Supporting Information

Solvent-controlled base-free synthesis of bis(trifluoromethyl)-cyclopropanes and -pyrazolines via cycloaddition of 2-trifluoromethyl-1,3-enynes with 2,2,2-trifluorodiazoethane

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General information

All reagents were of analytical grade, and were obtained from commercial suppliers and used without further purification. DCE、DMAc and other solvents were dried by a standard method prior to use. Melting points were measured in an open capillary using a Büchi melting point B-540 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR, respectively) using TMS as an internal standard. The ^{19}F NMR spectra were obtained using a 400 spectrometer (376 MHz) with $CDCl_3$ as the NMR solvent. The GC and GC-MS were recorded on HP 5973 MSD with 6890 GC. High resolution mass spectra (HRMS) were recorded under electron impact conditions using a MicroMass GCT CA 055 instrument and recorded on a MicroMass LCTTM spectrometer. Silica gel (300–400 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates.

Preparation of the stock solution of CF_3CHN_2

To an oven-dried 25 mL two-necked flask equipped with a stir bar were added $CF_3CH_2NH_2$·HCl (271 mg, 2 mmol) and 1,2-dichloroethane (DCE, 5 mL) under argon atmosphere. The tube was flushed with argon three times and sealed with a septum. Subsequently, the mixture was cooled to 0 ℃ and stirred for 30 min. To this mixture was slowly added a solution of $NaNO_2$ (0.5 mL, 4 M in water, degassed). The reaction mixture was stirred for 1 h at 0 ℃, then for an additional 30 min at 10 ℃ under Ar. The aqueous layer was frozen overnight. The organic layer was transferred with a Teflon needle to a flame-dried round-bottom flask and dried with Na_2SO_4. The light yellow solution of CF_3CHN_2 was stored in a refrigerator below 4 ℃ in the dark. The concentration of the stock solution of CF_3CHN_2 is about 0.5 M (^{19}F NMR using trifluorotoluene as an internal standard). Stock solutions of CF_3CHN_2 in DMAc (*N*,*N*-dimethylacetamide), CH_3CN, acetone, THF, EtOH, DMF (*N*,*N*-dimethylformamide), NMP (*N*-methylpyrrolidone), DMSO (dimethyl sulfoxide), CCl_4, hexane, ethyl acetate, dioxane, $CHCl_3$, toluene, Et_2O, DCM (dichloromethane), xylene, were prepared via the similar procedure.

General procedure for the synthesis of target compounds 3a−o

To a dried 10 mL Schlenk tube were added CF_3CHN_2 (3 mL, 1.5 mmol, 3.0 equiv., 0.5 M in DCE) and 2-CF_3-1,3-conjugated enynes (0.5 mmol, 1.0 equiv.) under an argon atmosphere. The reaction was stirred at 60 ℃ for 6 h. After the completion of the reaction, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (10 mL) and extracted with ethyl acetate (3 × 20 mL). The organic layer was separated and dried over Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (20/1) as eluent to afford the pure target compounds. The products have two isomers, of which **3a**, **3g**, **3m** and **3n** isomers have been separated, and the remaining products are mixtures of two isomers.

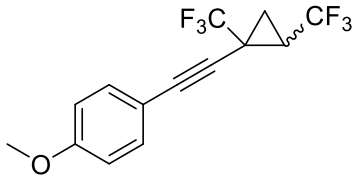
General procedure for the synthesis of target compounds 4a, 4f, 4h, 4j−o

To a dried 10 mL Schlenk tube were added CF_3CHN_2 (3 mL, 1.5 mmol, 3.0 equiv., 0.5 M in DMAc) and 2-trifluoromethyl-1,3-conjugated enynes (0.5 mmol, 1.0 equiv.) under an argon atmosphere. The reaction was stirred at 60 ℃ for 6 h. After the completion of the reaction, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (10 mL) and extracted with ethyl acetate (3 × 20 mL). The organic layer was separated and dried over Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (20/1) as eluent to afford the pure target compounds.

Reference:

1. Arkhipov, A. V.; Arkhipov, V. V.; Cossy, J.; Kovtunenko, V. O.; Mykhailiuk, P. K. *Org. Lett.* **2016**, *18*, 3406−3409.

Analytical data of compounds 3a−o



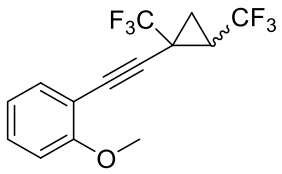
3a (isomer 1 + isomer 2)

1-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)-4-methoxybenzene (3a-isomer 1)

Oil; yield: 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 9.2 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.39−2.29 (m, 1H), 1.94−1.91 (m, 1H), 1.74−1.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 133.6, 123.5 (q, $^{1}J_{CF}$ = 272.0 Hz), 123.4 (q, $^{1}J_{CF}$ = 273.0 Hz), 114.0, 113.4, 81.8, 77.2, 55.3, 29.7 (q, $^{2}J_{CF}$ = 40.0 Hz), 22.6 (q, $^{2}J_{CF}$ = 40.0 Hz), 16.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −59.9 − −60.0 (m, 3F), −65.5 − −65.6 (m, 3F); HRMS (EI): calcd for $C_{14}H_{10}F_6O$ ([M]$^+$): 308.0636, found: 308.0638.

1-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)-4-methoxybenzene (3a-isomer 2)

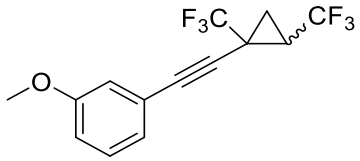
Oil; yield: 29%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 9.2 Hz, 2H), 3.69 (s, 3H), 2.22−2.13 (m, 1H), 1.63−1.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 132.5, 122.8 (q, $^{1}J_{CF}$ = 271.0 Hz), 122.6 (q, $^{1}J_{CF}$ = 273.0 Hz), 113.0, 112.8, 83.1, 76.1, 54.2, 23.7 (q, $^{2}J_{CF}$ = 37.6 Hz), 20.0 (q, $^{2}J_{CF}$ = 37.3 Hz), 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.6 (d, *J* = 6.4 Hz, 3F), −71.6 (s, 3F); HRMS (EI): calcd for $C_{14}H_{10}F_6O$ ([M]$^+$): 308.0636, found: 308.0638.



3b (isomer 1/isomer 2 = 66/34)

1-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)-2-methoxybenzene (3b (isomer 1 + isomer 2))

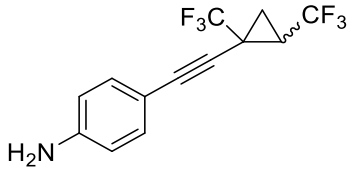
Oil; yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−6.86 (m, 4H, 0.66 × 4H isomer 1 + 0.34 × 4H isomer 2), 3.87 (s, 0.66 × 3H, isomer 1), 3.86 (s, 0.34 × 3H, isomer 2), 2.46−2.38 (m, 0.66 × 1H, isomer 1), 2.36−2.26 (m, 0.34 × 1H, isomer 2), 1.98−1.95 (m, 0.66 × 1H, isomer 1), 1.80−1.73 (m, 1.34H, 0.66 × 1H isomer 1 + 0.34 × 2H isomer 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 155.4, 128.6, 128.6, 125.3, 125.2, 118.5 (q, $^{1}J_{CF}$ = 271.0 Hz), 118.4 (q, $^{1}J_{CF}$ = 271.0 Hz), 118.2 (q, $^{1}J_{CF}$ = 273.0 Hz), 118.1 (q, $^{1}J_{CF}$ = 274.0 Hz), 115.1, 115.1, 105.8, 105.6, 105.5, 105.4, 81.7, 77.1, 75.4, 72.7, 50.4, 50.3, 24.5 (q, $^{2}J_{CF}$ = 41.0 Hz), 19.6 (q, $^{2}J_{CF}$ = 39.0 Hz), 17.6 (q, $^{2}J_{CF}$ = 38.0 Hz), 15.9 (q, $^{2}J_{CF}$ = 39.0 Hz), 11.3, 9.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −59.9 − −60.0 (m, 0.66 × 3F, isomer 1), −63.5 (d, *J* = 6.4 Hz, 0.34 × 3F, isomer 2), −65.3 − −65.4 (m, 0.66 × 3F, isomer 1), −71.5 (s, 0.34 × 3F, isomer 2); HRMS (EI): calcd for $C_{14}H_{10}F_6O$ ([M]$^+$): 308.0636, found: 308.0638.



3c (isomer 1/isomer 2 = 50/50)

1-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)-3-methoxybenzene (3c (isomer 1 + isomer 2))

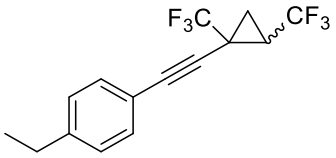
Oil; yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.19 (m, 1H, 0.5 × 1H isomer 1 + 0.5 × 1H isomer 2), 7.05−7.01 (m, 1H, 0.5 × 1H isomer 1 + 0.5 × 1H isomer 2), 6.95 (s, 1H, 0.5 × 1H isomer 1 + 0.5 × 1H isomer 2), 6.91−6.88 (m, 1H, 0.5 × 1H isomer 1 + 0.5 × 1H isomer 2), 3.78 (s, 3H, 0.5 × 3H isomer 1 + 0.5 × 3H isomer 2), 2.41−2.33 (m, 0.5 × 1H, isomer 1), 2.32−2.24 (m, 0.5 × 1H, isomer 2), 1.96−1.92 (m, 0.5 × 1H, isomer 1), 1.74−1.67 (m, 1.5H, 0.5 × 1H isomer 1 + 0.5 × 2H isomer 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 159.4, 129.5, 129.4, 124.5, 124.5, 123.7 (q, $^{1}J_{CF}$ = 273.0 Hz), 123.5 (q, $^{1}J_{CF}$ = 272.0 Hz), 123.4 (q, $^{1}J_{CF}$ = 273.0 Hz), 123.3 (q, $^{1}J_{CF}$ = 273.0 Hz), 122.6, 122.3, 116.8, 116.7, 115.8, 115.6, 84.0, 82.9, 81.3, 78.3, 55.2, 55.2, 29.3 (q, $^{2}J_{CF}$ = 40.0 Hz), 24.8 (q, $^{2}J_{CF}$ = 38.0 Hz), 22.5 (q, $^{2}J_{CF}$ = 40.0 Hz), 20.9 (q, $^{2}J_{CF}$ = 38.3 Hz), 16.4, 15.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.0 − −60.1 (m, 0.5 × 3F, isomer 1), −63.6 (d, *J* = 6.4 Hz, 0.5 × 3F, isomer 2), −65.4 − −65.5(m, 0.5 × 3F, isomer 1), −71.5 (s, 0.5 × 3F, isomer 2); HRMS (EI): calcd for $C_{14}H_{10}F_6O$ ($[M]^+$): 308.0636, found: 308.0634.



3d (isomer 1/isomer 2 = 25/75)

4-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)aniline (3d (isomer 1 + isomer 2))

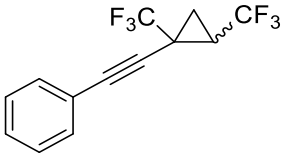
Oil; yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 2H, 0.25 × 2H isomer 1 + 0.75 × 2H isomer 2), 6.57 (d, *J* = 8.8 Hz, 2H, 0.25 × 2H isomer 1 + 0.75 × 2H isomer 2), 3.58 (s, 2H, 0.25 × 2H isomer 1 + 0.75 × 2H isomer 2), 2.35−2.30 (m, 0.25 × 1H isomer 1), 2.29−2.21 (m, 0.75 × 1H isomer 2), 1.92−1.89 (m, 0.25 × 1H isomer 1), 1.71−1.63 (m, 1.75H, 0.25 × 1H isomer 1 + 0.75 × 2H isomer 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 147.4, 133.5, 133.4, 123.8 (q, $^{1}J_{CF}$ = 271.0 Hz), 123.7 (q, $^{1}J_{CF}$ = 272.0 Hz), 123.6 (q, $^{1}J_{CF}$ = 273.0 Hz), 123.5 (q, $^{1}J_{CF}$ = 270.0 Hz), 114.6, 114.5, 110.8, 110.4, 84.7, 82.1, 81.0, 76.2, 29.7 (q, $^{2}J_{CF}$ = 40.0 Hz), 24.7 (q, $^{2}J_{CF}$ = 37.0 Hz), 22.6 (q, $^{2}J_{CF}$ = 37.0 Hz), 21.0 (q, $^{2}J_{CF}$ = 40.0 Hz), 16.5, 14.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −59.9 − −60.0 (m, 0.25 × 3F, isomer 1), −63.5 (d, *J* = 6.4 Hz, 0.75 × 3F, isomer 2), −65.5 − −65.6 (m, 0.25 × 3F, isomer 1), −71.6 (s, 0.75 × 3F, isomer 2); HRMS (EI): calcd for $C_{13}H_9F_6N$ ($[M]^+$): 293.0639, found: 293.0642.



3e (isomer 1/isomer 2 = 50/50)

1-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)-4-ethylbenzene (3e (isomer 1 + isomer 2))

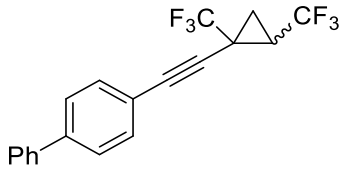
Oil; yield: 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 6.0 Hz, 0.5 × 1H × 2, isomer 1), 7.34 (d, *J* = 5.6 Hz, 0.5 × 1H × 2, isomer 2), 7.13 (d, *J* = 2.0 Hz, 0.5 × 1H × 2, isomer 1), 7.12 (d, *J* = 2.0 Hz, 0.5 × 1H × 2, isomer 2), 2.63−2.59 (m, 0.5 × 2H isomer 1 + 0.5 × 2H isomer 2), 2.39−2.31 (m, 0.5 × 1H, isomer 1), 2.30−2.22 (m, 0.5 × 1H, isomer 2), 1.94−1.90 (m, 0.5 × 1H, isomer 1), 1.72−1.64 (m, 1.5H, 0.5 × 1H isomer 1 + 0.5 × 2H isomer 2), 1.21 (t, *J* = 7.6 Hz, 0.5 × 3H, isomer 1), 1.20 (t, *J* = 7.6 Hz, 0.5 × 3H, isomer 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 145.6, 132.0, 131.9, 128.0, 127.9, 123.8 (q, $^{1}J_{CF}$ = 271 Hz), 123.6 (q, $^{1}J_{CF}$ = 271.8 Hz), 123.5 (q, $^{1}J_{CF}$ = 273.2 Hz), 123.4 (q, $^{1}J_{CF}$ = 273.1 Hz), 118.9, 118.5, 84.2, 82.5, 81.6, 77.8, 29.7 (q, $^{2}J_{CF}$ = 40.3 Hz), 28.9, 28.8, 24.8 (q, $^{2}J_{CF}$ = 37.7 Hz, $^{3}J_{CF}$ = 2.2 Hz), 22.6 (q, $^{2}J_{CF}$ = 39.8 Hz, $^{3}J_{CF}$ = 2.7 Hz), 21.0 (q, $^{2}J_{CF}$ = 38.3 Hz, $^{3}J_{CF}$ = 2.2 Hz), 16.4, 15.3, 15.2, 14.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.0 − −60.1 (m, 0.5 × 3F, isomer 1), −63.6 (d, *J* = 6.4 Hz, 0.5 × 3F, isomer 2), −65.5 − −65.6 (m, 0.5 × 3F, isomer 1), −71.6 (s, 0.5 × 3F, isomer 2); HRMS (EI): calcd for $C_{15}H_{12}F_6$ ($[M]^+$): 306.0843, found: 306.0841.



3f (isomer 1/isomer 2 = 50/50)

((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)benzene (3f (isomer 1 + isomer 2))

Oil; yield: 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.28 (m, 5H, 0.5 × 5H isomer 1 + 0.5 × 5H isomer 2), 2.40−2.32 (m, 0.5 × 1H, isomer 1), 2.32−2.24 (m, 0.5 × 1H, isomer 2), 1.95−1.92 (m, 0.5 × 1H, isomer 1), 1.73−1.66 (m, 1.5H, 0.5 × 1H isomer 1 + 0.5 × 2H isomer 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0, 131.9, 128.0, 127.9, 123.8 (q, $^{1}J_{CF}$ = 271 Hz), 123.6 (q, $^{1}J_{CF}$ = 271.8 Hz), 123.5 (q, $^{1}J_{CF}$ = 273.2 Hz), 123.4 (q, $^{1}J_{CF}$ = 273.1 Hz), 118.9, 118.5, 84.2, 82.5, 81.6, 77.8, 29.7 (q, $^{2}J_{CF}$ = 40.3 Hz), 28.9, 28.8, 24.8 (q, $^{2}J_{CF}$ = 37.7 Hz, $^{3}J_{CF}$ = 2.2 Hz), 22.6 (q, $^{2}J_{CF}$ = 39.8 Hz, $^{3}J_{CF}$ = 2.7 Hz), 21.0 (q, $^{2}J_{CF}$ = 38.3 Hz, $^{3}J_{CF}$ = 2.2 Hz), 16.4, 15.3, 15.2, 14.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.0 − −60.1 (m, 0.5 × 3F, isomer 1), −63.6 (d, *J* = 6.4 Hz, 0.5 × 3F, isomer 2), −65.4 − −65.5 (m, 0.5 × 3F, isomer 1), −71.5 (s, 0.5 × 3F, isomer 2); HRMS (EI): calcd for $C_{13}H_8F_6$ ($[M]^+$): 278.0530, found: 278.0532.



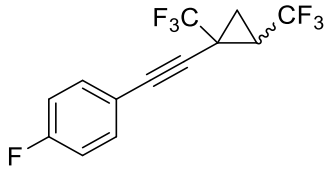
3g (isomer 1 + isomer 2)

4-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)-1,1'-biphenyl (3g-isomer 1)

Yellow soild; m.p.: 96.3−97.6 ℃; yield: 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.27 (m, 9H), 2.36−2.26 (m, 1H), 1.91−1.87 (m, 1H), 1.70−1.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 140.1, 132,5, 128.9, 127.9, 127.1, 123.5 (q, $^{1}J_{CF}$ = 272.0 Hz), 123.3 (q, $^{1}J_{CF}$ = 273.0 Hz), 120.2, 83.8, 81.3, 29.7 (q, $^{2}J_{CF}$ = 40.0 Hz), 22.6 (q, $^{2}J_{CF}$ = 43.0 Hz), 16.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −59.9 − −60.0 (m, 3F), −65.3 − −65.4 (m, 3F); HRMS (EI): calcd for $C_{19}H_{12}F_6$ ([M]$^+$): 354.0843, found: 354.0845.

4-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)-1,1'-biphenyl (3g-isomer 2)

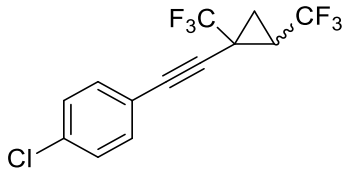
Yellow soild; m.p.: 96.9−97.7 ℃; yield: 28%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.32 (m, 9H), 2.34−2.25 (m, 1H), 1.75−1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 140.2, 132,4, 128.9, 127.8, 127.1, 127.0, 123.7 (q, $^{1}J_{CF}$ = 272.0 Hz), 123.5 (q, $^{1}J_{CF}$ = 273.0 Hz), 120.6, 84.0, 79.2, 24.9 (q, $^{2}J_{CF}$ = 38.0 Hz), 21.0 (q, $^{2}J_{CF}$ = 36.0 Hz), 15.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.5 (d, J = 6.4 Hz, 3F), −71.4 (s, 3F); HRMS (EI): calcd for $C_{19}H_{12}F_6$ ([M]$^+$): 354.0843, found: 354.0845.



3h (isomer 1/isomer 2 = 50/50)

1-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)-4-fluorobenzene (3h (isomer 1 + isomer 2))

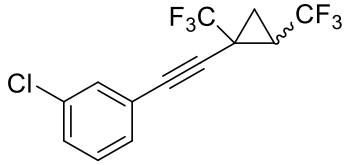
Oil; yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.39 (m, 2H, 0.5 × 2H isomer 1 + 0.5 × 2H isomer 2), 7.03−6.98 (m, 2H, 0.5 × 2H isomer 1 + 0.5 × 2H isomer 2), 2.40−2.32 (m, 0.5 × 1H, isomer 1), 2.31−2.25 (m, 0.5 × 1H, isomer 2), 1.96−1.93 (m, 0.5 × 1H, isomer 1), 1.75−1.66 (m, 1.5H, 0.5 × 1H isomer 1 + 0.5 × 2H isomer 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, $^{1}J_{CF}$ = 250.0 Hz), 162.9 (d, $^{1}J_{CF}$ = 249.0 Hz), 134.0 (d, $^{3}J_{CF}$ = 8.0 Hz), 133.9 (d, $^{3}J_{CF}$ = 8.0 Hz), 123.7 (q, $^{1}J_{CF}$ = 271.0 Hz), 123.5 (q, $^{1}J_{CF}$ = 272.0 Hz), 123.4 (q, $^{1}J_{CF}$ = 273.0 Hz), 123.3 (q, $^{1}J_{CF}$ = 273.0 Hz), 117.7 (d, $^{4}J_{CF}$ = 3.0 Hz), 117.4 (d, $^{4}J_{CF}$ = 4.0 Hz), 115.7 (d, $^{2}J_{CF}$ = 22.0 Hz), 115.6 (d, $^{2}J_{CF}$ = 23.0 Hz), 83.0, 82.9, 80.4, 78.3, 29.6 (q, $^{2}J_{CF}$ = 41.0 Hz), 24.8 (q, $^{2}J_{CF}$ = 36.0 Hz), 22.5 (q, $^{2}J_{CF}$ = 40.0 Hz), 20.9 (q, $^{2}J_{CF}$ = 41.0 Hz), 16.4, 14.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.0 − −60.1 (m, 0.5 × 3F, isomer 1), −63.7 (d, J = 6.4 Hz, 0.5 × 3F, isomer 2), −65.4 − −65.5 (m, 0.5 × 3F, isomer 1), −71.5 (s, 0.5 × 3F, isomer 2), −109.3 − −109.4 (m, 0.5 × 1F, isomer 1), −109.6 − −109.7 (m, 0.5 × 1F, isomer 2); HRMS (EI): calcd for $C_{13}H_7F_7$ ([M]$^+$): 296.0436, found: 296.0438.



3i (isomer 1/isomer 2 = 50/50)

1-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)-4-chlorobenzene (3i (isomer 1 + isomer 2))

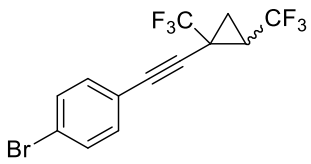
Oil; yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 3.6 Hz, 0.5 × 1H × 2, isomer 1), 7.35 (d, *J* = 3.6 Hz, 0.5 × 1H × 2, isomer 2), 7.29 (d, *J* = 2.8 Hz, 0.5 × 1H × 2, isomer 1), 7.27 (d, *J* = 2.4 Hz, 0.5 × 1H × 2, isomer 2), 2.41−2.33 (m, 0.5 × 1H, isomer 1), 2.31−2.26 (m, 0.5 × 1H, isomer 2), 1.97−1.93 (m, 0.5 × 1H, isomer 1), 1.76−1.67 (m, 1.5H, 0.5 × 1H isomer 1 + 0.5 × 2H isomer 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 135.2, 133.2, 133.1, 128.8, 128.7, 123.6 (q, $^{1}J_{CF}$ = 271.0 Hz), 123.4 (q, $^{1}J_{CF}$ = 272.0 Hz), 123.3 (q, $^{1}J_{CF}$ = 274.0 Hz), 123.2 (q, $^{1}J_{CF}$ = 273.0 Hz), 120.1, 119.8, 84.1, 83.0, 80.3, 79.6, 29.6 (q, $^{2}J_{CF}$ = 40.0 Hz), 24.8 (q, $^{2}J_{CF}$ = 40.0 Hz), 22.5 (q, $^{2}J_{CF}$ = 40.0 Hz), 20.9 (q, $^{2}J_{CF}$ = 38.0 Hz), 16.4, 15.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.0 − −60.1 (m, 0.5 × 3F, isomer 1), −63.6 (d, *J* = 6.4 Hz, 0.5 × 3F, isomer 2), −65.3 − −65.4 (m, 0.5 × 3F, isomer 1), −71.4 (s, 0.5 × 3F, isomer 2); HRMS (EI): calcd for $C_{13}H_7F_6Cl$ ($[M]^+$): 312.0140, found: 312.0141.



3j (isomer 1/isomer 2 = 70/30)

1-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)-3-chlorobenzene (3j (isomer 1 + isomer 2))

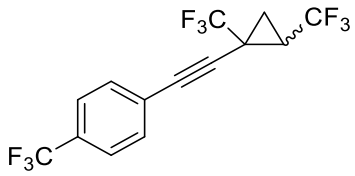
Oil; yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H, 0.7 × 1H isomer 1 + 0.3 × 1H isomer 2), 7.26−7.13 (m, 3H, 0.7 × 1H isomer 1 + 0.3 × 3H isomer 2), 2.33−2.26 (m, 0.7 × 1H, isomer 1), 2.25−2.19 (m, 0.3 × 1H, isomer 2), 1.90−1.86 (m, 0.7 × 1H, isomer 1), 1.69−1.60 (m, 1.3H, 0.7 × 1H isomer 1 + 0.3 × 2H isomer 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.3, 133.2, 130.9, 130.8, 129.1, 129.1, 128.6, 128.6, 128.5, 128.3, 122.6 (q, $^{1}J_{CF}$ = 271.0 Hz), 122.4 (q, $^{1}J_{CF}$ = 272.0 Hz), 122.3 (q, $^{1}J_{CF}$ = 273.0 Hz), 122.3, 122.2 (q, $^{1}J_{CF}$ = 271.0 Hz), 122.1, 83.3, 81.7, 79.0, 78.9, 28.7 (q, $^{2}J_{CF}$ = 40.0 Hz), 23.9 (q, $^{2}J_{CF}$ = 38.0 Hz), 21.5 (q, $^{2}J_{CF}$ = 40.0 Hz), 19.9 (q, $^{2}J_{CF}$ = 38.0 Hz), 15.4, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.1 − −60.2 (m, 0.7 × 3F, isomer 1), −63.7 (d, *J* = 6.4 Hz, 0.3 × 3F, isomer 2), −65.3 − −65.4 (m, 0.7 × 3F, isomer 1), −71.4 (s, 0.3 × 3F, isomer 2); HRMS (EI): calcd for $C_{13}H_7F_6Cl$ ($[M]^+$): 312.0140, found: 312.0142.



3k (isomer 1/isomer 2 = 50:50)

1-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)-4-bromobenzene (3k (isomer 1 + isomer 2))

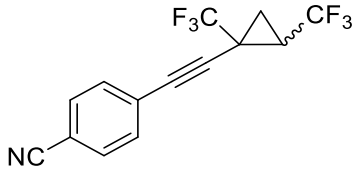
Oil; yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d *J* = 2.4 Hz, 0.5 × 1H × 2, isomer 1), 7.43 (d, *J* = 2.8 Hz, 0.5 × 1H × 2, isomer 2), 7.30 (d *J* = 4.0 Hz, 0.5 × 1H × 2, isomer 1), 7.27 (d, *J* = 3.6 Hz, 0.5 × 1H × 2, isomer 2), 2.41−2.33 (m, 0.5 × 1H, isomer 1), 2.32−2.26 (m, 0.5 × 1H, isomer 2), 1.97−1.94 (m, 0.5 × 1H, isomer 1), 1.76−1.67 (m, 1.5H, 0.5 × 1H isomer 1 + 0.5 × 2H isomer 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.4, 133.3, 131.7, 131.6, 123.6 (q, $^1J_{CF}$ = 271.0 Hz), 123.6, 123.4, 123.4 (q, $^1J_{CF}$ = 272.0 Hz), 123.3 (q, $^1J_{CF}$ = 273.0 Hz), 123.2 (q, $^1J_{CF}$ = 273.0 Hz), 120.6, 120.3, 84.3, 83.0, 80.4, 79.8, 29.6 (q, $^2J_{CF}$ = 40.0 Hz), 24.8 (q, $^2J_{CF}$ = 40.0 Hz), 22.5 (q, $^2J_{CF}$ = 40.0 Hz), 20.9 (q, $^2J_{CF}$ = 39.0 Hz), 16.4, 15.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.0 − −60.1 (m, 0.5 × 3F, isomer 1), −63.6 (d, *J* = 6.4 Hz, 0.5 × 3F, isomer 2), −65.3 − −65.4 (m, 0.5 × 3F, isomer 1), −71.4 (s, 0.5 × 3F, isomer 2); HRMS (EI): calcd for $C_{13}H_7F_6Br$ ($[M]^+$): 355.9635, found: 355.9636.



3l (isomer 1/isomer 2 = 50/50)

1-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)-4-(trifluoromethyl)benzene (3l (isomer 1 + isomer 2))

Oil; yield: 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.52 (m, 4H, 0.5 × 4H isomer 1 + 0.5 × 4H isomer 2), 2.44−2.36 (m, 0.5 × 1H, isomer 1), 2.34−2.29 (m, 0.5 × 1H, isomer 2), 2.00−1.96 (m, 0.5 × 1H, isomer 1), 1.79−1.71 (m, 1.5H, 0.5 × 1H isomer 1 + 0.5 × 2H isomer 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.8, 132.2, 132.1, 130.9 (q, $^2J_{CF}$ = 32.7 Hz), 130.8 (q, $^2J_{CF}$ = 32.6 Hz), 125.3−125.1 (m, 2C), 123.8 (q, $^1J_{CF}$ = 270.6 Hz), 123.7 (q, $^1J_{CF}$ = 270.5 Hz), 123.6 (q, $^1J_{CF}$ = 270.8 Hz), 123.4 (q, $^1J_{CF}$ = 271.8 Hz), 123.3 (q, $^1J_{CF}$ = 273.3 Hz), 123.2 (q, $^1J_{CF}$ = 273.2 Hz), 85.5, 82.7, 81.1, 80.0, 29.7 (q, $^2J_{CF}$ = 40.4 Hz), 24.9 (q, $^2J_{CF}$ = 37.8 Hz), 22.5 (q, $^2J_{CF}$ = 39.9 Hz), 20.9 (q, $^2J_{CF}$ = 38.6 Hz), 16.4, 15.0; ^{19}F NMR (376 MHz, $CDCl_3$ δ −60.2 − −60.3 (m, 0.5 × 3F, isomer 1), −63.1 (s, 0.5 × 3F, isomer 1), −63.1 (s, 0.5 × 3F, isomer 2), −63.8 (d, *J* = 6.4 Hz, 0.5 × 3F, isomer 2), −65.3 − −65.4 (m, 0.5 × 3F, isomer 1), −71.4 (s, 0.5 × 3F, isomer 2); HRMS (EI): calcd for $C_{14}H_7F_9$ ($[M]^+$): 346.0404, found: 346.0406.



3m (isomer 1 + isomer 2)

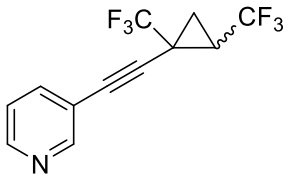
4-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)benzonitrile (3m-isomer 1)

Oil; yield: 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 2.46−2.36 (m, 1H), 2.04−1.99 (m, 1H), 1.82−1.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5, 132.1, 126.2, 123.3 (q, $^1J_{CF}$ = 272.0 Hz), 123.1 (q, $^1J_{CF}$ = 273.0 Hz), 118.1, 112.6, 87.4, 79.8, 29.7 (q, $^2J_{CF}$ = 39.0 Hz), 22.5 (q, $^2J_{CF}$ = 40.0 Hz),

16.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.1 – −60.2 (m, 3F), −65.1 – −65.2 (m, 3F); HRMS (EI): calcd for $C_{14}H_7F_6N$ ($[M]^+$): 303.0483, found: 303.0487.

4-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)benzonitrile (3m-isomer 2)

Oil; yield: 26%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 2.41−2.32 (m, 1H), 1.82−1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3, 132.0, 126.3, 123.5 (q, $^1J_{CF}$ = 270.0 Hz), 123.2 (q, $^1J_{CF}$ = 273.0 Hz), 118.1, 112.5, 83.0, 82.3, 25.0 (q, $^2J_{CF}$ = 37.0 Hz), 20.8 (q, $^2J_{CF}$ = 37.0 Hz), 15.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.7 (d, *J* = 3.7 Hz, 3F), −71.3 (s, 3F); HRMS (EI): calcd for $C_{14}H_7F_6N$ ($[M]^+$): 303.0483, found: 303.0487.



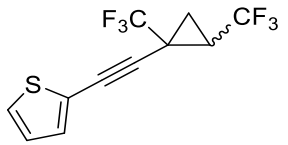
3n (isomer 1 + isomer 2)

3-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)pyridine (3n-isomer 1)

Oil; yield: 56%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.58 (d, *J* = 3.2 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.29−7.26 (m, 1H), 2.46−2.36 (m, 1H), 2.01−1.98 (m, 1H), 1.81−1.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 149.4, 139.0, 123.3 (q, $^1J_{CF}$ = 272.0 Hz), 123.1 (q, $^1J_{CF}$ = 274.0 Hz), 123.0, 118.6, 86.6, 78.2, 29.7 (q, $^2J_{CF}$ = 40.0 Hz), 22.5 (q, $^2J_{CF}$ = 40.0 Hz), 16.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.1 – −60.2 (m, 3F), −65.2 – −65.3 (m, 3F); HRMS (EI): calcd for $C_{12}H_7F_6N$ ($[M]^+$): 279.0483, found: 279.0486.

3-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)pyridine (3n-isomer 2)

Oil; yield: 30%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.57 (d, *J* = 3.6 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.29−7.25 (m, 1H), 2.40−2.31 (m, 1H), 1.81−1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 149.3, 138.9, 123.5 (q, $^1J_{CF}$ = 271.0 Hz), 123.2 (q, $^1J_{CF}$ = 273.0 Hz), 123.0, 118.9, 82.1, 80.8, 24.9 (q, $^2J_{CF}$ = 38.0 Hz), 20.8 (q, $^2J_{CF}$ = 38.0 Hz), 15.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.7 (d, *J* = 6.4 Hz, 3F), −71.4 (s, 3F); HRMS (EI): calcd for $C_{12}H_7F_6N$ ($[M]^+$): 279.0483, found: 279.0486.



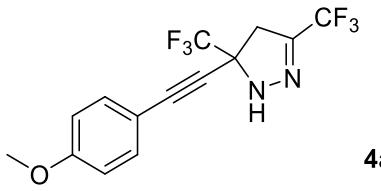
3o (isomer 1/isomer 2 = 50/50)

3-((1,2-Bis(trifluoromethyl)cyclopropyl)ethynyl)thiophene (3o (isomer 1 + isomer 2))

Oil; yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.48 (m, 1H, 0.5 × 1H isomer 1 + 0.5 × 1H isomer 2), 7.25−7.23 (m, 1H, 0.5 × 1H isomer 1 + 0.5 × 1H isomer 2), 7.11−7.09 (m, 1H, 0.5 × 1H isomer 1 + 0.5 × 1H isomer 2), 2.39−2.33 (m, 0.5 × 1H, isomer 1), 2.31−2.23 (m, 0.5 × 1H, isomer 2), 1.95−1.91 (m, 0.5 × 1H, isomer 1), 1.73−1.65 (m, 1.5H, 0. 5 × 1H isomer 1 + 0.5 × 2H isomer 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.3, 130.2, 129.9,

129.8, 125.6, 125.4, 123.8 (q, $^1J_{CF}$ = 271.0 Hz), 123.6 (q, $^1J_{CF}$ = 272.0 Hz), 123.5 (q, $^1J_{CF}$ = 273.0 Hz), 123.4 (q, $^1J_{CF}$ = 273.0 Hz), 120.8, 120.5, 82.8, 79.3, 78.3, 76.6, 29.6 (q, $^2J_{CF}$ = 40.0 Hz), 24.8 (q, $^2J_{CF}$ = 38.0 Hz), 22.6 (q, $^2J_{CF}$ = 40.0 Hz), 21.0 (q, $^2J_{CF}$ = 38.0 Hz), 16.3, 14.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.0 − −60.1 (m, 0.5 × 3F, isomer 1), −63.6 (d, *J* = 7.5 Hz, 0.5 × 3F, isomer 2), −65.4 − −65.5 (m, 0.5 × 3F, isomer 1), −71.5 (s, 0.5 × 3F, isomer 2); HRMS (EI): calcd for $C_{11}H_6F_6S$ ($[M]^+$): 284.0094, found: 284.0096.

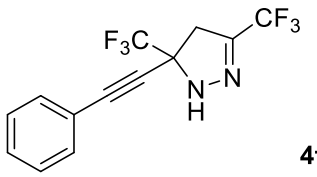
Analytical data of compounds 4a, 4f, 4h, 4j−o



4a

5-((4-Methoxyphenyl)ethynyl)-3,5-bis(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole (4a)

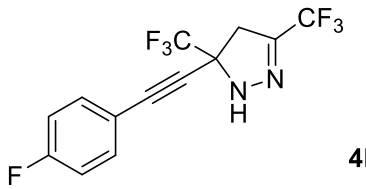
Oil; yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 9.2 Hz, 2H), 6.33 (s, 1H), 3.72 (s, 3H), 3.35 (d, *J* = 17.6 Hz, 1H), 3.27 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 140.2 (q, $^2J_{CF}$ = 38.0 Hz), 133.6, 123.6 (q, $^1J_{CF}$ = 280.0 Hz), 119.7 (q, $^1J_{CF}$ = 268.0 Hz), 114.1, 112.4, 88.7, 80.2, 66.2 (q, $^2J_{CF}$ = 32.0 Hz), 55.3, 40.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.0 (s, 3F), −78.0 (s, 3F); HRMS (EI): calcd for $C_{14}H_{10}F_6N_2O$ ($[M]^+$): 336.0697, found: 336.0695.



4f

5-(Phenylethynyl)-3,5-bis(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole (4f)

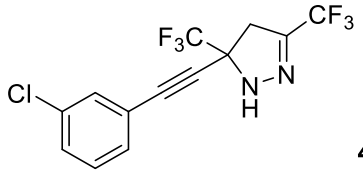
Oil; yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.33 (m, 5H), 6.43 (s, 1H), 3.45 (d, *J* = 17.6 Hz, 1H), 3.37 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4 (q, $^2J_{CF}$ = 38.0 Hz), 132.0, 129.8, 128.5, 123.5 (q, $^1J_{CF}$ = 280.0 Hz), 120.5, 119.7 (q, $^1J_{CF}$ = 268.0 Hz), 88.6, 81.4, 66.2 (q, $^2J_{CF}$ = 33.0 Hz), 40.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.0 (s, 3F), −78.0 (s, 3F); HRMS (EI): calcd for $C_{13}H_8F_6N_2$ ($[M]^+$): 306.0592, found: 306.0595.



4h

5-((4-Fluorophenyl)ethynyl)-3,5-bis(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole (4h)

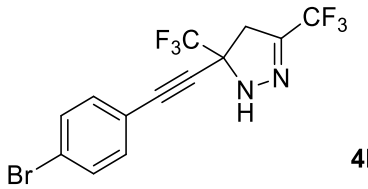
Oil; yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.42 (m, 2H), 7.07−7.01 (m, 2H), 6.41 (s, 1H), 3.46 (d, *J* = 17.6 Hz, 1H), 3.37 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, $^1J_{CF}$ = 250.0 Hz), 140.3 (q, $^2J_{CF}$ = 38.0 Hz), 134.1 (d, $^3J_{CF}$ = 9.0 Hz), 123.5 (q, $^1J_{CF}$ = 279.0 Hz), 119.6 (q, $^1J_{CF}$ = 268.0 Hz), 116.6 (d, $^4J_{CF}$ = 4.0 Hz), 115.9 (d, $^2J_{CF}$ = 22.0 Hz), 87.6, 81.2, 66.6 (q, $^2J_{CF}$ = 32.0 Hz), 40.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.1 (s, 3F), −78.0 (s, 3F), −108.2 − −108.3 (m, 1F); HRMS (EI): calcd for $C_{13}H_7F_7N_2$ ([M]$^+$): 324.0497, found: 324.0495.



4j

5-((3-Chlorophenyl)ethynyl)-3,5-bis(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole (4j)

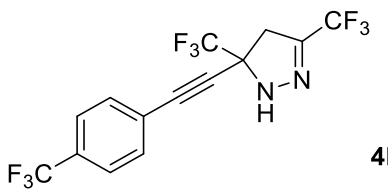
Oil; yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.28 (m, 4H), 6.43 (s, 1H), 3.47 (d, *J* = 17.6 Hz, 1H), 3.38 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3 (q, $^2J_{CF}$ = 39.0 Hz), 134.4, 131.8, 130.1, 129.7, 123.4 (q, $^1J_{CF}$ = 279.0 Hz), 122.1, 119.6 (q, $^1J_{CF}$ = 268.0 Hz), 87.1, 82.5, 66.1 (q, $^2J_{CF}$ = 33.0 Hz), 40.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.0 (s, 3F), −78.0 (s, 3F); HRMS (EI): calcd for $C_{13}H_7F_6N_2Cl$ ([M]$^+$): 340.0202, found: 340.0203.



4k

5-((4-Bromophenyl)ethynyl)-3,5-bis(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole (4k)

Oil; yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.43 (s, 1H), 3.47 (d, *J* = 17.6 Hz, 1H), 3.38 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3 (q, $^2J_{CF}$ = 39.0 Hz), 133.4, 131.9, 124.4, 123.4 (q, $^1J_{CF}$ = 280.0 Hz), 119.6 (q, $^1J_{CF}$ = 269.0 Hz), 119.3, 87.5, 82.5, 66.1 (q, $^2J_{CF}$ = 32.0 Hz), 40.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −66.9 (s, 3F), −77.9 (s, 3F); HRMS (EI): calcd for $C_{13}H_7F_6N_2Br$ ([M]$^+$): 385.9676, found: 385.9677.

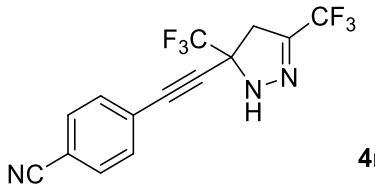


4l

3,5-Bis(trifluoromethyl)-5-((4-(trifluoromethyl)phenyl)ethynyl)-4,5-dihydro-1*H*-pyrazole (4l)

Oil; yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 6.50 (s, 1H), 3.49 (d, *J* = 17.6 Hz, 1H), 3.41 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4 (q, $^2J_{CF}$ = 39.0 Hz), 132.3,

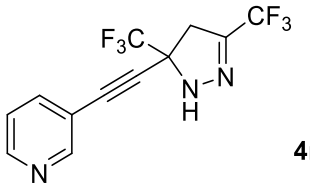
131.5 (q, $^{2}J_{CF}$ = 33.0 Hz), 125.4 (q, $^{3}J_{CF}$ = 4.0 Hz), 124.2, 123.6 (q, $^{1}J_{CF}$ = 271.0 Hz), 123.4 (q, $^{1}J_{CF}$ = 279.0 Hz), 119.6 (q, $^{1}J_{CF}$ = 269.0 Hz), 87.0, 83.5, 66.1 (q, $^{2}J_{CF}$ = 33.0 Hz), 40.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.2 (s, 3F), −67.1 (s, 3F), −78.0 (s, 3F); HRMS (EI): calcd for $C_{14}H_7F_9N_2$ ([M]$^+$): 374.0466, found: 374.0468.



4m

4-((3,5-Bis(trifluoromethyl)-4,5-dihydro-1*H*-pyrazol-5-yl)ethynyl)benzonitrile (4m)

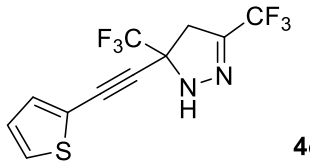
Oil; yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 6.53 (s, 1H), 3.50 (d, *J* = 17.6 Hz, 1H), 3.41 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2 (q, $^{2}J_{CF}$ = 38.0 Hz), 132.6, 132.2, 125.2, 123.3 (q, $^{1}J_{CF}$ = 279.0 Hz), 119.6 (q, $^{1}J_{CF}$ = 268.0 Hz), 118.0, 113.3, 86.6, 85.3, 66.0 (q, $^{2}J_{CF}$ = 32.0 Hz), 40.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.0 (s, 3F), −77.9 (s, 3F); HRMS (EI): calcd for $C_{14}H_7F_6N_3$ ([M]$^+$): 331.0544, found: 331.0541.



4n

3-((3,5-Bis(trifluoromethyl)-4,5-dihydro-1*H*-pyrazol-5-yl)ethynyl)pyridine (4n)

Oil; yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.61−8.60 (m, 1H), 7.77−7.74 (m, 1H), 7.65 (s, 1H), 7.32–7.29 (m, 1H), 3.50 (d, *J* = 17.6 Hz, 1H), 3.42 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 149.7, 139.4 (q, $^{2}J_{CF}$ = 39.0 Hz), 139.2, 123.5 (q, $^{1}J_{CF}$ = 279.0 Hz), 123.2, 119.7 (q, $^{1}J_{CF}$ = 268.0 Hz), 117.9, 85.2, 84.8, 66.0 (q, $^{2}J_{CF}$ = 32.0 Hz), 40.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −66.9 (s, 3F), −78.0 (s, 3F); HRMS (EI): calcd for $C_{12}H_7F_6N_3$ ([M]$^+$): 307.0544, found: 307.0541.



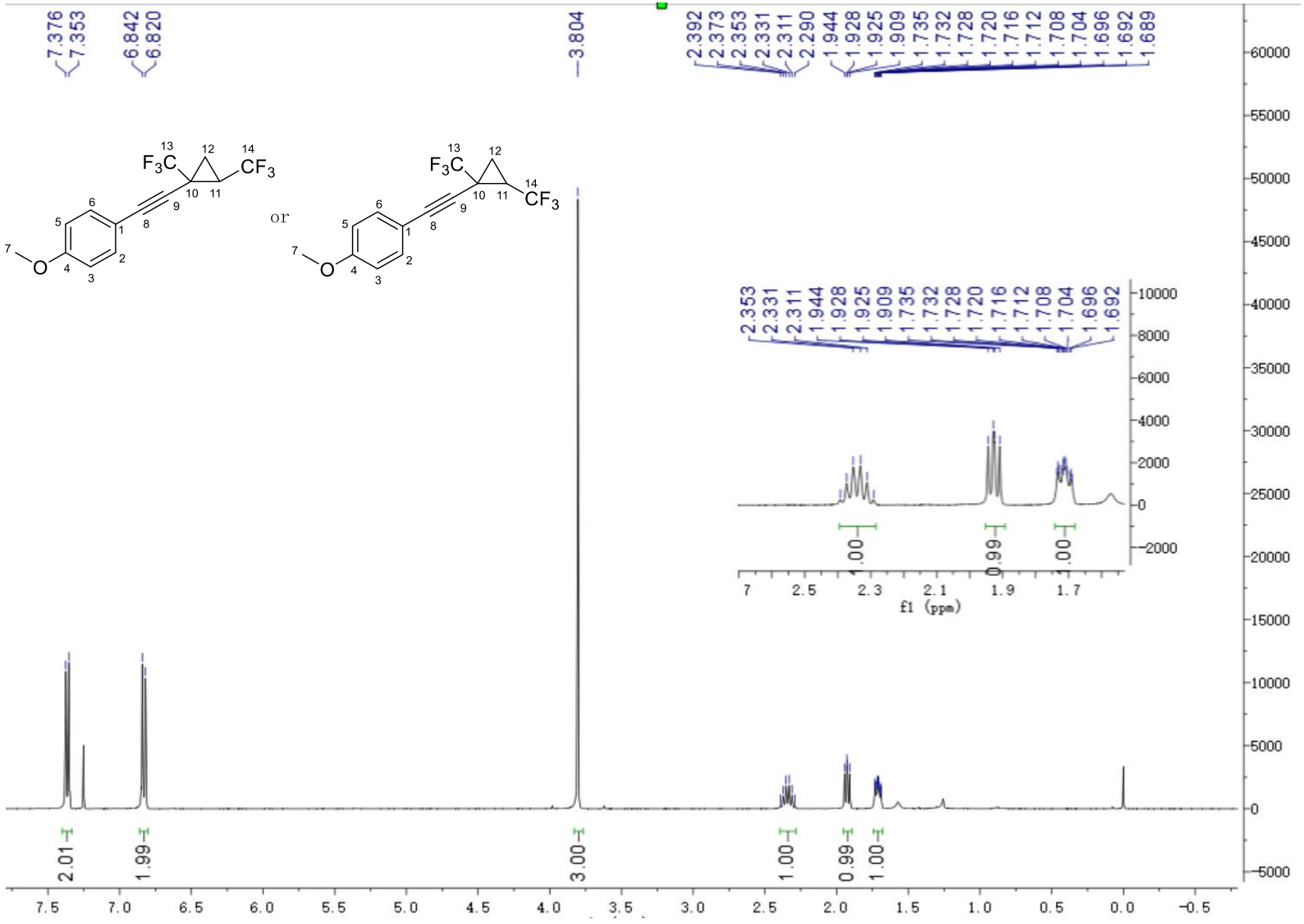
4o

5-(Thiophen-3-ylethynyl)-3,5-bis(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole (4o)

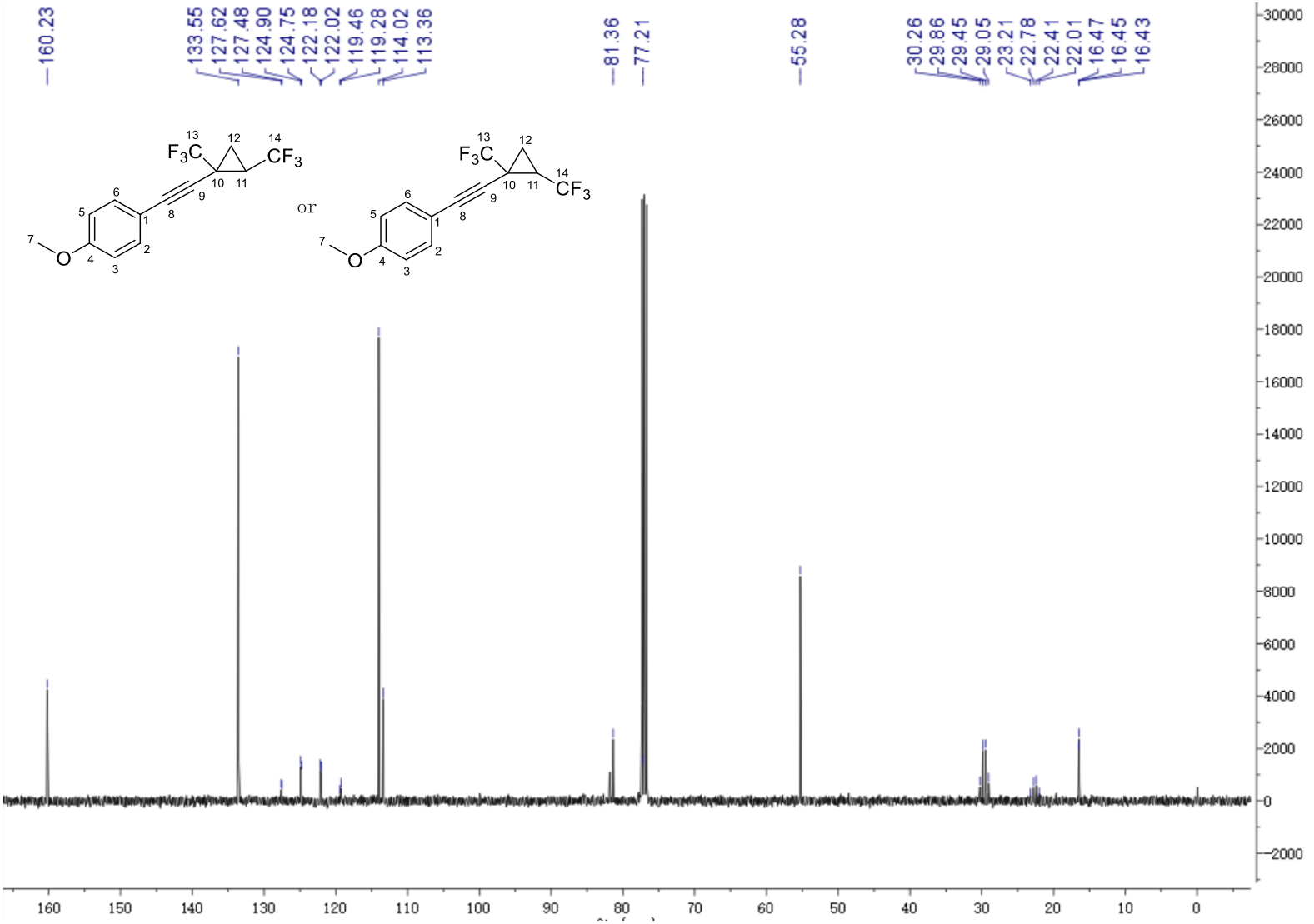
Oil; yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.55 (m, 1H), 7.30–7.28 (m, 1H), 7.13–7.12 (m, 1H), 6.37 (s, 1H), 3.45 (d, *J* = 17.6 Hz, 1H), 3.36 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3 (q, $^{2}J_{CF}$ = 38.0 Hz), 131.1, 129.7, 125.9, 123.5 (q, $^{1}J_{CF}$ = 279.0 Hz), 119.7 (q, $^{1}J_{CF}$ = 269.0 Hz), 119.5, 83.9, 81.2, 66.2 (q, $^{2}J_{CF}$ = 33.0 Hz), 40.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −66.9 (s, 3F), −77.9 (s, 3F); HRMS (EI): calcd for $C_{11}H_6F_6N_2S$ ([M]$^+$): 312.0156, found: 312.0154.

^{1}H, ^{13}C, ^{19}F NMR and HRMS (EI) spectra of compounds 3a−o

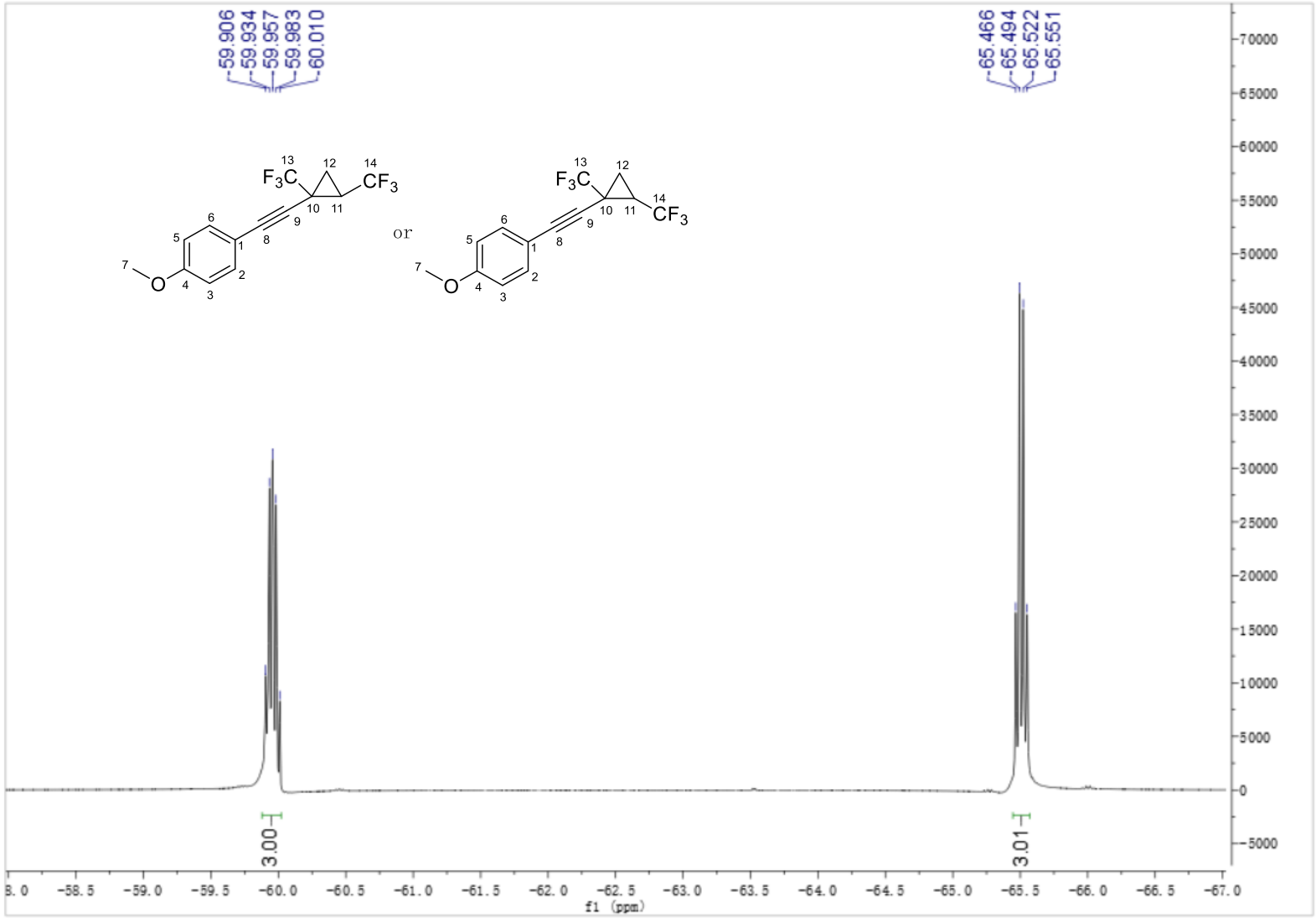
^{1}H NMR spectrum of 3a-isomer 1



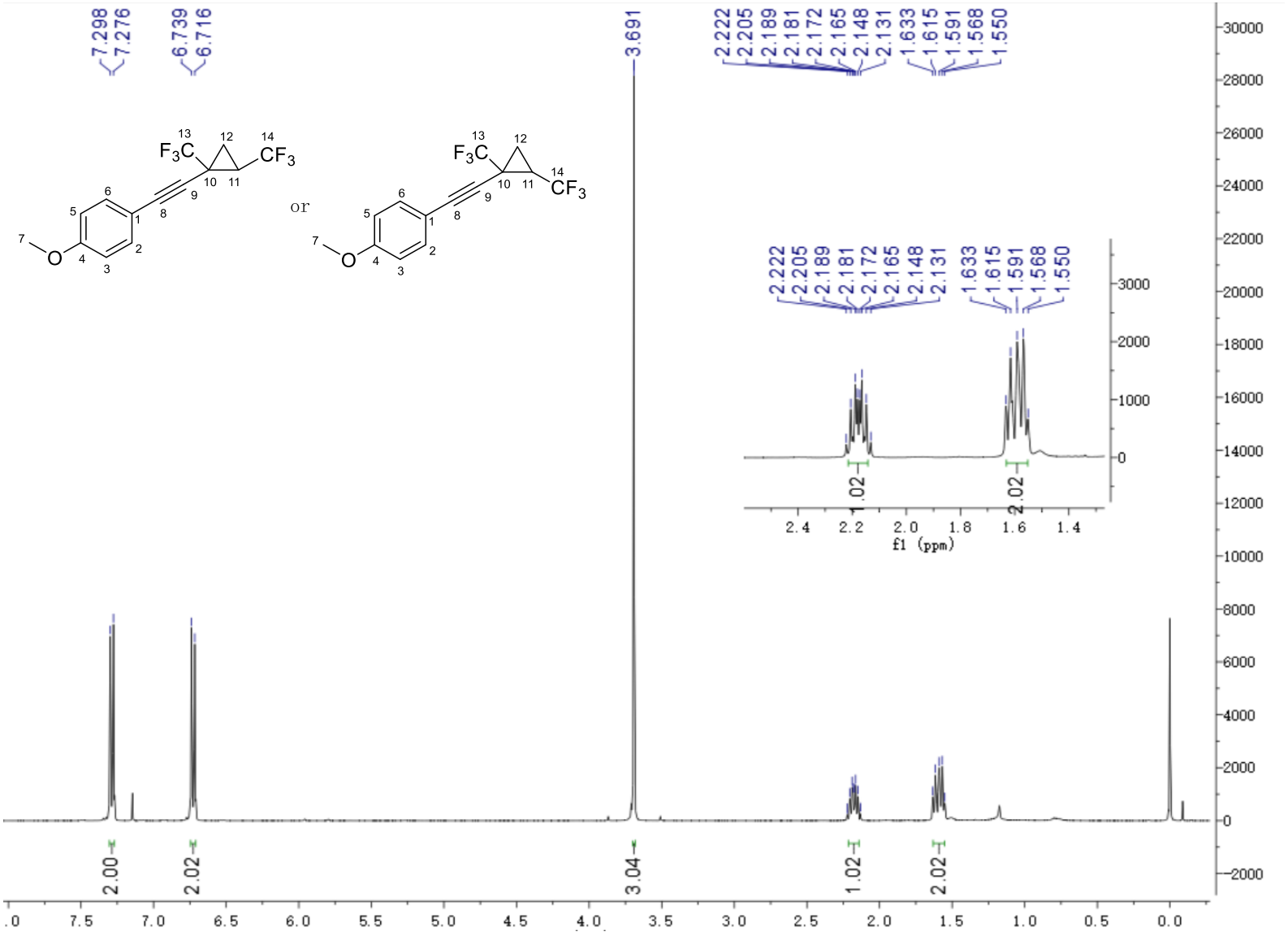
^{13}C NMR spectrum of 3a-isomer 1



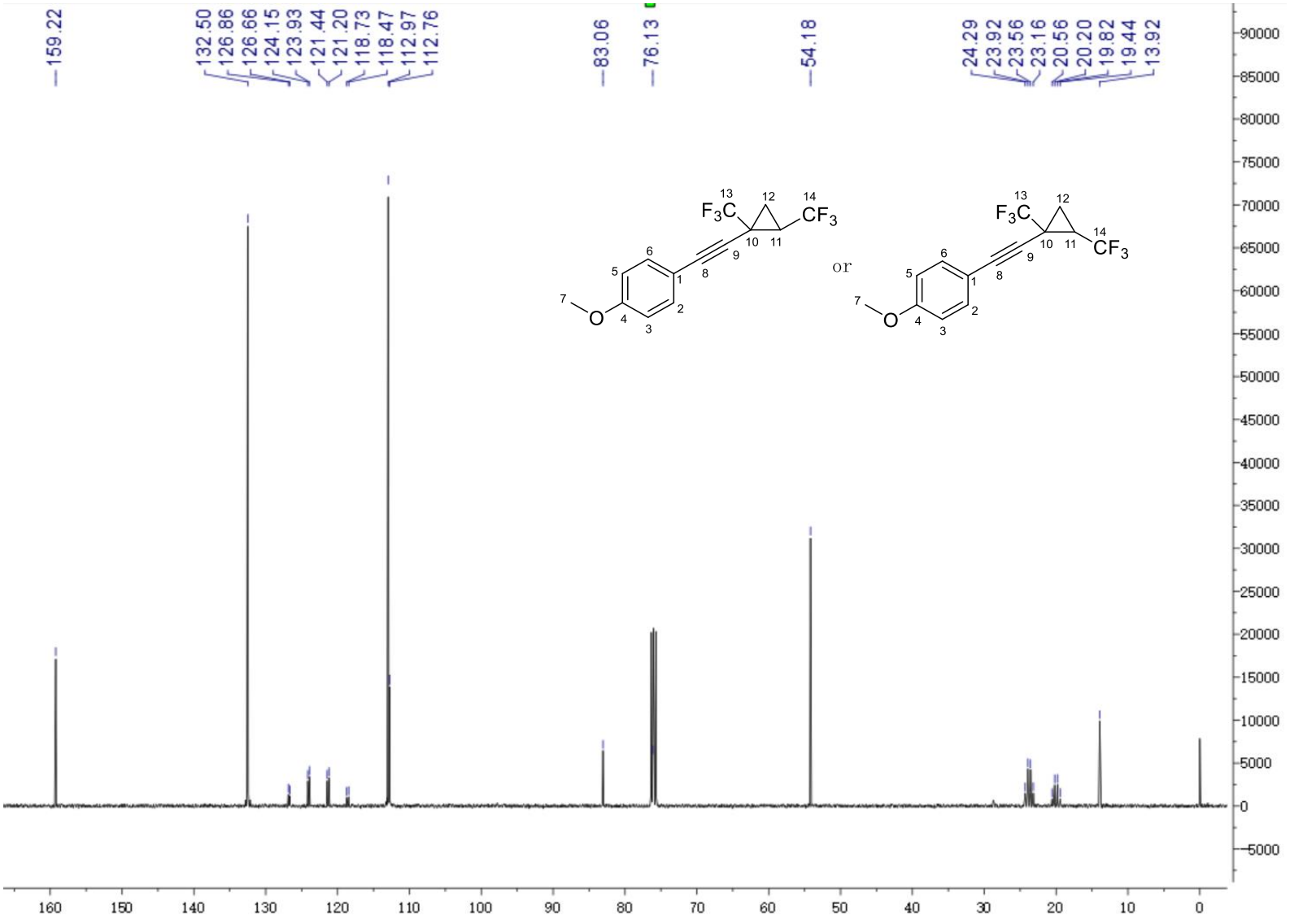
^{19}F NMR spectrum of 3a-isomer 1



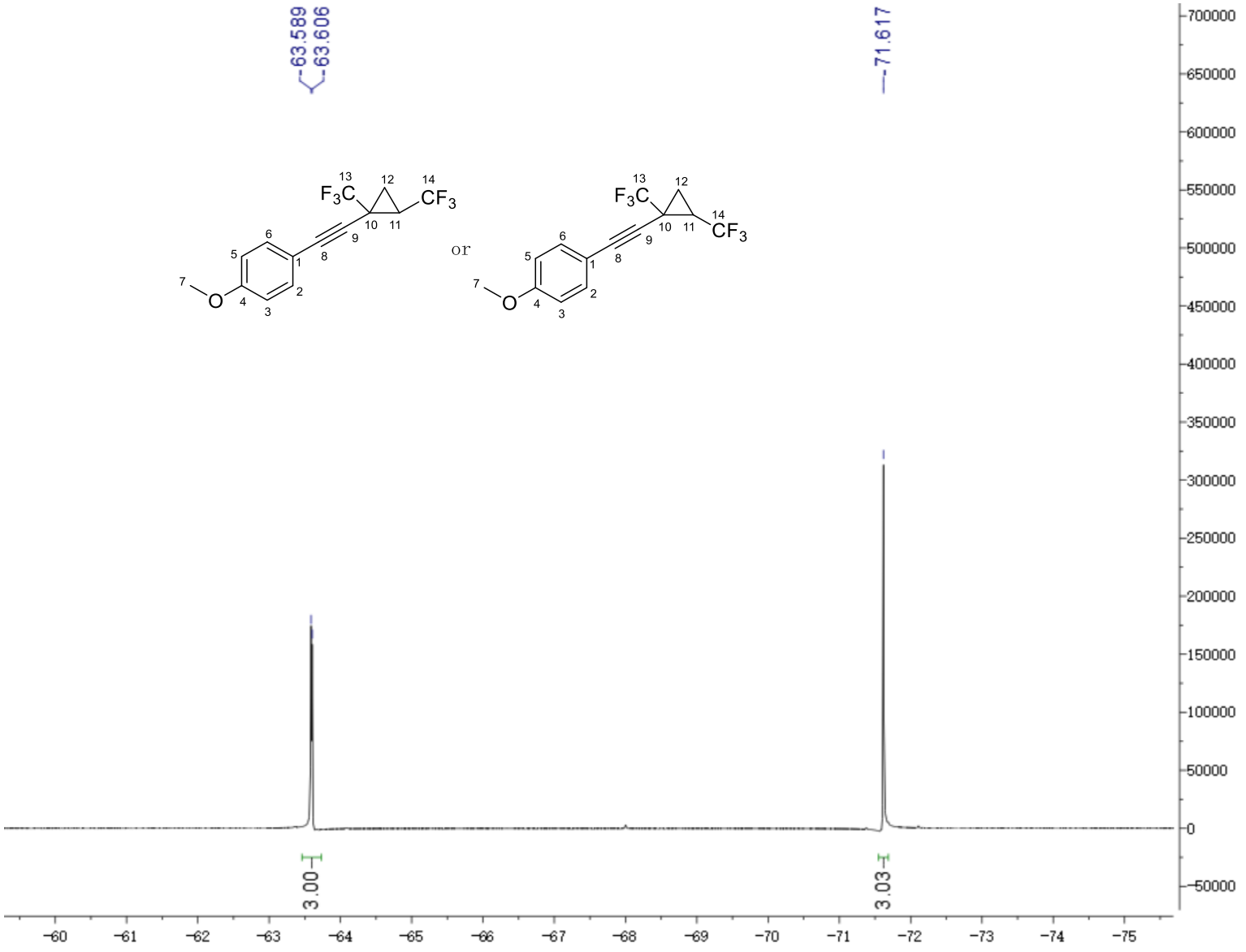
^{1}H NMR spectrum of 3a-isomer 2



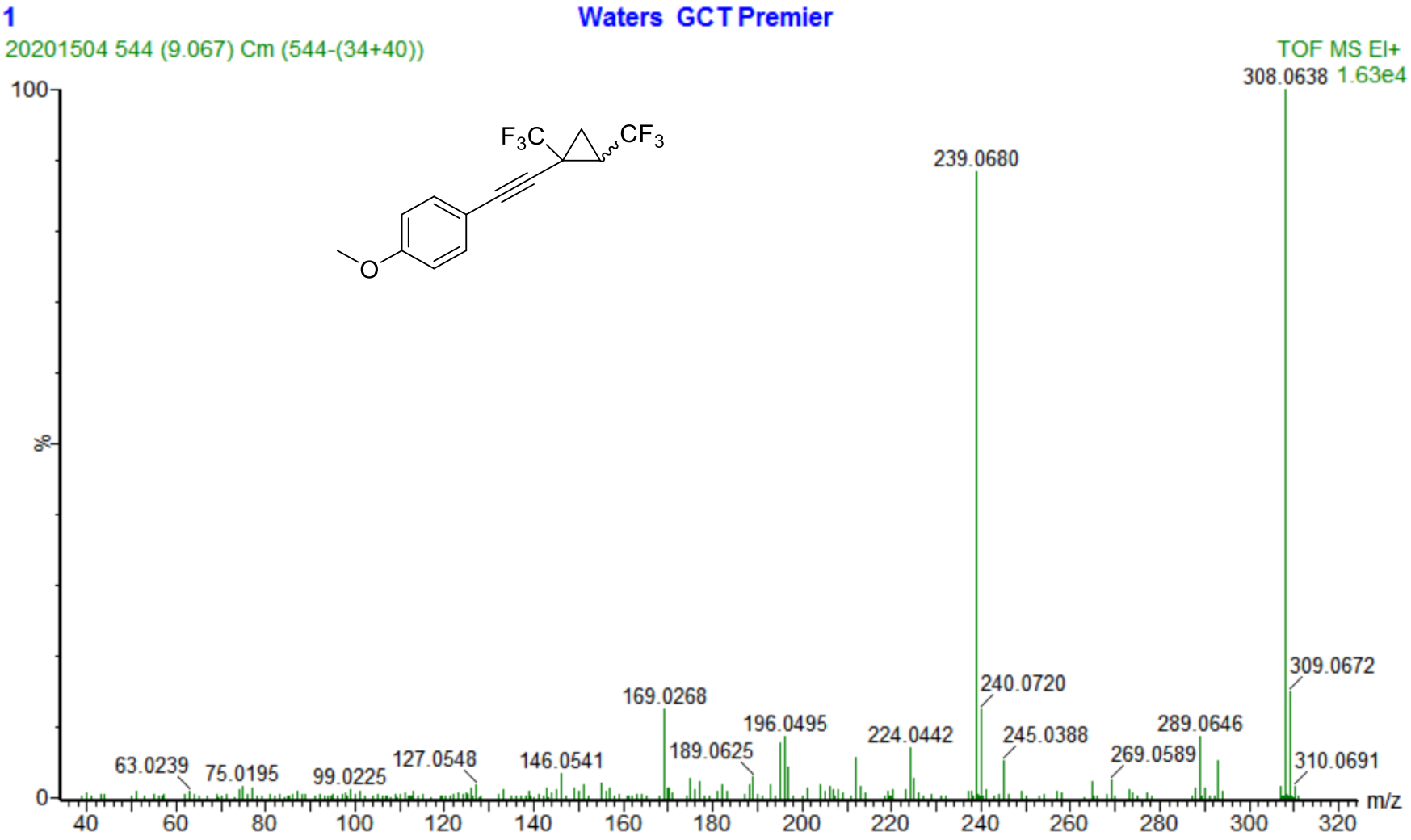
^{13}C NMR spectrum of 3a-isomer 2



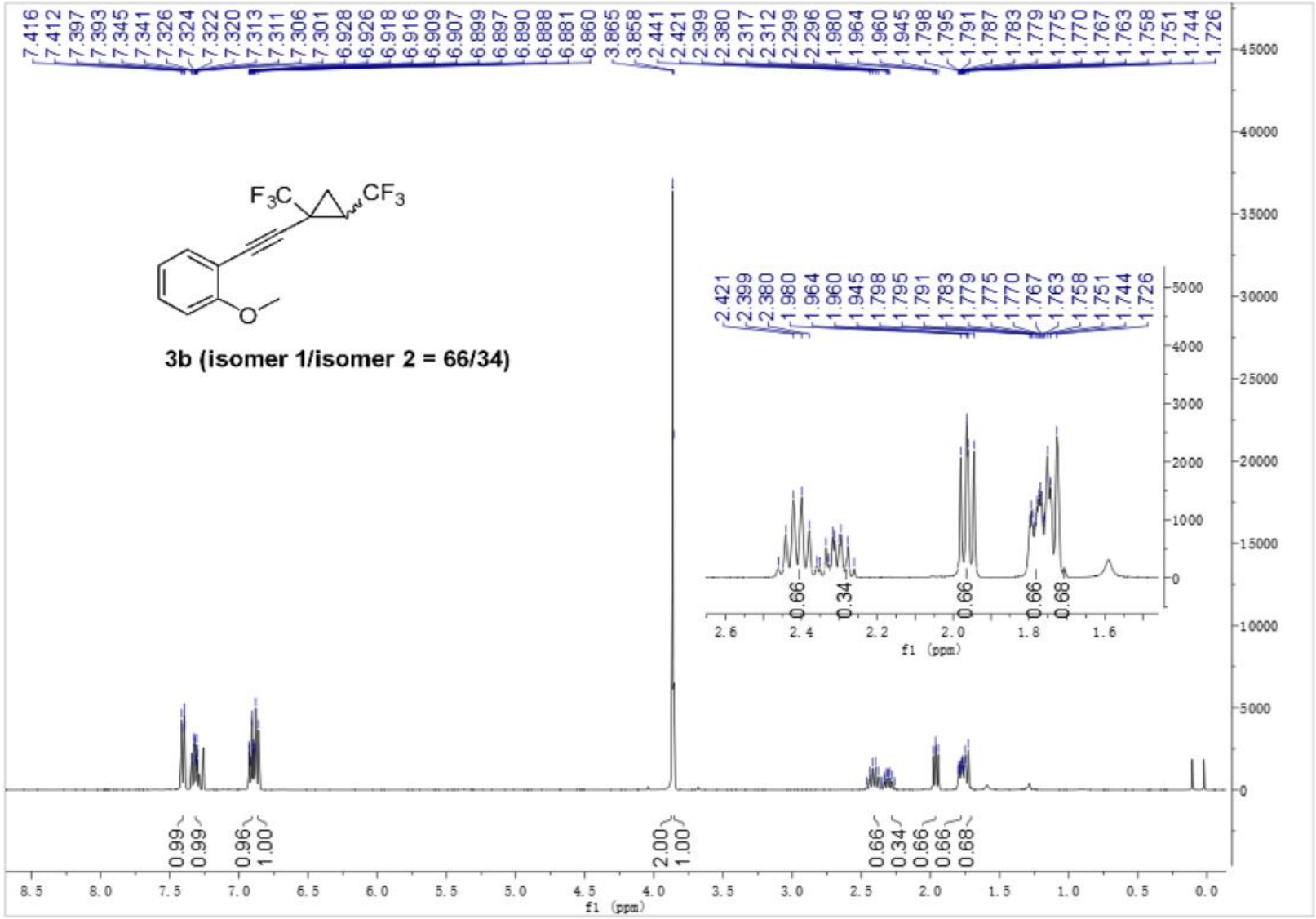
^{19}F NMR spectrum of 3a-isomer 2



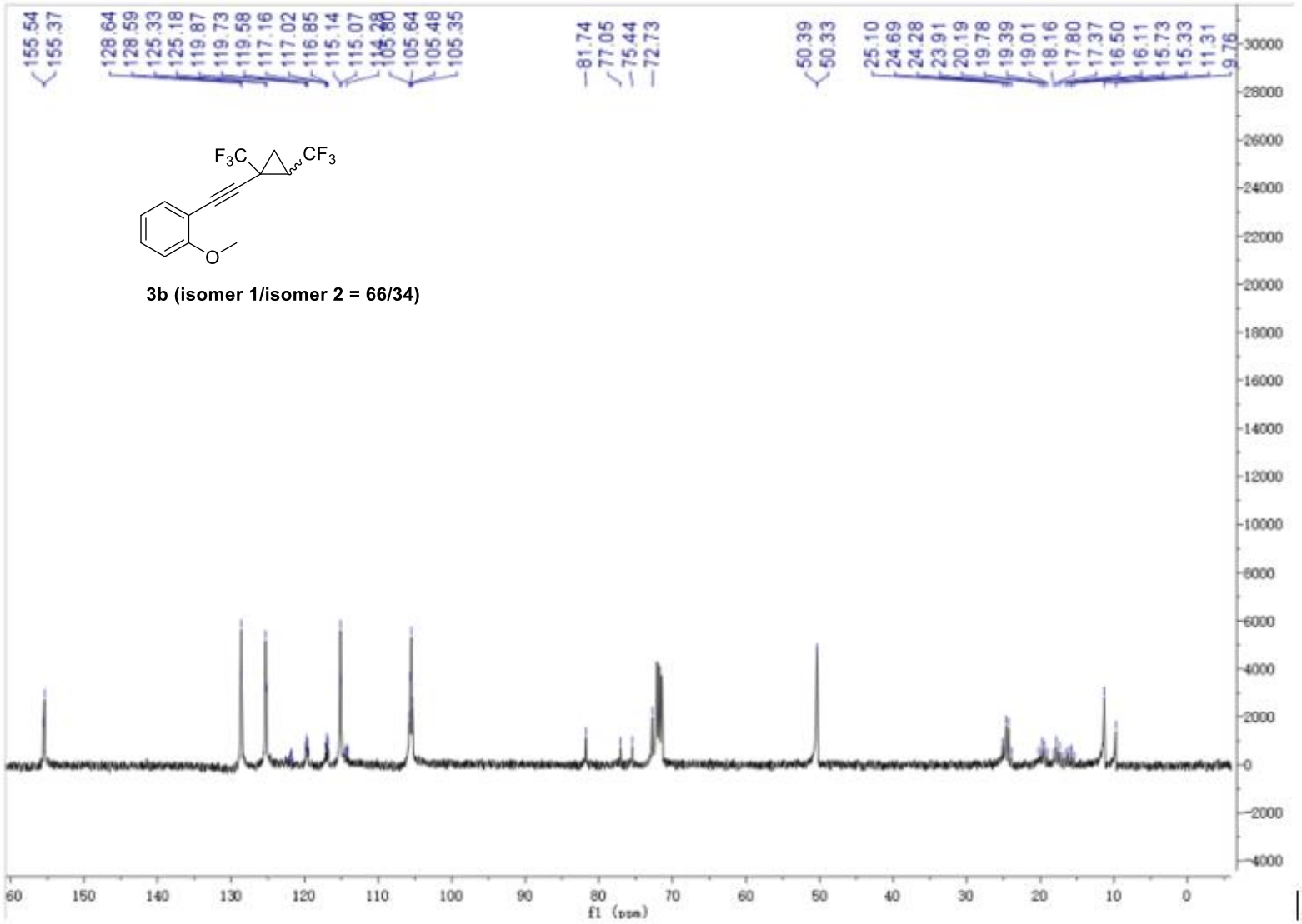
HRMS (EI) spectrum of 3a



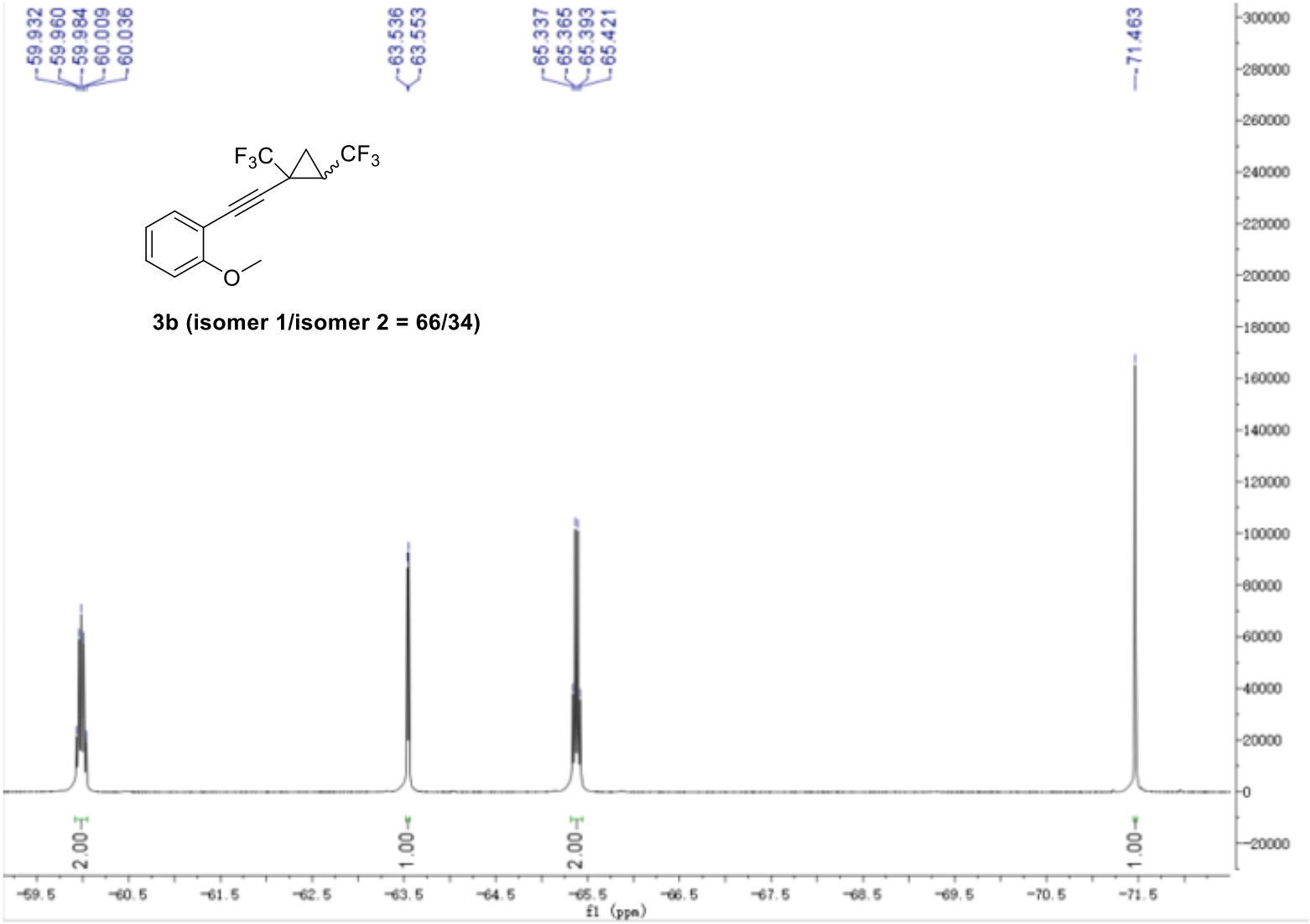
[1]H NMR spectrum of 3b



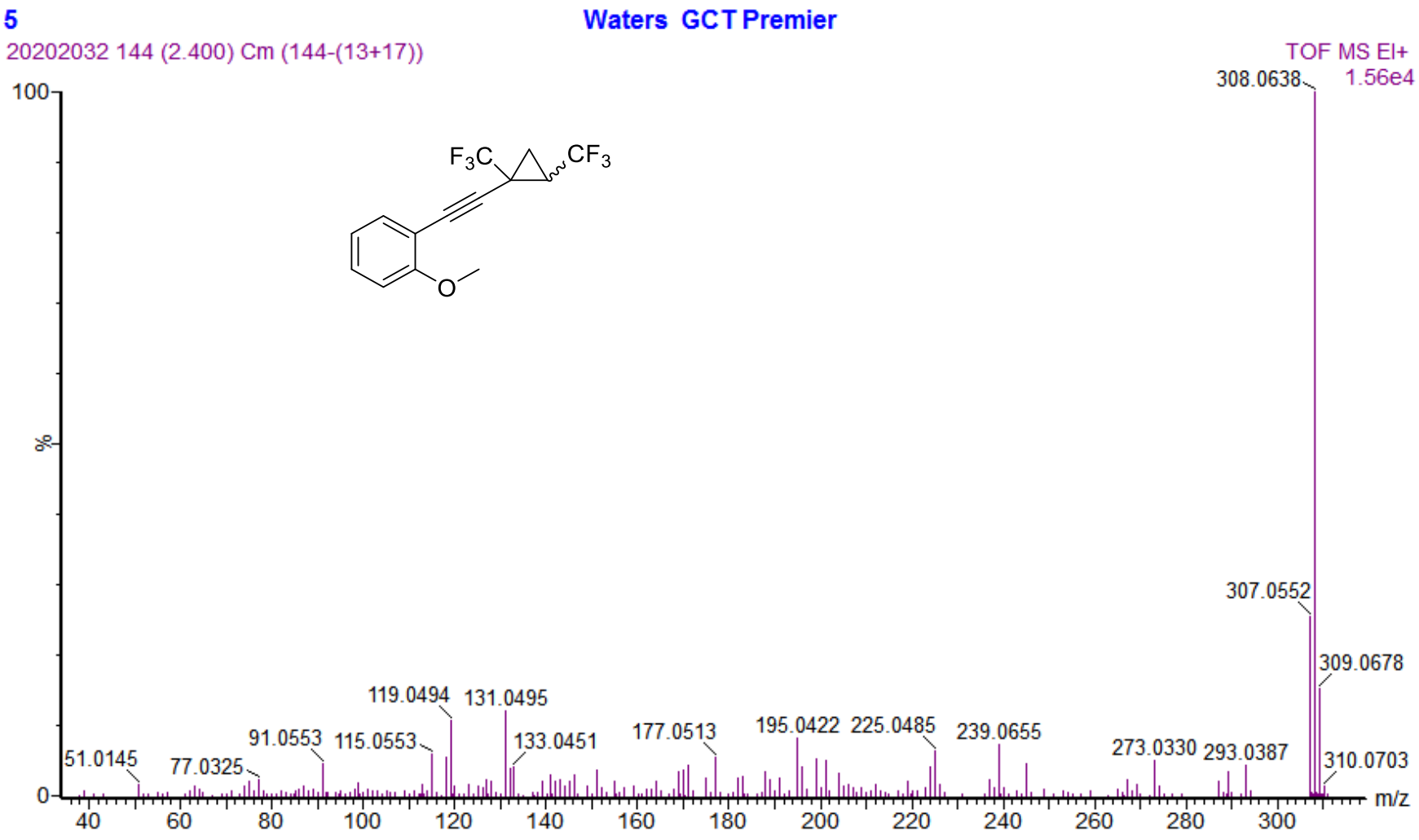
^{13}C NMR spectrum of 3b



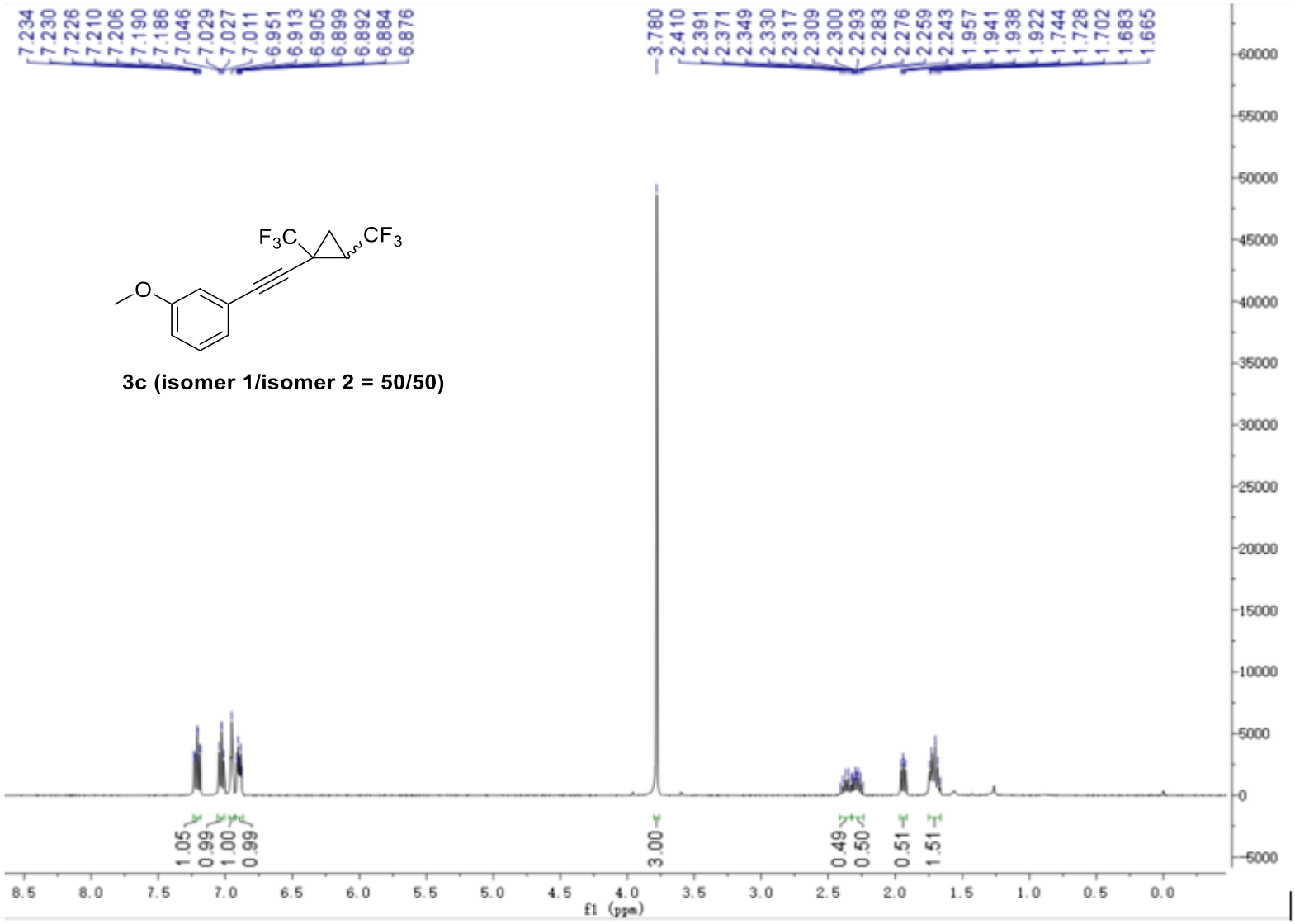
^{19}F NMR spectrum of 3b



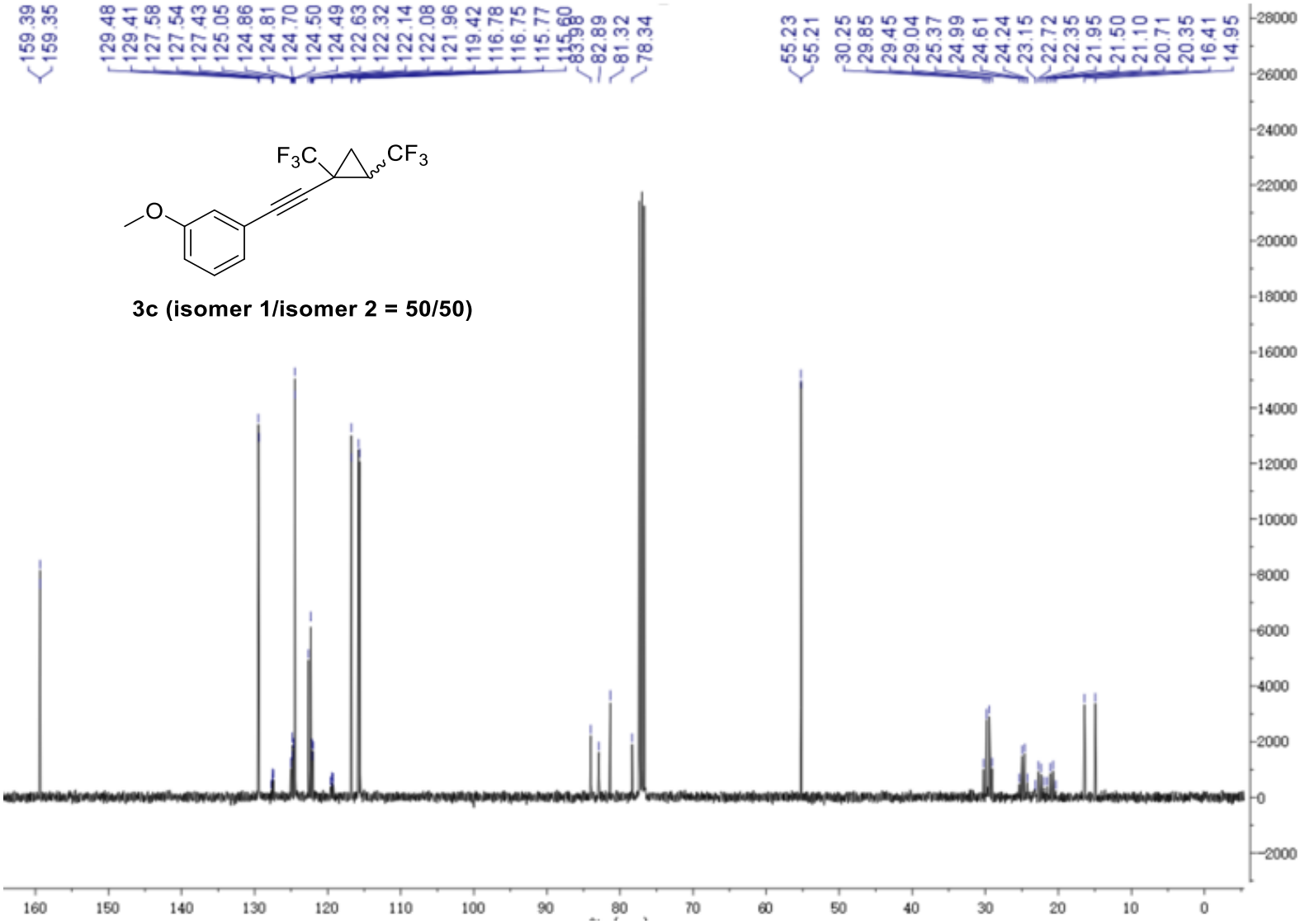
HRMS (EI) spectrum of 3b



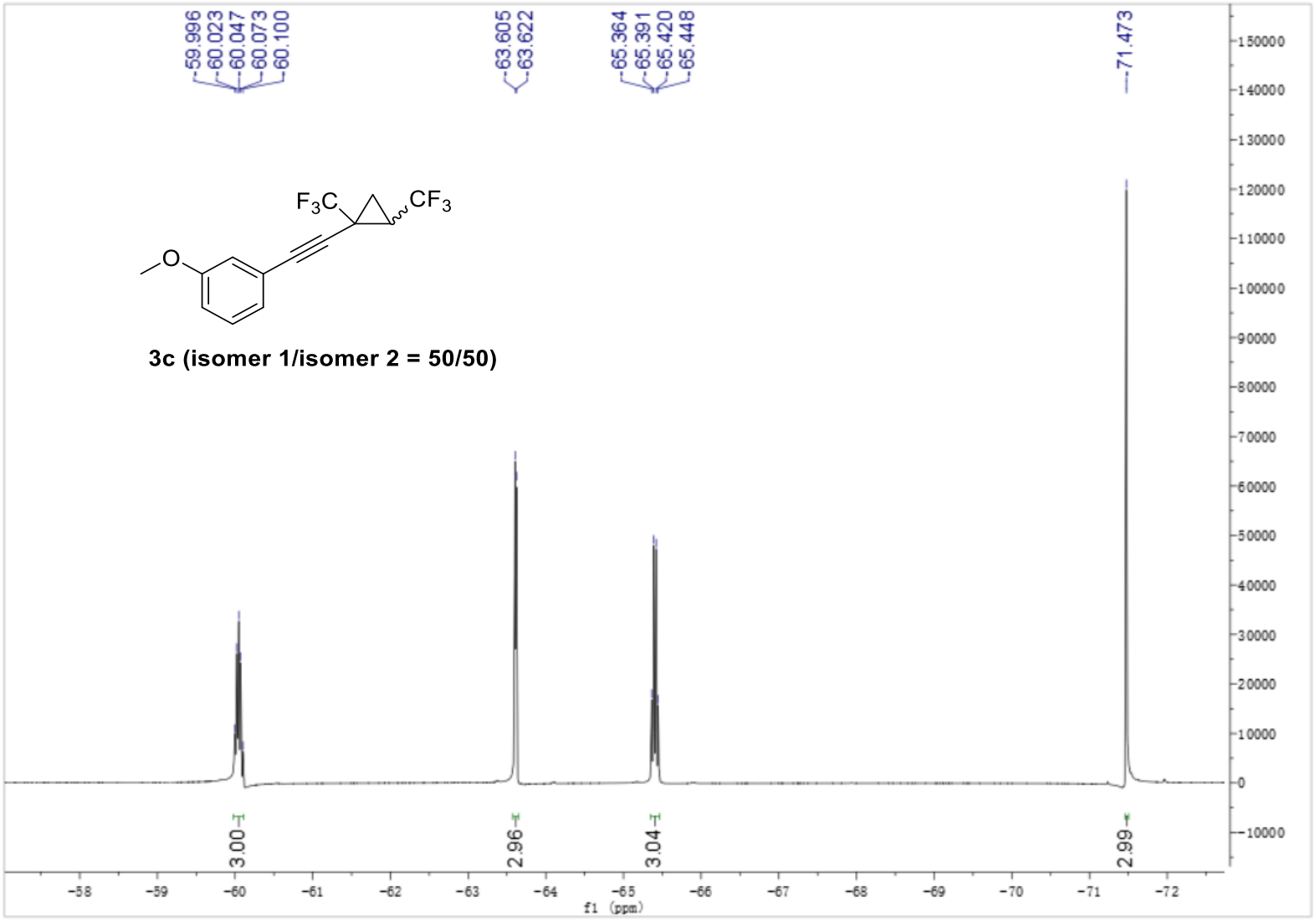
^{1}H NMR spectrum of 3c



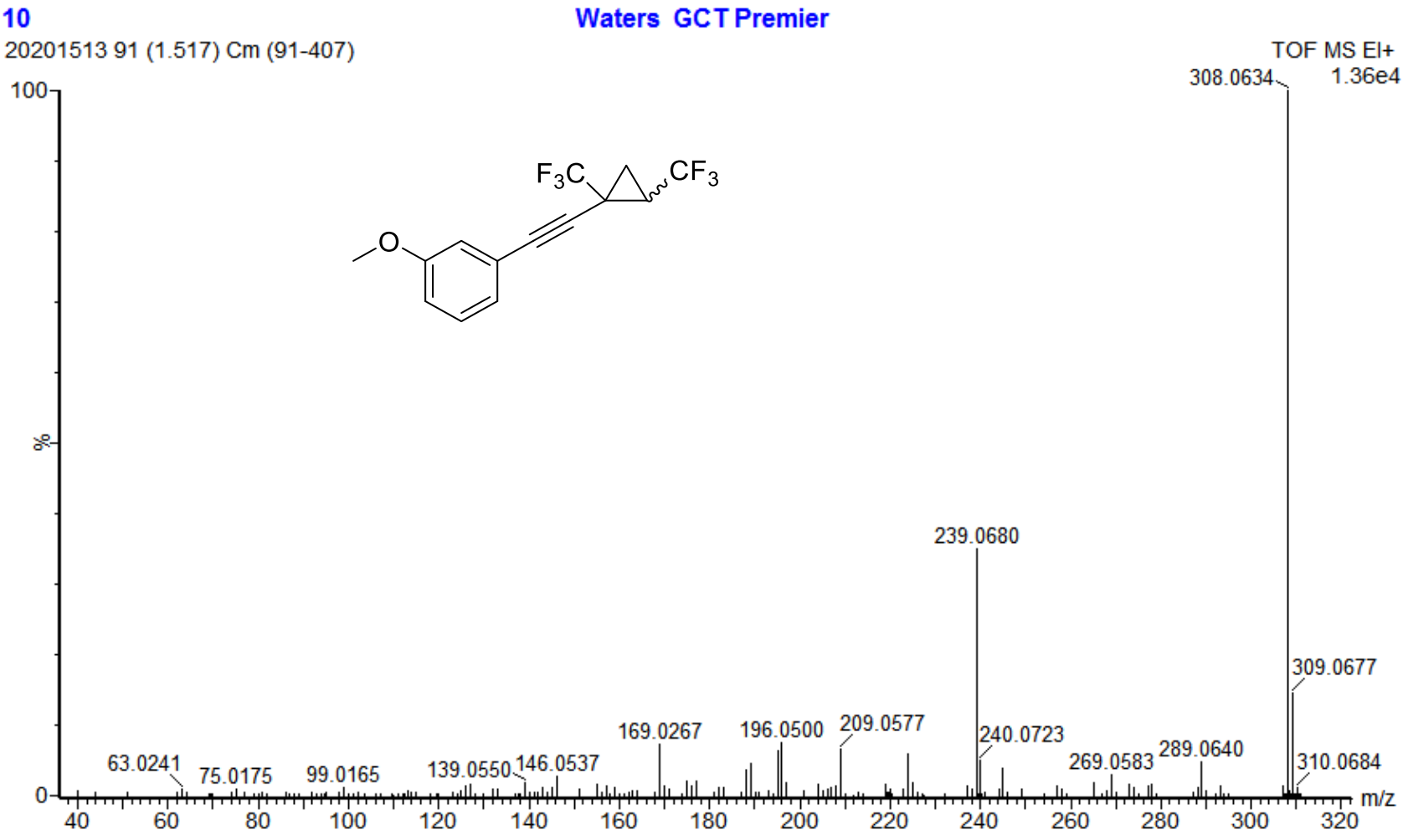
^{13}C NMR spectrum of 3c



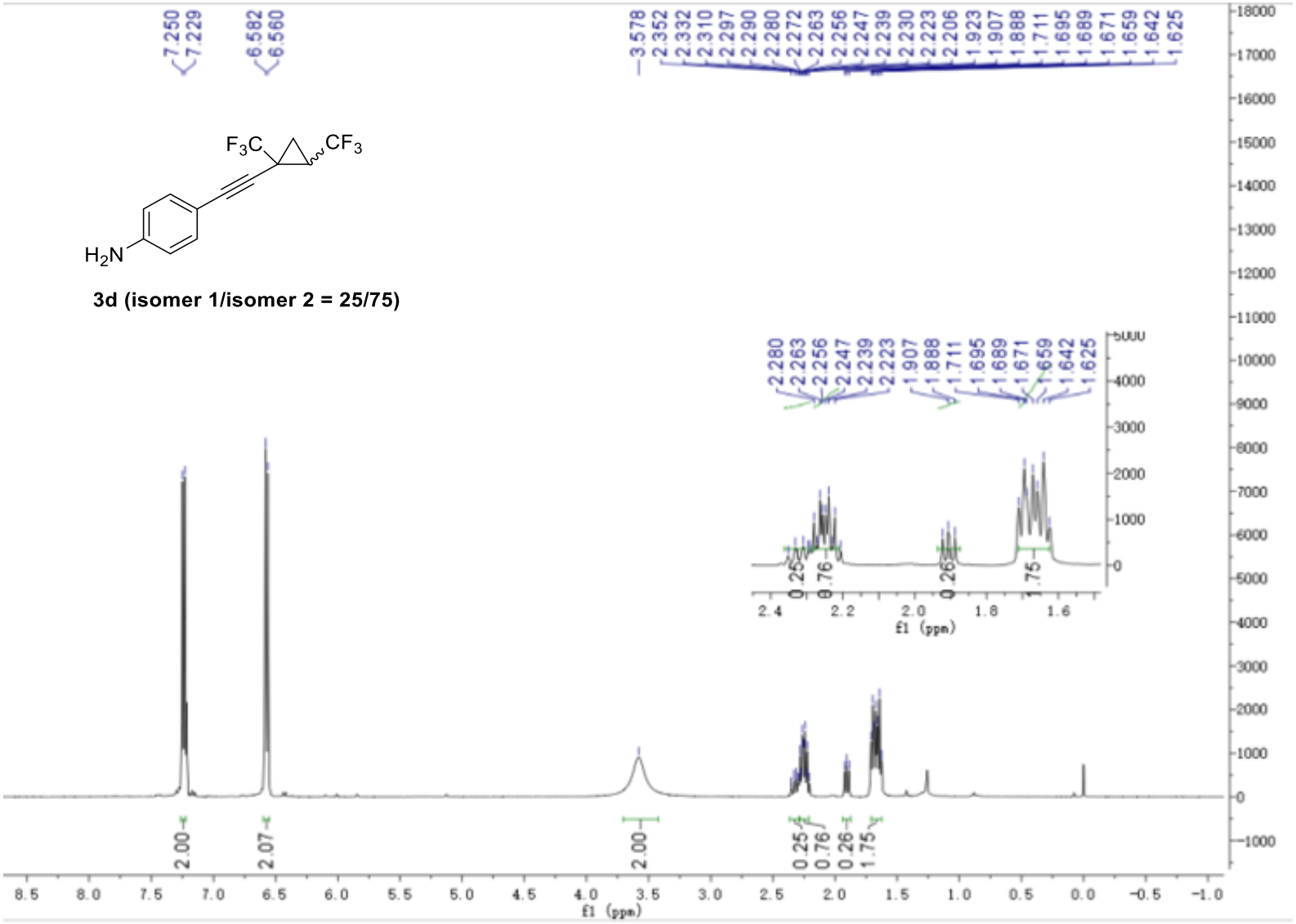
^{19}F NMR spectrum of 3c



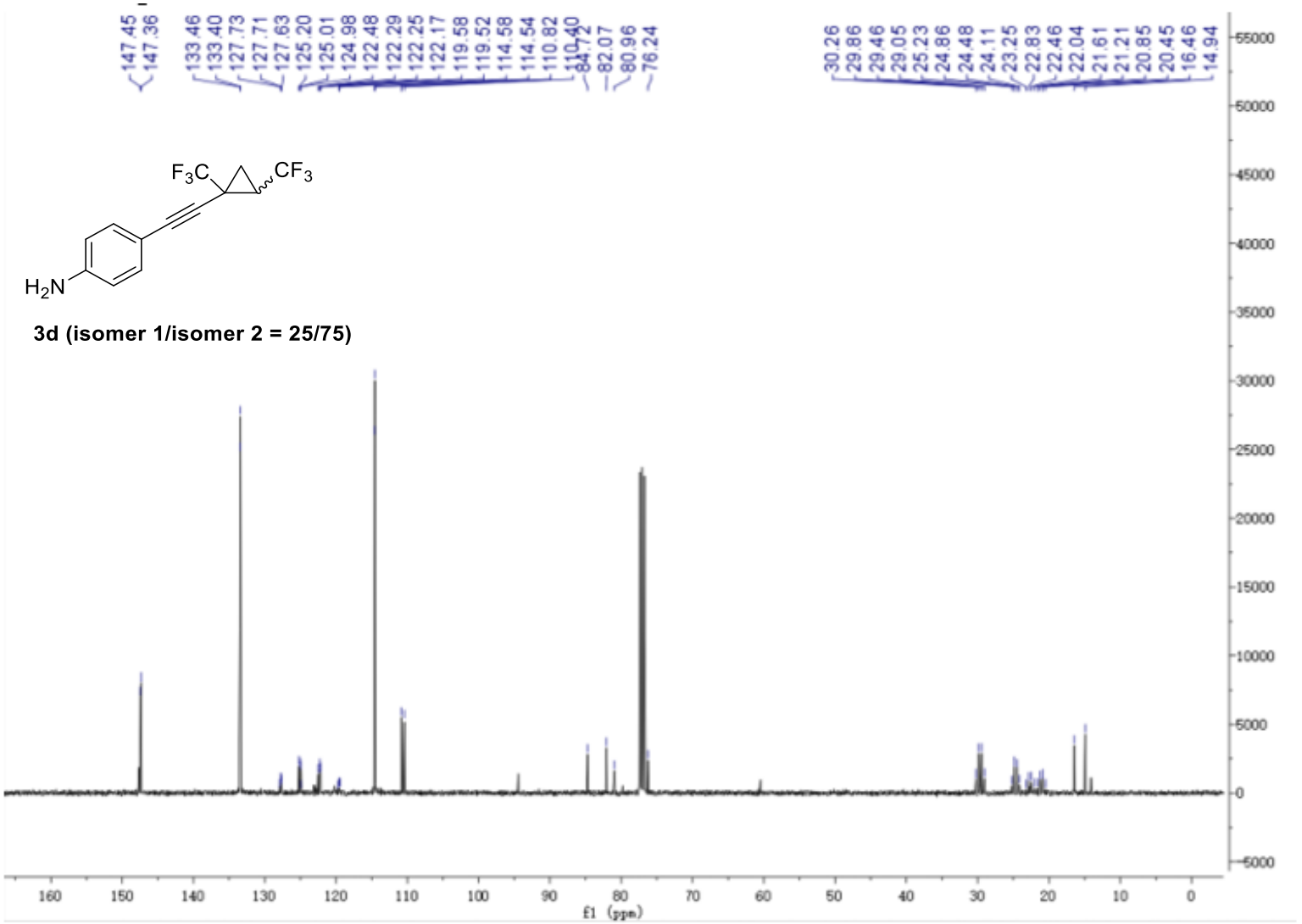
HRMS (EI) spectrum of 3c



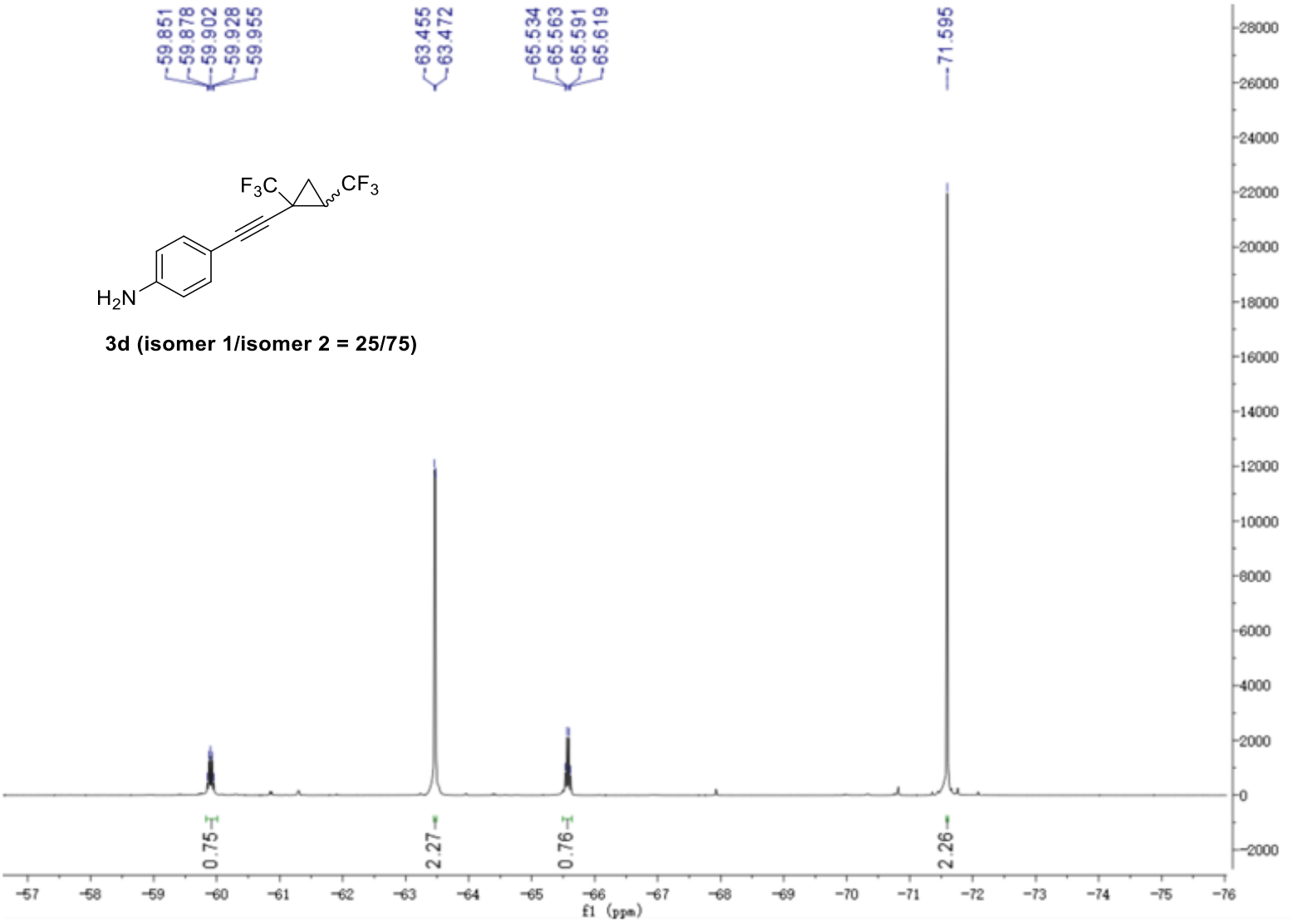
^{1}H NMR spectrum of 3d



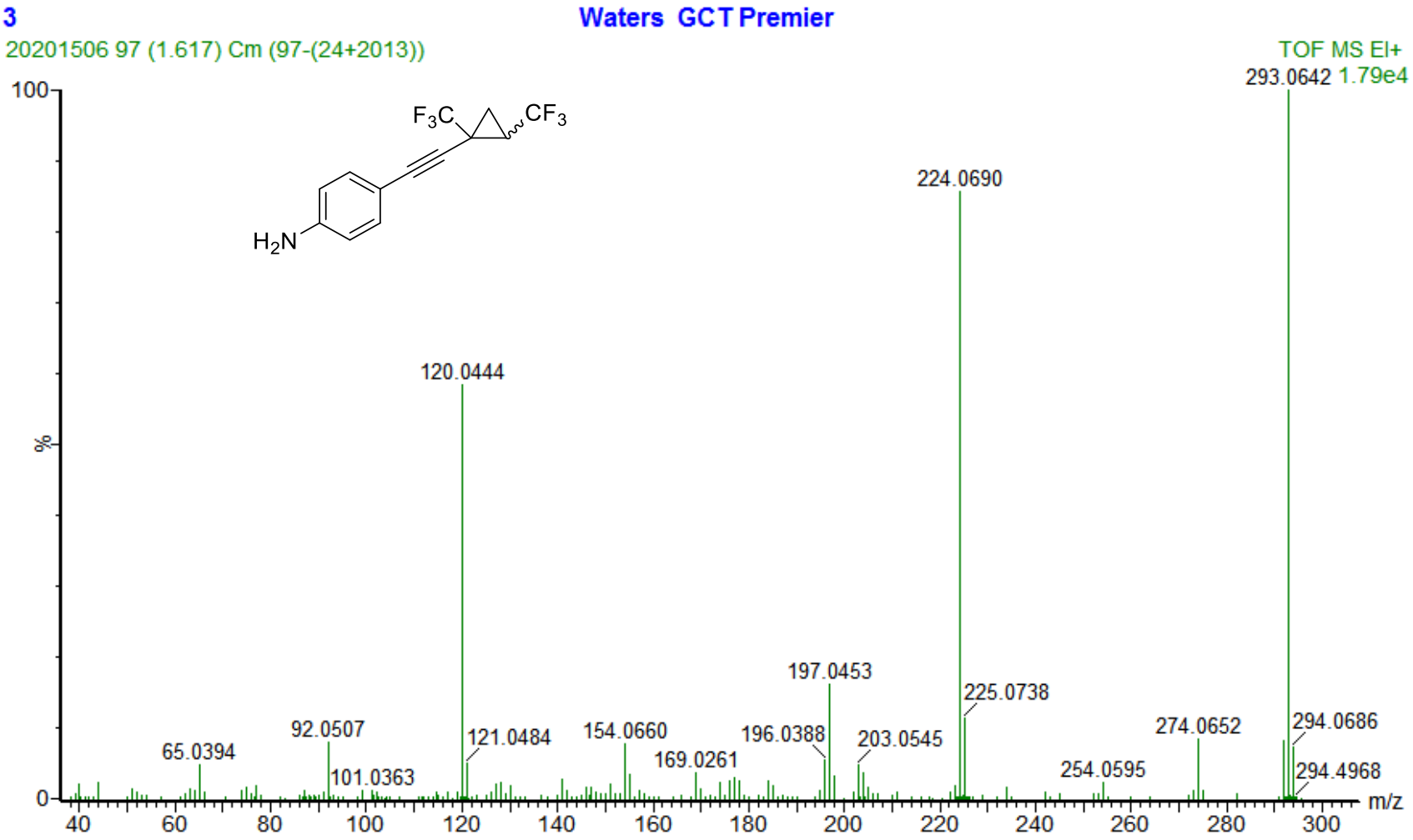
^{13}C NMR spectrum of 3d



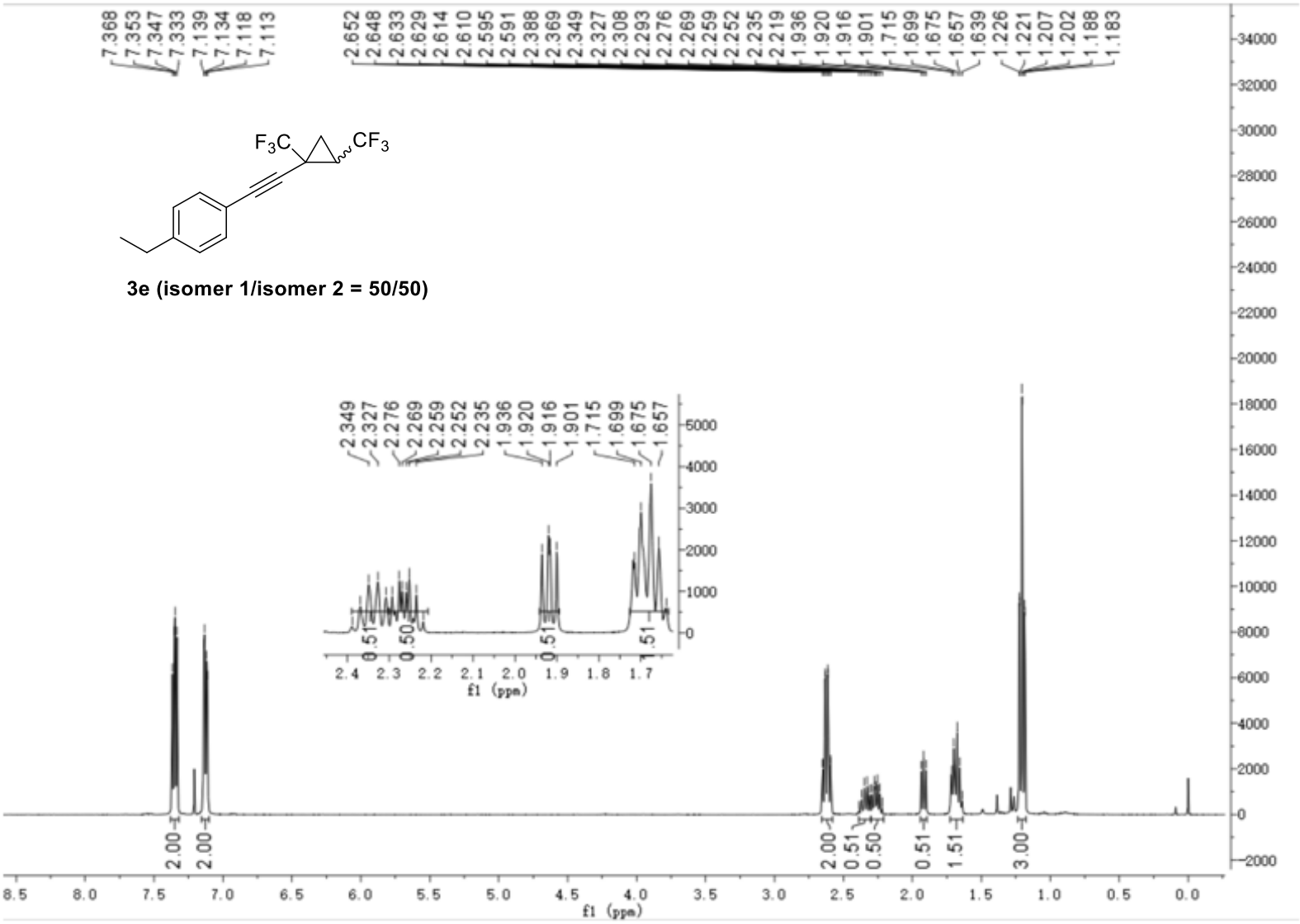
^{19}F NMR spectrum of 3d



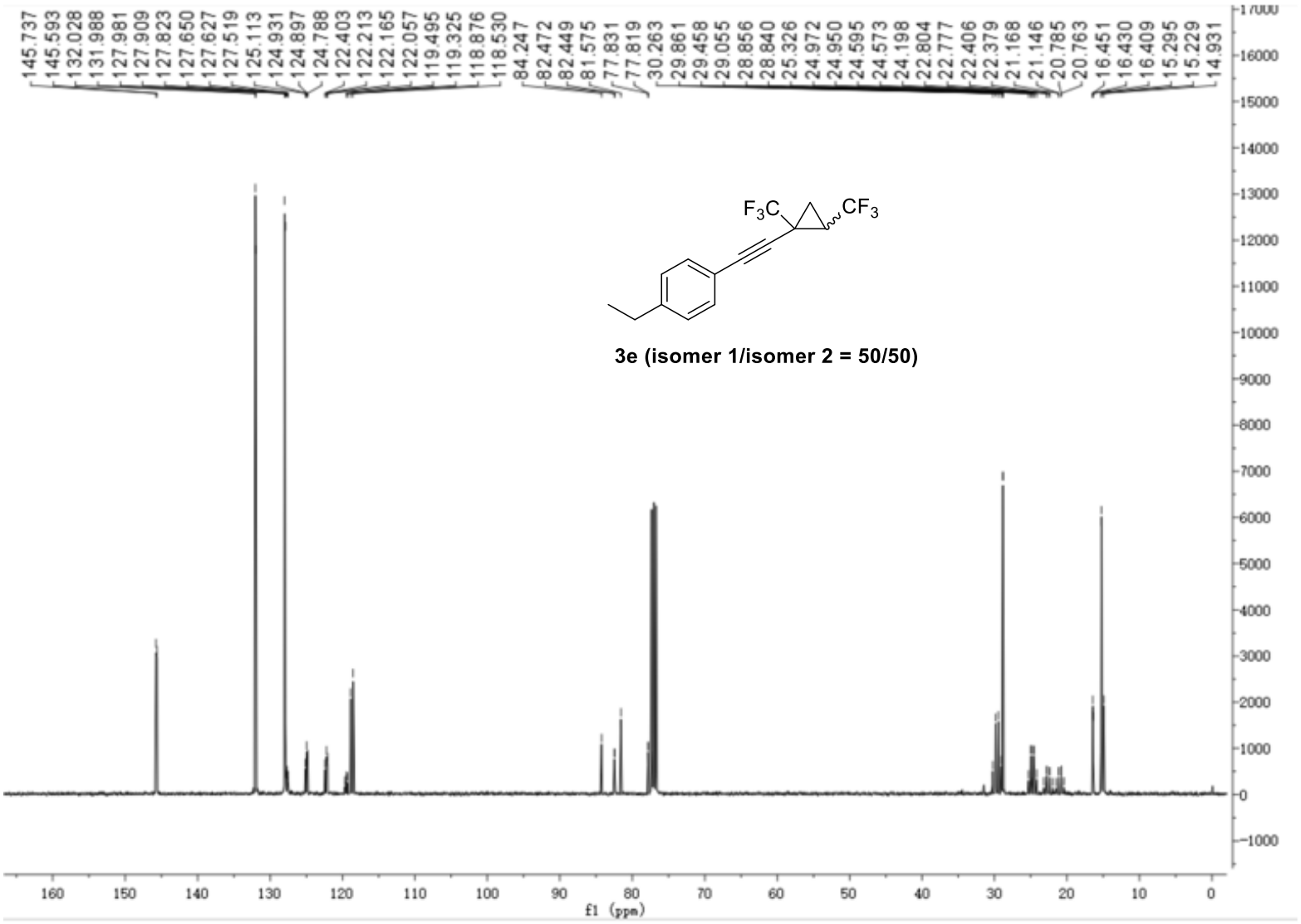
HRMS (EI) spectrum of 3d



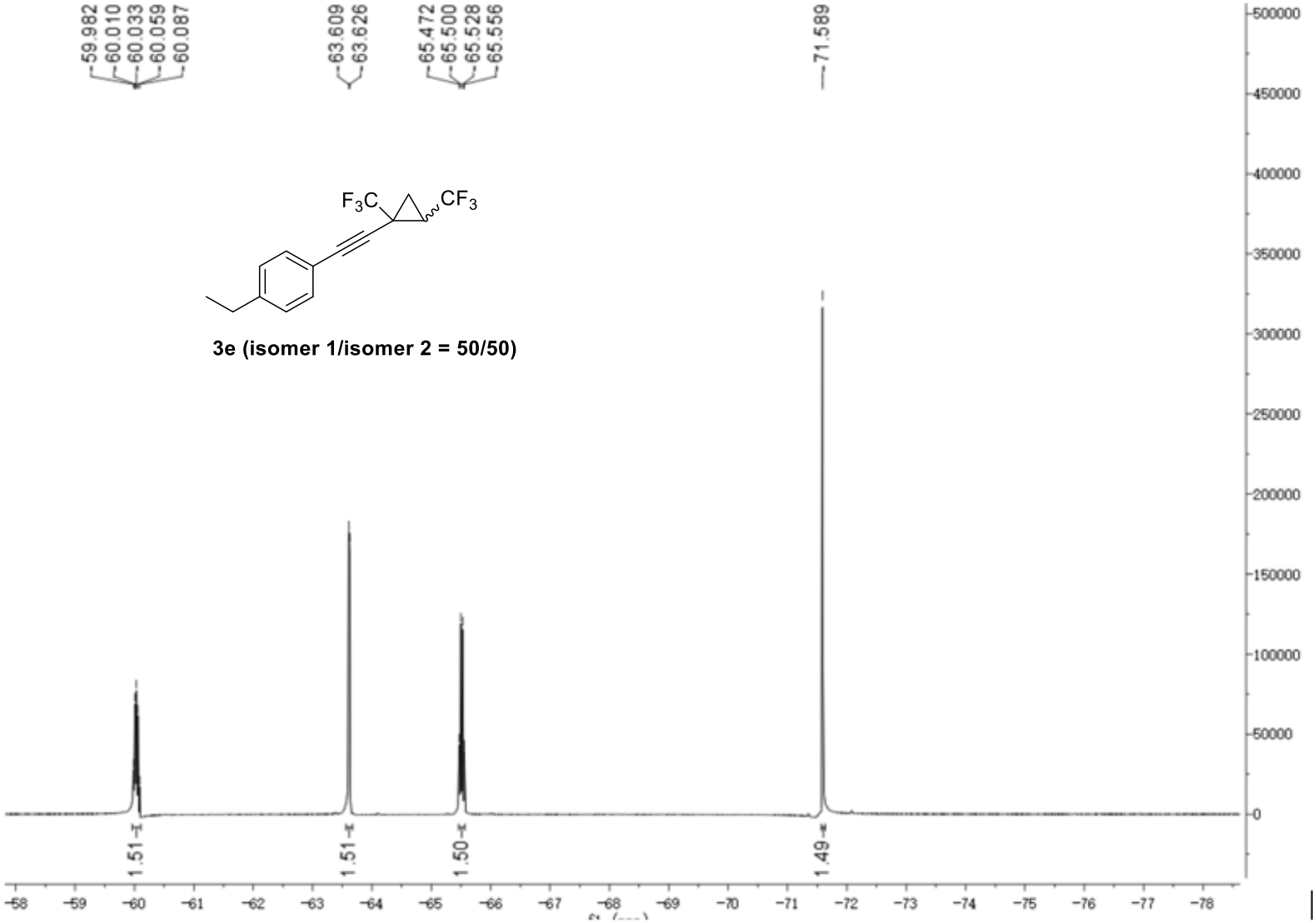
^{1}H NMR spectrum of 3e



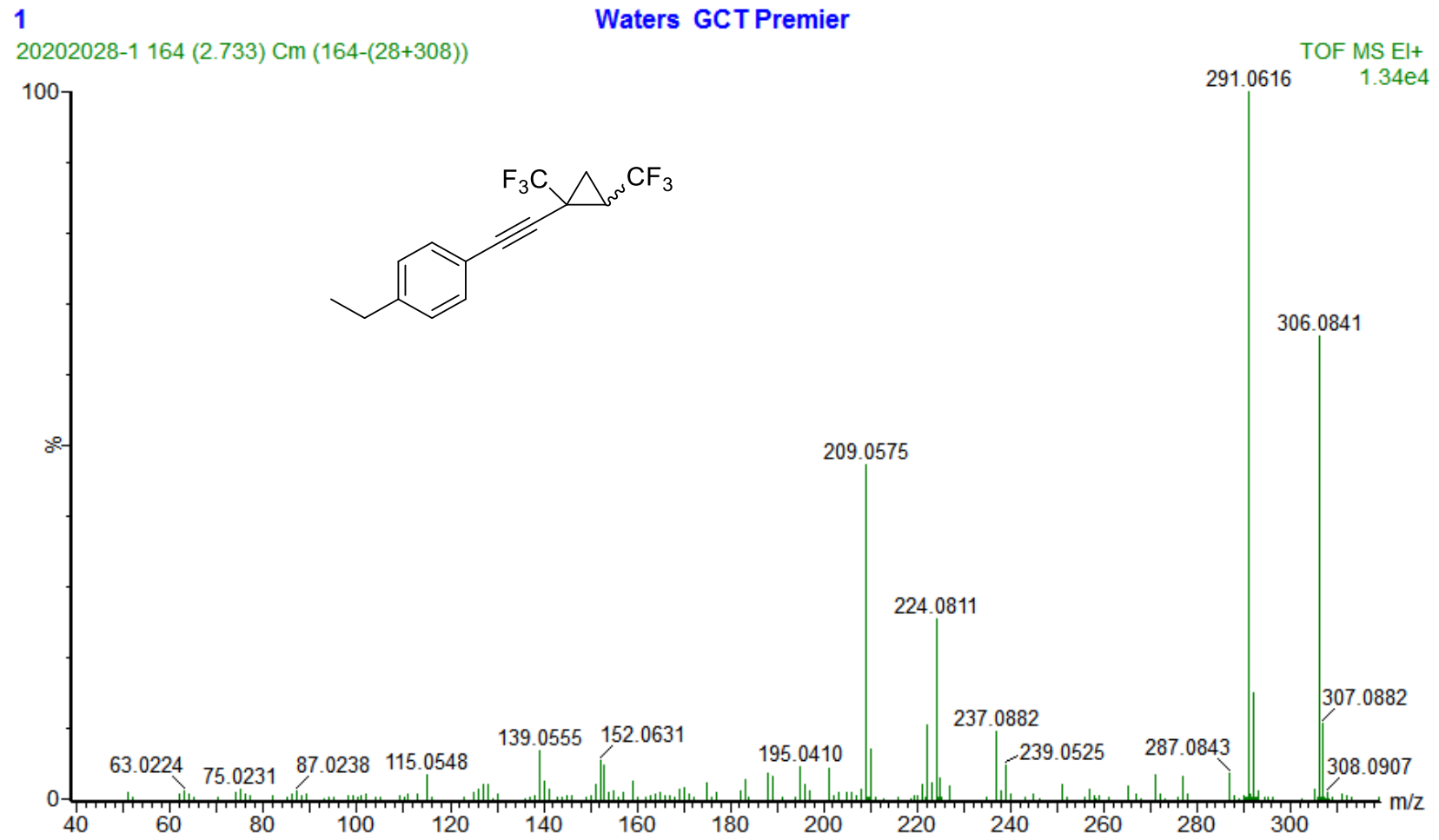
^{13}C NMR spectrum of 3e



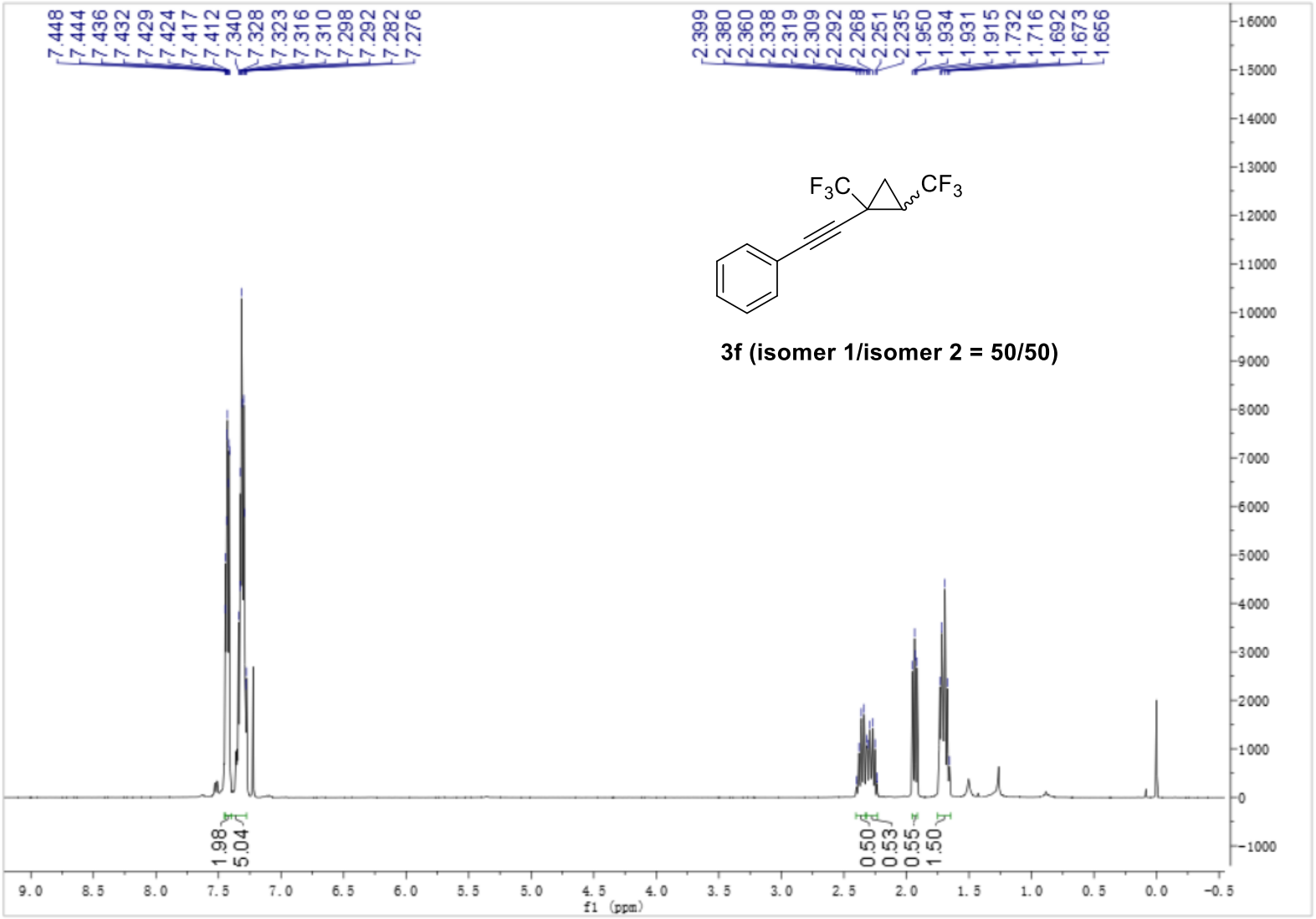
^{19}F NMR spectrum of 3e



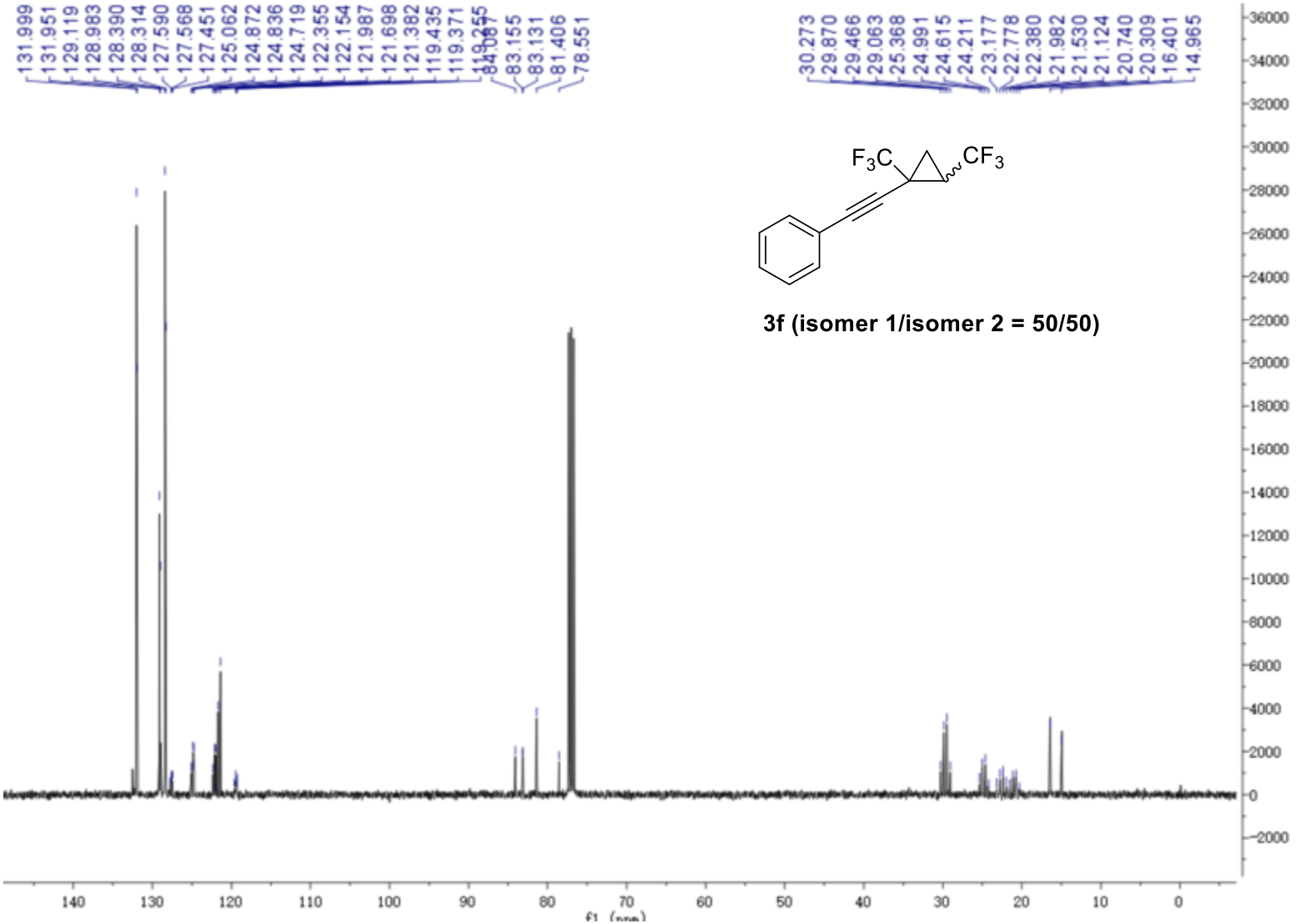
HRMS (EI) spectrum of 3e



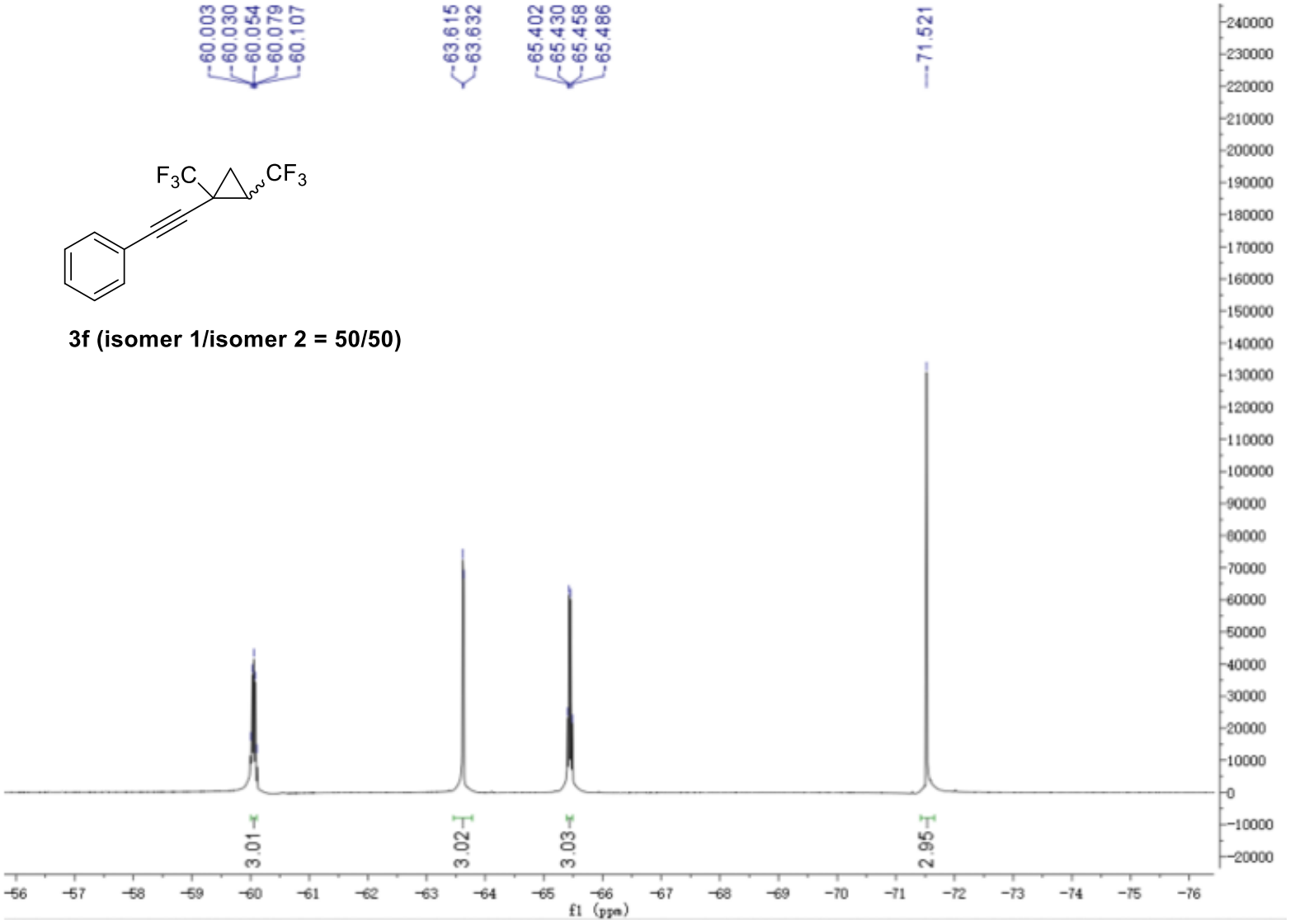
^{1}H NMR spectrum of 3f



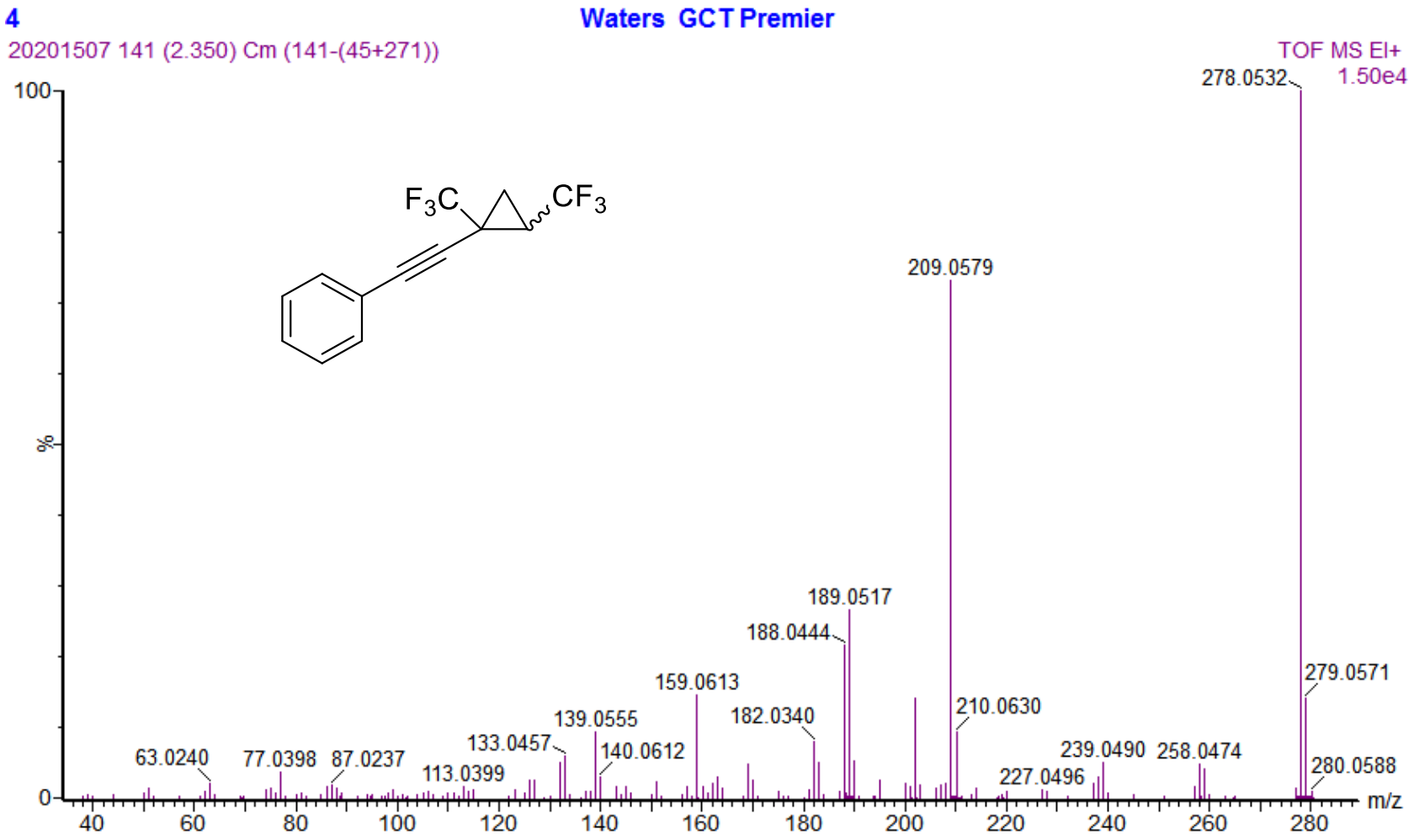
^{13}C NMR spectrum of 3f



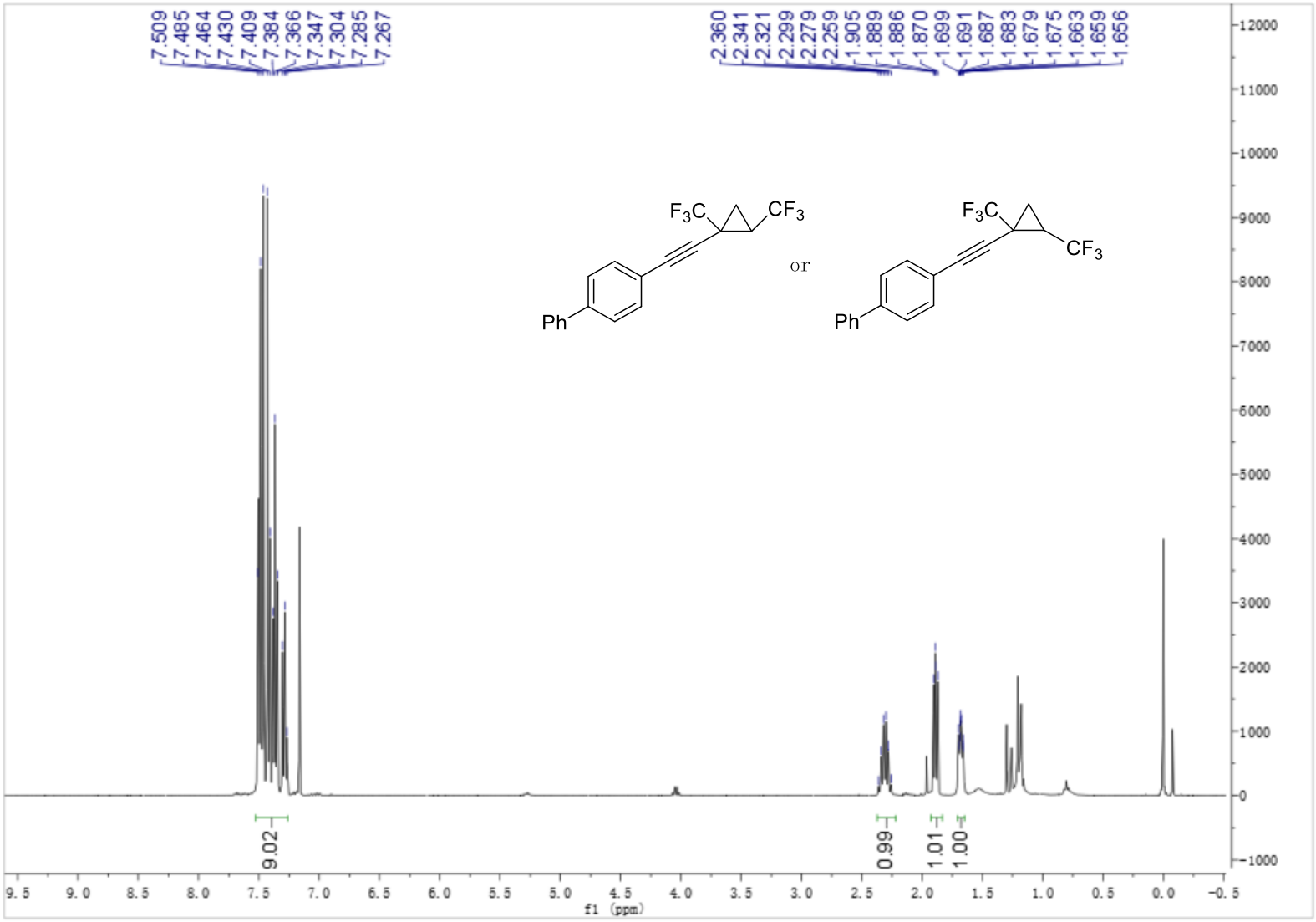
^{19}F NMR spectrum of 3f



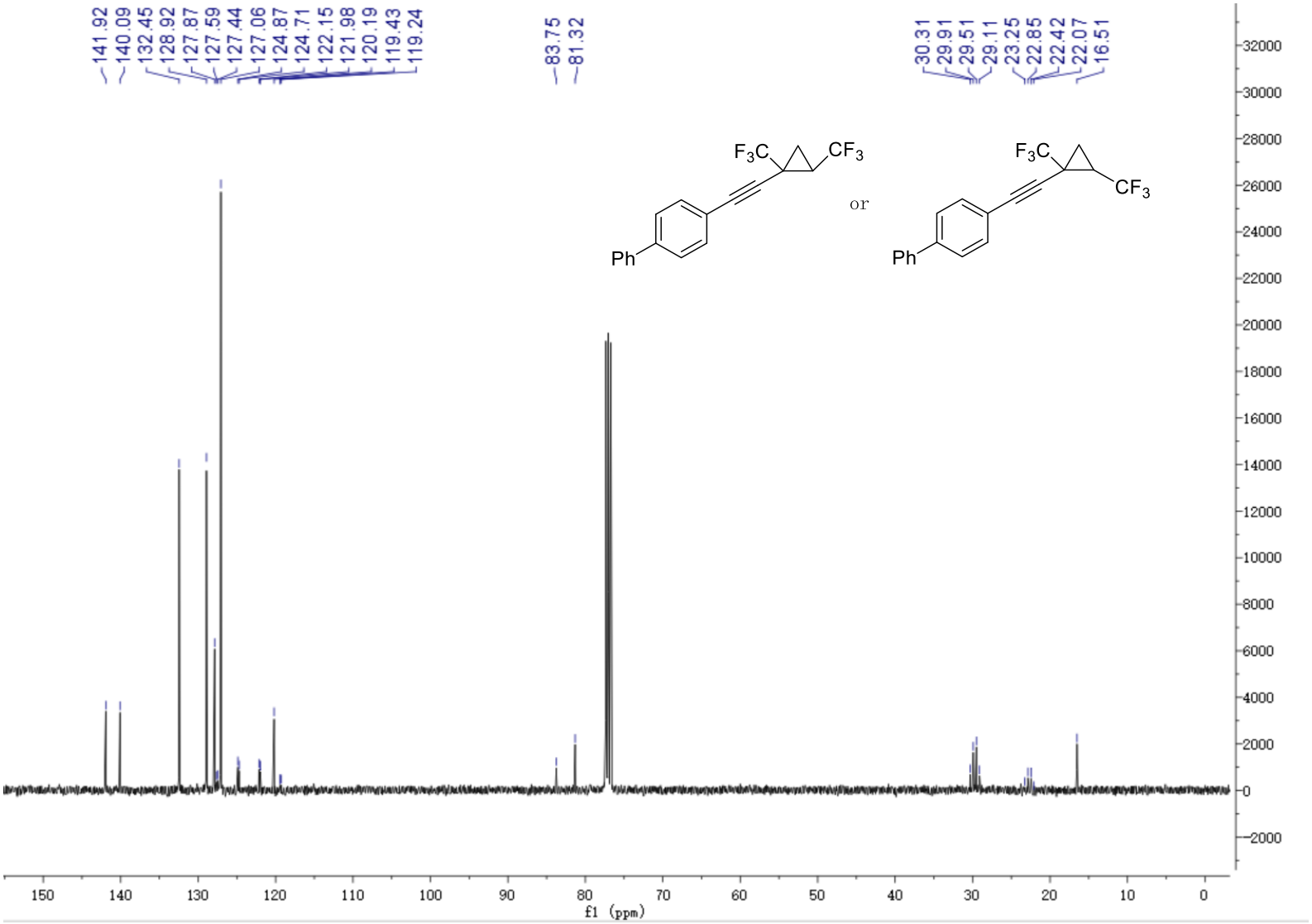
HRMS (EI) spectrum of 3f



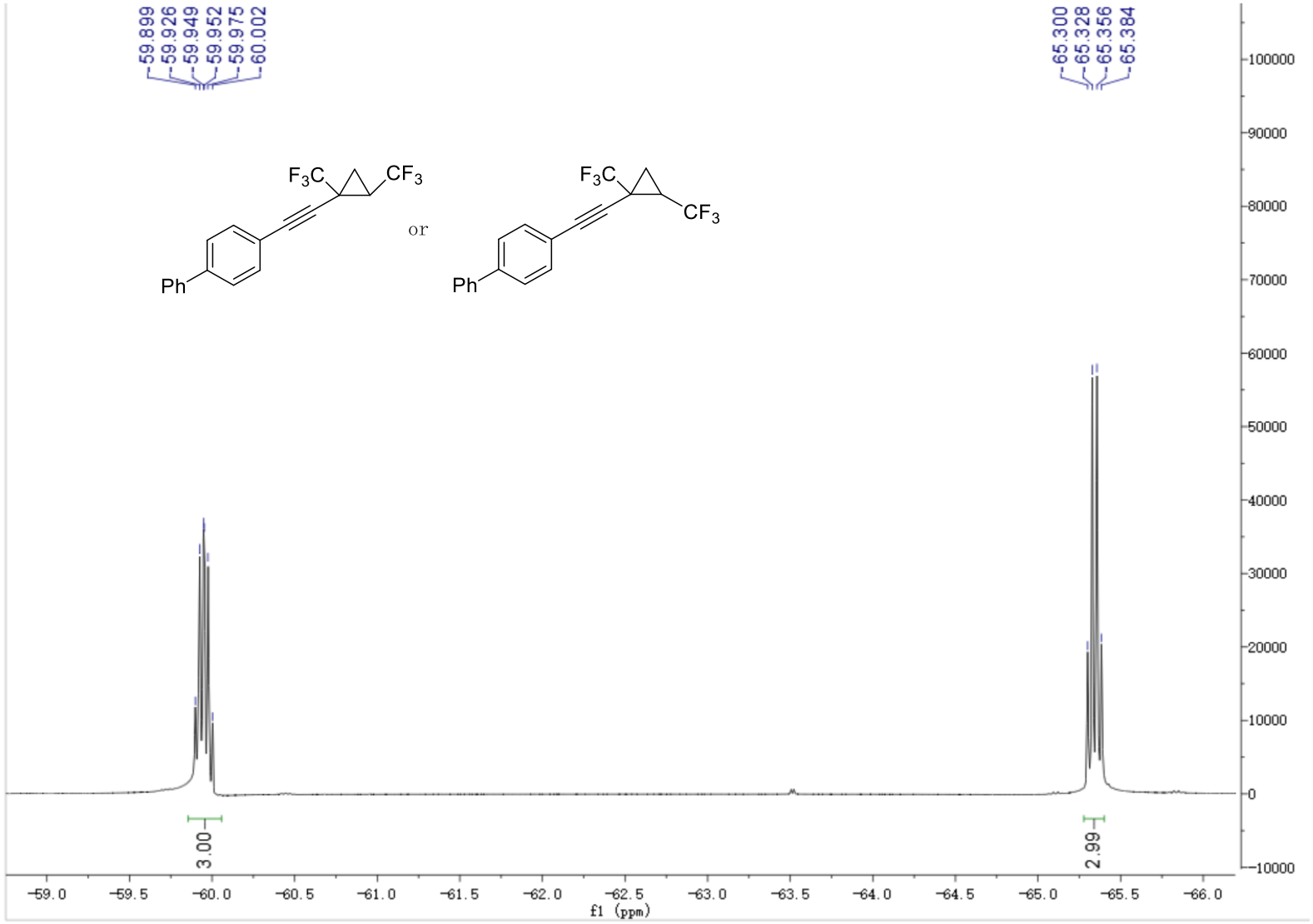
^{1}H NMR spectrum of 3g-isomer 1



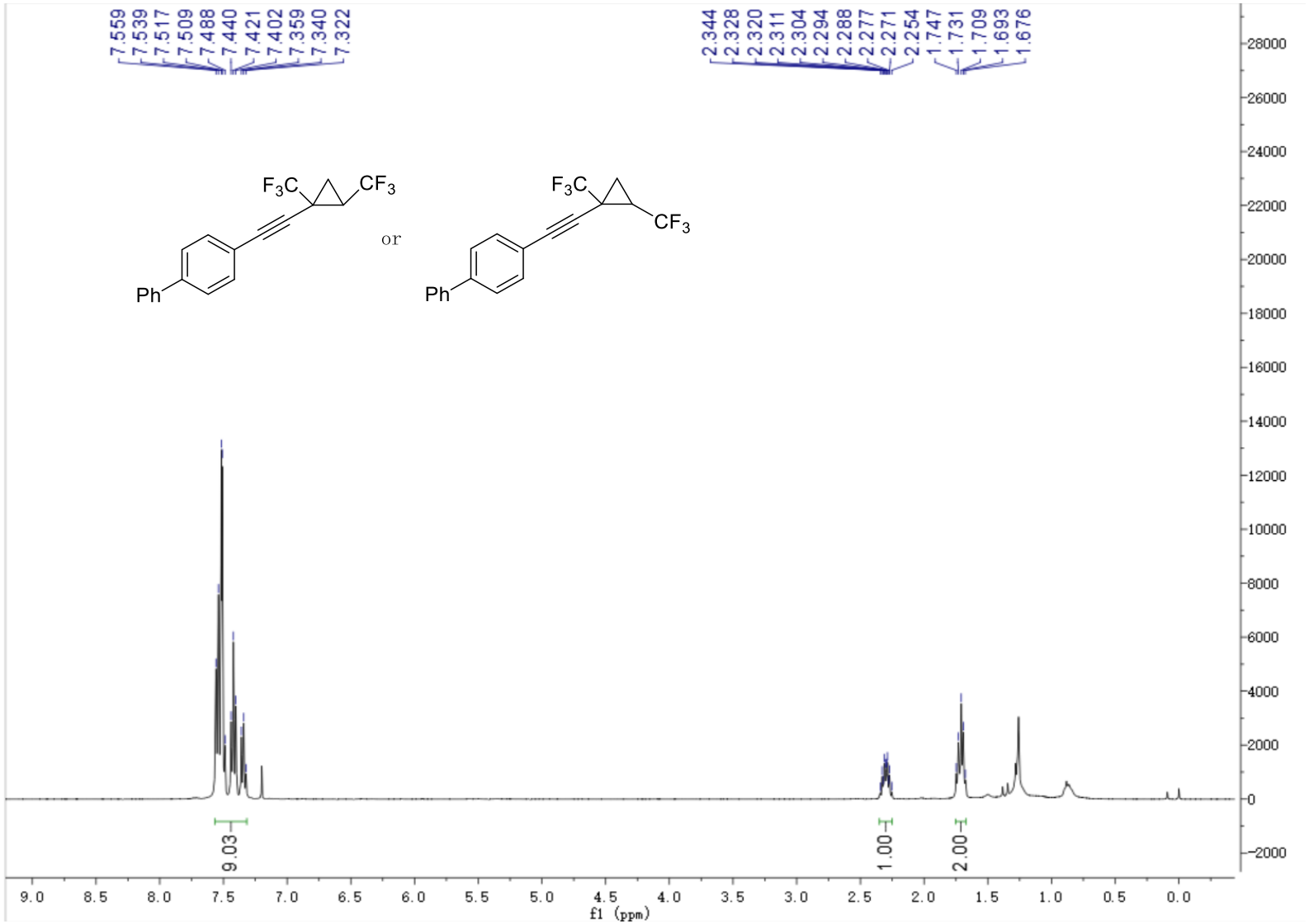
^{13}C NMR spectrum of 3g-isomer 1



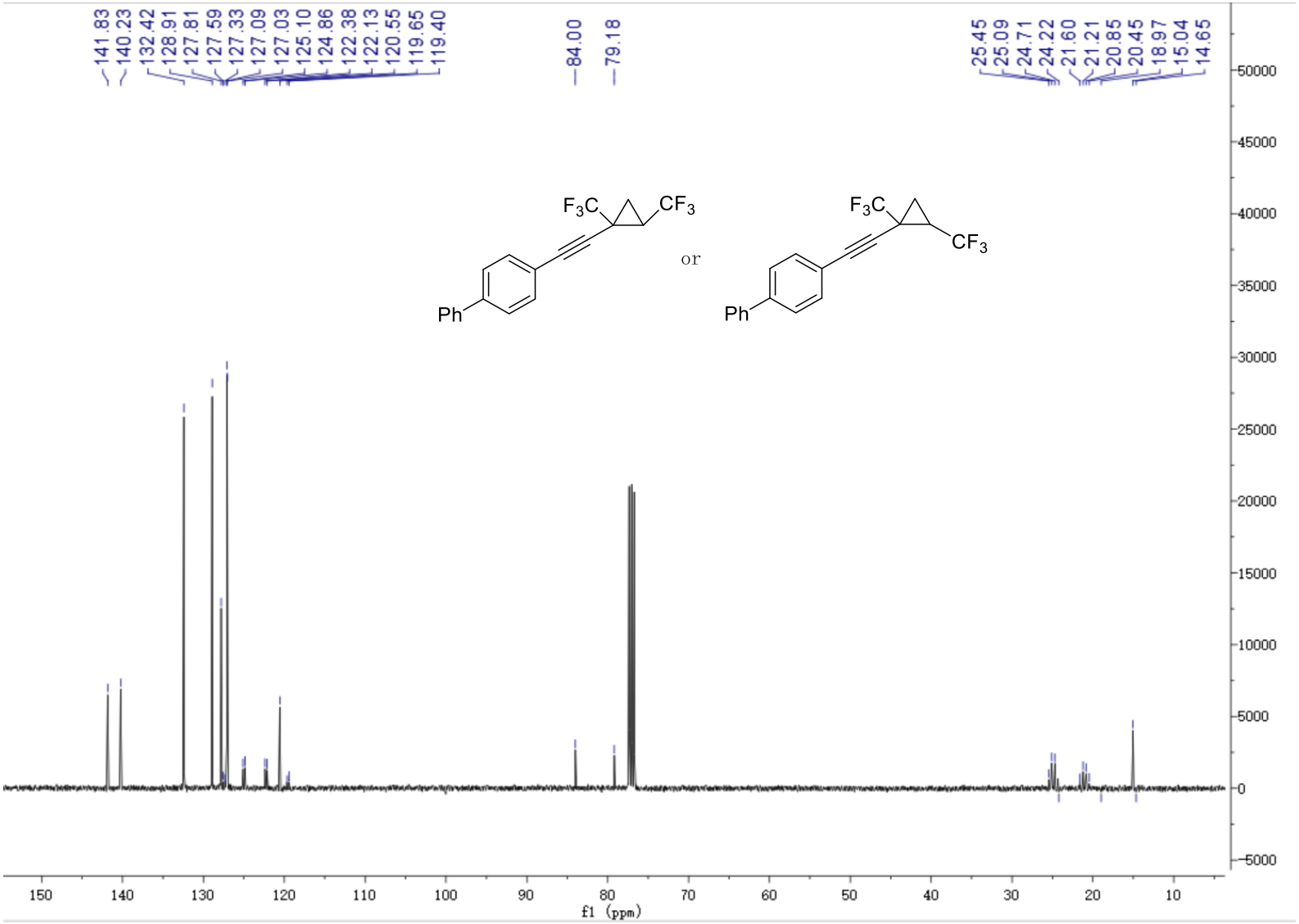
^{19}F NMR spectrum of 3g-isomer 1



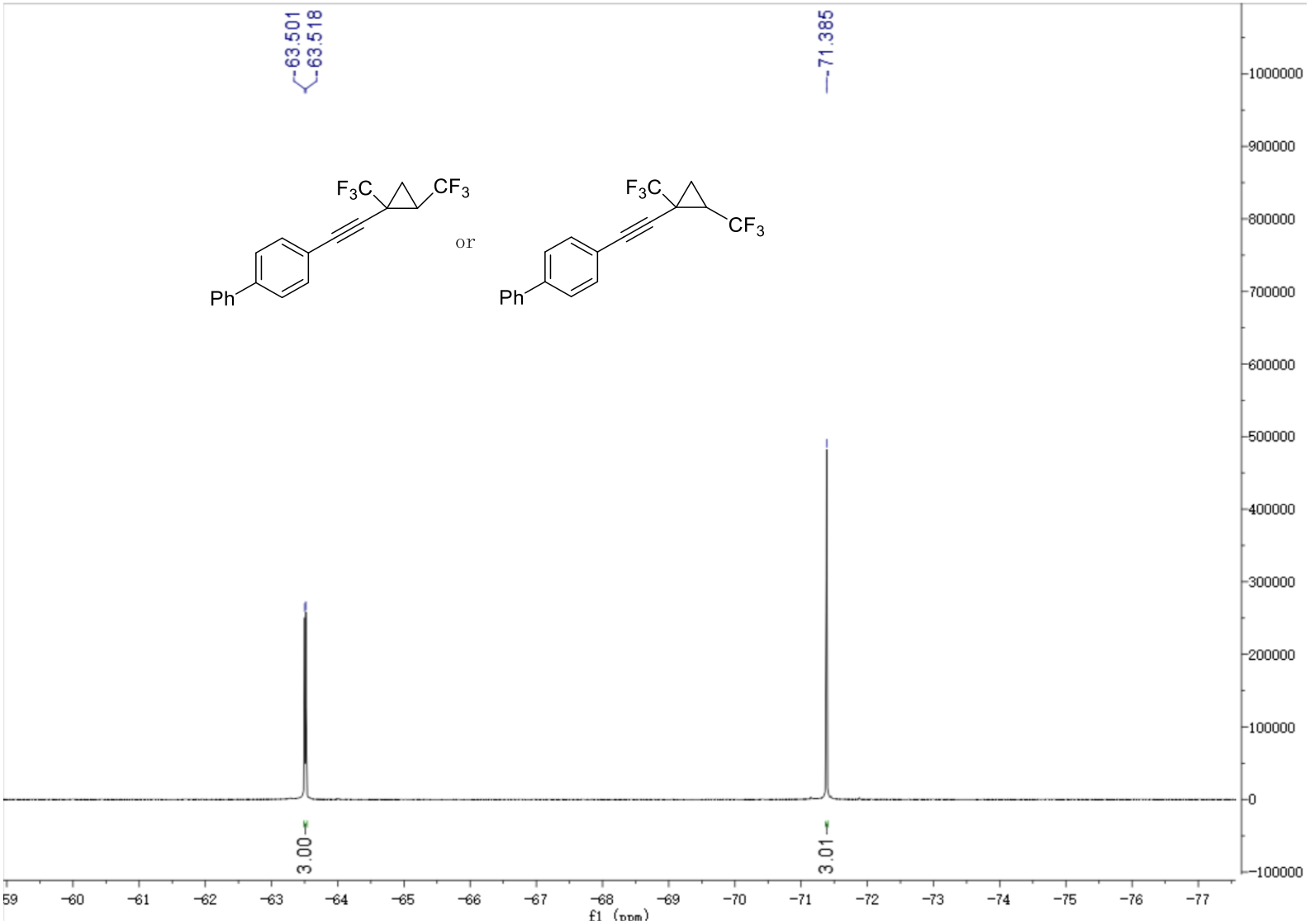
^{1}H NMR spectrum of 3g-isomer 2



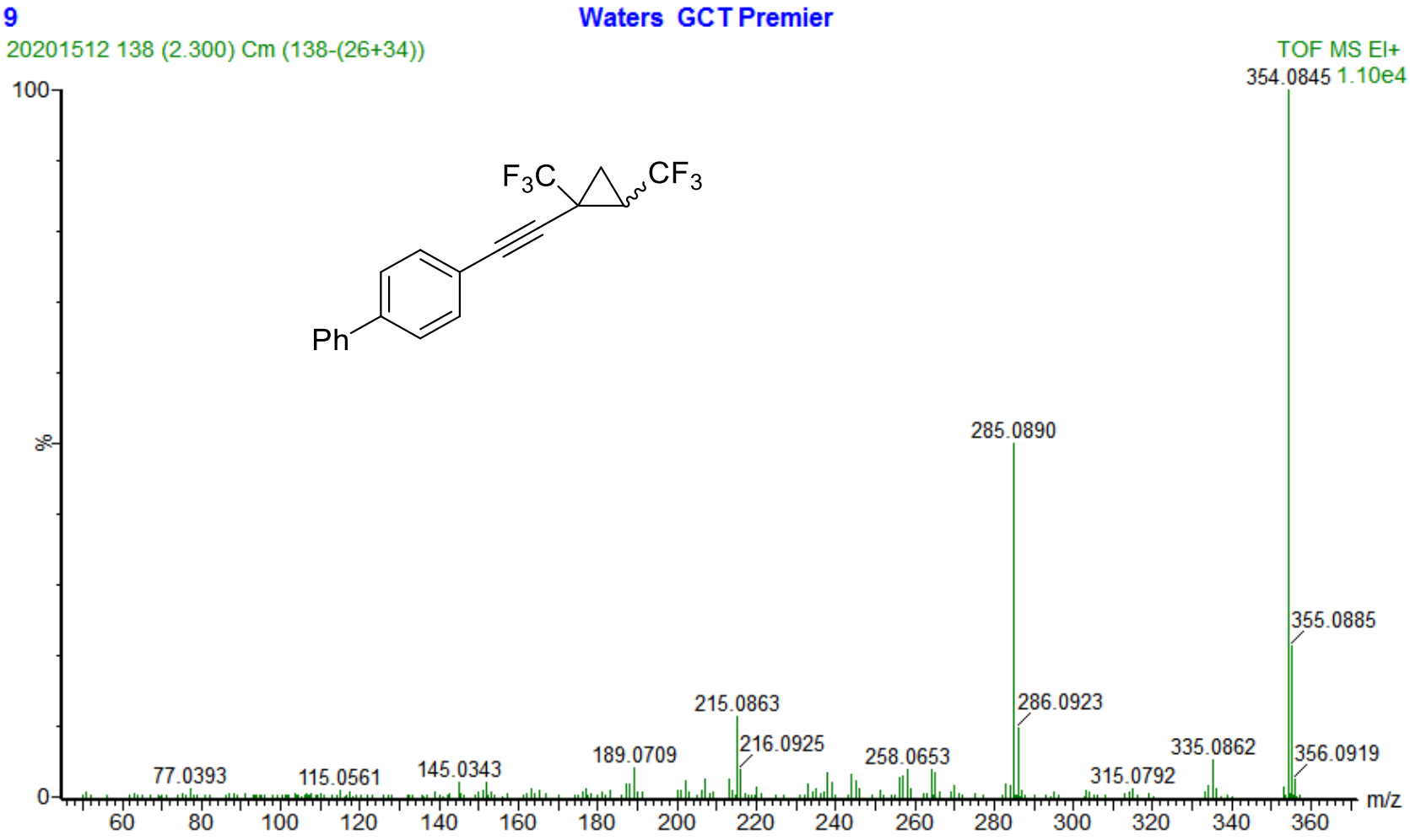
^{13}C NMR spectrum of 3g-isomer 2



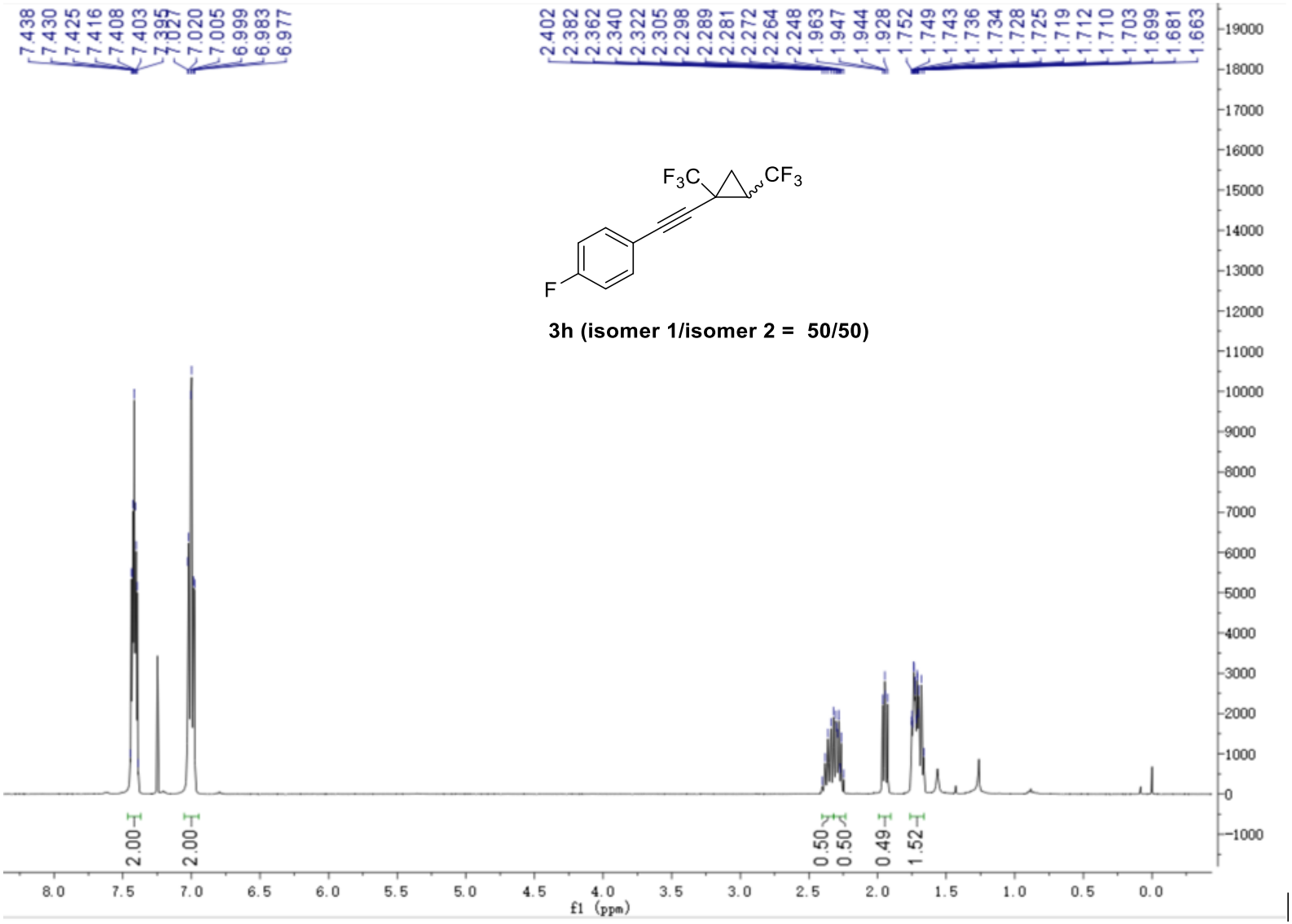
^{19}F NMR spectrum of 3g-isomer 2



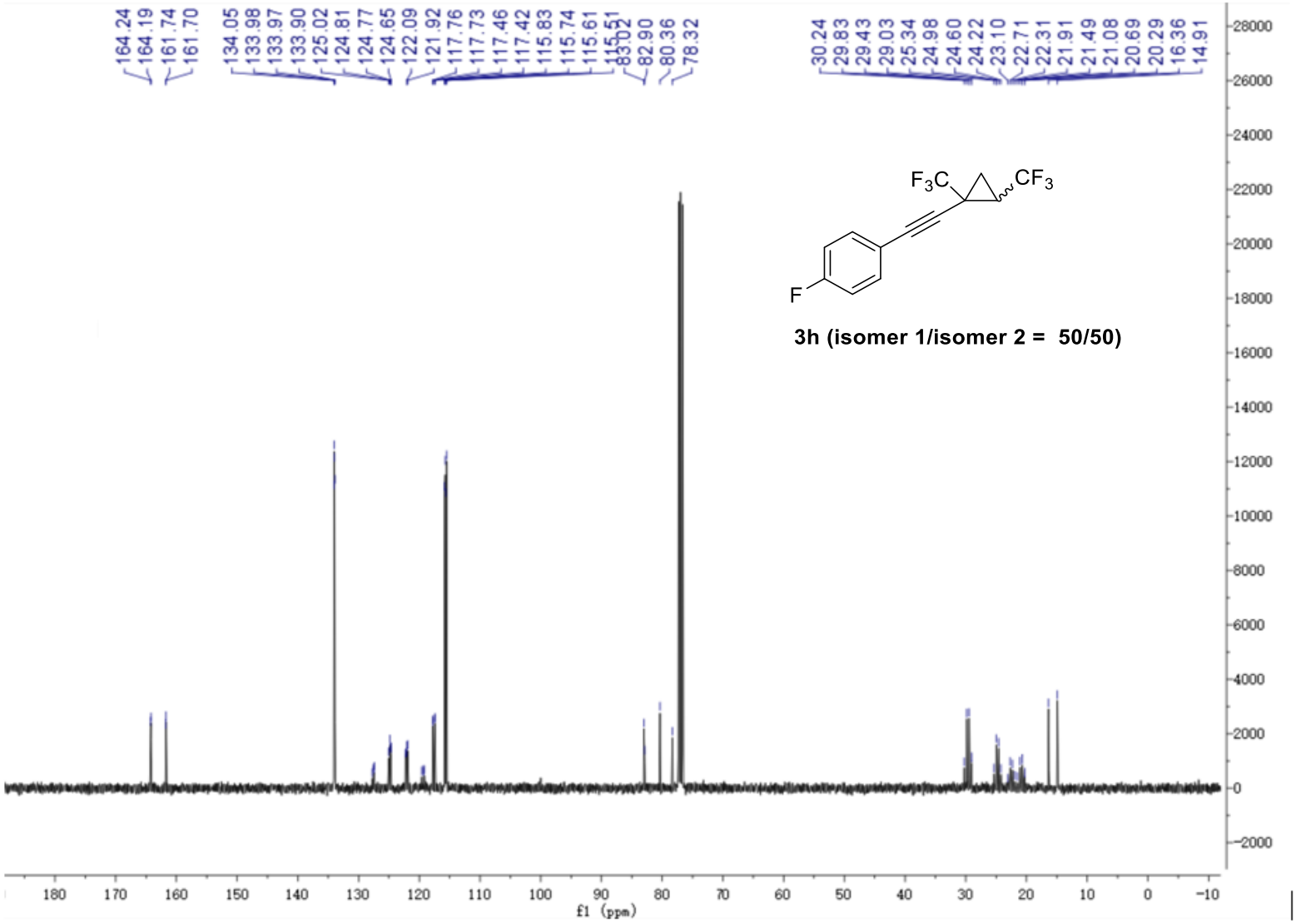
HRMS (EI) spectrum of 3g



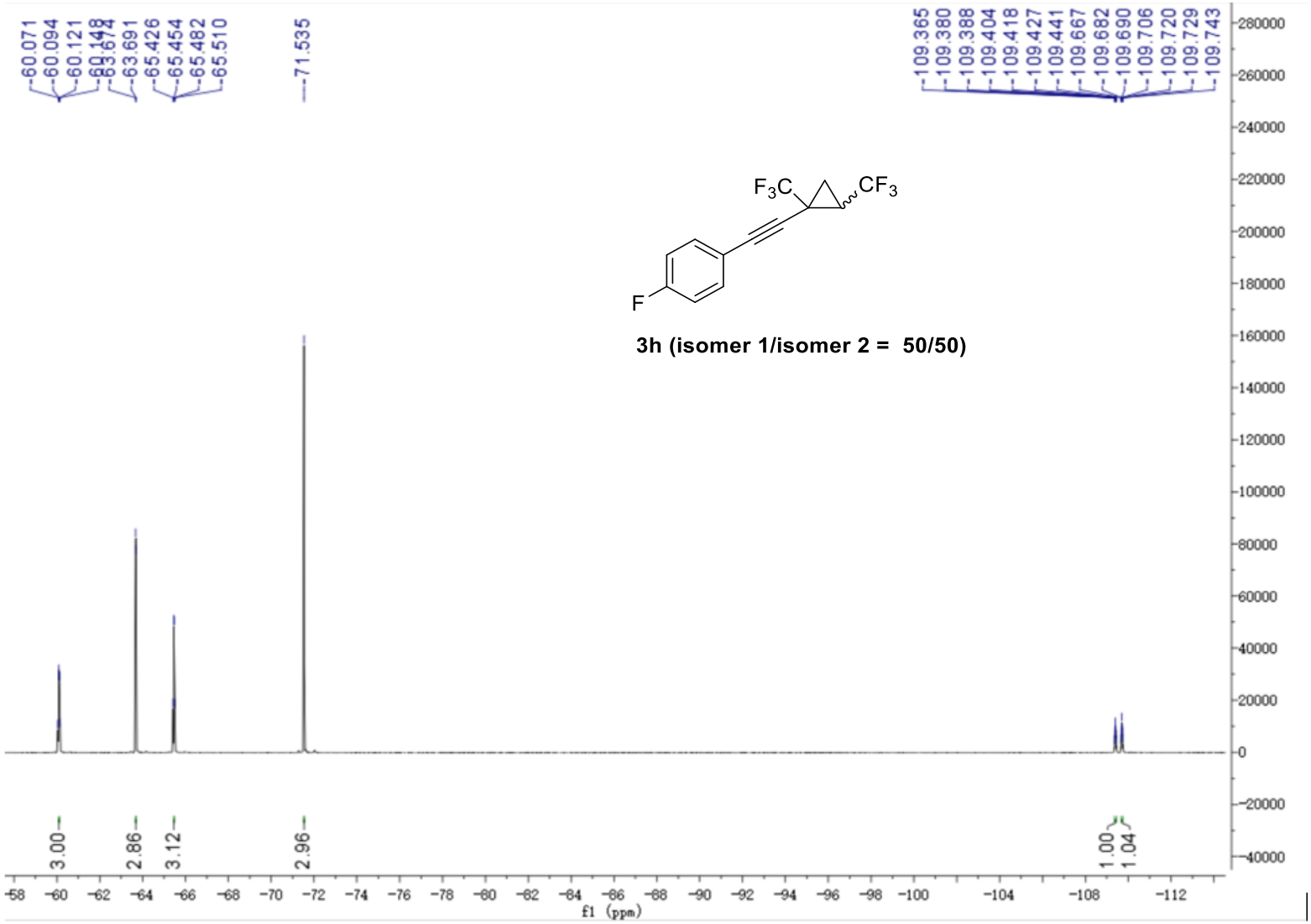
^{1}H NMR spectrum of 3h



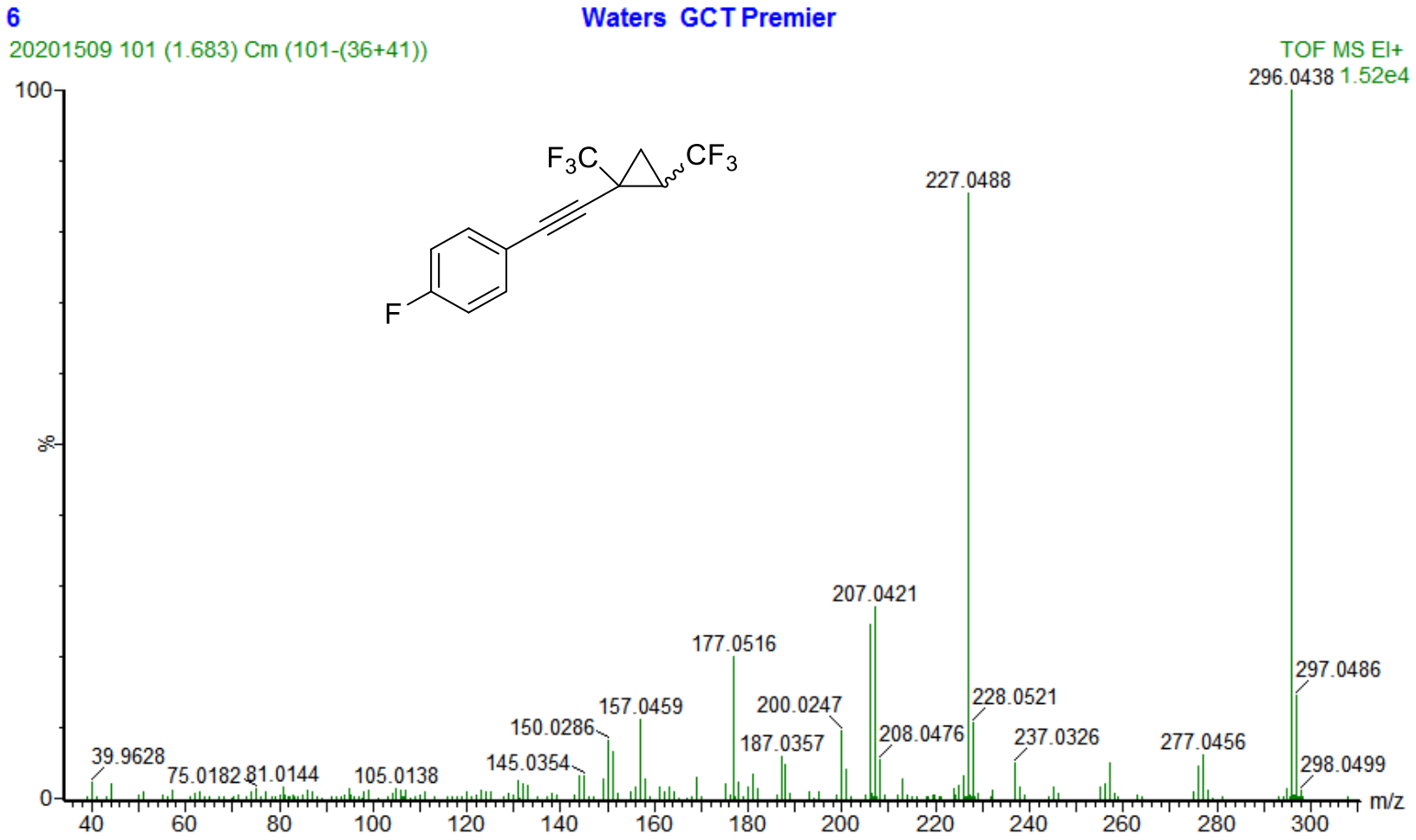
^{13}C NMR spectrum of 3h



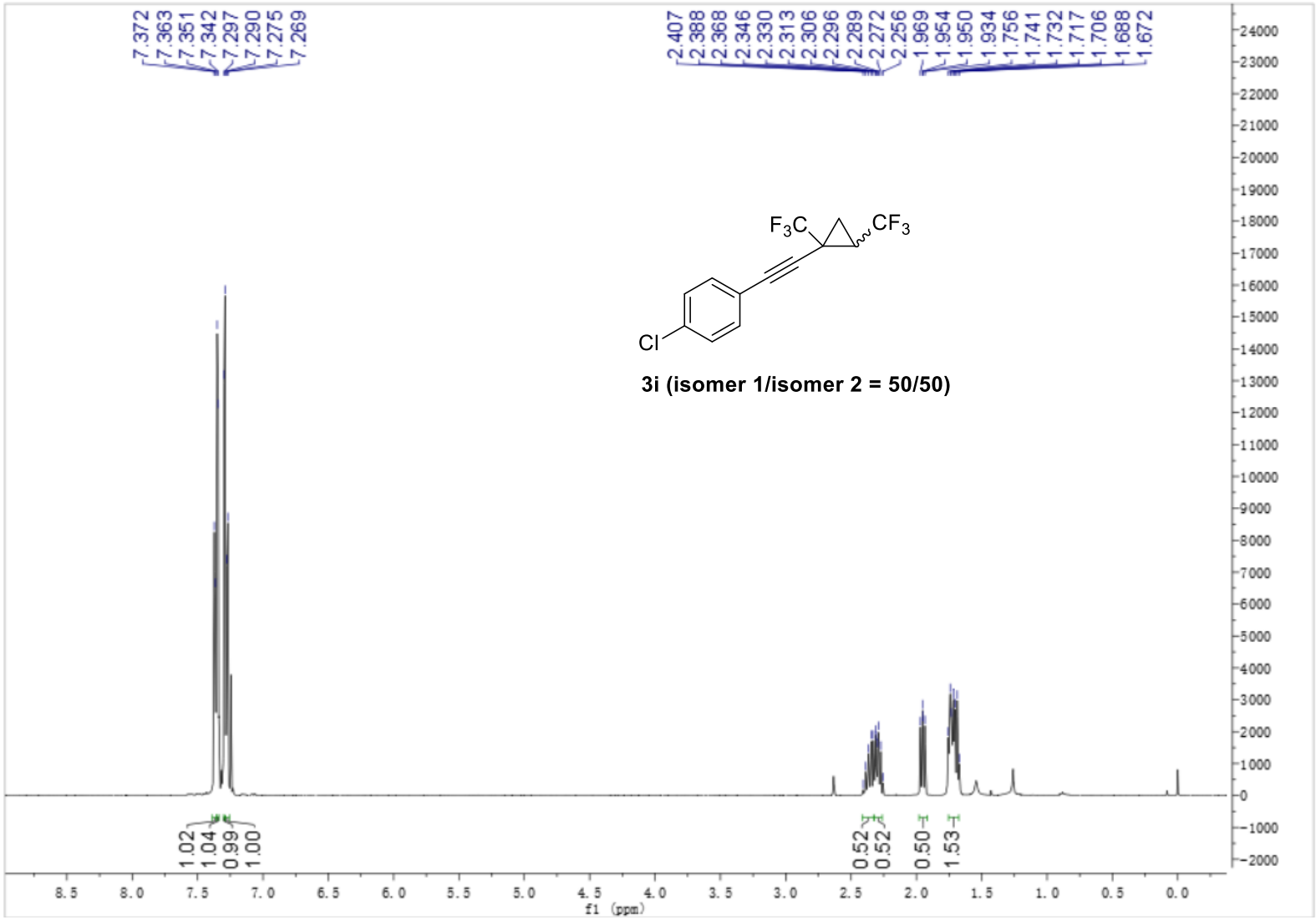
^{19}F NMR spectrum of 3h



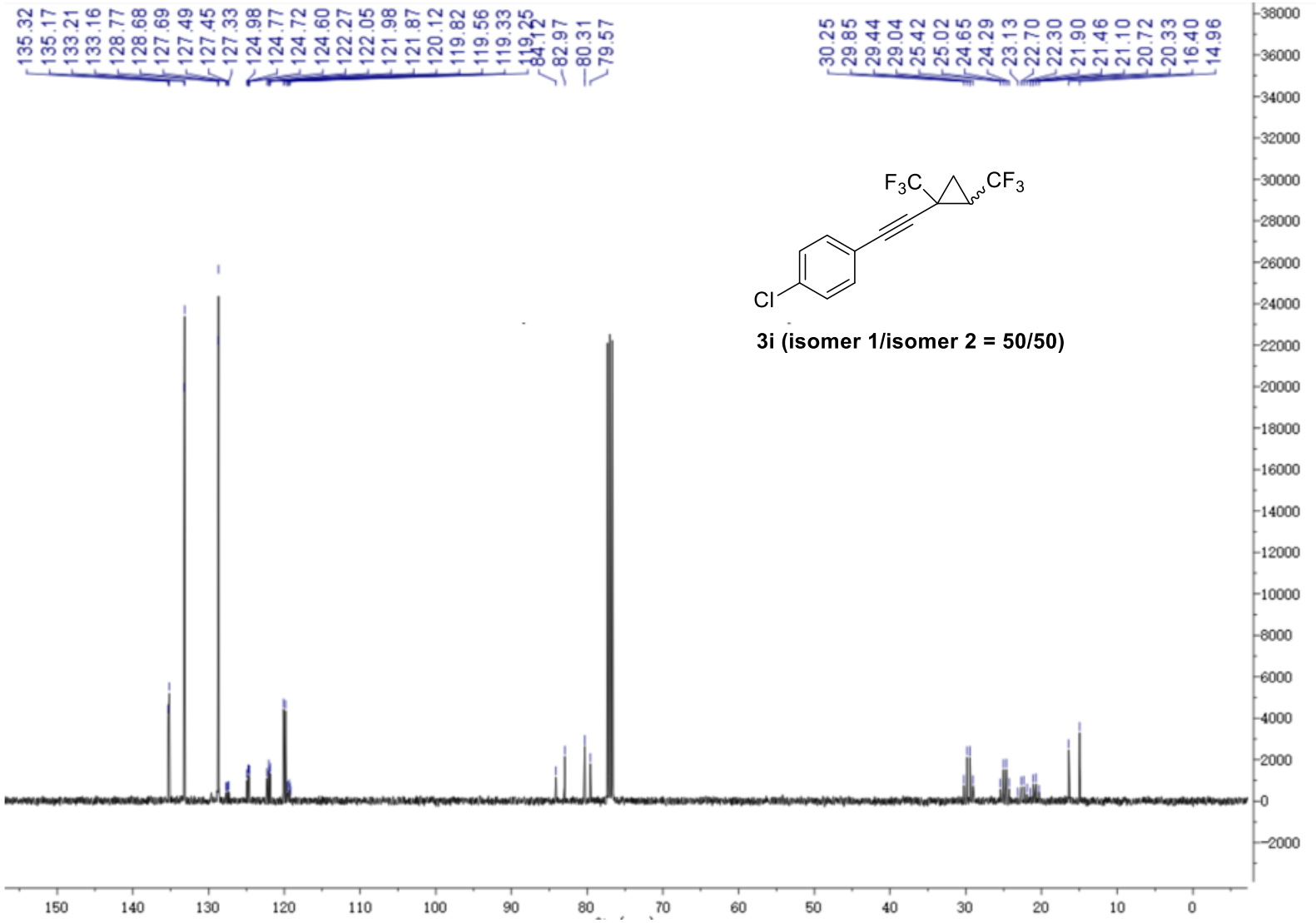
HRMS (EI) spectrum of 3h



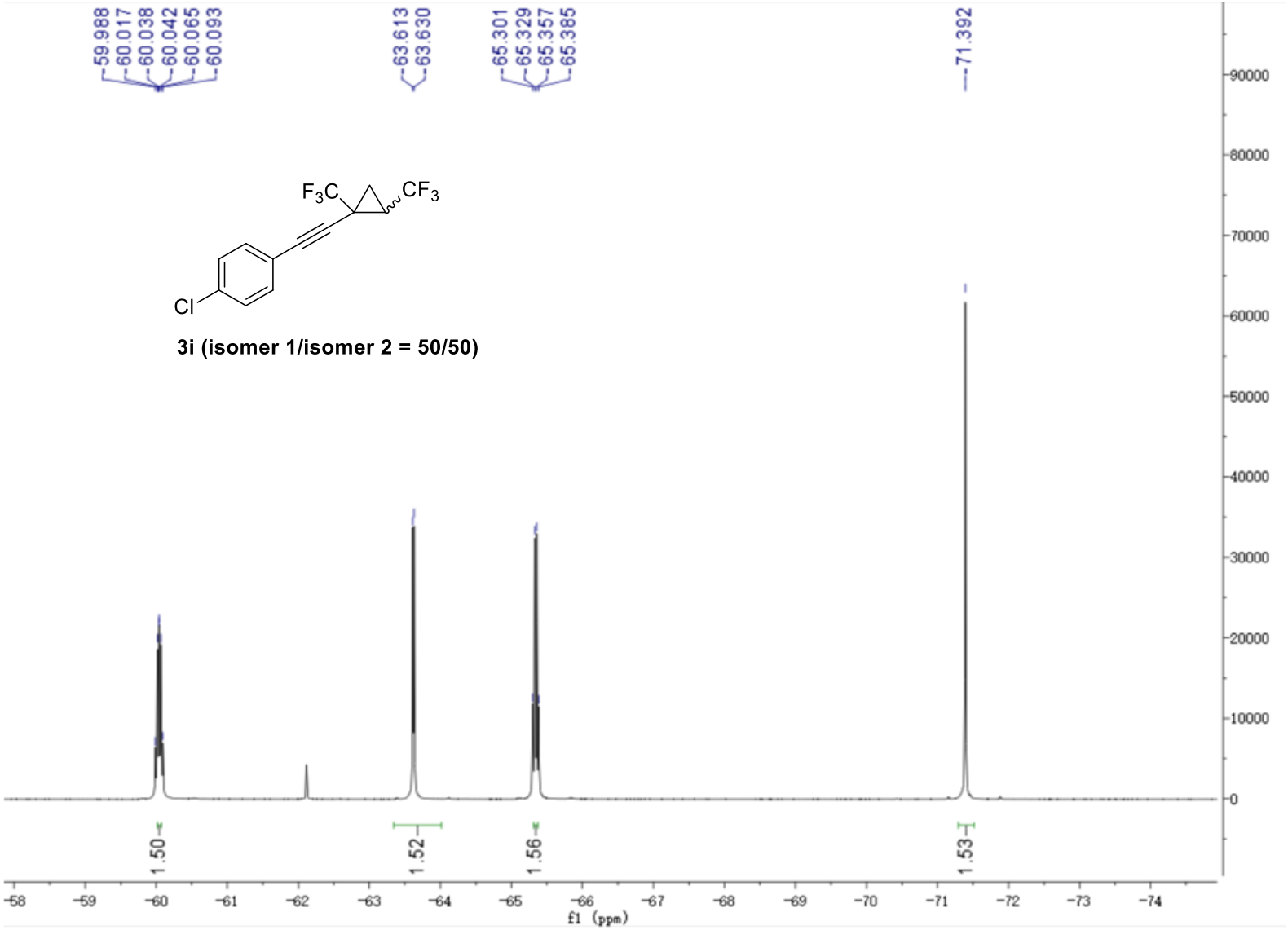
^{1}H NMR spectrum of 3i



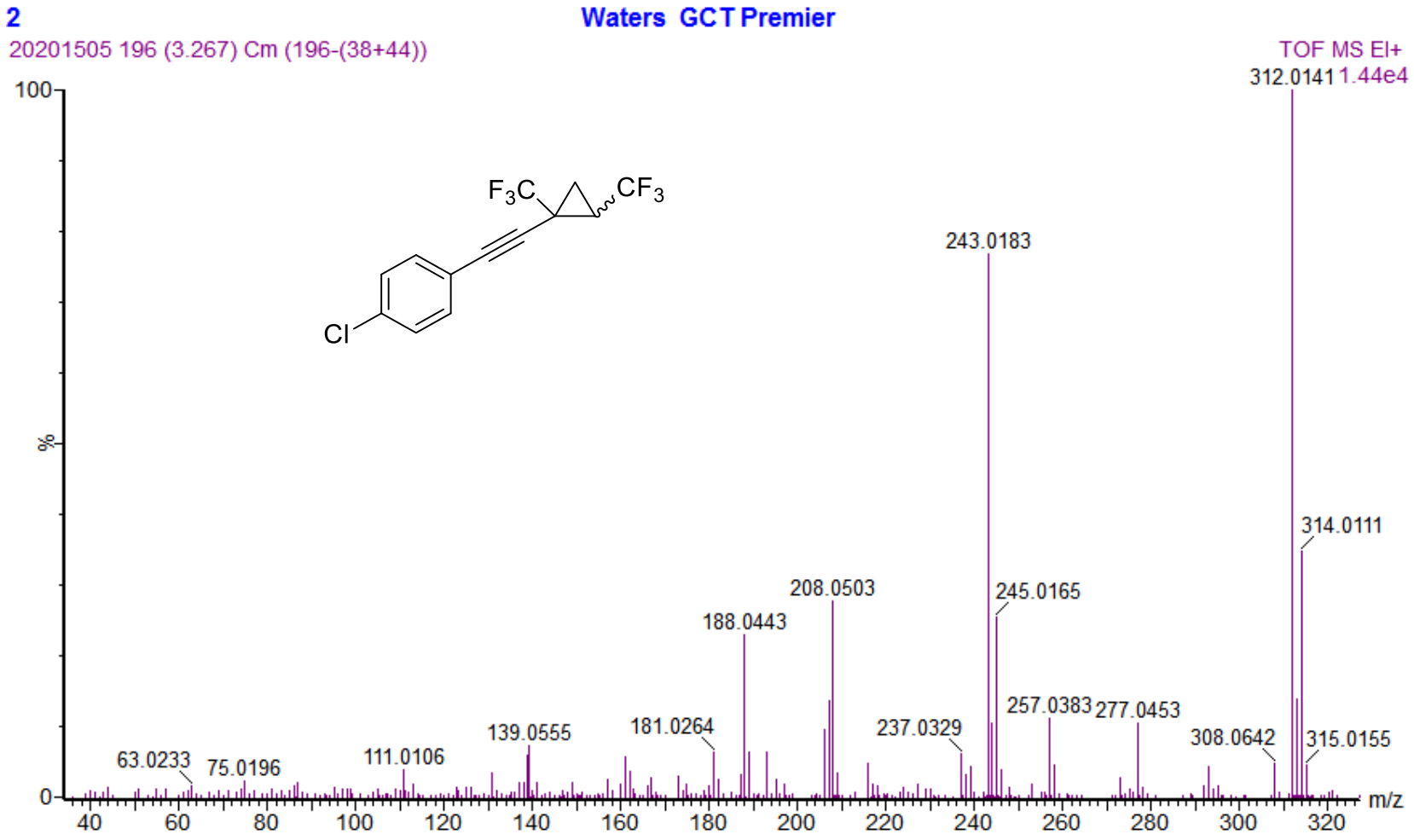
^{13}C NMR spectrum of 3i



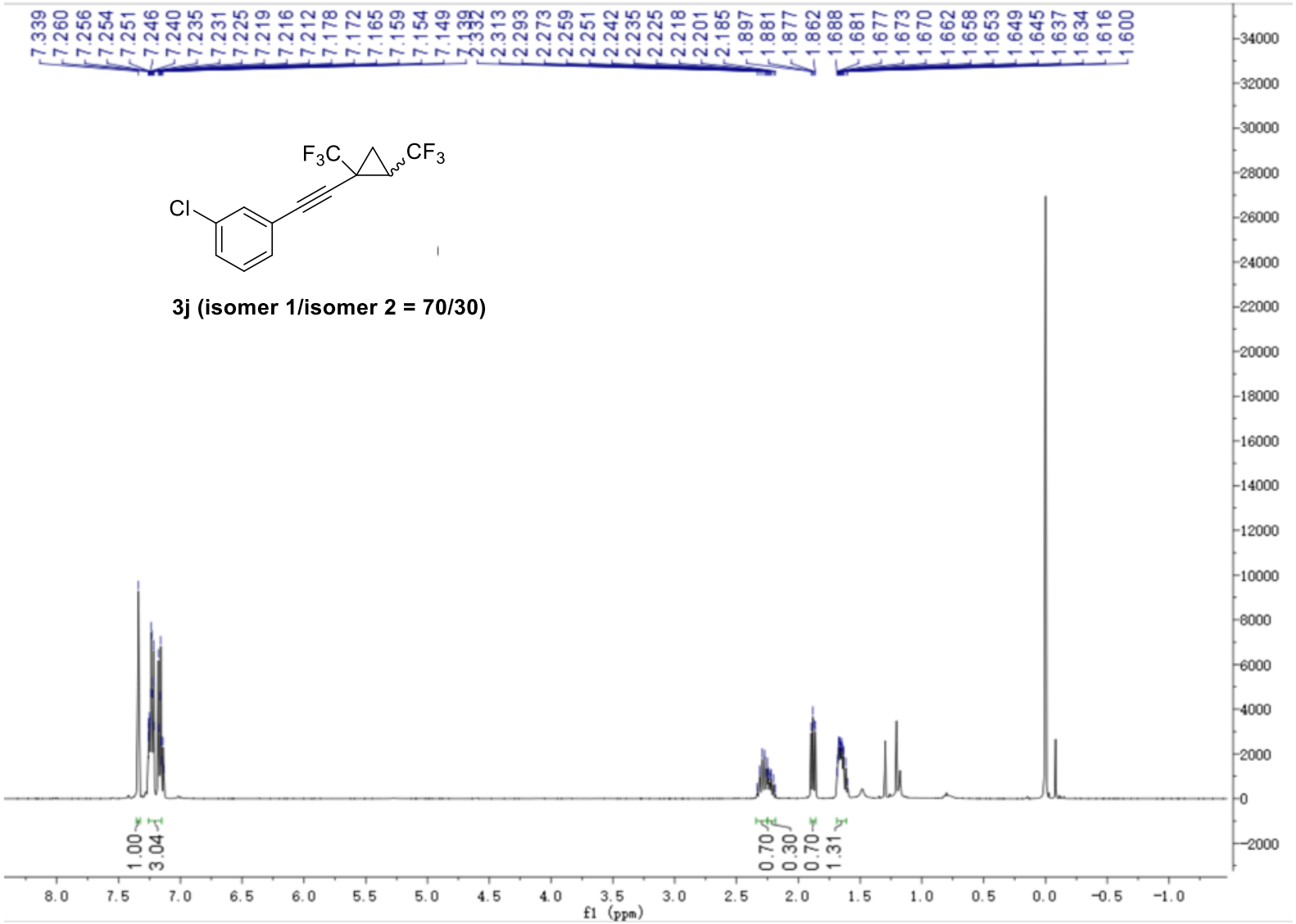
^{19}F NMR spectrum of 3i



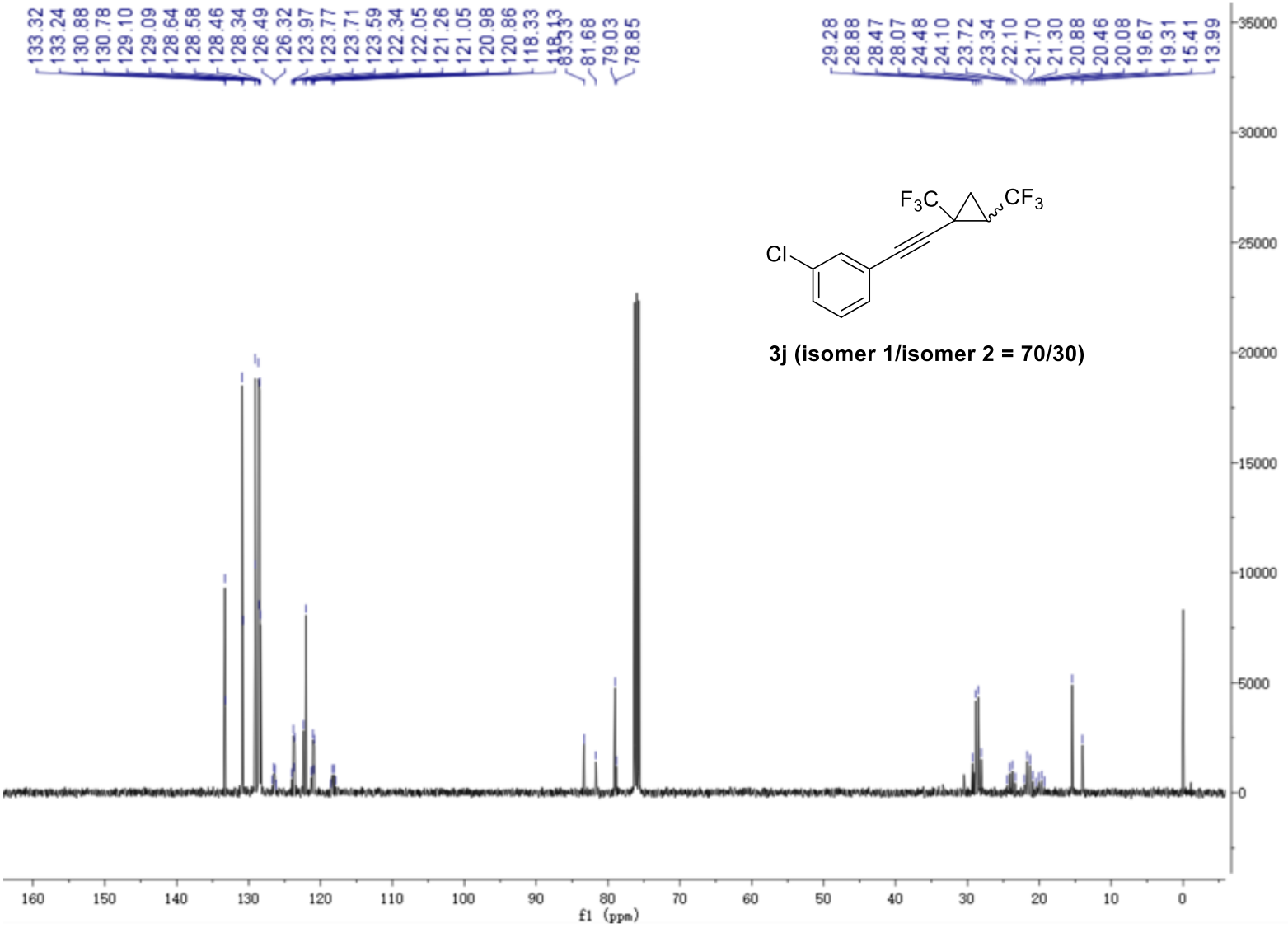
HRMS (EI) spectrum of 3i



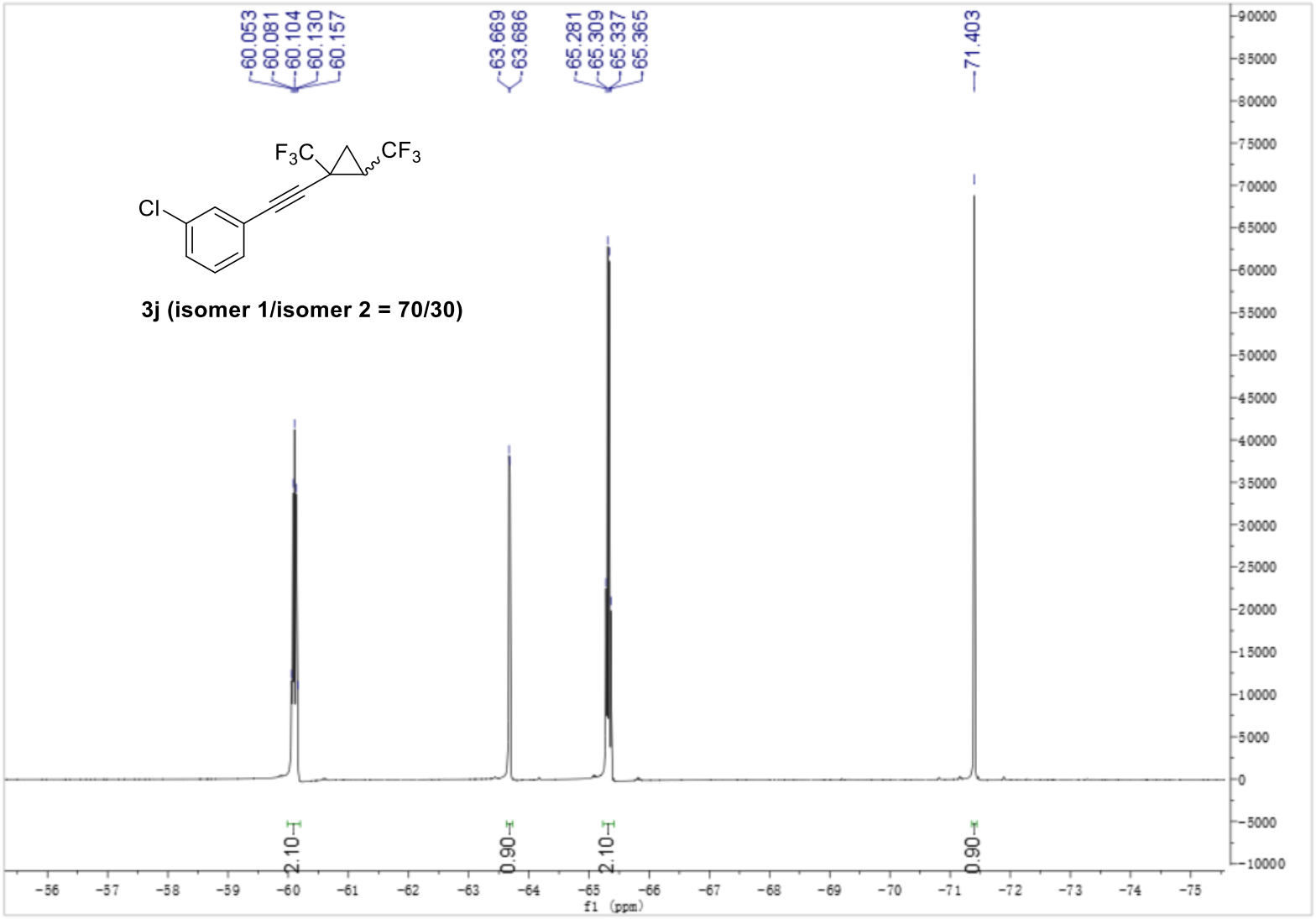
^{1}H NMR spectrum of 3j



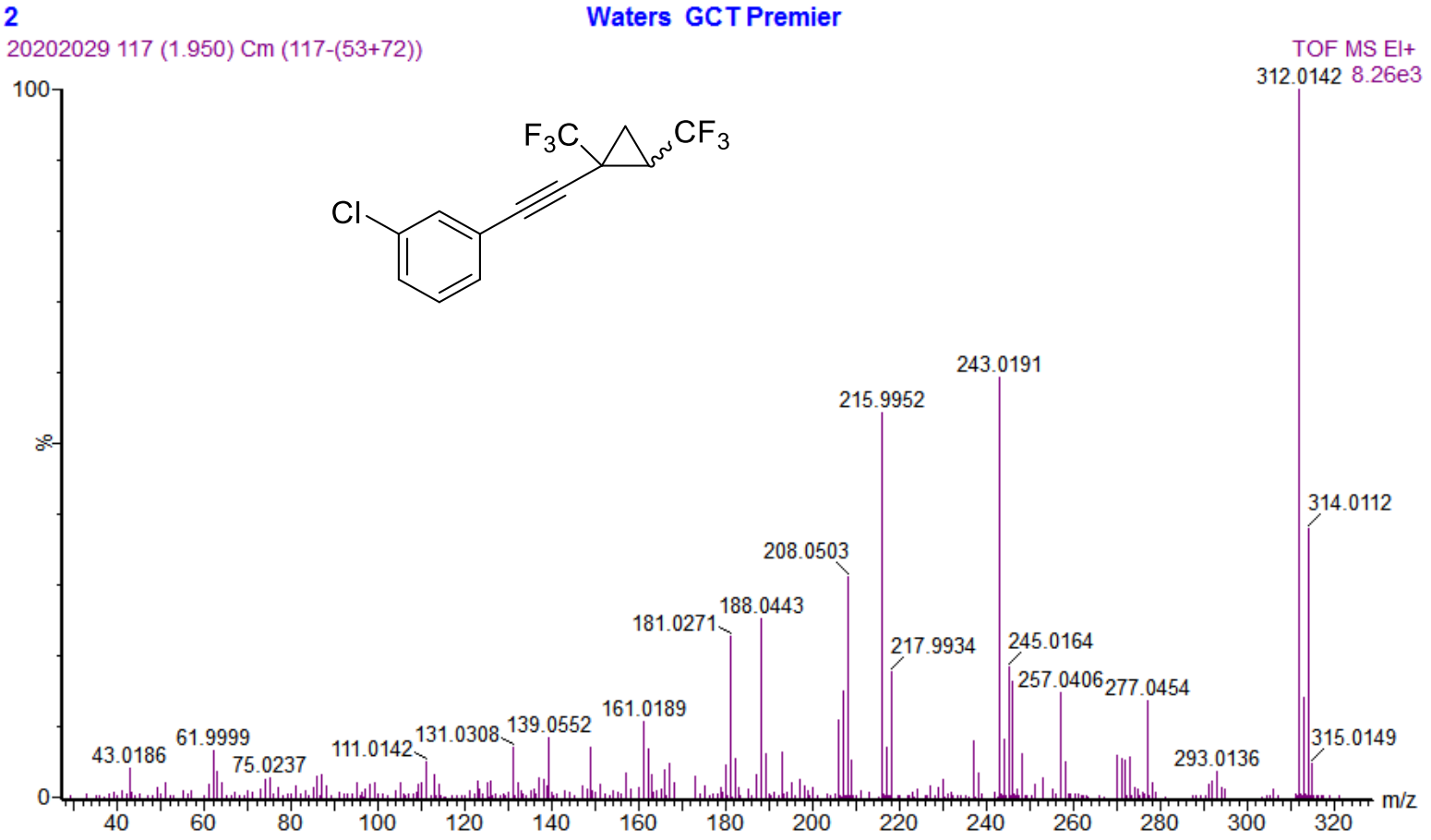
^{13}C NMR spectrum of 3j



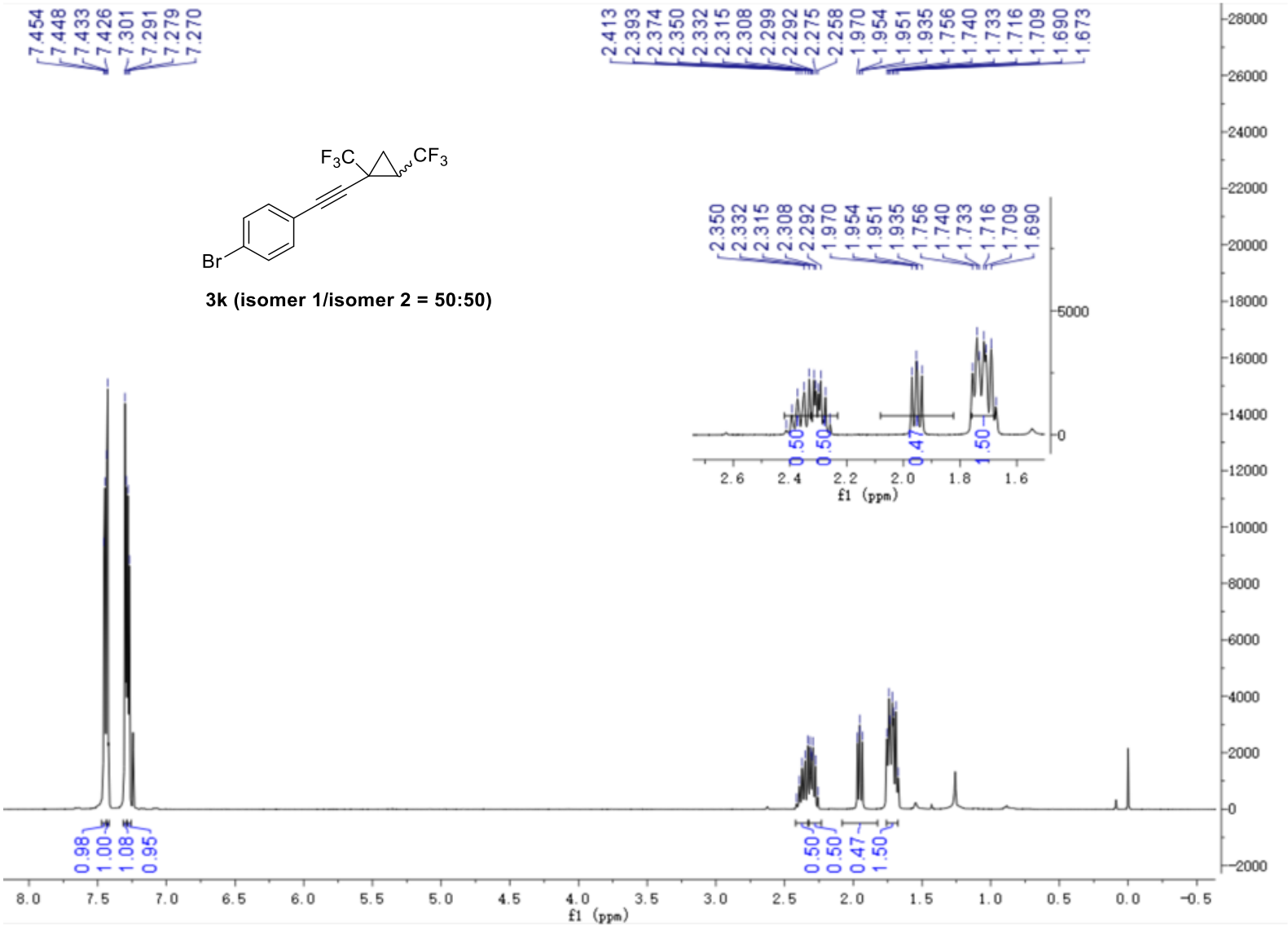
^{19}F NMR spectrum of 3j



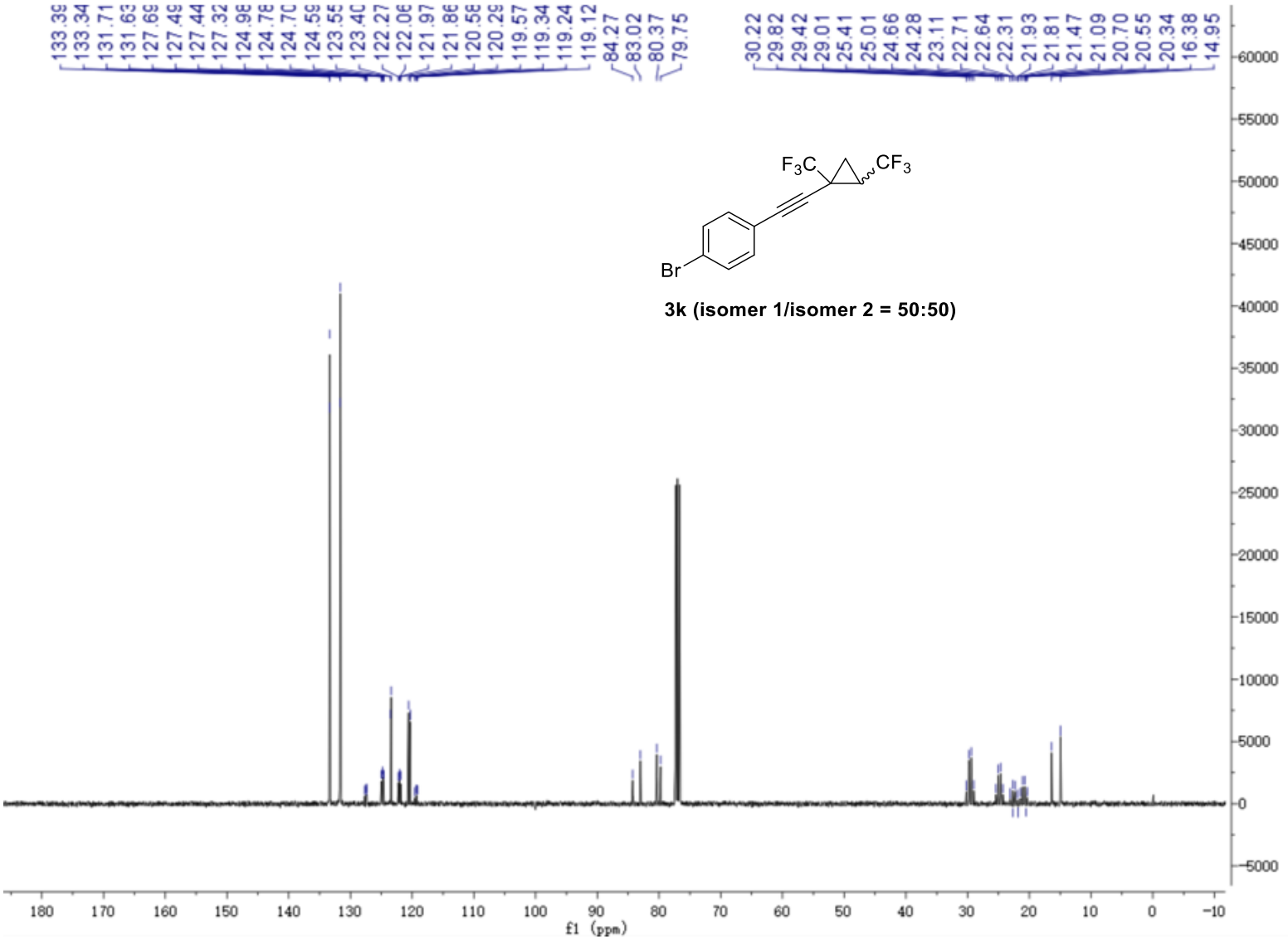
HRMS (EI) spectrum of 3j



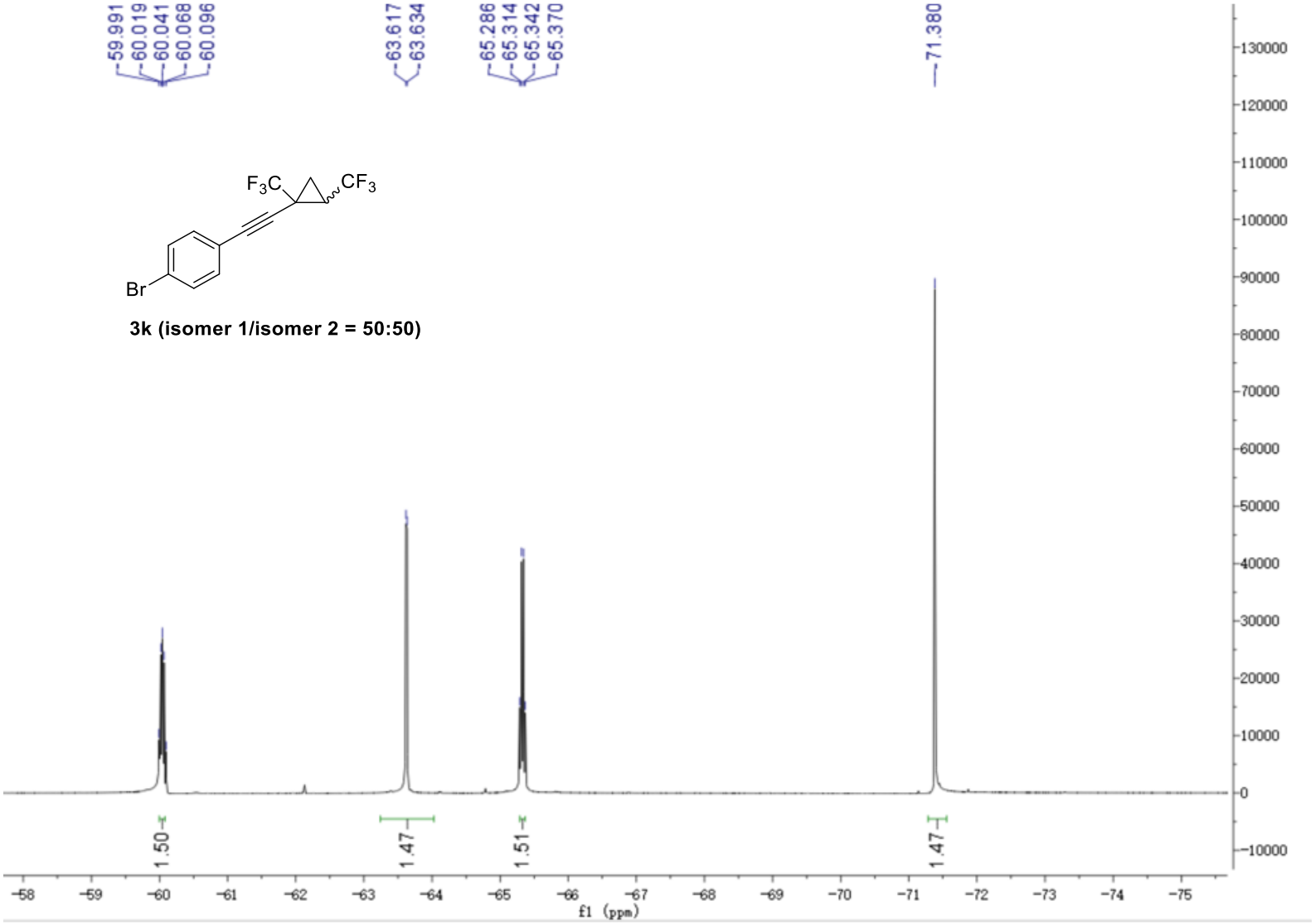
^{1}H NMR spectrum of 3k



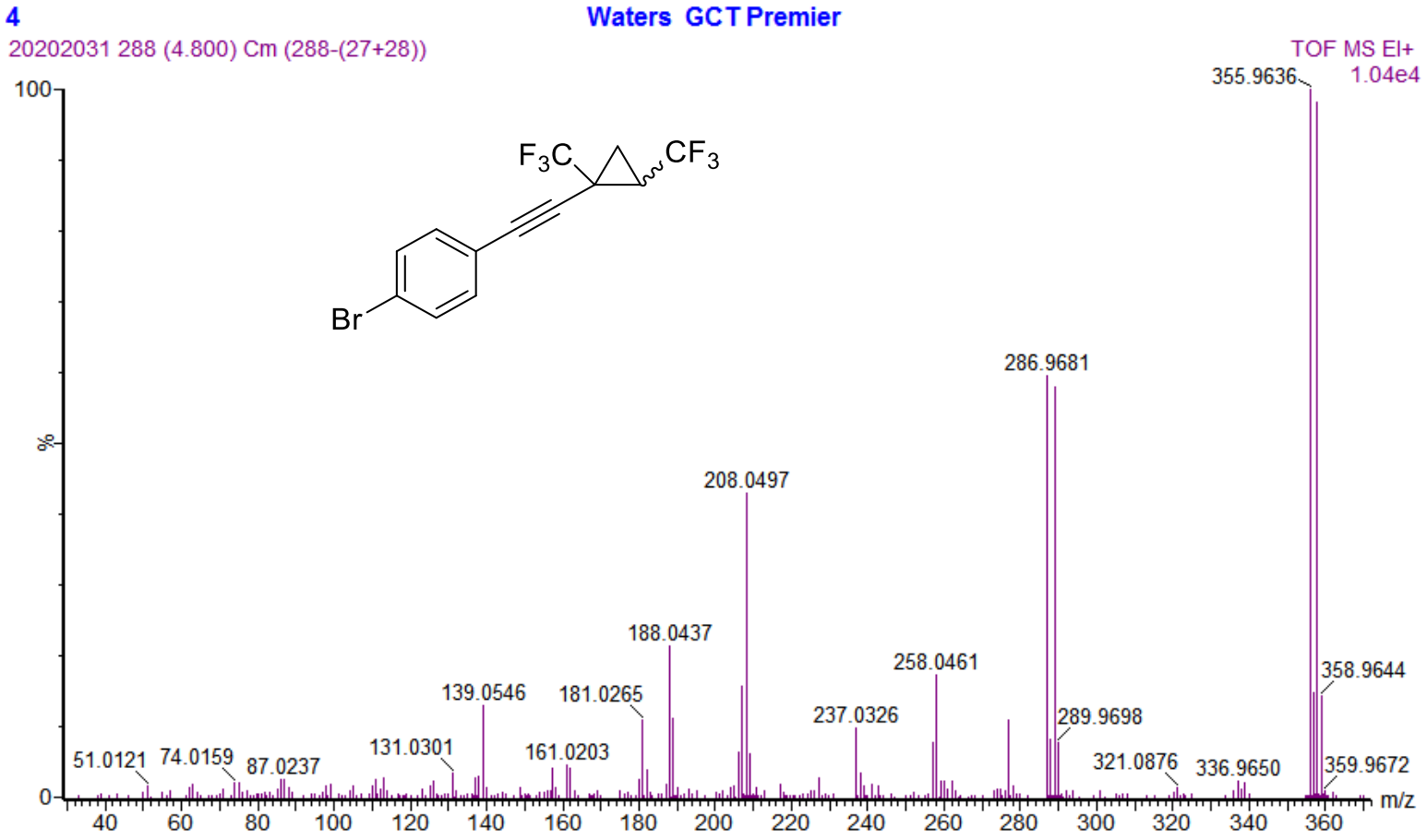
^{13}C NMR spectrum of 3k



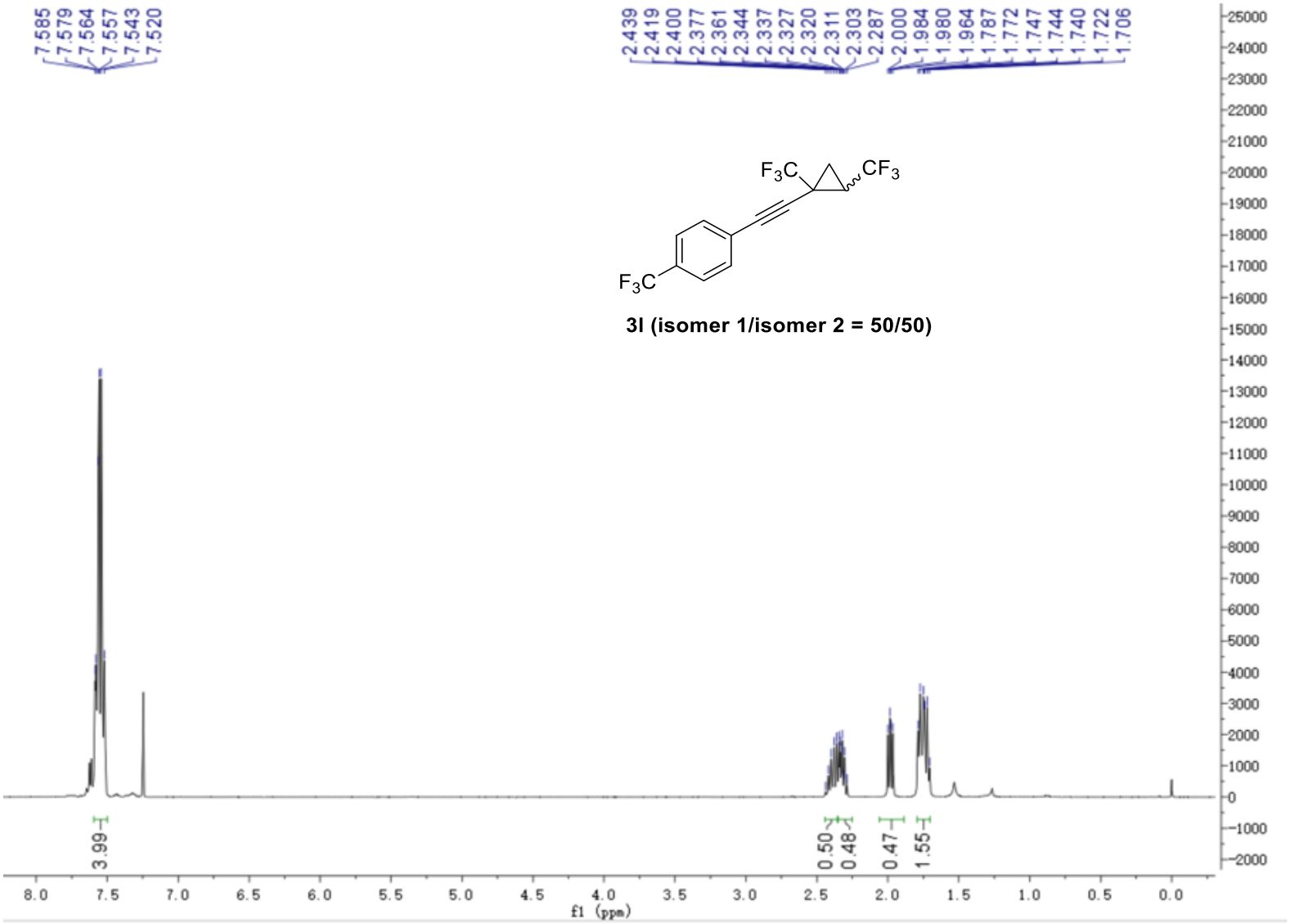
^{19}F NMR spectrum of 3k



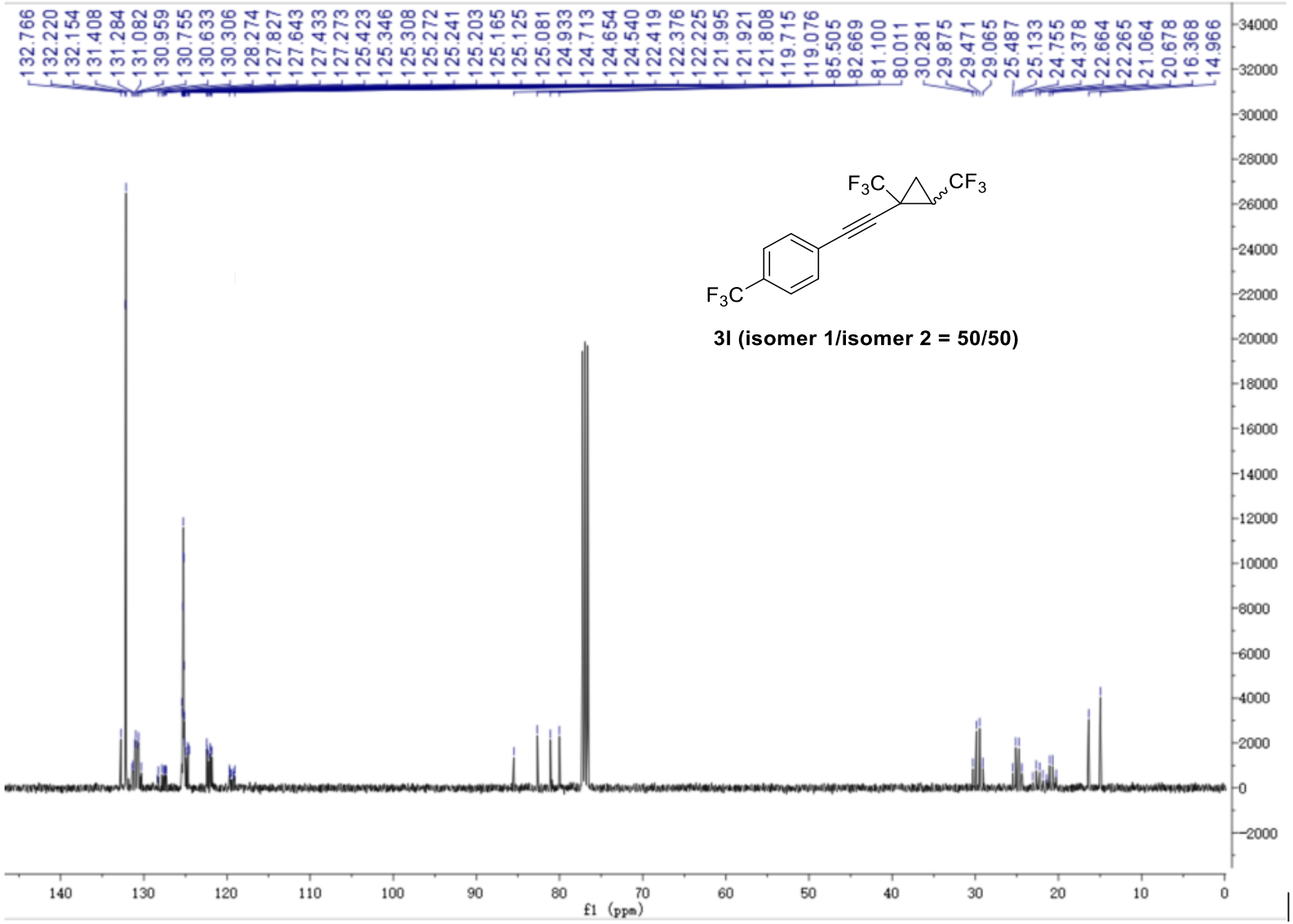
HRMS (EI) spectrum of 3k



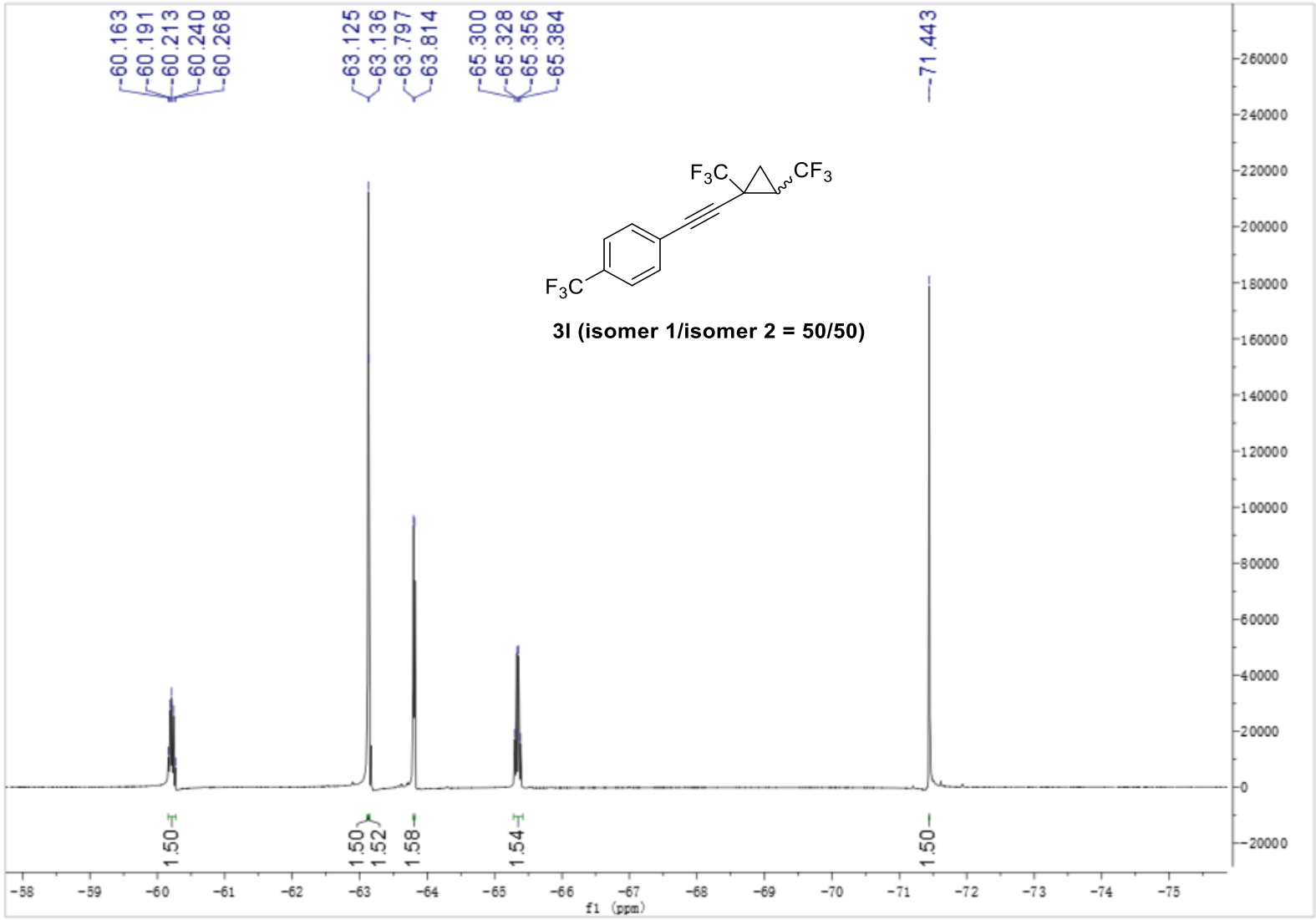
^{1}H NMR spectrum of 3l



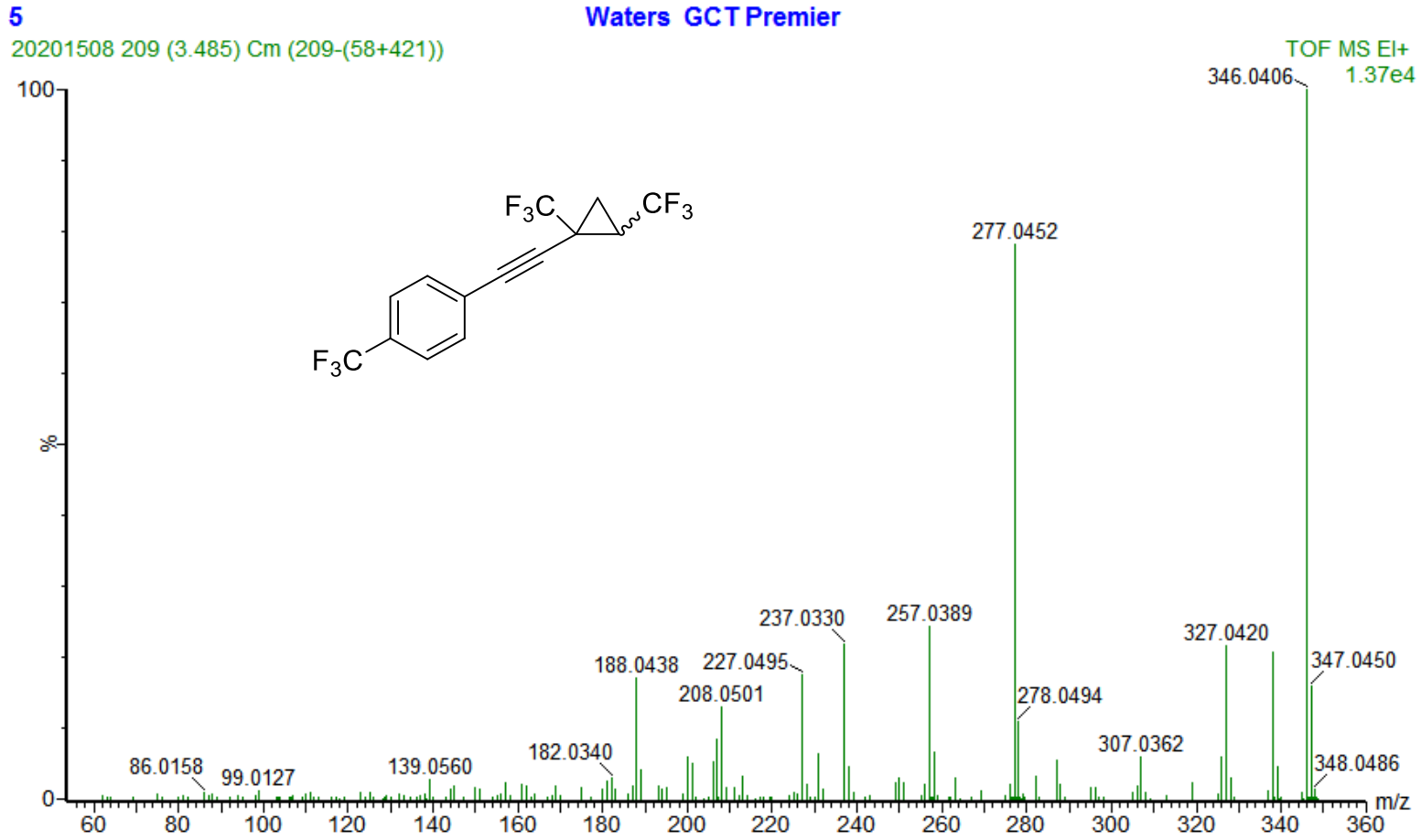
^{13}C NMR spectrum of 3l



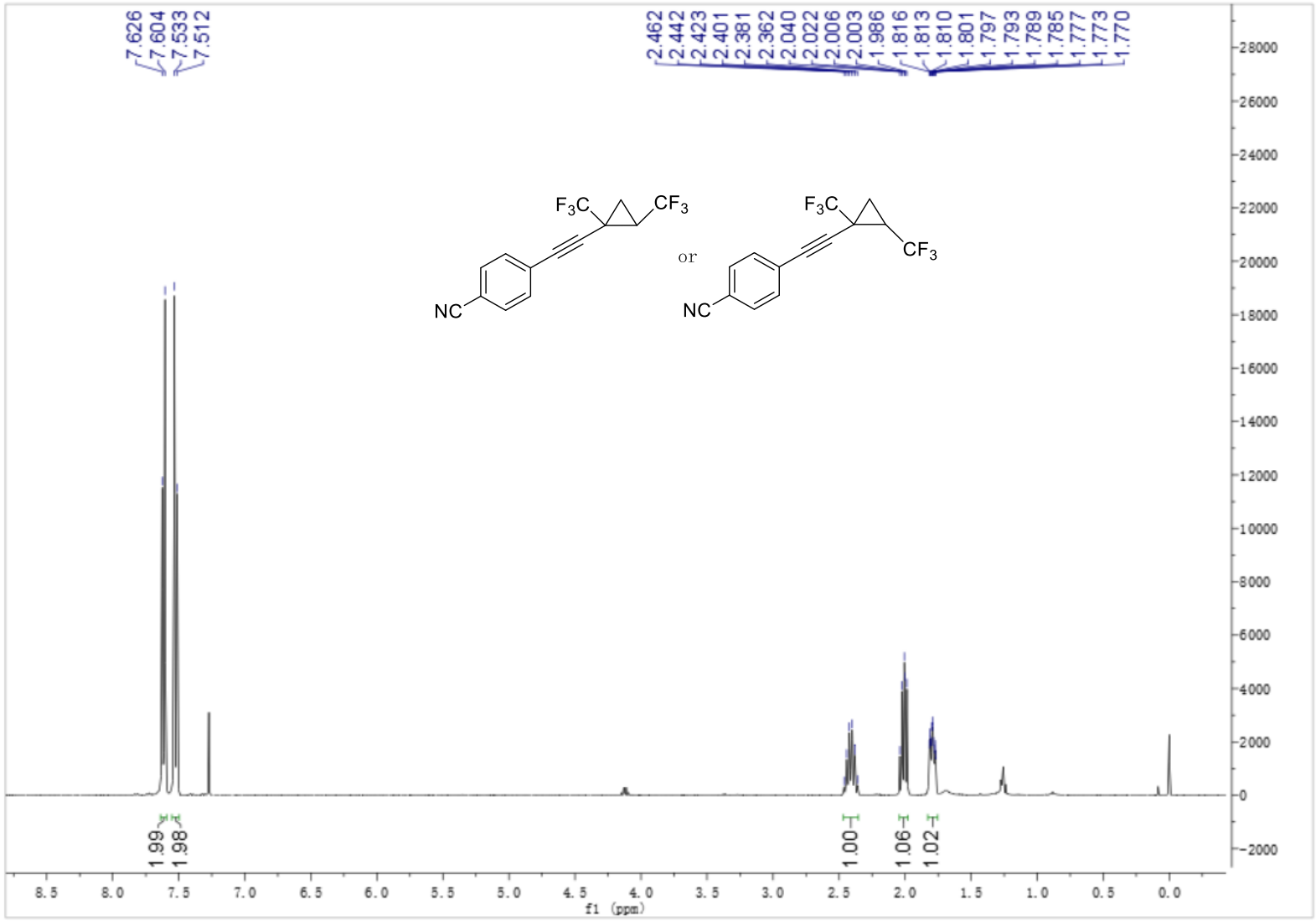
^{19}F NMR spectrum of 3l



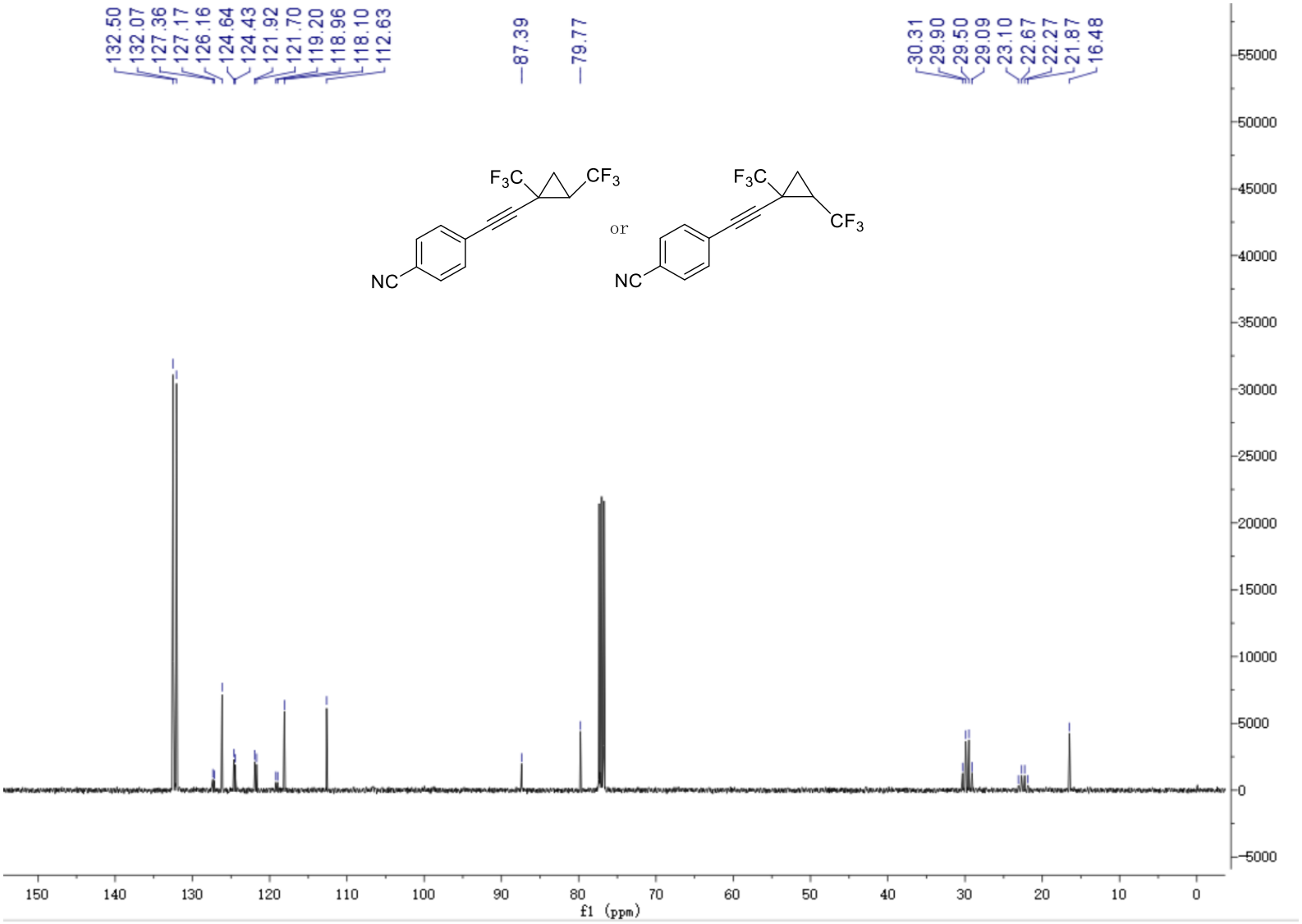
HRMS (EI) spectrum of 3l



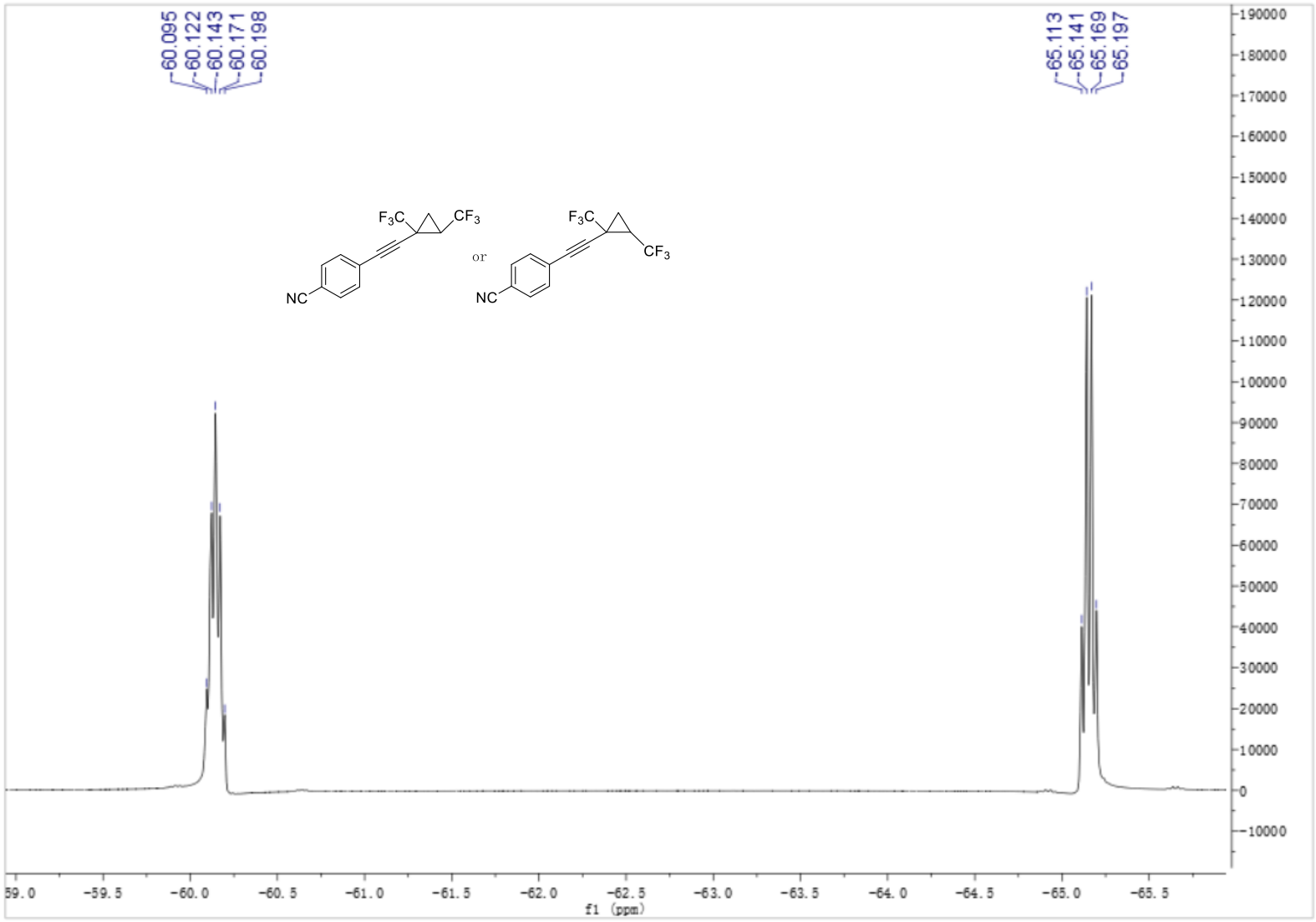
^{1}H NMR spectrum of 3m-isomer 1



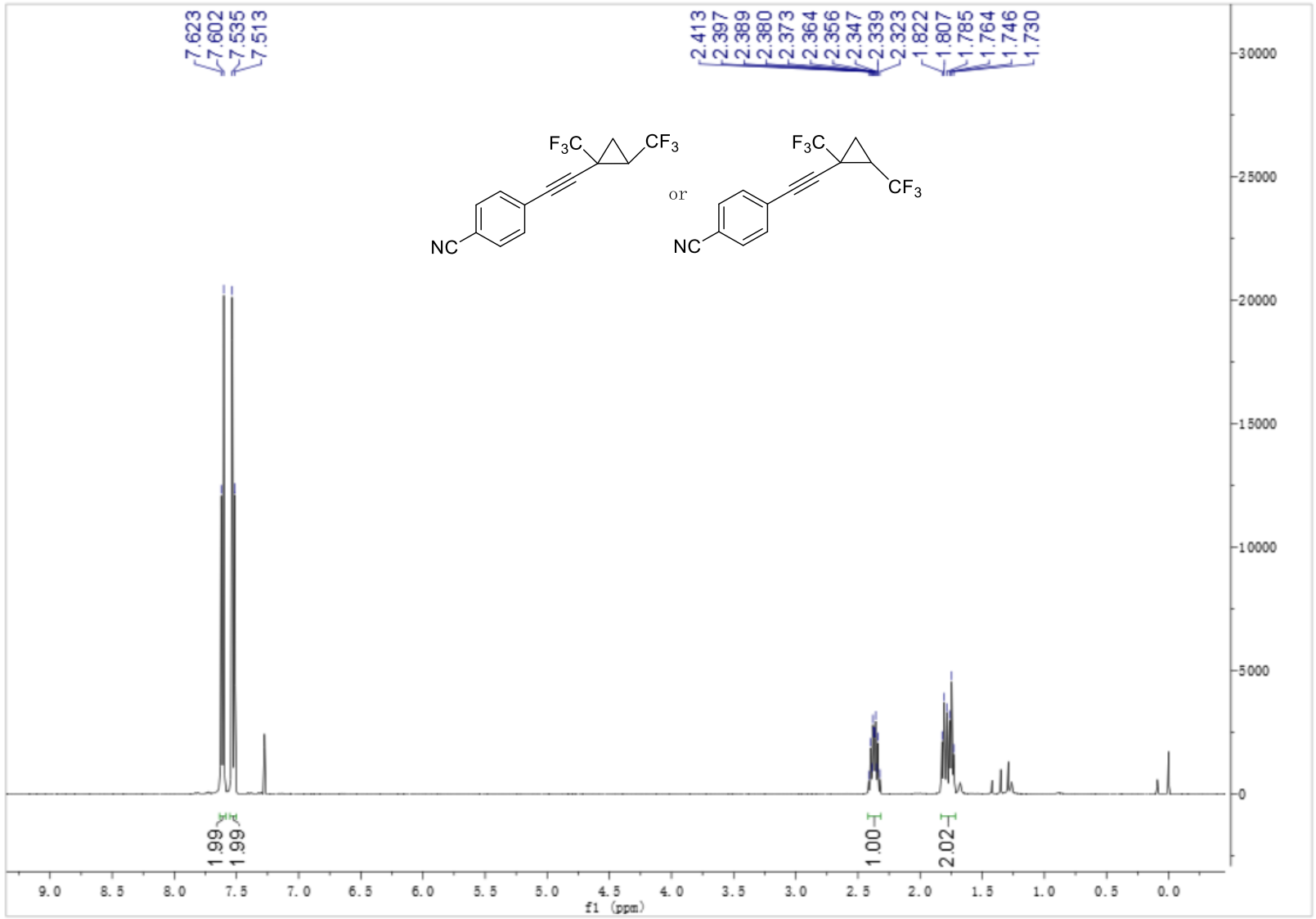
^{13}C NMR spectrum of 3m-isomer 1



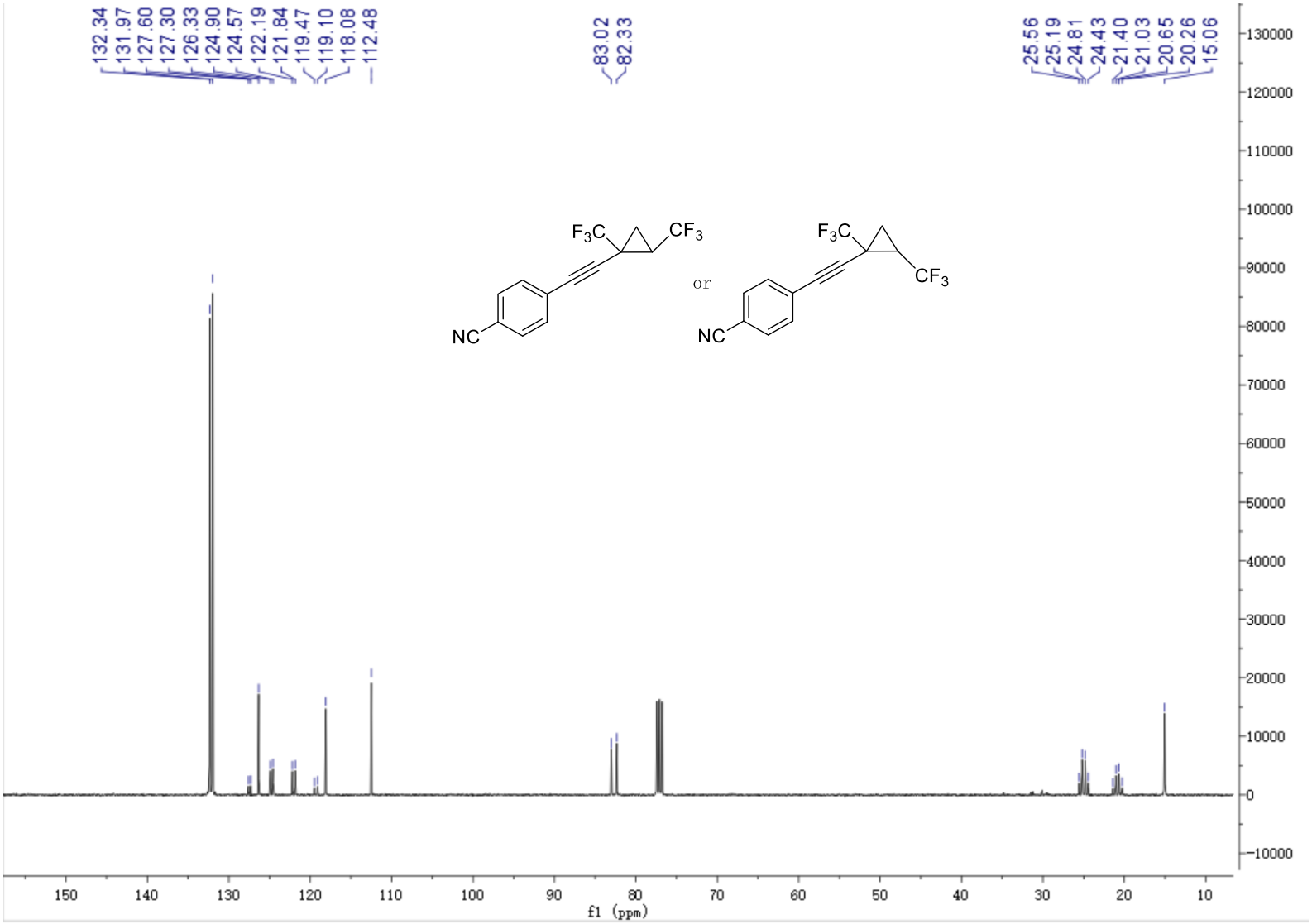
^{19}F NMR spectrum of 3m-isomer 1



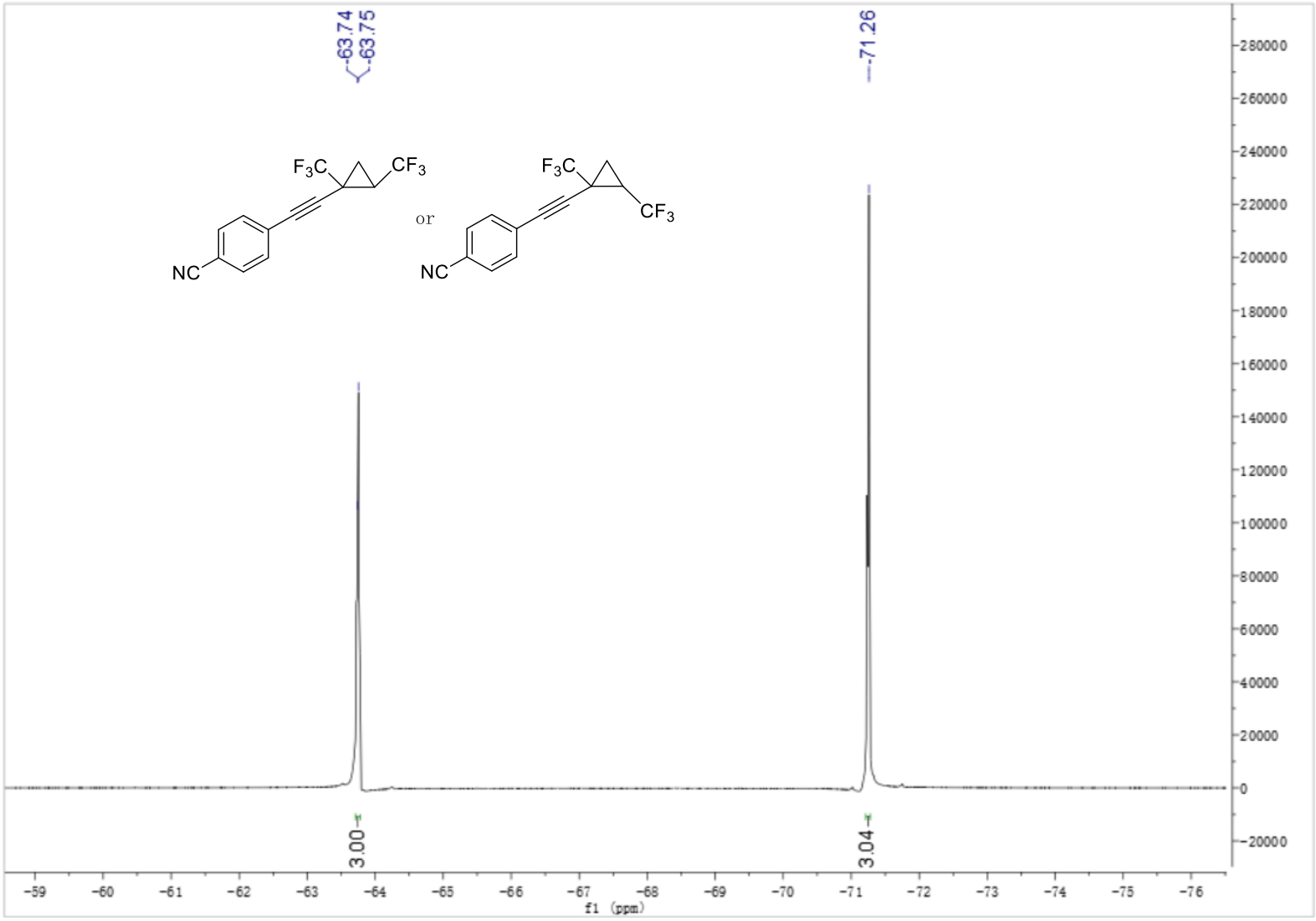
^{1}H NMR spectrum of 3m-isomer 2



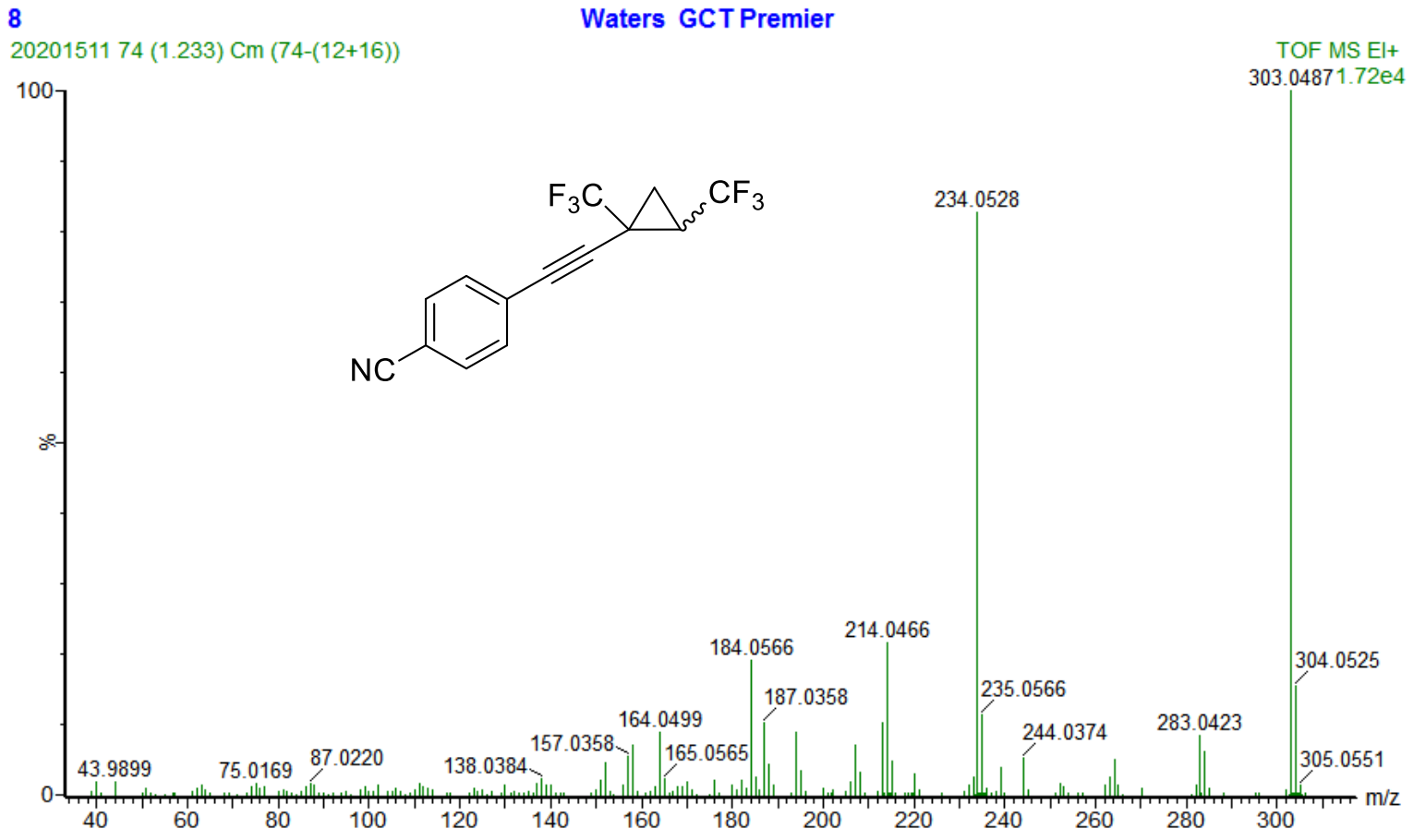
^{13}C NMR spectrum of 3m-isomer 2



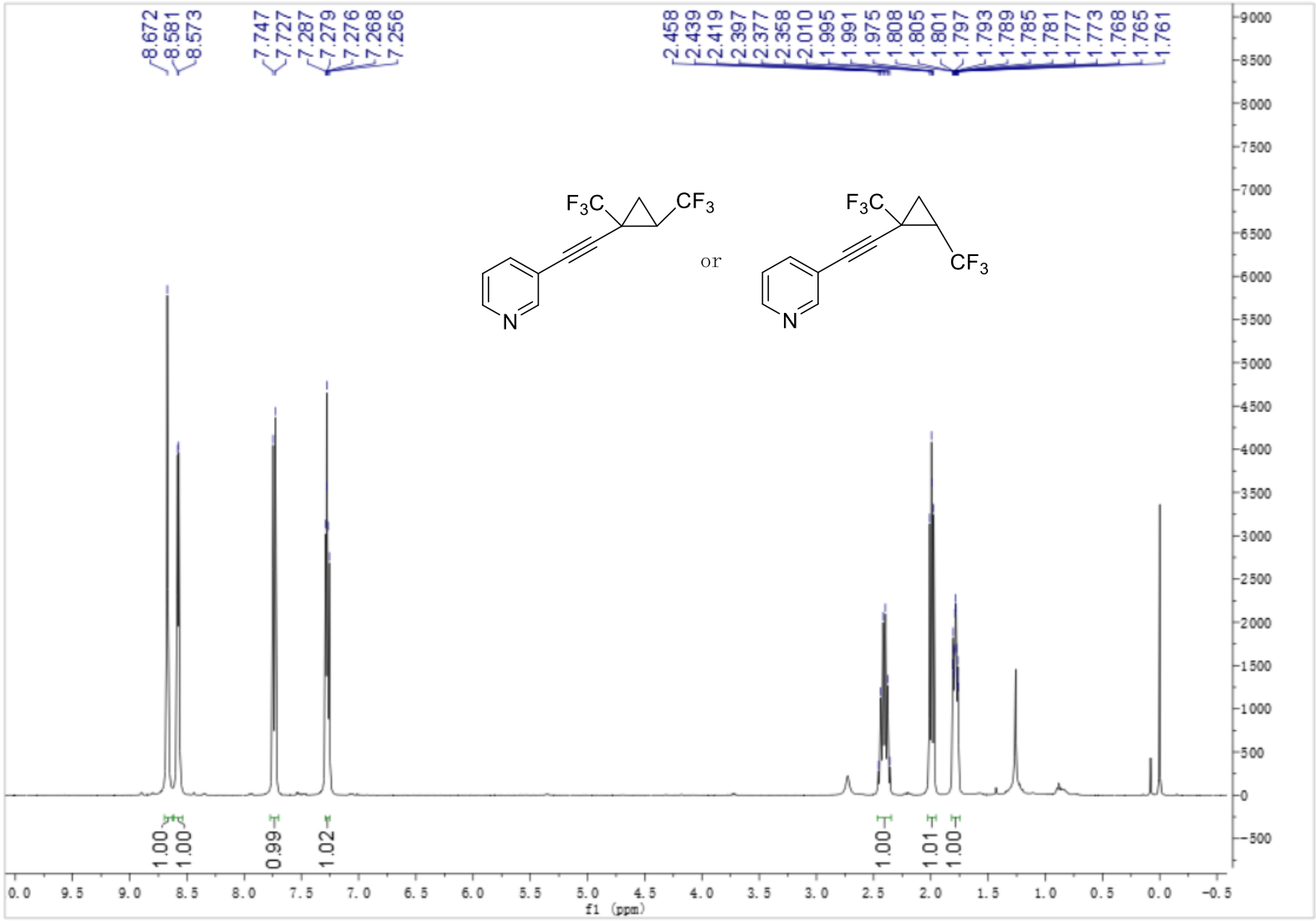
^{19}F NMR spectrum of 3m-isomer 2



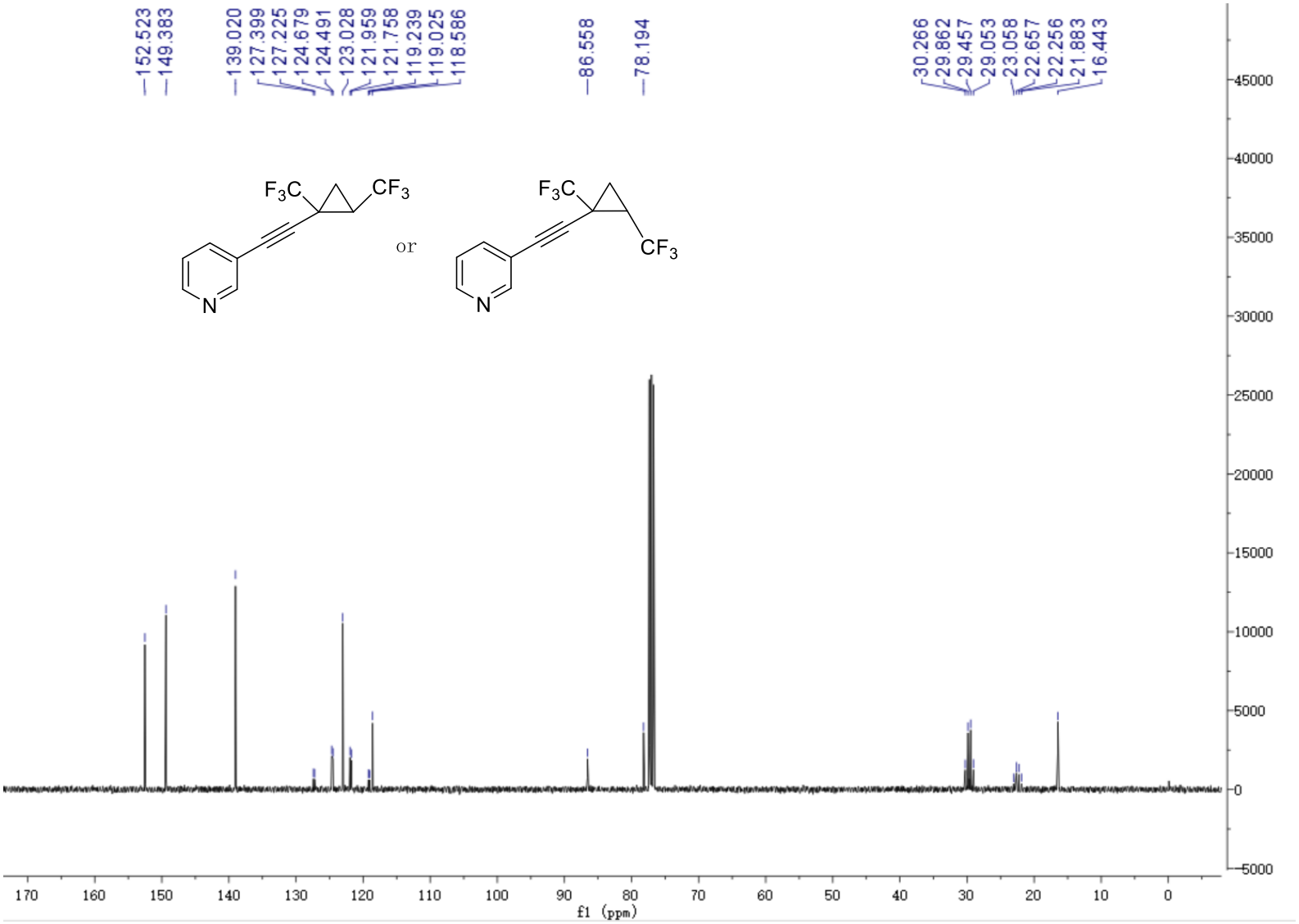
HRMS (EI) spectrum of 3m



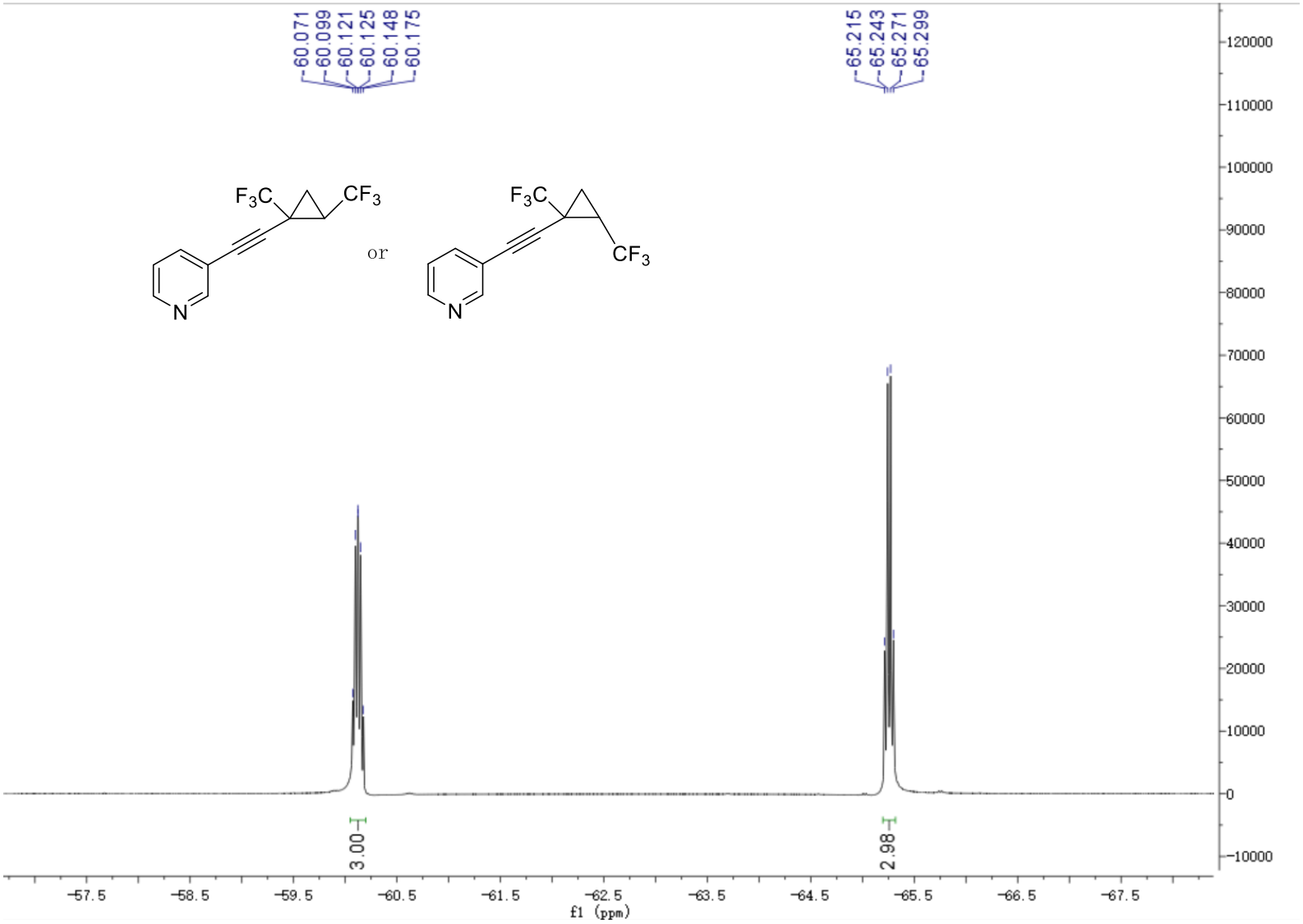
^{1}H NMR spectrum of 3n-isomer 1



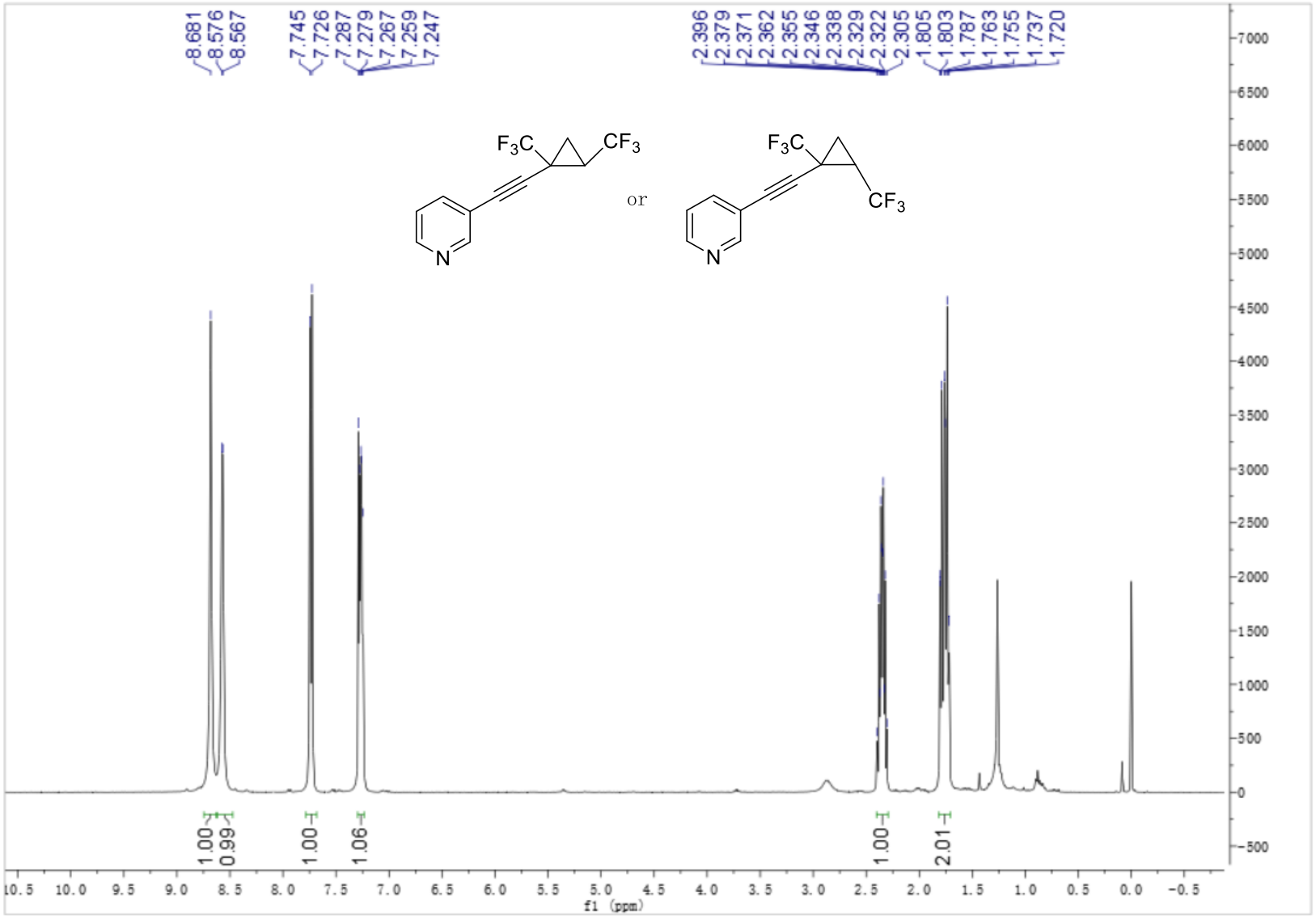
^{13}C NMR spectrum of 3n-isomer 1



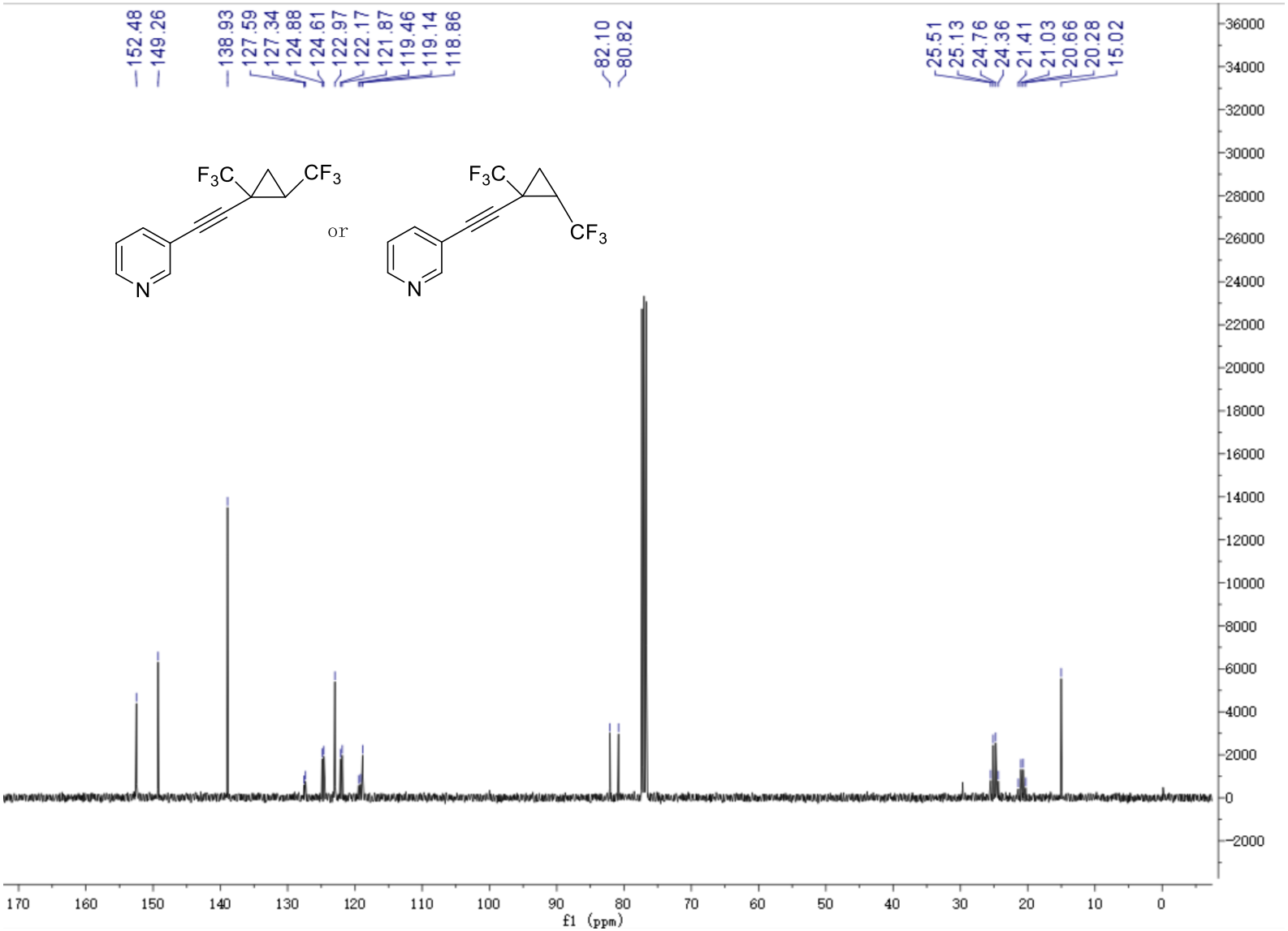
^{19}F NMR spectrum of 3n-isomer 1



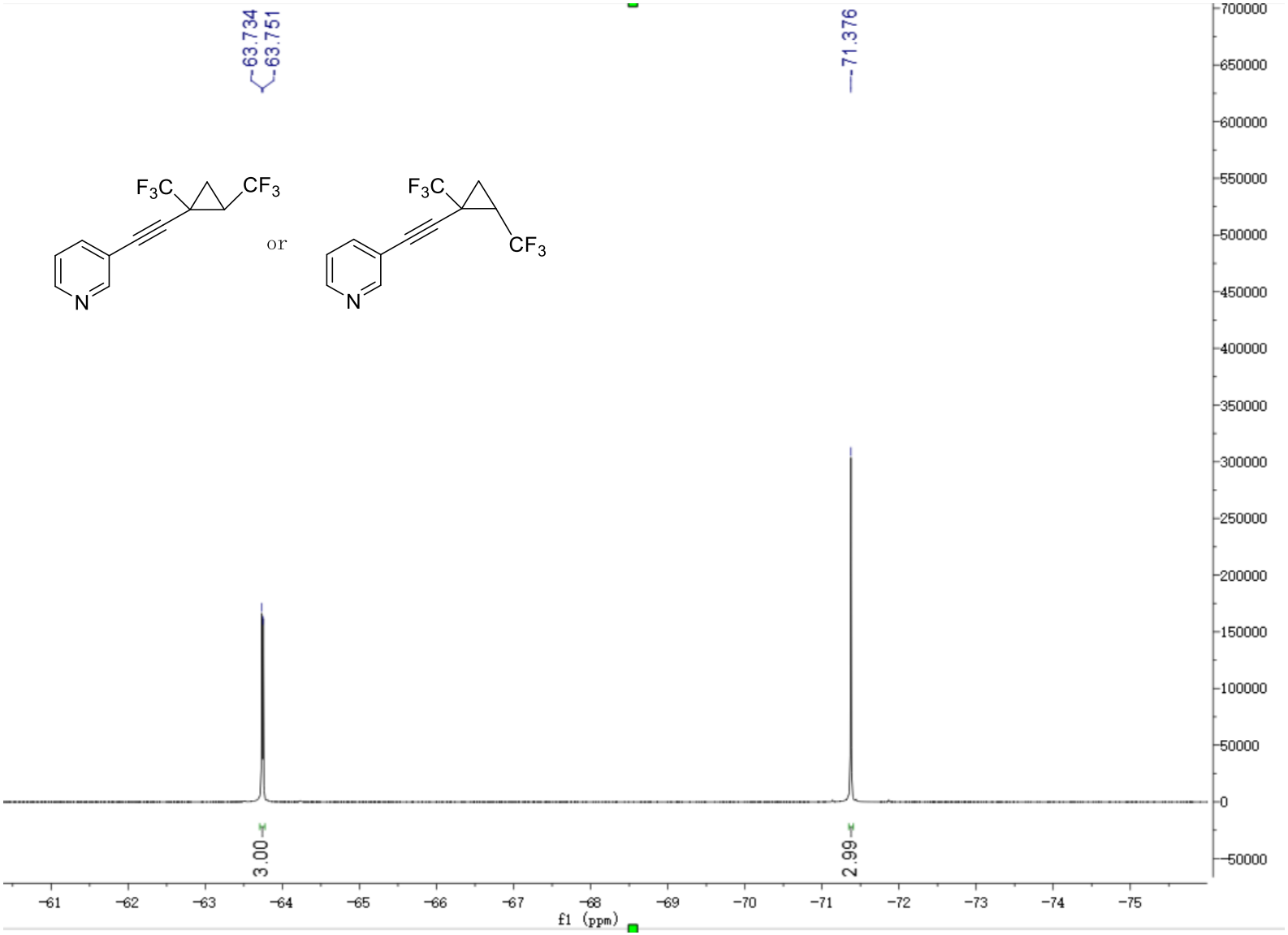
^{1}H NMR spectrum of 3n-isomer 2



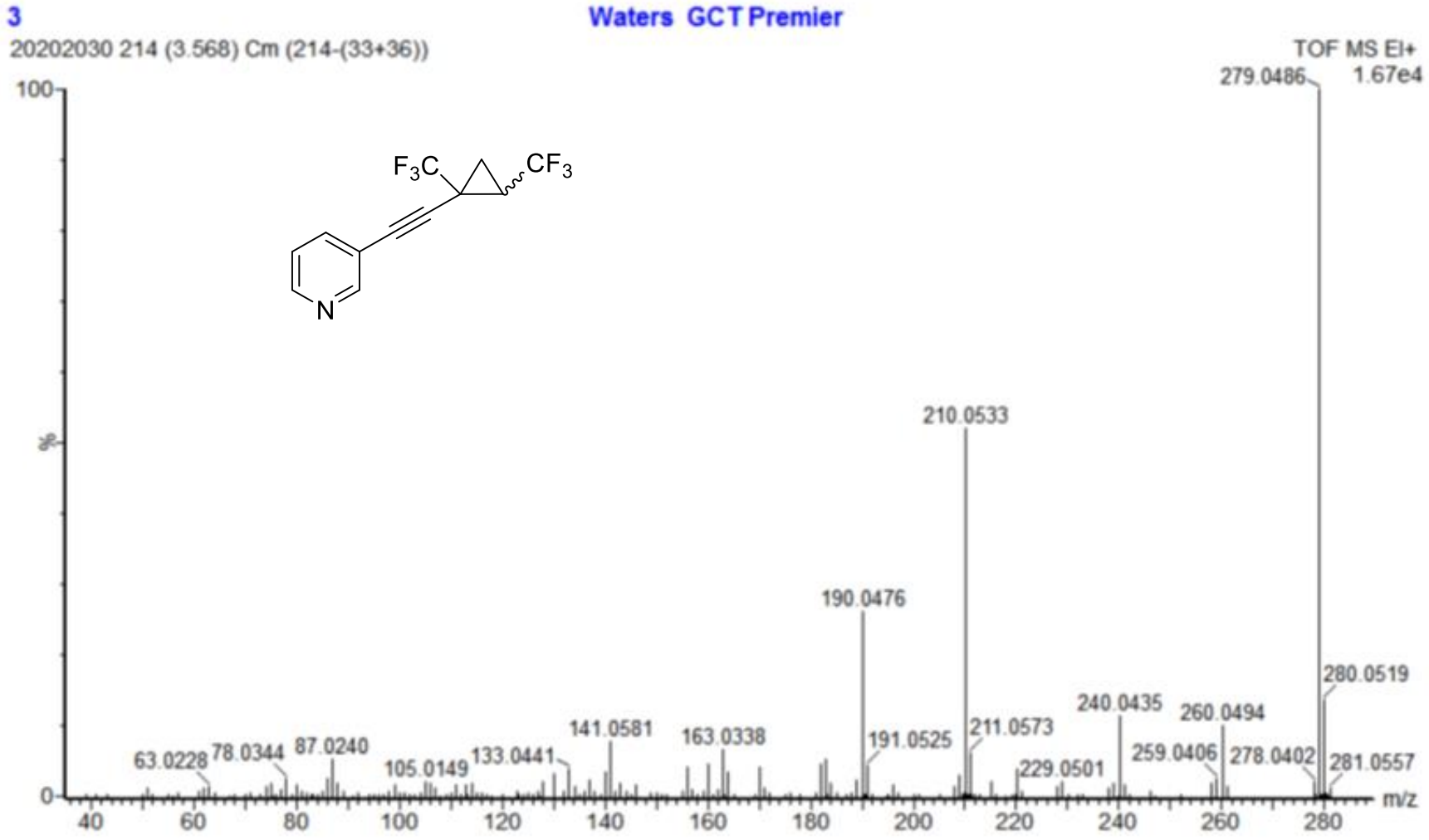
^{13}C NMR spectrum of 3n-isomer 2



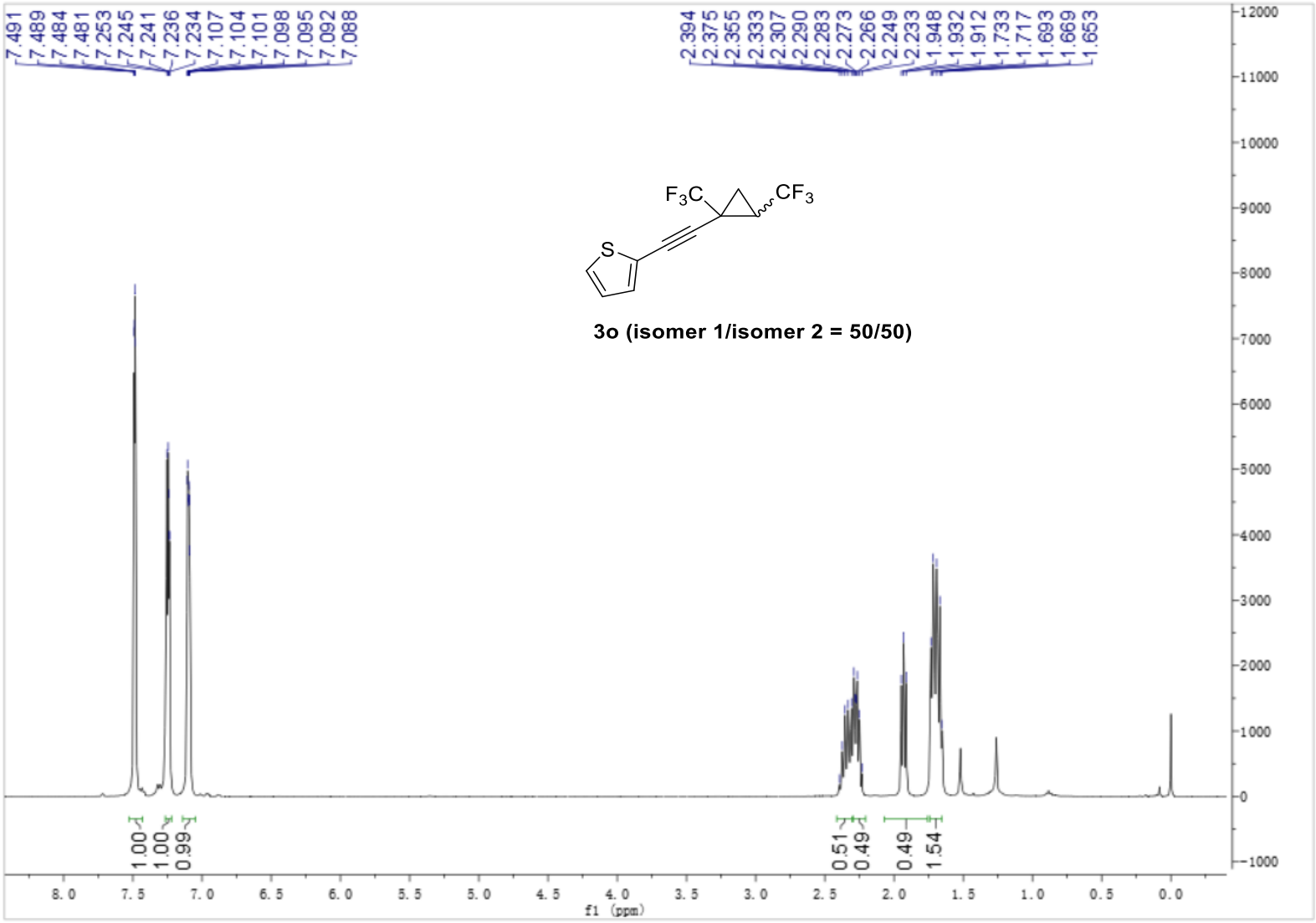
^{19}F NMR spectrum of 3n-isomer 2



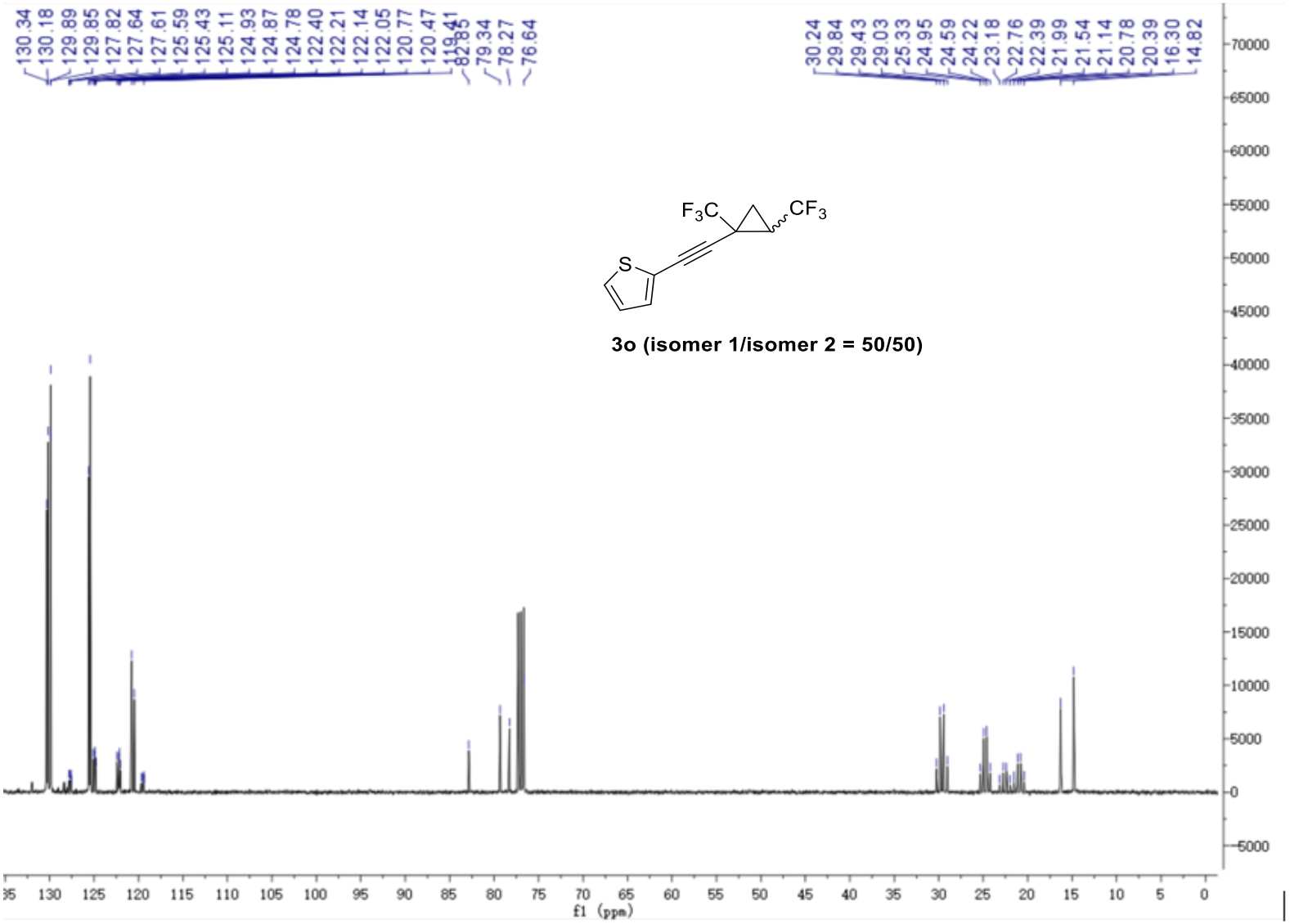
HRMS (EI) spectrum of 3n



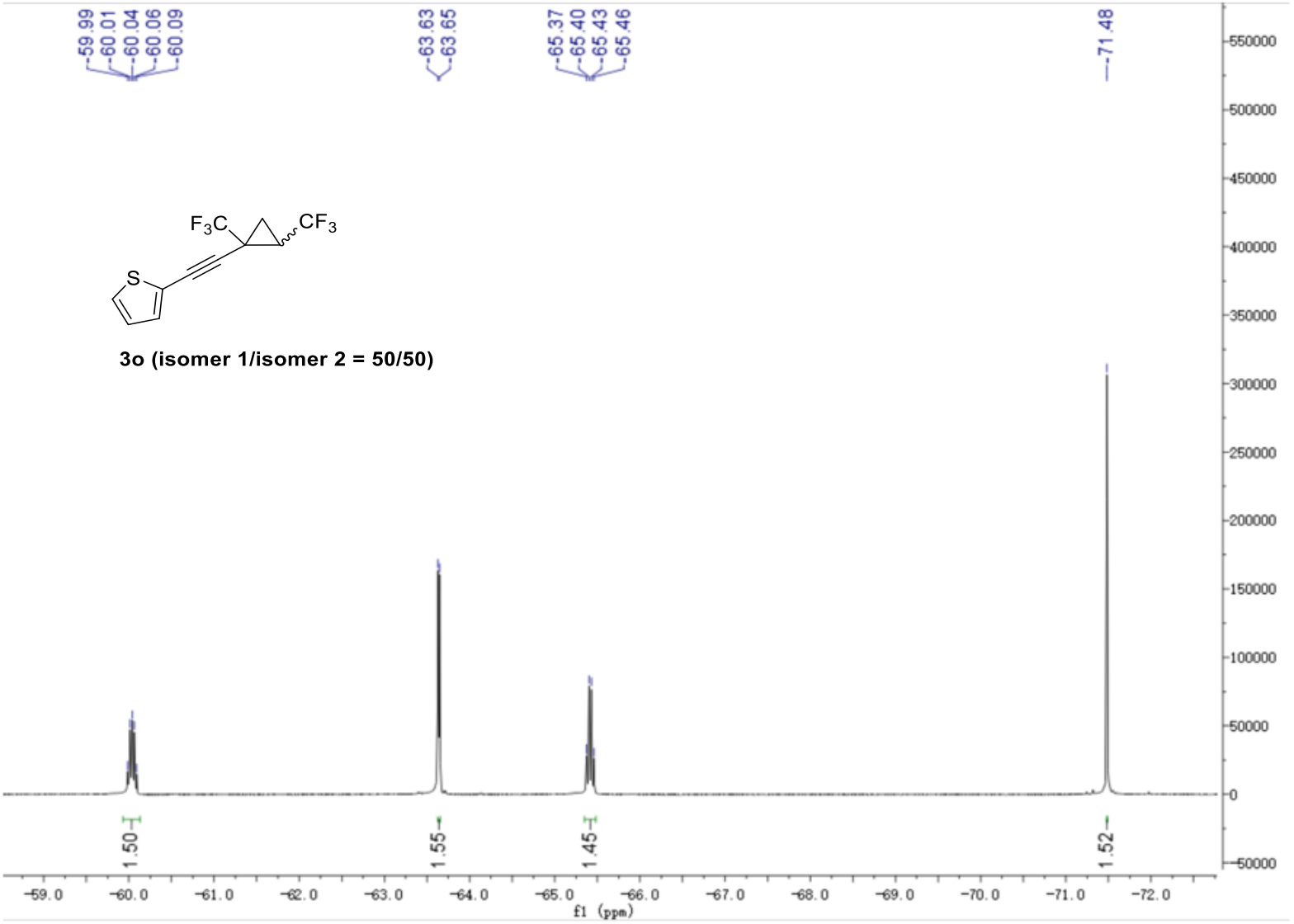
^{1}H NMR spectrum of 3o



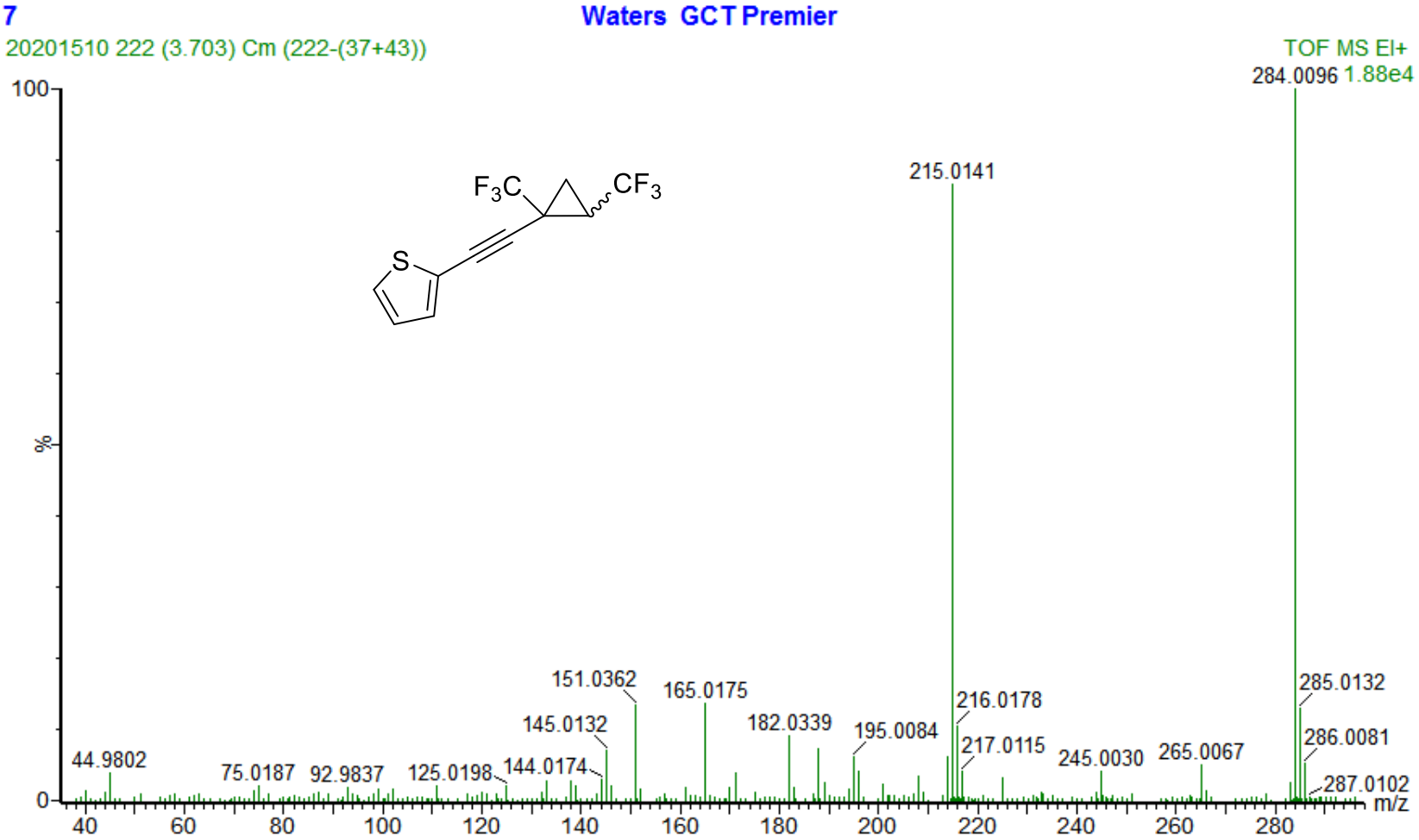
^{13}C NMR spectrum of 3o



^{19}F NMR spectrum of 3o

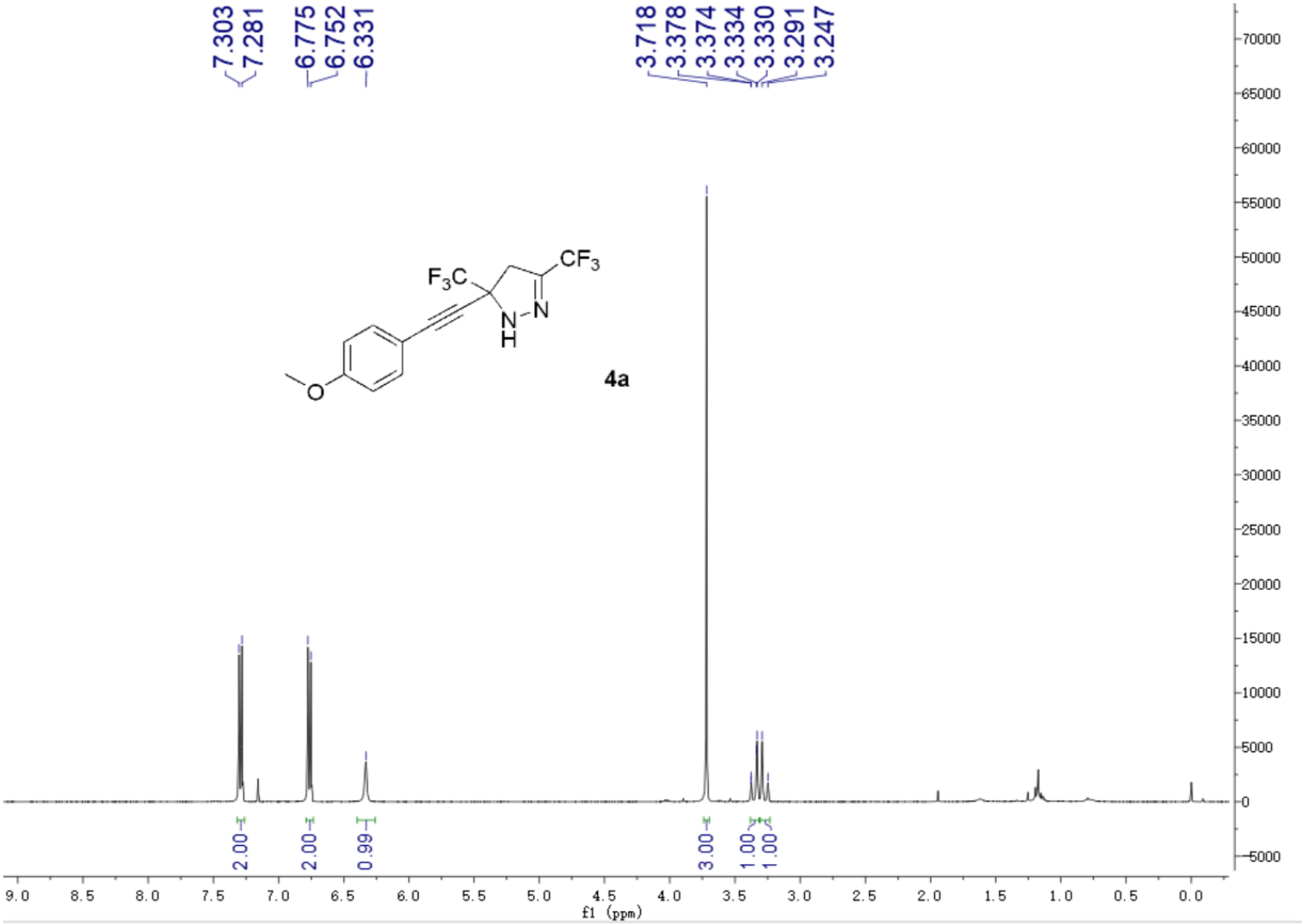


HRMS (EI) spectrum of 3o

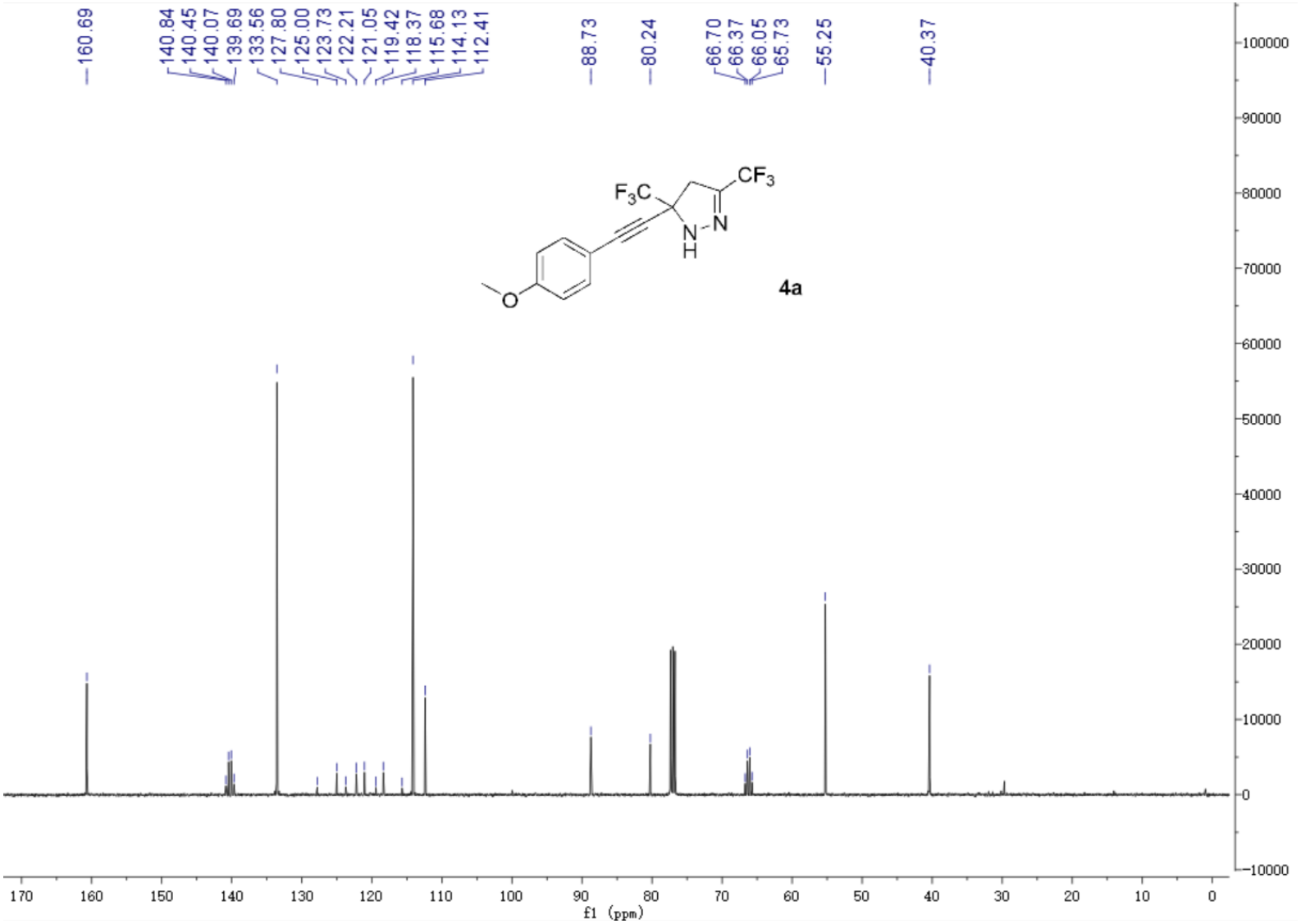


^{1}H, ^{13}C, ^{19}F NMR and HRMS (EI) spectra of compounds 4a, 4f, 4h, 4j−o

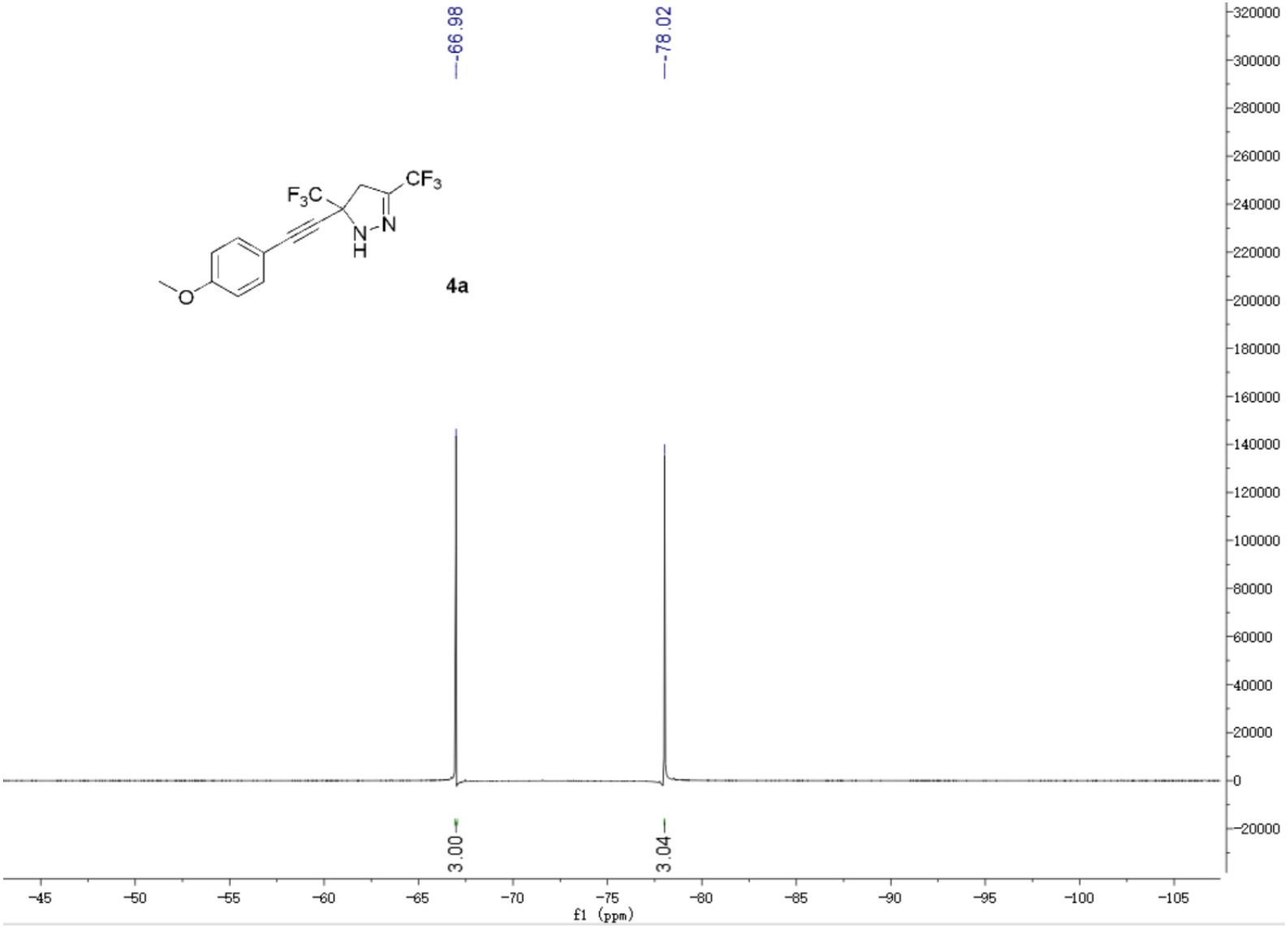
^{1}H NMR spectrum of 4a



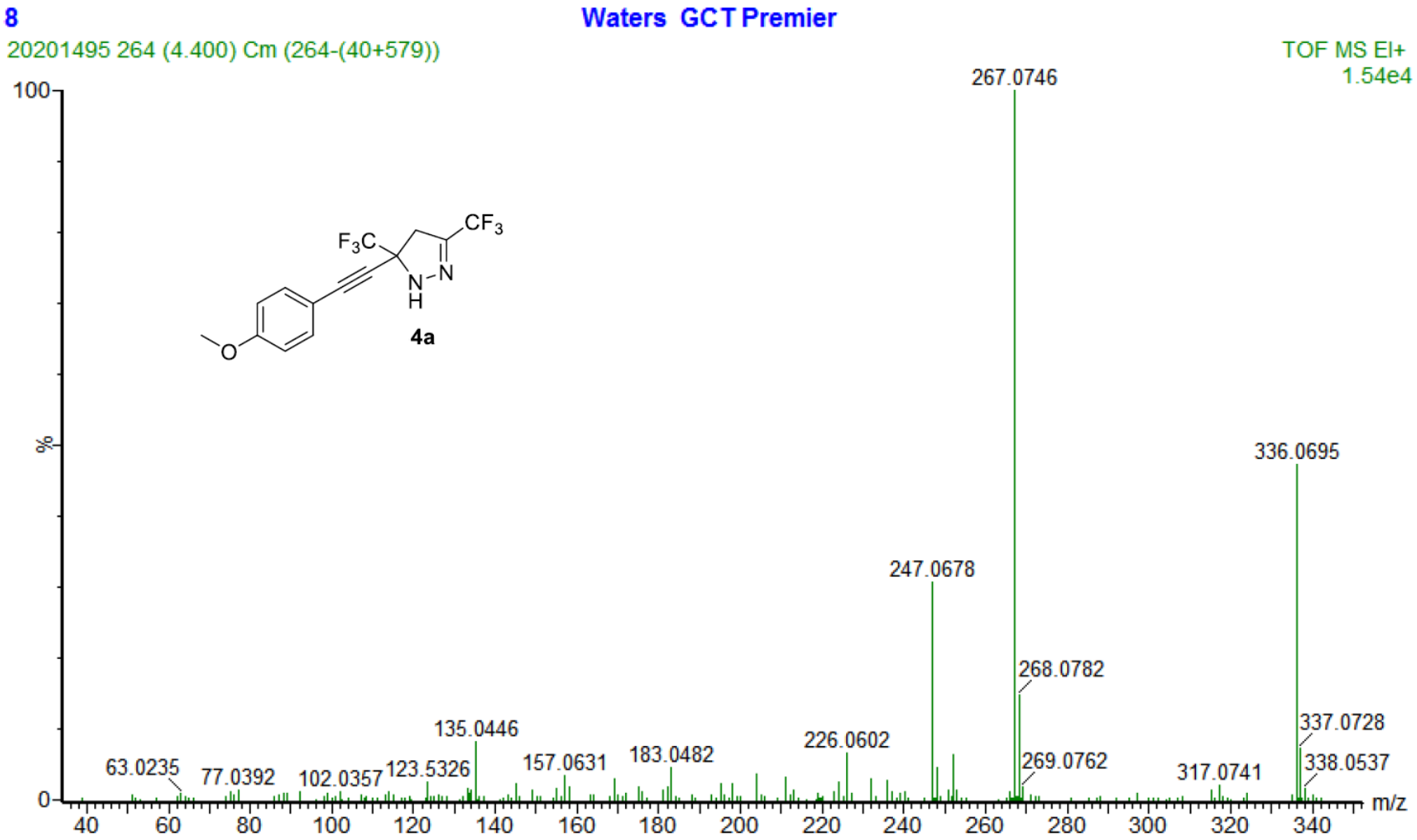
^{13}C NMR spectrum of 4a



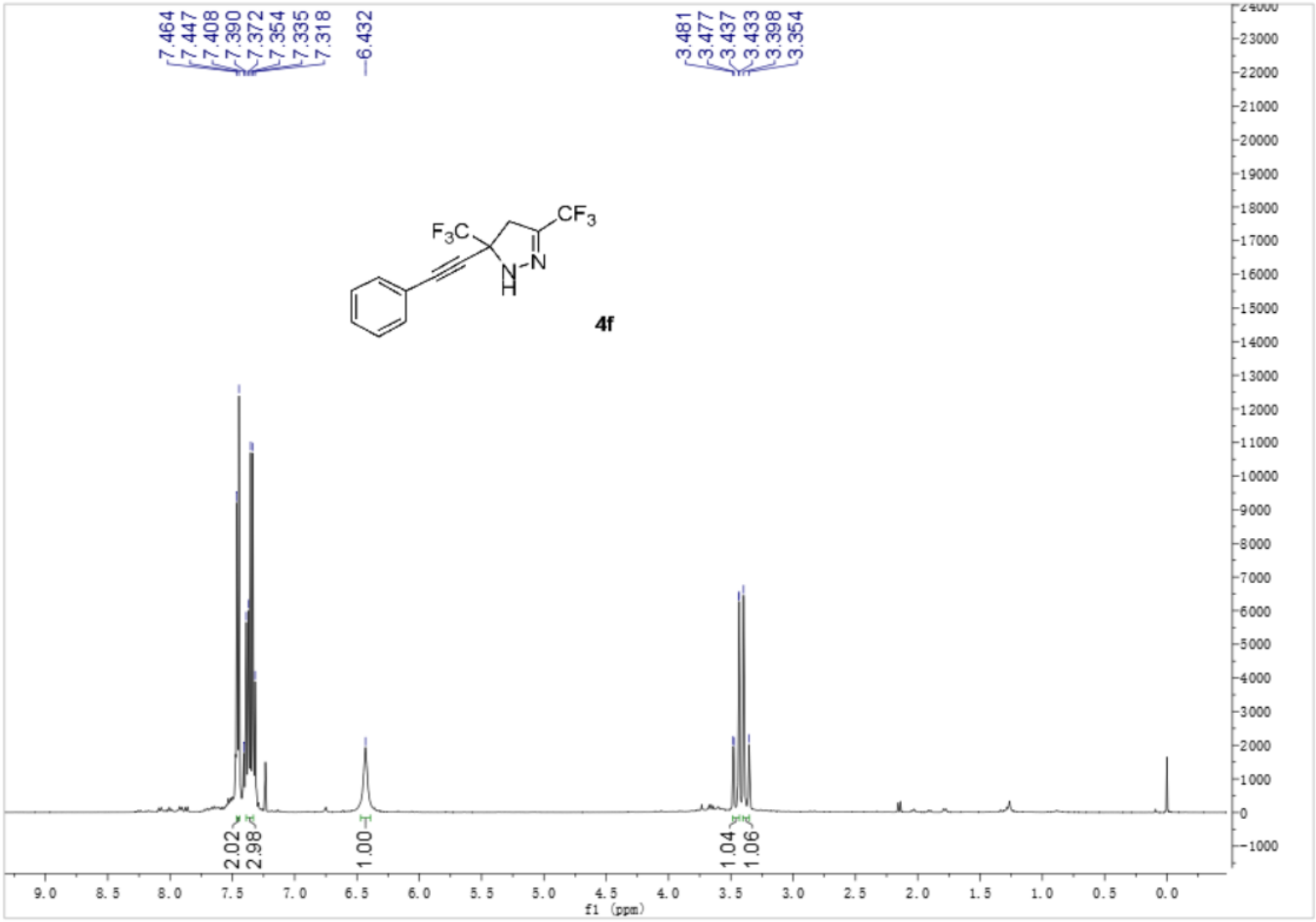
^{19}F NMR spectrum of 4a



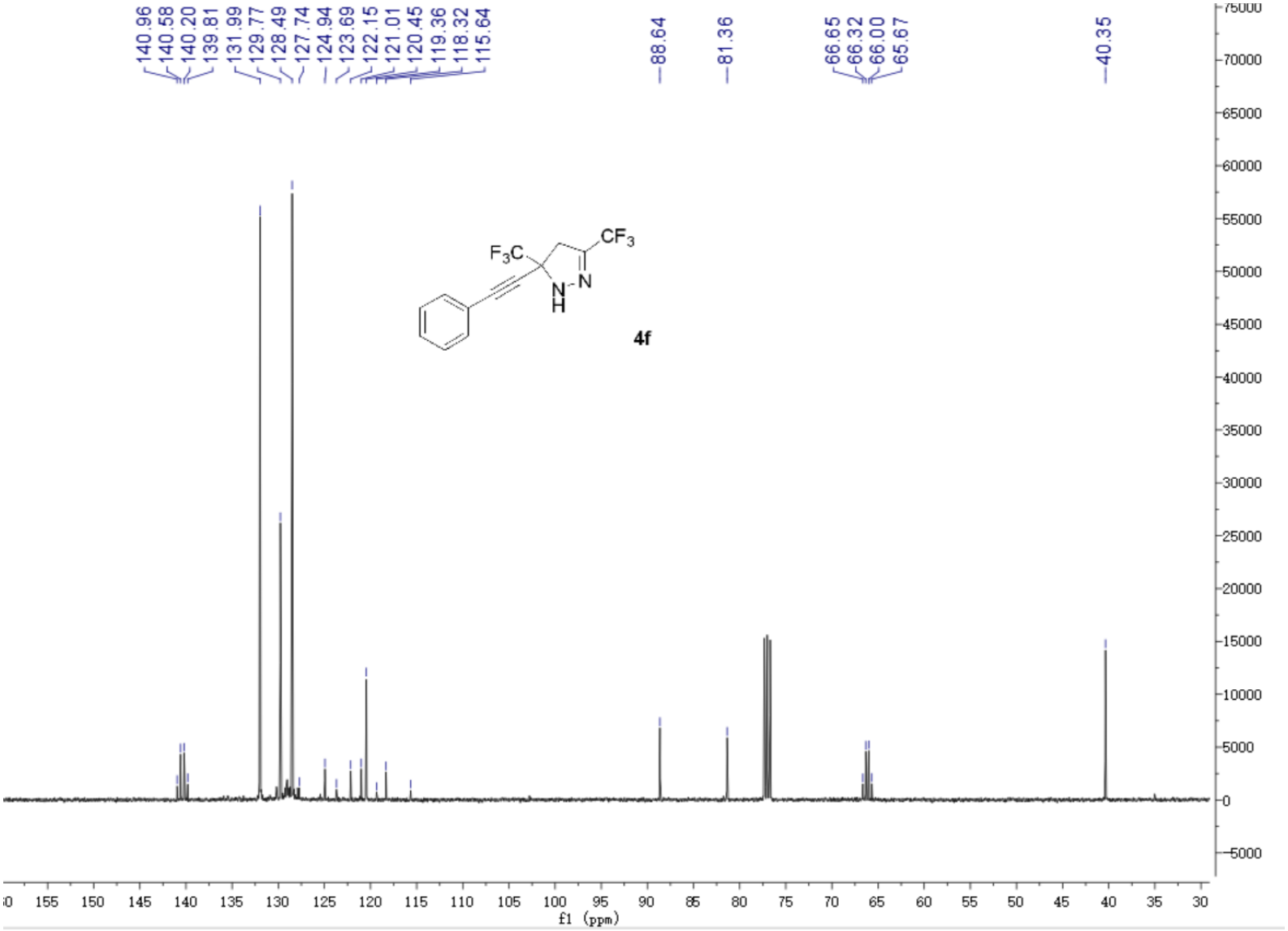
HRMS (EI) spectrum of 4a



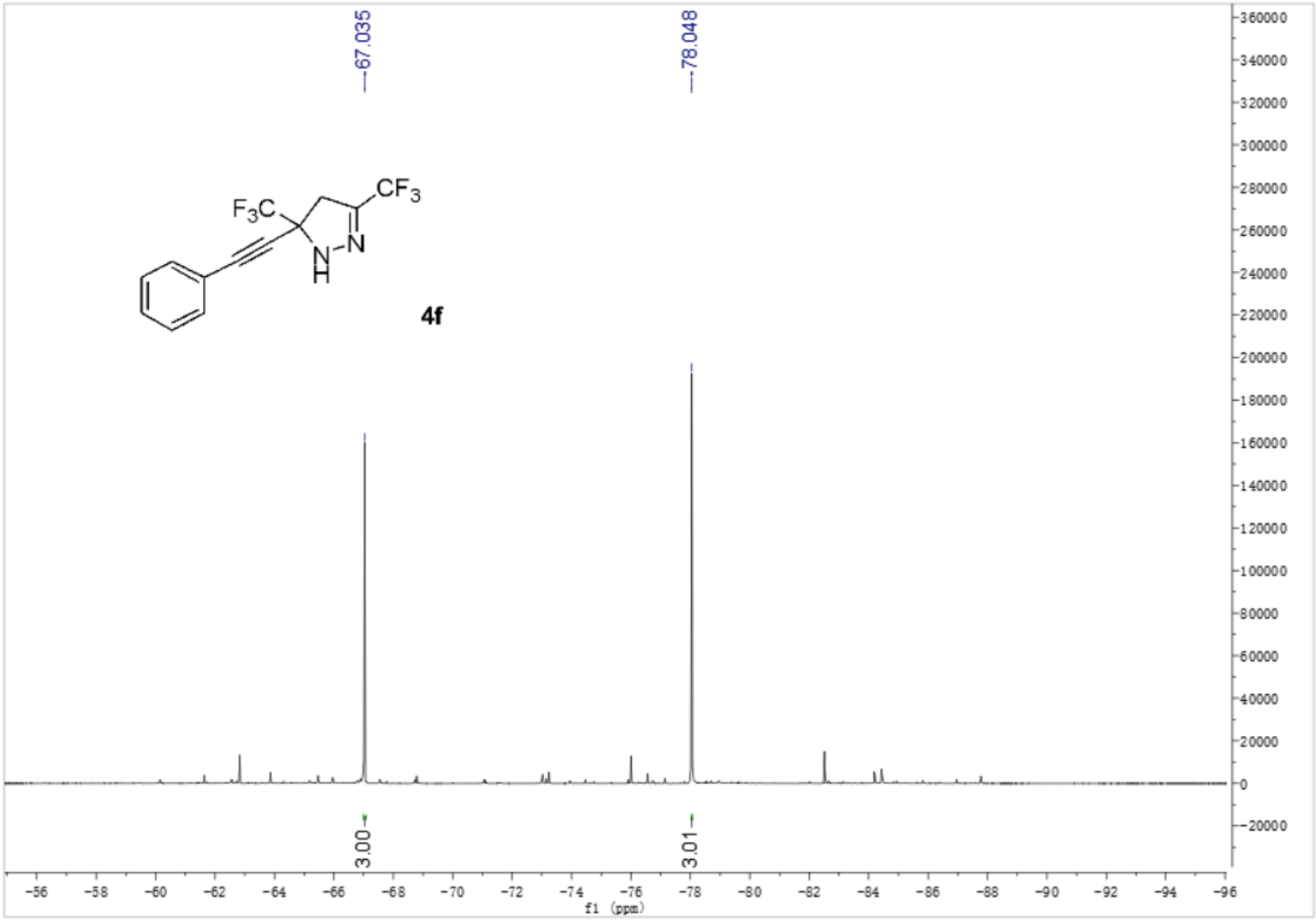
^{1}H NMR spectrum of 4f



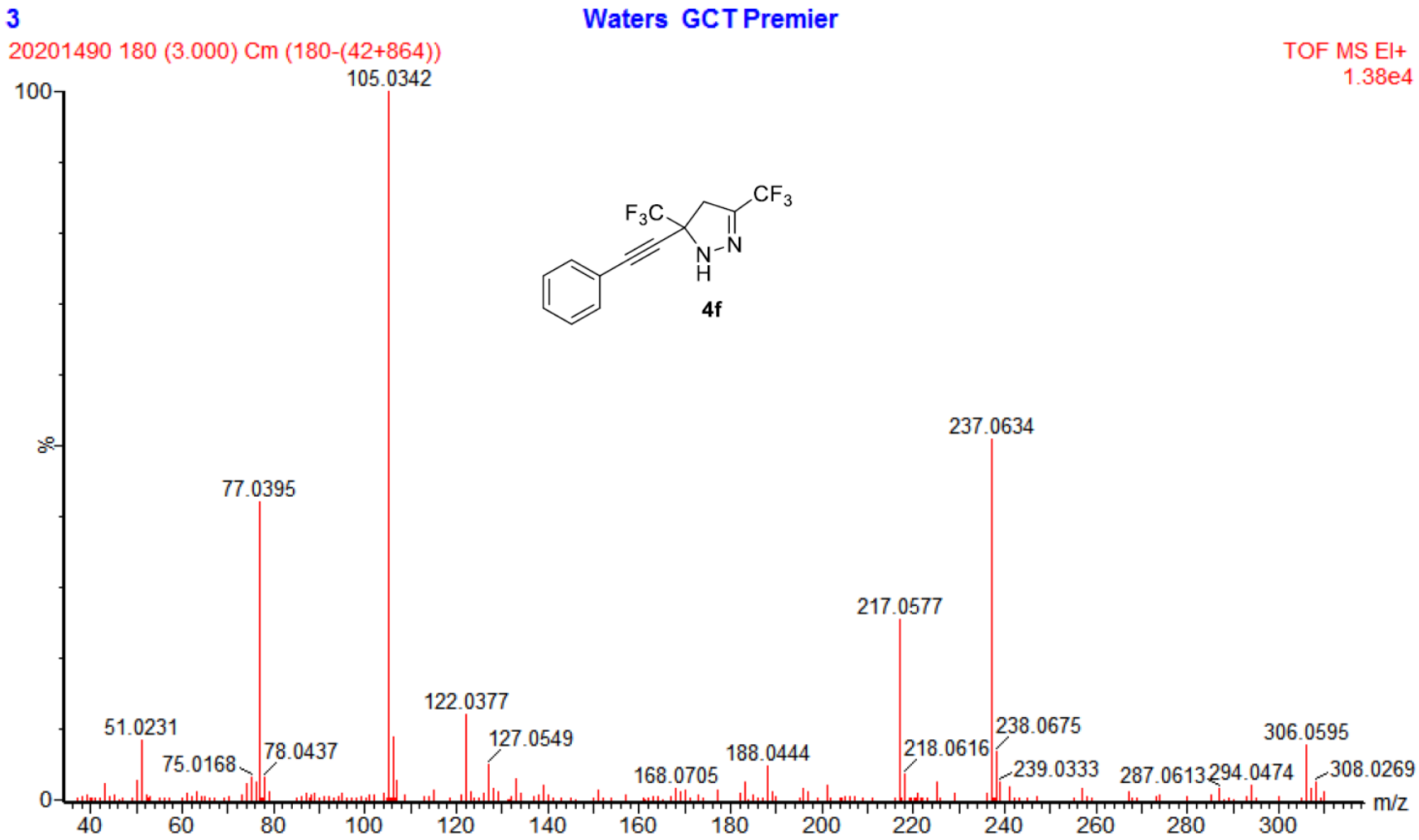
^{13}C NMR spectrum of 4f



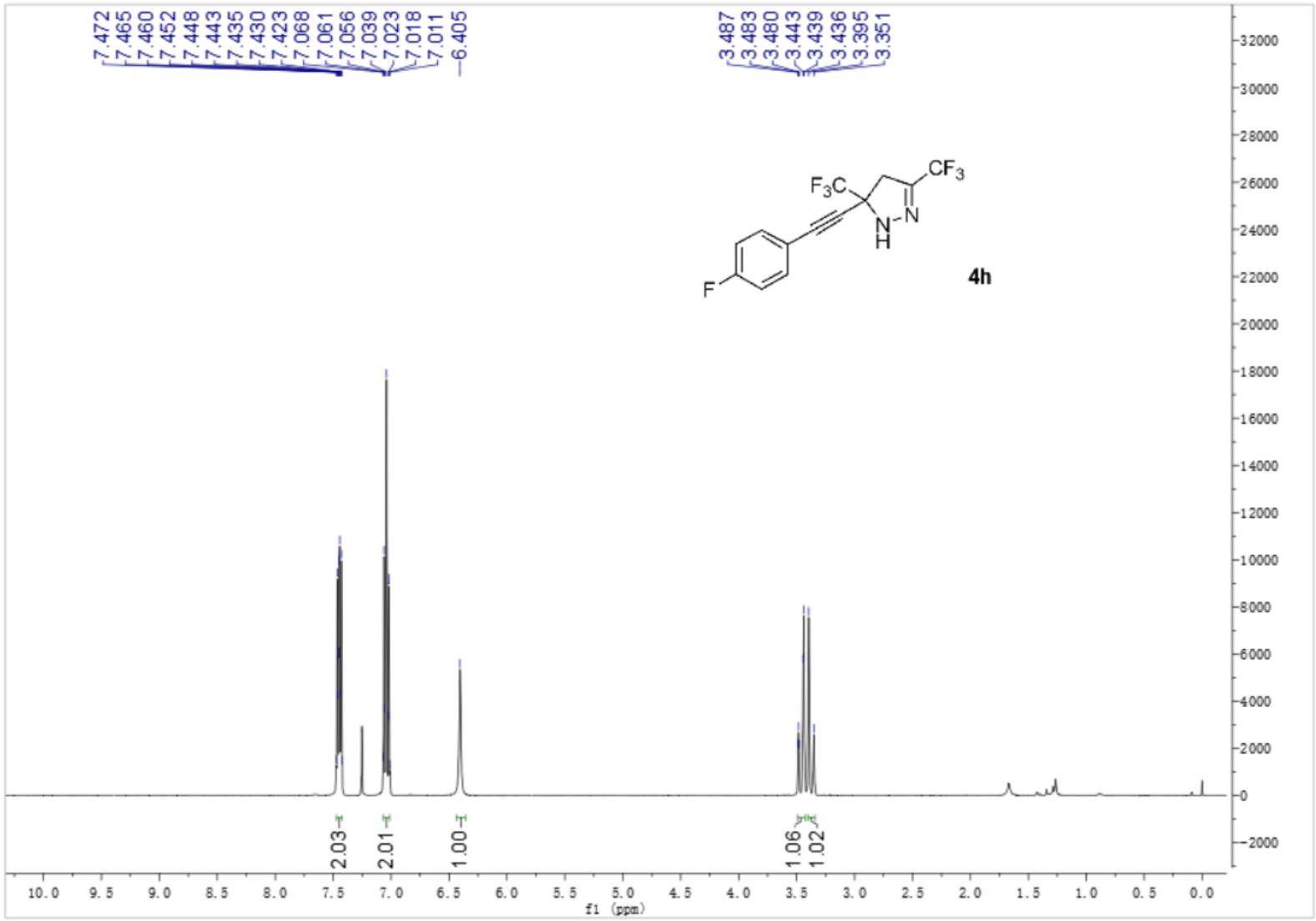
^{19}F NMR spectrum of 4f



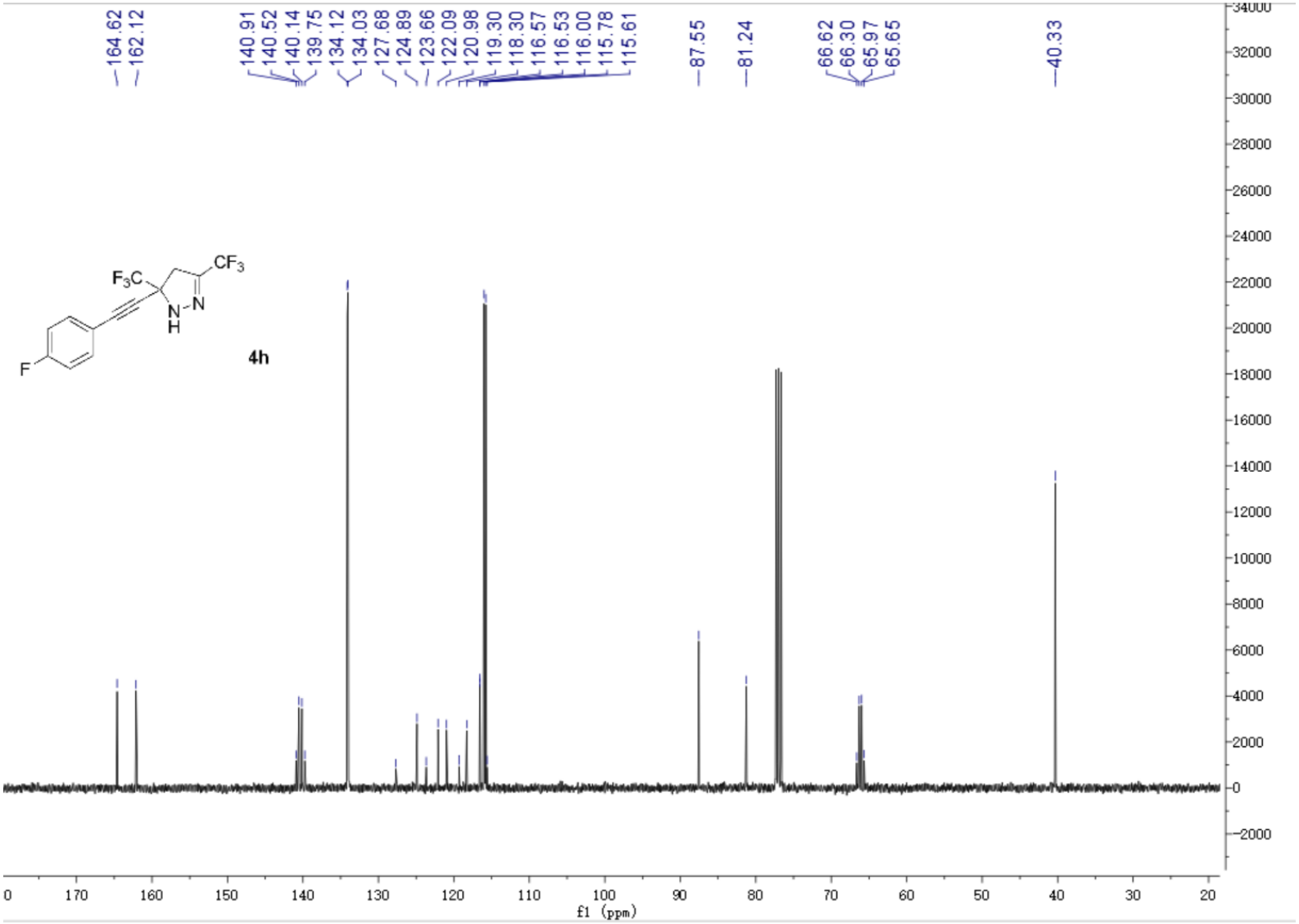
HRMS (EI) spectrum of 4f



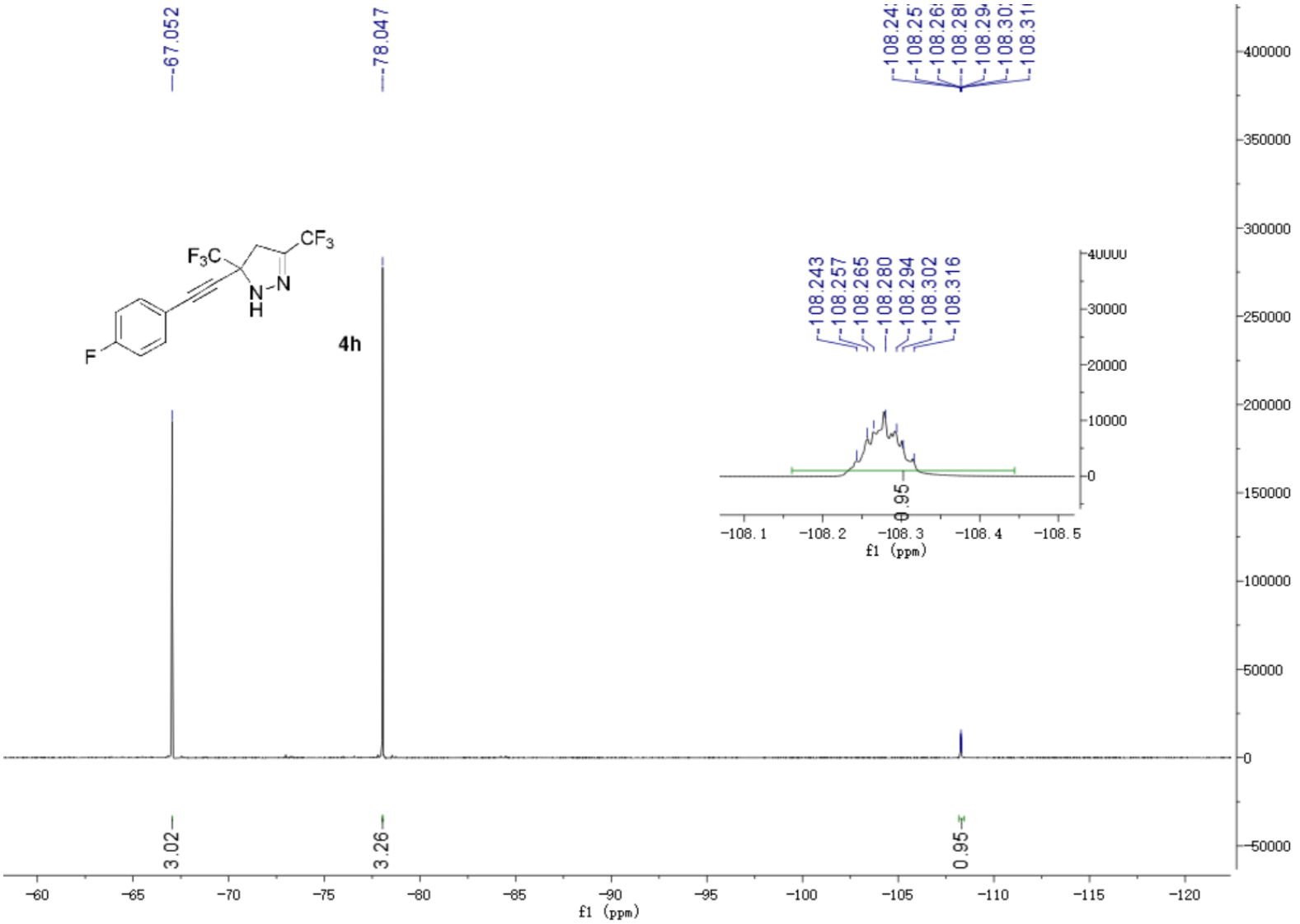
^{1}H NMR spectrum of 4h



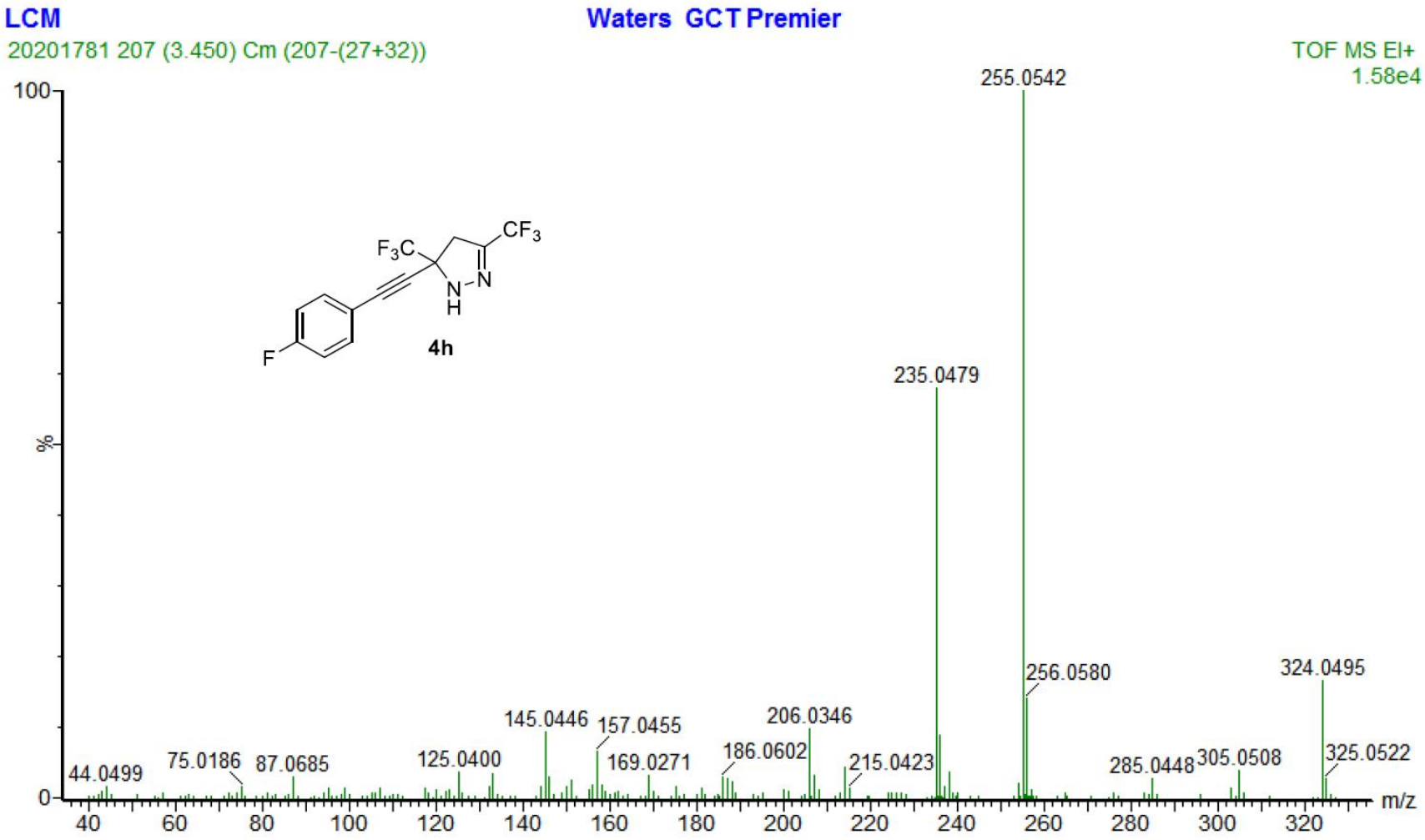
^{13}C NMR spectrum of 4h



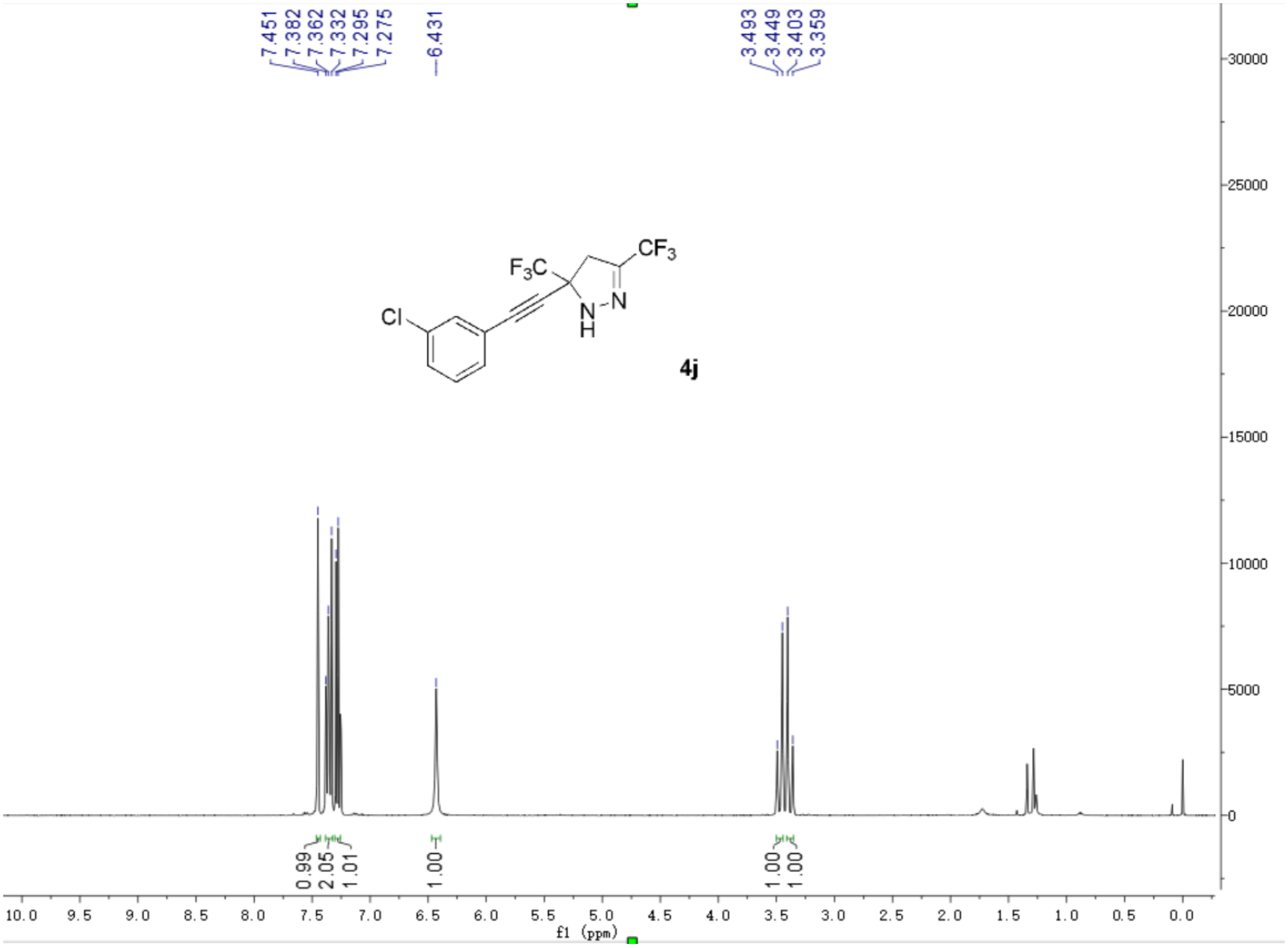
^{19}F NMR spectrum of 4h



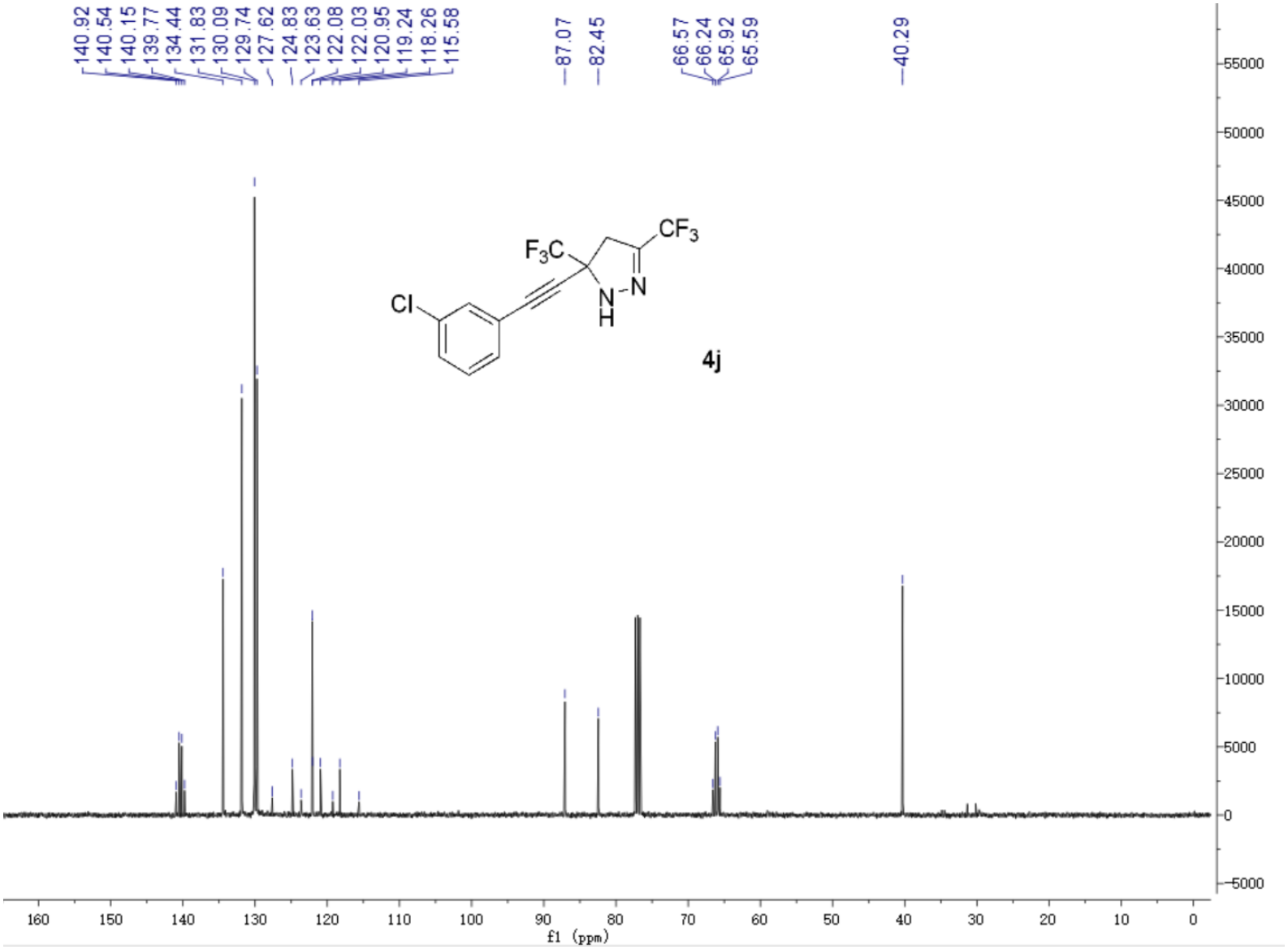
HRMS (EI) spectrum of 4h



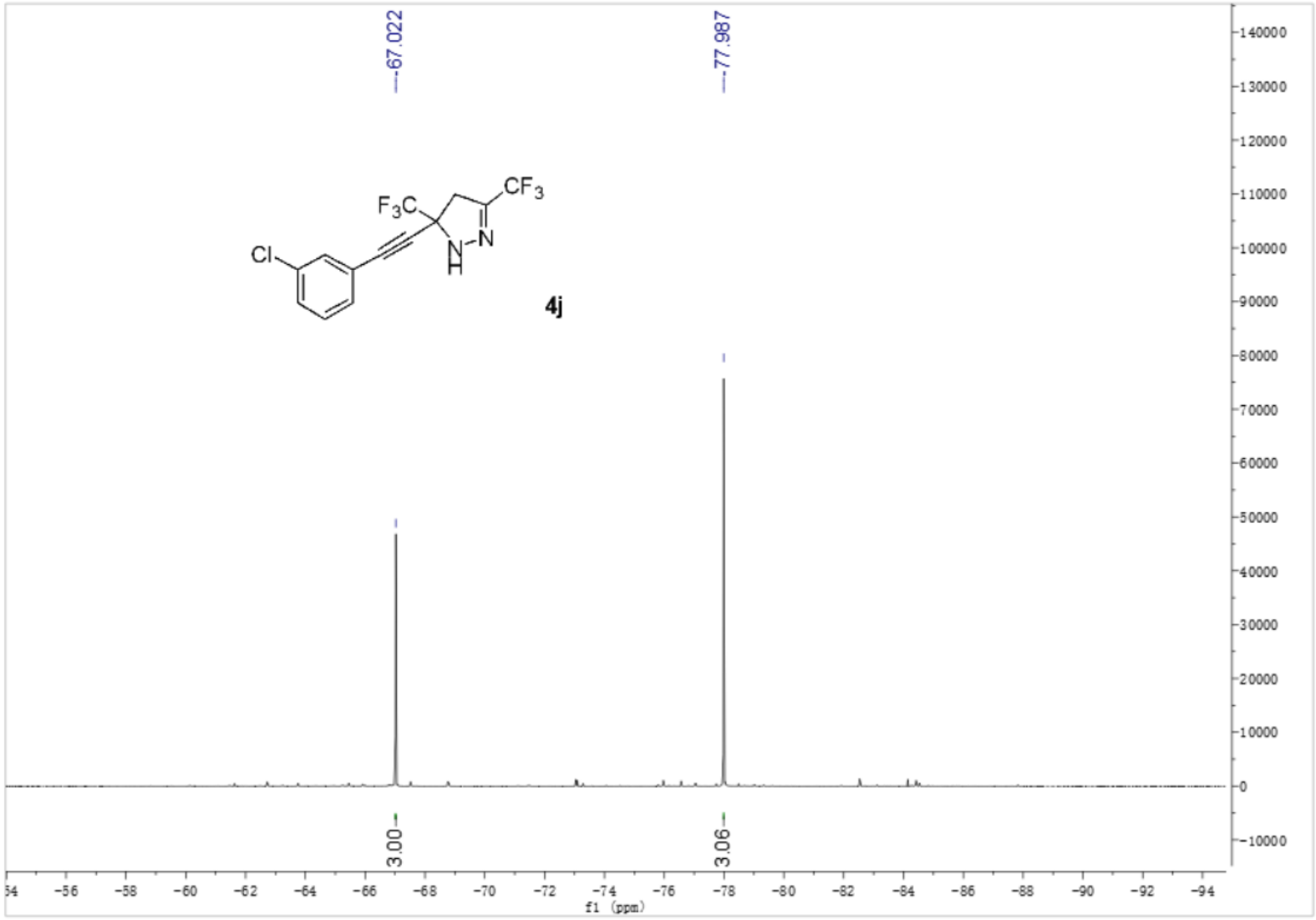
^{1}H NMR spectrum of 4j



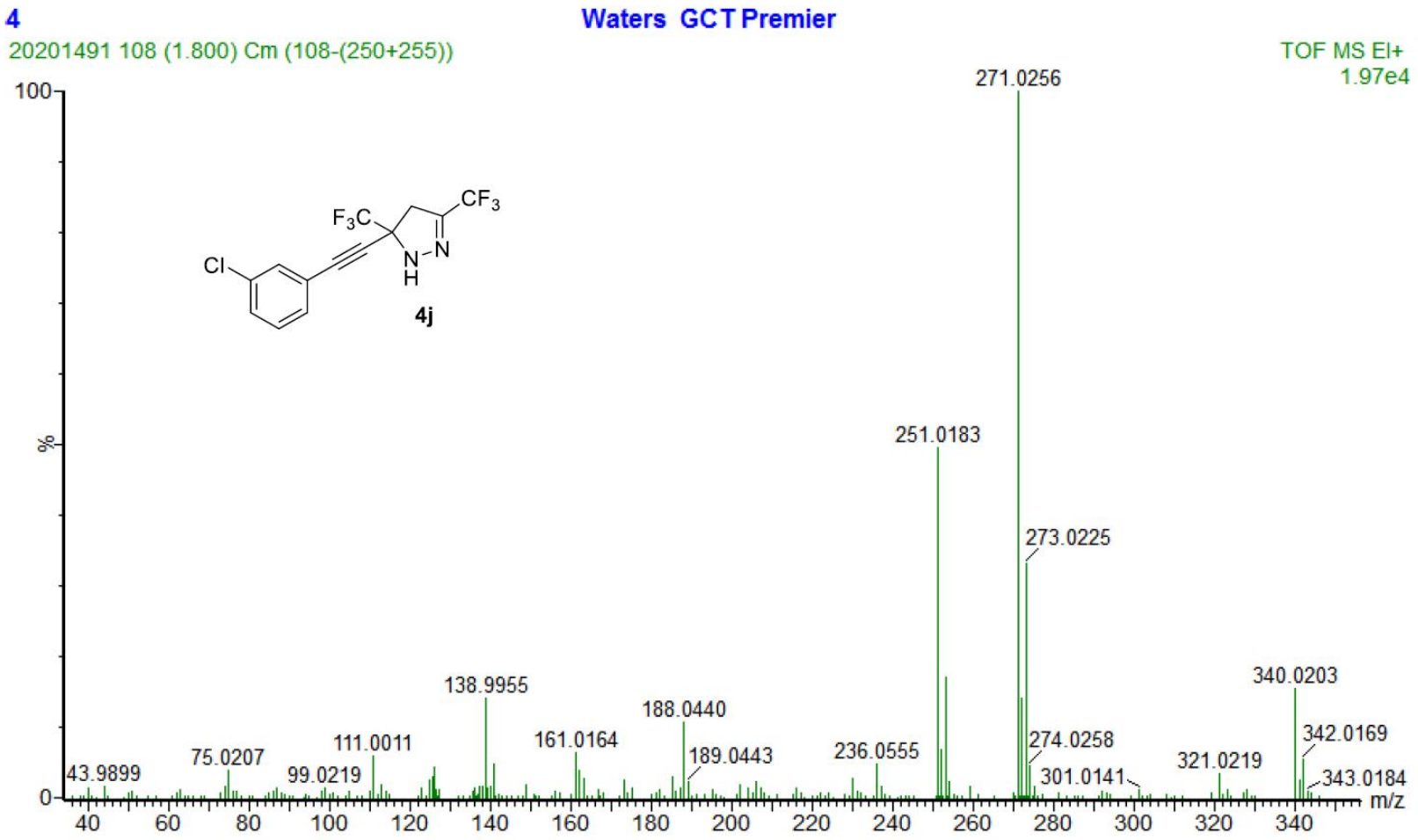
^{13}C NMR spectrum of 4j



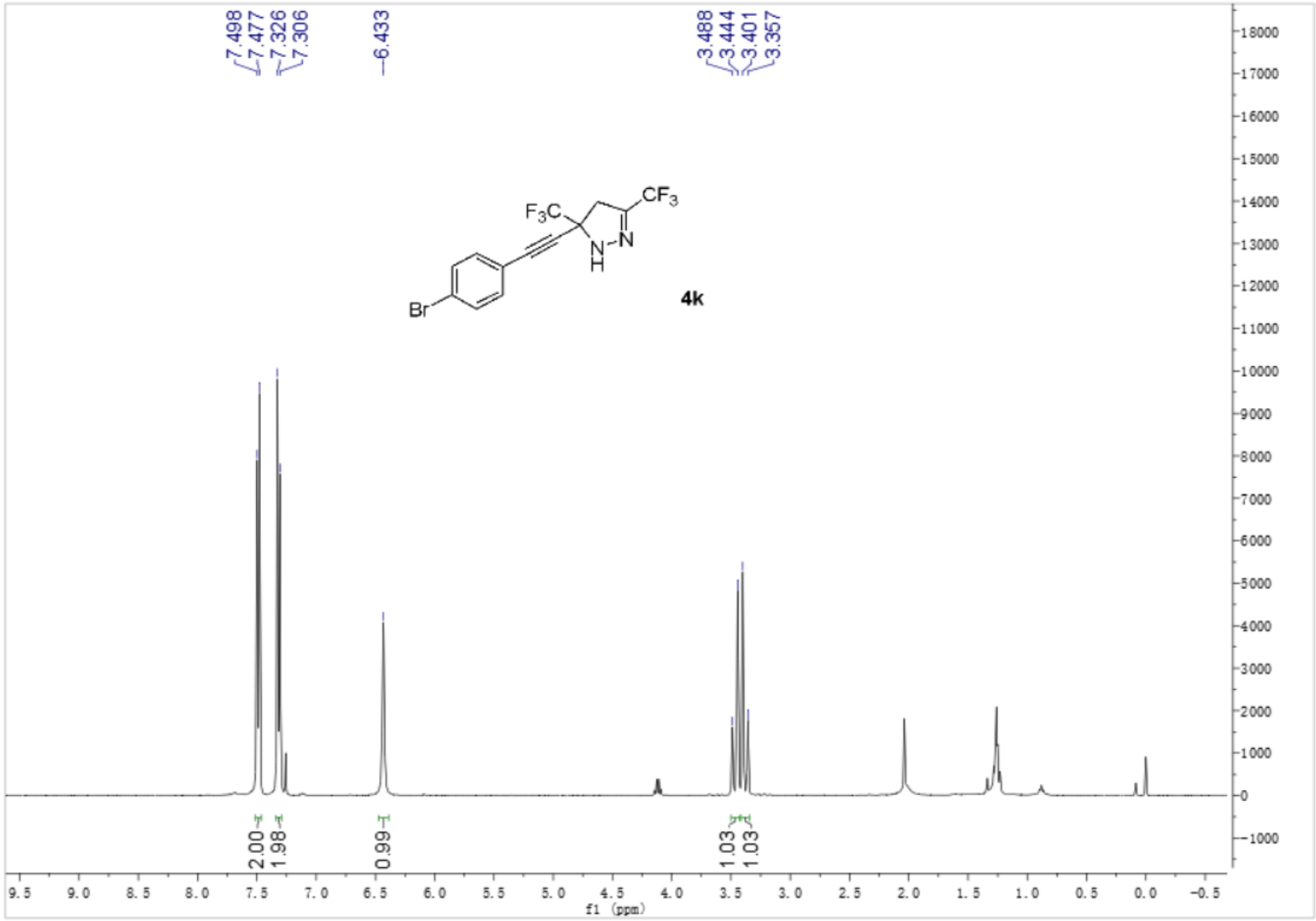
^{19}F NMR spectrum of 4j



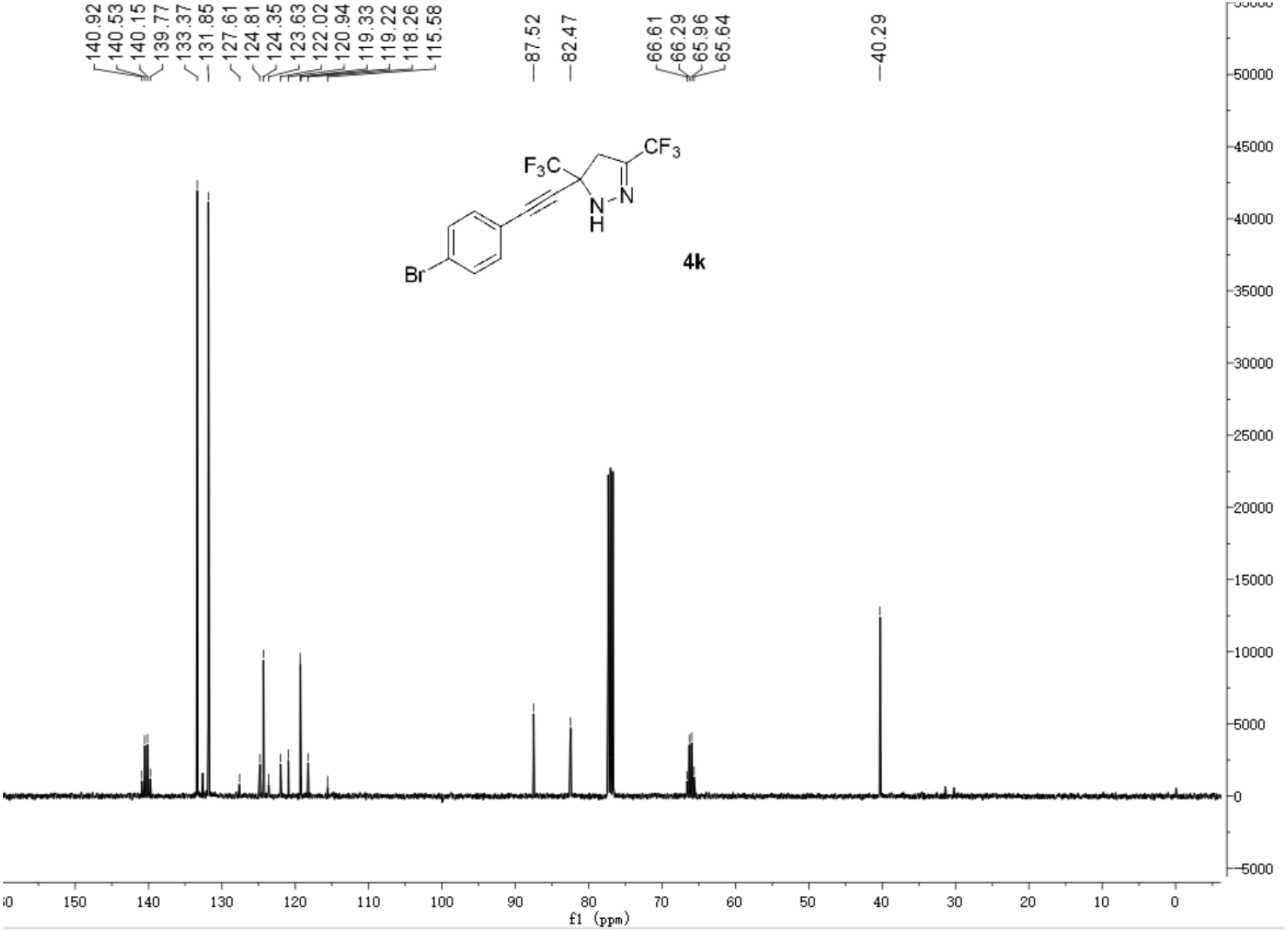
HRMS (EI) spectrum of 4j



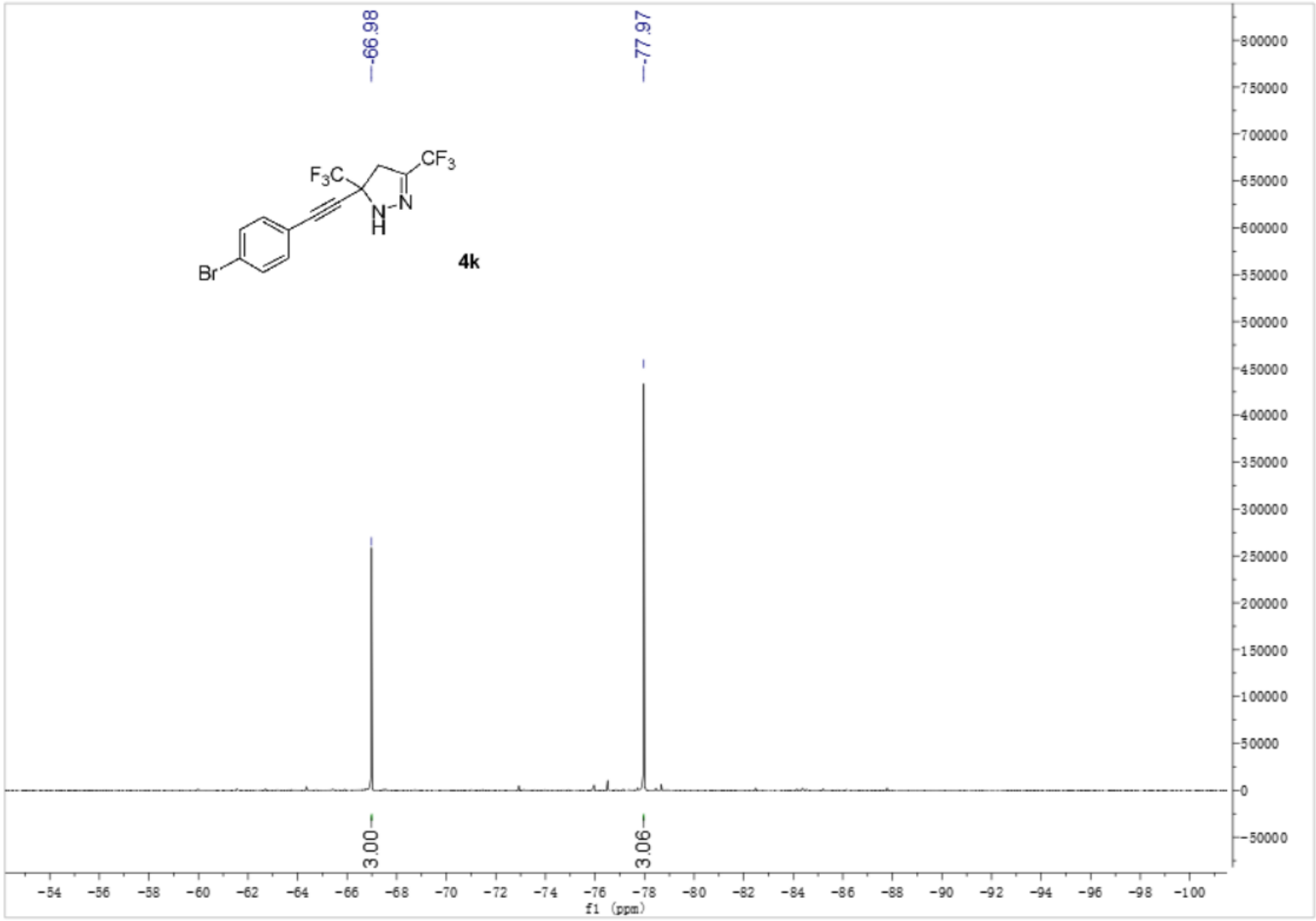
^{1}H NMR spectrum of 4k



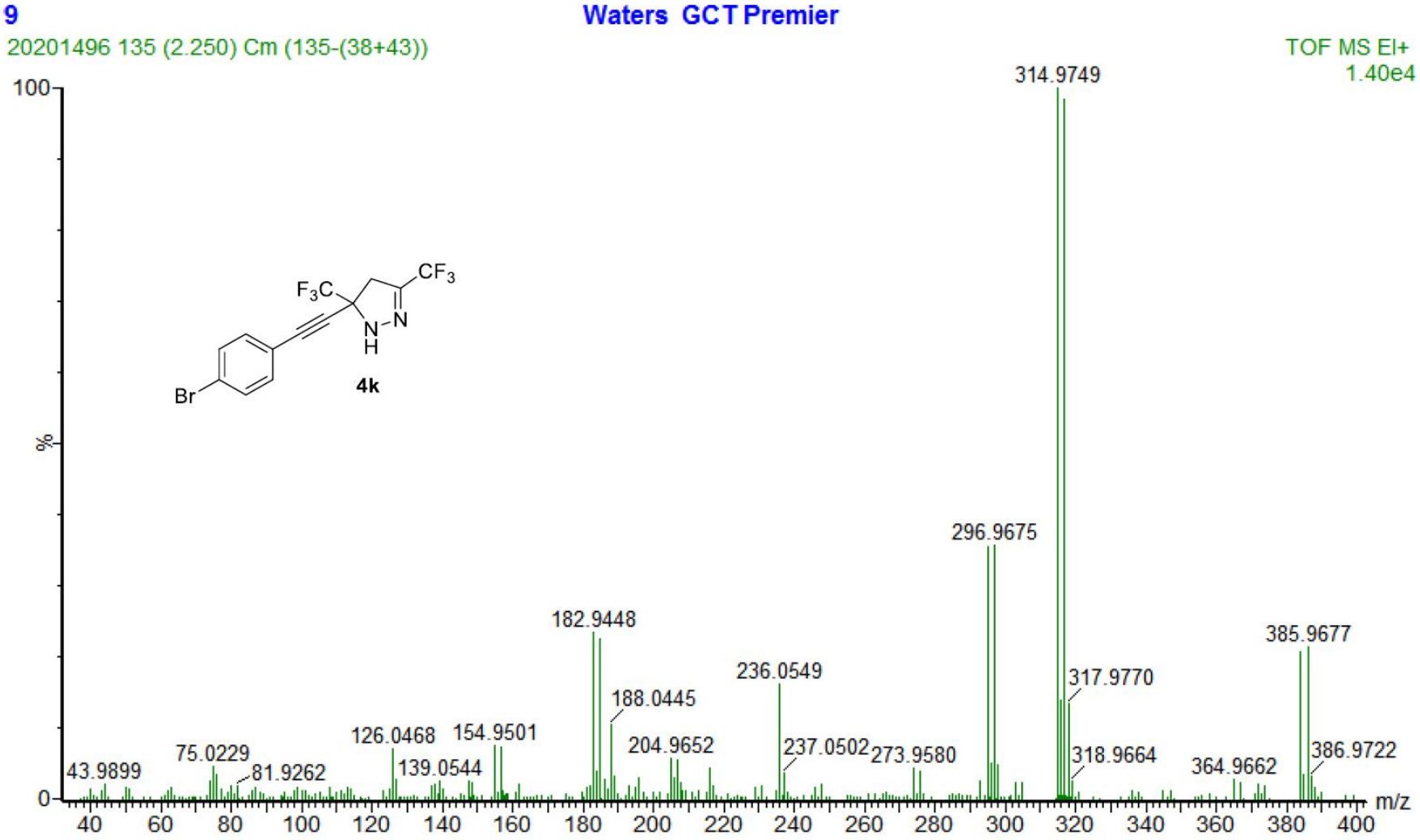
^{13}C NMR spectrum of 4k



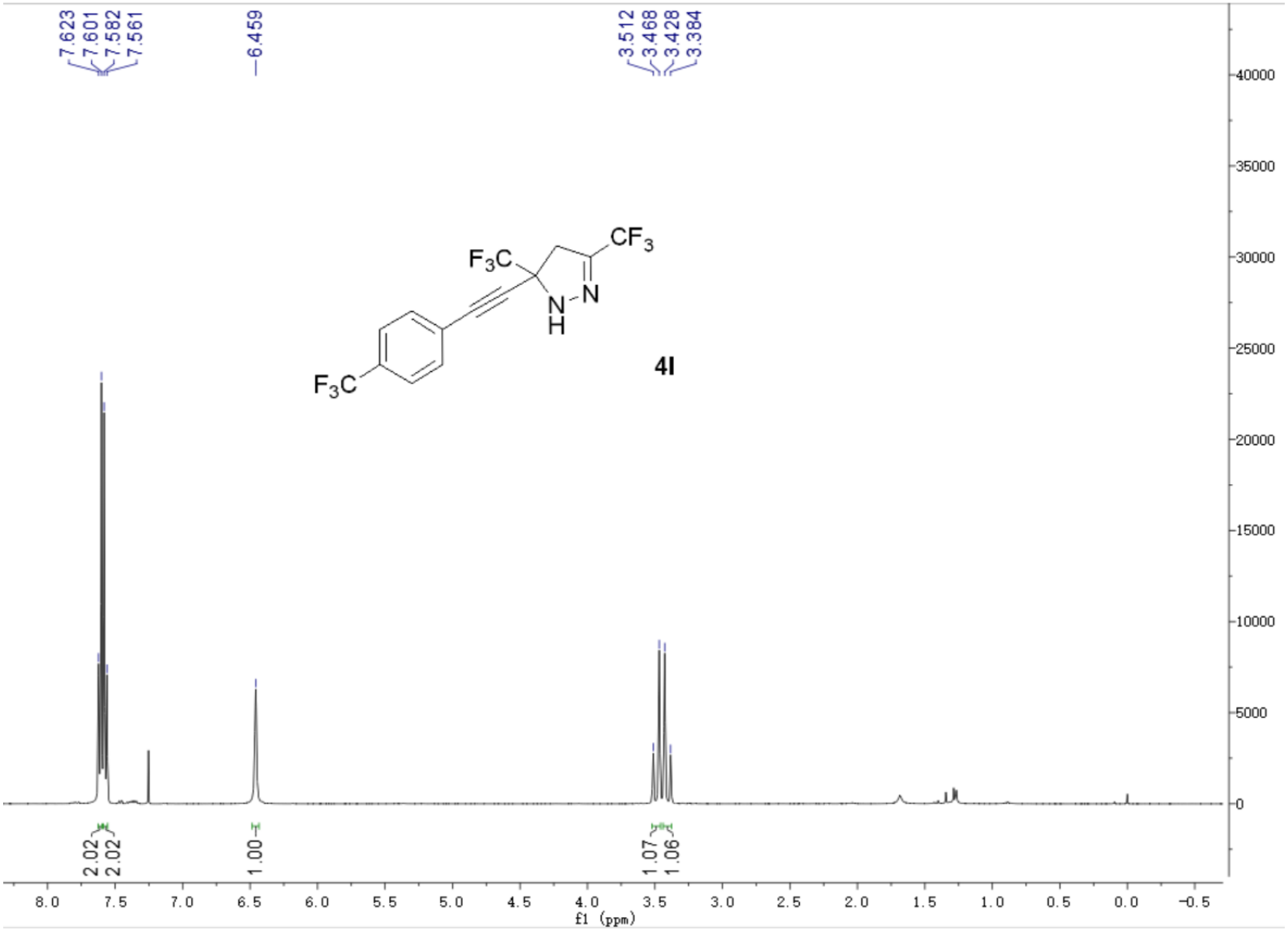
^{19}F NMR spectrum of 4k



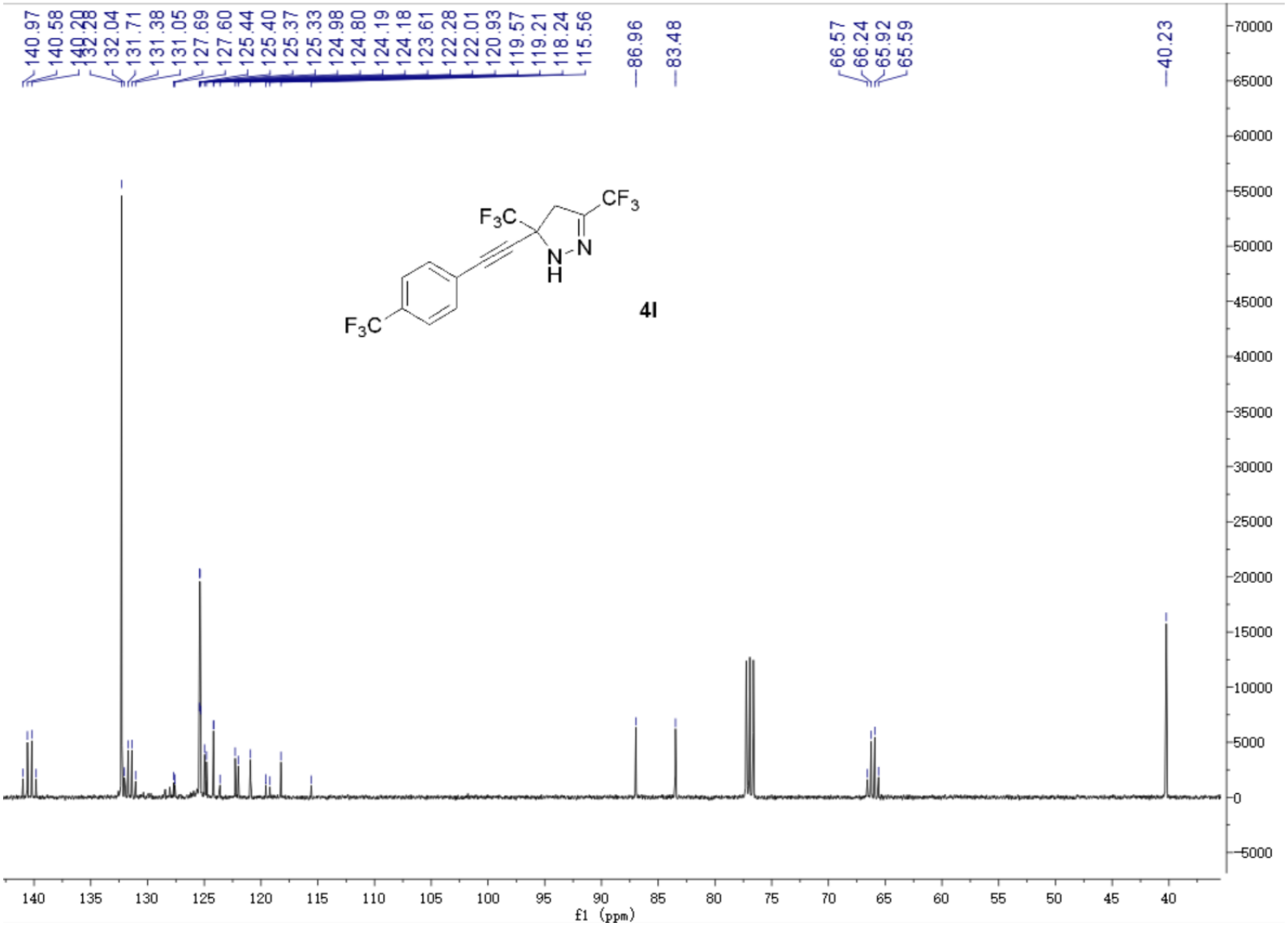
HRMS (EI) spectrum of 4k



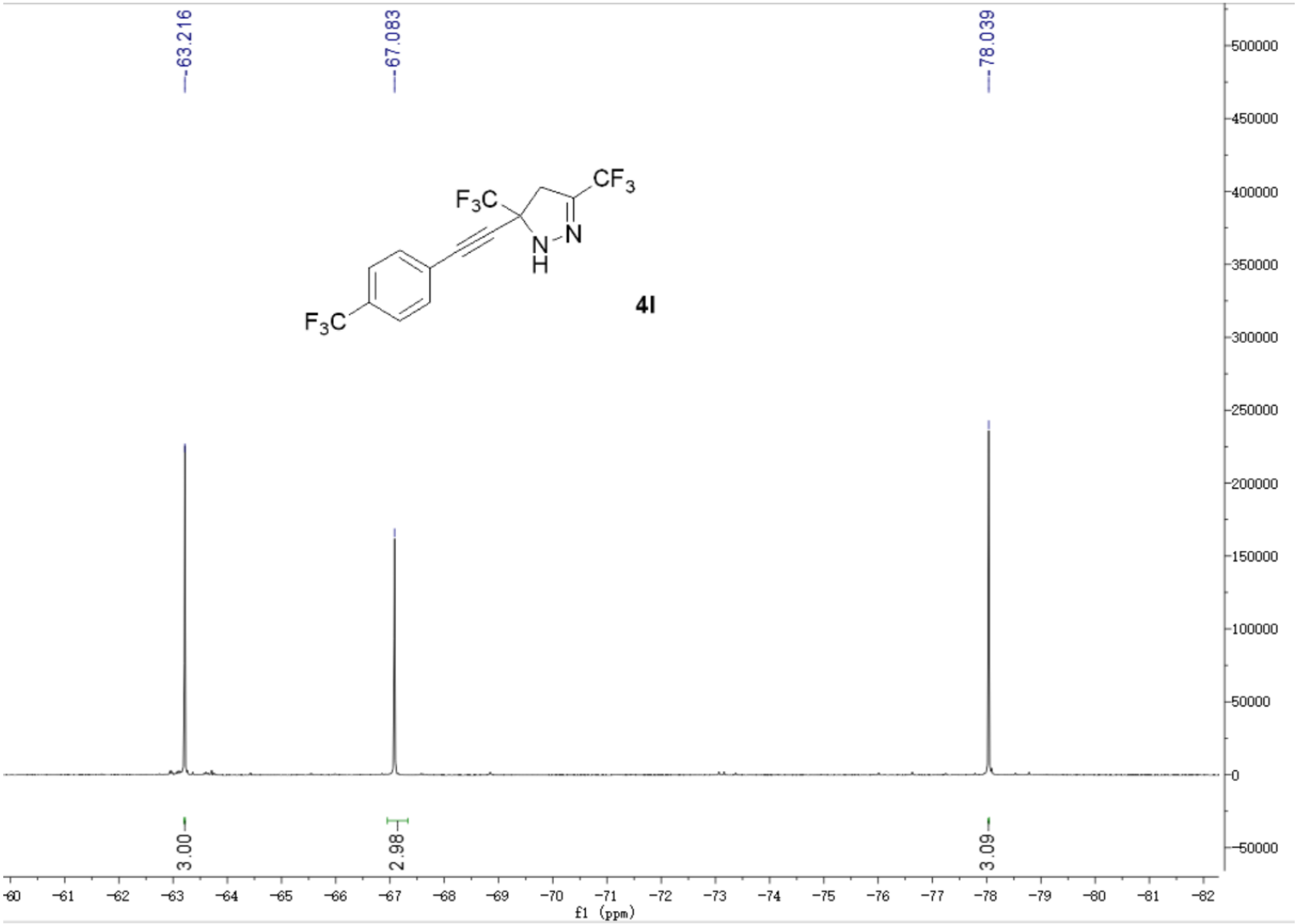
^{1}H NMR spectrum of 4l



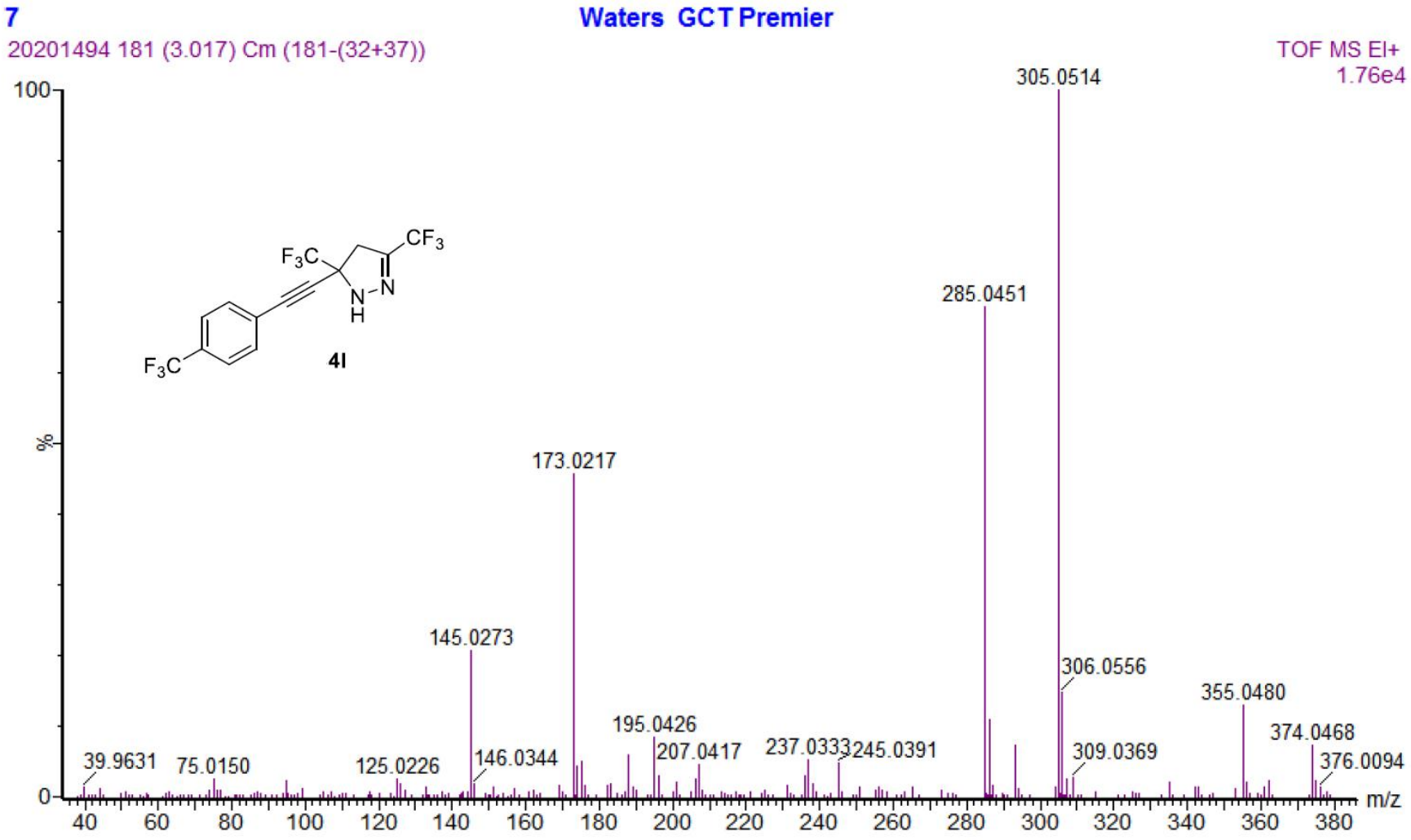
^{13}C NMR spectrum of 4l



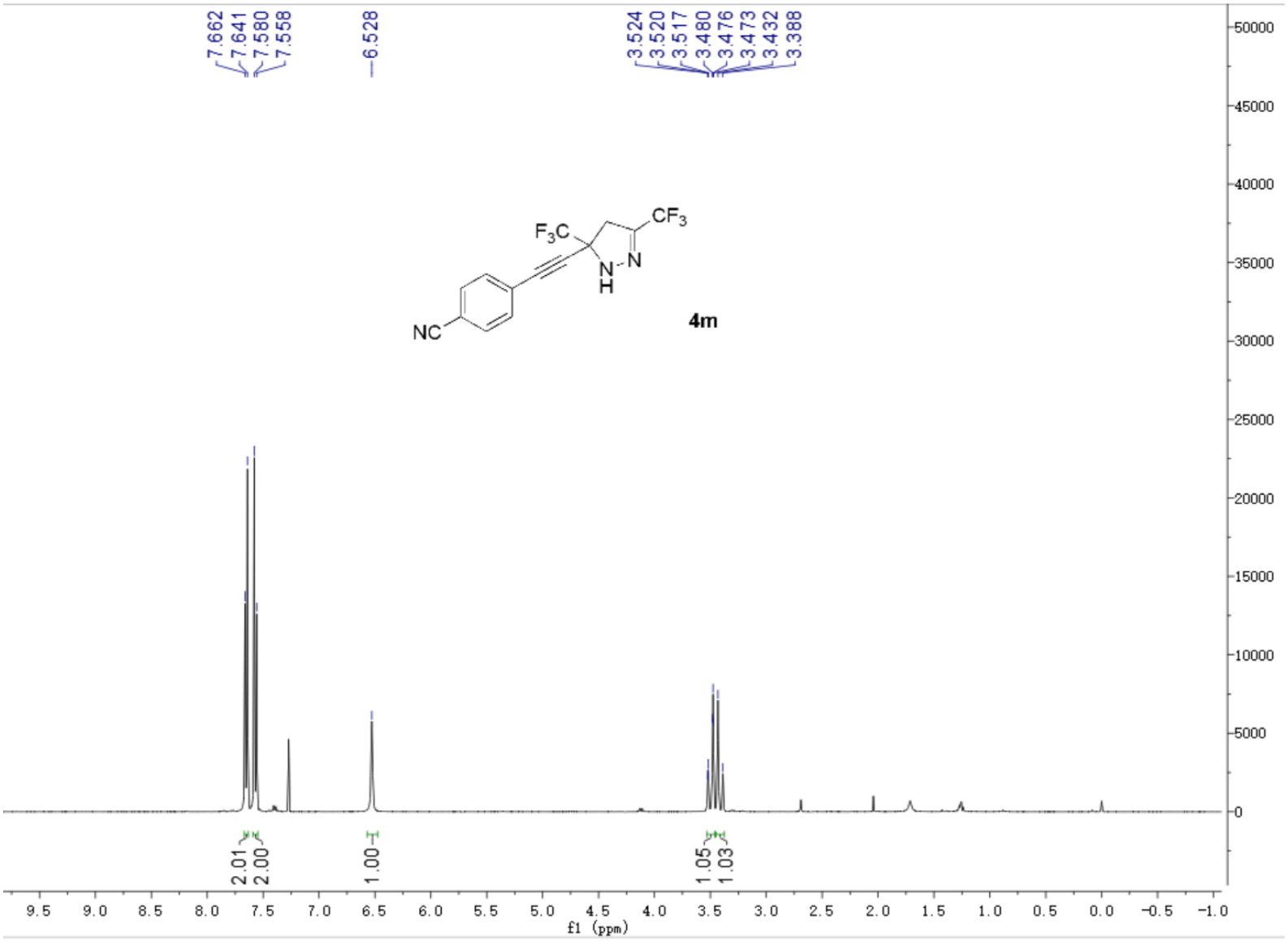
^{19}F NMR spectrum of 4l



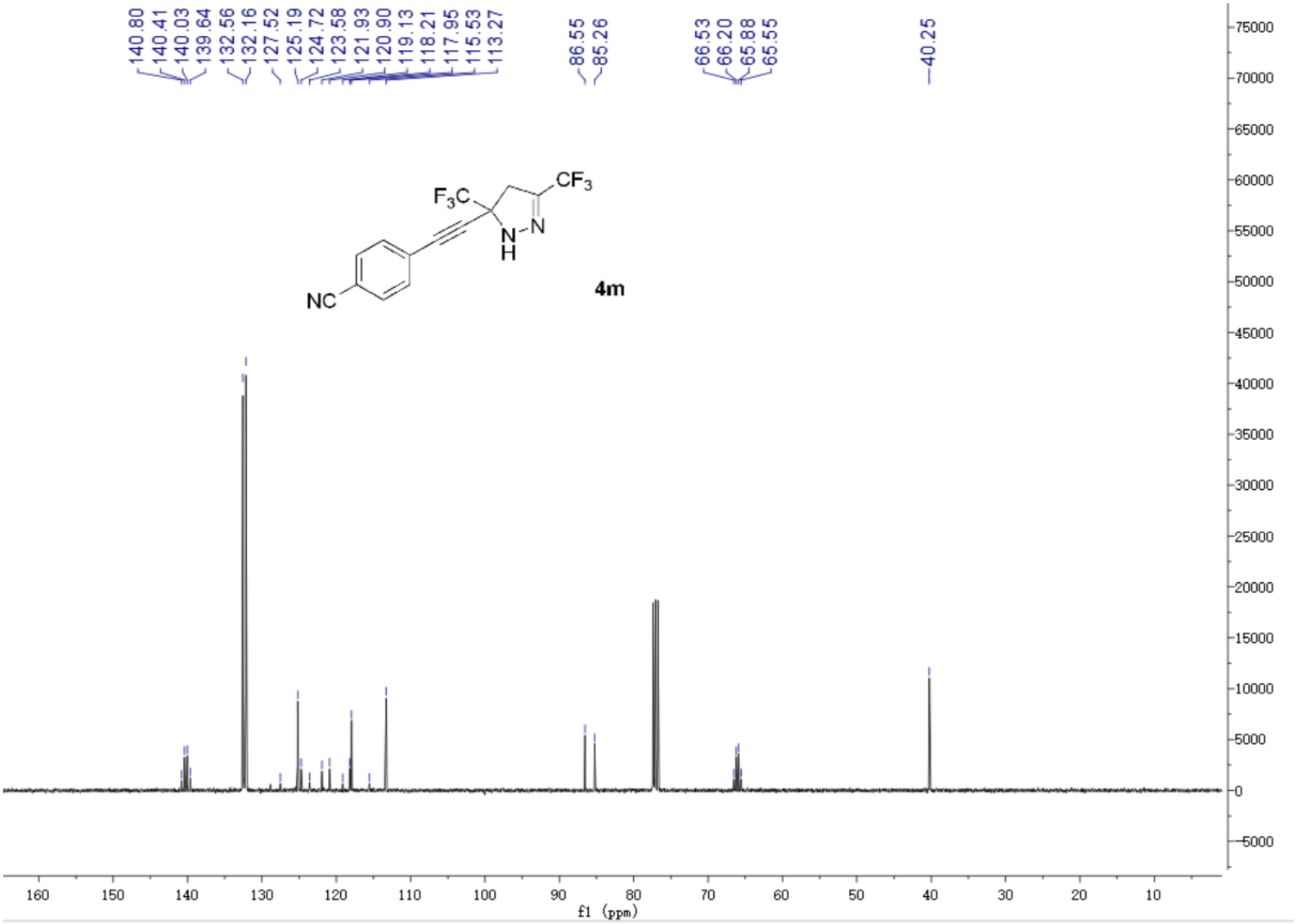
HRMS (EI) spectrum of 4l



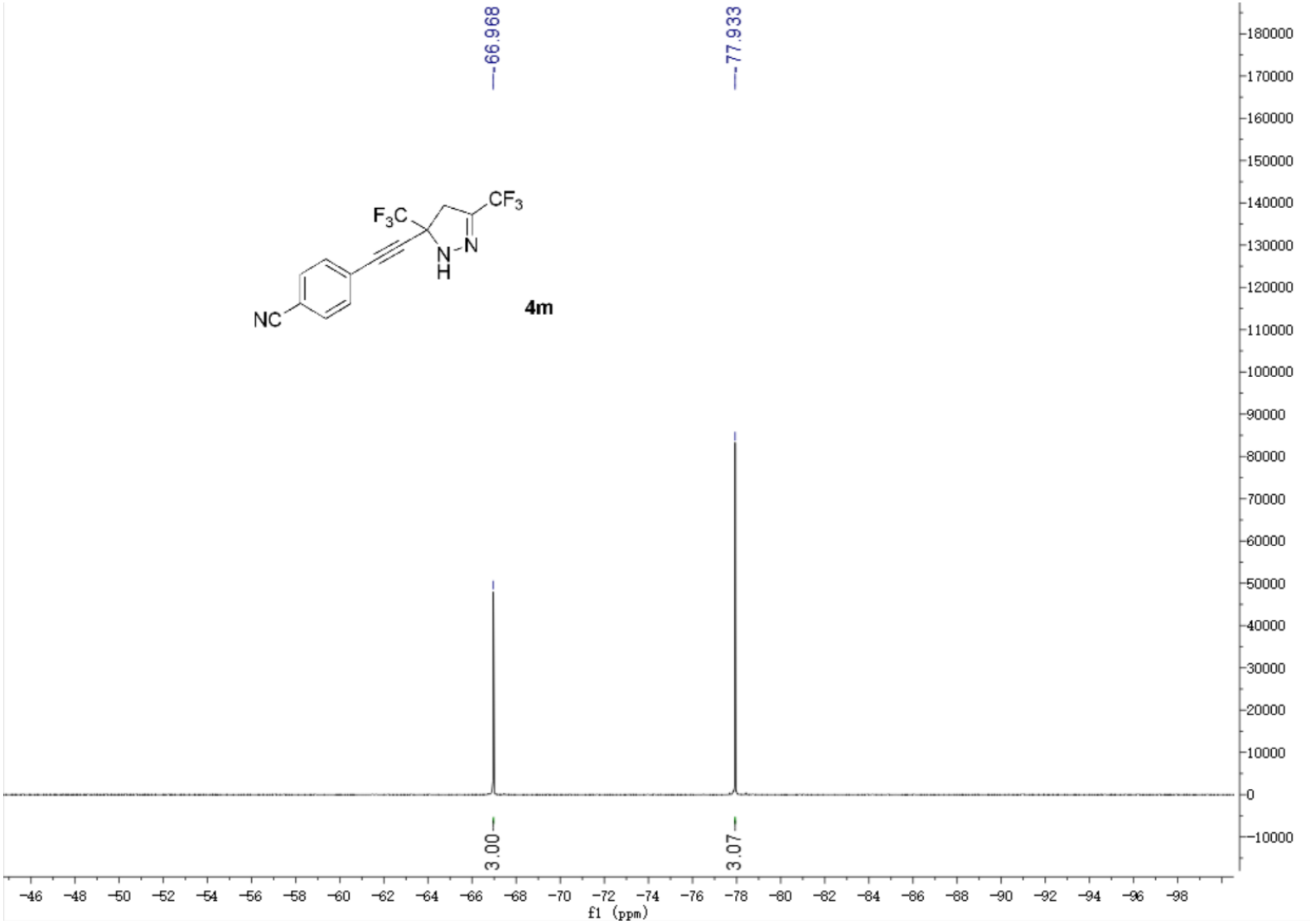
^{1}H NMR spectrum of 4m



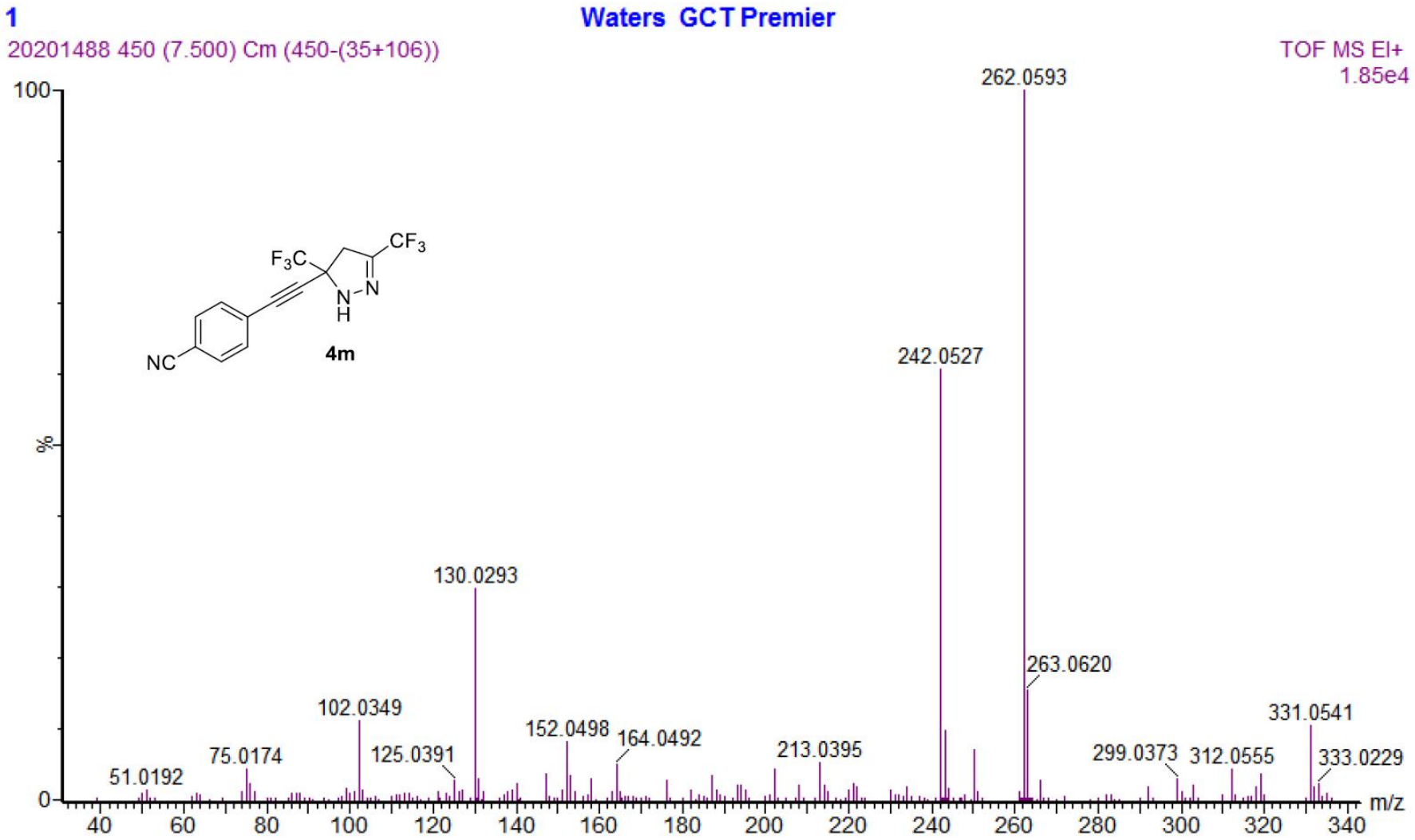
^{13}C NMR spectrum of 4m



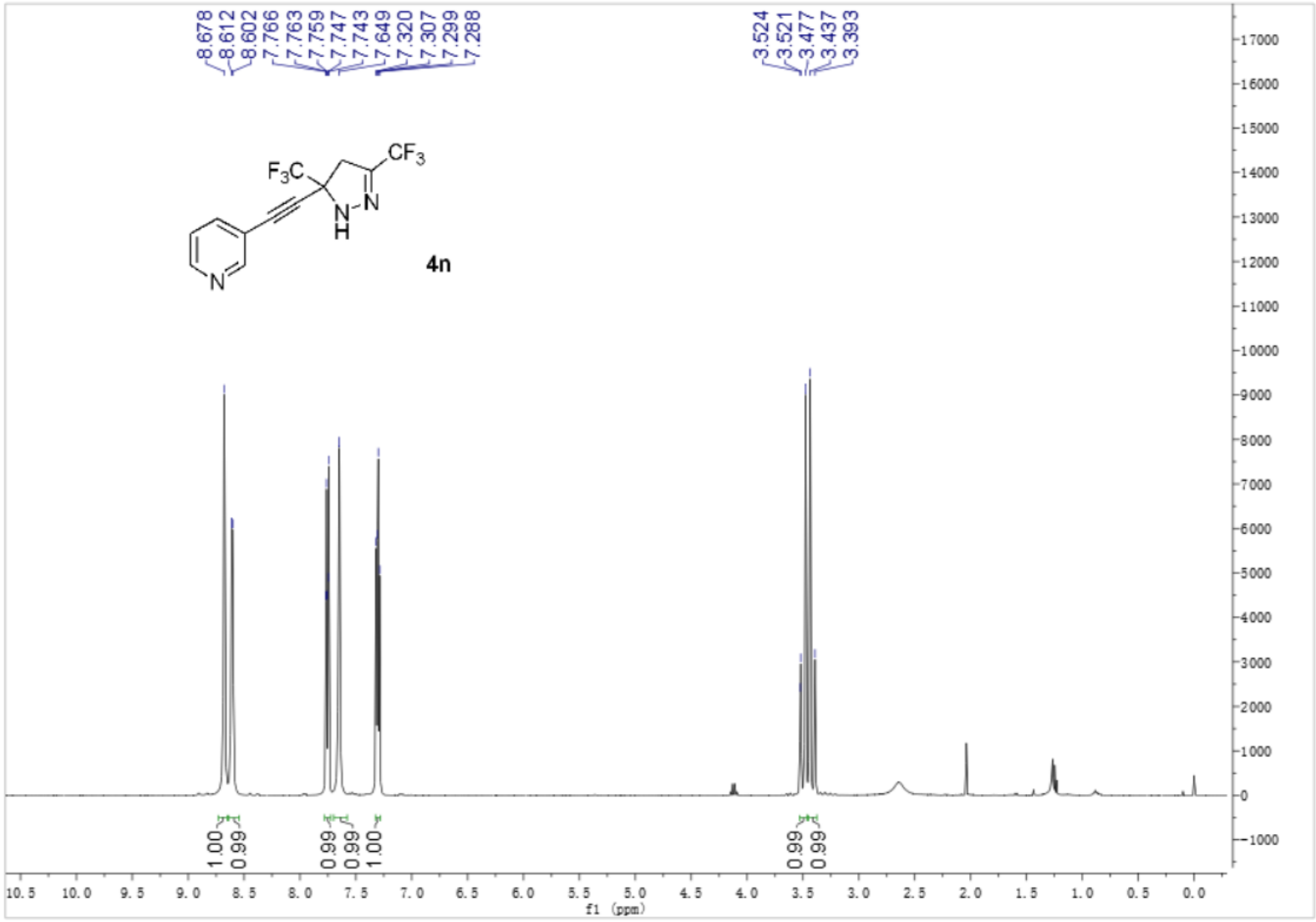
^{19}F NMR spectrum of 4m



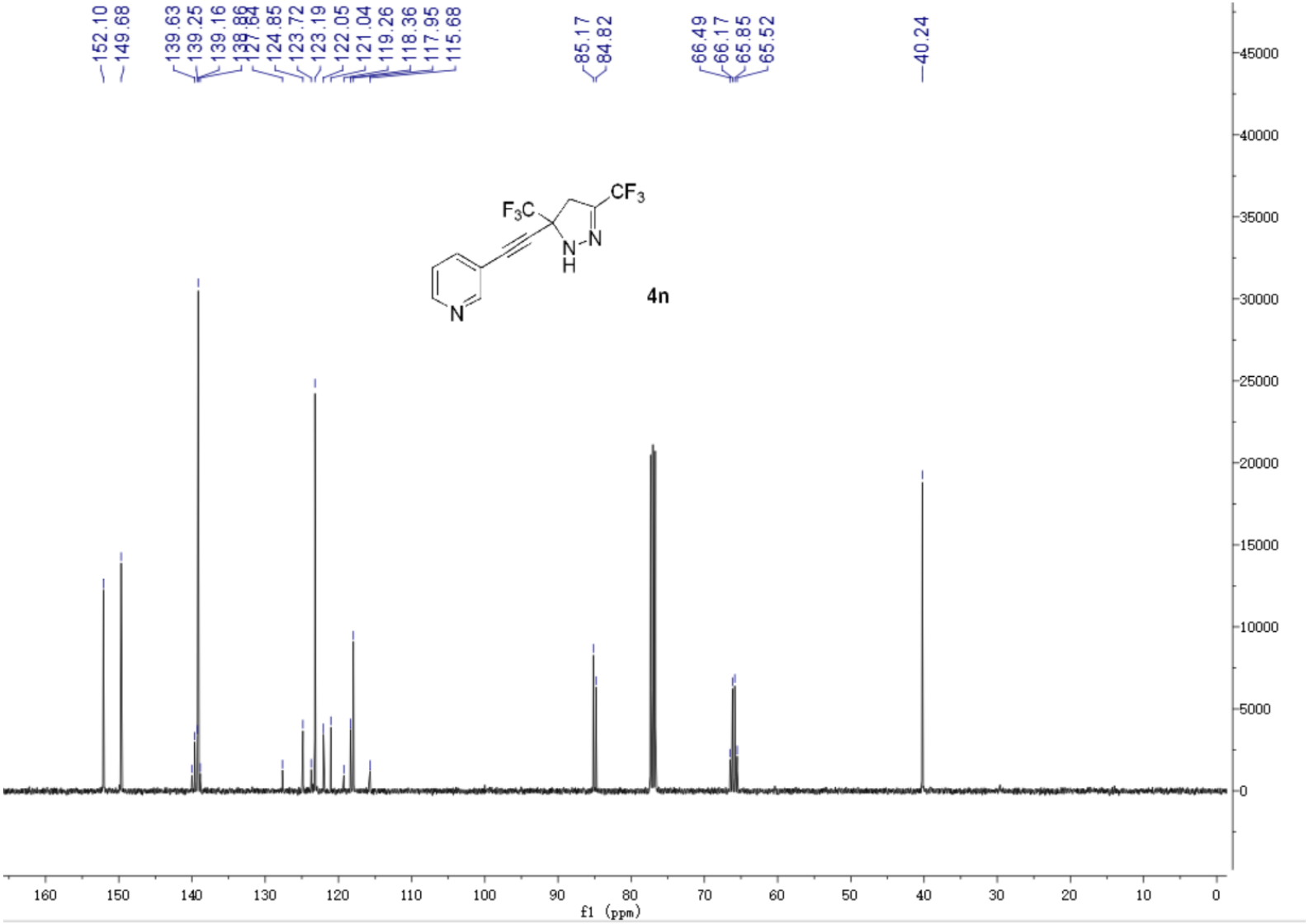
HRMS (EI) spectrum of 4m



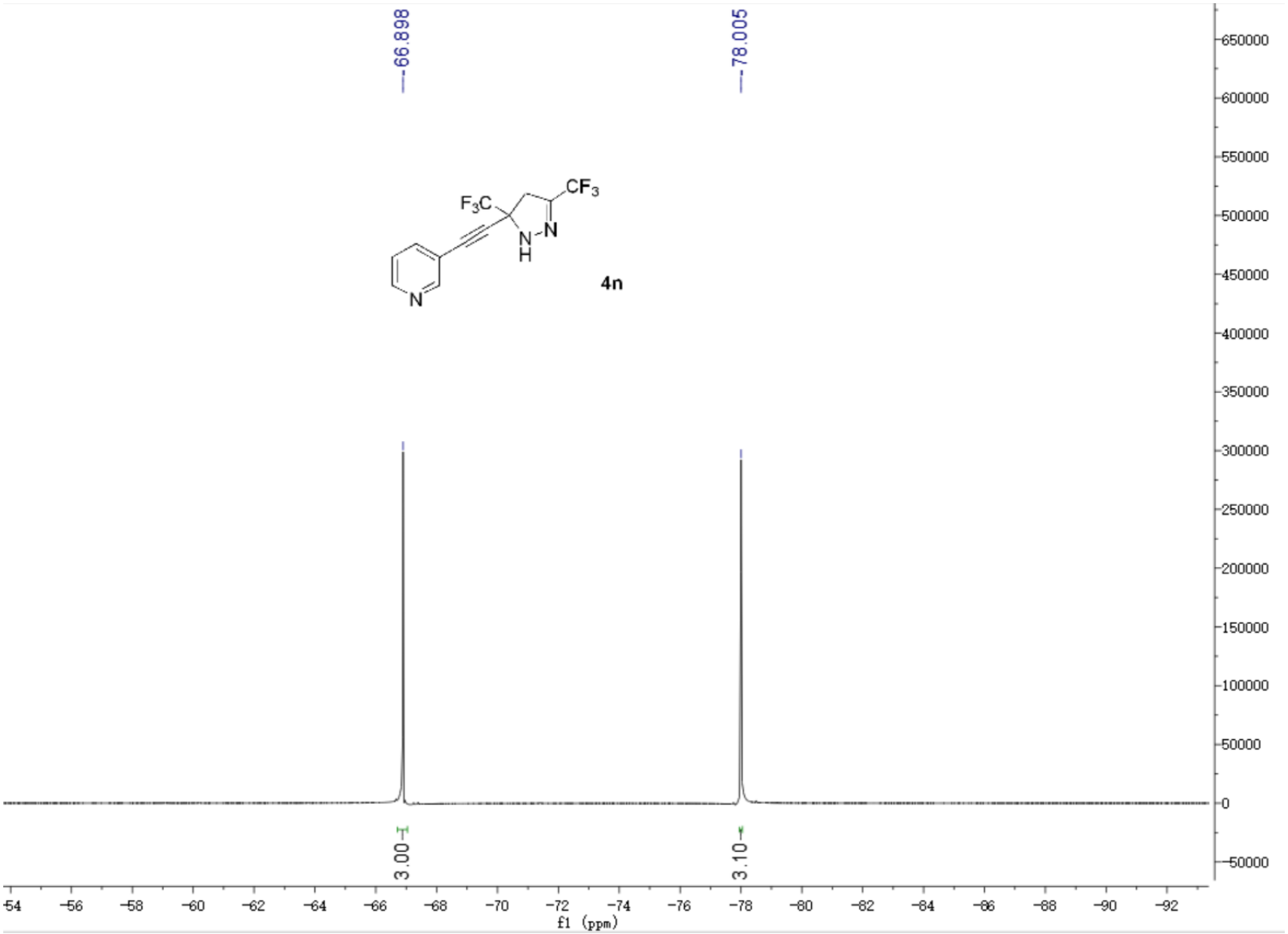
^{1}H NMR spectrum of 4n



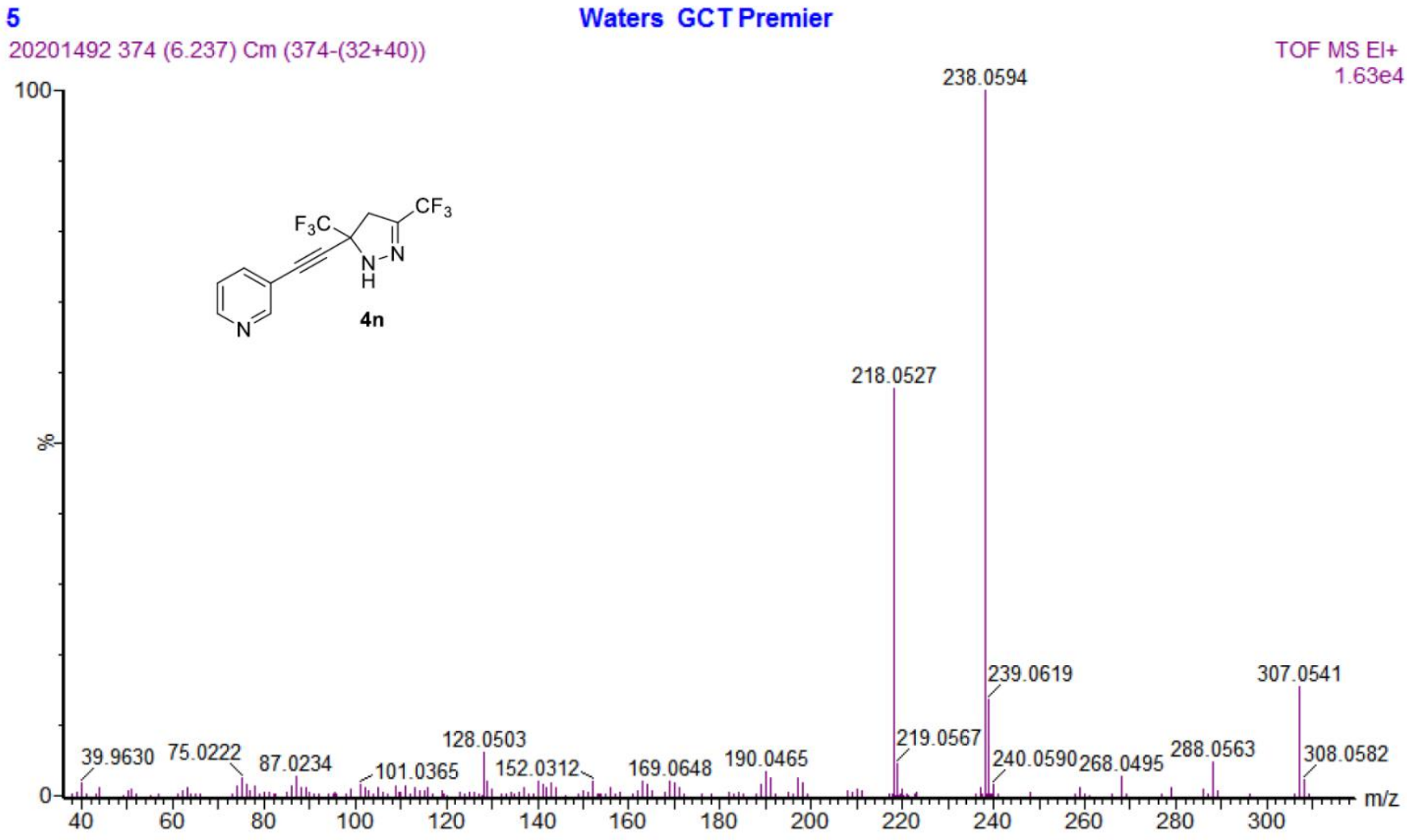
^{13}C NMR spectrum of 4n



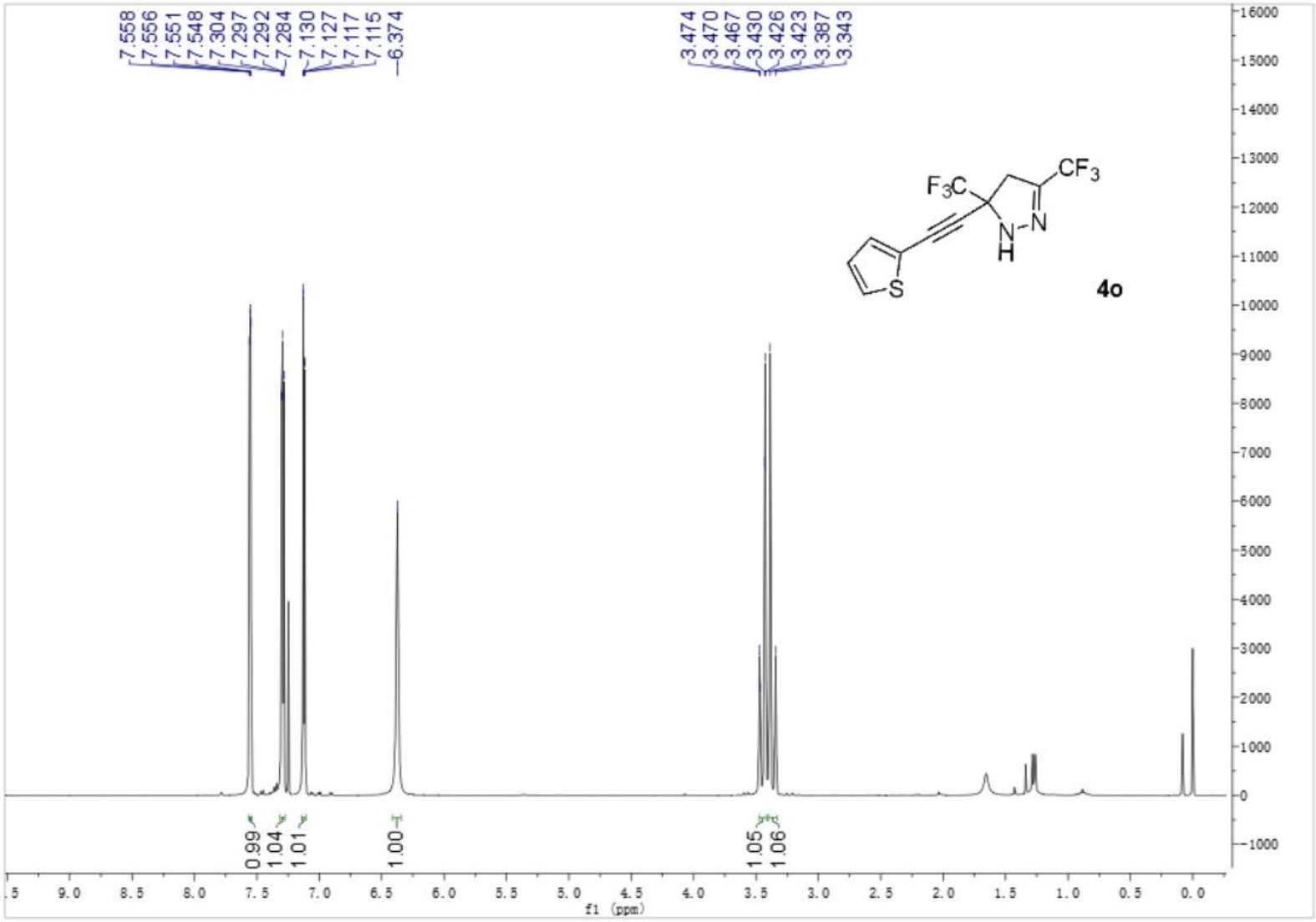
^{19}F NMR spectrum of 4n



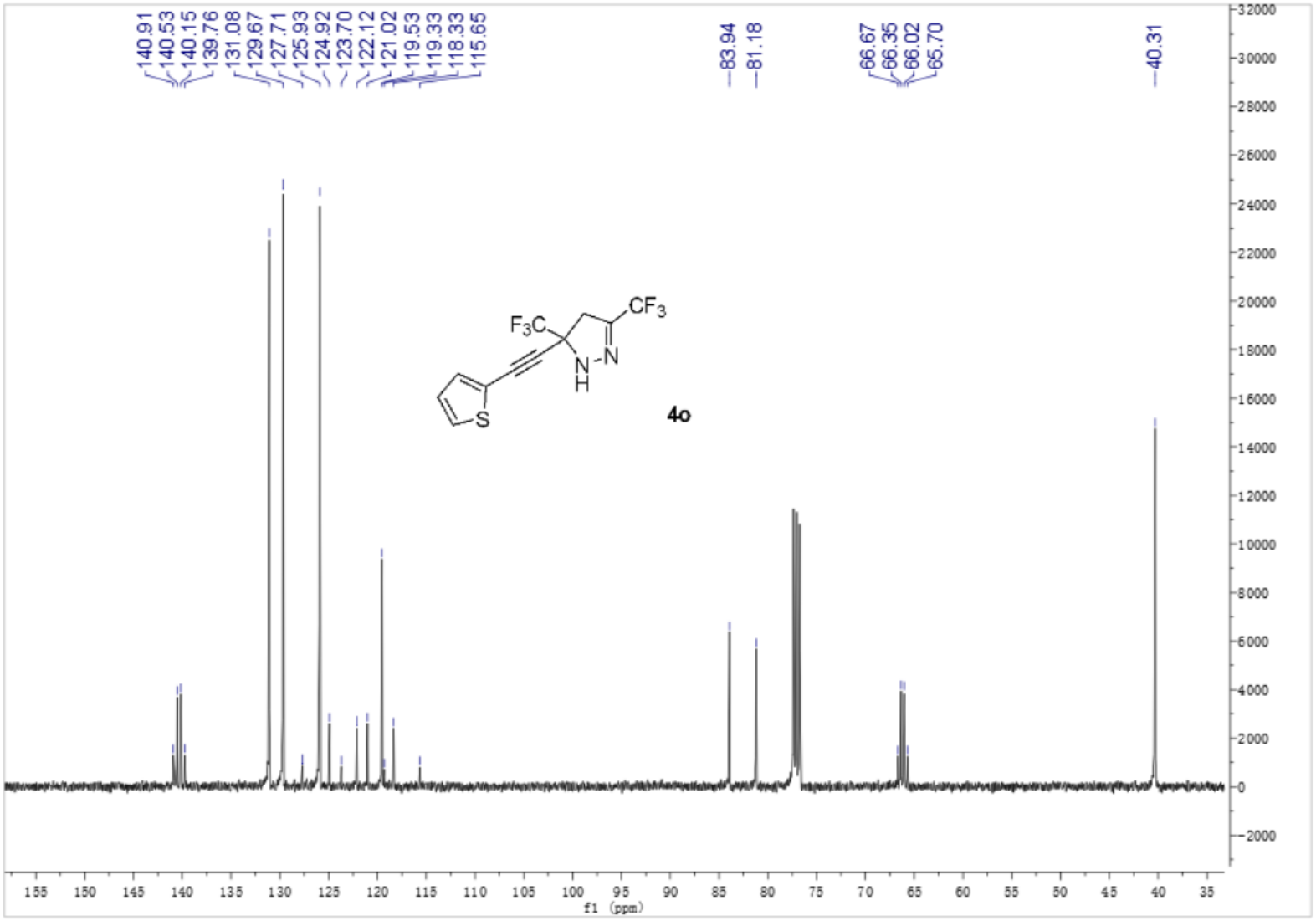
HRMS (EI) spectrum of 4n



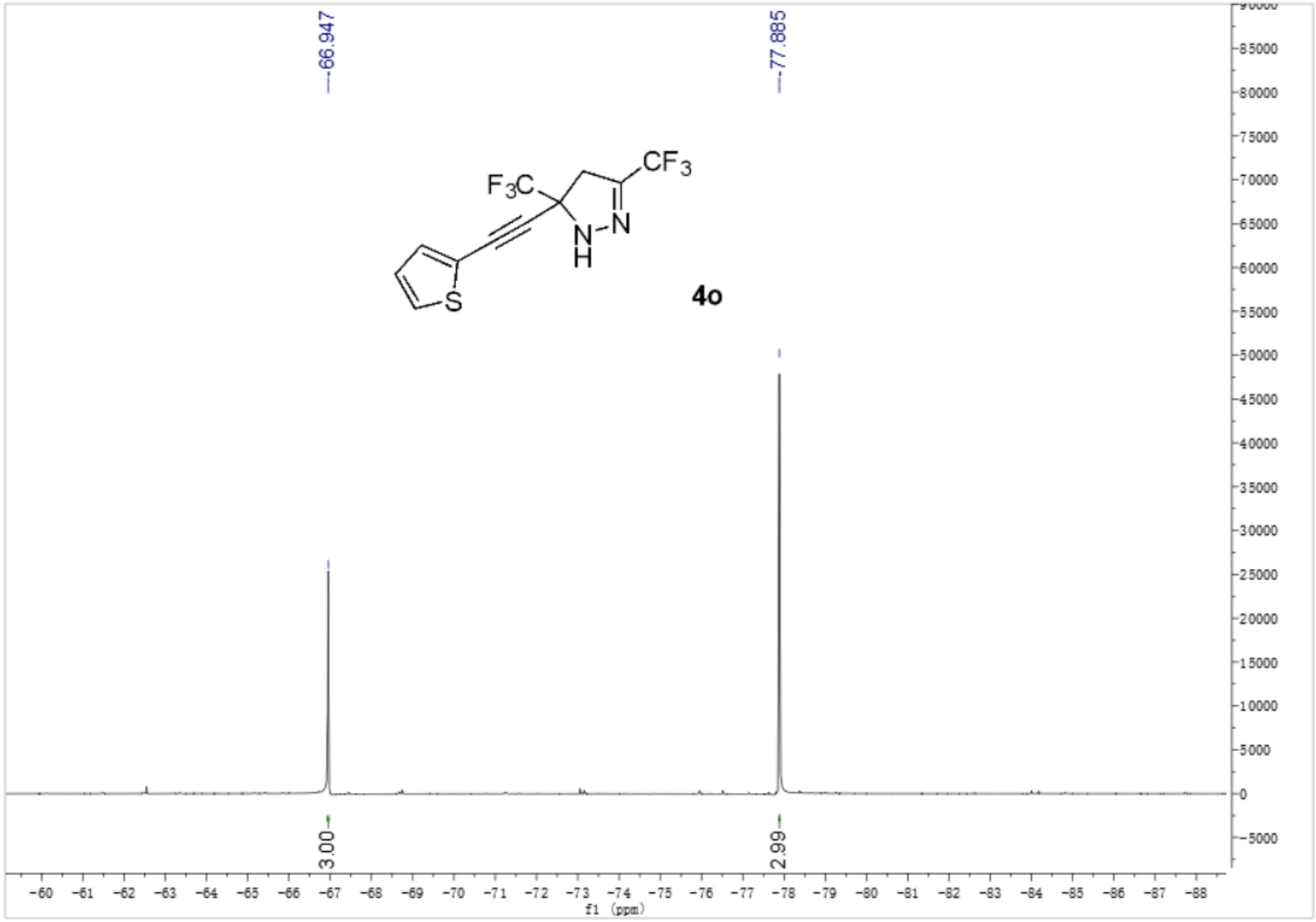
^{1}H NMR spectrum of 4o



^{13}C NMR spectrum of 4o



^{19}F NMR spectrum of 4o



HRMS (EI) spectrum of 4o