A Straightforward Access to Photochromic Diarylethene Derivatives via Palladium-Catalysed Direct Heteroarylation of 1,2-Dichloroperfluorocyclopentene

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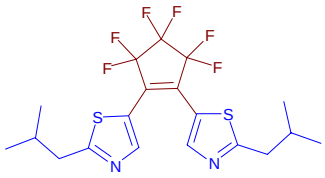
General. All reactions were perfomed in Schlenck tubes under argon. CPME analytical grade was not distilled before use. Potassium acetate 99+ was used. Commercial heteroaromatics and 1,2-dichlorohexafluorocyclopentene were used without purification. ^{1}H (400 or 500 MHz), ^{13}C (100 or 125 MHz) and ^{19}F (376 MHz) spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (^{1}H: 7.29 and ^{13}C: 77.0). Flash chromatography was performed on silica gel (230-400 mesh) using pentane\ether.

General procedure

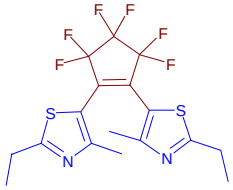
As a typical experiment, the reaction of the 1,2-dichlorohexafluorocyclopentene (0.122 g, 0.5 mmol), thiophene or furan derivative (1.5 mmol) and KOAc (0.147 g, 1.5 mmol) at 120 °C during 16 h in CPME (3 mL) in the presence of **(A):** $Pd(OAc)_2$ (0.011 g, 0.05 mmol) and PCy_3 (0.014 g, 0.05 mmol) or **(B):** $PdCl(dppb)(C_3H_5)$ (0.015 g, 0.025 mmol), under argon affords the corresponding coupling product **1-12** after evaporation of CPME and filtration on silica gel (pentane/ether).

(1a)



The reaction of 1,2-dichlorohexafluorocyclopentene (0.122 g, 0.5 mmol), 2-isobutyl-1,3-thiazole (0.211 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with $Pd(OAc)_2$ (0.011 g, 0.05 mmol) and PCy_3 (0.014 g, 0.05 mmol) in CPME (3 mL) at 120 °C during 16 h affords the corresponding product **1a** in 82% (0.186 g) isolated yield as a light green oil, and in 80% (0.181 g) isolated yield when using $PdCl(dppb)(C_3H_5)$ (0.015 g, 0.025 mmol) instead of $Pd(OAc)_2/PCy_3$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 2H), 2.92 (d, *J* = 7.0 Hz, 4H), 2.18-2.11 (m, 2H), 1.02 (d, *J* = 6.6 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.6, 146.2, 121.8, 42.5, 29.8, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.8 (t, *J* = 4.6 Hz, 4F), -130.6 (quint., *J* = 4.6 Hz, 2F). Elemental analysis: calcd (%) for $C_{19}H_{20}F_6N_2S_2$ (454.50): C 50.21, H 4.44; found: C 50.30, H 4.58.

(2)

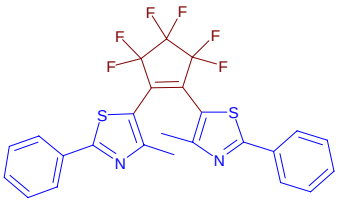


The reaction of 1,2-dichlorohexafluorocyclopentene (0.122 g, 0.5 mmol), 2-ethyl-4-methyl-1,3-thiazole (0.191 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with $Pd(OAc)_2$ (0.011 g, 0.05 mmol) and PCy_3 (0.014 g, 0.05 mmol) in CPME (3 mL) at 120 °C during 16 h affords the corresponding product **2** in 68% (0.145 g) isolated yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.99 (q, *J* = 7.5 Hz, 4H), 1.99 (s, 6H), 1.37 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.0, 154.8, 116.0, 27.0, 16.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.8 (t, *J* = 5.0 Hz, 4F), -131.4 (quint., *J* = 5.0 Hz, 2F). Elemental analysis: calcd (%) for $C_{17}H_{16}F_6N_2S_2$ (426.44): C 47.88, H 3.78; found: C 47.69, H 3.97.

(3a) (3b)

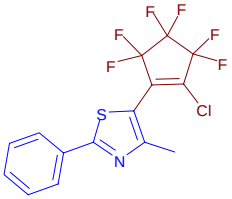
The reaction of 1,2-dichlorohexafluorocyclopentene (0.122 g, 0.5 mmol), 2-Phenyl-4-methyl-1,3-thiazole (0.262 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with $PdCl(dppb)(C_3H_5)$ (0.015 g, 0.025 mmol) in CPME (3 mL) at 120 °C during 24 h affords the corresponding product **3a** in 38% (0.099 g) isolated yield as a yellow oil and product **3b** in 43% (0.082 g) isolated yield as a colourless oil.

Compound 3a



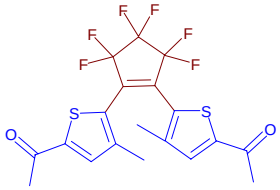
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 7.3 Hz, 4H), 7.53-7.42 (m, 6H), 2.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 156.5, 132.6, 131.1, 129.1, 126.8, 117.0, 17.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.2 (t, J = 4.6 Hz, 4F), -131.1 (quint., J = 4.6 Hz, 2F). Elemental analysis: calcd (%) for $C_{25}H_{16}F_6N_2S_2$ (522.53): C 57.46, H 3.09; found: C 57.57, H 3.01.

Compound 3b



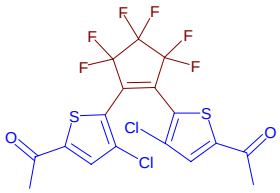
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 7.3 Hz, 2H), 7.55-7.44 (m, 3H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 157.0, 132.6, 131.2, 129.2, 126.8, 113.7, 17.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.4 (bs, 2F), -113.4 (bs, 2F), -130.1 (quint., J = 4.5 Hz, 2F).

(4)



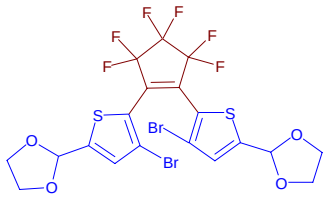
The reaction of 1,2-dichlorohexafluorocyclopentene (0.122 g, 0.5 mmol), 2-acetyl-4-methylthiophene (0.210 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with $Pd(OAc)_2$ (0.011 g, 0.05 mmol) and PCy_3 (0.014 g, 0.05 mmol) in CPME (3 mL) at 120 °C during 16 h affords the corresponding product **4** in 45% (0.100 g) isolated yield as a brown solid (mp: 154 °C) and in 69% (0.156 g) isolated yield when using $PdCl(dppb)(C_3H_5)$ (0.015 g, 0.025 mmol) instead of $Pd(OAc)_2/PCy_3$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 2H), 2.56 (s, 6H), 1.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 146.7, 141.9, 134.7, 129.6, 26.9, 15.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.6 (t, J = 5.0 Hz, 4F), -131.3 (quint., J = 5.0 Hz, 2F). Elemental analysis: calcd (%) for $C_{19}H_{14}F_6O_2S_2$ (452.44): C 50.44, H 3.12; found: C 50.59, H 3.20.

(5)



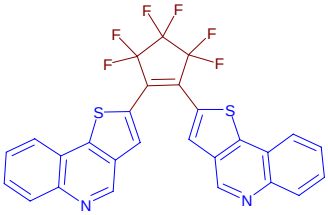
The reaction of 1,2-dichlorohexafluorocyclopentene (0.122 g, 0.5 mmol), 2-acetyl-4-chlorothiophene (0.240 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with $Pd(OAc)_2$ (0.011 g, 0.05 mmol) and PCy_3 (0.014 g, 0.05 mmol) in CPME (3 mL) at 120 °C during 24 h affords the corresponding product **5** in 54% (0.132 g) isolated yield as a light pink solid (mp: 183 °C) and in 67% (0.165 g) isolated yield when using $PdCl(dppb)(C_3H_5)$ (0.015 g, 0.025 mmol) instead of $Pd(OAc)_2/PCy_3$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 2H), 2.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 146.8, 132.2, 128.9, 128.8, 26.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.1 (t, J = 4.6 Hz, 4F), -130.8 (quint., J = 4.6 Hz, 2F). Elemental analysis: calcd (%) for $C_{17}H_8Cl_2F_6O_2S_2$ (493.27): C 41.39, H 1.63; found: C 41.50, H 1.80.

(6)



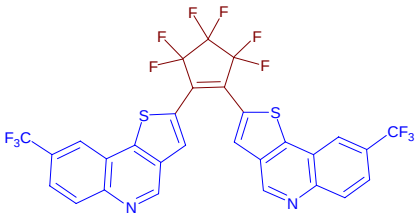
The reaction of 1,2-dichlorohexafluorocyclopentene (0.122 g, 0.5 mmol), 4-bromothiophene-2-carboxaldehyde dioxolane (0.352 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with $Pd(OAc)_2$ (0.011 g, 0.05 mmol) and PCy_3 (0.014 g, 0.05 mmol) in CPME (3 mL) at 120 °C during 24 h affords the corresponding product **6** in 68% (0.218 g) isolated yield as a yellow solid (mp: 137 °C) and in 80% (0.257 g) isolated yield when using $PdCl(dppb)(C_3H_5)$ (0.015 g, 0.025 mmol) instead of $Pd(OAc)_2/PCy_3$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (s, 2H), 6.16 (s, 2H), 4.13-4.04 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.3, 135.4, 128.0, 112.6, 112.4, 98.7, 65.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.3 (t, J = 4.5 Hz, 4F), -130.5 (quint., J = 4.5 Hz, 2F). Elemental analysis: calcd (%) for $C_{19}H_{12}Br_2F_6O_4S_2$ (642.23): C 35.53, H 1.88; found: C 35.68, H 1.69.

(7)



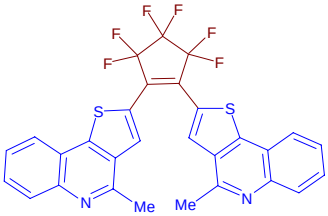
The reaction of 1,2-dichlorohexafluorocyclopentene (0.122 g, 0.5 mmol), [3-4]thienoquinoline (0.277 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with $Pd(OAc)_2$ (0.011 g, 0.05 mmol) and PCy_3 (0.014 g, 0.05 mmol) in CPME (3 mL) at 120 °C during 16 h affords the corresponding product **7** in 72% (0.195 g) isolated yield as a yellow solid (mp: 206 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.32 (s, 2H), 8.25 (d, J = 8.4 Hz, 2H), 8.07 (s, 2H), 7.96 (d, J = 8.1 Hz, 2H), 7.77 (t, J = 7.6 Hz, 2H), 7.60 (t, J = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.5, 146.8, 144.5, 133.0, 130.5, 129.9, 129.7, 127.8, 127.4, 123.7, 123.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.6 (t, J = 4.5 Hz, 4F), -130.4 (quint., J = 4.5 Hz, 2F). Elemental analysis: calcd (%) for $C_{27}H_{12}F_6N_2S_2$ (542.52): C 59.77, H 2.23; found: C 59.50, H 2.41.

(8)



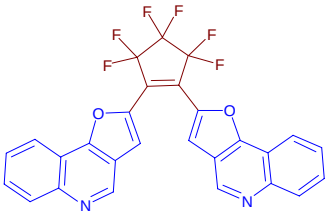
The reaction of 1,2-dichlorohexafluorocyclopentene (0.122 g, 0.5 mmol), 8-trifluoromethylthieno[3,2-c]quinoline (0.380 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with $Pd(OAc)_2$ (0.011 g, 0.05 mmol) and PCy_3 (0.014 g, 0.05 mmol) in CPME (3 mL) at 120 °C during 24 h affords the corresponding product **8** in 46% (0.156 g) isolated yield as a yellow solid (mp: 225 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.43 (s, 2H), 8.38 (d, J = 8.7 Hz, 2H), 8.26 (s, 2H), 8.12 (s, 2H), 7.97 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 147.7, 145.8, 133.8, 131.8, 129.7, 129.6 (q, J = 33.0 Hz), 128.2, 125.7 (q, J = 3.0 Hz), 123.7 (q, J = 272.6 Hz), 122.4, 121.4 (q, J = 4.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.2 (bs, 6F), -109.7 (t, J = 4.6 Hz, 4F), -130.4 (quint., J = 4.6 Hz, 2F). Elemental analysis: calcd (%) for $C_{29}H_{10}F_{12}N_2S_2$ (678.52): C 51.33, H 1.49; found: C 51.48, H 1.40.

(9)



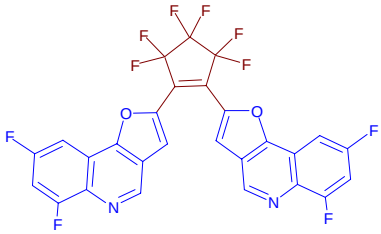
The reaction of 1,2-dichlorohexafluorocyclopentene (0.122 g, 0.5 mmol), 4-methylthieno[3,2-c]quinoline (0.298 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with $Pd(OAc)_2$ (0.011 g, 0.05 mmol) and PCy_3 (0.014 g, 0.05 mmol) in CPME (3 mL) at 120 °C during 24 h affords the corresponding product **9** in 53% (0.150 g) isolated yield as a yellow solid (mp: 214 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.33 (s, 2H), 8.29 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 8.1 Hz, 2H), 7.81 (s, 2H), 7.78 (t, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.9, 146.9, 145.8, 144.8, 130.2, 130.1, 127.6, 120.6, 120.2, 116.4, 113.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.0 (t, *J* = 5.0 Hz, 4F), -131.3 (quint., *J* = 5.0 Hz, 2F). Elemental analysis: calcd (%) for $C_{29}H_{16}F_6N_2S_2$ (570.57): C 61.05, H 2.83; found: C 61.19, H 2.99.

(10)



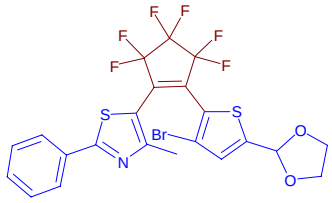
The reaction of 1,2-dichlorohexafluorocyclopentene (0.122 g, 0.5 mmol), furo[3,2-c]quinoline (0.253 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with $Pd(OAc)_2$ (0.011 g, 0.05 mmol) and PCy_3 (0.014 g, 0.05 mmol) in CPME (3 mL) at 120°C during 24 h affords the corresponding product **10** in 79 % (0.202 g) isolated yield as an orange solid (mp: 246 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.27 (s, 1H), 8.24 (d, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.87-7.83 (m, 3H), 7.78-7.73 (m, 3H), 7.76 (t, *J* = 8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.5, 145.2, 144.0, 142.4, 137.8, 134.5, 132.9, 130.5, 129.1, 127.6, 126.8, 123.8, 123.3, 121.4, 118.5, 112.0. δ -109.0 (t, *J* = 5.0 Hz, 4F), -131.3 (quint., *J* = 5.0 Hz, 2F). Elemental analysis: calcd (%) for $C_{27}H_{12}F_6N_2O_2$ (510.39): C 63.54, H 2.37; found: C 63.68, H 2.20.

(11)

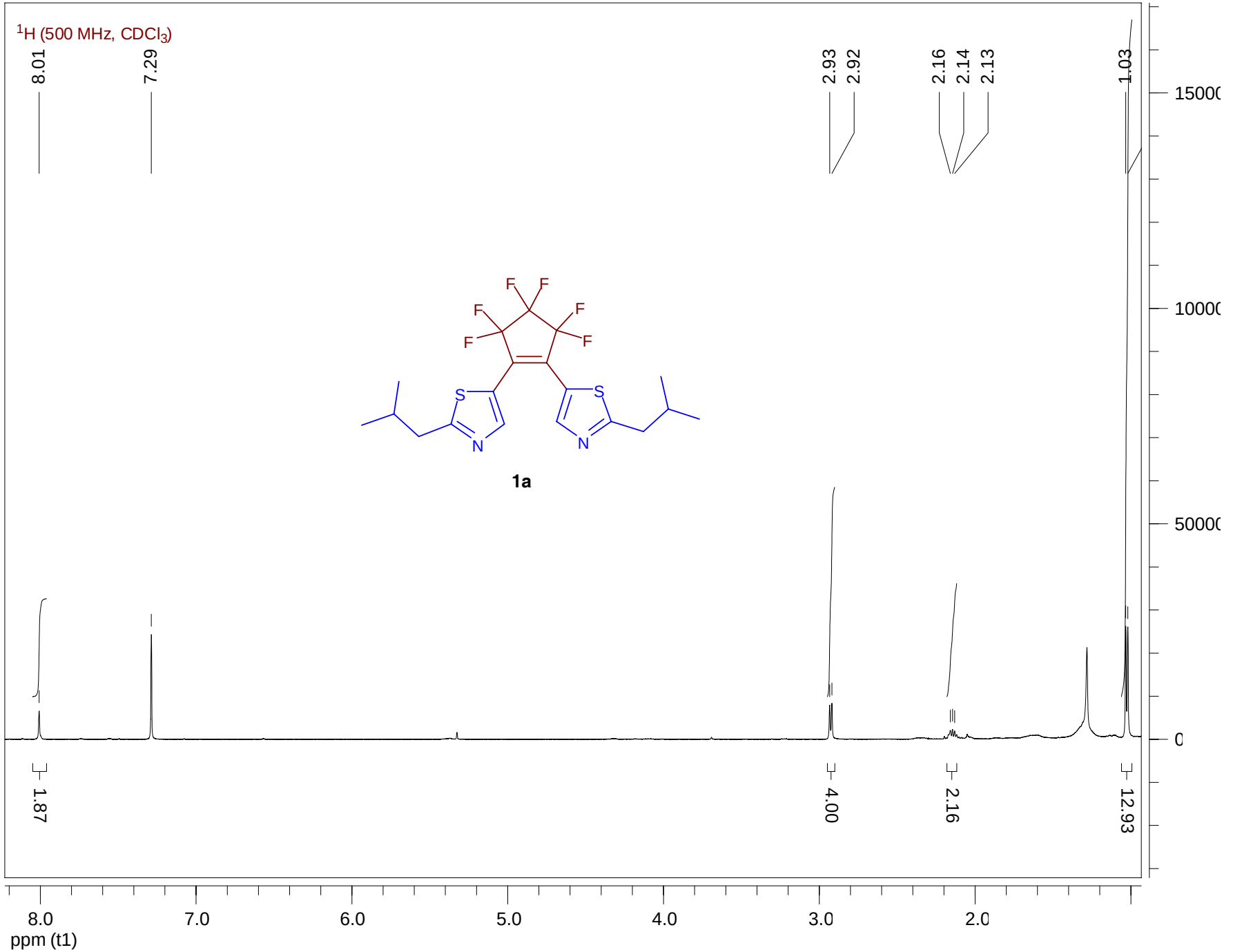


The reaction of 1,2-dichlorohexafluorocyclopentene (0.122 g, 0.5 mmol), 6,8-difluorofuro[3,2-c]quinoline (0.307 g, 1.5 mmol) and KOAc (0.147 g, 1.5 mmol) with $Pd(OAc)_2$ (0.011 g, 0.05 mmol) and PCy_3 (0.014 g, 0.05 mmol) in CPME (3 mL) at 120 °C during 16 h affords the corresponding product **11** in 59 % (0.172 g) isolated yield as a light brown solid (mp: > 265 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.33 (s, 2H), 7.82 (s, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5 (dd, *J* = 252.9 Hz, *J* = 11.5 Hz), 159.5 (dd, *J* = 262.0 Hz, *J* = 13.1 Hz), 156.0 (t, *J* = 5.5 Hz), 145.4, 145.1, 134.1 (dd, *J* = 11.6 Hz, *J* = 1.9 Hz), 122.0, 117.7 (dd, *J* = 11.8 Hz, *J* = 3.2 Hz), 113.4, 105.9 (dd, *J* = 28.8 Hz, *J* = 23.1 Hz), 100.1 (dd, *J* = 23.9 Hz, *J* = 4.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.5 (q, *J* = 8.6 Hz, 2F), -109.1 (t, *J* = 4.6 Hz, 4F), -115.0 (t, *J* = 9.7 Hz, 2F), -131.3 (quint., *J* = 4.6 Hz, 2F). Elemental analysis: calcd (%) for $C_{27}H_8F_{10}N_2O_2$ (582.35): C 55.69, H 1.38; found: C 55.42, H 1.38.

(12)



The reaction of **3b** (0.076 g, 0.2 mmol), 4-bromothiophene-2-carboxaldehyde dioxolane (0.141 g, 0.6 mmol) and KOAc (0.059 g, 0.6 mmol) with $PdCl(dppb)(C_3H_5)$ (0.006 g, 0.01 mmol) in CPME (2 mL) at 120 °C during 22 h affords the corresponding product **12** in 75% (0.088 g) isolated yield as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 6.1 Hz, 2H), 7.54-7.40 (m, 3H), 7.33 (s, 1H), 6.10 (s, 1H), 4.23-3.98 (m, 4H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 156.6, 149.2, 136.5, 132.5, 131.2, 129.1, 128.4, 126.9, 116.3, 112.9, 112.6, 98.8, 65.6, 17.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -108.7 (bs, 2F), -110.1 (bs, 2F), -130.9 (quint., *J* = 4.6 Hz, 2F). Elemental analysis: calcd (%) for $C_{22}H_{14}BrF_6NO_2S_2$ (583.32): C 45.37, H 2.42; found: C 45.38, H 2.11.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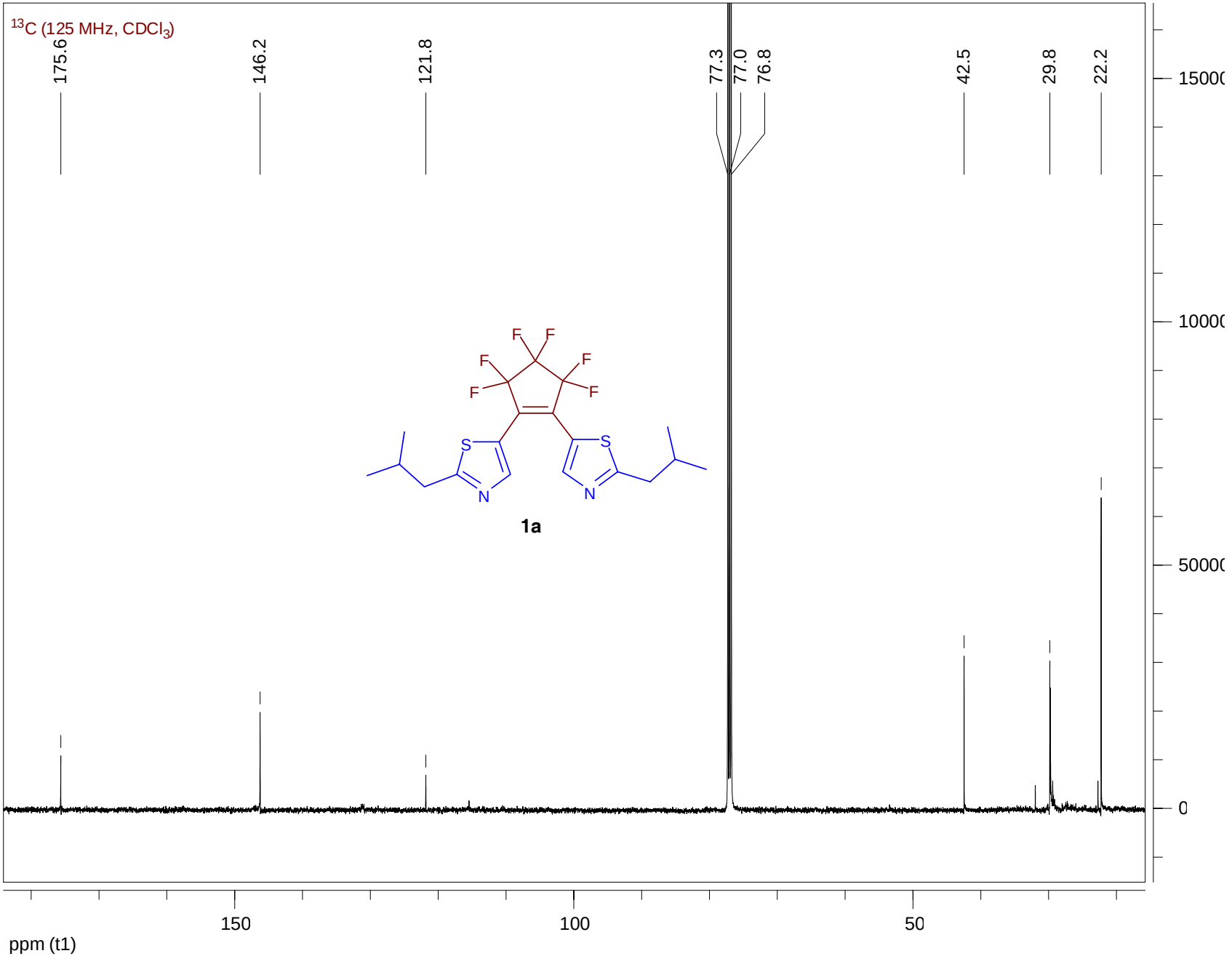
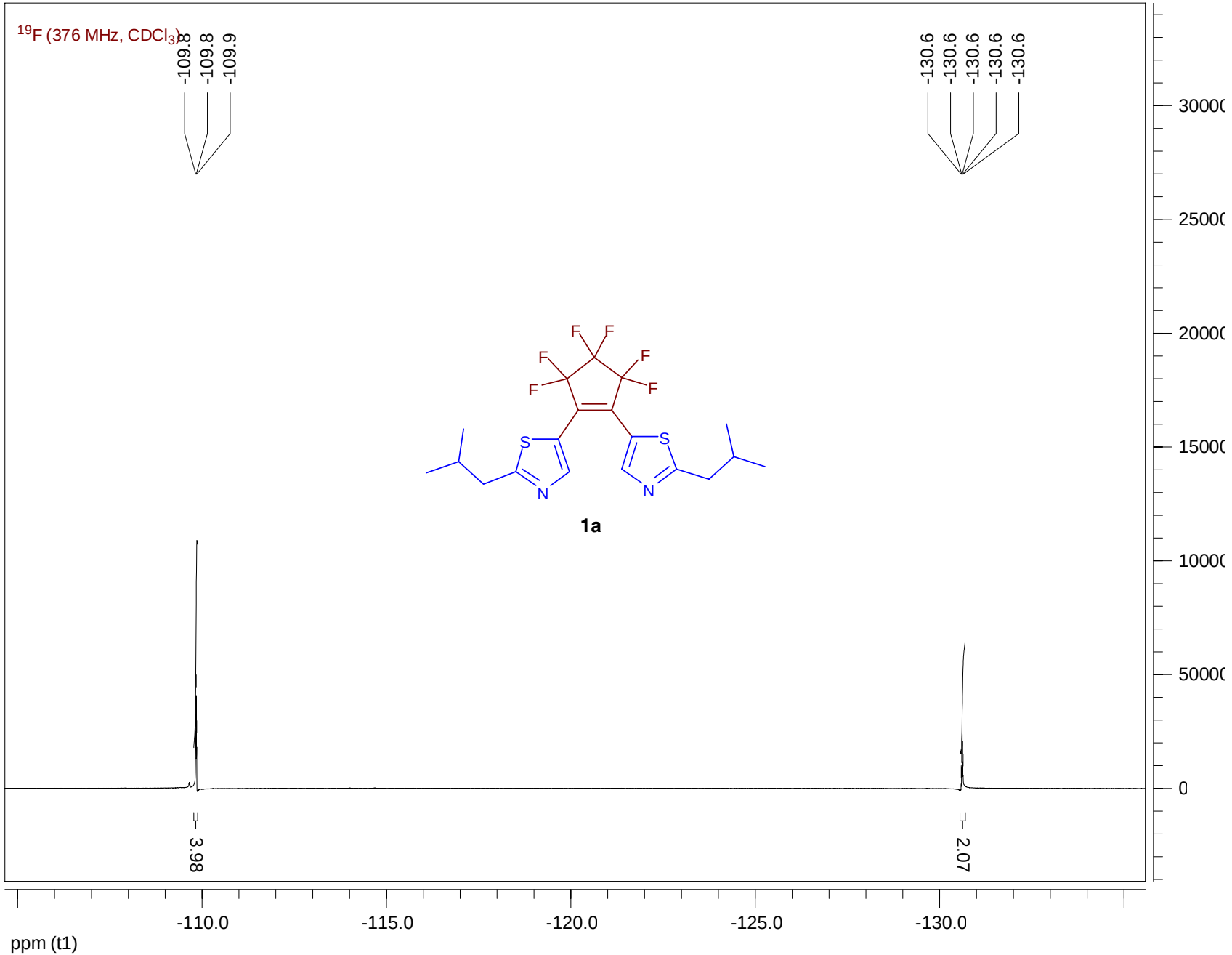
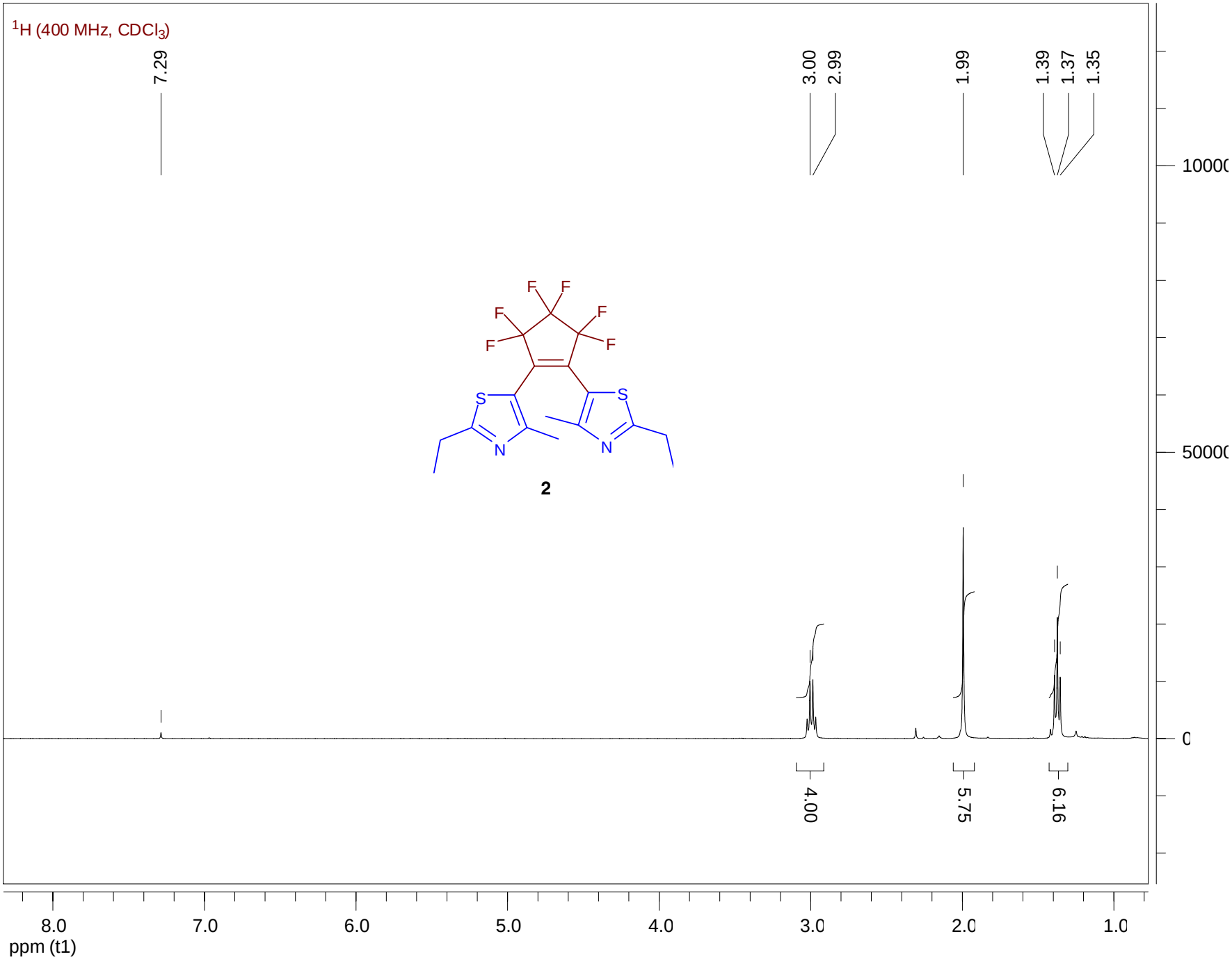
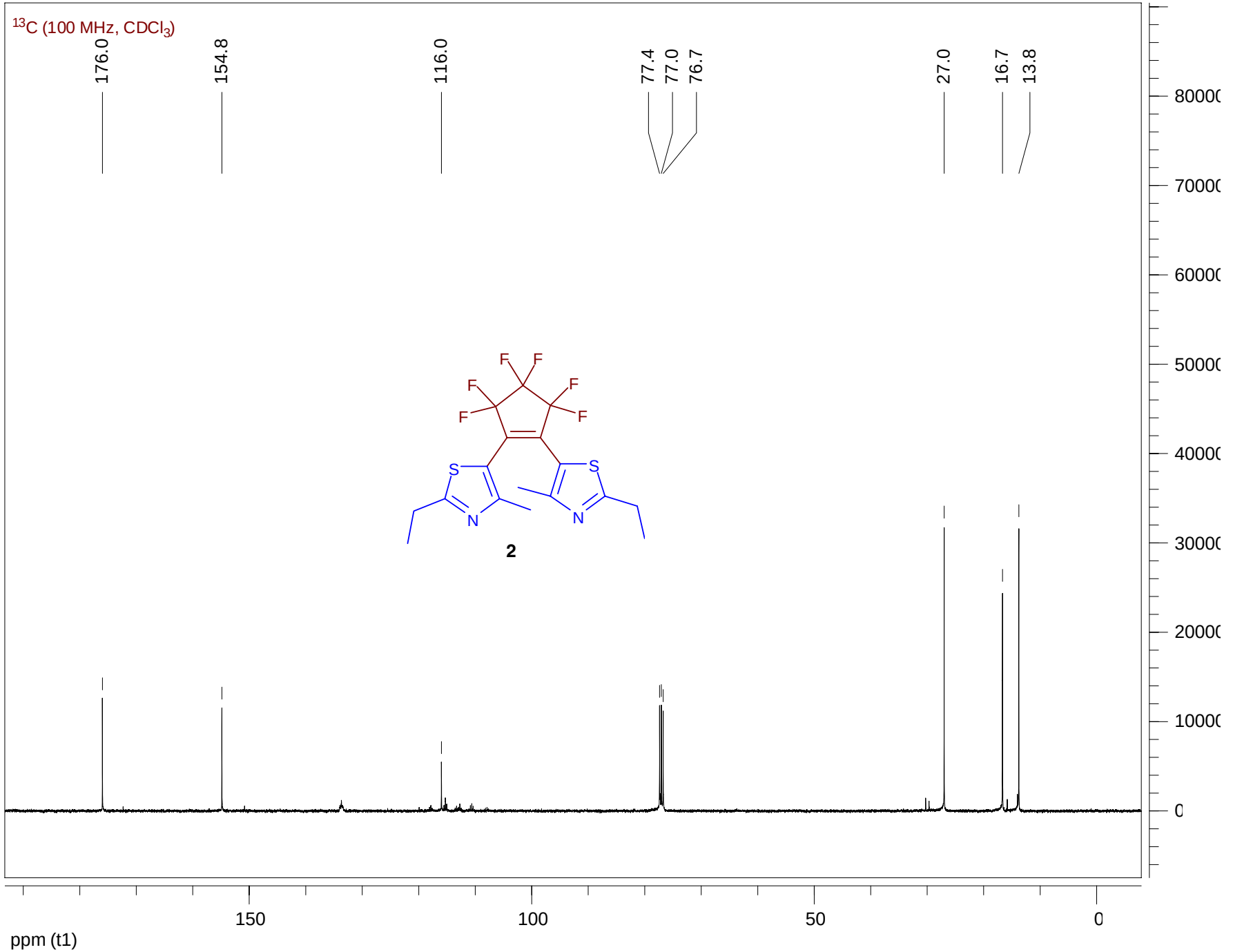
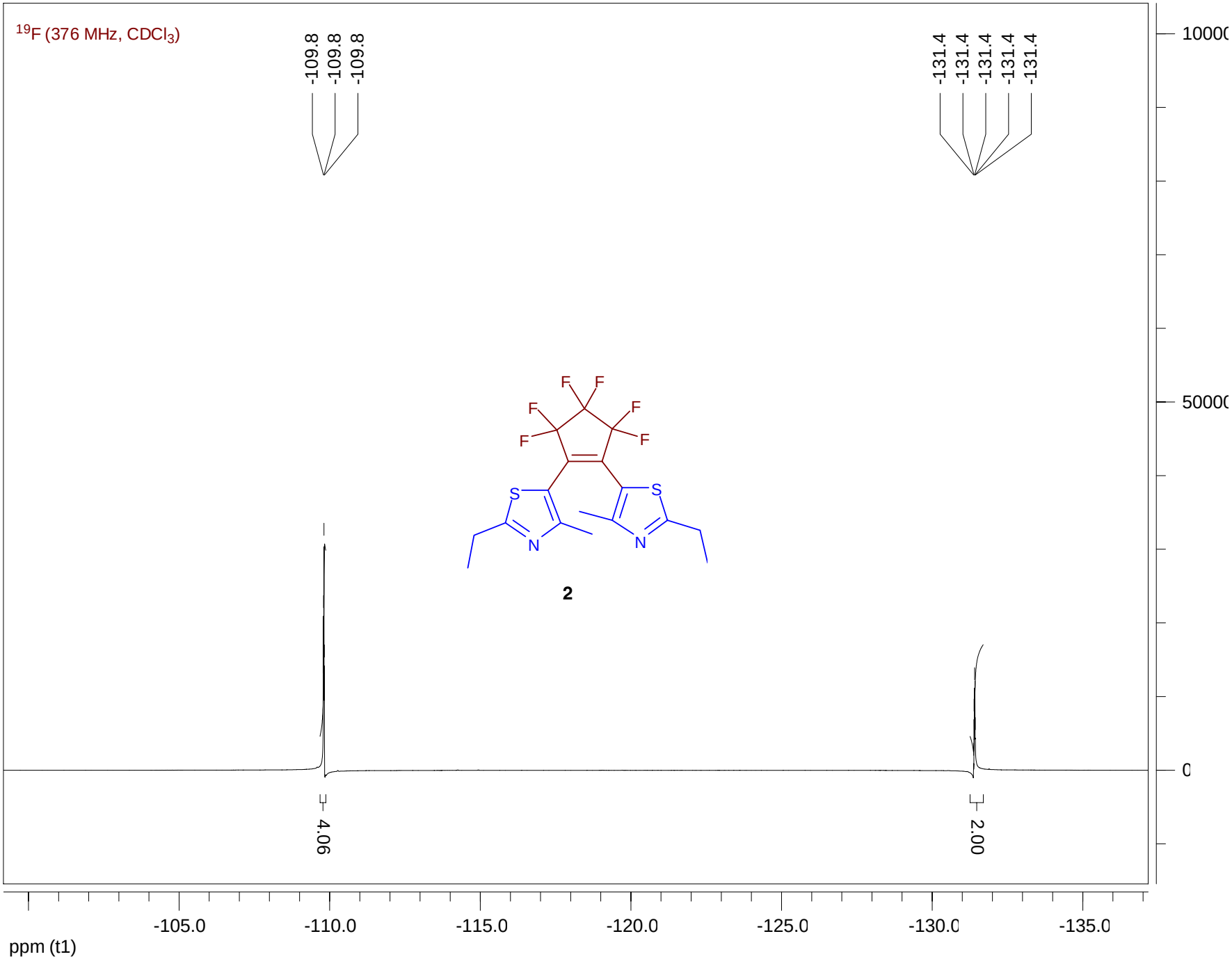
7.29
2.93
2.92
2.16
2.14
2.13
1.03
F
F
F
F
F
F
S
S
N
N
1a
15000
10000
50000
0
1.87
4.00
2.16
12.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

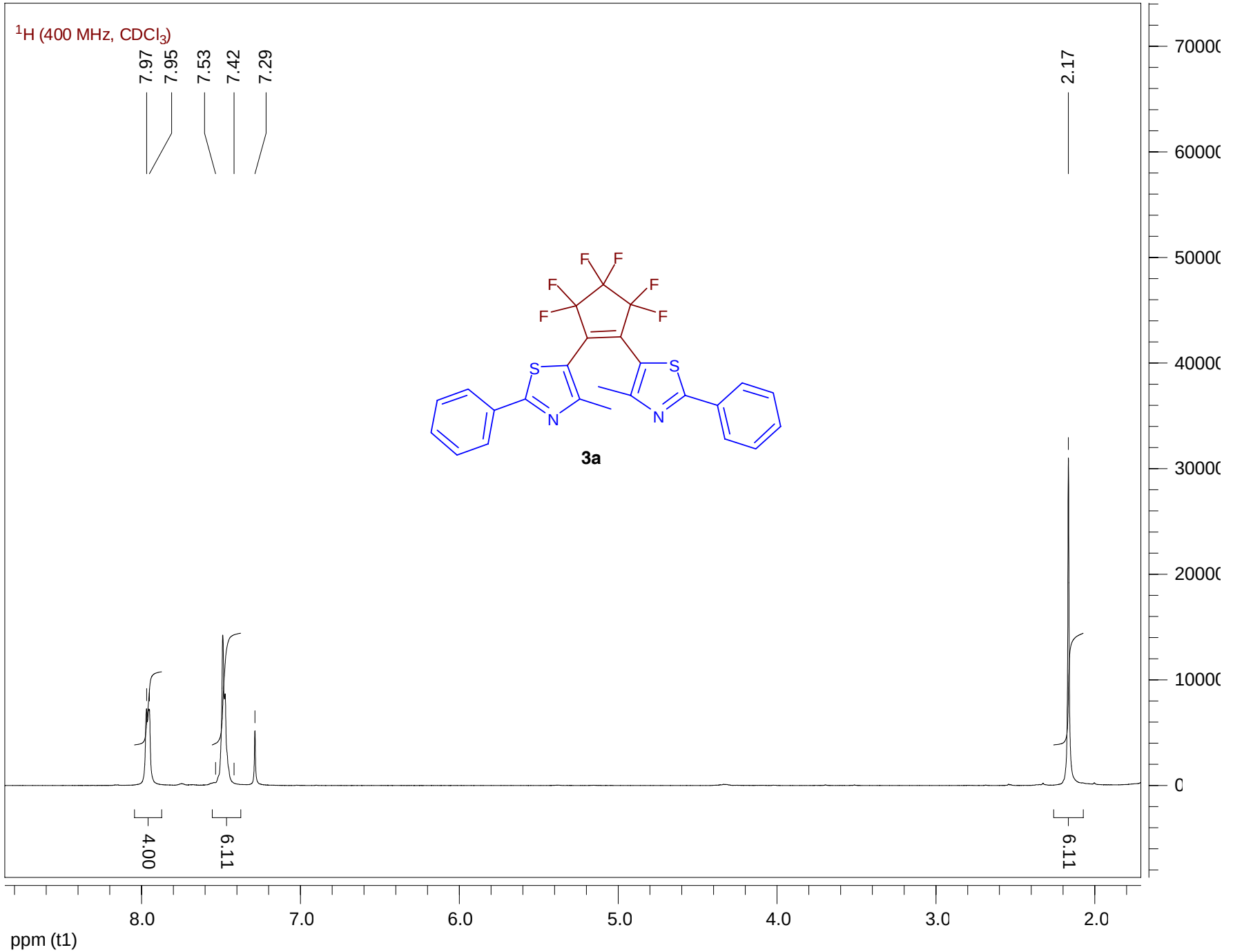

13C (125 MHz, CDCl3)
175.6
146.2
121.8
77.3
77.0
76.8
42.5
29.8
22.2
F
F
F
F
F
S
S
N
N
1a
150
100
50
ppm (t1)

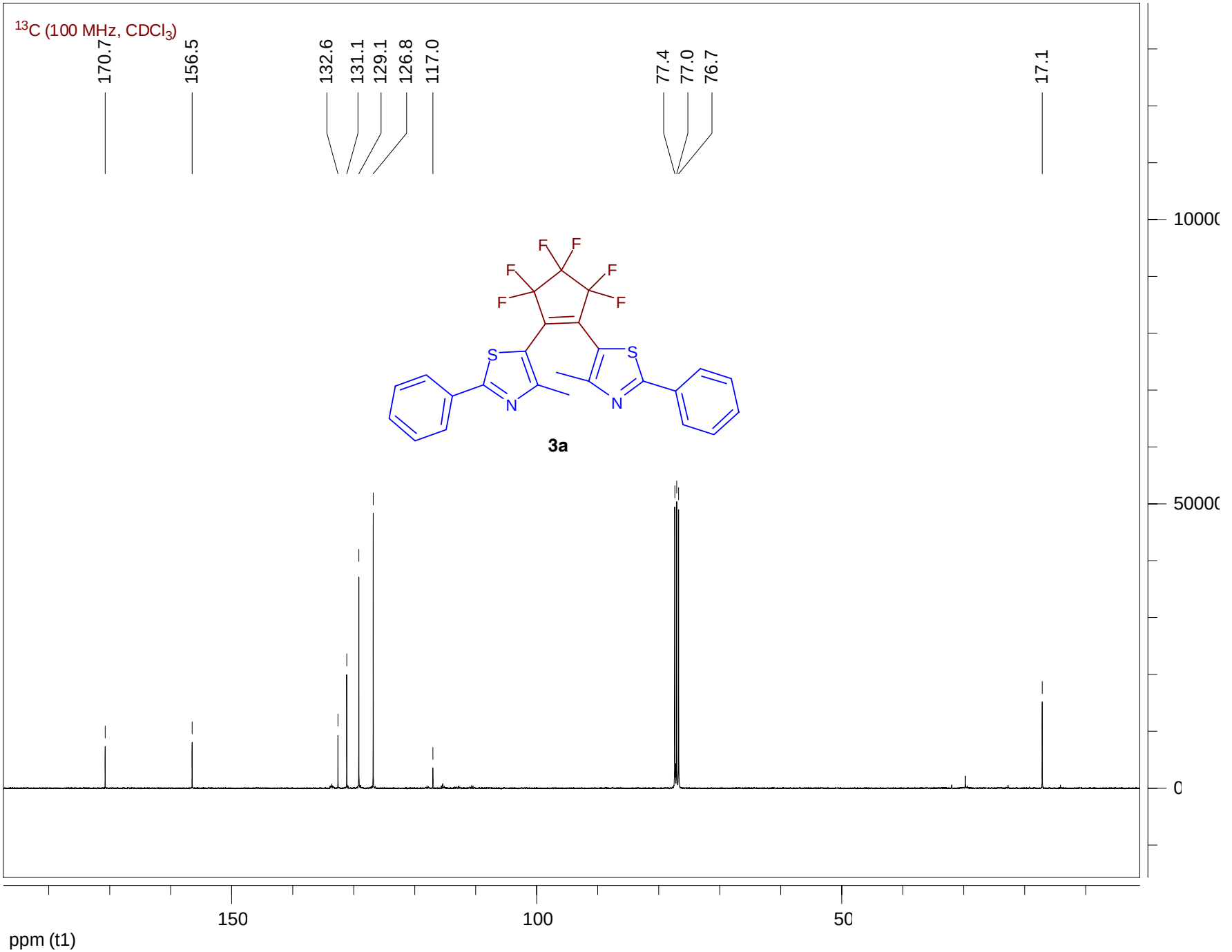

19F (376 MHz, CDCl3)
-109.8
-109.8
-109.9
-130.6
-130.6
-130.6
-130.6
-130.6
F
F
F
F
F
S
S
N
N
1a
3.98
2.07
-110.0
-115.0
-120.0
-125.0
-130.0
ppm (t1)
30000
25000
20000
15000
10000
5000
0

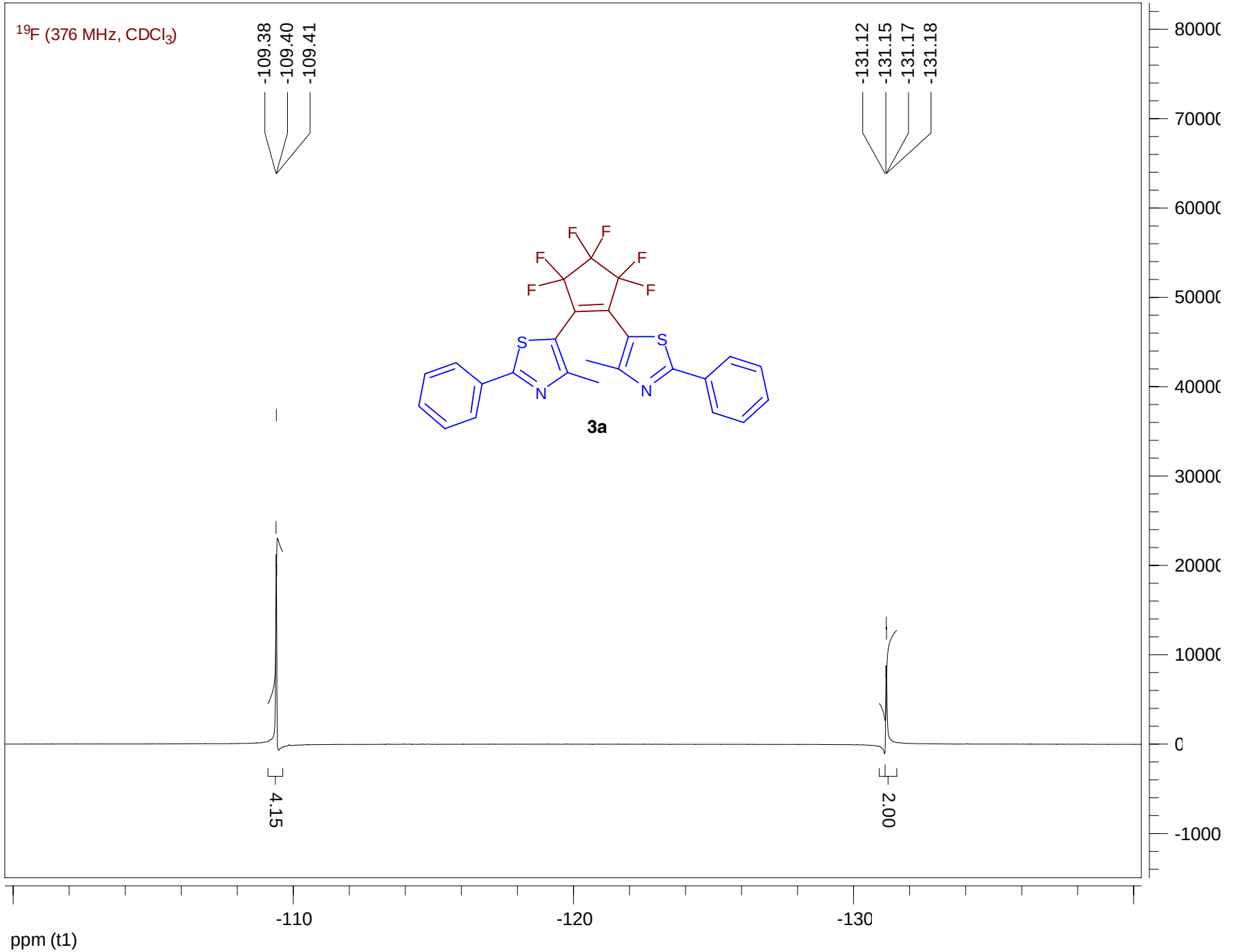

1H (400 MHz, CDCl3)
7.29
3.00
2.99
1.99
1.39
1.37
1.35
F
F
F
F
F
S
S
N
N
2
10000
50000
0
4.00
5.75
6.16
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

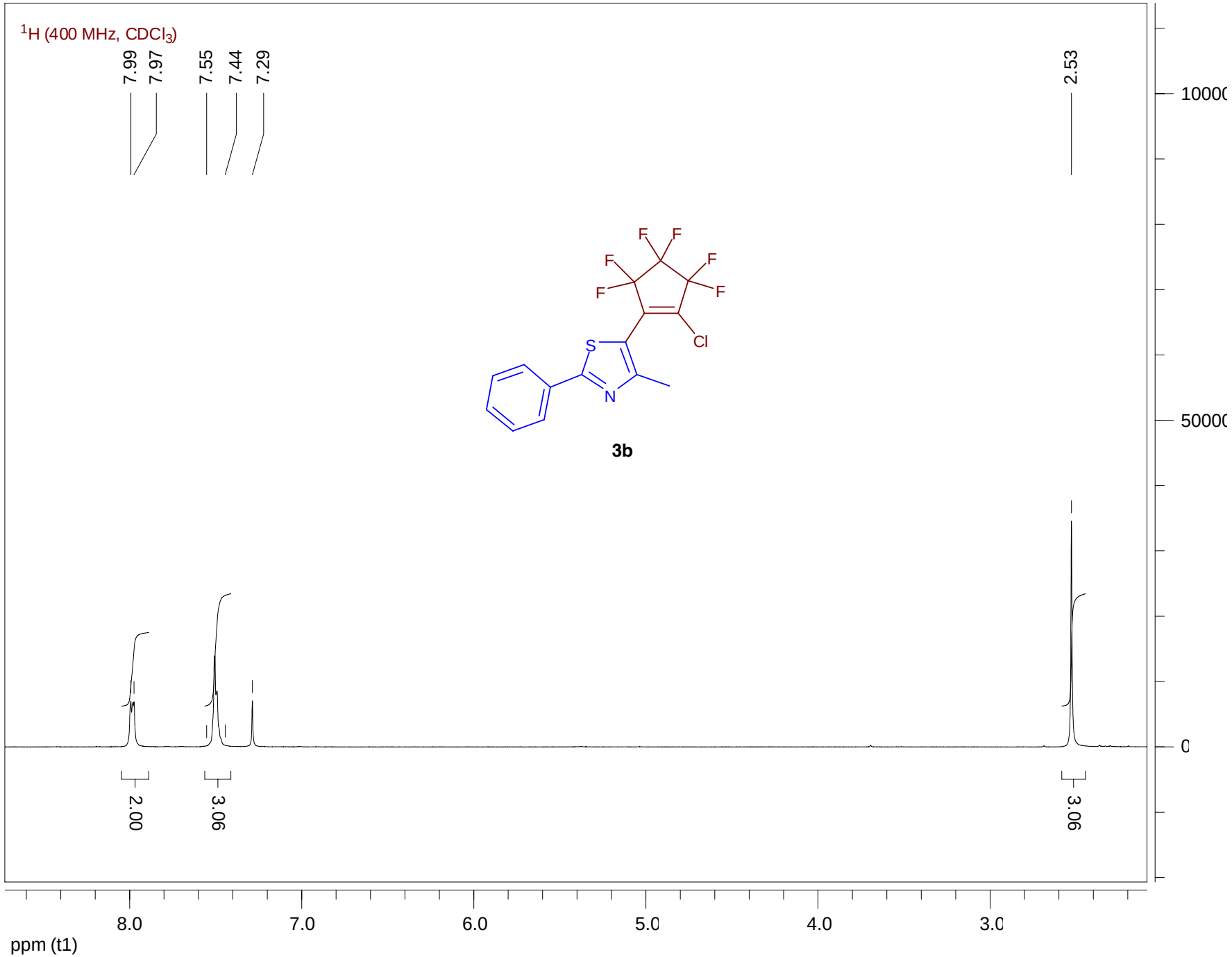

13C (100 MHz, CDCl3)
176.0
154.8
116.0
77.4
77.0
76.7
27.0
16.7
13.8
F
F
F
F
F
S
S
N
N
2
80000
70000
60000
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)

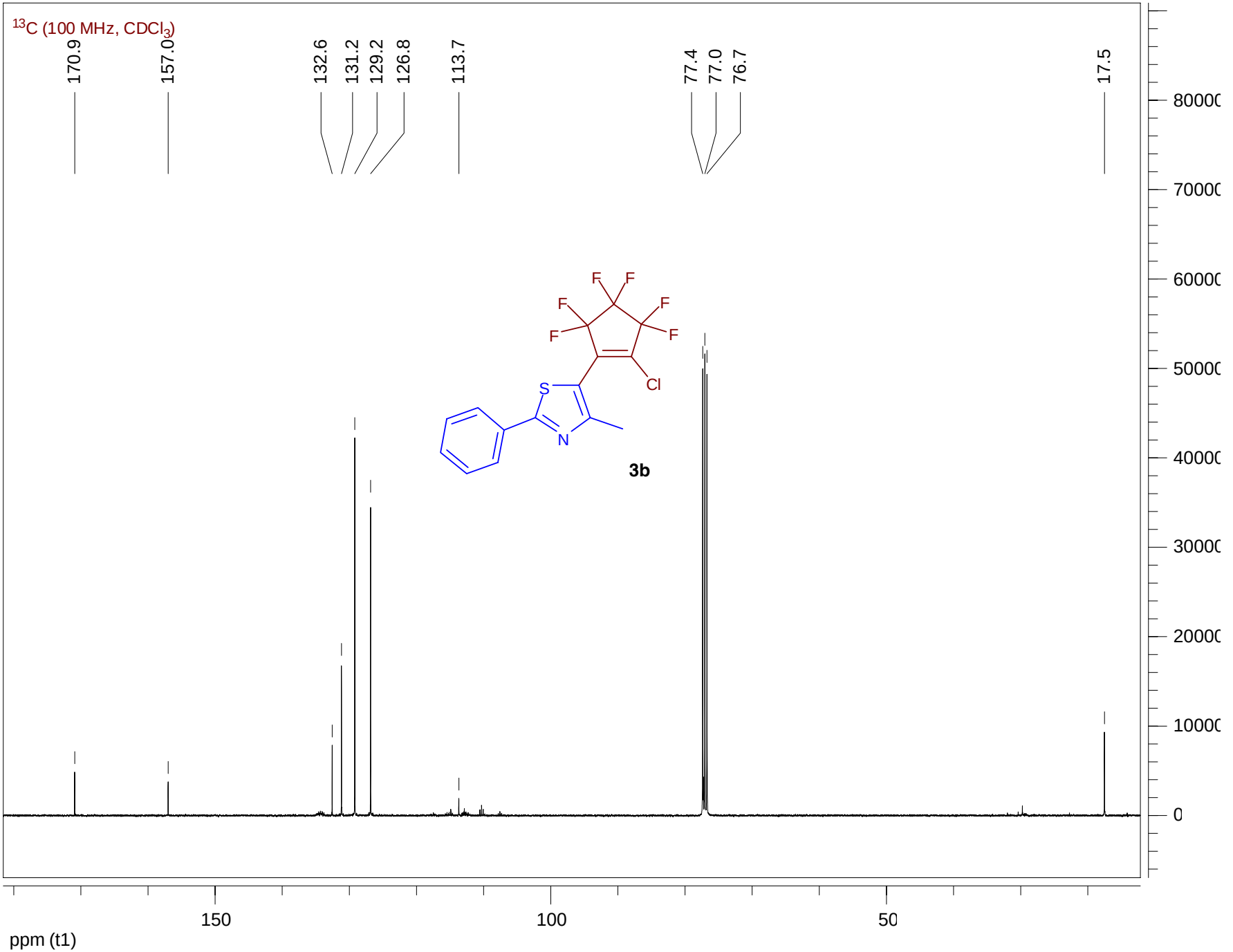

19F (376 MHz, CDCl3)
-109.8
-109.8
-109.8
-131.4
-131.4
-131.4
-131.4
-131.4
F
F
F
F
F
S
S
N
N
2
4.06
2.00
10000
50000
0
-105.0
-110.0
-115.0
-120.0
-125.0
-130.0
-135.0
ppm (t1)

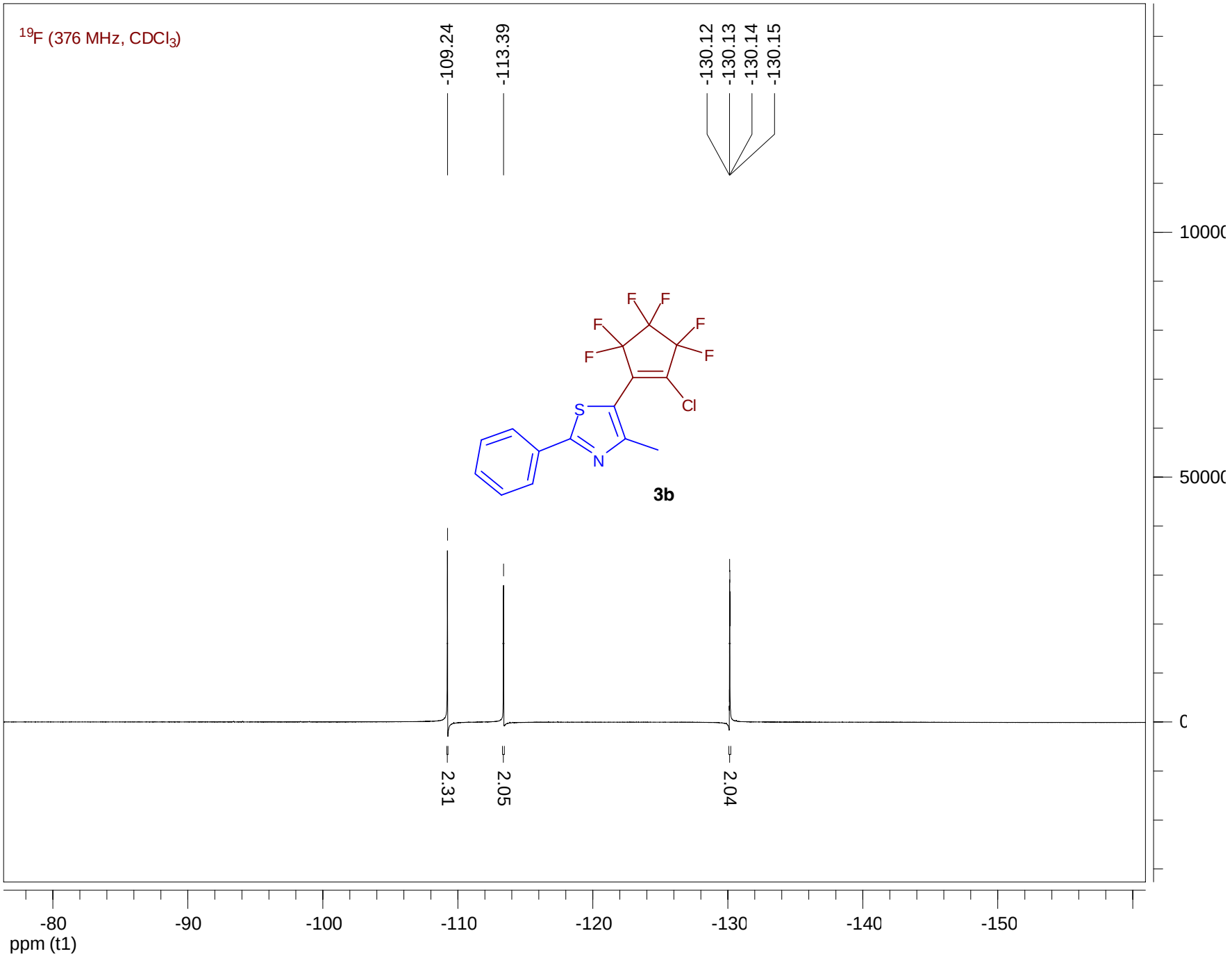

1H (400 MHz, CDCl3)
7.97
7.95
7.53
7.42
7.29
2.17
F
F
F
F
F
F
S
S
N
N
3a
4.00
6.11
6.11
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)
70000
60000
50000
40000
30000
20000
10000
0

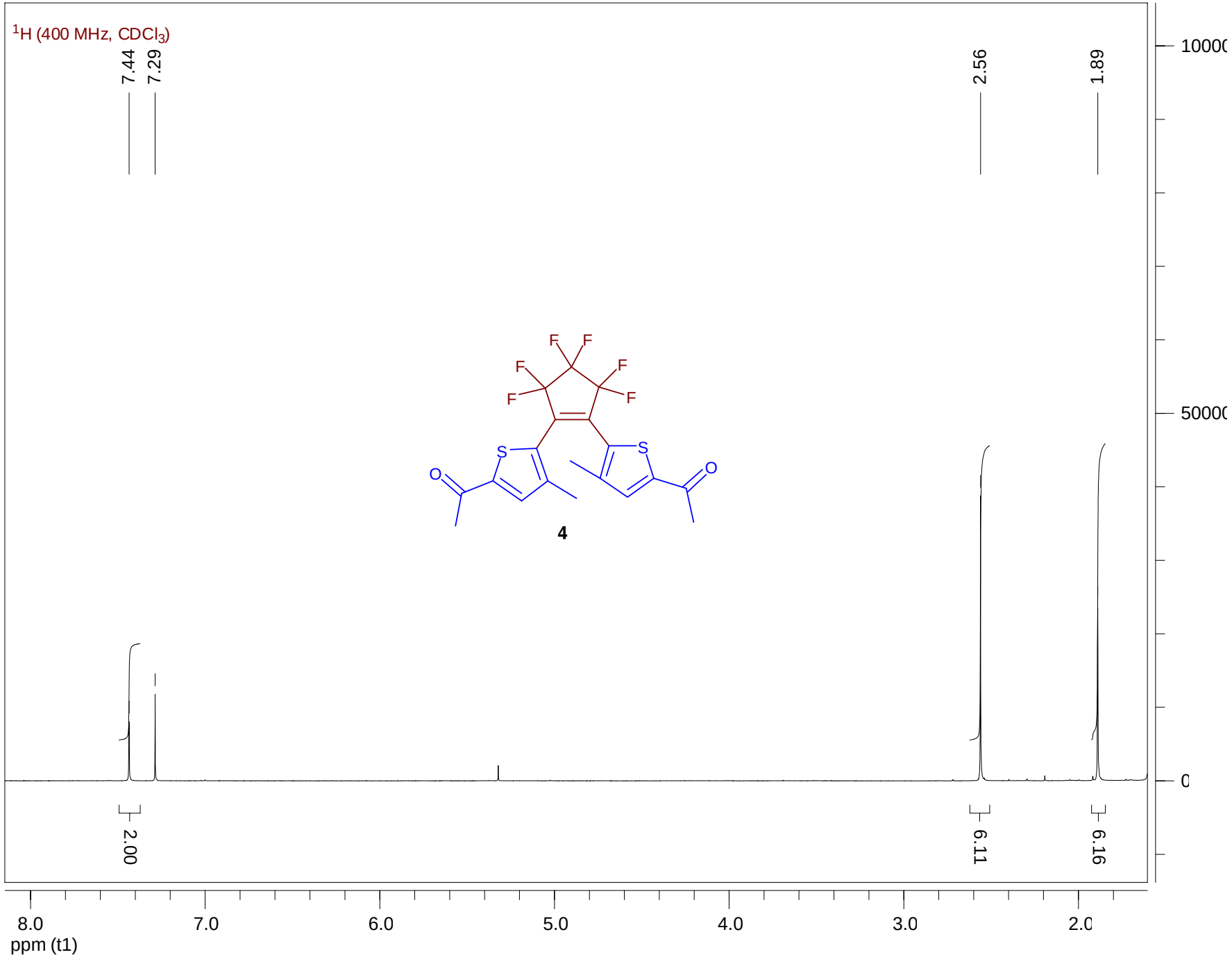

13C (100 MHz, CDCl3)
170.7
156.5
132.6
131.1
129.1
126.8
117.0
77.4
77.0
76.7
17.1
F
F
F
F
F
F
S
S
N
N
3a
10000
50000
0
150
100
50
ppm (t1)

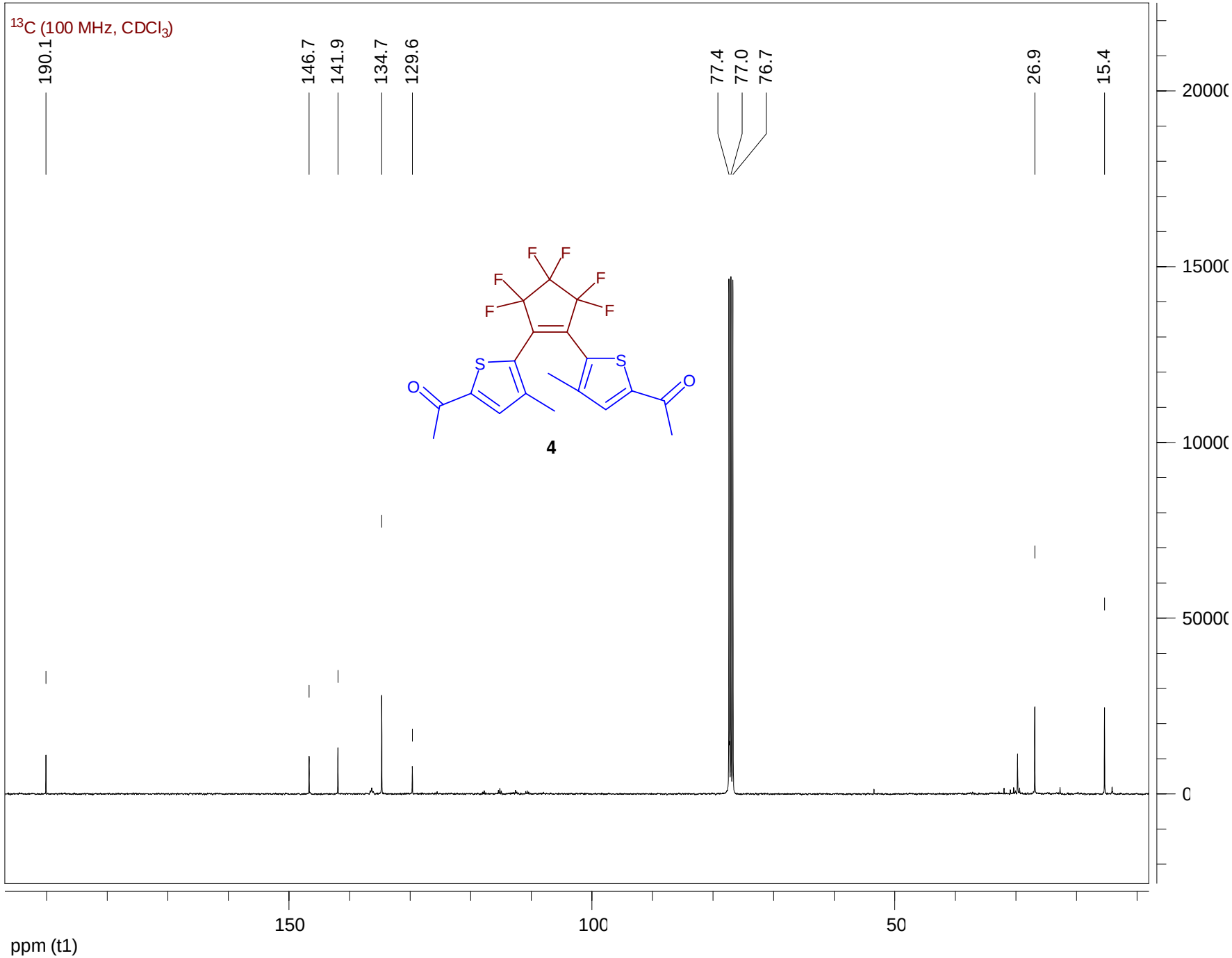

19F (376 MHz, CDCl3)
-109.38
-109.40
-109.41
-131.12
-131.15
-131.17
-131.18
F
F
F
F
F
S
S
N
N
3a
4.15
2.00
-110
-120
-130
ppm (t1)

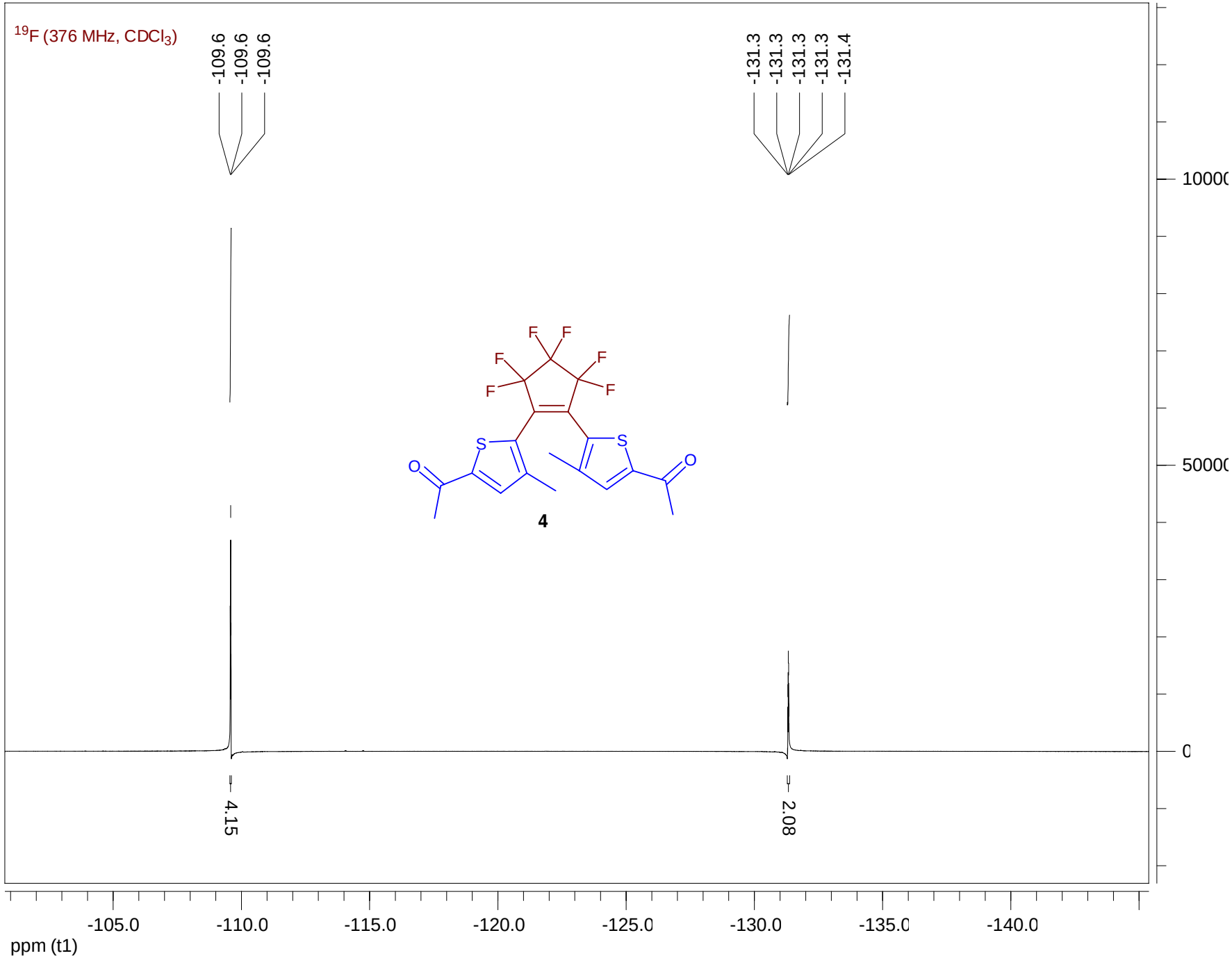

1H (400 MHz, CDCl3)
7.99
7.97
7.55
7.44
7.29
2.53
F
F
F
F
F
Cl
S
N
3b
10000
50000
0
2.00
3.06
3.06
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

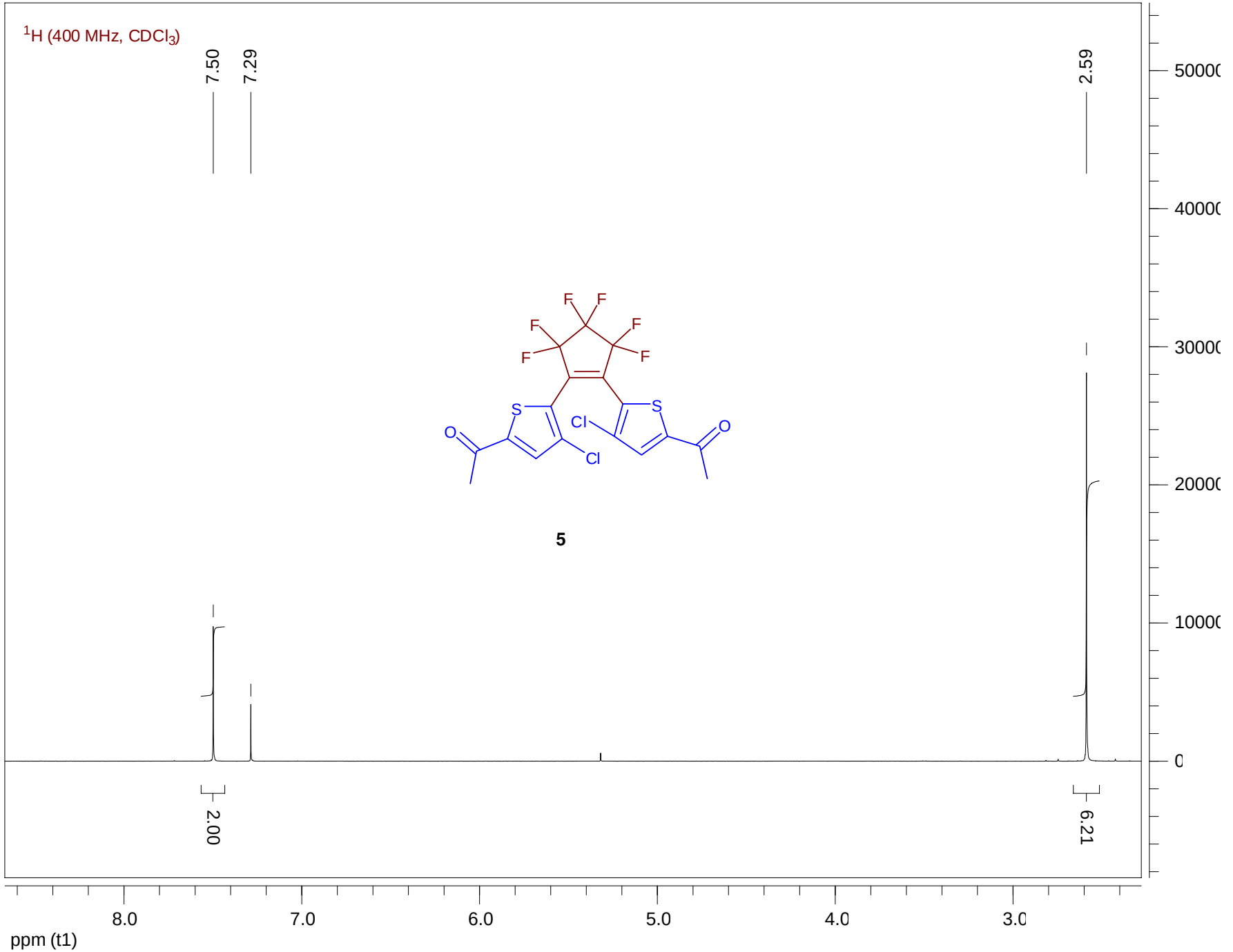

13C (100 MHz, CDCl3)
170.9
157.0
132.6
131.2
129.2
126.8
113.7
77.4
77.0
76.7
17.5
F
F
F
F
F
Cl
S
N
3b
80000
70000
60000
50000
40000
30000
20000
10000
0
150
100
50
ppm (t1)

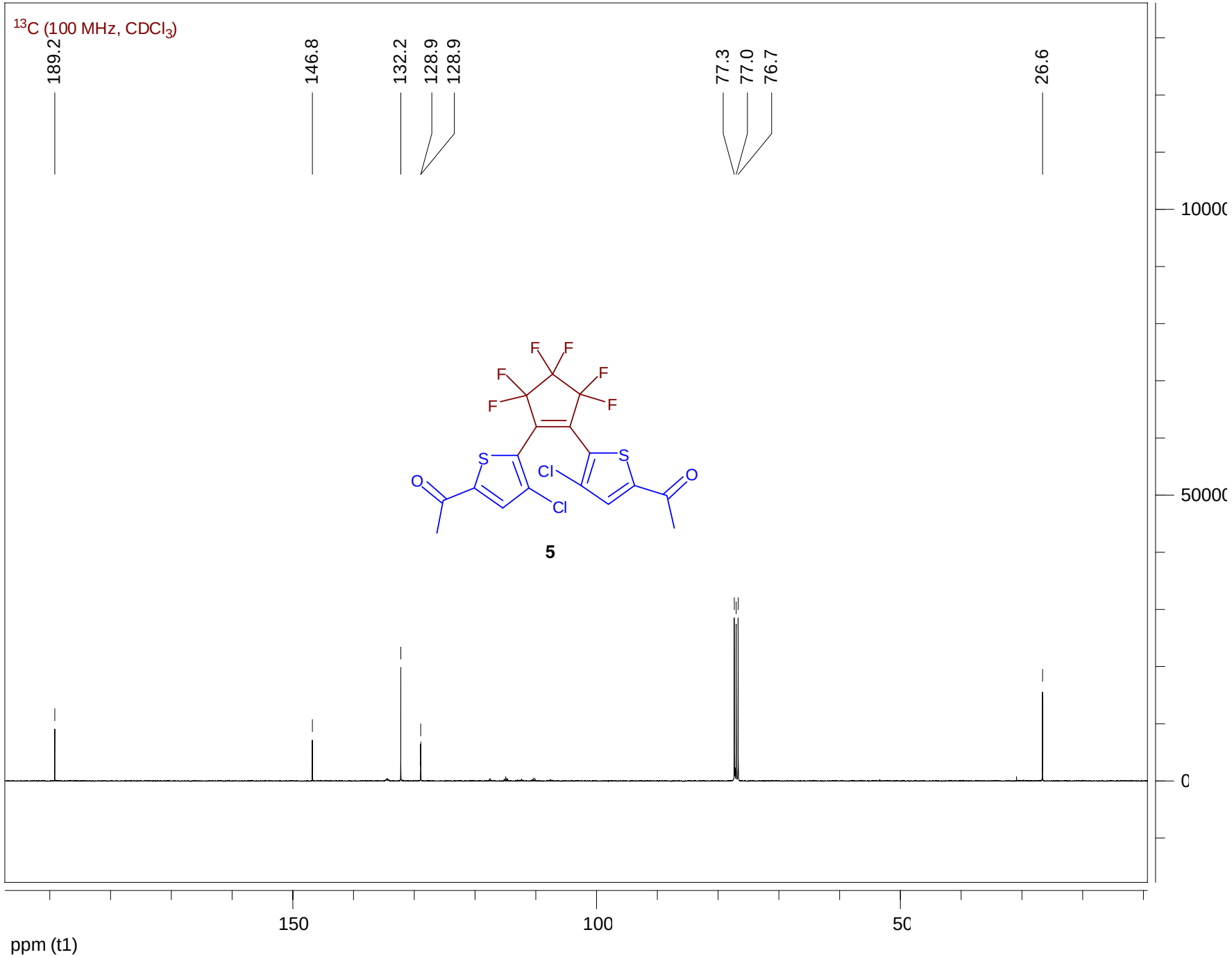

^{19}F (376 MHz, CDCl$_3$)
-109.24
-113.39
-130.12
-130.13
-130.14
-130.15
F
F
F
F
F
Cl
S
N
3b
2.31
2.05
2.04
10000
50000
0
-80
-90
-100
-110
-120
-130
-140
-150
ppm (t1)


1H (400 MHz, CDCl3)
7.44
7.29
2.56
1.88
10000
50000
0
2.00
6.11
6.16
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)
F
F
F
F
F
F
S
S
O
O
4

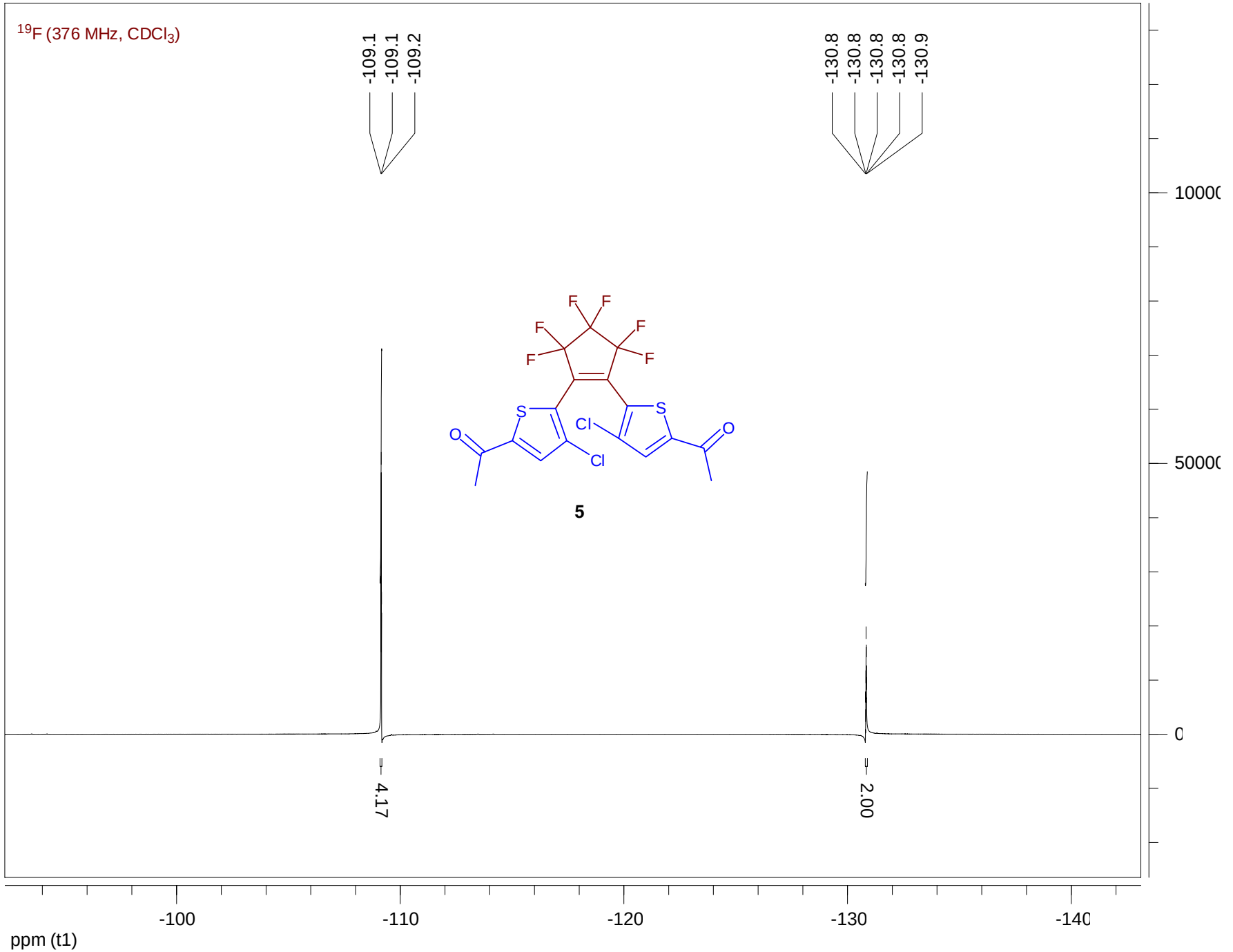

13C (100 MHz, CDCl3)
190.1
146.7
141.9
134.7
129.6
77.4
77.0
76.7
26.9
15.4
F
F
F
F
F
F
S
S
O
O
4
20000
15000
10000
50000
0
150
100
50
ppm (t1)

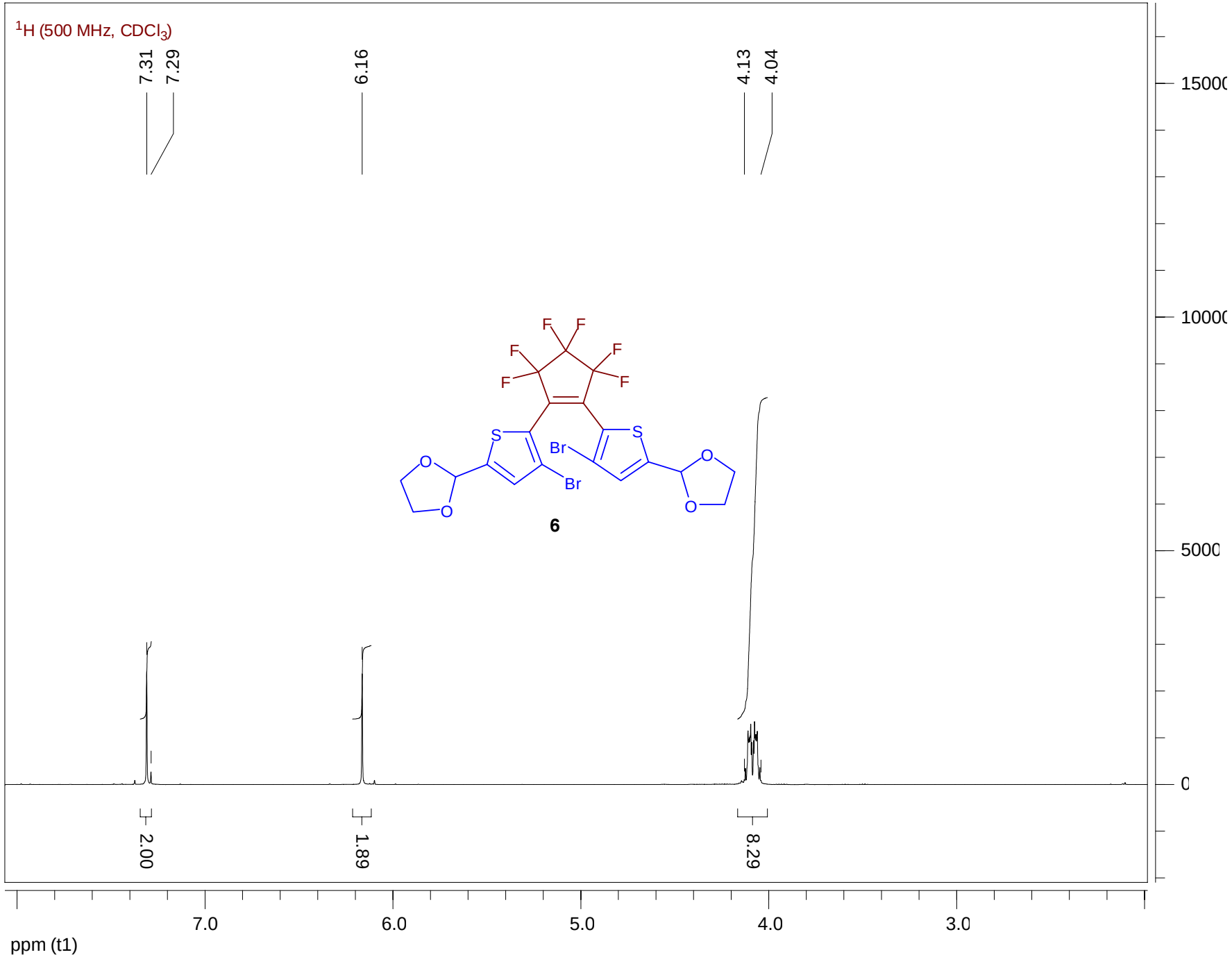

19F (376 MHz, CDCl3)
-109.6
-109.6
-109.6
-131.3
-131.3
-131.3
-131.3
-131.4
F
F
F
F
F
S
S
O
O
4
4.15
2.08
10000
50000
0
-105.0
-110.0
-115.0
-120.0
-125.0
-130.0
-135.0
-140.0
ppm (t1)

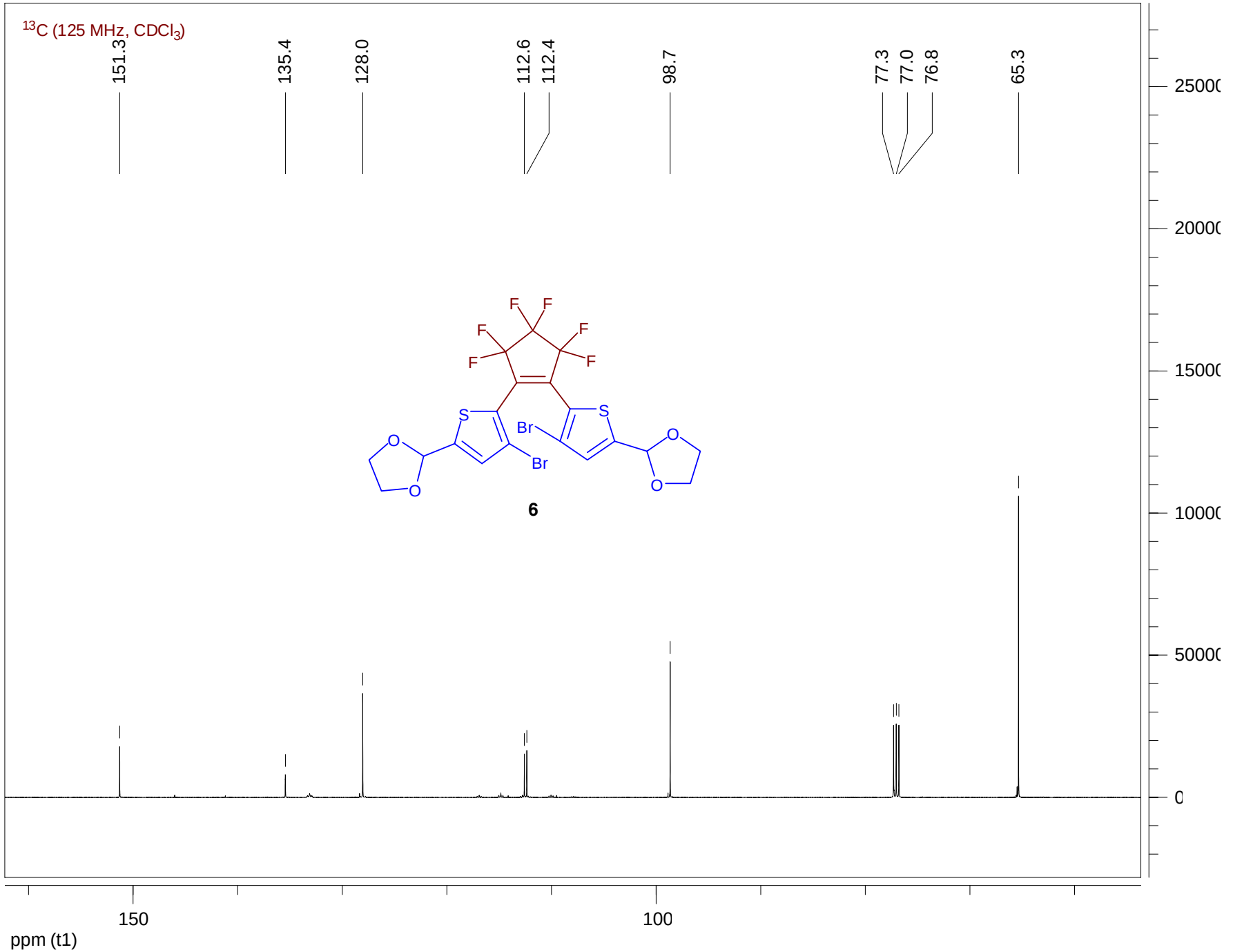

^{1}H (400 MHz, $CDCl_3$)
7.50
7.29
2.59
F
F
F
F
F
F
S
S
Cl
Cl
O
O
5
2.00
6.21
50000
40000
30000
20000
10000
0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

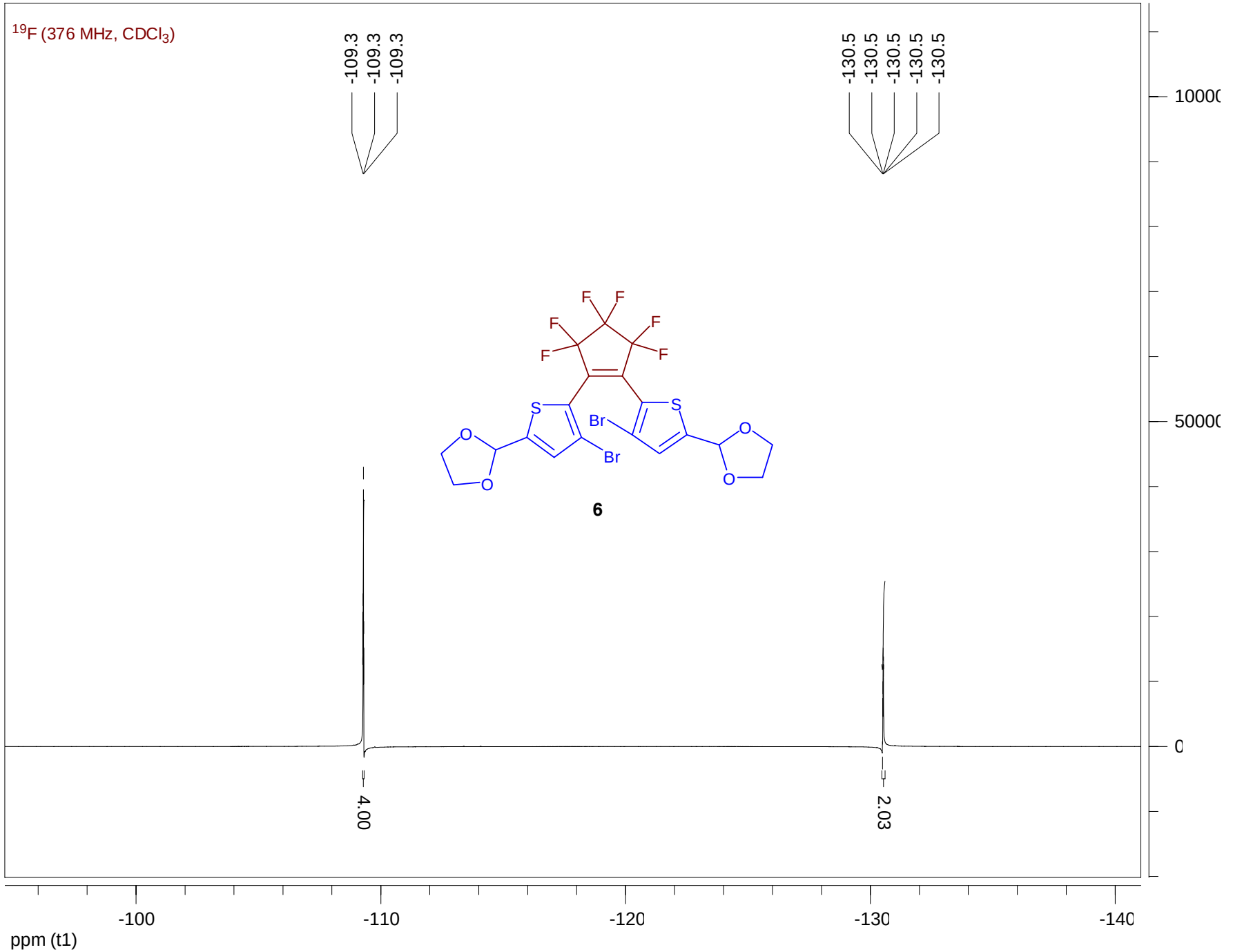

13C (100 MHz, CDCl3)
189.2
146.8
132.2
128.9
128.9
77.3
77.0
76.7
26.6
F
F
F
F
F
F
S
S
Cl
Cl
O
O
10000
50000
0
150
100
50
ppm (t1)

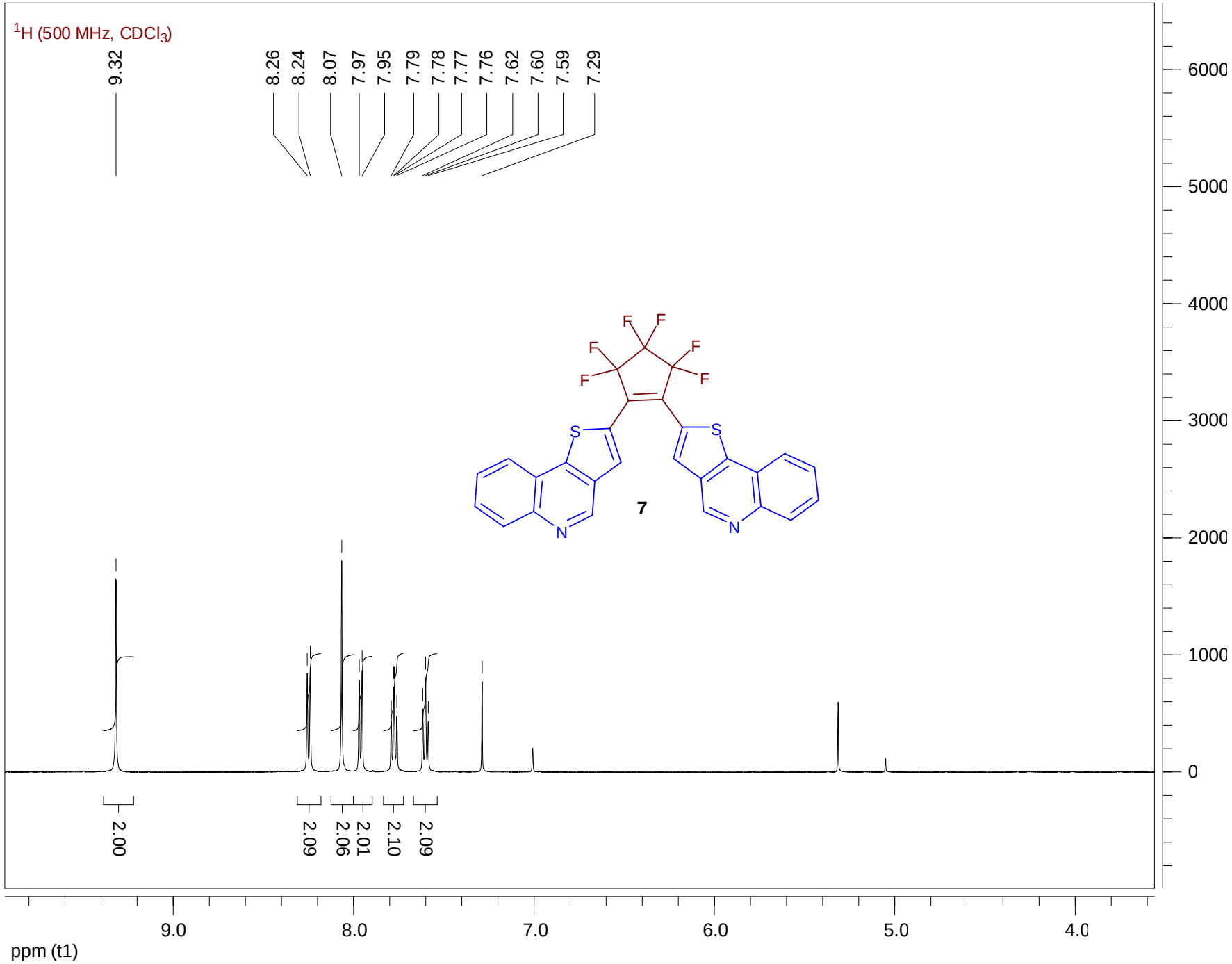
5

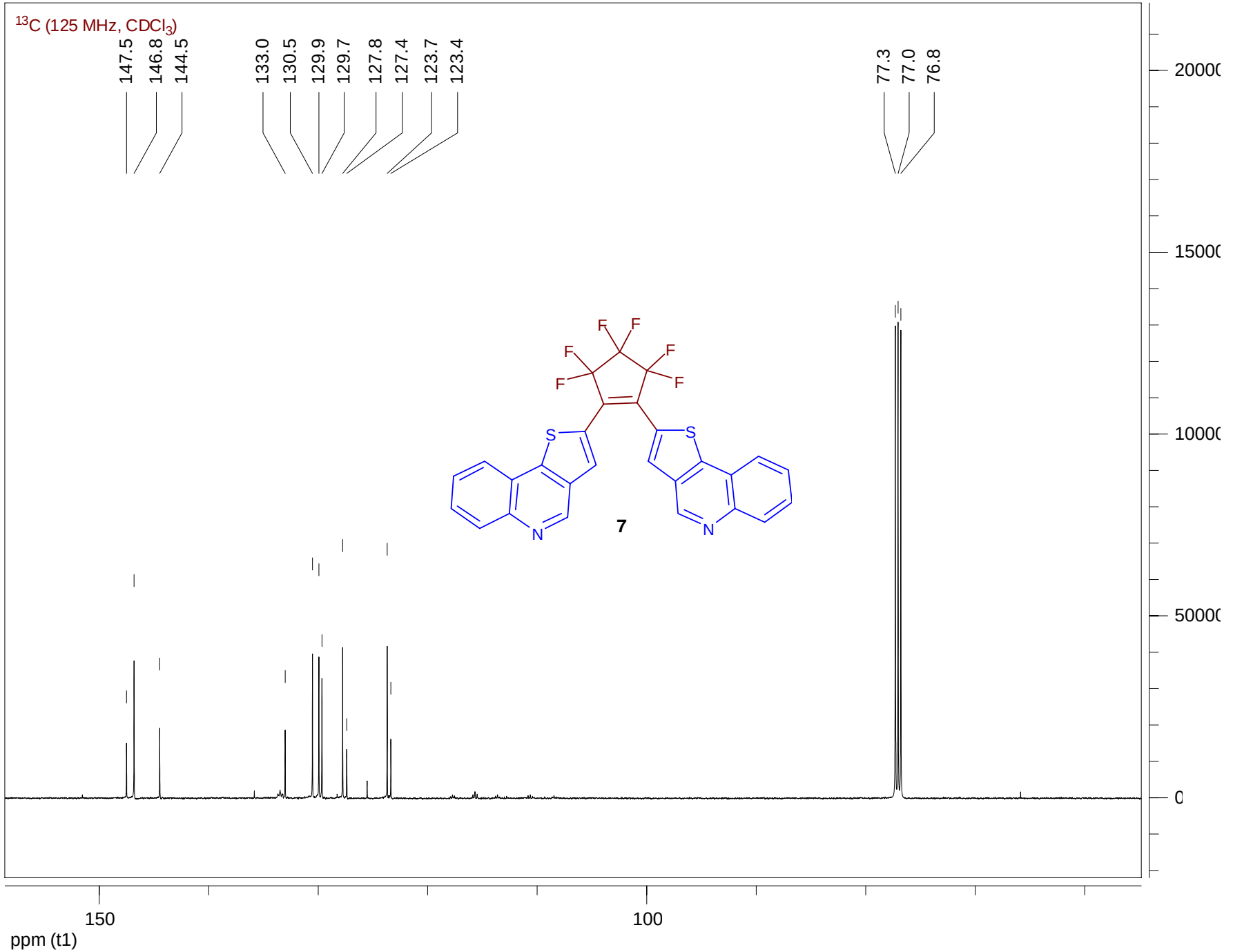

19F (376 MHz, CDCl3)
-109.1
-109.1
-109.2
-130.8
-130.8
-130.8
-130.8
-130.9
F
F
F
F
F
S
S
Cl
Cl
O
O
5
10000
50000
0
4.17
2.00
-100
-110
-120
-130
-140
ppm (t1)

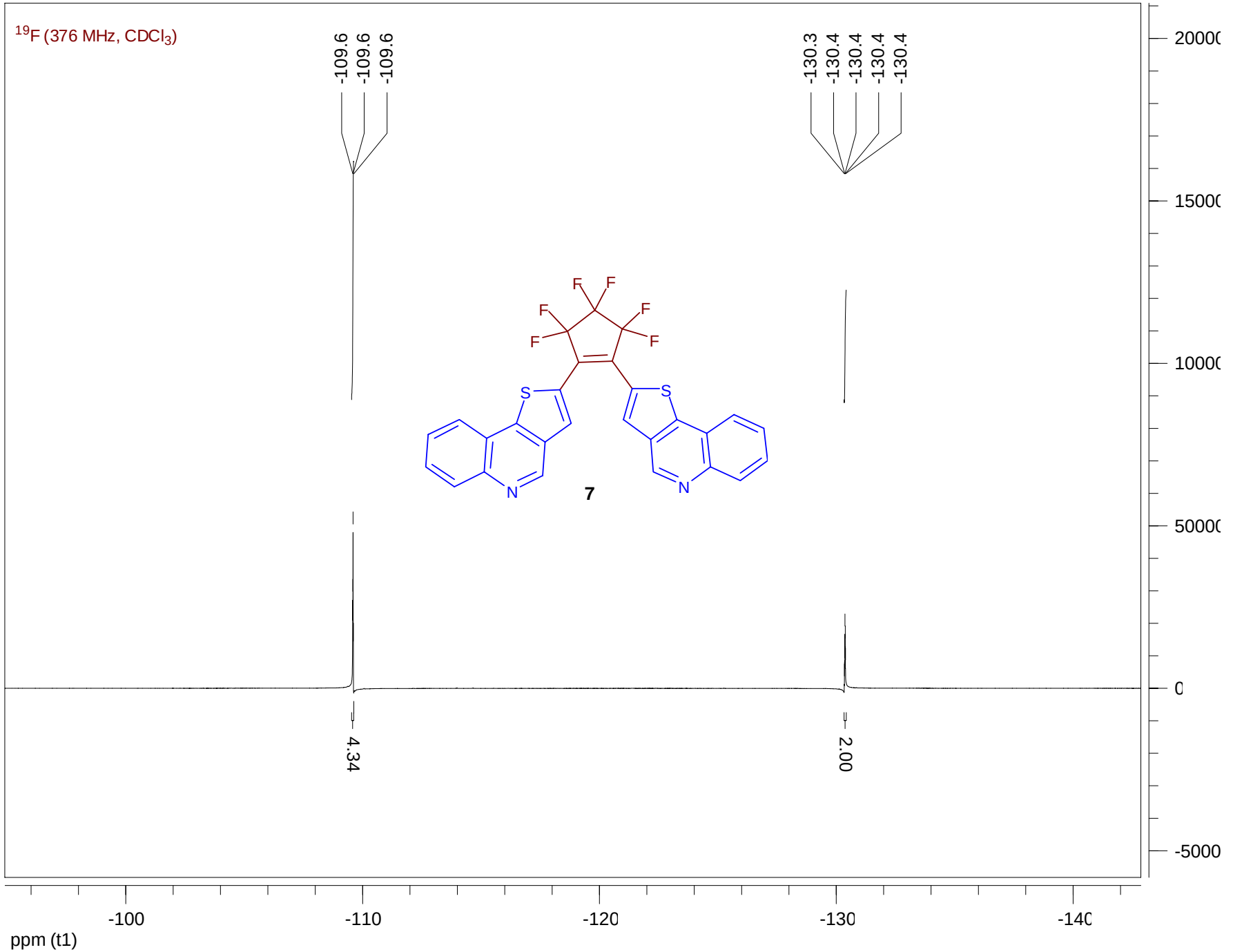

^{1}H (500 MHz, CDCl$_3$)
7.31
7.29
6.16
4.13
4.04
F
F
F
F
F
F
S
S
Br
Br
O
O
O
O
6
15000
10000
5000
0
2.00
1.89
8.29
7.0
6.0
5.0
4.0
3.0
ppm (t1)

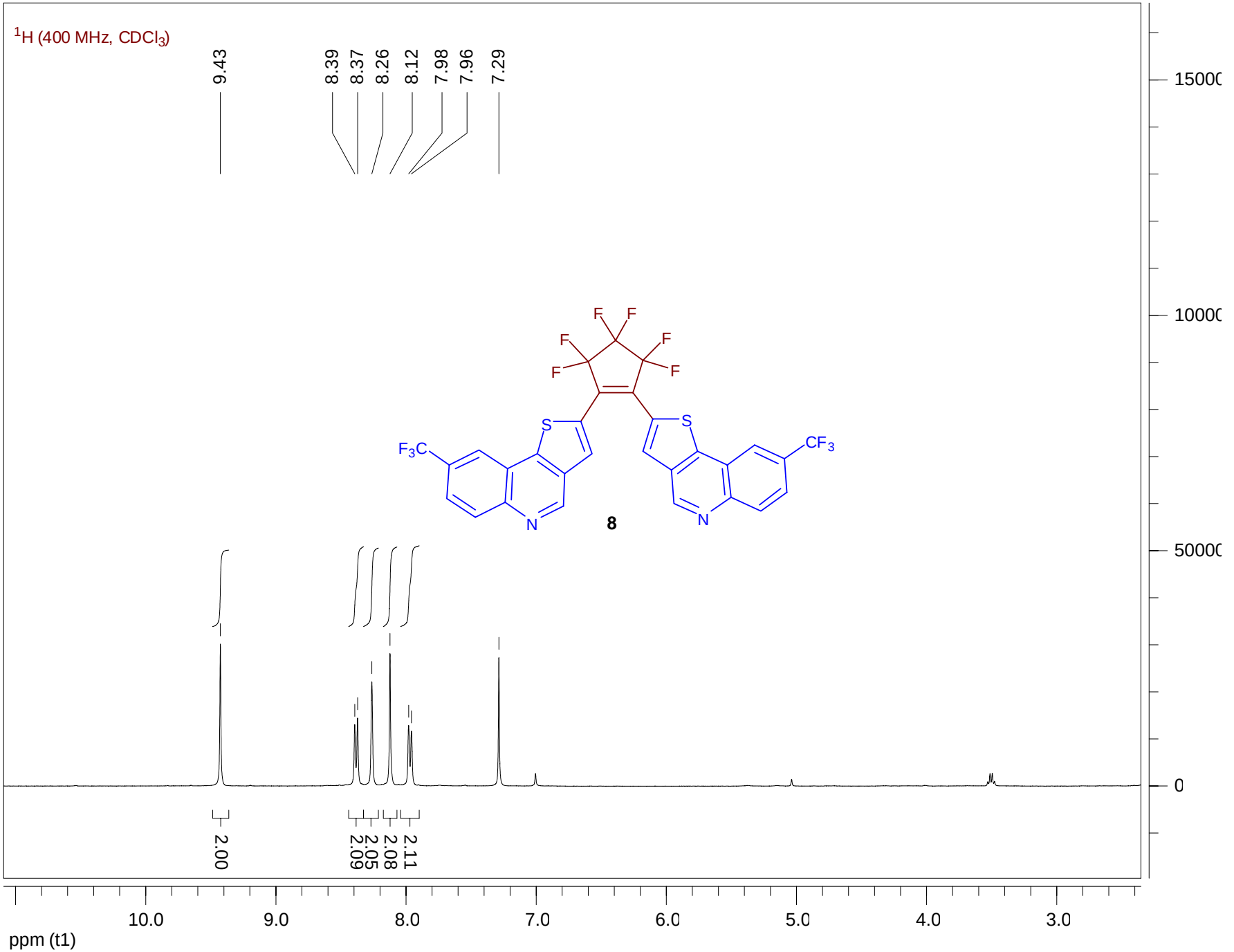

^{13}C (125 MHz, CDCl$_3$)
151.3
135.4
128.0
112.6
112.4
98.7
77.3
77.0
76.8
65.3
F
F
F
F
F
S
S
Br
Br
O
O
O
O
6
25000
20000
15000
10000
50000
0
150
100
ppm (t1)

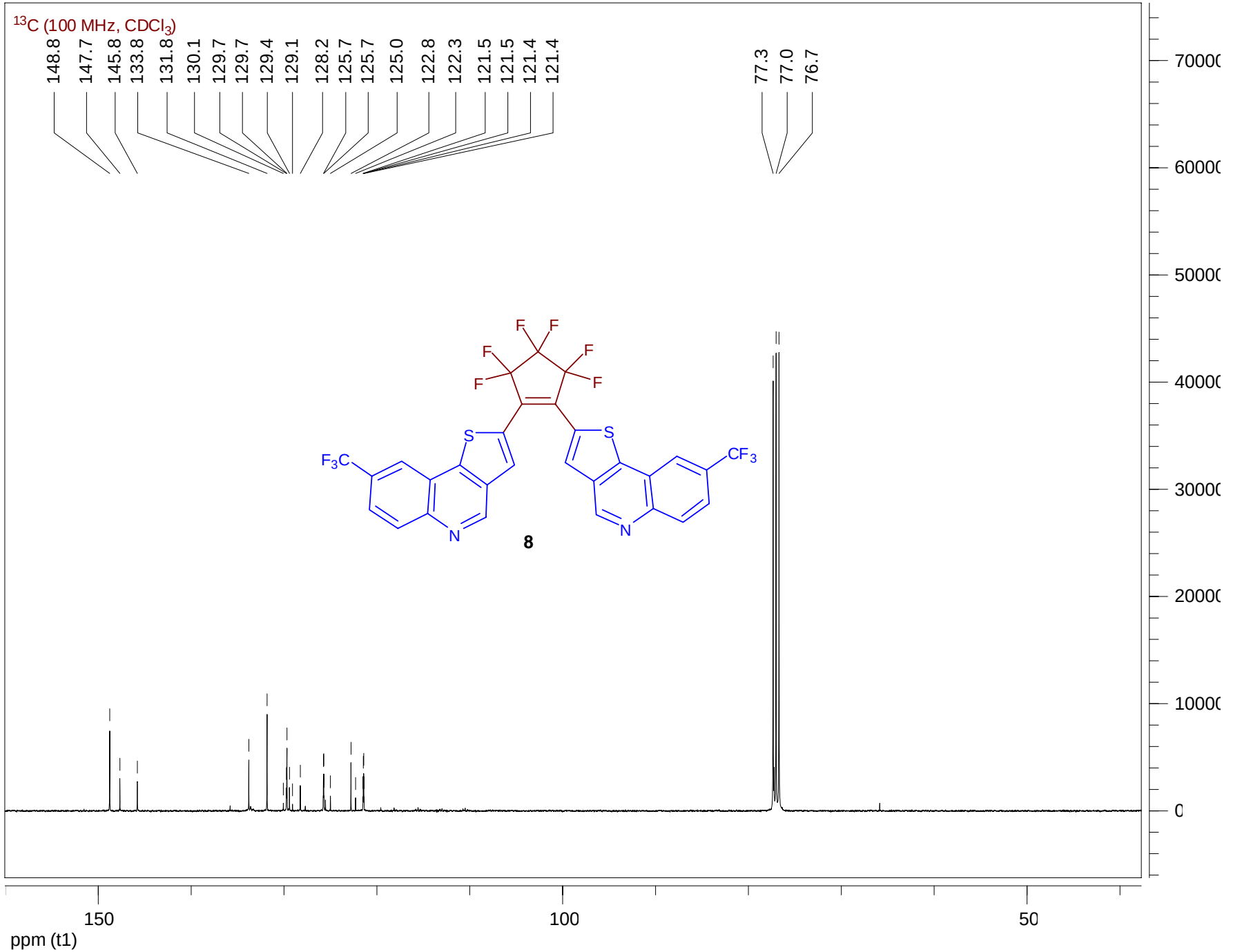

19F (376 MHz, CDCl3)
-109.3
-109.3
-109.3
-130.5
-130.5
-130.5
-130.5
-130.5
F
F
F
F
F
F
S
S
Br
Br
O
O
O
O
6
10000
50000
0
4.00
2.03
-100
-110
-120
-130
-140
ppm (t1)

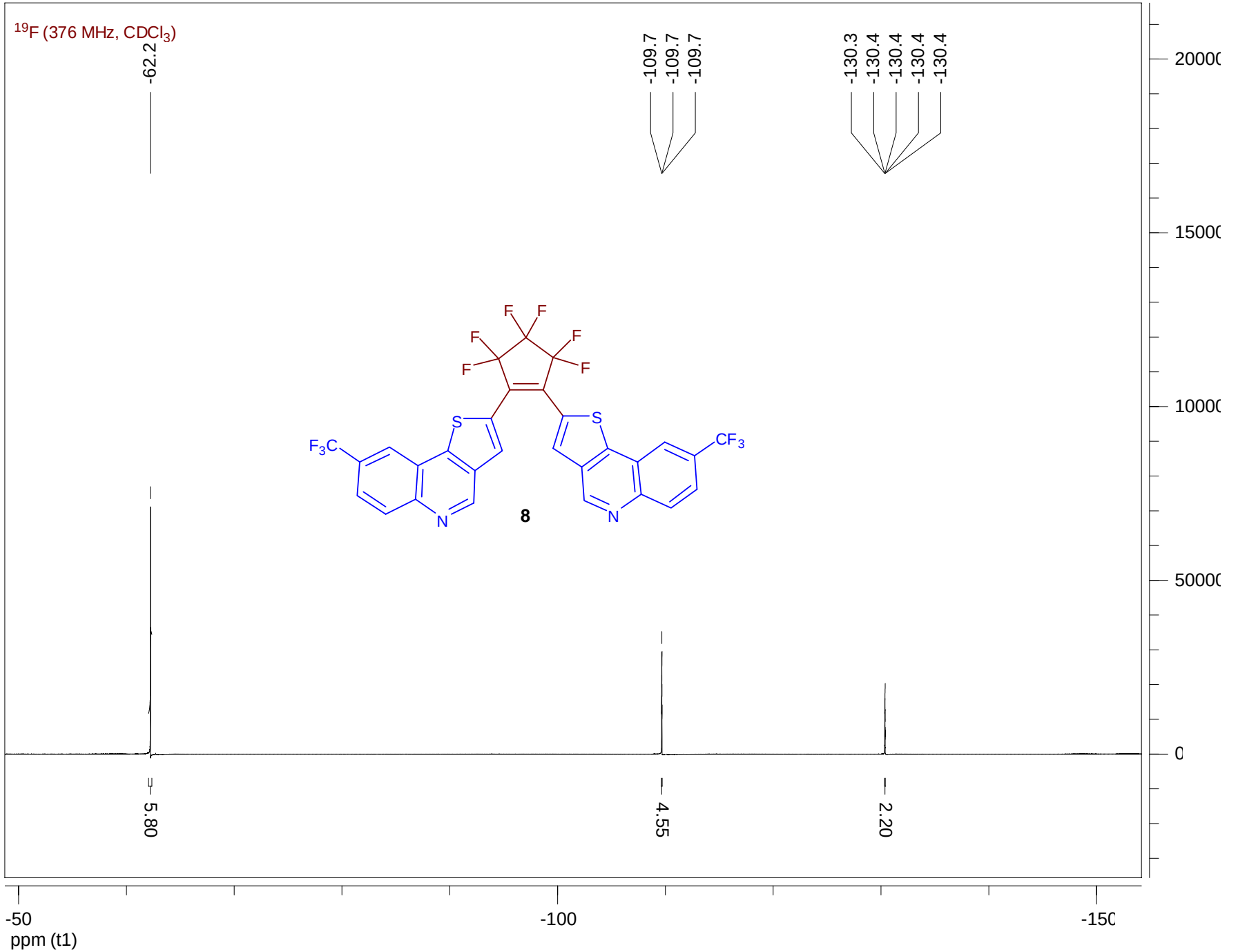

^{1}H (500 MHz, $CDCl_3$)
9.32
8.26
8.24
8.07
7.97
7.95
7.79
7.78
7.77
7.76
7.62
7.60
7.59
7.29
F
F
F
F
F
S
S
N
N
7
6000
5000
4000
3000
2000
1000
0
2.00
2.09
2.06
2.01
2.10
2.09
9.0
8.0
7.0
6.0
5.0
4.0
ppm (t1)

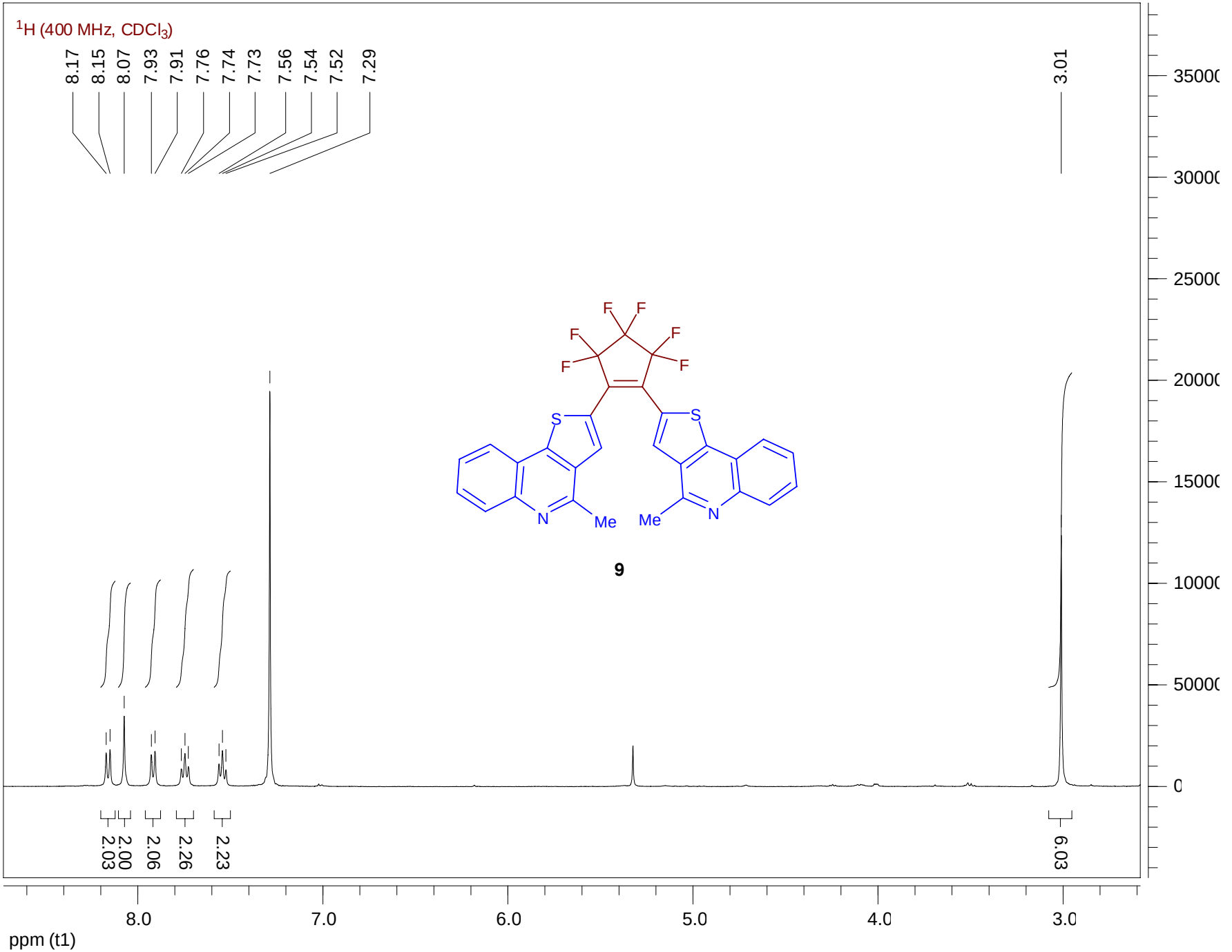

13C (125 MHz, CDCl3)
147.5
146.8
144.5
133.0
130.5
129.9
129.7
127.8
127.4
123.7
123.4
77.3
77.0
76.8
F
F
F
F
F
F
S
S
N
N
7
20000
15000
10000
50000
0
150
100
ppm (t1)

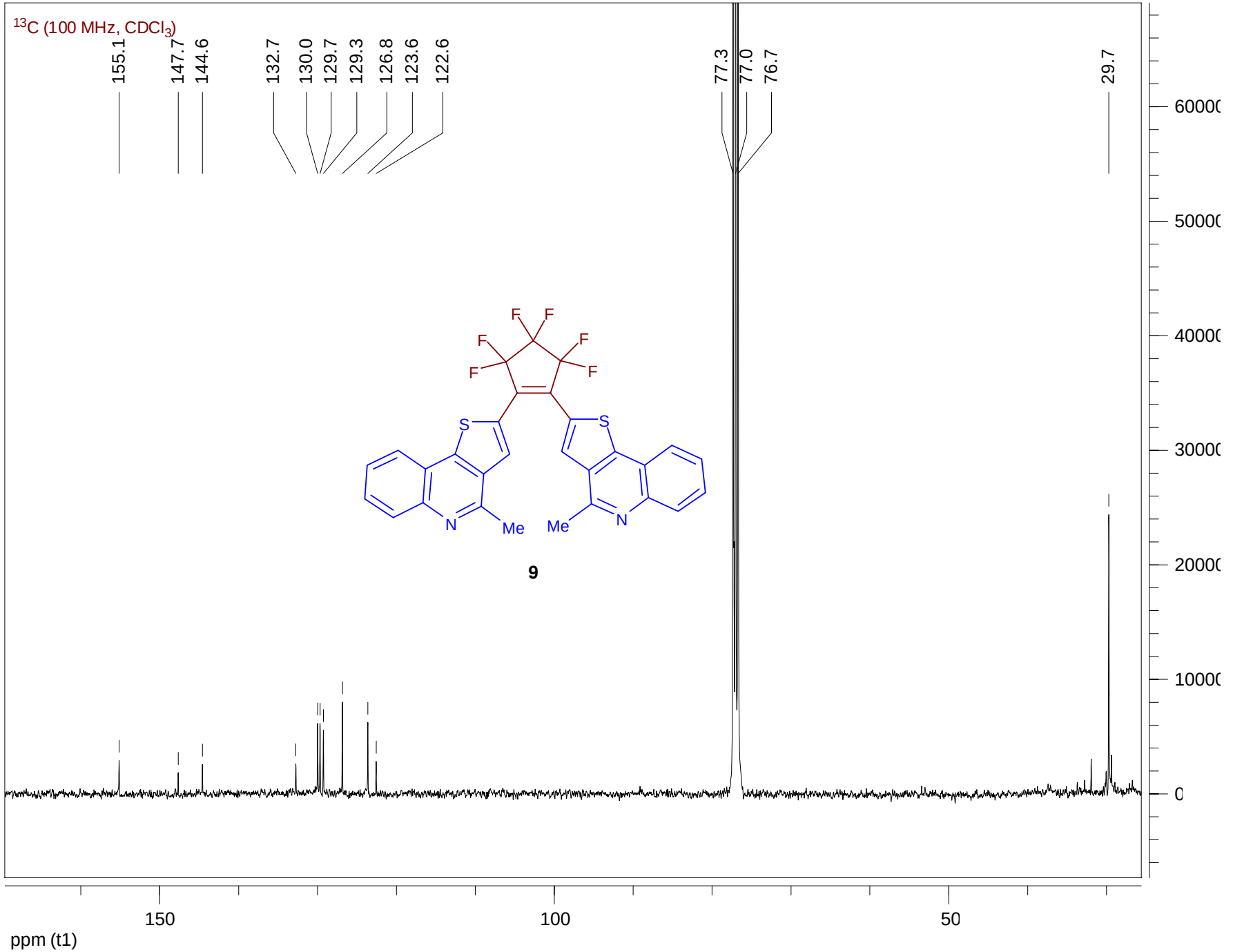

19F (376 MHz, CDCl3)
-109.6
-109.6
-109.6
-130.3
-130.4
-130.4
-130.4
-130.4
F
F
F
F
F
F
S
S
N
N
7
4.34
2.00
20000
15000
10000
50000
0
-5000
-100
-110
-120
-130
-140
ppm (t1)

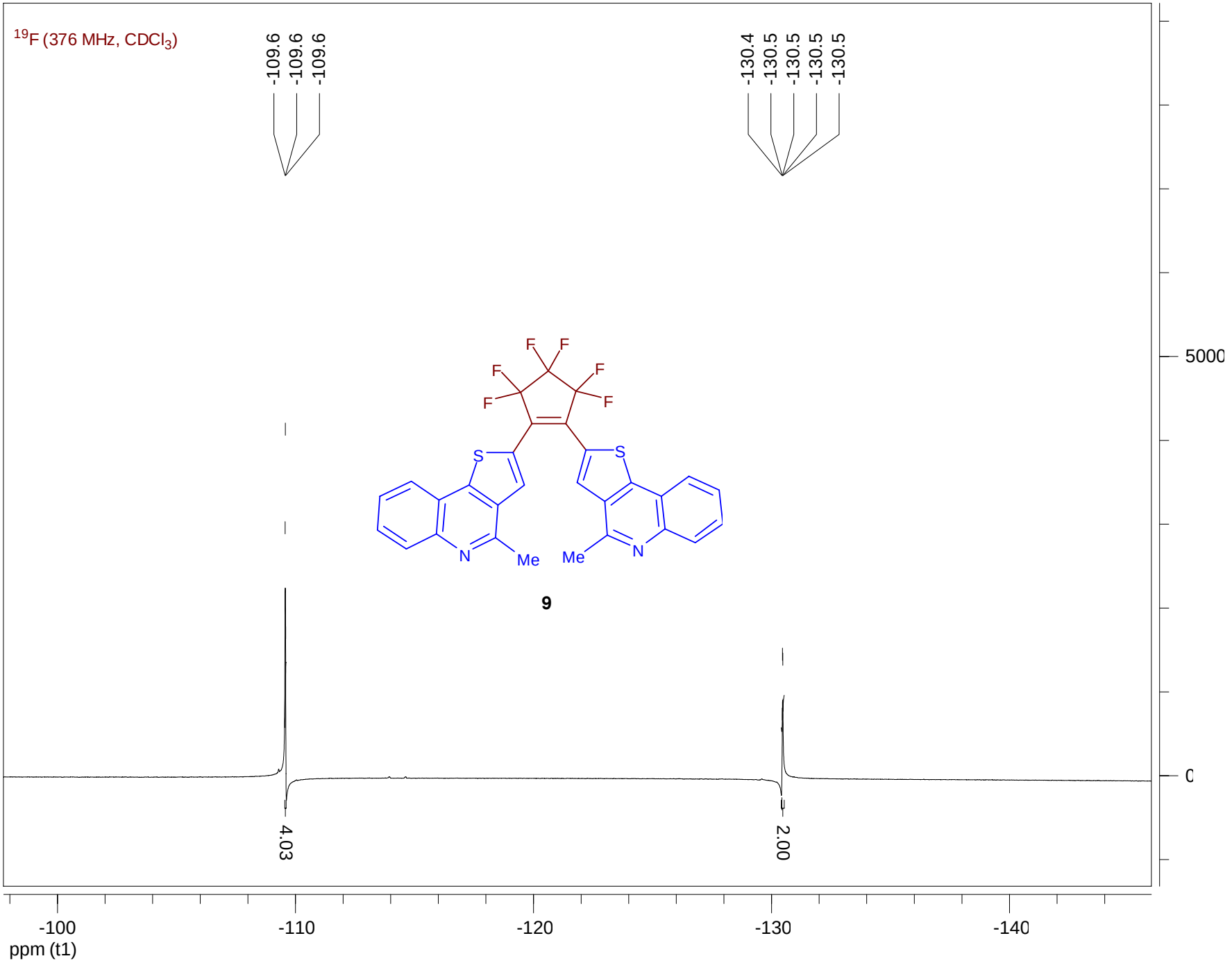

^{1}H (400 MHz, $CDCl_3$)
9.43
8.39
8.37
8.26
8.12
7.98
7.96
7.29
F
F
F
F
F
S
S
F_3C
CF_3
N
N
8
15000
10000
50000
0
2.00
2.09
2.05
2.08
2.11
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

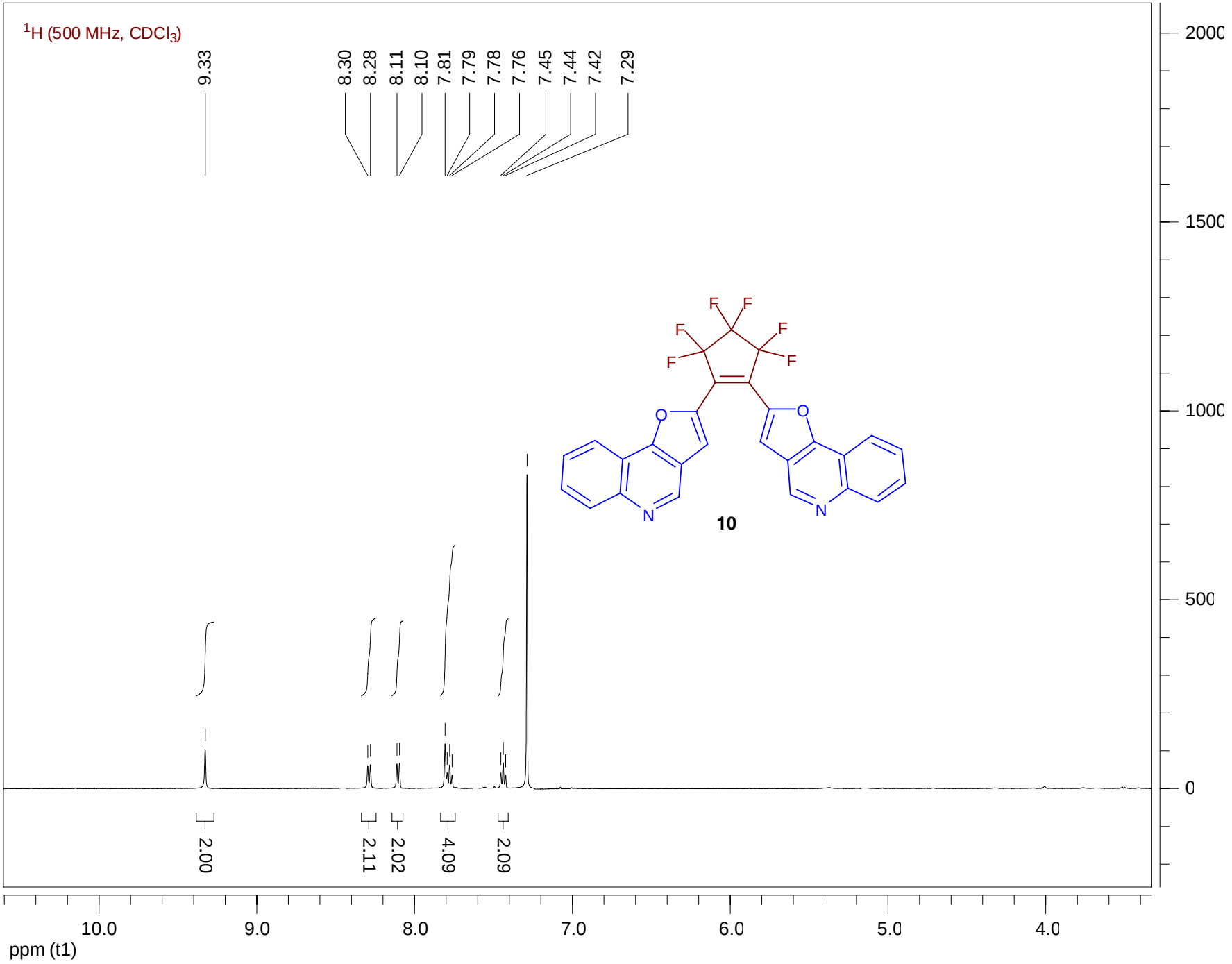

13C (100 MHz, CDCl3)
148.8
147.7
145.8
133.8
131.8
130.1
129.7
129.7
129.4
129.1
128.2
125.7
125.7
125.0
122.8
122.3
121.5
121.5
121.4
121.4
77.3
77.0
76.7
F
F
F
F
F
F
S
S
F3C
CF3
N
N
8
70000
60000
50000
40000
30000
20000
10000
0
150
100
50
ppm (t1)

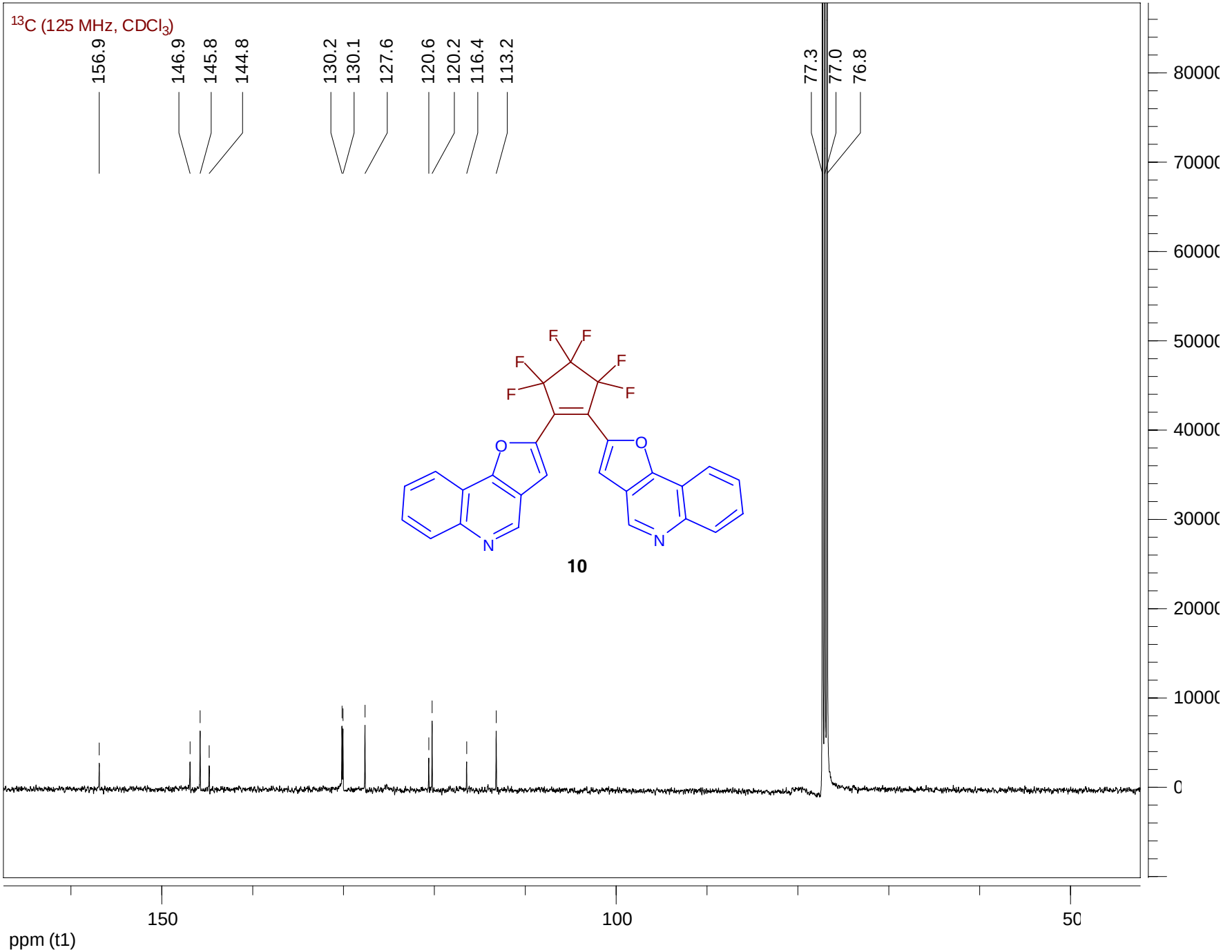

19F (376 MHz, CDCl3)
-62.2
-109.7
-109.7
-109.7
-130.3
-130.4
-130.4
-130.4
-130.4
F
F
F
F
F
F
S
S
F3C
CF3
N
N
8
5.80
4.55
2.20
20000
15000
10000
50000
0
-50
-100
-150
ppm (t1)

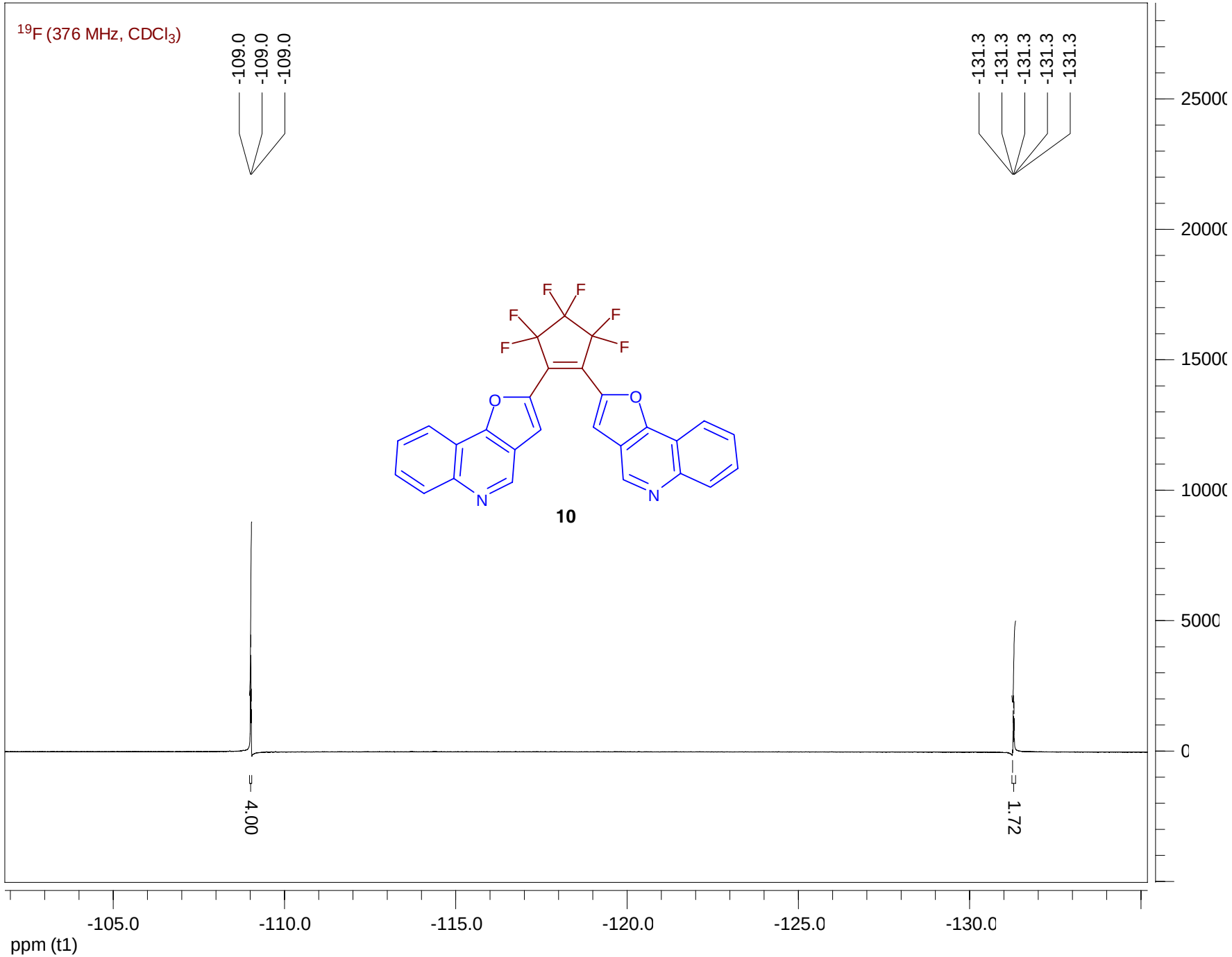

1H (400 MHz, CDCl3)
8.17
8.15
8.07
7.93
7.91
7.76
7.74
7.73
7.56
7.54
7.52
7.29
3.01
F
F
F
F
F
F
S
S
N
Me
Me
N
9
35000
30000
25000
20000
15000
10000
50000
0
2.03
2.00
2.06
2.26
2.23
6.03
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

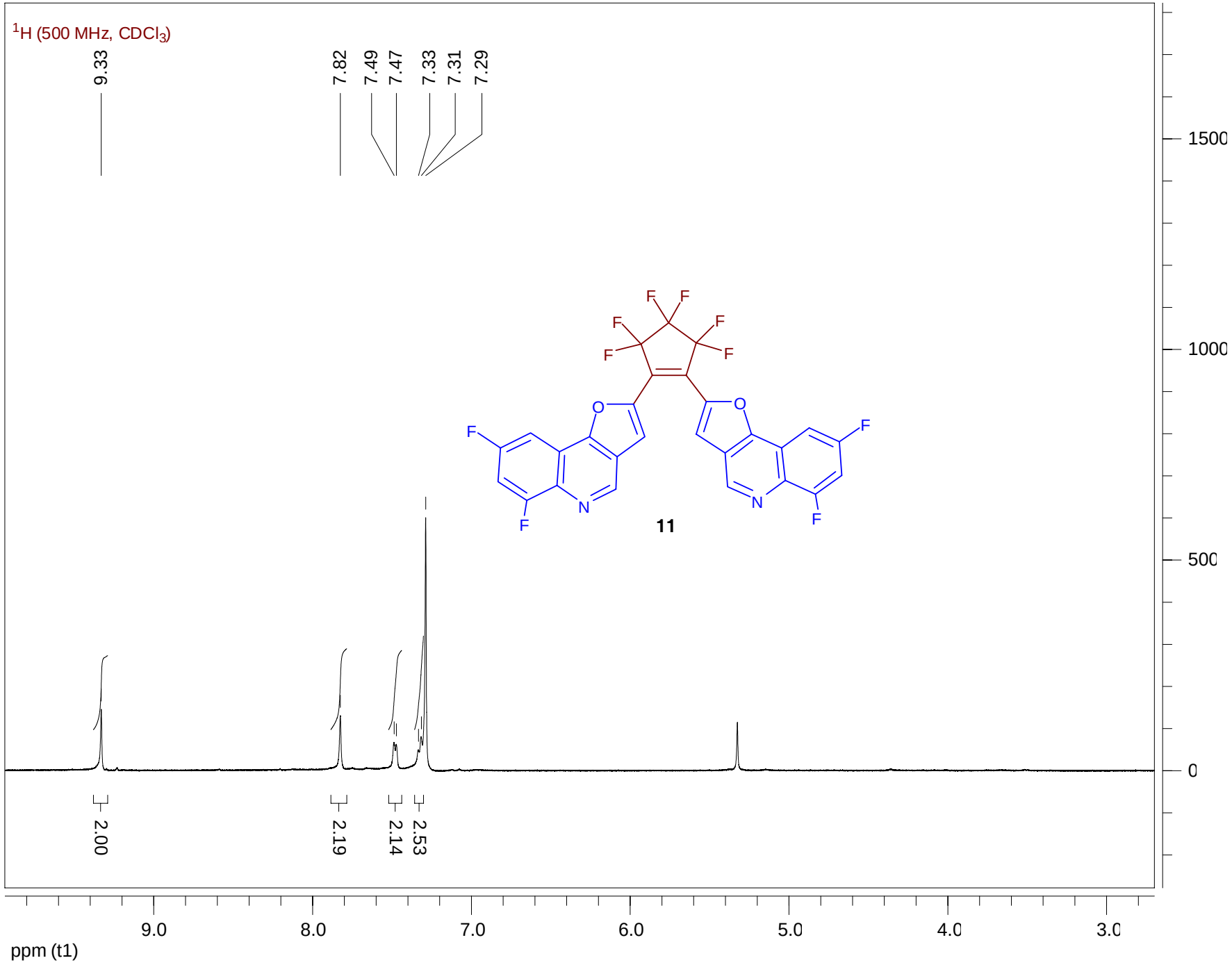

13C (100 MHz, CDCl3)
155.1
147.7
144.6
132.7
130.0
129.7
129.3
126.8
123.6
122.6
77.3
77.0
76.7
29.7
F
F
F
F
F
S
S
N
N
Me
Me
9
60000
50000
40000
30000
20000
10000
0
150
100
50
ppm (t1)

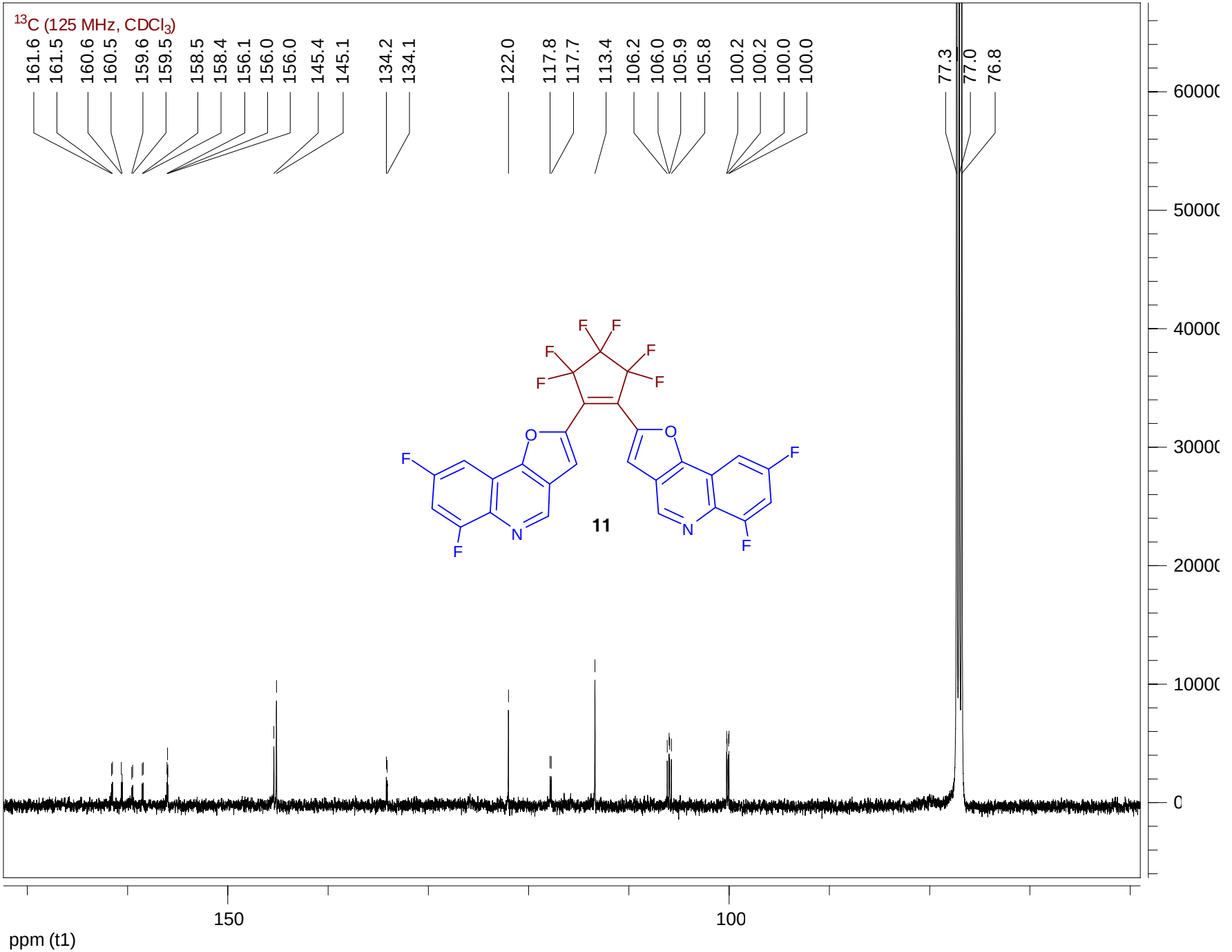

19F (376 MHz, CDCl3)
-109.6
-109.6
-109.6
-130.4
-130.5
-130.5
-130.5
-130.5
F
F
F
F
F
S
S
N
Me
Me
N
9
4.03
2.00
5000
0
-100
-110
-120
-130
-140
ppm (t1)

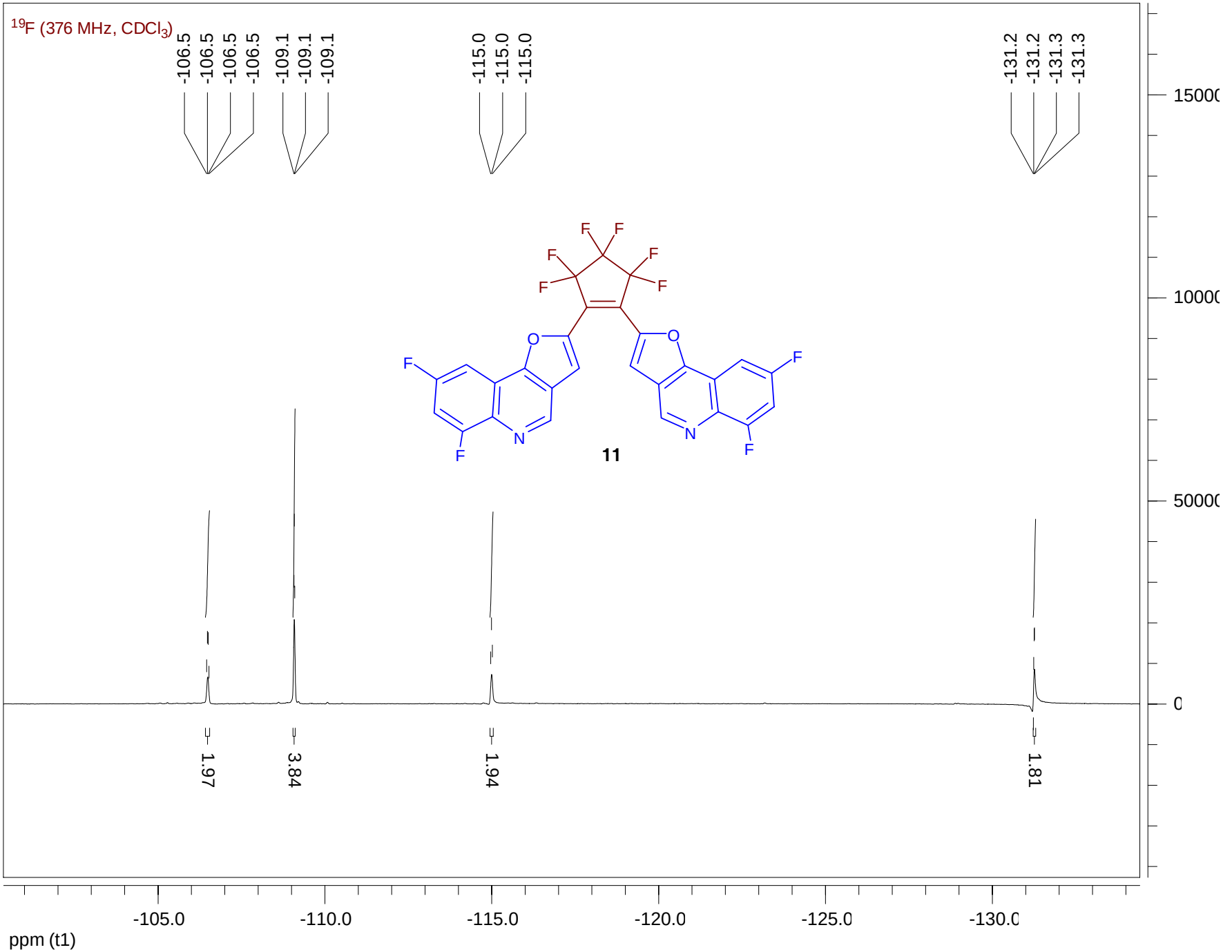

^{1}H (500 MHz, $CDCl_3$)
9.33
8.30
8.28
8.11
8.10
7.81
7.79
7.78
7.76
7.45
7.44
7.42
7.29
F
F
F
F
F
F
O
O
N
N
10
2000
1500
1000
500
0
2.00
2.11
2.02
4.09
2.09
10.0
9.0
8.0
7.0
6.0
5.0
4.0
ppm (t1)

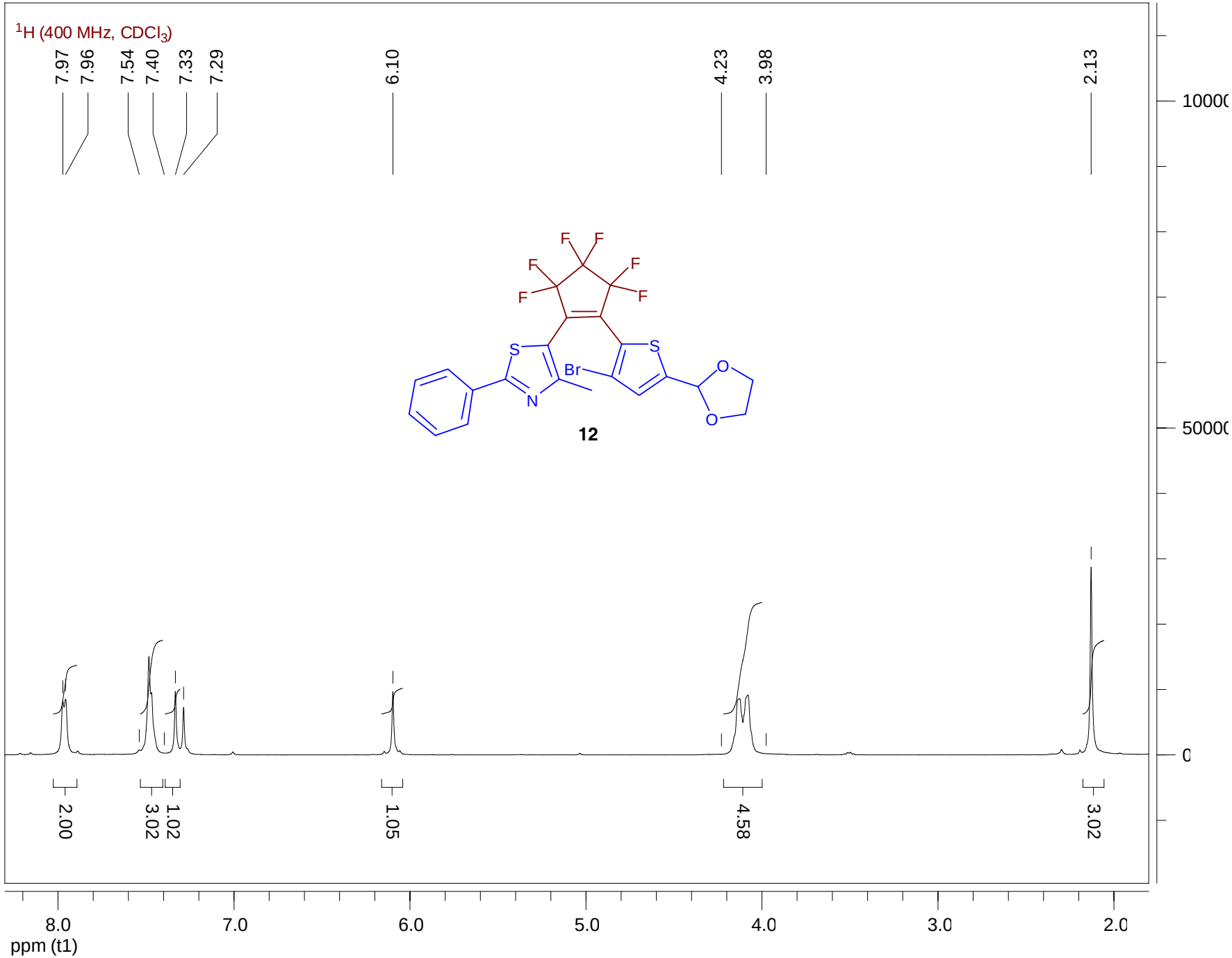

13C (125 MHz, CDCl3)
156.9
146.9
145.8
144.8
130.2
130.1
127.6
120.6
120.2
116.4
113.2
77.3
77.0
76.8
F
F
F
F
F
O
O
N
N
10
80000
70000
60000
50000
40000
30000
20000
10000
0
150
100
50
ppm (t1)

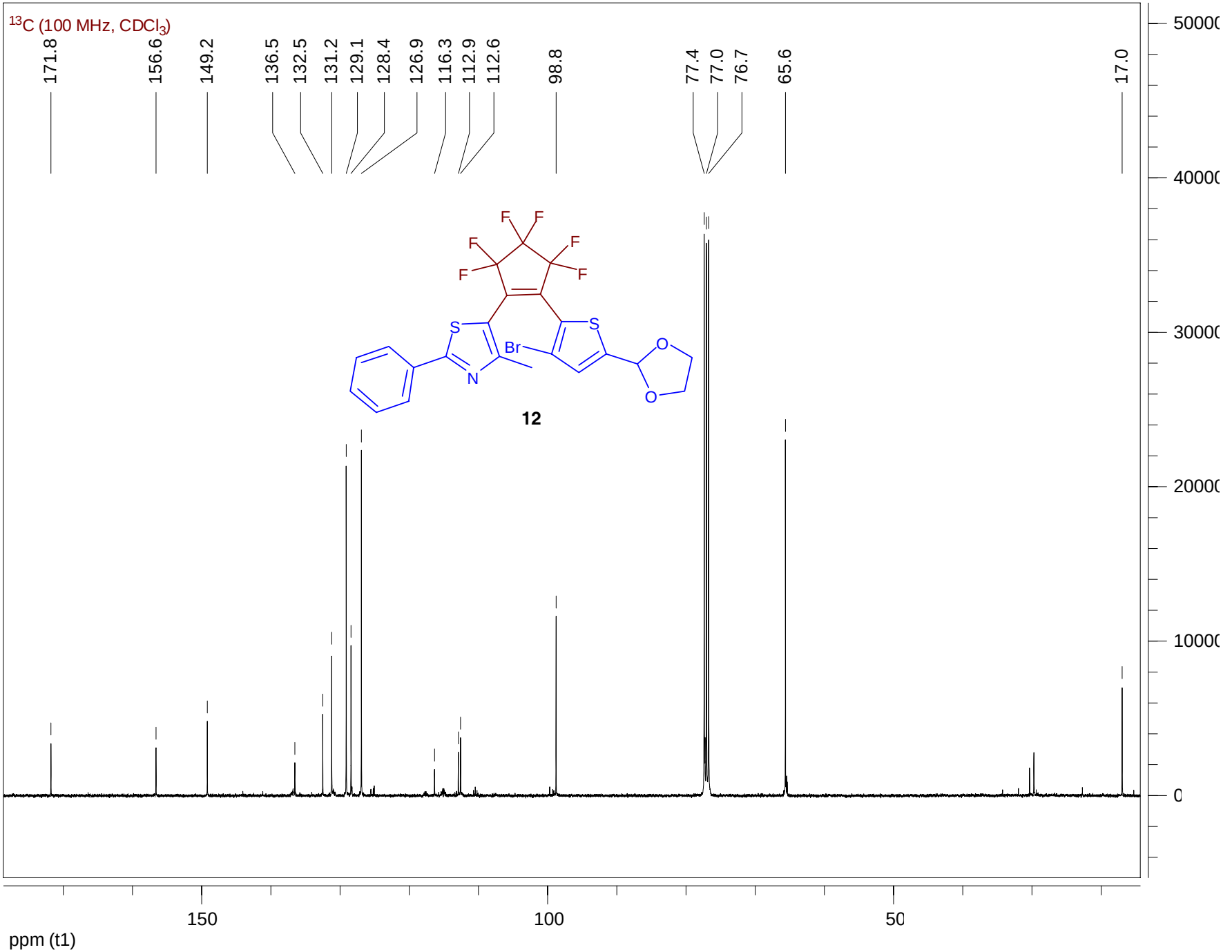

19F (376 MHz, CDCl3)
-109.0
-109.0
-109.0
-131.3
-131.3
-131.3
-131.3
-131.3
F
F
F
F
F
F
O
O
N
N
10
25000
20000
15000
10000
5000
0
4.00
1.72
-105.0
-110.0
-115.0
-120.0
-125.0
-130.0
ppm (t1)

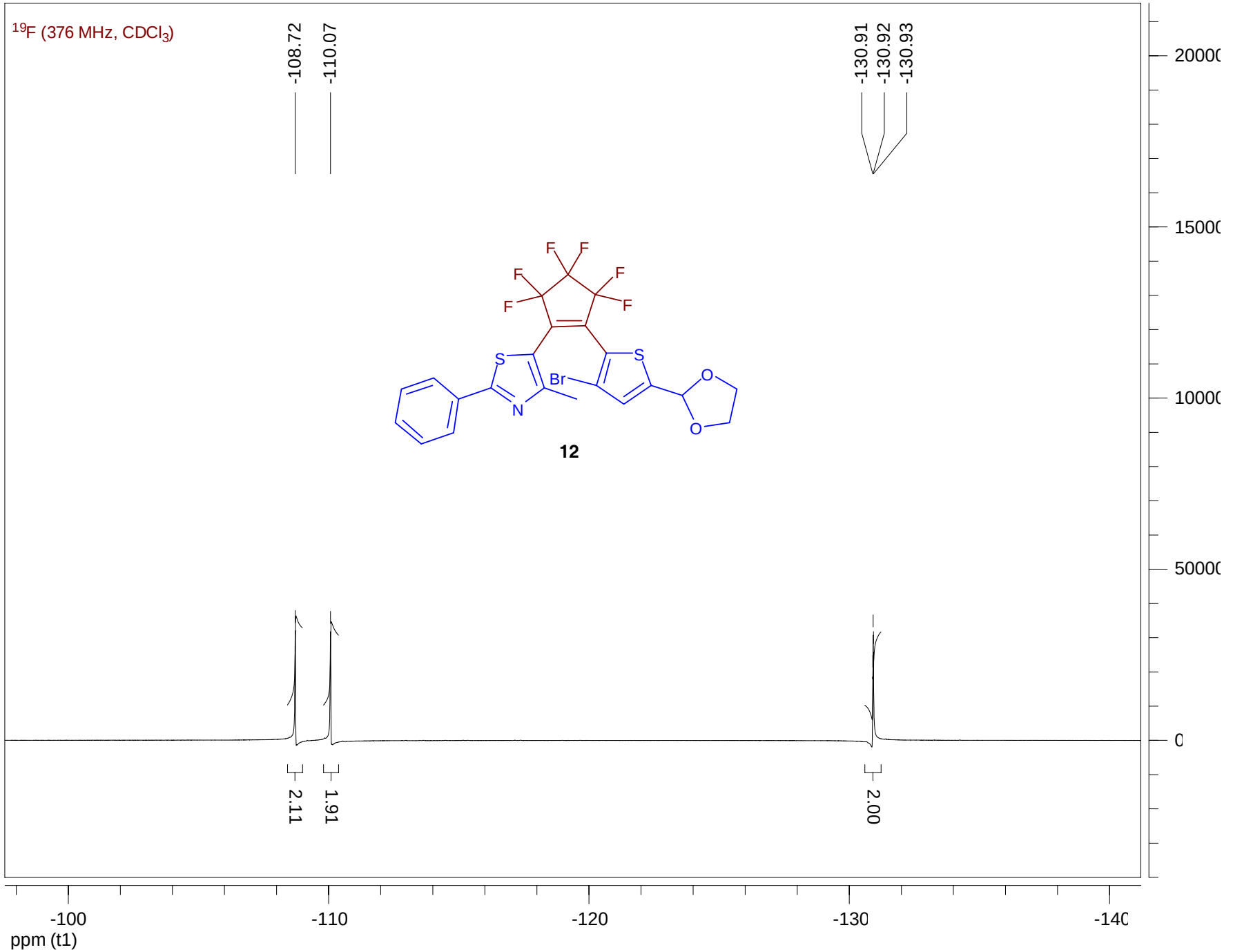

^{1}H (500 MHz, $CDCl_3$)
9.33
7.82
7.49
7.47
7.33
7.31
7.29
F
F
F
F
F
O
O
F
F
N
N
F
F
11
1500
1000
500
0
2.00
2.19
2.14
2.53
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)


13C (125 MHz, CDCl3)
161.6
161.5
160.6
160.5
159.6
159.5
158.5
158.4
156.1
156.0
156.0
145.4
145.1
134.2
134.1
122.0
117.8
117.7
113.4
106.2
106.0
105.9
105.8
100.2
100.2
100.0
100.0
77.3
77.0
76.8
F
F
F
F
F
F
O
O
F
F
N
N
F
F
11
60000
50000
40000
30000
20000
10000
0
150
100
ppm (t1)


19F (376 MHz, CDCl3)
-106.5
-106.5
-106.5
-106.5
-109.1
-109.1
-109.1
-115.0
-115.0
-115.0
-131.2
-131.2
-131.3
-131.3
F
F
F
F
F
F
O
O
F
F
N
N
F
F
11
1.97
3.84
1.94
1.81
15000
10000
5000
0
-105.0
-110.0
-115.0
-120.0
-125.0
-130.0
ppm (t1)


1H (400 MHz, CDCl3)
7.97
7.96
7.54
7.40
7.33
7.29
6.10
4.23
3.98
2.13
F
F
F
F
F
S
S
Br
N
O
O
12
10000
50000
0
2.00
3.02
1.02
1.05
4.58
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


13C (100 MHz, CDCl3)
171.8
156.6
149.2
136.5
132.5
131.2
129.1
128.4
126.9
116.3
112.9
112.6
98.8
77.4
77.0
76.7
65.6
17.0
F
F
F
F
F
S
S
Br
N
O
O
12
50000
40000
30000
20000
10000
0
150
100
50
ppm (t1)


19F (376 MHz, CDCl3)
-108.72
-110.07
-130.91
-130.92
-130.93
F
F
F
F
F
S
S
Br
N
O
O
12
2.11
1.91
2.00
20000
15000
10000
50000
0
-100
-110
-120
-130
-140
ppm (t1)

Photochromic studies

UV/vis absorption spectra were recorded using a Specord 205 UV-Vis-NIR spectrophotometer using quartz cuvettes of 1 cm pathlength. Irradiations of solutions have been made using a LS series Light Source of ABET technologies, Inc (150 W xenon lamp), with single wavelength light filters “350FS 10-25” and “450FS 40-25”.

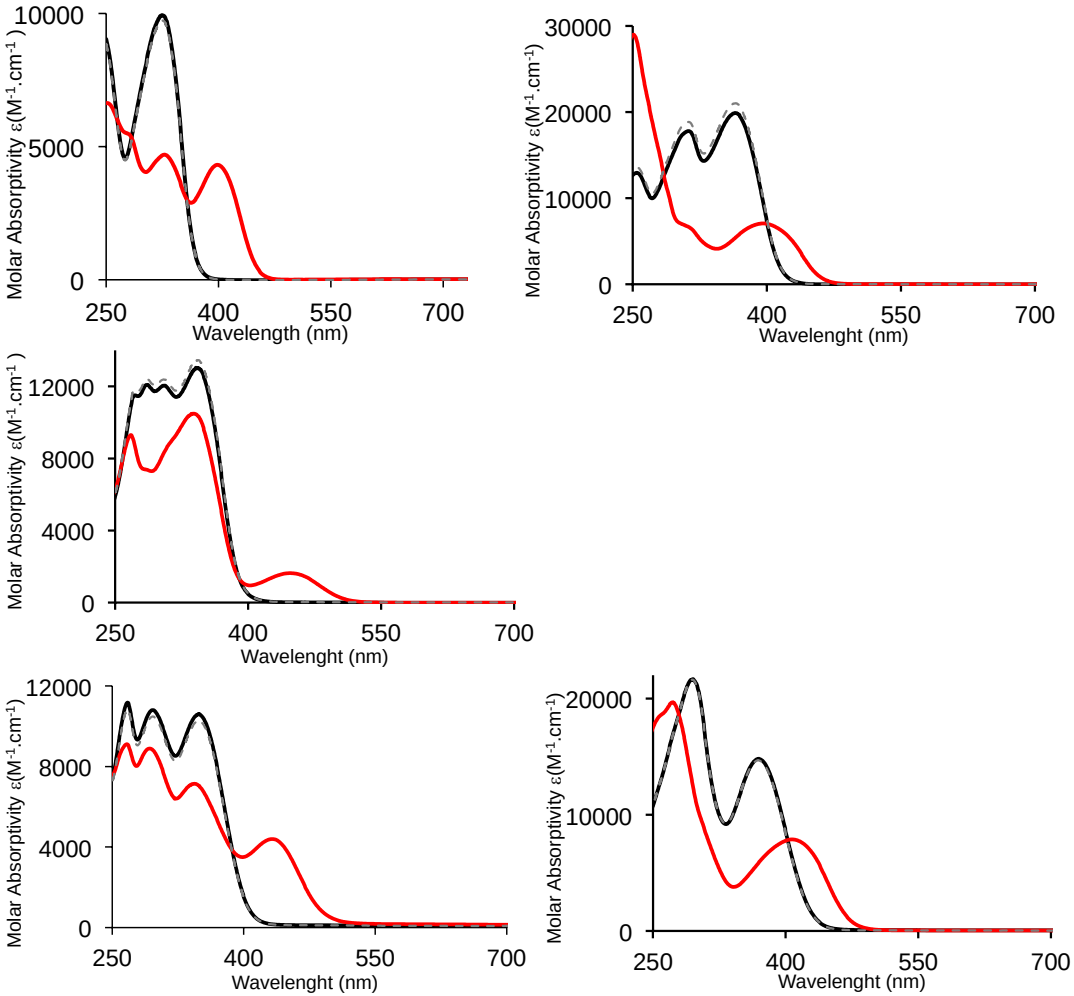


Fig. S1 UV-visible absorption spectrum of a) **2**; b) **3a**; c) **4**; d) **6** and e) **12** in their open form (black line), photostationary state after UV irradiation at 350 nm (red line) and after visible irradiation at 450 nm (dashed grey line).

Table S2 Absorption maximum (λ_{max}) and molar absorption coefficient at λ_{max} (ε) of compounds **2**, **3a**, **4**, **6** and **12** in the open and closed (PSS) forms

Compound	λ_{max} / nm (10^3 ε / M^{-1} cm^{-1})	
	open form	closed form (PSS)[a]
2	322 (9.7)	325, 397
3a	260 (13.0), 318 (18.0), 370 (20.5)	250, 310, 400
4	283 (12.0), 303 (12.0), 340 (12.9)	265, 336, 446
6	265 (11.0), 294 (10.7), 346 (10.5)	264, 290, 342, 430
12	300 (21.0), 367 (14.6)	270, 409

[a] Irradiation at λ = 350 nm, in dichloromethane (C ≈ 2.10^{-4} M) at 298 K.