# Supporting Information

## Copper-mediated Trifluoromethylation of Propargyl Acetates Leading to Trifluoromethyl-allenes

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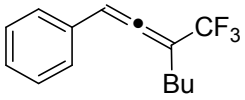
## Contents

## 1. General Information

$^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded in $CDCl_3$ on a 400 MHz instrument or a 300 MHz instrument. All chemical shifts are reported in ppm relative to TMS or $CFCl_3$ (positive for downfield shifts) as external standards. MS experiments were performed on an Agilent 5973N instrument for EI-MS and a Waters Micromass GCT Premier instrument for HRMS. DMF (⩾99.5%) and Cu (⩾99.0%) were used without purification. S-(Trifluoromethyl)diphenylsulfonium triflate[1] $[Ph_2SCF_3]^+[OTf]^-$ and propargyl acetates[2] were synthesized according to literature procedures. Other reagents were purchased from commercial sources.

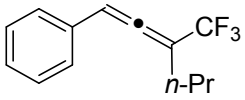
## 2. General Procedure for the Trifluoromethylation of Propargyl Acetates by Trifluoromethyl Sulfonium Salts.

Copper powder (38.4mg, 0.6 mmol) was added to a solution of the propargyl acetate (0.1 mmol) and $[Ph_2SCF_3]^+[OTf]^-$ (162 mg, 0.4 mmol) in DMF (0.5 mL) under $N_2$ in a 5 mL tube, which was then sealed. The reaction mixture was then stirred at 70 $^o$C for 2 to 9 h. After dilution with diethyl ether (30 mL), the reaction mixture was washed with water (3×20 mL), dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (eluent: pentane) to yield the desired allene.




**3a**

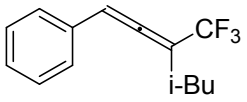
(3-(Trifluoromethyl)hepta-1,2-dien-1-yl)benzene(**3a**): Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.17 (m, 5H), 6.60-6.58 (m, 1H), 2.31-2.21 (m, 2H), 1.56-1.45 (m, 2H), 1.43-1.34 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.98 (d, *J* = 3.0 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 203.79 (q, *J* = 4.2 Hz), 132.11 (q, *J* = 1.1 Hz), 128.82, 128.10, 127.23, 123.58 (q, *J* = 274.2 Hz), 103.08 (q, *J* = 33.6 Hz), 101.47, 29.42, 26.35, 22.17, 13.70. IR(KBr): 2961, 2894, 2865, 1962, 1462, 1295, 1281, 1253, 1209, 1149, 1117, 1019, 914, 828, 745, 691 cm$^{-1}$. HRMS (EI): calcd. for $[C_{14}H_{15}F_3]$ 240.1126, found 240.1127.




**3b**

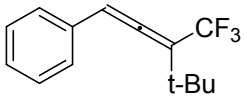
(3-(Trifluoromethyl)hexa-1,2-dien-1-yl)benzene(**3b**): Colorless oil. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.54-7.10 (m, 5H), 6.61-6.51 (m, 1H), 2.25 (t, *J* = 7.1 Hz, 2H), 1.61-1.46(m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). $^{19}$F NMR (376 MHz, CDCl3) δ -64.00 (d, *J* = 3.3 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 203.84 (q, *J* = 4.1 Hz), 132.08 (q, *J* = 1.1 Hz), 128.83, 128.11, 127.24, 123.57 (q, *J* = 274.1 Hz), 102.89 (q, *J* = 33.7 Hz), 101.28, 28.70, 20.69, 13.59. IR(KBr):2967, 2935, 2877, 1961, 1462, 1298, 1273, 1207, 1149, 1115, 1007, 996, 950, 914, 826, 745, 691 cm$^{-1}$. HRMS (EI): calcd. for

[$C_{13}H_{13}F_3$] 226.0969, found 226.0967.



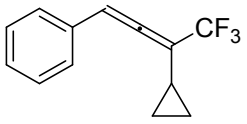

**3c**

(5-Methyl-3-(trifluoromethyl)hexa-1,2-dien-1-yl)benzene(**3c**): Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40-7.26 (m, 5H), 6.63-6.58 (m, 1H), 2.20-2.15 (m, 2H), 1.91-1.83 (m, 1H), 0.99 (t, *J* = 7.3 Hz, 6H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -64.19 (d, *J* = 5.8 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 204.45 (q, *J* = 4.1 Hz), 132.02 (q, *J* = 1.1 Hz), 128.85, 128.13, 127.35, 123.65 (q, *J* = 274.2 Hz), 101.82 (q, *J* = 33.6 Hz), 100.91, 36.08, 26.73, 22.45, 22.34. IR(KBr):2959, 2929, 2873, 1962, 1463, 1302, 1277, 1210, 1149, 1123, 1013, 746, 693cm$^{-1}$. HRMS (EI): calcd. for [$C_{14}H_{15}F_3$] 240.1126, found 240.1127.




**3d**

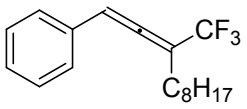
(4,4-Dimethyl-3-(trifluoromethyl)penta-1,2-dien-1-yl)benzene(**3d**): Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35-7.22 (m, 5H), 6.55 (q, *J* = 3.2 Hz, 1H), 1.26 (s, 9H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -57.29 (d, *J* = 1.7 Hz).$^{13}$C NMR (101 MHz, $CDCl_3$) δ 204.35 (q, *J* = 4.8 Hz), 132.24 (q, *J* = 1.2 Hz), 128.87, 127.99, 127.04, 124.03 (q, *J* = 276.1 Hz), 111.66 (q, *J* = 30.8 Hz), 100.94, 33.81, 30.00 (q, *J* = 1.2 Hz). IR(KBr): 2970, 2911, 1962, 1480, 1460, 1402, 1292, 1271, 1241, 1212, 1172, 1116, 1034, 974, 913, 825, 746, 733, 691, 648 cm$^{-1}$. HRMS (EI): calcd. for [$C_{14}H_{15}F_3$] 240.1126, found 240.1129.




**3e**

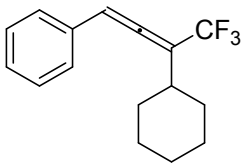
(3-Cyclopropyl-4,4,4-trifluorobuta-1,2-dien-1-yl)benzene(**3e**): Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35-7.21 (m, 5H), 6.74 -6.42 (m, 1H), 1.51-1.42 (m, 1H), 0.86-0.81 (m, 2H), 0.58-0.51 (m, 2H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.69 (d, J = 3.1 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.62 (q, *J* = 3.9 Hz), 131.82 (q, *J* = 1.1 Hz), 128.87, 128.26, 127.19, 123.52 (q, *J* = 274.5 Hz), 106.59 (q, *J* = 34.0 Hz), 102.26, 7.56, 7.08, 6.66. IR(KBr): 3089, 3035, 3013, 1959, 1497, 1461, 1313, 1293, 1280, 1202, 1151, 1119, 1076, 1027, 1007, 956, 914, 827, 747, 691 cm$^{-1}$. HRMS (EI):

calcd. for [$C_{13}H_{11}F_3$] 224.0813, found 224.0816.



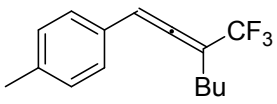

**3f**

(3-(Trifluoromethyl)undeca-1,2-dien-1-yl)benzene(**3f**): Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37-7.23 (m, 5H), 6.61-6.57 (m, 1H), 2.33-2.20 (m, 2H), 1.57-1.47 (m, 2H), 1.39-1.18 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -64.00 (d, *J* = 2.7 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 203.81 (q, *J* = 4.3 Hz), 132.12 (d, *J* = 1.1 Hz), 128.81, 128.10, 127.25, 123.60 (q, *J* = 274.2 Hz), 103.08 (q, *J* = 33.6 Hz), 101.32, 31.77, 29.25, 29.19, 29.07, 27.32, 26.66, 22.61, 14.03. IR(KBr): 2928, 2857, 1962, 1498, 1462, 1314, 1295, 1281, 1209, 1149, 1121, 1074, 913, 827, 745, 691 cm$^{-1}$. HRMS (EI): calcd. for [$C_{18}H_{23}F_3$] 296.1752, found 296.1748.




**3g**

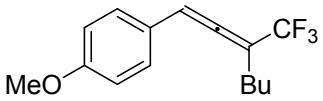
(3-Cyclohexyl-4,4,4-trifluorobuta-1,2-dien-1-yl)benzene(**3g**): Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.32-7.17 (m, 5H), 6.57-6.52 (m, 1H), 2.21-2.12 (m, 1H), 2.00-1.85 (m, 2H), 1.75-1.65 (m, 2H), 1.64-1.56 (m, 1H), 1.34-1.04 (m, 5H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.22 (d, *J* = 3.4 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 203.91 (q, *J* = 4.5 Hz), 132.15 (q, *J* = 1.2 Hz), 128.85, 128.08, 127.08, 123.78 (q, *J* = 274.6 Hz), 108.67 (q, *J* = 32.3 Hz), 101.93, 36.57, 33.03, 32.68, 26.24, 26.21, 25.72. IR(KBr): 2929, 2855, 1957, 1497, 1461, 1450, 1277, 1237, 1211, 1139, 1114, 984, 913, 891, 827, 745, 707, 691 cm$^{-1}$. HRMS (EI): calcd. for [$C_{16}H_{17}F_3$] 266.1282, found 266.1281.




**3h**

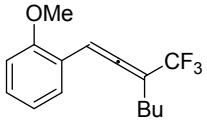
1-Methyl-4-(3-(trifluoromethyl)hepta-1,2-dien-1-yl)benzene(**3h**): Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.20-7.11 (m, 4H), 6.57-6.52 (m, 1H), 2.33 (s, 3H), 2.30-2.19 (m, 2H), 1.54-1.45 (m, 2H), 1.40-1.31 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).$^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.98 (d, *J* = 3.1 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 203.64 (q, *J* = 4.2 Hz), 138.13, 129.58, 129.14 (q, *J* = 1.2 Hz), 127.17, 123.66 (q, *J* = 274.2 Hz), 102.91 (q, *J* = 33.6 Hz), 101.18, 29.47, 26.42, 22.21, 21.21,

13.73. IR(KBr): 2958, 2929, 2865, 1960, 1515, 1460, 1315, 1293, 1279, 1252, 1206, 1149, 1117, 1020, 845, 798, 754, 688cm$^{-1}$. HRMS (EI): calcd. for [$C_{15}H_{17}F_3$] 254.1282, found 254.1281.



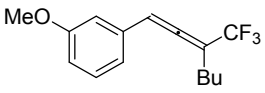

**3i**

1-Methoxy-4-(3-(trifluoromethyl)hepta-1,2-dien-1-yl)benzene (**3i**): Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.57-6.52 (m, 1H), 3.79 (s, 3H), 2.29-2.20 (m, 2H), 1.53-1.45 (m, 2H), 1.41-1.34 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -64.03 (d, *J* = 3.1 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 203.32 (q, *J* = 4.2 Hz), 159.63, 128.44, 124.29 (q, *J* = 1.2 Hz), 123.96 (q, *J* = 274.2 Hz), 114.34, 102.83 (q, *J* = 33.5 Hz), 100.80, 55.26, 29.46, 26.43, 22.17, 13.71. IR(KBr): 2959, 2933, 2864, 2840, 1960, 1608, 1512, 1465, 1401, 1284, 1250, 1147, 1115, 1033, 846, 739, 687cm$^{-1}$. HRMS (EI): calcd. for [$C_{15}H_{17}OF_3$] 270.1232, found 270.1234.




**3j**

1-Methoxy-2-(3-(trifluoromethyl)hepta-1,2-dien-1-yl)benzene (**3j**): Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39-7.16 (m, 2H), 7.08-6.73 (m, 3H), 3.83 (s, 3H), 2.27-2.20 (m, 2H), 1.56-1.45 (m, 2H), 1.42-1.33 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -64.07 (d, *J* = 3.4 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 204.51 (q, *J* = 4.3 Hz), 156.43, 129.26, 128.29, 123.84 (q, *J* = 273.9 Hz), 120.80,120.55(q, *J* = 1.2 Hz) , 111.01, 101.73 (q, *J* = 33.5 Hz), 95.50, 55.44, 29.62, 26.39, 22.20, 13.74. IR(KBr): 2959, 2933, 2865, 1962, 1598, 1495, 1465, 1285, 1249, 1210, 1147, 1116, 1050, 1029, 834, 750, 688 cm$^{-1}$. HRMS (EI): calcd. for [$C_{15}H_{17}OF_3$] 270.1232, found 270.1234.

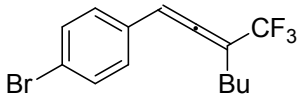



**3k**

1-Methoxy-3-(3-(trifluoromethyl)hepta-1,2-dien-1-yl)benzene (**3k**): Colorless oil.$^1$H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 1H), 6.91-6.79 (m, 3H), 6.63-6.49 (m, 1H), 3.80 (s, 3H), 2.30-2.22 (m, 2H), 1.53-1.45 (m, 2H), 1.42-1.33 (m, 2H), 0.89 (t, *J* = 7.3 Hz,3H). $^{19}$F NMR (376 MHz,

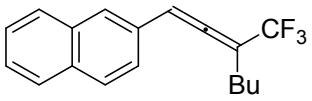
$CDCl_3$) δ -63.97 (d, *J* = 3.2 Hz). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 203.73 (q, *J* = 4.2 Hz), 159.78 , 133.36 (q, *J* = 1.2 Hz), 129.67 , 123.41 (q, *J* = 274.2 Hz), 119.73, 113.56, 112.42, 102.97 (q, *J* = 33.7 Hz), 101.14, 55.03, 29.27, 26.21, 22.03, 13.59. IR(KBr): 2959, 2934, 2865, 1963, 1599, 1584, 1493, 1467, 1440, 1286, 1258, 1207, 1153, 1117, 1048, 1020, 858, 825, 775, 736 ,687 $cm^{-1}$.

HRMS (EI): calcd. for $[C_{15}H_{17}OF_3]$ 270.1232, found 270.1227.




**3l**

1-Bromo-4-(3-(trifluoromethyl)hepta-1,2-dien-1-yl)benzene (**3l**): Colorless oil. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.55-6.51 (m, 1H), 2.30-2.23 (m, 2H), 1.55-1.44 (m, 2H), 1.41-1.32 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -63.98 (d, *J* = 3.0 Hz). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 203.83 (q, *J* = 4.2 Hz), 132.01, 131.10 (q, *J* = 1.2Hz) , 128.68, 123.37 (q, *J* = 274.4 Hz), 121.99, 103.64 (q, *J* = 33.7 Hz), 100.51, 29.37, 26.30, 22.15, 13.71. IR (KBr): 2959, 2932, 2864, 1963, 1489, 1465, 1305, 1287, 1192, 1149, 1071, 1010 ,846, 822 ,739, 688 $cm^{-1}$. HRMS (EI): calcd. for $[C_{14}H_{14}BrF_3]$ 318.0231, found 318.0234.



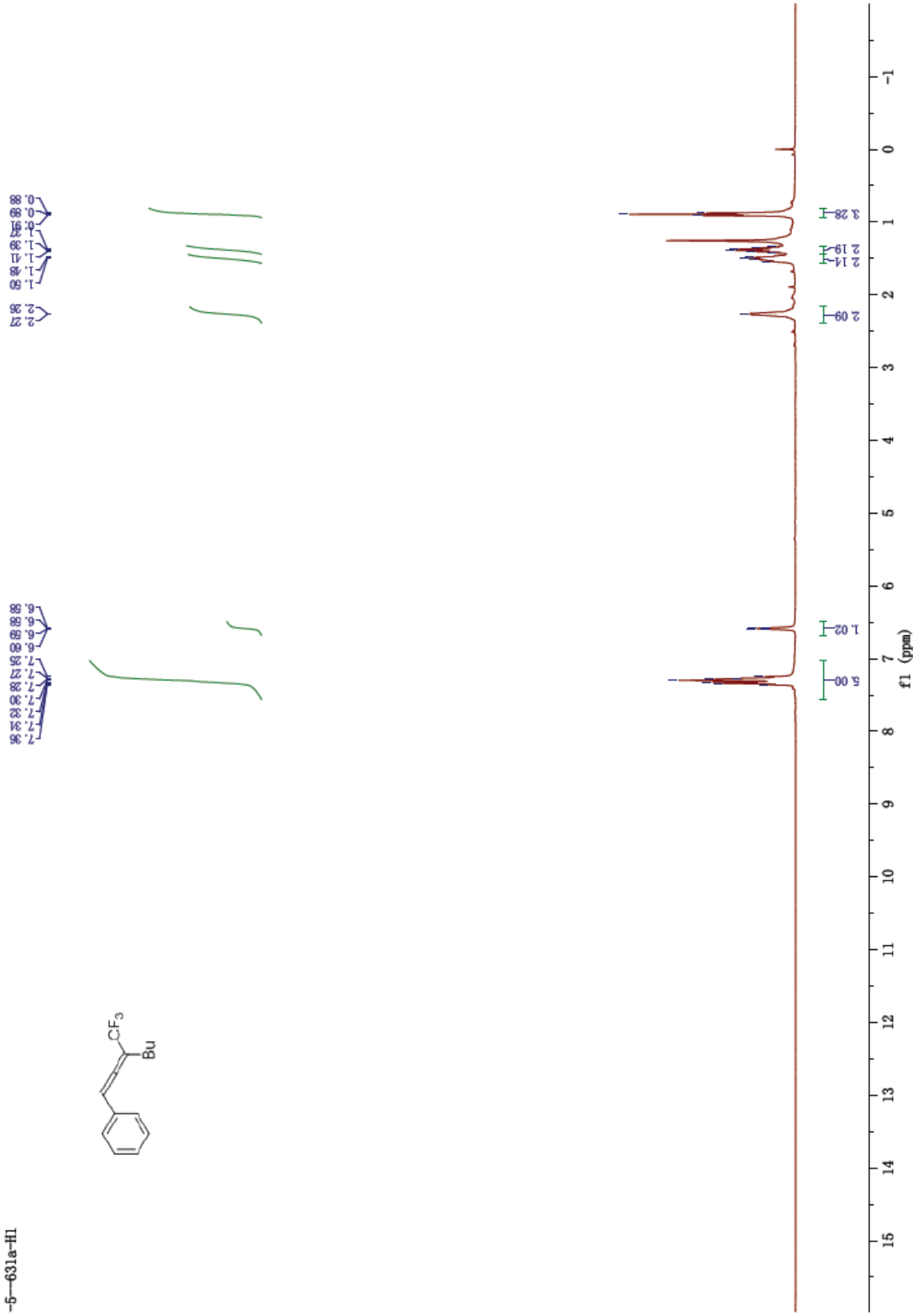

**3n**

2-(3-(Trifluoromethyl)hepta-1,2-dien-1-yl)naphthalene (**3n**): White solid. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.82-7.75 (m, 3H), 7.68 (s, 1H), 7.57-7.36 (m, 3H), 6.77-6.72 (m, 1H), 2.34-2.26 (m, 2H), 1.61-1.48 (m, 2H), 1.44-1.34 (m, 2H), 0.89 (t, *J* = 6.9 Hz, 3H). $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -63.93 (d, *J* = 3.1 Hz). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 204.33 (q, *J* = 4.1 Hz), 133.56, 133.14, 129.59(q, *J* = 1.2 Hz) , 128.64, 127.90, 127.78, 126.74, 126.50, 126.29, 124.44, 123.66 (q, *J* = 274.3 Hz), 103.34 (q, *J* = 33.7 Hz), 101.71, 29.48, 26.45, 22.21, 13.74. IR(KBr): 2962, 2928, 2861, 1959, 1467, 1335, 1285, 1251, 1208, 1152, 1116, 1020, 898, 865, 818, 746, 686 $cm^{-1}$. HRMS (EI): calcd. for $[C_{18}H_{17}F_3]$ 290.1282, found 290.1284.

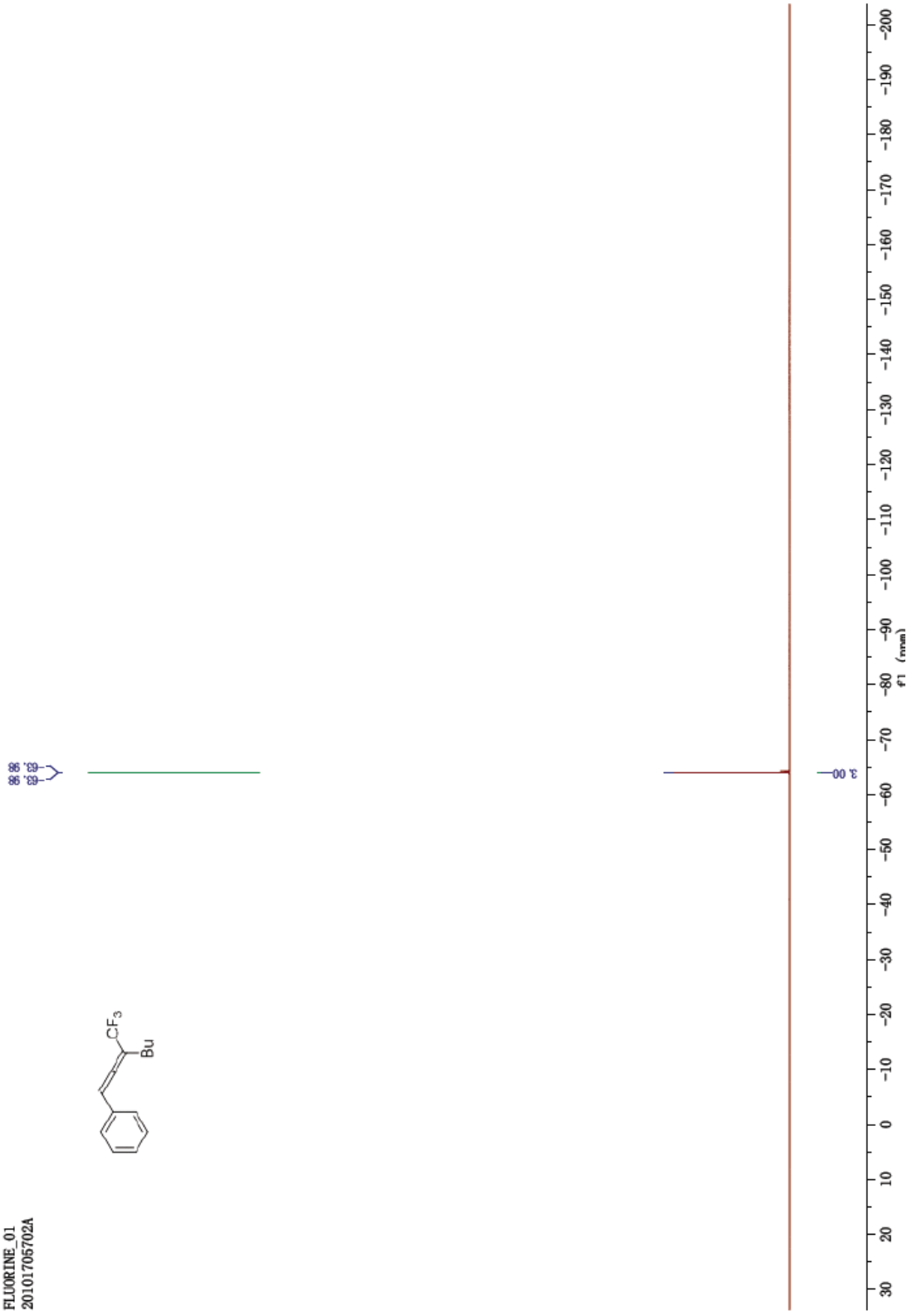
**References**


1. E. Magnier, J.-C. Blazejewski, M. Tordeux and C. Wakselman, *Angew. Chem., Int. Ed.*, 2006, **45**, 1279-1282.
2. (a)M. Yu, G. Zhang and L. Zhang, *Org. Lett.*, 2007, **9**, 2147-2150; (b)N. Marion, P. Carlqvist, R. Gealageas, P. de Fremont, F. Maseras and S. P. Nolan, *Chemistry*, 2007, **13**, 6437-6451; (c)D. Wang, X. Ye and X. Shi, *Org. Lett.*, 2010, **12**, 2088-2091.

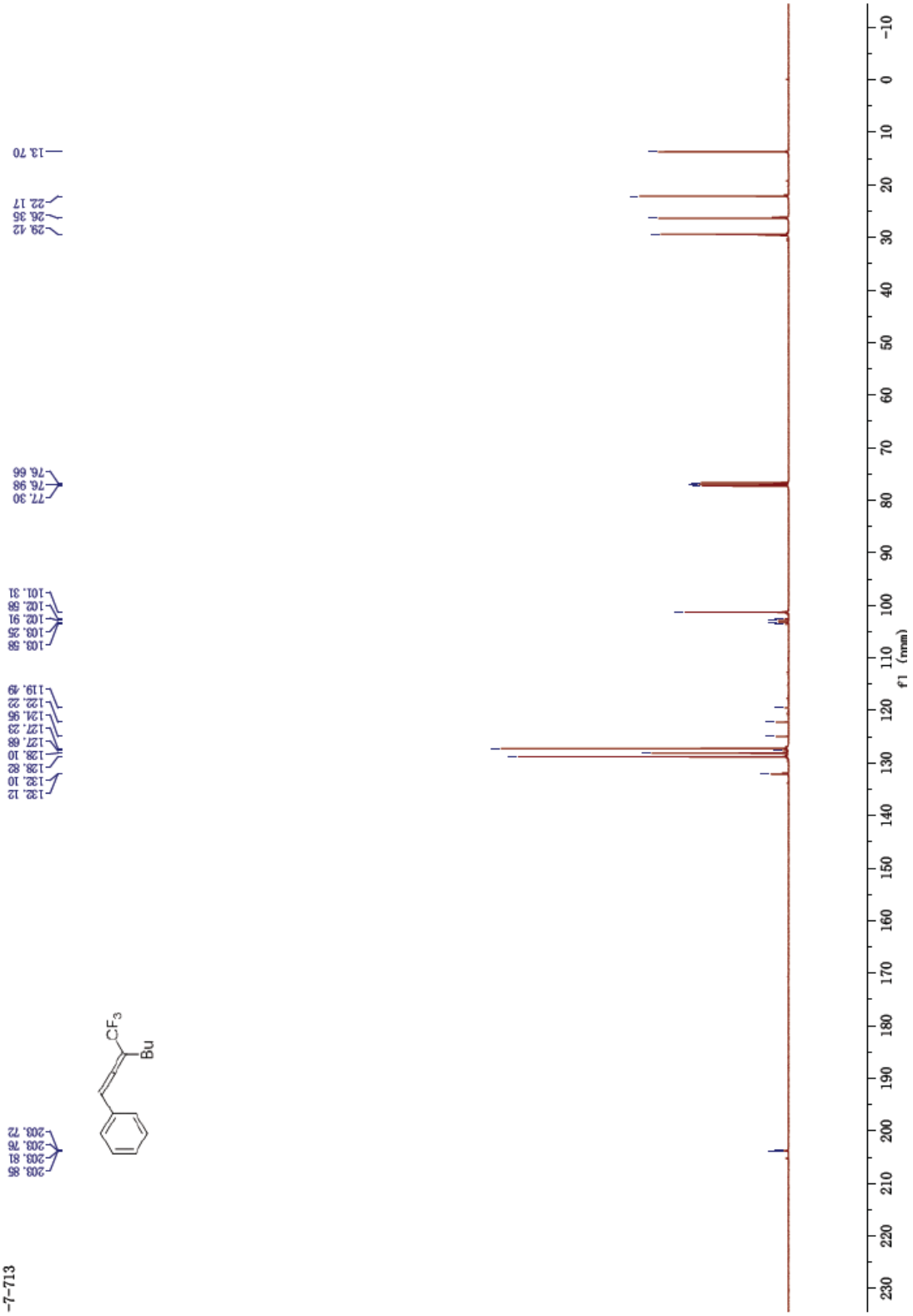
$^{1}$H NMR spectrum of compound **3a**



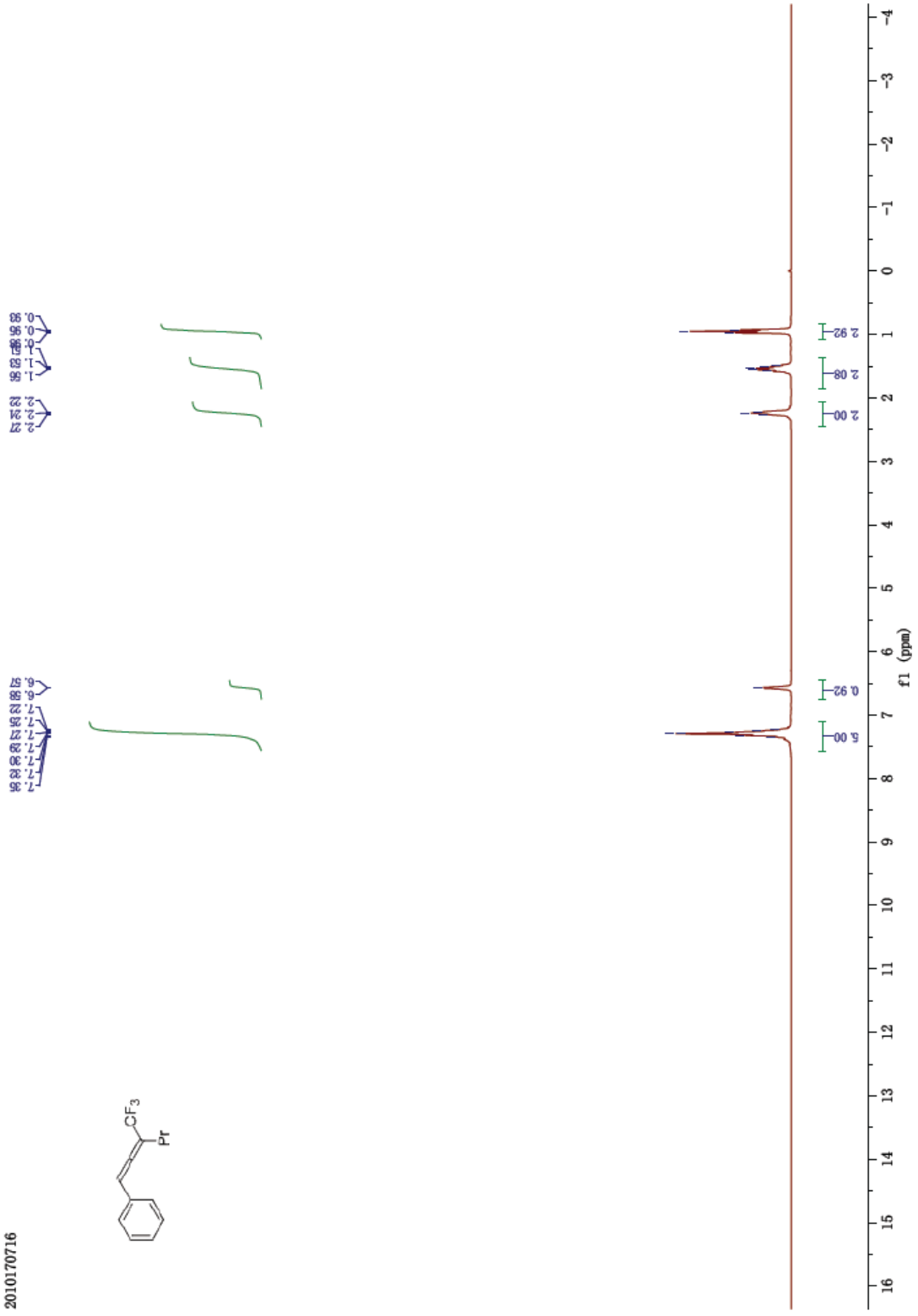
$^{19}F$ NMR spectrum of compound **3a**



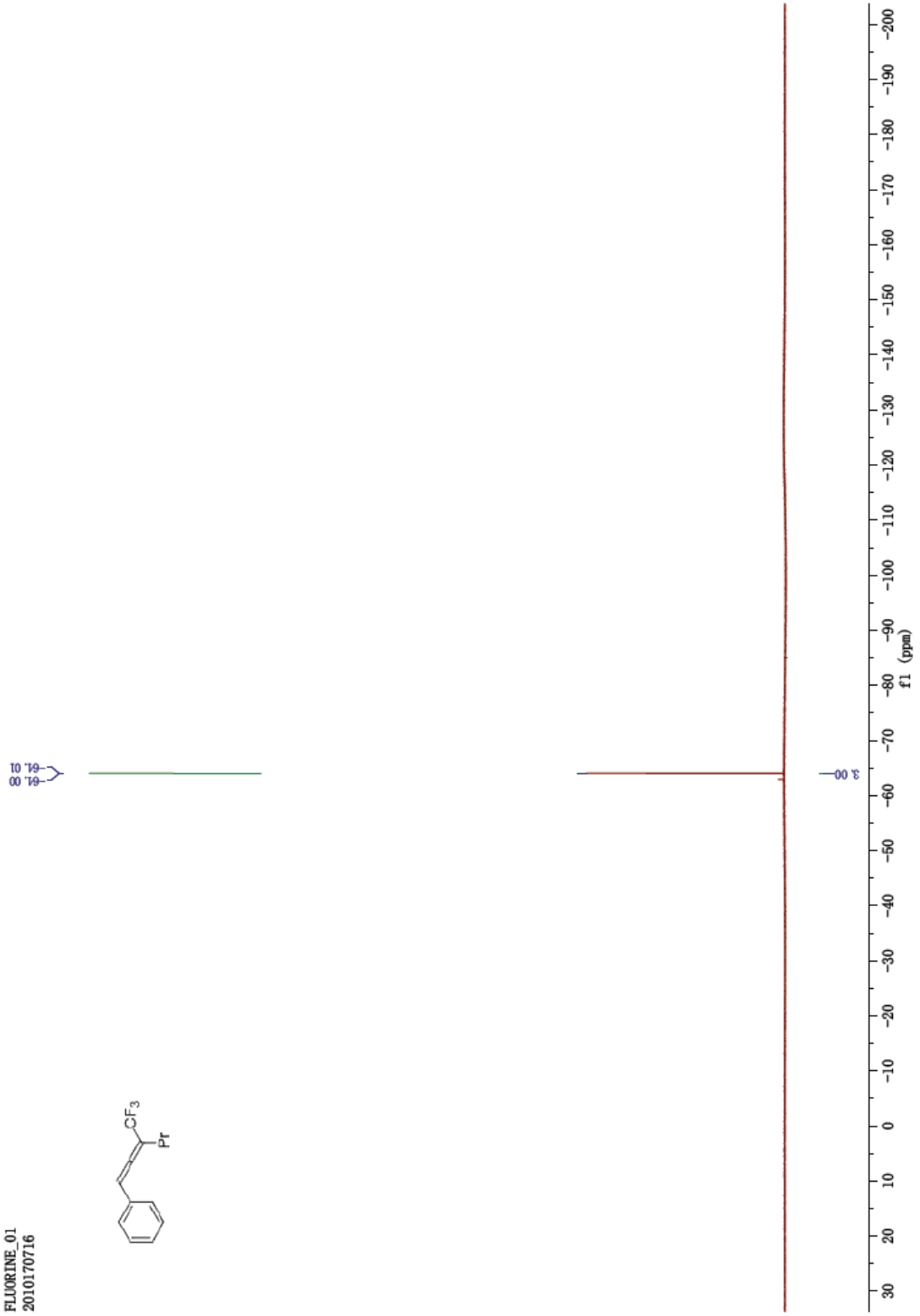
$^{13}C$ NMR spectrum of compound **3a**



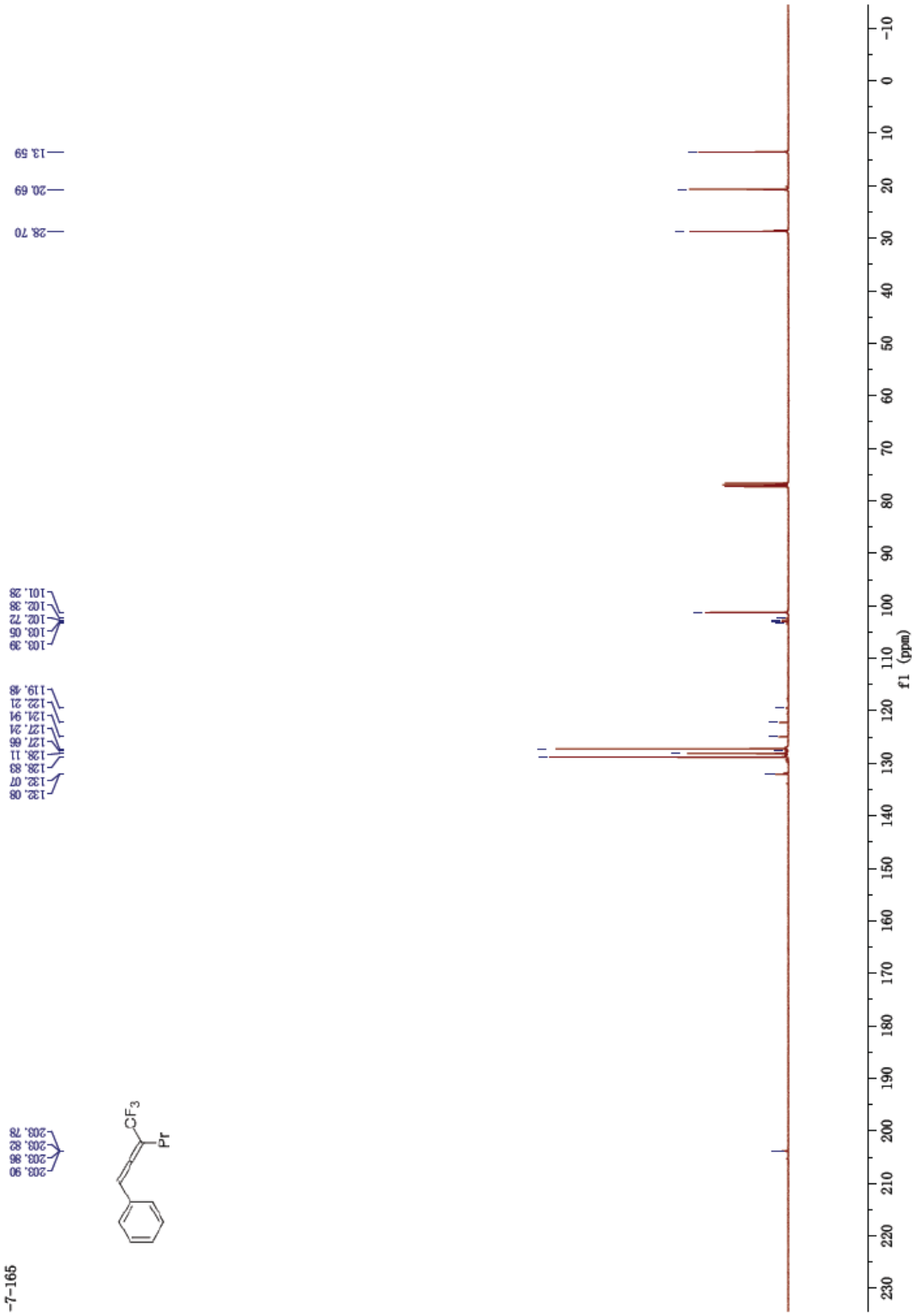
$^{1}$H NMR spectrum of compound **3b**



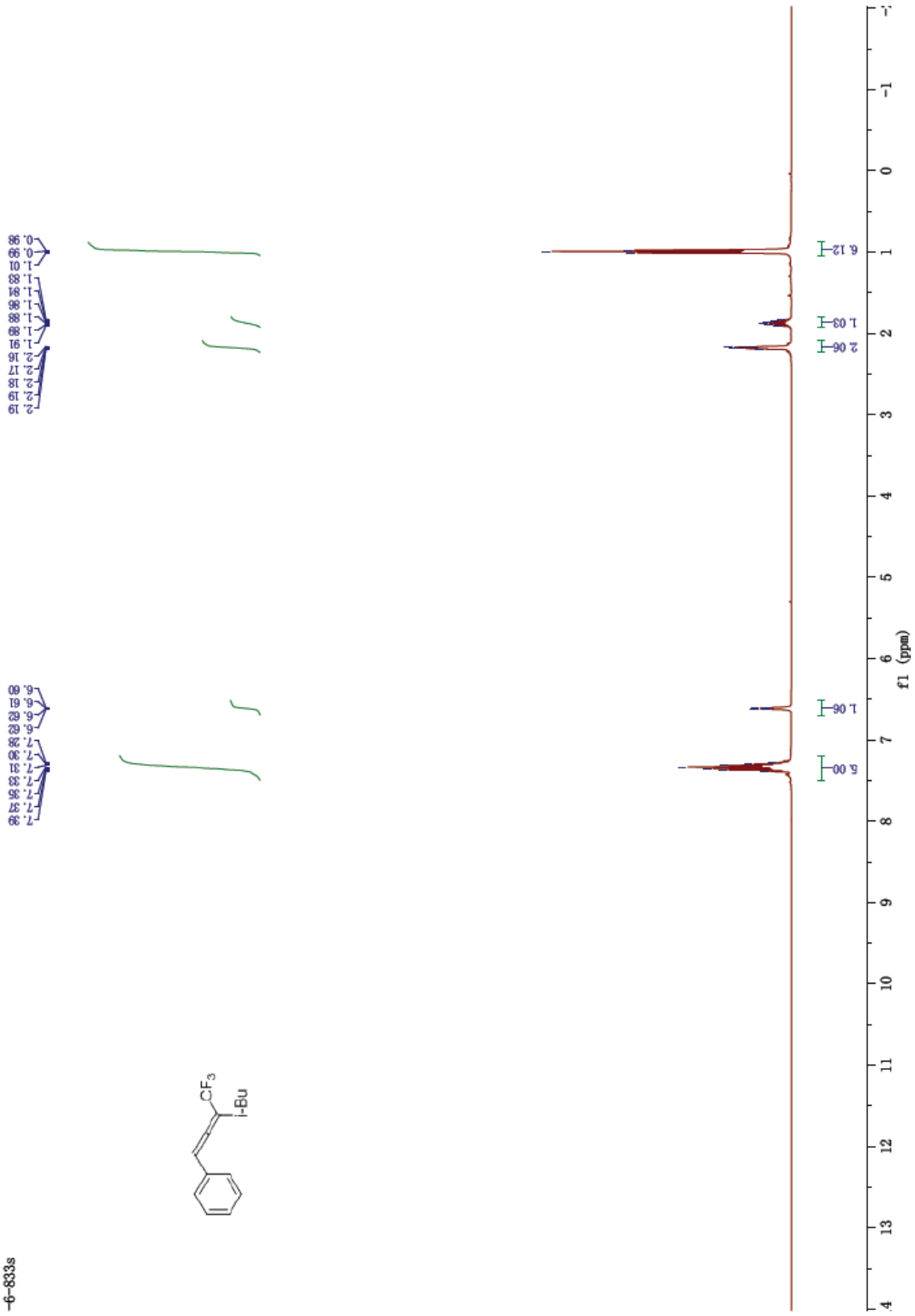
$^{19}F$ NMR spectrum of compound **3b**



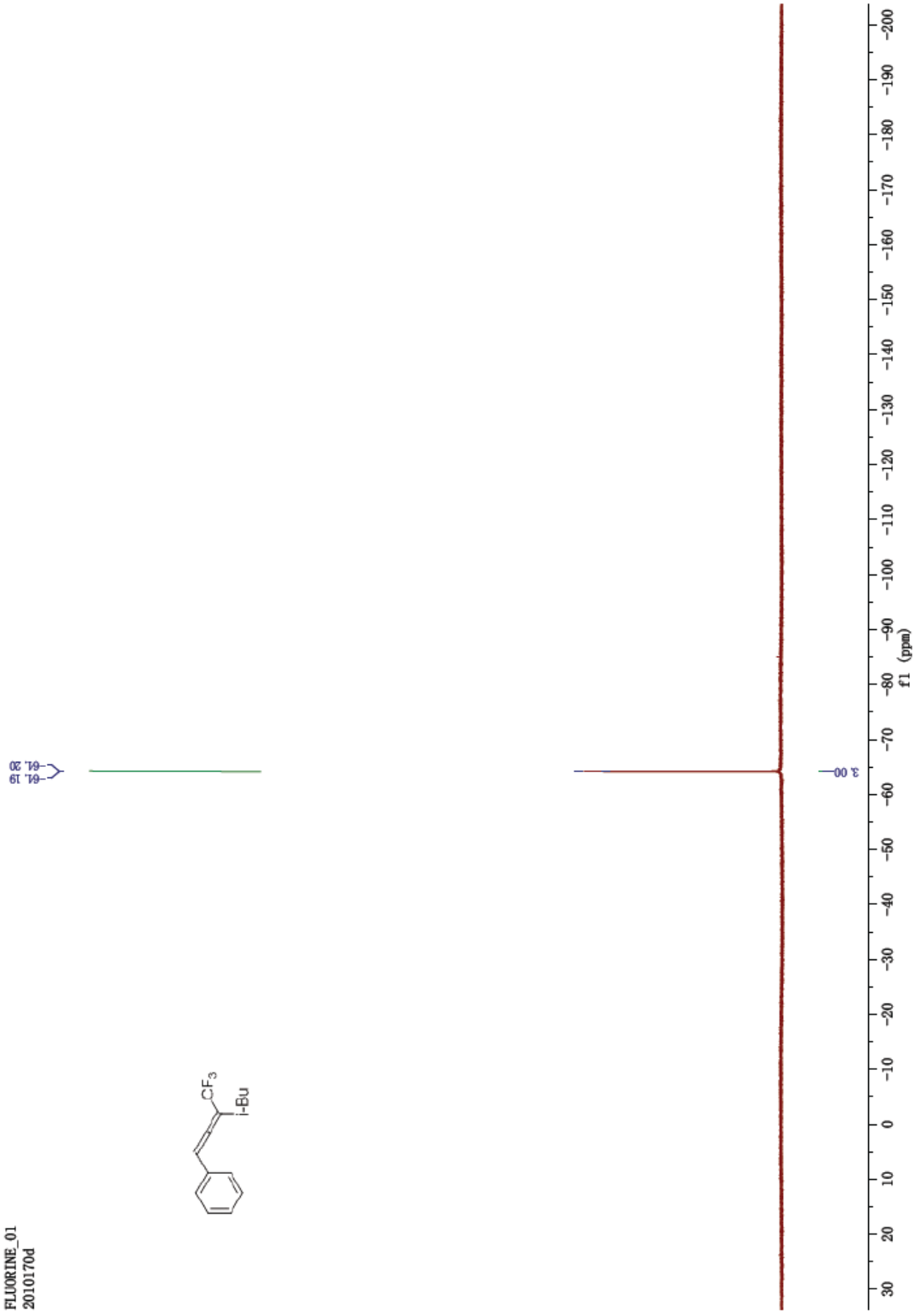
$^{13}C$ NMR spectrum of compound **3b**



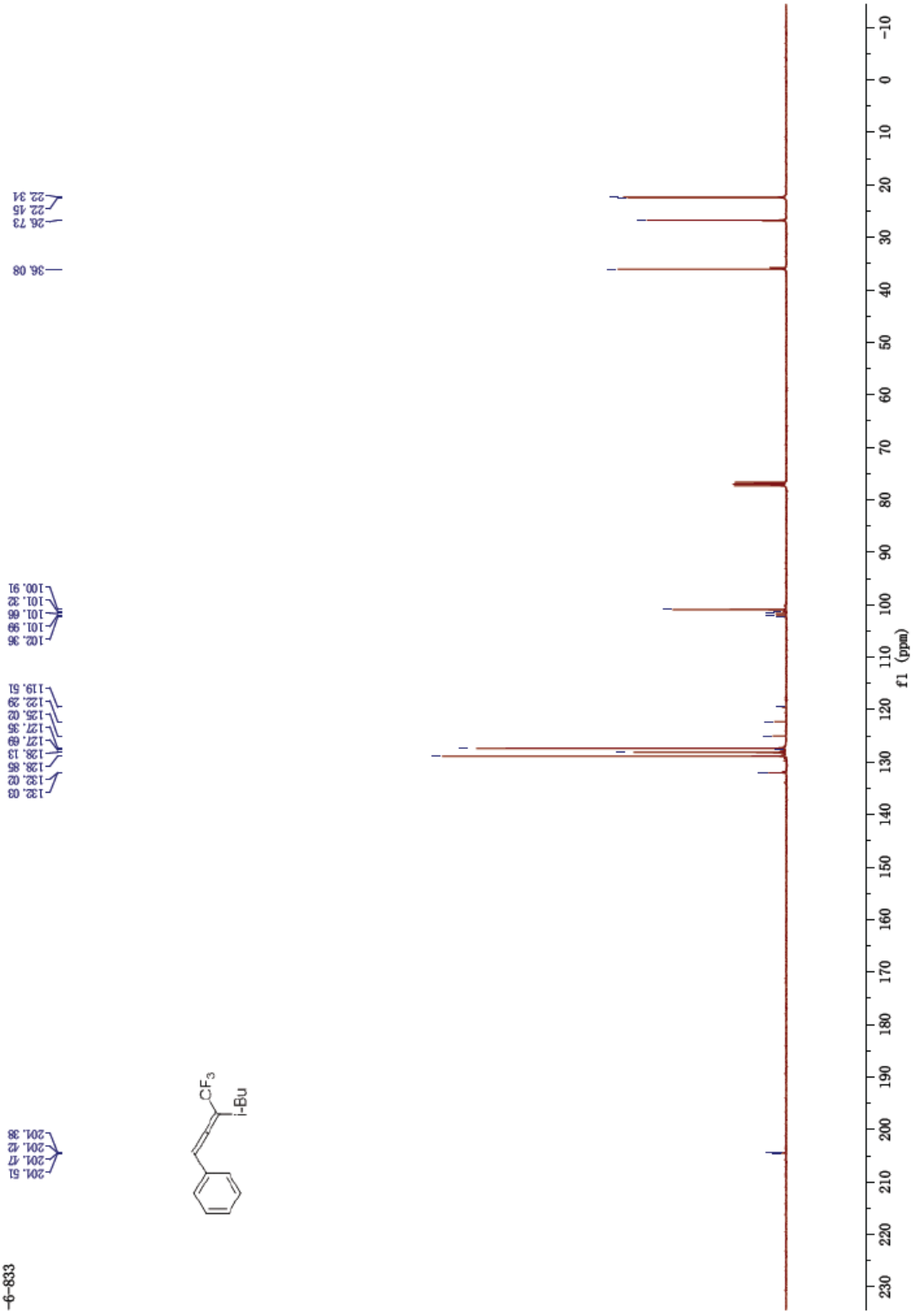
$^{1}$H NMR spectrum of compound **3c**



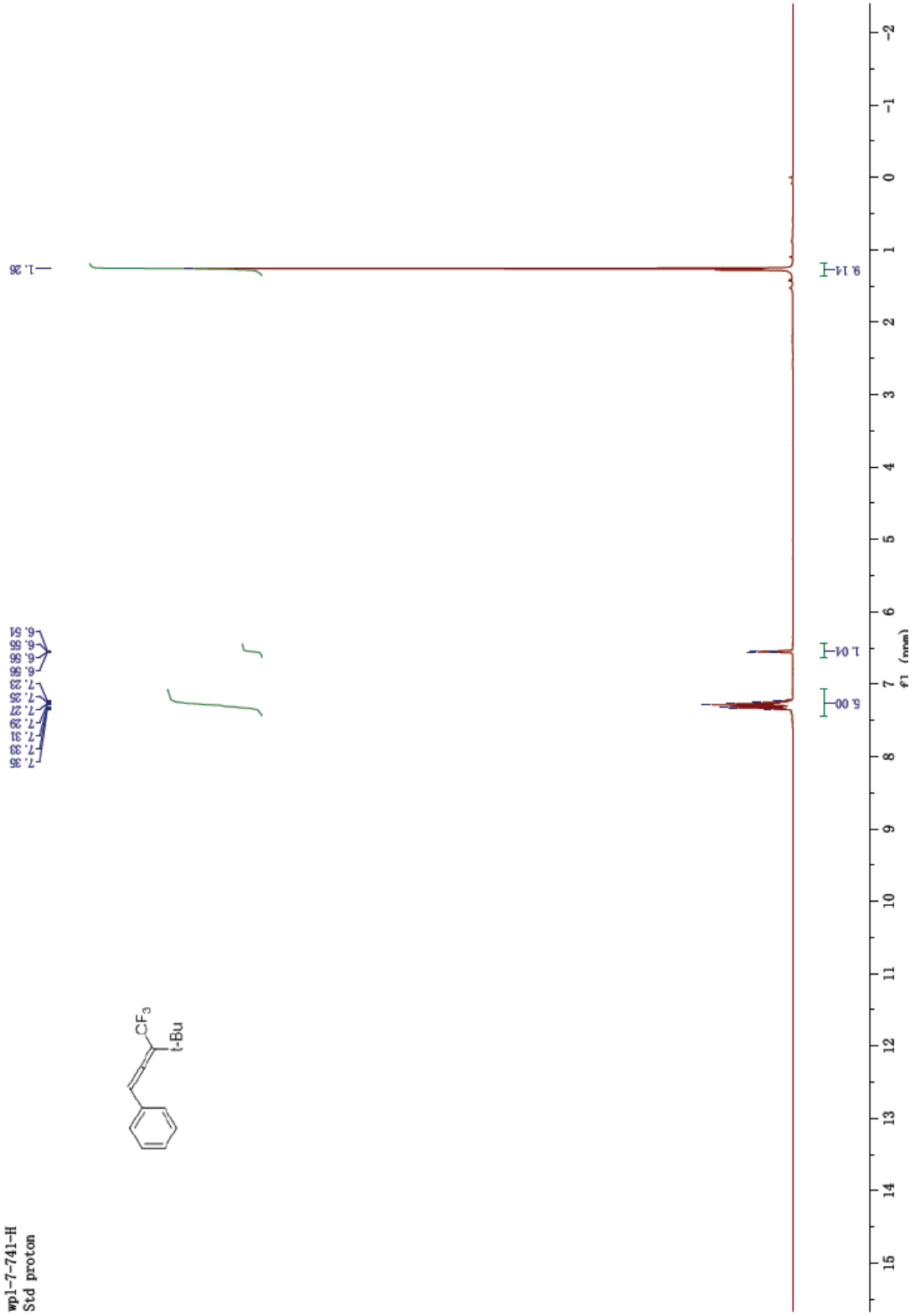
$^{19}F$ NMR spectrum of compound **3c**



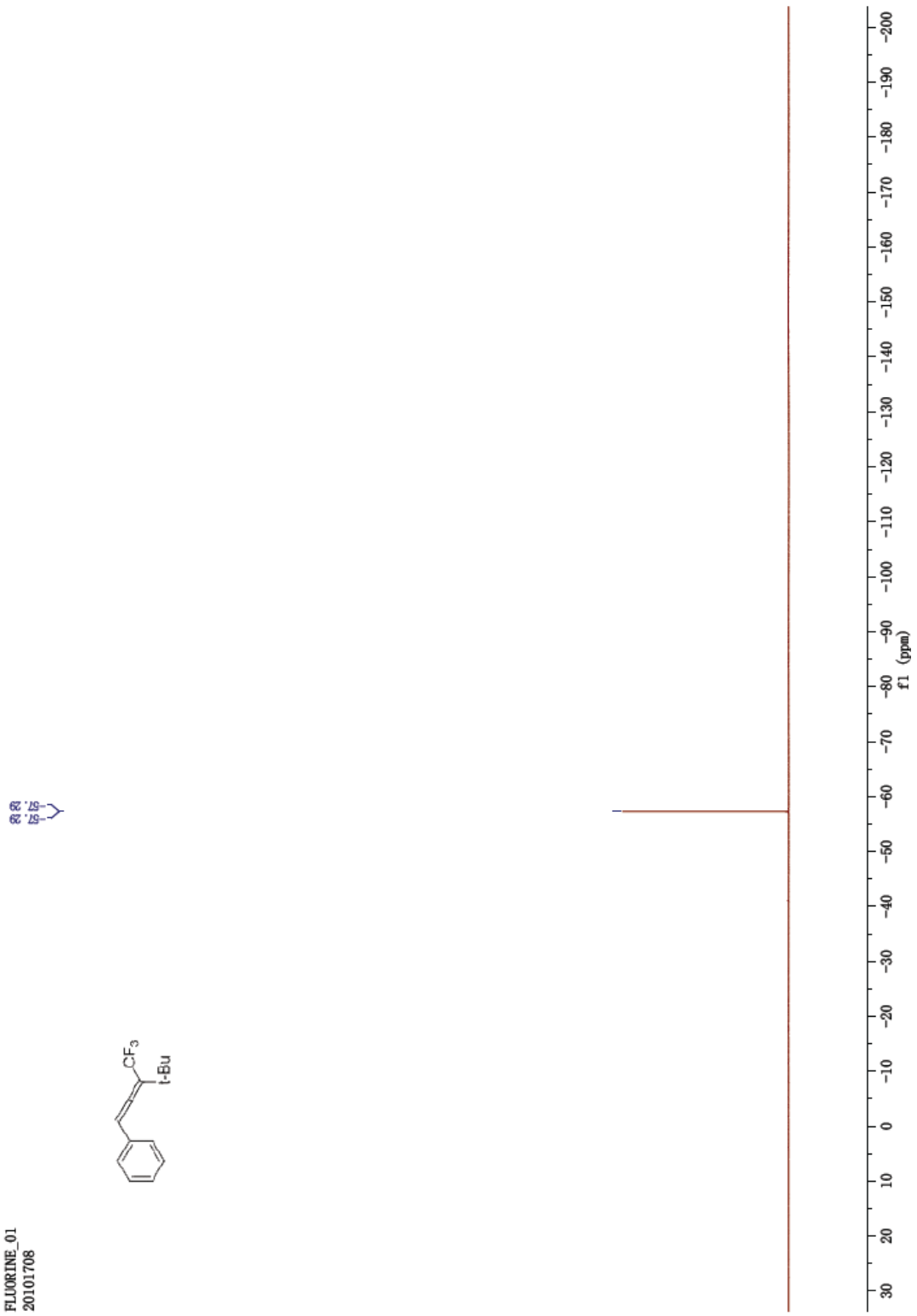
$^{13}$C NMR spectrum of compound **3c**



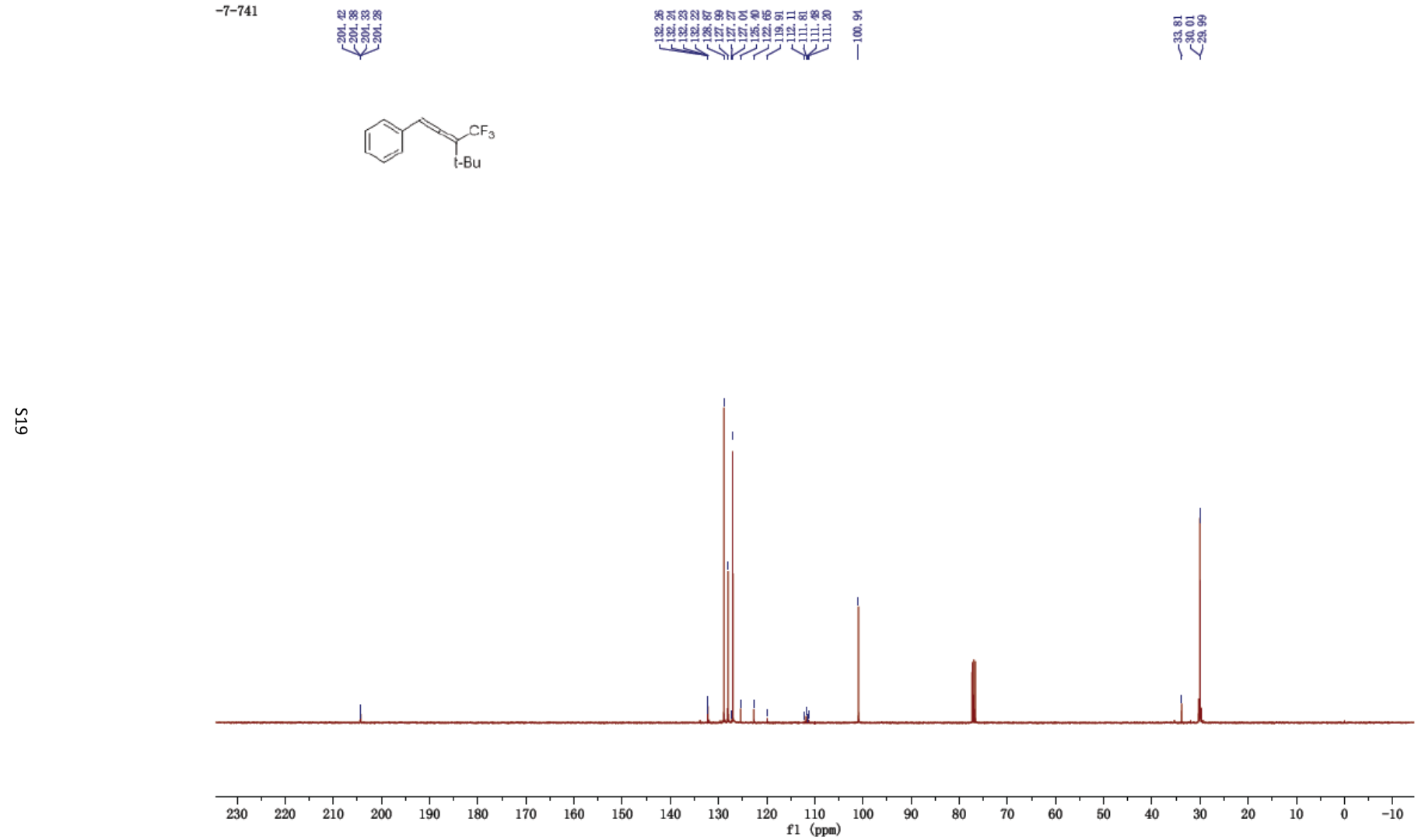
$^{1}$H NMR spectrum of compound **3d**



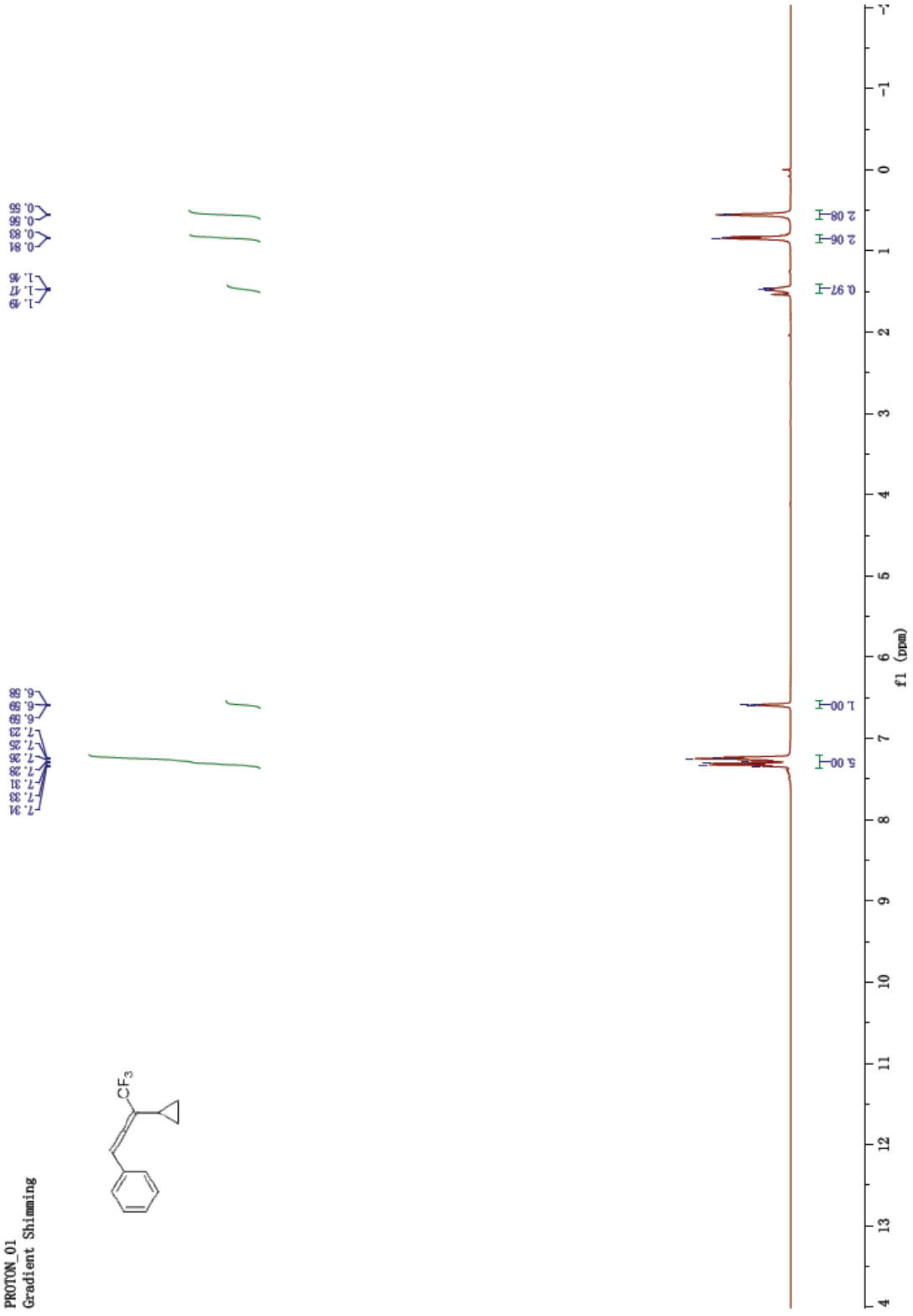

$^{19}F$ NMR spectrum of compound **3d**



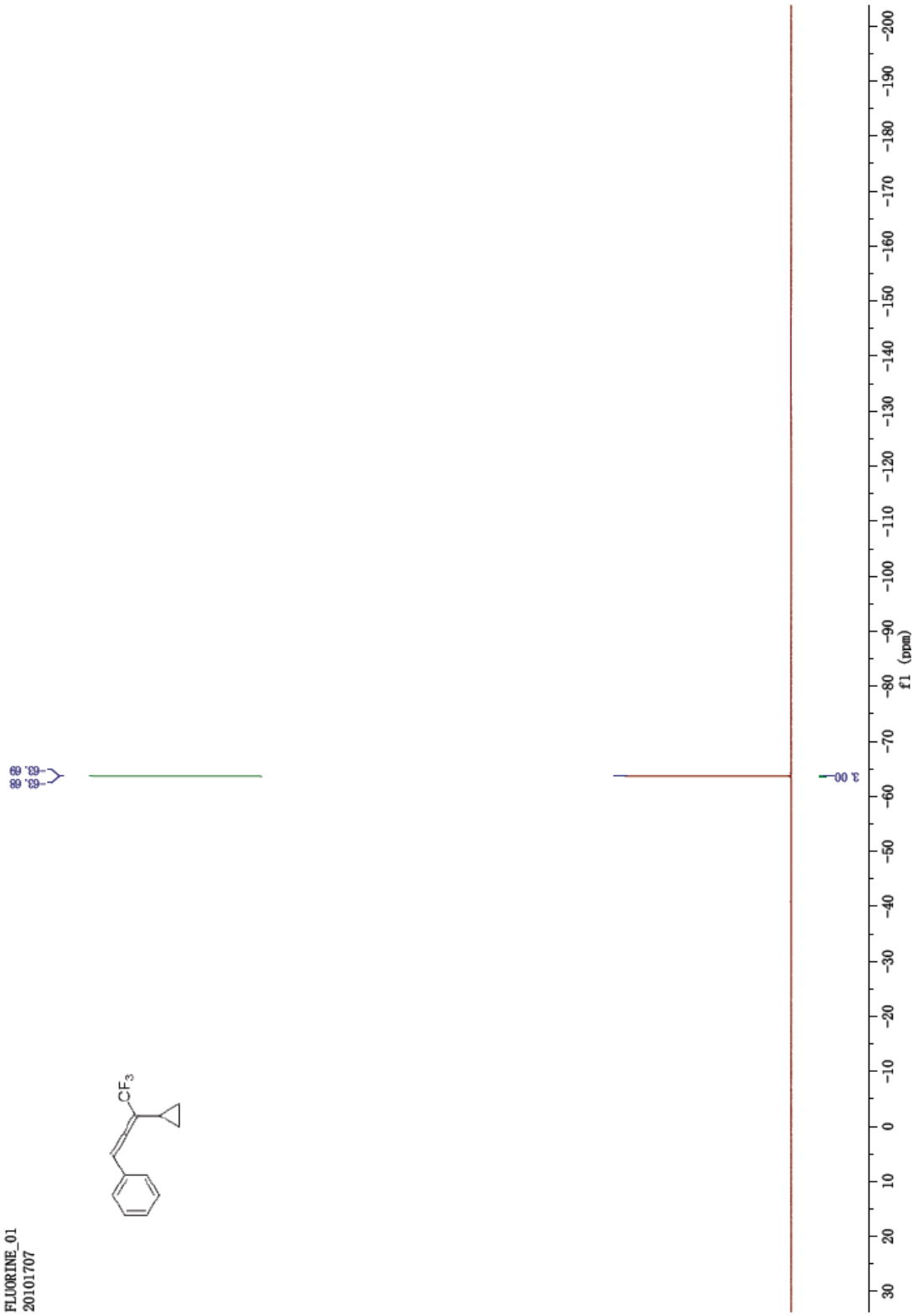

$^{13}$C NMR spectrum of compound **3d**


-7-741
204.42
204.38
204.33
204.28
132.26
132.24
132.23
132.22
128.67
127.99
127.27
127.01
125.40
122.65
119.91
112.11
111.81
111.49
111.20
100.94
33.81
30.01
29.99
CF3
t-Bu
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

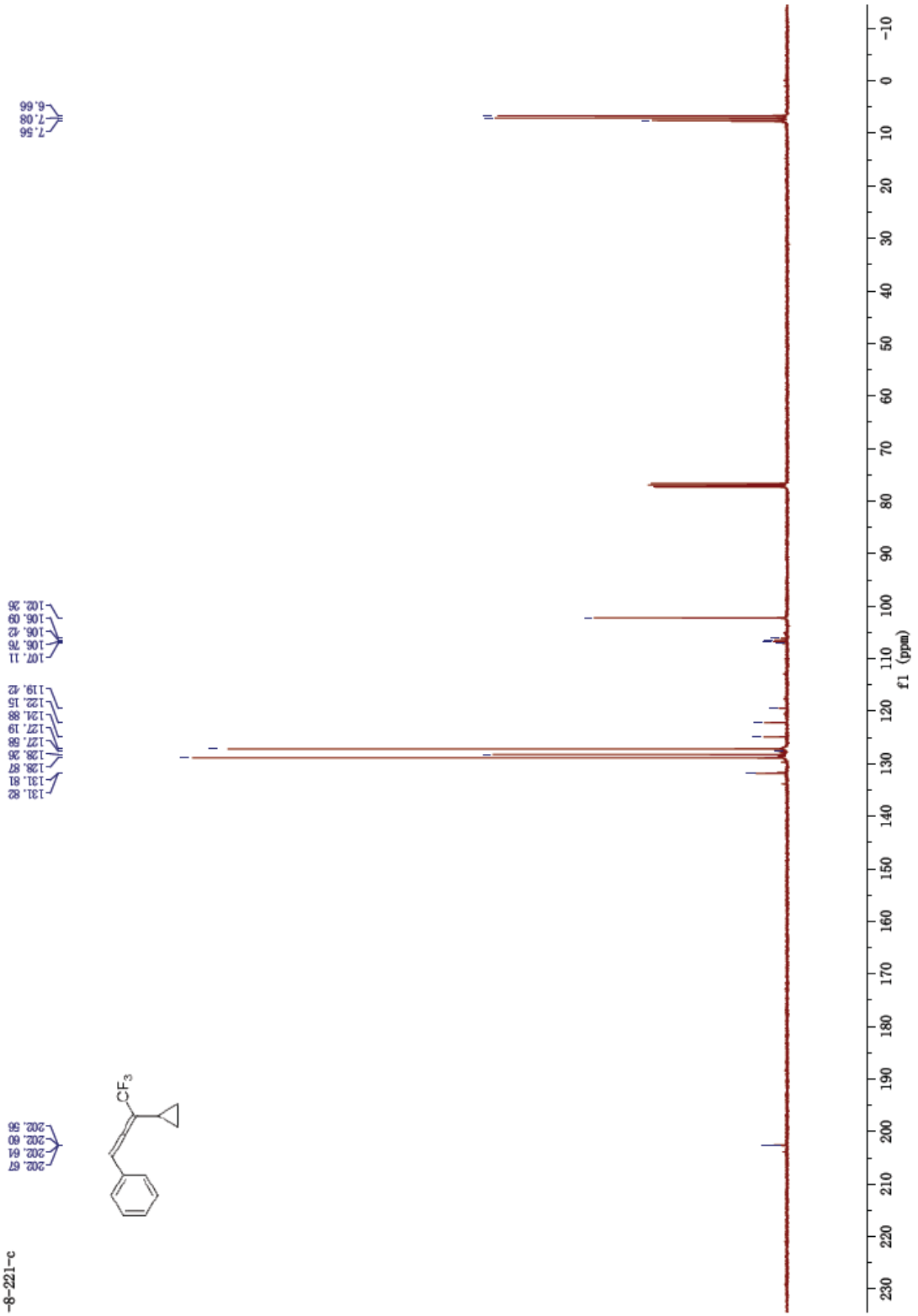
$^{1}$H NMR spectrum of compound **3e**



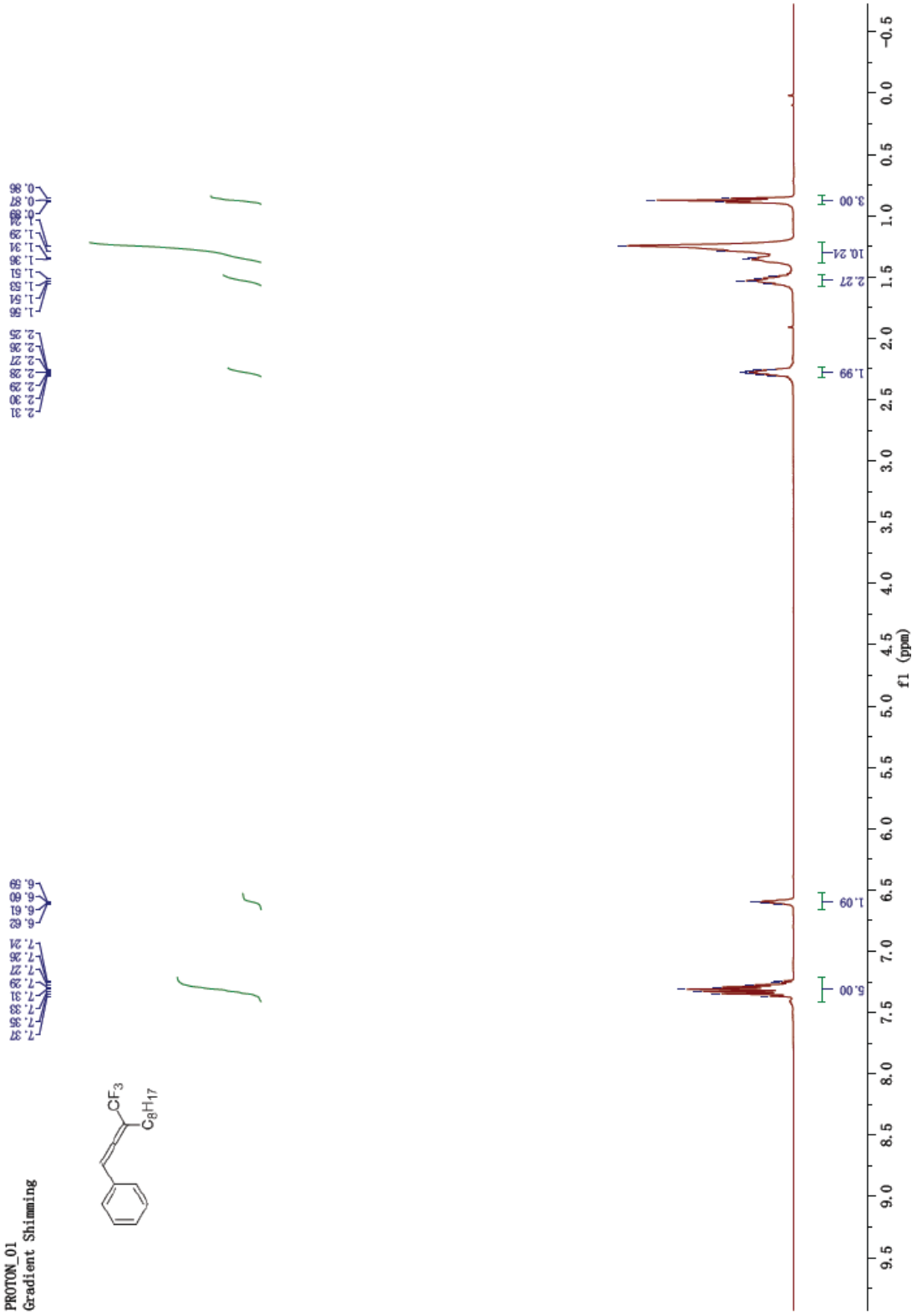
$^{19}F$ NMR spectrum of compound **3e**



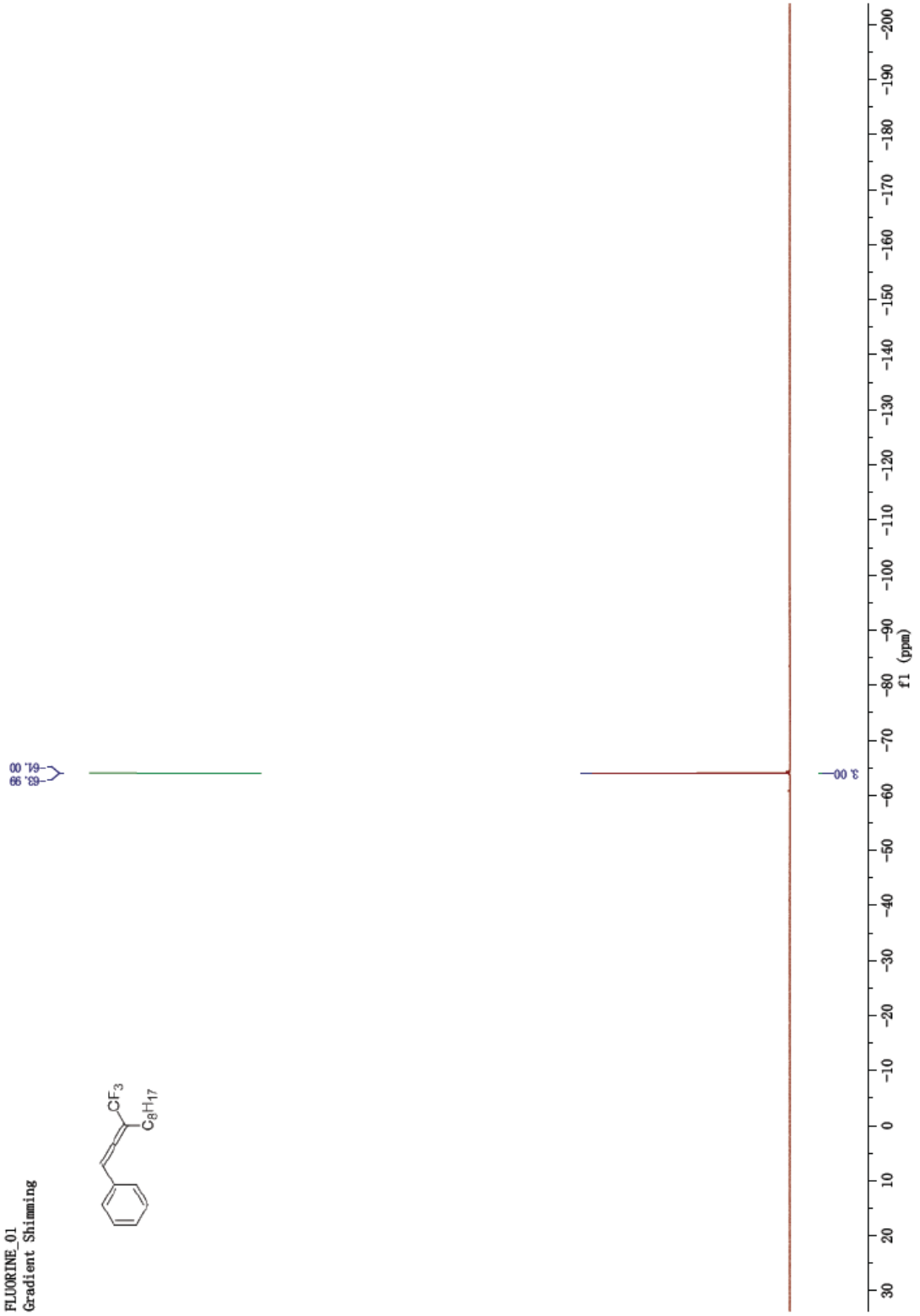
$^{13}C$ NMR spectrum of compound **3e**



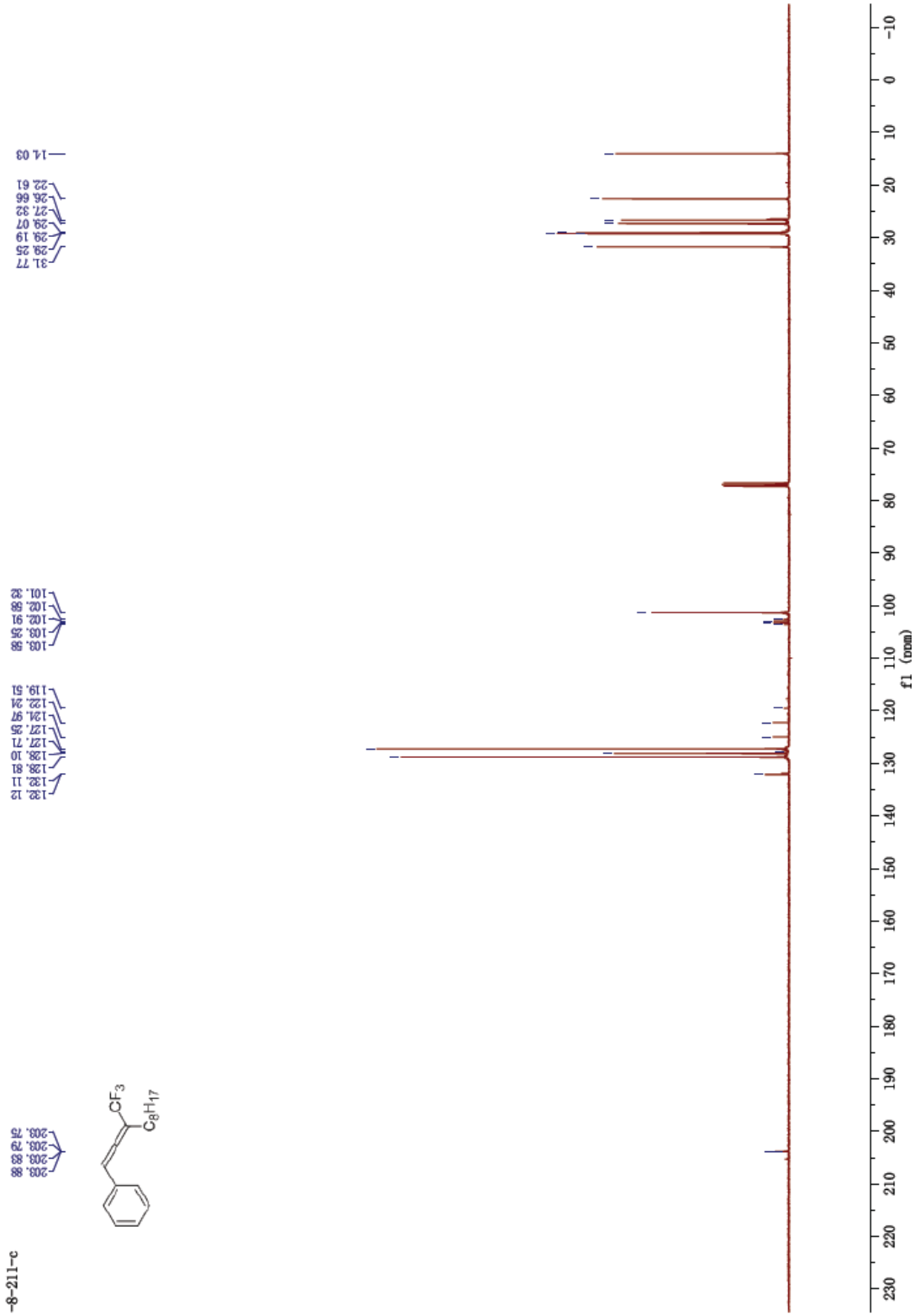
$^{1}$H NMR spectrum of compound **3f**



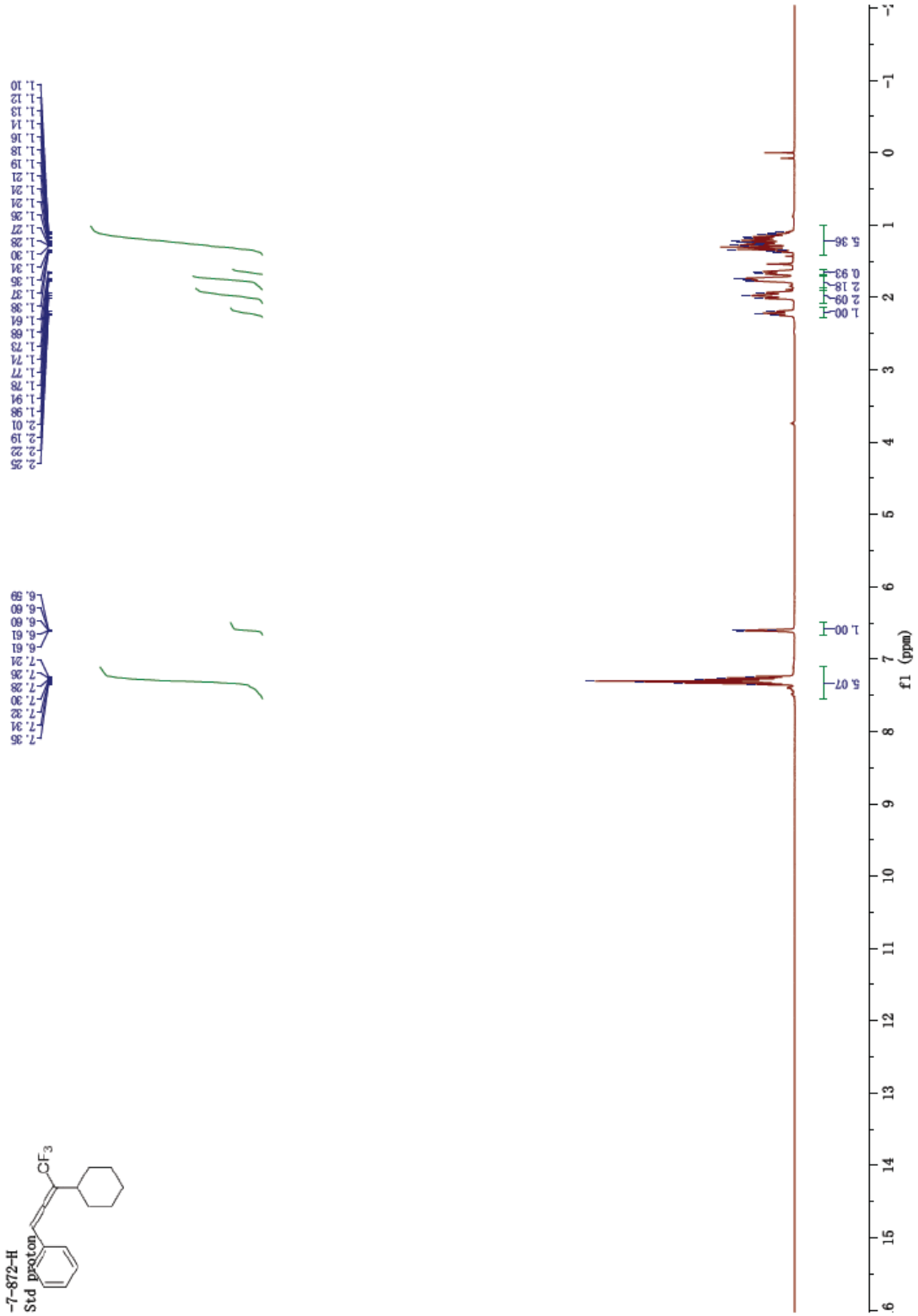
$^{19}F$ NMR spectrum of compound **3f**



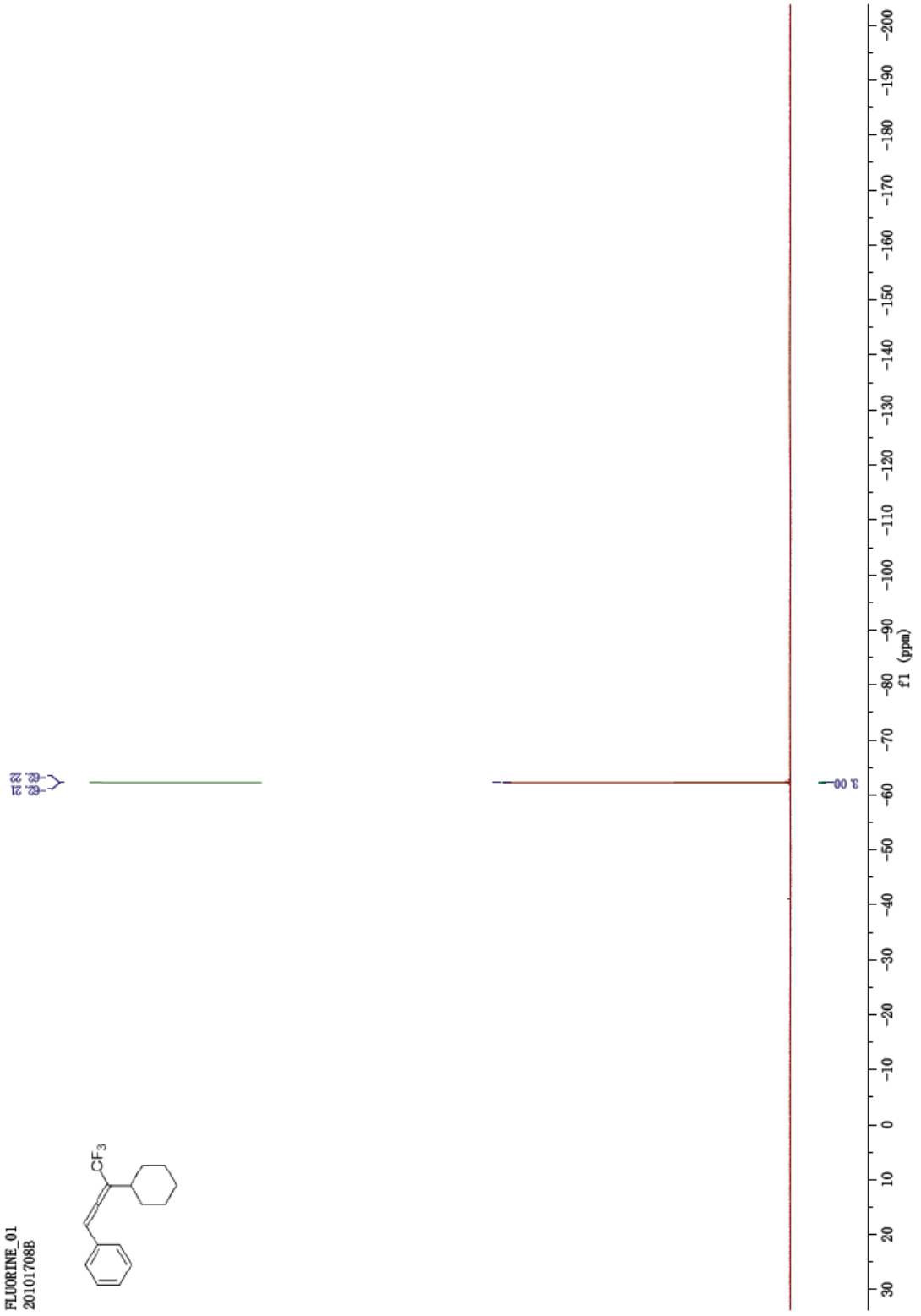
$^{13}C$ NMR spectrum of compound **3f**



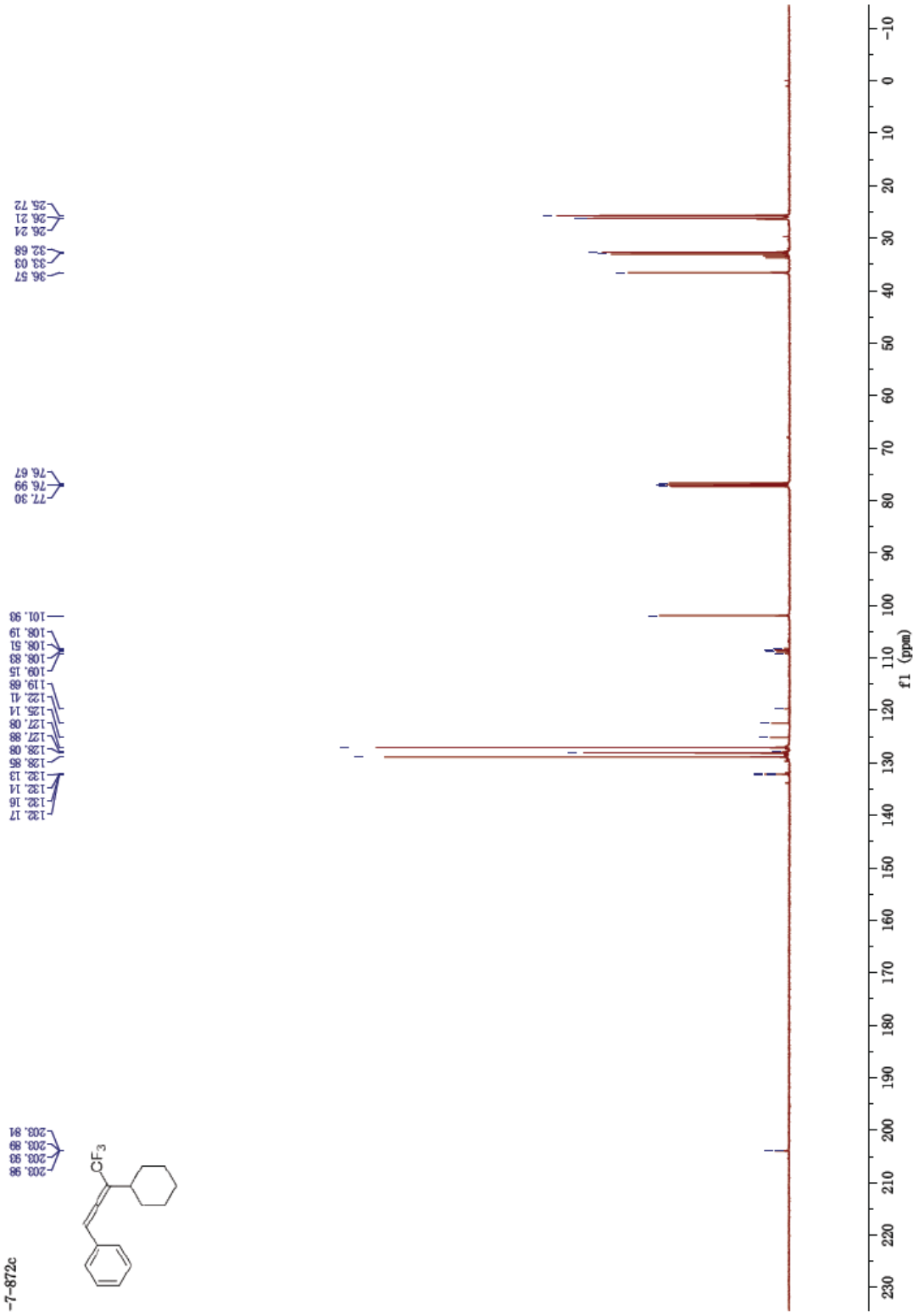
$^{1}$H NMR spectrum of compound **3g**



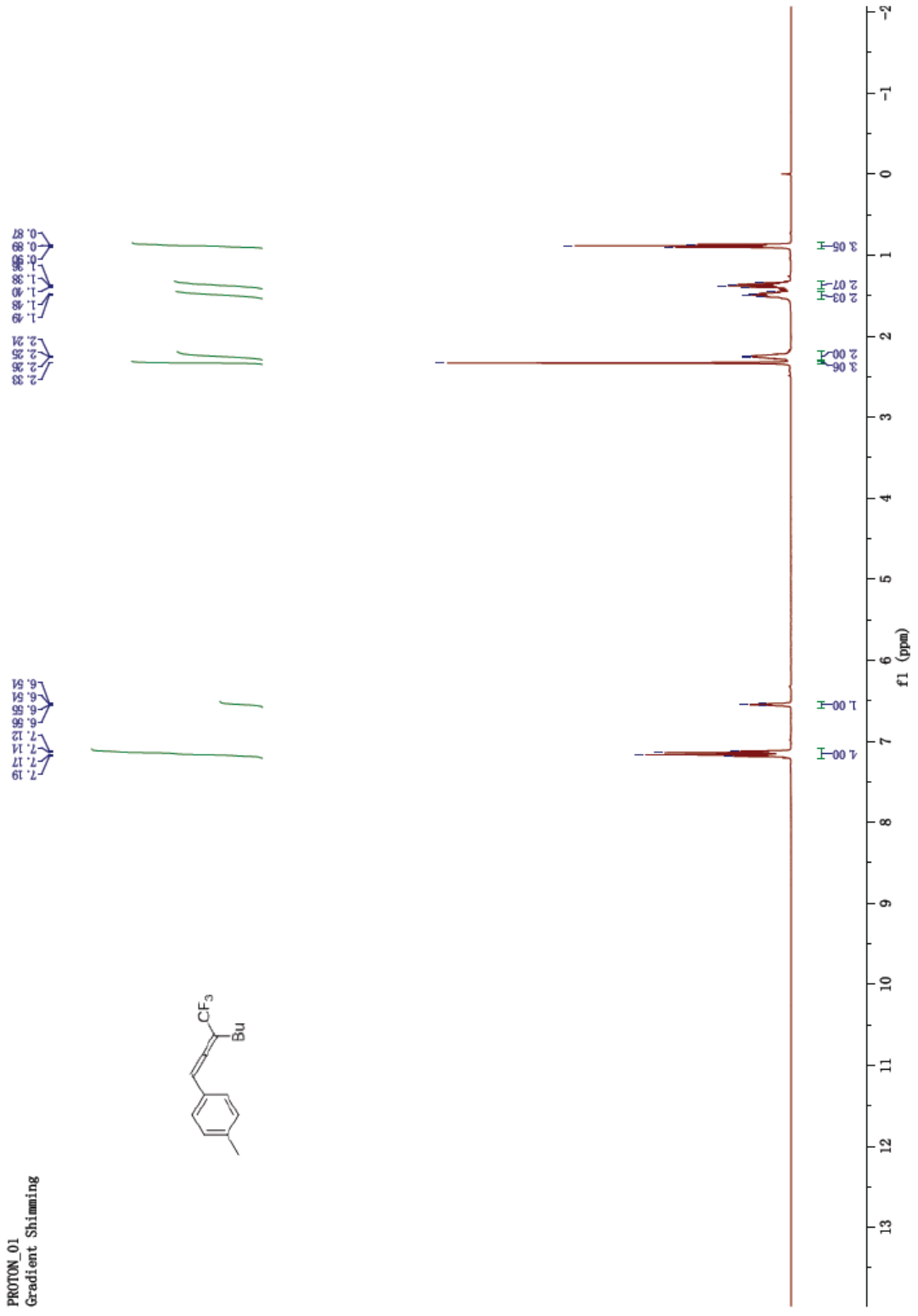
$^{19}F$ NMR spectrum of compound **3g**



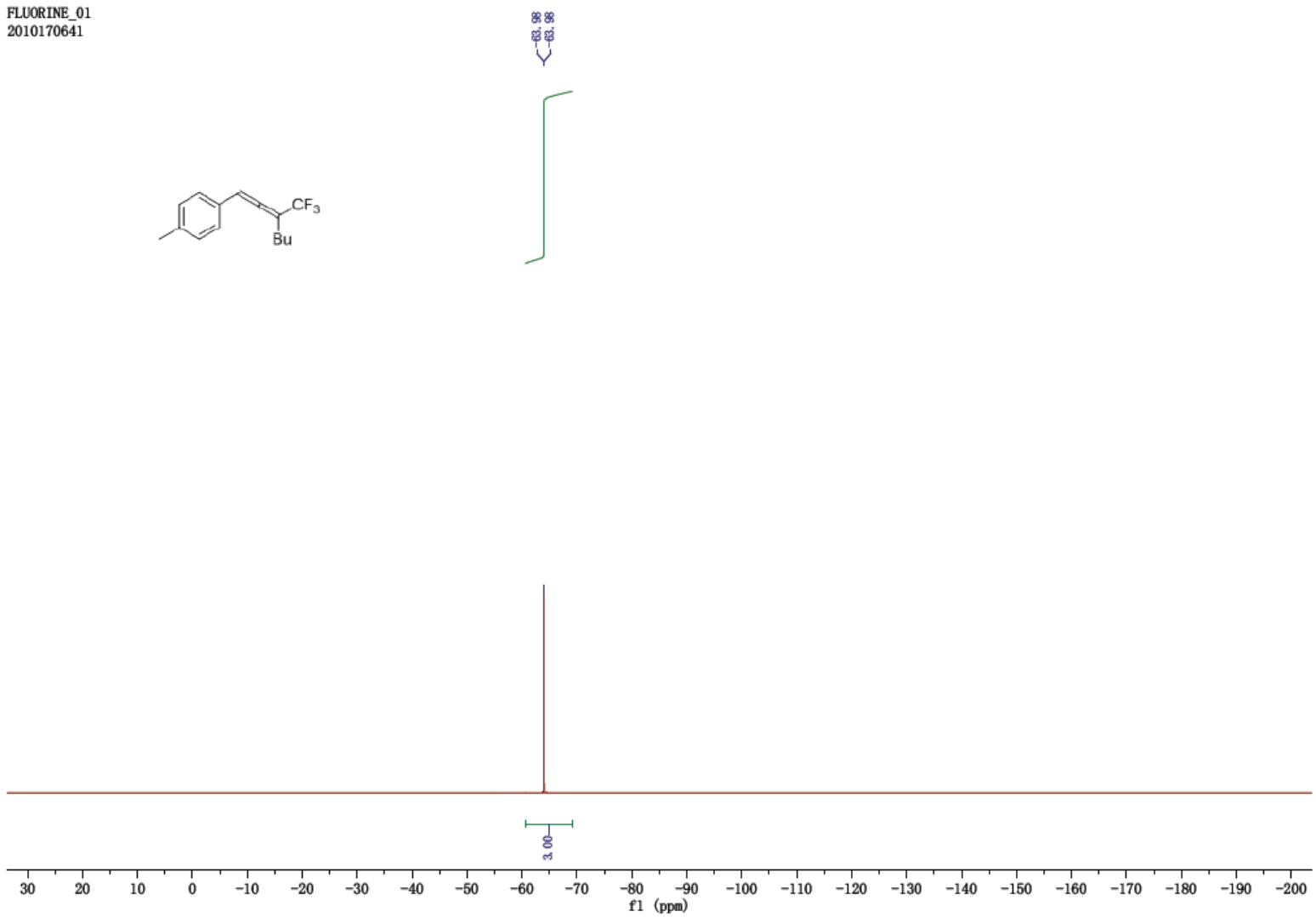
$^{13}C$ NMR spectrum of compound **3g**



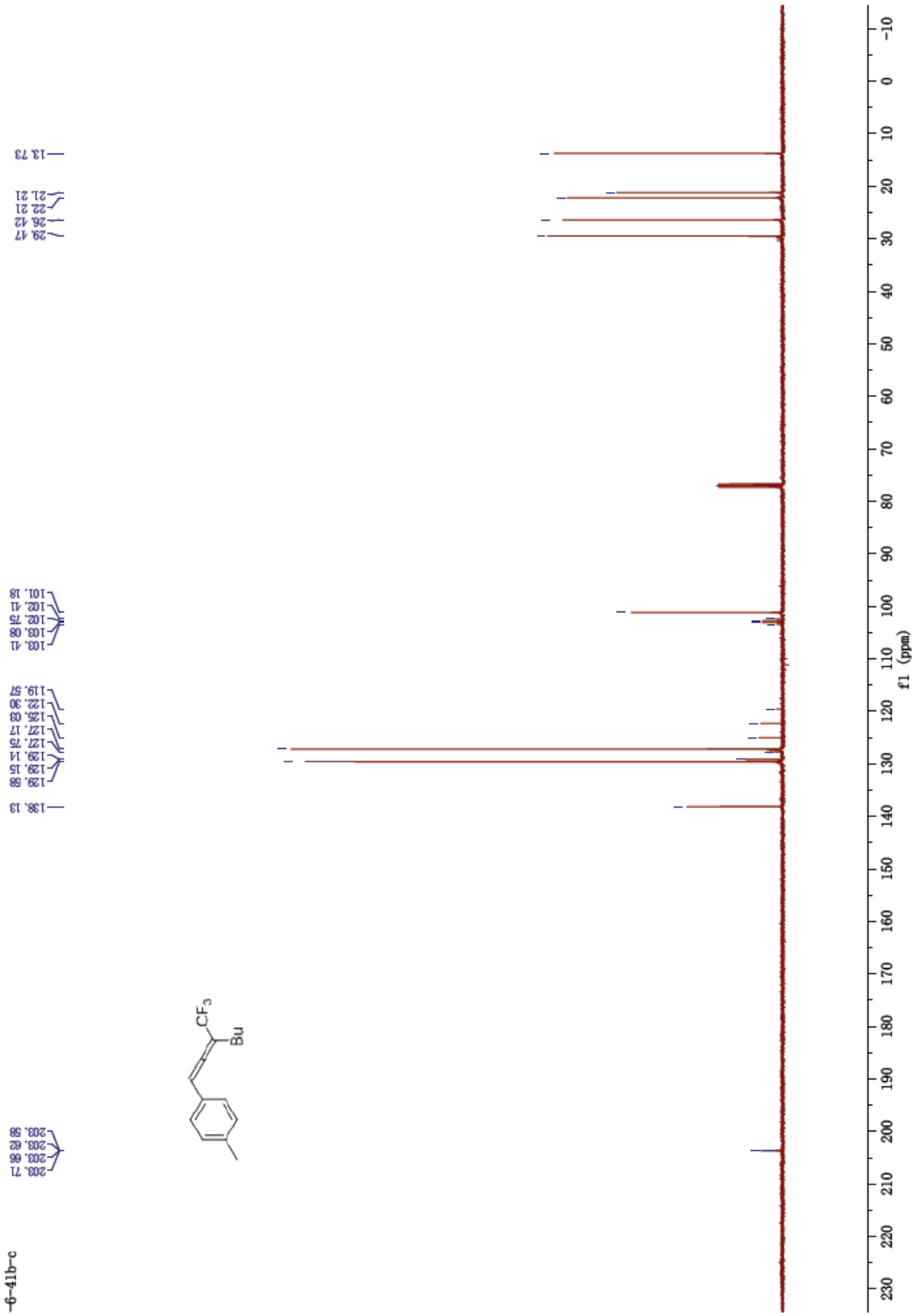
$^1$H NMR spectrum of compound **3h**



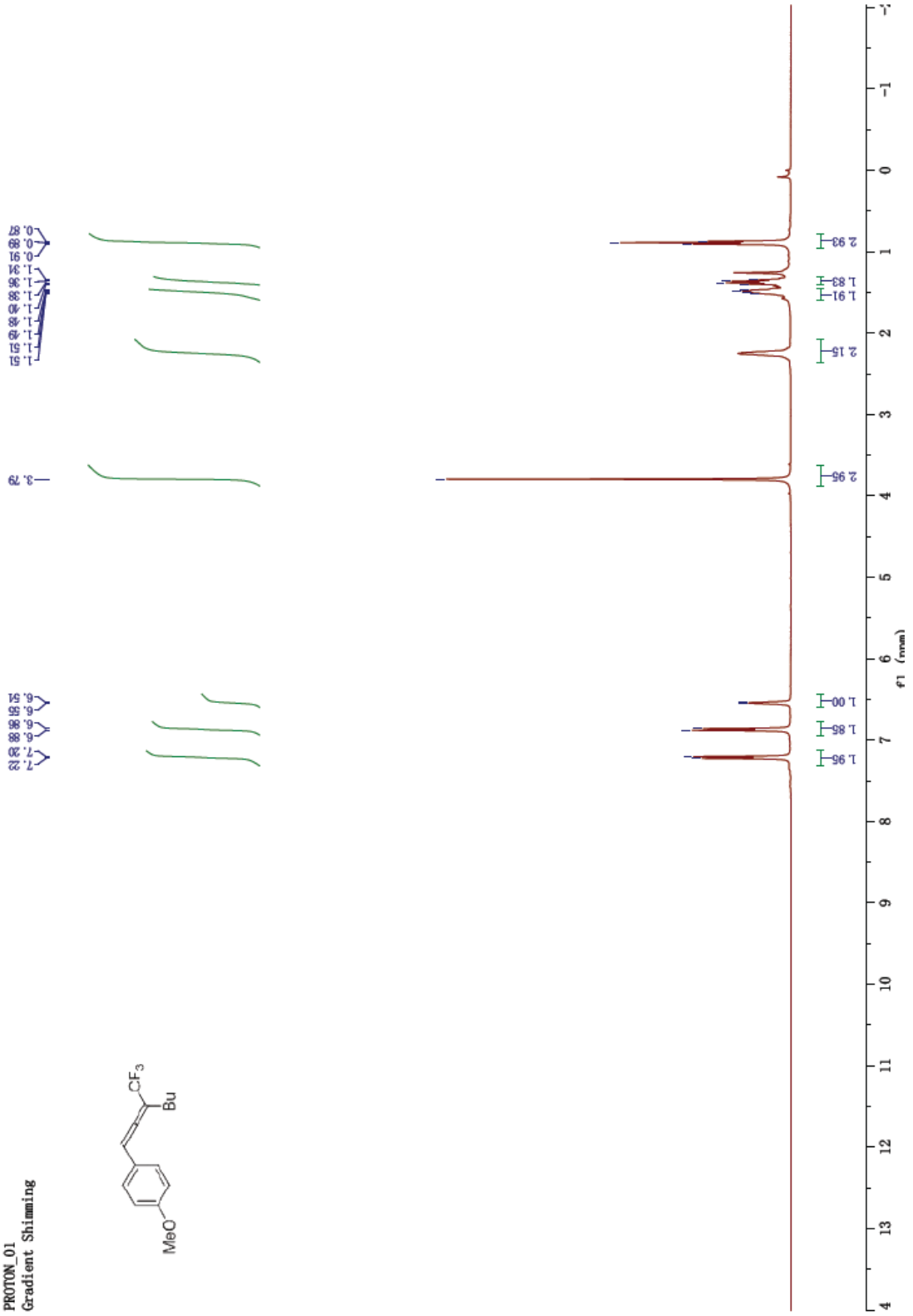
$^{19}$F NMR spectrum of compound **3h**


FLUORINE_01
2010170641
-63.98
-63.98
CF3
Bu
3.00
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

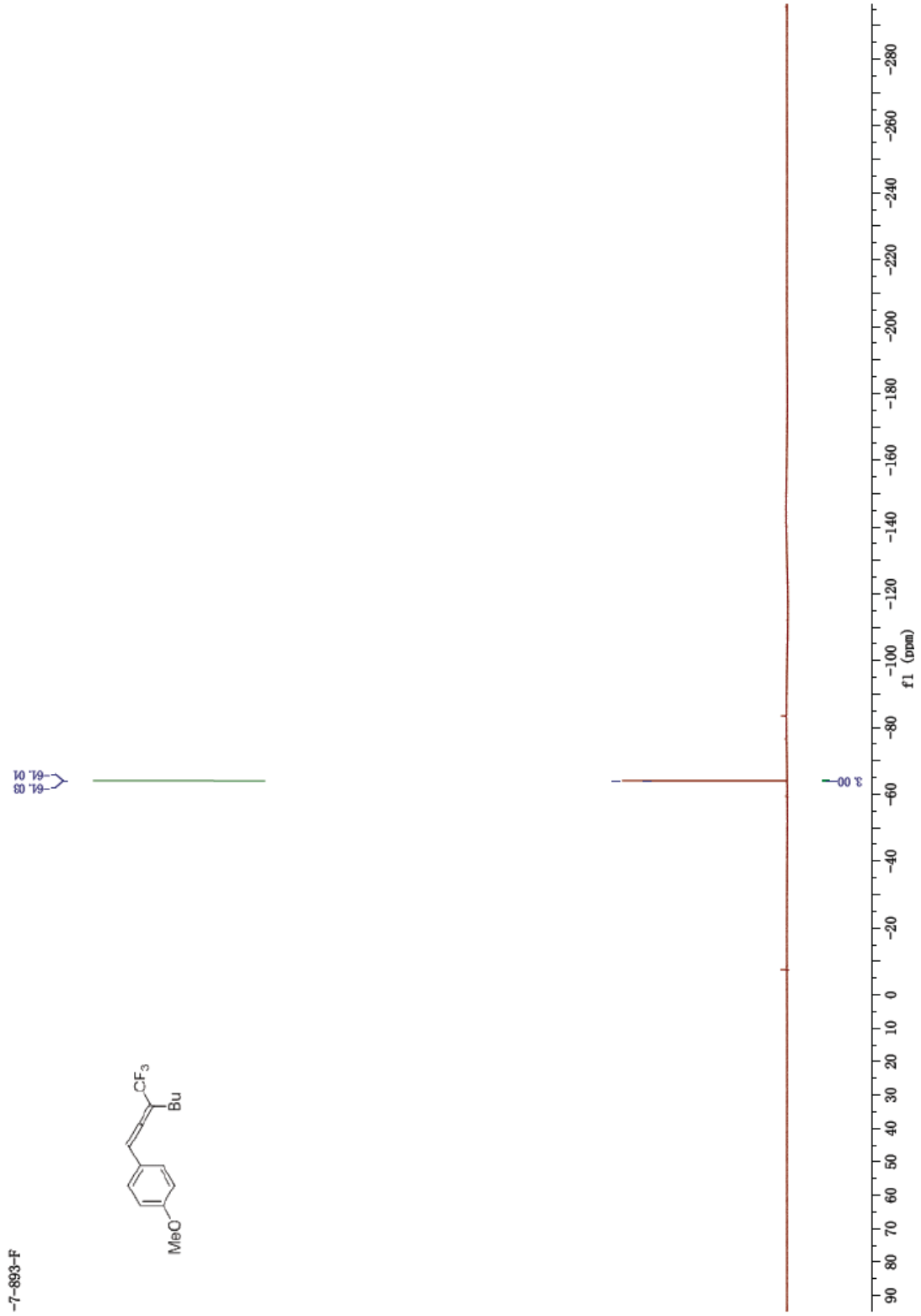
$^{13}C$ NMR spectrum of compound **3h**



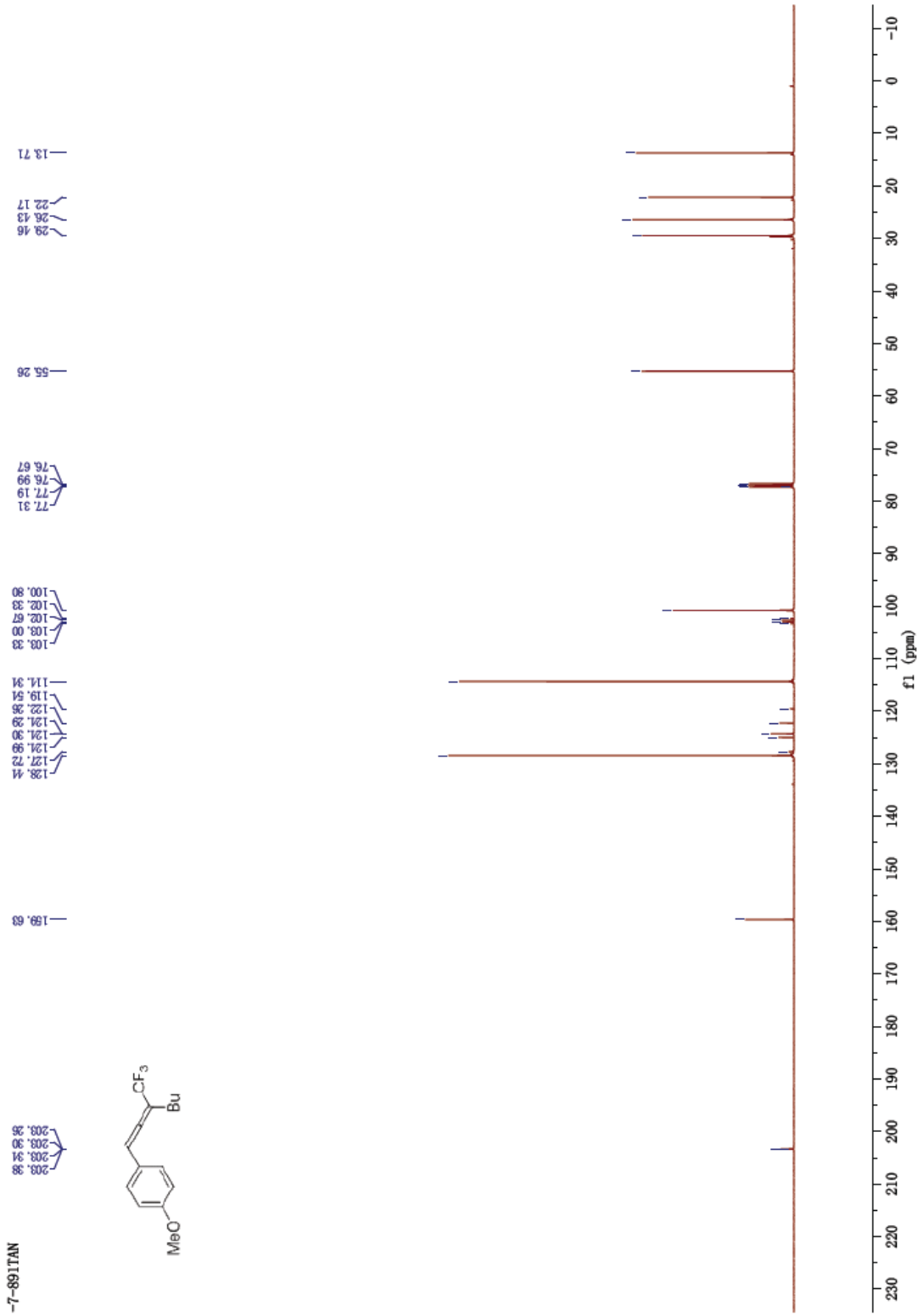
$^{1}$H NMR spectrum of compound **3i**



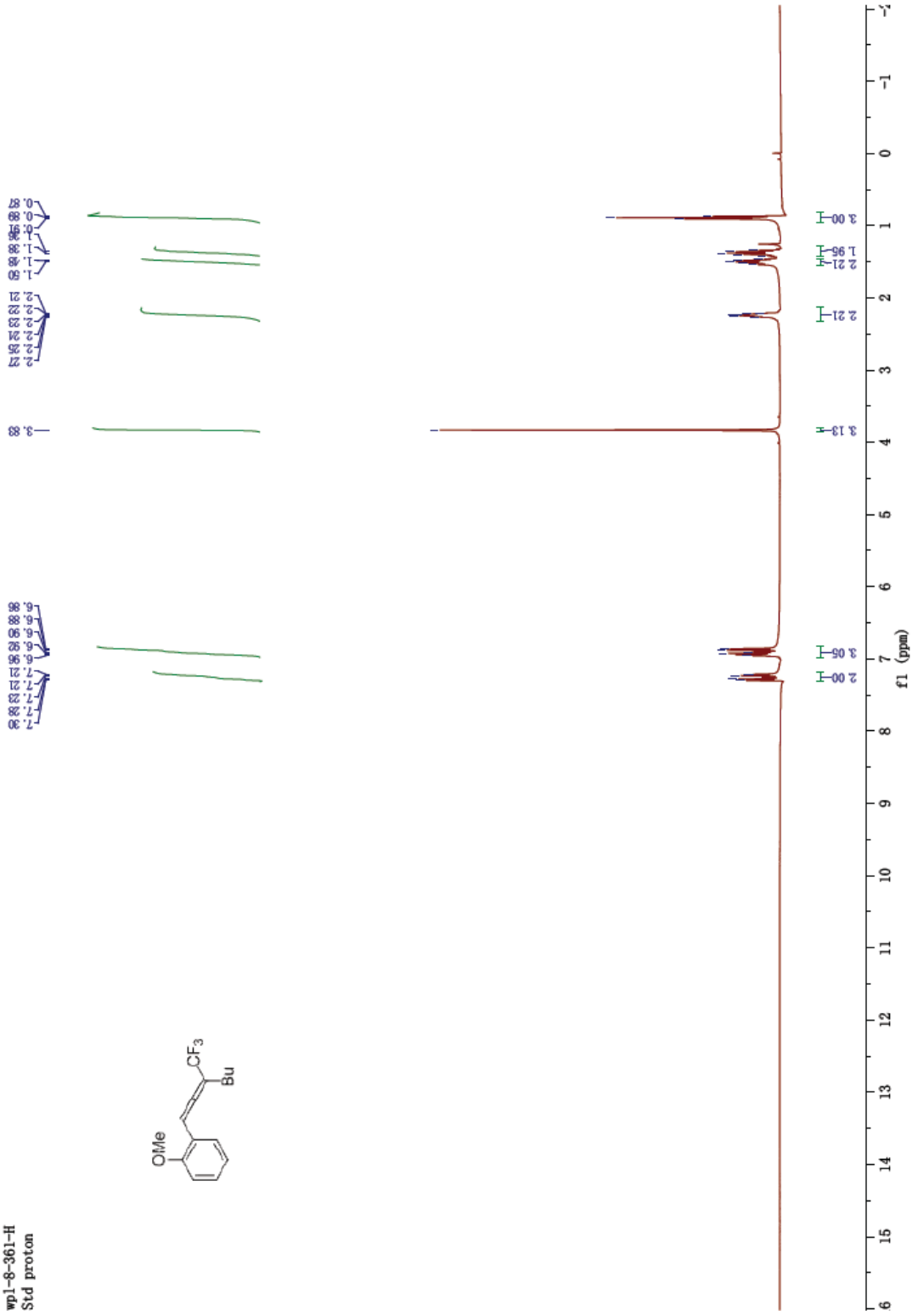
$^{19}F$ NMR spectrum of compound **3i**



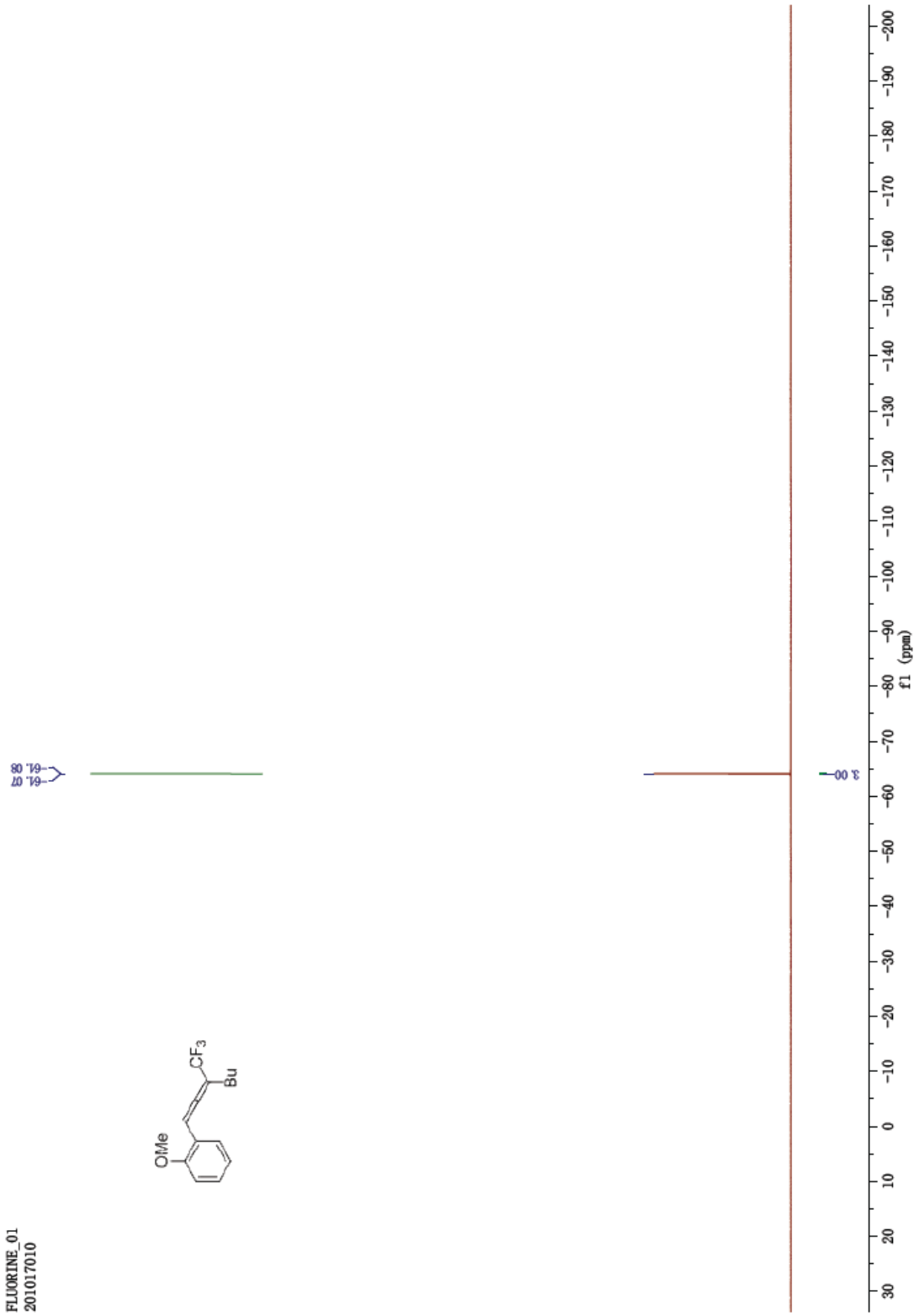
$^{13}C$ NMR spectrum of compound **3i**



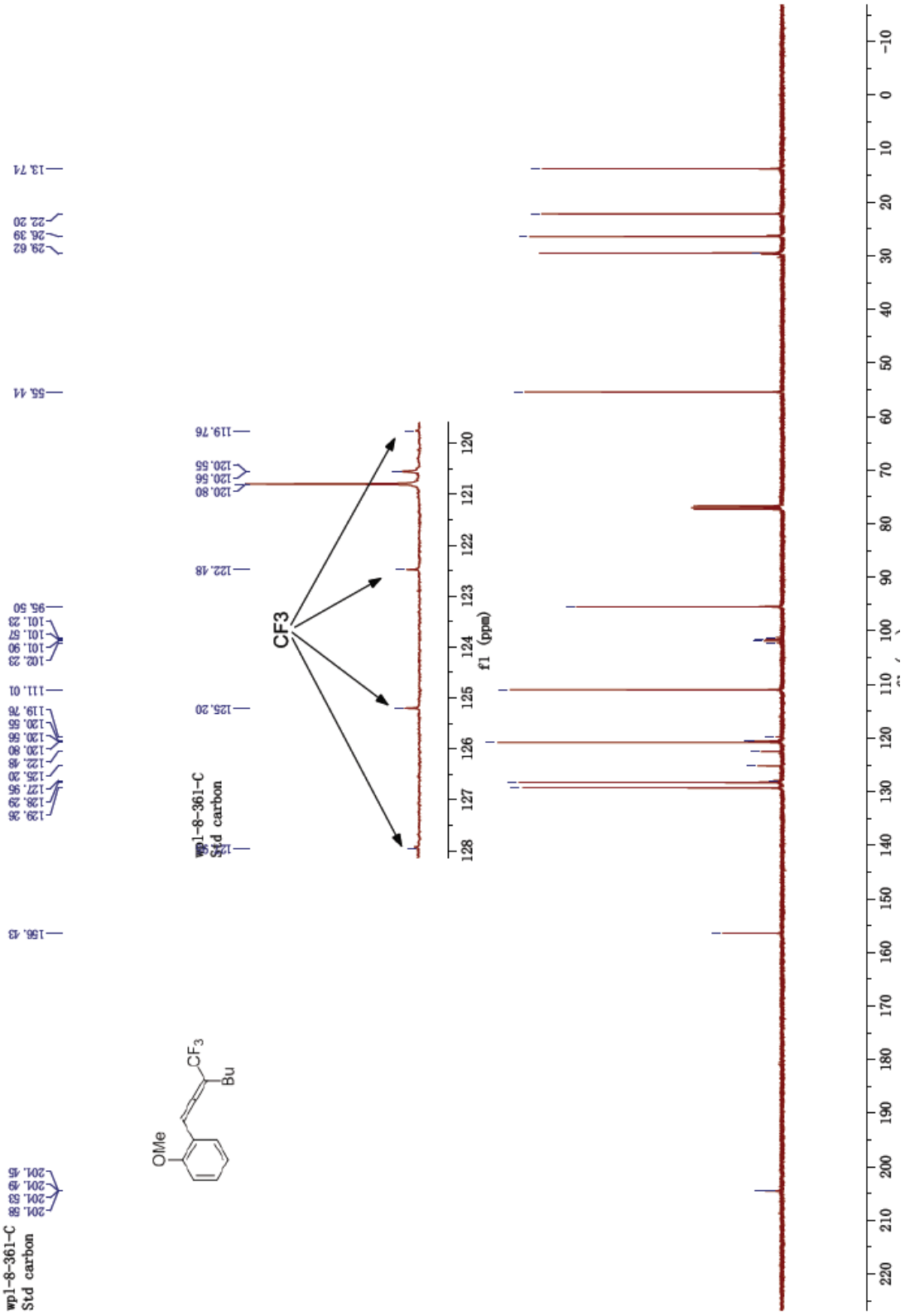
$^{1}$H NMR spectrum of compound **3j**



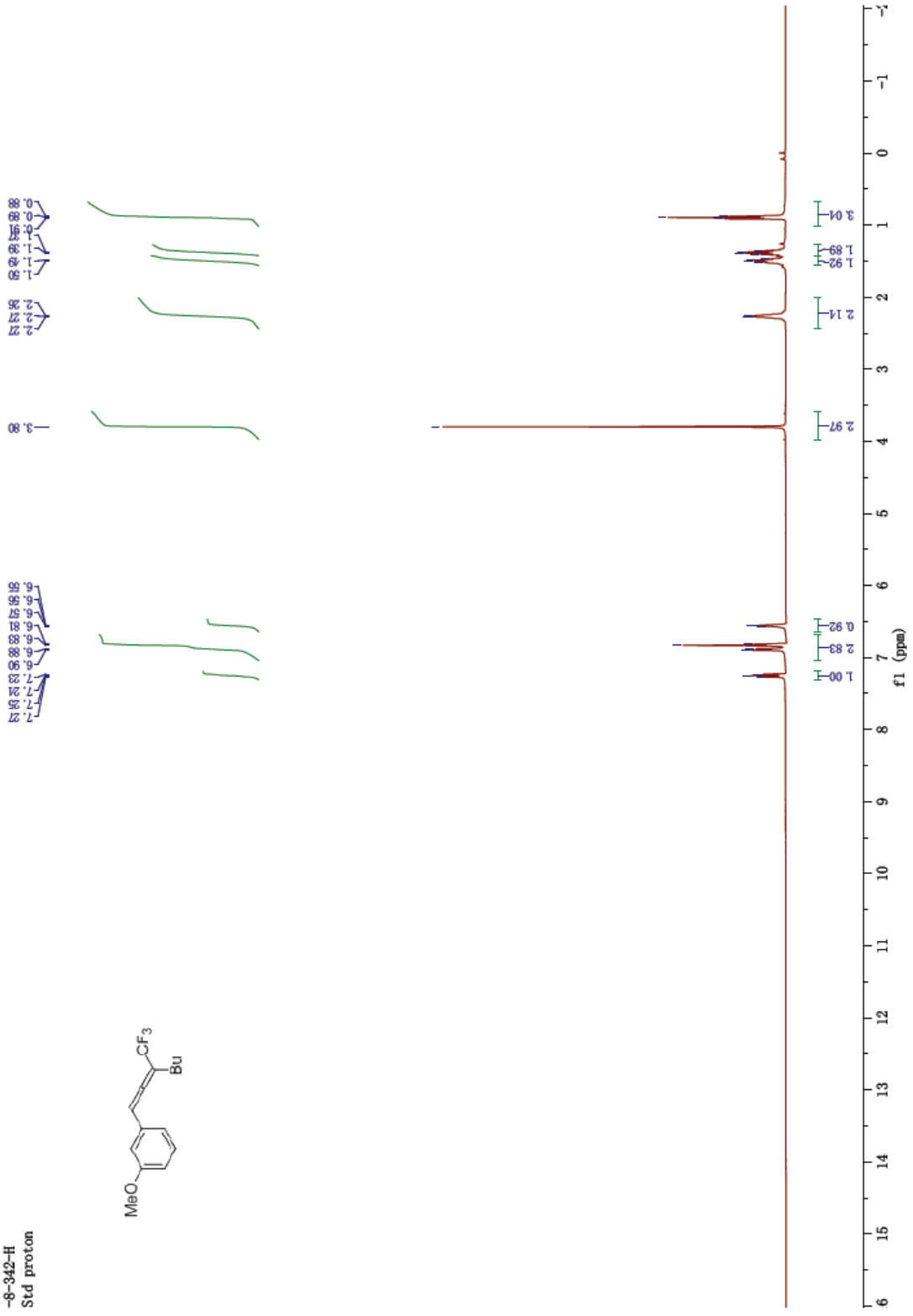
$^{19}F$ NMR spectrum of compound **3j**



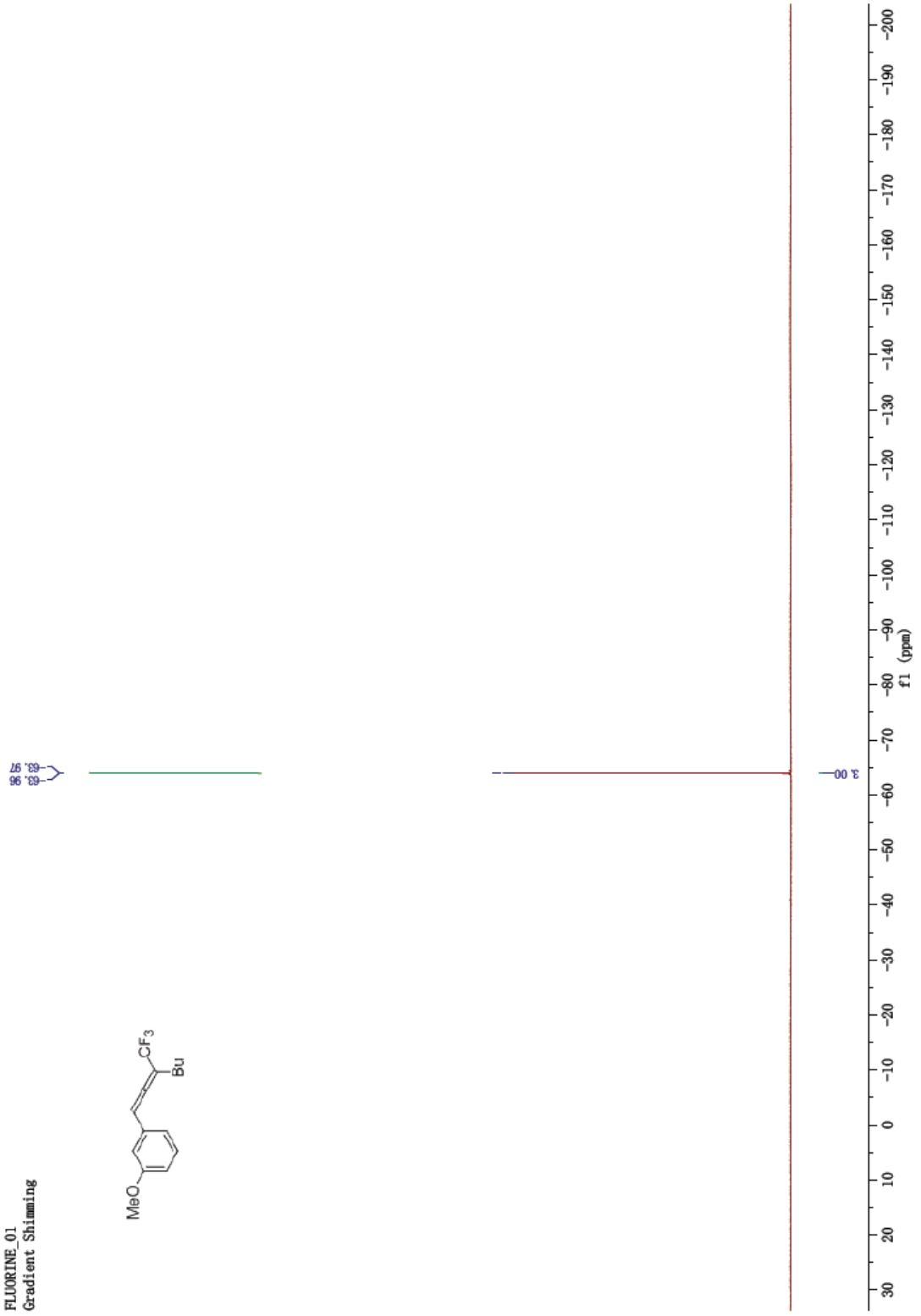
$^{13}$C NMR spectrum of compound **3j**



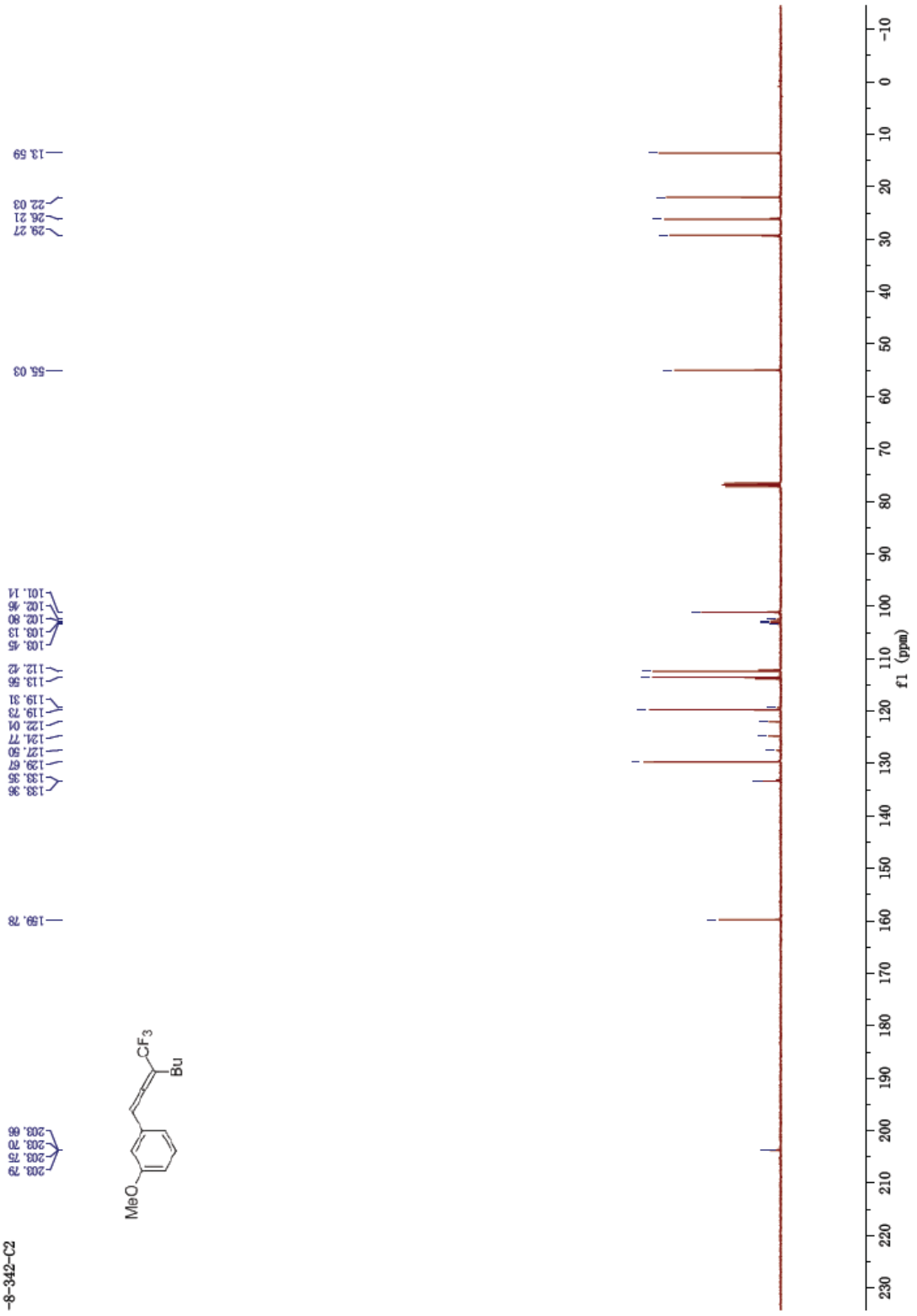
$^{1}$H NMR spectrum of compound **3k**



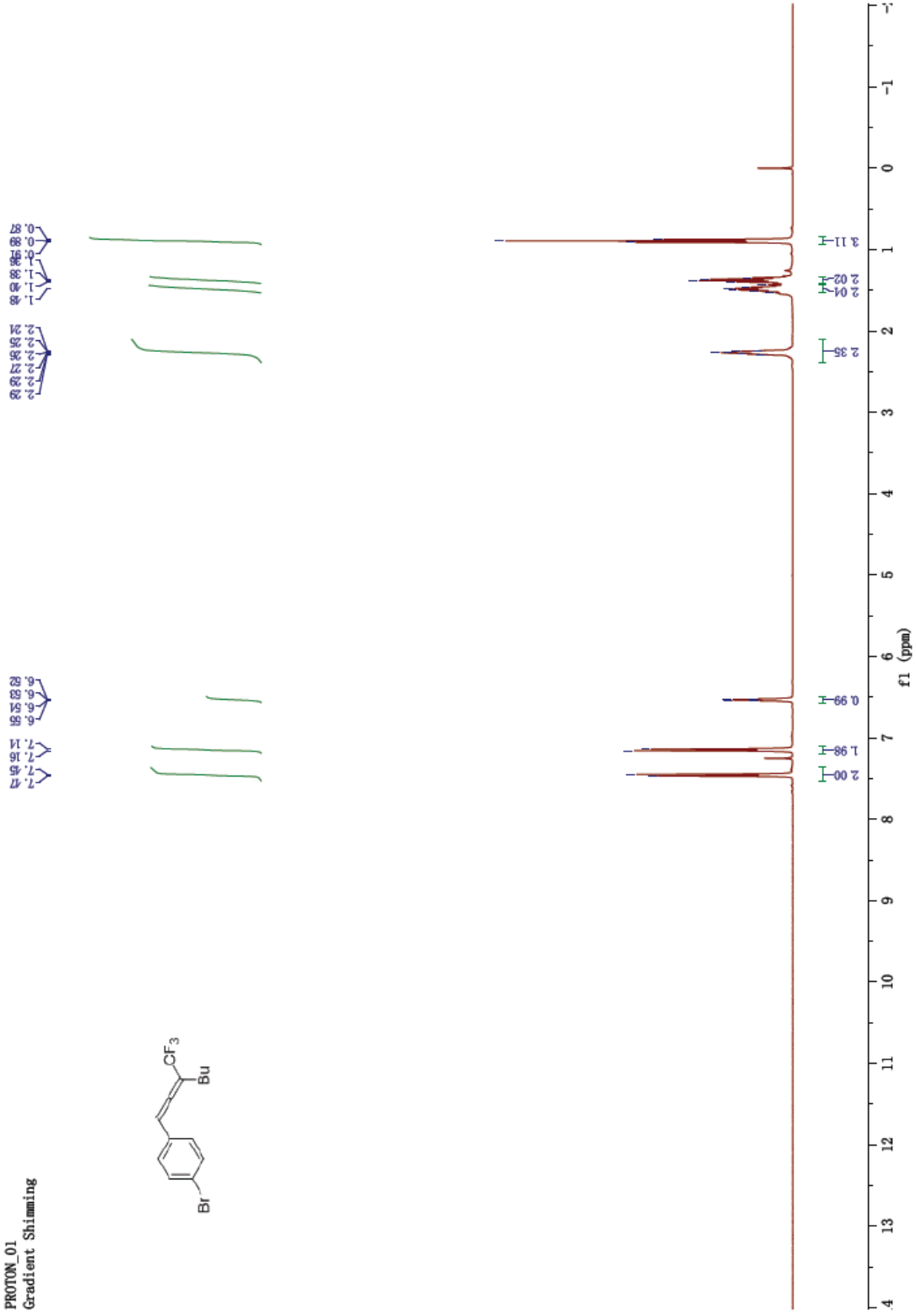
$^{19}F$ NMR spectrum of compound **3k**



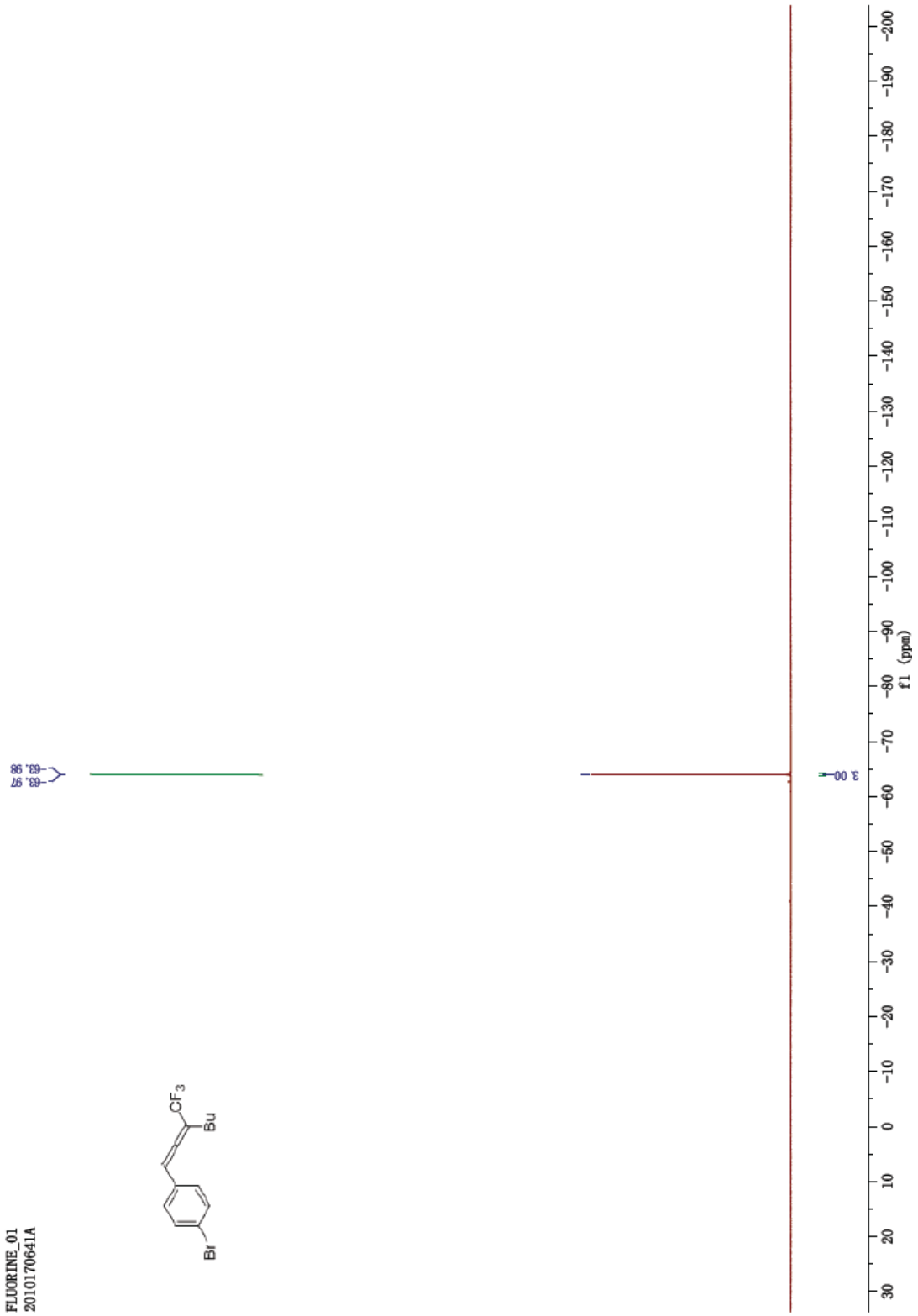
$^{13}C$ NMR spectrum of compound **3k**



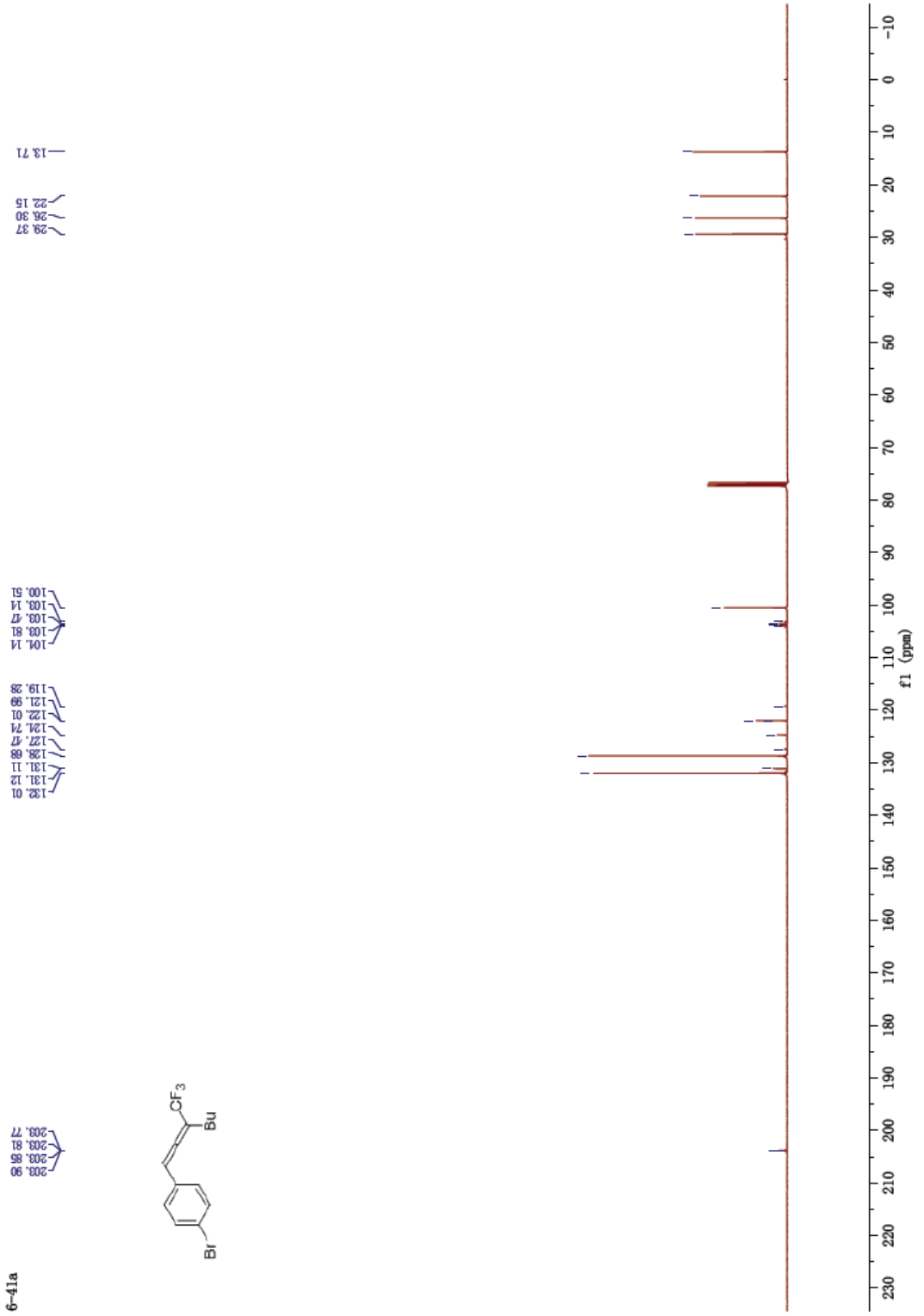
$^{1}$H NMR spectrum of compound o**3l**



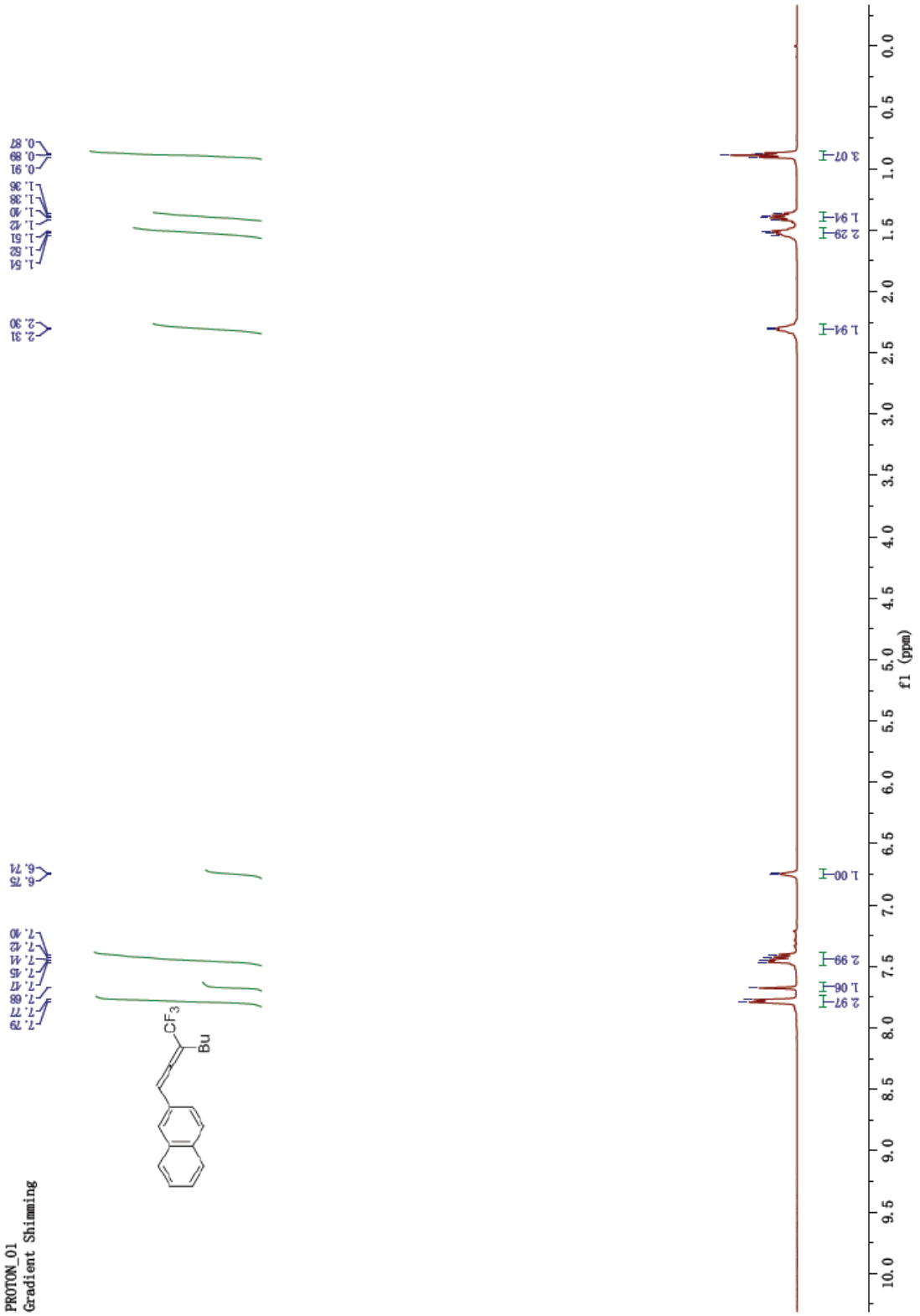
$^{19}F$ NMR spectrum of compound **3l**



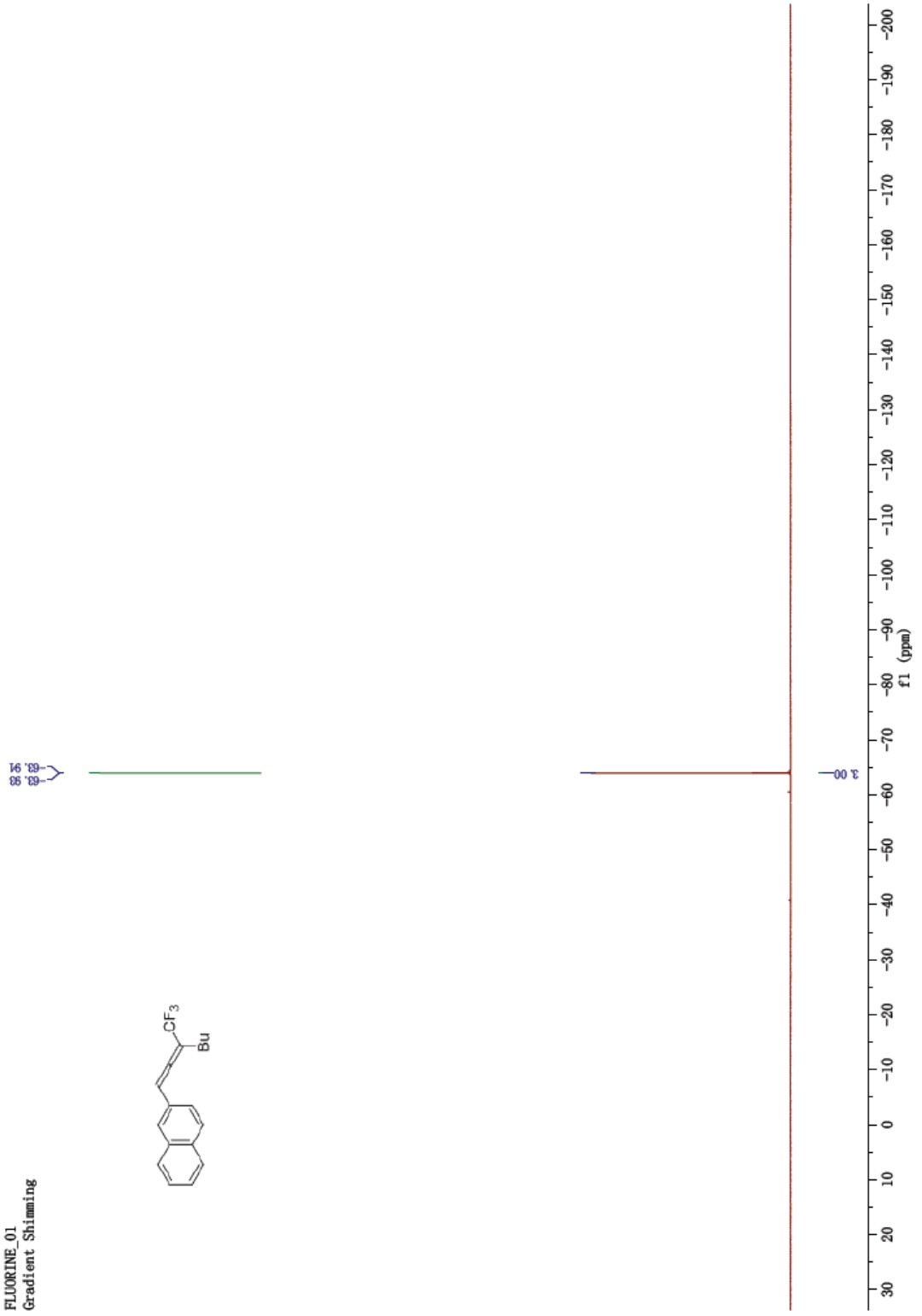
$^{13}C$ NMR spectrum of compound **3l**



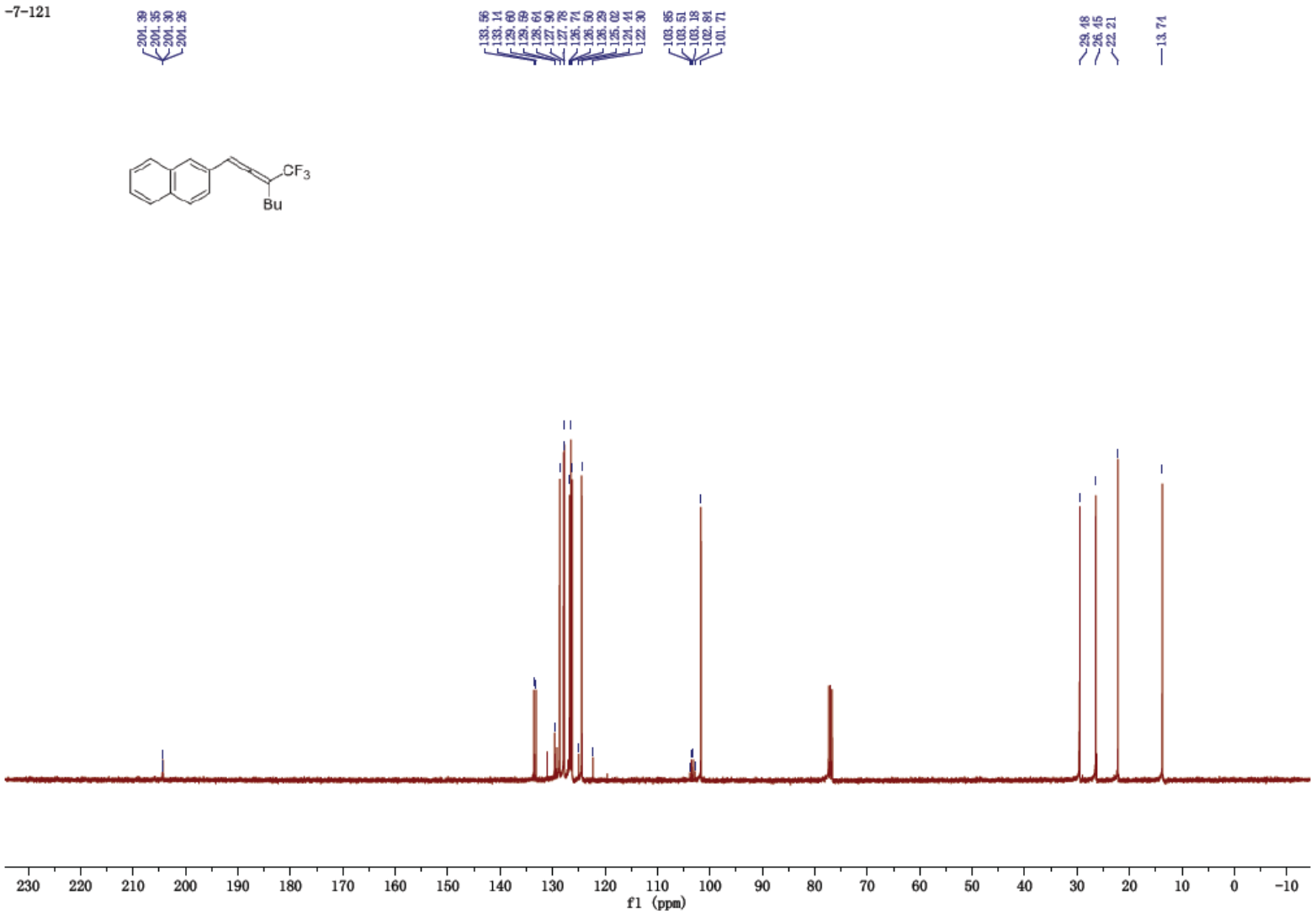
$^{1}$H NMR spectrum of compound **3n**



$^{19}F$ NMR spectrum of compound **3n**



$^{13}$C NMR spectrum of compound **3n**


-7-121
204.39
204.35
204.30
204.26
133.56
133.14
129.60
129.59
128.64
127.90
127.78
126.71
126.60
126.29
125.02
124.44
122.30
103.85
103.51
103.18
102.84
101.71
29.48
26.45
22.21
13.74
CF3
Bu
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)