, *J* = 5.2 Hz, 1H), 3.48 (d, *J* = 11.4 Hz, 1H), 3.39 (d, *J* = 11.3 Hz, 1H), 2.36 (d, *J* = 12.9 Hz, 1H), 1.91 – 1.81 (m, 1H), 1.81 – 1.71 (m, 2H), 1.70 – 1.63 (m, 2H), 1.61 – 1.51 (m, 2H), 1.38 (s, 1H), 1.28 – 1.14 (m, 2H), 1.05 (s, 3H), 1.00 (s, 3H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.51 (s, 3H).


2.37
2.34
1.88
1.87
1.86
1.85
1.84
1.84
1.84
1.83
1.83
1.80
1.79
1.78
1.77
1.76
1.75
1.73
1.72
1.69
1.67
1.65
1.64
1.59
1.58
1.57
1.56
1.55
1.54
1.53
1.52
1.38
1.24
1.23
1.20
1.20
1.18
1.17
1.15
1.05
1.00
0.87
0.85
0.51
OH
H
CH3
CH3
H3C
CH3
5
[1]H NMR (400 MHz, Chloroform-d) δ 5.43 (d, J = 5.2 Hz, 1H), 3.48 (d, J = 11.4 Hz, 1H), 3.39 (d, J = 11.3 Hz, 1H), 2.36 (d, J = 12.9 Hz, 1H), 1.91 – 1.81 (m, 1H), 1.81 – 1.71 (m, 2H), 1.70 – 1.63 (m, 2H), 1.61 – 1.51 (m, 2H), 1.38 (s, 1H), 1.28 – 1.14 (m, 2H), 1.05 (s, 3H), 1.00 (s, 3H), 0.86 (d, J = 6.5 Hz, 3H), 0.51 (s, 3H).
1.06
1.40
2.18
2.02
2.20
0.68
1.80
2.97
3.34
3.16
2.88
f1 (ppm)


146.12
116.11
65.78
41.07
39.33
38.05
36.27
31.93
31.33
29.86
28.86
27.74
22.26
15.09
11.63
OH
H
CH3
CH3
H3C
CH3
5
13C NMR (101 MHz, cdcl3) δ 146.12, 116.11, 65.78, 41.07, 39.33, 38.05, 36.27, 31.93, 31.33, 29.86, 28.86, 27.74, 22.26, 15.09, 11.63.
f1 (ppm)


146.12
116.11
65.78
41.07
39.33
38.05
36.27
31.93
31.33
29.87
28.86
27.74
22.26
15.09
11.63
OH
H
CH3
CH3
H3C
CH3
5
13C NMR (101 MHz, cdcl3) δ 146.12, 116.11, 65.78, 41.07, 39.33, 38.05, 36.27, 31.93, 31.33, 29.87, 28.86, 27.74, 22.26, 15.09, 11.63.
f1 (ppm)

S56

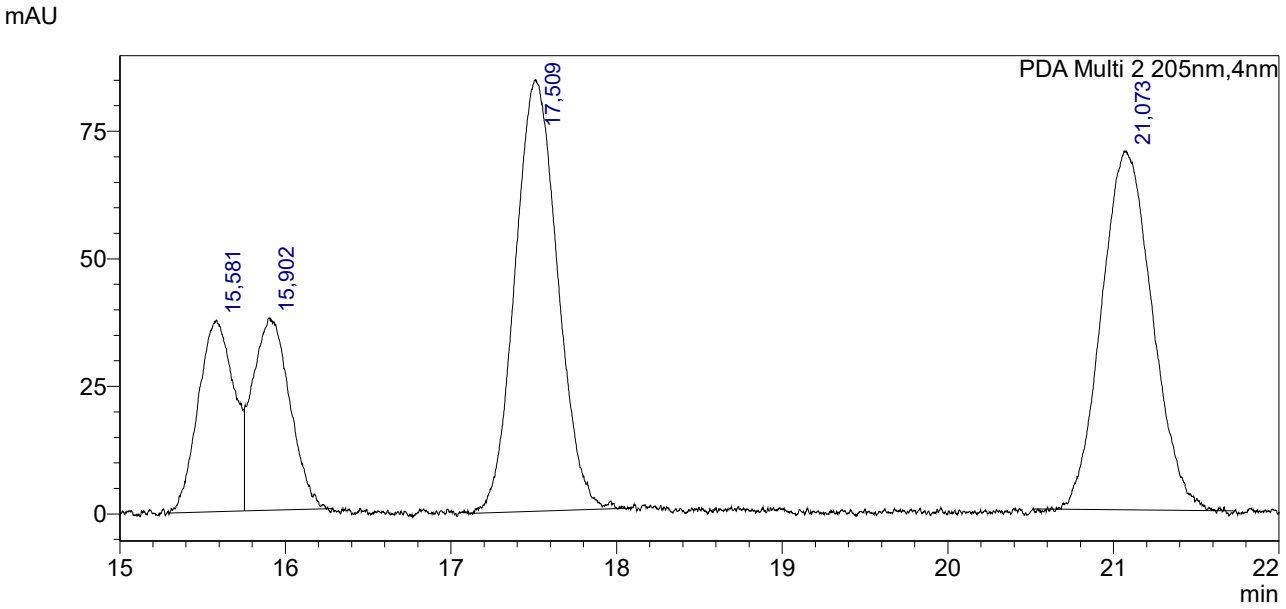
SHIMADZU LabSolutions

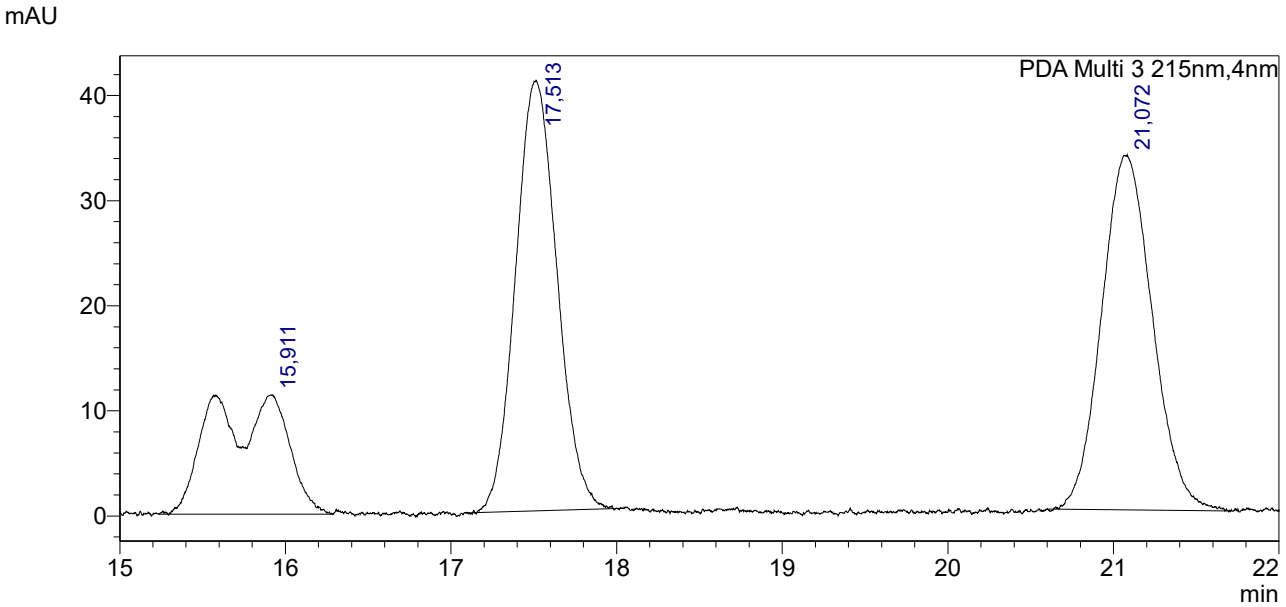
Analysis Report

<Sample Information>

Sample Name	: DA Sorenson Alcohol RAC AD-H		
Sample ID	:		
Data Filename	: DA Sorenson Alcohol RAC AD-H.lcd		
Method Filename	: C5 98-2 fl 0,5 60 min.lcm		
Batch Filename	: 20131112_all column screening - 2014.lcb		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 4 uL		
Date Acquired	: 23-12-2014 23:25:08	Acquired by	: System Administrator
Date Processed	: 24-12-2014 16:44:44	Processed by	: System Administrator

<Chromatogram>





<Peak Table>

PDA Ch2 205nm

S57

Peak#	Ret. Time	Area	Height	Area%
1	15,581	568516	37414	13,625
2	15,902	589478	37634	14,128
3	17,509	1513709	84449	36,278
4	21,073	1500803	70285	35,969
Total		4172506	229782	100,000

PDA Ch3 215nm

Peak#	Ret. Time	Area	Height	Area%
1	15,911	354004	11321	19,783
2	17,513	714835	40879	39,948
3	21,072	720568	33684	40,269
Total		1789407	85884	100,000

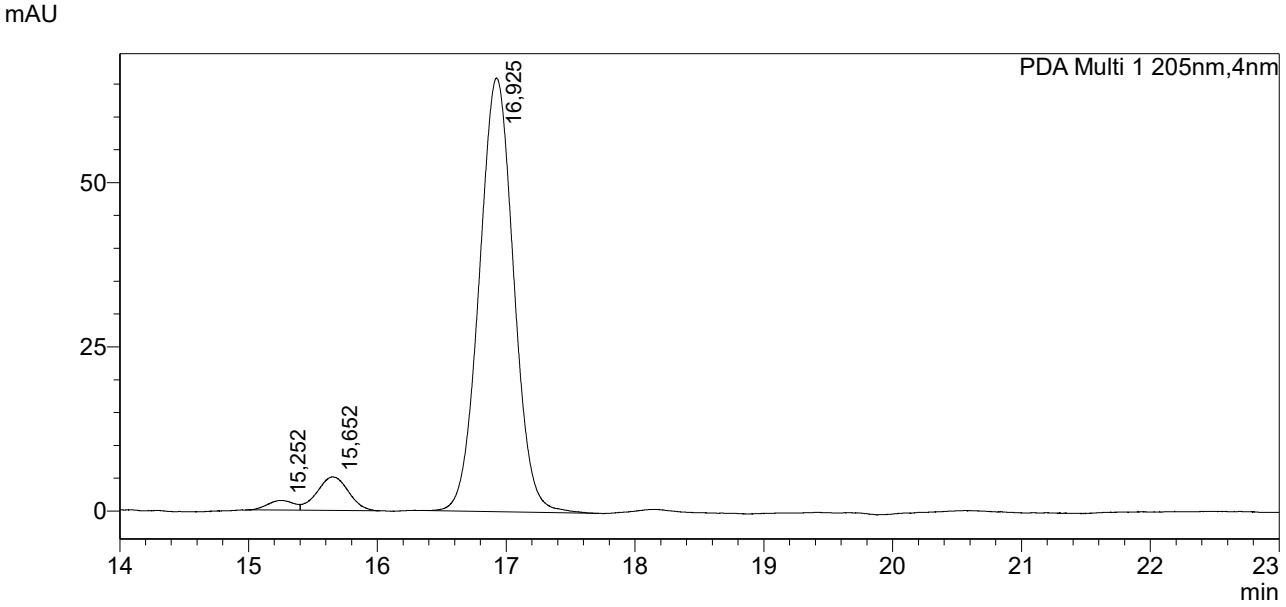
SHIMADZU LabSolutions

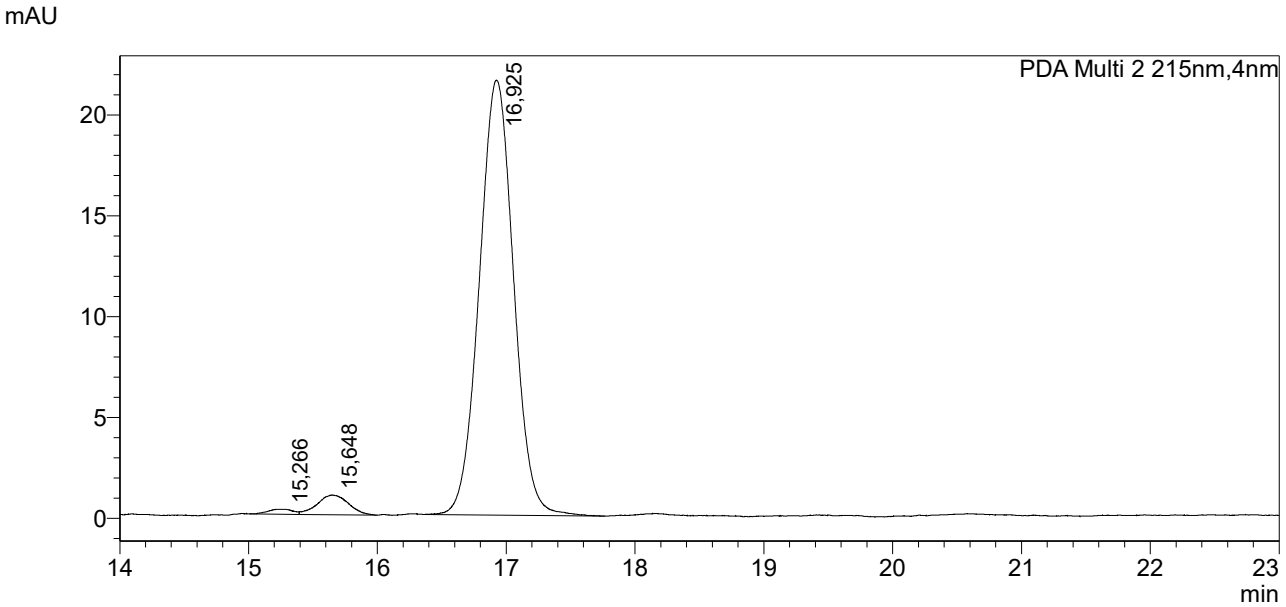
Analysis Report

<Sample Information>

Sample Name	: Diels-Alder adduct Alcohol 4 ENT first DA		
Sample ID	:		
Data Filename	: Diels-Alder adduct Alcohol 4 ENT first DA.lcd		
Method Filename	: C5 98-2 fl 0,5 40 min.lcm		
Batch Filename	: MHR-047.lcb		
Vial #	: 1-88	Sample Type	: Unknown
Injection Volume	: 1 uL	Level	: 3
Date Acquired	: 10-10-2015 17:35:06	Acquired by	: System Administrator
Date Processed	: 10-10-2015 18:15:08	Processed by	: System Administrator

<Chromatogram>





<Peak Table>

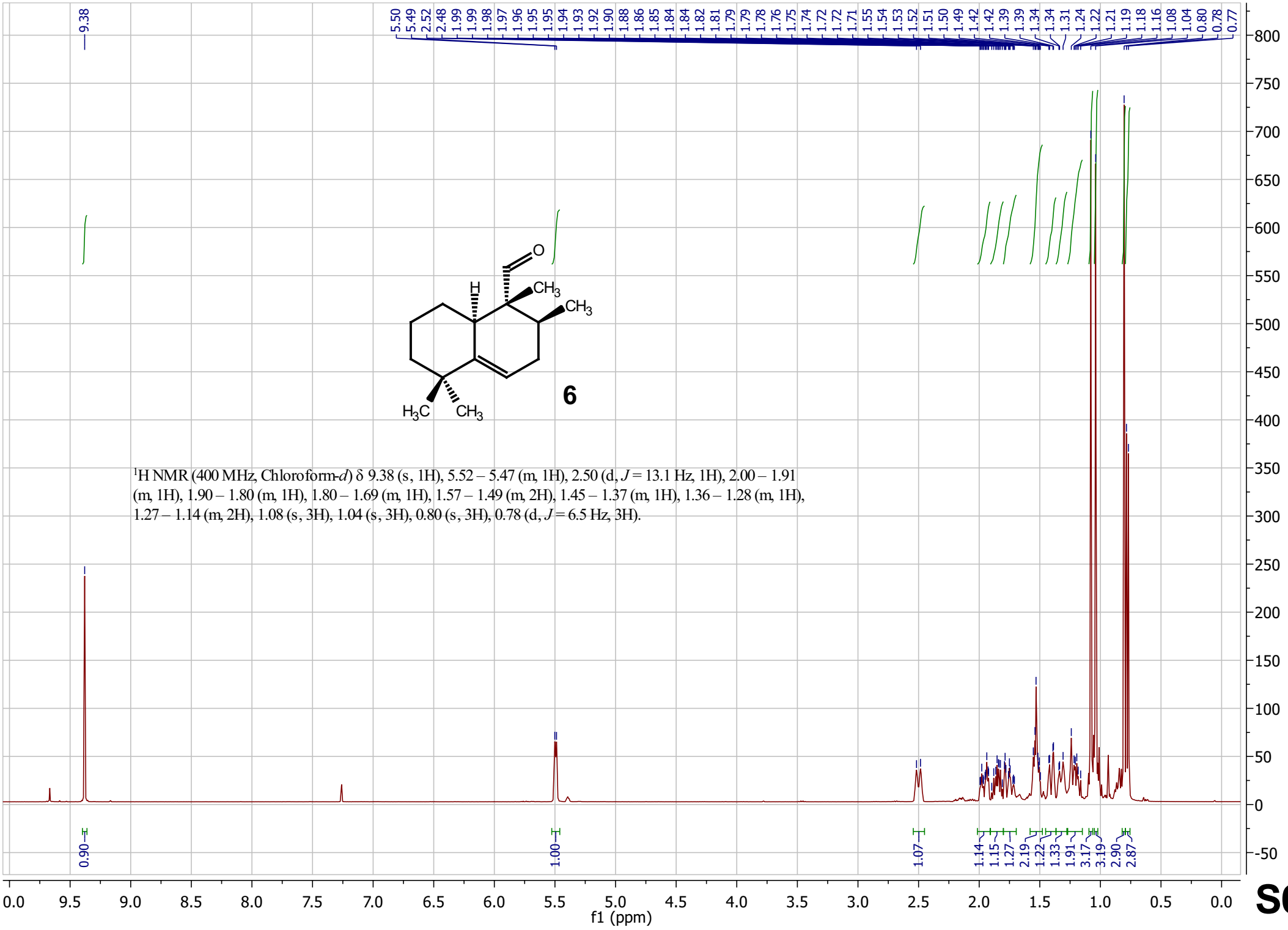
PDA Ch1 205nm

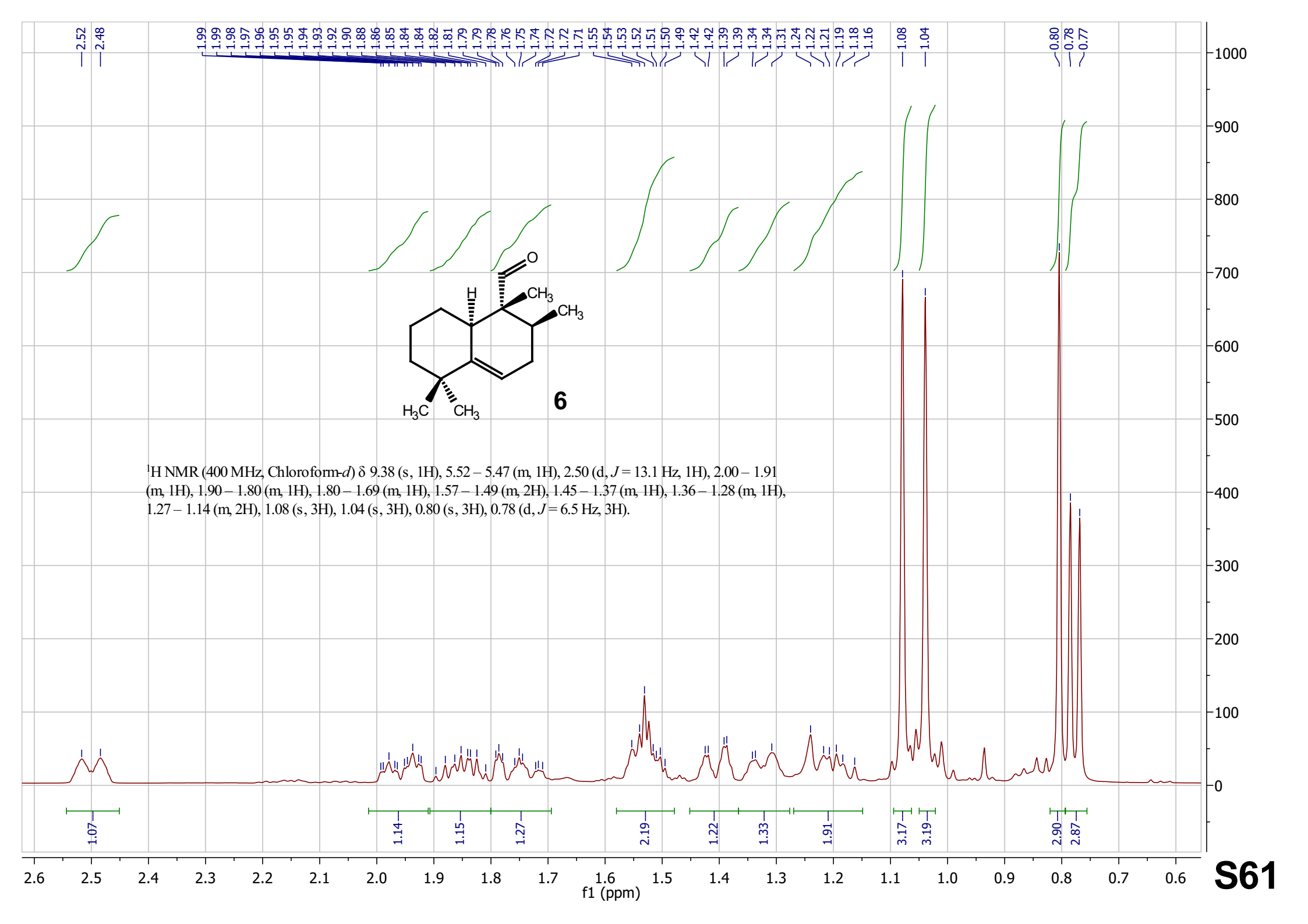
S59

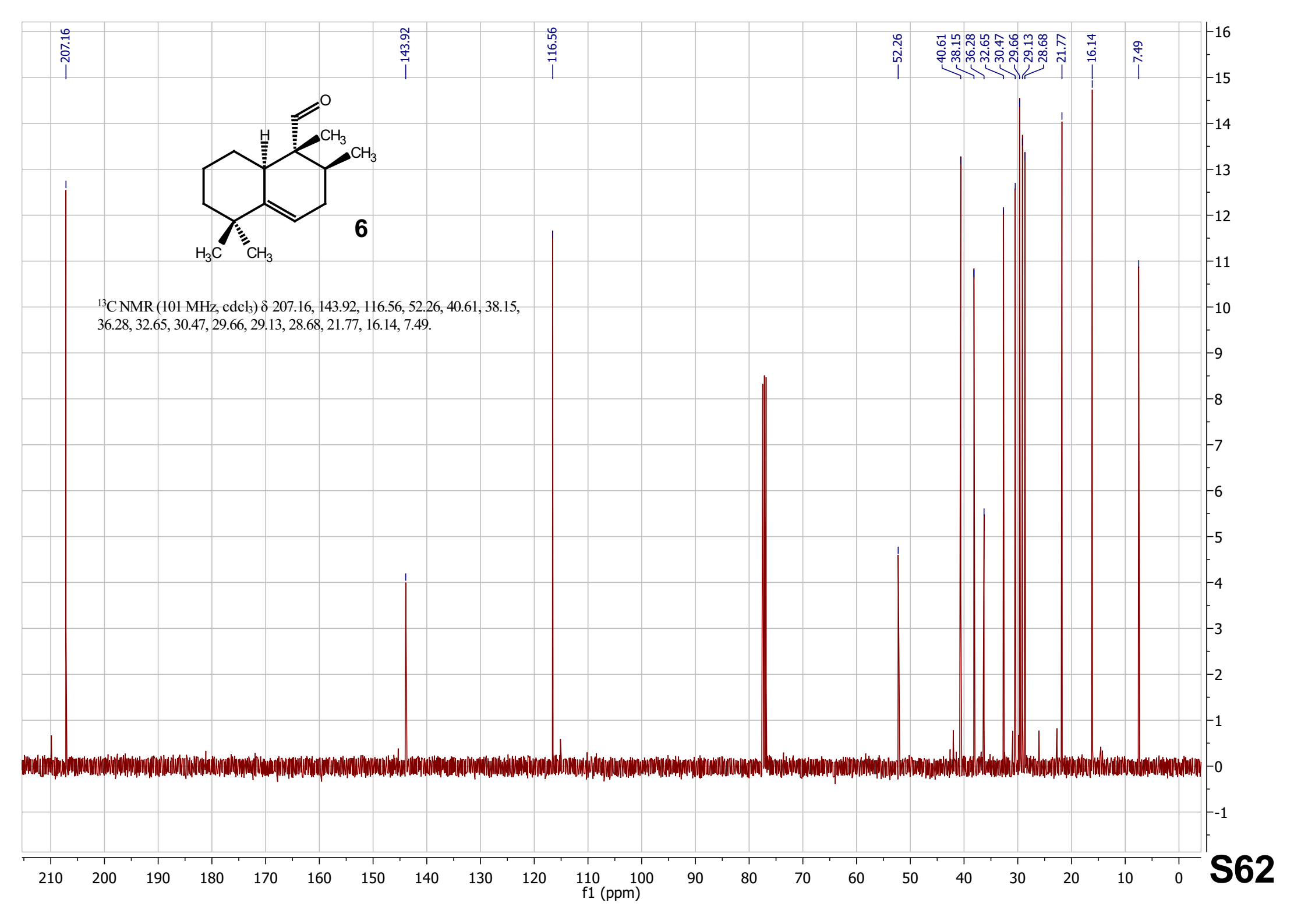
Peak#	Ret. Time	Area	Height	Area%
1	15,252	21156	1475	1,589
2	15,652	86592	5108	6,502
3	16,925	1224077	65981	91,910
Total		1331825	72564	100,000

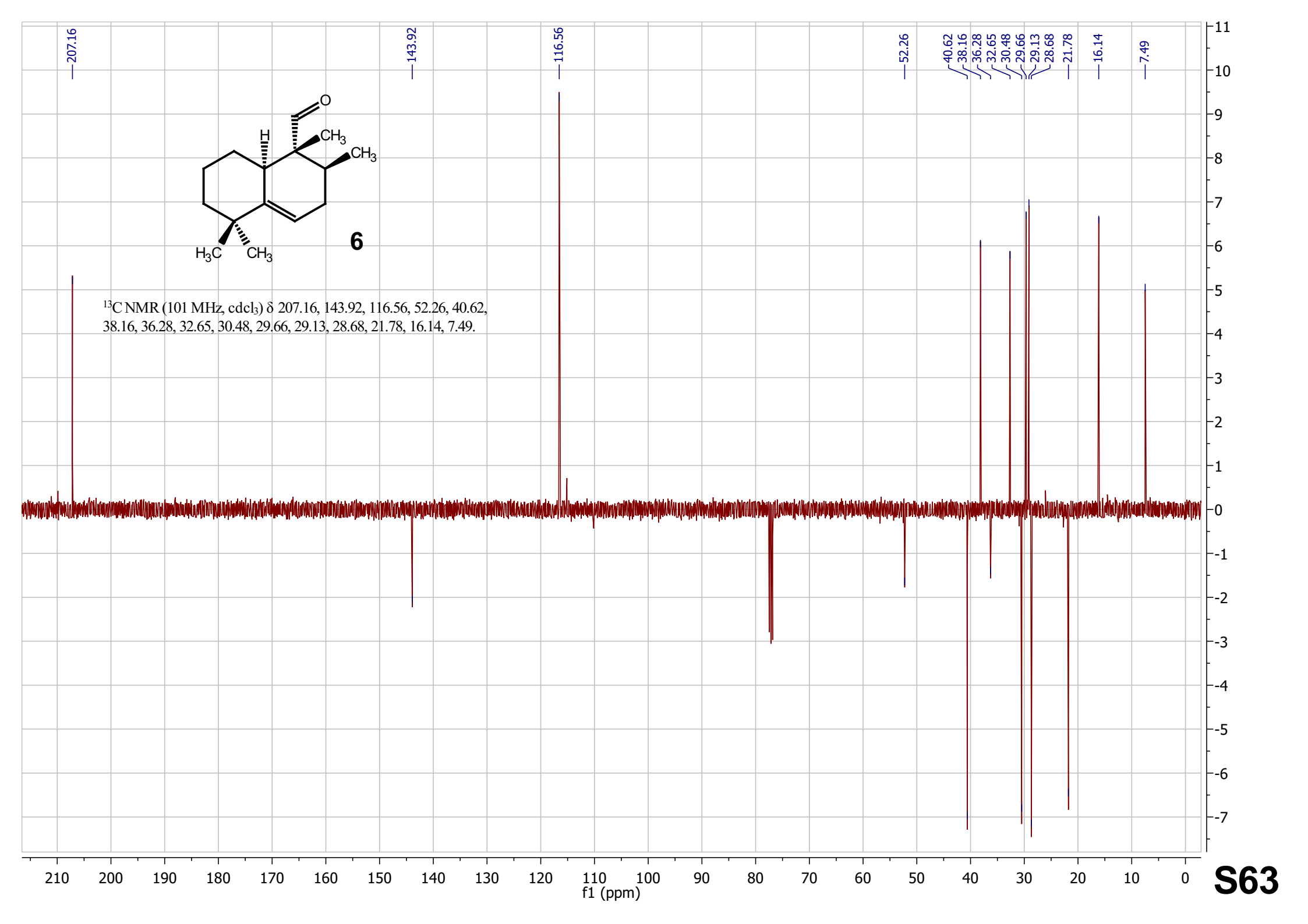
PDA Ch2 215nm

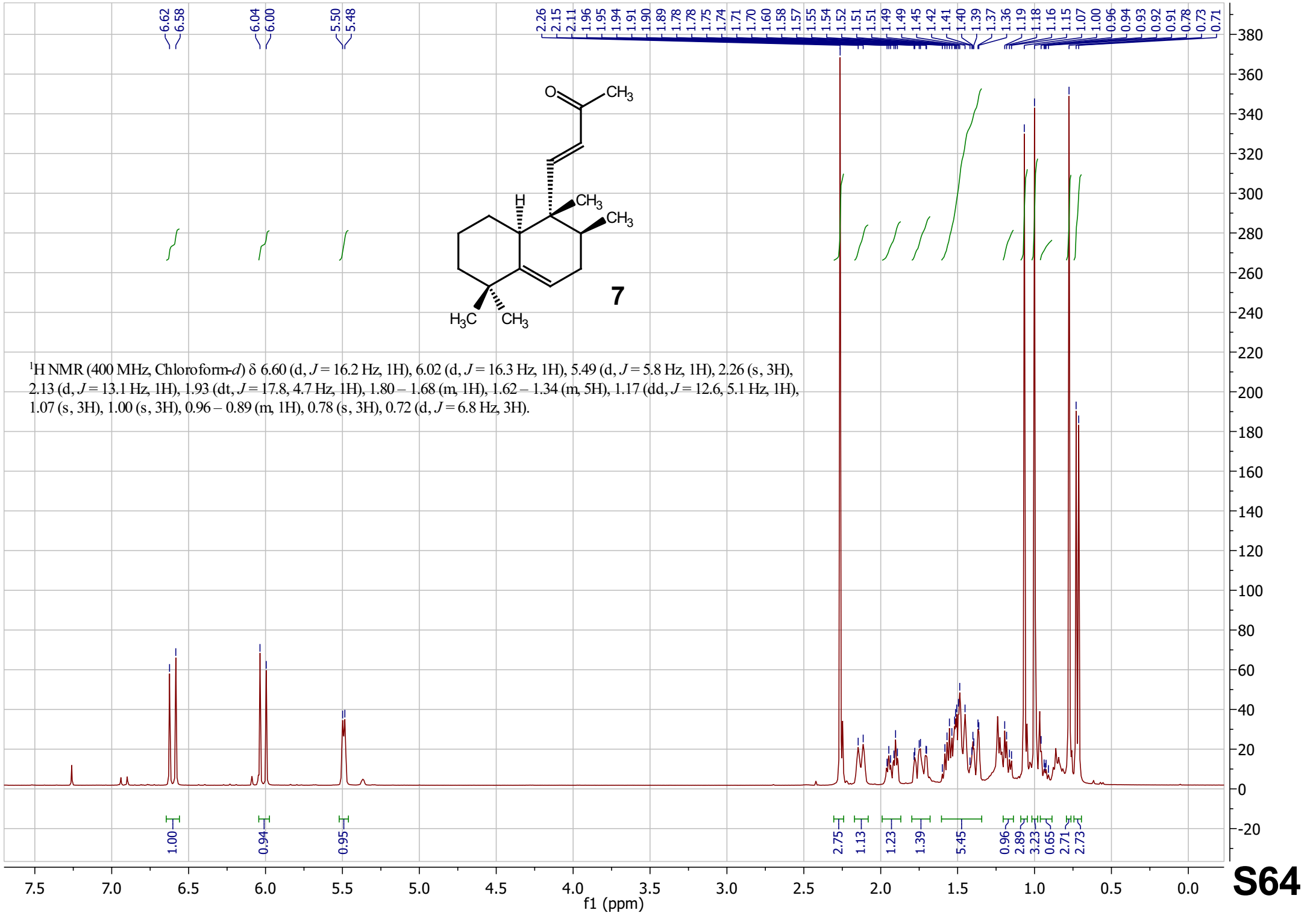
Peak#	Ret. Time	Area	Height	Area%
1	15,266	3376	248	0,807
2	15,648	16509	976	3,945
3	16,925	398634	21561	95,249
Total		418519	22785	100,000

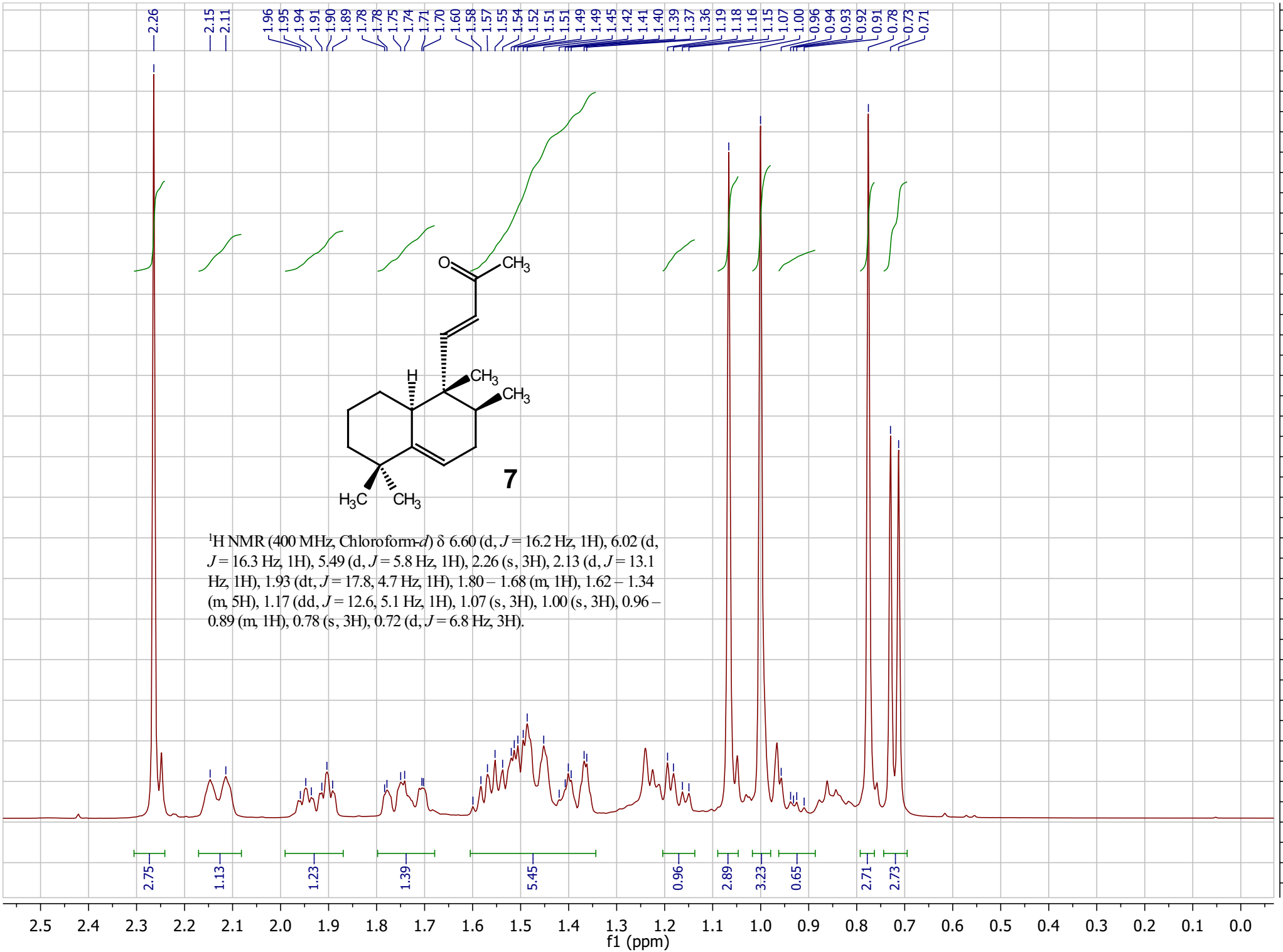

9.38
5.50 5.49 2.52 2.48 1.99 1.99 1.98 1.97 1.96 1.95 1.95 1.94 1.93 1.92 1.90 1.88 1.86 1.85 1.84 1.84 1.82 1.81 1.79 1.79 1.78 1.76 1.75 1.74 1.72 1.72 1.71 1.55 1.54 1.53 1.52 1.51 1.50 1.49 1.42 1.42 1.39 1.39 1.34 1.34 1.31 1.24 1.22 1.21 1.19 1.18 1.16 1.08 1.04 0.80 0.78 0.77
O
H
CH3
CH3
H3C
CH3
6
[1]H NMR (400 MHz, Chloroform-d) δ 9.38 (s, 1H), 5.52 – 5.47 (m, 1H), 2.50 (d, J = 13.1 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.90 – 1.80 (m, 1H), 1.80 – 1.69 (m, 1H), 1.57 – 1.49 (m, 2H), 1.45 – 1.37 (m, 1H), 1.36 – 1.28 (m, 1H), 1.27 – 1.14 (m, 2H), 1.08 (s, 3H), 1.04 (s, 3H), 0.80 (s, 3H), 0.78 (d, J = 6.5 Hz, 3H).
0.90
1.00
1.07
1.14 1.15 1.27 2.19 1.22 1.33 1.91 3.17 3.19 2.90 2.87
f1 (ppm)

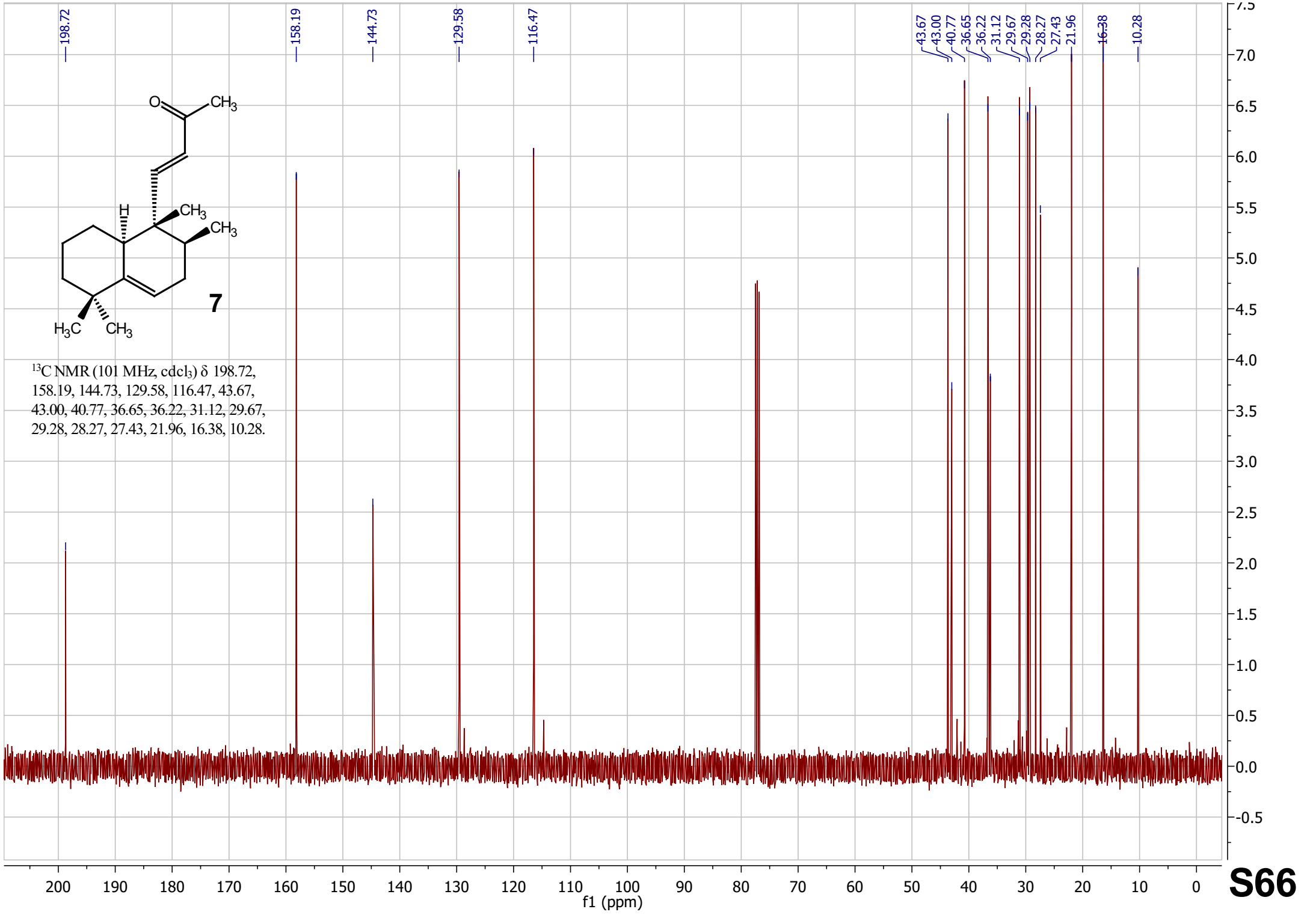

2.52 2.48
1.99 1.99 1.98 1.97 1.96 1.95 1.95 1.94 1.93 1.92 1.90 1.88 1.86 1.85 1.84 1.84 1.82 1.81 1.79 1.79 1.78 1.76 1.75 1.74 1.72 1.72 1.71 1.55 1.54 1.53 1.52 1.51 1.50 1.49 1.42 1.42 1.39 1.39 1.34 1.34 1.31 1.24 1.22 1.21 1.19 1.18 1.16
1.08 1.04
0.80 0.78 0.77
O
H
CH3
CH3
H3C
CH3
6
[1]H NMR (400 MHz, Chloroform-d) δ 9.38 (s, 1H), 5.52 – 5.47 (m, 1H), 2.50 (d, J = 13.1 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.90 – 1.80 (m, 1H), 1.80 – 1.69 (m, 1H), 1.57 – 1.49 (m, 2H), 1.45 – 1.37 (m, 1H), 1.36 – 1.28 (m, 1H), 1.27 – 1.14 (m, 2H), 1.08 (s, 3H), 1.04 (s, 3H), 0.80 (s, 3H), 0.78 (d, J = 6.5 Hz, 3H).
1.07
1.14
1.15
1.27
2.19
1.22
1.33
1.91
3.17
3.19
2.90
2.87
1000
900
800
700
600
500
400
300
200
100
0
2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6
f1 (ppm)

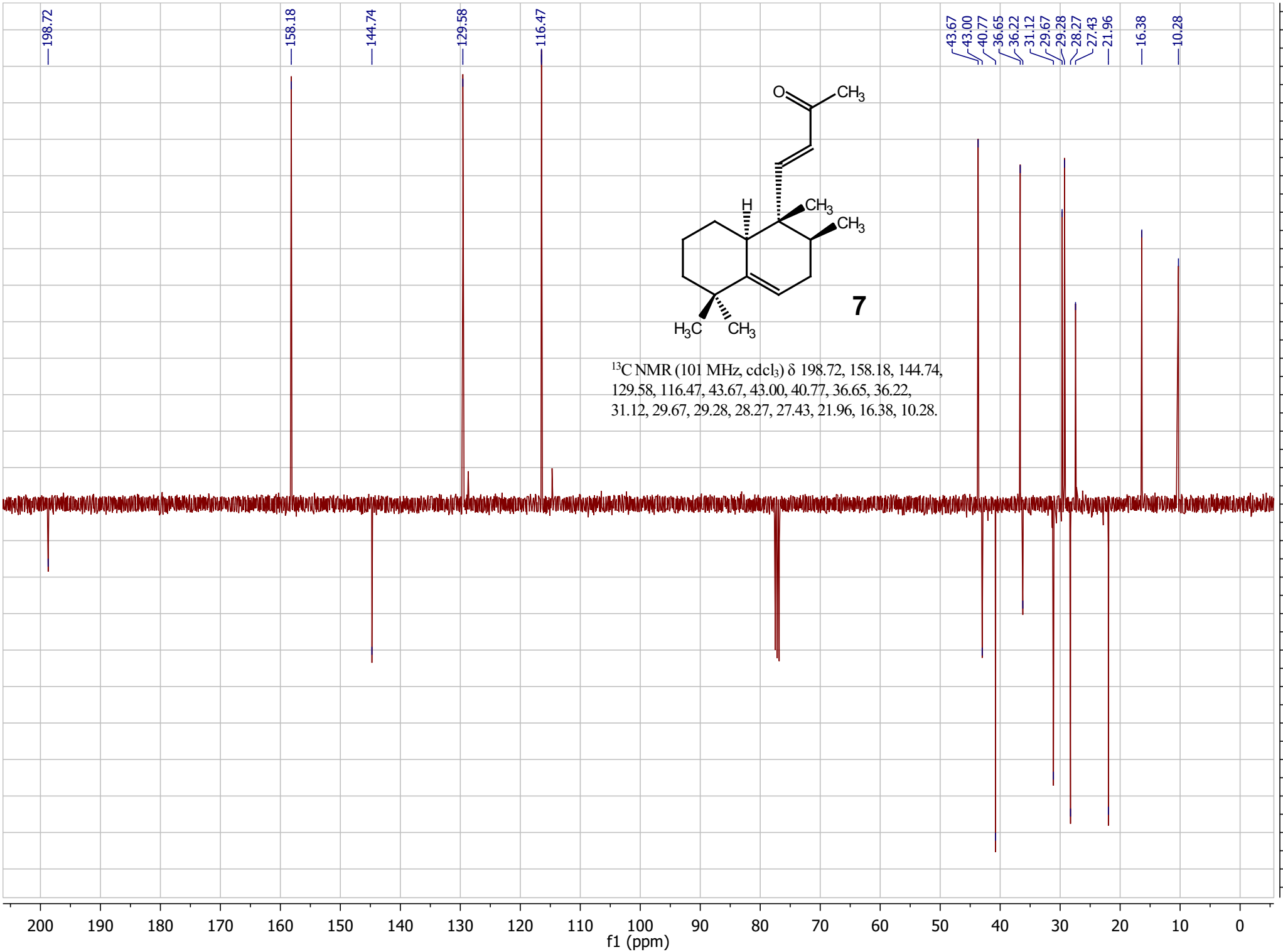

207.16
143.92
116.56
52.26
40.61
38.15
36.28
32.65
30.47
29.66
29.13
28.68
21.77
16.14
7.49
O
H
CH3
CH3
H3C
CH3
6
13C NMR (101 MHz, cdcl3) δ 207.16, 143.92, 116.56, 52.26, 40.61, 38.15, 36.28, 32.65, 30.47, 29.66, 29.13, 28.68, 21.77, 16.14, 7.49.
f1 (ppm)

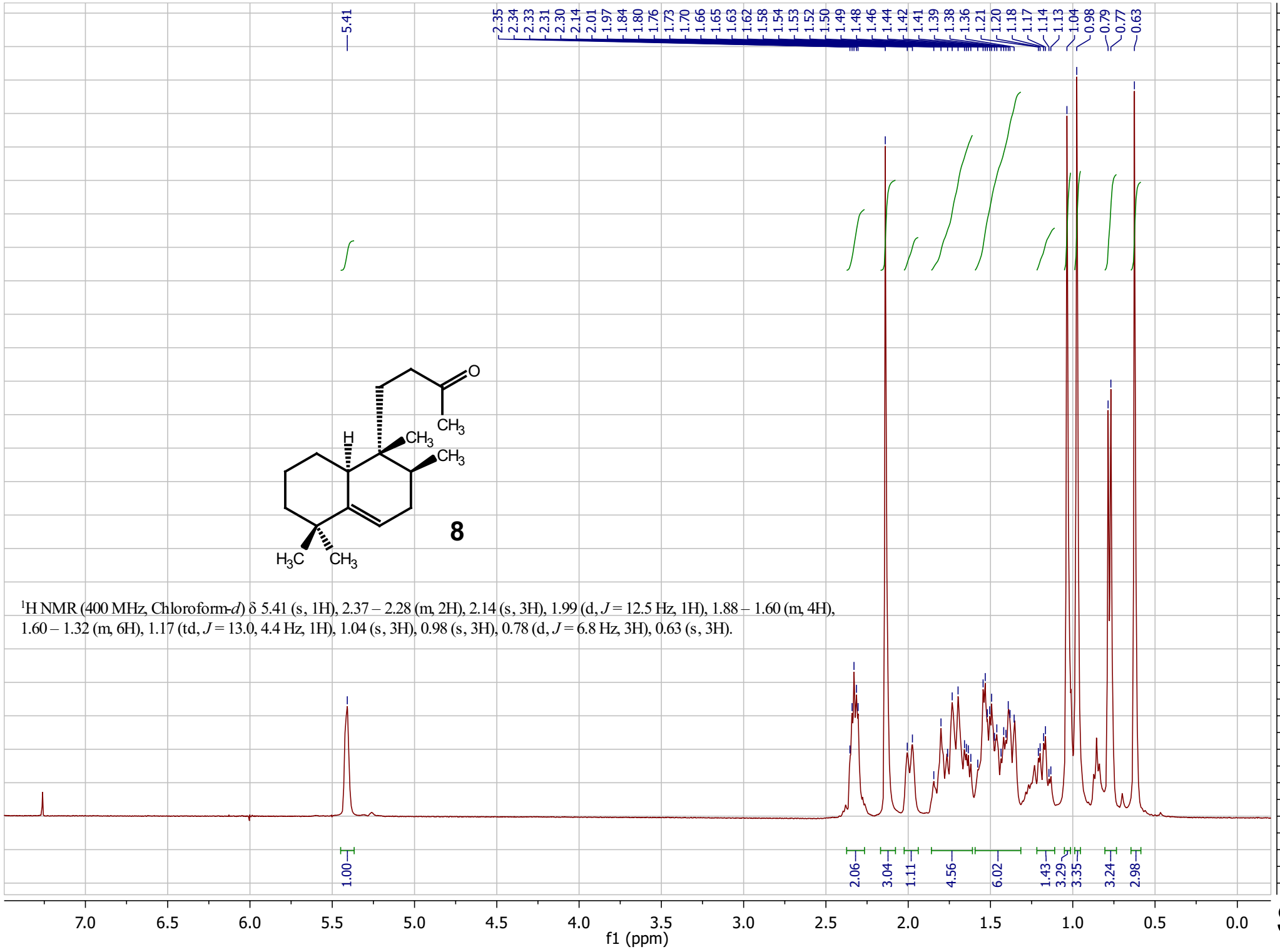

207.16
143.92
116.56
52.26
40.62
38.16
36.28
32.65
30.48
29.66
29.13
28.68
21.78
16.14
7.49
O
H
CH3
CH3
H3C
CH3
6
13C NMR (101 MHz, cdcl3) δ 207.16, 143.92, 116.56, 52.26, 40.62,
38.16, 36.28, 32.65, 30.48, 29.66, 29.13, 28.68, 21.78, 16.14, 7.49.
f1 (ppm)


6.62
6.58
6.04
6.00
5.50
5.48
2.26
2.15
2.11
1.96
1.95
1.94
1.91
1.90
1.89
1.78
1.78
1.75
1.74
1.71
1.70
1.60
1.58
1.57
1.55
1.54
1.52
1.51
1.51
1.49
1.49
1.45
1.42
1.41
1.40
1.39
1.37
1.36
1.19
1.18
1.16
1.15
1.07
1.00
0.96
0.94
0.93
0.92
0.91
0.78
0.73
0.71
O
CH3
H
CH3
CH3
H3C
CH3
7
[1]H NMR (400 MHz, Chloroform-d) δ 6.60 (d, J = 16.2 Hz, 1H), 6.02 (d, J = 16.3 Hz, 1H), 5.49 (d, J = 5.8 Hz, 1H), 2.26 (s, 3H), 2.13 (d, J = 13.1 Hz, 1H), 1.93 (dt, J = 17.8, 4.7 Hz, 1H), 1.80 – 1.68 (m, 1H), 1.62 – 1.34 (m, 5H), 1.17 (dd, J = 12.6, 5.1 Hz, 1H), 1.07 (s, 3H), 1.00 (s, 3H), 0.96 – 0.89 (m, 1H), 0.78 (s, 3H), 0.72 (d, J = 6.8 Hz, 3H).
1.00
0.94
0.95
2.75
1.13
1.23
1.39
5.45
0.96
2.89
3.23
0.65
2.71
2.73
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

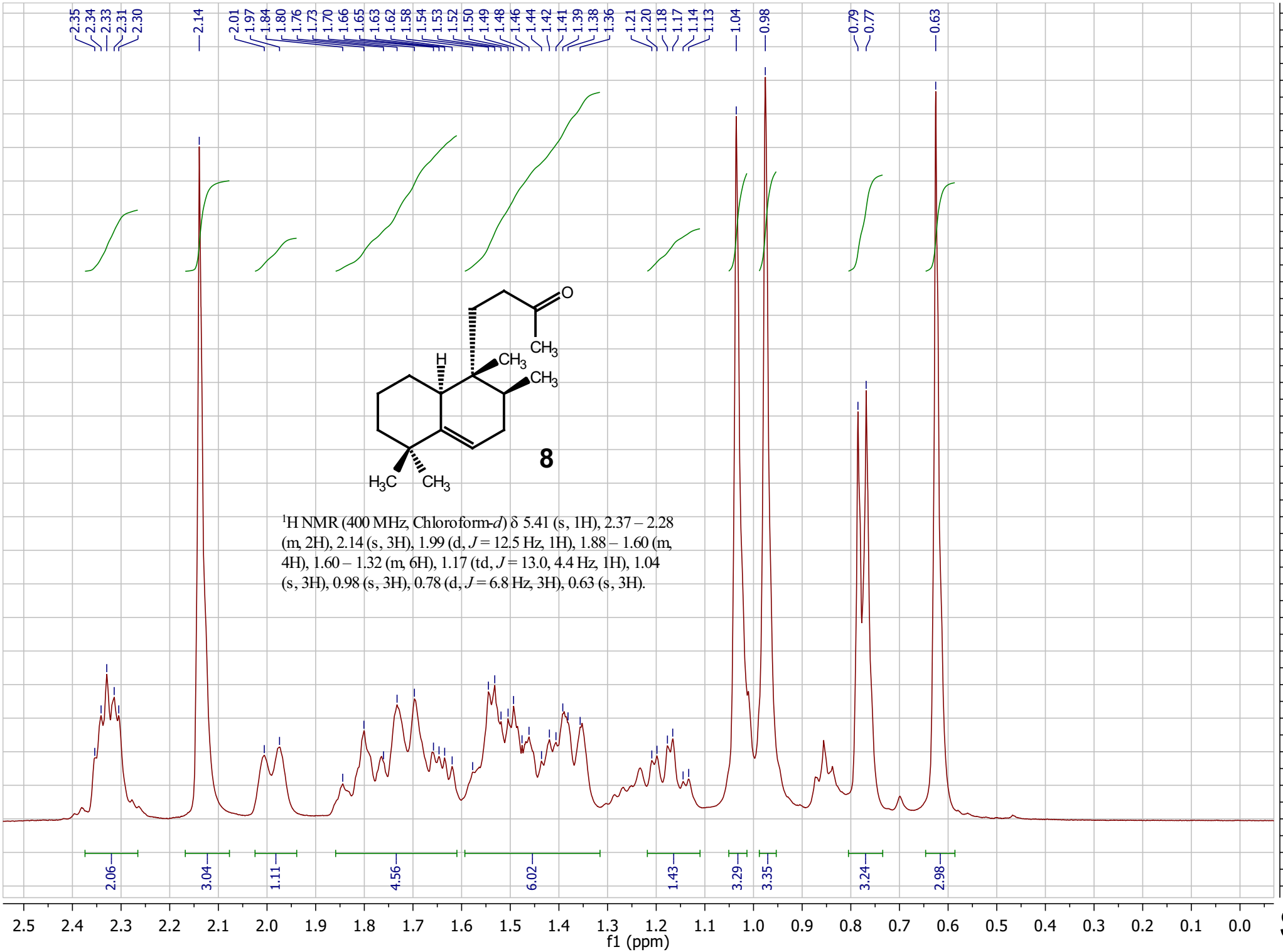

2.26
2.15
2.11
1.96
1.95
1.94
1.91
1.90
1.89
1.78
1.78
1.75
1.74
1.71
1.70
1.60
1.58
1.57
1.55
1.54
1.52
1.51
1.51
1.49
1.49
1.45
1.42
1.41
1.40
1.39
1.37
1.36
1.19
1.18
1.16
1.15
1.07
1.00
0.96
0.94
0.93
0.92
0.91
0.78
0.73
0.71
O
CH3
H
CH3
CH3
H3C
CH3
7
[1]H NMR (400 MHz, Chloroform-d) δ 6.60 (d, J = 16.2 Hz, 1H), 6.02 (d, J = 16.3 Hz, 1H), 5.49 (d, J = 5.8 Hz, 1H), 2.26 (s, 3H), 2.13 (d, J = 13.1 Hz, 1H), 1.93 (dt, J = 17.8, 4.7 Hz, 1H), 1.80 – 1.68 (m, 1H), 1.62 – 1.34 (m, 5H), 1.17 (dd, J = 12.6, 5.1 Hz, 1H), 1.07 (s, 3H), 1.00 (s, 3H), 0.96 – 0.89 (m, 1H), 0.78 (s, 3H), 0.72 (d, J = 6.8 Hz, 3H).
2.75
1.13
1.23
1.39
5.45
0.96
2.89
3.23
0.65
2.71
2.73
f1 (ppm)


198.72
158.19
144.73
129.58
116.47
43.67
43.00
40.77
36.65
36.22
31.12
29.67
29.28
28.27
27.43
21.96
16.38
10.28
O
CH3
H
CH3
CH3
H3C
CH3
7
13C NMR (101 MHz, cdcl3) δ 198.72, 158.19, 144.73, 129.58, 116.47, 43.67, 43.00, 40.77, 36.65, 36.22, 31.12, 29.67, 29.28, 28.27, 27.43, 21.96, 16.38, 10.28.
f1 (ppm)

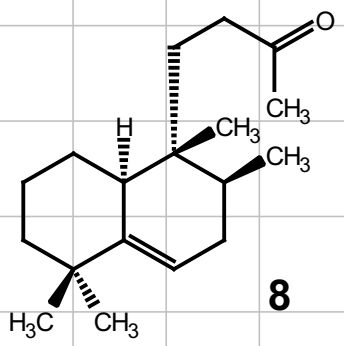

198.72
158.18
144.74
129.58
116.47
43.67
43.00
40.77
36.65
36.22
31.12
29.67
29.28
28.27
27.43
21.96
16.38
10.28
O
CH3
H
CH3
CH3
H3C
CH3
7
13C NMR (101 MHz, cdcl3) δ 198.72, 158.18, 144.74,
129.58, 116.47, 43.67, 43.00, 40.77, 36.65, 36.22,
31.12, 29.67, 29.28, 28.27, 27.43, 21.96, 16.38, 10.28.
f1 (ppm)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.41 (s, 1H), 2.37 – 2.28 (m, 2H), 2.14 (s, 3H), 1.99 (d, *J* = 12.5 Hz, 1H), 1.88 – 1.60 (m, 4H), 1.60 – 1.32 (m, 6H), 1.17 (td, *J* = 13.0, 4.4 Hz, 1H), 1.04 (s, 3H), 0.98 (s, 3H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.63 (s, 3H).

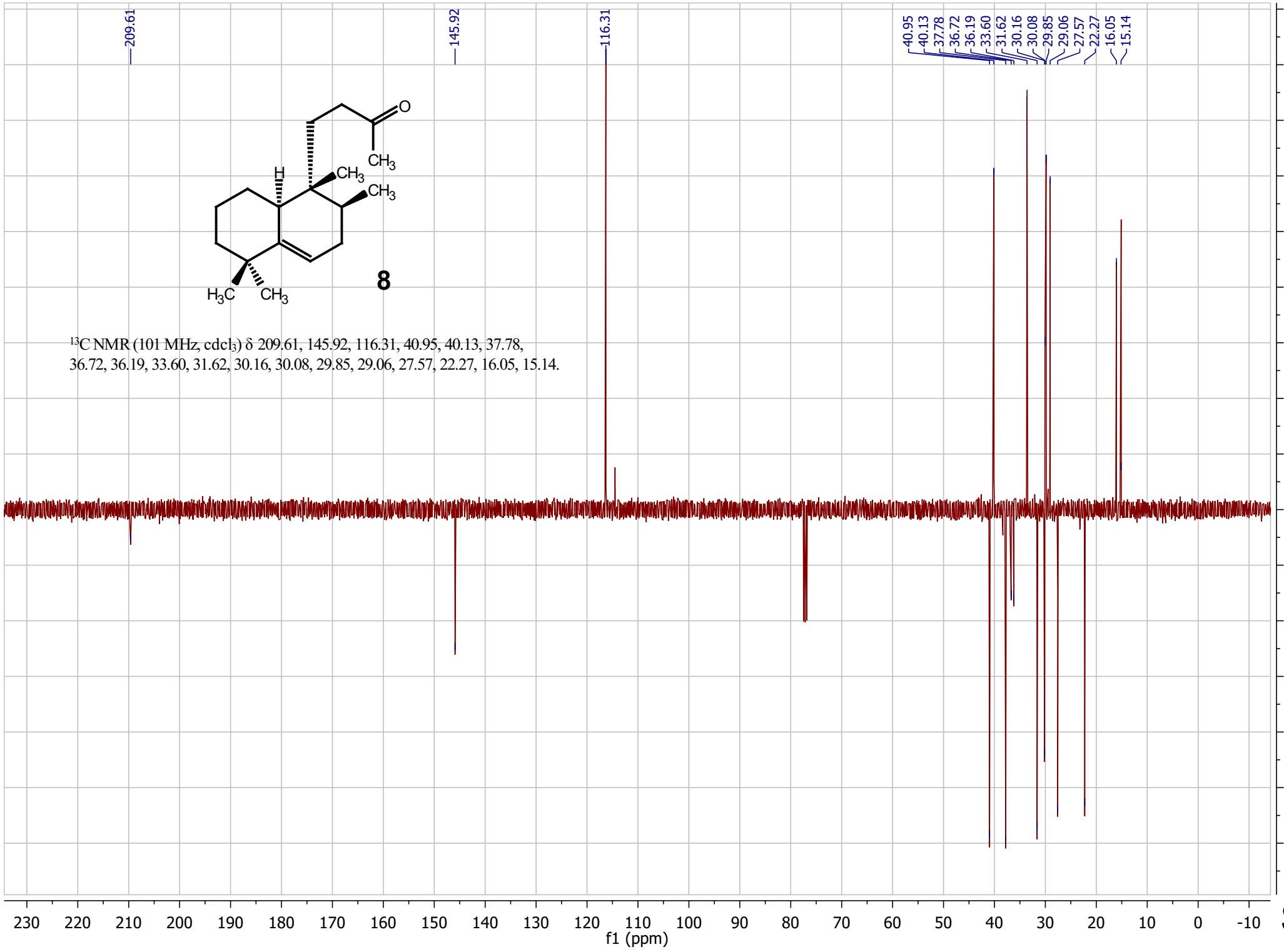


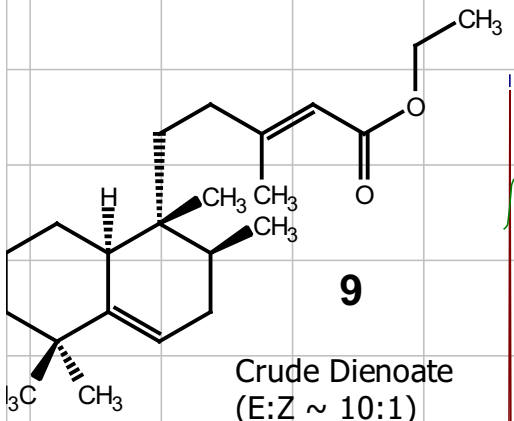
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.41 (s, 1H), 2.37 – 2.28 (m, 2H), 2.14 (s, 3H), 1.99 (d, *J* = 12.5 Hz, 1H), 1.88 – 1.60 (m, 4H), 1.60 – 1.32 (m, 6H), 1.17 (td, *J* = 13.0, 4.4 Hz, 1H), 1.04 (s, 3H), 0.98 (s, 3H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.63 (s, 3H).



8

^{13}C NMR (101 MHz, cdcl$_3$) δ 209.58, 145.91, 116.30, 40.95, 40.12, 37.77, 36.71, 36.18, 33.59, 31.61, 30.15, 30.07, 29.84, 29.04, 27.57, 22.26, 16.04, 15.11.

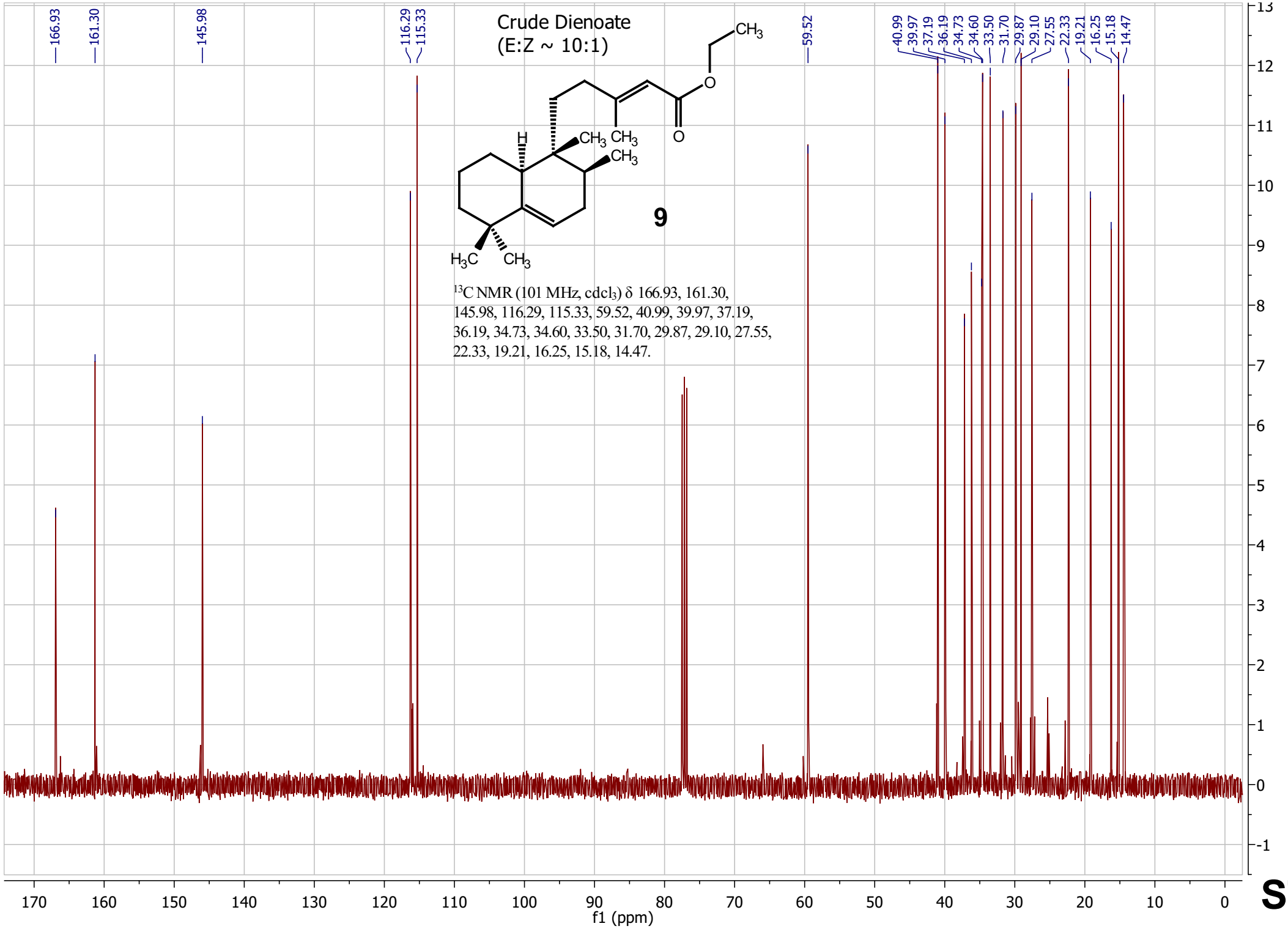

209.61
145.92
116.31
40.95
40.13
37.78
36.72
36.19
33.60
31.62
30.16
30.08
29.85
29.06
27.57
22.27
16.05
15.14
O
CH3
H
CH3
CH3
H3C
CH3
8
13C NMR (101 MHz, cdcl3) δ 209.61, 145.92, 116.31, 40.95, 40.13, 37.78,
36.72, 36.19, 33.60, 31.62, 30.16, 30.08, 29.85, 29.06, 27.57, 22.27, 16.05, 15.14.
f1 (ppm)

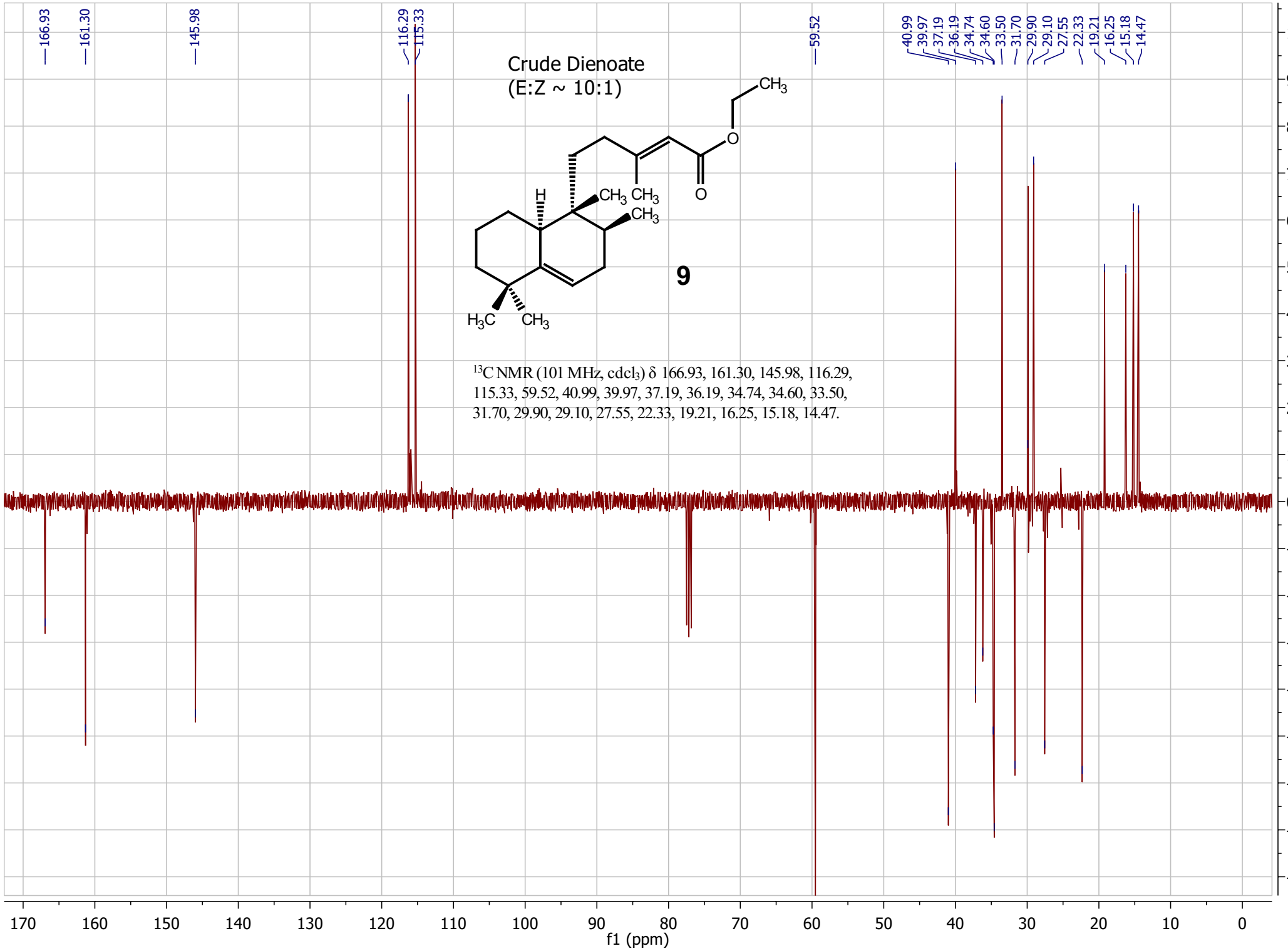


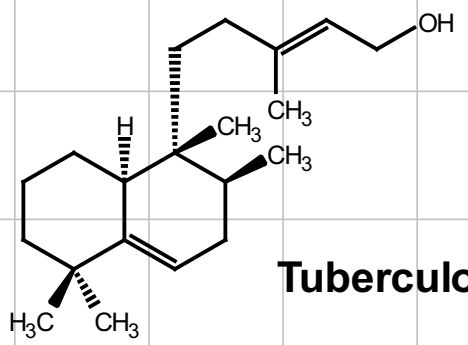
9

Crude Dienoate
(E:Z ~ 10:1)

^{1}H NMR (400 MHz, Chloroform-*d*)
δ 5.67 (s, 1H), 5.45 – 5.40 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.17 (s, 3H), 2.13 (d, *J* = 13.1 Hz, 1H), 2.03 (dt, *J* = 10.1, 4.4 Hz, 2H), 1.90 – 1.67 (m, 4H), 1.65 – 1.44 (m, 5H), 1.44 – 1.34 (m, 2H), 1.26 (d, *J* = 6.9 Hz, 2H), 1.22 – 1.14 (m, 1H), 1.05 (s, 3H), 0.99 (s, 3H), 0.81 (d, *J* = 6.7 Hz, 3H), 0.63 (s, 3H).

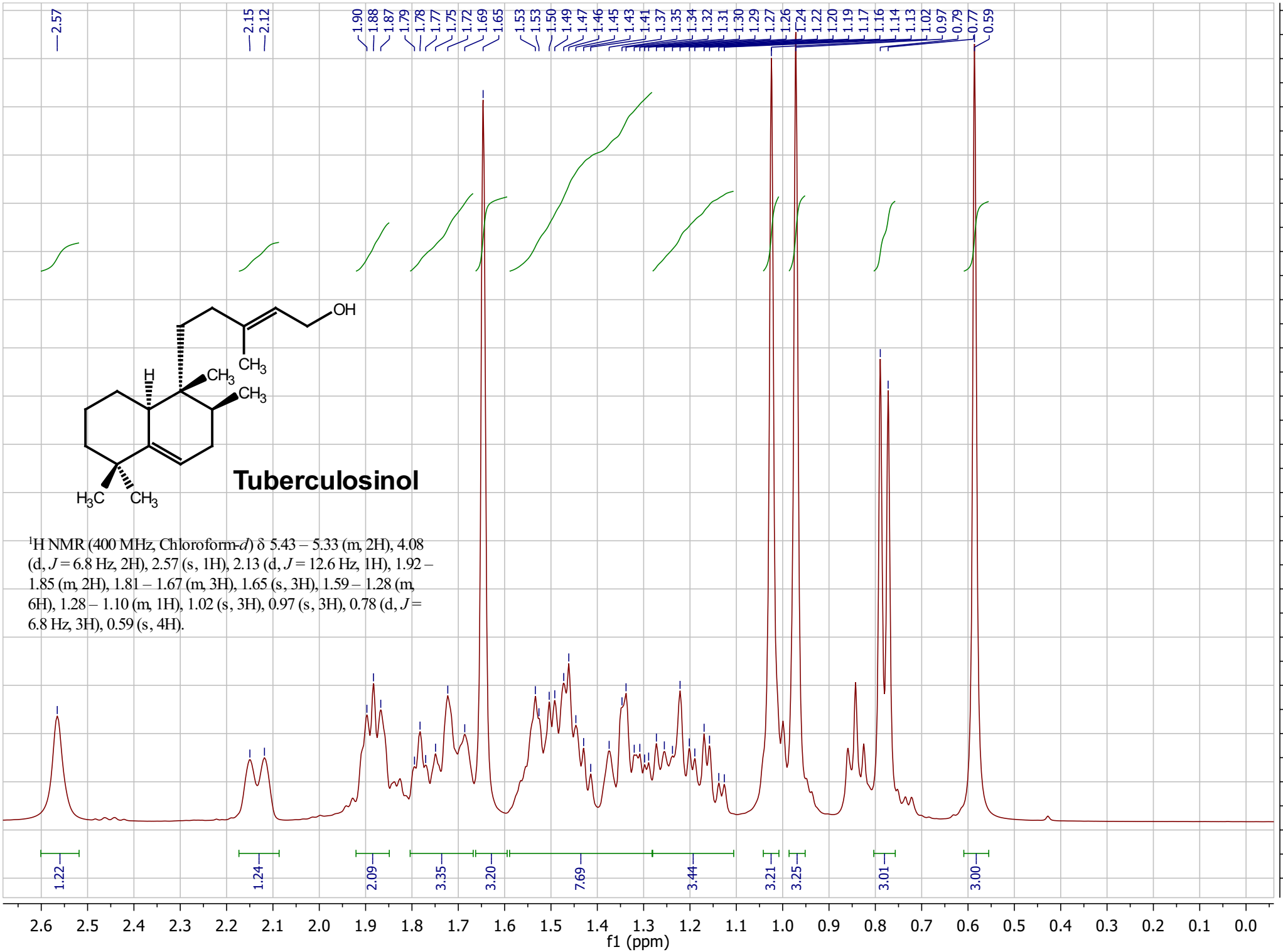

Crude Dienoate
(E:Z ~ 10:1)
9
^{13}C NMR (101 MHz, cdcl$_3$) δ 166.93, 161.30, 145.98, 116.29, 115.33, 59.52, 40.99, 39.97, 37.19, 36.19, 34.73, 34.60, 33.50, 31.70, 29.87, 29.10, 27.55, 22.33, 19.21, 16.25, 15.18, 14.47.
166.93
161.30
145.98
116.29
115.33
59.52
40.99
39.97
37.19
36.19
34.73
34.60
33.50
31.70
29.87
29.10
27.55
22.33
19.21
16.25
15.18
14.47
f1 (ppm)

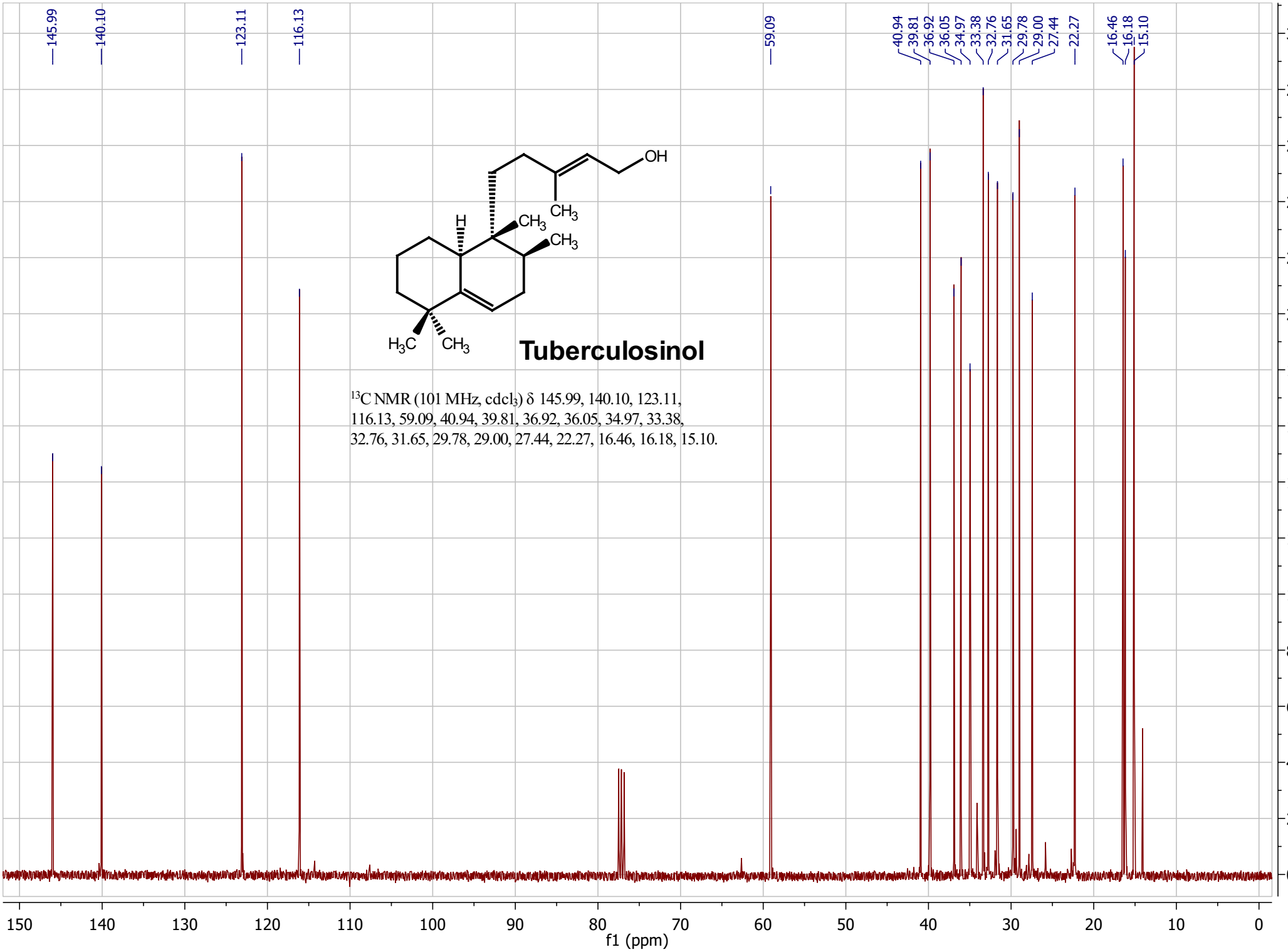

166.93
161.30
145.98
116.29
115.33
59.52
40.99
39.97
37.19
36.19
34.74
34.60
33.50
31.70
29.90
29.10
27.55
22.33
19.21
16.25
15.18
14.47
Crude Dienoate
(E:Z ~ 10:1)
CH3
O
O
H
CH3 CH3
CH3
H3C
CH3
9
13C NMR (101 MHz, cdcl3) δ 166.93, 161.30, 145.98, 116.29,
115.33, 59.52, 40.99, 39.97, 37.19, 36.19, 34.74, 34.60, 33.50,
31.70, 29.90, 29.10, 27.55, 22.33, 19.21, 16.25, 15.18, 14.47.
f1 (ppm)



Tuberculosinol

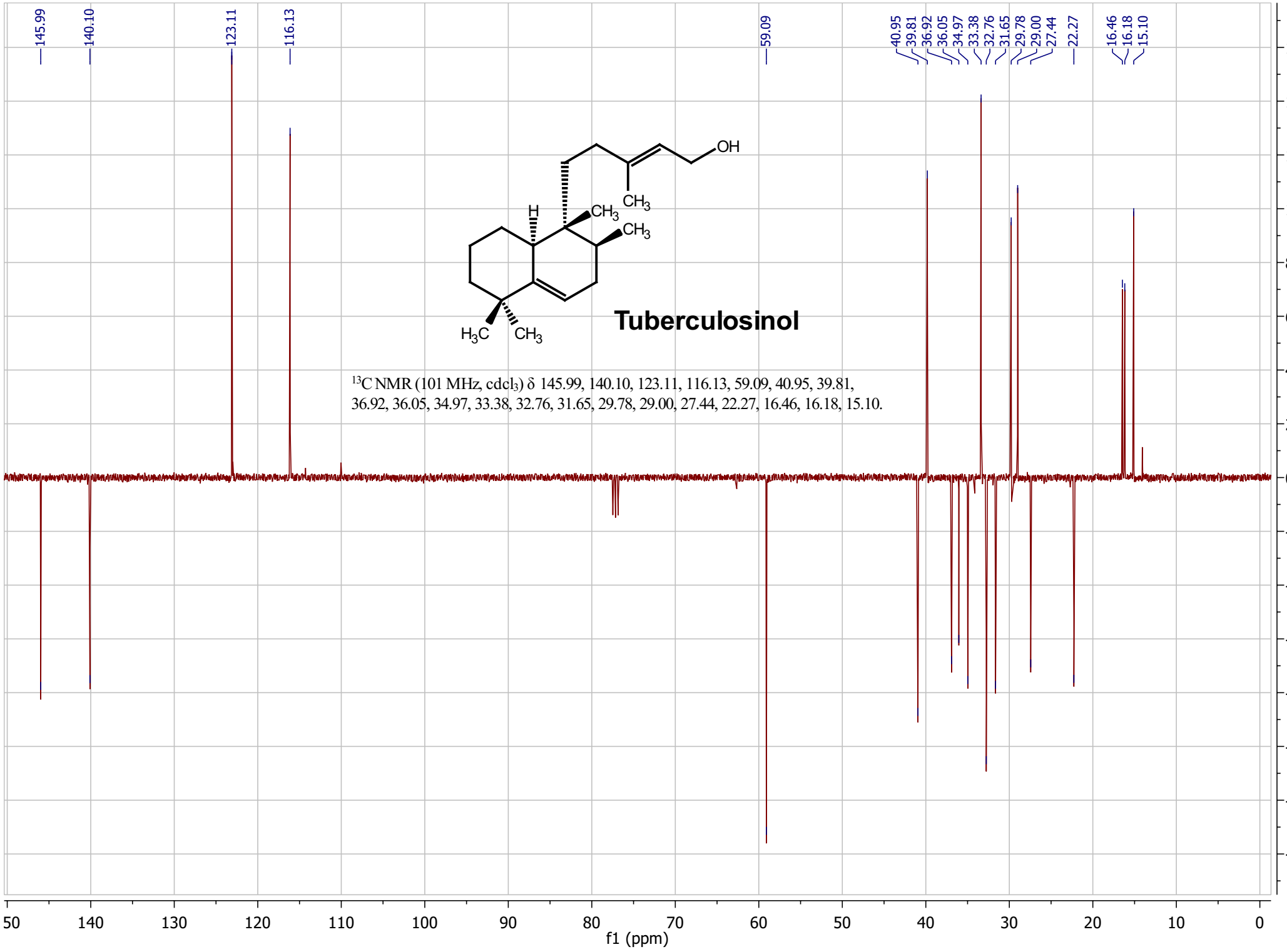
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.43 – 5.33 (m, 2H), 4.08 (d, *J* = 6.8 Hz, 2H), 2.57 (s, 1H), 2.13 (d, *J* = 12.6 Hz, 1H), 1.92 – 1.85 (m, 2H), 1.81 – 1.67 (m, 3H), 1.65 (s, 3H), 1.59 – 1.28 (m, 6H), 1.28 – 1.10 (m, 1H), 1.02 (s, 3H), 0.97 (s, 3H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.59 (s, 4H).

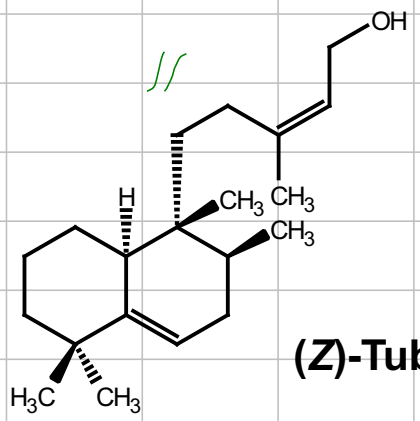

2.57
2.15
2.12
1.90
1.88
1.87
1.79
1.78
1.77
1.75
1.72
1.69
1.65
1.53
1.53
1.50
1.49
1.47
1.46
1.45
1.43
1.41
1.37
1.35
1.34
1.32
1.31
1.30
1.29
1.27
1.26
1.24
1.22
1.20
1.19
1.17
1.16
1.14
1.13
1.02
0.97
0.79
0.77
0.59
OH
CH3
H
CH3
CH3
H3C
CH3
Tuberculosinol
1H NMR (400 MHz, Chloroform-d) δ 5.43 – 5.33 (m, 2H), 4.08 (d, J = 6.8 Hz, 2H), 2.57 (s, 1H), 2.13 (d, J = 12.6 Hz, 1H), 1.92 – 1.85 (m, 2H), 1.81 – 1.67 (m, 3H), 1.65 (s, 3H), 1.59 – 1.28 (m, 6H), 1.28 – 1.10 (m, 1H), 1.02 (s, 3H), 0.97 (s, 3H), 0.78 (d, J = 6.8 Hz, 3H), 0.59 (s, 4H).
1.22
1.24
2.09
3.35
3.20
7.69
3.44
3.21
3.25
3.01
3.00
f1 (ppm)



Tuberculosinol

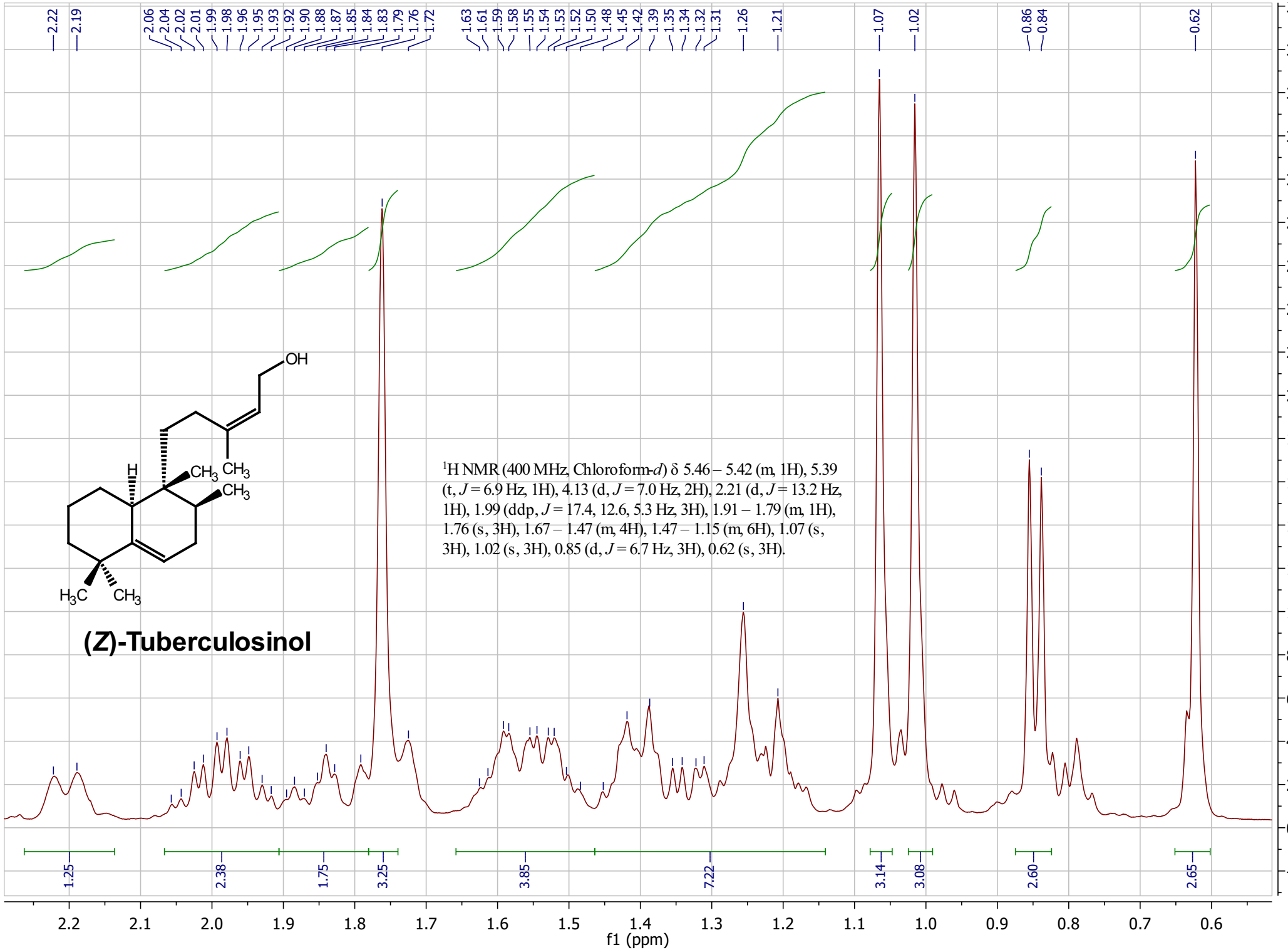
^{13}C NMR (101 MHz, cdcl$_3$) δ 145.99, 140.10, 123.11, 116.13, 59.09, 40.94, 39.81, 36.92, 36.05, 34.97, 33.38, 32.76, 31.65, 29.78, 29.00, 27.44, 22.27, 16.46, 16.18, 15.10.

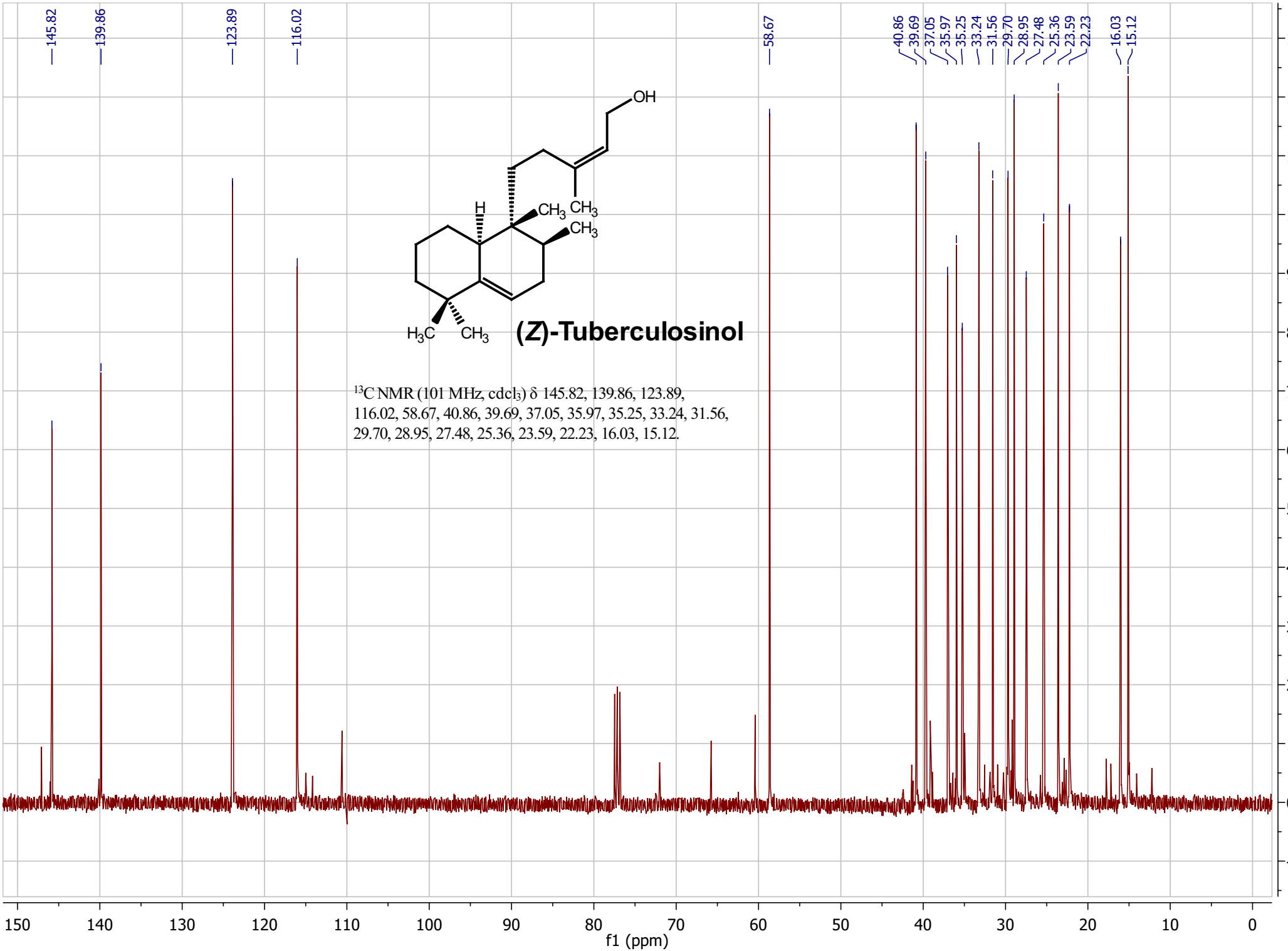

145.99
140.10
123.11
116.13
59.09
40.95
39.81
36.92
36.05
34.97
33.38
32.76
31.65
29.78
29.00
27.44
22.27
16.46
16.18
15.10
OH
CH3
CH3
CH3
H
H3C
CH3
Tuberculosinol
13C NMR (101 MHz, cdcl3) δ 145.99, 140.10, 123.11, 116.13, 59.09, 40.95, 39.81,
36.92, 36.05, 34.97, 33.38, 32.76, 31.65, 29.78, 29.00, 27.44, 22.27, 16.46, 16.18, 15.10.
f1 (ppm)

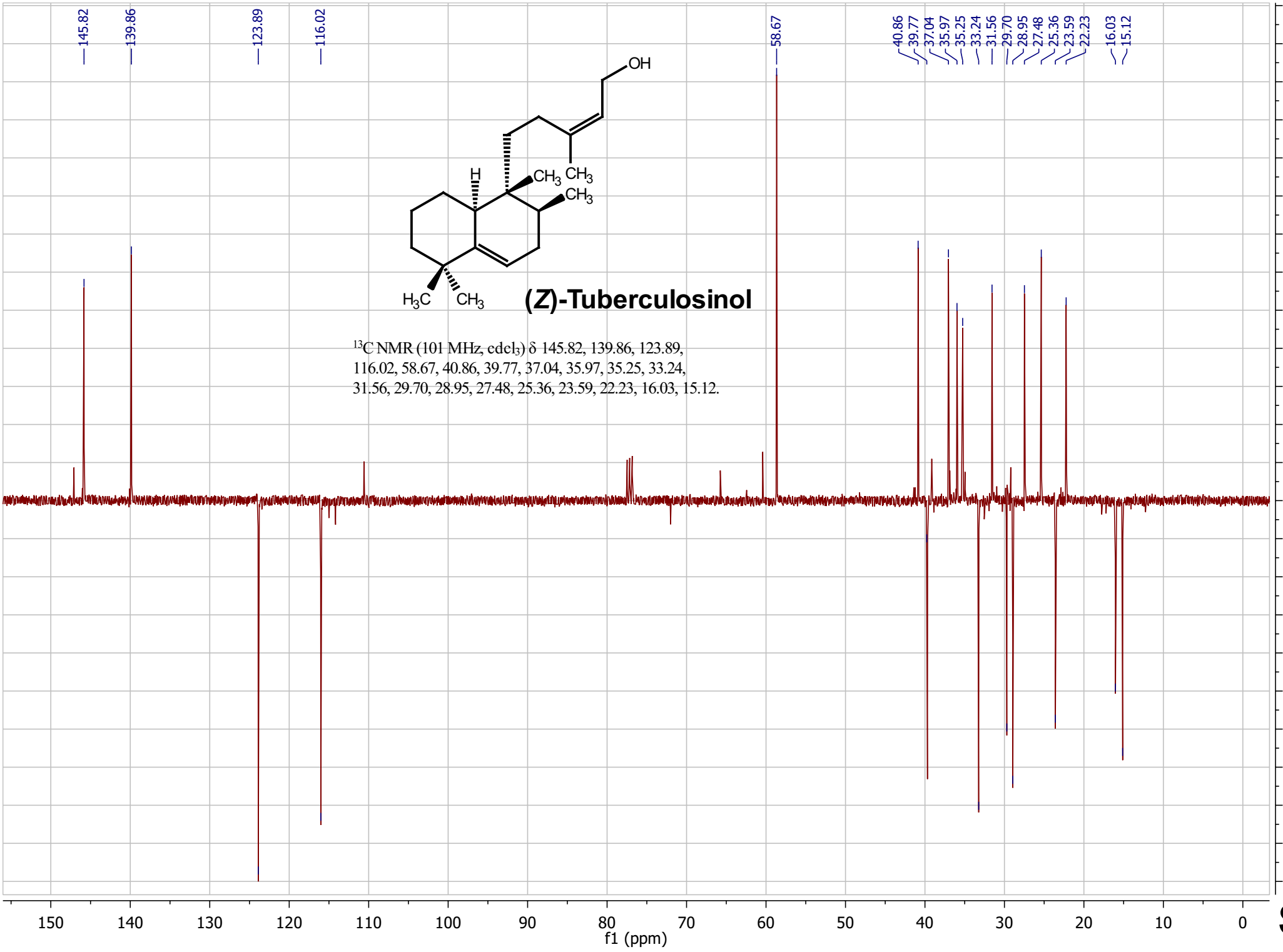


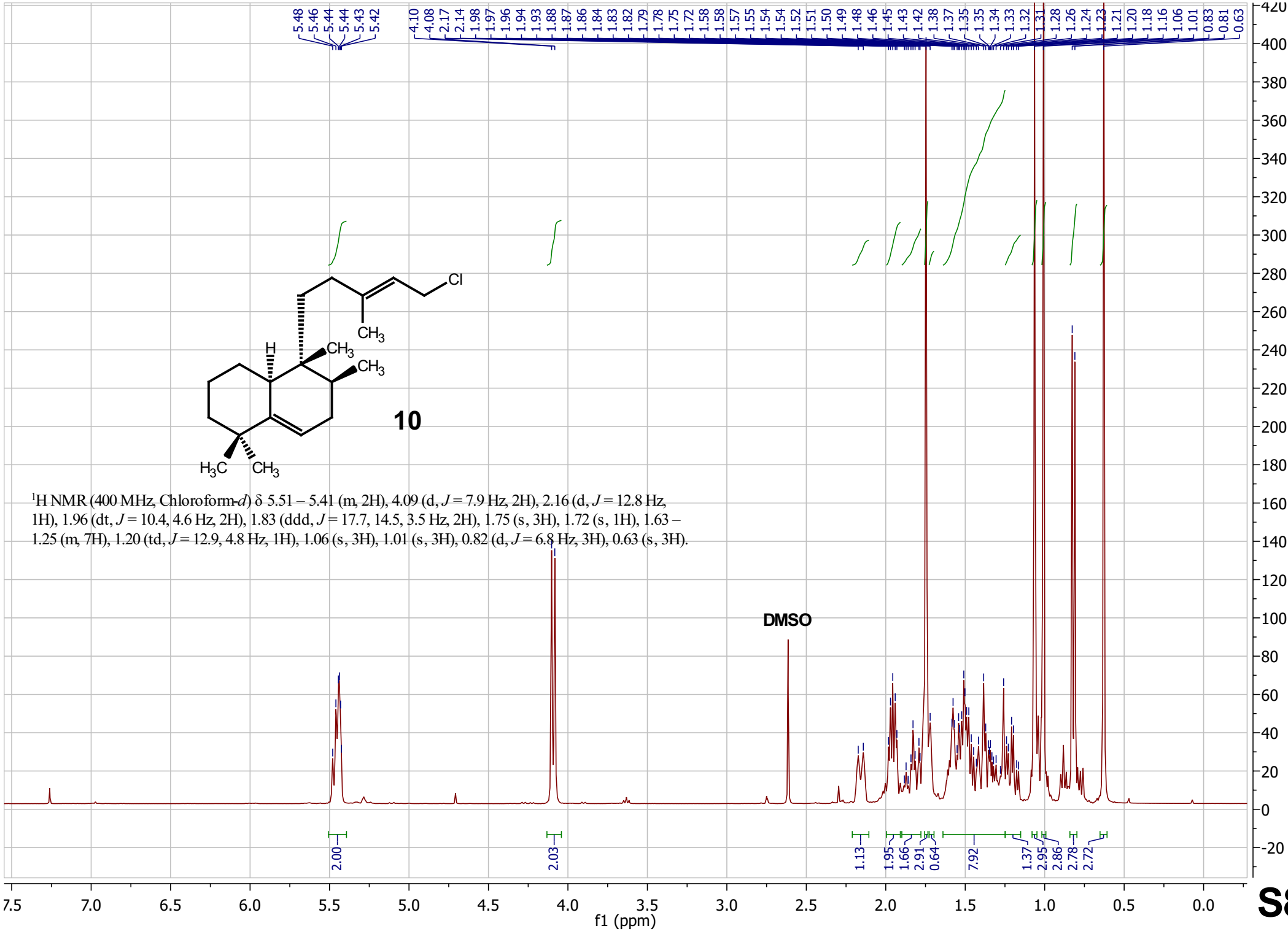
(*Z*)-Tuberculosinol

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.46 – 5.42 (m, 1H), 5.39 (t, *J* = 6.9 Hz, 1H), 4.13 (d, *J* = 7.0 Hz, 2H), 2.21 (d, *J* = 13.2 Hz, 1H), 1.99 (ddp, *J* = 17.4, 12.6, 5.3 Hz, 3H), 1.91 – 1.79 (m, 1H), 1.76 (s, 3H), 1.67 – 1.47 (m, 4H), 1.47 – 1.15 (m, 6H), 1.07 (s, 3H), 1.02 (s, 3H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.62 (s, 3H).

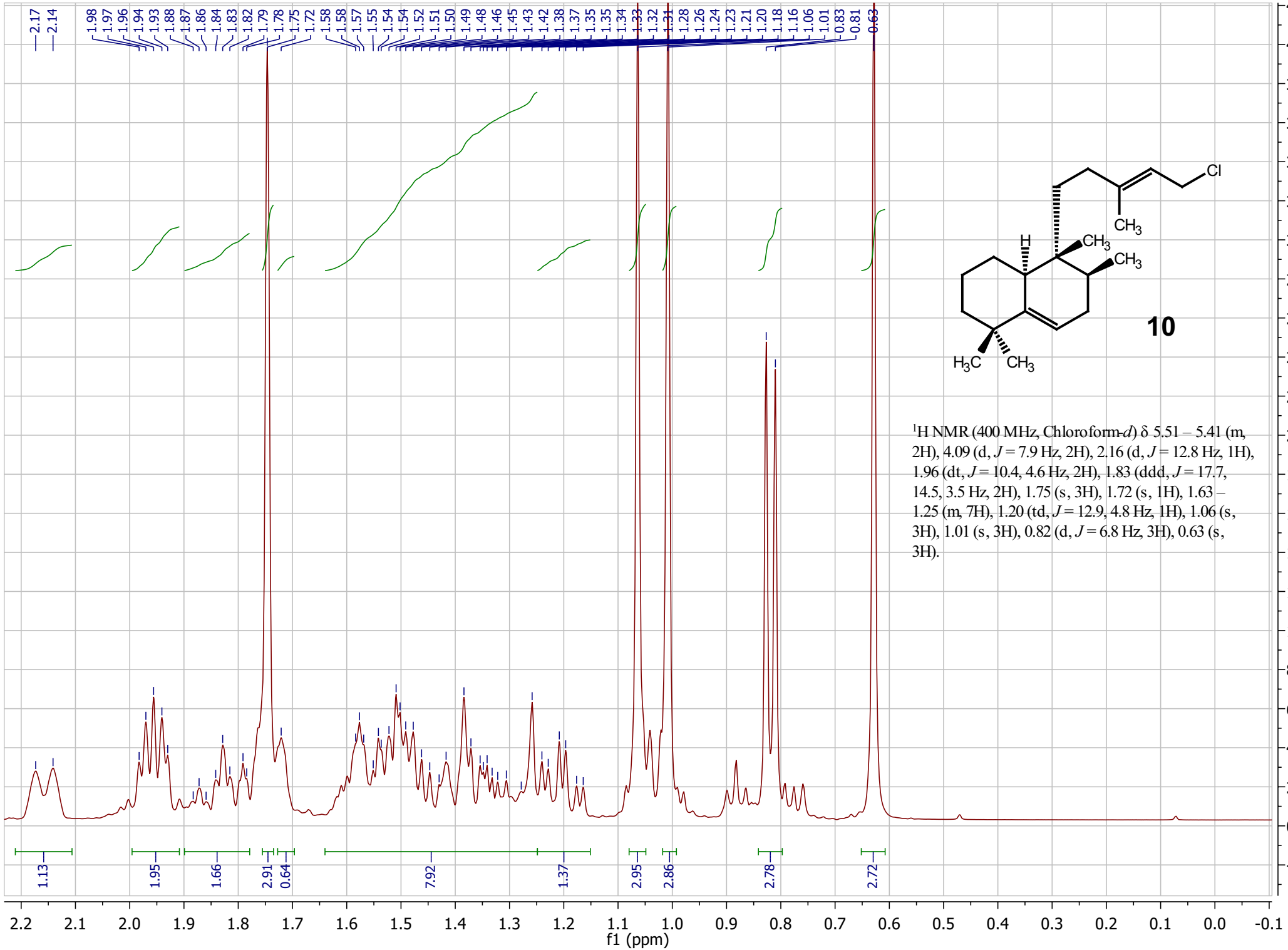

2.22
2.19
2.06
2.04
2.02
2.01
1.99
1.98
1.96
1.95
1.93
1.92
1.90
1.88
1.87
1.85
1.84
1.83
1.79
1.76
1.72
1.63
1.61
1.59
1.58
1.55
1.54
1.53
1.52
1.50
1.48
1.45
1.42
1.39
1.35
1.34
1.32
1.31
1.26
1.21
1.07
1.02
0.86
0.84
0.62
OH
H
CH3
CH3
CH3
H3C
CH3
(Z)-Tuberculosinol
1H NMR (400 MHz, Chloroform-d) δ 5.46 – 5.42 (m, 1H), 5.39 (t, J = 6.9 Hz, 1H), 4.13 (d, J = 7.0 Hz, 2H), 2.21 (d, J = 13.2 Hz, 1H), 1.99 (ddp, J = 17.4, 12.6, 5.3 Hz, 3H), 1.91 – 1.79 (m, 1H), 1.76 (s, 3H), 1.67 – 1.47 (m, 4H), 1.47 – 1.15 (m, 6H), 1.07 (s, 3H), 1.02 (s, 3H), 0.85 (d, J = 6.7 Hz, 3H), 0.62 (s, 3H).
1.25
2.38
1.75
3.25
3.85
7.22
3.14
3.08
2.60
2.65
f1 (ppm)

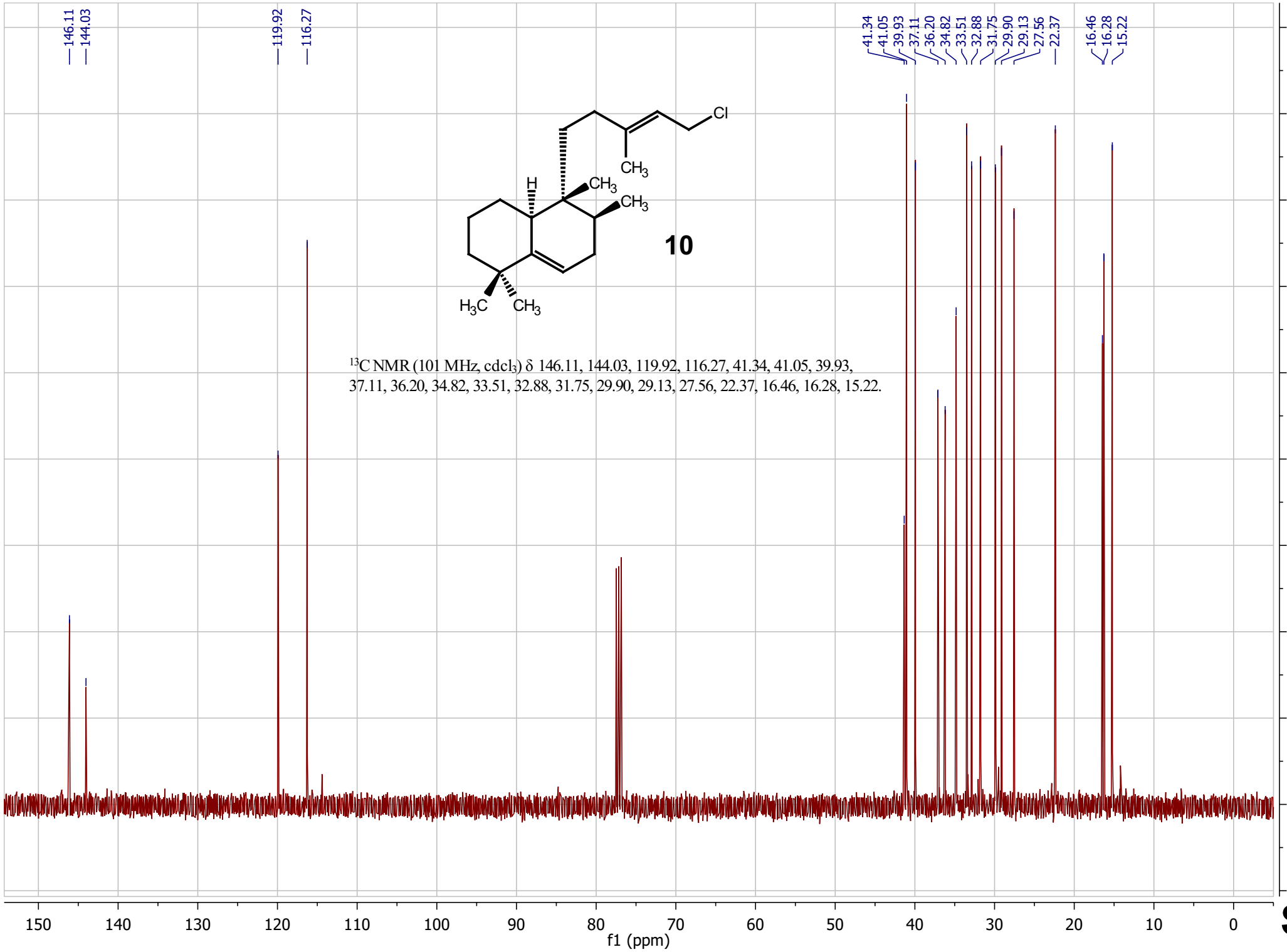

145.82
139.86
123.89
116.02
58.67
40.86
39.69
37.05
35.97
35.25
33.24
31.56
29.70
28.95
27.48
25.36
23.59
22.23
16.03
15.12
OH
H
CH3
CH3
CH3
H3C
CH3
(Z)-Tuberculosinol
13C NMR (101 MHz, cdcl3) δ 145.82, 139.86, 123.89, 116.02, 58.67, 40.86, 39.69, 37.05, 35.97, 35.25, 33.24, 31.56, 29.70, 28.95, 27.48, 25.36, 23.59, 22.23, 16.03, 15.12.
f1 (ppm)

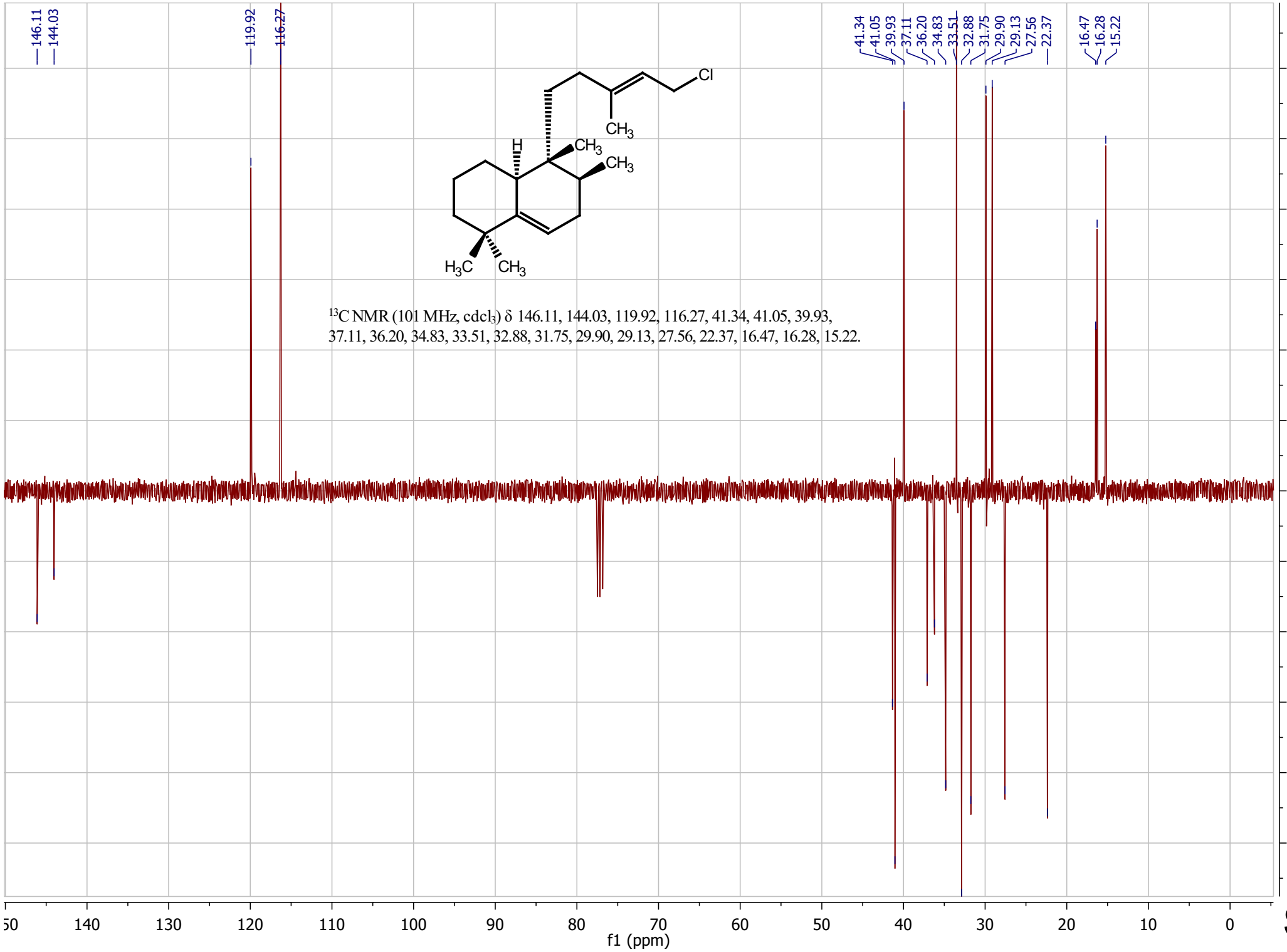

145.82
139.86
123.89
116.02
58.67
40.86
39.77
37.04
35.97
35.25
33.24
31.56
29.70
28.95
27.48
25.36
23.59
22.23
16.03
15.12
OH
H
CH3
CH3
CH3
H3C
CH3
(Z)-Tuberculosinol
13C NMR (101 MHz, cdcl3) δ 145.82, 139.86, 123.89,
116.02, 58.67, 40.86, 39.77, 37.04, 35.97, 35.25, 33.24,
31.56, 29.70, 28.95, 27.48, 25.36, 23.59, 22.23, 16.03, 15.12.
f1 (ppm)

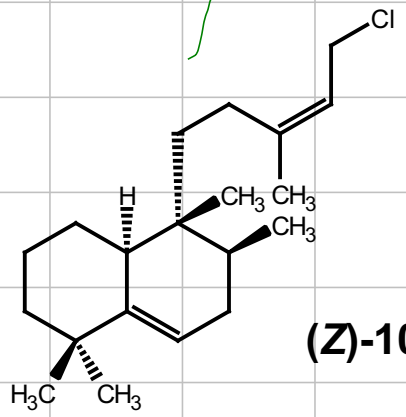


^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.51 – 5.41 (m, 2H), 4.09 (d, *J* = 7.9 Hz, 2H), 2.16 (d, *J* = 12.8 Hz, 1H), 1.96 (dt, *J* = 10.4, 4.6 Hz, 2H), 1.83 (ddd, *J* = 17.7, 14.5, 3.5 Hz, 2H), 1.75 (s, 3H), 1.72 (s, 1H), 1.63 – 1.25 (m, 7H), 1.20 (td, *J* = 12.9, 4.8 Hz, 1H), 1.06 (s, 3H), 1.01 (s, 3H), 0.82 (d, *J* = 6.8 Hz, 3H), 0.63 (s, 3H).


2.17
2.14
1.98
1.97
1.96
1.94
1.93
1.88
1.87
1.86
1.84
1.83
1.82
1.79
1.78
1.75
1.72
1.58
1.58
1.57
1.55
1.54
1.54
1.52
1.51
1.50
1.49
1.48
1.46
1.45
1.43
1.42
1.38
1.37
1.35
1.35
1.34
1.33
1.32
1.31
1.28
1.26
1.24
1.23
1.21
1.20
1.18
1.16
1.06
1.01
0.83
0.81
0.63
1.13
1.95
1.66
2.91
0.64
7.92
1.37
2.95
2.86
2.78
2.72
f1 (ppm)
Cl
CH3
H
CH3
CH3
H3C
CH3
10
[1]H NMR (400 MHz, Chloroform-d) δ 5.51 – 5.41 (m, 2H), 4.09 (d, J = 7.9 Hz, 2H), 2.16 (d, J = 12.8 Hz, 1H), 1.96 (dt, J = 10.4, 4.6 Hz, 2H), 1.83 (ddd, J = 17.7, 14.5, 3.5 Hz, 2H), 1.75 (s, 3H), 1.72 (s, 1H), 1.63 – 1.25 (m, 7H), 1.20 (td, J = 12.9, 4.8 Hz, 1H), 1.06 (s, 3H), 1.01 (s, 3H), 0.82 (d, J = 6.8 Hz, 3H), 0.63 (s, 3H).


146.11
144.03
119.92
116.27
41.34
41.05
39.93
37.11
36.20
34.82
33.51
32.88
31.75
29.90
29.13
27.56
22.37
16.46
16.28
15.22
Cl
CH3
H
CH3
CH3
H3C
CH3
10
13C NMR (101 MHz, cdcl3) δ 146.11, 144.03, 119.92, 116.27, 41.34, 41.05, 39.93,
37.11, 36.20, 34.82, 33.51, 32.88, 31.75, 29.90, 29.13, 27.56, 22.37, 16.46, 16.28, 15.22.
f1 (ppm)

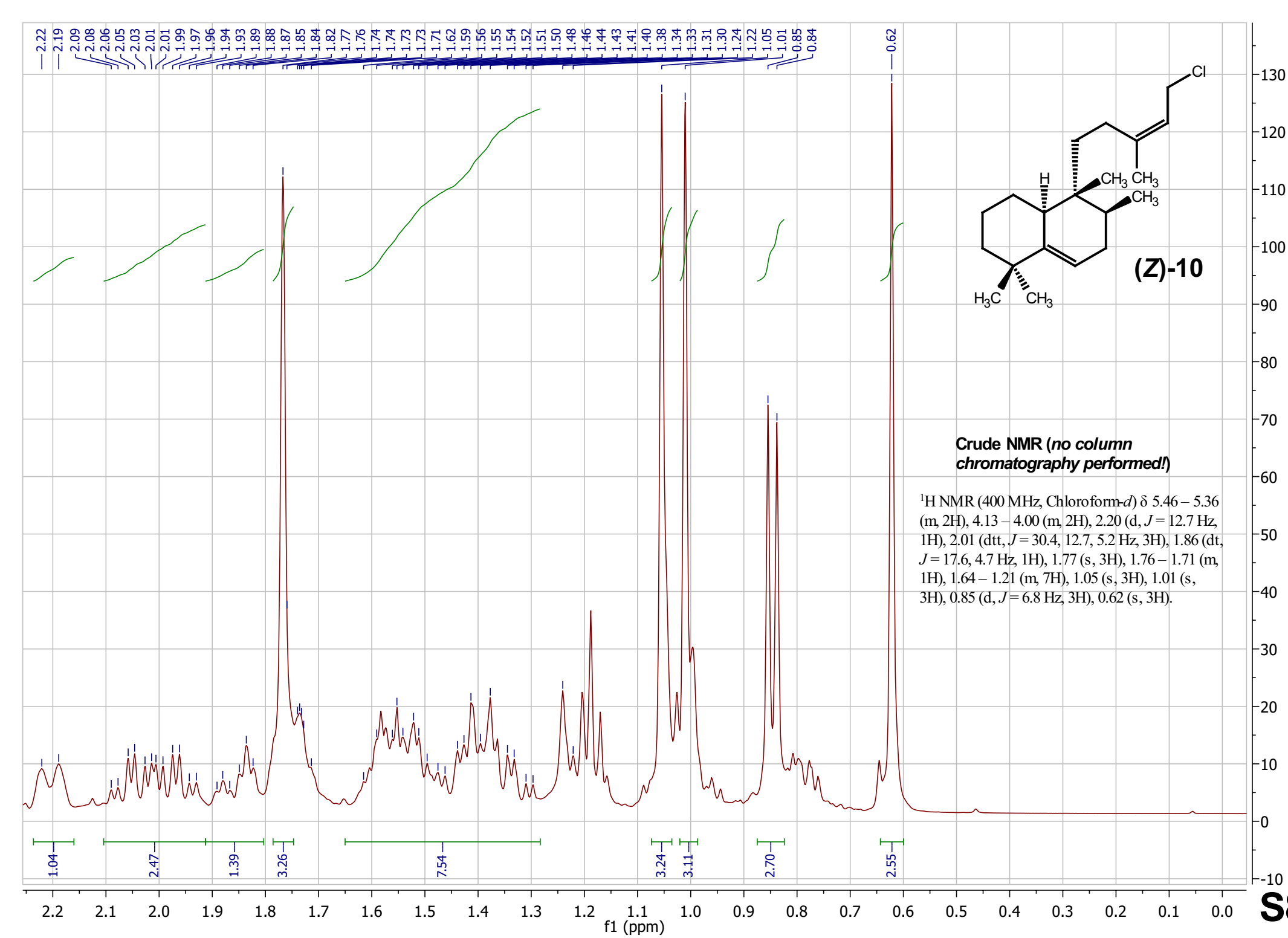

146.11
144.03
119.92
116.27
41.34
41.05
39.93
37.11
36.20
34.83
33.51
32.88
31.75
29.90
29.13
27.56
22.37
16.47
16.28
15.22
Cl
CH3
H
CH3
CH3
H3C
CH3
13C NMR (101 MHz, cdcl3) δ 146.11, 144.03, 119.92, 116.27, 41.34, 41.05, 39.93,
37.11, 36.20, 34.83, 33.51, 32.88, 31.75, 29.90, 29.13, 27.56, 22.37, 16.47, 16.28, 15.22.
f1 (ppm)

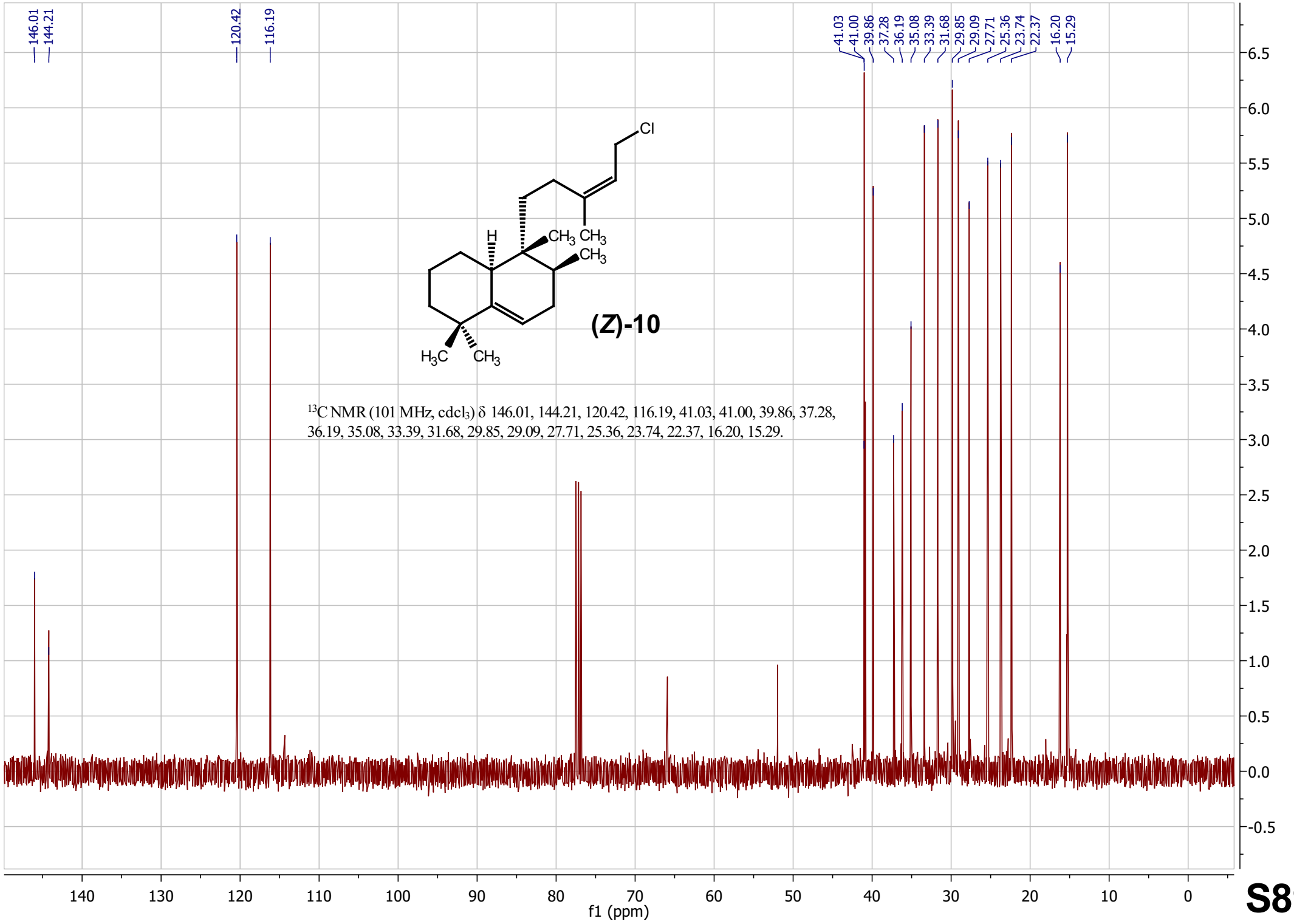


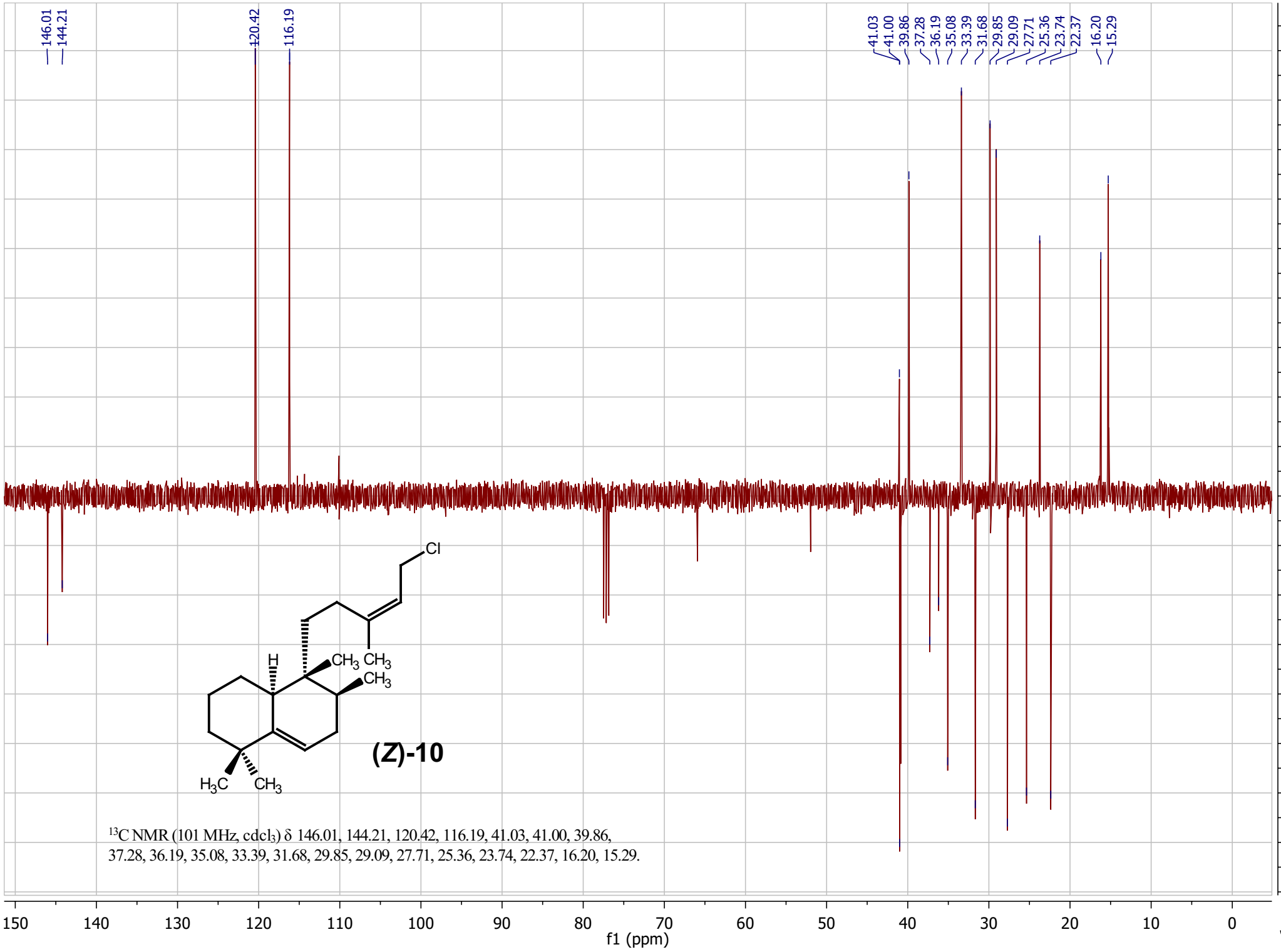
(*Z*)-10

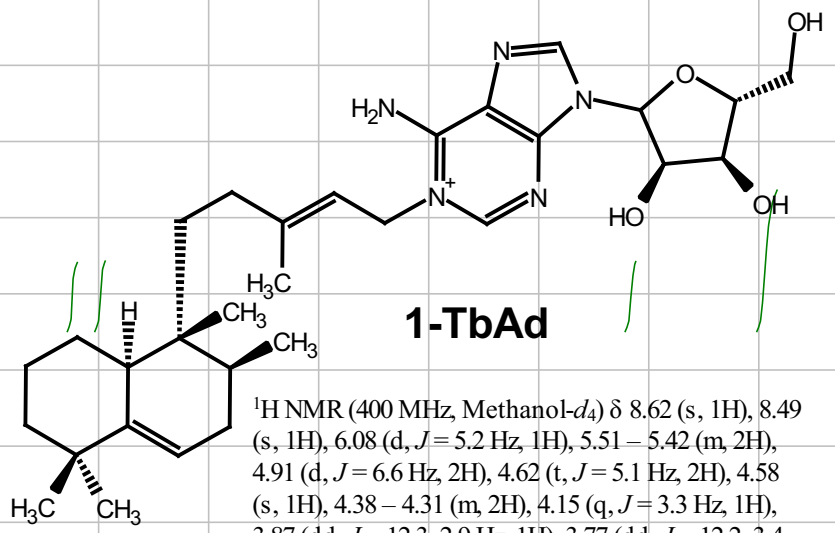
Crude NMR (*no column chromatography performed!*)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.46 – 5.36 (m, 2H), 4.13 – 4.00 (m, 2H), 2.20 (d, *J* = 12.7 Hz, 1H), 2.01 (dtt, *J* = 30.4, 12.7, 5.2 Hz, 3H), 1.86 (dt, *J* = 17.6, 4.7 Hz, 1H), 1.77 (s, 3H), 1.76 – 1.71 (m, 1H), 1.64 – 1.21 (m, 7H), 1.05 (s, 3H), 1.01 (s, 3H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.62 (s, 3H).


2.22 2.19 2.09 2.08 2.06 2.05 2.03 2.01 2.01 1.99 1.97 1.96 1.94 1.93 1.89 1.88 1.87 1.85 1.84 1.82 1.77 1.76 1.74 1.74 1.73 1.73 1.71 1.62 1.59 1.56 1.55 1.54 1.52 1.51 1.50 1.48 1.46 1.44 1.43 1.41 1.40 1.38 1.34 1.33 1.31 1.30 1.24 1.22 1.05 1.01 0.85 0.84
0.62
Cl
H
CH3 CH3
CH3
H3C CH3
(Z)-10
Crude NMR (no column chromatography performed!)
1H NMR (400 MHz, Chloroform-d) δ 5.46 – 5.36 (m, 2H), 4.13 – 4.00 (m, 2H), 2.20 (d, J = 12.7 Hz, 1H), 2.01 (dtt, J = 30.4, 12.7, 5.2 Hz, 3H), 1.86 (dt, J = 17.6, 4.7 Hz, 1H), 1.77 (s, 3H), 1.76 – 1.71 (m, 1H), 1.64 – 1.21 (m, 7H), 1.05 (s, 3H), 1.01 (s, 3H), 0.85 (d, J = 6.8 Hz, 3H), 0.62 (s, 3H).
1.04 2.47 1.39 3.26 7.54 3.24 3.11 2.70 2.55
f1 (ppm)


146.01
144.21
120.42
116.19
41.03
41.00
39.86
37.28
36.19
35.08
33.39
31.68
29.85
29.09
27.71
25.36
23.74
22.37
16.20
15.29
Cl
H
CH3 CH3
CH3
H3C CH3
(Z)-10
13C NMR (101 MHz, cdcl3) δ 146.01, 144.21, 120.42, 116.19, 41.03, 41.00, 39.86, 37.28, 36.19, 35.08, 33.39, 31.68, 29.85, 29.09, 27.71, 25.36, 23.74, 22.37, 16.20, 15.29.
f1 (ppm)

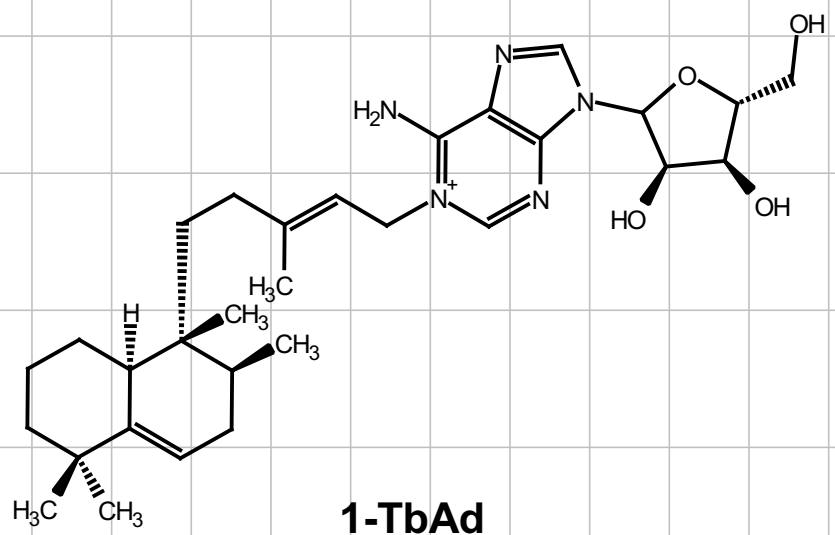

146.01
144.21
120.42
116.19
41.03
41.00
39.86
37.28
36.19
35.08
33.39
31.68
29.85
29.09
27.71
25.36
23.74
22.37
16.20
15.29
Cl
H
CH3 CH3
CH3
H3C
CH3
(Z)-10
13C NMR (101 MHz, cdcl3) δ 146.01, 144.21, 120.42, 116.19, 41.03, 41.00, 39.86,
37.28, 36.19, 35.08, 33.39, 31.68, 29.85, 29.09, 27.71, 25.36, 23.74, 22.37, 16.20, 15.29.
f1 (ppm)



1-TbAd

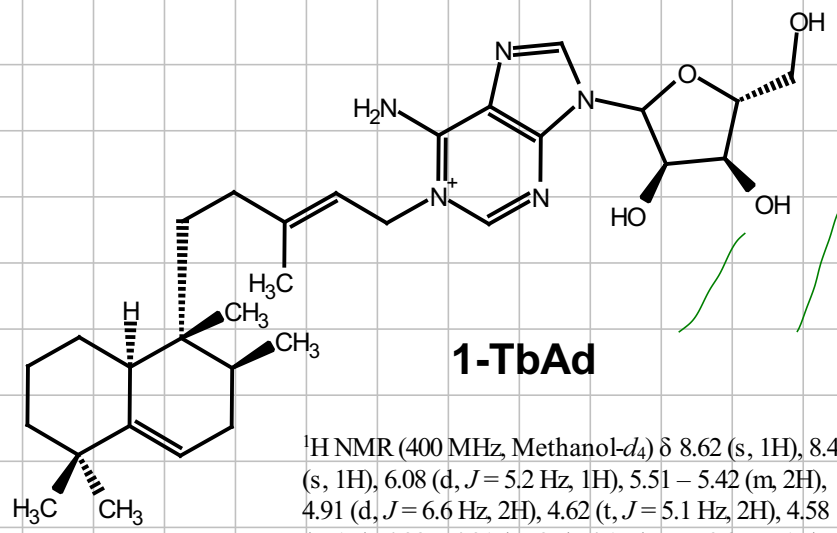
^{1}H NMR (400 MHz, Methanol-d_4) δ 8.62 (s, 1H), 8.49 (s, 1H), 6.08 (d, J = 5.2 Hz, 1H), 5.51 – 5.42 (m, 2H), 4.91 (d, J = 6.6 Hz, 2H), 4.62 (t, J = 5.1 Hz, 2H), 4.58 (s, 1H), 4.38 – 4.31 (m, 2H), 4.15 (q, J = 3.3 Hz, 1H), 3.87 (dd, J = 12.3, 2.9 Hz, 1H), 3.77 (dd, J = 12.2, 3.4 Hz, 1H), 2.23 (d, J = 12.1 Hz, 2H), 2.12 – 2.04 (m, 2H), 1.89 (s, 3H), 1.87 – 1.82 (m, 1H), 1.84 – 1.71 (m, 2H), 1.65 – 1.47 (m, 5H), 1.47 – 1.36 (m, 3H), 1.21 (ddd, J = 12.7, 5.7 Hz, 1H), 1.06 (s, 3H), 1.01 (s, 3H), 0.85 (d, J = 6.7 Hz, 3H), 0.66 (s, 3H).

f1 (ppm)



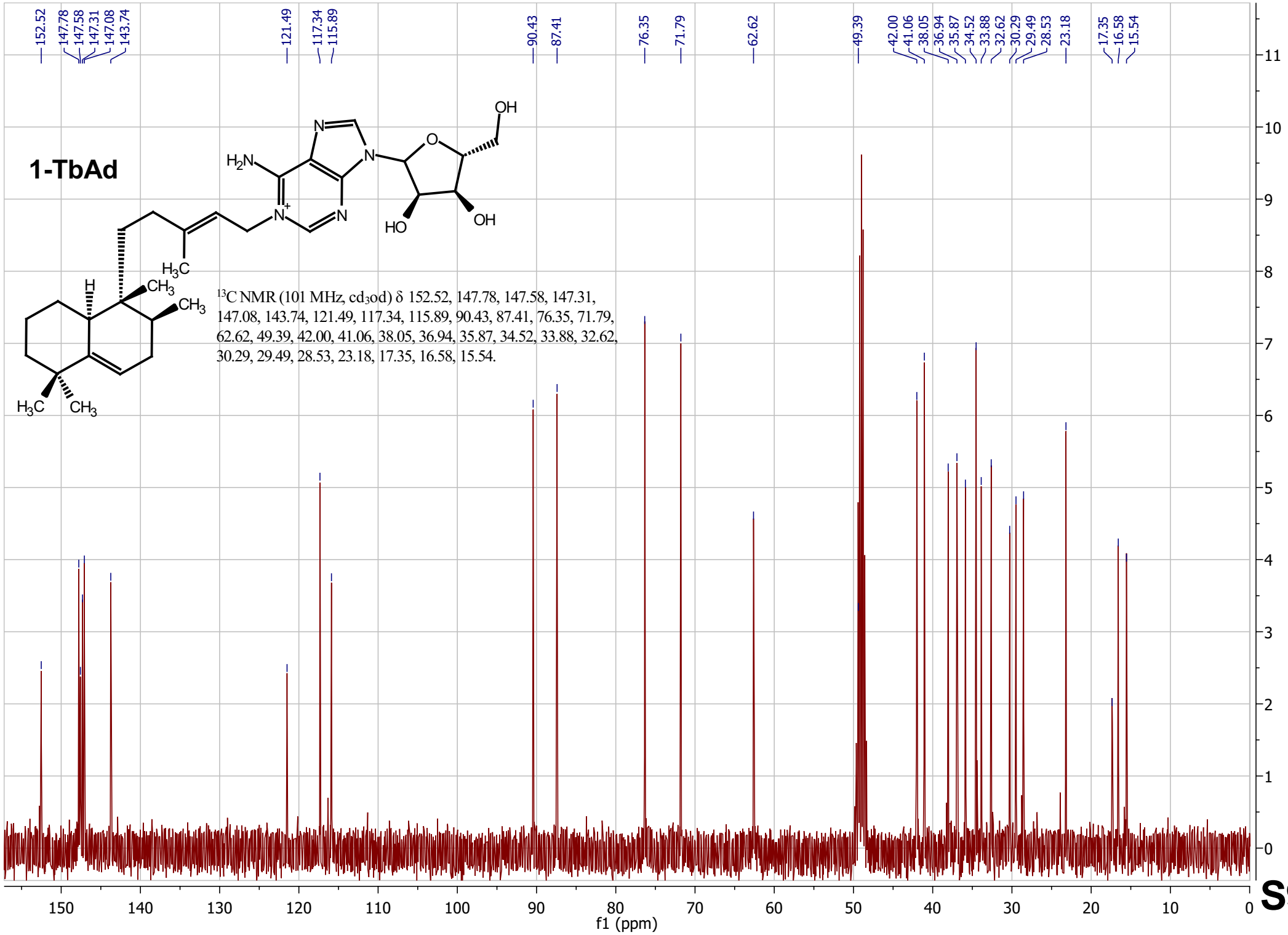
1-TbAd

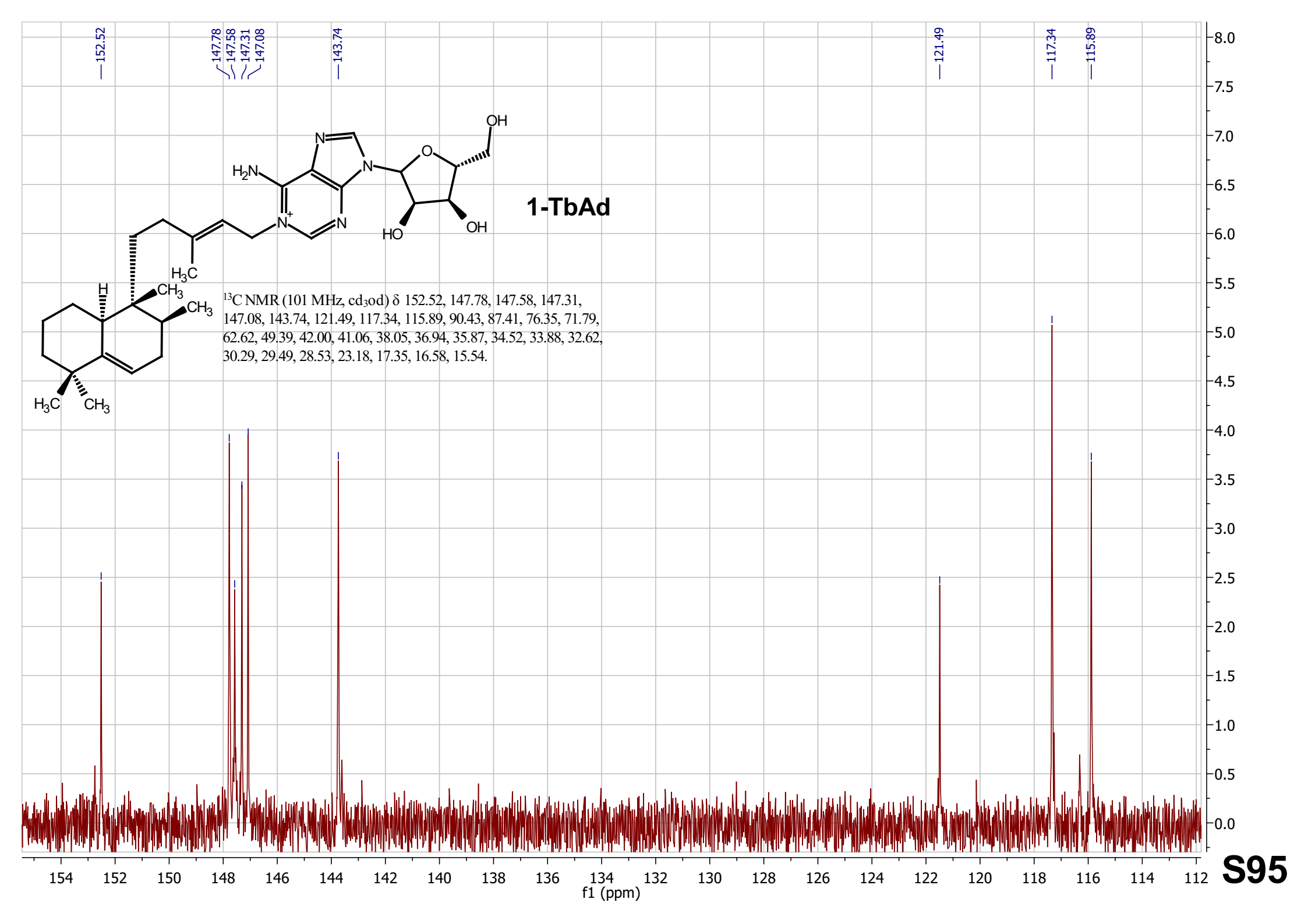
^{1}H NMR (400 MHz, Methanol-d_4) δ 8.62 (s, 1H), 8.49 (s, 1H), 6.08 (d, J = 5.2 Hz, 1H), 5.51 – 5.42 (m, 2H), 4.91 (d, J = 6.6 Hz, 2H), 4.62 (t, J = 5.1 Hz, 2H), 4.58 (s, 1H), 4.38 – 4.31 (m, 2H), 4.15 (q, J = 3.3 Hz, 1H), 3.87 (dd, J = 12.3, 2.9 Hz, 1H), 3.77 (dd, J = 12.2, 3.4 Hz, 1H), 2.23 (d, J = 12.1 Hz, 2H), 2.12 – 2.04 (m, 2H), 1.89 (s, 3H), 1.87 – 1.82 (m, 1H), 1.84 – 1.71 (m, 2H), 1.65 – 1.47 (m, 5H), 1.47 – 1.36 (m, 3H), 1.21 (ddd, J = 12.7, 5.7 Hz, 1H), 1.06 (s, 3H), 1.01 (s, 3H), 0.85 (d, J = 6.7 Hz, 3H), 0.66 (s, 3H).

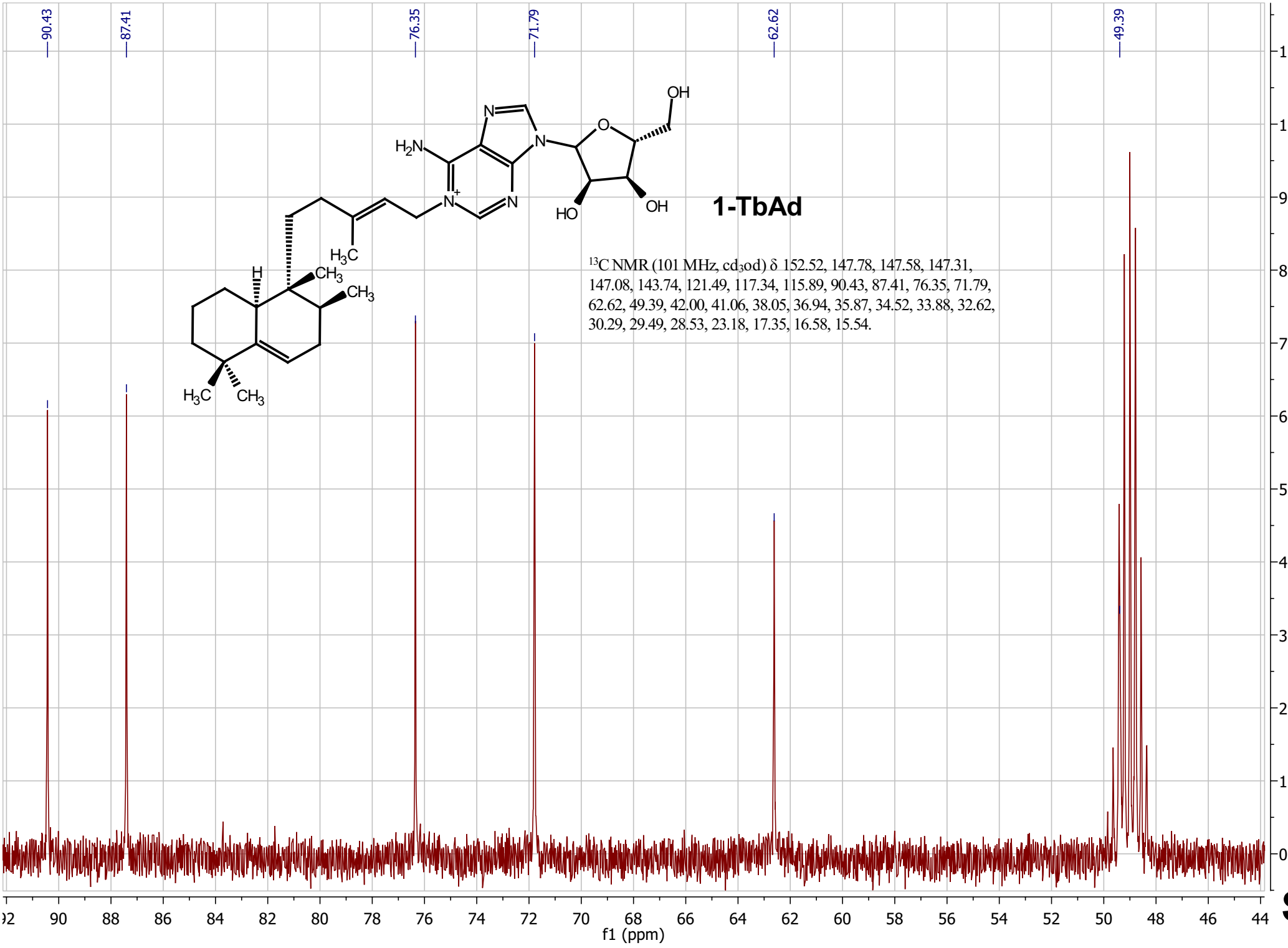


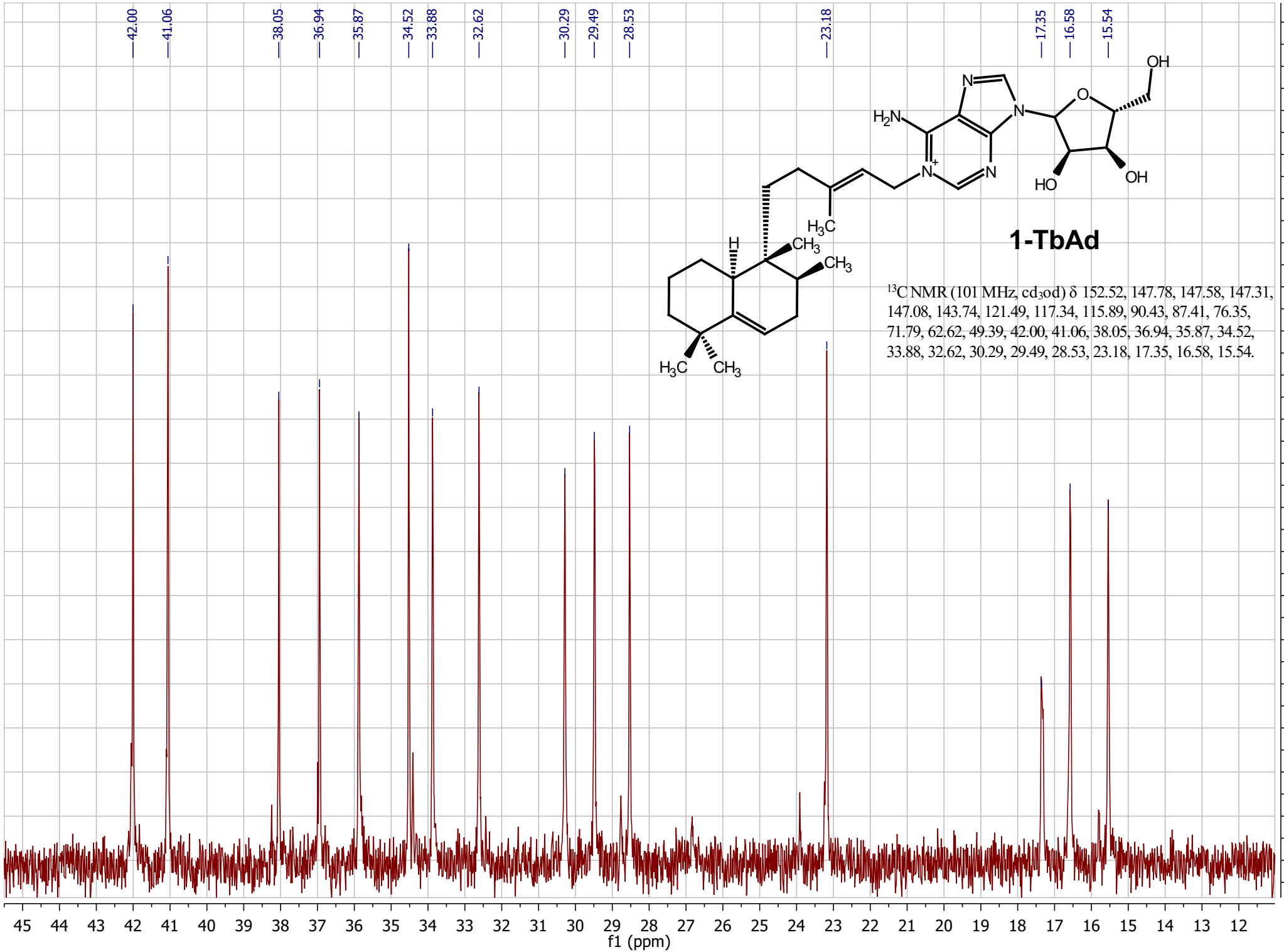
1-TbAd

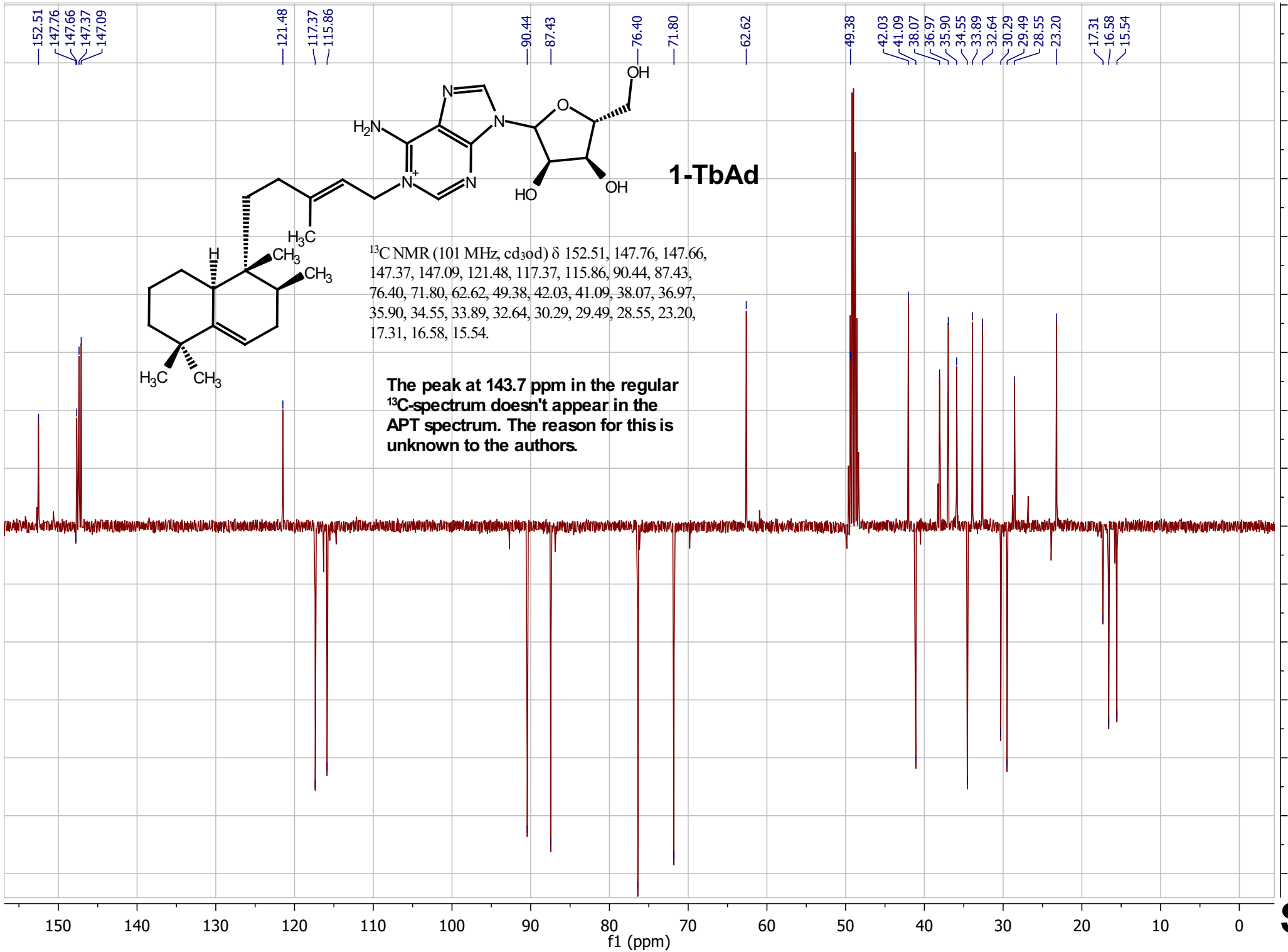
^{1}H NMR (400 MHz, Methanol-d_4) δ 8.62 (s, 1H), 8.49 (s, 1H), 6.08 (d, J = 5.2 Hz, 1H), 5.51 – 5.42 (m, 2H), 4.91 (d, J = 6.6 Hz, 2H), 4.62 (t, J = 5.1 Hz, 2H), 4.58 (s, 1H), 4.38 – 4.31 (m, 2H), 4.15 (q, J = 3.3 Hz, 1H), 3.87 (dd, J = 12.3, 2.9 Hz, 1H), 3.77 (dd, J = 12.2, 3.4 Hz, 1H), 2.23 (d, J = 12.1 Hz, 2H), 2.12 – 2.04 (m, 2H), 1.89 (s, 3H), 1.87 – 1.82 (m, 1H), 1.84 – 1.71 (m, 2H), 1.65 – 1.47 (m, 5H), 1.47 – 1.36 (m, 3H), 1.21 (ddd, J = 12.7, 5.7 Hz, 1H), 1.06 (s, 3H), 1.01 (s, 3H), 0.85 (d, J = 6.7 Hz, 3H), 0.66 (s, 3H).


152.52
147.78
147.58
147.31
147.08
143.74
121.49
117.34
115.89
90.43
87.41
76.35
71.79
62.62
49.39
42.00
41.06
38.05
36.94
35.87
34.52
33.88
32.62
30.29
29.49
28.53
23.18
17.35
16.58
15.54
1-TbAd
OH
N
O
N
H2N
N+
N
HO
OH
H3C
H
CH3
CH3
H3C
CH3
13C NMR (101 MHz, cd3od) δ 152.52, 147.78, 147.58, 147.31,
147.08, 143.74, 121.49, 117.34, 115.89, 90.43, 87.41, 76.35, 71.79,
62.62, 49.39, 42.00, 41.06, 38.05, 36.94, 35.87, 34.52, 33.88, 32.62,
30.29, 29.49, 28.53, 23.18, 17.35, 16.58, 15.54.
11
10
9
8
7
6
5
4
3
2
1
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

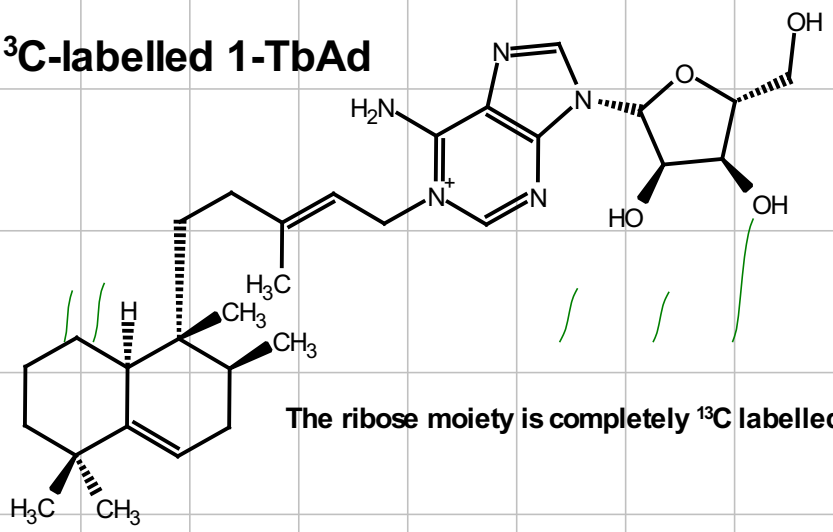

152.52
147.78
147.58
147.31
147.08
143.74
121.49
117.34
115.89
OH
N
O
N
H_2N
N
HO
OH
N
H_3C
H
CH_3
CH_3
H_3C
CH_3
1-TbAd
^{13}C NMR (101 MHz, cd$_3$od) δ 152.52, 147.78, 147.58, 147.31, 147.08, 143.74, 121.49, 117.34, 115.89, 90.43, 87.41, 76.35, 71.79, 62.62, 49.39, 42.00, 41.06, 38.05, 36.94, 35.87, 34.52, 33.88, 32.62, 30.29, 29.49, 28.53, 23.18, 17.35, 16.58, 15.54.
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
f1 (ppm)


90.43
87.41
76.35
71.79
62.62
49.39
OH
N
O
N
H_2N
N
N
HO
OH
H_3C
H
CH_3
CH_3
H_3C
CH_3
1-TbAd
^{13}C NMR (101 MHz, cd_3od) δ 152.52, 147.78, 147.58, 147.31, 147.08, 143.74, 121.49, 117.34, 115.89, 90.43, 87.41, 76.35, 71.79, 62.62, 49.39, 42.00, 41.06, 38.05, 36.94, 35.87, 34.52, 33.88, 32.62, 30.29, 29.49, 28.53, 23.18, 17.35, 16.58, 15.54.
f1 (ppm)


42.00
41.06
38.05
36.94
35.87
34.52
33.88
32.62
30.29
29.49
28.53
23.18
17.35
16.58
15.54
OH
N
N
O
H_2N
N
N
HO
OH
H_3C
H
CH_3
CH_3
H_3C
CH_3
1-TbAd
^{13}C NMR (101 MHz, cd$_3$od) δ 152.52, 147.78, 147.58, 147.31, 147.08, 143.74, 121.49, 117.34, 115.89, 90.43, 87.41, 76.35, 71.79, 62.62, 49.39, 42.00, 41.06, 38.05, 36.94, 35.87, 34.52, 33.88, 32.62, 30.29, 29.49, 28.53, 23.18, 17.35, 16.58, 15.54.
f1 (ppm)


152.51
147.76
147.66
147.37
147.09
121.48
117.37
115.86
90.44
87.43
76.40
71.80
62.62
49.38
42.03
41.09
38.07
36.97
35.90
34.55
33.89
32.64
30.29
29.49
28.55
23.20
17.31
16.58
15.54
1-TbAd
13C NMR (101 MHz, cd3od) δ 152.51, 147.76, 147.66, 147.37, 147.09, 121.48, 117.37, 115.86, 90.44, 87.43, 76.40, 71.80, 62.62, 49.38, 42.03, 41.09, 38.07, 36.97, 35.90, 34.55, 33.89, 32.64, 30.29, 29.49, 28.55, 23.20, 17.31, 16.58, 15.54.
The peak at 143.7 ppm in the regular 13C-spectrum doesn't appear in the APT spectrum. The reason for this is unknown to the authors.
f1 (ppm)

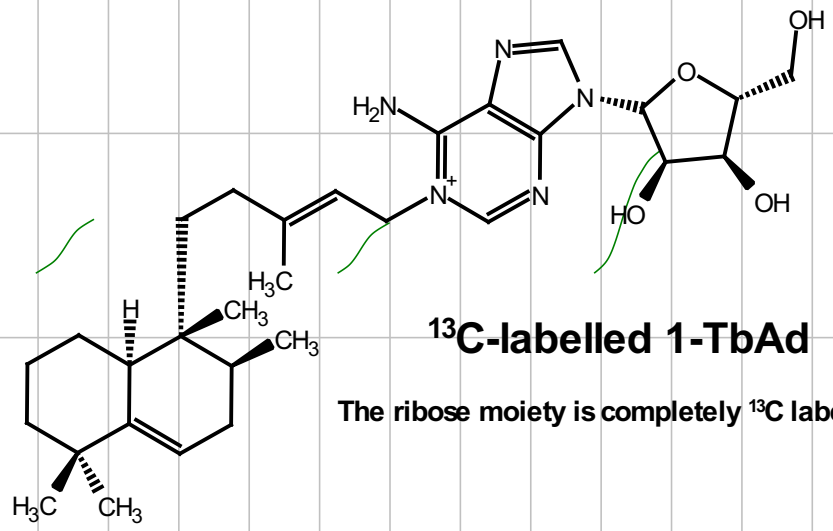
^{13}C-labelled 1-TbAd



The ribose moiety is completely ^{13}C labelled!

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.56 (s, 1H), 8.42 (s, 1H), 6.26 (s, 1H), 5.84 (s, 1H), 5.52 – 5.40 (m, 2H), 4.58 (s, 1H), 4.51 (s, 1H), 4.42 (s, 1H), 4.33 (s, 1H), 4.14 (s, 1H), 4.04 (d, J = 11.4 Hz, 1H), 3.94 (d, J = 9.7 Hz, 1H), 3.77 – 3.63 (m, 1H), 3.59 (d, J = 12.0 Hz, 1H), 2.22 (d, J = 13.3 Hz, 2H), 2.07 (t, J = 8.3 Hz, 2H), 1.88 (s, 3H), 1.86 – 1.70 (m, 3H), 1.65 – 1.47 (m, 4H), 1.47 – 1.35 (m, 2H), 1.21 (td, J = 12.4, 5.5 Hz, 1H), 1.06 (s, 3H), 1.01 (s, 3H), 0.84 (d, J = 6.7 Hz, 3H), 0.65 (s, 3H).

The allylic CH_2 (d, 2H) is missing from the ^{1}H-NMR spectrum. This signal most likely overlaps with the H_2O peak.

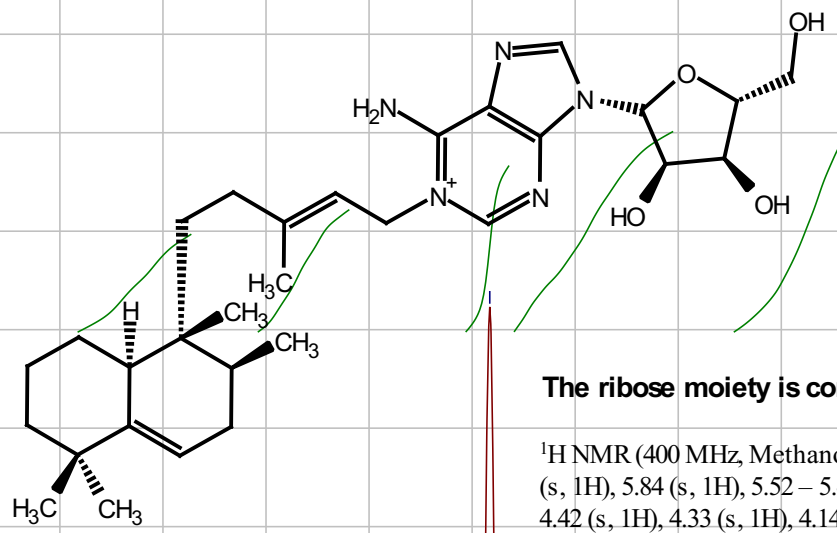


^{13}C-labelled 1-TbAd

The ribose moiety is completely ^{13}C labelled!

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.56 (s, 1H), 8.42 (s, 1H), 6.26 (s, 1H), 5.84 (s, 1H), 5.52 – 5.40 (m, 2H), 4.58 (s, 1H), 4.51 (s, 1H), 4.42 (s, 1H), 4.33 (s, 1H), 4.14 (s, 1H), 4.04 (d, J = 11.4 Hz, 1H), 3.94 (d, J = 9.7 Hz, 1H), 3.77 – 3.63 (m, 1H), 3.59 (d, J = 12.0 Hz, 1H), 2.22 (d, J = 13.3 Hz, 2H), 2.07 (t, J = 8.3 Hz, 2H), 1.88 (s, 3H), 1.86 – 1.70 (m, 3H), 1.65 – 1.47 (m, 4H), 1.47 – 1.35 (m, 2H), 1.21 (td, J = 12.4, 5.5 Hz, 1H), 1.06 (s, 3H), 1.01 (s, 3H), 0.84 (d, J = 6.7 Hz, 3H), 0.65 (s, 3H).

The allylic CH_2 (d, 2H) is missing from the ^{1}H-NMR spectrum. This signal most likely overlaps with the H_2O peak.

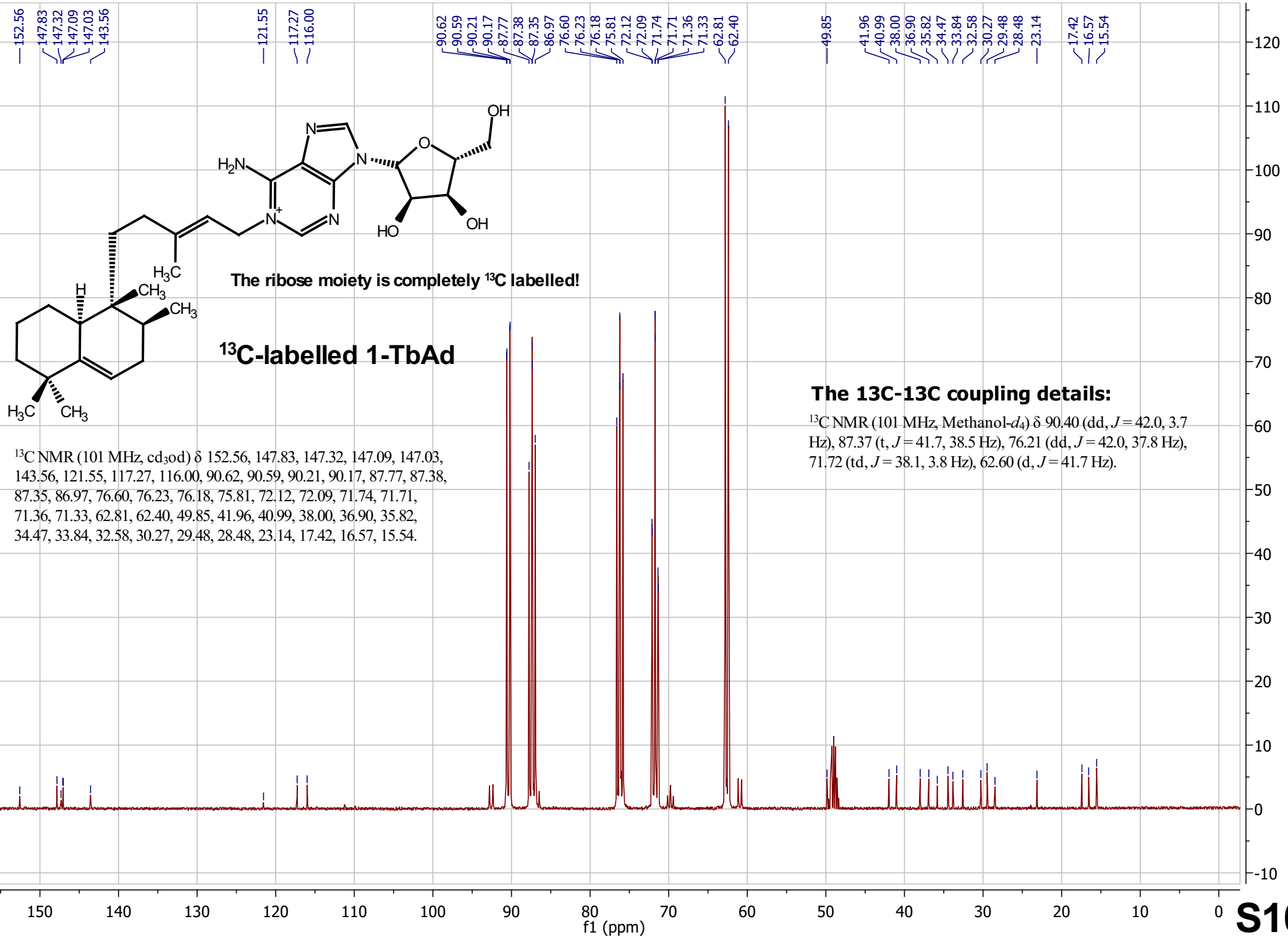


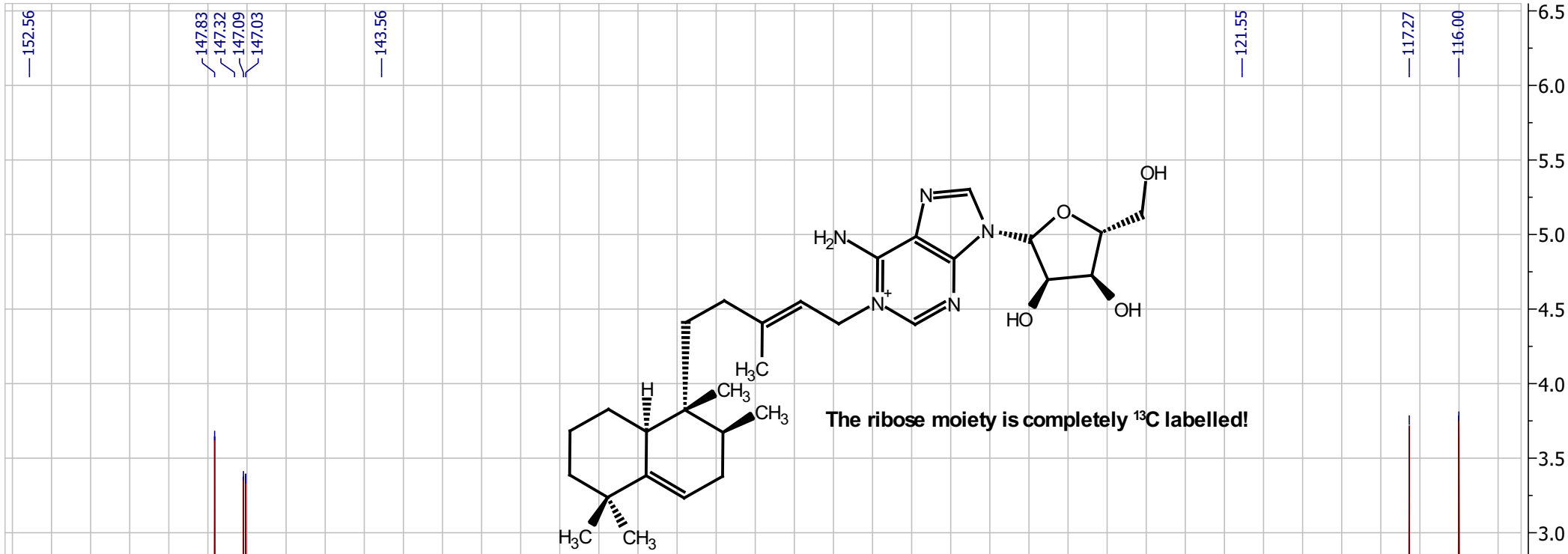
^{13}C-labelled 1-TbAd

The ribose moiety is completely ^{13}C labelled!

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.56 (s, 1H), 8.42 (s, 1H), 6.26 (s, 1H), 5.84 (s, 1H), 5.52 – 5.40 (m, 2H), 4.58 (s, 1H), 4.51 (s, 1H), 4.42 (s, 1H), 4.33 (s, 1H), 4.14 (s, 1H), 4.04 (d, J = 11.4 Hz, 1H), 3.94 (d, J = 9.7 Hz, 1H), 3.77 – 3.63 (m, 1H), 3.59 (d, J = 12.0 Hz, 1H), 2.22 (d, J = 13.3 Hz, 2H), 2.07 (t, J = 8.3 Hz, 2H), 1.88 (s, 3H), 1.86 – 1.70 (m, 3H), 1.65 – 1.47 (m, 4H), 1.47 – 1.35 (m, 2H), 1.21 (td, J = 12.4, 5.5 Hz, 1H), 1.06 (s, 3H), 1.01 (s, 3H), 0.84 (d, J = 6.7 Hz, 3H), 0.65 (s, 3H).

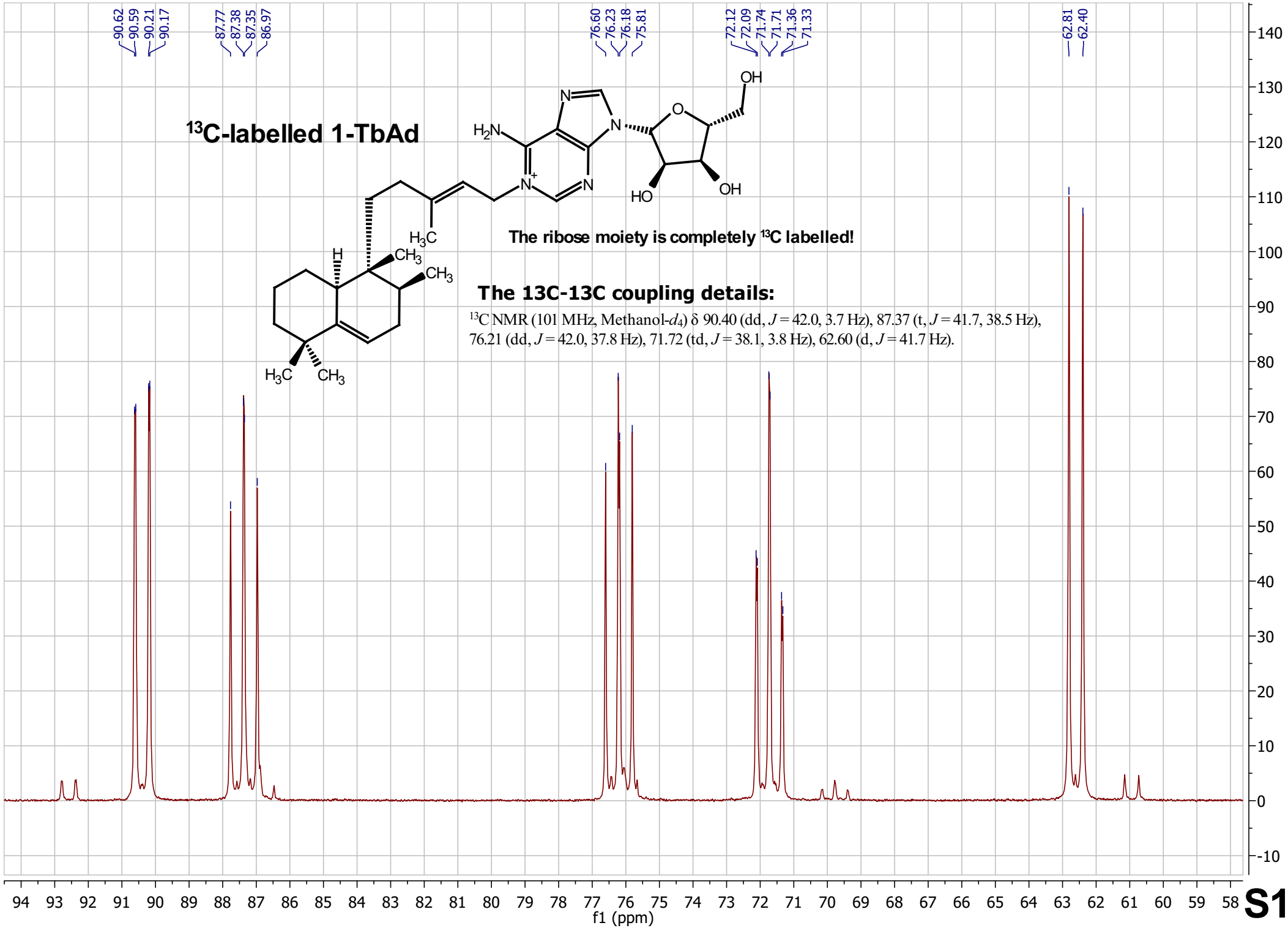
The allylic CH_2 (d, 2H) is missing from the ^{1}H-NMR spectrum. This signal most likely overlaps with the H_2O peak.

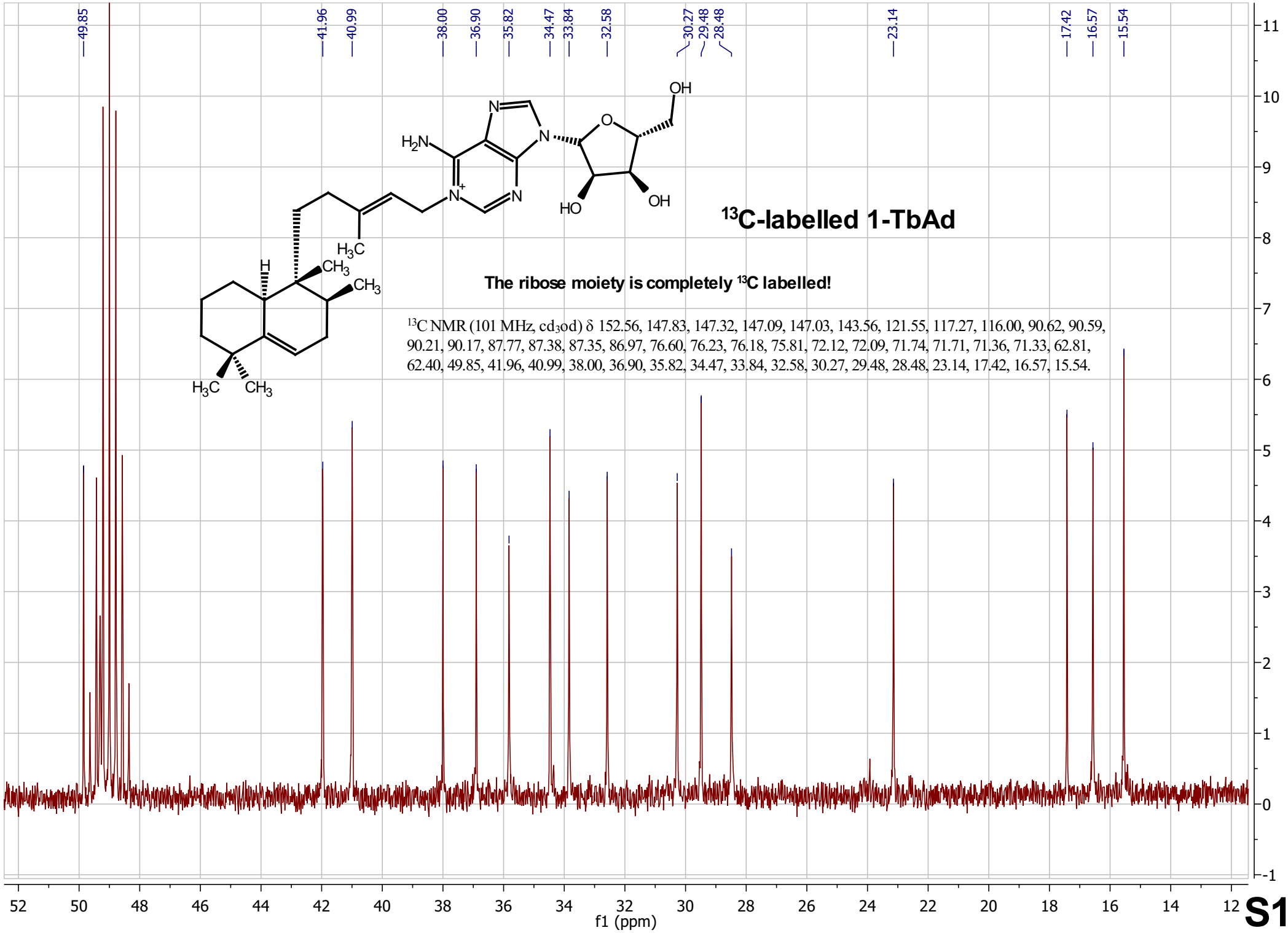

152.56
147.83
147.32
147.09
147.03
143.56
121.55
117.27
116.00
90.62
90.59
90.21
90.17
87.77
87.38
87.35
86.97
76.60
76.23
76.18
75.81
72.12
72.09
71.74
71.71
71.36
71.33
62.81
62.40
49.85
41.96
40.99
38.00
36.90
35.82
34.47
33.84
32.58
30.27
29.48
28.48
23.14
17.42
16.57
15.54
OH
N
O
N
H_2N
N
N
HO
OH
H_3C
H
CH_3
CH_3
H_3C
CH_3
The ribose moiety is completely ^{13}C labelled!
^{13}C-labelled 1-TbAd
^{13}C NMR (101 MHz, cd_3od) δ 152.56, 147.83, 147.32, 147.09, 147.03, 143.56, 121.55, 117.27, 116.00, 90.62, 90.59, 90.21, 90.17, 87.77, 87.38, 87.35, 86.97, 76.60, 76.23, 76.18, 75.81, 72.12, 72.09, 71.74, 71.71, 71.36, 71.33, 62.81, 62.40, 49.85, 41.96, 40.99, 38.00, 36.90, 35.82, 34.47, 33.84, 32.58, 30.27, 29.48, 28.48, 23.14, 17.42, 16.57, 15.54.
The 13C-13C coupling details:
^{13}C NMR (101 MHz, Methanol-d_4) δ 90.40 (dd, J = 42.0, 3.7 Hz), 87.37 (t, J = 41.7, 38.5 Hz), 76.21 (dd, J = 42.0, 37.8 Hz), 71.72 (td, J = 38.1, 3.8 Hz), 62.60 (d, J = 41.7 Hz).
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

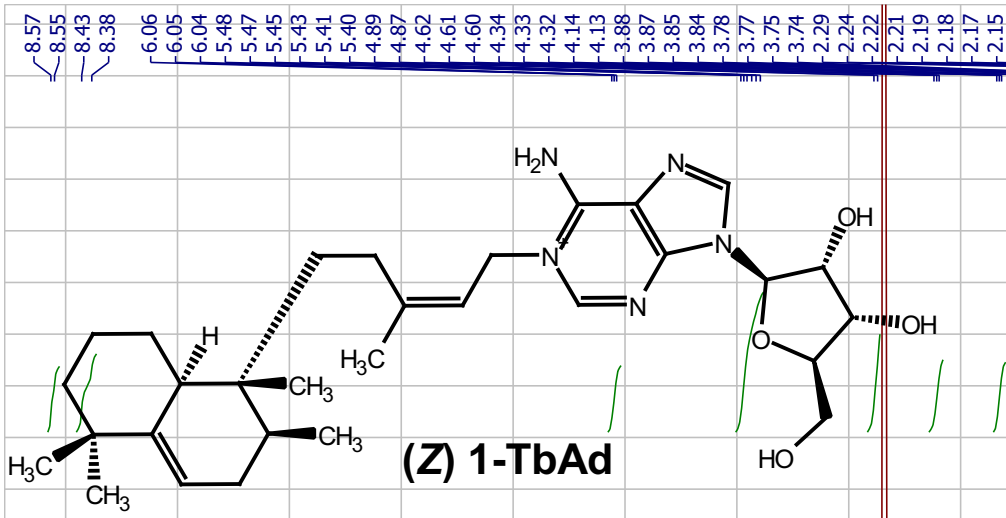


^{13}C NMR (101 MHz, cd_3od) δ 152.56, 147.83, 147.32, 147.09, 147.03, 143.56, 121.55, 117.27, 116.00, 90.62, 90.59, 90.21, 90.17, 87.77, 87.38, 87.35, 86.97, 76.60, 76.23, 76.18, 75.81, 72.12, 72.09, 71.74, 71.71, 71.36, 71.33, 62.81, 62.40, 49.85, 41.96, 40.99, 38.00, 36.90, 35.82, 34.47, 33.84, 32.58, 30.27, 29.48, 28.48, 23.14, 17.42, 16.57, 15.54.

f1 (ppm)

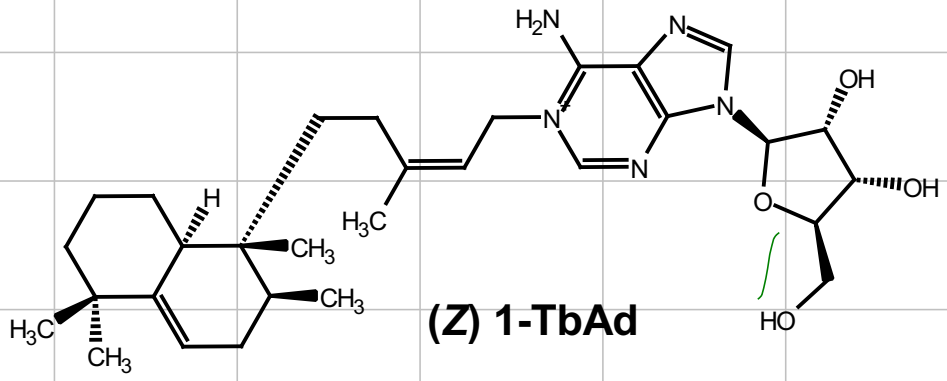

90.62
90.59
90.21
90.17
87.77
87.38
87.35
86.97
76.60
76.23
76.18
75.81
72.12
72.09
71.74
71.71
71.36
71.33
62.81
62.40
13C-labelled 1-TbAd
The ribose moiety is completely 13C labelled!
The 13C-13C coupling details:
13C NMR (101 MHz, Methanol-d4) δ 90.40 (dd, J = 42.0, 3.7 Hz), 87.37 (t, J = 41.7, 38.5 Hz), 76.21 (dd, J = 42.0, 37.8 Hz), 71.72 (td, J = 38.1, 3.8 Hz), 62.60 (d, J = 41.7 Hz).
f1 (ppm)


49.85
41.96
40.99
38.00
36.90
35.82
34.47
33.84
32.58
30.27
29.48
28.48
23.14
17.42
16.57
15.54
OH
N
O
N
H_2N
N+
N
HO
OH
H_3C
H
CH_3
CH_3
H_3C
CH_3
13C-labelled 1-TbAd
The ribose moiety is completely 13C labelled!
13C NMR (101 MHz, cd3od) δ 152.56, 147.83, 147.32, 147.09, 147.03, 143.56, 121.55, 117.27, 116.00, 90.62, 90.59, 90.21, 90.17, 87.77, 87.38, 87.35, 86.97, 76.60, 76.23, 76.18, 75.81, 72.12, 72.09, 71.74, 71.71, 71.36, 71.33, 62.81, 62.40, 49.85, 41.96, 40.99, 38.00, 36.90, 35.82, 34.47, 33.84, 32.58, 30.27, 29.48, 28.48, 23.14, 17.42, 16.57, 15.54.
f1 (ppm)



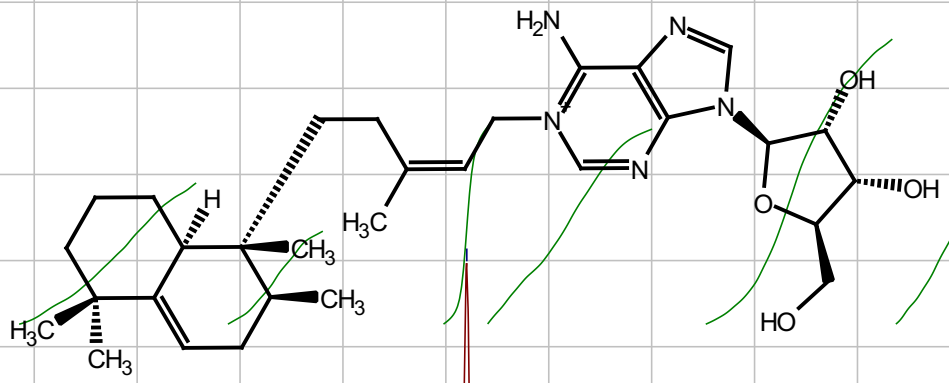
(*Z*) 1-TbAd

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.56 (d, J = 6.5 Hz, 2H), 8.41 (d, J = 18.0 Hz, 1H), 6.09 – 6.02 (m, 1H), 5.44 (dt, J = 23.8, 6.5 Hz, 2H), 4.88 (d, J = 6.6 Hz, 2H), 4.61 (t, J = 4.6 Hz, 1H), 4.33 (t, J = 4.3 Hz, 1H), 4.14 (d, J = 3.1 Hz, 1H), 3.91 – 3.82 (m, 1H), 3.76 (dd, J = 12.8, 2.5 Hz, 1H), 2.32 – 2.14 (m, 2H), 2.07 (t, J = 8.2 Hz, 1H), 1.88 (s, 3H), 1.85 – 1.71 (m, 3H), 1.65 – 1.47 (m, 5H), 1.43 (dd, J = 14.6, 8.6 Hz, 2H), 1.22 (dd, J = 12.4, 6.2 Hz, 1H), 1.06 (s, 3H), 1.02 (d, J = 10.1 Hz, 3H), 0.86 (dd, J = 19.7, 6.8 Hz, 3H), 0.66 (d, J = 10.9 Hz, 3H).



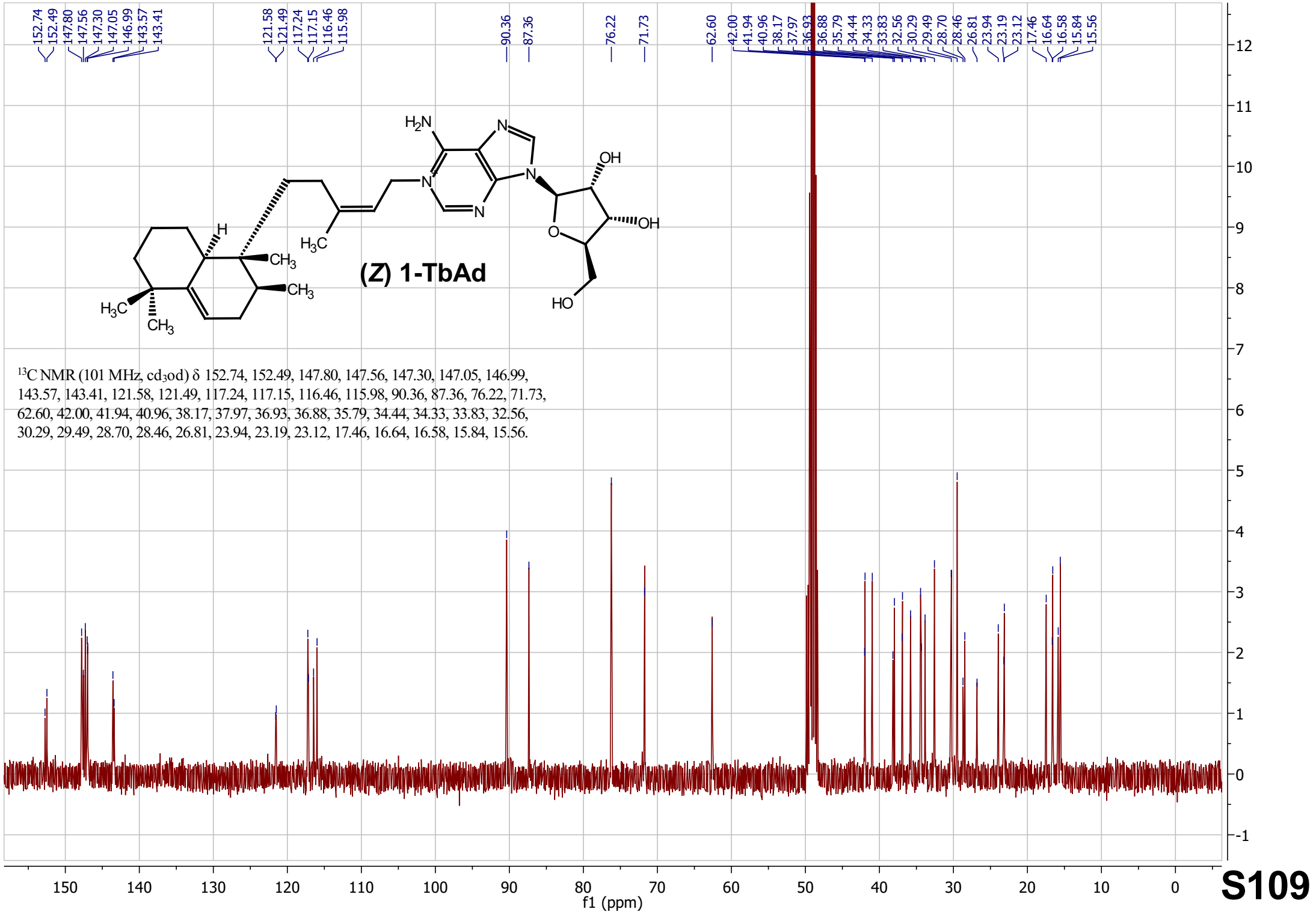
(*Z*) 1-TbAd

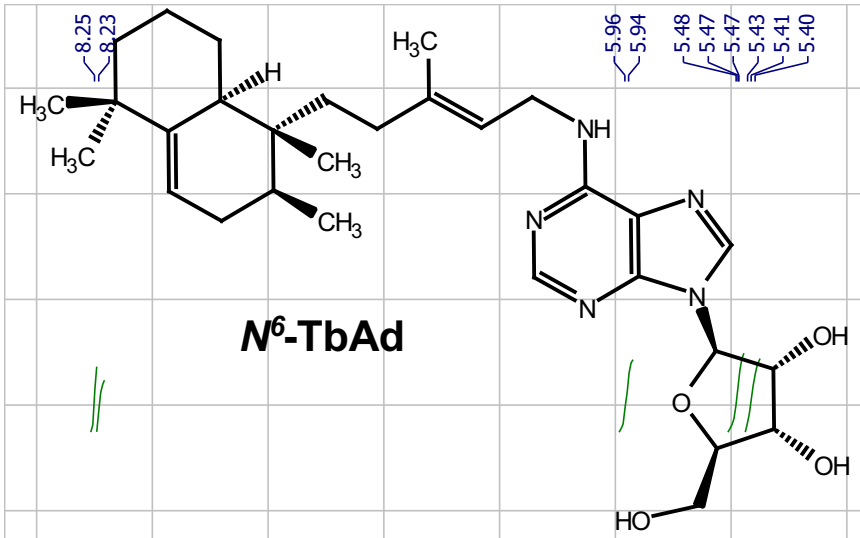
^{1}H NMR (400 MHz, Methanol-d_4) δ 8.56 (d, J = 6.5 Hz, 2H), 8.41 (d, J = 18.0 Hz, 1H), 6.09 – 6.02 (m, 1H), 5.44 (dt, J = 23.8, 6.5 Hz, 2H), 4.88 (d, J = 6.6 Hz, 2H), 4.61 (t, J = 4.6 Hz, 1H), 4.33 (t, J = 4.3 Hz, 1H), 4.14 (d, J = 3.1 Hz, 1H), 3.91 – 3.82 (m, 1H), 3.76 (dd, J = 12.8, 2.5 Hz, 1H), 2.32 – 2.14 (m, 2H), 2.07 (t, J = 8.2 Hz, 1H), 1.88 (s, 3H), 1.85 – 1.71 (m, 3H), 1.65 – 1.47 (m, 5H), 1.43 (dd, J = 14.6, 8.6 Hz, 2H), 1.22 (dd, J = 12.4, 6.2 Hz, 1H), 1.06 (s, 3H), 1.02 (d, J = 10.1 Hz, 3H), 0.86 (dd, J = 19.7, 6.8 Hz, 3H), 0.66 (d, J = 10.9 Hz, 3H).



(*Z*) 1-TbAd

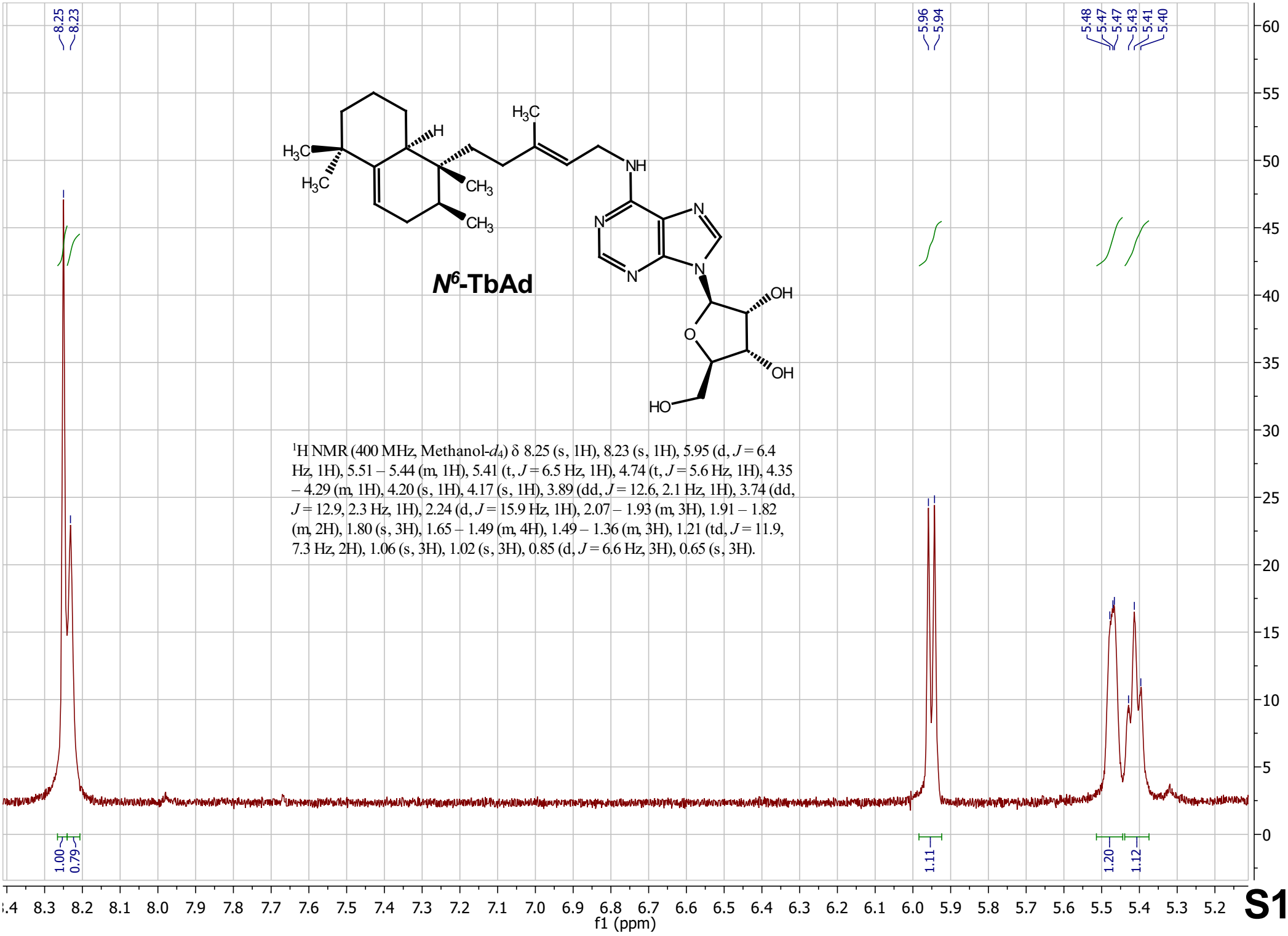
^{1}H NMR (400 MHz, Methanol-d_4) δ 8.56 (d, J = 6.5 Hz, 2H), 8.41 (d, J = 18.0 Hz, 1H), 6.09 – 6.02 (m, 1H), 5.44 (dt, J = 23.8, 6.5 Hz, 2H), 4.88 (d, J = 6.6 Hz, 2H), 4.61 (t, J = 4.6 Hz, 1H), 4.33 (t, J = 4.3 Hz, 1H), 4.14 (d, J = 3.1 Hz, 1H), 3.91 – 3.82 (m, 1H), 3.76 (dd, J = 12.8, 2.5 Hz, 1H), 2.32 – 2.14 (m, 2H), 2.07 (t, J = 8.2 Hz, 1H), 1.88 (s, 3H), 1.85 – 1.71 (m, 3H), 1.65 – 1.47 (m, 5H), 1.43 (dd, J = 14.6, 8.6 Hz, 2H), 1.22 (dd, J = 12.4, 6.2 Hz, 1H), 1.06 (s, 3H), 1.02 (d, J = 10.1 Hz, 3H), 0.86 (dd, J = 19.7, 6.8 Hz, 3H), 0.66 (d, J = 10.9 Hz, 3H).


152.74
152.49
147.80
147.56
147.30
147.05
146.99
143.57
143.41
121.58
121.49
117.24
117.15
116.46
115.98
90.36
87.36
76.22
71.73
62.60
42.00
41.94
40.96
38.17
37.97
36.93
36.88
35.79
34.44
34.33
33.83
32.56
30.29
29.49
28.70
28.46
26.81
23.94
23.19
23.12
17.46
16.64
16.58
15.84
15.56
(Z) 1-TbAd
13C NMR (101 MHz, cd3od) δ 152.74, 152.49, 147.80, 147.56, 147.30, 147.05, 146.99, 143.57, 143.41, 121.58, 121.49, 117.24, 117.15, 116.46, 115.98, 90.36, 87.36, 76.22, 71.73, 62.60, 42.00, 41.94, 40.96, 38.17, 37.97, 36.93, 36.88, 35.79, 34.44, 34.33, 33.83, 32.56, 30.29, 29.49, 28.70, 28.46, 26.81, 23.94, 23.19, 23.12, 17.46, 16.64, 16.58, 15.84, 15.56.
f1 (ppm)



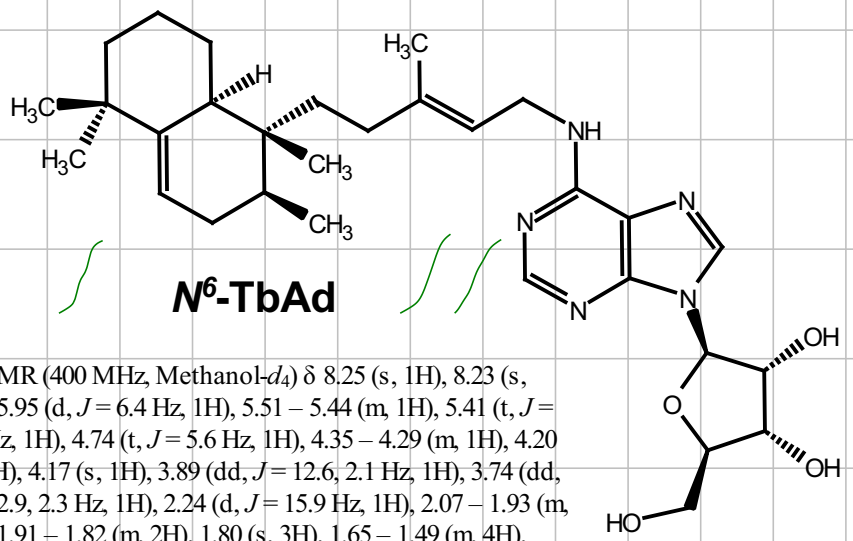
N^6-TbAd

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.25 (s, 1H), 8.23 (s, 1H), 5.95 (d, J = 6.4 Hz, 1H), 5.51 – 5.44 (m, 1H), 5.41 (t, J = 6.5 Hz, 1H), 4.74 (t, J = 5.6 Hz, 1H), 4.35 – 4.29 (m, 1H), 4.20 (s, 1H), 4.17 (s, 1H), 3.89 (dd, J = 12.6, 2.1 Hz, 1H), 3.74 (dd, J = 12.9, 2.3 Hz, 1H), 2.24 (d, J = 15.9 Hz, 1H), 2.07 – 1.93 (m, 3H), 1.91 – 1.82 (m, 2H), 1.80 (s, 3H), 1.65 – 1.49 (m, 4H), 1.49 – 1.36 (m, 3H), 1.21 (td, J = 11.9, 7.3 Hz, 2H), 1.06 (s, 3H), 1.02 (s, 3H), 0.85 (d, J = 6.6 Hz, 3H), 0.65 (s, 3H).



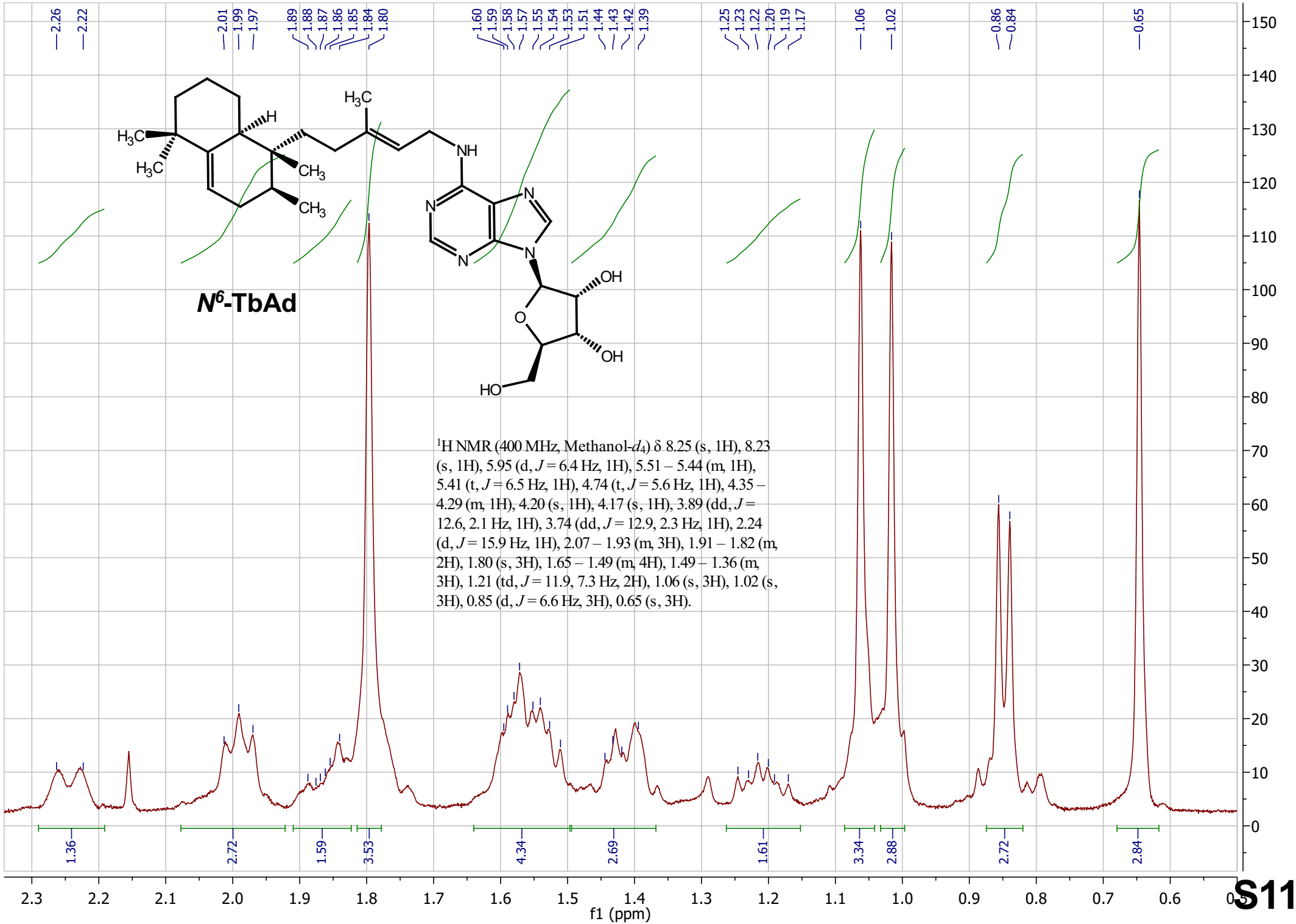
N^6-TbAd

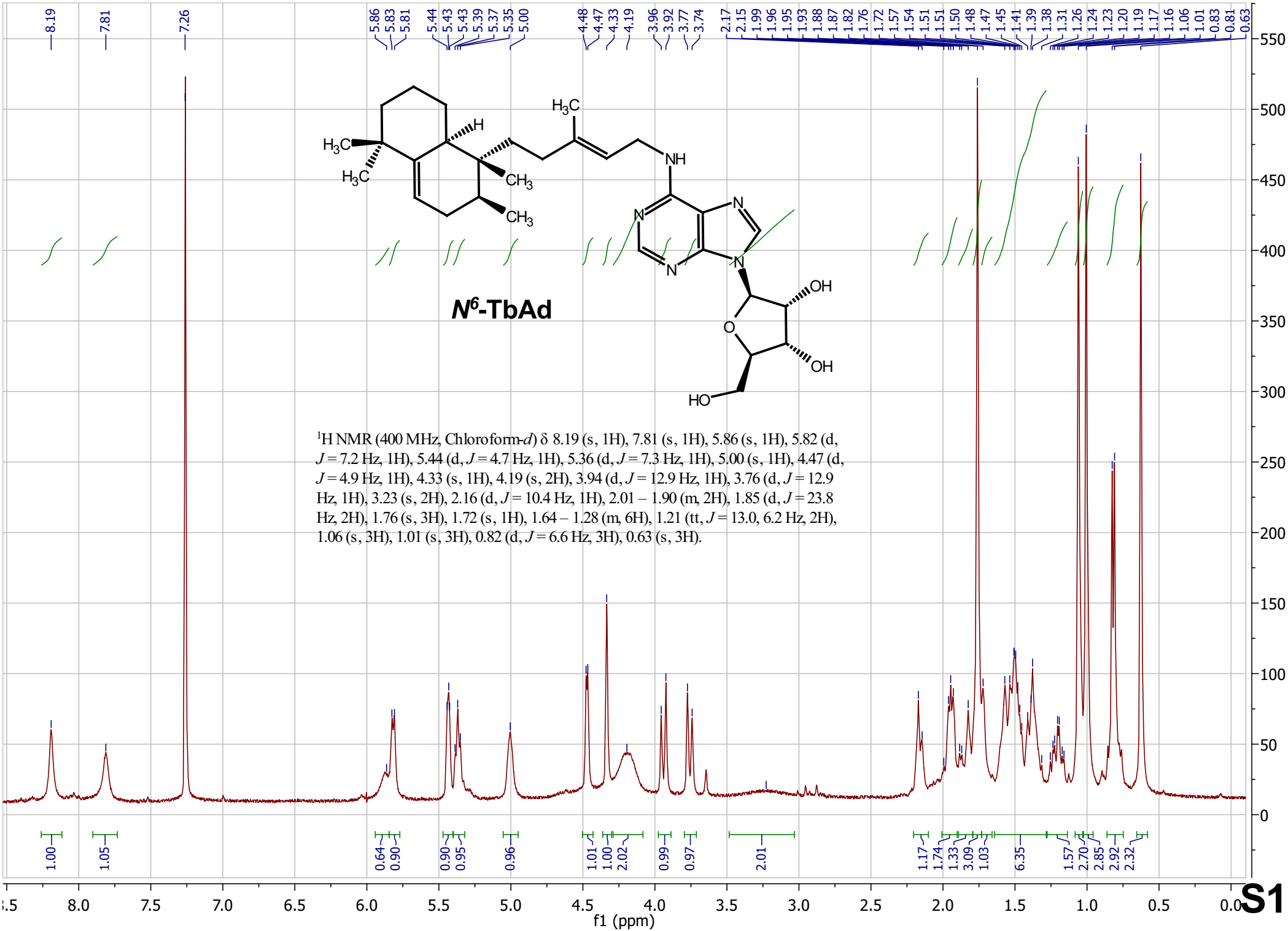
^{1}H NMR (400 MHz, Methanol-d_4) δ 8.25 (s, 1H), 8.23 (s, 1H), 5.95 (d, J = 6.4 Hz, 1H), 5.51 – 5.44 (m, 1H), 5.41 (t, J = 6.5 Hz, 1H), 4.74 (t, J = 5.6 Hz, 1H), 4.35 – 4.29 (m, 1H), 4.20 (s, 1H), 4.17 (s, 1H), 3.89 (dd, J = 12.6, 2.1 Hz, 1H), 3.74 (dd, J = 12.9, 2.3 Hz, 1H), 2.24 (d, J = 15.9 Hz, 1H), 2.07 – 1.93 (m, 3H), 1.91 – 1.82 (m, 2H), 1.80 (s, 3H), 1.65 – 1.49 (m, 4H), 1.49 – 1.36 (m, 3H), 1.21 (td, J = 11.9, 7.3 Hz, 2H), 1.06 (s, 3H), 1.02 (s, 3H), 0.85 (d, J = 6.6 Hz, 3H), 0.65 (s, 3H).



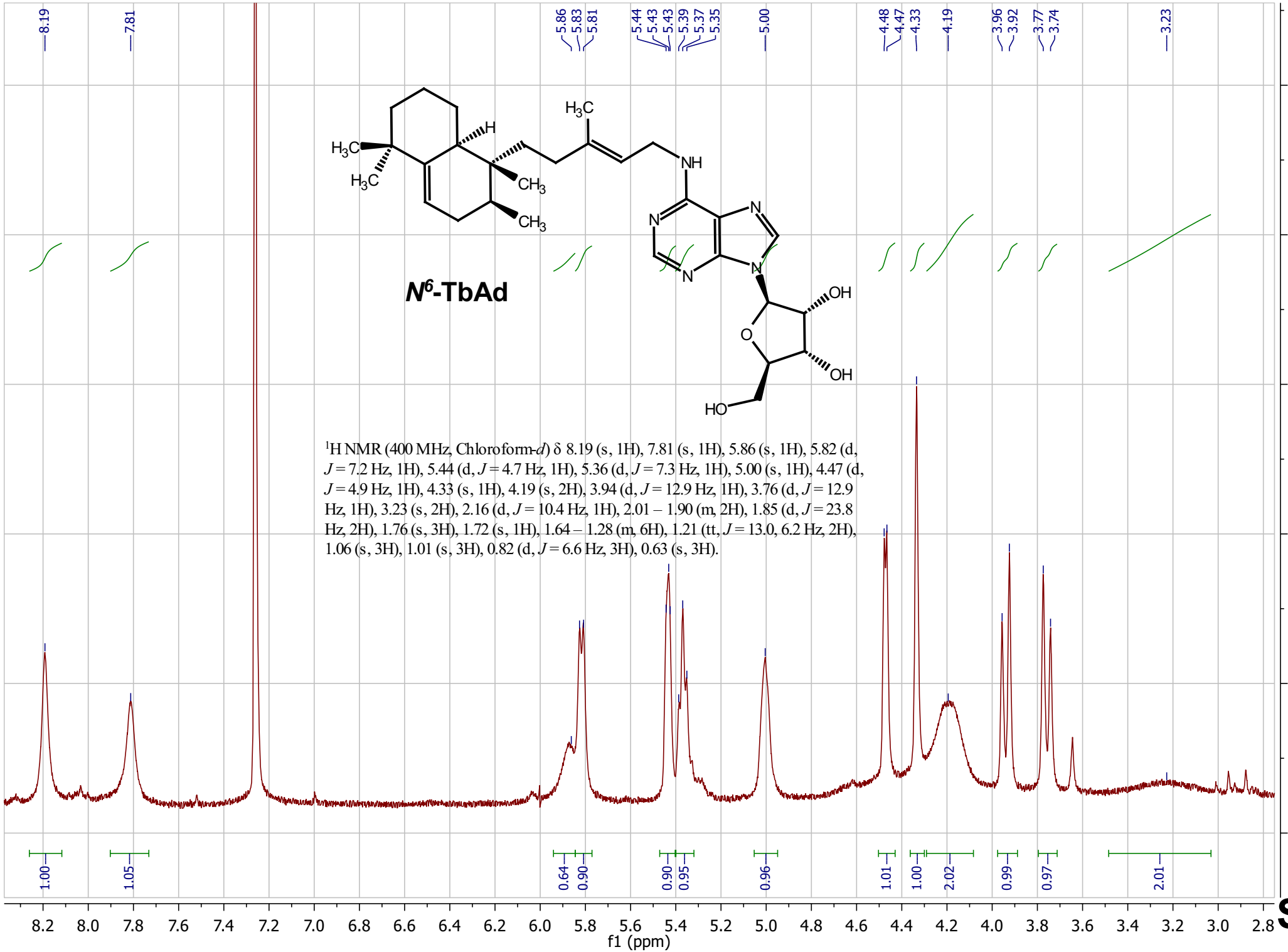
***N*^{6}-TbAd**

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.25 (s, 1H), 8.23 (s, 1H), 5.95 (d, J = 6.4 Hz, 1H), 5.51 – 5.44 (m, 1H), 5.41 (t, J = 6.5 Hz, 1H), 4.74 (t, J = 5.6 Hz, 1H), 4.35 – 4.29 (m, 1H), 4.20 (s, 1H), 4.17 (s, 1H), 3.89 (dd, J = 12.6, 2.1 Hz, 1H), 3.74 (dd, J = 12.9, 2.3 Hz, 1H), 2.24 (d, J = 15.9 Hz, 1H), 2.07 – 1.93 (m, 3H), 1.91 – 1.82 (m, 2H), 1.80 (s, 3H), 1.65 – 1.49 (m, 4H), 1.49 – 1.36 (m, 3H), 1.21 (td, J = 11.9, 7.3 Hz, 2H), 1.06 (s, 3H), 1.02 (s, 3H), 0.85 (d, J = 6.6 Hz, 3H), 0.65 (s, 3H).

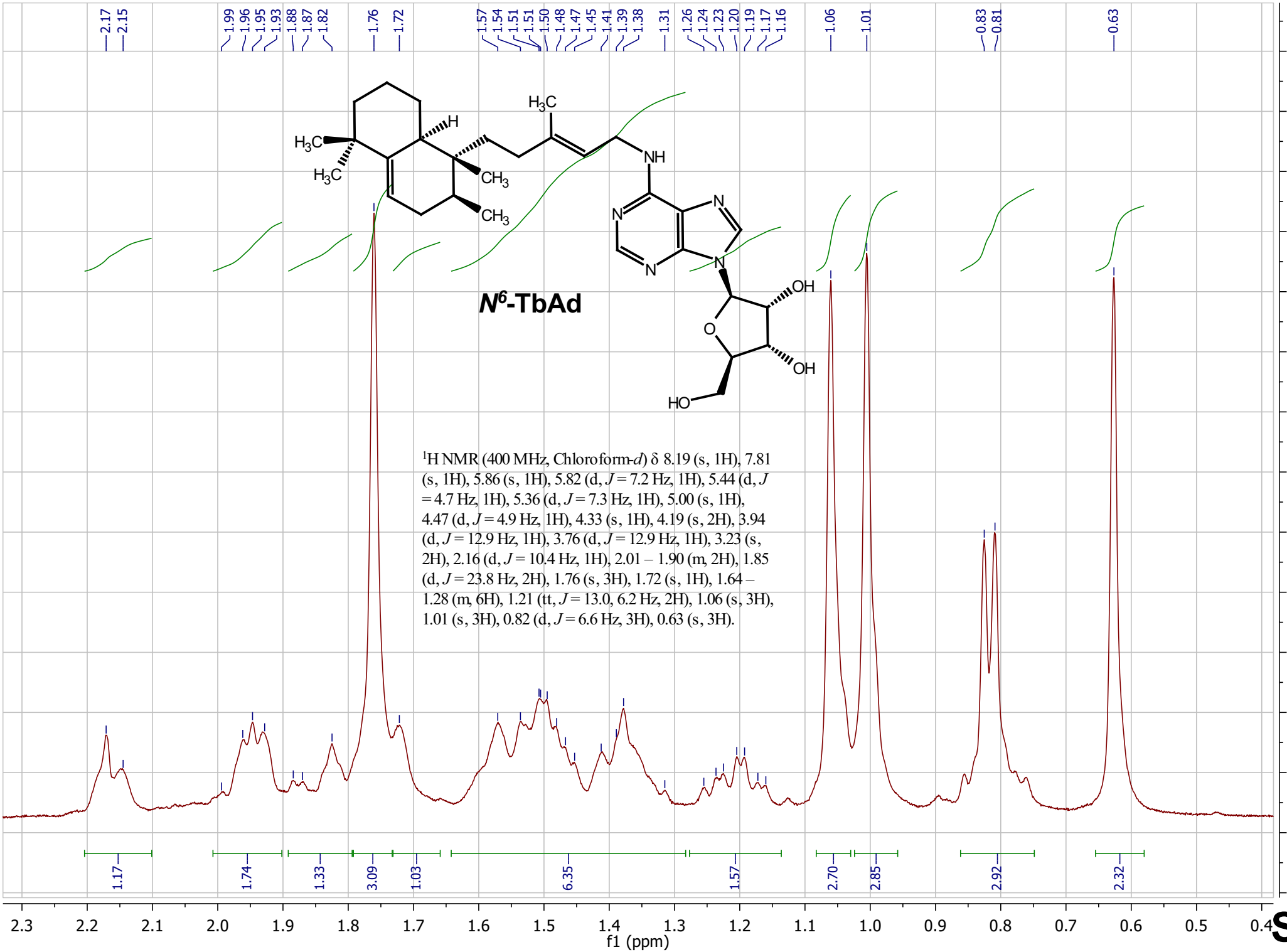

2.26
2.22
2.01
1.99
1.97
1.89
1.88
1.87
1.86
1.85
1.84
1.80
1.60
1.59
1.58
1.57
1.55
1.54
1.53
1.51
1.44
1.43
1.42
1.39
1.25
1.23
1.22
1.20
1.19
1.17
1.06
1.02
0.86
0.84
0.65
H3C
H3C
H
CH3
CH3
H3C
NH
N
N
N
N
OH
O
OH
HO
N6-TbAd
1H NMR (400 MHz, Methanol-d4) δ 8.25 (s, 1H), 8.23 (s, 1H), 5.95 (d, J = 6.4 Hz, 1H), 5.51 – 5.44 (m, 1H), 5.41 (t, J = 6.5 Hz, 1H), 4.74 (t, J = 5.6 Hz, 1H), 4.35 – 4.29 (m, 1H), 4.20 (s, 1H), 4.17 (s, 1H), 3.89 (dd, J = 12.6, 2.1 Hz, 1H), 3.74 (dd, J = 12.9, 2.3 Hz, 1H), 2.24 (d, J = 15.9 Hz, 1H), 2.07 – 1.93 (m, 3H), 1.91 – 1.82 (m, 2H), 1.80 (s, 3H), 1.65 – 1.49 (m, 4H), 1.49 – 1.36 (m, 3H), 1.21 (td, J = 11.9, 7.3 Hz, 2H), 1.06 (s, 3H), 1.02 (s, 3H), 0.85 (d, J = 6.6 Hz, 3H), 0.65 (s, 3H).
1.36
2.72
1.59
3.53
4.34
2.69
1.61
3.34
2.88
2.72
2.84
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
f1 (ppm)

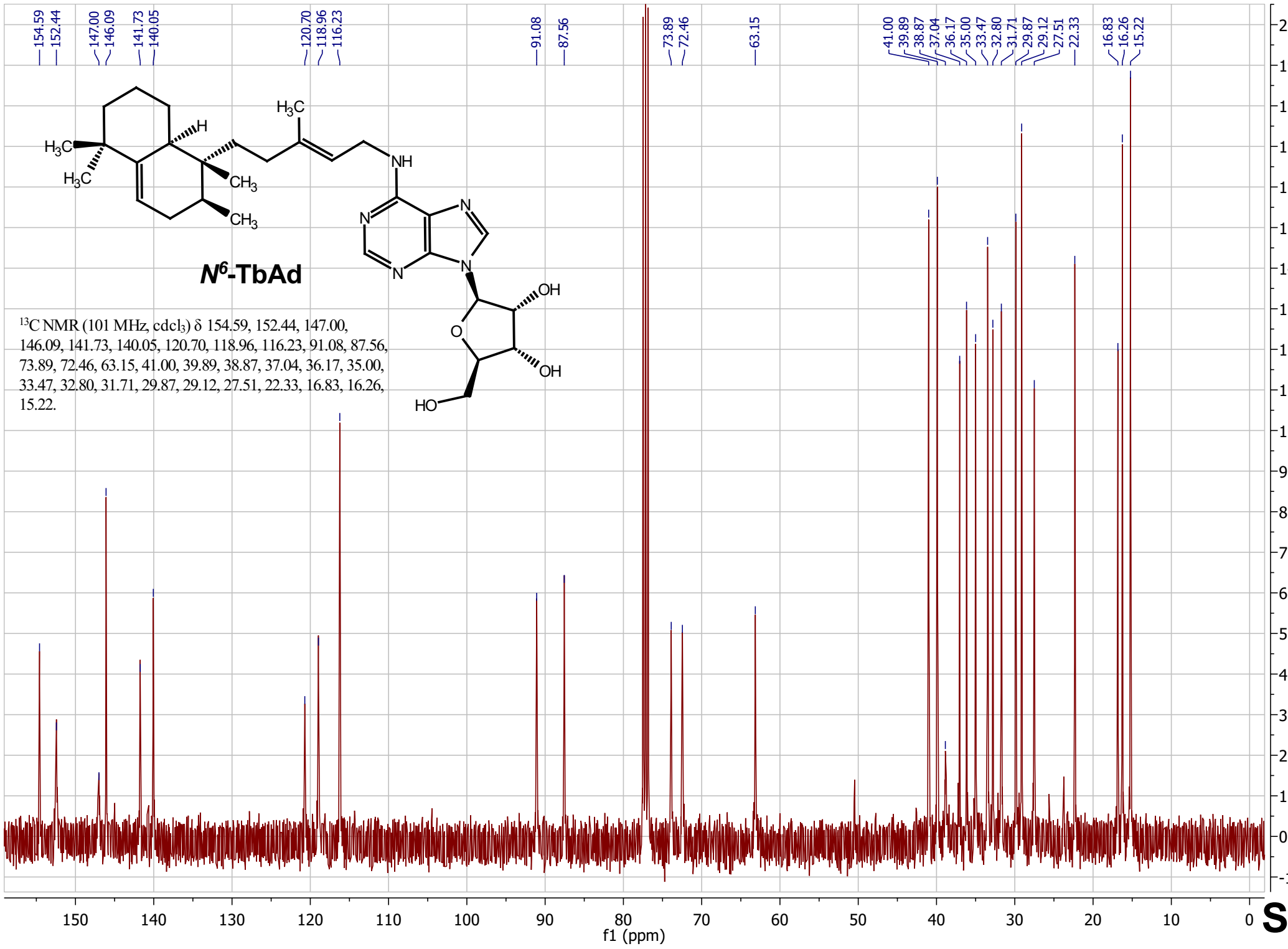


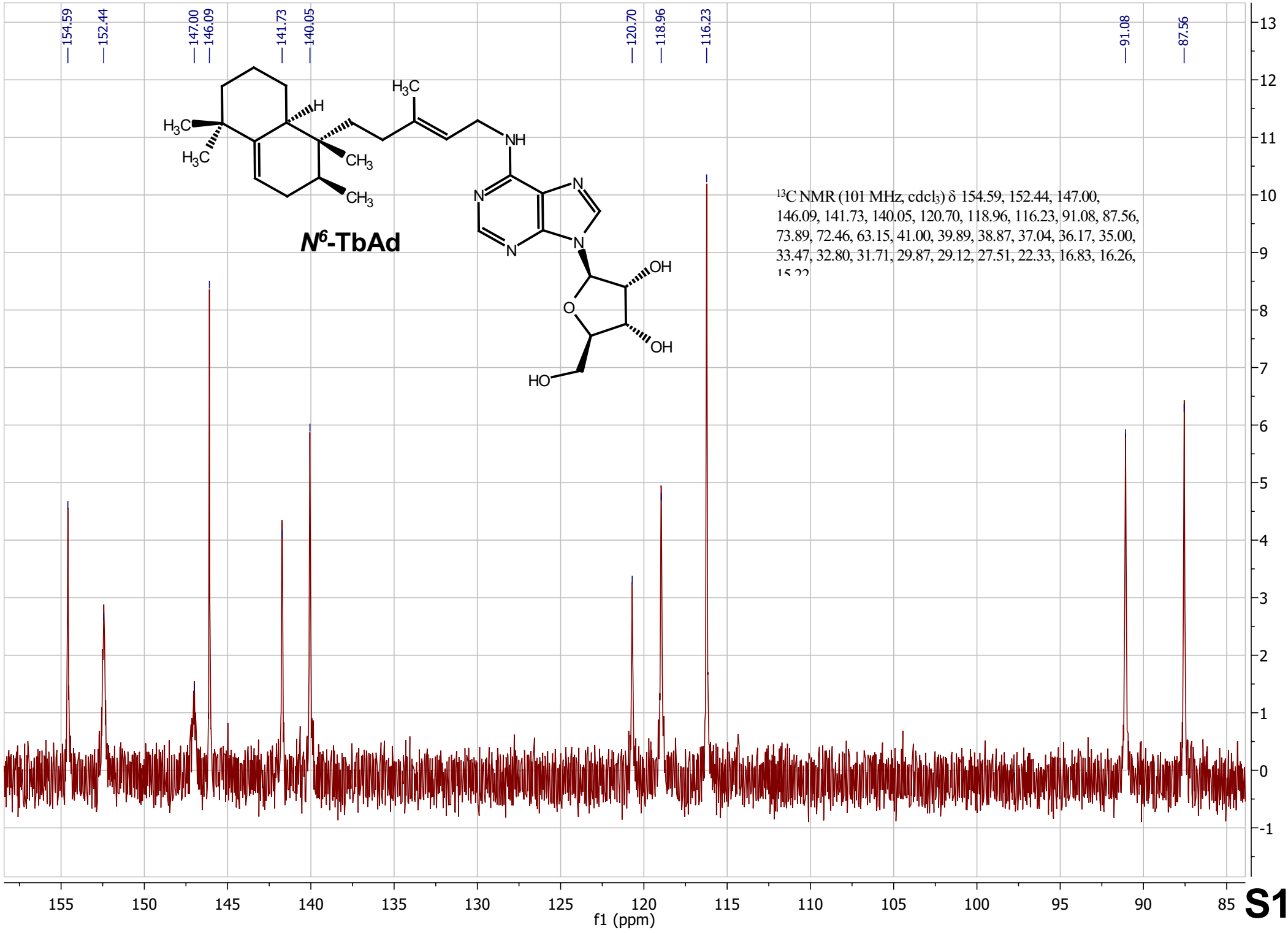
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.81 (s, 1H), 5.86 (s, 1H), 5.82 (d, *J* = 7.2 Hz, 1H), 5.44 (d, *J* = 4.7 Hz, 1H), 5.36 (d, *J* = 7.3 Hz, 1H), 5.00 (s, 1H), 4.47 (d, *J* = 4.9 Hz, 1H), 4.33 (s, 1H), 4.19 (s, 2H), 3.94 (d, *J* = 12.9 Hz, 1H), 3.76 (d, *J* = 12.9 Hz, 1H), 3.23 (s, 2H), 2.16 (d, *J* = 10.4 Hz, 1H), 2.01 – 1.90 (m, 2H), 1.85 (d, *J* = 23.8 Hz, 2H), 1.76 (s, 3H), 1.72 (s, 1H), 1.64 – 1.28 (m, 6H), 1.21 (tt, *J* = 13.0, 6.2 Hz, 2H), 1.06 (s, 3H), 1.01 (s, 3H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.63 (s, 3H).

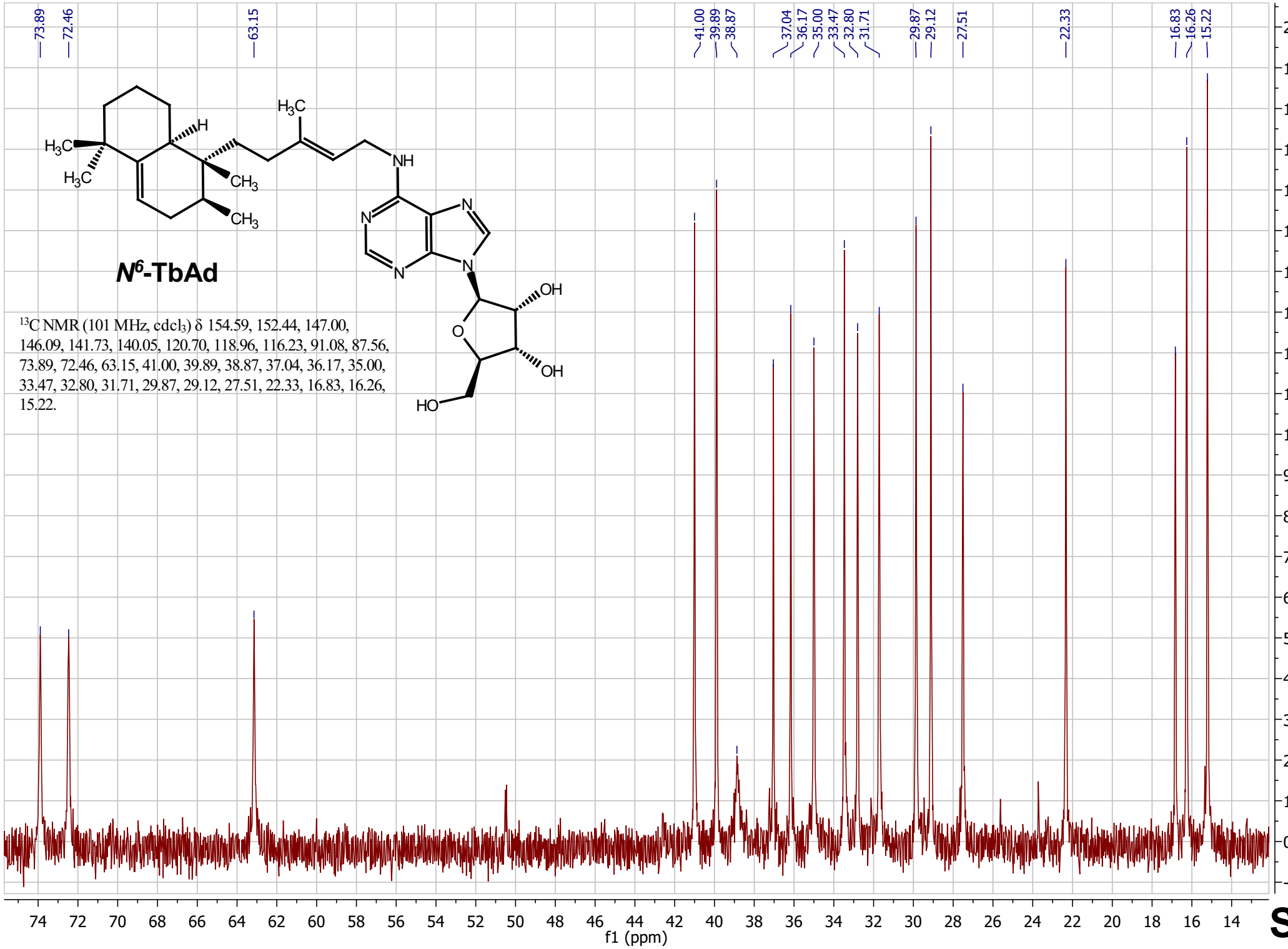


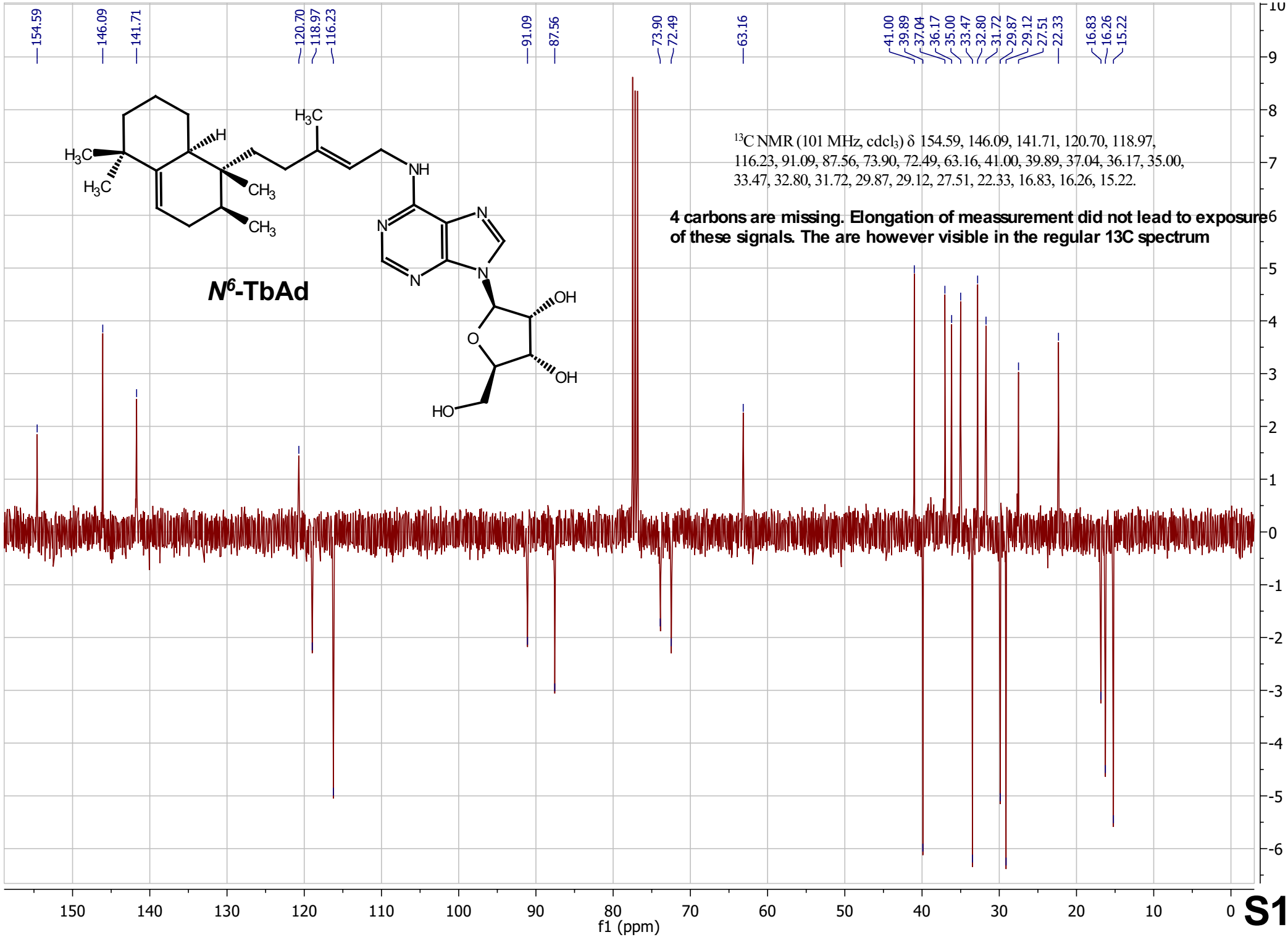
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.81 (s, 1H), 5.86 (s, 1H), 5.82 (d, *J* = 7.2 Hz, 1H), 5.44 (d, *J* = 4.7 Hz, 1H), 5.36 (d, *J* = 7.3 Hz, 1H), 5.00 (s, 1H), 4.47 (d, *J* = 4.9 Hz, 1H), 4.33 (s, 1H), 4.19 (s, 2H), 3.94 (d, *J* = 12.9 Hz, 1H), 3.76 (d, *J* = 12.9 Hz, 1H), 3.23 (s, 2H), 2.16 (d, *J* = 10.4 Hz, 1H), 2.01 – 1.90 (m, 2H), 1.85 (d, *J* = 23.8 Hz, 2H), 1.76 (s, 3H), 1.72 (s, 1H), 1.64 – 1.28 (m, 6H), 1.21 (tt, *J* = 13.0, 6.2 Hz, 2H), 1.06 (s, 3H), 1.01 (s, 3H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.63 (s, 3H).

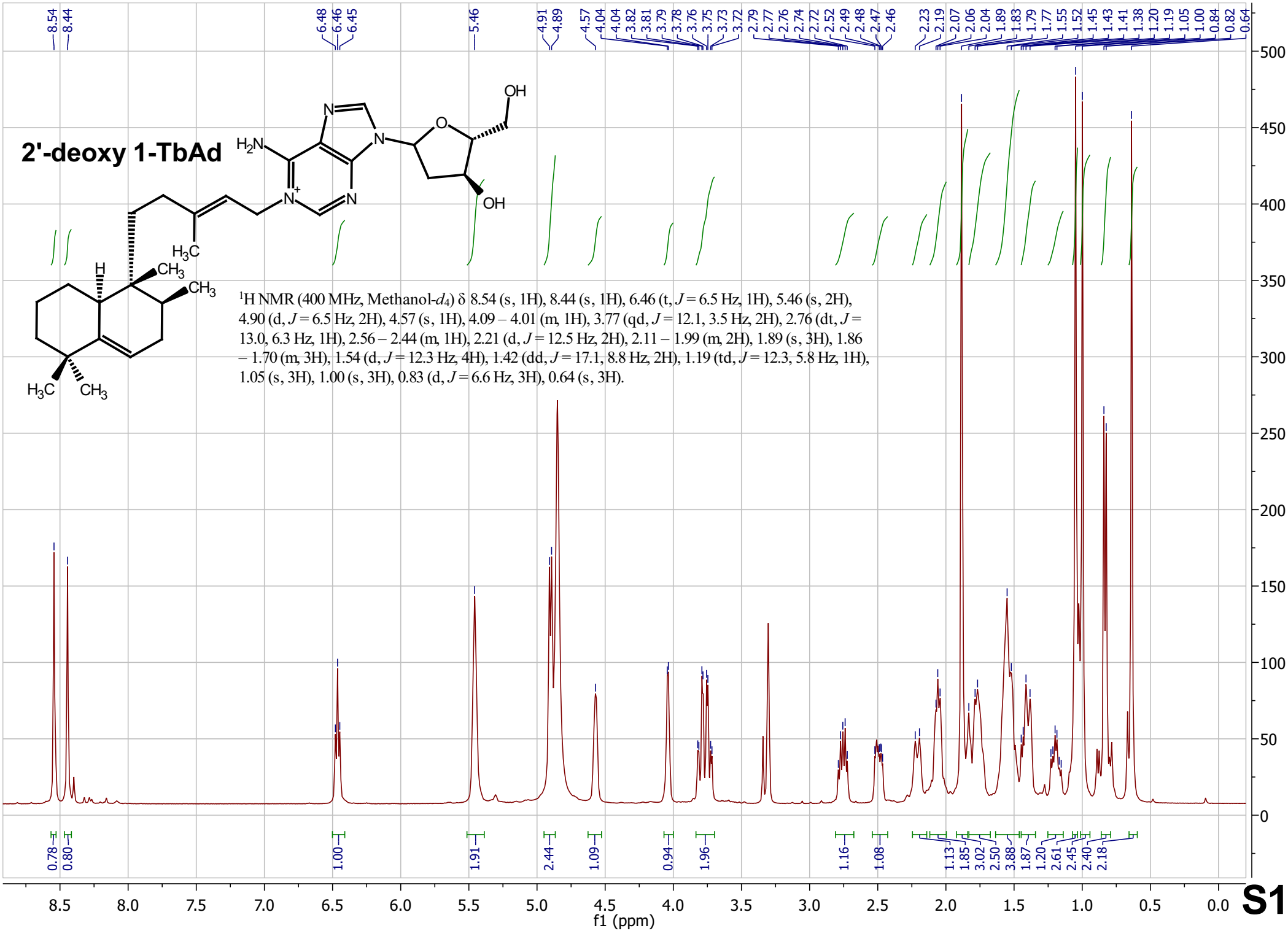

2.17
2.15
1.99
1.96
1.95
1.93
1.88
1.87
1.82
1.76
1.72
1.57
1.54
1.51
1.51
1.50
1.48
1.47
1.45
1.41
1.39
1.38
1.31
1.26
1.24
1.23
1.20
1.19
1.17
1.16
1.06
1.01
0.83
0.81
0.63
H3C
H
H3C
H3C
CH3
CH3
NH
N
N
N
N
OH
O
OH
HO
N6-TbAd
1H NMR (400 MHz, Chloroform-d) δ 8.19 (s, 1H), 7.81 (s, 1H), 5.86 (s, 1H), 5.82 (d, J = 7.2 Hz, 1H), 5.44 (d, J = 4.7 Hz, 1H), 5.36 (d, J = 7.3 Hz, 1H), 5.00 (s, 1H), 4.47 (d, J = 4.9 Hz, 1H), 4.33 (s, 1H), 4.19 (s, 2H), 3.94 (d, J = 12.9 Hz, 1H), 3.76 (d, J = 12.9 Hz, 1H), 3.23 (s, 2H), 2.16 (d, J = 10.4 Hz, 1H), 2.01 – 1.90 (m, 2H), 1.85 (d, J = 23.8 Hz, 2H), 1.76 (s, 3H), 1.72 (s, 1H), 1.64 – 1.28 (m, 6H), 1.21 (tt, J = 13.0, 6.2 Hz, 2H), 1.06 (s, 3H), 1.01 (s, 3H), 0.82 (d, J = 6.6 Hz, 3H), 0.63 (s, 3H).
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
1.17
1.74
1.33
3.09
1.03
6.35
1.57
2.70
2.85
2.92
2.32
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
f1 (ppm)

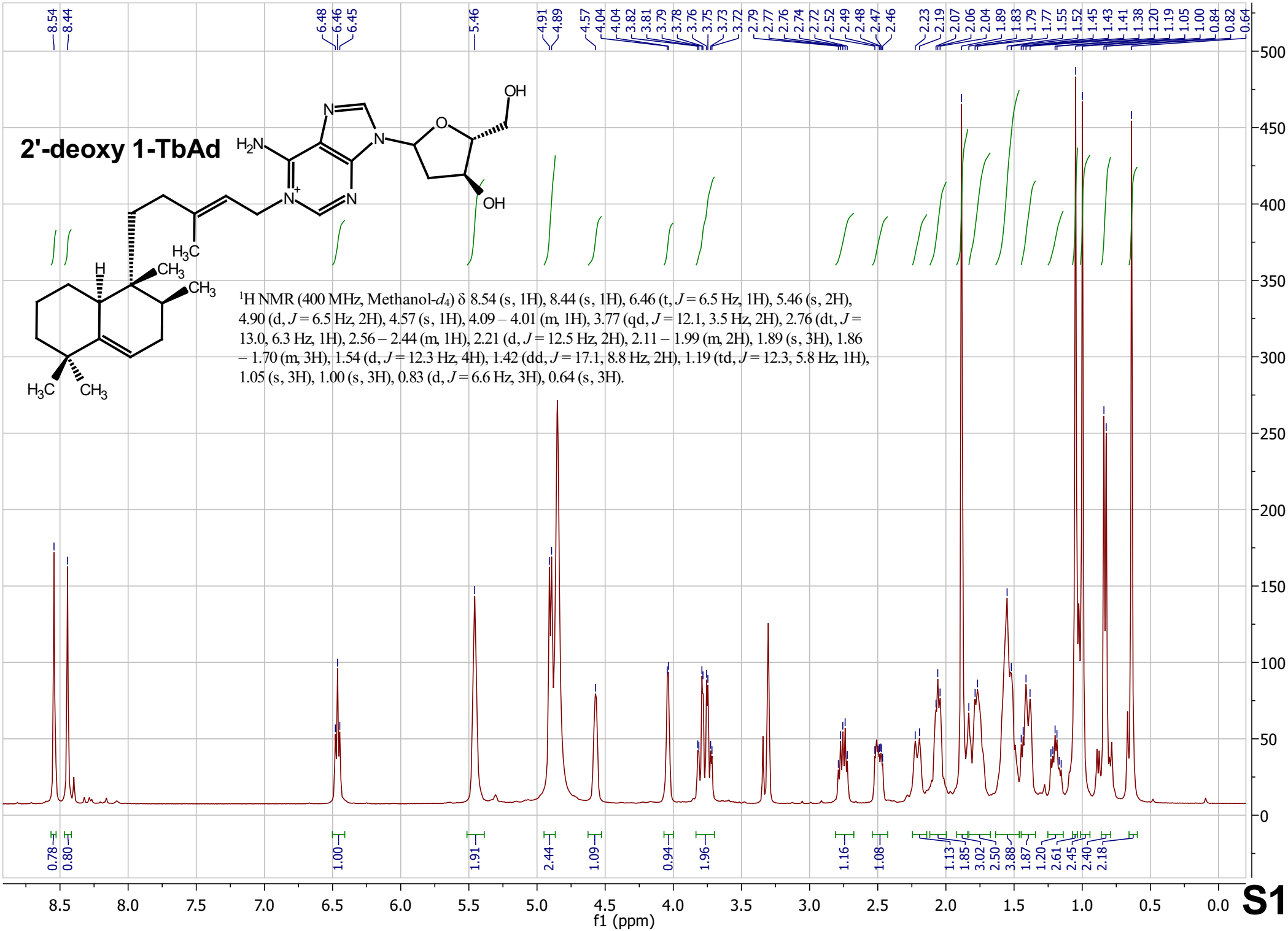

154.59
152.44
147.00
146.09
141.73
140.05
120.70
118.96
116.23
91.08
87.56
73.89
72.46
63.15
41.00
39.89
38.87
37.04
36.17
35.00
33.47
32.80
31.71
29.87
29.12
27.51
22.33
16.83
16.26
15.22
H3C
H
H3C
H3C
CH3
CH3
NH
N
N
N
N
O
OH
OH
HO
N6-TbAd
13C NMR (101 MHz, cdcl3) δ 154.59, 152.44, 147.00, 146.09, 141.73, 140.05, 120.70, 118.96, 116.23, 91.08, 87.56, 73.89, 72.46, 63.15, 41.00, 39.89, 38.87, 37.04, 36.17, 35.00, 33.47, 32.80, 31.71, 29.87, 29.12, 27.51, 22.33, 16.83, 16.26, 15.22.
f1 (ppm)

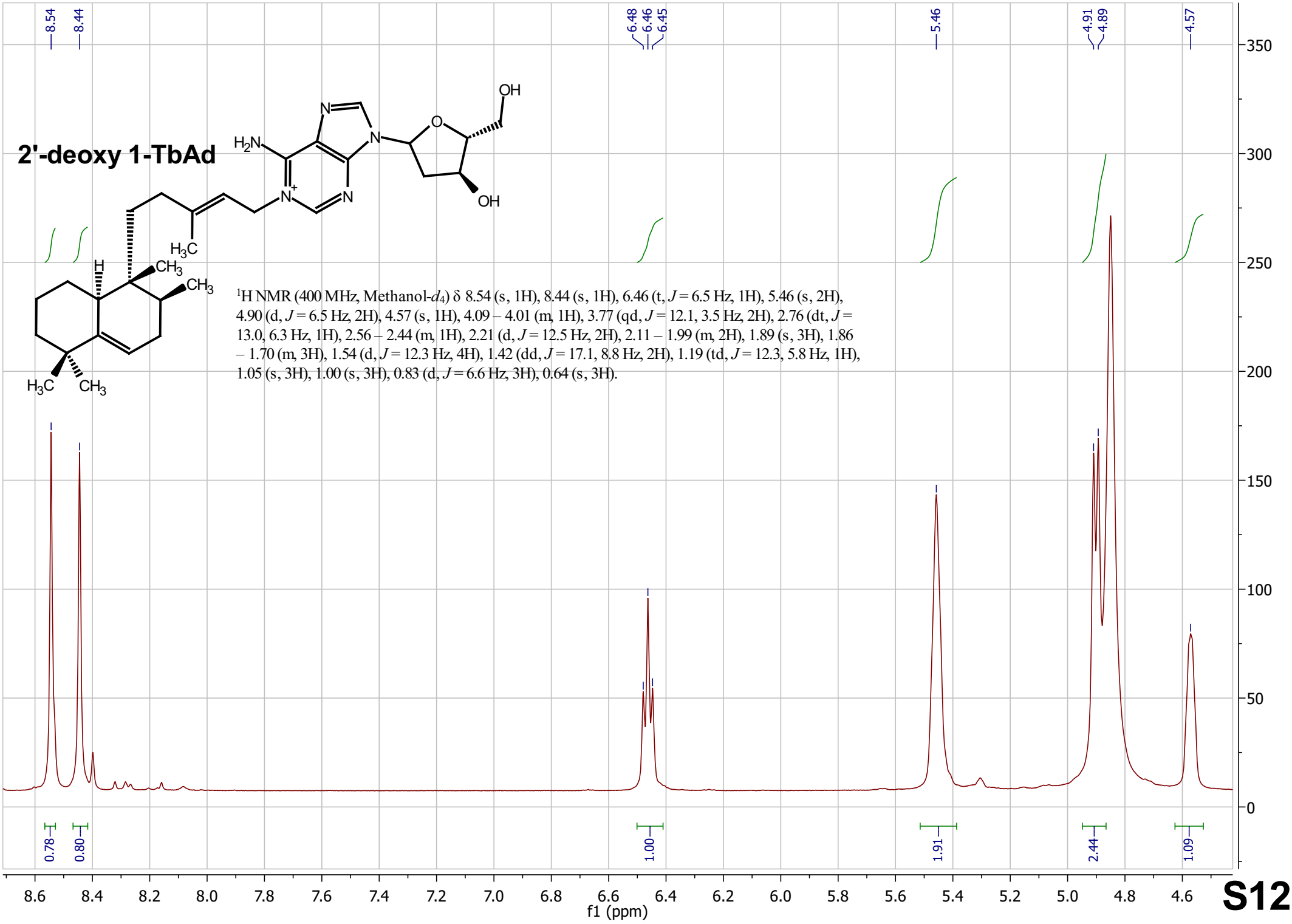

154.59
152.44
147.00
146.09
141.73
140.05
120.70
118.96
116.23
91.08
87.56
N^6-TbAd
^{13}C NMR (101 MHz, cdcl$_3$) δ 154.59, 152.44, 147.00, 146.09, 141.73, 140.05, 120.70, 118.96, 116.23, 91.08, 87.56, 73.89, 72.46, 63.15, 41.00, 39.89, 38.87, 37.04, 36.17, 35.00, 33.47, 32.80, 31.71, 29.87, 29.12, 27.51, 22.33, 16.83, 16.26, 15.22
f1 (ppm)


73.89
72.46
63.15
41.00
39.89
38.87
37.04
36.17
35.00
33.47
32.80
31.71
29.87
29.12
27.51
22.33
16.83
16.26
15.22
H3C
H
H3C
H3C
CH3
CH3
NH
N
N
N
N
O
OH
OH
HO
N6-TbAd
13C NMR (101 MHz, cdcl3) δ 154.59, 152.44, 147.00, 146.09, 141.73, 140.05, 120.70, 118.96, 116.23, 91.08, 87.56, 73.89, 72.46, 63.15, 41.00, 39.89, 38.87, 37.04, 36.17, 35.00, 33.47, 32.80, 31.71, 29.87, 29.12, 27.51, 22.33, 16.83, 16.26, 15.22.
f1 (ppm)

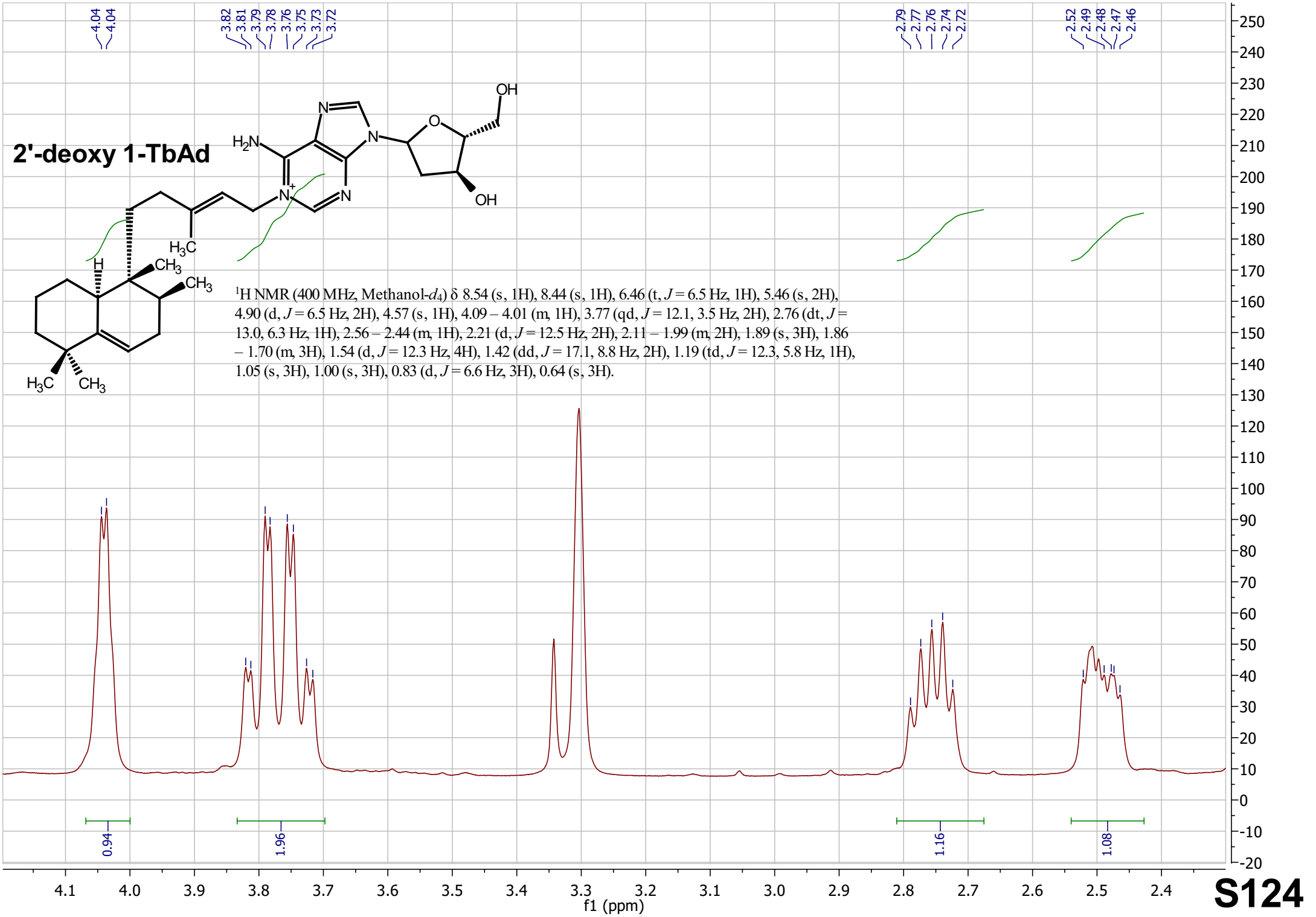

154.59
146.09
141.71
120.70
118.97
116.23
91.09
87.56
73.90
72.49
63.16
41.00
39.89
37.04
36.17
35.00
33.47
32.80
31.72
29.87
29.12
27.51
22.33
16.83
16.26
15.22
^{13}C NMR (101 MHz, cdcl$_3$) δ 154.59, 146.09, 141.71, 120.70, 118.97, 116.23, 91.09, 87.56, 73.90, 72.49, 63.16, 41.00, 39.89, 37.04, 36.17, 35.00, 33.47, 32.80, 31.72, 29.87, 29.12, 27.51, 22.33, 16.83, 16.26, 15.22.
4 carbons are missing. Elongation of meassurement did not lead to exposure of these signals. The are however visible in the regular 13C spectrum
N6-TbAd
f1 (ppm)

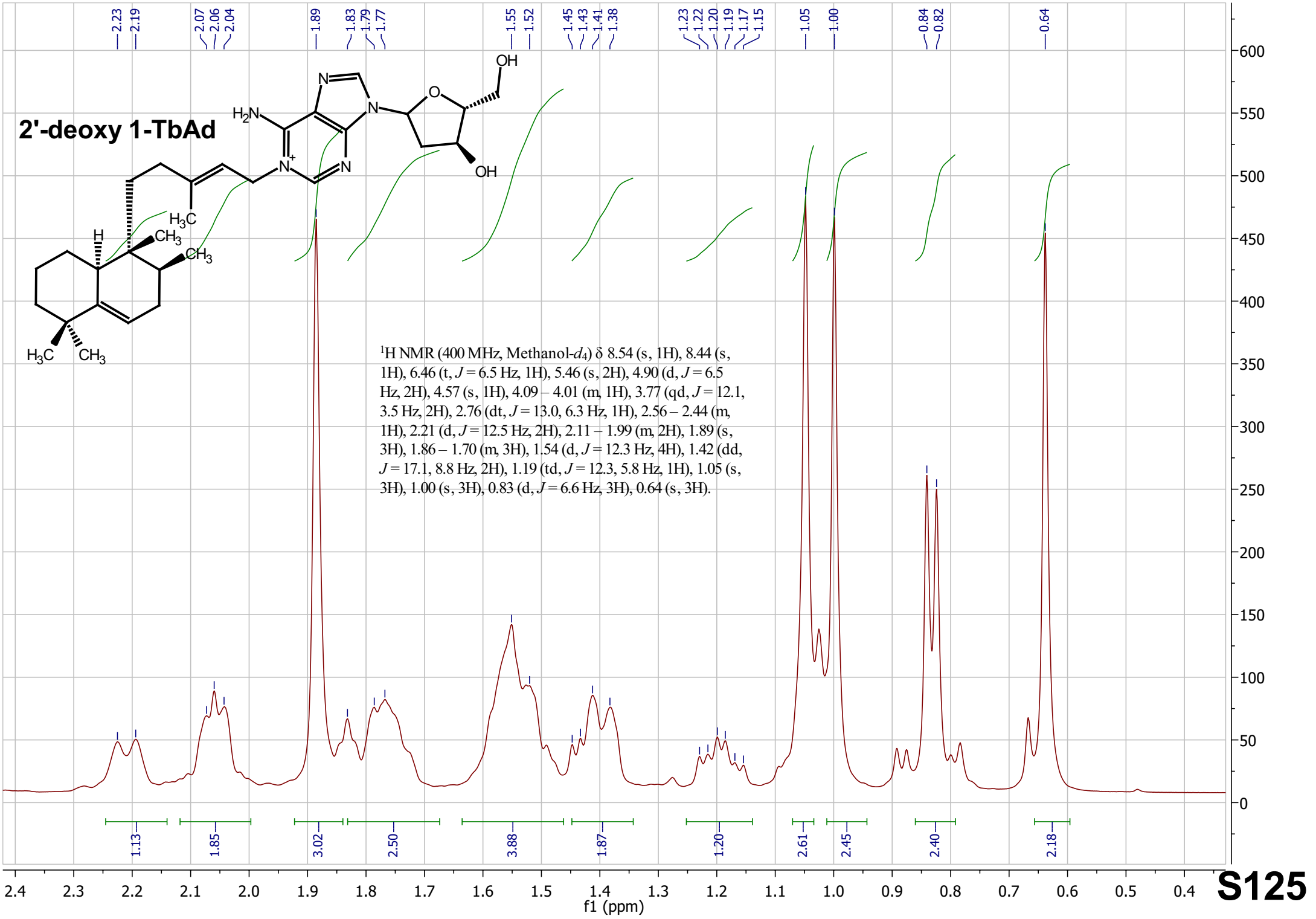

2'-deoxy 1-TbAd
^{1}H NMR (400 MHz, Methanol-d_4) δ 8.54 (s, 1H), 8.44 (s, 1H), 6.46 (t, J = 6.5 Hz, 1H), 5.46 (s, 2H), 4.90 (d, J = 6.5 Hz, 2H), 4.57 (s, 1H), 4.09 – 4.01 (m, 1H), 3.77 (qd, J = 12.1, 3.5 Hz, 2H), 2.76 (dt, J = 13.0, 6.3 Hz, 1H), 2.56 – 2.44 (m, 1H), 2.21 (d, J = 12.5 Hz, 2H), 2.11 – 1.99 (m, 2H), 1.89 (s, 3H), 1.86 – 1.70 (m, 3H), 1.54 (d, J = 12.3 Hz, 4H), 1.42 (dd, J = 17.1, 8.8 Hz, 2H), 1.19 (td, J = 12.3, 5.8 Hz, 1H), 1.05 (s, 3H), 1.00 (s, 3H), 0.83 (d, J = 6.6 Hz, 3H), 0.64 (s, 3H).
f1 (ppm)

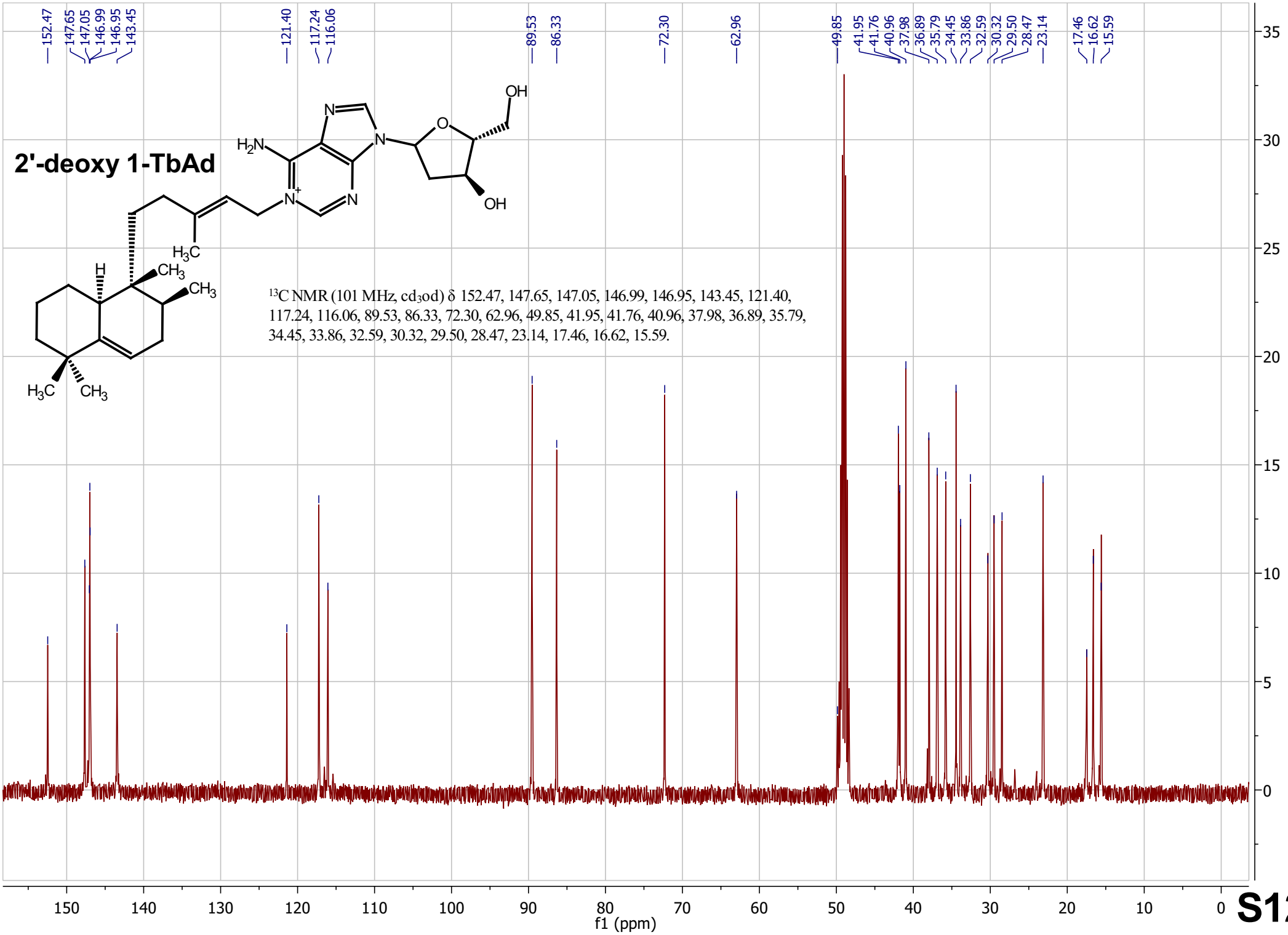

2'-deoxy 1-TbAd
OH
OH
H_2N
N
N
N
N
O
H_3C
H
CH_3
CH_3
H_3C
CH_3
^{1}H NMR (400 MHz, Methanol-d_4) δ 8.54 (s, 1H), 8.44 (s, 1H), 6.46 (t, J = 6.5 Hz, 1H), 5.46 (s, 2H), 4.90 (d, J = 6.5 Hz, 2H), 4.57 (s, 1H), 4.09 – 4.01 (m, 1H), 3.77 (qd, J = 12.1, 3.5 Hz, 2H), 2.76 (dt, J = 13.0, 6.3 Hz, 1H), 2.56 – 2.44 (m, 1H), 2.21 (d, J = 12.5 Hz, 2H), 2.11 – 1.99 (m, 2H), 1.89 (s, 3H), 1.86 – 1.70 (m, 3H), 1.54 (d, J = 12.3 Hz, 4H), 1.42 (dd, J = 17.1, 8.8 Hz, 2H), 1.19 (td, J = 12.3, 5.8 Hz, 1H), 1.05 (s, 3H), 1.00 (s, 3H), 0.83 (d, J = 6.6 Hz, 3H), 0.64 (s, 3H).
f1 (ppm)

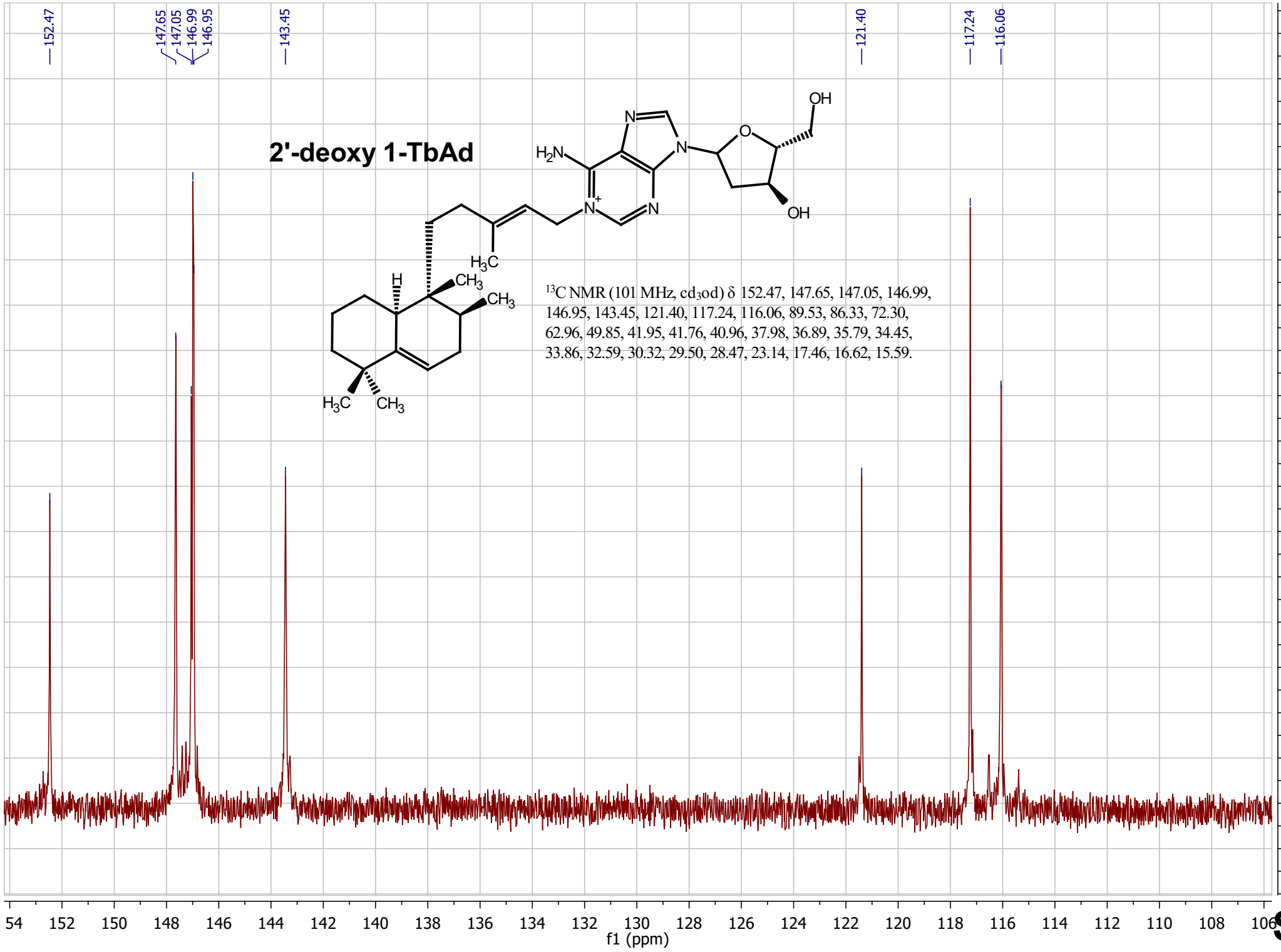


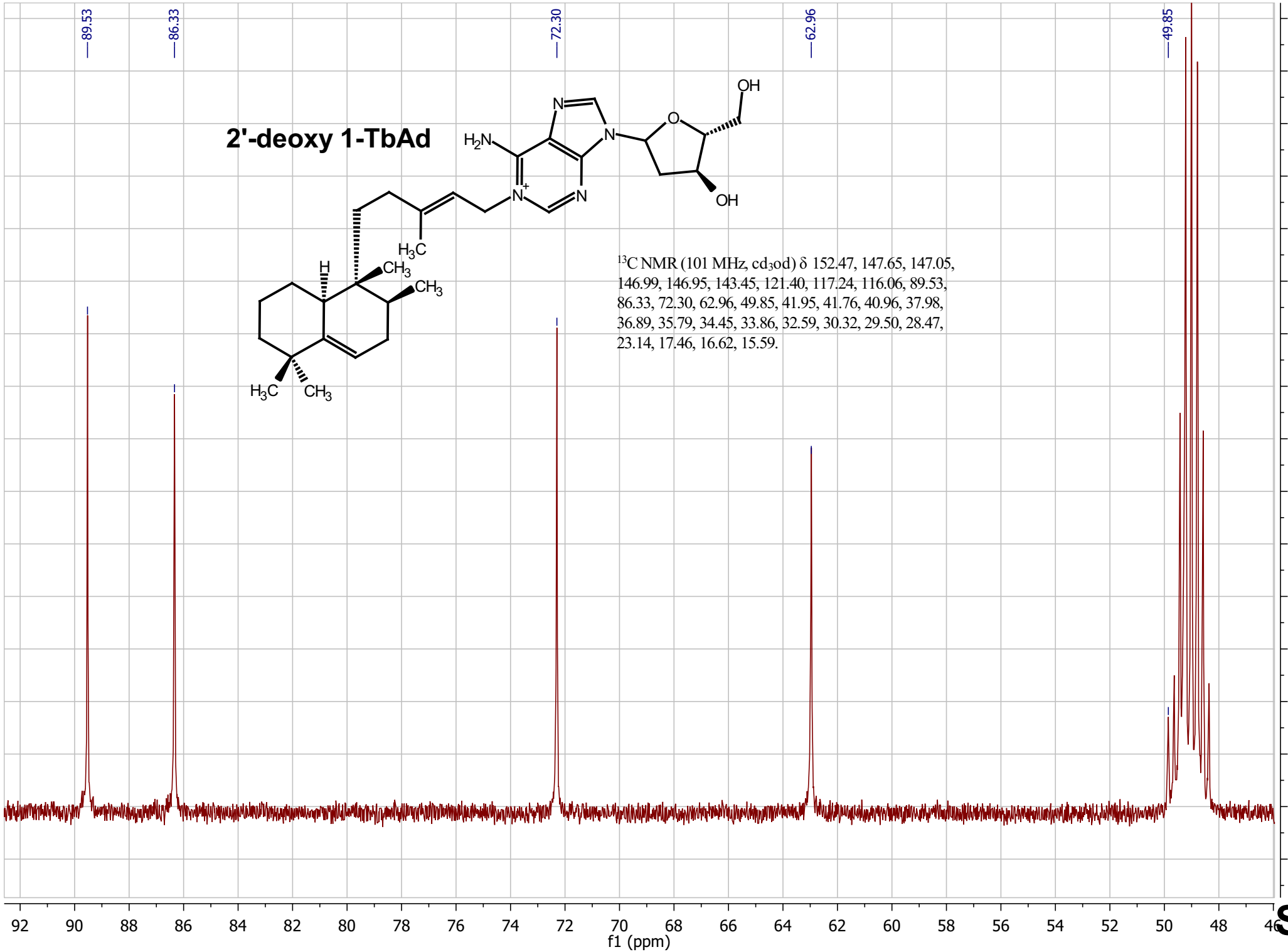
^{1}H NMR (400 MHz, Methanol-d_4) δ 8.54 (s, 1H), 8.44 (s, 1H), 6.46 (t, J = 6.5 Hz, 1H), 5.46 (s, 2H), 4.90 (d, J = 6.5 Hz, 2H), 4.57 (s, 1H), 4.09 – 4.01 (m, 1H), 3.77 (qd, J = 12.1, 3.5 Hz, 2H), 2.76 (dt, J = 13.0, 6.3 Hz, 1H), 2.56 – 2.44 (m, 1H), 2.21 (d, J = 12.5 Hz, 2H), 2.11 – 1.99 (m, 2H), 1.89 (s, 3H), 1.86 – 1.70 (m, 3H), 1.54 (d, J = 12.3 Hz, 4H), 1.42 (dd, J = 17.1, 8.8 Hz, 2H), 1.19 (td, J = 12.3, 5.8 Hz, 1H), 1.05 (s, 3H), 1.00 (s, 3H), 0.83 (d, J = 6.6 Hz, 3H), 0.64 (s, 3H).

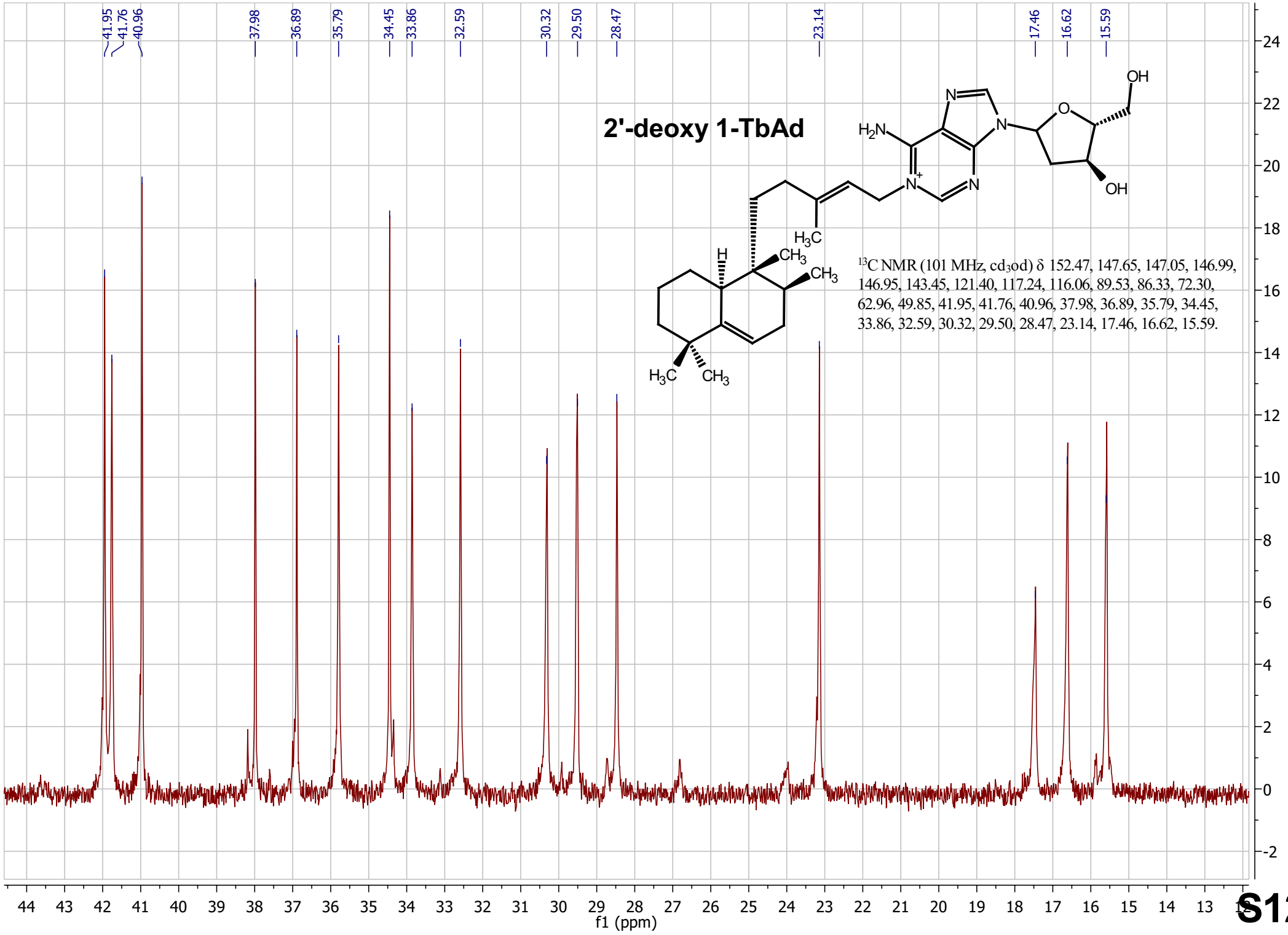

4.04
4.04
3.82
3.81
3.79
3.78
3.76
3.75
3.73
3.72
2.79
2.77
2.76
2.74
2.72
2.52
2.49
2.48
2.47
2.46
2'-deoxy 1-TbAd
OH
N
O
N
H_2N
N
N
OH
H_3C
H
CH_3
CH_3
H_3C
CH_3
[1]H NMR (400 MHz, Methanol-d_4) δ 8.54 (s, 1H), 8.44 (s, 1H), 6.46 (t, J = 6.5 Hz, 1H), 5.46 (s, 2H), 4.90 (d, J = 6.5 Hz, 2H), 4.57 (s, 1H), 4.09 – 4.01 (m, 1H), 3.77 (qd, J = 12.1, 3.5 Hz, 2H), 2.76 (dt, J = 13.0, 6.3 Hz, 1H), 2.56 – 2.44 (m, 1H), 2.21 (d, J = 12.5 Hz, 2H), 2.11 – 1.99 (m, 2H), 1.89 (s, 3H), 1.86 – 1.70 (m, 3H), 1.54 (d, J = 12.3 Hz, 4H), 1.42 (dd, J = 17.1, 8.8 Hz, 2H), 1.19 (td, J = 12.3, 5.8 Hz, 1H), 1.05 (s, 3H), 1.00 (s, 3H), 0.83 (d, J = 6.6 Hz, 3H), 0.64 (s, 3H).
0.94
1.96
1.16
1.08
f1 (ppm)

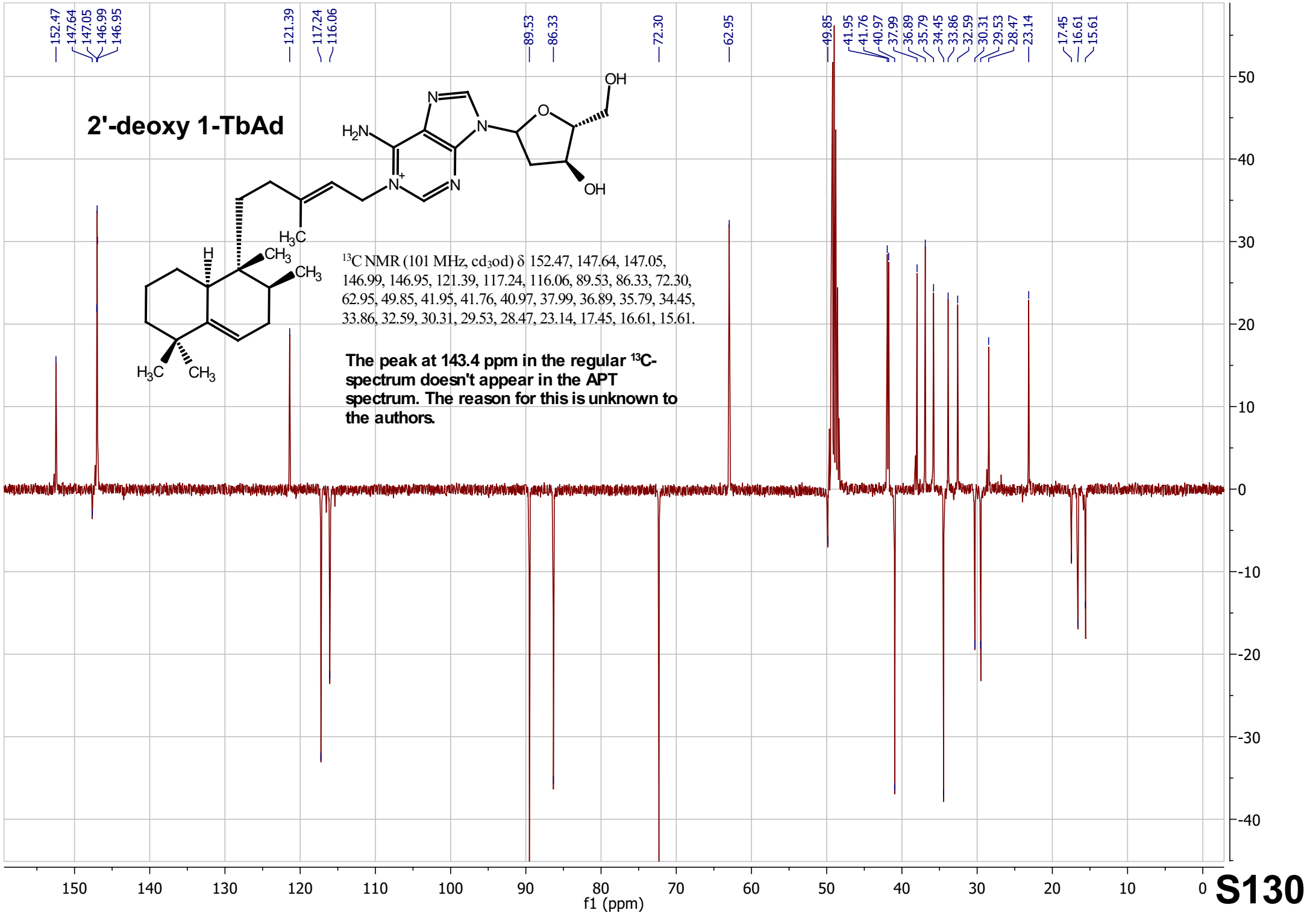

2'-deoxy 1-TbAd
^{1}H NMR (400 MHz, Methanol-d_4) δ 8.54 (s, 1H), 8.44 (s, 1H), 6.46 (t, J = 6.5 Hz, 1H), 5.46 (s, 2H), 4.90 (d, J = 6.5 Hz, 2H), 4.57 (s, 1H), 4.09 – 4.01 (m, 1H), 3.77 (qd, J = 12.1, 3.5 Hz, 2H), 2.76 (dt, J = 13.0, 6.3 Hz, 1H), 2.56 – 2.44 (m, 1H), 2.21 (d, J = 12.5 Hz, 2H), 2.11 – 1.99 (m, 2H), 1.89 (s, 3H), 1.86 – 1.70 (m, 3H), 1.54 (d, J = 12.3 Hz, 4H), 1.42 (dd, J = 17.1, 8.8 Hz, 2H), 1.19 (td, J = 12.3, 5.8 Hz, 1H), 1.05 (s, 3H), 1.00 (s, 3H), 0.83 (d, J = 6.6 Hz, 3H), 0.64 (s, 3H).
f1 (ppm)


152.47
147.65
147.05
146.99
146.95
143.45
121.40
117.24
116.06
89.53
86.33
72.30
62.96
49.85
41.95
41.76
40.96
37.98
36.89
35.79
34.45
33.86
32.59
30.32
29.50
28.47
23.14
17.46
16.62
15.59
2'-deoxy 1-TbAd
OH
N
O
N
H2N
N+
N
OH
H3C
H
CH3
CH3
H3C
CH3
13C NMR (101 MHz, cd3od) δ 152.47, 147.65, 147.05, 146.99, 146.95, 143.45, 121.40, 117.24, 116.06, 89.53, 86.33, 72.30, 62.96, 49.85, 41.95, 41.76, 40.96, 37.98, 36.89, 35.79, 34.45, 33.86, 32.59, 30.32, 29.50, 28.47, 23.14, 17.46, 16.62, 15.59.
35
30
25
20
15
10
5
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


152.47
147.65
147.05
146.99
146.95
143.45
121.40
117.24
116.06
2'-deoxy 1-TbAd
^{13}C NMR (101 MHz, cd$_3$od) δ 152.47, 147.65, 147.05, 146.99, 146.95, 143.45, 121.40, 117.24, 116.06, 89.53, 86.33, 72.30, 62.96, 49.85, 41.95, 41.76, 40.96, 37.98, 36.89, 35.79, 34.45, 33.86, 32.59, 30.32, 29.50, 28.47, 23.14, 17.46, 16.62, 15.59.
f1 (ppm)


89.53
86.33
72.30
62.96
49.85
2'-deoxy 1-TbAd
^{13}C NMR (101 MHz, cd$_3$od) δ 152.47, 147.65, 147.05, 146.99, 146.95, 143.45, 121.40, 117.24, 116.06, 89.53, 86.33, 72.30, 62.96, 49.85, 41.95, 41.76, 40.96, 37.98, 36.89, 35.79, 34.45, 33.86, 32.59, 30.32, 29.50, 28.47, 23.14, 17.46, 16.62, 15.59.
f1 (ppm)


41.95
41.76
40.96
37.98
36.89
35.79
34.45
33.86
32.59
30.32
29.50
28.47
23.14
17.46
16.62
15.59
2'-deoxy 1-TbAd
^{13}C NMR (101 MHz, cd$_3$od) δ 152.47, 147.65, 147.05, 146.99, 146.95, 143.45, 121.40, 117.24, 116.06, 89.53, 86.33, 72.30, 62.96, 49.85, 41.95, 41.76, 40.96, 37.98, 36.89, 35.79, 34.45, 33.86, 32.59, 30.32, 29.50, 28.47, 23.14, 17.46, 16.62, 15.59.
f1 (ppm)


2'-deoxy 1-TbAd
152.47
147.64
147.05
146.99
146.95
121.39
117.24
116.06
89.53
86.33
72.30
62.95
49.85
41.95
41.76
40.97
37.99
36.89
35.79
34.45
33.86
32.59
30.31
29.53
28.47
23.14
17.45
16.61
15.61
^{13}C NMR (101 MHz, cd$_3$od) δ 152.47, 147.64, 147.05, 146.99, 146.95, 121.39, 117.24, 116.06, 89.53, 86.33, 72.30, 62.95, 49.85, 41.95, 41.76, 40.97, 37.99, 36.89, 35.79, 34.45, 33.86, 32.59, 30.31, 29.53, 28.47, 23.14, 17.45, 16.61, 15.61.
The peak at 143.4 ppm in the regular ^{13}C-spectrum doesn't appear in the APT spectrum. The reason for this is unknown to the authors.
f1 (ppm)