Supporting Information

Stereoselective Synthesis of Both Tetrahydropyran Rings of Antitumor Macrolide, (-)-Lasonolide A

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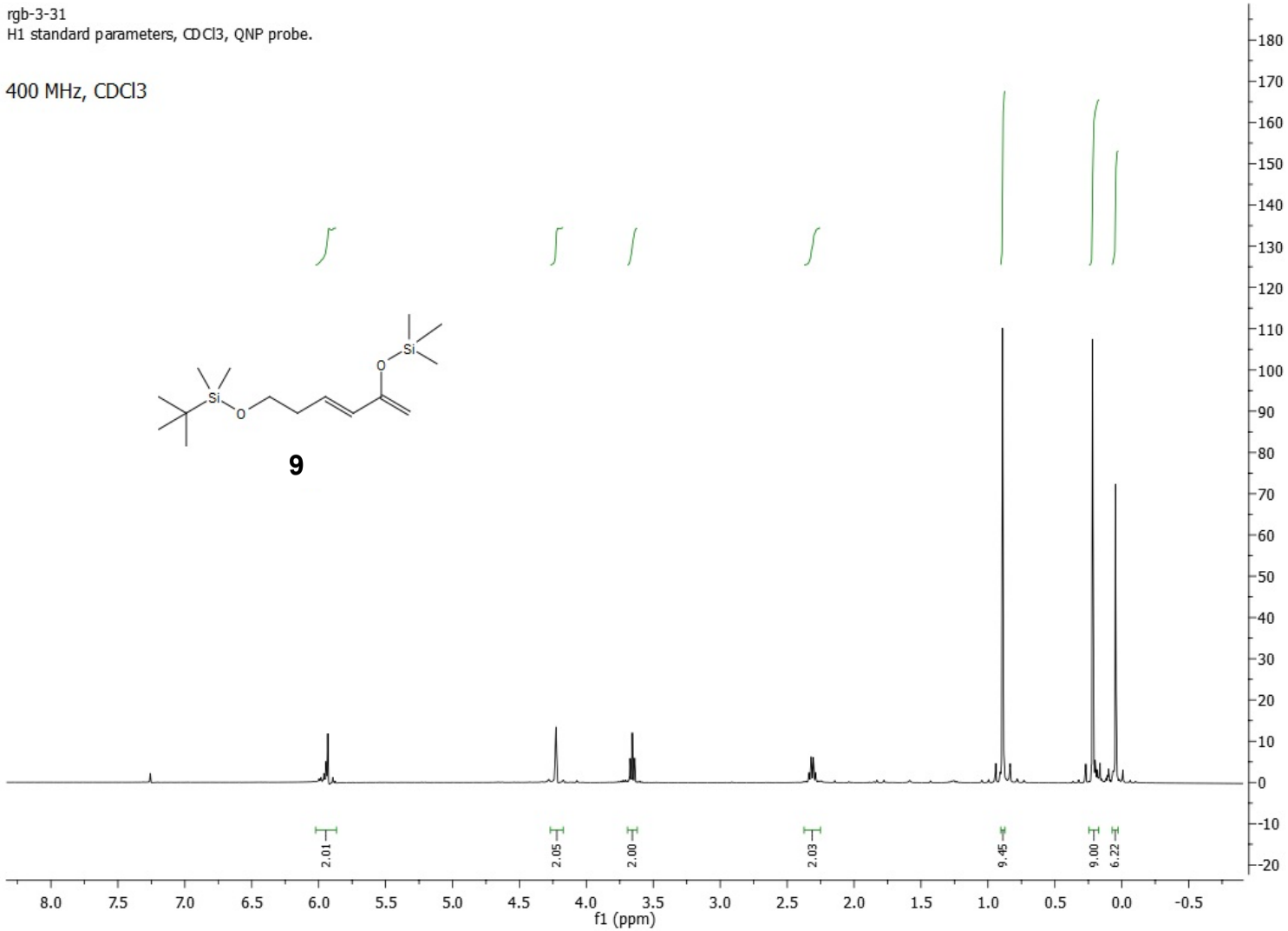
(All spectra of the new compounds are arranged in the order of their appearance in the manuscript)

General experimental methods

All moisture sensitive reactions were carried out in flame dried flask under nitrogen or argon atmosphere. Anhydrous solvents were obtained as follows: THF, DME, diethyl ether and toluene by distillation from sodium and benzophenone; dichloromethane, pyridine, acetonitrile and triethylamine from CaH2. All other solvents were HPLC grade. Column chromatography was performed with 240-400 mesh silica gel under low pressure of 5-10 psi. TLC was carried out with silica gel 60-F-254 plates visualized under UV light and stained with either phosphomolybdic acid or acidic *p*-anisaldehyde. 1H NMR spectra were recorded at 300, 400 or 500 MHz with chemical shifts reported in ppm (δ). 13C NMR spectra were recorded at 75, 100 or 125 MHz with chemical shifts reported in ppm (δ). Infrared spectra were recorded as thin films on NaCl plates on a Fourier transform spectrometer. Optical rotations were measured using a sodium (589, D line) lamp polarimeter. Mass spectra were obtained at the Purdue University Campus-wide Mass Spectrometry Center facility.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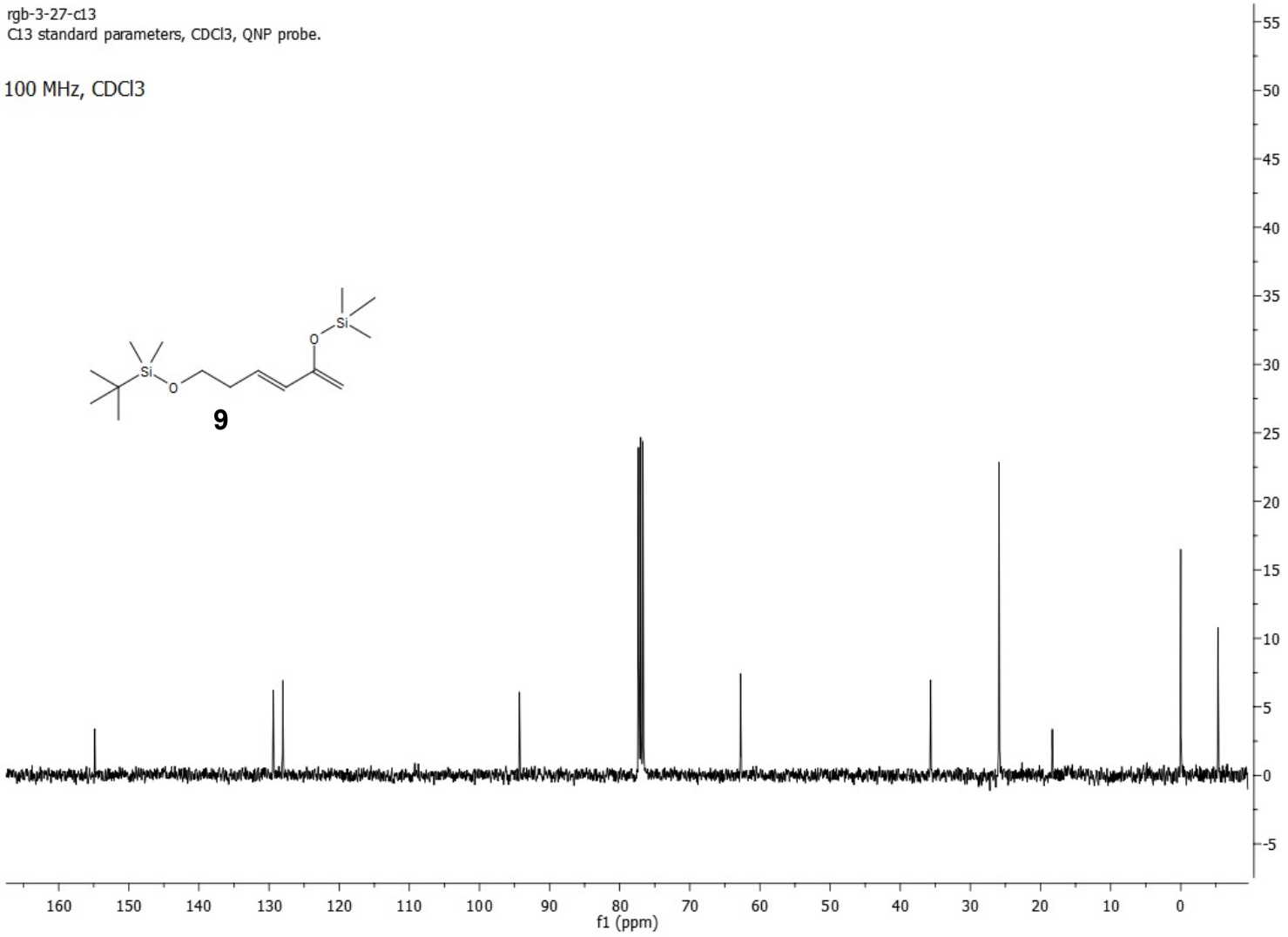
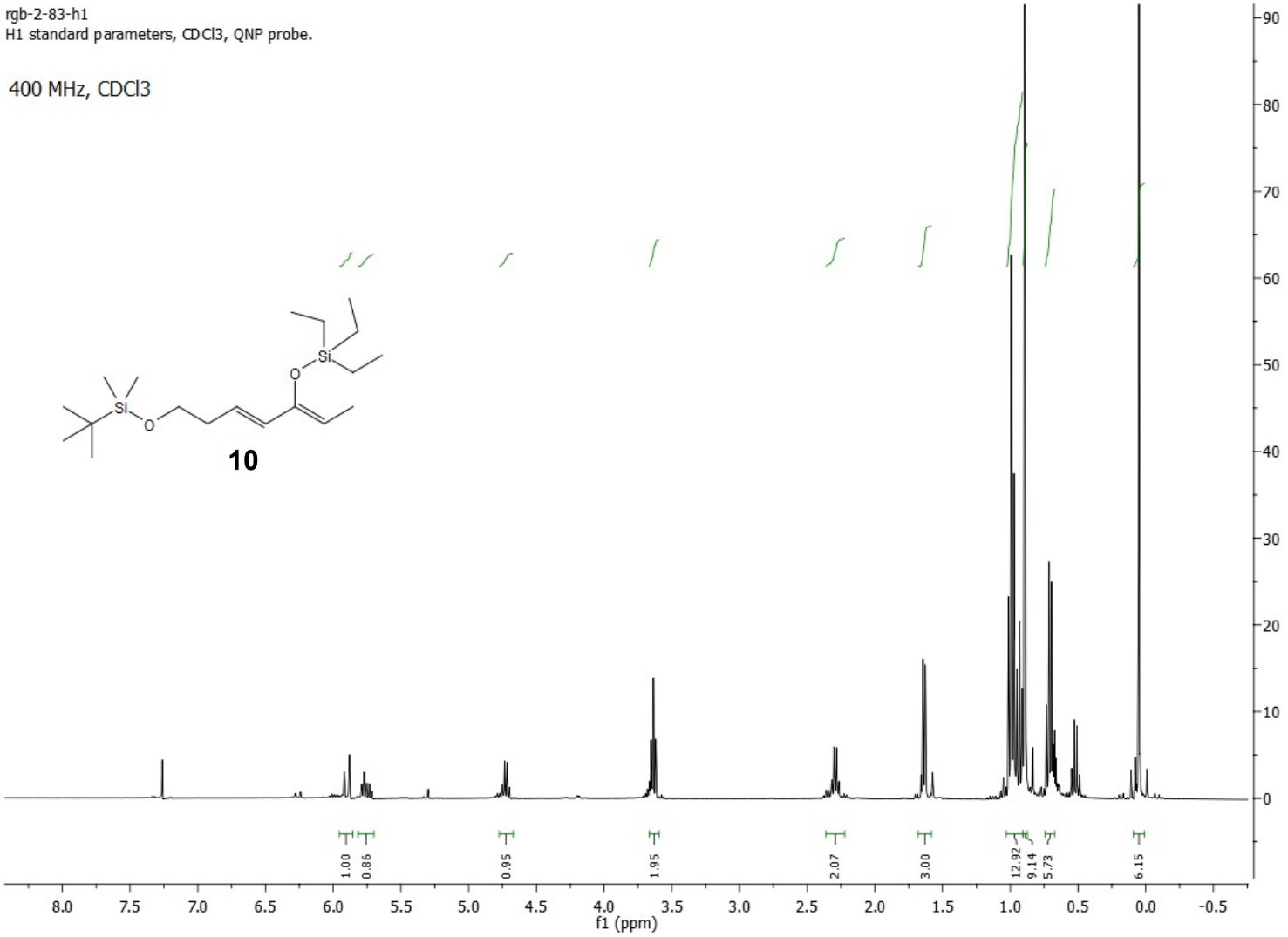
400 MHz, CDCl3
Si
O
Si
O
9
2.01
2.05
2.00
2.03
9.45
9.00
6.22
f1 (ppm)


rgb-3-27-c13
C13 standard parameters, CDCl3, QNP probe.
100 MHz, CDCl3
Si
O
Si
O
9
55
50
45
40
35
30
25
20
15
10
5
0
-5
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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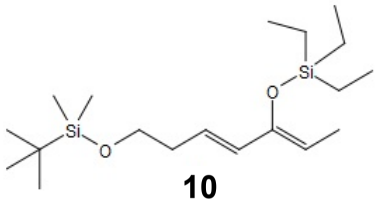
400 MHz, CDCl3
Si
O
Si
O
10
1.00
0.86
0.95
1.95
2.07
3.00
12.92
9.14
5.73
6.15
f1 (ppm)

rgb-2-83-c13
C13 standard parameters, CDCl3, QNP probe.

100 MHz, CDCl3



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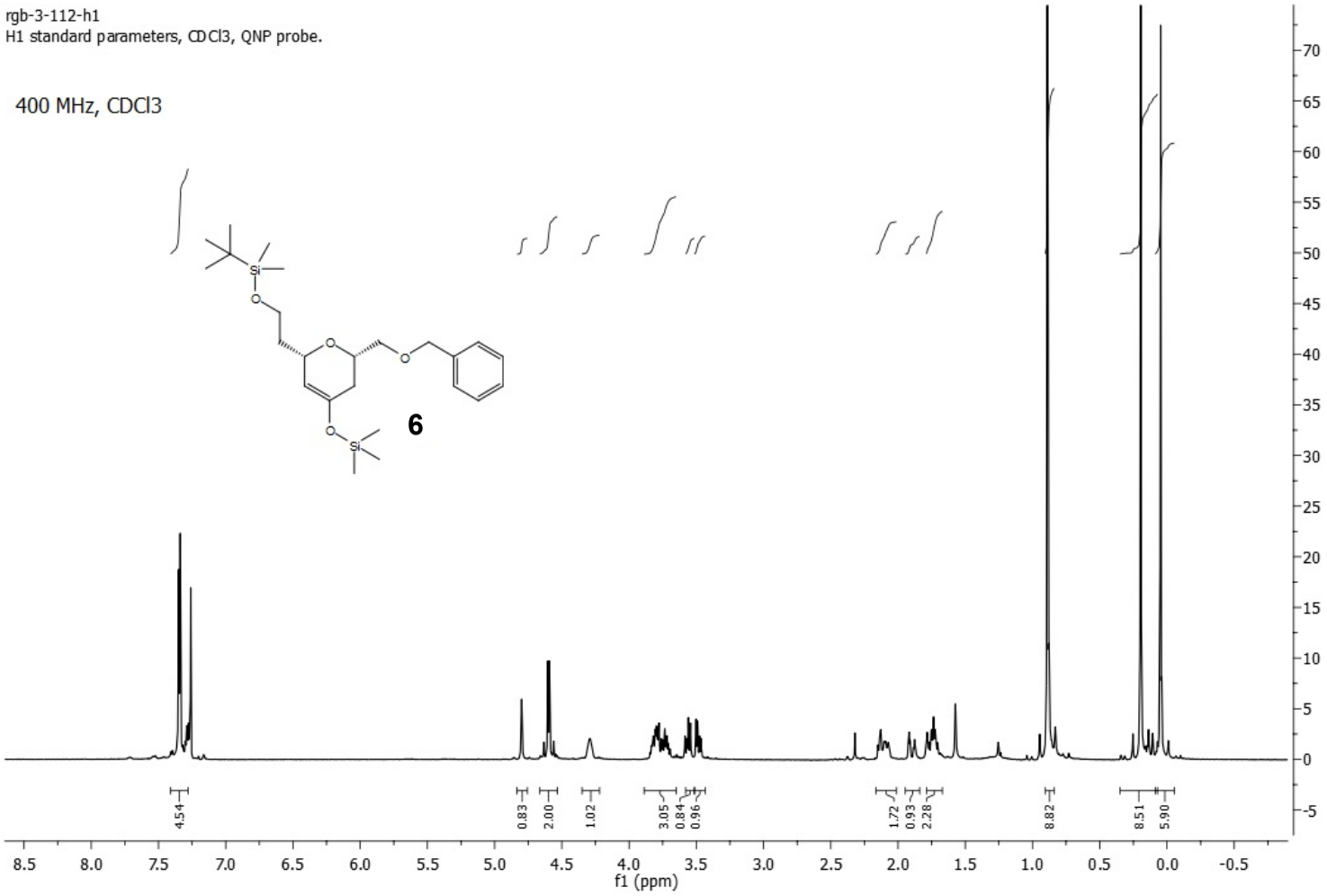
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400 MHz, CDCl3
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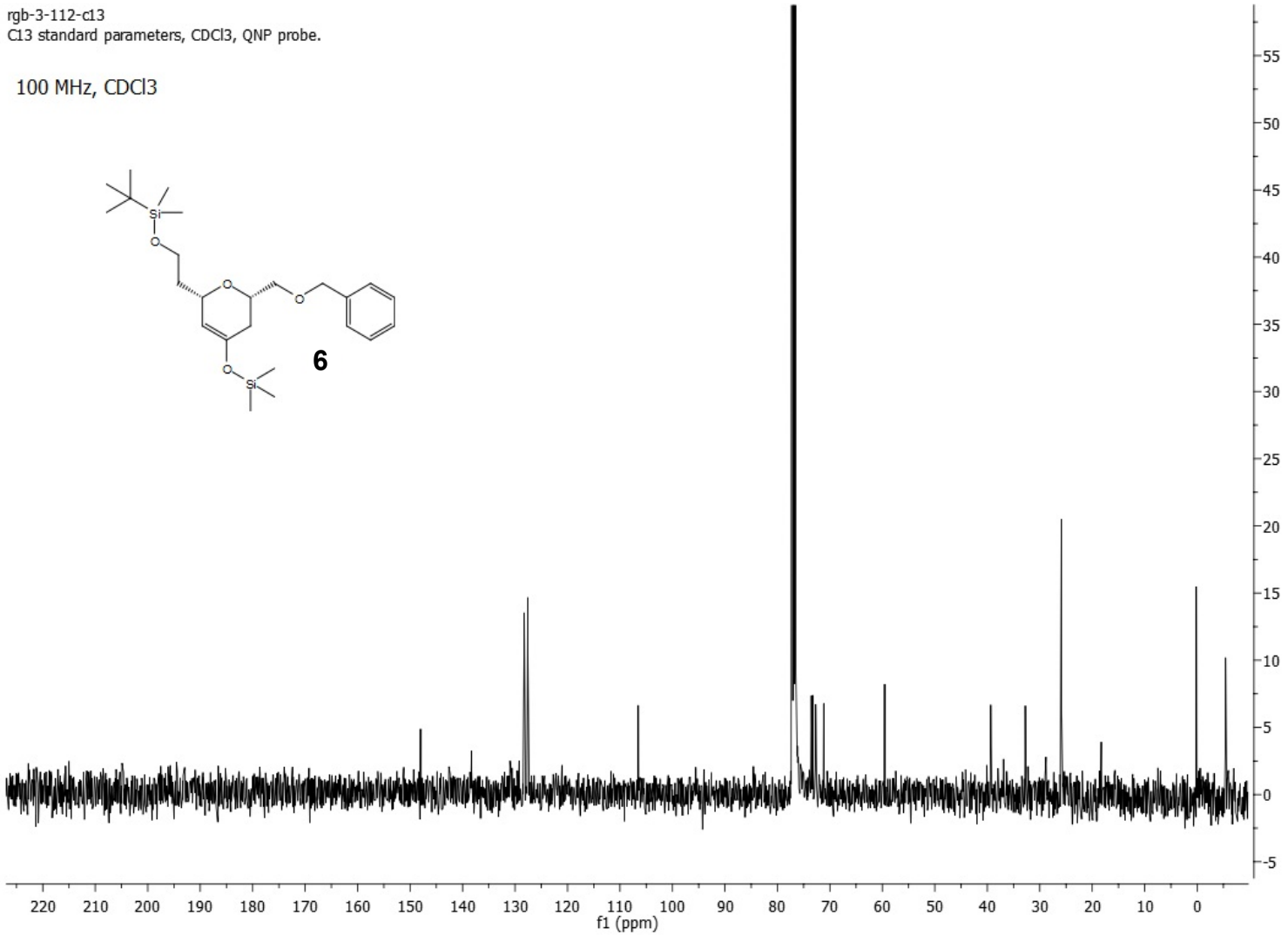
4.54
0.83
2.00
1.02
3.05
0.84
0.96
1.72
0.93
2.28
8.82
8.51
5.90
f1 (ppm)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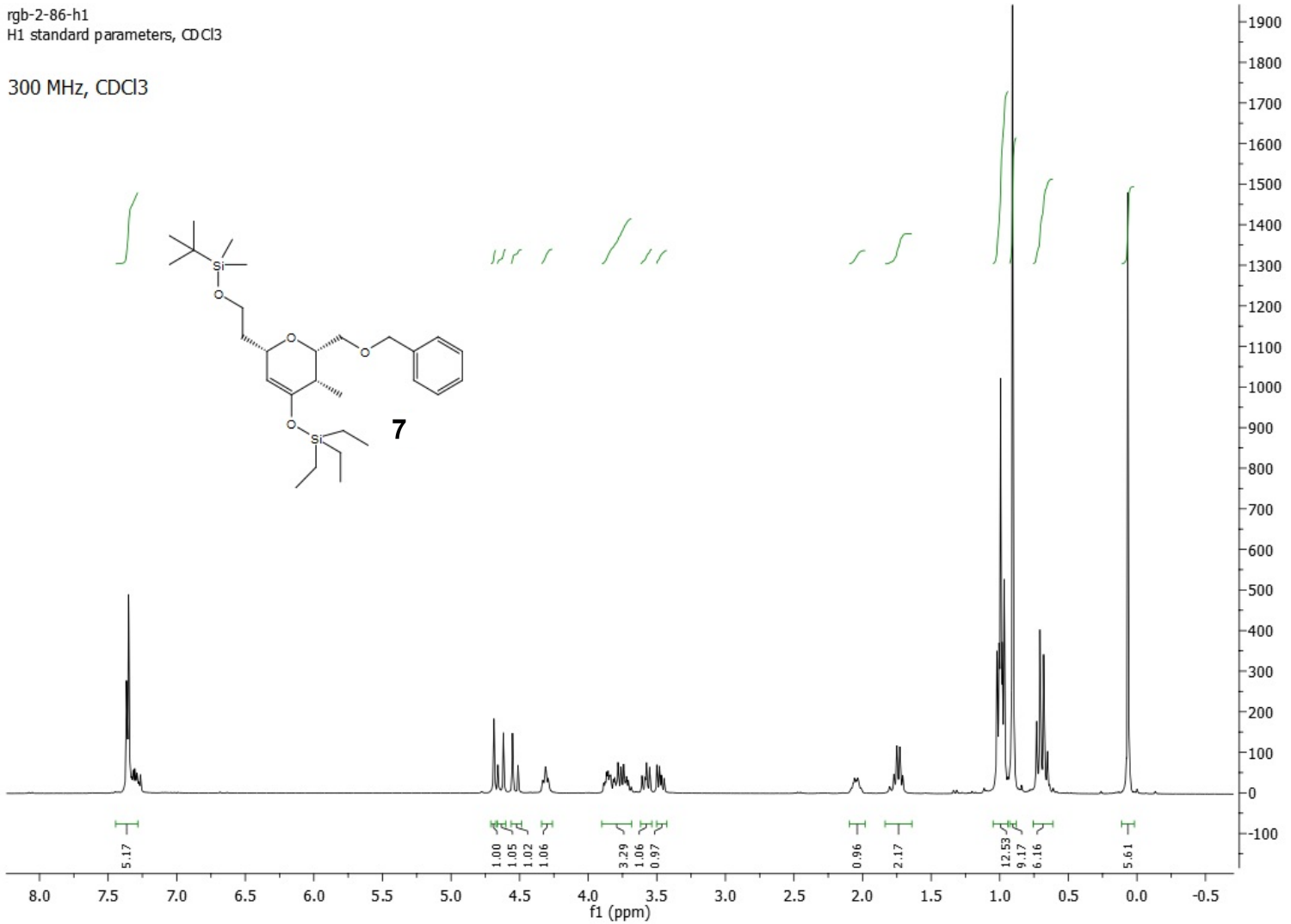
100 MHz, CDCl3
6
f1 (ppm)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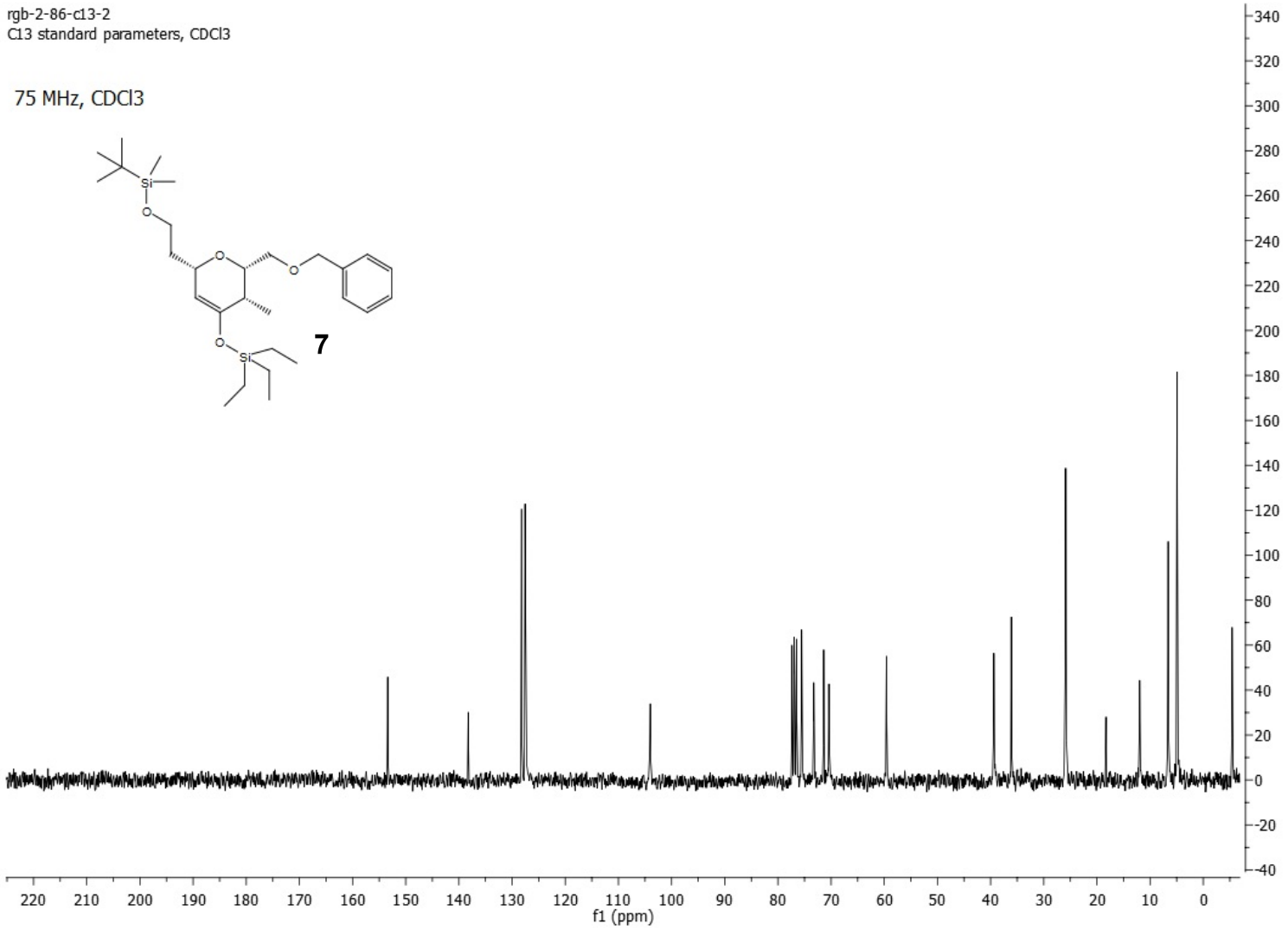
H1 standard parameters, CDCl3
300 MHz, CDCl3
7
5.17
1.00
1.05
1.02
1.06
3.29
1.06
0.97
0.96
2.17
12.53
9.17
6.16
5.61
f1 (ppm)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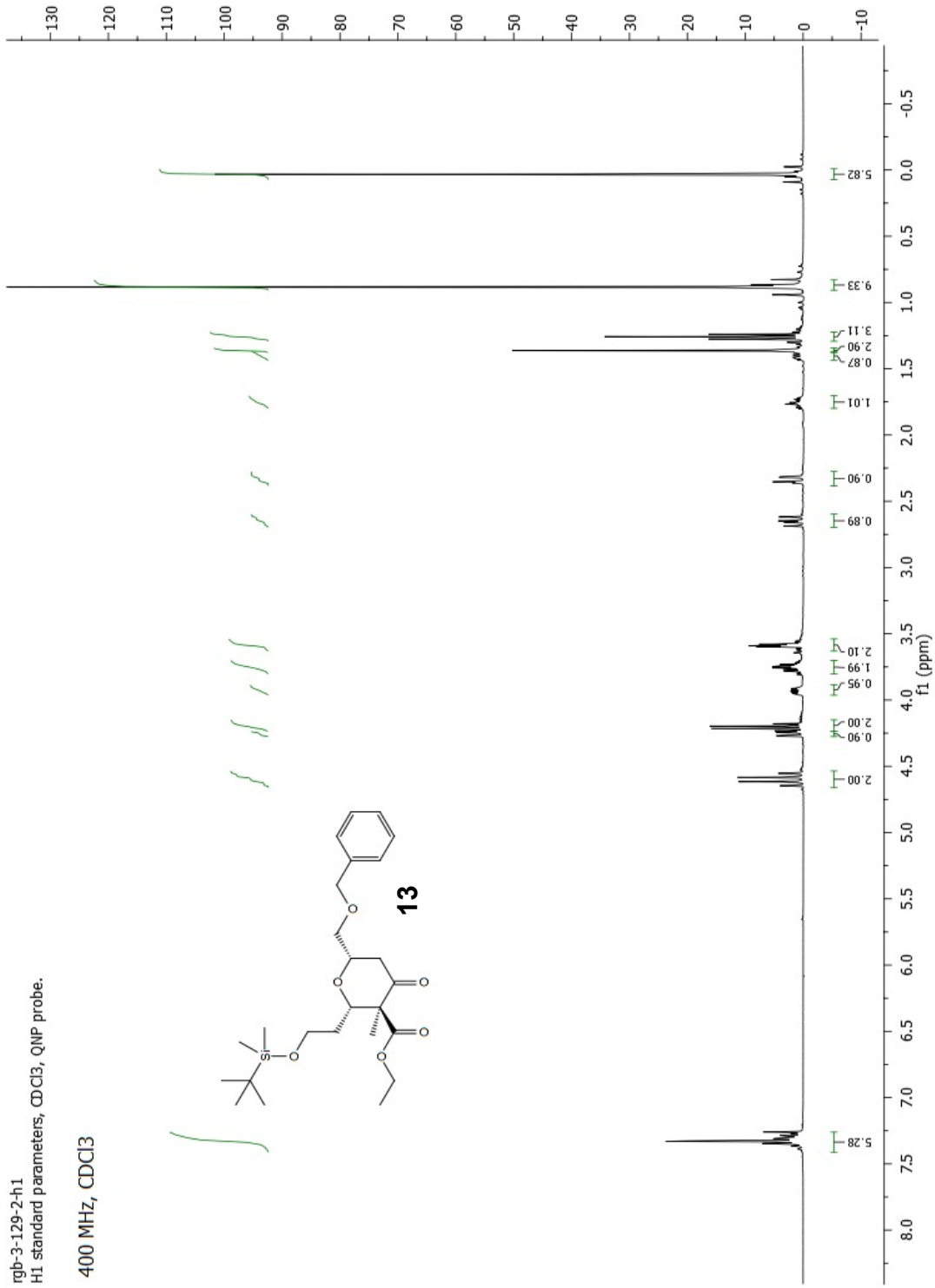
75 MHz, CDCl3
7
f1 (ppm)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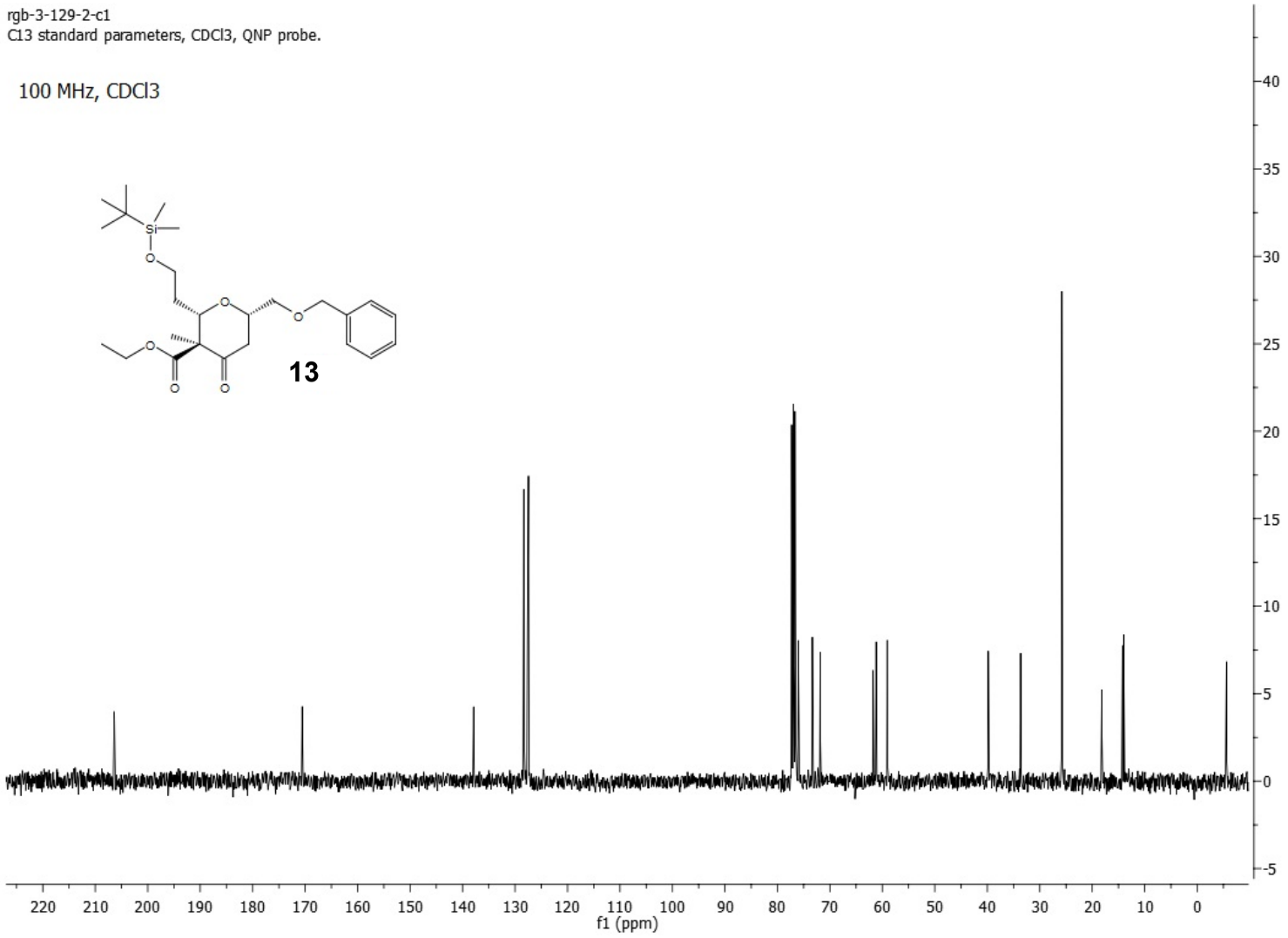
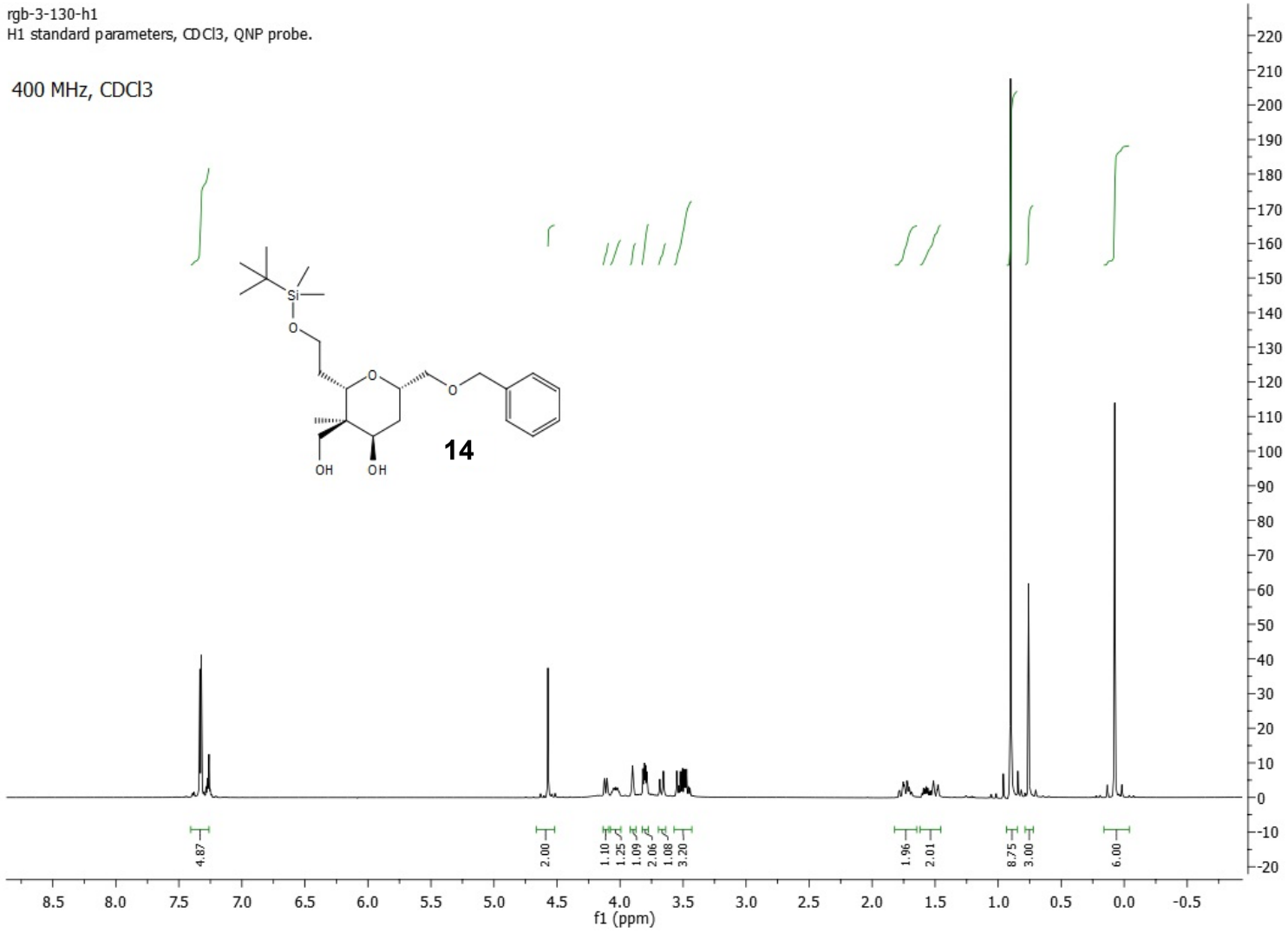
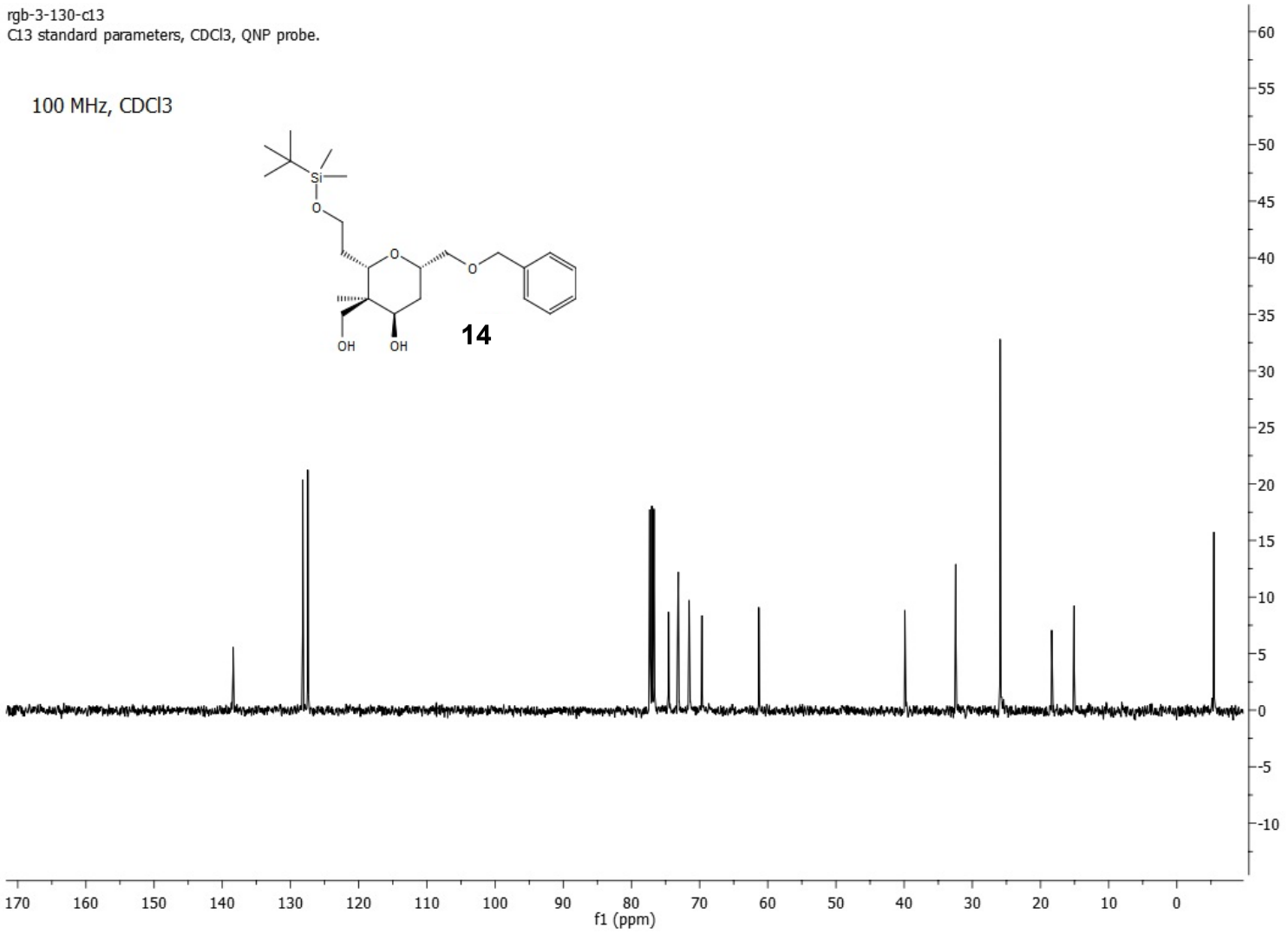
H1 standard parameters, CDCl3, QNP probe.
400 MHz, CDCl3
13
f1 (ppm)

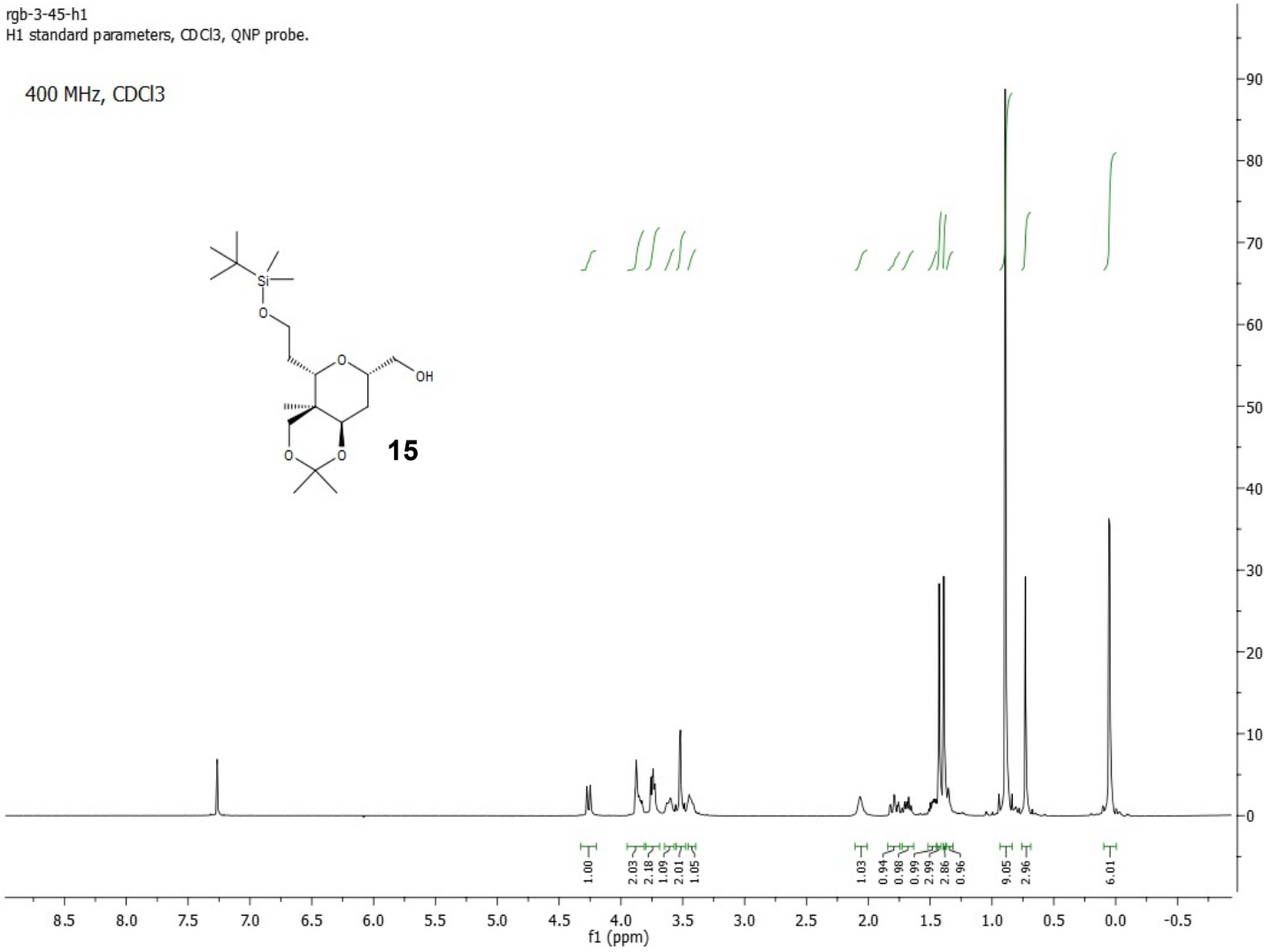
rgb-3-129-2-c1
C13 standard parameters, CDCl3, QNP probe.

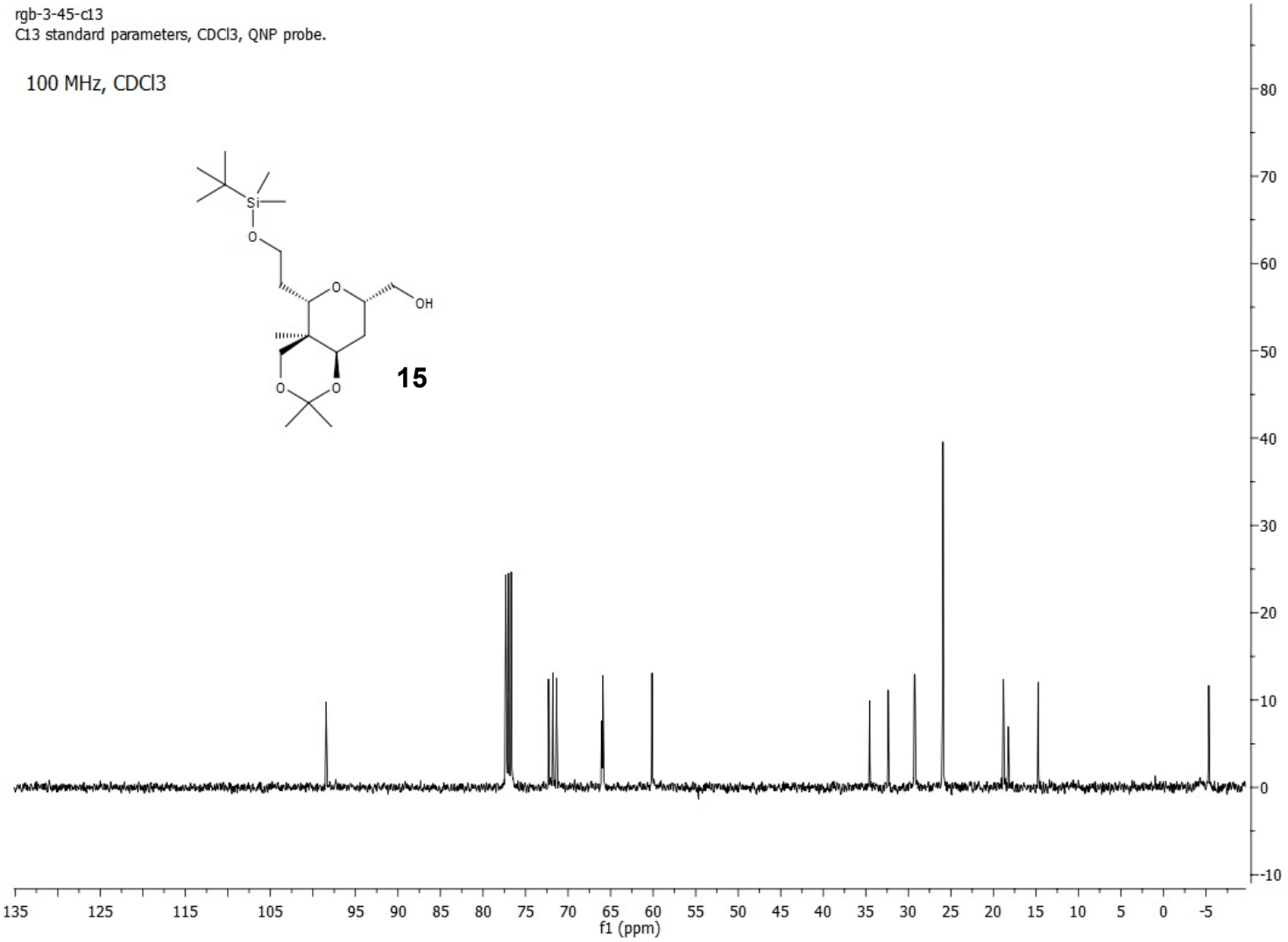


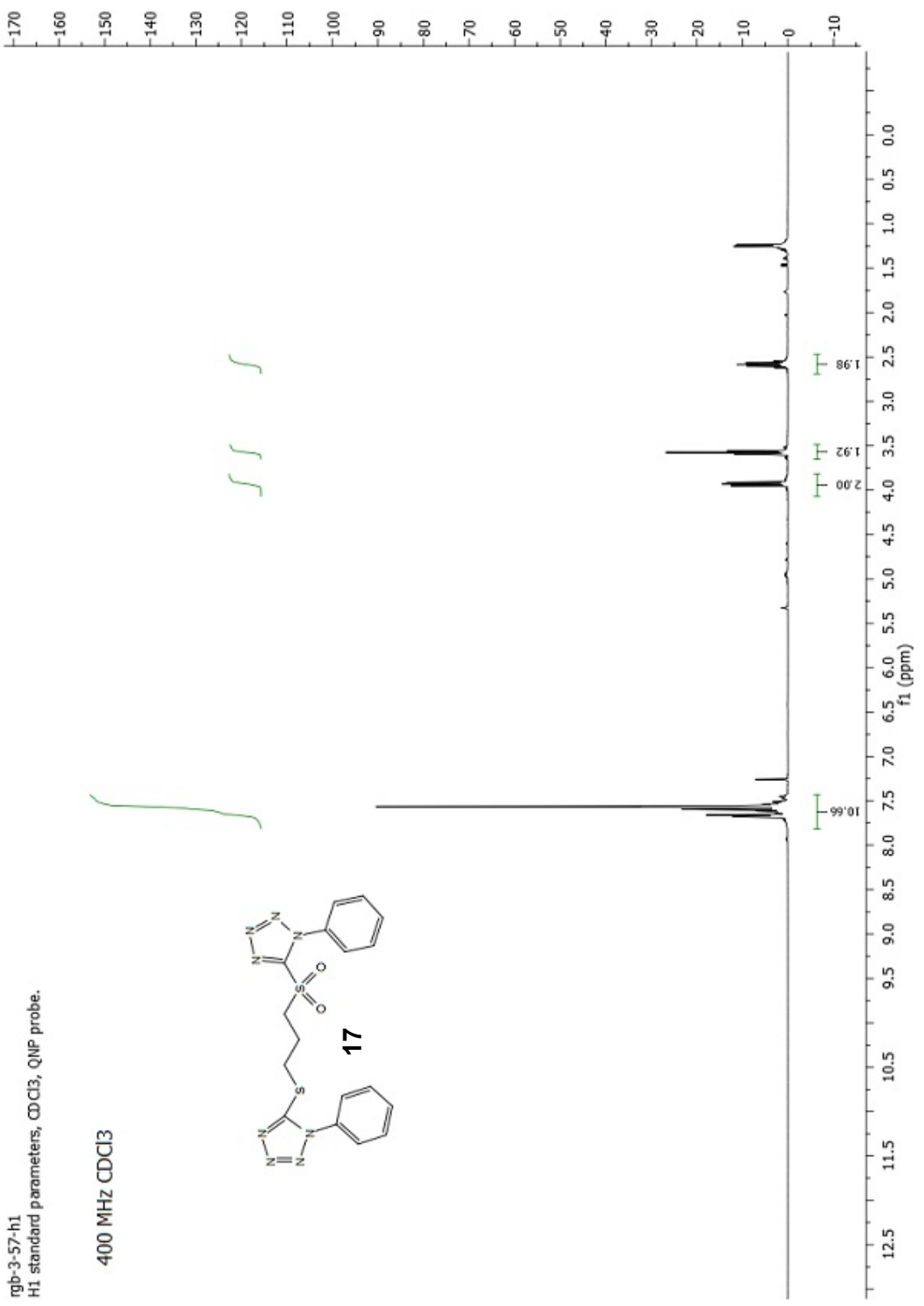

rgb-3-130-h1
H1 standard parameters, CDCl3, QNP probe.
400 MHz, CDCl3
14
OH
OH
4.87
2.00
1.10
1.25
1.09
2.06
1.08
3.20
1.96
2.01
8.75
3.00
6.00
f1 (ppm)

rgb-3-130-c13
C13 standard parameters, CDCl3, QNP probe.



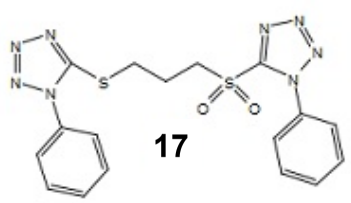

rgb-3-45-h1
H1 standard parameters, CDCl3, QNP probe.
400 MHz, CDCl3
Si
O
O
O
OH
O
O
15
1.00
2.03
2.18
1.09
2.01
1.05
1.03
0.94
0.98
0.99
2.99
2.86
0.96
9.05
2.96
6.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
90
80
70
60
50
40
30
20
10
0


rgb-3-45-c13
C13 standard parameters, CDCl3, QNP probe.
100 MHz, CDCl3
Si
O
O
OH
O
O
15
80
70
60
50
40
30
20
10
0
-10
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
f1 (ppm)


rgb-3-57-h1
H1 standard parameters, CDCl3, QNP probe.
400 MHz CDCl3
17
10.66
2.00
1.92
1.98
f1 (ppm)

rgb-3-57-c13
C13 standard parameters, CDCl3, QNP probe.

100 MHz CDCl3



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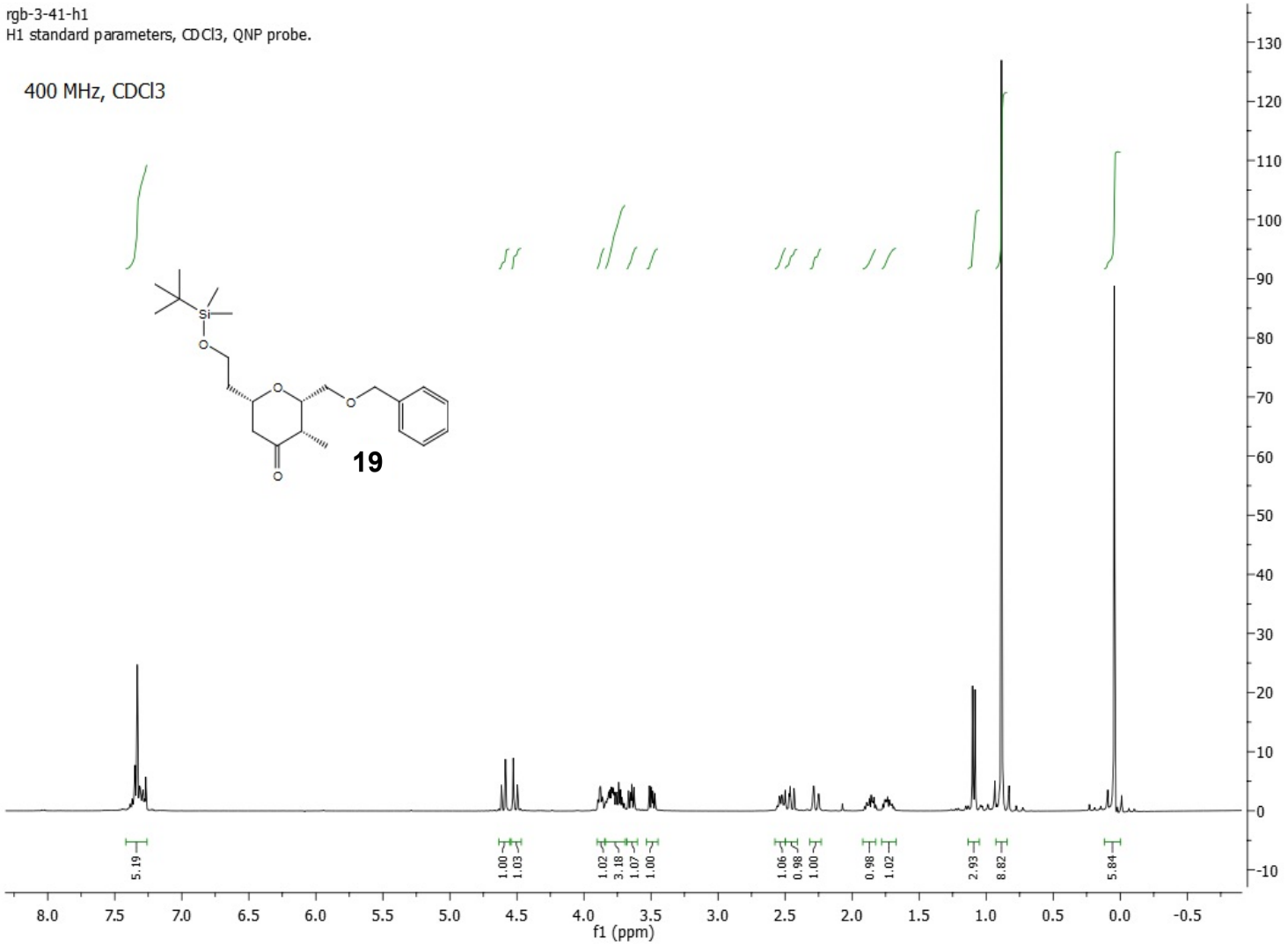
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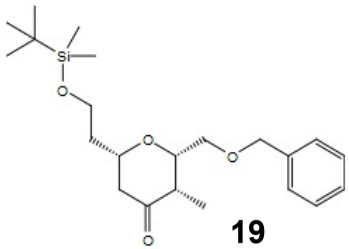
400 MHz, CDCl3
19
5.19
1.00
1.03
1.02
3.18
1.07
1.00
1.06
0.98
1.00
0.98
1.02
2.93
8.82
5.84
f1 (ppm)

rgb-3-41-c13
C13 standard parameters, CDCl3, QNP probe.

100 MHz, CDCl3



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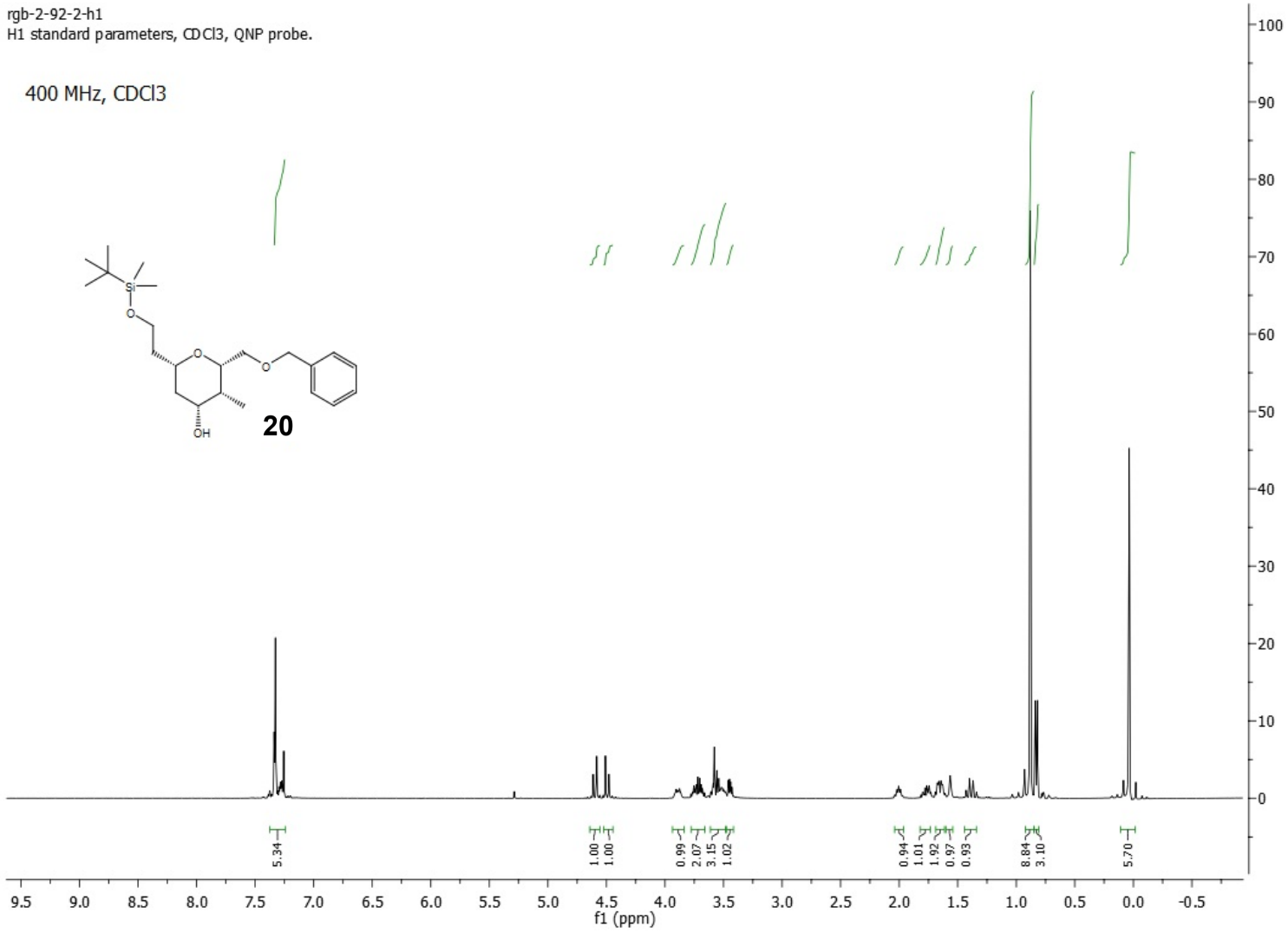
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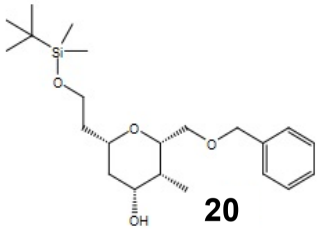
H1 standard parameters, CDCl3, QNP probe.
400 MHz, CDCl3
20
5.34
1.00
1.00
0.99
2.07
3.15
1.02
0.94
1.01
1.92
0.97
0.93
8.84
3.10
5.70
f1 (ppm)

rgb-2-92-2-c13
C13 standard parameters, CDCl3, QNP probe.

100 MHz, CDCl3



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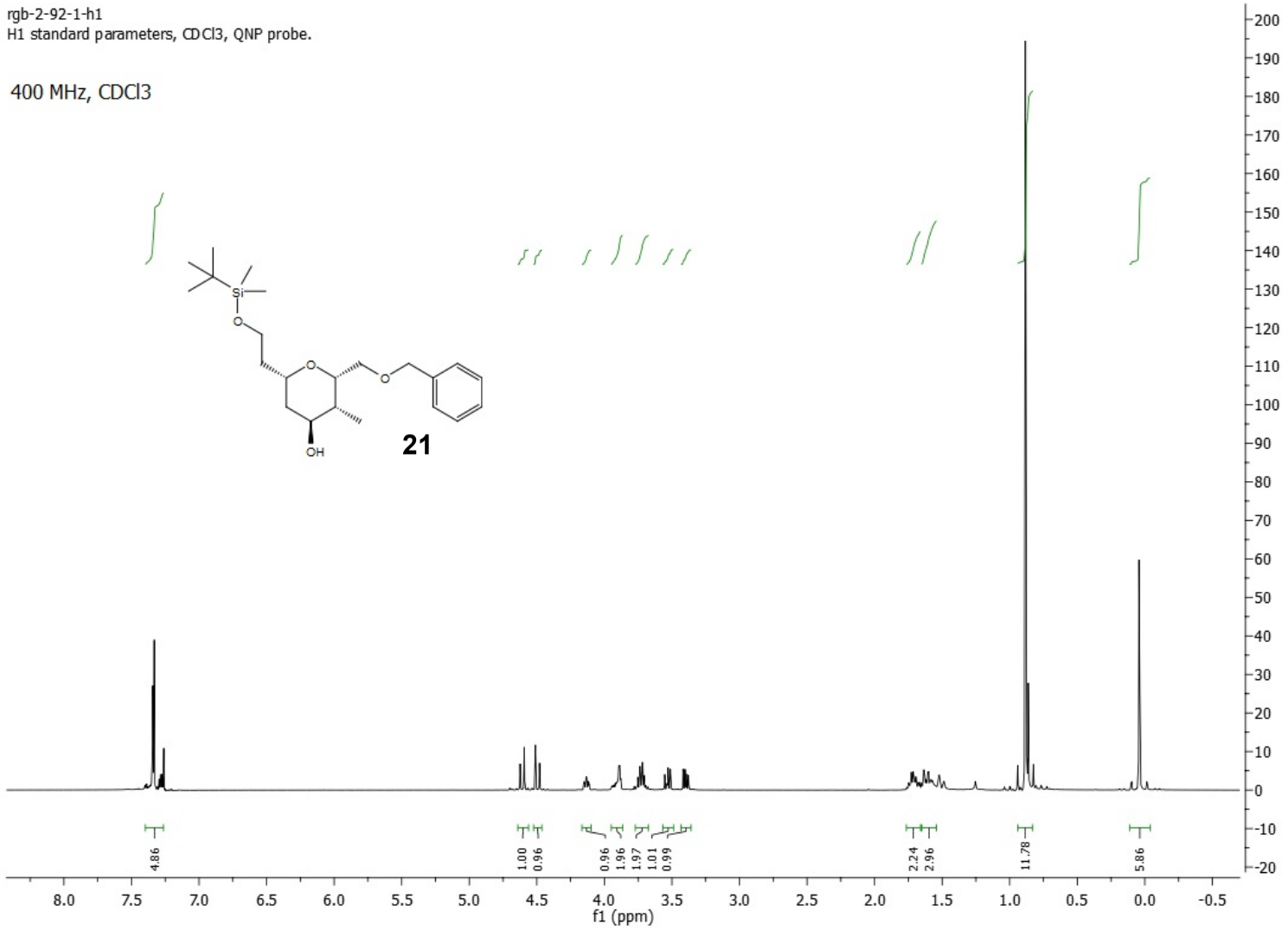
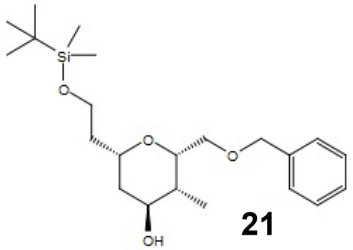

rgb-2-92-1-h1
H1 standard parameters, CDCl3, QNP probe.
400 MHz, CDCl3
Si
O
O
O
OH
21
4.86
1.00
0.96
0.96
1.96
1.97
1.01
0.99
2.24
2.96
11.78
5.86
f1 (ppm)

rgb-2-92-1-c13
C13 standard parameters, CDCl3, QNP probe.

100 MHz, CDCl3



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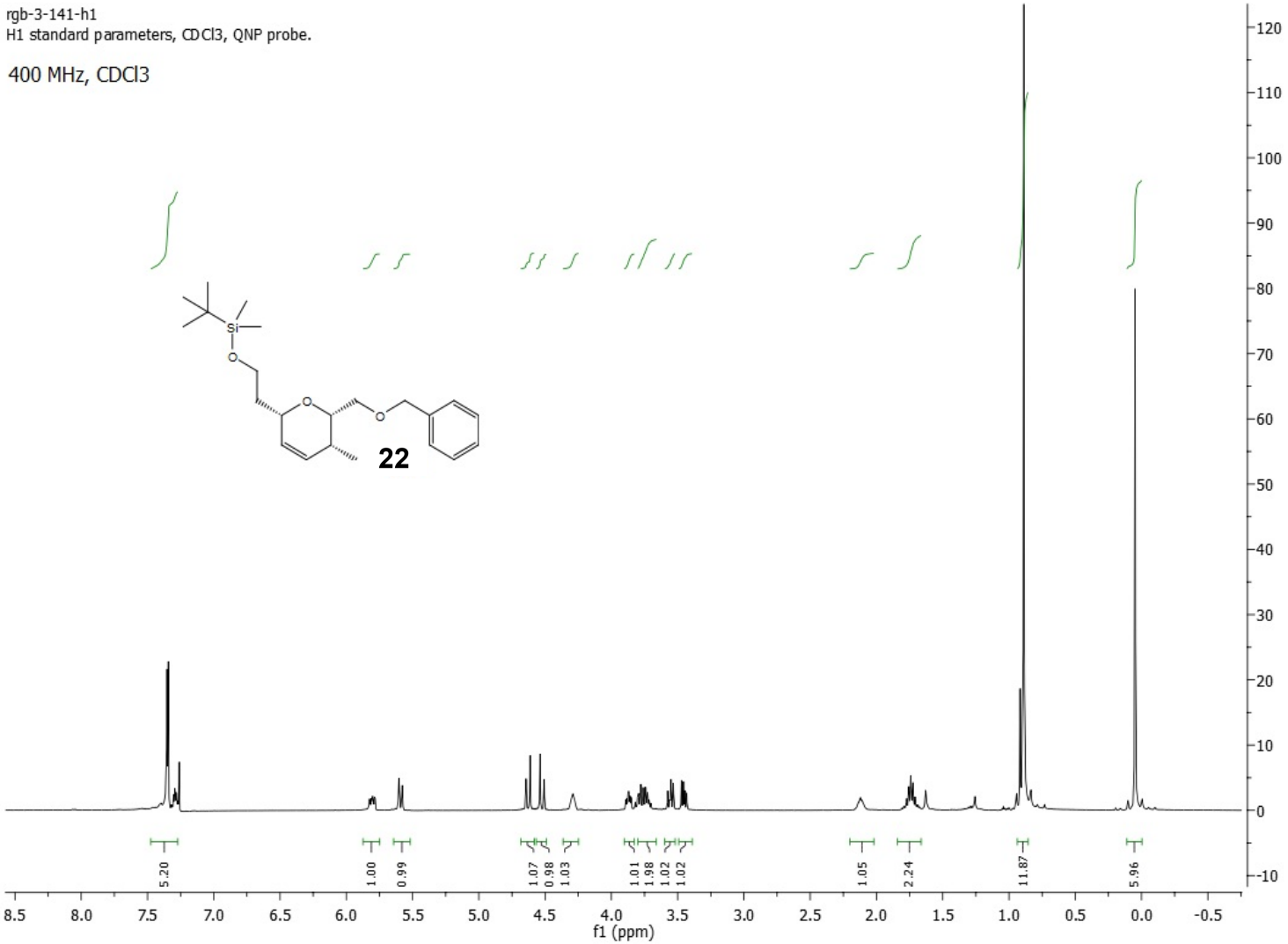
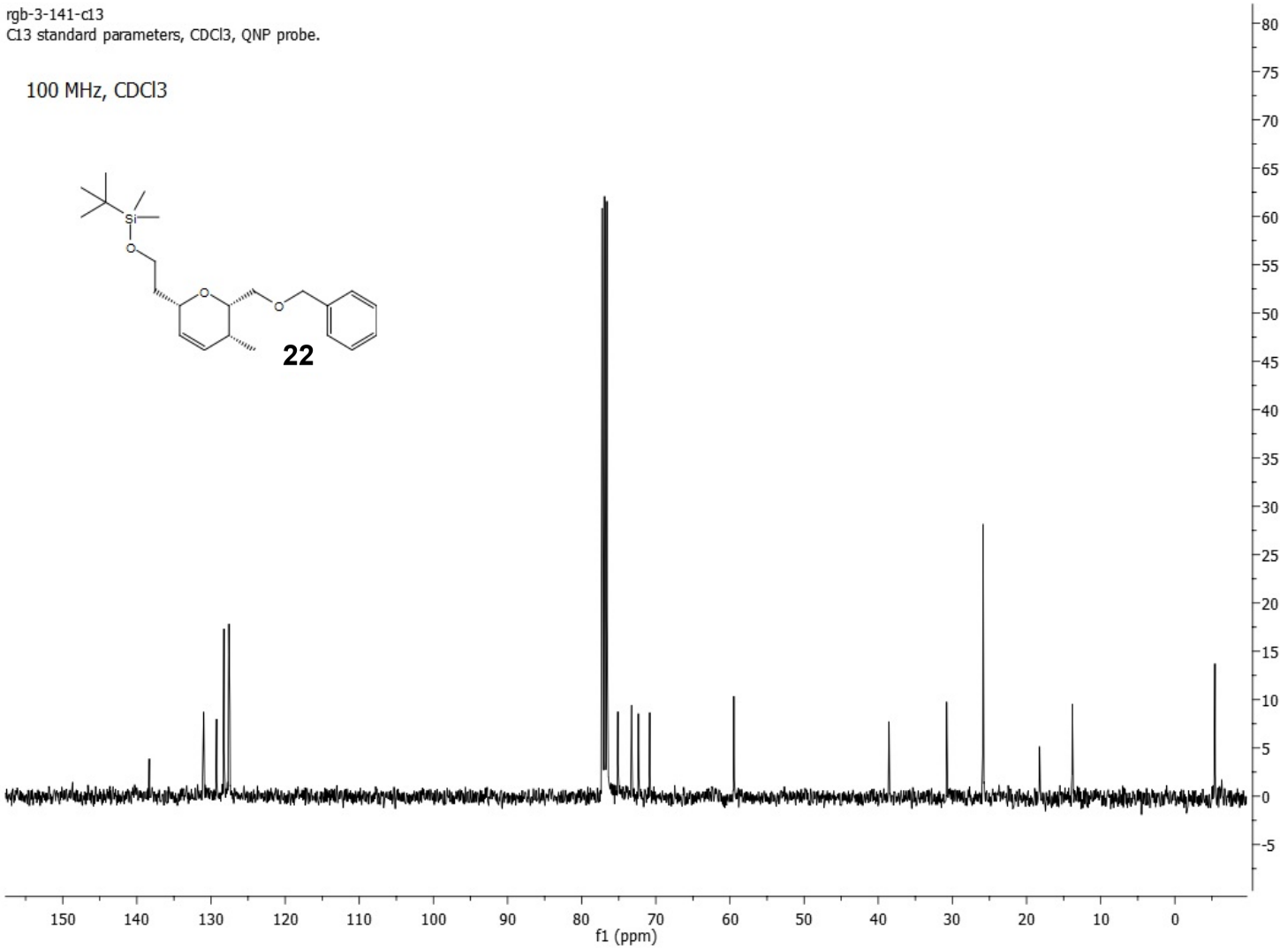

rgb-3-141-h1
H1 standard parameters, CDCl3, QNP probe.
400 MHz, CDCl3
Si
O
O
O
22
5.20
1.00
0.99
1.07
0.98
1.03
1.01
1.98
1.02
1.02
1.05
2.24
11.87
5.96
f1 (ppm)


rgb-3-141-c13
C13 standard parameters, CDCl3, QNP probe.
100 MHz, CDCl3
Si
O
O
O
22
80
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70
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60
55
50
45
40
35
30
25
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15
10
5
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50
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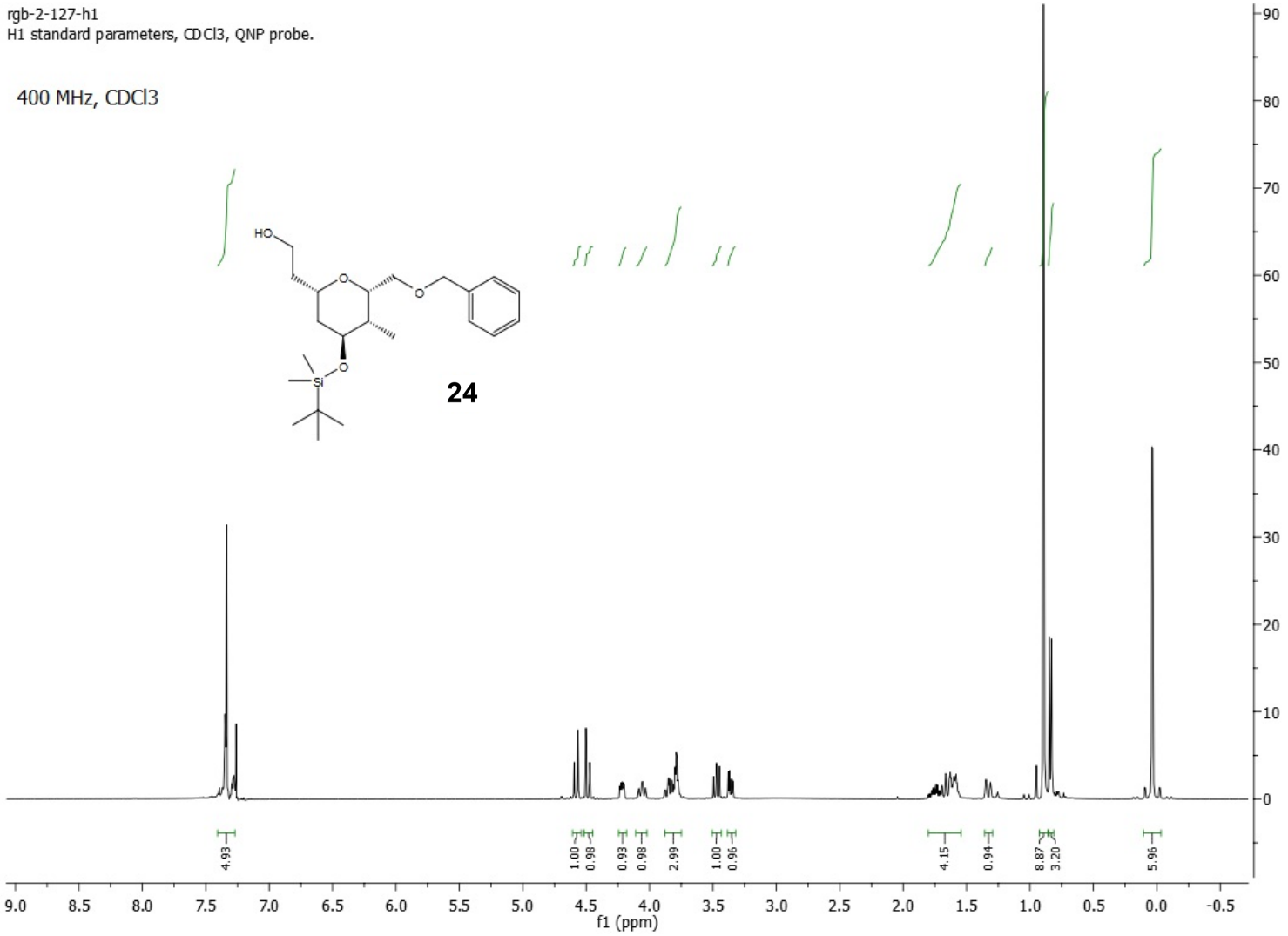
10
0
f1 (ppm)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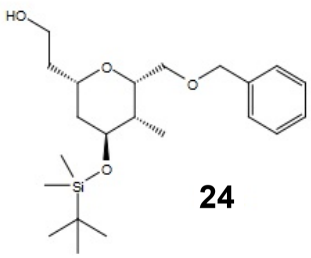
400 MHz, CDCl3
HO
O
O
O
Si
O
24
4.93
1.00
0.98
0.93
0.98
2.99
1.00
0.96
4.15
0.94
8.87
3.20
5.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
90
80
70
60
50
40
30
20
10
0

rgb-2-127-c13
C13 standard parameters, CDCl3, QNP probe.

100 MHz, CDCl3



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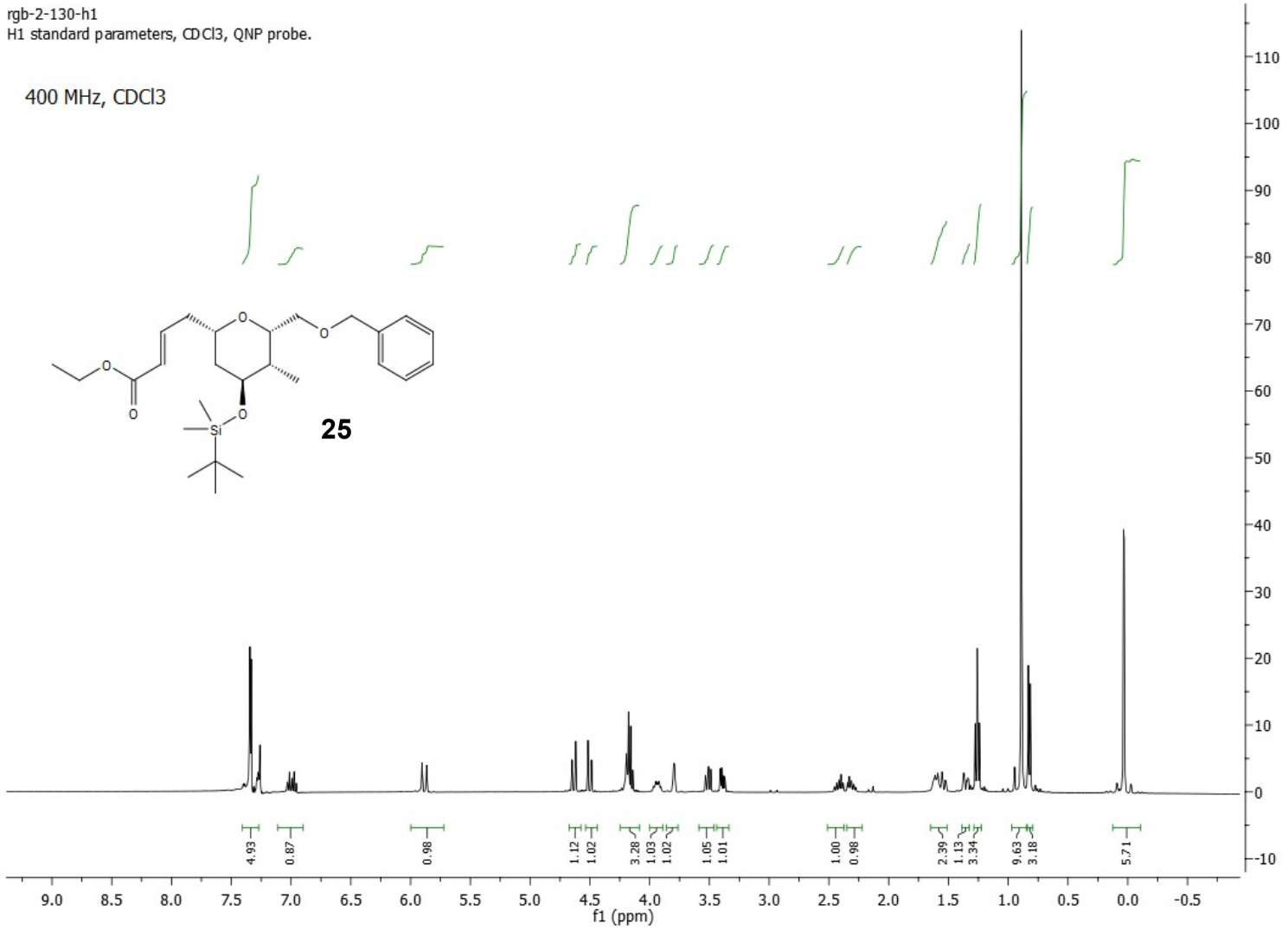
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400 MHz, CDCl3
25
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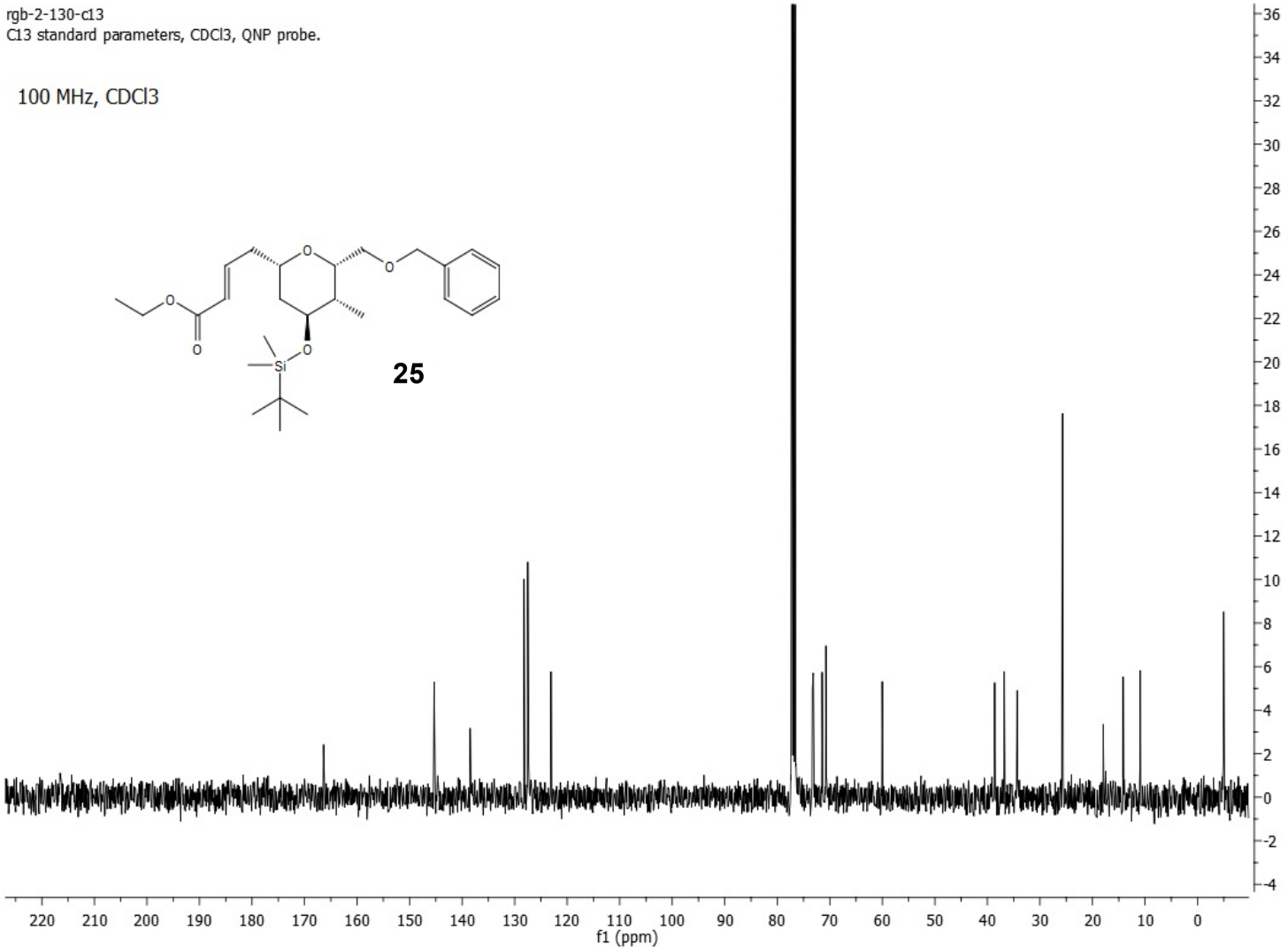
0.87
0.98
1.12
1.02
3.28
1.03
1.02
1.05
1.01
1.00
0.98
2.39
1.13
3.34
9.63
3.18
5.71
f1 (ppm)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C13 standard parameters, CDCl3, QNP probe.
100 MHz, CDCl3
25
f1 (ppm)