A concise synthesis of (alkynyl)(trifluoromethyl)sulfanes via a bismuth(III)-promoted reaction of trimethyl(alkynyl)silane with trifluoromethanesulfanylamide

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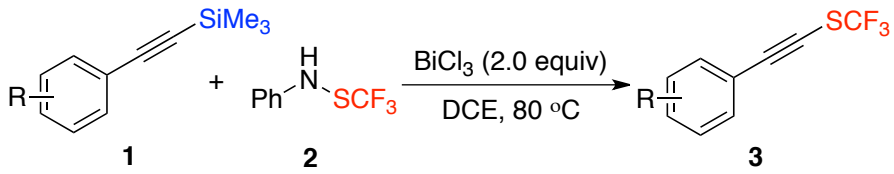
Supporting Information

General experimental methods:

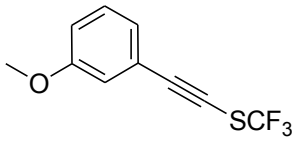
Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

*General procedure of the synthesis of (alkynyl)(trifluoromethyl)sulfanes **3** via a bismuth(III)-promoted reaction of trimethyl(alkynyl)silane **1** with trifluoromethanesulfanylamide **2**:*



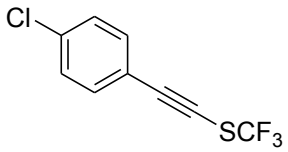
1 **2** **3**

Trifluoromethanesulfanylamide **2** (0.3 mmol, 58.0 mg) was added to a solution of trimethyl(alkynyl)silane **1** (0.2 mmol) and bismuth(III) chloride (0.4 mmol, 126.2 mg) in DCE (2.0 mL). The mixture was stirred at 80 °C for 8-12 hours. After completion of the reaction as indicated by TLC, the reaction mixture was filtered with silica gel and washed by CH_2Cl_2 (3 × 5.0 mL). The mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel to provide the product **3**.



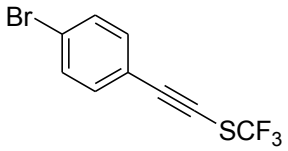
(2-(3-Methoxyphenyl)ethynyl)(trifluoromethyl)sulfane (**3a**)

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 6.93–7.00 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 66.5, 101.2, 116.4, 116.8, 122.4, 124.7, 128.1 (q, *J* = 310.3 Hz), 129.6, 159.3; ^{19}F NMR (378 MHz, $CDCl_3$) δ -44.00 (s); HRMS (ESI) calcd for $C_{10}H_8F_3OS$: 233.0242 (M + H^+), found: 233.0248.



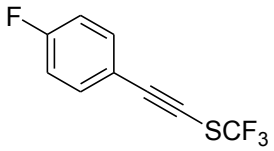
(2-(4-Chlorophenyl)ethynyl)(trifluoromethyl)sulfane (**3b**)

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J_1 = 6.8 Hz, J_2 = 1.8 Hz, 2H), 7.43 (dd, J_1 = 6.8 Hz, J_2 = 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.9, 100.1, 120.0, 128.0 (q, *J* = 311.0 Hz), 128.9, 133.4, 136.0; ^{19}F NMR (378 MHz, $CDCl_3$) δ -43.86 (s); HRMS (ESI) calcd for $C_9H_5ClF_3S$: 236.9747 (M + H^+), found: 236.9758.



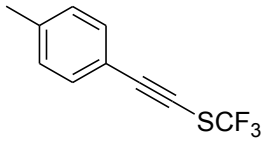
(2-(4-Bromophenyl)ethynyl)(trifluoromethyl)sulfane (**3c**)

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dt, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 2H), 7.49 (dt, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.1, 100.2, 120.4, 124.3, 127.9 (q, *J* = 311.0 Hz), 131.8, 133.5; ^{19}F NMR (378 MHz, $CDCl_3$) δ -43.83 (s); HRMS (ESI) calcd for $C_9H_5BrF_3S$: 280.9242 (M + H^+), found: 280.9240.



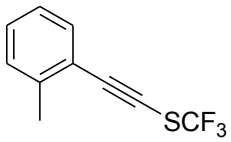
(2-(4-Fluorophenyl)ethynyl)(trifluoromethyl)sulfane (**3d**)

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03–7.07 (m, 2H), 7.48–7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.7, 100.2, 111.8, 115.9 (d, $^{2}J_{CF}$ = 22.6 Hz), 128.1 (q, J = 310.8 Hz), 134.52 (d, $^{3}J_{CF}$ = 8.6 Hz), 163.4 (d, $^{1}J_{CF}$ = 251.6 Hz); ^{19}F NMR (378 MHz, $CDCl_3$) δ -44.03 (s), -108.37(s); HRMS (ESI) calcd for $C_9H_5F_4S$: 221.0043 (M + H^+), found: 221.0057.



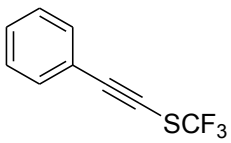
(2-*p*-Tolylethynyl)(trifluoromethyl)sulfane (**3e**)

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 7.16 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 65.8, 101.6, 118.5, 128.2 (q, J = 310.8 Hz), 129.3, 132.3, 140.3; ^{19}F NMR (378 MHz, $CDCl_3$) δ -44.26 (s); HRMS (ESI) calcd for $C_{10}H_8F_3S$: 217.0293 (M + H^+), found: 217.0281.



(2-*o*-Tolylethynyl)(trifluoromethyl)sulfane (**3f**)

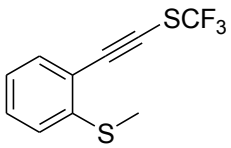
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.17 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.29 (td, J = 7.6, 1.2 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 70.1, 100.4, 121.4, 125.7, 128.2 (q, J = 303.9 Hz), 129.7, 132.3, 141.3; ^{19}F NMR (378 MHz, $CDCl_3$) δ -44.32 (s); HRMS (ESI) calcd for $C_{10}H_8F_3S$: 217.0293, found: 217.0295.



(2-Phenylethynyl)(trifluoromethyl)sulfane (**3g**)

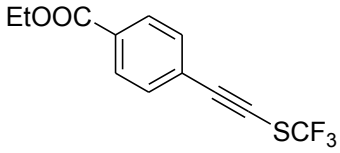
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.39 (m, 2H), 7.42–7.43 (m, 1H),

7.50–7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.7, 101.3, 121.5, 128.0 (q, J = 294.8 Hz), 128.5, 129.7, 132.2; ^{19}F NMR (378 MHz, $CDCl_3$) δ -44.08 (s); HRMS (ESI) calcd for $C_9H_6F_3S$: 203.0137 ($M + H^+$), found: 203.0131.



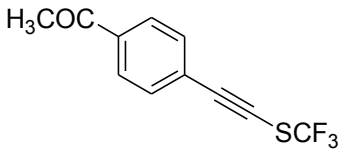
1-(Methylthio)-2-(2-(trifluoromethylthio)ethynyl)benzene (**3h**)

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 3H), 7.11 (td, J_1 = 7.6 Hz, J_2 = 0.7 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.33 – 7.37 (m, 1H), 7.45 (dd, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1, 73.0, 98.7, 119.7, 124.3, 124.4, 128.0 (q, J = 311.0 Hz), 130.1, 133.1, 143.1; ^{19}F NMR (378 MHz, $CDCl_3$) δ -43.86 (s); HRMS (ESI) calcd for $C_{10}H_8F_3S_2$: 249.0014 ($M + H^+$), found: 249.0028.



Ethyl 4-(2-(trifluoromethylthio)ethynyl)benzoate (**3i**)

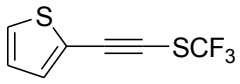
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (t, J = 7.1 Hz, 3H), 4.39 (q, J = 7.1 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 61.3, 69.9, 100.5, 125.9, 127.9 (q, J = 293.9Hz), 129.5, 131.1, 131.6, 165.7; ^{19}F NMR (378 MHz, $CDCl_3$) δ -43.62 (s); HRMS (ESI) calcd for $C_{12}H_{10}F_3O_2S$: 275.0348 ($M + H^+$), found: 275.0342.



1-(4-(2-(Trifluoromethylthio)ethynyl)phenyl)ethanone (**3j**)

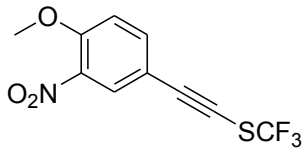
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 3H), 7.55 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.6, 70.4, 100.4, 127.9 (q, J = 311.2 Hz), 128.2, 128.3, 131.8, 137.2, 197.1; ^{19}F NMR (378 MHz, $CDCl_3$) δ -43.59

(s); HRMS (ESI) calcd for $C_{11}H_8F_3OS$: 245.0242 ($M + H^+$), found: 245.0236.



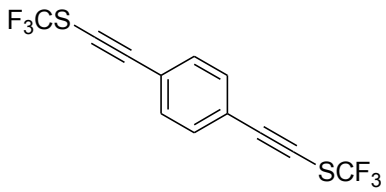
2-(2-(Trifluoromethylthio)ethynyl)thiophene (**3k**)

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00–7.04 (m, 1H), 7.27–7.30 (m, 1H), 7.38–7.42 (m, H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.4, 99.5, 123.4, 126.7, 127.9 (q, J = 314.9 Hz), 127.7, 130.3; ^{19}F NMR (378 MHz, $CDCl_3$) δ -44.18 (s); HRMS (ESI) calcd for $C_7H_4F_3S_2$: 208.9701($M + H^+$), found: 208.9707.



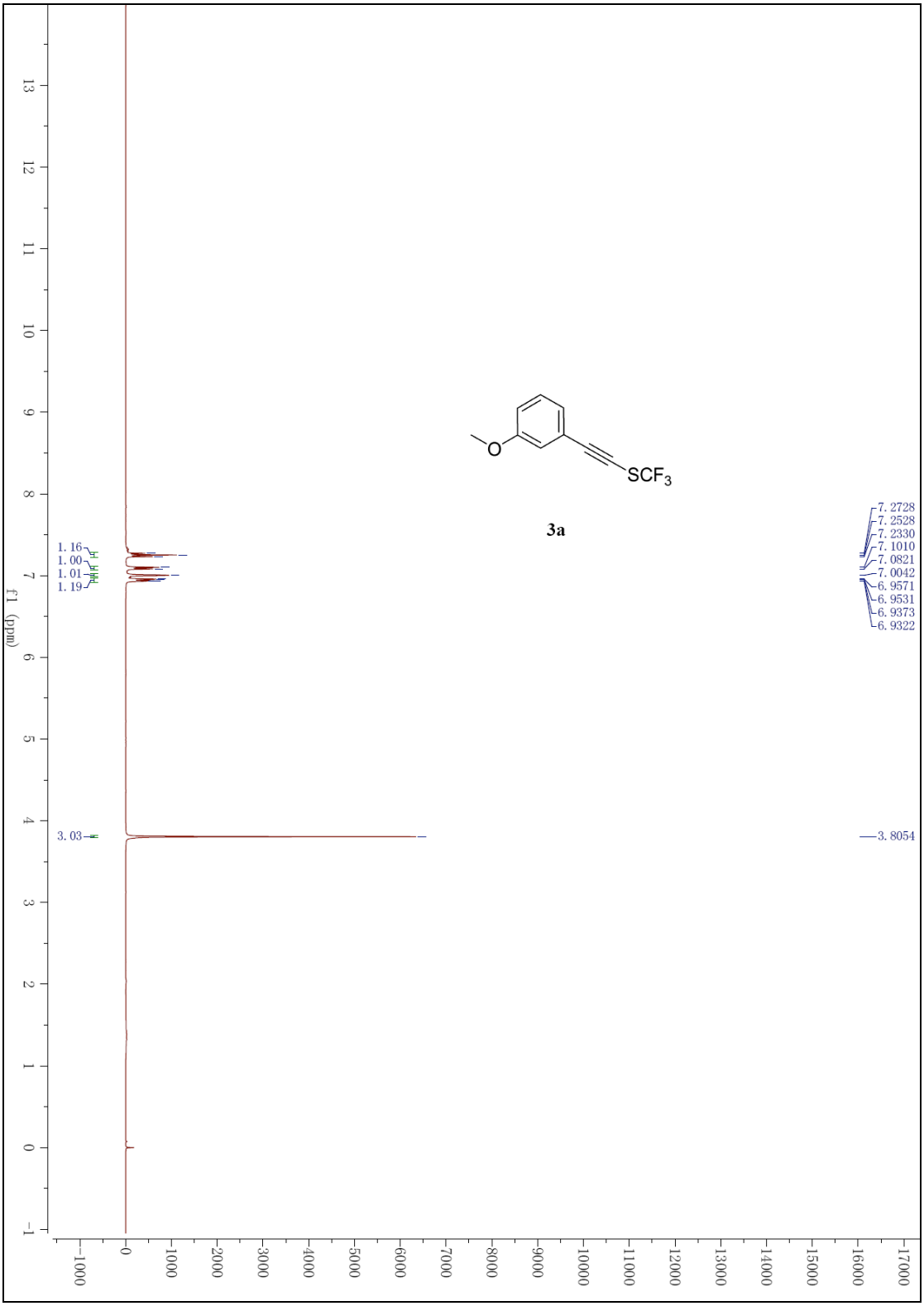
(2-(4-Methoxy-3-nitrophenyl)ethynyl)(trifluoromethyl)sulfane (**3l**)

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 3H), 7.04 (d, J = 8.7 Hz, 1H), 7.64 (dd, J_1 = 8.7 Hz, J_2 = 2.1 Hz, 1H), 7.97 (d, J = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 78.0, 81.0, 113.5, 114.6, 128.8 (q, J = 313.3 Hz), 129.3, 131.7, 137.6, 153.0; ^{19}F NMR (378 MHz, $CDCl_3$) δ -43.69 (s); HRMS (ESI) calcd for $C_{10}H_7F_3NO_3S$: 278.0093 ($M + H^+$), found: 278.0085.



1,4-Bis(2-(trifluoromethylthio)ethynyl)benzene (**3m**)

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.6, 100.4, 122.6, 127.9 (q, J = 312.5 Hz), 131.9; ^{19}F NMR (378 MHz, $CDCl_3$) δ -43.71 (s); HRMS (ESI) calcd for $C_{12}H_5F_6S_2$: 326.9731 ($M + H^+$), found: 326.9745.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SCF3
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7.0821
7.0042
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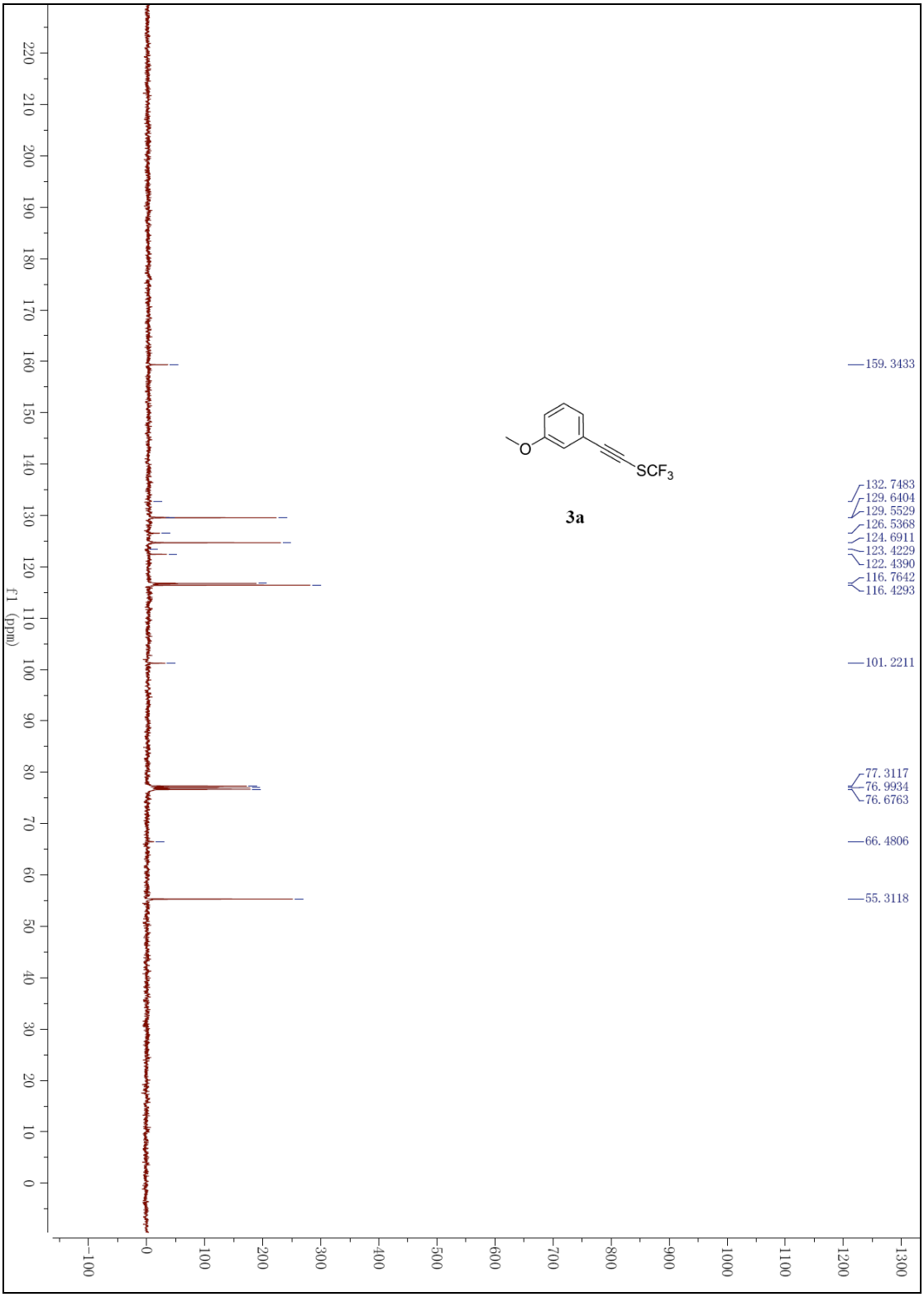
6.9531
6.9373
6.9322
3.8054
1.16
1.00
1.01
1.19
3.03
f1 (ppm)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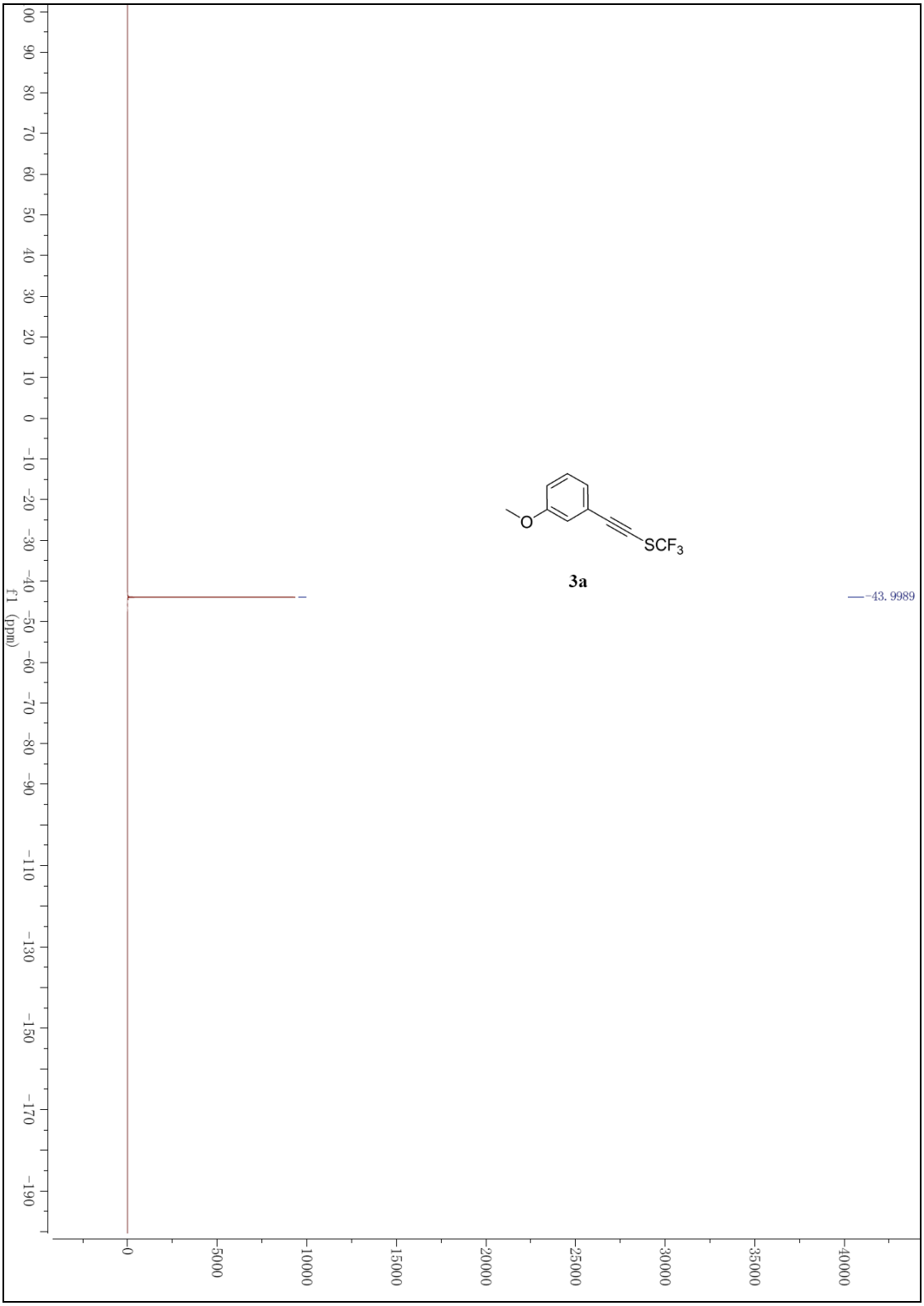
SCF3
3a
f1 (ppm)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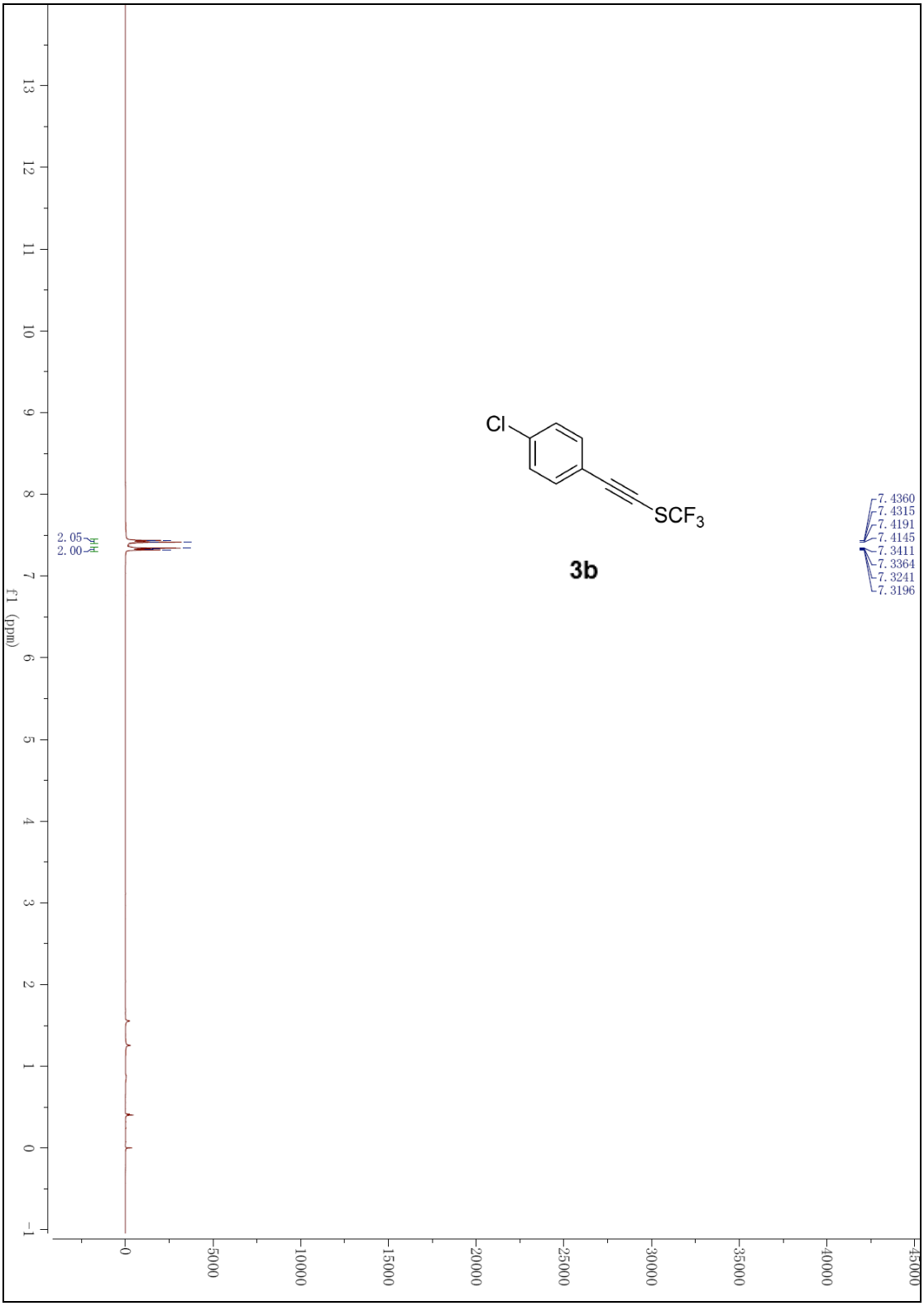
f1 (ppm)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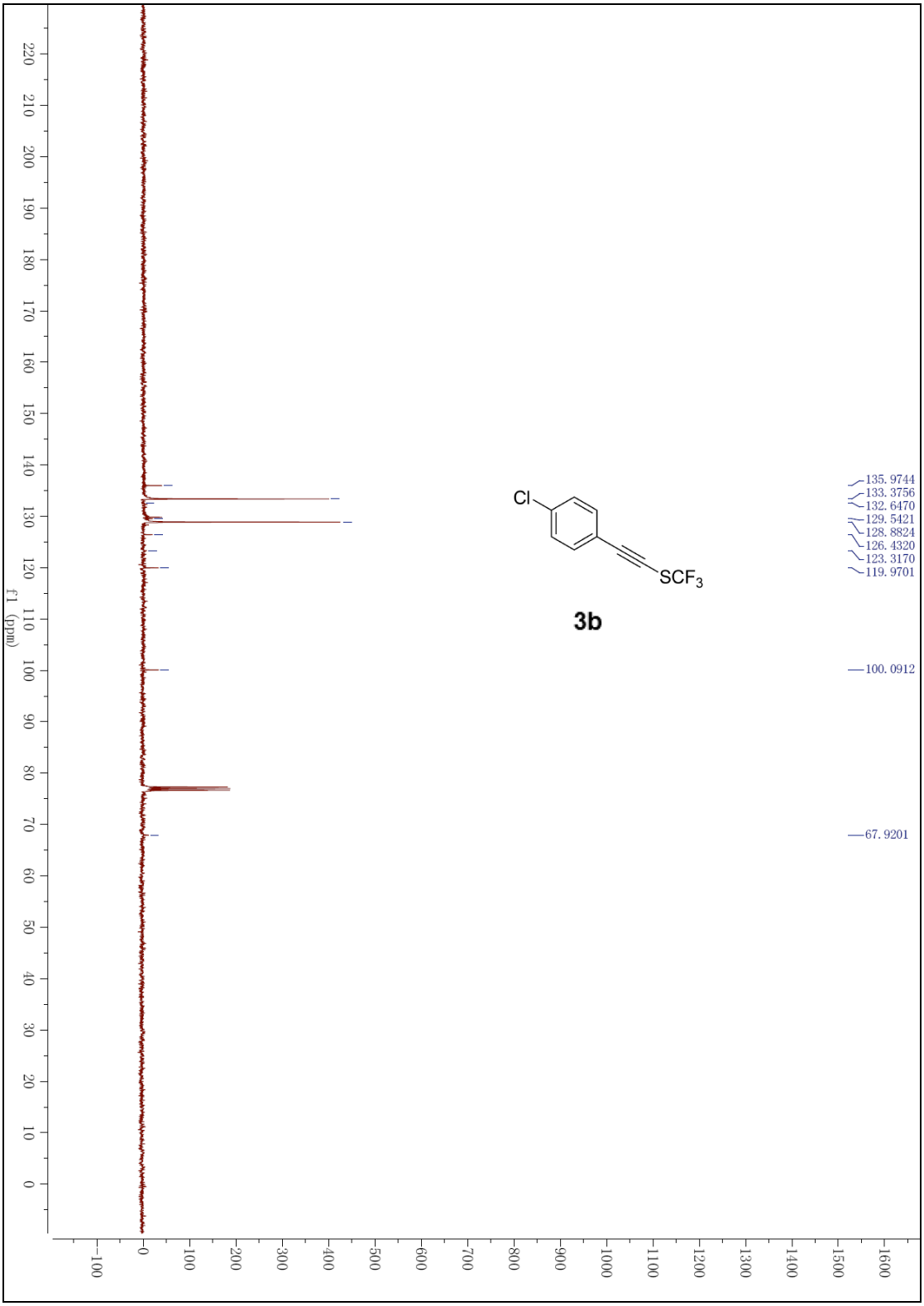
2.00
f1 (ppm)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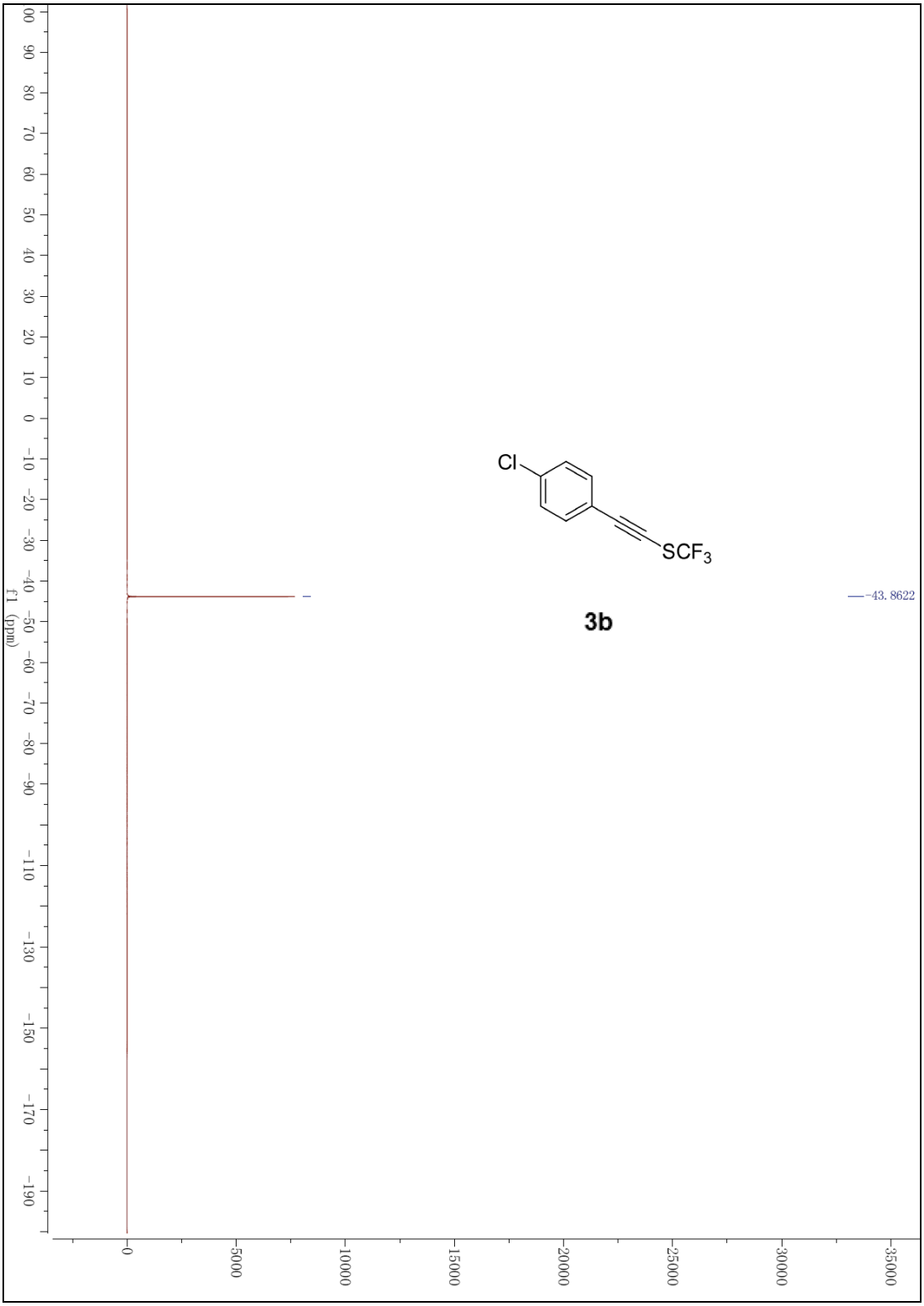
Cl
SCF3
3b
f1 (ppm)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-60
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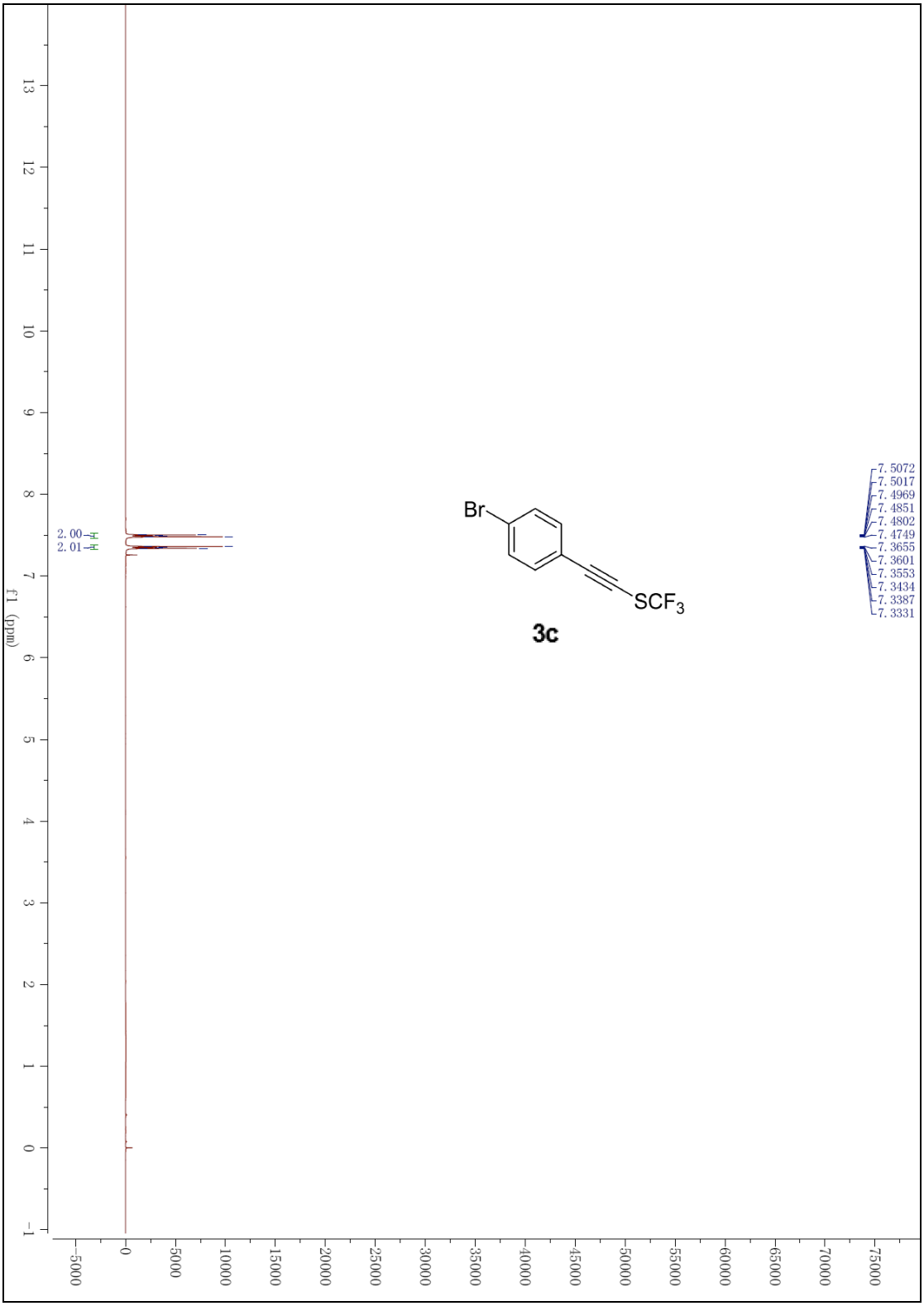
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2.01
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SCF3
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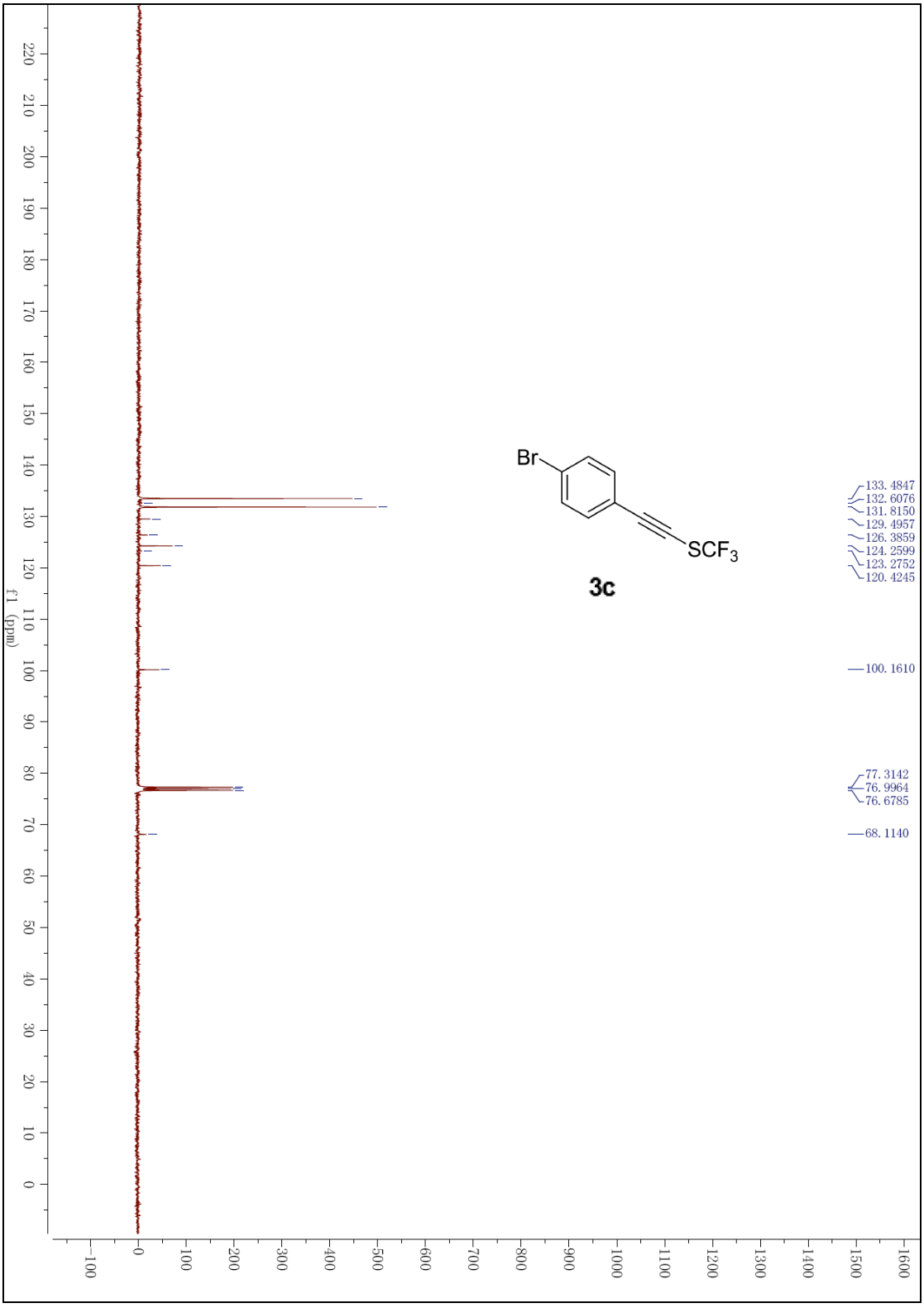
f1 (ppm)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SCF3
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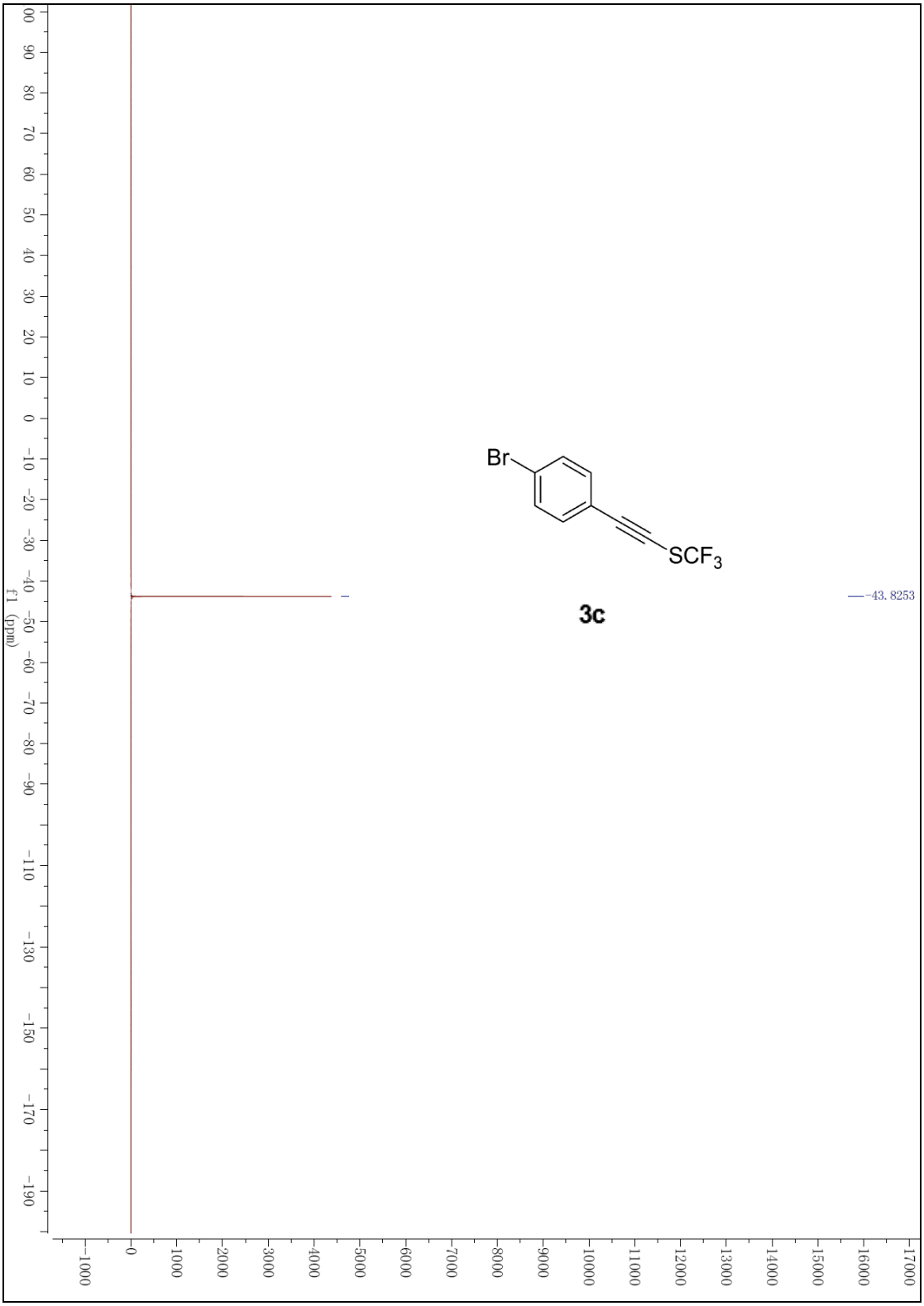
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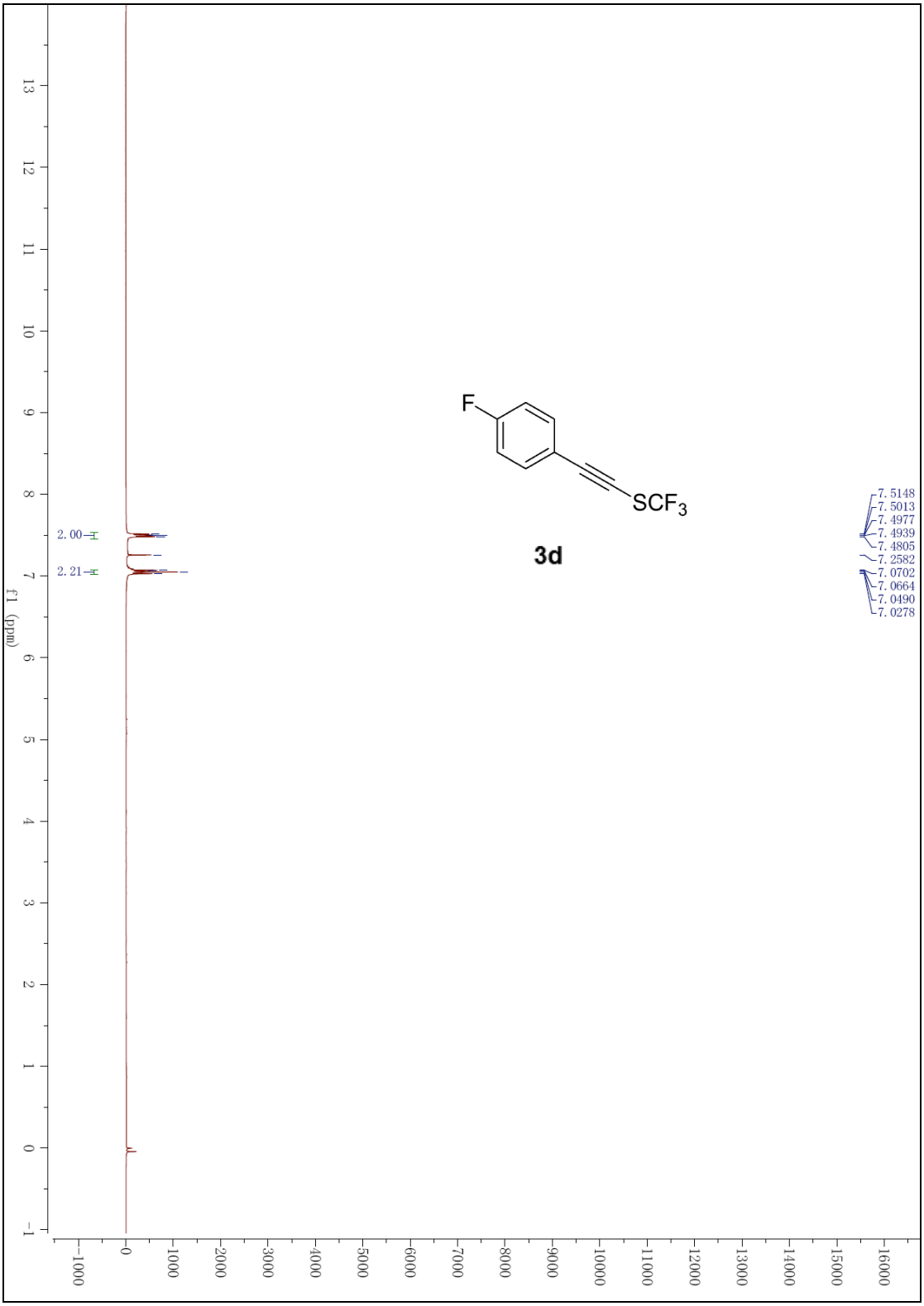
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3d
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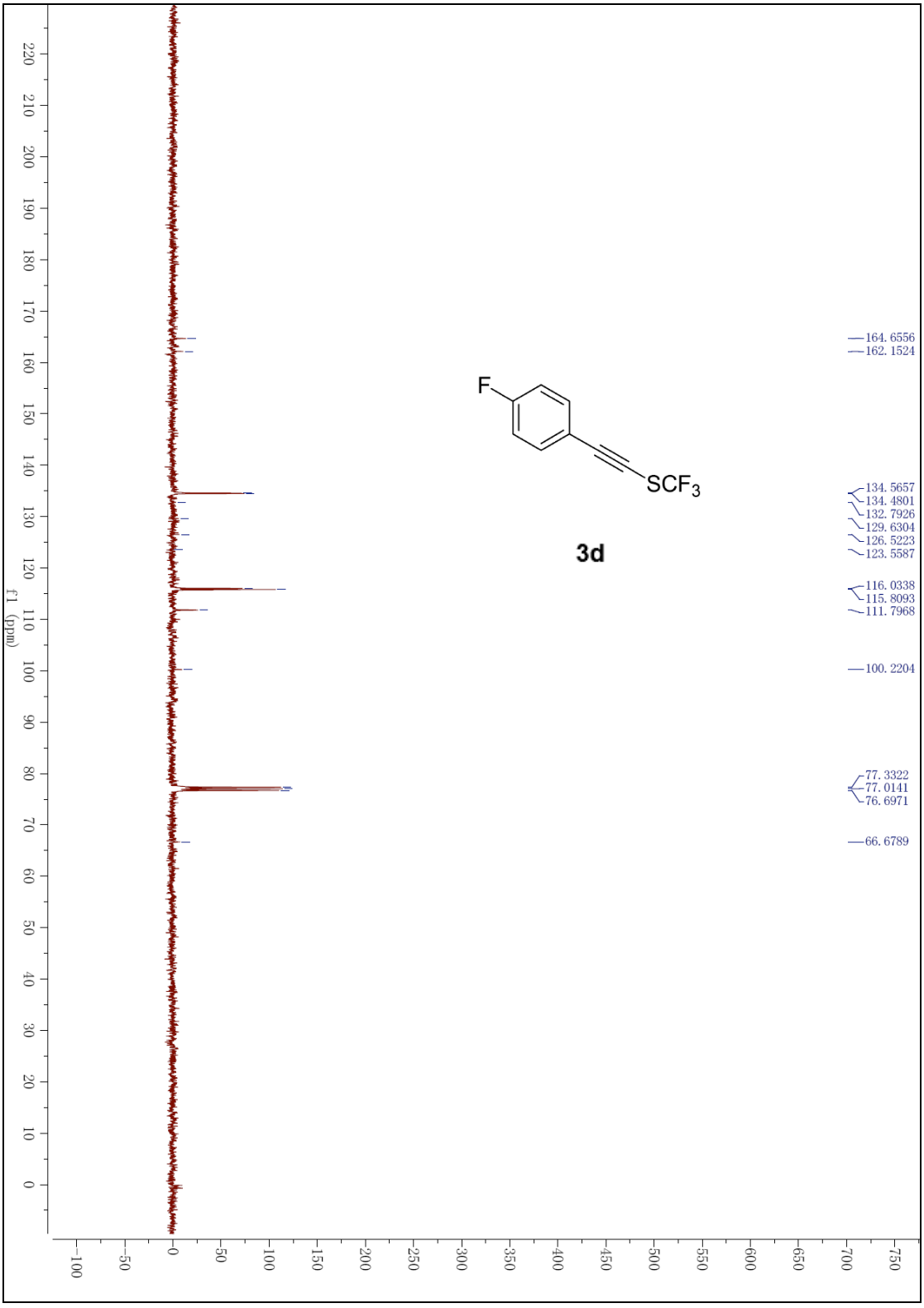
f1 (ppm)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SCF3
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134.4801
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77.0141
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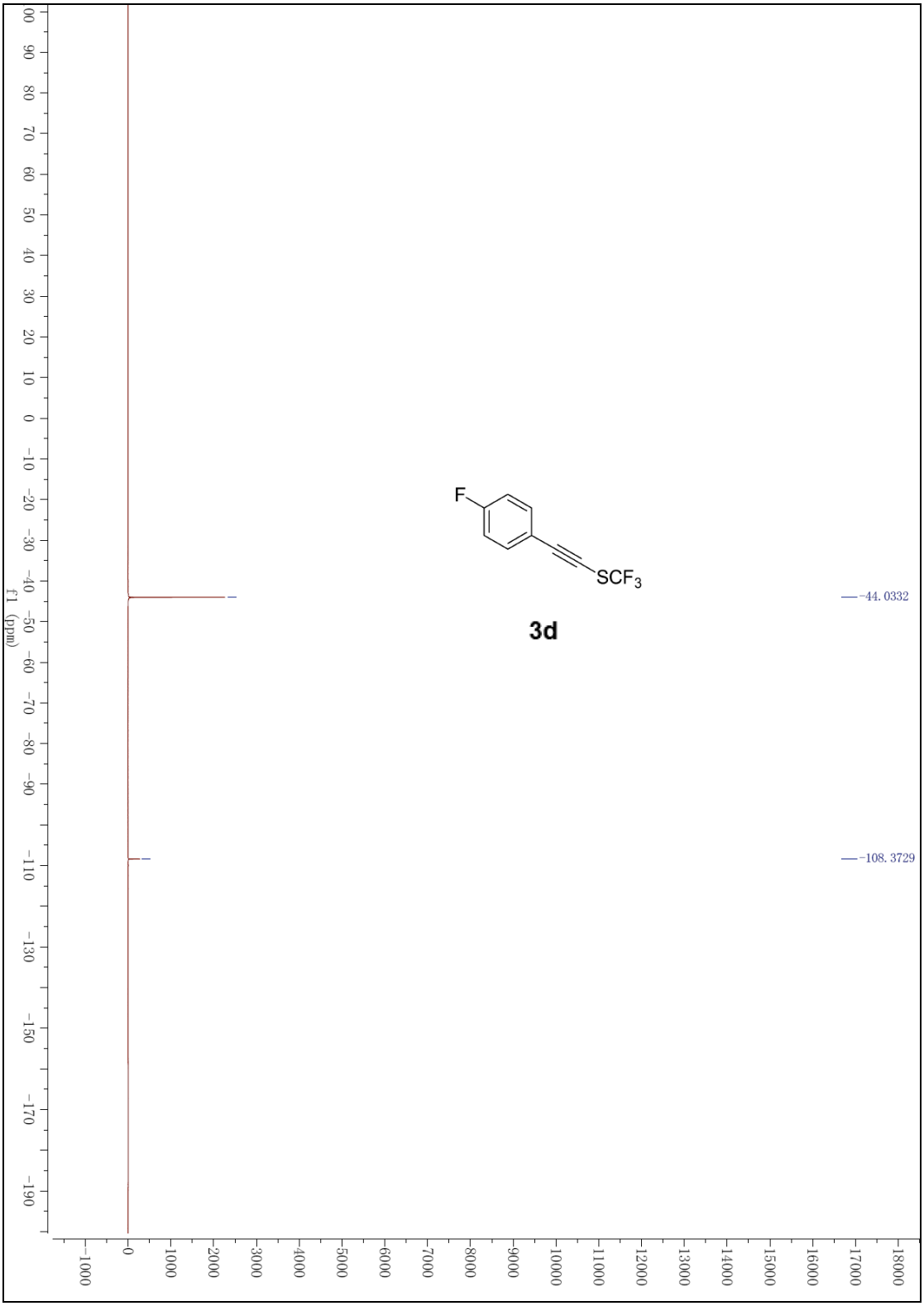
66.6789
f1 (ppm)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SCF3
3d
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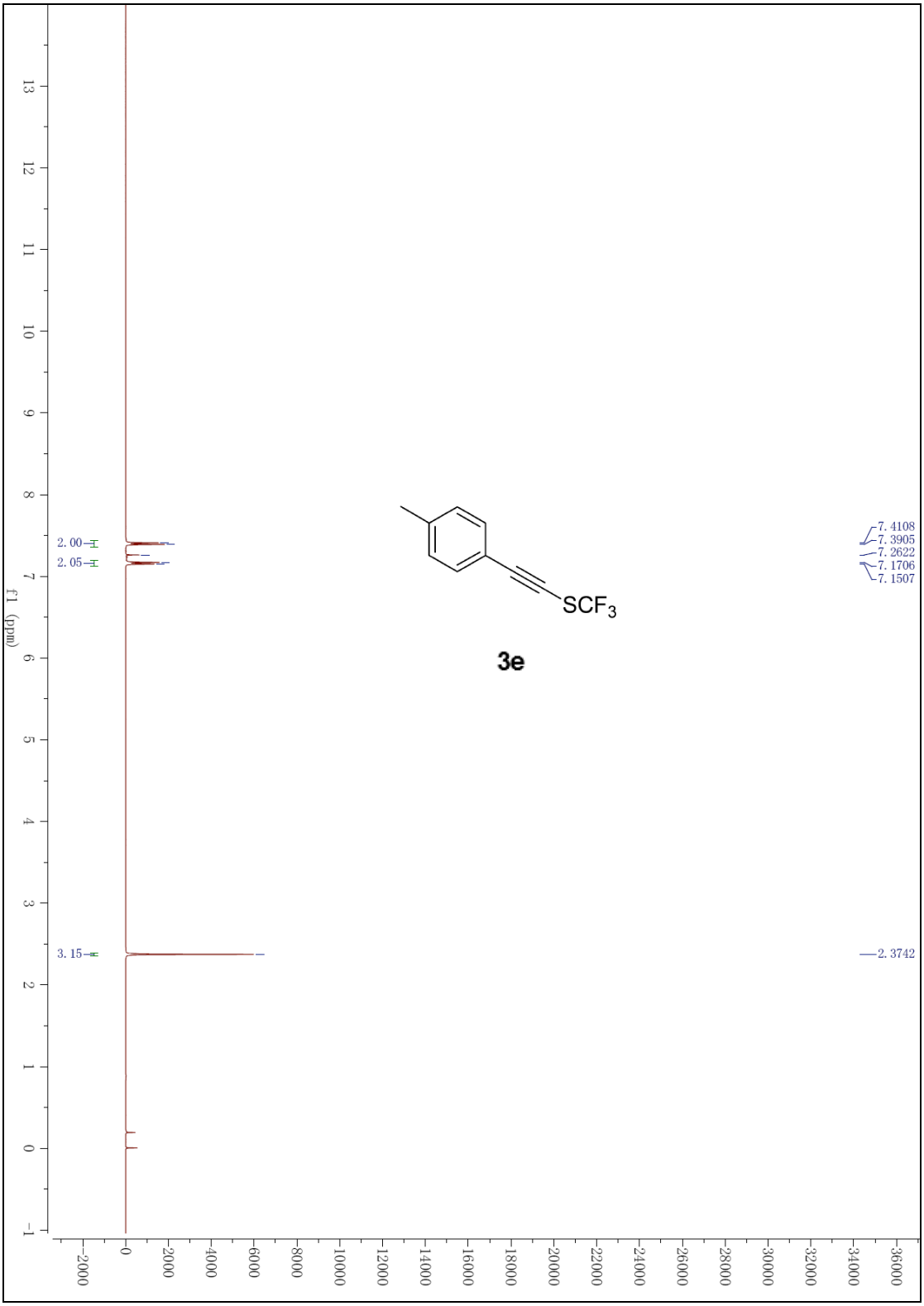
f1 (ppm)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7.2622
7.1706
7.1507
2.00
2.05
3.15
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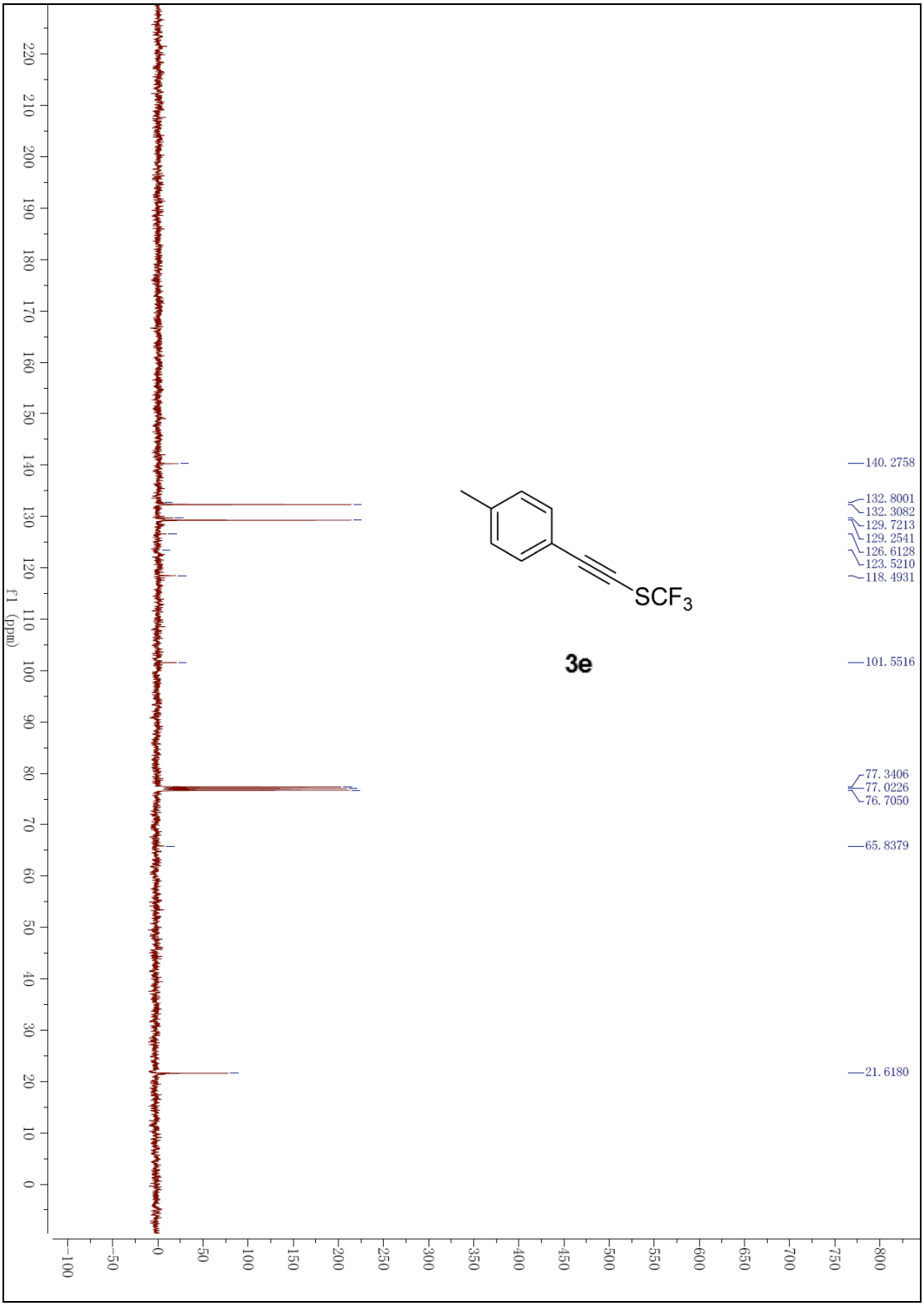
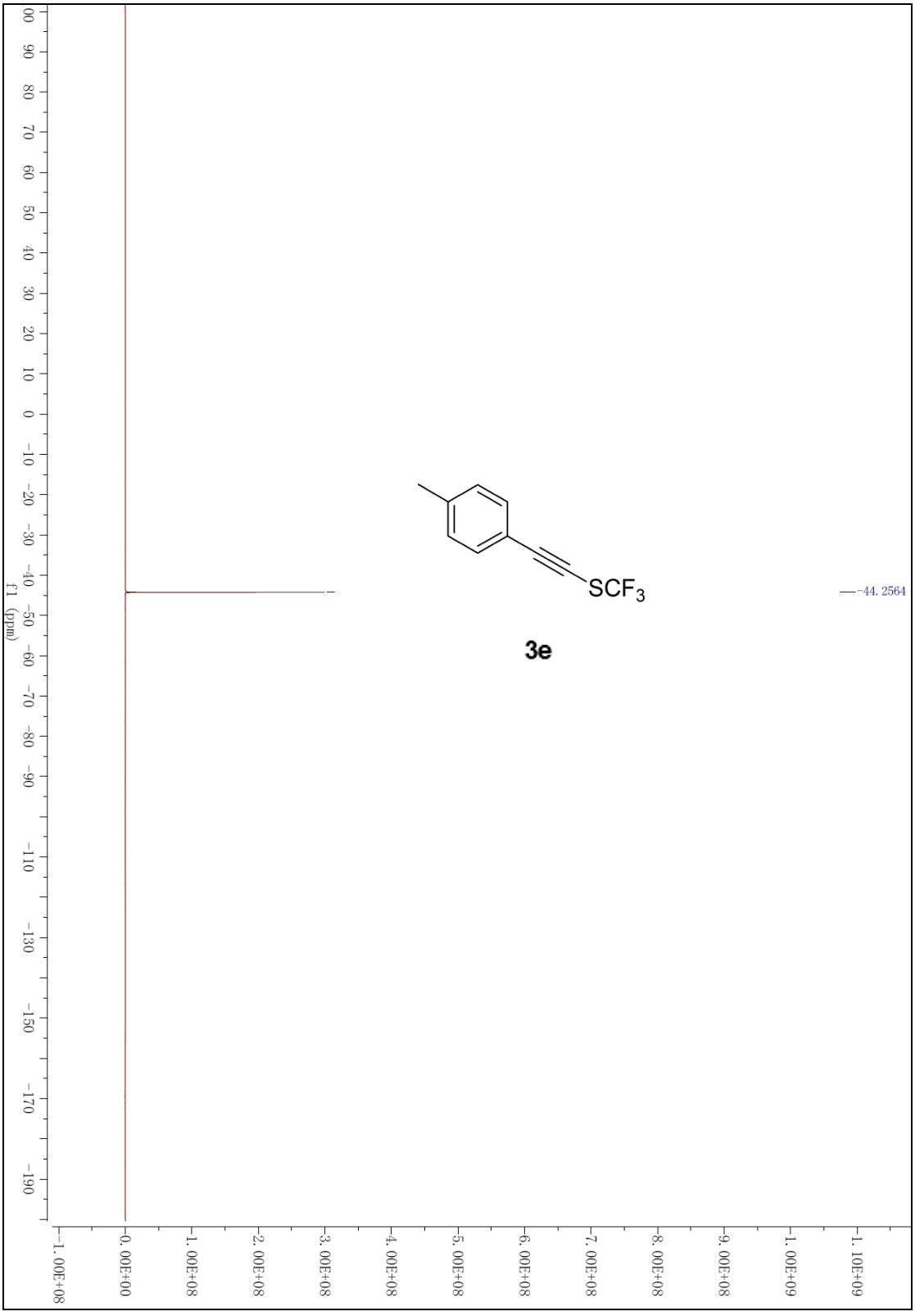
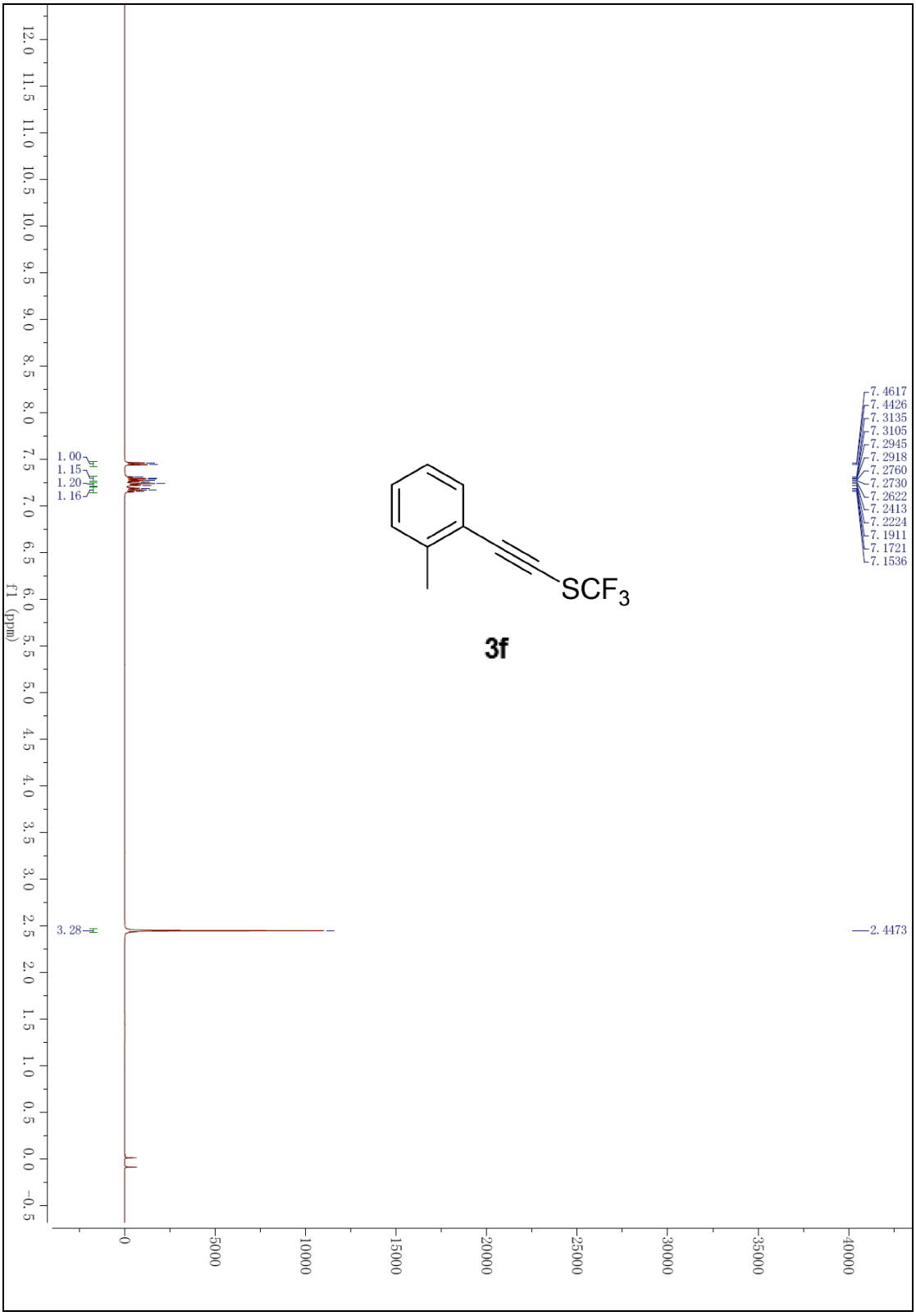
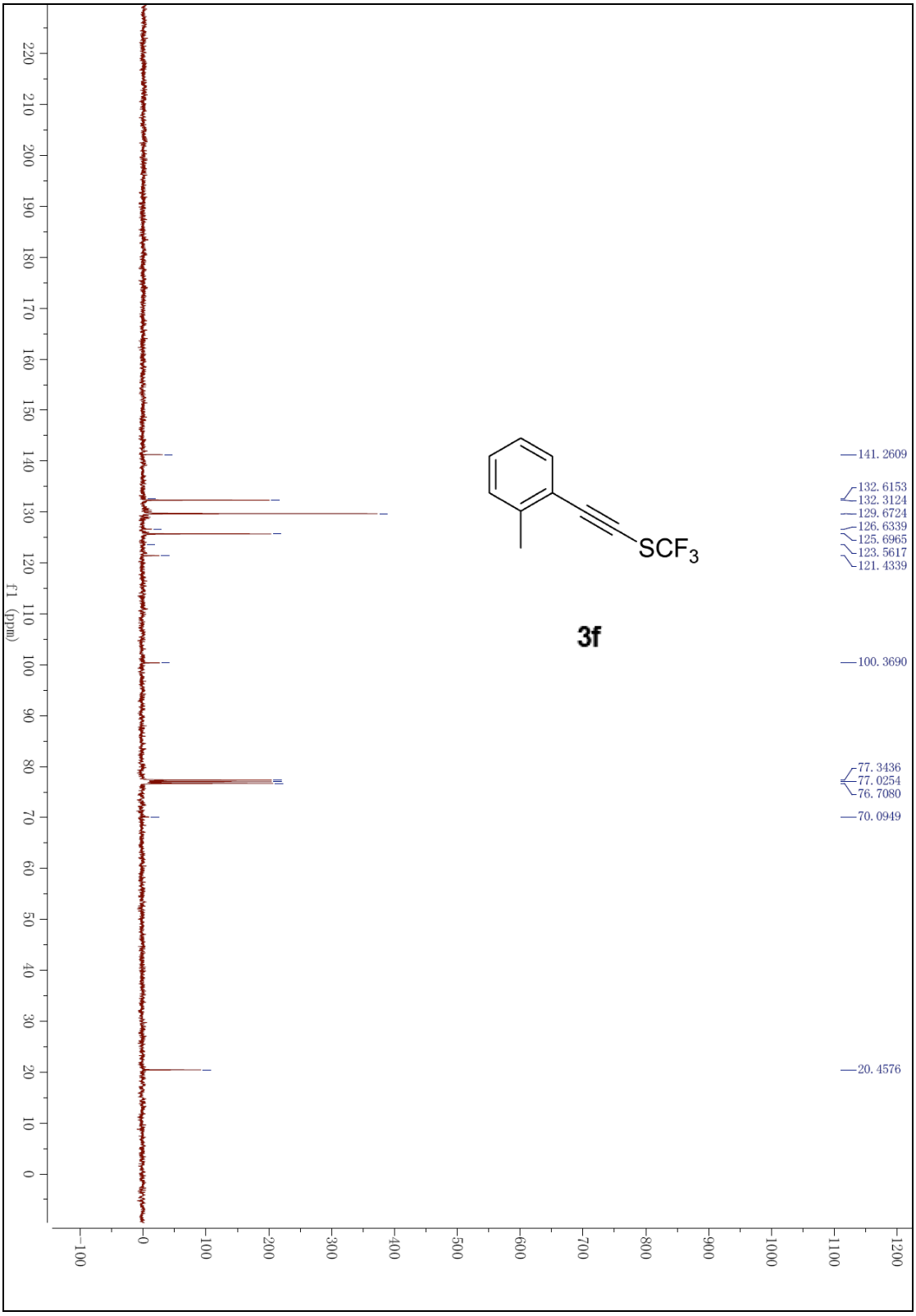
SCF3
3e
f1 (ppm)

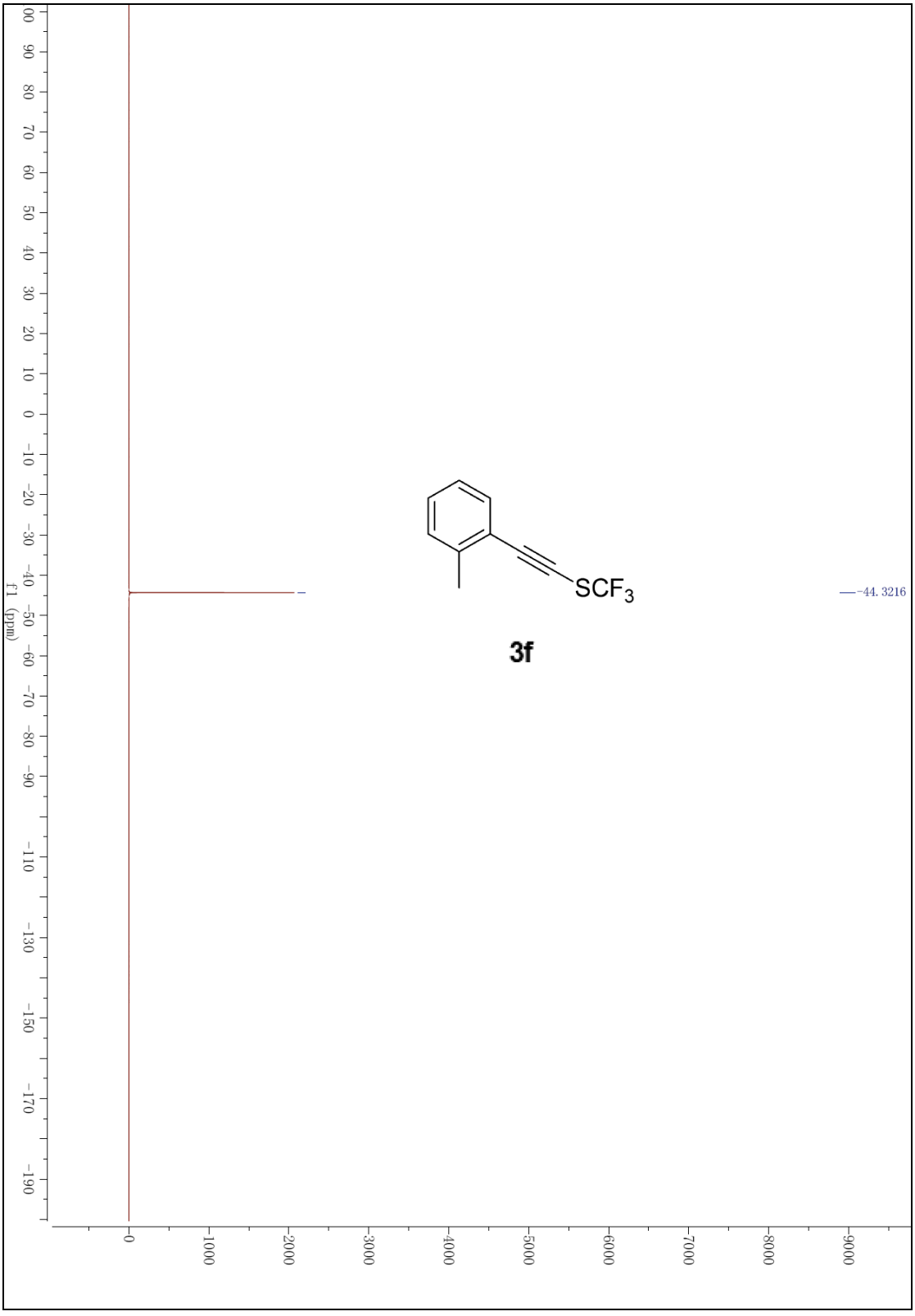

140.2758
132.8001
132.3082
129.7213
129.2541
126.6128
123.5210
118.4931
101.5516
77.3406
77.0226
76.7050
65.8379
21.6180
SCF3
3e
f1 (ppm)

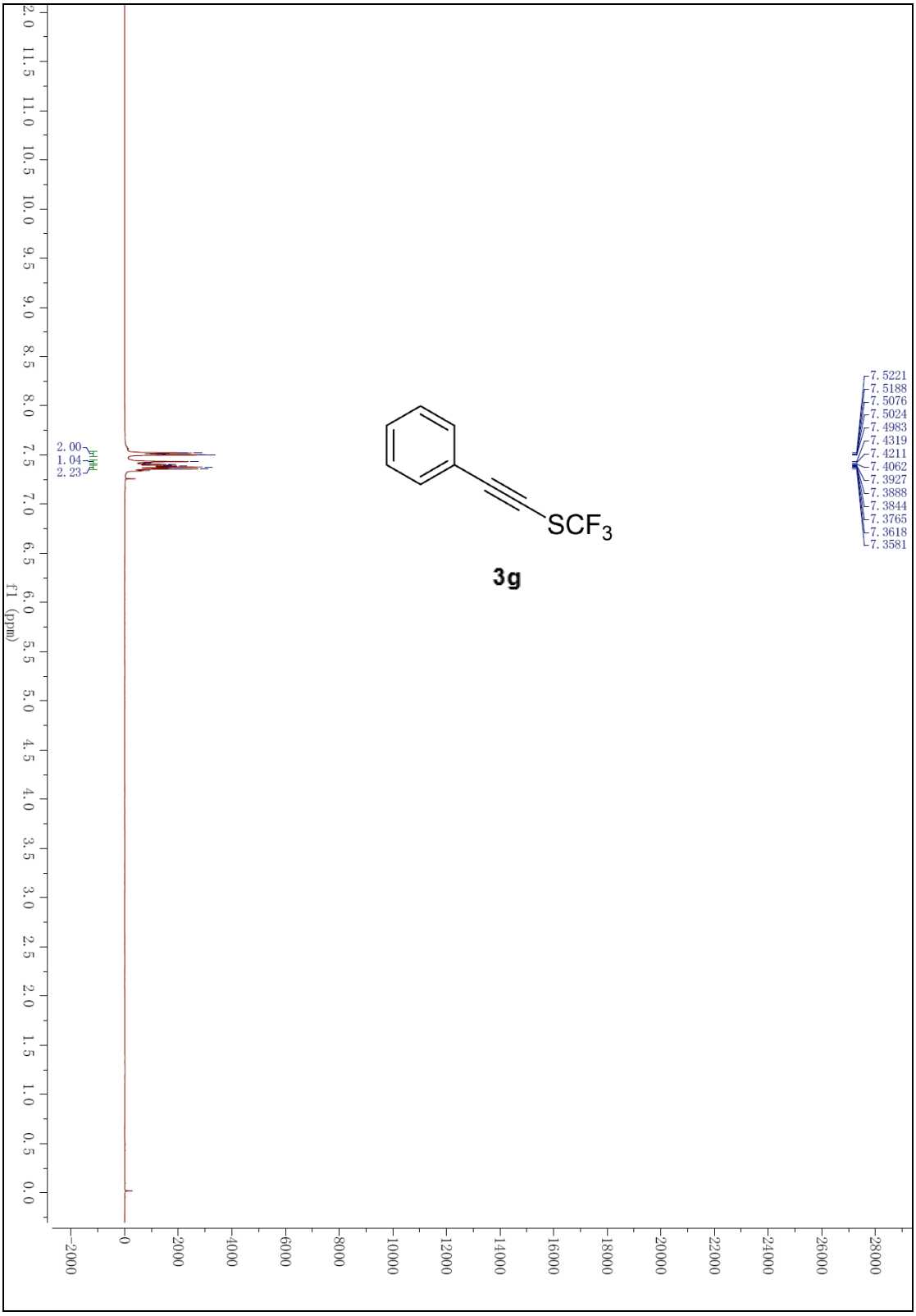


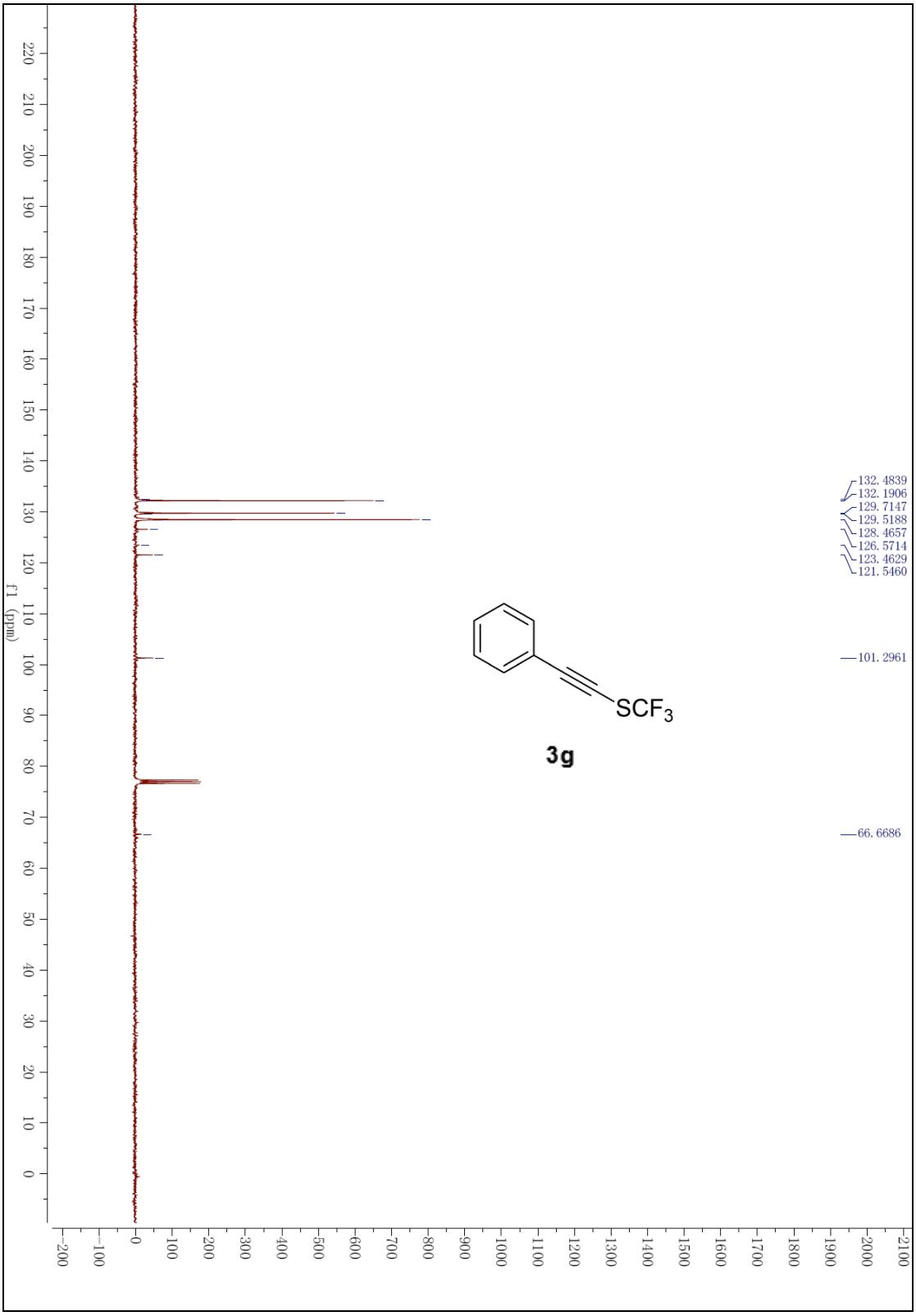
3e

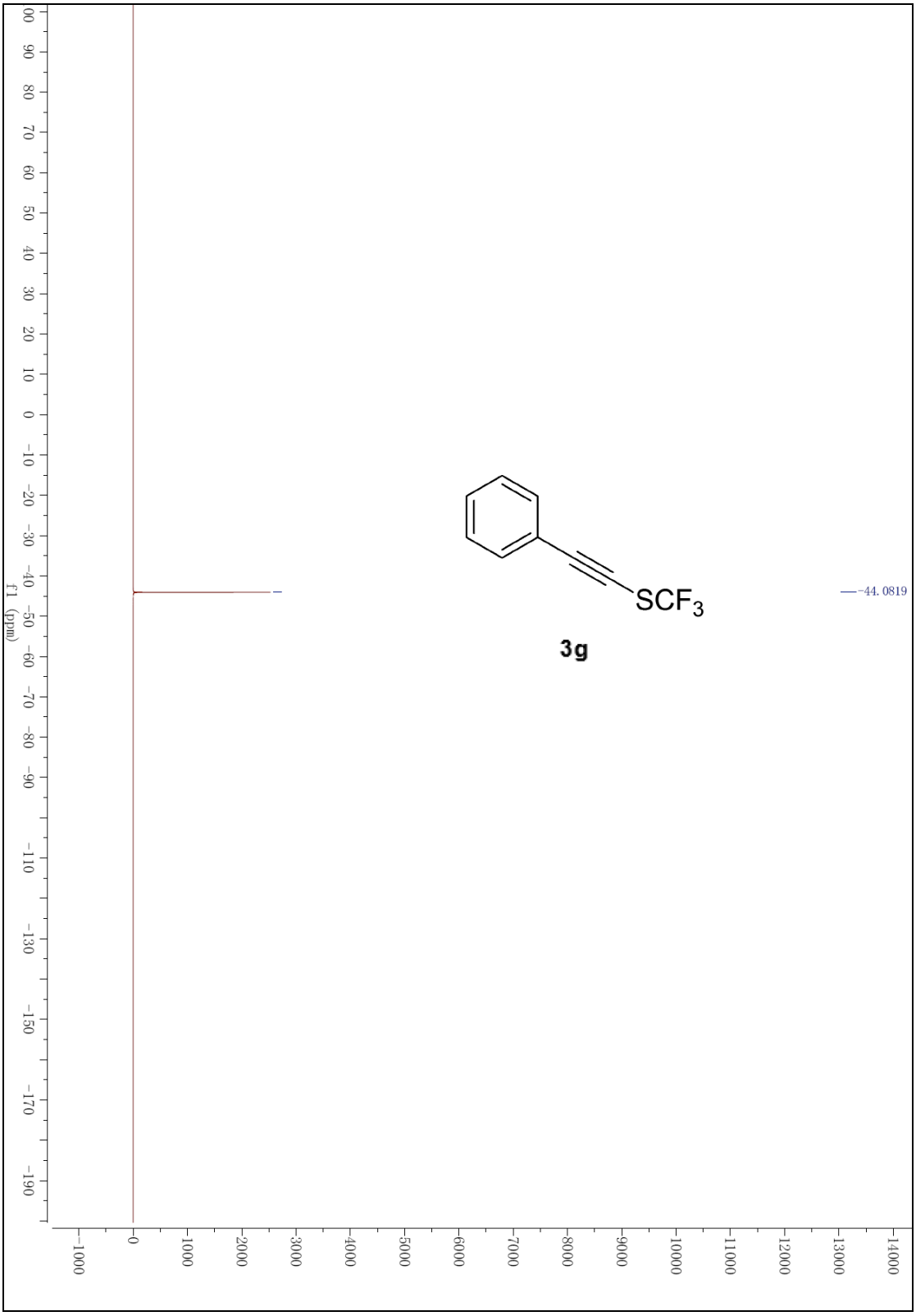

7.4617
7.4426
7.3135
7.3105
7.2945
7.2918
7.2760
7.2730
7.2622
7.2413
7.2224
7.1911
7.1721
7.1536
1.00
1.15
1.20
1.16
3.28
2.4473
SCF3
3f
f1 (ppm)


141.2609
132.6153
132.3124
129.6724
126.6339
125.6965
123.5617
121.4339
100.3690
77.3436
77.0254
76.7080
70.0949
20.4576
SCF3
3f
f1 (ppm)

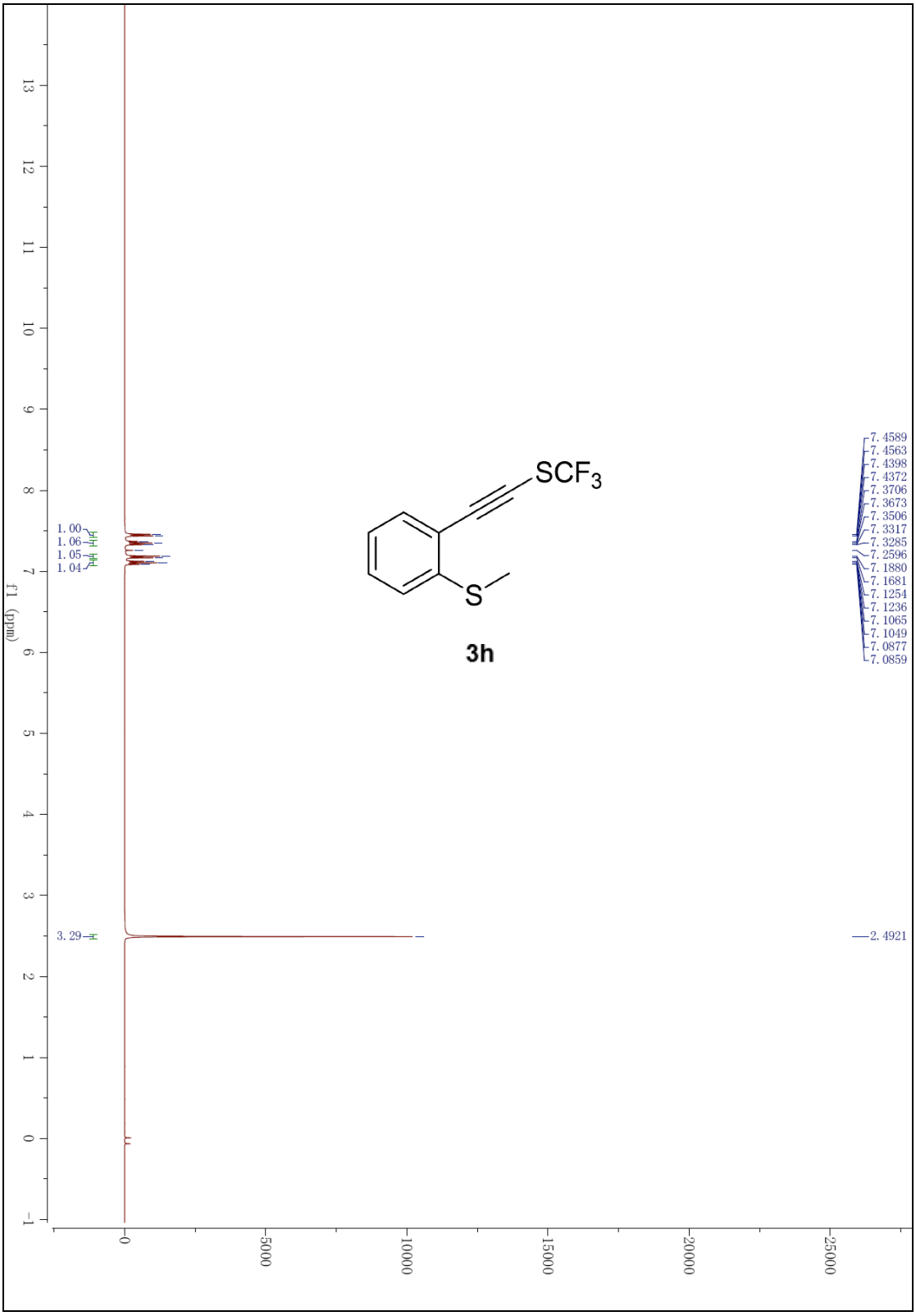

SCF3
−44.3216
3f
f1 (ppm)

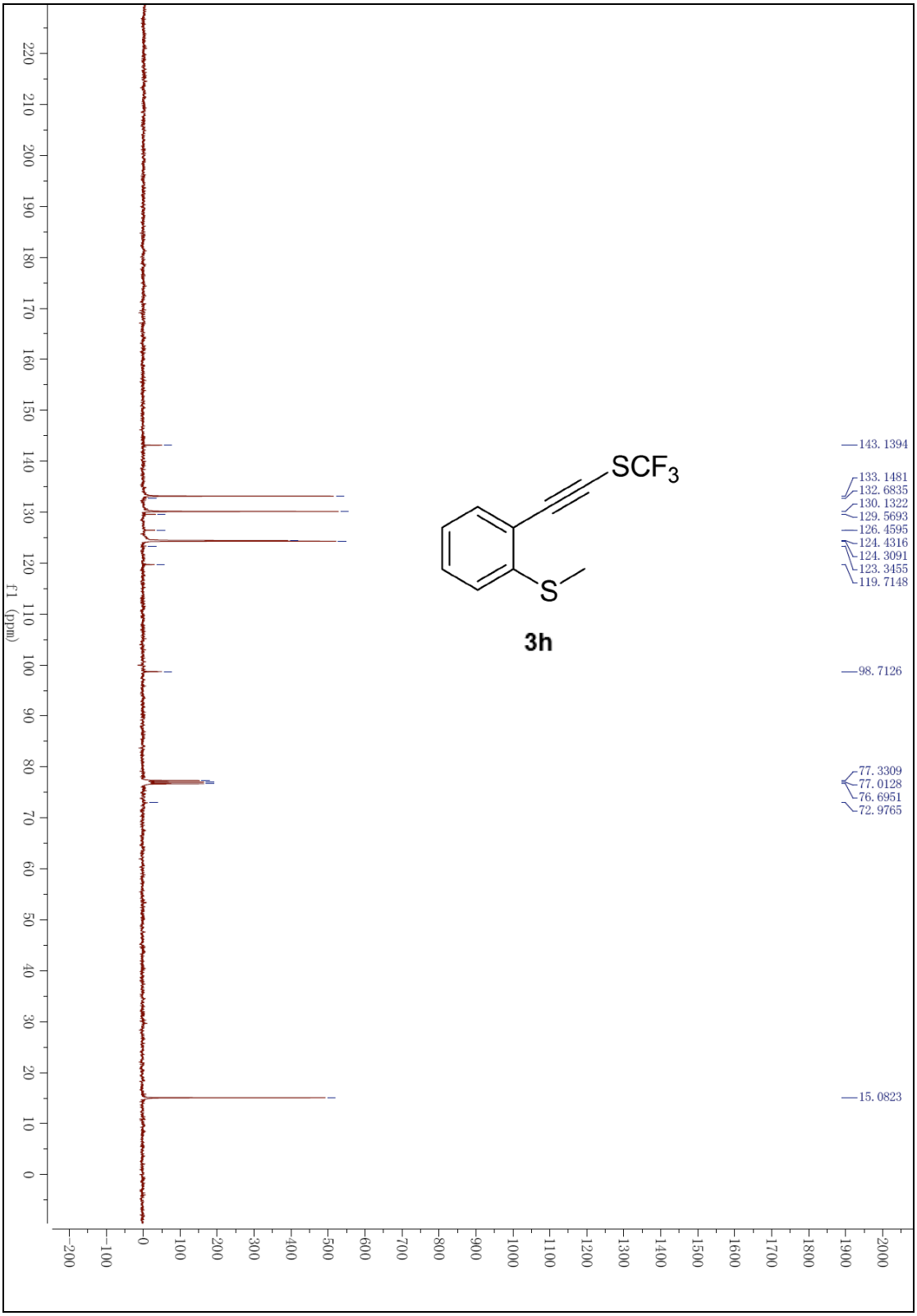

2.00
1.04
2.23
7.5221
7.5188
7.5076
7.5024
7.4983
7.4319
7.4211
7.4062
7.3927
7.3888
7.3844
7.3765
7.3618
7.3581
SCF3
3g
f1 (ppm)

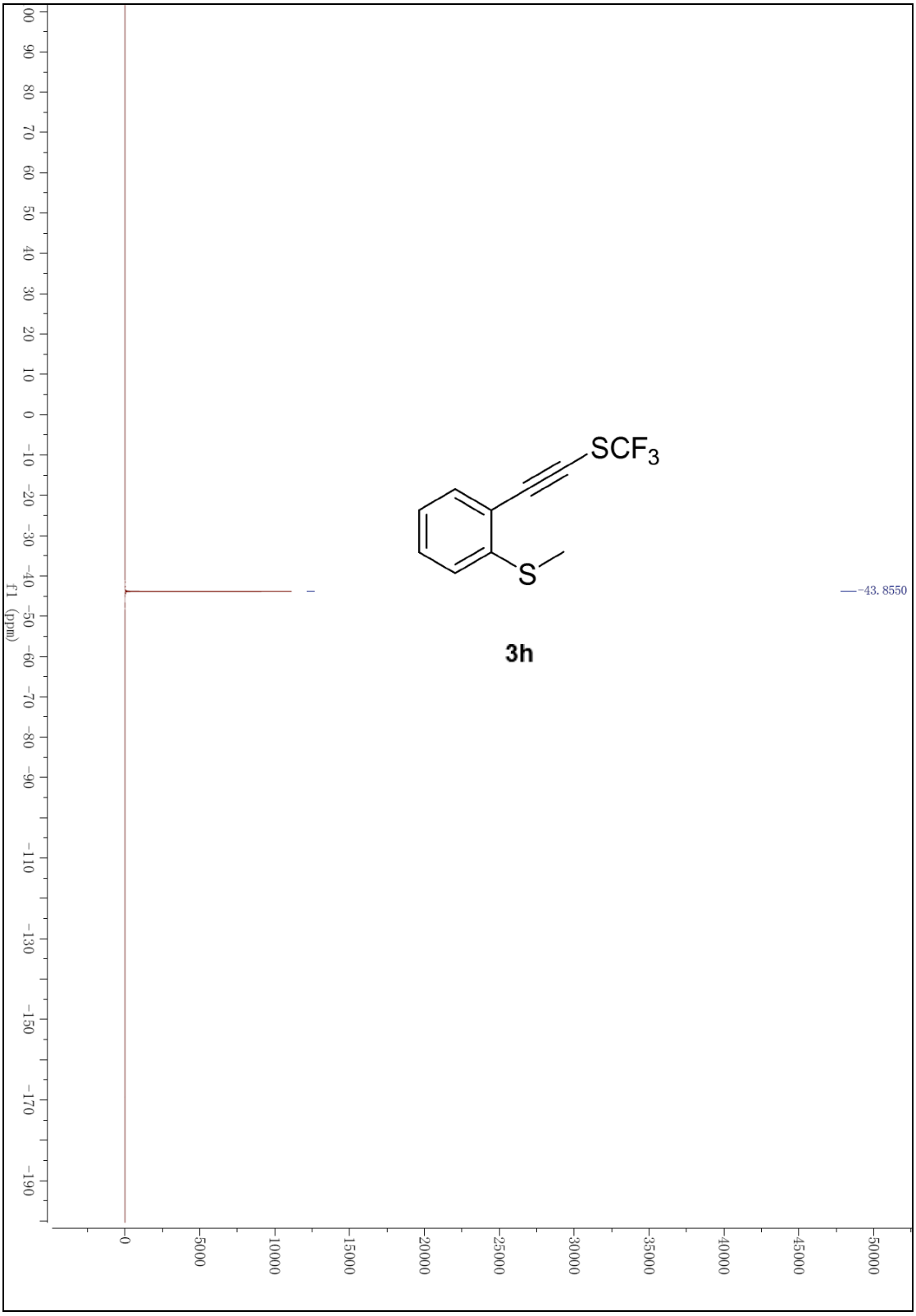

132.4839
132.1906
129.7147
129.5188
128.4657
126.5714
123.4629
121.5460
101.2961
66.6686
SCF3
3g
f1 (ppm)

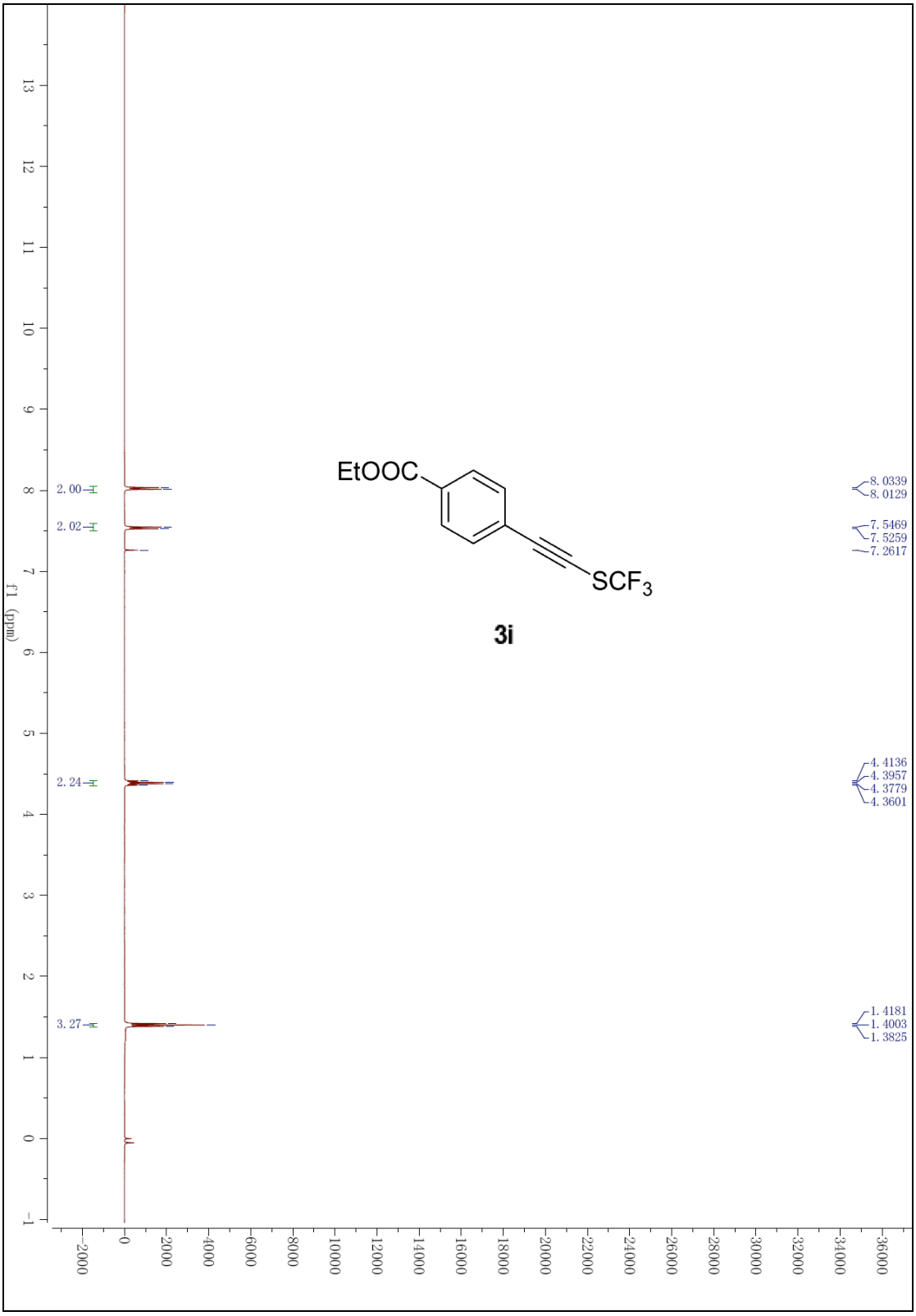


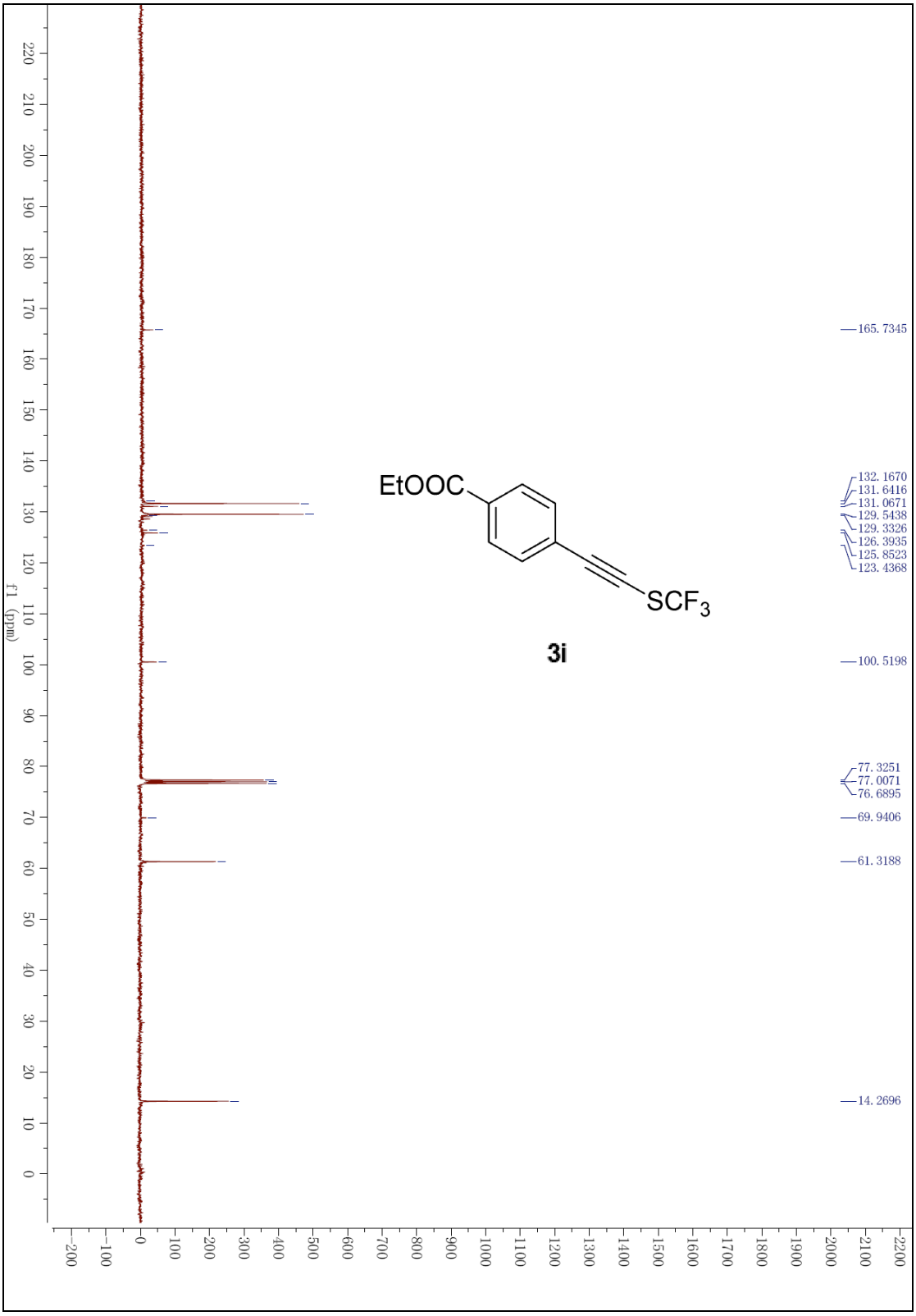
3g

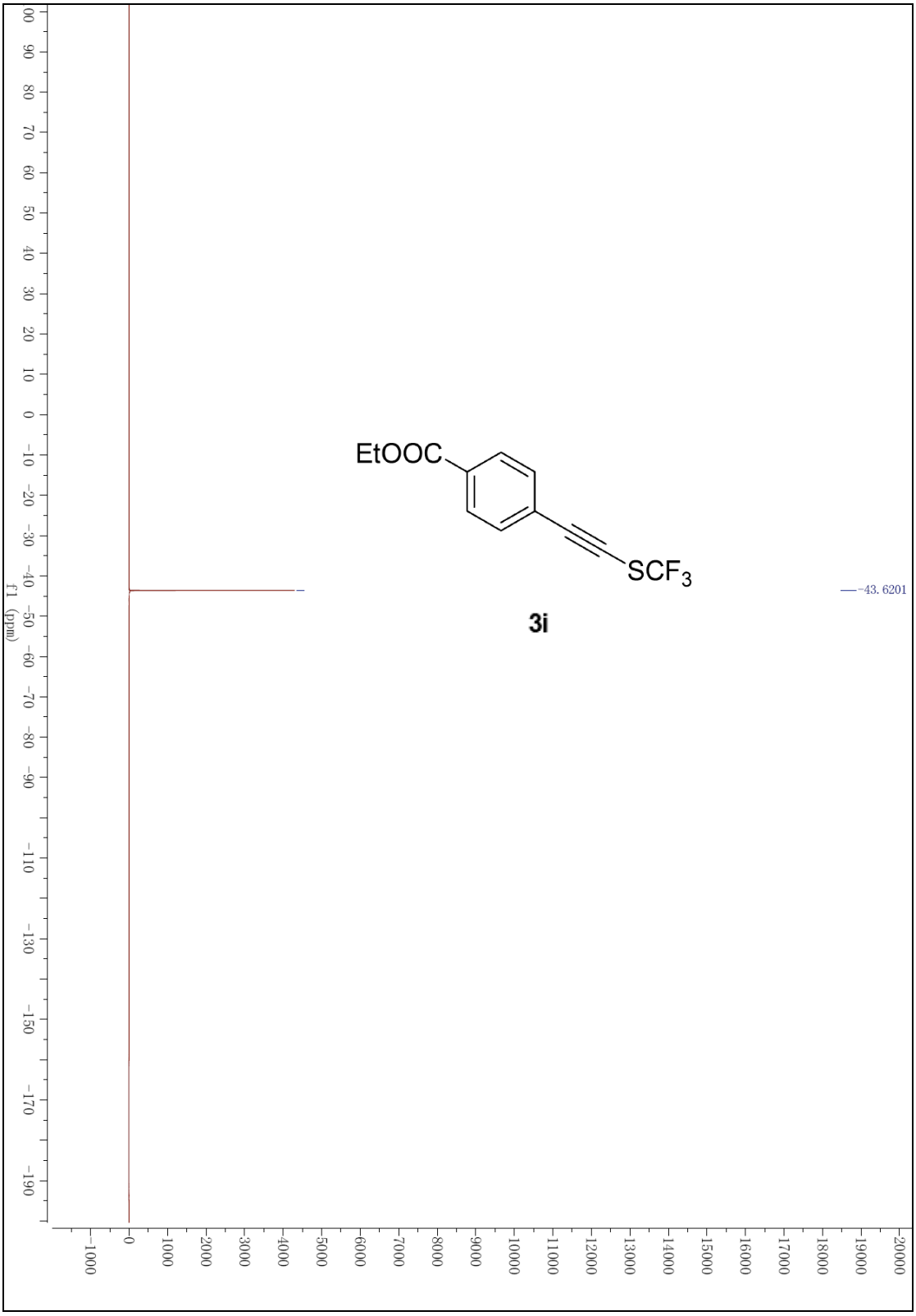

SCF3
S
3h
1.00
1.06
1.05
1.04
3.29
2.4921
7.4589
7.4563
7.4398
7.4372
7.3706
7.3673
7.3506
7.3317
7.3285
7.2596
7.1880
7.1681
7.1254
7.1236
7.1065
7.1049
7.0877
7.0859
f1 (ppm)

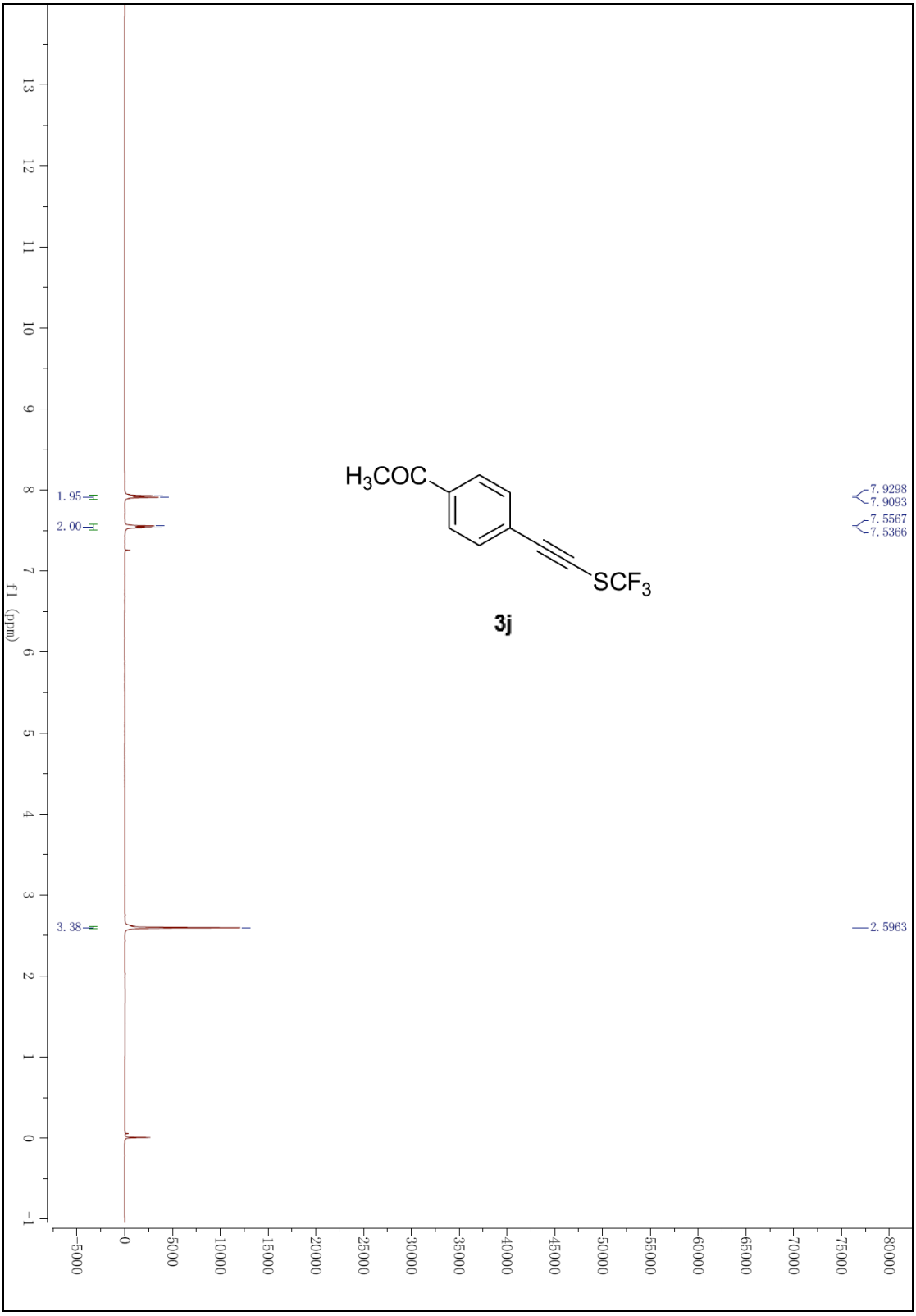

SCF3
S
3h
143.1394
133.1481
132.6835
130.1322
129.5693
126.4595
124.4316
124.3091
123.3455
119.7148
98.7126
77.3309
77.0128
76.6951
72.9765
15.0823
f1 (ppm)

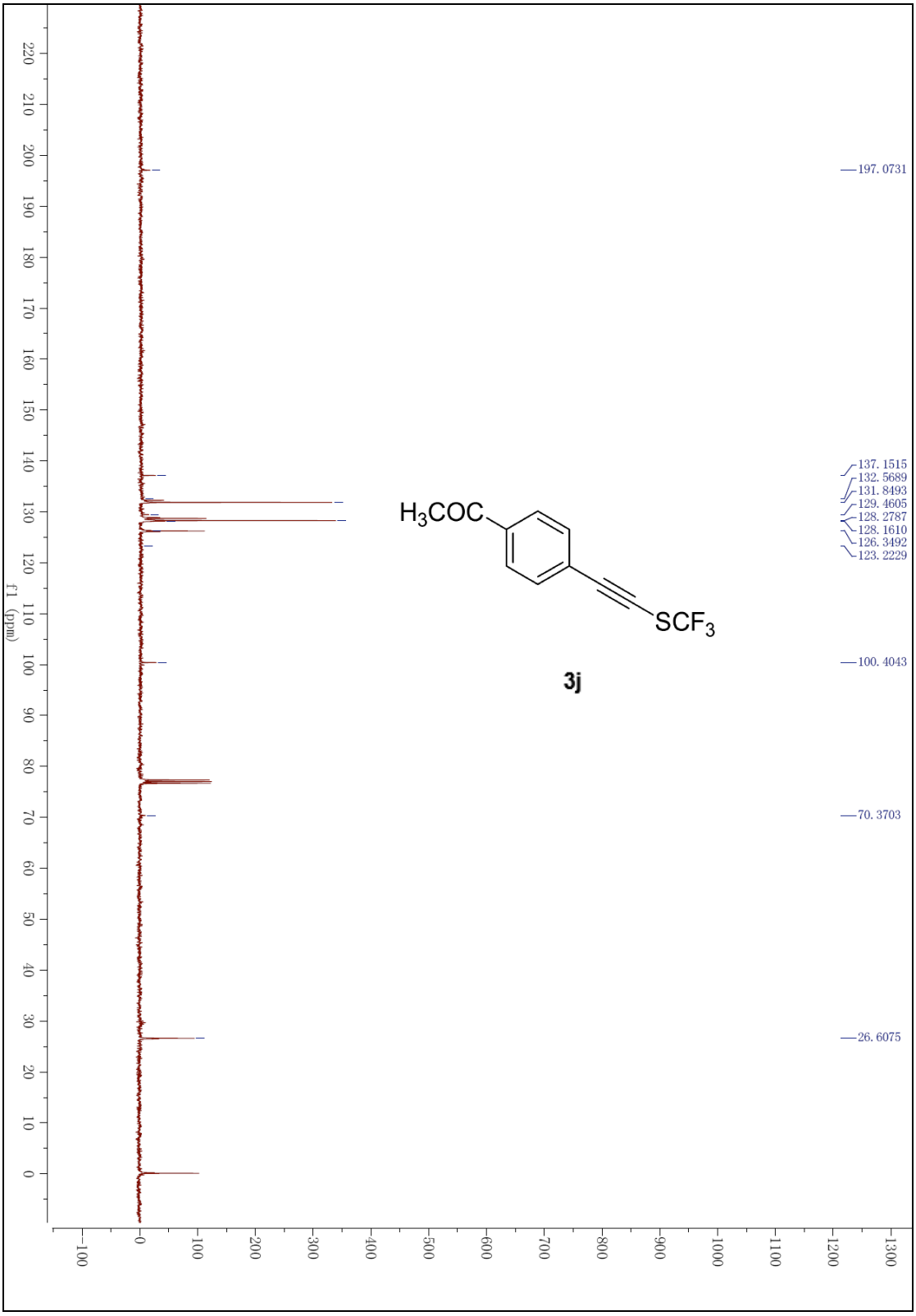

SCF3
S
-43.8550
f1 (ppm)
3h

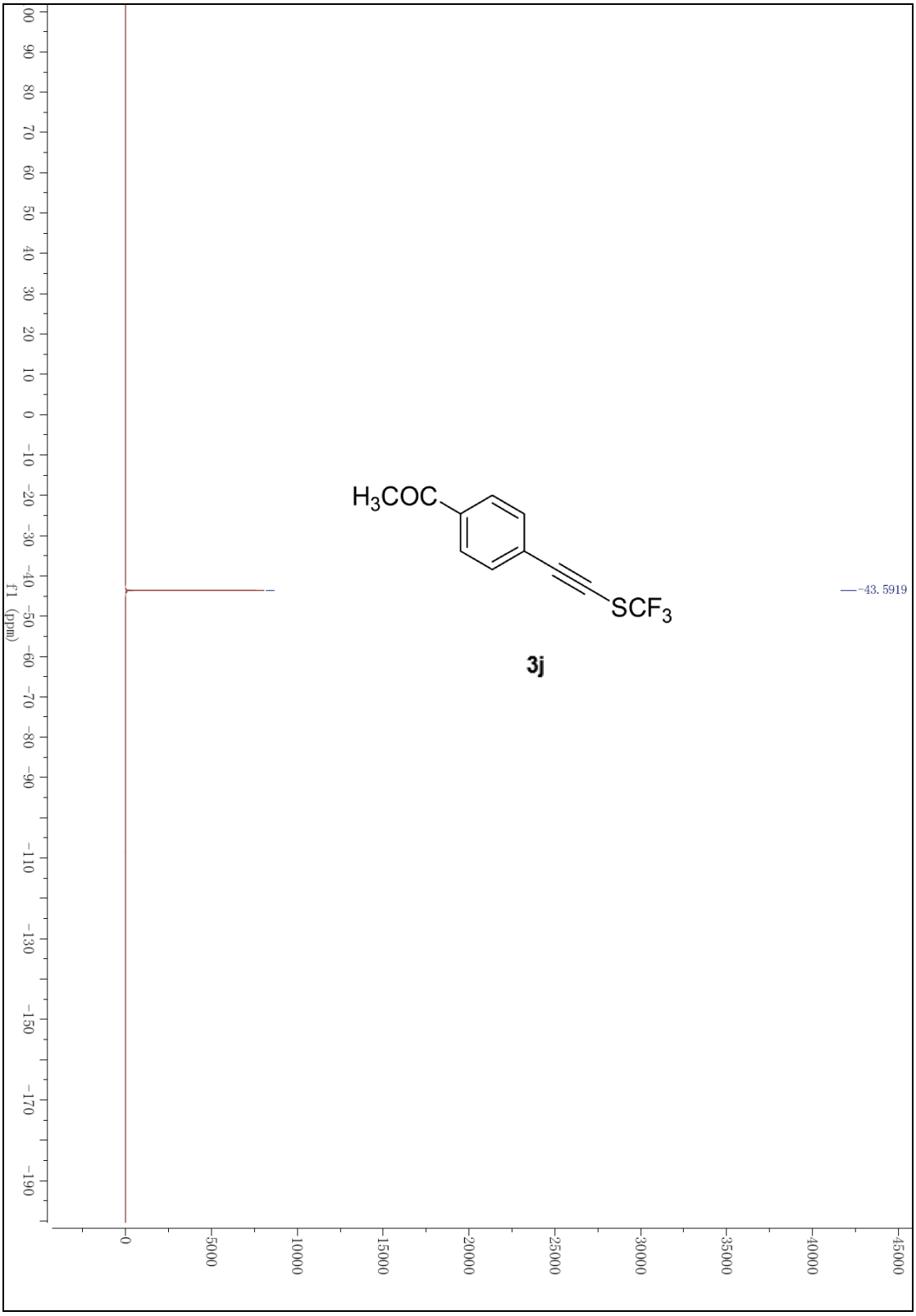

EtOOC
SCF3
3i
2.00
2.02
2.24
3.27
8.0339
8.0129
7.5469
7.5259
7.2617
4.4136
4.3957
4.3779
4.3601
1.4181
1.4003
1.3825
f1 (ppm)


EtOOC
SCF3
3i
165.7345
132.1670
131.6416
131.0671
129.5438
129.3326
126.3935
125.8523
123.4368
100.5198
77.3251
77.0071
76.6895
69.9406
61.3188
14.2696
f1 (ppm)

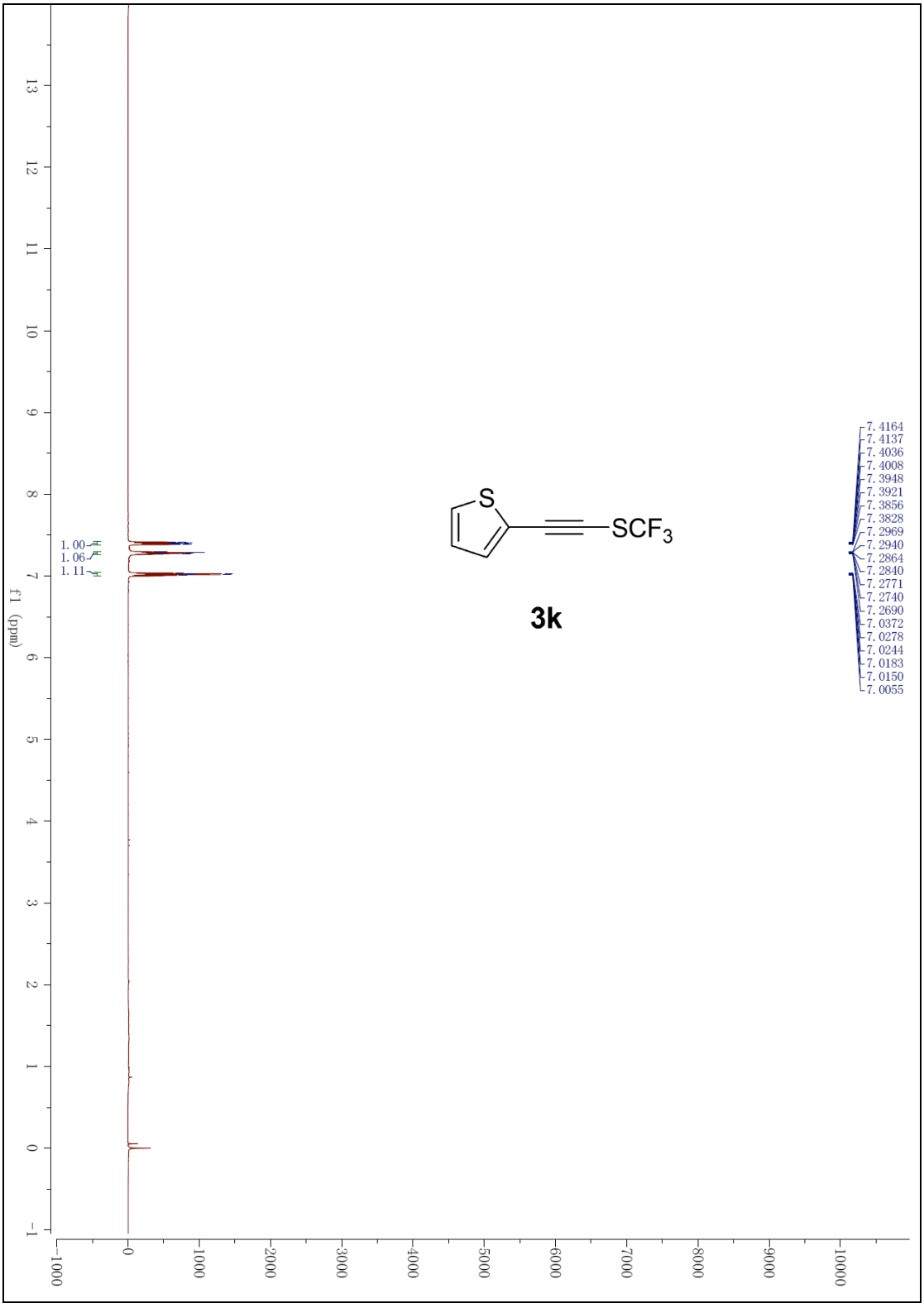

EtOOC
SCF3
3i
-43.6201
f1 (ppm)

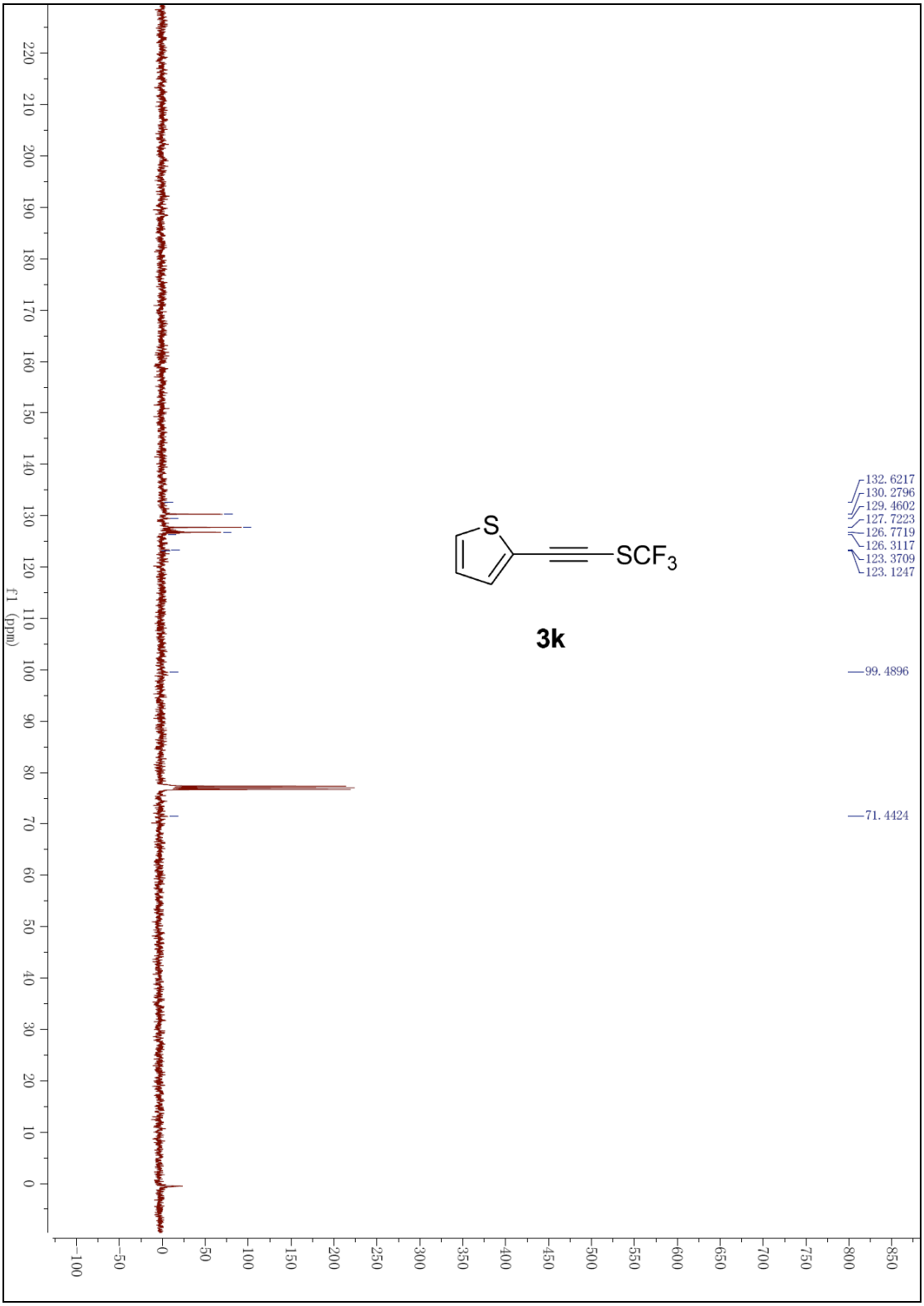

H3COC
SCF3
3j
1.95
2.00
3.38
7.9298
7.9093
7.5567
7.5366
2.5963
f1 (ppm)

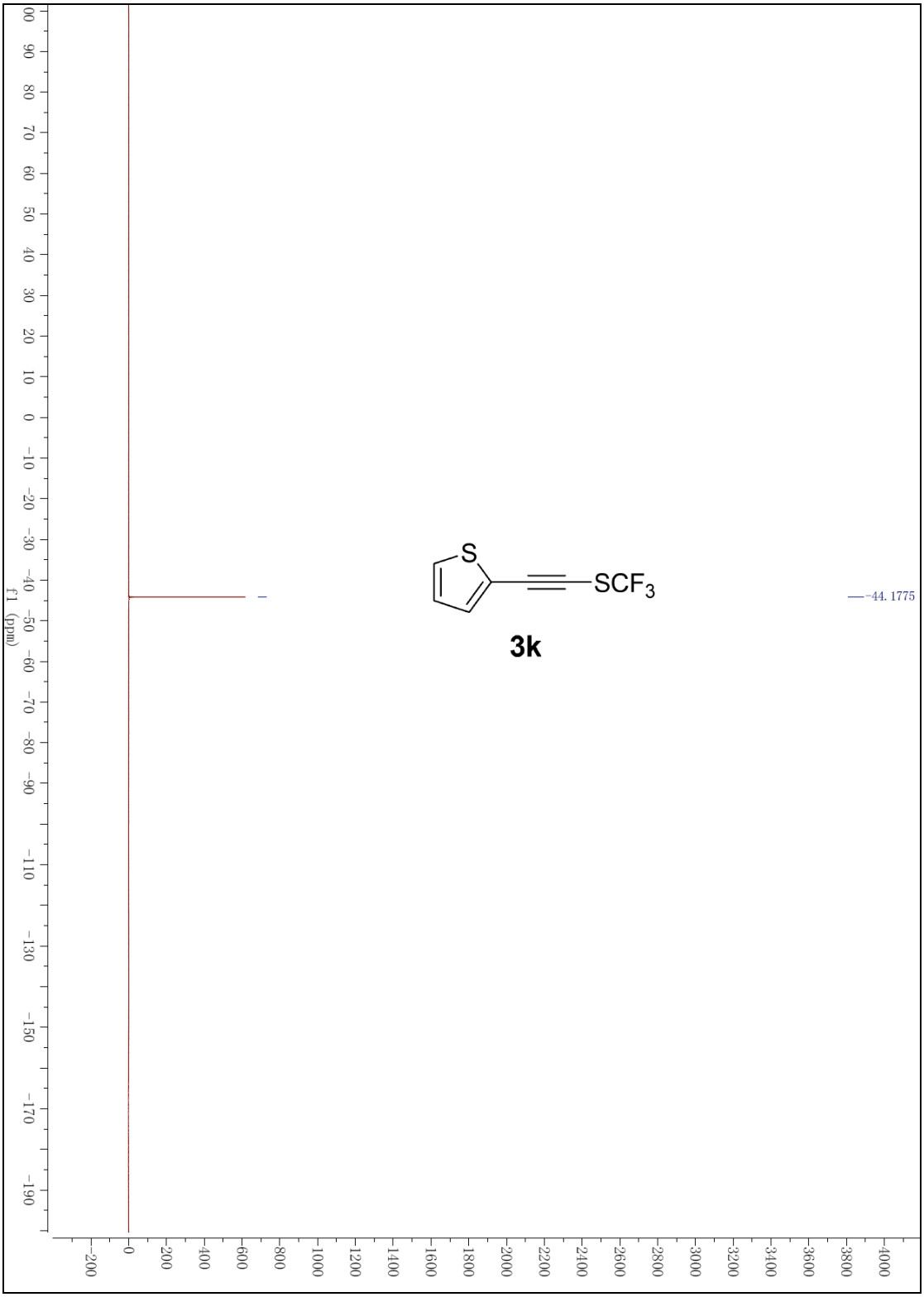

197.0731
137.1515
132.5689
131.8493
129.4605
128.2787
128.1610
126.3492
123.2229
100.4043
70.3703
26.6075
H3COC
SCF3
3j
f1 (ppm)

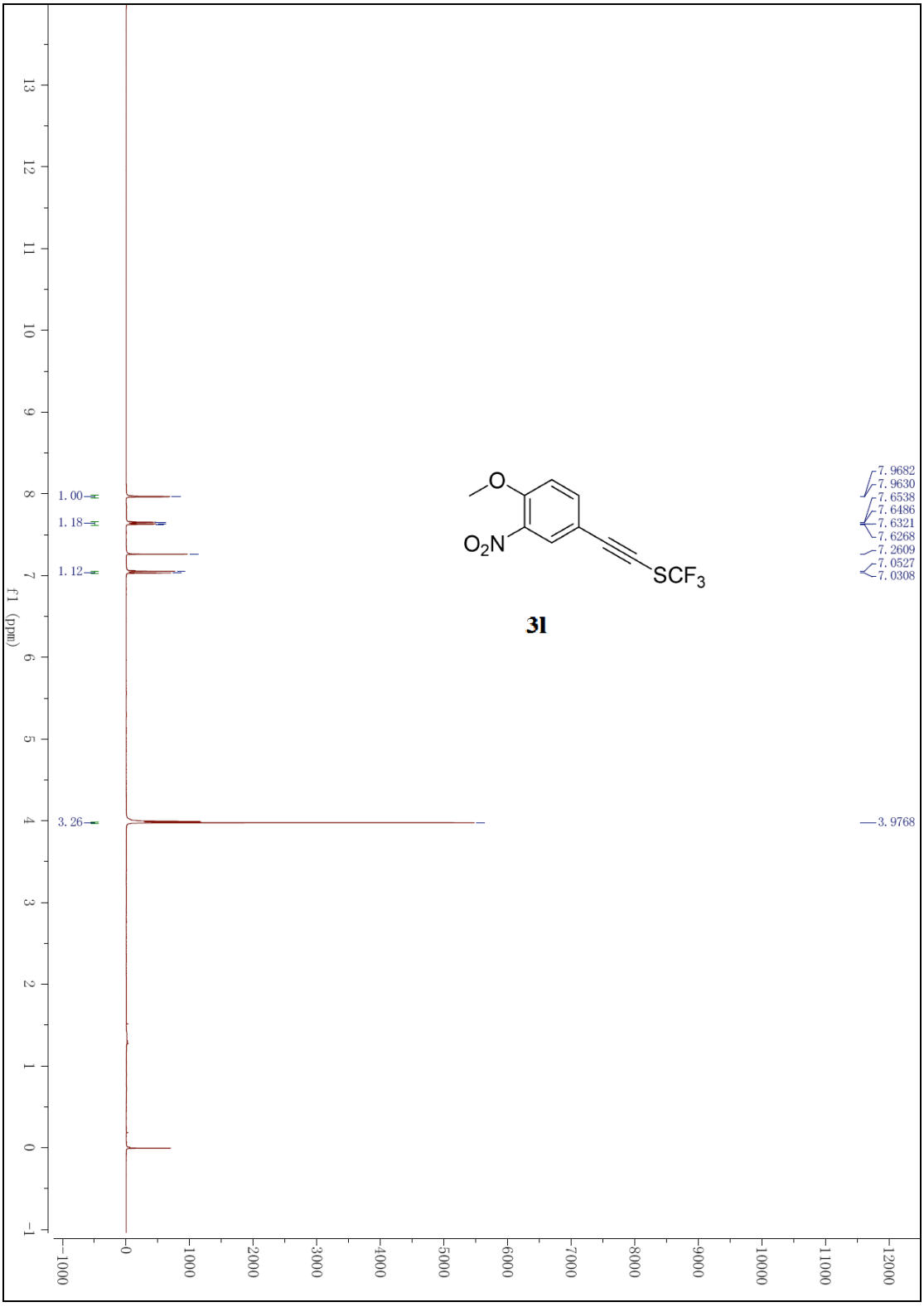


3j

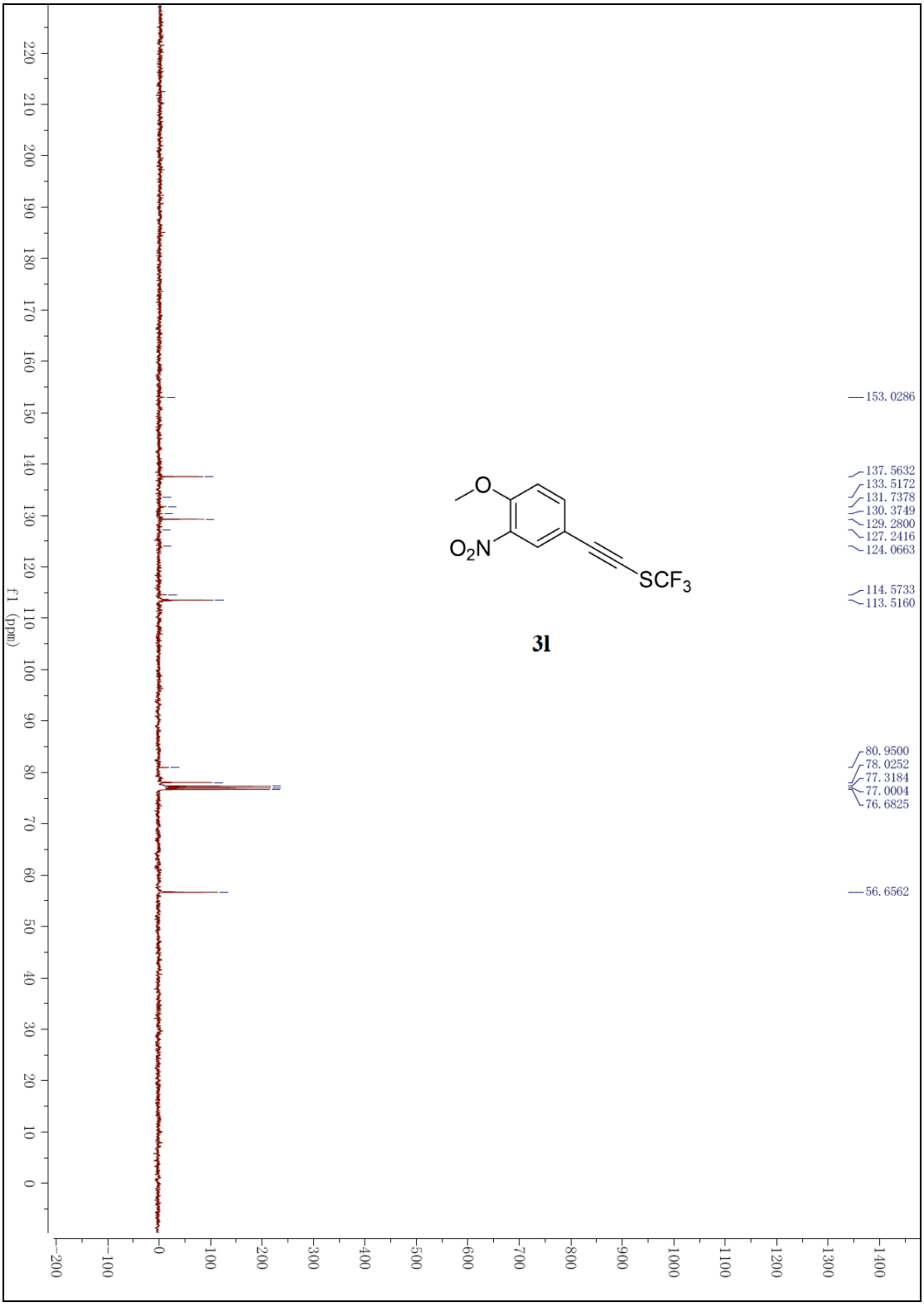

S
SCF3
3k
1.00
1.06
1.11
7.4164
7.4137
7.4036
7.4008
7.3948
7.3921
7.3856
7.3828
7.2969
7.2940
7.2864
7.2840
7.2771
7.2740
7.2690
7.0372
7.0278
7.0244
7.0183
7.0150
7.0055
f1 (ppm)


S
SCF3
3k
132.6217
130.2796
129.4602
127.7223
126.7719
126.3117
123.3709
123.1247
99.4896
71.4424
f1 (ppm)

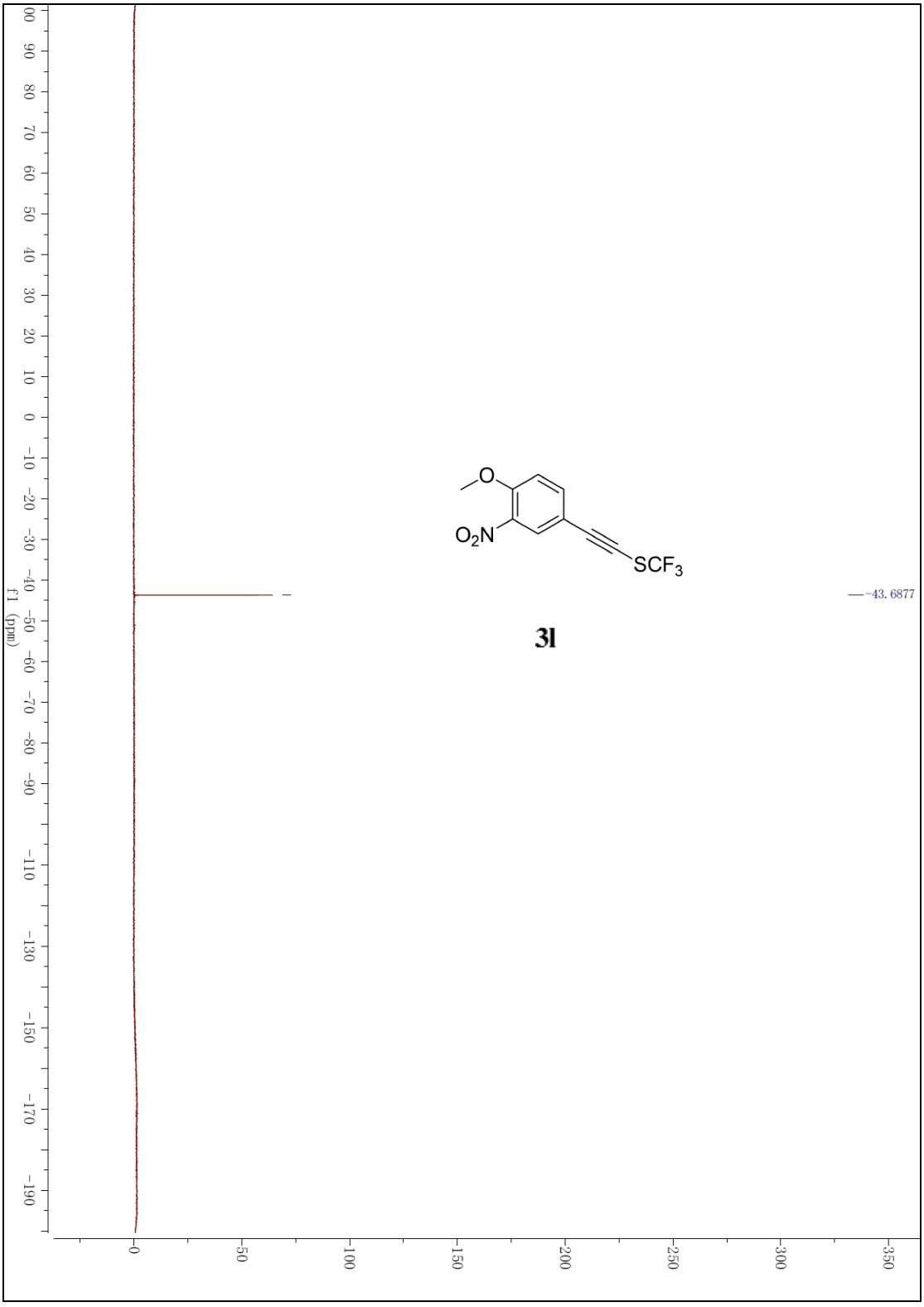

S
SCF3
3k
−44.1775
f1 (ppm)


7.9682
7.9630
7.6538
7.6486
7.6321
7.6268
7.2609
7.0527
7.0308
3.9768
1.00
1.18
1.12
3.26
O
O2N
SCF3
f1 (ppm)

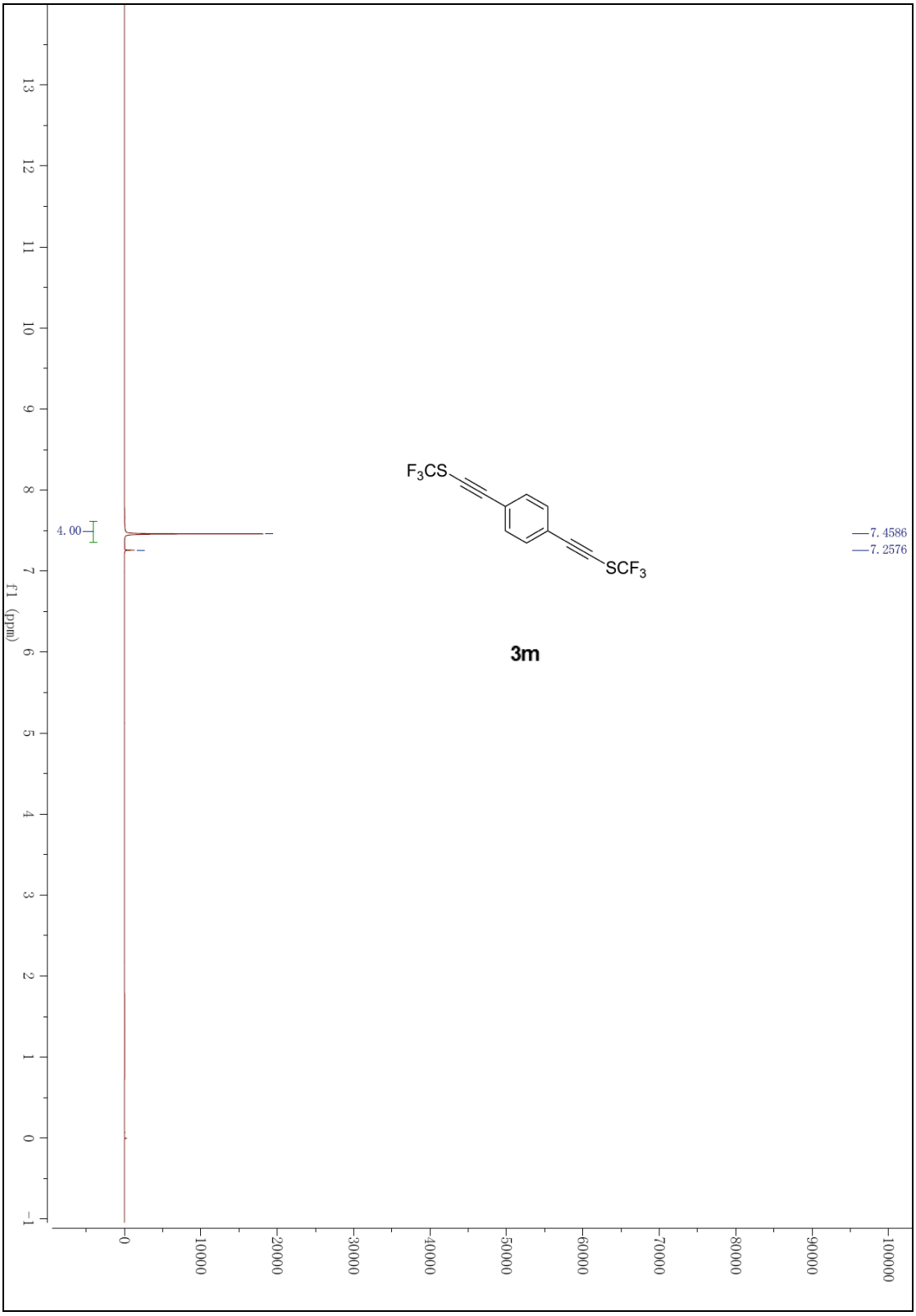
3l

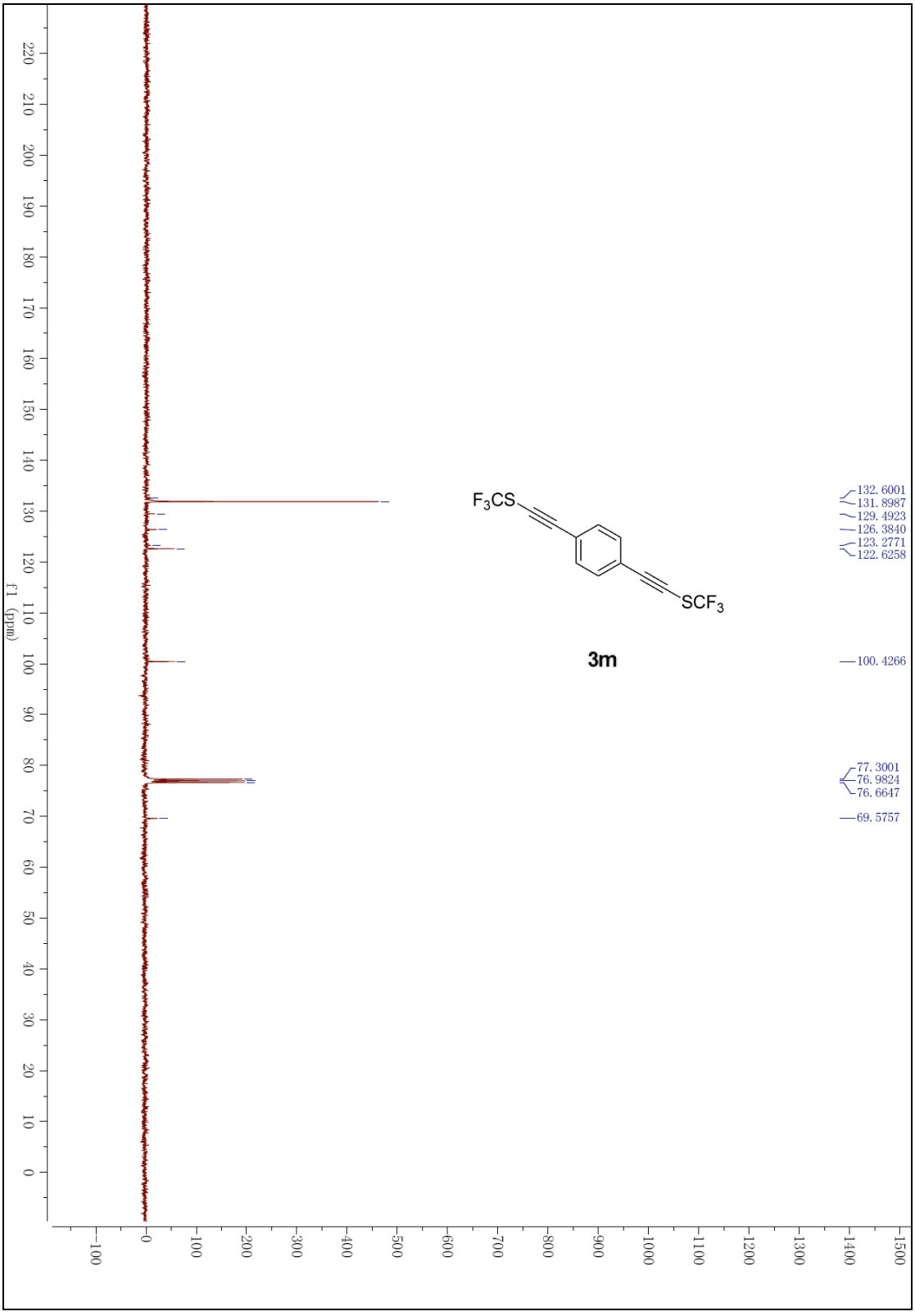

153.0286
137.5632
133.5172
131.7378
130.3749
129.2800
127.2416
124.0663
114.5733
113.5160
80.9500
78.0252
77.3184
77.0004
76.6825
56.6562
O
O2N
SCF3
f1 (ppm)

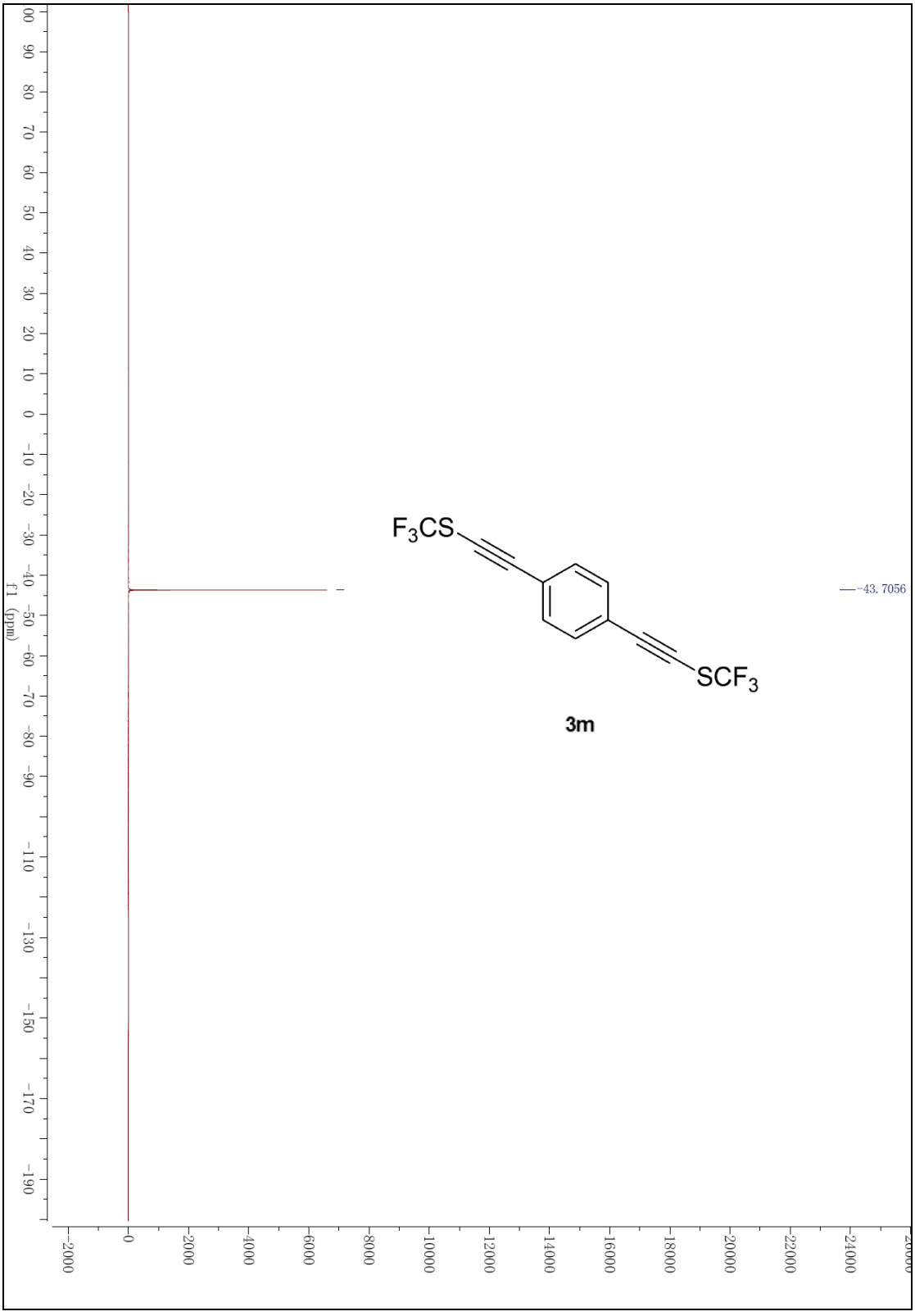
3l



3l


F3CS
SCF3
4.00
7.4586
7.2576
f1 (ppm)
3m


F3CS
SCF3
3m
132.6001
131.8987
129.4923
126.3840
123.2771
122.6258
100.4266
77.3001
76.9824
76.6647
69.5757
f1 (ppm)


F3CS
SCF3
3m
-43.7056
f1 (ppm)