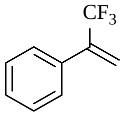
Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 684–685

One-pot synthesis of α-trifluoromethylstyrenes from aryl ketones and the Ruppert–Prakash reagent

Vitalij V. Levin and Alexander D. Dilman

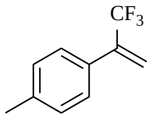
Synthesis of α-trifluoromethylstyrenes (General procedure). A solution of ketone (5 g) in THF (10 ml) was cooled with to 0 °C (water/salt bath), and cesium fluoride CsF (0.5 mol%) was added. Then, (trifluoromethyl)trimethylsilane (1.1 equiv) was added gradually; after induction period, the temperature may rise. The addition was carried out at such a rate that the temperature of the mixture did not exceed 20 °C. After the addition was complete, the cooling bath was removed and the mixture stirred for one hour. THF was evaporated under reduced pressure (20 Torr) with heating the mixture to 60 °C on water bath. The residual oil was treated with phosphorus pentoxide (0.5 equiv) and acid [for **1a-k,m**, concentrated H_2SO_4 (0.25 equiv); for **1l**, MsOH (0.25 equiv)] with stirring. The mixture becomes warm, and after 5 min it was immersed in a glycerol bath preheated to 100 °C. The mixture was stirred at this temperature for 15-60 min and then worked-up (the exact reaction time and the work-up procedure are indicated in compound characterization part).

(3,3,3-Trifluoroprop-1-en-2-yl)benzene (1a).



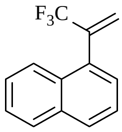
Reaction time 30 min. The product was distilled directly from the reaction mixture at atmospheric pressure. Bp 143–147 °C. Yield 6.24 g (87%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.73–7.32 (m, 6H), 6.03 (q, *J* = 1.8 Hz, 1H), 5.83 (q, *J* = 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 139.2 (q, *J* = 30.0 Hz), 133.8, 129.1, 128.7, 127.5 (q, *J* = 1.2 Hz), 123.5 (q, *J* = 273.9 Hz), 120.5 (q, *J* = 5.8 Hz). ^{19}F NMR ($CDCl_3$, 262 MHz) δ: –65.6 (s). The spectral properties are in good agreement with the literature.[S1]

1-Methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1b).



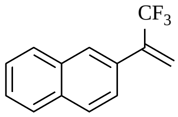
Reaction time 30 min The product was extracted with pentane (3×10 ml), the combined extracts were filtered through Na_2SO_4 and evaporated at atmospheric pressure. Then, was the product was distilled under vacuum. Bp 85–90 °C/43 Torr. Yield 5.69 g (82%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.41 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.95 (q, *J* = 1.4 Hz, 1H), 5.78 (q, *J* = 1.7 Hz, 1H), 2.42 (s, 3H). ^{19}F NMR ($CDCl_3$, 262 MHz) δ: –65.6 (s). The spectral properties are in good agreement with the literature.[S1]

1-(3,3,3-Trifluoroprop-1-en-2-yl)naphthalene (1c).



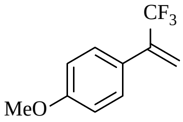
Reaction time 30 min. The product was extracted with petroleum ether (3×10 ml), the combined extracts were filtered through Na_2SO_4 and concentrated on a rotary evaporator. The residue was distilled under reduced pressure. Bp 125–129 °C/22 Torr. Yield 5.35 g (82%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.07–7.90 (m, 3H), 7.64–7.48 (m, 4H), 6.41 (s, 1H), 5.74 (s, 1H). ^{19}F NMR ($CDCl_3$, 262 MHz) δ: –67.5 (s). The spectral properties are in good agreement with the literature.[S1]

2-(3,3,3-Trifluoroprop-1-en-2-yl)naphthalene (1d).



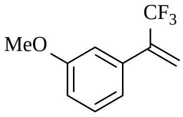
Reaction time 30 min. The product was extracted with petroleum ether (3×10 ml), the combined extracts were filtered through Na_2SO_4 and concentrated on a rotary evaporator. The residue was distilled under reduced pressure. Bp 134–137 °C/21 Torr. Yield 5.62 g (86%). The product solidifies on storage, mp 31–32 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.99 (s, 1H), 7.94–7.84 (m, 3H), 7.64–7.58 (m, 1H), 7.57–7.51 (m, 2H), 6.09 (s, 1H), 5.93 (q, *J* = 1.7 Hz, 1H). ^{19}F NMR($CDCl_3$, 262MHz) δ: –65.2 (s). The spectral properties are in good agreement with the literature.[S2]

1-Methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1e).



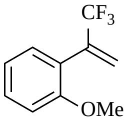
Reaction time 15 min. Cold water (10 ml) was added to the reaction mixture followed by extraction with hexane (3×10 ml). The combined extracts were filtered through Na_2SO_4 and concentrated on a rotary evaporator. The residue was distilled under reduced pressure. Bp 99–102 °C/24 Torr. Yield 4.17 g (62%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.42 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 5.88 (d, J = 1.6 Hz, 1H), 5.71 (q, J = 1.6 Hz, 1H), 3.84 (s, 3H). ^{19}F NMR ($CDCl_3$, 262 MHz) δ: –65.6 (s). The spectral properties are in good agreement with the literature.[S3]

1-Methoxy-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1f).



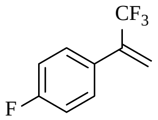
Reaction time 30 min. Cold water (10 ml) was added to the reaction mixture followed by extraction with hexane (3×10 ml). The combined extracts were filtered through Na_2SO_4 and concentrated on a rotary evaporator. The residue was distilled under reduced pressure. Bp 81–84 °C/9 Torr. Yield 2.90 g (43%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.32 (t, J = 8.0 Hz, 1H), 7.07 (d, J = 8.6 Hz, 1H), 7.03–7.00 (m, 1H), 6.95 (dd, J = 8.3, 2.6 Hz, 1H), 5.97 (q, J = 1.4 Hz, 1H), 5.79 (q, J = 1.7 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.7, 139.0 (q, J = 30.1 Hz), 135.1, 129.7, 123.4 (q, J = 273.9 Hz), 120.7 (q, J = 5.7 Hz), 120.0, 114.5, 113.5 (q, J = 1.2 Hz), 55.4. ^{19}F NMR ($CDCl_3$, 262 MHz) δ: -65.5 (s). The spectral properties are in good agreement with the literature.[S3]

1-Methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1g).



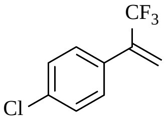
Reaction time 30 min. Cold water (10 ml) was added to the reaction mixture followed by extraction with hexane (3×10 ml). The combined extracts were filtered through Na_2SO_4 and concentrated at atmospheric pressure. The residue was distilled under vacuum. Bp 91–93 °C/22 Torr. Yield 4.31 g (64%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.39 (td, J = 7.8, 1.8 Hz, 1H), 7.30–7.23 (m, 1H), 7.06–6.95 (m, 2H), 6.13 (q, J = 1.5 Hz, 1H), 5.69 (q, J = 1.4 Hz, 1H), 3.86 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 157.5, 136.2 (q, J = 31.6 Hz), 130.9, 130.4, 123.4 (q, J = 5.1 Hz), 123.3 (q, J = 274.0 Hz), 120.5, 111.3, 55.8. ^{19}F NMR ($CDCl_3$, 262 MHz) δ: –66.4 (s). The spectral properties are in good agreement with the literature.[S1]

1-Fluoro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1h).



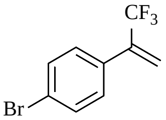
Reaction time 1 h. The product was distilled directly from the reaction mixture under reduced pressure. Bp 79–82 °C/35 Torr. Yield 5.78 g (84%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.44 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 5.96 (s, 1H), 5.74 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 163.3 (d, *J* = 248.9 Hz), 138.2 (q, *J* = 30.3 Hz), 129.9 (d, *J* = 3.4 Hz), 129.5 (dq, *J* = 8.3, 1.2 Hz), 123.4 (q, *J* = 273.8 Hz), 120.6 (qd, *J* = 5.7, 1.2 Hz), 115.7 (d, *J* = 21.8 Hz). ^{19}F NMR ($CDCl_3$, 262 MHz) δ: –65.91 (s, 3F), –113.26 (t, *J* = 5.3 Hz, 1F). The spectral properties are in good agreement with the literature.[S4]

1-Chloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1i).



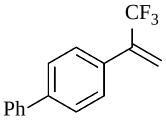
Reaction time 1 h. The product was extracted with petroleum ether (3×10 ml), the combined extracts were filtered through Na_2SO_4 and concentrated on a rotary evaporator. The residue was distilled under reduced pressure. Bp 102–105 °C/20 Torr. Yield 5.03 g (80%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ:7.43–7.34 (m, 4H), 5.98 (q, *J* = 1.4 Hz, 1H), 5.77 (q, *J* = 1.7 Hz, 1H). ^{19}F NMR ($CDCl_3$, 262 MHz) δ: –65.7 (s). The spectral properties are in good agreement with the literature.[S4]

1-Bromo-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1j).



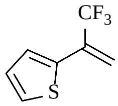
Reaction time 1 h. Cold water (10 ml) was added to the reaction mixture followed by extraction with hexane (3×10 ml). The combined extracts were filtered through Na_2SO_4 and concentrated on a rotary evaporator. The residue was distilled under reduced pressure. Bp 108–111 °C/12 Torr. Yield 4.04 g (64%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.57 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 6.03 (d, *J* = 1.6 Hz, 1H), 5.82 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 138.2 (q, *J* = 30.5 Hz), 132.6, 131.9, 129.1 (q, *J* = 1.3 Hz), 123.5, 123.2 (q, *J* = 273.8 Hz), 121.0 (q, *J* = 5.7 Hz). ^{19}F NMR ($CDCl_3$, 262 MHz) δ: –65.7 (s). The spectral properties are in good agreement with the literature.[S4]

4-(3,3,3-Trifluoroprop-1-en-2-yl)-1,1'-biphenyl (1k).



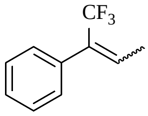
Reaction time 1 h. Cold water (10 ml) was added to the reaction mixture followed by extraction withCH_2Cl_2 (3×10 ml). The combined extracts were filtered through Na_2SO_4 and concentrated on a rotary evaporator. The residue was recrystallized from methanol. Yield 4.49 g (71%). Mp 60–61 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.70–7.36 (m, 9H), 6.01 (s, 1H), 5.86 (q, *J* = 1.7 Hz, 1H). ^{19}F NMR (CDCl$_3$, 262 MHz) δ: –65.4 (s). The spectral properties are in good agreement with the literature.[S2]

2-(3,3,3-Trifluoroprop-1-en-2-yl)thiophene (1l).



Reaction time 30 min. Cold water (10 ml) was added to the reaction mixture followed by extraction with pentane (3×10 ml). The combined extracts were filtered through Na$_2$SO$_4$ and the solvent was evaporated at atmospheric pressure. The residue was distilled under vacuum. Bp 69–71 °C/50 Torr. Yield 3.81 g (54%). ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.35 (d, *J* = 5.2 Hz, 1H), 7.31–7.24 (m, 1H), 7.09 (dd, *J* = 5.2, 3.8 Hz, 1H), 5.89 (d, *J* = 2.0 Hz, 1H), 5.87 (s, 1H). ^{13}C NMR (CDCl$_3$, 75 MHz) δ: 135.8, 132.8 (q, *J* = 31.5 Hz), 128.0, 127.0 (q, *J* = 1.6 Hz), 126.2, 122.8 (q, *J* = 274.1 Hz), 117.8 (q, *J* = 5.6 Hz). ^{19}F NMR (CDCl$_3$, 262 MHz) δ: –66.8 (s). The spectral properties are in good agreement with the literature.[S5]

(1,1,1-Trifluorobut-2-en-2-yl)benzene (1m).



Mixture of *E*/*Z* isomers, ratio 1:1. Reaction time 1 h. The product was distilled directly from the reaction mixture under vacuum. Bp 77–82 °C/50 Torr. Yield 4.30 g (62%). ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.60–7.17 (m, 5H), 6.61 (qd, *J* = 7.0, 1.8 Hz, 1H), 6.21 (q, *J* = 7.4 Hz, 1H), 2.10 (dq, *J* = 6.1, 3.0 Hz, 3H), 1.73 (dq, *J* = 7.4, 2.6 Hz, 3H). ^{19}F NMR (CDCl$_3$, 262 MHz) δ: –58.10 (s), –66.46 (s). The spectral properties are in good agreement with the literature.[S6]

References

S1. R.-q. Pan, X.-x. Liu and M.-z. Deng, *J. Fluorine Chem.*, 1999, **95**, 167.

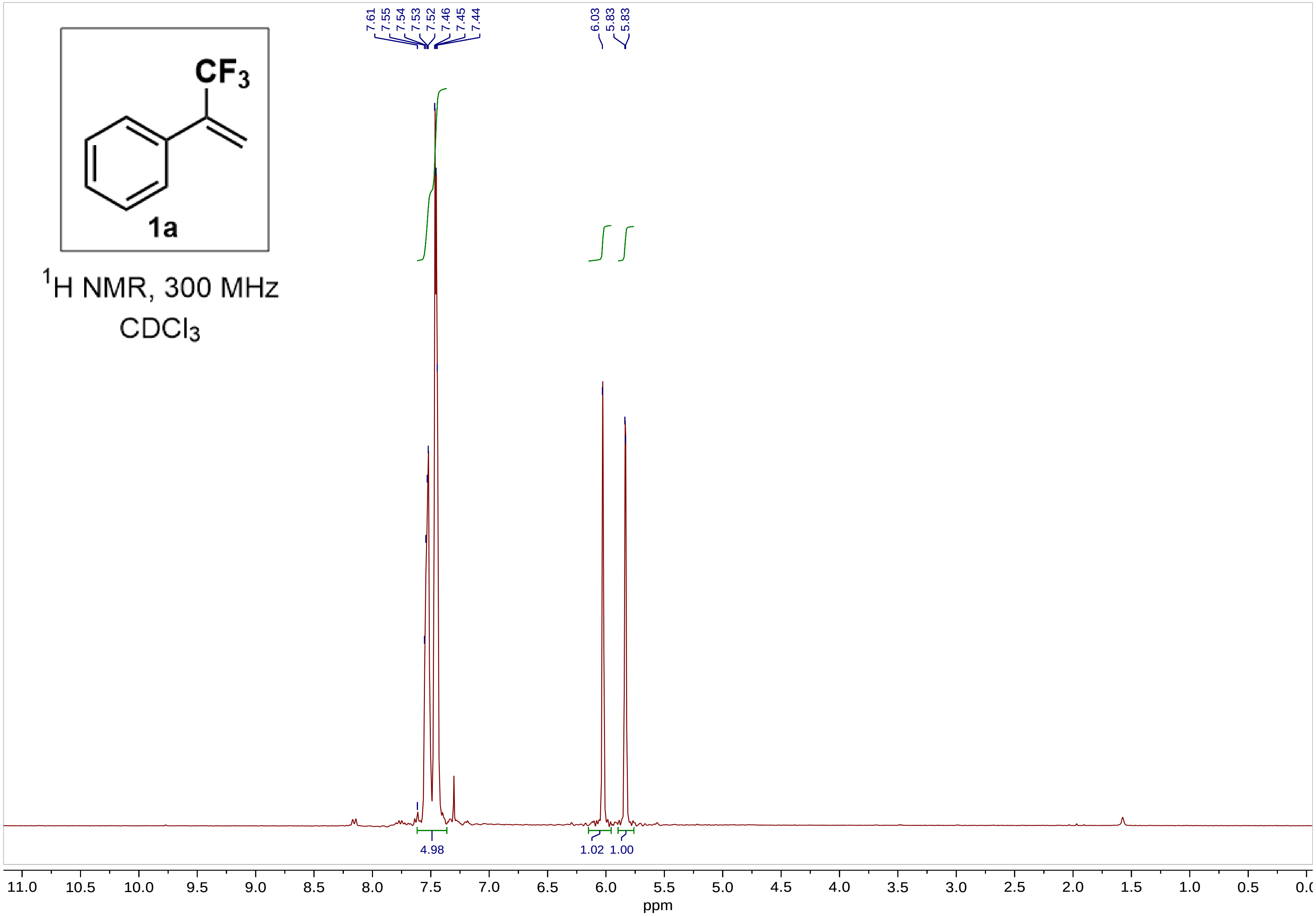
S2. X. Wang, Y. Xu, Y. Deng, Y. Zhou, J. Feng, G. Ji, Y. Zhang and J. Wang, *Chem. Eur. J.*, 2014, **20**, 961.

S3. Y. Li, B. Zhao, K. Dai, D.-H. Tu, B. Wang, Y.-Y. Wang, Z.-T. Liu, Z.-W. Liu and J. Lu, *Tetrahedron*, 2016, **72**, 5684.

S4. H. Tian, H. Shimakoshi, K. Imamura, Y. Shiota, K. Yoshizawa and Y. Hisaeda, *Chem. Commun.*, 2017, **53**, 9478.

S5. P. Poutrel, X. Pannecoucke, P. Jubault and T. Poisson, *Org. Lett.*, 2020, **22**, 4858.

S6. T. Xiao, L. Li and L. Zhou, *J. Org. Chem.*, 2016, **81**, 7908.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7.53
7.52
7.46
7.45
7.44
6.03
5.83
5.83
4.98
1.02
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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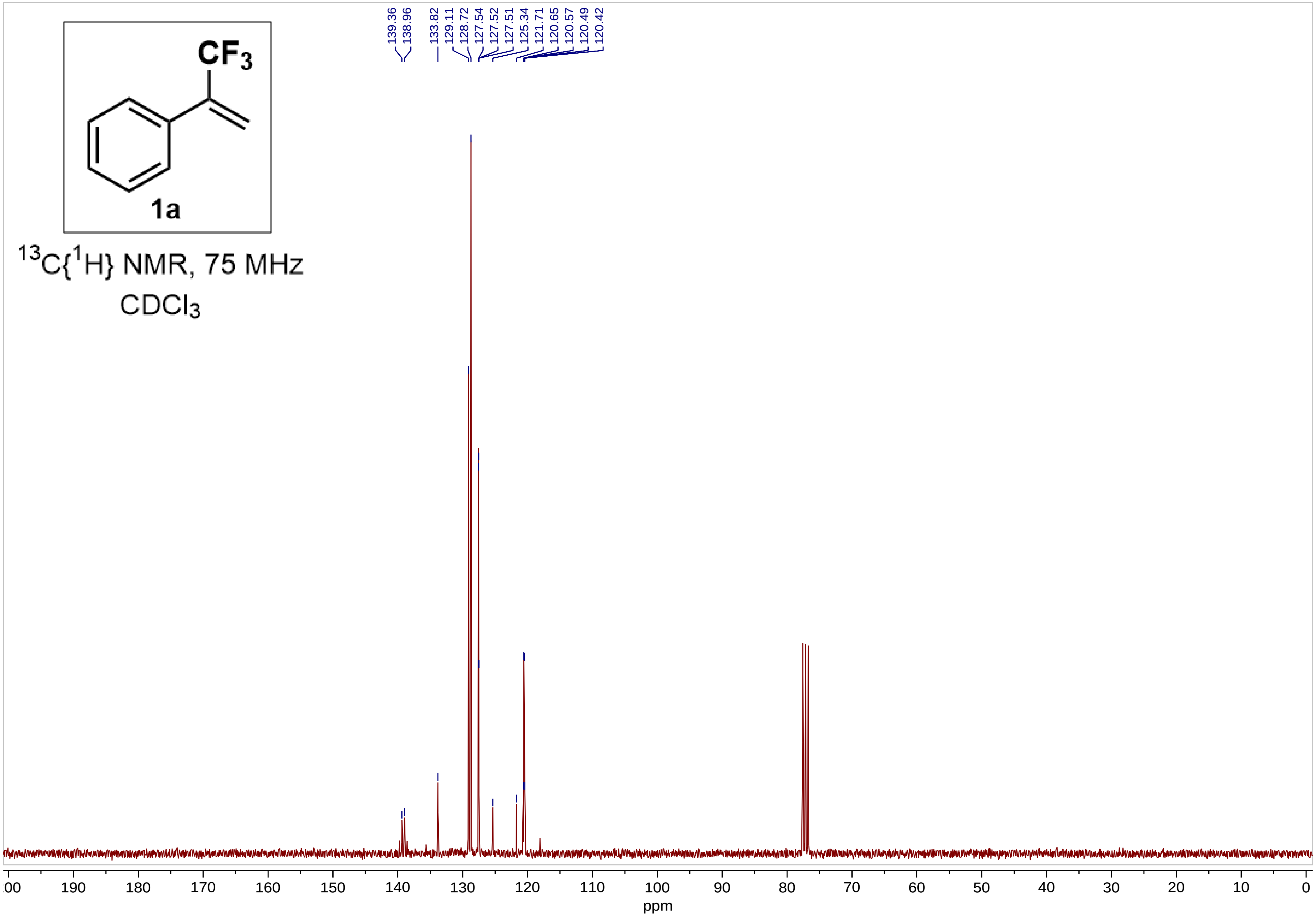
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127.51
125.34
121.71
120.65
120.57
120.49
120.42
00
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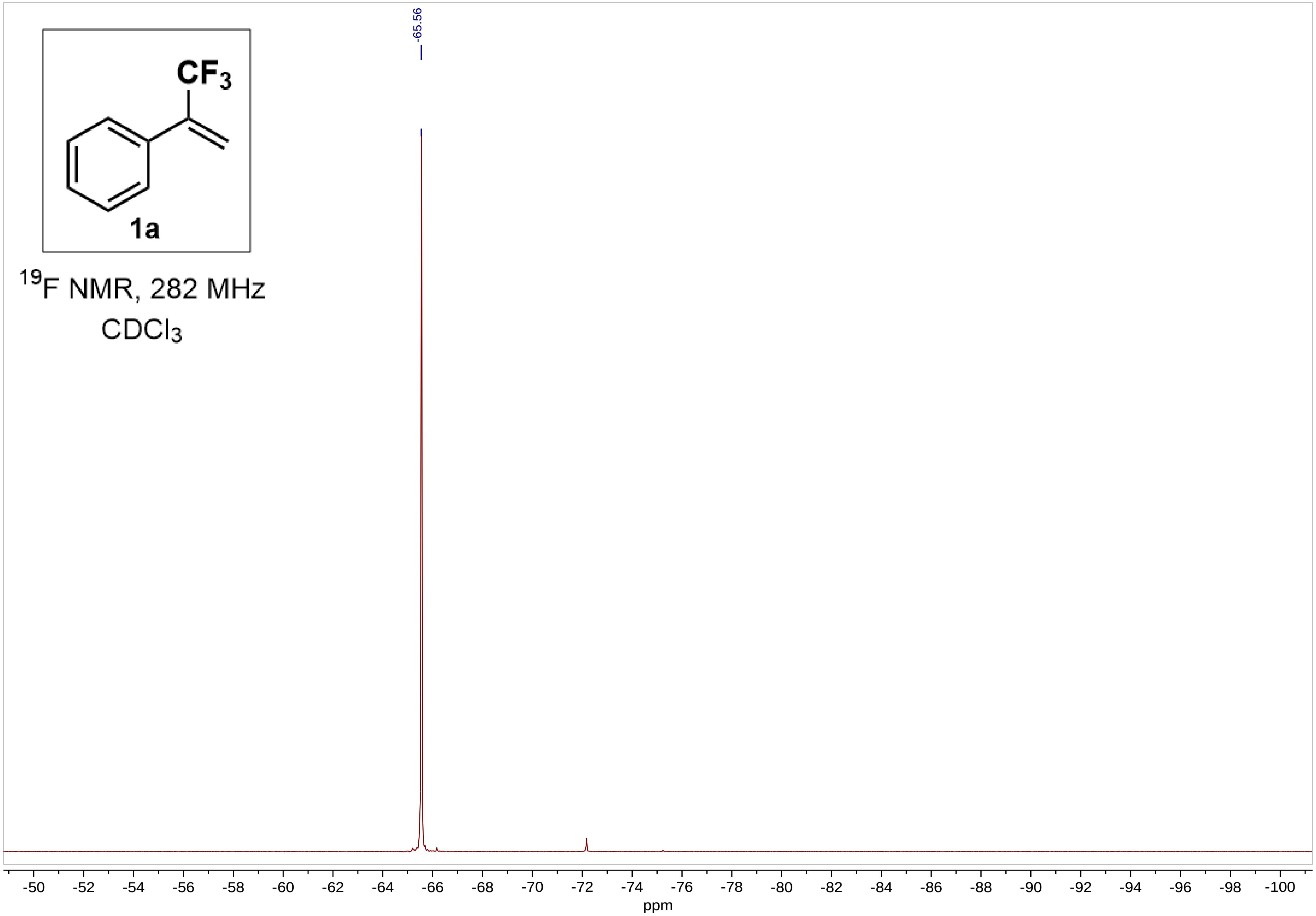
CF_3
1a
^{19}F NMR, 282 MHz
$CDCl_3$
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-62
-64
-66
-68
-70
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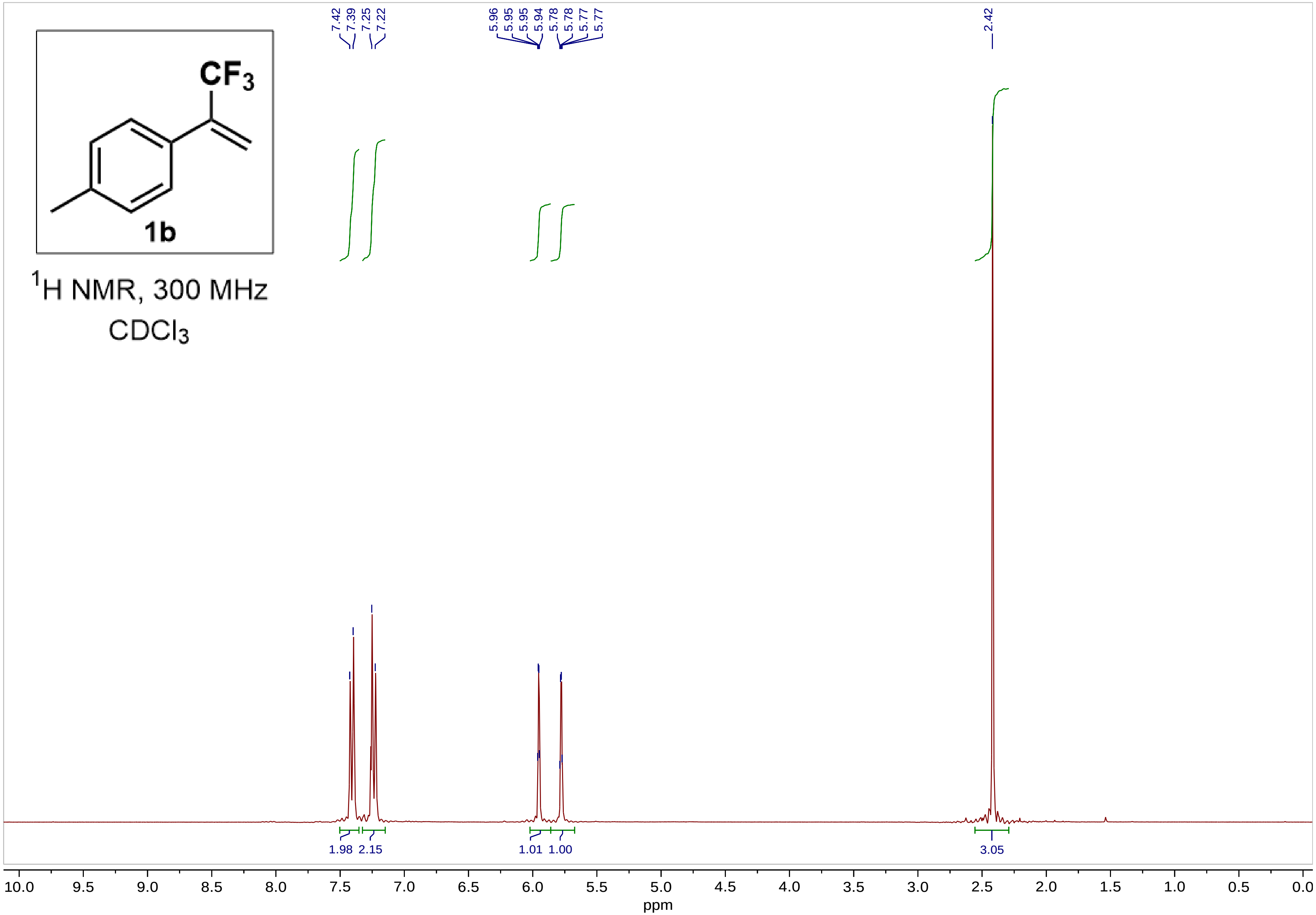
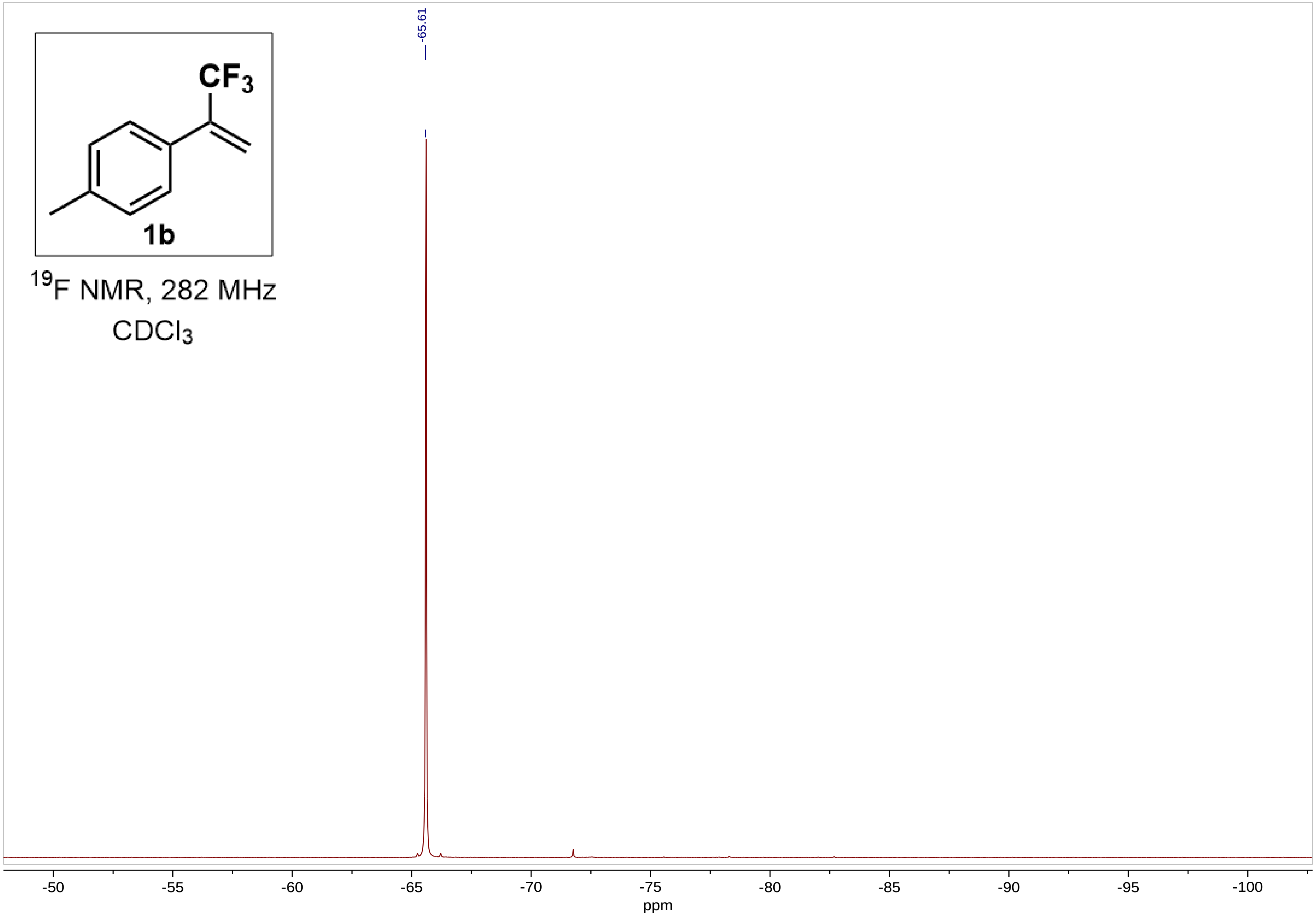


1b

^{1}H NMR, 300 MHz

CDCl$_3$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1b
19F NMR, 282 MHz
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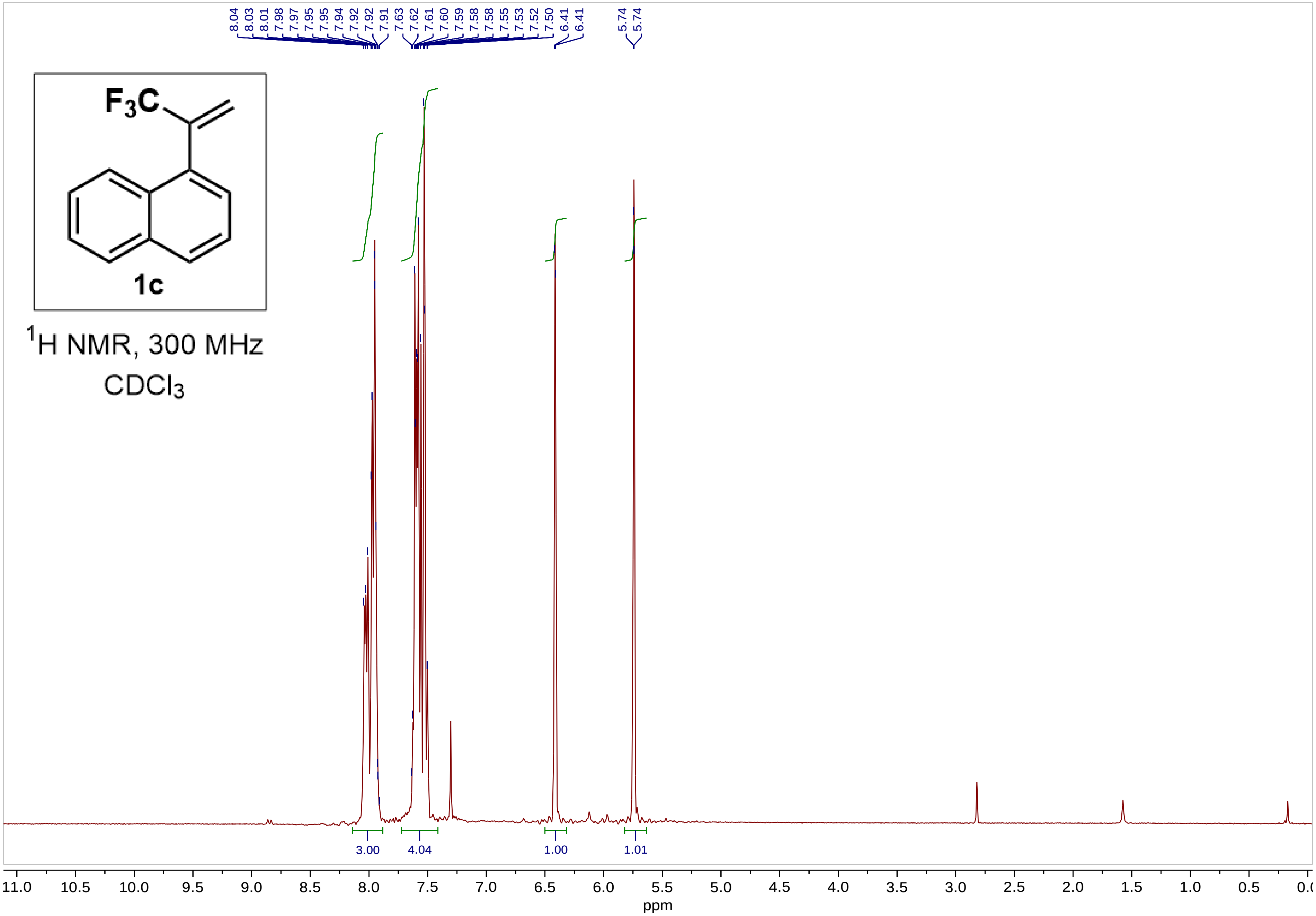
ppm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8.03
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7.59
7.58
7.58
7.55
7.53
7.52
7.50
6.41
6.41
5.74
5.74
F3C
1c
1H NMR, 300 MHz
CDCl3
3.00
4.04
1.00
1.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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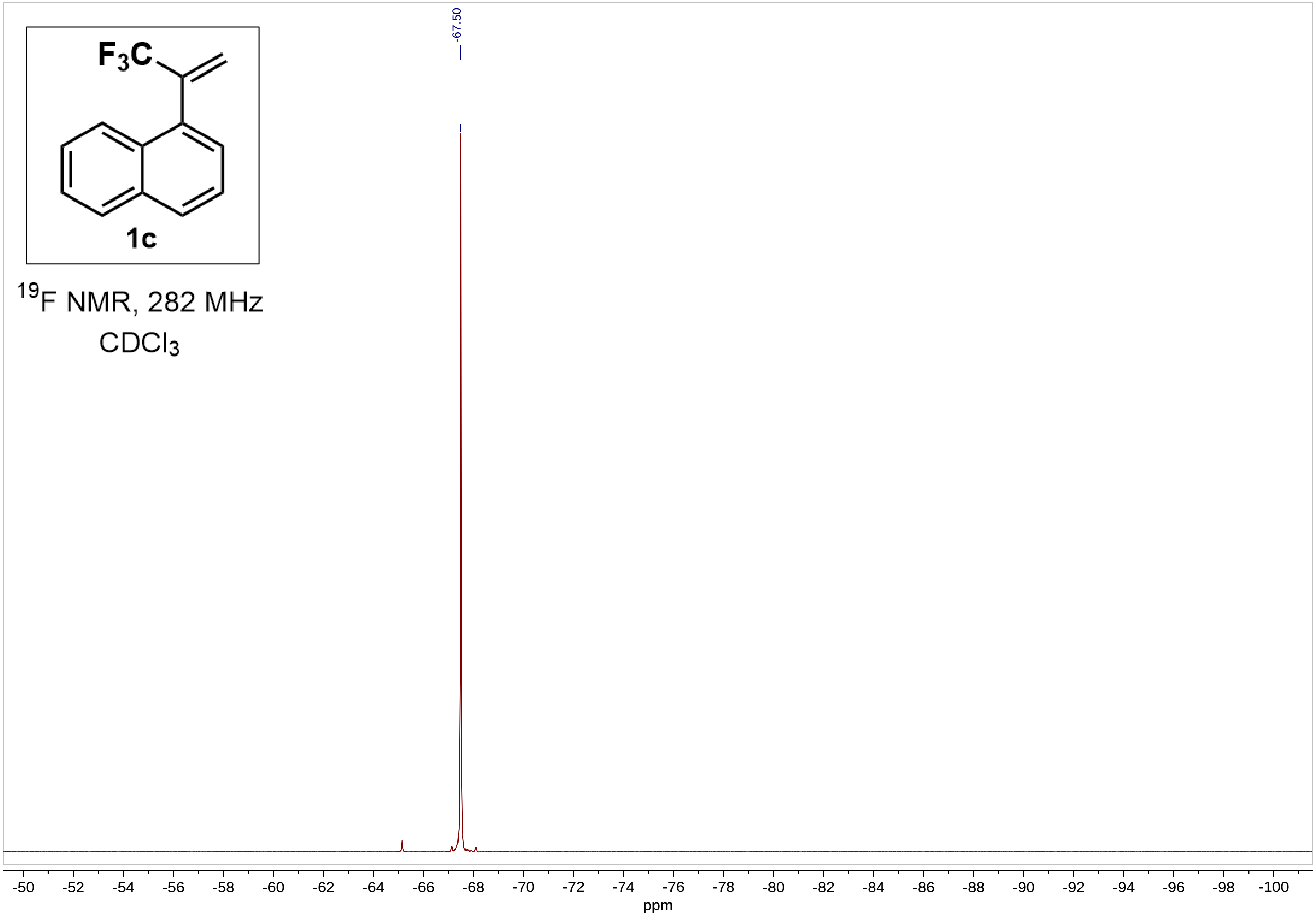
-67.50
F$_3$C
1c
^{19}F NMR, 282 MHz
CDCl$_3$
-50
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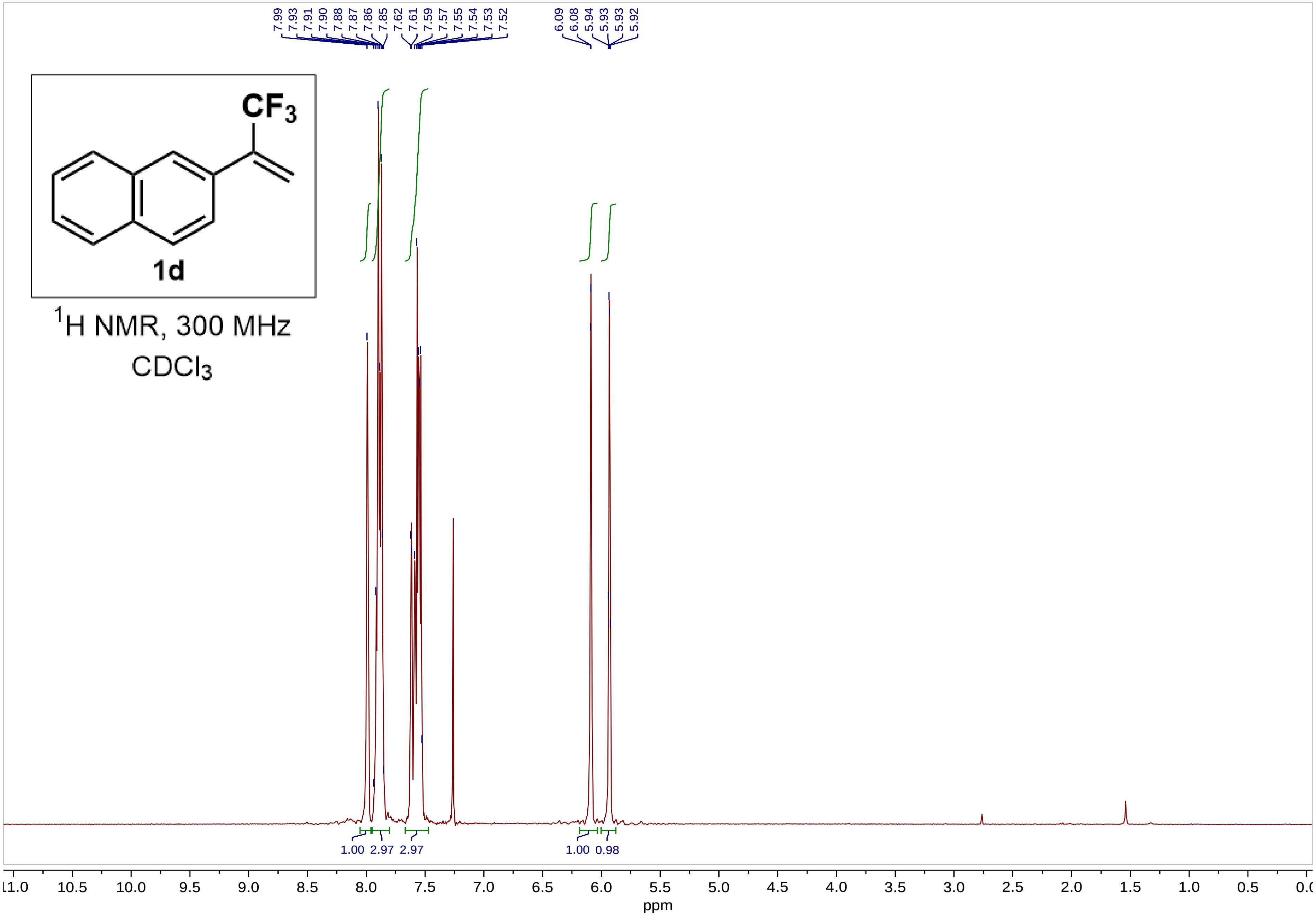
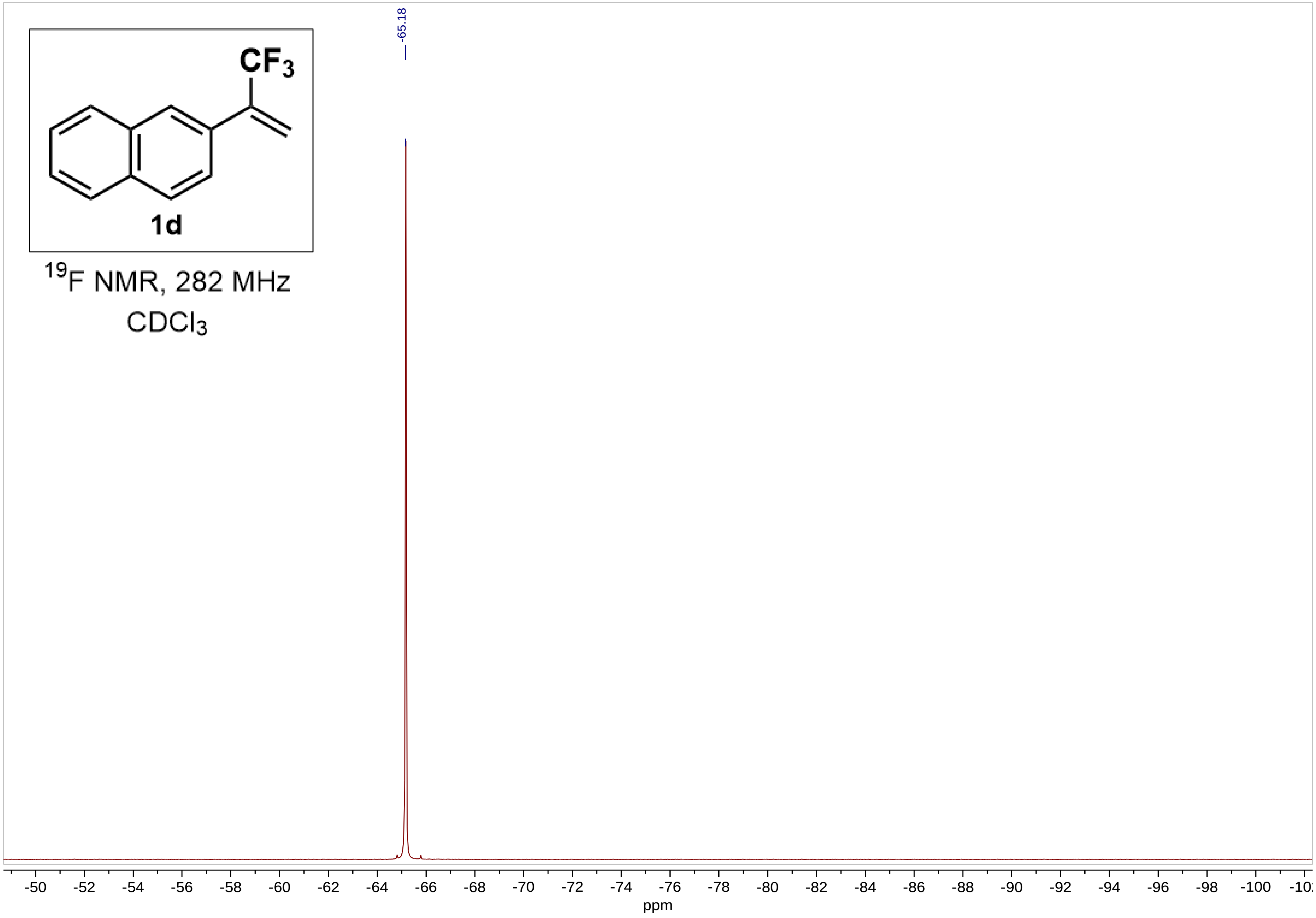


1d

^{1}H NMR, 300 MHz

$CDCl_3$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1d
^{19}F NMR, 282 MHz
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-98
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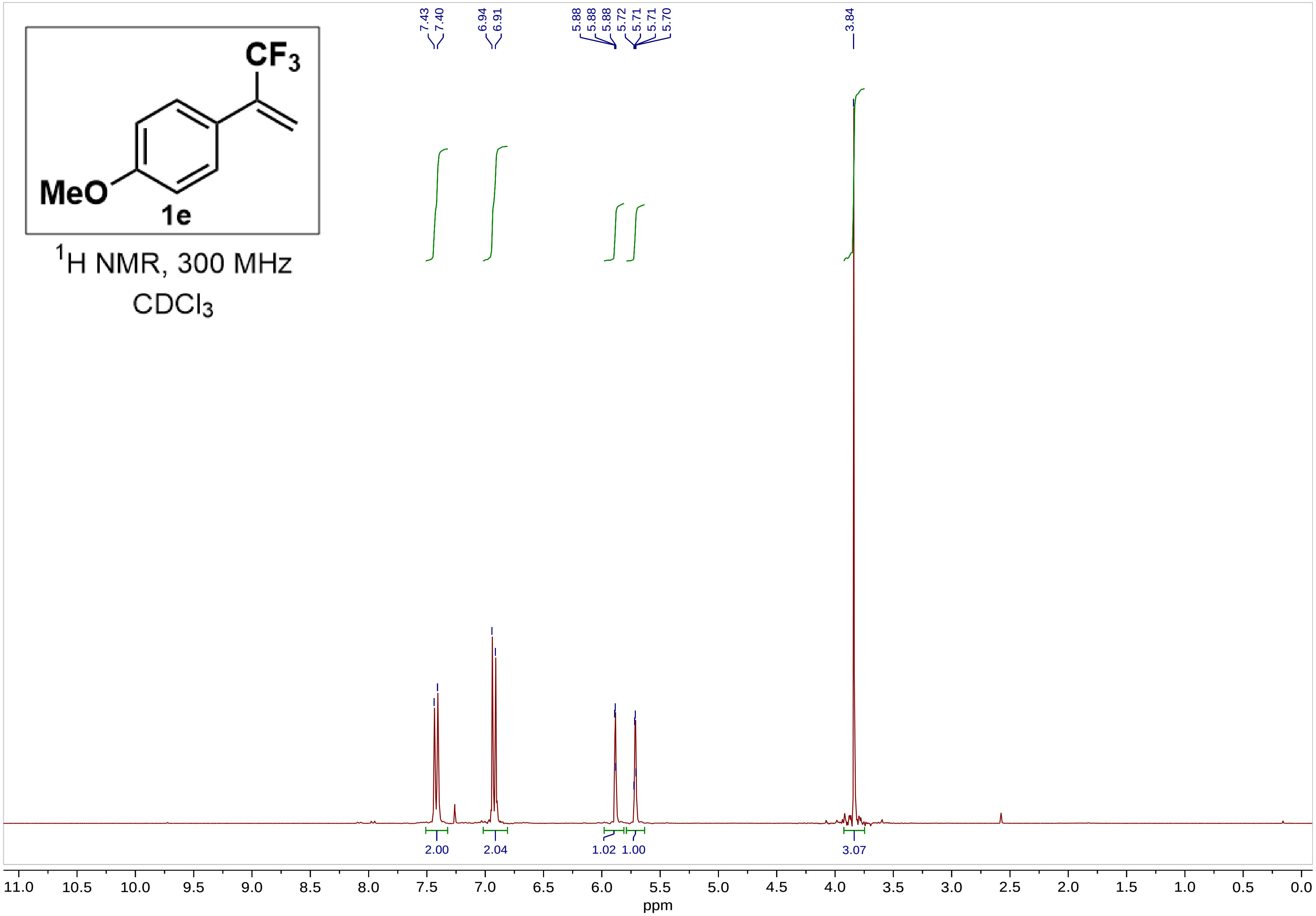
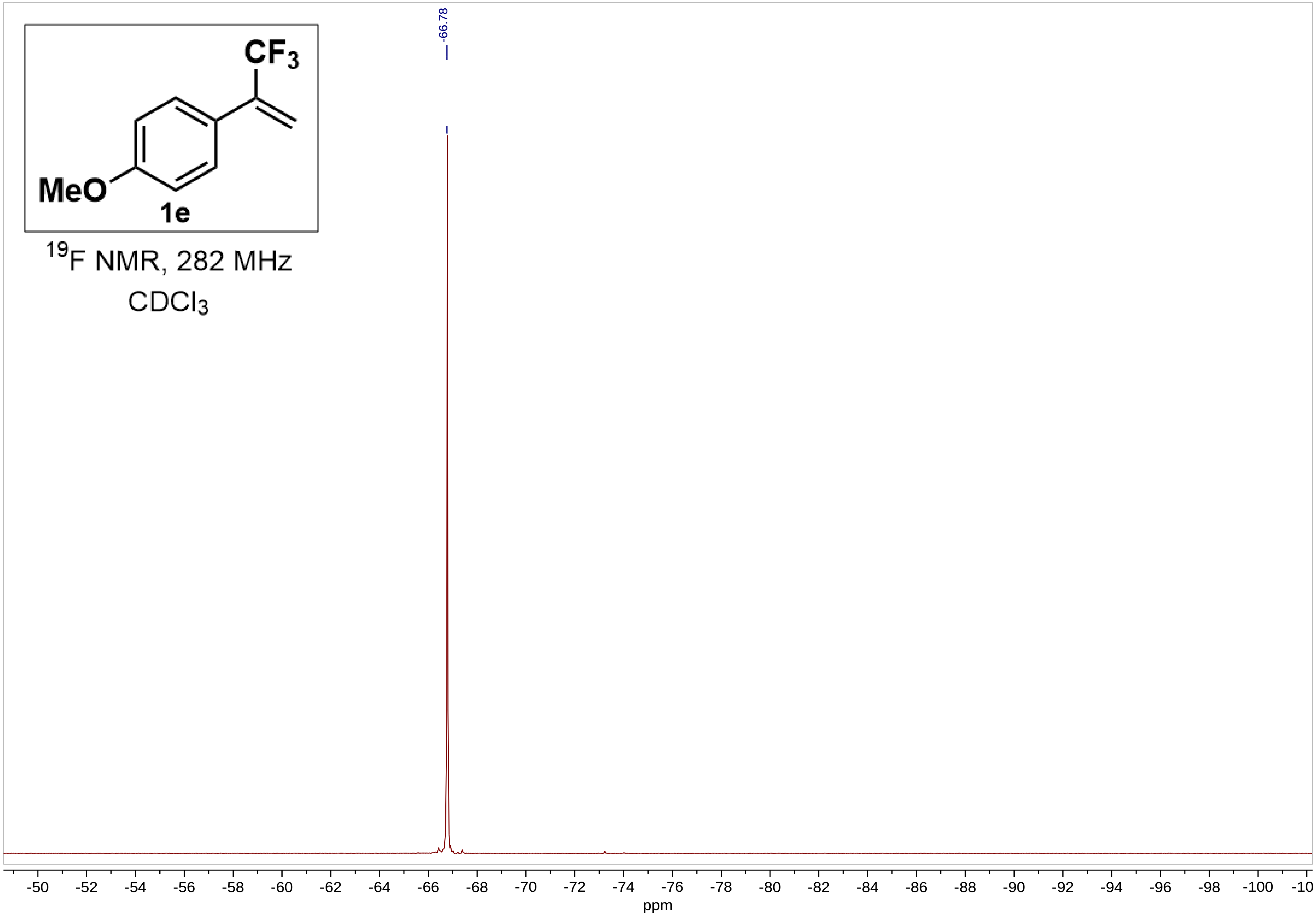
ppm



1e

^{1}H NMR, 300 MHz

CDCl$_3$


-66.78
CF3
MeO
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19F NMR, 282 MHz
CDCl3
-50
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-56
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-66
-68
-70
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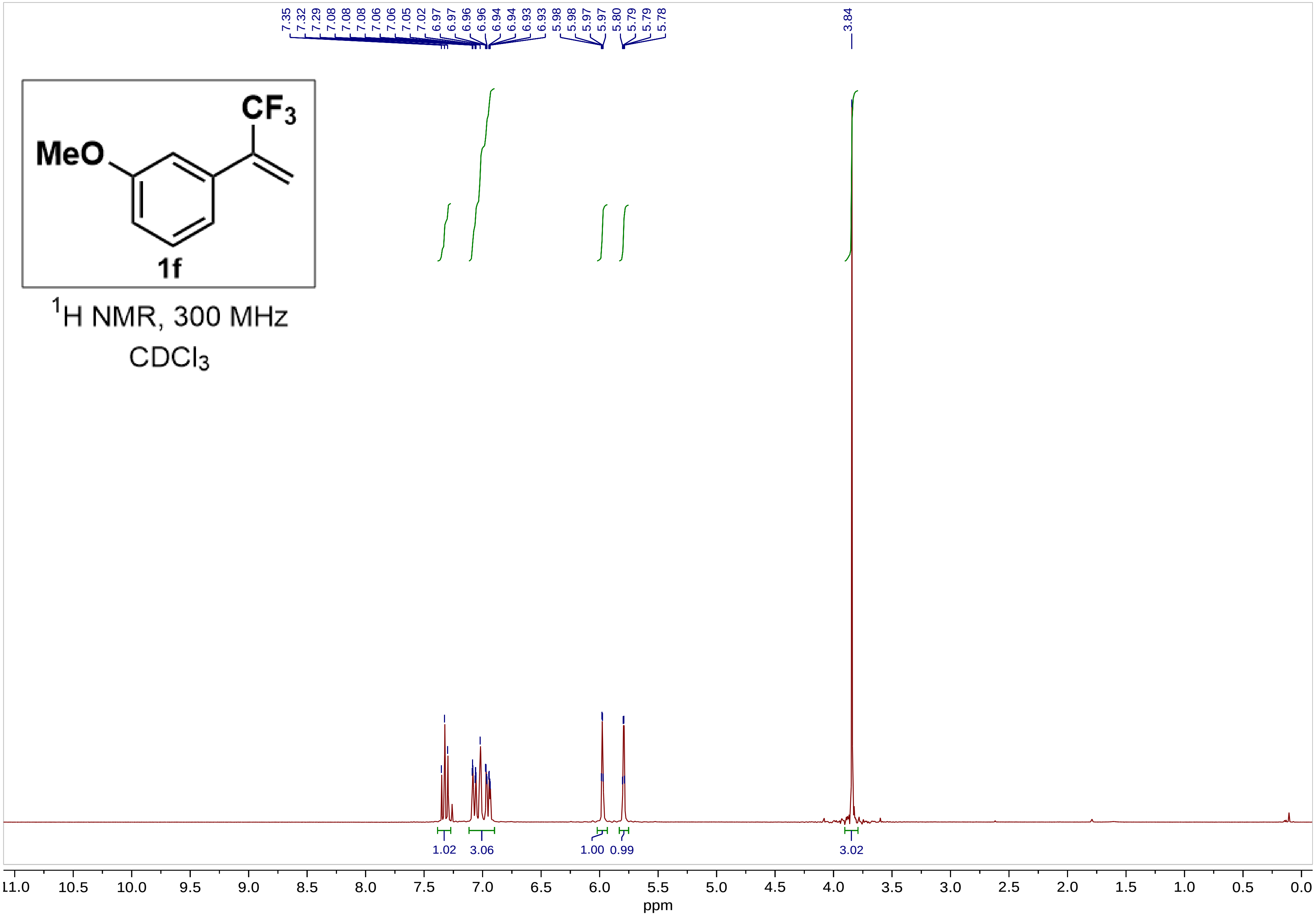
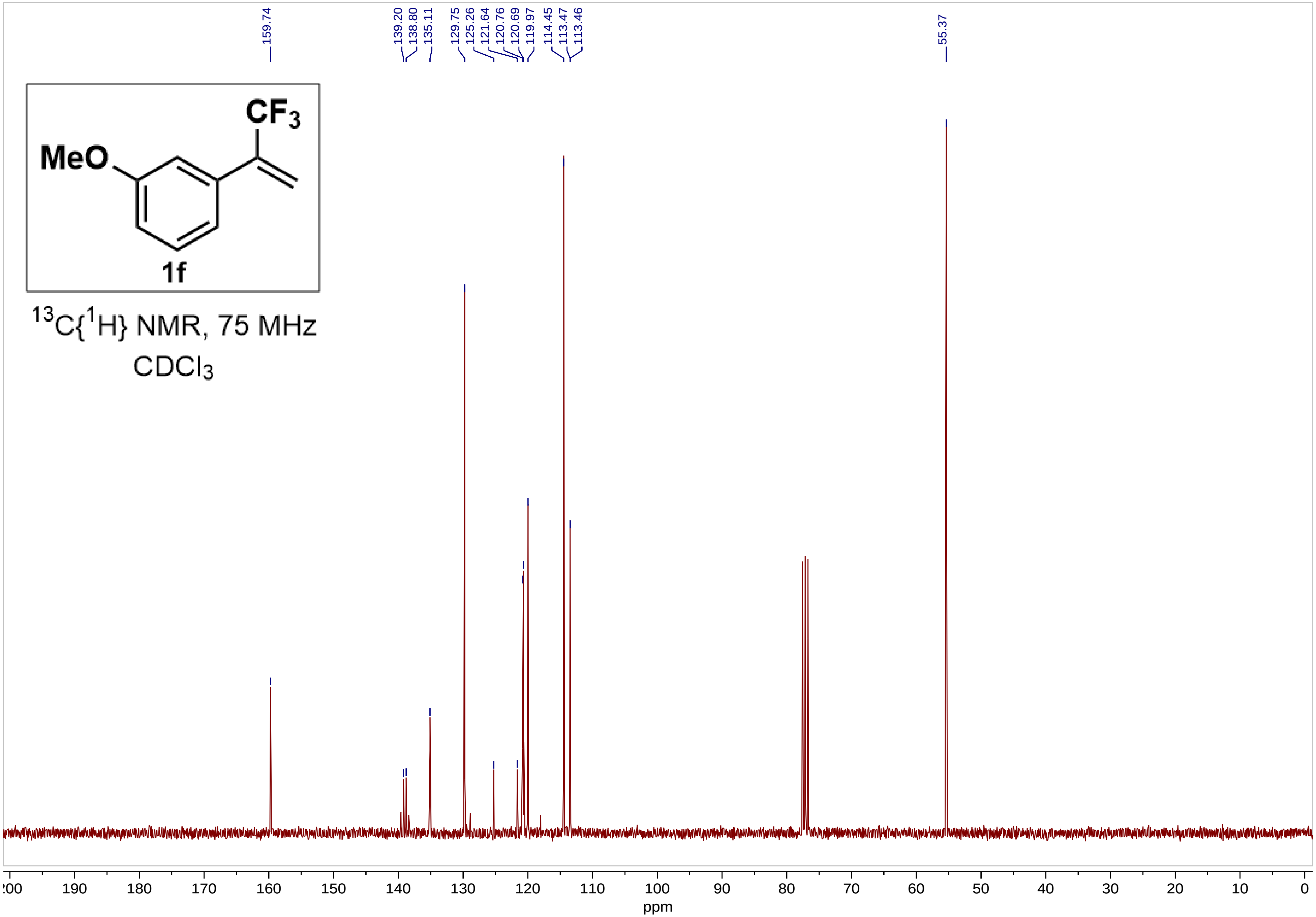
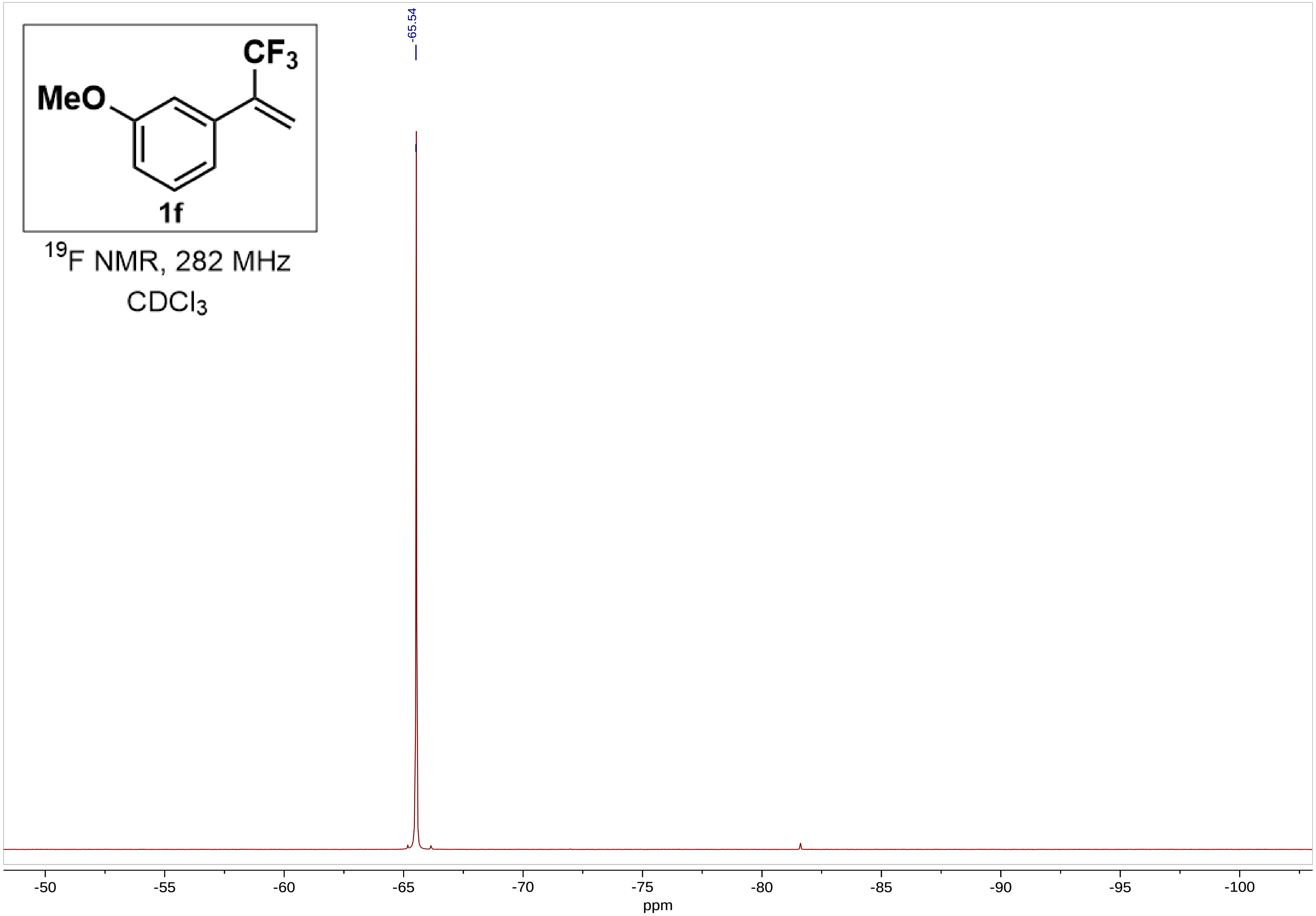
ppm


7.35
7.32
7.29
7.08
7.08
7.06
7.06
7.05
7.02
6.97
6.97
6.96
6.96
6.94
6.94
6.93
6.93
5.98
5.98
5.97
5.97
5.80
5.79
5.79
5.78
3.84
MeO
CF$_3$
1f
^{1}H NMR, 300 MHz
CDCl$_3$
1.02
3.06
1.00
0.99
3.02
11.0
10.5
10.0
9.5
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
ppm

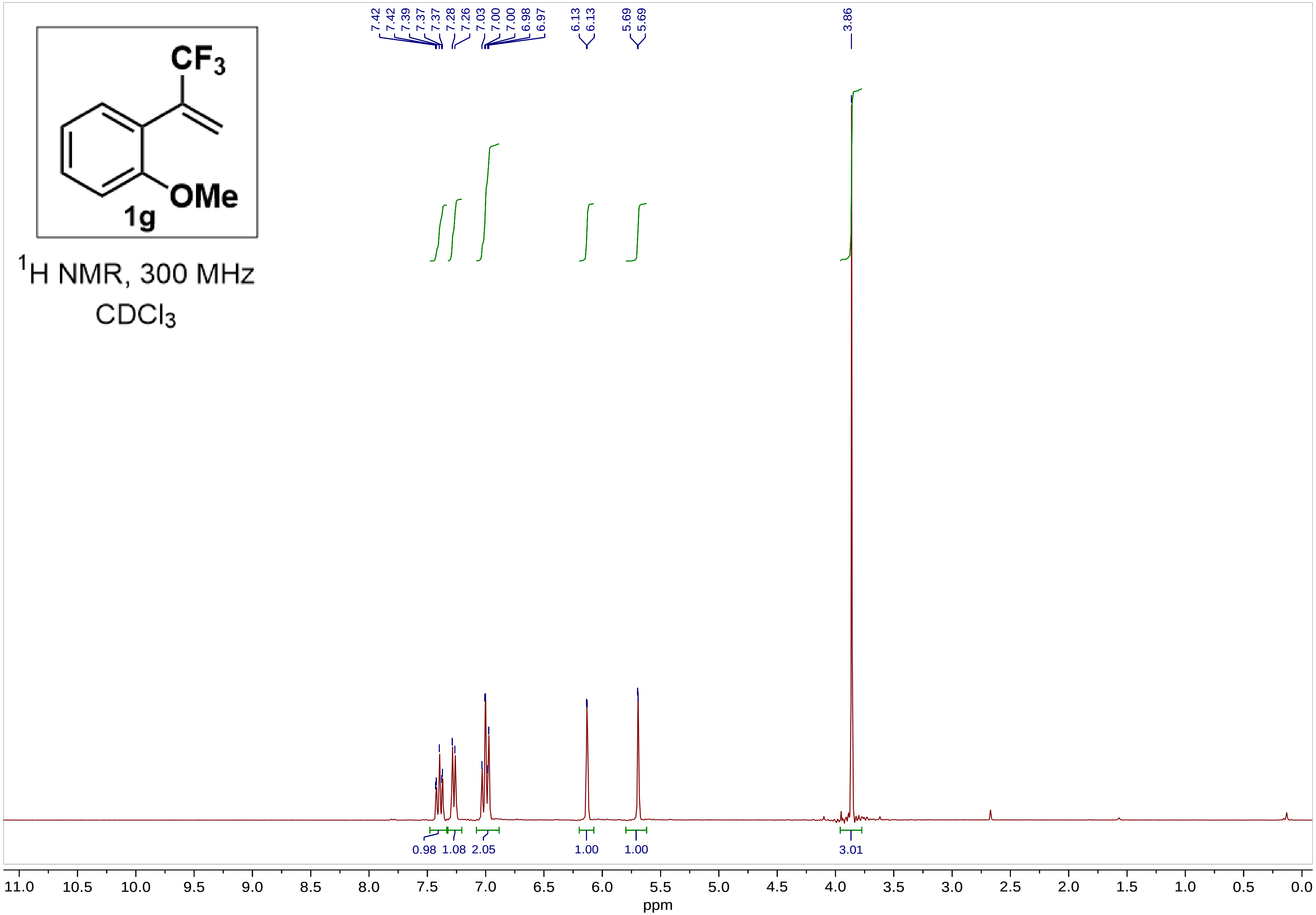

159.74
139.20
138.80
135.11
129.75
125.26
121.64
120.76
120.69
119.97
114.45
113.47
113.46
55.37
CF3
MeO
1f
13C{1H} NMR, 75 MHz
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

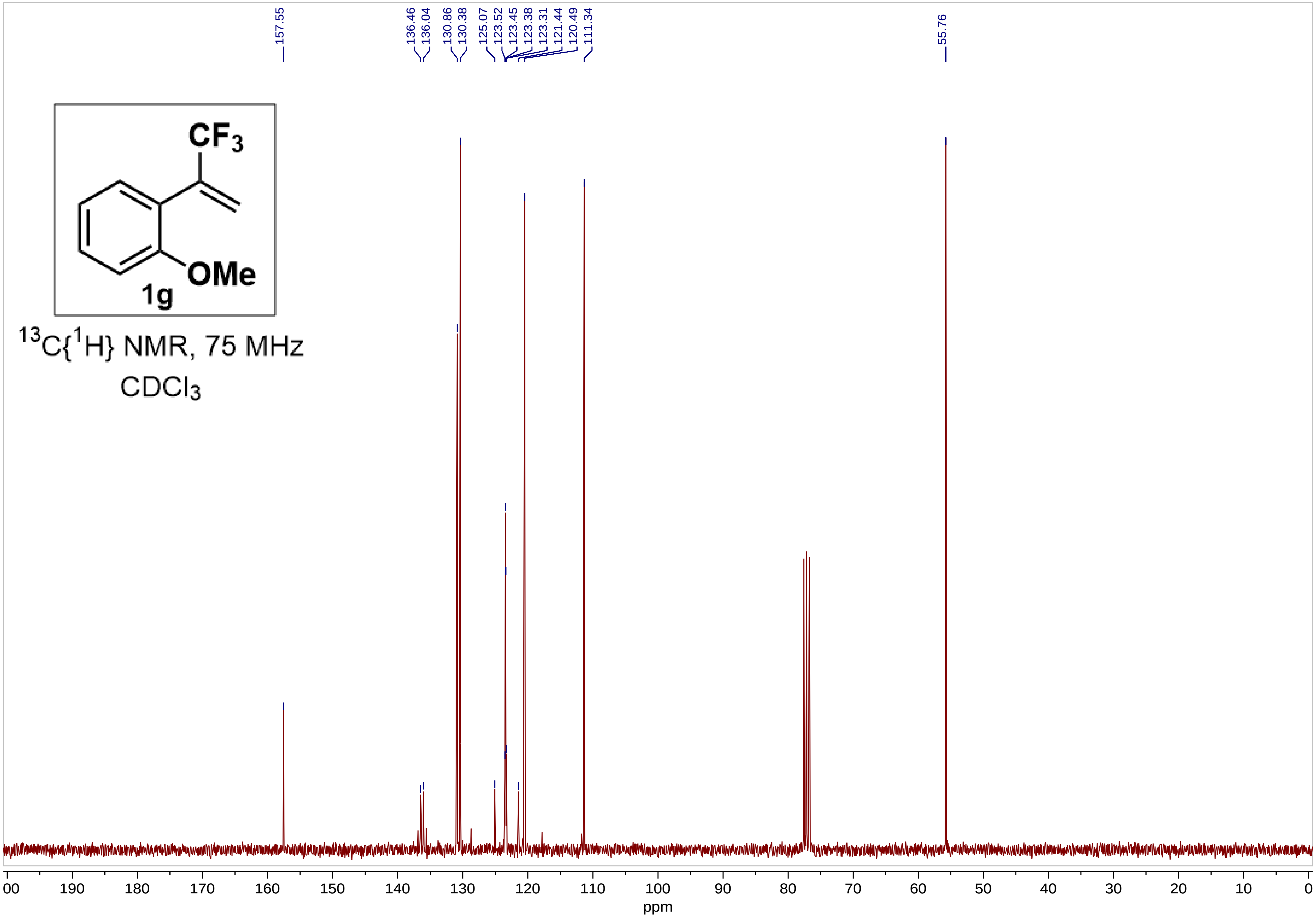

CF3
MeO
1f
^{19}F NMR, 282 MHz
$CDCl_3$
-65.54
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
ppm

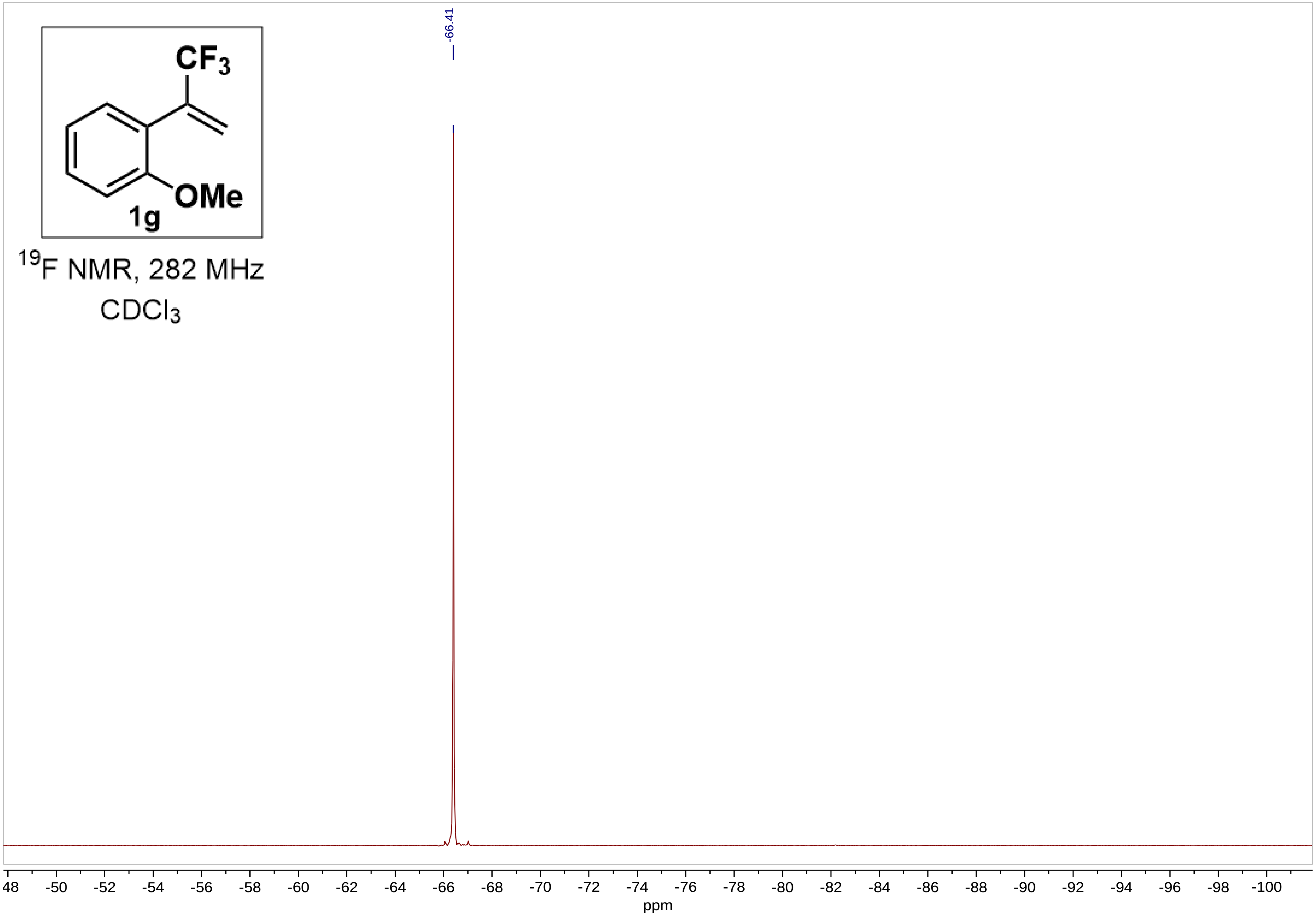
1g

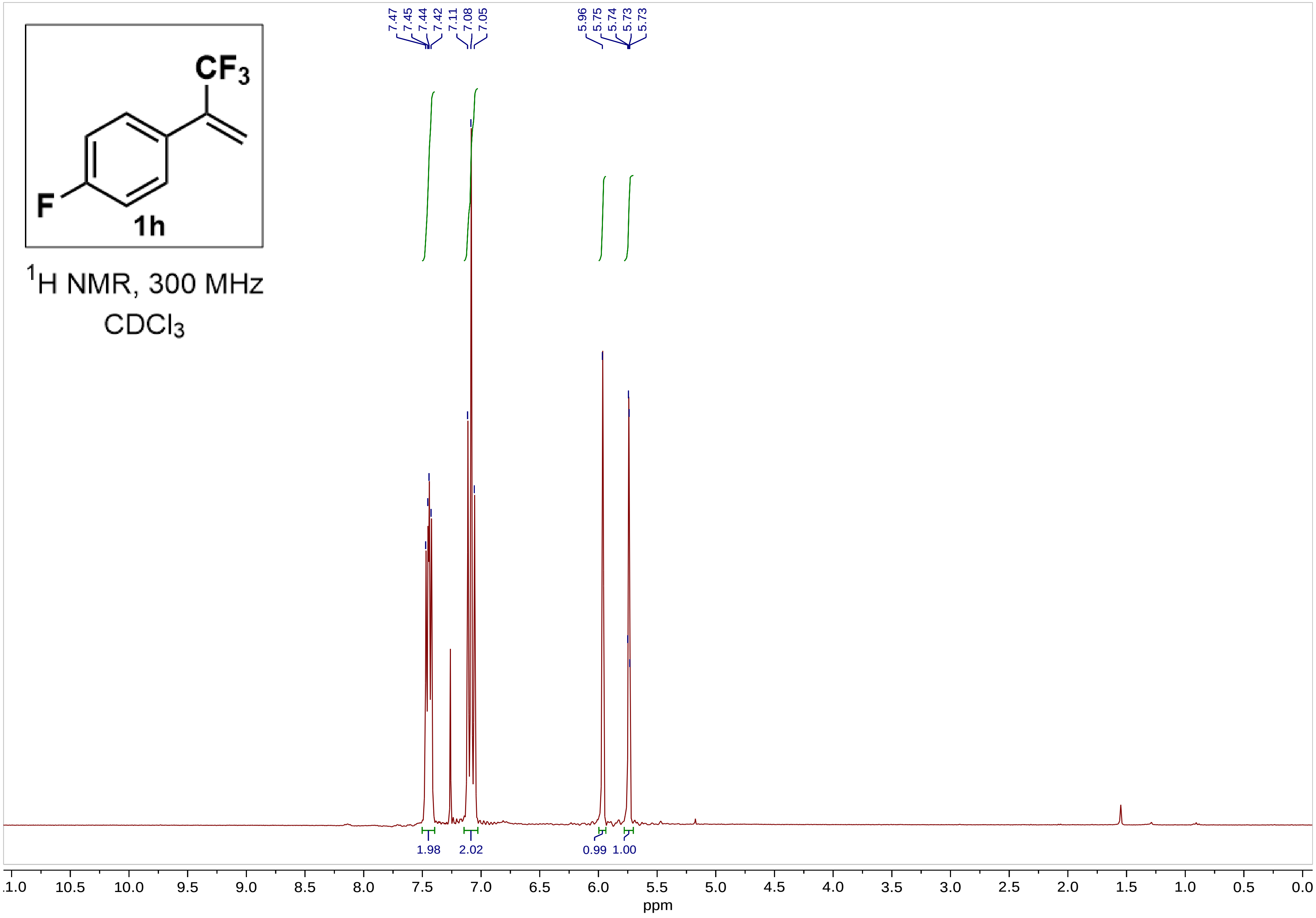
^{1}H NMR, 300 MHz

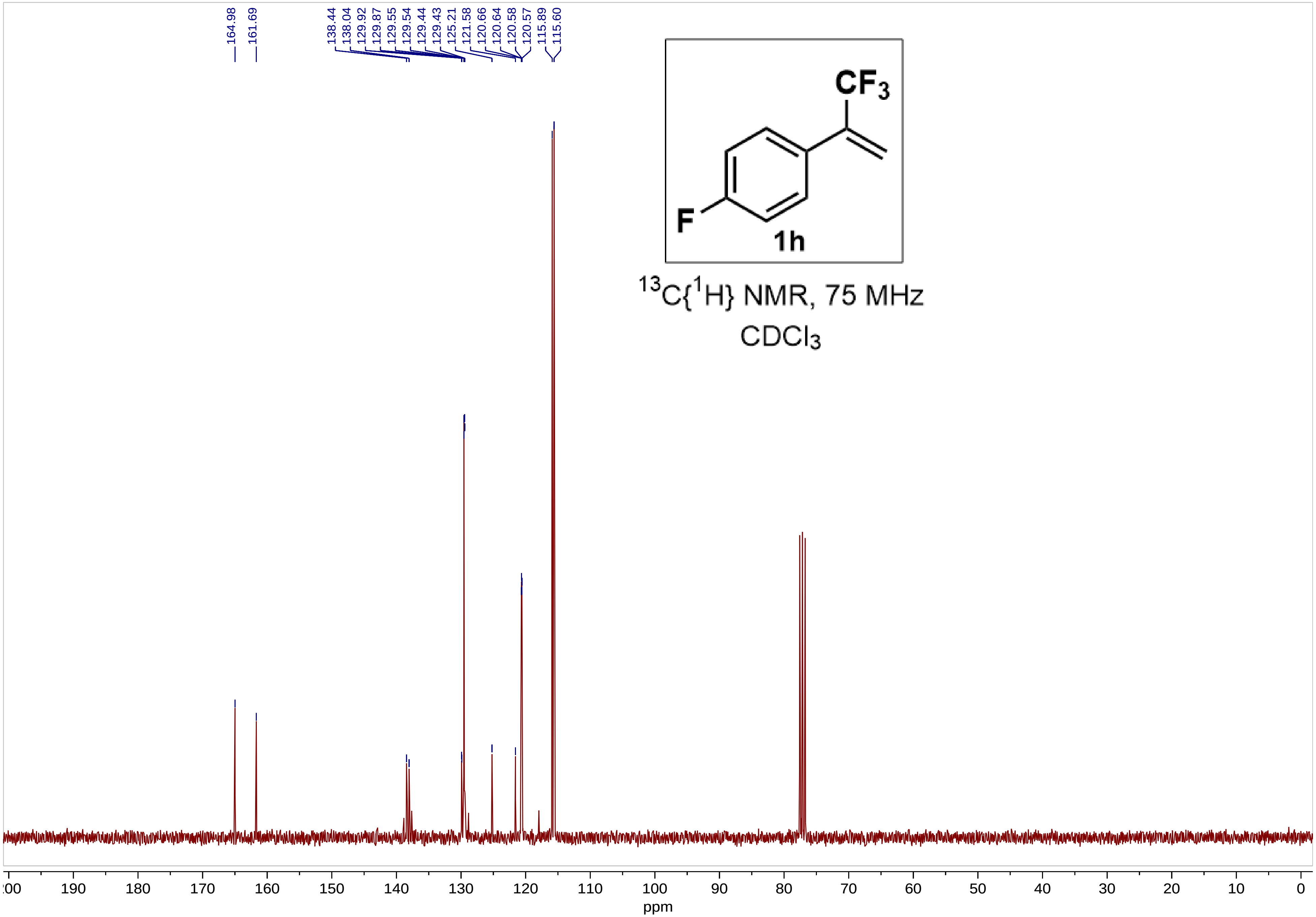
$CDCl_3$

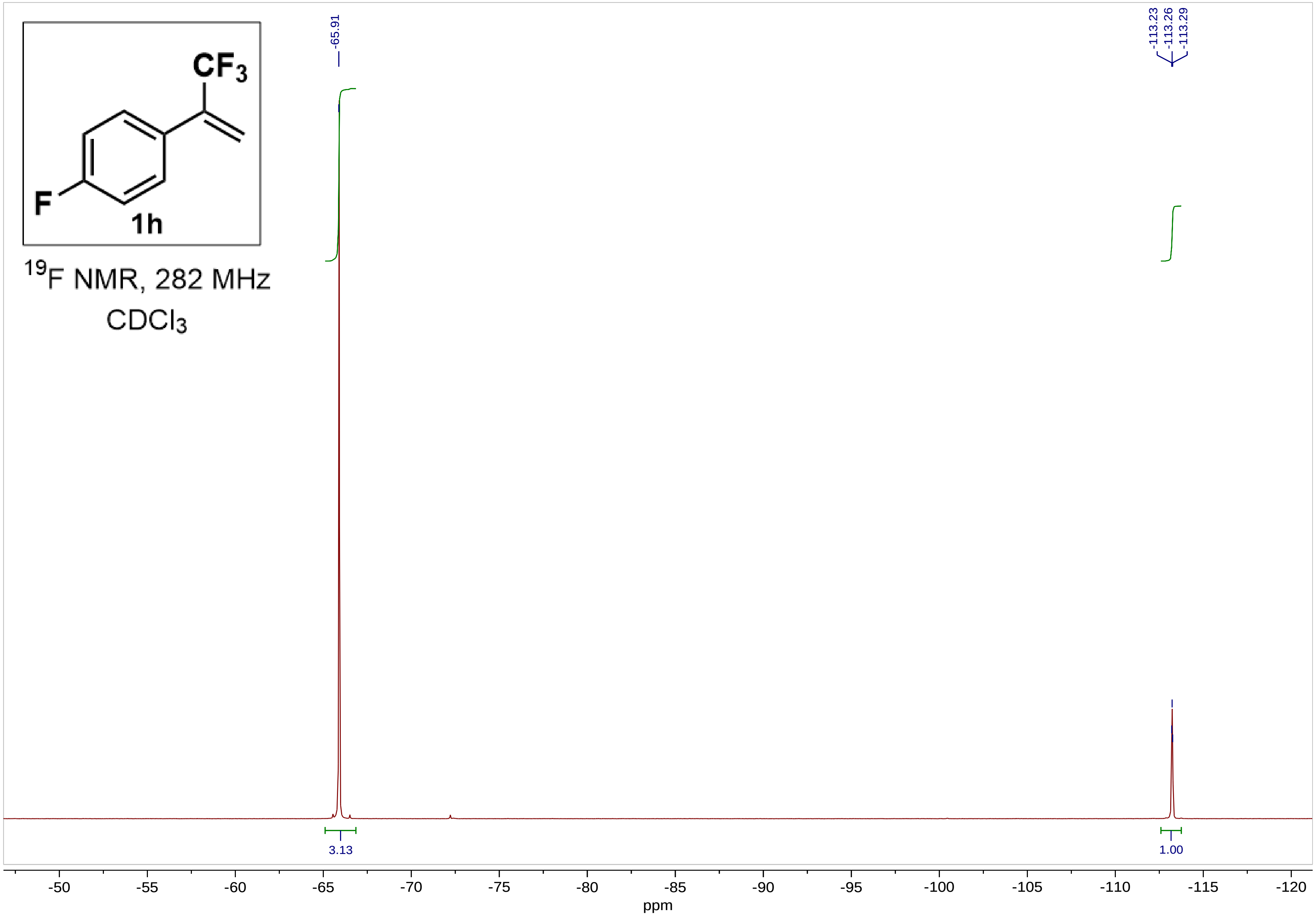


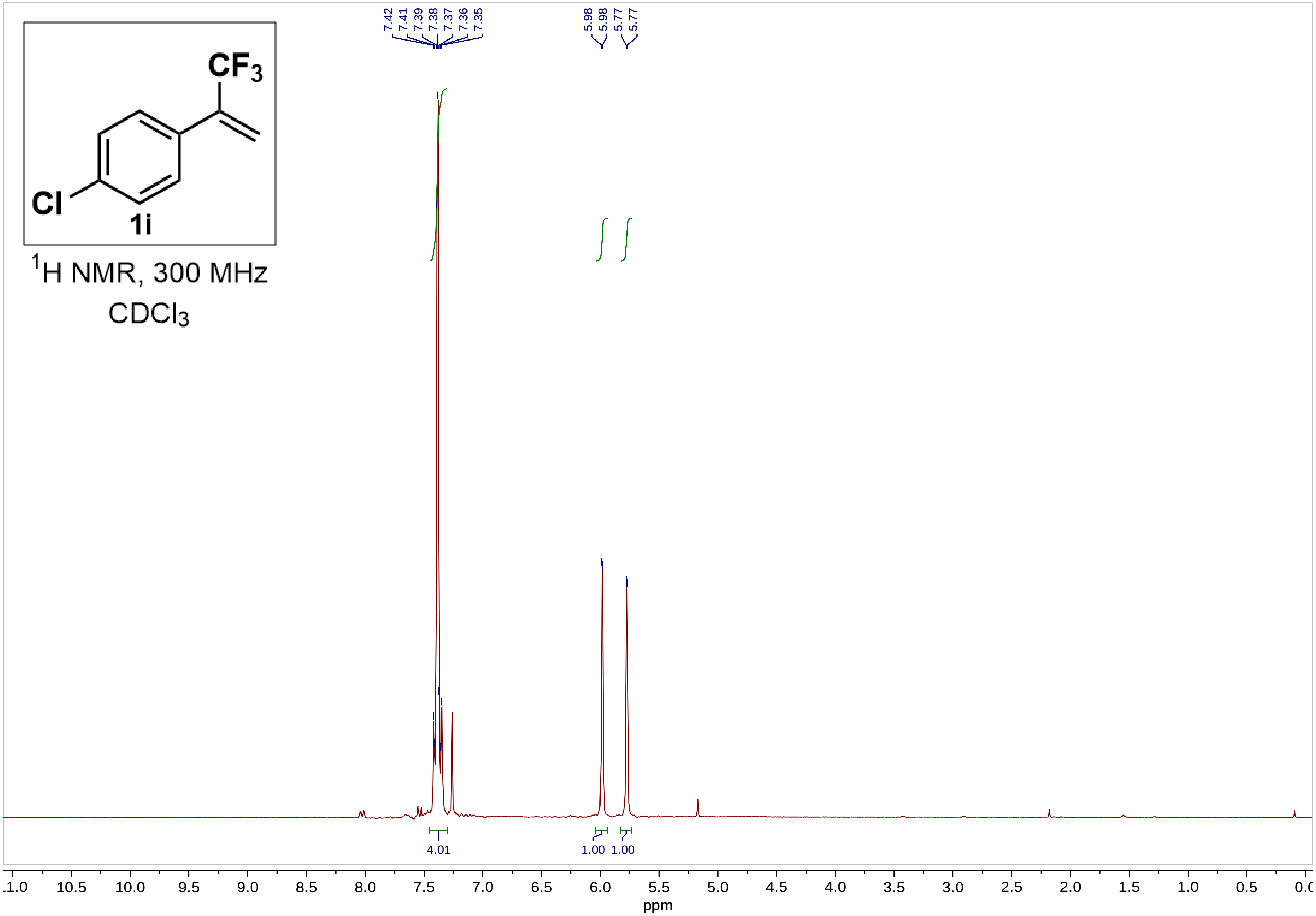

157.55
136.46
136.04
130.86
130.38
125.07
123.52
123.45
123.38
123.31
121.44
120.49
111.34
55.76
CF3
OMe
1g
13C{1H} NMR, 75 MHz
CDCl3
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-66.41
CF3
OMe
1g
19F NMR, 282 MHz
CDCl3
48
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
ppm


CF3
F
1h
1H NMR, 300 MHz
CDCl3
7.47
7.45
7.44
7.42
7.11
7.08
7.05
5.96
5.75
5.74
5.73
5.73
1.98
2.02
0.99
1.00
.1.0
10.5
10.0
9.5
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
ppm


164.98
161.69
138.44
138.04
129.92
129.87
129.55
129.54
129.44
129.43
125.21
121.58
120.66
120.64
120.58
120.57
115.89
115.60
CF3
F
1h
13C{1H} NMR, 75 MHz
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

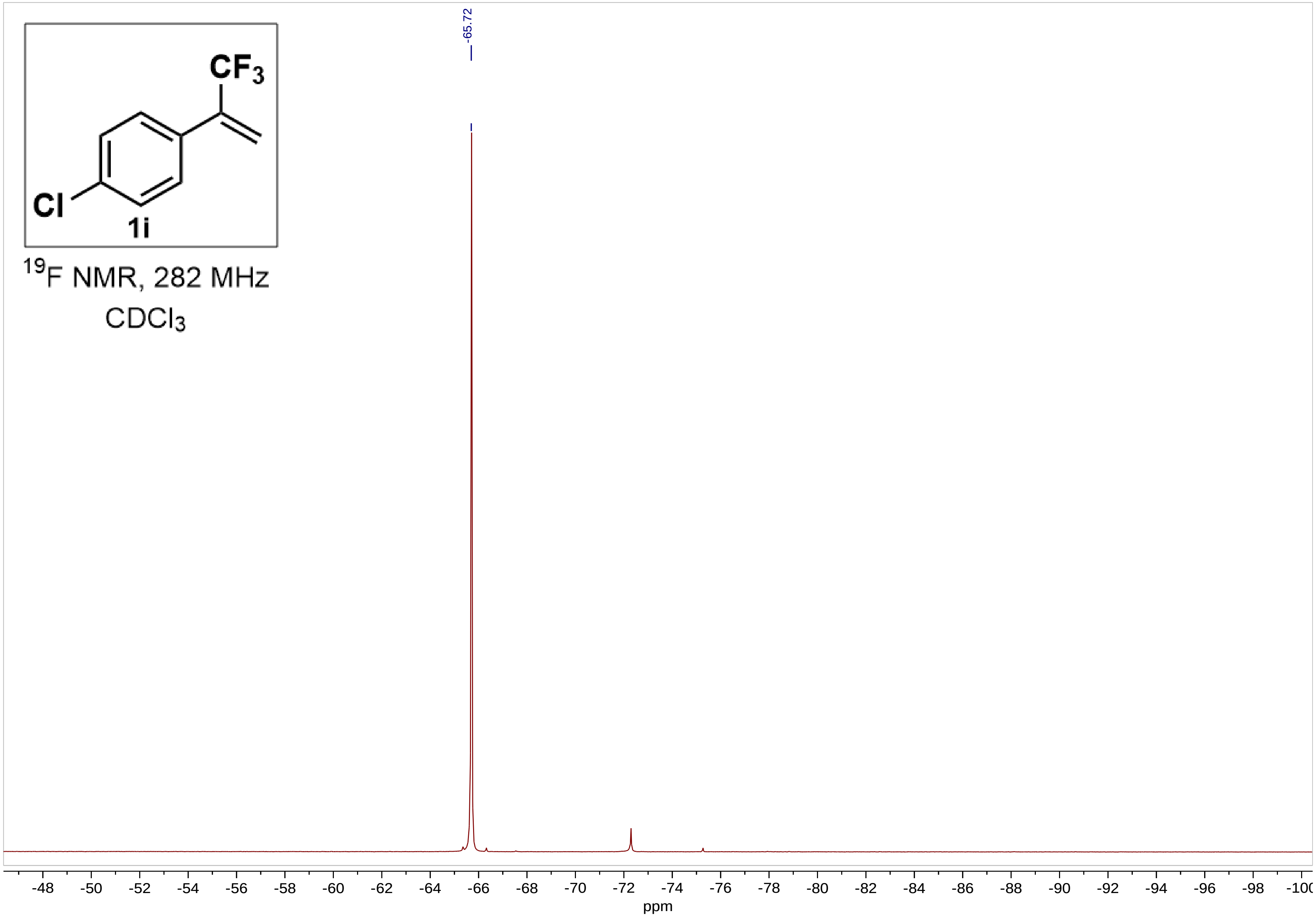

CF$_3$
F
1h
^{19}F NMR, 282 MHz
CDCl$_3$
-65.91
-113.23
-113.26
-113.29
3.13
1.00
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
ppm



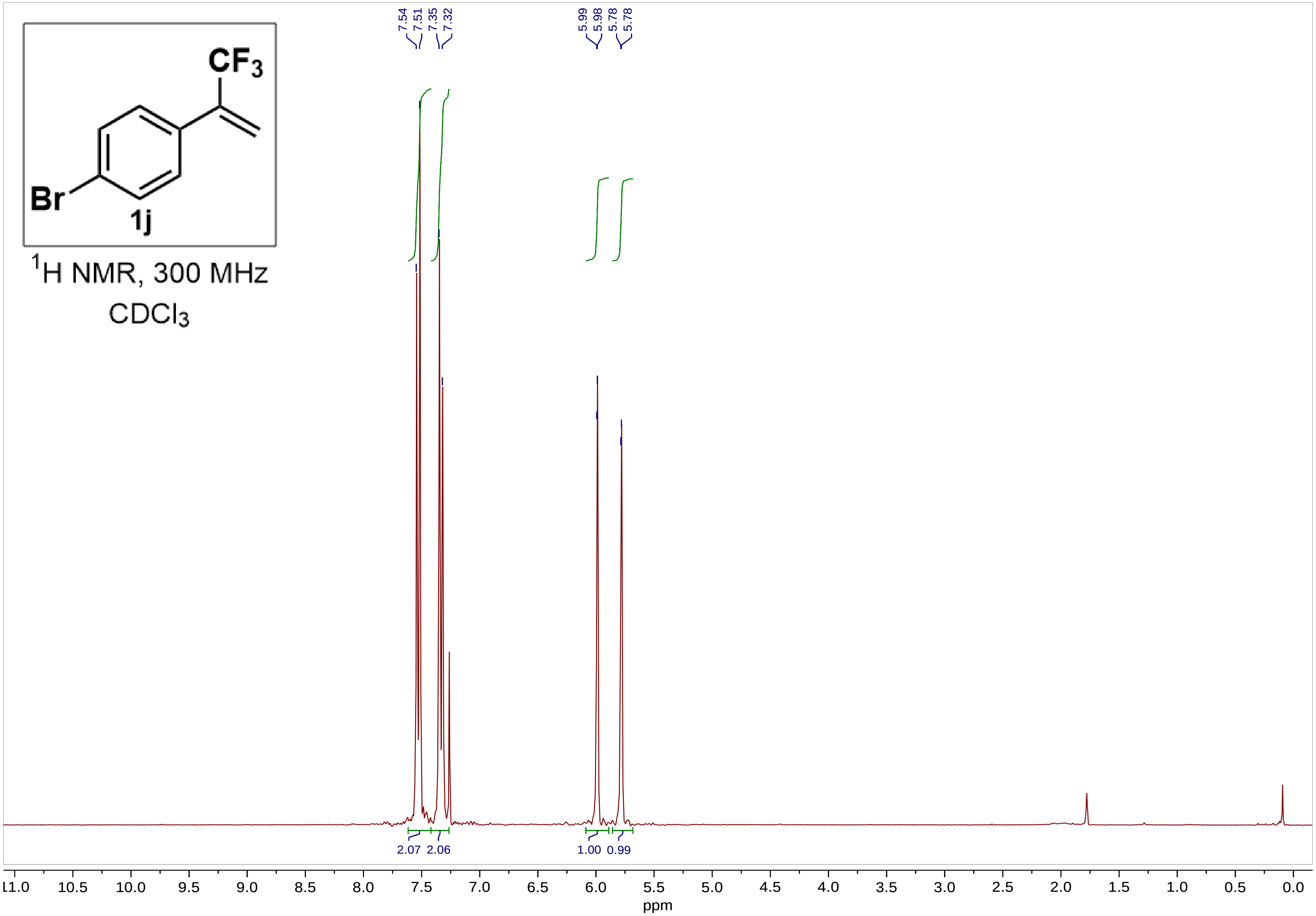
1i

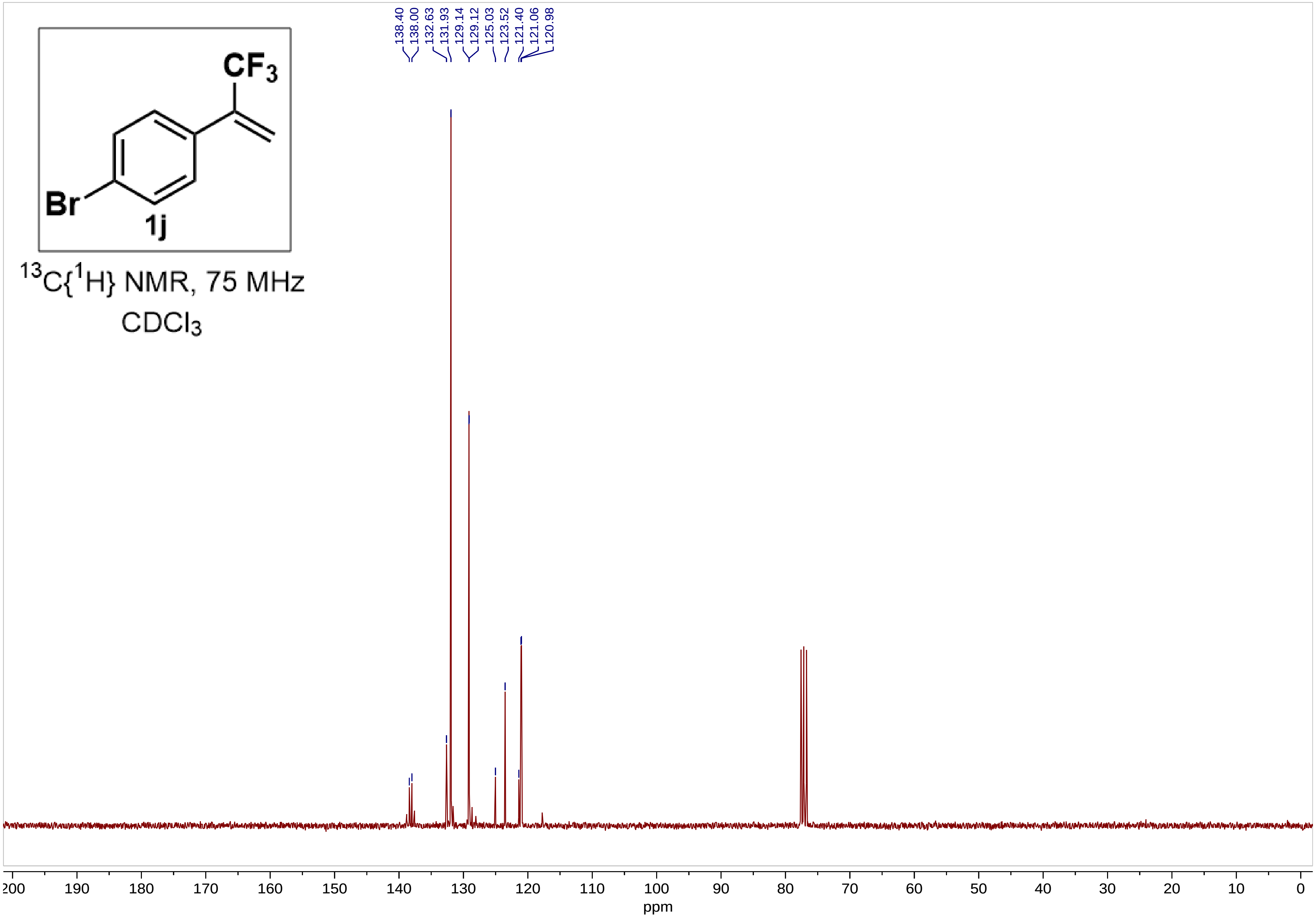
^{1}H NMR, 300 MHz

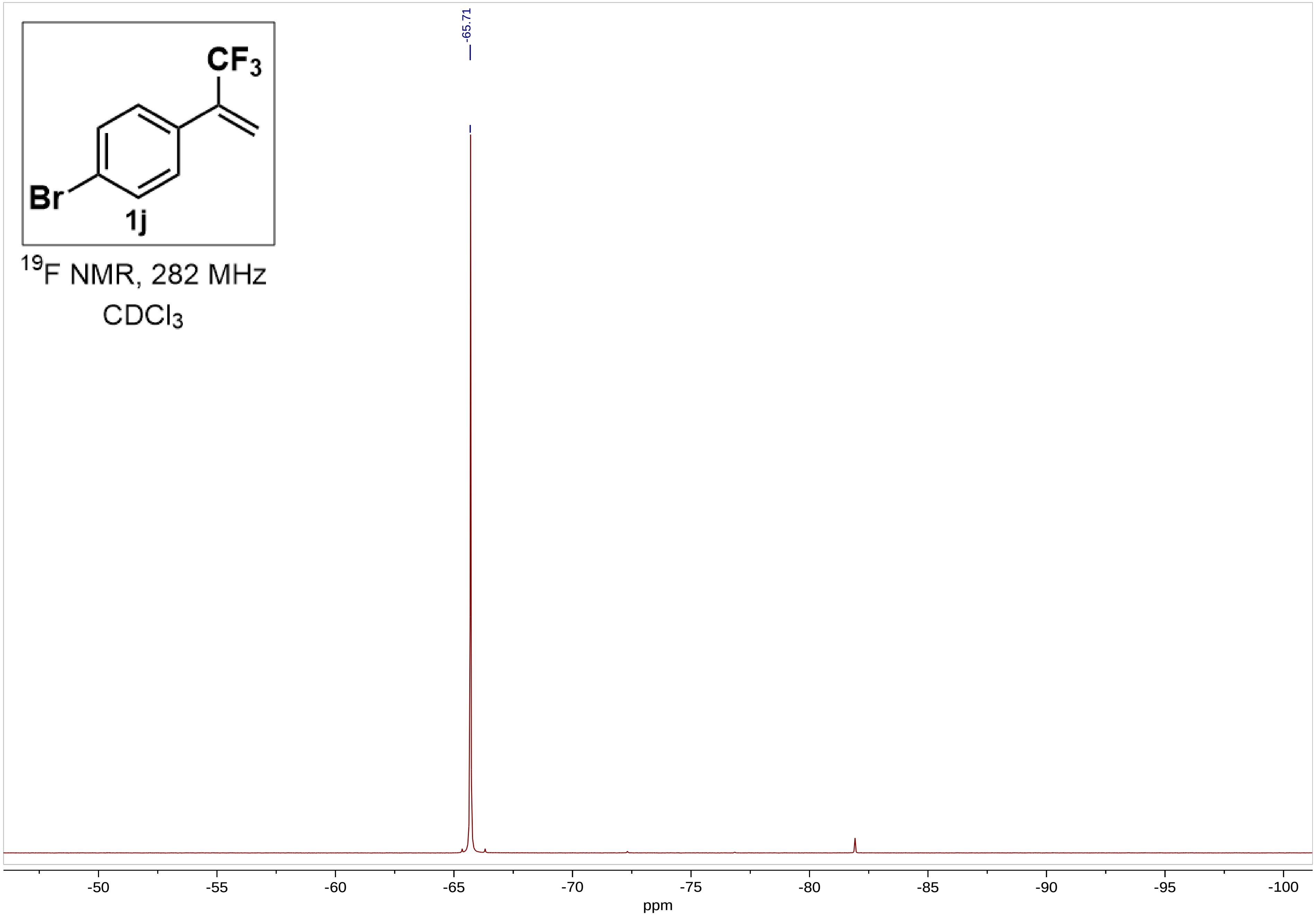
$CDCl_3$

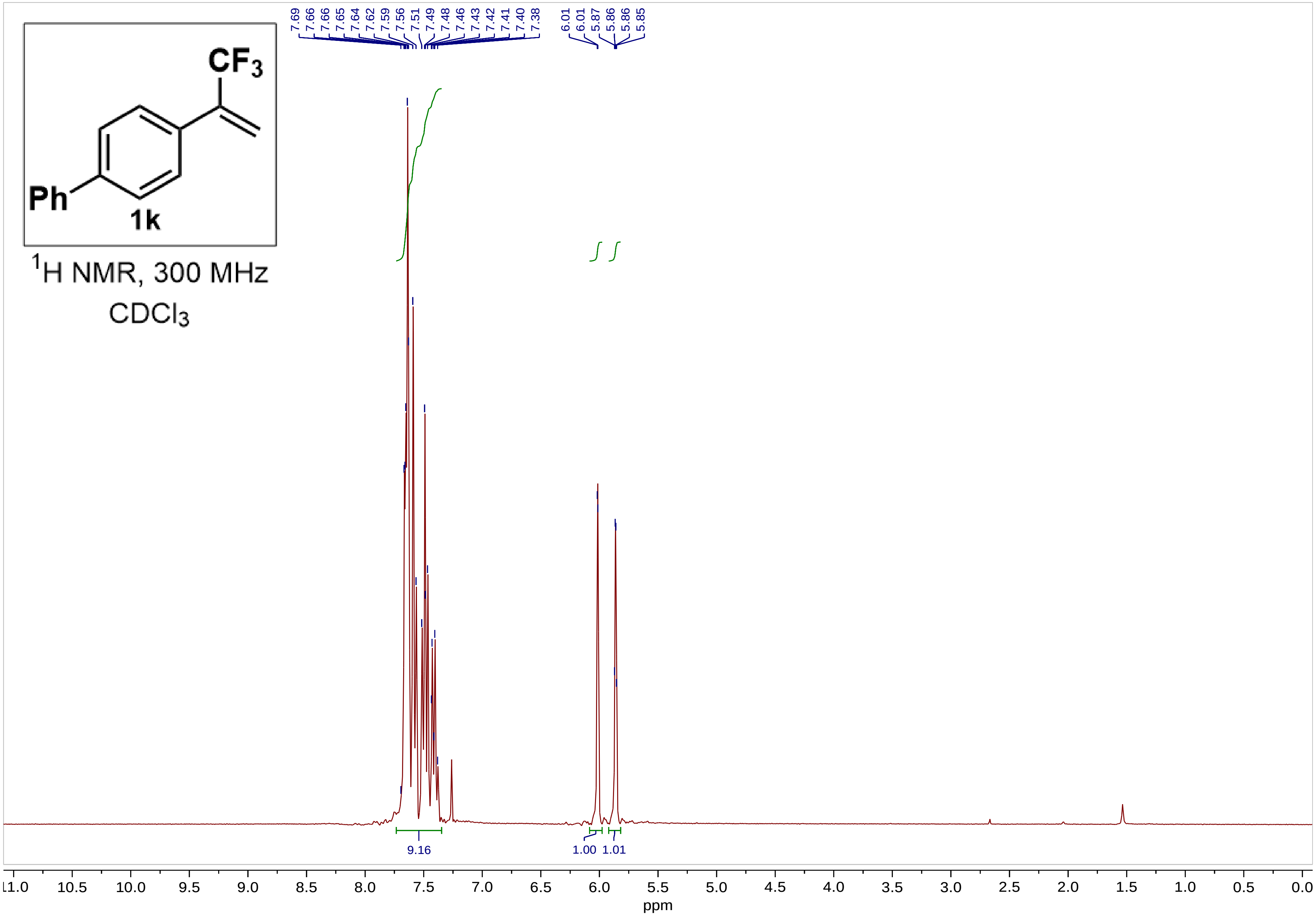


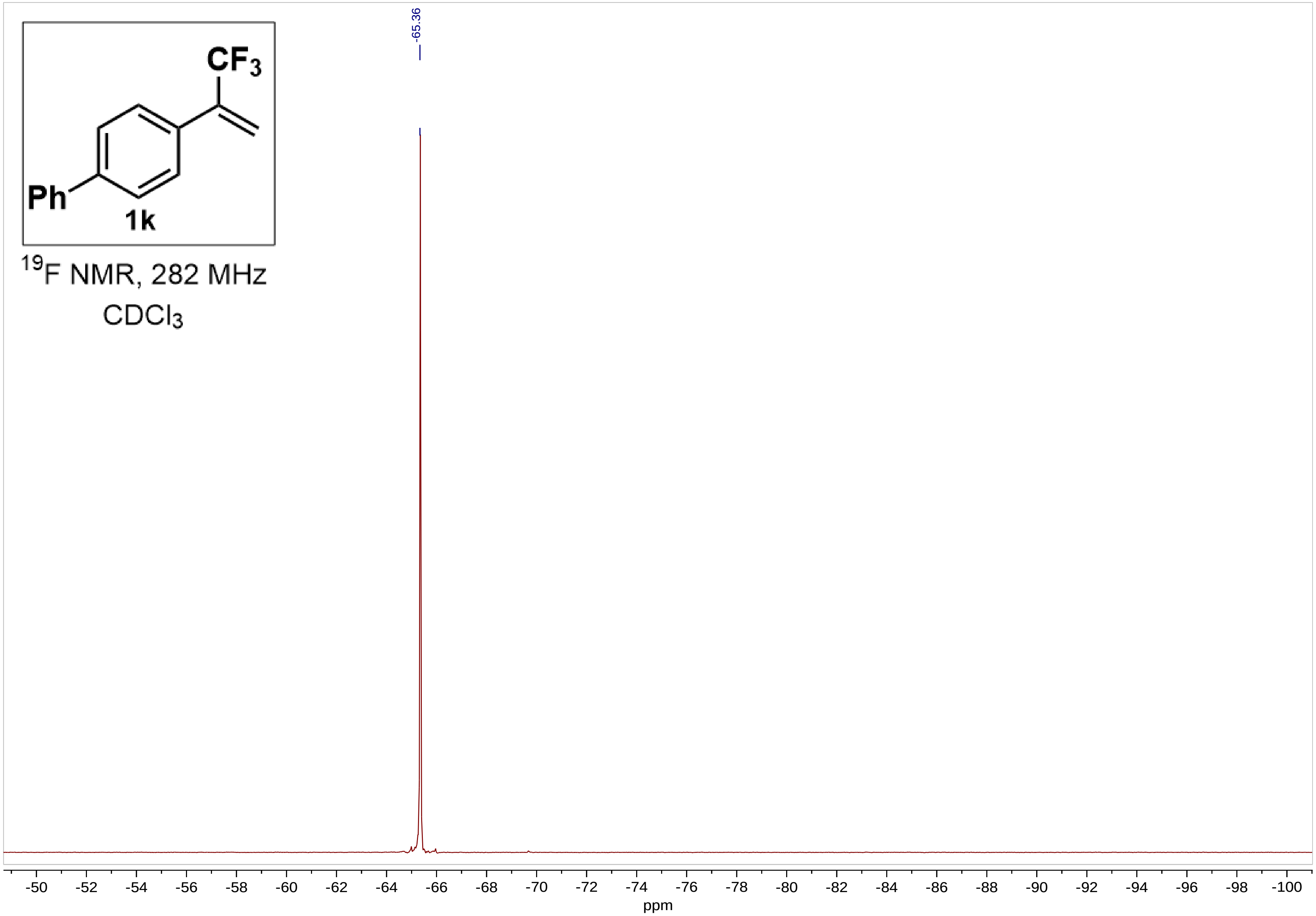
CF3
Cl
1i
^{19}F NMR, 282 MHz
CDCl$_3$
-65.72
-48
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
ppm

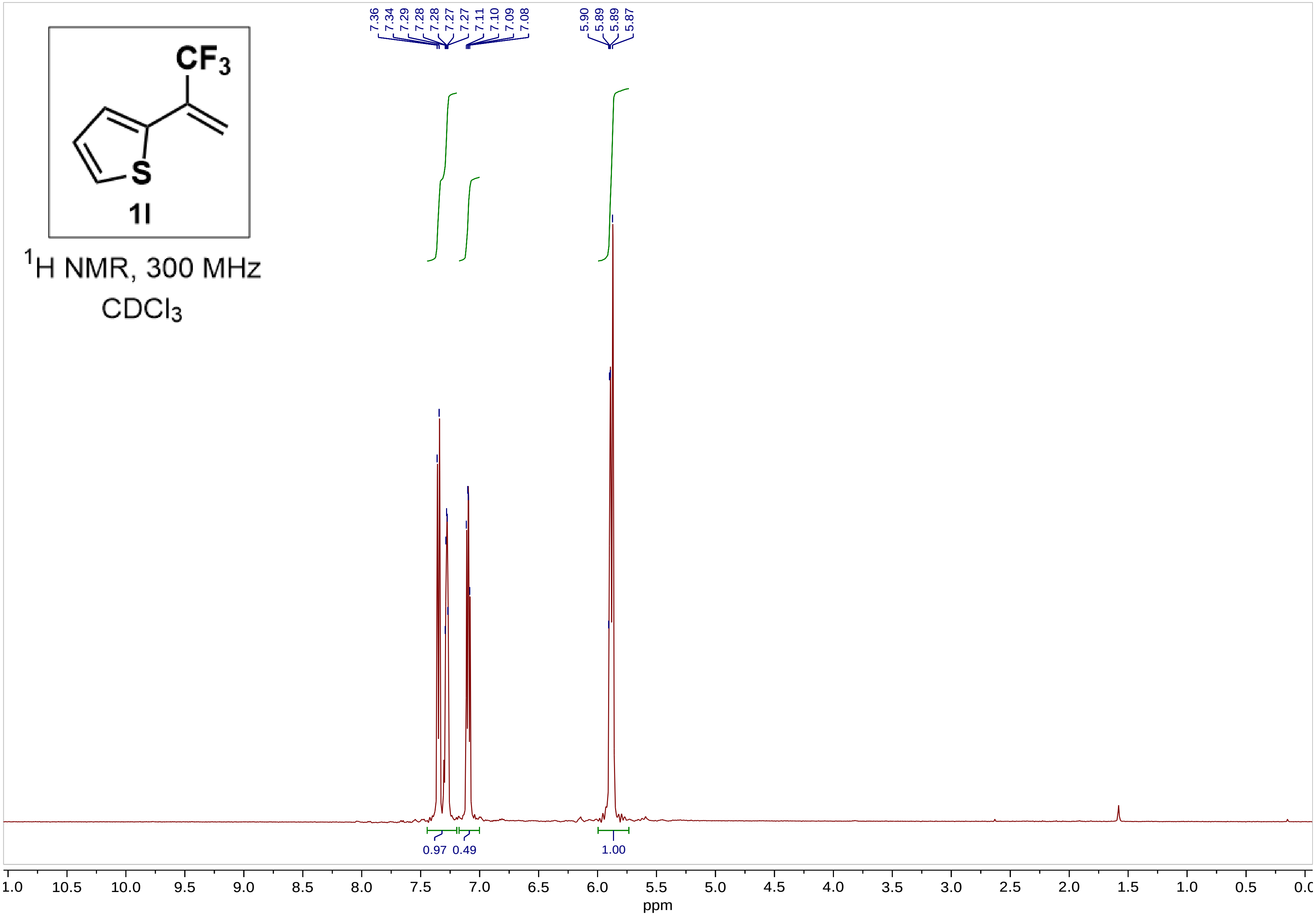

CF3
Br
1j
1H NMR, 300 MHz
CDCl3
7.54
7.51
7.35
7.32
5.99
5.98
5.78
5.78
2.07
2.06
1.00
0.99
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

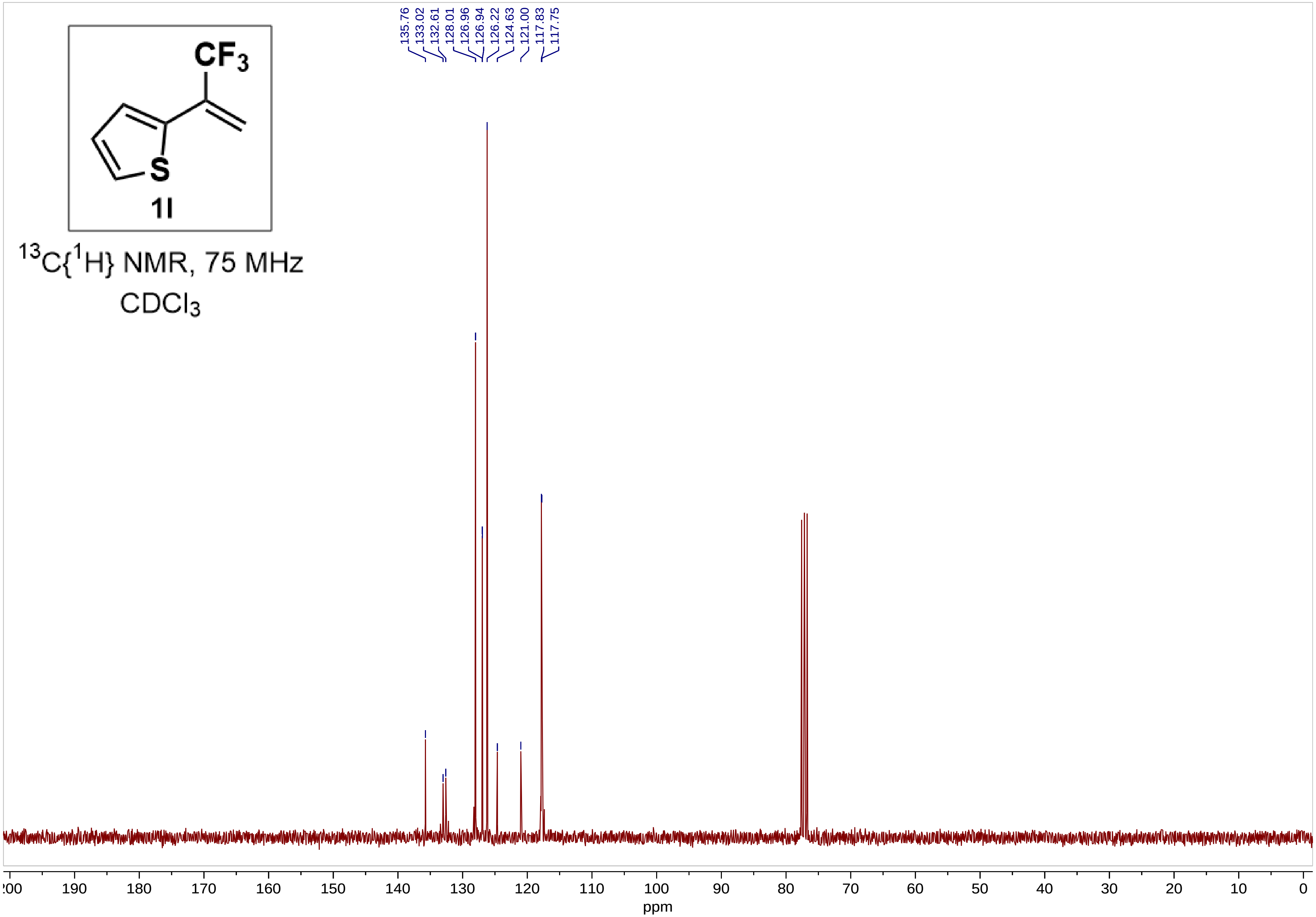

CF3
Br
1j
13C{1H} NMR, 75 MHz
CDCl3
138.40
138.00
132.63
131.93
129.14
129.12
125.03
123.52
121.40
121.06
120.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


CF3
Br
1j
19F NMR, 282 MHz
CDCl3
-65.71
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
ppm


CF3
Ph
1k
1H NMR, 300 MHz
CDCl3
7.69
7.66
7.66
7.65
7.64
7.62
7.59
7.56
7.51
7.49
7.48
7.46
7.43
7.42
7.41
7.40
7.38
6.01
6.01
5.87
5.86
5.86
5.85
9.16
1.00
1.01
11.0
10.5
10.0
9.5
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
ppm


CF3
Ph
1k
19F NMR, 282 MHz
CDCl3
-65.36
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
ppm

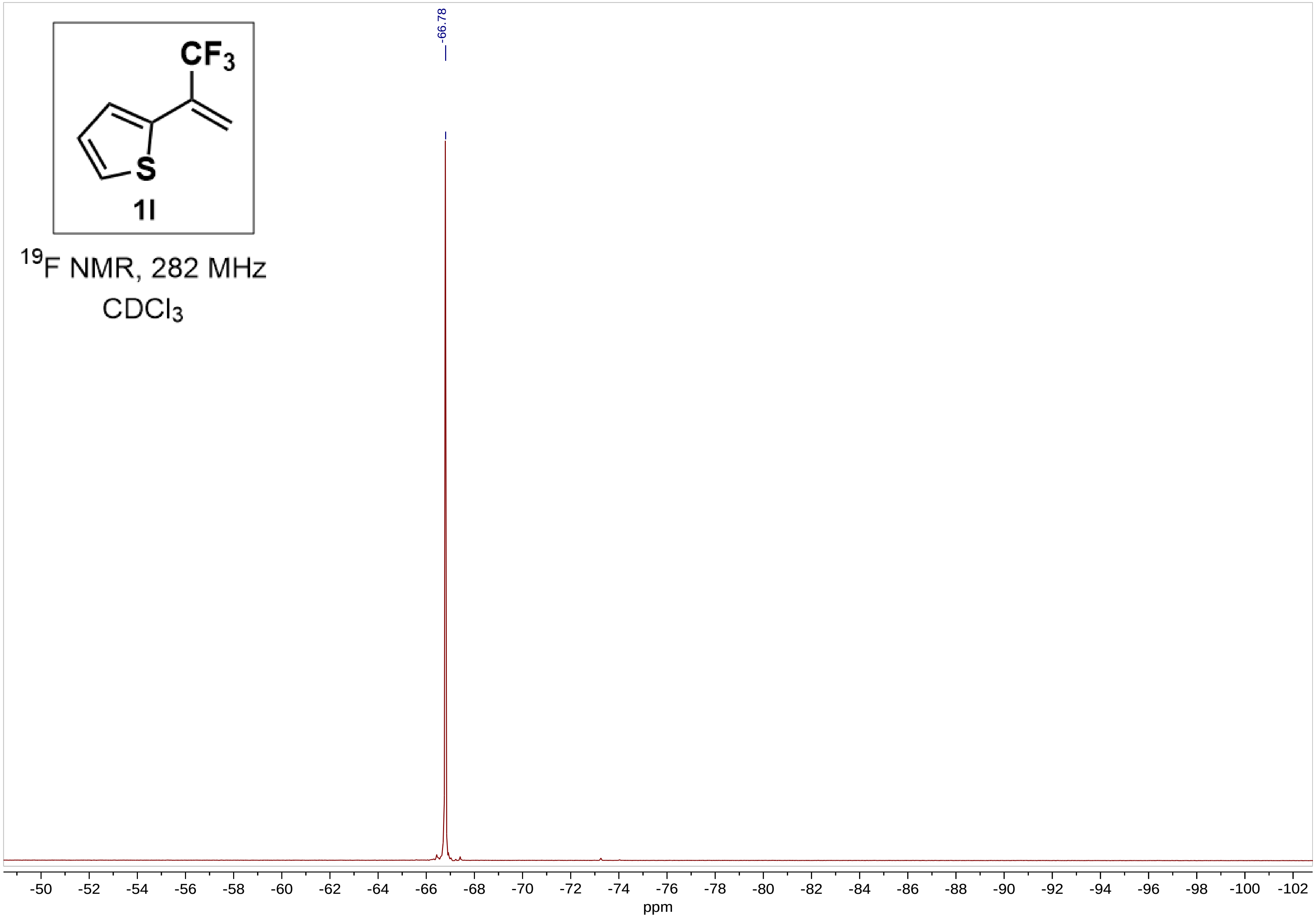

CF3
S
1l
1H NMR, 300 MHz
CDCl3
7.36
7.34
7.29
7.28
7.28
7.27
7.27
7.11
7.10
7.09
7.08
5.90
5.89
5.89
5.87
0.97
0.49
1.00
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



1l

$^{13}C\{^{1}H\}$ NMR, 75 MHz

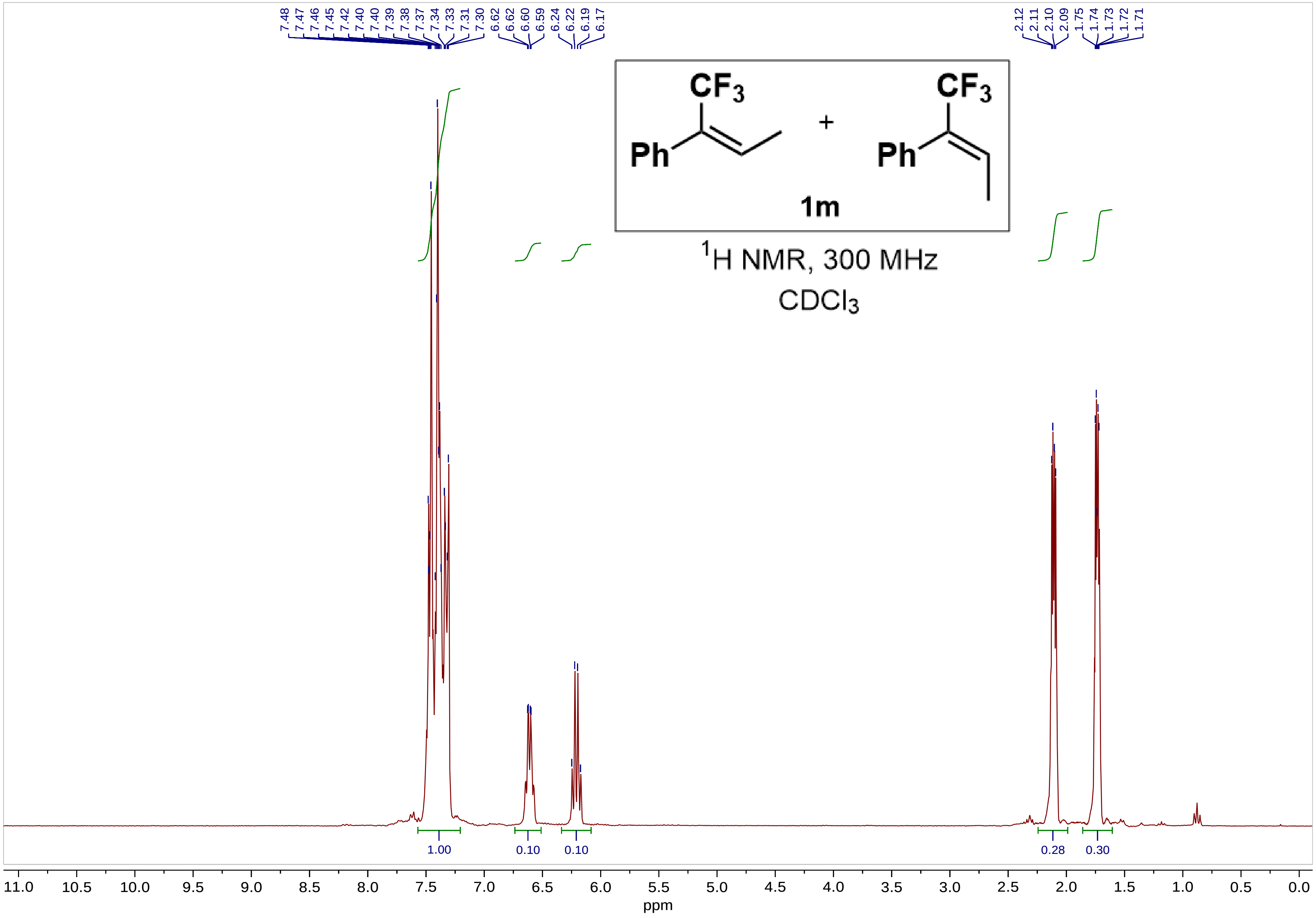
$CDCl_3$

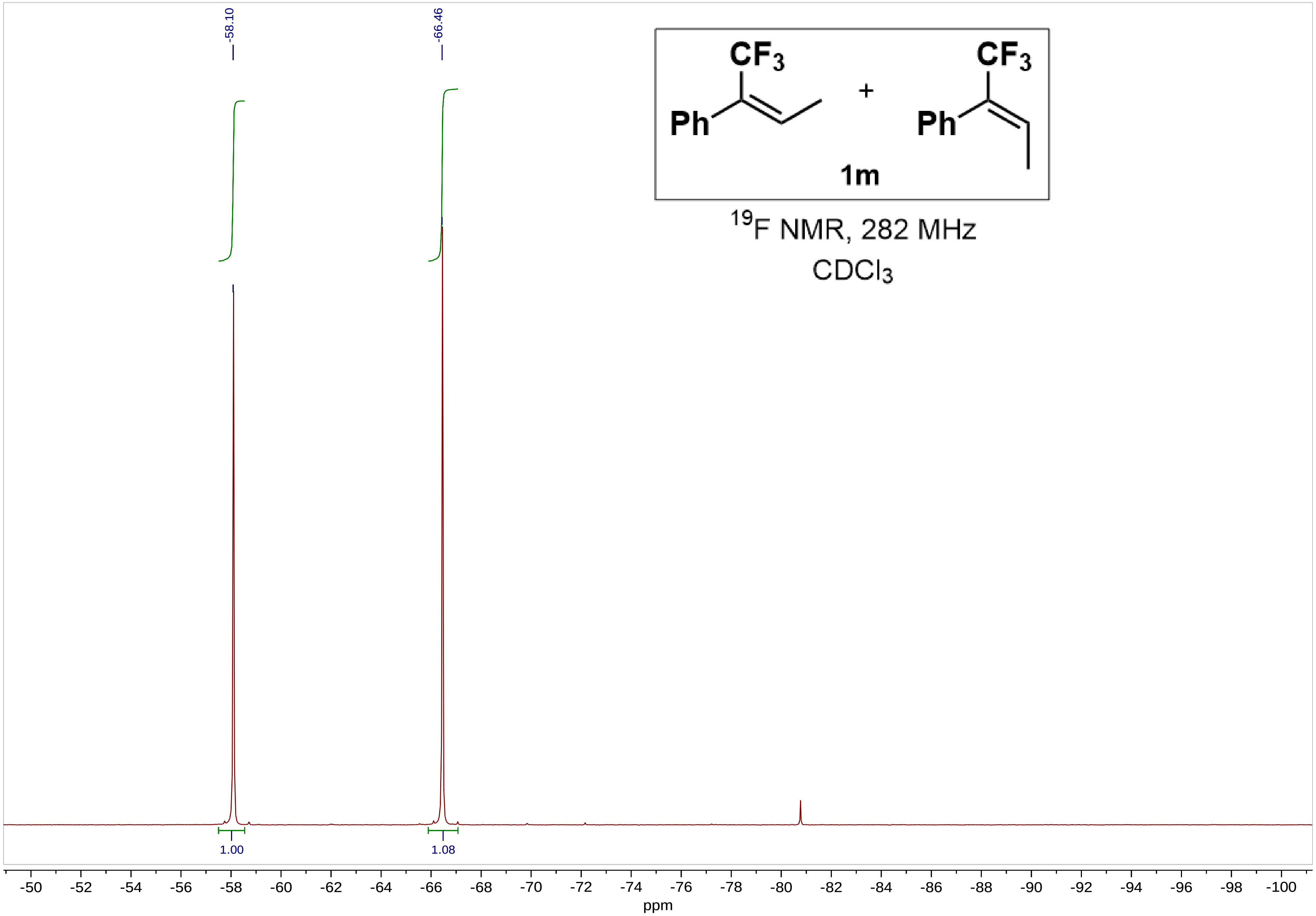


1l

^{19}F NMR, 282 MHz

$CDCl_3$


7.48
7.47
7.46
7.45
7.42
7.40
7.40
7.39
7.38
7.37
7.34
7.33
7.31
7.30
6.62
6.62
6.60
6.59
6.24
6.22
6.19
6.17
2.12
2.11
2.10
2.09
1.75
1.74
1.73
1.72
1.71
CF3
Ph
+
CF3
Ph
1m
1H NMR, 300 MHz
CDCl3
1.00
0.10
0.10
0.28
0.30
11.0
10.5
10.0
9.5
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
ppm


-58.10
-66.46
CF$_3$
Ph
+
CF$_3$
Ph
1m
^{19}F NMR, 282 MHz
CDCl$_3$
1.00
1.08
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
ppm