Introduction of Aryl Fluorosulfates into the Realm of Catellani Reaction Substrates

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1 The two-chamber reactors

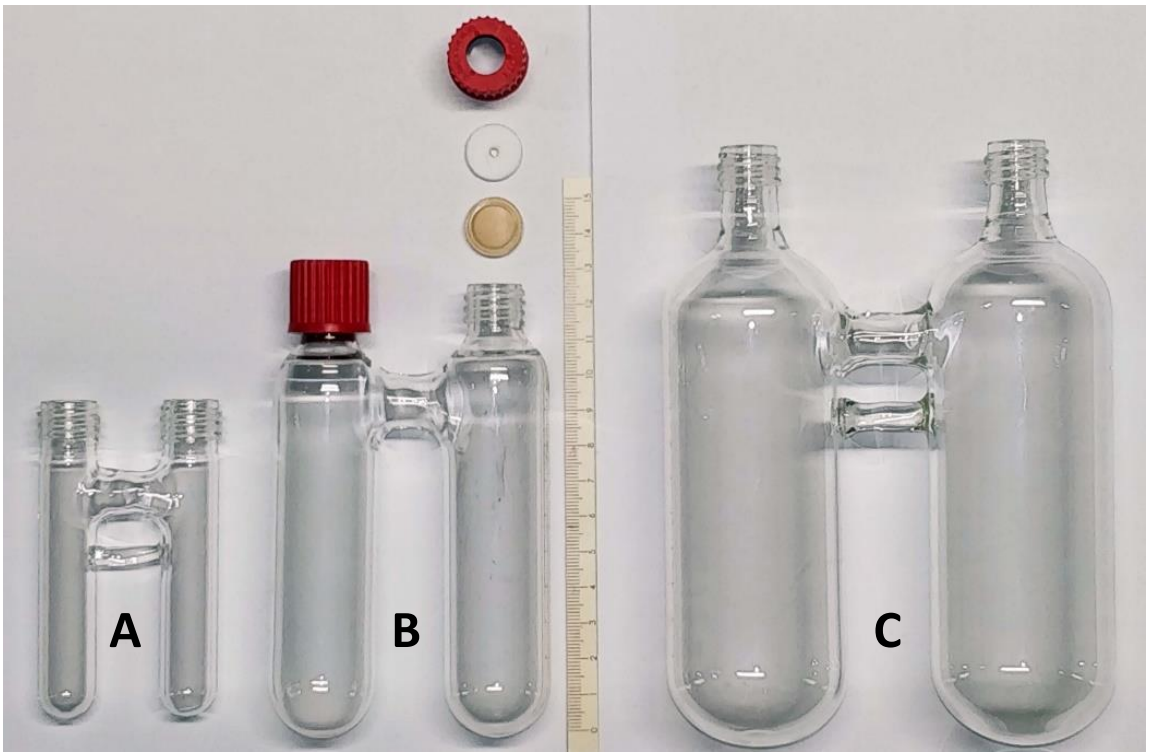


Figure S1-1. A small two chamber reactor (**A**, V_{total} = 10–12 mL), an intermediate-size two-chamber reactor (**B**, V_{total} = 100–110 mL) with GL14 hollow cap, PTFE disk and septum assembly, and a large two-chamber reactor (**C**, V_{total} = 400–425 mL). Invented by the Skrydstrup group.[2]

2 Optimization of reaction parameters for activated substrates

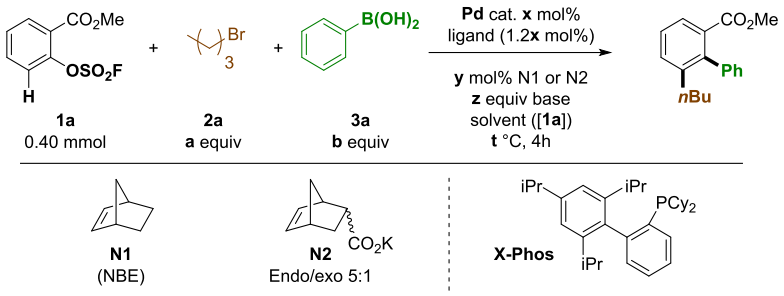


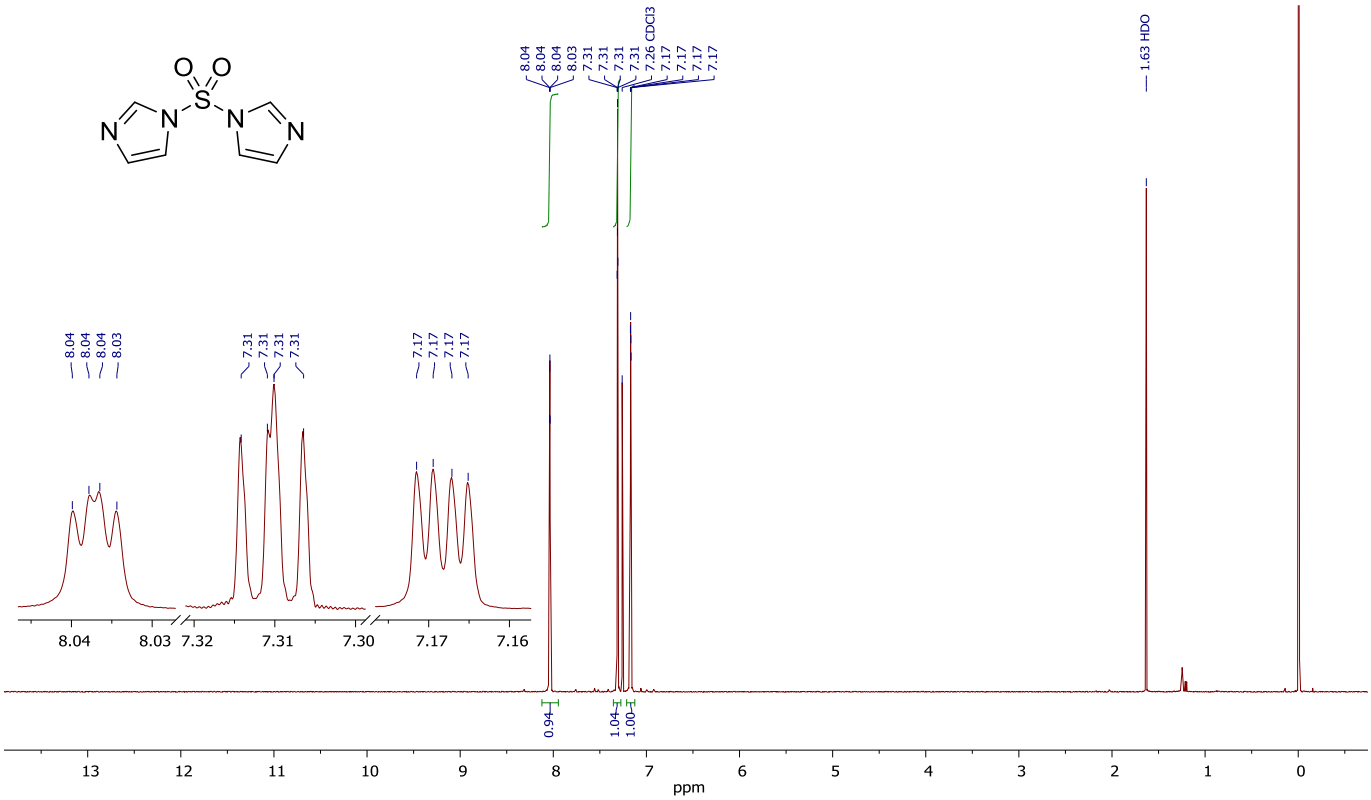
Table S1. Optimization of reaction conditions. *Groups of directly comparable single-variable changes are shaded accordingly.*

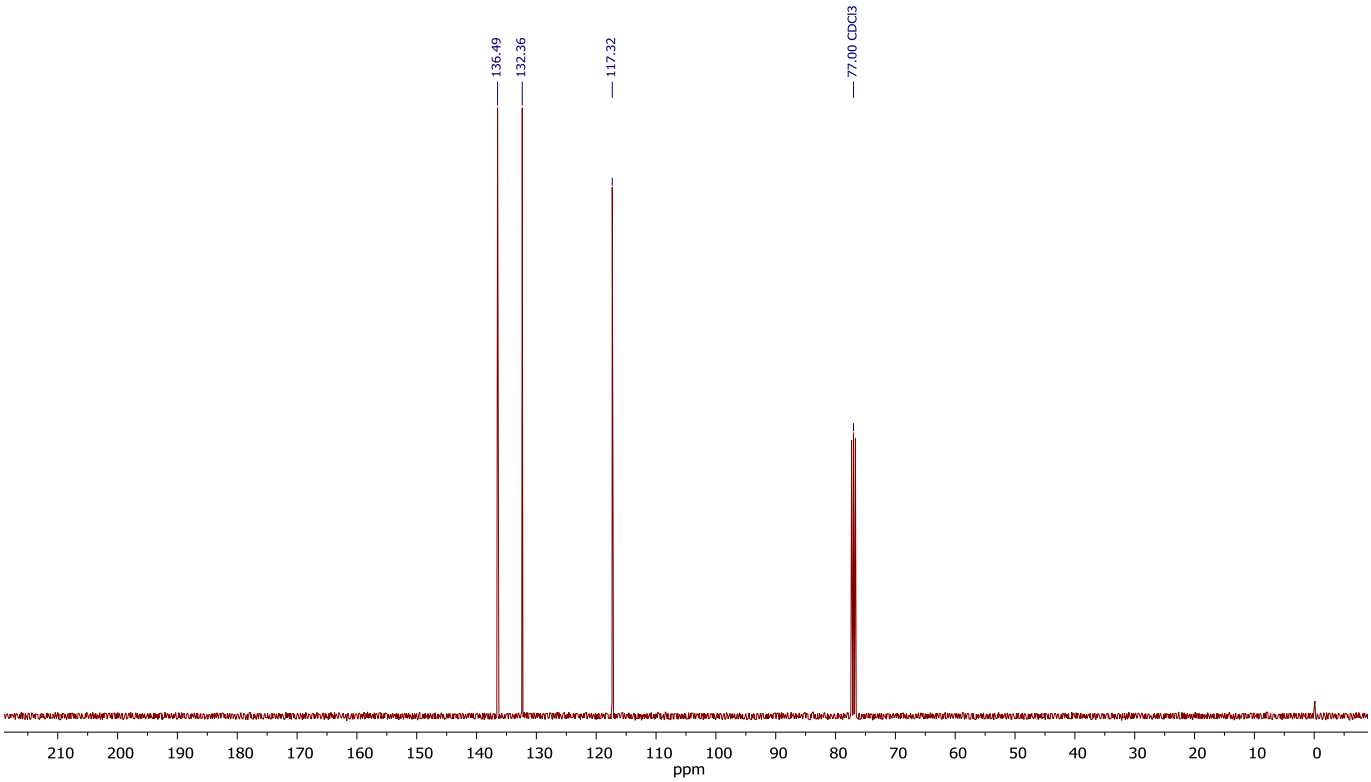
Entry	**a**	**b**	**Pd** cat.	**x**	Ligand	**y**	Base (**z**)	Solvent	[**1a**], M	**t**, °C	Yield
1	2.00	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	DMF	0.20	100	35%
2	2.00	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	DMF	0.20	90	46%
3	2.00	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	DMF	0.20	80	65%
4	3.00	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	DMF	0.20	80	57%
5	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	DMF	0.20	80	**69%**
6	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	DMF	0.20	70	**74%**
7	1.50	1.20	$Pd(OAc)_2$	2	—	100 (**N1**)	K_2CO_3 (6.0)	DMF	0.20	70	59%
8	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N2**)	K_2CO_3 (5.0)	DMF	0.20	70	49%[a]
9	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	DMAc	0.20	70	65%
10	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	NMP	0.20	70	60%
11	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	MeCN	0.20	70	4%
12	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	GVL[b]	0.20	70	0%
13	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	DMF	0.20	60	61%[c]
14	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	DMF	0.20	50	10%[c]
15	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	Cs_2CO_3 (6.0)	DMF	0.20	70	68%
16	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	KOAc (6.0)	DMF	0.20	70	26%
17	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	TEA (6.0)	DMF	0.20	70	0%
18	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	Bu_4NOAc (6.0)	DMF	0.20	70	0%
19	1.50	1.20	Pd/C (10%)	10	—	100 (**N1**)	K_2CO_3 (6.0)	DMF	0.20	70	5%
20	1.50	1.20	$Pd(PPh_3)_4$	5	—	100 (**N1**)	K_2CO_3 (6.0)	DMF	0.20	70	0%[d]
21	1.50	1.20	$Pd(OAc)_2$	5	—	100 (**N1**)	K_2CO_3 (6.0)	DMF	0.50	70	64%
22	1.50	1.20	$Pd(OAc)_2$	5	—	50 (**N1**)	K_2CO_3 (6.0)	DMF	0.50	70	**78%**
23	1.20	1.20	$Pd(OAc)_2$	5	—	50 (**N1**)	K_2CO_3 (6.0)	DMF	0.50	70	**81%**
24	1.20	1.20	$Pd(OAc)_2$	5	—	50 (**N1**)	K_2CO_3 (6.0)	DMF	1.00	70	54%
25	1.20	1.20	$Pd(OAc)_2$	5	—	25 (**N1**)	K_2CO_3 (6.0)	DMF	0.50	70	76%[e]
26	1.10	1.20	$Pd(OAc)_2$	5	—	50 (**N1**)	K_2CO_3 (6.0)	DMF	0.50	70	79%
27	1.20	1.25[f]	$Pd(OAc)_2$	5	—	50 (**N1**)	K_2CO_3 (6.0)	DMF	0.50	70	**82%**
28	1.20	1.25[f]	$Pd(OAc)_2$	7.5	—	50 (**N1**)	K_2CO_3 (6.0)	DMF	0.50	70	83%[g]
29	1.20	1.25[f]	$Pd(OAc)_2$	5	X-Phos	50 (**N1**)	K_2CO_3 (6.0)	DMF	0.50	70	74%

[a]Complicated purification. [b]γ-valerolactone. [c]Reaction conducted for 8 hours. [d]2-Carboxymethylbiphenyl was formed exclusively. [e]Sharply increased amount of 2-Carboxymethylbiphenyl. [f]The amount was increased to ensure complete conversion over multiple repetitions. [g]The increase in yield was insufficient to justify the 50% increase in catalyst loading.

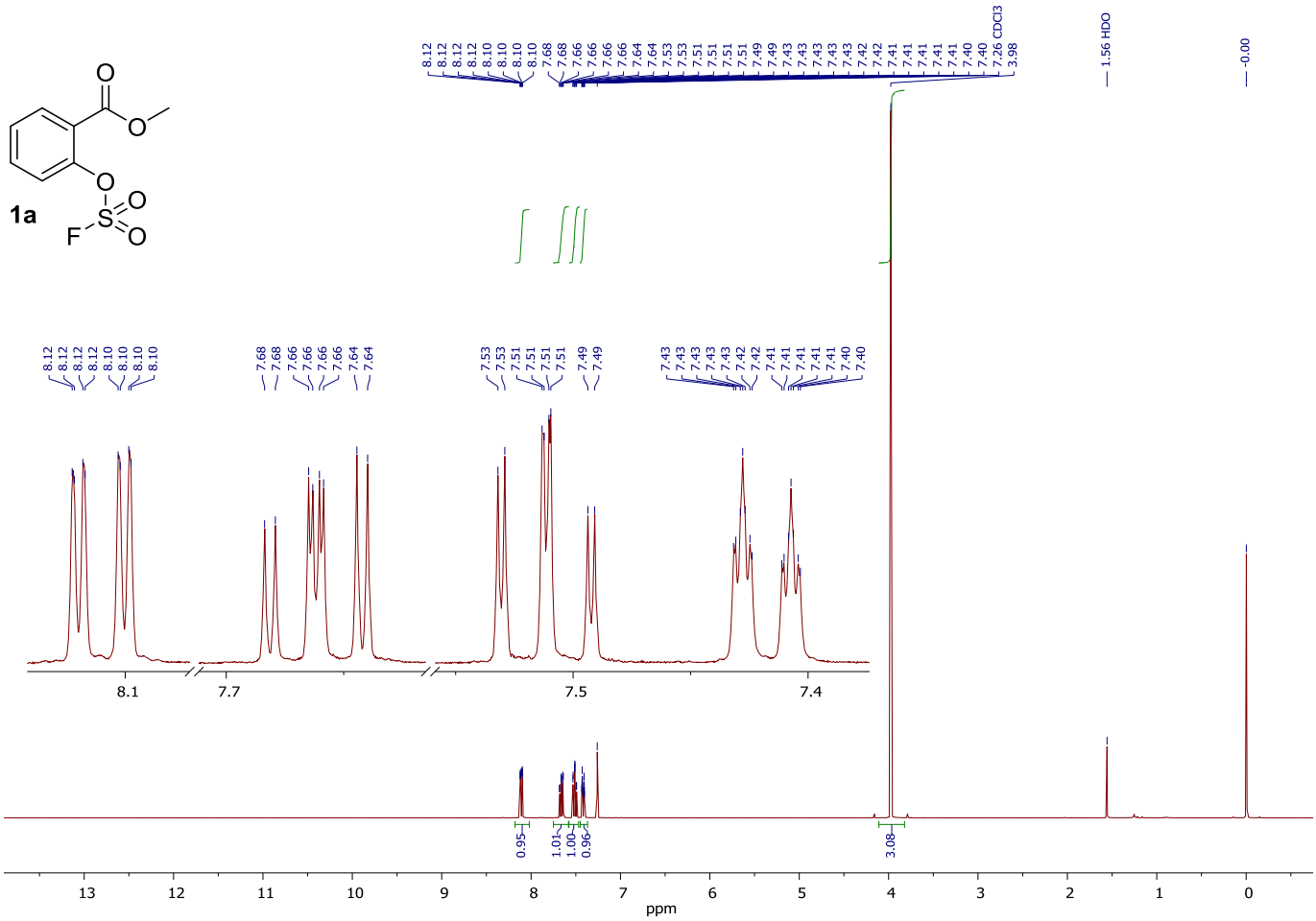
3 NMR spectra of the synthesized compounds

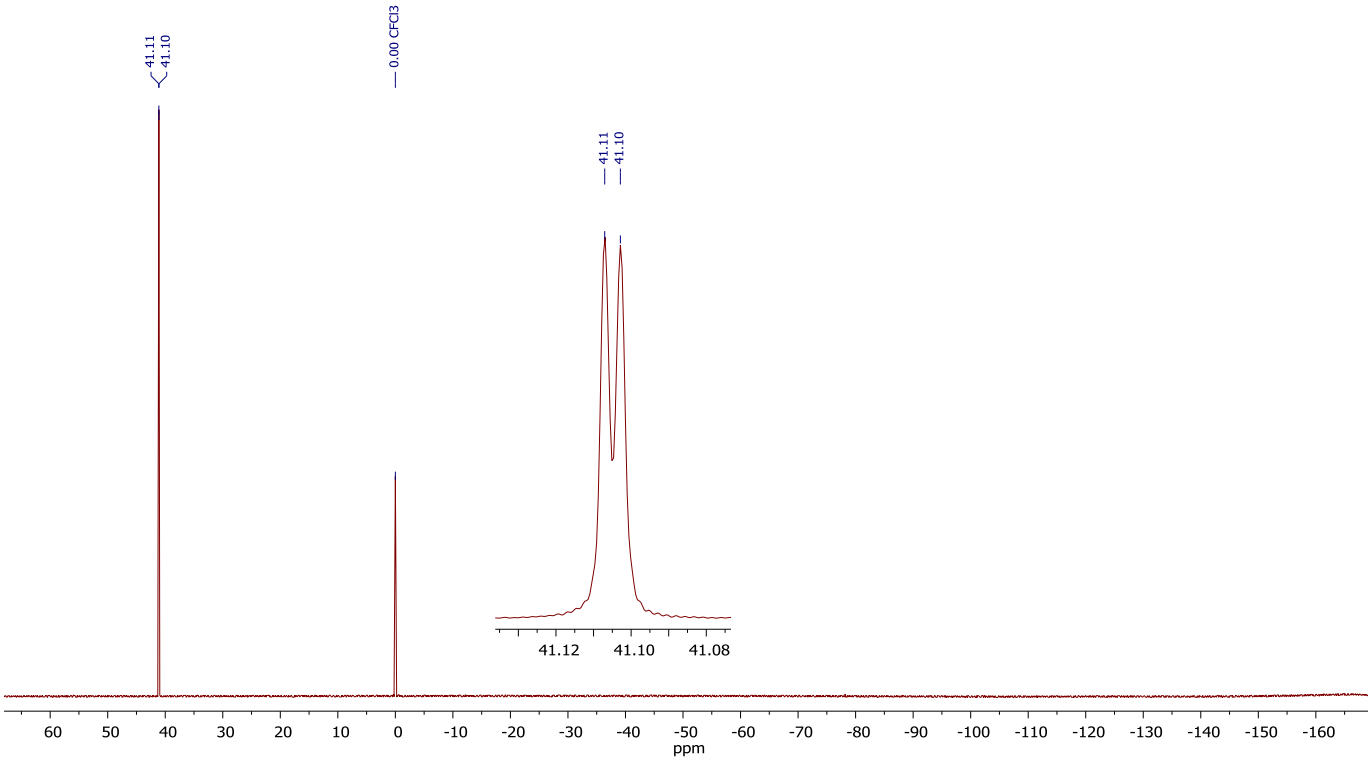
3.1 1,1'-sulfonyldiimidazole

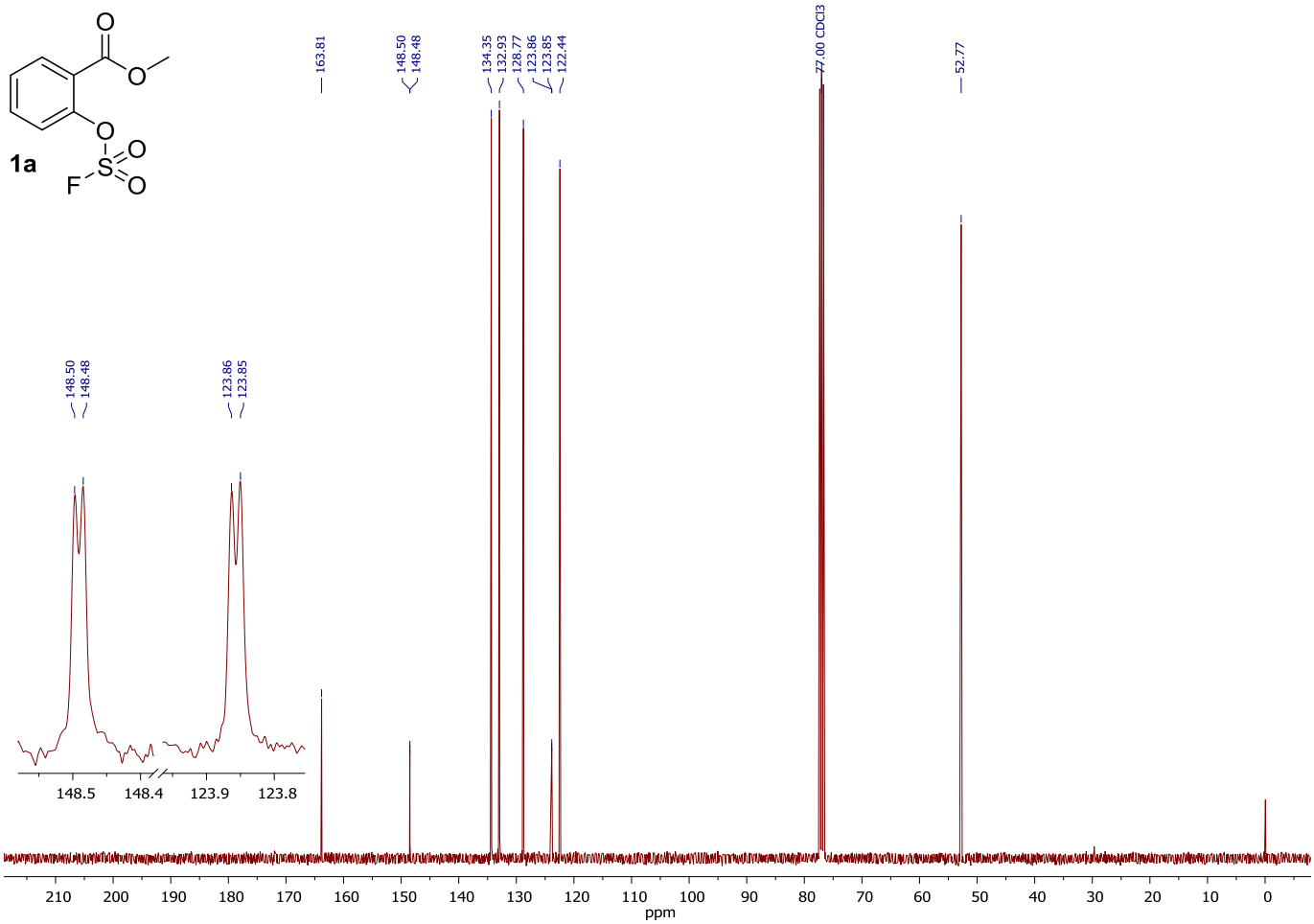




3.2 Fluorosulfates 1a-1u



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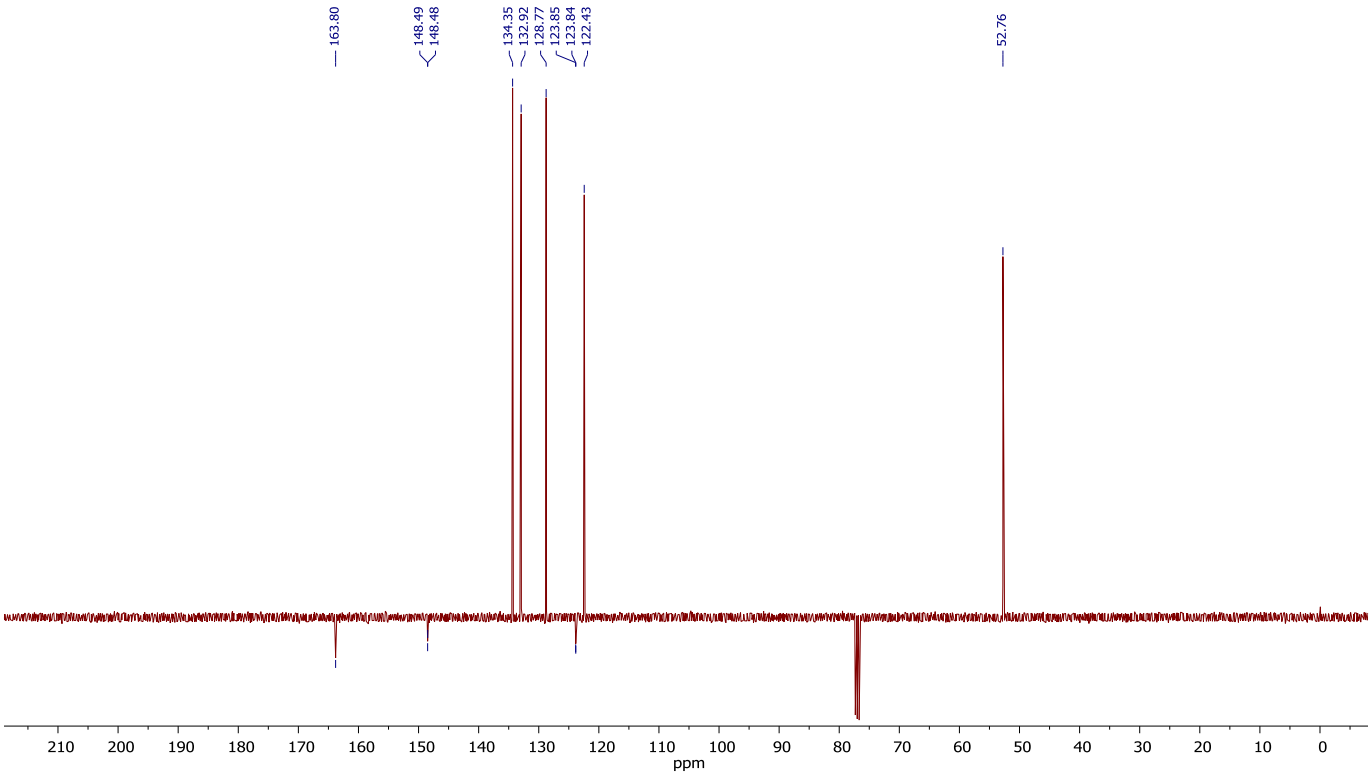
148.4
123.9
123.8
ppm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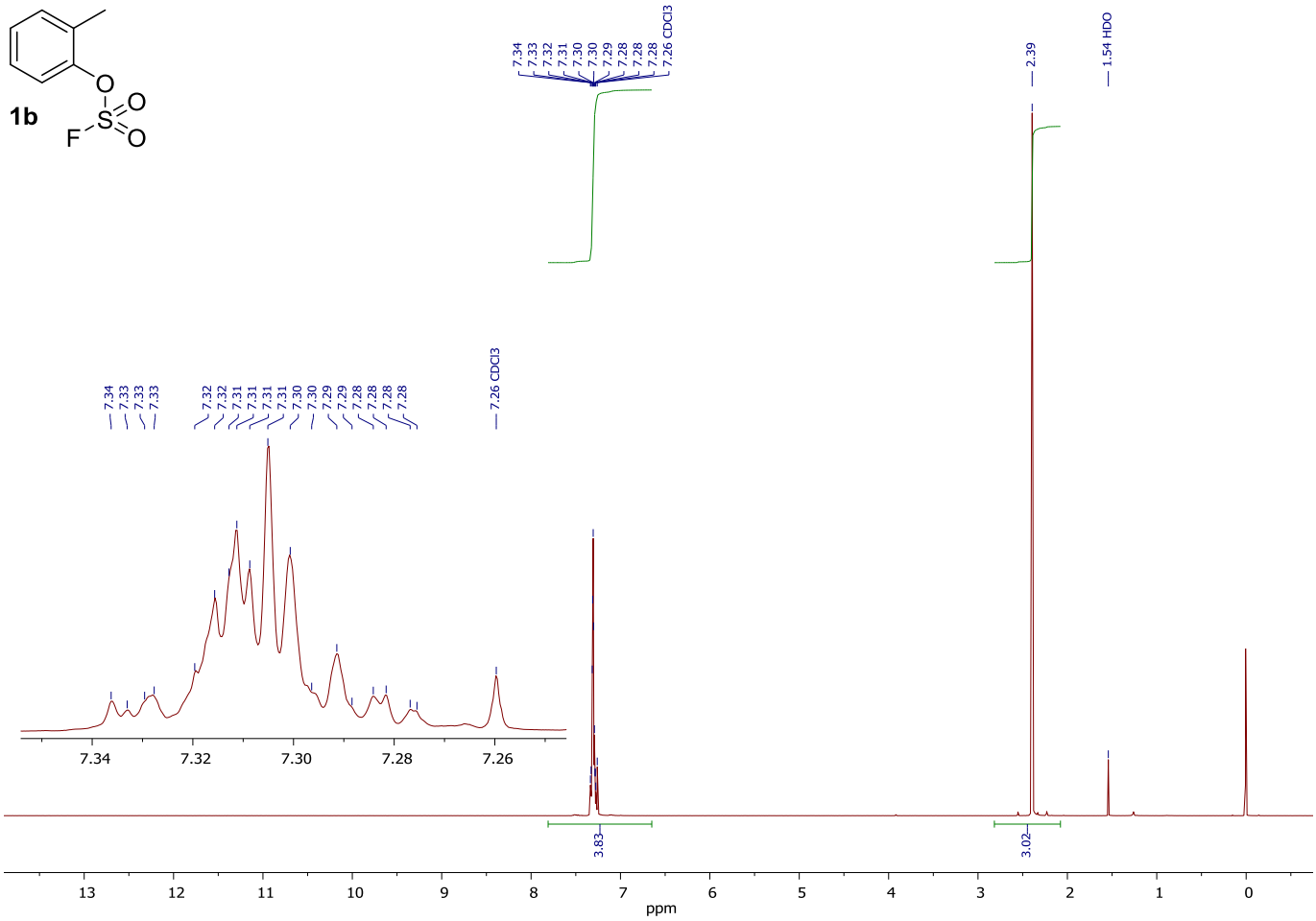
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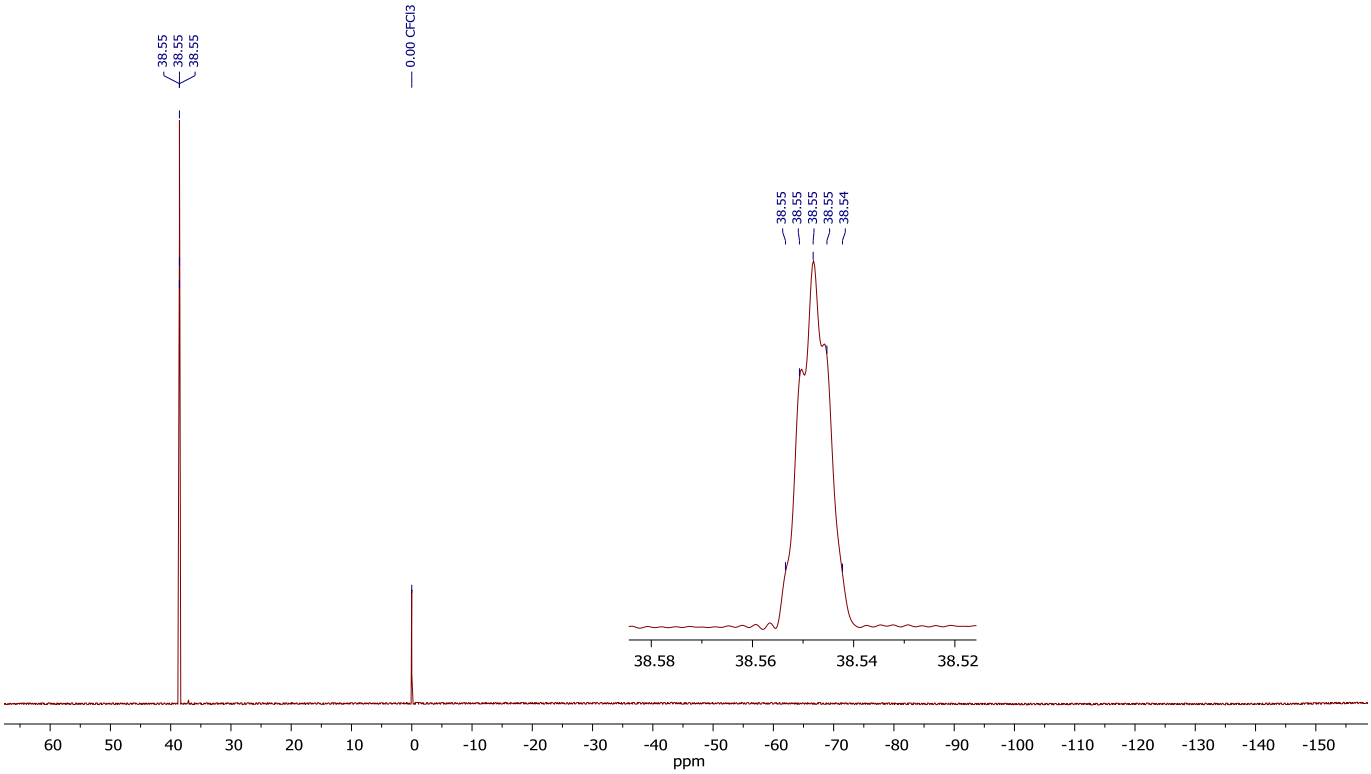
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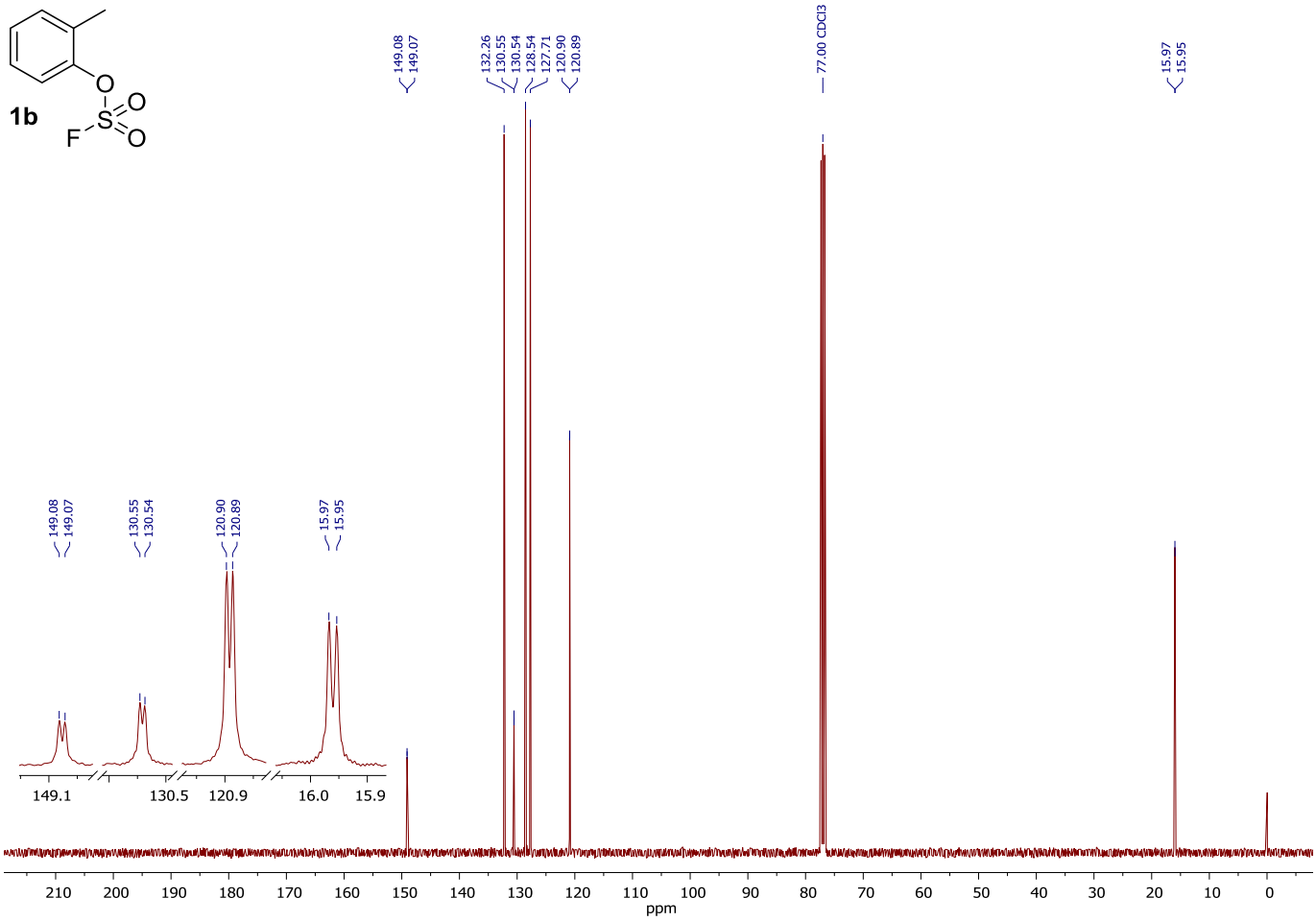
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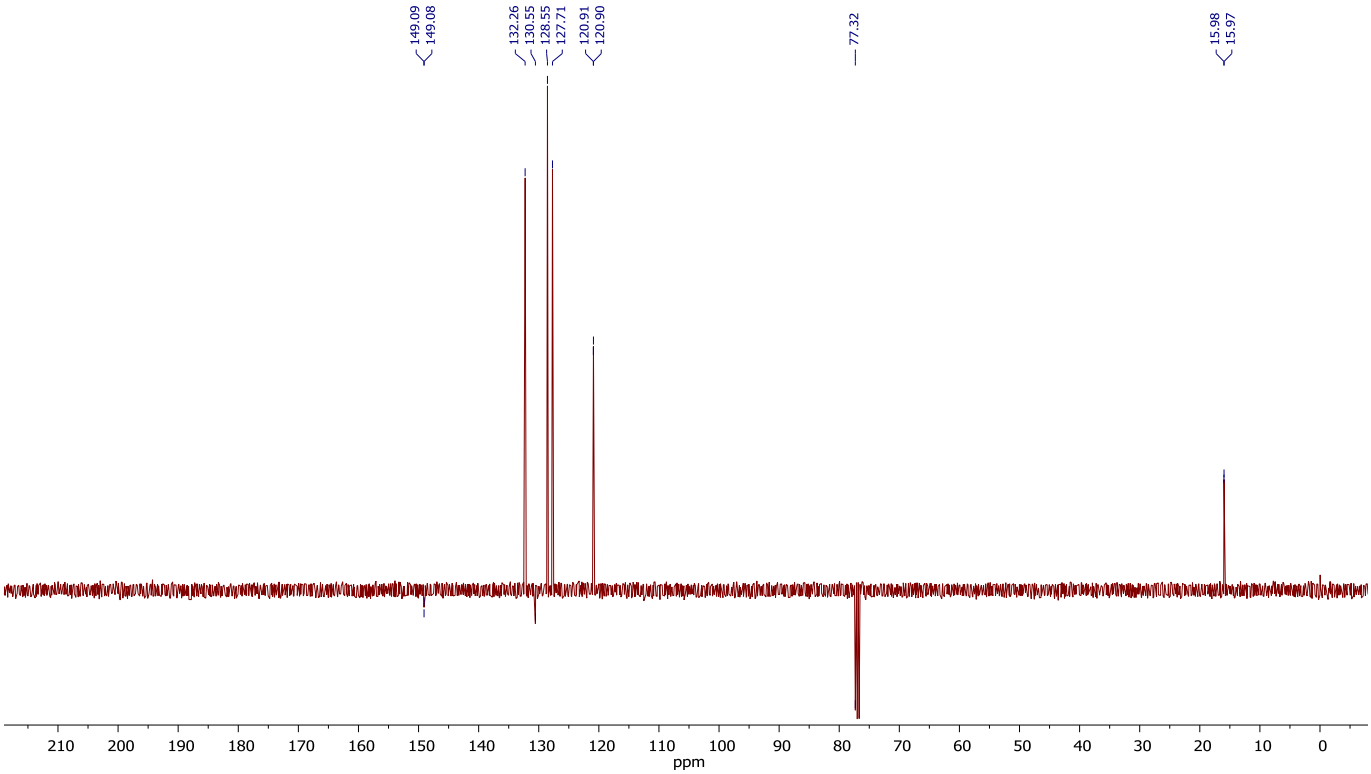
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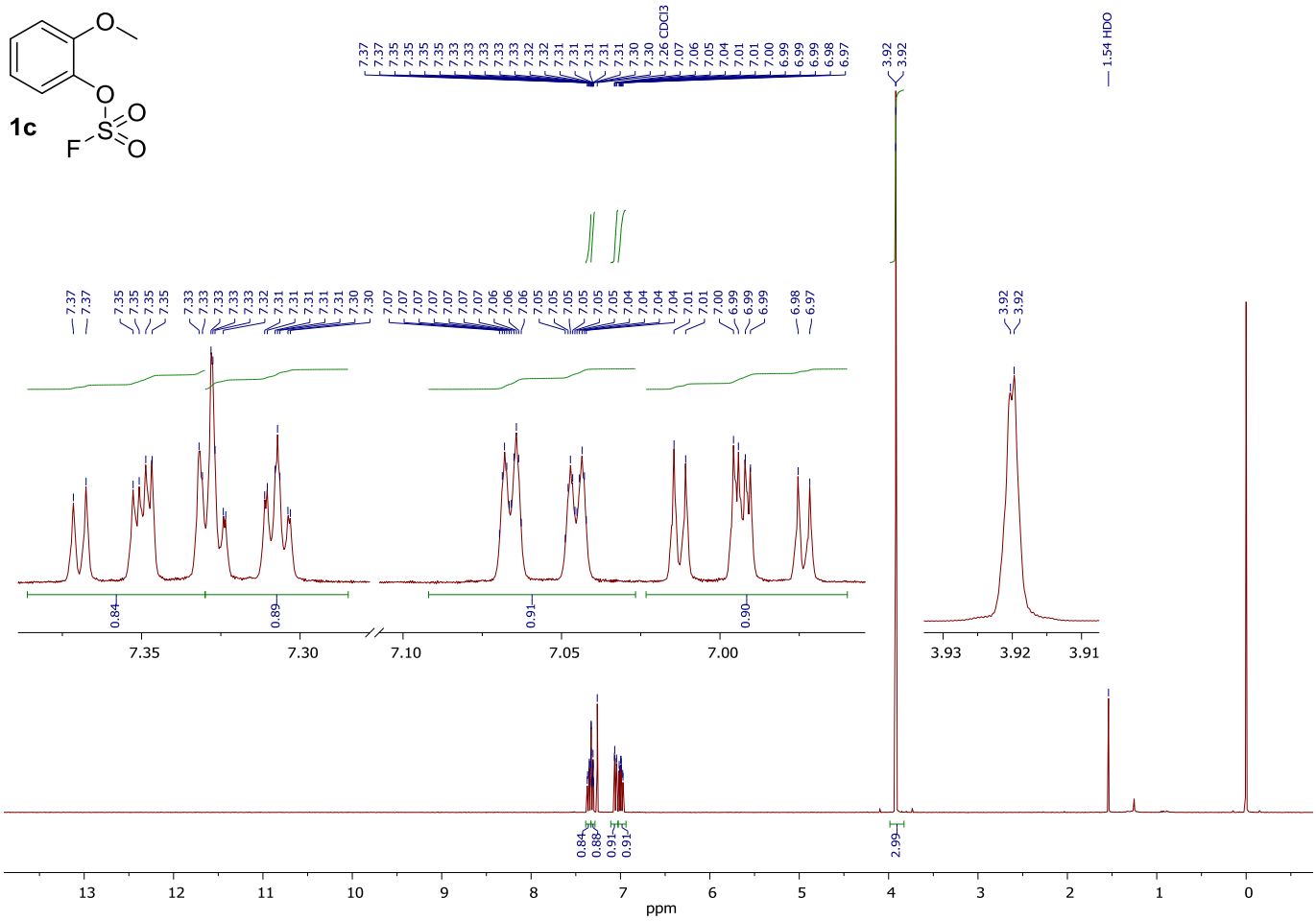
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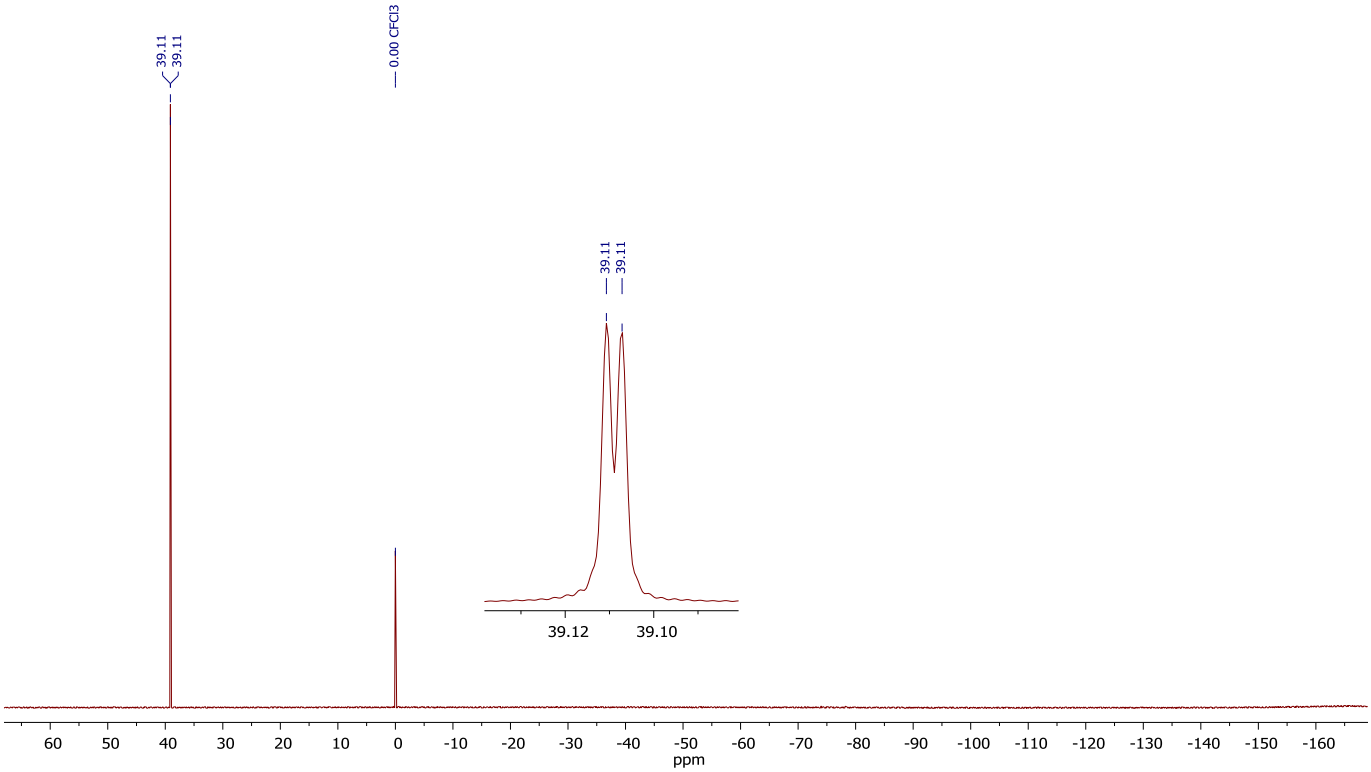
ppm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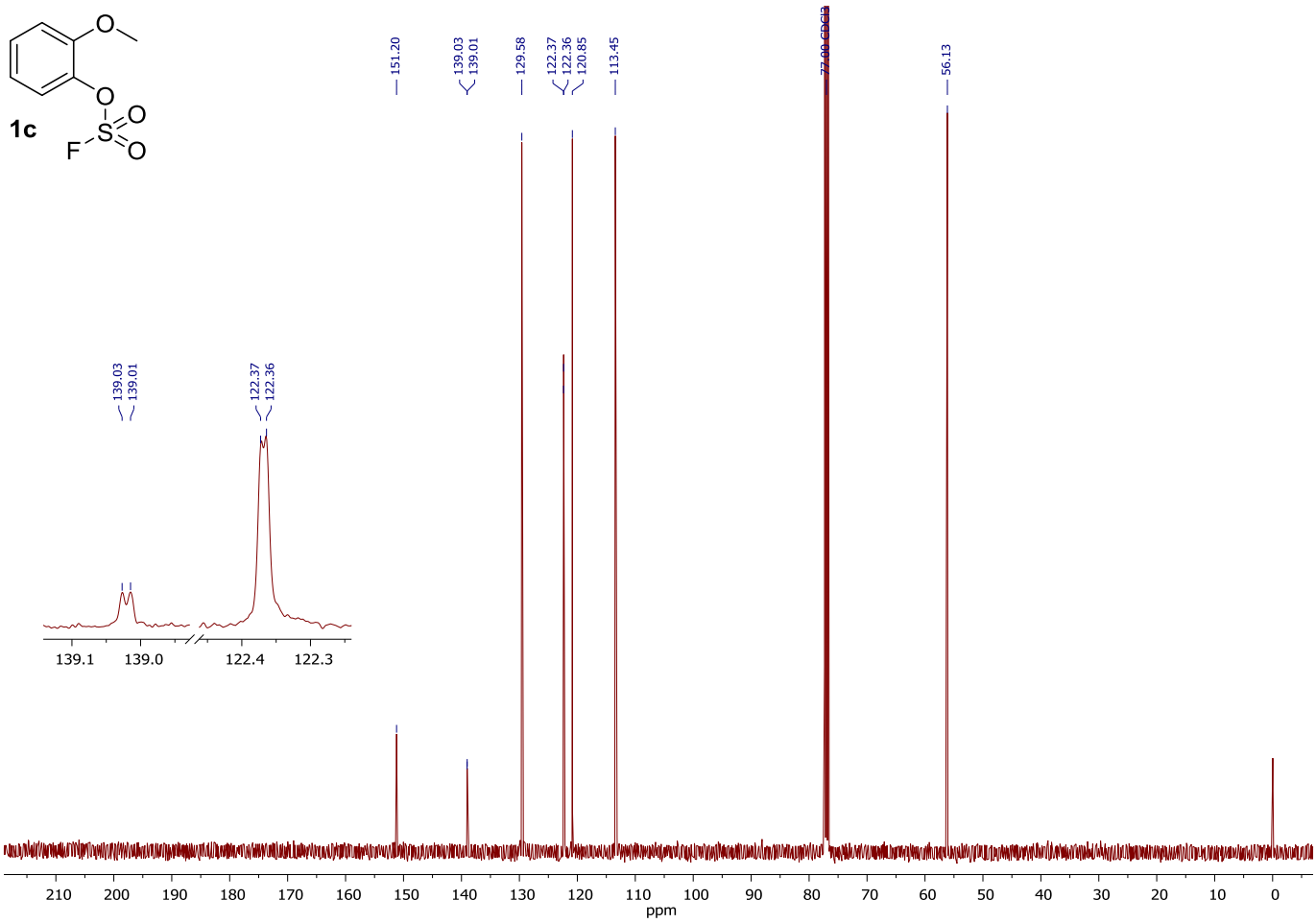
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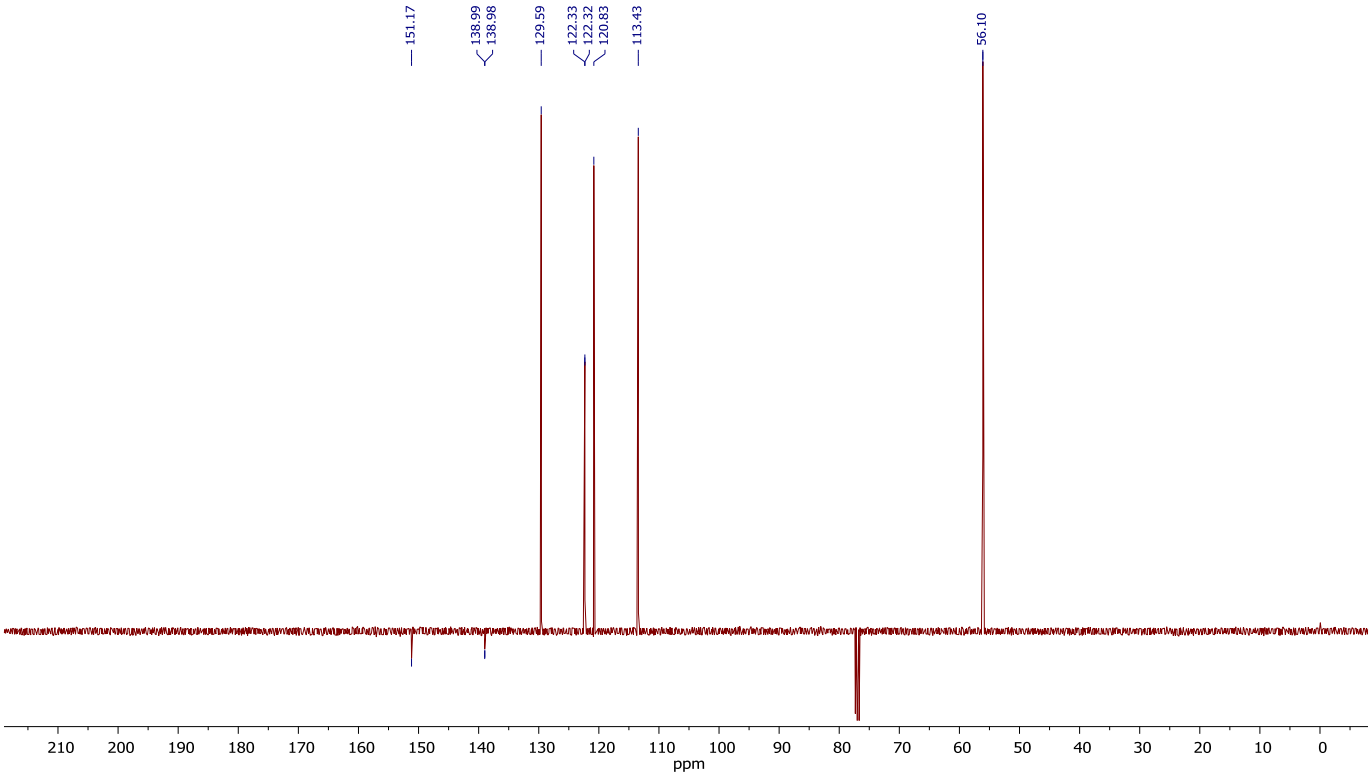
122.3
ppm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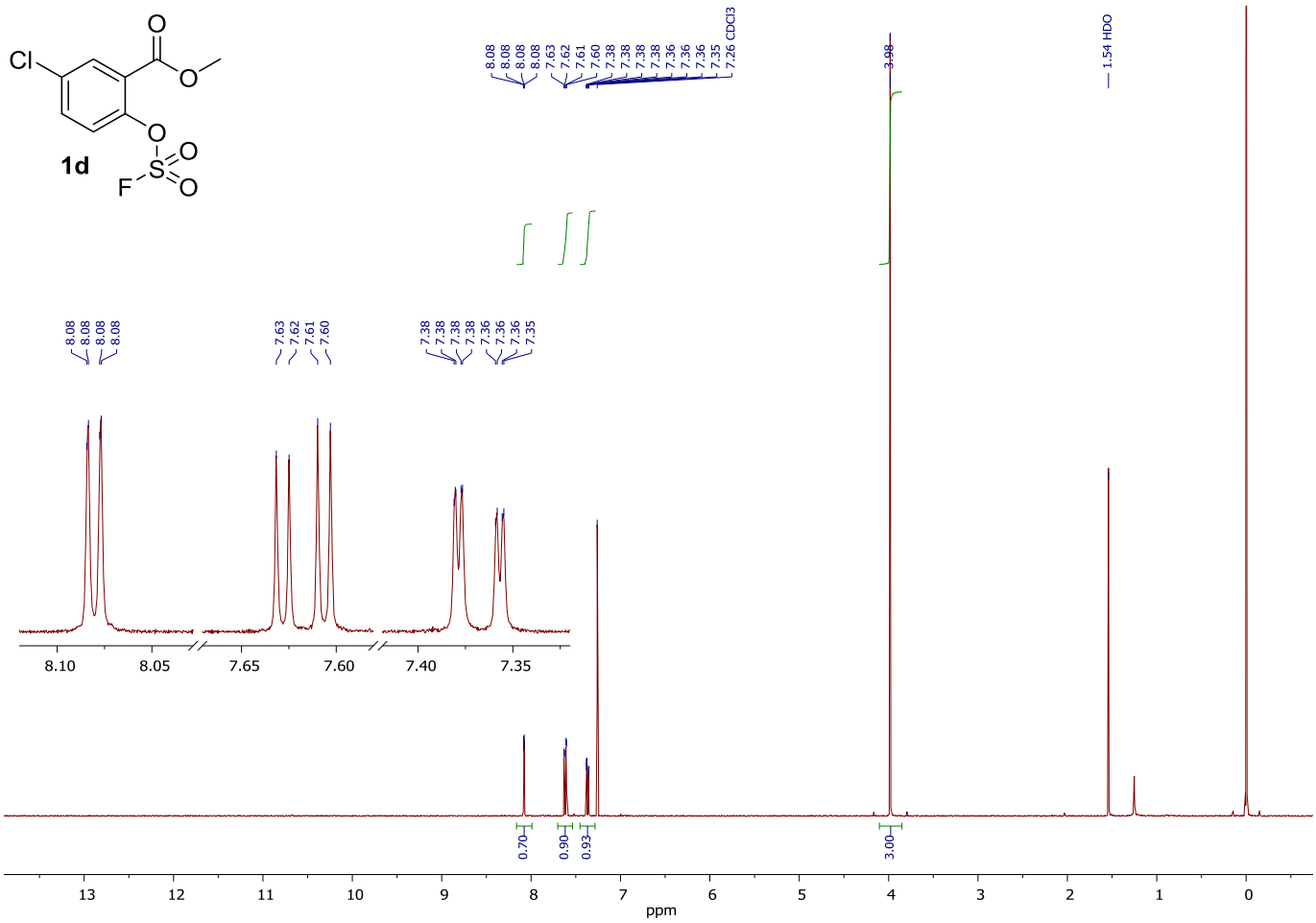
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O
O
F
S
O
O
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8.08
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7.38
7.38
7.38
7.38
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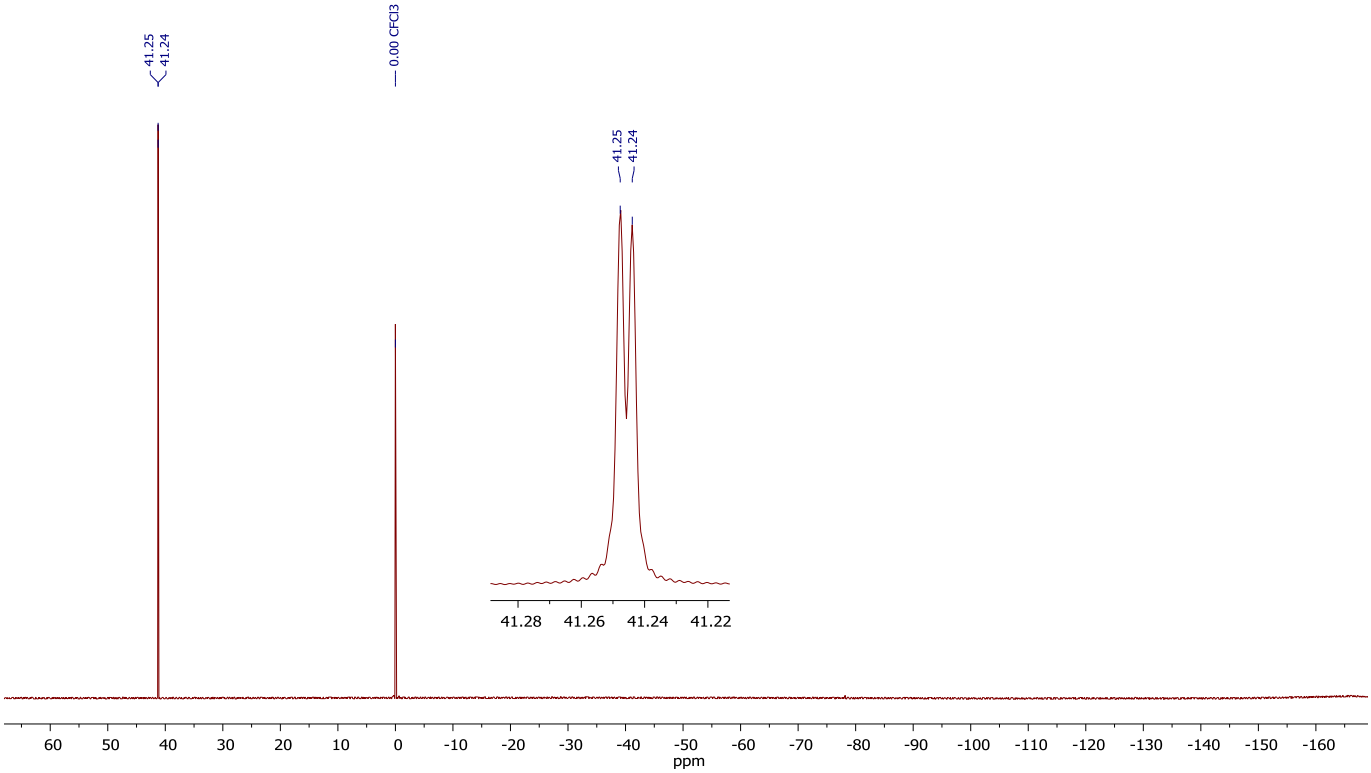
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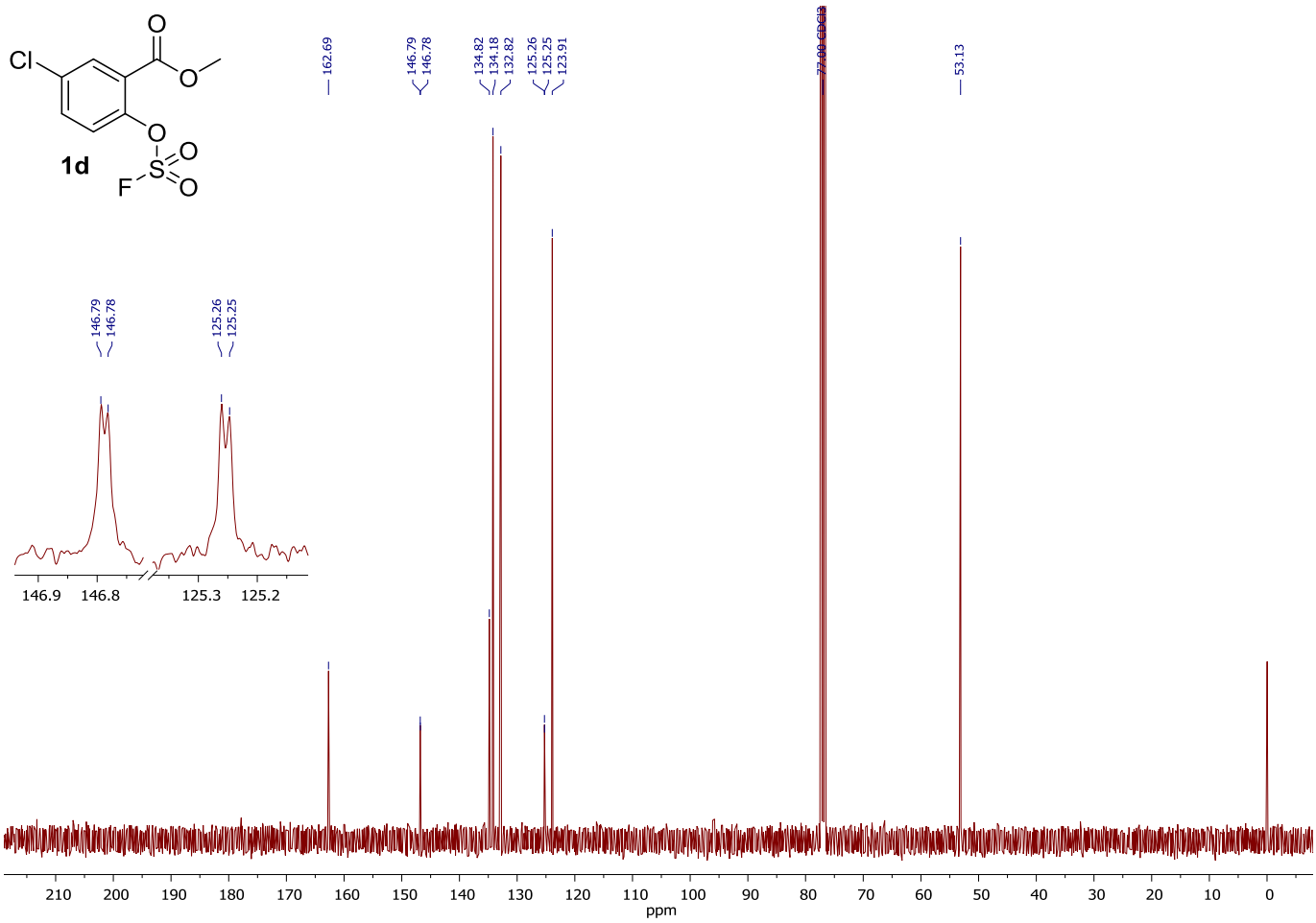
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O
O
S
O
F
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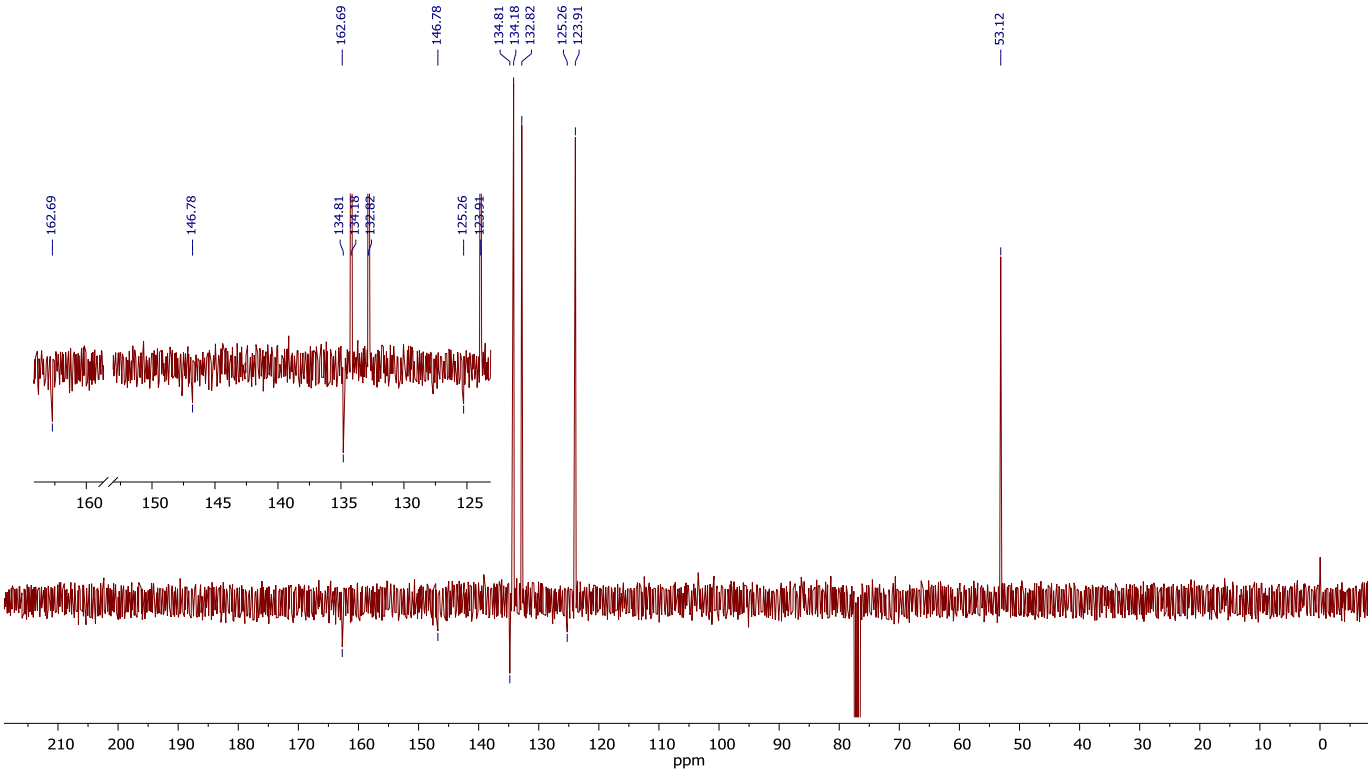
125.2
ppm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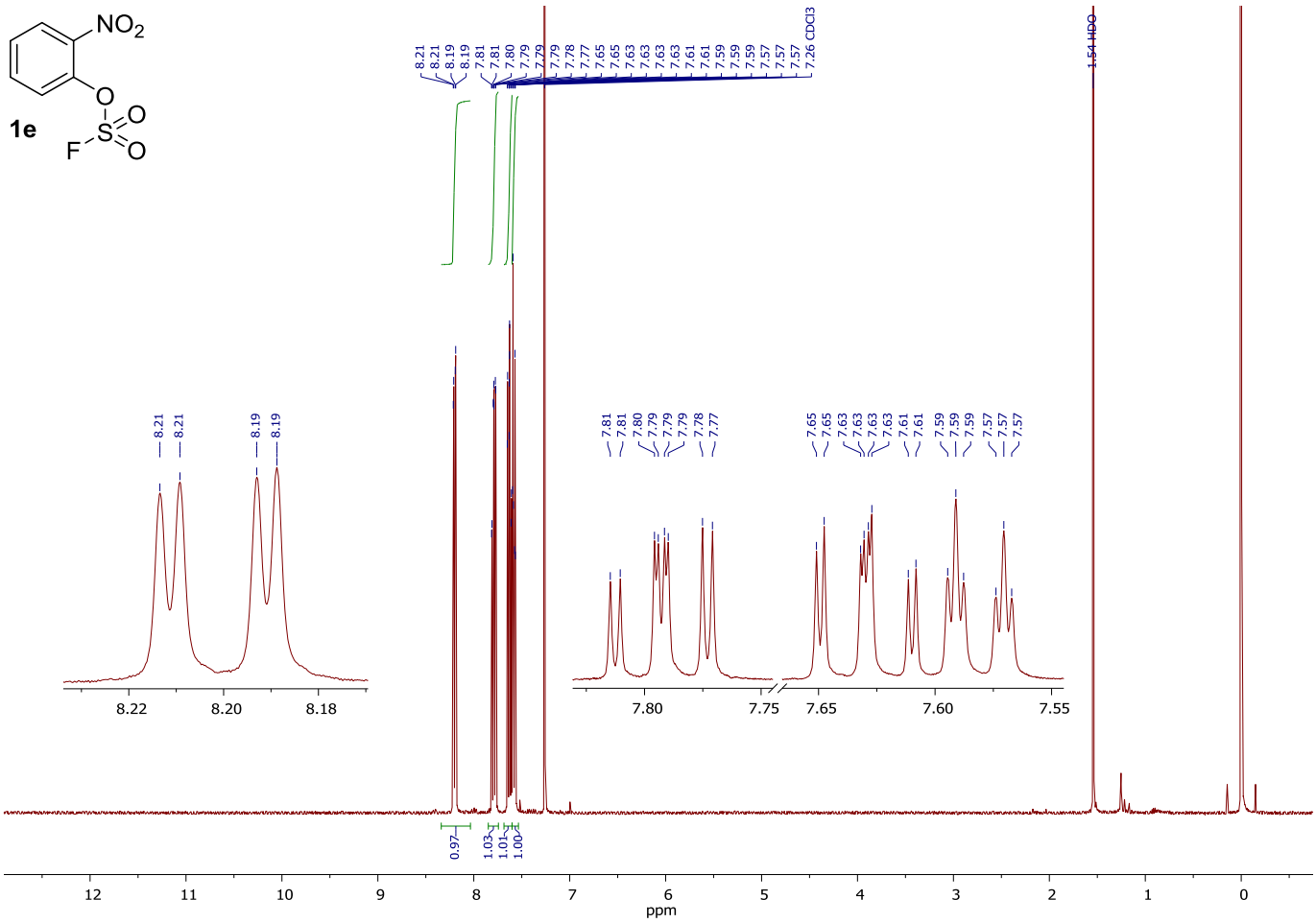
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O
O
S
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7.63
7.63
7.61
7.61
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1.00
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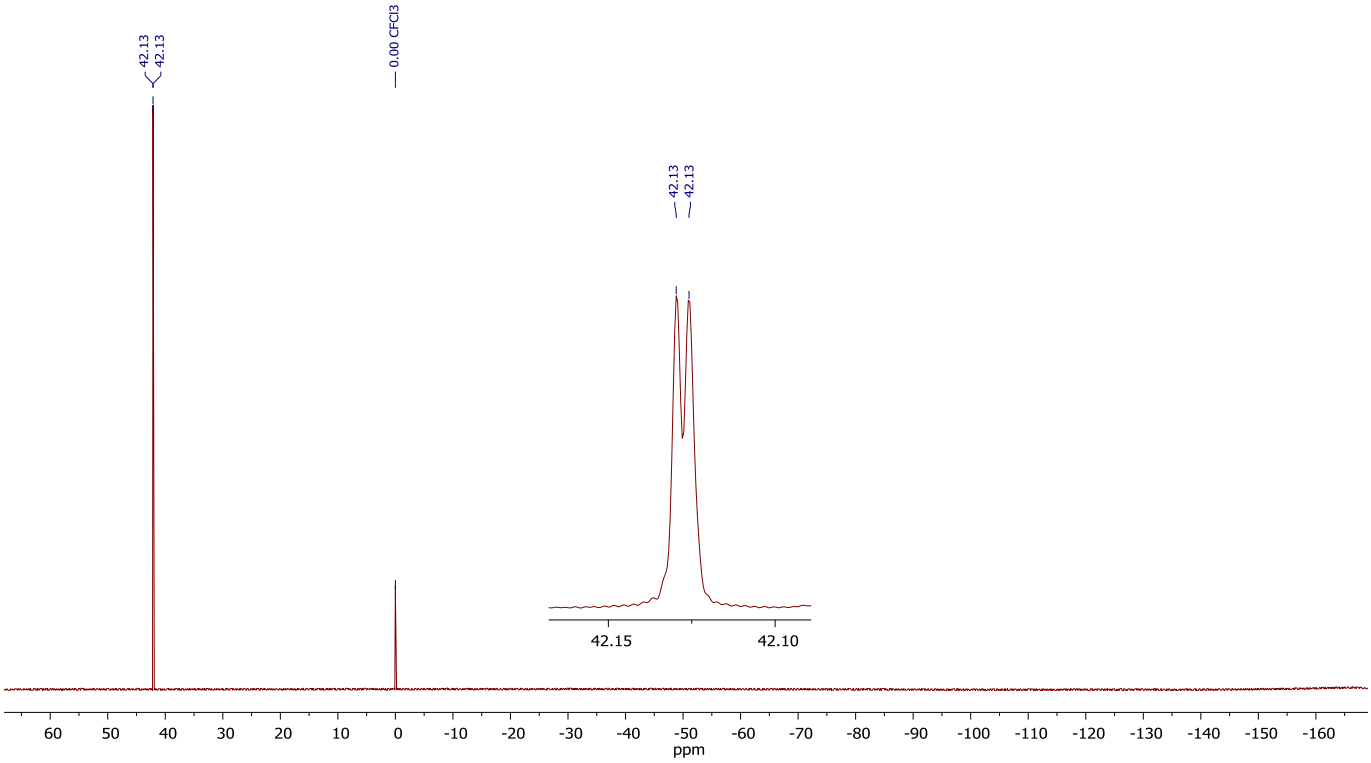
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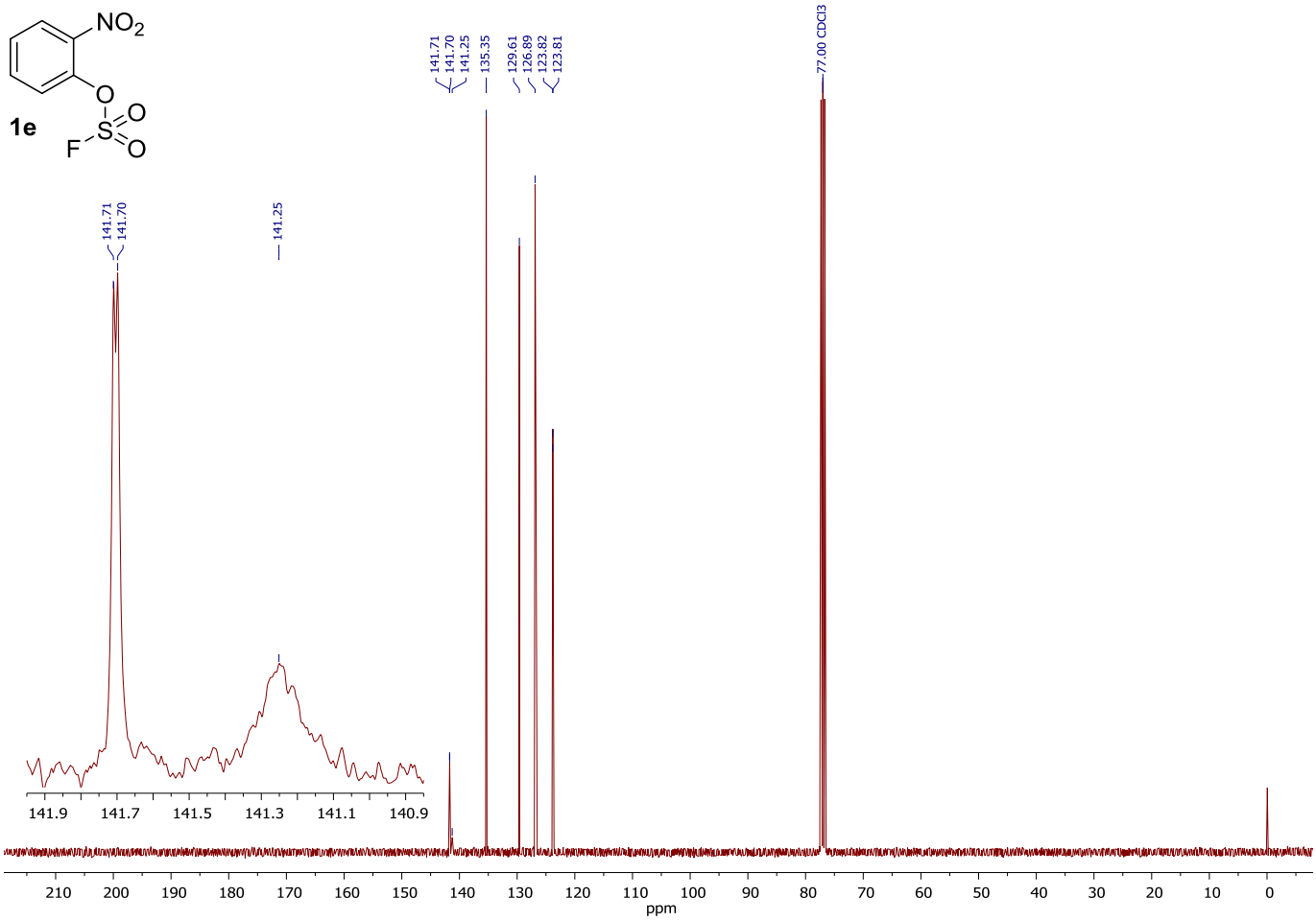
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77.00 CDCl3
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141.7
141.5
141.3
141.1
140.9
210
200
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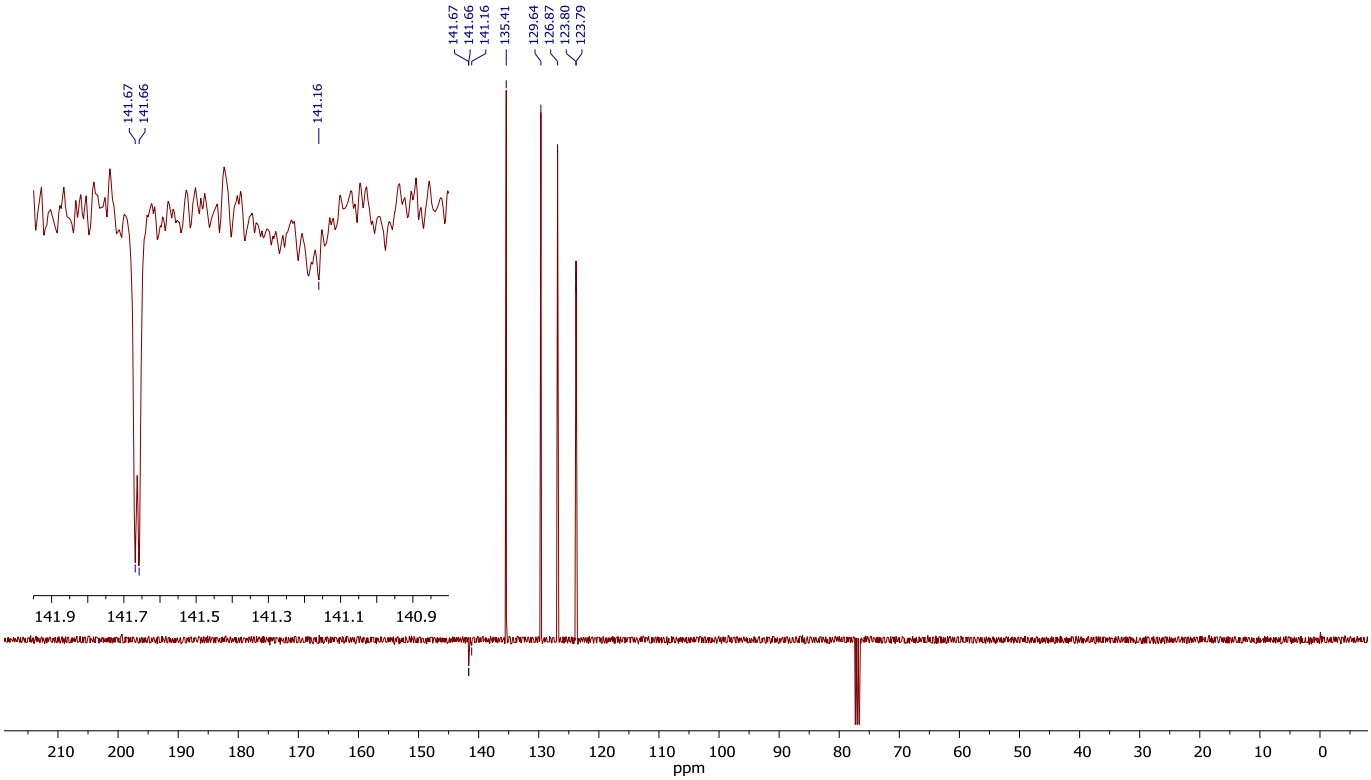
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200
190
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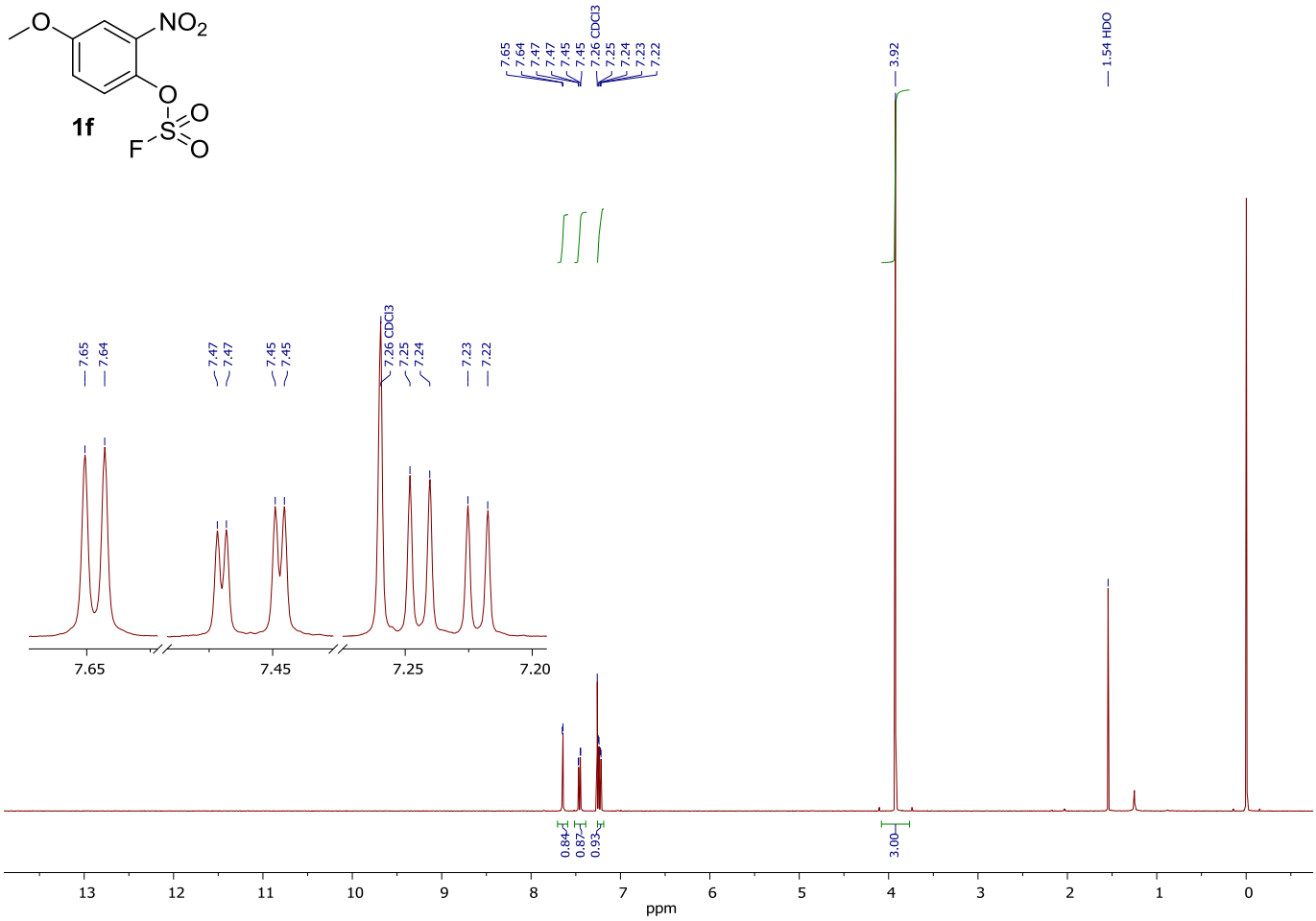
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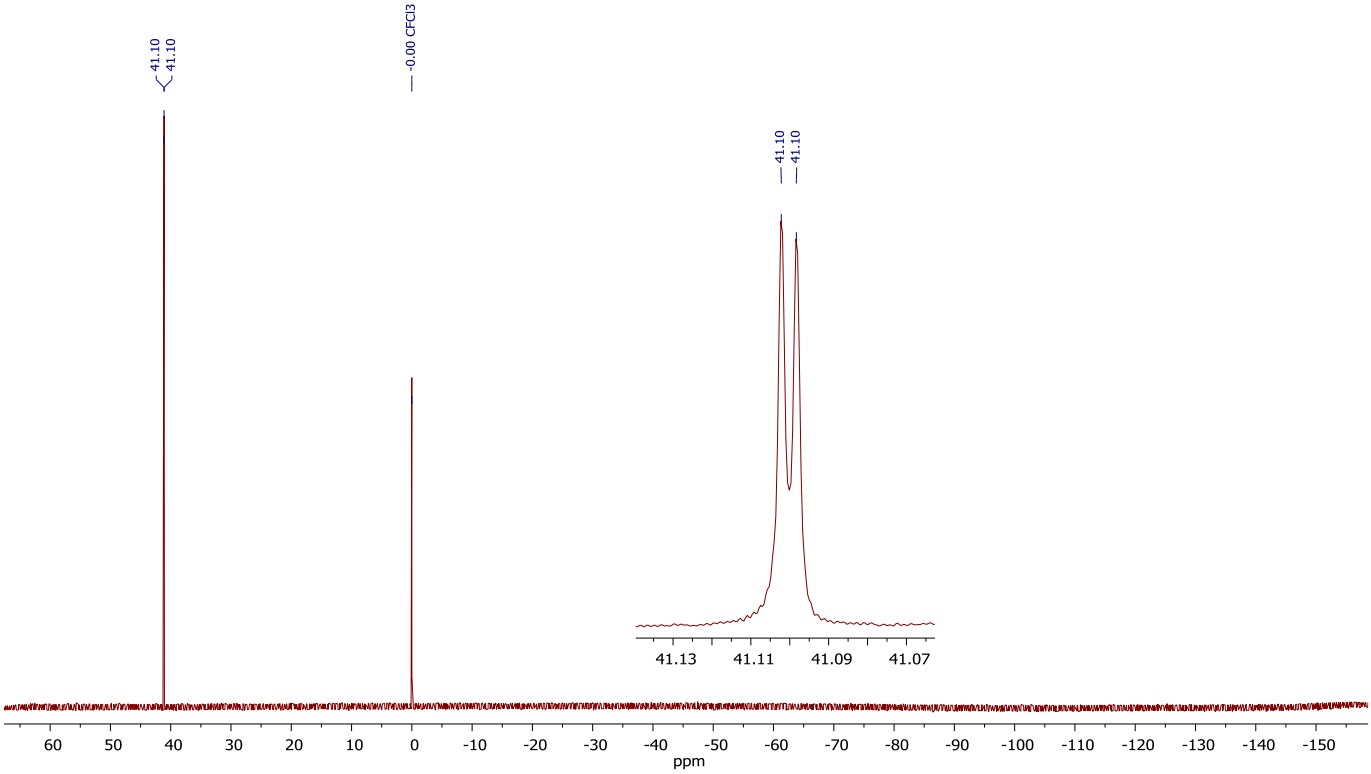
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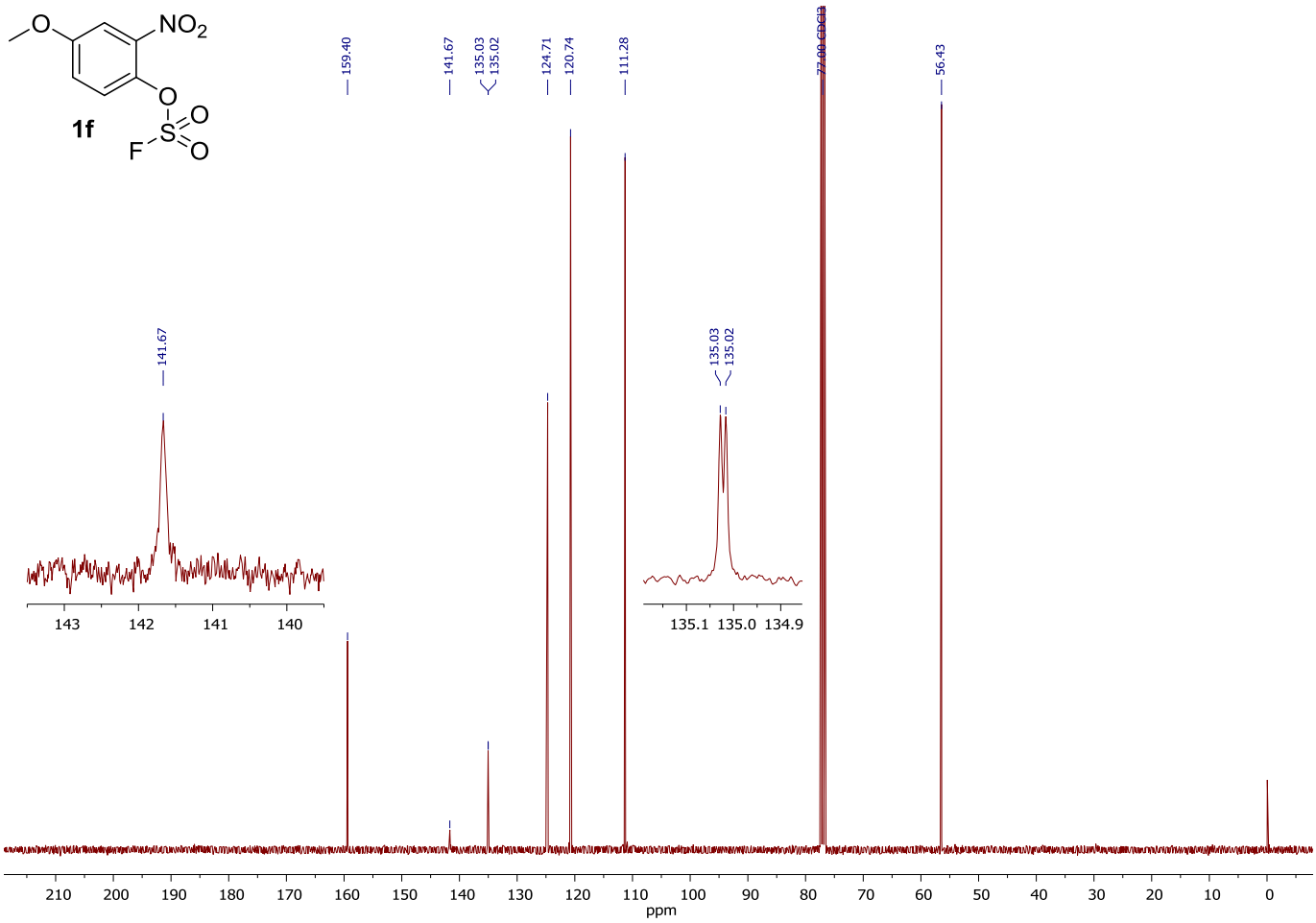
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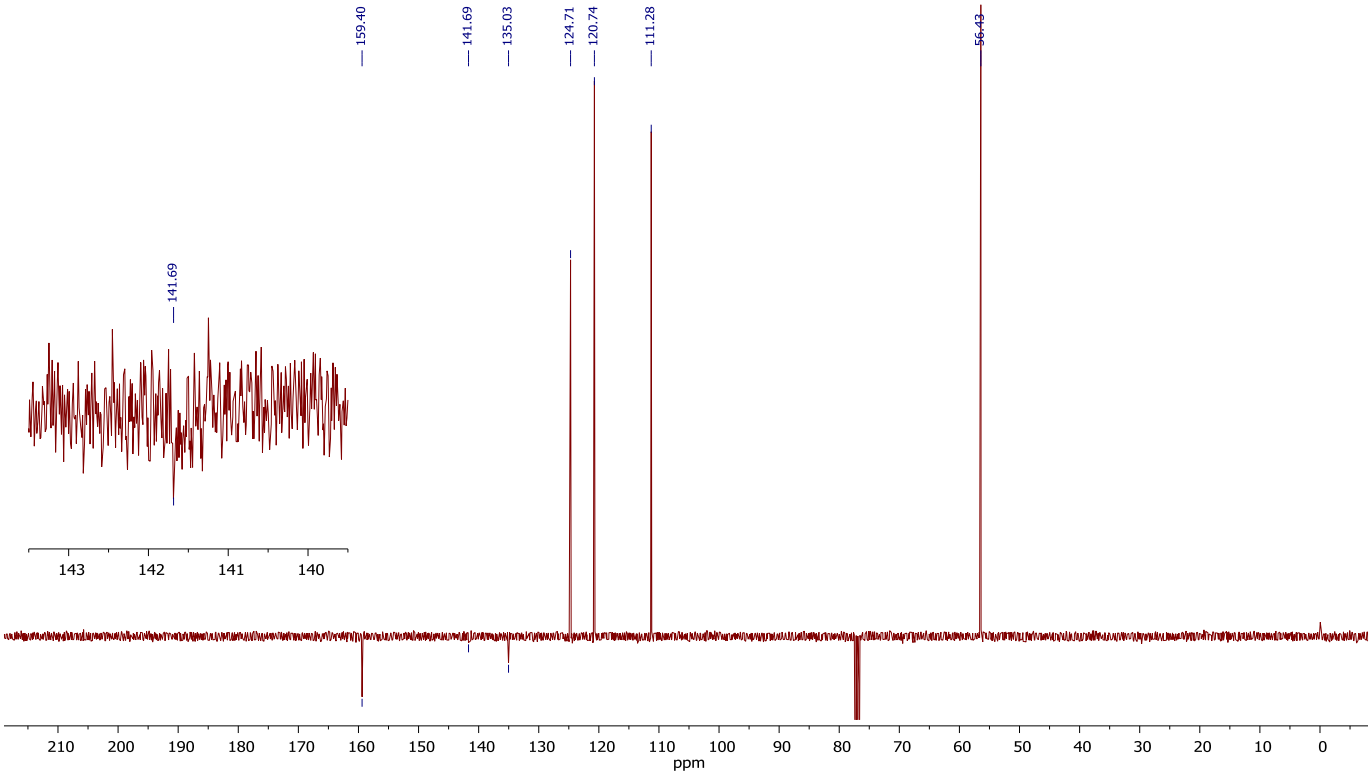
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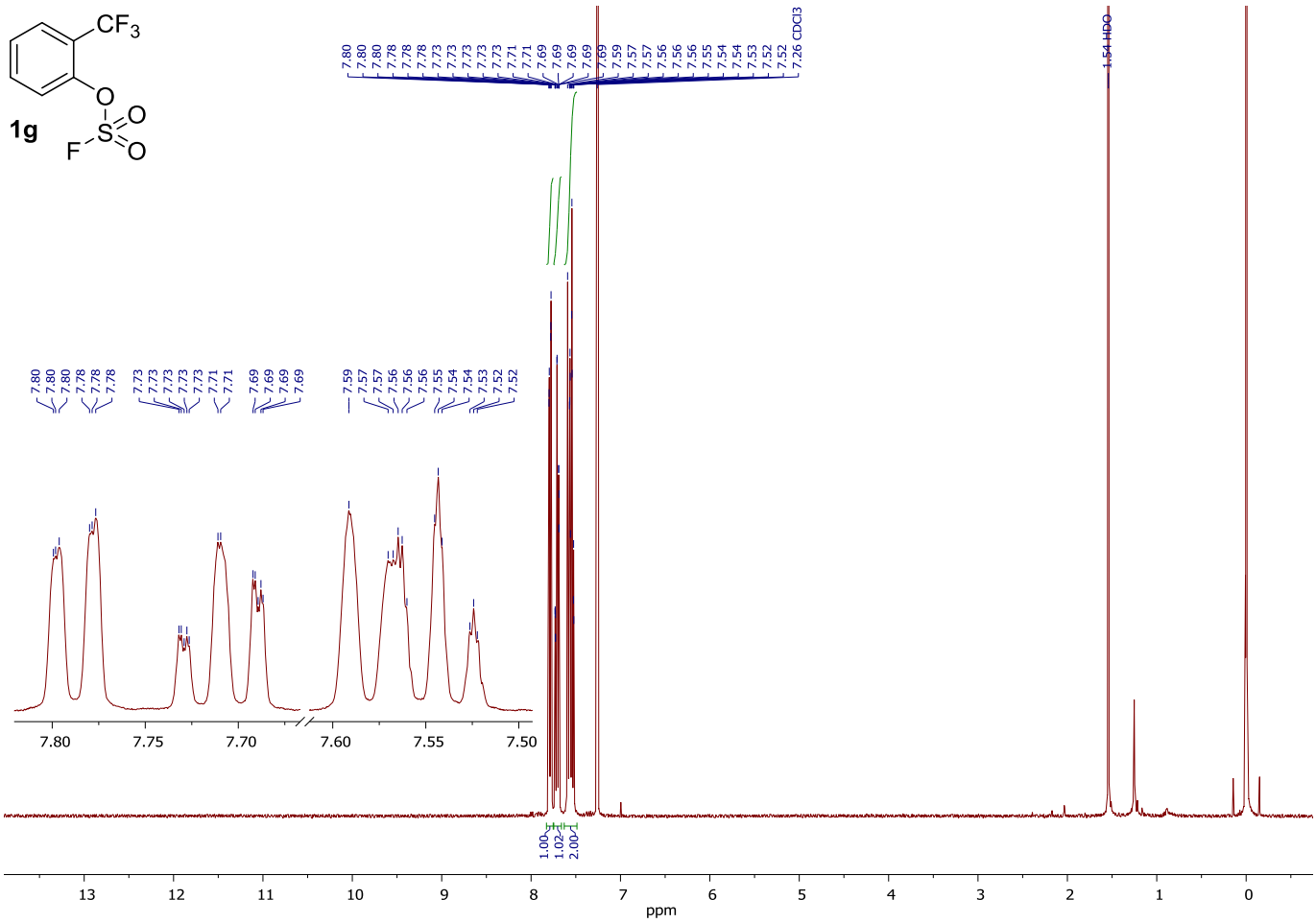
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O
O
F
S
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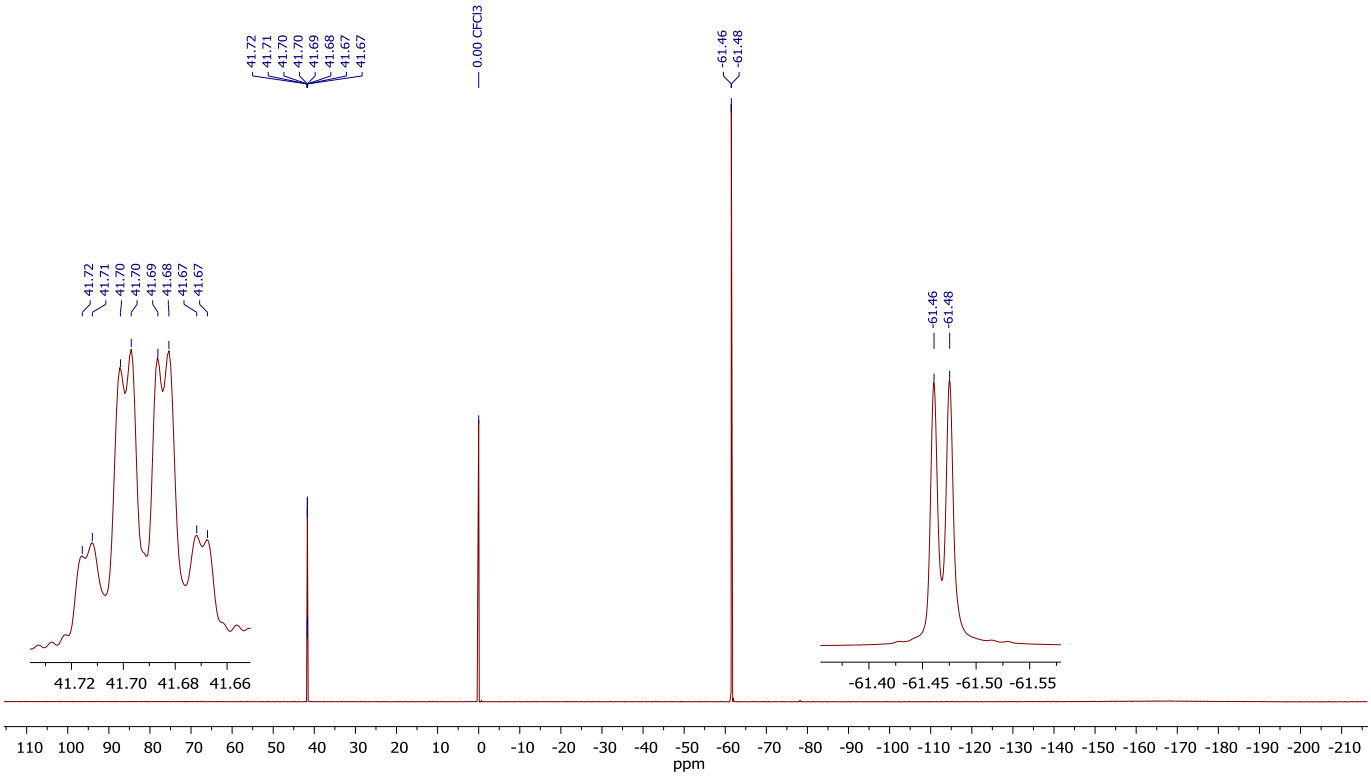
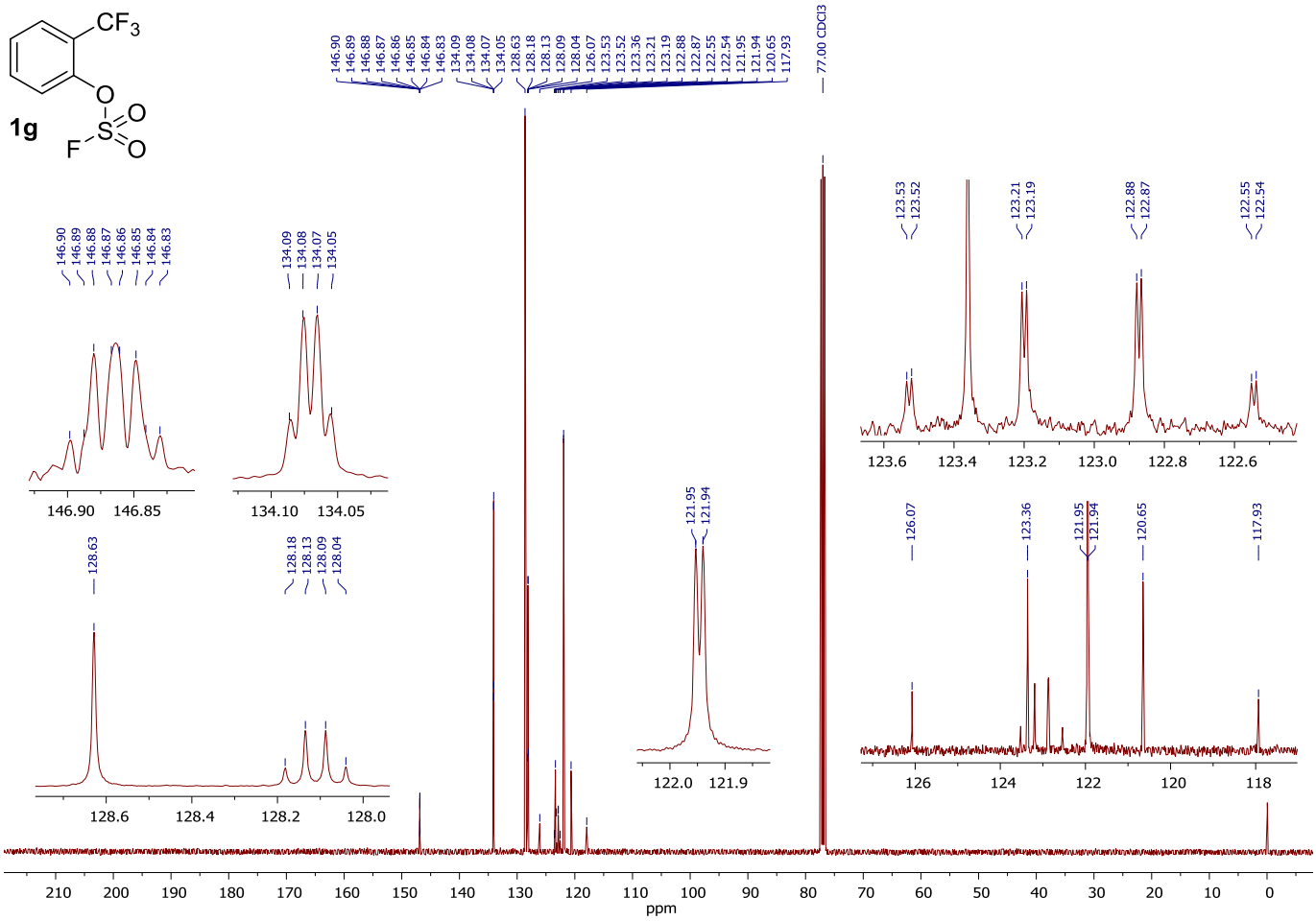
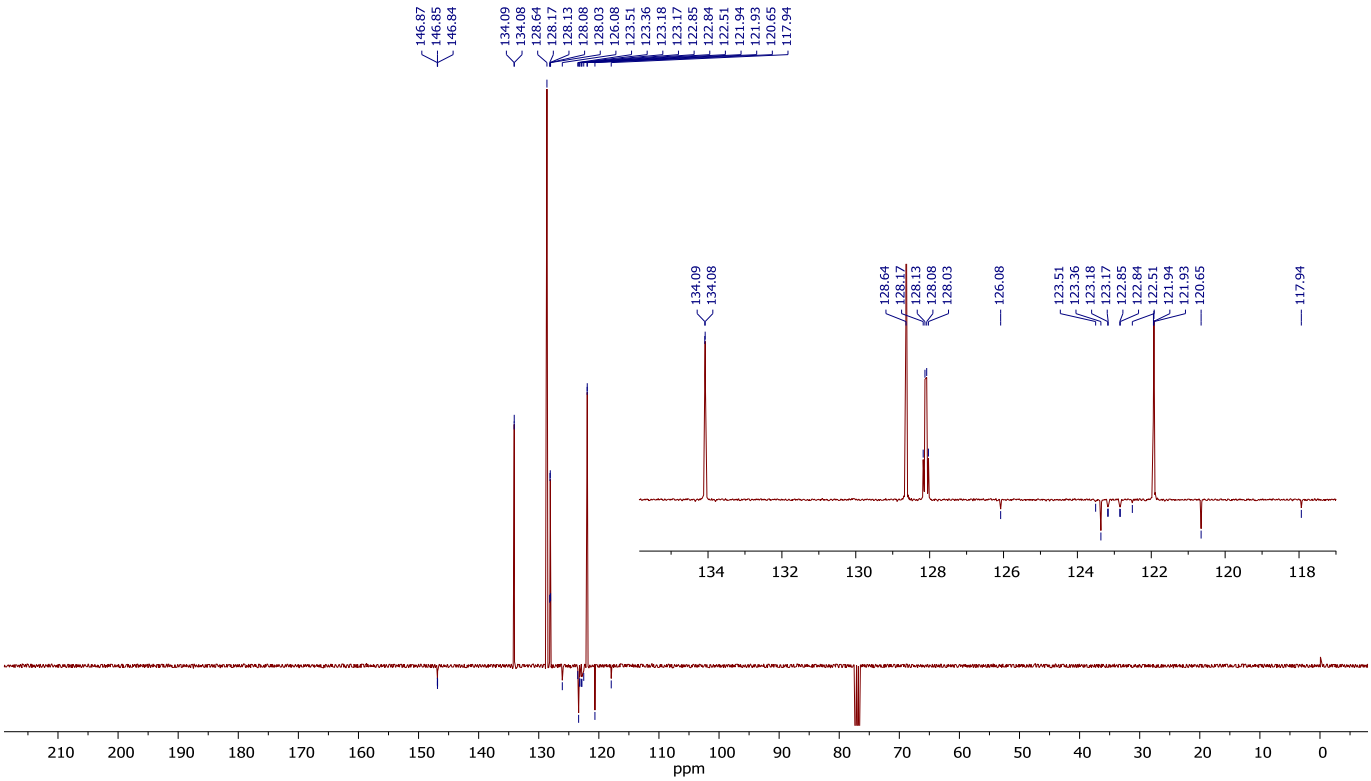
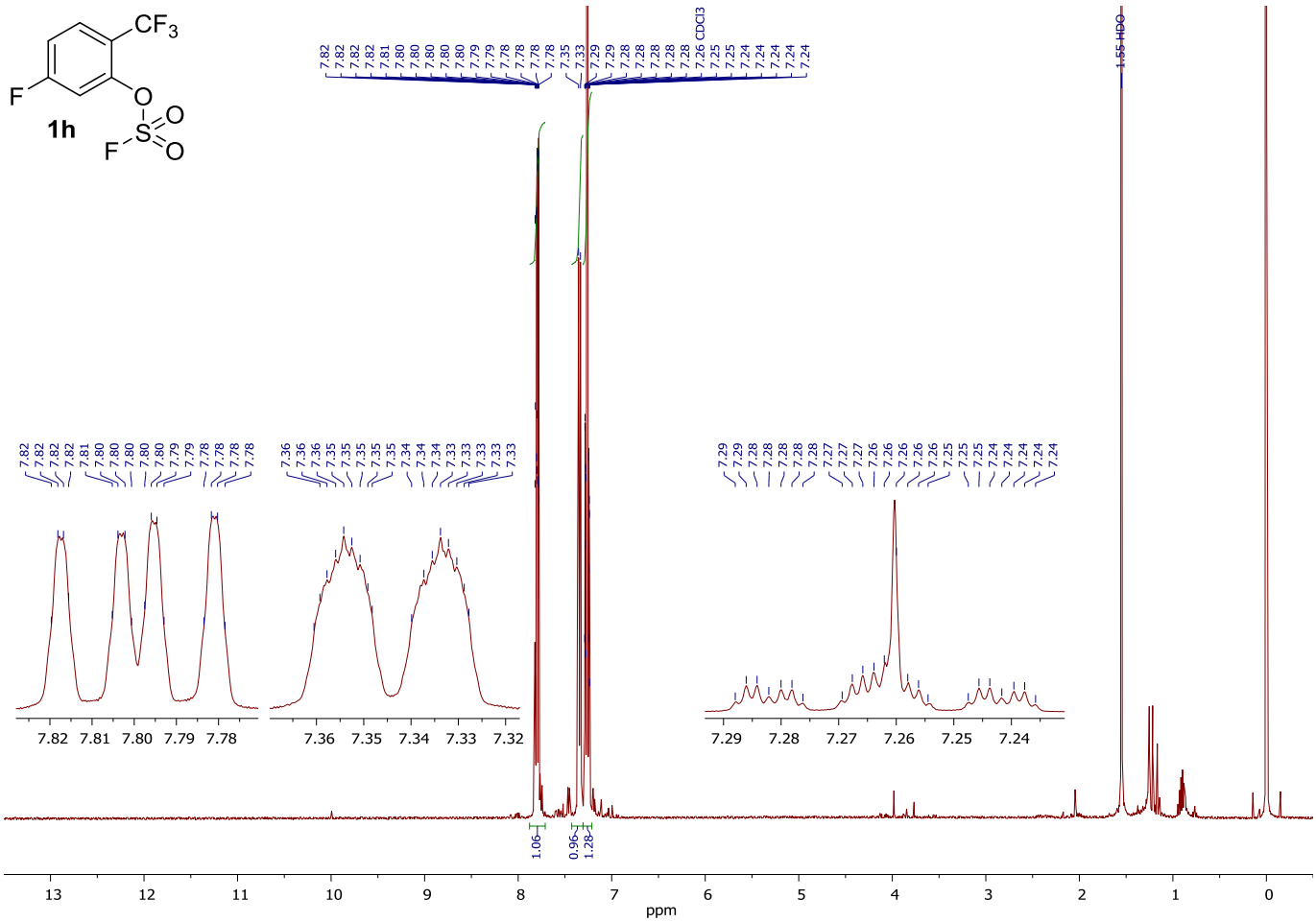
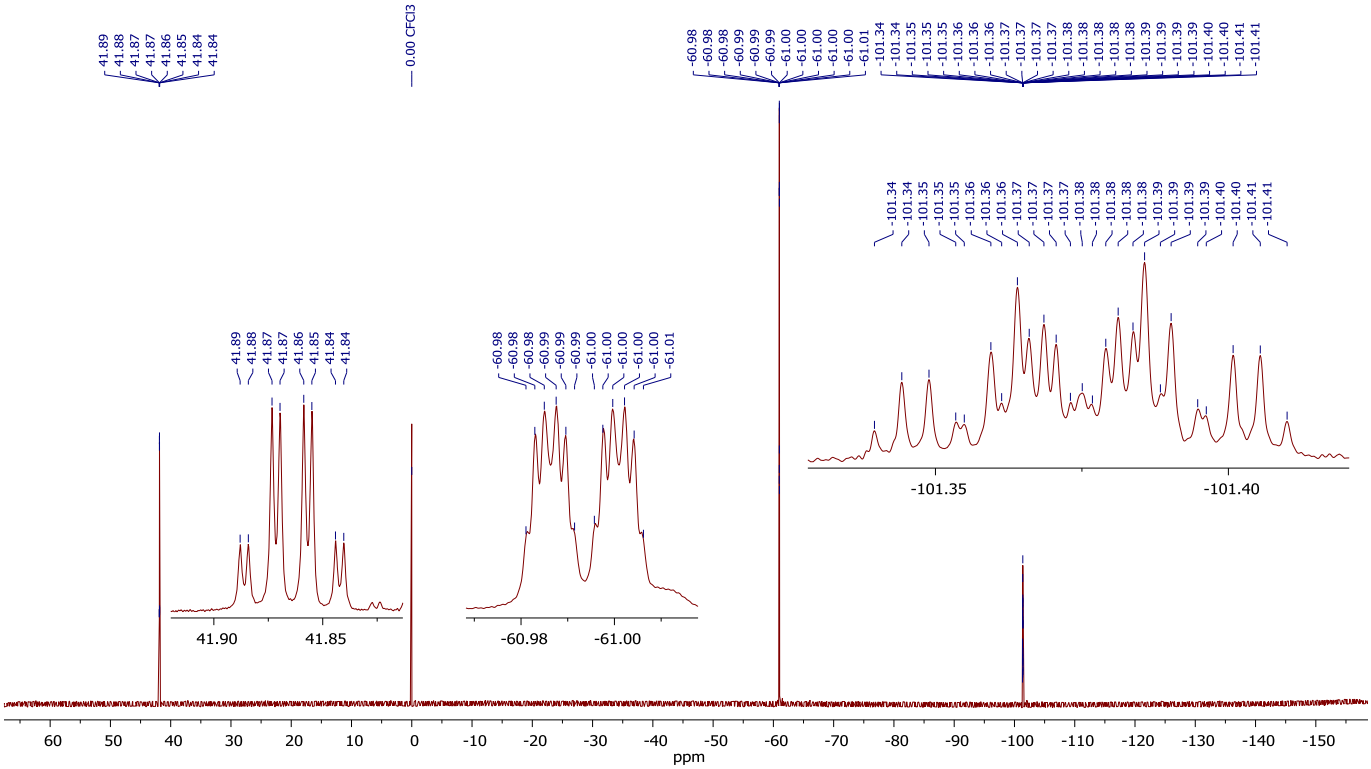
7.26 CDCl3
1.54 HDO
1.00
1.02
2.00
ppm

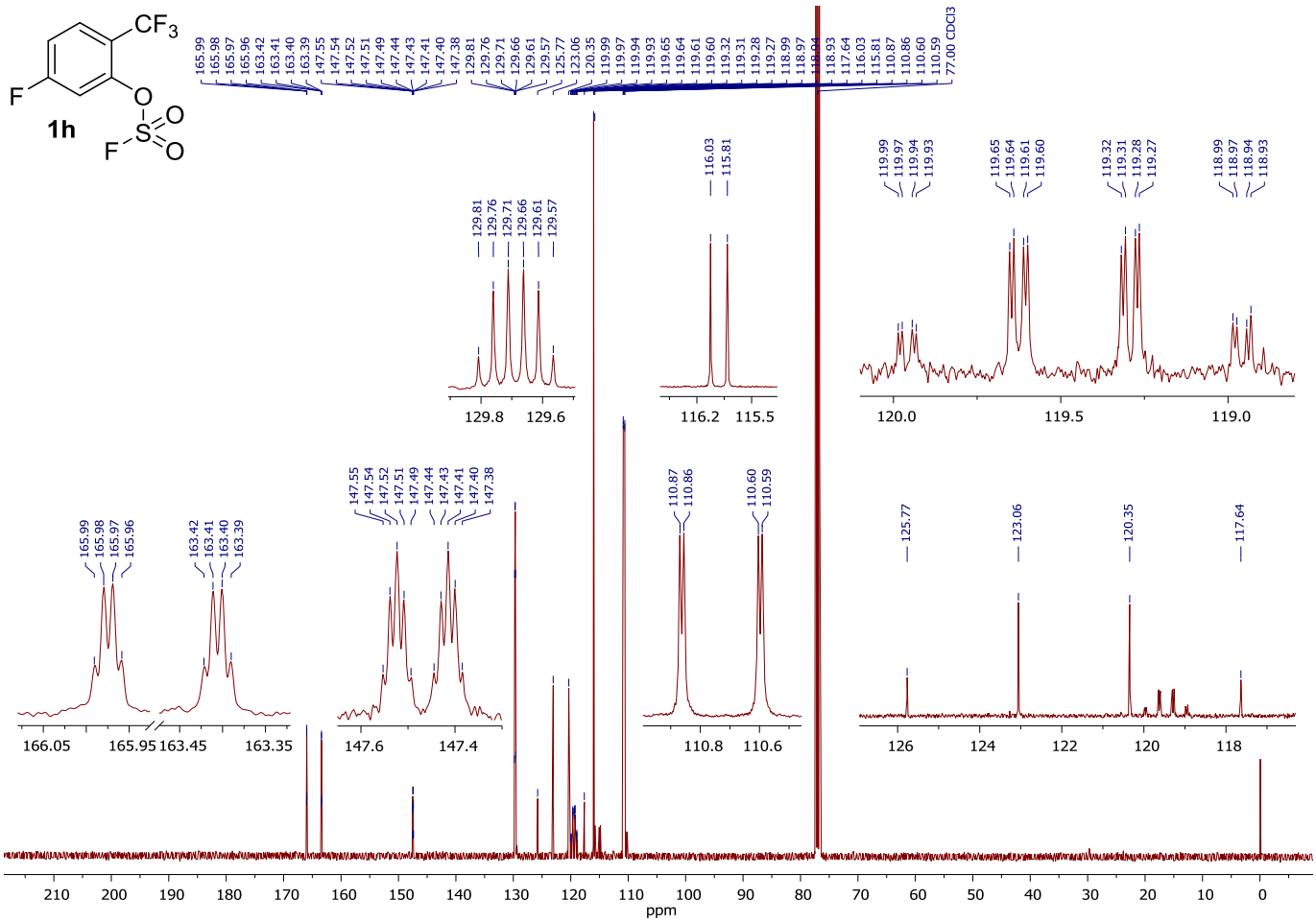

41.72 41.71 41.70 41.70 41.69 41.68 41.67 41.67
0.00 CFCl3
-61.46
-61.48
ppm

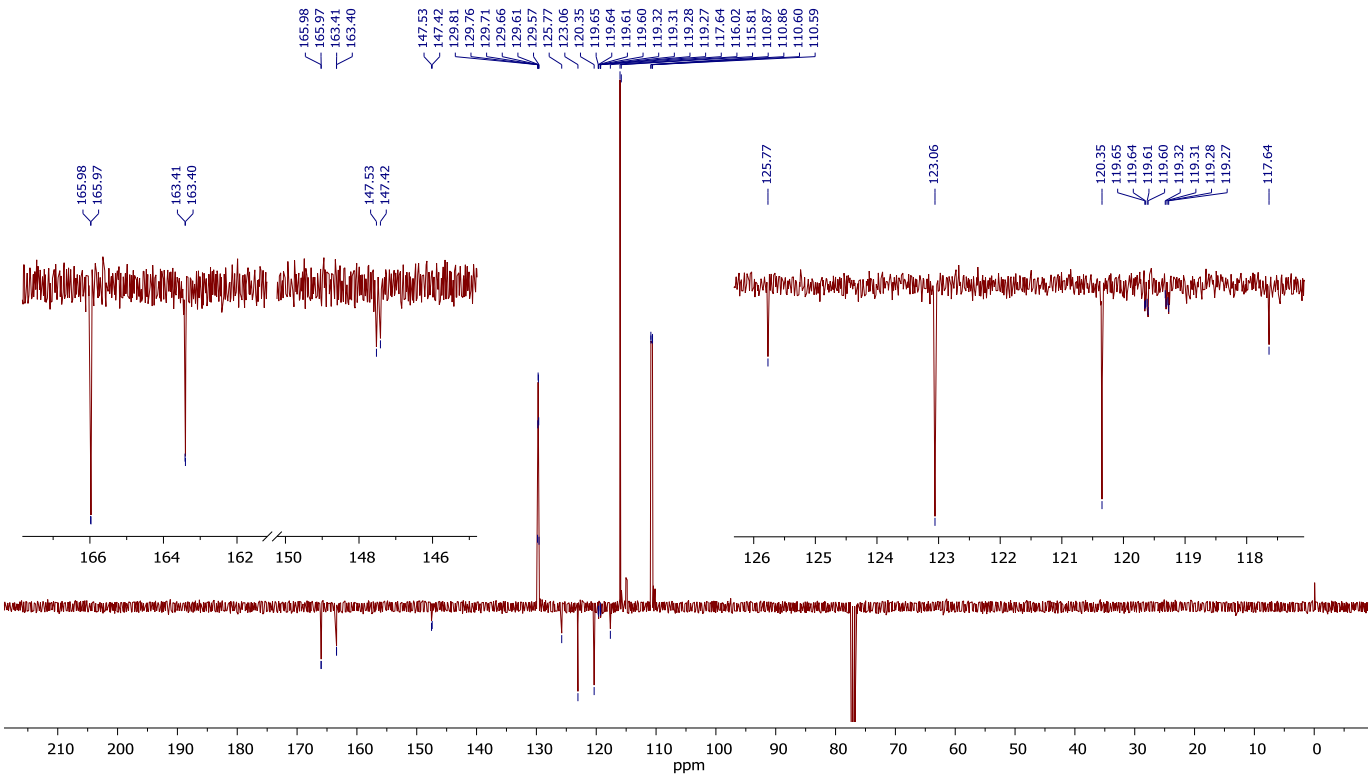

1g
CF3
O
O
S
O
F
146.90
146.89
146.88
146.87
146.86
146.85
146.84
146.83
134.09
134.08
134.07
134.05
128.63
128.18
128.13
128.09
128.04
128.64
128.17
128.08
128.03
126.08
123.53
123.52
123.51
123.36
123.21
123.19
123.18
123.17
122.88
122.87
122.85
122.84
122.55
122.54
122.51
121.95
121.94
121.93
120.65
117.93
117.94
77.00 CDCl3
ppm

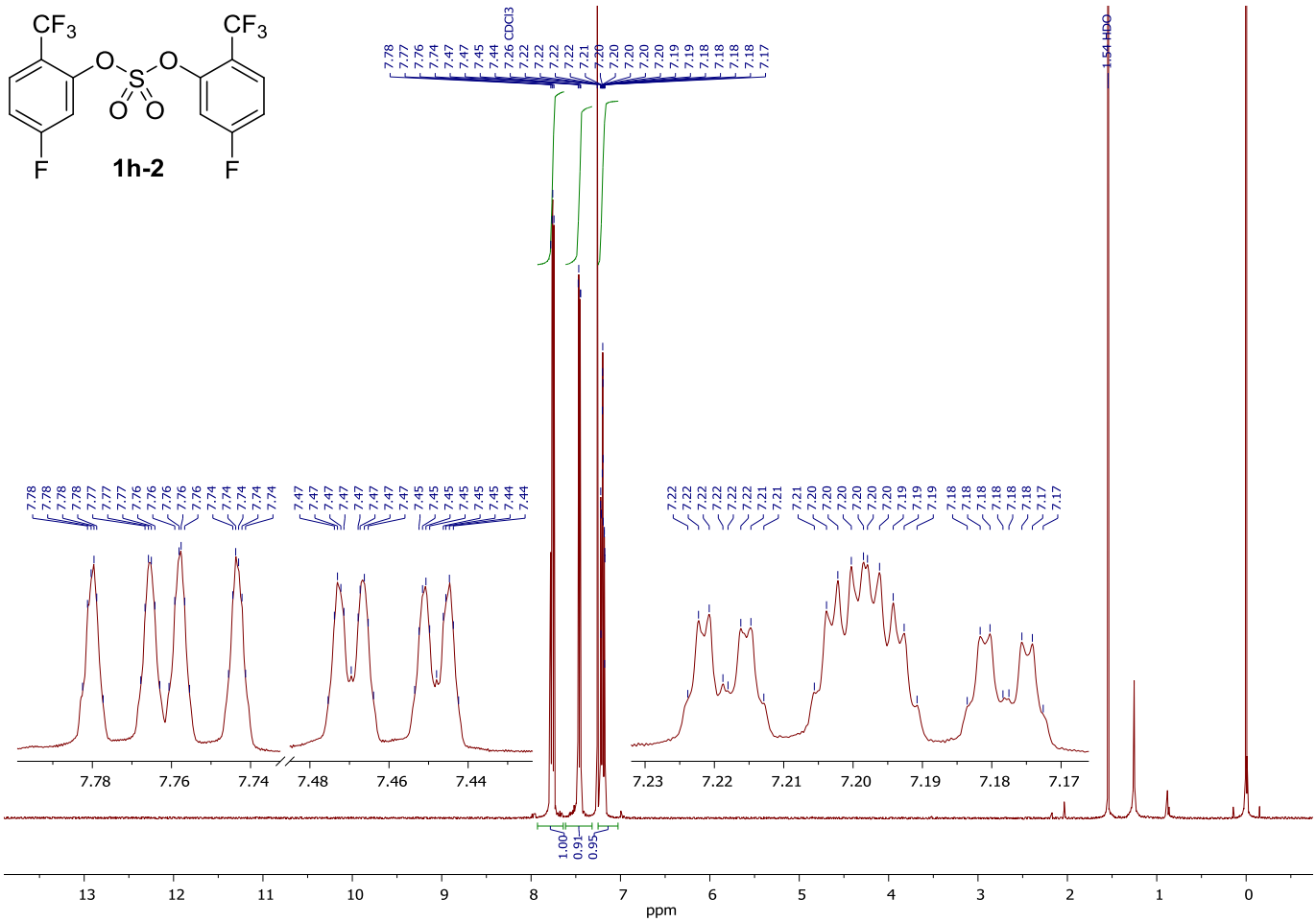

146.87
146.85
146.84
134.09
134.08
128.64
128.17
128.13
128.08
128.03
126.08
123.51
123.36
123.18
123.17
122.85
122.84
122.51
121.94
121.93
120.65
117.94
ppm

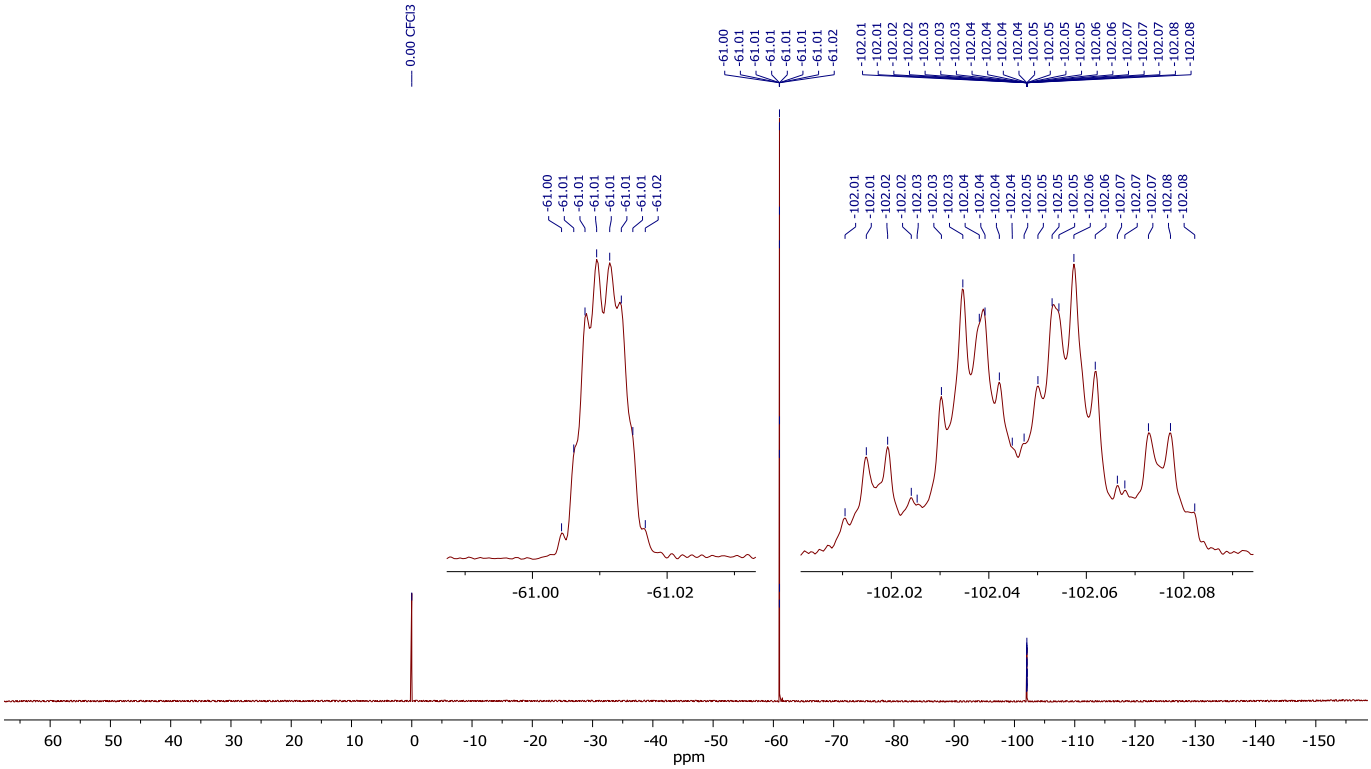

1h
CDCl3
1.55 HDO
1.06
0.96
1.28
ppm

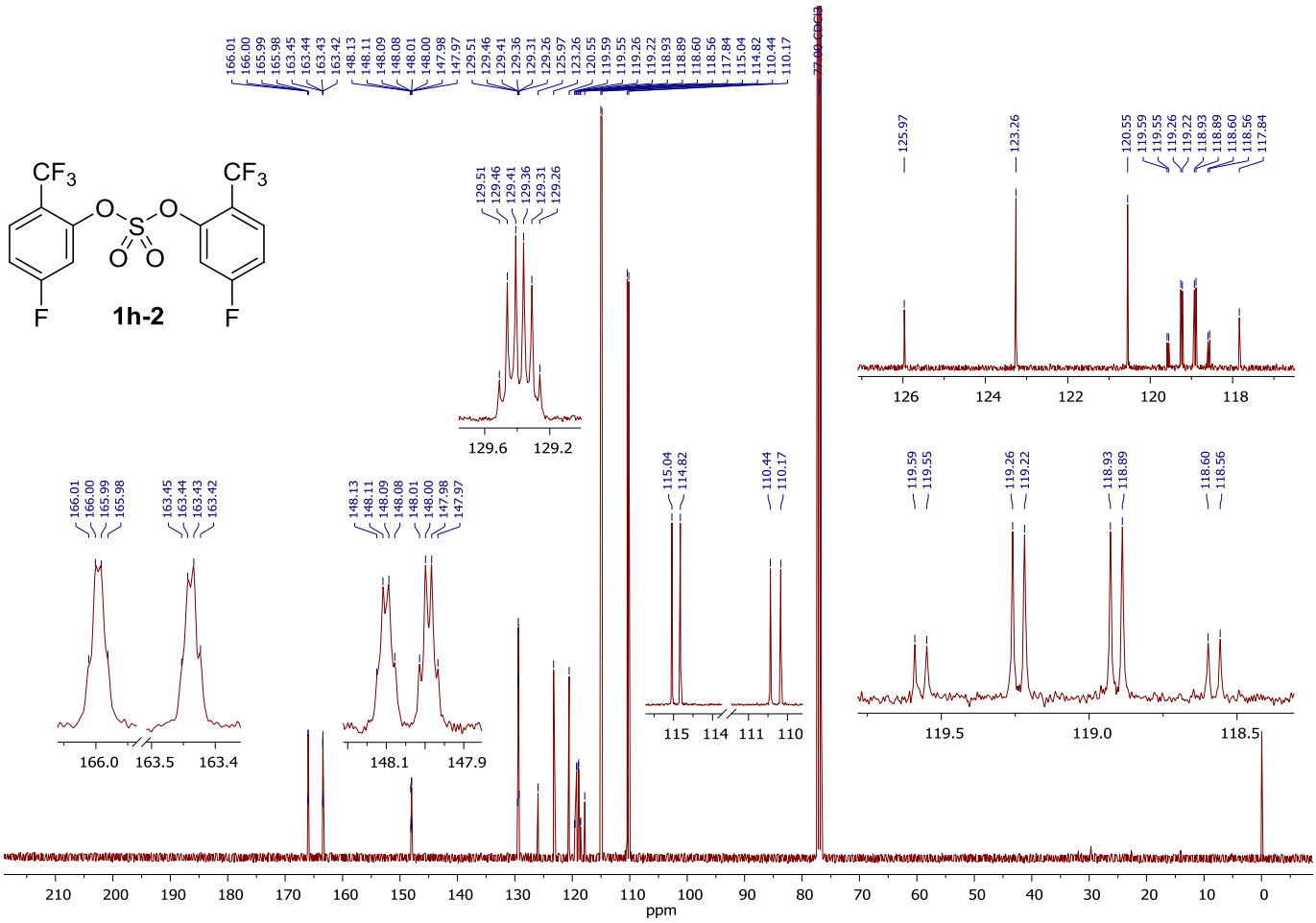

0.00 CFCl3
ppm

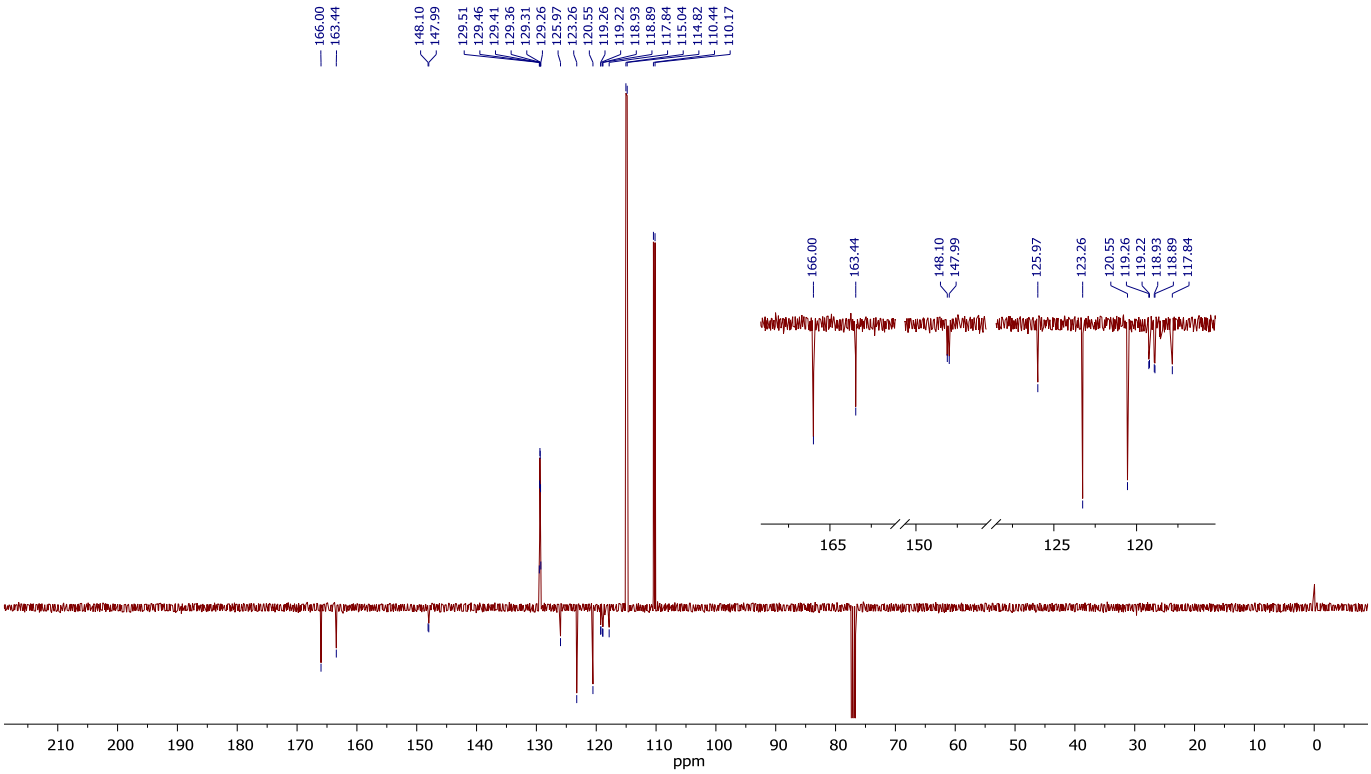

1h
CF3
F
O
S
O
O
F
77.00 CDCl3
ppm

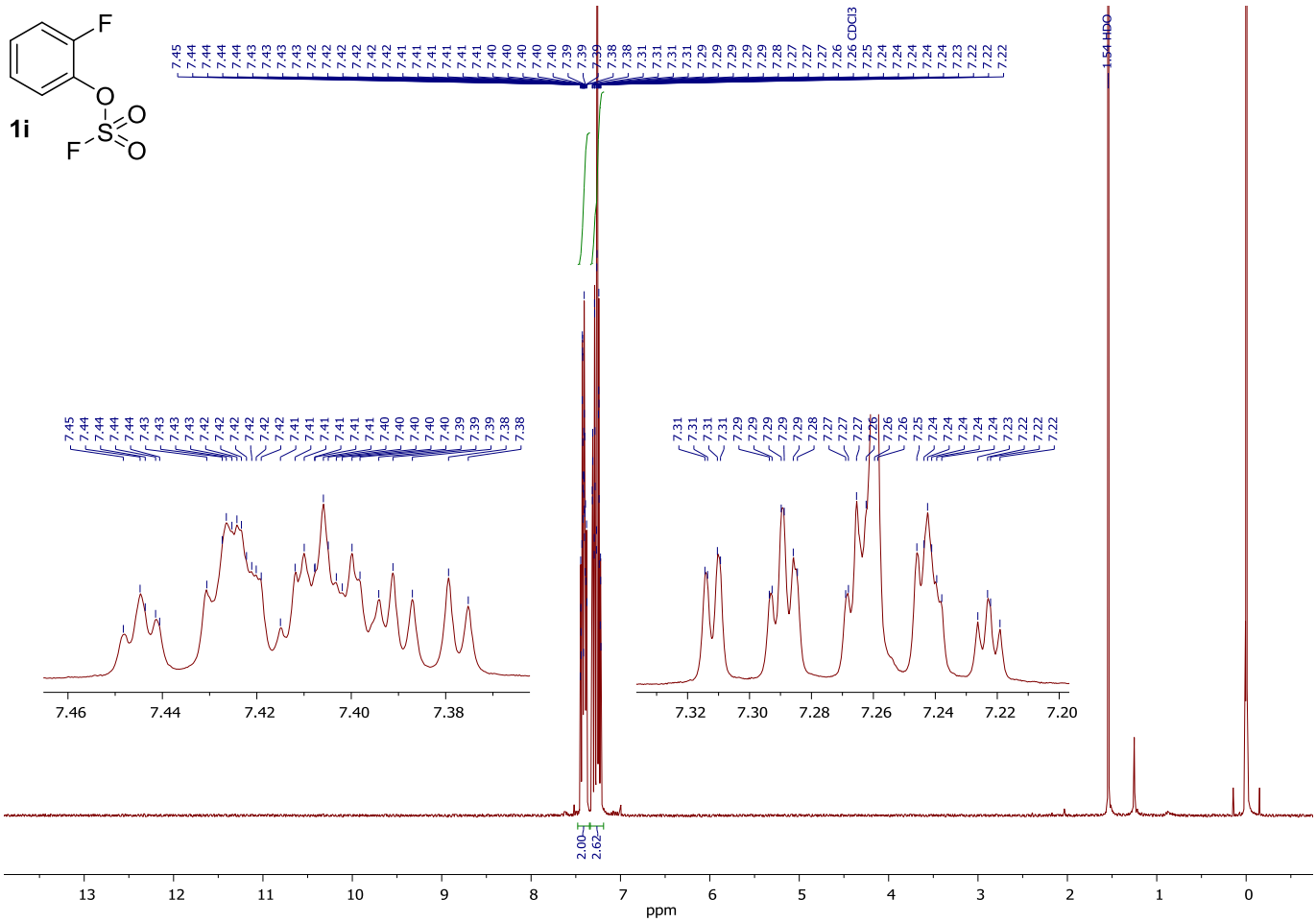

ppm

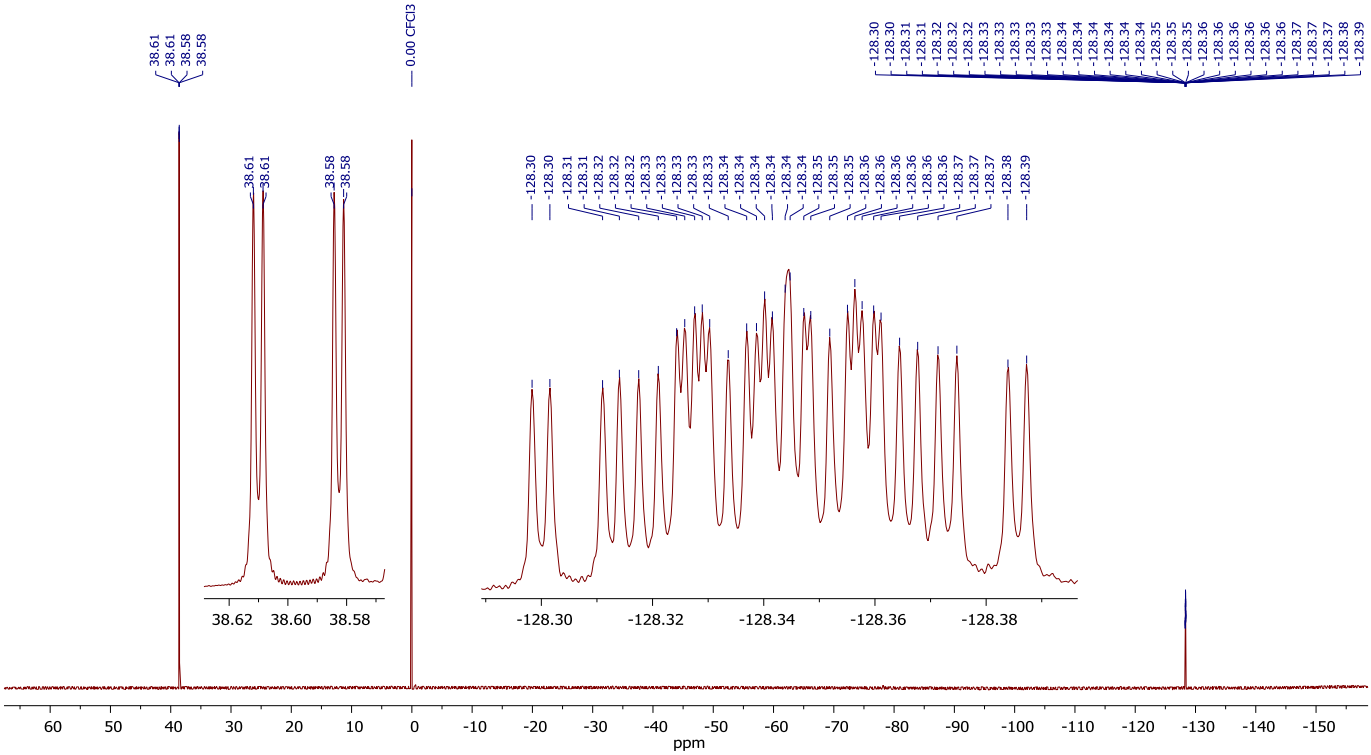

CF3
CF3
O
S
O
O
O
F
F
1h-2
7.26 CDCl3
1.54 HDO
1.00
0.91
0.95
ppm

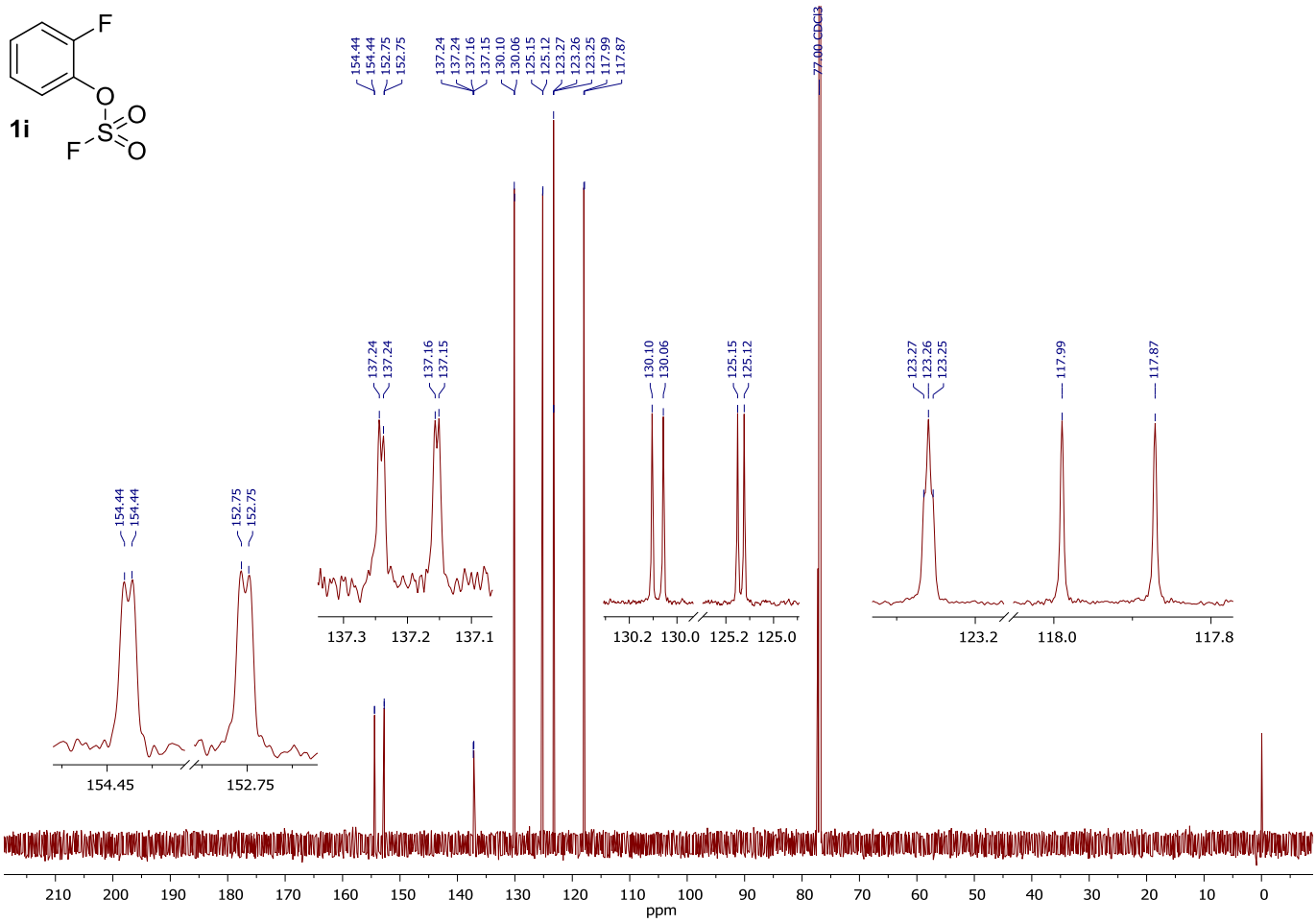

0.00 CFCl3
-61.00
-61.02
-102.02
-102.04
-102.06
-102.08
ppm

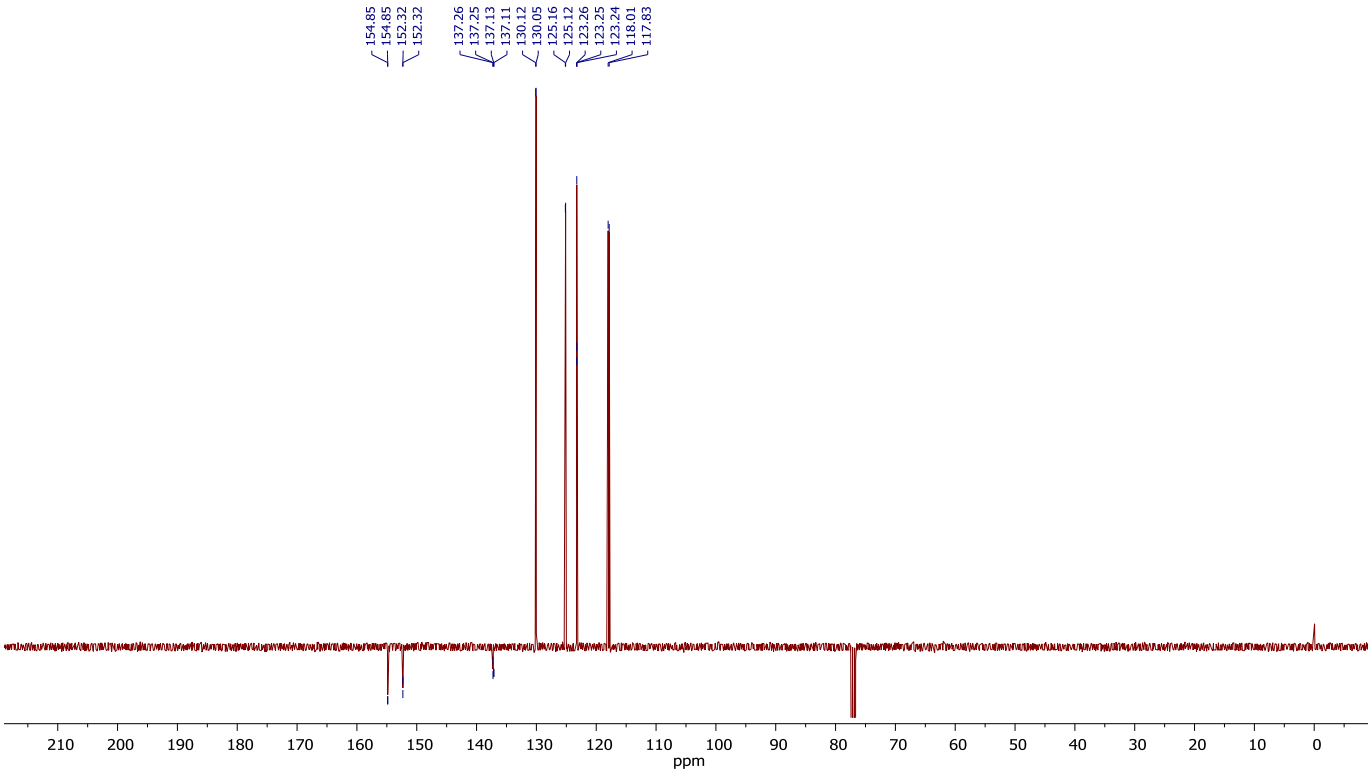

CF3
CF3
O
S
O
O
O
F
F
1h-2
166.01
166.00
165.99
165.98
163.45
163.44
163.43
163.42
148.13
148.11
148.09
148.08
148.01
148.00
147.98
147.97
129.51
129.46
129.41
129.36
129.31
129.26
125.97
123.26
120.55
119.59
119.55
119.26
119.22
118.93
118.89
118.60
118.56
117.84
115.04
114.82
110.44
110.17
77.00 CDCl3
ppm

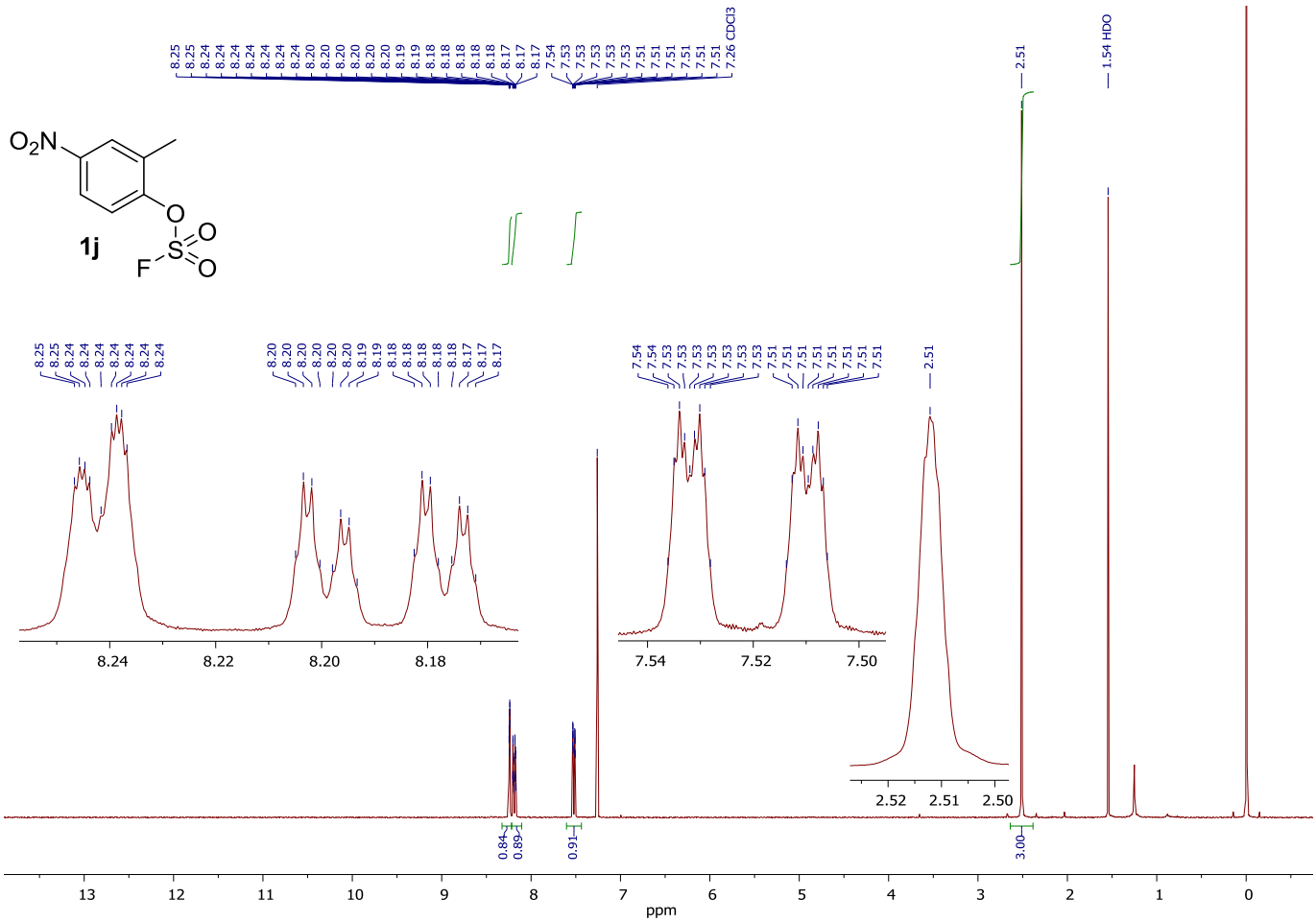

166.00
163.44
148.10
147.99
129.51
129.46
129.41
129.36
129.31
129.26
125.97
123.26
120.55
119.26
119.22
118.93
118.89
117.84
115.04
114.82
110.44
110.17
ppm

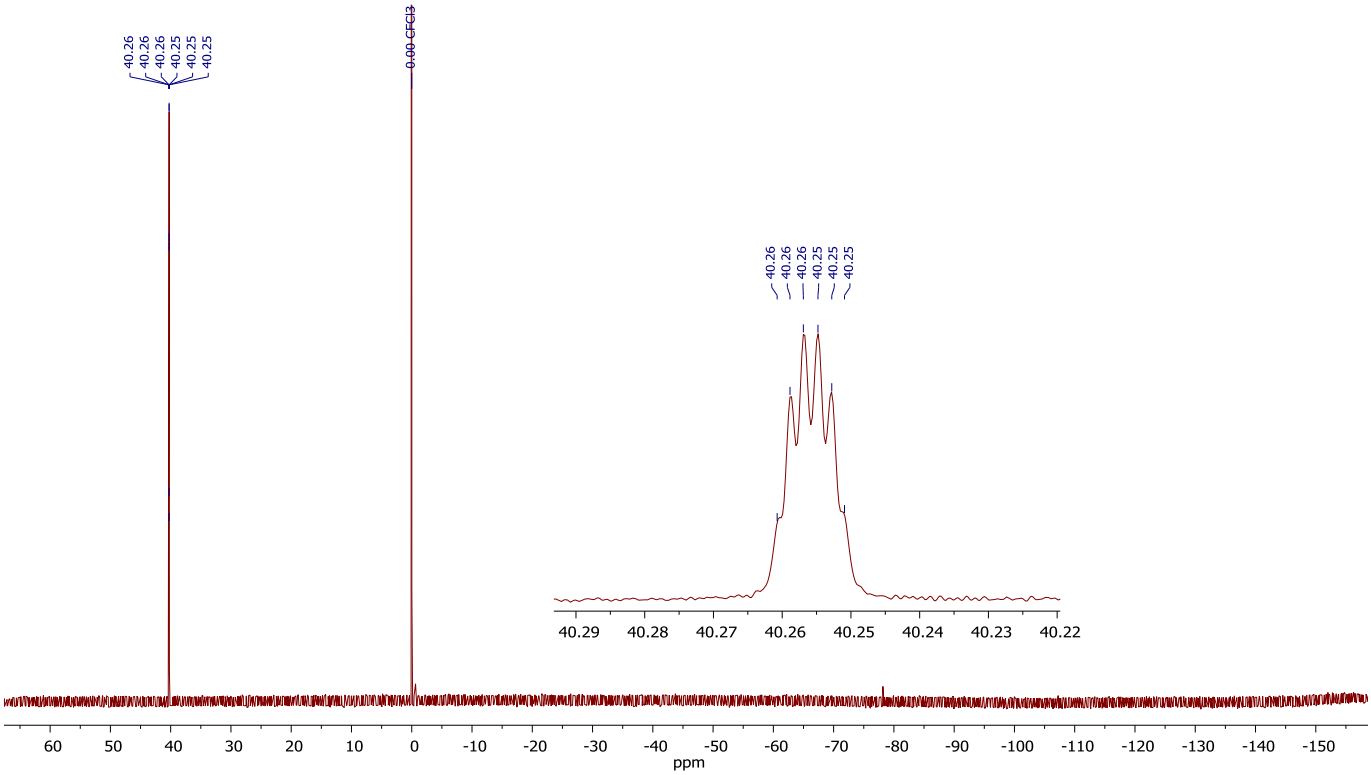

1i
7.26 CDCl3
1.54 HDO
2.00
2.62
ppm

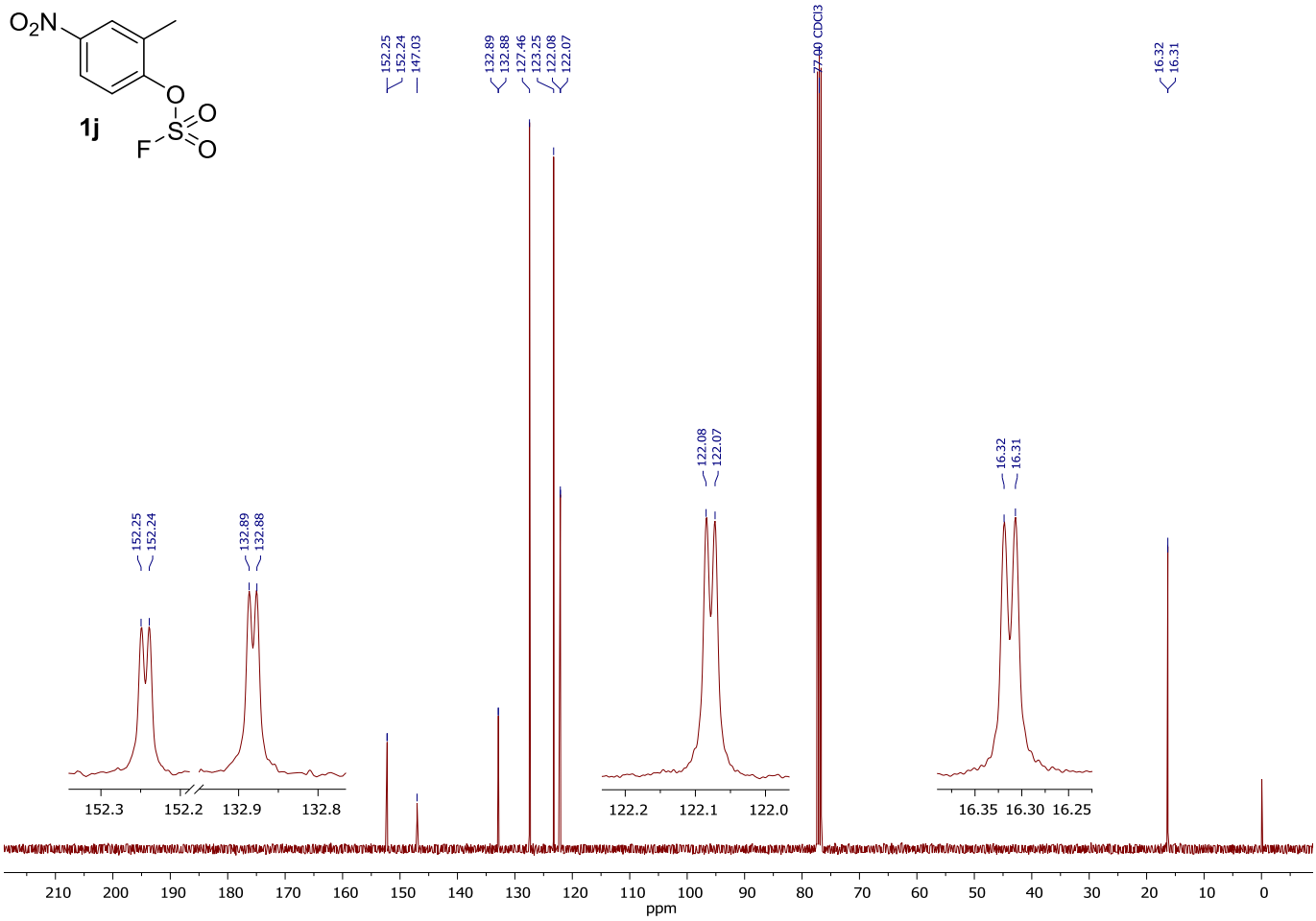

38.61
38.58
0.00 CFCl3
-128.30
-128.31
-128.32
-128.33
-128.34
-128.35
-128.36
-128.37
-128.38
-128.39
ppm

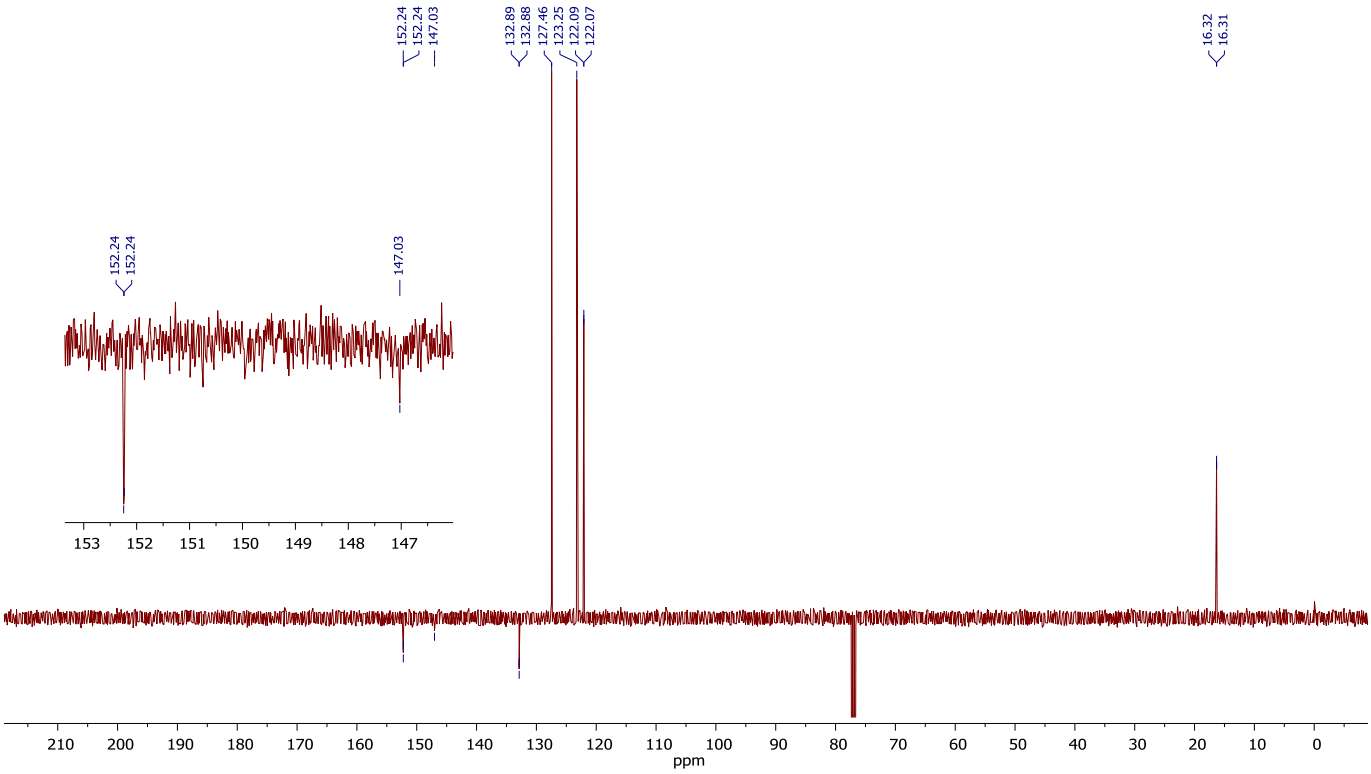

1i
F
O
O
O
F
S
154.44
154.44
152.75
152.75
137.24
137.24
137.16
137.15
130.10
130.06
125.15
125.12
123.27
123.26
123.25
117.99
117.87
77.00 CDCl3
154.45
152.75
137.3
137.2
137.1
130.2
130.0
125.2
125.0
123.2
118.0
117.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

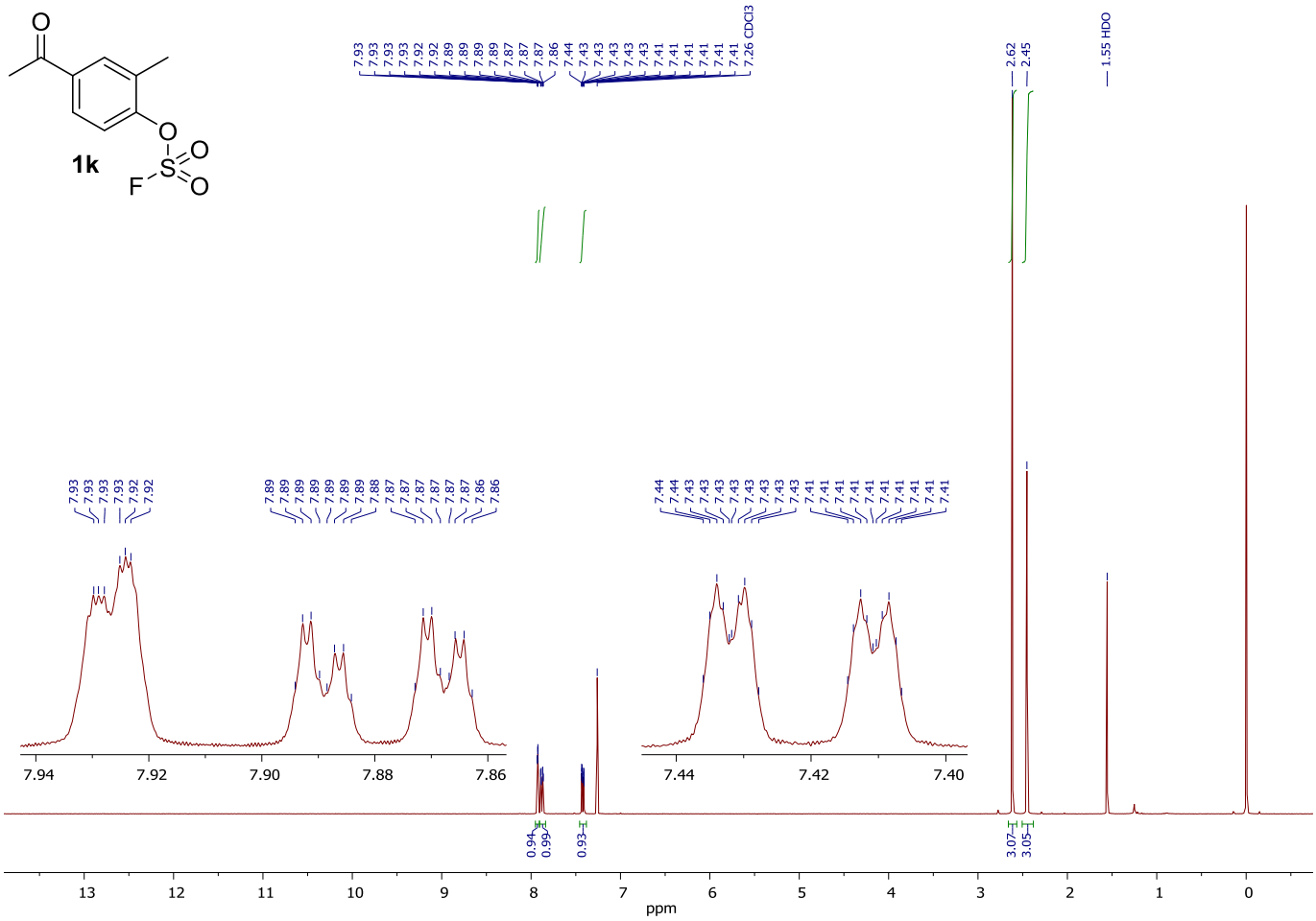

154.85
154.85
152.32
152.32
137.26
137.25
137.13
137.11
130.12
130.05
125.16
125.12
123.26
123.25
123.24
118.01
117.83
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

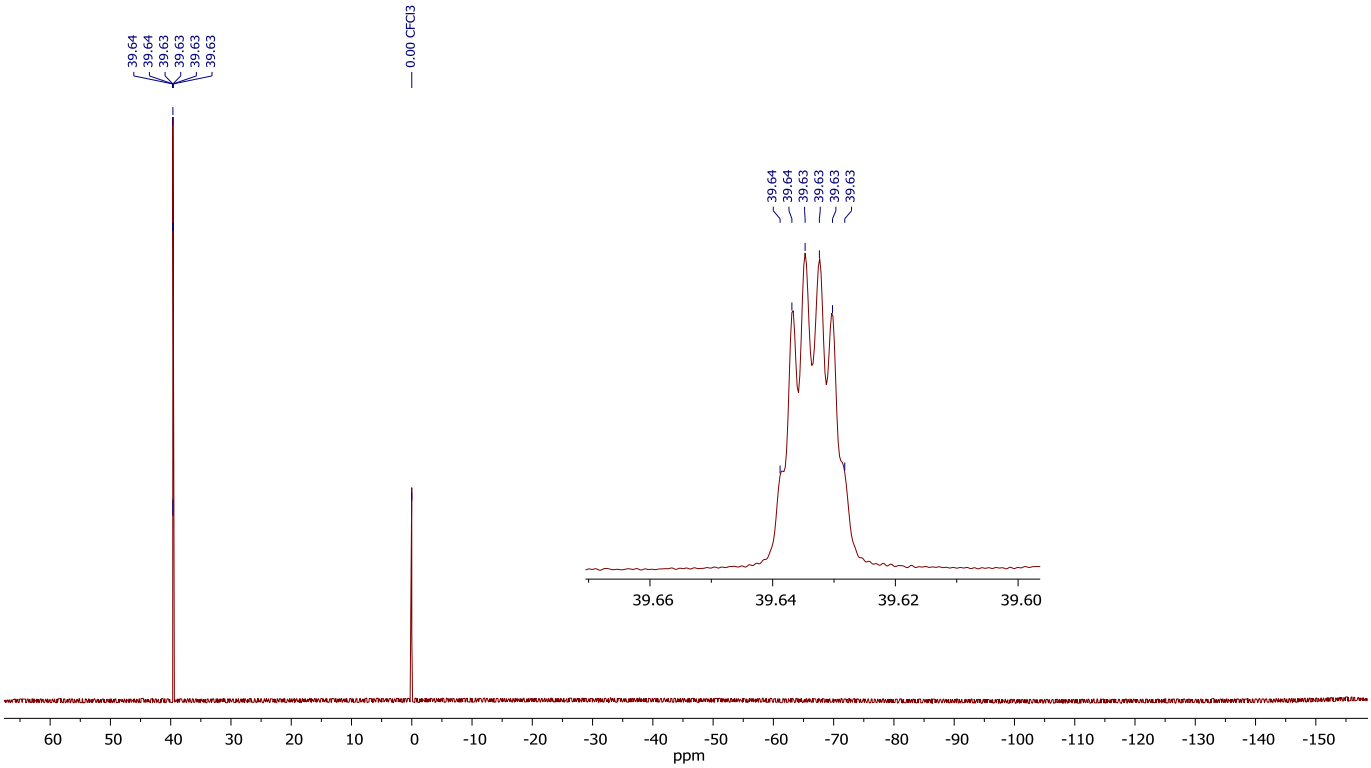

1j
7.26 CDCl3
2.51
1.54 HDO
0.84
0.89
0.91
3.00
ppm

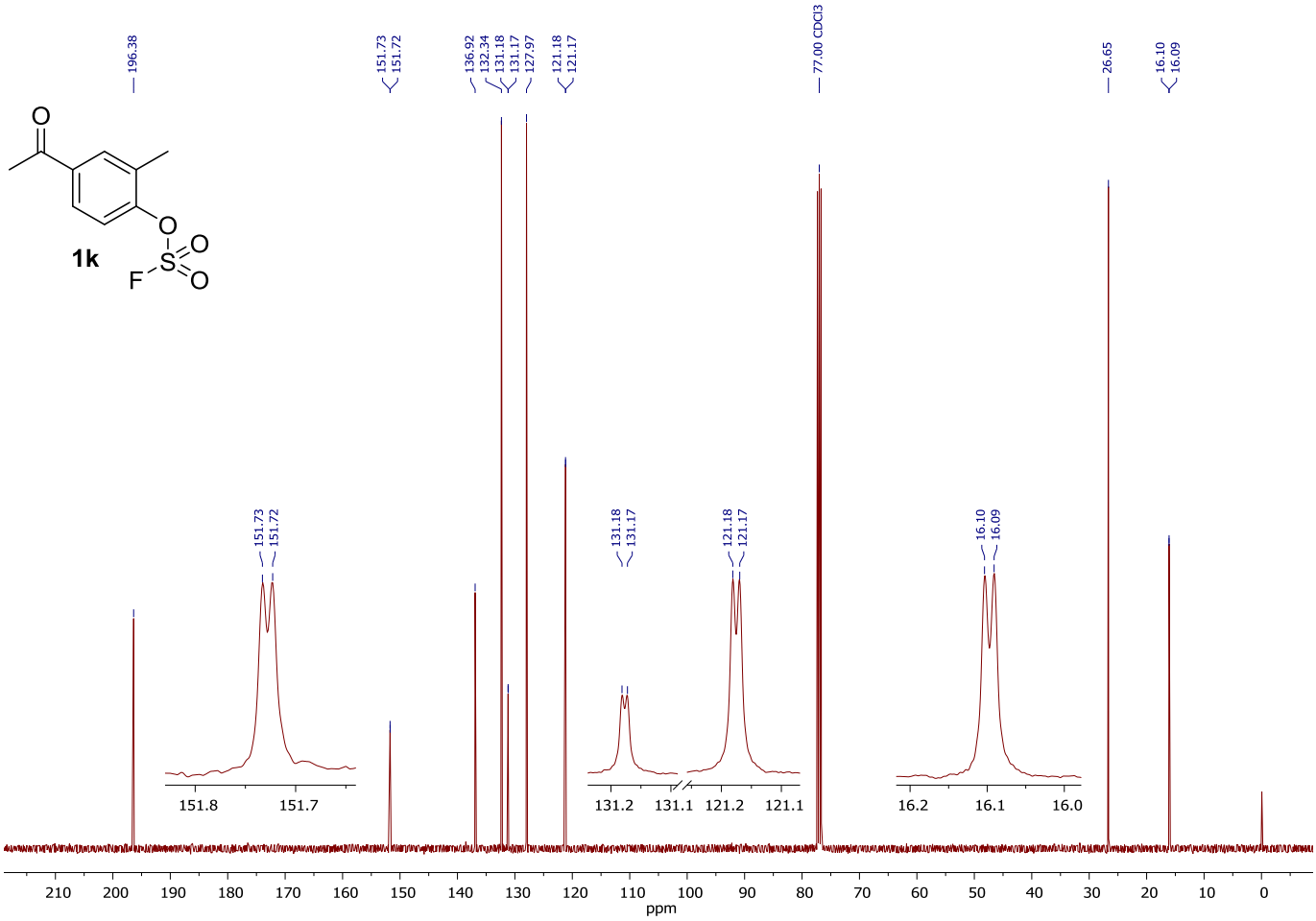

40.26
40.25
0.00 CFCl3
ppm

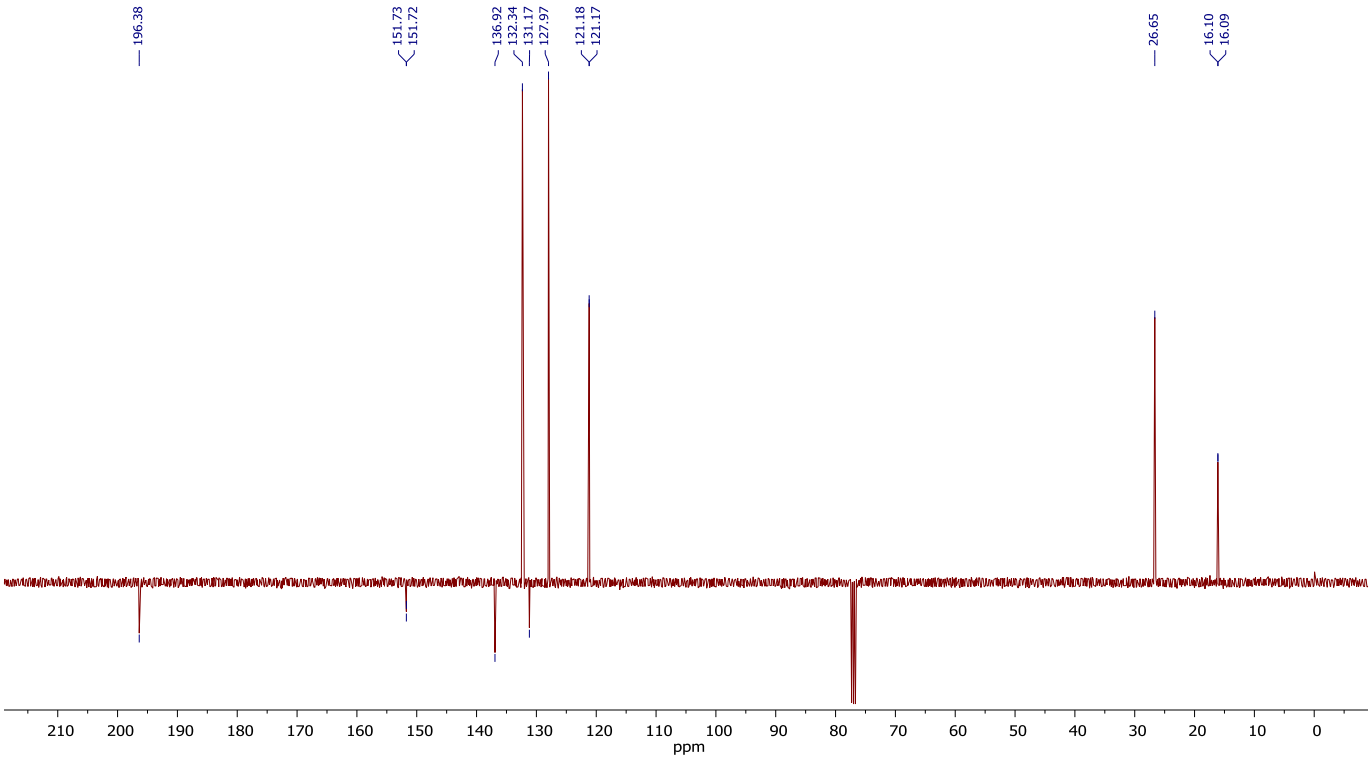

O2N
O
O
S
F
O
1j
152.25
152.24
147.03
132.89
132.88
127.46
123.25
122.08
122.07
77.00 CDCl3
16.32
16.31
152.3
152.2
132.9
132.8
122.2
122.1
122.0
16.35
16.30
16.25
ppm

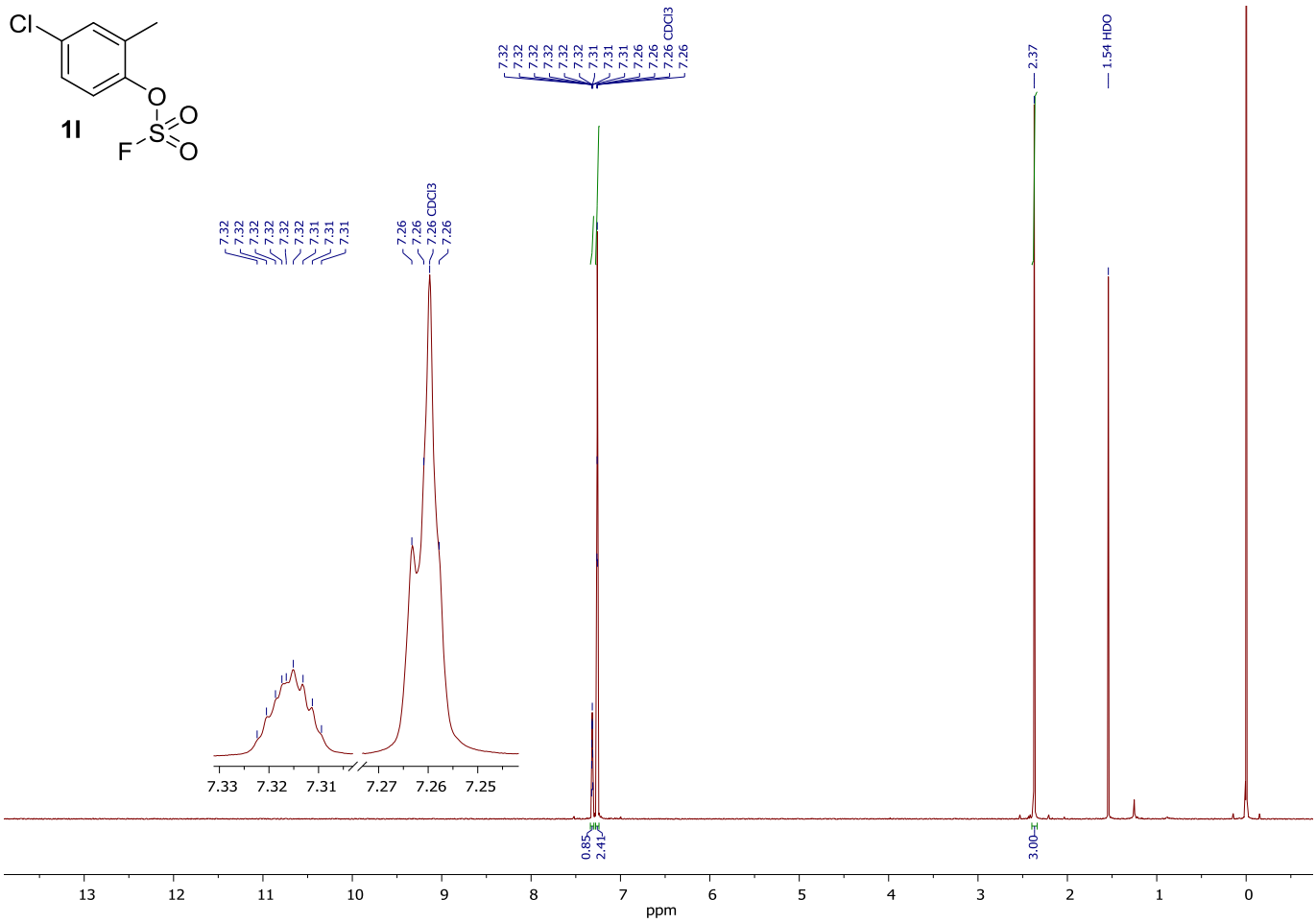

152.24
152.24
147.03
132.89
132.88
127.46
123.25
122.09
122.07
16.32
16.31
153
152
151
150
149
148
147
ppm

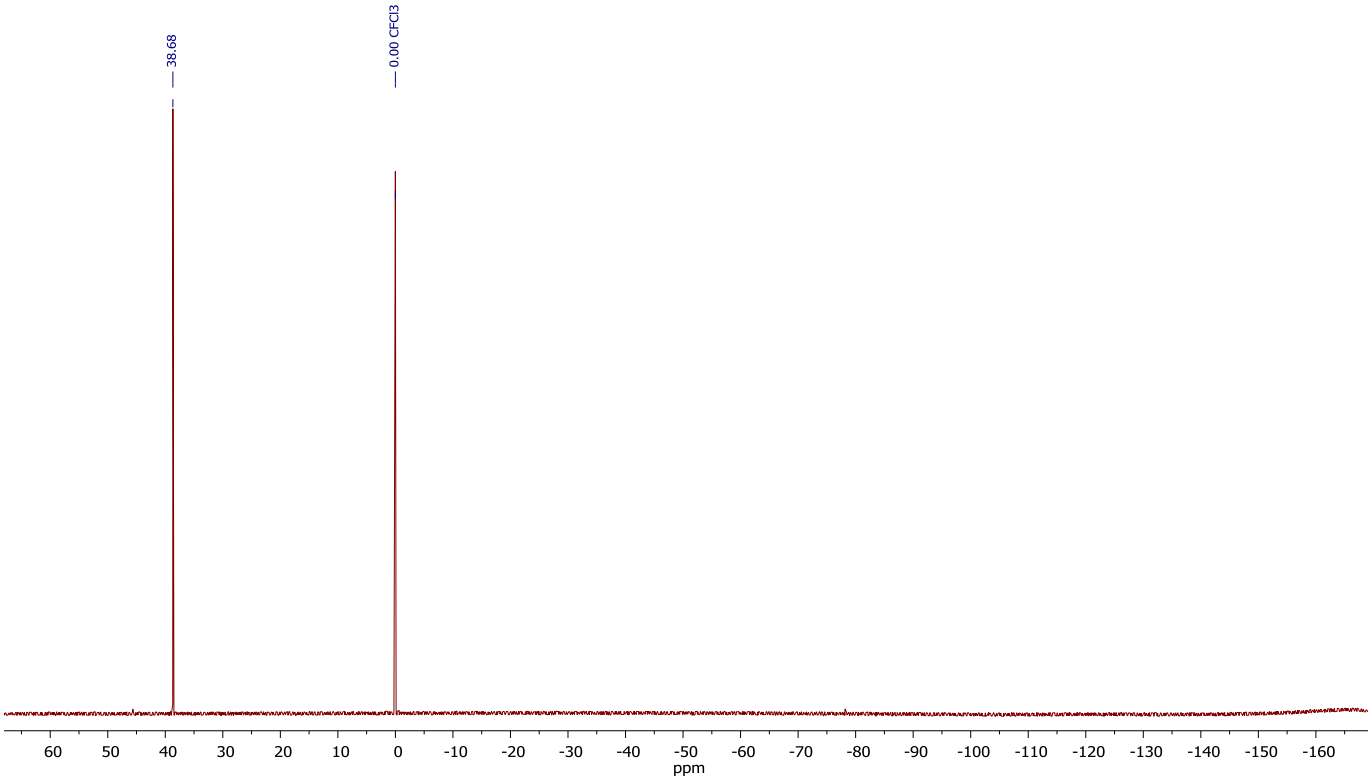

1k
7.26 CDCl3
2.62
2.45
1.55 HDO
0.94
0.99
0.93
3.07
3.05
ppm

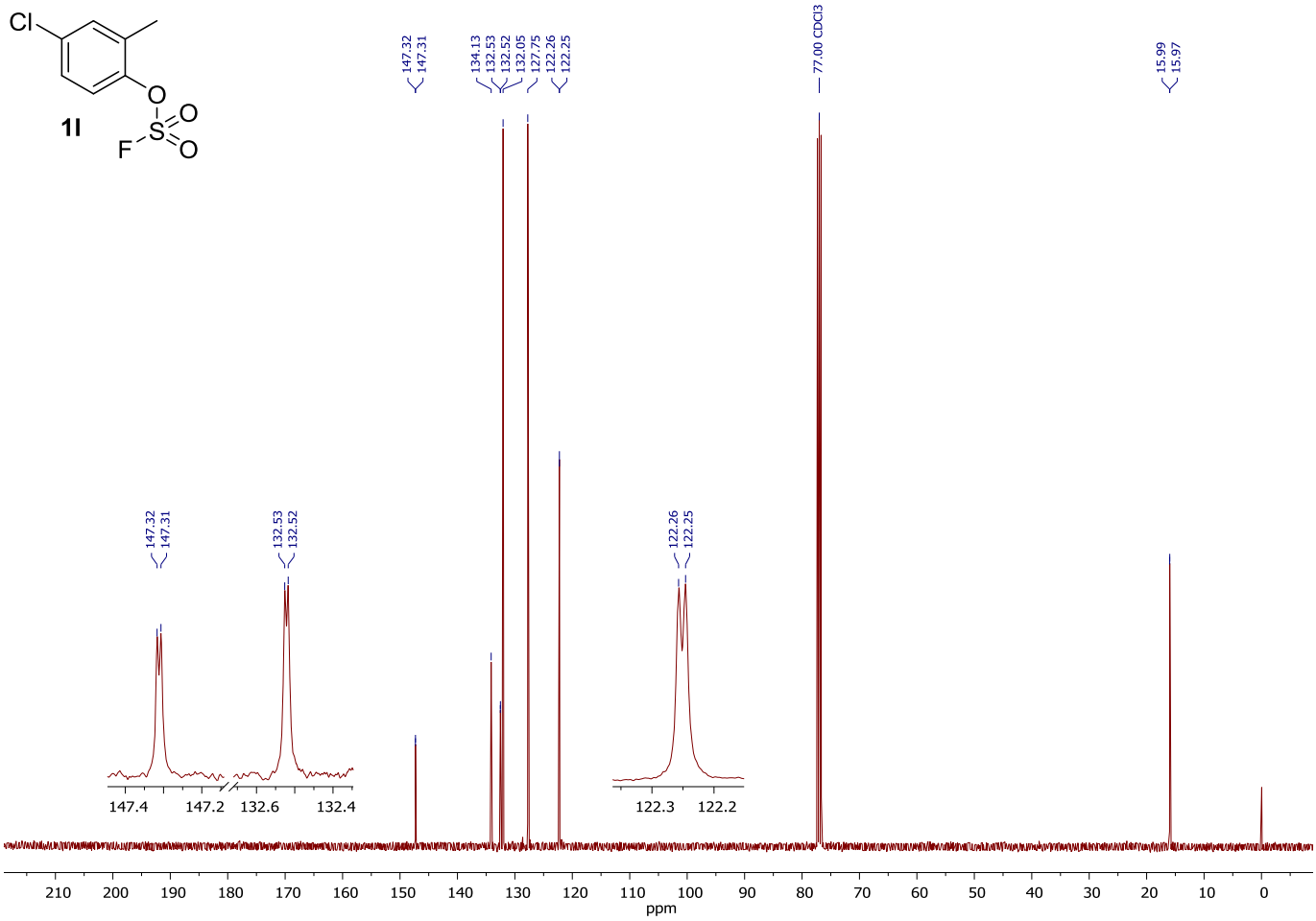

39.64
39.63
0.00 CFCl3
ppm

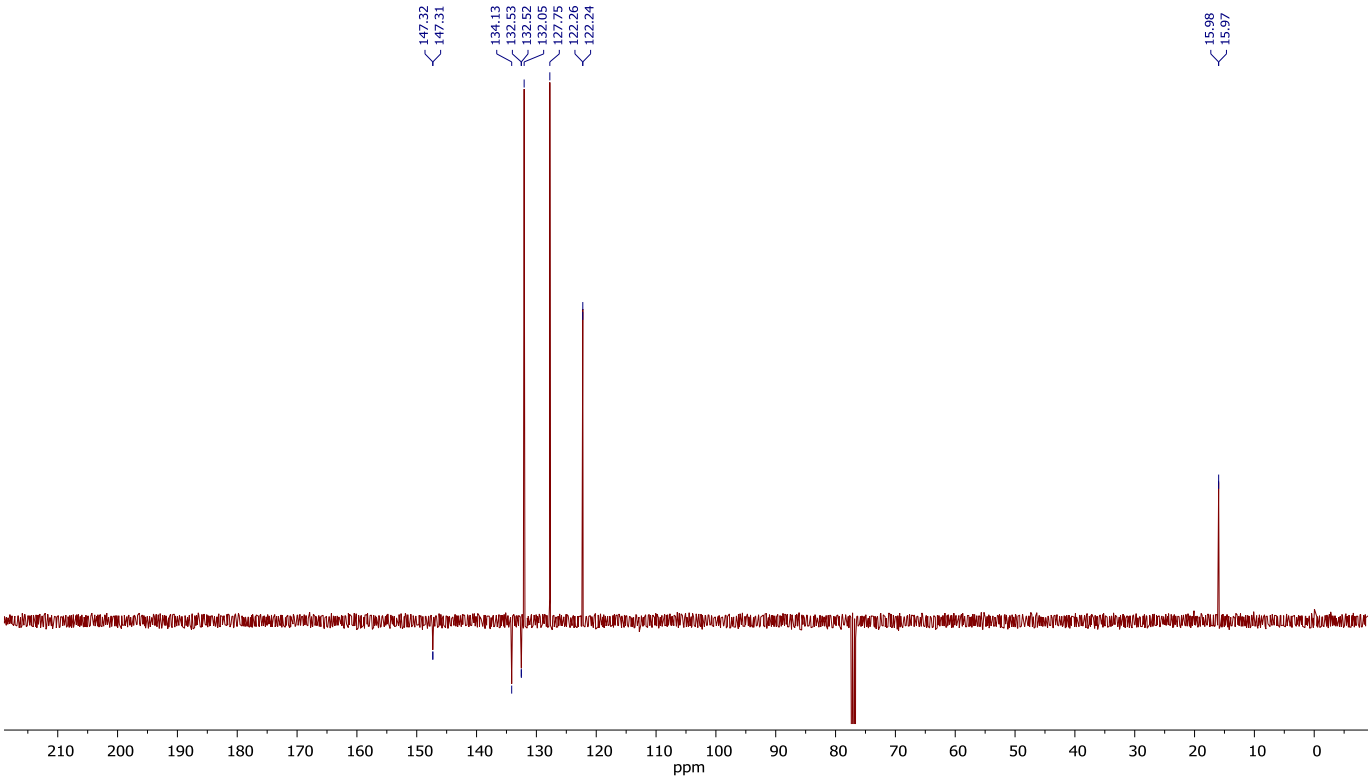

1k
196.38
151.73
151.72
136.92
132.34
131.18
131.17
127.97
121.18
121.17
77.00 CDCl3
26.65
16.10
16.09
151.8
151.7
131.2
131.1
121.2
121.1
16.2
16.1
16.0
ppm

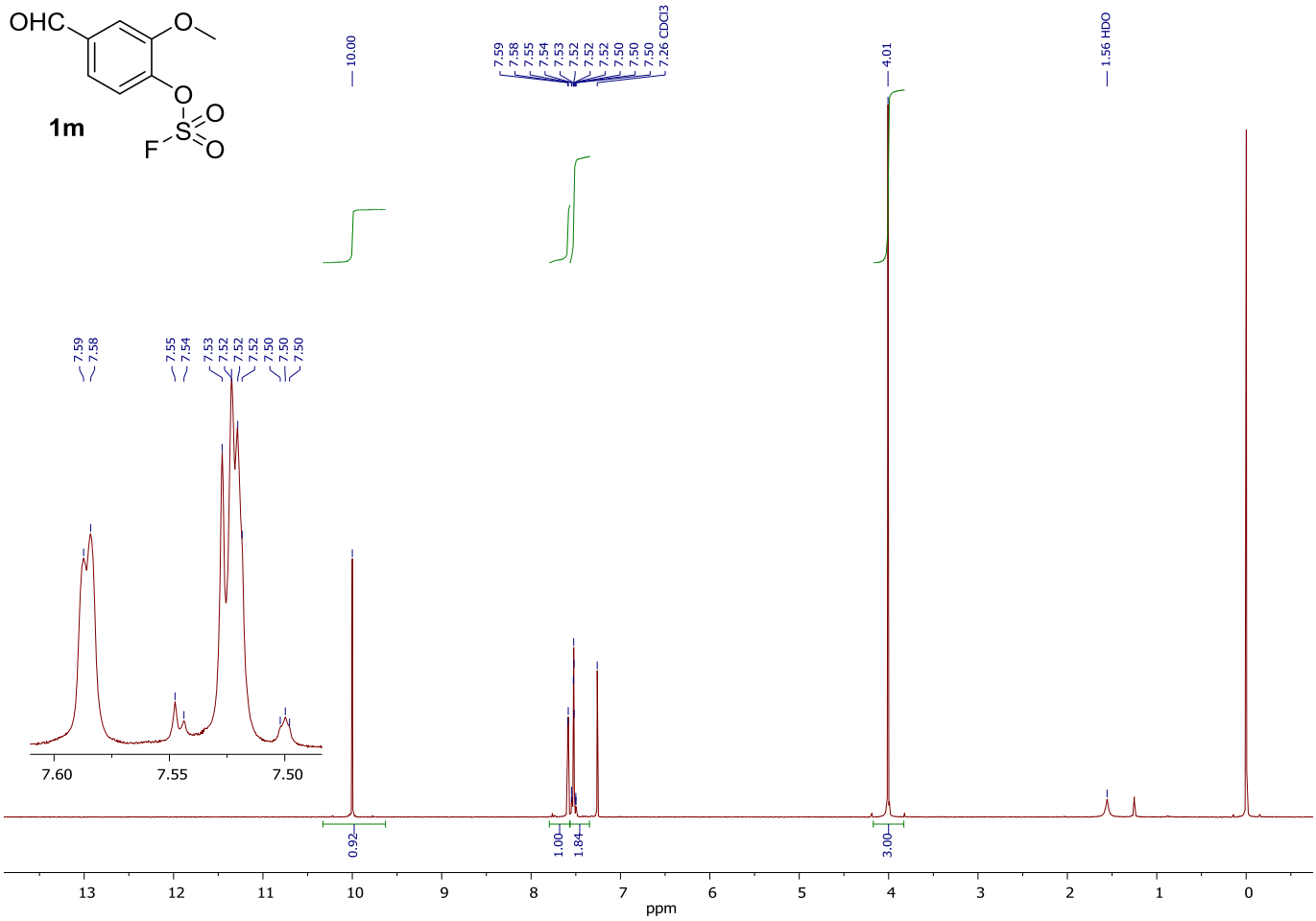

196.38
151.73
151.72
136.92
132.34
131.17
127.97
121.18
121.17
26.65
16.10
16.09
ppm

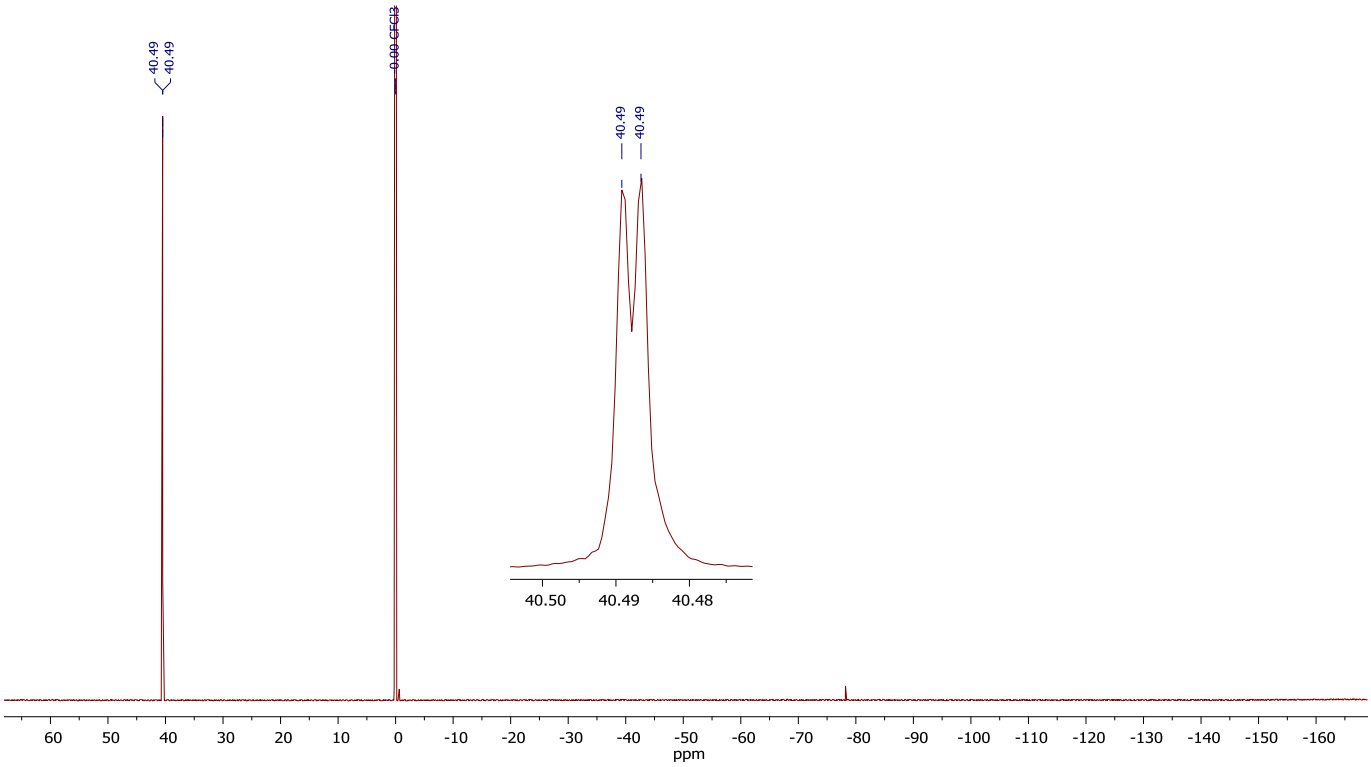

Cl
O
O
S
O
F
1l
7.32
7.32
7.32
7.32
7.32
7.32
7.31
7.31
7.31
7.26
7.26
7.26 CDCl3
7.26
2.37
1.54 HDO
7.33
7.32
7.31
7.27
7.26
7.25
0.85
2.41
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

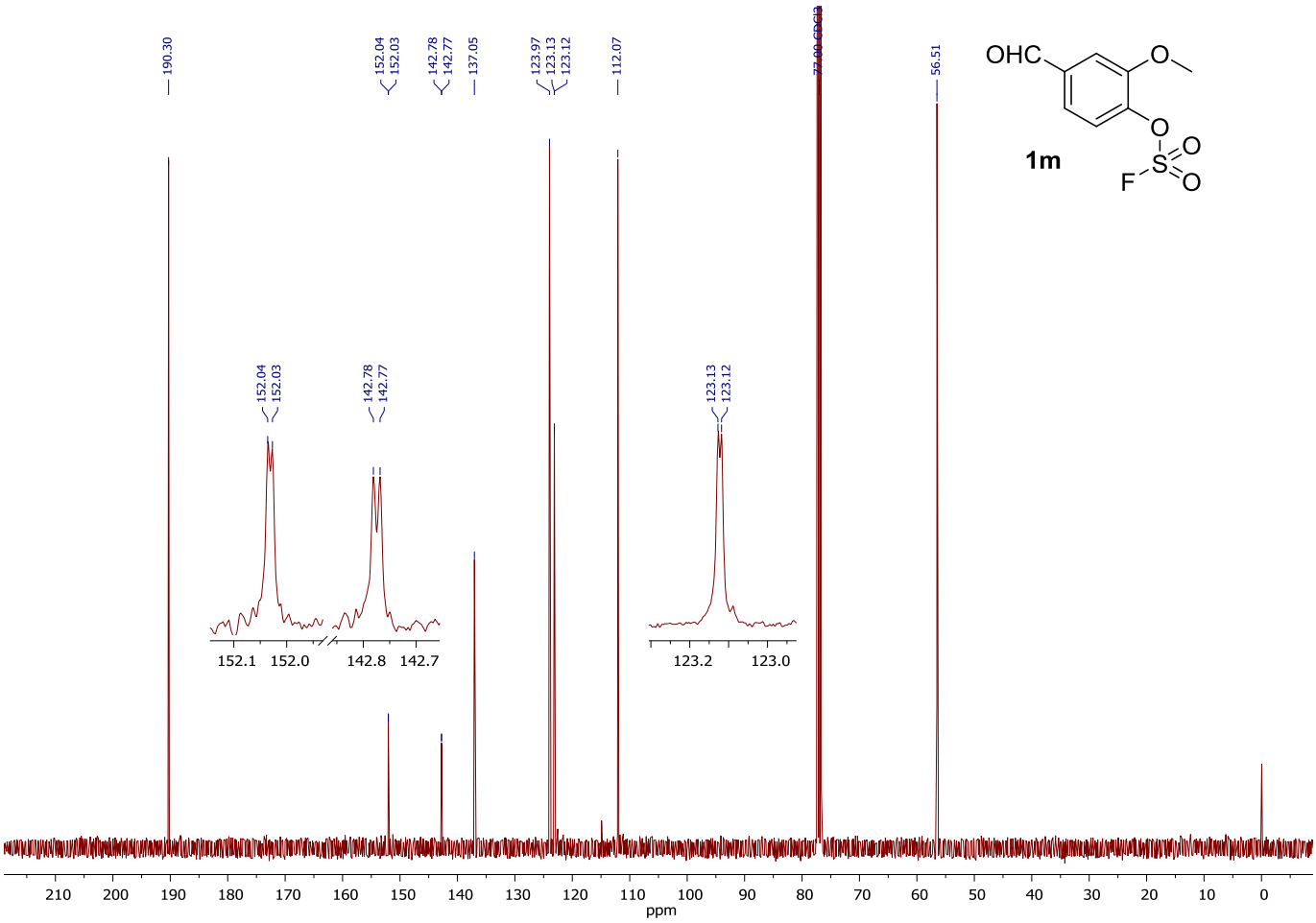

38.68
0.00 CFCl3
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
ppm

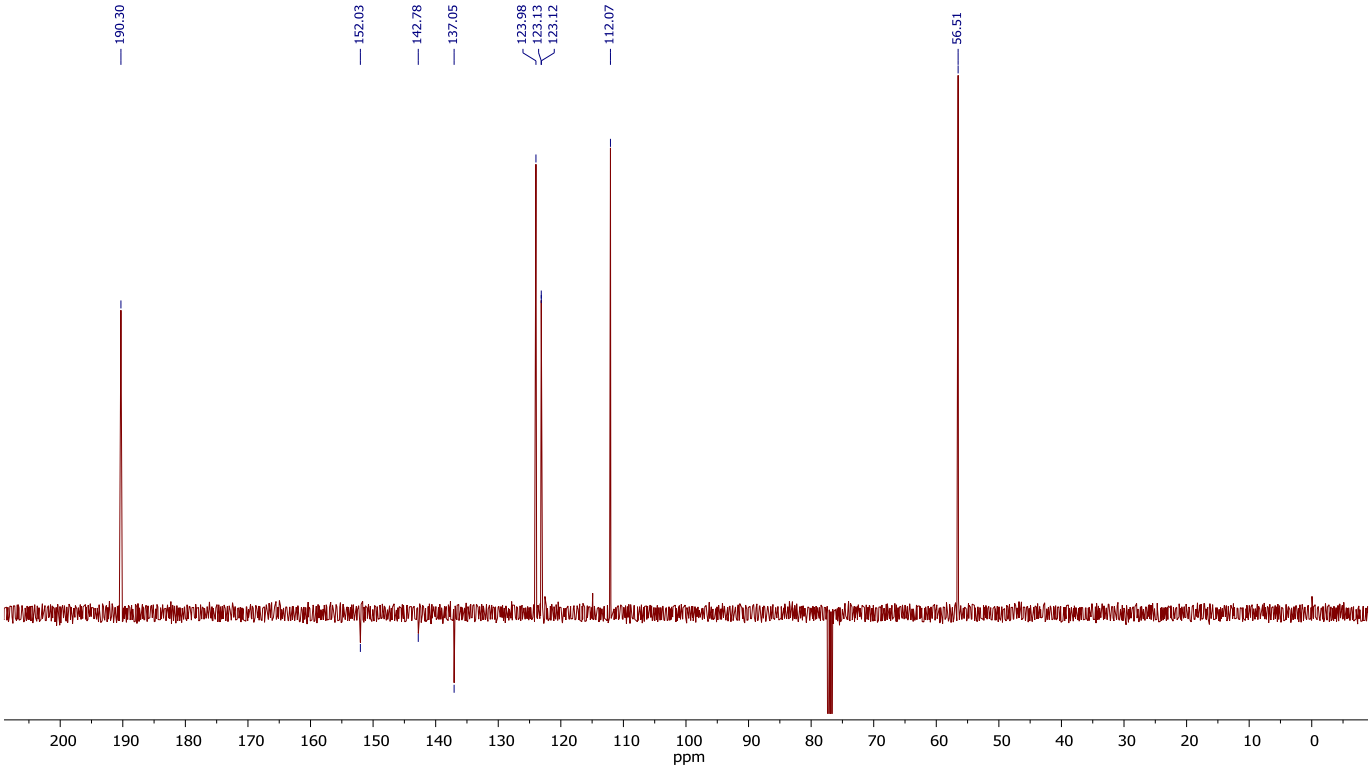

Cl
O
O
O
F
S
1l
147.32
147.31
134.13
132.53
132.52
132.05
127.75
122.26
122.25
77.00 CDCl3
15.99
15.97
147.4
147.2
132.6
132.4
122.3
122.2
ppm

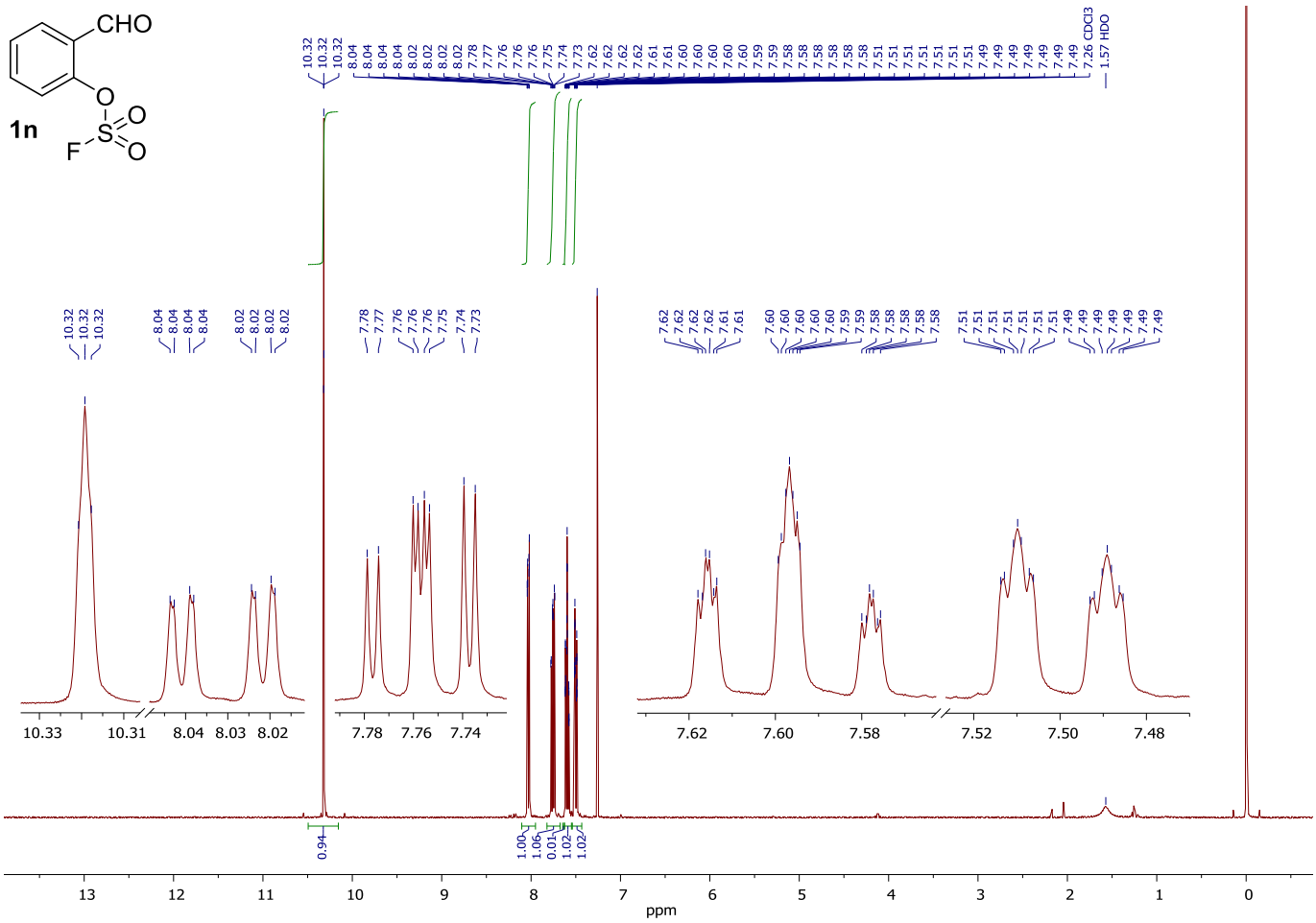

147.32
147.31
134.13
132.53
132.52
132.05
127.75
122.26
122.24
15.98
15.97
ppm

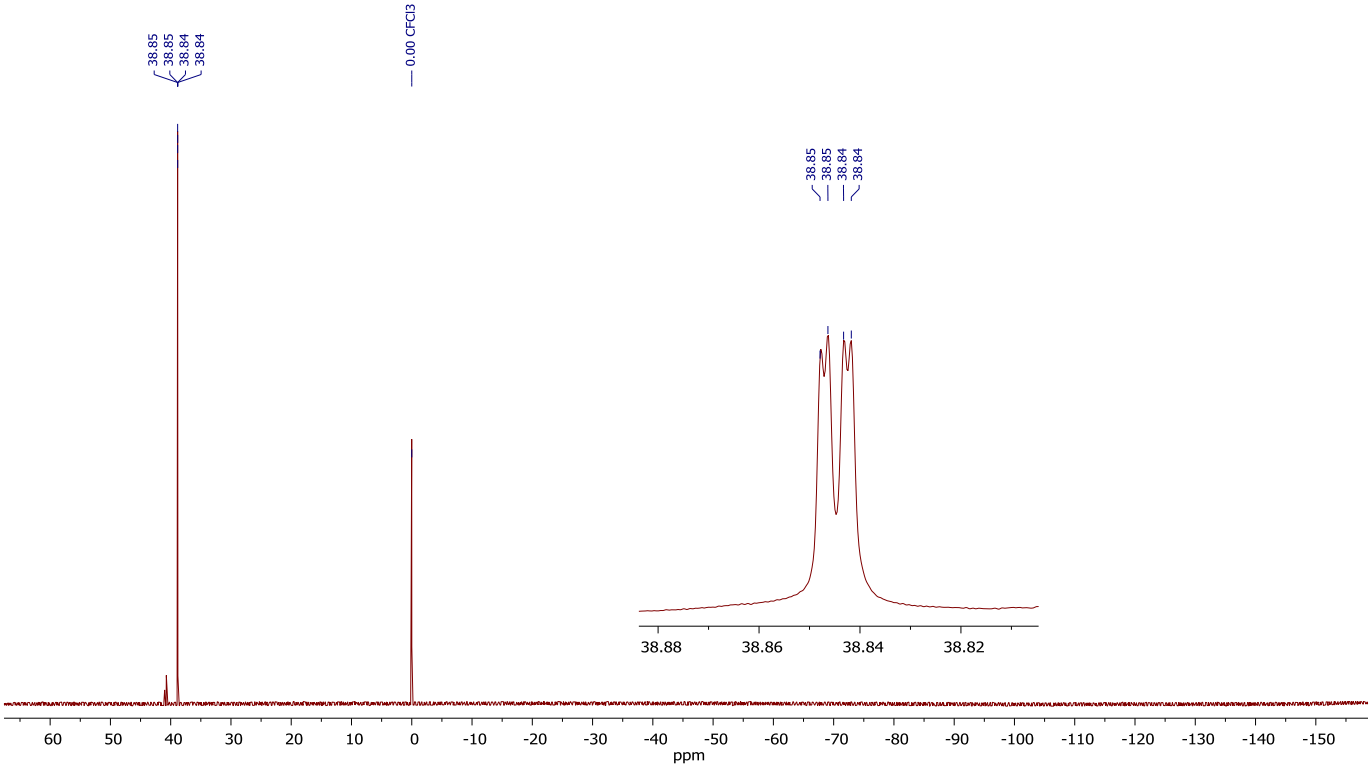

OHC
O
O
S
O
O
F
1m
10.00
7.59
7.58
7.55
7.54
7.53
7.52
7.52
7.52
7.50
7.50
7.50
7.26 CDCl3
4.01
1.56 HDO
7.60
7.55
7.50
0.92
1.00
1.84
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

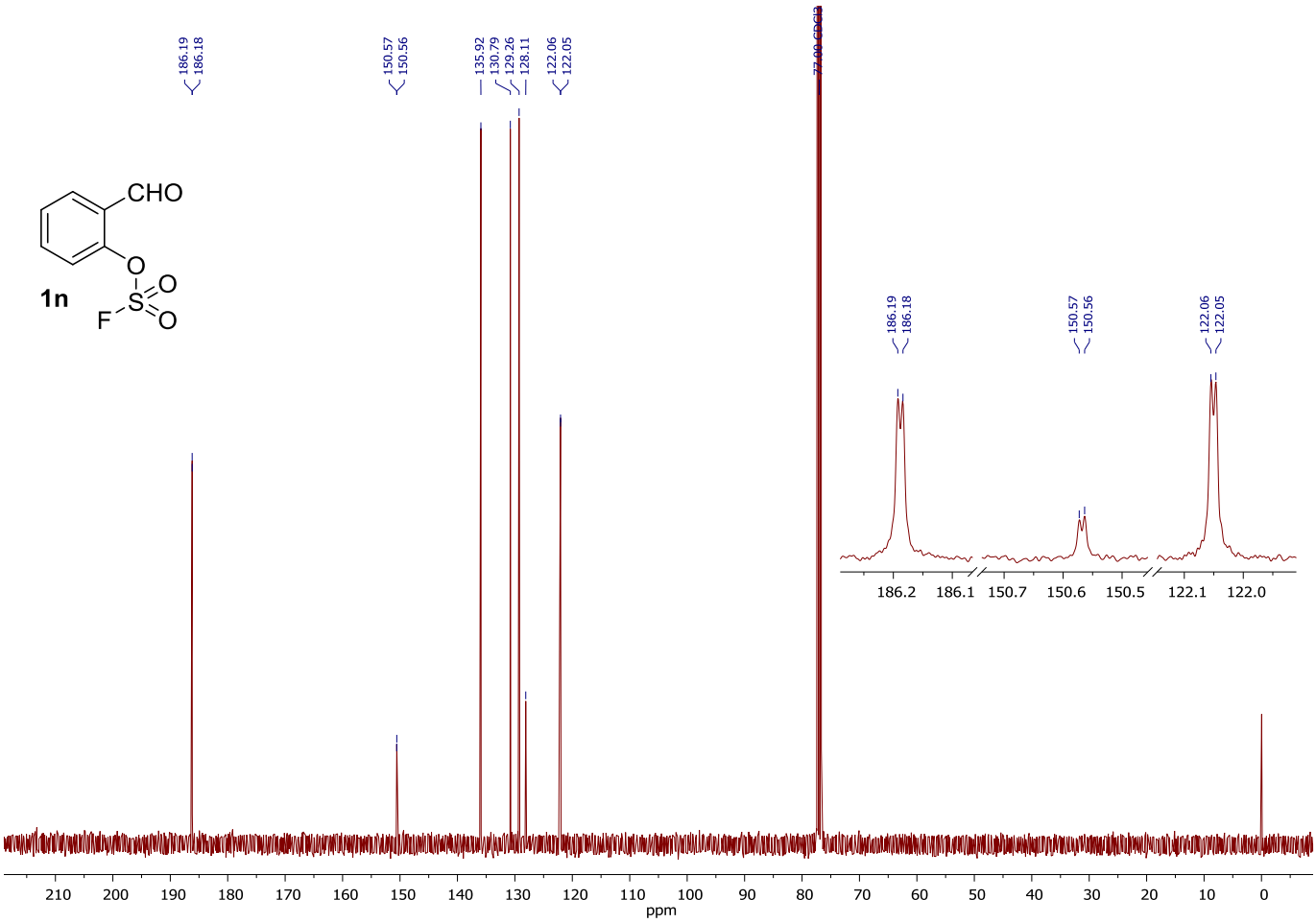

40.49
40.49
0.00 CFCl3
40.50
40.49
40.48
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
ppm

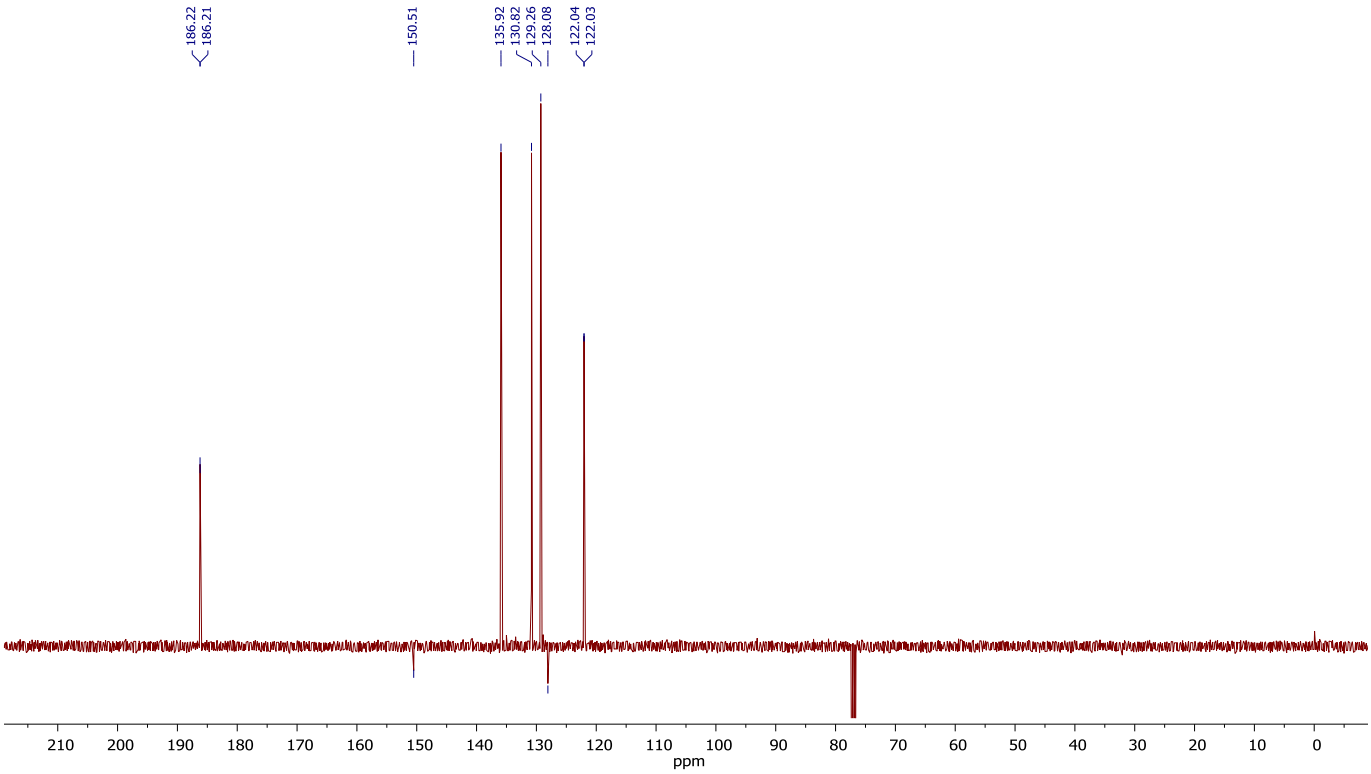

190.30
152.04
152.03
142.78
142.77
137.05
123.97
123.13
123.12
112.07
77.00 CDCl3
56.51
OHC
O
O
S
O
O
F
1m
152.1
152.0
142.8
142.7
123.2
123.0
ppm

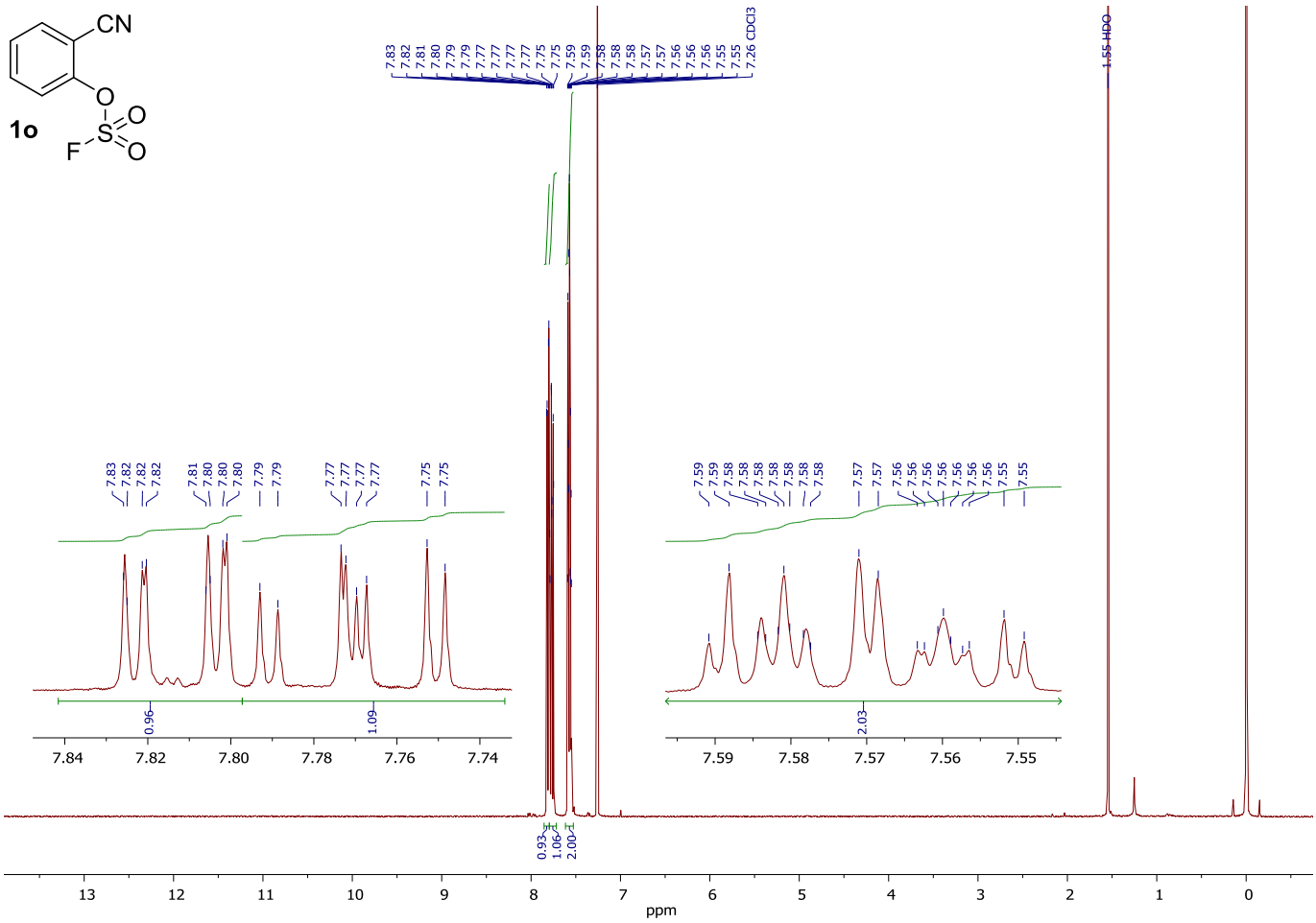

190.30
152.03
142.78
137.05
123.98
123.13
123.12
112.07
56.51
ppm

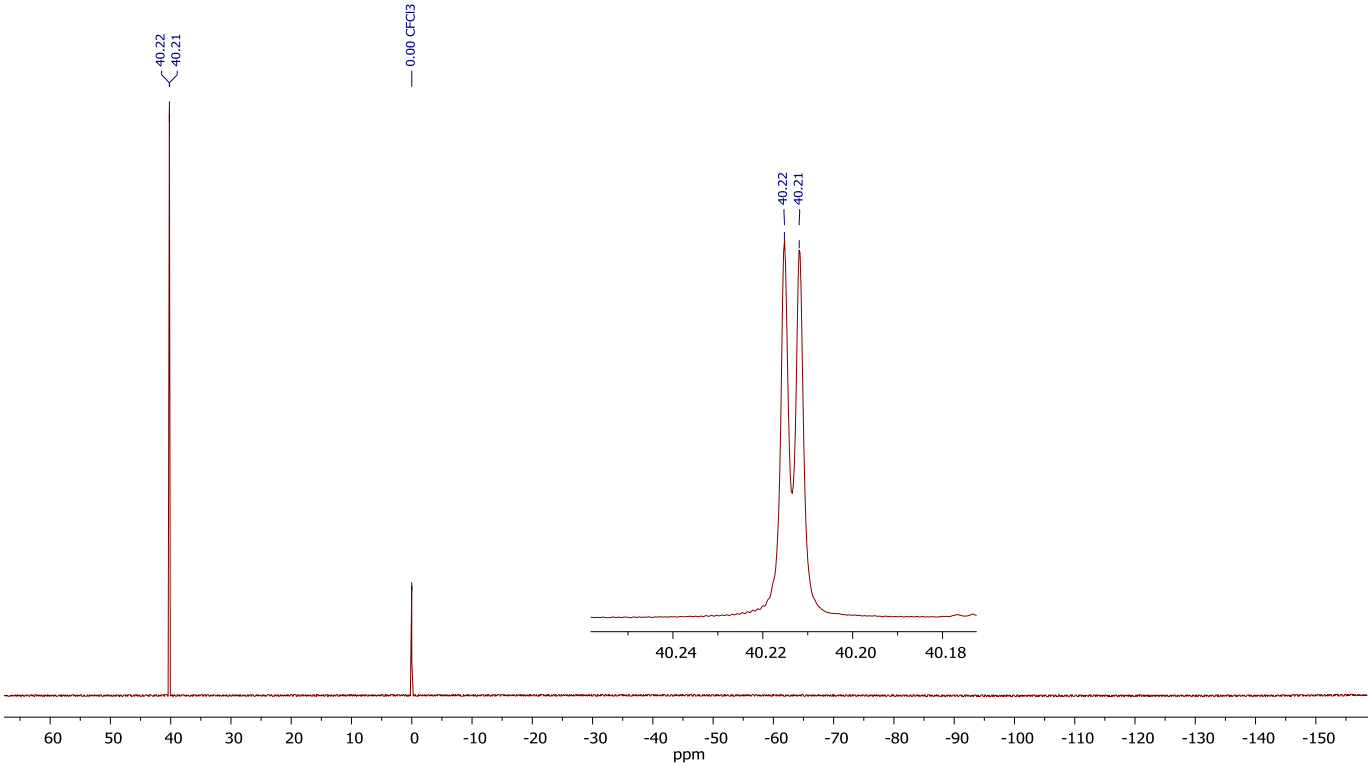

CHO
O
O
O
F
S
1n
7.26 CDCl3
1.57 HDO
0.94
1.00
1.06
0.01
1.02
1.02
ppm

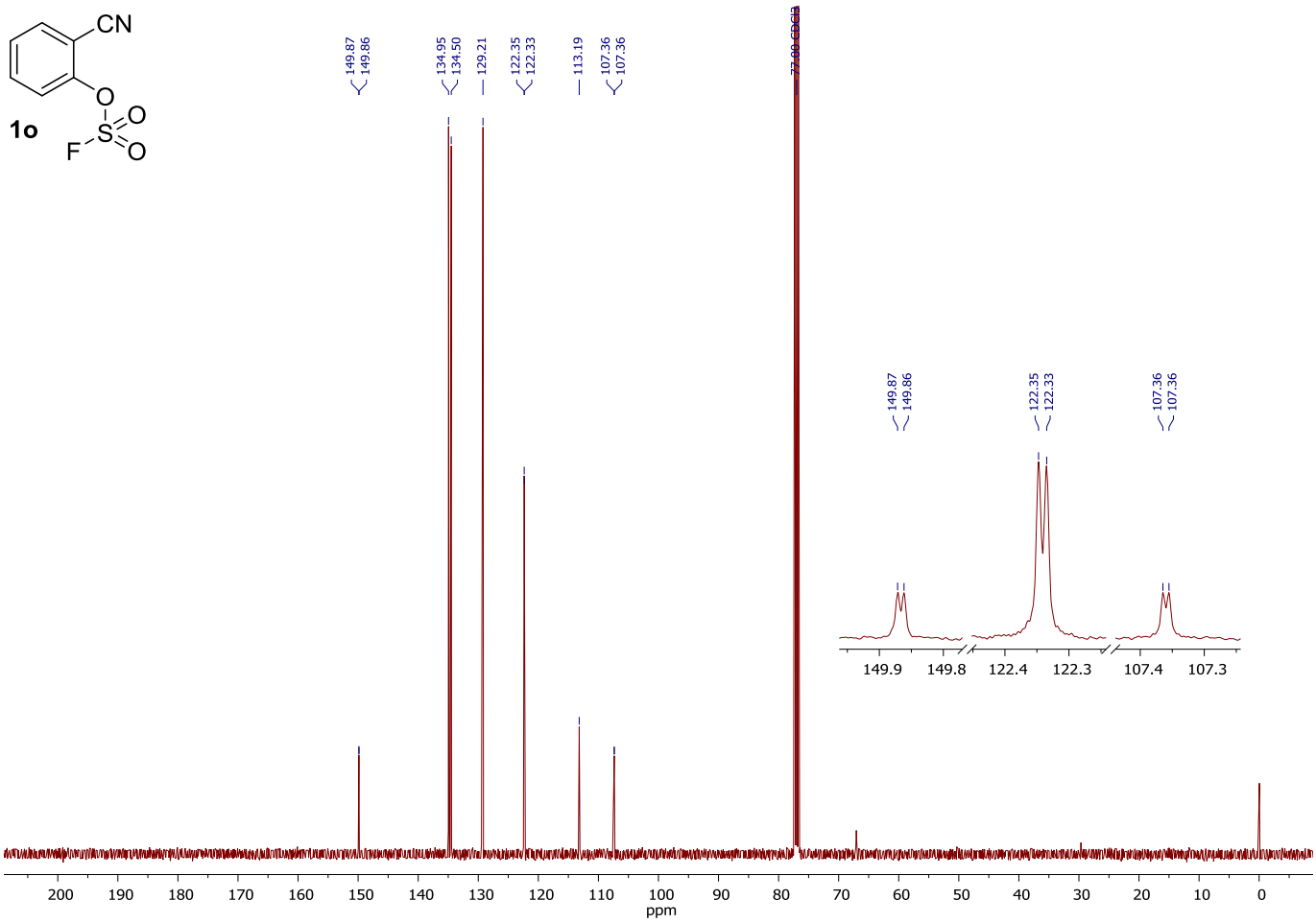

38.85
38.85
38.84
38.84
0.00 CFCl3
ppm

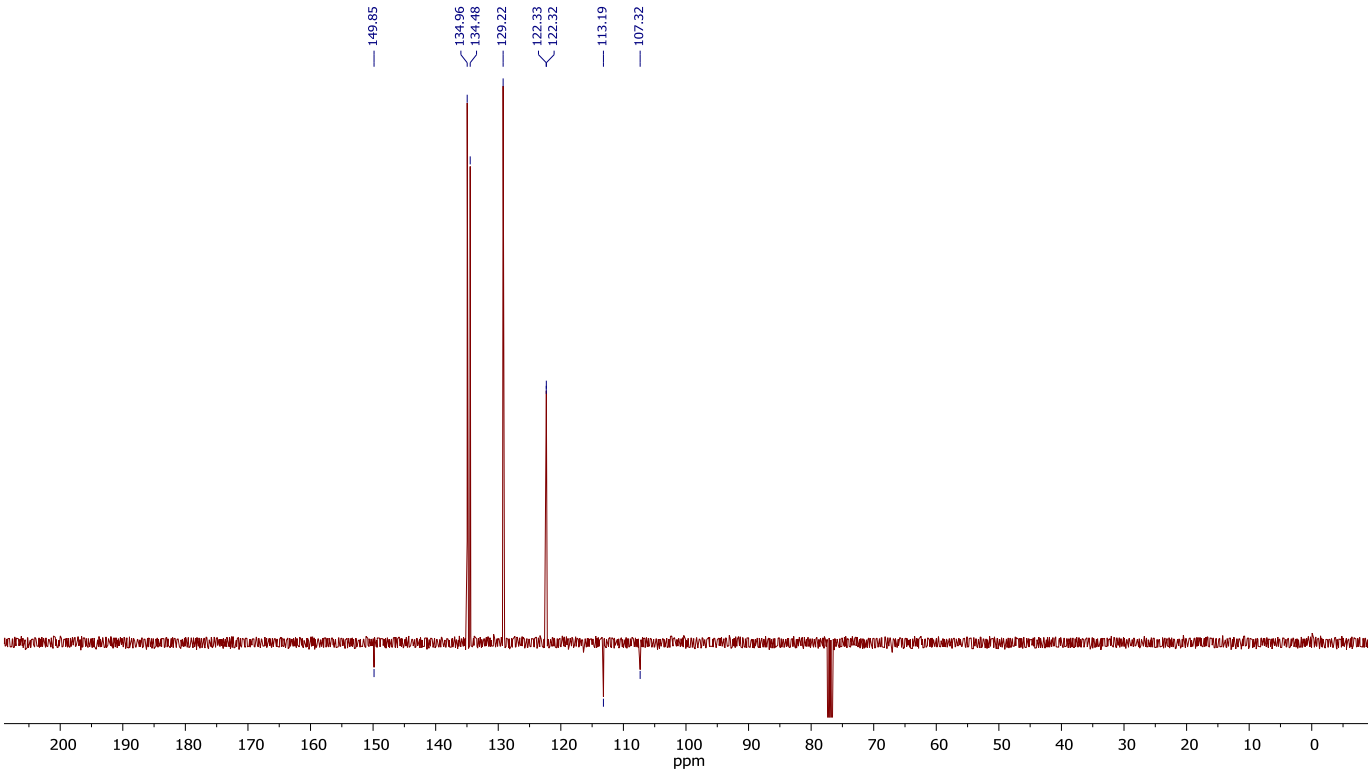

186.19
186.18
150.57
150.56
135.92
130.79
129.26
128.11
122.06
122.05
77.00 CDCl3
CHO
O
O
O
F
S
1n
186.2
186.1
150.7
150.6
150.5
122.1
122.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

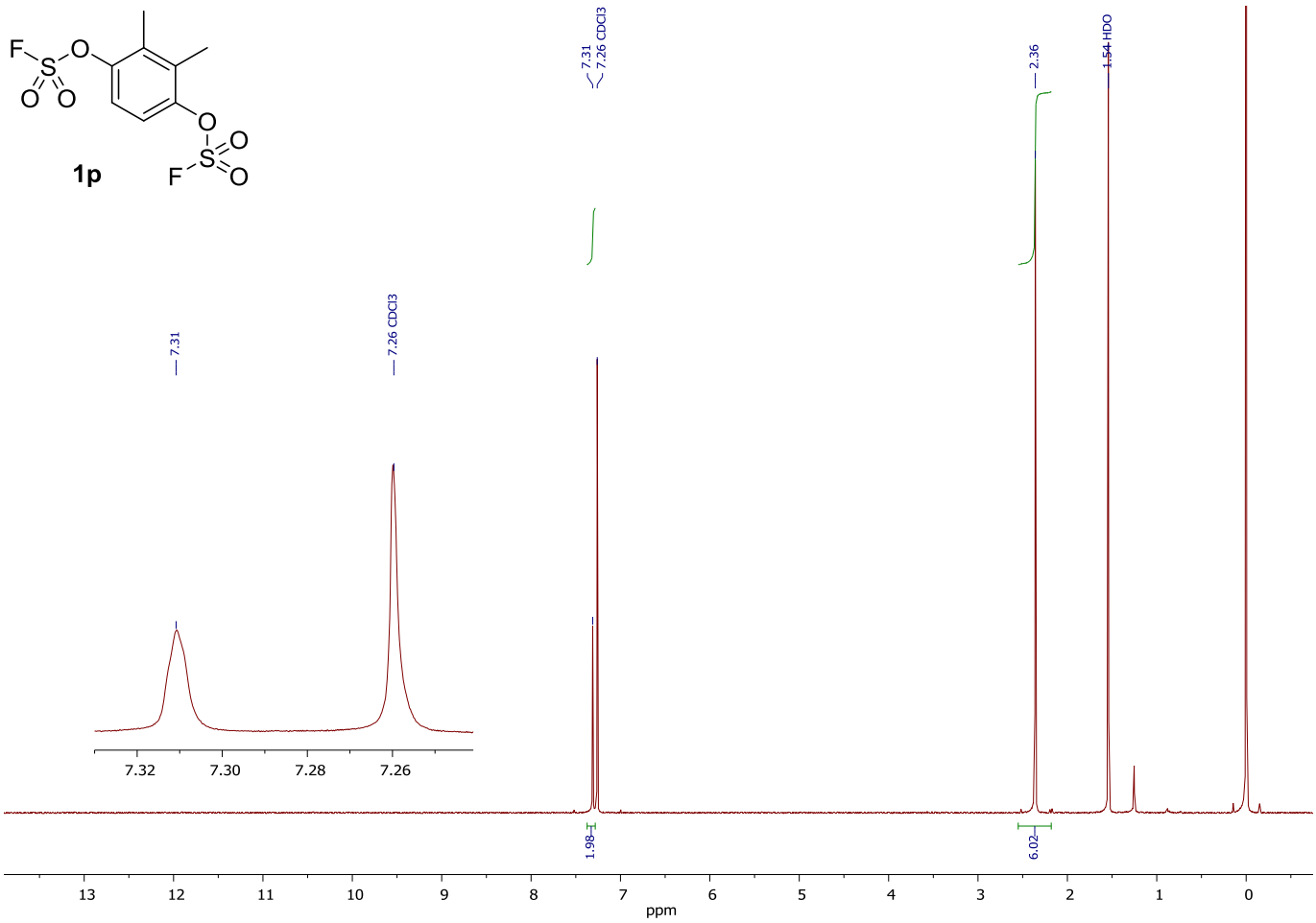

186.22
186.21
150.51
135.92
130.82
129.26
128.08
122.04
122.03
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

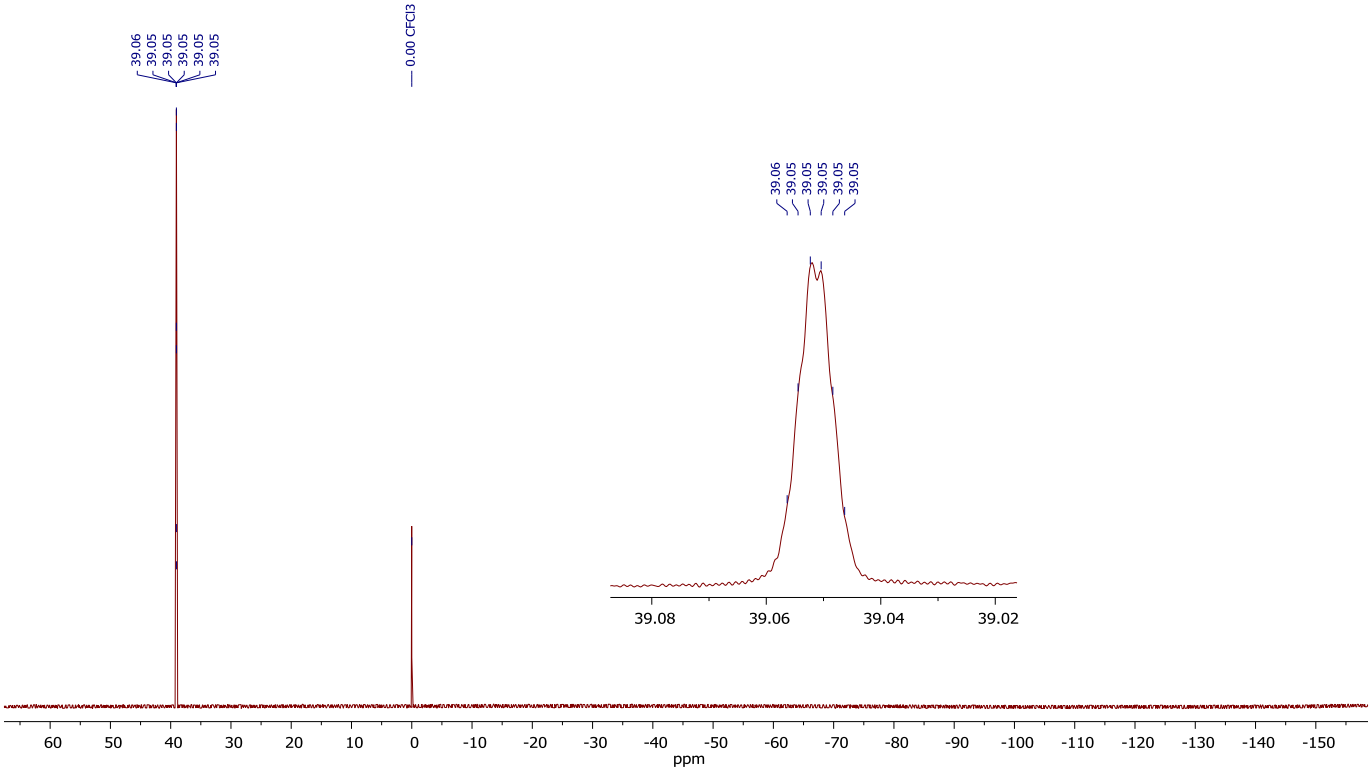

CN
O
O
O
F
S
1o
7.83 7.82 7.81 7.80 7.79 7.79 7.77 7.77 7.77 7.77 7.77 7.75 7.75 7.59 7.59 7.58 7.58 7.58 7.57 7.57 7.56 7.56 7.56 7.55 7.26 CDCl3
1.55 HDO
0.96
1.09
2.03
0.93
1.06
2.00
ppm

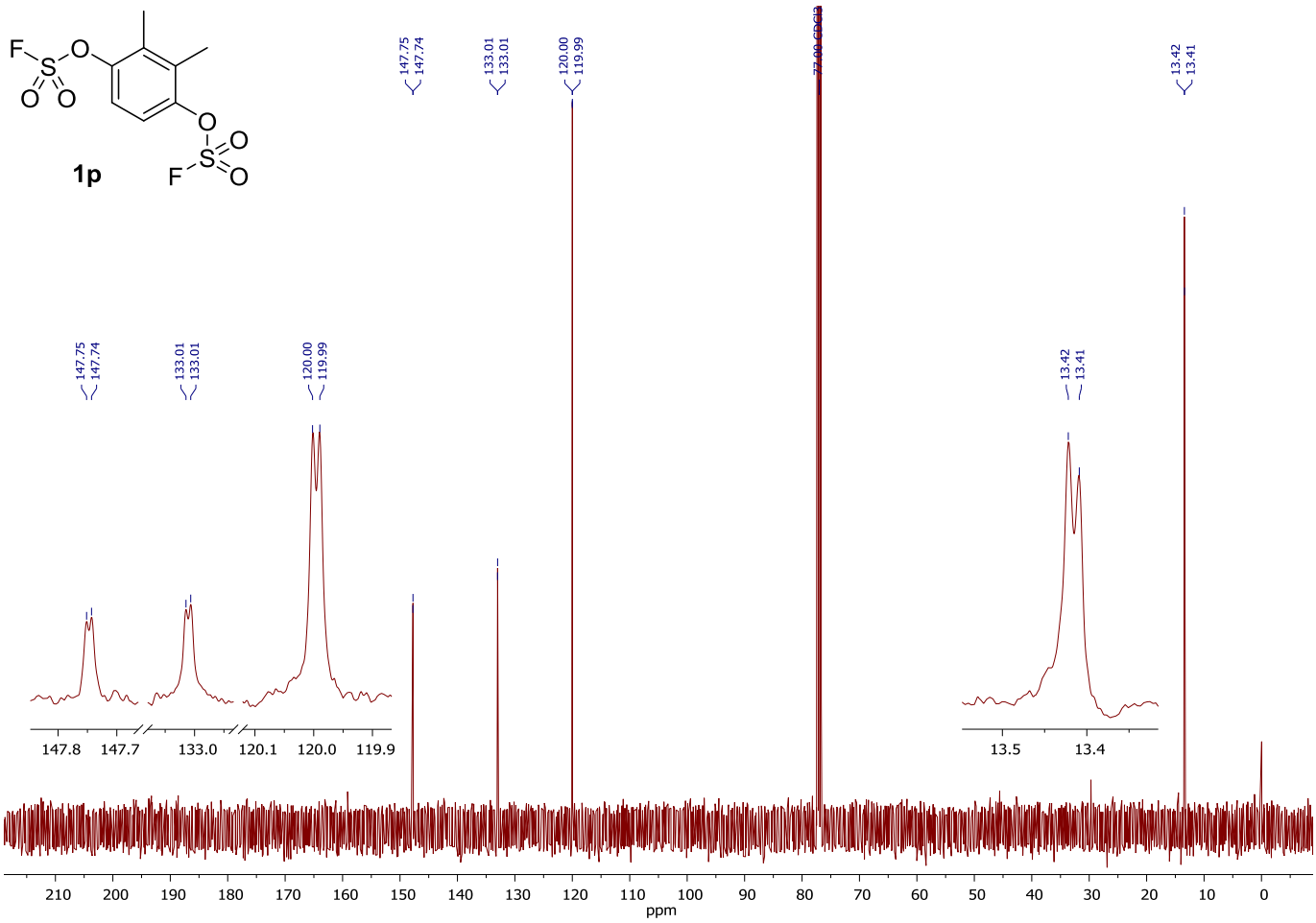

40.22
40.21
0.00 CFCl3
ppm

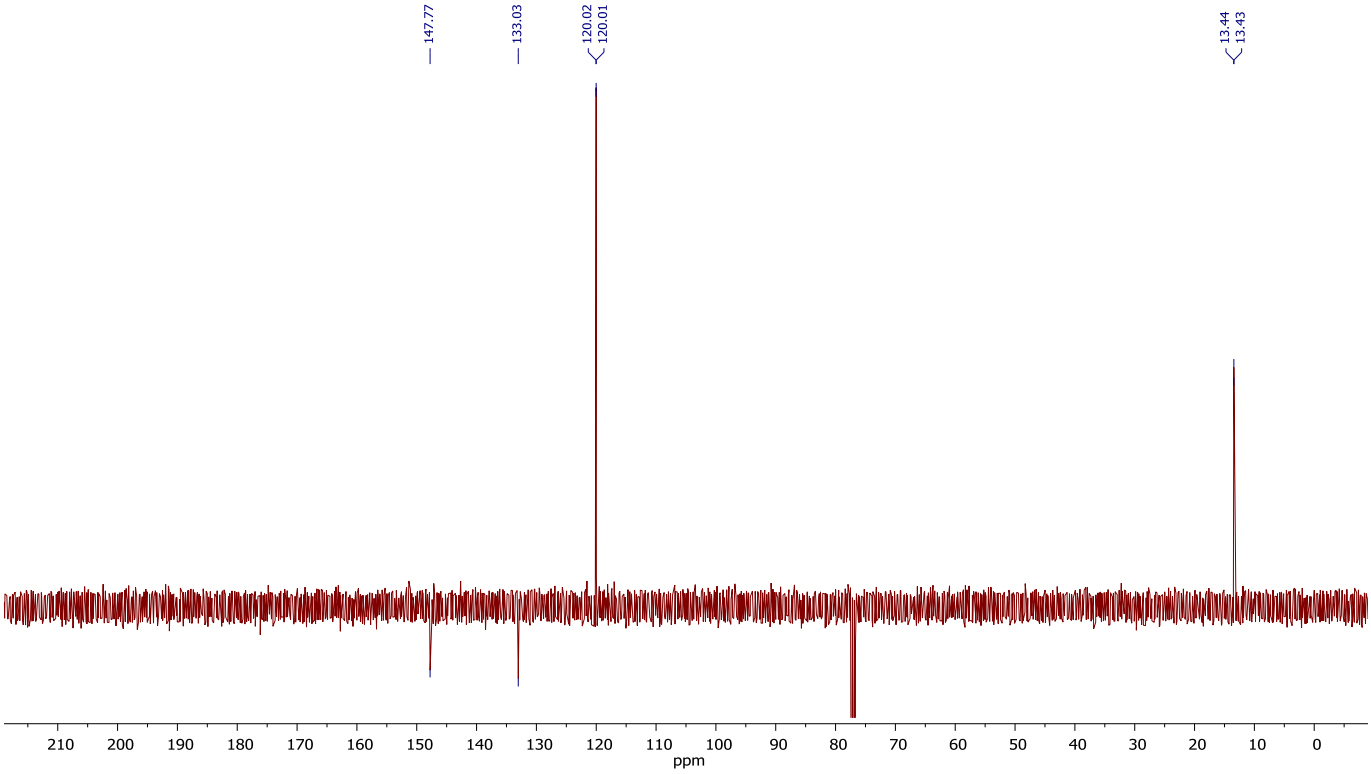

CN
O
O
O
F
S
1o
149.87
149.86
134.95
134.50
129.21
122.35
122.33
113.19
107.36
107.36
77.00 CDCl3
149.9
149.8
122.4
122.3
107.4
107.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

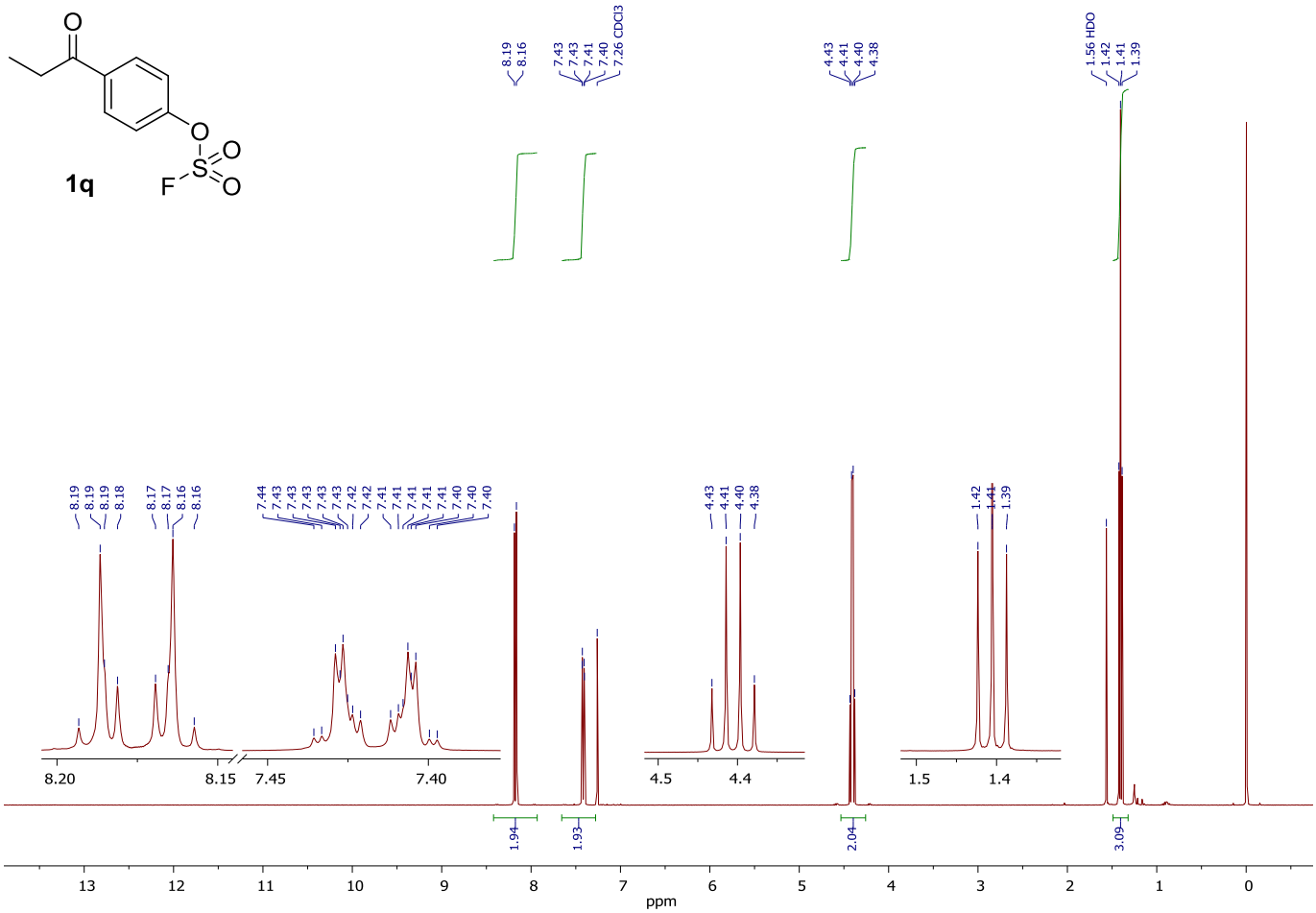

149.85
134.96
134.48
129.22
122.33
122.32
113.19
107.32
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

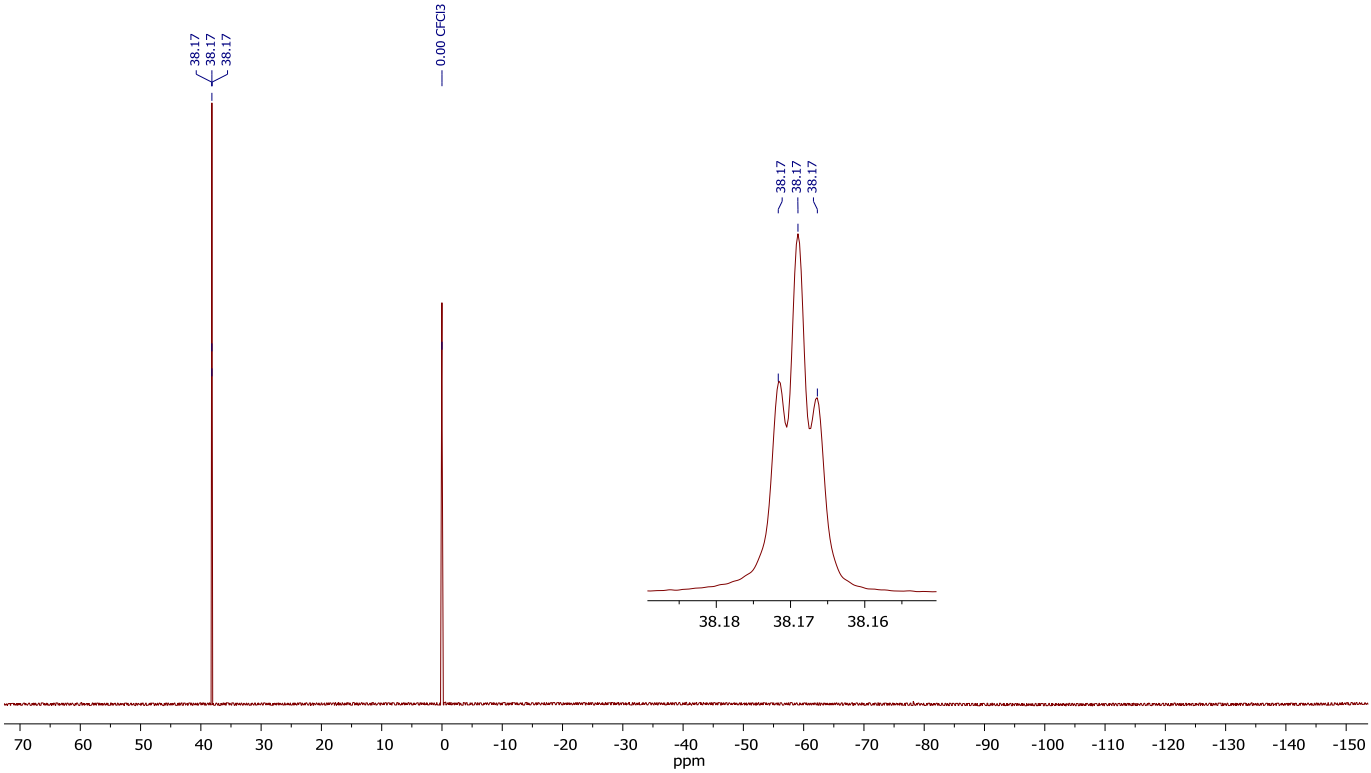

1p
7.31
7.26 CDCl3
2.36
1.54 HDO
1.98
6.02
ppm

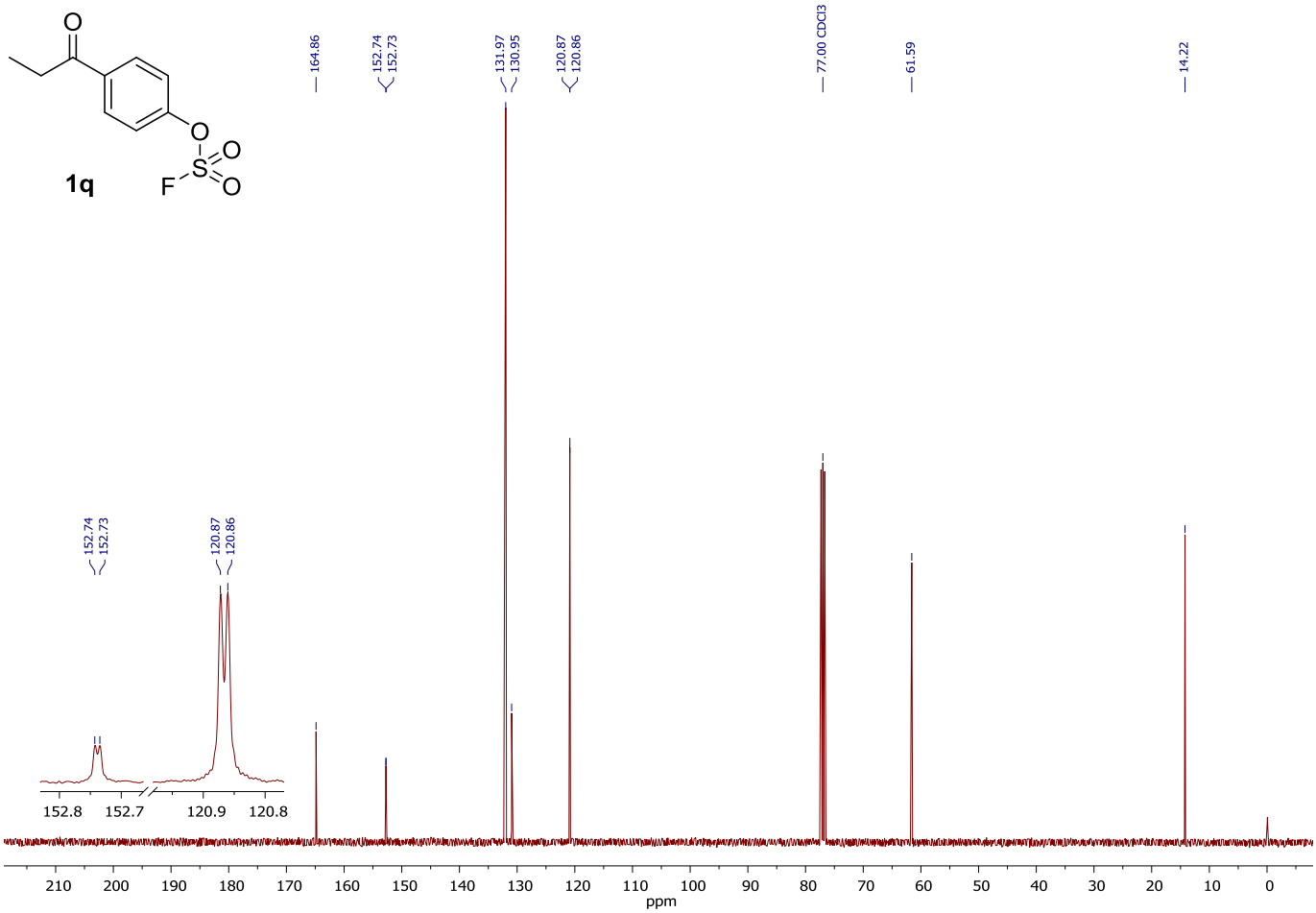

39.06
39.05
0.00 CFCl3
ppm

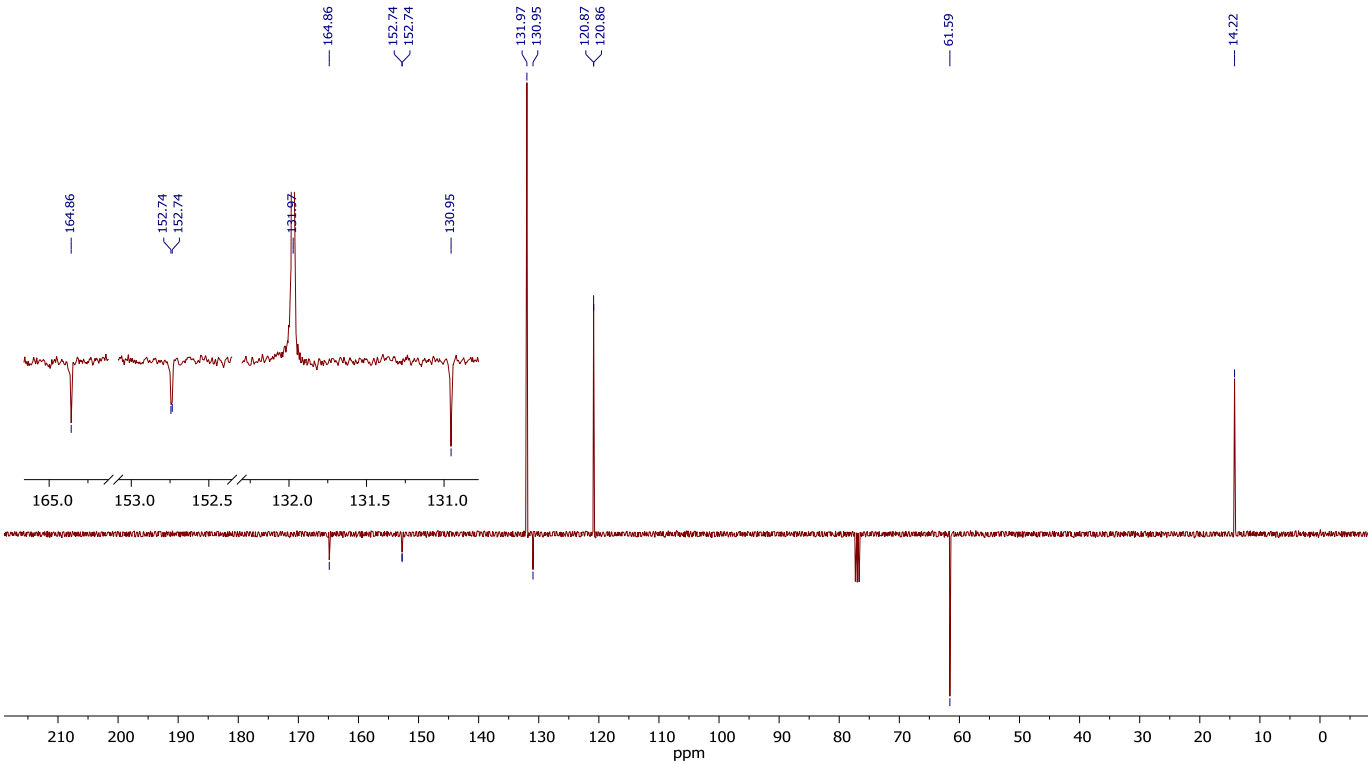

1p
147.75
147.74
133.01
133.01
120.00
119.99
77.00 CDCl3
13.42
13.41
147.8
147.7
133.0
120.1
120.0
119.9
13.5
13.4
ppm

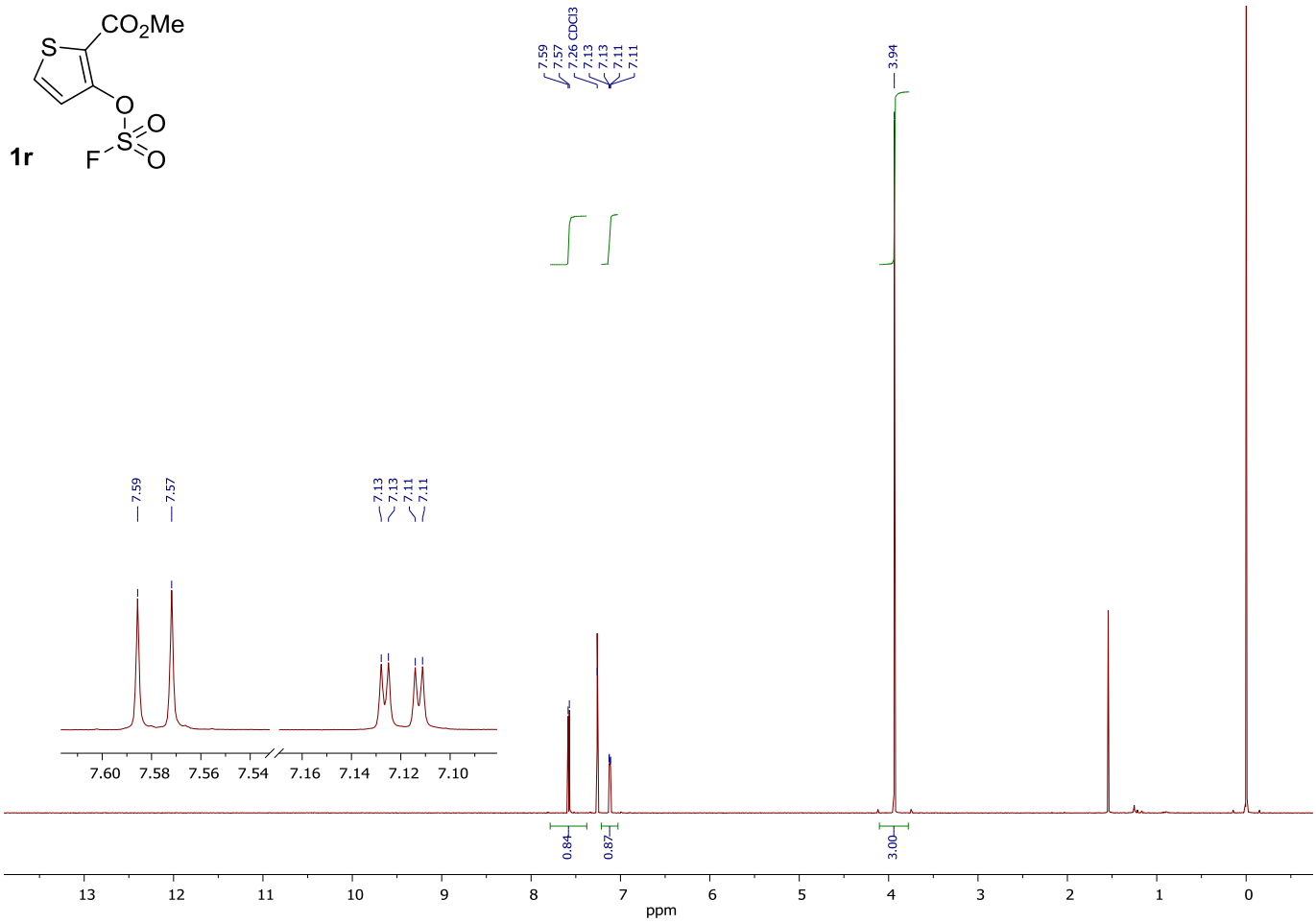

147.77
133.03
120.02
120.01
13.44
13.43
ppm

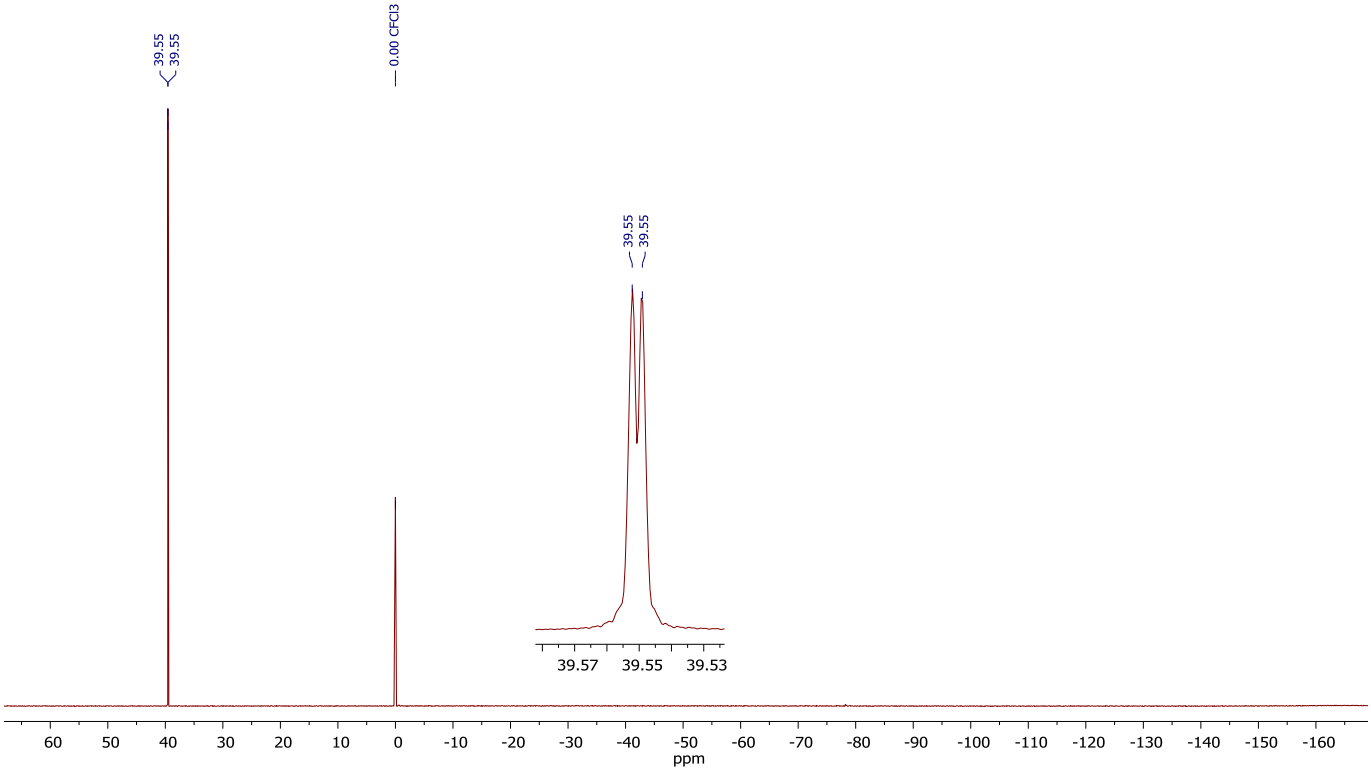

1q
8.19
8.16
7.43
7.43
7.41
7.40
7.26 CDCl3
4.43
4.41
4.40
4.38
1.56 HDO
1.42
1.41
1.39
1.94
1.93
2.04
3.09
ppm

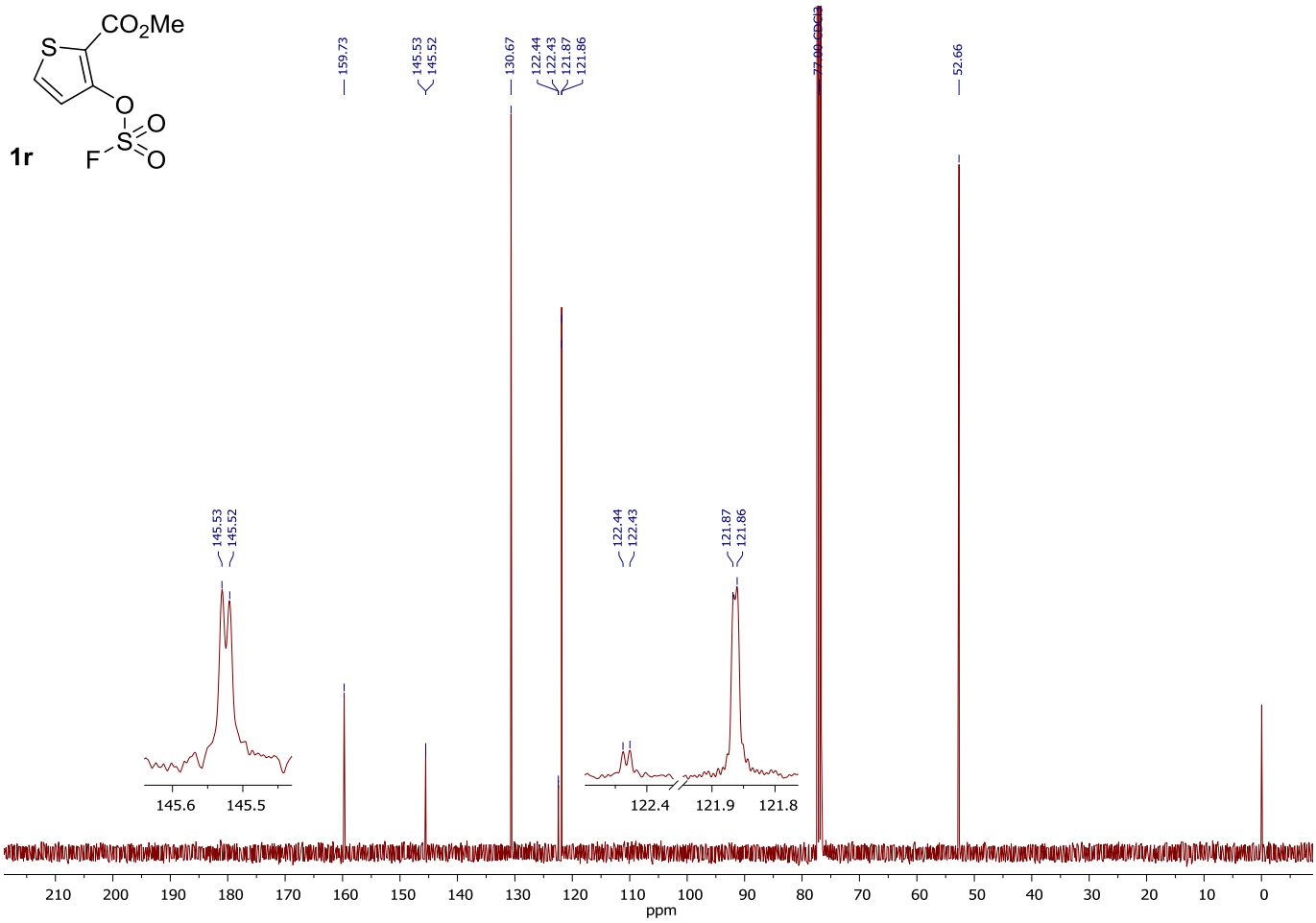

38.17
38.17
38.17
0.00 CFCl3
ppm

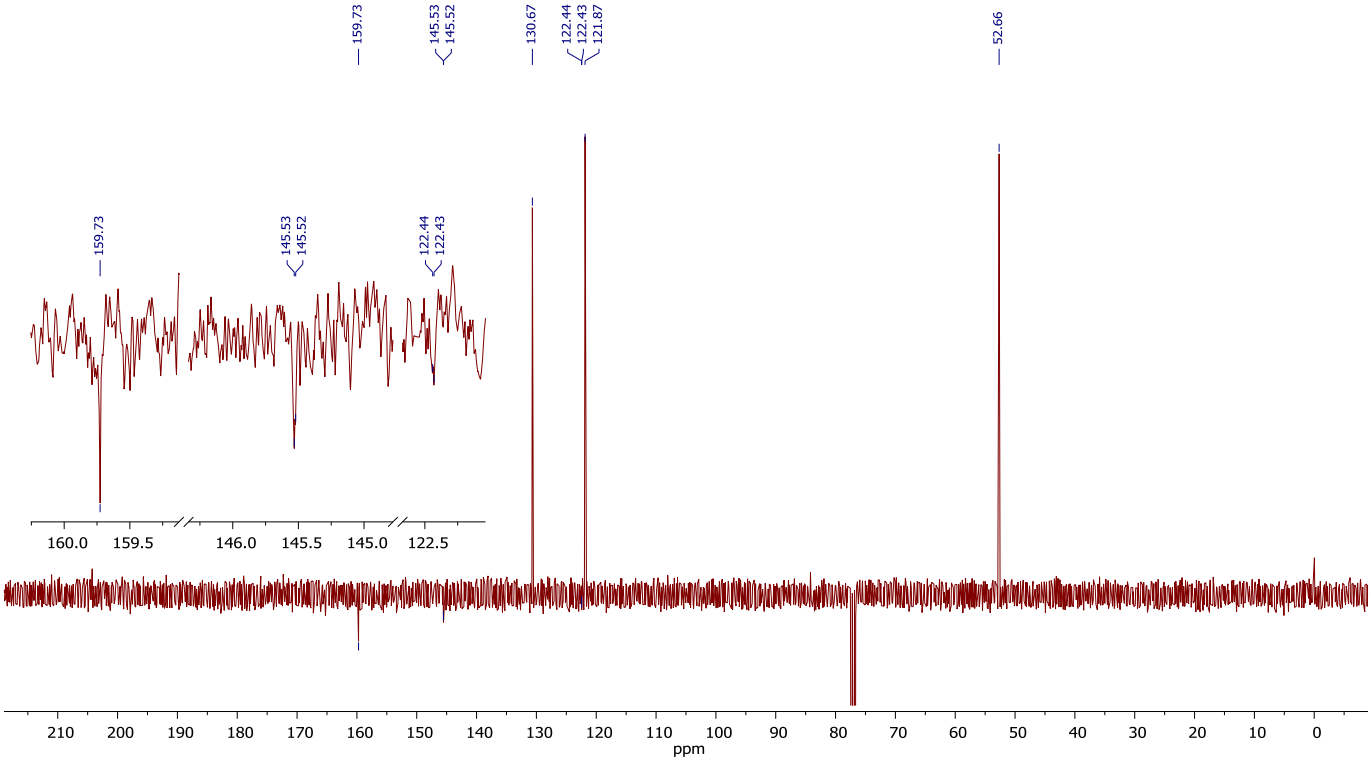

1q
164.86
152.74
152.73
131.97
130.95
120.87
120.86
77.00 CDCl3
61.59
14.22
152.8
152.7
120.9
120.8
ppm

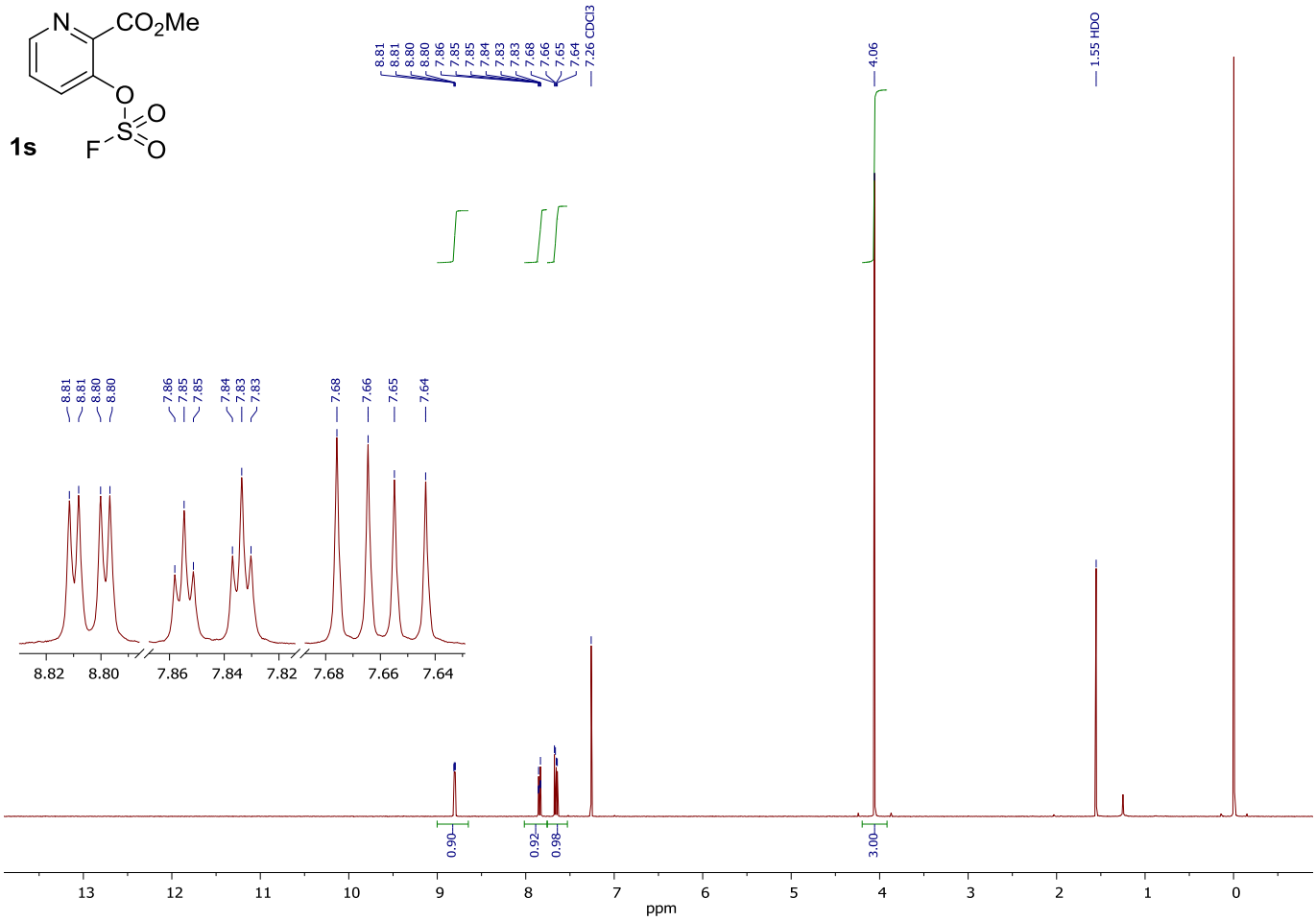

164.86
152.74
152.74
131.97
130.95
120.87
120.86
61.59
14.22
165.0
153.0
152.5
132.0
131.5
131.0
ppm

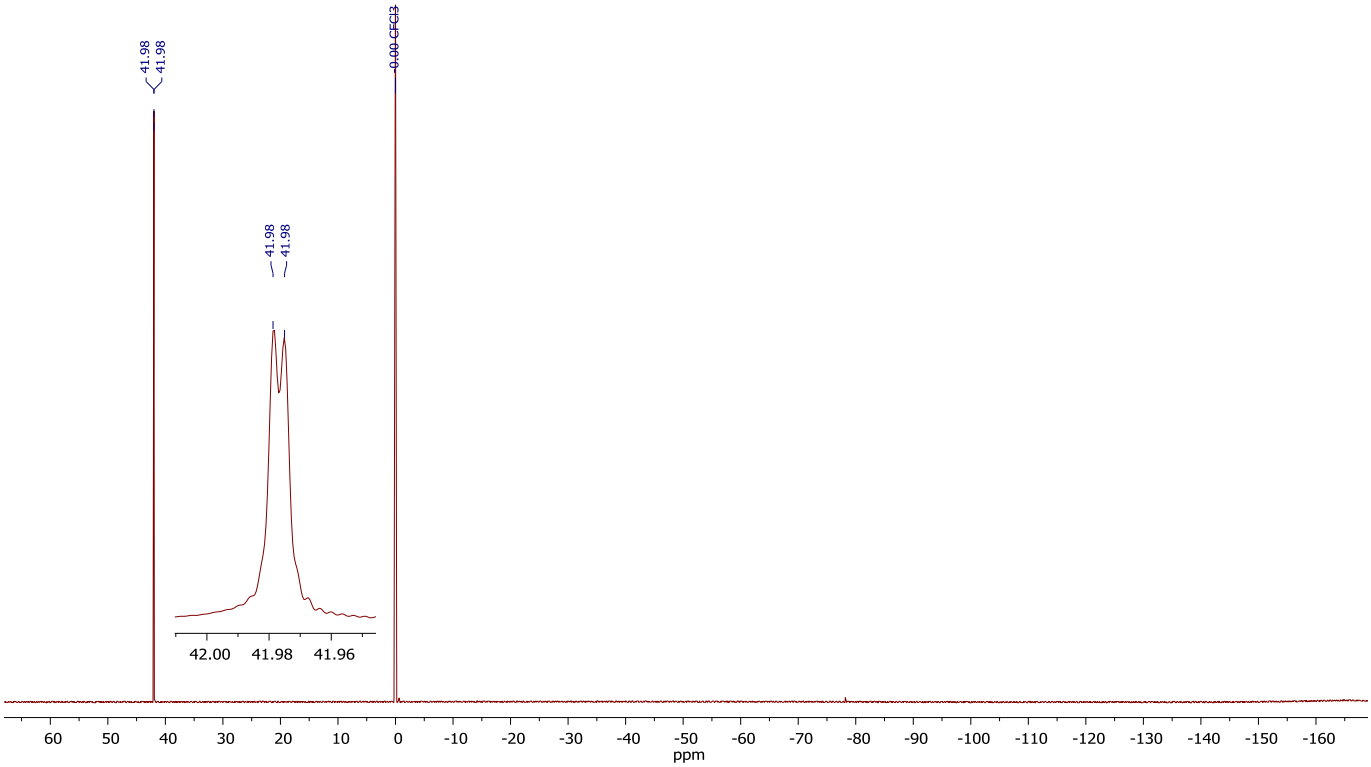

CO2Me
S
O
O
S
O
F
1r
7.59
7.57
7.26 CDCl3
7.13
7.13
7.11
7.11
3.94
7.59
7.57
7.13
7.13
7.11
7.11
7.60 7.58 7.56 7.54 7.16 7.14 7.12 7.10
0.84
0.87
3.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm

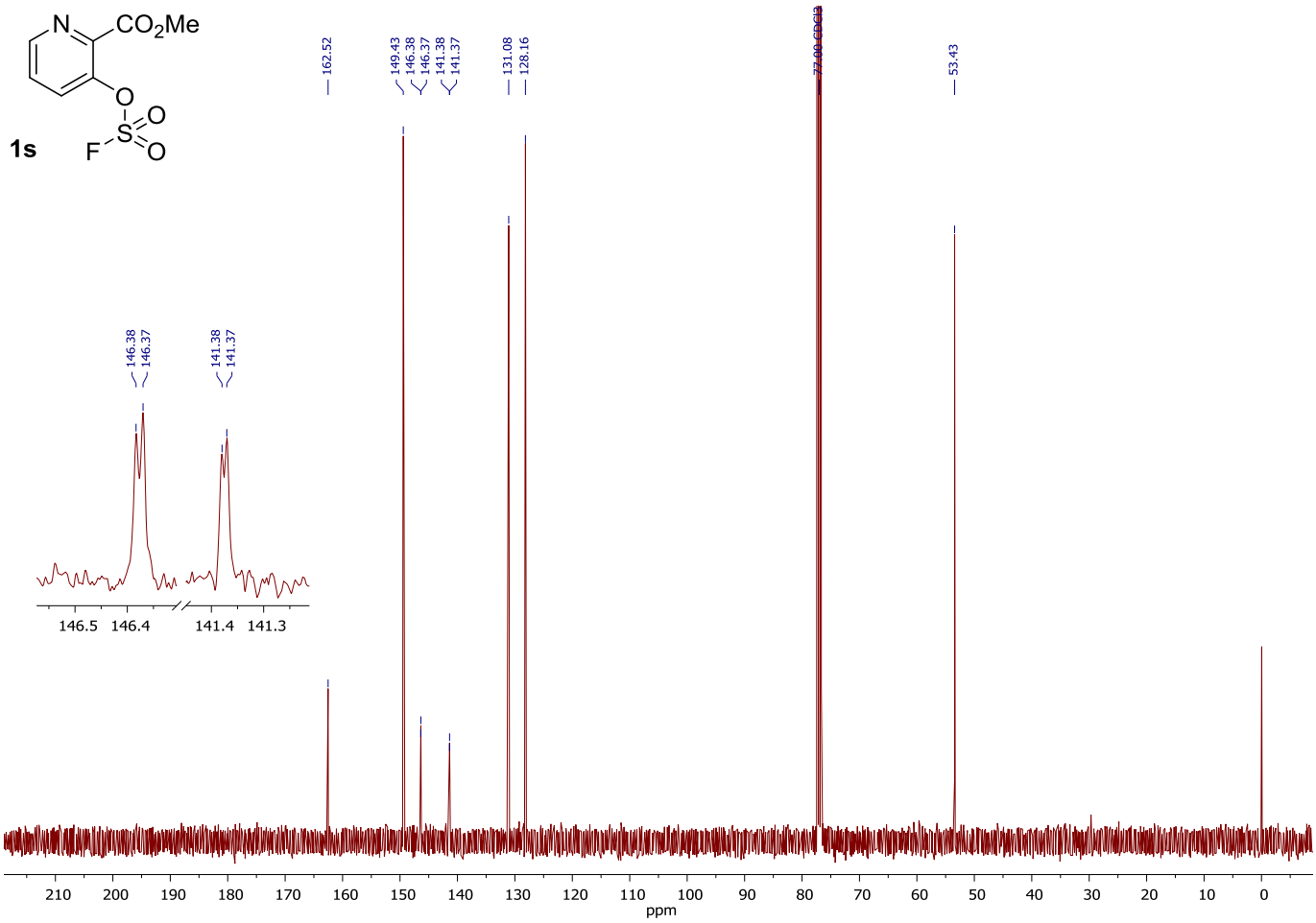

39.55
39.55
0.00 CFCl3
39.55
39.55
39.57 39.55 39.53
60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
ppm

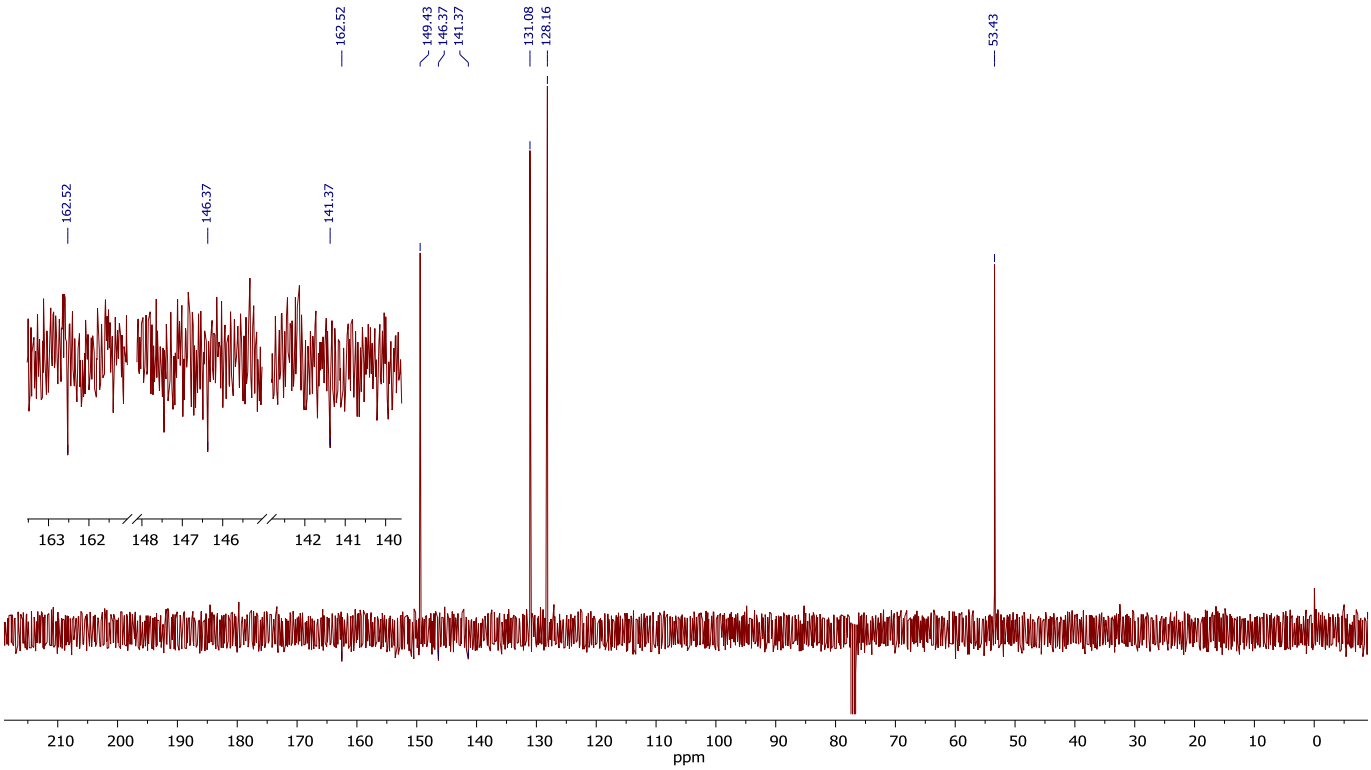

1r
CO2Me
S
O
O
S
O
F
159.73
145.53
145.52
130.67
122.44
122.43
121.87
121.86
77.00 CDCl3
52.66
145.6
145.5
122.4
121.9
121.8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

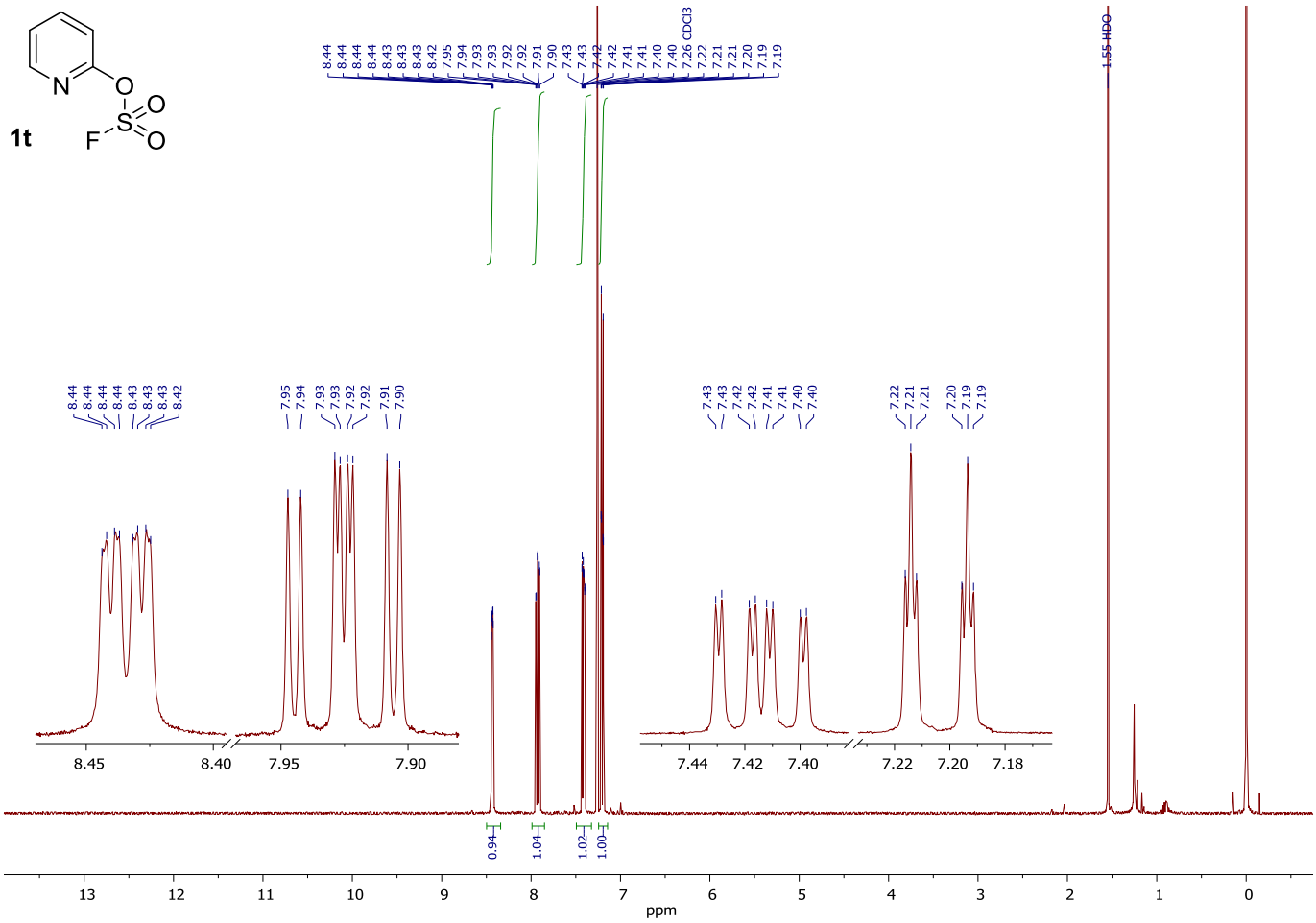

159.73
145.53
145.52
130.67
122.44
122.43
121.87
52.66
160.0
159.5
146.0
145.5
145.0
122.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

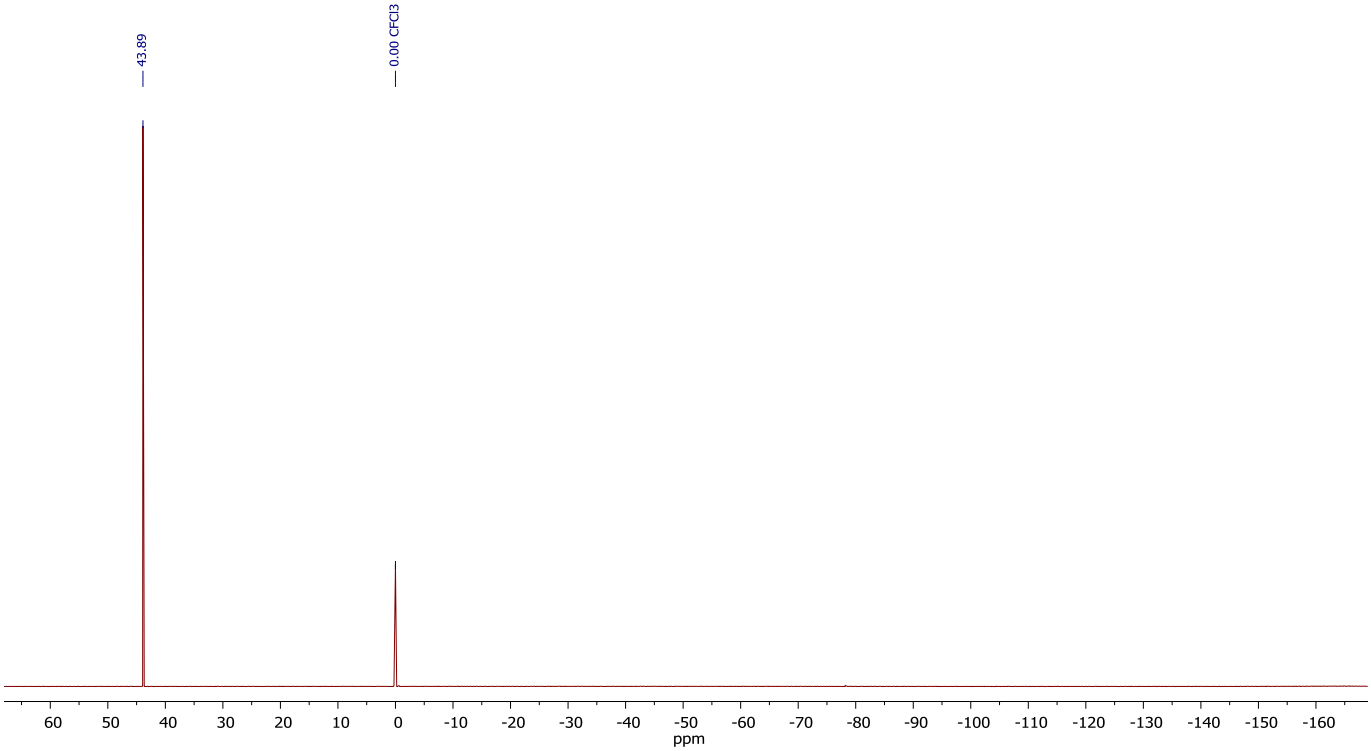

1s
8.81
8.81
8.80
8.80
7.86
7.85
7.85
7.84
7.83
7.83
7.68
7.66
7.65
7.64
7.26 CDCl3
4.06
1.55 HDO
0.90
0.92
0.98
3.00
ppm

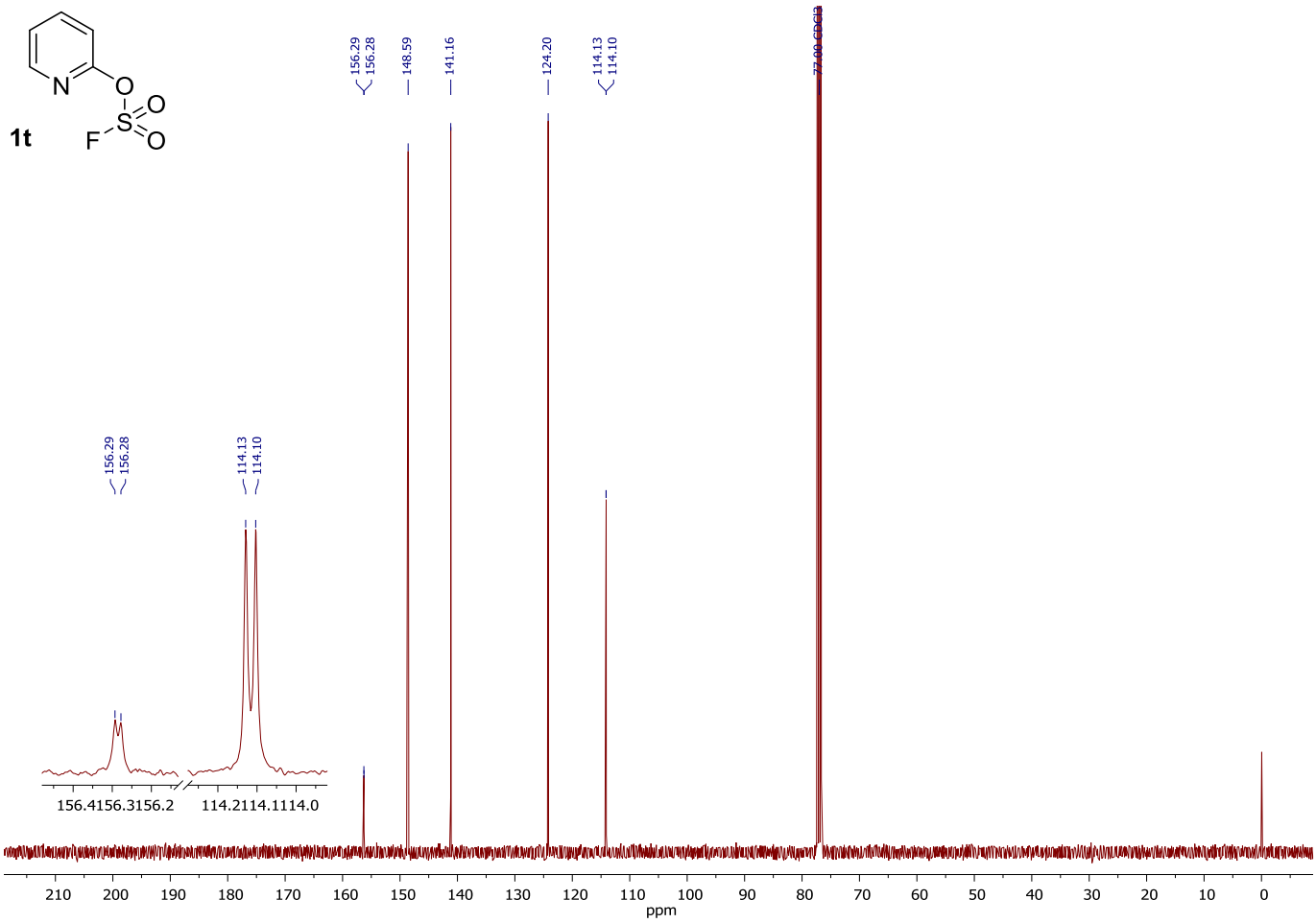

41.98
41.98
0.00 CFCl3
ppm

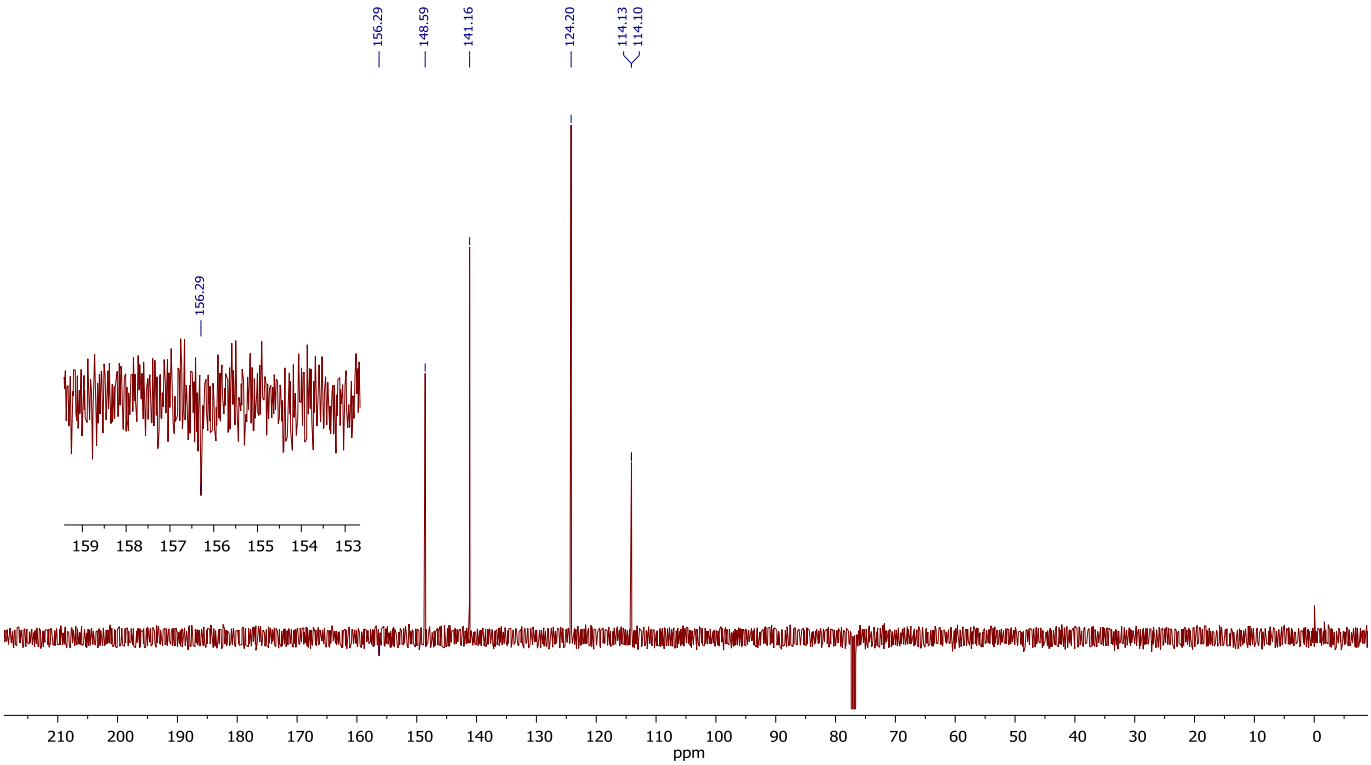

1s
162.52
149.43
146.38
146.37
141.38
141.37
131.08
128.16
77.00 CDCl3
53.43
146.5 146.4
141.4 141.3
ppm

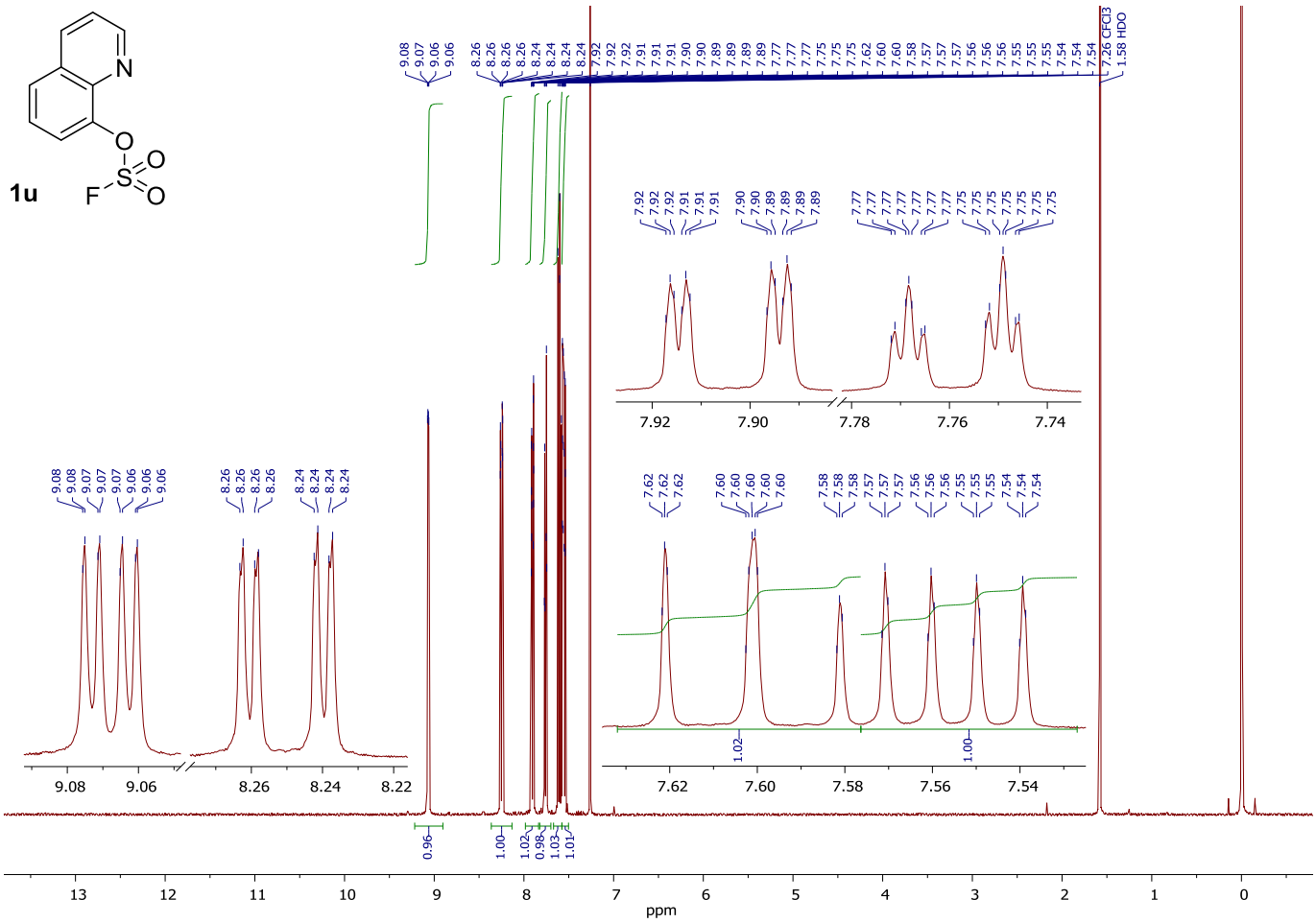

162.52
149.43
146.37
141.37
131.08
128.16
53.43
163 162 148 147 146 142 141 140
ppm

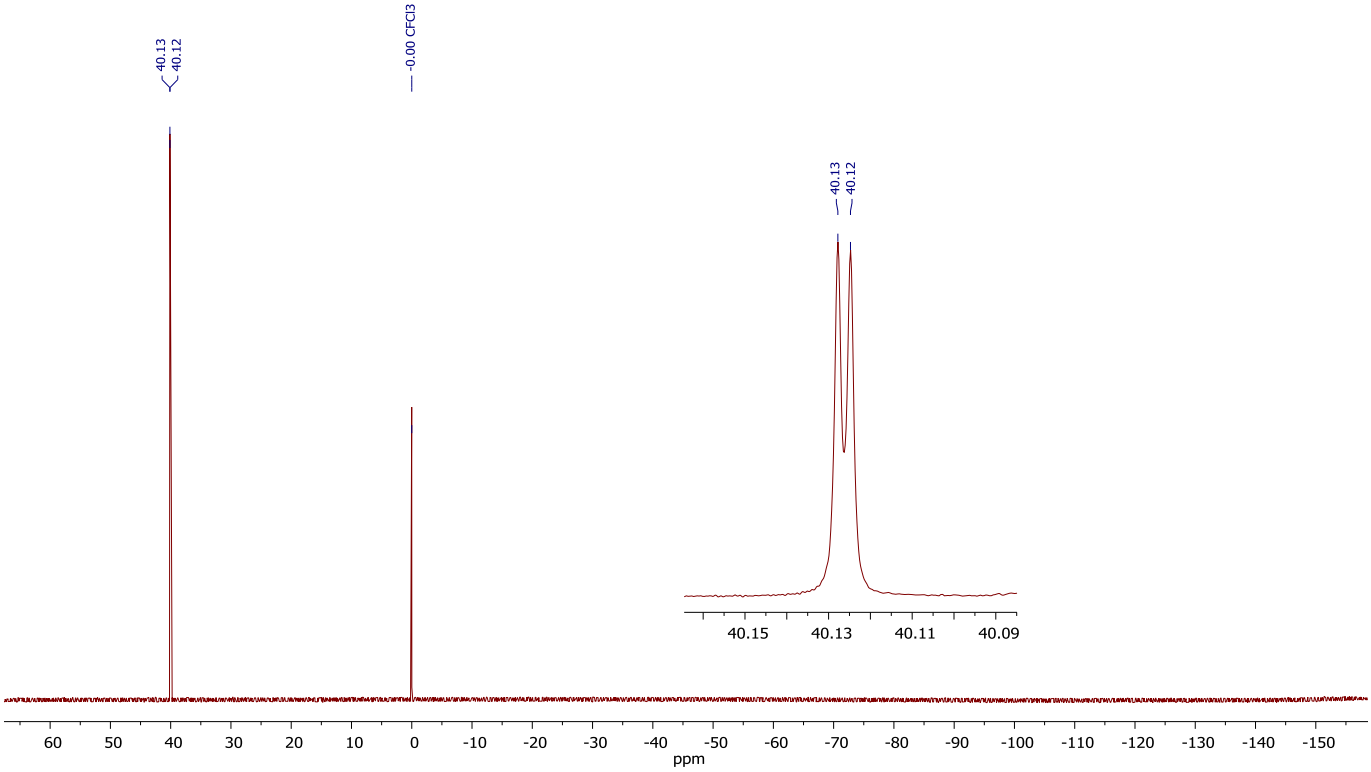

1t
8.44
8.44
8.44
8.44
8.43
8.43
8.43
8.43
8.42
7.95
7.94
7.93
7.93
7.92
7.92
7.91
7.90
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.26 CDCl3
7.22
7.21
7.21
7.20
7.19
7.19
1.55 HDO
0.94
1.04
1.02
1.00
ppm

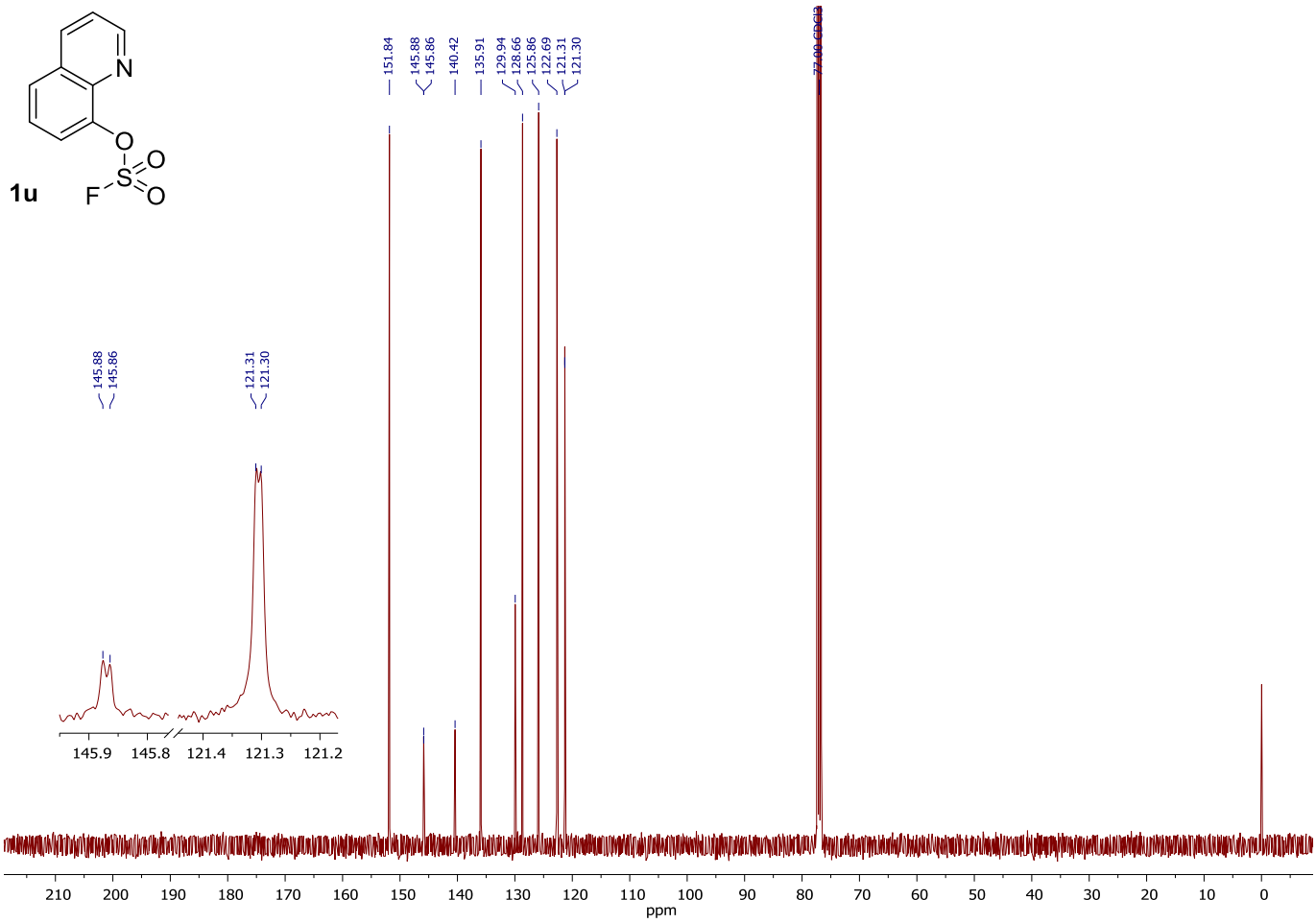

43.89
0.00 CFCl3
ppm

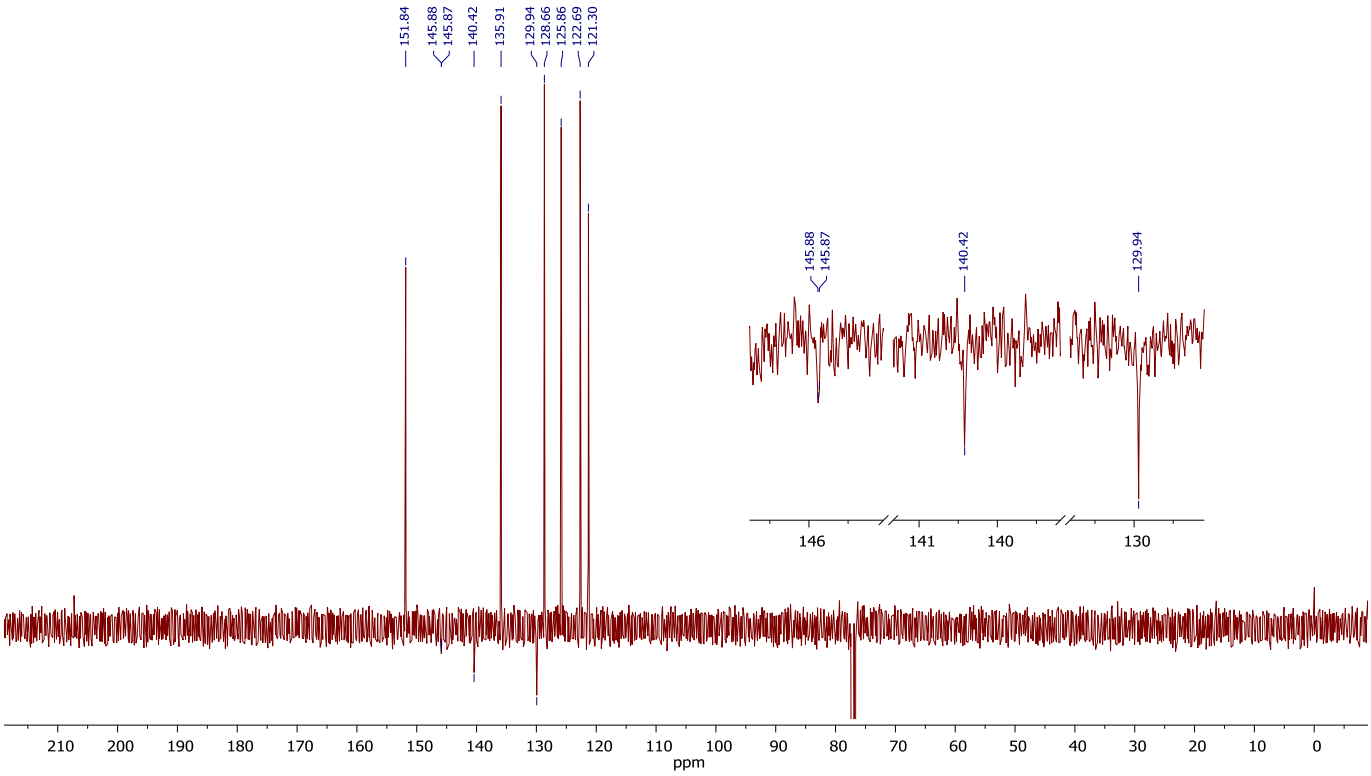

1t
156.29
156.28
148.59
141.16
124.20
114.13
114.10
77.00 CDCl3
156.4156.3156.2
114.2114.1114.0
ppm

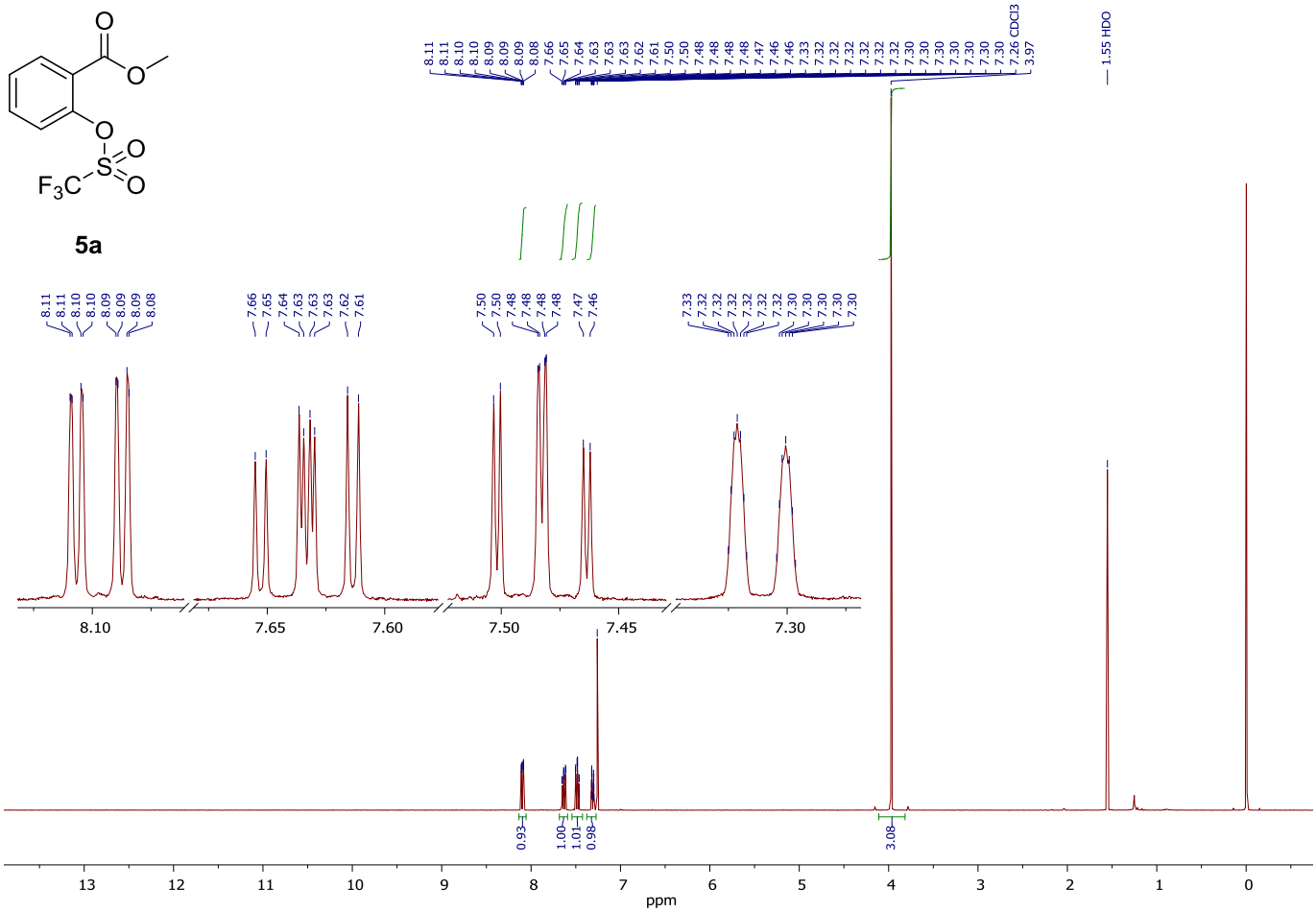

156.29
148.59
141.16
124.20
114.13
114.10
159 158 157 156 155 154 153
ppm

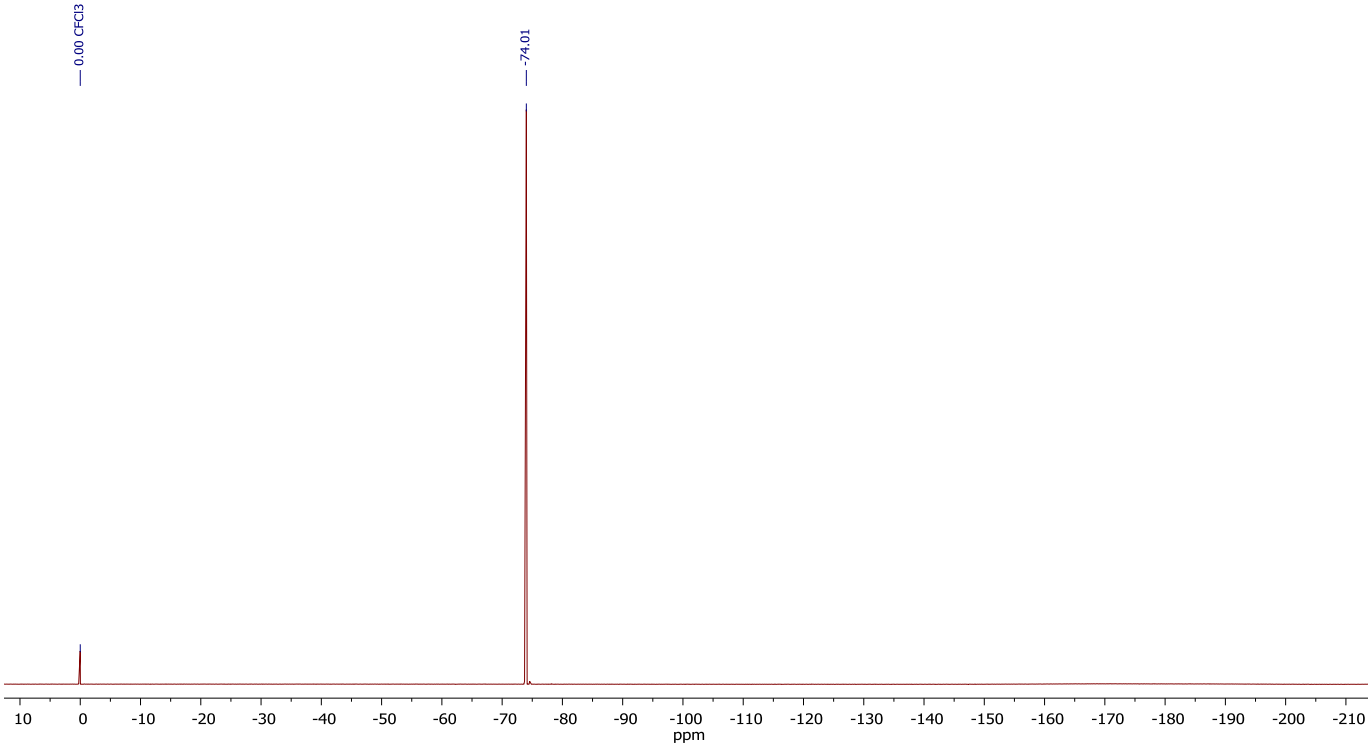

1u
7.26 CFCl3
1.58 HDO
0.96
1.00
1.02
0.98
1.03
1.01
1.02
1.00
ppm

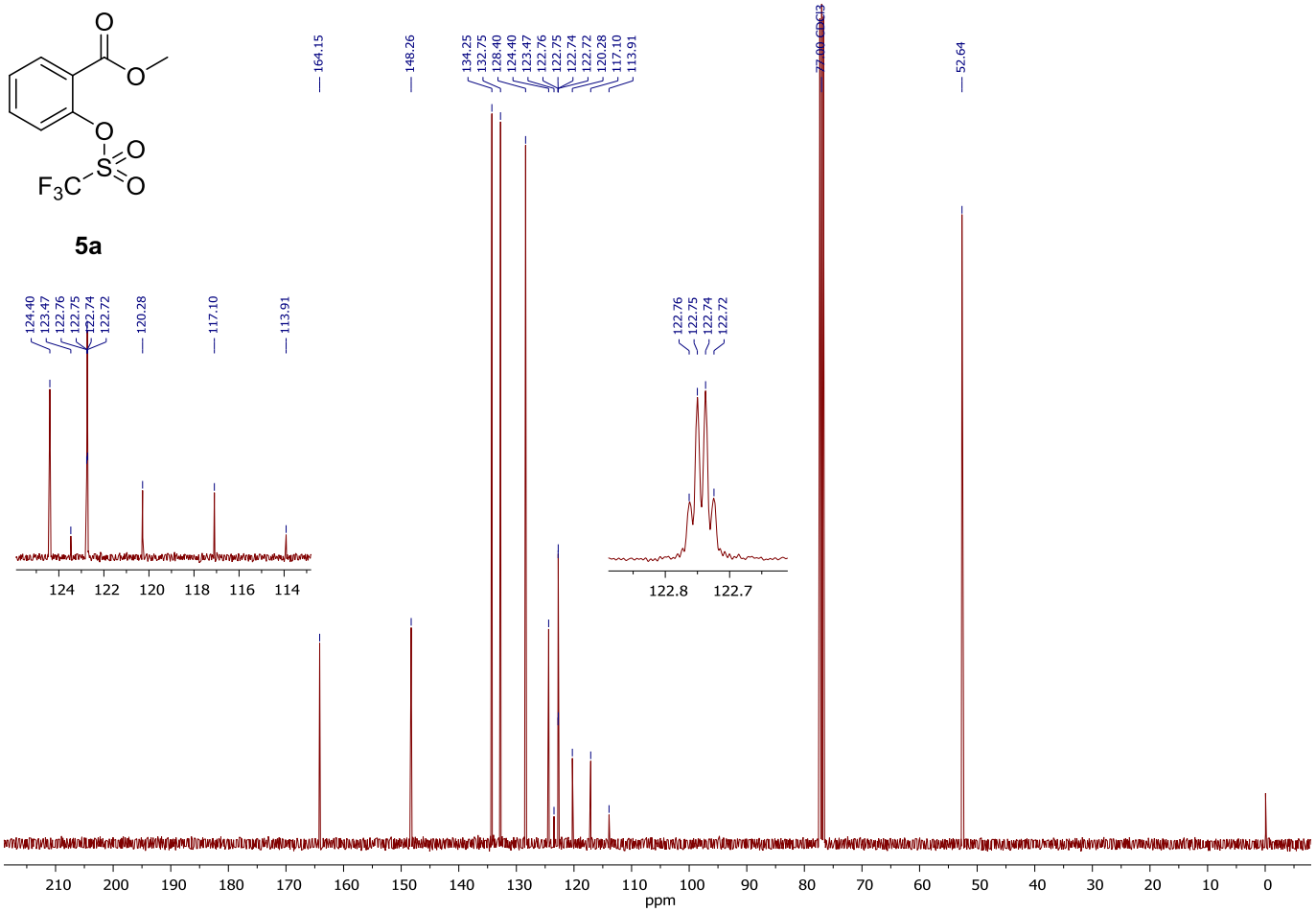

40.13
40.12
-0.00 CFCl3
ppm

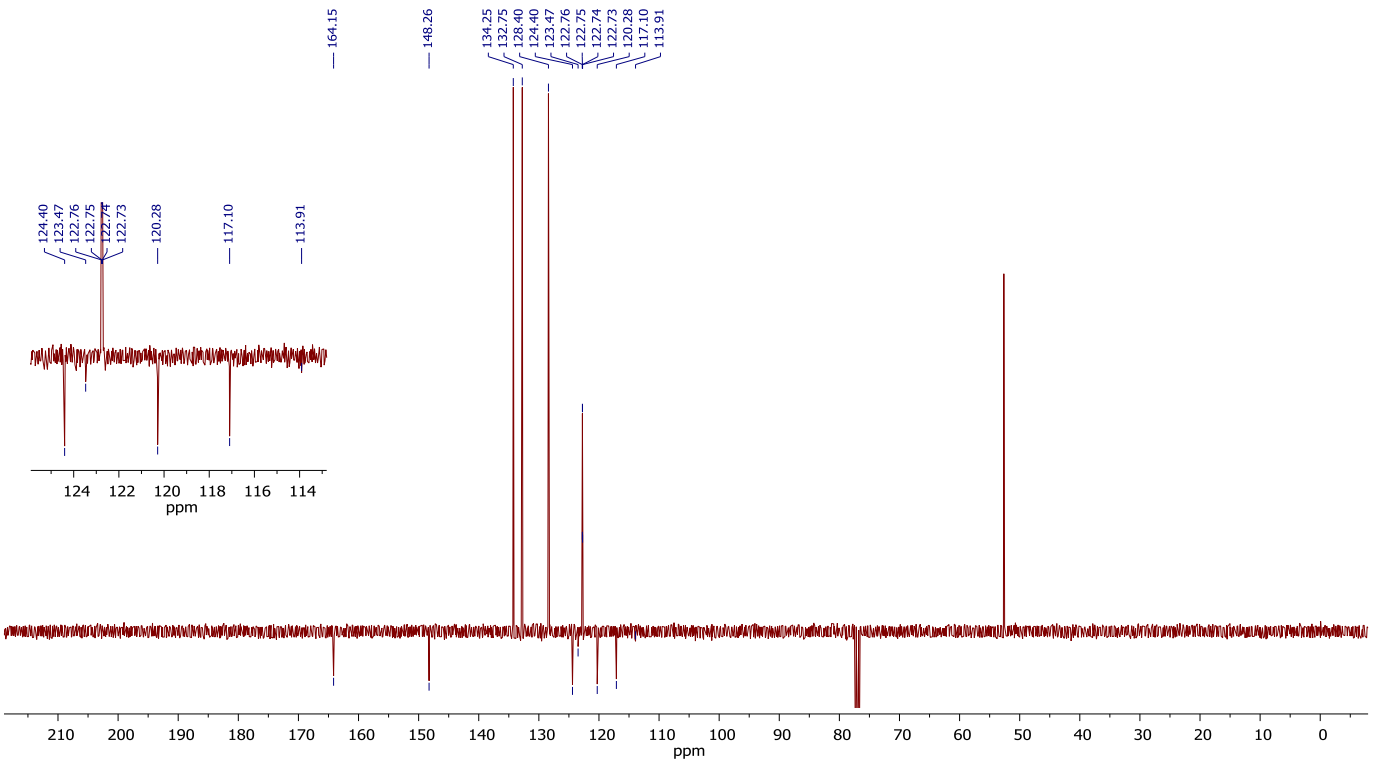

1u
151.84
145.88
145.86
140.42
135.91
129.94
128.66
125.86
122.69
121.31
121.30
77.00 CDCl3
145.9
145.8
121.4
121.3
121.2
ppm

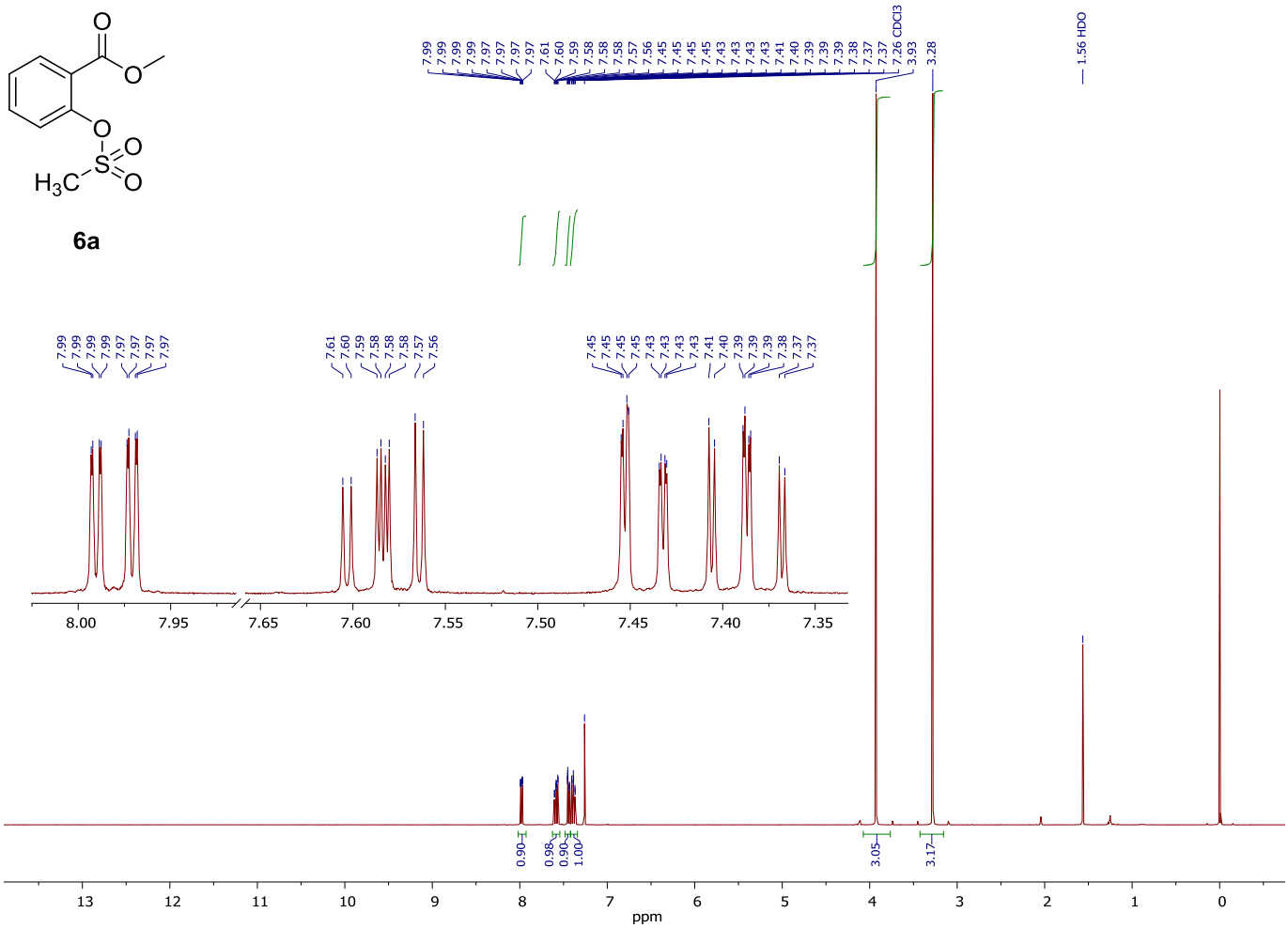

151.84
145.88
145.87
140.42
135.91
129.94
128.66
125.86
122.69
121.30
146
141
140
130
ppm

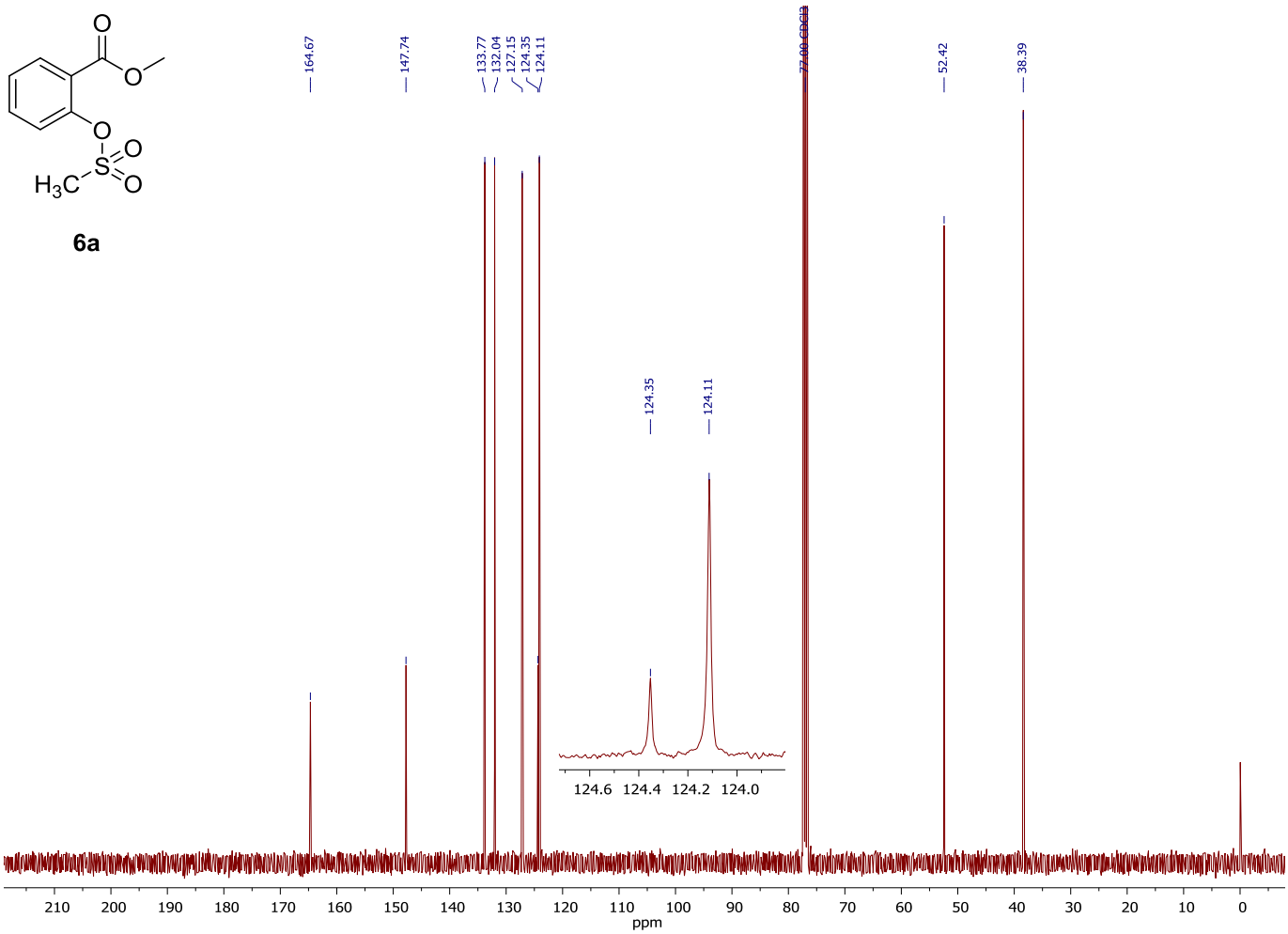

5a
8.11 8.11 8.10 8.10 8.09 8.09 8.09 8.08 8.08 7.66 7.65 7.64 7.63 7.63 7.63 7.62 7.61 7.50 7.50 7.48 7.48 7.48 7.48 7.47 7.46 7.33 7.32 7.32 7.32 7.32 7.32 7.32 7.30 7.30 7.30 7.30
8.10 7.65 7.60 7.50 7.45 7.30
7.26 CDCl3
3.97
1.55 HDO
0.93 1.00 1.01 0.98 3.08
13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm


0.00 CFCl3
-74.01
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm

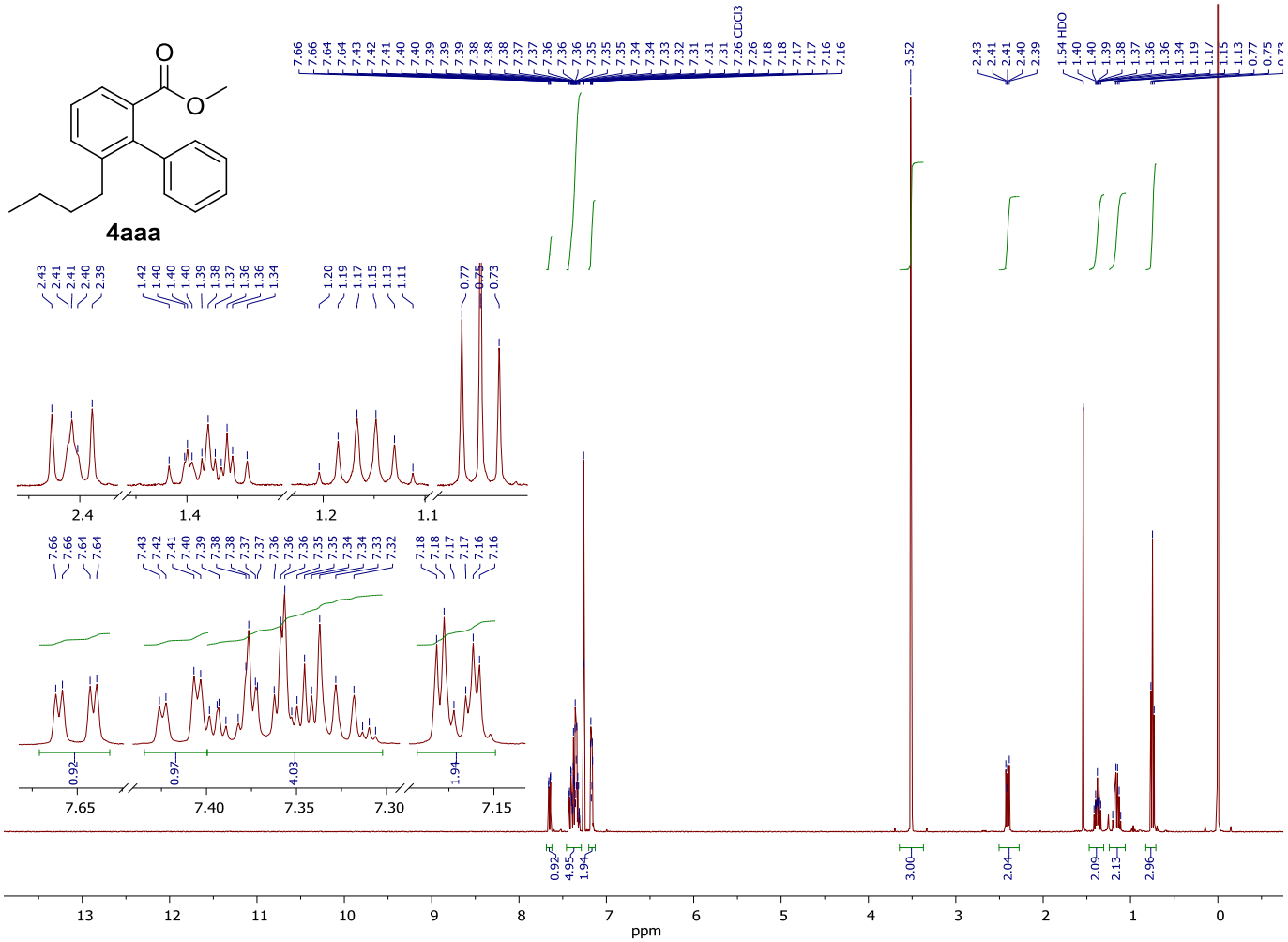

5a
164.15
148.26
134.25
132.75
128.40
124.40
123.47
122.76
122.75
122.74
122.72
120.28
117.10
113.91
77.00 CDCl3
52.64
122.76
122.75
122.74
122.72
122.8
122.7
124
122
120
118
116
114
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

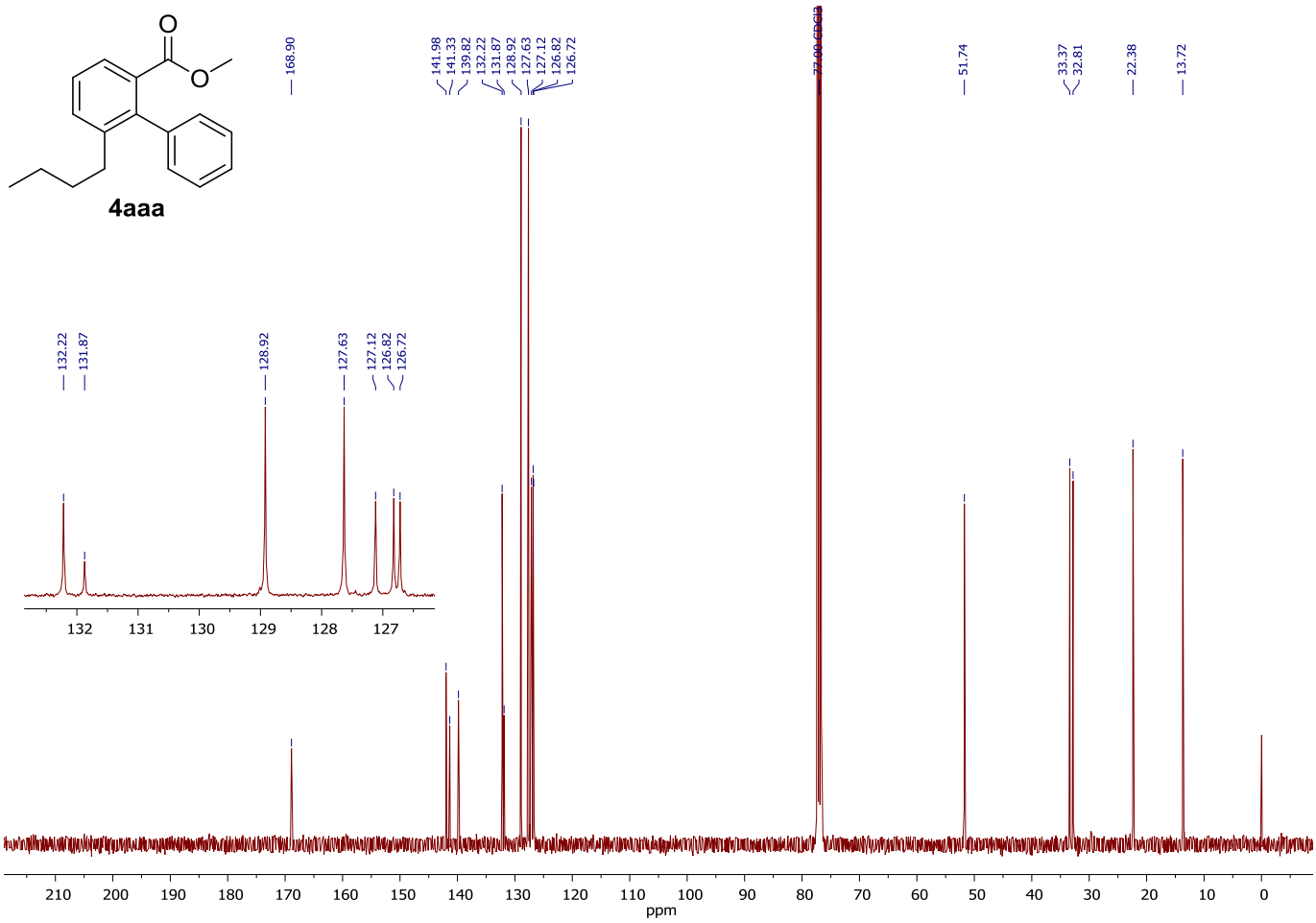

164.15
148.26
134.25
132.75
128.40
124.40
123.47
122.76
122.75
122.74
122.73
120.28
117.10
113.91
124
122
120
118
116
114
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


6a
7.99 7.99 7.99 7.99 7.97 7.97 7.97 7.97 7.61 7.60 7.59 7.58 7.58 7.58 7.57 7.56 7.45 7.45 7.45 7.45 7.43 7.43 7.43 7.43 7.41 7.40 7.39 7.39 7.39 7.38 7.37 7.37 7.26 CDCl3 3.93 3.28
1.56 HDO
0.90 0.98 0.90 1.00 3.05 3.17
ppm


6a
164.67
147.74
133.77
132.04
127.15
124.35
124.11
77.00 CDCl3
52.42
38.39
124.35
124.11
124.6 124.4 124.2 124.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

3.3 Catellani products 4, 9 and 10

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141.98
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139.82
132.22
131.87
128.92
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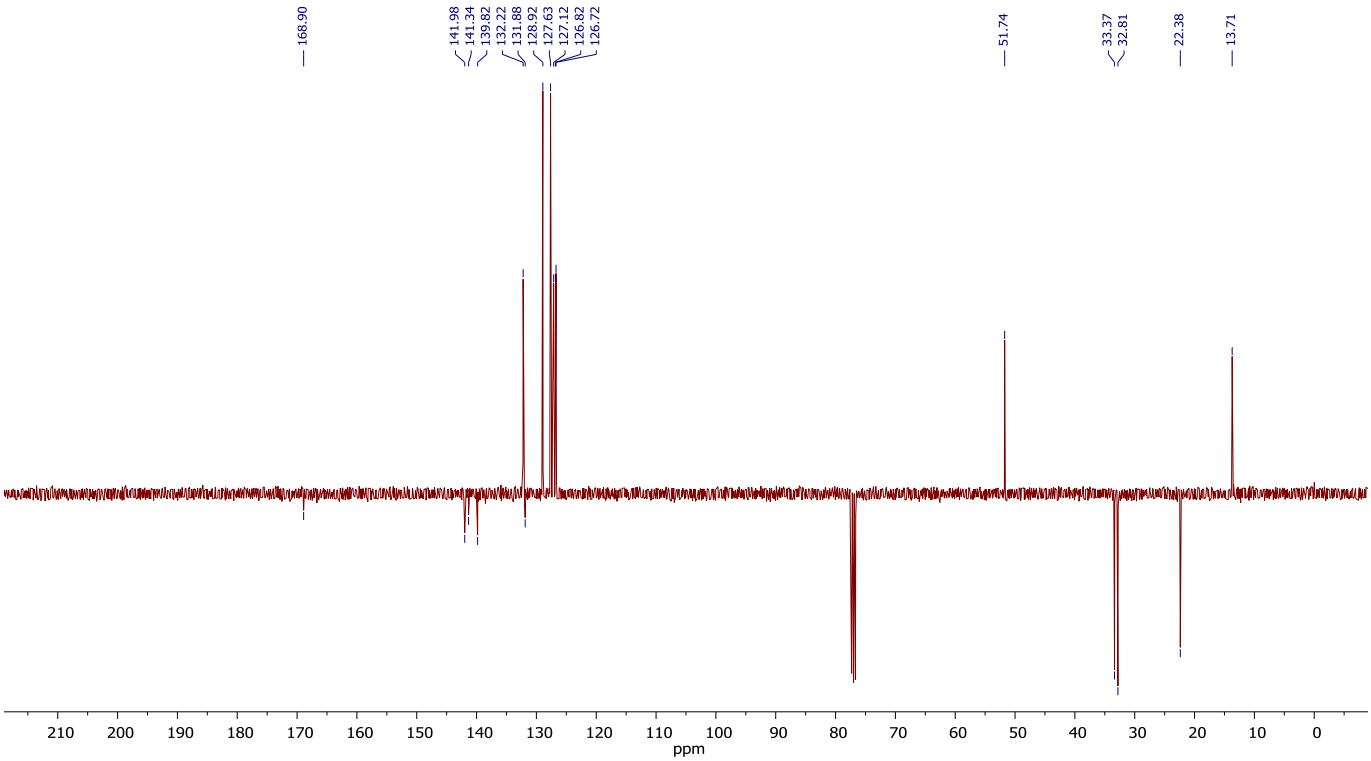
126.82
126.72
77.00 CDCl3
51.74
33.37
32.81
22.38
13.72
ppm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141.98
141.34
139.82
132.22
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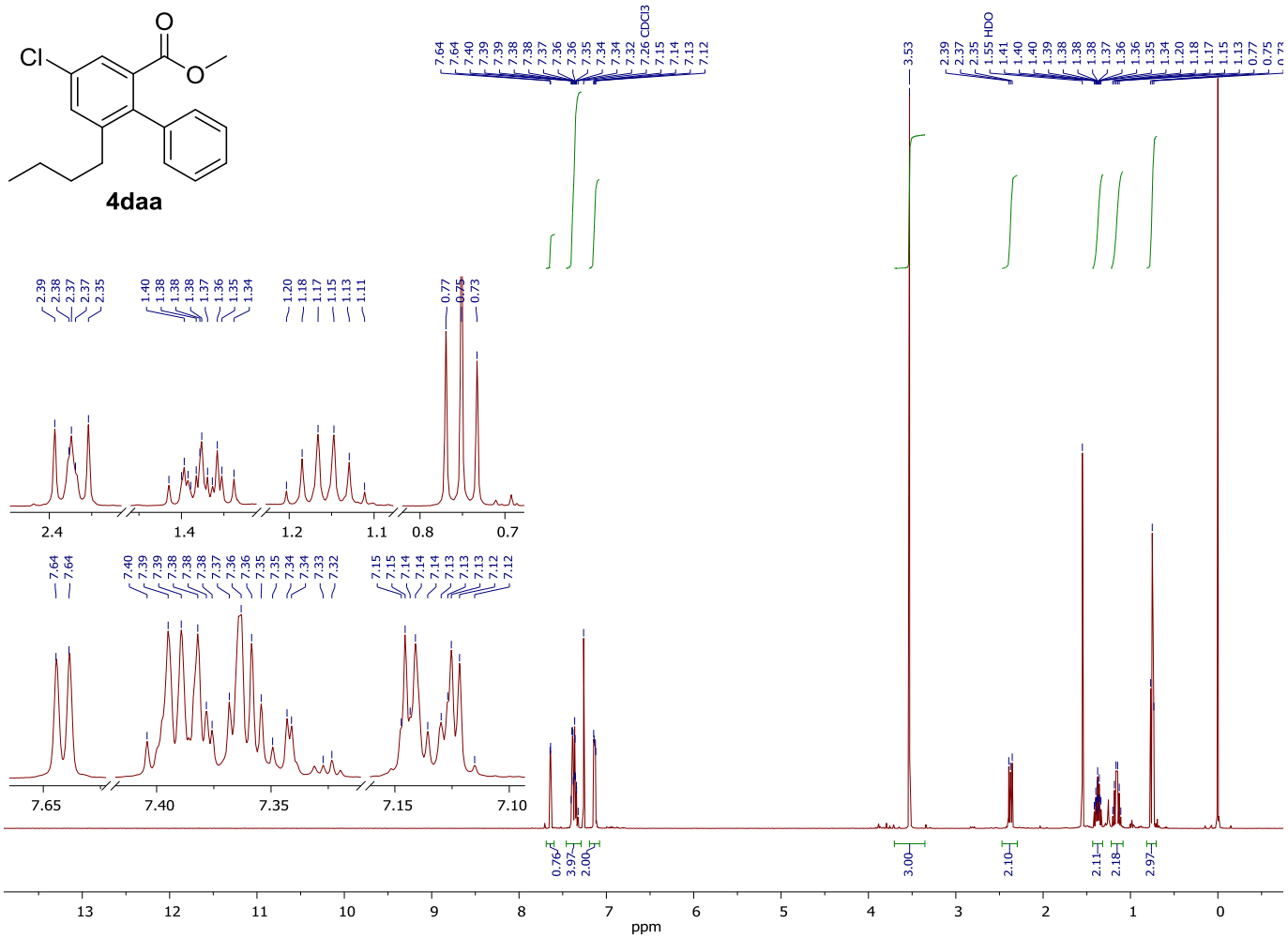
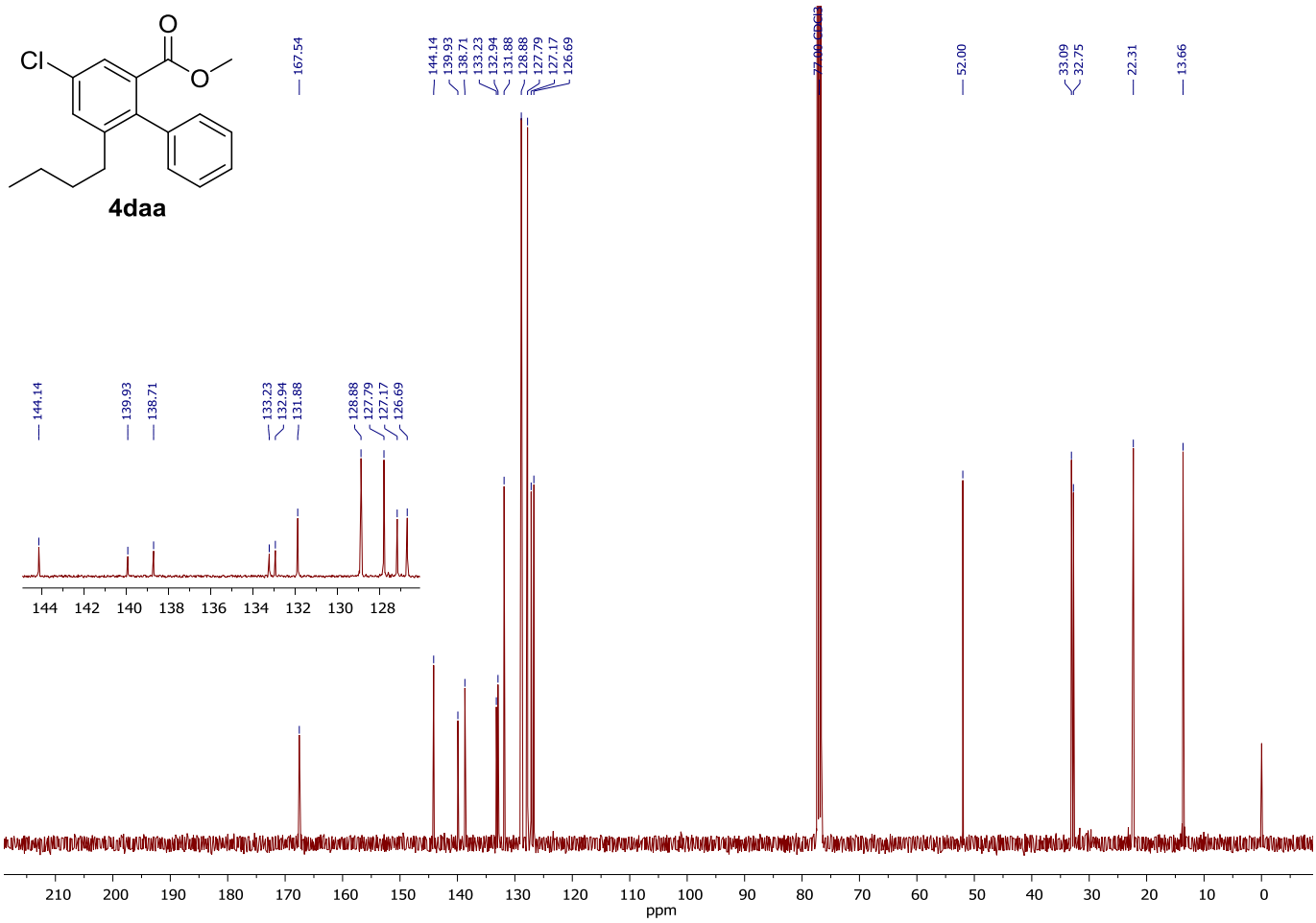
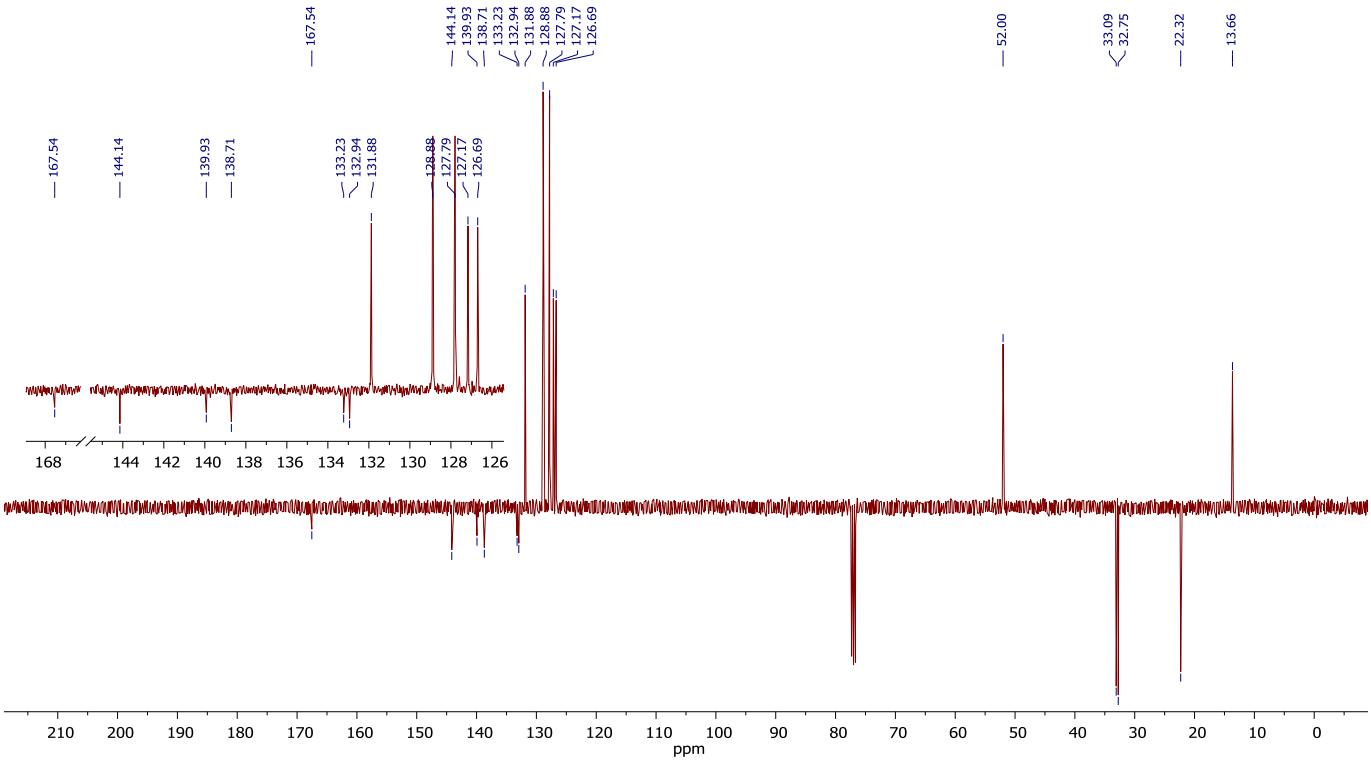
127.63
127.12
126.82
126.72
51.74
33.37
32.81
22.38
13.71
ppm


Cl
O
O
4daa
CDCl3
HDO
ppm


Cl
O
O
4daa
167.54
144.14
139.93
138.71
133.23
132.94
131.88
128.88
127.79
127.17
126.69
77.00 CDCl3
52.00
33.09
32.75
22.31
13.66
ppm


167.54
144.14
139.93
138.71
133.23
132.94
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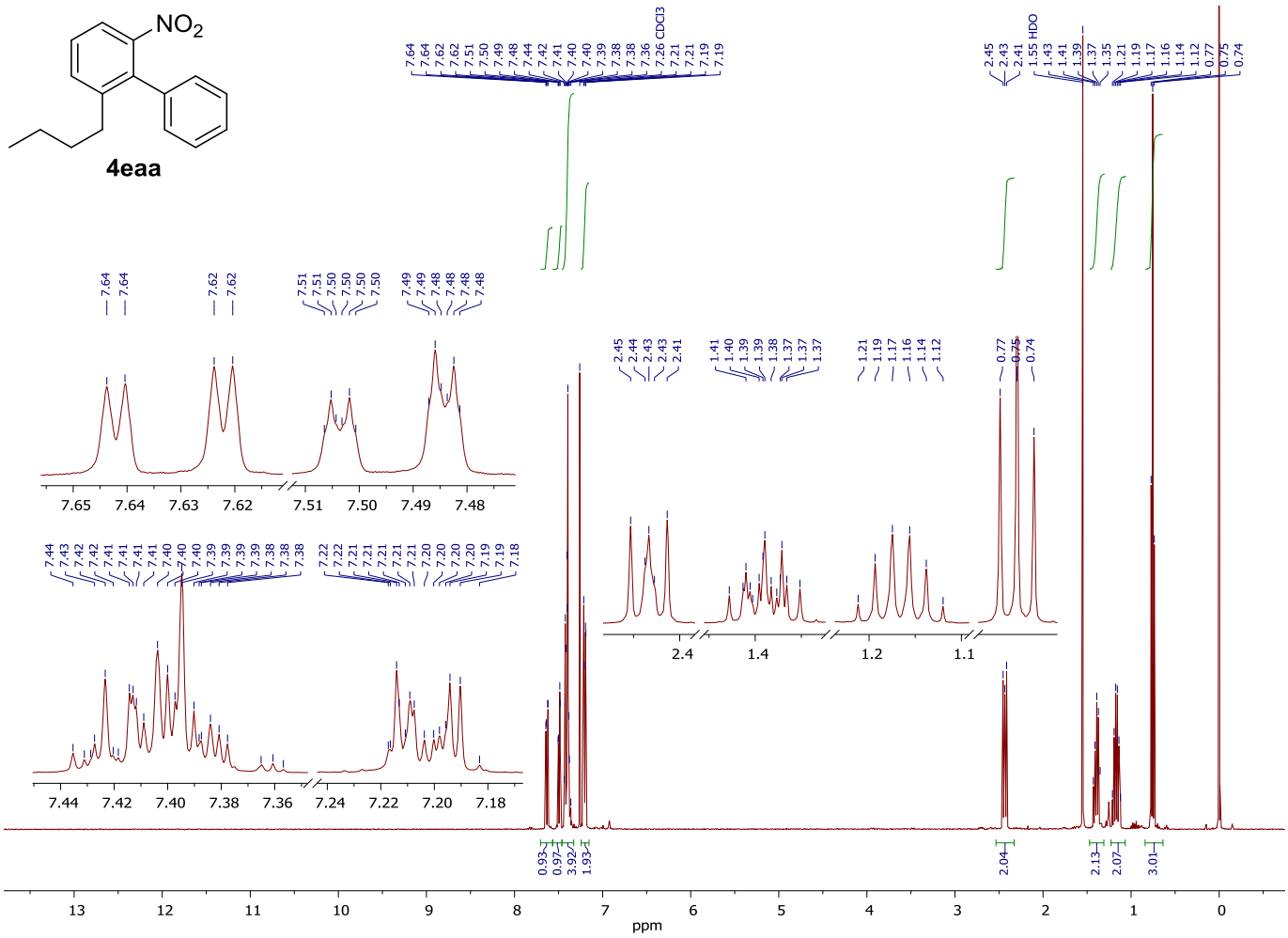
128.88
127.79
127.17
126.69
52.00
33.09
32.75
22.32
13.66
ppm


NO2
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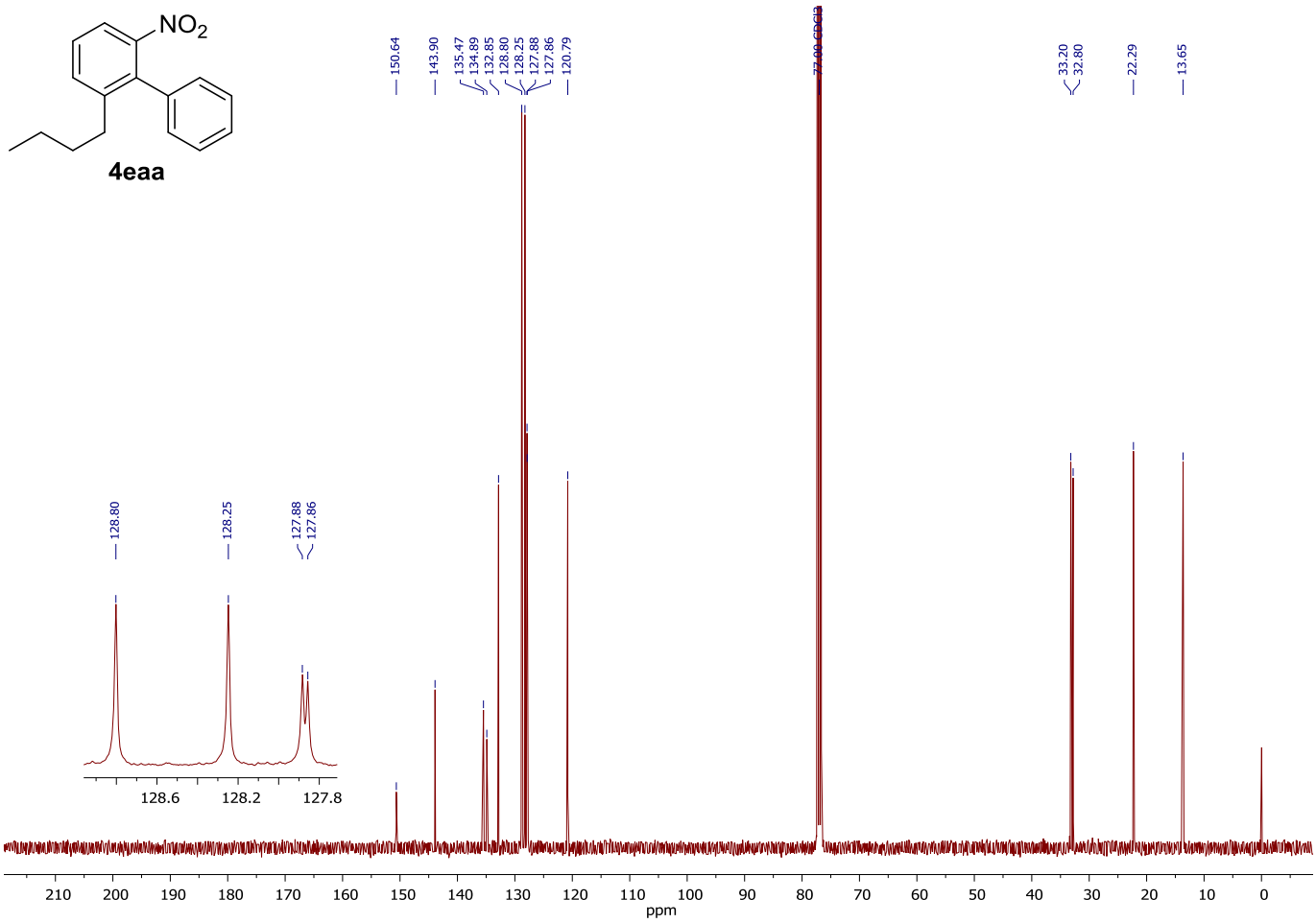
CDCl3
HDO
ppm


NO2
4eaa
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143.90
135.47
134.89
132.85
128.80
128.25
127.88
127.86
120.79
77.00 CDCl3
33.20
32.80
22.29
13.65
128.80
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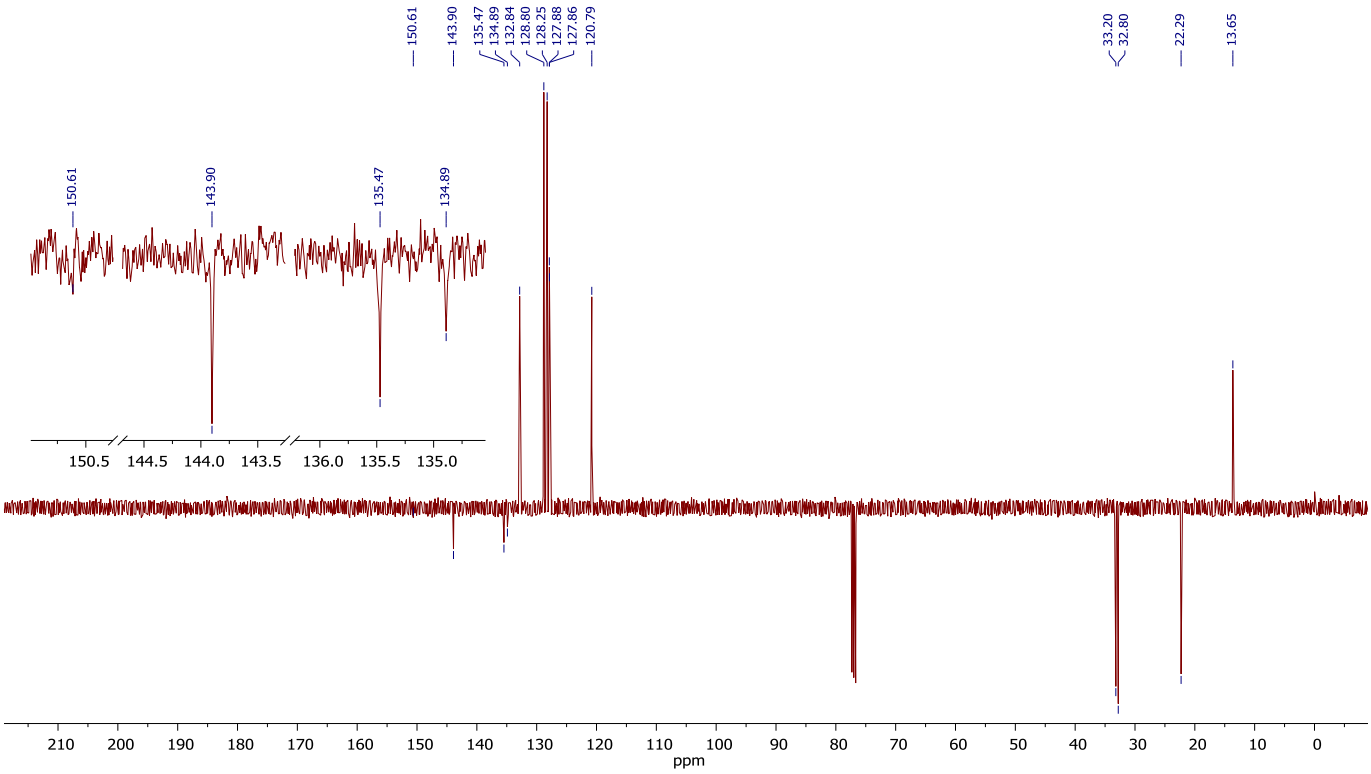
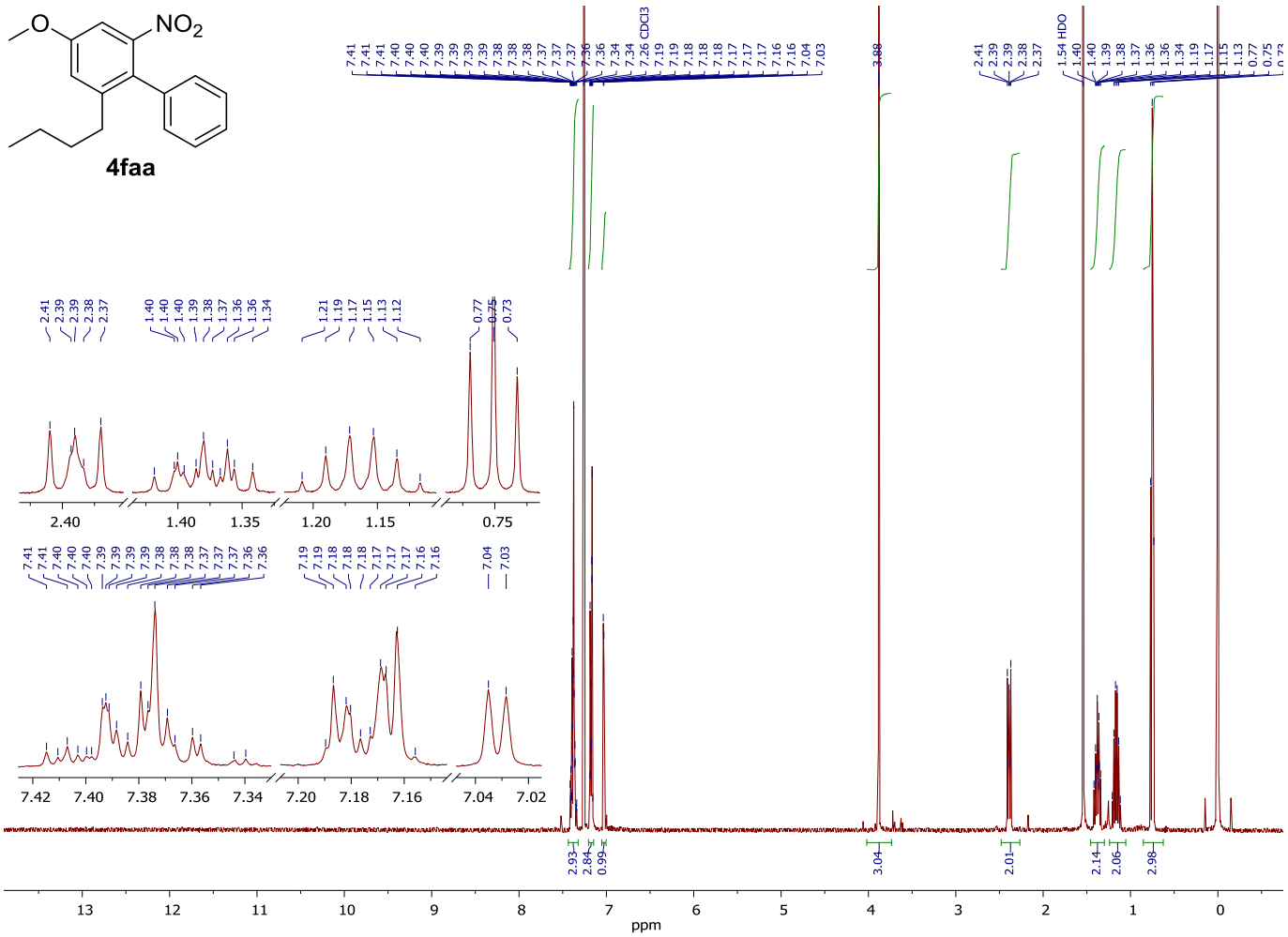
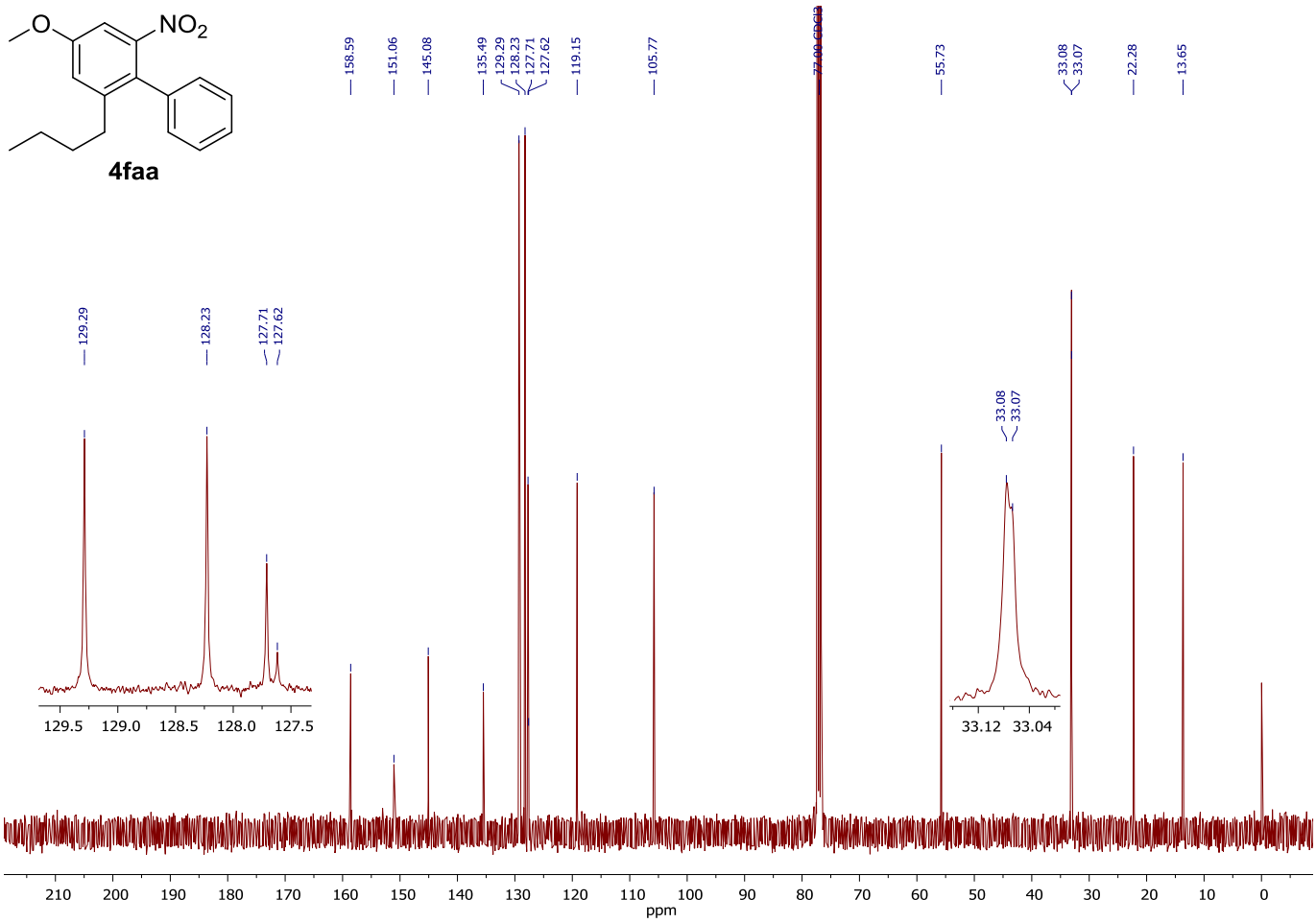
127.86
128.6
128.2
127.8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


150.61
143.90
135.47
134.89
132.84
128.80
128.25
127.88
127.86
120.79
33.20
32.80
22.29
13.65
150.61
143.90
135.47
134.89
150.5 144.5 144.0 143.5 136.0 135.5 135.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
NO2
4faa
CDCl3
HDO
ppm


O
NO2
4faa
158.59
151.06
145.08
135.49
129.29
128.23
127.71
127.62
119.15
105.77
77.00 CDCl3
55.73
33.08
33.07
22.28
13.65
129.29
128.23
127.71
127.62
129.5 129.0 128.5 128.0 127.5
33.08
33.07
33.12 33.04
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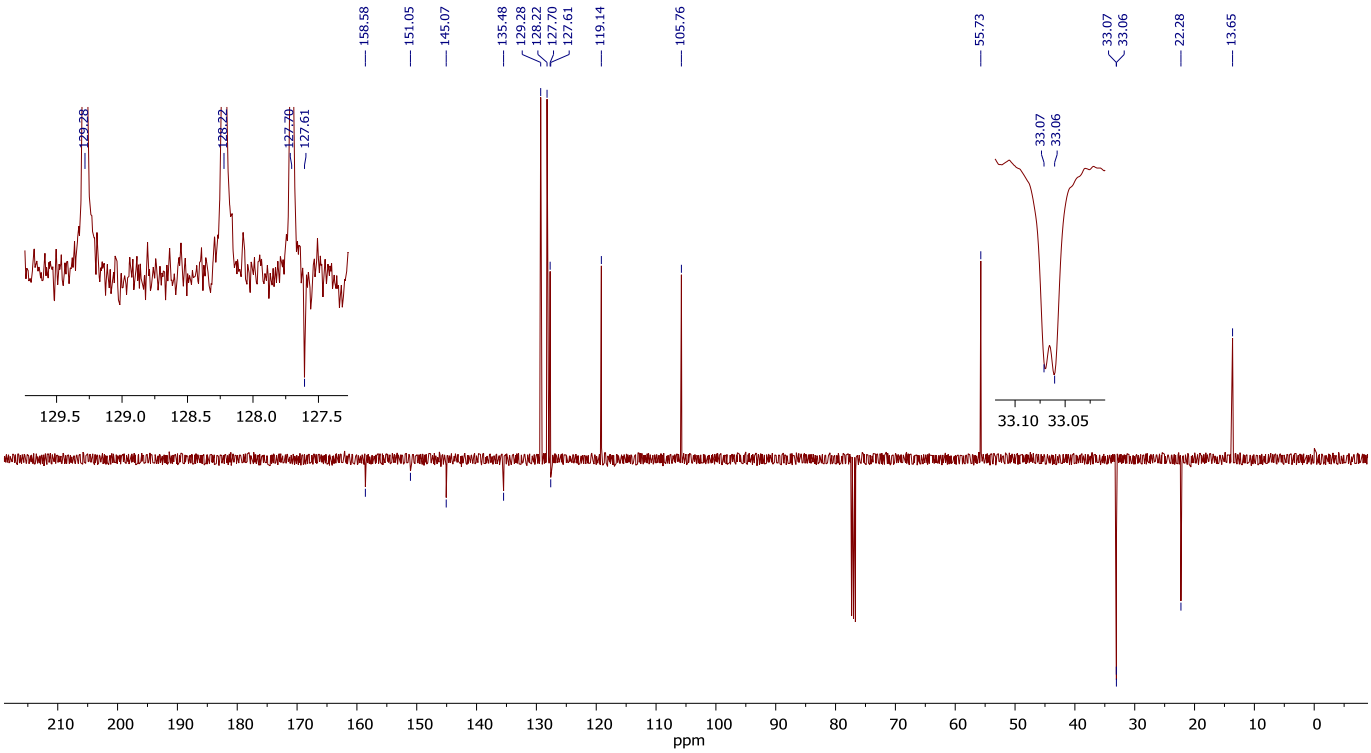
ppm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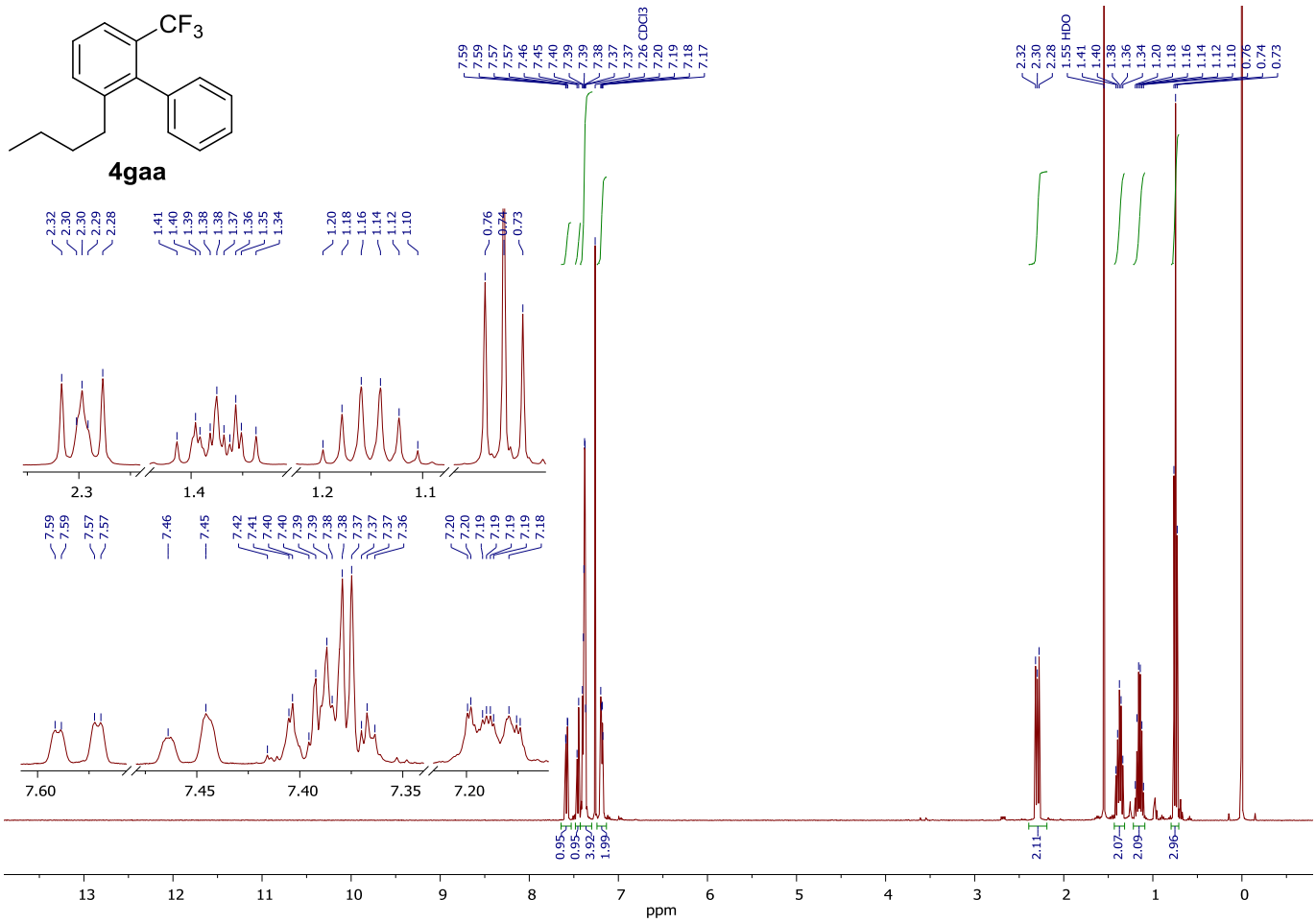
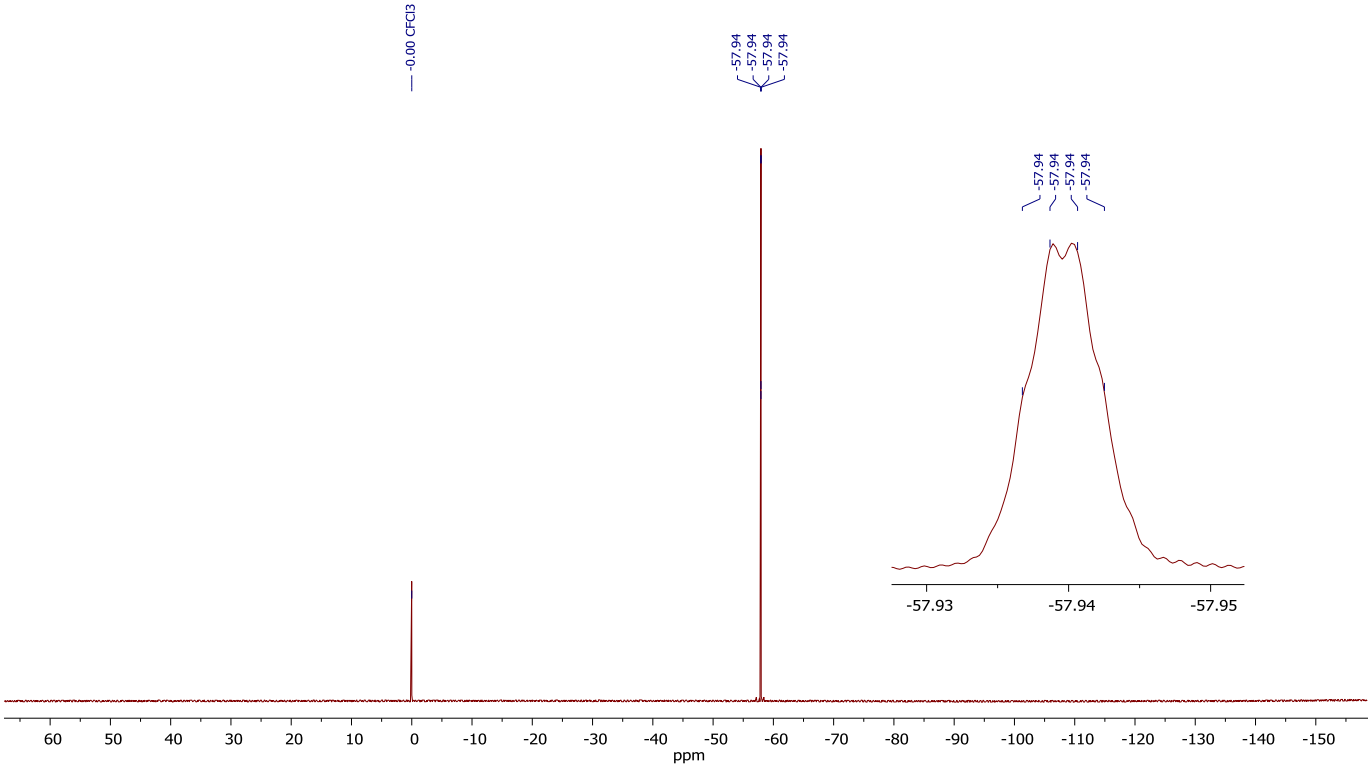
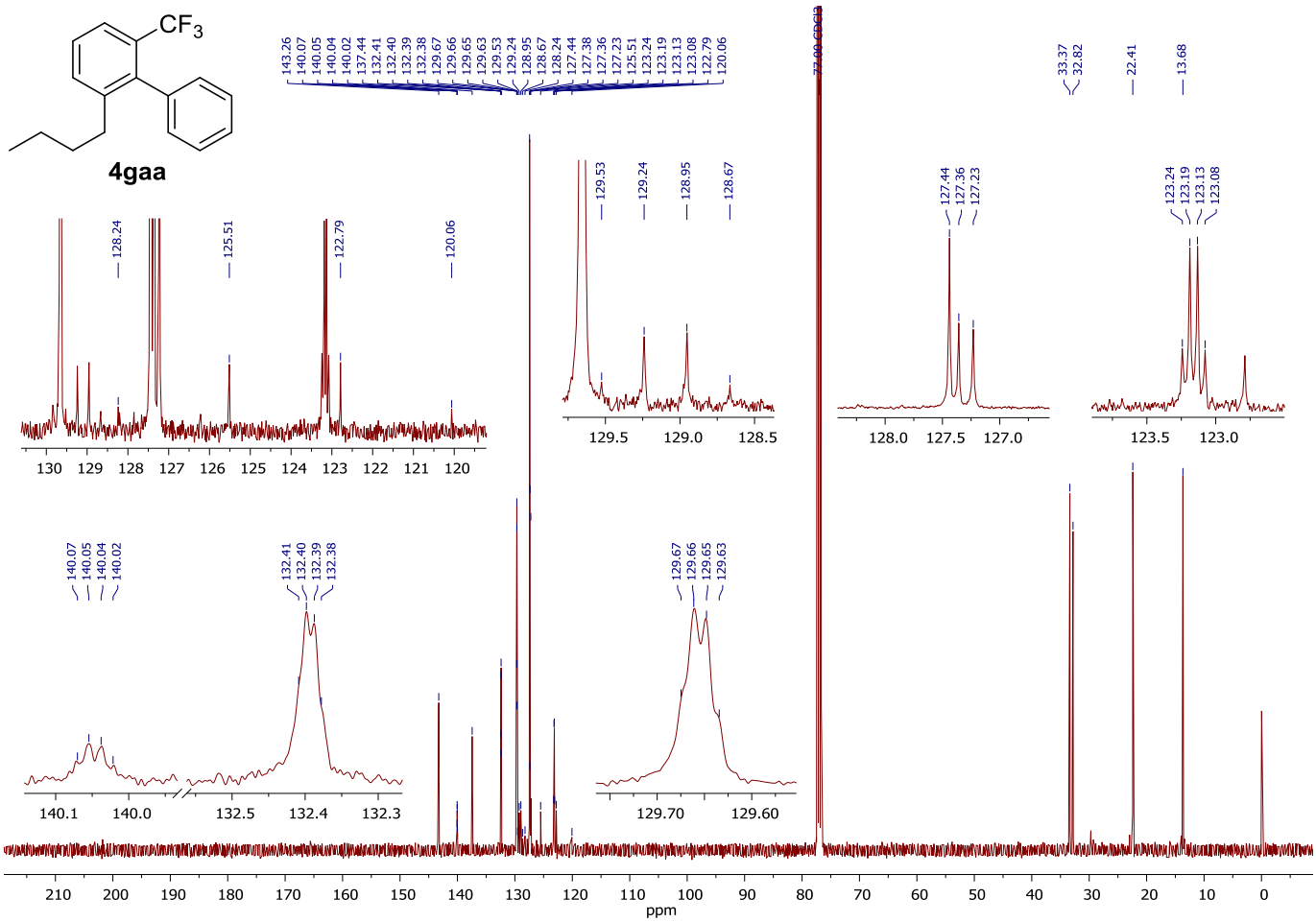
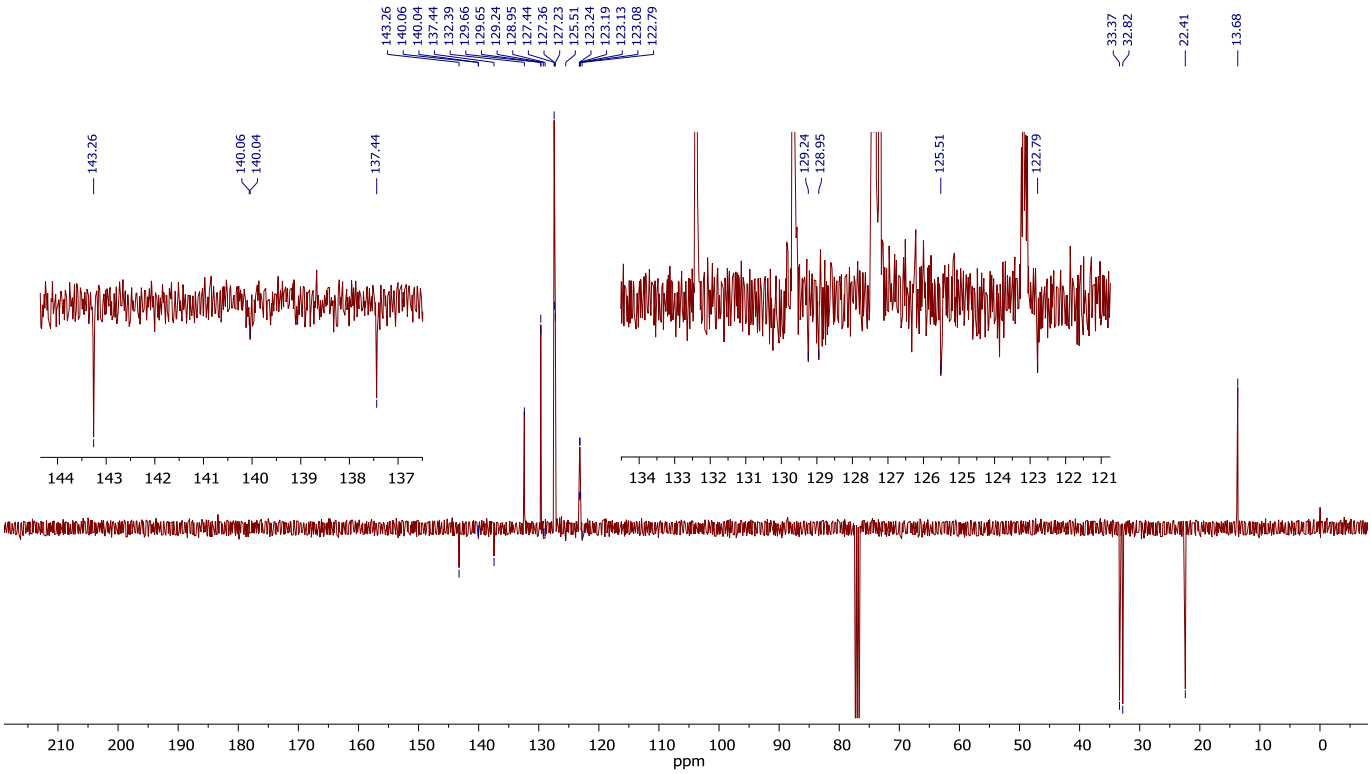
151.05
145.07
135.48
129.28
128.22
127.70
127.61
119.14
105.76
55.73
33.07
33.06
22.28
13.65
129.28
128.22
127.70
127.61
129.5 129.0 128.5 128.0 127.5
33.07
33.06
33.10 33.05
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


CF3
4gaa
7.26 CDCl3
1.55 HDO
ppm


-0.00 CFCl3
-57.94
ppm


CF3
4gaa
143.26
140.07
140.05
140.04
140.02
137.44
132.41
132.40
132.39
132.38
129.67
129.66
129.65
129.63
129.53
129.24
128.95
128.67
128.24
127.44
127.36
127.23
125.51
123.24
123.19
123.13
123.08
122.79
120.06
77.00 CDCl3
33.37
32.82
22.41
13.68
ppm


143.26
140.06
140.04
137.44
132.39
129.66
129.65
129.24
128.95
127.44
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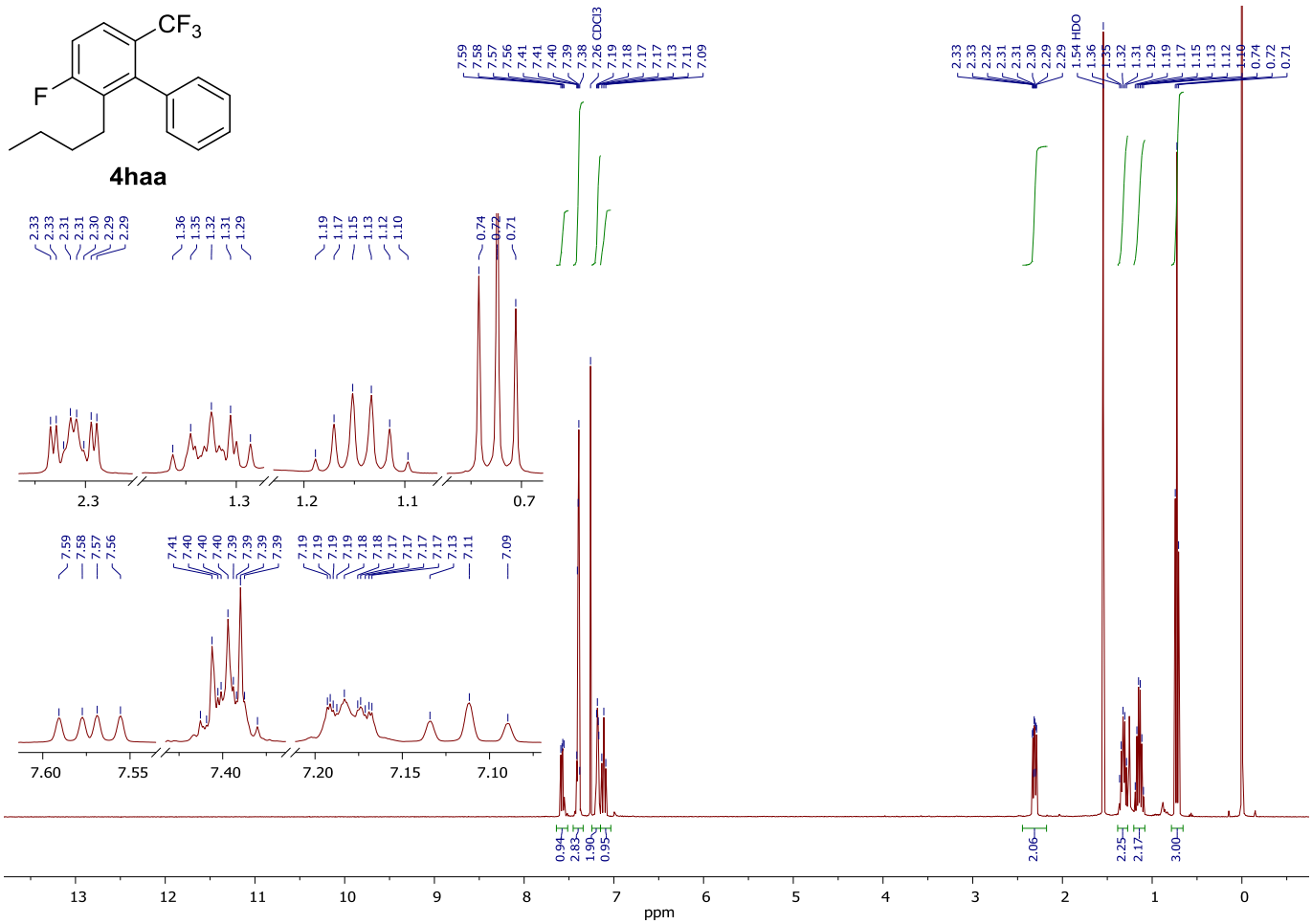
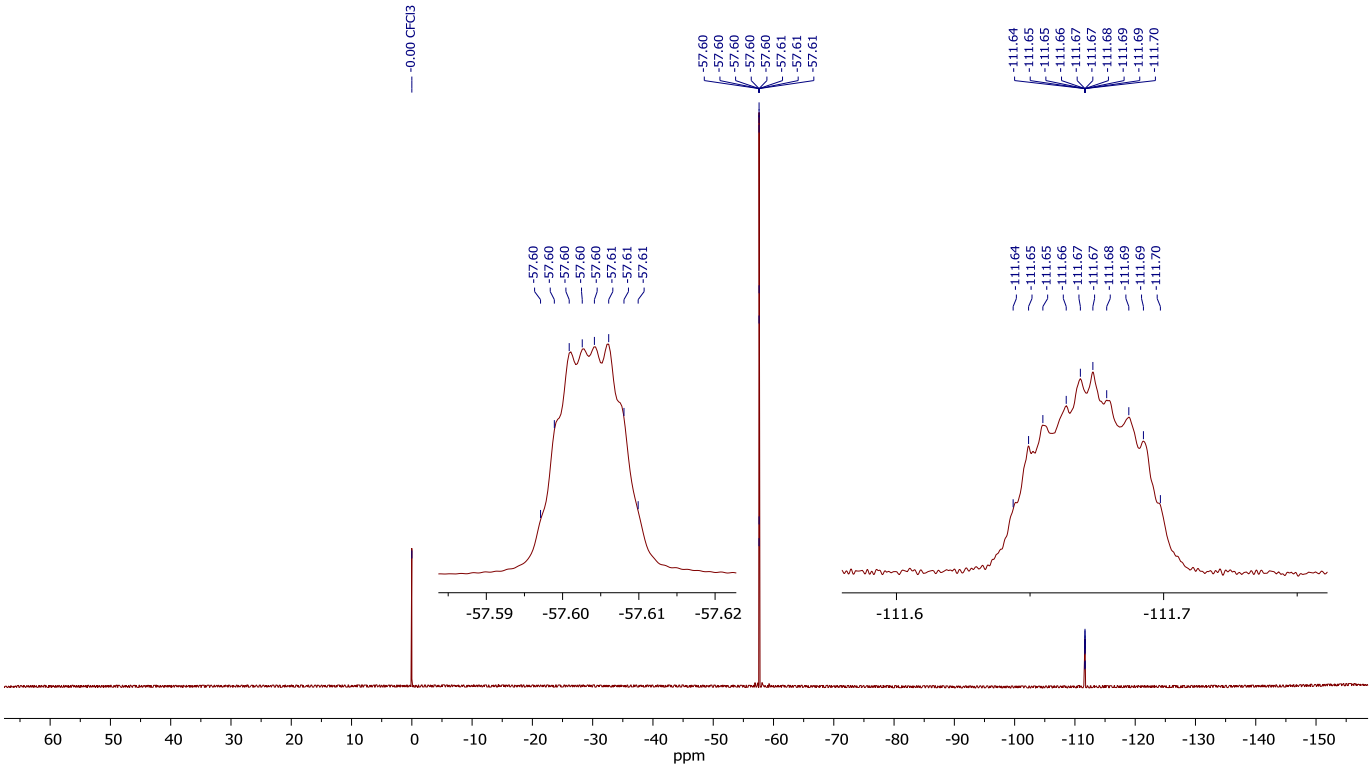
127.23
125.51
123.24
123.19
123.13
123.08
122.79
33.37
32.82
22.41
13.68
ppm


CF3
F
4haa
7.26 CDCl3
1.54 HDO
ppm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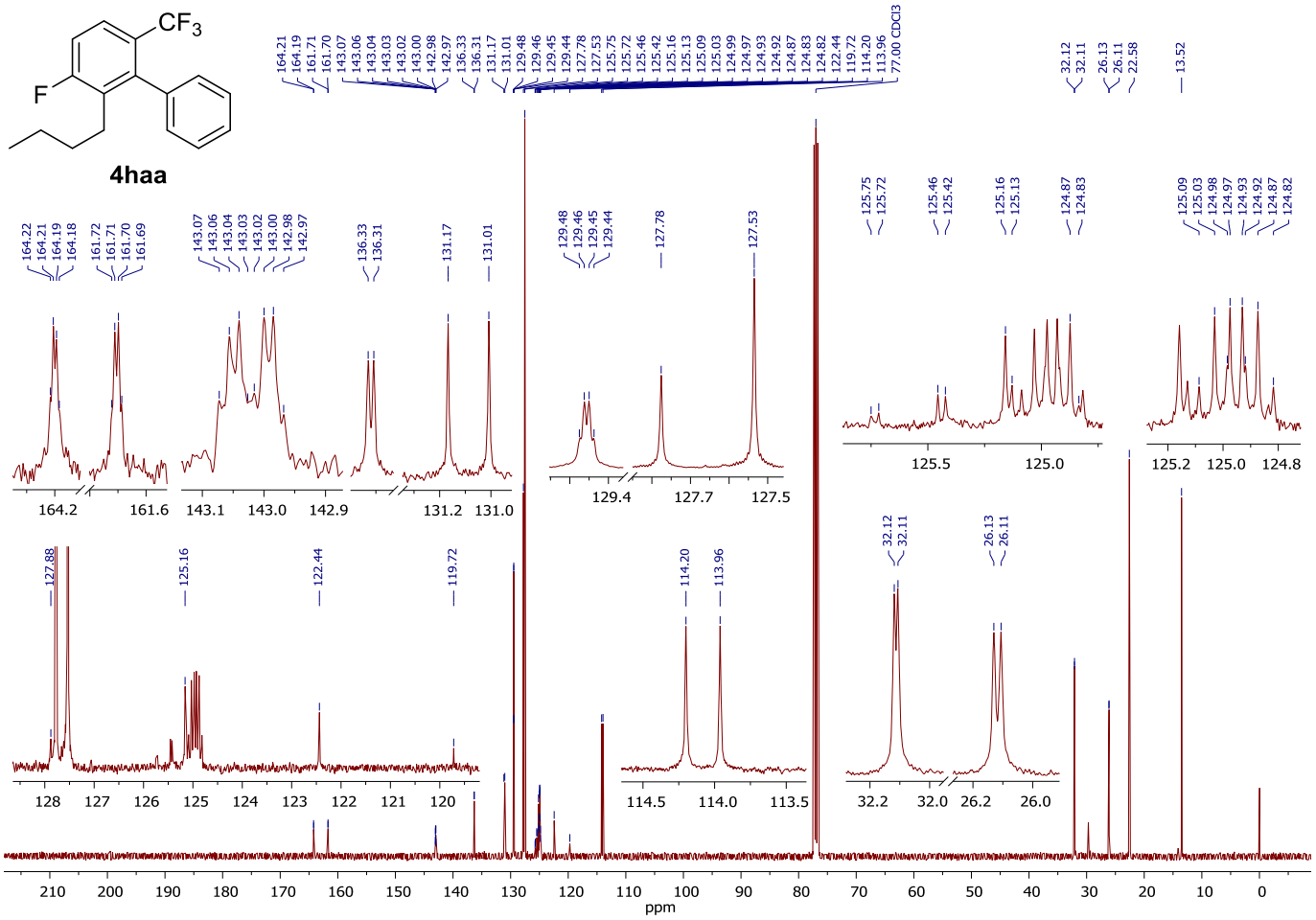
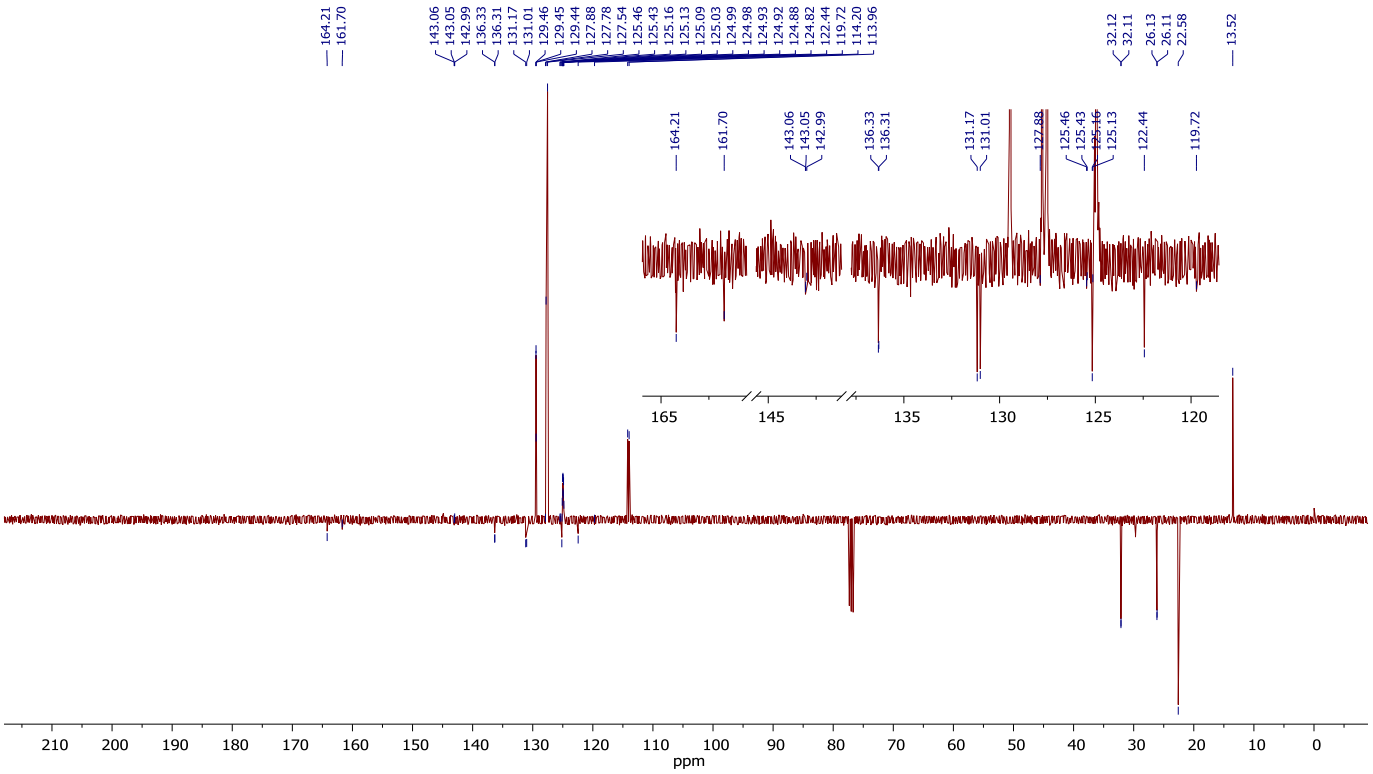
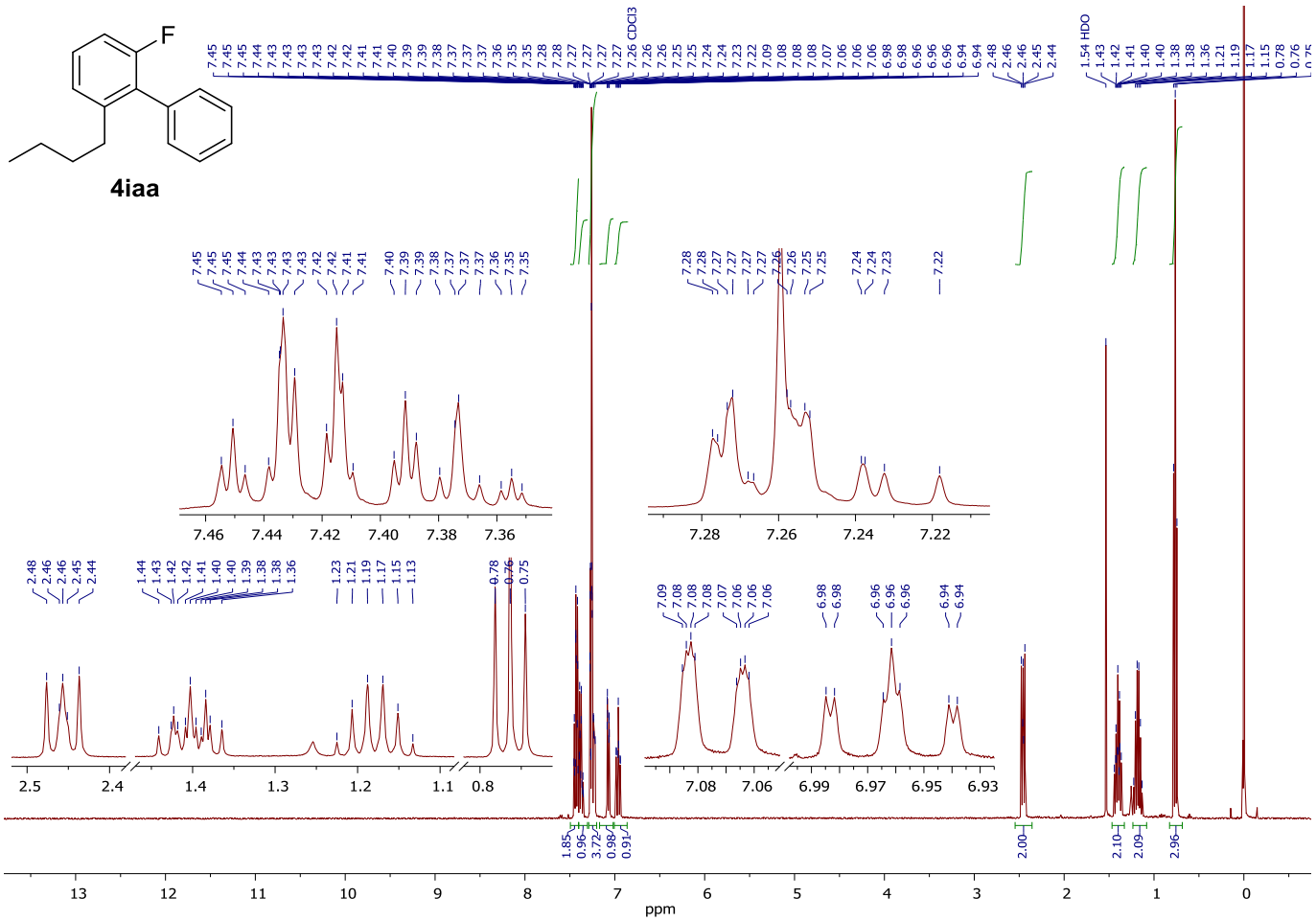
ppm


CF3
F
4haa
ppm


ppm


F
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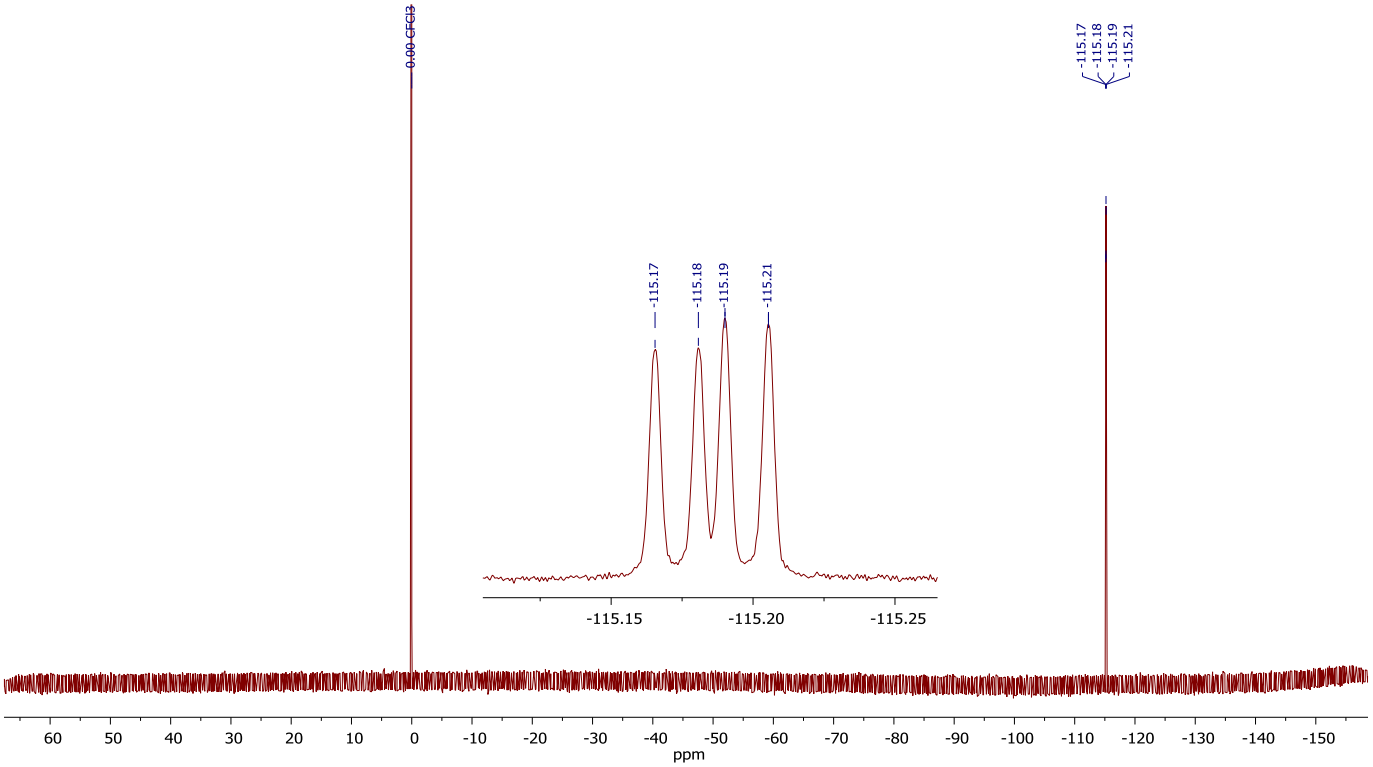
CDCl3
HDO
ppm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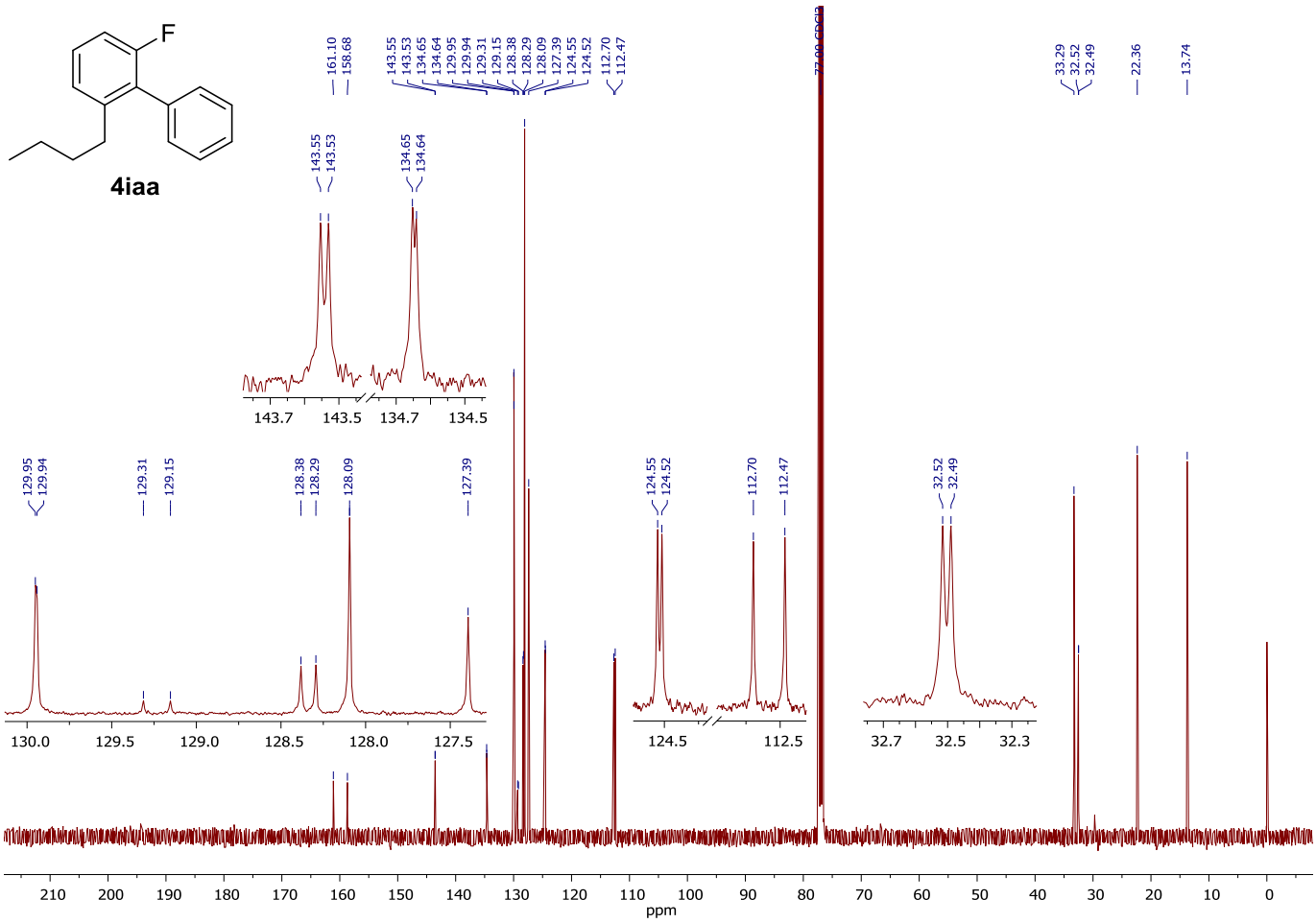
ppm


F
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129.94
129.31
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128.38
128.29
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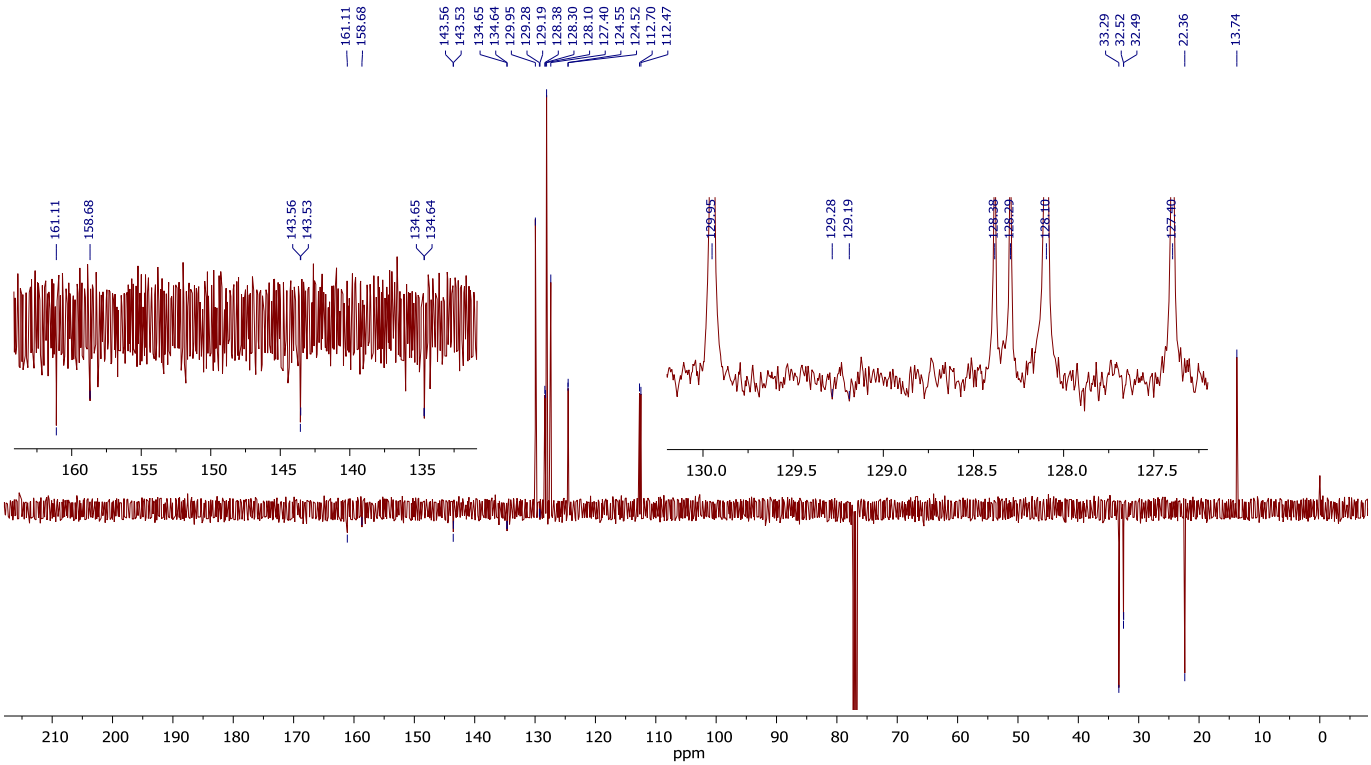
124.55
124.52
112.70
112.47
33.29
32.52
32.49
22.36
13.74
ppm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129.28
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128.38
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128.10
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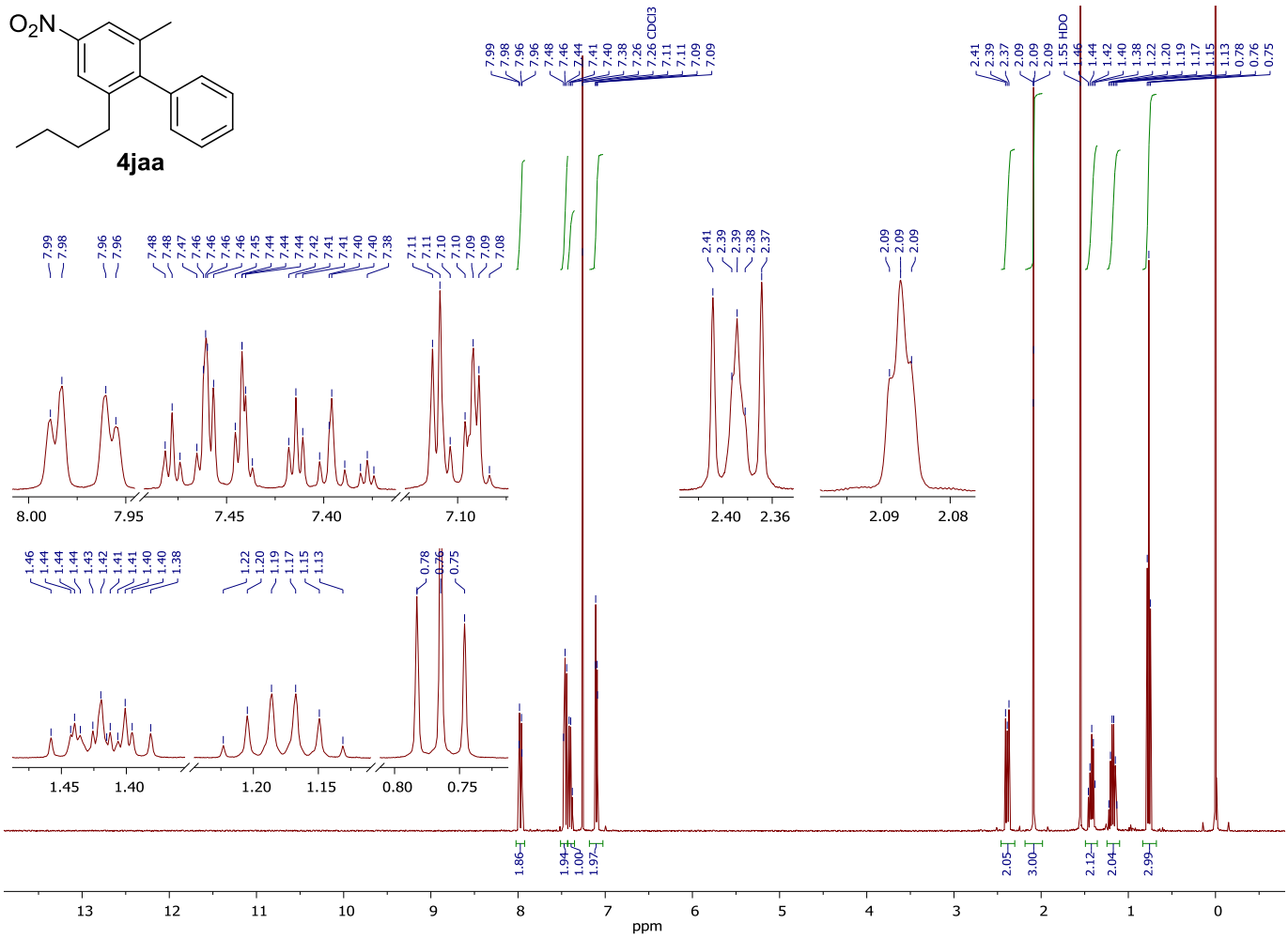
124.55
124.52
112.70
112.47
33.29
32.52
32.49
22.36
13.74
ppm


O2N
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7.99 7.98 7.96 7.96 7.48 7.46 7.44 7.41 7.40 7.38 7.26 CDCl3 7.11 7.11 7.09 7.09
2.41 2.39 2.37 2.09 2.09 1.55 HDO 1.46 1.44 1.42 1.40 1.38 1.22 1.20 1.19 1.17 1.15 1.13 0.78 0.76 0.75
7.99 7.98 7.96 7.96 7.48 7.48 7.47 7.46 7.46 7.46 7.46 7.45 7.44 7.44 7.44 7.42 7.41 7.41 7.40 7.40 7.38 7.11 7.11 7.10 7.10 7.09 7.09 7.08
2.41 2.39 2.39 2.38 2.37
2.09 2.09 2.09
8.00 7.95 7.45 7.40 7.10
2.40 2.36
2.09 2.08
1.46 1.44 1.44 1.44 1.43 1.42 1.41 1.41 1.40 1.40 1.38
1.22 1.20 1.19 1.17 1.15 1.13
0.78 0.76 0.75
1.45 1.40 1.20 1.15 0.80 0.75
1.86 1.94 1.00 1.97 2.05 3.00 2.12 2.04 2.99
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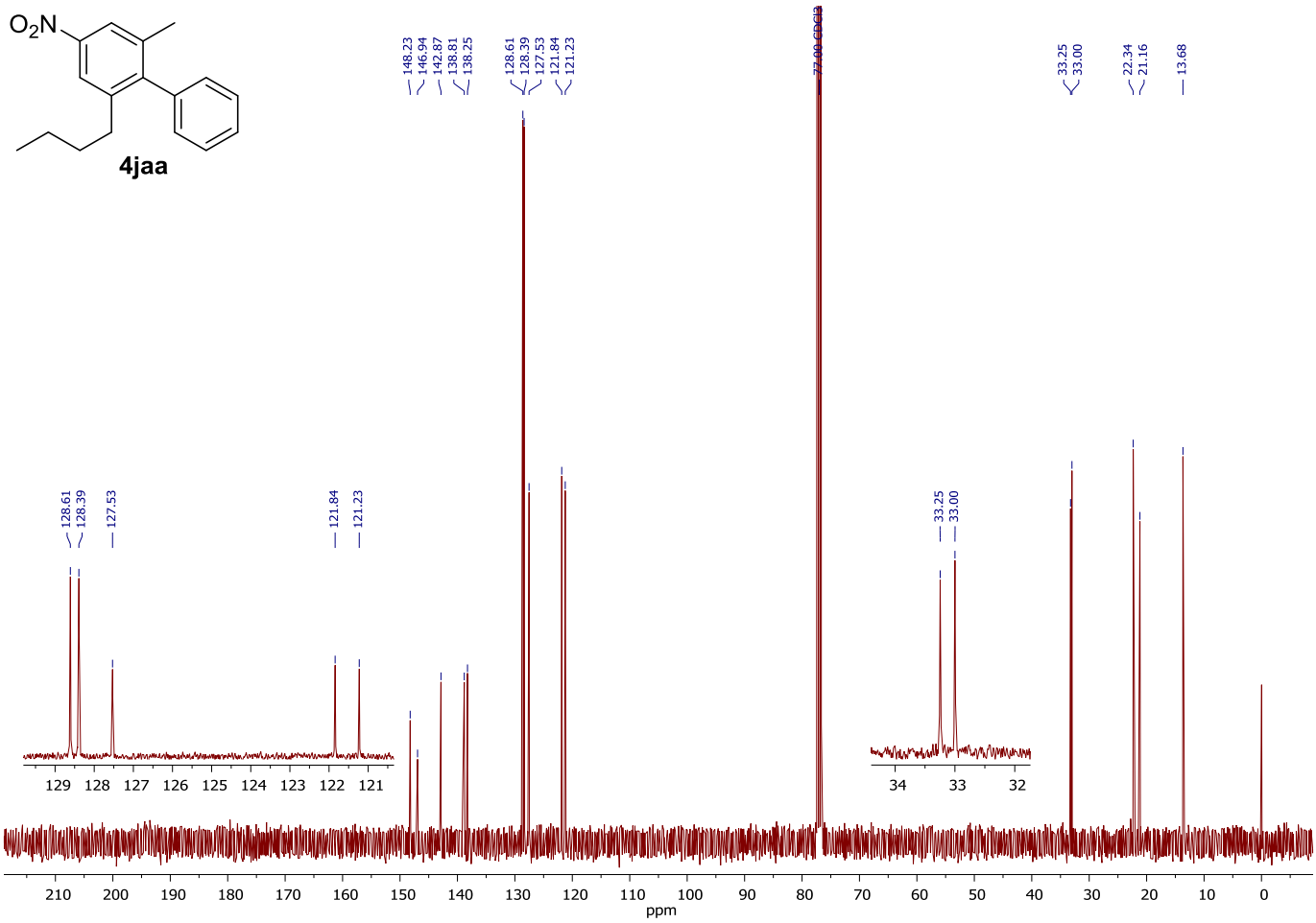
O2N
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121.23
77.00 CDCl3
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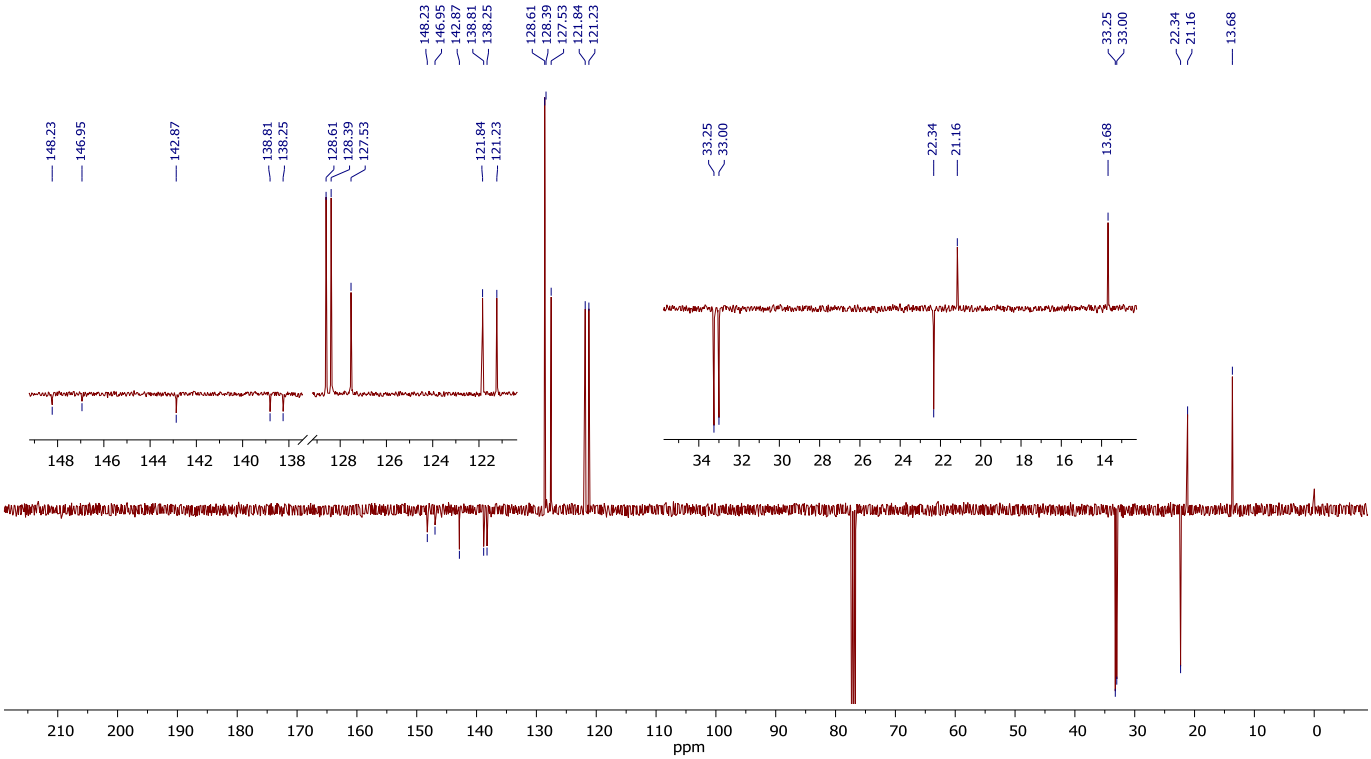
33.00
22.34
21.16
13.68
ppm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142.87
138.81
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127.53
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121.23
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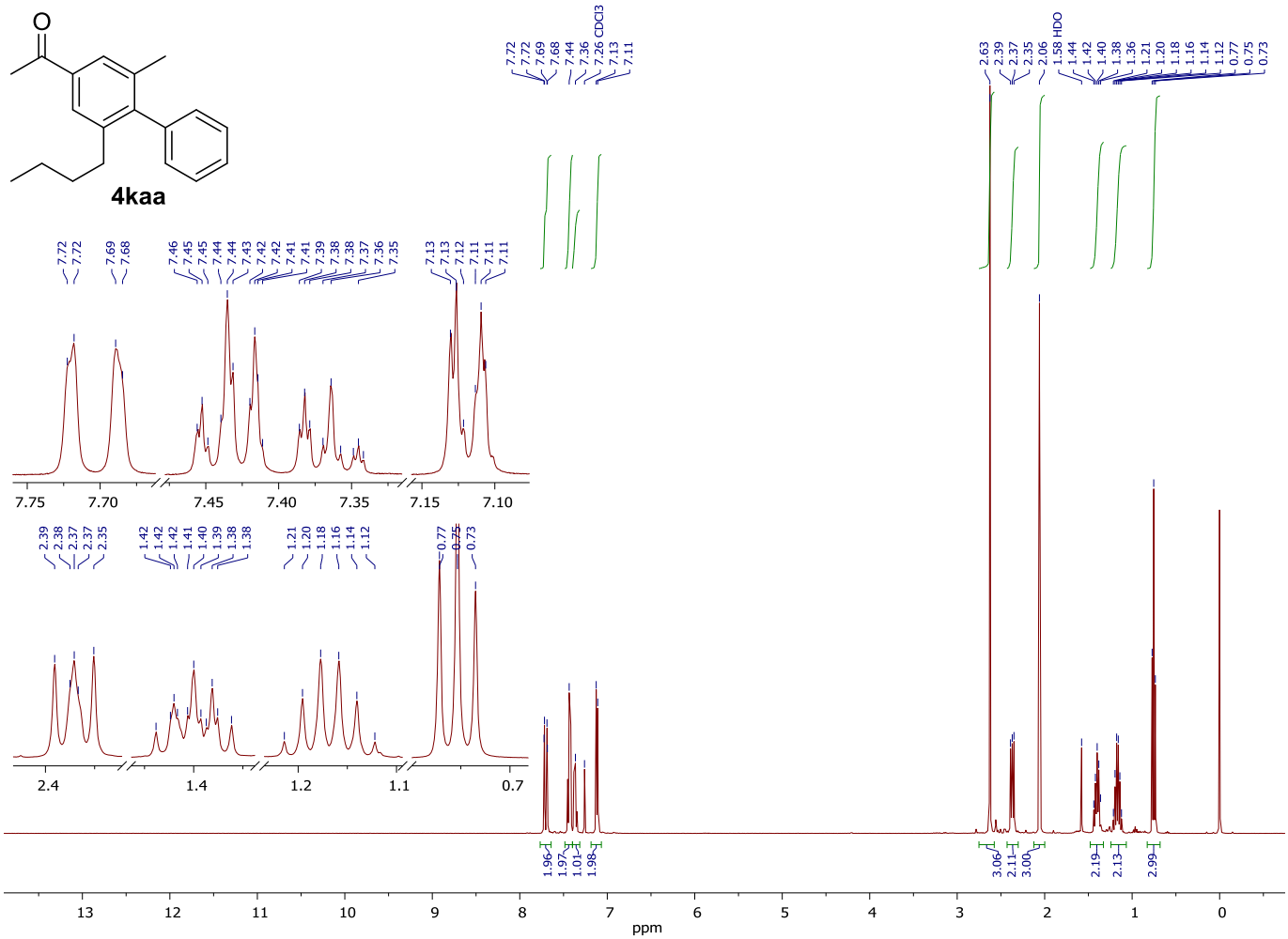
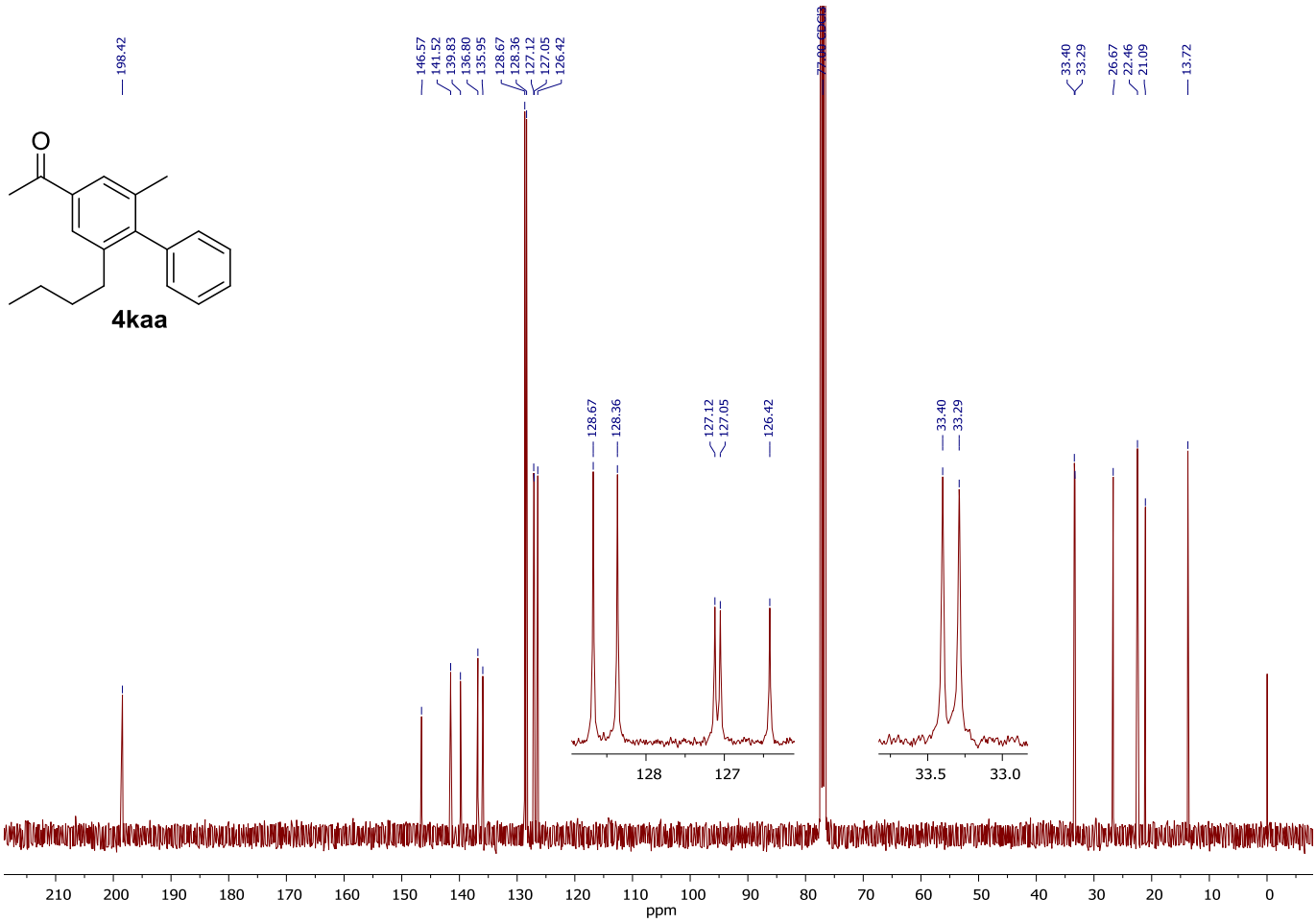
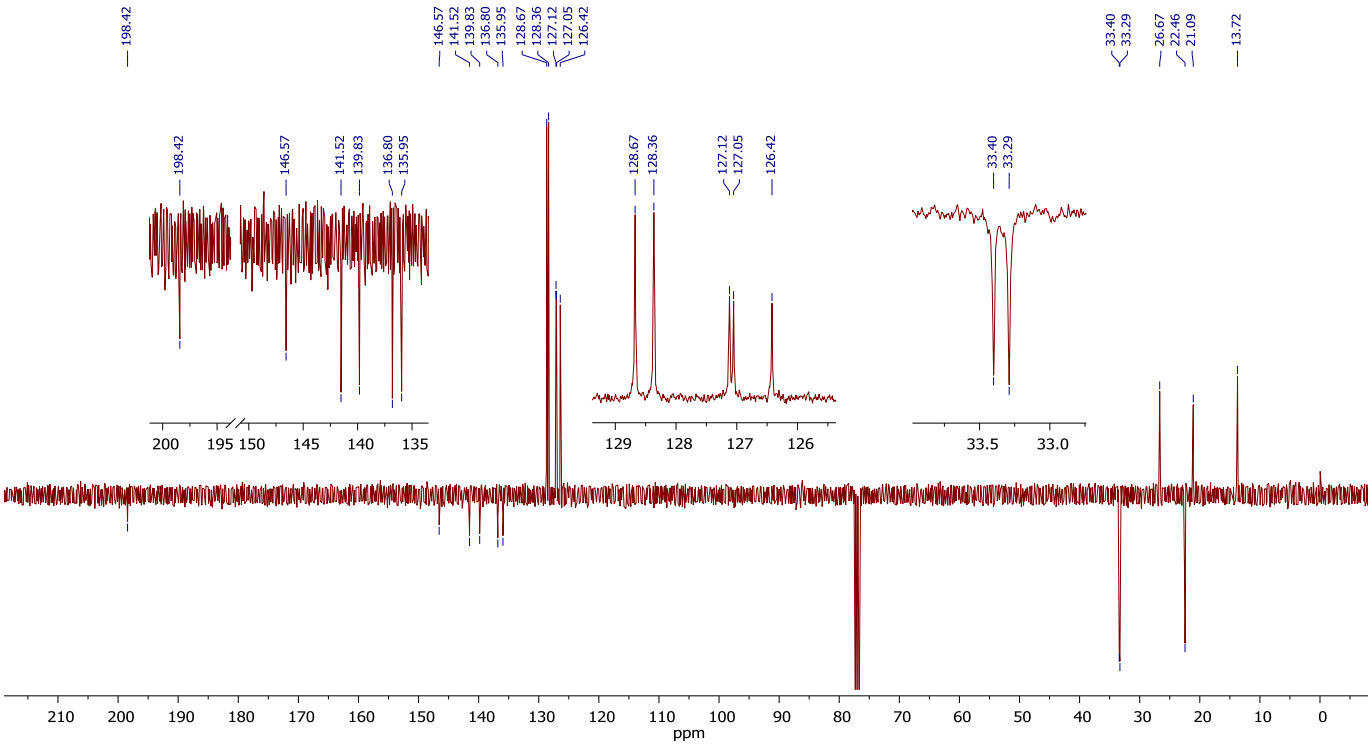
33.00
22.34
21.16
13.68
ppm


4kaa
7.72 7.72 7.69 7.68 7.44 7.36 7.26 CDCl3 7.13 7.11
2.63 2.39 2.37 2.35 2.06 1.58 HDO 1.44 1.42 1.40 1.38 1.36 1.21 1.20 1.18 1.16 1.14 1.12 0.77 0.75 0.73
7.72 7.72 7.69 7.68 7.46 7.45 7.45 7.44 7.44 7.43 7.42 7.42 7.41 7.41 7.39 7.38 7.38 7.37 7.36 7.35 7.13 7.13 7.12 7.11 7.11 7.11
7.75 7.70 7.45 7.40 7.35 7.15 7.10
2.39 2.38 2.37 2.37 2.35 1.42 1.42 1.42 1.41 1.40 1.39 1.38 1.38 1.21 1.20 1.18 1.16 1.14 1.12 0.77 0.75 0.73
2.4 1.4 1.2 1.1 0.7
1.96 1.97 1.01 1.98 3.06 2.11 3.00 2.19 2.13 2.99
13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm


198.42
146.57
141.52
139.83
136.80
135.95
128.67
128.36
127.12
127.05
126.42
77.04 CDCl3
33.40
33.29
26.67
22.46
21.09
13.72
O
4kaa
128
127
33.5
33.0
ppm


198.42
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128.67
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127.05
126.42
33.40
33.29
26.67
22.46
21.09
13.72
200
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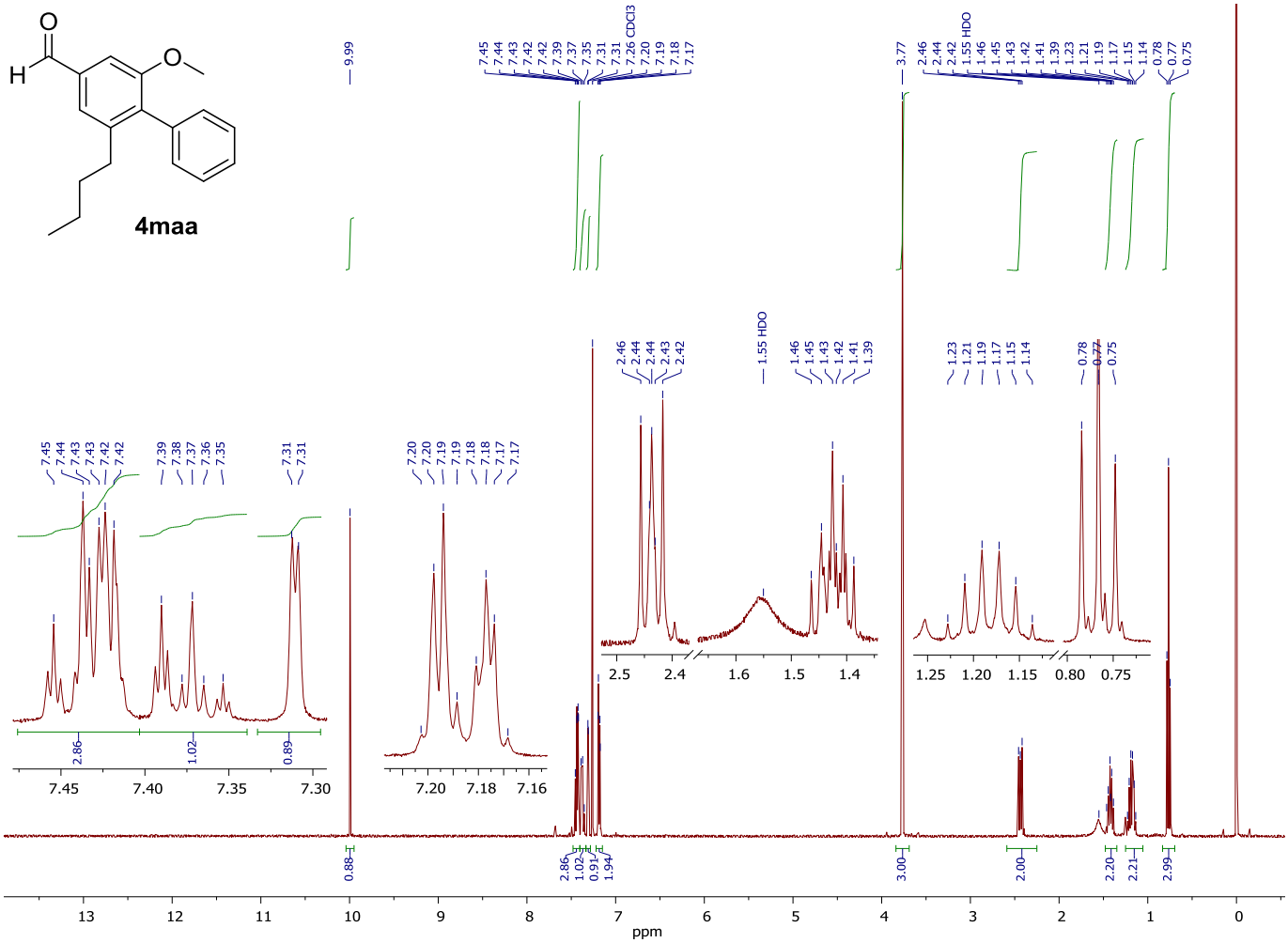
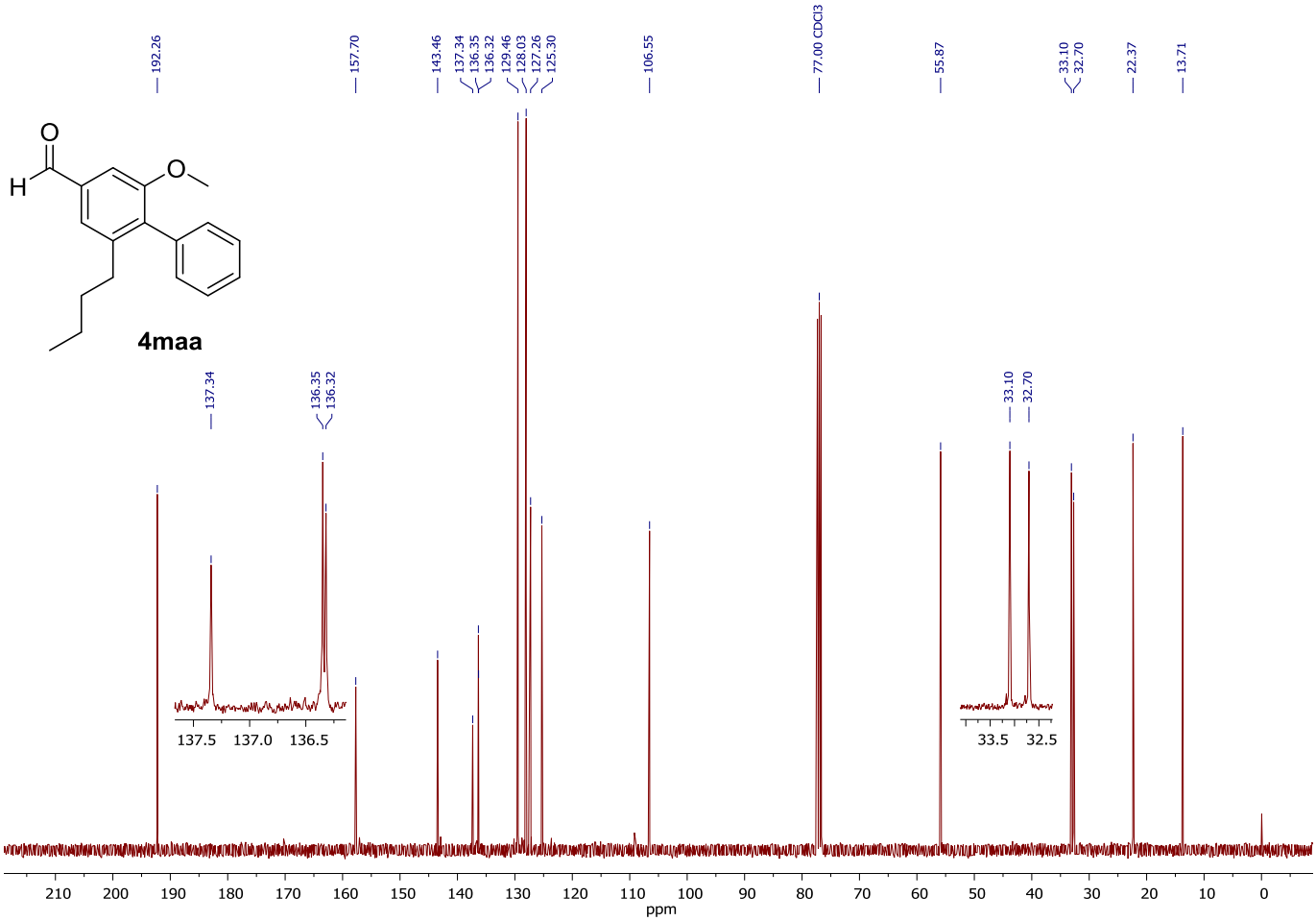
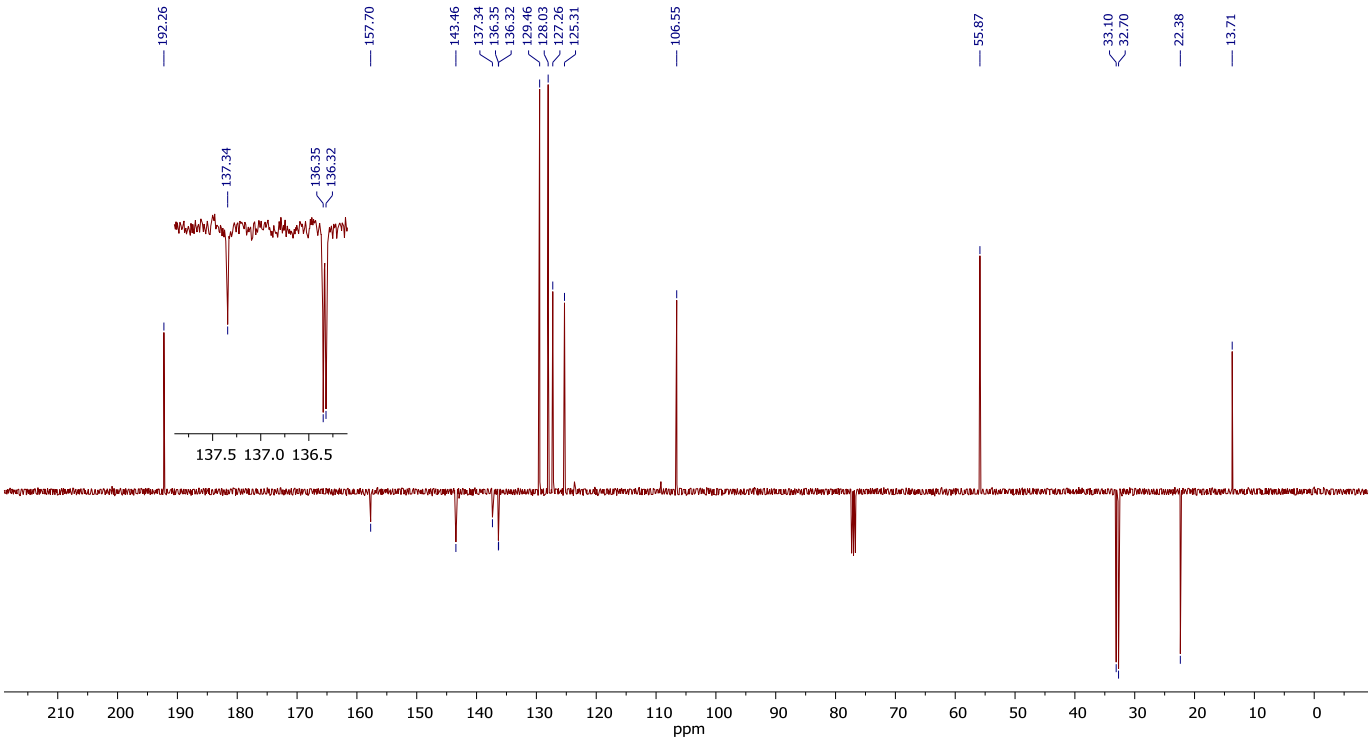
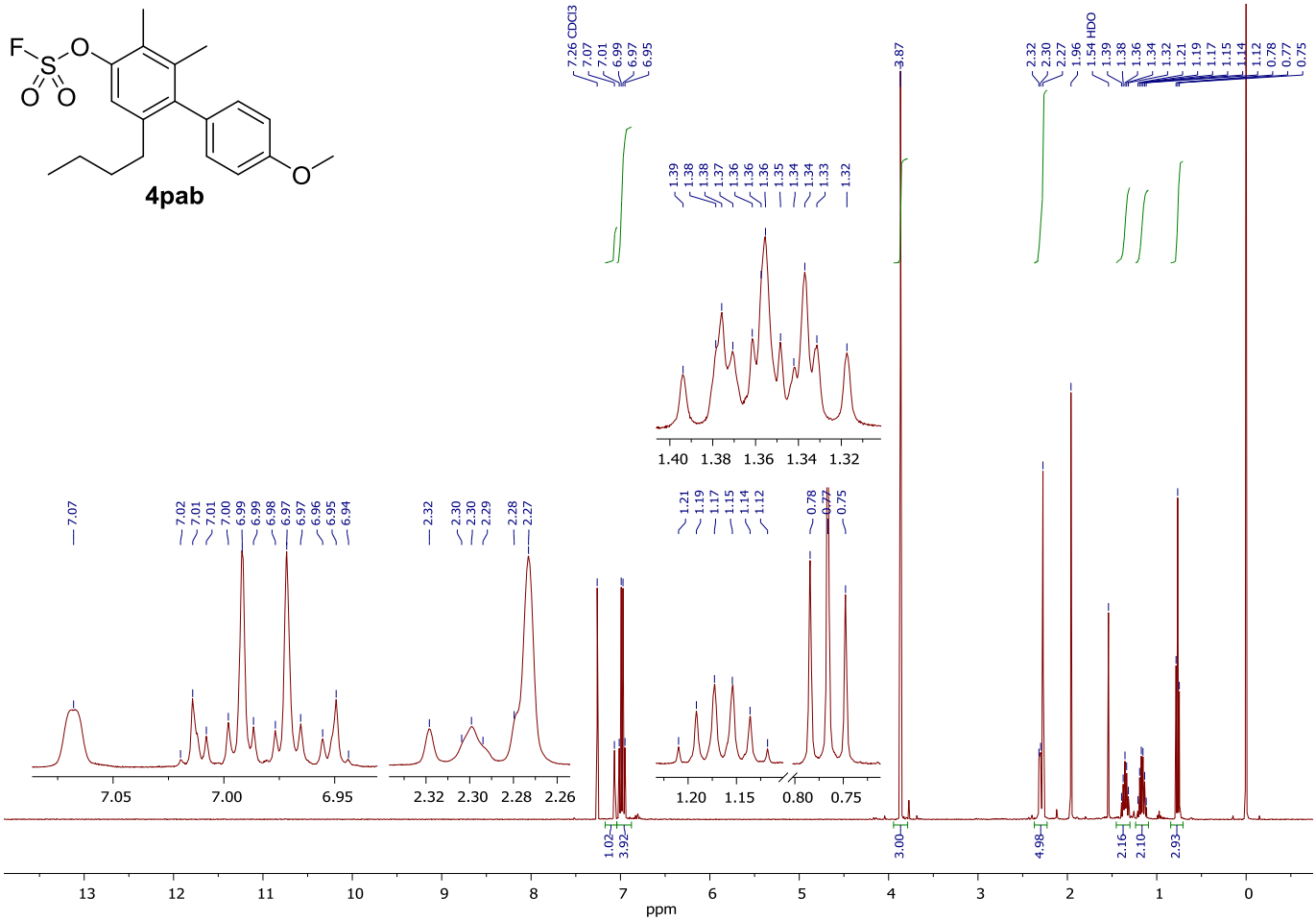
150
145
140
135
129
128
127
126
33.5
33.0
ppm


4maa
9.99
7.45 7.44 7.43 7.42 7.42 7.39 7.37 7.35 7.31 7.26 CDCl3 7.20 7.19 7.18 7.17
3.77
2.46 2.44 2.42 1.55 HDO 1.46 1.45 1.43 1.42 1.41 1.39 1.23 1.21 1.19 1.17 1.15 1.14 0.78 0.77 0.75
2.86
1.02
0.89
0.88
2.86
1.02
0.91
1.94
3.00
2.00
2.20
2.21
2.99
ppm


192.26
157.70
143.46
137.34
136.35
136.32
129.46
128.03
127.26
125.30
106.55
77.00 CDCl3
55.87
33.10
32.70
22.37
13.71
O
H
O
4maa
137.5 137.0 136.5
33.5 32.5
ppm


192.26
157.70
143.46
137.34
136.35
136.32
129.46
128.03
127.26
125.31
106.55
55.87
33.10
32.70
22.38
13.71
137.5 137.0 136.5
ppm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2.32
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2.27
1.96
1.54 HDO
1.39
1.38
1.36
1.34
1.32
1.21
1.19
1.17
1.15
1.14
1.12
0.78
0.77
0.75
7.07
7.02
7.01
7.00
6.99
6.98
6.97
6.96
6.95
6.94
2.29
2.28
1.40 1.38 1.36 1.34 1.32
7.05 7.00 6.95
2.32 2.30 2.28 2.26
1.20 1.15 0.80 0.75
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2.93
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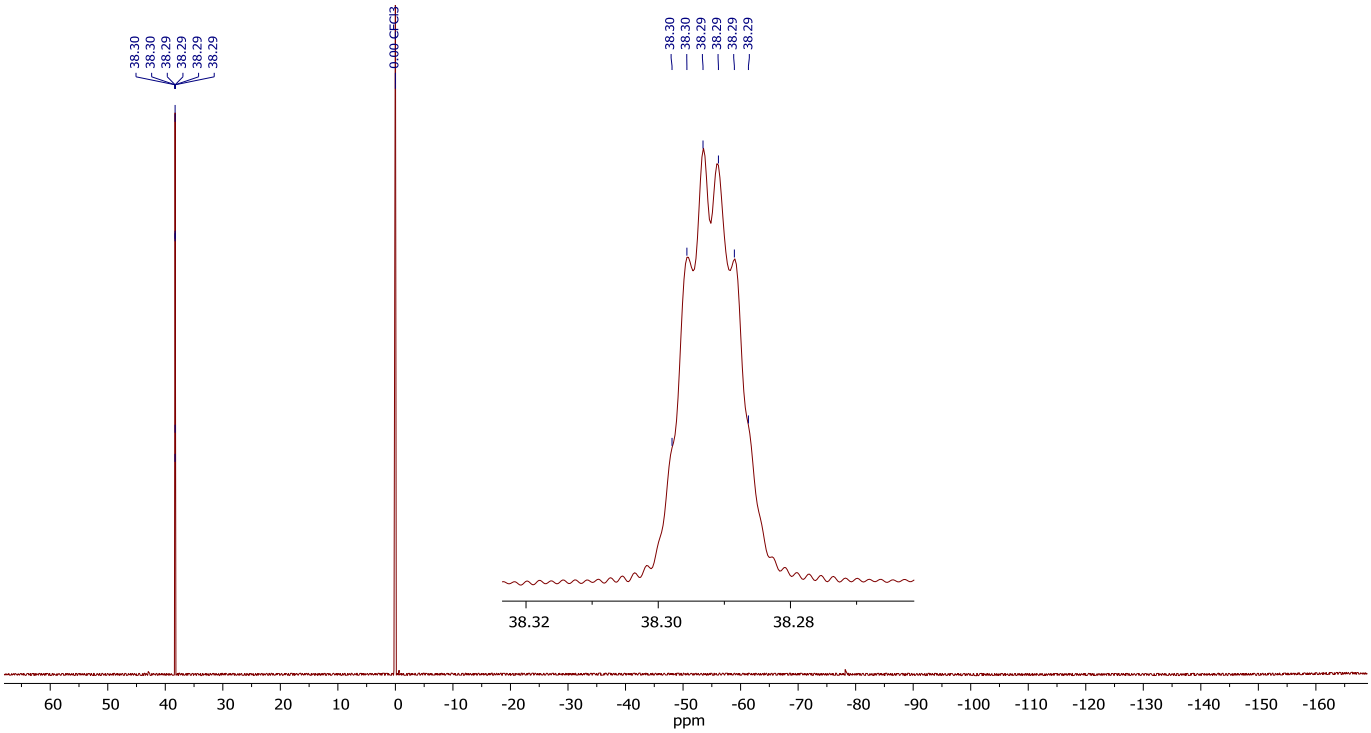
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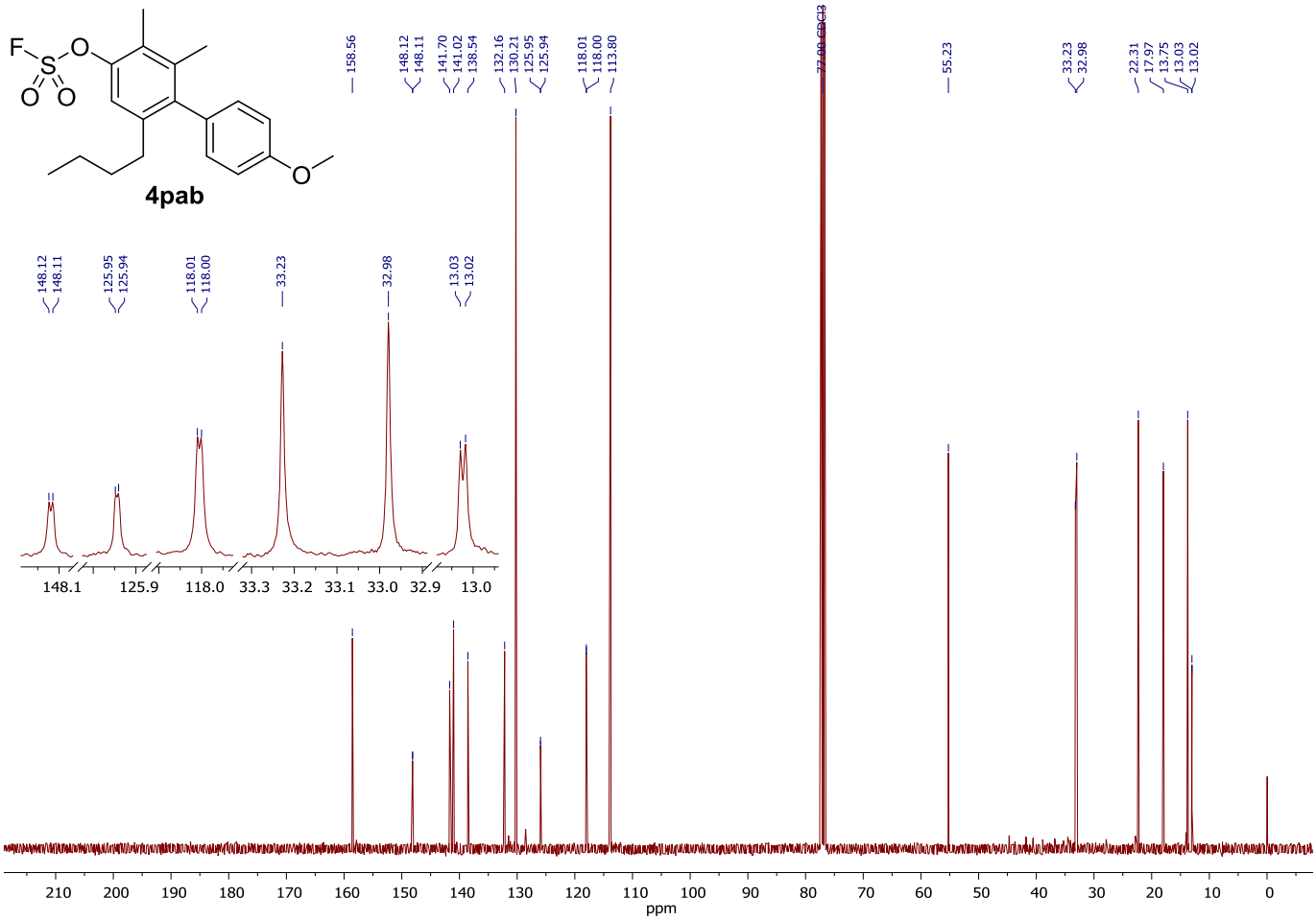
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118.01
118.00
113.80
77.00 CDCl3
55.23
33.23
32.98
22.31
17.97
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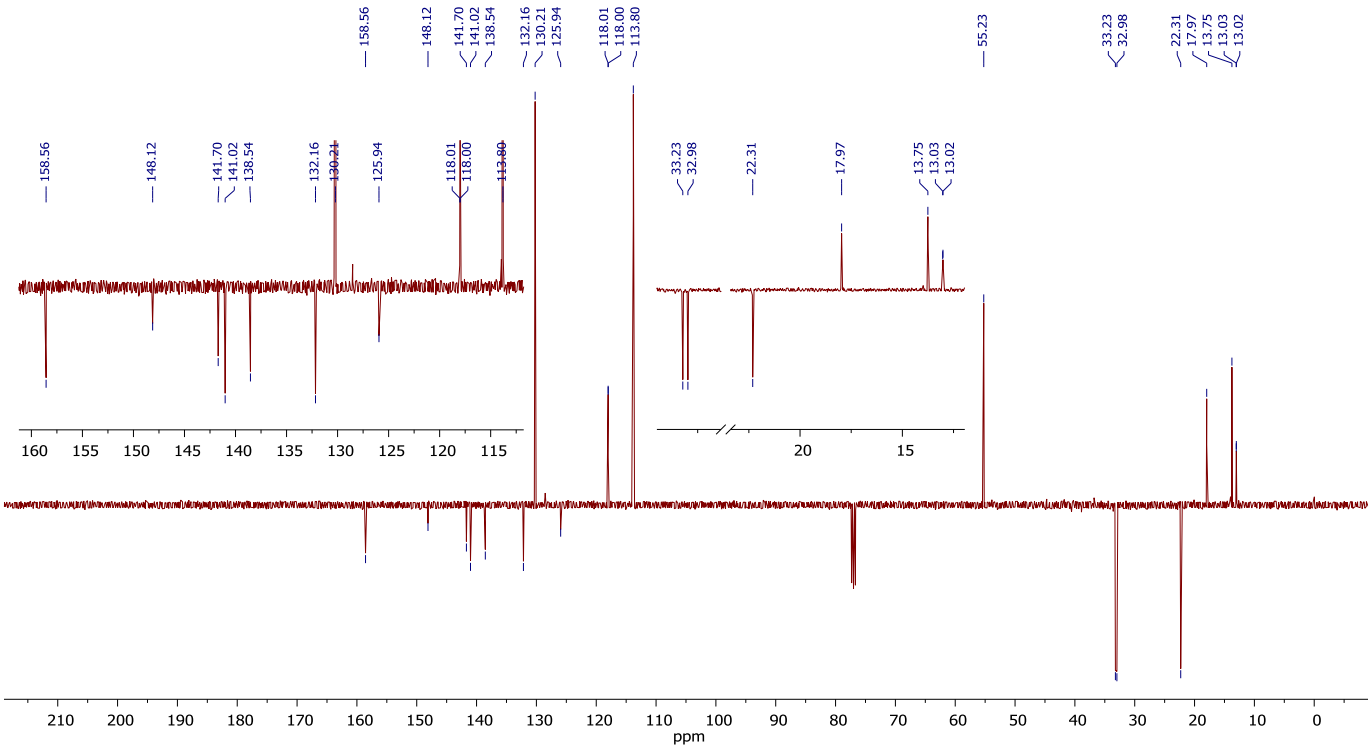
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22.31
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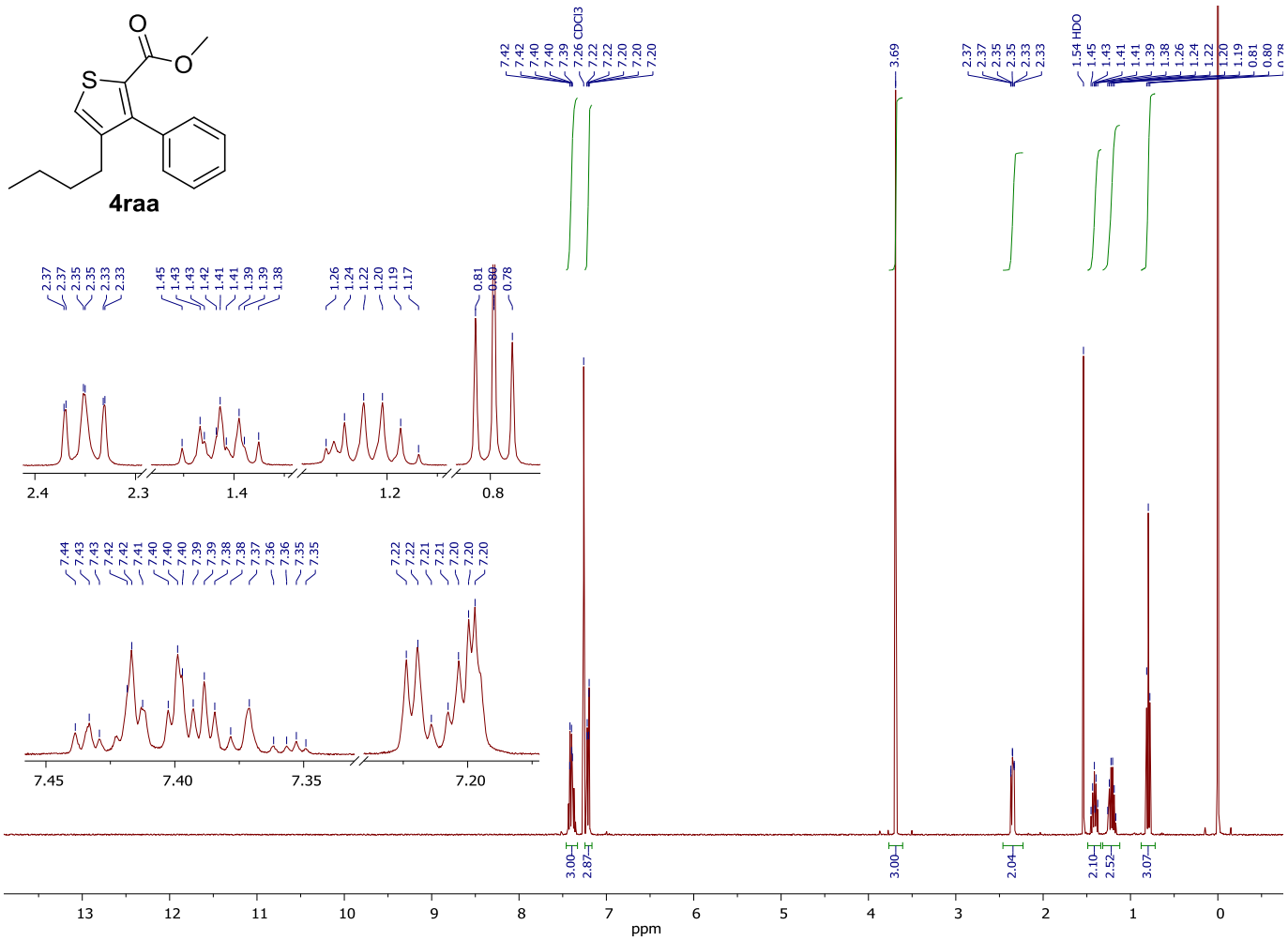
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3.69
2.37 2.37 2.35 2.35 2.33 2.33 2.33
1.54 HDO 1.45 1.43 1.41 1.41 1.39 1.38 1.26 1.24 1.22 1.20 1.19 0.81 0.80 0.78
2.37 2.37 2.35 2.35 2.33 2.33
1.45 1.43 1.43 1.42 1.41 1.41 1.39 1.39 1.38
1.26 1.24 1.22 1.20 1.19 1.17
0.81 0.80 0.78
2.4 2.3 1.4 1.2 0.8
7.44 7.43 7.43 7.42 7.42 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.36 7.36 7.35 7.35
7.22 7.22 7.21 7.21 7.20 7.20 7.20
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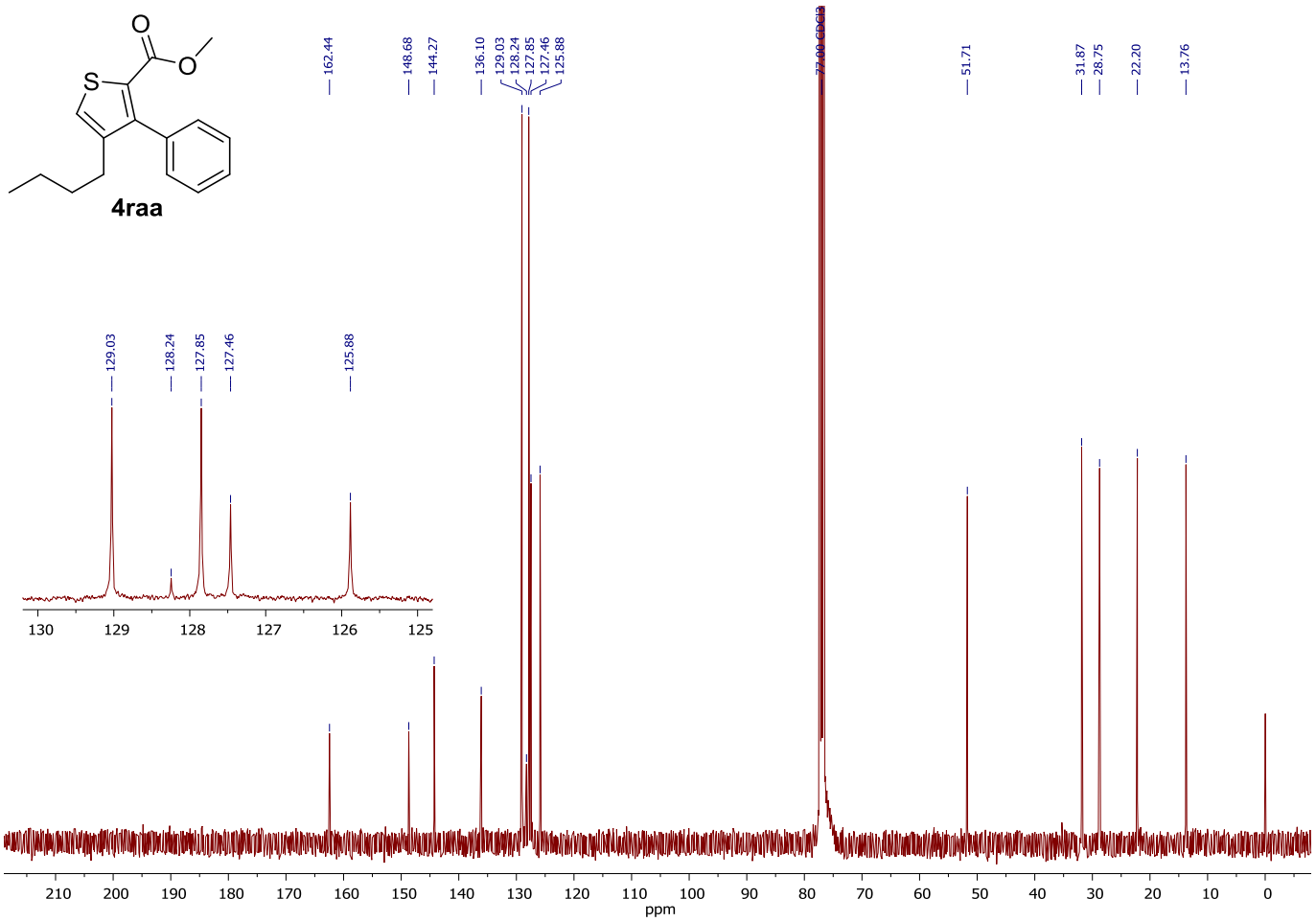
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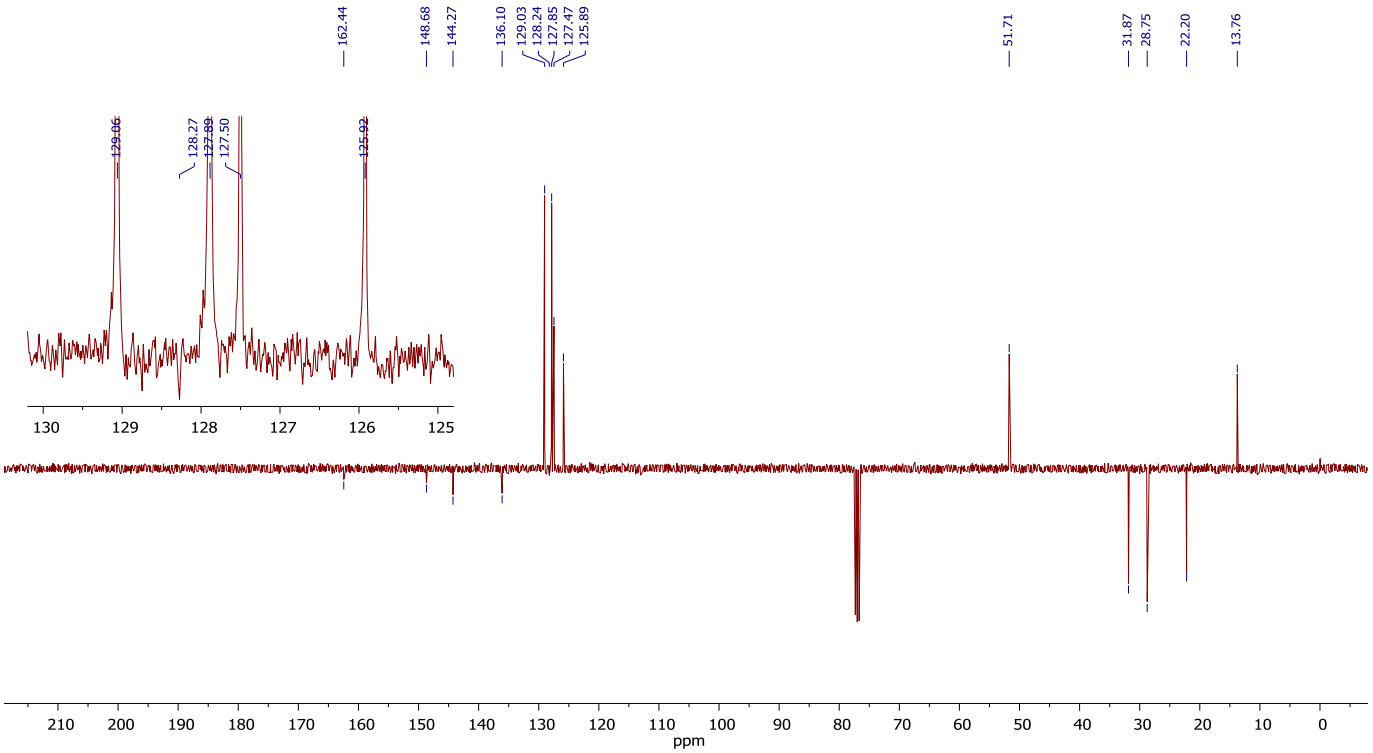
13.76
ppm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136.10
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128.24
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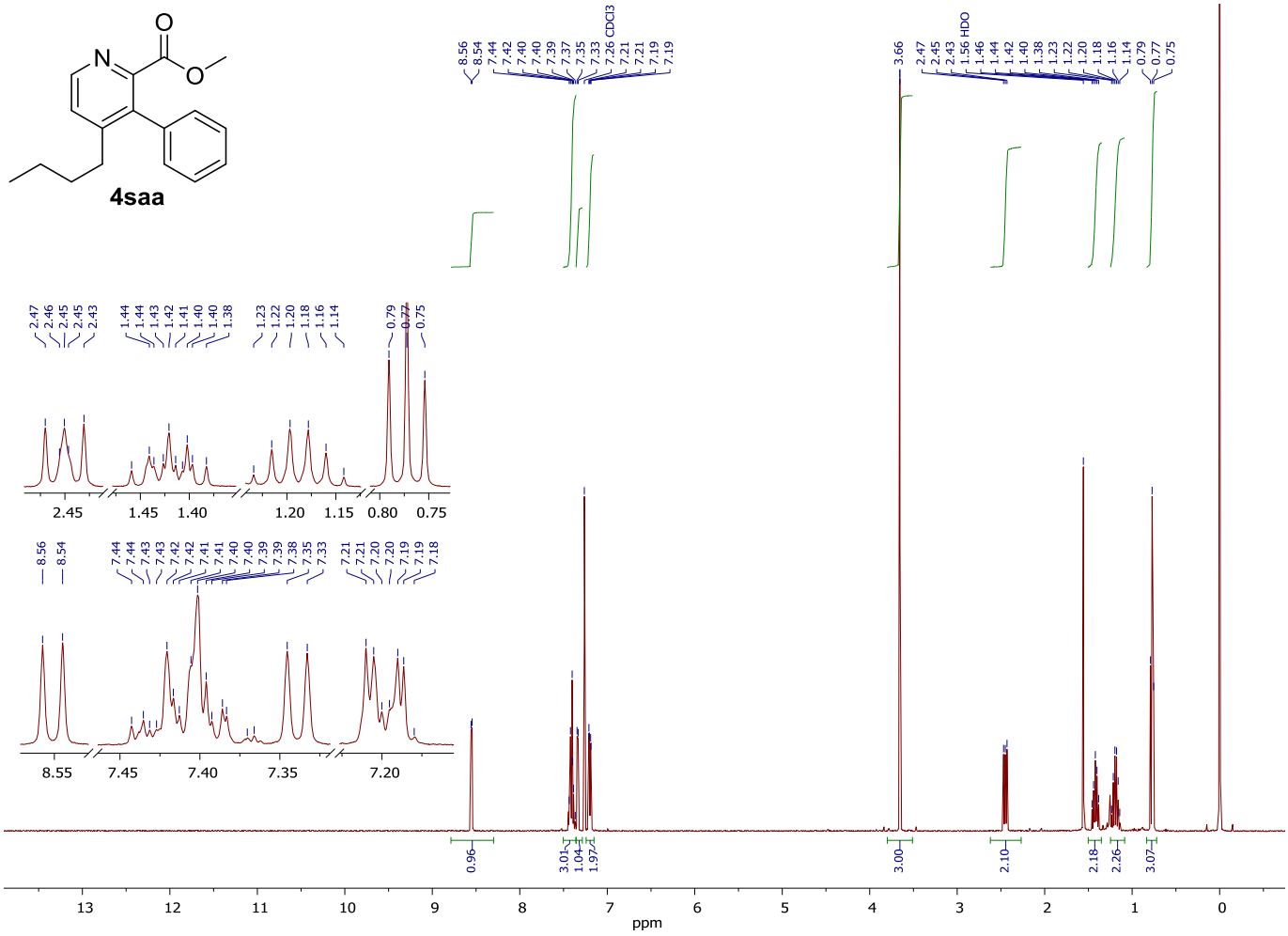
28.75
22.20
13.76
129.06
128.27
127.89
127.50
125.92
ppm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8.54
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7.40
7.40
7.39
7.37
7.35
7.33
7.26 CDCl3
7.21
7.21
7.19
7.19
3.66
2.47
2.45
2.43
1.56 HDO
1.46
1.44
1.42
1.40
1.38
1.23
1.22
1.20
1.18
1.16
1.14
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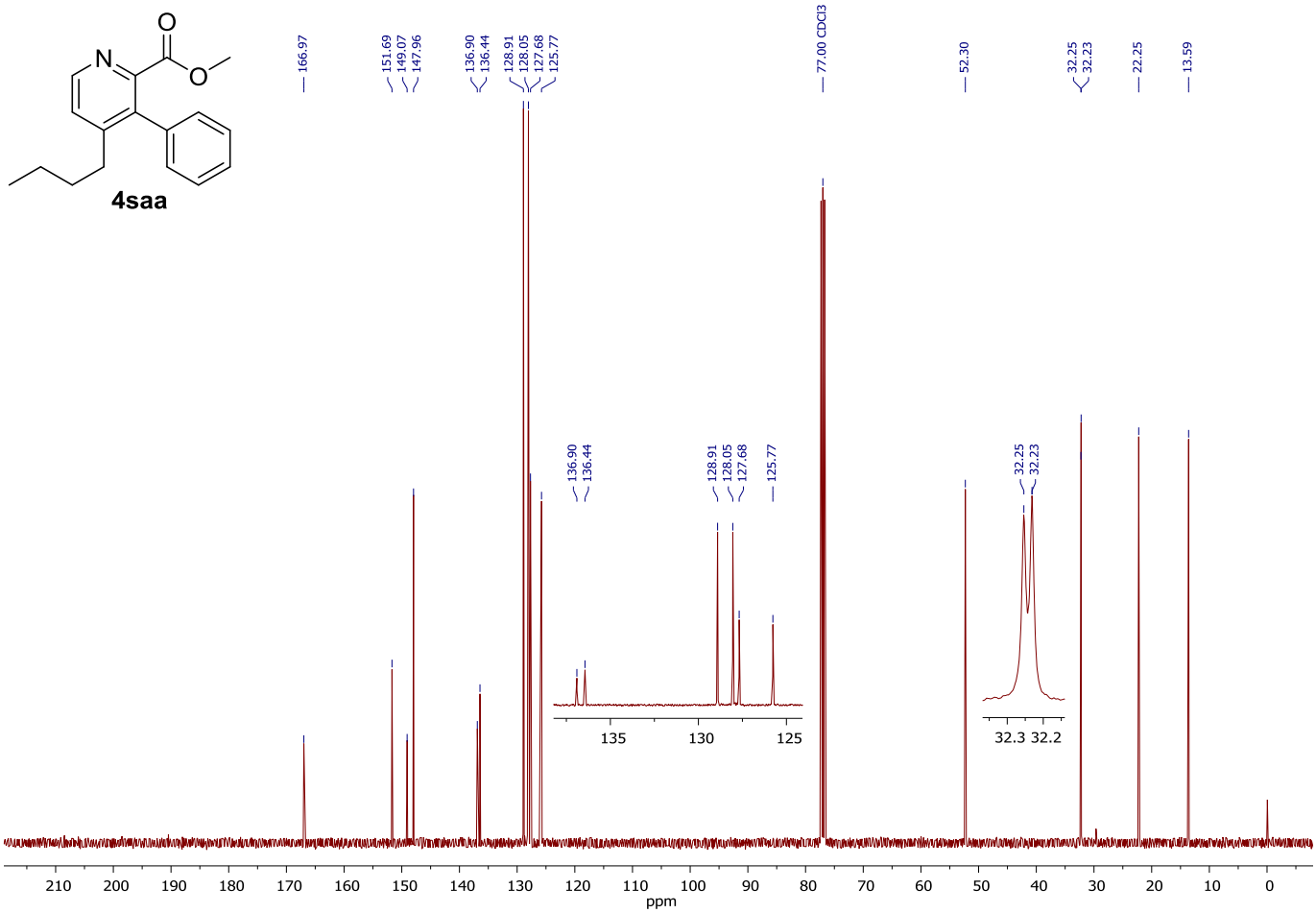
1.04
1.97
3.00
2.10
2.18
2.26
3.07
ppm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32.23
22.25
13.59
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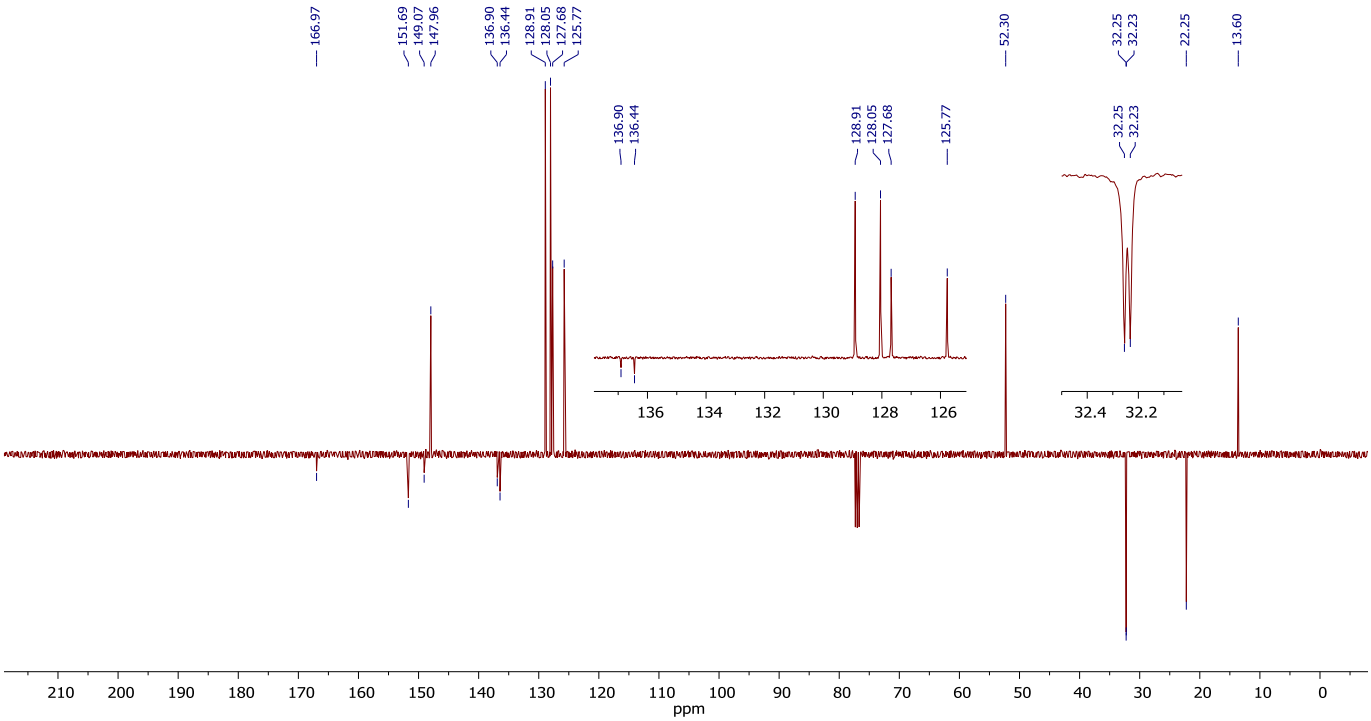
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32.25
32.23
22.25
13.60
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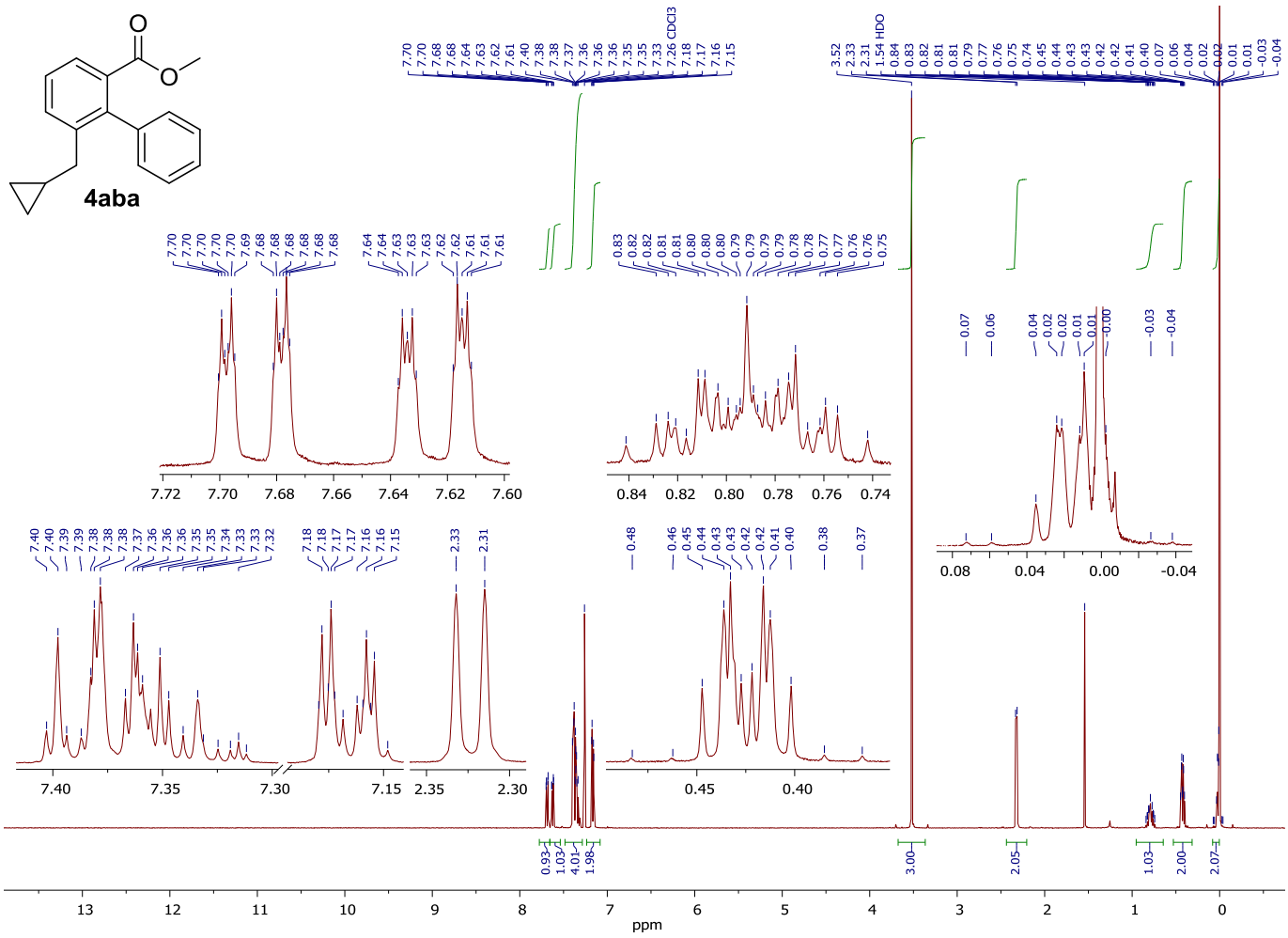
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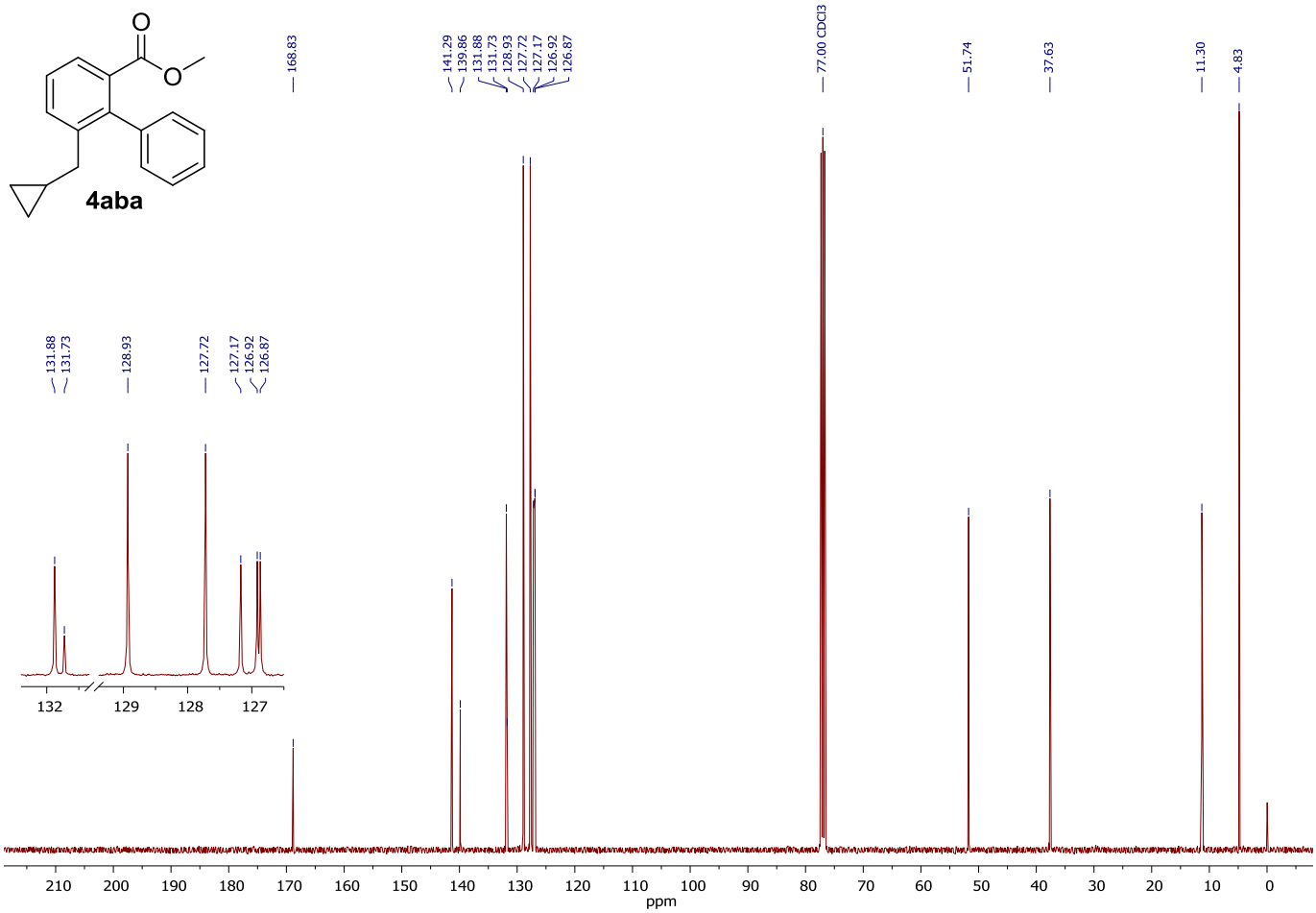
CDCl3
HDO
ppm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127.17
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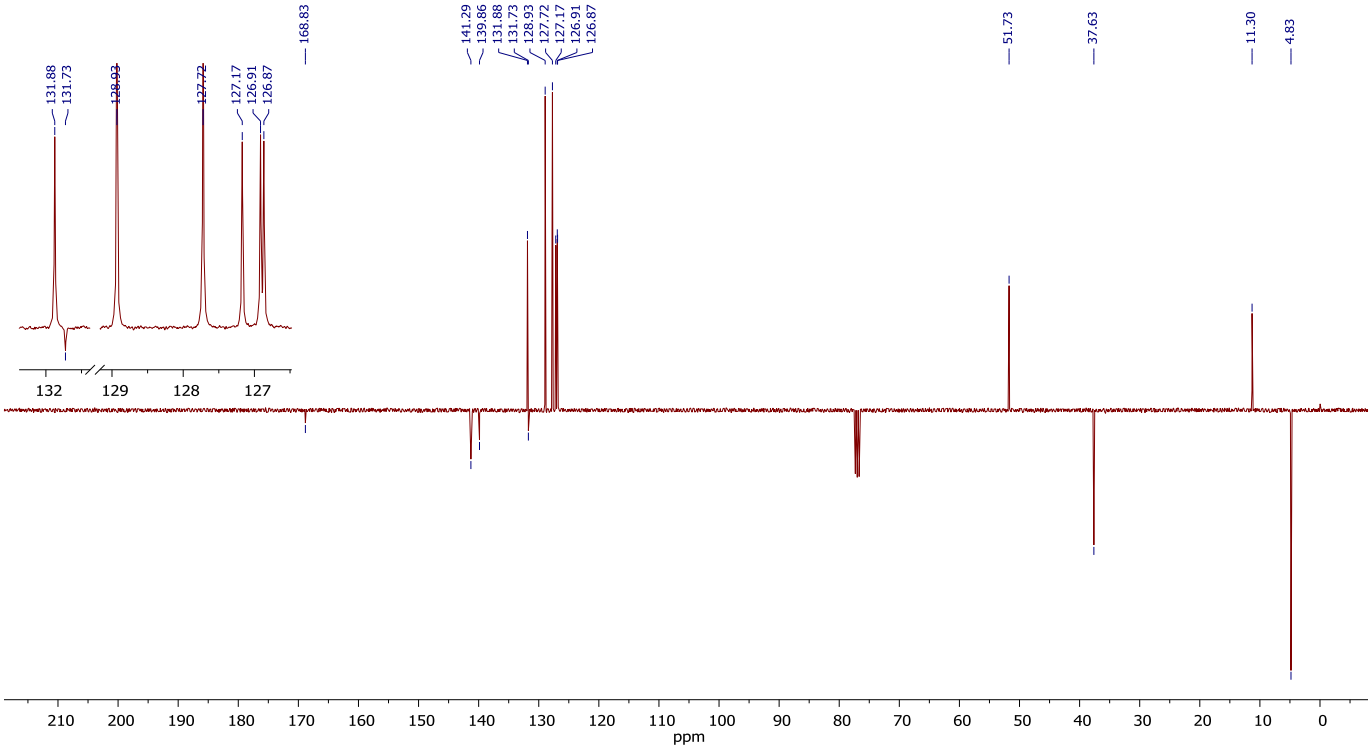
11.30
4.83
ppm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127.17
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11.30
4.83
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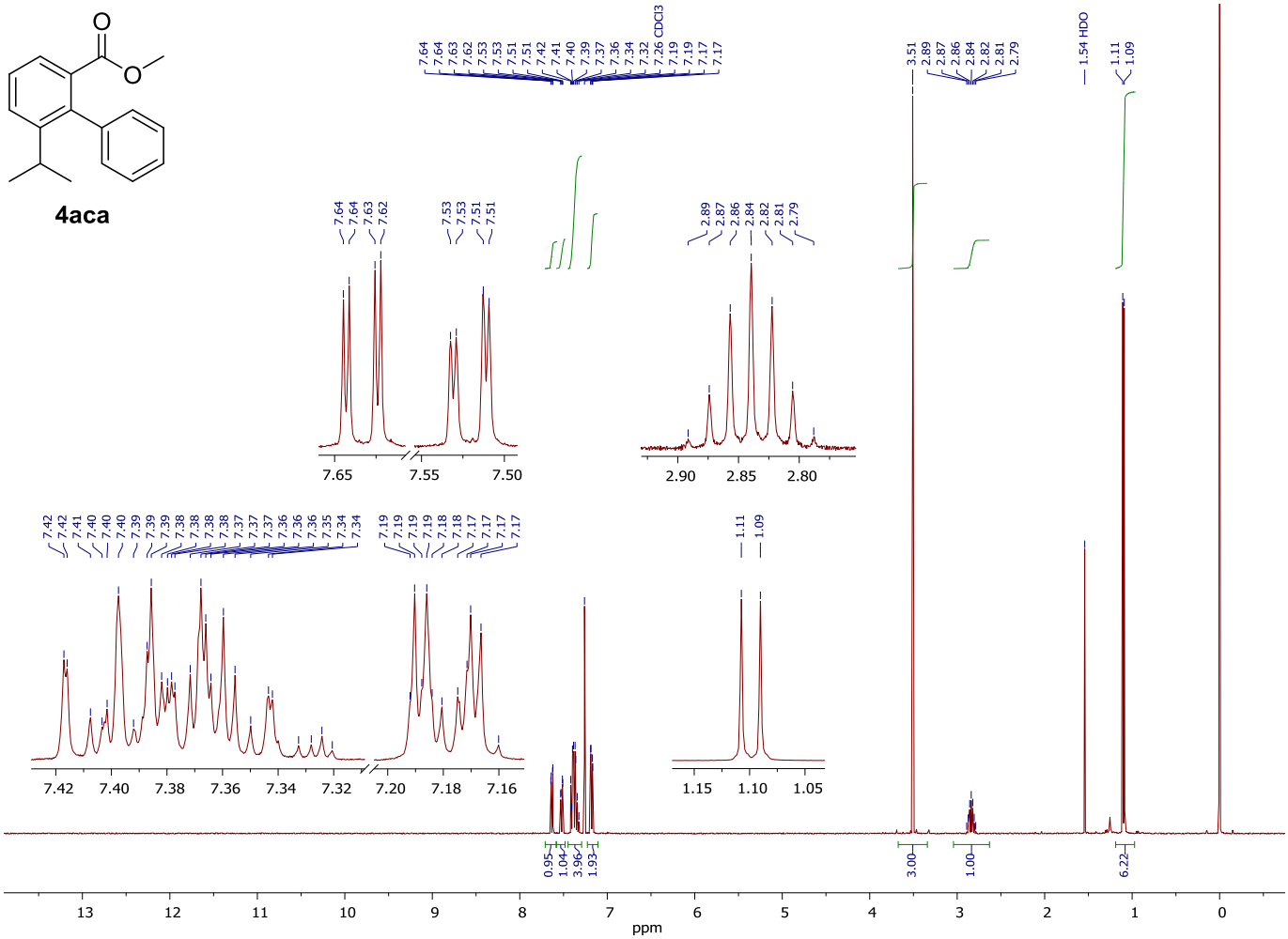
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CDCl3
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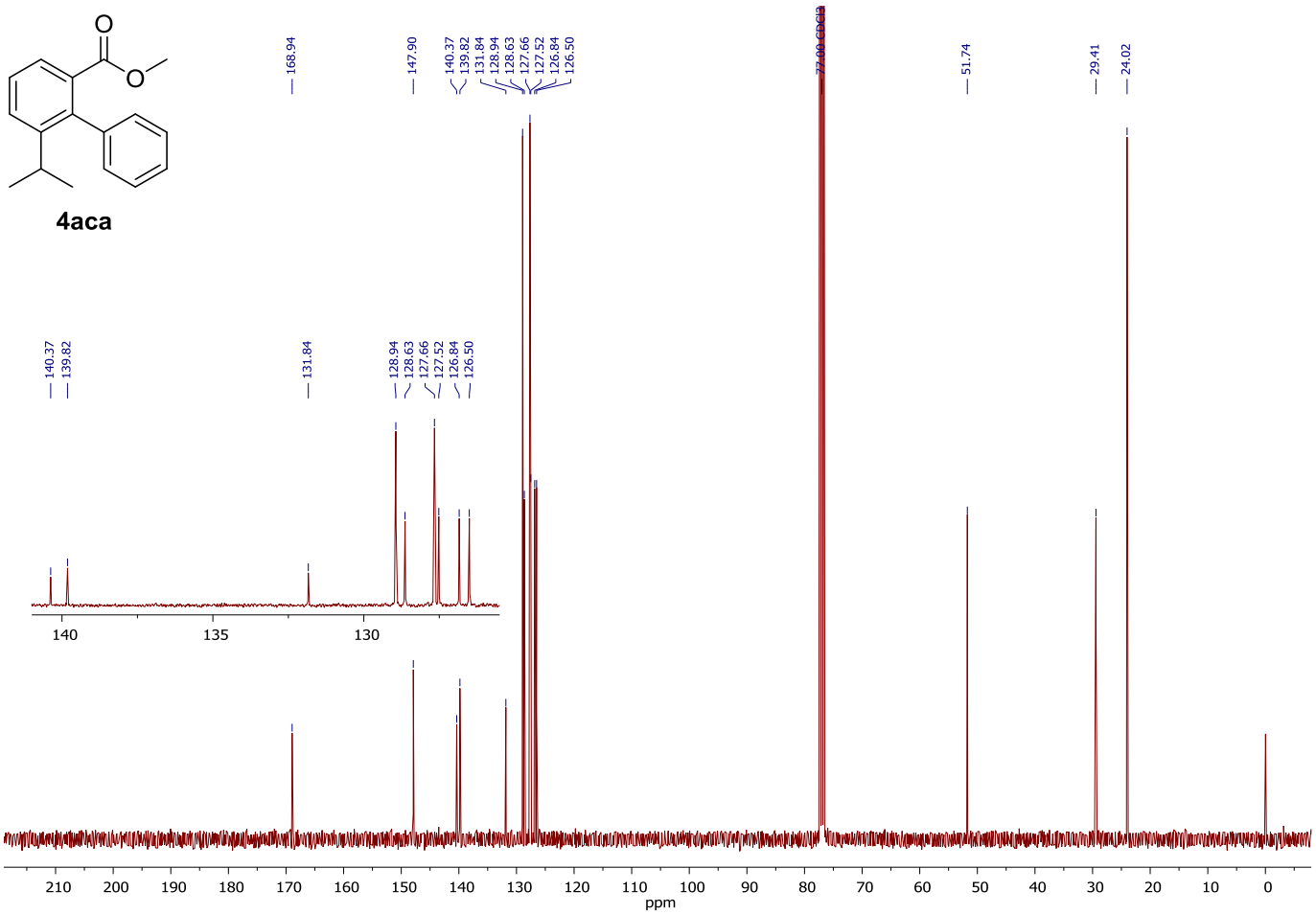
ppm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29.41
24.02
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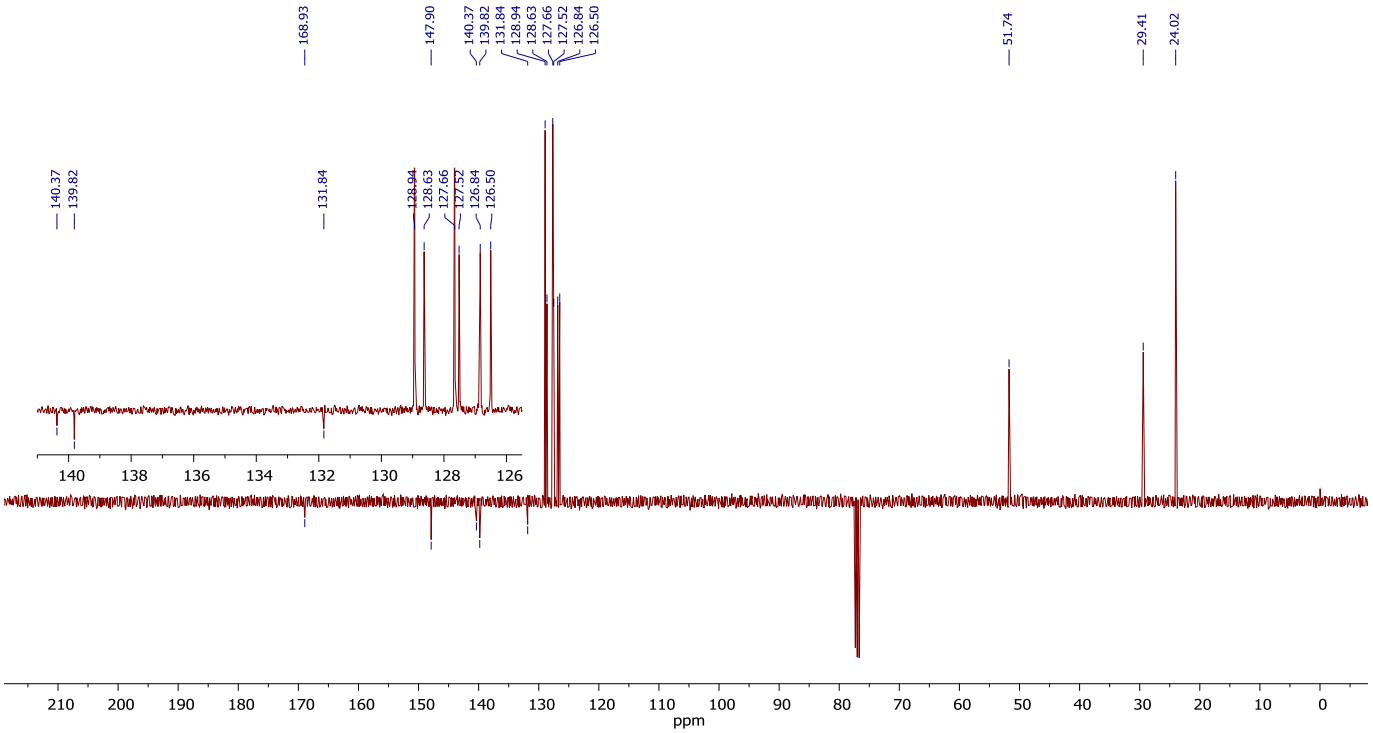
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126.50
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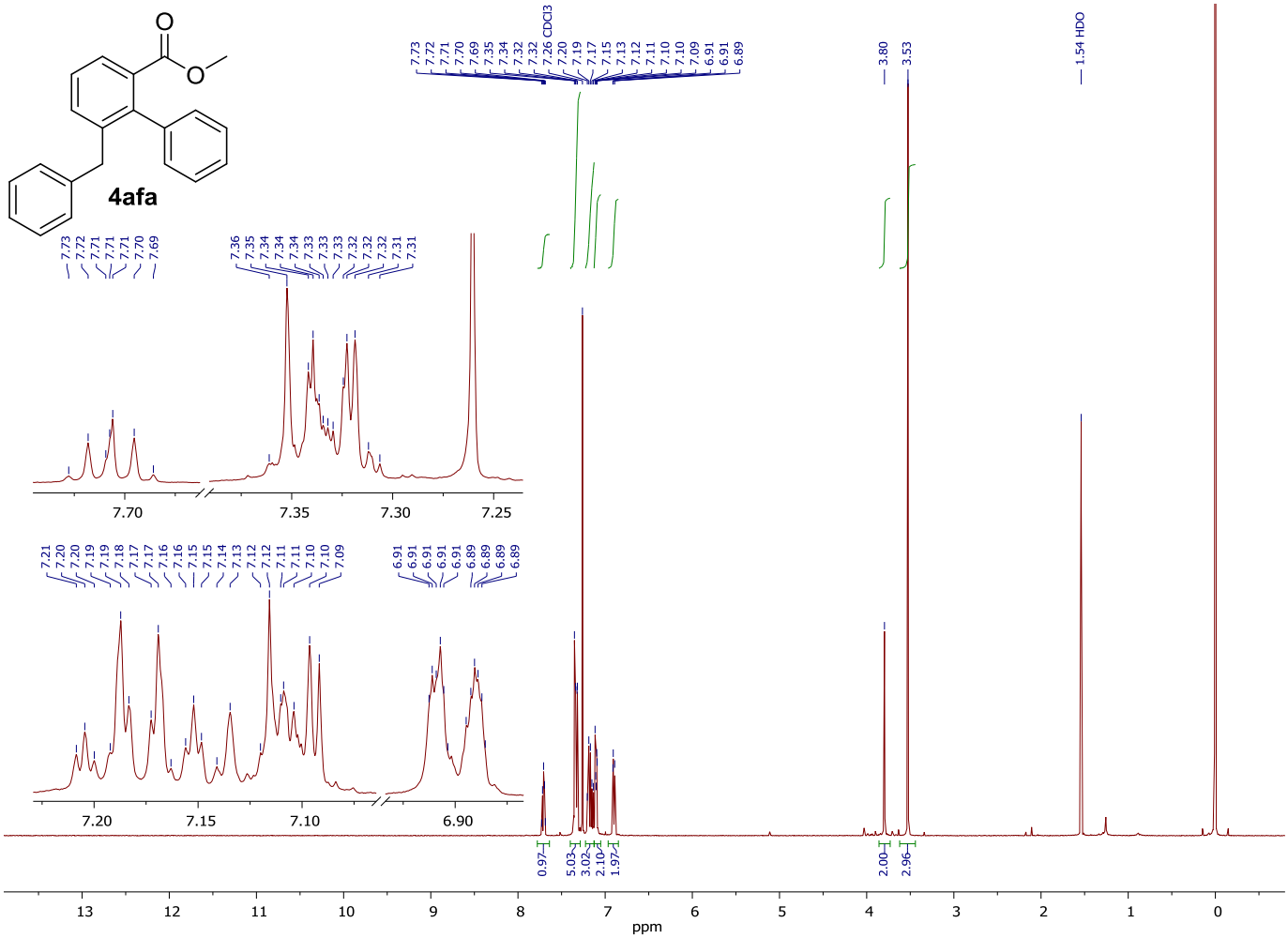
24.02
ppm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7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.26 CDCl3
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7.19
7.17
7.15
7.13
7.12
7.11
7.10
7.10
7.09
6.91
6.89
3.80
3.53
1.54 HDO
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.17
7.16
7.16
7.15
7.15
7.14
7.13
7.12
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7.11
7.10
7.10
7.09
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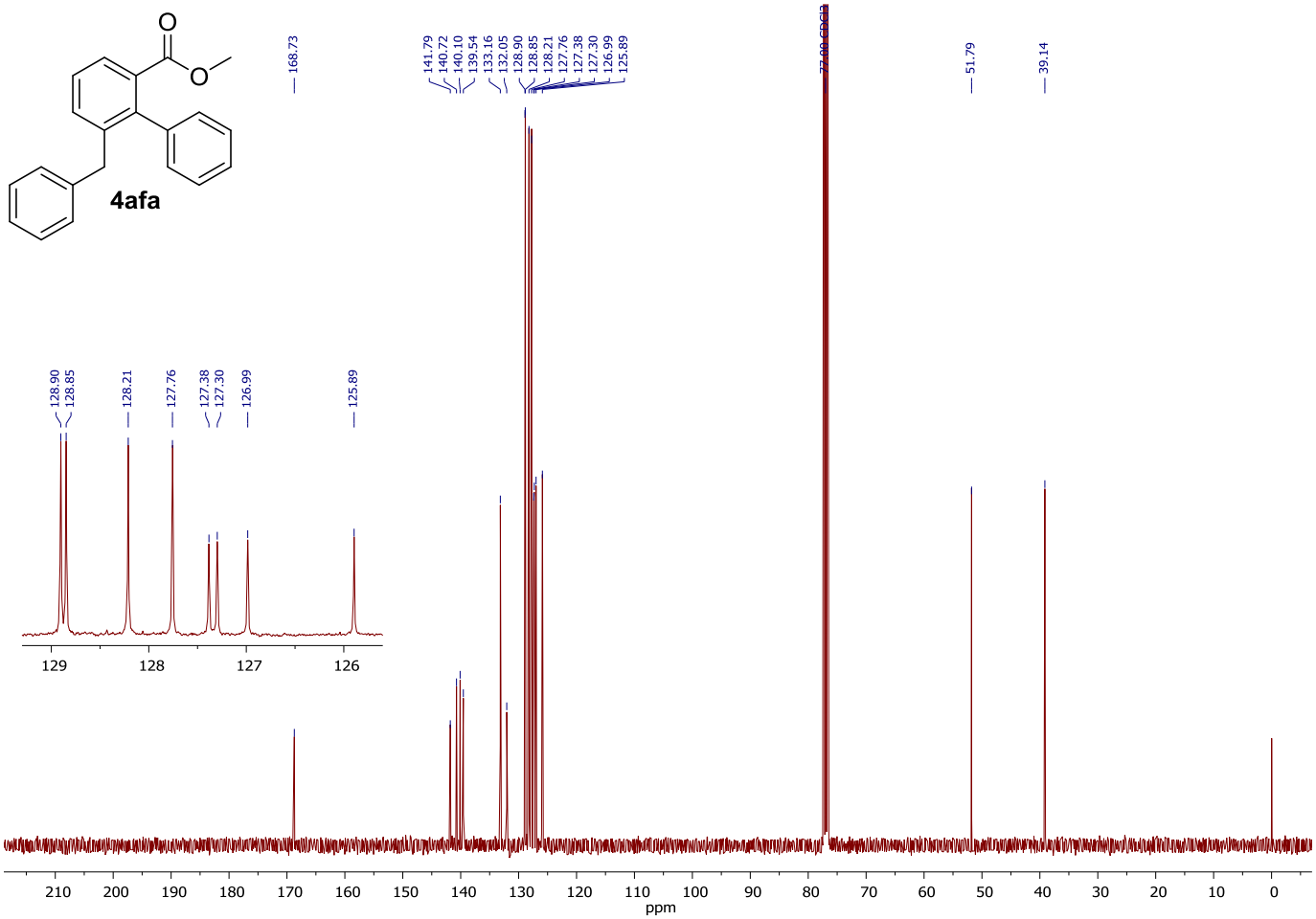
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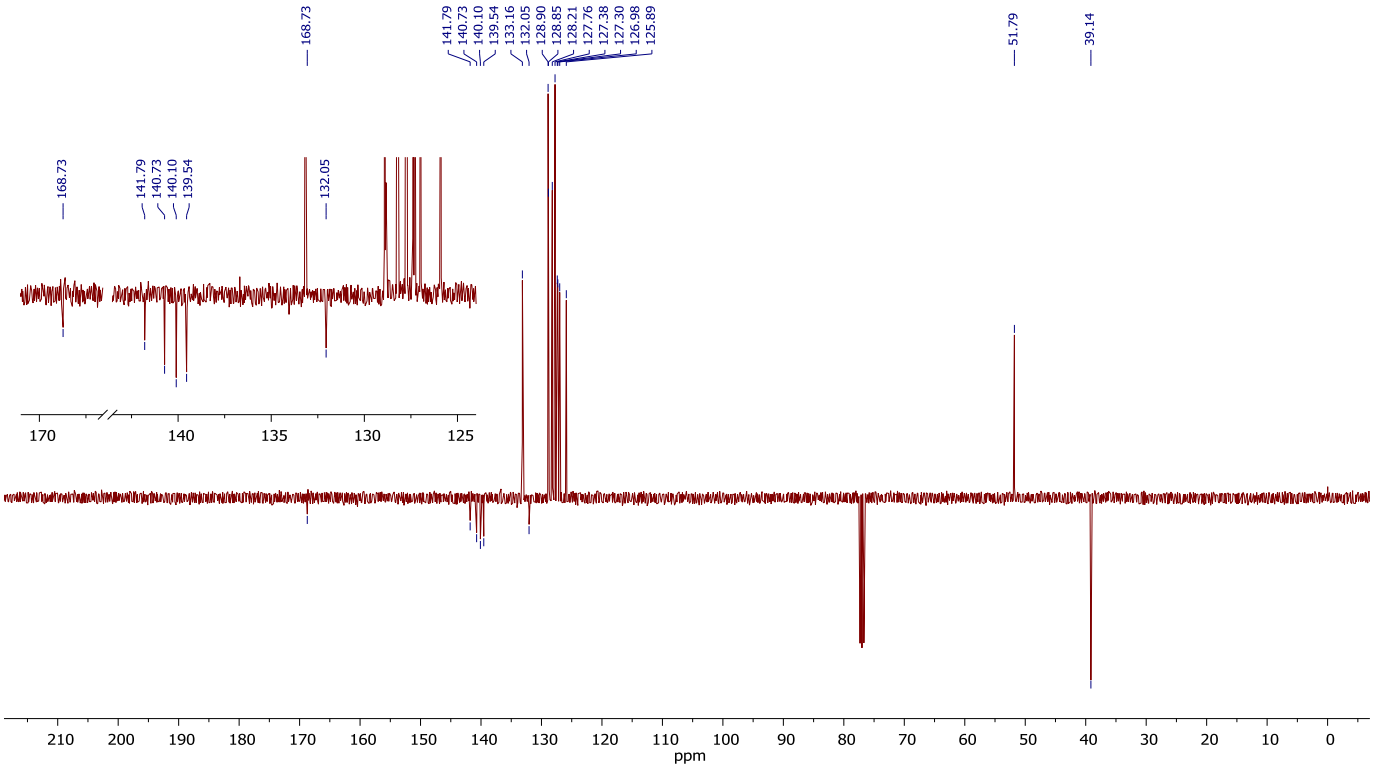
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125.89
51.79
39.14
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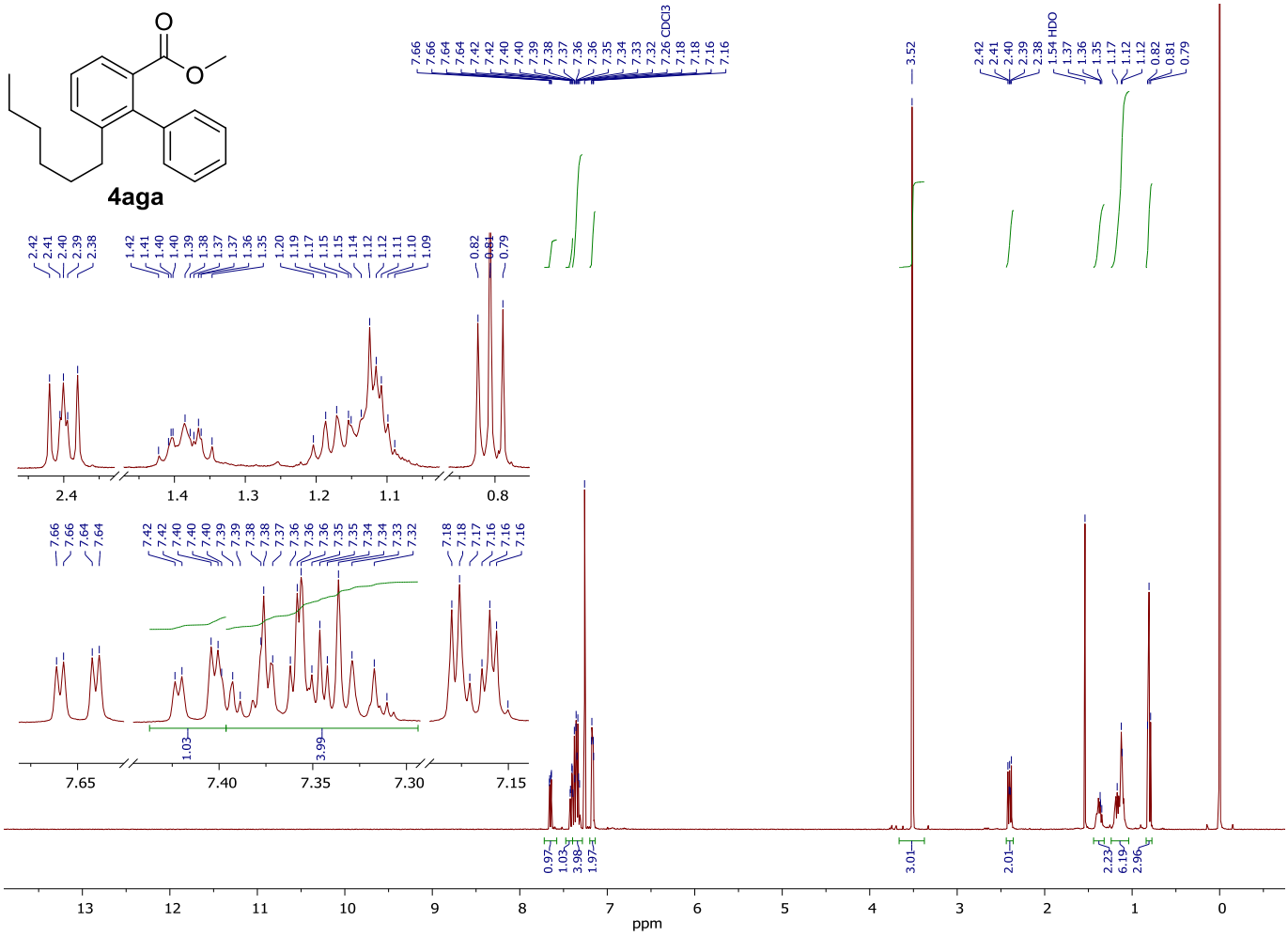
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3.52
2.42 2.41 2.40 2.39 2.38 1.54 HDO 1.37 1.36 1.35 1.17 1.12 1.12 0.82 0.81 0.79
2.42 2.41 2.40 2.39 2.38 1.42 1.41 1.40 1.40 1.39 1.38 1.37 1.37 1.36 1.35 1.20 1.19 1.17 1.15 1.15 1.14 1.12 1.12 1.11 1.10 1.09 0.82 0.81 0.79
2.4 1.4 1.3 1.2 1.1 0.8
7.66 7.66 7.64 7.64 7.42 7.42 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.18 7.18 7.17 7.16 7.16 7.16
1.03 3.99
7.65 7.40 7.35 7.30 7.15
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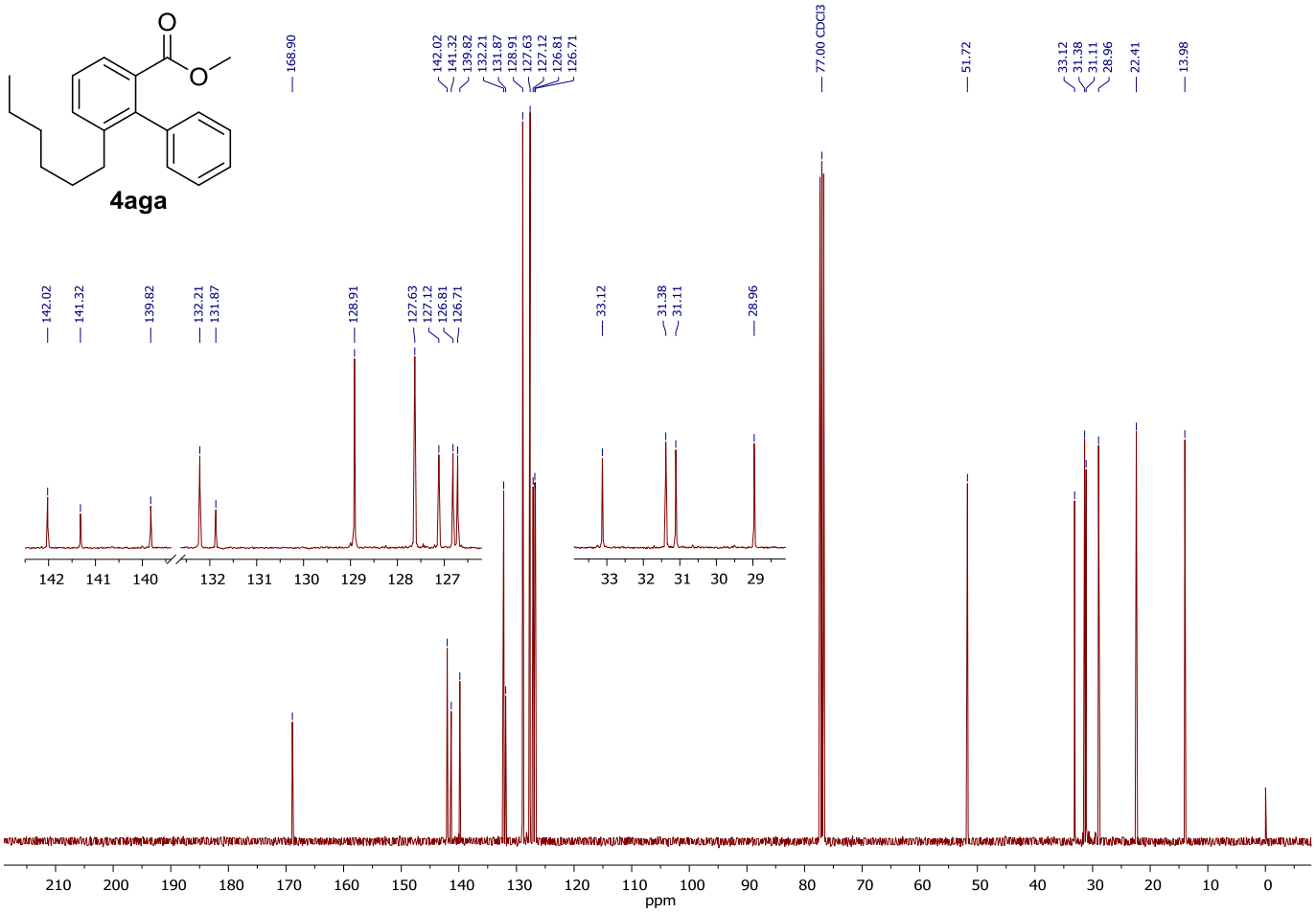
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77.00 CDCl3
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33.12
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31.11
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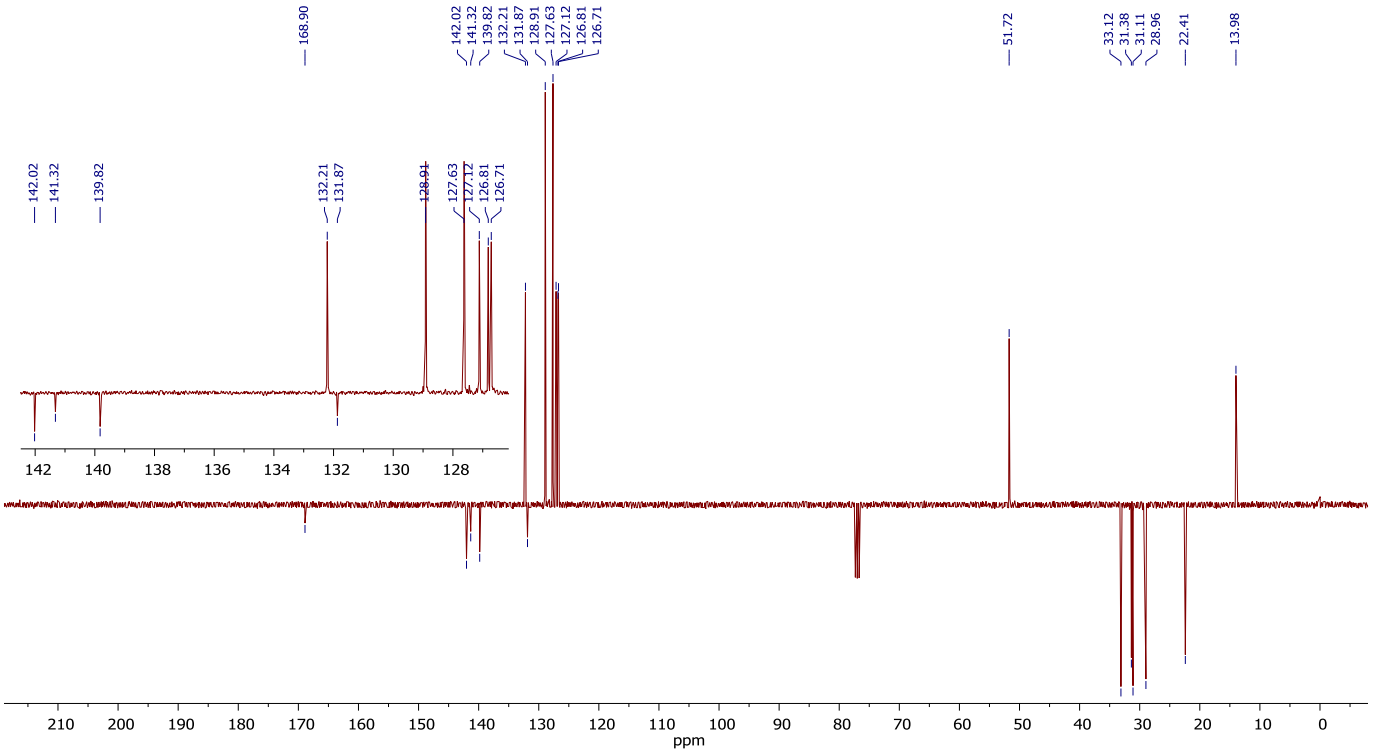
22.41
13.98
ppm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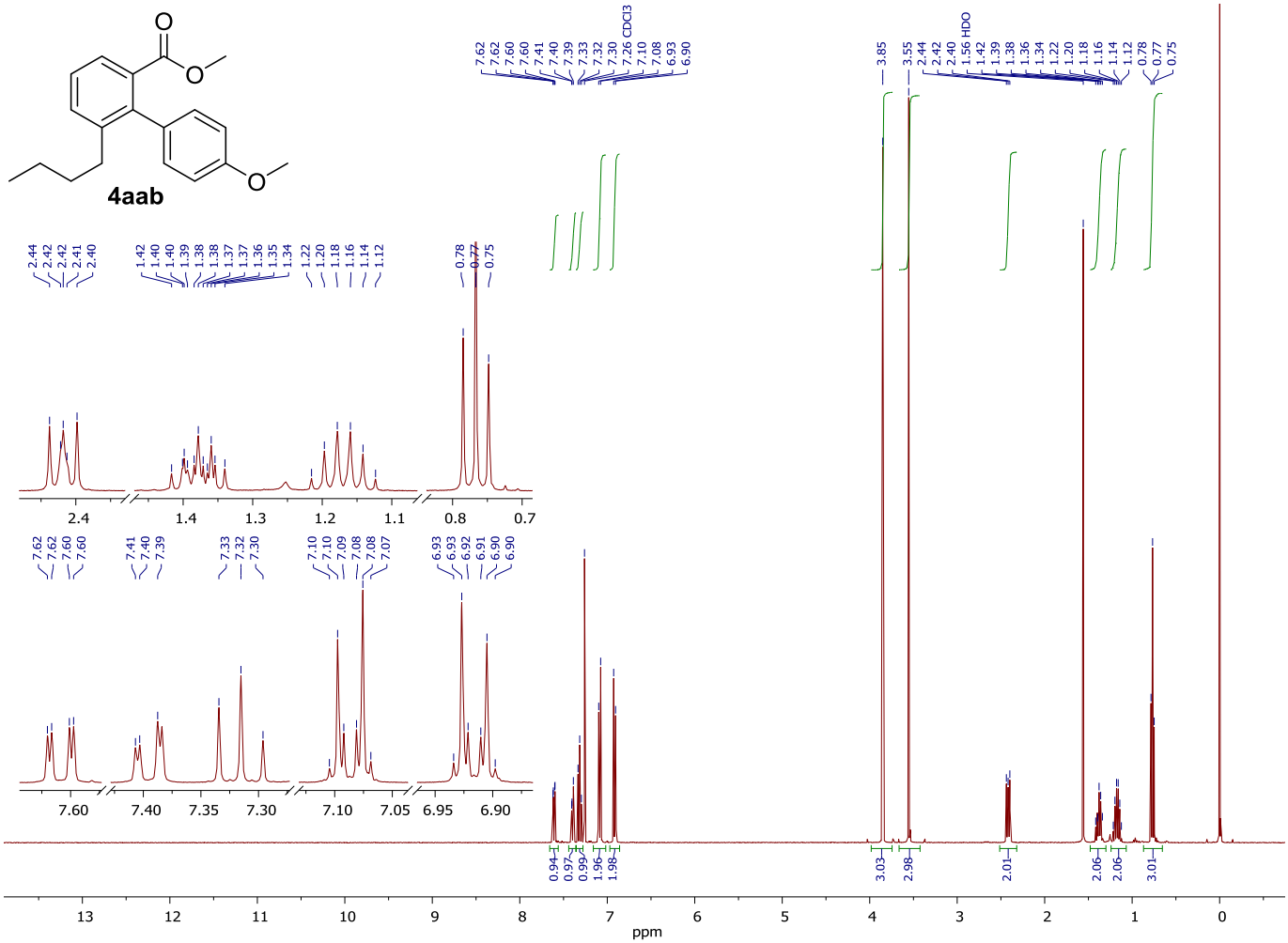
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3.85
3.55
2.44 2.42 2.42 2.40 1.56 HDO 1.42 1.39 1.38 1.36 1.34 1.22 1.20 1.18 1.16 1.14 1.12
0.78 0.77 0.75
2.44 2.42 2.42 2.41 2.40
1.42 1.40 1.40 1.39 1.38 1.38 1.37 1.37 1.36 1.35 1.34
1.22 1.20 1.18 1.16 1.14 1.12
0.78 0.77 0.75
7.62 7.62 7.60 7.60
7.41 7.40 7.39
7.33 7.32 7.30
7.10 7.10 7.09 7.08 7.08 7.07
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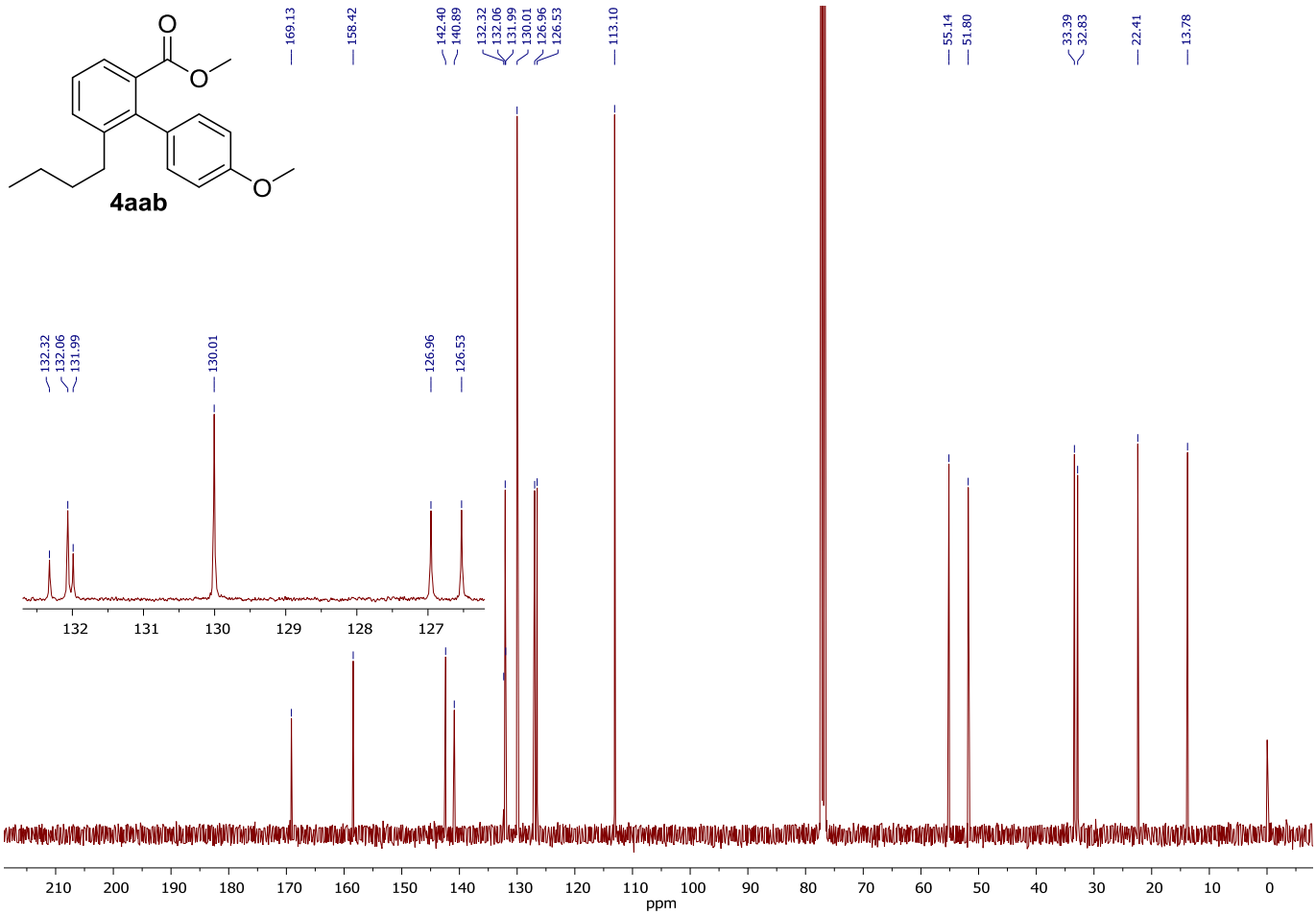
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132.32
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22.41
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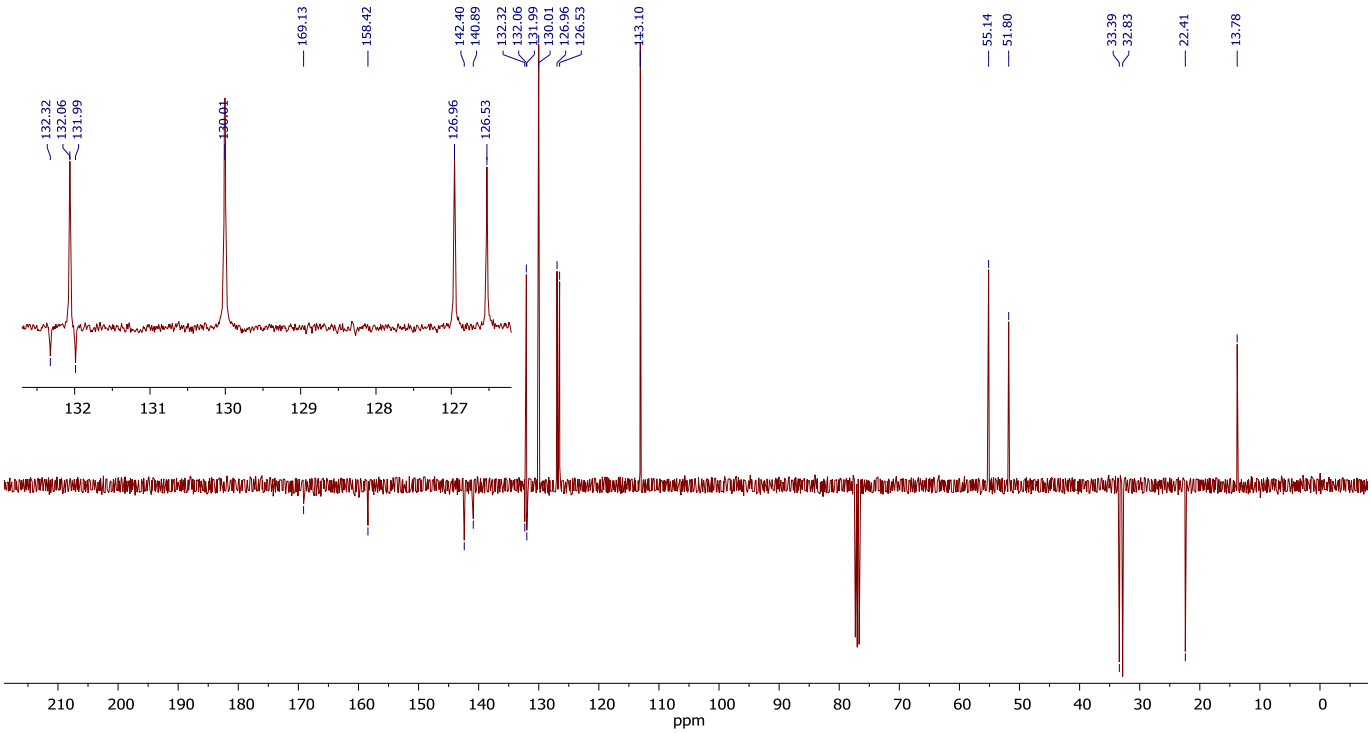
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22.41
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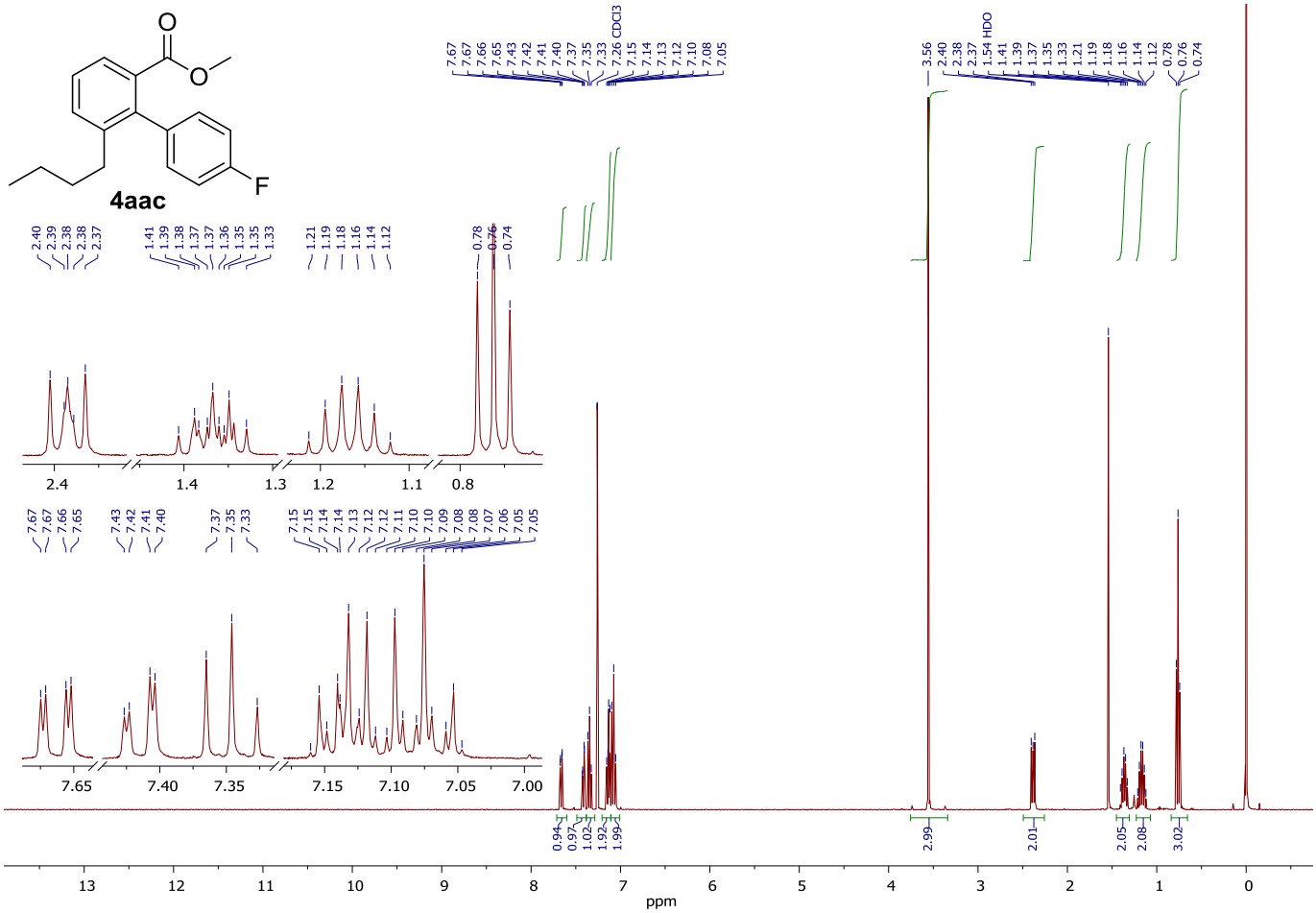
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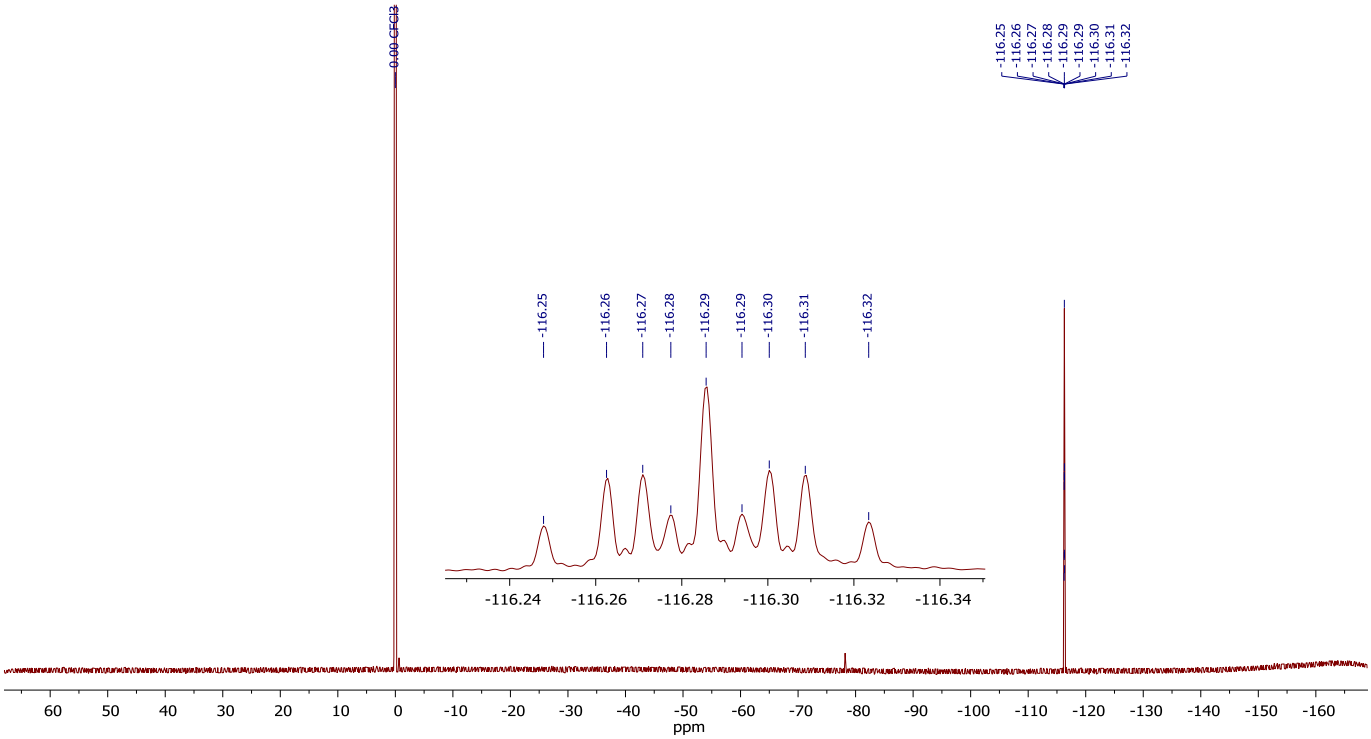
1.54 HDO
ppm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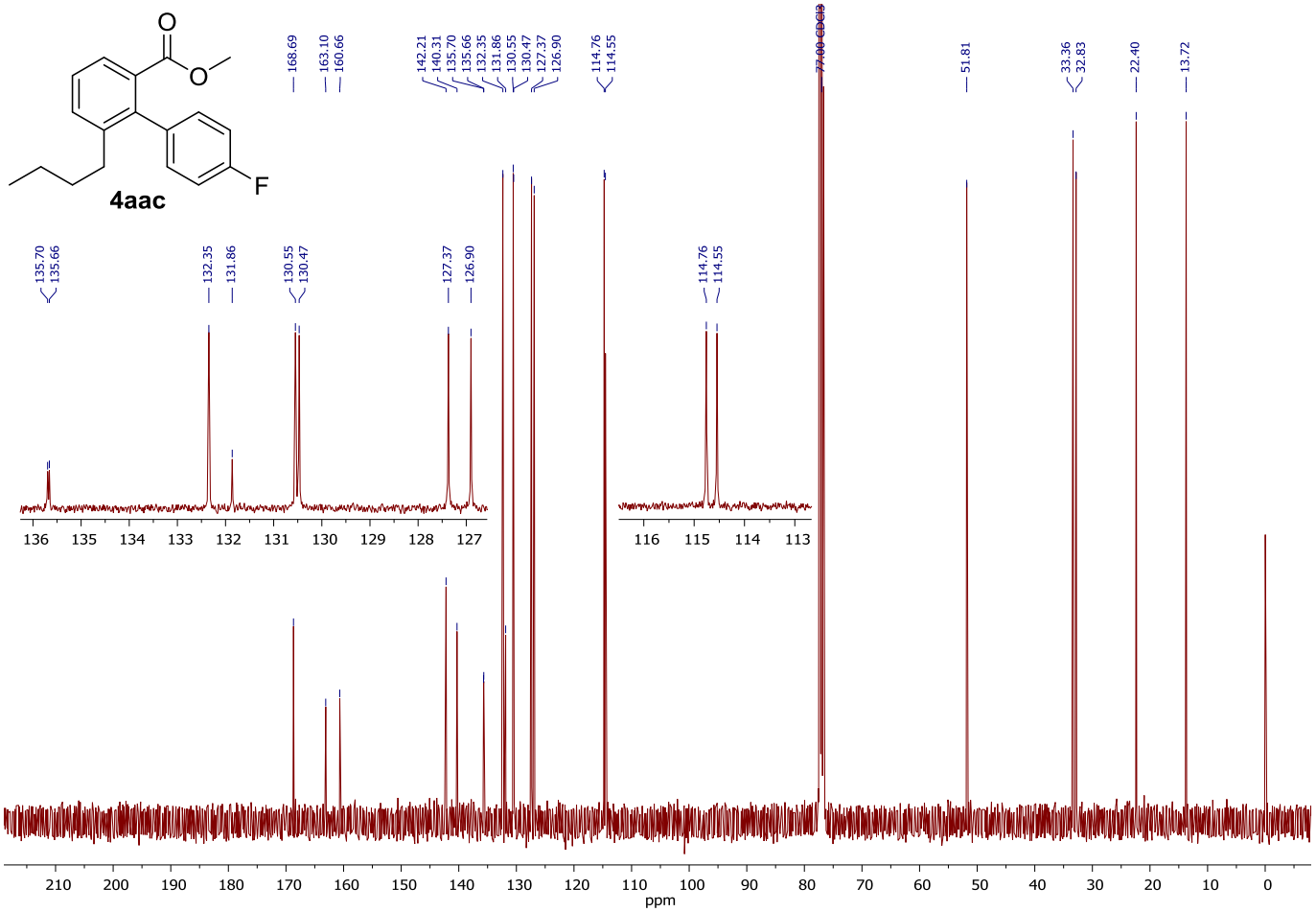
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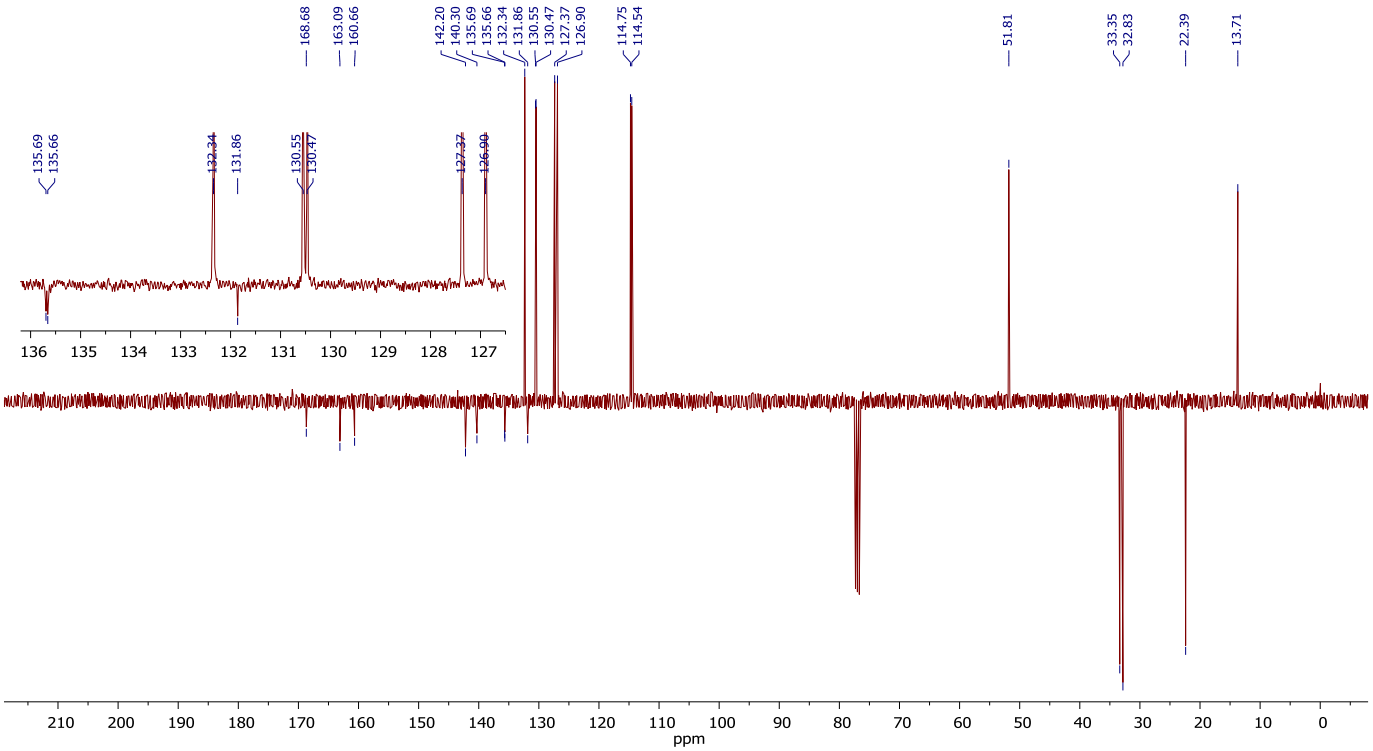
ppm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33.35
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22.39
13.71
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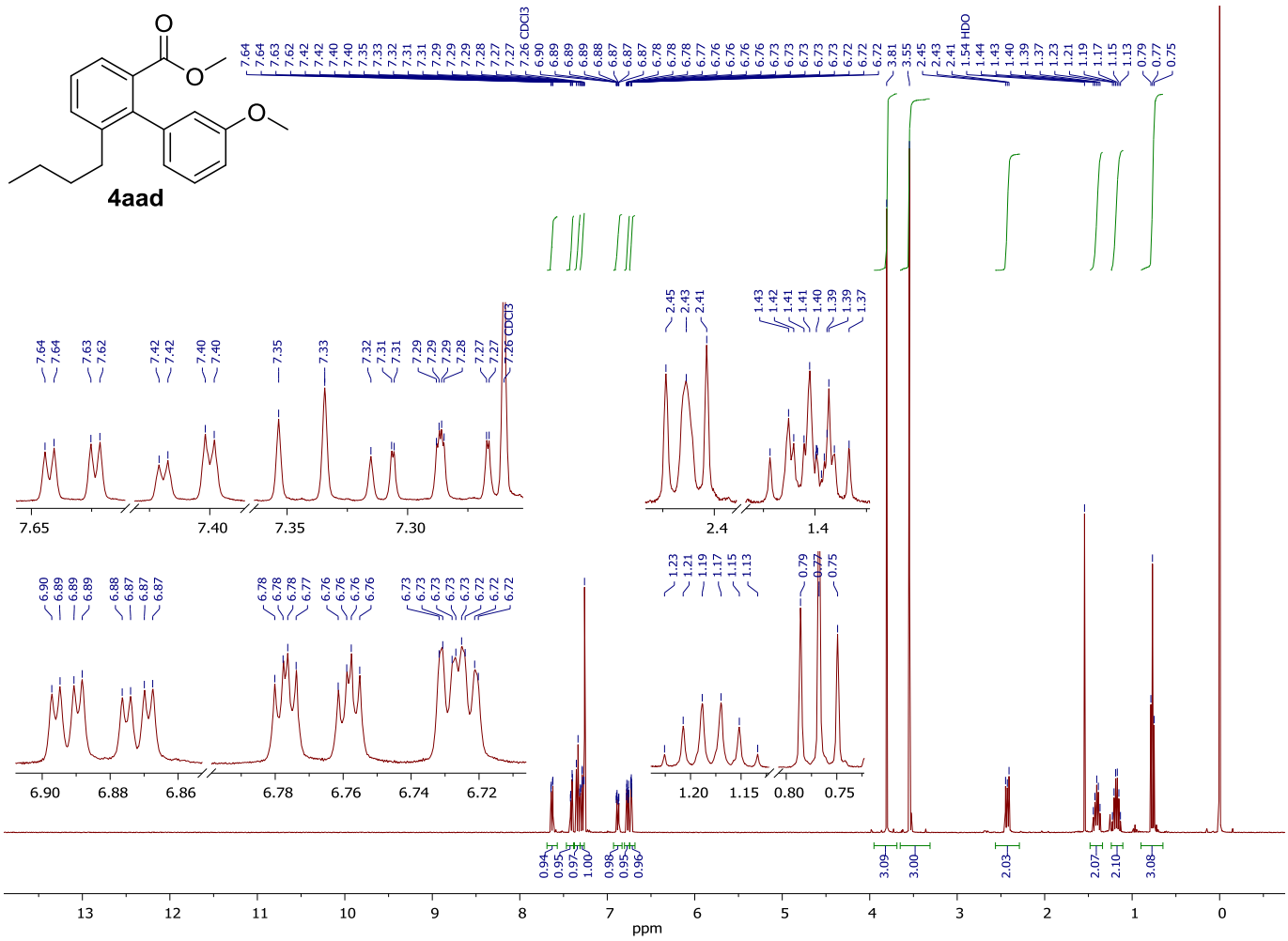
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1.54 HDO
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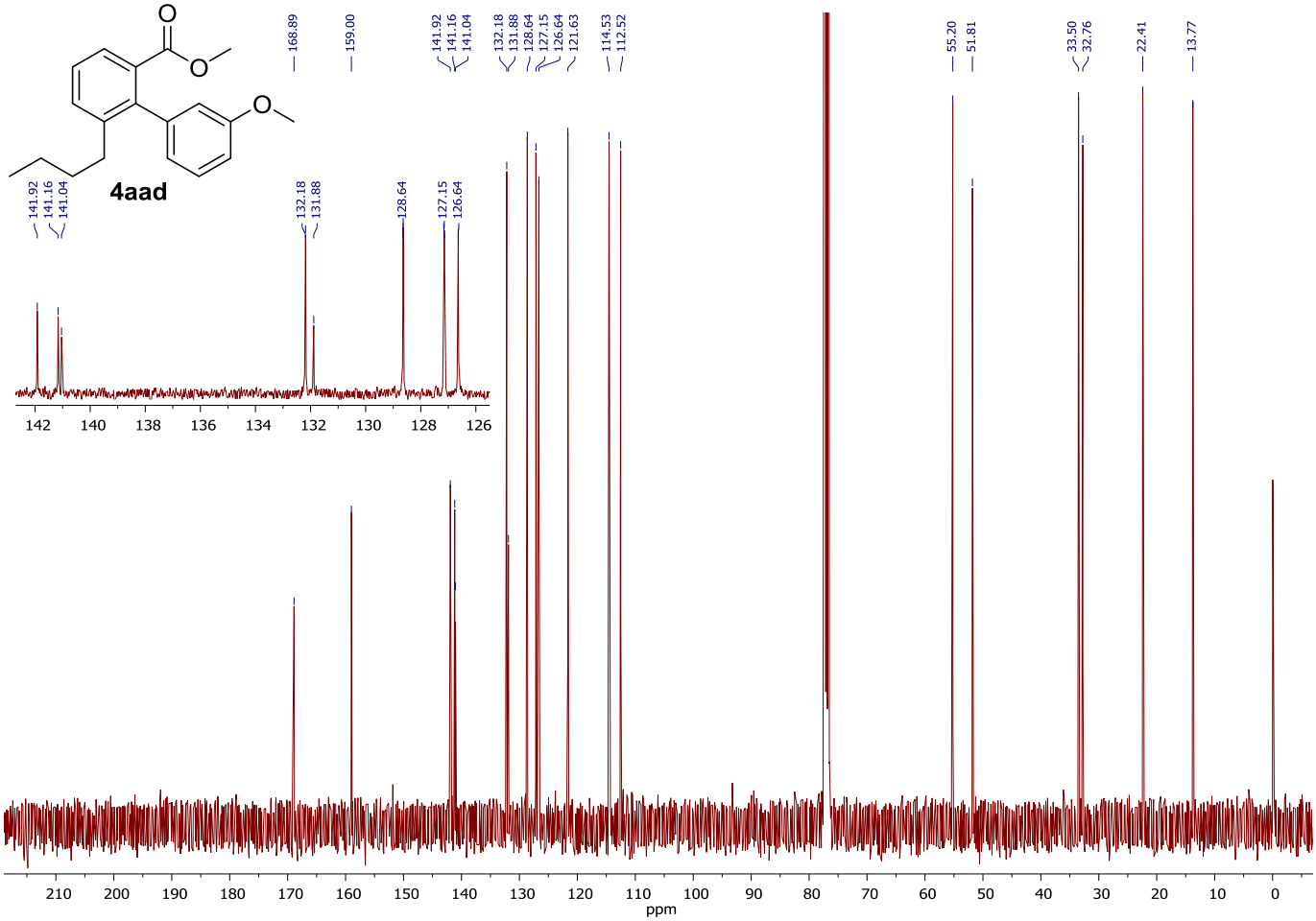
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141.92
141.16
141.04
132.18
131.88
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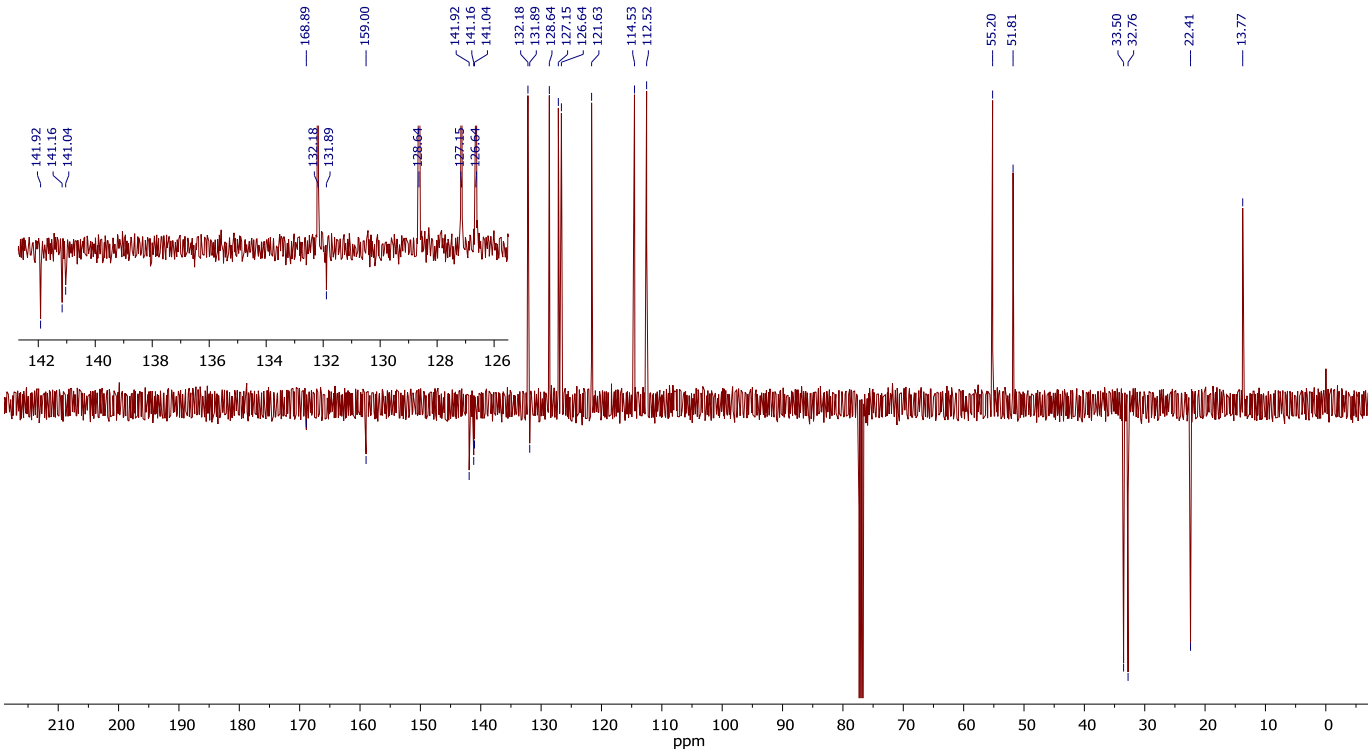
121.63
114.53
112.52
55.20
51.81
33.50
32.76
22.41
13.77
ppm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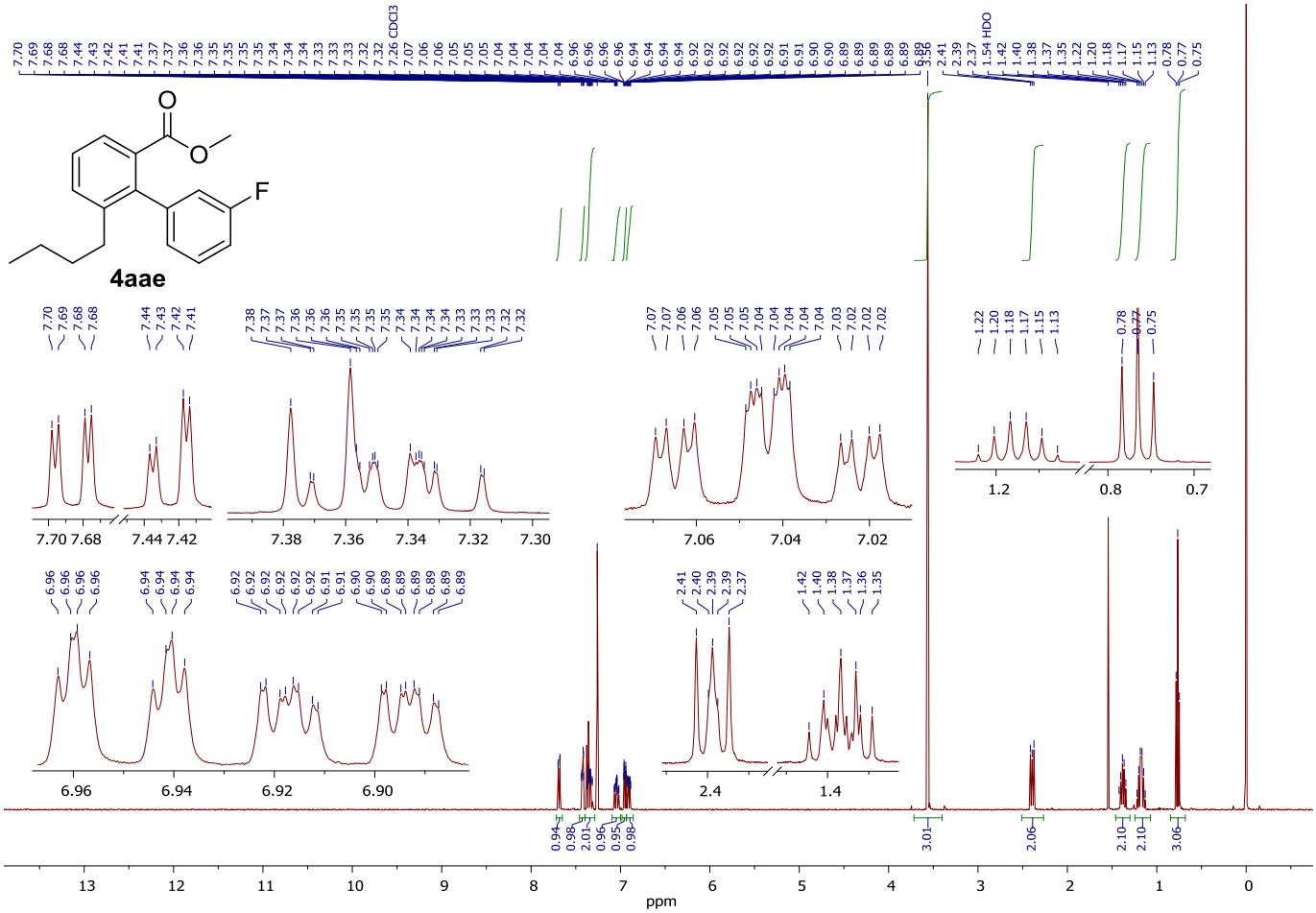
51.81
33.50
32.76
22.41
13.77
ppm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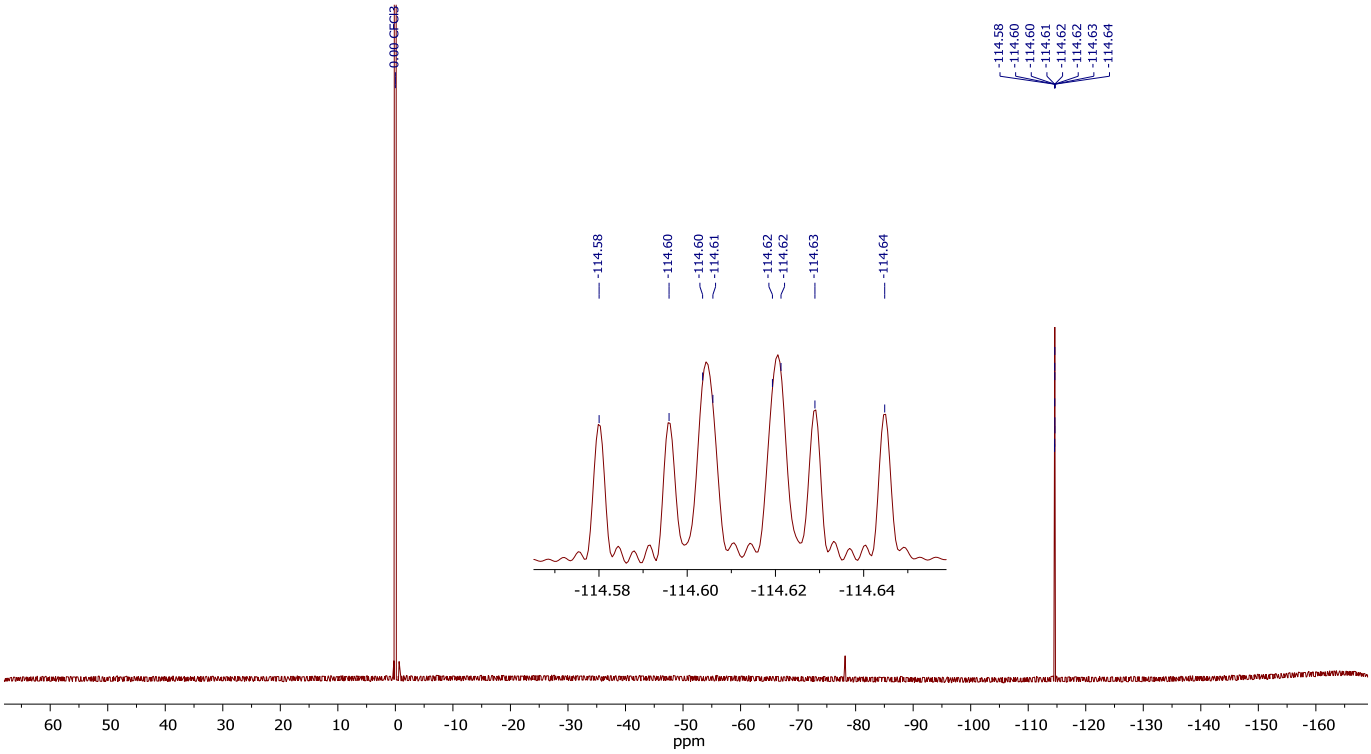
F
ppm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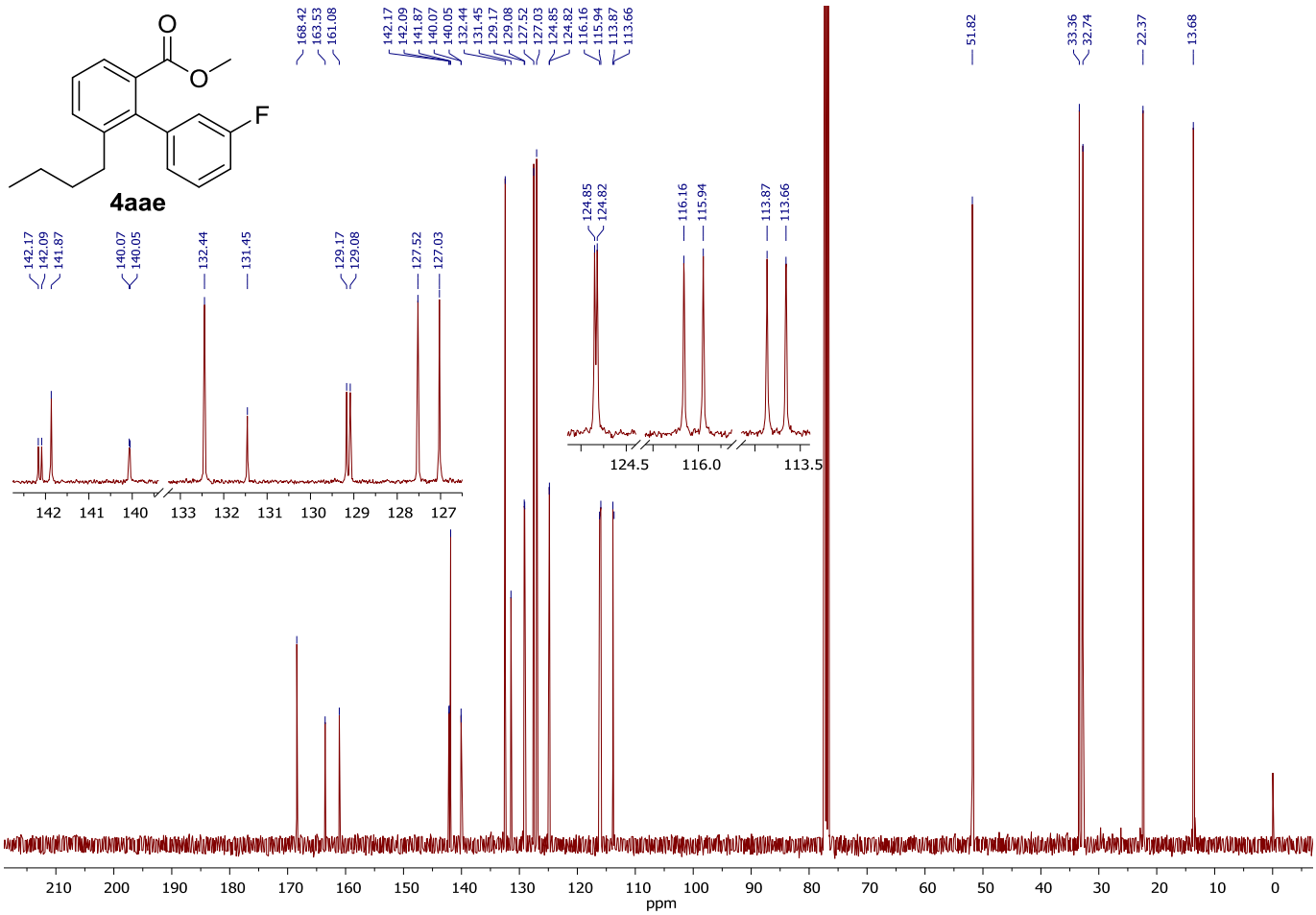
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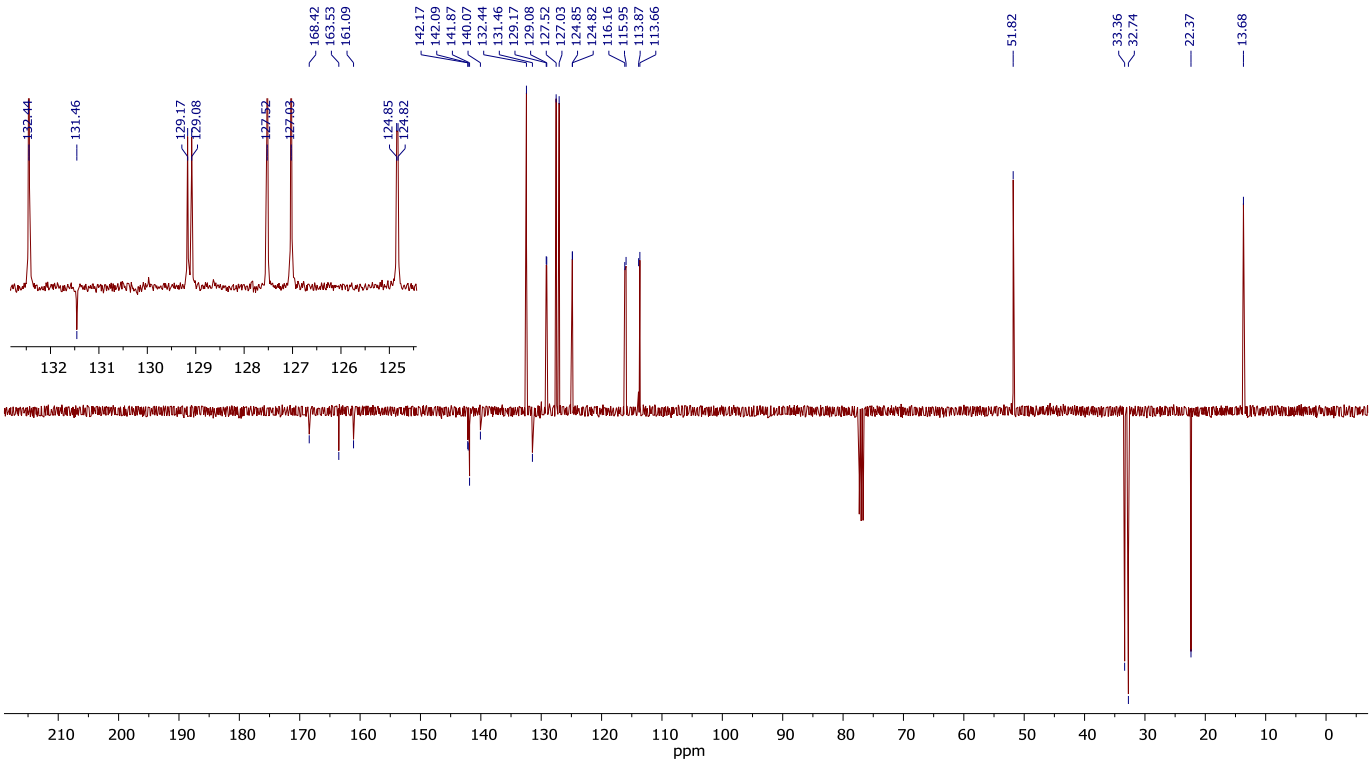
142.09
141.87
140.07
140.05
132.44
131.45
129.17
129.08
127.52
127.03
124.85
124.82
116.16
115.94
113.87
113.66
51.82
33.36
32.74
22.37
13.68
ppm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142.09
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140.07
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129.17
129.08
127.52
127.03
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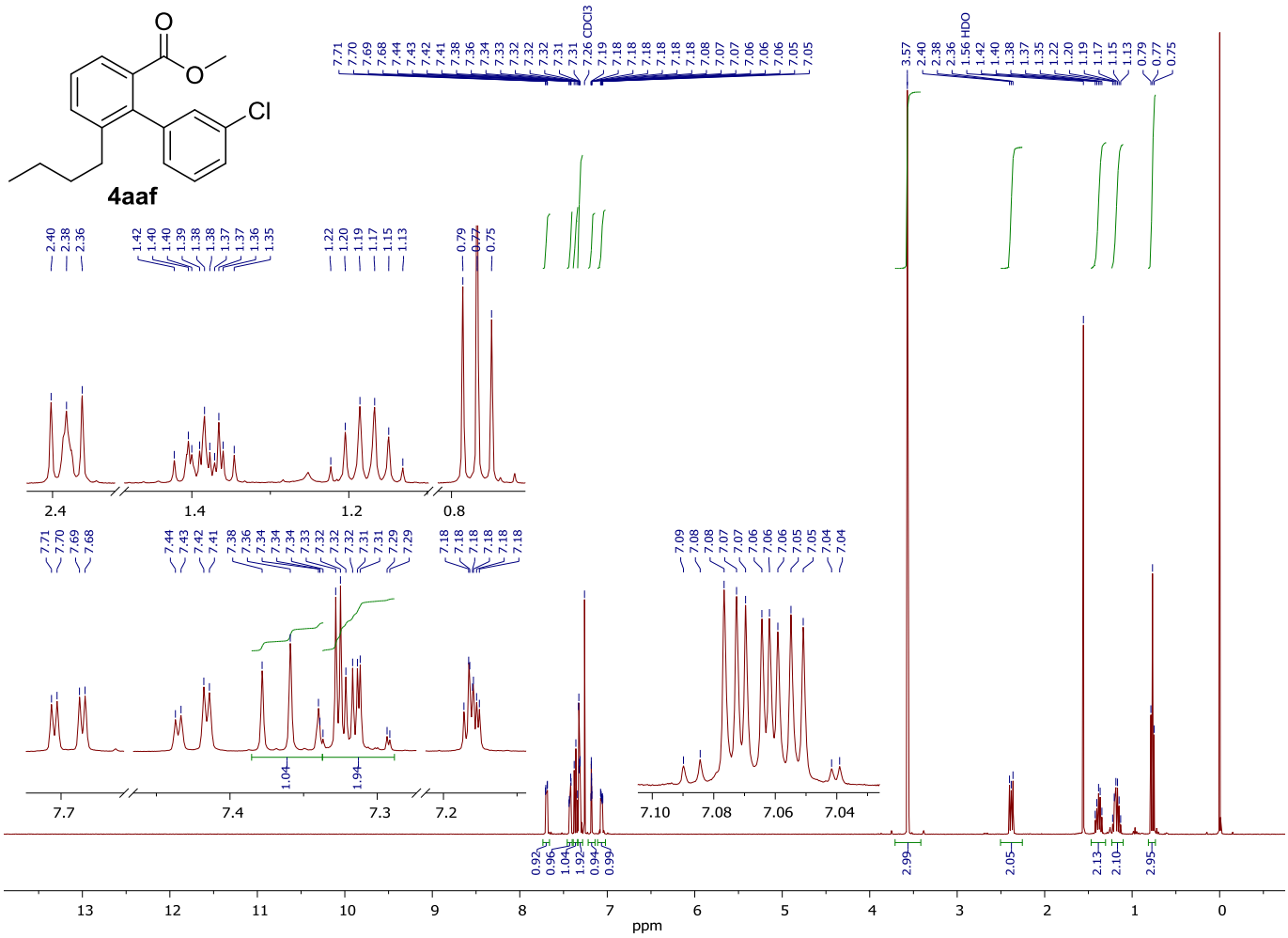
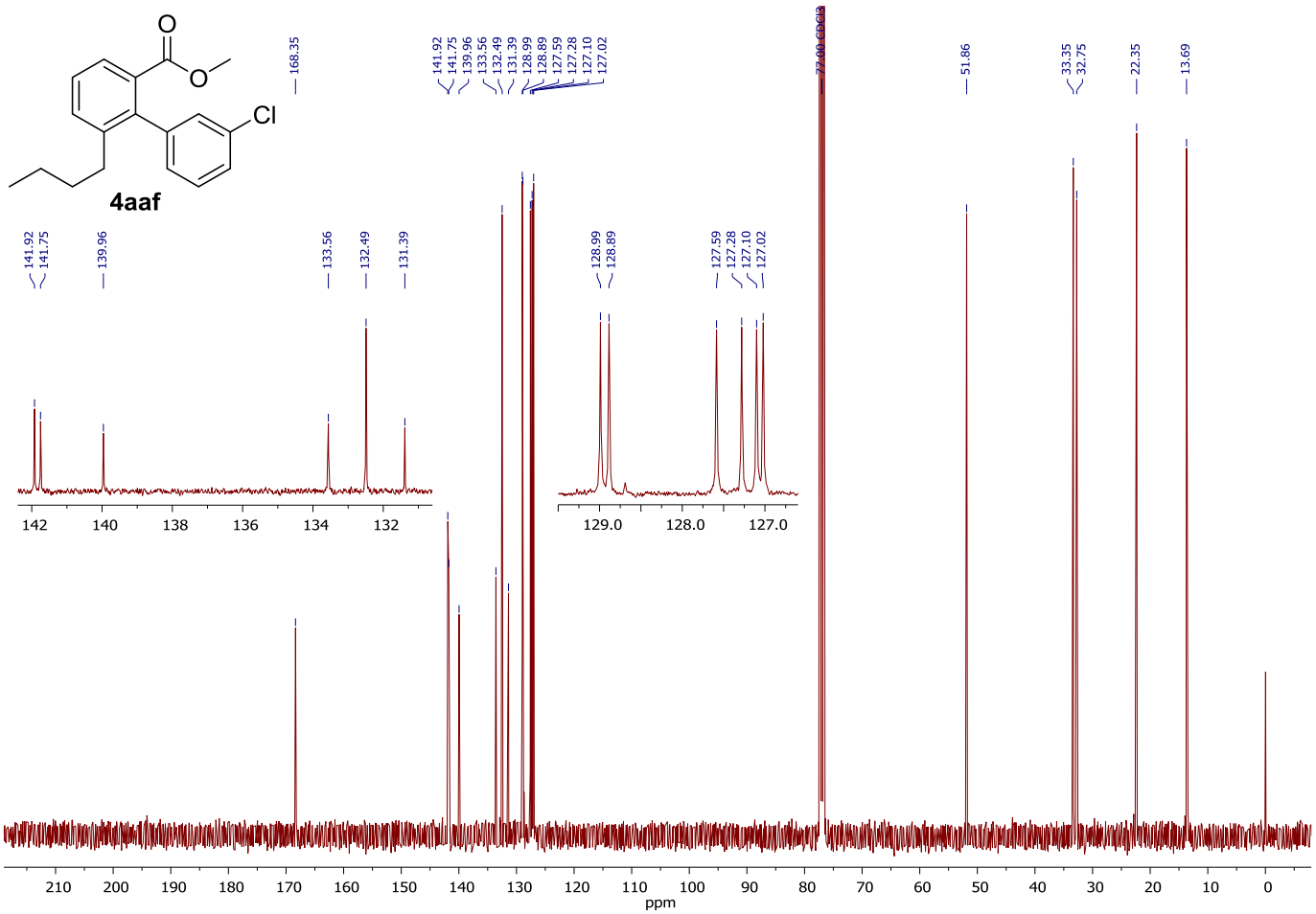
116.16
115.95
113.87
113.66
51.82
33.36
32.74
22.37
13.68
ppm


4aaf
7.26 CDCl3
1.56 HDO
ppm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139.96
133.56
132.49
131.39
128.99
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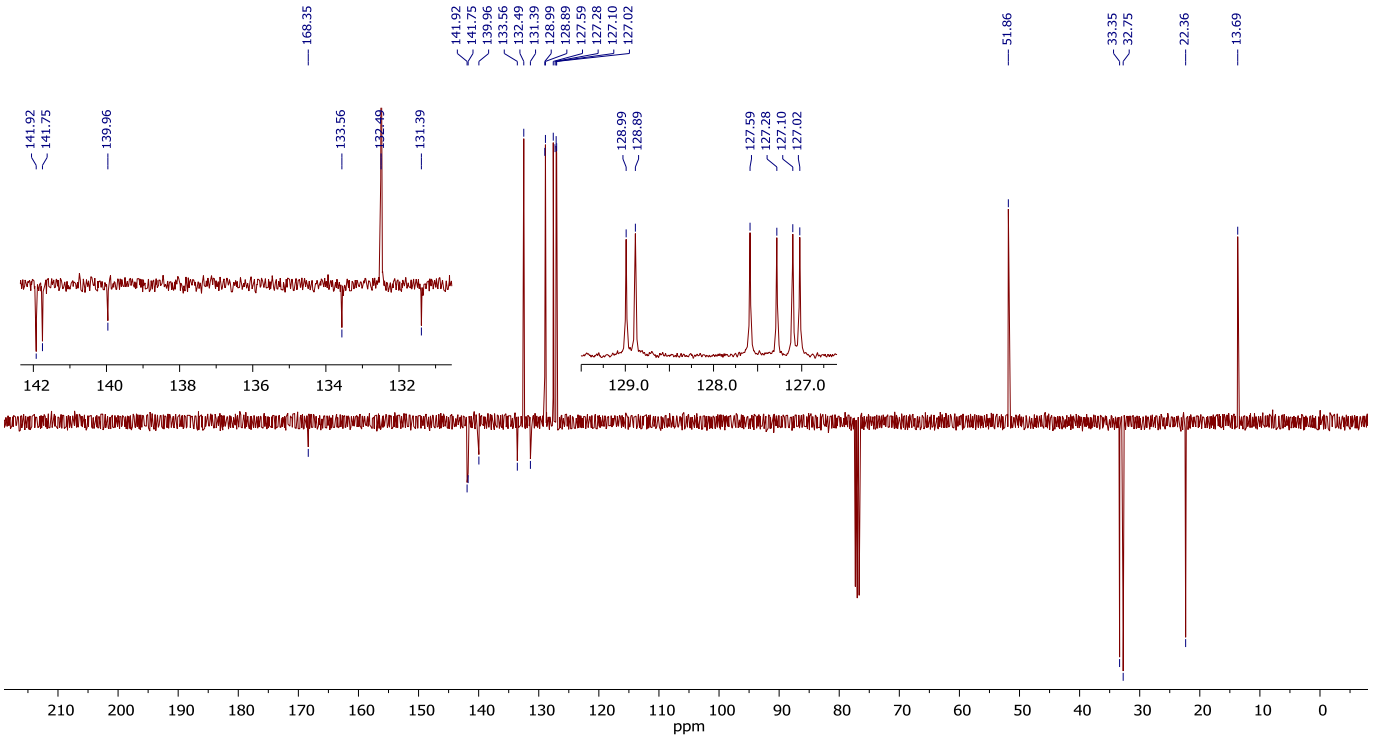
127.59
127.28
127.10
127.02
77.00 CDCl3
51.86
33.35
32.75
22.35
13.69
ppm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141.75
139.96
133.56
132.49
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127.59
127.28
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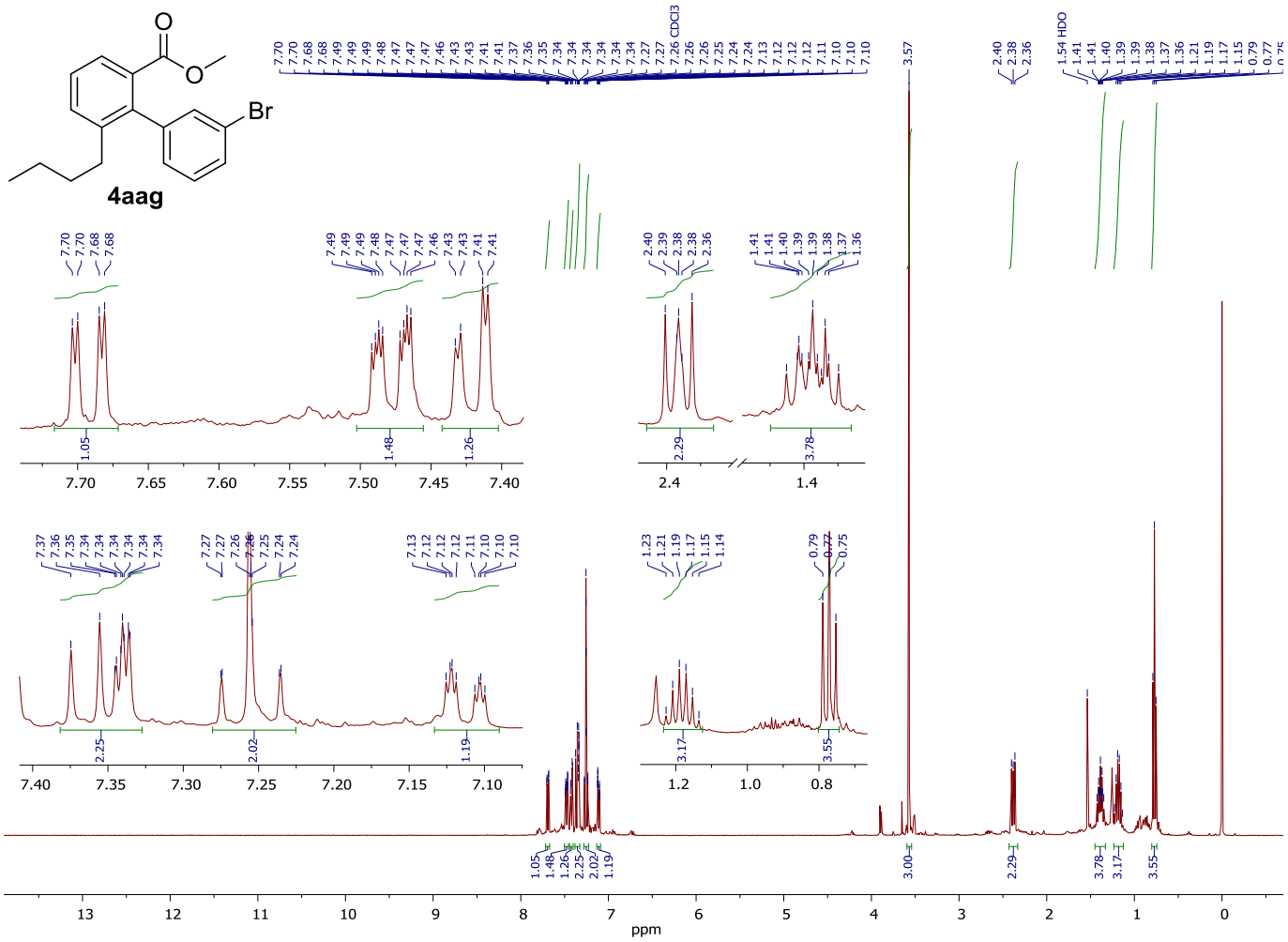
127.02
51.86
33.35
32.75
22.36
13.69
ppm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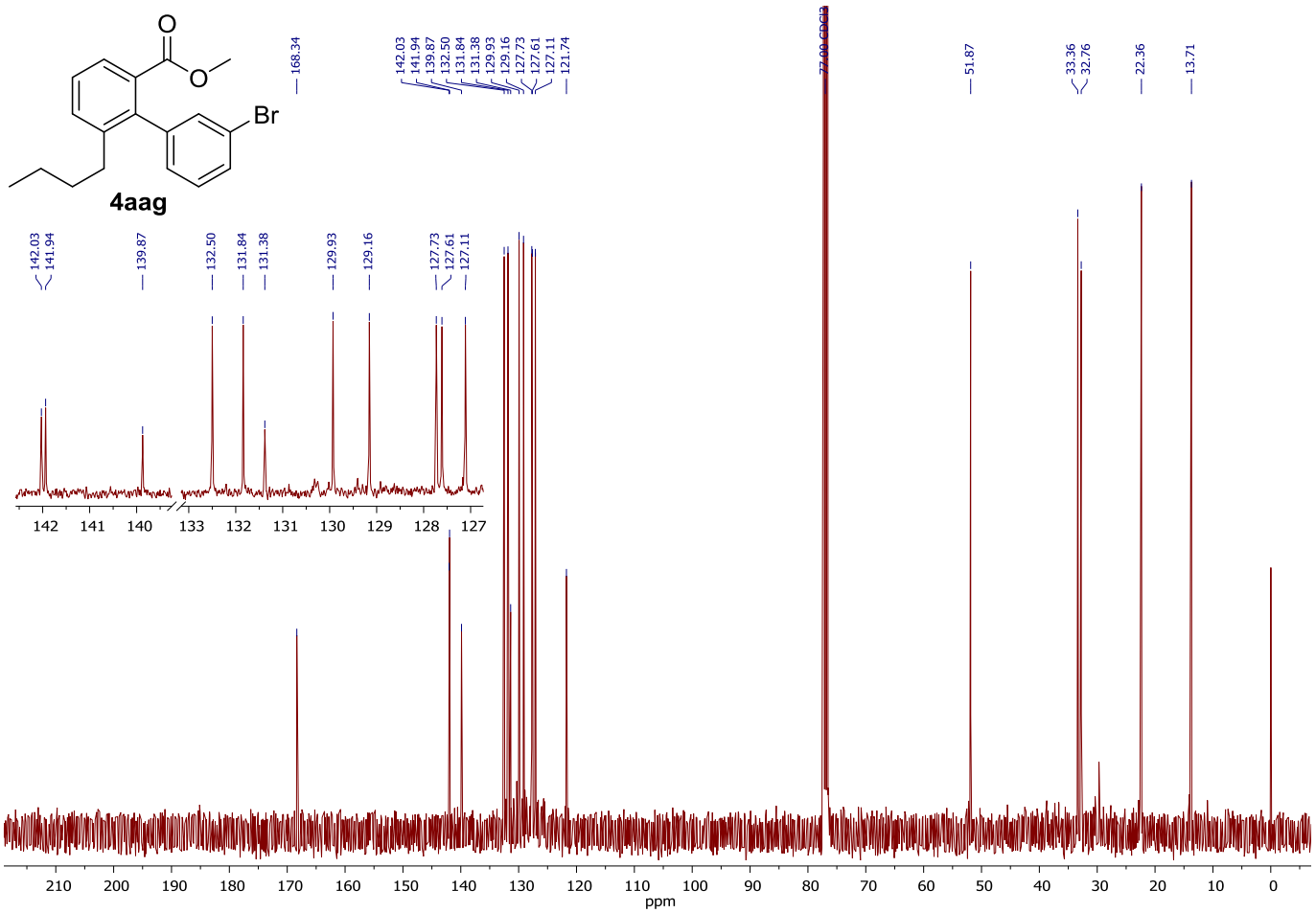
Br
CDCl3
HDO
ppm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Br
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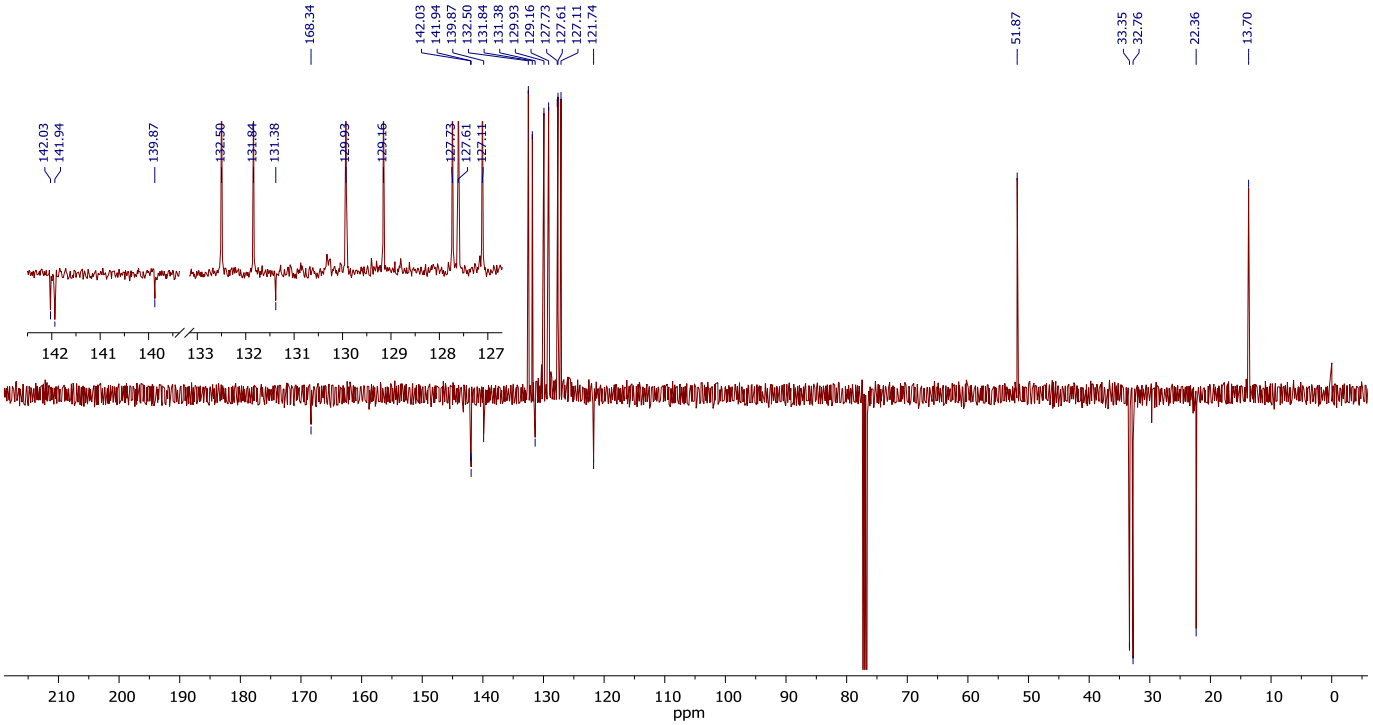
142.03
141.94
139.87
132.50
131.84
131.38
129.93
129.16
127.73
127.61
127.11
121.74
77.00 CDCl3
51.87
33.36
32.76
22.36
13.71
ppm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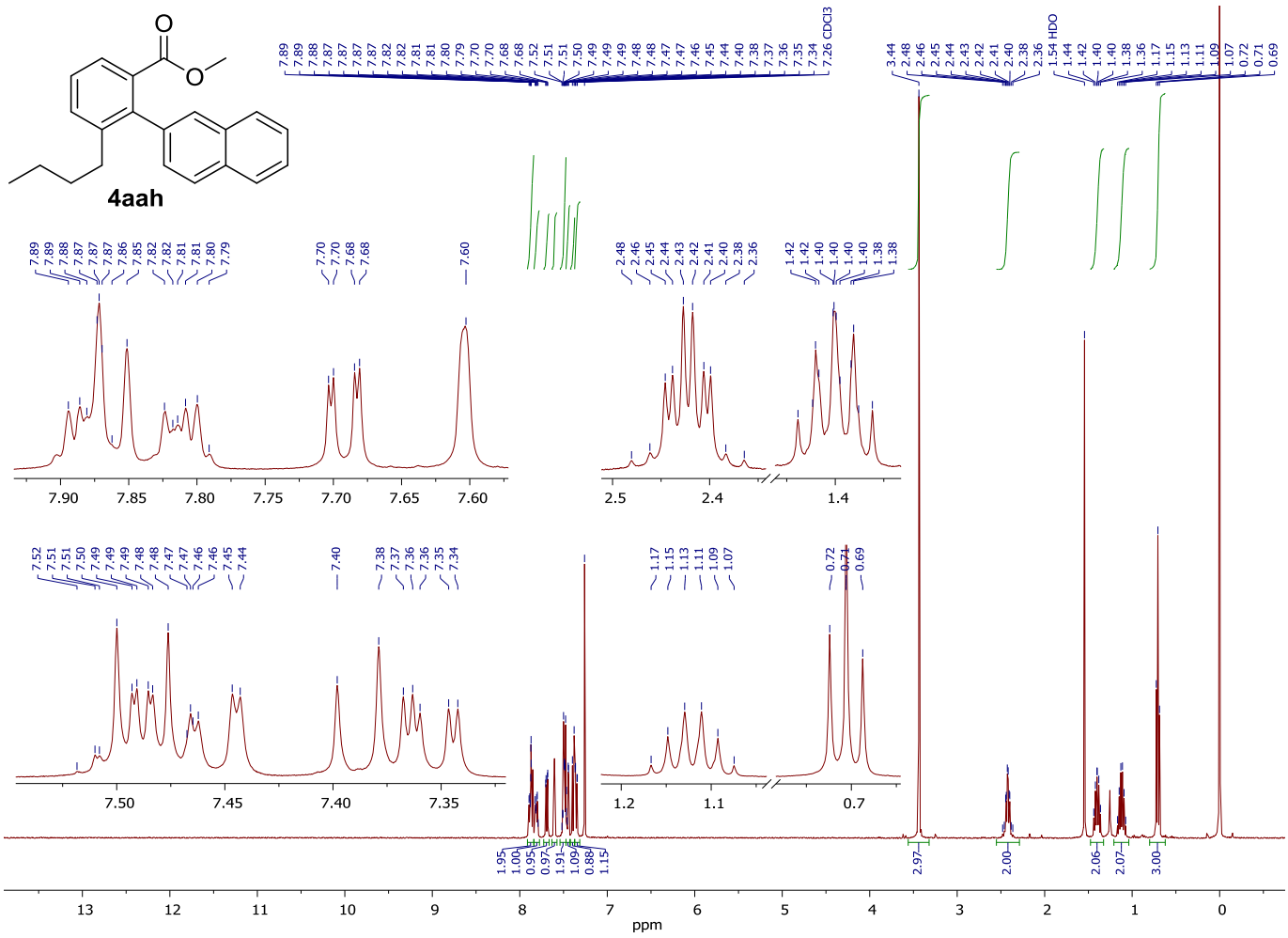
142.03
141.94
139.87
132.50
131.84
131.38
129.93
129.16
127.73
127.61
127.11
121.74
51.87
33.35
32.76
22.36
13.70
ppm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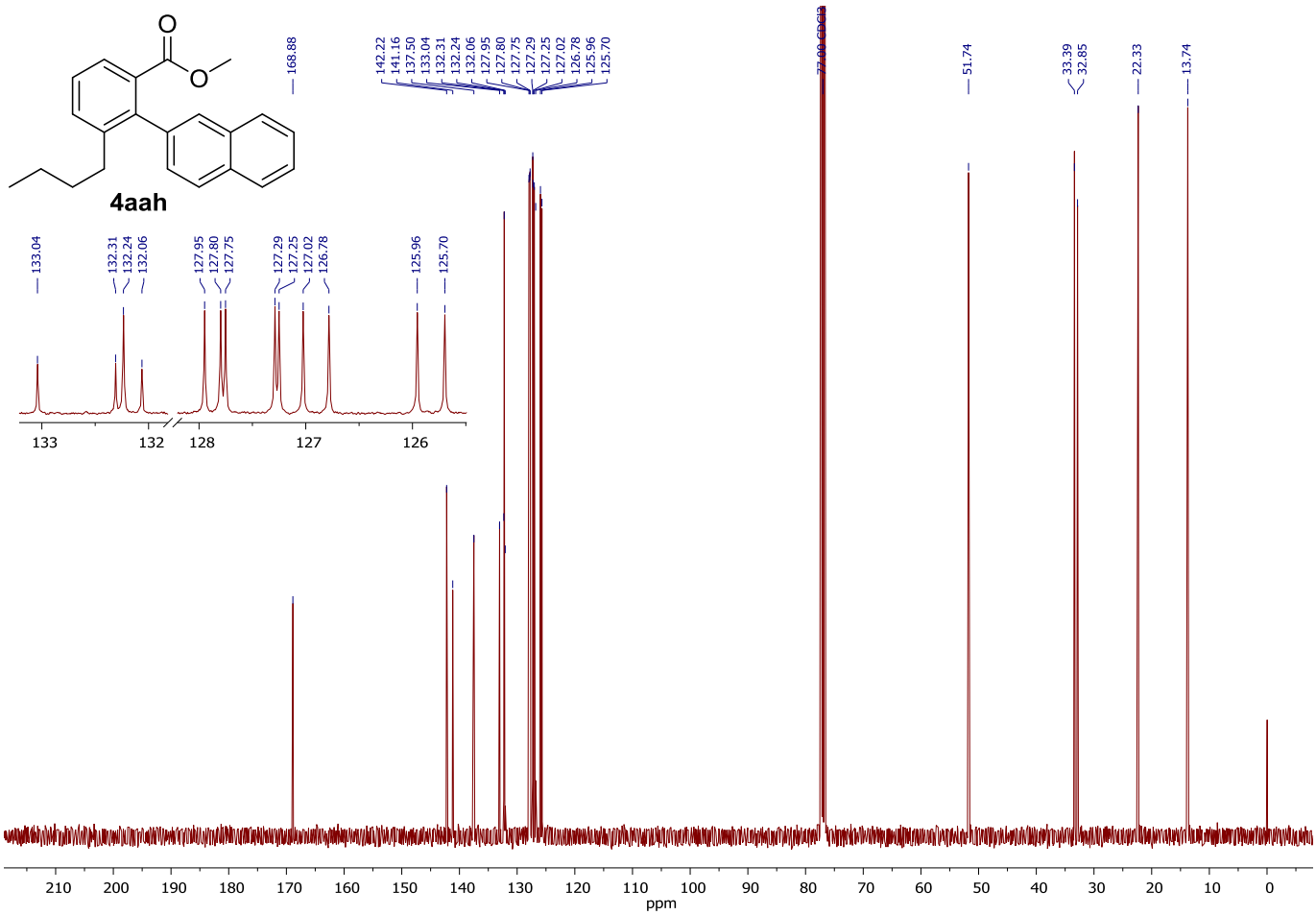
7.26 CDCl3
1.54 HDO
ppm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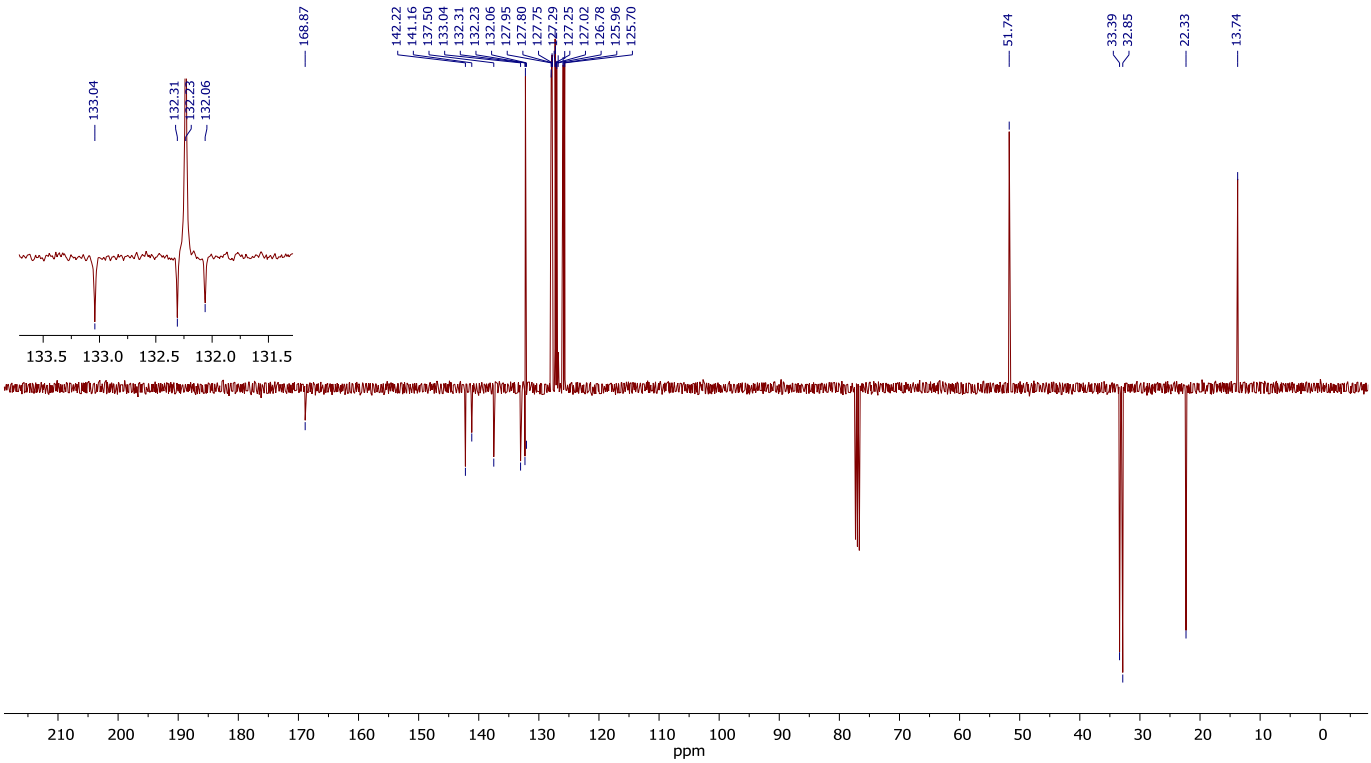
141.16
137.50
133.04
132.31
132.24
132.06
127.95
127.80
127.75
127.29
127.25
127.02
126.78
125.96
125.70
77.00 CDCl3
51.74
33.39
32.85
22.33
13.74
ppm


168.87
142.22
141.16
137.50
133.04
132.31
132.23
132.06
127.95
127.80
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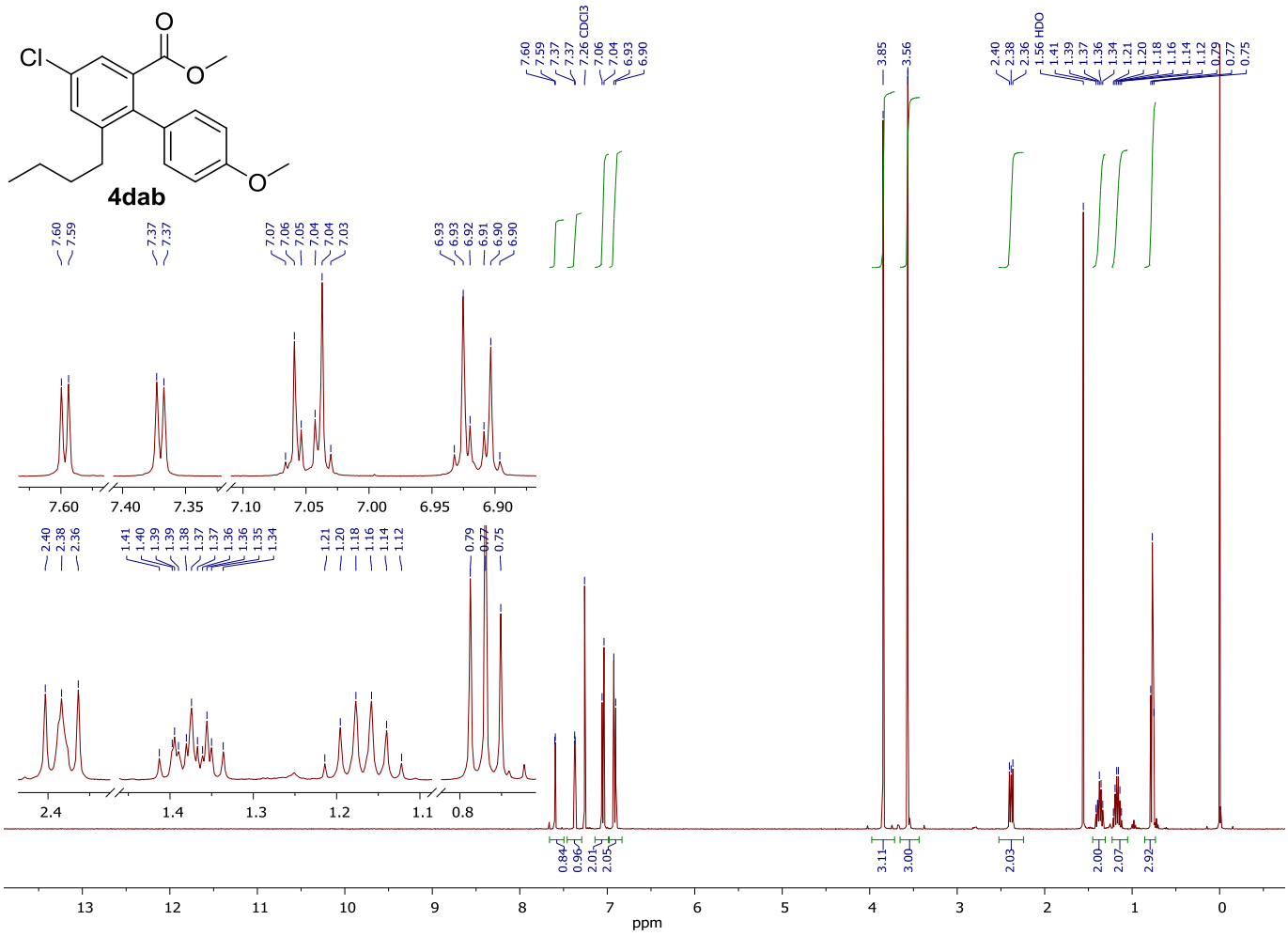
127.25
127.02
126.78
125.96
125.70
51.74
33.39
32.85
22.33
13.74
ppm


4dab
Cl
O
O
O
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7.59
7.37
7.37
7.26 CDCl3
7.06
7.04
6.93
6.90
3.85
3.56
2.40
2.38
2.36
1.56 HDO
1.41
1.39
1.37
1.36
1.34
1.21
1.20
1.18
1.16
1.14
1.12
0.79
0.77
0.75
7.07
7.06
7.05
7.04
7.04
7.03
6.93
6.93
6.92
6.91
6.90
6.90
7.60
7.40
7.35
7.10
7.05
7.00
6.95
6.90
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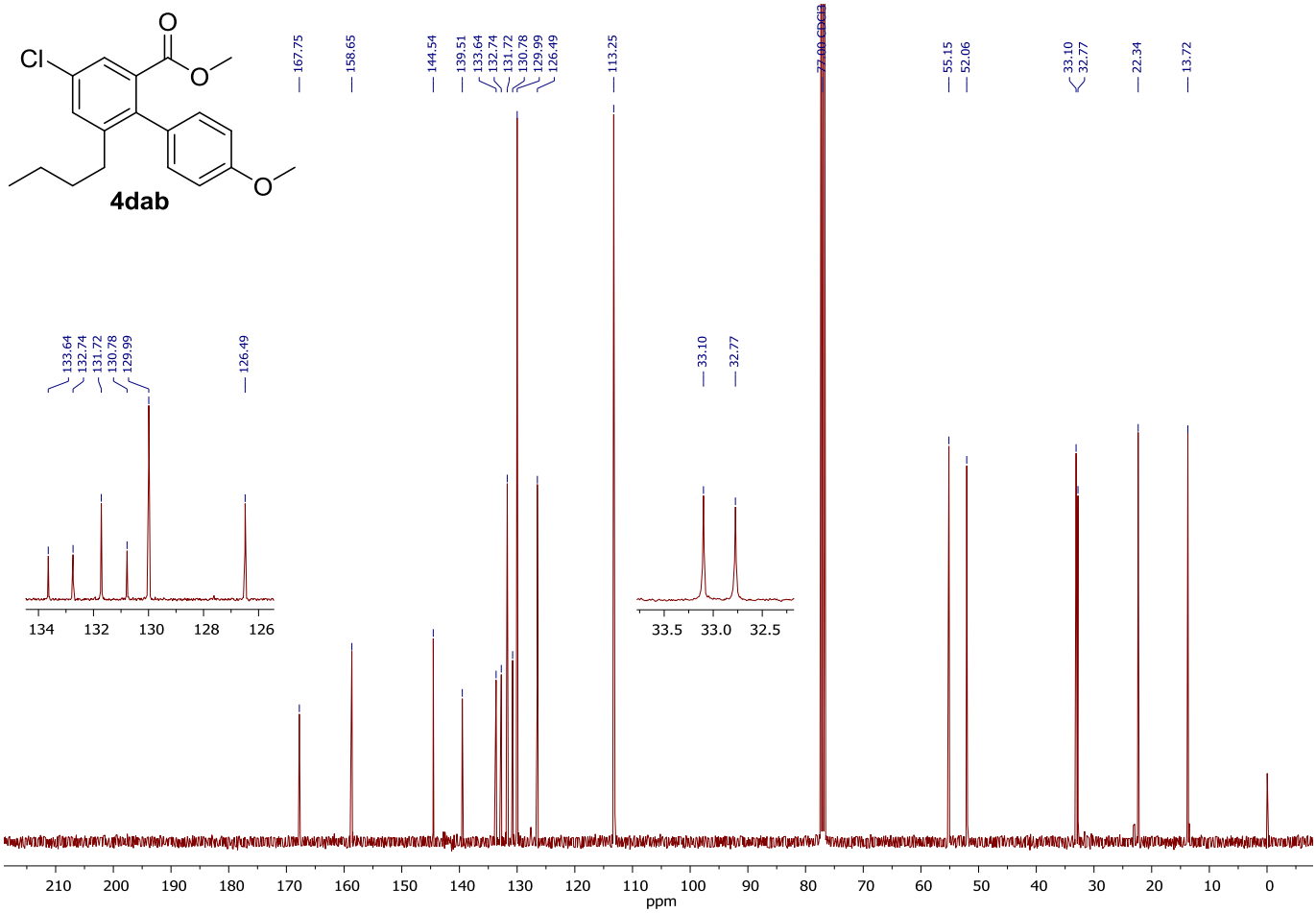
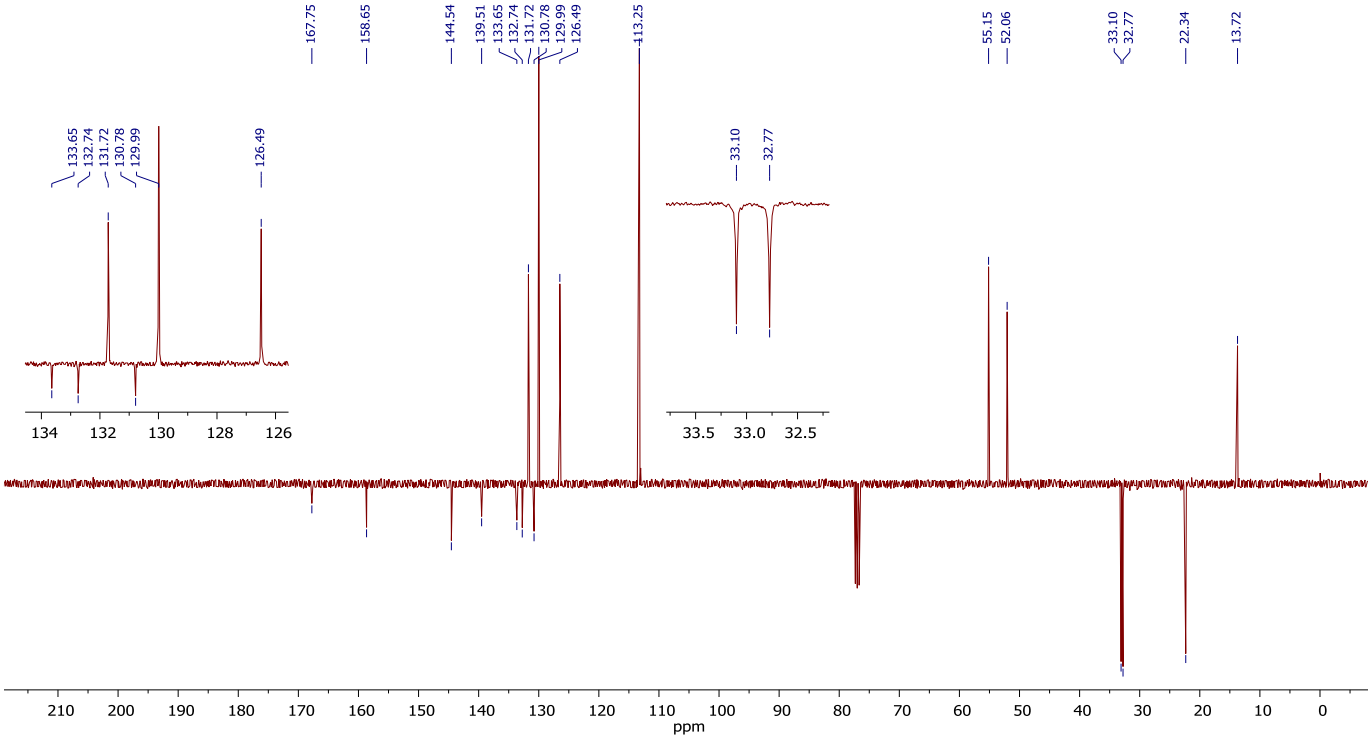
2.38
2.36
1.41
1.40
1.39
1.39
1.38
1.37
1.37
1.36
1.36
1.35
1.34
1.21
1.20
1.18
1.16
1.14
1.12
0.79
0.77
0.75
2.4
1.4
1.3
1.2
1.1
0.8
0.84
0.96
2.01
2.05
3.11
3.00
2.03
2.00
2.07
2.92
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm


Cl
O
O
O
4dab
167.75
158.65
144.54
139.51
133.64
132.74
131.72
130.78
129.99
126.49
113.25
77.00 CDCl3
55.15
52.06
33.10
32.77
22.34
13.72
ppm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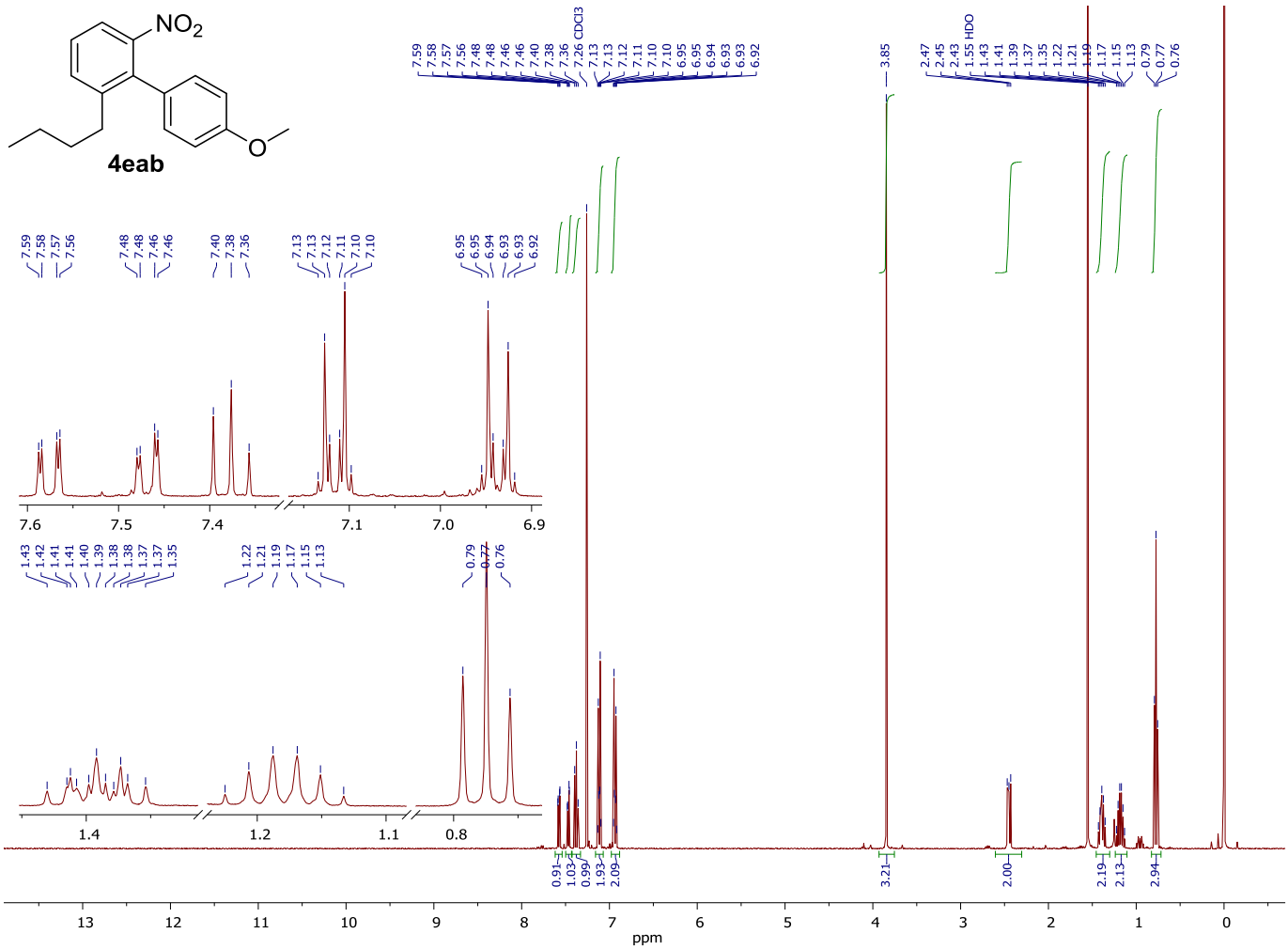
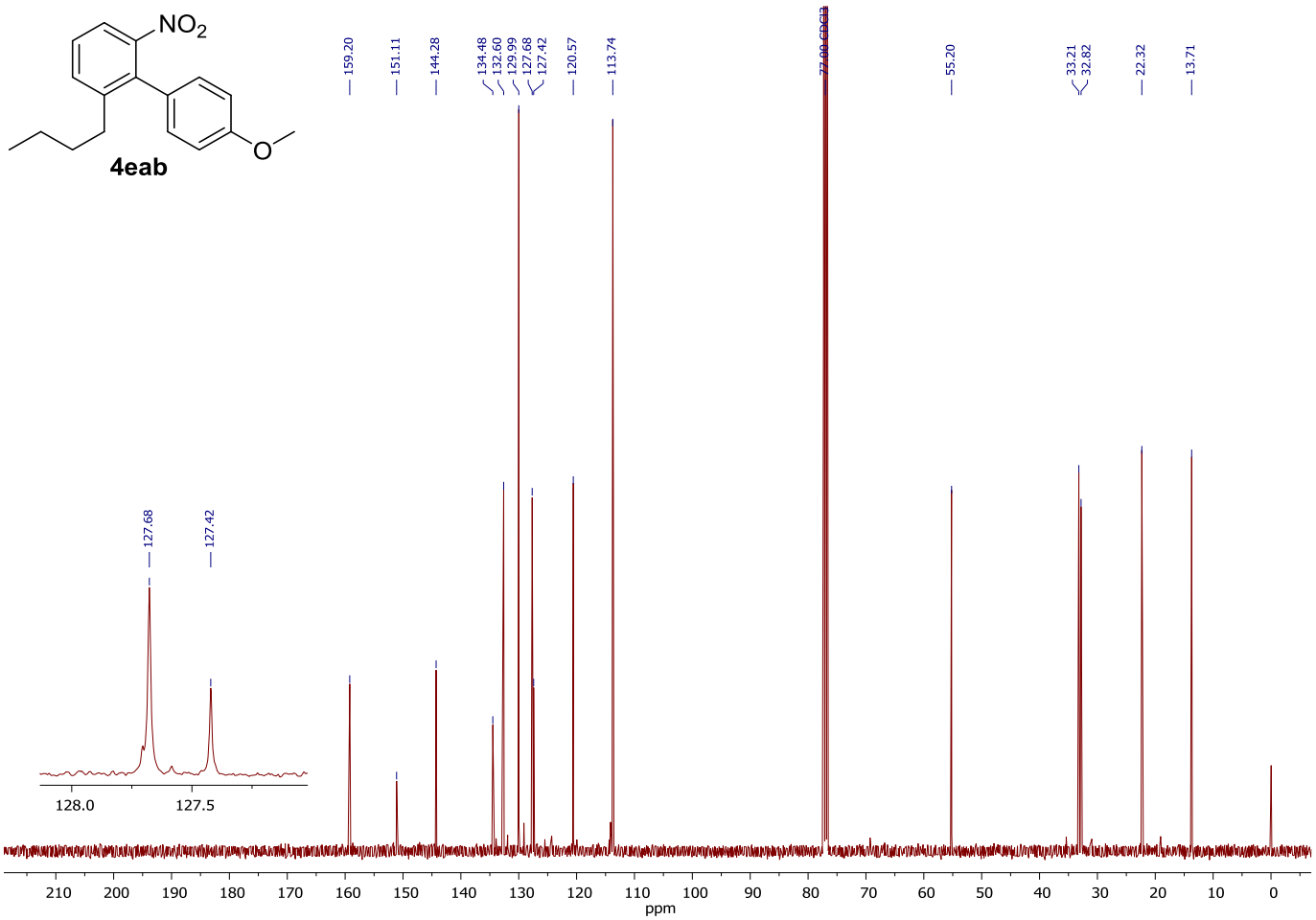
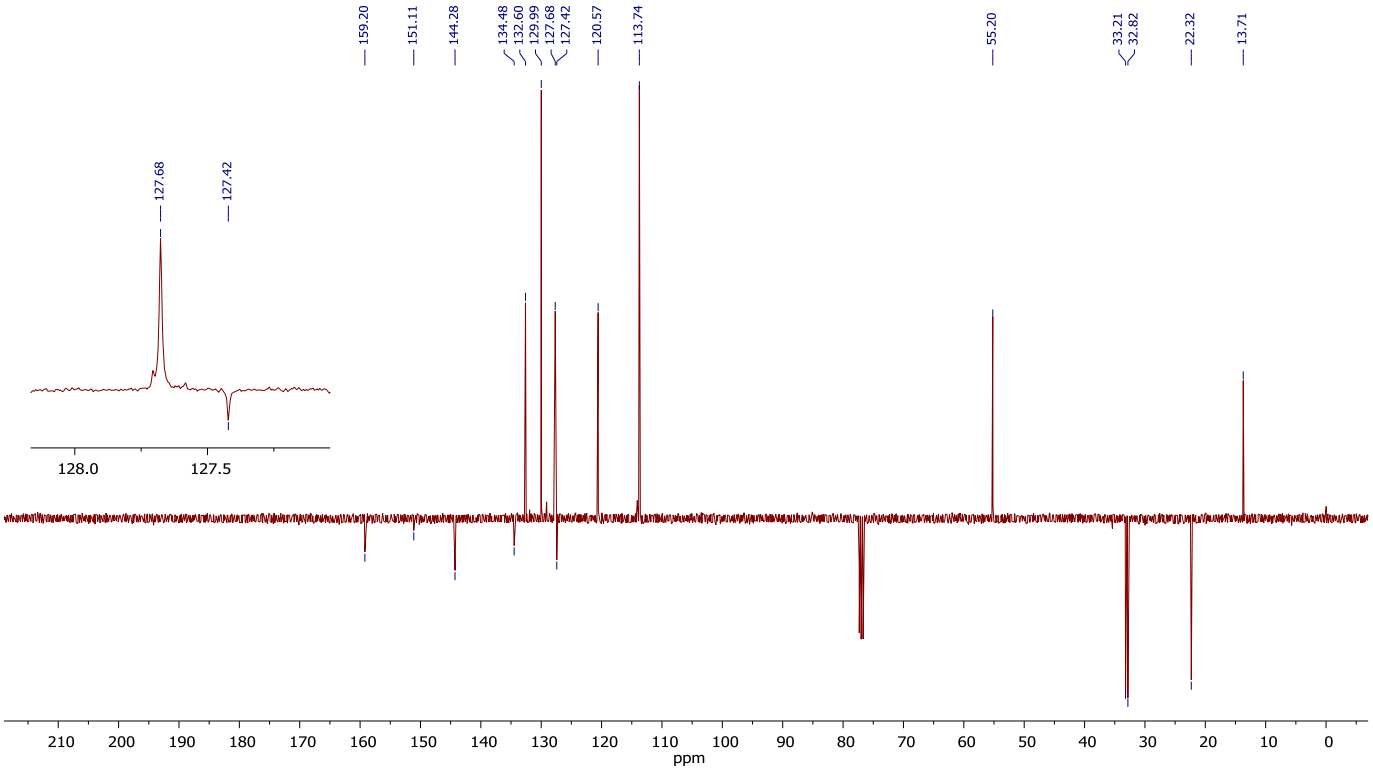
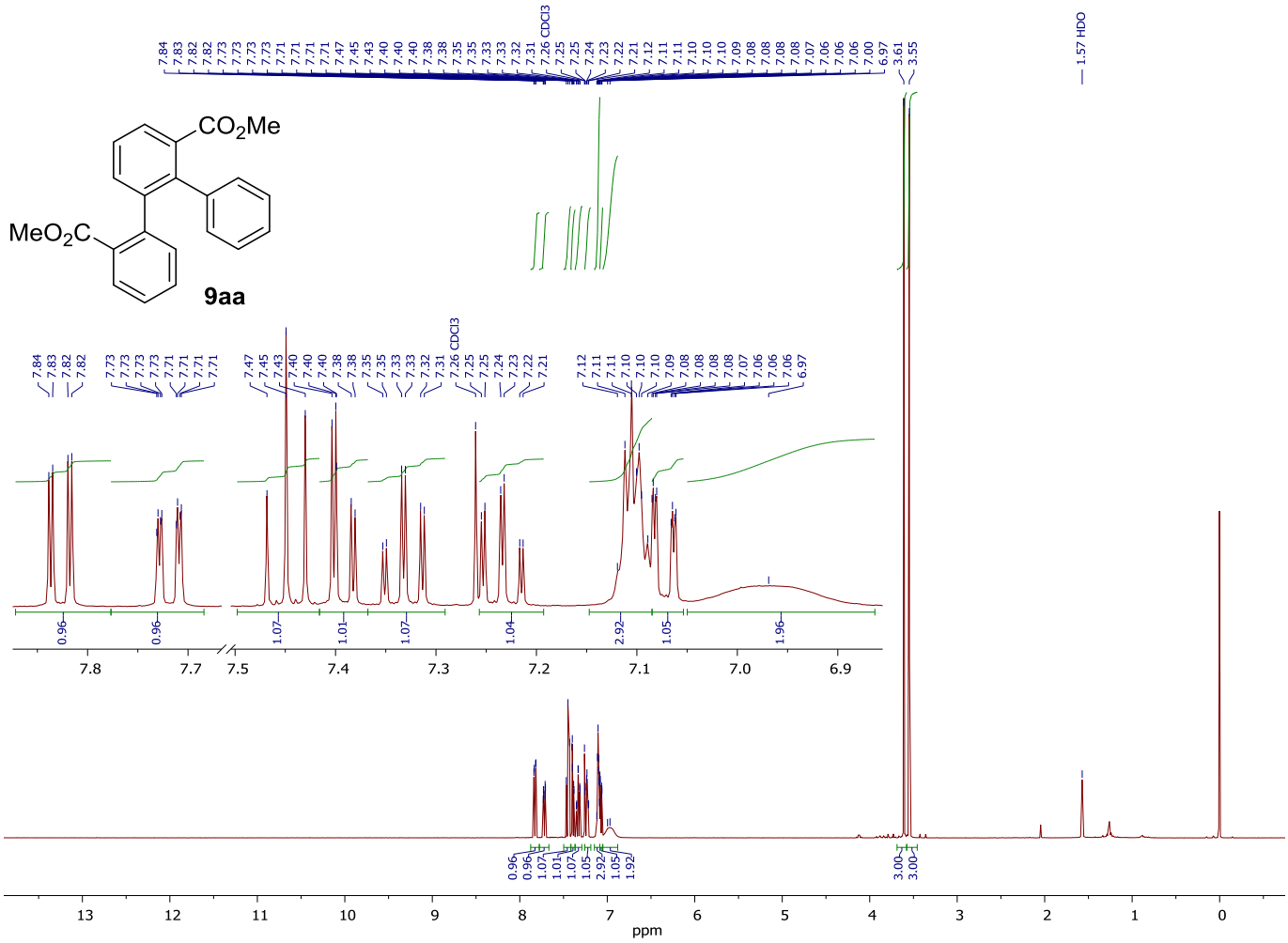
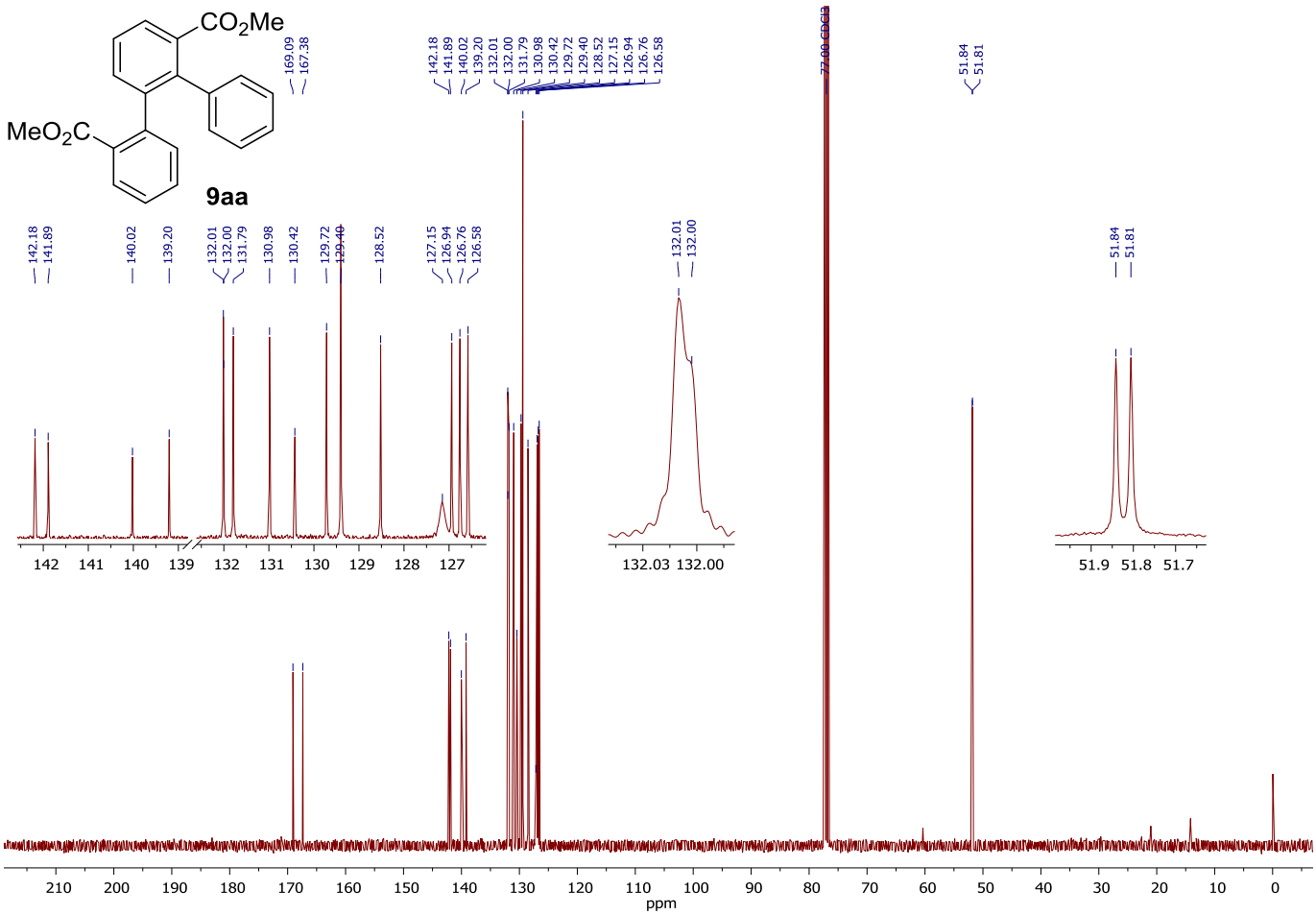
158.65
144.54
139.51
133.65
132.74
131.72
130.78
129.99
126.49
113.25
55.15
52.06
33.10
32.77
22.34
13.72
ppm

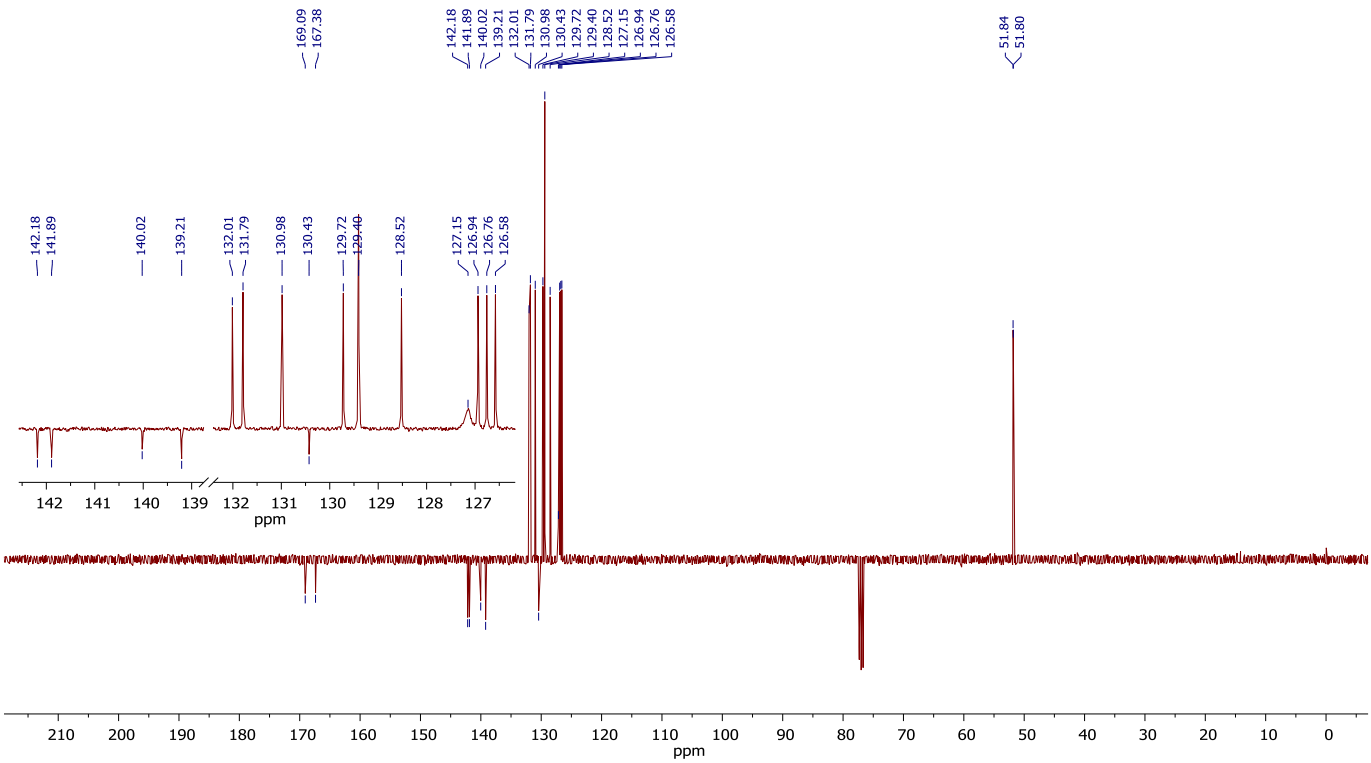

NO2
O
4eab
7.59 7.58 7.57 7.56 7.48 7.48 7.46 7.46 7.40 7.38 7.36 7.26 CDCl3 7.13 7.13 7.12 7.11 7.10 7.10 6.95 6.95 6.94 6.93 6.93 6.92
3.85
2.47 2.45 2.43 1.55 HDO 1.43 1.41 1.39 1.37 1.35 1.22 1.21 1.19 1.17 1.15 1.13 0.79 0.77 0.76
1.43 1.42 1.41 1.41 1.40 1.39 1.38 1.38 1.37 1.37 1.35
1.22 1.21 1.19 1.17 1.15 1.13
0.79 0.77 0.76
0.91 1.03 0.99 1.93 2.09
3.21
2.00
2.19 2.13
2.94
ppm

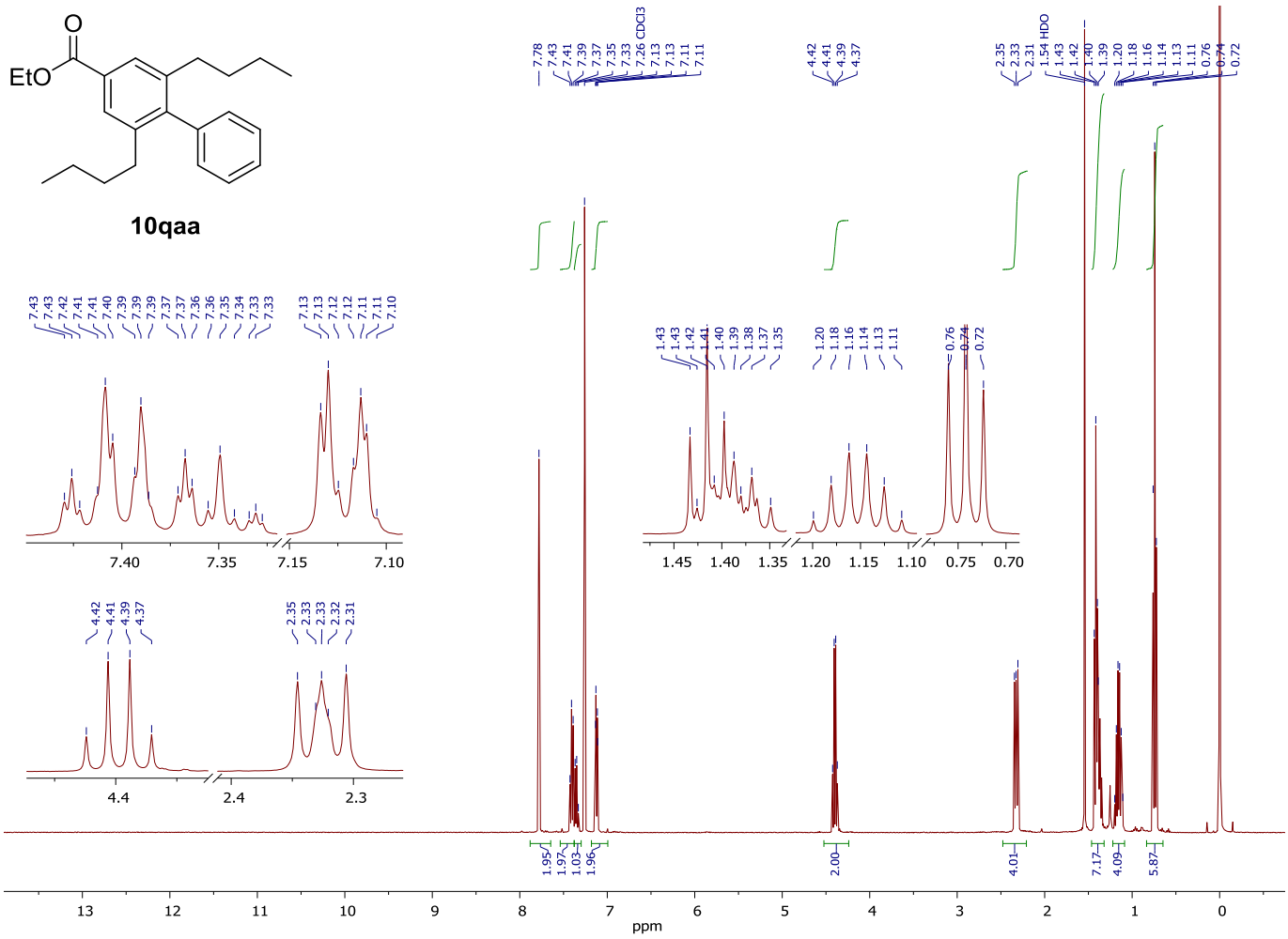

NO2
O
4eab
159.20
151.11
144.28
134.48
132.60
129.99
127.68
127.42
120.57
113.74
77.00 CDCl3
55.20
33.21
32.82
22.32
13.71
127.68
127.42
128.0
127.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

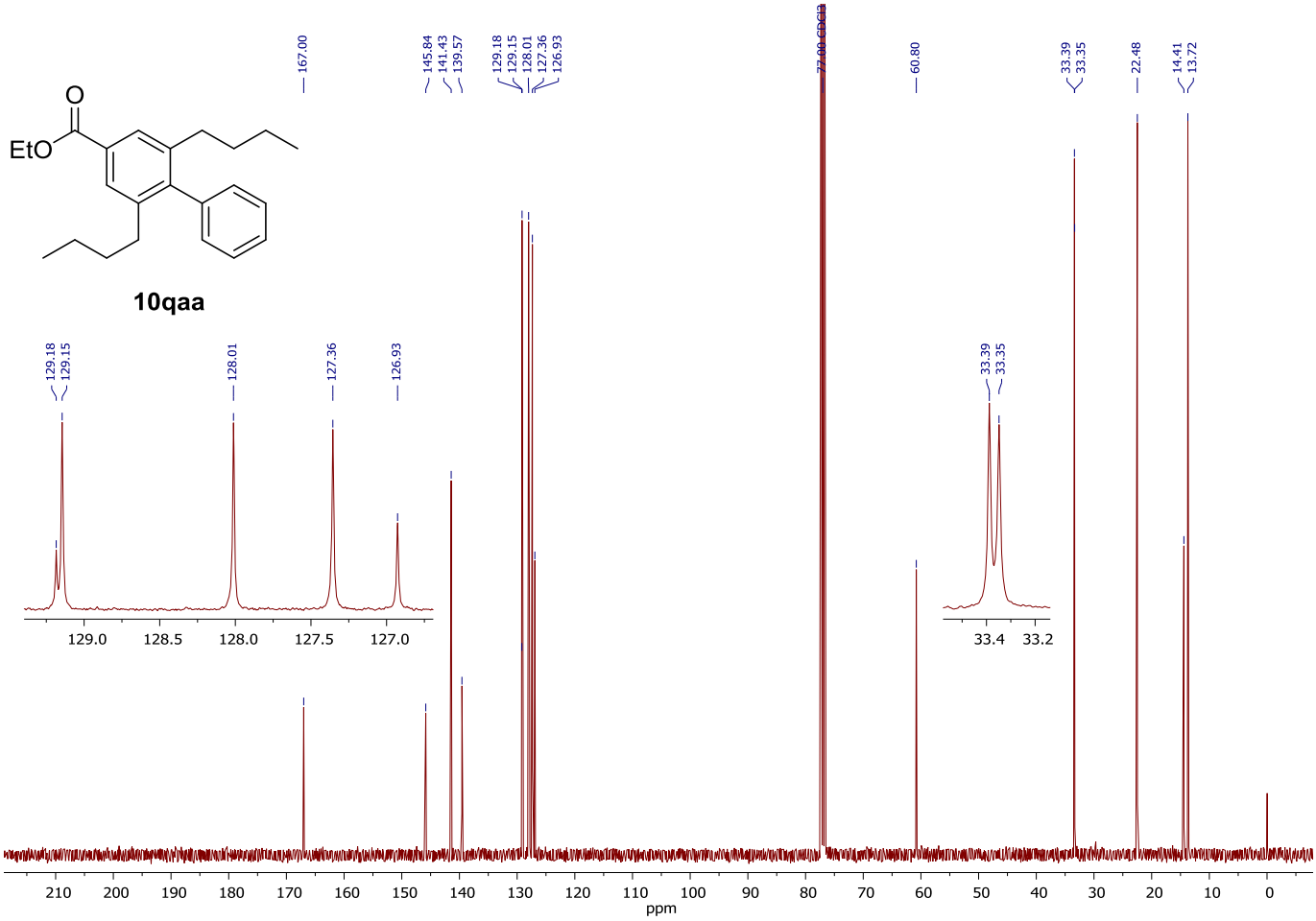

159.20
151.11
144.28
134.48
132.60
129.99
127.68
127.42
120.57
113.74
55.20
33.21
32.82
22.32
13.71
127.68
127.42
128.0
127.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

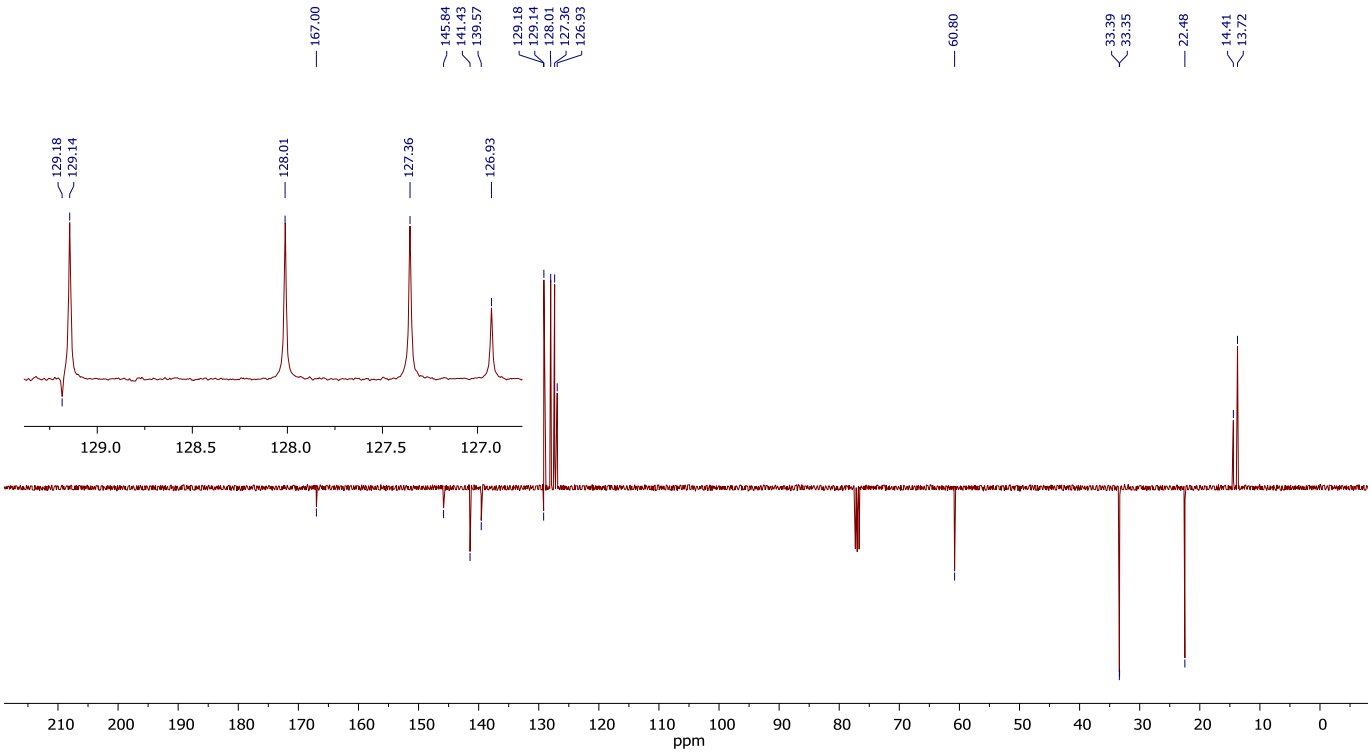

CO2Me
MeO2C
9aa
CDCl3
HDO
ppm


CO2Me
MeO2C
9aa
169.09
167.38
142.18
141.89
140.02
139.20
132.01
132.00
131.79
130.98
130.42
129.72
129.40
128.52
127.15
126.94
126.76
126.58
77.00 CDCl3
51.84
51.81
132.03 132.00
51.9 51.8 51.7
ppm


169.09
167.38
142.18
141.89
140.02
139.21
132.01
131.79
130.98
130.43
129.72
129.40
128.52
127.15
126.94
126.76
126.58
51.84
51.80
ppm


EtO
O
10qaa
7.78
7.43
7.41
7.39
7.37
7.35
7.33
7.26 CDCl3
7.13
7.11
4.42
4.41
4.39
4.37
2.35
2.33
2.31
1.54 HDO
1.43
1.42
1.40
1.39
1.20
1.18
1.16
1.14
1.13
1.11
0.76
0.74
0.72
1.95
1.97
1.03
1.96
2.00
4.01
7.17
4.09
5.87
ppm


EtO
O
10qaa
167.00
145.84
141.43
139.57
129.18
129.15
128.01
127.36
126.93
77.00 CDCl3
60.80
33.39
33.35
22.48
14.41
13.72
ppm


167.00
145.84
141.43
139.57
129.18
129.14
128.01
127.36
126.93
60.80
33.39
33.35
22.48
14.41
13.72
ppm