Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Thioether-Functionalized Trifluoromethyl-alkynes, 1, 3-Dienes and Allenes: Divergent Synthesis from Reaction of 2-Trifluoromethyl-1, 3-Conjugated Enynes with Sulfur Nucleophiles

Huayu Cheng, Xiaofan Zhou, Anjing Hu, Shiteng Ding, Yimo Wang, Yuanjing Xiao* and Junliang Zhang*

Department of Chemistry, School of Chemistry and Molecular

Engineering, East China Normal University, Shanghai, 200241, P. R.

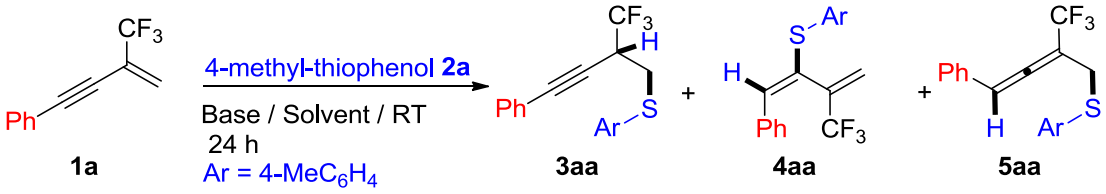
China, Fax: (+86)-21-54345471

E-mail: yjxiao@chem.ecnu.edu.cn, jlzhang@chem.ecnu.edu.cn

1. General information.

^{1}H NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in CDCl33. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). All reactions were carried out under an atmosphere of Argon in flame-dried glassware with magnetic stirring, CH_2Cl_2 (DCM), CH_3CN, DMSO, DMF, chlorobenzene were freshly distilled from CaH_2; Et_2O, MTBE (methyl *tert*-butyl ether), toluene and THF was freshly distilled from sodium metal prior to use. Chloroform ($CHCl_3$) was freshly distilled from phosphorous pentoxide (P_2O_5) prior to use. 2- trifluoromethyl 1,3-enynes **1** and 2-methyl 1,3-enynes **1z** were prepared in good yields according to the literature.[1]

2. Table S1. Screening results of reaction conditions.[a]



Entry	Base (equiv)	Solvent	**2a** (equiv)	**3aa** [%][b]	**4aa** [%][b]	**5aa** [%][b]
1	--	Toluene	1.5	-	-	-
2	Et_3N(0.5)	Toluene	1.5	70	13	5
3	Et_3N(2.0)	Toluene	1.5	75	11	7
4	Et_3N(2.0)	Toluene	3.0	77	8	5
5	**Et_3N(2.0)**	**ether**	**1.5**	**82(77)**	**8**	**3**
6	Et_3N(1.0)	ether	1.5	78	9	10
7	TMG(2.0)	ether	1.5	15	48	8
8	DBU(2.0)	ether	1.5	29	62	10
9	DIEA(2.0)	ether	1.5	39	21	6
10	DMAP(2.0)	ether	1.5	74	22	1
11	BDMA(2.0)	ether	1.5	35	1	17
12	$^{n}Bu_4N$(2.0)	ether	1.5	34	1	7
13	Et_3N(2.0)	DCM	1.5	43	16	8
14	Et_3N(2.0)	THF	1.5	64	21	5
15	Et_3N(2.0)	MeCN	1.5	21	45	7
16	Et_3N(2.0)	DMF	1.5	13	61	3
17	Et_3N(2.0)	DMSO	1.5	12	72	3
18	Et_3N(2.0)	MeOH	1.5	30	54	11
19	Et_3N(2.0)	EtOH	1.5	20	66	1
20	Et_3N(2.0)	DMSO	1.2	5	77	1

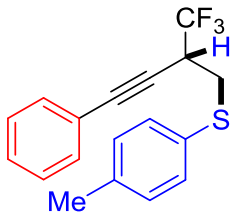
21	**Et_3N(2.0)**	**DMSO**	**1.1**	**4**	**84(80)**	**1**

[a] Reaction conditions: **1a** (0.2 mmol), Slovent (2.0 mL), RT, N_2, 24 h; [b] Determined by ^1H NMR of the reaction mixture containing CH_2Br_2 as an internal standard. TMG =Tetramethylguanidine; DBU= 1,8-Diazabicyclo[5.4.0]undec-ene; DIEA= N,N-Diisopropylethylamine; DMAP: 4-Dimethylaminopyridine; BDMA: N,N-Dimethylbenzylamine.

We initiated this project using enyne **1a** and 4-methyl-thiophenol **2a** as model substrates for screening reaction conditions. Under base free conditions, no reaction occurred (Table 1 entry 1), the result prompted us to test base as additives. Considering that the replacement of the alkaline metal ion with ammonium cation formed by deprotonation of hydrosulfuryl of thiophenol will weaken the metalfluorine interaction, thus suppress the defluorination process,[2] we choose organic base such as tertiary amine for reaction screening. A series of commonly used tertiary amine such as Et_3N, $^nBu_4N$, DBU, DIEA, and DMAP at room temperatures in various solvents were investigated. Nucleophilic addition pattern relied heavily on the solvent and base used. The combination of Et_3N as base and ether as solvent was found to be the optimal reaction conditions for 1,2–nucleophilic addition pattern, and functionalized alkyne **3aa** could be obtained in 77% isolated yield (Table 1 entry 5). Interestingly, simply use DMSO instead of ether as solvent invert the regioselectivity to 3,4–nucleophilic addition pattern, and functionalized 1,3-diene **4aa** could be obtained in 80% isolated yield (Table 1 entry 21).

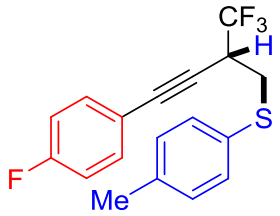
3. General procedure for the synthesis of thioether-functionalized trifluoromethyl-alkynes 3

To the solution of 2-trifluoromethyl 1,3-conjugated enynes **1** (1.0 mmol), thiophenol **2** (1.5 mmol) in toluene (5.0 mL) under nitrogen at room temperature was added Et_3N (2.0 mmol), the reaction was stirred at room temperature for 24 h. After **1** was completely consumed, which was determined by TLC analysis, the solvent was removed under reduced pressure and the crude reaction mixture was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 1:0~5:1) to give the desired **3**.



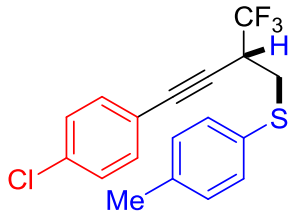
3aa

77% isolated yield. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.25 (m, 5H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 3.56 – 3.39 (m, 1H), 3.33 (dd, *J* = 13.4, 4.0 Hz, 1H), 3.12 (dd, *J* = 13.3, 10.5 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.65, 131.95, 131.70, 130.44, 130.02, 128.69, 128.20, 124.57 (q, *J* = 280.9 Hz), 122.05, 85.66, 81.02 (d, *J* = 3.3 Hz), 39.24 (q, *J* = 30.0 Hz), 34.16, 21.03. ^{19}F NMR (283 MHz, $CDCl_3$) δ -70.59. MS (70 eV): m/z (%): 320 (M^+, 45.55), 137 (100). HRMS(EI) calcd for $C_{18}H_{15}F_3S$: 320.0847, found: 320.0842.



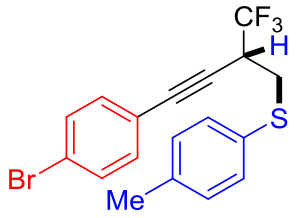
3ba

75% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 3.51 – 3.39 (m, 1H), 3.32 (dd, *J* = 13.4, 4.0 Hz, 1H), 3.11 (dd, *J* = 13.4, 10.5 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.73 (d, *J* = 250.0 Hz), 137.66, 133.90 (d, *J* = 8.4 Hz), 131.65, 130.42, 130.02, 124.52 (q, *J* = 280.8 Hz), 118.12 (d, *J* = 3.5 Hz), 115.50 (d, *J* = 22.1 Hz), 84.63, 80.79 (d, *J* = 2.1 Hz), 39.25 (q, *J* = 30.1 Hz), 34.06, 21.00. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.60, -110.11. MS (70 eV): m/z (%): 338 (M^+, 36.12), 141 (100). HRMS(EI) calcd for $C_{18}H_{14}F_4S$: 338.0752, found: 338.0750.



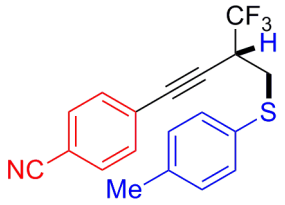
3ca

57% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 3.50 – 3.41 (m, 1H), 3.32 (dd, *J* = 13.4, 3.6 Hz, 1H), 3.17 – 3.05 (m, 1H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.68, 134.79, 133.16, 131.65, 130.35, 130.02, 128.54, 124.46 (q, *J* = 280.9 Hz), 120.50, 84.58, 82.06 (q, *J* = 6.3, 3.0 Hz), 39.31 (q, *J* = 30.0 Hz), 34.00, 21.00. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.52. MS (70 eV): m/z (%): 354 (M^+, 25.12), 137 (100). HRMS(EI) calcd for $C_{18}H_{14}F_3ClS$: 354.0457, found: 354.0458.



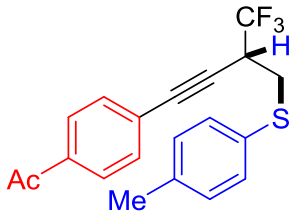
3da

89% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.50-3.40 (m, 1H), 3.32 (dd, *J* = 13.5, 3.9 Hz, 1H), 3.11 (dd, *J* = 13.4, 10.5 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.63, 133.33, 131.61, 131.44, 130.35, 130.00, 124.42 (q, *J* = 280.9 Hz), 123.02, 120.93, 84.63, 82.24 (q, *J* = 3.2 Hz), 39.33 (q, *J* = 30.0 Hz), 33.93, 20.97. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.45.MS (70 eV): m/z (%): 398 (M^+, 52.65), 137 (100). HRMS(EI) calcd for $C_{18}H_{14}F_3BrS$: 397.9952, found: 397.9962.



3ea

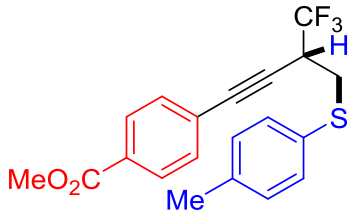
This compound has the same polarity as corresponding allene and can't be separated with each other, we can't get it's pure spectrum.



3fa

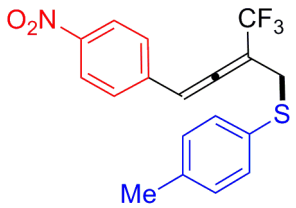
33% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 3.52 – 3.42 (m, 1H), 3.34 (dd, *J* = 13.5, 4.0 Hz, 1H), 3.13 (dd, *J* = 13.4, 10.5 Hz, 1H), 2.33 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.44, 137.72, 136.64, 132.04, 131.72, 130.37, 130.05, 125.79, 124.50 (q, *J* = 280.8 Hz), 122.86, 85.30, 82.41 (q, *J* =2.7 Hz), 39.34 (q, *J* = 30.2 Hz), 34.10, 21.06, 11.85. ^{19}F NMR (471 MHz, $CDCl_3$) δ

-70.54. MS (70 eV): m/z (%): 362 (M^+, 27.84), 43 (100). HRMS(EI) calcd for $C_{20}H_{17}NOF_3S$: 362.0952, found: 362.0938.



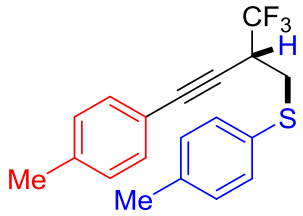
3ga

53% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 3.92 (s, 3H), 3.57-3.47 (m, 1H), 3.34 (dd, *J* = 13.5, 4.0 Hz, 1H), 3.13 (dd, *J* = 13.5, 10.5 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.39, 137.77, 131.88, 131.72, 130.24, 130.05, 130.00, 129.34, 126.64, 124.39 (q, *J* = 280.9 Hz), 84.90, 84.01 (q, *J* = 3.3 Hz), 52.23, 39.40 (q, *J* = 30.1 Hz), 33.96, 21.03. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.47. MS (70 eV): m/z (%): 378 (M^+, 19.72), 191 (100). HRMS(EI) calcd for $C_{20}H_{17}NO_2F_3S$: 378.0901, found: 378.0899.



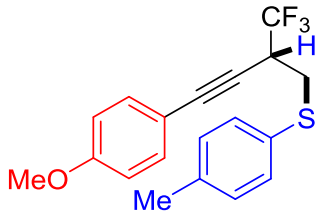
5ha

61% isolated yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.55 – 6.50 (m, 1H), 3.82 – 3.71 (m, 2H), 2.27 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.20. ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.77 (q, *J* = 3.8 Hz), 147.27, 137.96, 137.51, 131.36, 130.01, 129.90, 128.02, 123.86, 122.59 (q, *J* = 275.5 Hz), 101.32 (q, *J* = 34.2 Hz), 100.75, 31.69, 20.98. MS (70 eV): m/z (%): 365 (M^+, 100), 365 (100). HRMS(EI) calcd for $C_{18}H_{14}NO_2F_3S$: 365.0697, found: 365.0698.



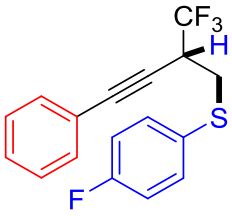
3ia

66% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 3.50 – 3.39 (m, 1H), 3.33 (dd, *J* = 13.3, 3.6 Hz, 1H), 3.11 (dd, *J* = 12.9, 10.8 Hz, 1H), 2.34 (d, *J* = 11.6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.85, 137.61, 131.84, 131.68, 130.52, 130.01, 128.96, 124.61 (q, *J* = 281.0 Hz), 118.99, 85.78, 80.29 (q, *J* = 3.3 Hz), 39.22 (q, *J* = 30.1 Hz), 34.23, 21.48, 21.05. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.65. MS (70 eV): m/z (%): 334 (M^+, 34.37), 137 (100). HRMS(EI) calcd for $C_{19}H_{17}F_3S$: 334.1003, found: 334.0999.



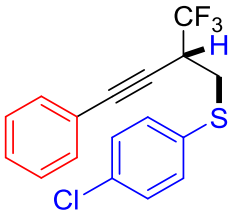
3ja

53% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ7.37 (d, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 2H), 3.79 (s, 3H), 3.52 – 3.39 (m, 1H), 3.32 (dd, *J* = 13.4, 3.5 Hz, 1H), 3.16 – 3.02 (m, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.88, 137.56, 133.41, 131.61, 130.56, 129.99, 124.64 (q, *J* = 280.8 Hz), 114.13, 113.82, 85.58, 79.58 (q, *J* = 3.2 Hz), 55.24, 39.21 (q, *J* = 29.9 Hz), 34.23, 21.02. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.65. MS (70 eV): m/z (%): 350 (M^+,18.47), 137 (100). HRMS(EI) calcd for $C_{19}H_{17}F_3OS$: 350.0952, found: 350.0948.



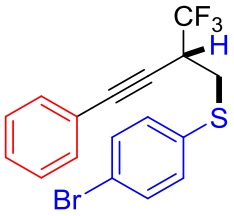
3ab

70% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 4H), 7.30 (dd, *J* = 14.3, 6.9 Hz, 3H), 6.99 (t, *J* = 8.5 Hz, 2H), 3.45 (d, *J* = 1.4 Hz, 1H), 3.30 (dd, *J* = 13.4, 2.5 Hz, 1H), 3.11 (dd, *J* = 12.4, 11.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.48 (d, *J* = 248.2 Hz), 134.01 (d, *J* = 8.2 Hz), 131.90 (s), 129.21, 128.80, 128.25, 124.50 (q, *J* = 280.8 Hz), 121.90, 116.36 (d, *J* = 21.9 Hz), 85.91, 80.78 (q, *J* = 2.7 Hz), 39.28 (q, *J* = 30.1 Hz), 34.62. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.55, -113.48. MS (70 eV): m/z (%): 324 (M^+,45.92), 141 (100). HRMS(EI) calcd for $C_{17}H_{12}F_4S$: 324.0596, found: 324.0593.



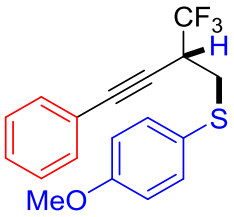
3ac

80% isolated yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 4H), 7.39 – 7.27 (m, 5H), 3.57 – 3.46 (m, 1H), 3.38 (dd, *J* = 13.5, 4.0 Hz, 1H), 3.20 (dd, *J* = 13.4, 10.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.48, 132.87, 132.22, 131.90, 129.37, 128.83, 128.26, 124.43 (q, *J* = 280.9 Hz), 121.81, 85.99, 80.63 (q, *J* = 3.2 Hz), 39.33 (q, *J* = 30.2 Hz), 33.70. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.60. MS (70 eV): m/z (%): 340 (M^+,31.44), 157 (100). HRMS(EI) calcd for $C_{17}H_{12}F_3ClS$: 340.0300, found: 340.0298.



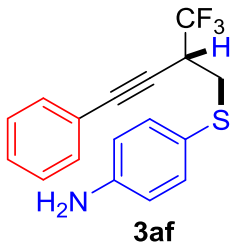
3ad

93% isolated yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.35-7.27 (m, 5H), 3.54 – 3.45 (m, 1H), 3.35 (dd, *J* = 13.5, 3.8 Hz, 1H), 3.17 (dd, *J* = 13.2, 10.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.59, 132.30, 132.29, 131.90, 128.83, 128.26, 124.42 (q, *J* = 280.9 Hz), 121.78, 121.37, 86.01, 80.60 (q, *J* = 3.2 Hz), 39.34 (q, *J* = 30.2 Hz), 33.49. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.60. MS (70 eV): m/z (%): 384 (M^+,64.44), 128 (100). HRMS(EI) calcd for $C_{17}H_{12}F_3BrS$: 383.9795, found: 383.9792.



3ae

85% isolated yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.33 – 7.29 (m, 3H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.46-3.37 (m, 1H), 3.26 (dd, *J* = 13.4, 4.0 Hz, 1H), 3.05 (dd, *J* = 13.4, 10.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.77, 134.72, 131.95, 128.69, 128.22, 124.59 (q, *J* = 280.9 Hz), 124.21, 122.09, 114.86, 85.66, 81.10 (q, *J* = 3.2 Hz), 55.29, 39.22 (q, *J* = 30.0 Hz), 35.26. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.52. MS (70 eV): m/z (%): 336 (M^+, 67.43), 153 (100). HRMS(EI) calcd for $C_{18}H_{15}OF_3S$: 336.0796, found: 336.0792.

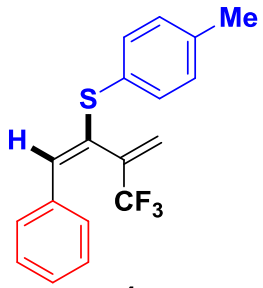


3af

69% isolated yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.27 (m, 5H), 6.61 (d, *J* = 8.5 Hz, 2H), 3.75 (s, 2H), 3.48 – 3.33 (m, 1H), 3.20 (dd, *J* = 13.3, 4.0 Hz, 1H), 2.99 (dd, *J* = 13.2, 10.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.91, 135.28, 131.96, 128.64, 128.22, 124.65 (q, *J* = 280.8 Hz), 122.16, 120.82, 115.66, 85.49, 81.30 (q, *J* = 3.2 Hz), 39.02 (q, *J* = 29.8 Hz), 35.68. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.44. HRMS(ESI) calcd for $C_{17}H_{15}F_3SN$ [M+H$^+$]: 322.0872, found: 322.0878.

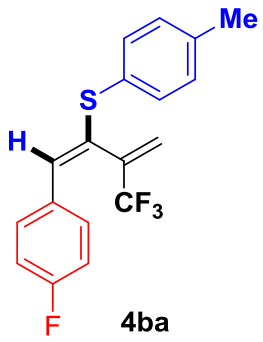
4. General procedure for the synthesis of products 4

To the solution of 2-trifluoromethyl 1,3-conjugated enynes **1** (1,0 mmol), thiophenol **2** (1.1 mmol) in DMSO (5.0 mL) under nitrogen at room temperature was added Et_3N (2.0 mmol), the reaction was stirred at room temperature for 24 h. After **1** was completely consumed, which was determined by TLC analysis, water (15 mL) was added to reaction mixture and extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography on silica gel (petroleum ether: ethyl acetate = 1:0~5:1) to give the desired **4**.



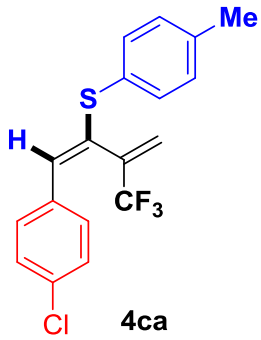
4aa

80% isolated yield. Colorless solid. Mp 38.5-40.6 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.21 (m, 7H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.91-6.96 (m, 1H), 5.78 (s, 1H), 5.36 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.48, 135.55, 135.45, 135.02 (q, *J* = 31.9 Hz), 133.62, 130.45, 129.91, 128.87, 128.70, 128.30, 127.85, 125.42 (q, *J* = 4.4 Hz), 122.43 (q, *J* = 275.7 Hz), 21.18. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.92. MS (70 eV): m/z (%): 320 (M^+, 100), 320 (100). HRMS(EI) calcd for $C_{18}H_{15}F_3S$: 320.0847, found: 320.0848.



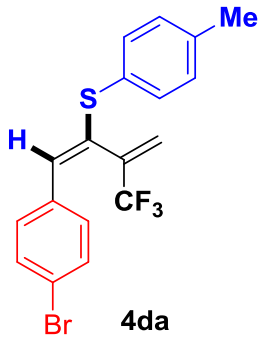
4ba

77% isolated yield. Colorless solid. Mp 31.9-34.5 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.26 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.92 (dd, *J* = 8.7 Hz, 5.5 Hz, 2H), 6.84 (s, 1H), 5.75 (s, 1H), 5.32 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.17 (d, *J* = 248.5 Hz), 138.60, 134.91 (q, *J* = 31.6 Hz), 134.03, 133.69, 131.61 (d, *J* = 3.4 Hz), 130.42, 130.35, 129.94, 128.67, 125.57 (q, *J* = 4.7 Hz), 122.38 (q, 275.5 Hz), 115.28 (d, *J* = 21.5 Hz), 21.10. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.88, -113.02. MS (70 eV): m/z (%): 338(M^+, 100), 137 (100). HRMS(EI) calcd for $C_{18}H_{14}F_4S$: 338.0752, found: 338.0753.



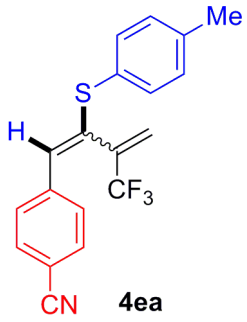
4ca

77% isolated yield. Colorless solid. Mp 41.7-43.8 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.19 (m, 4H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.77 (s, 1H), 5.79 (s, 1H), 5.36 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.78, 134.86 (q, *J* = 31.6 Hz), 133.94, 133.89, 133.54, 133.16, 131.63, 129.99, 129.84, 128.49, 128.38, 125.75 (q, *J* = 4.7 Hz), 122.30 (q, *J* = 275.6 Hz), 21.17. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.98. MS (70 eV): m/z (%): 354(M^+, 100). HRMS(EI) calcd for $C_{18}H_{14}F_3ClS$: 354.0457, found: 354.0458.



4da

94% isolated yield. Colorless solid. Mp 44.5-45.8 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 8.5 Hz, 2H), 7.40(t, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 4H), 6.77 (s, 1H), 5.82 (s, 1H), 5.39 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.80, 134.85 (q, *J* = 31.6 Hz), 134.39, 133.93, 133.07, 131.83, 131.44, 130.11, 130.00, 128.32, 125.77 (q, *J* = 4.7 Hz), 122.27 (q, *J* = 275.6 Hz), 121.76), 21.18. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.89. MS (70 eV): m/z (%): 398(M^+, 97.08), 400 (100). HRMS(EI) calcd for $C_{18}H_{14}F_3BrS$: 397.9952, found: 397.9949.

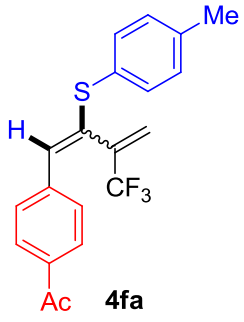


4ea

91% isolated yield. *E/Z* =2.8:1

Major isomer. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.15(d, *J* = 8.0 Hz, 2H), 7.16 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.97 (s, 1H), 5.91 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.98 (s), 137.33, 136.53 (q, *J* = 29.8 Hz), 134.99, 131.66, 131.63, 130.20, 130.04, 129.84, 129.28, 124.93 (q, *J* = 5.2 Hz), 122.51 (q, *J* = 275.1 Hz), 118.52, 111.36, 20.84. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.50. MS (70 eV): m/z (%): 345 (M^+, 100). HRMS(EI) calcd for $C_{19}H_{14}NF_3S$: 345.0799, found: 345.0793.

Minor isomer. Colorless solid. Mp 82.3-84.1 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.58 (s, 1H), 5.89 (s, 1H), 5.48 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.03, 139.50, 135.85, 134.78 (q, *J* = 32.1 Hz), 134.56, 131.99, 130.23, 129.82, 128.90, 127.34, 126.47 (q, *J* = 4.8 Hz), 122.09 (q, *J* = 275.5 Hz), 118.66, 110.71, 21.22. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.09. MS (70 eV): m/z (%): 345 (M^+, 100). HRMS(EI) calcd for $C_{19}H_{14}NF_3S$: 345.0799, found: 345.0795.



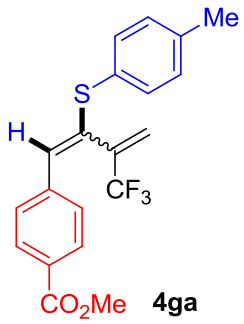
4fa

89% isolated yield. *E/Z* =1.8:1

Major isomer. Colorless solid. Mp 53.3-55.5 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.24 (s, 1H), 7.18 (d, *J* = 8.2 Hz, 2H),

7.10 (d, *J* = 8.2 Hz, 2H), 5.98 (d, *J* = 1.8 Hz, 1H), 5.91 (s, 1H), 2.61 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.21, 140.16, 137.06, 136.78 (q, *J* = 29.7 Hz), 136.28, 136.27, 136.26, 130.35, 130.03, 129.80, 129.74, 127.99, 124.52 (q, *J* = 5.2 Hz), 122.65 (q, *J* = 275.2 Hz), 26.42, 20.87. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.42. MS (70 eV): m/z (%): 362 (M^+, 100). HRMS(EI) calcd for $C_{20}H_{17}OF_3S$: 362.0952, found: 362.0949.

Minor isomer. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 5.84 (s, 1H), 5.43 (s, 1H), 2.56 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.39, 140.18, 139.17, 135.79, 134.97 (q, *J* = 31.9 Hz), 134.26, 131.81, 130.13, 128.62, 128.34, 127.88, 126.12 (q, *J* = 4.9 Hz), 122.22 (q, *J* = 275.4 Hz), 26.53, 21.24. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.01. MS (70 eV): m/z (%): 362 (M^+, 20.08), 141 (100). HRMS(EI) calcd for $C_{20}H_{17}OF_3S$: 362.0952, found: 362.0949.



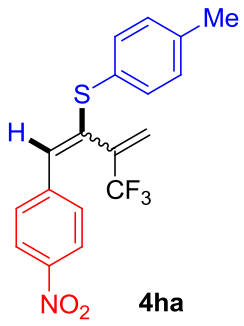
4ga

84% isolated yield. *E*/*Z* =1.2:1

Major isomer. Colorless solid. Mp 54.6-56.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.19 (s, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 5.93 (d, *J* = 1.5 Hz, 1H), 5.87 (s, 1H), 3.90 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.61, 140.11, 137.08, 136.89 (q, *J* =29.7 Hz), 136.48 (d, *J* = 1.1 Hz), 130.23, 130.07, 129.95, 129.86, 129.61, 129.56, 129.31, 124.51 (q, *J* = 5.2 Hz), 122.73 (q, *J* = 275.2 Hz), 52.09, 20.98. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.47. MS (70 eV): m/z (%): 378 (M^+, 100). HRMS(EI) calcd for $C_{20}H_{17}NO_2F_3S$: 378.0901, found: 378.0904.

Minor isomer. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H),

7.39 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.75 (s, 1H), 5.84 (d, *J* = 1.2 Hz, 1H), 5.44 (d, *J* = 1.1 Hz, 1H), 3.89 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.52, 139.94, 139.02, 134.86 (q, *J* = 31.8 Hz), 134.17, 133.89, 132.05, 130.05, 129.47, 128.88, 128.37, 127.90, 126.04 (q, *J* = 4.7 Hz), 122.20 (q, *J* = 275.5 Hz), 51.95, 21.12. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.96. MS (70 eV): m/z (%): 378 (M^+, 100). HRMS(EI) calcd for $C_{20}H_{17}NO_2F_3S$: 378.0901, found: 378.0898.

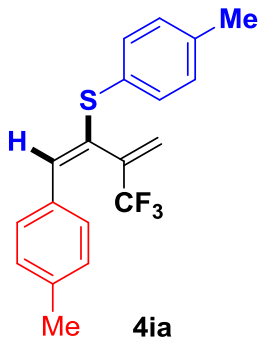


4ha

94% isolated yield. *E/Z* =4:1

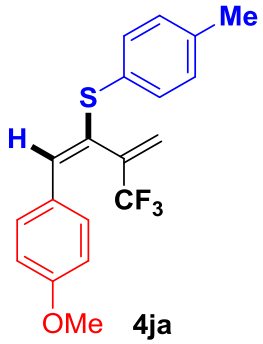
Major isomer. Colorless solid. Mp 30.3-32.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.17 (s, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 5.96 (d, *J* = 1.5 Hz, 1H), 5.92 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.99, 142.10, 137.59, 136.61 (q, *J* = 29.7 Hz), 134.54, 132.54, 130.43, 130.39, 130.36, 130.00, 129.27, 125.26 (q, *J* =4.5 Hz), 123.34, 122.59 (q, *J* = 275.4 Hz), 21.02. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.59. MS (70 eV): m/z (%): 365 (M^+, 100). HRMS(EI) calcd for $C_{18}H_{14}NO_2F_3S$: 365.0697, found: 365.0695.

Minor isomer. Colorless solid. Mp 41.8-43.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.57 (s, 1H), 5.93 (s, 1H), 5.53 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.50, 142.09, 139.73, 136.95, 135.13 (q, *J* = 32.3 Hz), 134.76, 130.35, 129.01, 128.81, 127.16, 126.71 (q, *J* = 4.7 Hz), 123.60, 122.09 (q, *J* = 275.5 Hz), 21.29. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.14. MS (70 eV): m/z (%): 365 (M^+, 100). HRMS(EI) calcd for $C_{18}H_{14}NO_2F_3S$: 365.0697, found: 365.0699.



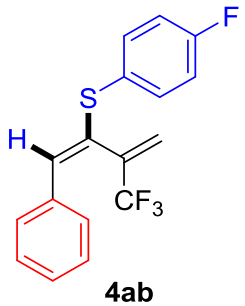
4ia

80% isolated yield. Colorless solid. Mp 53.4-55.5 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.92 (s, 1H), 5.71 (s, 1H), 5.29 (s, 1H), 2.29 (d, *J* = 11.4 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.25, 137.92, 136.25, 135.12 (q, *J* = 31.4 Hz), 133.36, 132.56, 129.82, 129.16, 129.02, 129.00, 128.67, 125.12 (q, *J* = 4.7 Hz), 122.48 (q, *J* = 275.7 Hz), 21.13, 21.09. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.72. MS (70 eV): m/z (%): 334(M^+, 100), 137 (100). HRMS(EI) calcd for $C_{19}H_{17}F_3S$: 334.1003, found: 334.1000.



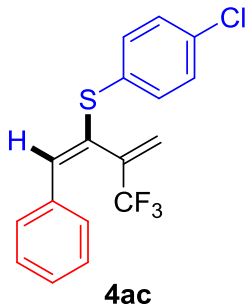
4ja

89% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 6.96 (s, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 5.75 (s, 1H), 5.31 (s, 1H), 3.80 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.37, 138.13, 136.49, 135.17 (q, *J* = 31.0 Hz), 133.17, 130.21, 129.79, 129.40, 128.02, 127.31, 124.98 (q, *J* = 4.8 Hz), 122.49 (q, *J* = 275.4 Hz), 113.74, 55.21, 21.16. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.88. MS (70 eV): m/z (%): 350(M^+, 96.43), 137 (100). HRMS (EI) calcd for $C_{19}H_{17}F_3OS$: 350.0952, found: 350.0947.



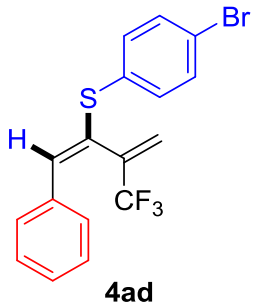
4ab

86% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.9, 5.7 Hz, 2H), 7.39-7.24 (m, 5 H), 7.07 (t, *J* = 8.5 Hz, 2H), 6.99 (s, 1H), 5.79 (s, 1H), 5.33 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.86 (d, *J* = 249.0 Hz), 136.35, 135.67 (d, *J* = 8.4 Hz), 135.18, 134.85 (q, *J* = 31.5 Hz), 130.00, 128.74, 128.36, 128.08, 127.71 (d, *J* = 3.3 Hz), 125.54 (q, *J* = 4.7 Hz), 122.36 (q, *J* =275.5 Hz), 116.25 (d, *J* = 22.0 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.85, -112.41. MS (70 eV): m/z (%): 324 (M^+, 92.23), 128 (100). HRMS (EI) calcd for $C_{17}H_{12}F_4S$: 324.0596, found: 324.0587.



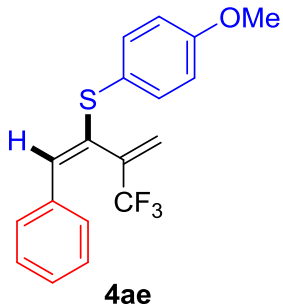
4ac

85% isolated yield. Colorless solid. Mp 32.3-33.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.27 - 7.36 (m, 7H), 7.07 (s, 1H), 5.79 (s, 1H), 5.35 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.81, 135.07, 134.73 (q, *J* = 31.5 Hz), 134.33, 134.25, 131.30, 129.26, 129.12, 128.81, 128.41, 128.24, 125.66 (q, *J* = 4.8 Hz), 122.31 (q, *J* = 275.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.87. MS (70 eV): m/z (%): 340 (M^+, 94.58), 128 (100). HRMS(EI) calcd for $C_{17}H_{12}F_3ClS$: 340.0300, found: 340.0294.



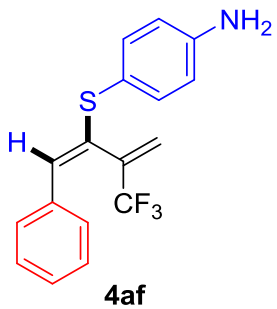
4ad

94% isolated yield. Colorless solid. Mp 34.5-36.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.24 (m, 7H), 7.09 (s, 1H), 5.79 (s, 1H), 5.36 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.10, 135.00, 134.64 (d, *J* = 31.5 Hz), 134.31, 132.15, 132.00, 128.82, 128.79, 128.38, 128.24, 125.66 (q, *J* = 4.8 Hz), 122.35, 122.30 (q, *J* =275.7 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.88. MS (70 eV): m/z (%): 384 (M^+, 61.37), 128 (100). HRMS(EI) calcd for $C_{17}H_{12}F_3BrS$: 383.9795, found: 383.9789.



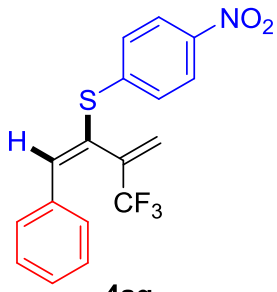
4ae

78% isolated yield. Colorless solid. Mp 32.8-34.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.21 (m, 5H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.84 (s, 1H), 5.82 (s, 1H), 5.36 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.12, 135.99, 135.48, 135.09 (d, *J* = 31.5 Hz), 133.96, 131.29, 128.62, 128.26, 127.71, 125.44 (q, *J* = 4.8 Hz), 122.69, 122.41 (q, *J* = 275.6 Hz), 114.71, 55.27. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.94. MS (70 eV): m/z (%): 336 (M^+, 100), 336 (100). HRMS(EI) calcd for $C_{18}H_{15}OF_3S$: 336.0796, found: 336.0789.



4af

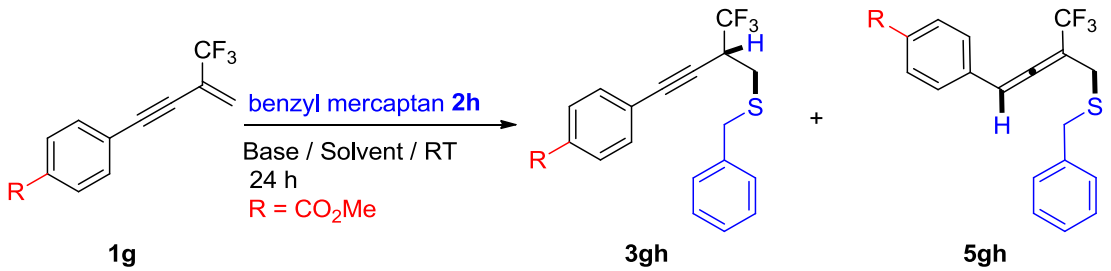
65% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.20 (m, 5H), 7.30 (d, *J* = 7.5 Hz, 2H), 6.75 (s, 1H), 6.68 (d, *J* = 7.9 Hz, 2H), 5.84 (s, 1H), 5.39 (s, 1H), 3.83 (brs, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.28, 136.34, 135.64, 135.19 (q, *J* = 31.5 Hz), 132.45, 132.09, 128.52, 128.19, 127.48, 125.39 (q, *J* = 4.8 Hz), 122.44 (q, *J* = 275.5 Hz), 119.19, 115.52. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.84. HRMS(ESI) calcd for $C_{17}H_{15}F_3SN$ [M+H$^+$]: 322.0872, found: 322.0873.



4ag

84% isolated yield. Colorless solid. Mp 53.8-55.7 ^{o}C ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.9 Hz, 2H), 7.49 (d, *J* = 8.9 Hz, 2H), 7.46 – 7.38 (m, 2H), 7.37 – 7.29 (m, 3H), 7.34 (s, 1H), 5.84 (d, *J* = 1.0 Hz, 1H), 5.51 (d, *J* = 1.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.50, 143.40, 143.30, 134.49 (q, *J* = 31.5 Hz), 134.45, 130.19, 128.97, 128.92, 128.56, 126.18 (q, *J* =4.8 Hz), 125.68, 123.93, 122.18 (q, *J* = 275.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.74. MS (70 eV): m/z (%): 351 (M$^+$, 54.70), 128 (100). HRMS(EI) calcd for $C_{17}H_{12}NO_2F_3S$: 351.0541, found: 351.0536.

5. Table S2. Screening results of reaction conditions.[a]



1g **3gh** **5gh**

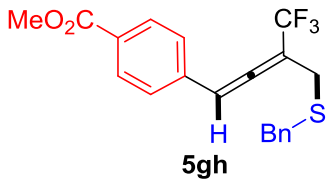
Entry	Solvent[c]	Base	**3gh**[%][b]	**5gh**[%][b]
1	MeOH	TMEDA	33	59
2	Toluene	TMEDA	69	22
3	$CHCl_3$	TMEDA	65	29
4	MTBE	TMEDA	53	27
5	DMSO	TMEDA	52	47
6	DMSO/MeOH	TMEDA	23	60
7	**DMSO/$CHCl_3$**	**TMEDA**	**19**	**80(75)**
8	DMSO/$CHCl_3$	Et_3N	26	71
9	DMSO/$CHCl_3$	pyridine	50	42
10	DMSO/$CHCl_3$	DMAP	31	26
11	DMSO/$CHCl_3$	Diisopropylamine	22	73
12	DMSO/$CHCl_3$	DIEA	48	43
13	DMSO/$CHCl_3$	BDMA	44	46
14[d]	DMSO/$CHCl_3$	TMEDA	18	78

[a] Reaction conditions: enyne **1g** (0.32 mmol), benzyl mercaptan **2h** (0.2 mmol) Slovent (2.0 mL), Base (10% mol), RT, N_2, 24 h; [b] Determined by ^1H NMR of the reaction mixture containing CH_2Br_2 as an internal standard; [c] co-solvent (*v* : *v*= 1:1); [d] the reaction was carried out at 0^oC; DIEA= N,N-Diisopropylethylamine; DMAP:

4-Dimethylaminopyridine; BDMA: N,N-Dimethylbenzylamine.

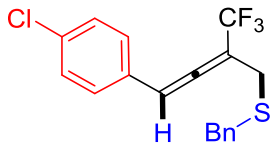
6. General procedure for the synthesis of thioether-functionalized trifluoromethyl-allenes 5

To the solution of benzyl mercaptan **2** (1.0 mmol) in DMSO/$CHCl_3$ (*V*:*V* = 1:1, 5.0 mL) under nitrogen at room temperature was added TMEDA (0.1 mmol), then added 2-trifluoromethyl 1,3-conjugated enynes **1** (1.6 mmol), the reaction was stirred at room temperature for 4 h. After **2** was completely consumed, which was determined by TLC analysis, water (2.0 mL) was added and the reaction mixture was extracted with ethyl acetate (3x4.0 mL). The combined organic extracts were washed with brine (4.0 mL) and dried over $MgSO_4$. After filtration and evaporation, the residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 100:0~50:1) to give the desired **5**.



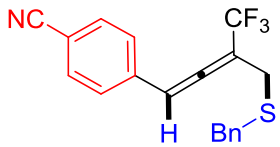
5gh

75 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.18 (m, 5H), 6.78 (q, *J* = 3.1 Hz, 1H), 3.95 (s, 3H), 3.77 (d, *J* = 13.5 Hz, 1H), 3.73 (d, *J* = 13.5 Hz, 1H), 3.32 (s, *2*H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.05 (q, *J* = 3.7 Hz), 166.36, 137.09, 136.04, 130.15, 130.02, 128.78, 128.47, 127.37, 127.16, 122.73 (q, *J* = 275.3 Hz), 101.72, 101.14 (q, *J* = 33.8 Hz), 52.07, 35.99, 27.65. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.51. HRMS (ESI) calcd for $C_{20}H_{17}F_3NaO_2S$: 401.0794, found: 401.0810



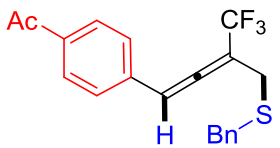
5ch

52 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.03 (m, 9H), 6.70 (q, J = 3.0 Hz, 1H), 3.73 (d, *J* = 13.5 Hz, 1H), 3.69 (d, *J* = 13.5 Hz, 1H), 3.26 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.42 (q, *J* = 3.6 Hz), 137.23, 134.46, 129.89, 129.23, 128.87, 128.73, 128.56, 127.25, 122.86 (q, J = 273.4 Hz), 101.50, 100.97 (q, *J* = 34.0 Hz), 36.10, 27.79. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.71. MS (70 ev): m/z(%): 354 (M^+,0.17), 91(100). HRMS (EI) calcd for $C_{18}H_{14}F_3ClS$: 354.0457, found: 354.0459.



5eh

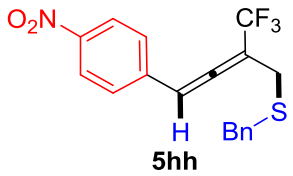
71 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.23 (m, 5H), 6.74 (q, *J* = 2.8 Hz, 1H), 3.76 (d, *J* = 13.5 Hz, 1H), 3.72 (d, *J* = 13.5 Hz, 1H), 3.30 (dd, *J* = 2.3, 0.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.13 (q, *J* = 3.7 Hz), 136.97, 136.25, 132.60, 128.73, 128.50, 127.91, 127.23, 122.55 (q, *J* = 275.4 Hz), 118.38, 111.87, 101.97 (q, *J* = 34.2 Hz), 101.37, 36.18, 27.58. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.57. HRMS (ESI) calcd for $C_{19}H_{14}F_3NNaS$:368.0691, found: 368.0698



5fh

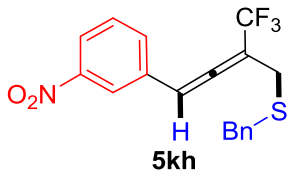
63 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.24 (m, 5H), 6.79 (q, J = 3.0 Hz, 1H), 3.77 (d, *J* = 13.5 Hz, 1H), 3.72 (d, *J* = 13.5 Hz, 1H), 3.40 – 3.25 (m, 2H), 2.62 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.11 (d, *J* = 3.9 Hz), 197.11, 137.05, 136.76, 136.16, 128.91,

128.77, 128.46, 127.55, 127.16, 122.69 (d, J = 275.2 Hz), 101.65 , 101.14 (d, J = 33.8 Hz), 35.97, 27.59, 26.49. ^{19}F NMR (500 MHz, $CDCl_3$) δ -62.51. HRMS (ESI) calcd for $C_{20}H_{17}F_3NaOS$:385.0844, found: 385.0851



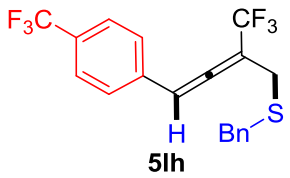
5hh

77 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.43 – 7.14 (m, 5H), 6.78 (q, J = 2.7 Hz, 1H), 3.76 (d, J = 13.5 Hz, 1H), 3.72 (d, J = 13.5 Hz, 1H), 3.31 (d, J = 1.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.50 (q, J = 3.7 Hz), 147.53, 138.28, 137.00, 128.80, 128.58, 128.09, 127.32, 124.25, 122.56 (q, J = 275.3 Hz), 102.18 (q, J = 34.4 Hz), 101.11, 36.28, 27.57. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.58. HRMS (ESI) calcd for $C_{18}H_{14}F_3NNaO_2S$: 388.0590, found: 388.0591.



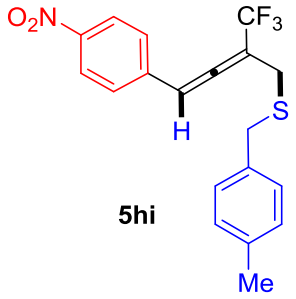
5kh

80 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18-8.13 (m, 2H), 7.68-7.65 (m, 1H), 7.58-7.53 (m, 1H), 7.33 – 7.23 (m, 5H), 6.79 (q, J = 2.8 Hz, 1H), 3.77 (d, J = 13.5 Hz, 1H), 3.73 (d, J = 13.5 Hz, 1H), 3.37 – 3.22 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.69 (q, J = 3.8 Hz), 148.65, 137.03, 133.44, 133.00, 129.91, 128.81, 128.56, 127.28, 123.20, 122.57 (q, J = 275.3 Hz), 122.14, 102.27 (q, J = 34.2 Hz), 100.95, 36.21, 27.62. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.66. HRMS (ESI) calcd for $C_{18}H_{14}F_3NNaO_2S$: 388.0590, found: 388.0594.



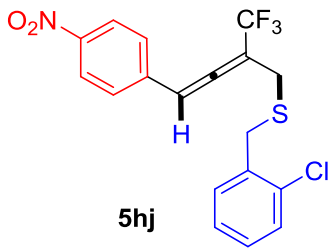
5lh

56 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.22 (m, 5H), 6.77 (q, 2.7 Hz, 1H), 3.77 (d, *J* = 13.5 Hz, 1H), 3.73 (d, *J* = 13.5 Hz, 1H), 3.35 – 3.26 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.95 (q, *J* = 3.8 Hz), 137.16, 135.23, 130.52 (q, *J* = 32.6 Hz), 128.87, 128.60, 127.74, 127.31, 125.96 (q, *J* = 3.8 Hz), 123.89 (q, *J* = 272.1 Hz), 122.75 (q, *J* = 275.1 Hz), 101.67 (q, *J* = 34.2 Hz), 101.50, 36.22, 27.71. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.59, -62.61. MS(70 ev): m/z(%): 388(M^+,4.67),91(100). HRMS(EI) calcd for $C_{19}H_{14}F_6S$: 388.0720, found: 388.0718.



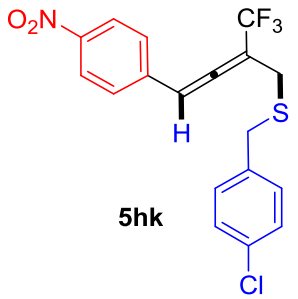
5hi

73 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.80 (q, *J* = 2.9 Hz, 1H), 3.73 (d, *J* = 13.5 Hz, 1H), 3.69 (d, *J* = 13.4 Hz, 1H), 3.31 (d, *J* = 2.5 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.48 (q, *J* = 3.8 Hz), 147.48, 138.30, 136.99, 133.84, 129.23, 128.67, 128.06, 124.20, 122.56 (q, *J* = 275.3 Hz), 102.19 (q, *J* = 34.2 Hz), 101.06, 35.92, 27.46, 20.98. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.58. HRMS (ESI) calcd for $C_{19}H_{16}F_3NNaO_2S$: 402.0746, found: 402.0748



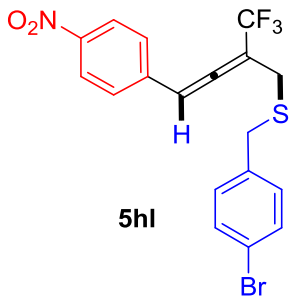
5hj

65 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.38-7.34 (m, 1H), 7.32– 7.28 (m, 1H), 7.24 – 7.17 (m, 2H), 6.80 (q, J = 2.8 Hz, 1H), 3.88 (d, *J* = 13.6 Hz, 1H), 3.83 (d, *J* = 13.6 Hz, 1H), 3.42 – 3.36 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.45 (q, *J* = 3.7 Hz), 147.47, 138.16, 134.92, 133.93, 130.56, 129.81, 128.72, 128.08, 126.86, 124.16, 122.52 (q, *J* = 275.4 Hz), 102.19 (q, *J* = 34.4 Hz), 101.28, 33.91, 28.09. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.60. HRMS(ESI) calcd for $C_{18}H_{13}ClF_3NNaO_2S$: 422.0200, found: 422.0201



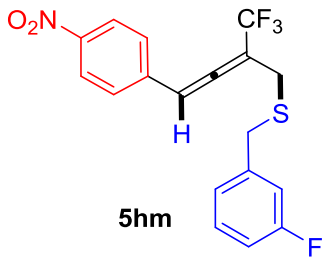
5hk

63 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.86 (q, J = 2.8 Hz, 1H), 3.74 (d, *J* = 13.7 Hz, 1H), 3.70 (d, *J* = 13.7 Hz, 1H), 3.31 (d, *J* = 1.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.49 (q, *J* = 3.7 Hz), 147.62, 138.15, 135.57, 133.15, 130.12, 128.75, 128.10, 124.28, 122.52 (q, *J* = 275.4 Hz), 102.07 (q, *J* = 34.4 Hz), 101.17, 35.66, 27.64. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.71. HRMS (ESI) calcd for $C_{18}H_{13}ClF_3NNaO_2S$: 422.0200, found: 422.0206



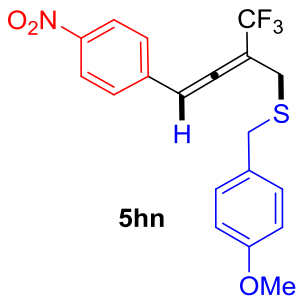
5hl

80 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.76 (q, *J* = 2.7 Hz, 1H), 3.70 (d, *J* = 13.7 Hz, 1H), 3.66 (d, *J* = 13.7 Hz, 1H), 3.28 (d, *J* = 2.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.51 (q, *J* = 3.6 Hz), 147.67, 138.16, 136.11, 131.75, 130.49, 128.13, 124.32, 122.54 (q, *J* = 273.6 Hz), 121.27, 102.11 (q, *J* = 34.5 Hz), 101.20, 35.78, 27.67. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.53. HRMS(ESI) calcd for $C_{18}H_{13}BrF_3NNaO_2S$: 465.9695, found: 465.9695.



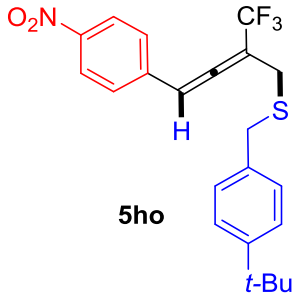
5hm

80 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.21 (dd, *J* = 8.5, 5.4 Hz, 2H), 6.97 (t, *J* = 8.6 Hz, 2H), 6.80 (q, *J* = 2.7 Hz, 1H), 3.73 (d, *J* = 13.6 Hz, 1H), 3.69 (d, *J* = 13.6 Hz, 1H), 3.29 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.47 (q, *J* = 3.7 Hz), 161.92 (d, *J* = 246.2 Hz), 147.55, 138.18, 132.72 (d, *J* = 3.3 Hz), 130.38, 130.31, 128.08, 124.24, 122.52 (q, *J* = 275.3 Hz), 115.44 (d, *J* = 21.4 Hz), 102.06 (q, *J* = 34.4 Hz), 101.13, 35.50, 27.55. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.62, -114.83. HRMS(ESI) calcd for $C_{18}H_{13}F_4NNaO_2S$: 406.0495, found: 406.0499



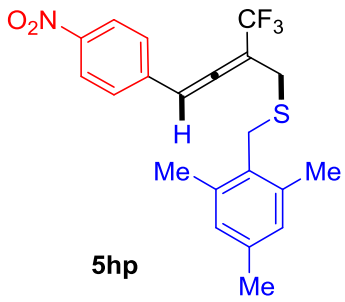
5hn

81 % isolated yield. Colorless oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.79 (q, *J* = 2.7 Hz, 1H), 3.78 (s, 3H), 3.71 (d, *J* = 13.4 Hz, 1H), 3.67 (d, *J* = 13.4 Hz, 1H), 3.32 – 3.29 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.49 (q, *J* = 3.7 Hz), 158.79, 147.51, 138.29, 129.88, 128.85, 128.06, 124.20, 122.57 (q, *J* = 275.3 Hz), 113.93, 102.26 (q, *J* = 34.2 Hz), 101.05, 55.15, 35.69, 27.46. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.57. HRMS (ESI) calcd for $C_{19}H_{16}F_3NNaO_3S$: 418.0695, found: 418.0698



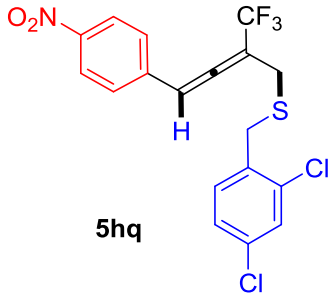
5ho

81 % isolated yield. Colorless oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.79 (q, *J* = 2.7 Hz, 1H), 3.79 – 3.61 (m, 2H), 3.74 (d, *J* = 13.4 Hz, 1H), 3.70 (d, *J* = 13.4 Hz, 1H), 3.33 (d, *J* = 1.7 Hz, 2H), 1.31 (s, 9H). ^{13}C NMR (125MHz, $CDCl_3$) δ 206.62 (q, *J* = 3.8 Hz), 150.39, 147.54, 138.34, 133.90, 128.48, 128.10, 125.52, 124.26, 122.59 (q, *J* = 275.3 Hz), 102.28 (q, *J* = 34.2 Hz), 101.09, 35.87, 34.45, 31.24, 27.68. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.57. HRMS(ESI) calcd for $C_{22}H_{22}F_3NNaO_2S$: 444.1216, found: 444.1226



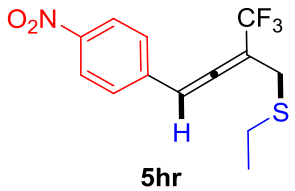
5hp

81 % isolated yield. Colorless oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 6.84 (s, 2H), 6.82 (q, *J* = 2.9 Hz, 1H), 3.84 (d, *J* = 11.4 Hz, 1H), 3.81 (d, *J* = 11.4 Hz, 1H), 3.52 (t, *J* = 2.5 Hz, 2H), 2.35 (s, 6H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.44 (q, *J* = 3.6 Hz), 147.53, 138.27, 136.91, 136.90, 129.75, 129.05, 128.07, 124.20, 122.63 (q, *J* = 275.5 Hz), 102.64 (q, *J* = 34.0 Hz), 101.19, 31.75, 29.65, 20.82, 19.42. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.65. HRMS(ESI) calcd for $C_{21}H_{20}F_3NNaO_2S$:430.1059, found: 430.1062



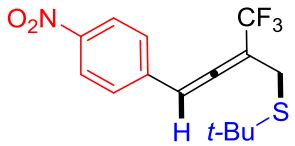
5hq

71 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.34 (d, J = 2.2 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 6.80 (q, J = 2.9 Hz, 1H), 3.83 (d, *J* = 13.7 Hz, 1H), 3.79 (d, *J* = 13.7 Hz, 1H), 3.40 – 3.36 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.45, 147.52, 138.05, 134.62, 133.75, 133.63, 131.28, 129.58, 128.08, 127.17, 124.19, 122.48 (q, *J* = 275.6 Hz), 102.06 (q, *J* = 34.4 Hz), 101.34, 33.37, 28.15. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.71. HRMS (ESI) calcd for $C_{18}H_{12}Cl_2F_3NNaO_2S$: 455.9810, found: 455.9811



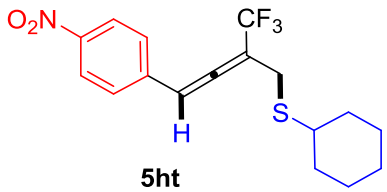
5hr

78 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 6.79 (q, *J* = 2.8 Hz, 1H), 3.42 (d, *J* = 2.5 Hz, 2H), 2.62 – 2.53 (m, 2H), 1.23 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.49 (q, *J* = 3.8 Hz), 147.55, 138.34, 128.07, 124.20, 122.61 (q, *J* = 272.5 Hz), 102.39 (q, *J* = 34.2 Hz), 100.99, 28.10, 26.11, 14.13. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.70. HRMS (ESI) calcd for $C_{13}H_{12}F_3NNaO_2S$: 326.0433, found: 326.0432.



5hs

62 % isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.76 (q, *J* = 2.9 Hz, 1H), 3.42 (d, *J* = 2.9 Hz, 2H), 1.33 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.51 (q, *J* = 3.4 Hz), 147.51, 138.32 , 128.16, 124.17, 122.69 (q, *J* = 275.1 Hz), 102.75 (q, *J* = 34.3 Hz), 101.32, 43.20, 30.65, 24.90. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.01. HRMS (ESI) calcd for $C_{15}H_{16}F_3NNaO_2S$: 354.0746, found: 354.0754.



5ht

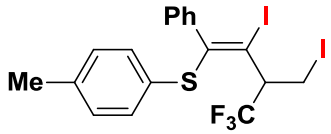
65 % isolated yield. Colorless oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 6.78 (q, *J* = 2.8 Hz, 1H), 3.43 (d, *J* = 2.7 Hz, 2H), 2.70 – 2.61(m, 1H), 1.98 – 1.84 (m, 2H), 1.78 – 1.65 (m, 2H), 1.61 – 1.51 (m, 1H), 1.38–1.07 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.51 (q, *J* = 3.6 Hz), 147.48, 138.40,

128.08, 124.12, 122.63 (q, J = 275.3 Hz), 102.77 (q, J = 34.2 Hz), 101.01, 43.69, 33.12, 33.08, 26.60, 25.94, 25.85, 25.57. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.72. HRMS (ESI) calcd for $C_{17}H_{18}F_3NNaO_2S$: 380.0905, found: 380.0903.

7. Derivatizations of alkyne **3aa**, 1,3-diene **4aa** and allene **5eh**, **5hh**

(1) Synthesis of diiodic compound 6

Under N_2, to a solution of **3aa** (0.5 mmol, 160 mg) in toluene (2.0 mL) was added I_2 (0.5 mmol, 127 mg) at room temperature. The reaction mixture was stirred for 12 h, saturated $Na_2S_2O_3$ (5.0 mL) solution was added then stirring for 10 min until the reaction mixture turn to colorless, then extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography (silica gel, PE) to afford **6** (143 mg, 50% yield) as a colorless solid.

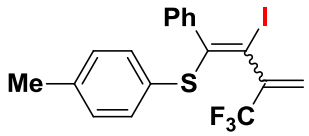


6

50% isolated yield. Colorless solid. Mp 35.1-37.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.06 (m, 7H), 6.91 (d, J = 7.6 Hz, 2H), 4.88 – 4.77 (m, 1H), 3.64 (dd, J = 10.1, 2.6 Hz, 1H), 3.51 (dd, J = 10.8 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.89, 142.64, 138.55, 133.85, 129.43, 129.21, 128.25, 127.99, 127.73, 124.18 (q, J = 283.9 Hz), 96.61, 52.37 (q, J = 27.6 Hz), 21.12, 3.18. ^{19}F NMR (471 MHz, $CDCl_3$) δ-66.71. HRMS(ESI) calcd for $C_{18}H_{15}F_3IS$ [M-I$^+$]: 446.9886, found: 446.9892.

(2) Synthesis of *β*-iodo alkenyl sulfides 7

Under N_2, to a solution of **3aa** (0.2 mmol, 64 mg) in toluene (2.0 mL) was added NIS (0.6 mmol, 135 mg) at room temperature. The reaction was monitored through TLC (hexanes). After stirring for 12 h, saturated $Na_2S_2O_3$ (2.0 mL) solution was added then stirring for 10 min until the reaction mixture turn to colorless, then extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography (silica gel, PE) to afford **7** (86 mg, 96% yield, *E/Z* = 2:3) as a colorless oil.



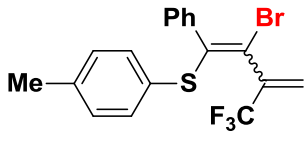
7

96% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ [7.22– 6.84 (m, 9H)], [6.01 (s, 0.38H, 5.57 (s, 0.60H)], [5.80 (s, 0.38H), 5.34 (s, 0.58H)], [2.20 (s, 1.1H), 2.1 8(s, 1.8H)]. ^{13}C NMR (125 MHz, $CDCl_3$) δ (152.94, 148.00), [140.33 (q, *J* = 32.1 Hz), 140.19 (q, *J* = 31.7 Hz)], (141.13, 138.48), (138.20, 136.10), 134.69, (133.47, 129.55), (129.30, 129.22), (128.92, 128.68), (128.09, 127.72), (127.56, 127.40), [124.85 (q, *J* = 4.3 Hz), 124.38 (q, *J* = 4.5 Hz)], [122.26 (q, *J* = 275.5 Hz), 122.07 (q, *J* = 276.0 Hz)], (82.87, 82.13), (21.09, 21.06). ^{19}F NMR (471 MHz, $CDCl_3$) δ (-63.35, -64.33). MS (70 eV): m/z (%): 446 (M^+, 56.93), 123 (100). HRMS(EI) calcd for $C_{18}H_{14}IF_3S$: 445.9813, found: 445.9810

(3) Synthesis of *β*-bromo alkenyl sulfides 8

Under N_2, to a solution of **3aa** (0.2 mmol, 64 mg) in toluene (2.0 mL) was added NBS (0.6 mmol, 106 mg) at room temperature. The reaction

was monitored through TLC (hexanes). After stirring for 12 h, saturated $Na_2S_2O_3$ (2.0 mL) solution was added then stirring for 10 min until the reaction mixture turn to colorless, then extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography (silica gel, PE) to afford **8** (78 mg, 98% yield, *E/Z* = 10:1) as a colorless oil.



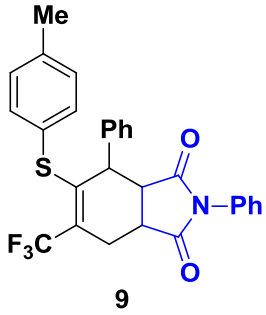
8

98% isolated yield. Colorless solid. Mp 47.2-49.0 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ [7.25-7.13 (m. 5H)], [7.07 (d, *J* = 8.1 Hz, 0.2H), 7.01 (d, *J* = 8.1 Hz, 1.8H)], [6.89 (d, *J* = 7.9 Hz, 1.8H), 6.85 (d, *J* = 7.9 Hz, 0.2H)], [6.14 (d, *J* = 1.1 Hz, 0.9H), 5.67 (d, *J* = 1.1 Hz, 0.1H)], [5.87 (d, *J* = 1.3 Hz, 0.9H), 5.36 (d, *J* = 1.3 Hz, 0.1H)], [2.20 (s, 2.7H), 2.19 (s, 0.3H)]. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.08, 138.05, 138.03, 137.63 (q, *J* = 32.4 Hz), (134.89, 132.99), (129.66, 129.46), (129.39, 129.21), 128.68, 128.12, 127.69, 125.81 (q, *J* = 4.5 Hz), 122.15 (q, *J* = 275.4 Hz), 109.36, 21.06. ^{19}F NMR (471 MHz, $CDCl_3$) δ (-63.99, -64.86). MS (70 eV): m/z (%): 398 (M^+, 53.32), 228 (100). HRMS(EI) calcd for $C_{18}H_{14}BrF_3S$: 397.9952, found: 397.9954.

(4) Synthesis of cycloaddition product 9

Under N_2, **4aa** (0.3 mmol, 96 mg) and N-phenyl-Maleimidein (0.6 mmol, 104 mg) in PhCl (4 mL) was heated at 150 ℃ in a sealed tube for 48 h. The reaction solvent was removed under reduced pressure and residue was purified by column chromatography (silica gel, PE:EA =

20:1) to afford the desired product **9** (92 mg, 62%, dr = 8:1) as a colorless solid.



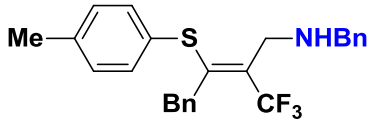
9

62% isolated yield. Colorless solid. Mp 137.2-139.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 6H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.42 – 6.38 (m, 2H), 4.11 (d, *J* = 6.9 Hz, 1H), 3.45 – 3.36 (m, 1H), 3.30 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.20 (dd, *J* = 19.0, 2.7 Hz, 1H), 3.10 (dd, *J* = 19.4, 11.4 Hz, 1H), 2.37 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.43. ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.28, 175.15, 142.43 (d, *J* = 2.4 Hz), 139.67, 134.89, 134.78, 130.93, 130.03, 128.89, 128.86, 128.76, 128.52, 128.12, 126.11, 125.79, 124.32 (q, *J* = 30.0 Hz), 123.66 (q, *J* = 275.6 Hz), 45.38, 36.45, 22.31 (q, *J* = 3.3 Hz), 21.16, 0.95. ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.43. HRMS(ESI) calcd for $C_{28}H_{22}F_3NNaO_2S$ [M+H$^+$]: 516.1216, found: 516.1224.

(5) Synthesis of alkenyl sulfides 10

Under N_2, to a solution of **4-4aa** (0.5 mmol, 160 mg) in DMSO (4.0 mL) was added $BnNH_2$ (1.0 mmol, 107 mg) at room temperature. The reaction was monitored through TLC (petroleum ether: ethyl acetate = 5:1). After stirring for 12 h, water (15 mL) was added to reaction mixture and extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash

column chromatography on silica gel (silica gel, PE:EA = 5:1) to afford **10** (169 mg, 86% yield) as a colorless oil.

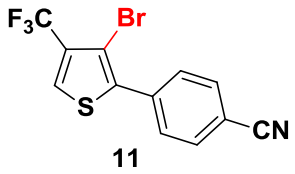


10

86% isolated yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.16 (m, 10H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 6.7 Hz, 2H), 3.74 (s, 2H), 3.51 (s, 2H), 3.44 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.87, 139.69, 138.98, 137.57, 134.39, 129.83, 128.40, 128.38, 128.07, 127.85, 127.58, 127.53 (d, *J* = 27.6 Hz), 127.06, 126.46, 124.31 (d, *J* = 276.2 Hz), 53.03, 46.74 (d, *J* = 2.2 Hz), 37.37, 21.16. ^{19}F NMR (471 MHz, $CDCl_3$) δ -57.57.HRMS(ESI) calcd for $C_{25}H_{25}F_3NS$ [M+H$^+$]: 428.1654, found: 428.1658.

(6) Synthesis of 3-bromo-thiophene derivative 11

Under N_2, to a solution of **5eh** (0.2 mmol, 69 mg) in toluene (2.0 mL) was added NBS (0.6 mmol, 107 mg) at room temperature. The reaction was monitored through TLC (petroleum ether: ethyl acetate = 20:1). After stirring for 4 h, saturated $Na_2S_2O_3$ (2.0 mL) solution was added then stirring for 10 min until the reaction mixture turn to colorless, then extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography silica gel (petroleum ether: ethyl acetate = 100:1~50:1)) to afford **11** (54 mg, 81% yield) as a colorless solid.

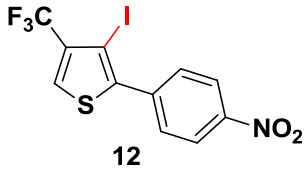


11

81% isolated yield. White solid; Mp 92.8-94.5 ^{o}C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.47, 136.36, 132.40, 132.05 (q, *J* = 35.0 Hz), 129.94, 128.28 (q, *J* = 5.1 Hz), 120.76 (q, *J* = 270.8 Hz), 118.18, 112.69, 106.06. ^{19}F NMR (471MHz, $CDCl_3$) δ -62.53. MS(70 ev): m/z(%): 331(M^+, 99.39), 333(100). HRMS (EI) calcd for $C_{12}H_5F_3NBrS$: 330.9278, found: 330.9274.

(7) Synthesis of 3-iodo-thiophene derivative 12

Under N_2, to a solution of **5hh** (0.2 mmol, 69 mg) in toluene (2.0 mL) was added NIS (0.6 mmol, 135 mg) at room temperature. The reaction was monitored through TLC (petroleum ether: ethyl acetate = 20:1). After stirring for 4 h, saturated $Na_2S_2O_3$ (2.0 mL) solution was added then stirring for 10 min until the reaction mixture turn to colorless, then extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography silica gel (petroleum ether: ethyl acetate = 100:1~50:1)) to afford **12** (63 mg, 79% yield) as a yellow solid.

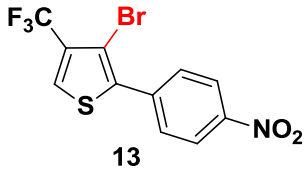


12

79% isolated yield. Yellow solid. Mp 110.2-112.8 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 2H), 7.95 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.93, 143.27, 140.04, 135.19 (q, *J* = 34.5 Hz), 130.88, 129.55 (q, *J* = 5.3 Hz), 123.84, 120.86 (q, *J* = 271.2 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.44. MS (70 ev): m/z(%): 399(M^+, 100), 399(100). HRMS (EI) calcd for $C_{11}H_5IF_3NO_2S$: 398.9038, found: 398.9041.

(8) Synthesis of 3-bromo-thiophene derivative 13

Under N_2, to a solution of **5eh** (0.2 mmol, 69 mg) in toluene (2.0 mL) was added NBS (0.6 mmol, 107 mg) at room temperature. The reaction was monitored through TLC (petroleum ether: ethyl acetate = 20:1). After stirring for 12 h, saturated $Na_2S_2O_3$ (2.0 mL) solution was added then stirring for 10 min until the reaction mixture turn to colorless, then extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography silica gel (petroleum ether: ethyl acetate = 100:1~50:1)) to afford **13** (59 mg, 84% yield) as a colorless solid.



13

84% isolated yield. White solid. Mp 108.3-110.9 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.3 Hz, 2H), 7.91 (s, 1H), 7.81 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.92, 139.14, 138.28, 132.33 (q, *J* = 35.0 Hz), 130.29, 128.48 (q, *J* = 5.2 Hz), 123.97, 120.80 (q, *J* = 268.8Hz), 106.53. ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.18.

MS(70 ev): m/z(%): 351(M^+, 39.03), 99(100). HRMS(EI) calcd for $C_{11}H_5BrF_3NO_2S$: 350.9176, found: 350.9181.

8. Reference:

[1] Q. Zeng, L. Zhang, J. Yang, B. Xu, Y. Xiao and J. Zhang, *Chem. Commun.*, **2014**, *50*, 4203.

[2] K. Uneyama, T. Katagiri, H. Amii, *Acc. Chem. Res*. **2008**, *41*, 817–829.

9. X-ray structures for 1,3-diene 4ag and diiodic compounds 6

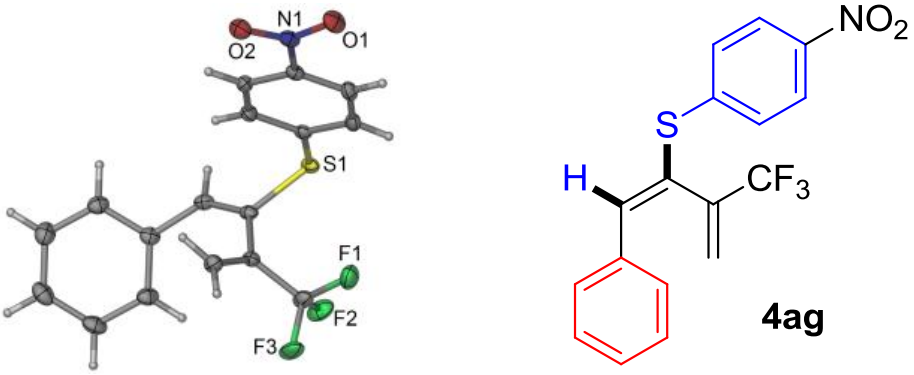


Figure 1. ORTEP depiction of compound **4ag**, CCDC1867549

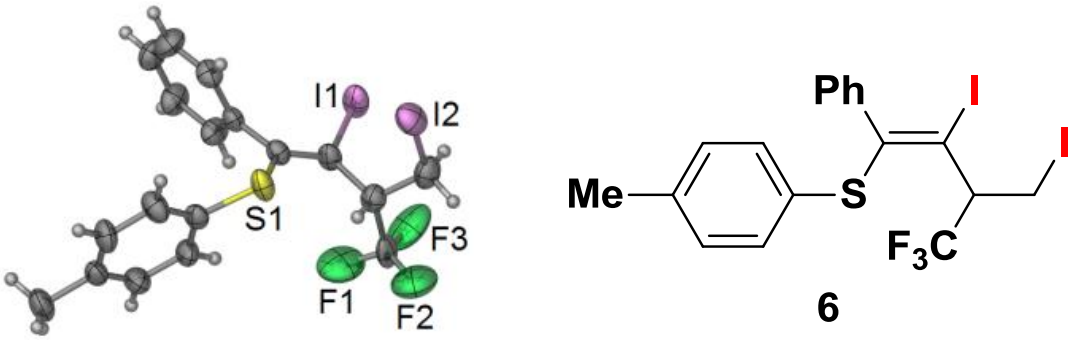
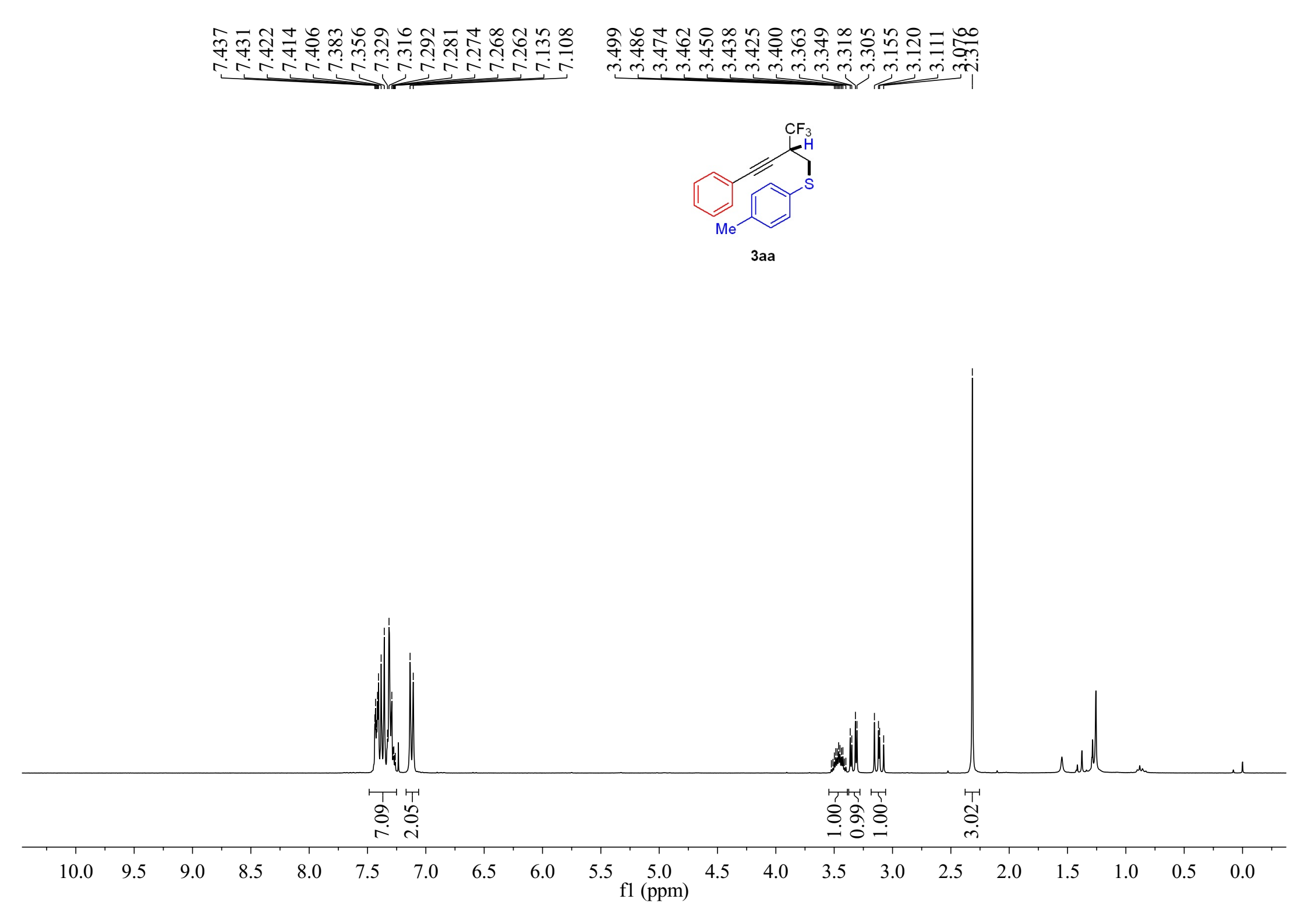


Figure 2. ORTEP depiction of compound **6**, CCDC1860794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7.268
7.262
7.135
7.108
3.499
3.486
3.474
3.462
3.450
3.438
3.425
3.400
3.363
3.349
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3.305
3.155
3.120
3.111
3.076
2.318
CF3
H
S
Me
3aa
7.09
2.05
1.00
0.99
1.00
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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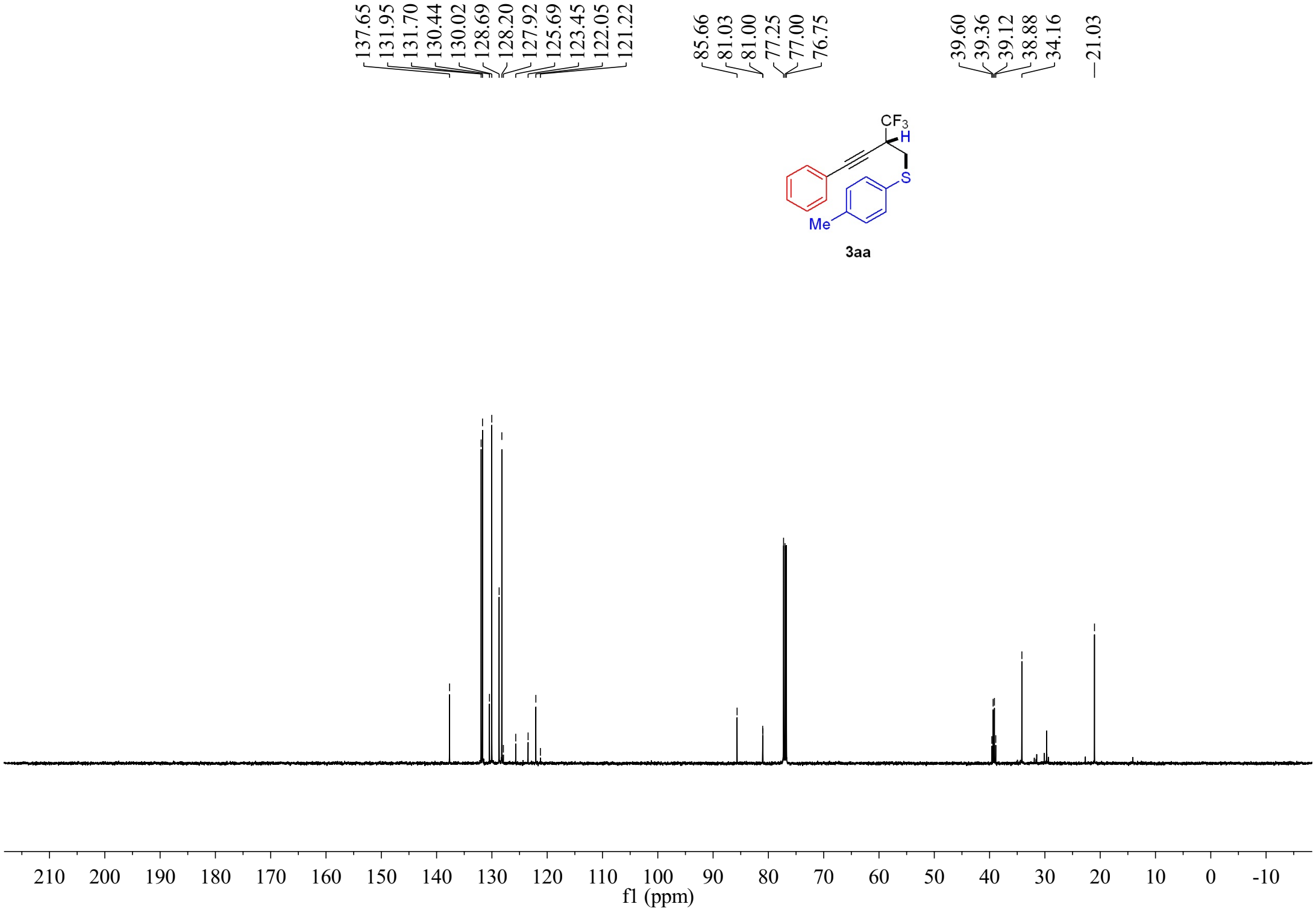
f1 (ppm)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81.00
77.25
77.00
76.75
39.60
39.36
39.12
38.88
34.16
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Me
3aa
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190
180
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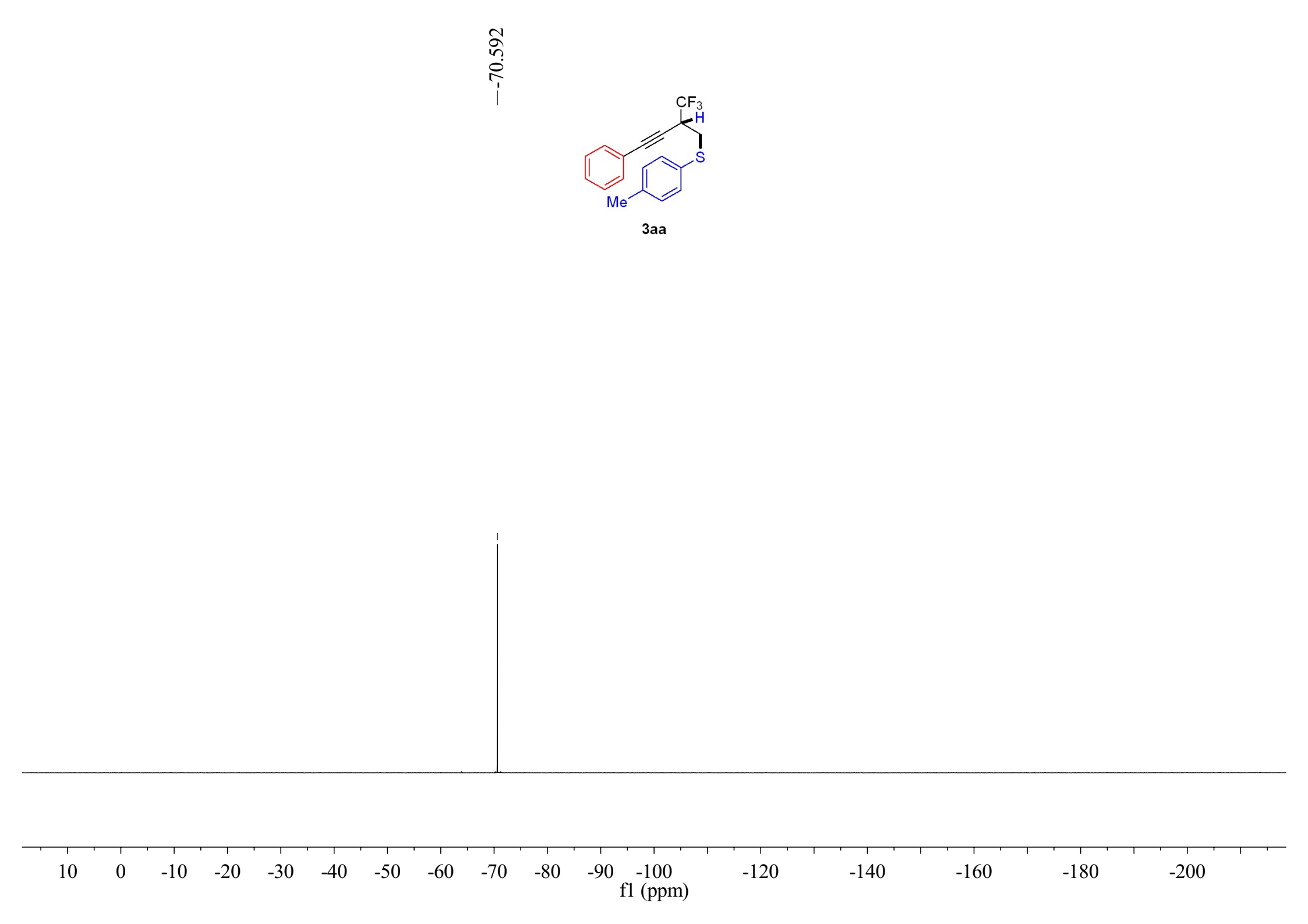
f1 (ppm)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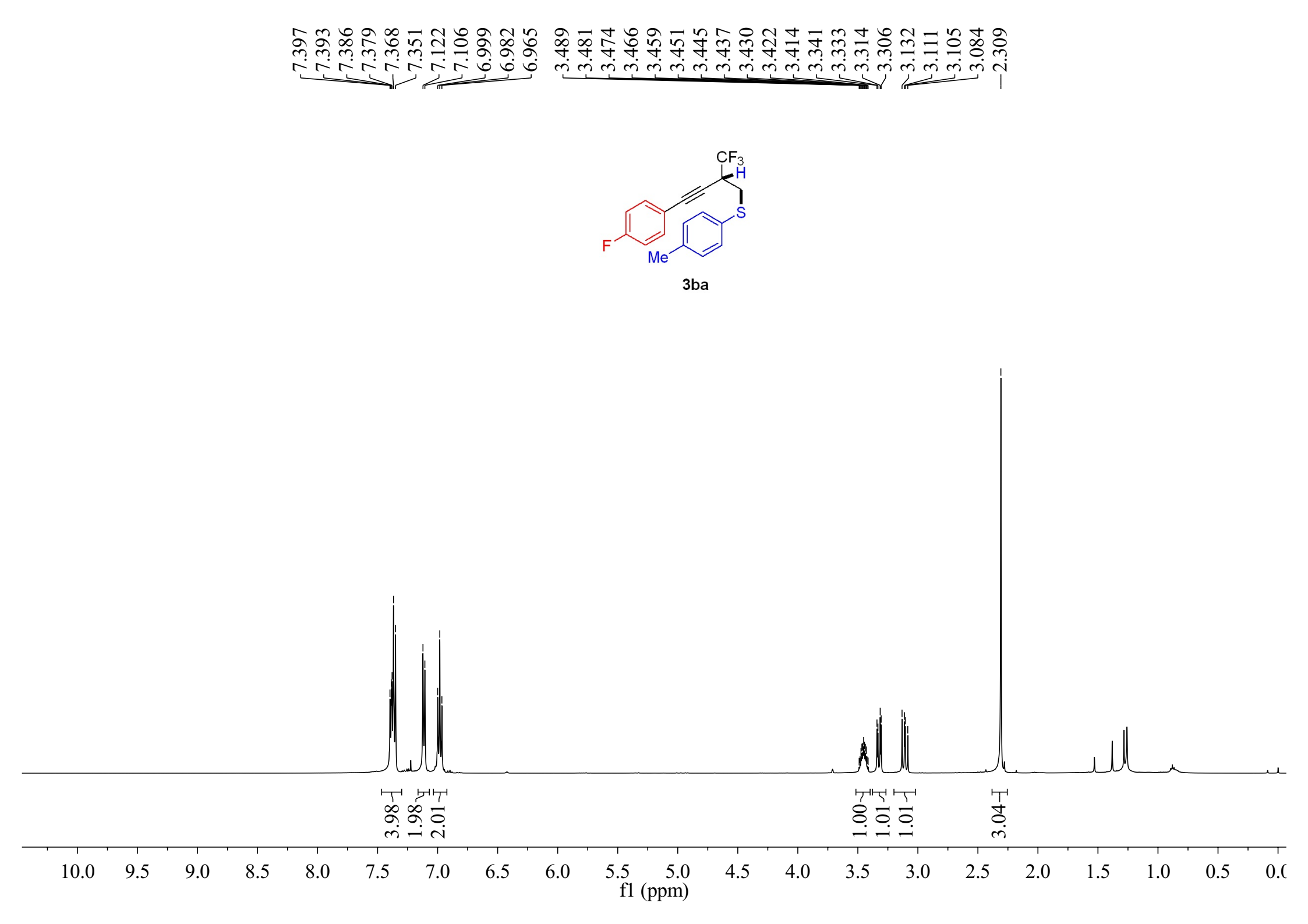
f1 (ppm)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3.306
3.132
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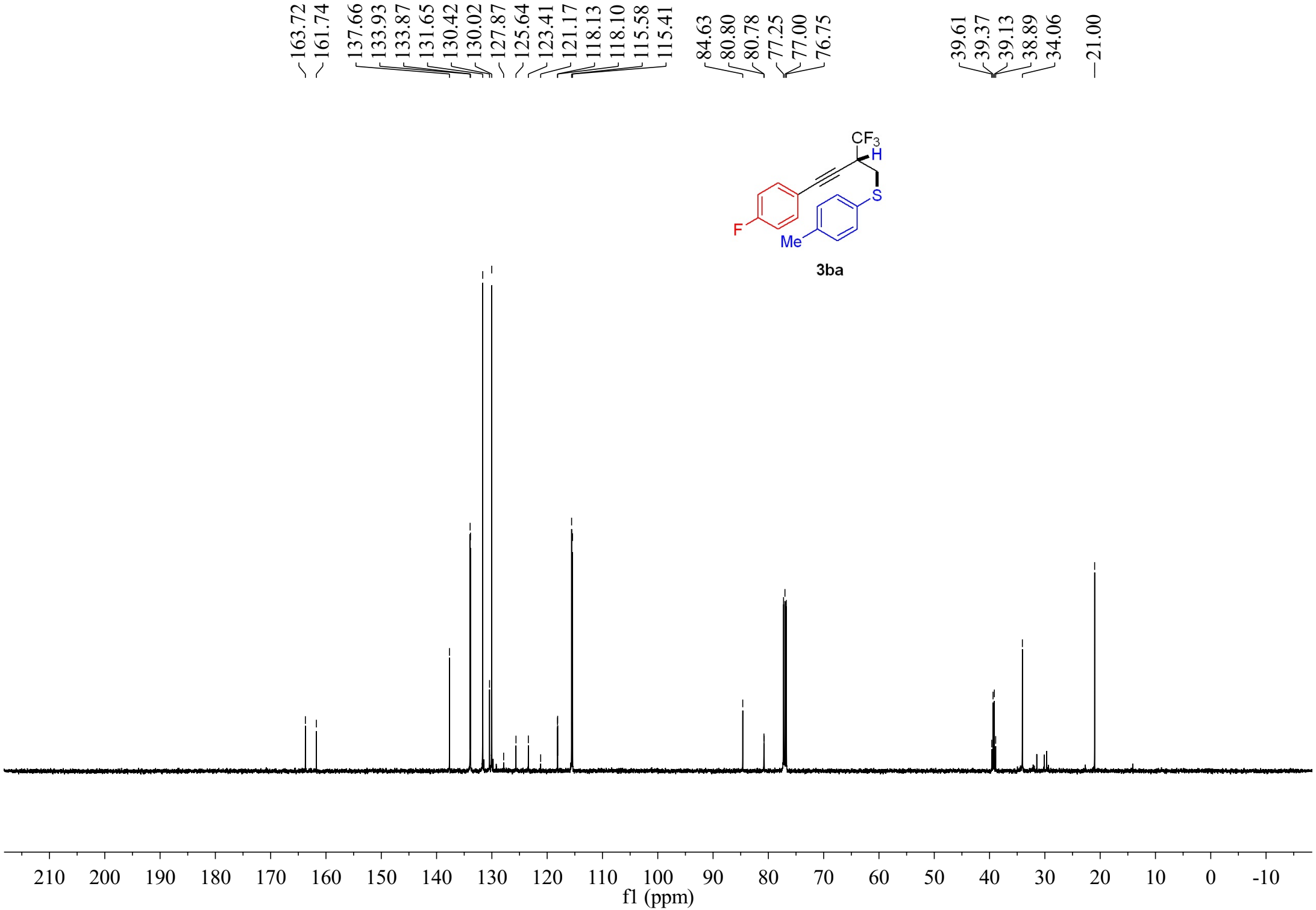
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118.13
118.10
115.58
115.41
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80.80
80.78
77.25
77.00
76.75
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39.37
39.13
38.89
34.06
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H
S
F
Me
3ba
210
200
190
180
170
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120
110
100
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80
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30
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0
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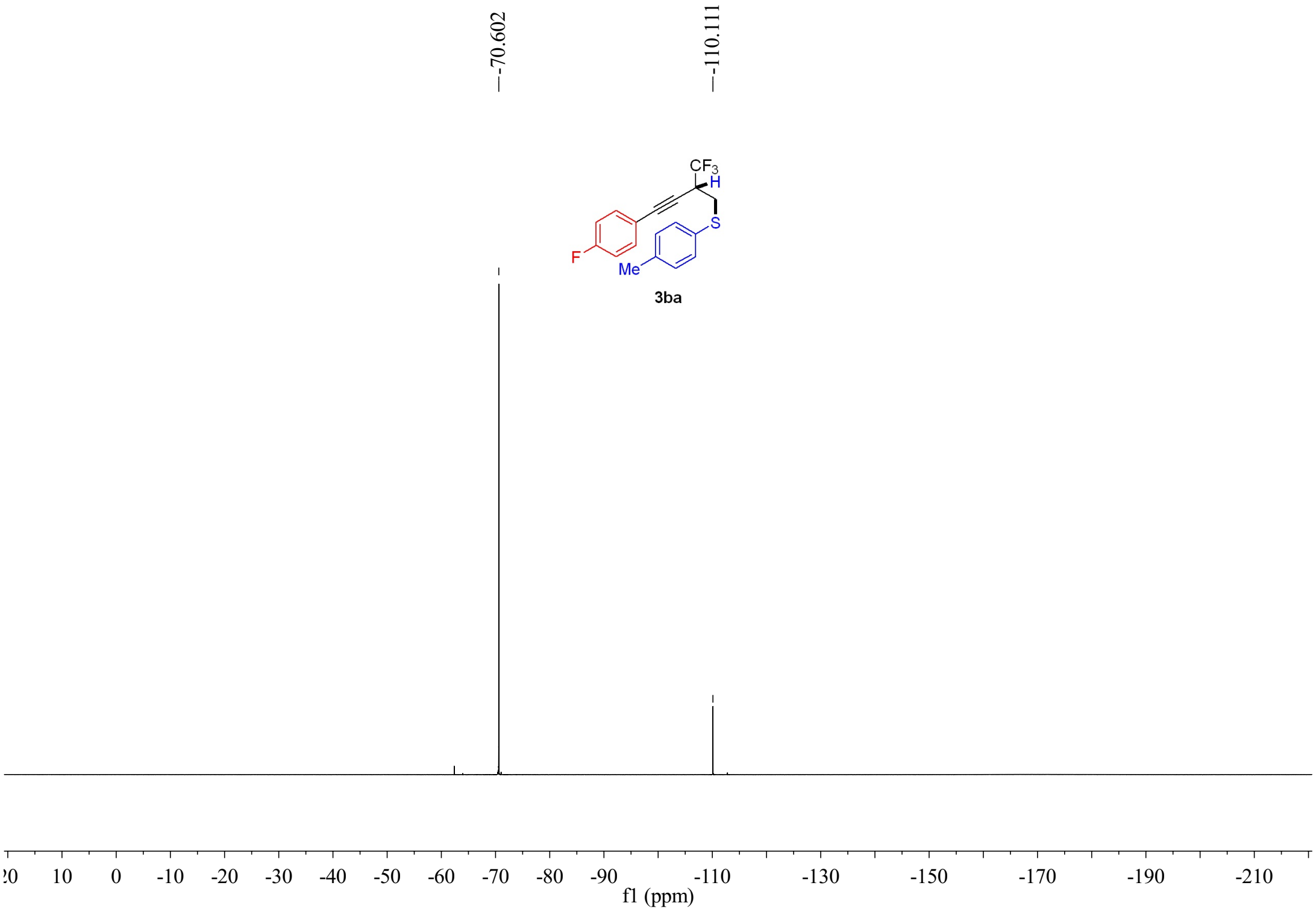
f1 (ppm)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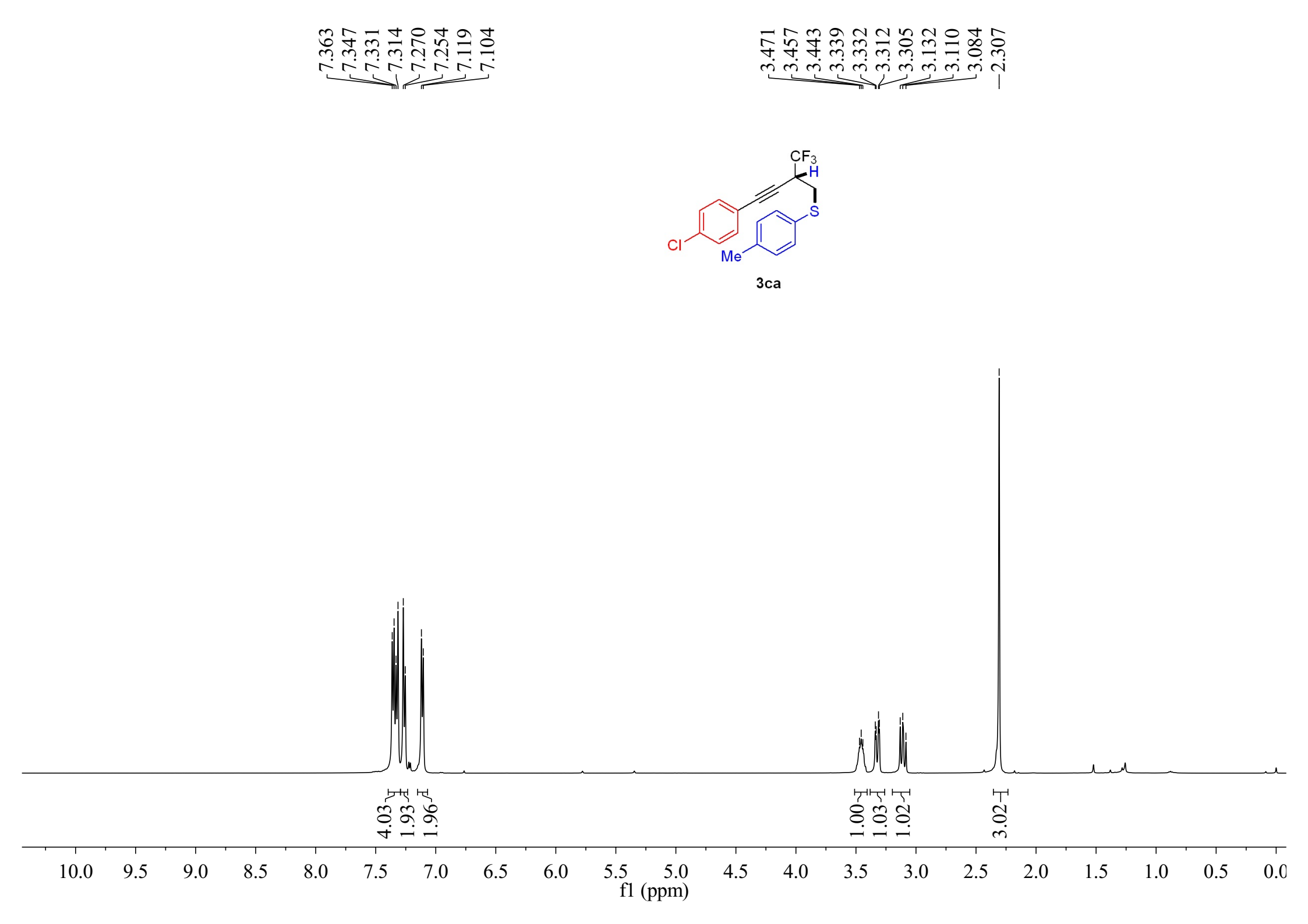
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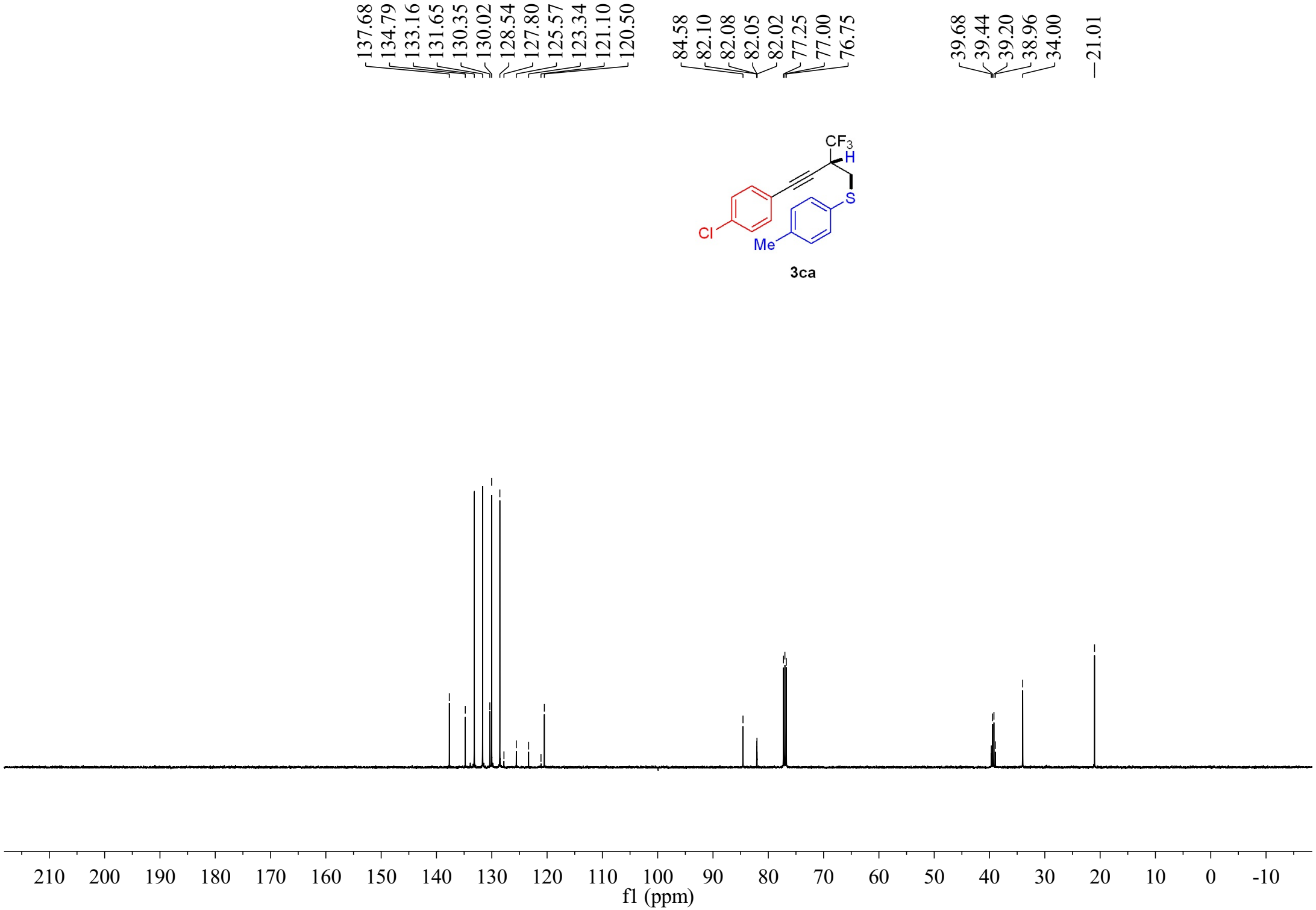
f1 (ppm)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21.01
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S
Cl
Me
3ca
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200
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180
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100
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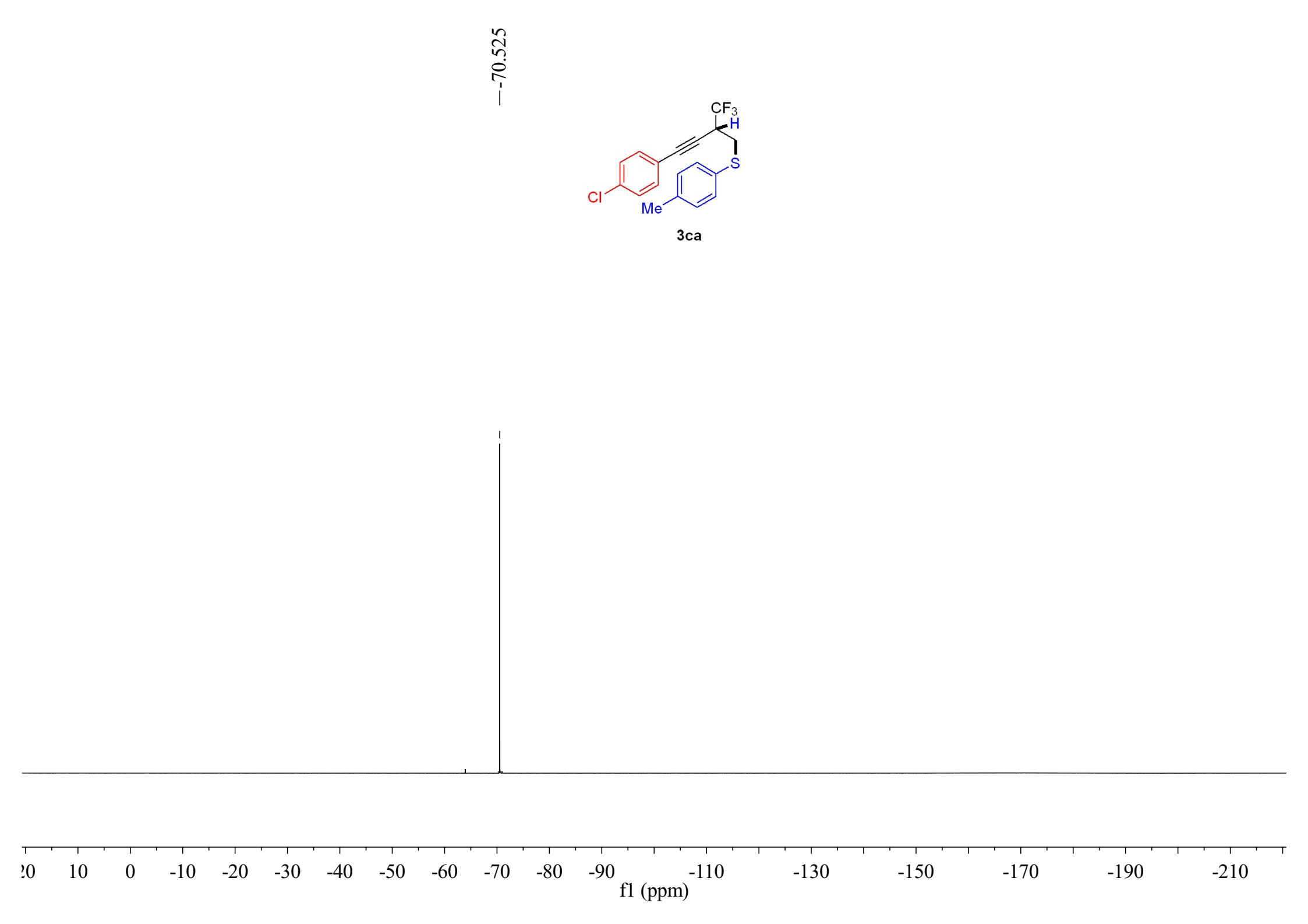
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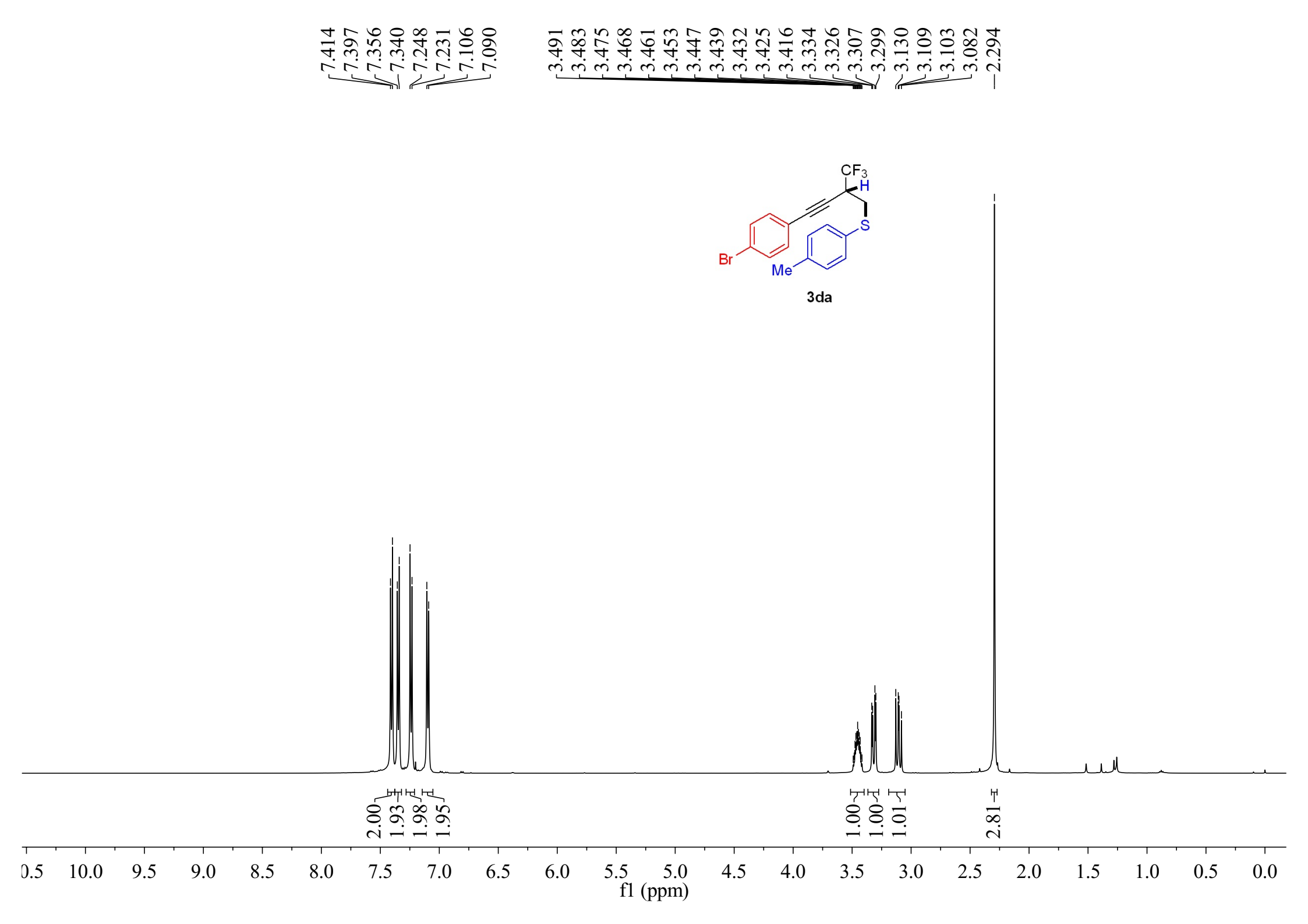
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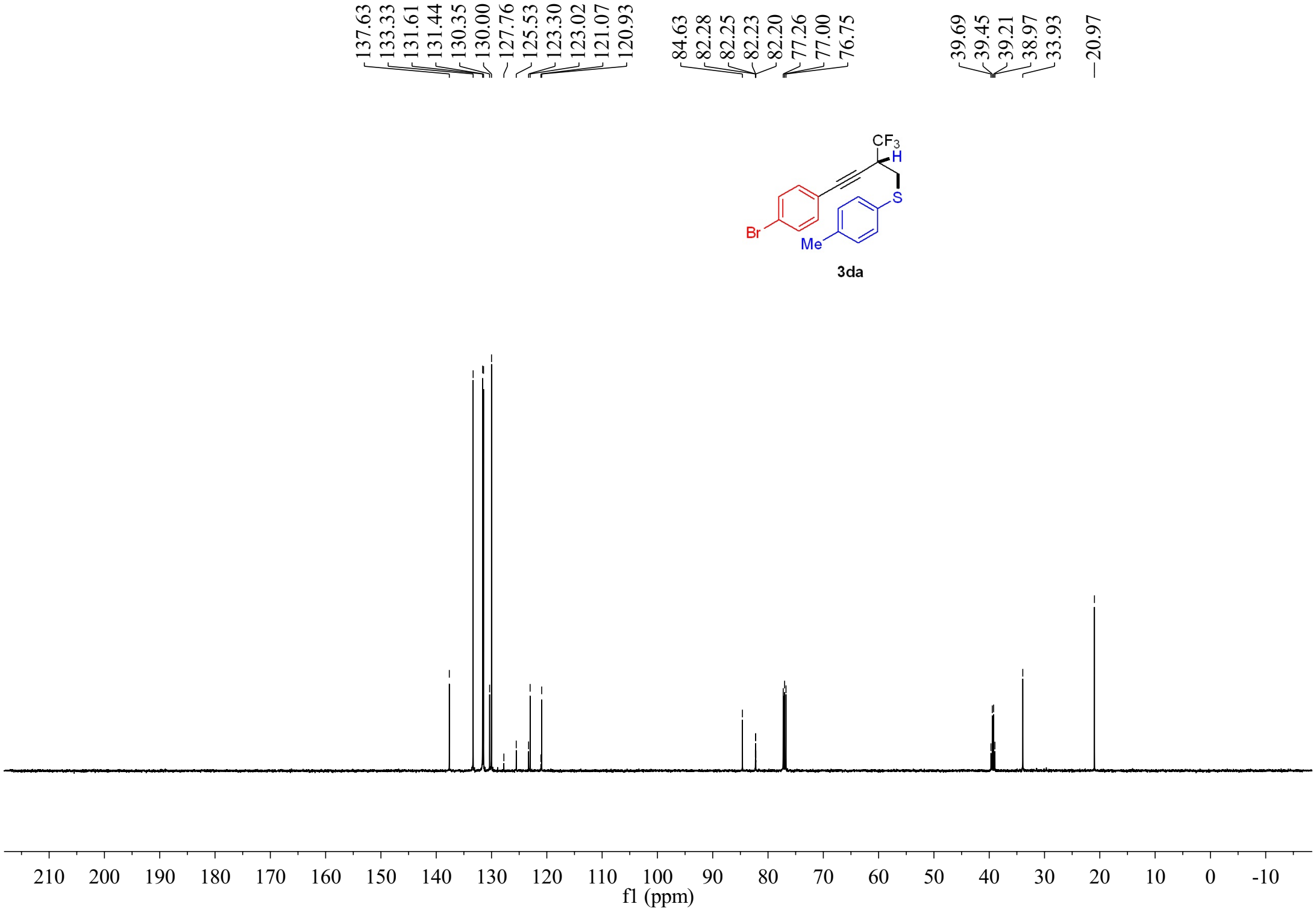
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S
Br
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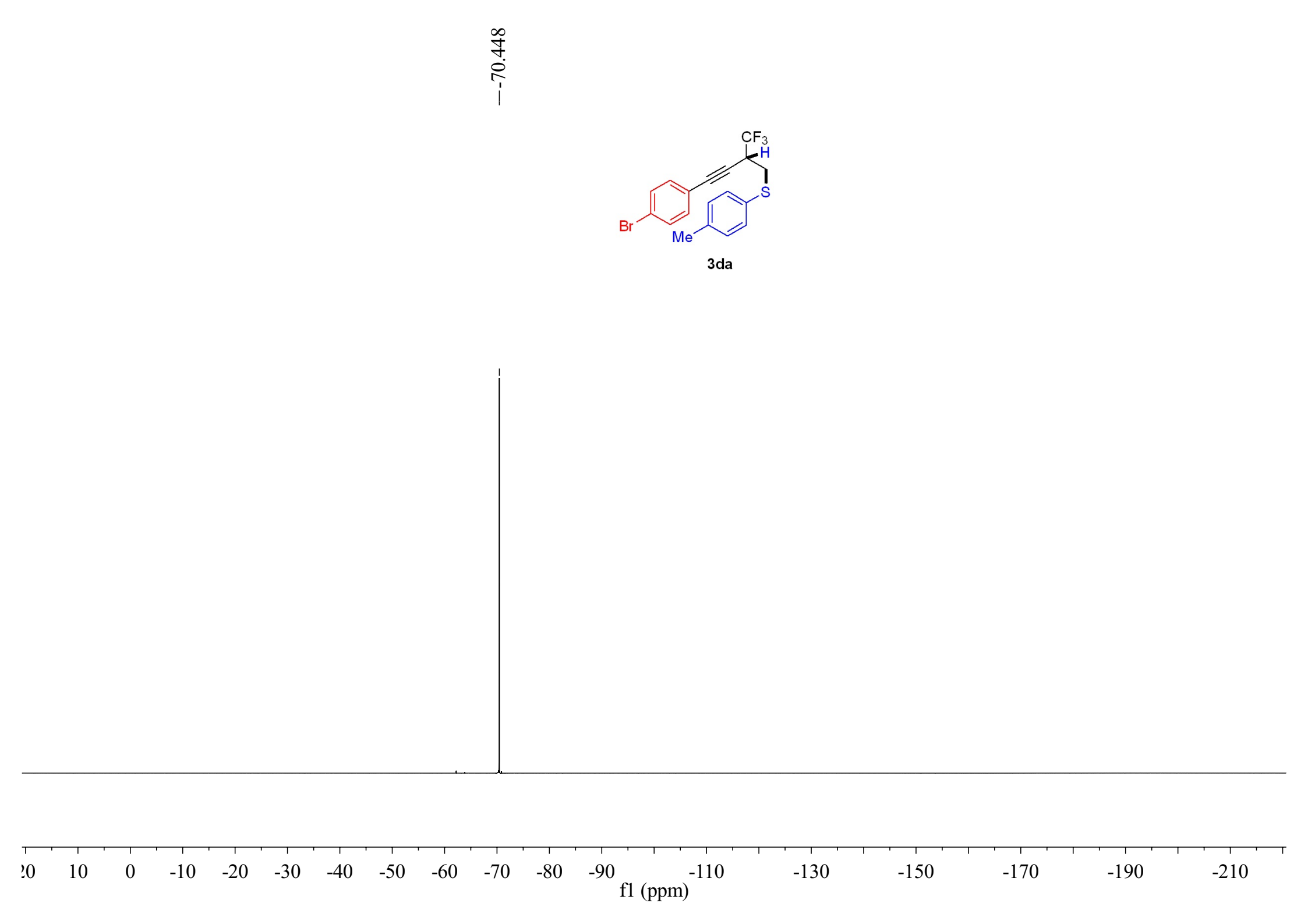
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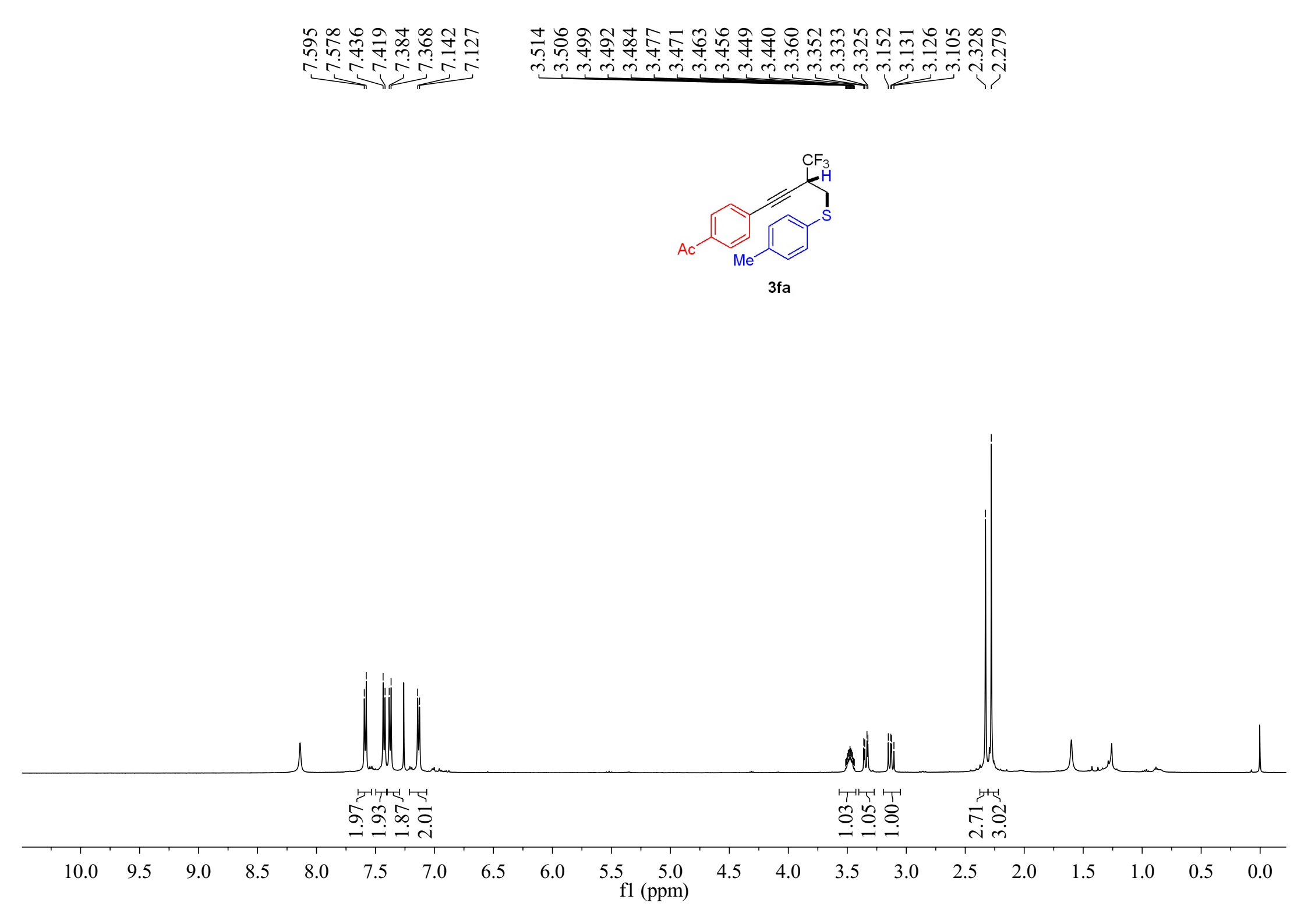
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1.05
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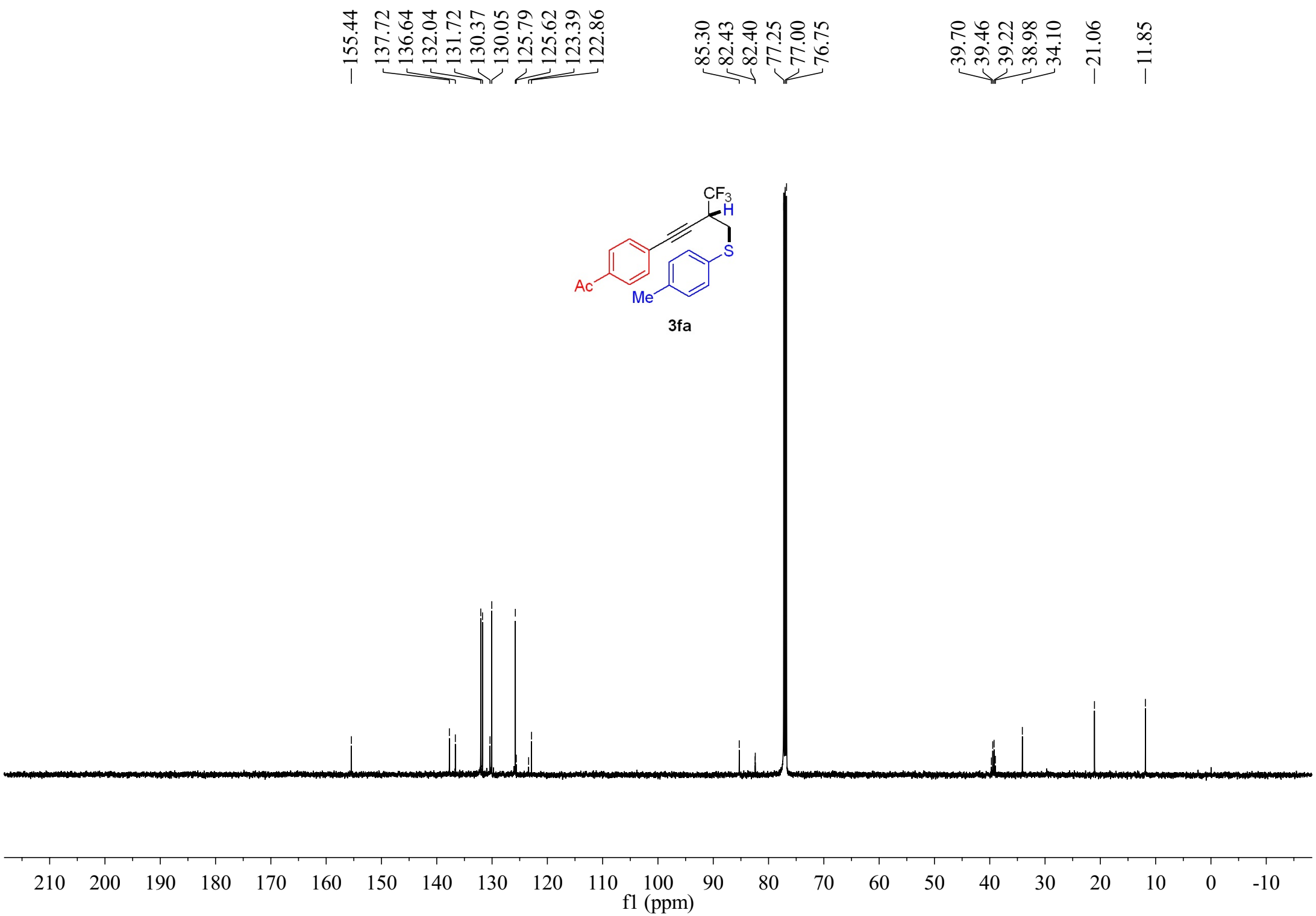
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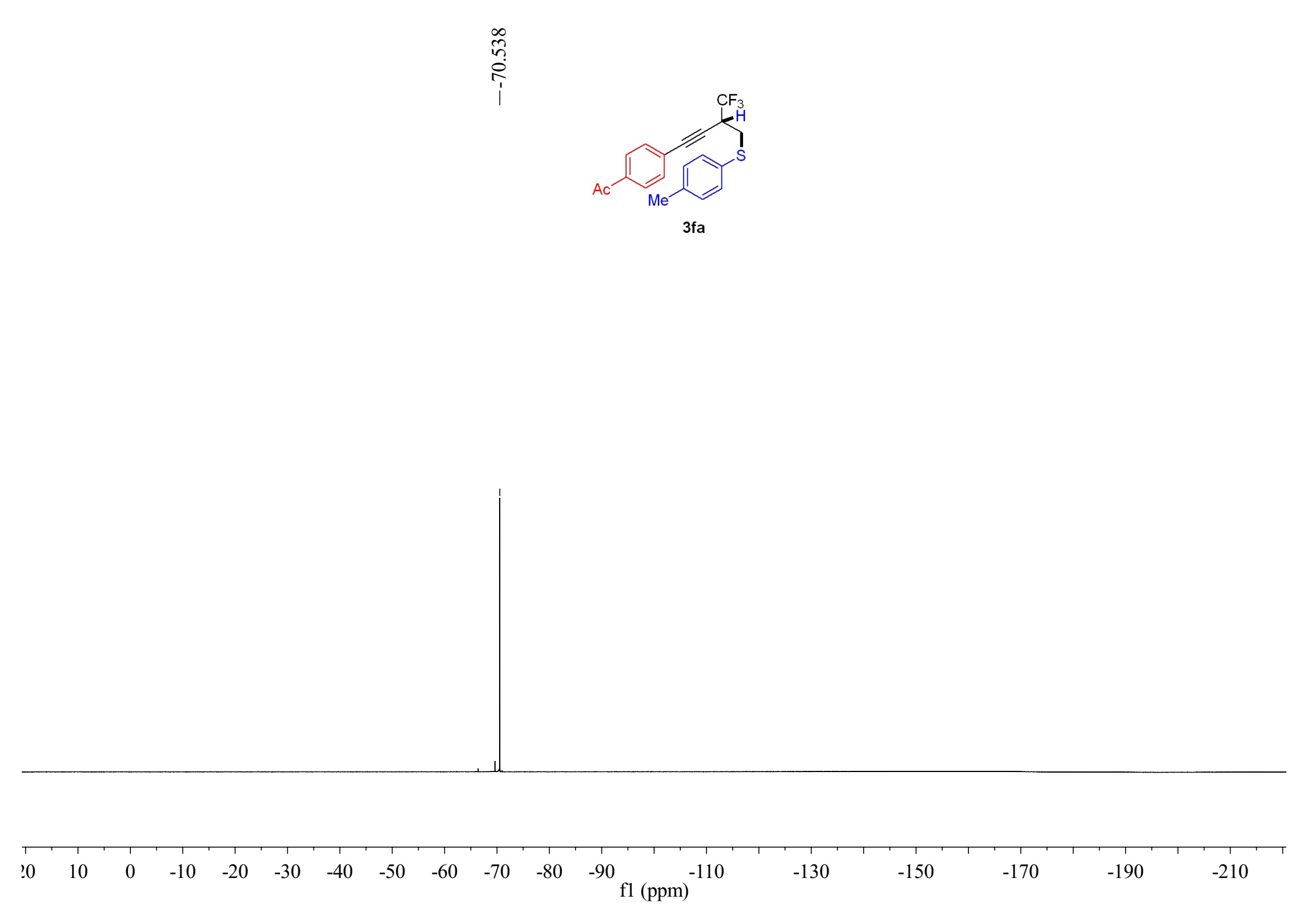
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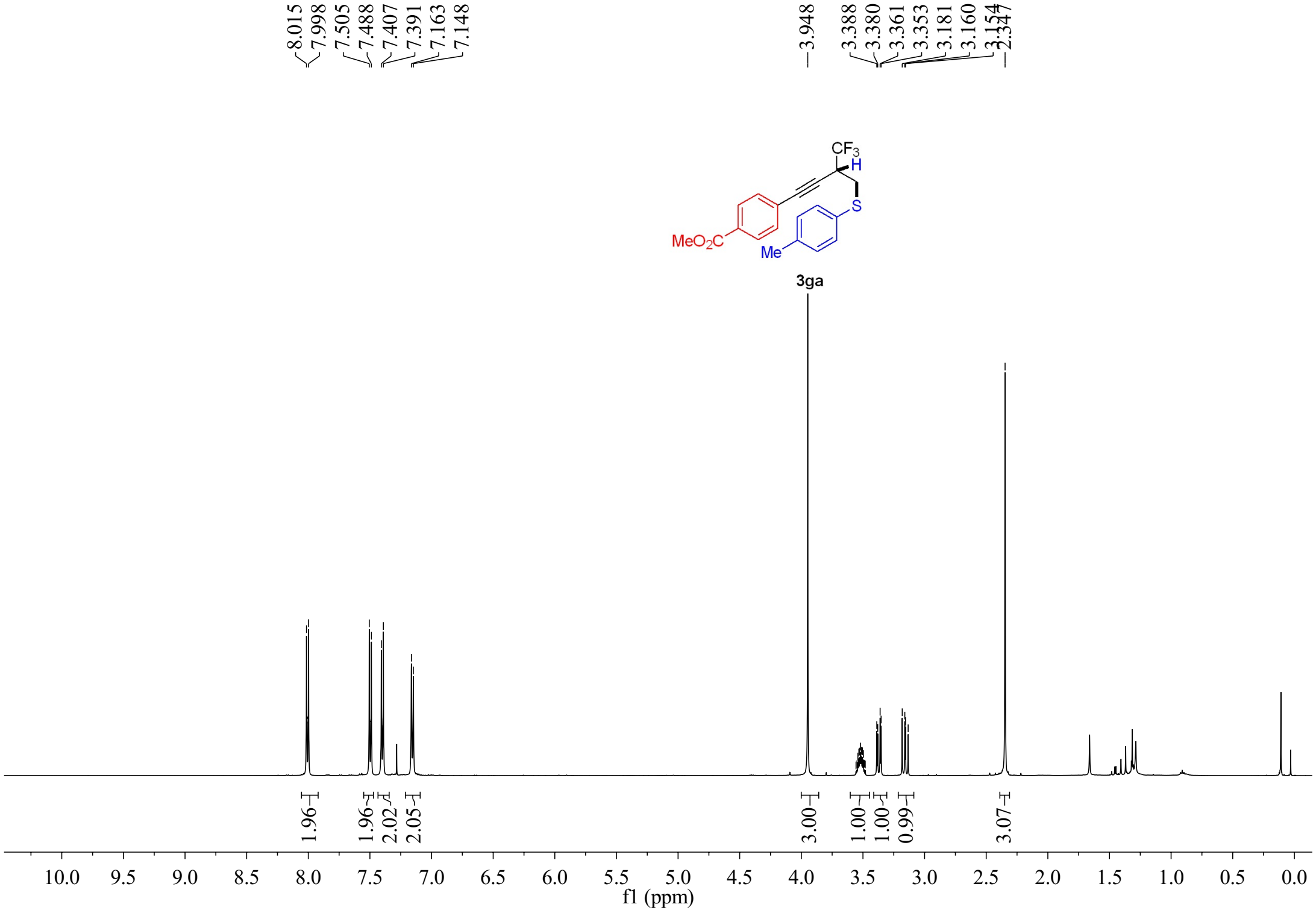
f1 (ppm)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1.00
0.99
3.07
10.0
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7.0
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6.0
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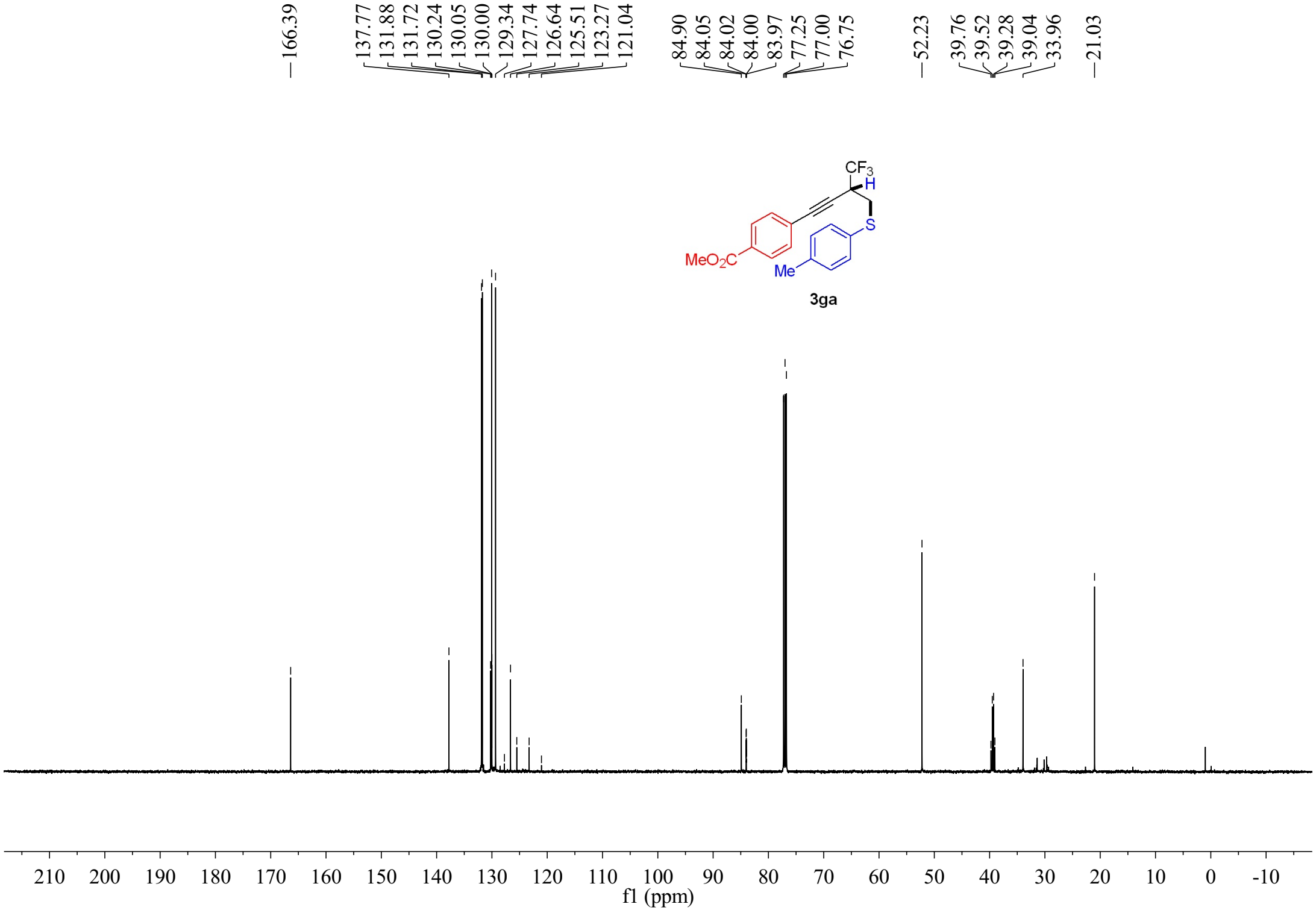
f1 (ppm)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84.05
84.02
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77.00
76.75
52.23
39.76
39.52
39.28
39.04
33.96
21.03
CF3
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S
MeO2C
Me
3ga
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200
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180
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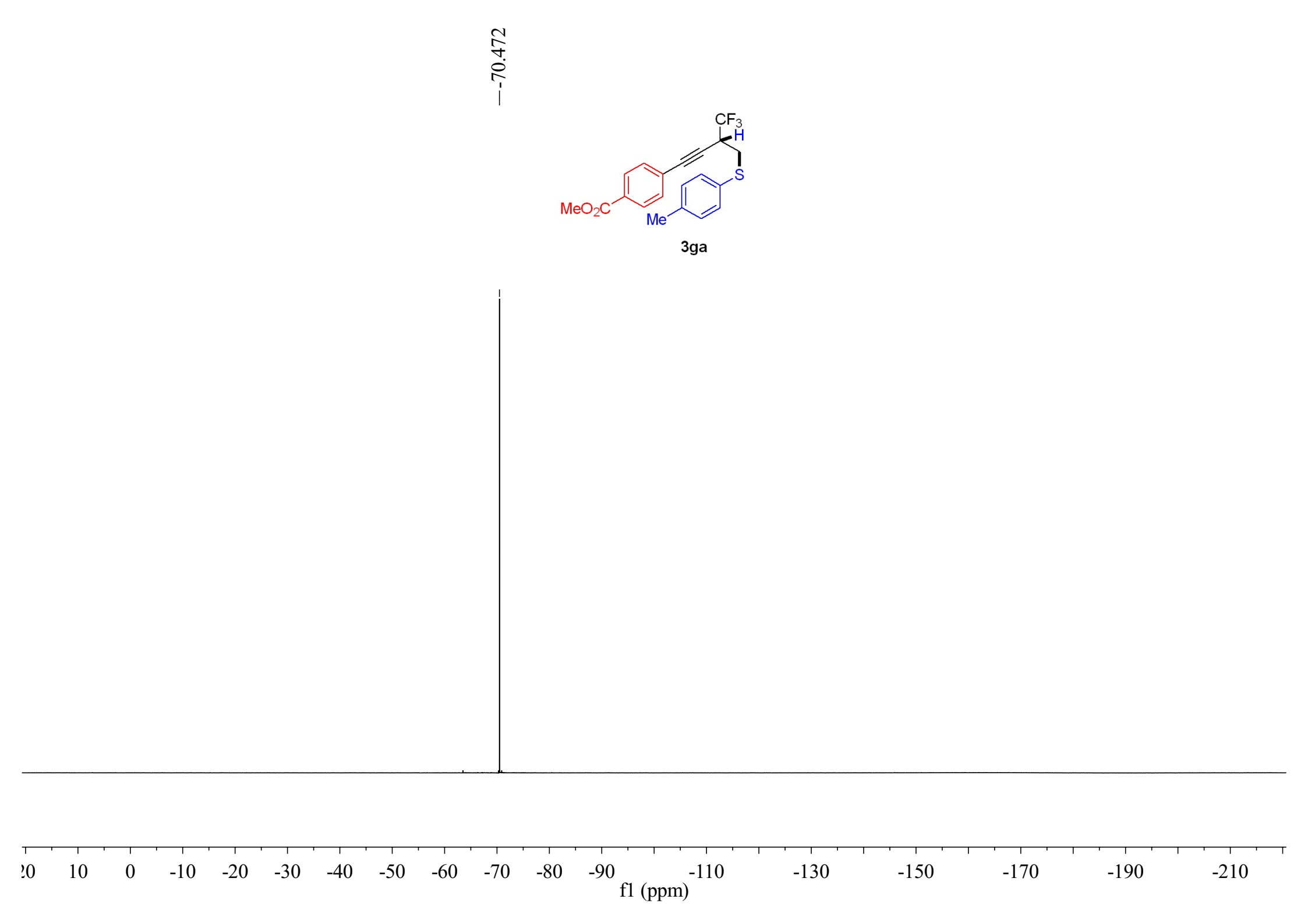
f1 (ppm)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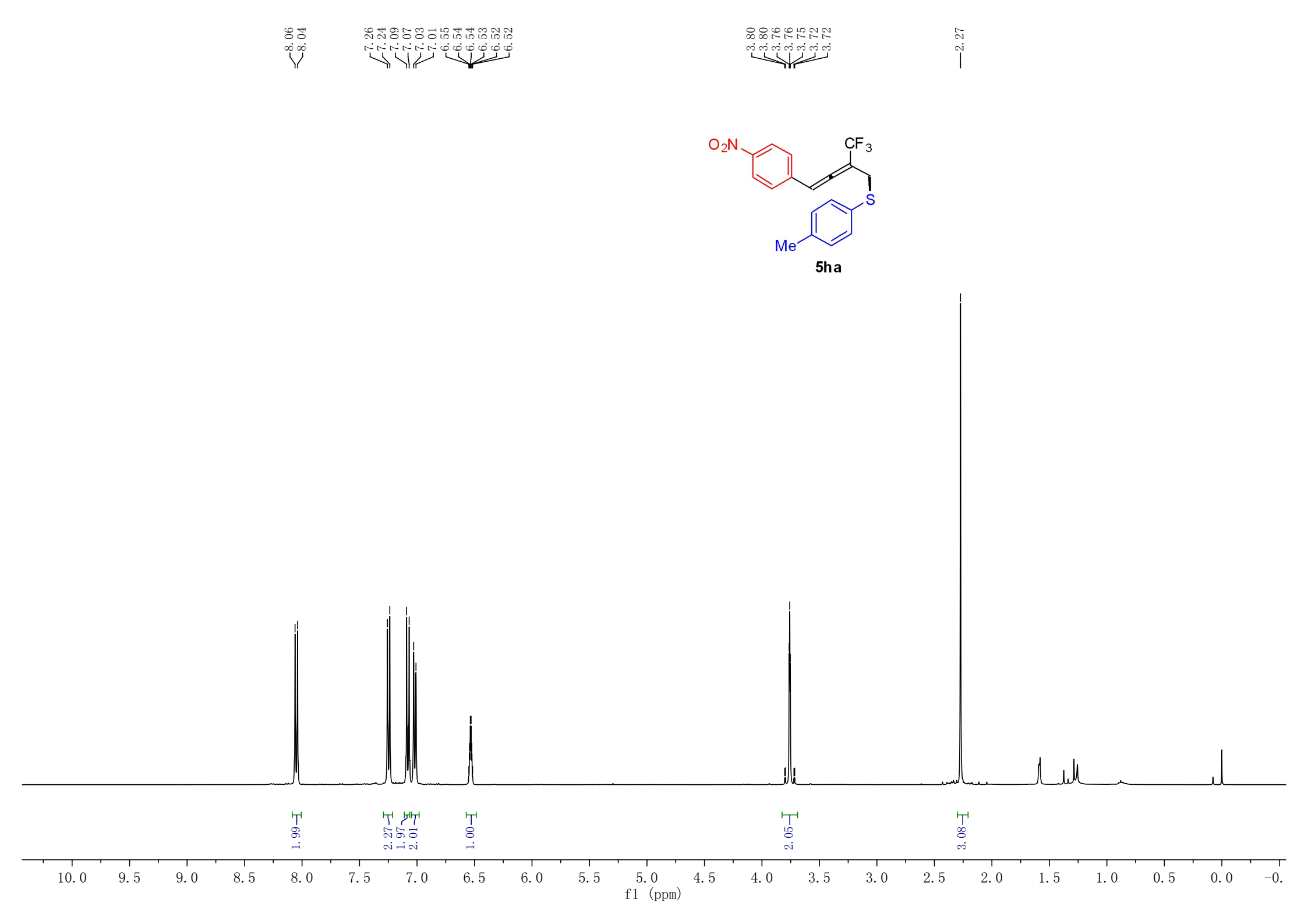
-150
-170
-190
-210
f1 (ppm)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3.75
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3.72
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CF3
S
Me
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2.01
1.00
2.05
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8.0
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6.0
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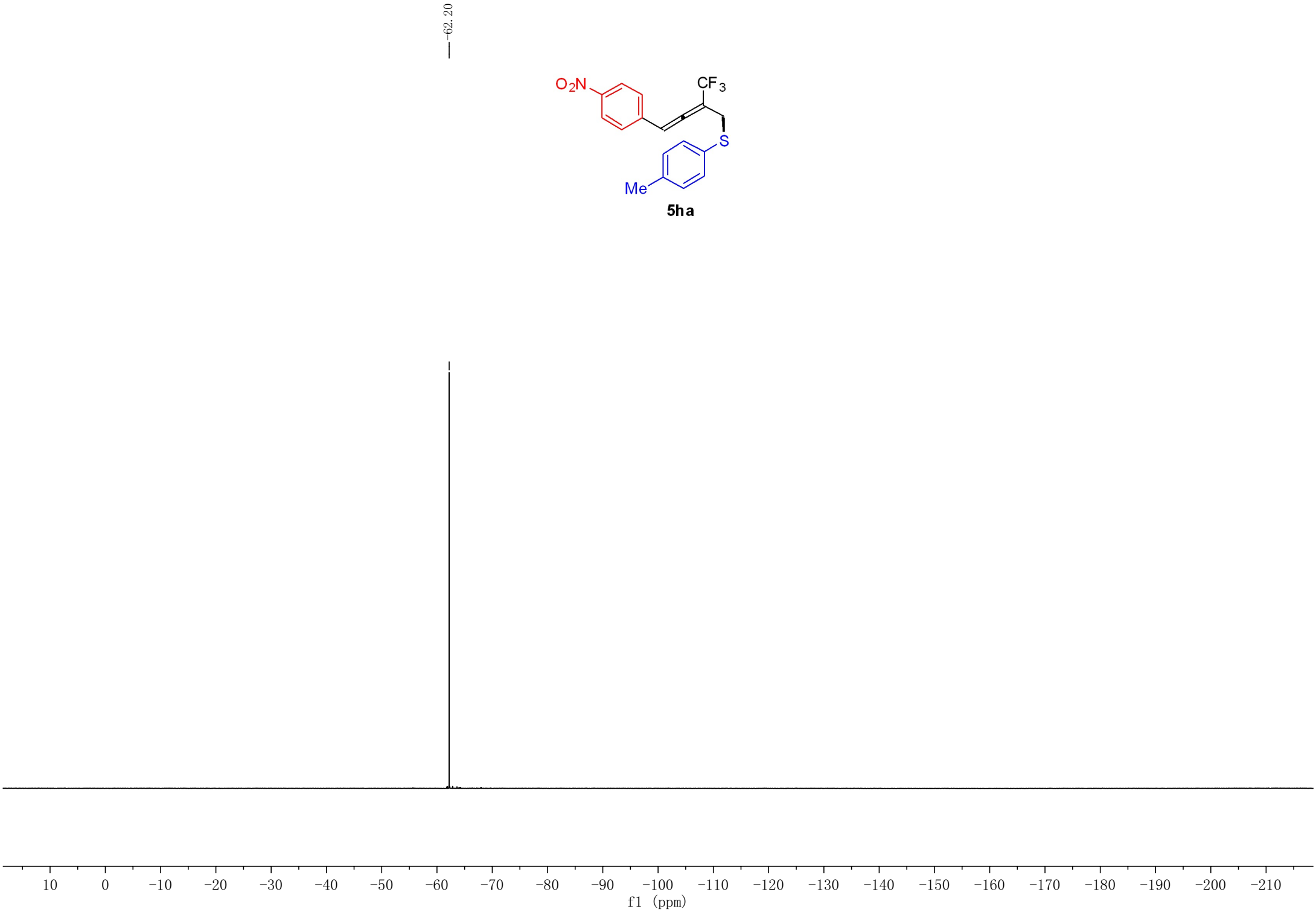
f1 (ppm)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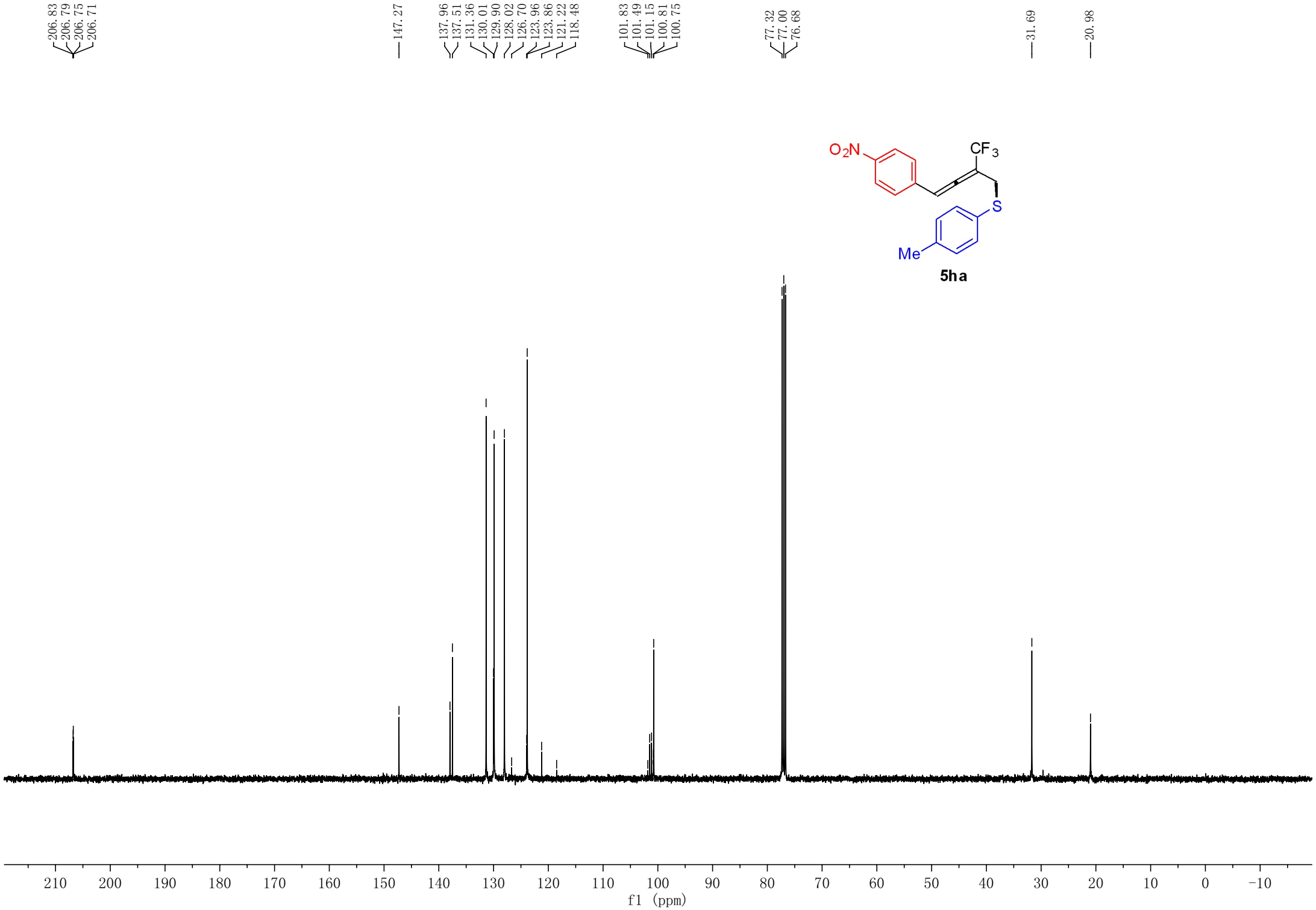
-160
-170
-180
-190
-200
-210
f1 (ppm)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137.51
131.36
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129.90
128.02
126.70
123.96
123.86
121.22
118.48
101.83
101.49
101.15
100.81
100.75
77.32
77.00
76.68
31.69
20.98
O2N
CF3
S
Me
5ha
210
200
190
180
170
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100
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70
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30
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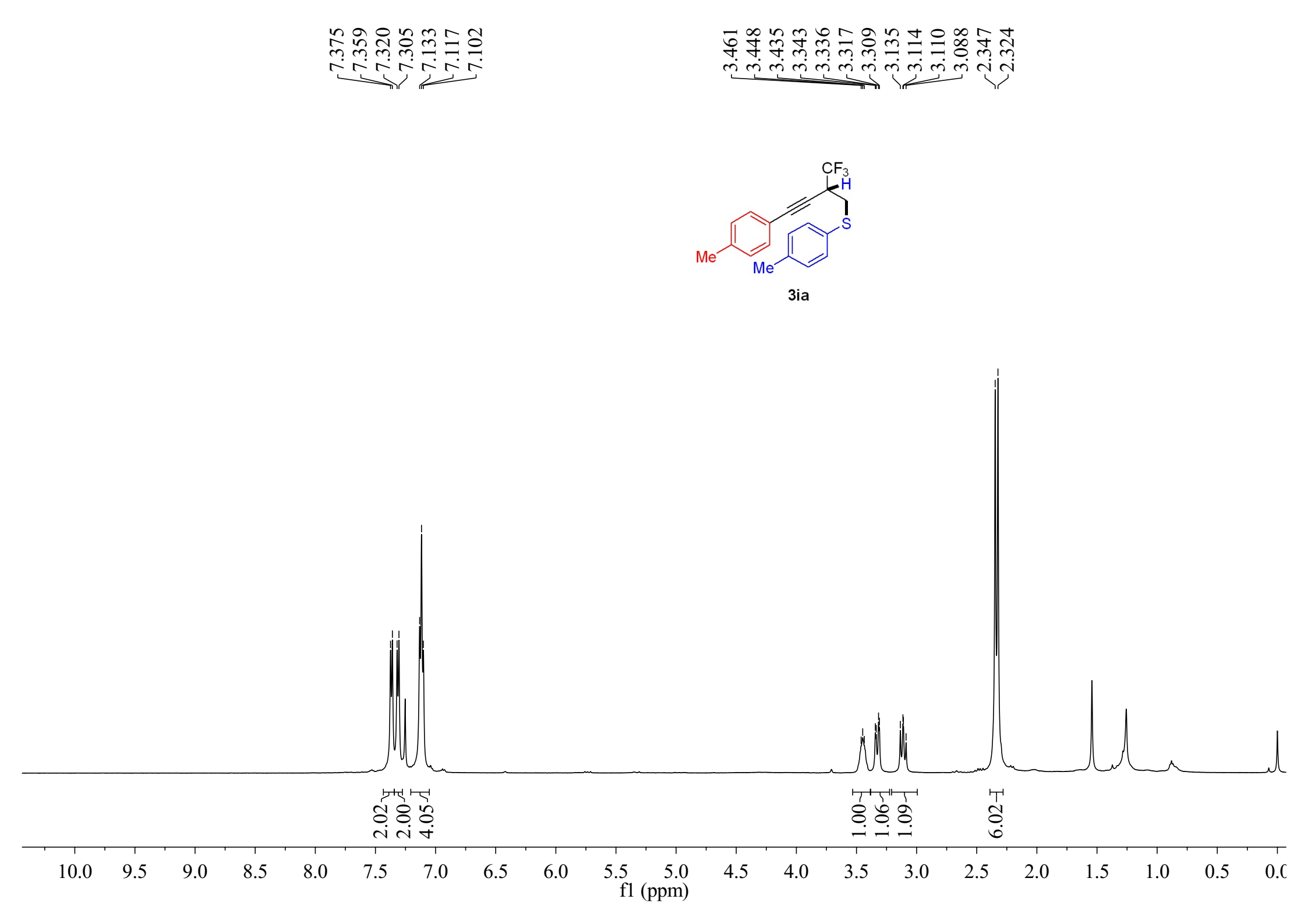
0
-10
f1 (ppm)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3.448
3.435
3.343
3.336
3.317
3.309
3.135
3.114
3.110
3.088
2.347
2.324
CF3
H
S
Me
Me
3ia
2.02
2.00
4.05
1.00
1.06
1.09
6.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
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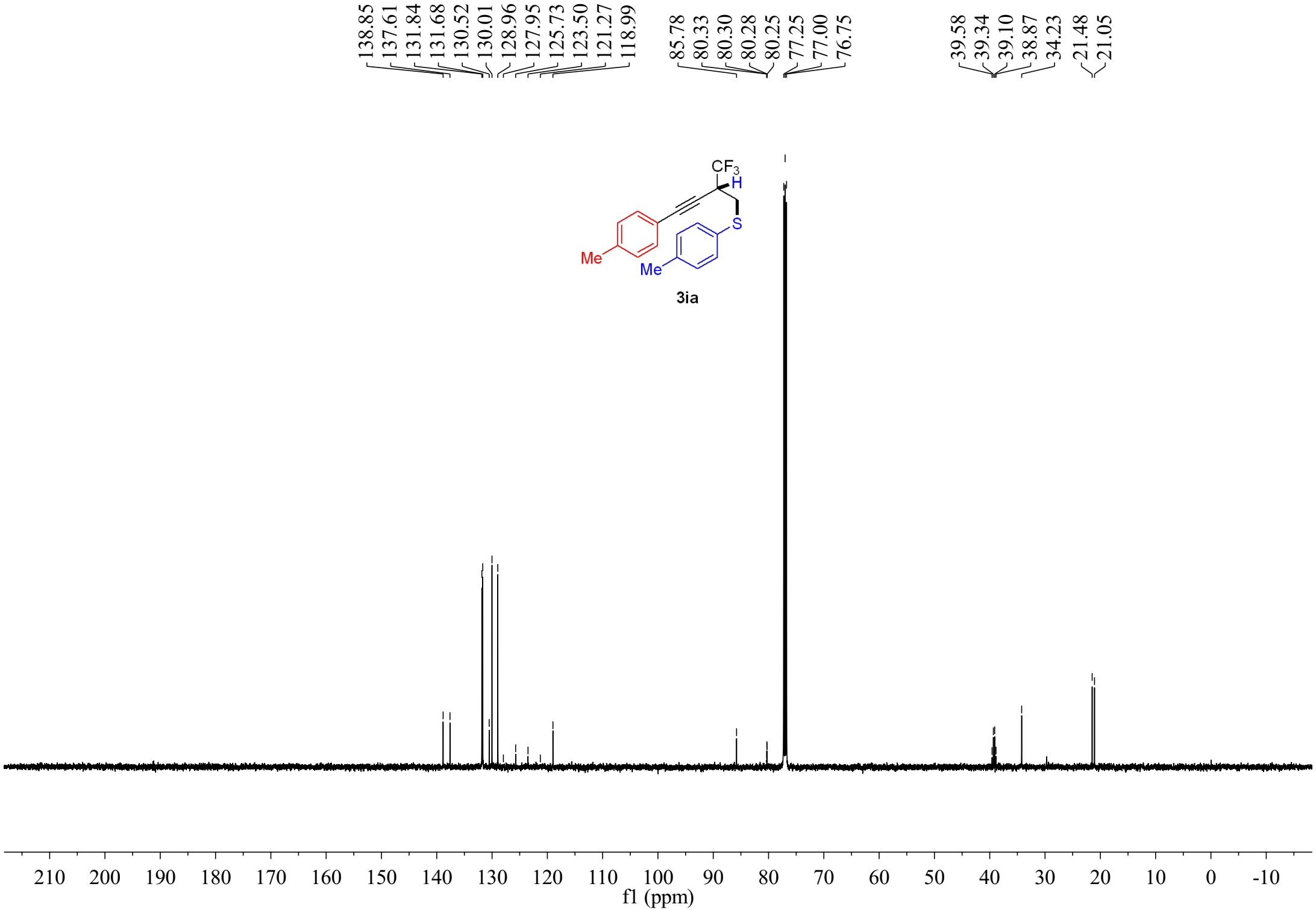
0.0
f1 (ppm)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128.96
127.95
125.73
123.50
121.27
118.99
85.78
80.33
80.30
80.28
80.25
77.25
77.00
76.75
39.58
39.34
39.10
38.87
34.23
21.48
21.05
CF3
H
S
Me
Me
3ia
210
200
190
180
170
160
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140
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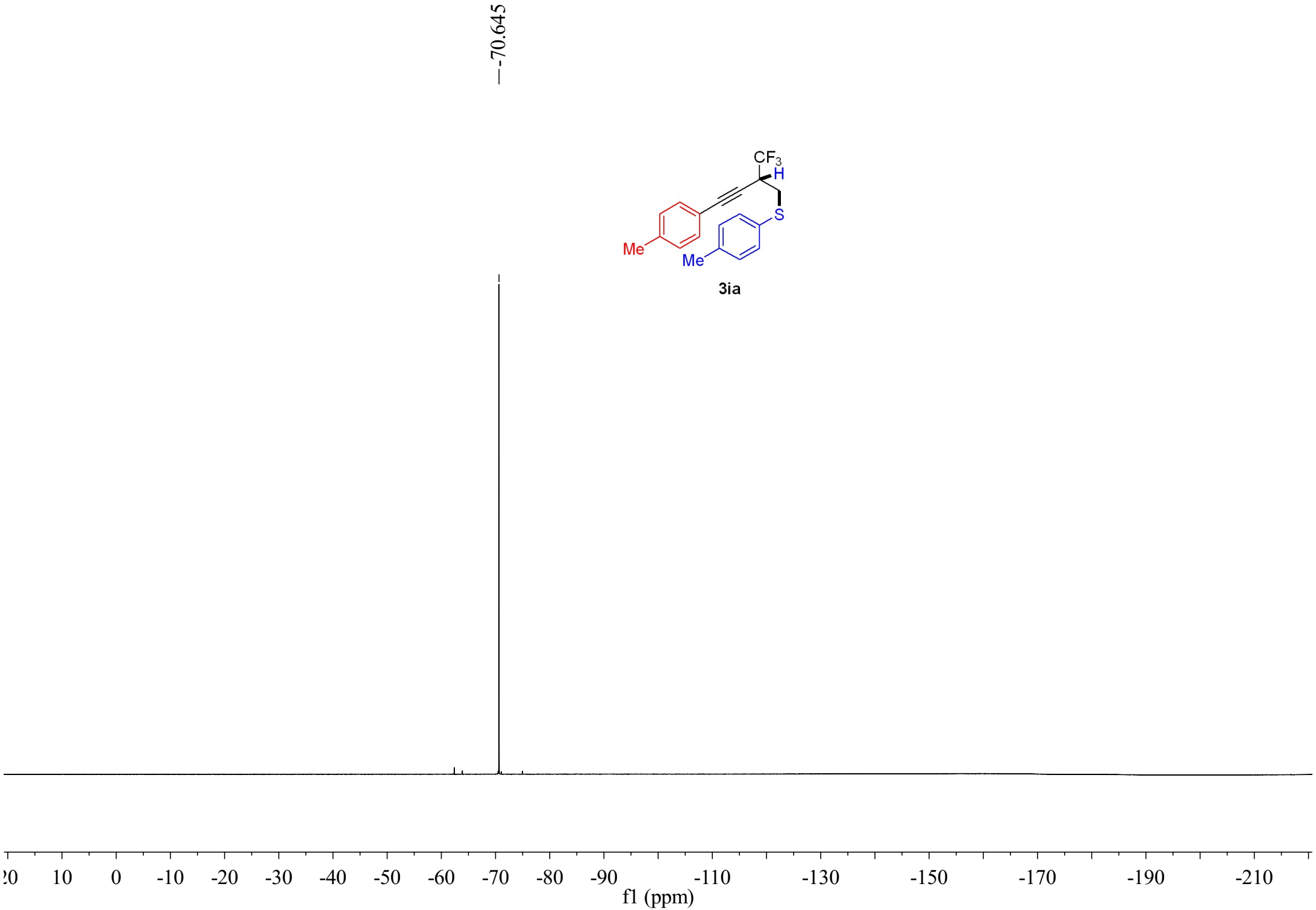
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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S
Me
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3ia
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-10
-20
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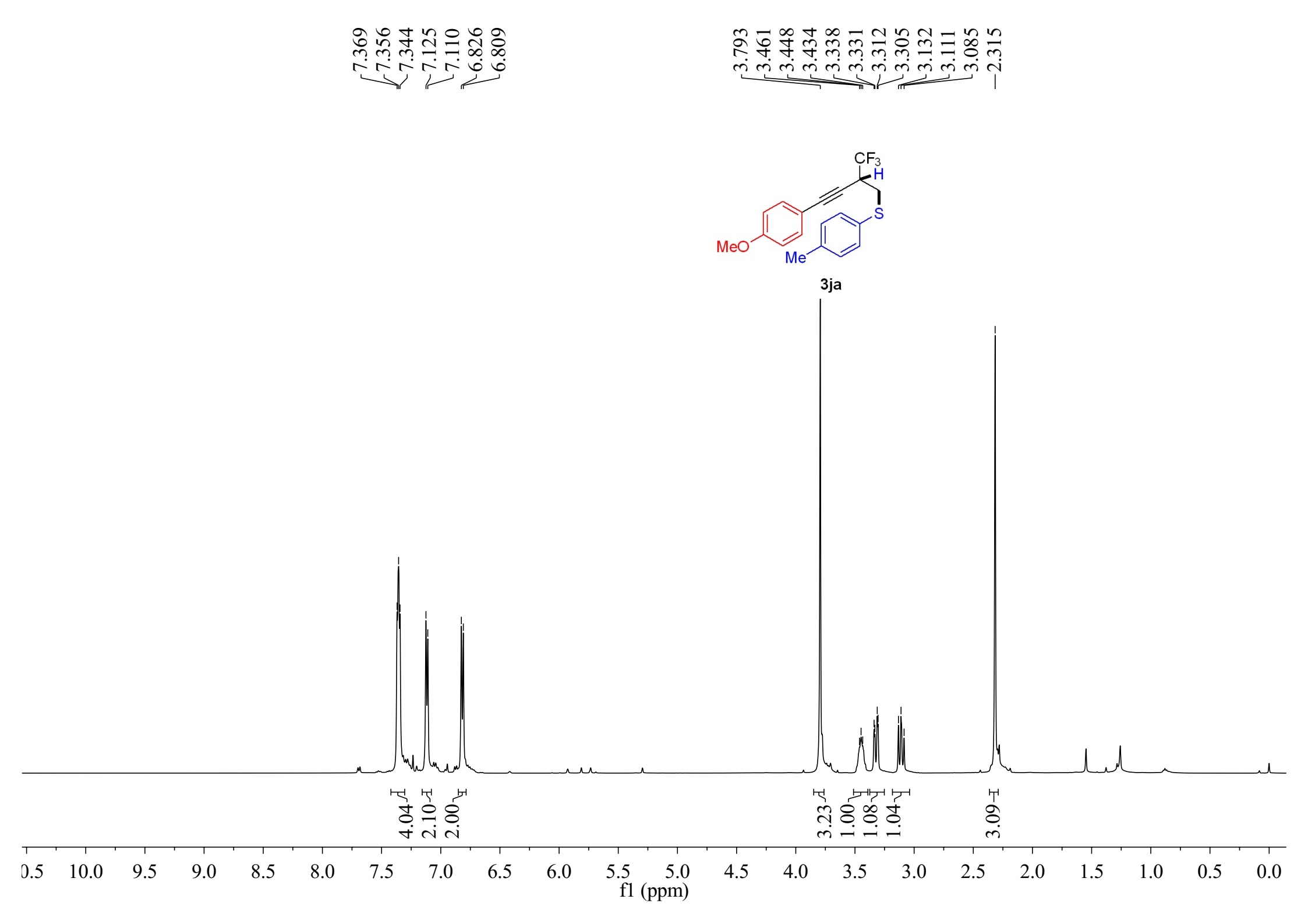
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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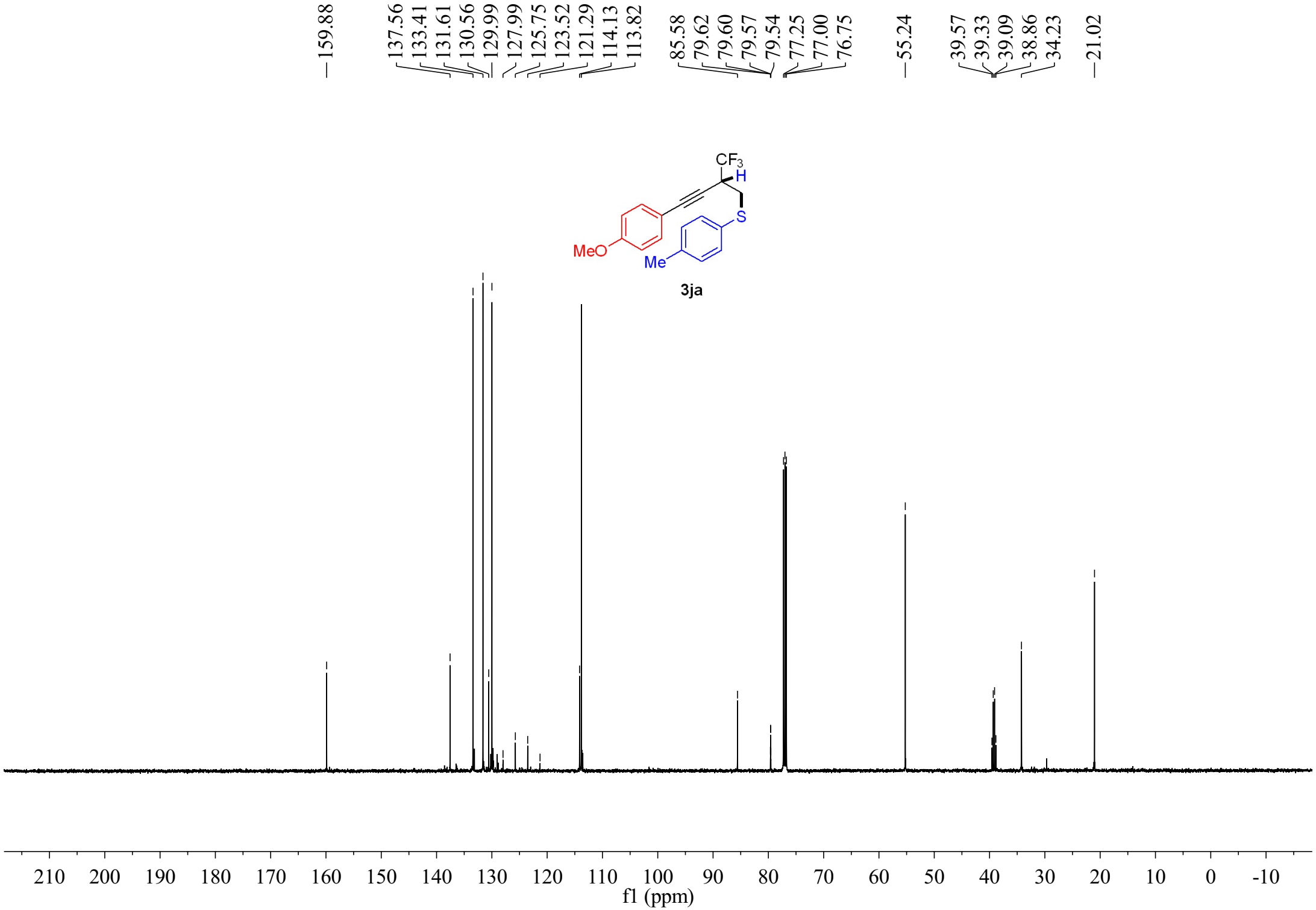
7.356
7.344
7.125
7.110
6.826
6.809
3.793
3.461
3.448
3.434
3.338
3.331
3.312
3.305
3.132
3.111
3.085
2.315
CF3
H
S
MeO
Me
3ja
4.04
2.10
2.00
3.23
1.00
1.08
1.04
3.09
f1 (ppm)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129.99
127.99
125.75
123.52
121.29
114.13
113.82
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79.62
79.60
79.57
79.54
77.25
77.00
76.75
55.24
39.57
39.33
39.09
38.86
34.23
21.02
CF3
H
S
MeO
Me
3ja
210
200
190
180
170
160
150
140
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120
110
100
90
80
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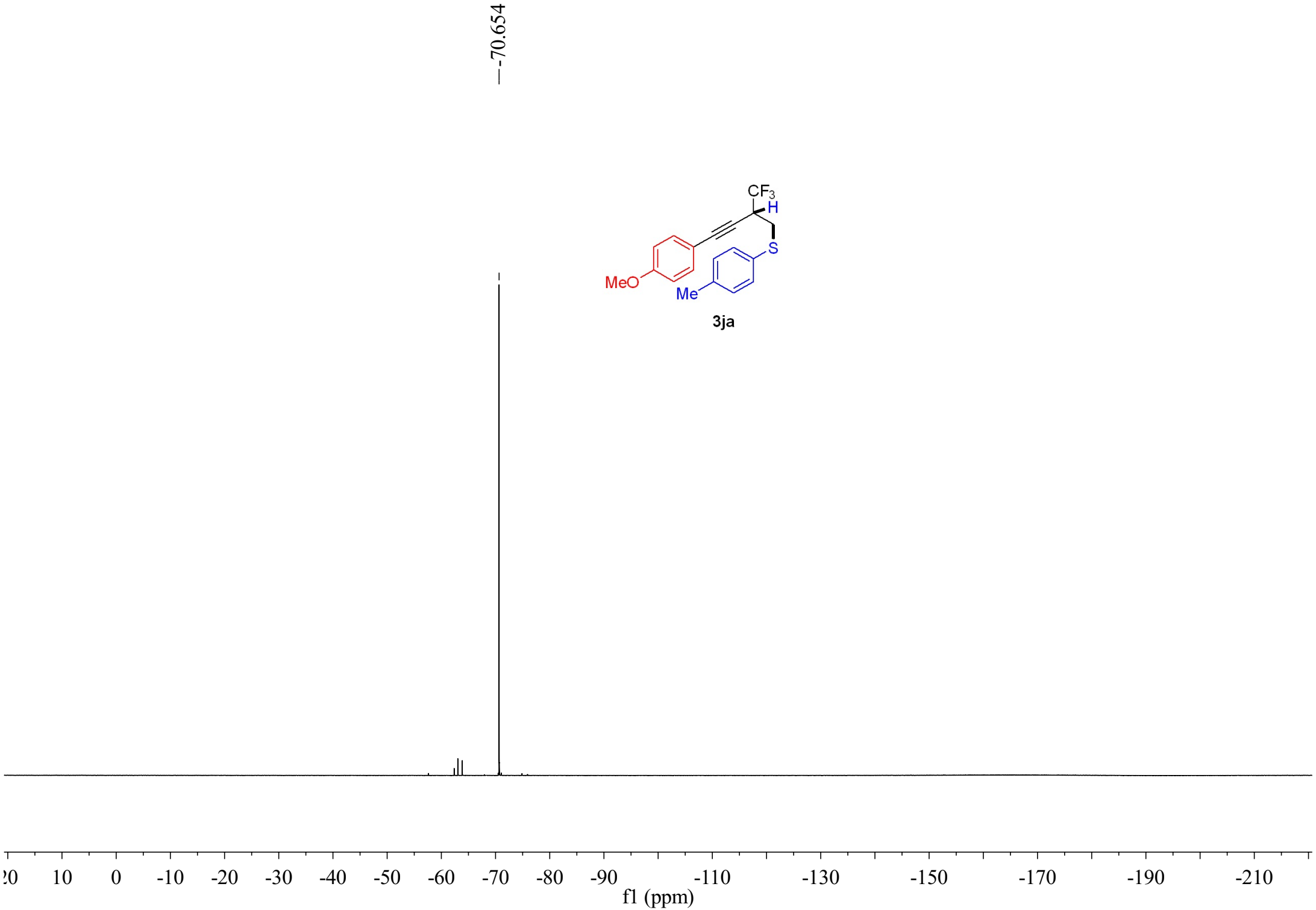
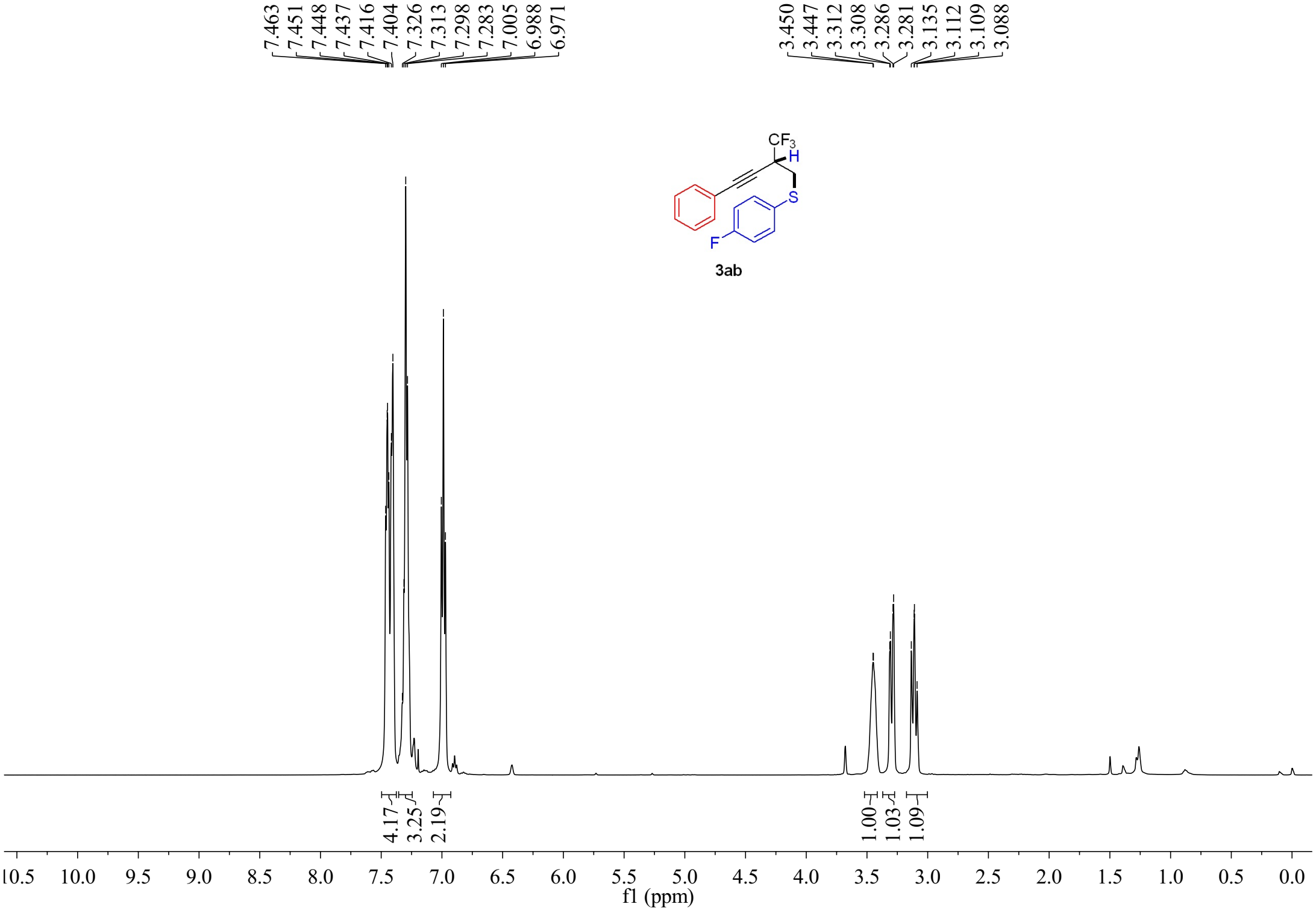
60
50
40
30
20
10
0
-10
f1 (ppm)


-70.654
CF3
H
S
MeO
Me
3ja
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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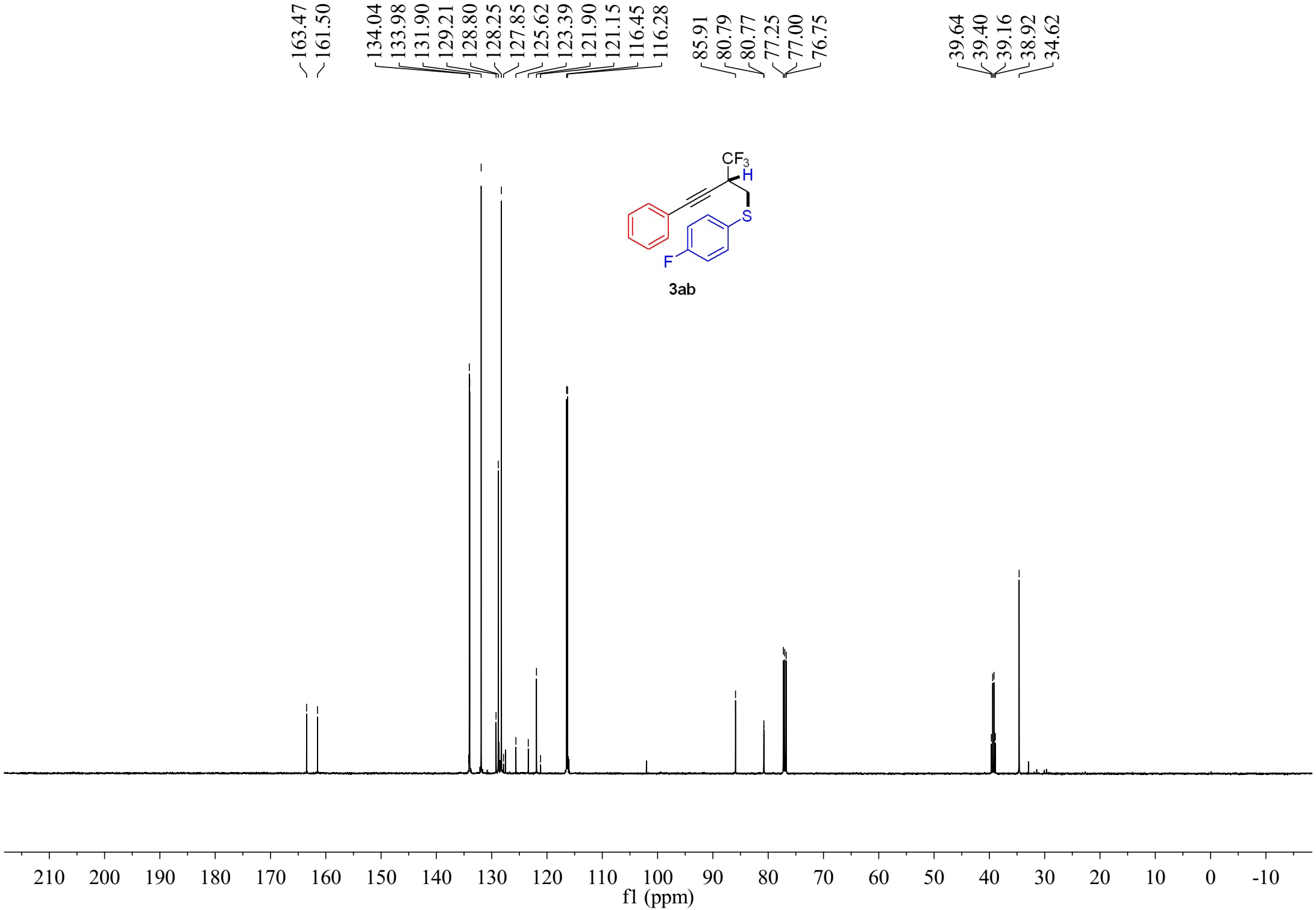
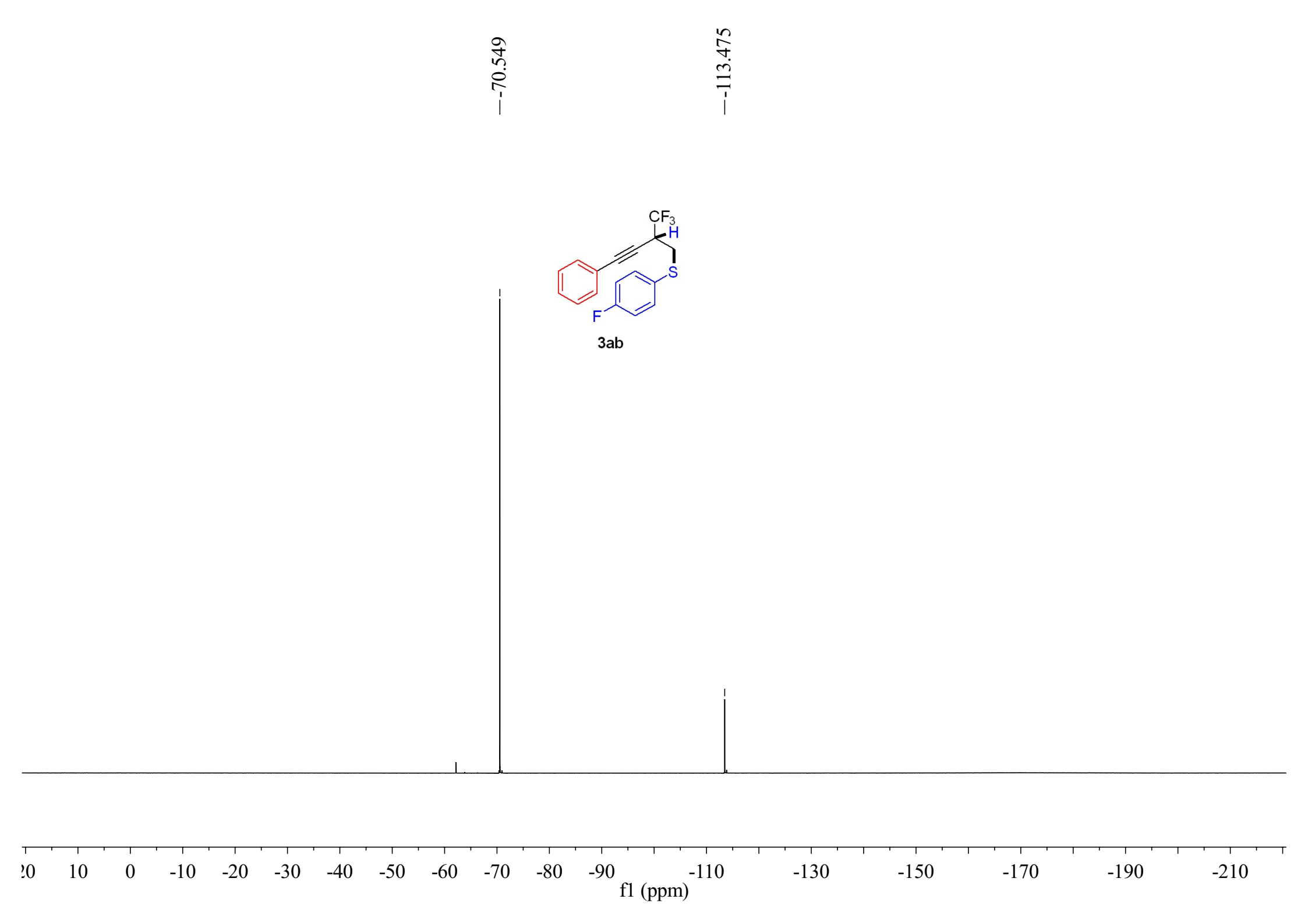
7.451
7.448
7.437
7.416
7.404
7.326
7.313
7.298
7.283
7.005
6.988
6.971
3.450
3.447
3.312
3.308
3.286
3.281
3.135
3.112
3.109
3.088
CF3
H
S
F
3ab
4.17
3.25
2.19
1.00
1.03
1.09
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.47
161.50
134.04
133.98
131.90
129.21
128.80
128.25
127.85
125.62
123.39
121.90
121.15
116.45
116.28
85.91
80.79
80.77
77.25
77.00
76.75
39.64
39.40
39.16
38.92
34.62
CF3
H
S
F
3ab
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)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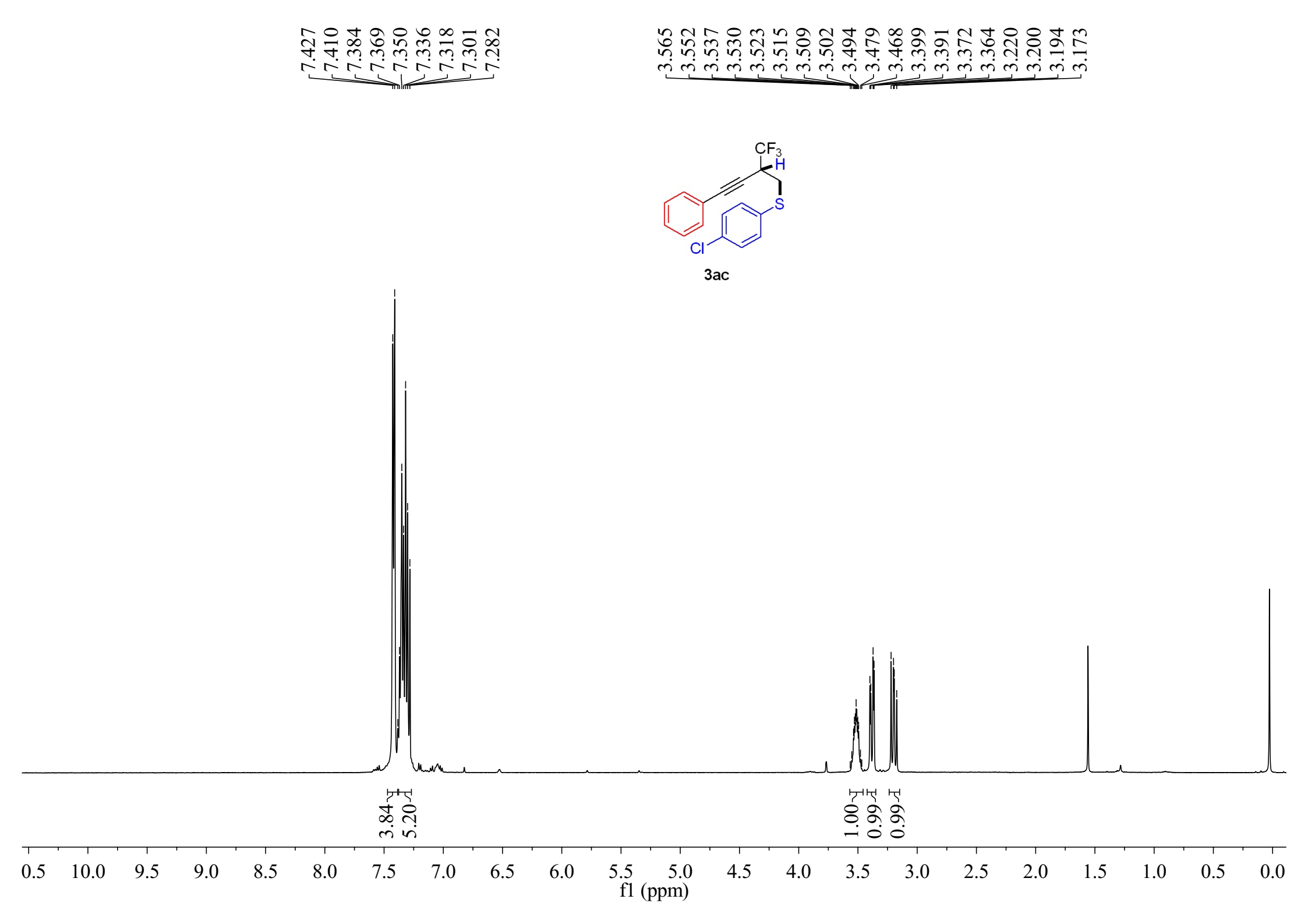
CF3
H
S
F
3ab
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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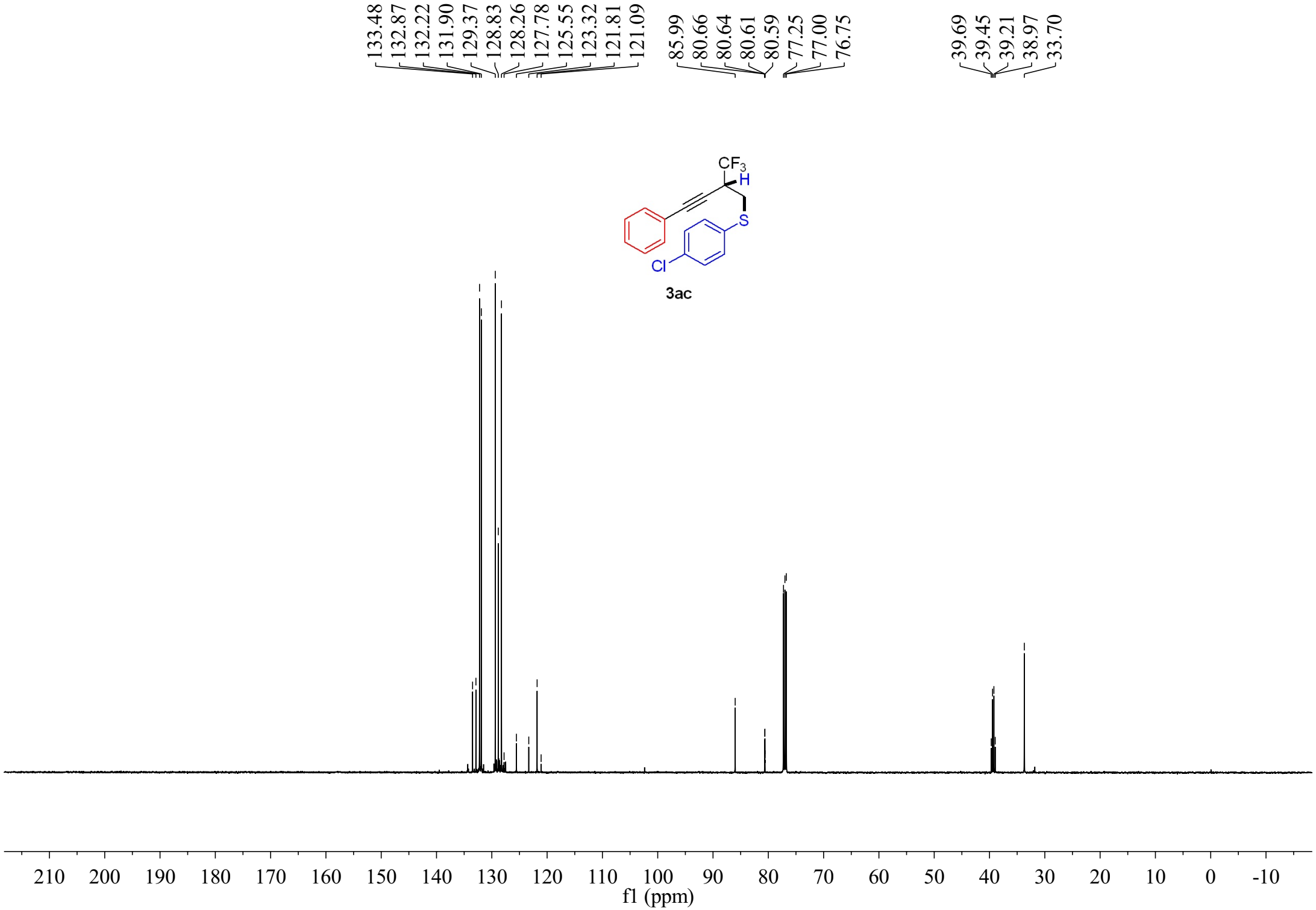
7.384
7.369
7.350
7.336
7.318
7.301
7.282
3.565
3.552
3.537
3.530
3.523
3.515
3.509
3.502
3.494
3.479
3.468
3.399
3.391
3.372
3.364
3.220
3.200
3.194
3.173
CF3
H
S
Cl
3ac
3.84
5.20
1.00
0.99
0.99
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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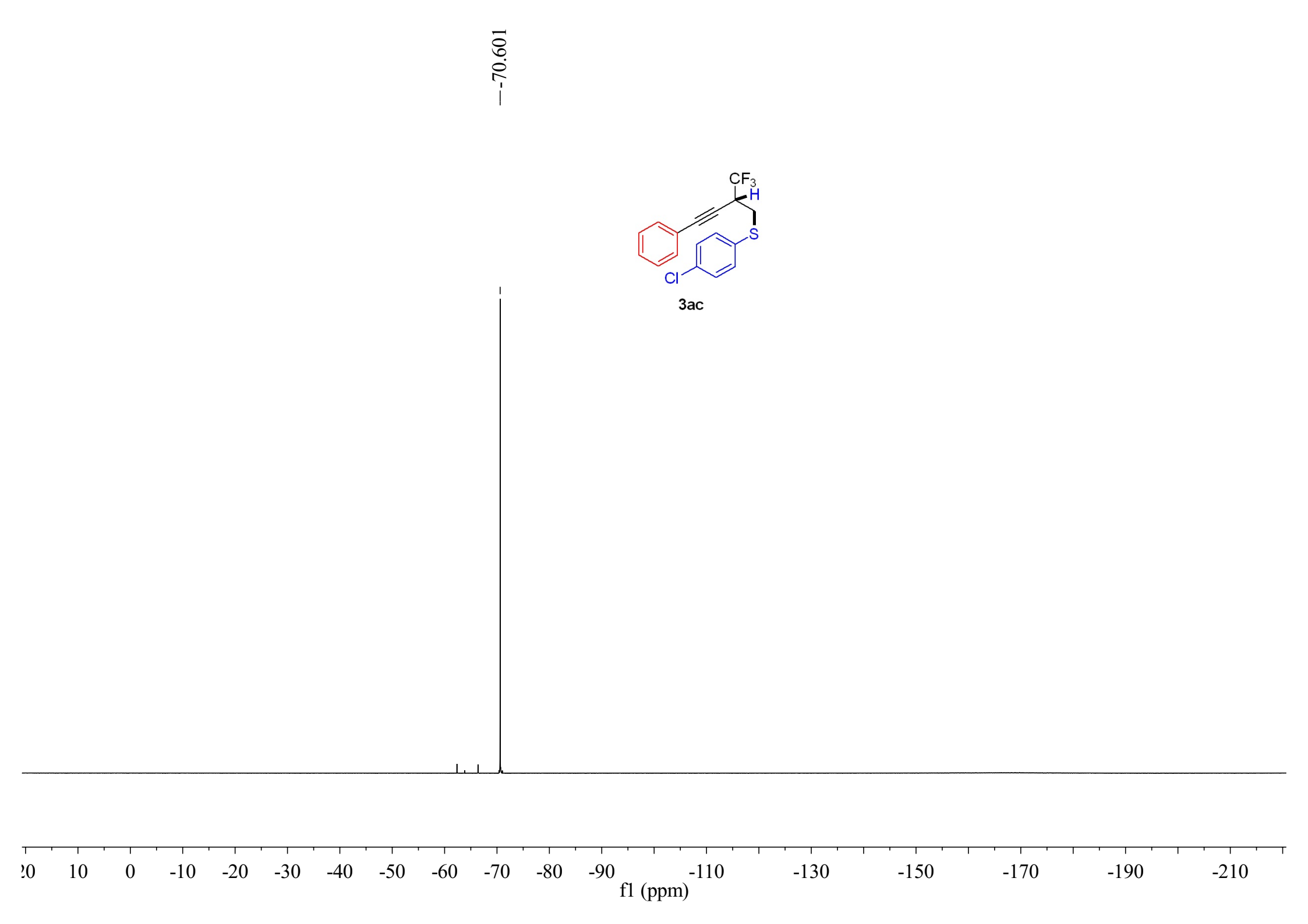
132.22
131.90
129.37
128.83
128.26
127.78
125.55
123.32
121.81
121.09
85.99
80.66
80.64
80.61
80.59
77.25
77.00
76.75
39.69
39.45
39.21
38.97
33.70
CF3
H
S
Cl
3ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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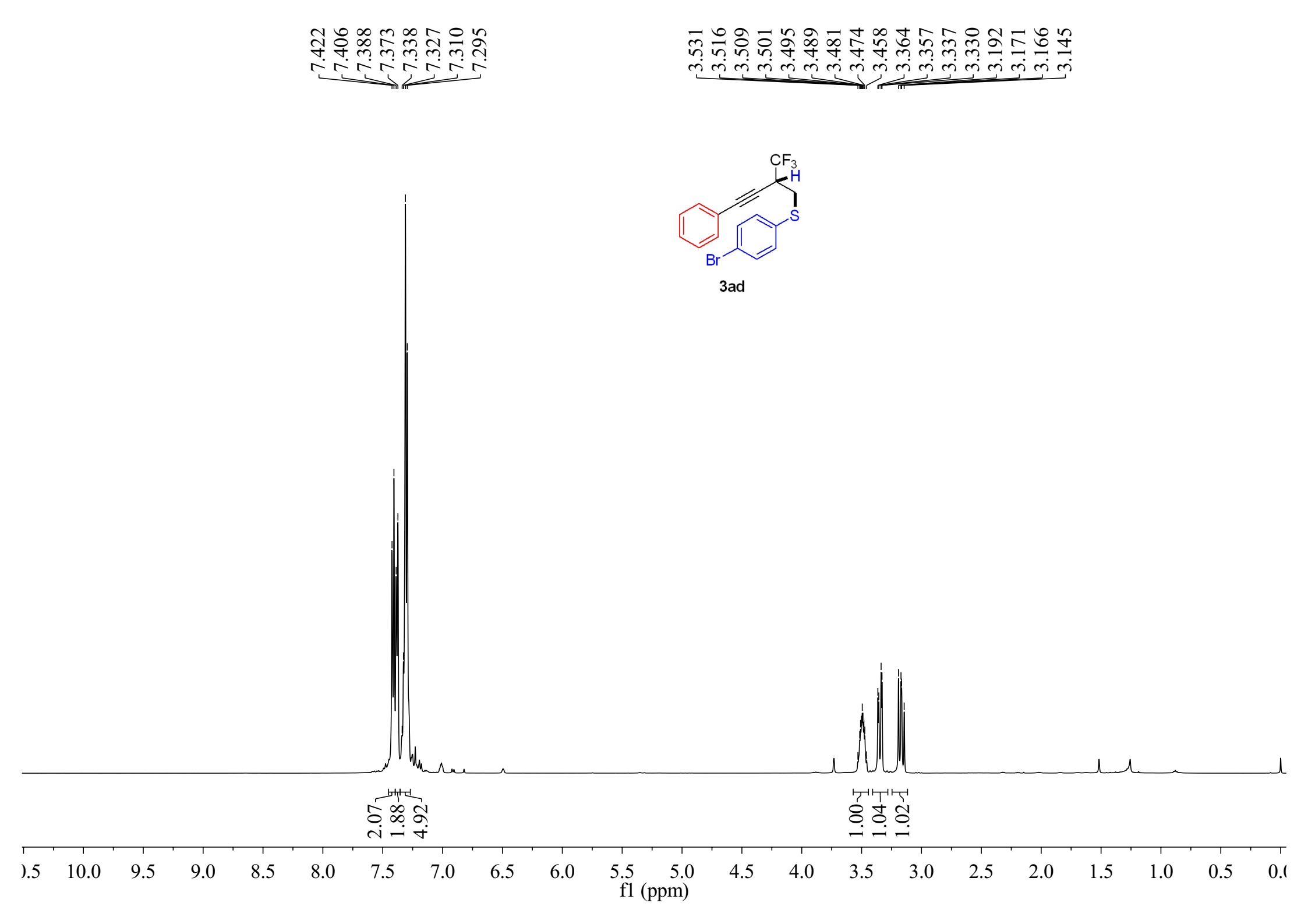
CF3
H
S
Cl
3ac
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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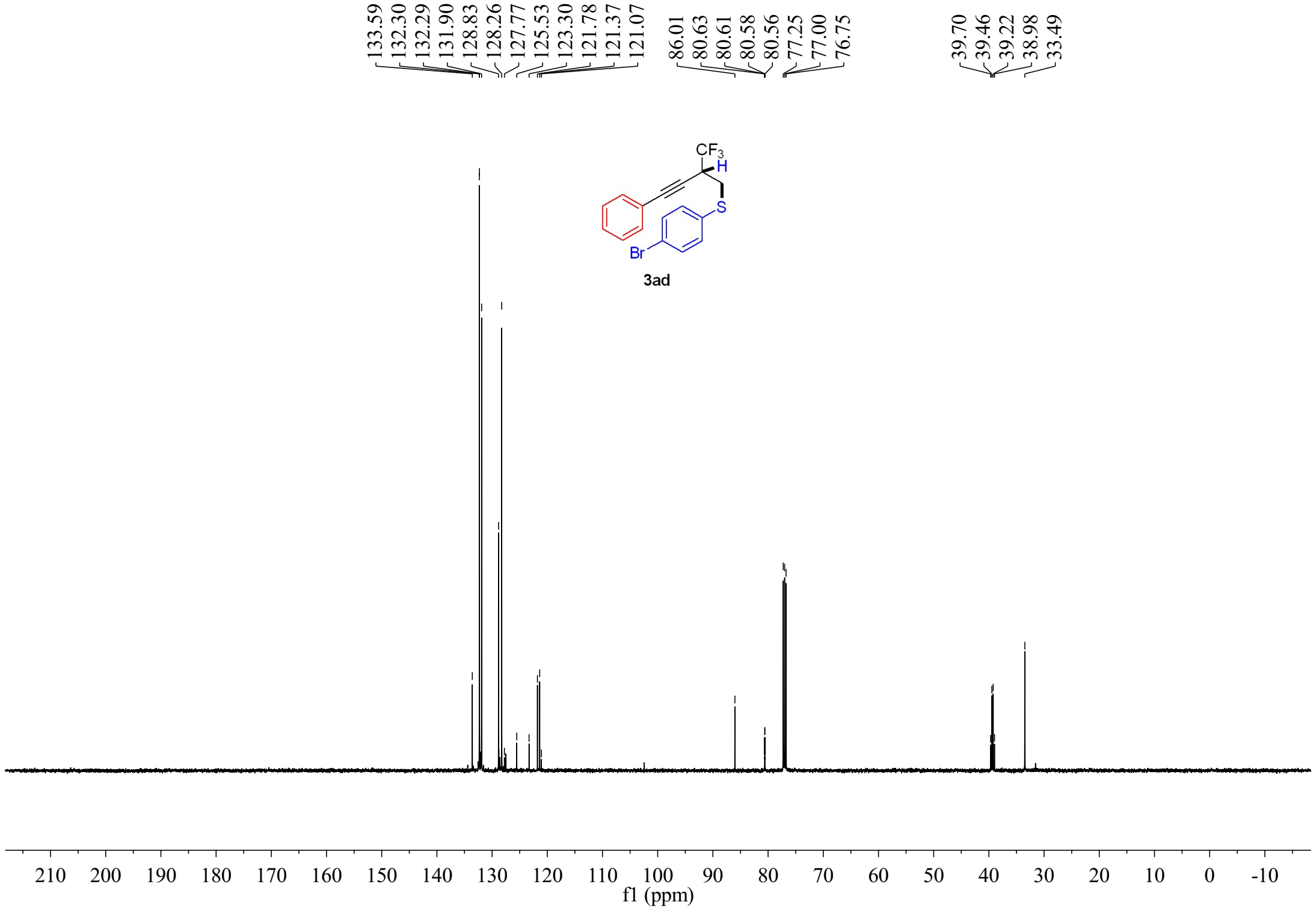
7.406
7.388
7.373
7.338
7.327
7.310
7.295
3.531
3.516
3.509
3.501
3.495
3.489
3.481
3.474
3.458
3.364
3.357
3.337
3.330
3.192
3.171
3.166
3.145
CF3
H
S
Br
3ad
2.07
1.88
4.92
1.00
1.04
1.02
f1 (ppm)


133.59
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132.29
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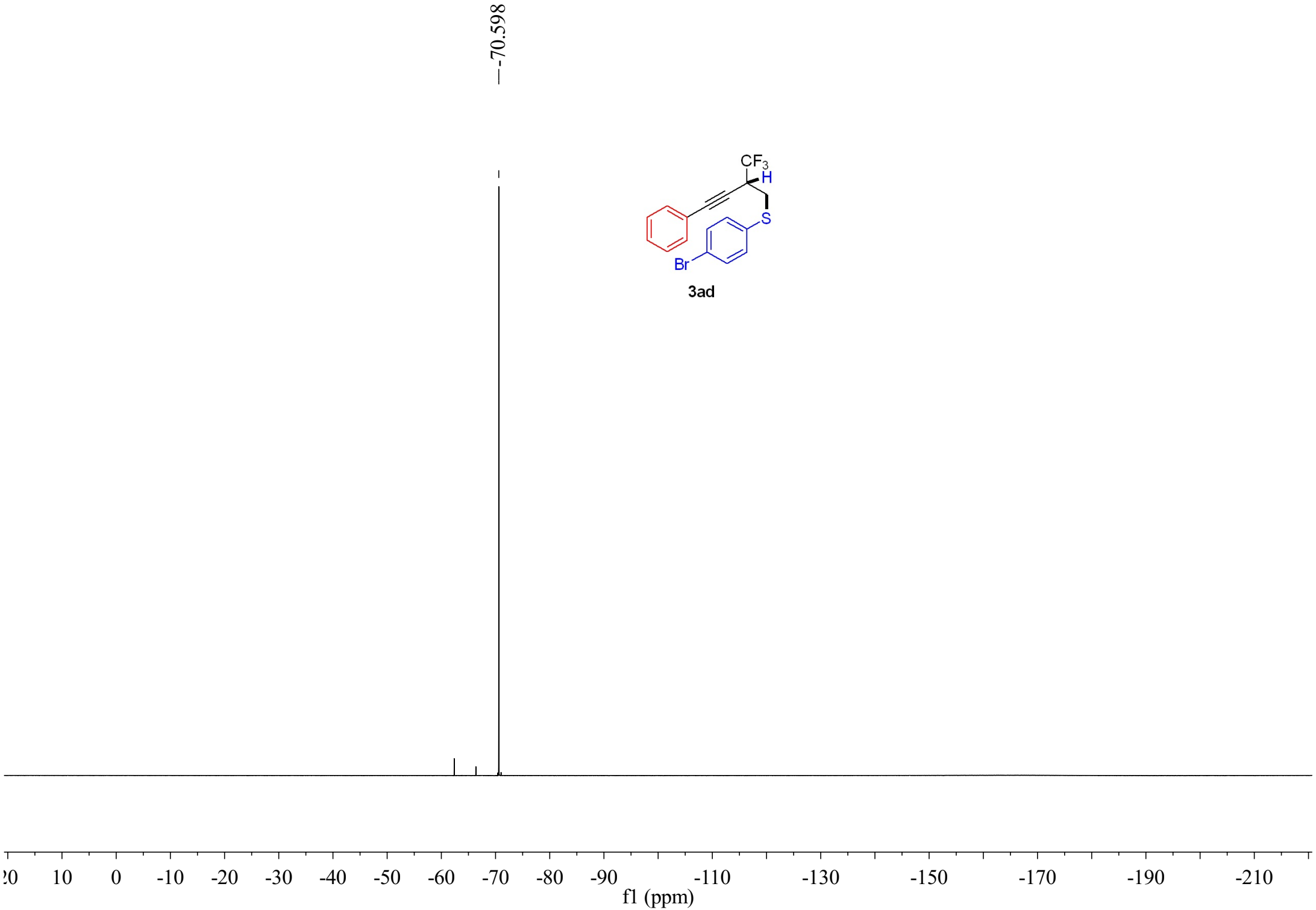
128.26
127.77
125.53
123.30
121.78
121.37
121.07
86.01
80.63
80.61
80.58
80.56
77.25
77.00
76.75
39.70
39.46
39.22
38.98
33.49
CF3
H
S
Br
3ad
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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Br
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-20
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-40
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-60
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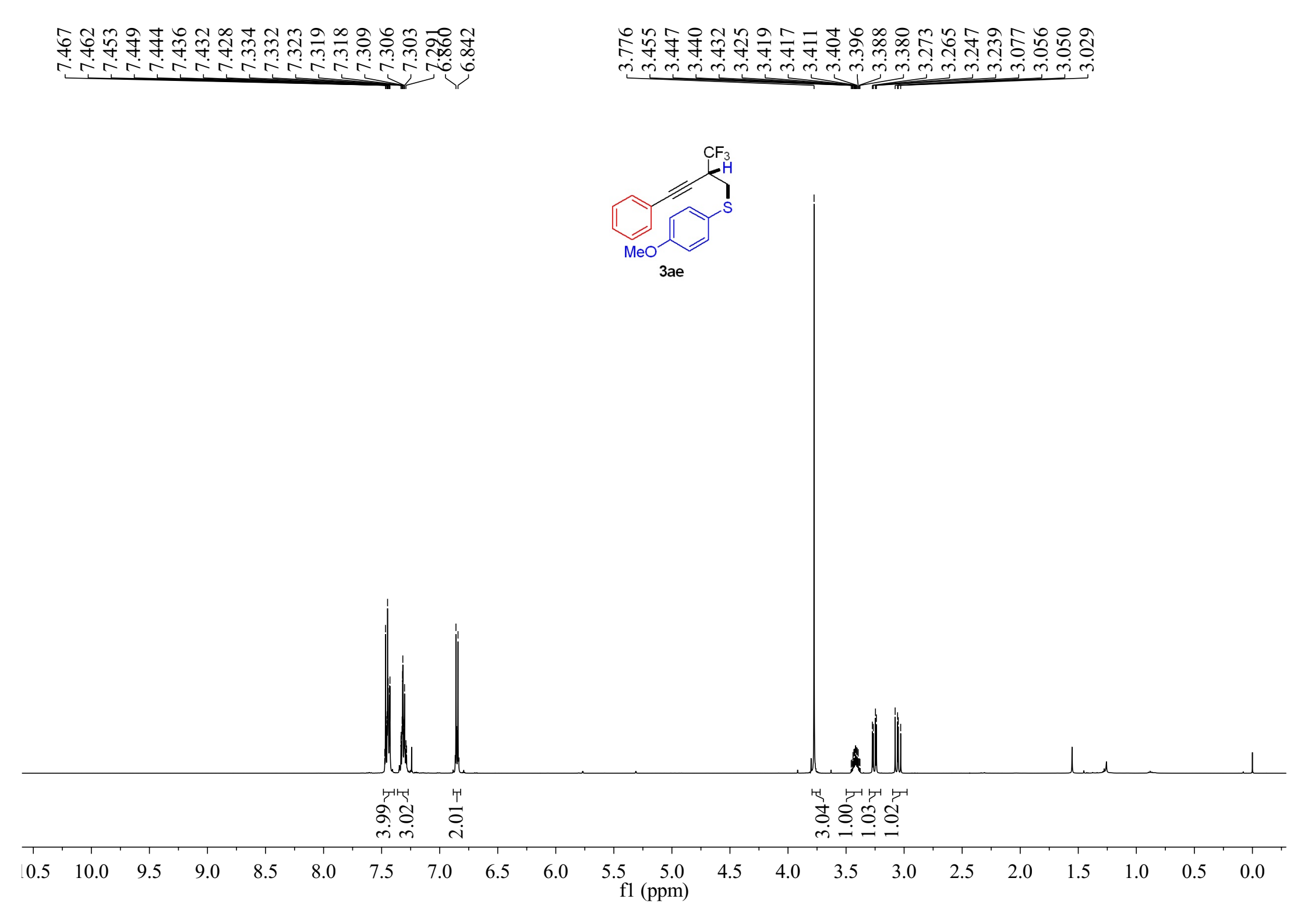
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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7.436
7.432
7.428
7.334
7.332
7.323
7.319
7.318
7.309
7.306
7.303
7.291
6.860
6.842
3.776
3.455
3.447
3.440
3.432
3.425
3.419
3.417
3.411
3.404
3.396
3.388
3.380
3.273
3.265
3.247
3.239
3.077
3.056
3.050
3.029
CF3
H
S
MeO
3ae
3.99
3.02
2.01
3.04
1.00
1.03
1.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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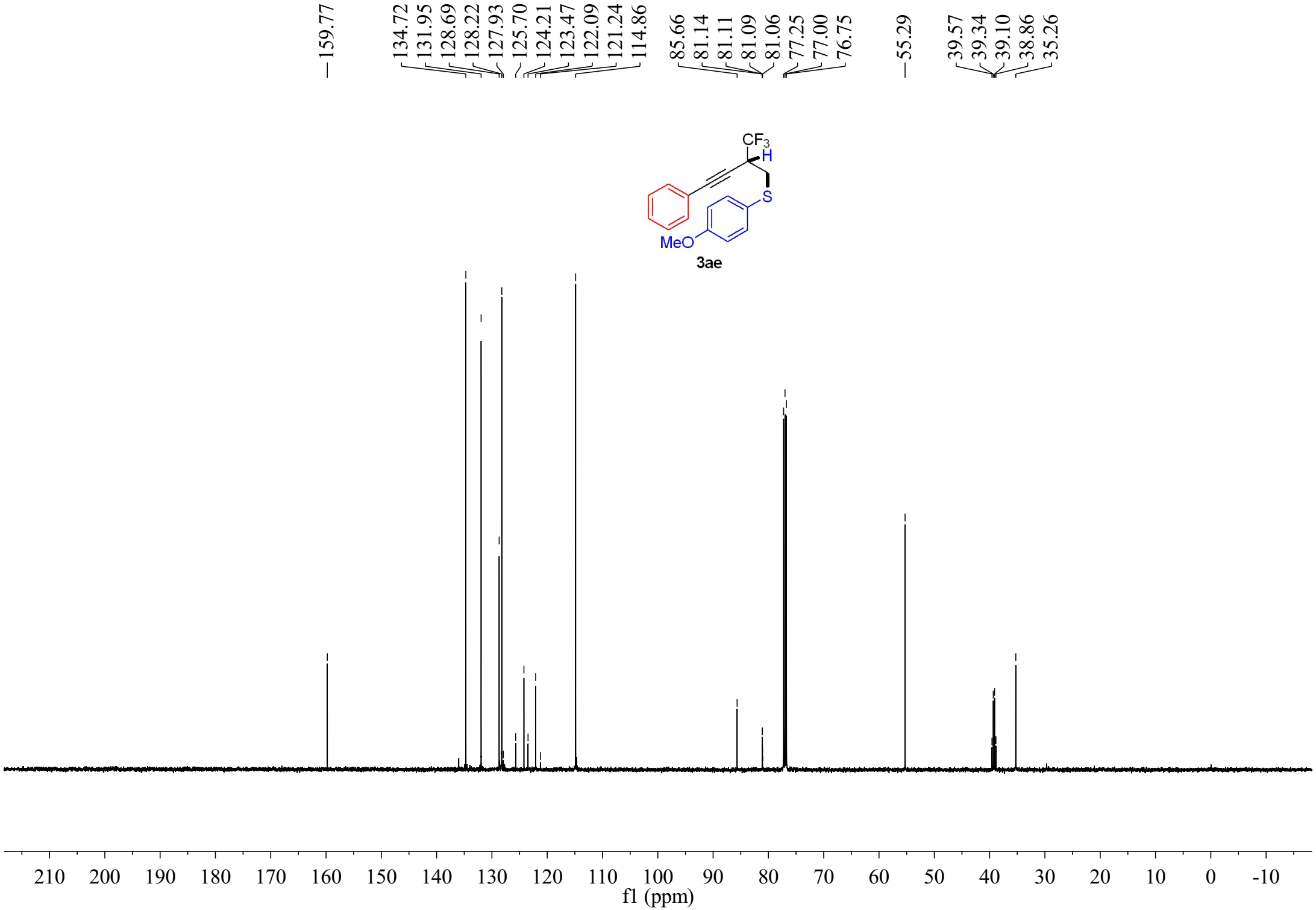
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.22
127.93
125.70
124.21
123.47
122.09
121.24
114.86
85.66
81.14
81.11
81.09
81.06
77.25
77.00
76.75
55.29
39.57
39.34
39.10
38.86
35.26
CF3
H
S
MeO
3ae
210
200
190
180
170
160
150
140
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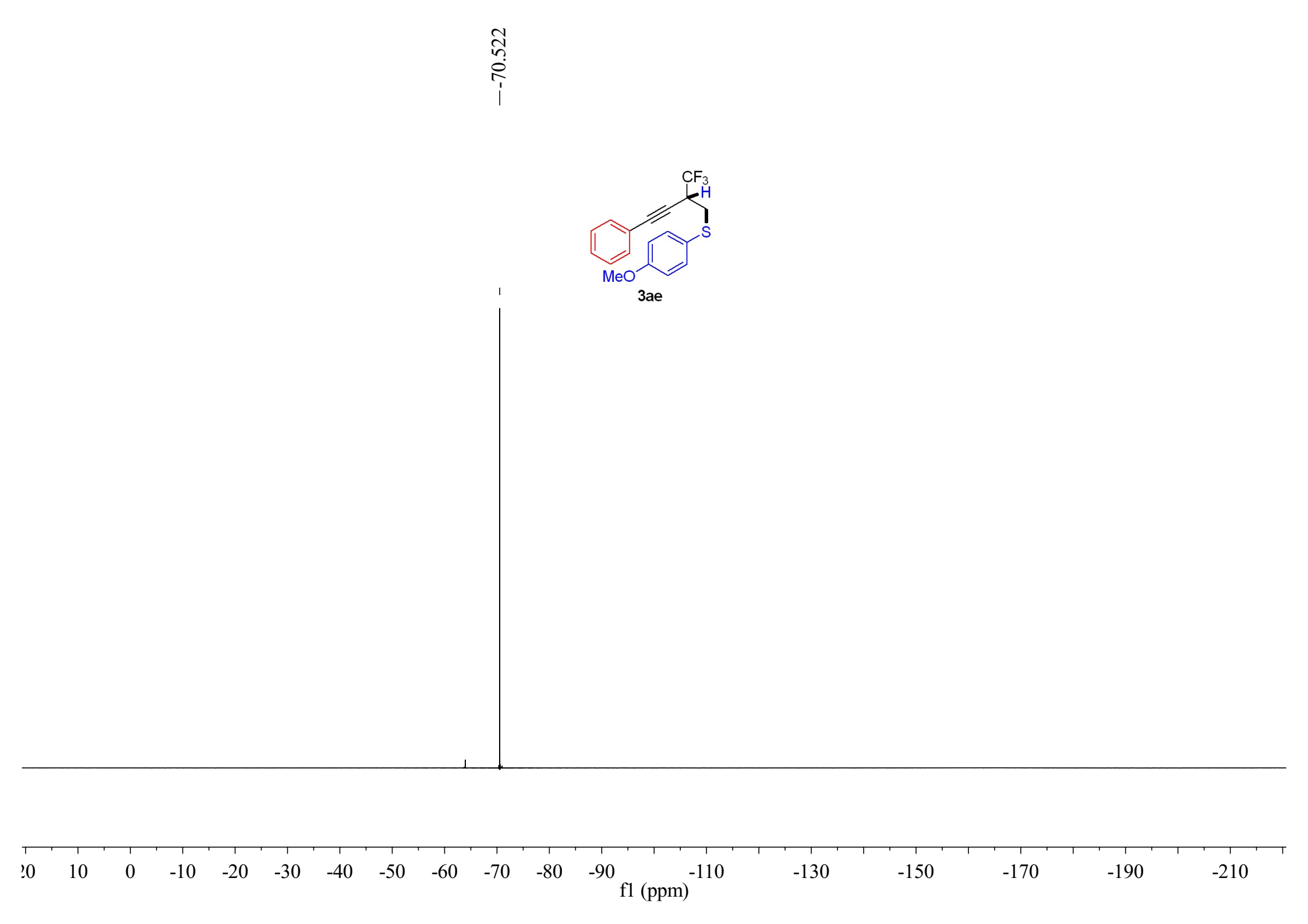
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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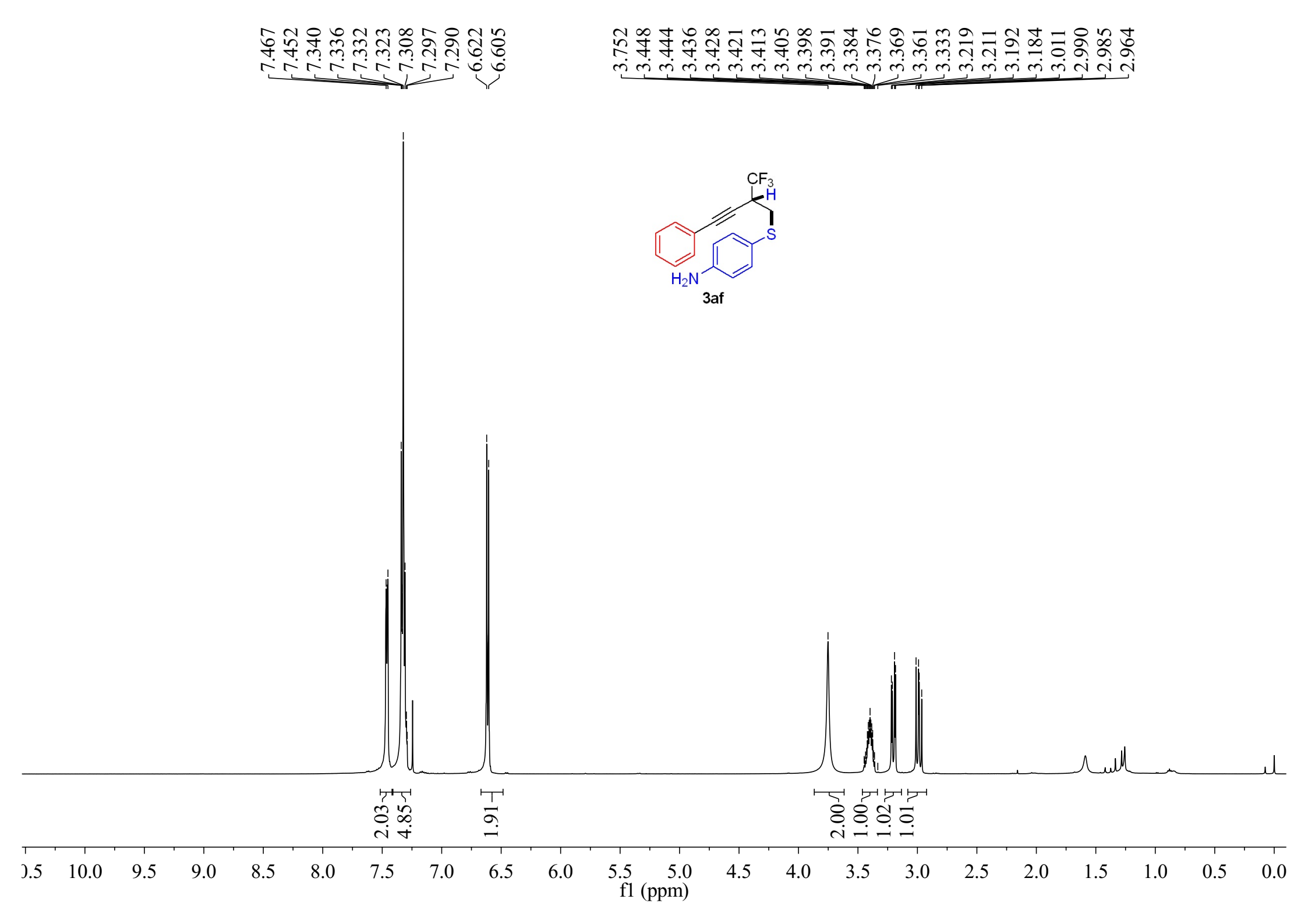
CF3
H
S
MeO
3ae
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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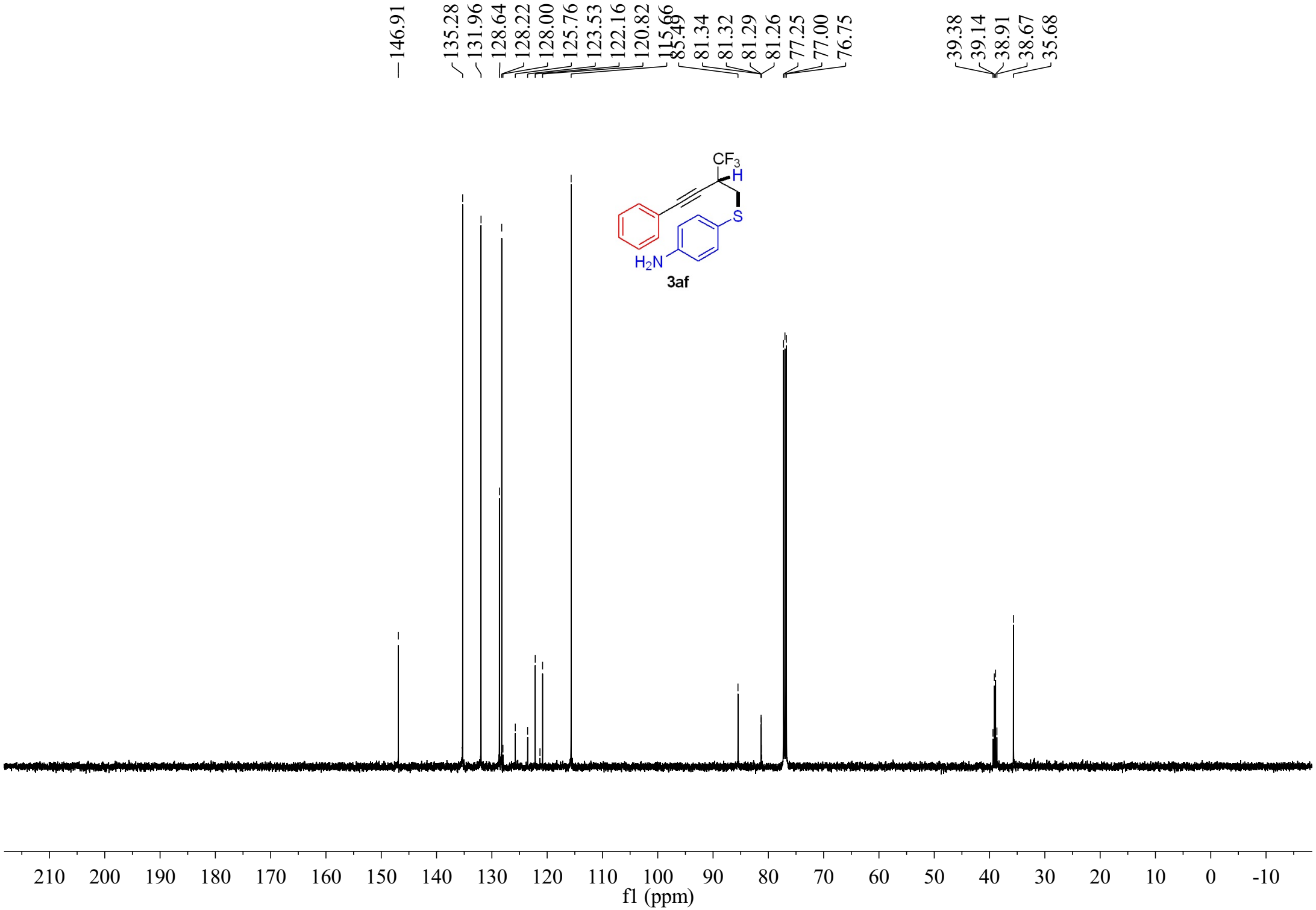
7.452
7.340
7.336
7.332
7.323
7.308
7.297
7.290
6.622
6.605
3.752
3.448
3.444
3.436
3.428
3.421
3.413
3.405
3.398
3.391
3.384
3.376
3.369
3.361
3.333
3.219
3.211
3.192
3.184
3.011
2.990
2.985
2.964
CF3
H
S
H2N
3af
2.03
4.85
1.91
2.00
1.00
1.02
1.01
f1 (ppm)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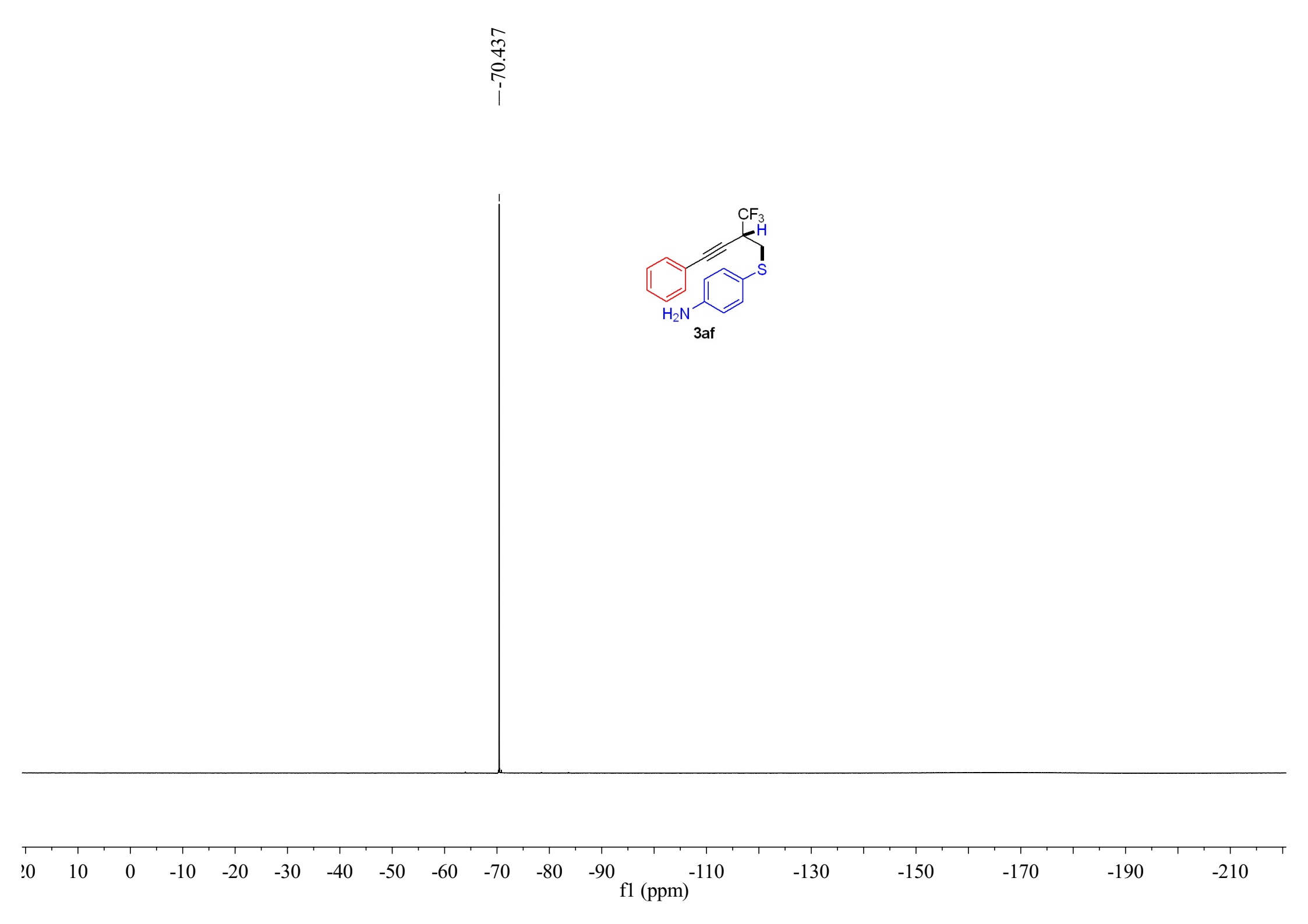
128.64
128.22
128.00
125.76
123.53
122.16
120.82
115.66
85.49
81.34
81.32
81.29
81.26
77.25
77.00
76.75
39.38
39.14
38.91
38.67
35.68
CF3
H
S
H2N
3af
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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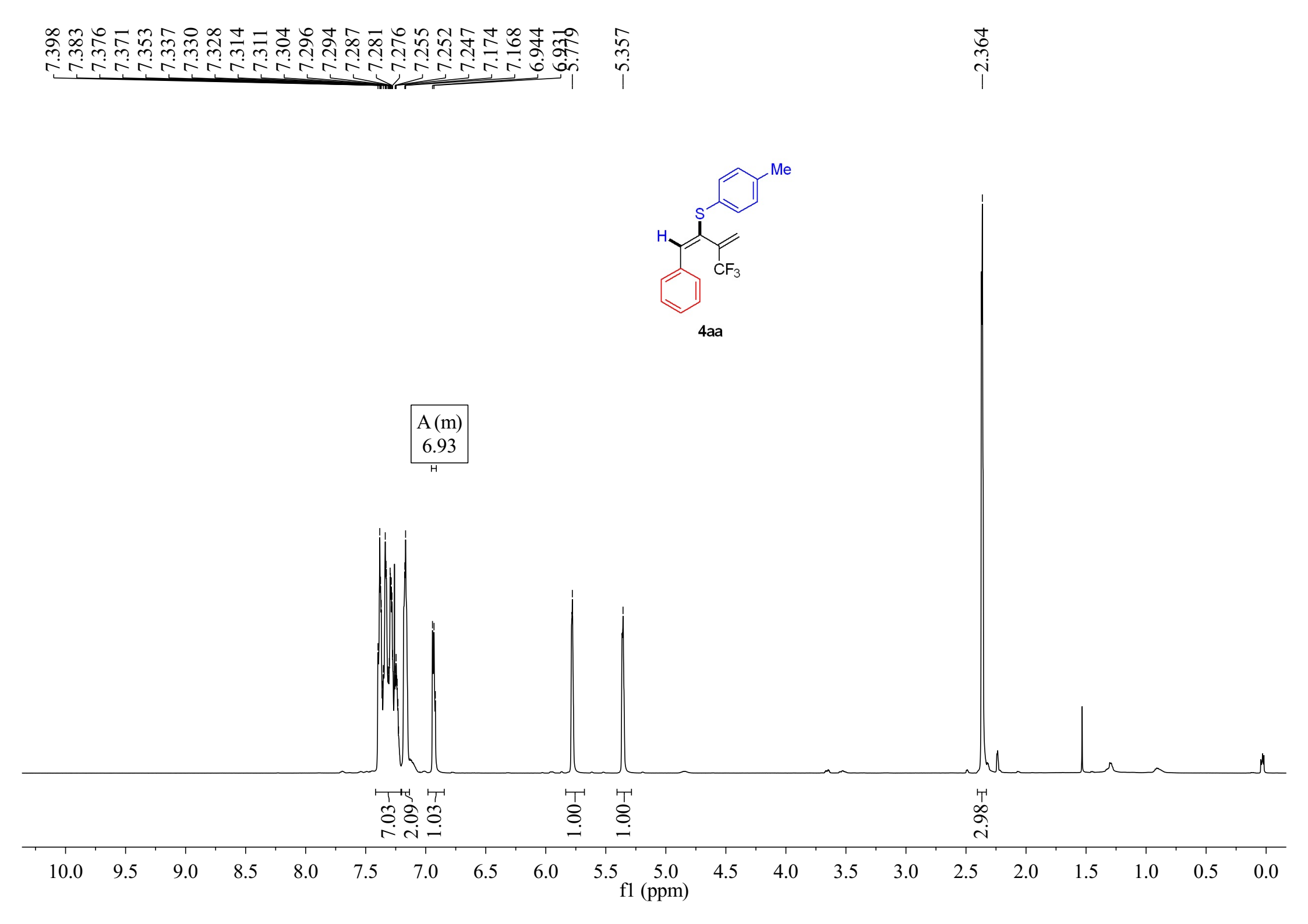
S
H2N
3af
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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7.337
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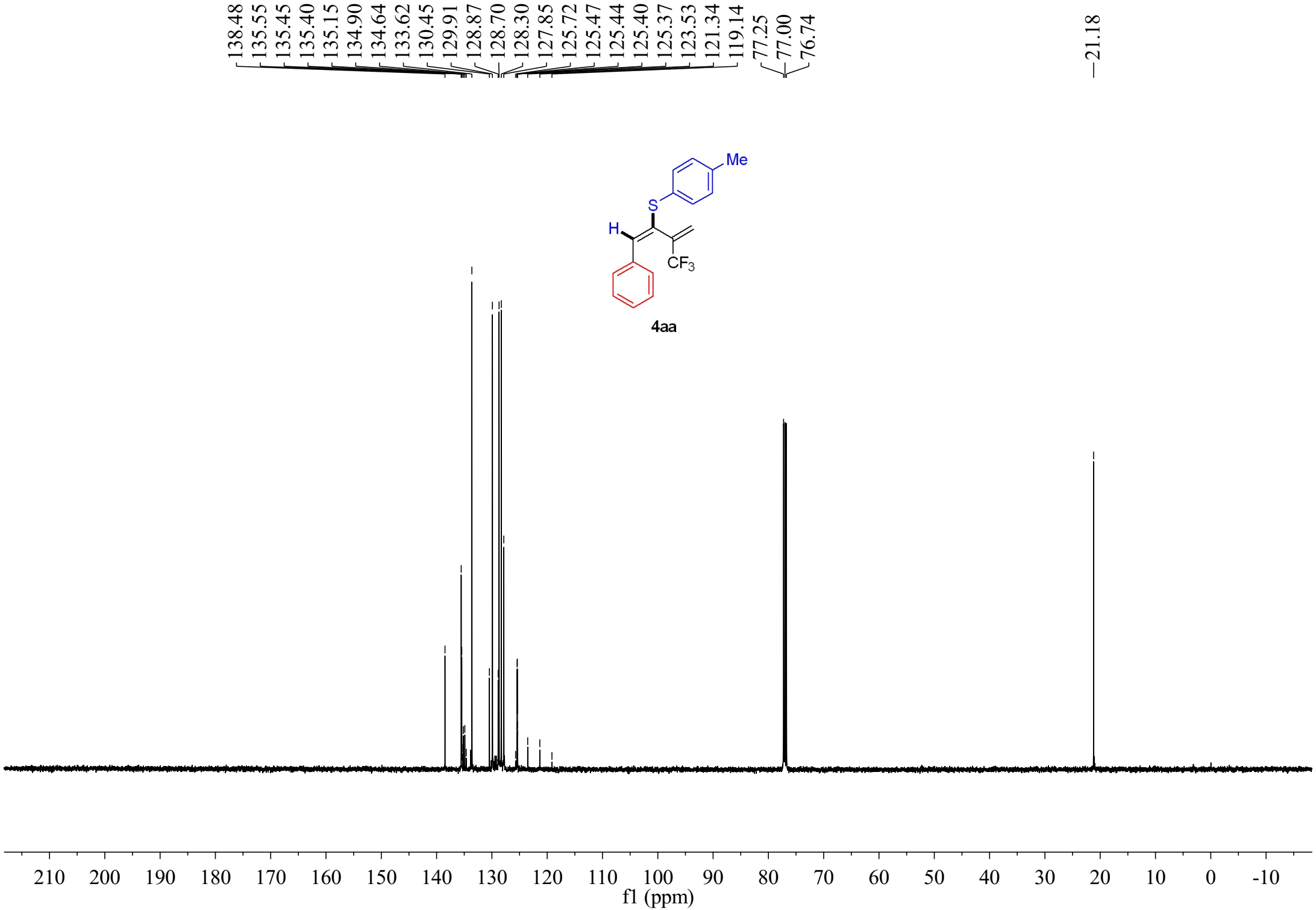
7.328
7.314
7.311
7.304
7.296
7.294
7.287
7.281
7.276
7.255
7.252
7.247
7.174
7.168
6.944
6.931
5.779
5.357
2.364
Me
S
H
CF3
4aa
A (m)
6.93
H
7.03
2.09
1.03
1.00
1.00
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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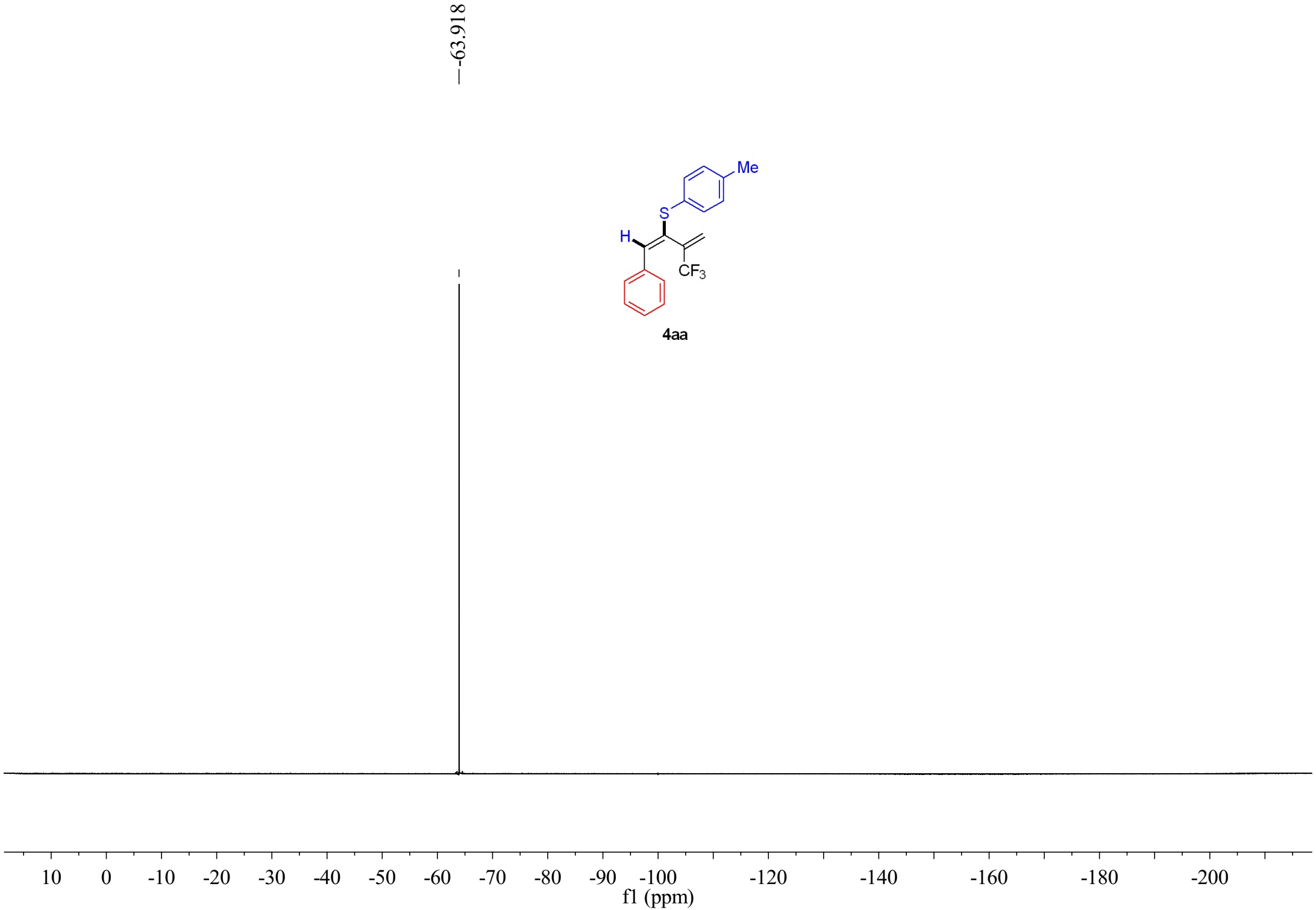
134.64
133.62
130.45
129.91
128.87
128.70
128.30
127.85
125.72
125.47
125.44
125.40
125.37
123.53
121.34
119.14
77.25
77.00
76.74
21.18
Me
S
H
CF3
4aa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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Me
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H
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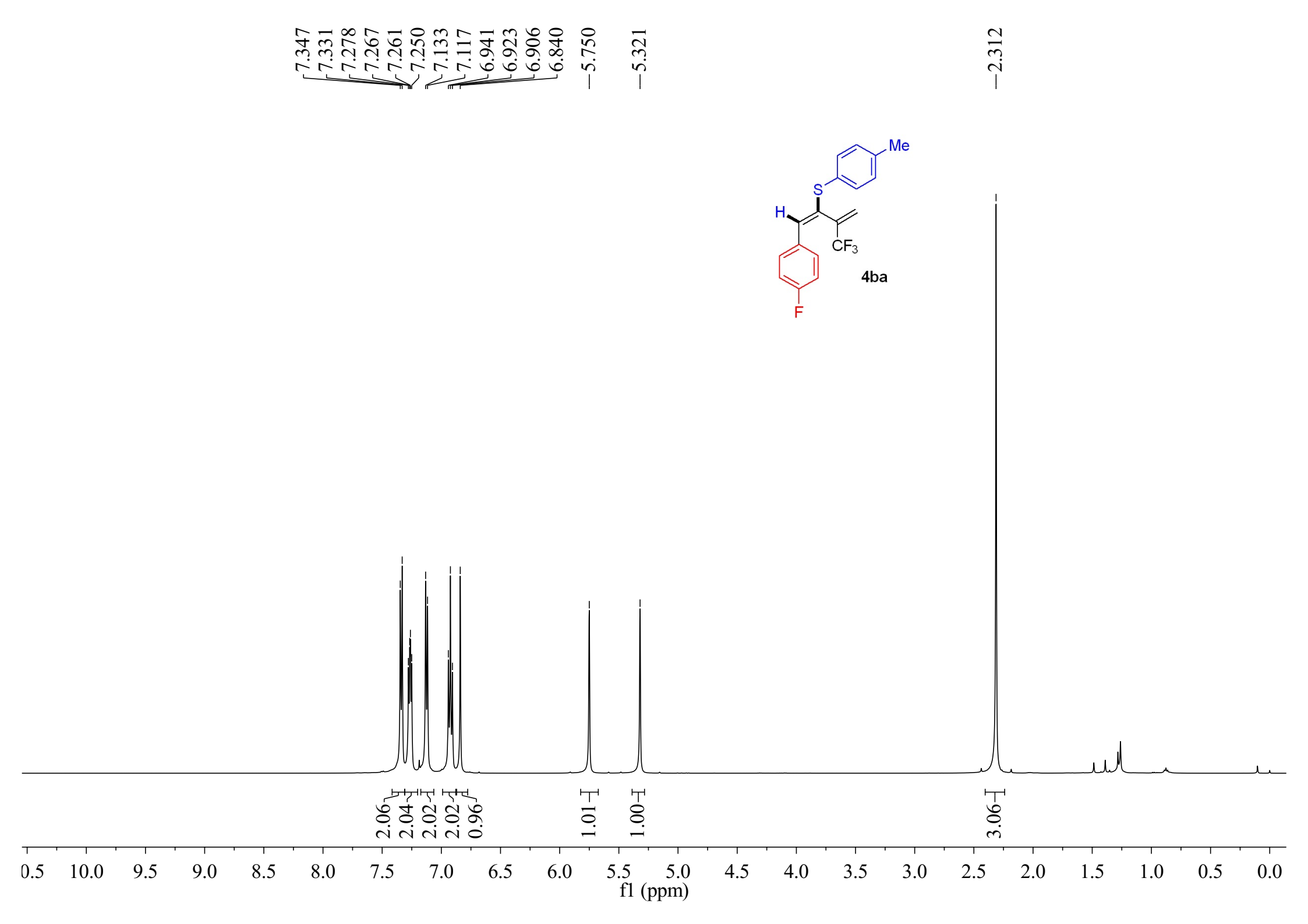
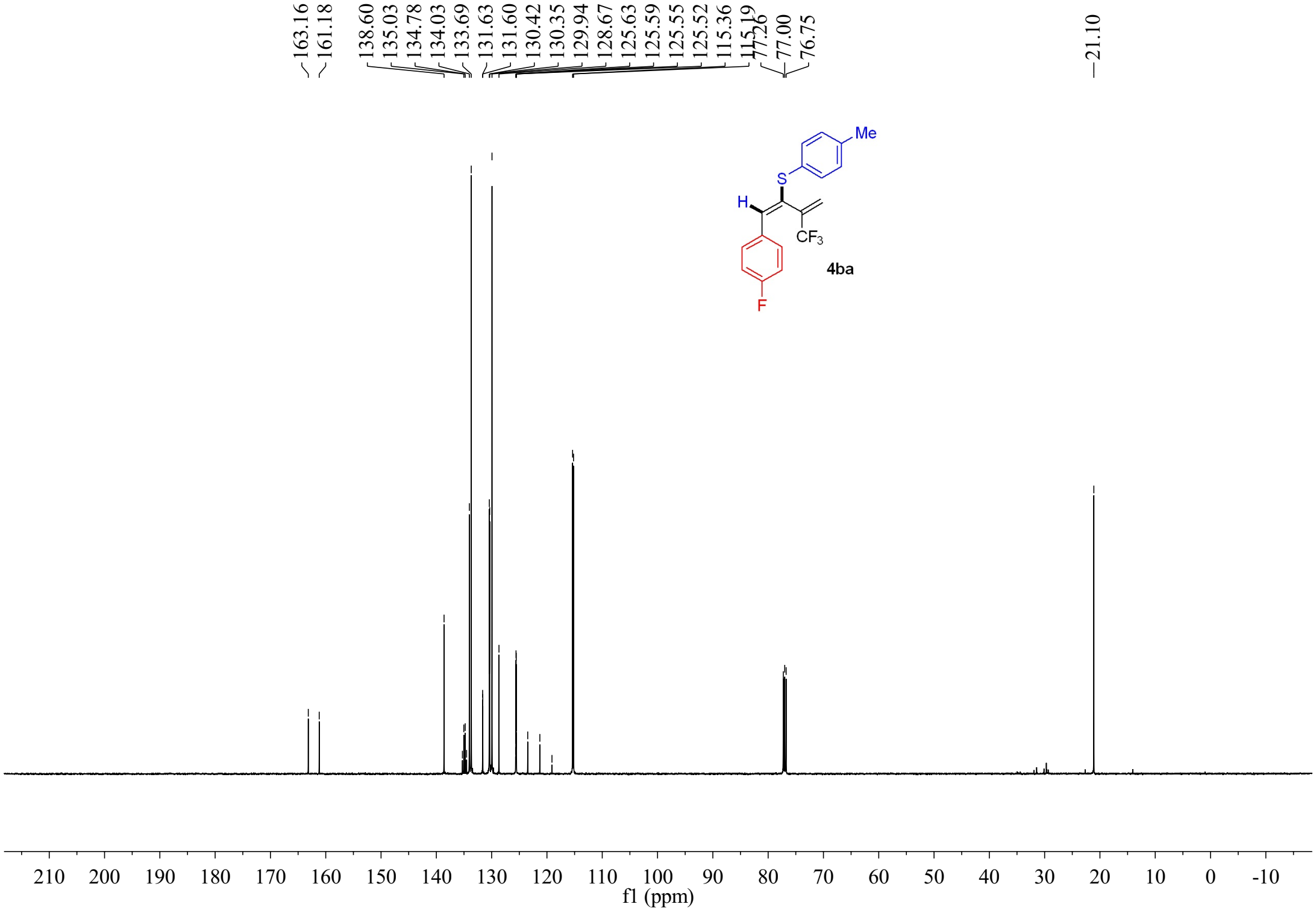
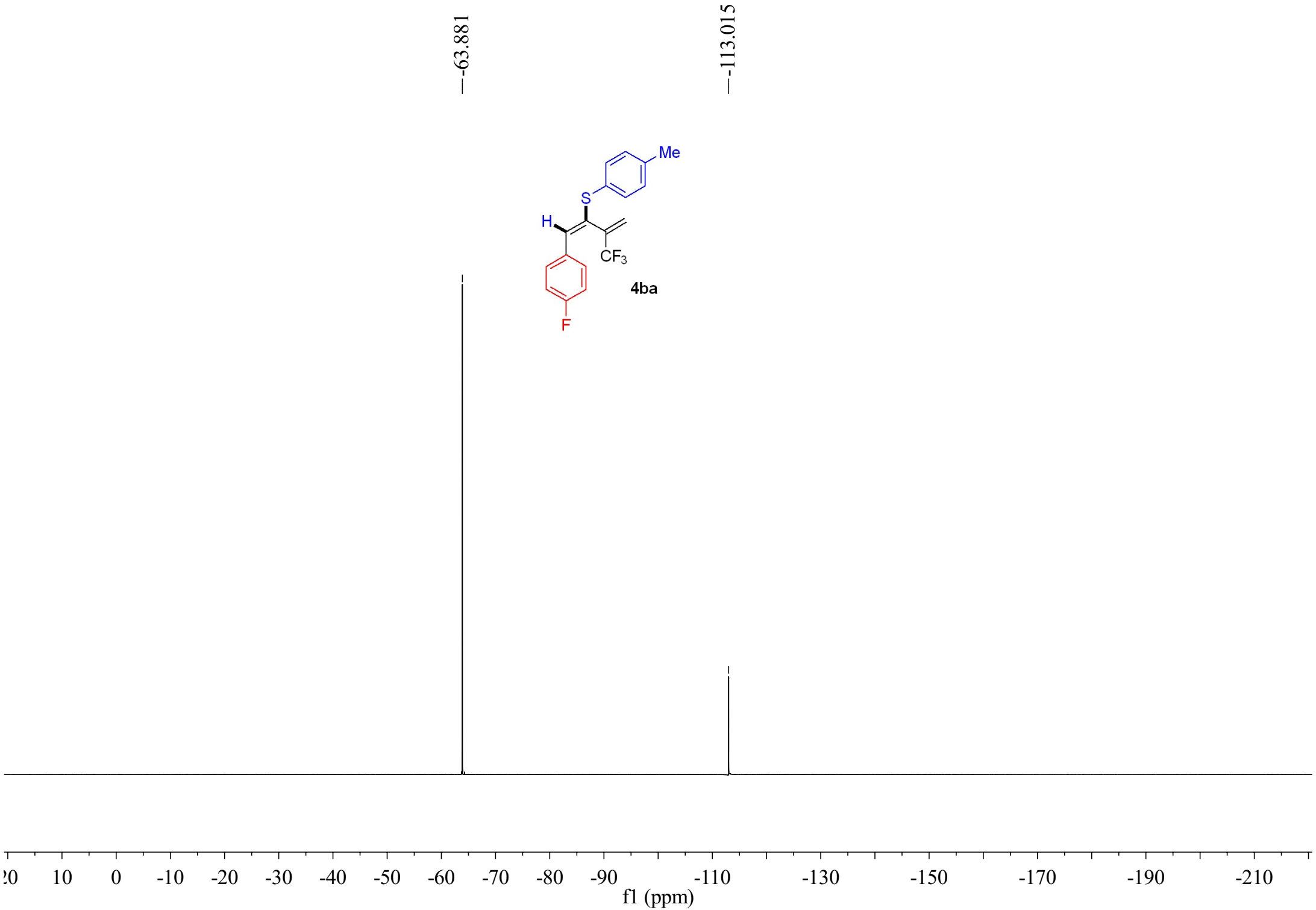
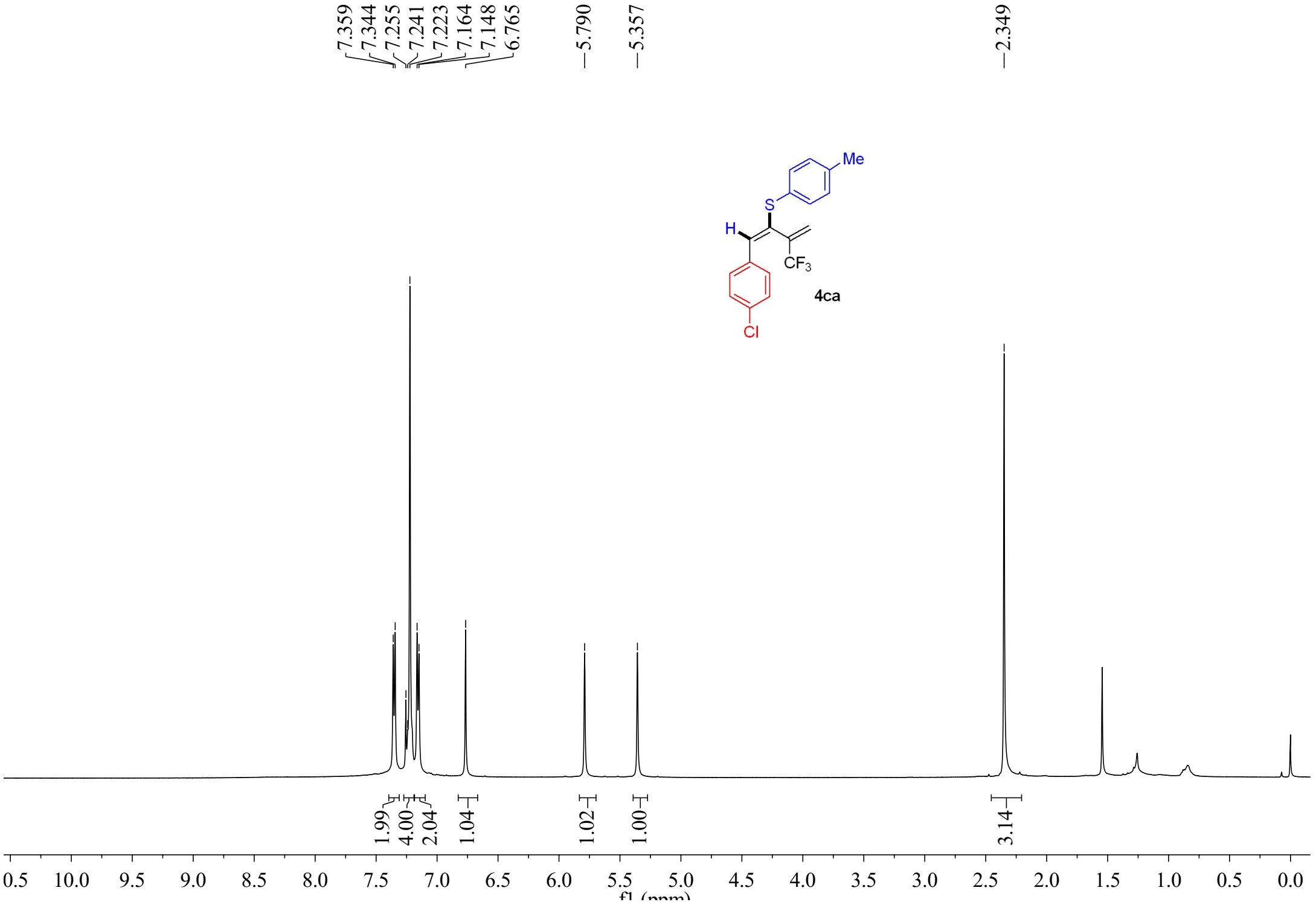
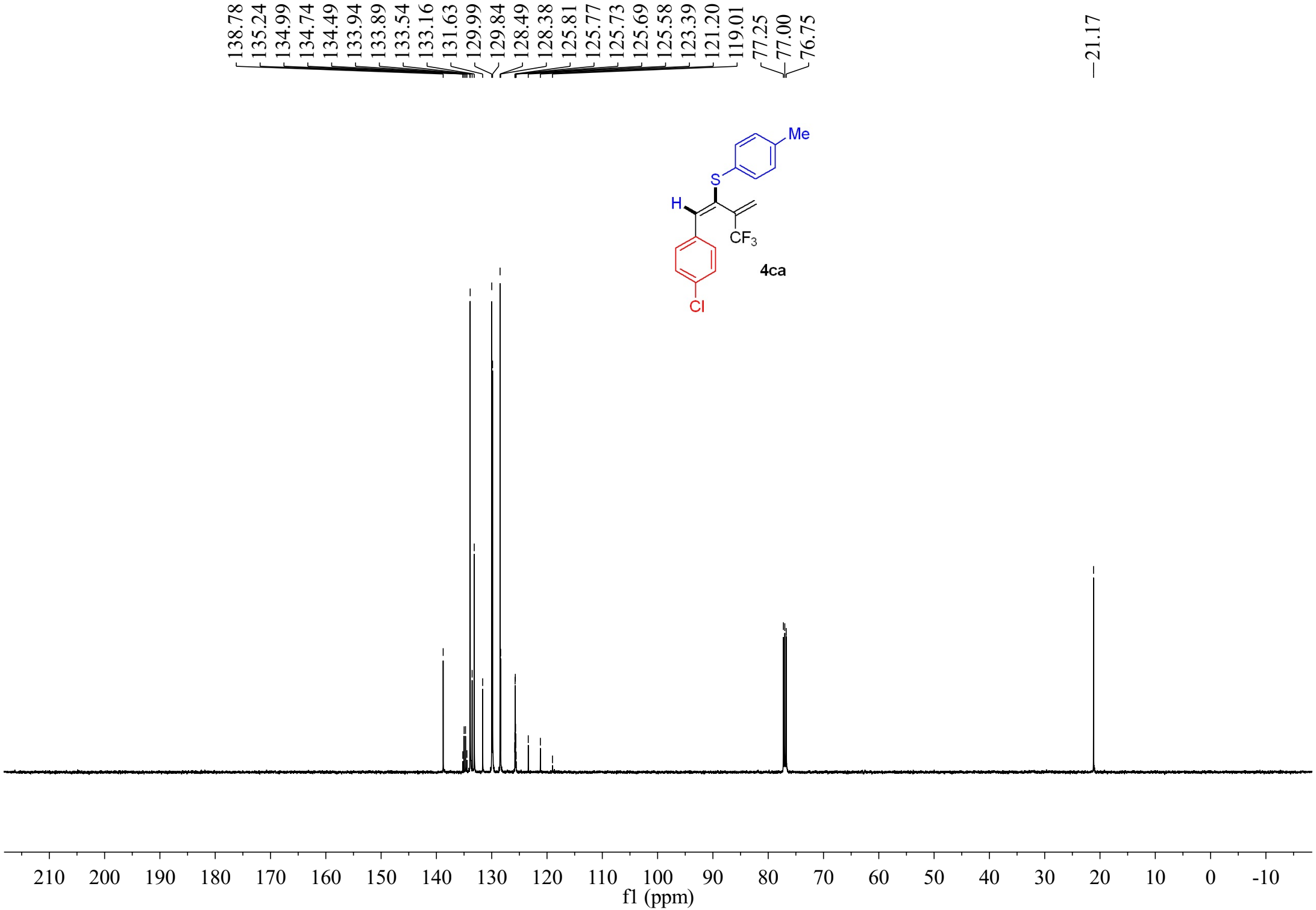
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

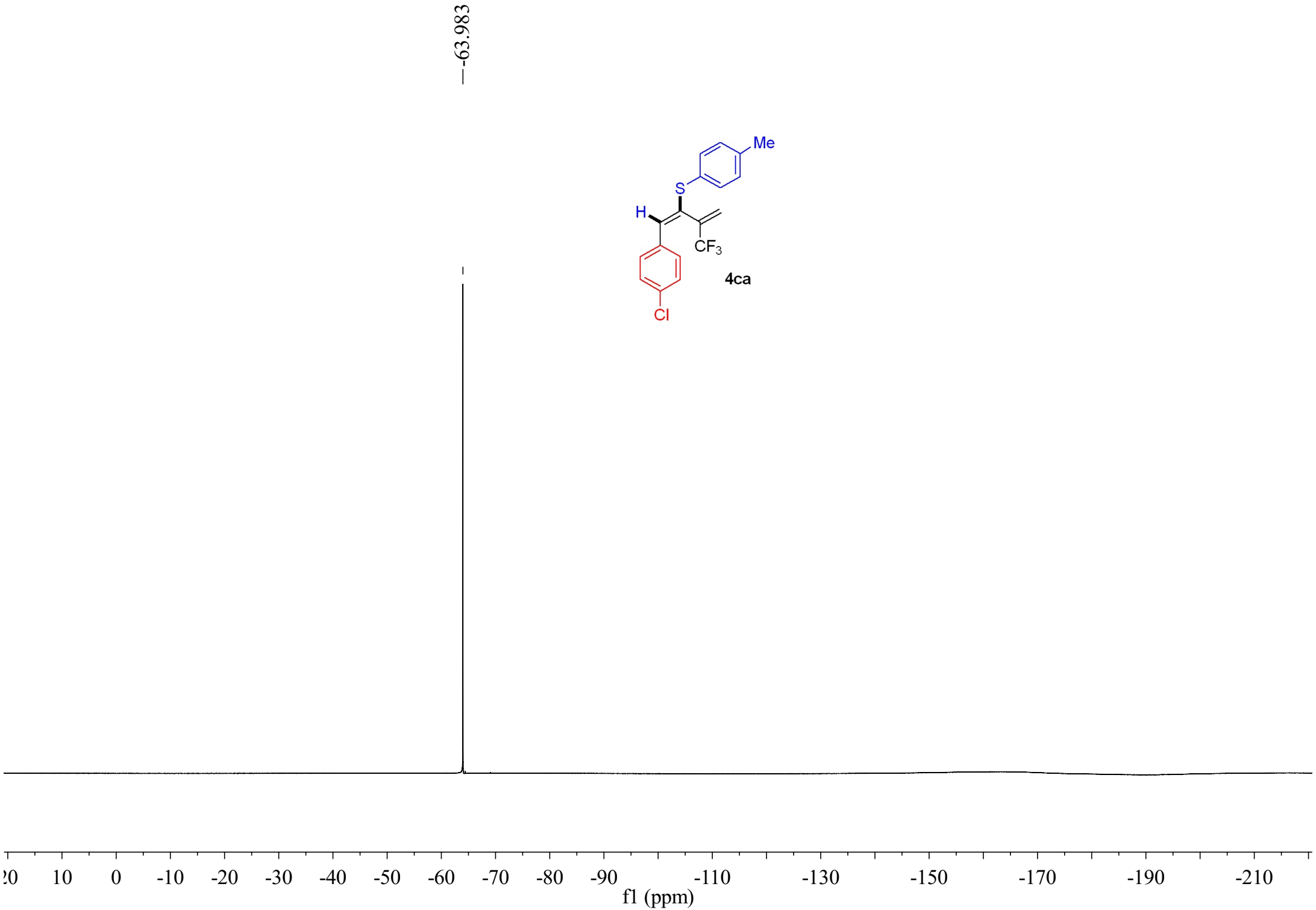

7.347
7.331
7.278
7.267
7.261
7.250
7.133
7.117
6.941
6.923
6.906
6.840
5.750
5.321
2.312
Me
S
H
CF3
F
4ba
2.06
2.04
2.02
2.02
0.96
1.01
1.00
3.06
f1 (ppm)

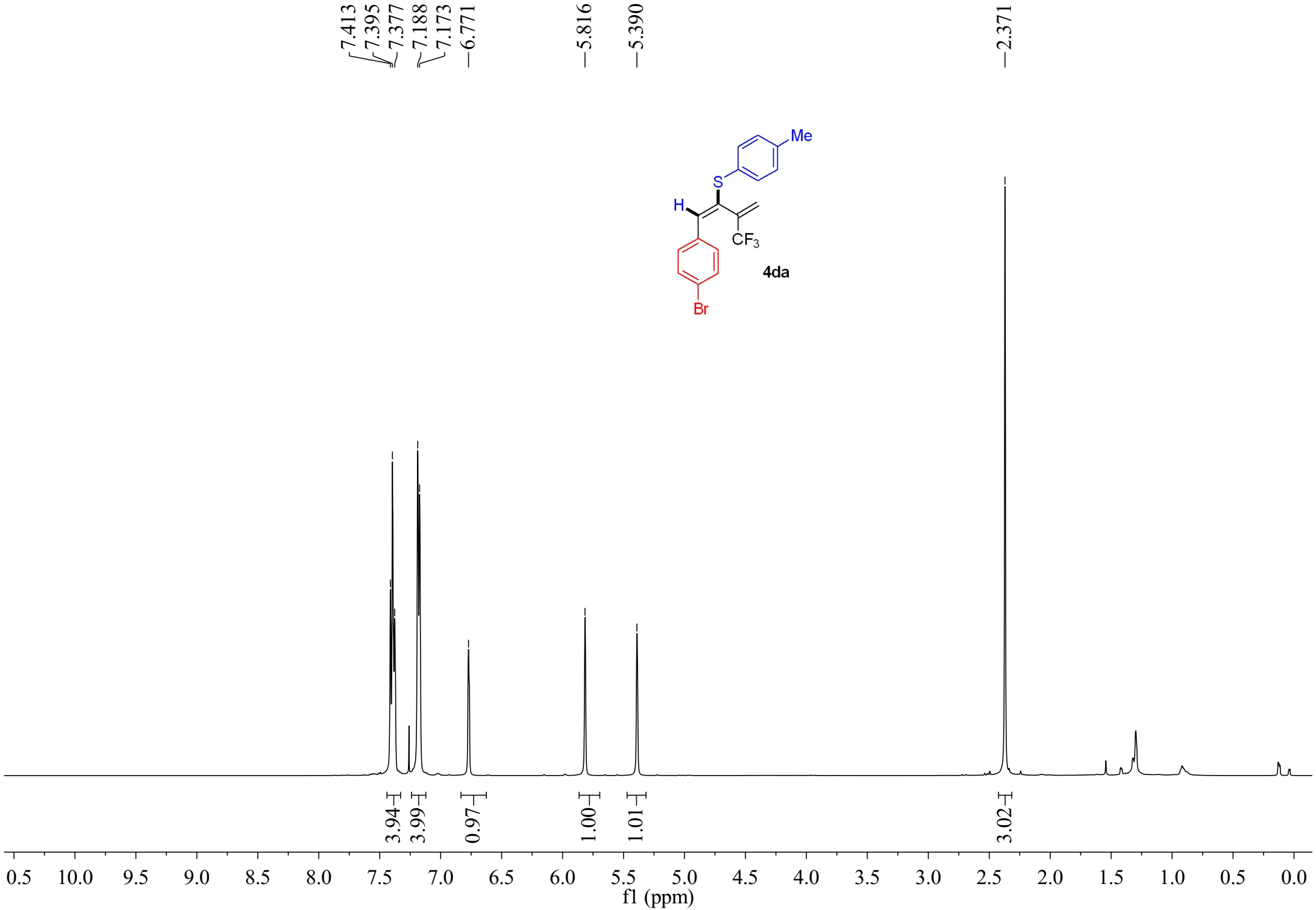

163.16
161.18
138.60
135.03
134.78
134.03
133.69
131.63
131.60
130.42
130.35
129.94
128.67
125.63
125.59
125.55
125.52
115.36
115.19
77.26
77.00
76.75
21.10
Me
S
H
CF3
F
4ba
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

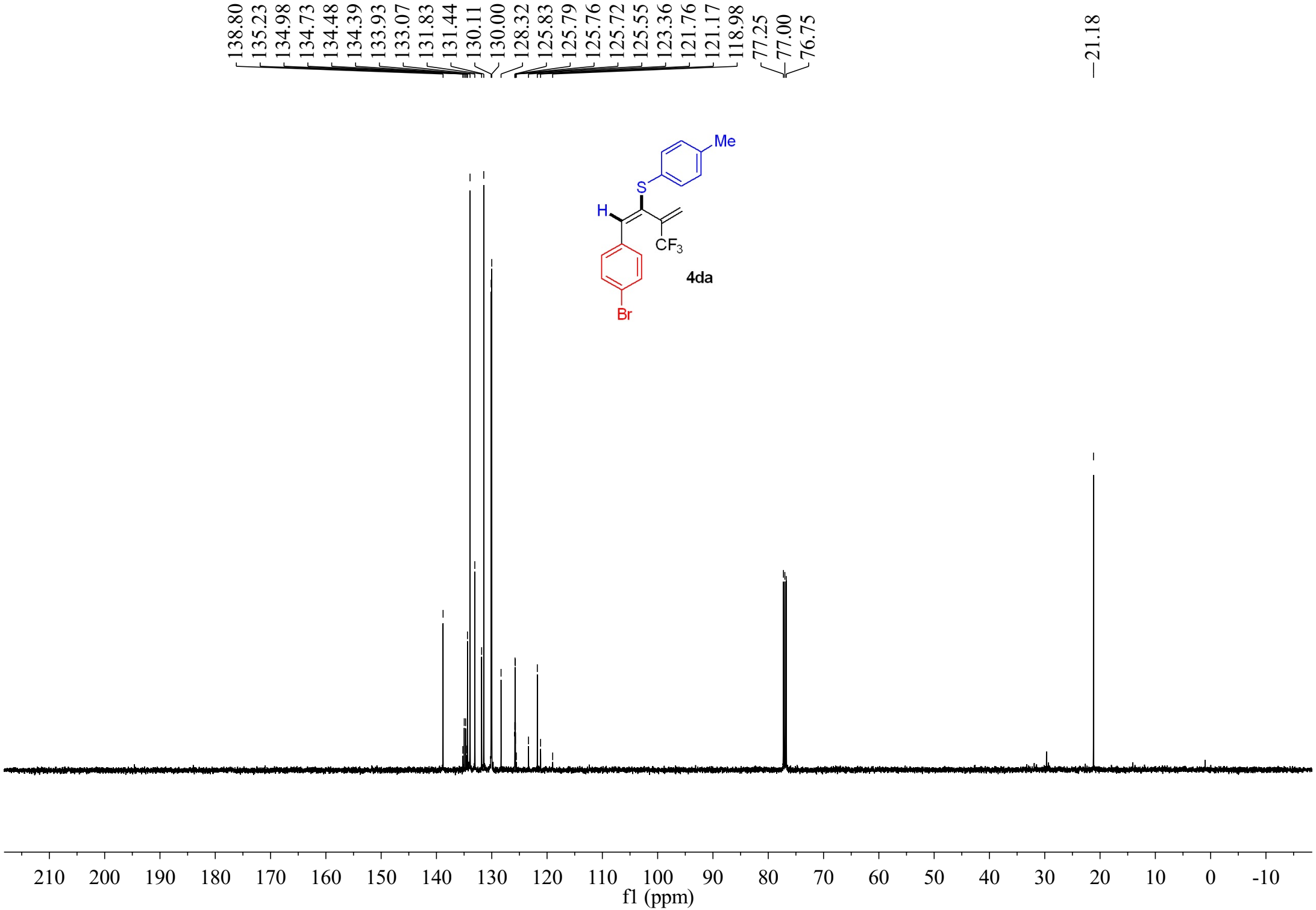

-63.881
-113.015
Me
S
H
CF3
F
4ba
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

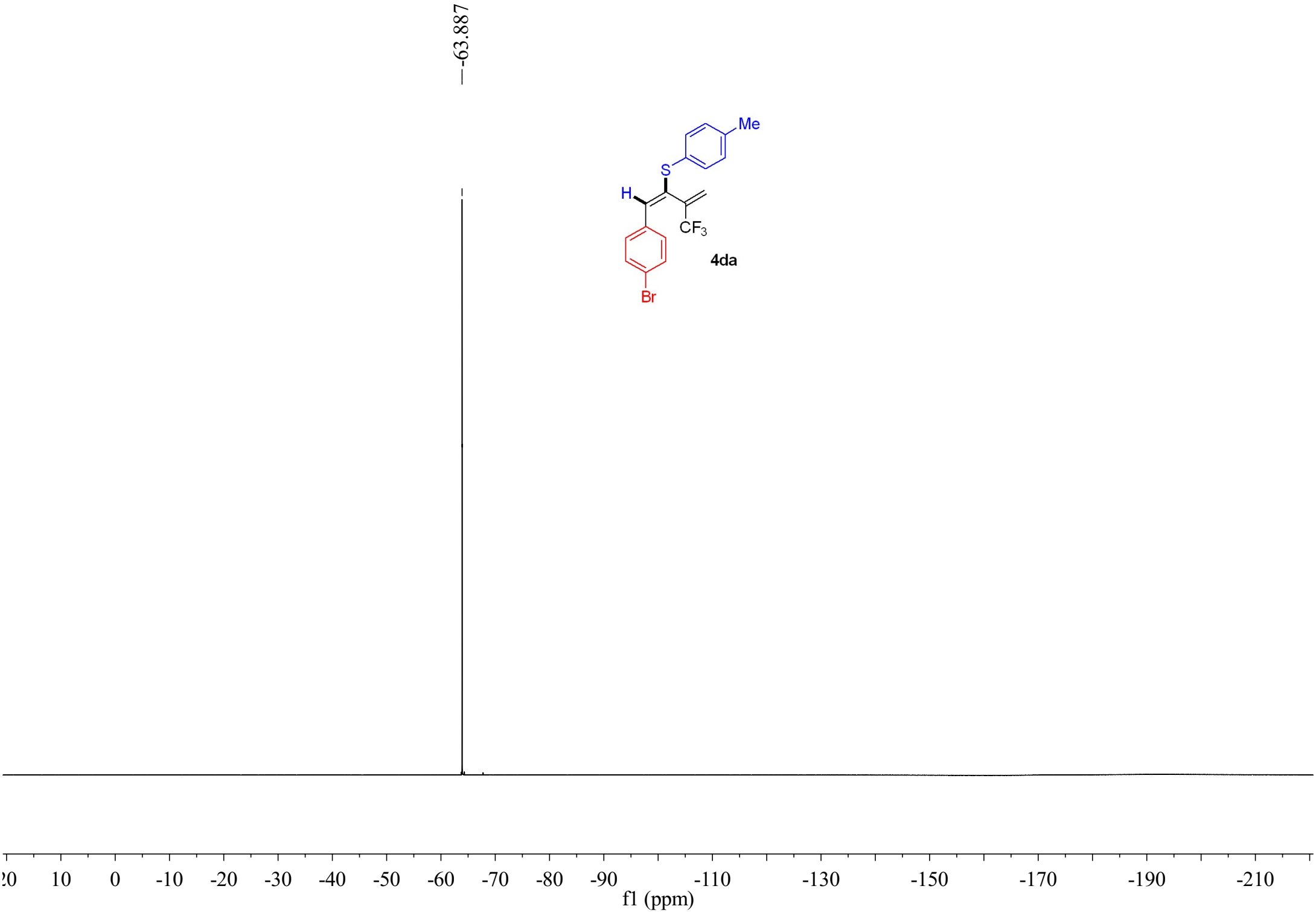

7.359
7.344
7.255
7.241
7.223
7.164
7.148
6.765
5.790
5.357
2.349
Me
S
H
CF3
Cl
4ca
1.99
4.00
2.04
1.04
1.02
1.00
3.14
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

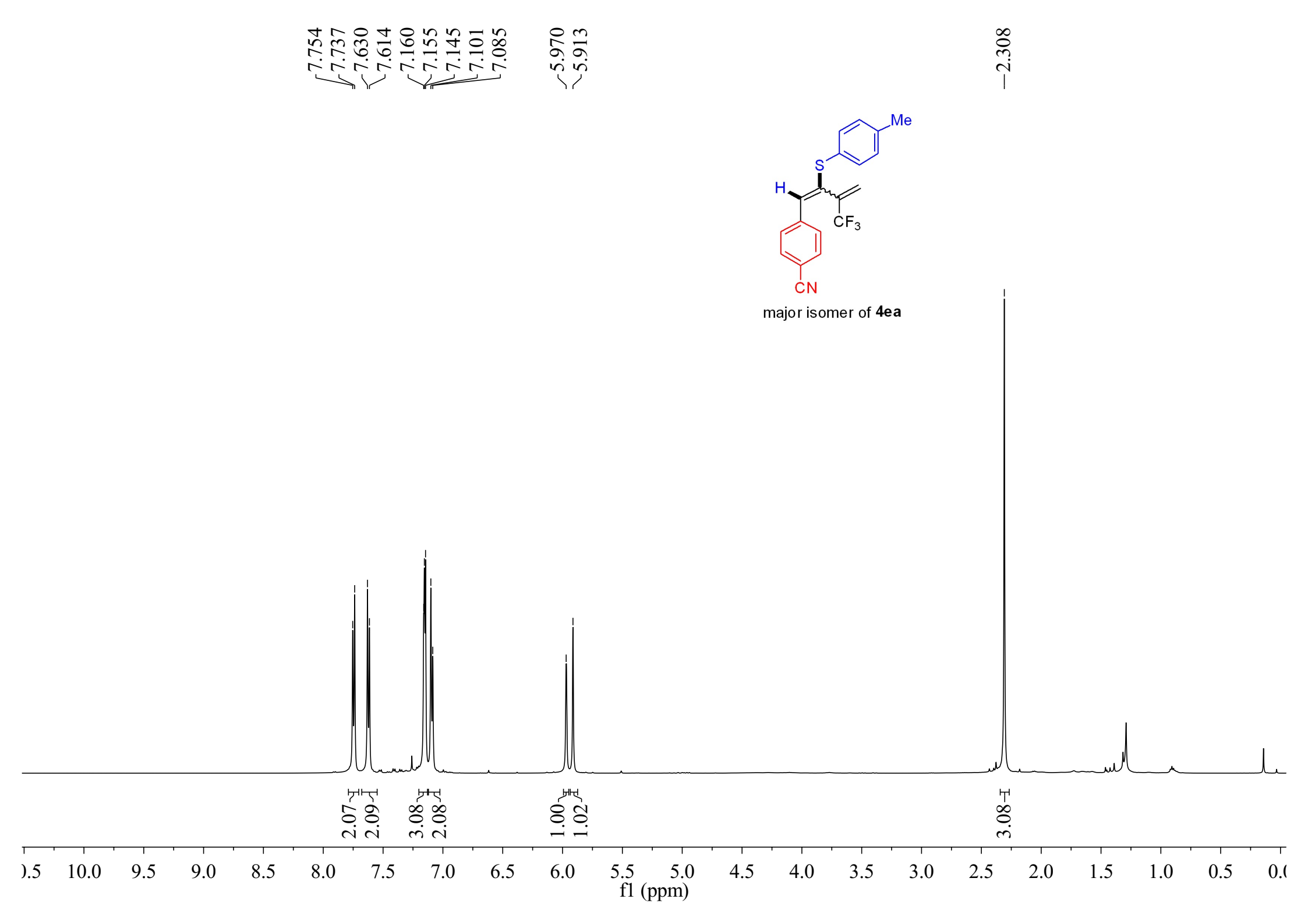

138.78
135.24
134.99
134.74
134.49
133.94
133.89
133.54
133.16
131.63
129.99
129.84
128.49
128.38
125.81
125.77
125.73
125.69
125.58
123.39
121.20
119.01
77.25
77.00
76.75
21.17
Me
S
H
CF3
Cl
4ca
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

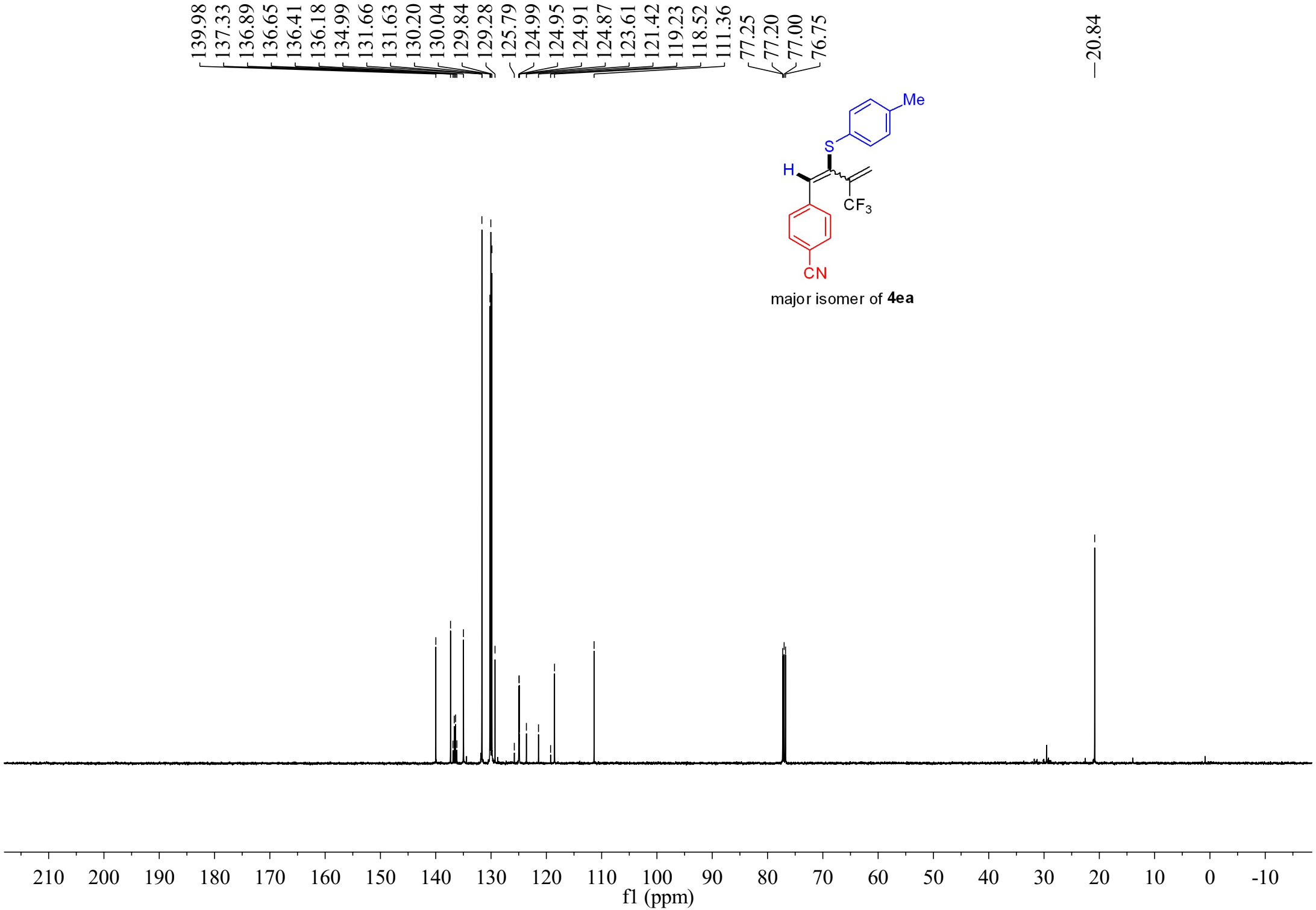

-63.983
Me
S
H
CF3
Cl
4ca
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

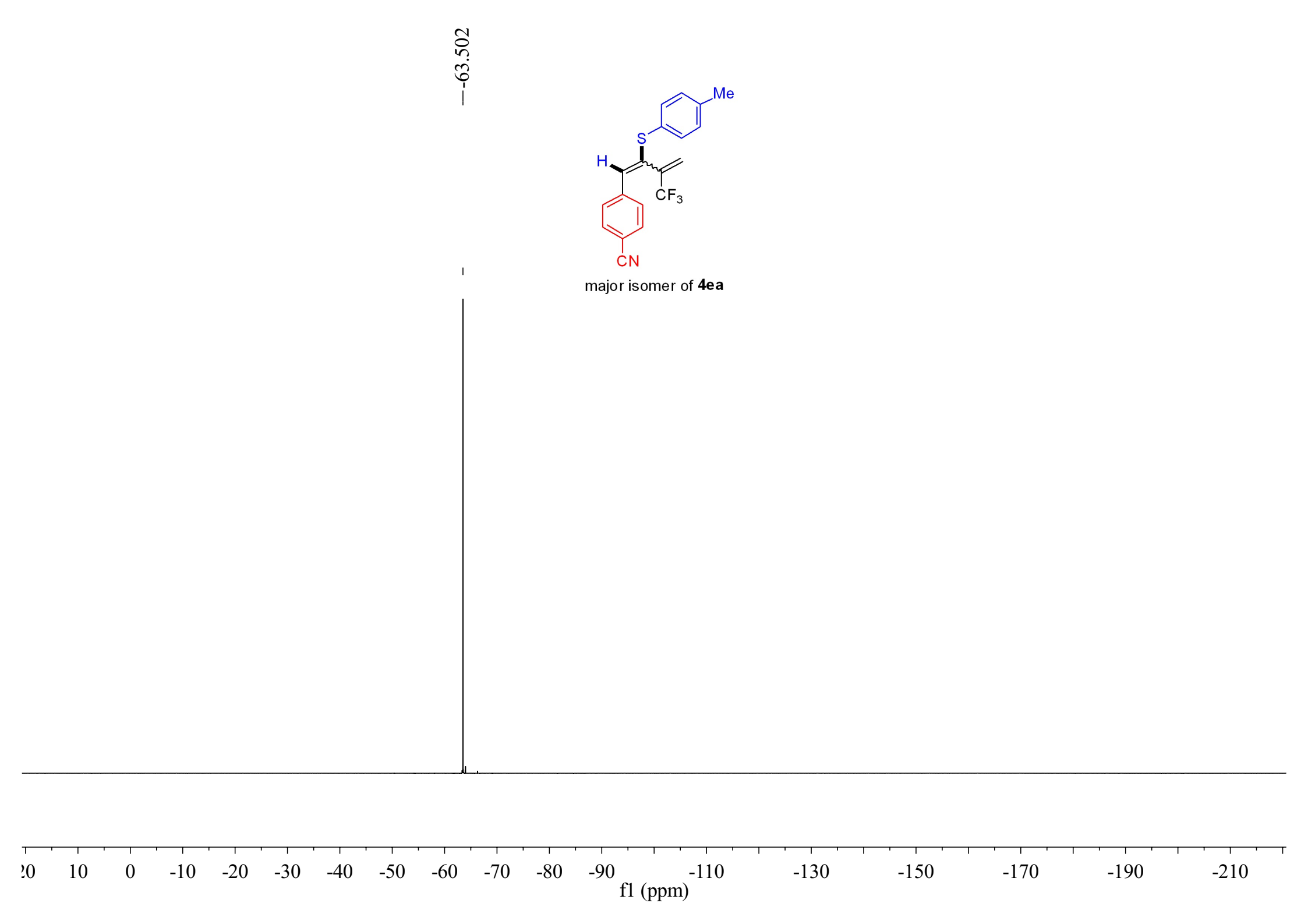

7.413
7.395
7.377
7.188
7.173
6.771
5.816
5.390
2.371
Me
S
H
CF3
Br
4da
3.94
3.99
0.97
1.00
1.01
3.02
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

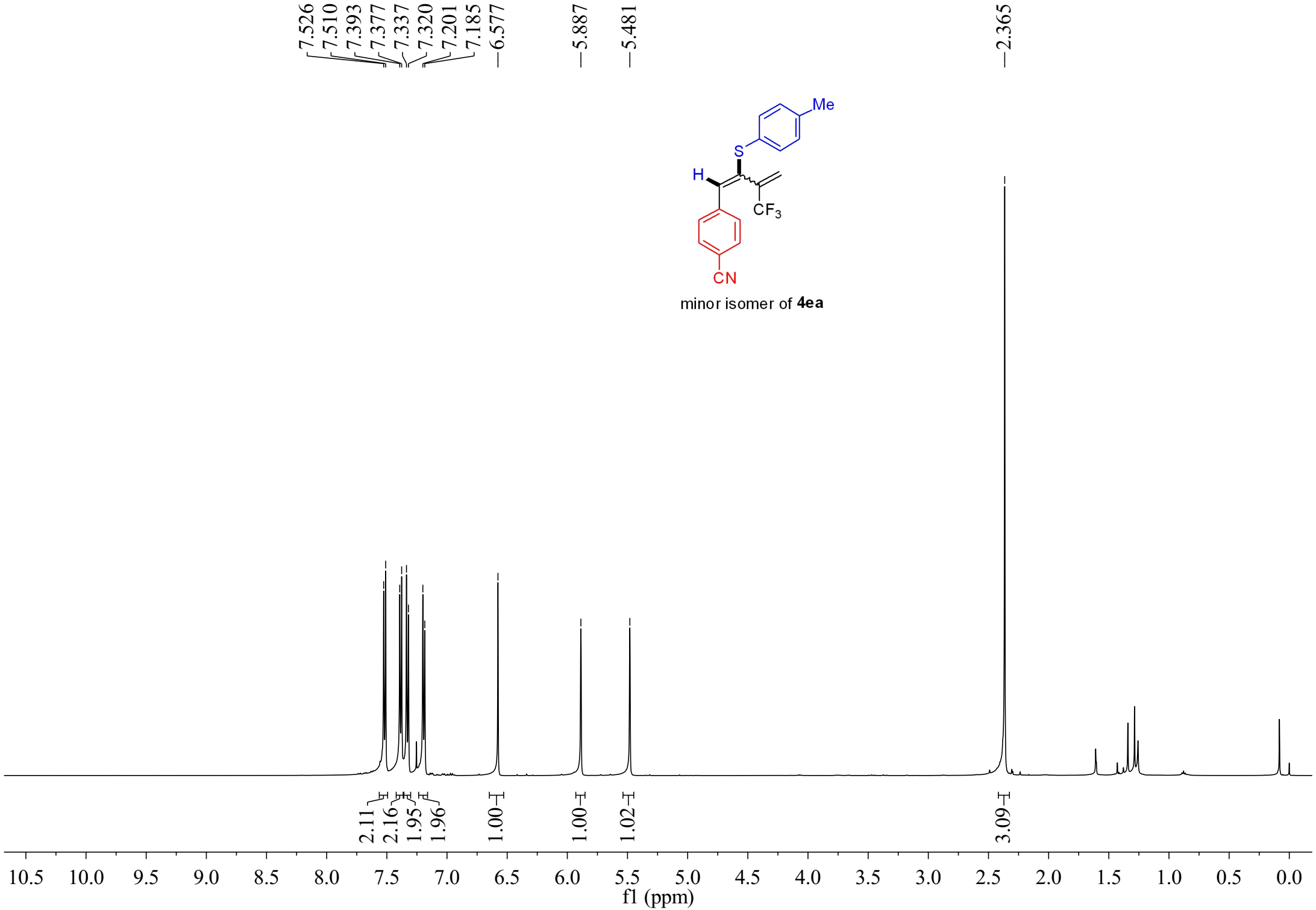

138.80
135.23
134.98
134.73
134.48
134.39
133.93
133.07
131.83
131.44
130.11
130.00
128.32
125.83
125.79
125.76
125.72
125.55
123.36
121.76
121.17
118.98
77.25
77.00
76.75
21.18
Me
S
H
CF3
Br
4da
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

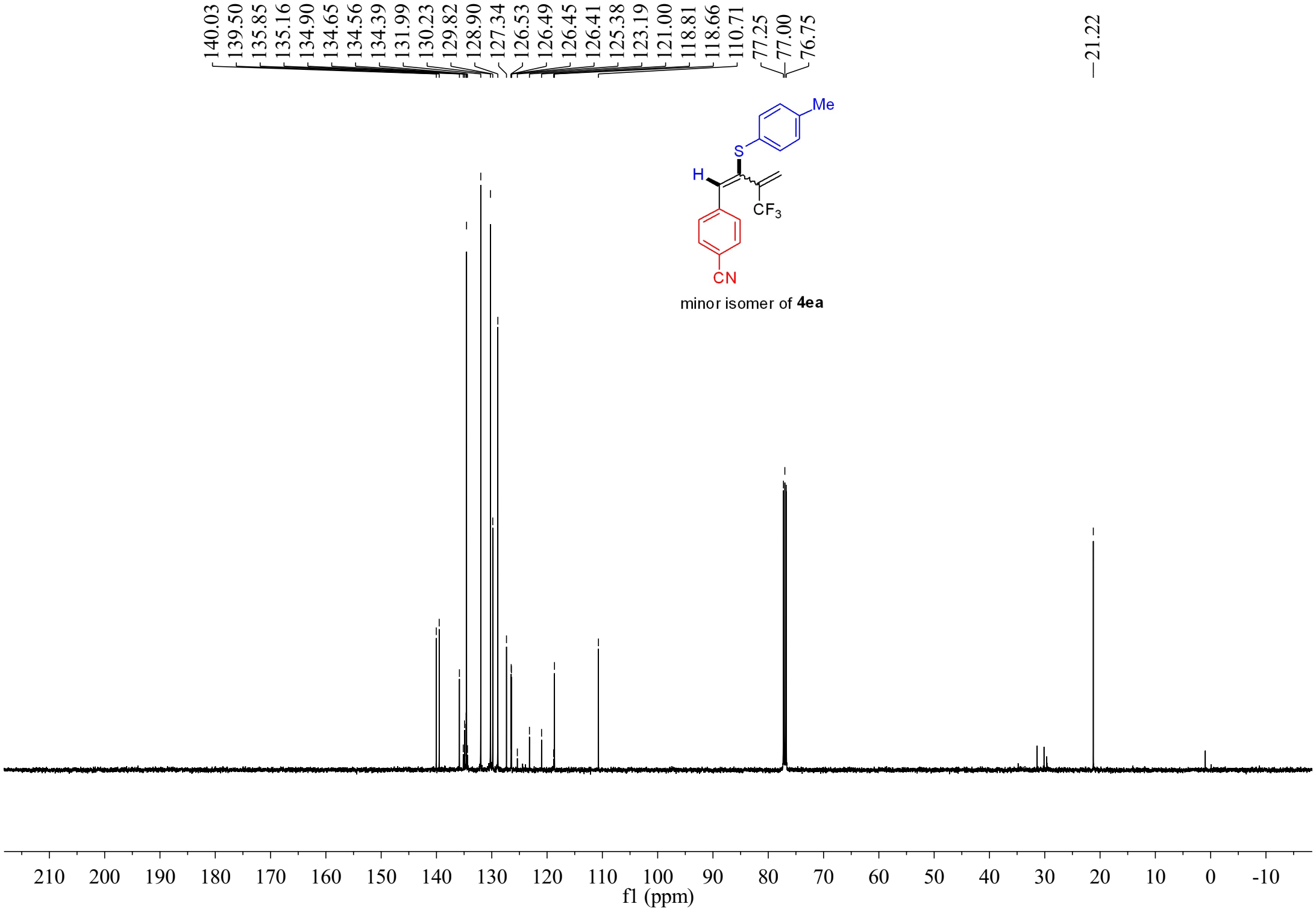

-63.887
Me
S
H
CF3
Br
4da
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

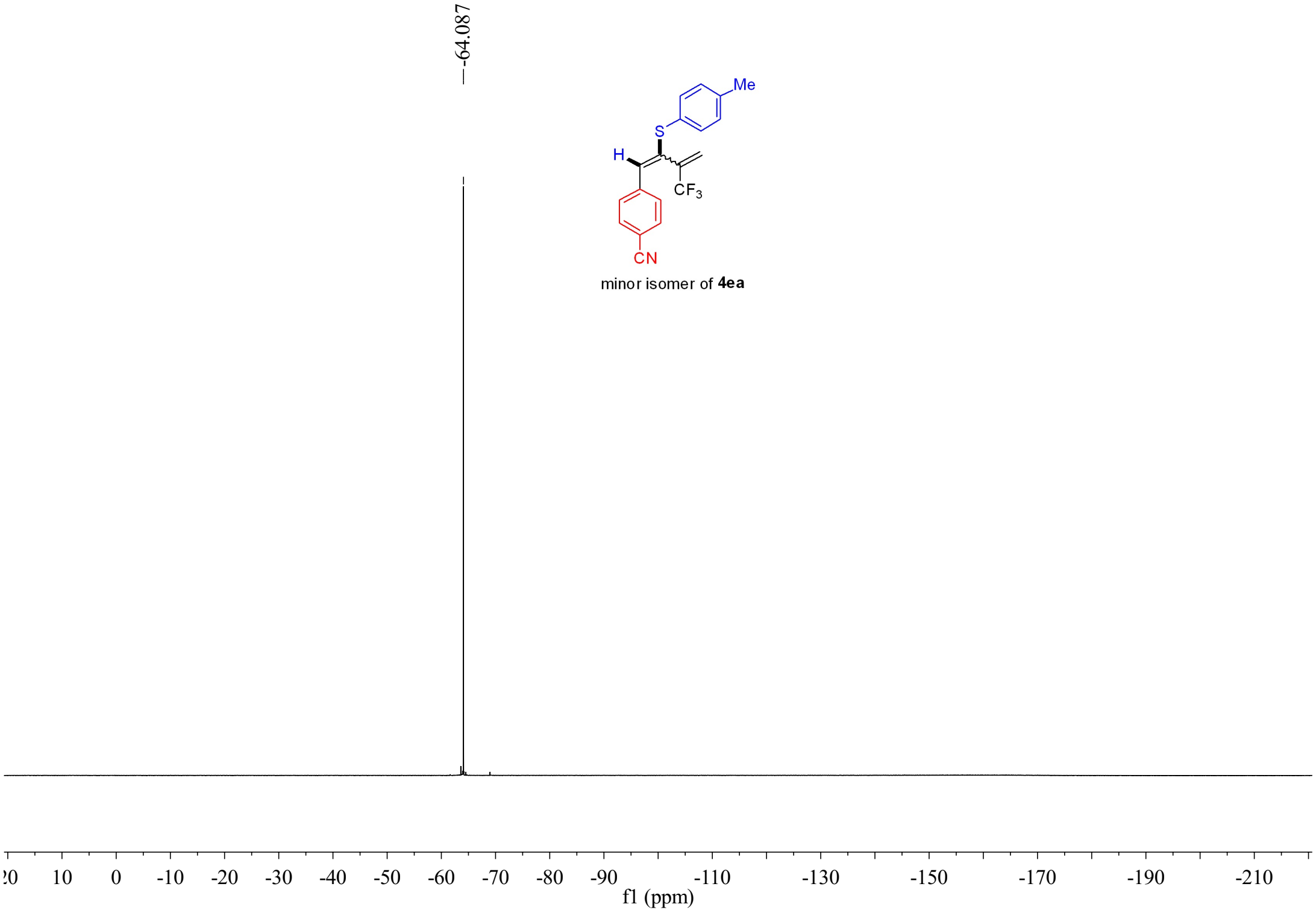

7.754
7.737
7.630
7.614
7.160
7.155
7.145
7.101
7.085
5.970
5.913
2.308
Me
S
H
CF3
CN
major isomer of 4ea
2.07
2.09
3.08
2.08
1.00
1.02
3.08
f1 (ppm)

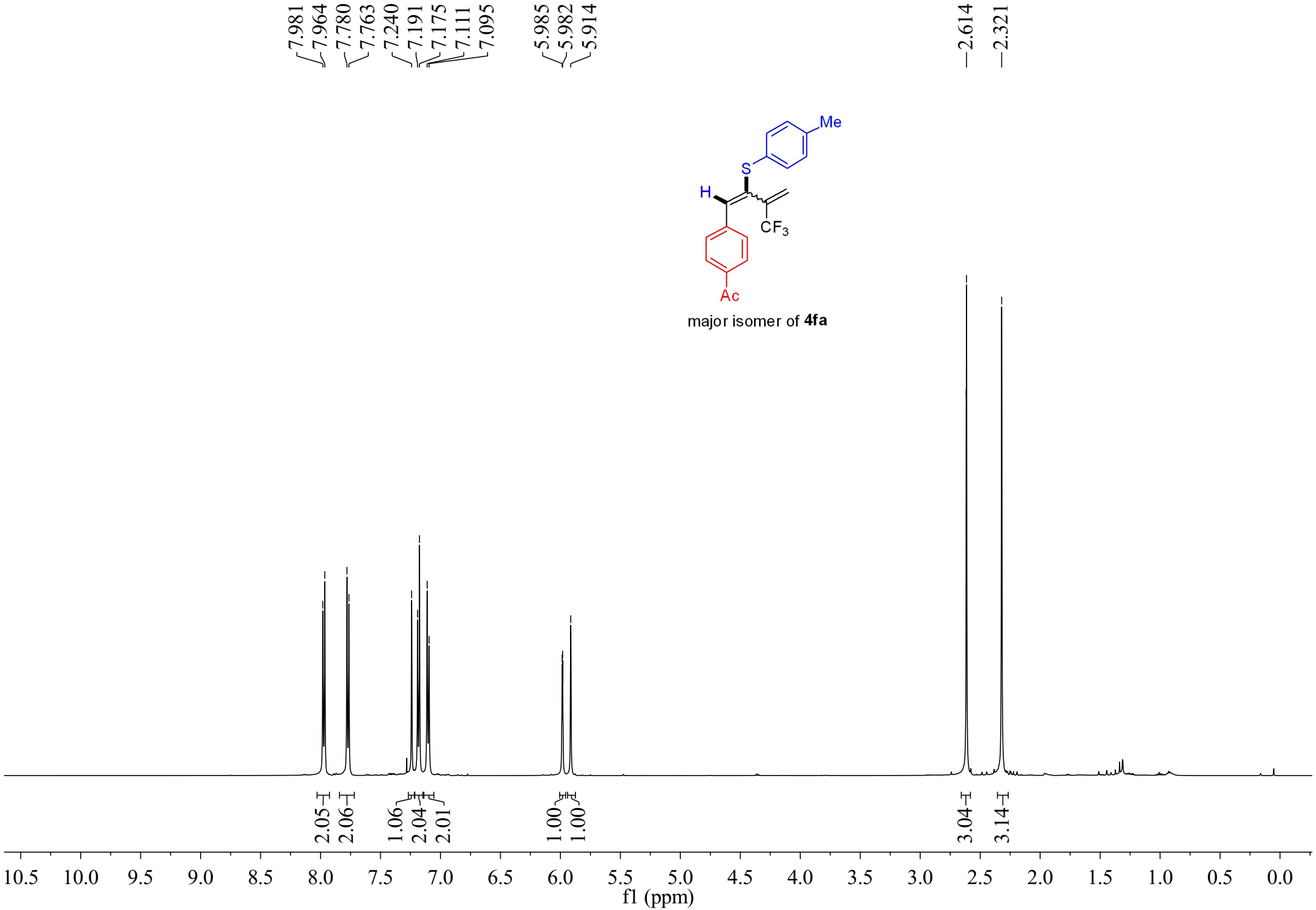

139.98
137.33
136.89
136.65
136.41
136.18
134.99
131.66
131.63
130.20
130.04
129.84
129.28
125.79
124.99
124.95
124.91
124.87
123.61
121.42
119.23
118.52
111.36
77.25
77.20
77.00
76.75
20.84
Me
S
H
CF3
CN
major isomer of 4ea
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

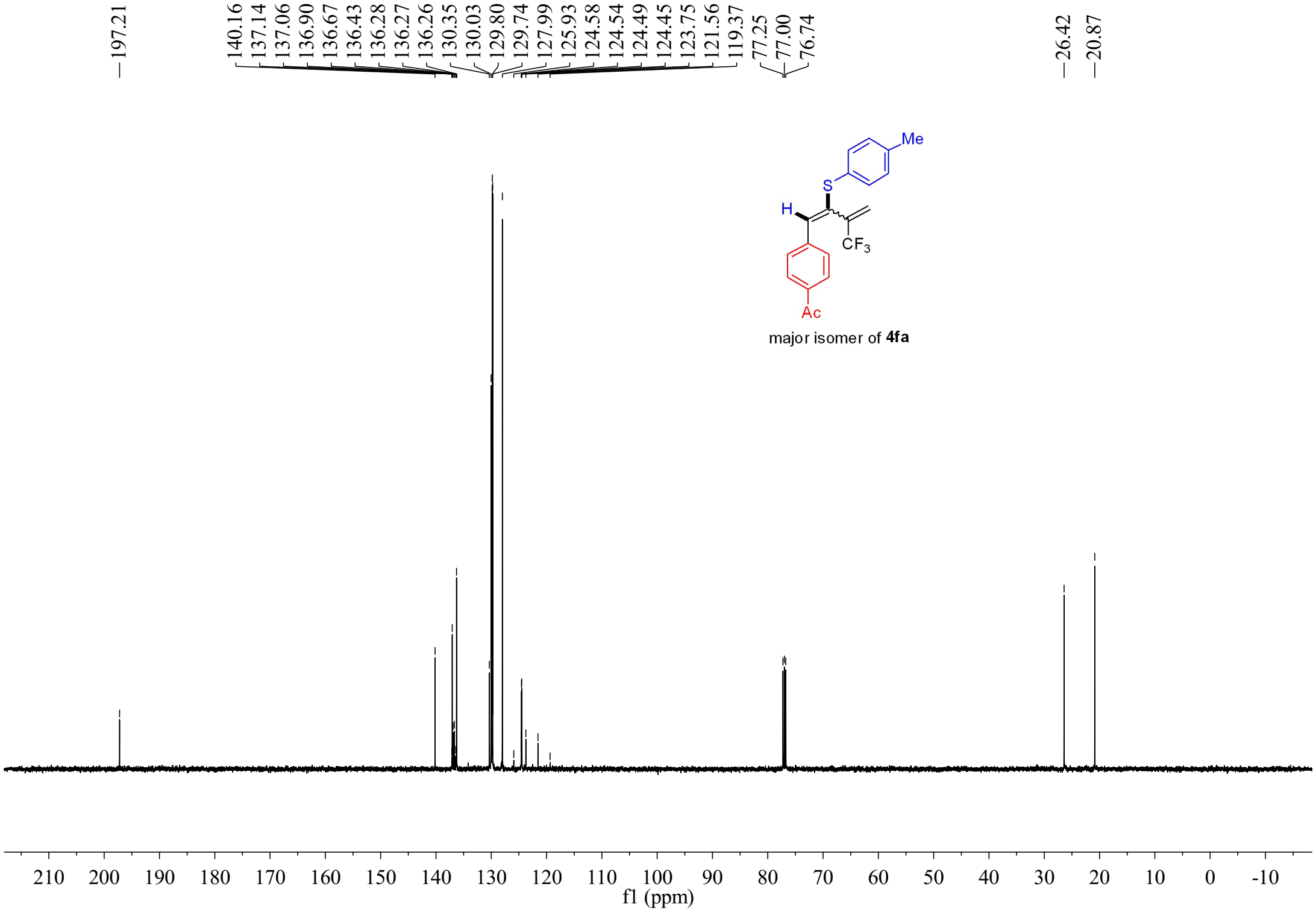

-63.502
Me
S
H
CF3
CN
major isomer of 4ea
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

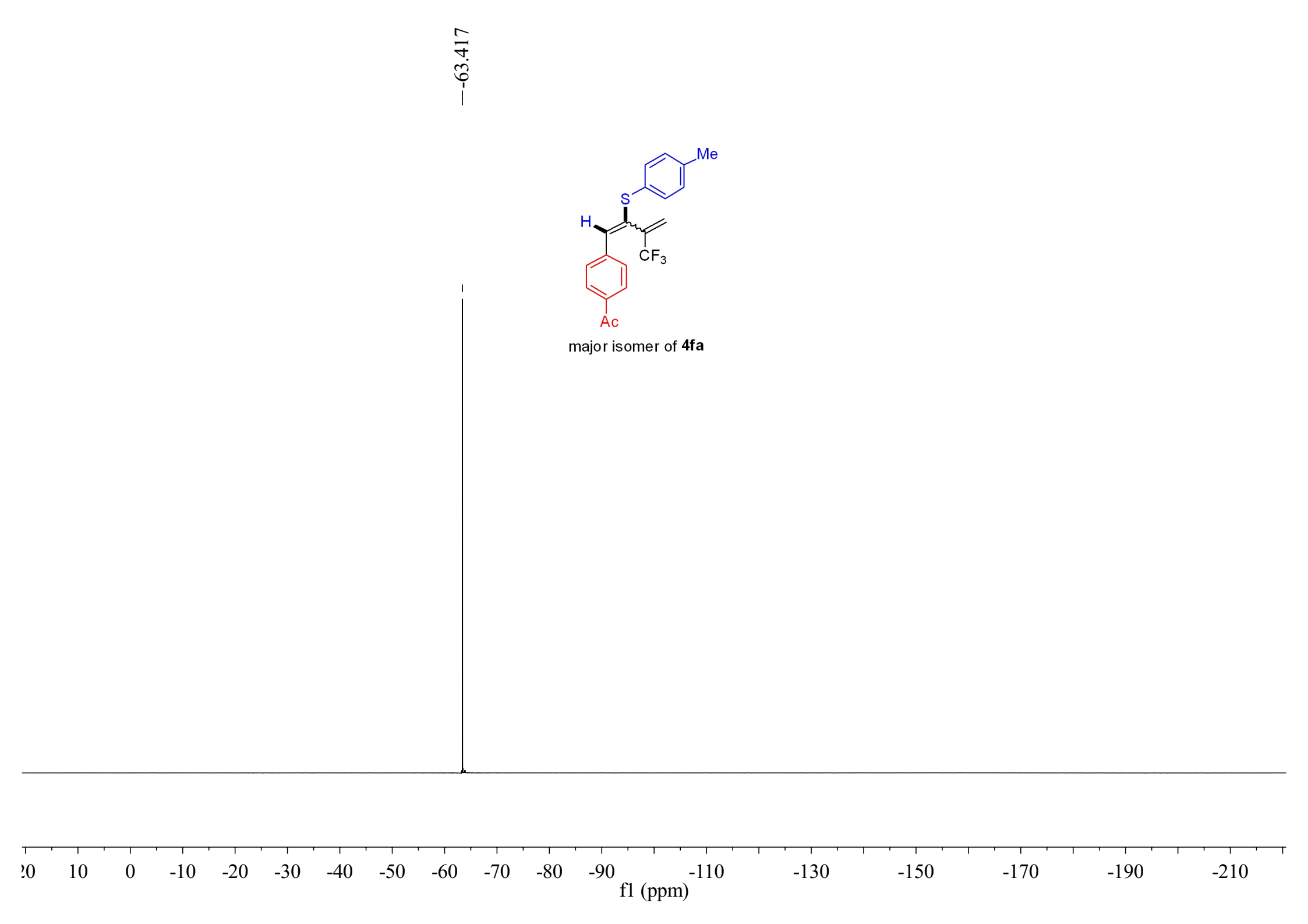

7.526
7.510
7.393
7.377
7.337
7.320
7.201
7.185
6.577
5.887
5.481
2.365
Me
S
H
CF3
CN
minor isomer of 4ea
2.11
2.16
1.95
1.96
1.00
1.00
1.02
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

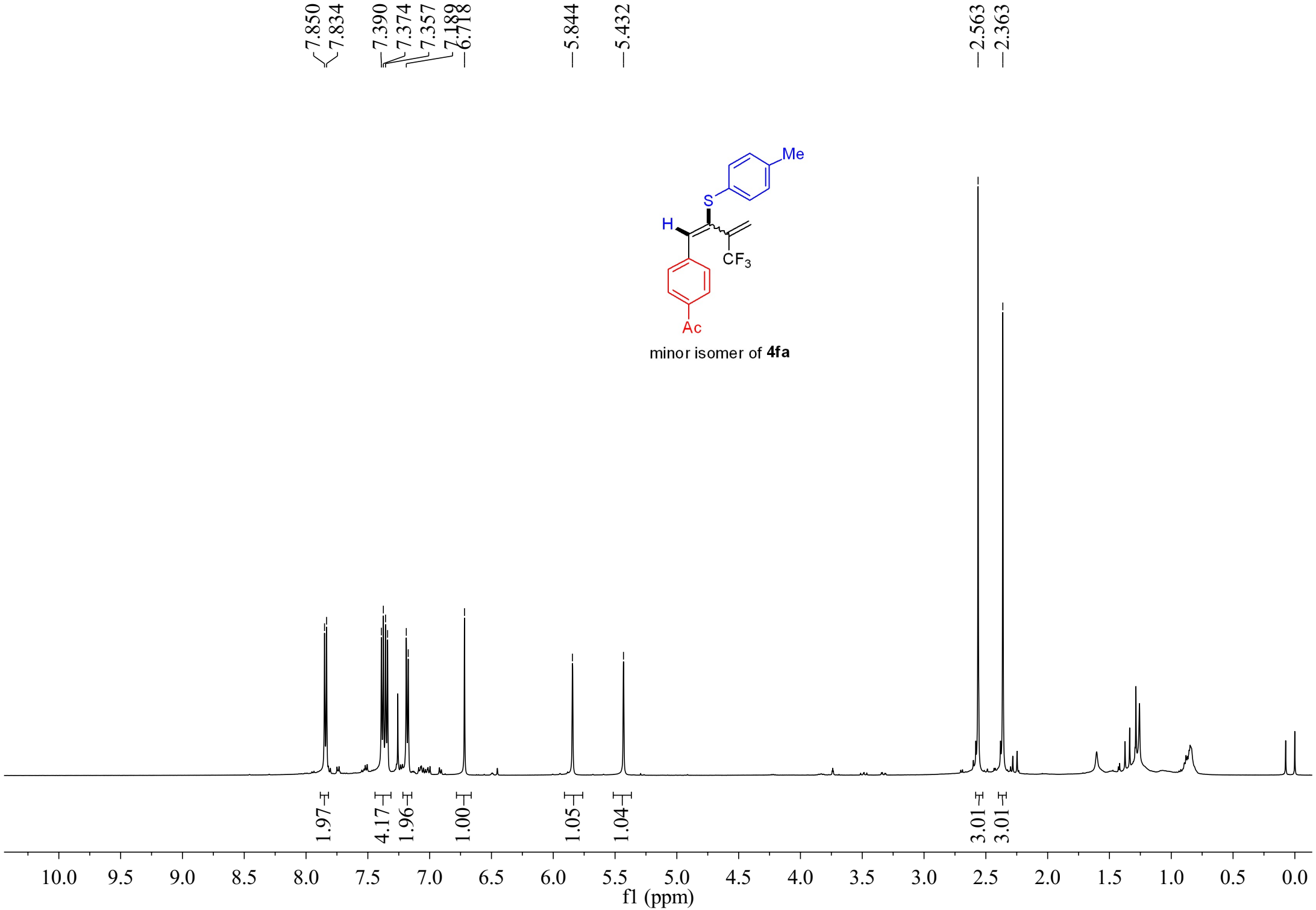

140.03
139.50
135.85
135.16
134.90
134.65
134.56
134.39
131.99
130.23
129.82
128.90
127.34
126.53
126.49
126.45
126.41
125.38
123.19
121.00
118.81
118.66
110.71
77.25
77.00
76.75
21.22
Me
S
H
CF3
CN
minor isomer of 4ea
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

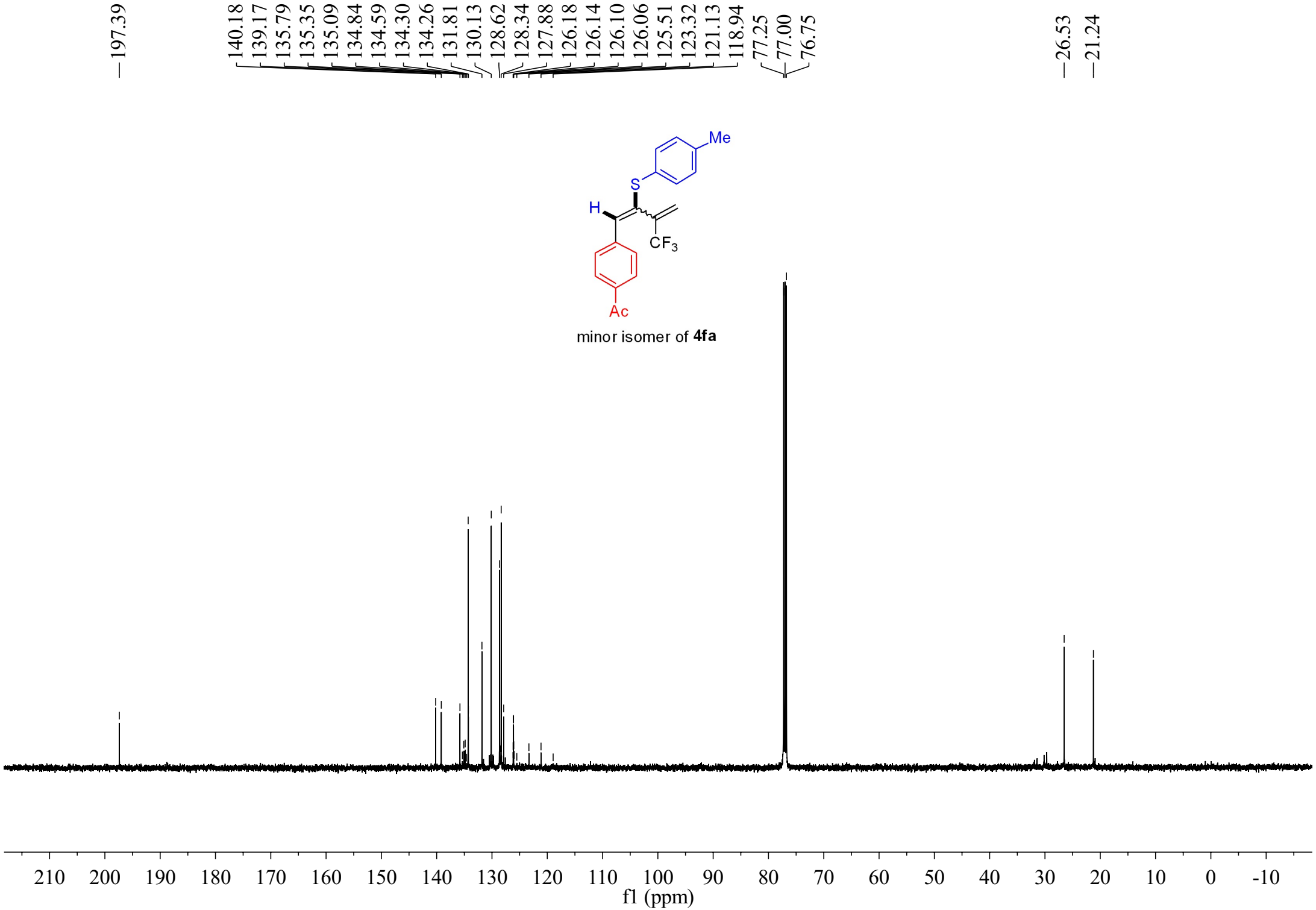

-64.087
Me
S
H
CF3
CN
minor isomer of 4ea
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

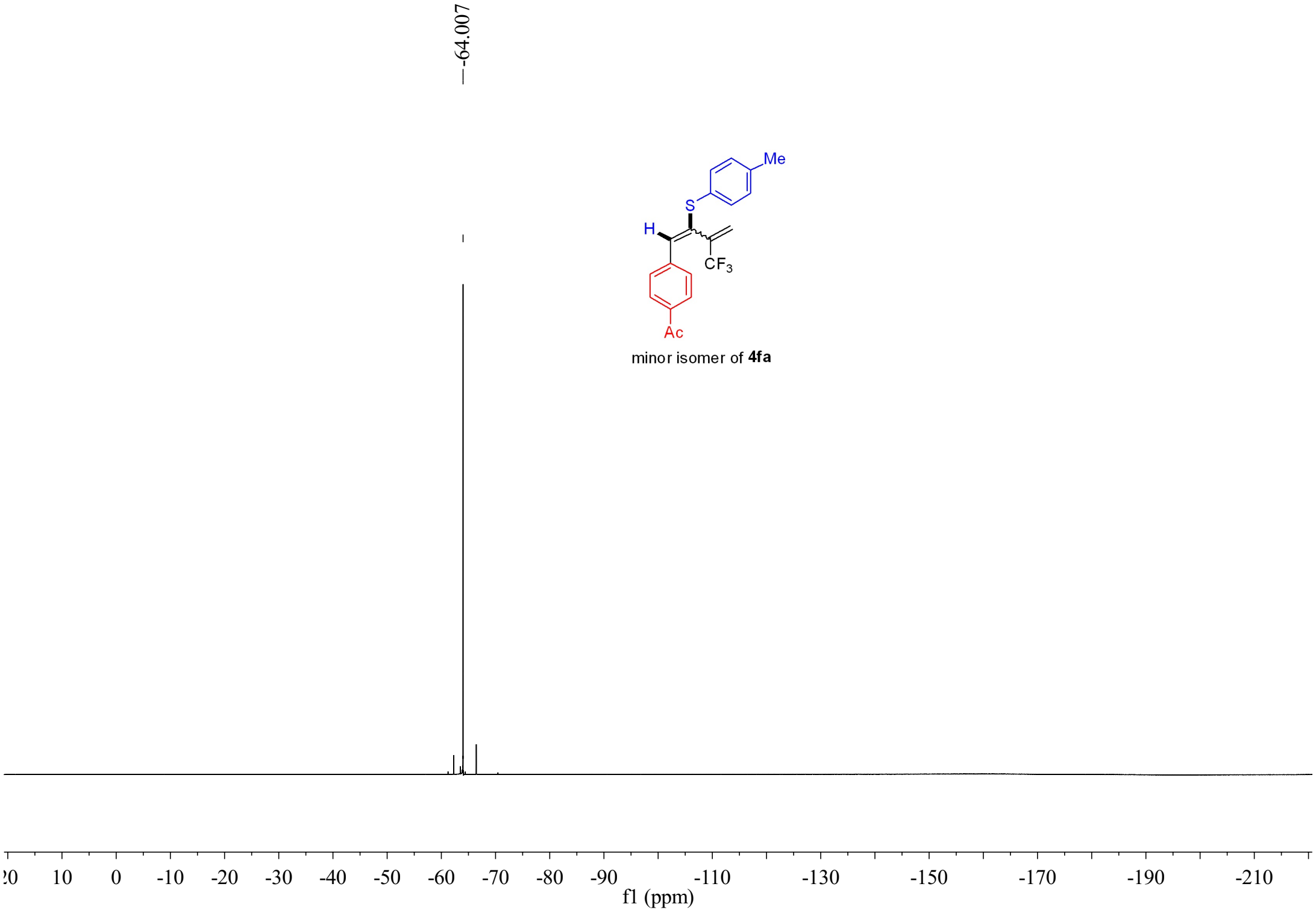

7.981
7.964
7.780
7.763
7.240
7.191
7.175
7.111
7.095
5.985
5.982
5.914
2.614
2.321
Me
S
H
CF3
Ac
major isomer of 4fa
2.05
2.06
1.06
2.04
2.01
1.00
1.00
3.04
3.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

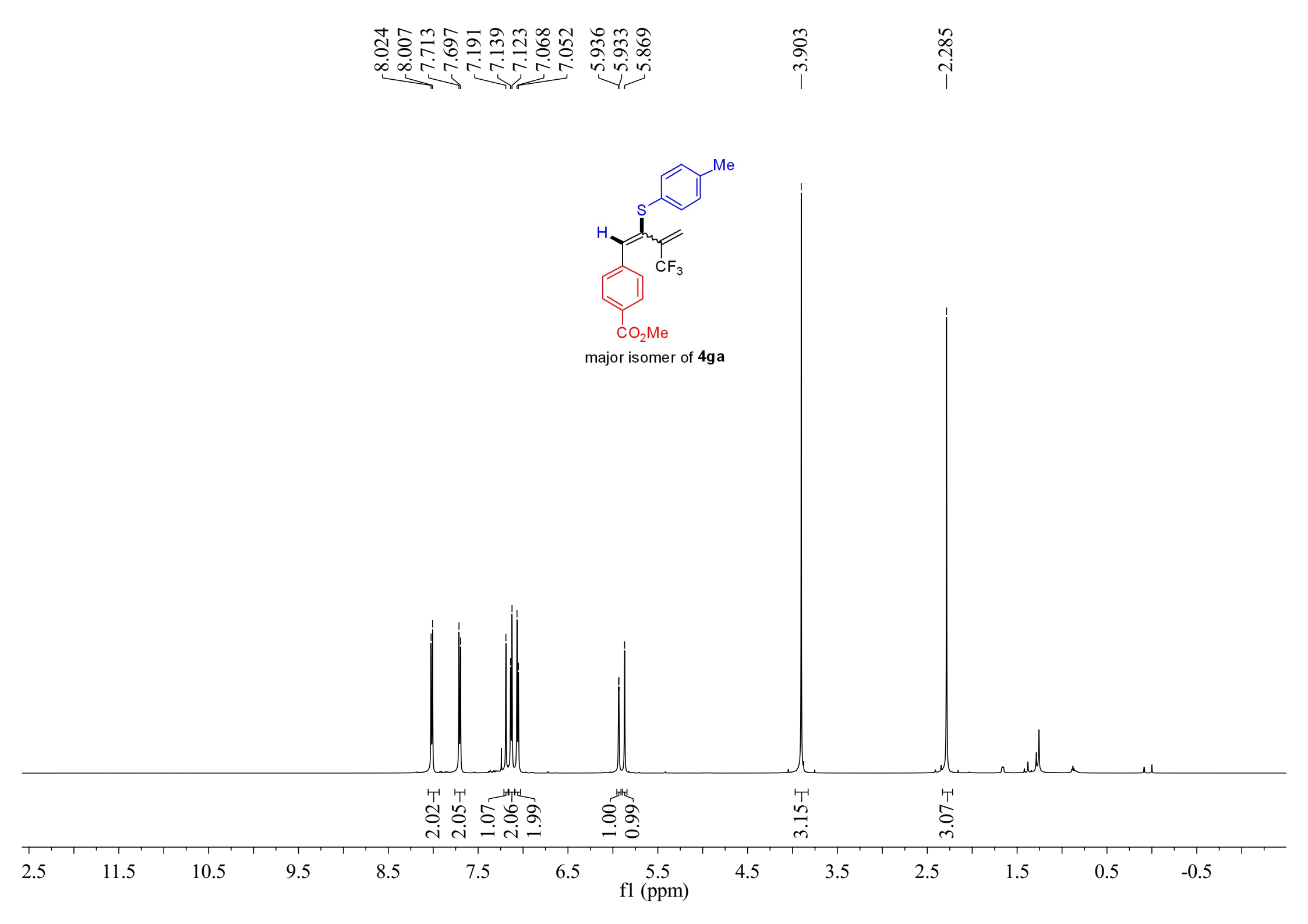

197.21
140.16
137.14
137.06
136.90
136.67
136.43
136.28
136.27
136.26
130.35
130.03
129.80
129.74
127.99
125.93
124.58
124.54
124.49
124.45
123.75
121.56
119.37
77.25
77.00
76.74
26.42
20.87
Me
S
H
CF3
Ac
major isomer of 4fa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

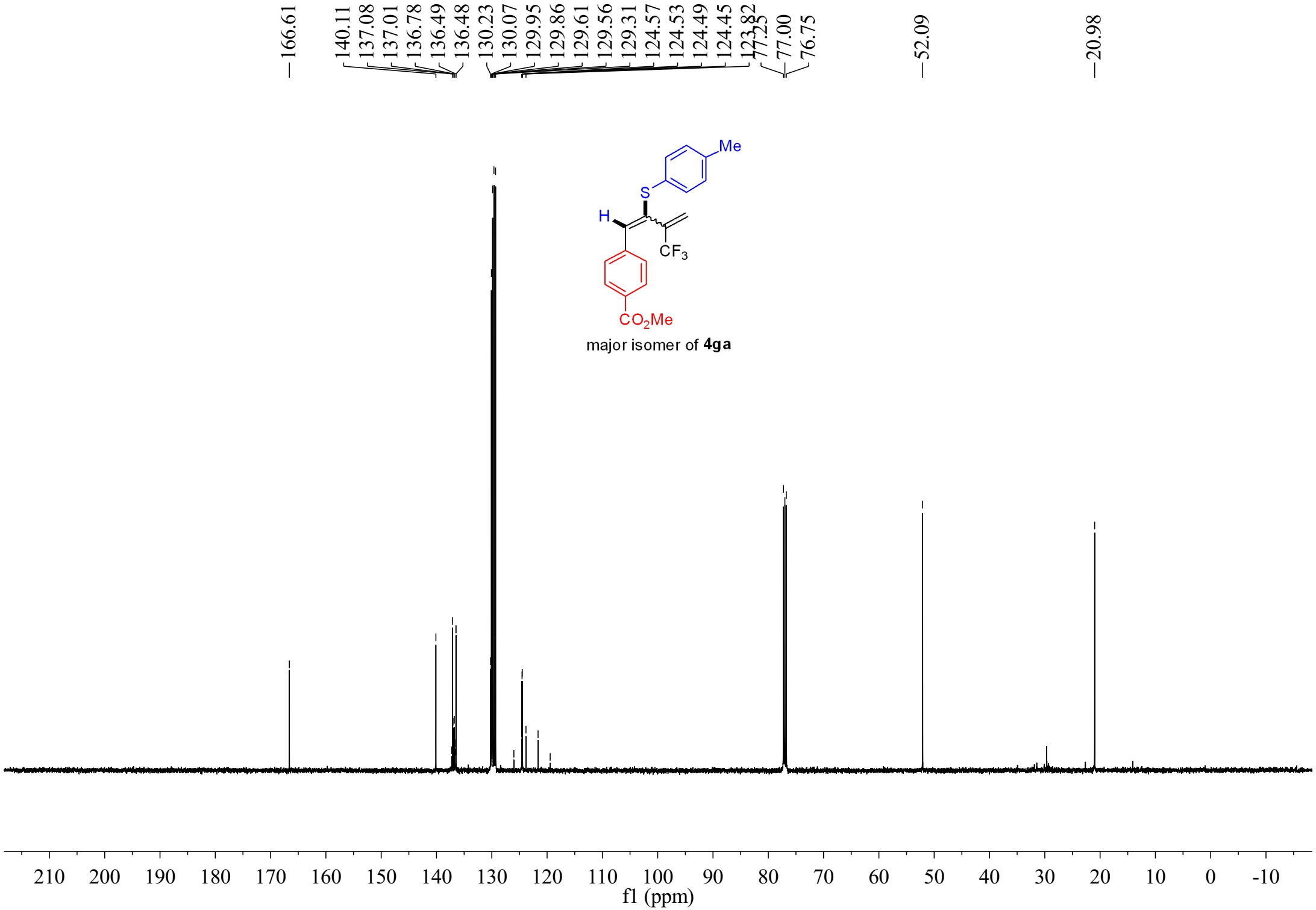

-63.417
Me
S
H
CF3
Ac
major isomer of 4fa
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

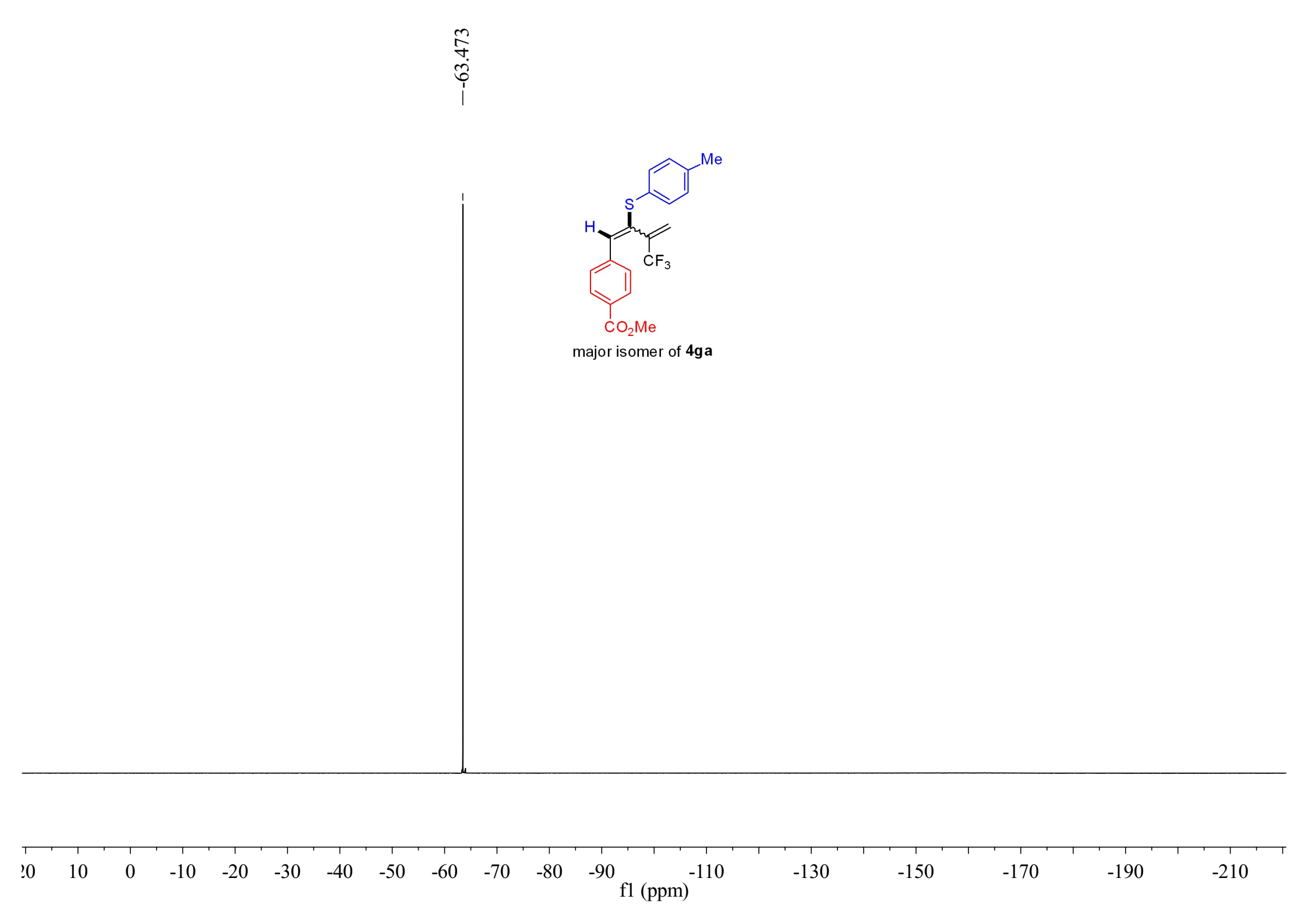

7.850
7.834
7.390
7.374
7.357
7.189
6.718
5.844
5.432
2.563
2.363
Me
S
H
CF3
Ac
minor isomer of 4fa
1.97
4.17
1.96
1.00
1.05
1.04
3.01
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

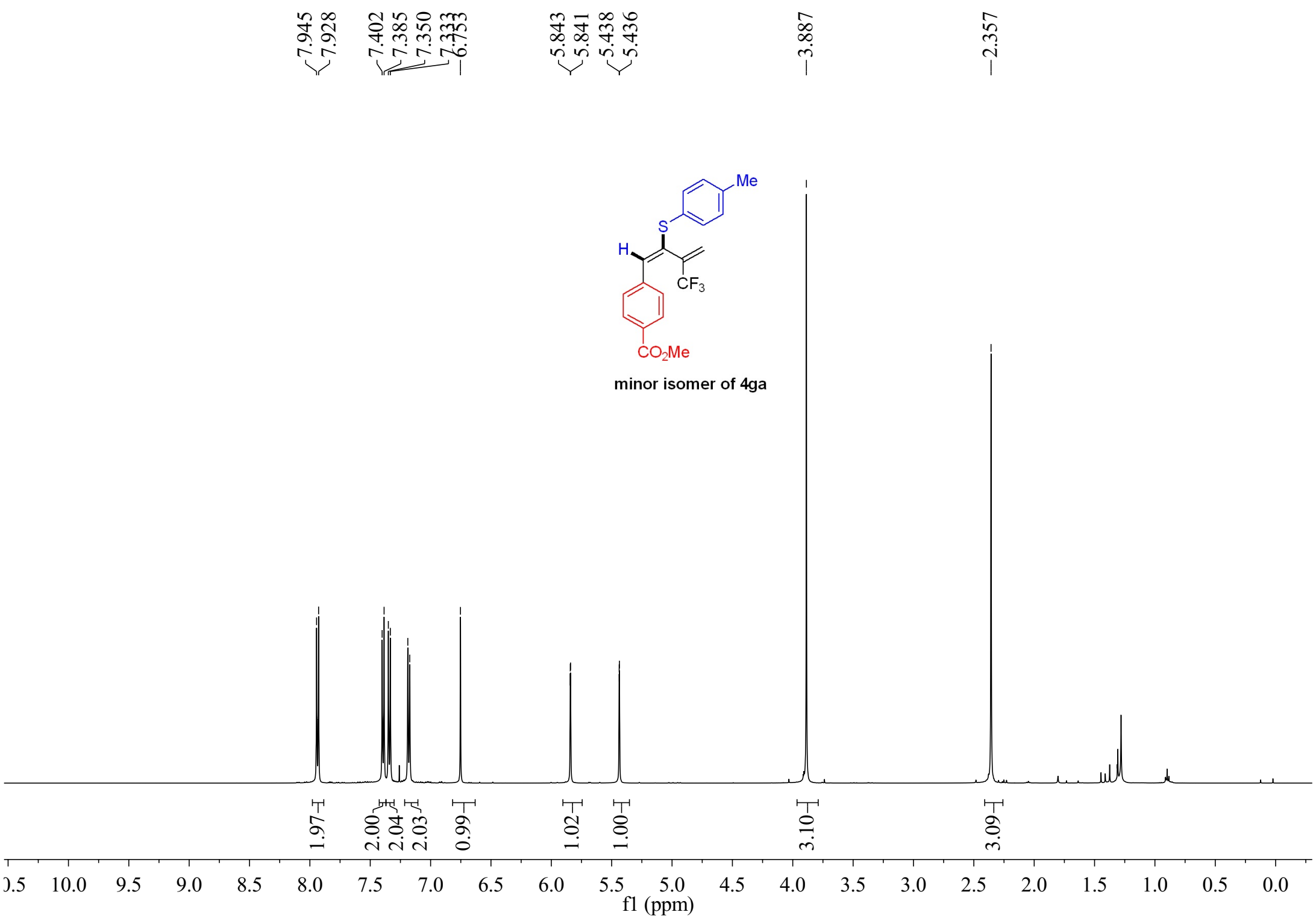

197.39
140.18
139.17
135.79
135.35
135.09
134.84
134.59
134.30
134.26
131.81
130.13
128.62
128.34
127.88
126.18
126.14
126.10
126.06
125.51
123.32
121.13
118.94
77.25
77.00
76.75
26.53
21.24
Me
S
H
CF3
Ac
minor isomer of 4fa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

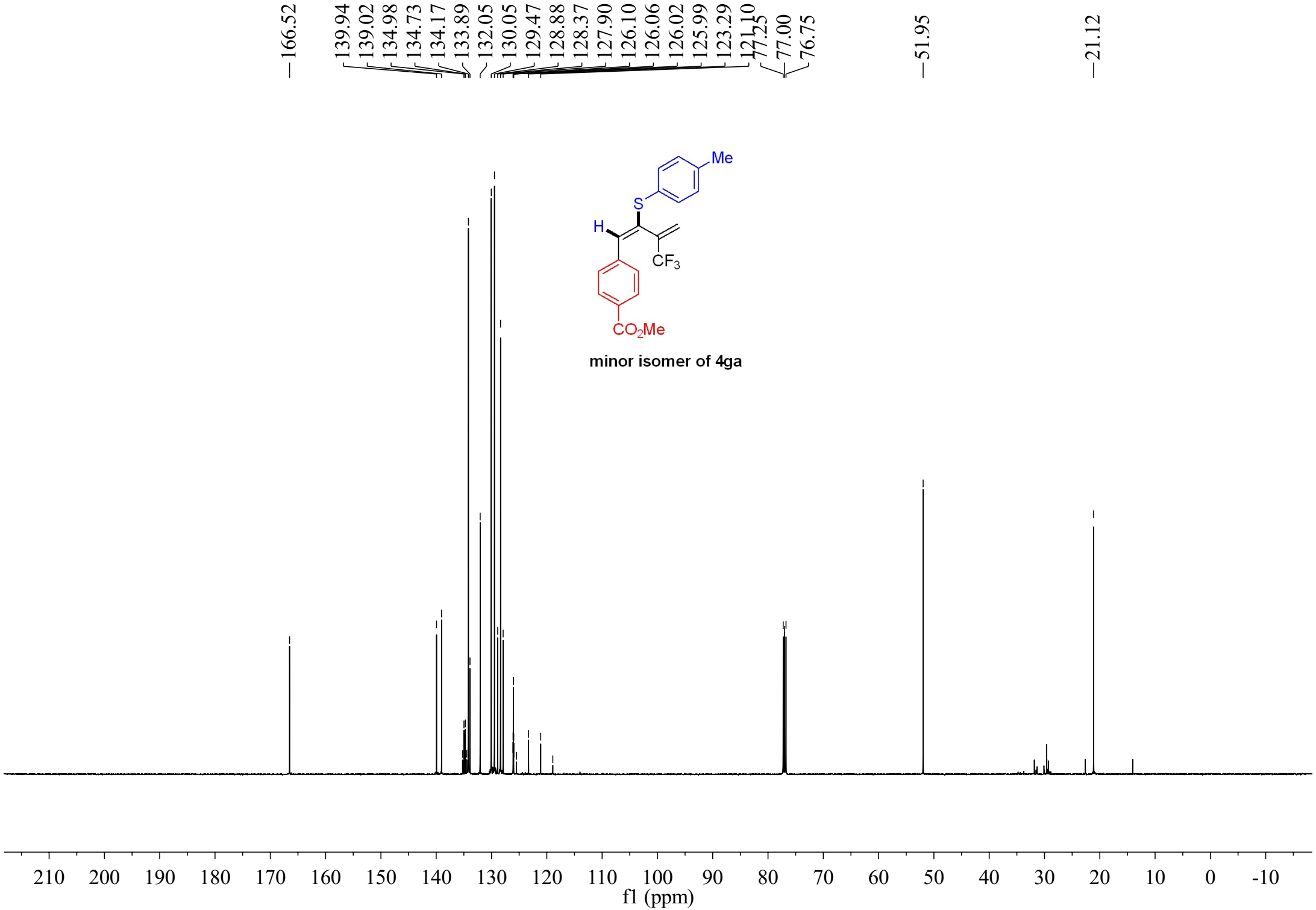

-64.007
Me
S
H
CF3
Ac
minor isomer of 4fa
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

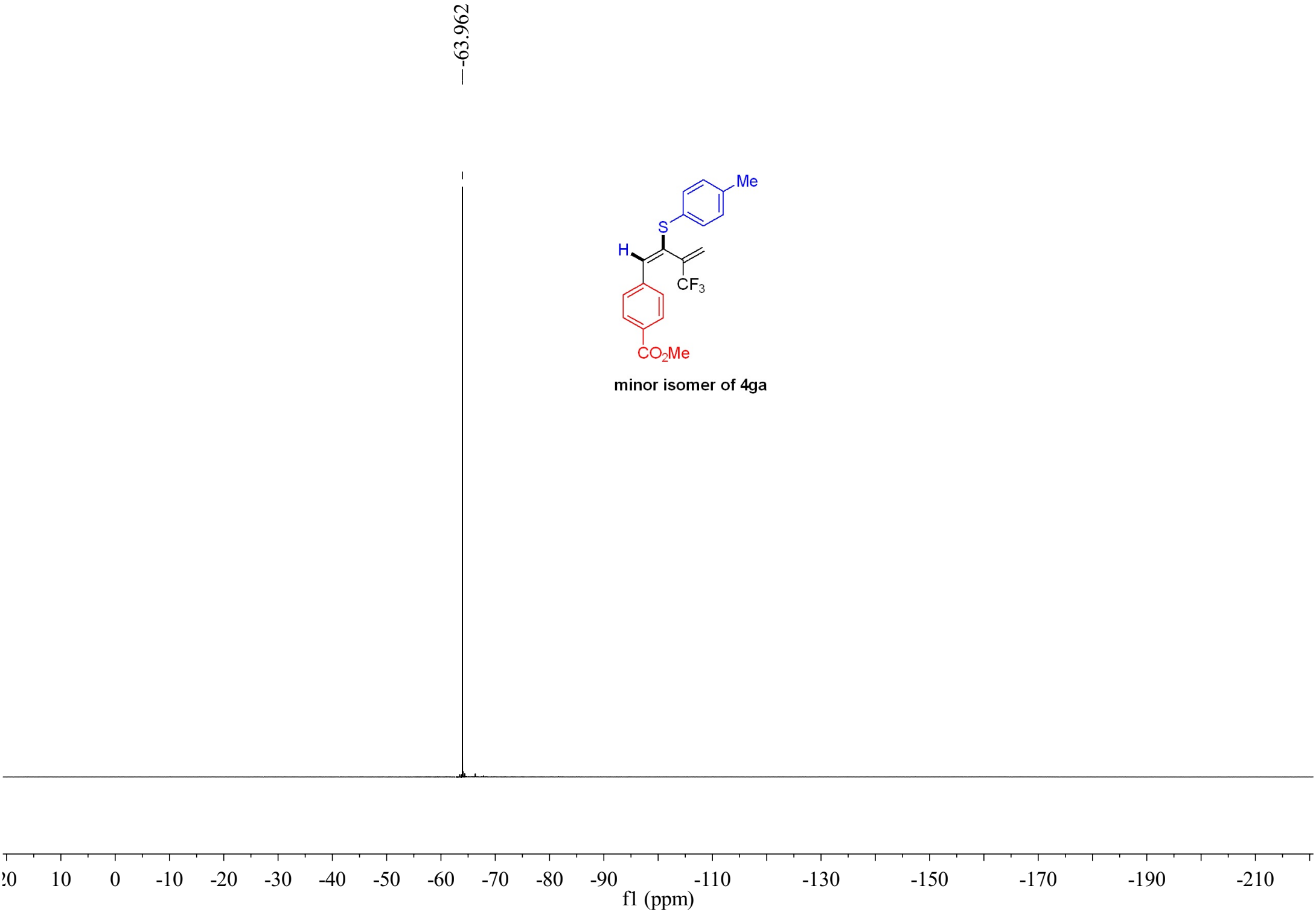

8.024
8.007
7.713
7.697
7.191
7.139
7.123
7.068
7.052
5.936
5.933
5.869
3.903
2.285
Me
S
H
CF3
CO2Me
major isomer of 4ga
2.02
2.05
1.07
2.06
1.99
1.00
0.99
3.15
3.07
2.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

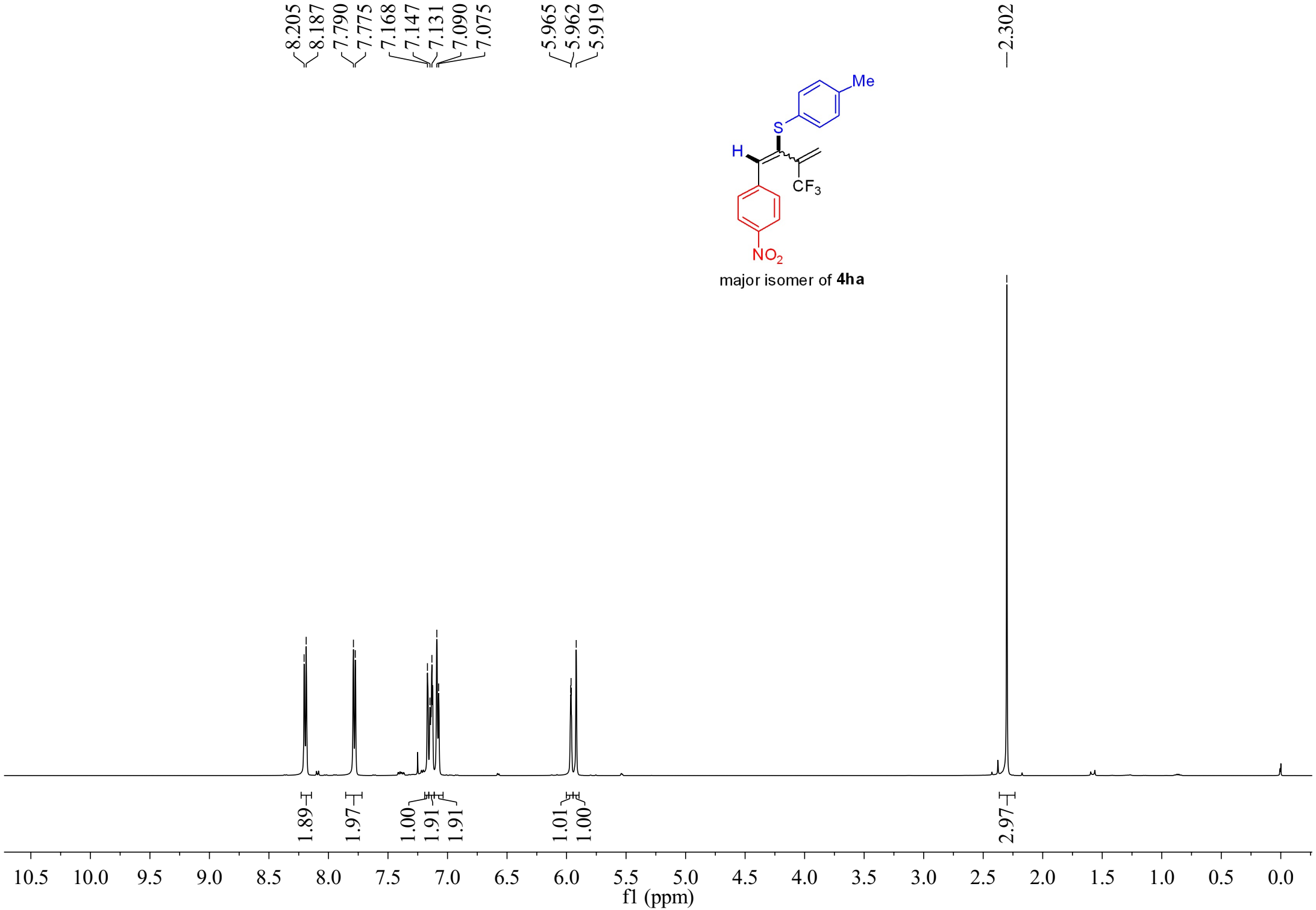

166.61
140.11
137.08
137.01
136.78
136.49
136.48
130.23
130.07
129.95
129.86
129.61
129.56
129.31
124.57
124.53
124.49
124.45
123.82
77.25
77.00
76.75
52.09
20.98
Me
S
H
CF3
CO2Me
major isomer of 4ga
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

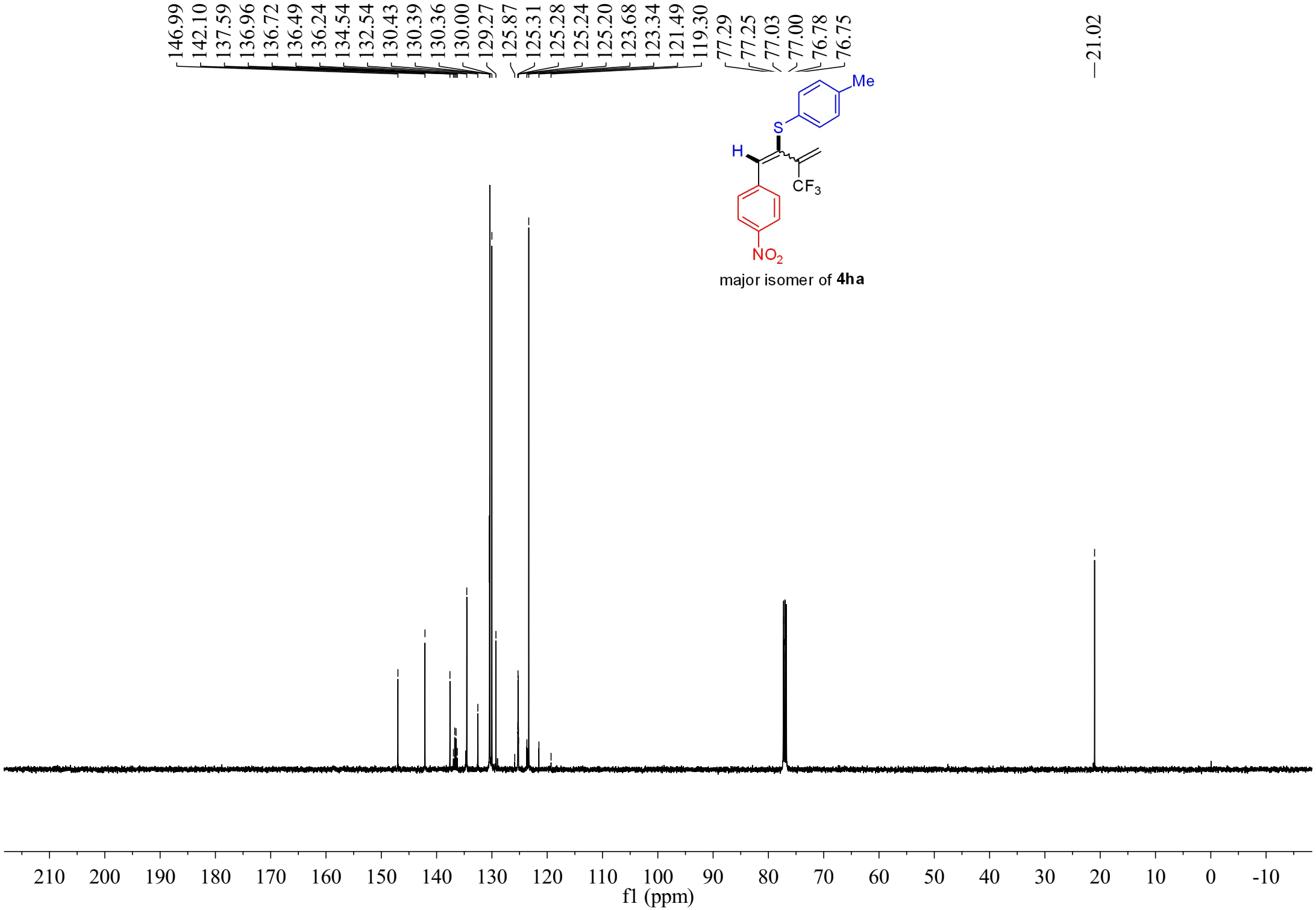

-63.473
Me
S
H
CF3
CO2Me
major isomer of 4ga
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

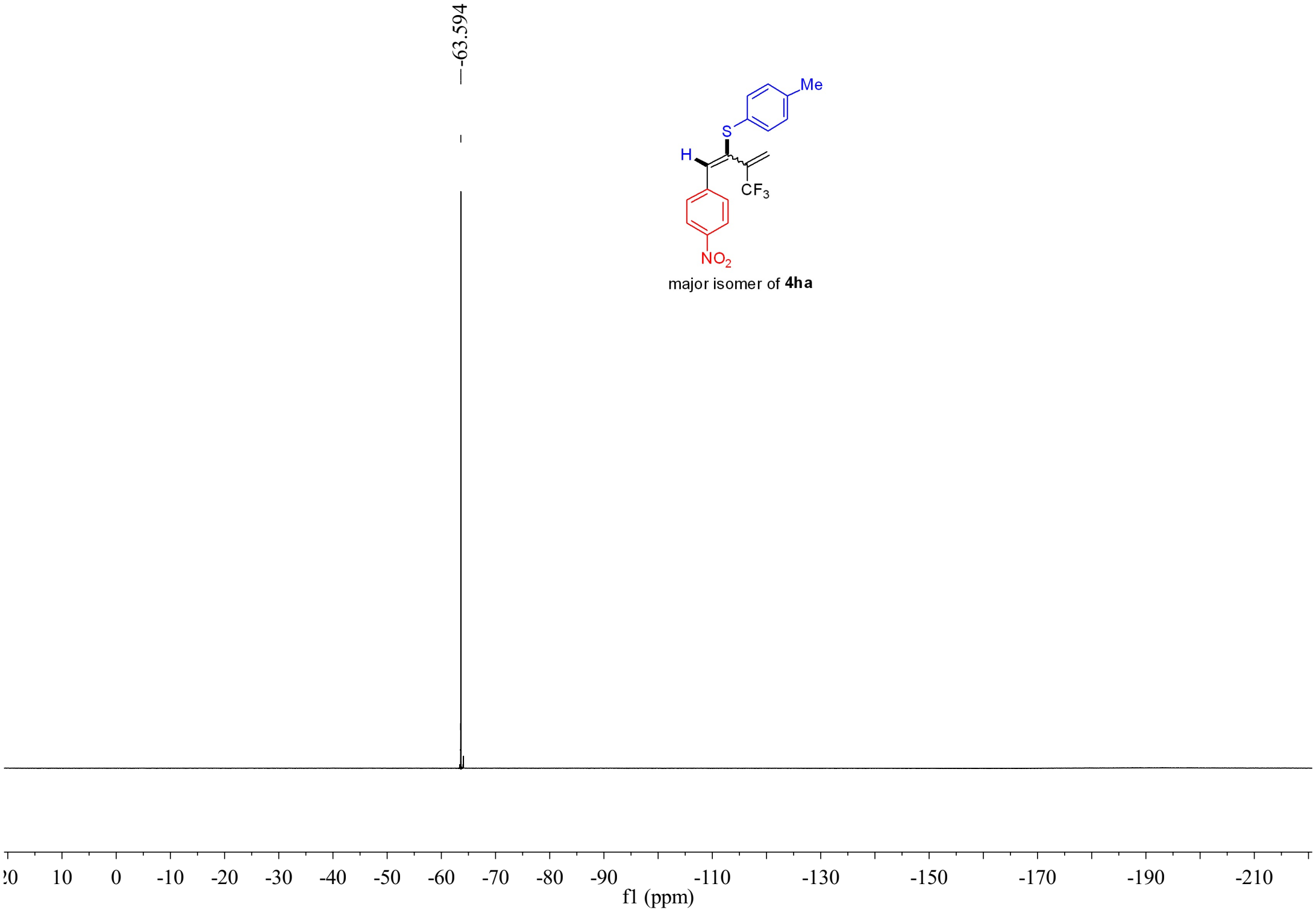

7.945
7.928
7.402
7.385
7.350
7.333
6.753
5.843
5.841
5.438
5.436
3.887
2.357
Me
S
H
CF3
CO2Me
minor isomer of 4ga
1.97
2.00
2.04
2.03
0.99
1.02
1.00
3.10
3.09
f1 (ppm)

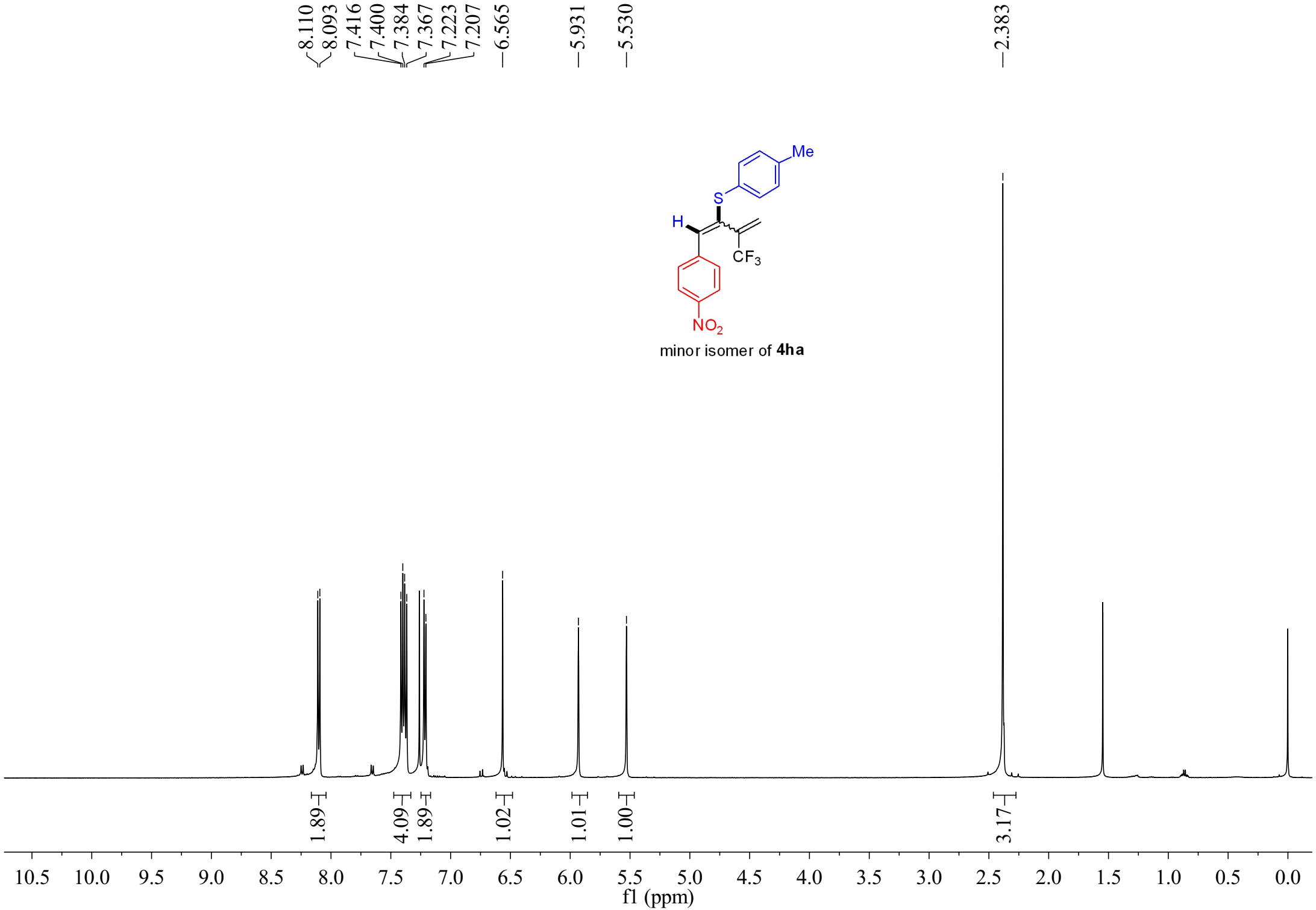

166.52
139.94
139.02
134.98
134.73
134.17
133.89
132.05
130.05
129.47
128.88
128.37
127.90
126.10
126.06
126.02
125.99
123.29
121.10
77.25
77.00
76.75
51.95
21.12
Me
S
H
CF3
CO2Me
minor isomer of 4ga
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

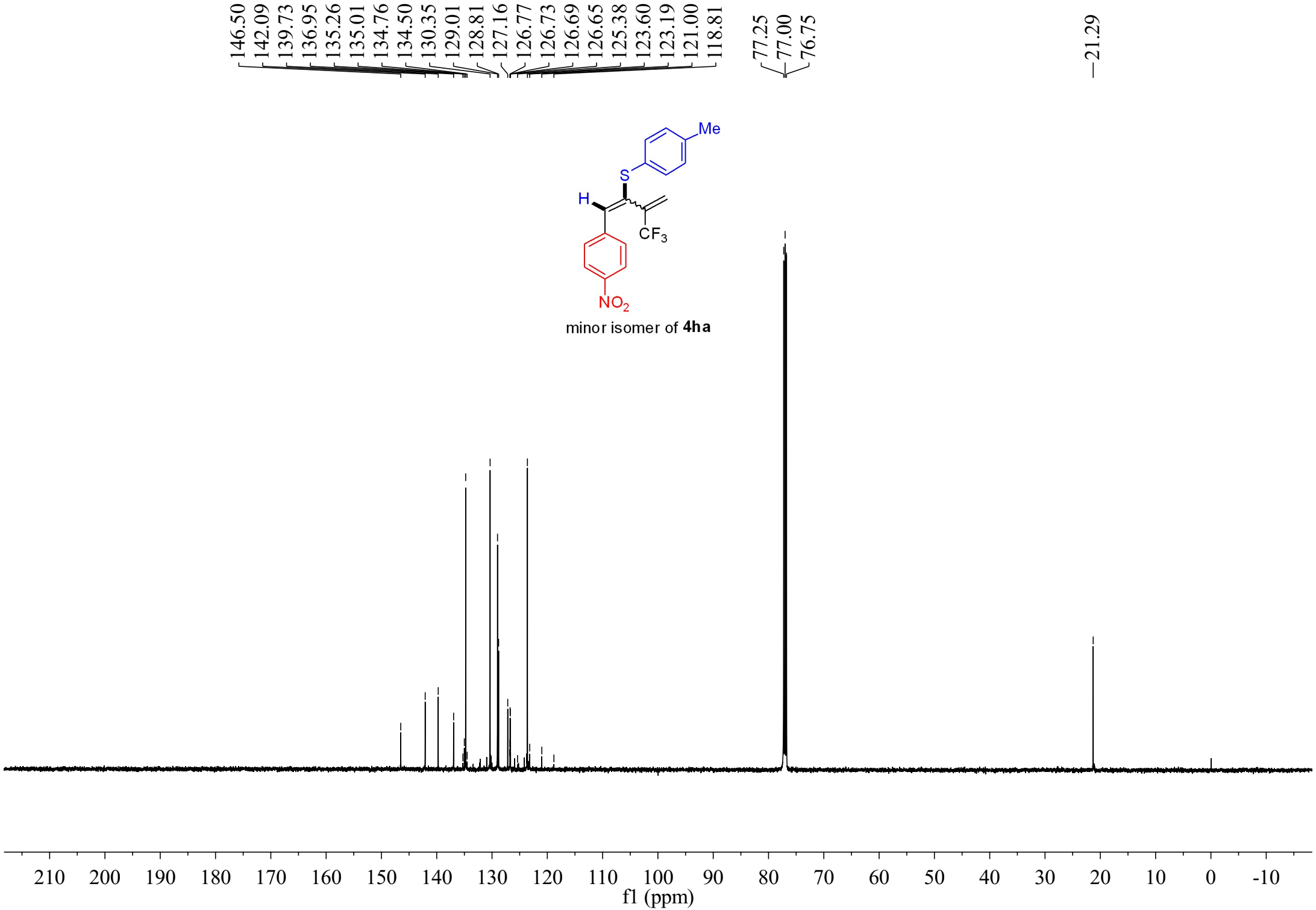

-63.962
Me
S
H
CF3
CO2Me
minor isomer of 4ga
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

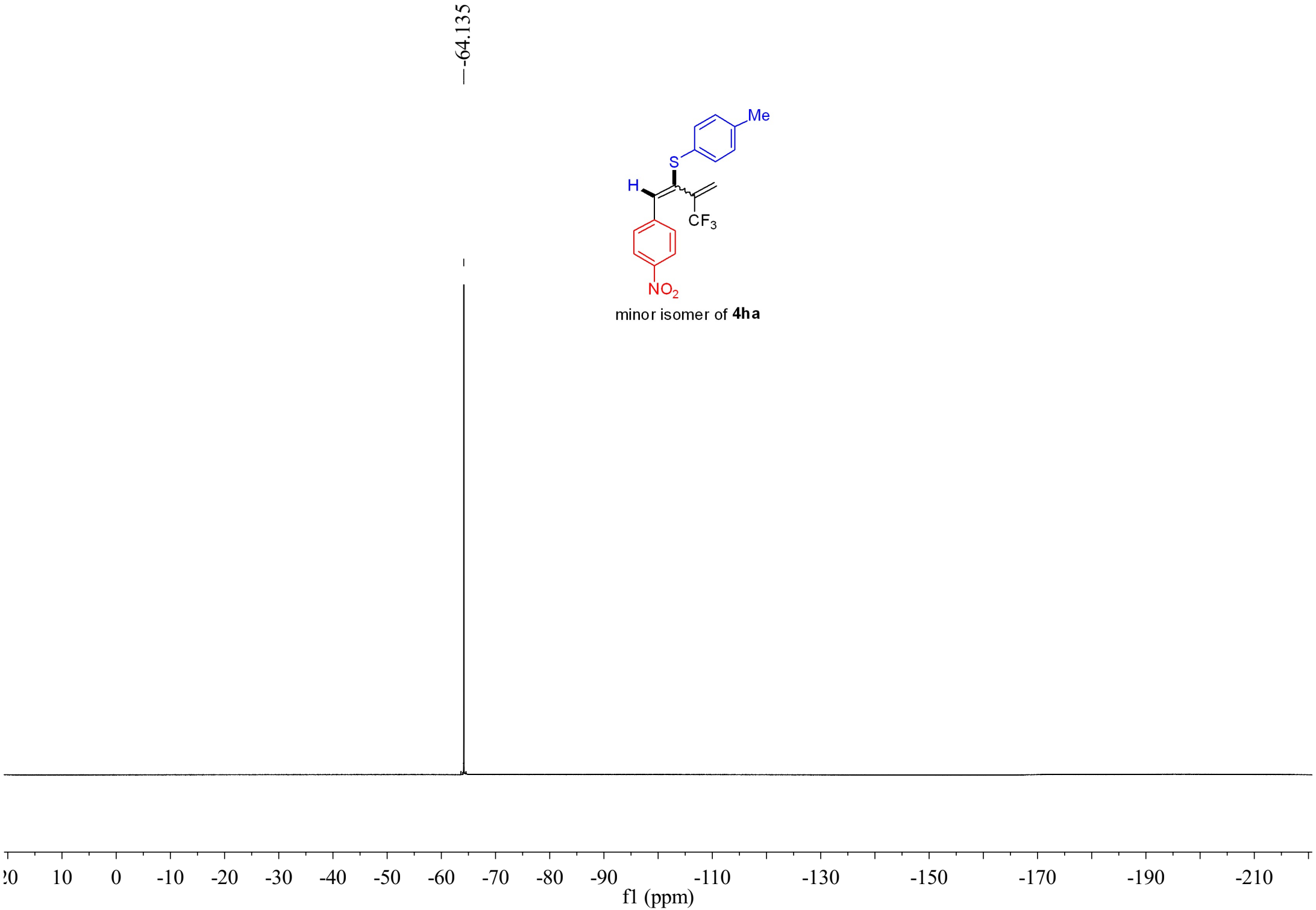

8.205
8.187
7.790
7.775
7.168
7.147
7.131
7.090
7.075
5.965
5.962
5.919
2.302
Me
S
H
CF3
NO2
major isomer of 4ha
1.89
1.97
1.00
1.91
1.91
1.01
1.00
2.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

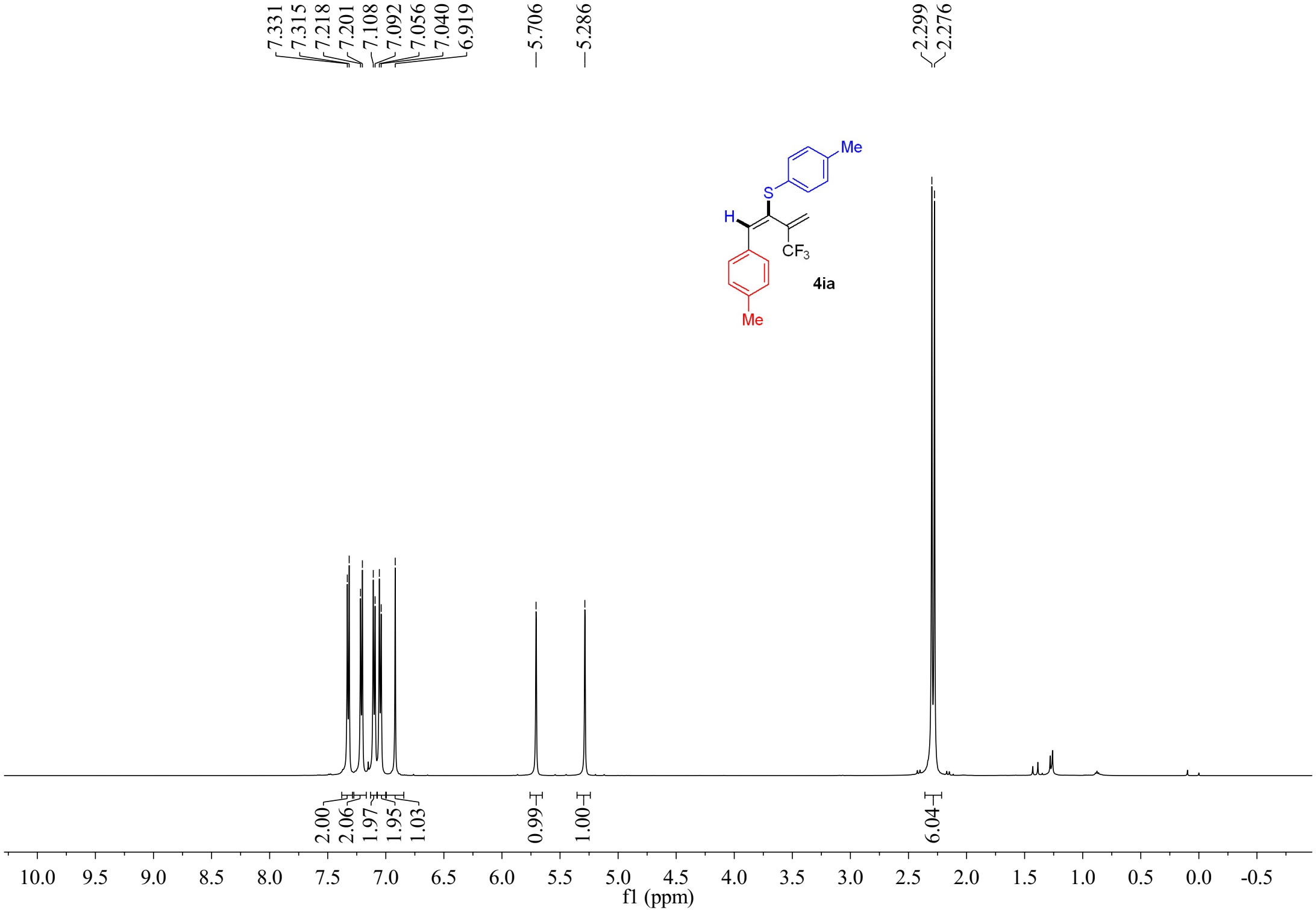

146.99
142.10
137.59
136.96
136.72
136.49
136.24
134.54
132.54
130.43
130.39
130.36
130.00
129.27
125.87
125.31
125.28
125.24
125.20
123.68
123.34
121.49
119.30
77.29
77.25
77.03
77.00
76.78
76.75
21.02
Me
S
H
CF3
NO2
major isomer of 4ha
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

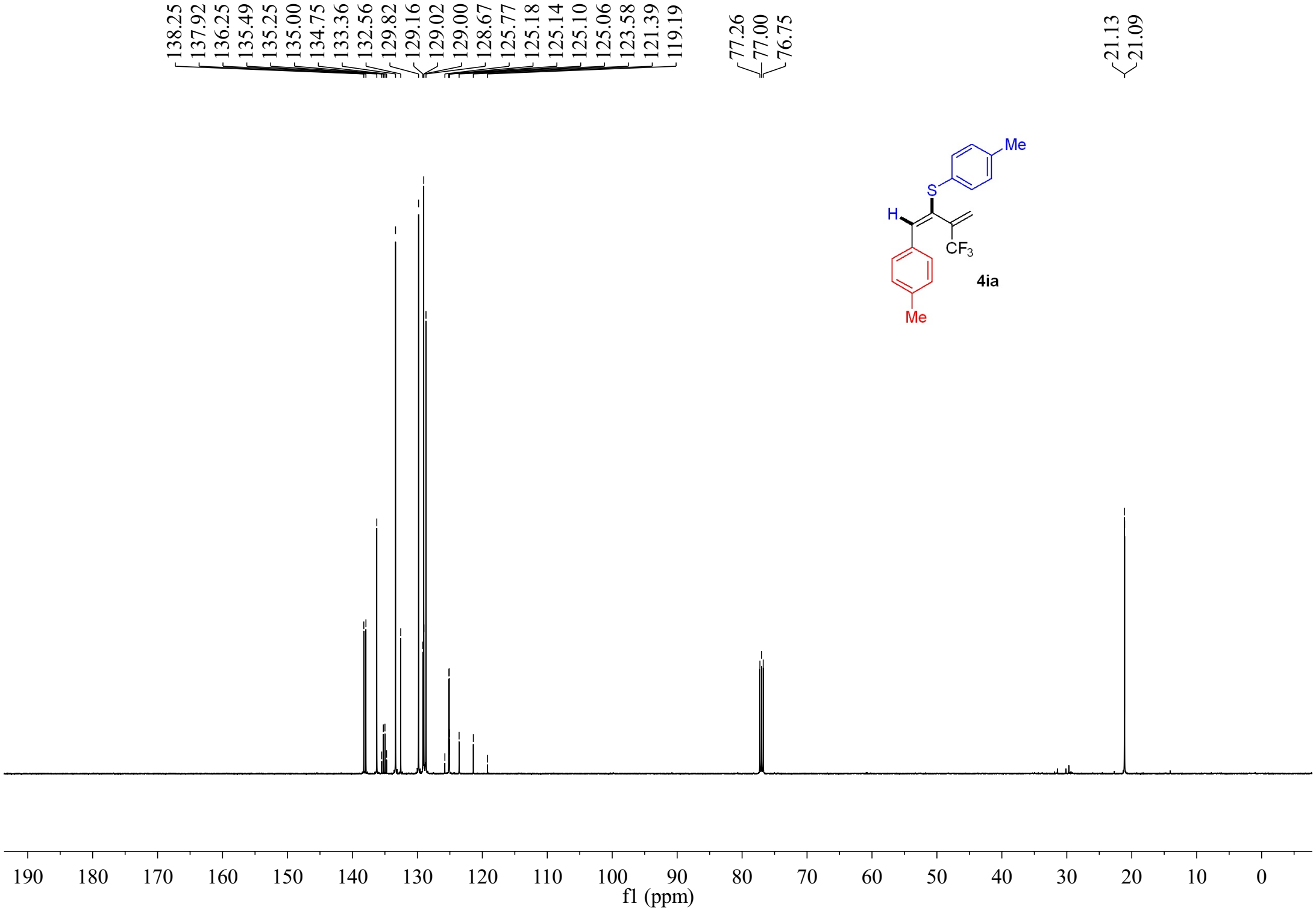

-63.594
Me
S
H
CF3
NO2
major isomer of 4ha
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

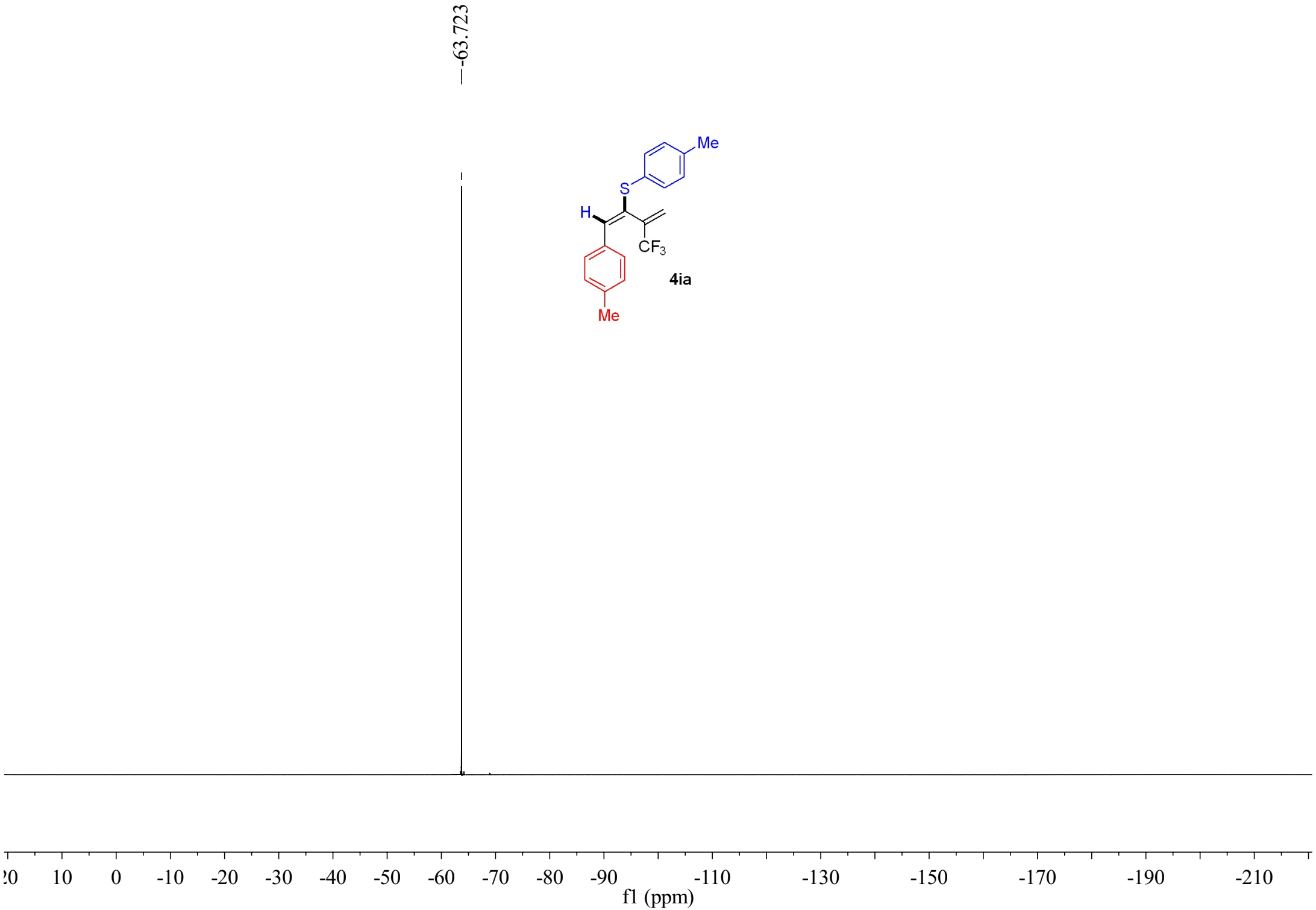

8.110
8.093
7.416
7.400
7.384
7.367
7.223
7.207
6.565
5.931
5.530
2.383
Me
S
H
CF3
NO2
minor isomer of 4ha
1.89
4.09
1.89
1.02
1.01
1.00
3.17
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

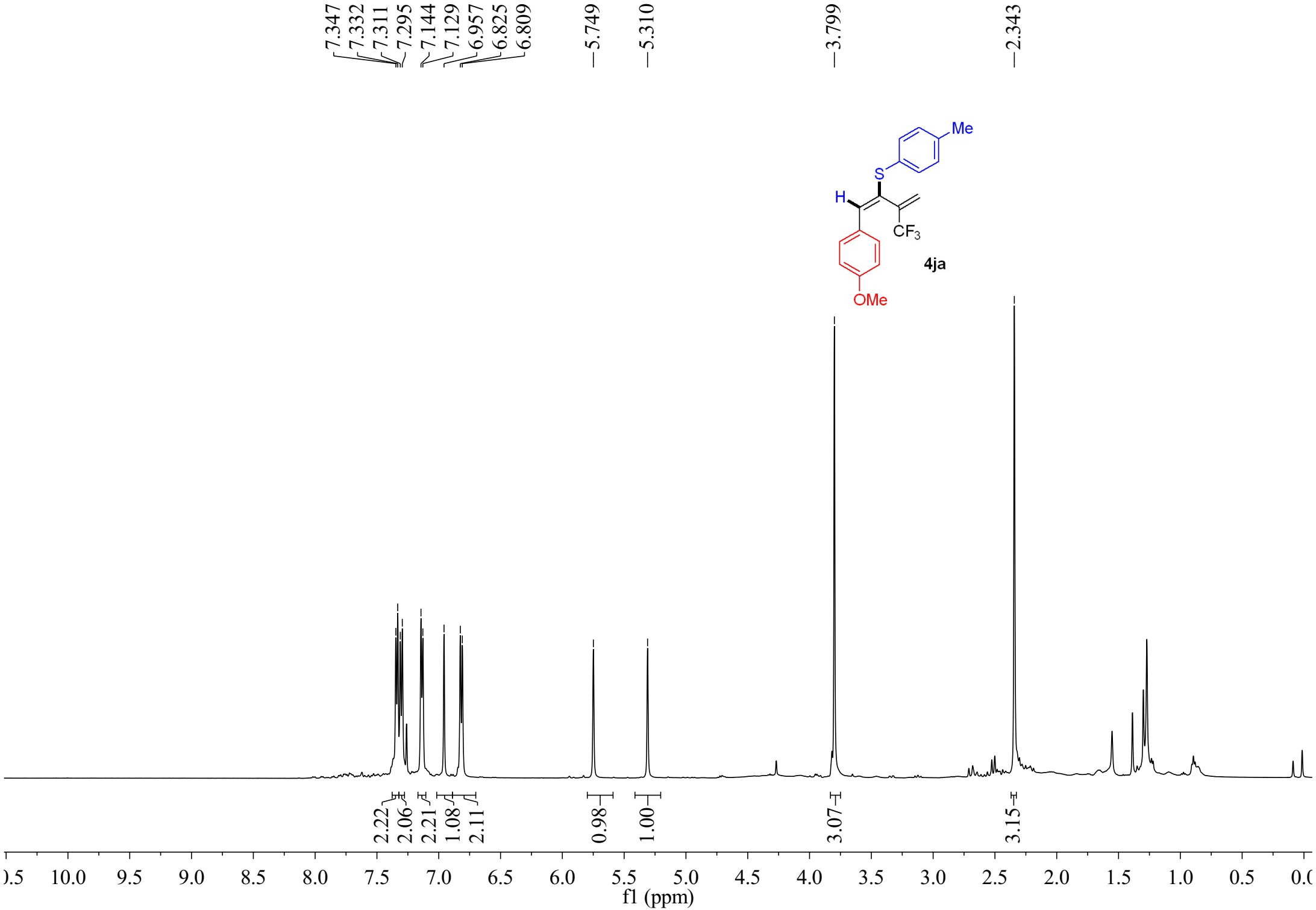

146.50
142.09
139.73
136.95
135.26
135.01
134.76
134.50
130.35
129.01
128.81
127.16
126.77
126.73
126.69
126.65
125.38
123.60
123.19
121.00
118.81
77.25
77.00
76.75
21.29
Me
S
H
CF3
NO2
minor isomer of 4ha
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

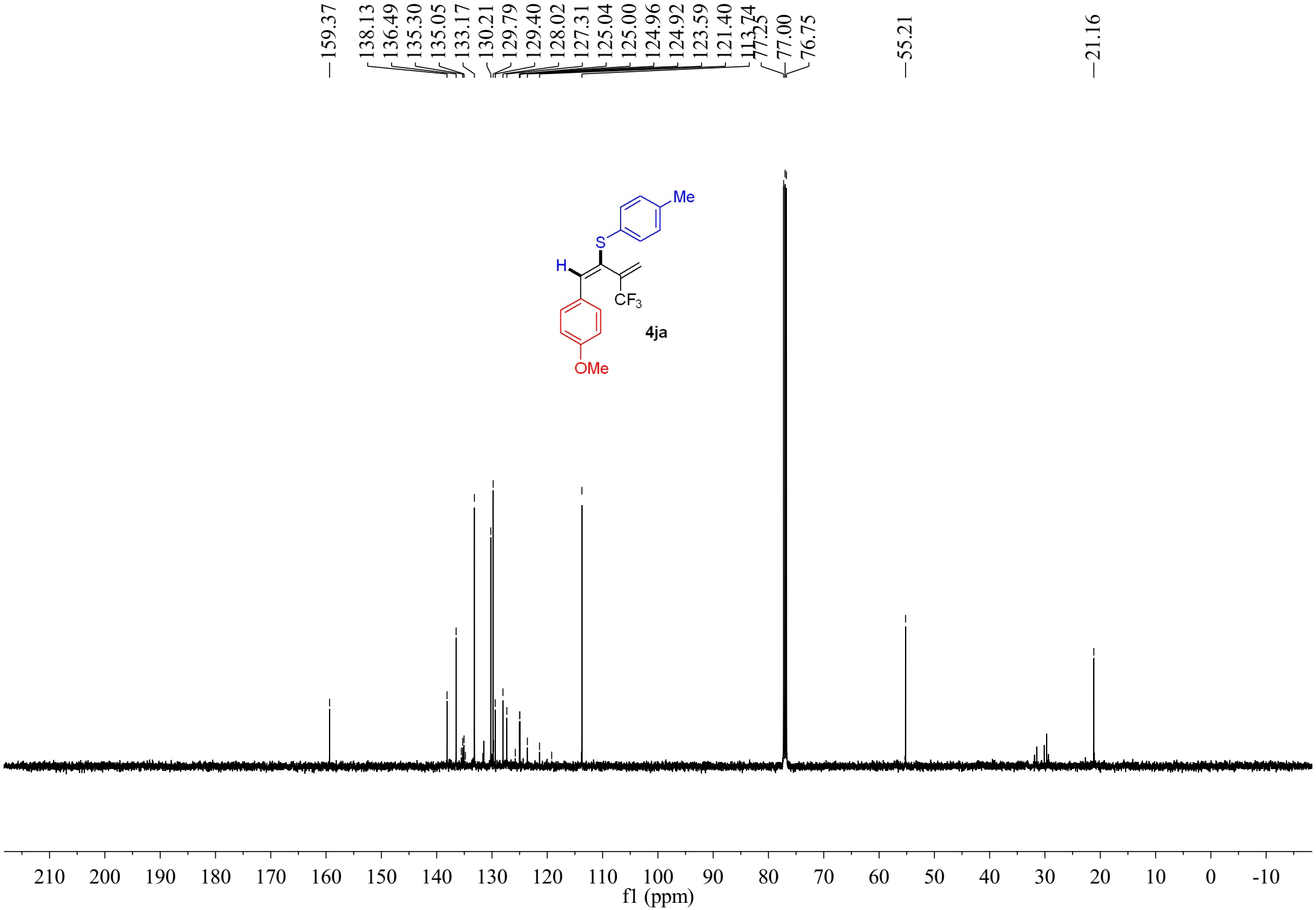

-64.135
Me
S
H
CF3
NO2
minor isomer of 4ha
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

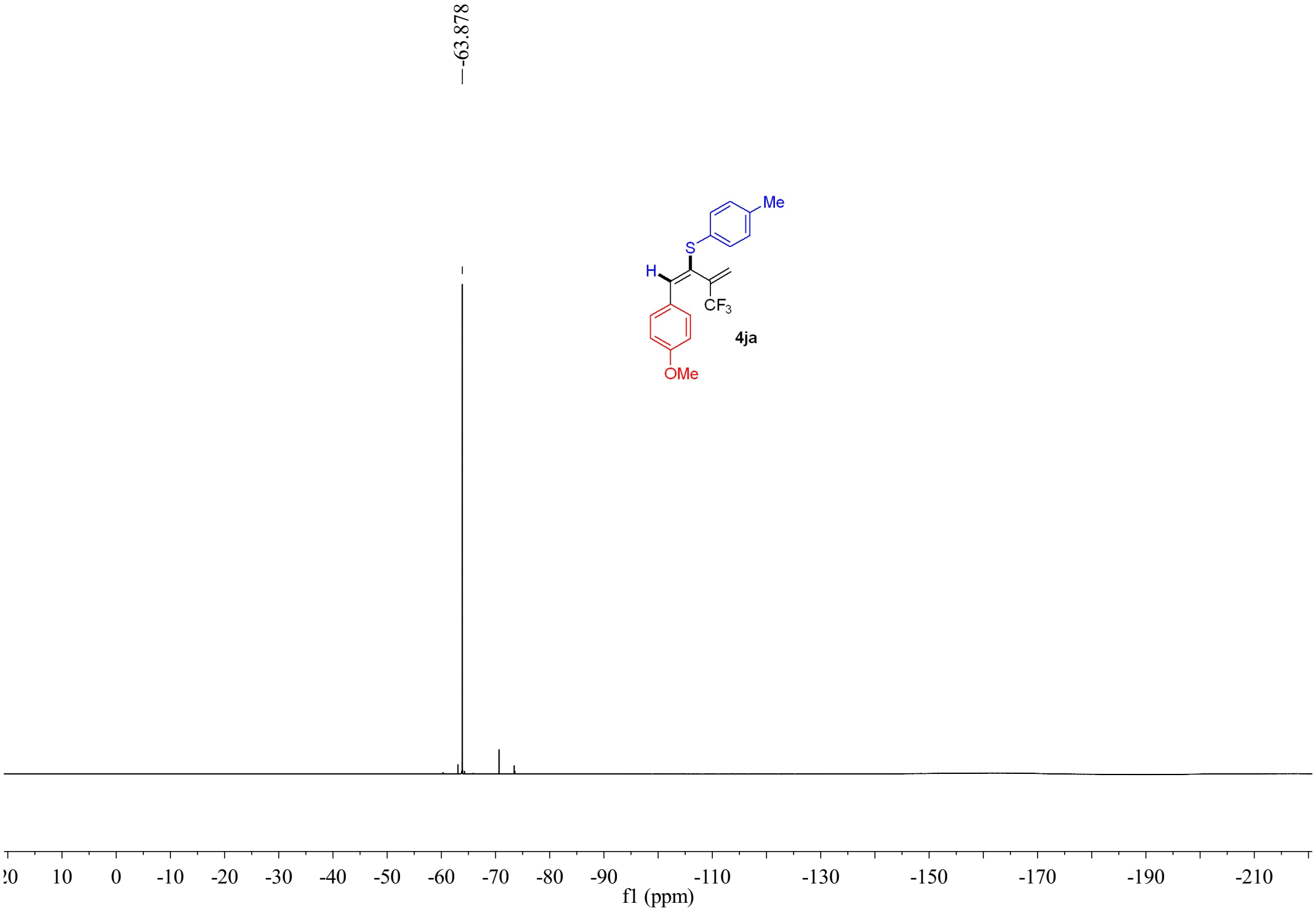

7.331
7.315
7.218
7.201
7.108
7.092
7.056
7.040
6.919
5.706
5.286
2.299
2.276
Me
S
H
CF3
Me
4ia
2.00
2.06
1.97
1.95
1.03
0.99
1.00
6.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

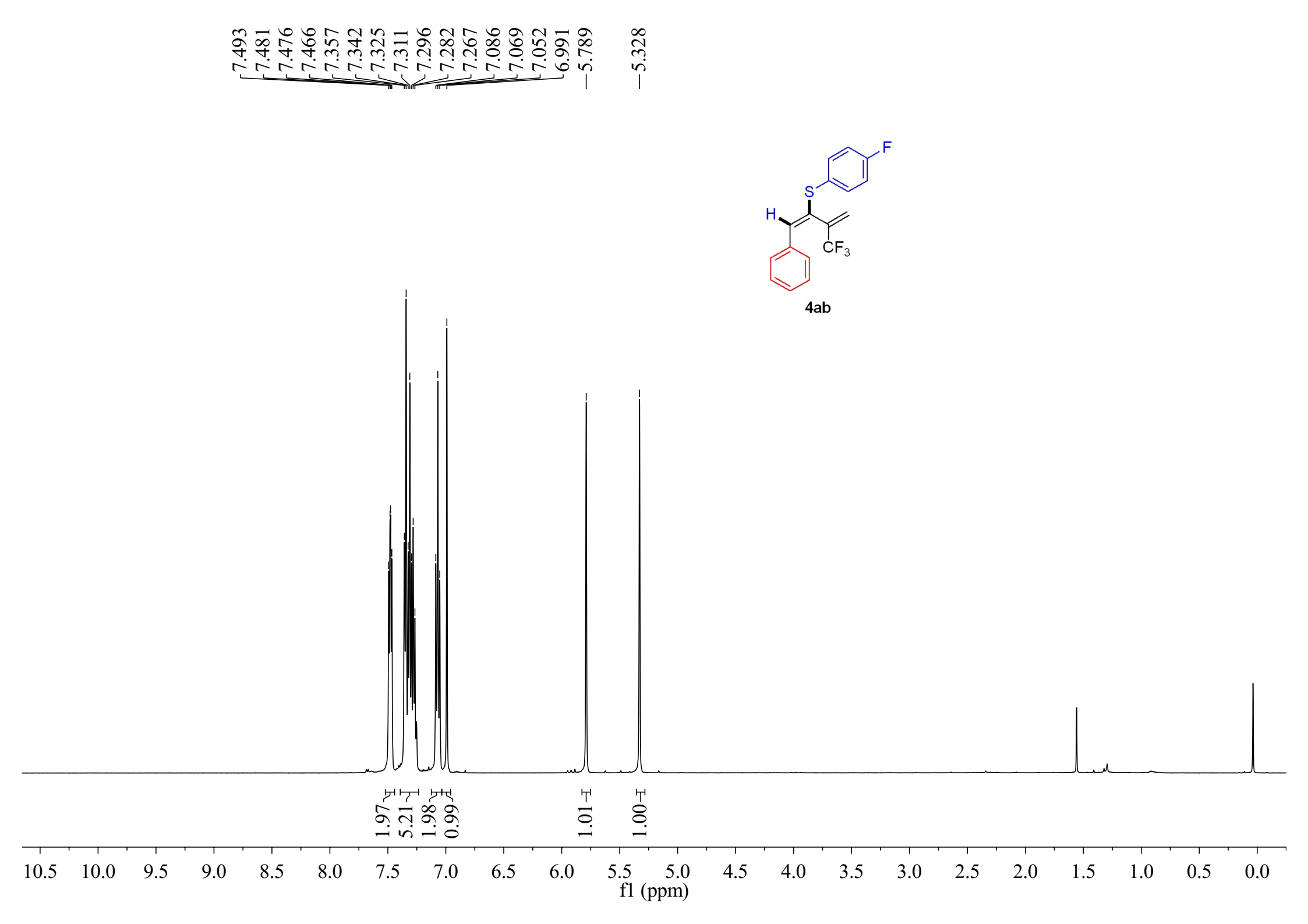

138.25
137.92
136.25
135.49
135.25
135.00
134.75
133.36
132.56
129.82
129.16
129.02
129.00
128.67
125.77
125.18
125.14
125.10
125.06
123.58
121.39
119.19
77.26
77.00
76.75
21.13
21.09
Me
S
H
CF3
Me
4ia
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

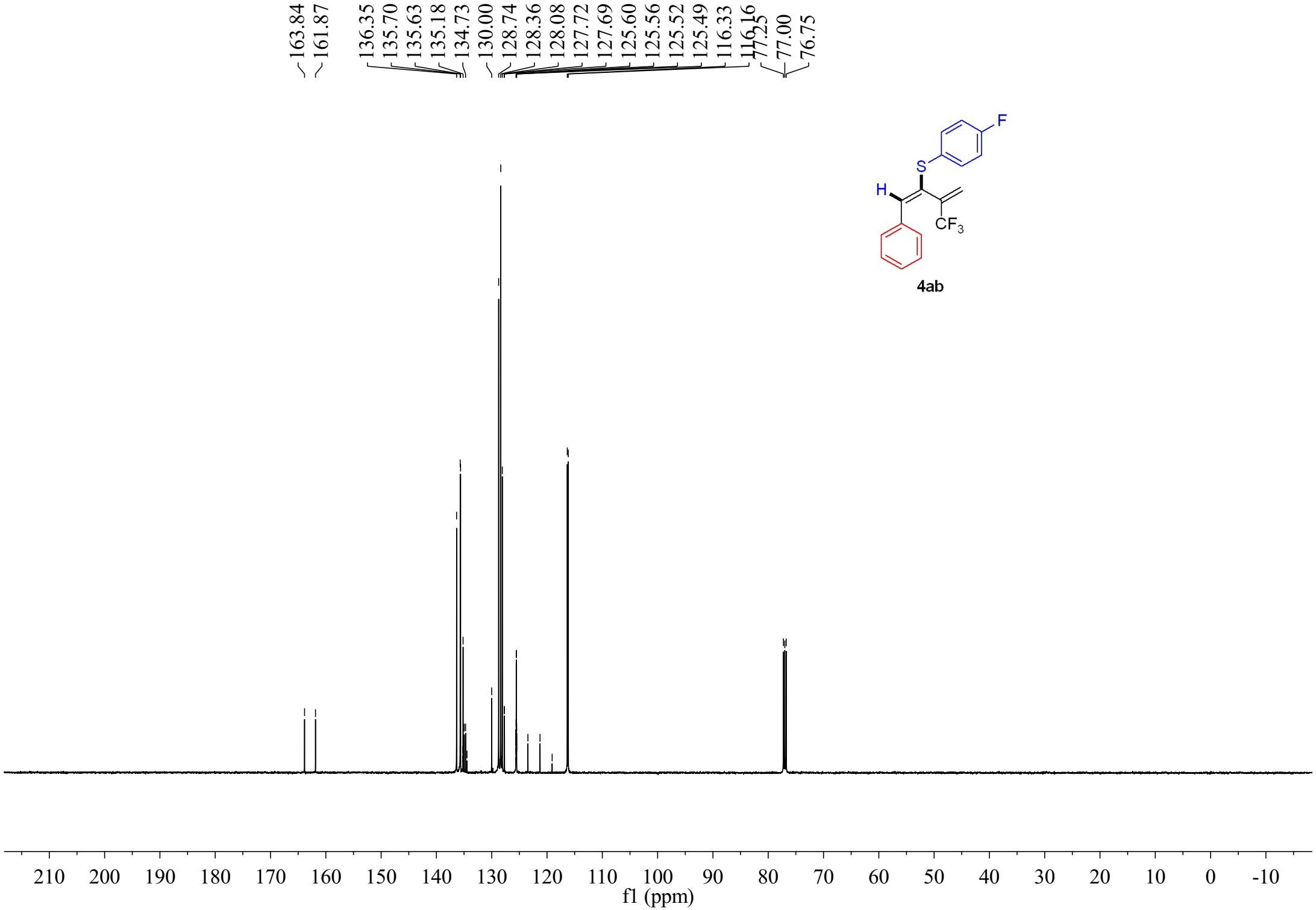

-63.723
Me
S
H
CF3
4ia
Me
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

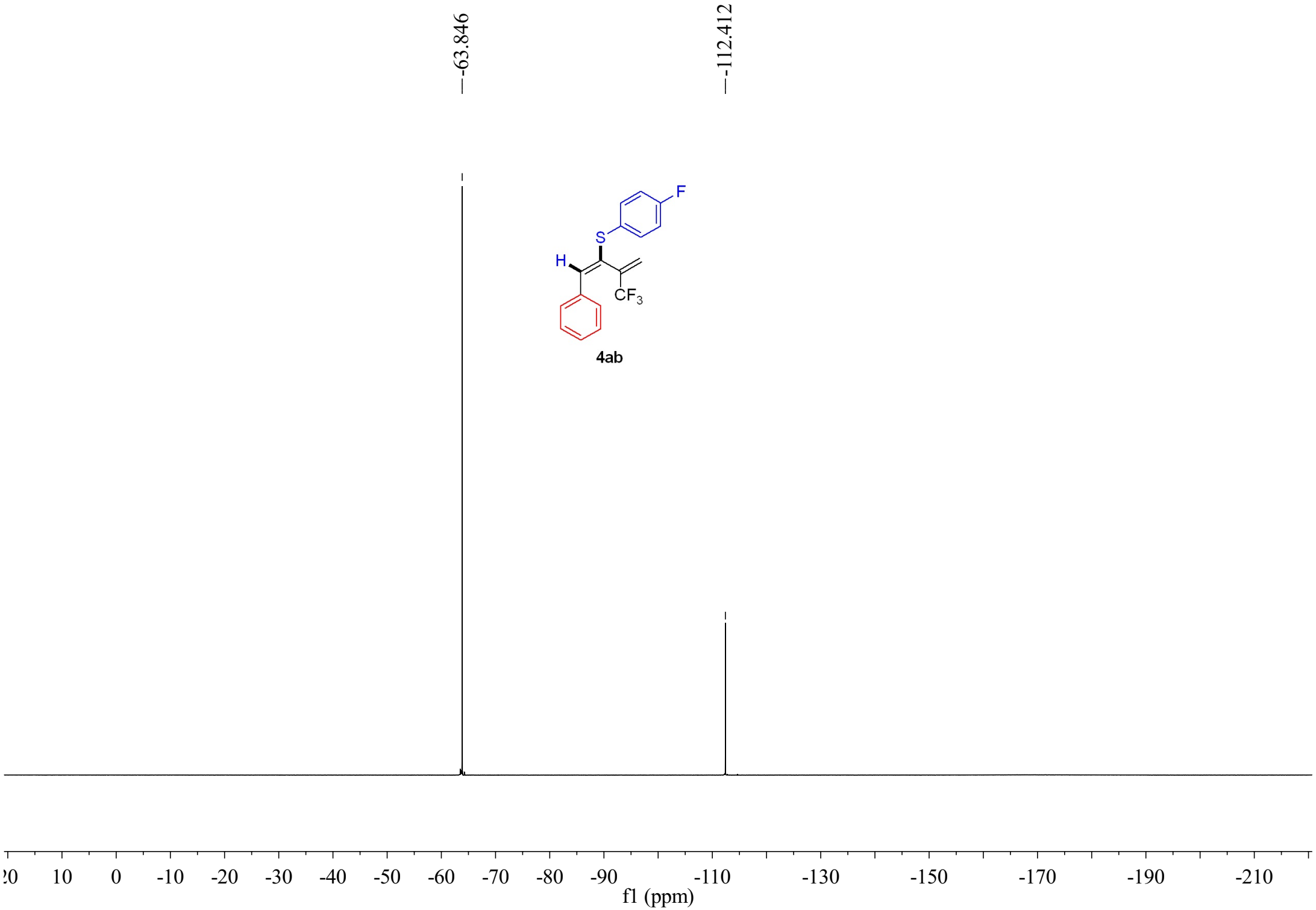

7.347
7.332
7.311
7.295
7.144
7.129
6.957
6.825
6.809
5.749
5.310
3.799
2.343
Me
S
H
CF3
OMe
4ja
2.22
2.06
2.21
1.08
2.11
0.98
1.00
3.07
3.15
f1 (ppm)

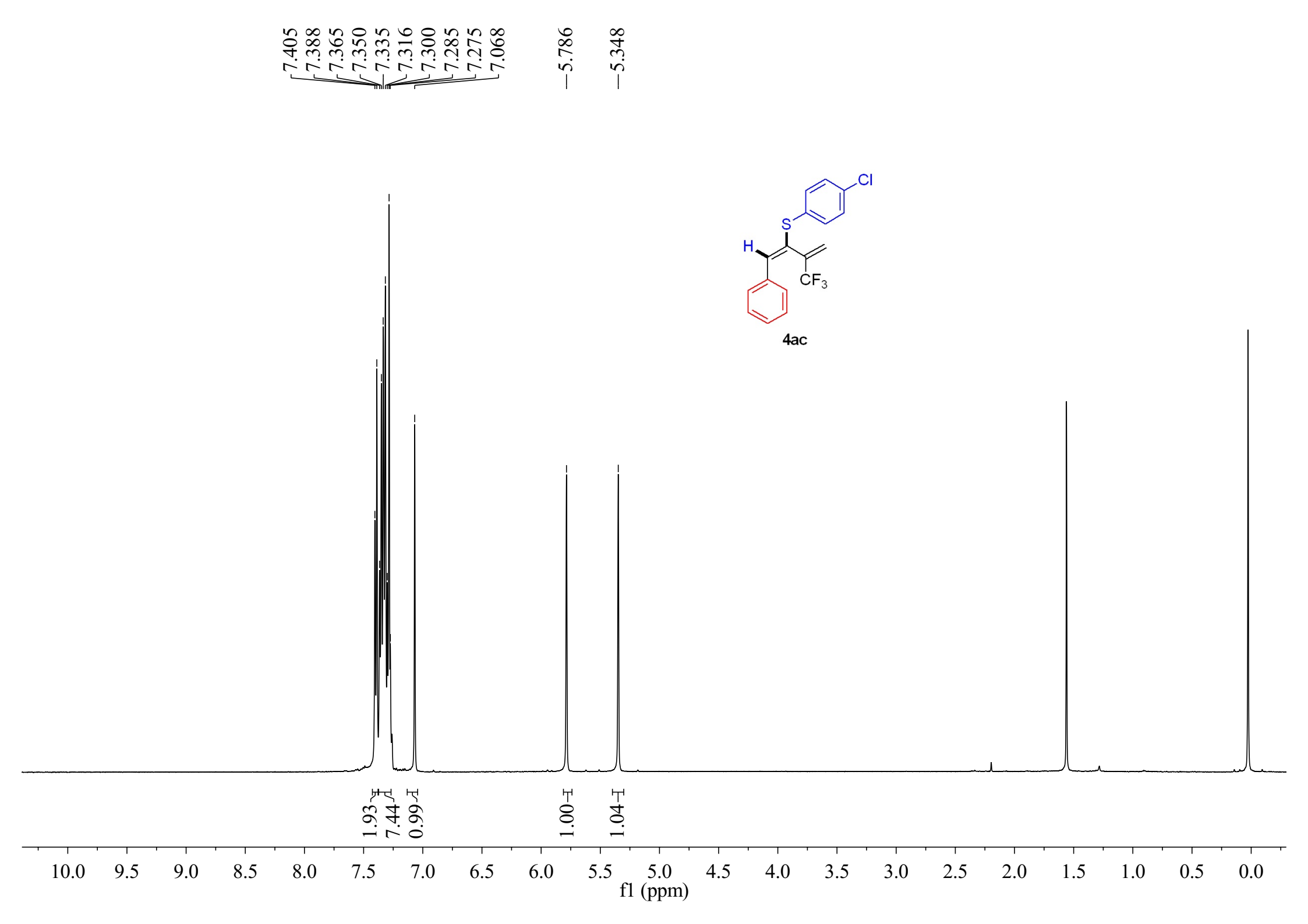

159.37
138.13
136.49
135.30
135.05
133.17
130.21
129.79
129.40
128.02
127.31
125.04
125.00
124.96
124.92
123.59
121.40
113.74
77.25
77.00
76.75
55.21
21.16
Me
S
H
CF3
OMe
4ja
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

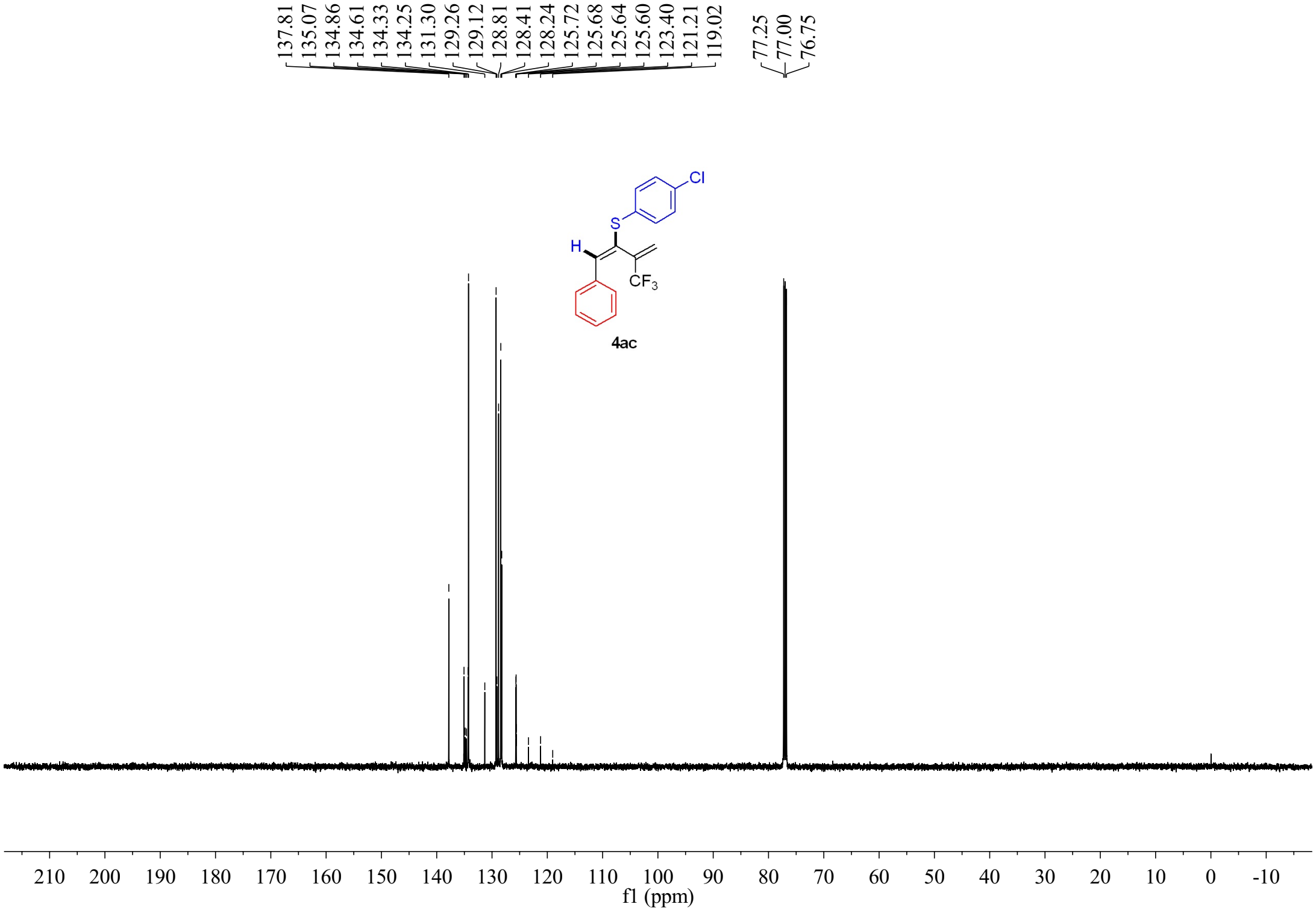

-63.878
Me
S
H
CF3
OMe
4ja
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

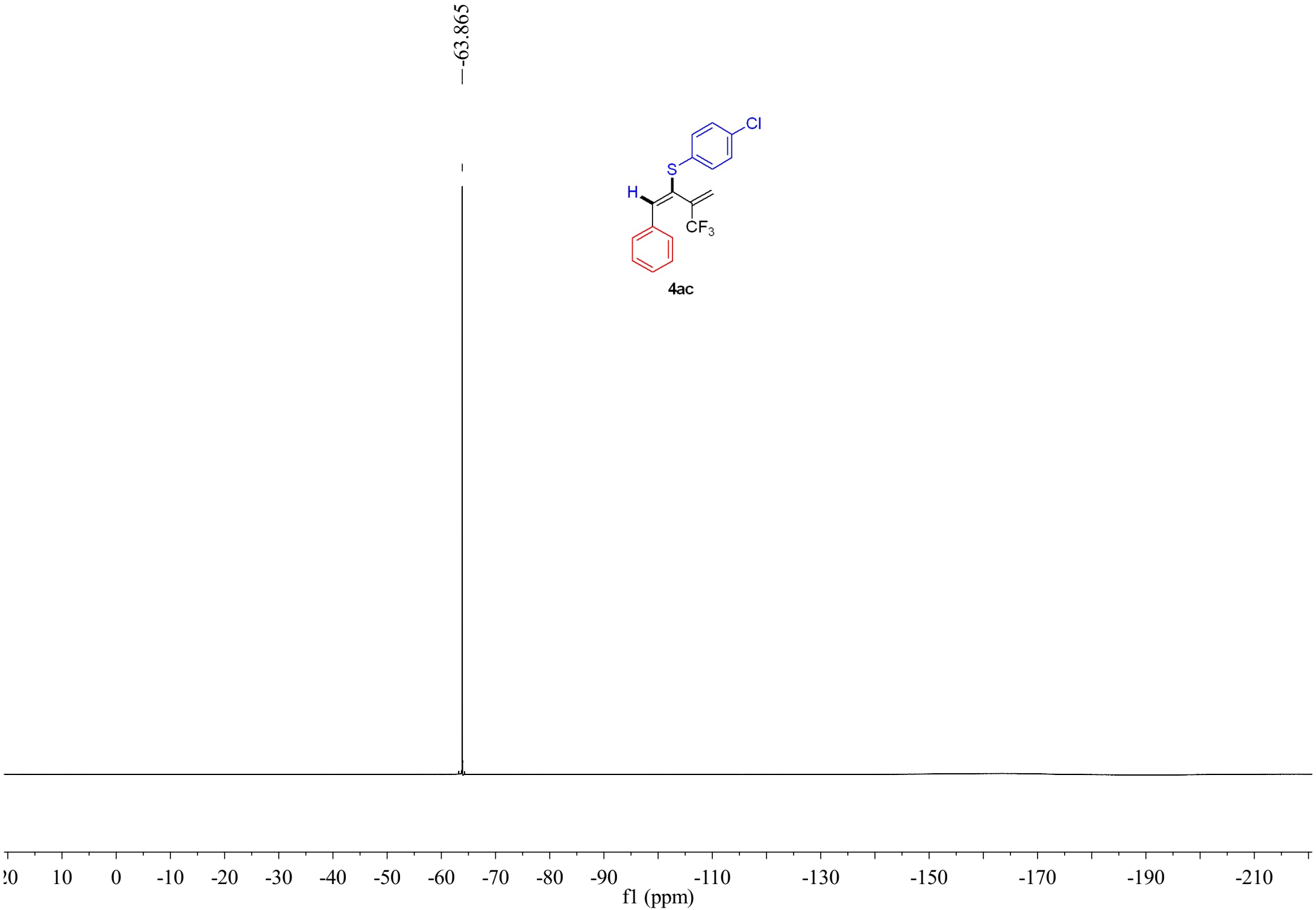

7.493
7.481
7.476
7.466
7.357
7.342
7.325
7.311
7.296
7.282
7.267
7.086
7.069
7.052
6.991
5.789
5.328
F
S
H
CF3
4ab
1.97
5.21
1.98
0.99
1.01
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


163.84
161.87
136.35
135.70
135.63
135.18
134.73
130.00
128.74
128.36
128.08
127.72
127.69
125.60
125.56
125.52
125.49
116.33
116.16
77.25
77.00
76.75
F
S
H
CF3
4ab
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)


-63.846
-112.412
F
S
H
CF3
4ab
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


7.405
7.388
7.365
7.350
7.335
7.316
7.300
7.285
7.275
7.068
5.786
5.348
Cl
S
H
CF3
4ac
1.93
7.44
0.99
1.00
1.04
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
f1 (ppm)


137.81
135.07
134.86
134.61
134.33
134.25
131.30
129.26
129.12
128.81
128.41
128.24
125.72
125.68
125.64
125.60
123.40
121.21
119.02
77.25
77.00
76.75
Cl
S
H
CF3
4ac
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)


-63.865
Cl
S
H
CF3
4ac
20
10
0
-10
-20
-30
-40
-50
-60
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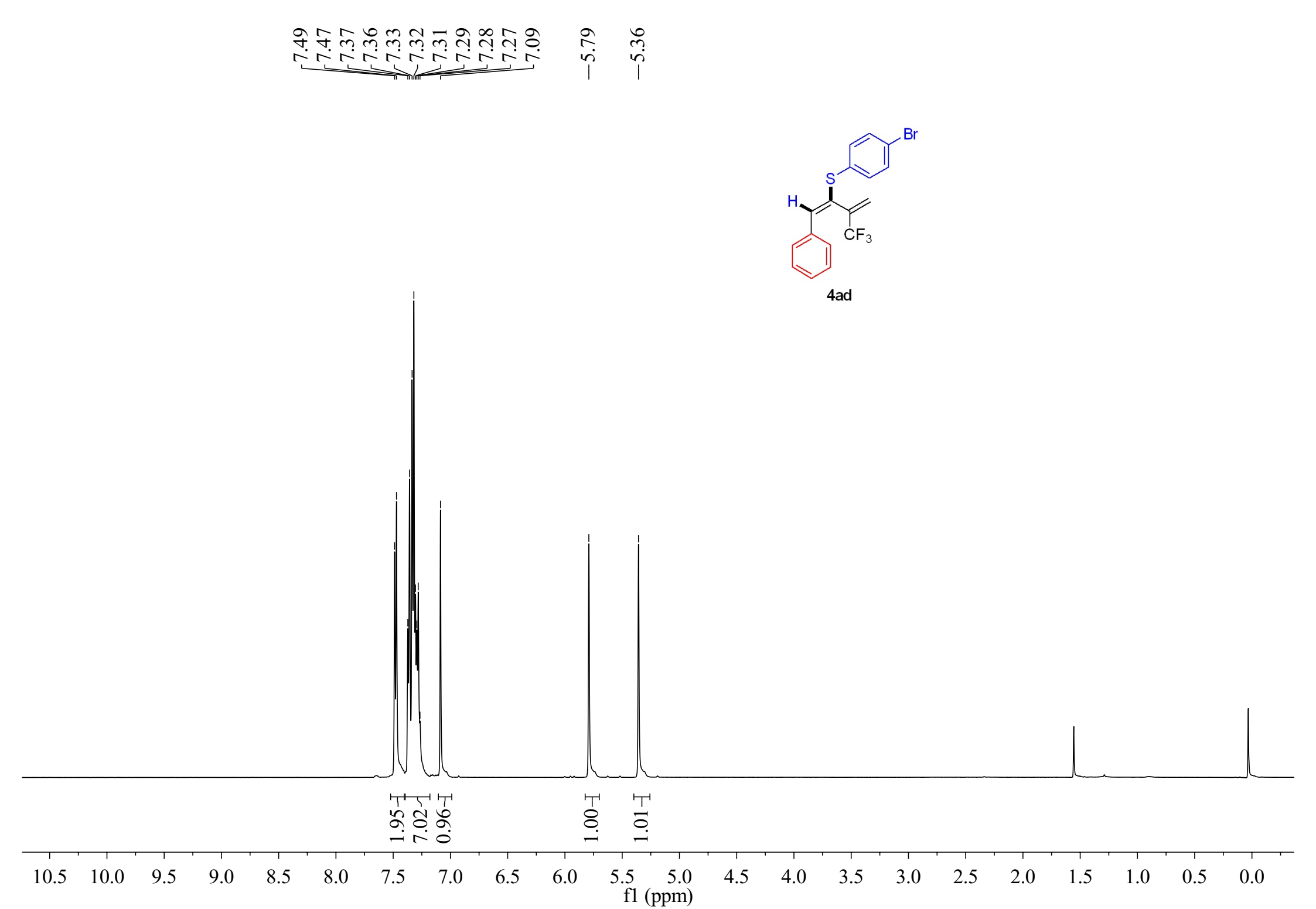
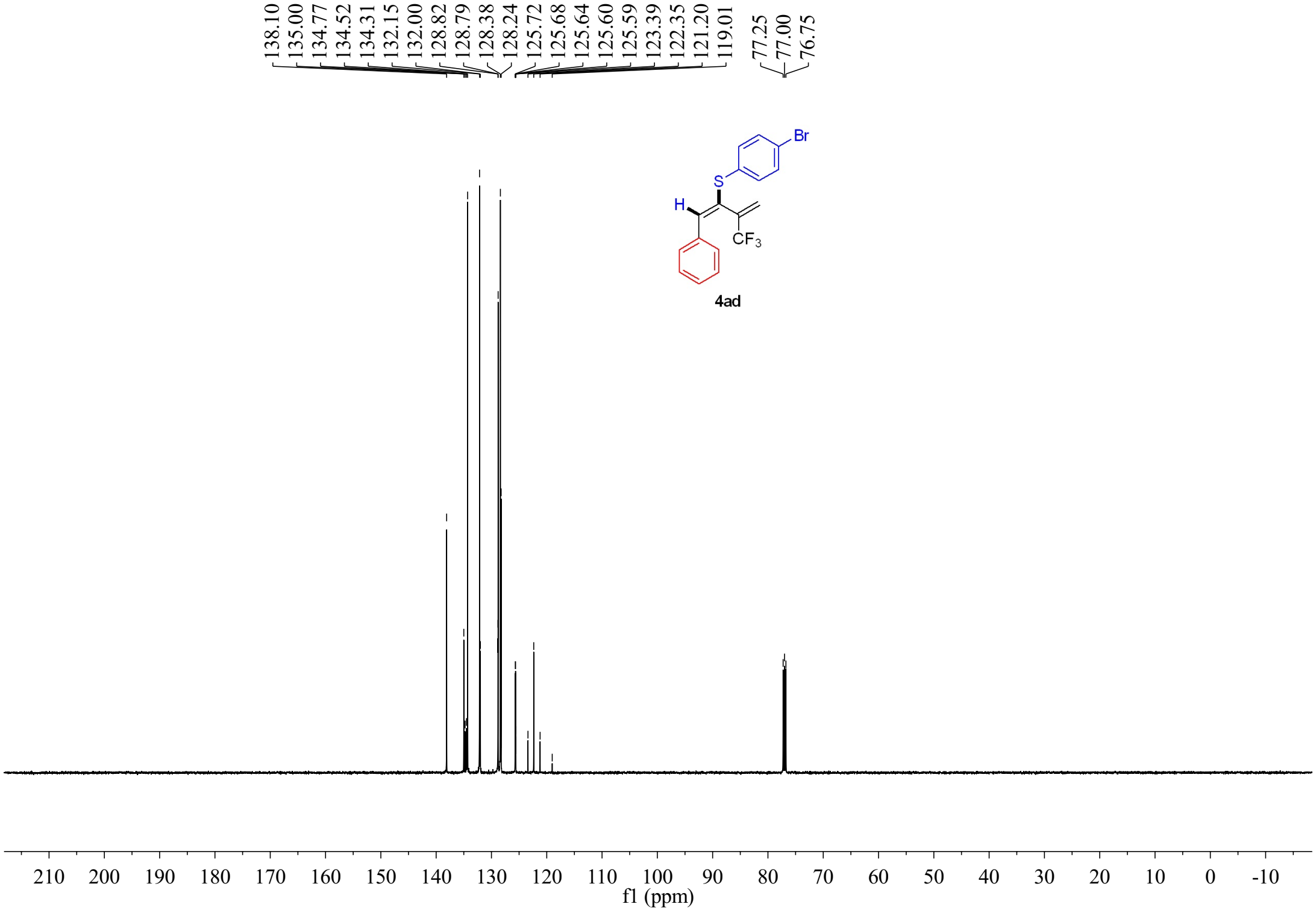
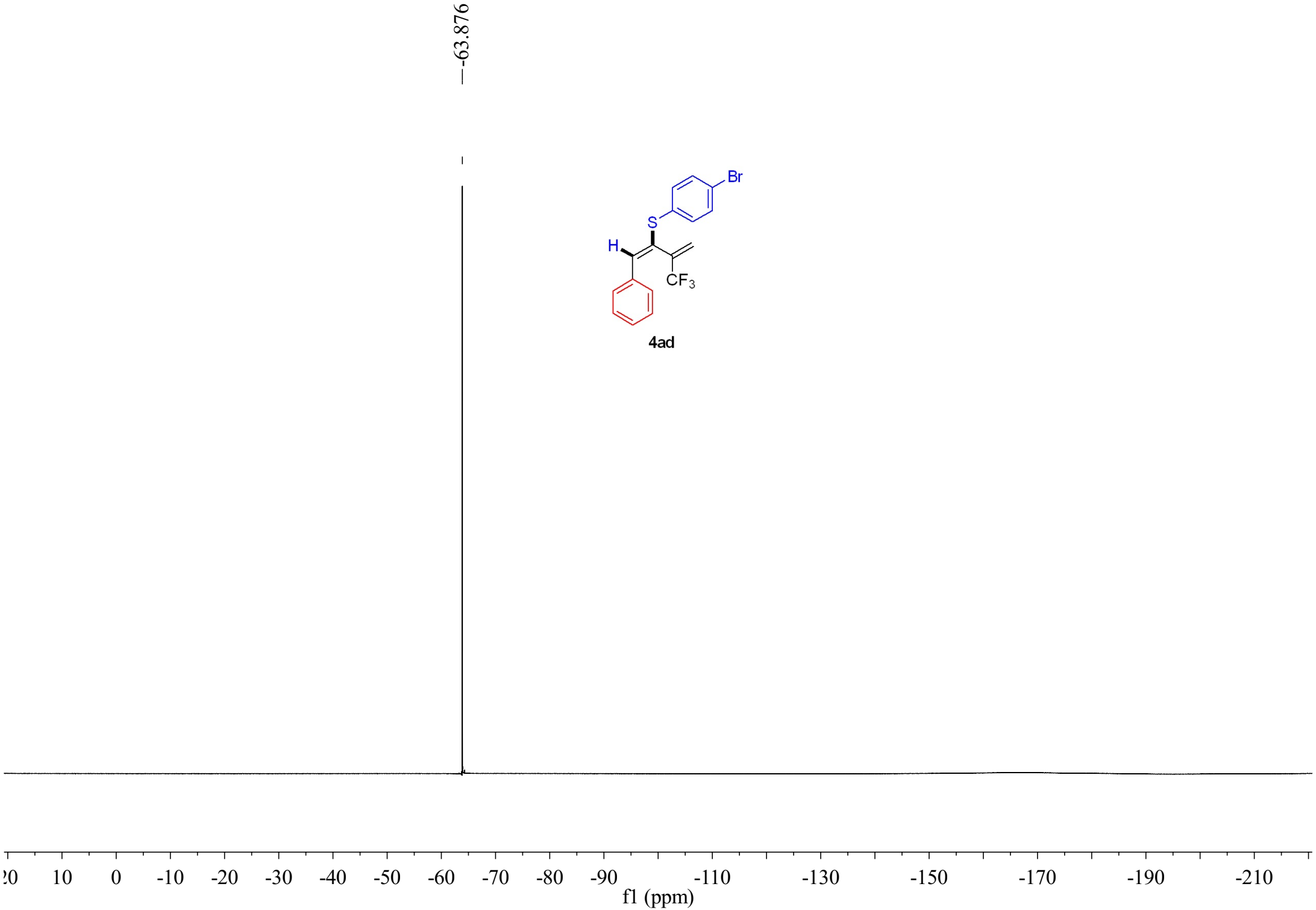
-110
-130
-150
-170
-190
-210
f1 (ppm)


7.49
7.47
7.37
7.36
7.33
7.32
7.31
7.29
7.28
7.27
7.09
5.79
5.36
Br
S
H
CF3
4ad
1.95
7.02
0.96
1.00
1.01
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
f1 (ppm)


138.10
135.00
134.77
134.52
134.31
132.15
132.00
128.82
128.79
128.38
128.24
125.72
125.68
125.64
125.60
125.59
123.39
122.35
121.20
119.01
77.25
77.00
76.75
Br
S
H
CF3
4ad
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)


-63.876
Br
S
H
CF3
4ad
20
10
0
-10
-20
-30
-40
-50
-60
-70
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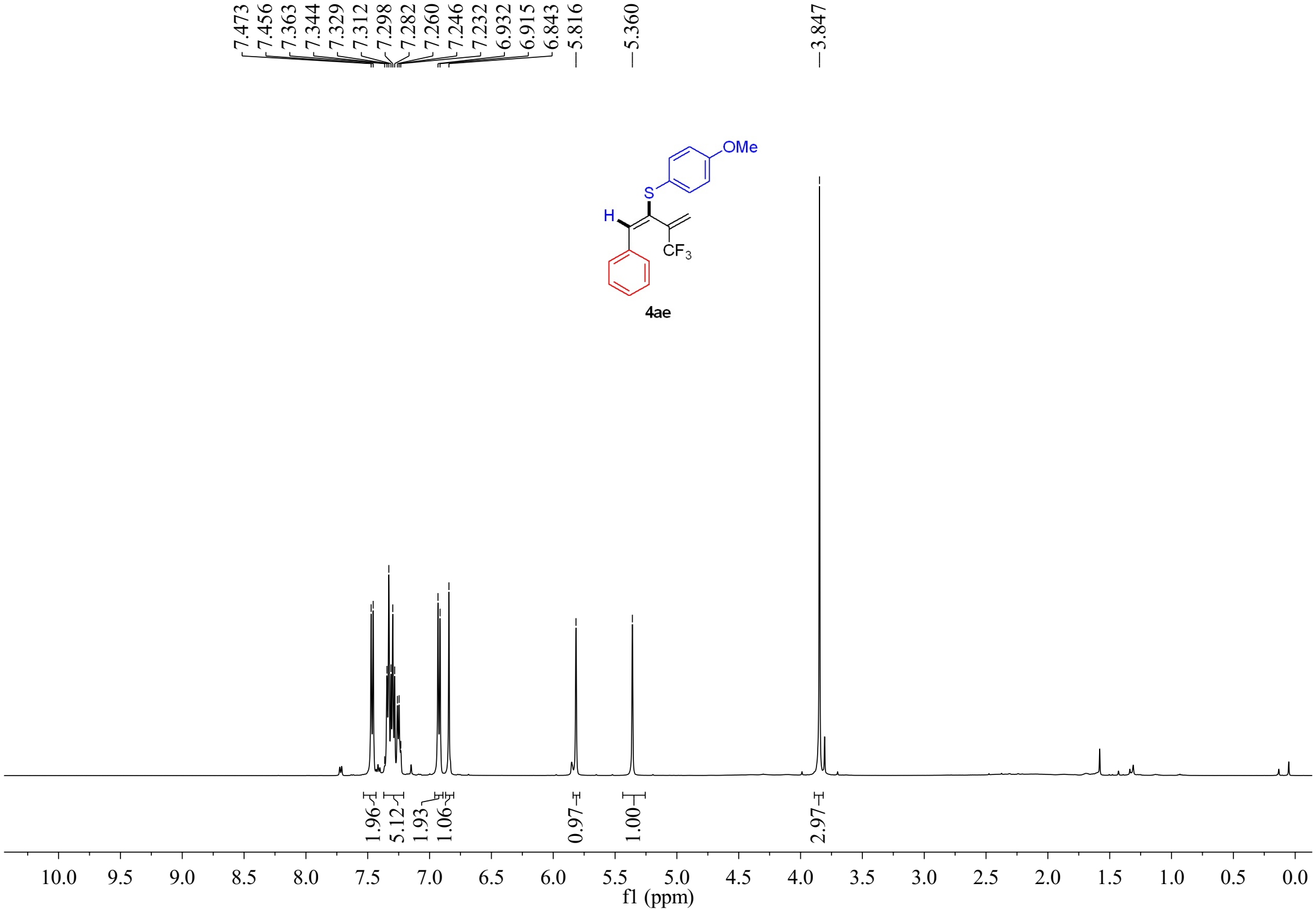
-110
-130
-150
-170
-190
-210
f1 (ppm)


7.473
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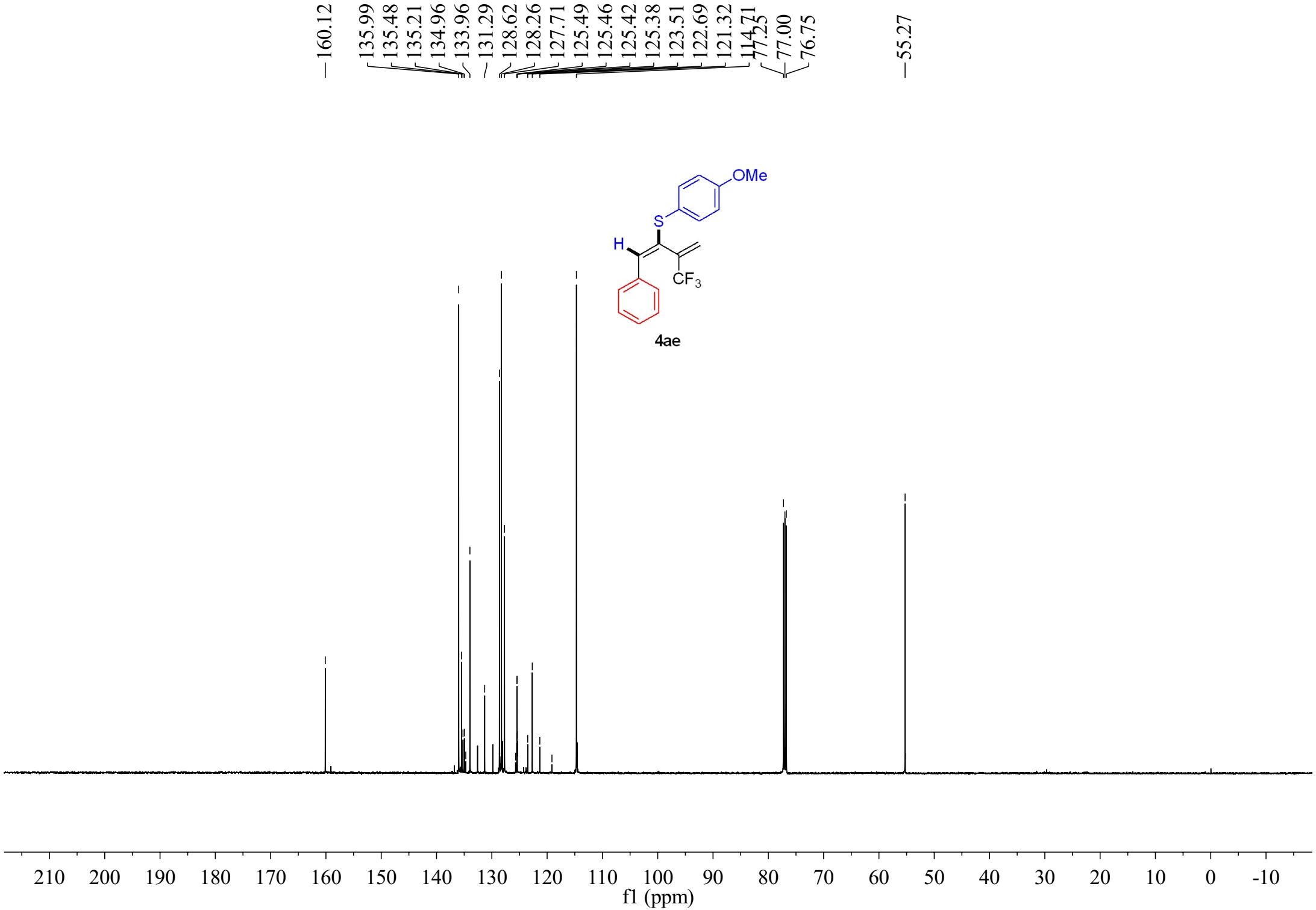
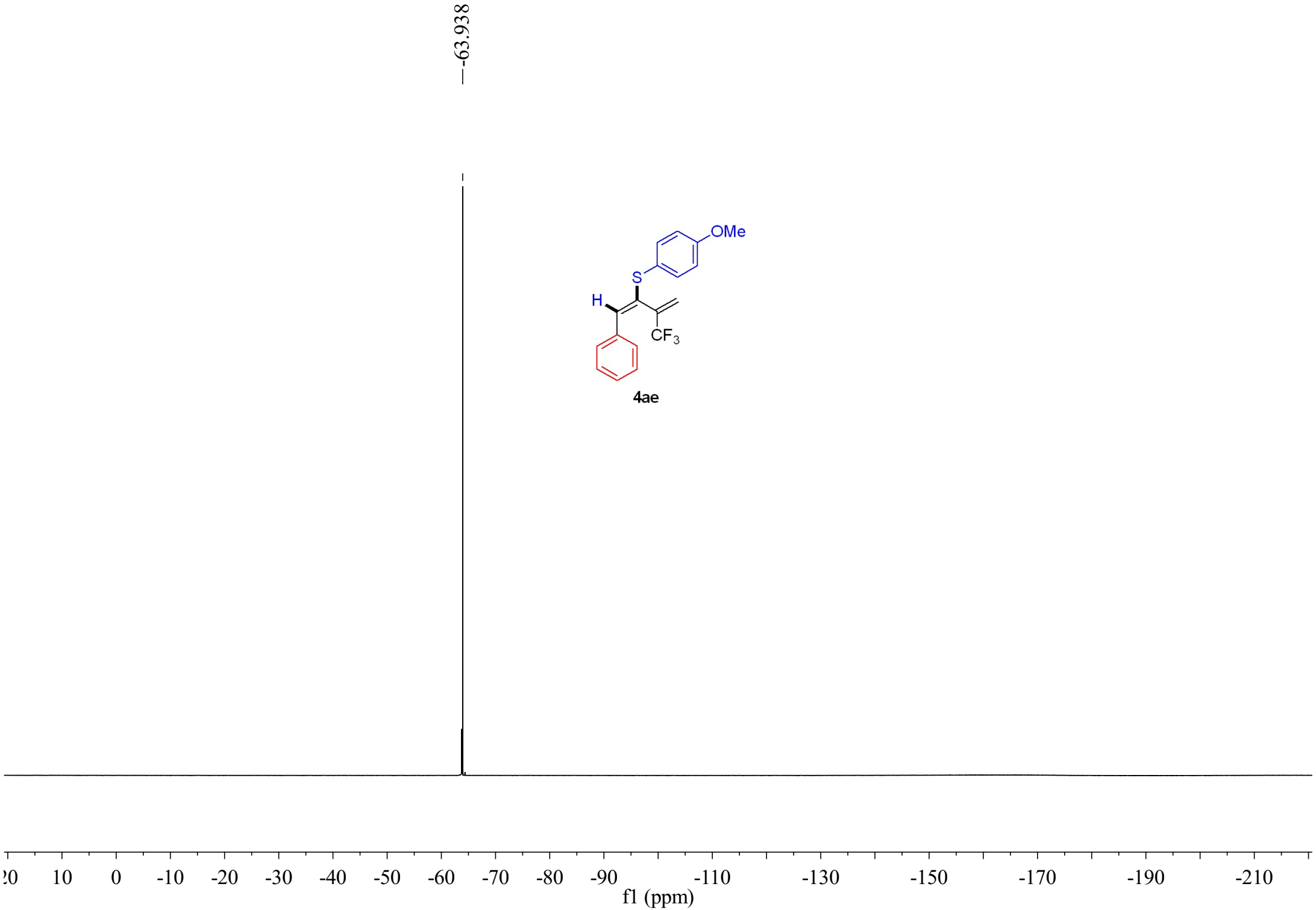
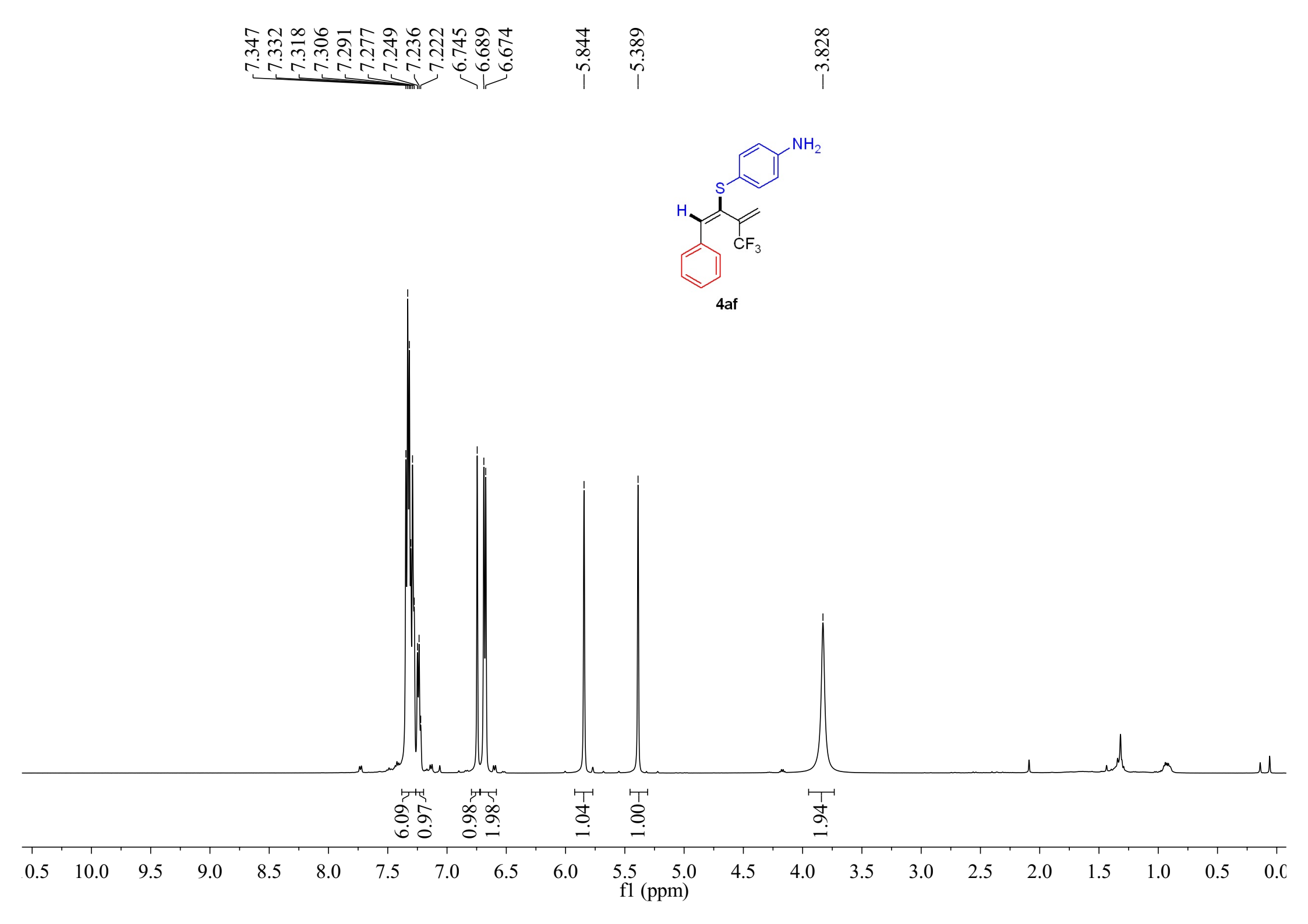
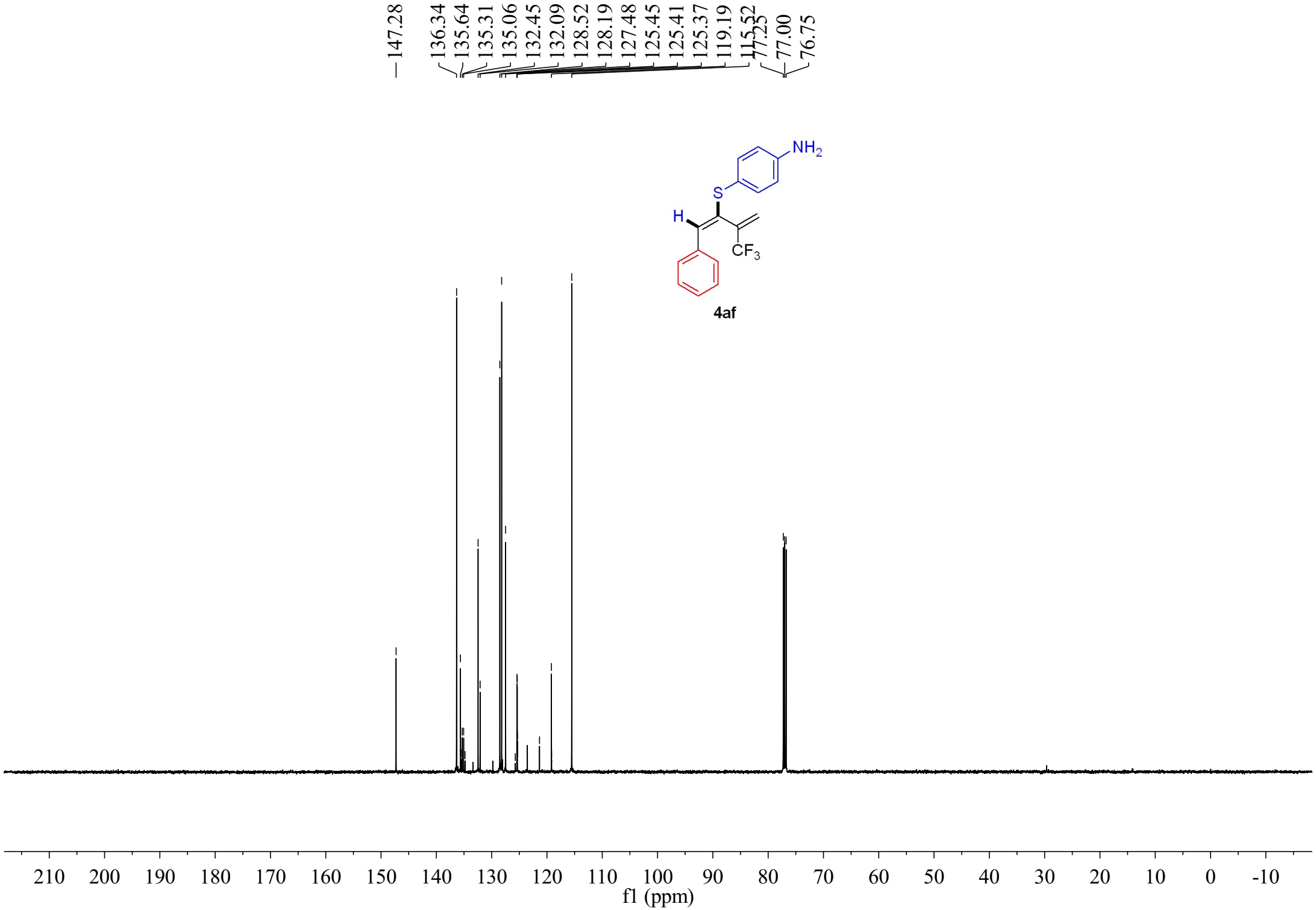
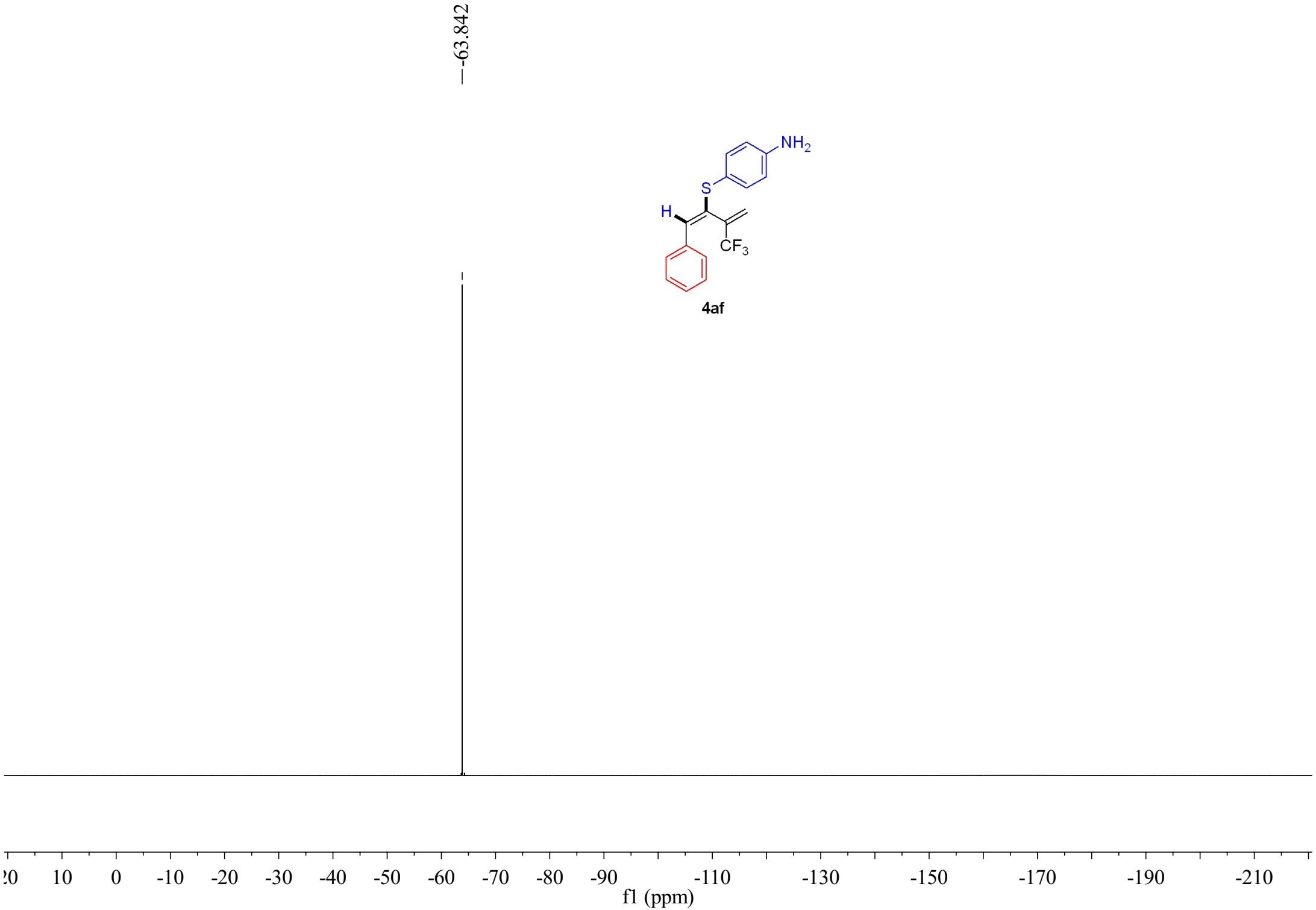
7.363
7.344
7.329
7.312
7.298
7.282
7.260
7.246
7.232
6.932
6.915
6.843
5.816
5.360
3.847
OMe
S
H
CF3
4ae
1.96
5.12
1.93
1.06
0.97
1.00
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

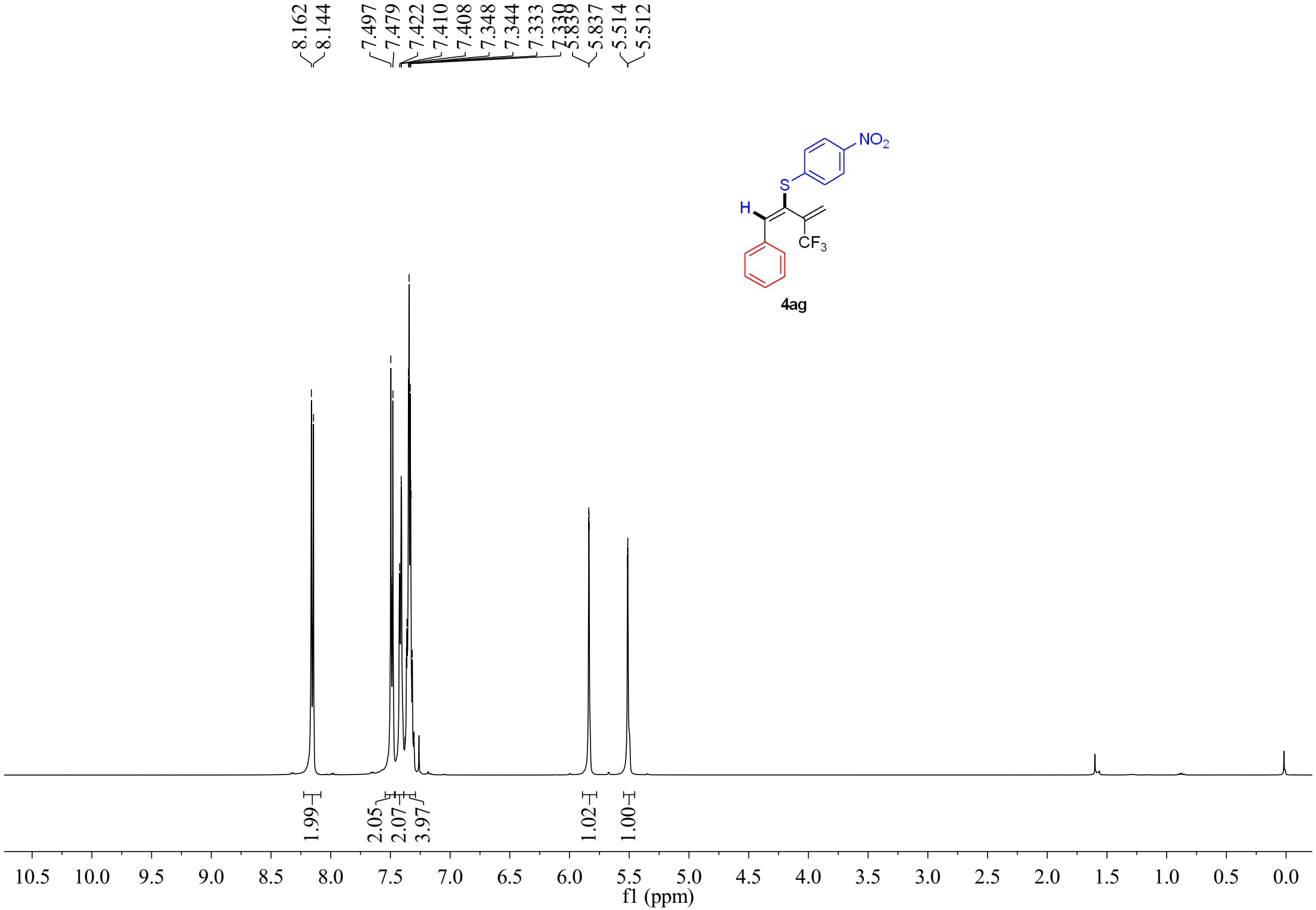

160.12
135.99
135.48
135.21
134.96
133.96
131.29
128.62
128.26
127.71
125.49
125.46
125.42
125.38
123.51
122.69
121.32
114.71
77.25
77.00
76.75
55.27
OMe
S
H
CF3
4ae
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

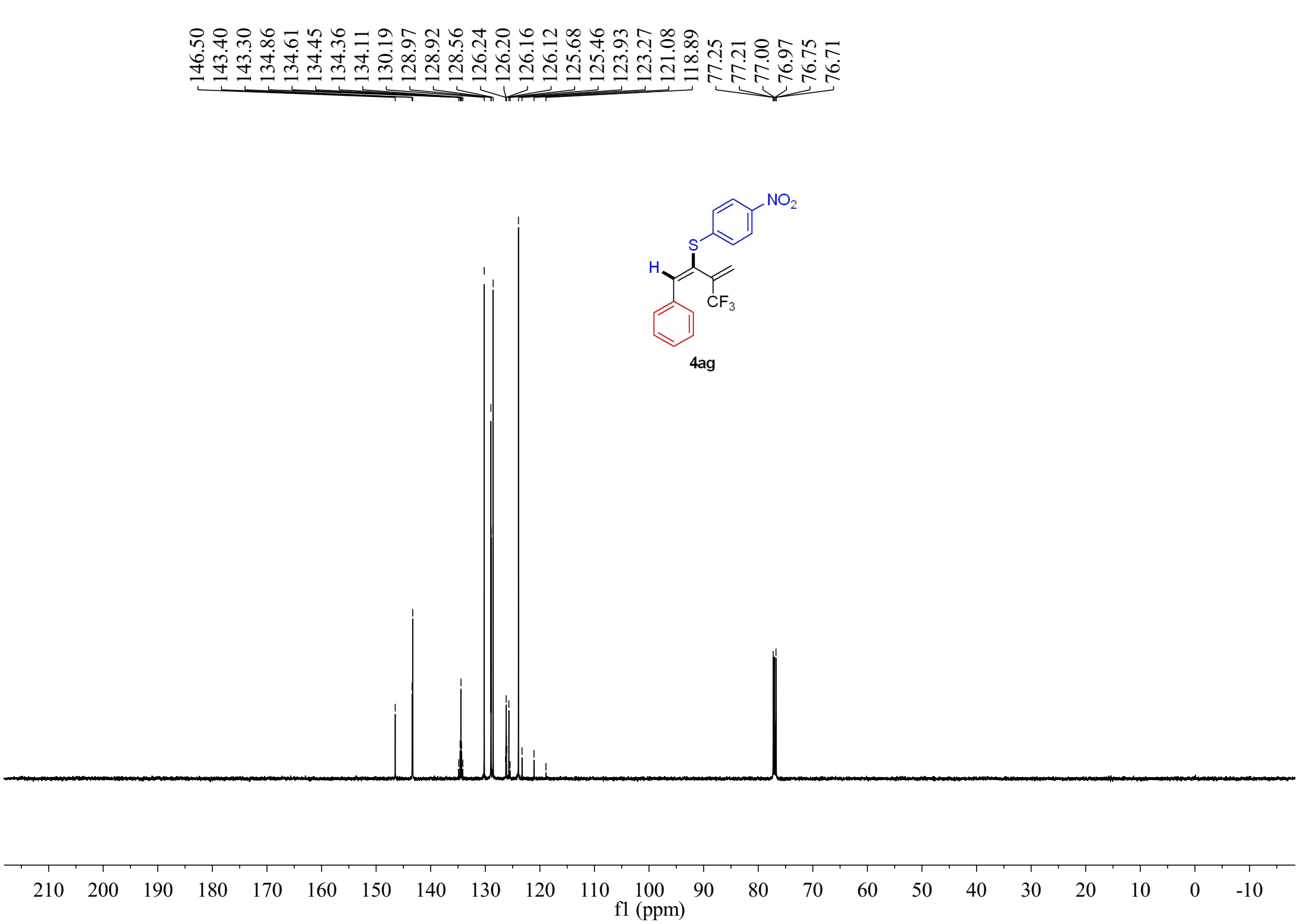

-63.938
OMe
S
H
CF3
4ae
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

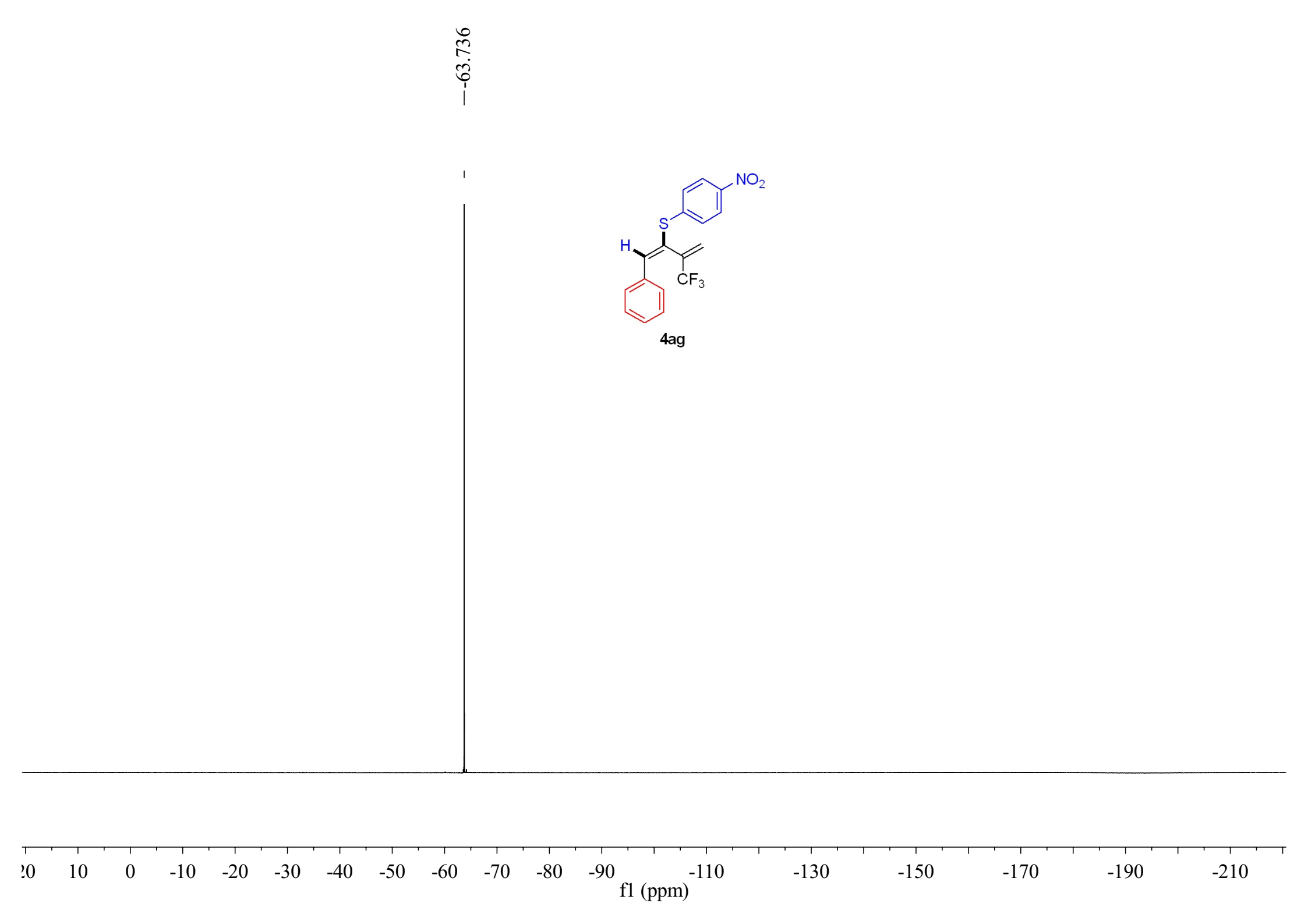

7.347
7.332
7.318
7.306
7.291
7.277
7.249
7.236
7.222
6.745
6.689
6.674
5.844
5.389
3.828
NH2
S
H
CF3
4af
6.09
0.97
0.98
1.98
1.04
1.00
1.94
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

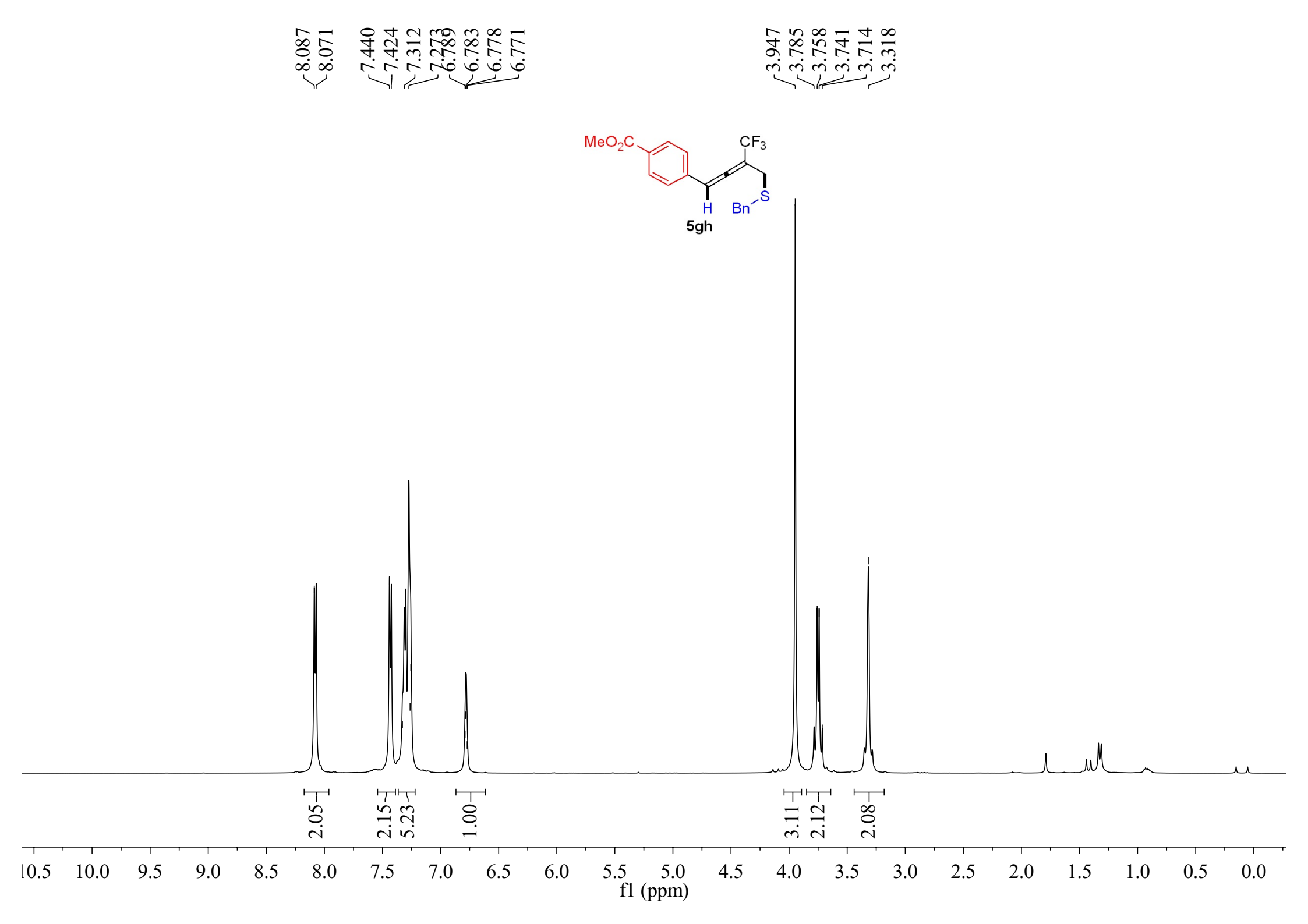

147.28
136.34
135.64
135.31
135.06
132.45
132.09
128.52
128.19
127.48
125.45
125.41
125.37
119.19
115.52
77.25
77.00
76.75
NH2
S
H
CF3
4af
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

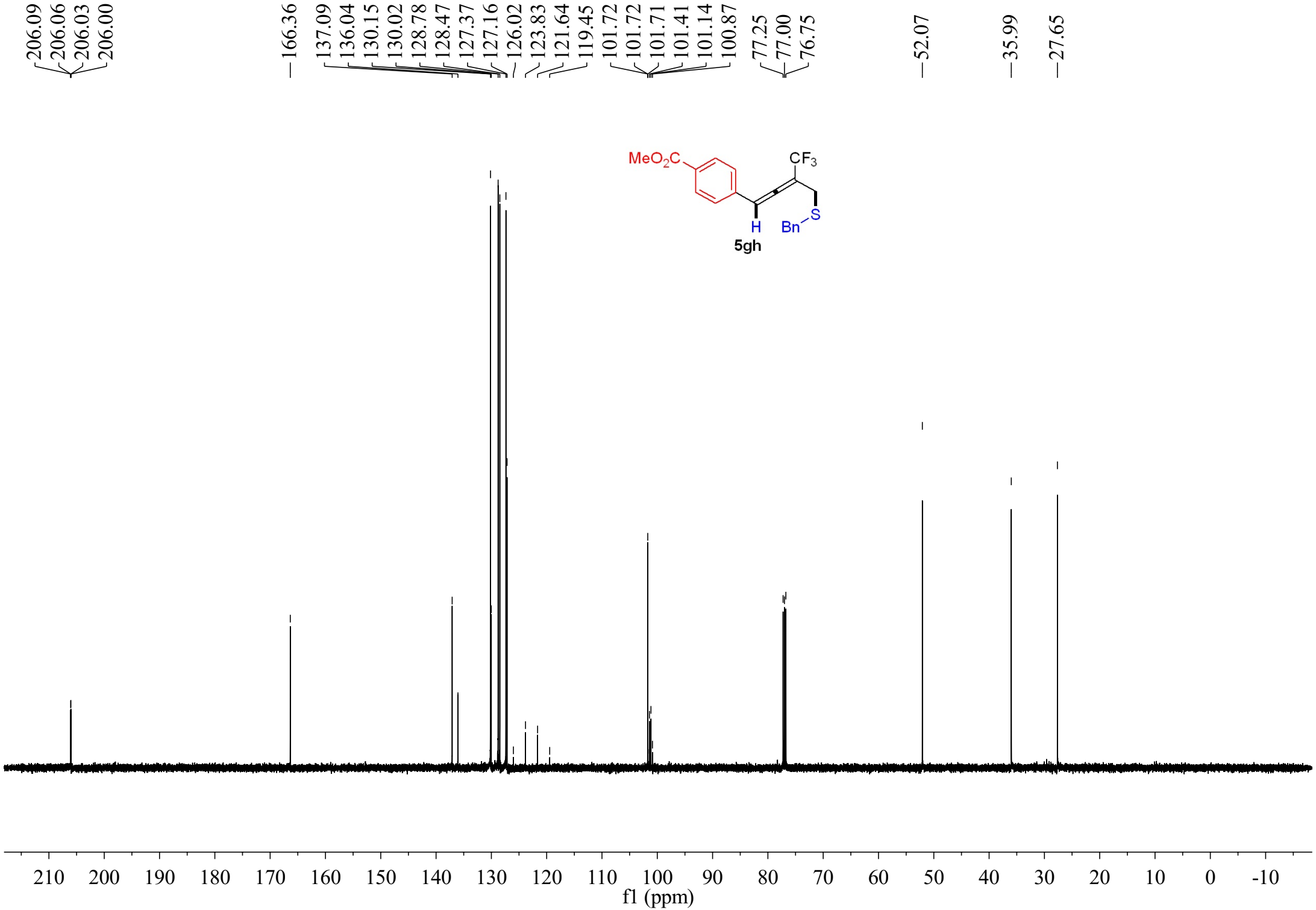

-63.842
NH2
S
H
CF3
4af
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

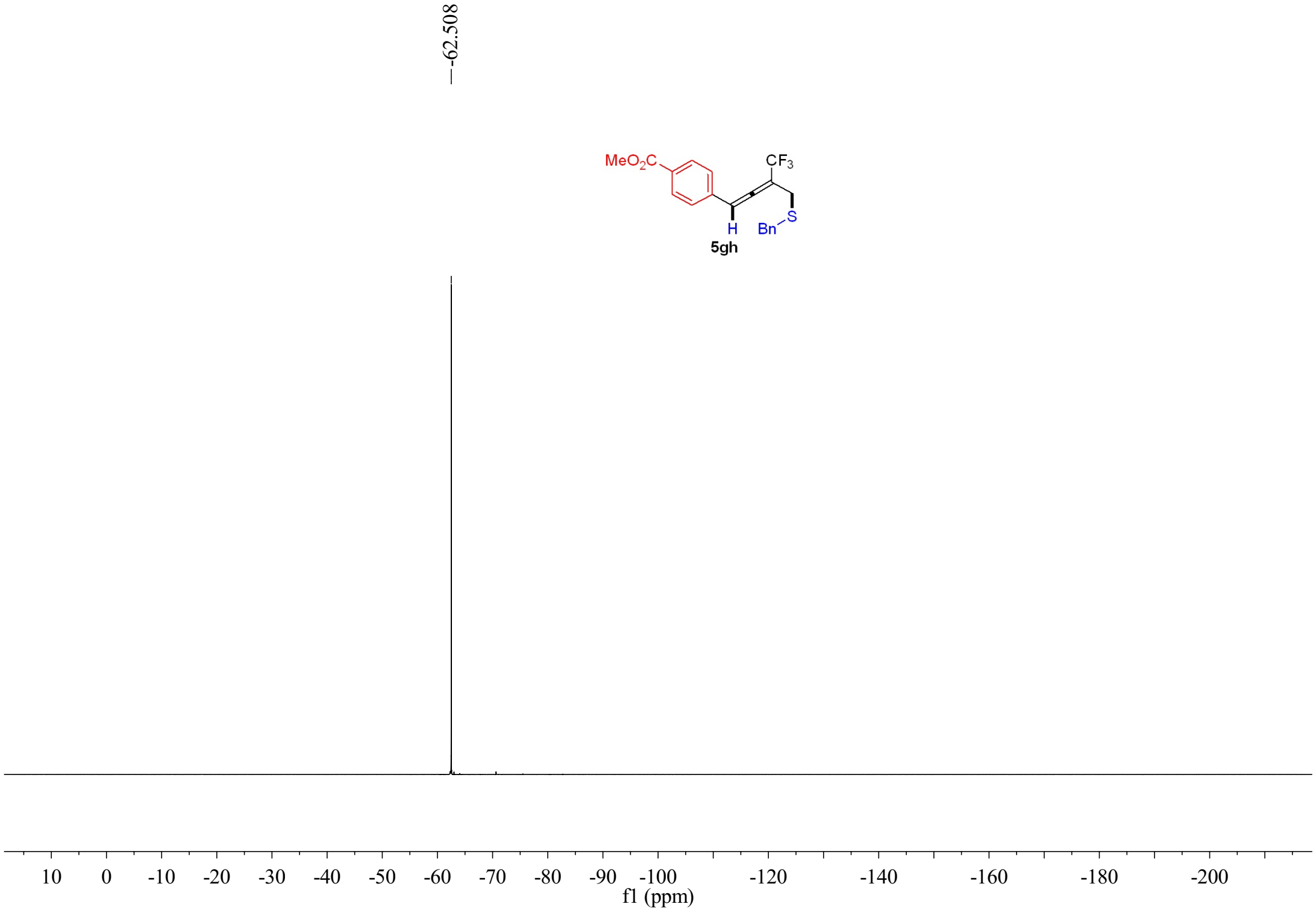

8.162
8.144
7.497
7.479
7.422
7.410
7.408
7.348
7.344
7.333
7.330
5.839
5.837
5.514
5.512
NO2
S
H
CF3
4ag
1.99
2.05
2.07
3.97
1.02
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

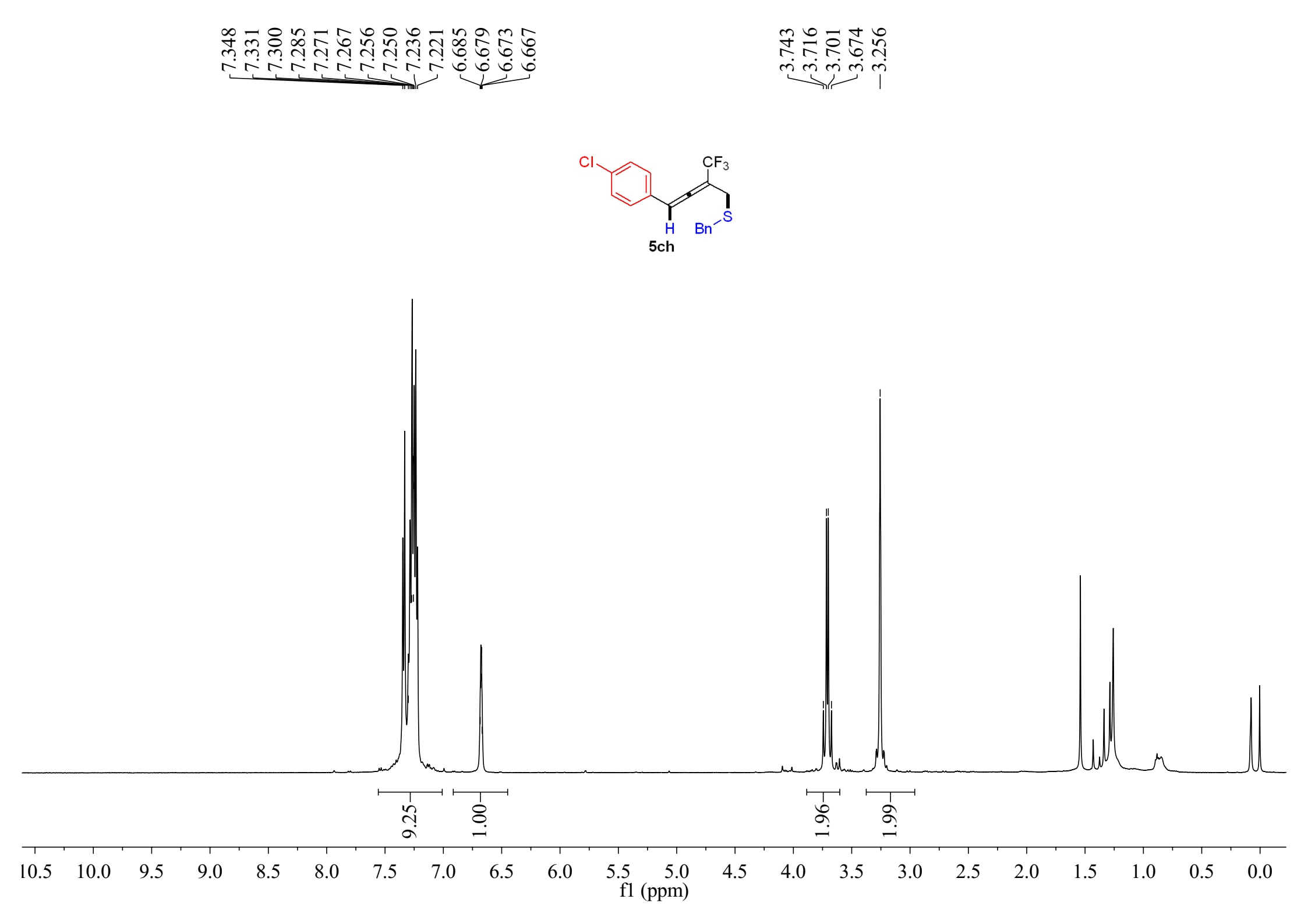

146.50
143.40
143.30
134.86
134.61
134.45
134.36
134.11
130.19
128.97
128.92
128.56
126.24
126.20
126.16
126.12
125.68
125.46
123.93
123.27
121.08
118.89
77.25
77.21
77.00
76.97
76.75
76.71
NO2
S
H
CF3
4ag
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

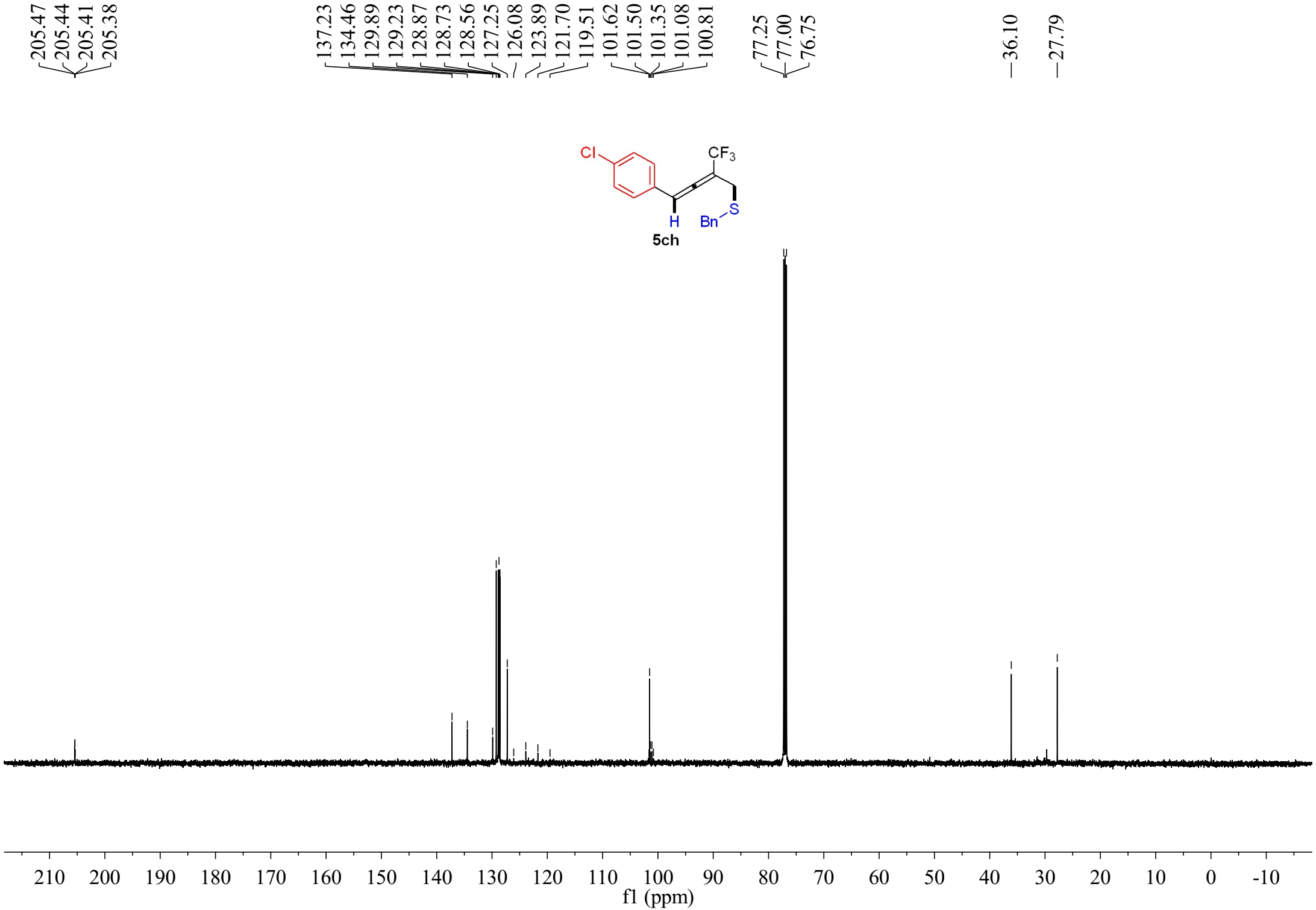

-63.736
NO2
S
H
CF3
4ag
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

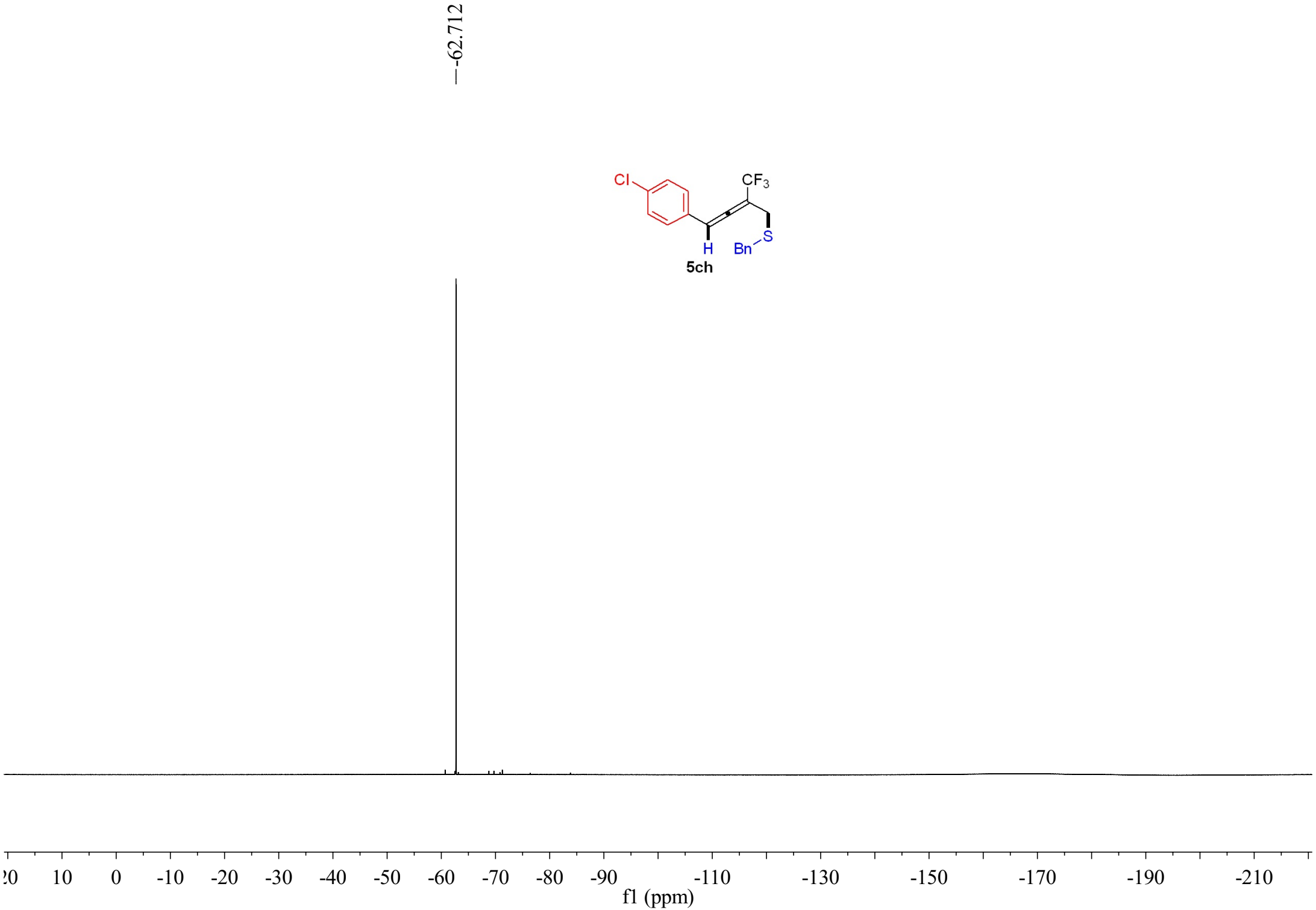

8.087
8.071
7.440
7.424
7.312
7.273
6.789
6.783
6.778
6.771
3.947
3.785
3.758
3.741
3.714
3.318
MeO2C
CF3
H
Bn
S
5gh
2.05
2.15
5.23
1.00
3.11
2.12
2.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

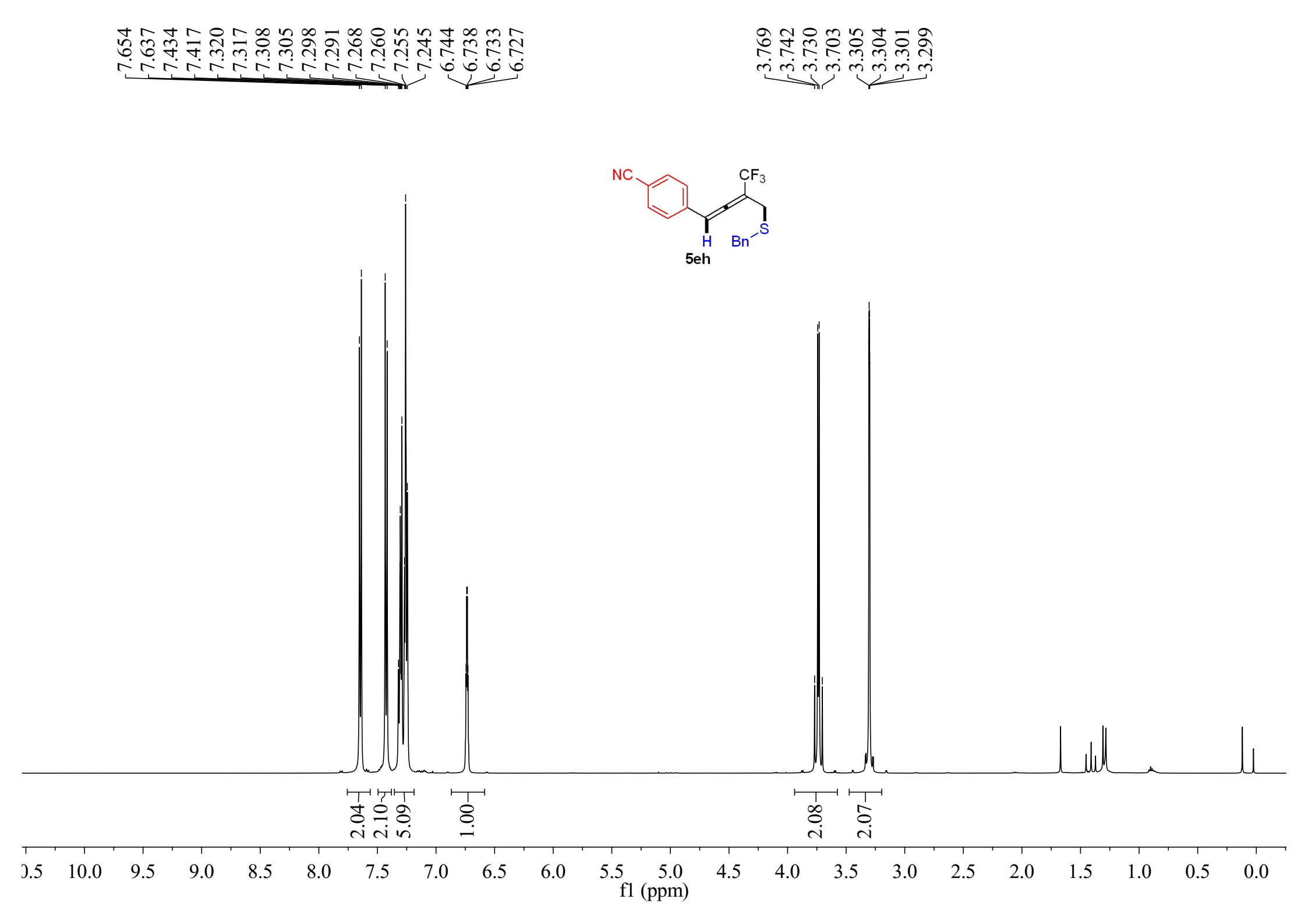

206.09
206.06
206.03
206.00
166.36
137.09
136.04
130.15
130.02
128.78
128.47
127.37
127.16
126.02
123.83
121.64
119.45
101.72
101.72
101.71
101.41
101.14
100.87
77.25
77.00
76.75
52.07
35.99
27.65
MeO2C
CF3
H
Bn
S
5gh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-62.508
MeO2C
CF3
H
Bn
S
5gh
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

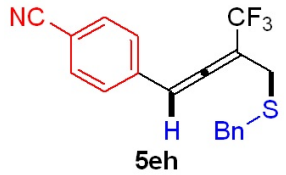

7.348
7.331
7.300
7.285
7.271
7.267
7.256
7.250
7.236
7.221
6.685
6.679
6.673
6.667
3.743
3.716
3.701
3.674
3.256
Cl
CF3
H
Bn
S
5ch
9.25
1.00
1.96
1.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


205.47
205.44
205.41
205.38
137.23
134.46
129.89
129.23
128.87
128.73
128.56
127.25
126.08
123.89
121.70
119.51
101.62
101.50
101.35
101.08
100.81
77.25
77.00
76.75
36.10
27.79
Cl
CF3
H
Bn
S
5ch
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)

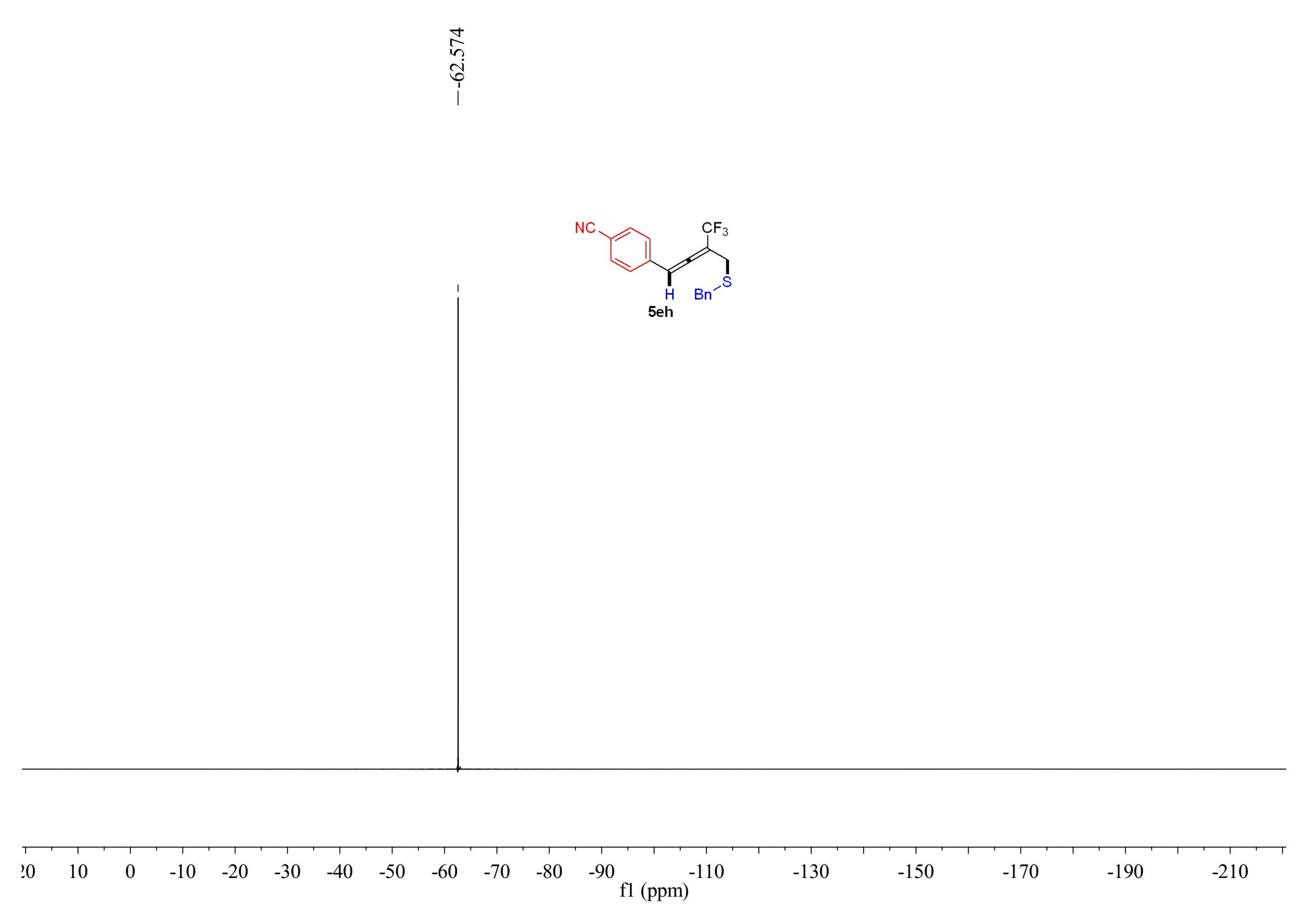

-62.712
Cl
CF3
H
Bn
S
5ch
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

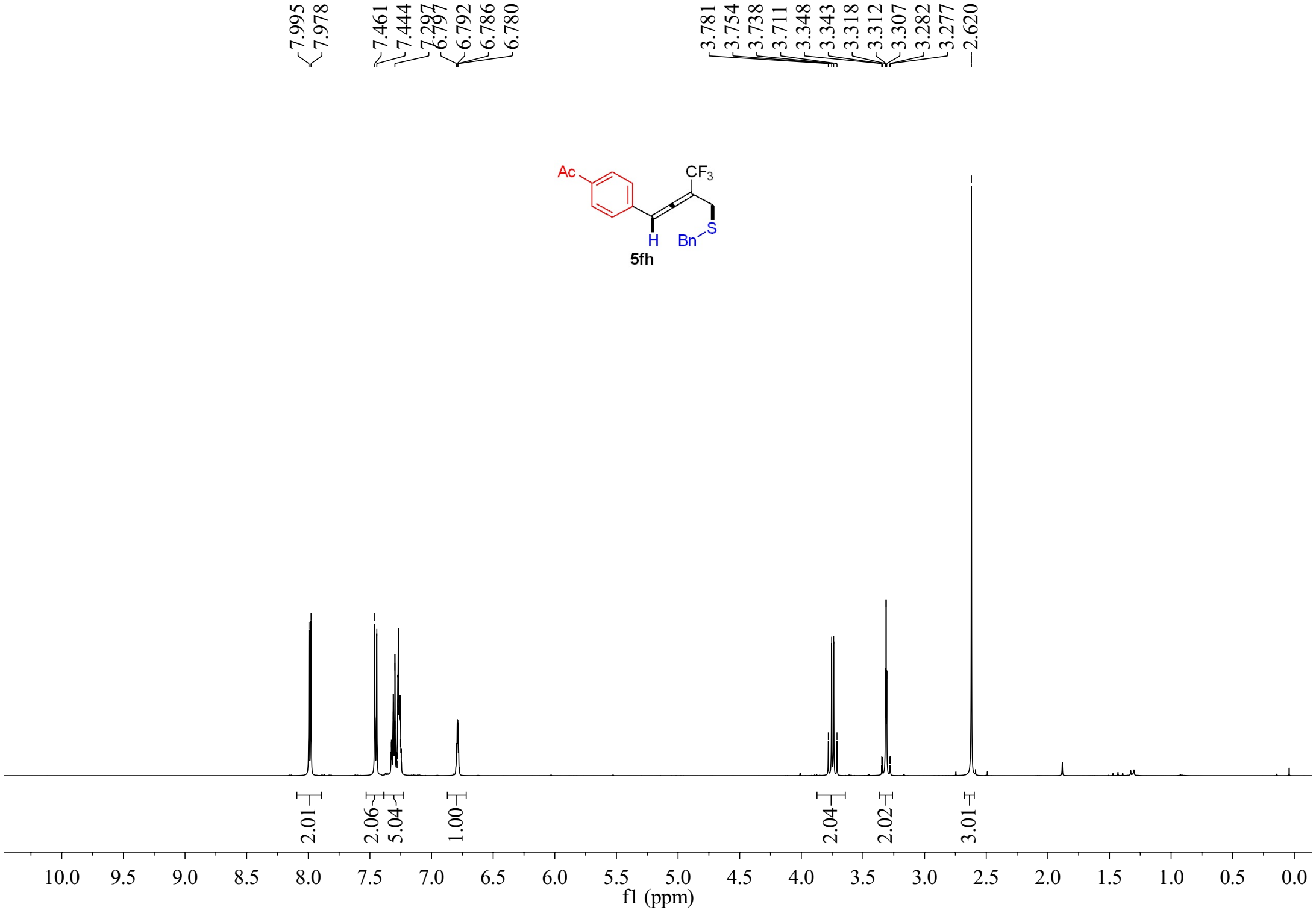

7.654
7.637
7.434
7.417
7.320
7.317
7.308
7.305
7.298
7.291
7.268
7.260
7.255
7.245
6.744
6.738
6.733
6.727
3.769
3.742
3.730
3.703
3.305
3.304
3.301
3.299
NC
CF3
H
Bn
S
5eh
2.04
2.10
5.09
1.00
2.08
2.07
f1 (ppm)

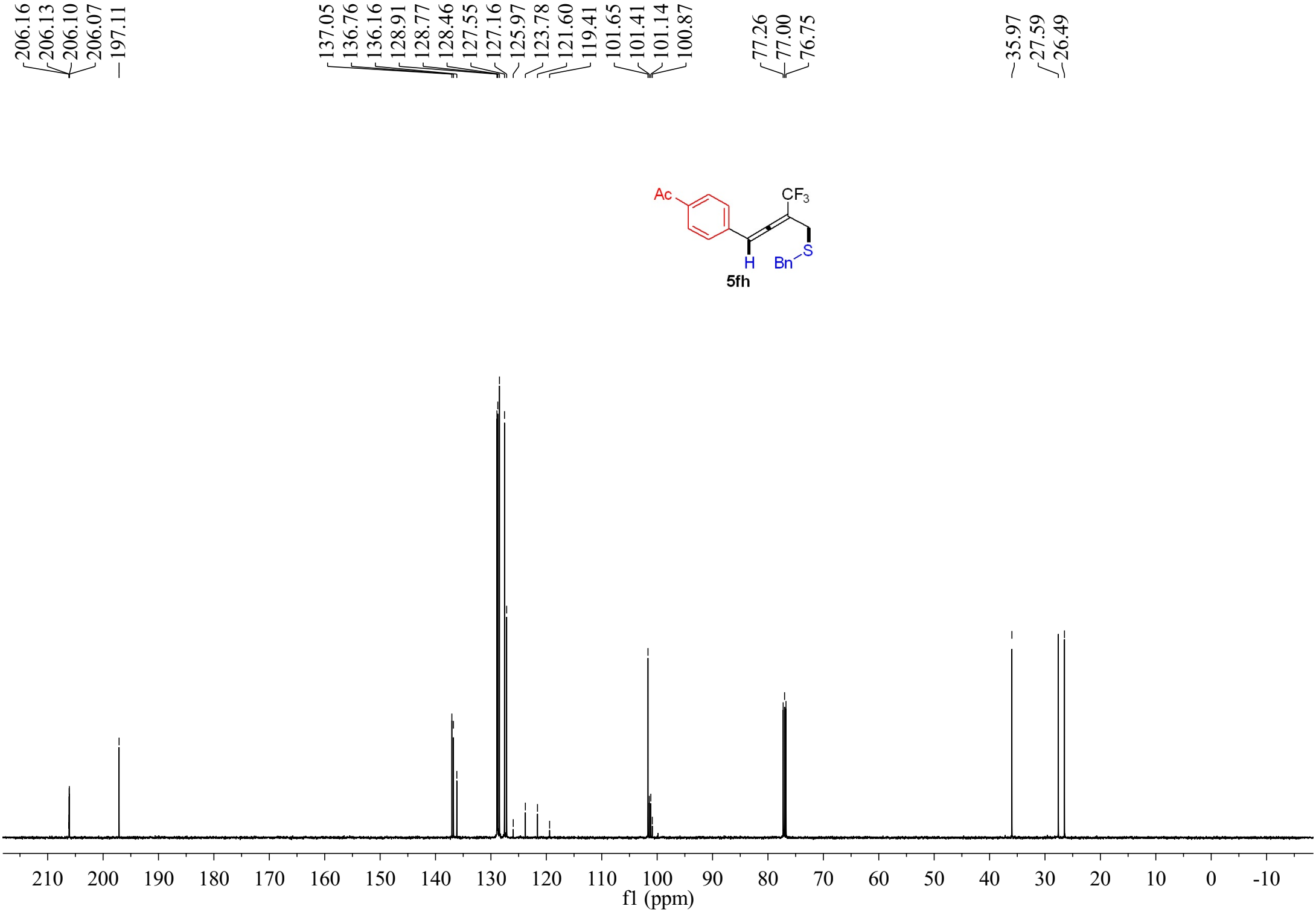
206.18
206.15
206.12
206.09
136.97
136.25
132.83
132.60
128.73
128.57
128.50
128.29
127.91
127.23
125.83
123.64
121.45
119.27
118.38
111.87
102.38
102.11
101.84
101.57
101.37
77.25
77.00
76.75
36.18
27.58

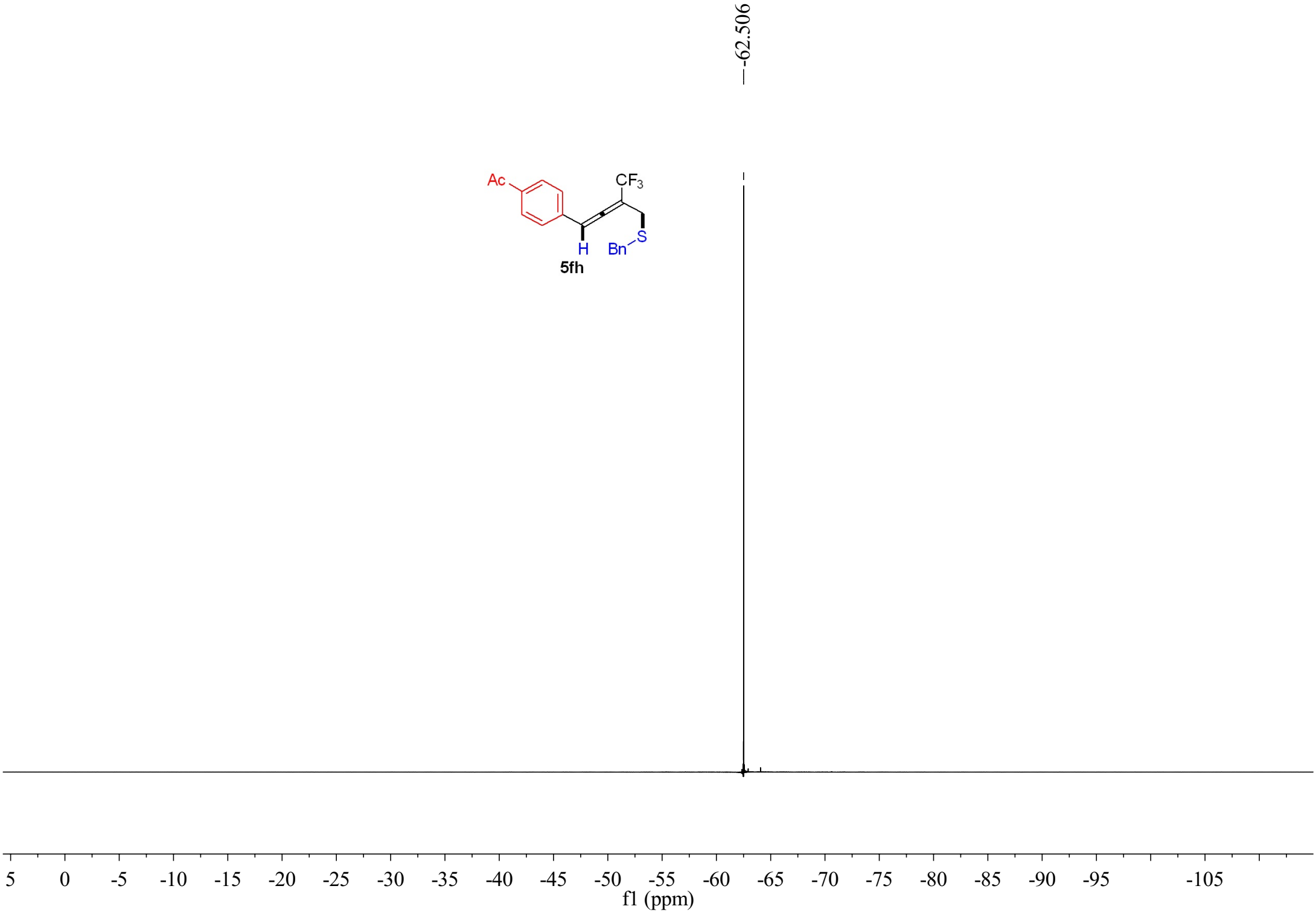


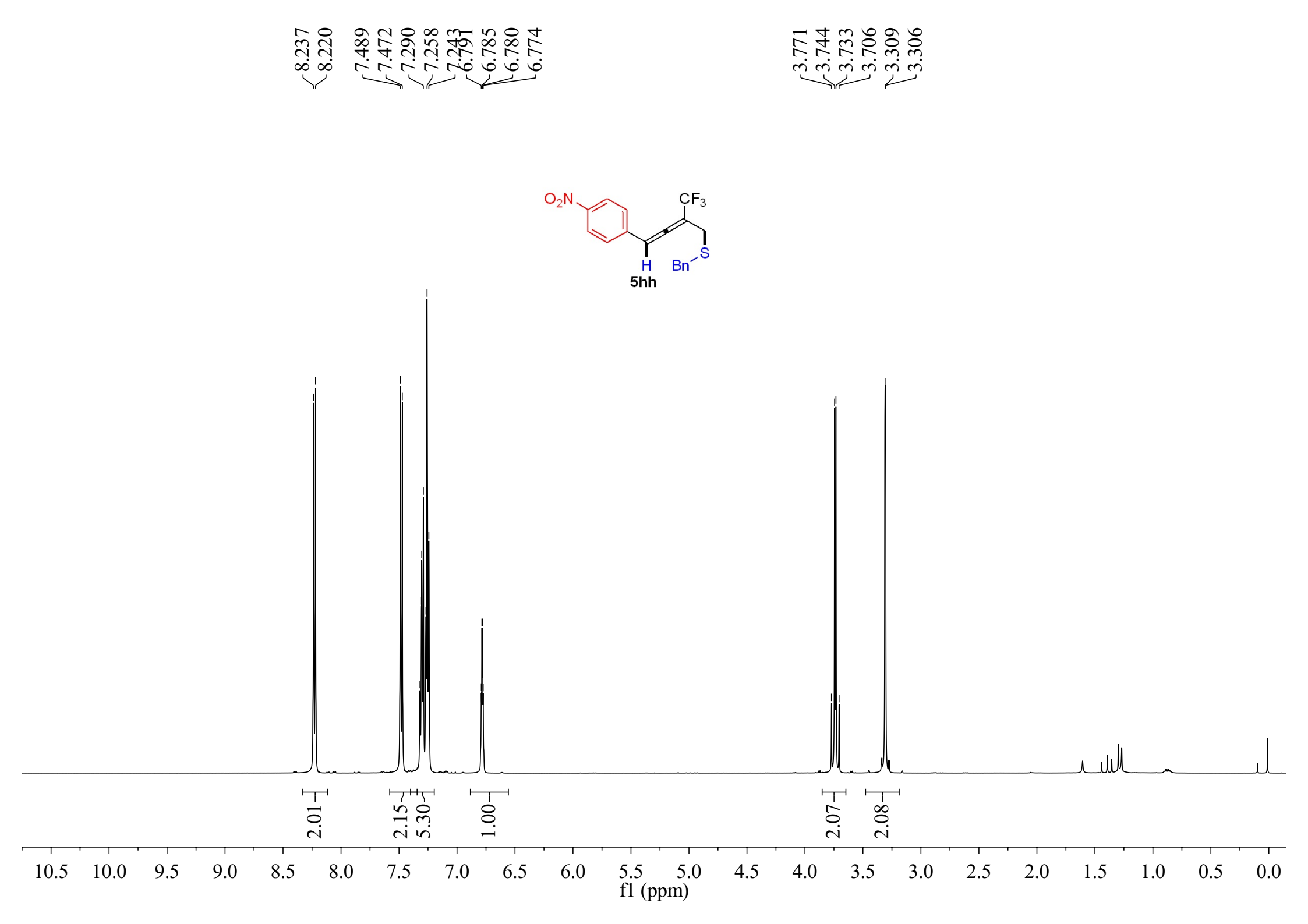
5eh

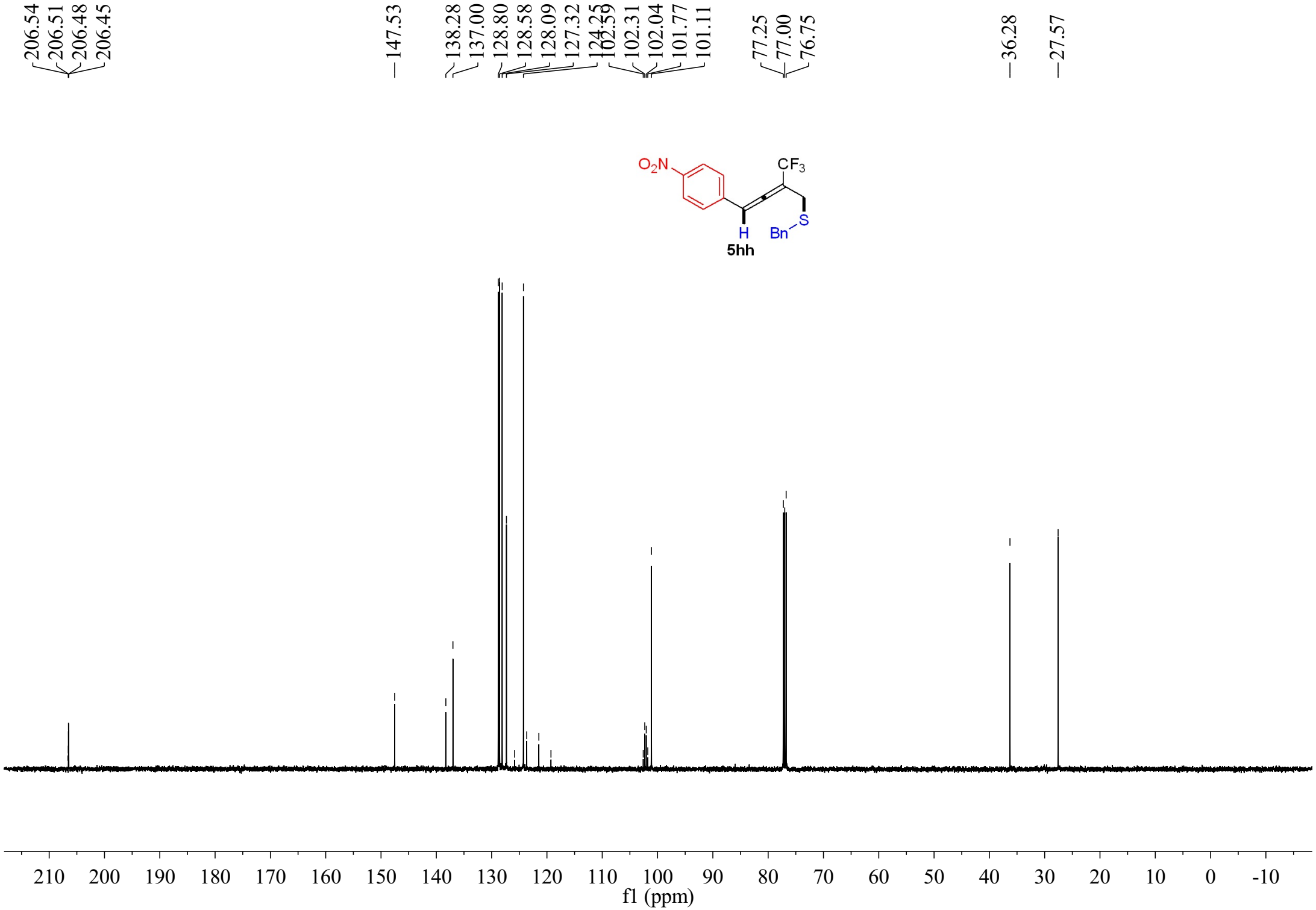

-62.574
NC
CF3
H
Bn
S
5eh
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

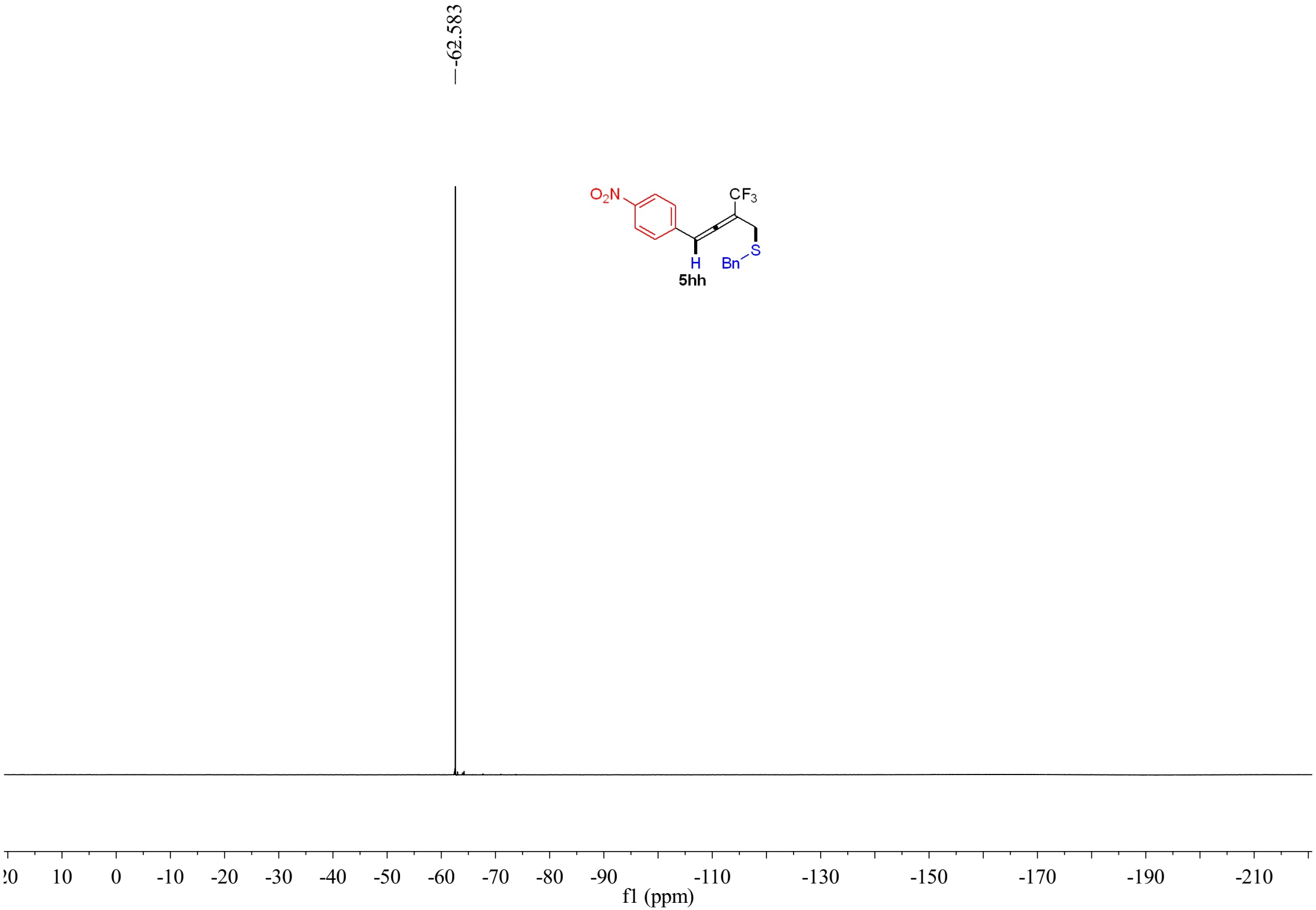

7.995
7.978
7.461
7.444
7.297
6.797
6.792
6.786
6.780
3.781
3.754
3.738
3.711
3.348
3.343
3.318
3.312
3.307
3.282
3.277
2.620
Ac
CF3
H
Bn
S
5fh
2.01
2.06
5.04
1.00
2.04
2.02
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

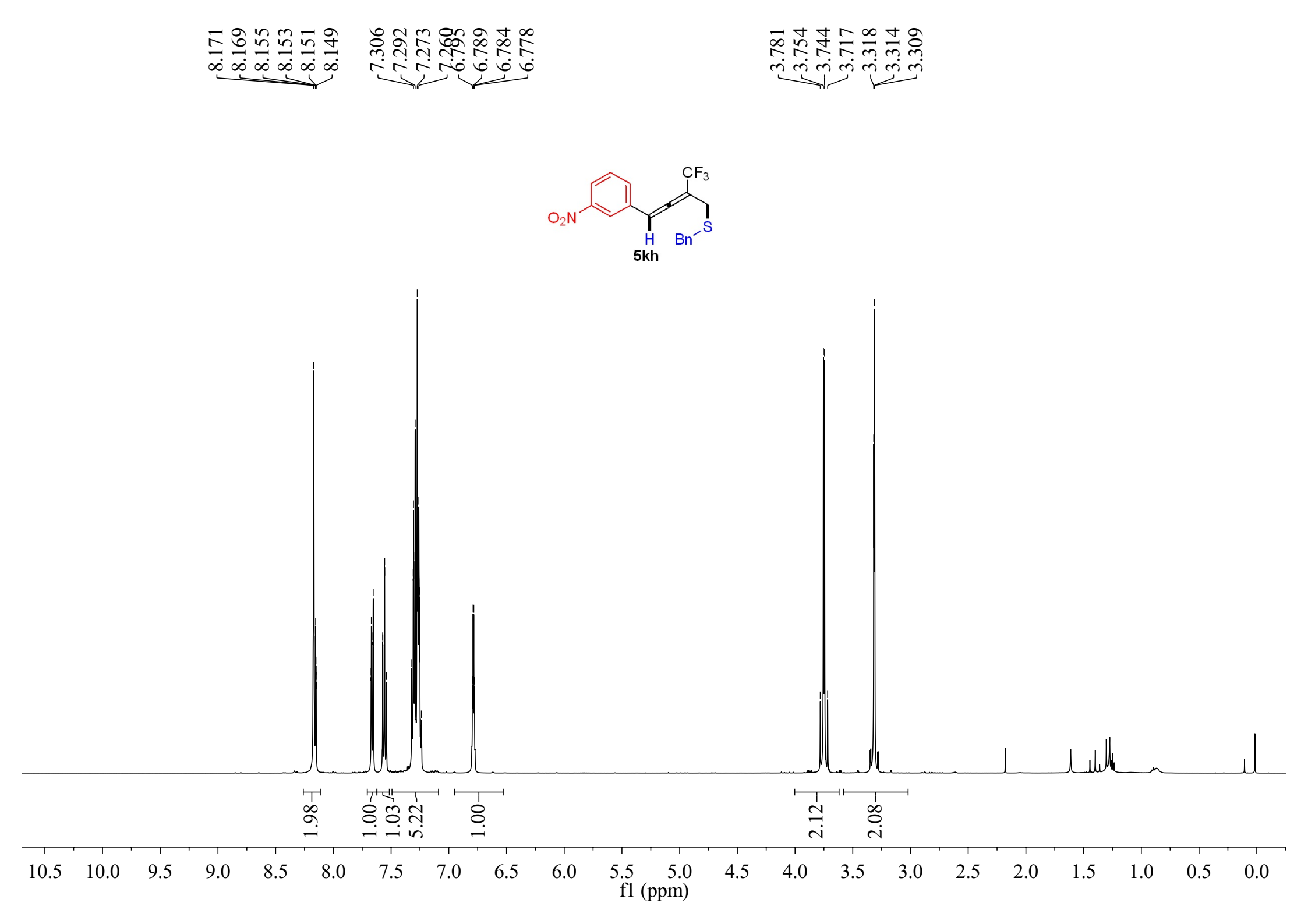

206.16
206.13
206.10
206.07
197.11
137.05
136.76
136.16
128.91
128.77
128.46
127.55
127.16
125.97
123.78
121.60
119.41
101.65
101.41
101.14
100.87
77.26
77.00
76.75
35.97
27.59
26.49
Ac
CF3
H
Bn
S
5fh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

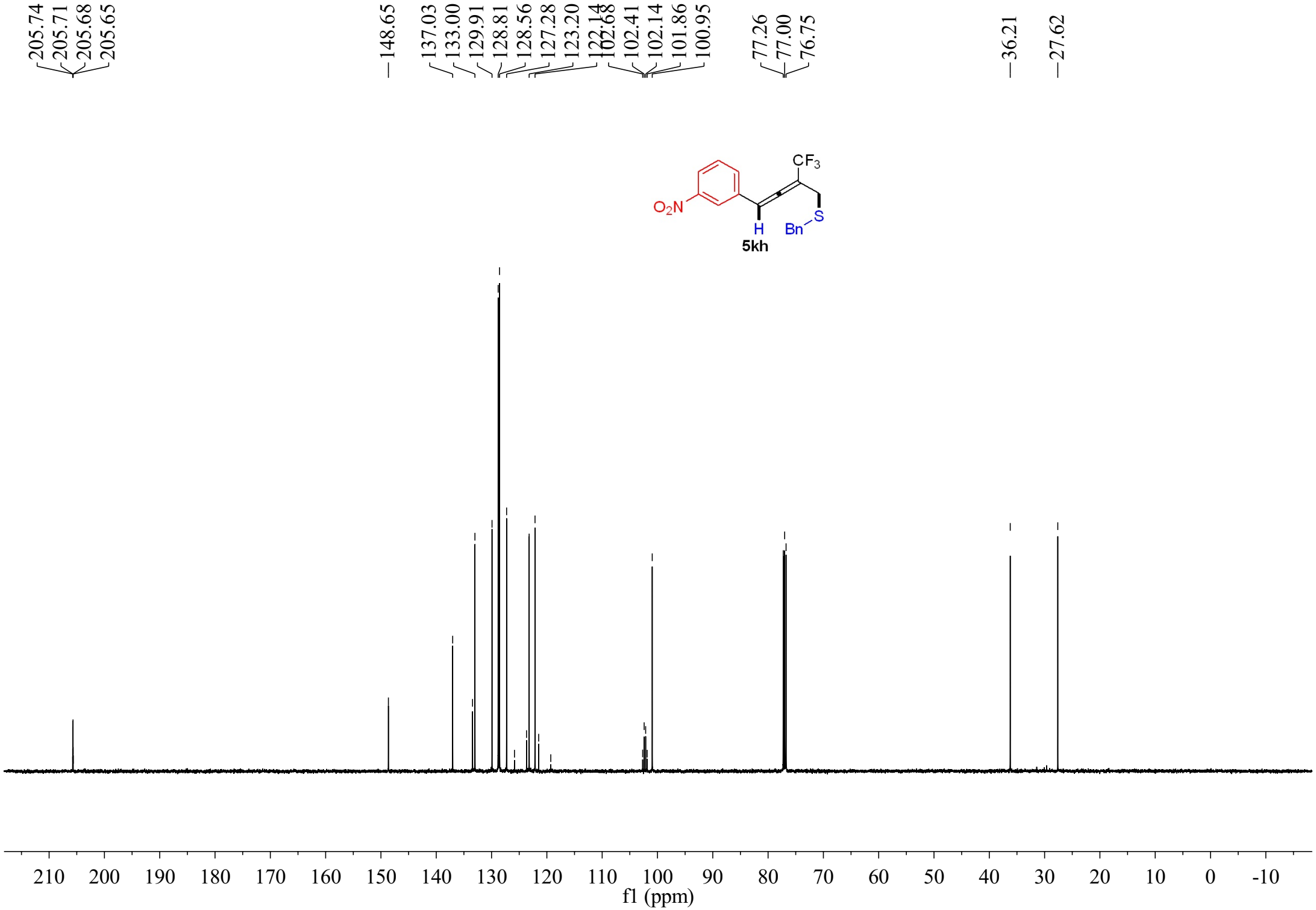

-62.506
Ac
CF3
H
Bn
S
5fh
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-105
f1 (ppm)

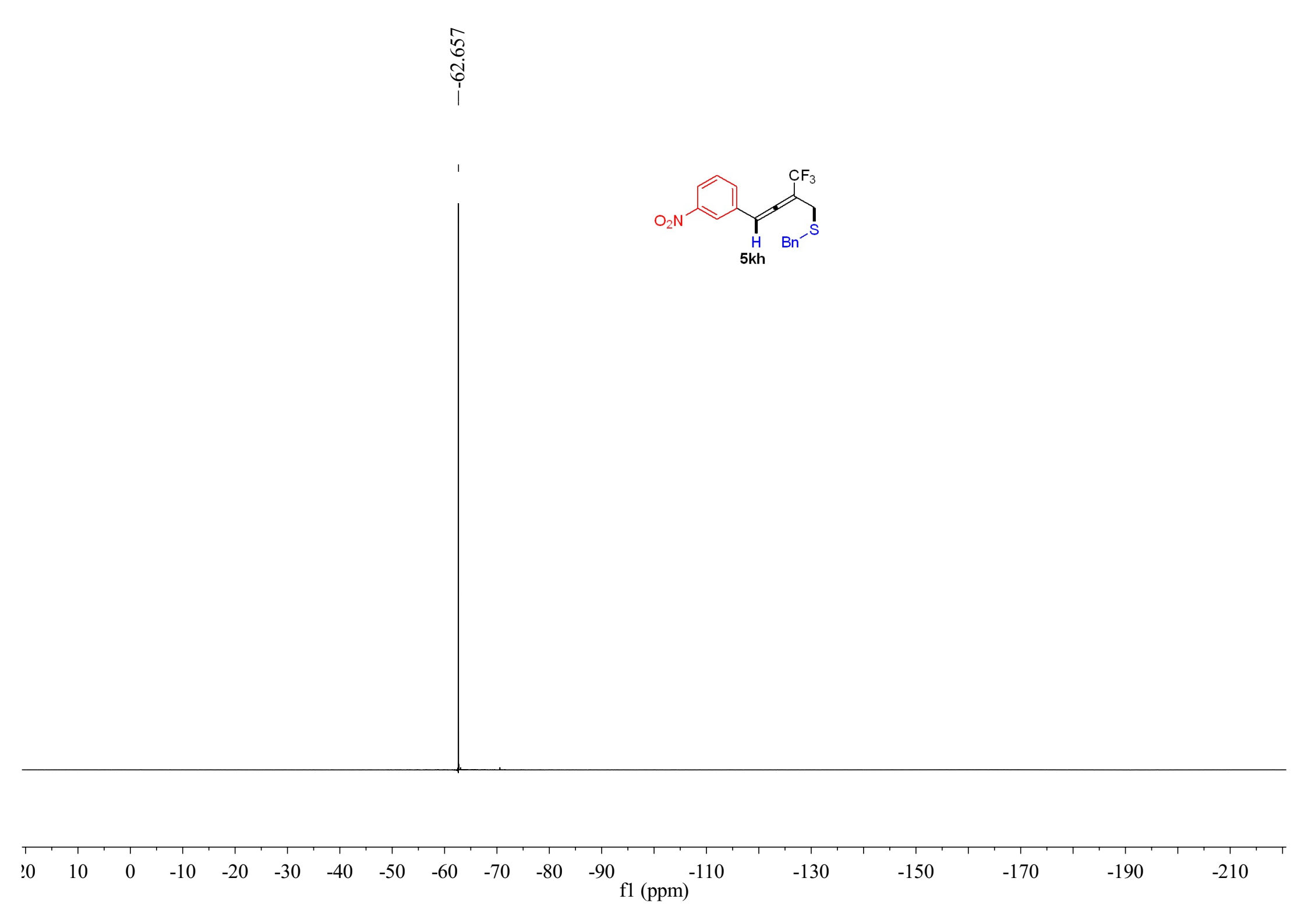

8.237
8.220
7.489
7.472
7.290
7.258
7.243
6.791
6.785
6.780
6.774
3.771
3.744
3.733
3.706
3.309
3.306
O2N
CF3
H
Bn
S
5hh
2.01
2.15
5.30
1.00
2.07
2.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

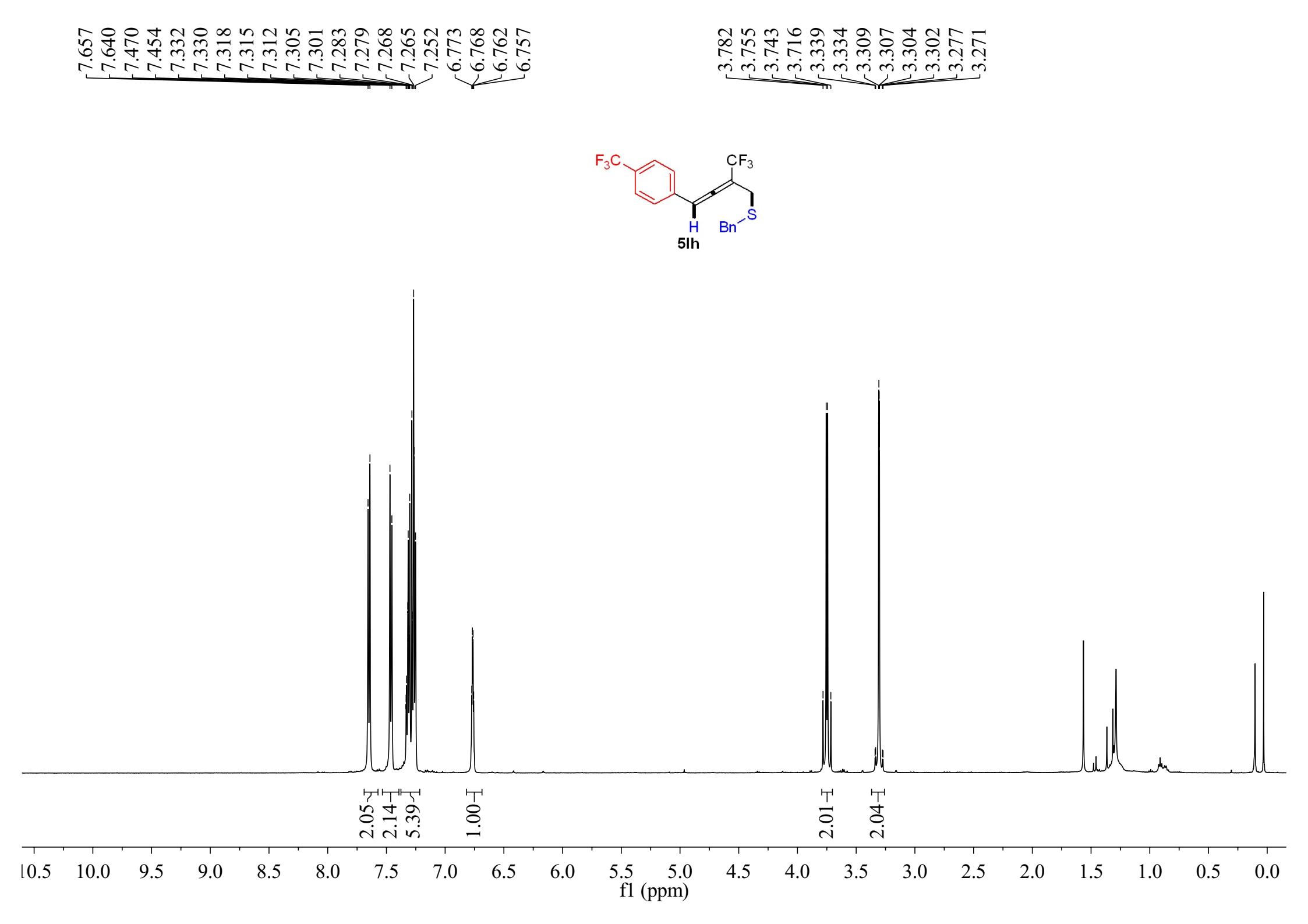

206.54
206.51
206.48
206.45
147.53
138.28
137.00
128.80
128.58
128.09
127.32
124.25
102.59
102.31
102.04
101.77
101.11
77.25
77.00
76.75
36.28
27.57
O2N
CF3
H
Bn
S
5hh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

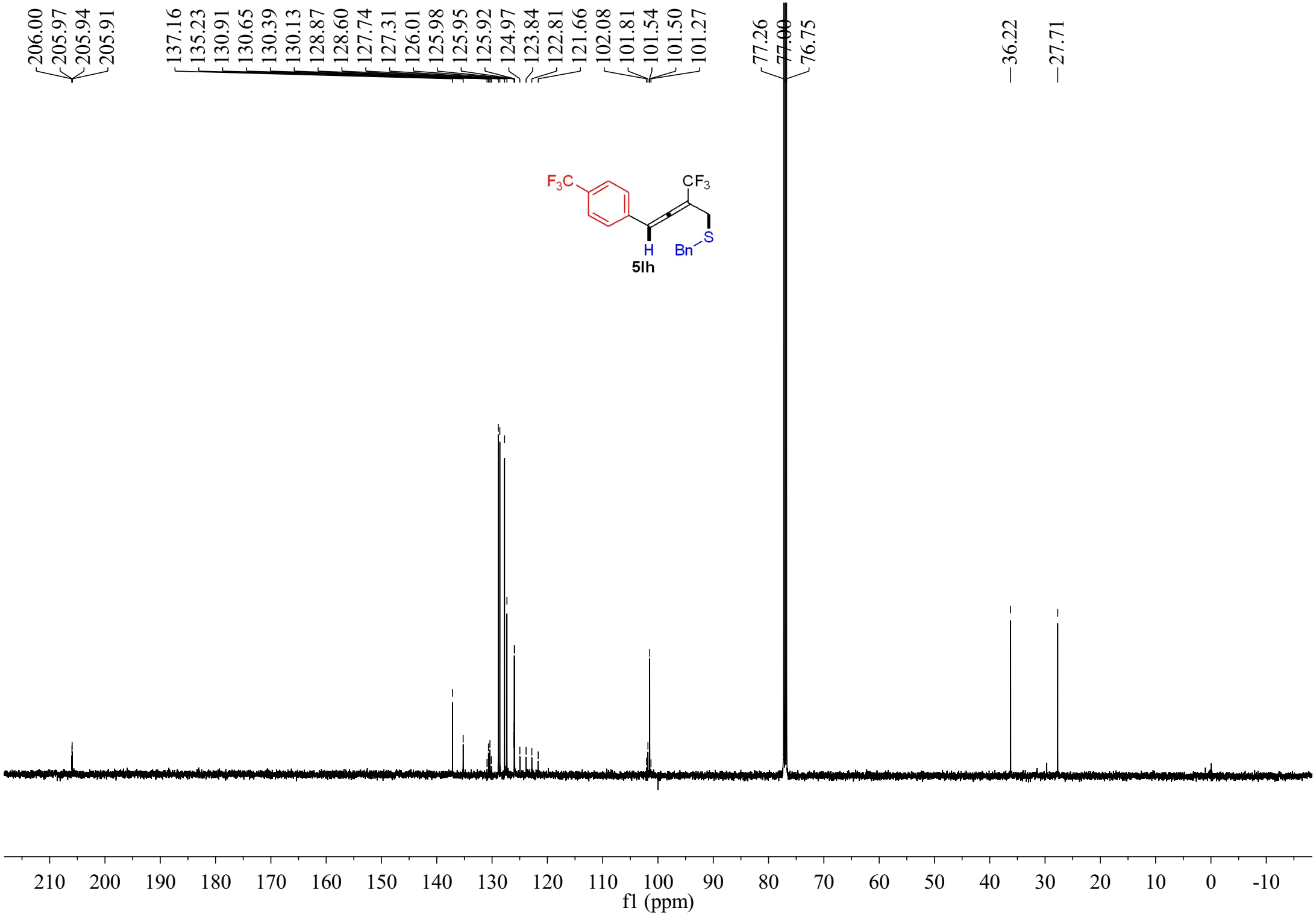

-62.583
O2N
CF3
H
Bn
S
5hh
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

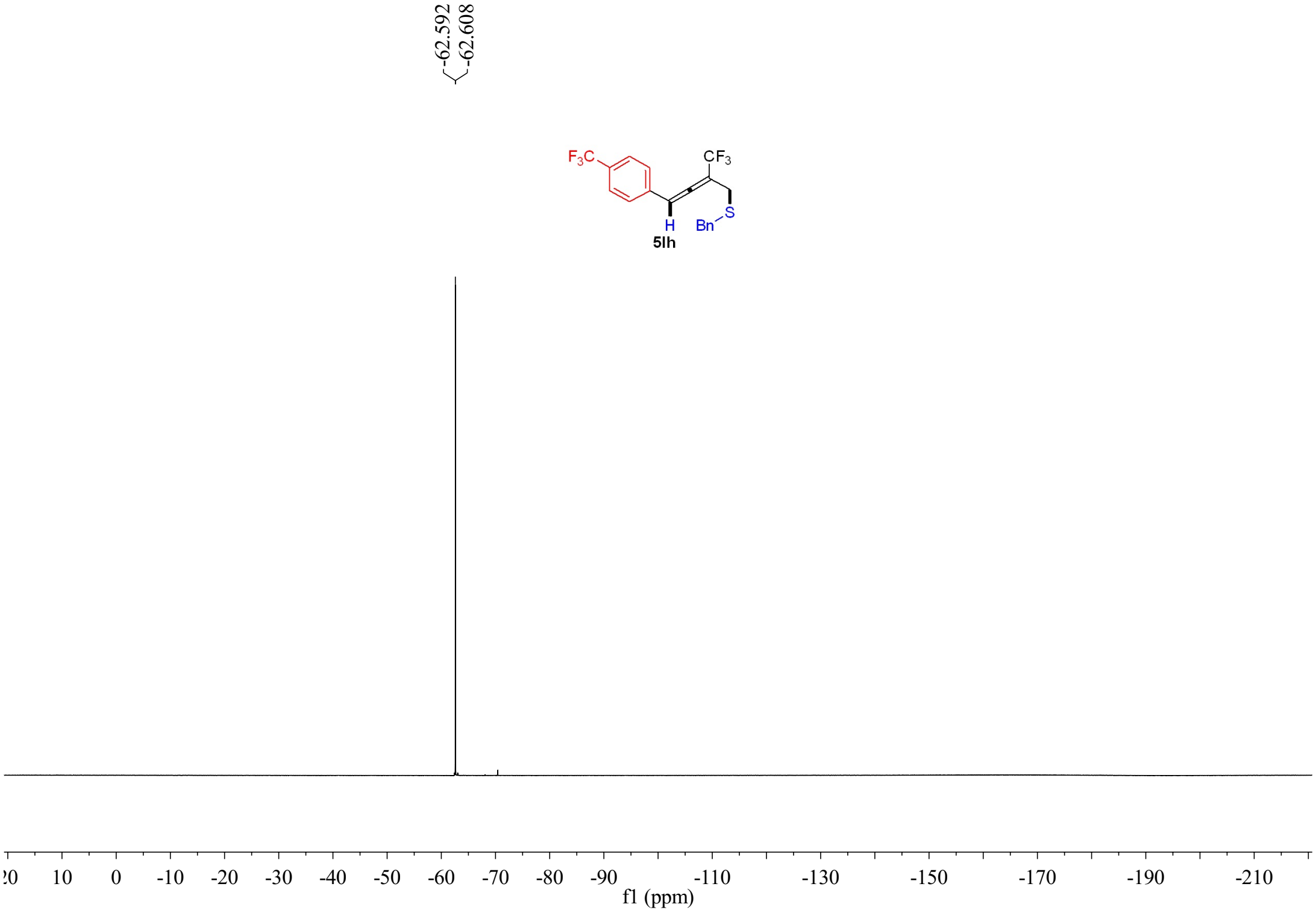

8.171
8.169
8.155
8.153
8.151
8.149
7.306
7.292
7.273
7.260
6.795
6.789
6.784
6.778
3.781
3.754
3.744
3.717
3.318
3.314
3.309
CF3
O2N
H
Bn
S
5kh
1.98
1.00
1.03
5.22
1.00
2.12
2.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

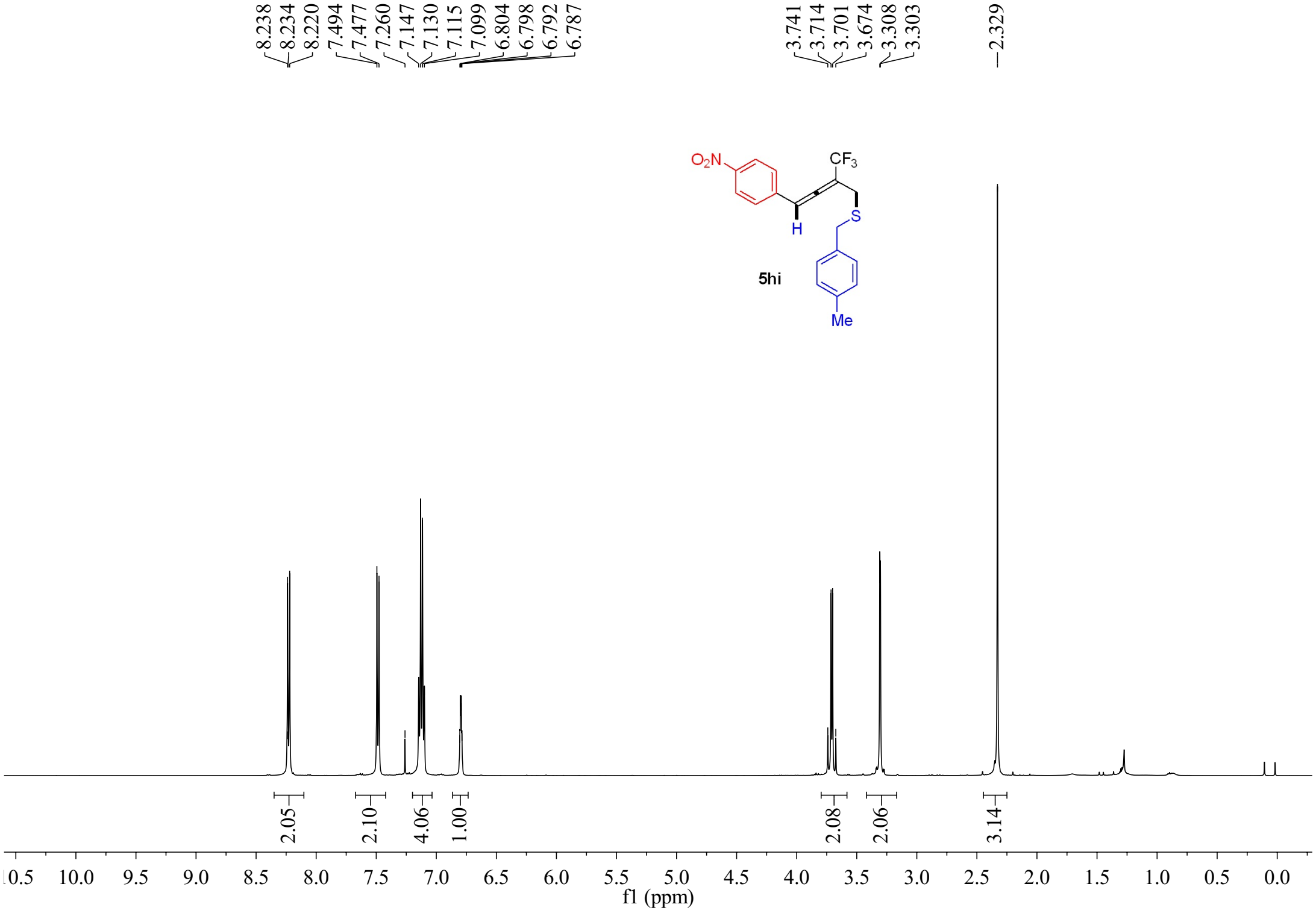

205.74
205.71
205.68
205.65
148.65
137.03
133.00
129.91
128.81
128.56
127.28
123.20
122.14
102.68
102.41
102.14
101.86
100.95
77.26
77.00
76.75
36.21
27.62
CF3
O2N
H
Bn
S
5kh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-62.657
CF3
O2N
H
Bn
S
5kh
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


7.657
7.640
7.470
7.454
7.332
7.330
7.318
7.315
7.312
7.305
7.301
7.283
7.279
7.268
7.265
7.252
6.773
6.768
6.762
6.757
3.782
3.755
3.743
3.716
3.339
3.334
3.309
3.307
3.304
3.302
3.277
3.271
F3C
CF3
H
Bn
S
5Ih
2.05
2.14
5.39
1.00
2.01
2.04
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
f1 (ppm)


206.00
205.97
205.94
205.91
137.16
135.23
130.91
130.65
130.39
130.13
128.87
128.60
127.74
127.31
126.01
125.98
125.95
125.92
124.97
123.84
122.81
121.66
102.08
101.81
101.54
101.50
101.27
77.26
77.00
76.75
36.22
27.71
F3C
CF3
H
Bn
S
5Ih
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)


-62.592
-62.608
F3C
CF3
H
Bn
S
5Ih
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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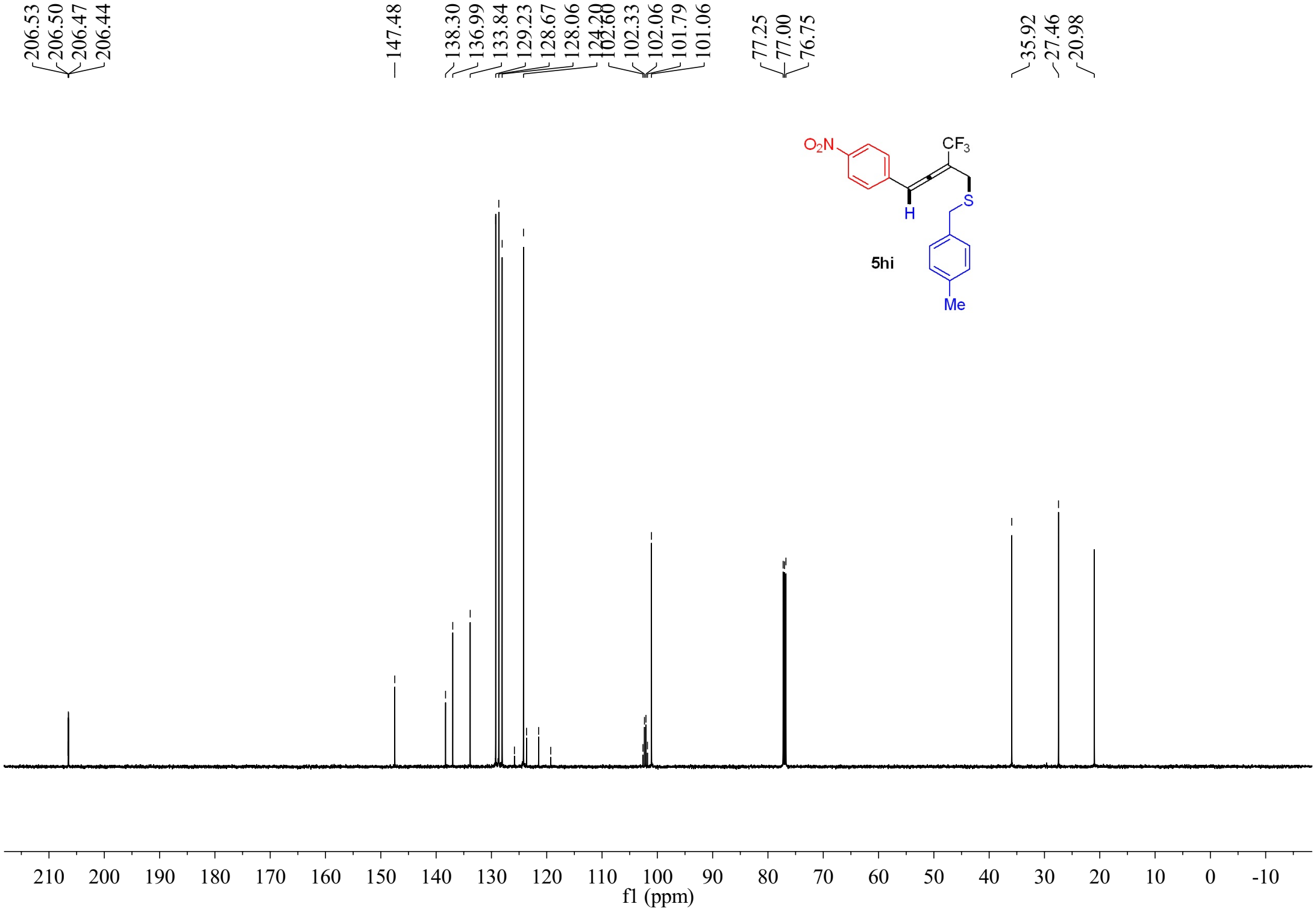
8.234
8.220
7.494
7.477
7.260
7.147
7.130
7.115
7.099
6.804
6.798
6.792
6.787
3.741
3.714
3.701
3.674
3.308
3.303
2.329
O2N
CF3
H
S
Me
5hi
2.05
2.10
4.06
1.00
2.08
2.06
3.14
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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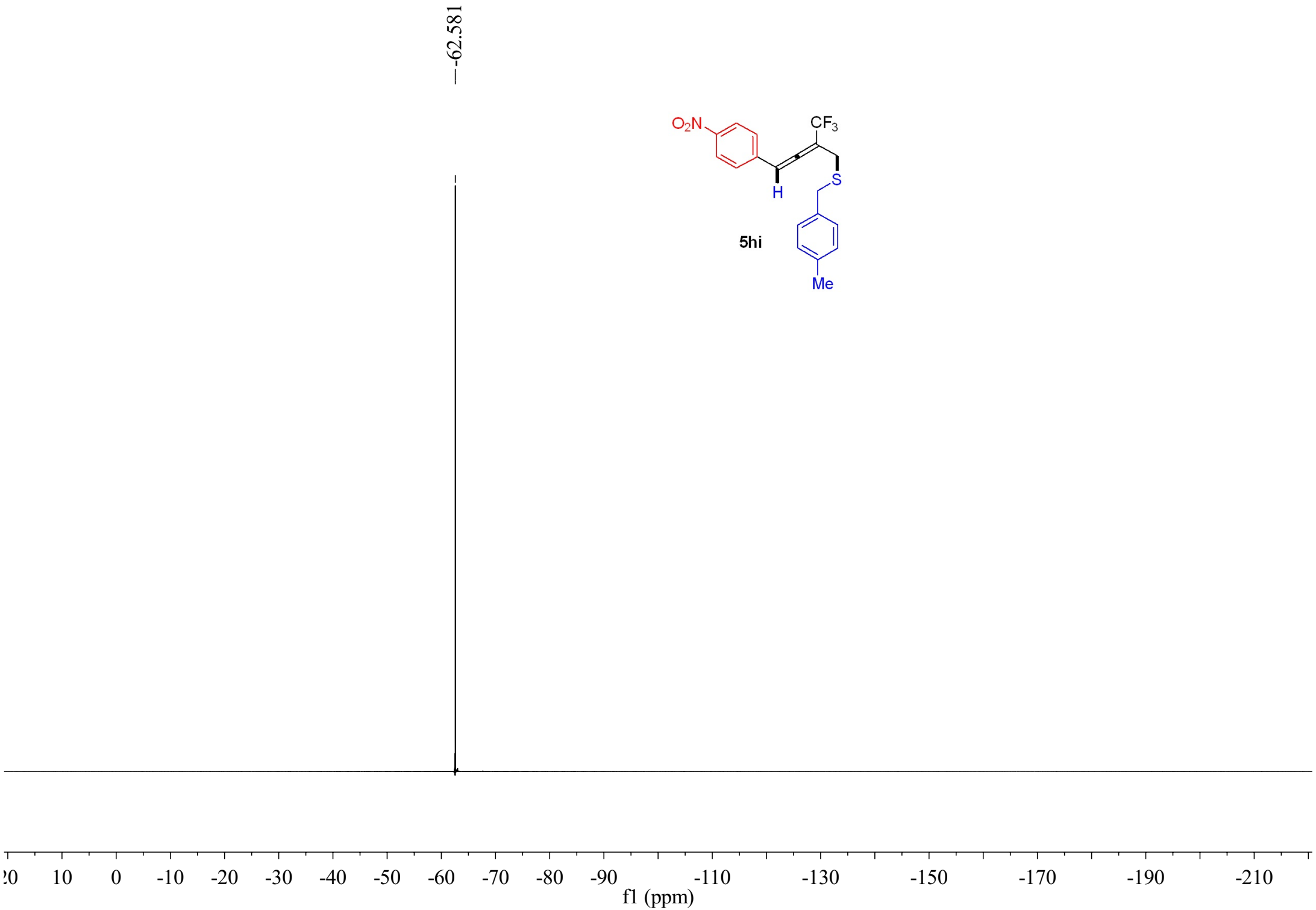
206.47
206.44
147.48
138.30
136.99
133.84
129.23
128.67
128.06
124.20
102.60
102.33
102.06
101.79
101.06
77.25
77.00
76.75
35.92
27.46
20.98
O2N
CF3
H
S
Me
5hi
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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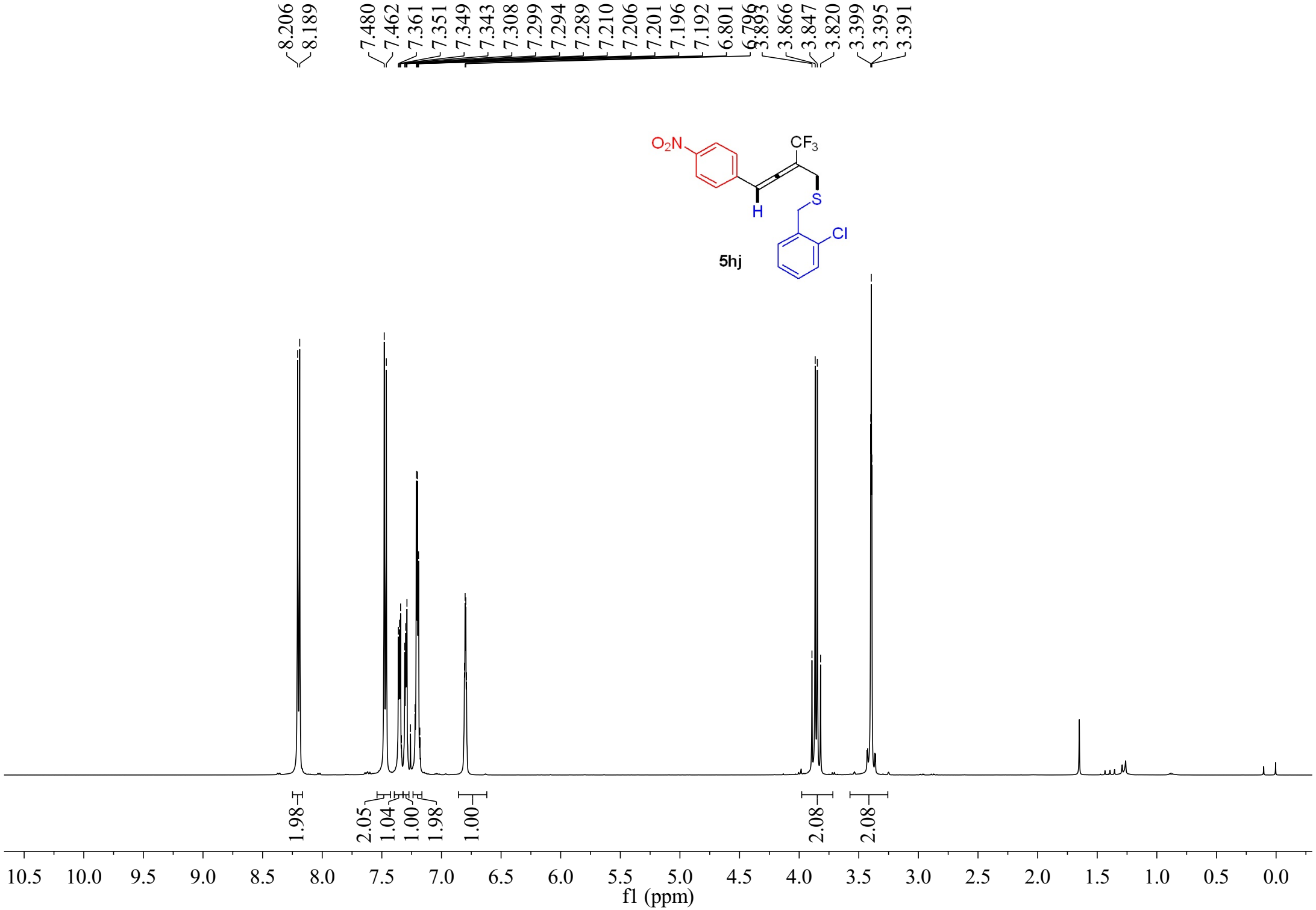
CF3
H
S
Me
5hi
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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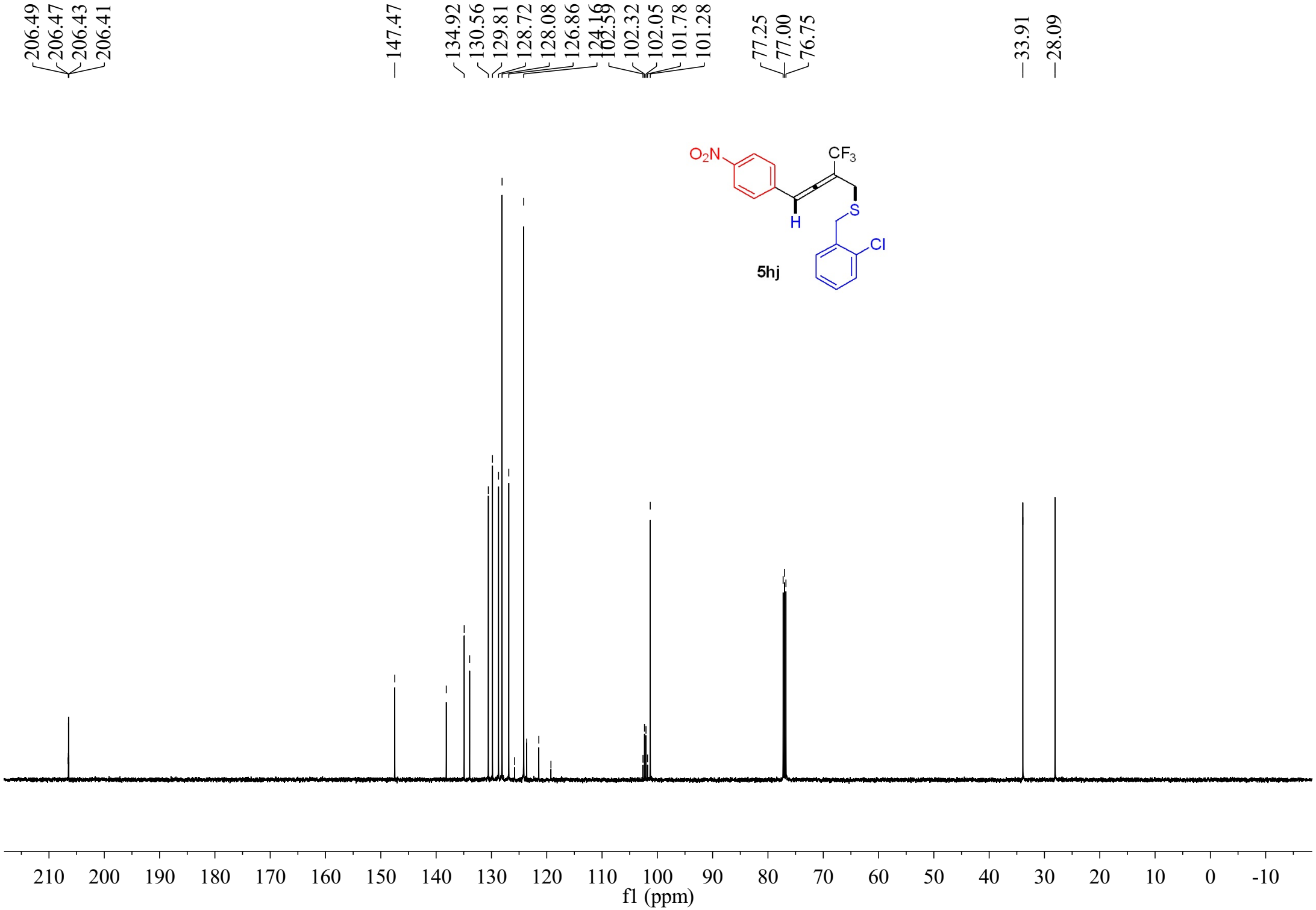
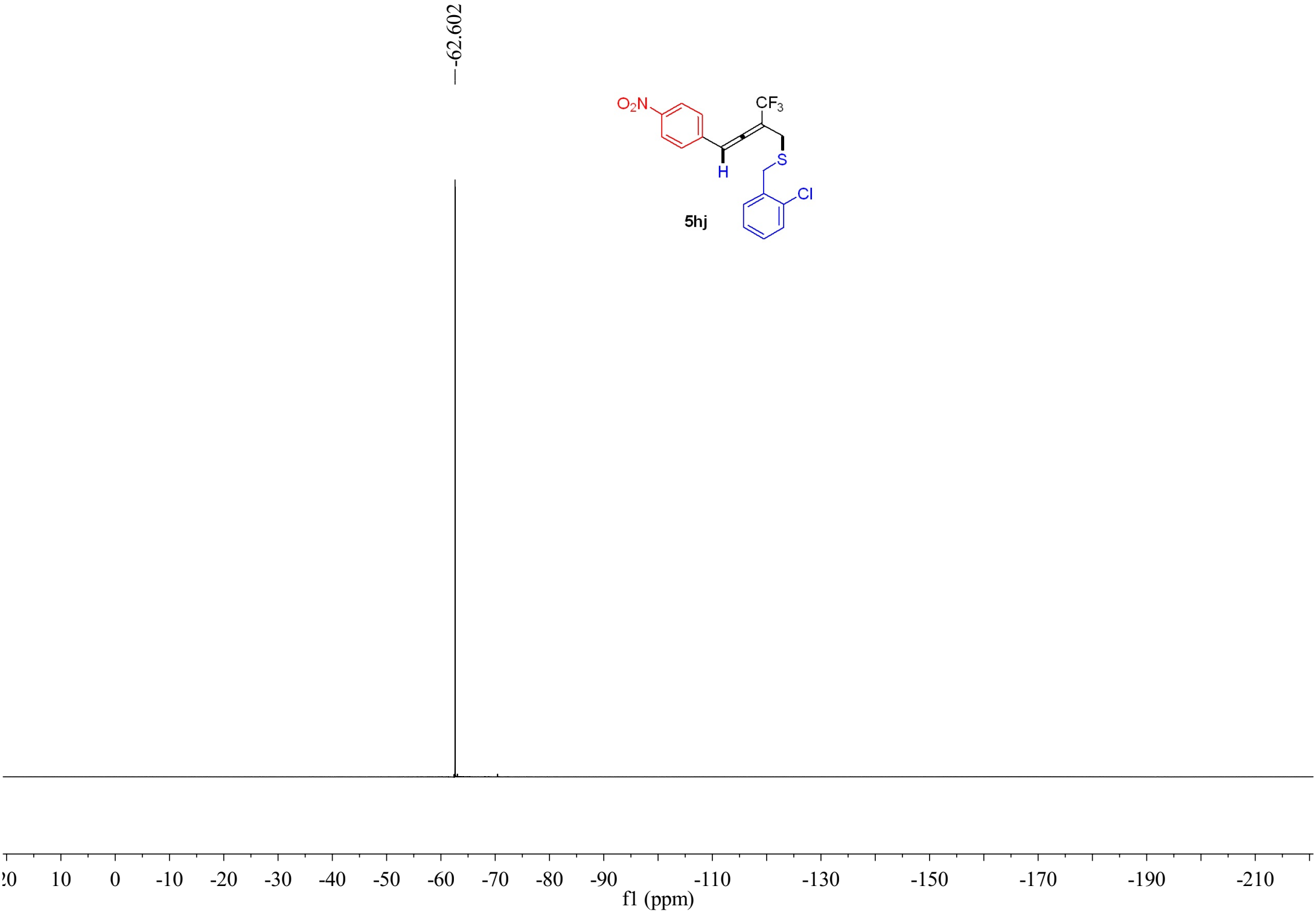
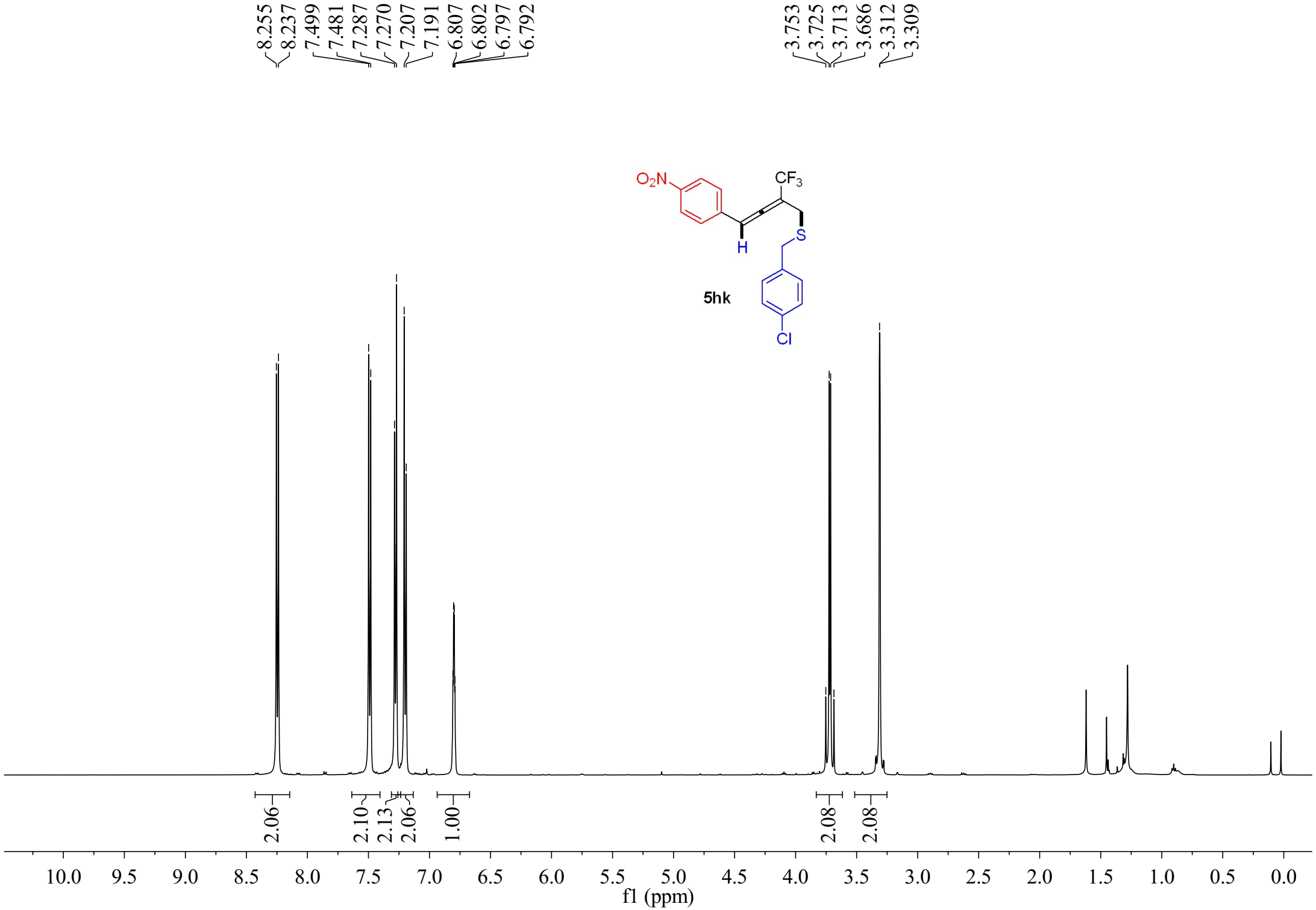
8.189
7.480
7.462
7.361
7.351
7.349
7.343
7.308
7.299
7.294
7.289
7.210
7.206
7.201
7.196
7.192
6.801
6.796
3.893
3.866
3.847
3.820
3.399
3.395
3.391
O2N
CF3
H
S
Cl
5hj
1.98
2.05
1.04
1.00
1.98
1.00
2.08
2.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


206.49
206.47
206.43
206.41
147.47
134.92
130.56
129.81
128.72
128.08
126.86
124.16
102.59
102.32
102.05
101.78
101.28
77.25
77.00
76.75
33.91
28.09
O2N
CF3
H
S
Cl
5hj
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)


-62.602
O2N
CF3
H
S
Cl
5hj
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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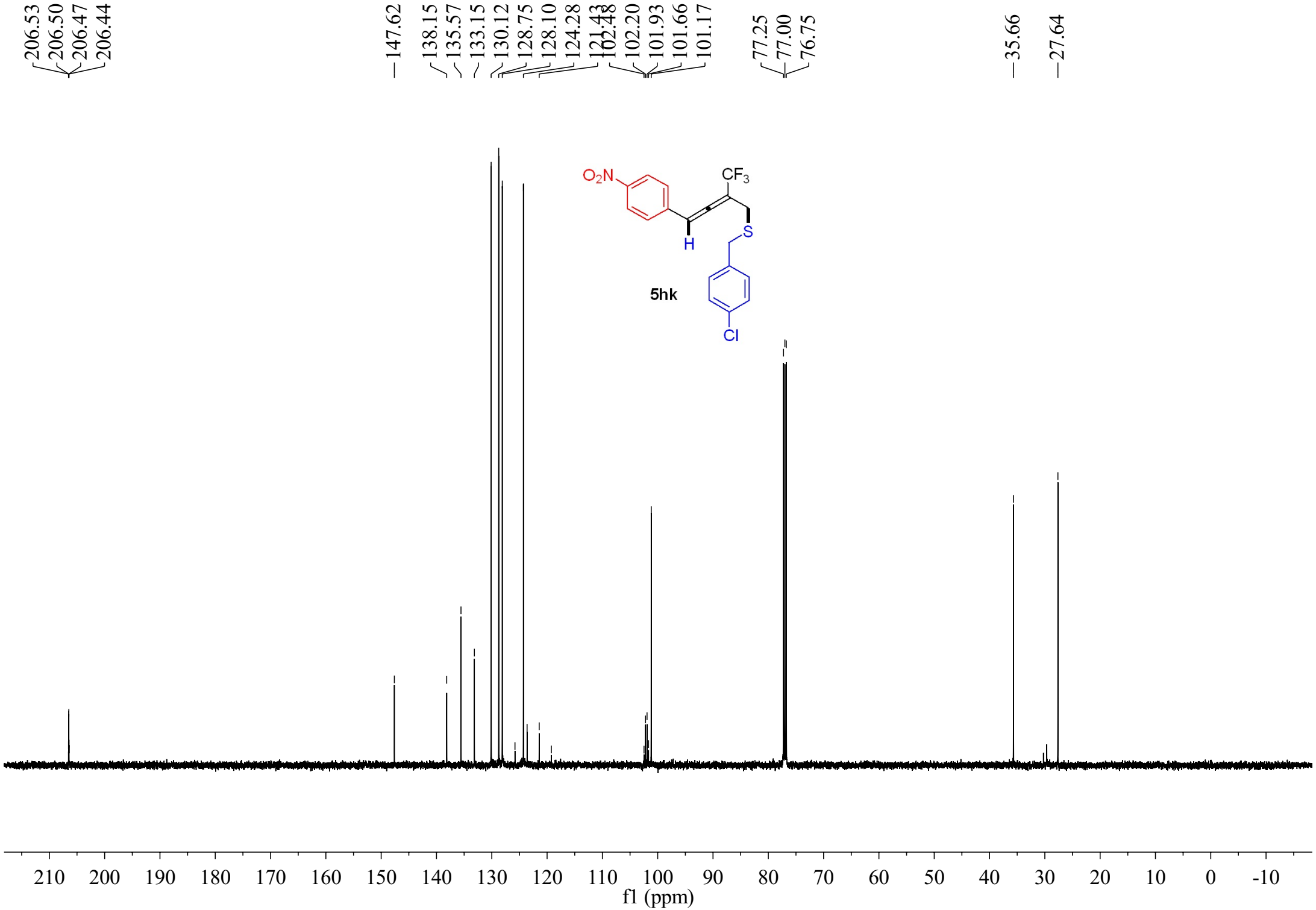
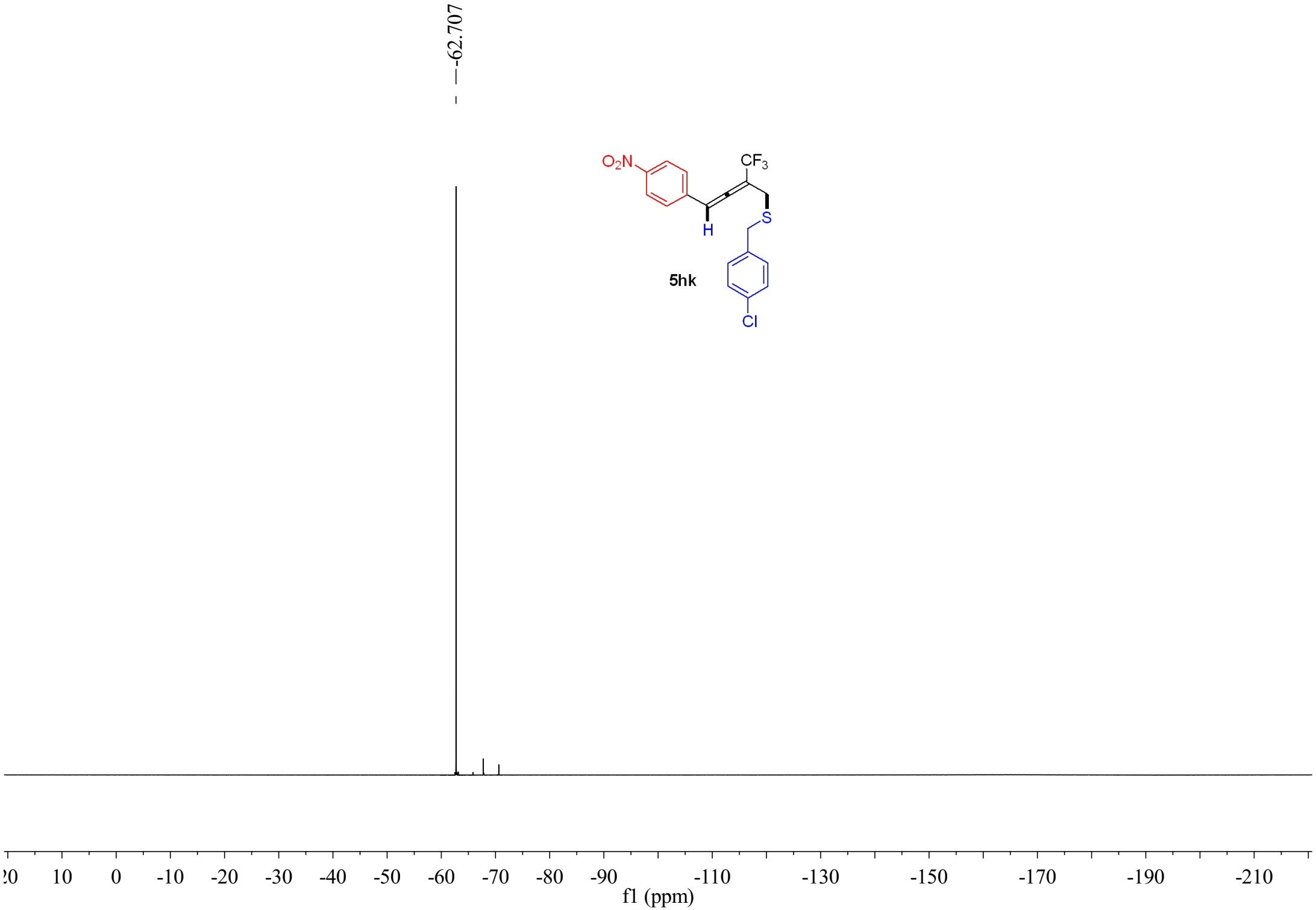
8.237
7.499
7.481
7.287
7.270
7.207
7.191
6.807
6.802
6.797
6.792
3.753
3.725
3.713
3.686
3.312
3.309
O2N
CF3
H
S
Cl
5hk
2.06
2.10
2.13
2.06
1.00
2.08
2.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


206.53
206.50
206.47
206.44
147.62
138.15
135.57
133.15
130.12
128.75
128.10
124.28
121.43
102.48
102.20
101.93
101.66
101.17
77.25
77.00
76.75
35.66
27.64
O2N
CF3
H
S
Cl
5hk
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)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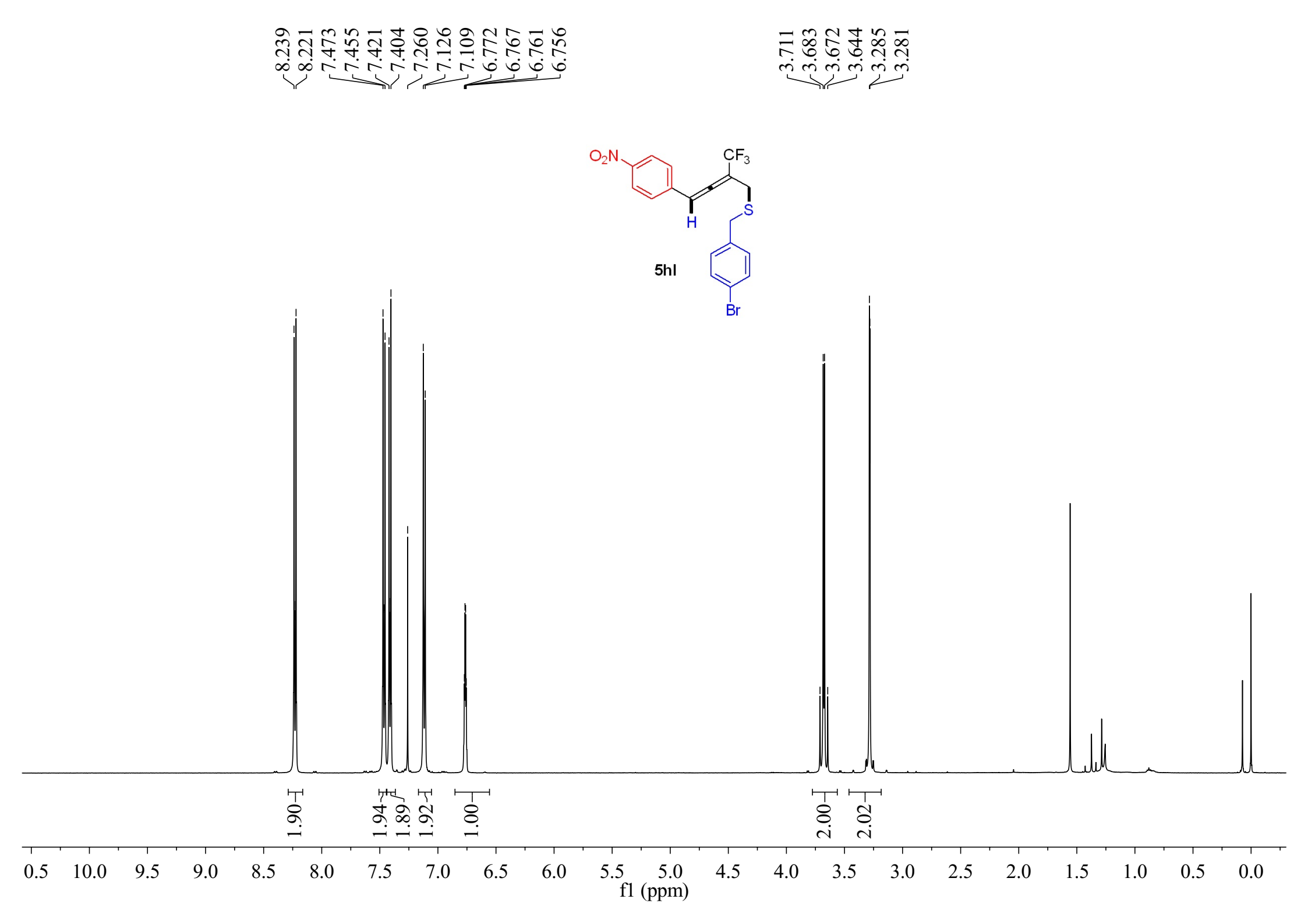
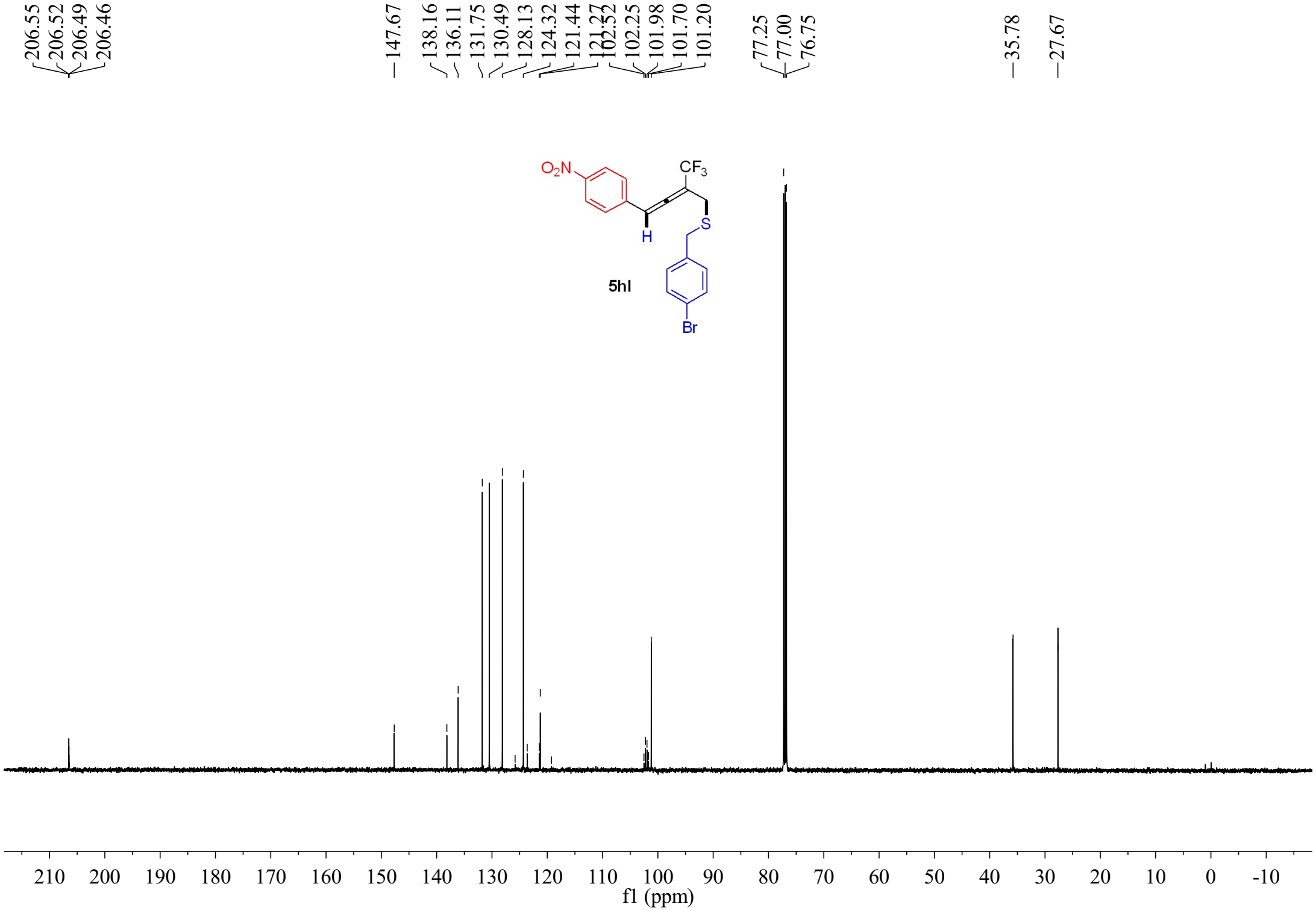
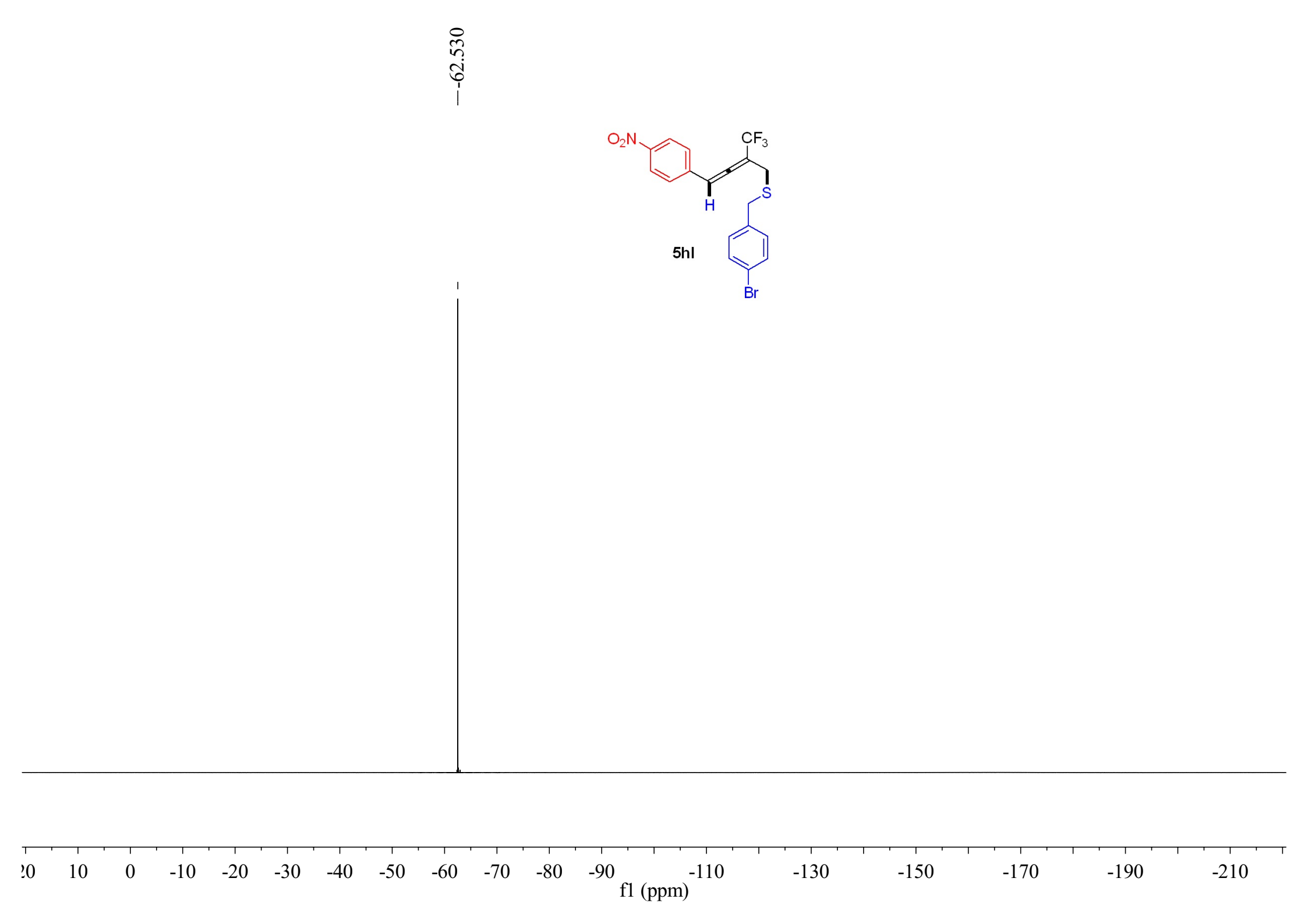
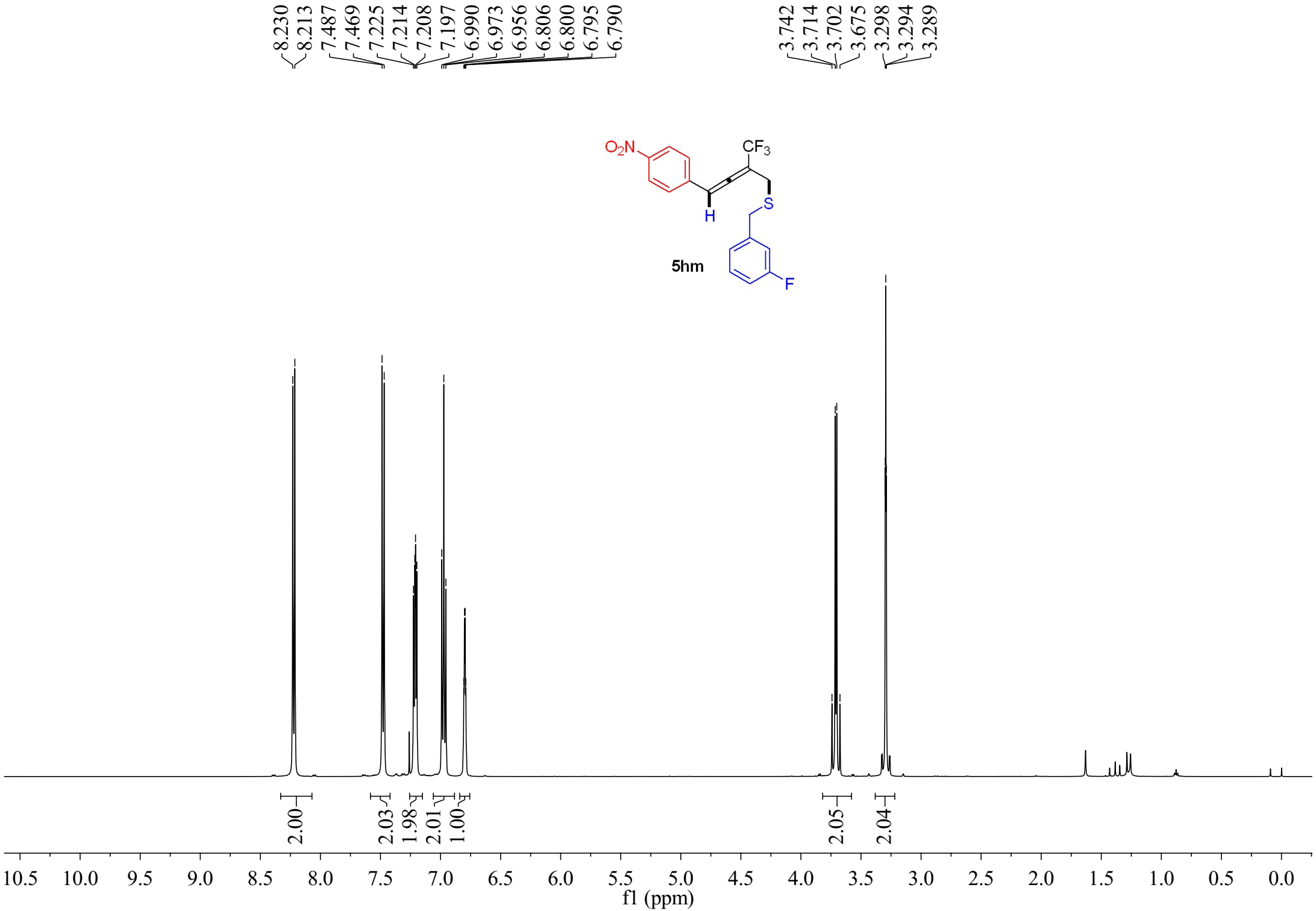
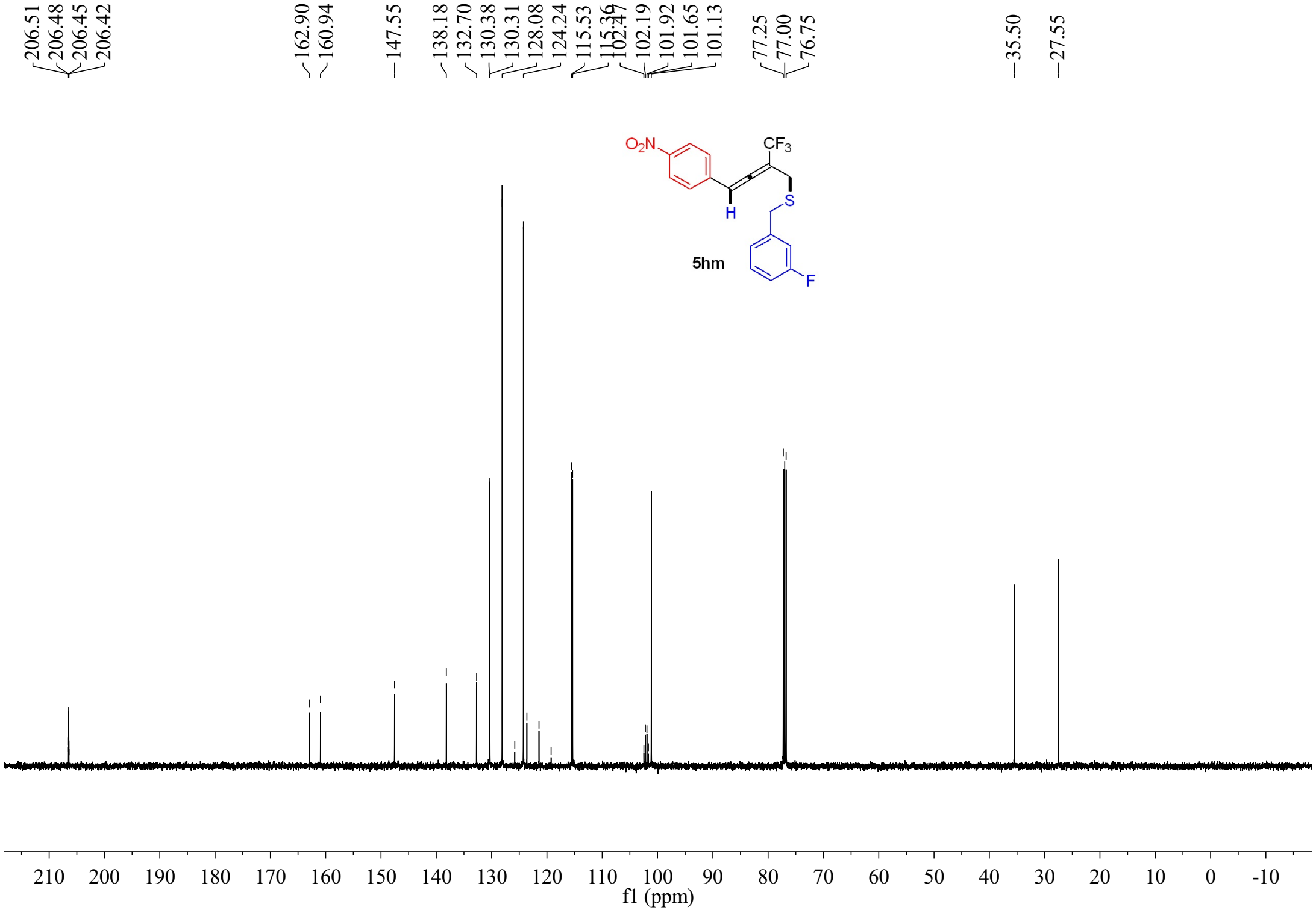
O2N
CF3
H
S
Cl
5hk
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

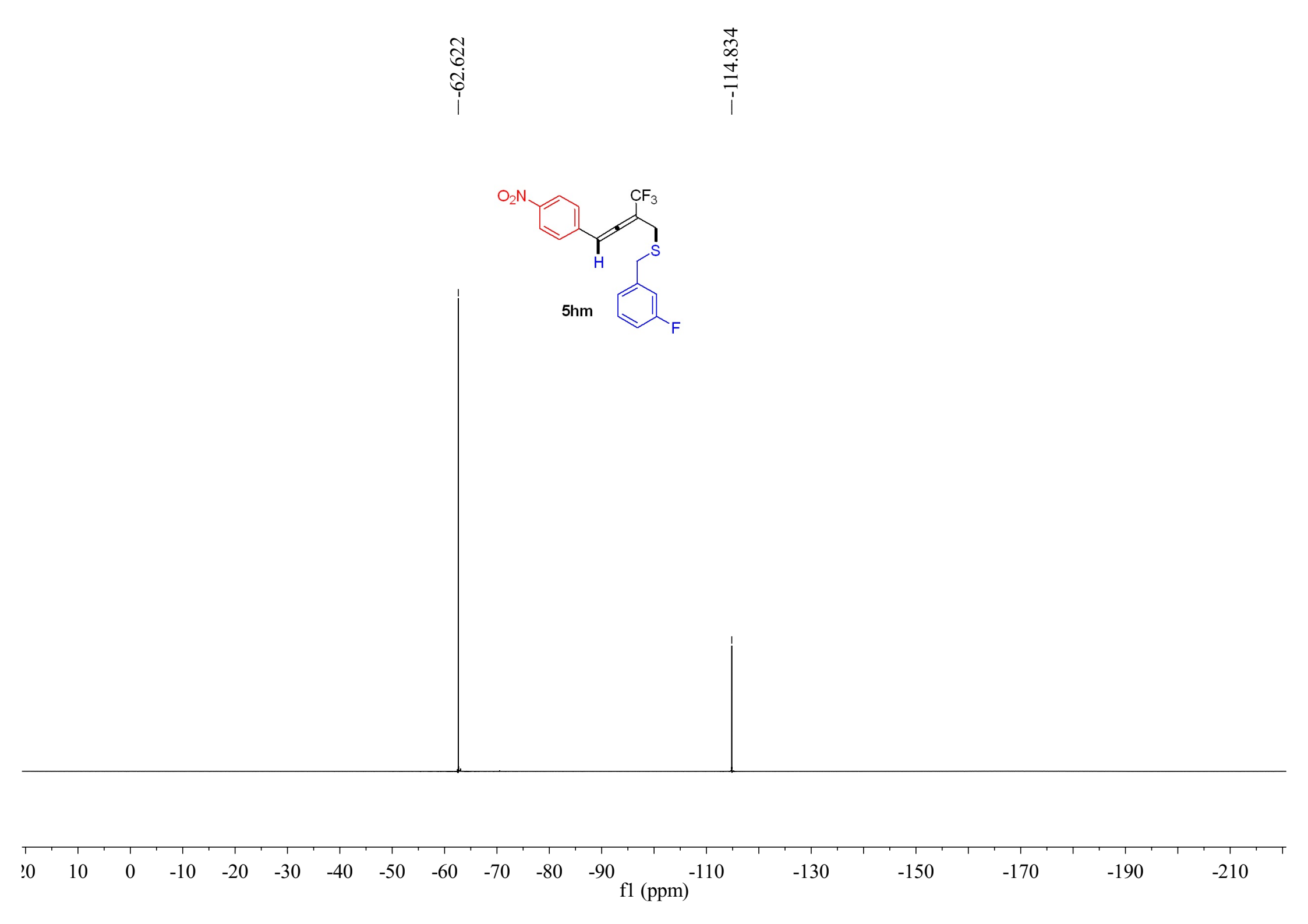

8.239
8.221
7.473
7.455
7.421
7.404
7.260
7.126
7.109
6.772
6.767
6.761
6.756
3.711
3.683
3.672
3.644
3.285
3.281
O2N
CF3
H
S
Br
5hl
1.90
1.94
1.89
1.92
1.00
2.00
2.02
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

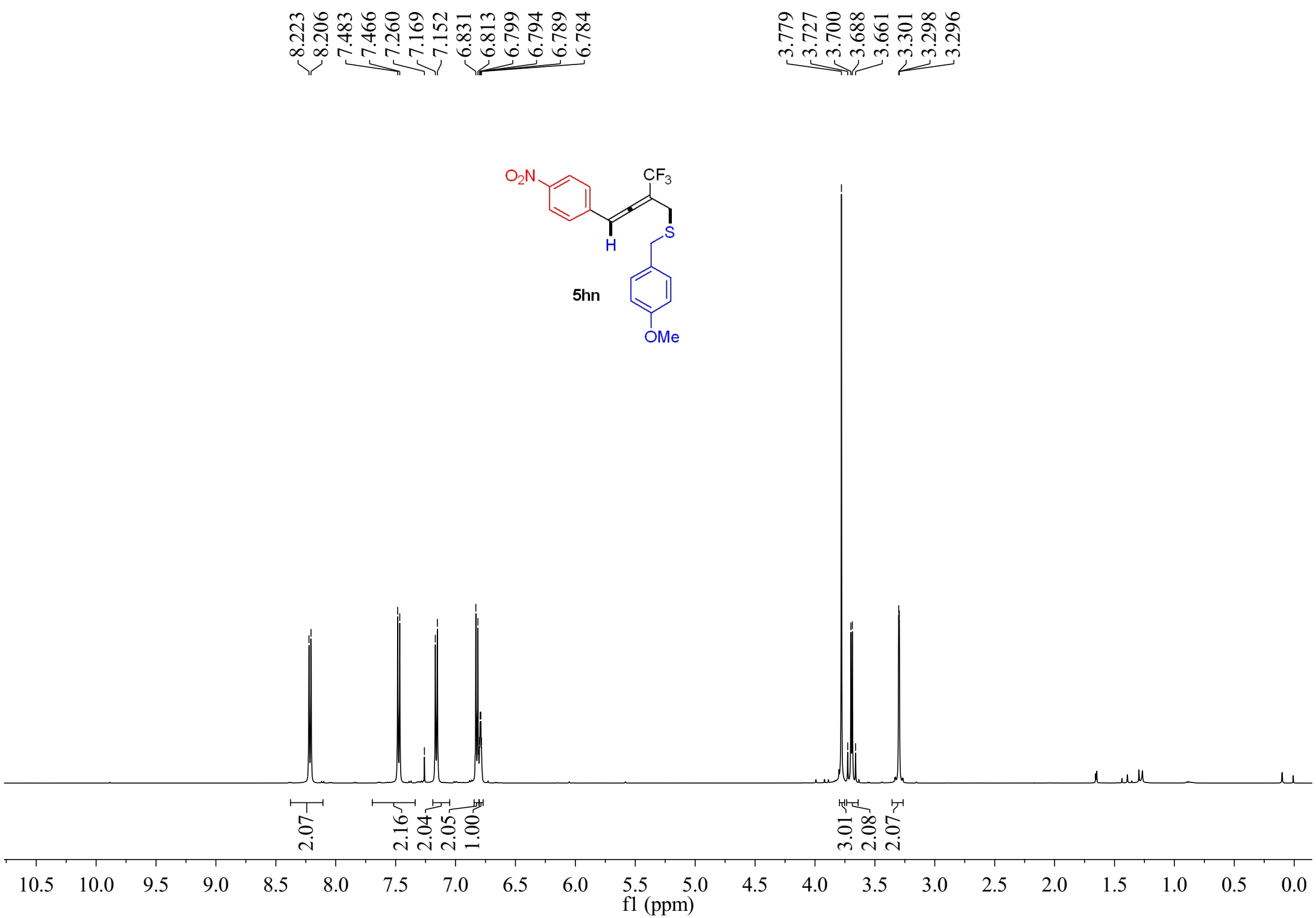

206.55
206.52
206.49
206.46
147.67
138.16
136.11
131.75
130.49
128.13
124.32
121.44
121.27
102.52
102.25
101.98
101.70
101.20
77.25
77.00
76.75
35.78
27.67
O2N
CF3
H
S
Br
5hl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

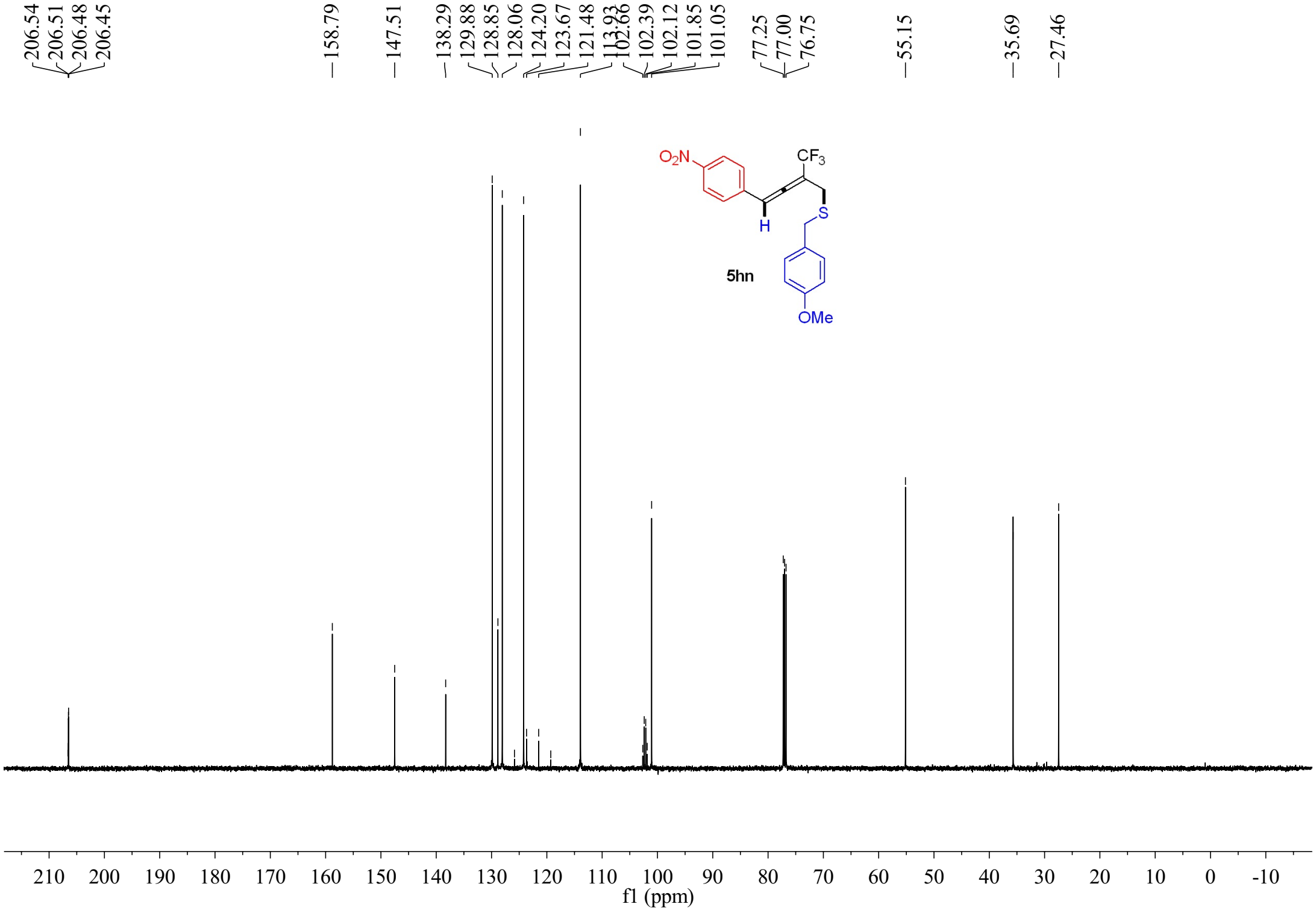

-62.530
O2N
CF3
H
S
Br
5hl
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

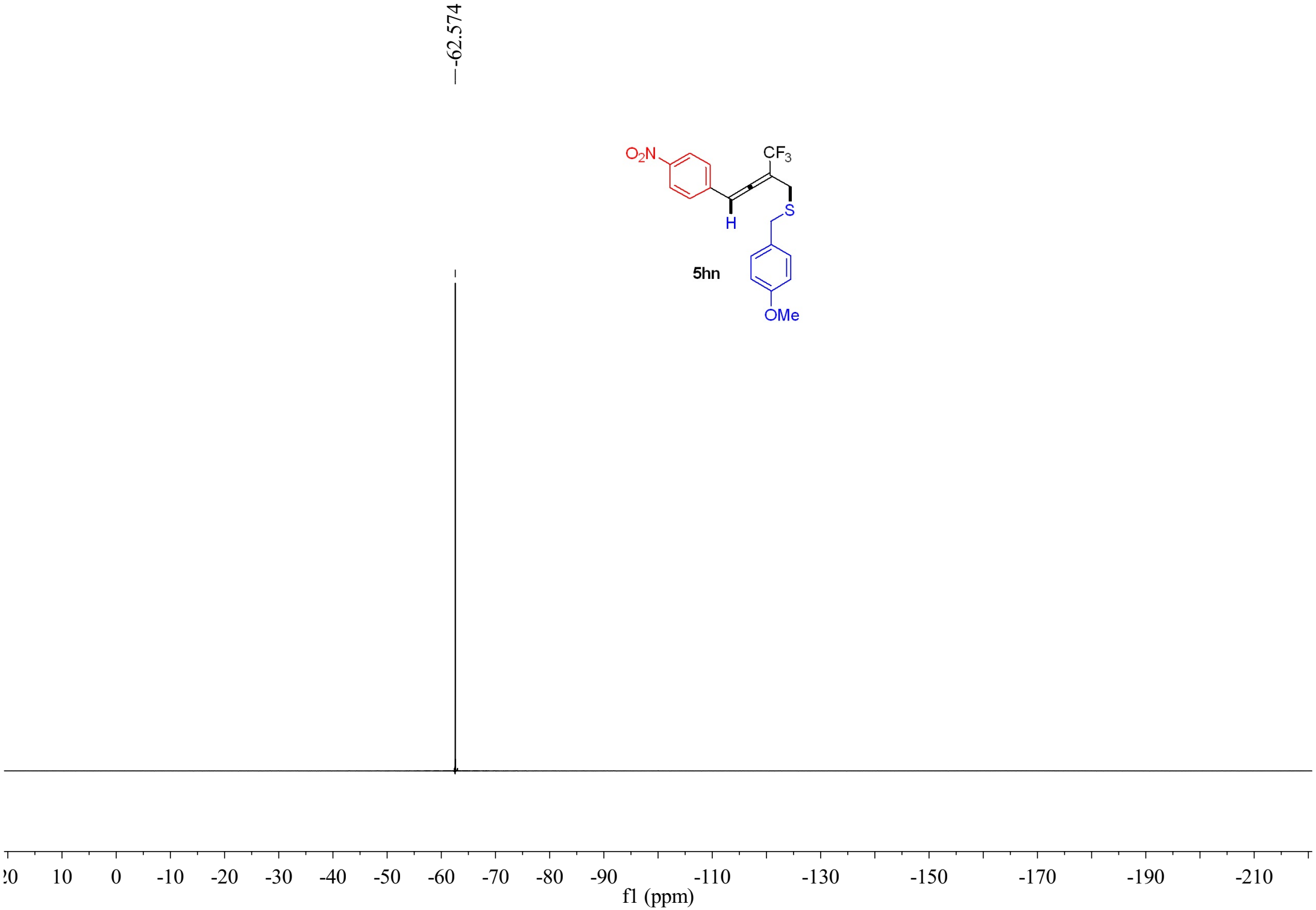

8.230
8.213
7.487
7.469
7.225
7.214
7.208
7.197
6.990
6.973
6.956
6.806
6.800
6.795
6.790
3.742
3.714
3.702
3.675
3.298
3.294
3.289
O2N
CF3
H
S
F
5hm
2.00
2.03
1.98
2.01
1.00
2.05
2.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

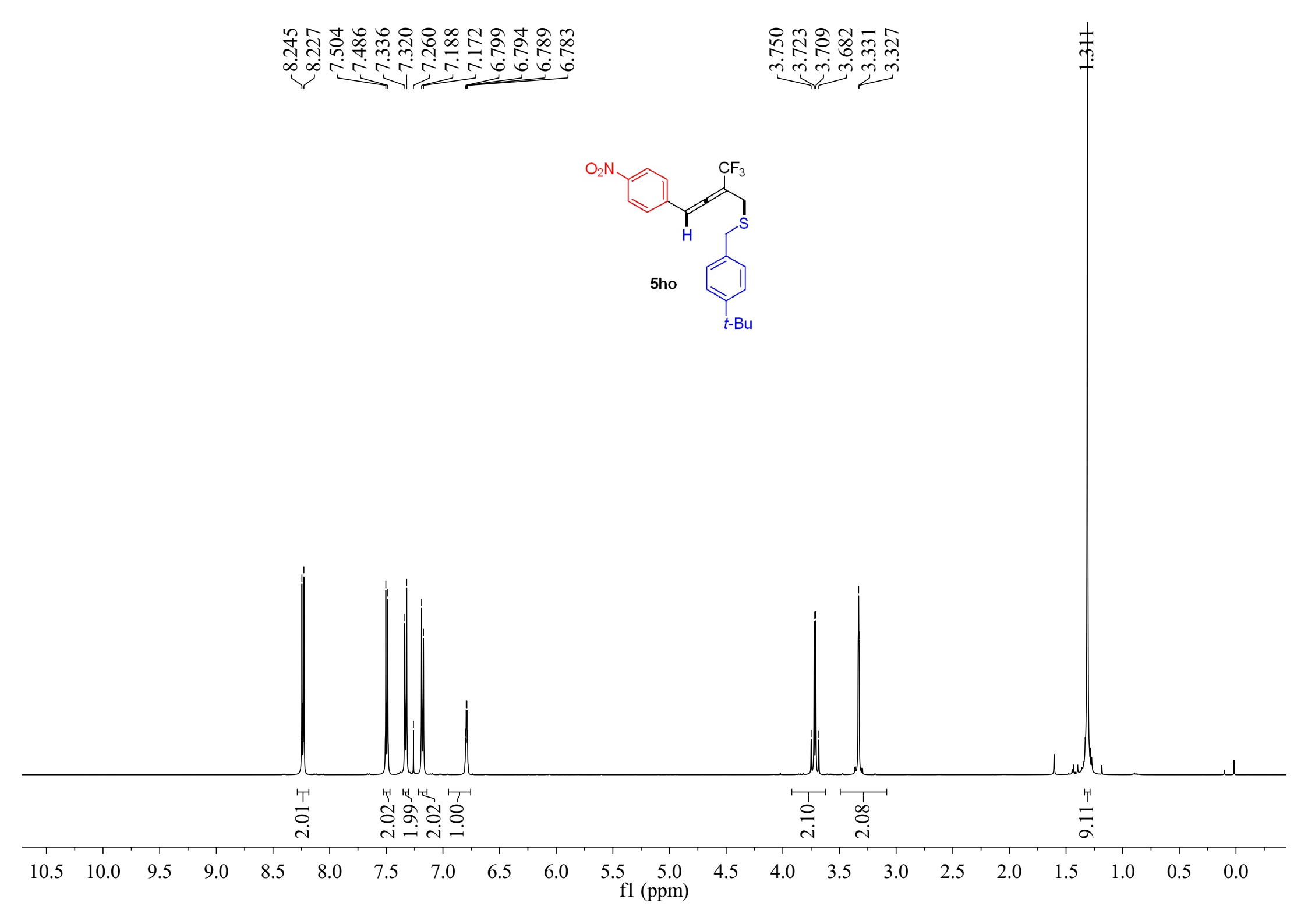

206.51
206.48
206.45
206.42
162.90
160.94
147.55
138.18
132.70
130.38
130.31
128.08
124.24
115.53
115.36
102.47
102.19
101.92
101.65
101.13
77.25
77.00
76.75
35.50
27.55
O2N
CF3
H
S
F
5hm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

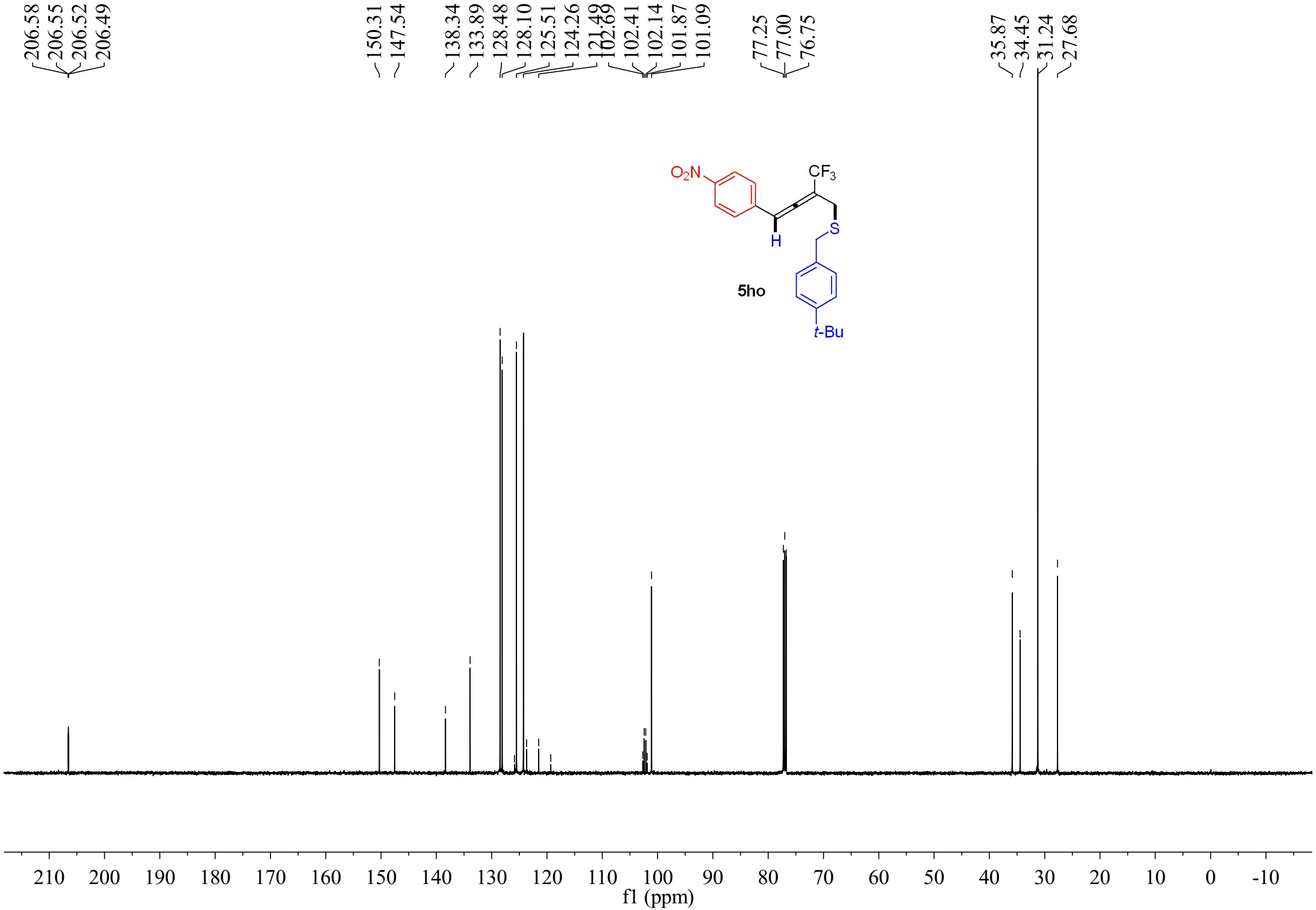

-62.622
-114.834
O2N
CF3
H
S
F
5hm
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

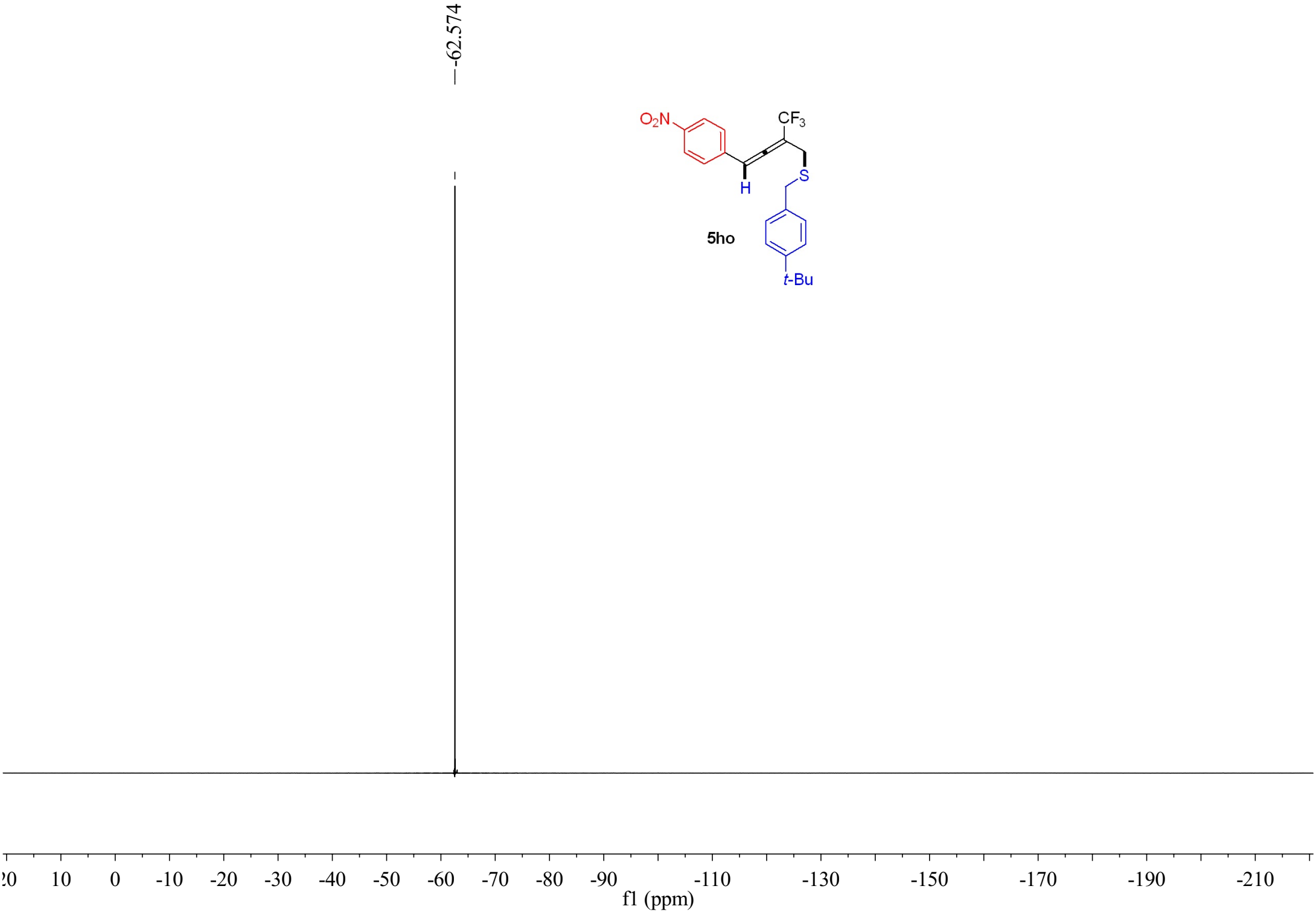

8.223
8.206
7.483
7.466
7.260
7.169
7.152
6.831
6.813
6.799
6.794
6.789
6.784
3.779
3.727
3.700
3.688
3.661
3.301
3.298
3.296
O2N
CF3
H
S
OMe
5hn
2.07
2.16
2.04
2.05
1.00
3.01
2.08
2.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

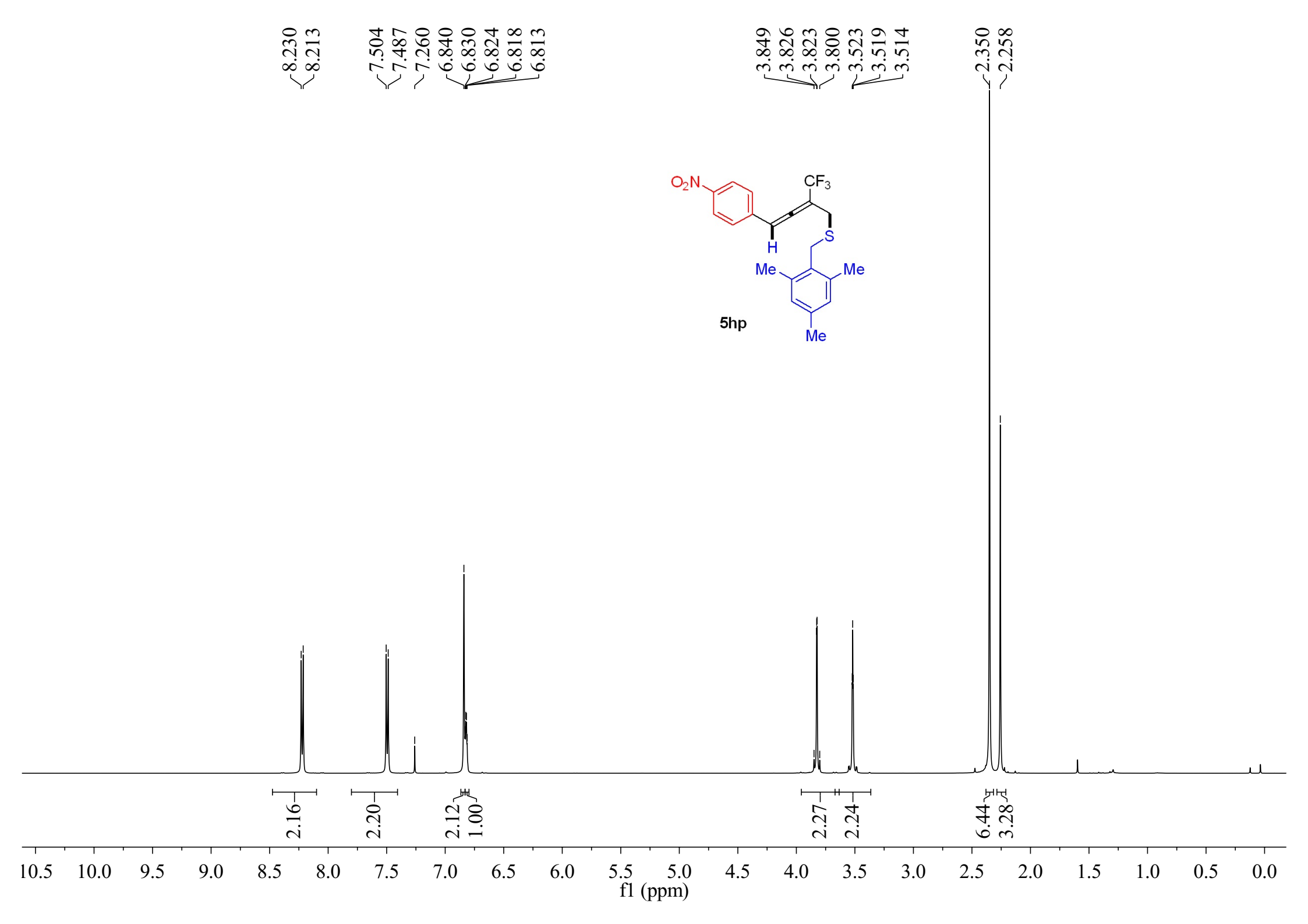

206.54
206.51
206.48
206.45
158.79
147.51
138.29
129.88
128.85
128.06
124.20
123.67
121.48
113.93
102.66
102.39
102.12
101.85
101.05
77.25
77.00
76.75
55.15
35.69
27.46
O2N
CF3
H
S
OMe
5hn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

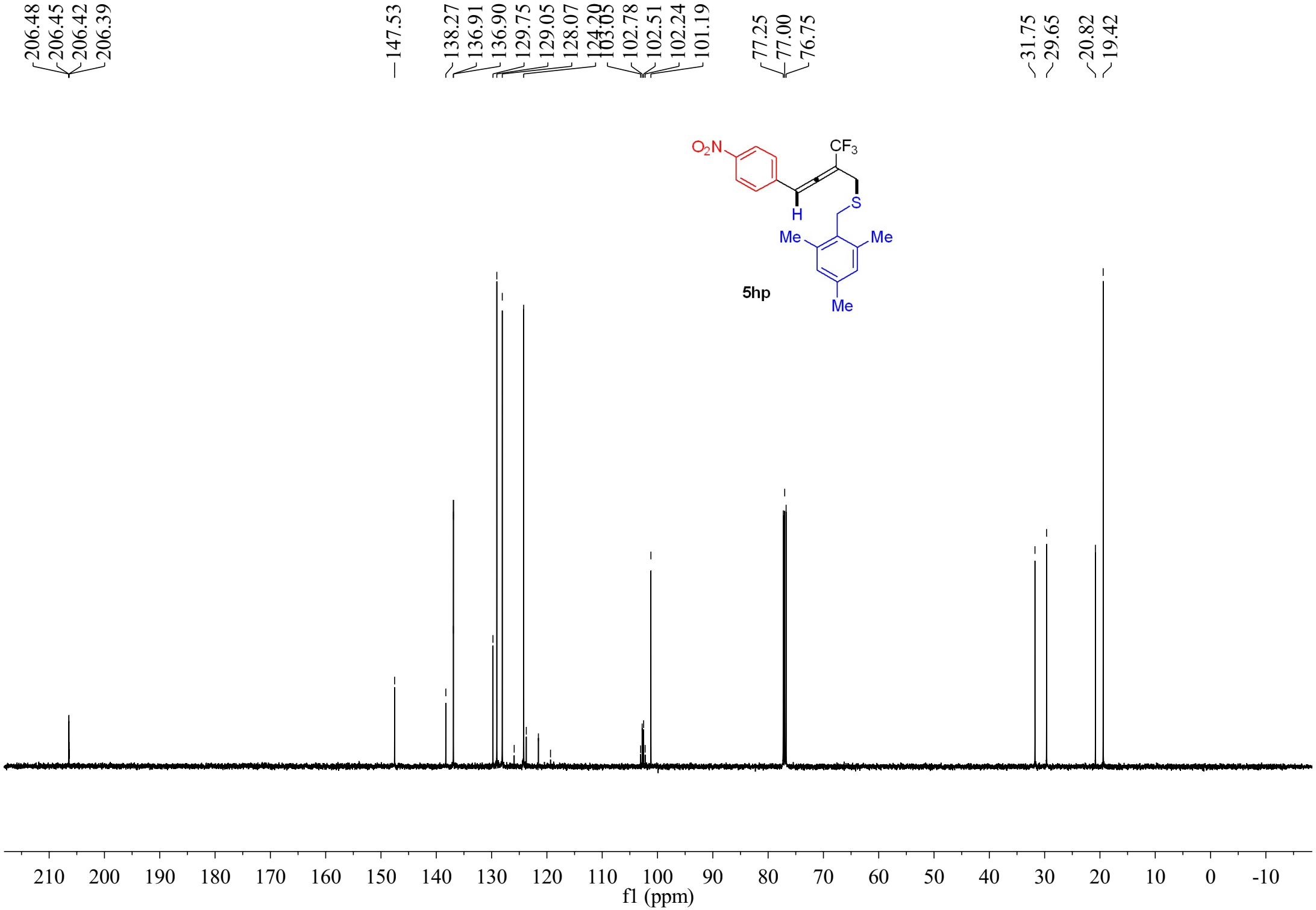

-62.574
O2N
CF3
H
S
OMe
5hn
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

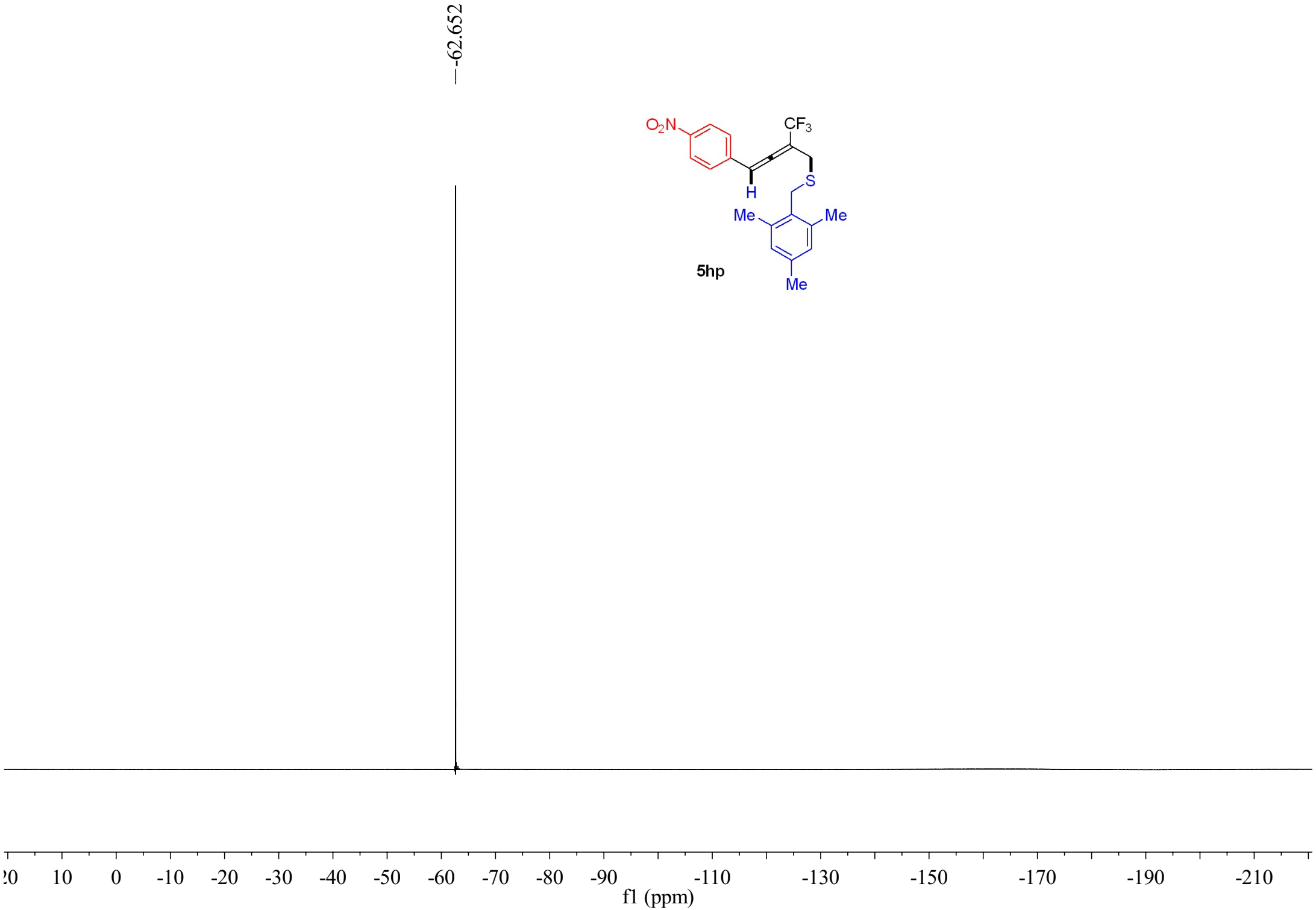

8.245
8.227
7.504
7.486
7.336
7.320
7.260
7.188
7.172
6.799
6.794
6.789
6.783
3.750
3.723
3.709
3.682
3.331
3.327
1.311
O2N
CF3
H
S
5ho
t-Bu
2.01
2.02
1.99
2.02
1.00
2.10
2.08
9.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

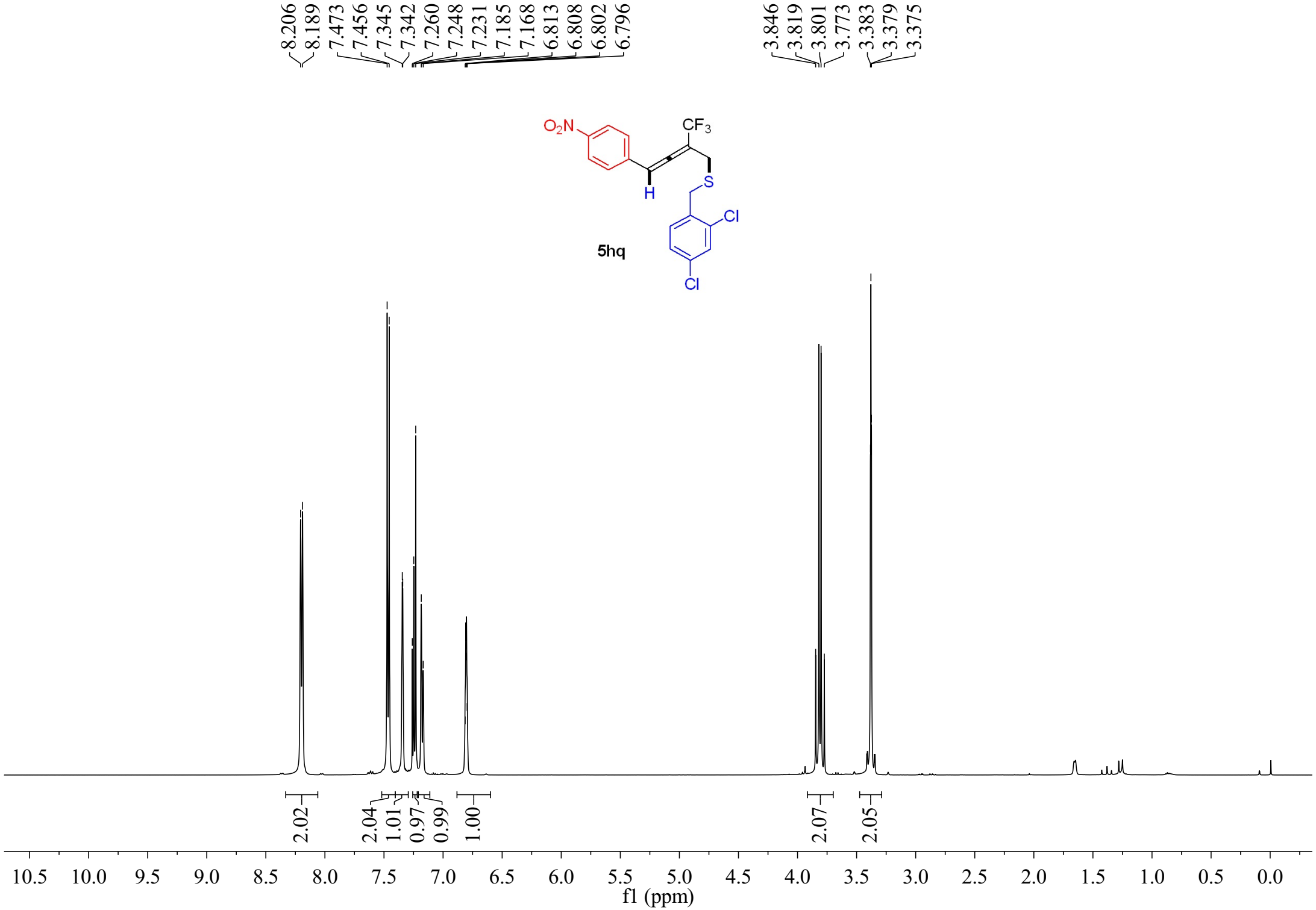

206.58
206.55
206.52
206.49
150.31
147.54
138.34
133.89
128.48
128.10
125.51
124.26
121.49
102.69
102.41
102.14
101.87
101.09
77.25
77.00
76.75
35.87
34.45
31.24
27.68
O2N
CF3
H
S
5ho
t-Bu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

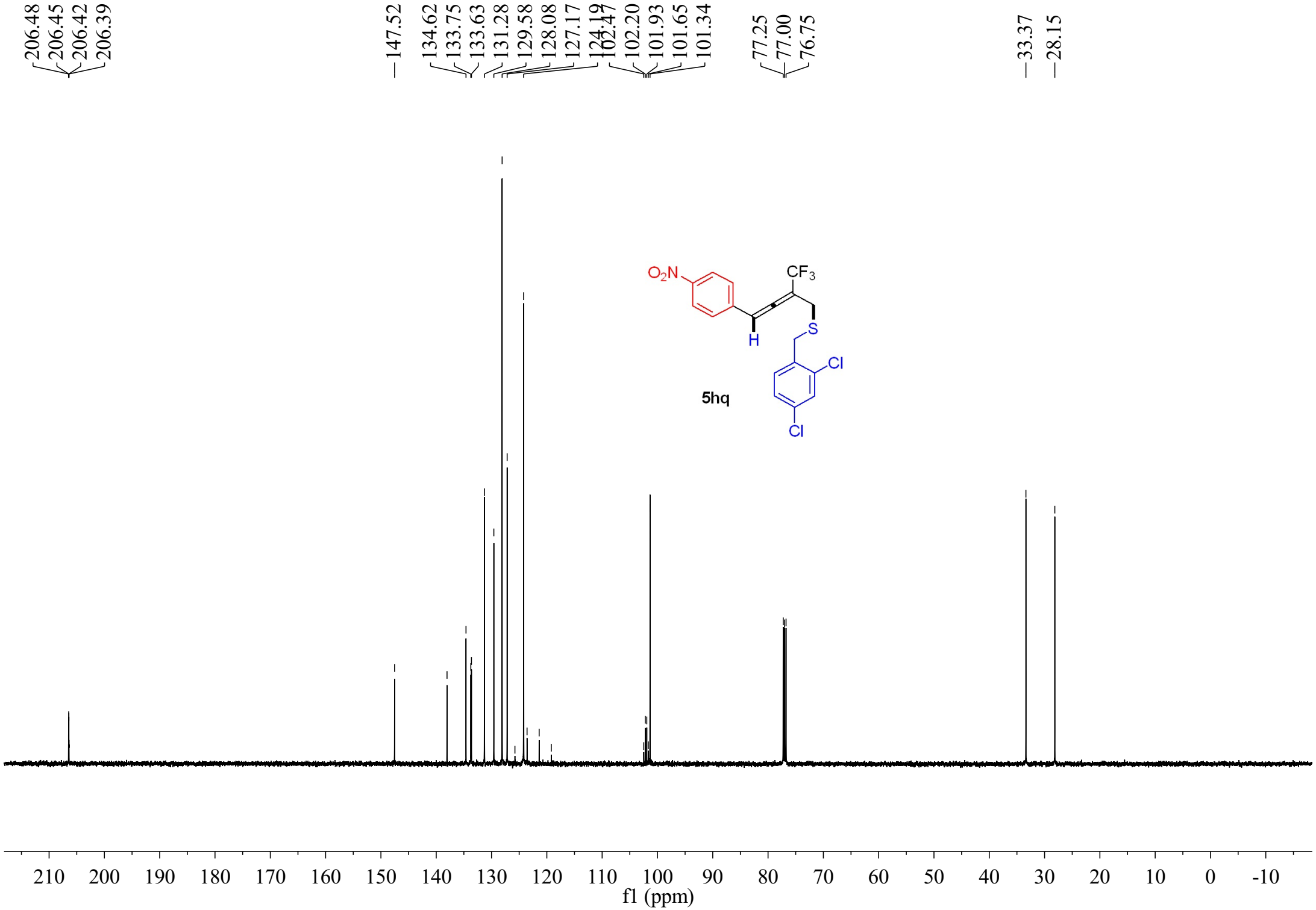

-62.574
O2N
CF3
H
S
5ho
t-Bu
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


8.230
8.213
7.504
7.487
7.260
6.840
6.830
6.824
6.818
6.813
3.849
3.826
3.823
3.800
3.523
3.519
3.514
2.350
2.258
O2N
CF3
H
S
Me
Me
Me
5hp
2.16
2.20
2.12
1.00
2.27
2.24
6.44
3.28
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
f1 (ppm)


206.48
206.45
206.42
206.39
147.53
138.27
136.91
136.90
129.75
129.05
128.07
124.20
103.05
102.78
102.51
102.24
101.19
77.25
77.00
76.75
31.75
29.65
20.82
19.42
O2N
CF3
S
H
Me
Me
Me
5hp
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)


-62.652
O2N
CF3
H
S
Me
Me
Me
5hp
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


8.206
8.189
7.473
7.456
7.345
7.342
7.260
7.248
7.231
7.185
7.168
6.813
6.808
6.802
6.796
3.846
3.819
3.801
3.773
3.383
3.379
3.375
O2N
CF3
H
S
Cl
Cl
5hq
2.02
2.04
1.01
0.97
0.99
1.00
2.07
2.05
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
f1 (ppm)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206.45
206.42
206.39
147.52
134.62
133.75
133.63
131.28
129.58
128.08
127.17
124.19
102.47
102.20
101.93
101.65
101.34
77.25
77.00
76.75
33.37
28.15
O2N
CF3
H
S
Cl
Cl
5hq
210
200
190
180
170
160
150
140
130
120
110
100
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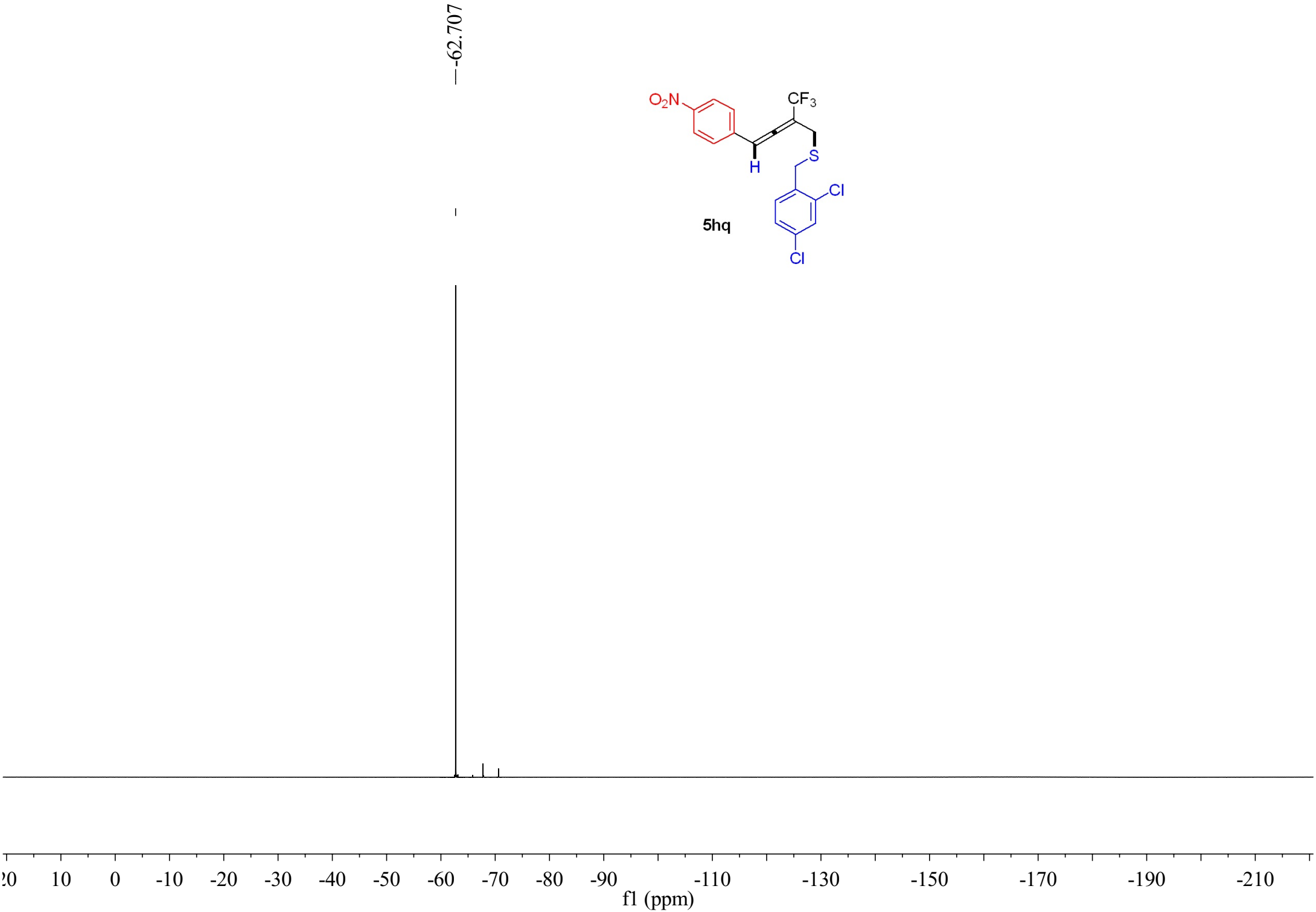
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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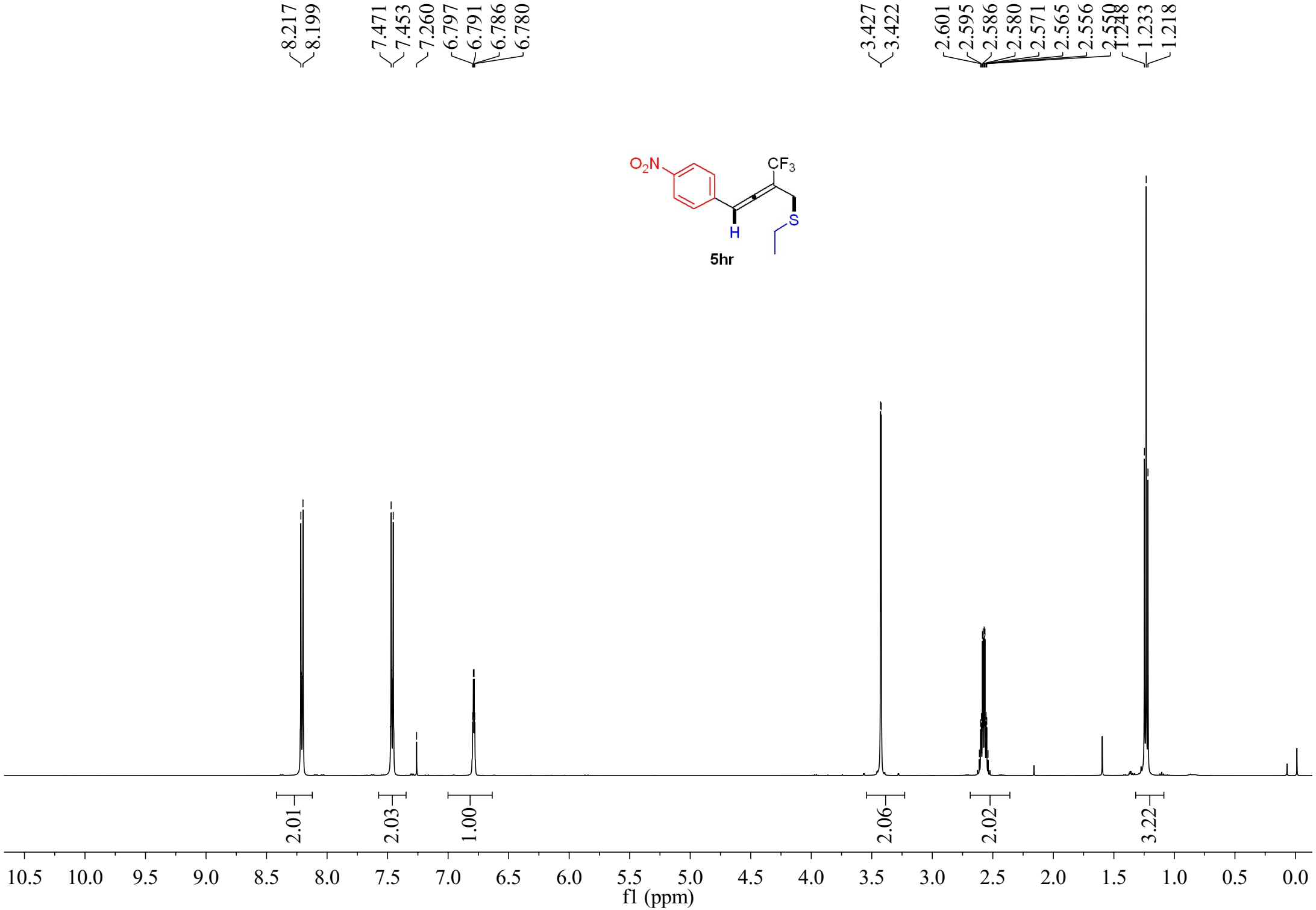
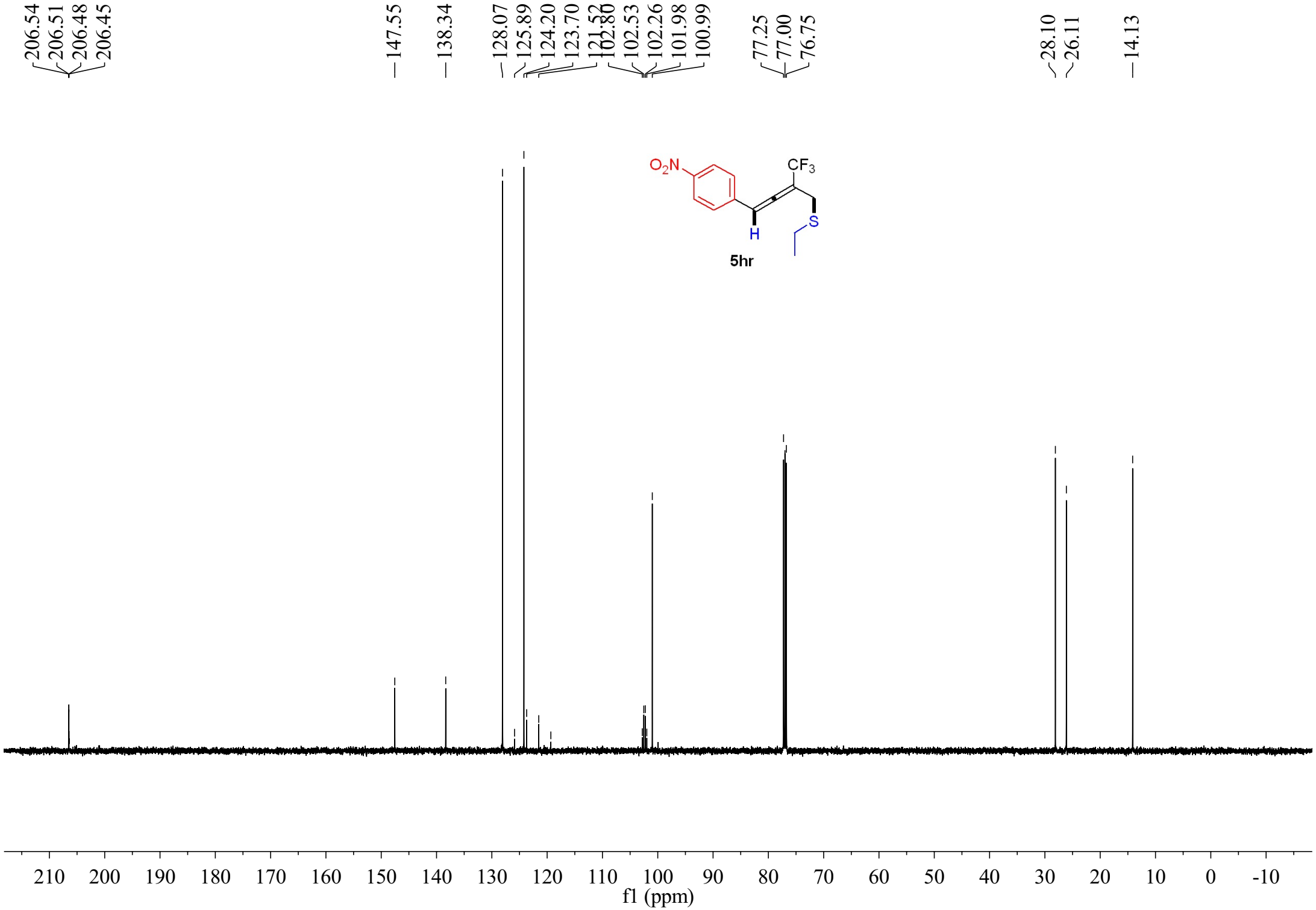
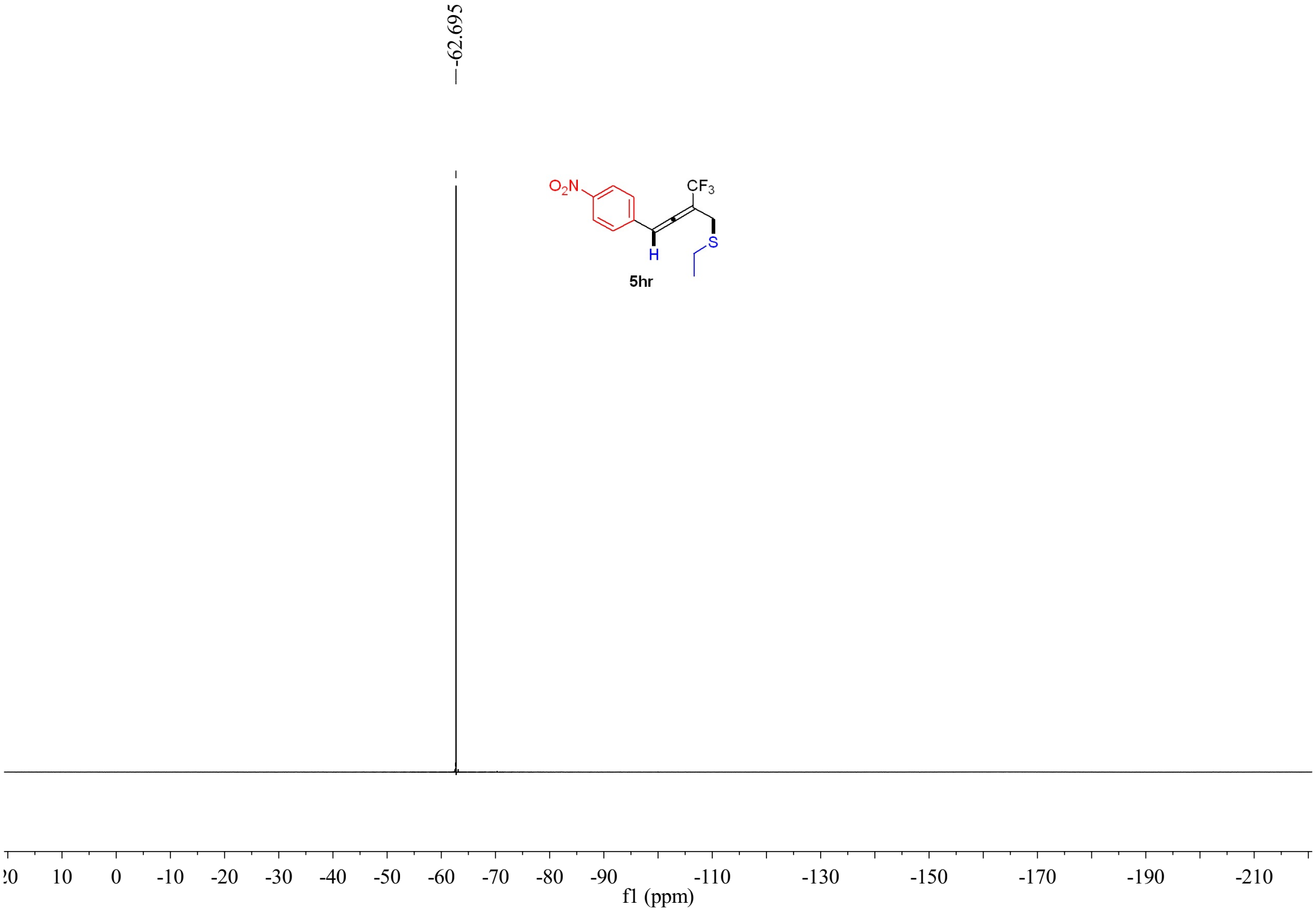
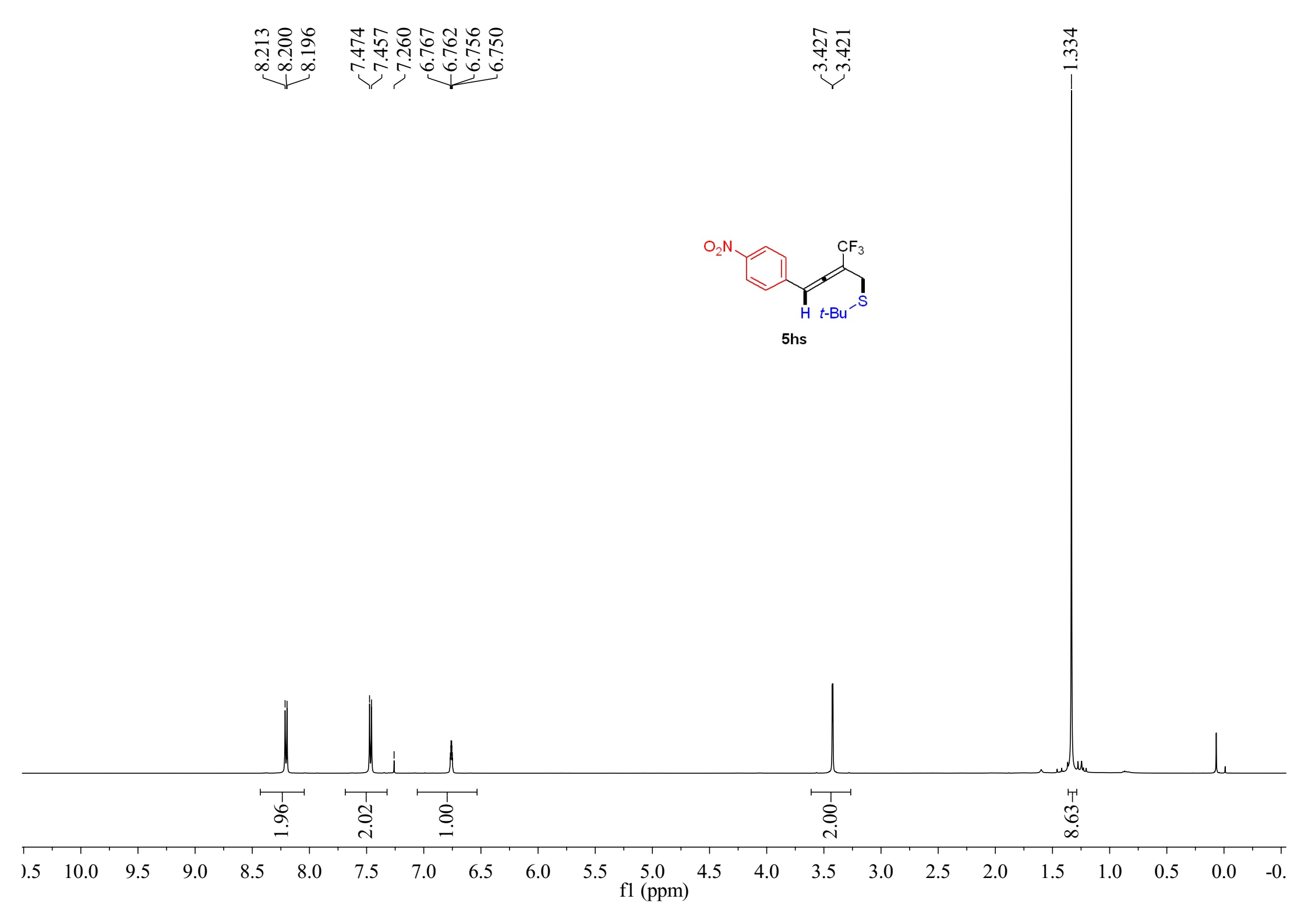
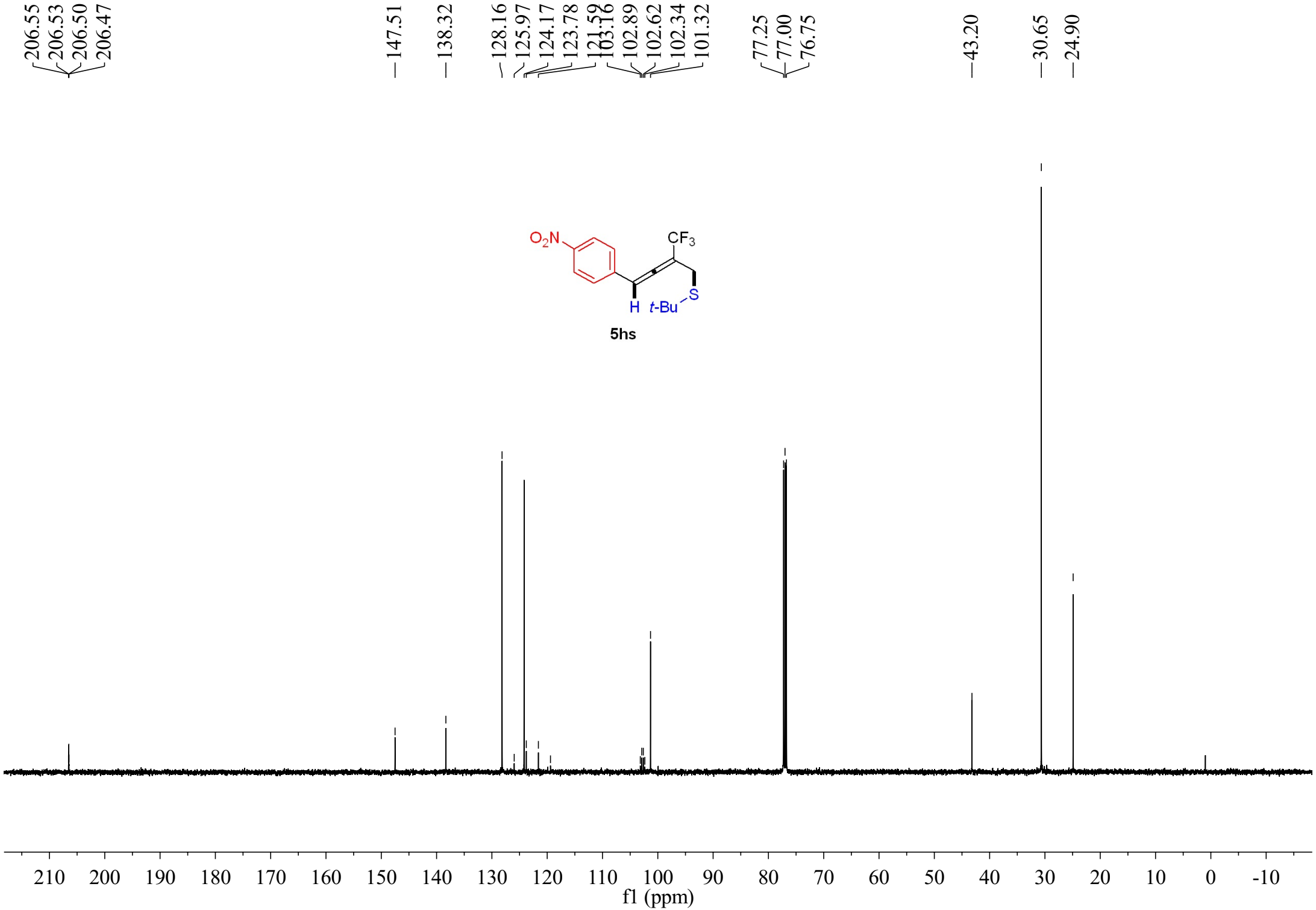
CF3
H
S
Cl
Cl
5hq
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

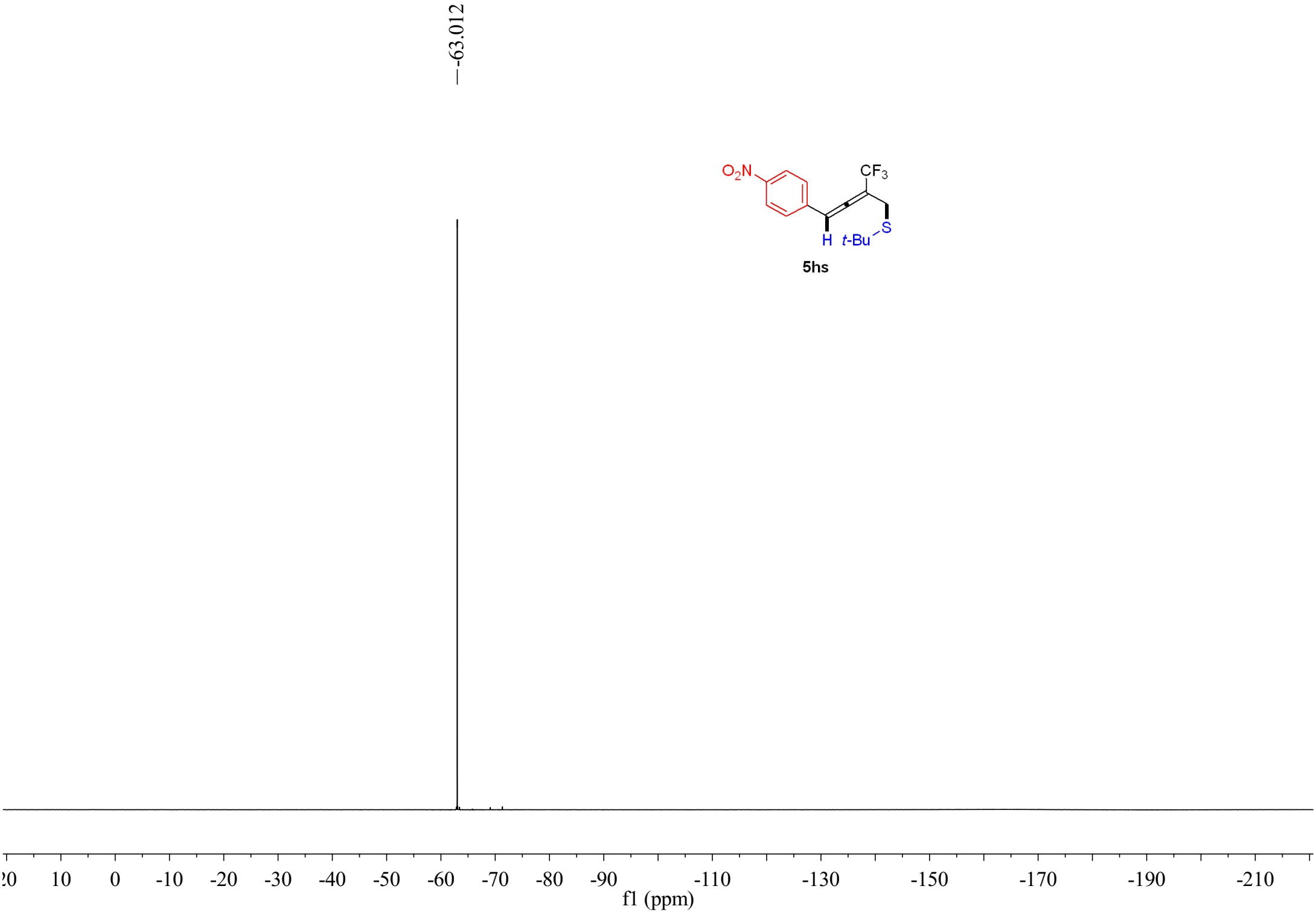

8.217
8.199
7.471
7.453
7.260
6.797
6.791
6.786
6.780
3.427
3.422
2.601
2.595
2.586
2.580
2.571
2.565
2.556
2.550
1.248
1.233
1.218
O2N
CF3
H
S
5hr
2.01
2.03
1.00
2.06
2.02
3.22
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

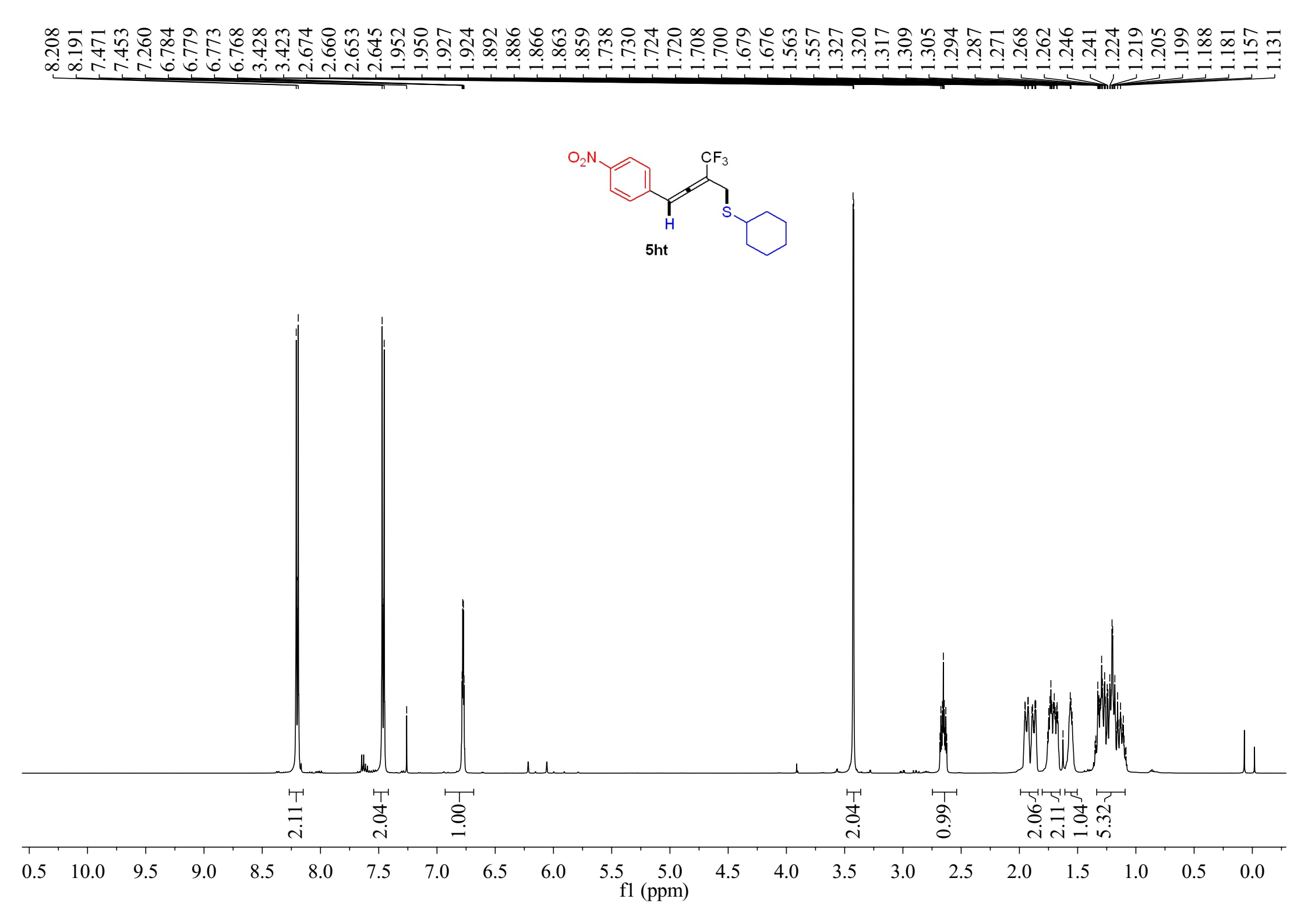

206.54
206.51
206.48
206.45
147.55
138.34
128.07
125.89
124.20
123.70
121.52
102.80
102.53
102.26
101.98
100.99
77.25
77.00
76.75
28.10
26.11
14.13
O2N
CF3
H
S
5hr
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

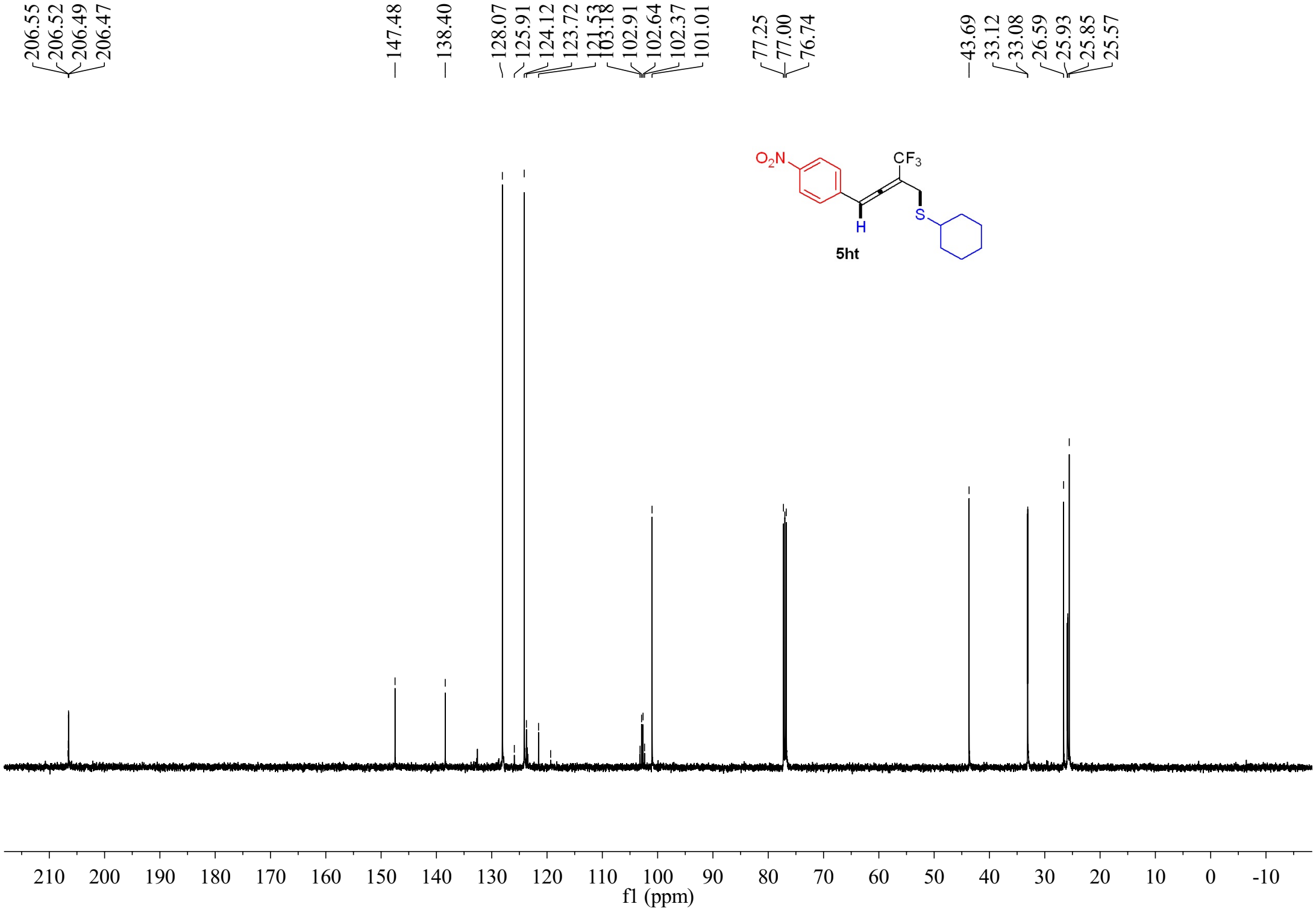

-62.695
O2N
CF3
H
S
5hr
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

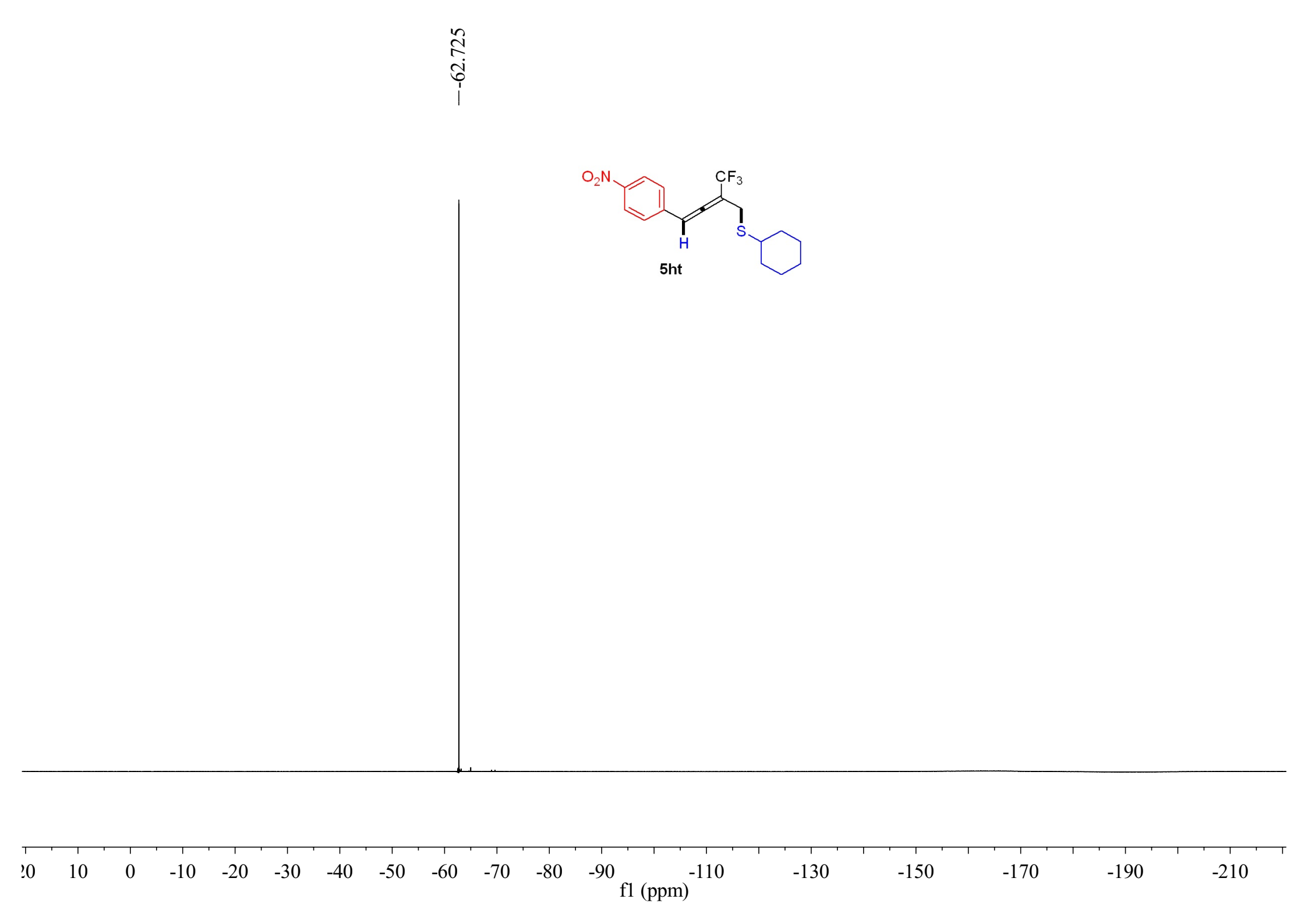

8.213
8.200
8.196
7.474
7.457
7.260
6.767
6.762
6.756
6.750
3.427
3.421
1.334
O2N
CF3
H
t-Bu
S
5hs
1.96
2.02
1.00
2.00
8.63
f1 (ppm)

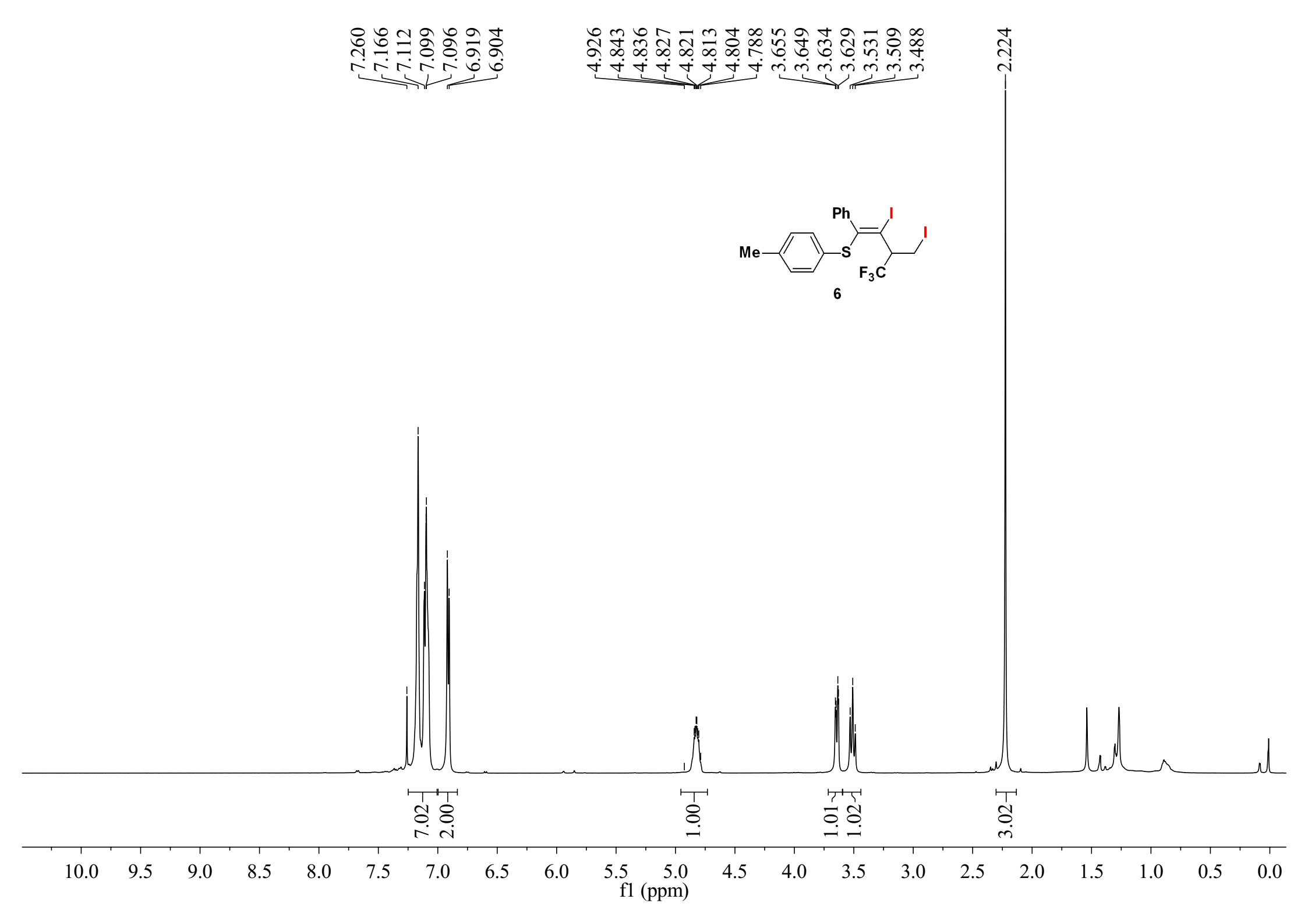

206.55
206.53
206.50
206.47
147.51
138.32
128.16
125.97
124.17
123.78
121.59
103.16
102.89
102.62
102.34
101.32
77.25
77.00
76.75
43.20
30.65
24.90
O2N
CF3
H
t-Bu
S
5hs
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

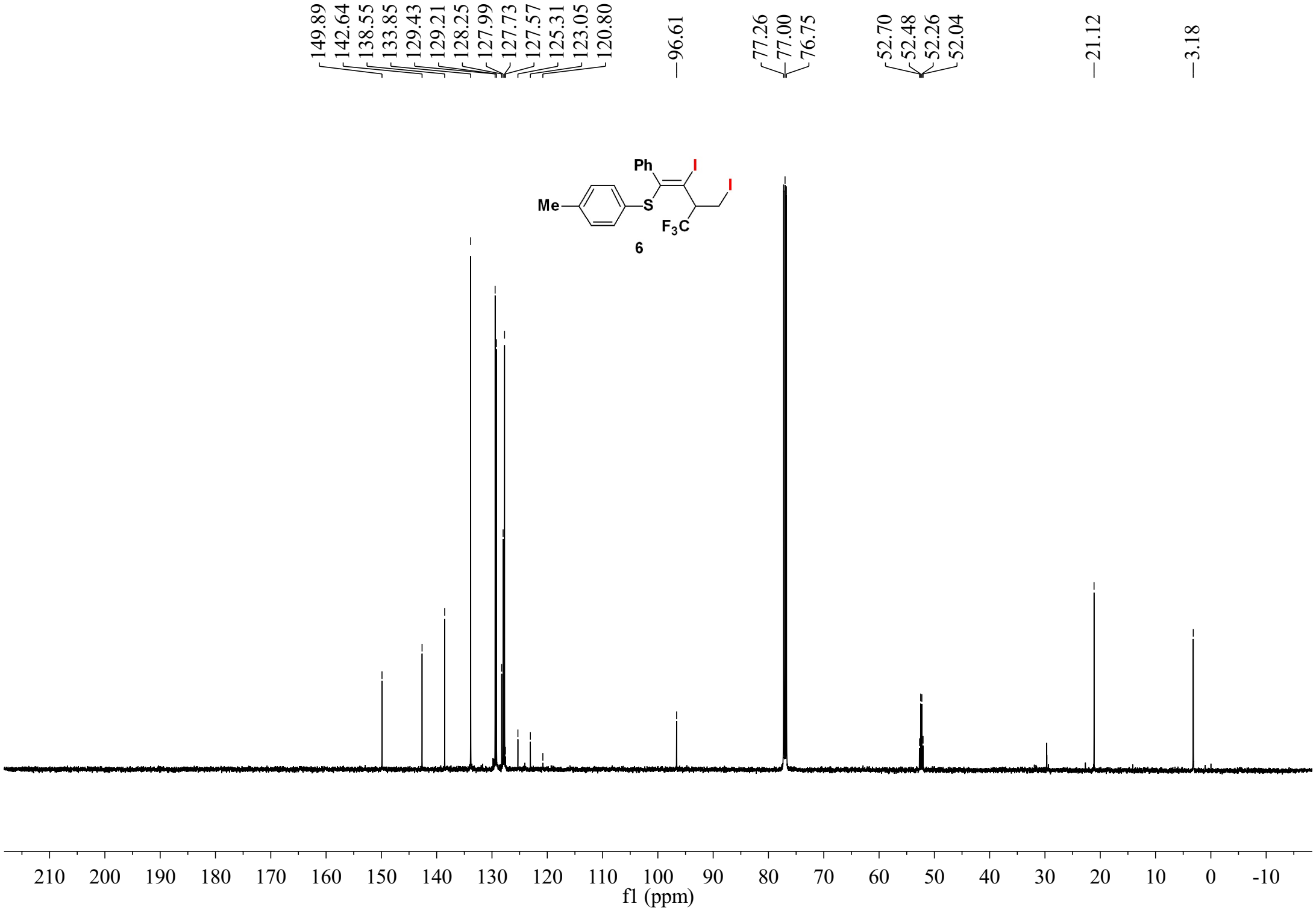

-63.012
O2N
CF3
H
t-Bu
S
5hs
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

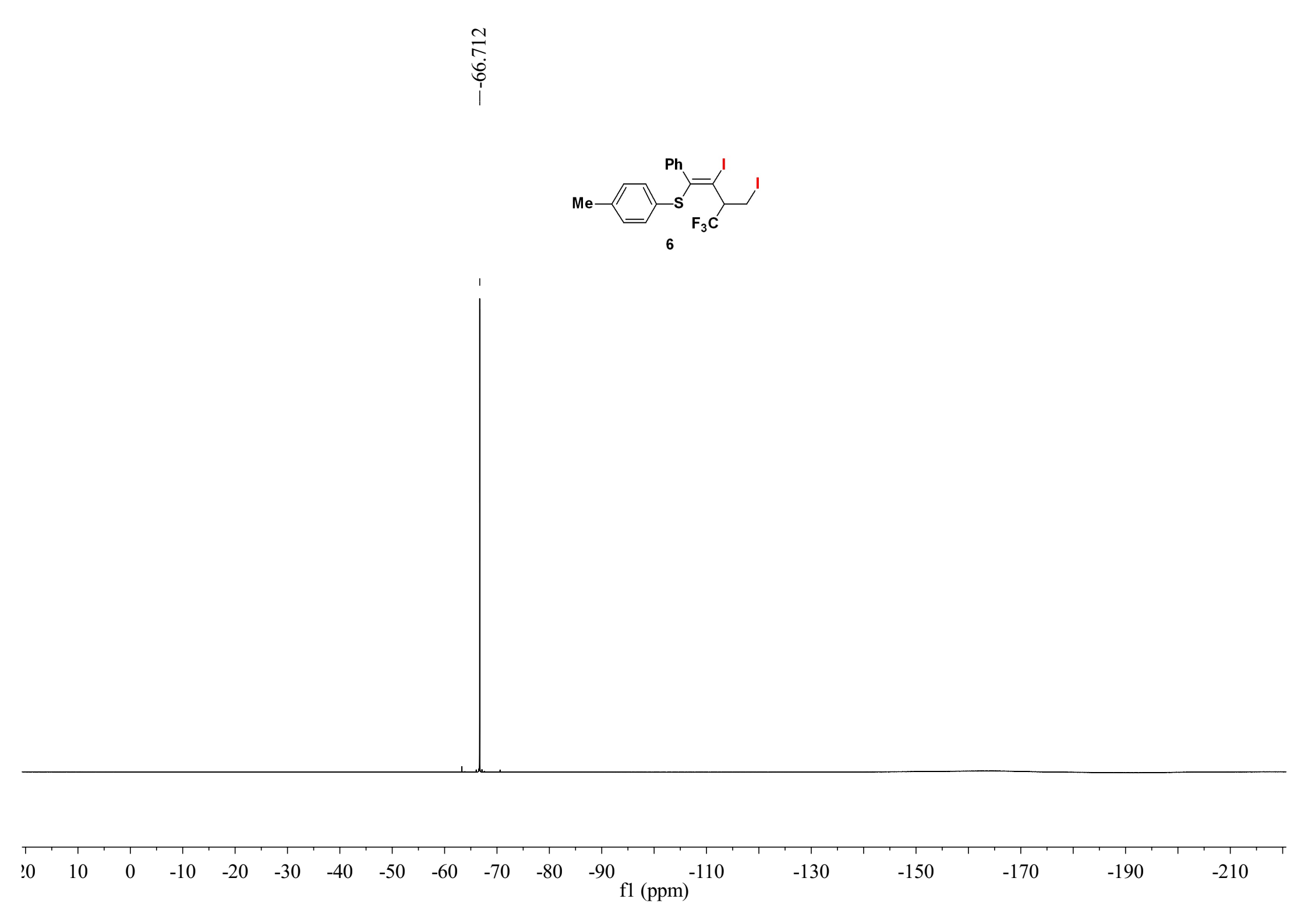

8.208
8.191
7.471
7.453
7.260
6.784
6.779
6.773
6.768
3.428
3.423
2.674
2.660
2.653
2.645
1.952
1.950
1.927
1.924
1.892
1.886
1.866
1.863
1.859
1.738
1.730
1.724
1.720
1.708
1.700
1.679
1.676
1.563
1.557
1.327
1.320
1.317
1.309
1.305
1.294
1.287
1.271
1.268
1.262
1.246
1.241
1.224
1.219
1.205
1.199
1.188
1.181
1.157
1.131
O2N
CF3
H
S
5ht
2.11
2.04
1.00
2.04
0.99
2.06
2.11
1.04
5.32
0.5
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
f1 (ppm)

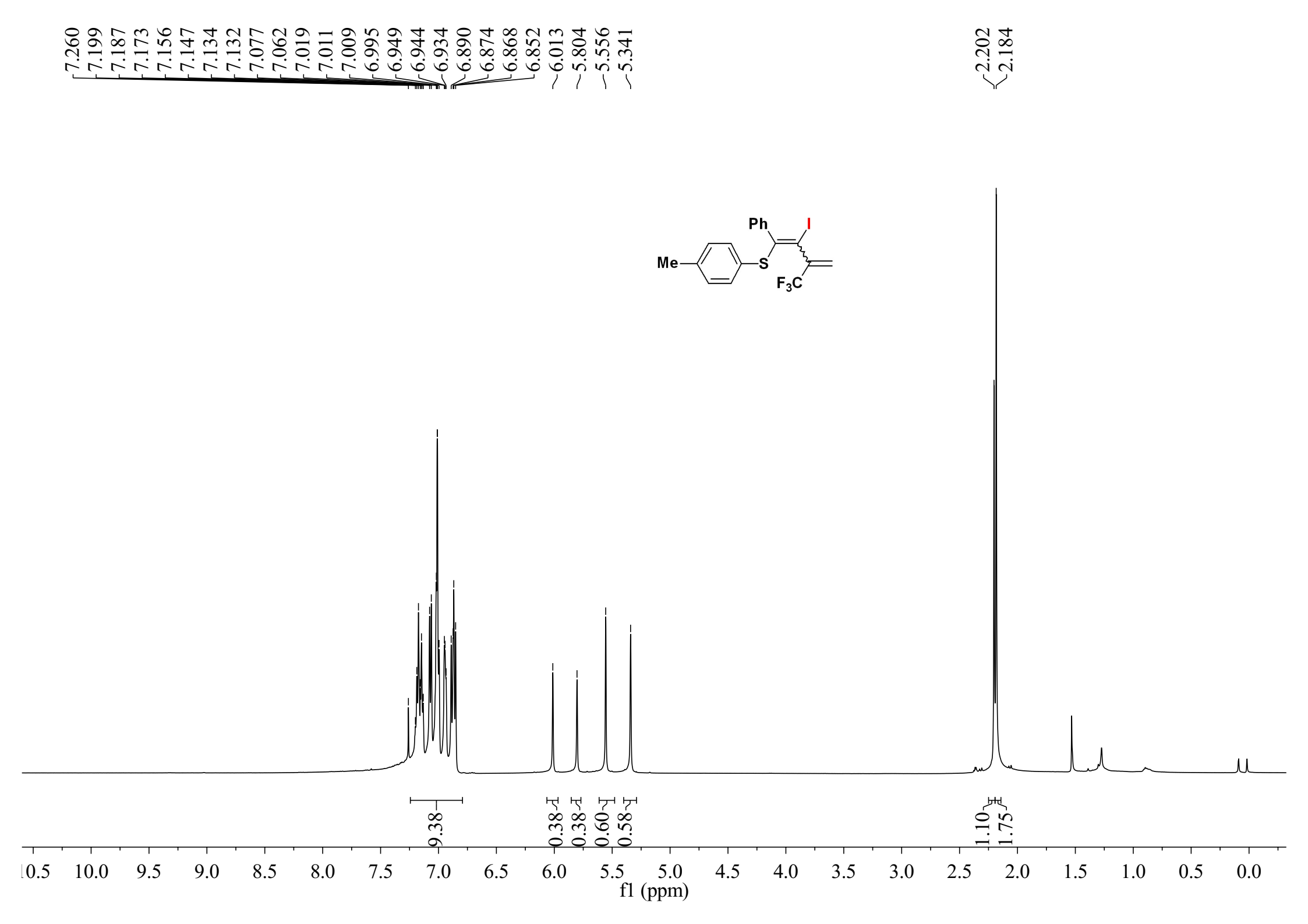

206.55
206.52
206.49
206.47
147.48
138.40
128.07
125.91
124.12
123.72
121.53
103.18
102.91
102.64
102.37
101.01
77.25
77.00
76.74
43.69
33.12
33.08
26.59
25.93
25.85
25.57
O2N
CF3
H
S
5ht
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

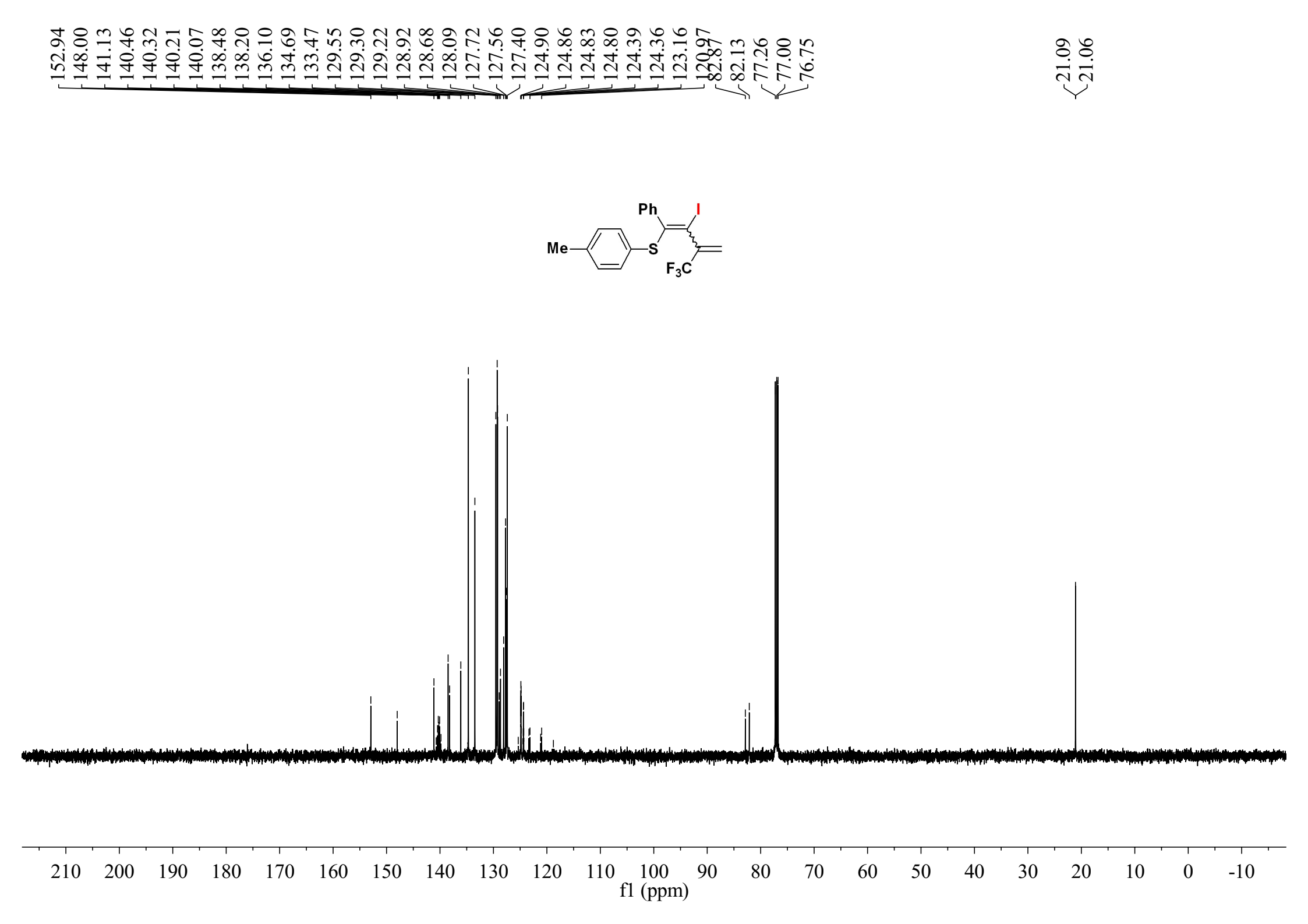

-62.725
O2N
CF3
H
S
5ht
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

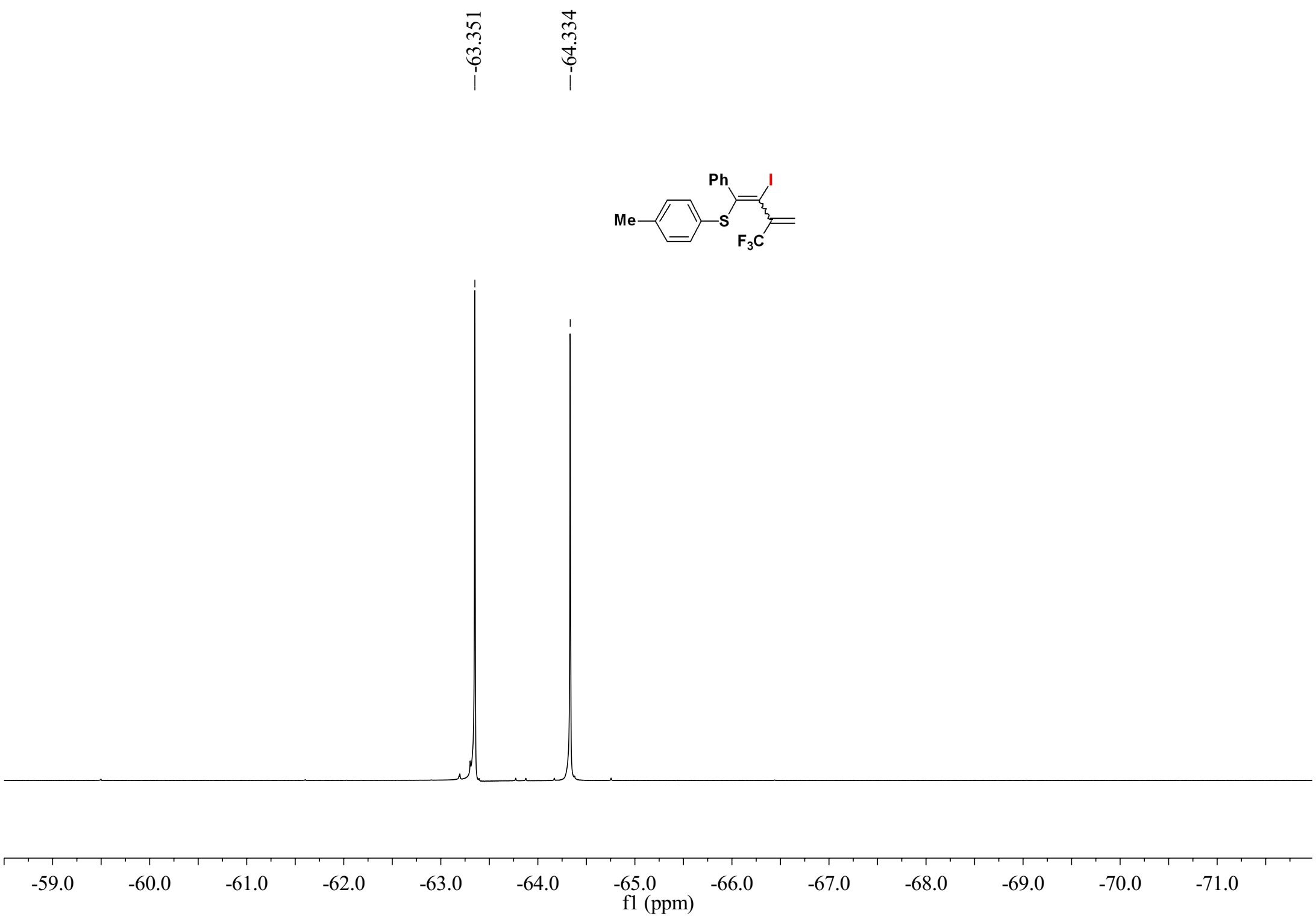

7.260
7.166
7.112
7.099
7.096
6.919
6.904
4.926
4.843
4.836
4.827
4.821
4.813
4.804
4.788
3.655
3.649
3.634
3.629
3.531
3.509
3.488
2.224
Ph
I
I
Me
S
F3C
6
7.02
2.00
1.00
1.01
1.02
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

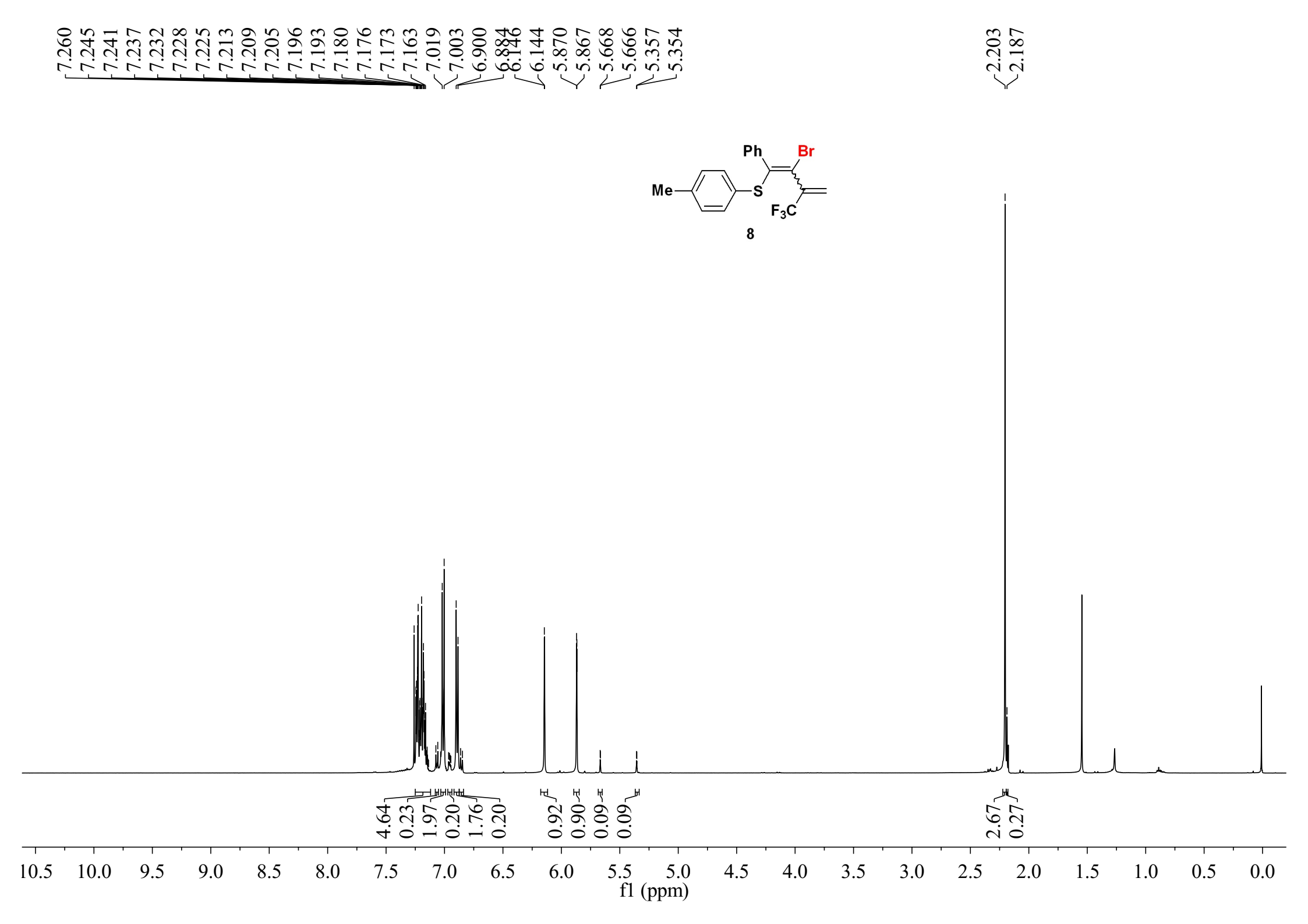

149.89
142.64
138.55
133.85
129.43
129.21
128.25
127.99
127.73
127.57
125.31
123.05
120.80
96.61
77.26
77.00
76.75
52.70
52.48
52.26
52.04
21.12
3.18
Ph
I
I
Me
S
F3C
6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

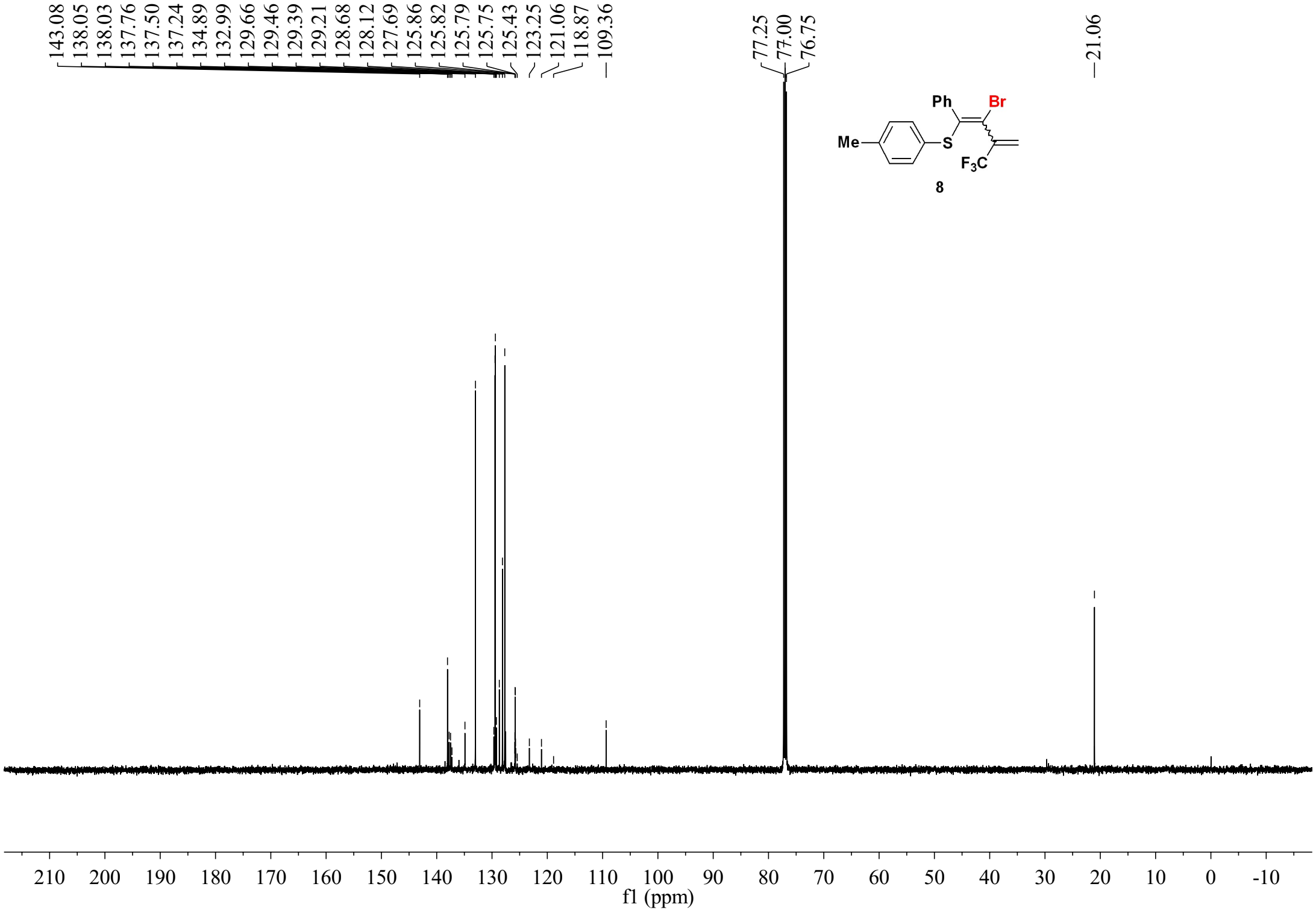

-66.712
Ph
I
I
Me
S
F3C
6
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

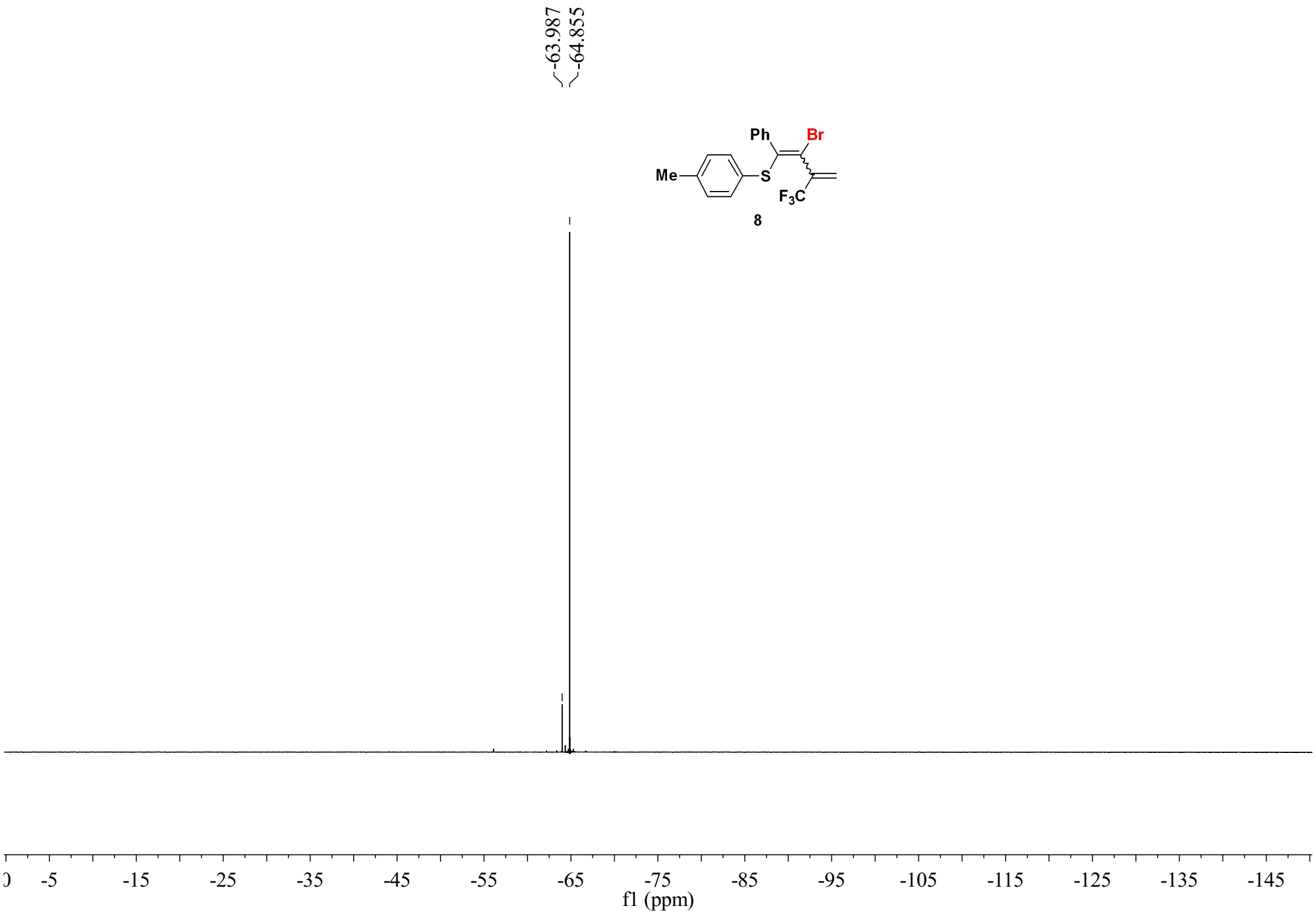

7.260
7.199
7.187
7.173
7.156
7.147
7.134
7.132
7.077
7.062
7.019
7.011
7.009
6.995
6.949
6.944
6.934
6.890
6.874
6.868
6.852
6.013
5.804
5.556
5.341
2.202
2.184
Ph
I
Me
S
F3C
9.38
0.38
0.38
0.60
0.58
1.10
1.75
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

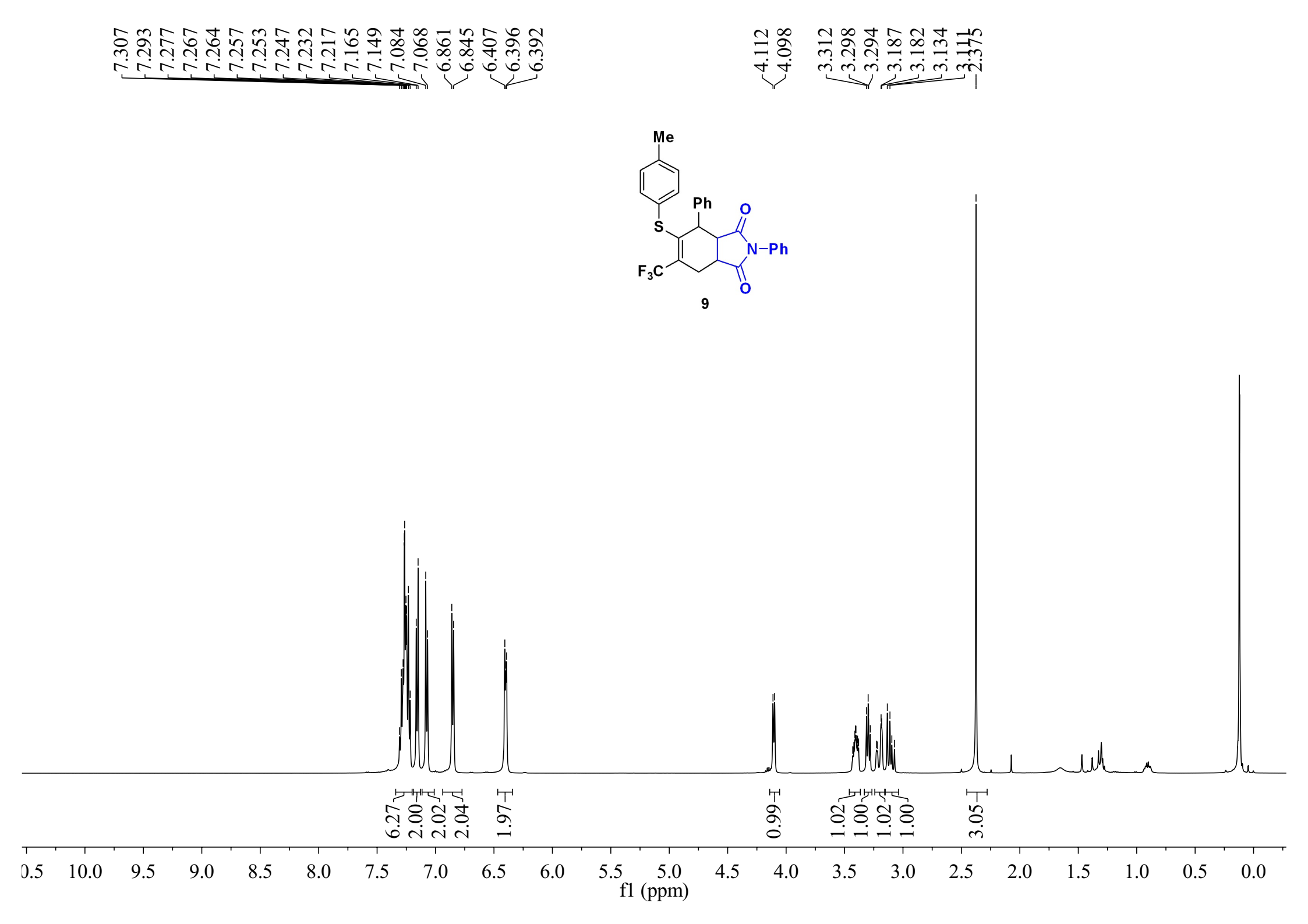

152.94
148.00
141.13
140.46
140.32
140.21
140.07
138.48
138.20
136.10
134.69
133.47
129.55
129.30
129.22
128.92
128.68
128.09
127.72
127.56
127.40
124.90
124.86
124.83
124.80
124.39
124.36
123.16
120.97
82.87
82.13
77.26
77.00
76.75
21.09
21.06
Ph
I
Me
S
F3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

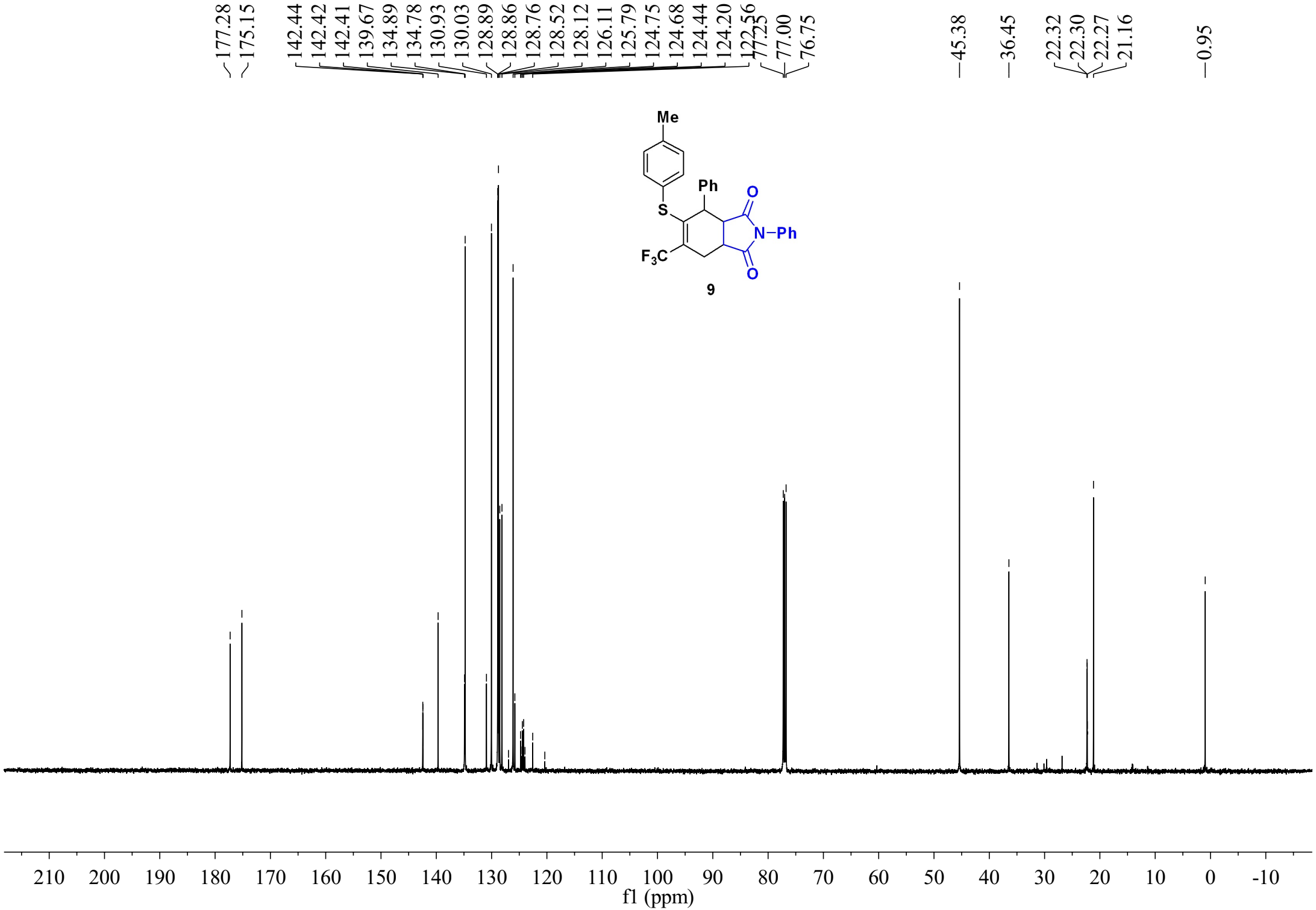

-63.351
-64.334
Ph
I
Me
S
F3C
-59.0
-60.0
-61.0
-62.0
-63.0
-64.0
-65.0
-66.0
-67.0
-68.0
-69.0
-70.0
-71.0
f1 (ppm)

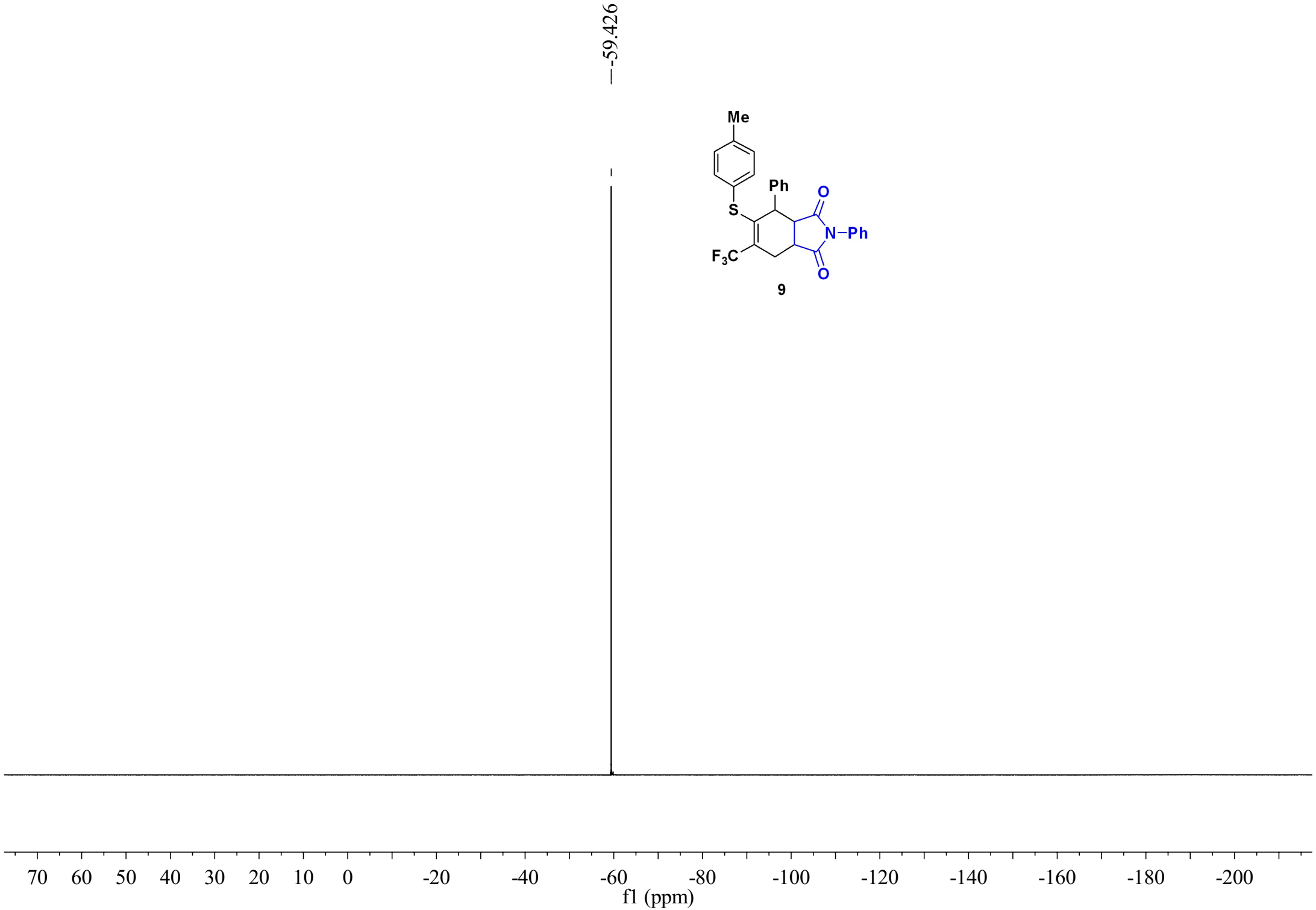

7.260
7.245
7.241
7.237
7.232
7.228
7.225
7.213
7.209
7.205
7.196
7.193
7.180
7.176
7.173
7.163
7.019
7.003
6.900
6.884
6.146
6.144
5.870
5.867
5.668
5.666
5.357
5.354
2.203
2.187
Ph
Br
Me
S
F3C
8
4.64
0.23
1.97
0.20
1.76
0.20
0.92
0.90
0.09
0.09
2.67
0.27
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

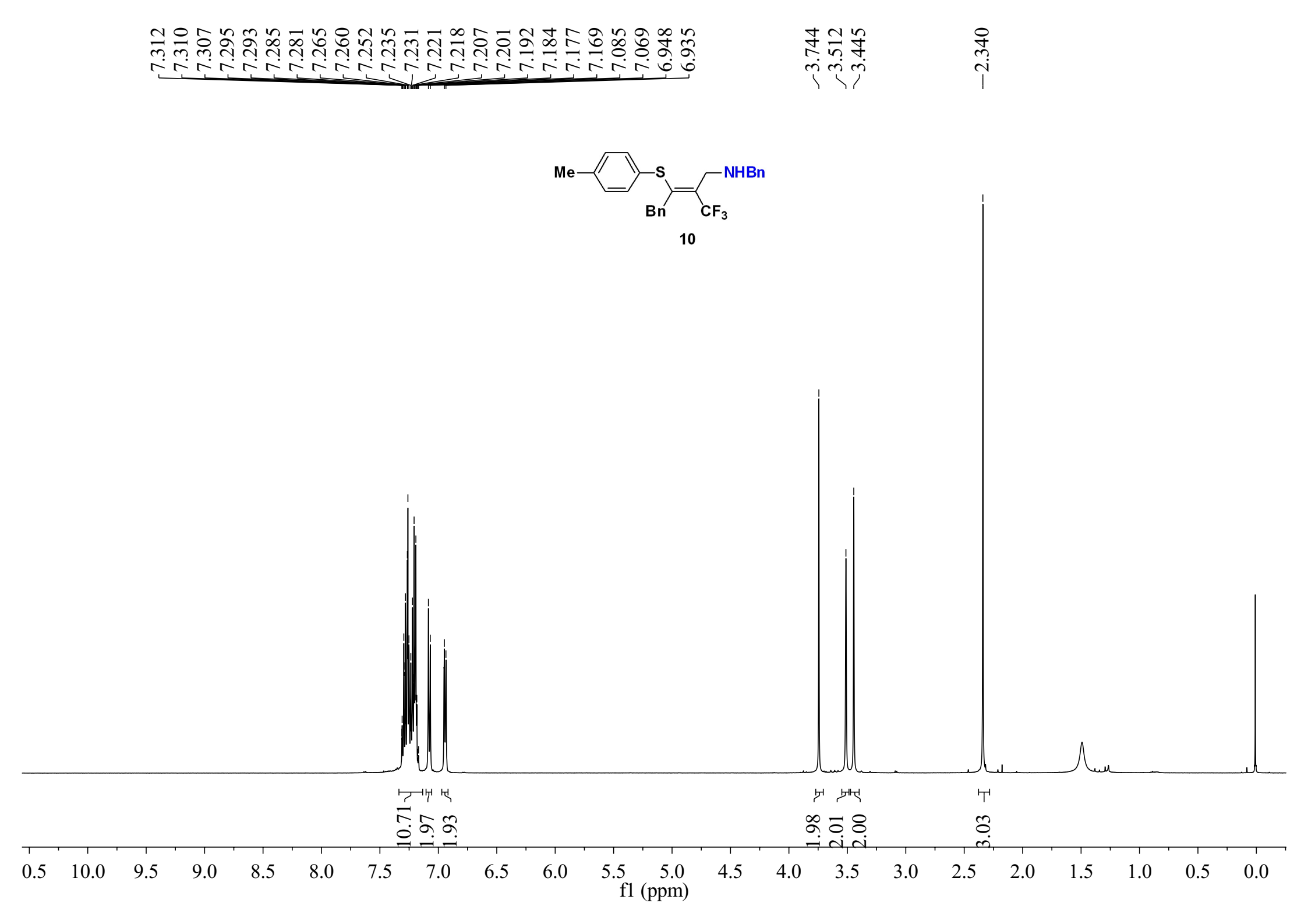

143.08
138.05
138.03
137.76
137.50
137.24
134.89
132.99
129.66
129.46
129.39
129.21
128.68
128.12
127.69
125.86
125.82
125.79
125.75
125.43
123.25
121.06
118.87
109.36
77.25
77.00
76.75
21.06
Ph
Br
Me
S
F3C
8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

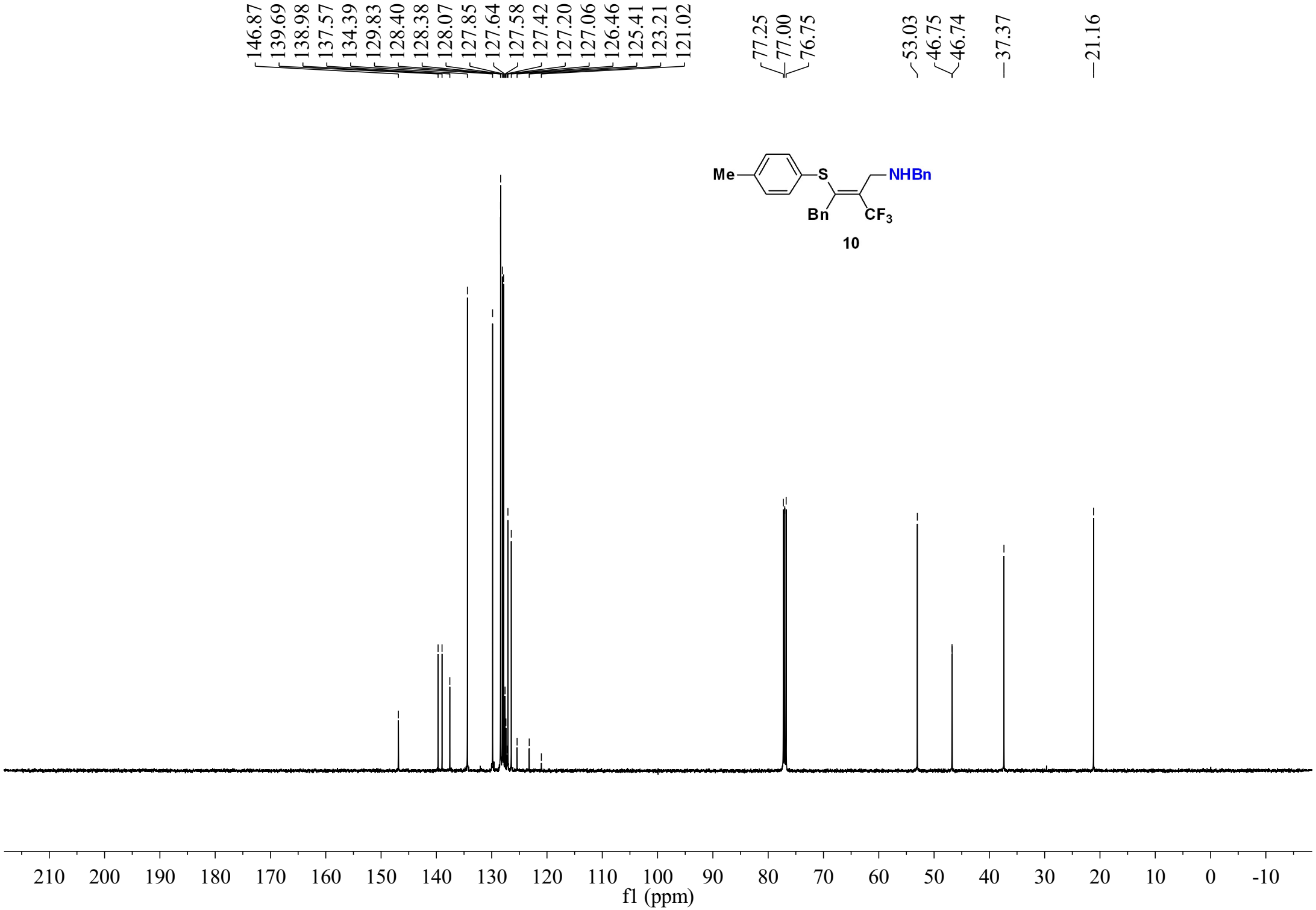

-63.987
-64.855
Ph
Br
Me
S
F3C
8
0
-5
-15
-25
-35
-45
-55
-65
-75
-85
-95
-105
-115
-125
-135
-145
f1 (ppm)

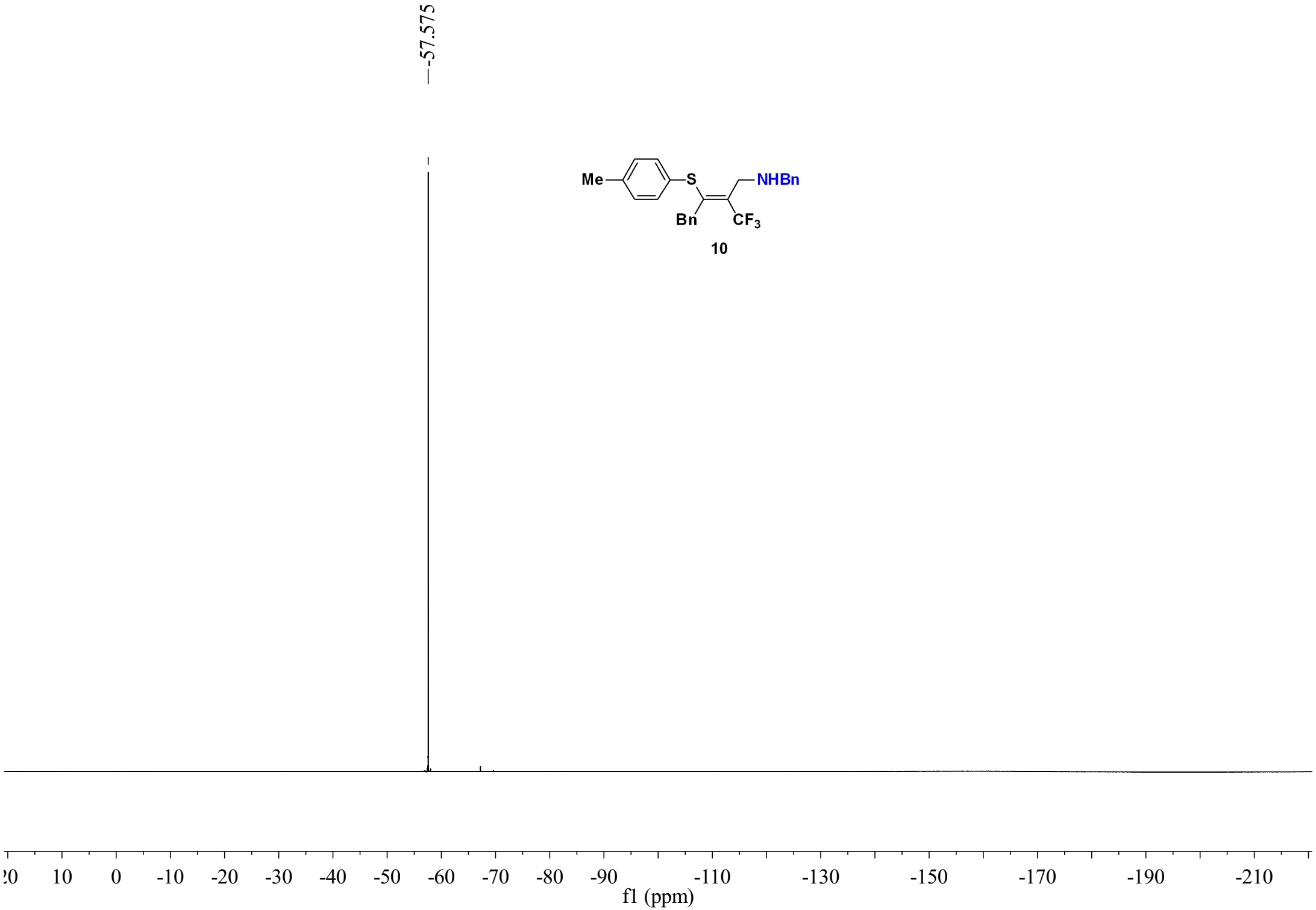

7.307
7.293
7.277
7.267
7.264
7.257
7.253
7.247
7.232
7.217
7.165
7.149
7.084
7.068
6.861
6.845
6.407
6.396
6.392
4.112
4.098
3.312
3.298
3.294
3.187
3.182
3.134
3.111
2.375
Me
Ph
S
O
N–Ph
F3C
O
9
6.27
2.00
2.02
2.04
1.97
0.99
1.02
1.00
1.02
1.00
3.05
f1 (ppm)

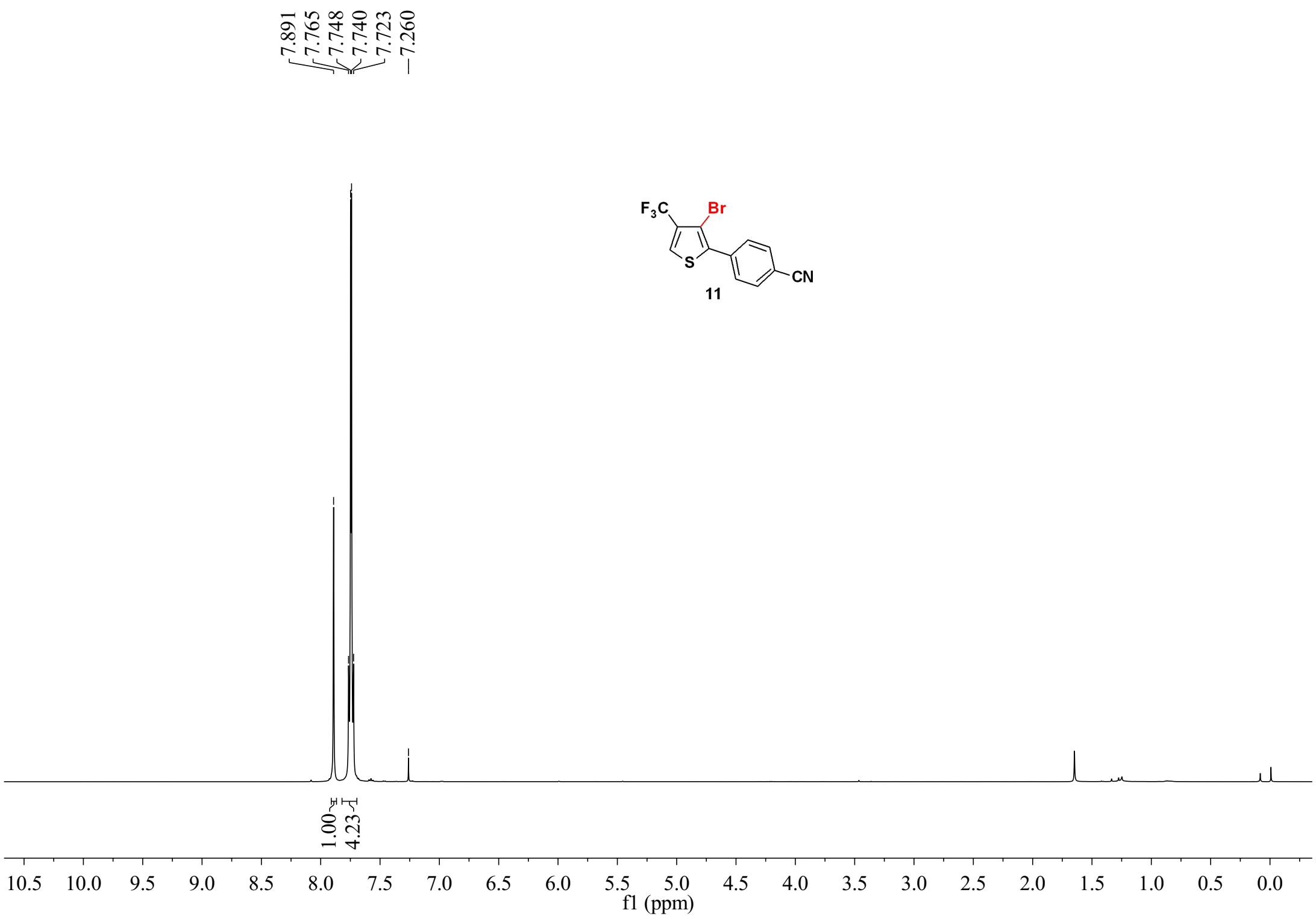

177.28
175.15
142.44
142.42
142.41
139.67
134.89
134.78
130.93
130.03
128.89
128.86
128.76
128.52
128.12
126.11
125.79
124.75
124.68
124.44
124.20
122.56
77.25
77.00
76.75
45.38
36.45
22.32
22.30
22.27
21.16
0.95
Me
Ph
S
O
N–Ph
F3C
O
9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

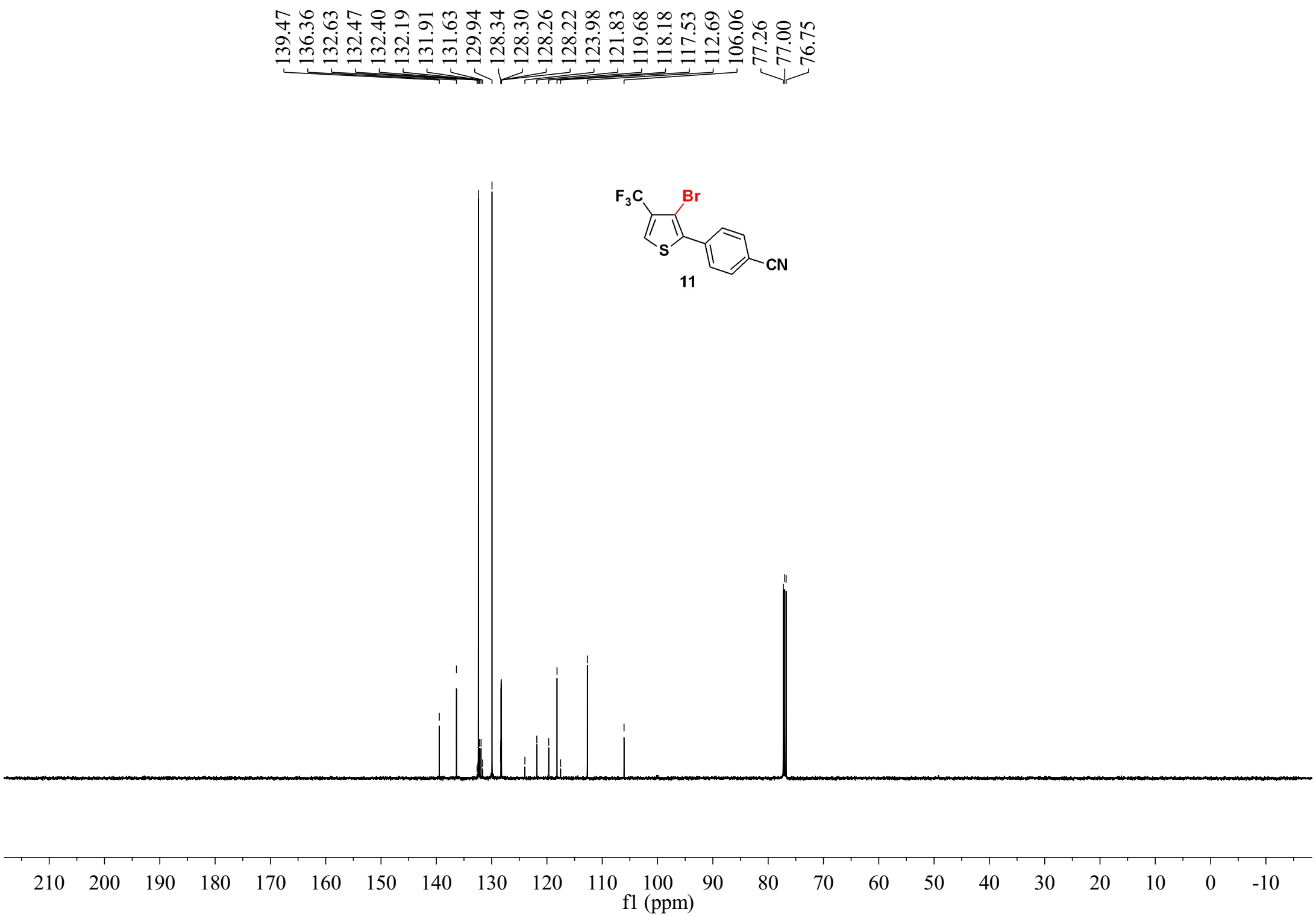

-59.426
Me
Ph
S
O
N–Ph
F3C
O
9
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

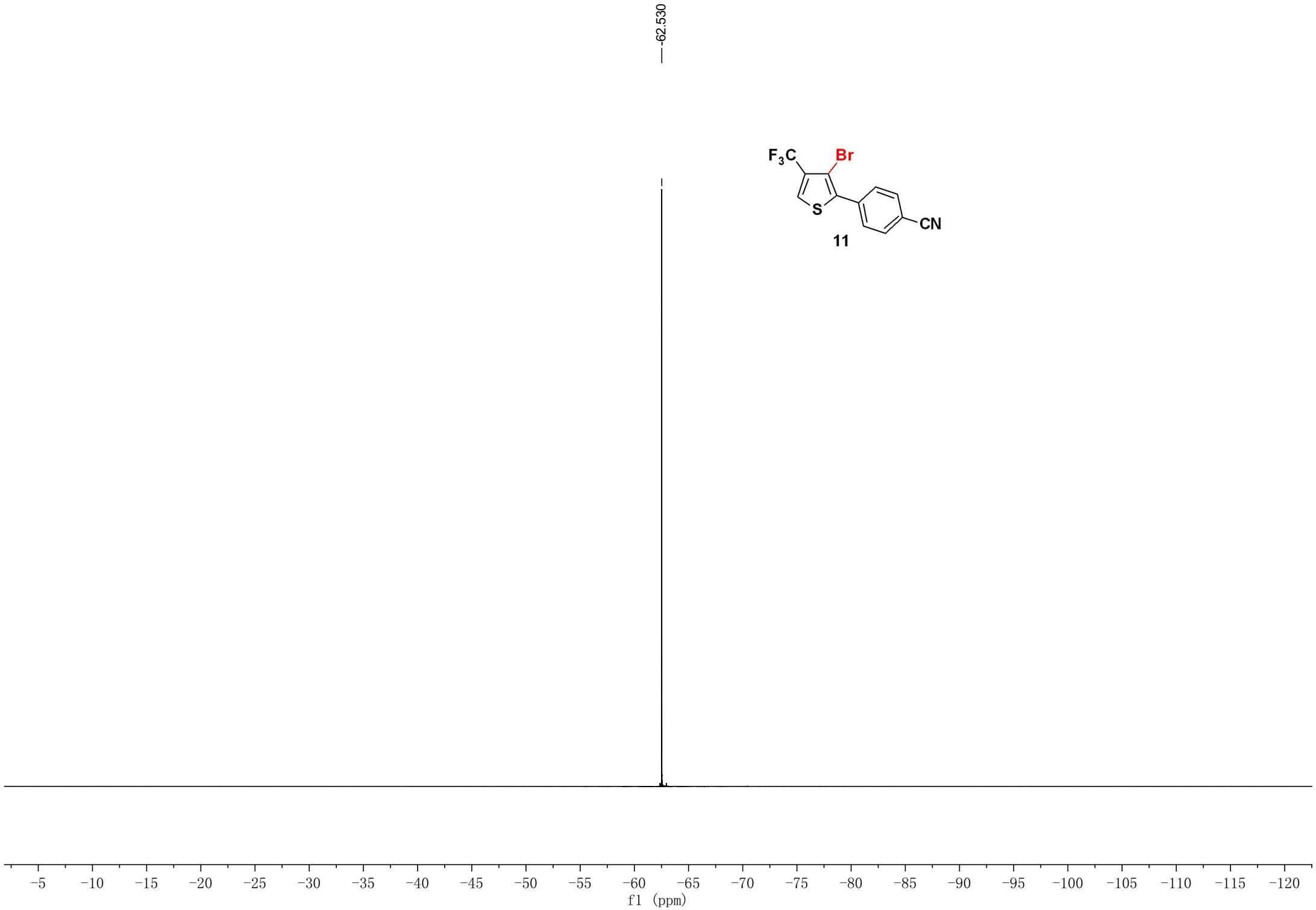

7.312
7.310
7.307
7.295
7.293
7.285
7.281
7.265
7.260
7.252
7.235
7.231
7.221
7.218
7.207
7.201
7.192
7.184
7.177
7.169
7.085
7.069
6.948
6.935
3.744
3.512
3.445
2.340
Me
S
NHBn
Bn
CF3
10
10.71
1.97
1.93
1.98
2.01
2.00
3.03
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

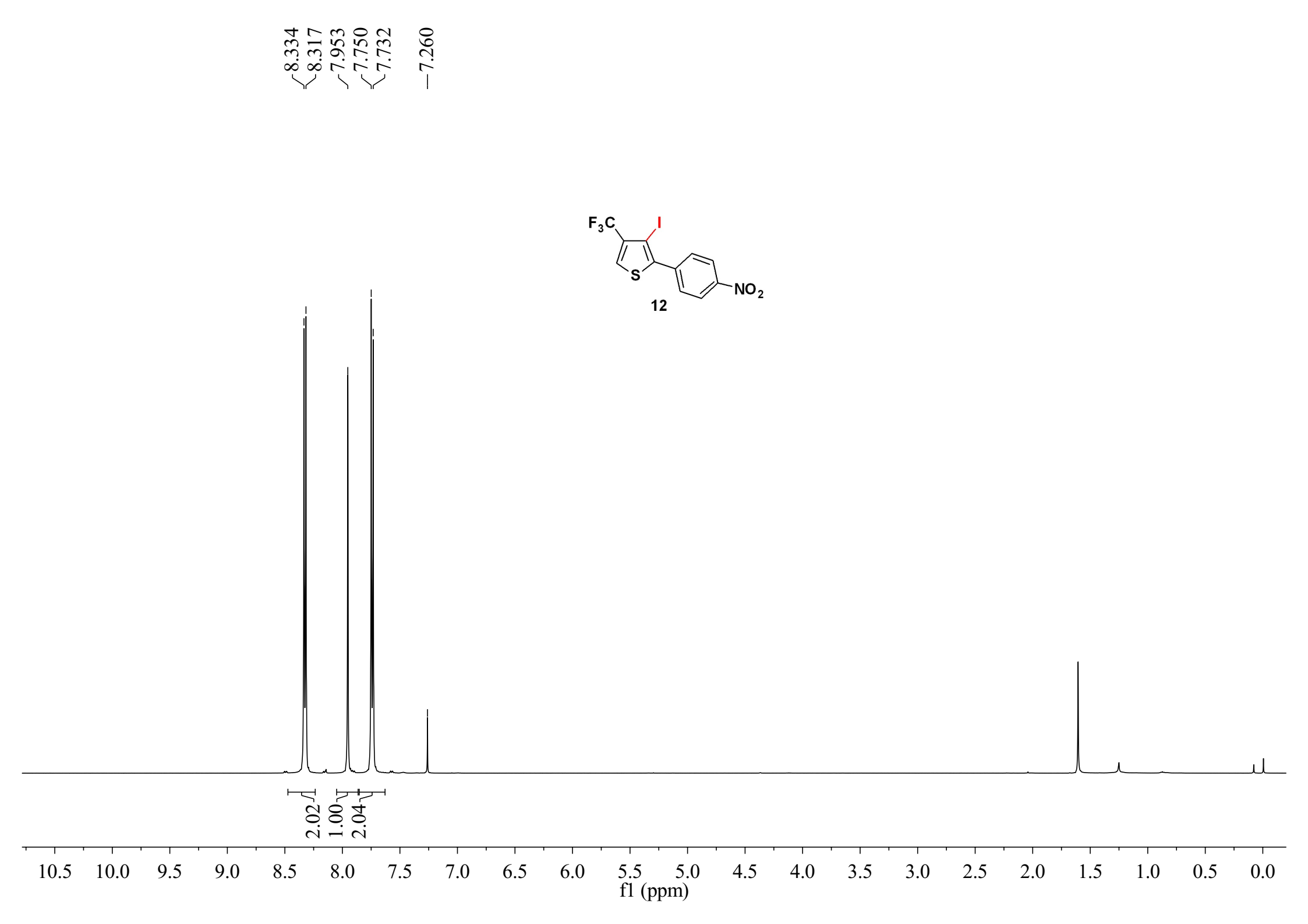

146.87
139.69
138.98
137.57
134.39
129.83
128.40
128.38
128.07
127.85
127.64
127.58
127.42
127.20
127.06
126.46
125.41
123.21
121.02
77.25
77.00
76.75
53.03
46.75
46.74
37.37
21.16
Me
S
NHBn
Bn
CF3
10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

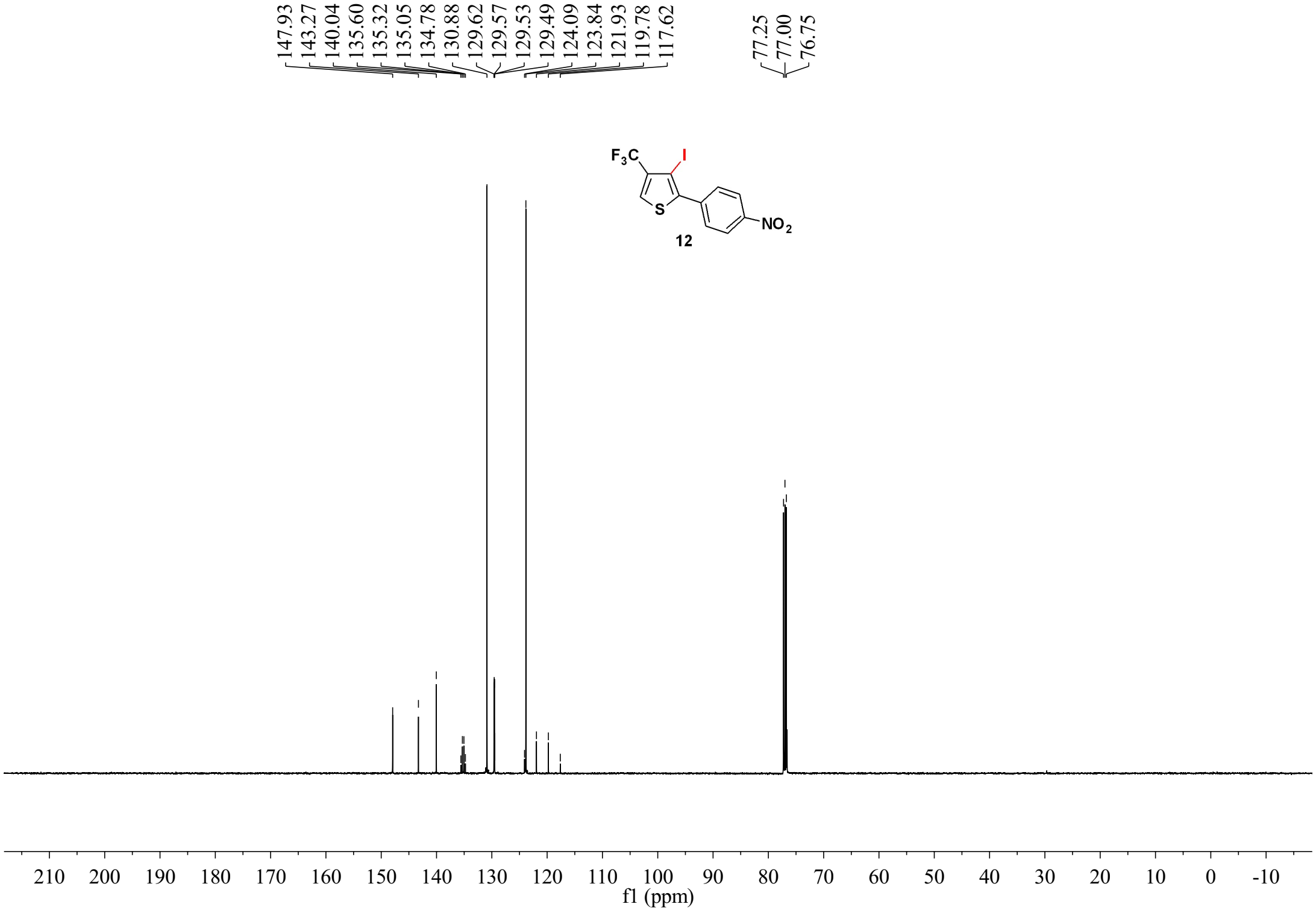

-57.575
Me
S
NHBn
Bn
CF3
10
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

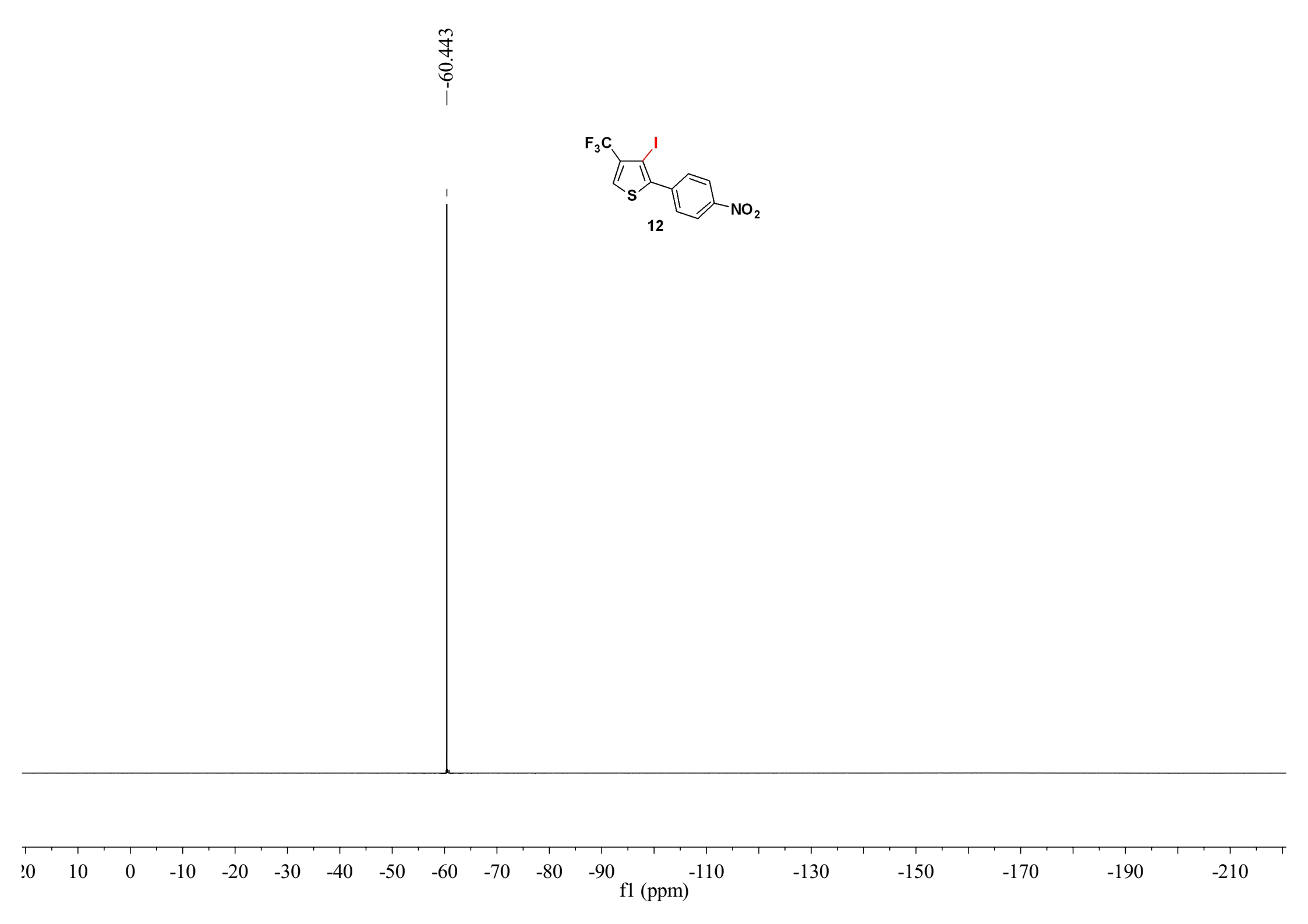

7.891
7.765
7.748
7.740
7.723
7.260
F3C
Br
S
CN
11
1.00
4.23
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

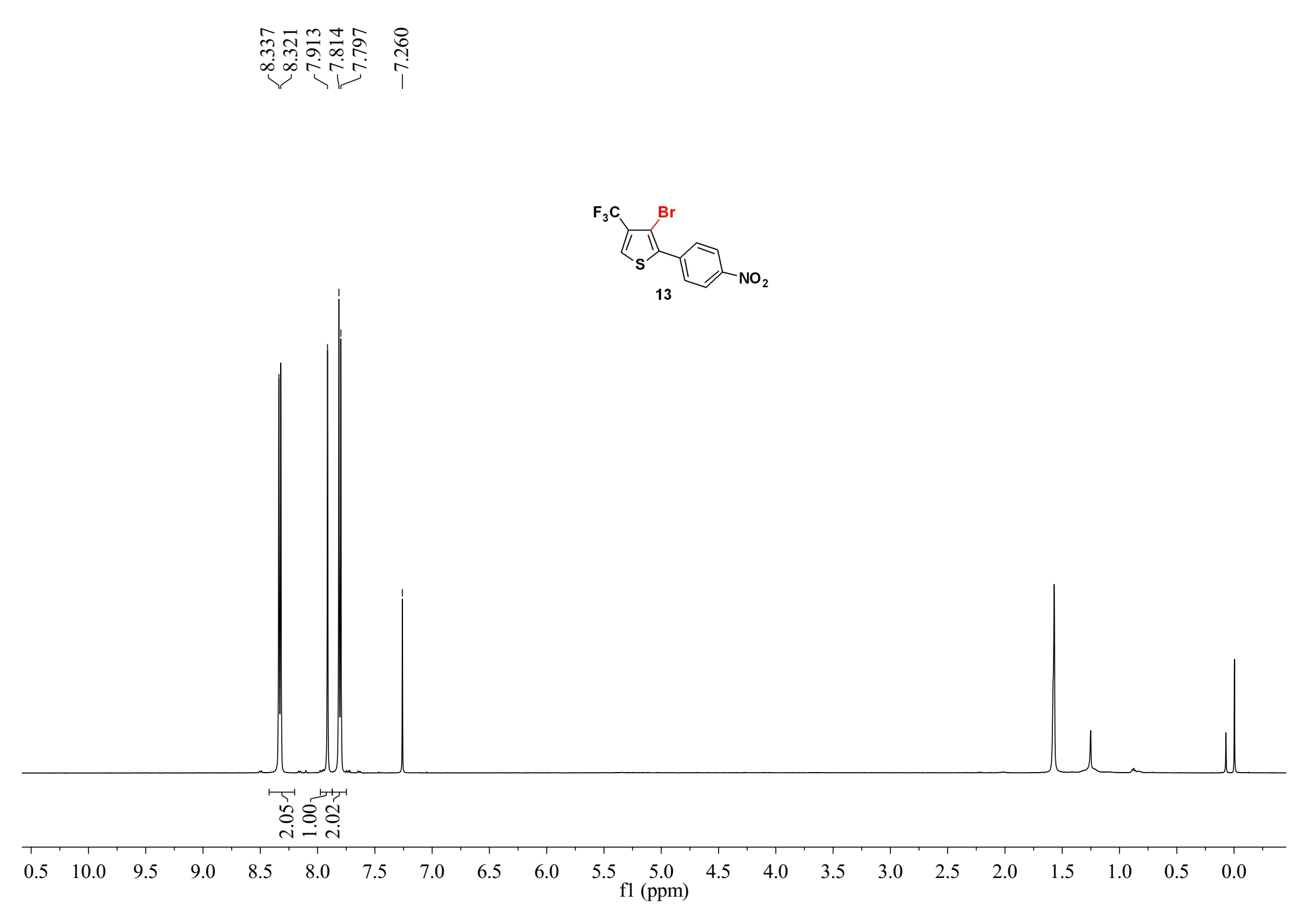

139.47
136.36
132.63
132.47
132.40
132.19
131.91
131.63
129.94
128.34
128.30
128.26
128.22
123.98
121.83
119.68
118.18
117.53
112.69
106.06
77.26
77.00
76.75
F3C
Br
S
CN
11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

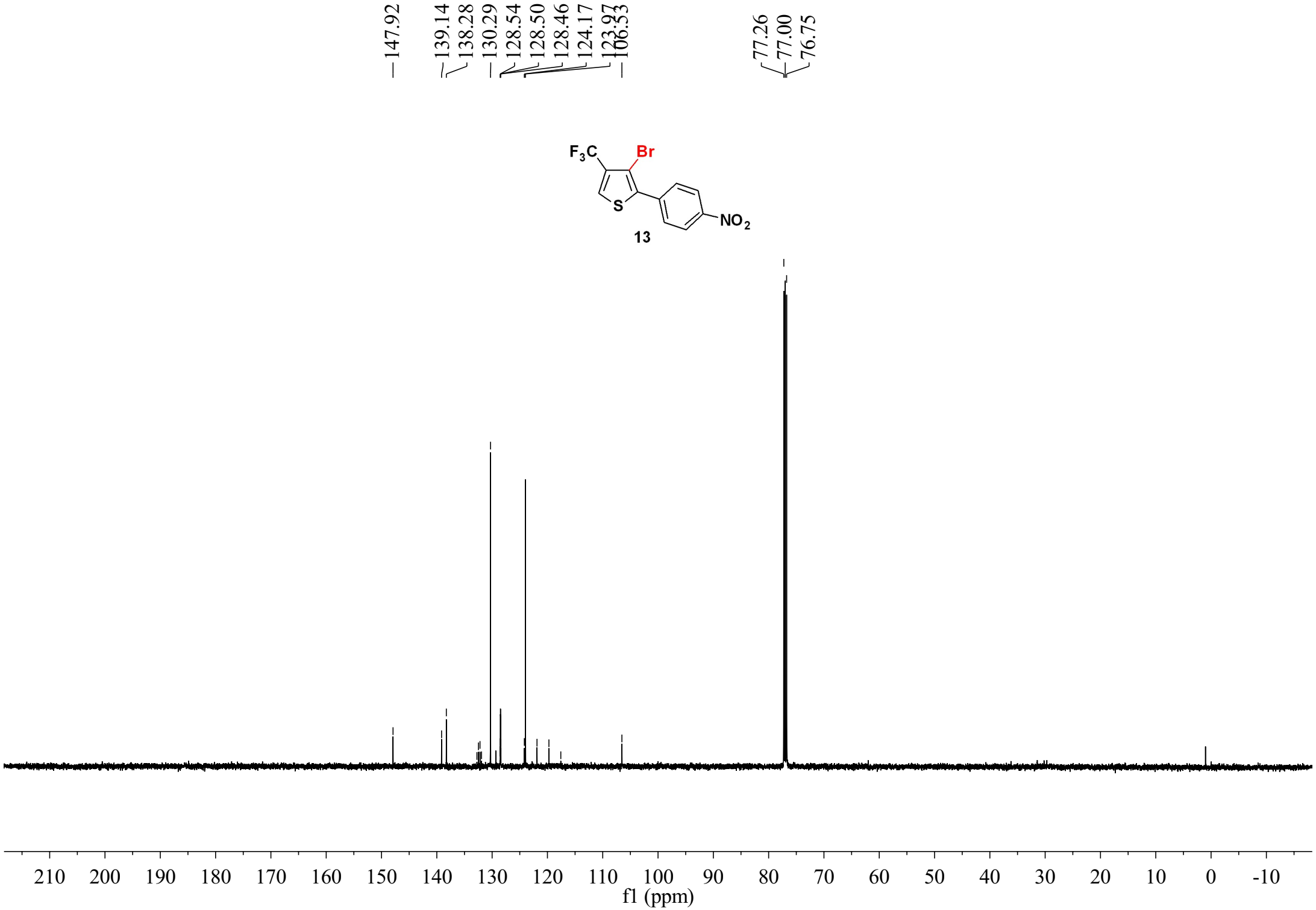

-62.530
F3C
Br
S
CN
11
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
f1 (ppm)

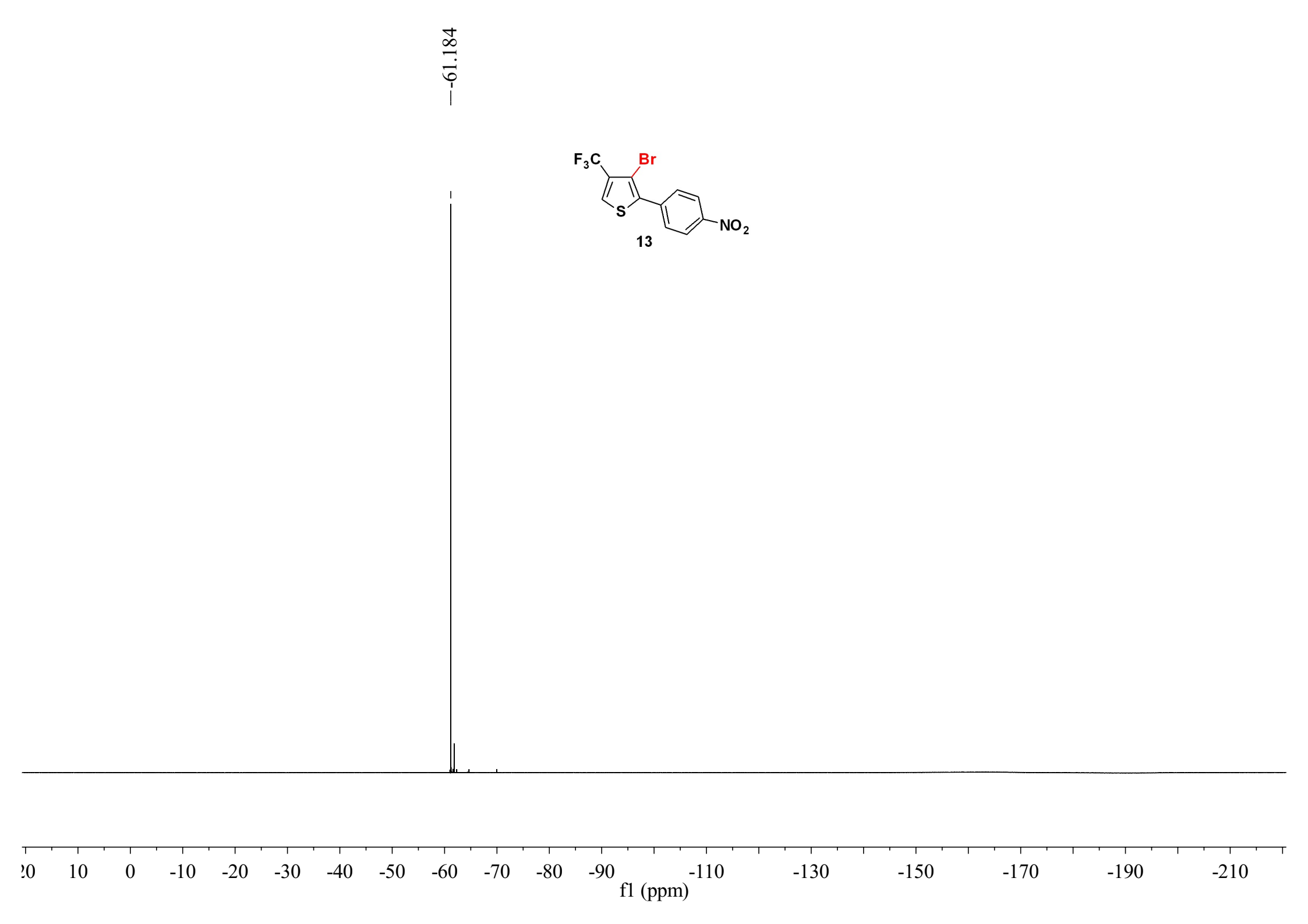

8.334
8.317
7.953
7.750
7.732
7.260
F3C
I
S
NO2
12
2.02
1.00
2.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


147.93
143.27
140.04
135.60
135.32
135.05
134.78
130.88
129.62
129.57
129.53
129.49
124.09
123.84
121.93
119.78
117.62
77.25
77.00
76.75
F3C
I
S
NO2
12
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)


-60.443
F3C
I
S
NO2
12
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


8.337
8.321
7.913
7.814
7.797
7.260
F3C
Br
S
NO2
13
2.05
1.00
2.02
0.5 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
f1 (ppm)


147.92
139.14
138.28
130.29
128.54
128.50
128.46
124.17
123.97
106.53
77.26
77.00
76.75
F3C
Br
S
NO2
13
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)


-61.184
F3C
Br
S
NO2
13
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)