Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Pyrroles *versus* Cyclic Nitrones: Catalyst-Controlled Divergent Cyclization of *N*-(2-perfluoroalkyl-3-alkynyl)hydroxylamines

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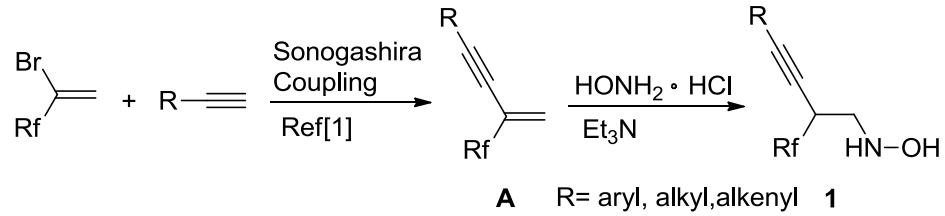
1. General information.

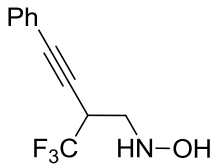
^{1}H NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in chloroform-d3. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). All reactions were carried out under an atmosphere of Argon in flame-dried glassware with magnetic stirring. $ClCH_2CH_2Cl$ (DCE), CH_2Cl_2 (DCM), CH_3CN, DMSO, DMF were freshly distilled from CaH_2; toluene and THF was freshly distilled from sodium metal prior to use. 4 Å molecular sieves were powdered and dried at 300 ℃ in muffle furnace for 8-10 hours prior to use. 2-Perfluoroalkyl 1, 3-enynes **A** were prepared in good yields according to the literature.[1]

2. Preparation of N-(2–(perfluoroalkyl)-3-alkynyl) hydroxylamines 1



To the solution of 2-perfluoroalkyl 1, 3-enyne **A** (0.3 mmol), hydroxylamine hydrochloride (0.45 mmol) in DCM (3.0 ml) at 0 ^{o}C was added Et_3N (170 mol %), the reaction was stirred at 0 ^{o}C for 24 h. After the enyne was completely consumed, which was determined by TLC analysis, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether : acetate =5:1～1:1) to afford *N*-(2–(Perfluoroalkyl)-3-alkynyl)hydroxylamines **1** in 40%～75% yield.

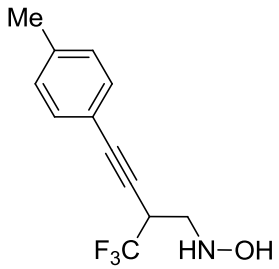
Synthesis of 1a.



1a

1a 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.37 – 7.29 (m, 3H), 5.82 (s, 1H), 5.62 (brs, 1H), 4.03 – 3.90 (m, 1H), 3.45 (dd, *J* = 13.2, 4.4 Hz, 1H), 3.17 (dd, *J* = 13.2, 9.6 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.61. ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.97, 128.90, 128.33, 124.83 (q, *J* = 278.0 Hz), 121.73, 85.90, 80.13, 52.21, 36.20 (q, *J* = 30.0 Hz). MS (70 eV): m/z (%): 229 (M^+, 1.17), 46 (100). HRMS calcd for $C_{11}H_{10}NOF_3$: 229.0714, found: 229.0715.

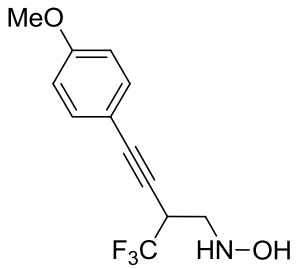
Synthesis of 1b.



1b

66% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.03 (brs, 1H), 5.62 (brs, 1H), 4.02 – 3.88 (m, 1H), 3.44 (dd, *J* = 13.2, 4.4 Hz, 1H), 3.16 (dd, *J* = 13.2, 9.6 Hz, 1H), 2.35 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.67. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.10, 131.85, 129.06, 124.86 (q, *J* = 278.0 Hz), 118.64, 86.08, 79.36, 52.22, 36.19 (q, *J* = 30.0 Hz), 21.49. MS (70 eV): m/z (%): 243 (M^+, 6.54), 46 (100). HRMS calcd for $C_{12}H_{12}NOF_3$: 243.0871, found: 243.0869.

Synthesis of 1c.

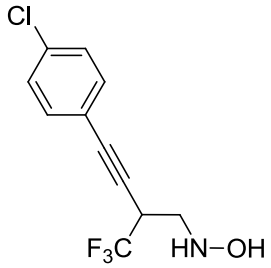


1c

75% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.99 (brs, 2H), 4.02-3.87 (m, 1H), 3.81 (s, 3H), 3.43 (dd, *J* = 13.2, 4.4 Hz, 1H), 3.15 (dd, *J* = 13.2, 9.6 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.72. ^{13}C NMR (100 MHz, $CDCl_3$) δ

160.00, 133.44, 124.83 (q, J = 278.0 Hz), 113.92, 113.76, 85.92, 78.65, 78.61, 77.32, 77.00, 76.68, 55.25, 52.16, 36.12 (q, J = 30.0 Hz). MS (70 eV): m/z (%): 259 (M^+, 10.66), 46 (100). HRMS calcd for $C_{12}H_{12}NO_2F_3$: 259.0820 , found:259.0822.

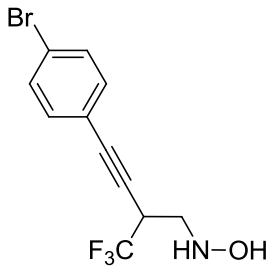
Synthesis of 1d.



1d

66% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H). 5.57 (brs, 1H), 5.33 (brs, 1H), 4.01 – 3.88 (m, 1H), 3.45 (dd, J = 13.3, 4.5 Hz, 1H), 3.17 (dd, J = 13.3, 9.4 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.55. ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.08, 133.18, 128.70, 124.72 (q, J = 278.0 Hz), 120.18, 84.85, 81.19, 52.07, 36.20 (q, J = 30.0 Hz). MS (70 eV): m/z (%): 263 (M^+, 2.49), 265 (M^+ + 2, 0.75), 46 (100). HRMS calcd for $C_{11}H_9NOF_3Cl$: 263.0325, found: 263.0326.

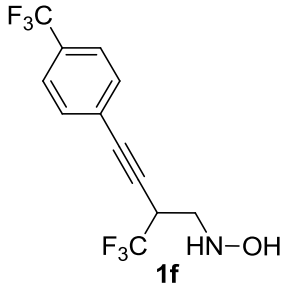
Synthesis of 1e.



1e

63% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.28 (brs, 1H), 5.59 (brs, 1H), 4.02 – 3.89 (m, 1H), 3.45 (dd, *J* = 13.2, 4.4 Hz, 1H), 3.17 (dd, *J* = 13.2, 9.5 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.55. ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.39, 131.64, 124.70 (q, *J* = 279.0 Hz), 123.31, 120.69, 84.88, 81.46, 81.42, 52.13, 36.28 (q, *J* = 30.0 Hz). MS (70 eV): m/z (%): 307 (M^+, 1.96), 309 (M^+ + 2, 1.69), 46 (100). HRMS calcd for $C_{11}H_9NOF_3Br$: 306.9820, found: 306.9809.

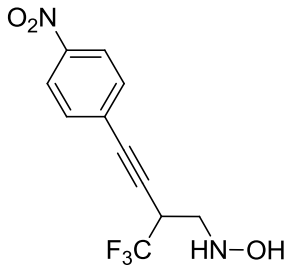
Synthesis of 1f.



1f

66% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 4H), 6.56 (brs, 1H), 5.53 (brs, 1H), 4.08 – 3.90 (m, 1H), 3.47 (dd, *J* = 13.3, 4.4 Hz, 1H), 3.20 (dd, *J* = 13.2, 9.5 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.01, -69.50. ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.26, 130.76 (q, *J* = 32.9 Hz), 125.50, 124.67 (q, *J* = 278.0 Hz), 125.29 (q, *J* = 3.7 Hz), 123.75 (q, *J* = 271.0 Hz), 84.55, 82.77 (q, *J* = 3.5 Hz), 52.09, 36.26 (q, *J* = 30.1 Hz). LRMS-ESI $[M-H]^-$: 296.0 (100); HRMS calcd for $C_{12}H_9NF_6O$: 297.0588, found: 297.0586.

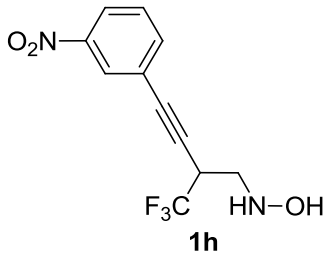
Synthesis of 1g.



1g

1g 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 6.16 (s, 1H), 5.58 (brs, 1H), 4.08-3.95 (m, 1H), 3.48 (dd, *J* = 13.3, 4.5 Hz, 1H), 3.21 (dd, *J* = 13.3, 9.4 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.27. ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.51, 132.82, 128.48, 124.53 (q, *J* = 278.0 Hz), 123.57, 85.67, 83.87, 52.04, 36.34 (q, *J* = 30.0 Hz). LRMS-ESI: 272.95 (M^+-H)(100); HRMS calcd for $C_{11}H_9N_2O_3F_3$: 274.0565, found: 274.0566.

Synthesis of 1h.

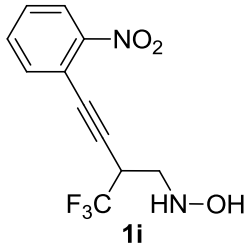


1h

66% isolated yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.28 (s, 1H), 8.26 – 8.21 (m, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.66 (s, 1H), 6.05 (brs, 1H), 4.19 – 4.03 (m, 1H), 3.24 (dd, *J* = 12.9, 4.1 Hz, 1H), 3.11 (dd, *J* = 12.8, 9.0 Hz, 1H). ^{19}F NMR (377 MHz, d_6-DMSO) δ -63.51. ^{13}C NMR (100 MHz, d_6-DMSO) δ 148.27, 138.30, 130.85, 126.77, 125.66 (q, *J* = 279.0 Hz), 124.26, 123.51, 85.17 (q, *J* = 3.7 Hz), 82.68, 52.74, 36.38 (q, *J* = 28.5 Hz). MS (70 eV): m/z (%): 274 (M^+, 15.57), 66 (100).

HRMS calcd for $C_{11}H_9N_2O_3F_3$: 274.0565, found: 274.0567.

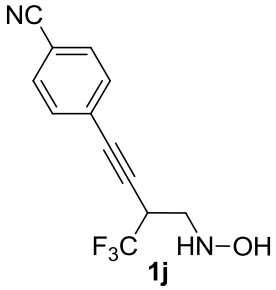
Synthesis of 1i.



1i

48% isolated yield .^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.67 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.60 (td, *J* = 7.6, 1.2 Hz, 1H), 7.53 – 7.47 (m, 1H), 6.54 (brs, 1H), 5.82 (brs, 1H), 4.15-4.03 (m, 1H), 3.49 (dd, *J* = 13.3, 4.3 Hz, 1H), 3.22 (dd, *J* = 13.3, 9.8 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.19. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.81, 135.09, 133.08, 129.39, 124.58 (q, *J* = 279.0 Hz), 124.79, 117.31, 88.52 (q, *J* = 3.8 Hz), 81.39, 51.86, 36.61 (q, *J* = 30.1 Hz). MS (70 eV): m/z (%): 275 ($M+H^+$, 10.0), 209 (100). HRMS-ESI calcd for $C_{11}H_{10}N_2O_3F_3$ [$M+H^+$]: 275.0638, found: 275.0656.

Synthesis of 1j.

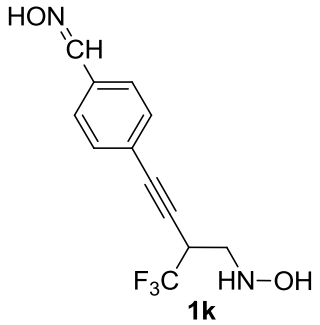


1j

53% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 5.76 (s, 1H), 5.56 (brs, 1H), 4.07 – 3.93 (m, 1H),

3.47 (dd, J = 13.3, 3.1 Hz, 1H), 3.19 (dd, J = 13.3, 9.4 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.34. ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.53, 132.04, 126.61, 124.58 (q, J = 278.0 Hz), 118.16, 112.42, 84.89, 84.11, 52.11, 36.35 (q, J = 30.0 Hz). MS (70 eV): m/z (%): 254 (M^+, 1.99), 46 (100). HRMS calcd for $C_{12}H_9N_2F_3O$: 254.0667, found: 254.0666.

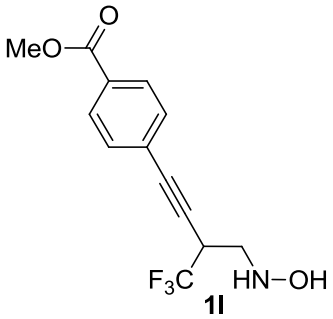
Synthesis of 1k.



1k

48% isolated yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.43 (s, 1H), 8.16 (s, 1H), 7.65 (s, 1H), 7.60 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 6.01 (brs, 1H), 4.08-3.97 (m, 1H), 3.20 (dd, J = 12.8, 4.2 Hz, 1H), 3.06 (dd, J = 12.8, 8.9 Hz, 1H). ^{19}F NMR (377 MHz, d_6-DMSO) δ -63.55. ^{13}C NMR (100 MHz, d_6-DMSO) δ 148.05, 134.07, 132.54, 127.06, 125.80 (q, J = 278.0 Hz), 122.55, 84.55, 84.07, 53.00, 36.42 (q, J = 28.2 Hz). MS (70 eV): m/z (%) : 272.0 (M^+, 23.0)，210 (100). HRMS-ESI calcd for $C_{12}H_{12}N_2O_2F_3$[M+H^+]: 273.0845, found: 273.0859.

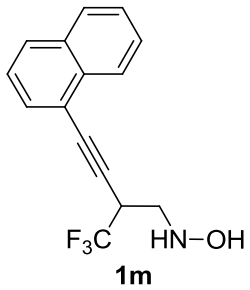
Synthesis of 1l.



1l

1l 71% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 6.19 (brs, 1H), 5.59 (brs, 1H), 4.06 – 3.95 (m, 1H), 3.92 (s, 3H), 3.47 (dd, *J* = 13.0, 3.8 Hz, 1H), 3.19 (dd, *J* = 13.1, 9.6 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.46. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.37, 131.92, 130.19, 129.47, 126.35, 124.69 (q, *J* = 278.0 Hz), 85.08, 83.20, 52.29, 52.13, 36.30 (q, *J* = 30.1 Hz). MS (70 eV): m/z (%): 287 (M^+, 5.38), 46 (100). HRMS calcd for $C_{13}H_{12}NO_3F_3$: 287.0769, found: 287.0767.

Synthesis of 1m.

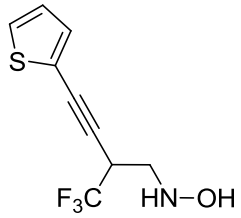


1m

63% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 7.1 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.53 (dd, *J* = 11.0, 4.0 Hz, 1H), 7.46 – 7.39 (m, 1H), 6.26 (brs, 1H), 5.55 (brs, 1H), 4.21 – 4.08 (m, 1H), 3.55 (dd, *J* = 13.3, 4.6 Hz, 1H), 3.30 (dd, *J* = 13.3, 9.4 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.47. ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.36, 133.09, 131.03, 129.42, 128.34, 127.10, 126.52,

124.96 (q, *J* = 278.0 Hz) 125.74, 125.05, 119.35, 85.05 (q, *J* = 3.7 Hz), 84.14, 52.37, 36.60 (q, *J* = 29.0 Hz). MS (70 eV): m/z (%): 279 (M^+, 8.22), 46 (100). HRMS calcd for $C_{15}H_{12}NOF_3$: 279.0871, found: 279.0879.

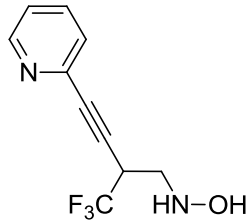
Synthesis of 1n.



1n

57% isolated yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.04 (brs, 1H), 6.97 (dd, *J* = 4.9, 3.9 Hz, 1H), 5.61 (brs, 1H), 4.08-3.94 (m, 1H), 3.44 (dd, *J* = 13.2, 4.5 Hz, 1H), 3.17 (dd, *J* = 13.2, 9.5 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.44.^{13}C NMR (100 MHz, $CDCl_3$) δ 133.12, 127.77, 126.93, 124.67 (q, *J* = 279.9 Hz), 121.52, 84.04 (q, *J* = 3.7 Hz), 79.33, 51.99, 36.42 (q, *J* = 30.1 Hz). MS (70 eV): m/z (%): 235 (M^+, 17.6), 46 (100). HRMS calcd for $C_9H_8NOSF_3$: 235.0279, found : 235.0277.

Synthesis of 1o.

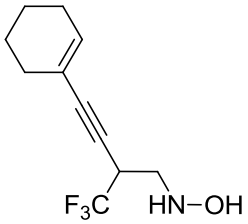


1o

40% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.53 (m, 1H), 7.70-7.64 (m, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.36 (brs, 1H), 7.30 – 7.23 (m, 1H), 5.68 (brs, 1H), 4.14-4.02 (m, 1H), 3.46 (dd, *J* = 13.2, 4.4 Hz, 1H), 3.20 (dd, *J* = 13.2, 9.8 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.22. ^{13}C

NMR (100 MHz, $CDCl_3$) δ 149.74, 141.99, 136.52, 127.45, 124.72 (q, *J* = 278.0 Hz), 123.49, 84.72, 81.26 (q, *J* = 3.4 Hz), 52.03, 36.21 (q, *J* = 29.8 Hz). MS (70 eV): m/z (%): 230 (M^+, 68.15), 66 (100). HRMS calcd for $C_{10}H_9N_2OF_3$: 230.0667, found: 230.0665.

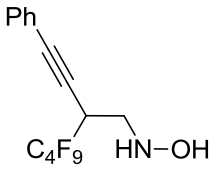
Synthesis of 1p.



1p

57% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (brs, 1H), 6.17 (dd, *J* = 3.8, 1.9 Hz, 1H), 5.54 (brs, 1H), 3.97 – 3.70 (m, 1H), 3.36 (dd, *J* = 13.1, 4.4 Hz, 1H), 3.05 (dd, *J* = 13.1, 9.6 Hz, 1H), 2.17 – 2.05 (m, 4H), 1.69 – 1.51 (m, 4H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.96. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.58, 124.90 (q, *J* = 279.6 Hz), 119.58, 87.84, 77.20, 52.24, 36.09 (q, *J* = 29.8 Hz), 28.97, 25.56, 22.12, 21.34. MS (70 eV): m/z (%): 233 (M^+, 1.79), 46 (100). HRMS calcd for $C_{11}H_{14}NOF_3$: 233.1027, found: 233.1026.

Synthesis of 1q.

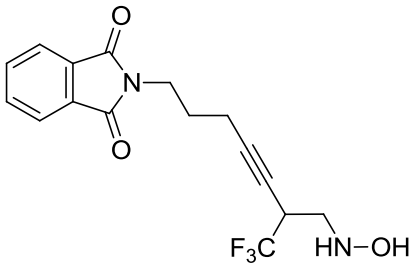


1q

60% isolated yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.3 Hz, 2H), 7.39 – 7.29 (m, 3H), 4.19 – 3.95 (m, 1H), 3.55 (dd, *J* = 13.2, 3.8 Hz, 1H),

3.20 (dd, *J* = 13.0, 10.0 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -80.79 – -81.04 (m, 3F), -113.04 – -117.18 (m, 2F), -120.12 – -122.74 (m, 2F), -124.60 – -127.60 (m, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.90, 128.96, 128.34, 121.75, 119.23-108.28 (m, 4C), 86.93, 79.49 (d, *J* = 10.4 Hz), 51.26, 34.11 (dd, *J* = 26.6, 22.8 Hz). MS (70 eV): m/z (%): 379 (M^+, 2.10), 46 (100). HRMS calcd for $C_{14}H_{10}NOF_9$: 379.0619, found: 379.0617.

Synthesis of 1r.

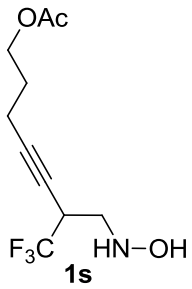


1r

2-(7,7,7-trifluoro-6-((hydroxyamino)methyl)hept-4-yn-1-yl)isoindoline-1,3-dione

47% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.77 (brs, 2H), 3.89 – 3.77 (m, 2H), 3.72 – 3.60 (m, 1H), 3.34 (dd, *J* = 13.1, 4.3 Hz, 1H), 3.01 (dd, *J* = 13.1, 9.9 Hz, 1H), 2.34-2.25 (m, 2H), 1.97-1.88 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -70.11. ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.36, 133.96, 132.00, 124.94 (q, *J* = 279.6 Hz), 123.24, 85.16, 72.29, 52.05, 36.82, 35.69 (q, *J* = 28.8 Hz), 27.20, 16.27. LRMS-ESI[$M+H^+$]: 341.0 (100); HRMS calcd for $C_{16}H_{15}N_2F_3O_3$: 340.1035, found: 340.1036.

Synthesis of 1s.



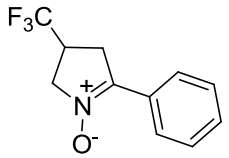
1s

53% isolated yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (brs, 1H), δ 5.60 (brs, 1H), δ 4.15 (t, *J* = 6.3 Hz, 2H), 3.76 – 3.60 (m, 1H), 3.32 (dd, *J* = 13.0, 4.2 Hz, 1H), 3.00 (dd, *J* = 13.0, 9.7 Hz, 1H), 2.31 (t, *J* = 7.0 Hz, 2H), 2.04 (s, 3H), 1.89 – 1.80 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -70.14. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.12, 124.94 (q, *J* = 279.5 Hz), 85.17, 72.06 (q, *J* = 3.5 Hz), 62.83, 52.14, 35.60 (q, *J* = 29.8 Hz), 27.47, 20.84, 15.37. MS (70 eV): m/z (%): 253 (M^+, 2.79), 43 (100). HRMS calcd for $C_{10}H_{14}NO_3F_3$: 253.0926, found: 253.0927.

3. Synthesis of cyclic nitrones 2

The solution of *N*-(2–(perfluoroalkyl)-3-alkynyl)hydroxylamine **1** (0.2 mmol), AgOTf (2.57mg. 5mol %) in 1, 2-dichloroethane (2.0 mL) was stirred at room temperature for 0.5-5 h under argon atmosphere. After complete conversion (monitored by TLC), the solvent was evaporated under reduced pressure and the residue was purified by silica gel flash column chromatography [eluent: Et_2O or EtOAc or dichloromethane: MeOH (*v:v*) = 100:5] to give the desired cyclic nitrone **2**.

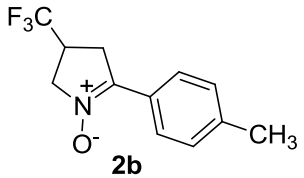
Synthesis of 2a.



2a

95% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.21 (m, 2H), 7.52 – 7.38 (m, 3H), 4.46 – 4.29 (m, 2H), 3.41 (dd, *J* = 18.5, 11.0 Hz, 1H), 3.35-3.19 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.13. ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.07, 130.81, 128.53, 128.19, 127.00, 126.17 (q, *J* = 275.0 Hz), 63.27 (q, *J* = 2.4 Hz), 34.12 (q, *J* = 30.5 Hz), 30.92 (q, *J* = 2.8 Hz). MS (70 eV): m/z (%): 229 (M^+, 100). HRMS calcd for $C_{11}H_{10}F_3NO$: 229.0714, found: 229.0712.

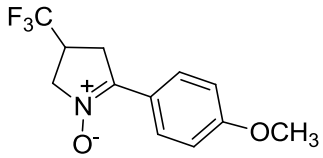
Synthesis of 2b.



2b

2b 84% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 4.55 – 4.24 (m, 2H), 3.42 (dd, *J* = 18.3, 11.0 Hz, 1H), 3.35-3.20 (m, 2H), 2.39 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.08. ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.51, 138.53, 129.26, 127.12, 126.19 (q, *J* = 276.0 Hz), 125.45, 63.05, 34.17 (q, *J* = 30.5 Hz), 30.99 (q, *J* = 2.7 Hz), 21.61. MS (70 eV): m/z (%): 243(M^+, 100). HRMS calcd for $C_{12}H_{12}NOF_3$: 243.0871, found: 243.0872.

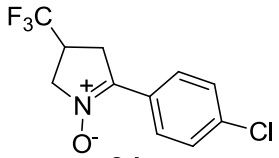
Synthesis of 2c.



2c

97% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.47 – 4.26 (m, 2H), 3.85 (s, 3H), 3.40 (dd, *J* = 18.2, 10.8 Hz, 1H), 3.34 – 3.17 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.08. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.34, 137.96, 129.07, 126.23 (q, *J* = 277.2 Hz), 121.13, 113.89, 62.84, 55.33, 34.20 (q, *J* = 30.5 Hz), 30.98 (q, *J* = 2.9 Hz). MS (70 eV): m/z (%): 259 (M^+, 100). HRMS calcd for $C_{12}H_{12}NO_2F_3$: 259.0820, found: 259.0818.

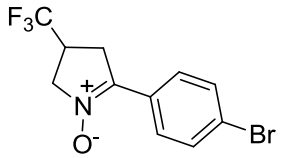
Synthesis of 2d.



2d

82% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 4.50 – 4.25 (m, 2H), 3.41 (dd, *J* = 18.4, 11.0 Hz, 1H), 3.36 – 3.21 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.12. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.26, 136.53, 128.84, 128.28, 126.63, 126.10 (q, *J* = 277.0 Hz), 63.29, 34.09 (q, *J* = 30.6 Hz), 30.85 (q, *J* = 2.8 Hz). MS (70 eV): m/z (%): 263(M^+, 100), 265 (M^+ + 2, 32.19). HRMS calcd for $C_{11}H_9NOF_3Cl$: 263.0321, found: 263.0325.

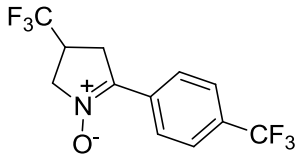
Synthesis of 2e.



2e

87% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 4.48 – 4.27 (m, 2H), 3.42 (dd, *J* = 18.1, 10.9 Hz, 1H), 3.36 – 3.22 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.10. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.35, 131.82, 128.41, 127.02, 126.09 (q, *J* = 278.0 Hz), 125.00, 63.35, 34.09 (q, *J* = 30.6 Hz), 30.80 (q, *J* = 2.8 Hz). MS (70 eV): m/z (%): 307 (M^+, 100), 309 (M^+ + 2, 99.70). HRMS calcd for $C_{11}H_9NOF_3Br$: 306.9820, found: 306.9824

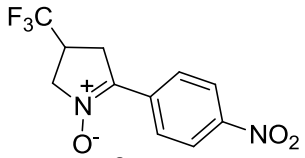
Synthesis of 2f.



2f

2f 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 4.63 – 4.28 (m, 2H), 3.47 (dd, *J* = 18.5, 11.0 Hz, 1H), 3.40 – 3.25 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.07, -73.21. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.87, 131.99 (q, *J* = 32.7 Hz), 131.31, 127.11, 126.07 (q, *J* = 276.0 Hz), 125.49 (q, *J* = 3.8 Hz), 123.60 (q, *J* = 271.0 Hz), 63.66, 34.20 (q, *J* = 30.7 Hz), 30.86 (q, *J* = 2.8 Hz). MS (70 eV): m/z (%): 297(M^+, 100). HRMS calcd for $C_{12}H_9NF_6O$: 297.0588, found: 297.0587.

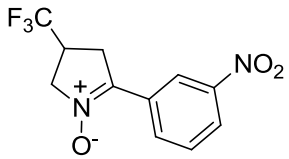
Synthesis of 2g.



2g

98% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 9.1 Hz, 2H), 8.27 (d, *J* = 9.1 Hz, 2H), 4.55-4.37 (m, 2 H), 3.52 (dd, *J* = 18.5, 11.1 Hz, 1H), 3.46 – 3.30 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.16. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.01, 136.38, 133.65, 127.55, 125.97 (q, *J* = 277.4 Hz), 123.78, 63.88, 34.12 (q, *J* = 30.7 Hz), 30.82 (q, *J* = 2.8 Hz). MS (70 eV): m/z (%): 274 (M^+,100). HRMS calcd for $C_{11}H_9N_2O_3F_3$: 274.0565, found: 274.0561.

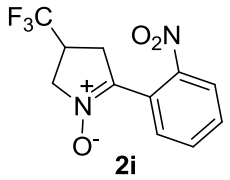
Synthesis of 2h.



2h

85% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.79 (d, *J* = 7.8 Hz, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 8.1 Hz, 1H), 4.56 – 4.37 (m, 2H), 3.53 (dd, *J* = 18.3, 10.9 Hz, 1H), 3.46 – 3.32 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.93. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.25, 136.11, 132.23, 129.81, 129.76, 126.03 (q, *J* = 276.0 Hz), 125.00, 121.58, 63.75, 34.21 (q, *J* = 26.4 Hz), 30.85. MS (70 eV): m/z (%): 274 (M^+, 100), HRMS calcd for $C_{11}H_9N_2O_3F_3$: 274.0565, found: 274.0563.

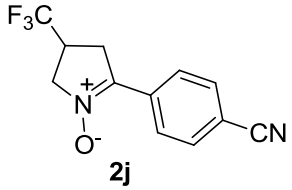
Synthesis of 2i.



2i

90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.72 (td, *J* = 7.6, 1.2 Hz, 1H), 7.61 (td, *J* = 8.1, 1.4 Hz, 1H), 7.53 (dd, *J* = 7.7, 1.3 Hz, 1H), 4.42 – 4.33 (m, 1H), 4.32 – 4.24 (m, 1H), 3.50 – 3.37 (m, 2H), 3.34 – 3.23 (m, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.22. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.17, 136.77, 133.44, 130.93, 129.57, 125.00, 123.39, 126.05 (q, *J* = 275.0 Hz), 61.93 (q, *J* = 2.5 Hz), 35.19 (q, *J* = 30.7 Hz), 31.93 (q, *J* = 2.9 Hz). MS (70 eV): m/z (%): 274 (M^+, 13.95), 104 (100). HRMS calcd for $C_{11}H_9N_2O_3F_3$: 274.0565, found: 274.0555.

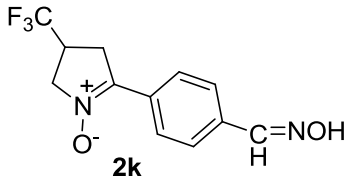
Synthesis of 2j.



2j

96% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 4.53 – 4.34 (m, 2H), 3.47 (dd, *J* = 18.4, 11.0 Hz, 1H), 3.40-3.28 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.18. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.50, 132.26, 131.95, 127.08, 126.00 (q, *J* = 276.0 Hz), 118.20, 113.58, 63.81 (q, *J* = 2.5 Hz), 34.13 (q, *J* = 30.7 Hz), 30.68 (q, *J* = 2.9 Hz). MS (70 eV): m/z (%): 254 (M^+, 100). HRMS calcd for $C_{12}H_9N_2F_3O$: 254.0667, found: 254.0668.

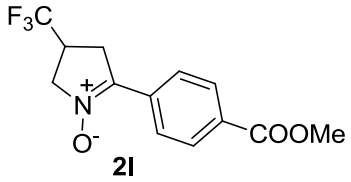
Synthesis of 2k.



2k

77% isolated yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.43 (s, 1H), 8.38 (d, *J* = 8.5 Hz, 2H), 8.17 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 4.48 (dd, *J* = 14.7, 9.7 Hz, 1H), 4.18 (dd, *J* = 14.7, 5.1 Hz, 1H), 3.75-3.61 (m, 1H), 3.55 (dd, *J* = 17.5, 9.9 Hz, 1H), 3.28 (dd, *J* = 17.5, 3.9 Hz, 1H). ^{19}F NMR (377 MHz, d_6-DMSO) δ -73.44. ^{13}C NMR (100 MHz, d_6-DMSO) δ 148.10, 137.12, 135.00, 129.59, 127.51 (q, *J* = 276.0 Hz), 127.47, 126.74, 63.77, 33.74 (q, *J* = 29.2 Hz), 30.6. MS (70 eV): m/z (%): 272 (M^+, 5.13), 66 (100). HRMS calcd for $C_{12}H_{11}N_2O_2F_3$: 272.0773, found: 272.0774.

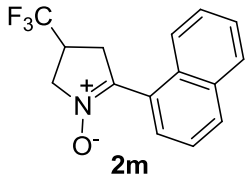
Synthesis of 2l.



2l

96% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.6 Hz, 2H), 8.10 (d, *J* = 8.6 Hz, 2H), 4.54 – 4.31 (m, 2H), 3.93 (s, 3H), 3.48 (dd, *J* = 18.4, 10.9 Hz, 1H), 3.41 – 3.27 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.10. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.21, 137.36, 131.97, 131.59, 129.73, 126.10 (q, *J* = 275.0 Hz), 126.77, 63.66 (q, *J* = 2.4 Hz), 52.31, 34.22 (q, *J* = 30.6 Hz), 30.92 (q, *J* = 2.7 Hz). MS (70 eV): m/z(%): 287 (M^+, 0.85), 175 (100). HRMS calcd for $C_{13}H_{12}NO_3F_3$: 287.0769, found: 287.0768.

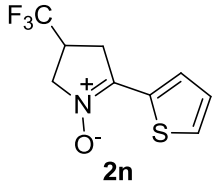
Synthesis of 2m.



2m

92% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.81 (m, 2H), 7.80 – 7.41 (m, 5H), 4.67 – 4.32 (m, 2H), 3.62 – 3.21 (m, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.43. ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.88, 133.62, 131.02, 129.35, 128.71, 126.97, 126.77, 126.52, 126.24 (q, *J* = 278 Hz), 126.19, 125.49, 124.92, 62.26, 35.12 (q, *J* = 30.4 Hz), 33.98. MS (70 eV): m/z(%): 279 (M^+, 0.77), 262 (100). HRMS calcd for $C_{15}H_{12}NOF_3$: 279.087, found: 279.0873.

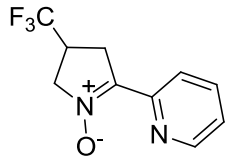
Synthesis of 2n.



2n

95% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 5.0 Hz, 1H), 7.31 (d, *J* = 3.7 Hz, 1H), 7.13 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.44 – 4.21 (m, 2H), 3.52 – 3.20 (m, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.98. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.14, 129.69, 129.31, 128.35, 126.53, 126.07 (q, *J* = 276.0 Hz), 35.12 (q, *J* = 30.6 Hz), 29.97 (q, *J* = 2.9 Hz). MS (70 eV): m/z (%): 235 (M^+, 100). HRMS calcd for $C_9H_8NF_3OS$: 235.0279, found: 235.0278.

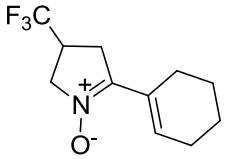
Synthesis of 2o.



2o

94% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 4.3 Hz, 1H), 7.80 (t, *J* = 7.4 Hz, 1H), 7.34 – 7.27 (m, 1H), 4.53 – 4.33 (m, 2H), 3.64 (dd, *J* = 18.8, 9.9 Hz, 1H), 3.52 (dd, *J* = 18.8, 4.7 Hz, 1H), 3.36 – 3.19 (m, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.21. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.37, 147.29, 140.49, 136.63, 126.27 (q, *J* = 277.2 Hz), 124.73, 123.16, 64.19 (q, *J* = 2.4 Hz), 34.15 (q, *J* = 30.5 Hz), 30.89 (q, *J* = 2.8 Hz). MS (70 eV): m/z (%): 230 (M^+, 72.12), 144 (100). HRMS calcd for $C_{10}H_9N_2F_3O$: 230.0667, found: 230.0665.

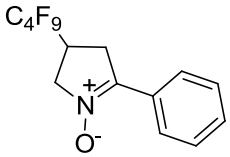
Synthesis of 2p.



2p

92% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 4.34 – 4.15 (m, 2H), 3.20-3.08 (m, 2H), 2.96 (d, *J* = 12.7 Hz, 1H), 2.43 – 2.32 (m, 2H), 2.25 (s, 2H), 1.80-1.65 (m, 2H), 1.65 – 1.57 (m, 2H).^{19}F NMR (377 MHz, $CDCl_3$) δ -73.14. ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.19, 135.45, 127.39, 126.19 (q, *J* = 275.0 Hz), 62.62 (q, *J* = 2.4 Hz), 34.15 (q, *J* = 30.4 Hz), 30.96 (q, *J* = 2.8 Hz), 26.33, 25.94, 22.28, 21.21. MS (70 eV): m/z (%): 233 (M^+, 98.57), 148 (100). HRMS calcd for $C_{11}H_{14}NOF_3$: 233.1027, found: 233.1029.

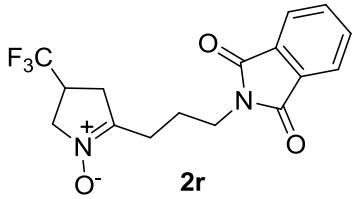
Synthesis of 2q.



2q

95% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.24 (m, 2H), 7.50 – 7.39 (m, 3H), 4.56-4.43 (m, 1H), 4.38 – 4.28 (m, 1H), 3.53 – 3.33 (m, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -80.74 – -81.20 (m, 3F), -118.67 – -118.80 (m, 1F), -118.80 – -118.95 (m, 1F), -122.56 – -122.61 (m, 1F), -122.67 – -122.79 (m, 1F), -126.08 (t, *J* = 13.9 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.98, 130.90, 128.59, 128.18, 127.06, 119.46-105.69(m, 4C), 62.85, 32.88 (t, *J* = 23.1 Hz), 30.43. MS (70 eV): m/z (%): 379 (M^+, 87.88), 378 (100). HRMS calcd for $C_{14}H_{10}NOF_9$: 379.0619, found: 379.0616.

Synthesis of 2r.

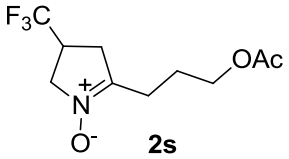


2r

93% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 2H), 7.71 – 7.65 (m, 2H), 4.25 – 4.03 (m, 2H), 3.68 (t, *J* = 7.2 Hz, 2H), 3.30 – 3.11 (m, 1H), 3.04 (dd, *J* = 18.6, 9.7 Hz, 1H), 2.91 (d, *J* = 18.6 Hz, 1H), 2.54 (t, *J* = 7.7 Hz, 2H), 2.01 – 1.84 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.35. ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.12, 144.03, 133.98, 131.89, 126.09 (q, *J* = 277.2 Hz), 123.20, 61.07, 37.14, 34.52 (q, *J* = 30.4 Hz), 31.29 (q, *J* = 2.8 Hz), 23.80, 23.57. MS (70 eV): m/z (%): 340 (M^+, 2.90),

151 (100). HRMS calcd for $C_{16}H_{15}N_2F_3O_3$: 340.1035, found: 340.1038.

Synthesis of 2s.



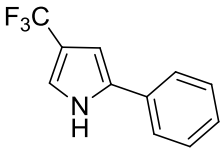
2s

89% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 – 4.11 (m, 2H), 4.07 (t, *J* = 6.4 Hz, 2H), 3.28 – 3.11 (m, 1H), 3.00 (dd, *J* = 18.7, 9.6 Hz, 1H), 2.88 (d, *J* = 18.7 Hz, 1H), 2.62 – 2.49 (m, 2H), 2.02 (s, 3H), 1.93 – 1.82 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.40. ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.92, 144.44, 126.09 (q, *J* = 277.2 Hz), 63.45, 61.09 (q, *J* = 2.5 Hz), 34.57 (q, *J* = 30.5 Hz), 31.49 (q, *J* = 2.8 Hz), 23.93, 23.16, 20.83. MS (70 eV): m/z (%): 253 (M^+, 6.01), 43 (100). HRMS calcd for $C_{10}H_{14}NO_3F_3$: 253.0926, found: 253.0927.

4. Synthesis of pyrroles 3.

The solution of *N*-(2–(perfluoroalkyl)-3-alkynyl)hydroxylamine **1** (0.2 mmol), $IPrAuNTf_2$ (8.7 mg. 5 mol %) and $HNTf_2$ (10 or 40 mol %) in DMF (2.0 mL) was stirred at room temperature for 10-21 h under argon atmosphere. After complete conversion (monitored by TLC), the solvent was removed under reduced pressure and the crude reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane 1:2 ~ 5:1) to give the desired pyrrole **3**.

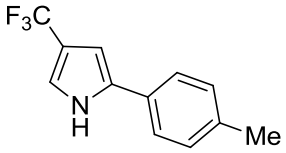
Synthesis of 3a.



3a

87% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (brs, 1H), 7.47 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.41 (dd, *J* = 10.4, 5.0 Hz, 2H), 7.33 – 7.27 (m, 1H), 7.15 (s, 1H), 6.67 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.59. ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.40, 131.44, 129.08, 127.37, 124.24, 123.75 (q, *J* = 264.0 Hz), 118.08 (q, *J* = 5.0 Hz), 116.66 (q, *J* = 37.0 Hz). 103.32 (q, *J* = 2.8 Hz). MS (70 eV): m/z (%): 211(M^+, 100). HRMS calcd for $C_{11}H_8F_3N$: 211.0609, found: 211.0608.

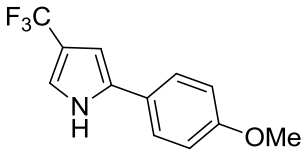
Synthesis of 3b.



3b

86% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (brs, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.11 (m, 1H), 6.61 (s, 1H), 2.37 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.60. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.25, 133.56, 129.74, 128.73, 124.21, 123.80 (q, *J* = 264.0 Hz), 117.70 (q, *J* = 5.1 Hz), 116.56 (q, *J* = 36.9 Hz), 102.80 (q, *J* = 2.7 Hz), 21.12. MS (70 eV): m/z (%): 225 (M^+, 100). HRMS calcd for $C_{12}H_{10}NF_3$: 225.0765, found: 225.0766.

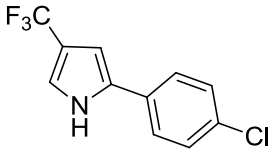
Synthesis of 3c.



3c

86% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (brs, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.11 (s, 1H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.54 (s, 1H), 3.84 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.59. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.06, 133.44, 125.72, 124.45, 123.83 (q, *J* = 264.0 Hz), 117.48 (q, *J* = 5.1 Hz), 116.49 (q, *J* = 36.9 Hz), 114.52, 102.30 (q, *J* = 2.6 Hz), 55.36. MS (70 eV): m/z (%): 241 (M^+, 100). HRMS calcd for $C_{12}H_{10}NF_3O$: 241.0714, found: 241.0716.

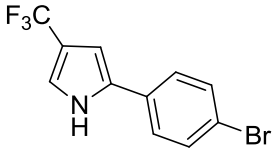
Synthesis of 3d.



3d

90%isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (brs, 1H), 7.38 (d, *J* = 8.0, 4H), 7.18 – 7.14 (m, 1H), 6.64 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.73. ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.13, 132.30, 129.98, 129.28, 125.48, 123.60 (q, *J* = 266.0 Hz), 118.42 (q, *J* = 5.0 Hz), 116.91 (q, *J* = 37.1 Hz), 103.78 (q, *J* = 2.8 Hz). MS (70 V): m/z (%): 245 (M^+, 100), 247 (M^+ + 2, 32.32). HRMS calcd for $C_{11}H_7NF_3Cl$: 245.0219, found: 245.0218

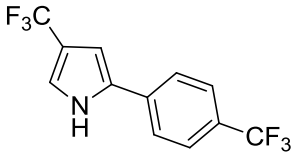
Synthesis of 3e.



3e

90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (brs, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.33 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.16 (s, 1H), 6.65 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.69. ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.29, 132.20, 130.39, 125.73, 123.59 (q, *J* = 266.1 Hz), 121.11, 118.49 (q, *J* = 5.0 Hz), 116.91 (q, *J* = 37.2 Hz), 103.82 (q, *J* = 2.7 Hz). MS (70 eV): m/z (%): 289 (M^+, 98.86), 291 (M^+ + 2, 100). HRMS calcd for $C_{11}H_7NF_3Br$: 288.9714, found: 288.9715.

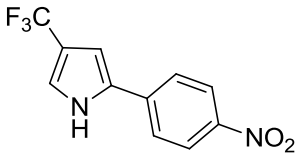
Synthesis of 3f.



3f

84% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (brs, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.16 (m, 1H), 6.76 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.58, -57.75. ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.64, 131.84, 129.12 (q, *J* = 32.7 Hz), 126.12 (q, *J* = 3.8 Hz), 124.16, 124.04 (q, *J* = 270.0 Hz), 123.52 (q, *J* = 265.0 Hz), 119.18 (q, *J* = 4.9 Hz), 117.12 (q, *J* = 37.2 Hz), 104.87 (q, *J* = 2.7 Hz). MS (70 eV): m/z (%): 279 (M^+, 100). HRMS calcd for $C_{12}H_7NF_6$: 279.0483, found: 279.0484.

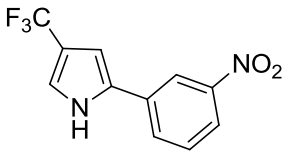
Synthesis of 3g.



3g

86% isolated yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.36 (s, 1H), 8.24 (d, J = 8.7 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.59 (s, 1H), 7.16 (s, 1H).^{19}F NMR (377 MHz, d_6-DMSO) δ -55.45. ^{13}C NMR (100 MHz, d_6-DMSO) δ 145.84, 138.25, 131.33, 124.86, 124.78, 124.49 (q, J = 264.0 Hz) 122.33, 115.22 (q, J = 36.2 Hz), 106.88. MS (70 eV): m/z (%): 256 (M^+, 100). HRMS calcd for $C_{11}H_7N_2F_3O_2$: 256.0460, found: 256.0462.

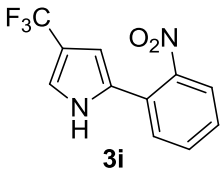
Synthesis of 3h.



3h

89% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (brs, 1H), 8.33 (t, J = 1.9 Hz, 1H), 8.14-8.09 (m, 1H), 7.85 – 7.77 (m, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.29 – 7.21 (m, 1H), 6.80 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.80. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.79, 133.11, 130.84, 130.16, 130.02, 123.38 (q, J = 266.2 Hz), 121.72, 119.56 (q, J = 4.8 Hz), 118.54, 117.23 (q, J = 37.4 Hz), 105.22 (q, J = 2.8 Hz). MS (70 eV): m/z (%): 256 (M^+, 95.76), 151 (100). HRMS calcd for $C_{11}H_7N_2F_3O_2$: 256.0460, found: 256.0461.

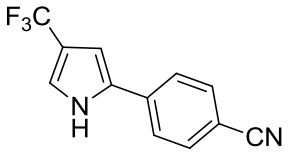
Synthesis of 3i.



3i

94% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 7.82 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.50 – 7.43 (m, 1H), 7.23 – 7.17 (m, 1H), 6.61 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$). δ -57.49. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.39, 132.80, 131.61, 128.49, 127.67, 125.86, 124.66, 123.48 (q, *J* = 264.0 Hz), 119.35 (q, *J* = 4.7 Hz), 116.35 (q, *J* = 37.2 Hz), 108.36. MS (70 eV): m/z (%): 256 (M^+, 100), HRMS calcd for $C_{11}H_7N_2F_3O_2$: 256.0460, found: 256.0456.

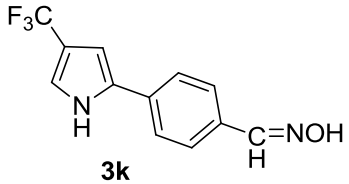
Synthesis of 3j.



3j

91% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.25 (s, 1H), 6.80 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.86, ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.53, 132.95, 131.29, 123.34 (q, *J* = 264.0 Hz), 124.31, 119.86 (q, *J* = 4.8 Hz), 118.69, 117.27, 110.32, 105.80 (q, *J* = 2.7 Hz). MS (70 eV): m/z (%): 236 (M^+, 100). HRMS calcd for $C_{12}H_7N_2F_3$: 236.0561, found: 236.0563.

Synthesis of 3k.

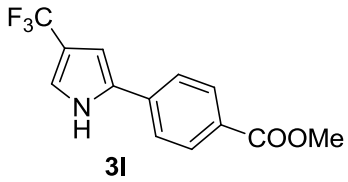


3k

68% isolated yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.03 (s, 1H), 11.22 (s, 1H), 8.13 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H),

7.43 (s, 1H), 6.88 (s, 1H). ^{19}F NMR (377 MHz, d_6-DMSO) δ -55.25. ^{13}C NMR (100 MHz, d_6-DMSO) δ 148.26, 133.00, 132.70, 131.78, 127.37, 124.76 (q, J = 264.0 Hz), 124.64, 120.31 (q, J = 4.9 Hz), 114.56 (q, J = 36.1 Hz), 103.87. MS (70 eV): m/z (%): 254 (M^+, 54.51), 66 (100). HRMS calcd for $C_{12}H_9N_2OF_3$: 254.0667, found: 254.0662.

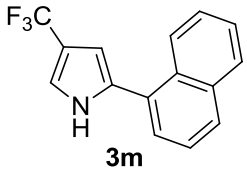
Synthesis of 3l.



3l

90% isolated yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.18 (s, 1H), 7.96 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.5 Hz, 2H), 7.49 (s, 1H), 7.00 (s, 1H), 3.85 (s, 3H). ^{19}F NMR (377 MHz, d_6-DMSO) δ -55.39, ^{13}C NMR (100 MHz, d_6-DMSO) δ 166.38, 136.36, 132.27, 130.26, 127.79, 124.63 (q, J = 264.0 Hz), 124.31, 121.20 (q, J = 4.8 Hz), 114.86 (q, J = 36.2 Hz), 105.27 (d, J = 2.6 Hz), 52.44 (d, J = 1.4 Hz). MS (70 eV): m/z (%): 269 (M^+, 84.89), 238 (100). HRMS calcd for $C_{13}H_{10}NF_3O_2$: 269.0664, found: 269.0666.

Synthesis of 3m.

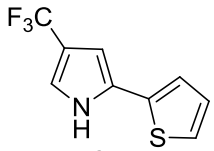


3m

90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (brs, 1H), 8.20 – 8.10 (m, 1H), 7.95 – 7.90 (m, 1H), 7.88 (dd, J = 7.4, 1.8 Hz, 1H), 7.60 – 7.42 (m, 4H), 7.26 – 7.24 (m, 1H), 6.67 (s, 1H). ^{19}F NMR (377 MHz,

$CDCl_3$) δ -57.20. ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.93, 131.77, 131.37, 129.96, 128.57, 128.55, 126.79, 126.77, 126.23, 125.33, 125.16, 123.92 (q, *J* = 264.0 Hz), 117.79 (q, *J* = 5.0 Hz), 116.13 (q, *J* = 37.0 Hz), 106.74 (q, *J* = 2.7 Hz). MS (70 eV): m/z (%): 261 (M^+, 100). HRMS calcd for $C_{15}H_{10}NF_3$: 261.0765, found: 261.0767.

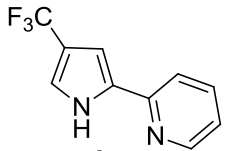
Synthesis of 3n.



3n

90% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (brs, 1H), 7.24 (d, *J* = 5.0 Hz, 1H), 7.09 (dd, *J* = 4.4, 2.6 Hz, 2H), 7.05 (dd, *J* = 4.9, 3.7 Hz, 1H), 6.57 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.61. ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.30, 127.82, 127.79, 124.03, 123.57 (q, *J* = 264.0 Hz), 122.39, 117.84 (q, *J* = 5.0 Hz), 116.50 (q, *J* = 37.2 Hz), 103.95 (q, *J* = 2.7 Hz). MS (70 eV): m/z (%): 217 (M^+, 100). HRMS calcd for $C_9H_6NF_3S$: 217.0173, found: 217.0172.

Synthesis of 3o.

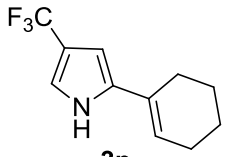


3o

70% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ 10.24 (brs, 1H), 8.48 (d, *J* = 4.7 Hz, 1H), 7.69 (td, *J* = 7.8, 1.6 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.18 (s, 1H), 7.14 (dd, *J* = 6.9, 5.4 Hz, 1H), 6.86 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.45. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.50, 148.73,

137.04, 132.49, 123.67 (q, J = 265.9 Hz), 121.63, 119.17, 118.68 (q, J = 2.1 Hz), 116.57 (q, J = 36.8 Hz), 104.52 (q, J = 2.6 Hz). MS (70 eV): m/z (%): 212 (M^+, 100), HRMS calcd for $C_{10}H_7N_2F_3$: 212.0561, found: 212.0560.

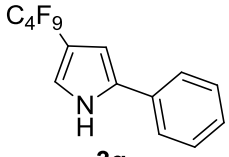
Synthesis of 3p.



3p

70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (brs, 1H), 7.04 – 6.93 (m, 1H), 6.29 (s, 1H), 5.98 – 5.84 (m, 1H), 2.35-2.28 (m, 2H), 2.22-2.15 (m, 2H), 1.80 – 1.71 (m, 2H), 1.69 – 1.61 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$). δ -57.56. ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.00, 128.16, 123.94 (q, J = 265.8 Hz), 120.74, 116.86 (q, J = 5.0 Hz), 115.54 (q, J = 36.7 Hz), 101.69 (q, J = 2.7 Hz), 25.97, 25.19, 22.40, 22.10. MS (70 eV): m/z (%): 215 (M^+, 72.87), 84 (100). HRMS calcd for $C_{11}H_{12}NF_3$: 215.0922, found: 215.0923.

Synthesis of 3q.

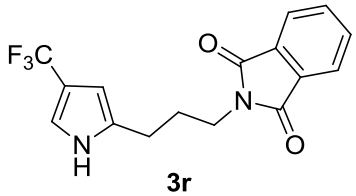


3q

87% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.48 (dd, J = 8.2, 1.1 Hz, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 7.14 (dd, J = 2.7, 1.3 Hz, 1H), 6.66 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.10 (t, J = 9.7 Hz, 3F), -105.25 (t, J = 12.8 Hz, 2F), -123.20—123.35

(m, 2F), -124.26 – -126.44 (m, 2F).^{13}C NMR (100 MHz, $CDCl_3$) δ 133.54, 131.40, 129.09, 127.39, 124.24, 119.43 (t, *J* = 7.5 Hz), 119.05-115.26 (m, 2C), 114.54 (t, *J* = 28.2 Hz), 113.47-110.04 (m, 2C), 104.46. MS (70 eV): m/z (%): 361 (M^+, 44.97), 192 (100). HRMS calcd for $C_{14}H_8NF_9$: 361.0513, found: 361.0511.

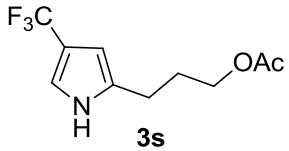
Synthesis of 3r.



3r

63% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (brs, 1H), 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.04 – 6.96 (m, 1H), 6.10 (s, 1H), 3.77 – 3.71 (m, 2H), 2.63 – 2.53 (m, 2H), 2.02-1.93 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.16. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.06, 134.22, 132.60, 131.82, 124.03 (q, *J* = 246.0 Hz), 123.34, 116.39 (q, *J* = 5.1 Hz), 114.81 (q, *J* = 36.4 Hz), 103.28 (q, *J* = 2.6 Hz), 36.91, 29.15, 23.97. MS (70 eV): m/z (%): 322 (M^+, 39.30), 66 (100). HRMS calcd for $C_{16}H_{13}N_2O_2F_3$: 322.0929, found: 322.0927.

Synthesis of 3s.



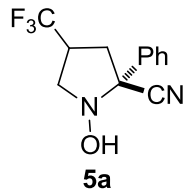
3s

54% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (brs, 1H), 6.97 – 6.96 (m, 1H), 6.10 (s, 1H), 4.14 (t, *J* = 6.2 Hz, 2H), 2.65 (t, *J* = 7.3 Hz, 2H), 2.08 (s, 3H), 1.98 – 1.90 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ

-57.28. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.63, 132.57, 123.96 (q, *J* = 265.6 Hz), 116.36 (q, *J* = 5.1 Hz), 114.97 (q, *J* = 36.7 Hz), 103.19 (q, *J* = 2.7 Hz), 63.36, 28.74, 23.65, 20.96. MS (70 eV): m/z (%): 235 (M^+, 20.67), 148 (100). HRMS calcd for $C_{10}H_{12}NO_2F_3$: 235.0820, found: 235.0819.

5. Synthesis of 5a and 5a'.

To a solution of nitrone **2a** (0.23 g, 1.0 mmol) in THF (10 mL) was added dropwise a 2.0 M solution of Et_2AlCl in hexanes (0.5 mL, 1.0 mmol). The resulting mixture was stirred for 5 min at ambient temperature and then cooled to -20 ℃. Trimethylsilyl cyanide (0.38ml, 3.0 mmol) was then added dropwise to this cold reaction mixture. After stirring for 2 h at this temperature, the solvent was rotatory evaporated. The residue was taken up into 5% methanolic citric acid (10 mL) and the resulting mixture was stirred for 1 h, saturated aqueous sodium bicarbonate (25 mL) was then added. The reaction mixture was extracted with dichloromethane (3x15 mL) and the combined organic extracts were dried ($MgSO_4$). After filtration and evaporation, the residue was urified by flash column chromatography on silica gel [eluent: petroleum ether:ethyl acetate=10:1] to give **5a** (73% yield) and its diastereoisomer **5a'**(5 % yield).



5a

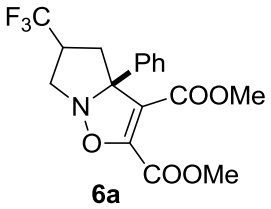
The major isomer, **5a** 73% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.48 – 7.36 (m, 3H), 5.18 (s, 1H), 3.65 (dd, *J* = 11.0,

2.7 Hz, 1H), 3.43 (t, *J* = 10.7 Hz, 1H), 3.24 – 3.03 (m, 1H), 2.72 (dd, *J* = 14.1, 9.8 Hz, 1H), 2.22 (dd, *J* = 14.1, 8.0 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.19. ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.03, 129.50, 129.11 126.66 (q, *J* = 276 Hz), 126.21, 117.14, 72.69, 53.33 (q, *J* = 2.4 Hz), 37.83 (q, *J* = 2.5 Hz), 36.65 (q, *J* = 30.1 Hz). MS (70 eV): m/z (%): 256 (M^+, 65.0), 229 (100). HRMS-ESI calcd for $C_{12}H_{12}F_3N_2O$ [$M+H^+$]: 257.0896, found: 257.0909.

The minor isomer, **5a'** 5% isolated yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.50-7.35(m, 3H), 5.09 (brs, 1H), 3.72 (dd, *J* = 9.8, 8.0 Hz, 1H), 3.45 (t, *J* = 10.0 Hz, 1H), 3.20 – 2.96 (m, 1H), 2.73 (dd, *J* = 14.7, 5.0 Hz, 1H), 2.35 (dd, *J* = 14.7, 11.4 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -70.77. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.09, 129.39, 129.13, 126.18, 126.16 (q, *J* =275.0 Hz), 117.15, 71.74, 54.26 (q, *J* = 2.5 Hz), 37.72, 36.52 (q, *J* = 30.5 Hz). MS (70 eV): m/z (%): 256 (M^+, 36.0), 229 (100). HRMS-ESI calcd for $C_{12}H_{12}F_3N_2O$ [$M+H^+$]: 257.0896, found: 257.0906.

6. Synthesis of 6a and 6a'.

The solution of nitrone **2a** (114 mg, 0.5 mmol) and dimethyl acetylenedicarboxylate (DMAD) (0.09 mL, 1.5 mmol) in dichloromethane (6.5 mL) was stirred at ambient temperature for 12 h under argon atmosphere. After complete conversion (monitored by TLC), the solvent was evaporated under reduced pressure and the crude reaction mixture was directly purified by silica gel flash column chromatography [eluent: petroleum ether : ethyl acetate = 20:1] to give the desired **6a** and its diastereoisomer **6a'**.



6a

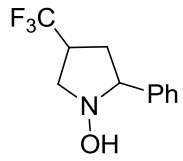
The major isomer **6a**, 52% isolated yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.39-7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 3.98 (dd, *J* = 9.5, 5.9 Hz, 1H), 3.89 (s, 3H), 3.73 (s, 3H), 3.34 – 3.28 (m, 1H), 2.99 – 2.85 (m, 2H), 2.84 – 2.76 (m, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.88. ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.57, 159.25, 150.23, 142.69, 128.56, 127.91, 126.0 (q, *J* = 275.0 Hz), 125.76, 112.61, 79.82, 56.90 53.29, 52.06, 39.22 (q, *J* = 30.1 Hz), 35.84. MS (70 eV): m/z (%): 371 (M^+, 86.81), 216 (100). HRMS-ESI calcd for $C_{17}H_{16}F_3NNaO_5$ [M+Na^+]: 394.0873, found: 394.0883.

The minor isomer **6a'**, 24% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.40-7.34 (m, 2H), 7.32 – 7.27 (m, 1H), 3.90 (s, 3H), 3.80 (ddd, *J* = 14.4, 6.7, 1.9 Hz, 1H), 3.64 (s, 3H), 3.42 (dd, *J* = 14.4, 11.1 Hz, 1H), 3.27 (ddd, *J* = 12.8, 6.6, 1.8 Hz, 1H), 3.23-3.10 (m, 1H), 2.48 (t, *J* = 12.1 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -68.97. ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.12, 159.05, 152.03, 141.77, 128.29, 127.98, 126.67, 126.16 (q, *J* = 276.0 Hz), 110.57, 83.50, 58.73 (q, *J* = 2.1 Hz), 53.34, 51.87, 42.39 (q, *J* = 28.7 Hz), 36.33. MS (70 eV): m/z (%): 371 (M^+, 86.81), 216 (100). HRMS-ESI calcd for $C_{17}H_{16}F_3NNaO_5$ [M+Na^+]: 394.0873, found: 394.0888.

7. Synthesis of 7a.

To a solution of nitrone **2a** (230mg, 1.0 mmol) in THF (10 mL) at 0℃was added $LiAlH_4$ (190mg, 5.0 mmol). After stirring at 0 ℃ for 15 mins, the

reaction was warmed up to room temperature and was stirred for additional 5 h under argon atmosphere. After complete conversion (monitored by TLC), the reaction was cooled to 0 ℃ and quenched with saturated NH_4Cl (8.0 mL).The reaction mixture was extracted with dichloromethane (3x15 mL) and the combined organic extracts were dried over $MgSO_4$. After filtration and evaporation, the residue was purified by flash column chromatography on silica gel to afford **7a** (162 mg) in 70% isolated yield. [Eluent: petroleum ether : ethyl acetate = 10:1].



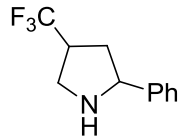
7a

7a 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 6.34 (brs, 1H), 3.80 (dd, *J* = 11.1, 7.2 Hz, 1H), 3.29 (dd, *J* = 7.6, 2.7 Hz, 1H), 3.05 – 2.82 (m, 2H), 2.39 (ddd, *J* = 13.6, 9.7, 7.3 Hz, 1H), 2.00 – 1.85 (m, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.88. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.26, 128.52, 127.98, 127.68, 127.32 (q, *J* = 275.0 Hz), 71.95, 56.01, 37.92 (q, *J* = 30.4 Hz), 30.38. MS (70 eV): m/z (%): 231 (M^+, 100). HRMS-ESI calcd for $C_{11}H_{13}F_3NO$ [$M+H^+$]: 232.0944, found: 232.0968.

8. Synthesis of compound 8a.

A mixture of 125 mg (0.54 mmol) of compound **7a** and 700mg (10.8 mmol) of zinc powder in MeOH /AcOH(v: v = 1:1 6.0 mL) was vigorously stirred for 3 h at 60℃ under nitrogen atmosphere. The reaction mixture was neutralized with solid Na_2CO_3, followed by filtration, concentration, and the residue was purified by column chromatography on silica gel (DCM/MeOH/NH_4OH = 100:1:0.5) to give the corresponding product **8a**

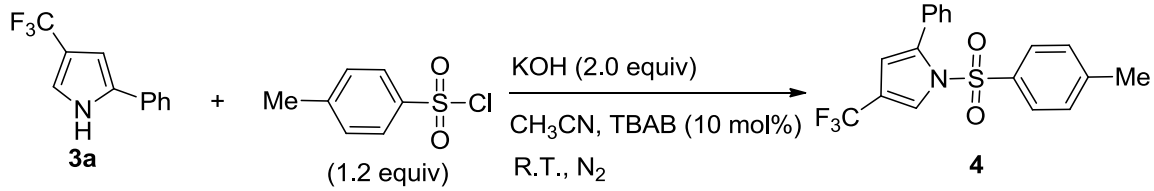
(94 mg) in 81% isolated yield.



8a

8a 81% isolated yield.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.32 (m, 4H), 7.28 (t, *J* = 7.1 Hz, 1H), 4.13 (dd, *J* = 10.2, 6.4 Hz, 1H), 3.39 (dd, *J* = 11.8, 4.2 Hz, 1H), 3.26 – 3.14 (m, 1H), 3.01-2.90 (m, 1H), 2.52 – 2.39 (m, 1H), 1.89 (s, 1H), 1.86 – 1.78 (m, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.87. ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.69, 128.56, 128.0 (q, *J* = 277.2 Hz), 127.50, 126.51, 63.34, 47.01 (q, *J* = 2.6 Hz), 43.45 (q, *J* = 27.1 Hz), 34.78. MS (70 eV): m/z (%): 214(M-H^+, 25.7), 94(100). HRMS-ESI calcd for $C_{11}H_{13}NF_3$ [M+H^+]: 216.0995, found: 216.0992.

9. Synthesis of pyrrole 3a derivative 4



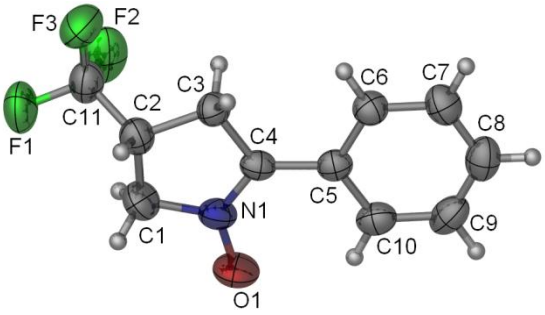
To a solution of **3a**(80mg, 0.38mmol) in CH_3CN (1.0 mL), KOH(42.6mg, 0.76mmol) and TBAB(12.3mg, 10 mol%) were added at room temperature under N_2 atmosphere, and the mixture was stirred for 1h at room temperature, then 4-methylbenzene-1-sulfonyl chloride (87mg, 0.46 mmol) was added . the mixture was allowed to react under room temperature for another 1h. And the solvent was then evaporated under vacuum. The residue was purified by column chromatography on silica gel eluting using hexane / DCM = 3 : 1 mixture as eluent to afford 2-phenyl-1-tosyl-4-(trifluoromethyl)-1H-pyrrole **4** 115mg in 83% isolated yield.

4 83% isolated yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.20 – 7.16 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.30 (d, *J* = 1.5 Hz, 1H), 2.38 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -59.05. ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.63, 136.43, 134.47, 131.11, 129.84, 129.61, 128.98, 127.54, 127.50, 122.66 (q, *J* = 266.0 Hz), 122.34 (q, *J* = 5.3 Hz), 117.06 (q, *J* = 37.6 Hz), 111.38 (q, *J* = 2.3 Hz), 21.58. MS (70 eV): m/z (%): 365(M^+, 85.2), 210(100). HRMS-ESI calcd for $C_{18}H_{14}F_3NNaO_2S$ [$M+Na^+$]: 388.0590, found: 388.0588.

9. Reference

[1] C. M. Hu, F. Hong, Y. Y. Xu, *J. Fluorine. Chem.* 1993, **64**, 1

10. X-ray structures of 2a, 3a and 4.



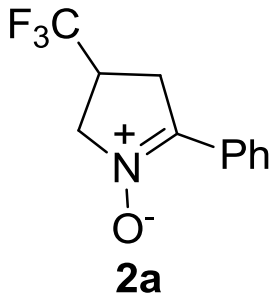
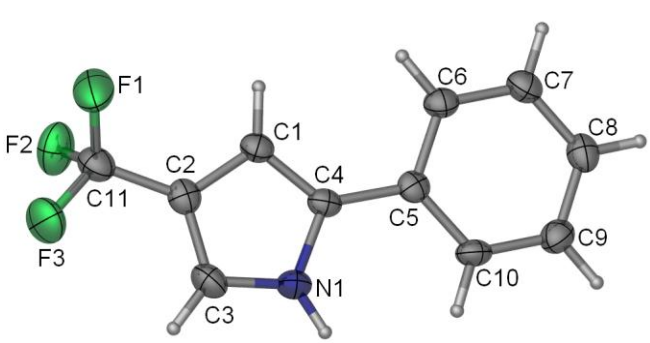
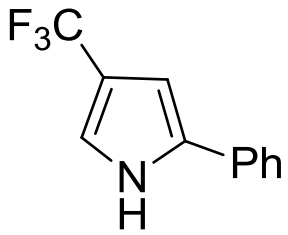


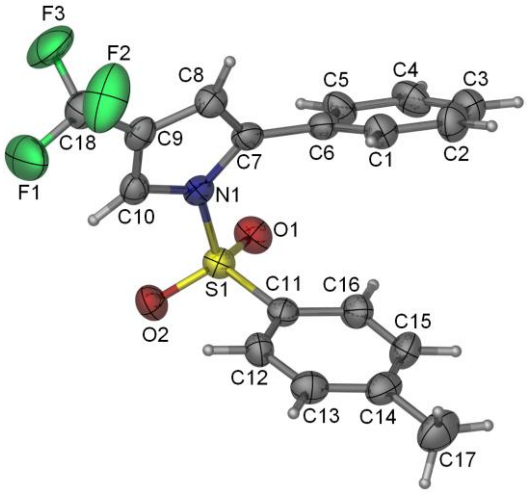
Figure 1. ORTEP depiction of compound **2a**, CCDC 973252.

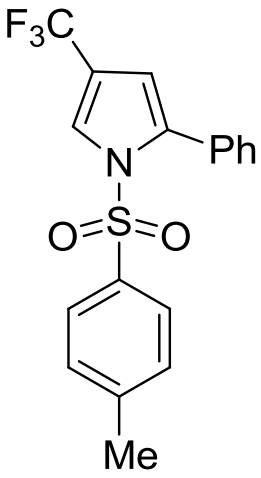




3a

Figure 2. ORTEP depiction of compound **3a**, CCDC 973253



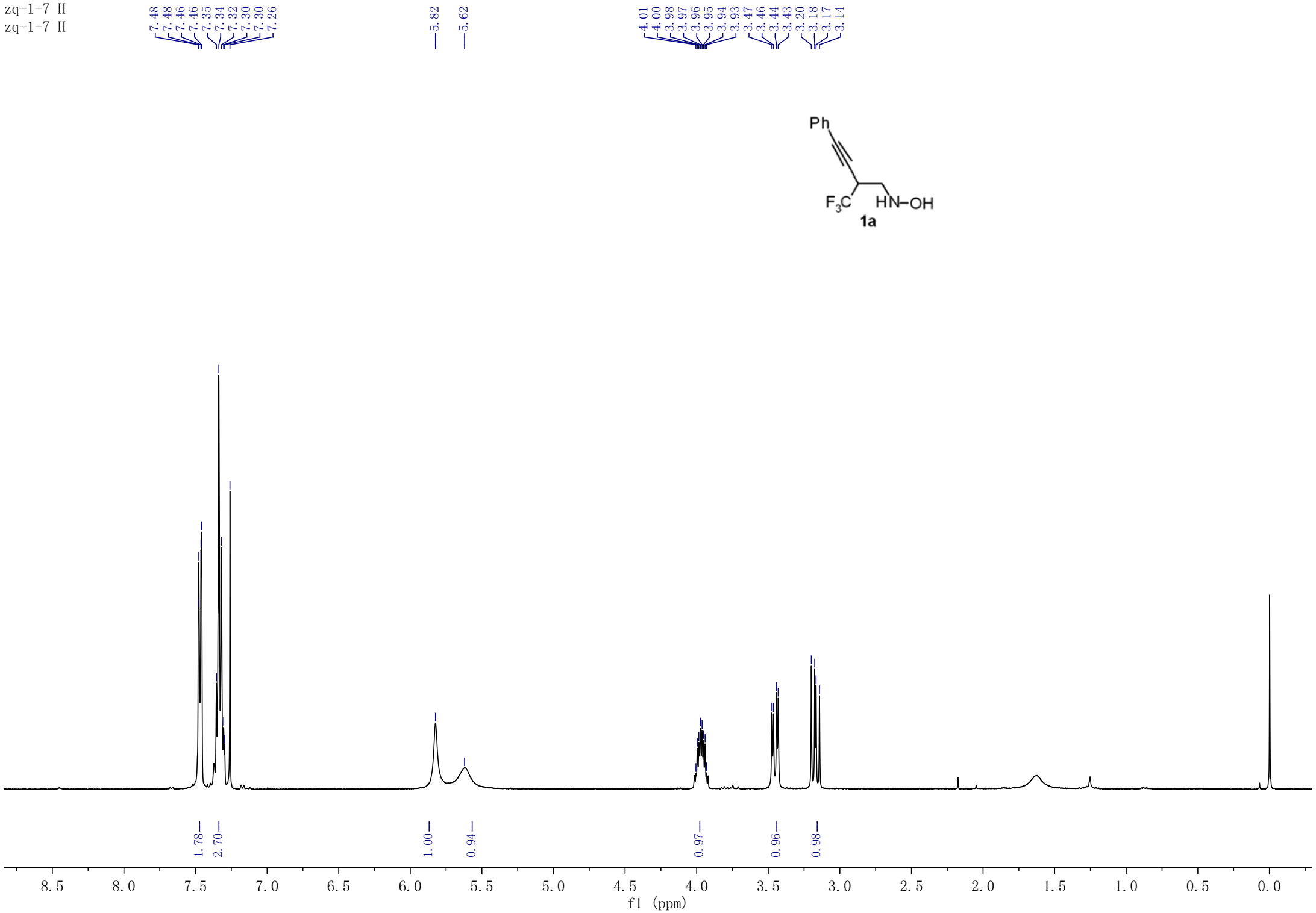


4

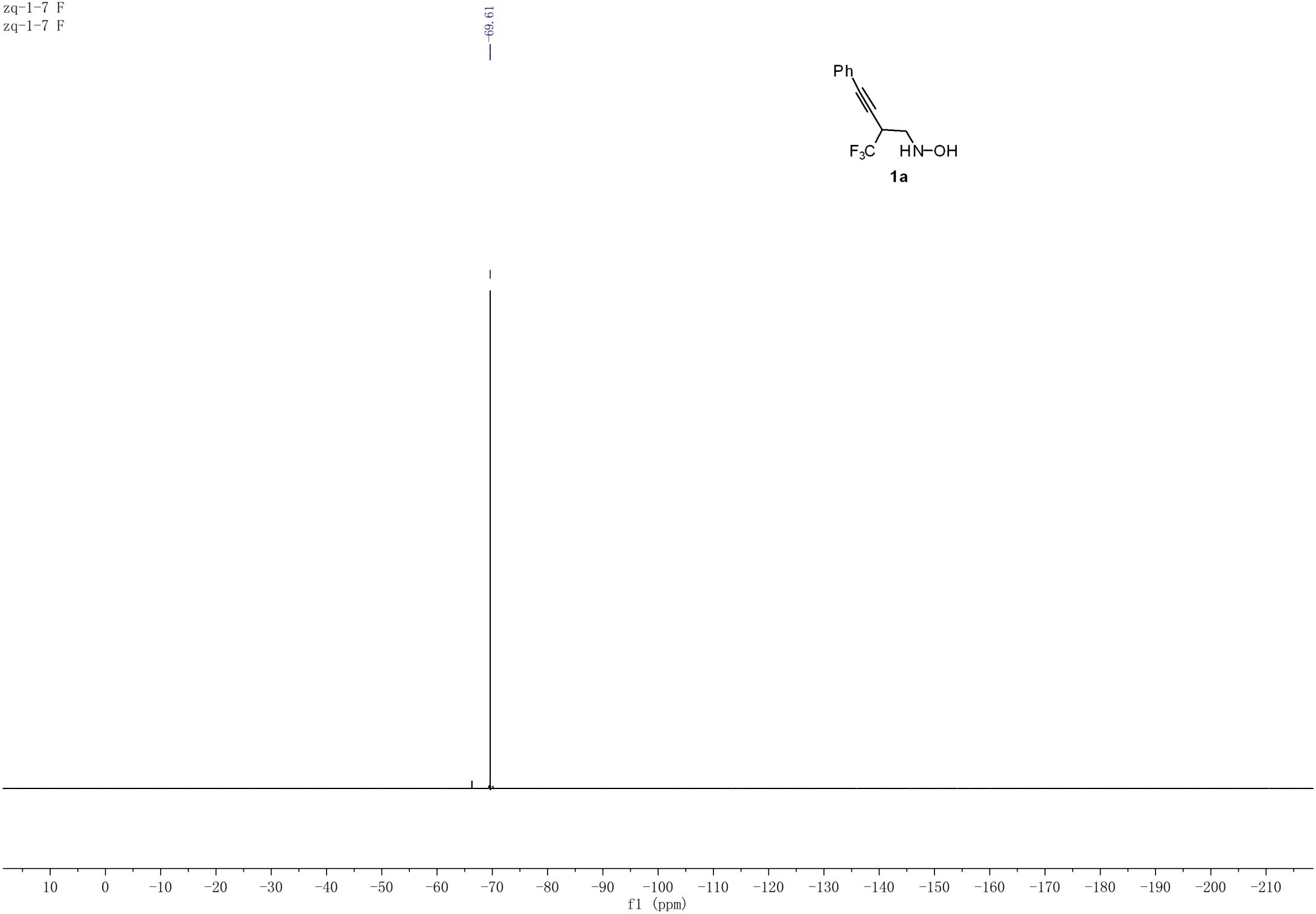
Figure 3. ORTEP depiction of compound **4**, CCDC

11. NMR Spectra.

zq-1-7 H
zq-1-7 H


7.48
7.48
7.46
7.46
7.35
7.34
7.32
7.30
7.30
7.26
5.82
5.62
4.01
4.00
3.98
3.97
3.96
3.95
3.94
3.93
3.47
3.46
3.44
3.43
3.20
3.18
3.17
3.14
Ph
F3C
HN–OH
1a
1.78
2.70
1.00
0.94
0.97
0.96
0.98
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)

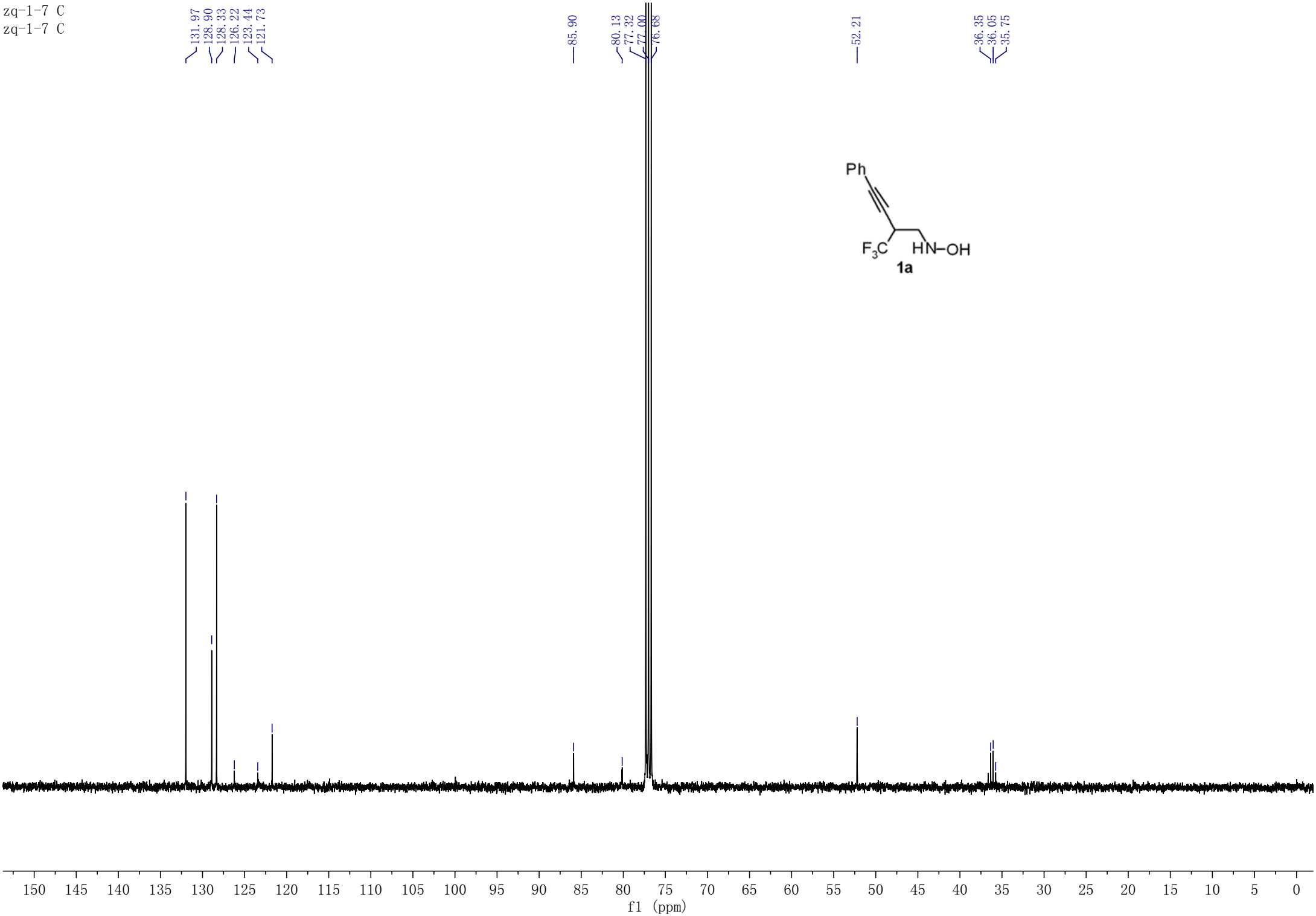
zq-1-7 F
zq-1-7 F


-69.61
Ph
F3C
HN–OH
1a
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

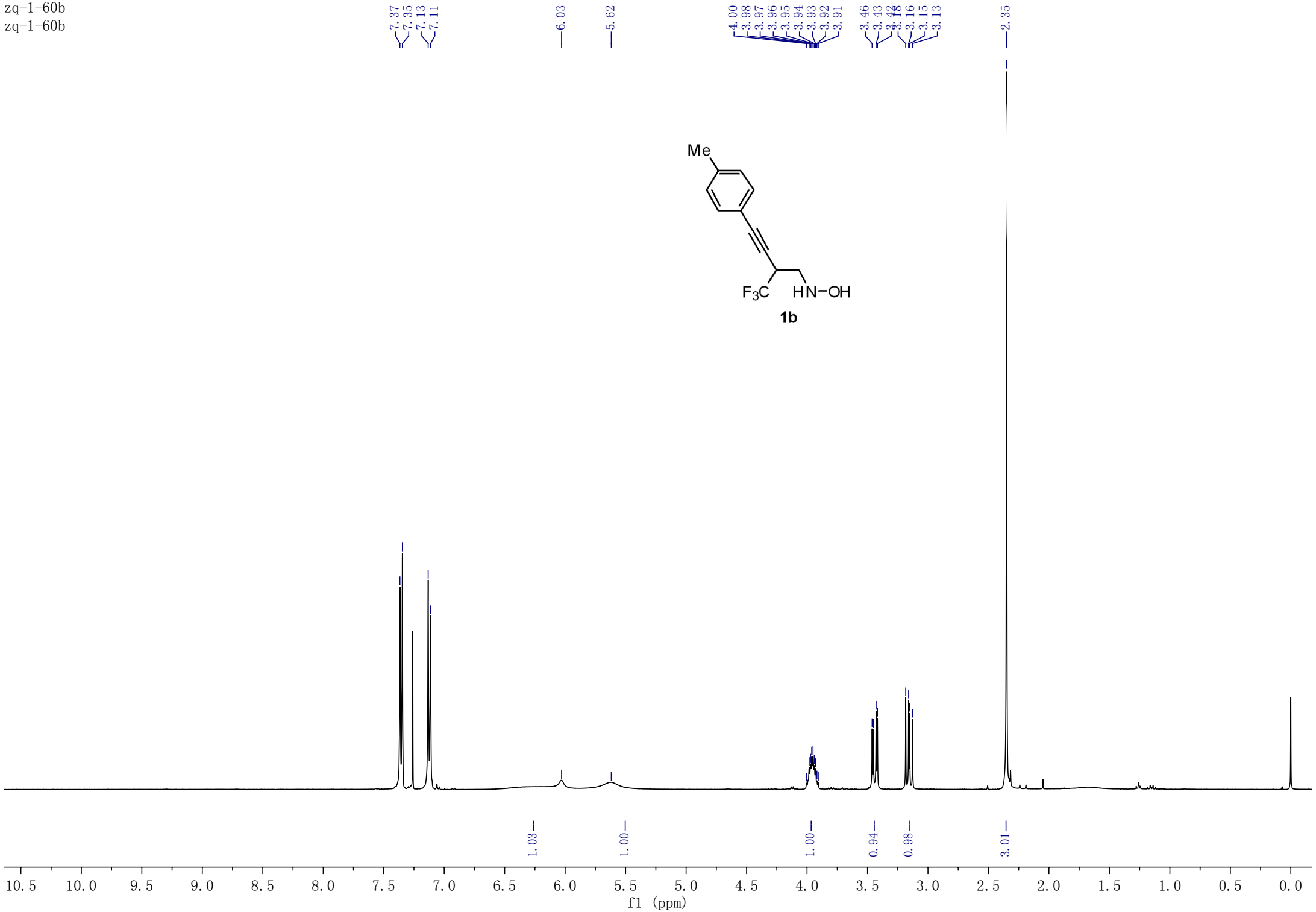
zq-1-7 C
zq-1-7 C

131.97
128.90
128.33
126.22
123.44
121.73
85.90
80.13
77.32
77.00
76.68
52.21
36.35
36.05
35.75

1a

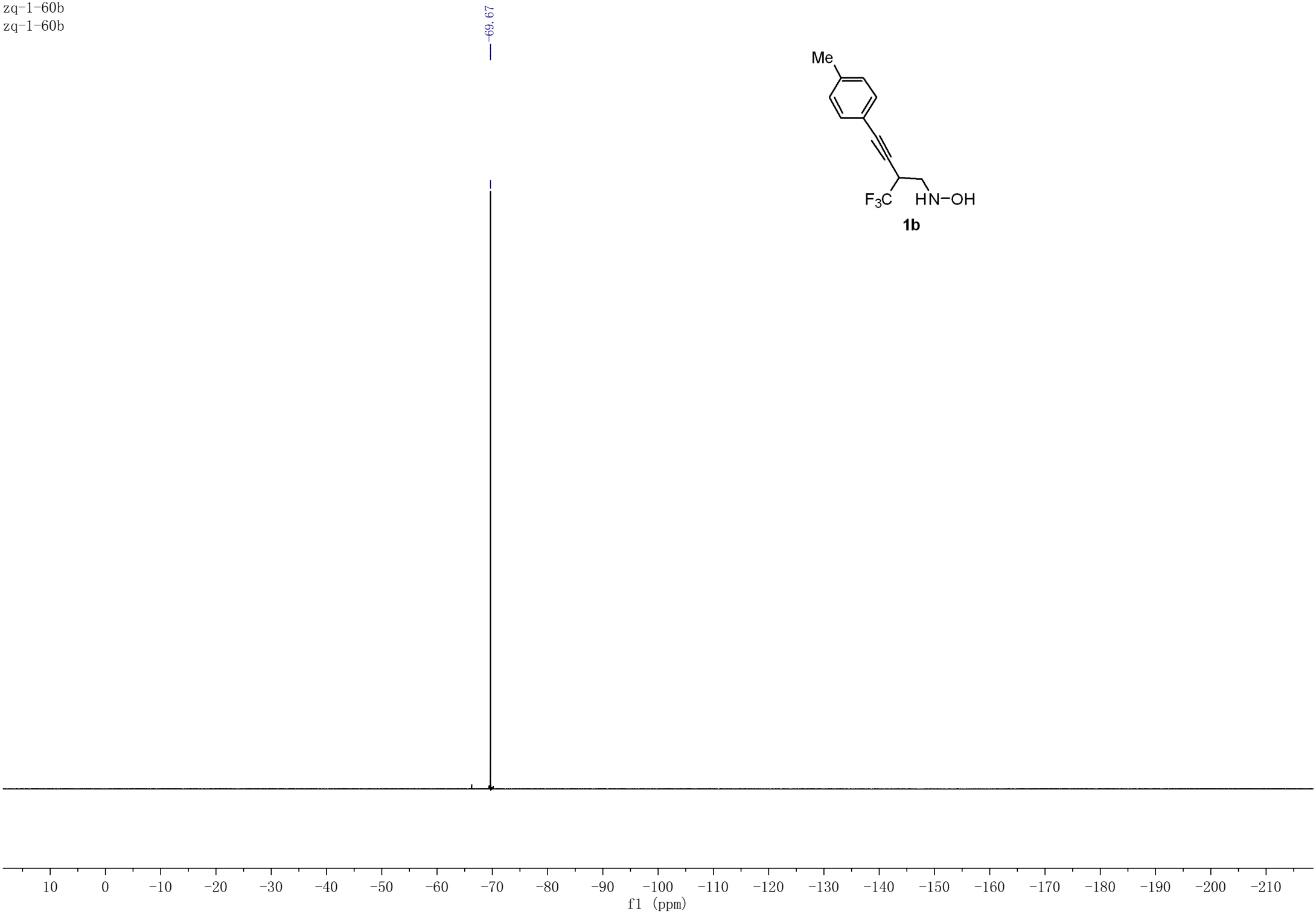


zq-1-60b
zq-1-60b



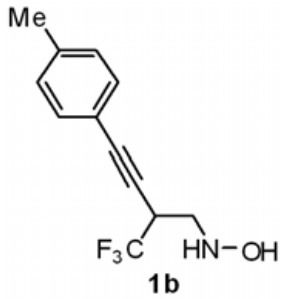
zq-1-60b
zq-1-60b

1b



zq-1-60b
zq-1-b-2

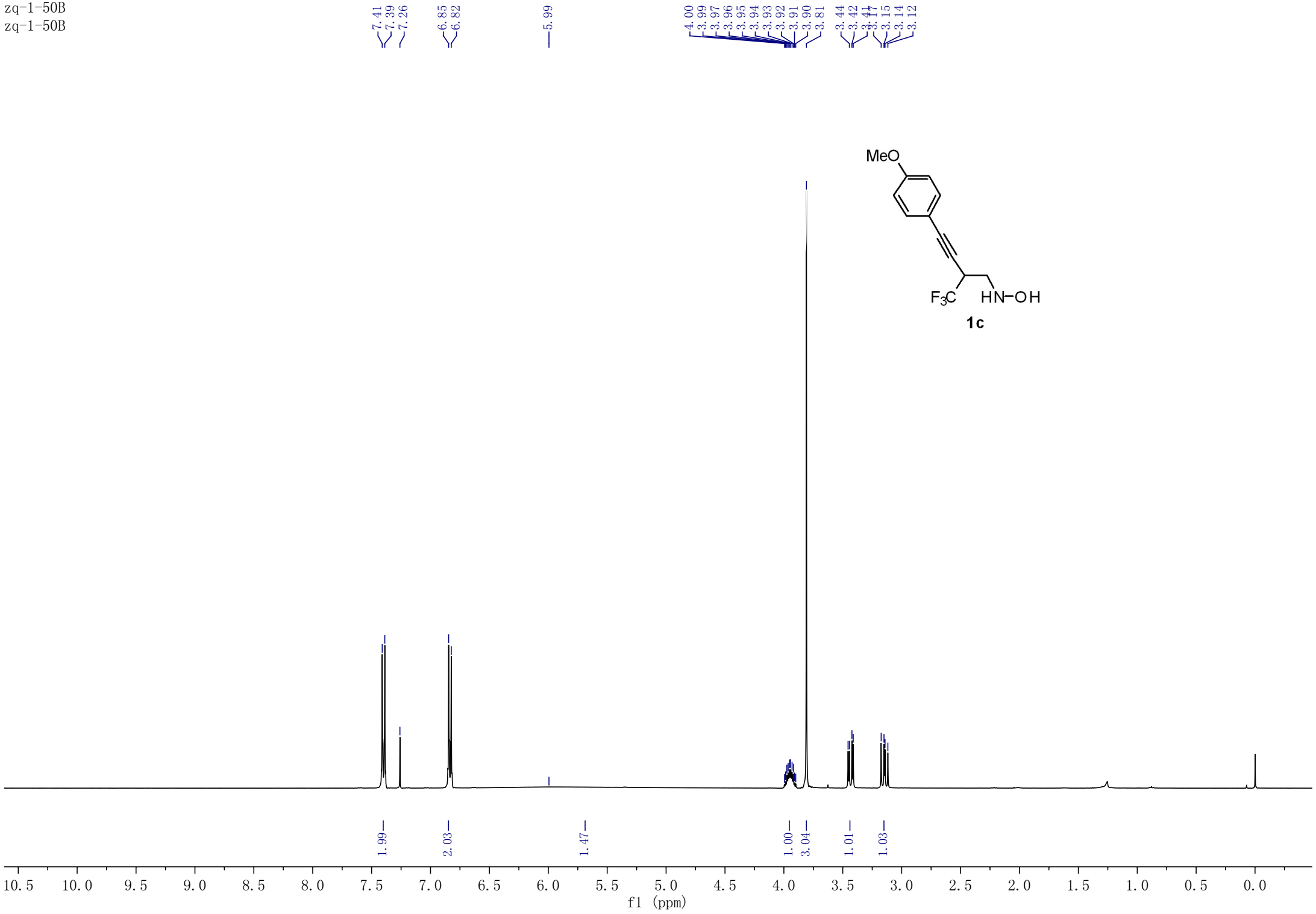
139.10
131.85
129.06
126.25
123.47
118.64
86.08
79.36
77.32
77.00
76.68
52.22
36.64
36.34
36.04
35.75
21.49



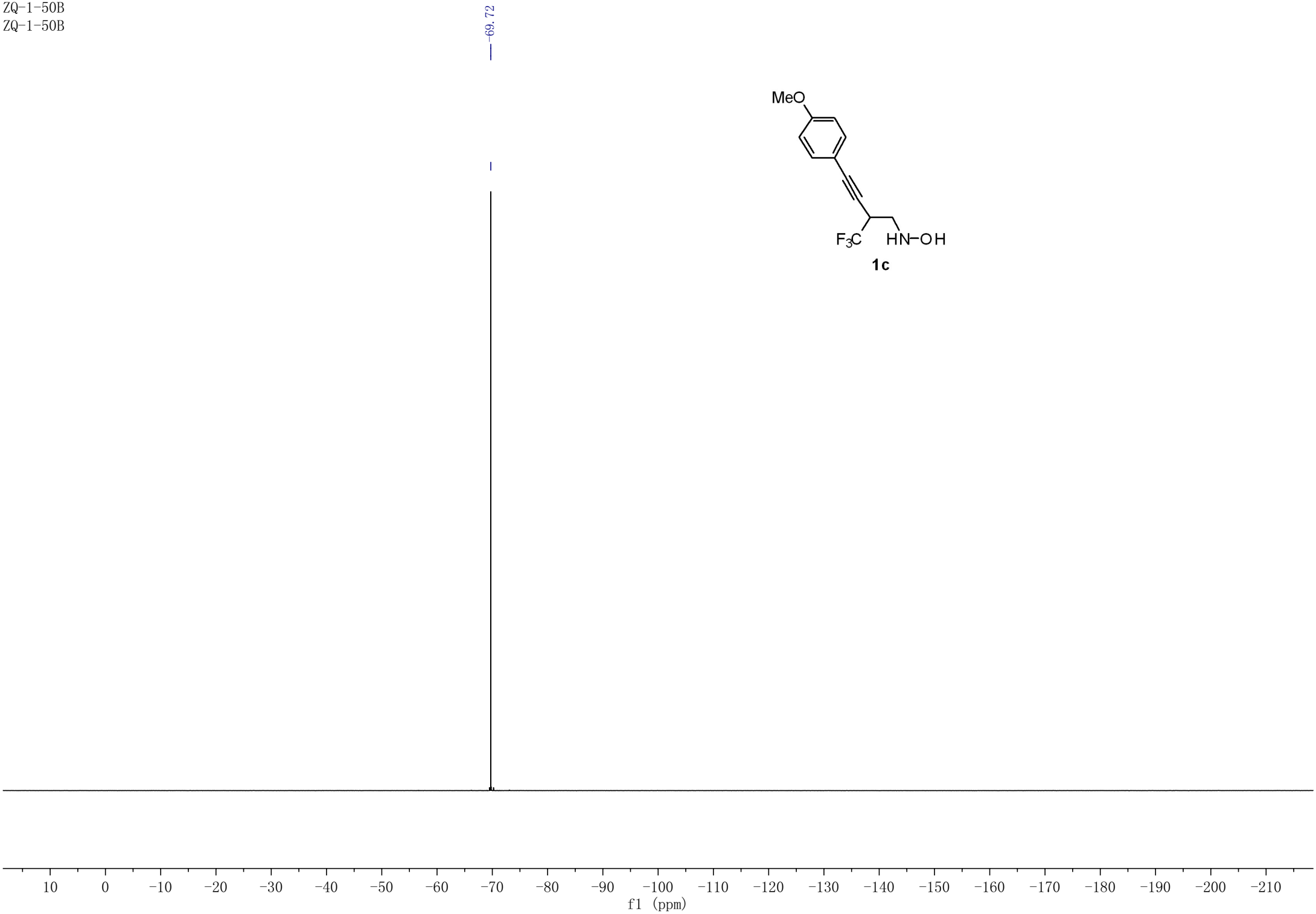
1b

f1 (ppm)

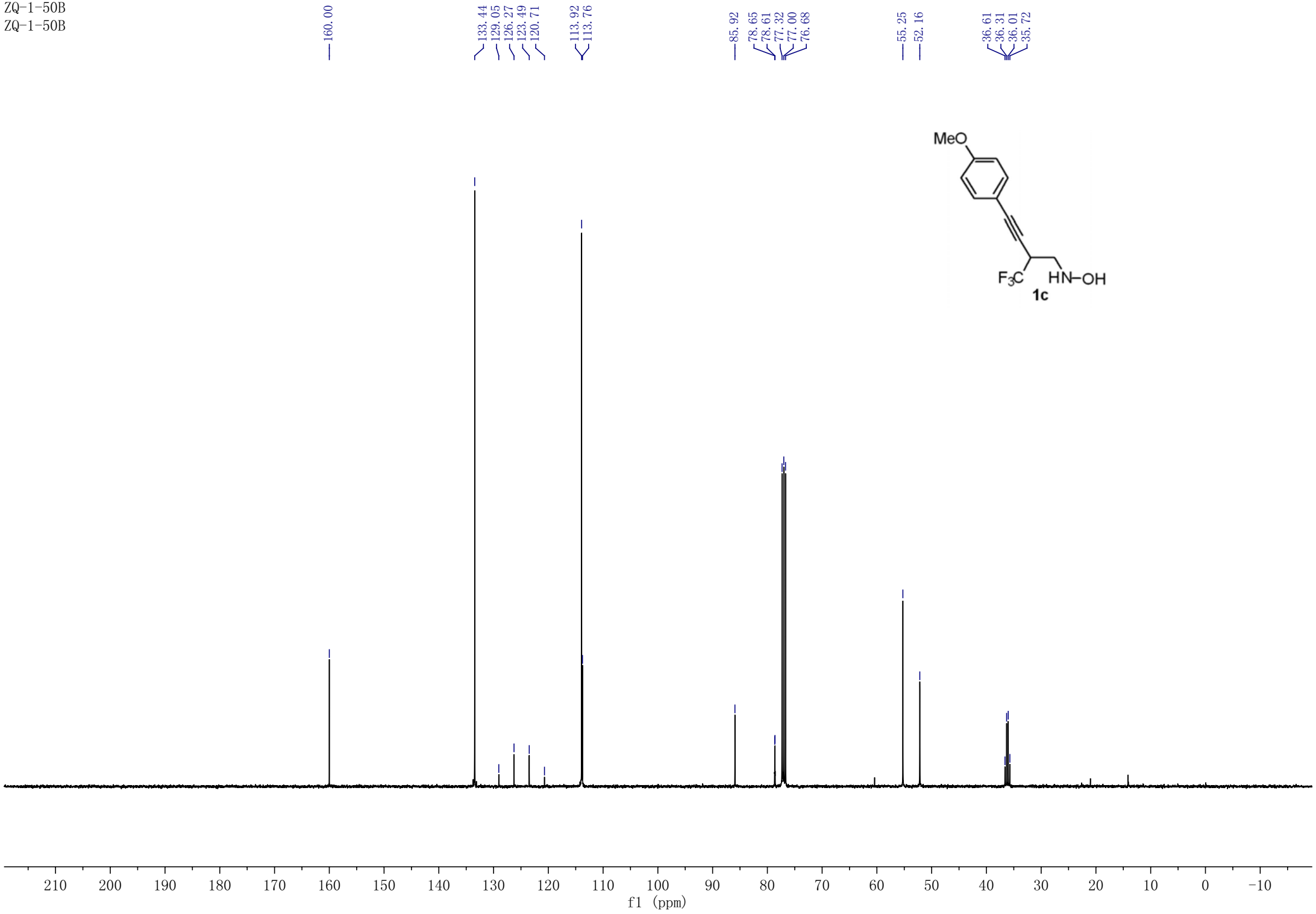
zq-1-50B
zq-1-50B



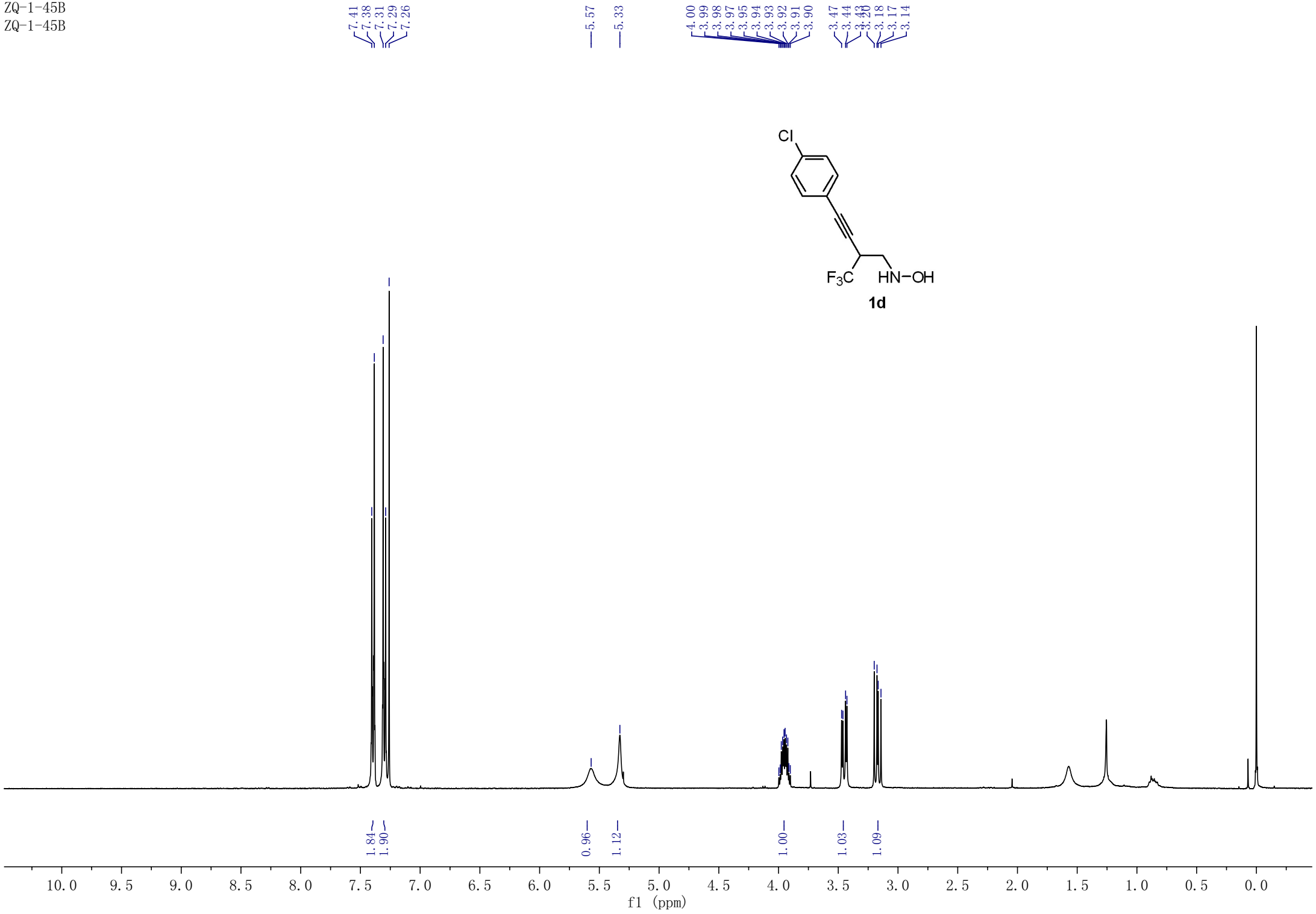
ZQ-1-50B
ZQ-1-50B



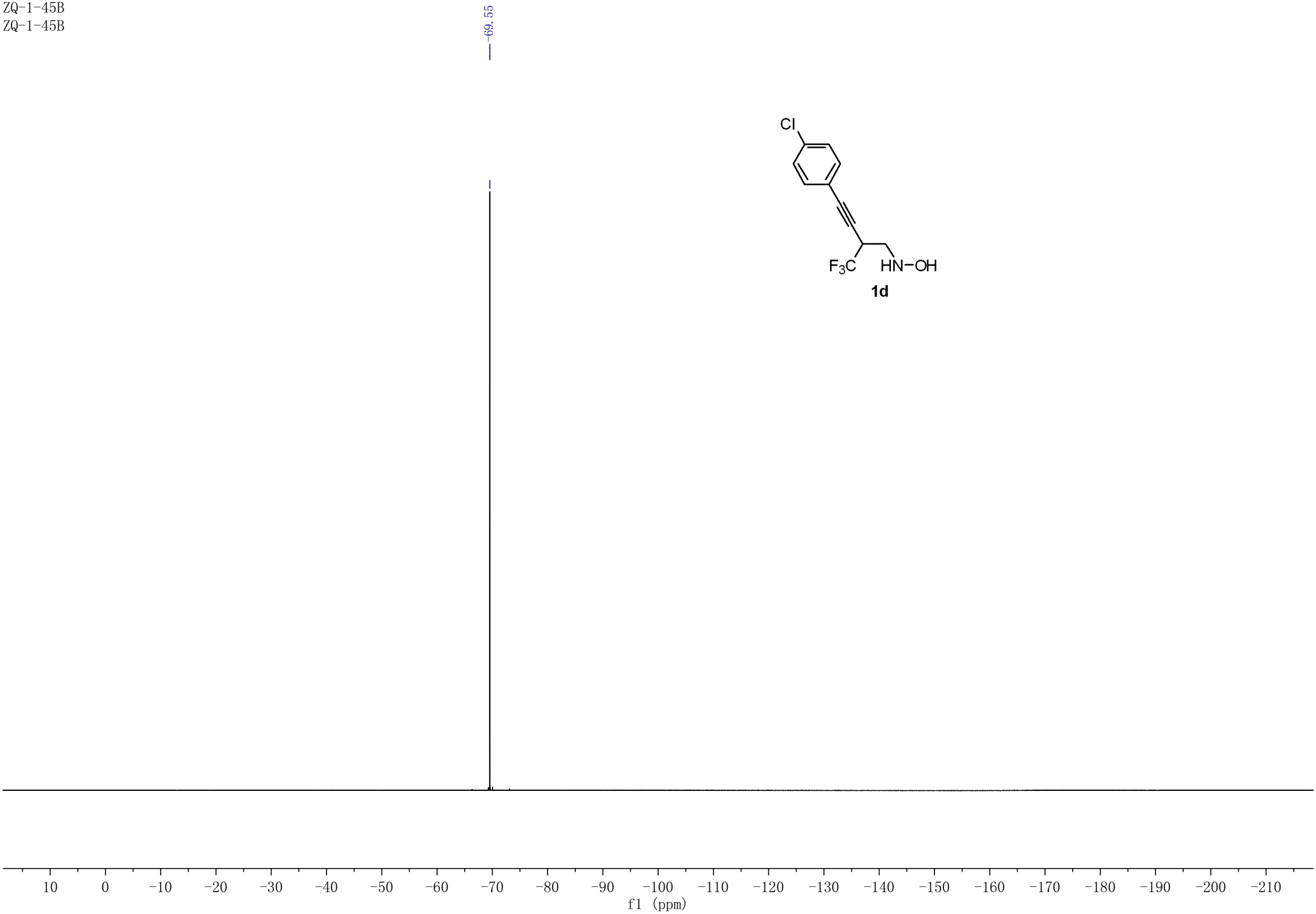
ZQ-1-50B
ZQ-1-50B



ZQ-1-45B
ZQ-1-45B

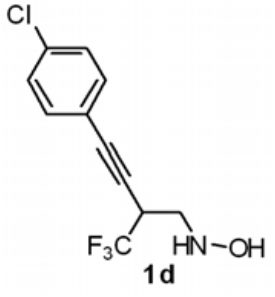


ZQ-1-45B
ZQ-1-45B

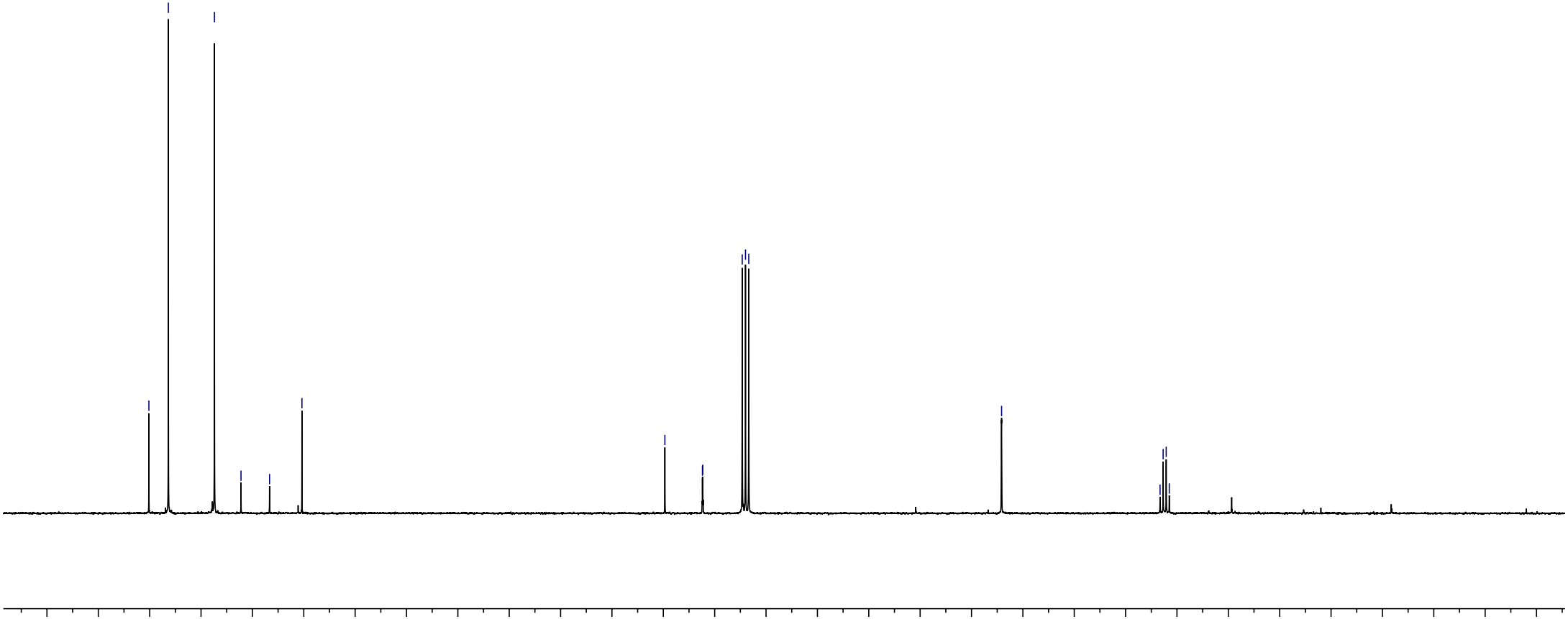


ZQ-1-45B
ZQ-1-45B

135.08
133.18
128.70
126.11
123.33
120.18
84.85
81.19
81.16
77.32
77.00
76.68
52.07
36.64
36.35
36.05
35.75



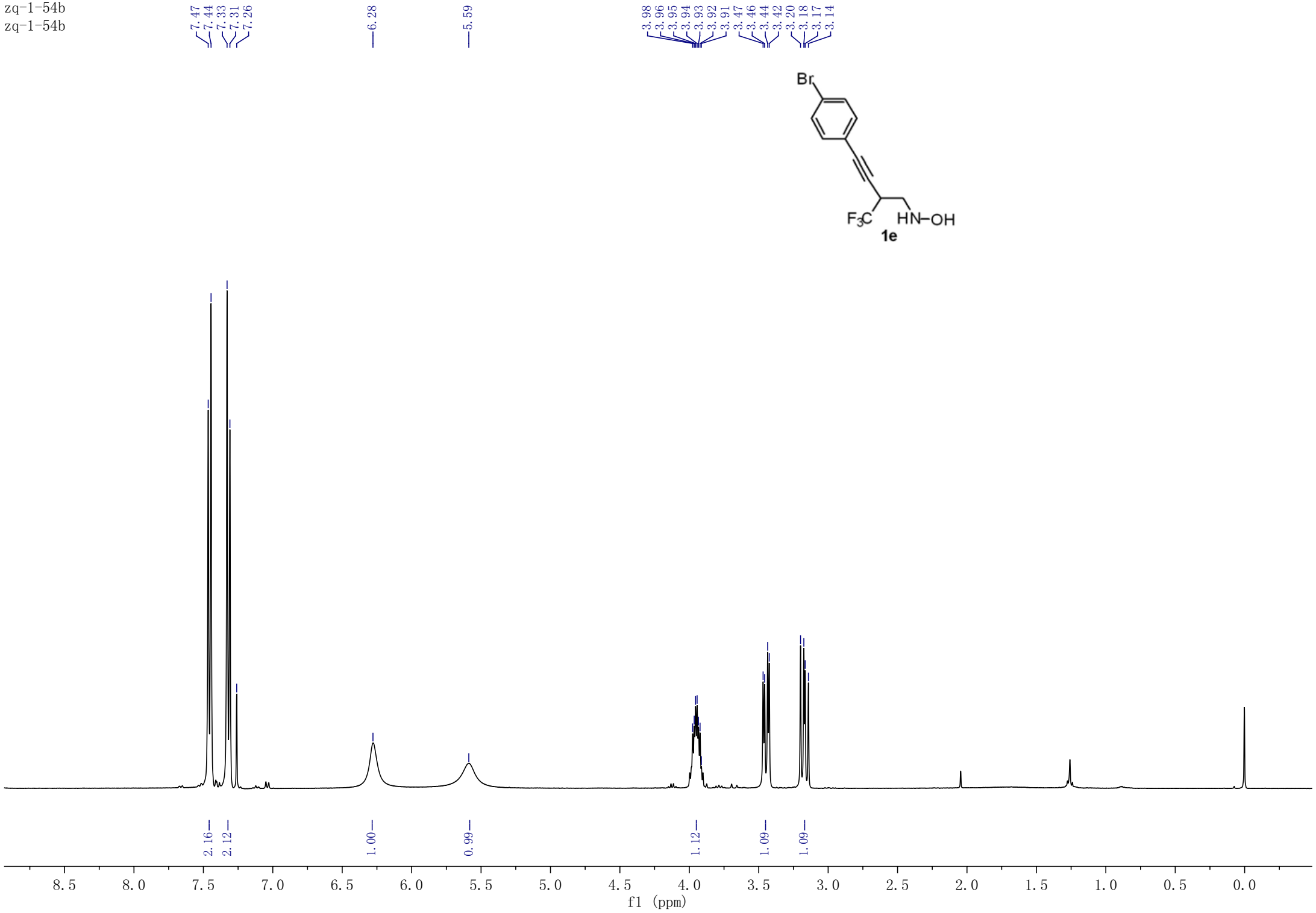
1d



145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0

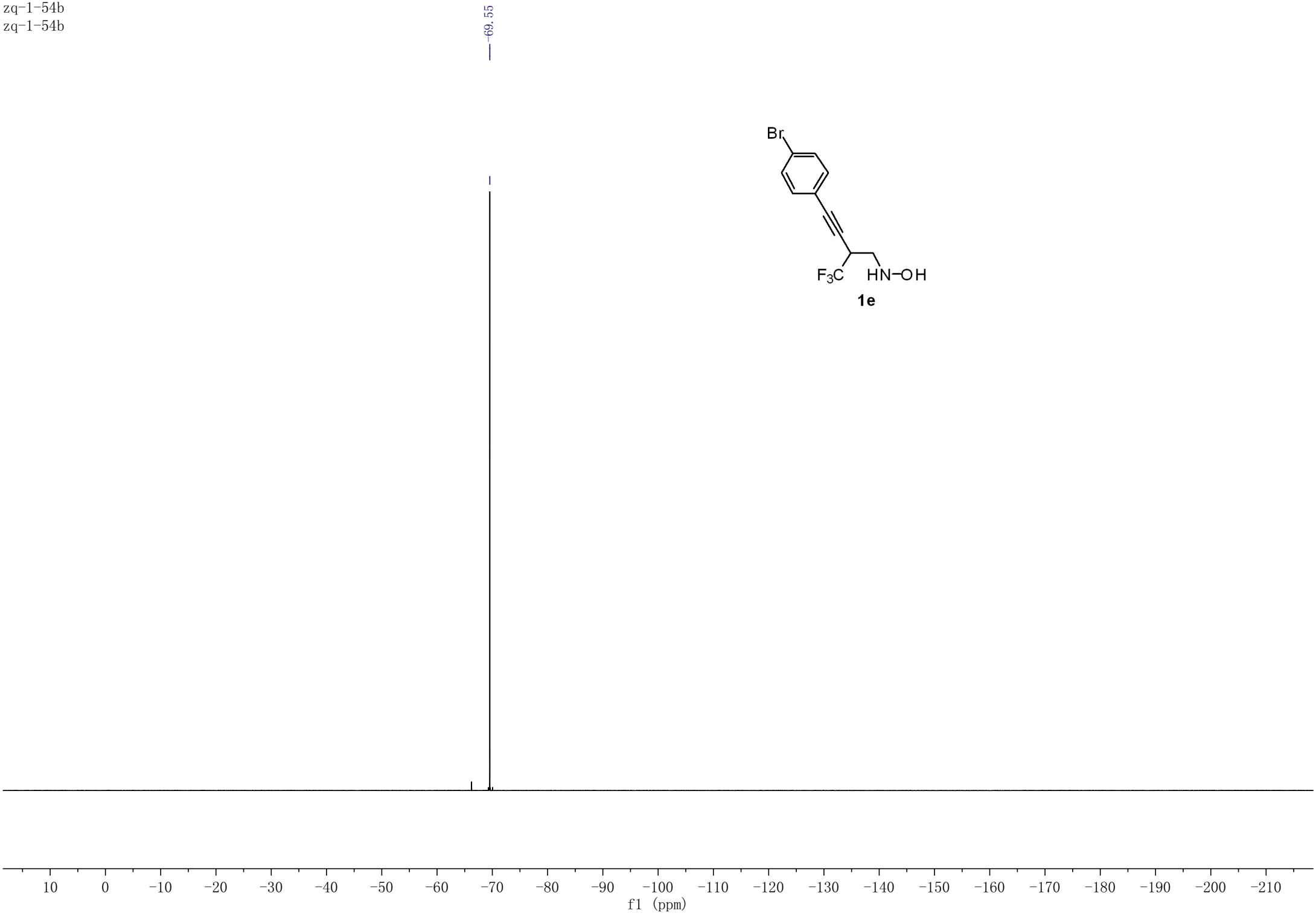
f1 (ppm)

zq-1-54b
zq-1-54b



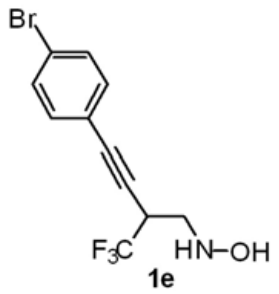
zq-1-54b
zq-1-54b

1e

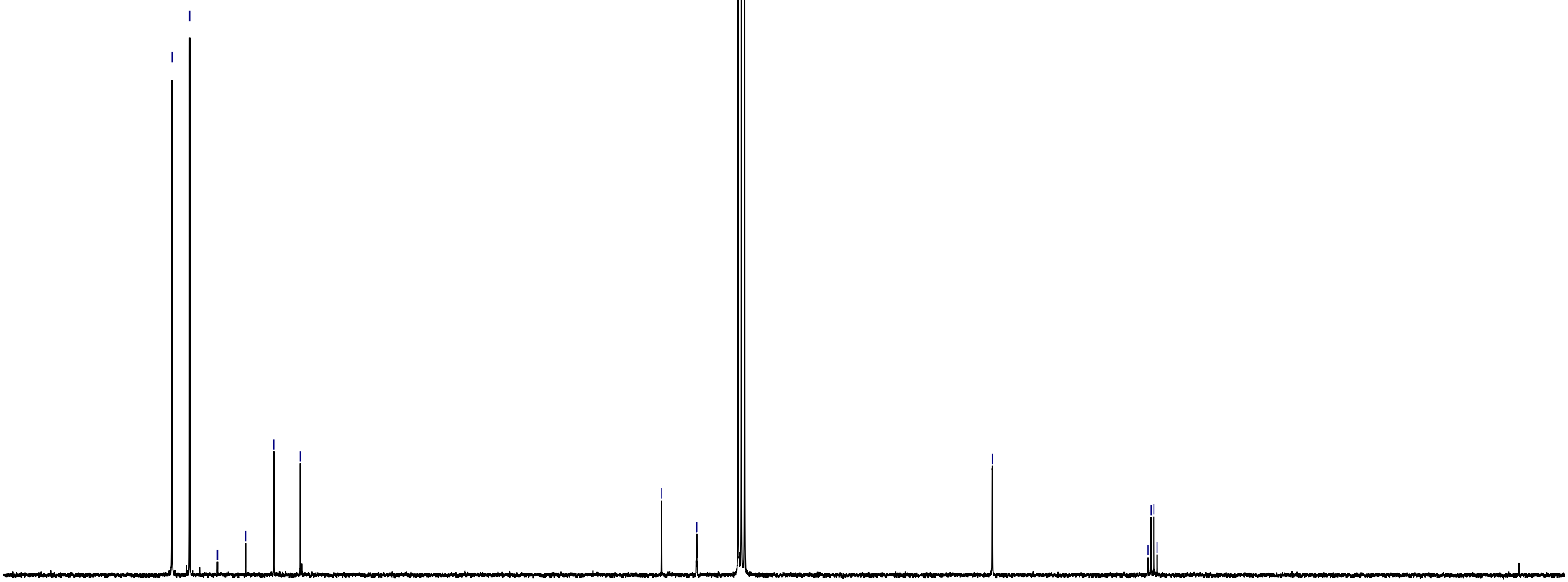


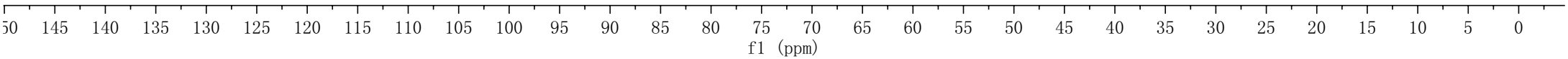
zq-1-54b
zq-1-54b

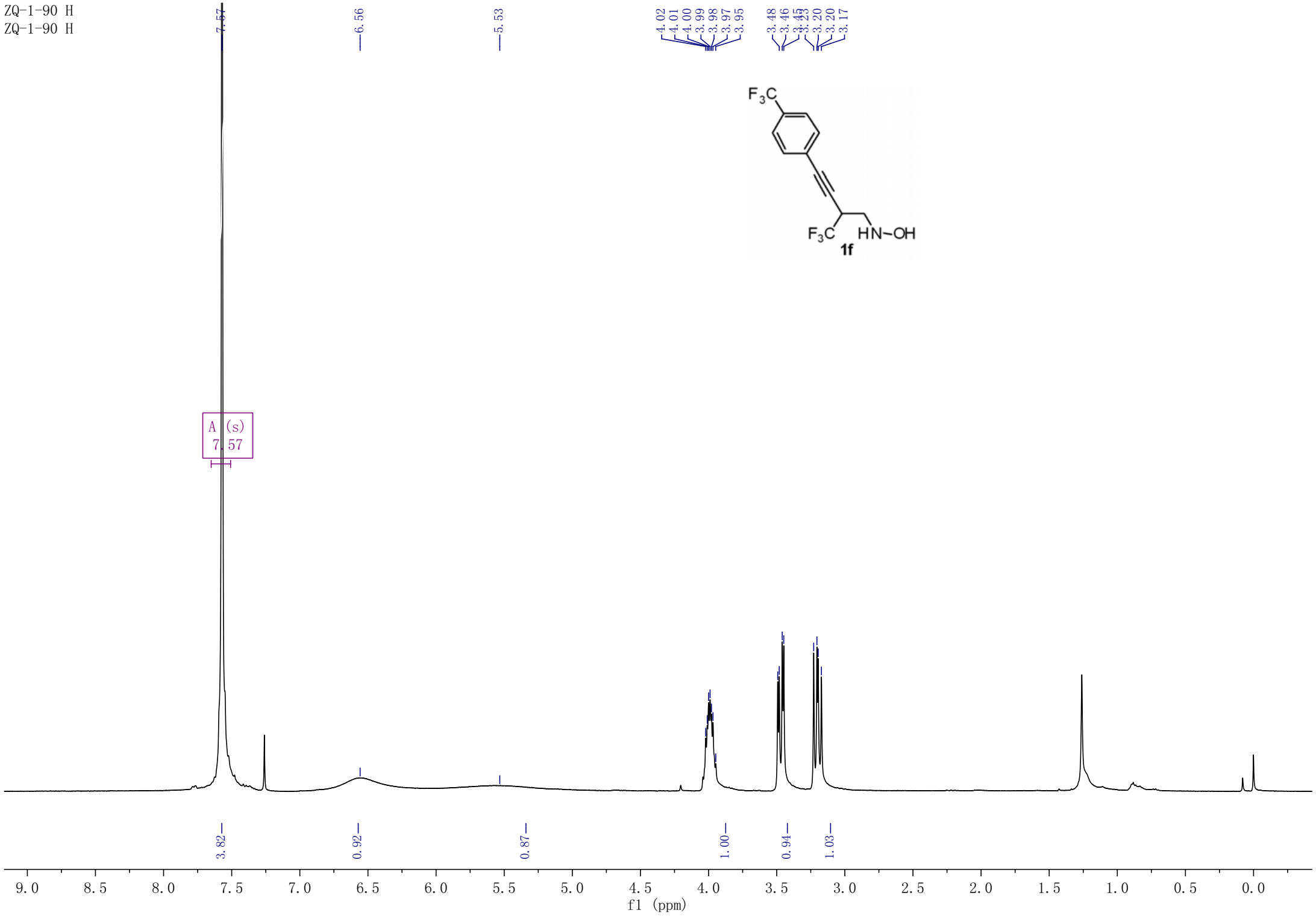
133.39
131.64
128.88
126.10
123.31
120.69
84.88
81.46
81.42
77.32
77.00
76.68
52.13
36.72
36.43
36.13
35.83



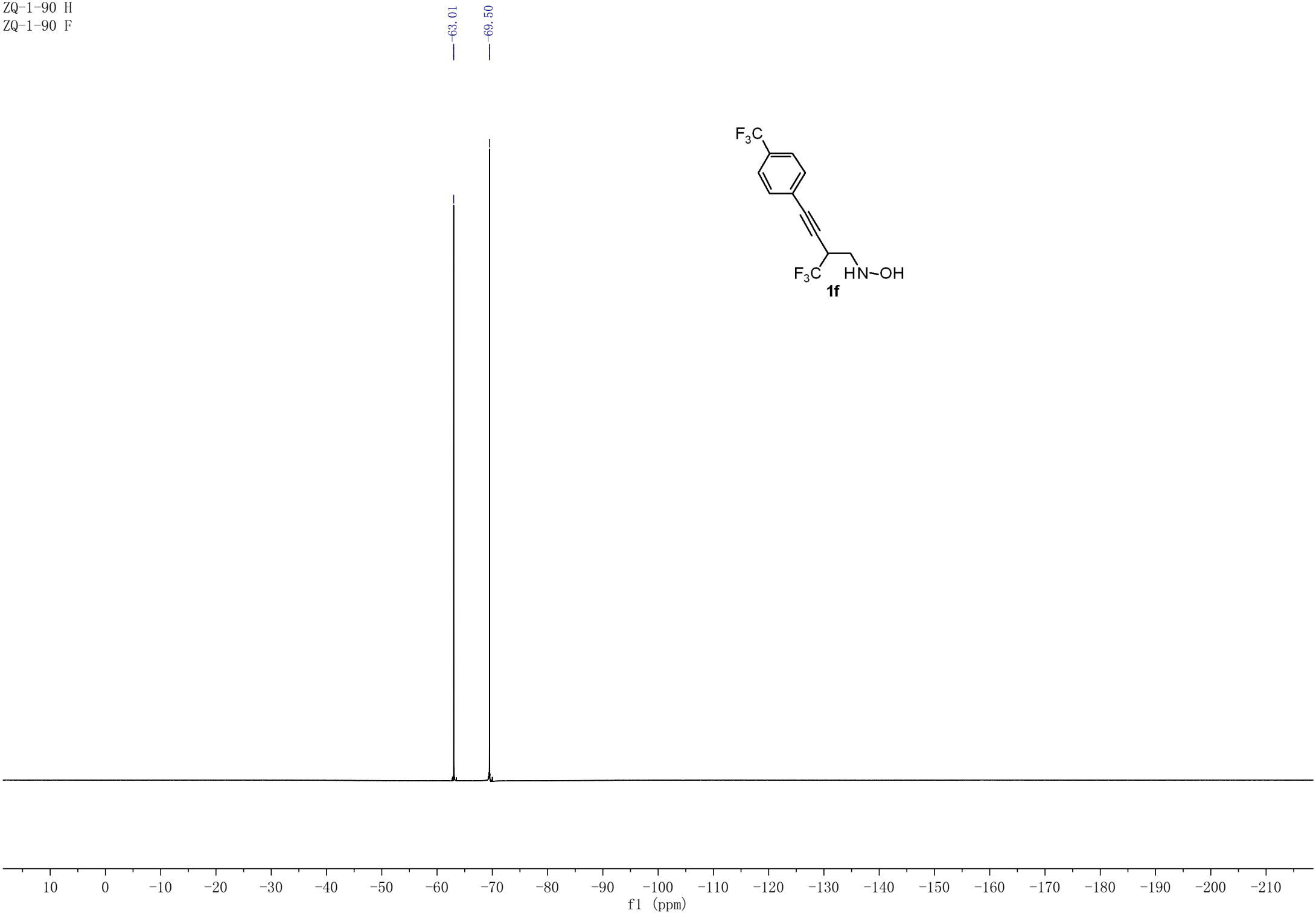
1e






ZQ-1-90 H
ZQ-1-90 H
7.57
6.56
5.53
4.02
4.01
4.00
3.99
3.98
3.97
3.95
3.48
3.46
3.20
3.20
3.17
F3C
F3C
HN-OH
1f
A (s)
7.57
3.82
0.92
0.87
1.00
0.94
1.03
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)

ZQ-1-90 H
ZQ-1-90 F



ZQ-1-90 H
ZQ-1-90 C

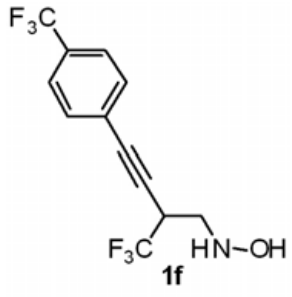
132.26
131.25
130.92
130.59
130.27
126.06
125.50
125.35
125.31
125.28
125.24
125.10
123.28
122.39

84.55
82.78
82.75

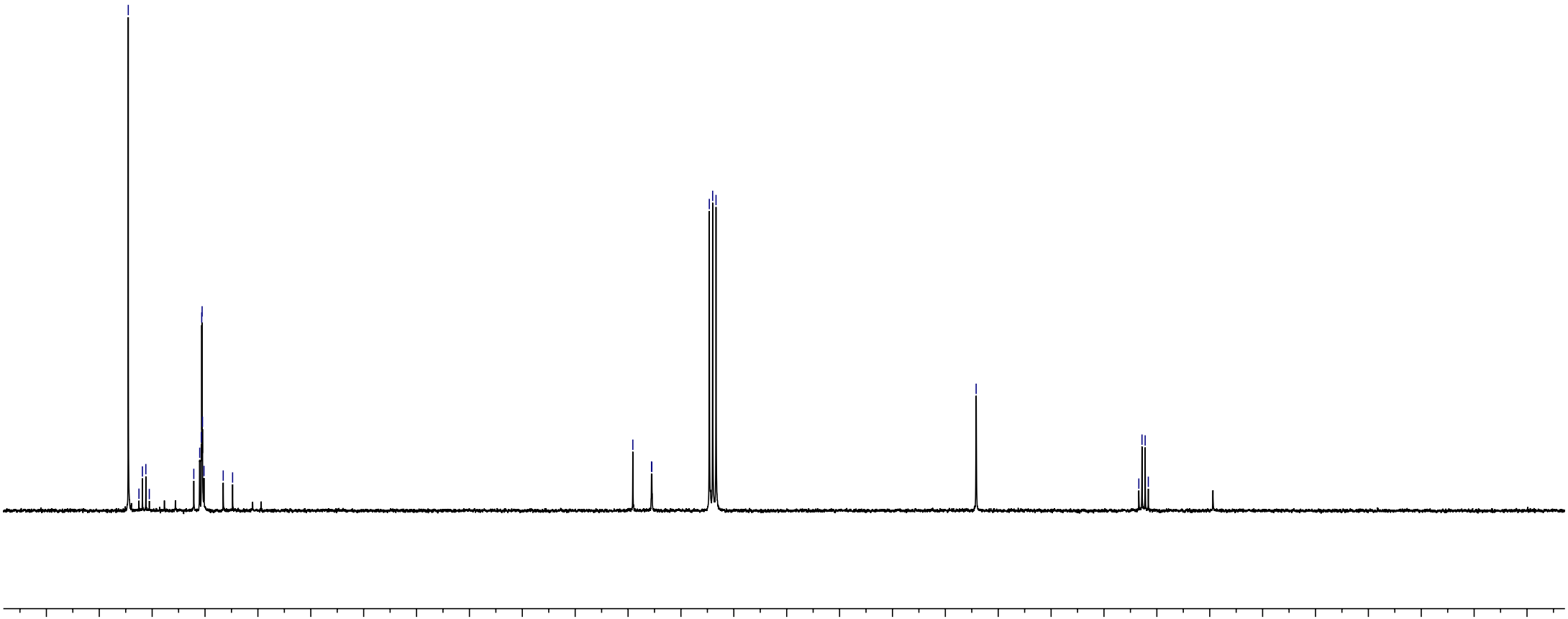
77.32
77.00
76.68

52.09

36.70
36.40
36.11
35.81

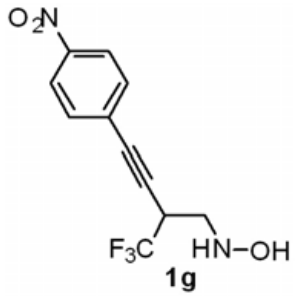


1f

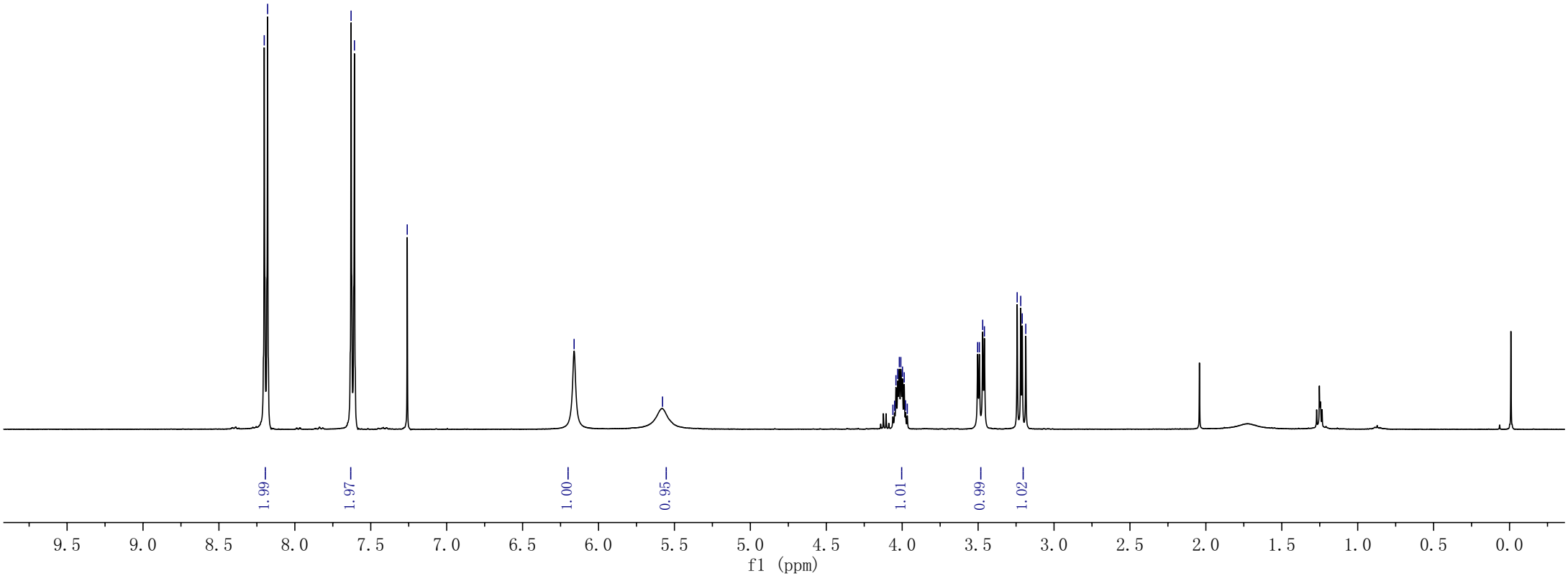


ZQ-1-65 B H
ZQ-1-65 B H

8.20
8.18
7.63
7.61
7.26
6.16
5.58
4.06
4.05
4.04
4.03
4.02
4.01
4.00
3.99
3.98
3.97
3.49
3.47
3.46
3.24
3.22
3.21
3.19

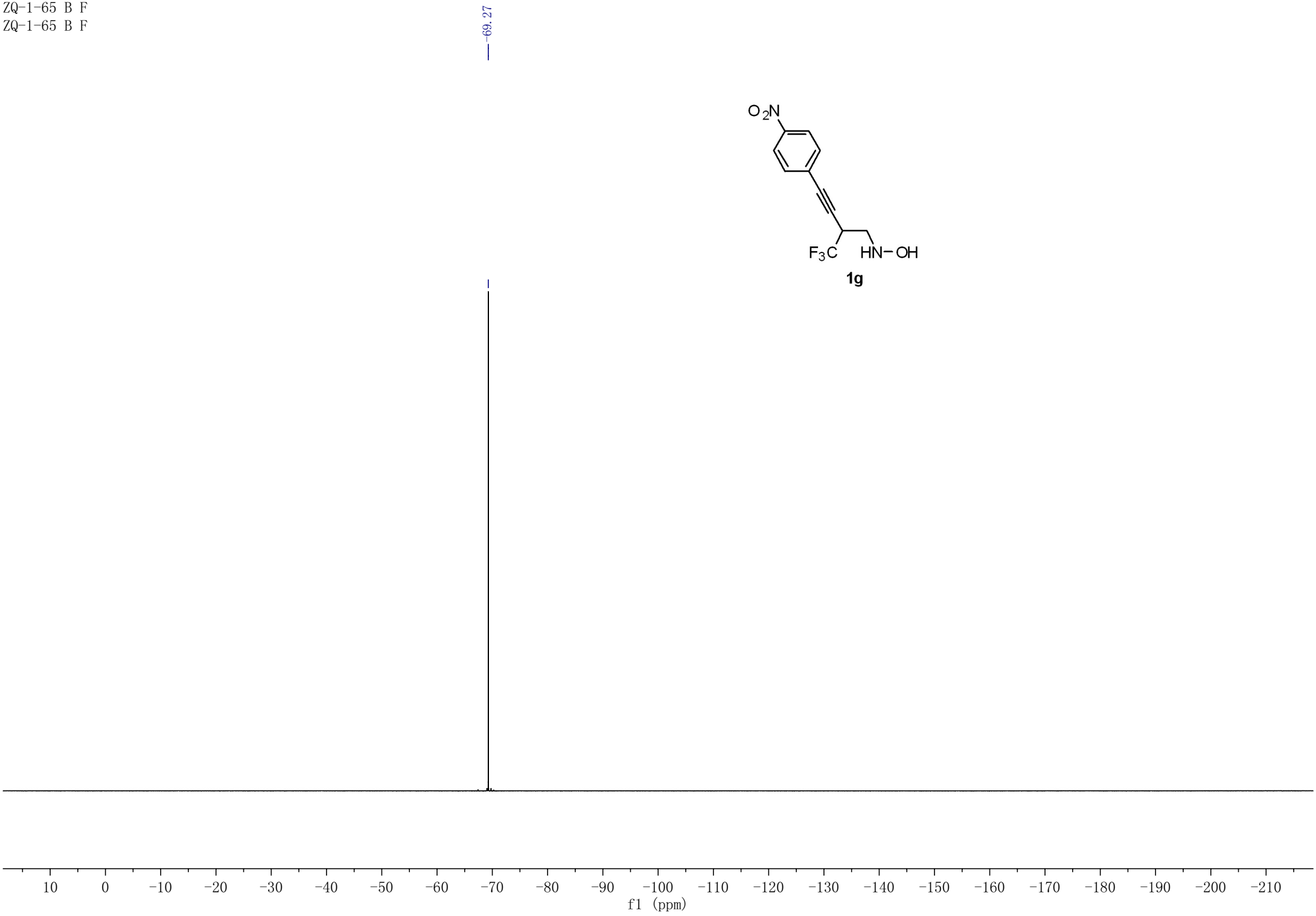


1g



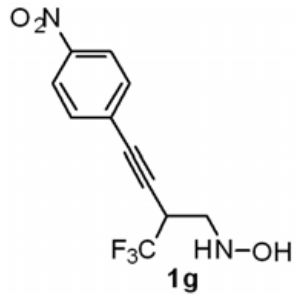
ZQ-1-65 B F
ZQ-1-65 B F

1g

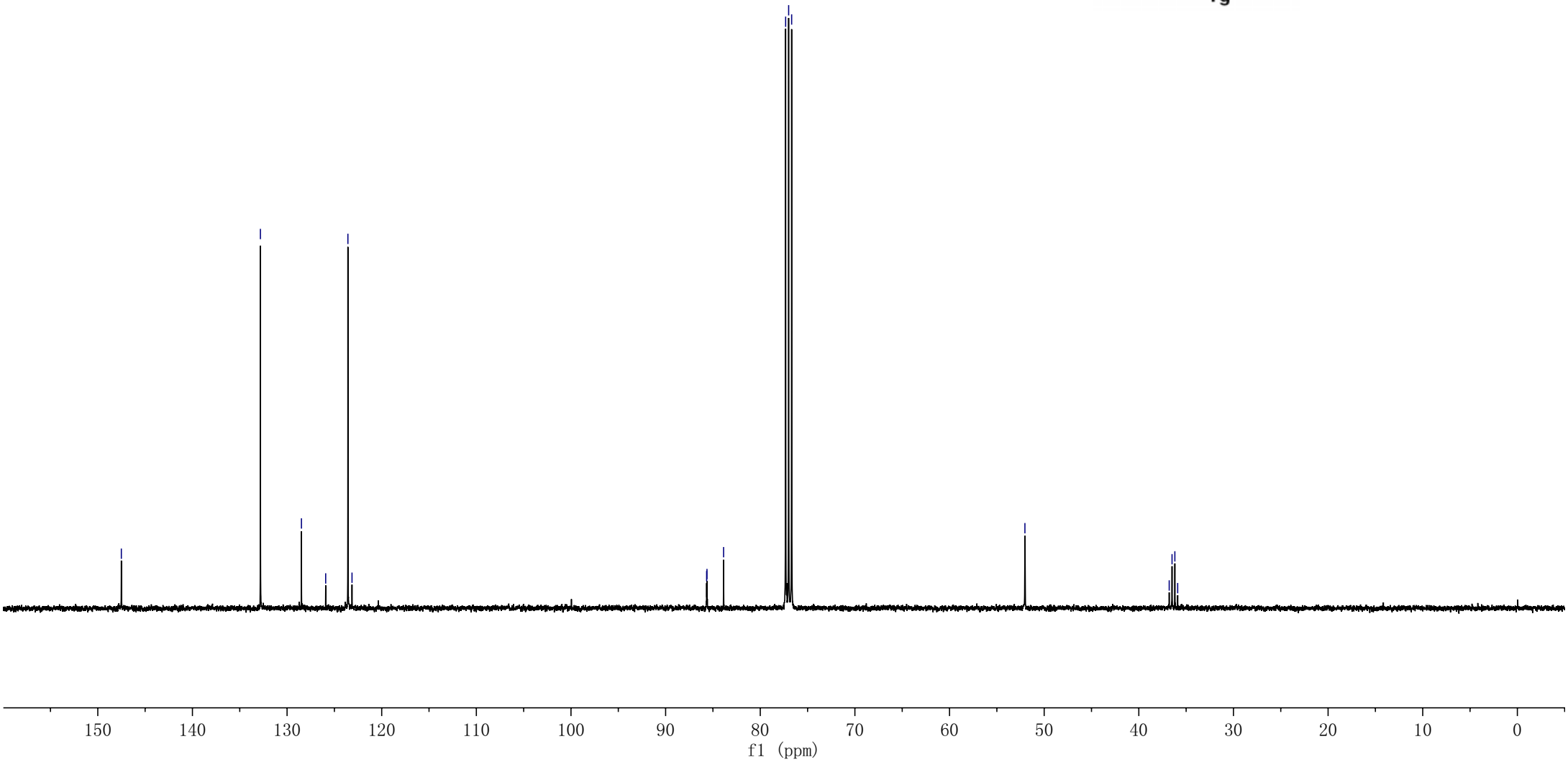


ZQ-1-65 B C
ZQ-1-65 B C

147.51
132.82
128.48
125.92
123.57
123.14
85.67
85.63
83.87
77.32
77.00
76.68
52.04
36.79
36.49
36.19
35.89

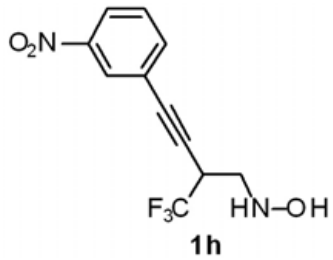


1g

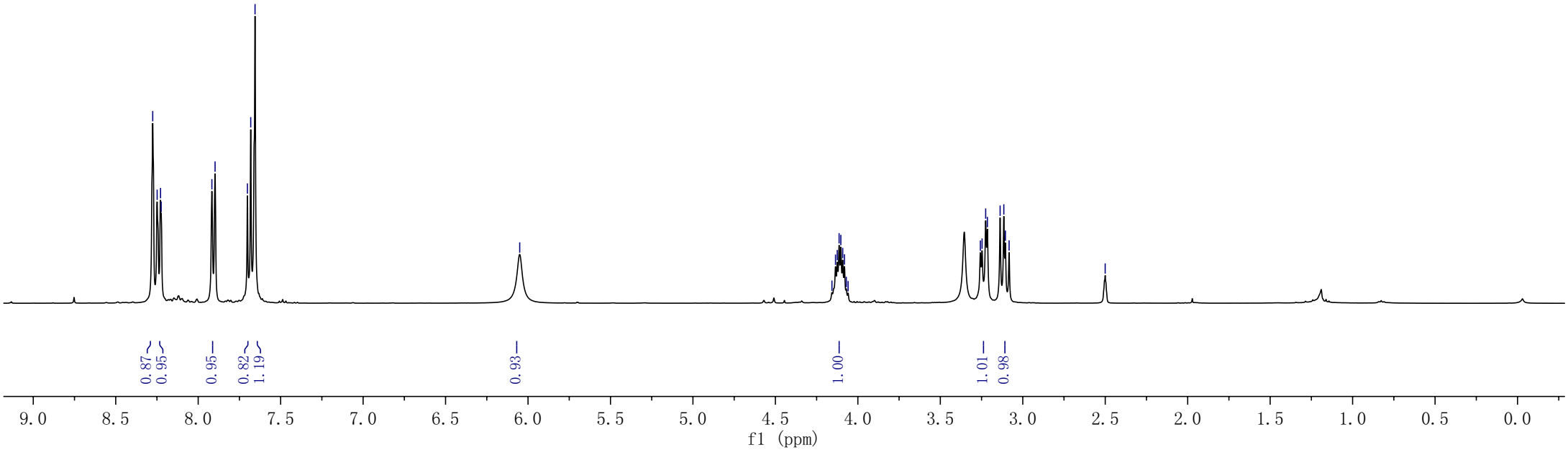


ZL-1-144
ZL-1-144

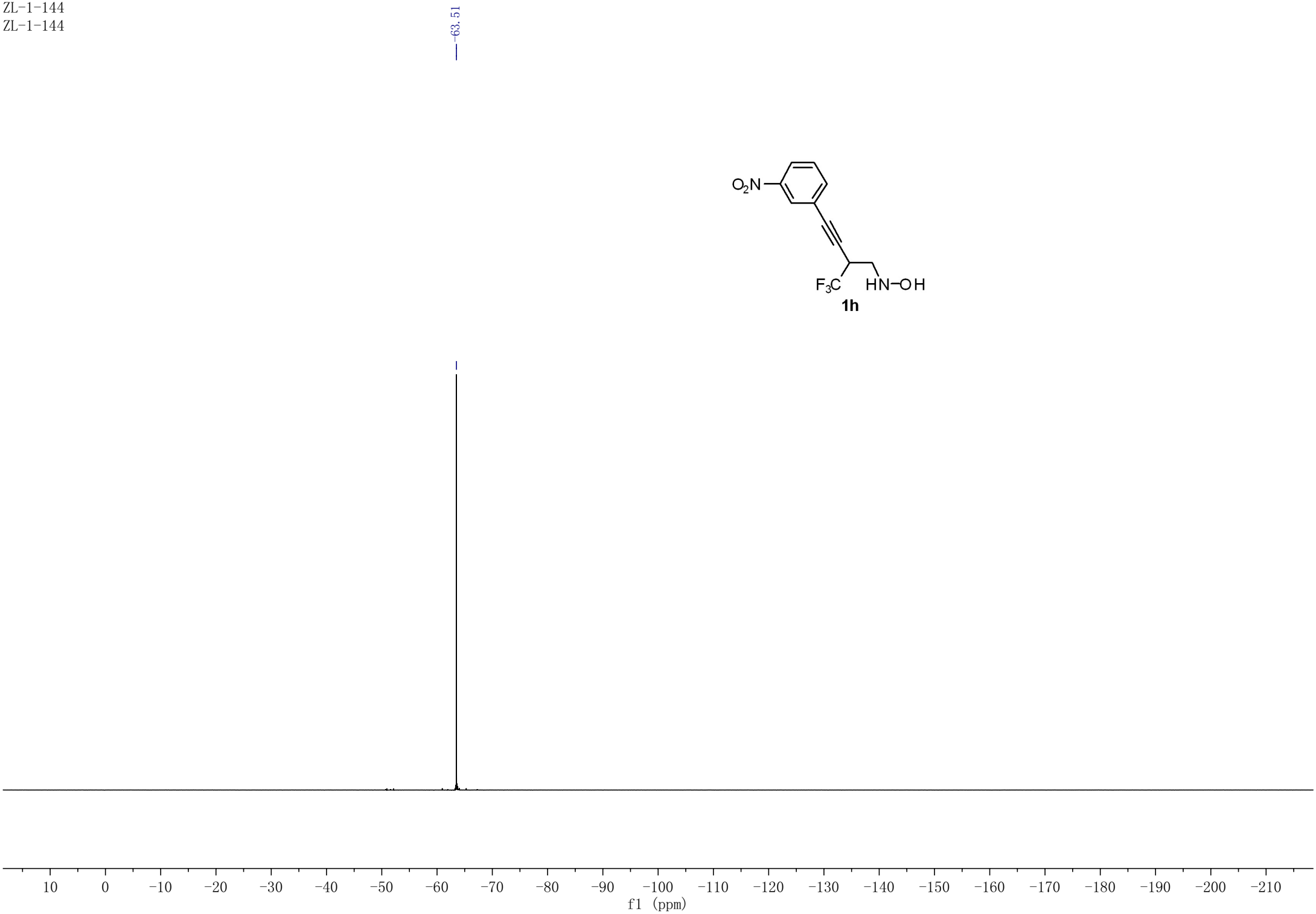
8.28 8.25 8.23 8.22 7.92 7.90 7.70 7.68 7.66 6.05 4.16 4.14 4.12 4.11 4.10 4.09 4.08 4.07 4.06 3.26 3.25 3.22 3.21 3.14 3.11 3.11 3.08 2.50



1h



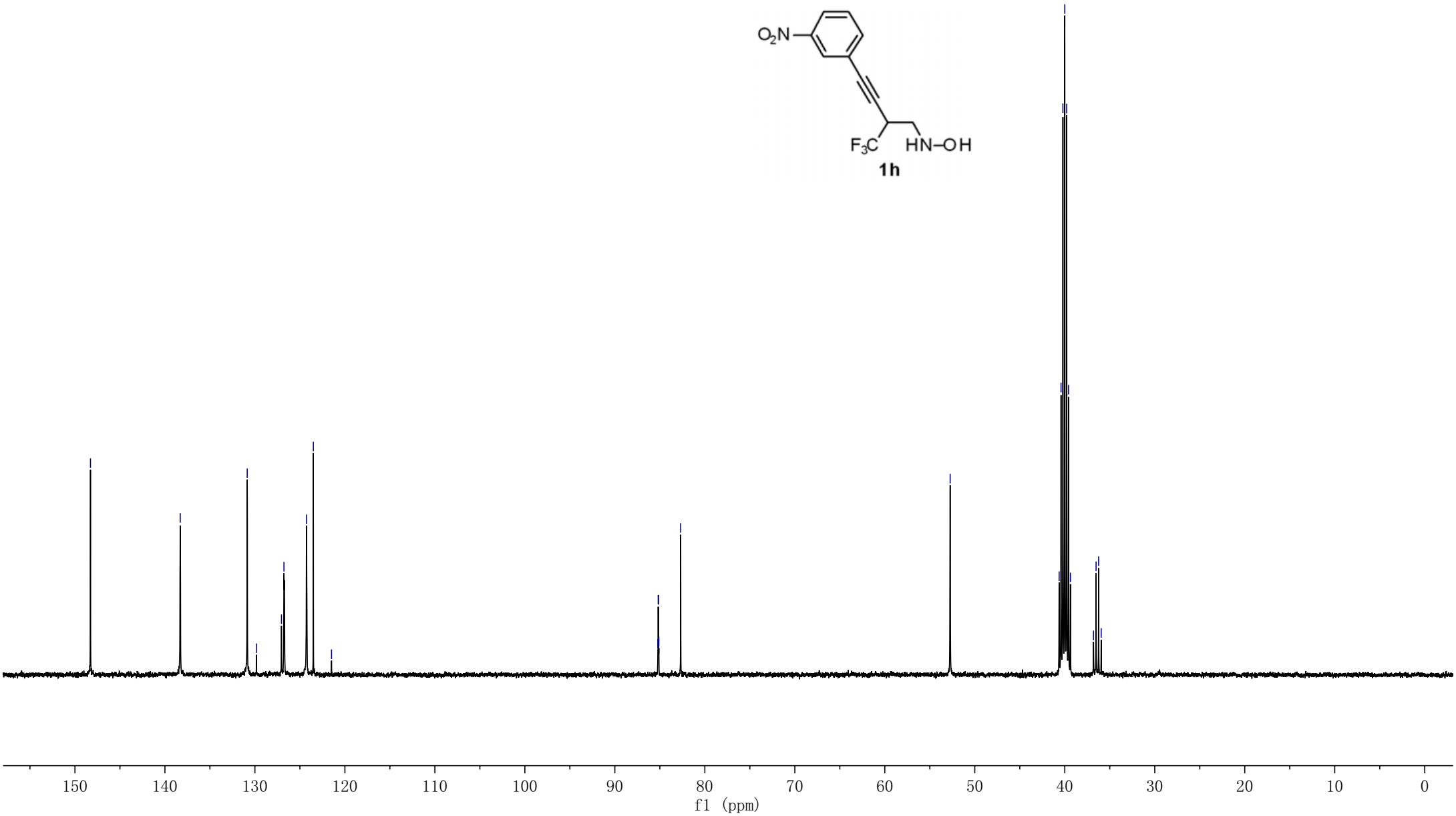
ZL-1-144
ZL-1-144



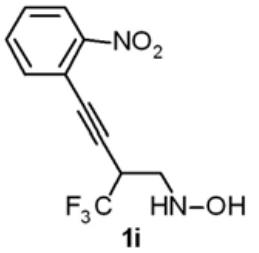
ZL-1-144
ZL-1-144

148.27
138.30
130.85
129.83
127.05
126.77
124.26
123.51
121.49
85.22
85.18
85.15
85.11
82.68
52.74
40.63
40.42
40.21
40.00
39.79
39.58
39.37
36.81
36.52
36.24
35.96

1h



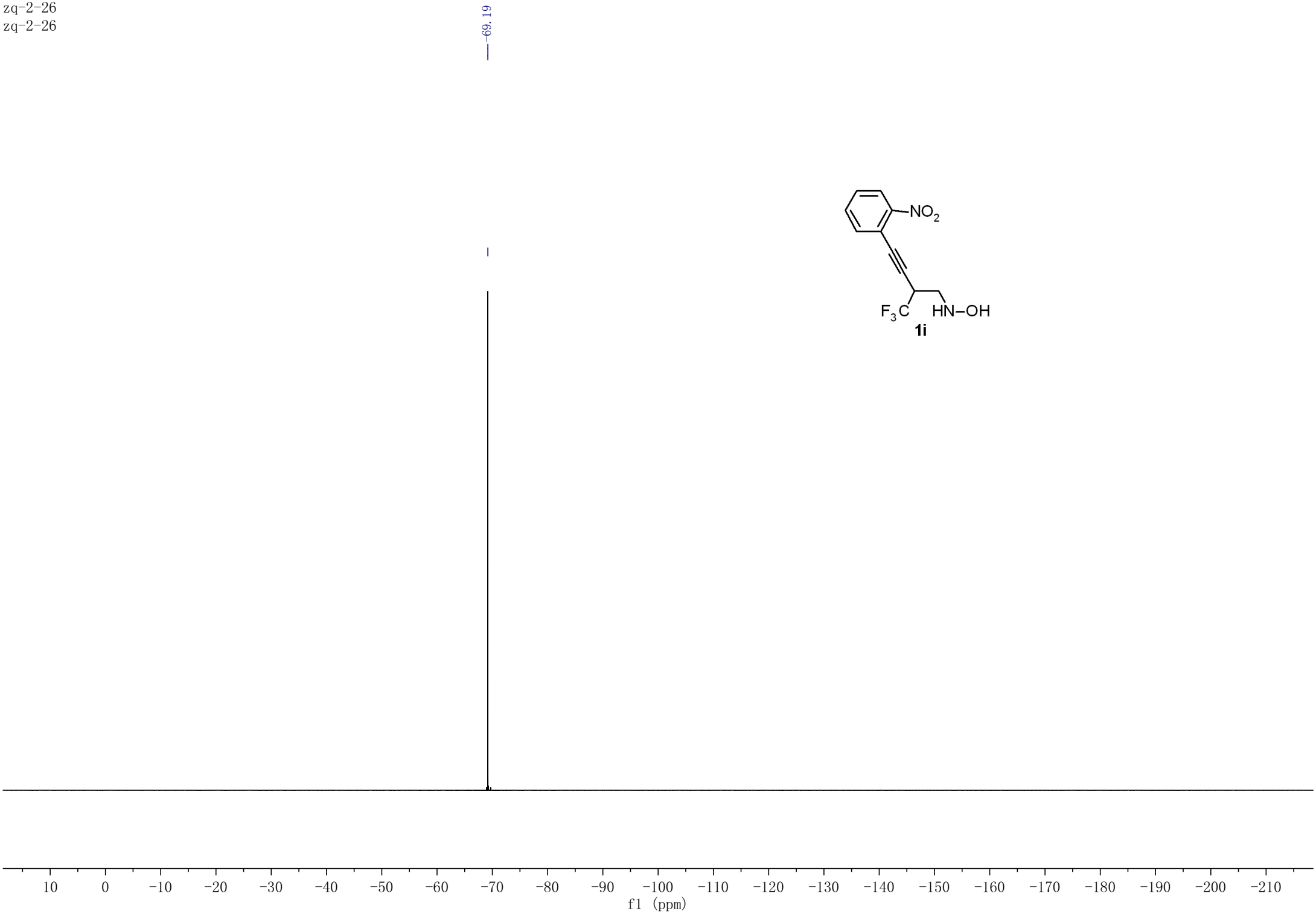
zq-2-26
zq-2-26



1i

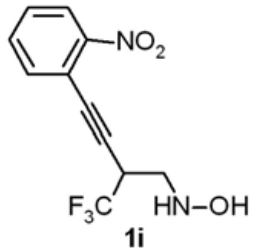
f1 (ppm)

zq-2-26
zq-2-26


-69.19
NO2
F3C
HN–OH
1i
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

zq-2-26
zq-2-26

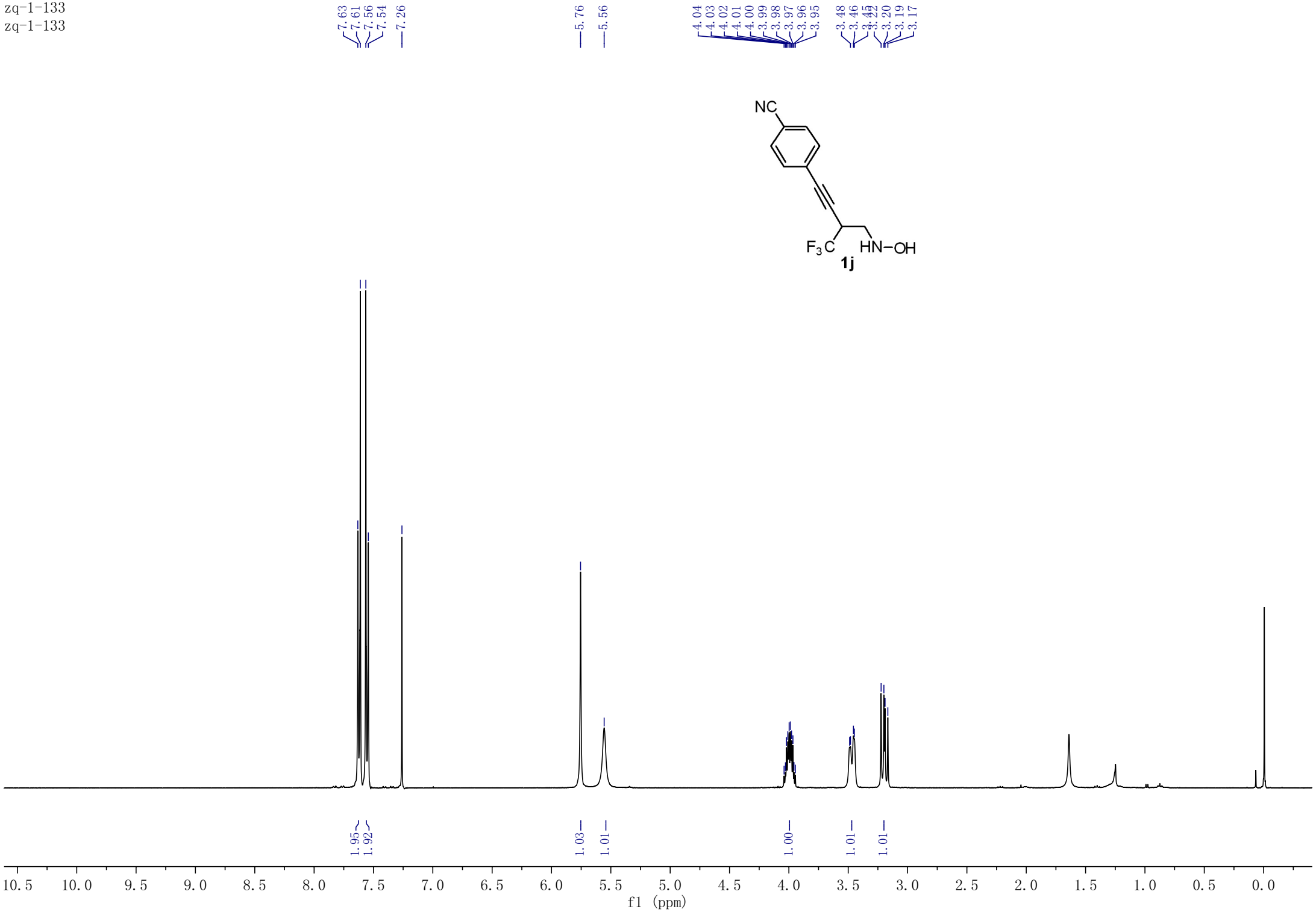
149.81
135.09
133.08
129.39
128.75
125.97
124.79
123.18
120.40
117.31
88.57
88.54
88.50
88.46
81.39
77.32
77.00
76.68
51.86
37.05
36.76
36.46
36.16



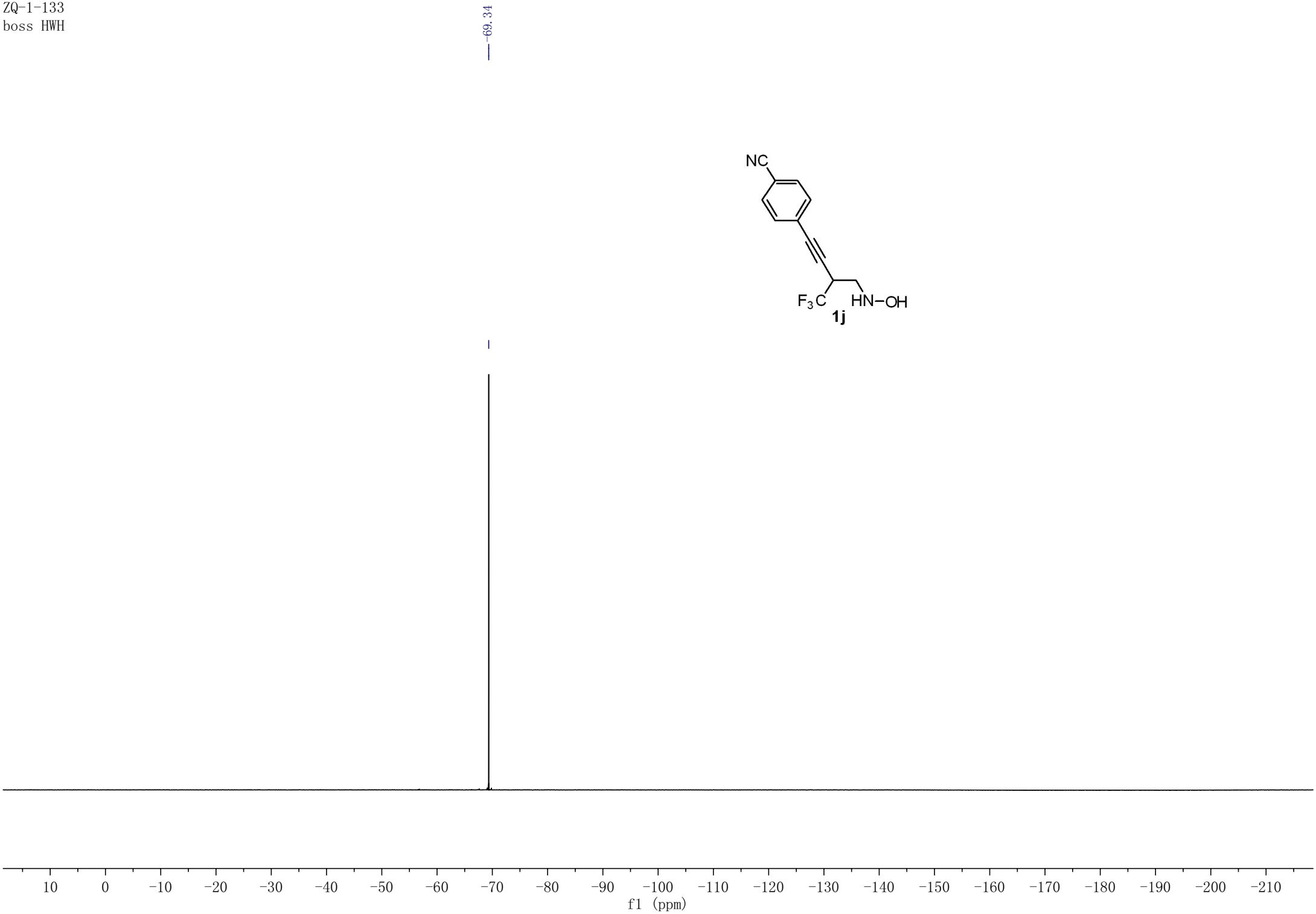
1i

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

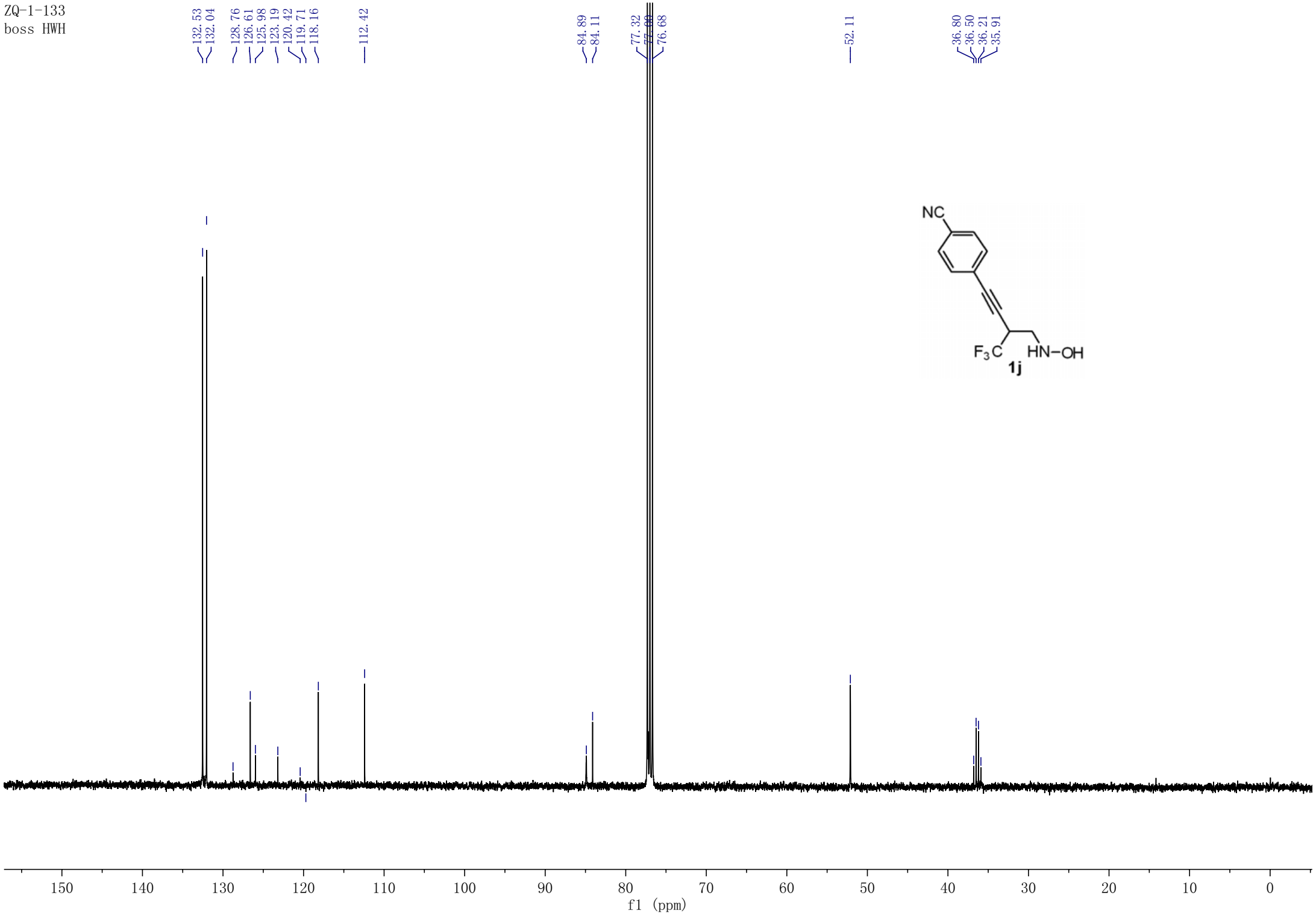
zq-1-133
zq-1-133

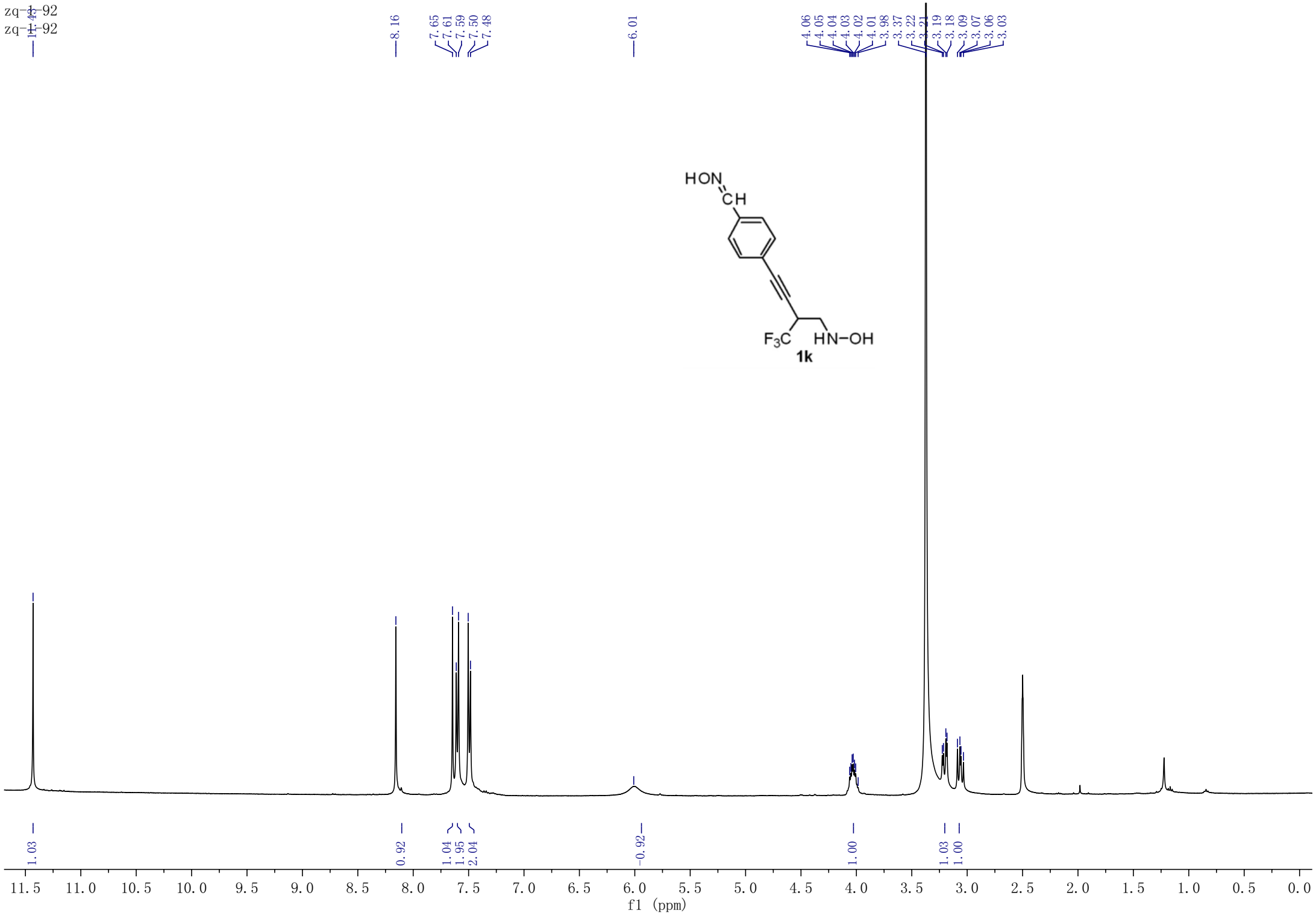


ZQ-1-133
boss HWH

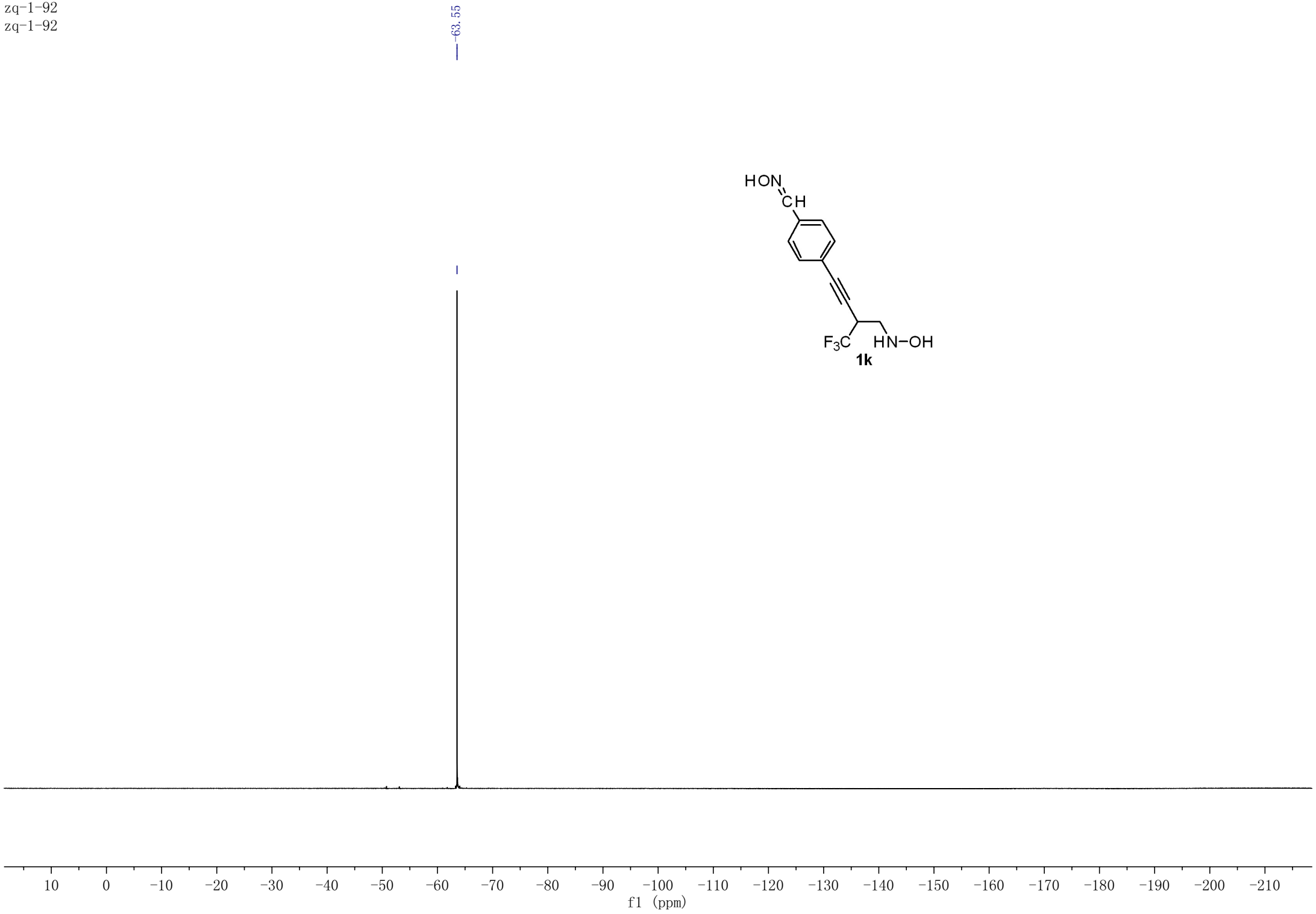


ZQ-1-133
boss HWH



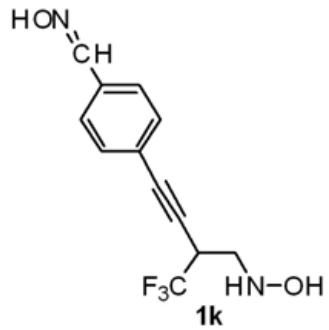

zq-1-92
zq-1-92
11.48
8.16
7.65
7.61
7.59
7.50
7.48
6.01
4.06
4.05
4.04
4.03
4.02
4.01
3.98
3.37
3.22
3.21
3.19
3.18
3.09
3.07
3.06
3.03
HON
CH
F3C
HN−OH
1k
1.03
0.92
1.04
1.95
2.04
0.92
1.00
1.03
1.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

zq-1-92
zq-1-92


-63.55
HON
CH
F3C
HN−OH
1k
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

zq-1-92
zq-1-92

148.05
134.07
132.54
127.19
127.06
124.41
122.55
84.55
84.07
53.00
40.63
40.42
40.21
40.00
39.58
39.37
36.84
36.56
36.28
35.99

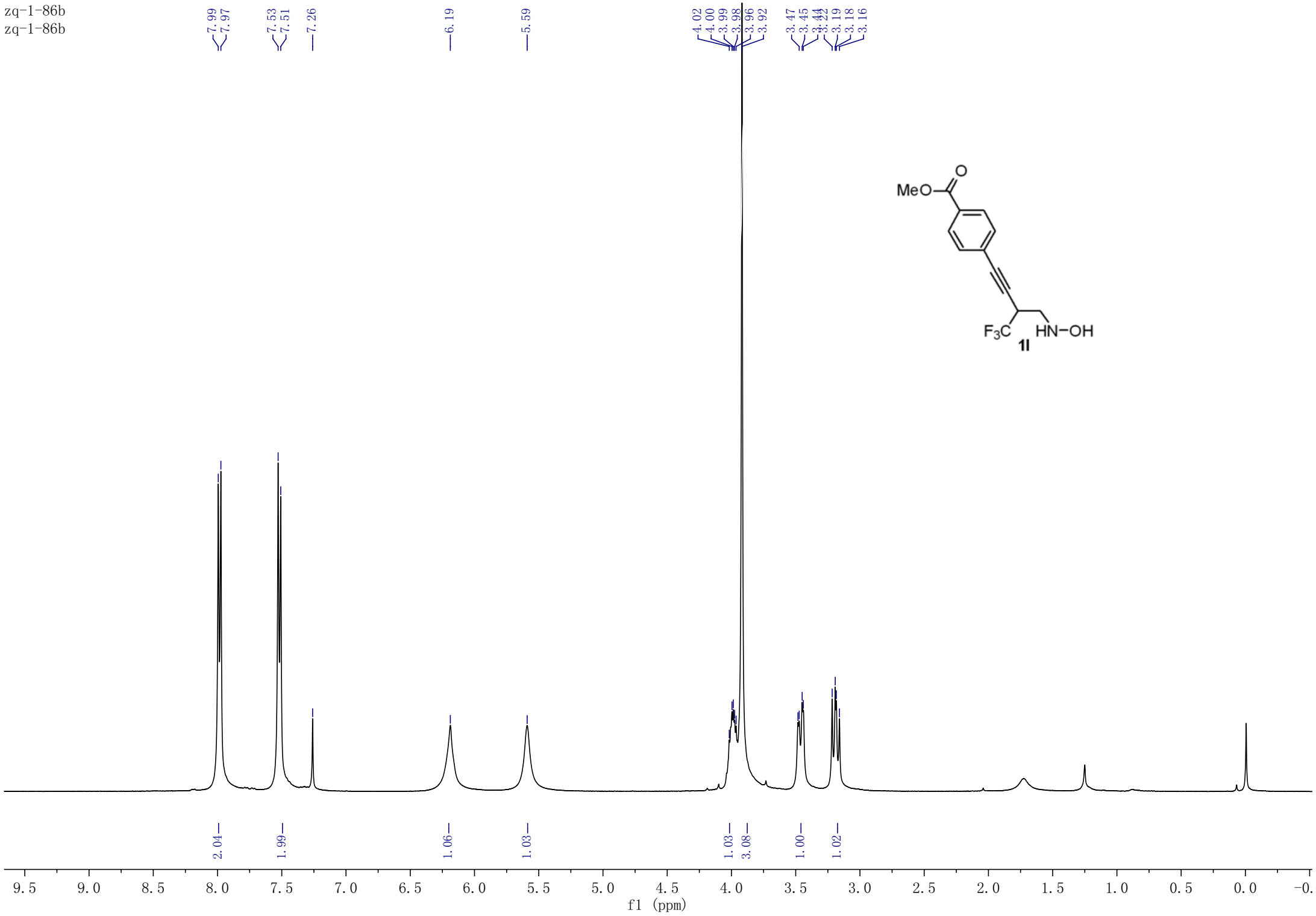


1k

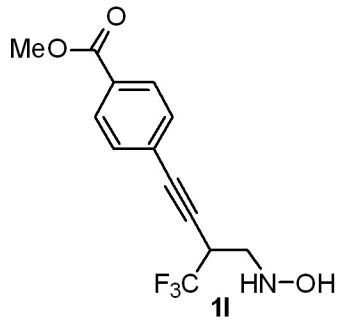
f1 (ppm)

zq-1-86b

zq-1-86b



zq-1-86b
zq-1-86b



1l

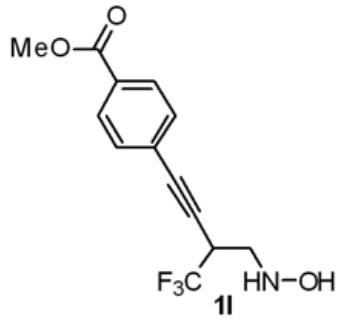
-69.46

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

f1 (ppm)

zq-1-86b
zq-1-86b

166.37
131.92
130.19
129.47
126.35
126.08
123.30
85.08
83.20
77.32
77.00
76.68
52.29
52.13
36.75
36.45
36.15
35.85



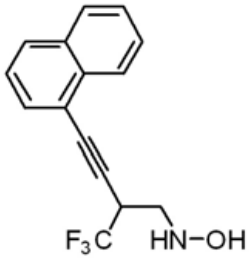
1l

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

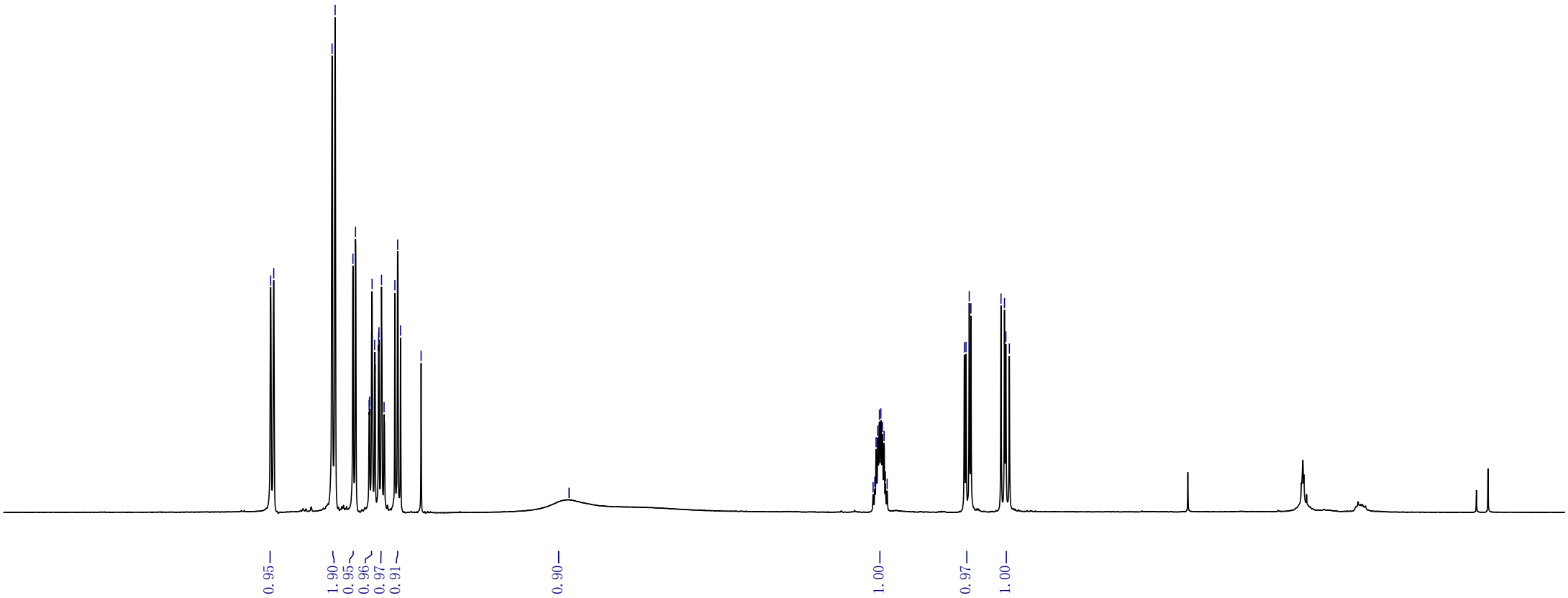
ZQ-1-43
ZQ-1-43

8.28 8.26 7.86 7.84 7.72 7.71 7.61 7.61 7.59 7.58 7.57 7.55 7.55 7.53 7.51 7.44 7.42 7.40 7.26 6.26

4.19 4.18 4.17 4.16 4.15 4.14 4.13 4.12 4.11 4.10 3.57 3.56 3.54 3.53 3.32 3.30 3.29 3.27



1m

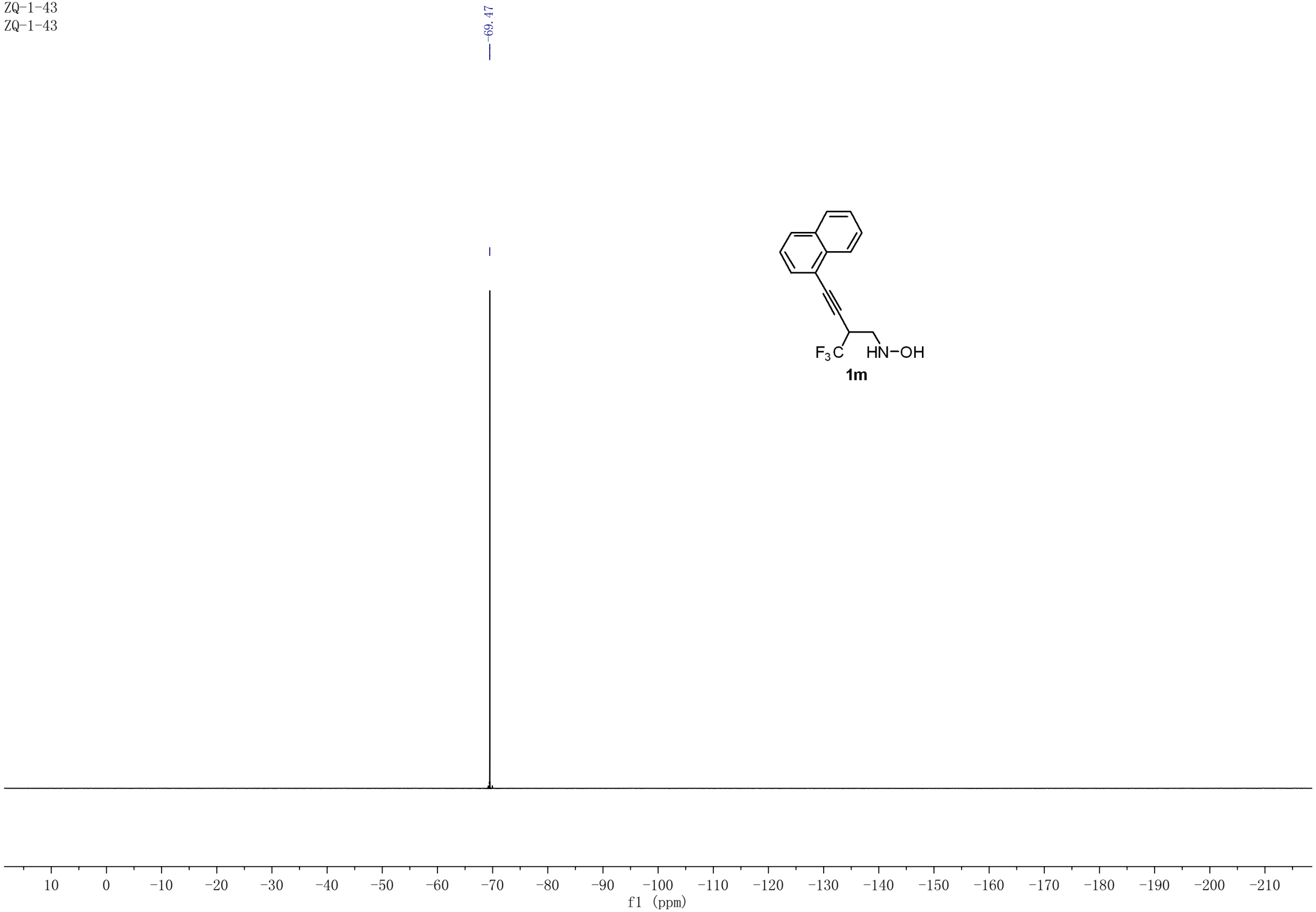


0.95 1.90 0.95 0.96 0.97 0.91 0.90 1.00 0.97 1.00

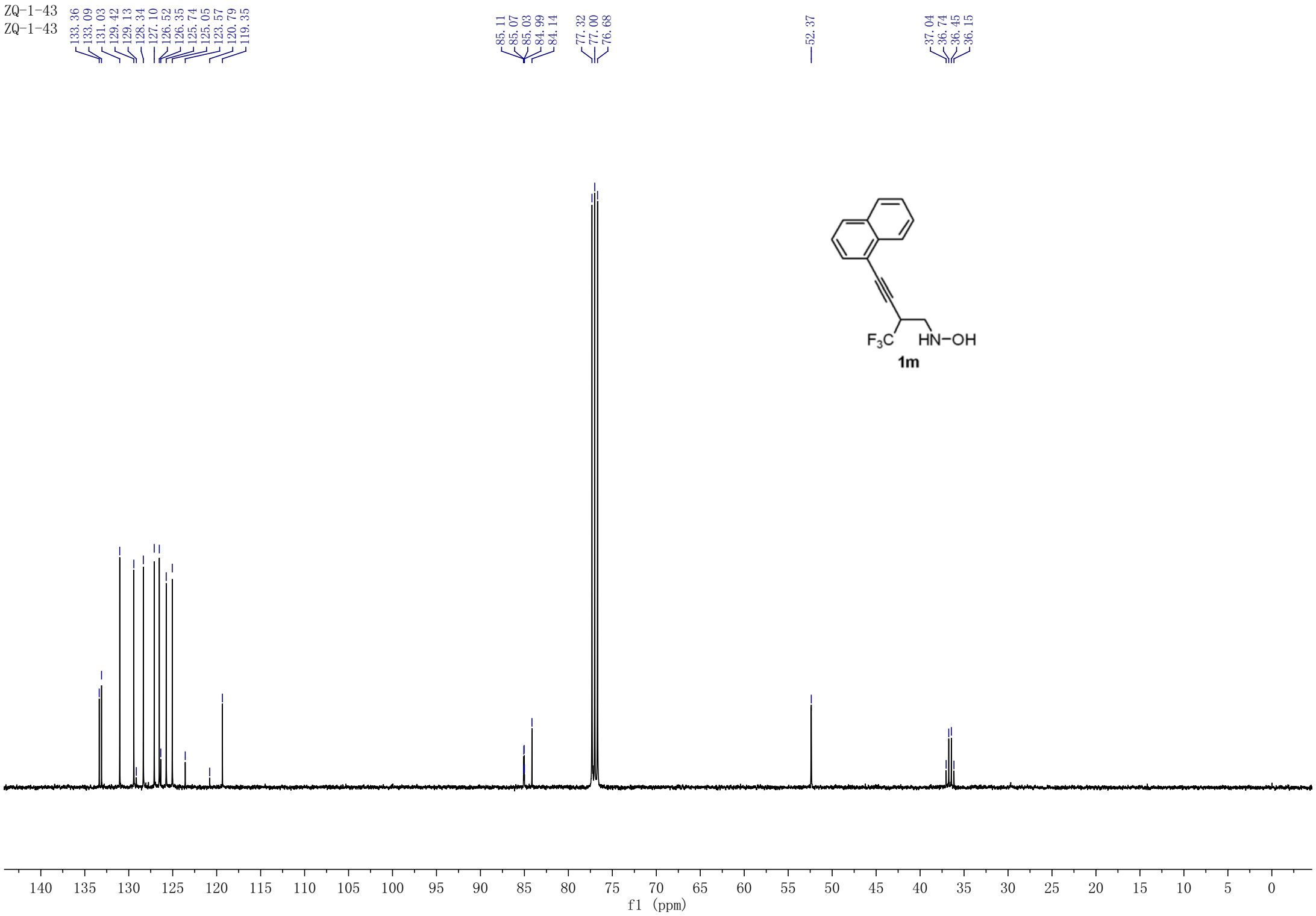
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

f1 (ppm)

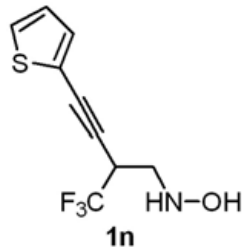
ZQ-1-43
ZQ-1-43


-69.47
F3C
HN−OH
1m
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

ZQ-1-43


ZQ-1-43
133.36
133.09
131.03
129.42
129.13
128.34
127.10
126.52
126.35
125.74
125.05
123.57
120.79
119.35
85.11
85.07
85.03
84.99
84.14
77.32
77.00
76.68
52.37
37.04
36.74
36.45
36.15
F3C
HN−OH
1m
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

zl-1-101
zl-1-101

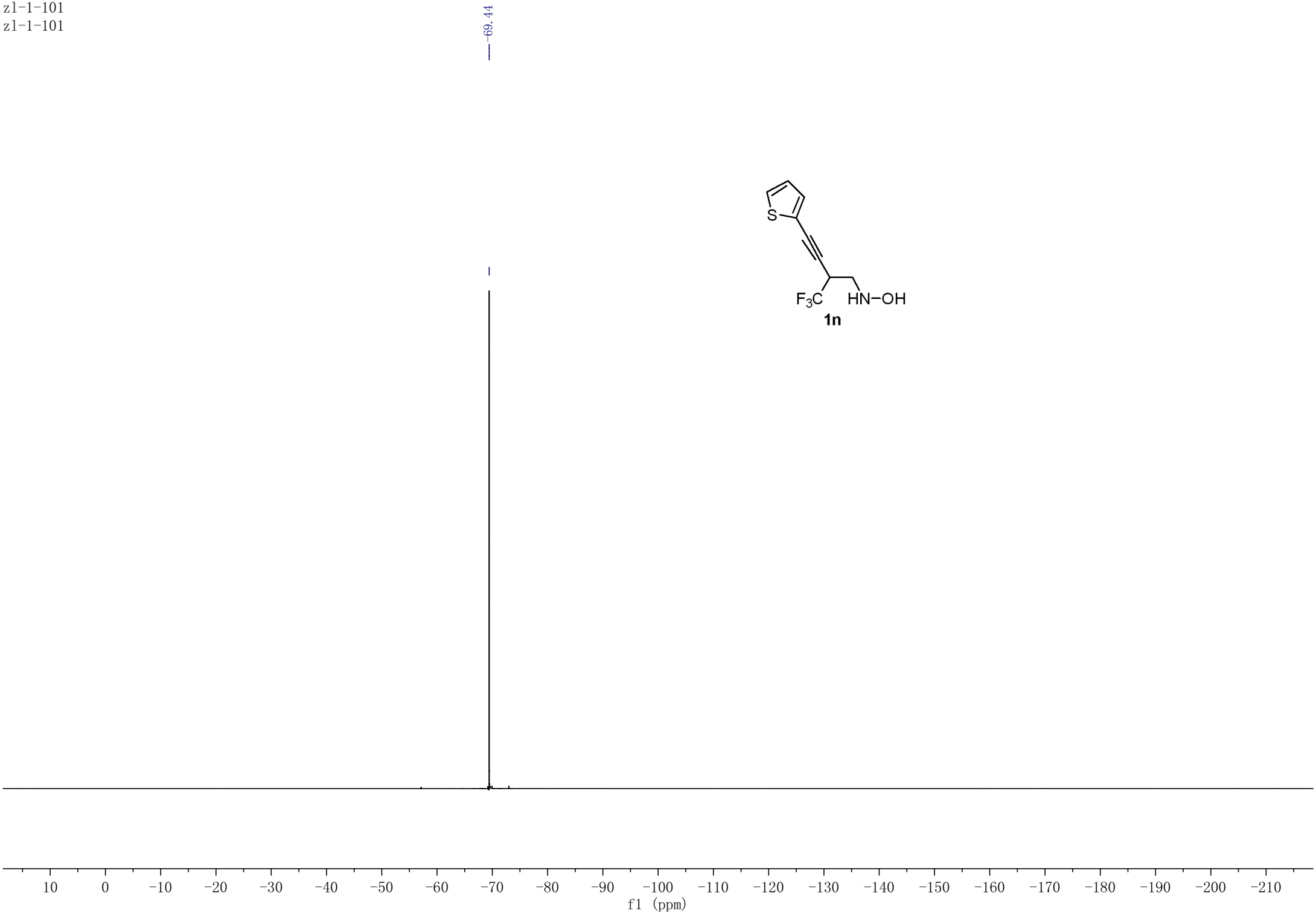


1n

f1 (ppm)

zl-1-101
zl-1-101

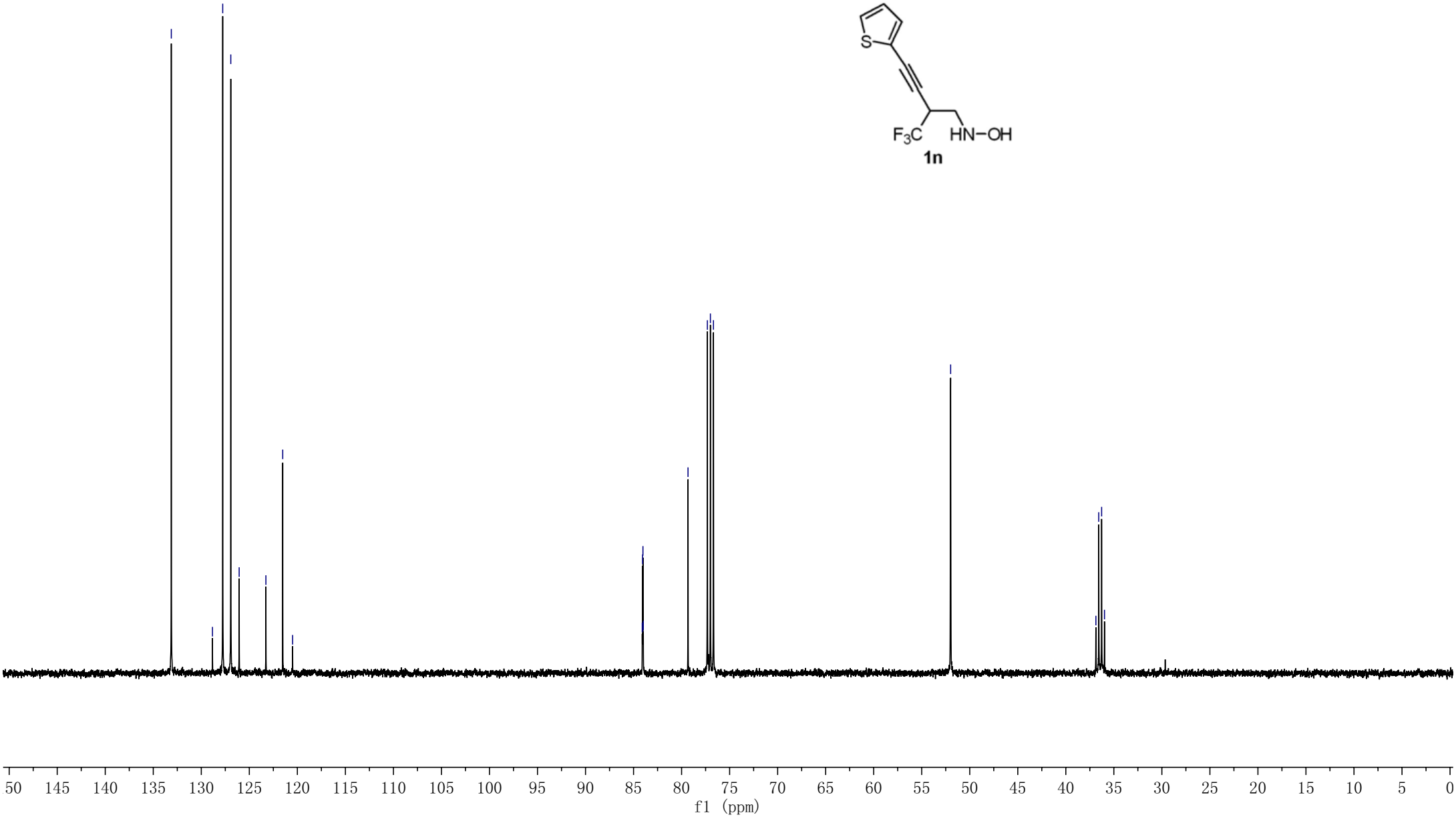
1n



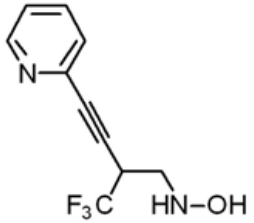
zl-1-101
zl-1-101

133.12
128.84
127.77
126.93
126.06
123.28
121.52
120.49
84.10
84.06
84.02
83.99
79.33
77.32
77.00
76.68
51.99
36.87
36.57
36.27
35.97

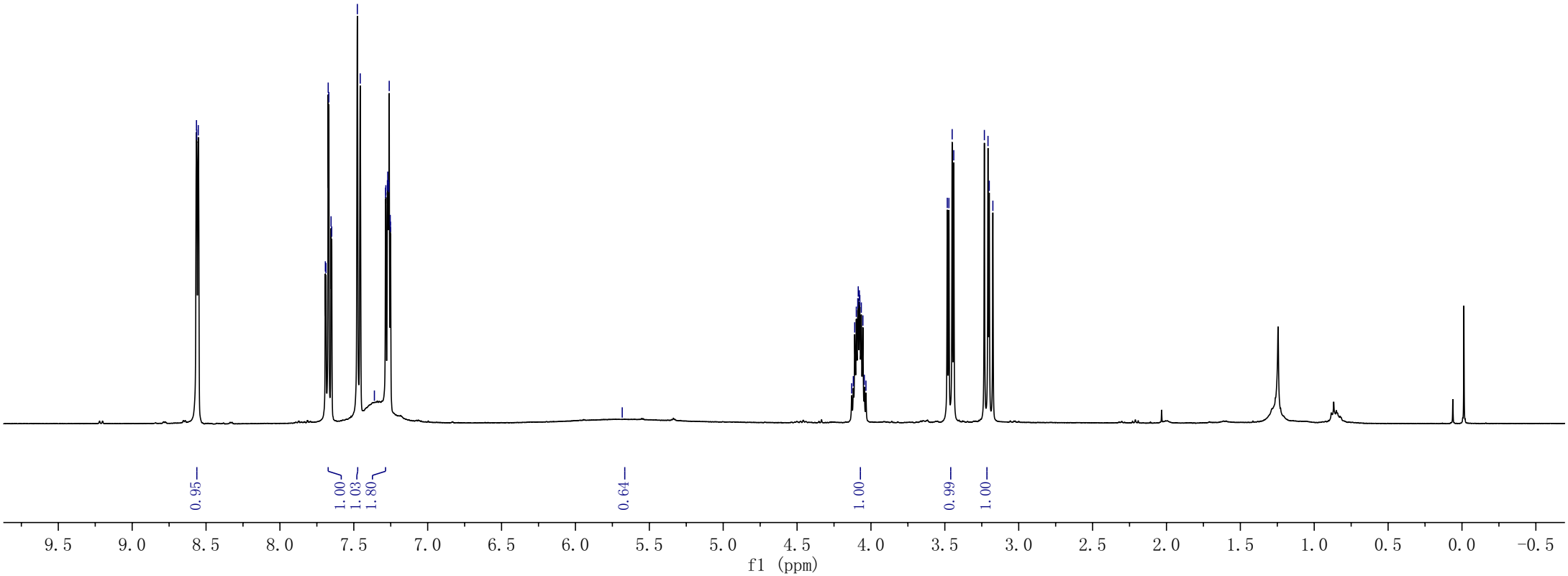
1n



zq-2-40
zq-2-40

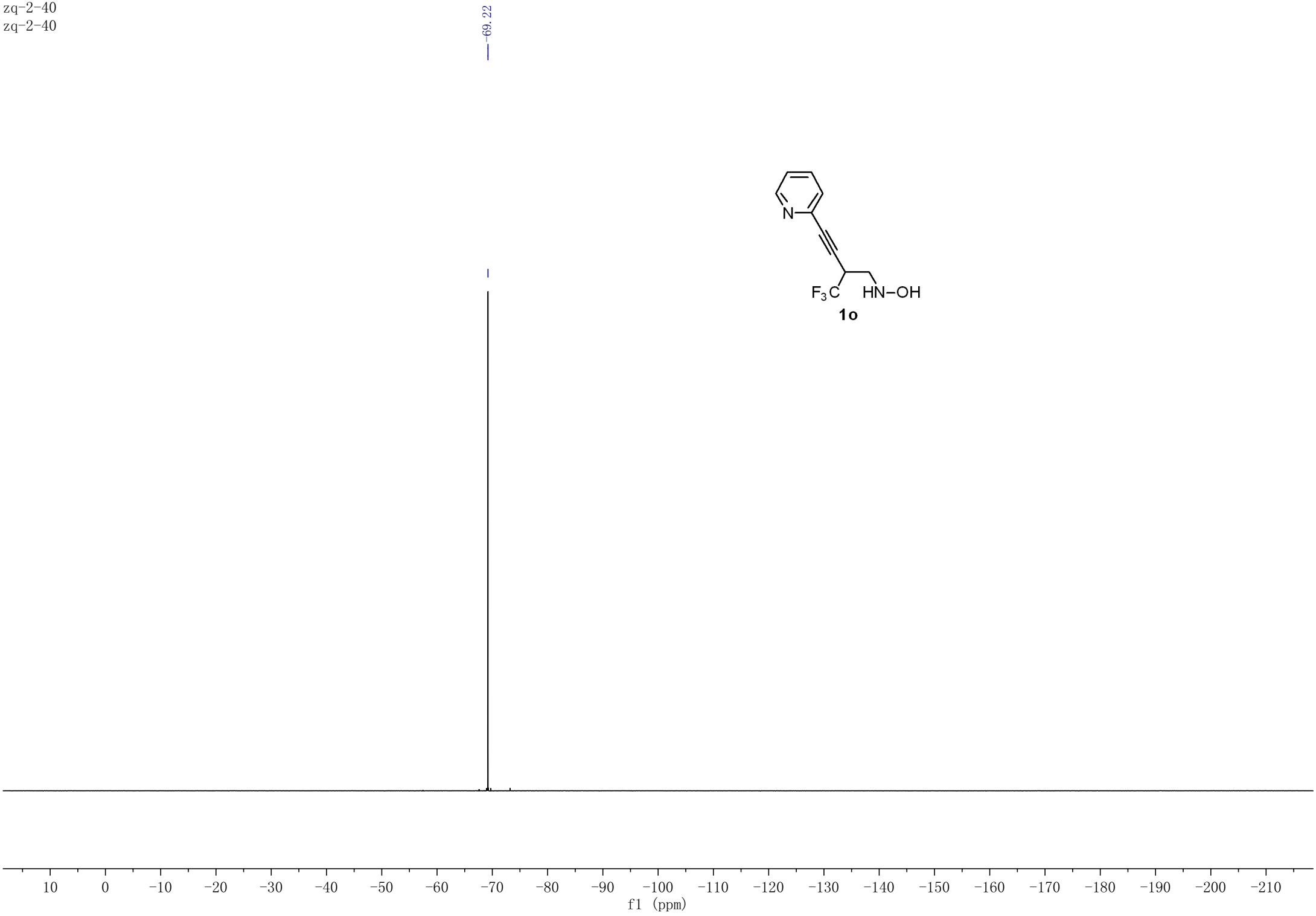


1o



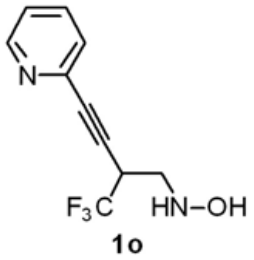
zq-2-40
zq-2-40

1o



zq-2-40
zq-2-40

149.74
141.99
128.89
127.45
126.11
123.49
123.33
120.55
84.72
81.28
77.32
77.00
76.68
52.03
36.66
36.36
36.07
35.77



1o

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

zq-2-23
zq-2-23

7.26

6.24 6.18 6.18 6.17 6.17

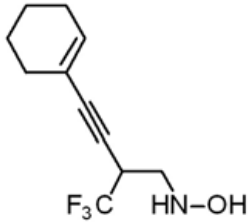
5.54

3.88 3.87 3.86 3.85 3.84 3.83 3.82 3.81 3.80 3.79

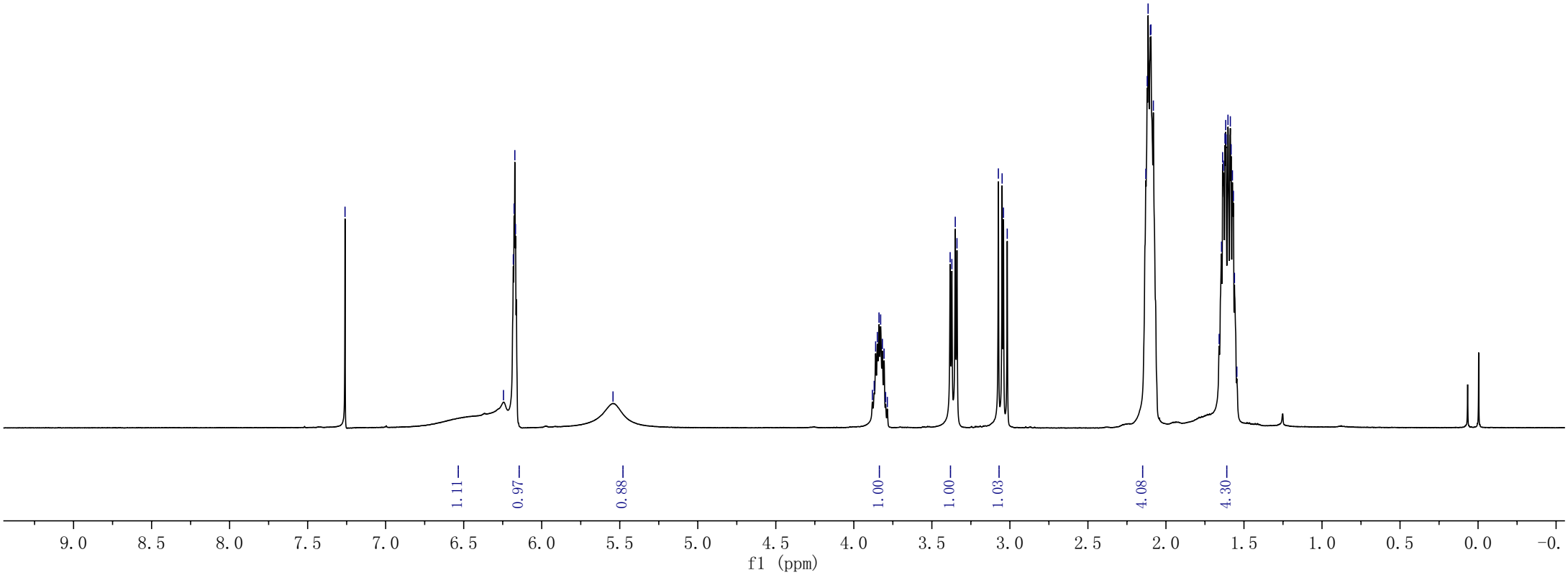
3.38 3.35 3.34 3.07 3.05 3.04 3.02

2.13 2.12 2.11 2.10 2.10 2.08

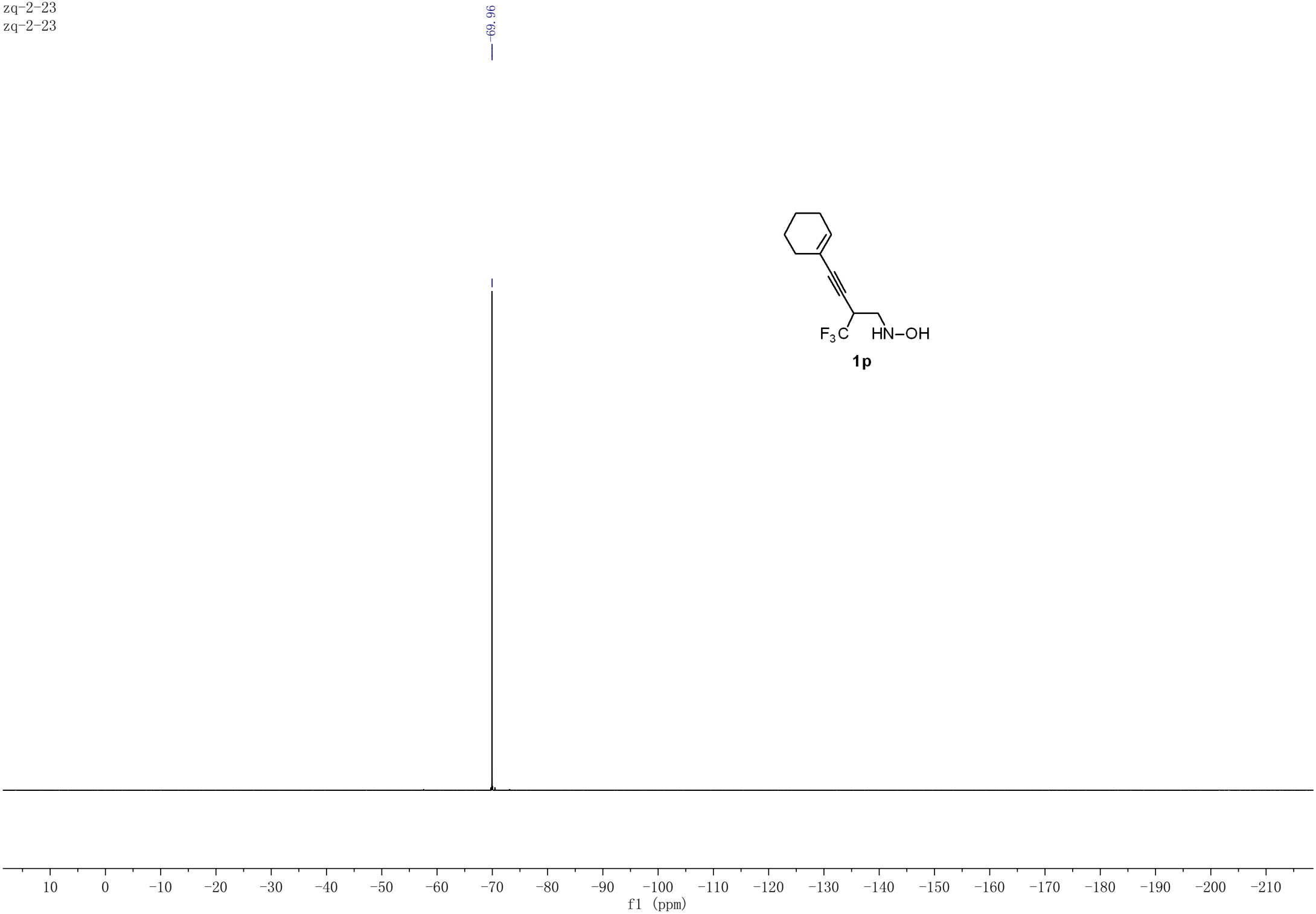
1.66 1.64 1.64 1.63 1.62 1.62 1.61 1.60 1.59 1.58 1.57 1.57 1.56 1.55



1p



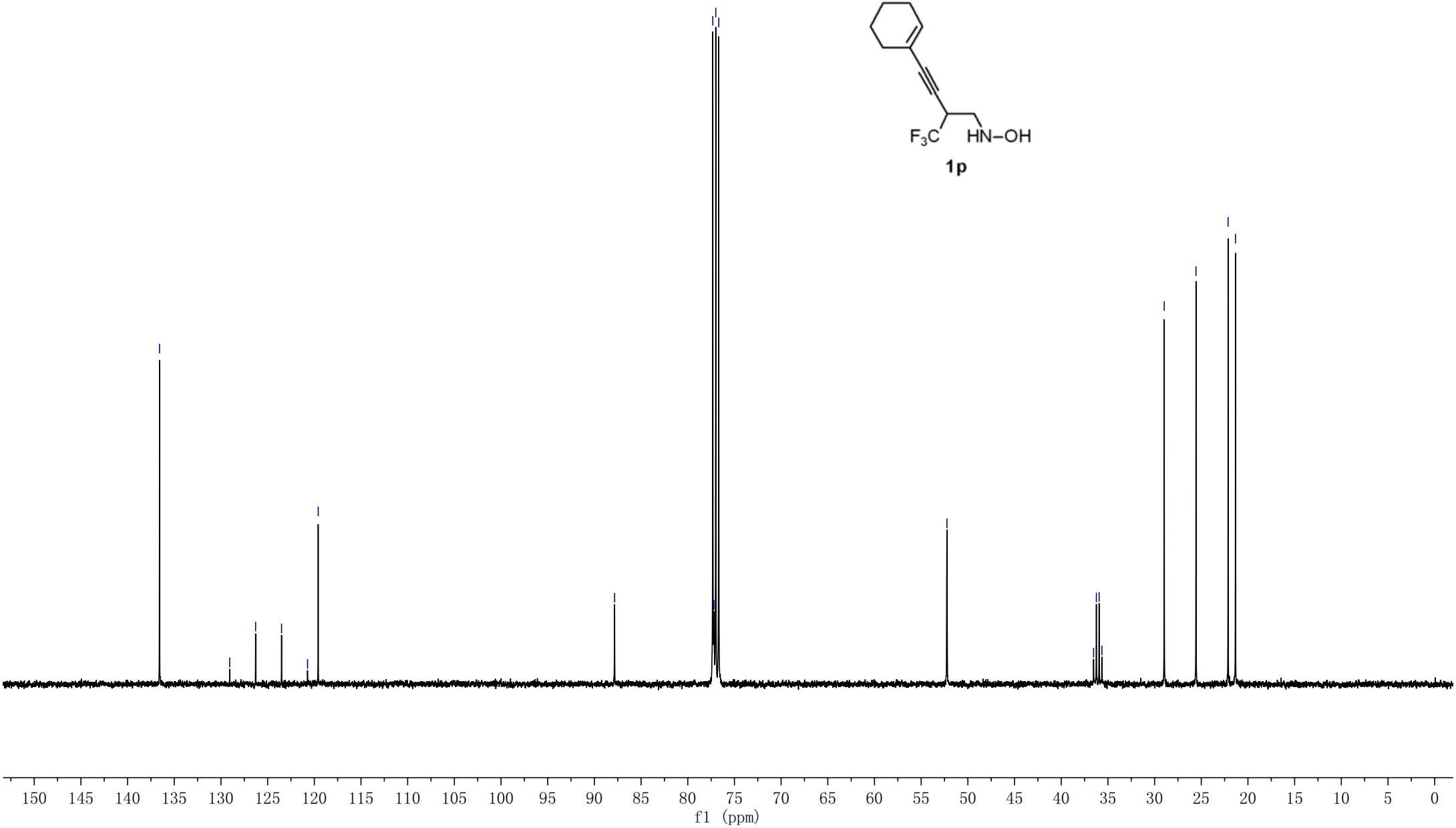
zq-2-23
zq-2-23


-69.96
F3C
HN–OH
1p
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

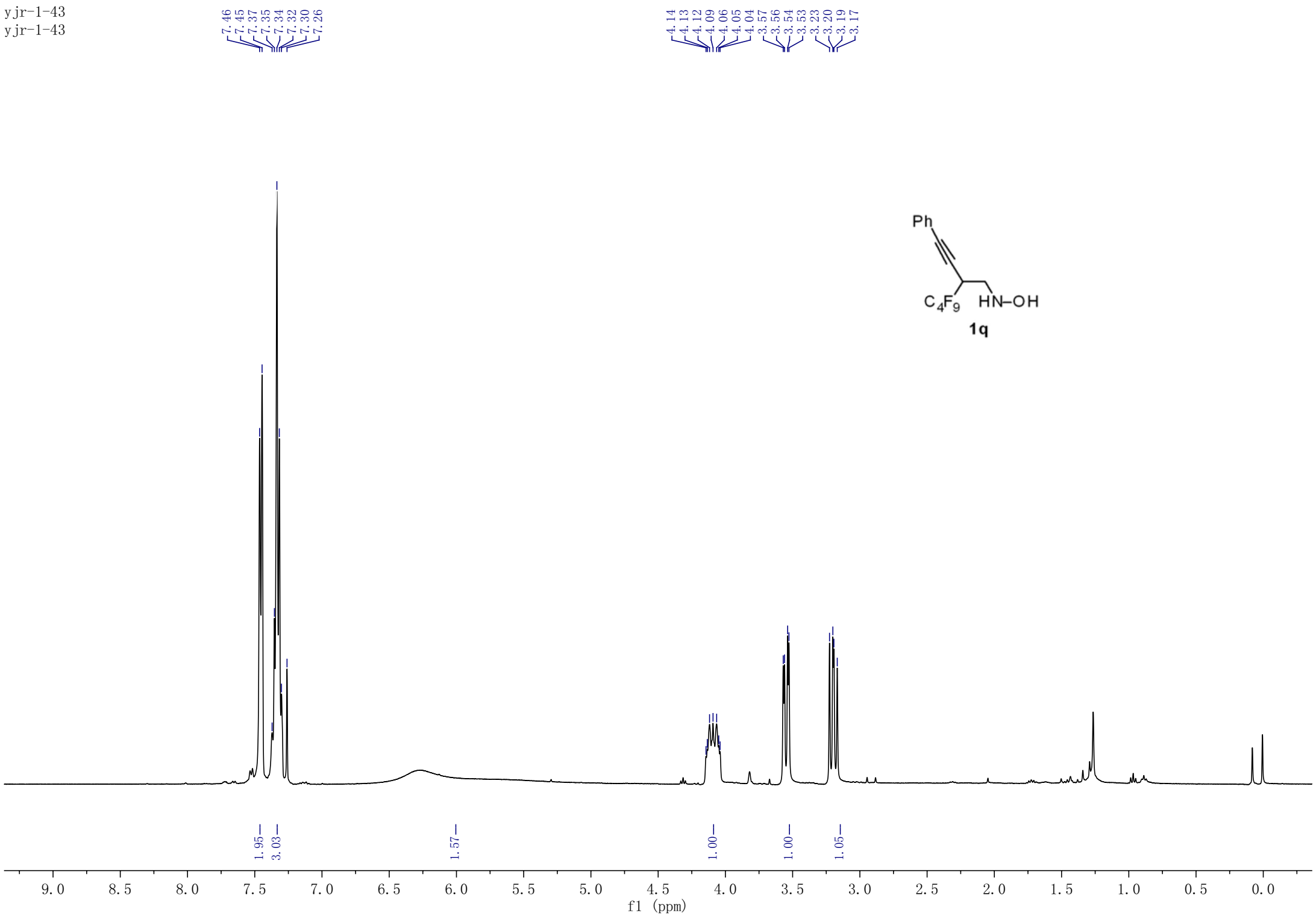
zq-2-23
zq-2-23

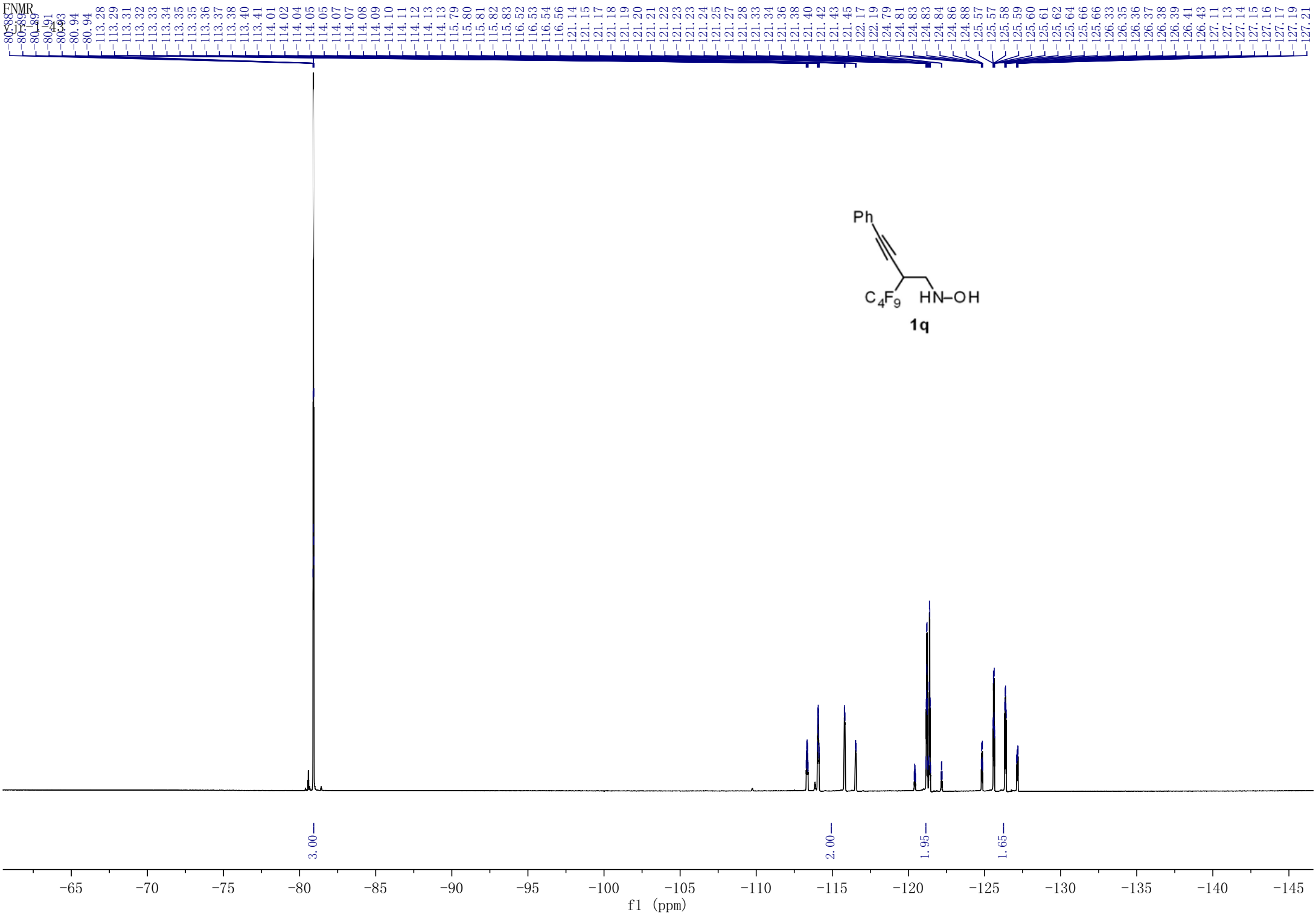
136.58
129.07
126.29
123.51
120.73
119.58
87.84
77.32
77.20
77.00
76.68
52.24
36.53
36.24
35.94
35.64
28.97
25.56
22.12
21.34

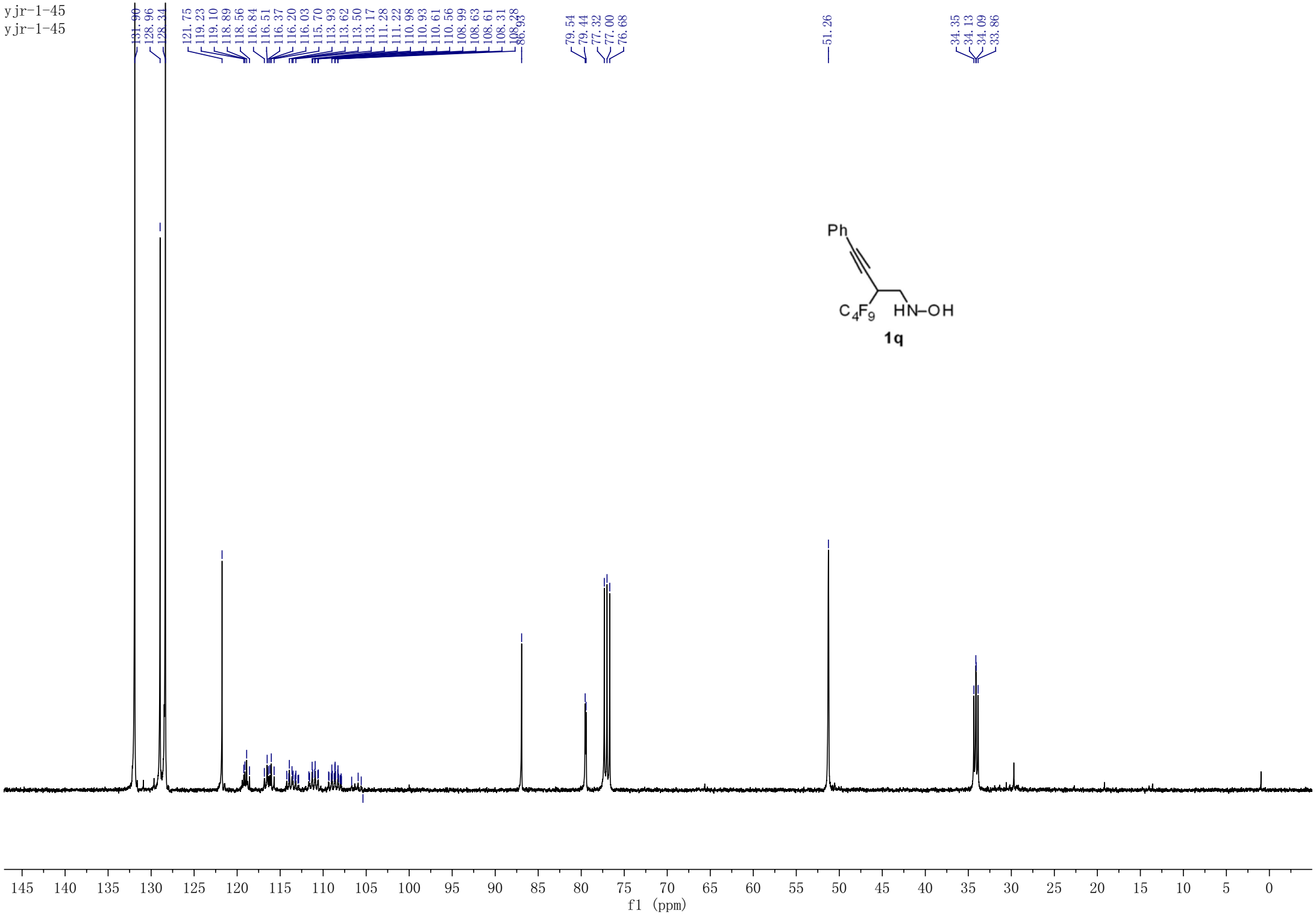
1p

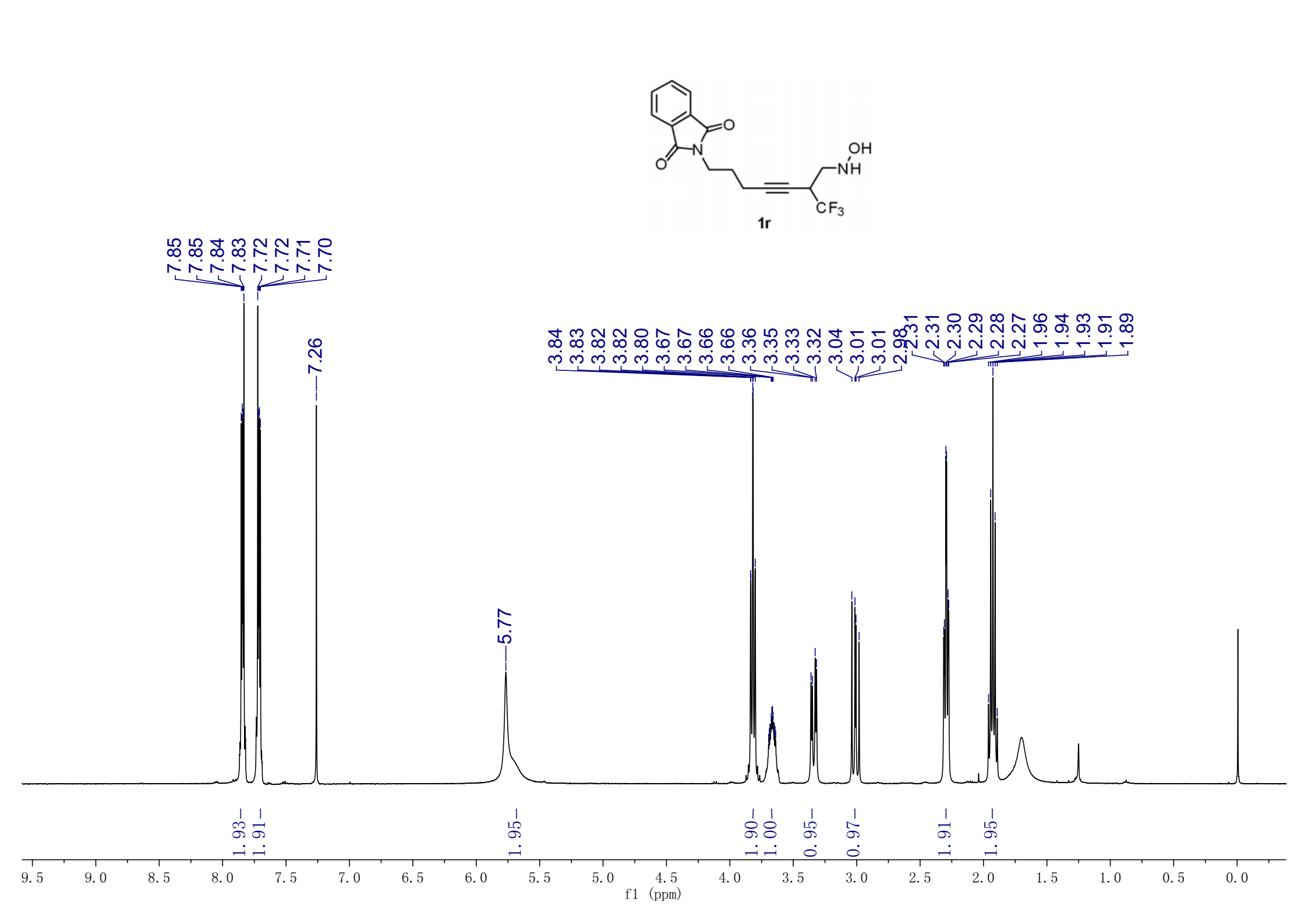


yjr-1-43
yjr-1-43

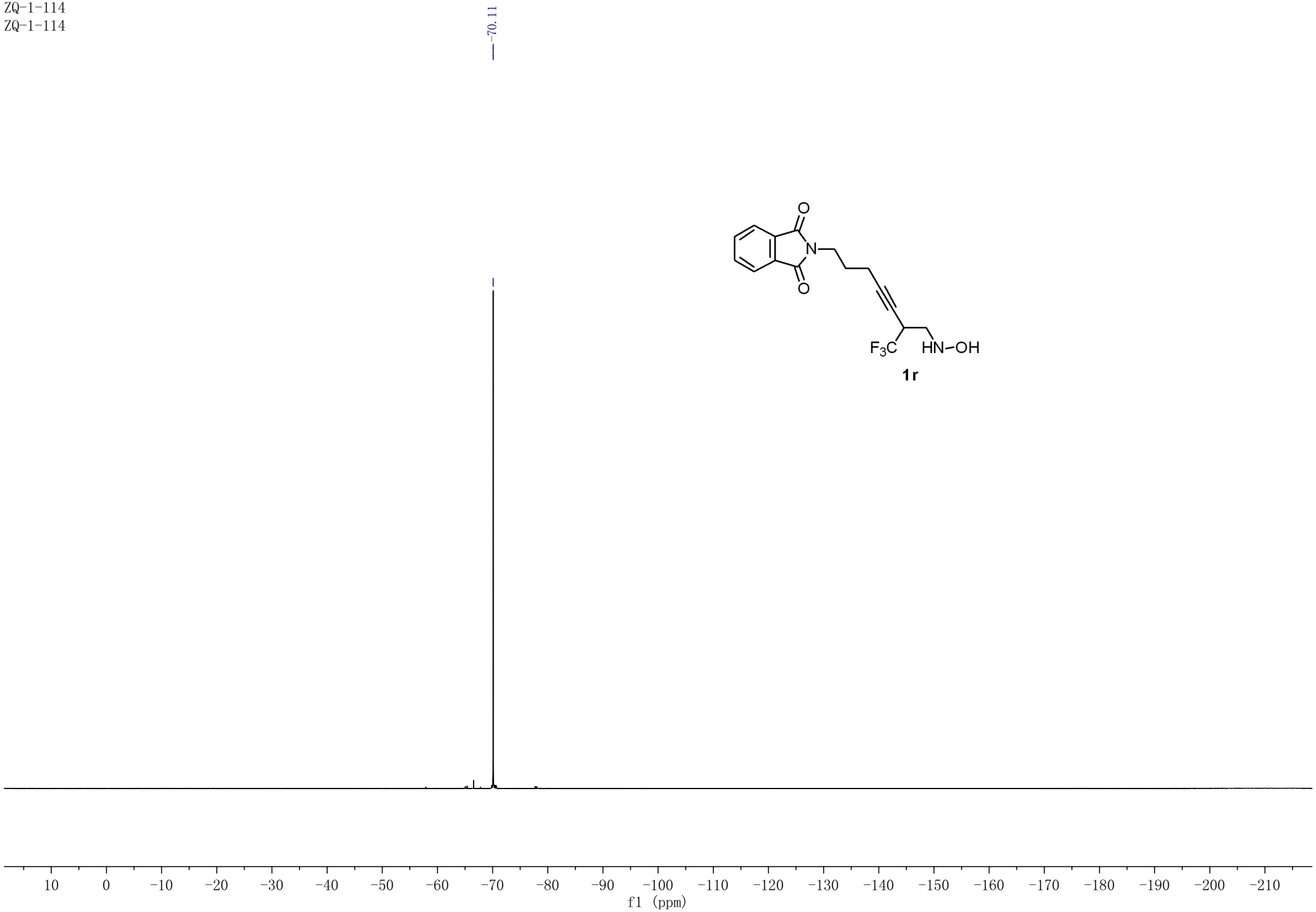


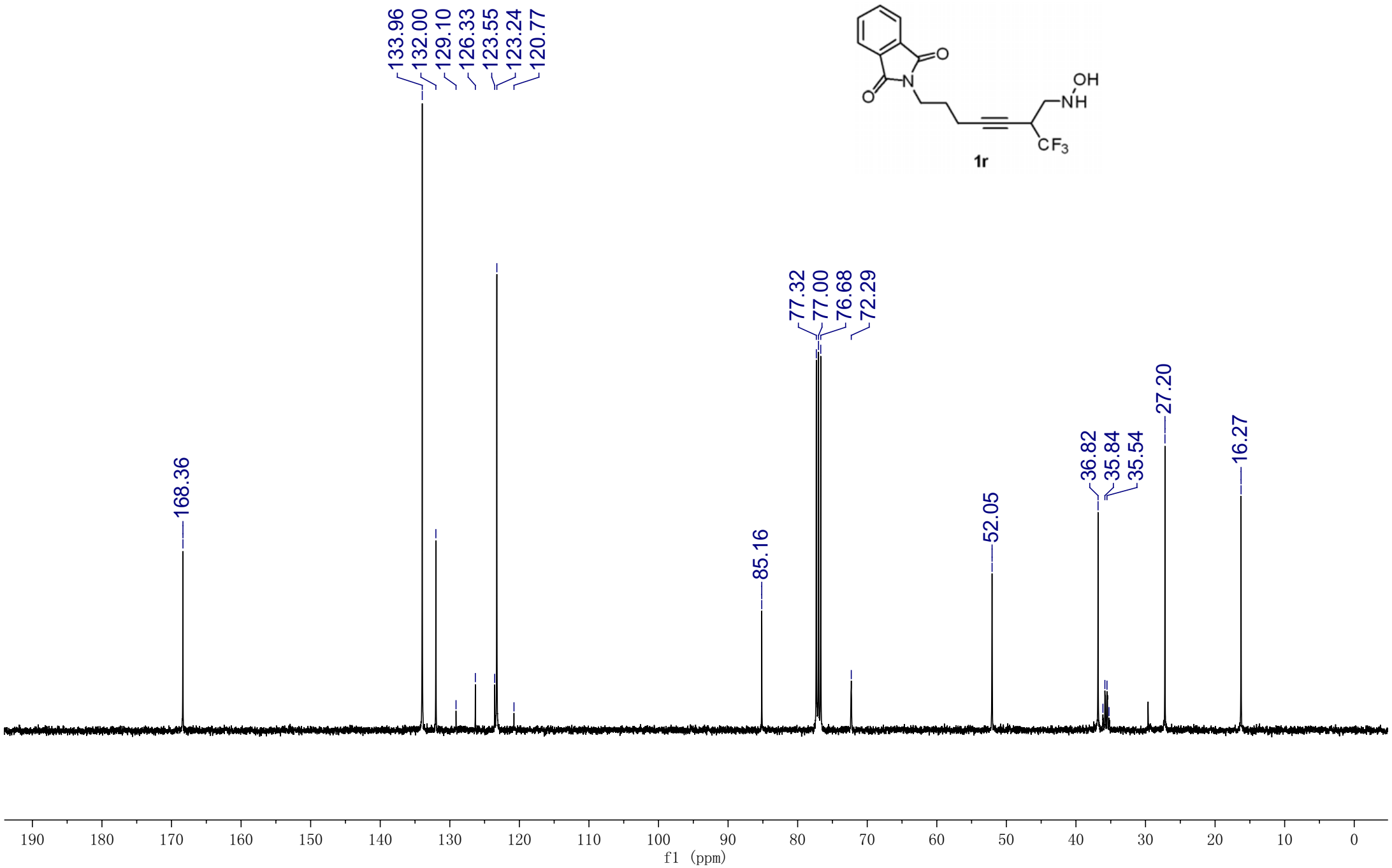

FNMR
Ph
C4F9
HN–OH
1q
3.00
2.00
1.95
1.65
f1 (ppm)


yjr-1-45
yjr-1-45
131.90
128.96
128.34
121.75
119.23
119.10
118.89
118.56
116.84
116.51
116.37
116.20
116.03
115.70
113.93
113.62
113.50
113.17
111.28
111.22
110.98
110.93
110.61
110.56
108.99
108.63
108.61
108.31
108.28
88.93
79.54
79.44
77.32
77.00
76.68
51.26
34.35
34.13
34.09
33.86
Ph
C4F9
HN–OH
1q
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

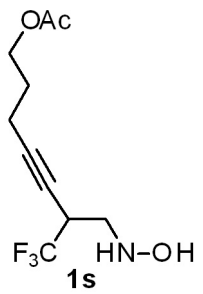

O
O
N
OH
NH
CF3
1r
7.85
7.85
7.84
7.83
7.72
7.72
7.71
7.70
7.26
5.77
3.84
3.83
3.82
3.82
3.80
3.67
3.67
3.66
3.66
3.36
3.35
3.33
3.32
3.04
3.01
3.01
2.98
2.31
2.31
2.30
2.29
2.28
2.27
1.96
1.94
1.93
1.91
1.89
1.93
1.91
1.95
1.90
1.00
0.95
0.97
1.91
1.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

ZQ-1-114
ZQ-1-114



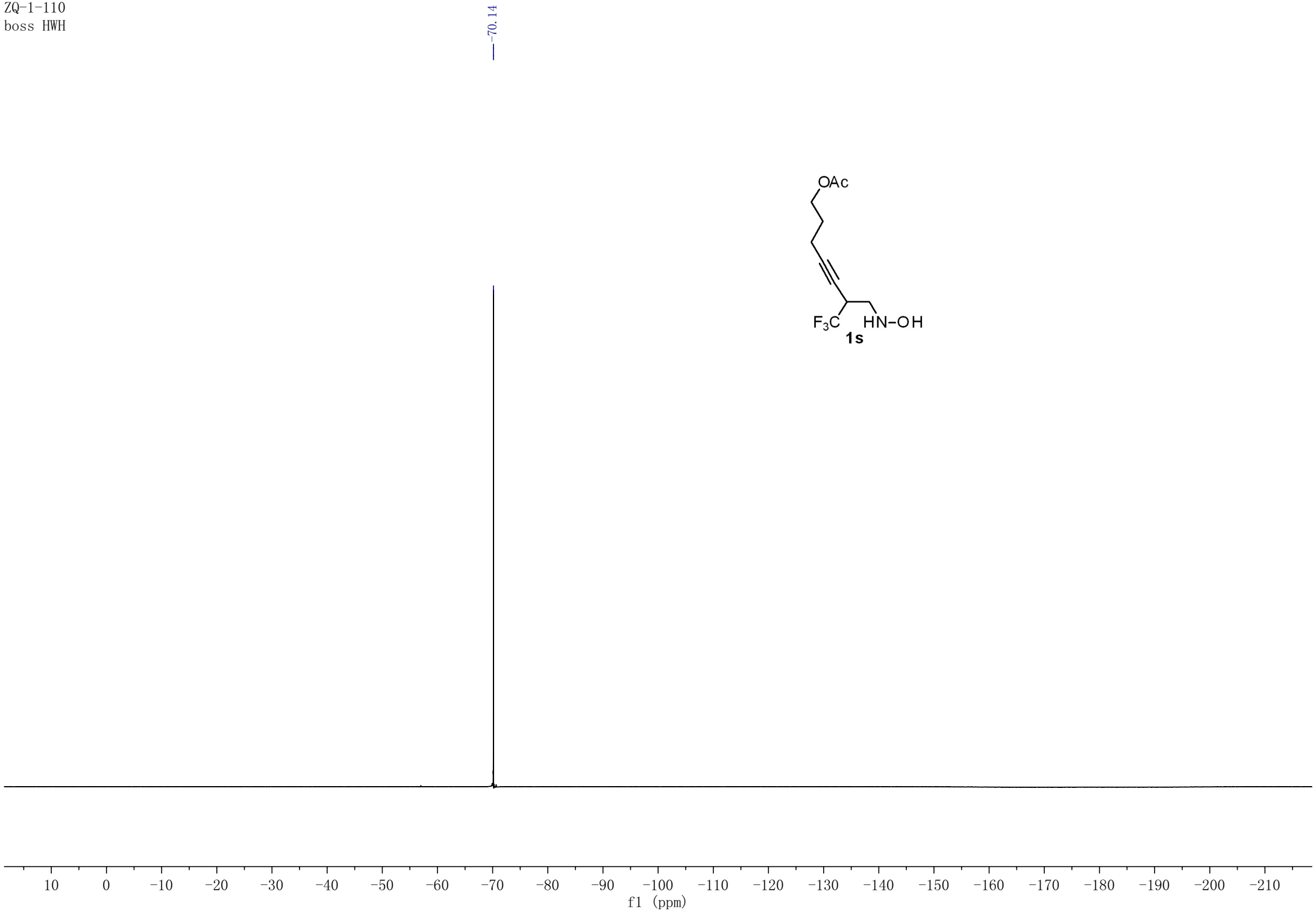

133.96
132.00
129.10
126.33
123.55
123.24
120.77
77.32
77.00
76.68
72.29
168.36
85.16
52.05
36.82
35.84
35.54
27.20
16.27
O
O
N
OH
NH
CF3
1r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

ZQ-1-110
boss HWH



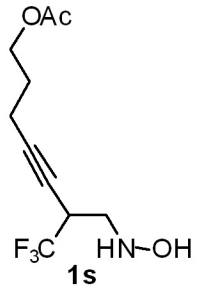
1s

ZQ-1-110
boss HWH

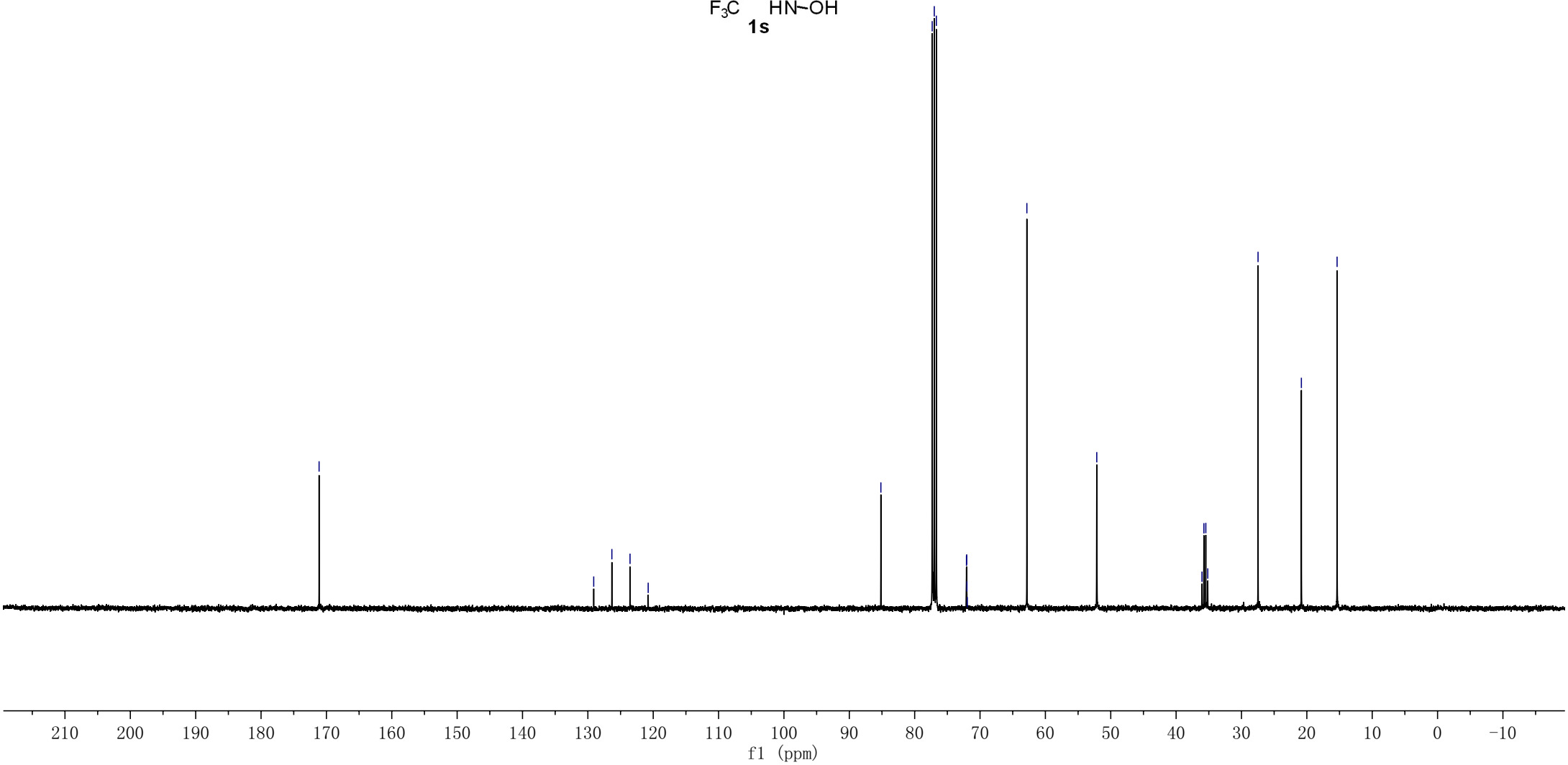


ZQ-1-110
boss HWH

171.12
129.10
126.33
123.55
120.77
85.17
77.32
77.00
76.68
72.08
72.04
72.01
71.96
62.83
52.14
36.05
35.75
35.45
35.16
27.47
20.84
15.37



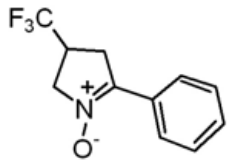
1s



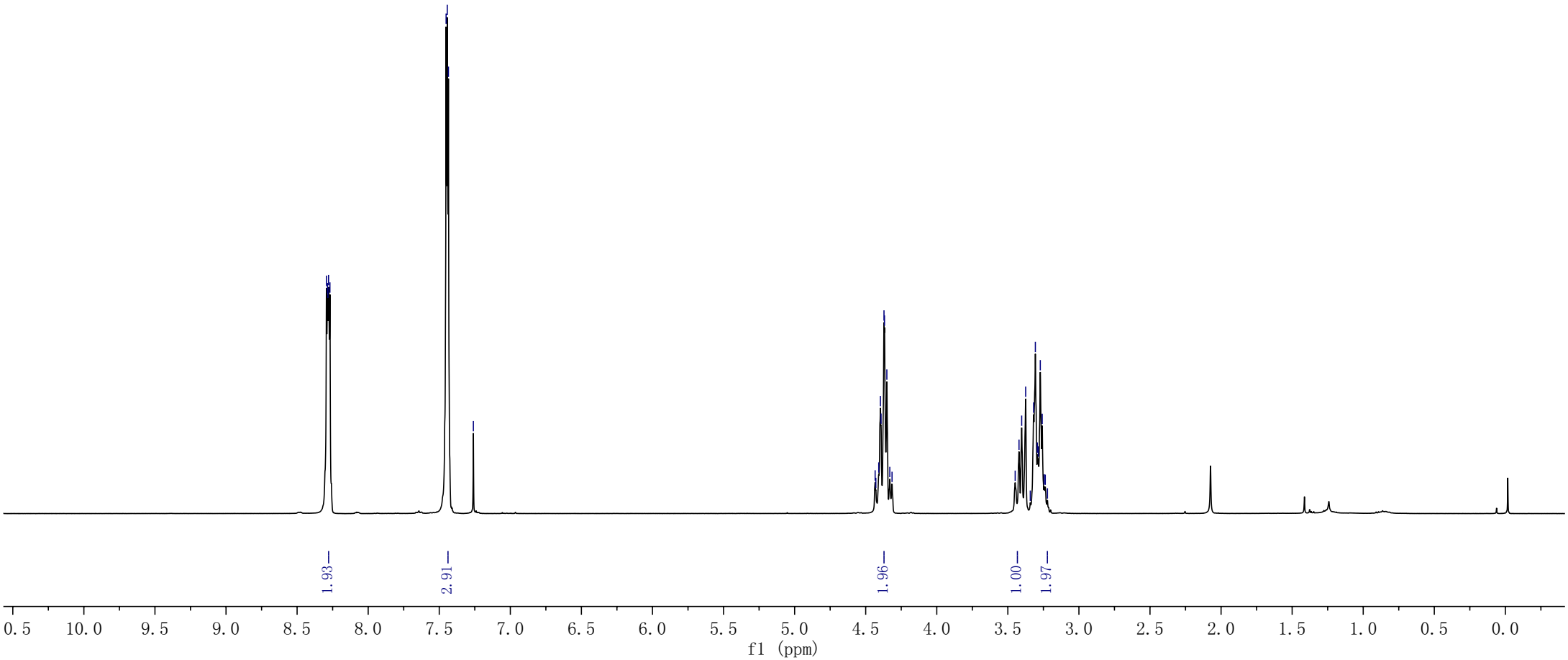
xiaoyj01-05-2-2
xiaoyj01-05-2-2

8.29 8.29 8.28 8.28 8.27 7.45 7.44 7.44 7.26

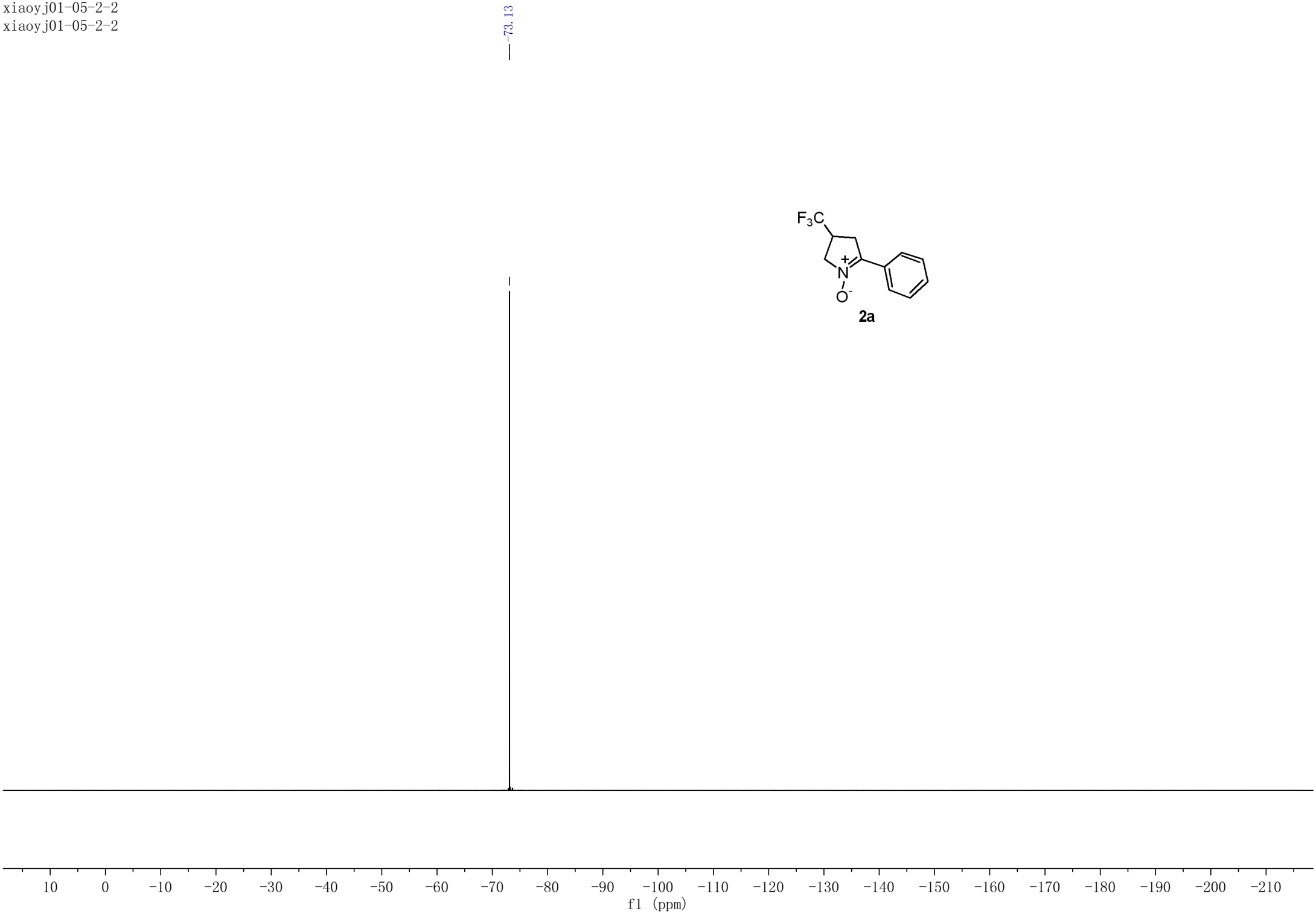
4.43 4.43 4.41 4.40 4.39 4.37 4.37 4.35 4.33 4.31 3.45 3.42 3.40 3.37 3.34 3.32 3.31 3.29 3.29 3.27 3.26 3.24 3.24 3.22



2a



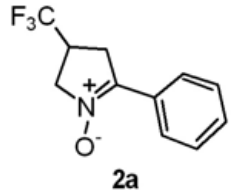
xiaoyj01-05-2-2
xiaoyj01-05-2-2



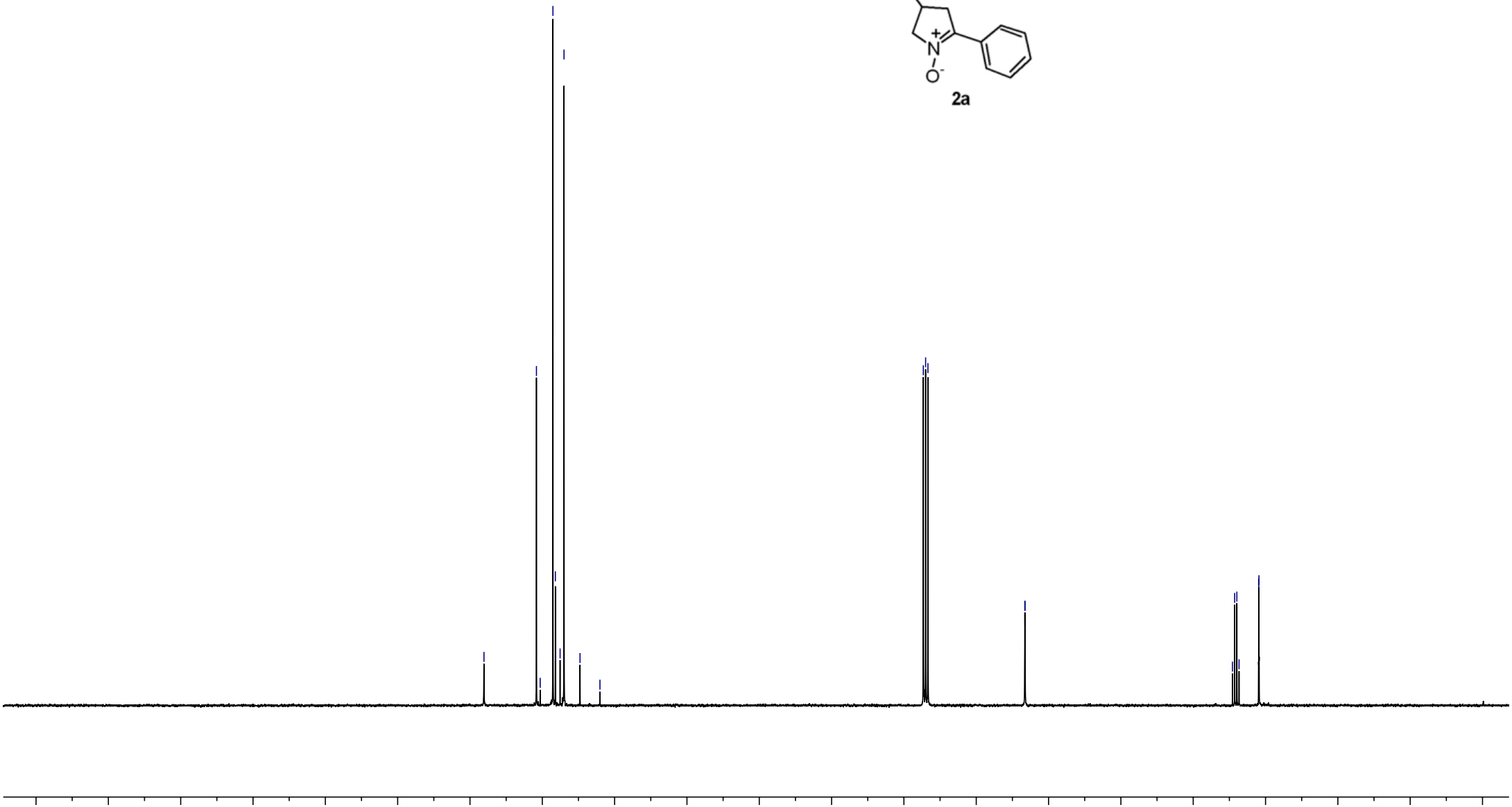
xiaoyj01-05-2-2

xiaoyj01-05-2-2

138.07
130.81
130.30
128.53
128.19
127.54
127.00
124.79
122.03
77.32
77.00
76.68
63.28
63.26
34.57
34.27
33.97
33.66
30.94
30.91



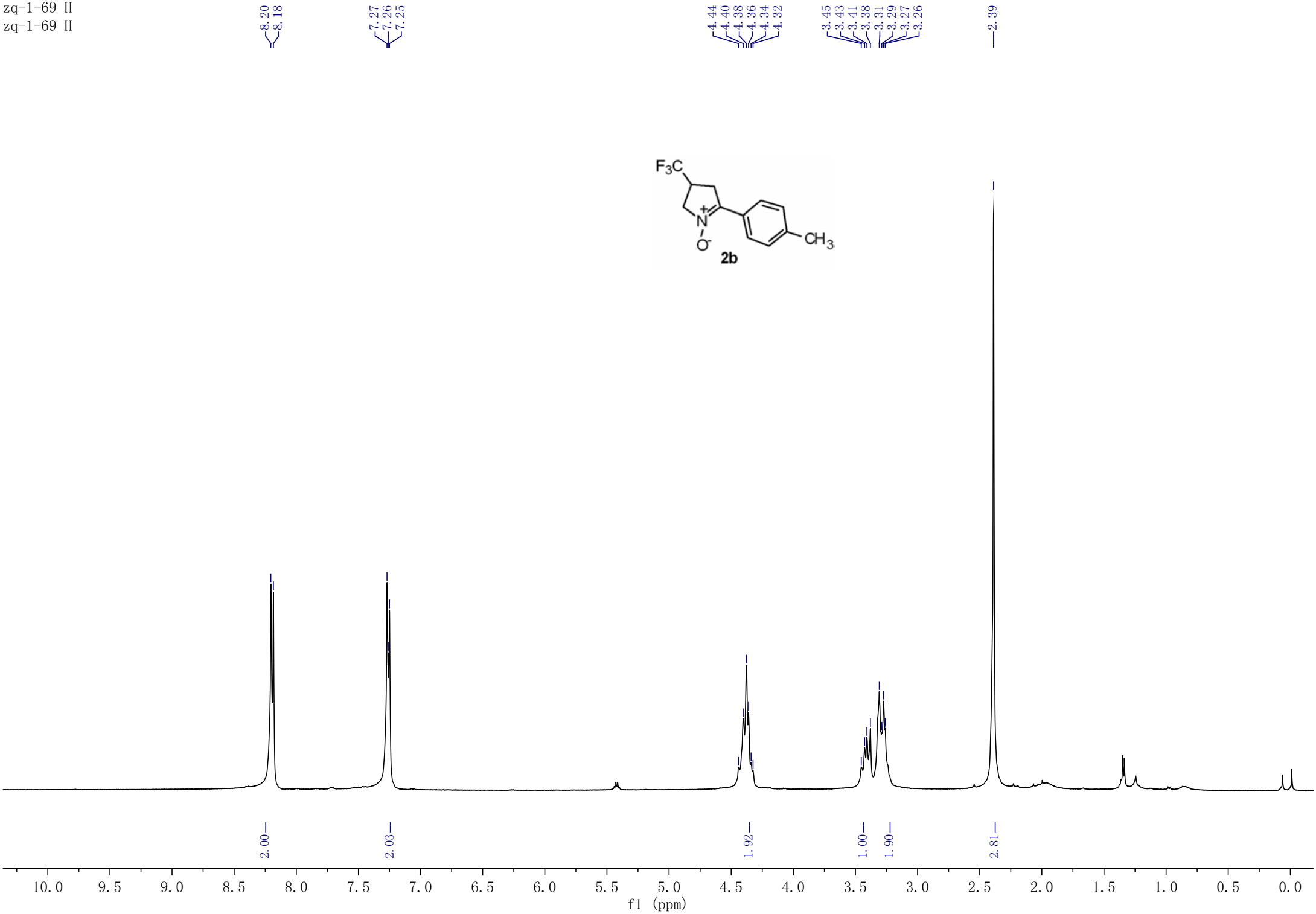
2a



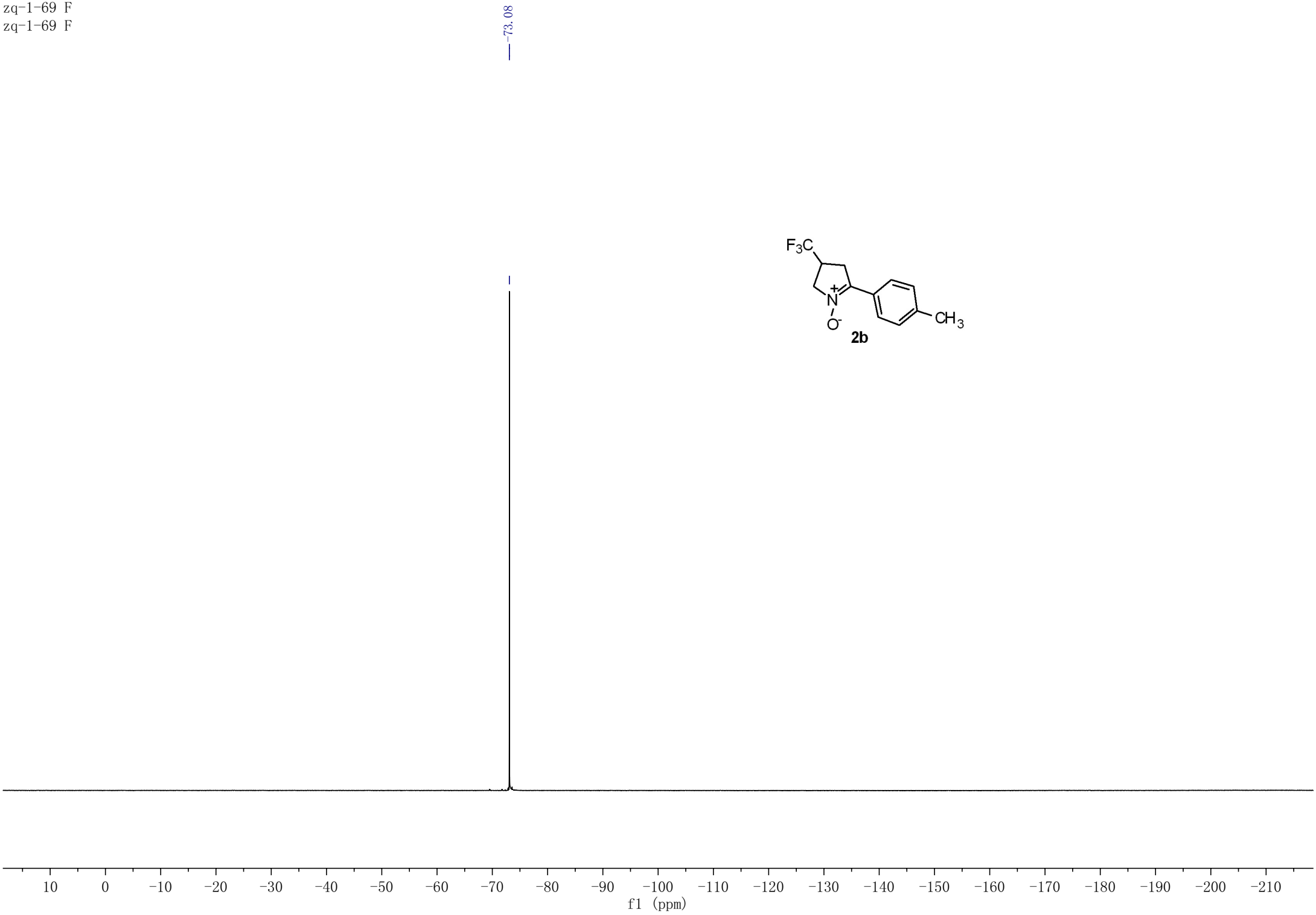
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

zq-1-69 H
zq-1-69 H

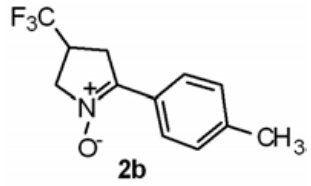


zq-1-69 F
zq-1-69 F

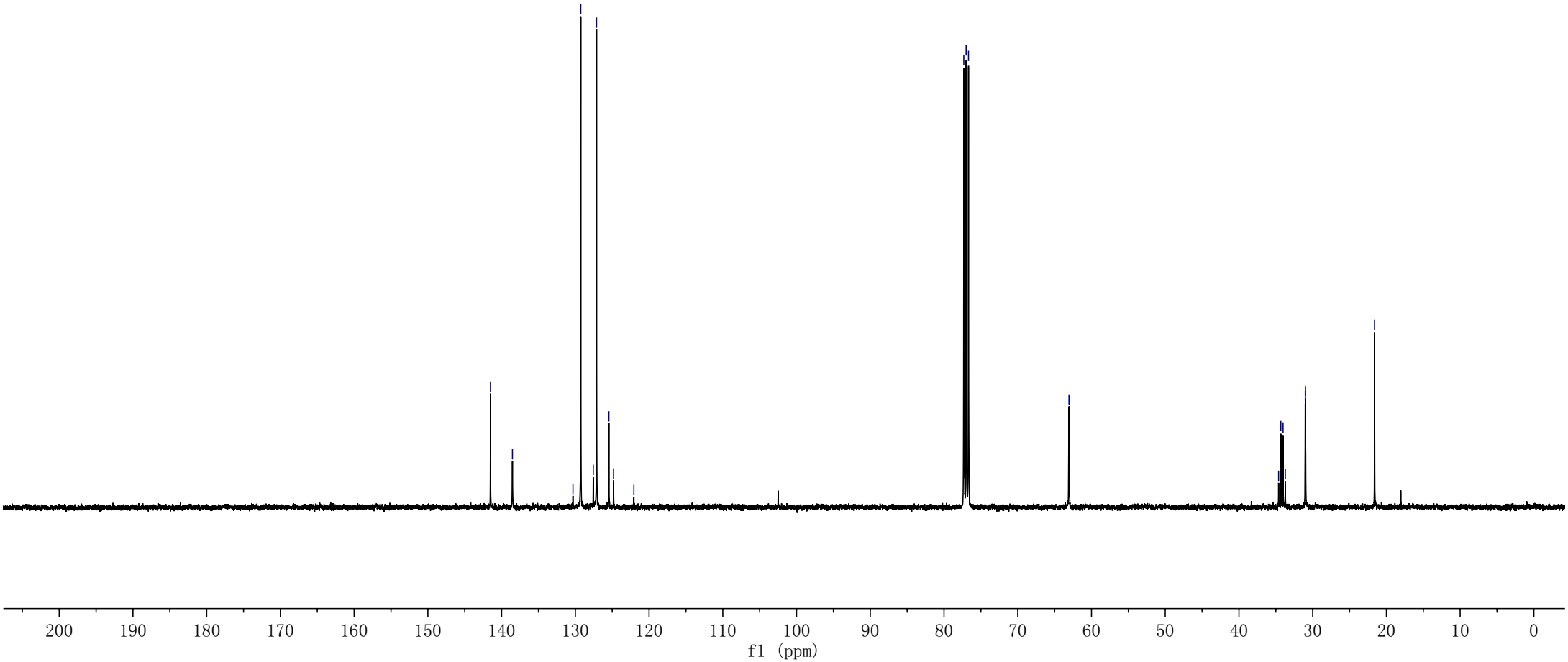


xiaoyj-1-69 C
xiaoyj-1-69 C

141.51
138.53
130.32
129.26
127.57
127.12
125.45
124.81
122.06
77.32
77.00
76.68
63.05
34.62
34.32
34.02
33.71
31.00
30.98
21.61

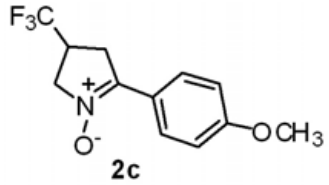


2b

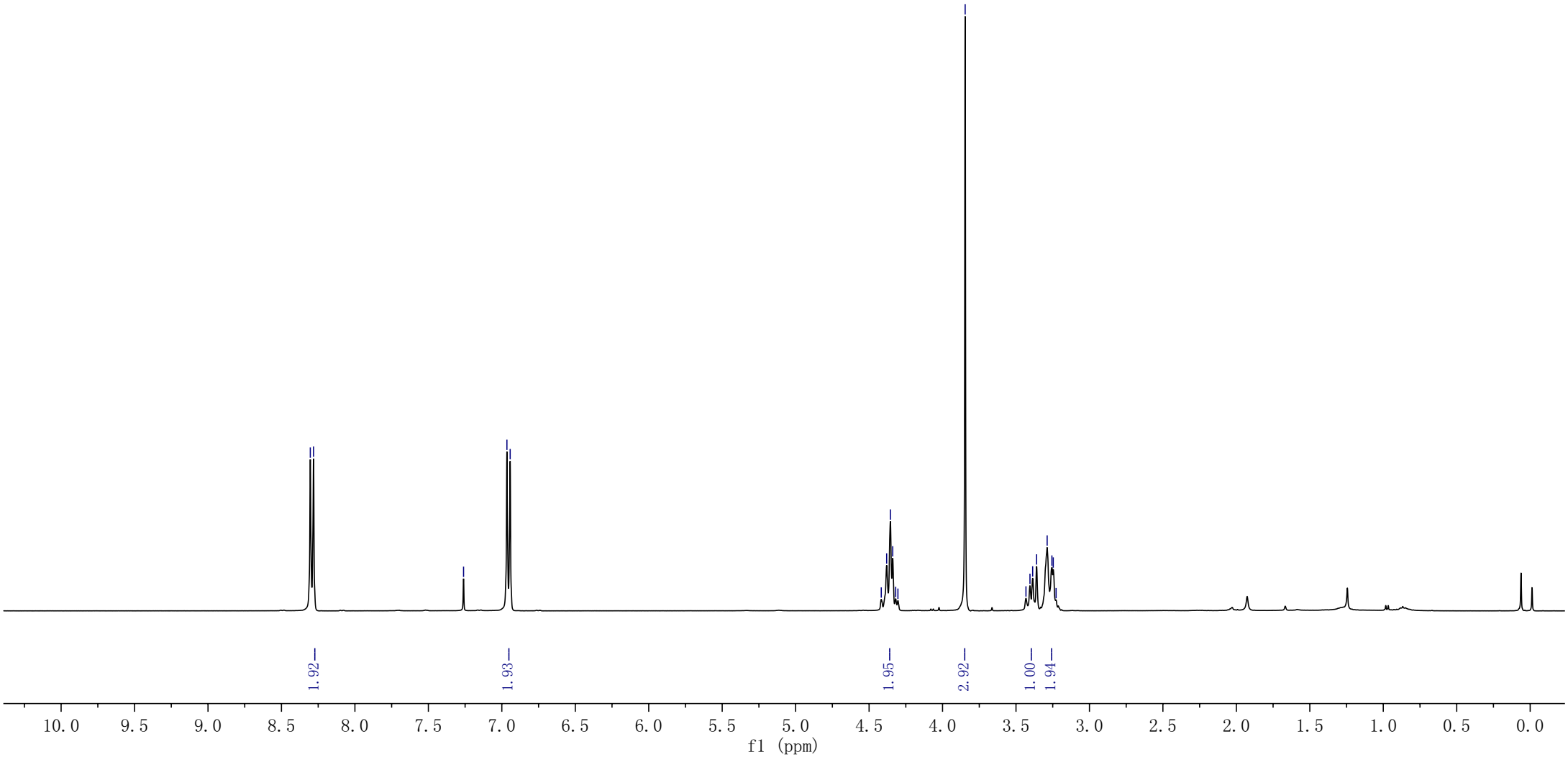


zq-1-56
zq-1-56

8.30
8.28
7.26
6.97
6.94
4.42
4.38
4.36
4.34
4.32
4.30
3.85
3.43
3.40
3.39
3.36
3.29
3.26
3.25
3.23

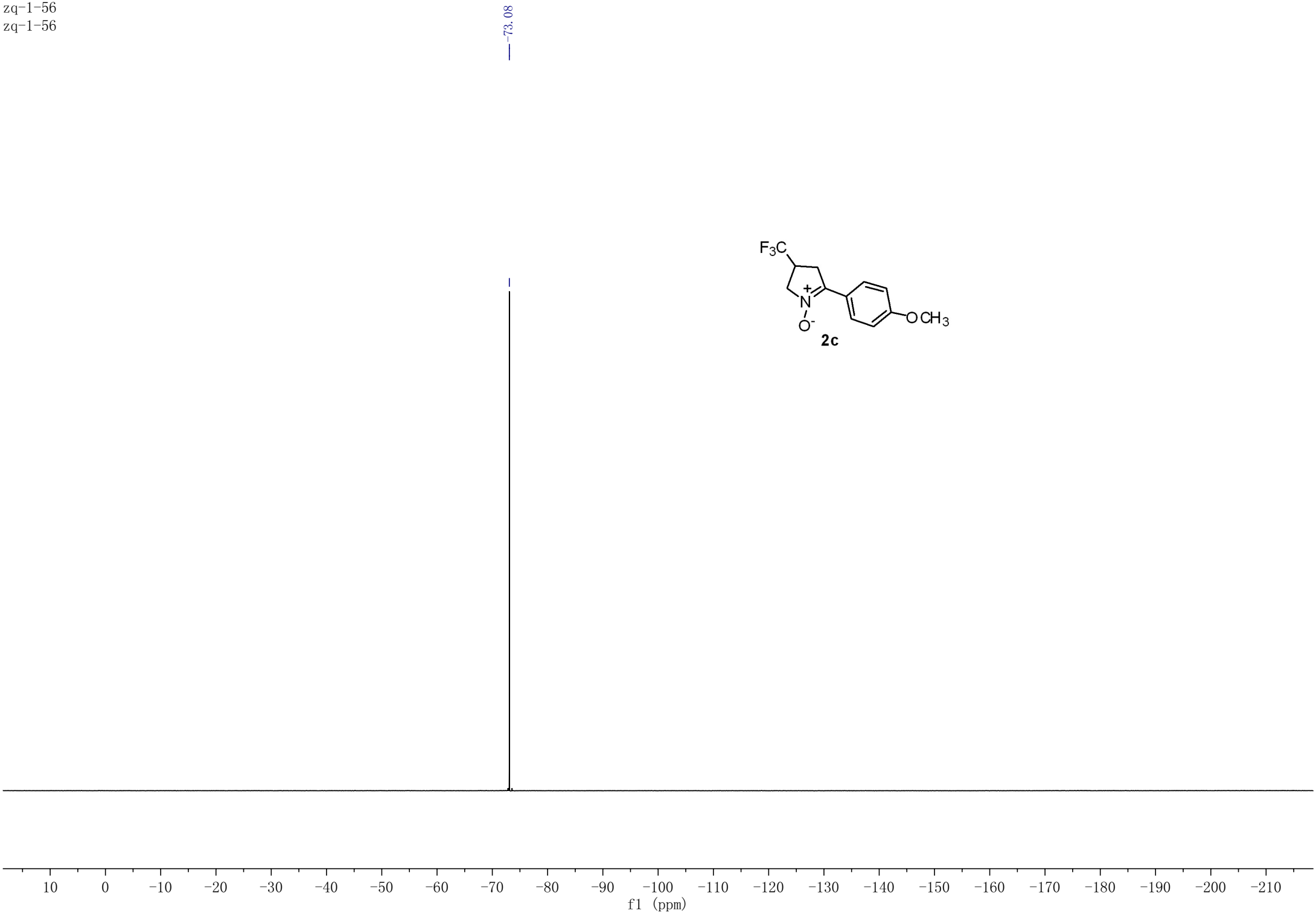


2c



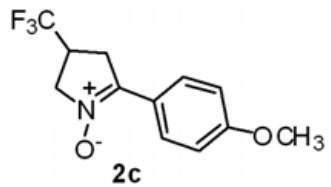
zq-1-56
zq-1-56

2c

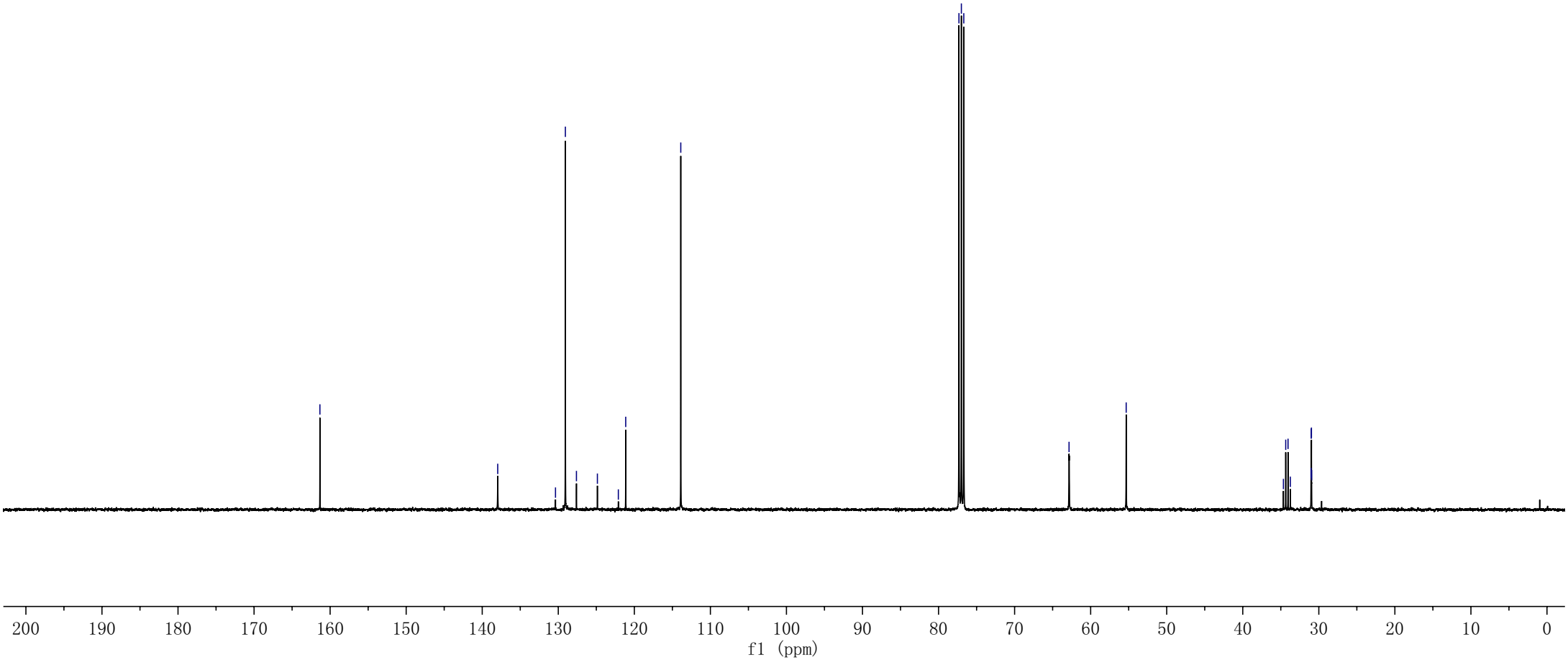


zq-1-56
zq-1-56

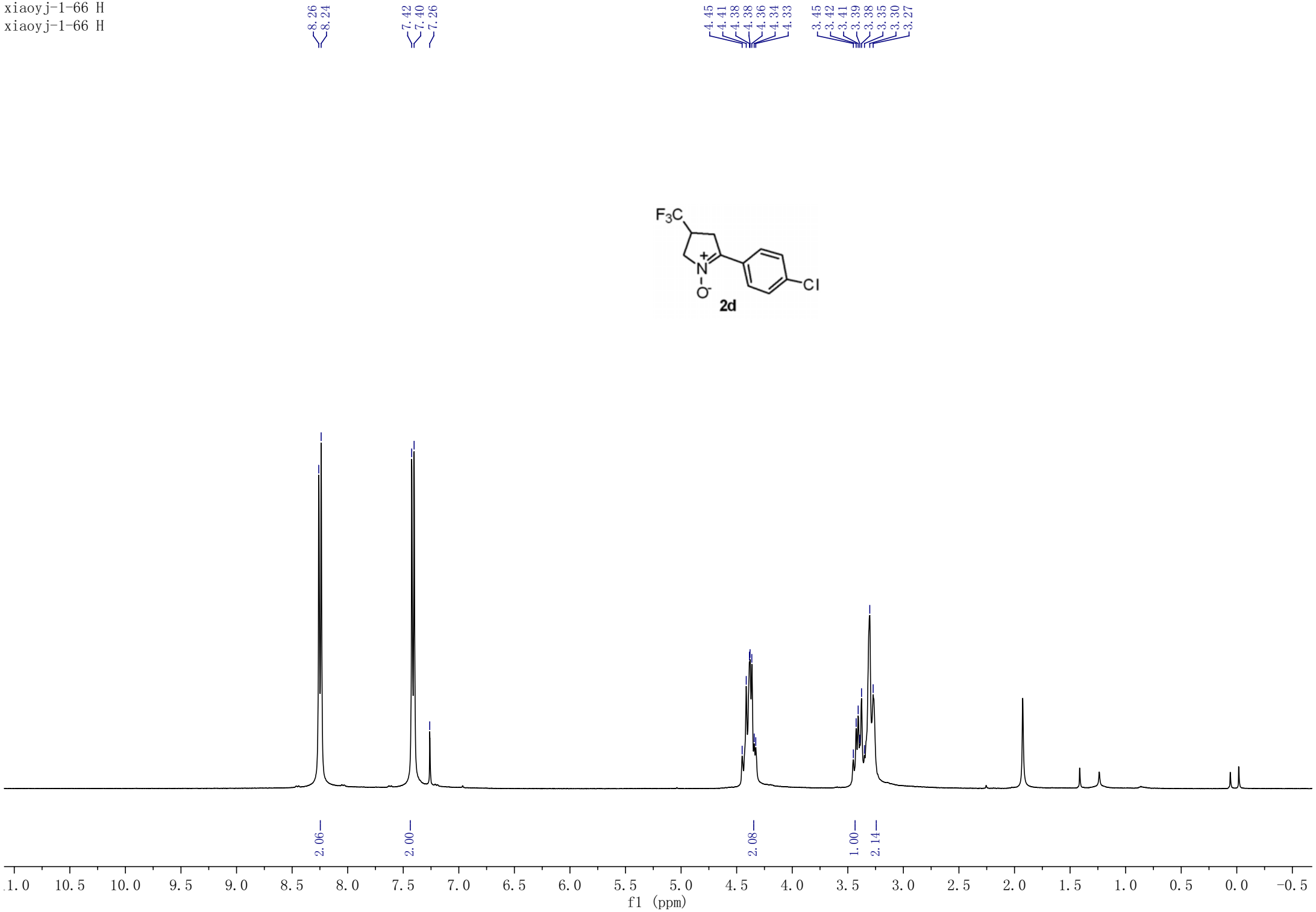
161.34
137.96
130.37
129.07
127.61
124.86
122.10
121.13
113.89
77.32
77.00
76.68
62.84
55.33
34.65
34.35
34.05
33.75
31.02
31.00
30.97
30.94



2c

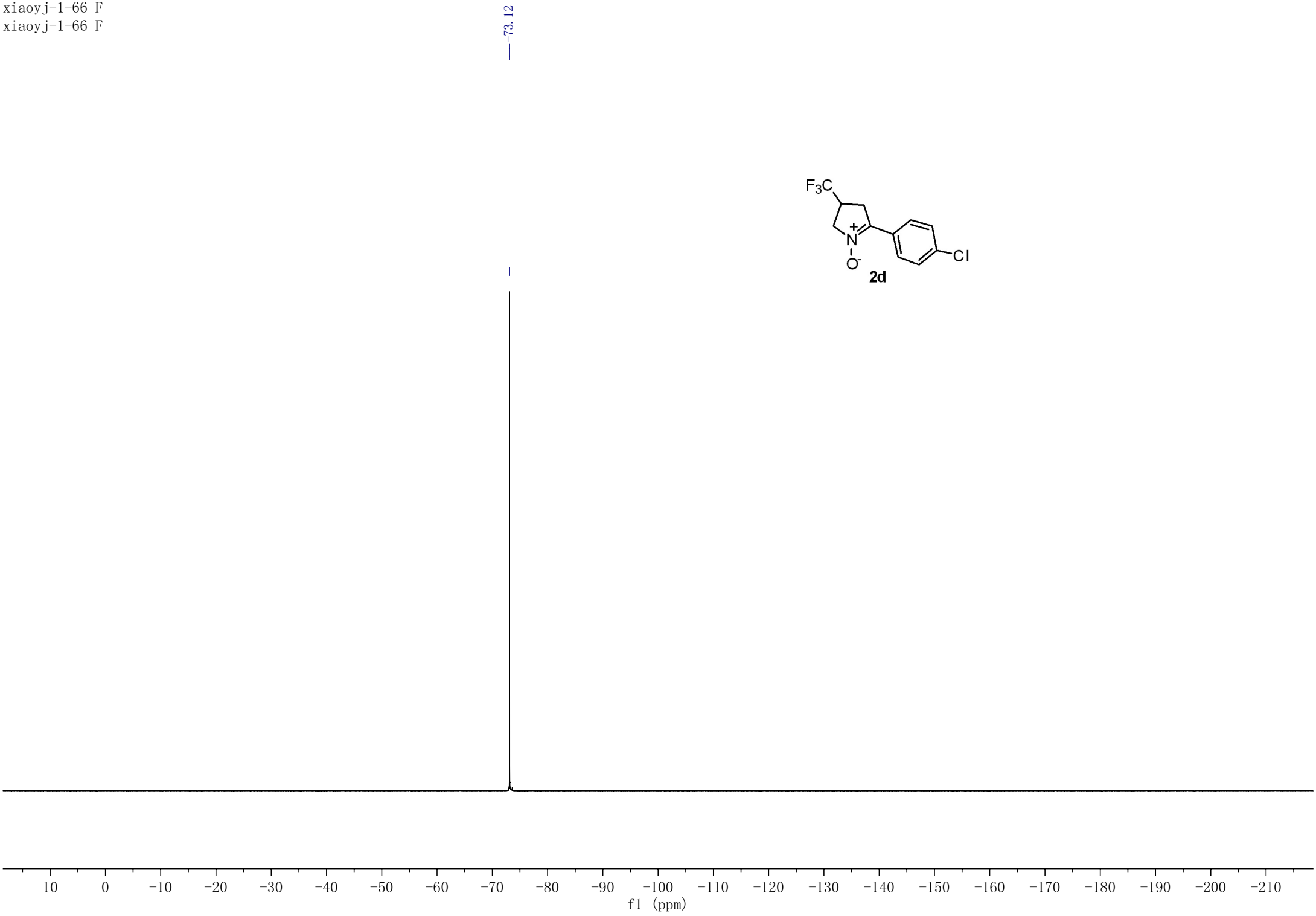


xiaoyj-1-66 H
xiaoyj-1-66 H



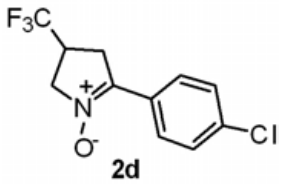
xiaoyj-1-66 F
xiaoyj-1-66 F

2d

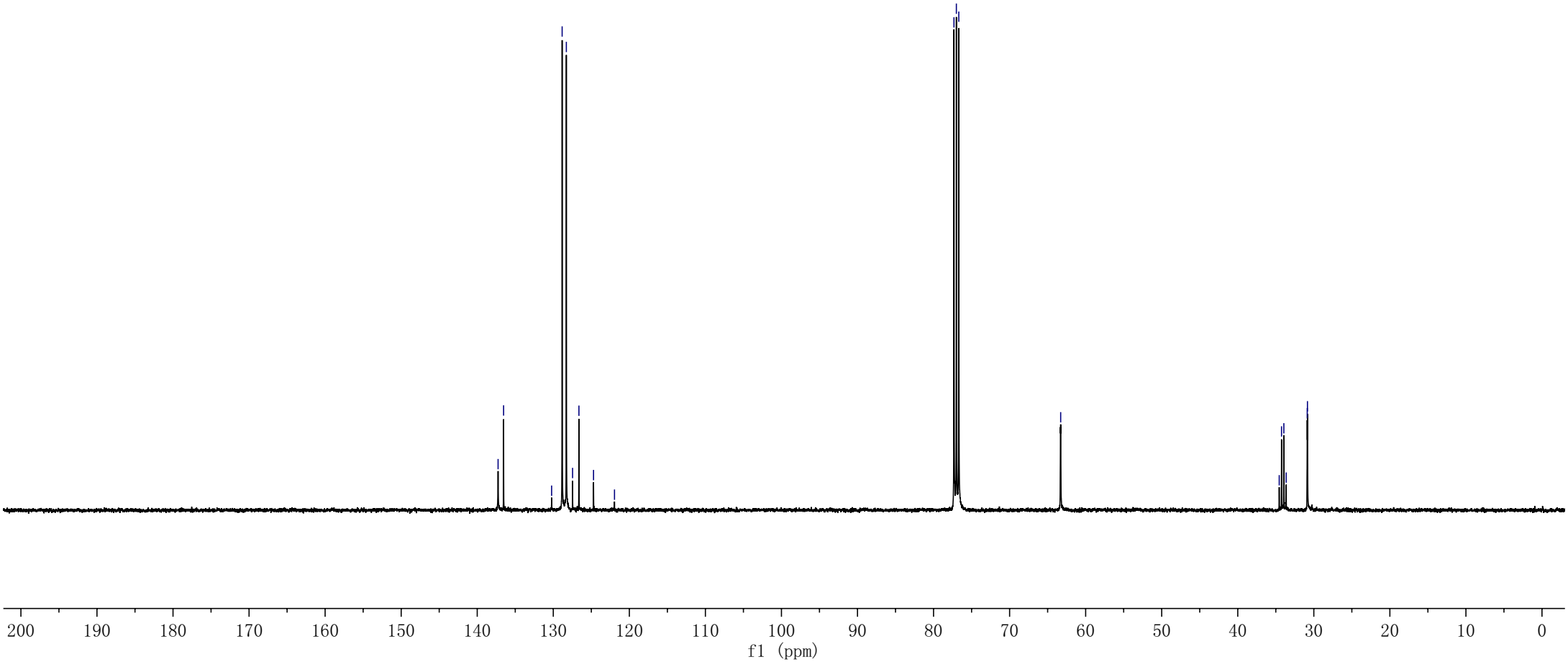


xiaoyj-1-66 C
xiaoyj-1-66 C

137.26
136.53
130.22
128.84
128.28
127.46
126.63
124.71
121.95
77.32
77.00
76.68
63.29
34.55
34.25
33.94
33.64
30.86
30.84

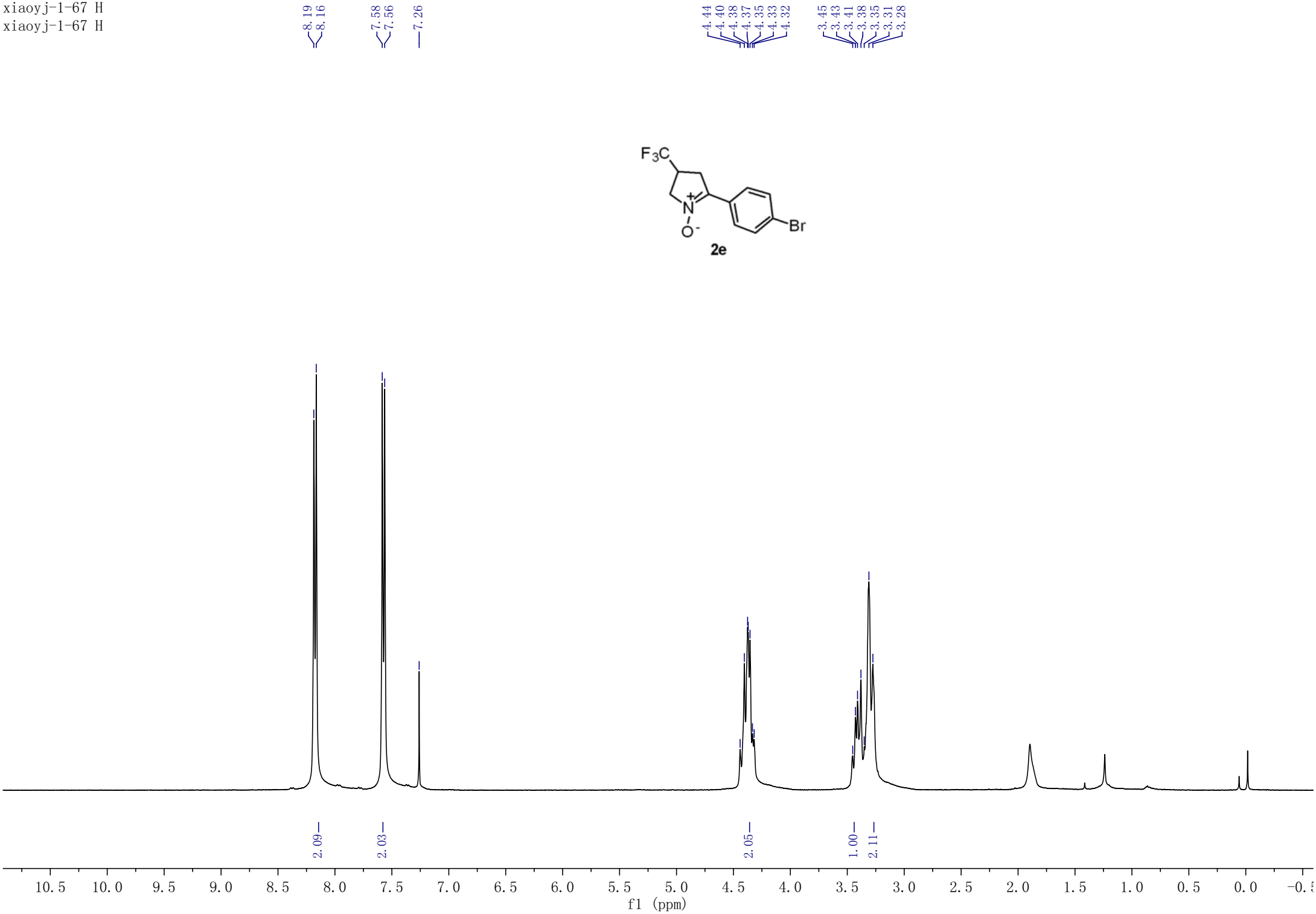


2d



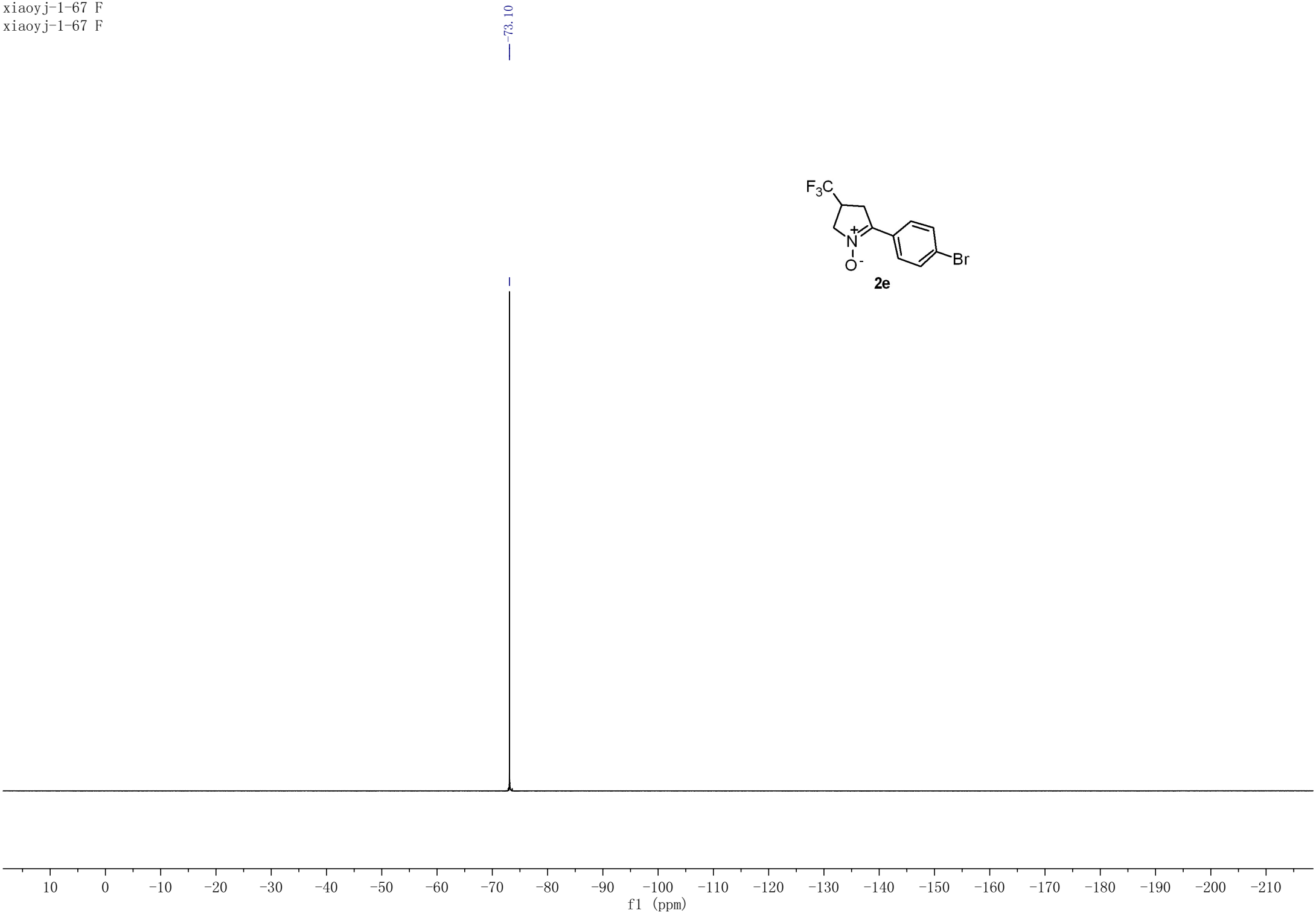
xiaoyj-1-67 H
xiaoyj-1-67 H

2e



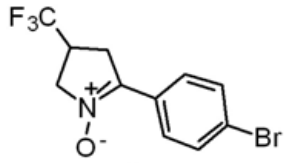
xiaoyj-1-67 F
xiaoyj-1-67 F

2e

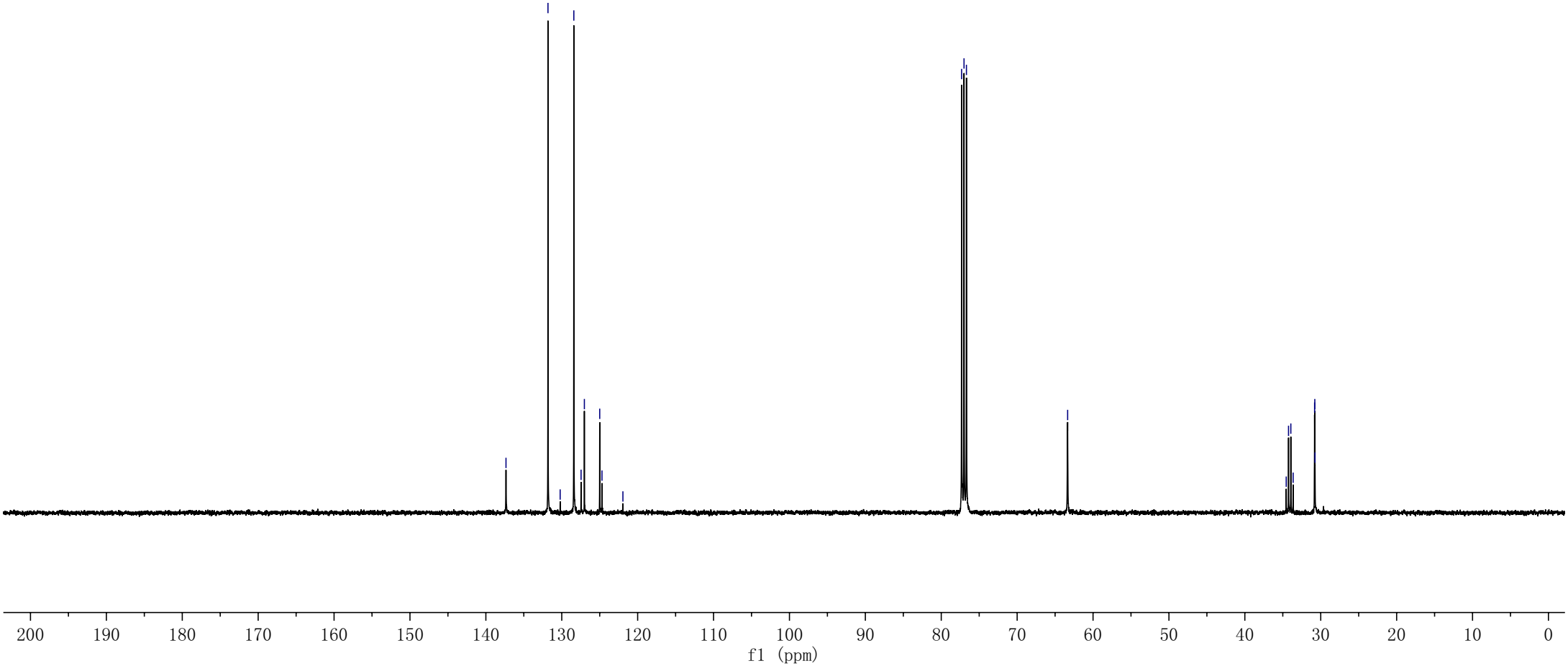


xiaoyj-1-67 C
xiaoyj-1-67 C

137.35
131.82
130.21
128.41
127.46
127.02
125.00
124.70
121.94
77.32
77.00
76.68
63.35
34.55
34.24
33.94
33.64
30.81
30.78
30.75

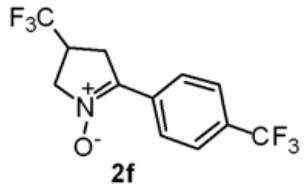


2e

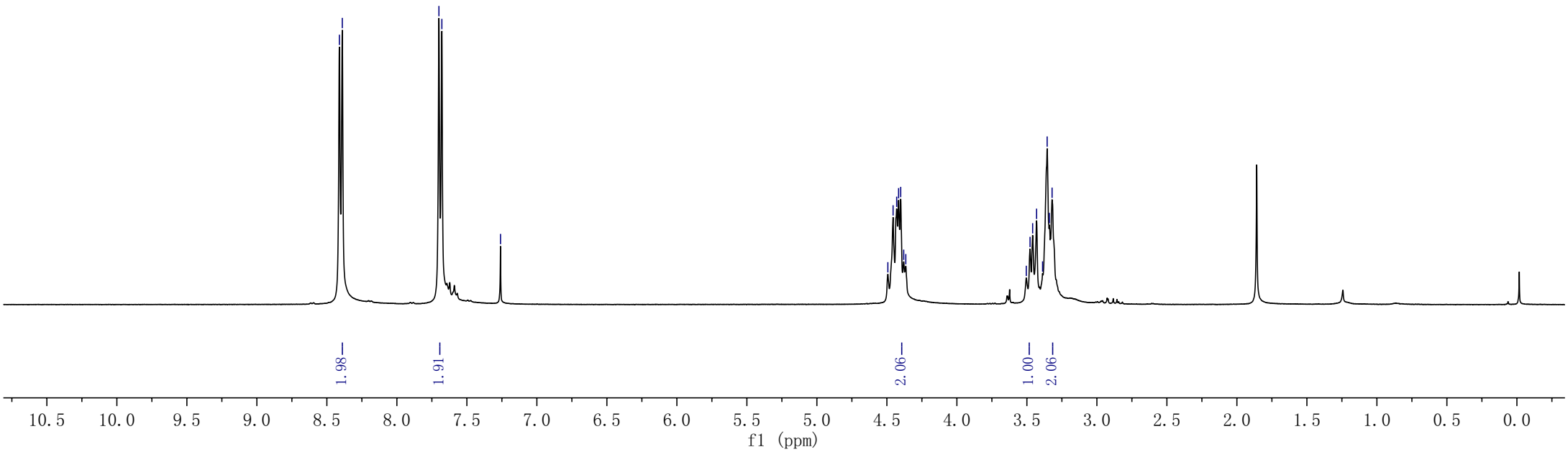


zq-1-105 H
zq-1-105 H

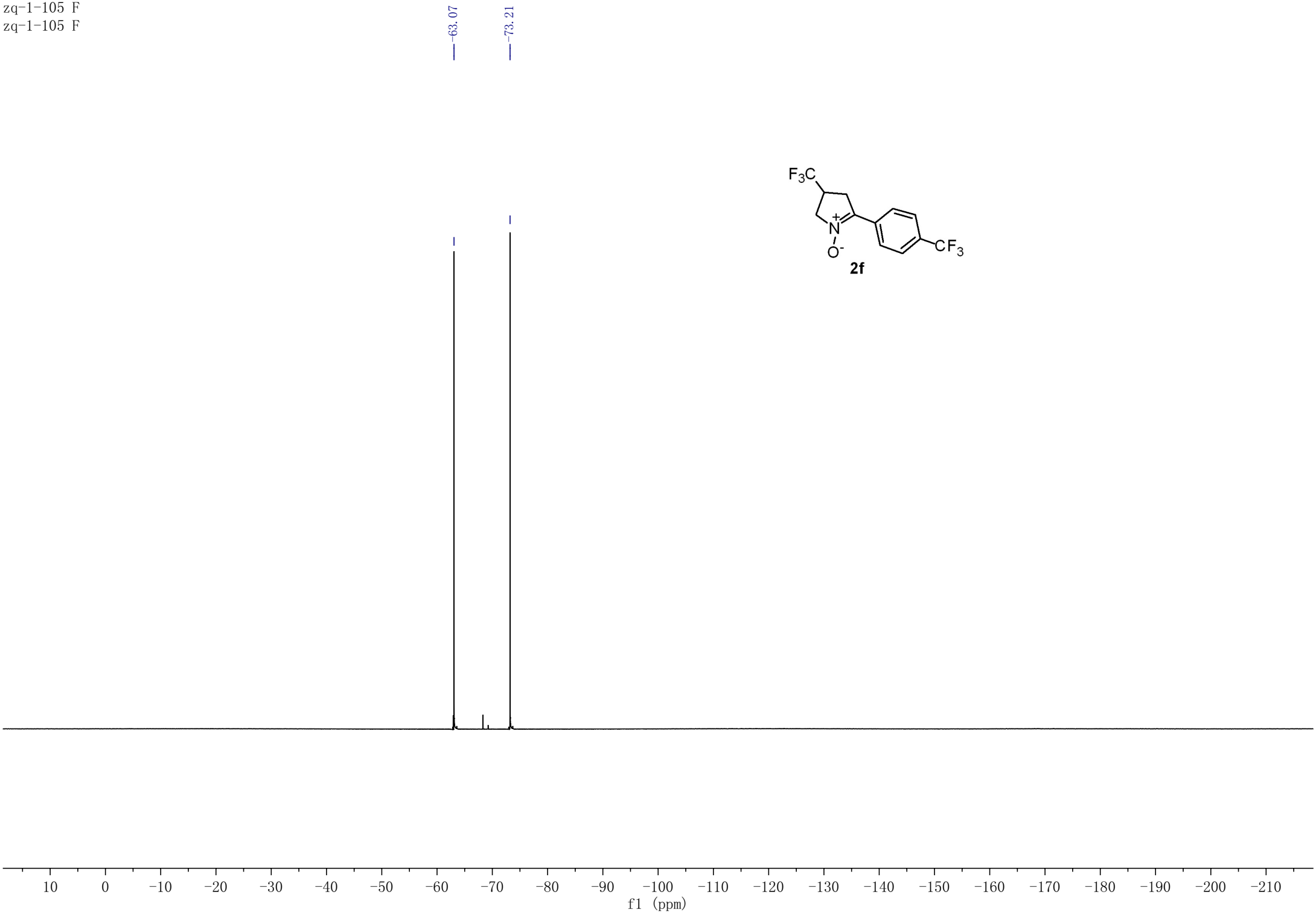
8.41
8.39
7.70
7.68
7.26
4.49
4.46
4.43
4.42
4.40
4.38
4.36
3.50
3.48
3.46
3.43
3.39
3.36
3.34
3.32



2f

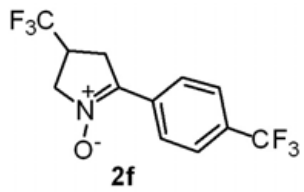


zq-1-105 F
zq-1-105 F

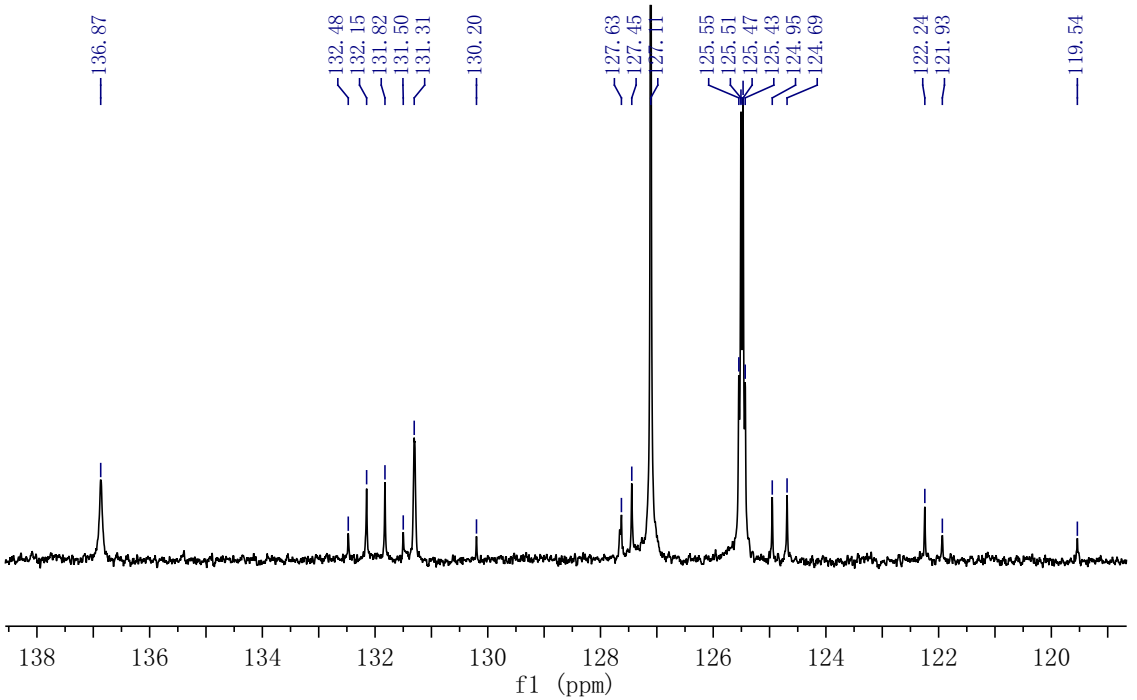


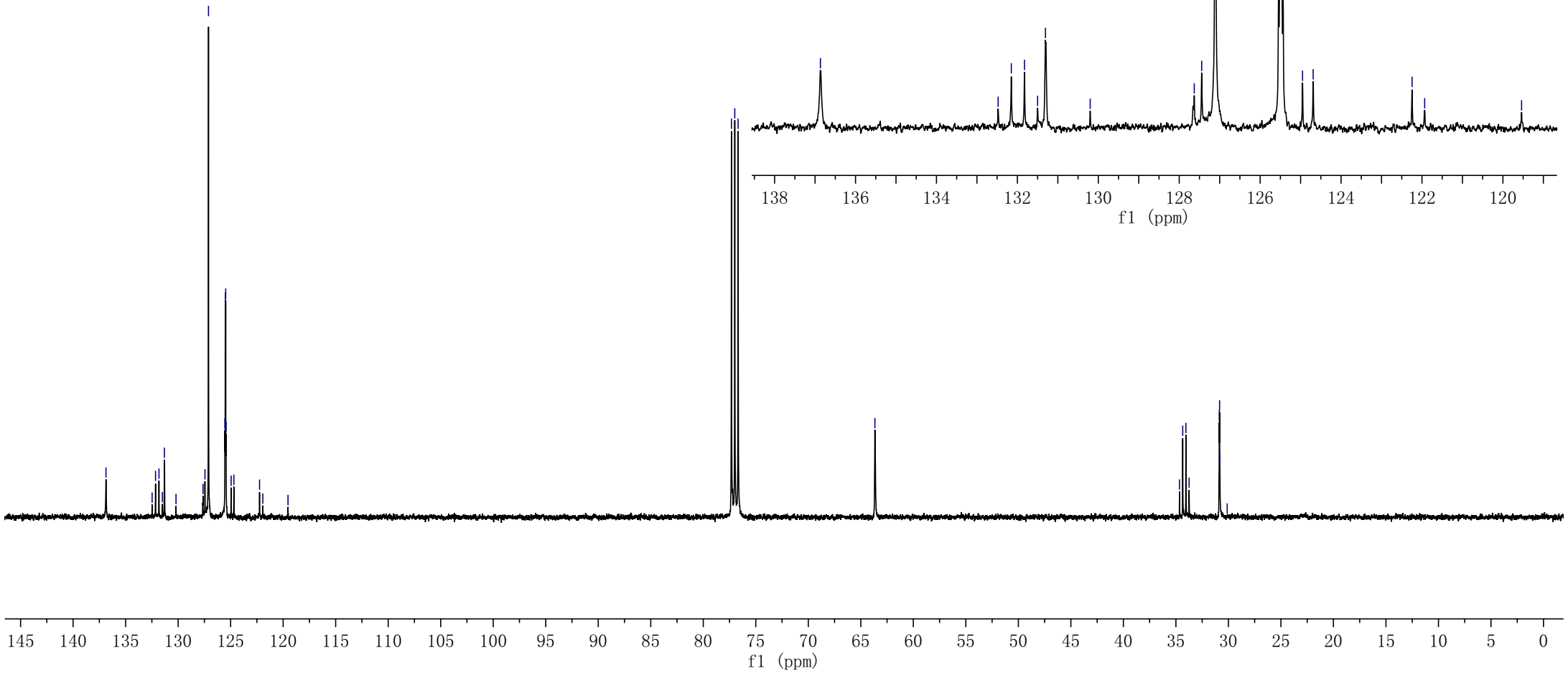
zq-1-105 C
zq-1-105 C

136.87
132.48
132.15
131.82
131.50
131.31
130.20
127.63
127.45
127.11
125.55
125.51
125.47
125.43
124.95
124.69
122.24
121.93
119.54
77.32
77.00
76.68
63.66
34.66
34.35
34.05
33.74
30.87
30.84
30.82
30.12



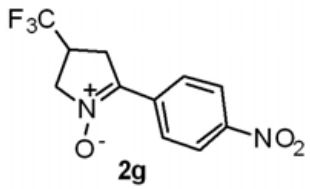
2f



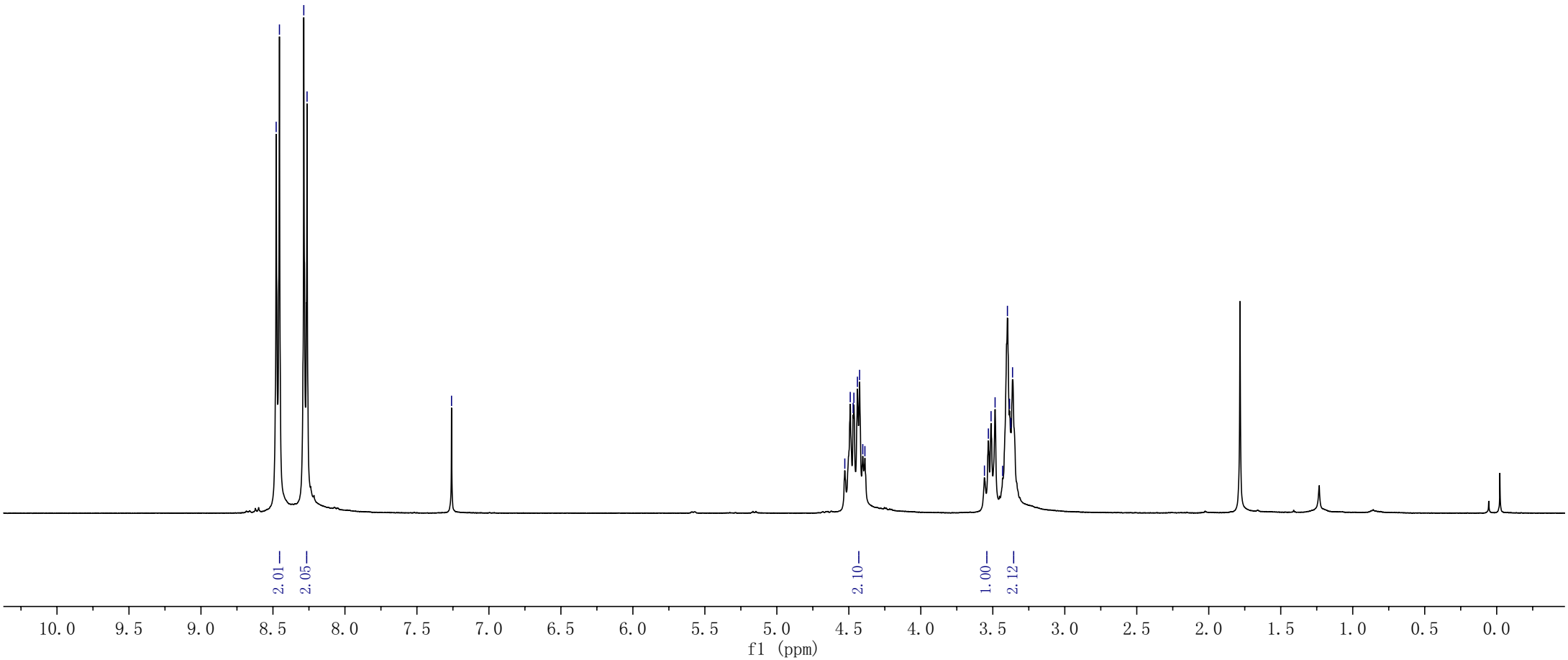


xiaoyj-1-73 H
xiaoyj-1-73 H

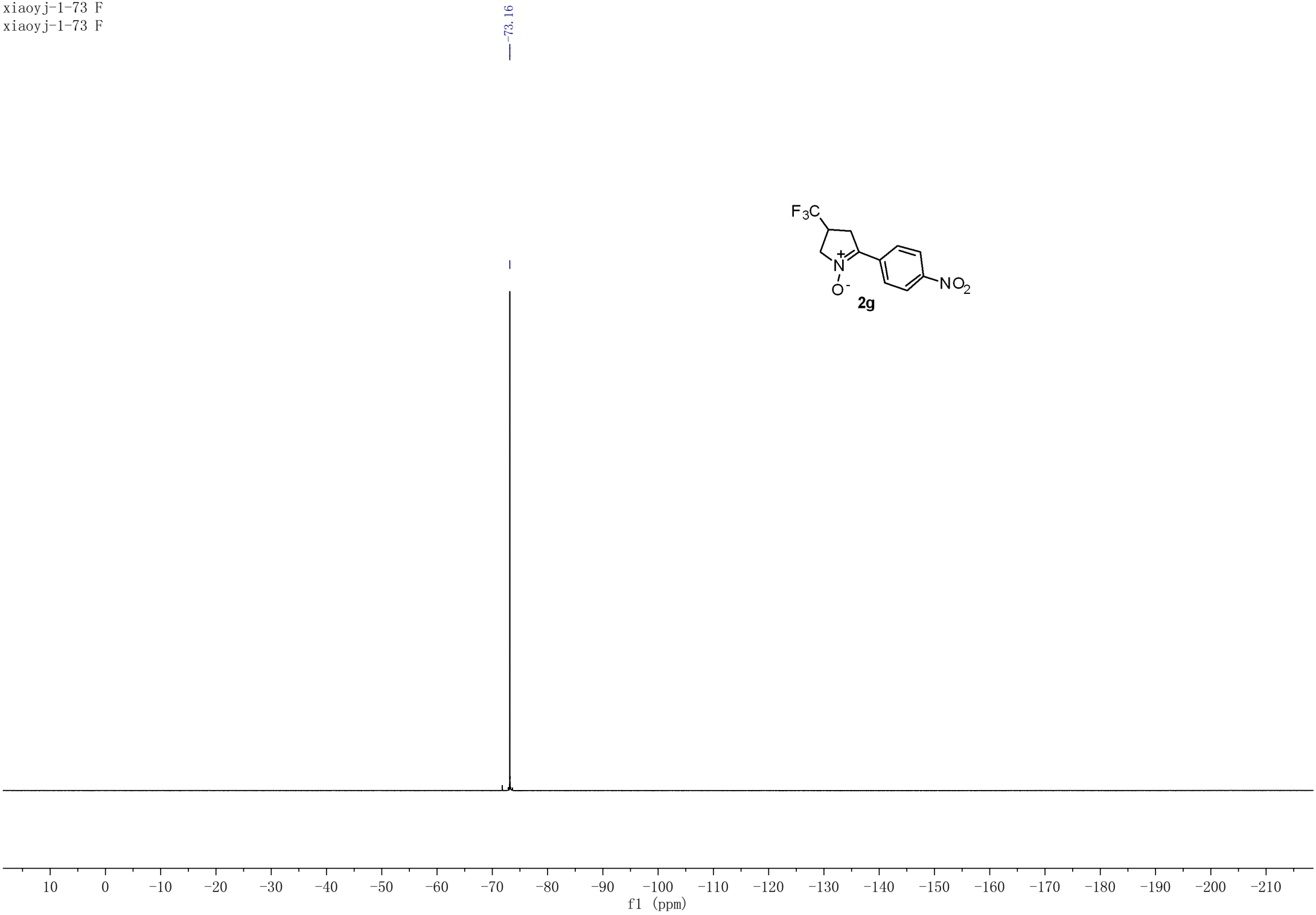
8.48 8.45 8.29 8.26 7.26 4.53 4.49 4.47 4.46 4.44 4.43 4.40 4.39 3.56 3.53 3.51 3.48 3.43 3.40 3.38 3.38 3.36



2g

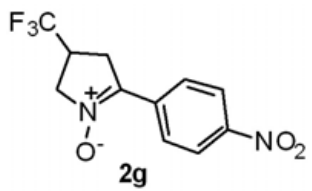


xiaoyj-1-73 F
xiaoyj-1-73 F

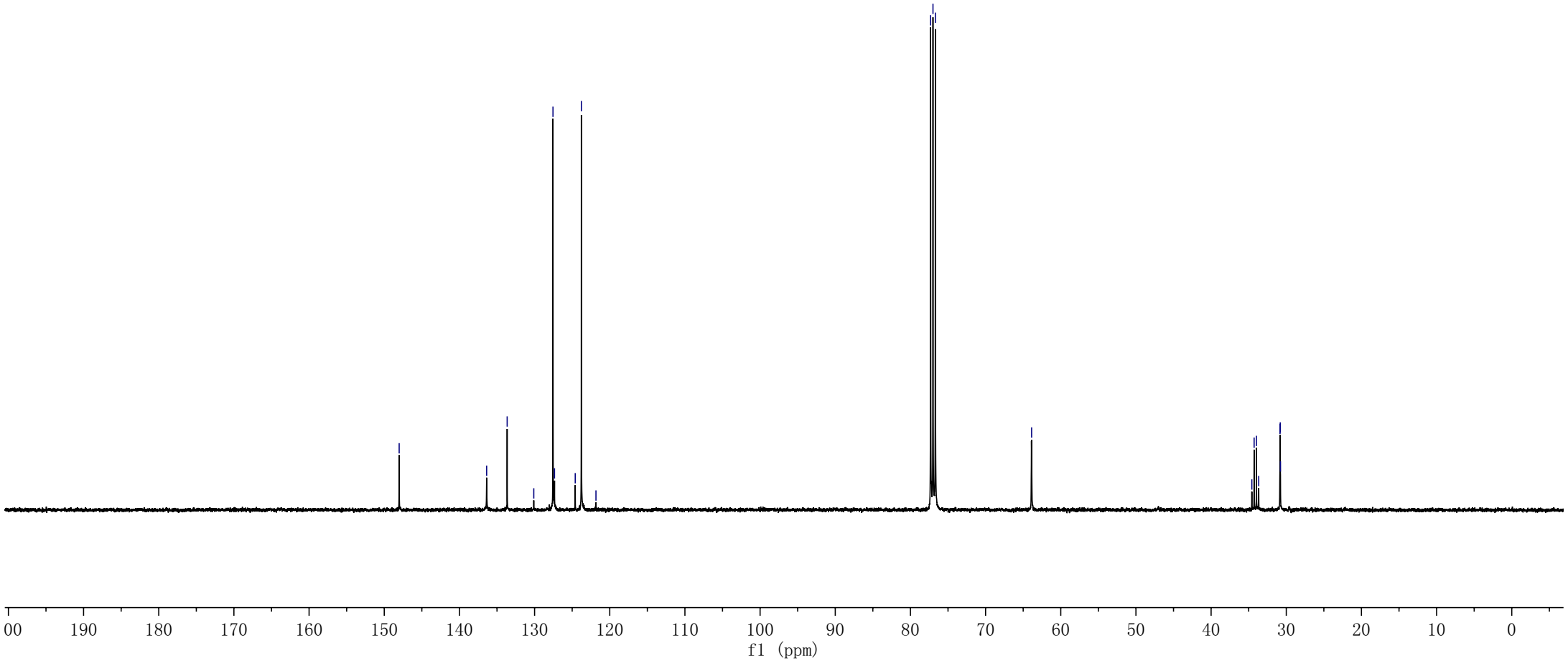


xiaoyj-1-73 C
xiaoyj-1-73 C

148.01
136.38
133.65
130.11
127.55
127.35
124.59
123.78
121.84
77.32
77.00
76.68
63.88
34.58
34.28
33.97
33.66
30.83
30.80
30.78

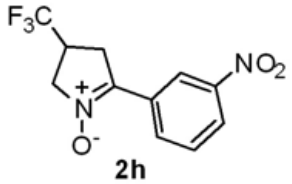


2g

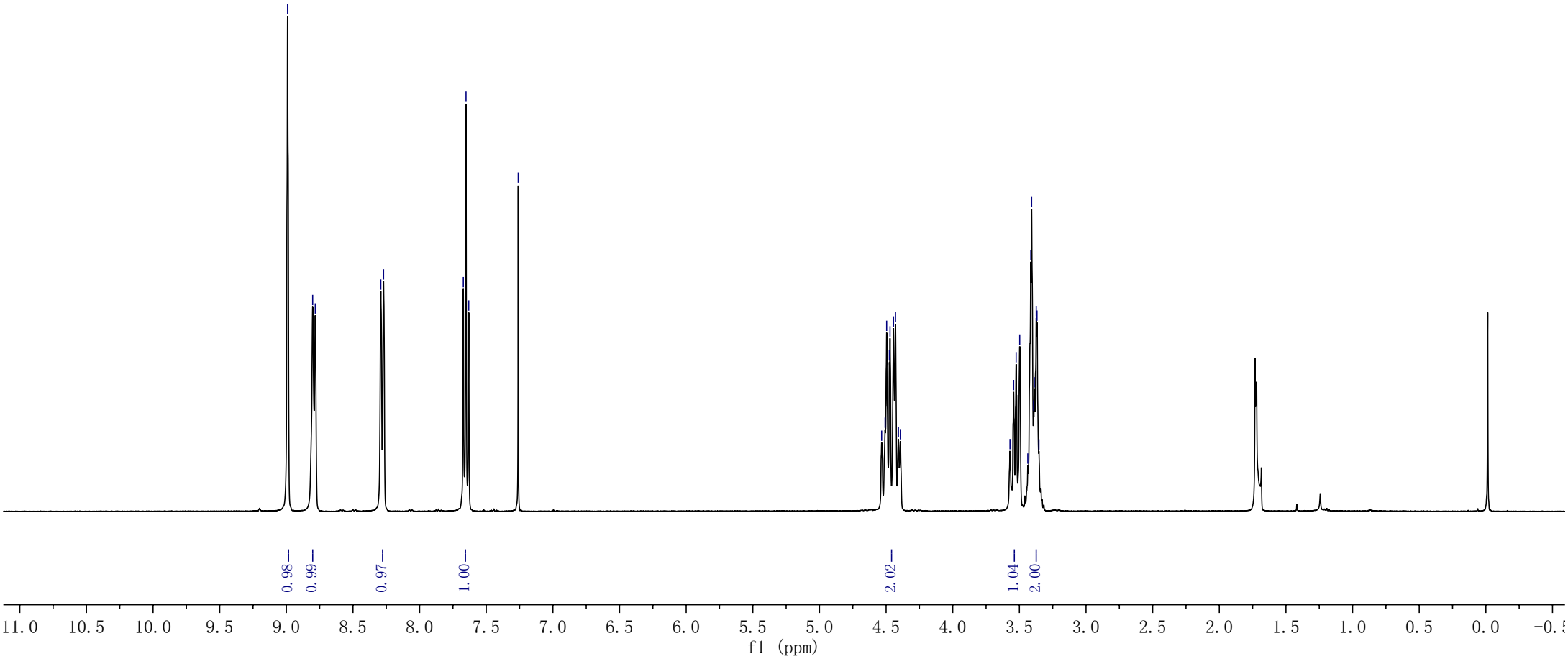


zl-1-147
zl-1-147

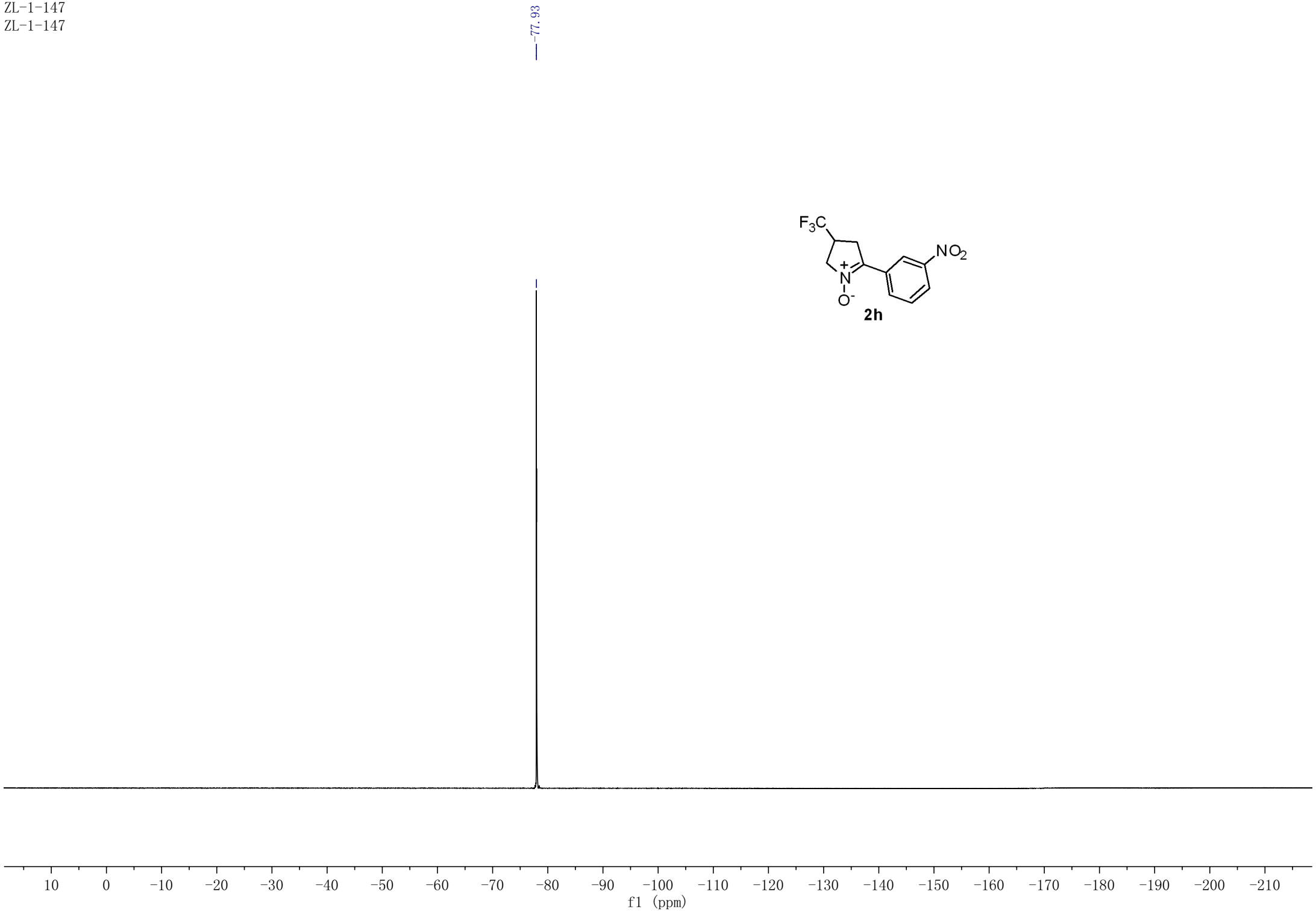
8.99
8.80
8.78
8.29
8.27
7.67
7.65
7.63
7.26
4.53
4.51
4.50
4.48
4.47
4.44
4.43
4.41
4.39
3.57
3.54
3.52
3.50
3.44
3.41
3.41
3.39
3.39
3.37
3.37
3.35



2h

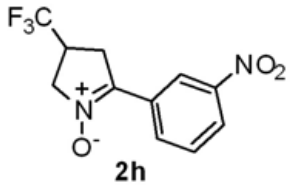


ZL-1-147
ZL-1-147



ZL-1-147
ZL-1-147

148.25
136.11
132.23
129.81
129.76
128.09
127.41
125.00
124.65
123.31
121.58
77.32
77.00
76.68
63.75
34.63
34.34
34.08
33.78
30.85



2h

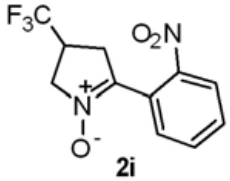
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

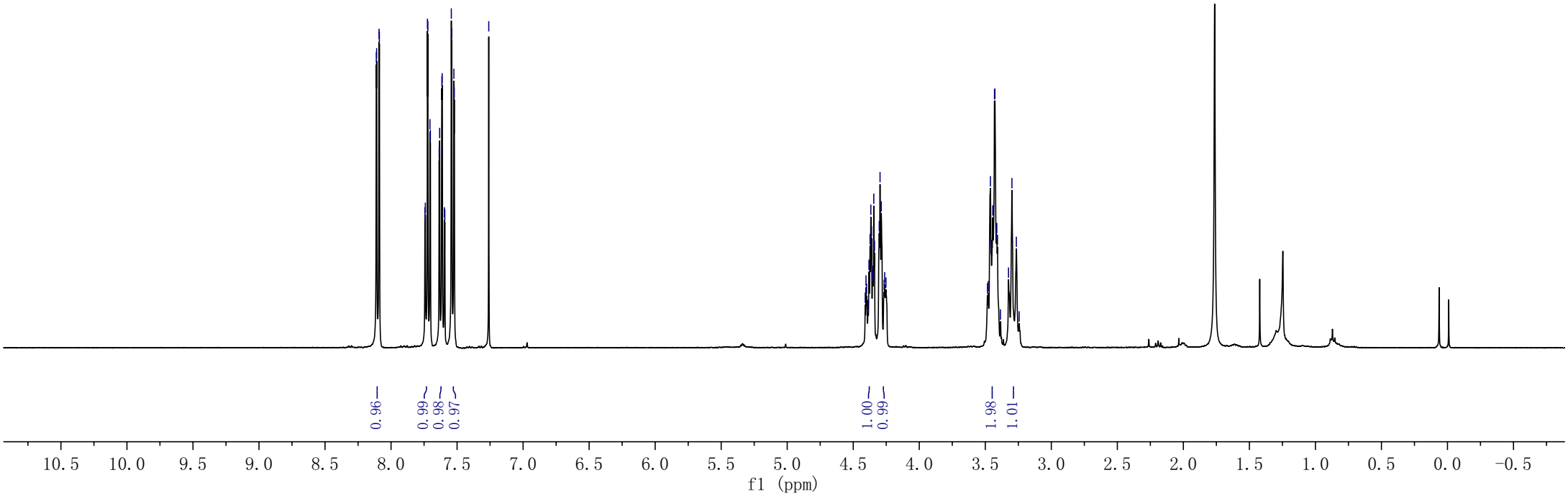
ZQ-2-30-H
ZQ-2-30-H

8.11 8.11 8.09 8.09 7.72 7.72 7.54 7.54 7.52 7.26

4.41 4.40 4.40 4.39 4.38 4.37 4.37 4.36 4.35 4.35 4.34 4.34 4.30 4.30 4.29 4.27 4.26 4.25 3.48 3.48 3.46 3.45 3.44 3.43 3.43 3.42 3.41 3.41 3.39 3.32 3.30 3.26 3.24



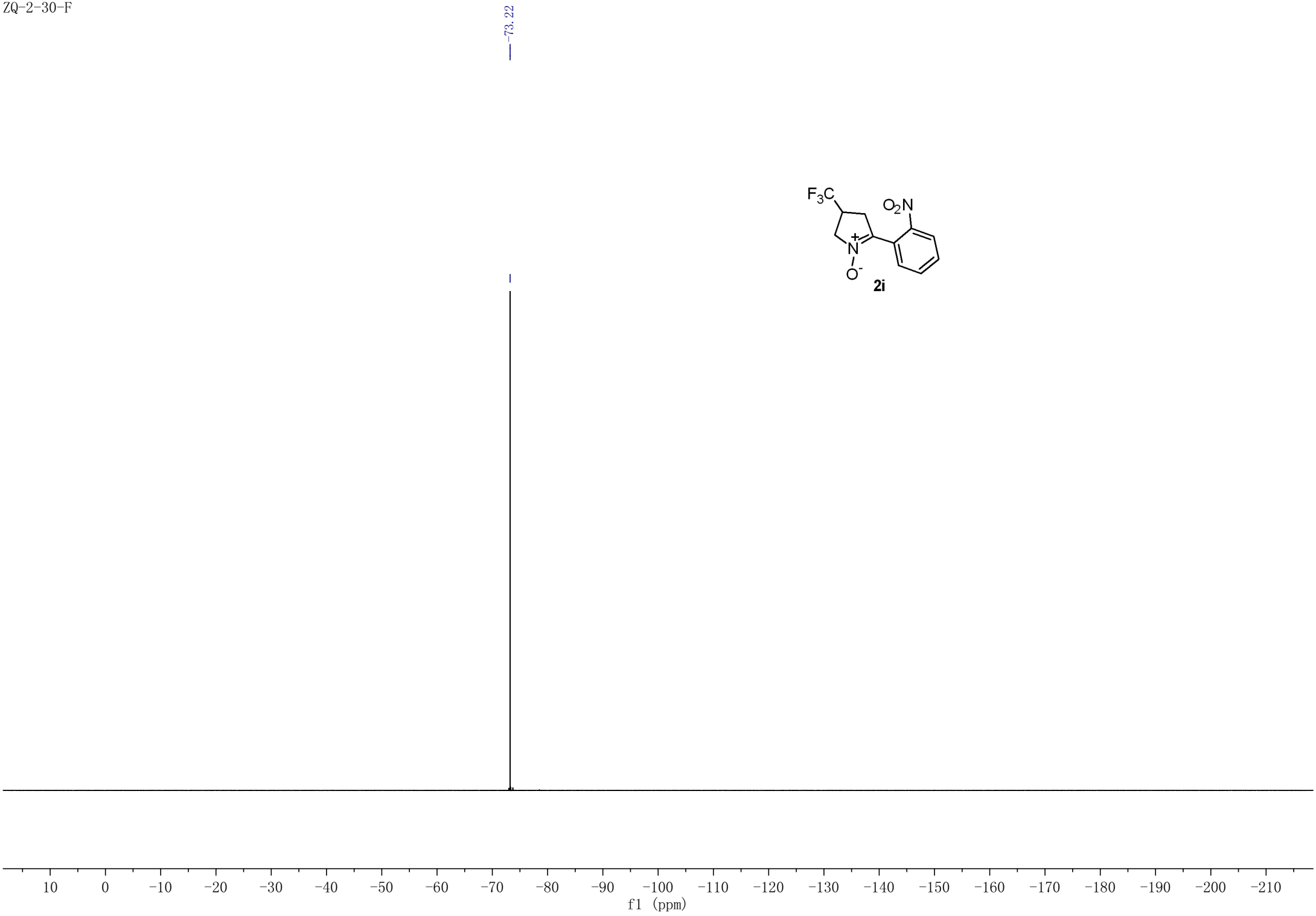
2i



ZQ-2-30-F

F3C
O2N
N
O-

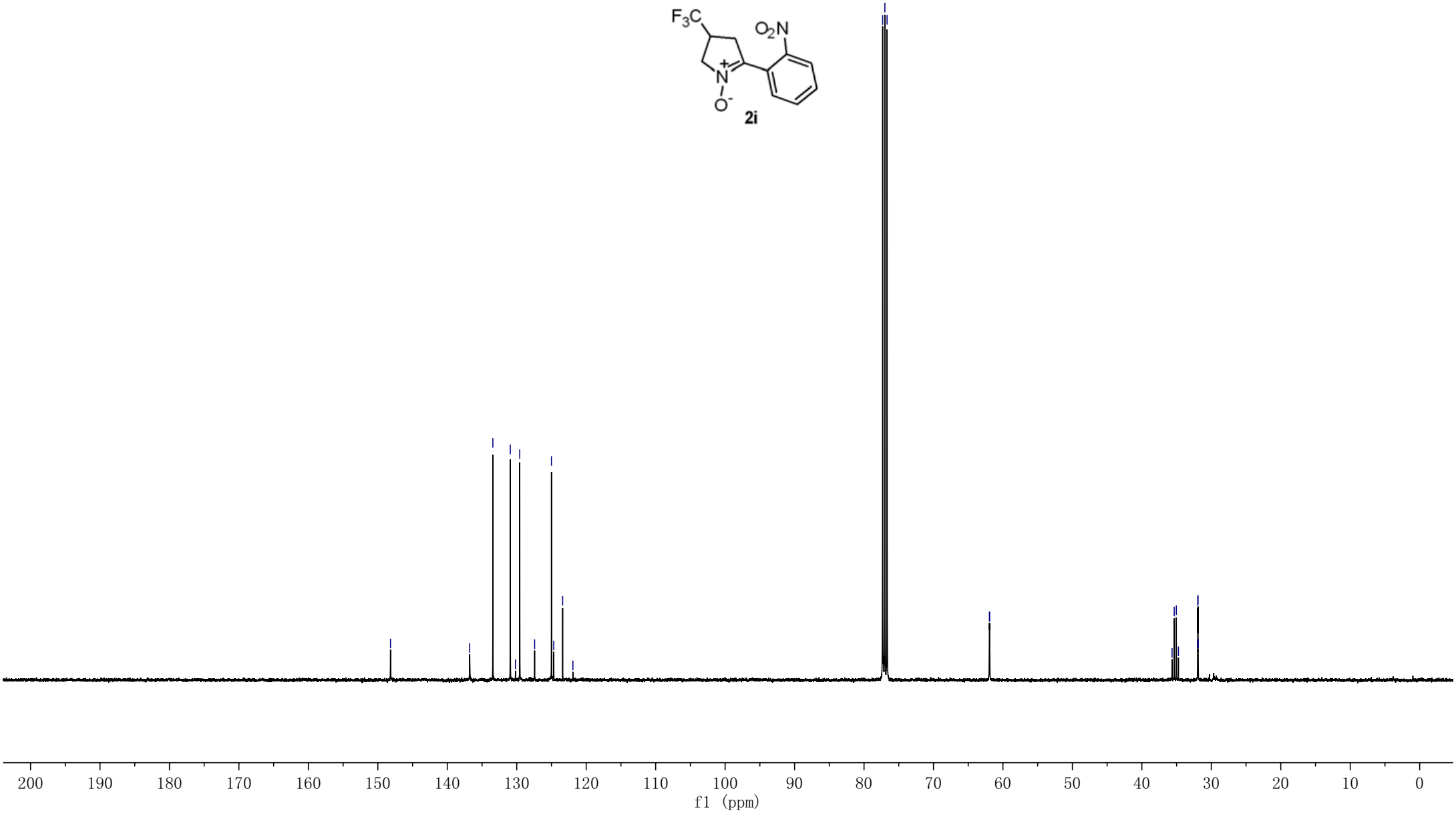
2i


-73.22
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

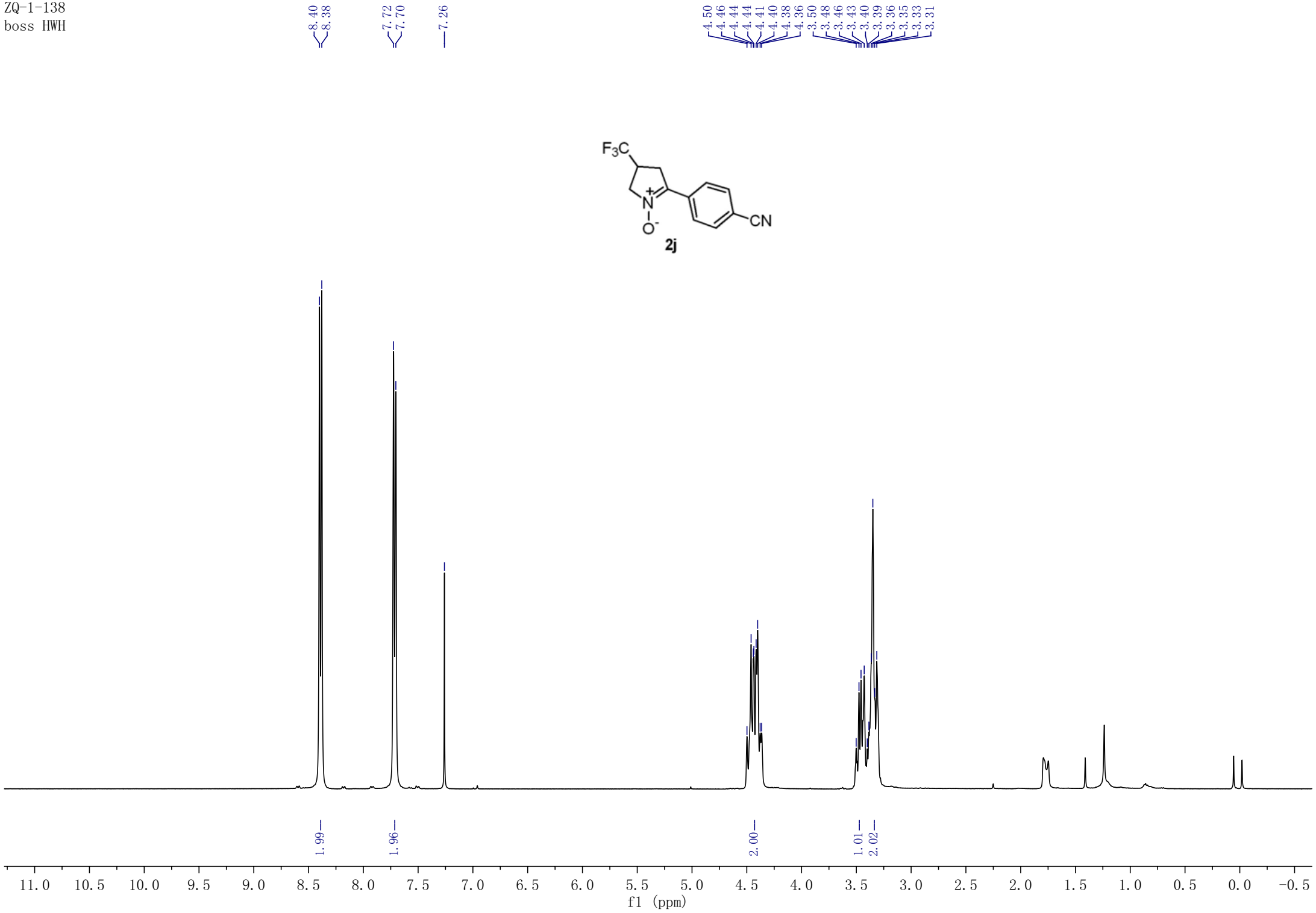
ZQ-2-30-C
ZQ-2-30-C

148.17
136.77
133.44
130.93
130.18
129.57
127.42
125.00
124.67
123.39
121.91
77.32
77.00
76.68
61.95
61.92
35.65
35.34
35.04
34.74
31.97
31.94
31.92
31.89

2i

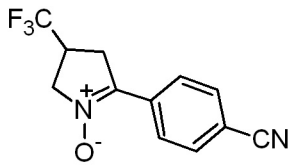


ZQ-1-138
boss HWH



ZQ-1-138
boss HWH

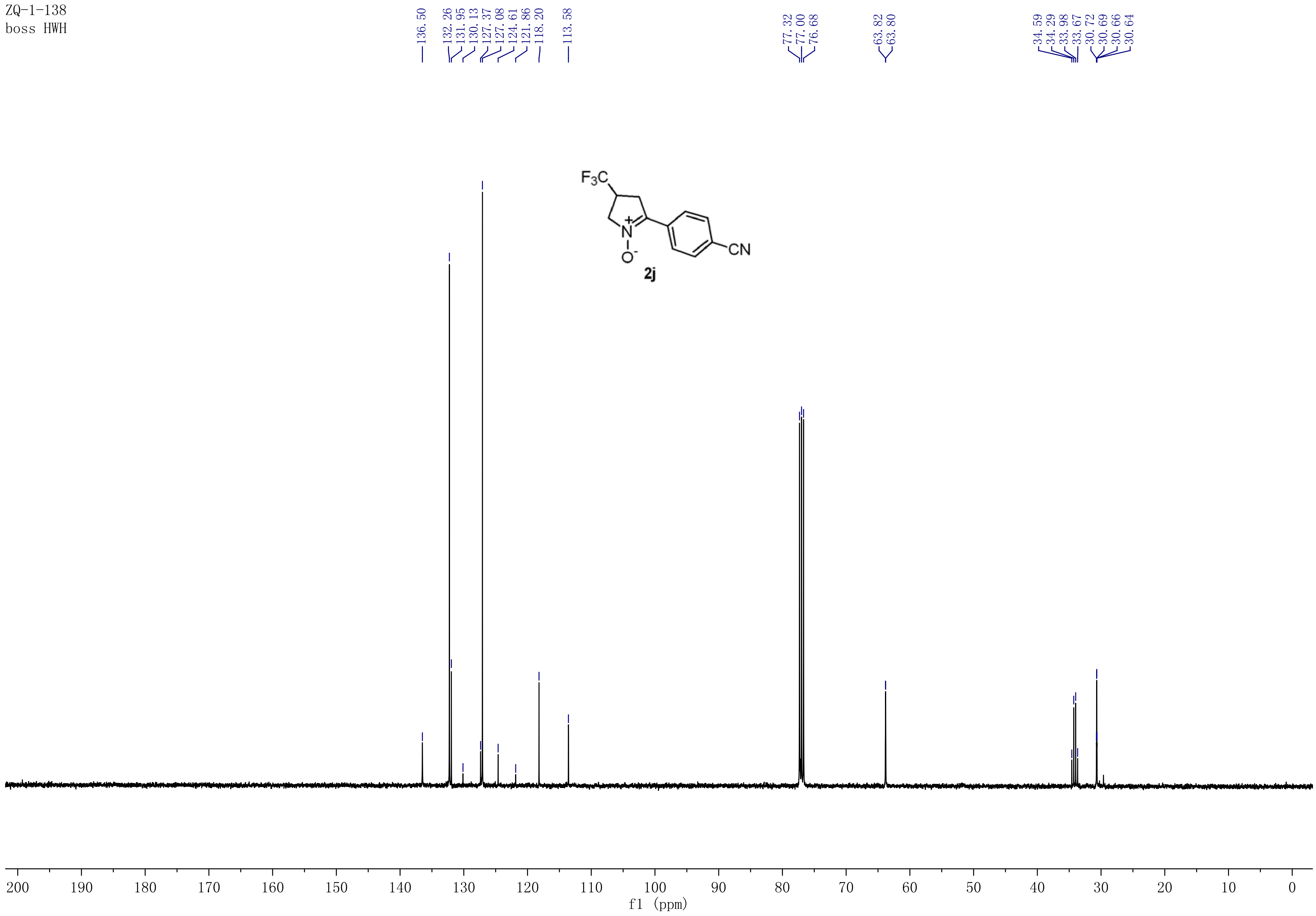
-73.18



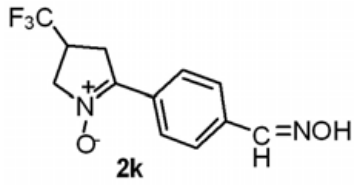
2j

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

f1 (ppm)


ZQ-1-138
boss HWH
136.50
132.26
131.95
130.13
127.37
127.08
124.61
121.86
118.20
113.58
77.32
77.00
76.68
63.82
63.80
34.59
34.29
33.98
33.67
30.72
30.69
30.66
30.64
F3C
N
O
CN
2j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

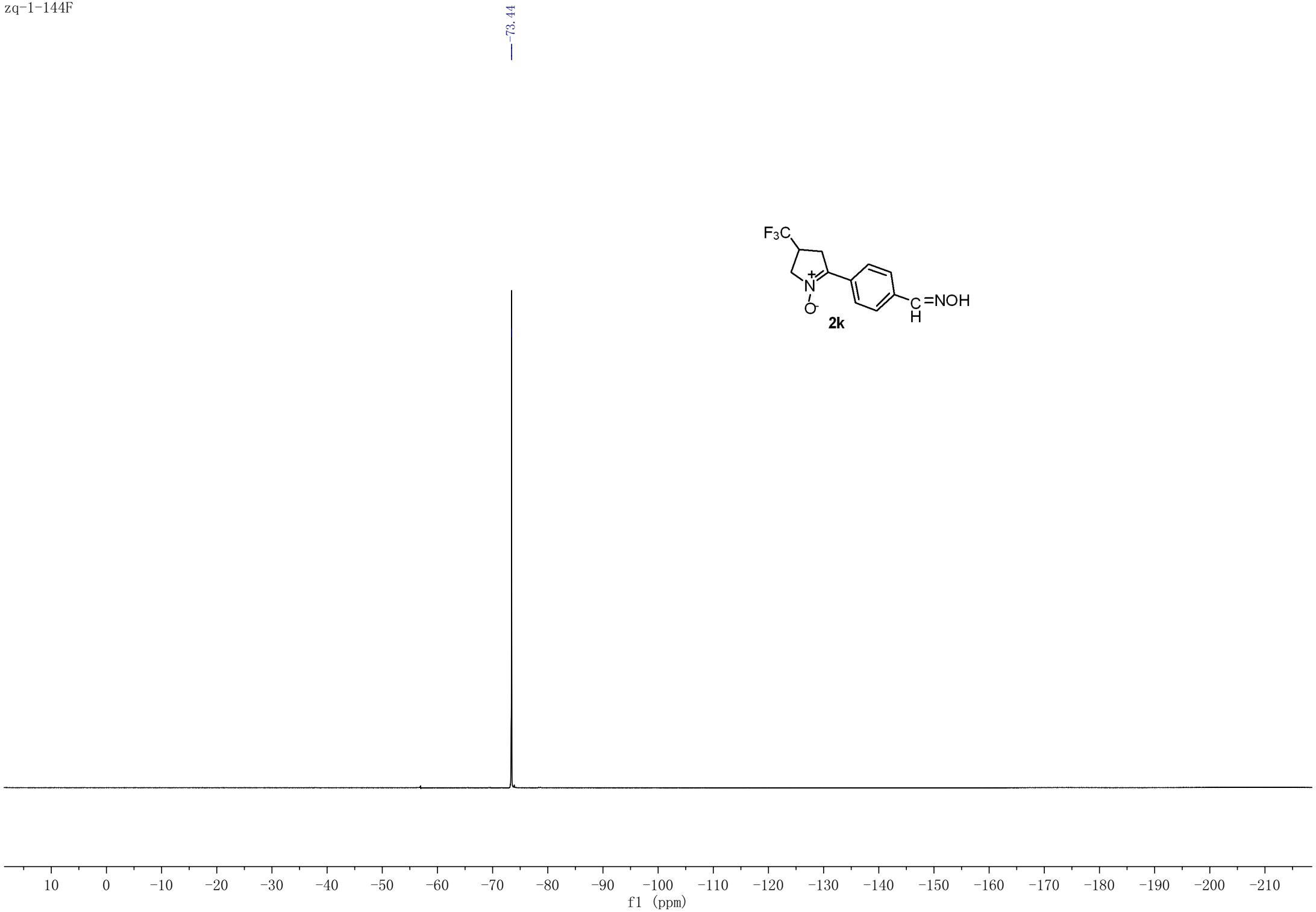
ZQ-1-144
ZQ-1-144



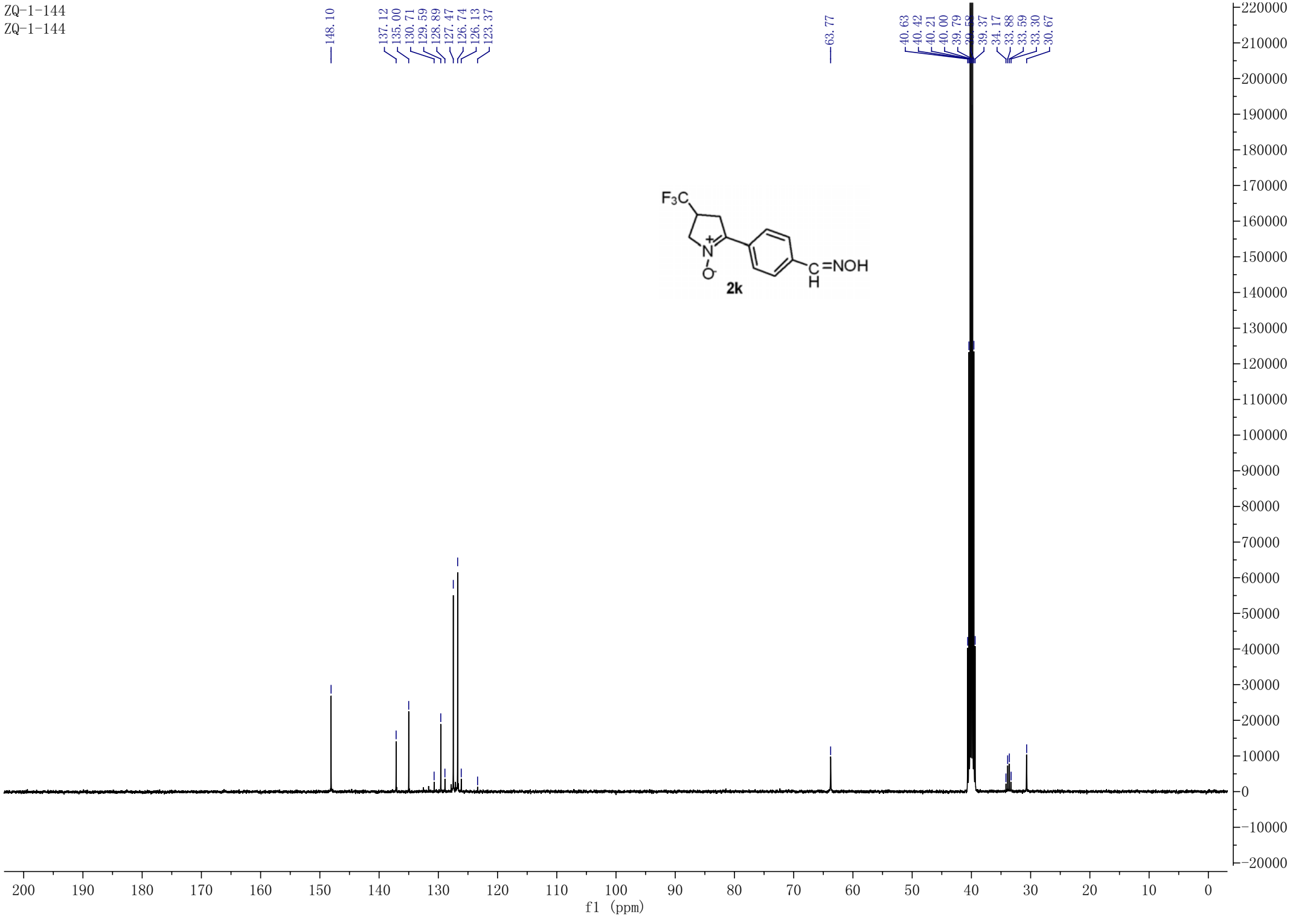
2k

f1 (ppm)

zq-1-144F

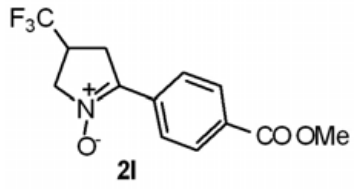

-73.44
F3C
N+
O-
C
H
=NOH
2k
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

ZQ-1-144
ZQ-1-144



zq-1-91
zq-1-91

8.36
8.34
8.11
8.09
7.26
4.49
4.45
4.43
4.40
4.38
4.37
3.93
3.52
3.49
3.47
3.44
3.37
3.35
3.33
3.32

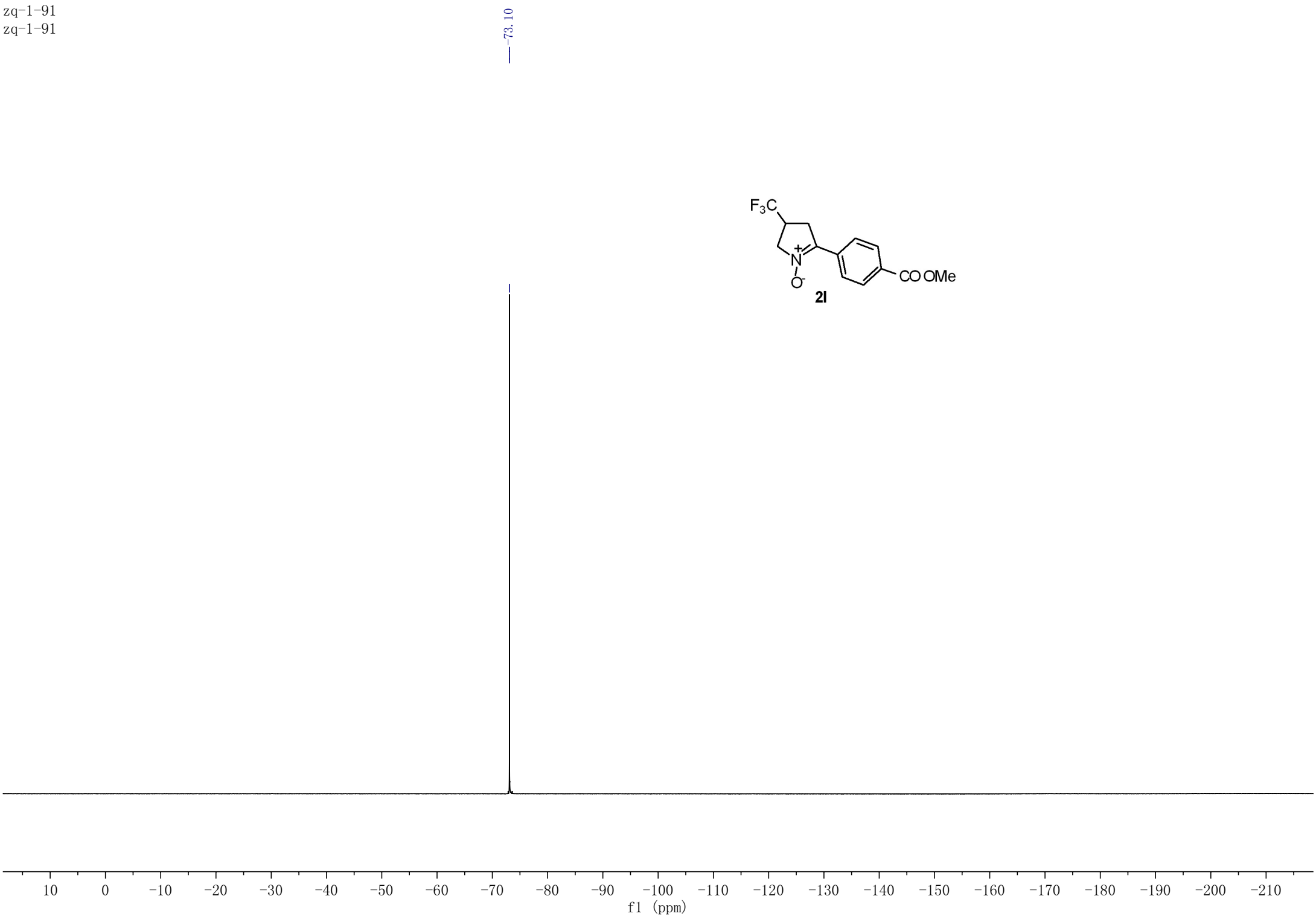


2l

2.05
2.13
2.01
3.04
1.00
2.14

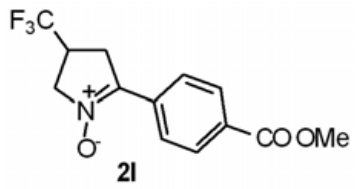
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

zq-1-91
zq-1-91

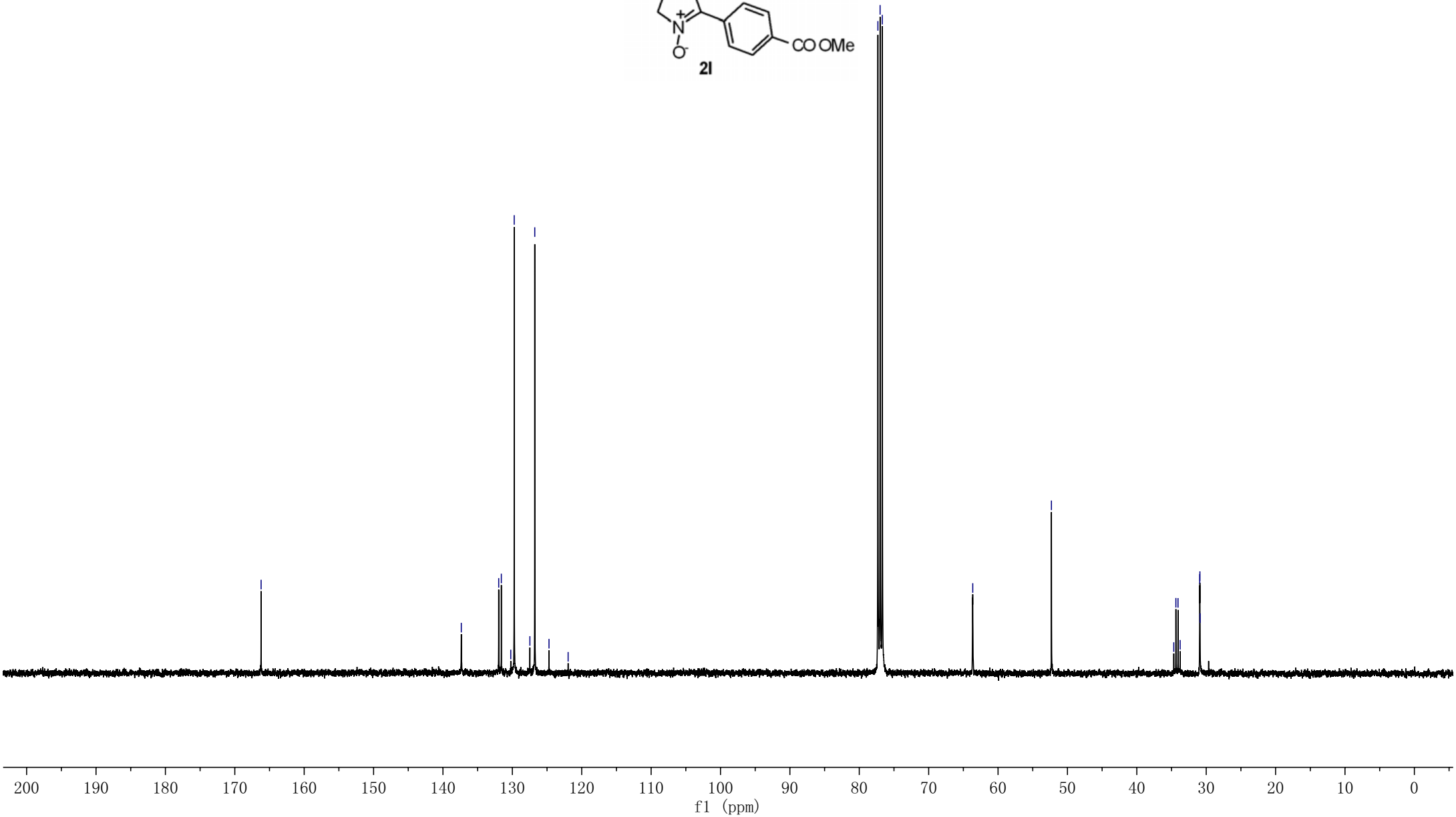

-73.10
F3C
N
O
CO OMe
2l
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

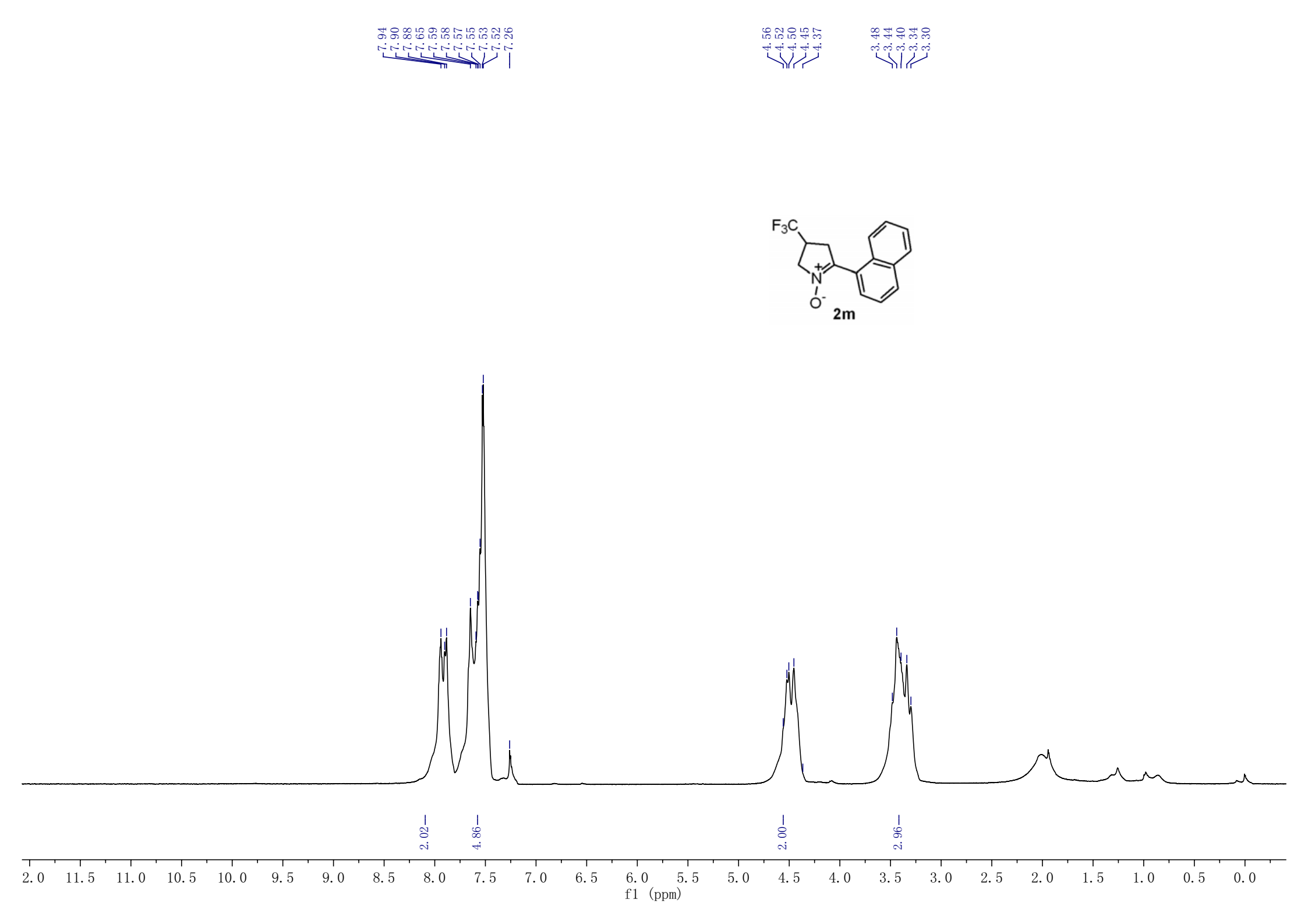
zq-1-91
zq-1-91

166.21
137.36
131.97
131.59
130.23
129.73
127.47
126.77
124.72
121.96
77.32
77.00
76.68
63.65
52.31
34.67
34.37
34.06
33.76
30.94
30.91
30.88



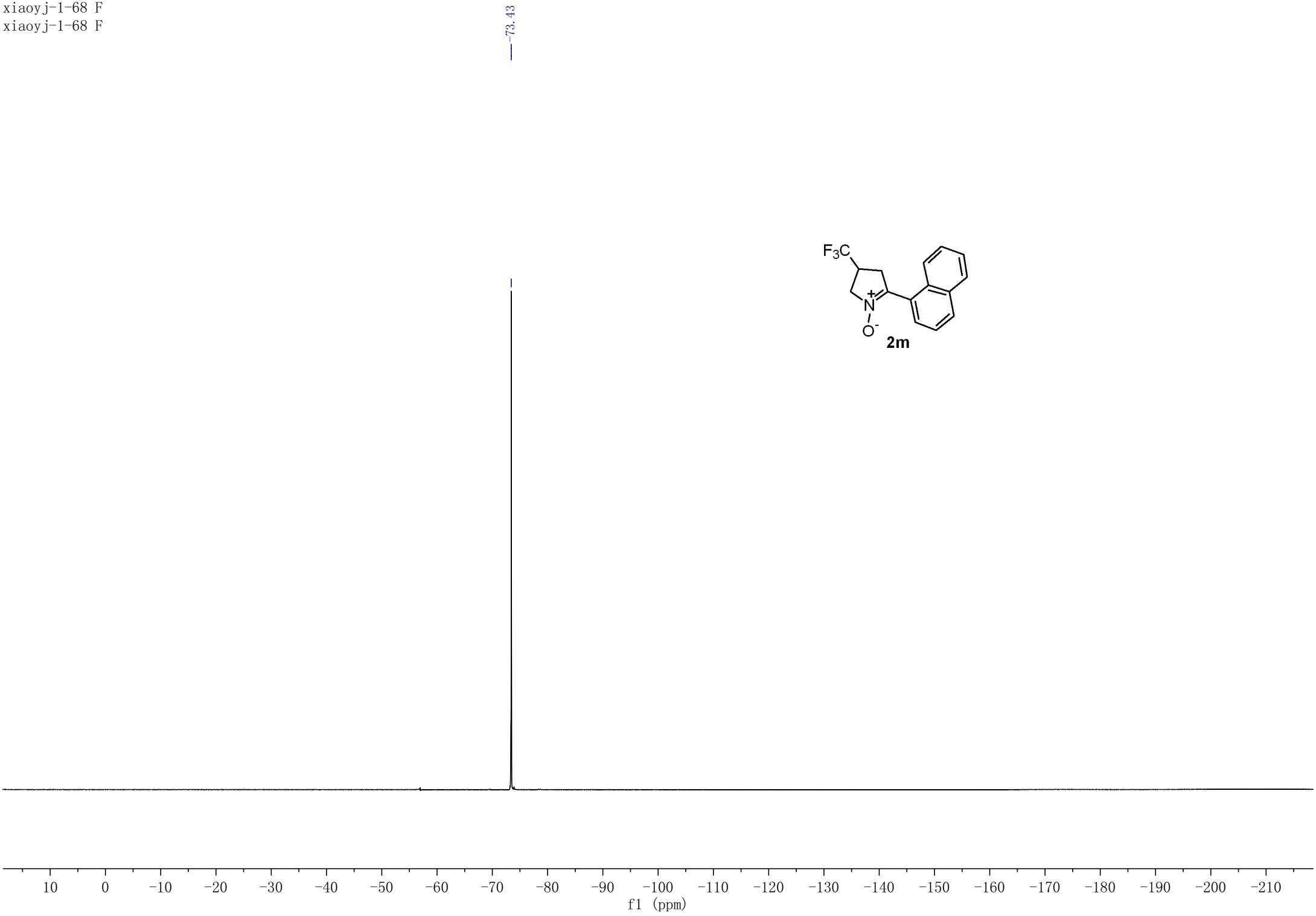
2l

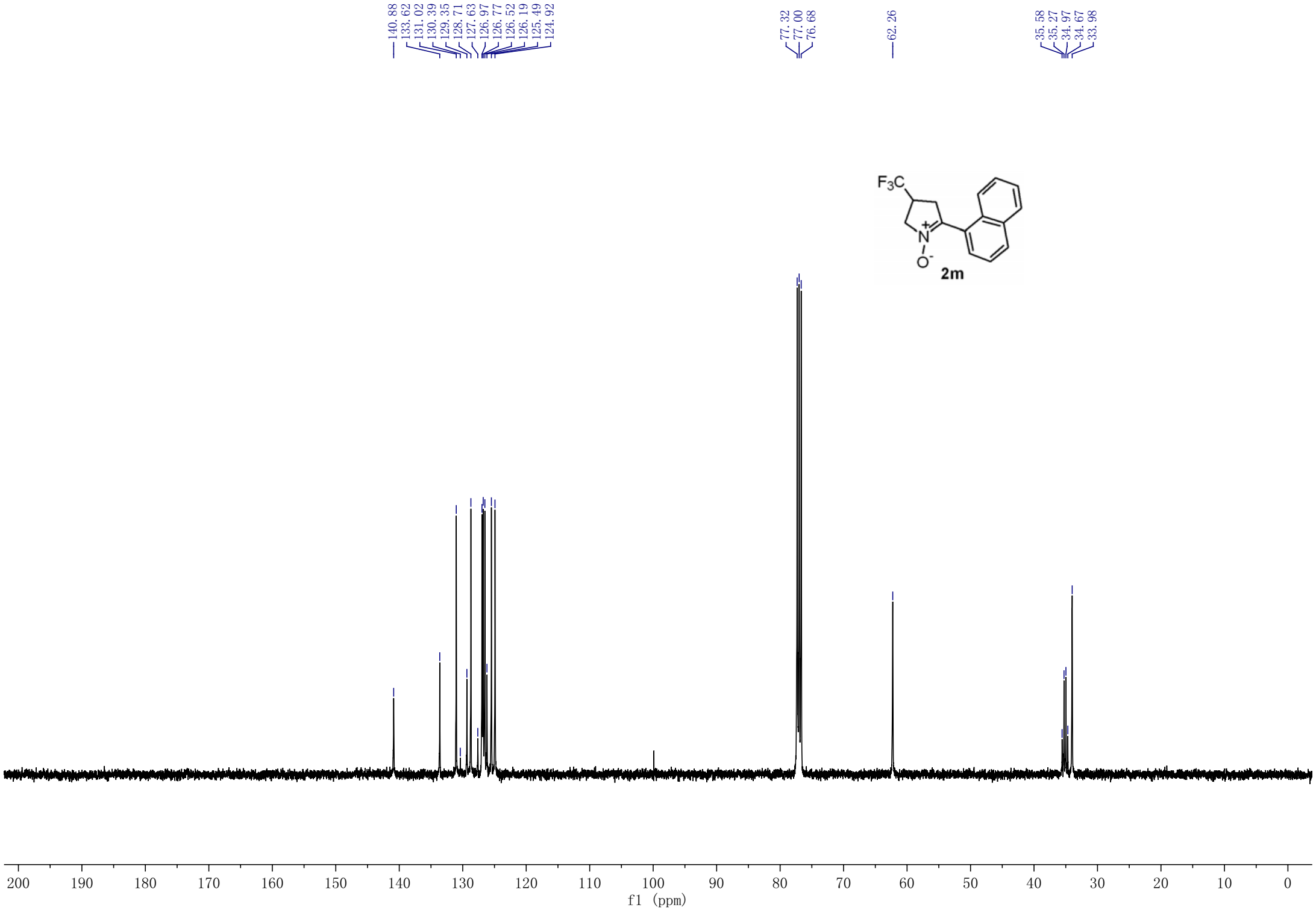



7.94
7.90
7.88
7.65
7.59
7.58
7.57
7.55
7.53
7.52
7.26
4.56
4.52
4.50
4.45
4.37
3.48
3.44
3.40
3.34
3.30
F3C
N
O
2m
2.02
4.86
2.00
2.96
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

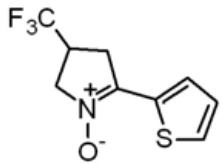
xiaoyj-1-68 F
xiaoyj-1-68 F

2m

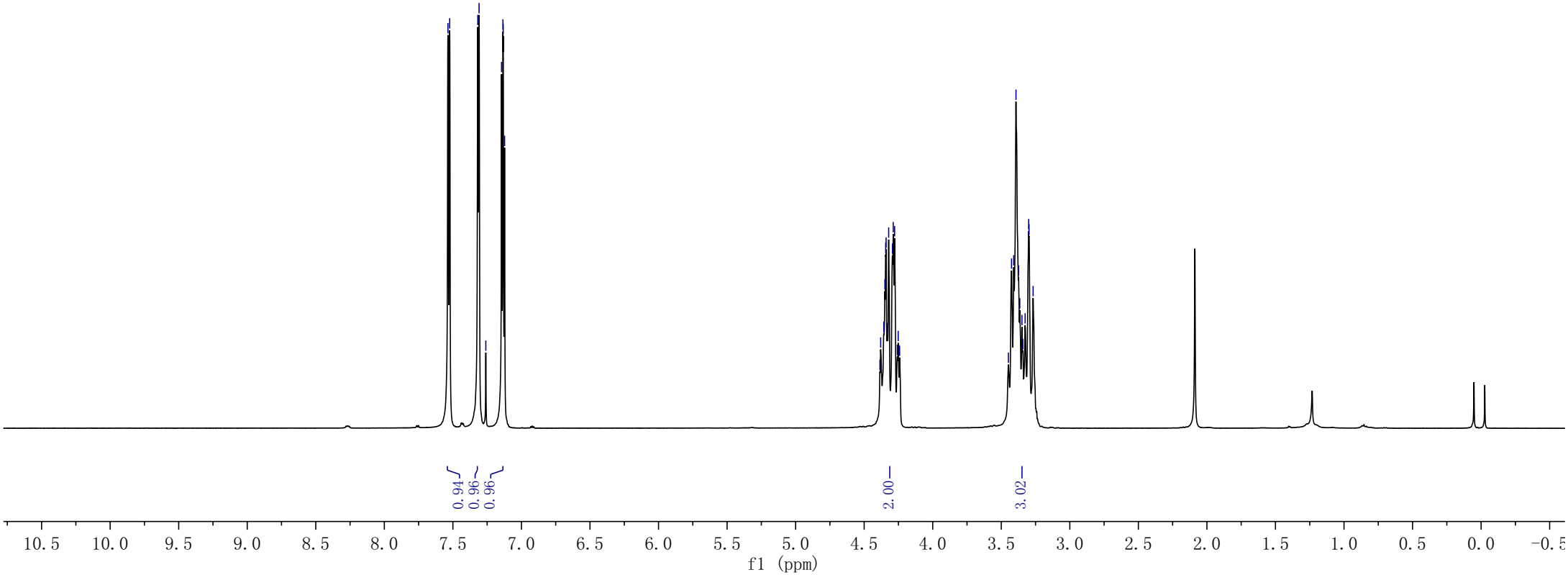



140.88
133.62
131.02
130.39
129.35
128.71
127.63
126.97
126.77
126.52
126.19
125.49
124.92
77.32
77.00
76.68
62.26
35.58
35.27
34.97
34.67
33.98
F3C
N
O
2m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

z1-1-102
z1-1-102

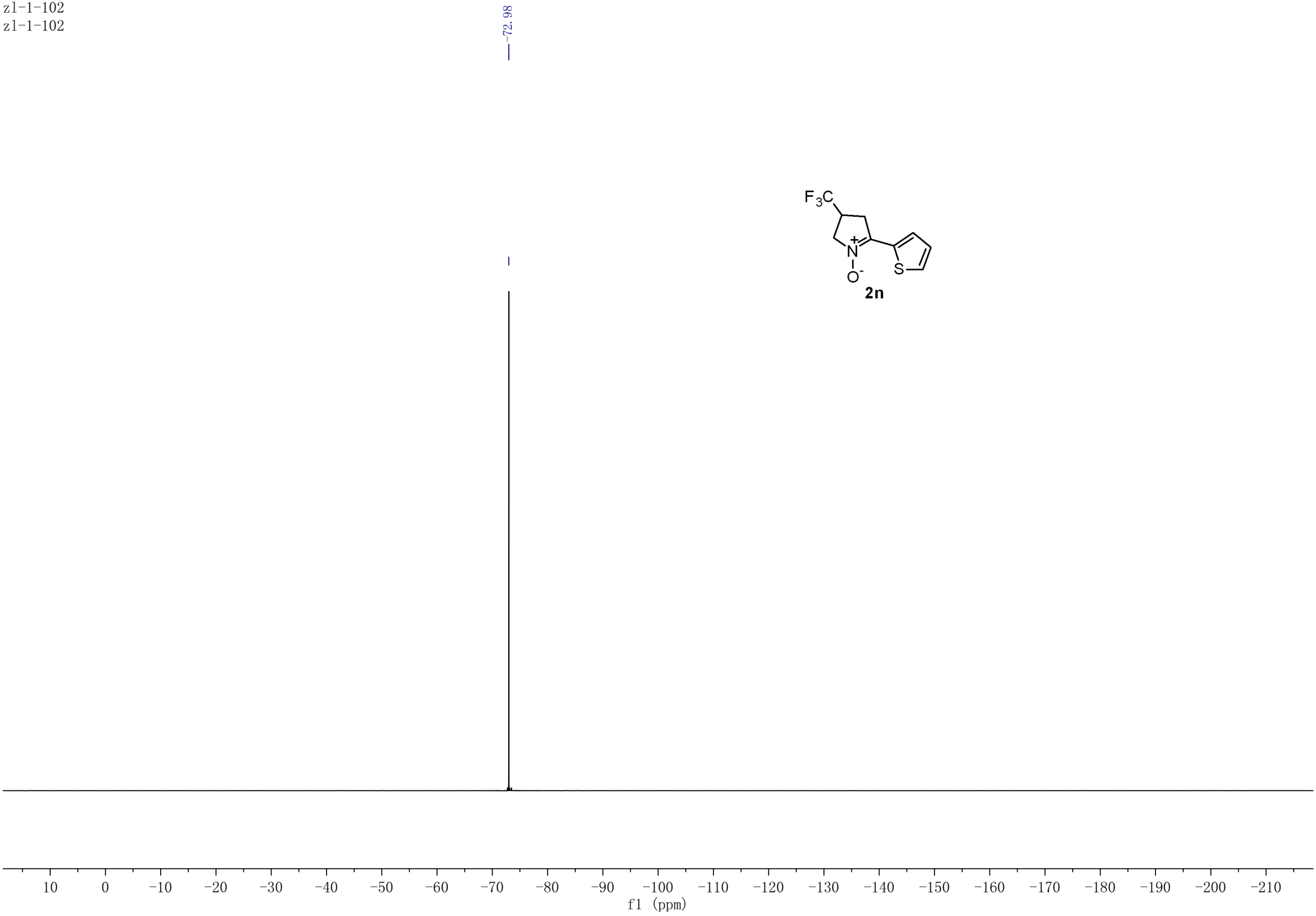


2n



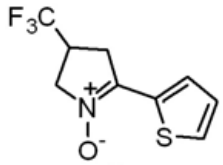
zl-1-102
zl-1-102

2n

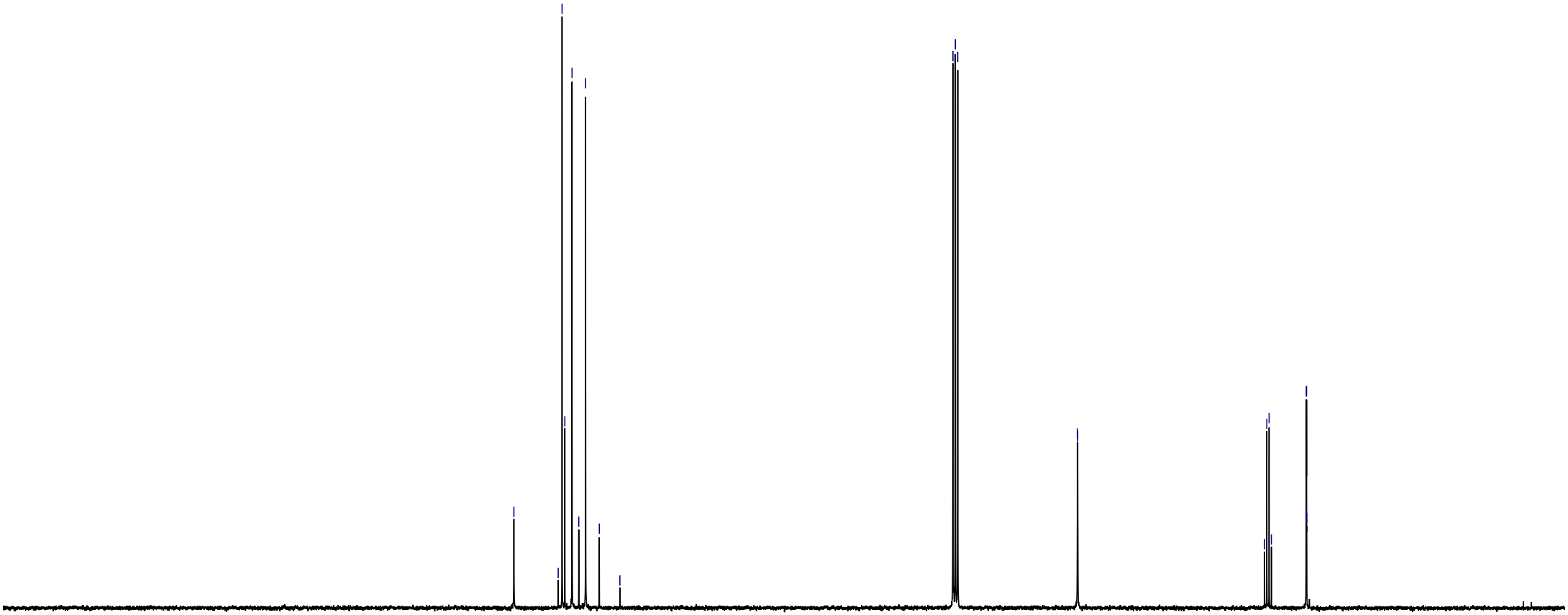


zl-102
zl-1-102

136.14
130.20
129.69
129.31
128.35
127.45
126.53
124.69
121.94
77.32
77.00
76.68
60.64
60.61
35.58
35.28
34.97
34.67
30.01
29.98
29.95
29.93



2n



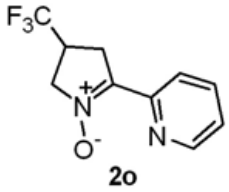
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

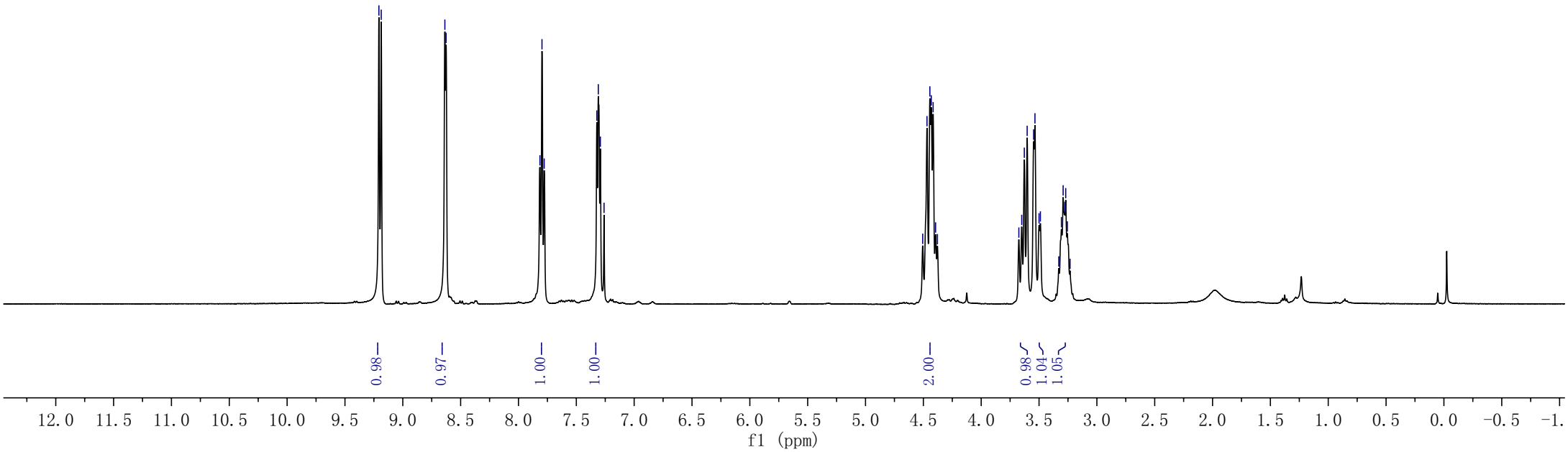
zq-1-118
zq-1-118

9.21 9.19 8.64 8.63 7.81 7.80 7.78 7.32 7.31 7.29 7.26

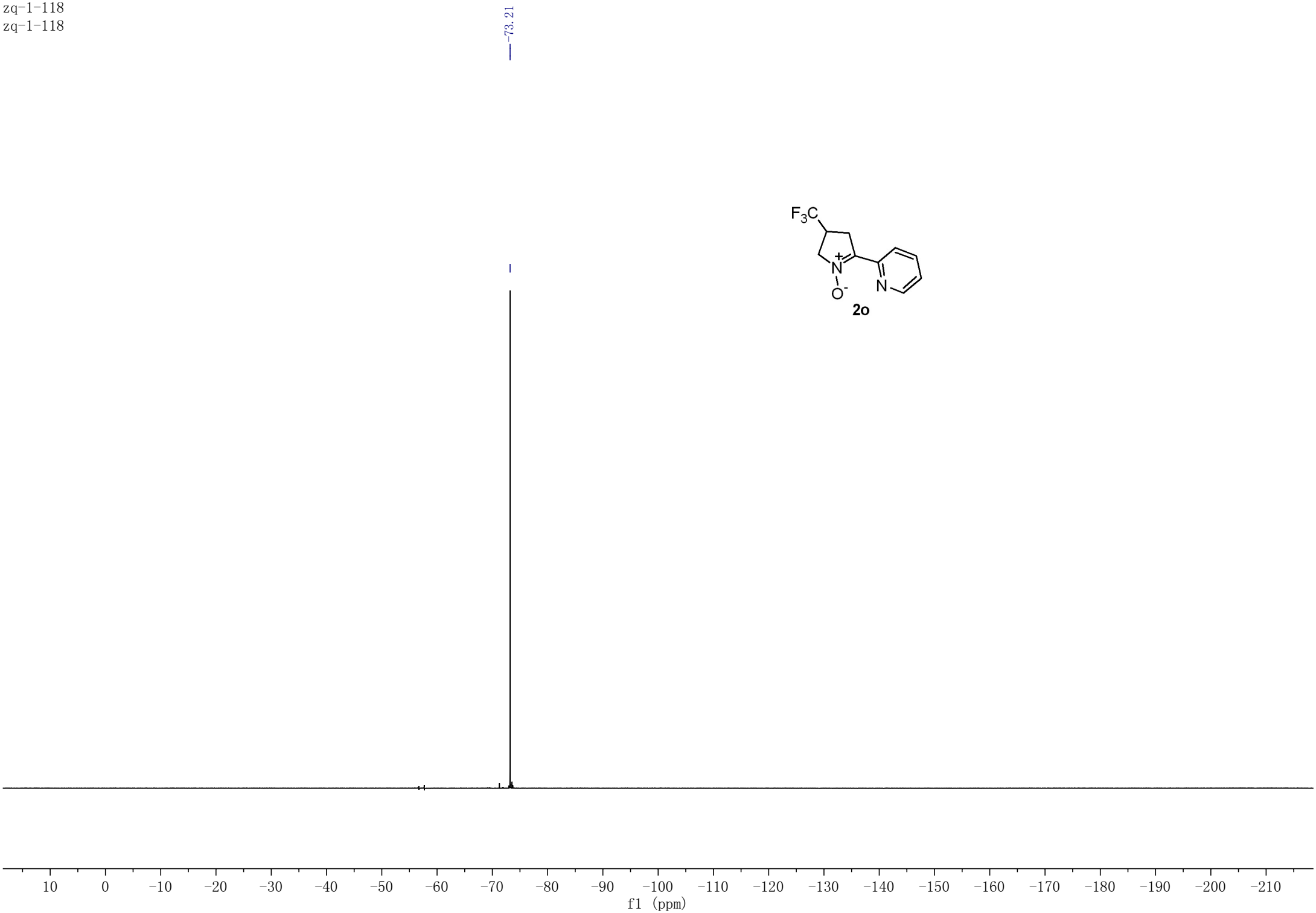
4.51 4.47 4.44 4.43 4.42 4.39 4.38 3.67 3.65 3.63 3.60 3.55 3.54 3.50 3.49 3.33 3.31 3.29 3.28 3.27 3.26 3.23



2o

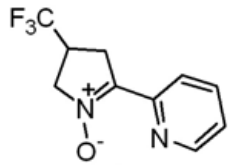


zq-1-118
zq-1-118



zq-1-118
zq-1-118

149.37
147.29
140.49
136.63
130.41
127.65
124.90
124.73
123.16
122.14
77.32
77.00
76.68
64.20
64.18
34.60
34.30
34.00
33.69
30.90
30.88
30.85



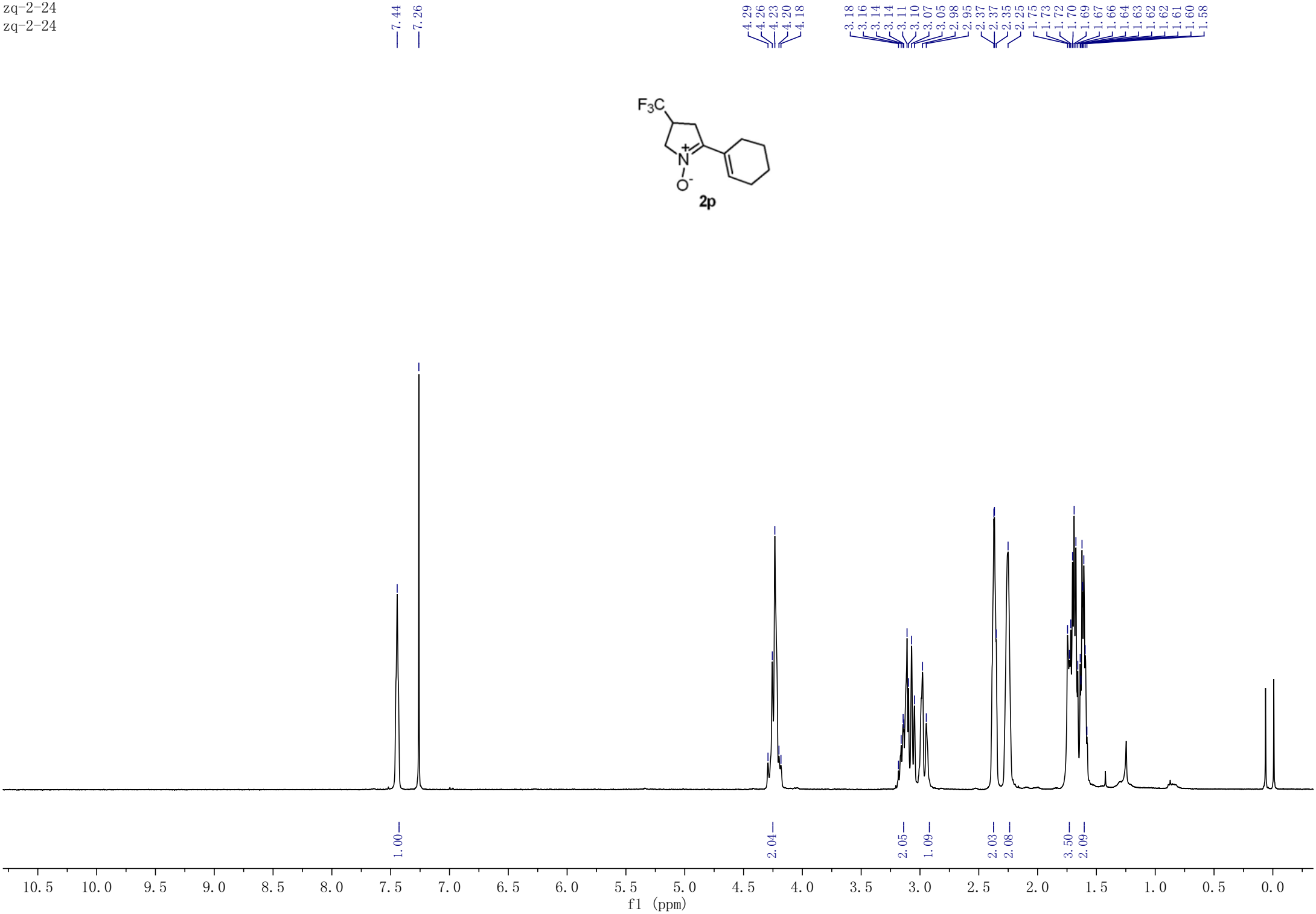
2o

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

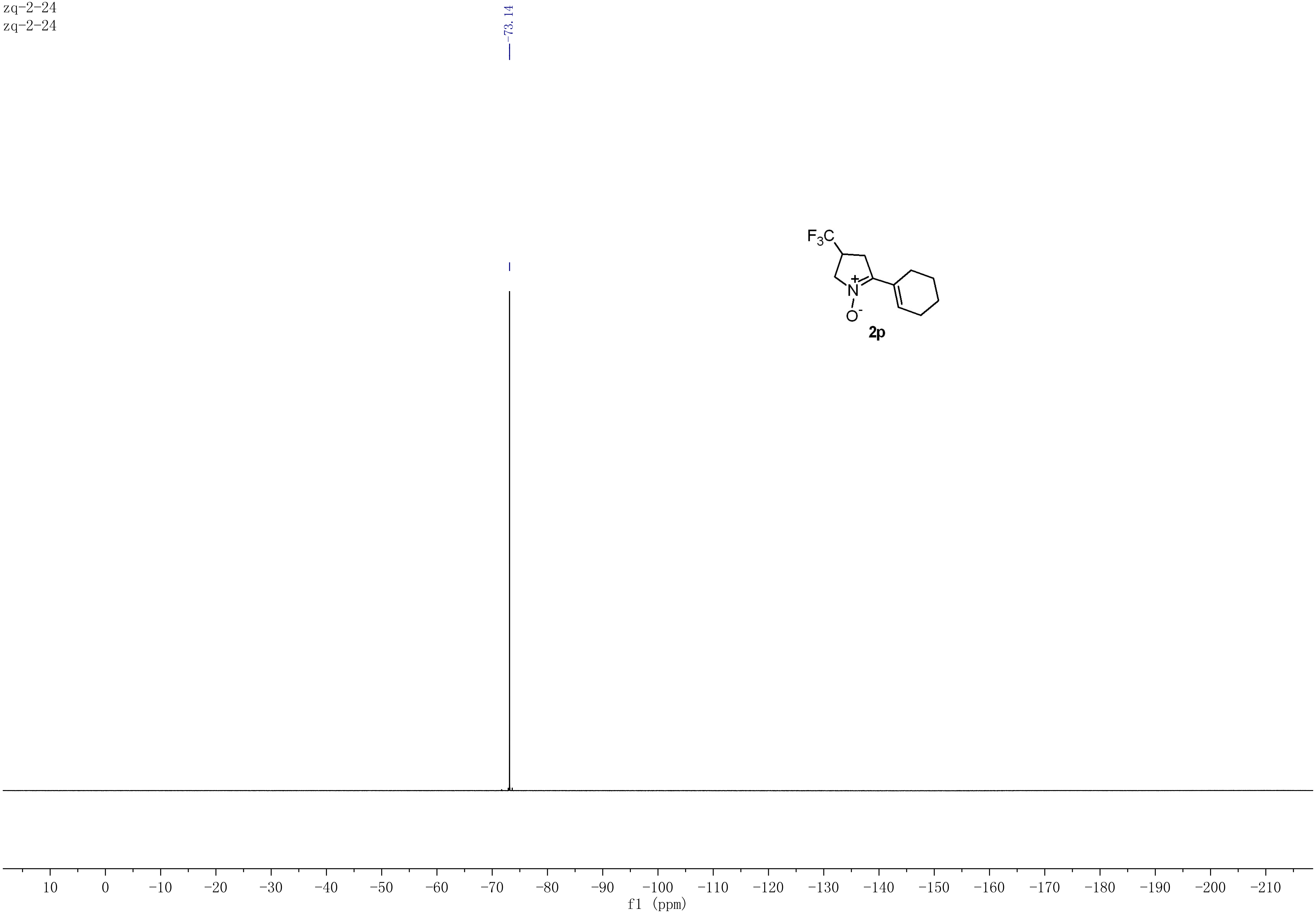
f1 (ppm)

zq-2-24
zq-2-24

F3C
N
O
2p


7.44
7.26
4.29
4.26
4.23
4.20
4.18
3.18
3.16
3.14
3.14
3.11
3.10
3.07
3.05
2.98
2.95
2.37
2.37
2.35
2.25
1.75
1.73
1.72
1.70
1.69
1.67
1.66
1.64
1.63
1.62
1.62
1.61
1.60
1.58
1.00
2.04
2.05
1.09
2.03
2.08
3.50
2.09
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)

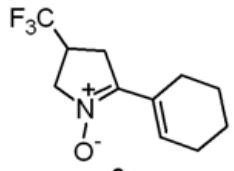
zq-2-24
zq-2-24



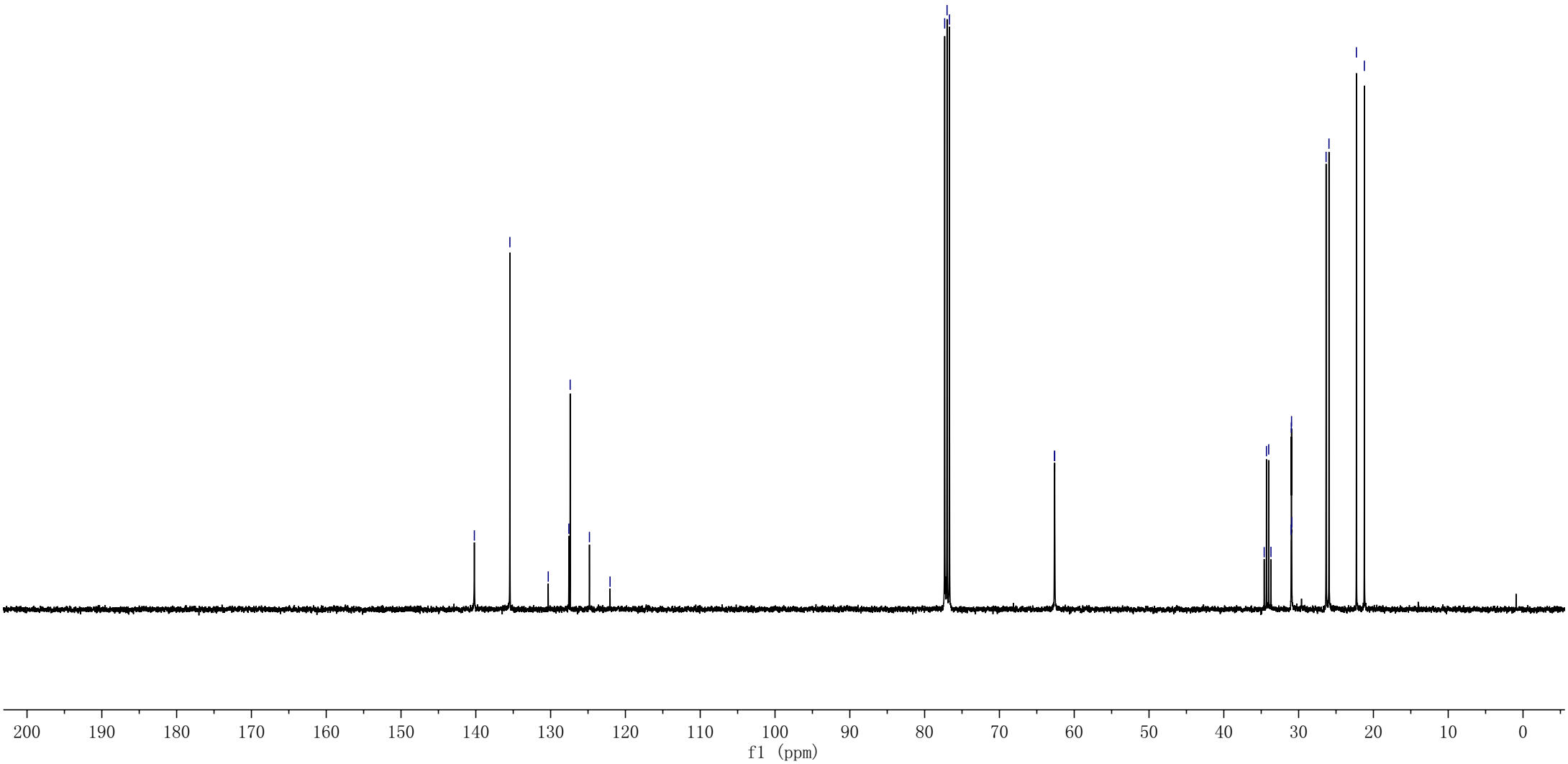
2p

zq-2-24
zq-2-24

140.19
135.45
130.32
127.56
127.39
124.81
122.05
77.32
77.00
76.68
62.63
62.61
34.60
34.30
34.00
33.70
31.00
30.97
30.95
30.92
26.33
25.94
22.28
21.21

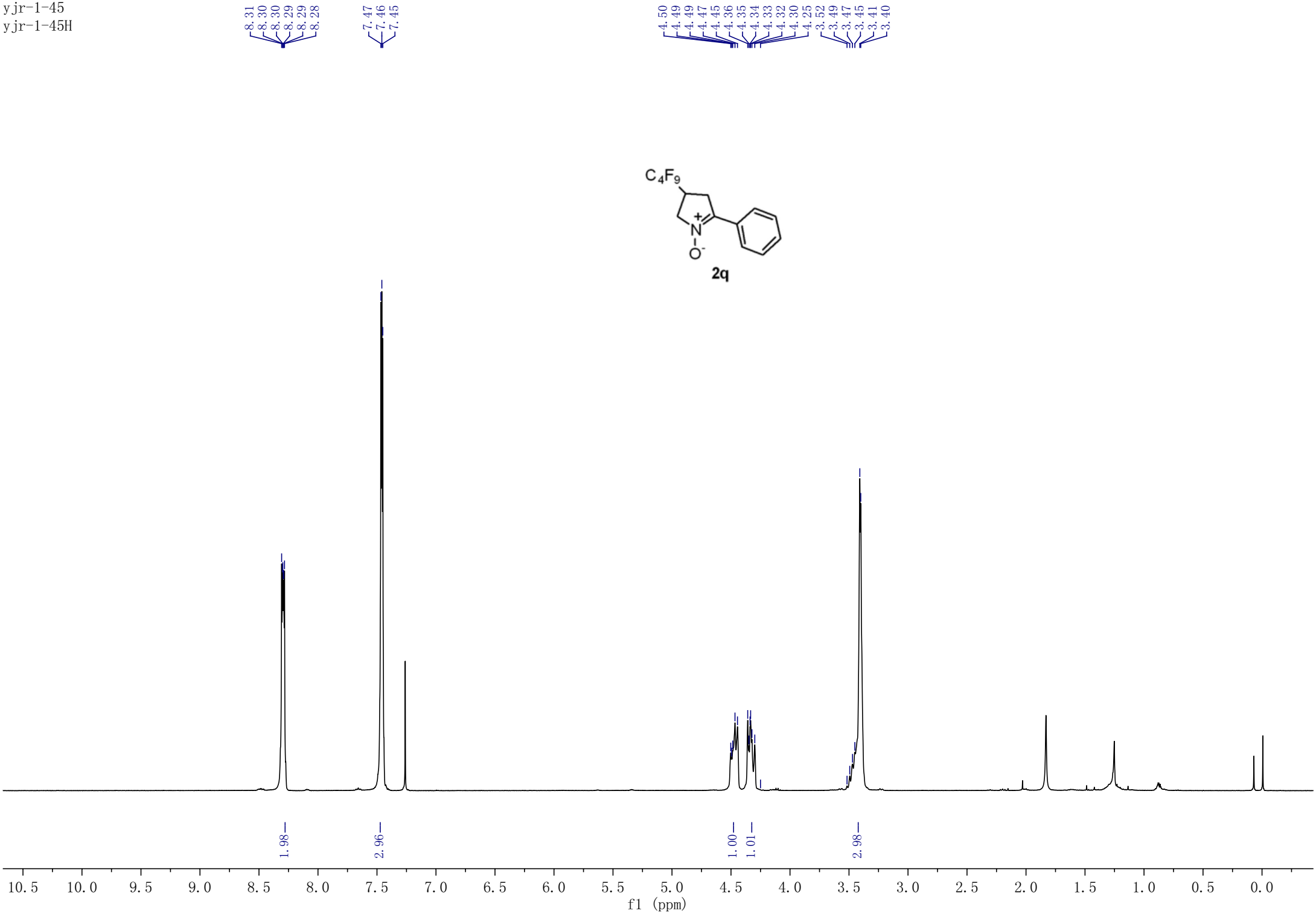


2p

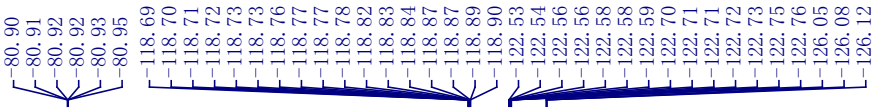


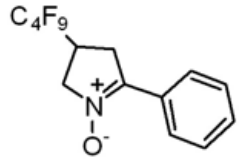
yjr-1-45
yjr-1-45H

2q

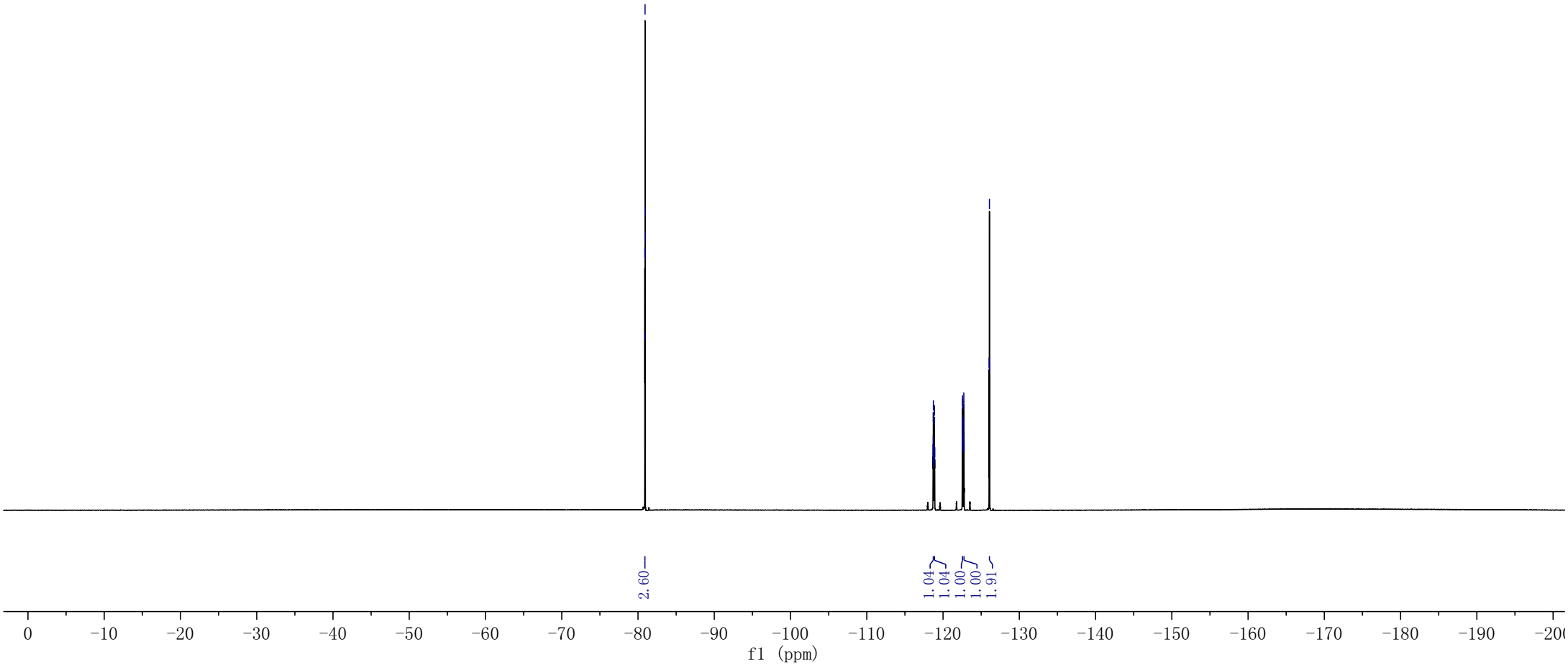


yjr-1-45
yjr-1-45F



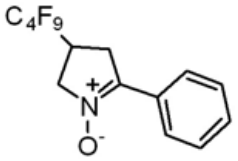


2q



yjr-1-45
YJR-1-45

137.98
130.90
128.59
128.18
127.06
119.46
118.66
118.33
117.22
116.90
116.58
115.79
115.46
114.66
114.31
114.07
111.38
111.02
110.69
110.43
108.71
108.43
106.01
105.69
77.32
77.00
76.68
62.85
33.10
32.87
32.65
30.43



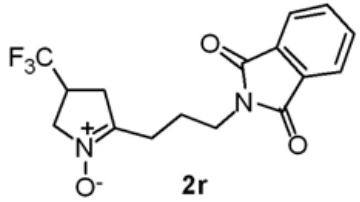
2q

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

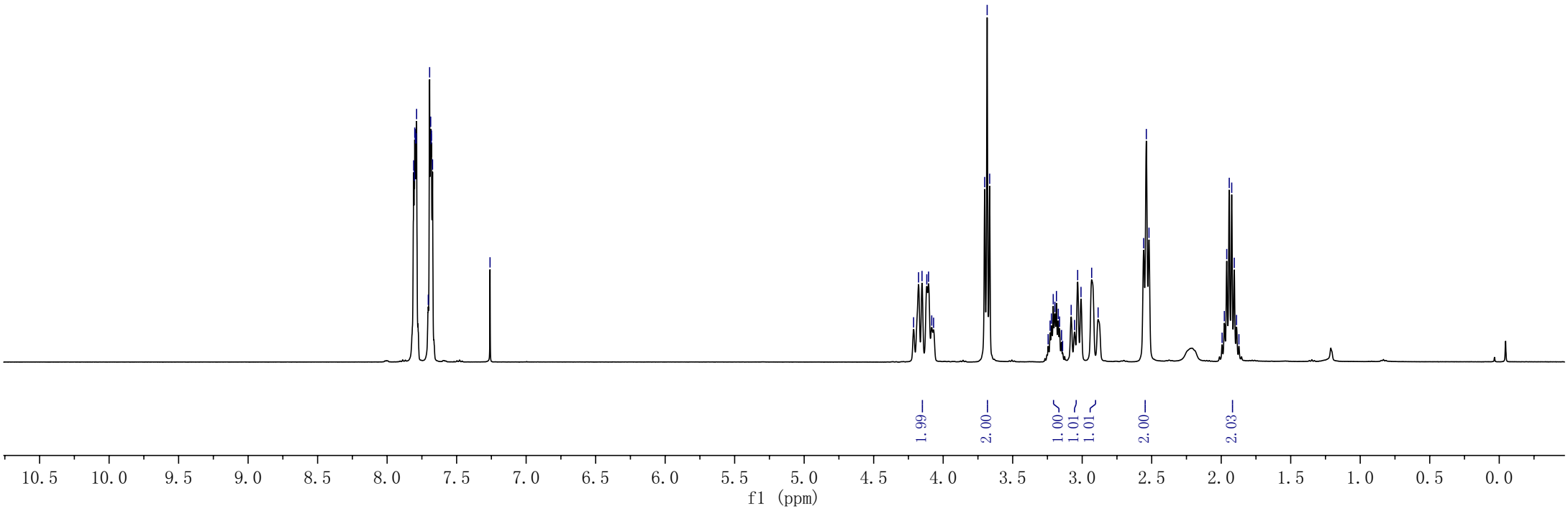
zq-1-120
zq-1-120

7.81 7.80 7.80 7.80 7.80 7.79 7.79 7.70 7.69 7.69 7.68 7.68 7.67 7.26

4.21 4.18 4.15 4.12 4.11 4.08 4.07 3.70 3.68 3.67 3.21 3.20 3.19 3.08 3.03 3.01 2.93 2.56 2.54 2.52 1.99 1.98 1.96 1.94 1.92 1.91 1.89 1.87

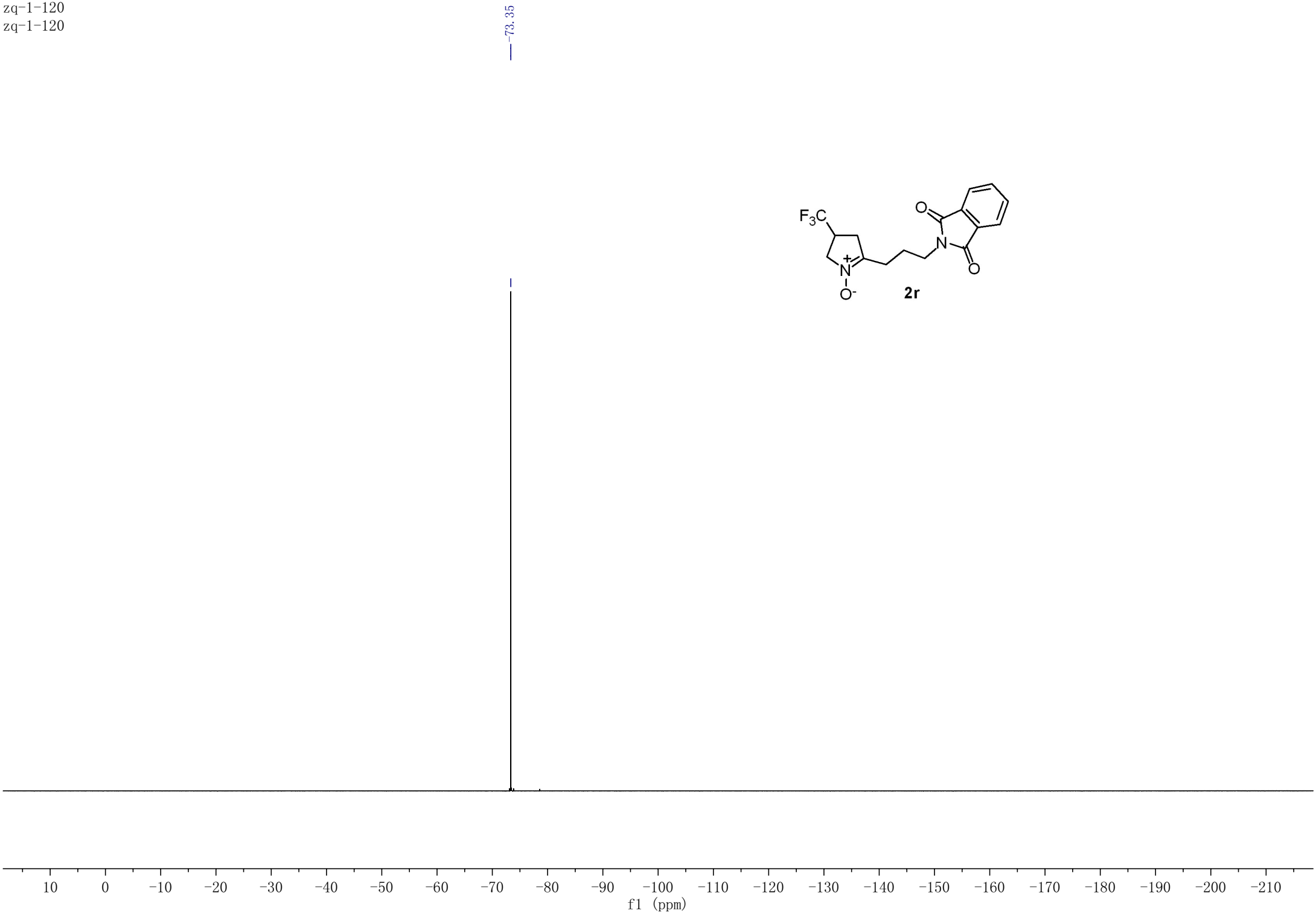


2r



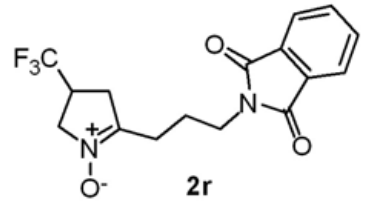
zq-1-120
zq-1-120

2r

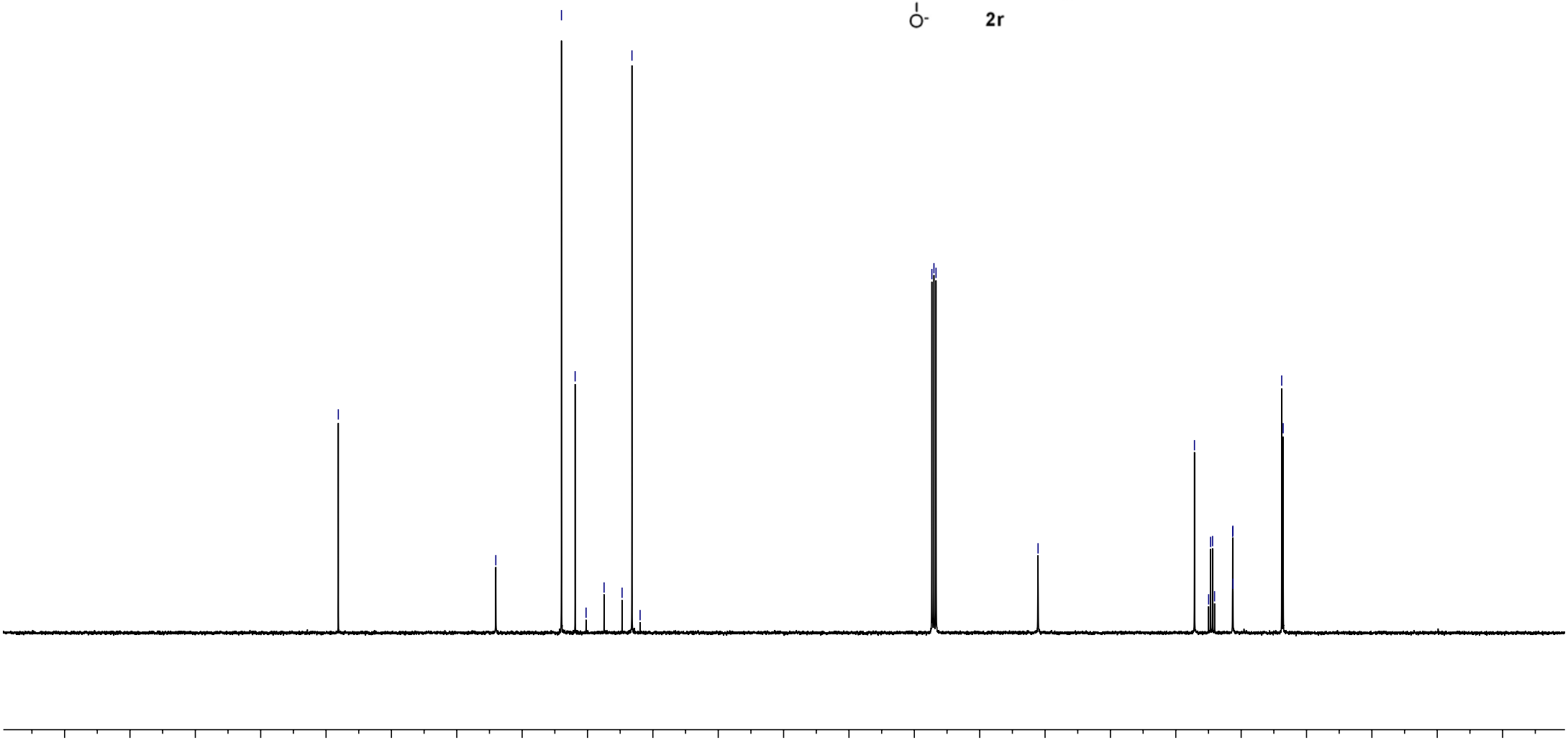


zq-1-120
zq-1-120

168.12
144.03
133.98
131.89
130.22
127.46
124.71
123.20
121.95
77.32
77.00
76.68
61.07
37.14
34.98
34.68
34.37
34.07
31.30
31.27
31.25
23.80
23.57



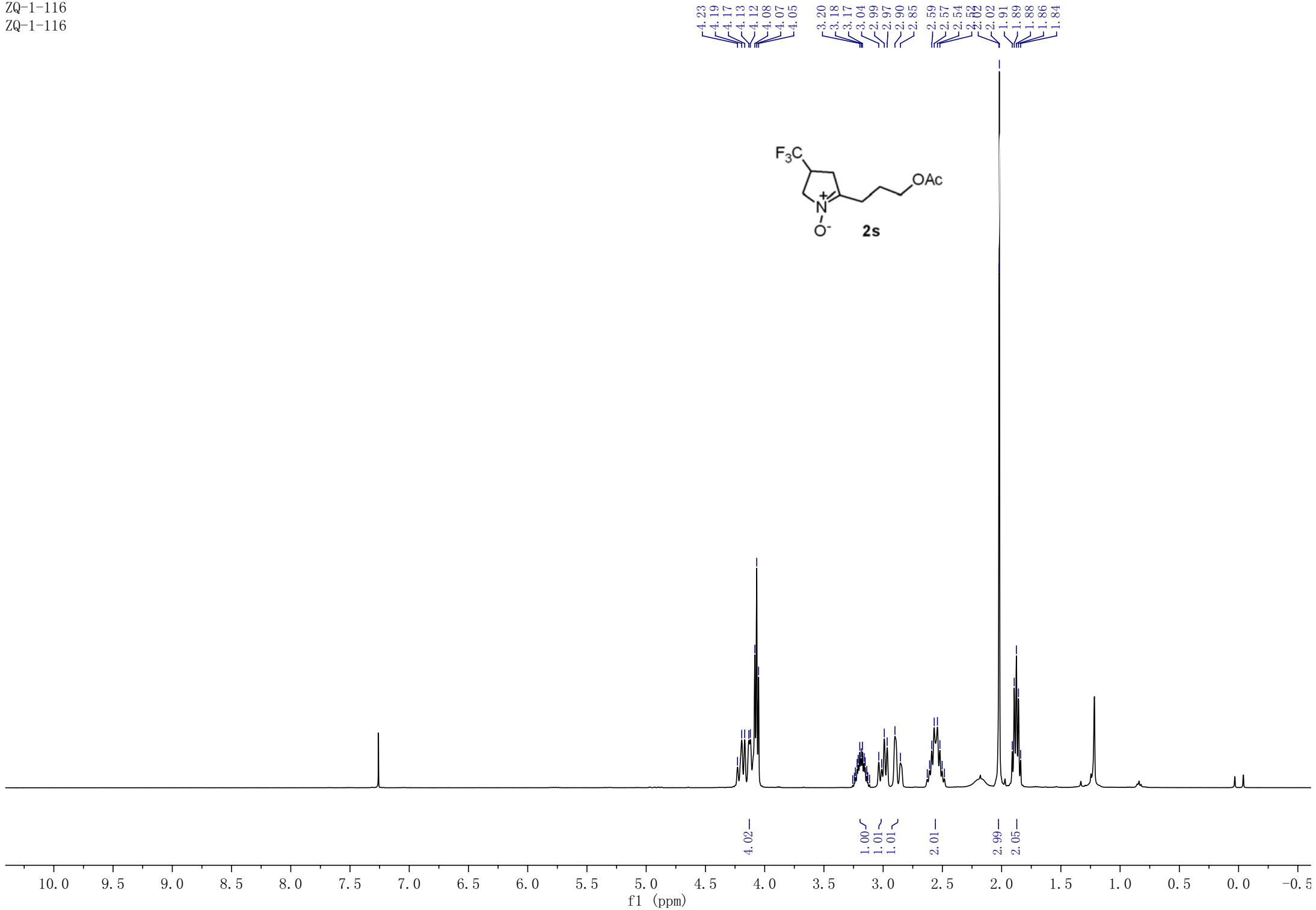
2r



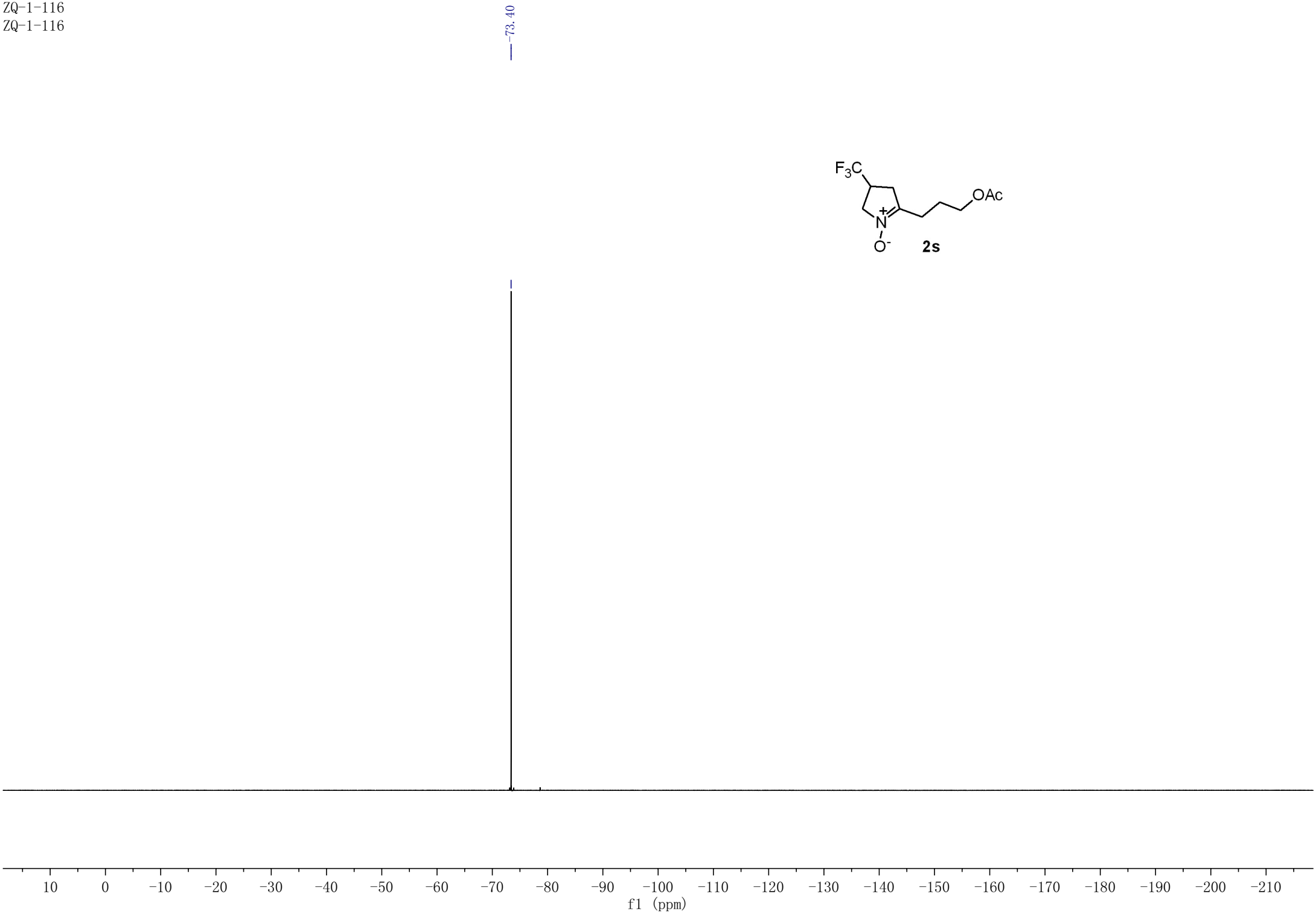
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

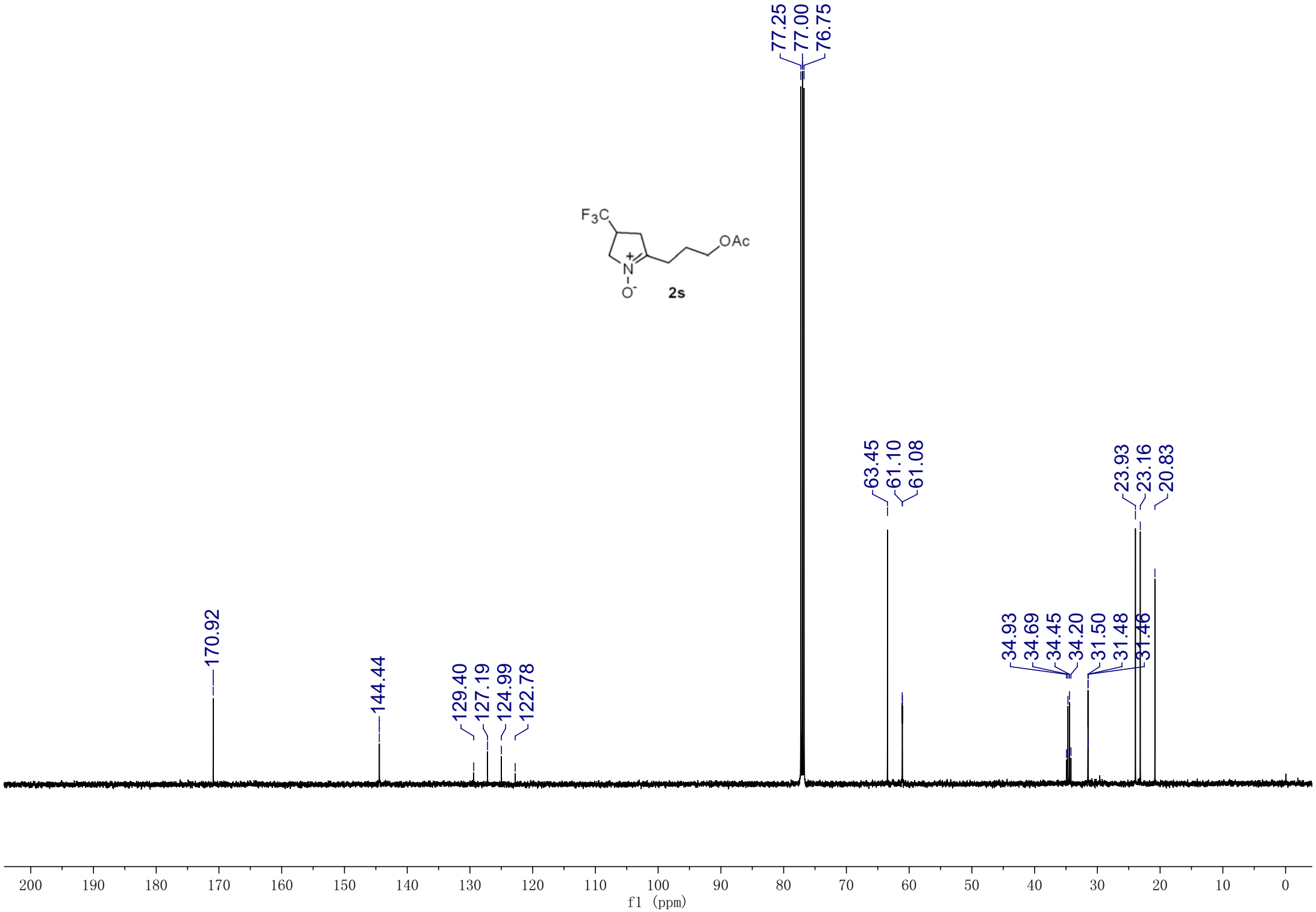
f1 (ppm)

ZQ-1-116
ZQ-1-116

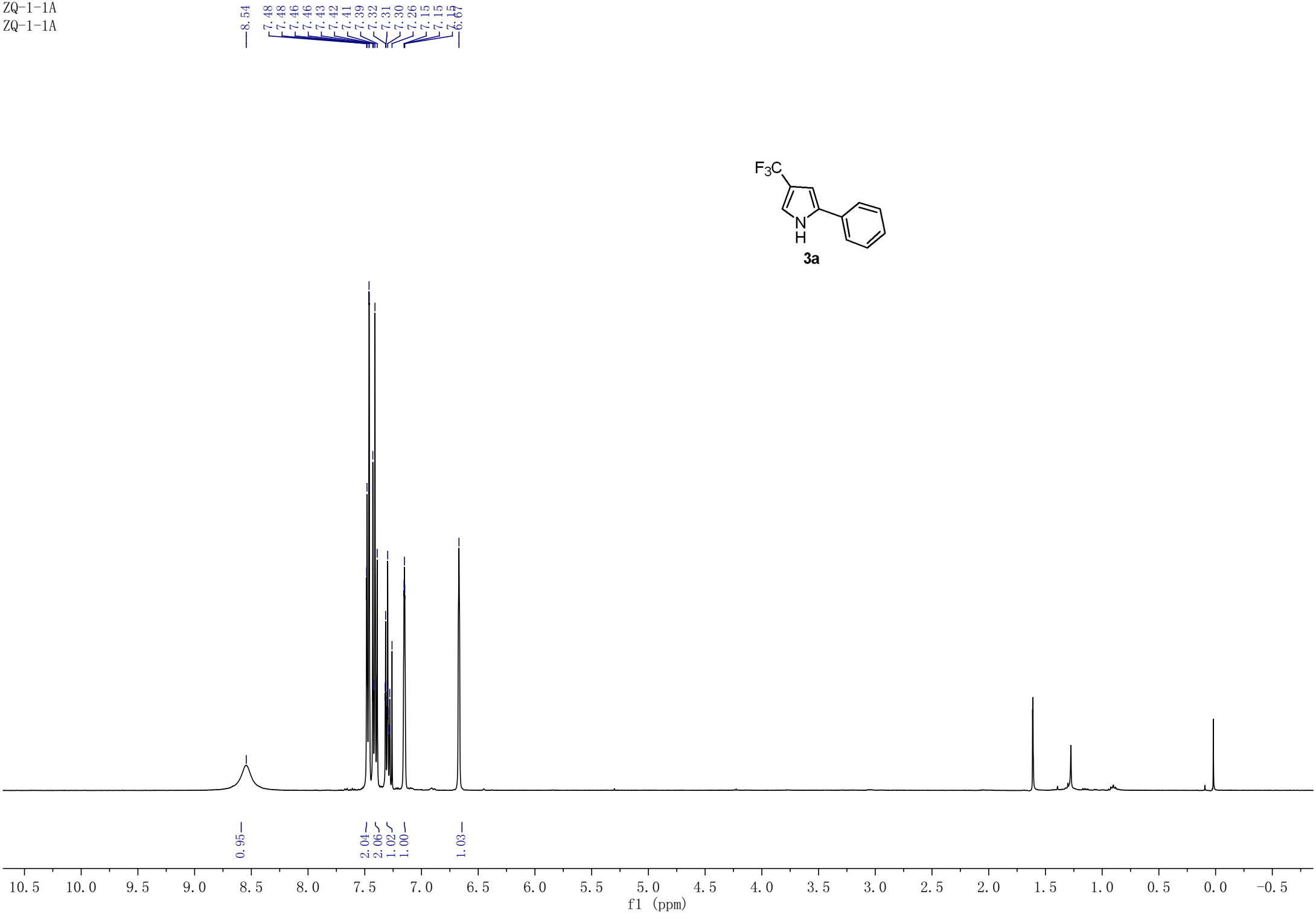


ZQ-1-116
ZQ-1-116

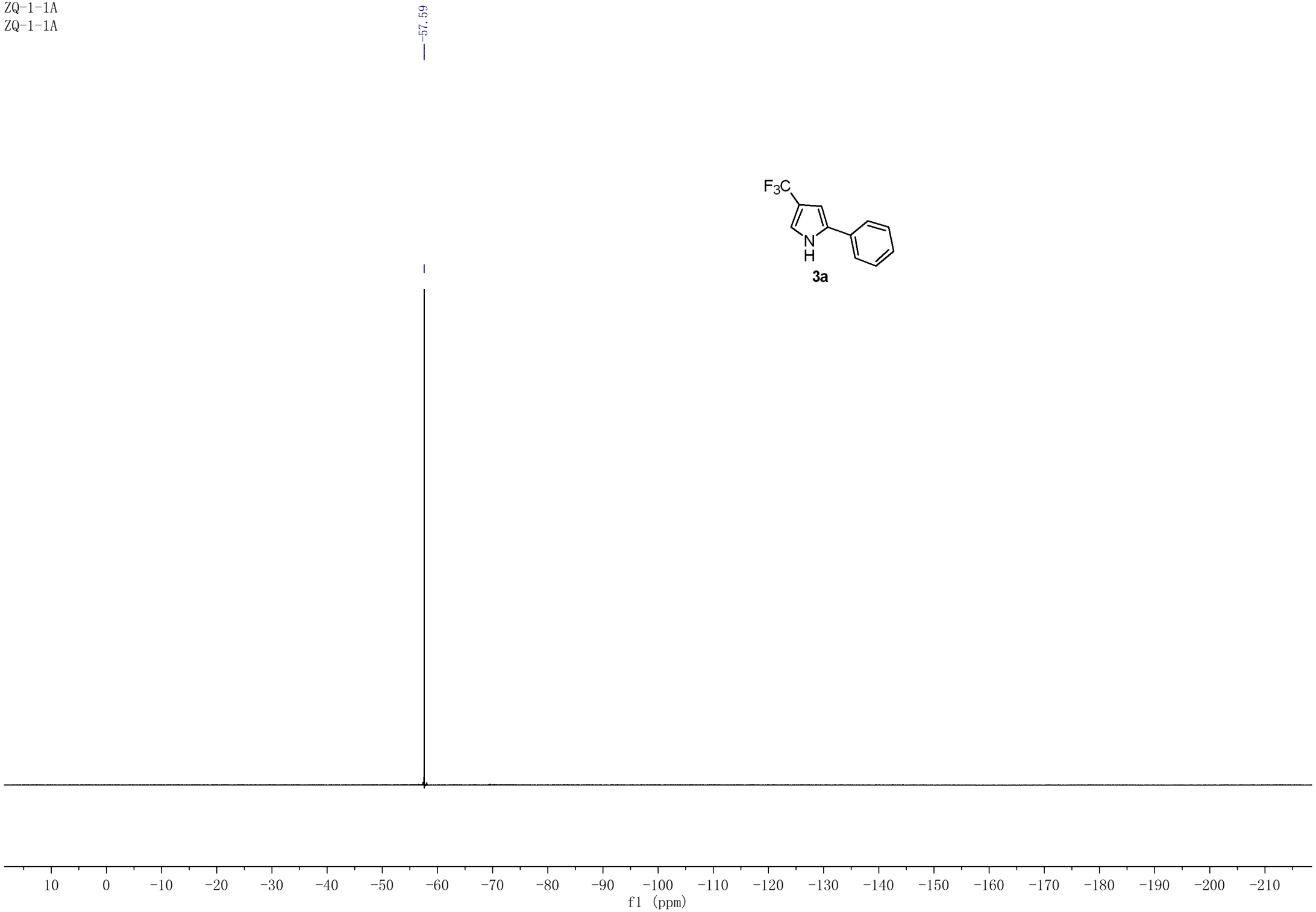


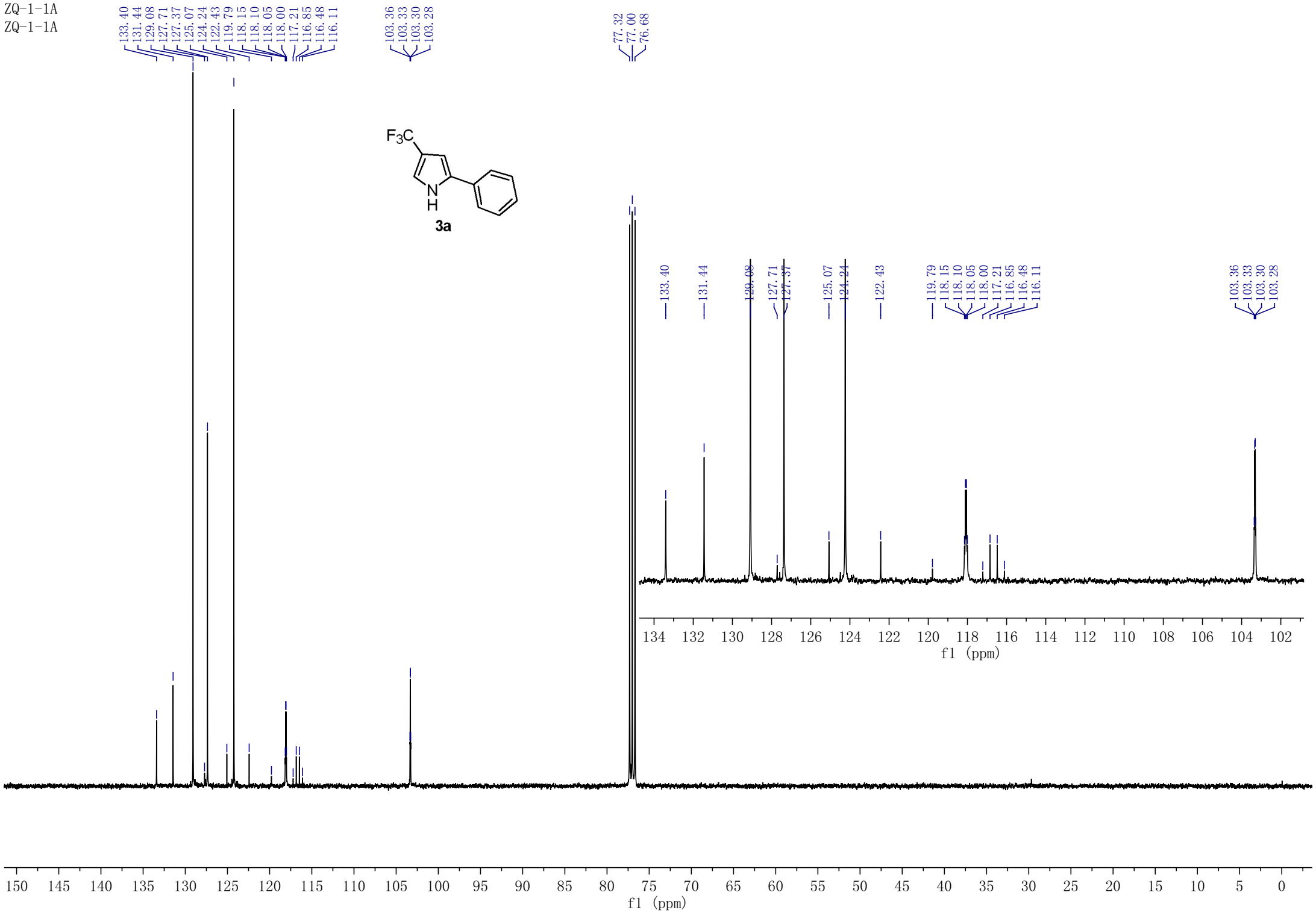

77.25
77.00
76.75
63.45
61.10
61.08
23.93
23.16
20.83
170.92
144.44
129.40
127.19
124.99
122.78
34.93
34.69
34.45
34.20
31.50
31.48
31.46
F3C
OAc
N
O
2s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

ZQ-1-1A
ZQ-1-1A

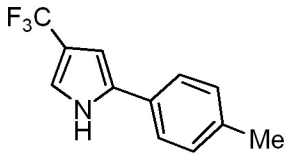

8.54
7.48
7.48
7.46
7.46
7.43
7.42
7.41
7.39
7.32
7.31
7.30
7.26
7.15
7.15
6.67
F3C
N
H
3a
0.95
2.04
2.06
1.02
1.00
1.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

ZQ-1-1A
ZQ-1-1A


-57.59
F3C
N
H
3a
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


ZQ-1-1A
ZQ-1-1A
133.40
131.44
129.08
127.71
127.37
125.07
124.24
122.43
119.79
118.15
118.10
118.05
118.00
117.21
116.85
116.48
116.11
103.36
103.33
103.30
103.28
77.32
77.00
76.68
F3C
N
H
3a
f1 (ppm)

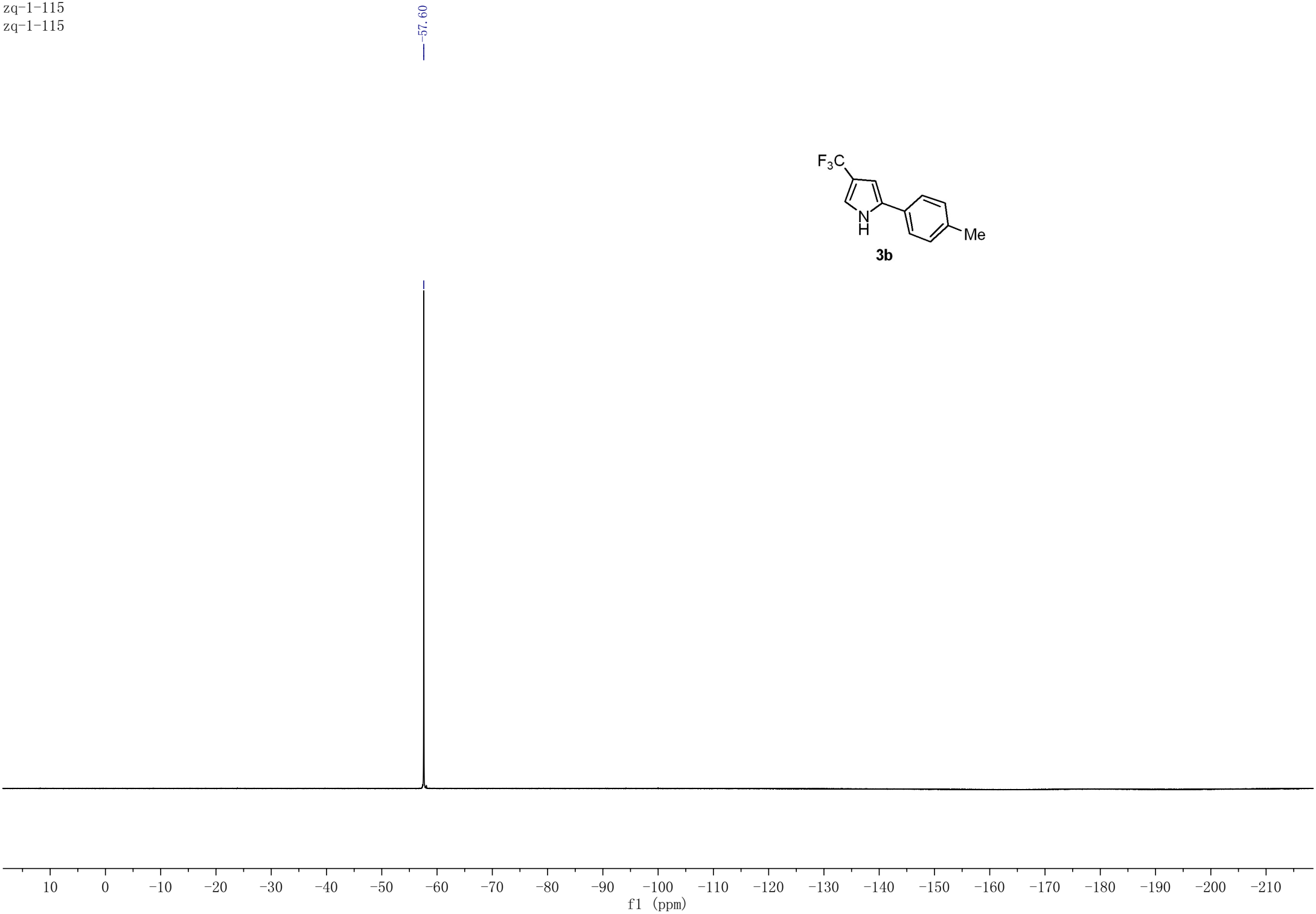
zq-1-115
zq-1-115



3b

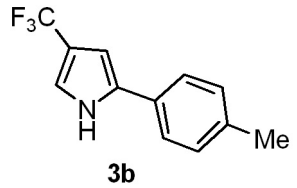
zq-1-115
zq-1-115

3b



zq-1-115
zq-1-115

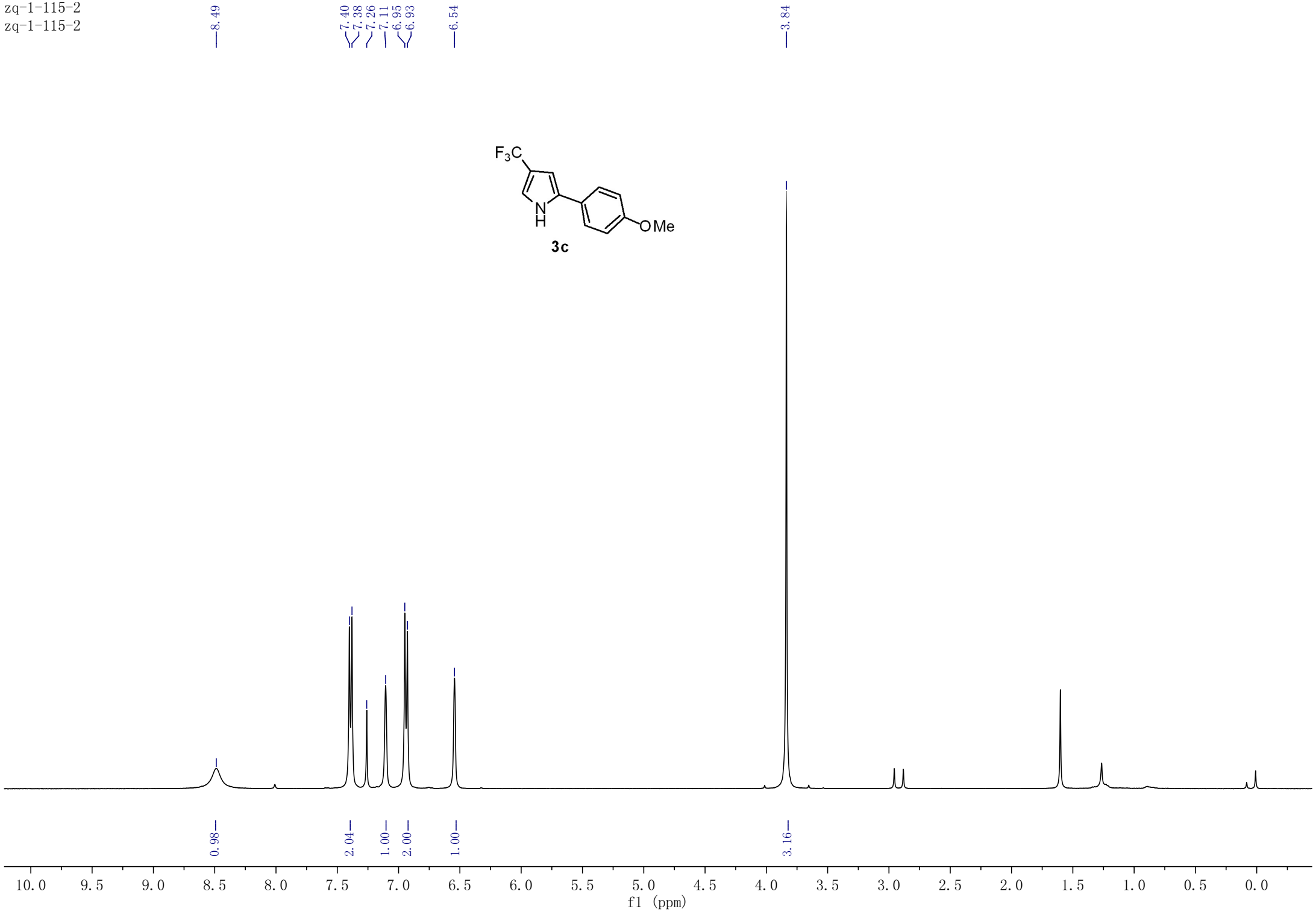
137.25
133.56
129.74
128.73
125.12
124.21
122.48
117.78
117.73
117.68
117.63
116.74
116.37
116.00
103.06
102.81
102.79
102.76
77.32
77.00
76.68
21.12



3b

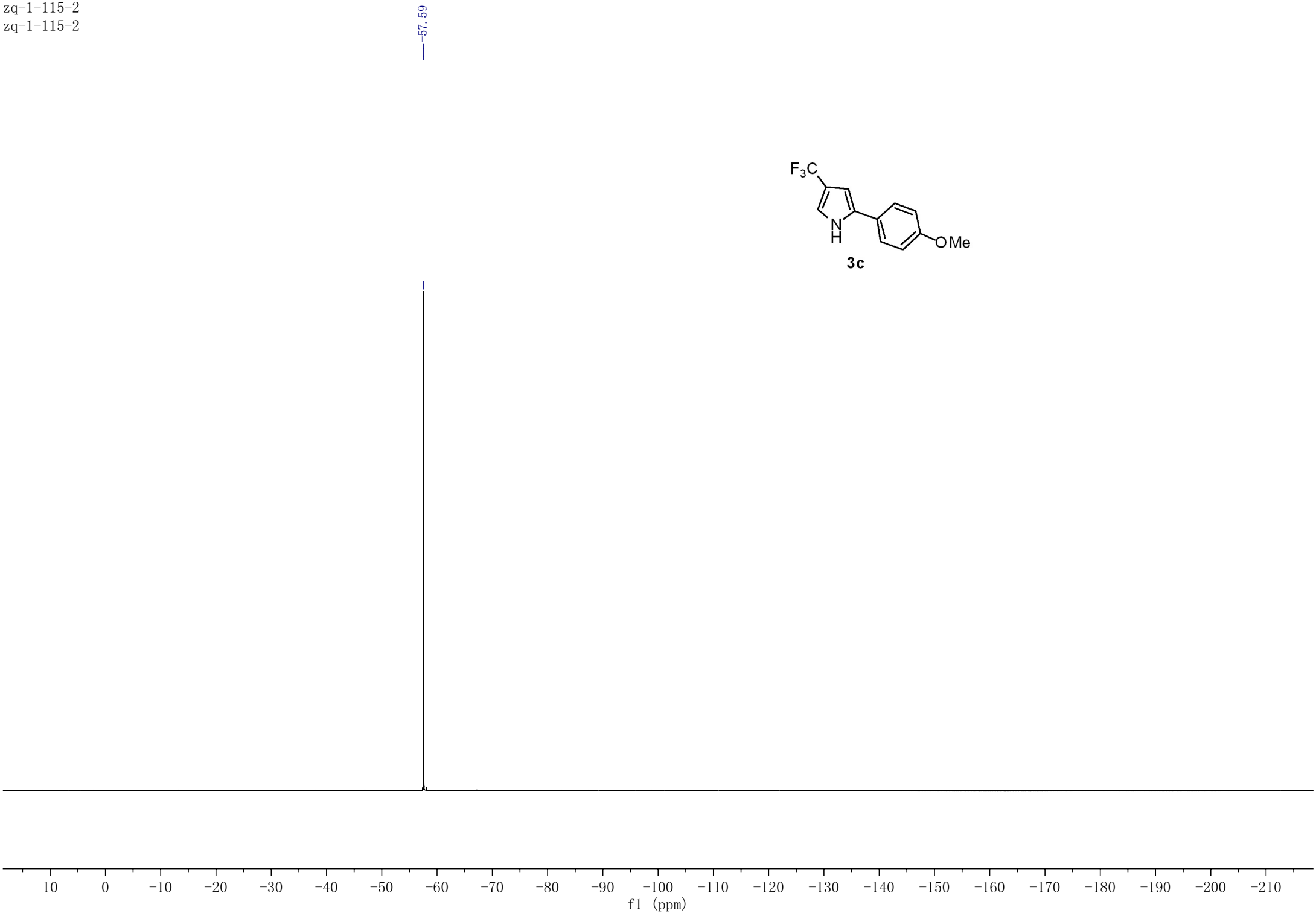
f1 (ppm)

zq-1-115-2
zq-1-115-2

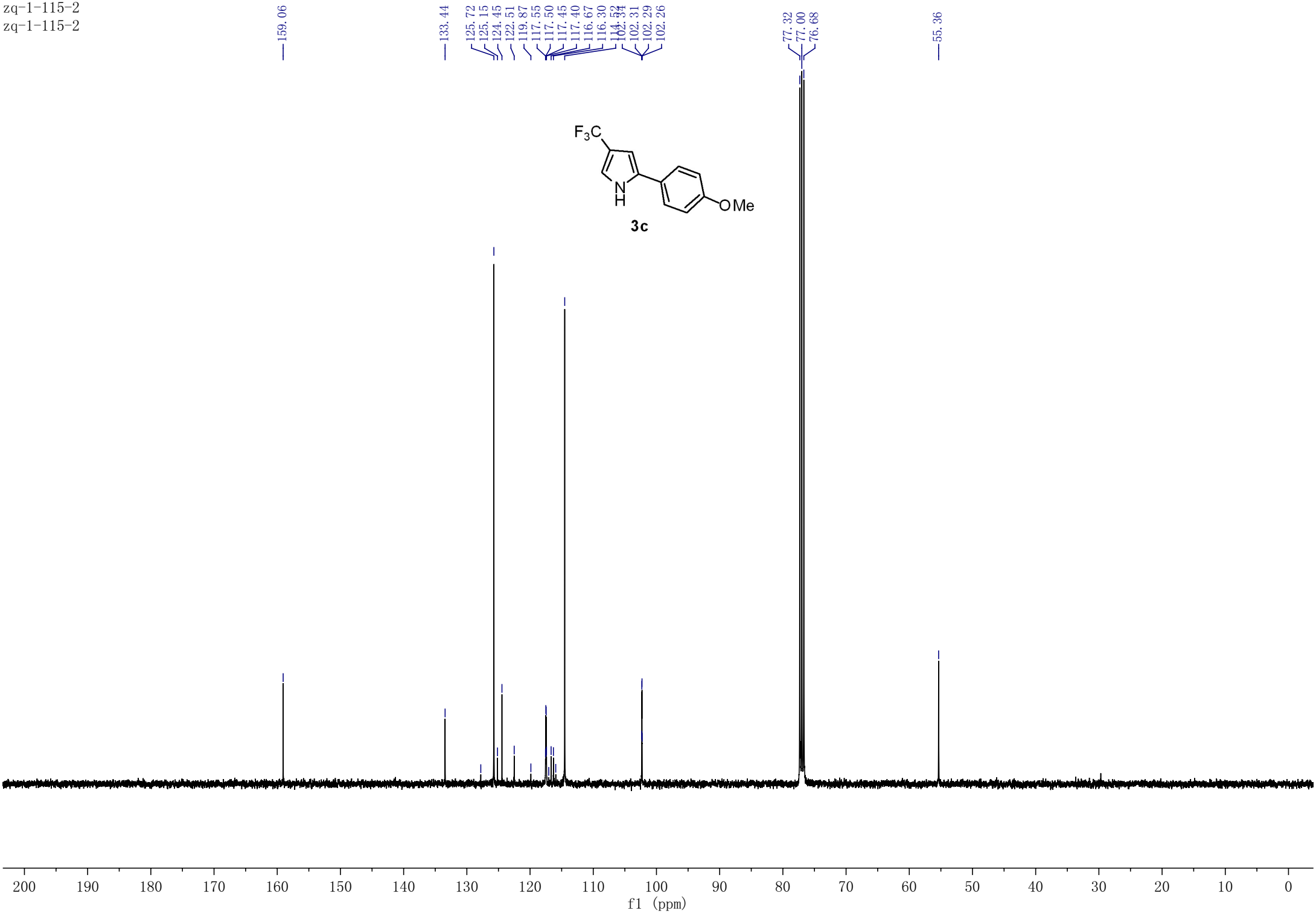


zq-1-115-2
zq-1-115-2

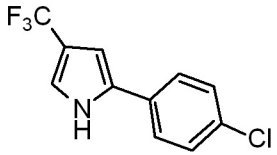
3c



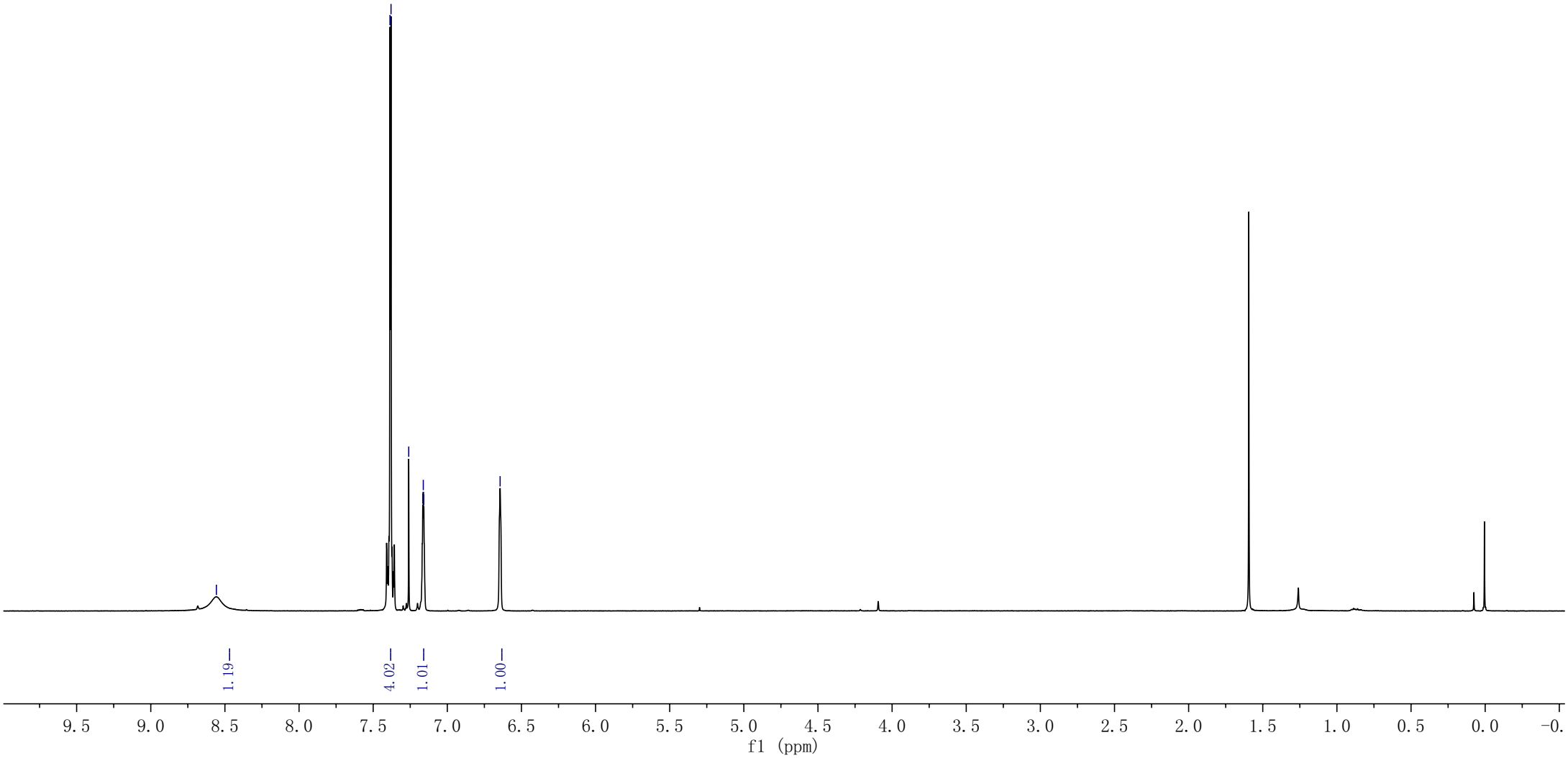
zq-1-115-2
zq-1-115-2



zl-1-100
zl-1-100

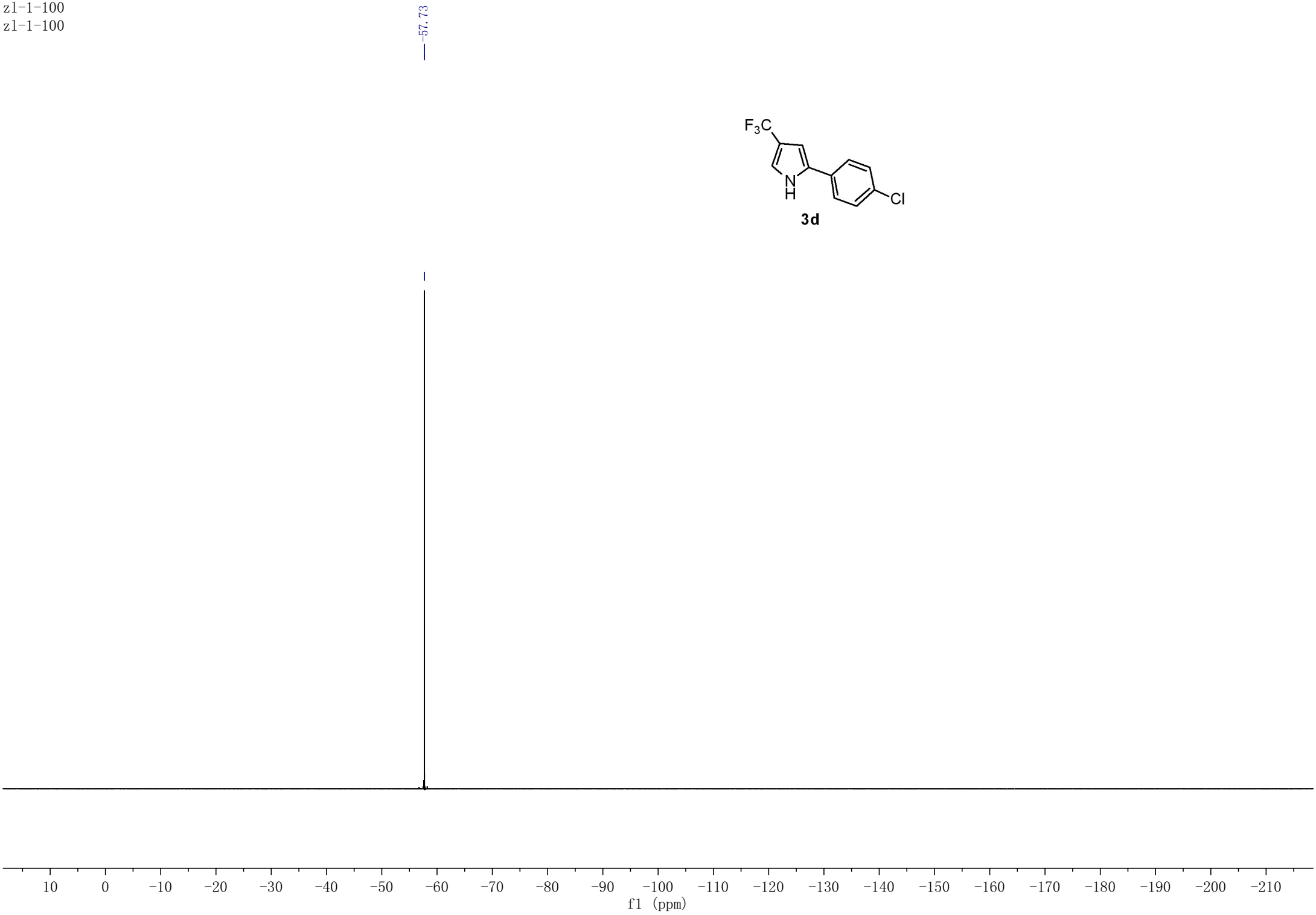


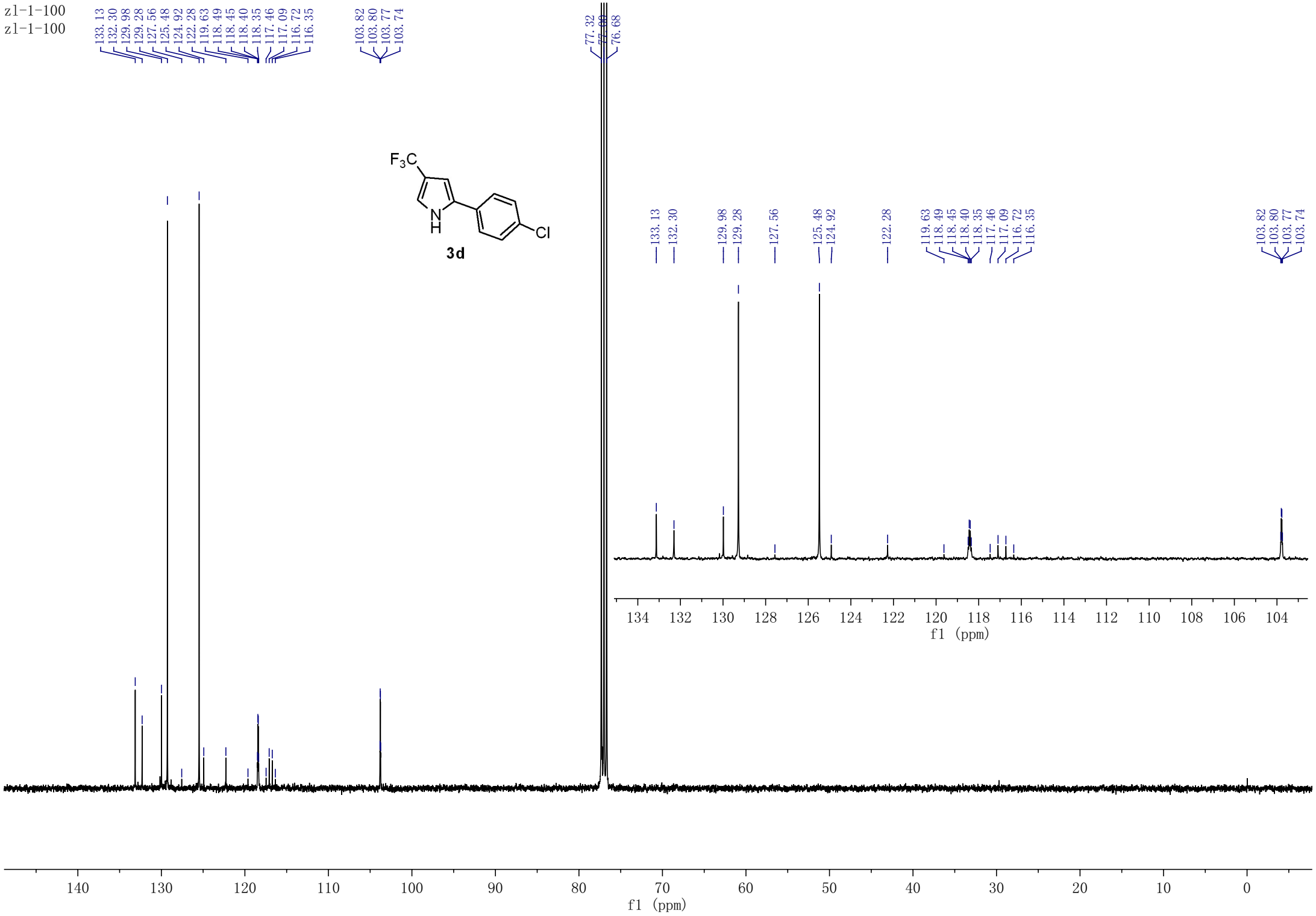
3d



zl-1-100
zl-1-100

3d

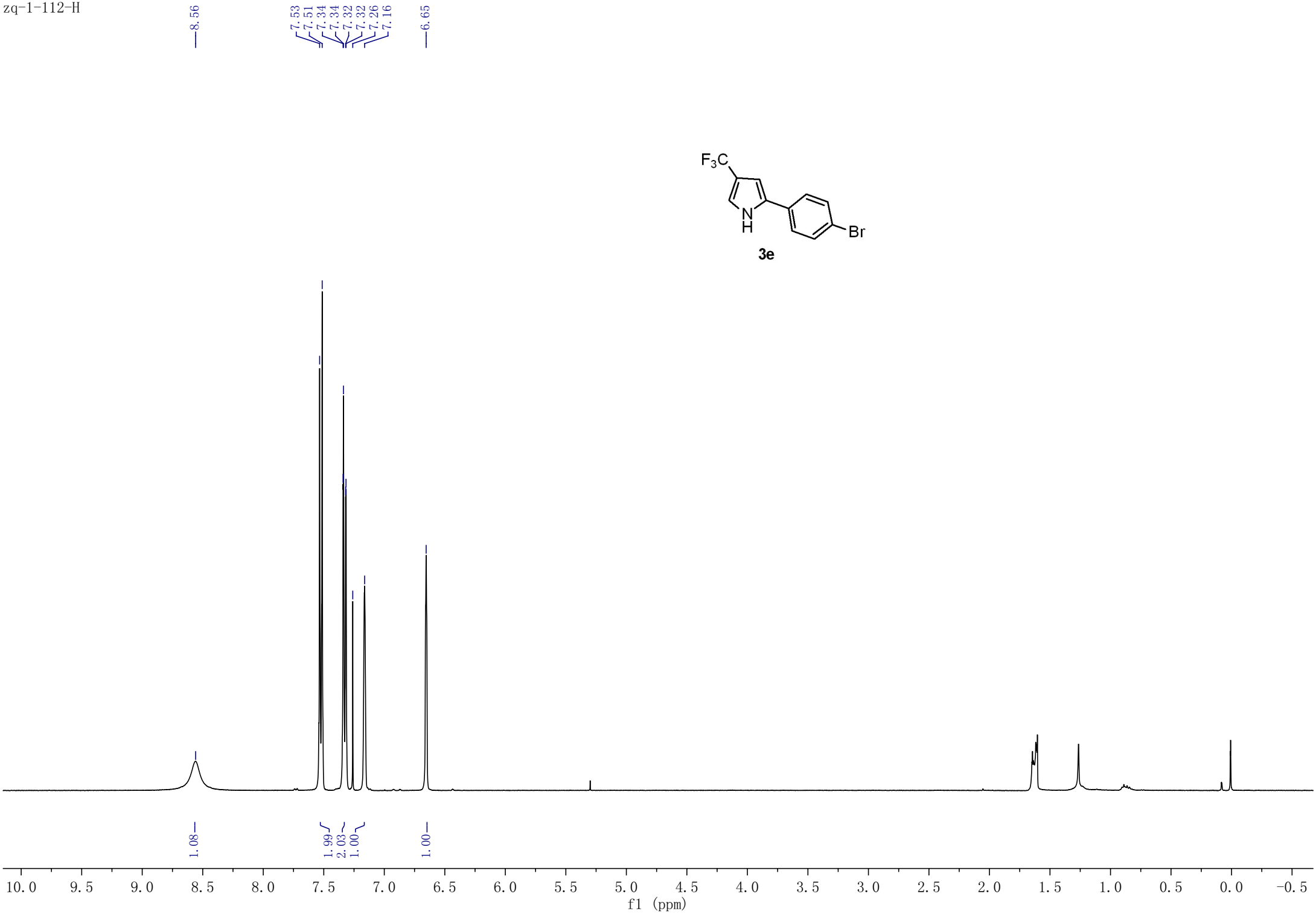



zl-1-100
zl-1-100
133.13
132.30
129.98
129.28
127.56
125.48
124.92
122.28
119.63
118.49
118.45
118.40
118.35
117.46
117.09
116.72
116.35
103.82
103.80
103.77
103.74
77.32
77.00
76.68
F3C
N
H
Cl
3d
f1 (ppm)

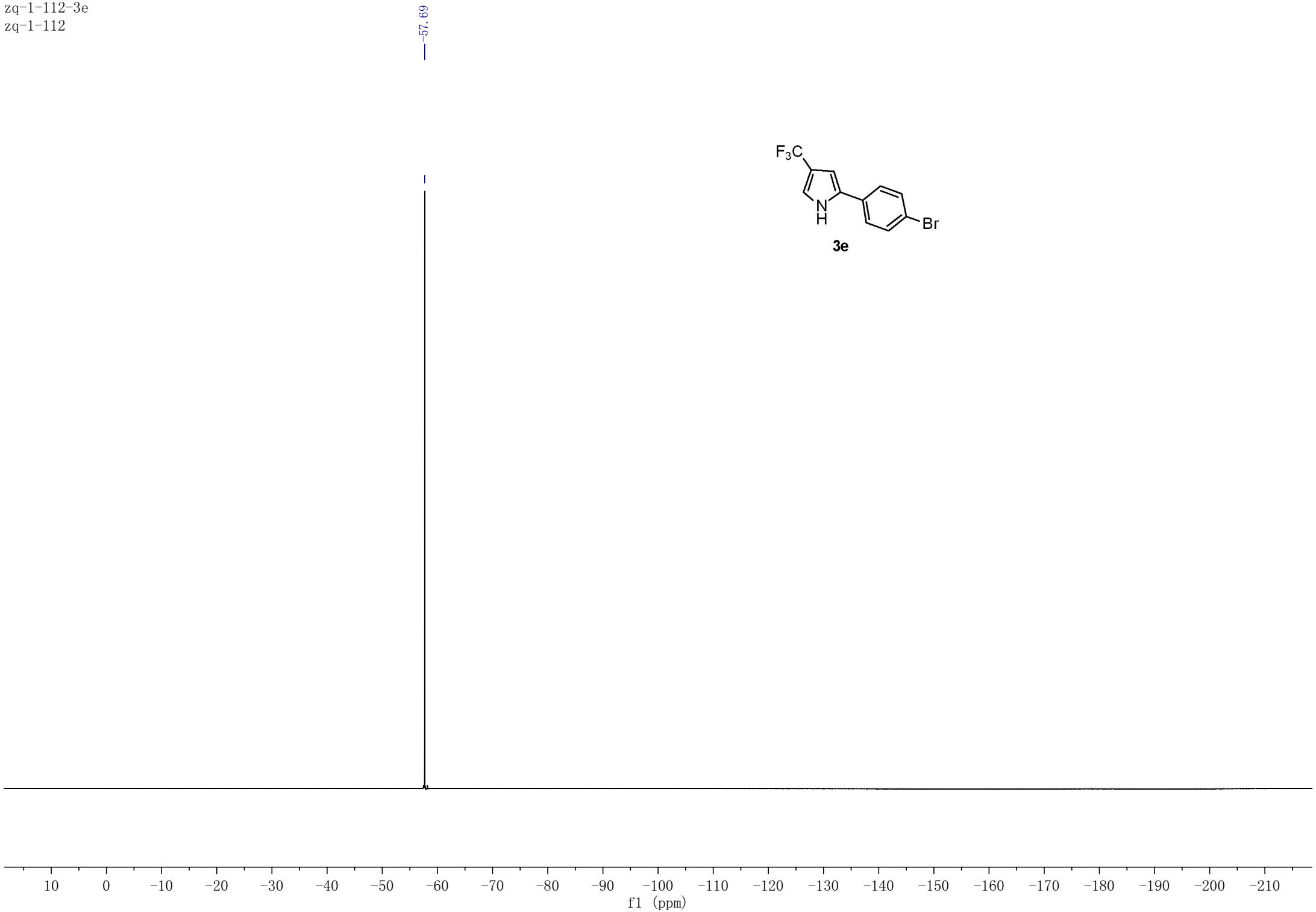
zq-1-112-H

F3C
N
H
Br

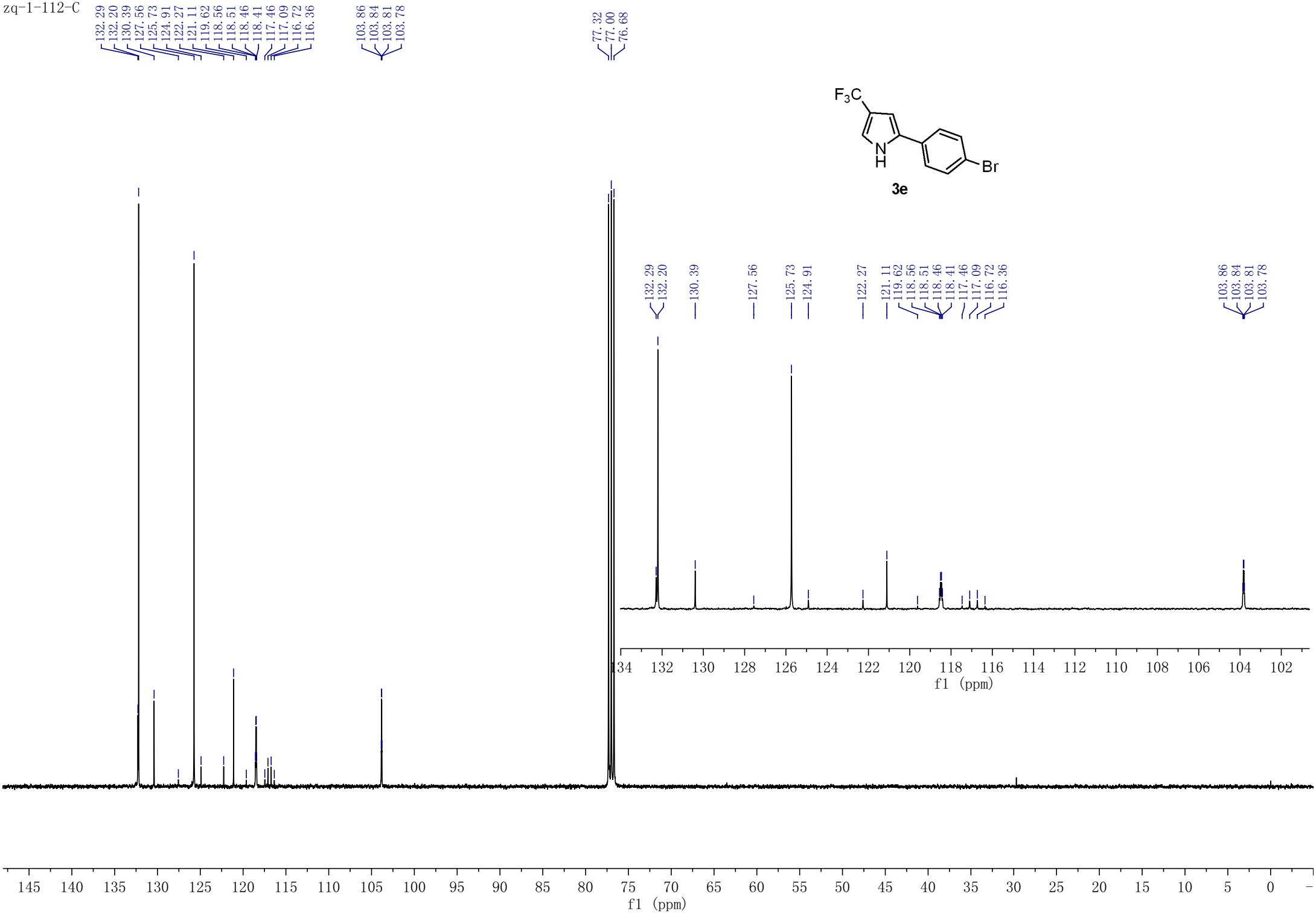
3e


8.56
7.53
7.51
7.34
7.34
7.32
7.32
7.26
7.16
6.65
1.08
1.99
2.03
1.00
1.00
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)

zq-1-112-3e
zq-1-112

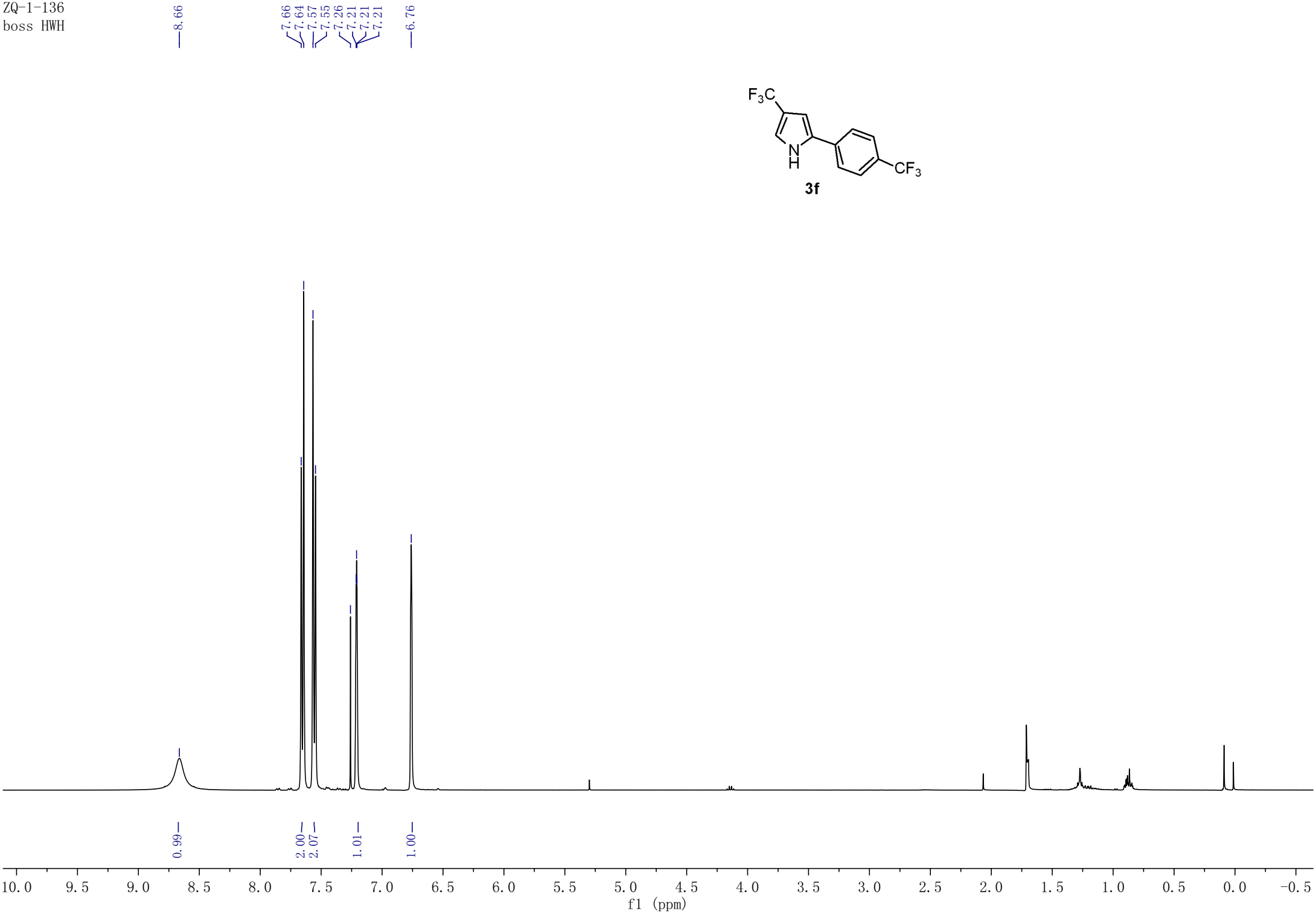


zq-1-112-C

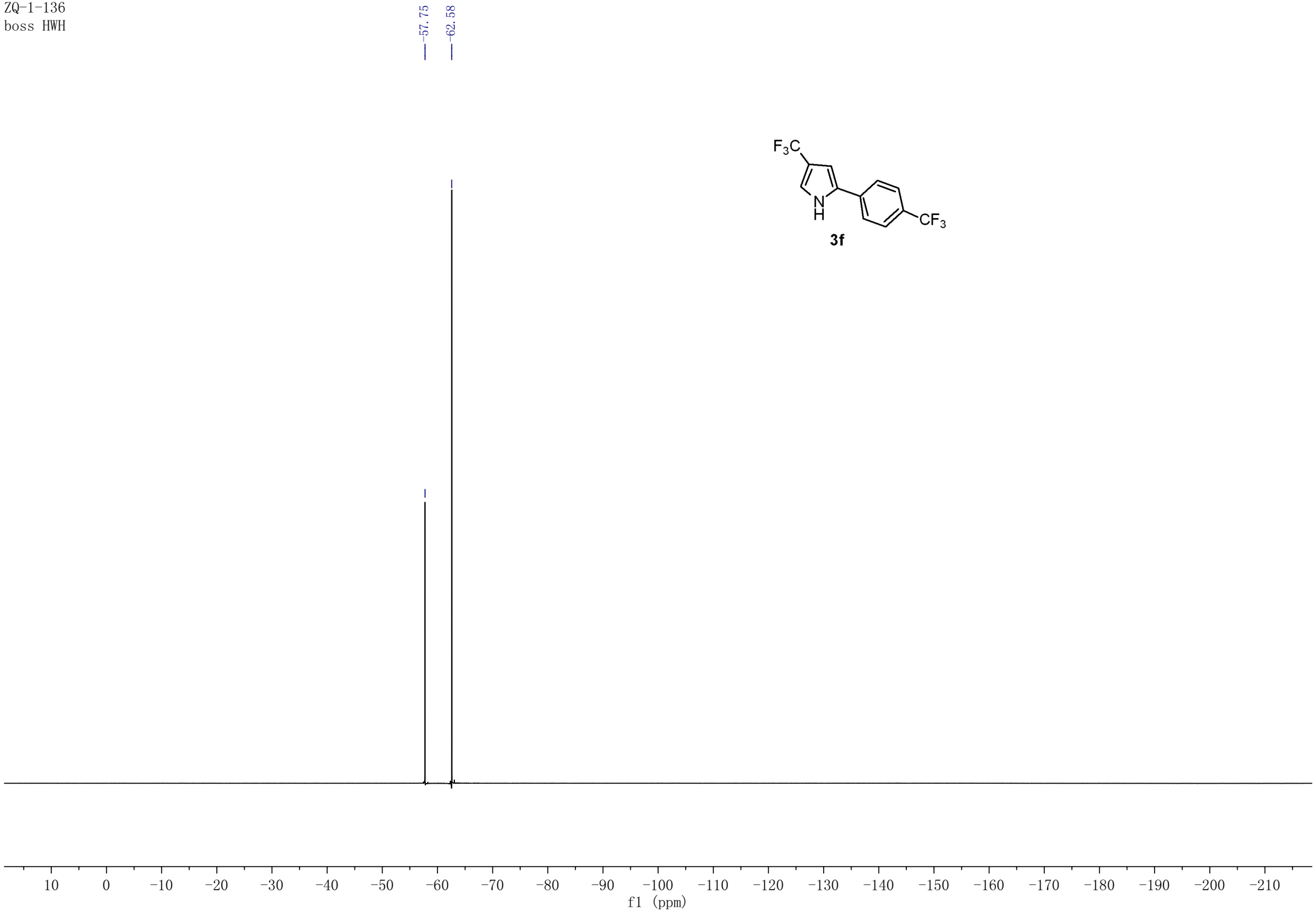

132.29
132.20
130.39
127.56
125.73
124.91
122.27
121.11
119.62
118.56
118.51
118.46
118.41
117.46
117.09
116.72
116.36
103.86
103.84
103.81
103.78
77.32
77.00
76.68
F3C
N
H
Br
3e
f1 (ppm)

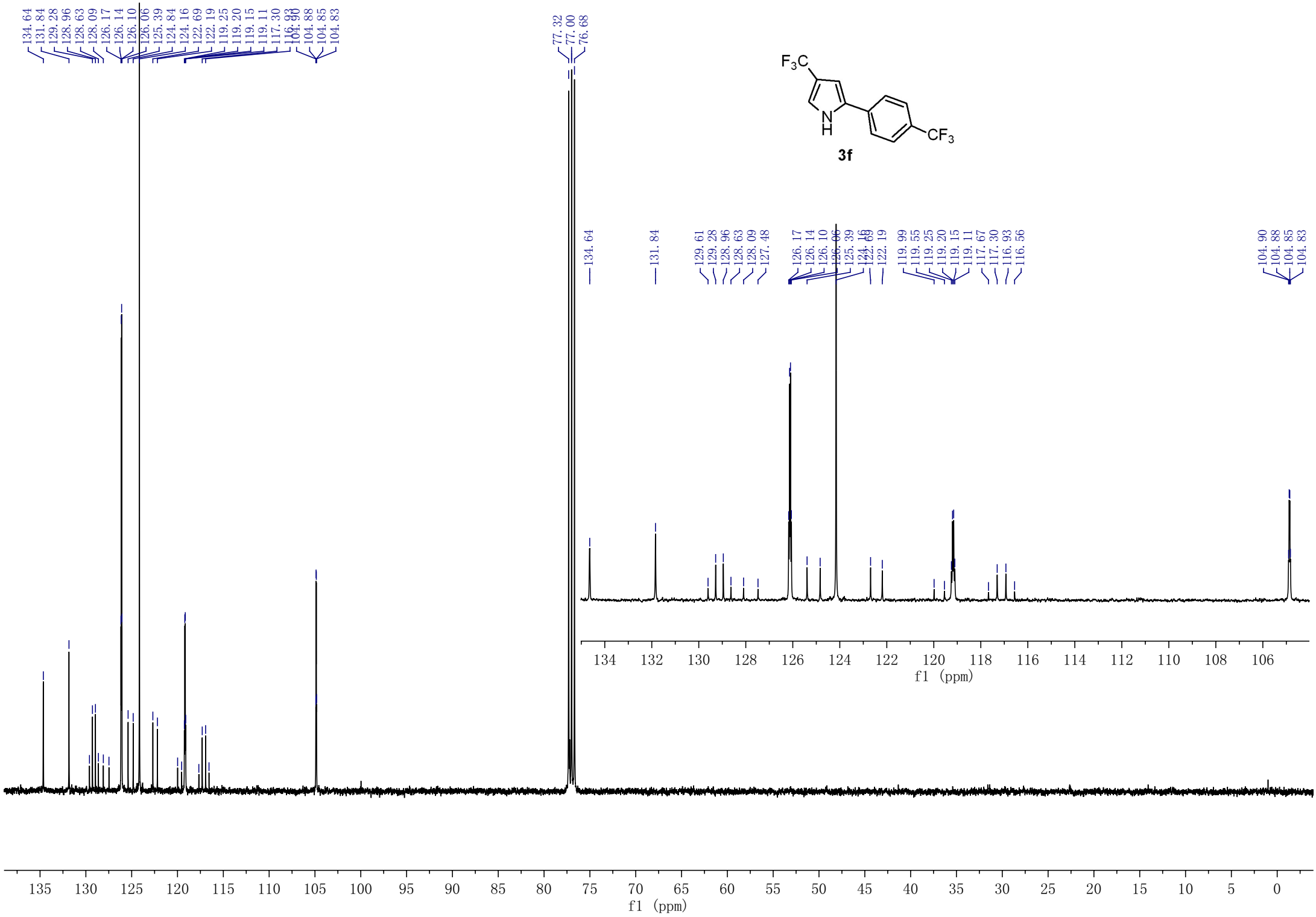
ZQ-1-136
boss HWH

3f



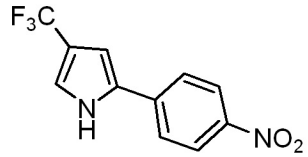
ZQ-1-136
boss HWH



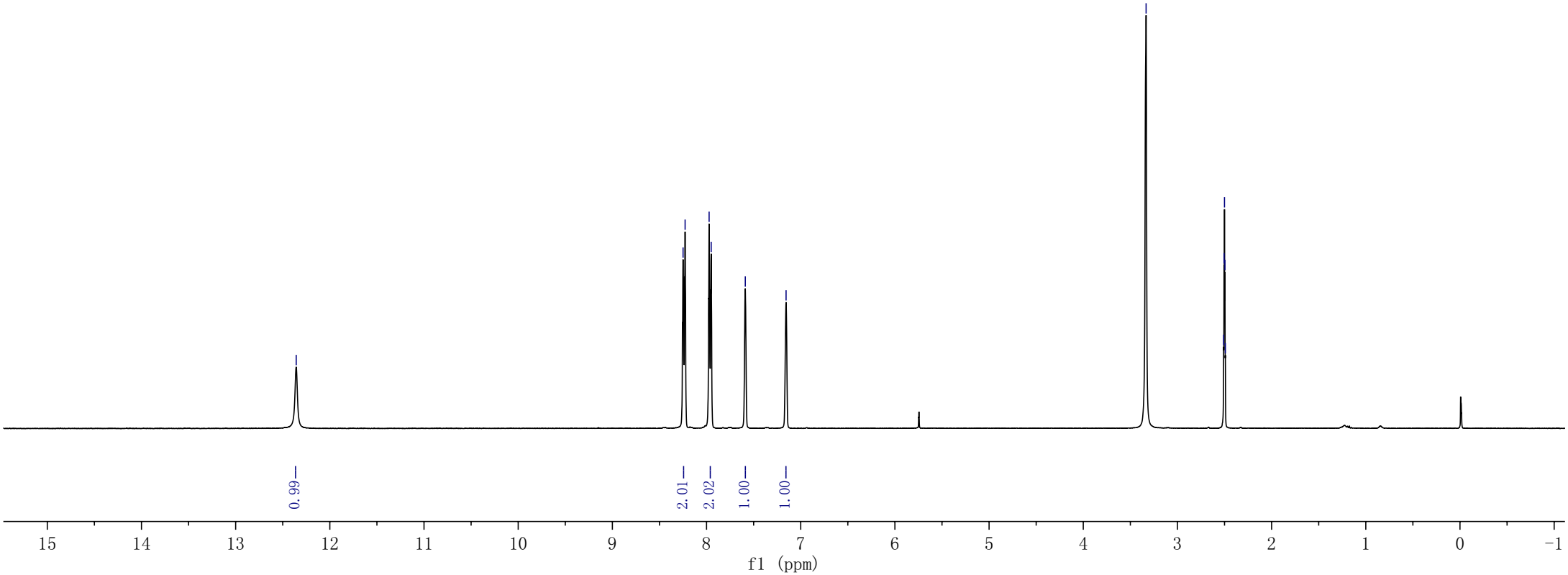

134.64
131.84
129.28
128.96
128.63
128.09
126.17
126.14
126.10
126.06
125.39
124.84
124.16
122.69
122.19
119.25
119.20
119.15
119.11
117.30
104.90
104.88
104.85
104.83
77.32
77.00
76.68
F3C
N
H
CF3
3f
f1 (ppm)
f1 (ppm)

zq-1-135
zq-1-135

12.36
8.25
8.23
7.97
7.95
7.59
7.16
3.33
2.51
2.50
2.50
2.50
2.49

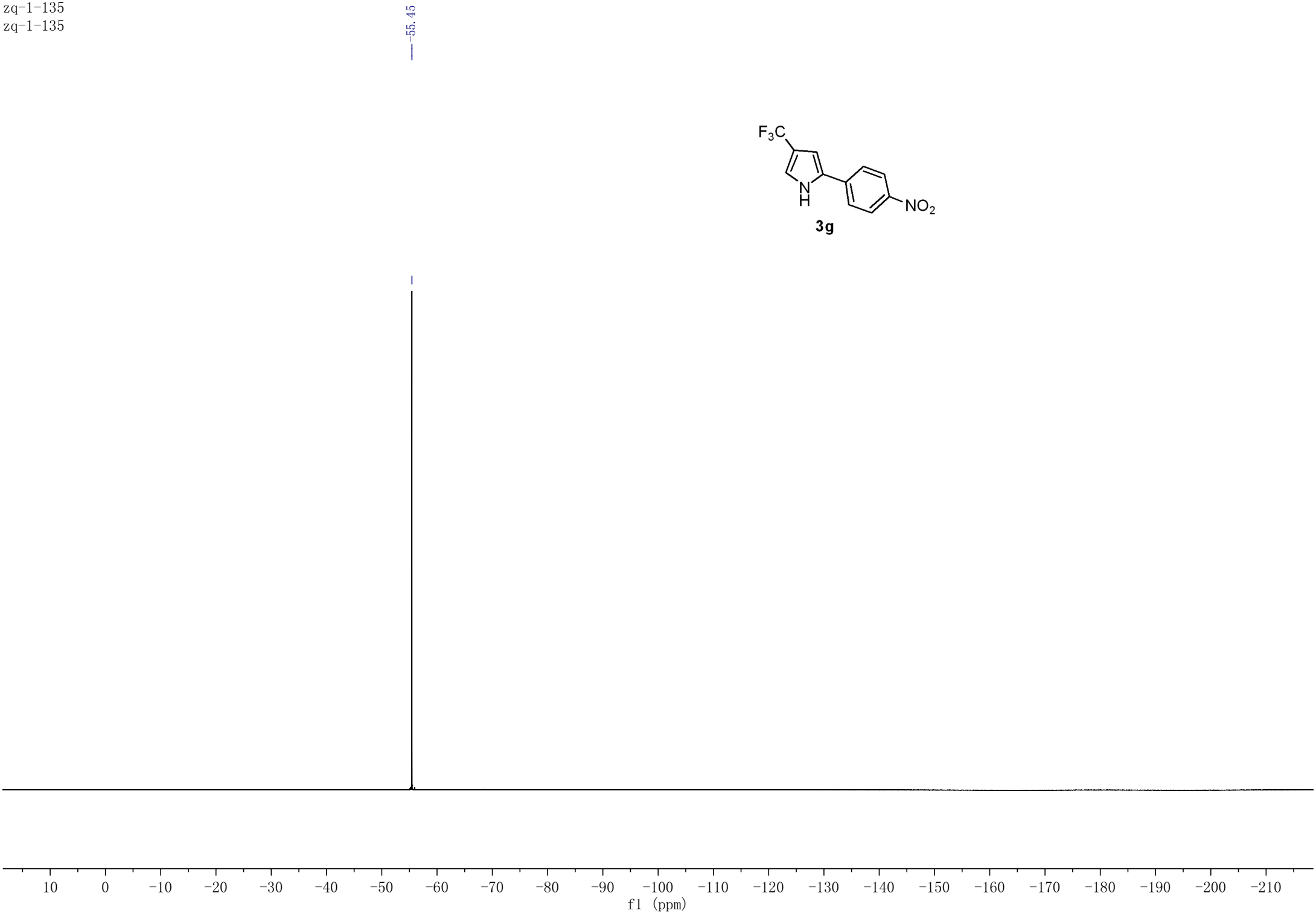


3g



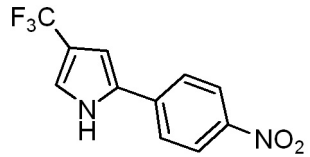
zq-1-135
zq-1-135

3g



zq-1-135
zq-1-135

145.84
138.25
131.33
128.45
125.81
124.86
124.78
123.17
122.33
120.52
115.76
115.40
115.04
114.68
106.88
40.63
40.42
40.21
39.79
39.58
39.37

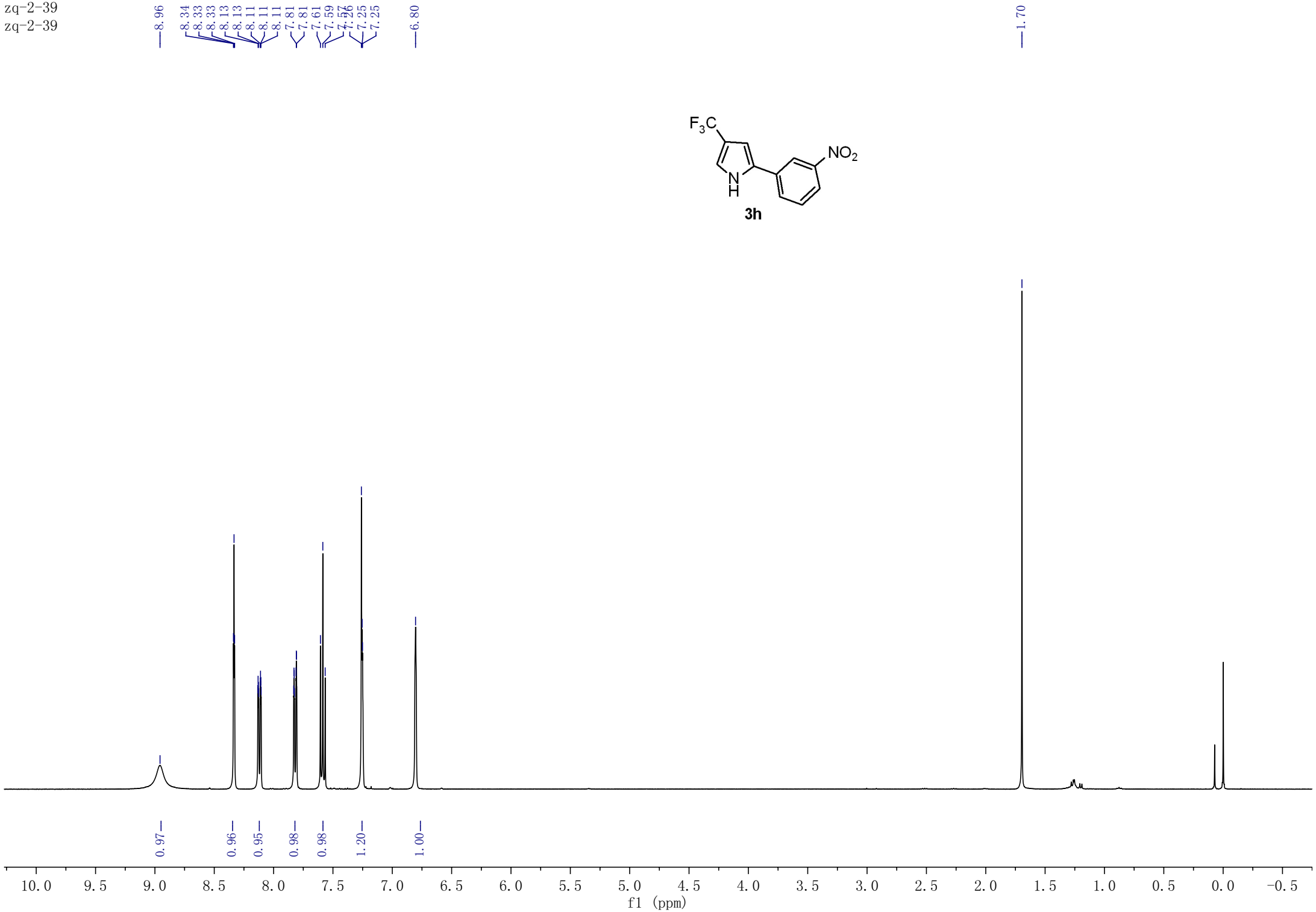


3g

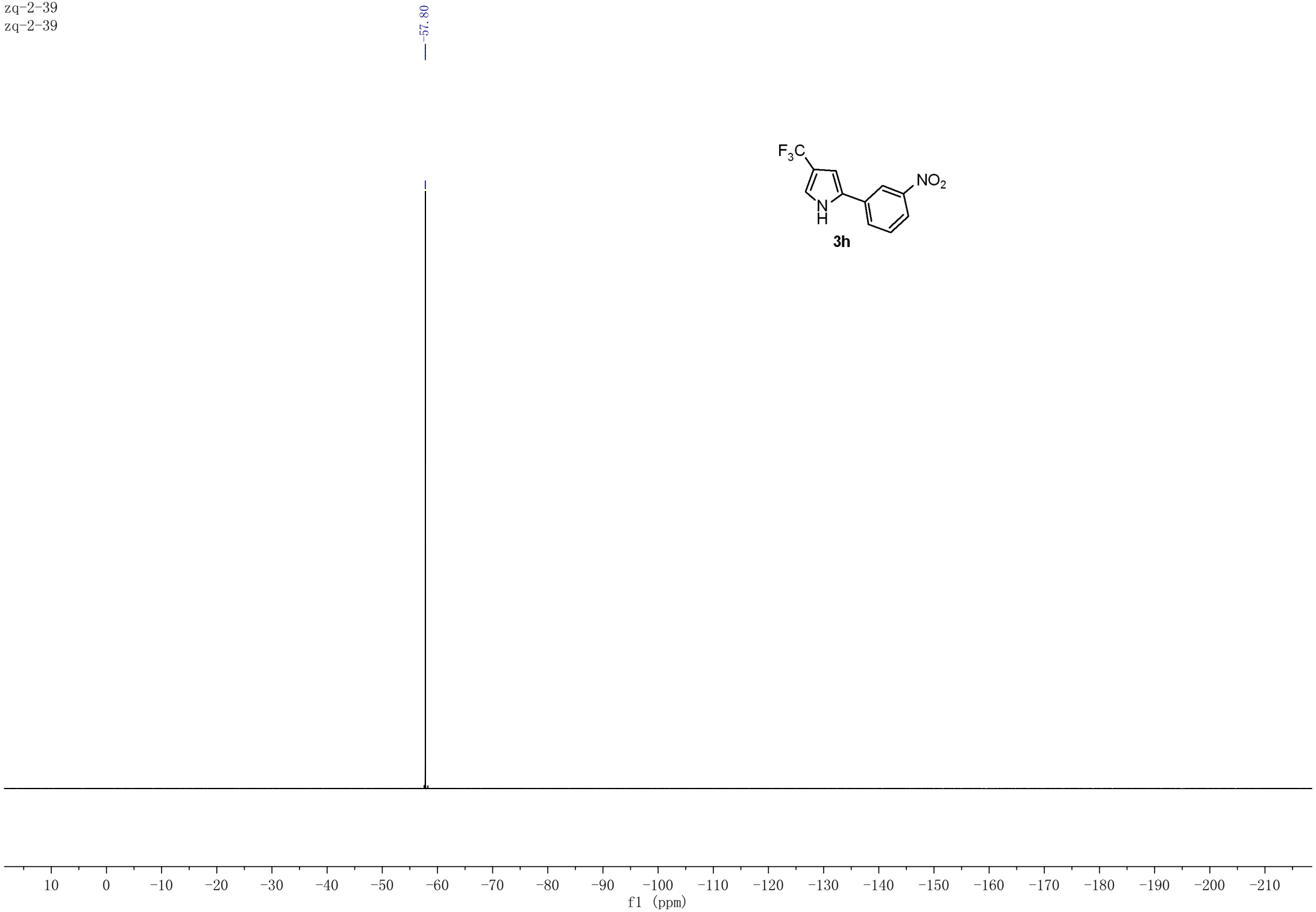
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

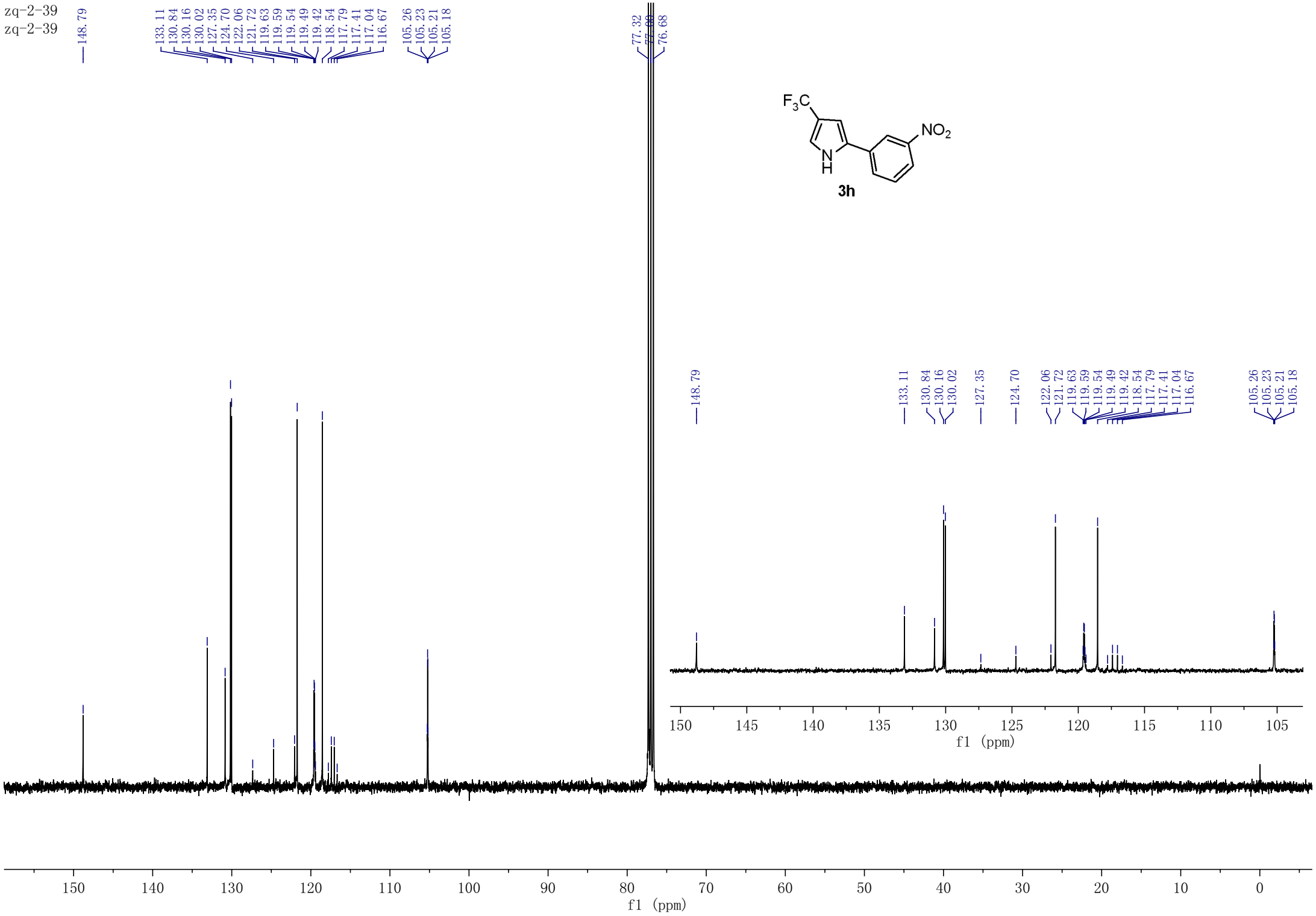
f1 (ppm)

zq-2-39
zq-2-39


8.96
8.34
8.33
8.33
8.13
8.13
8.11
8.11
8.11
7.81
7.81
7.61
7.59
7.57
7.56
7.25
7.25
6.80
1.70
F3C
NO2
N
H
3h
0.97
0.96
0.95
0.98
0.98
1.20
1.00
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)

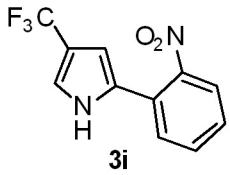
zq-2-39
zq-2-39


-57.80
F3C
NO2
N
H
3h
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

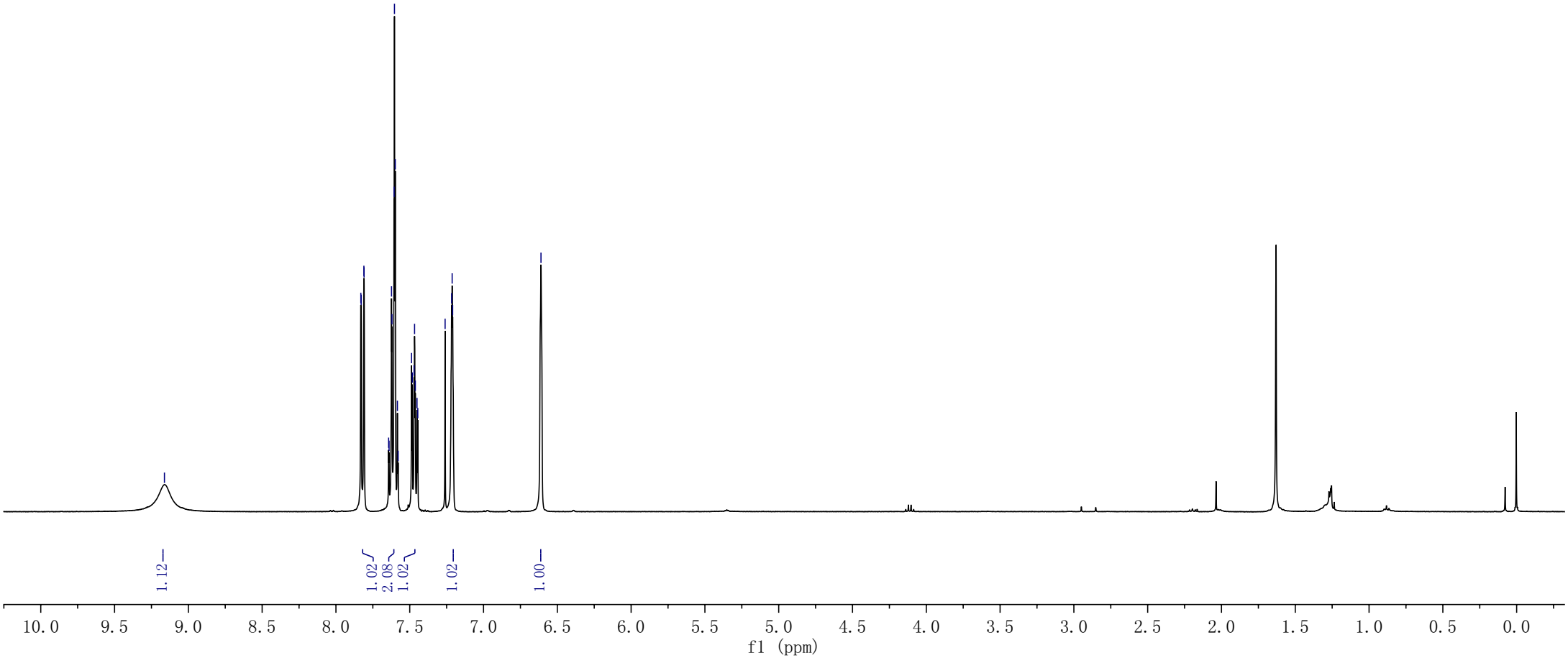

zq-2-39
zq-2-39
148.79
133.11
130.84
130.16
130.02
127.35
124.70
122.06
121.72
119.63
119.59
119.54
119.49
119.42
118.54
117.79
117.41
117.04
116.67
105.26
105.23
105.21
105.18
77.32
77.00
76.68
F3C
NO2
N
H
3h
f1 (ppm)

ZQ-2-31
ZQ-2-31

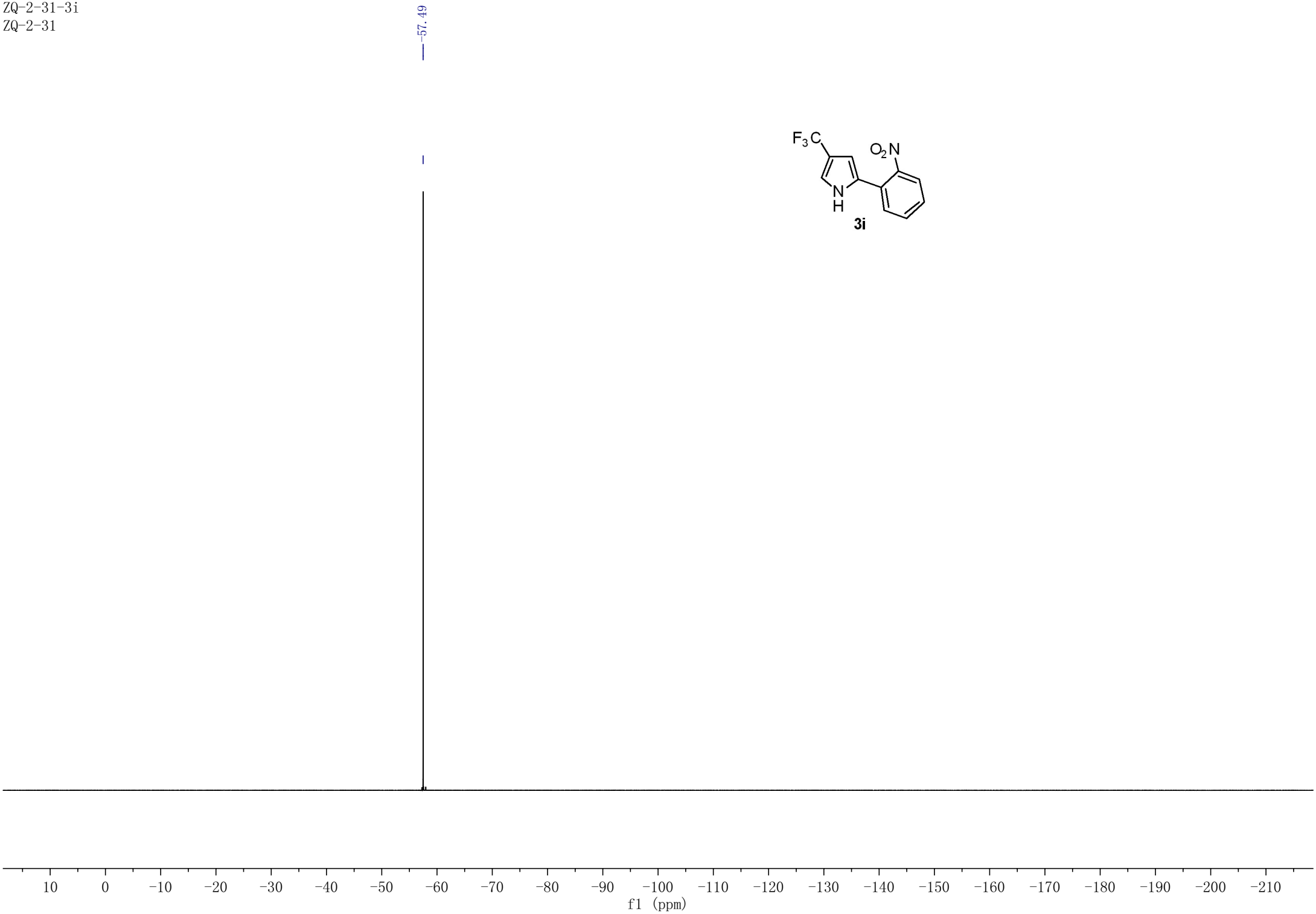
9.16
7.83
7.83
7.81
7.81
7.64
7.64
7.62
7.62
7.61
7.60
7.60
7.58
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.26
7.22
7.21
6.61

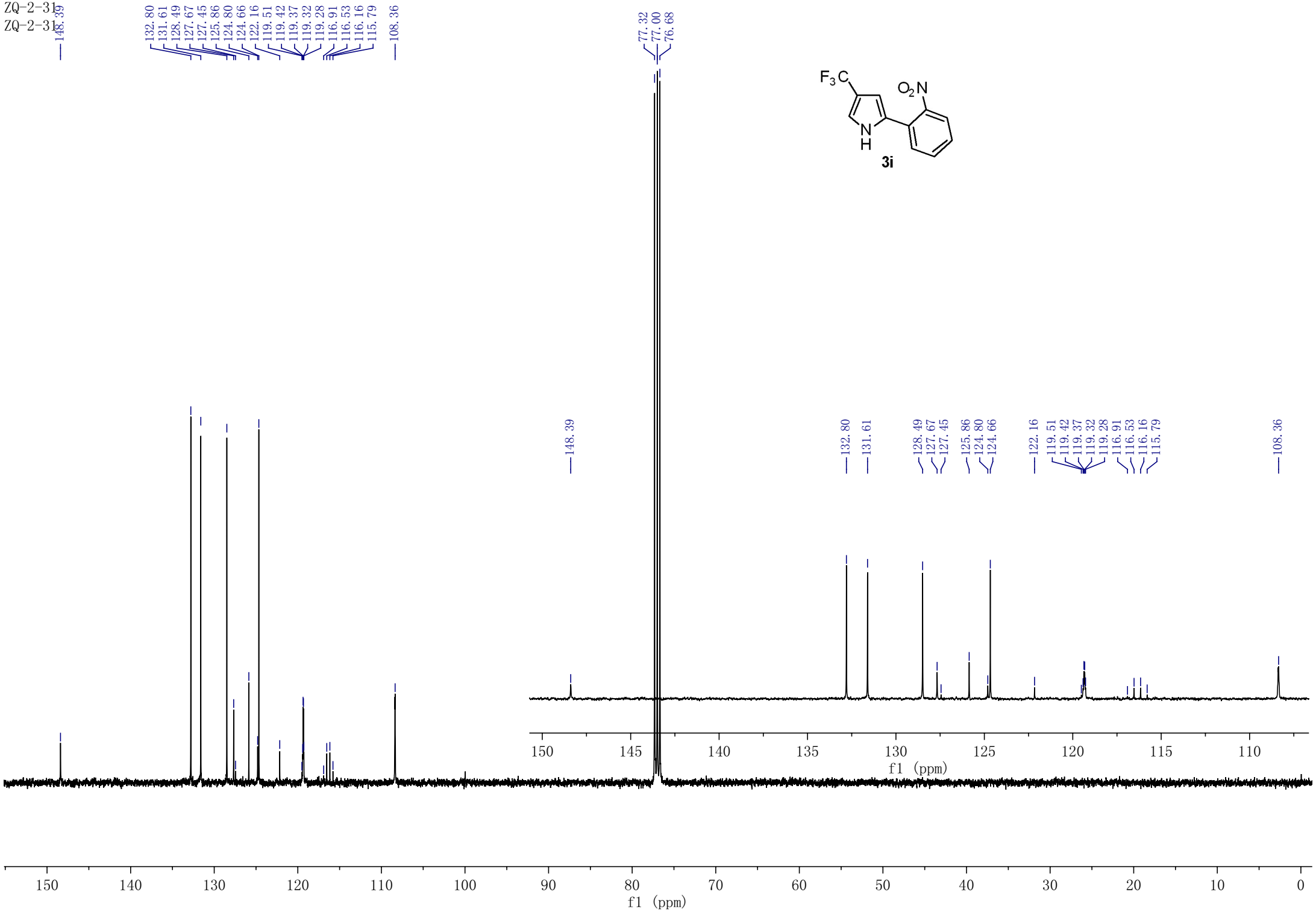


3i

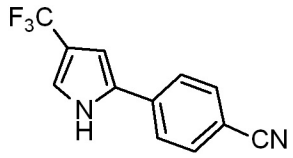


ZQ-2-31-3i
ZQ-2-31

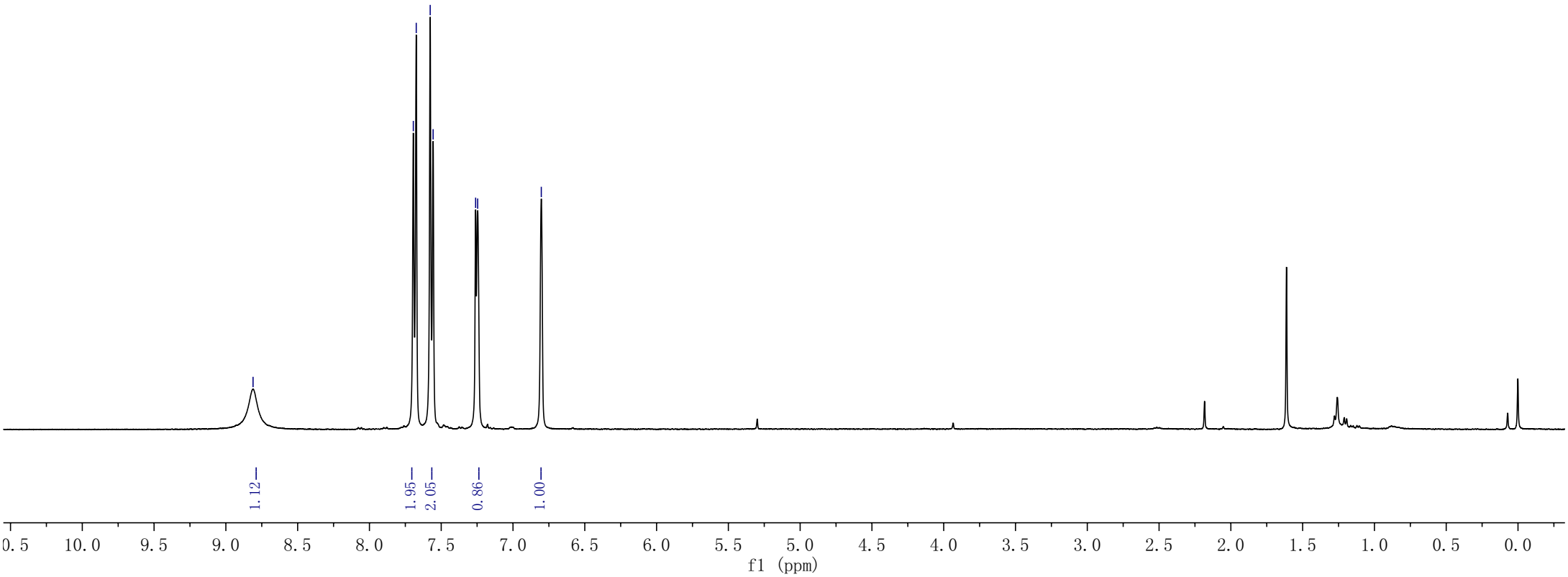



ZQ-2-31
ZQ-2-31
148.39
132.80
131.61
128.49
127.67
127.45
125.86
124.80
124.66
122.16
119.51
119.42
119.37
119.32
119.28
116.91
116.53
116.16
115.79
108.36
77.32
77.00
76.68
F3C
O2N
N
H
3i
f1 (ppm)
f1 (ppm)

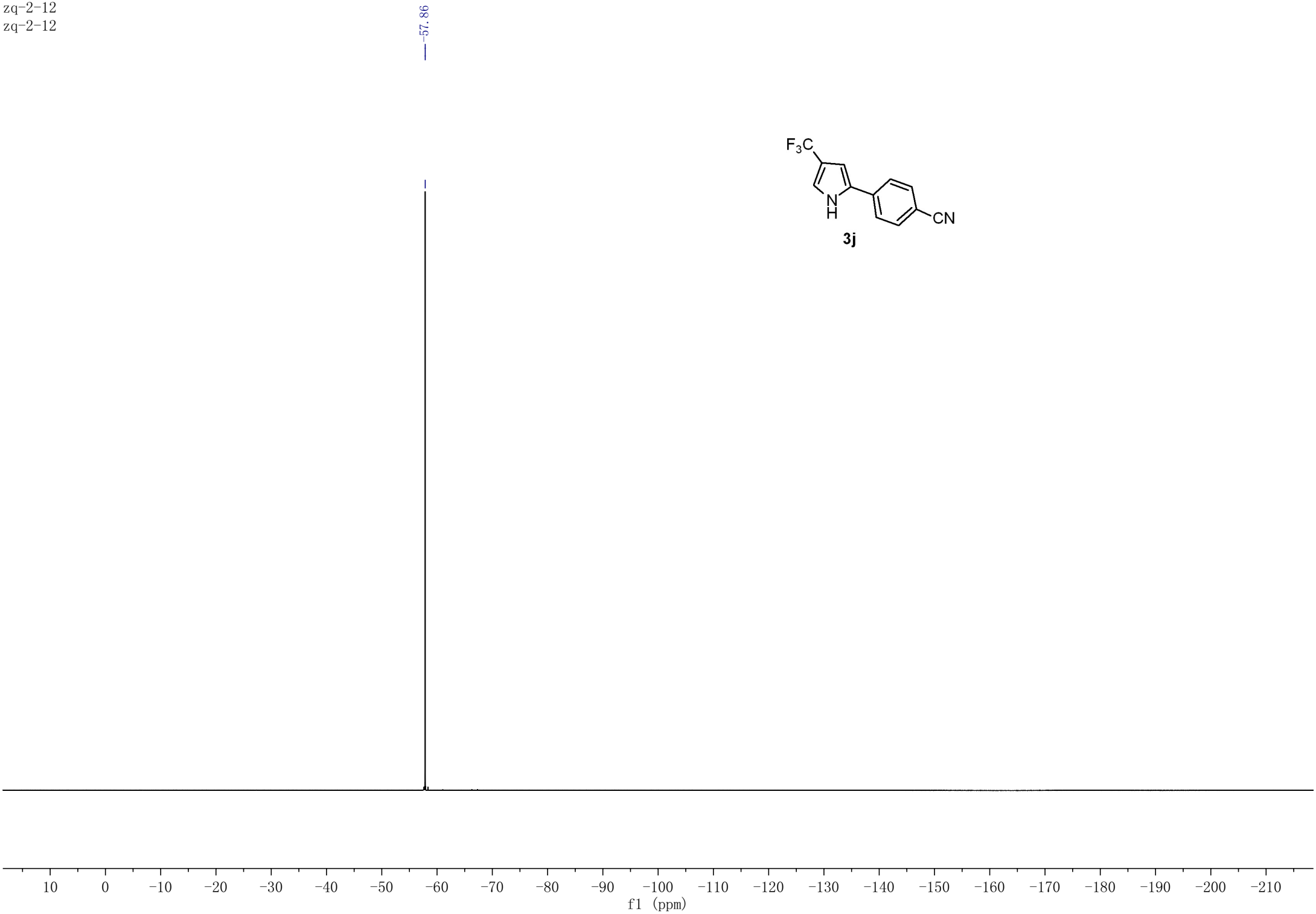
zq-2-12
zq-2-12

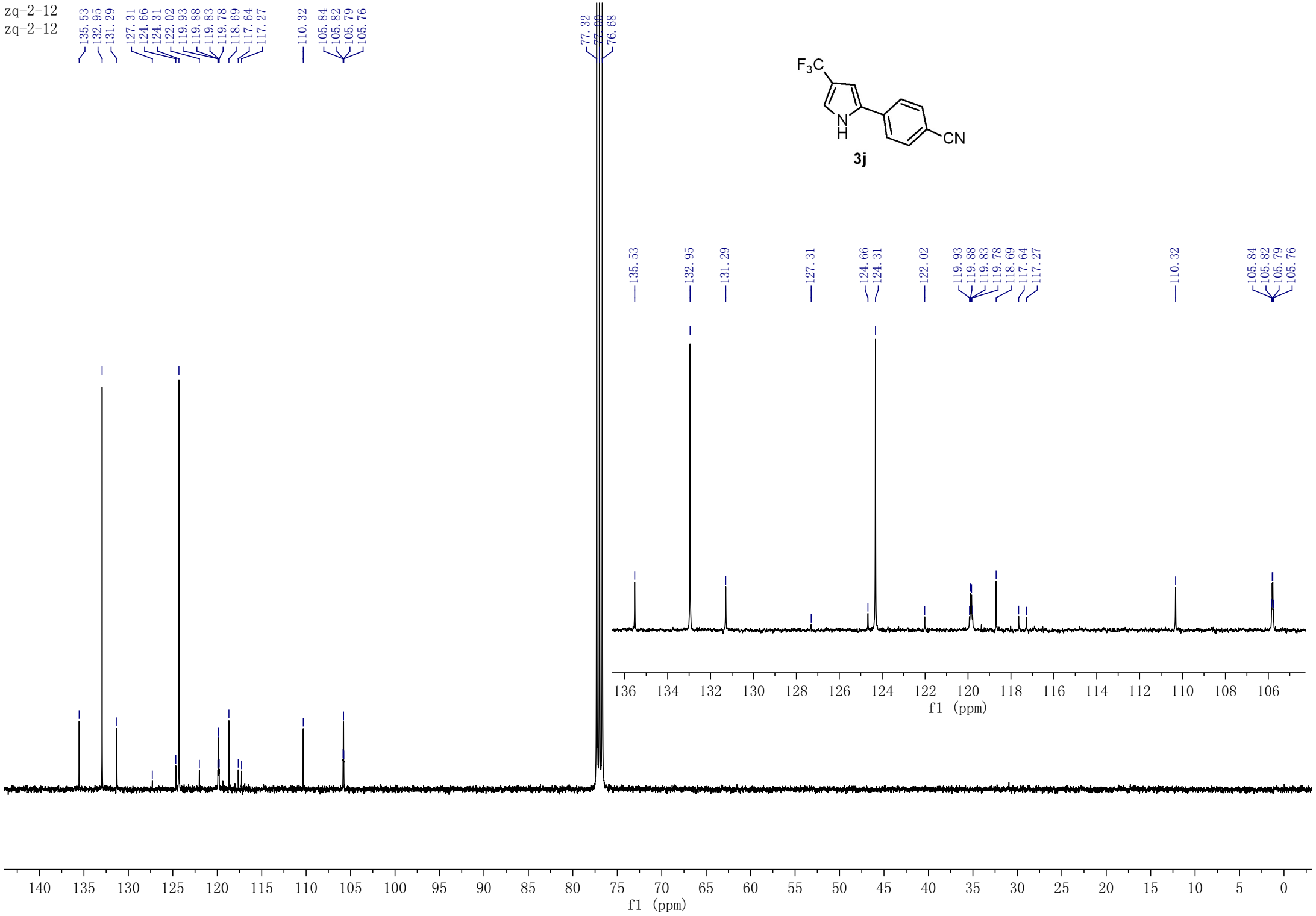


3j

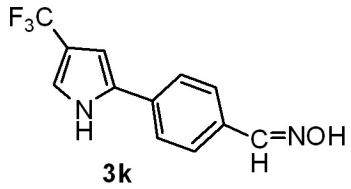


zq-2-12
zq-2-12

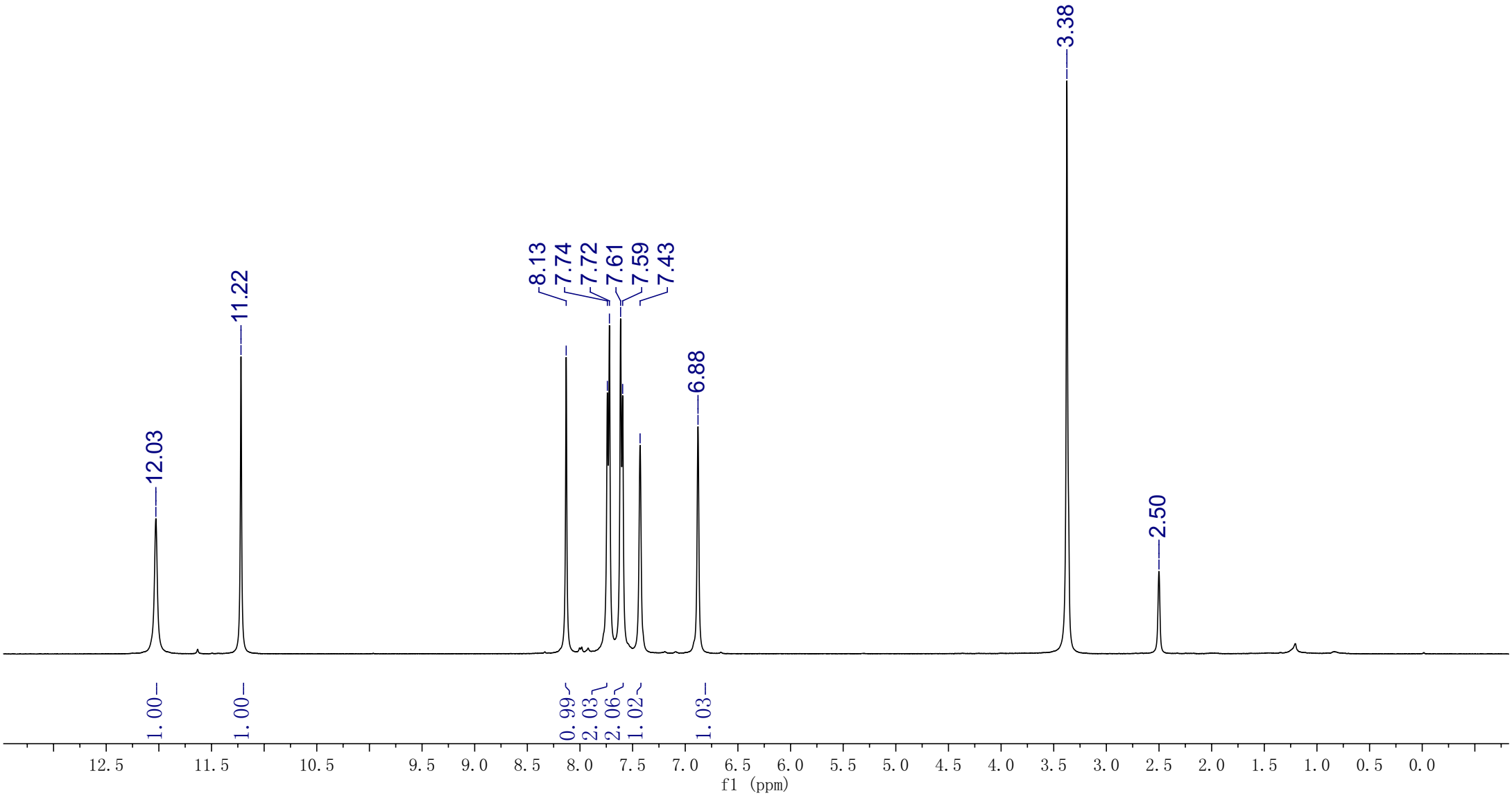

-57.86
F3C
N
H
CN
3j
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


zq-2-12
zq-2-12
135.53
132.95
131.29
127.31
124.66
124.31
122.02
119.93
119.88
119.83
119.78
118.69
117.64
117.27
110.32
105.84
105.82
105.79
105.76
77.32
77.00
76.68
F3C
N
H
CN
3j
f1 (ppm)

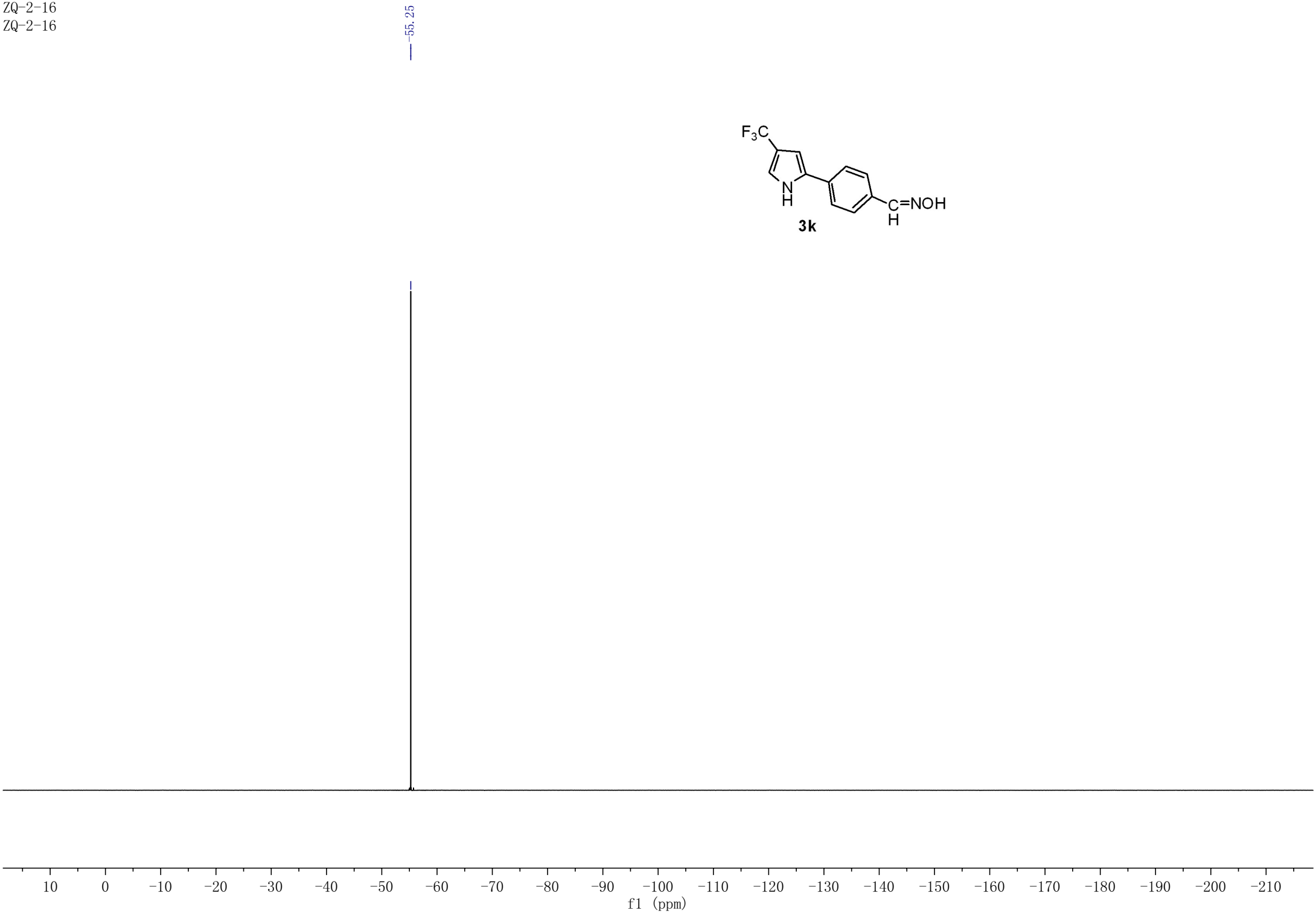
zq-2-16


F3C
N
H
C=NOH
H

3k


12.03
11.22
8.13
7.74
7.72
7.61
7.59
7.43
6.88
3.38
2.50
1.00
1.00
0.99
2.03
2.06
1.02
1.03
12.5
11.5
10.5
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)

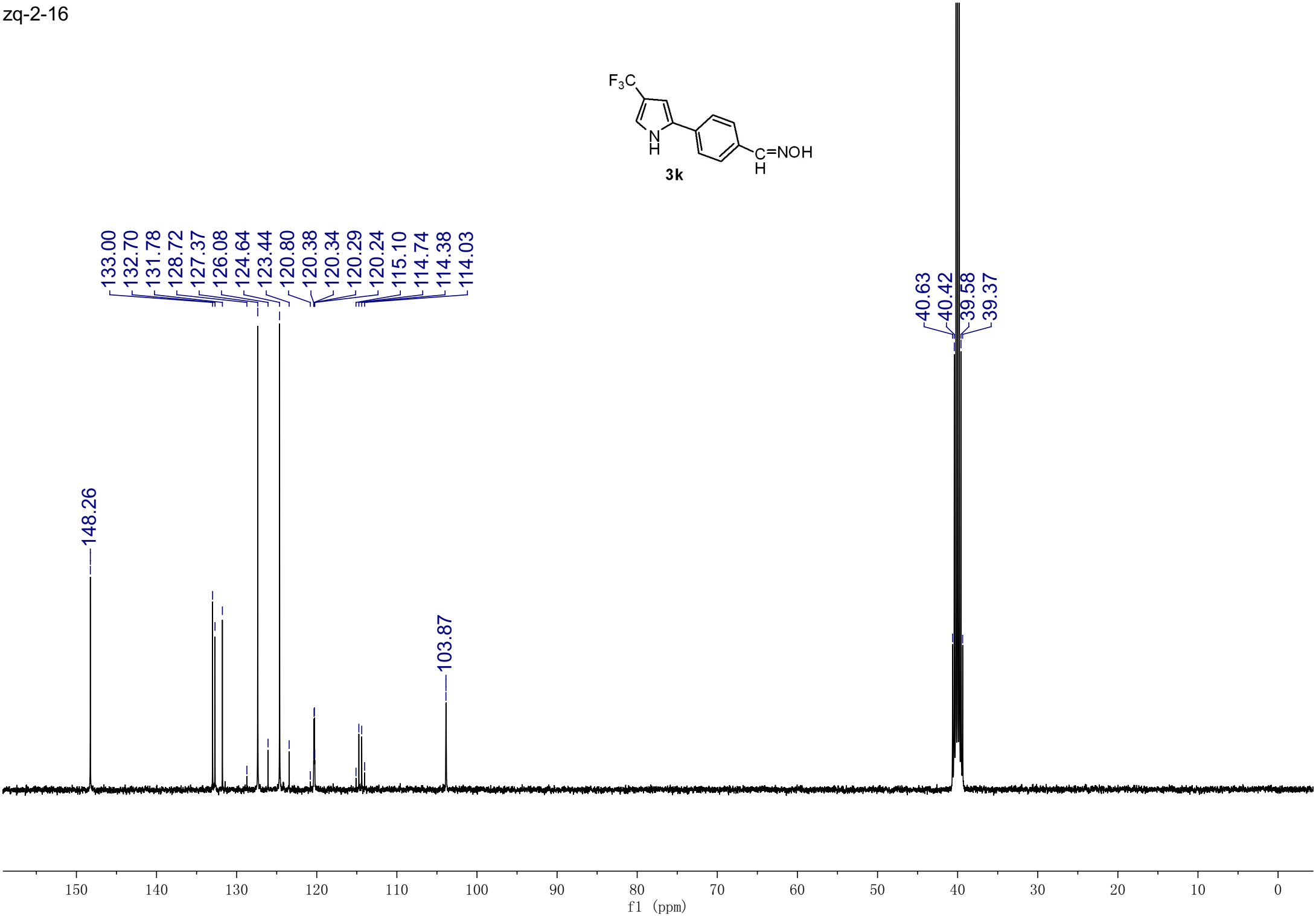
ZQ-2-16
ZQ-2-16


-55.25
F3C
N
H
C=NOH
H
3k
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

zq-2-16

F3C
N
H
C=NOH
H

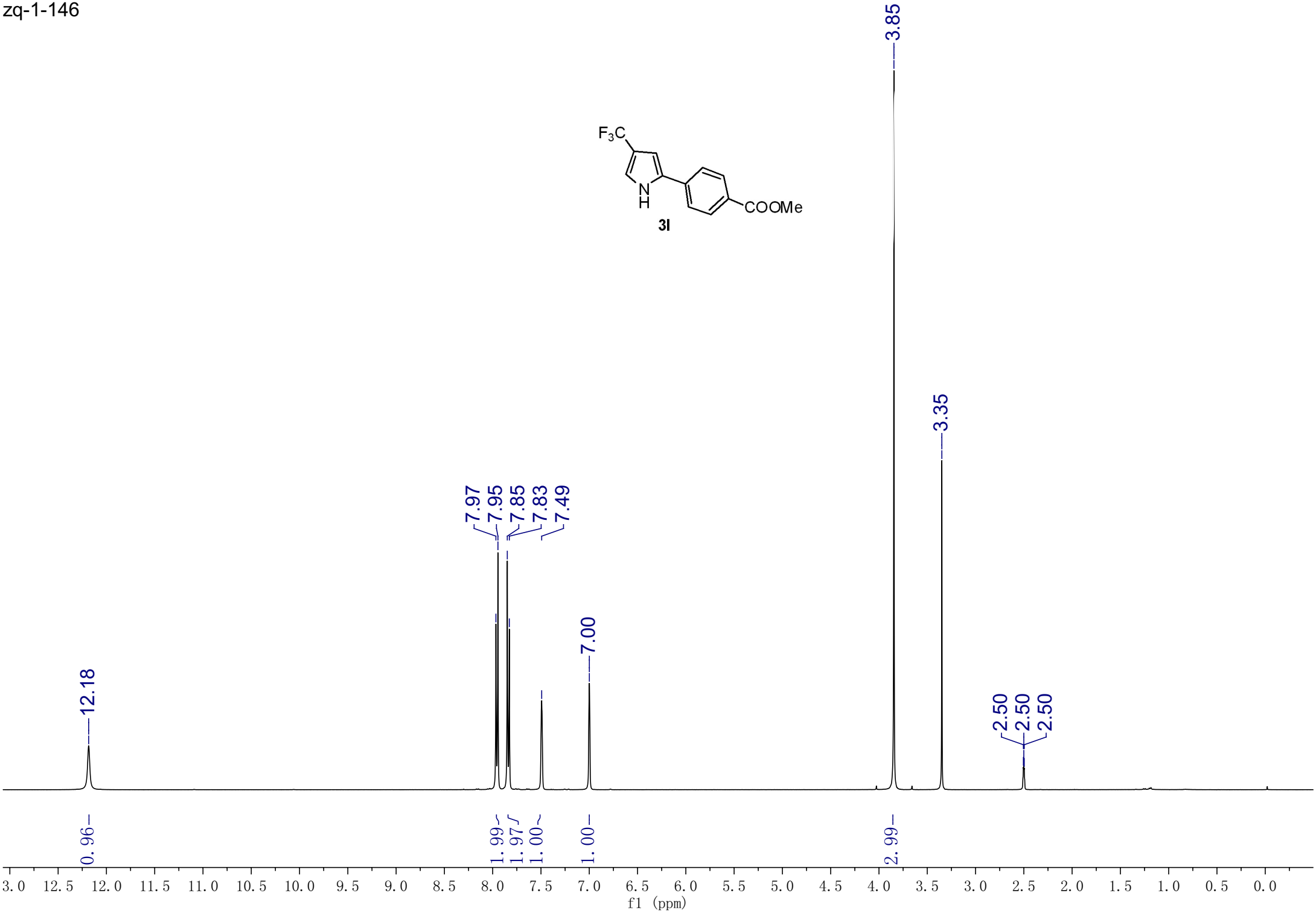
3k


133.00
132.70
131.78
128.72
127.37
126.08
124.64
123.44
120.80
120.38
120.34
120.29
120.24
115.10
114.74
114.38
114.03
148.26
103.87
40.63
40.42
39.58
39.37
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

zq-1-146

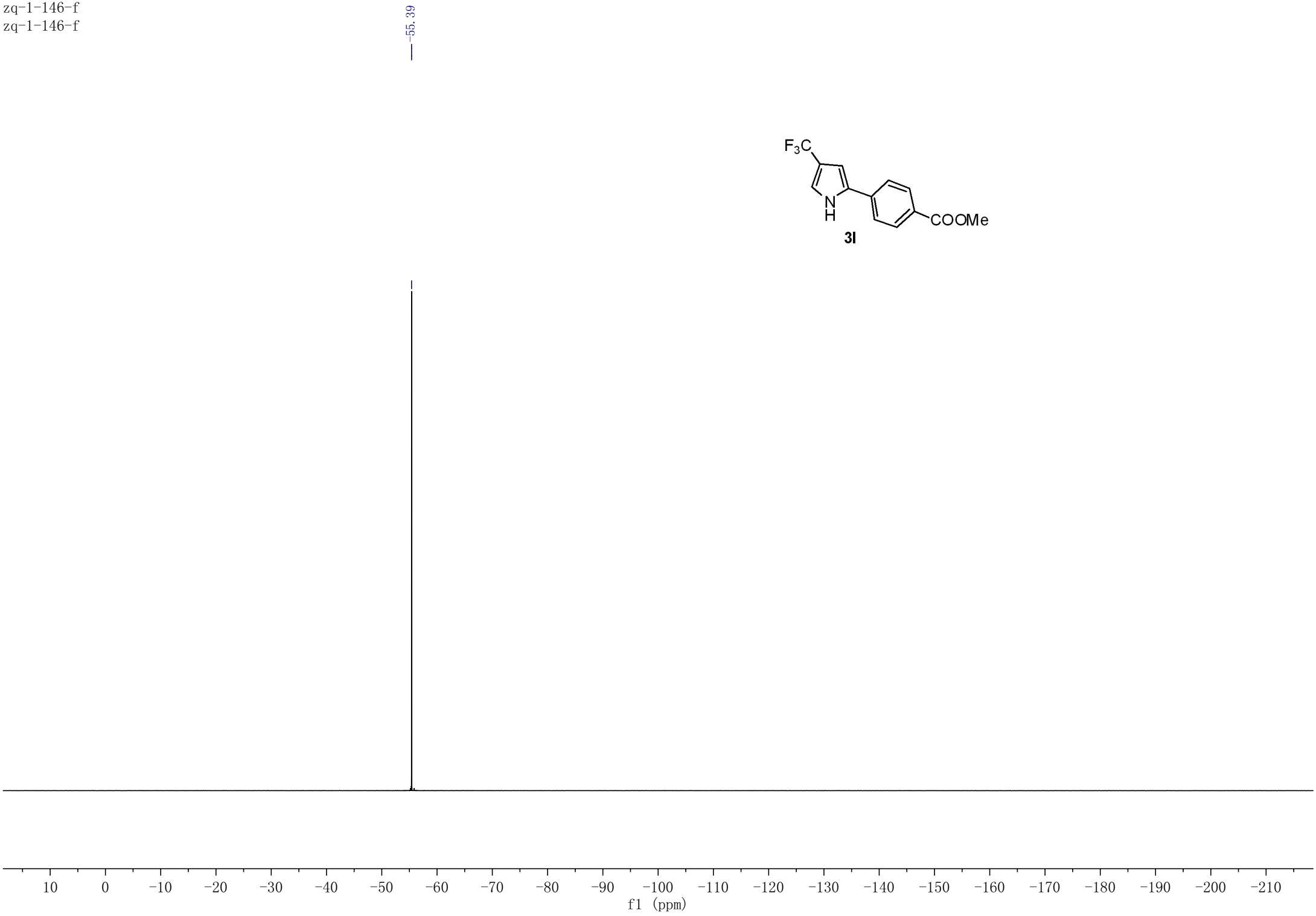
F3C
N
H
COOMe

3l

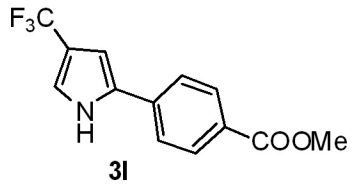

12.18
7.97
7.95
7.85
7.83
7.49
7.00
3.85
3.35
2.50
2.50
2.50
0.96
1.99
1.97
1.00
1.00
2.99
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

zq-1-146-f
zq-1-146-f

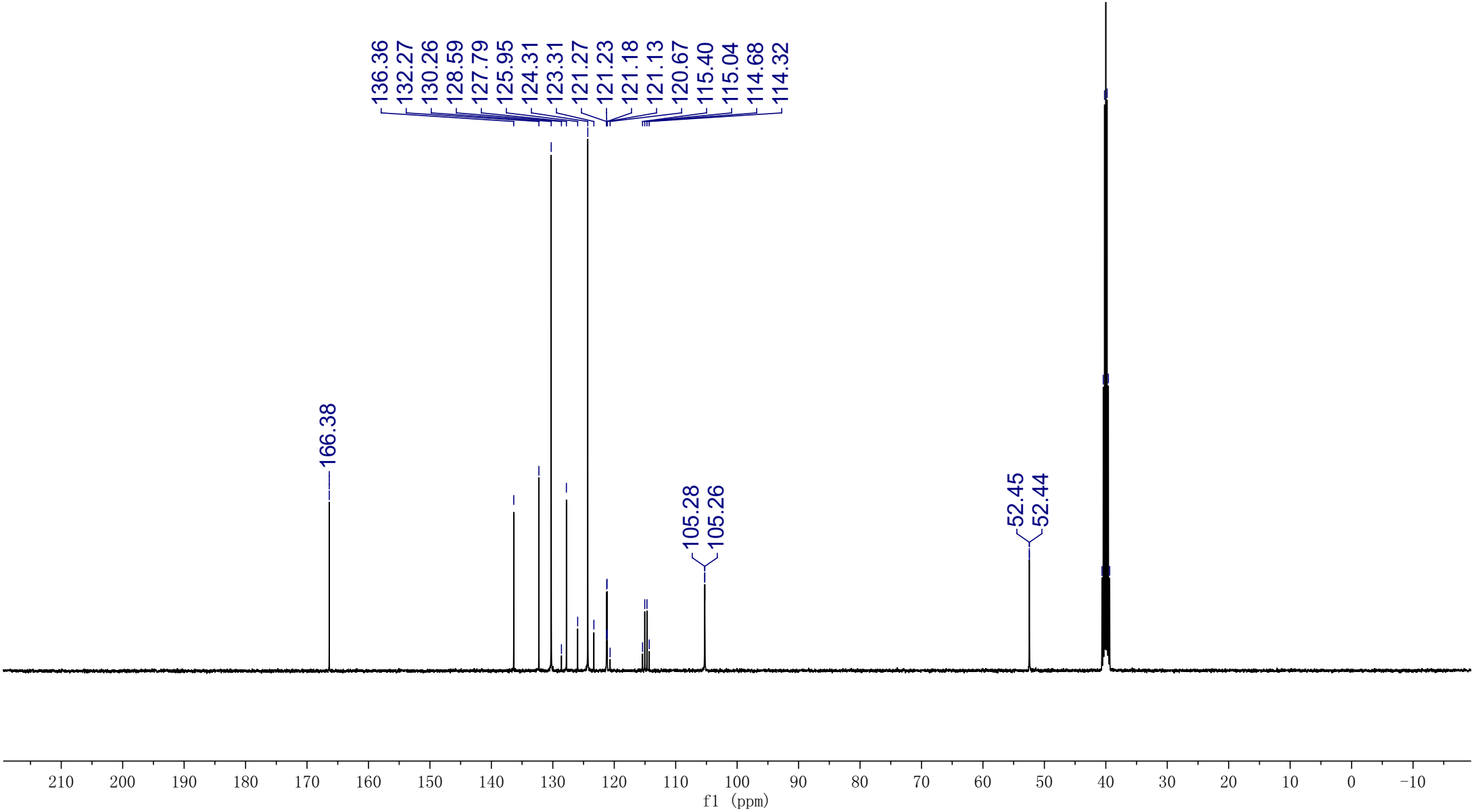
3l



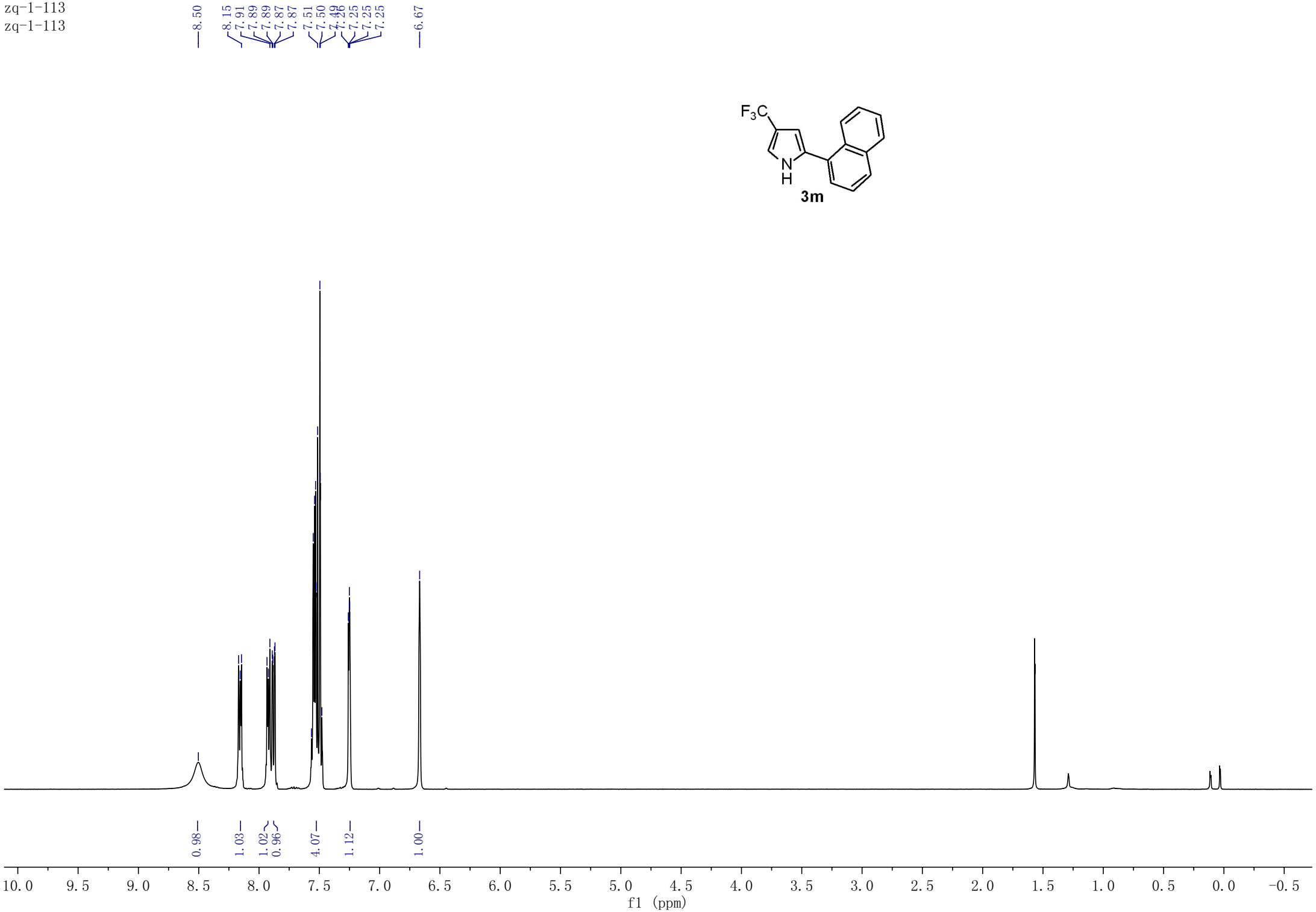
zq-1-146-c


F3C
N
H
COOMe

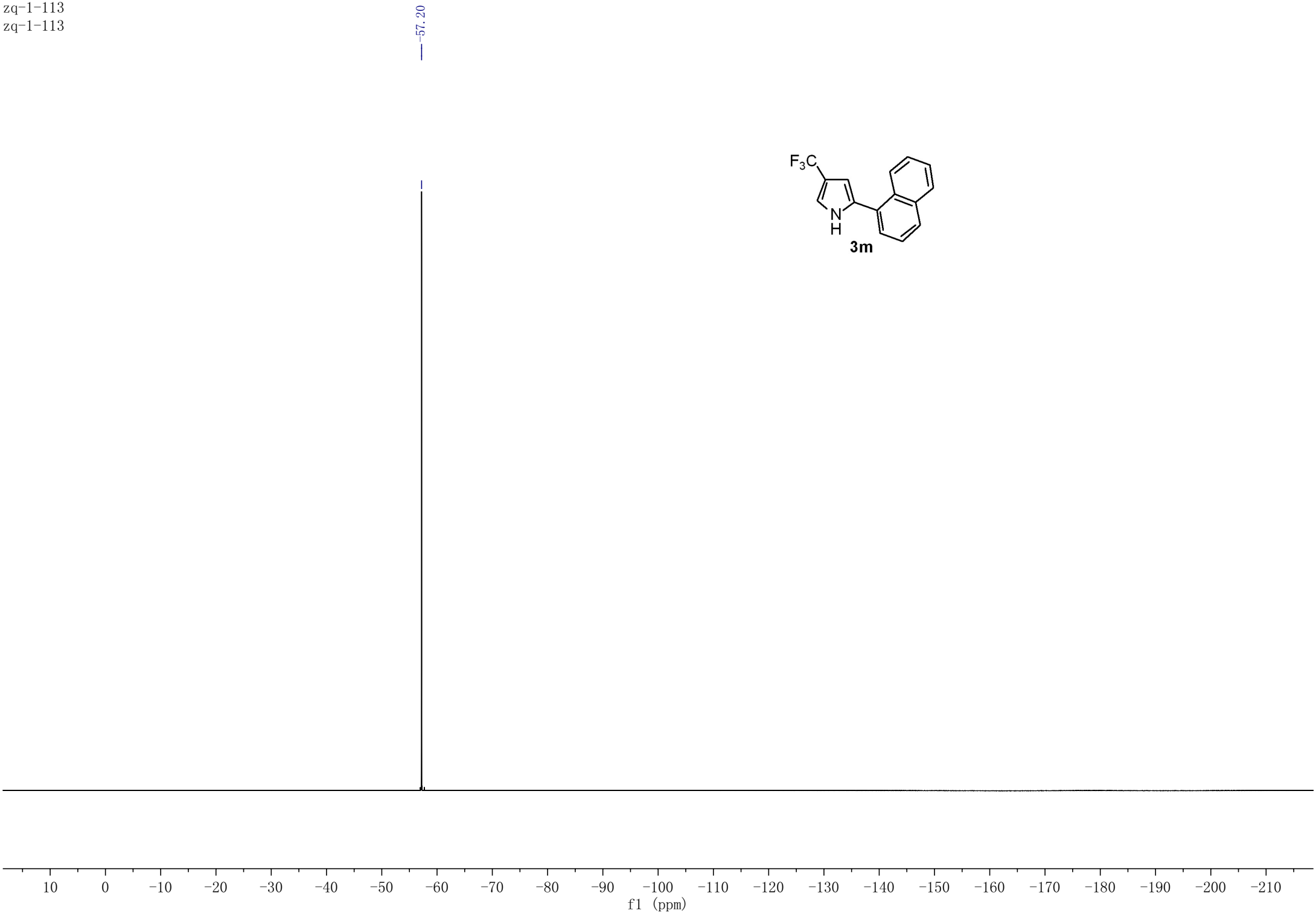
3l

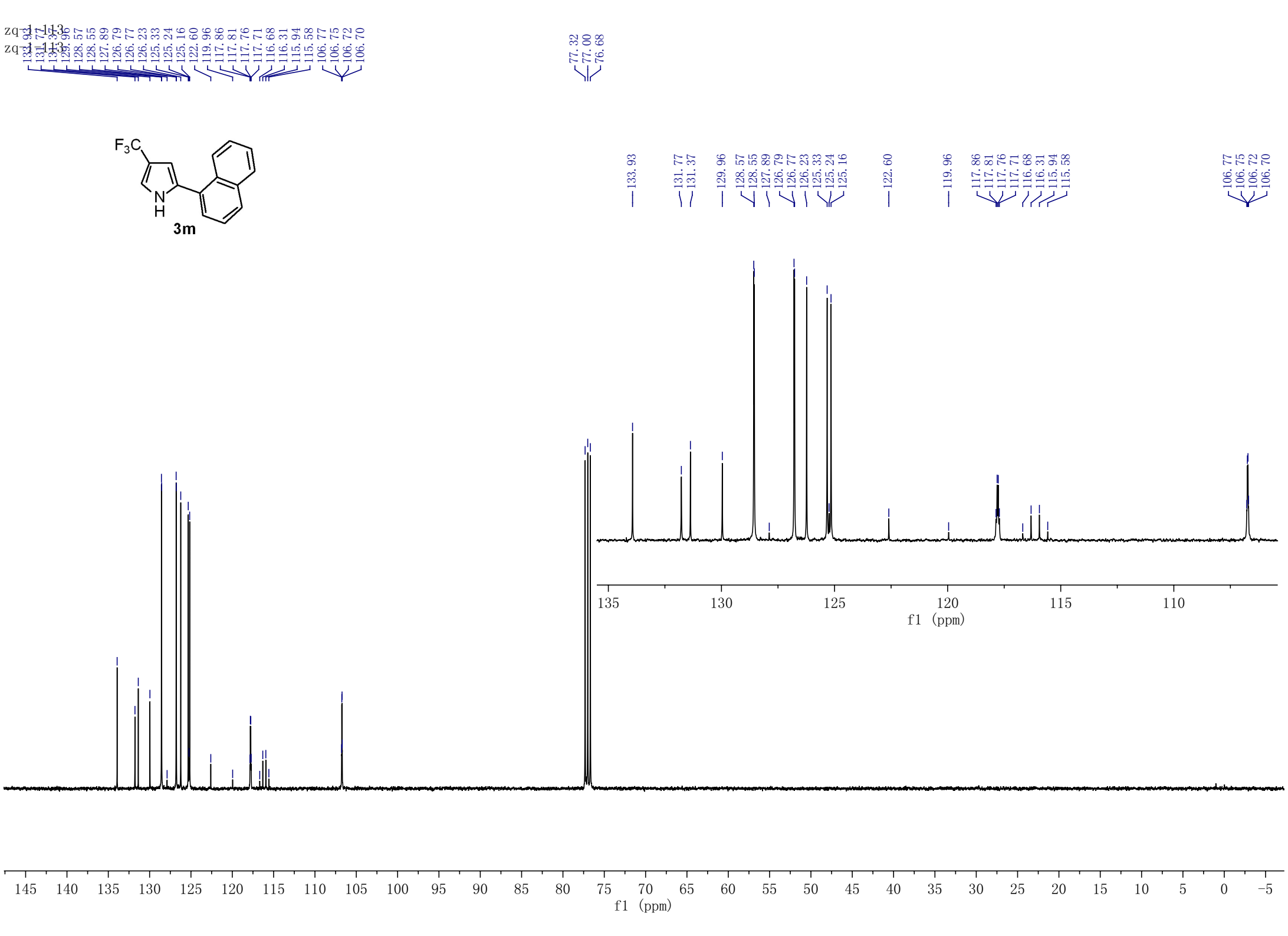

166.38
136.36
132.27
130.26
128.59
127.79
125.95
124.31
123.31
121.27
121.23
121.18
121.13
120.67
115.40
115.04
114.68
114.32
105.28
105.26
52.45
52.44
40.63
40.42
40.21
40.00
39.79
39.58
39.37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

zq-1-113
zq-1-113

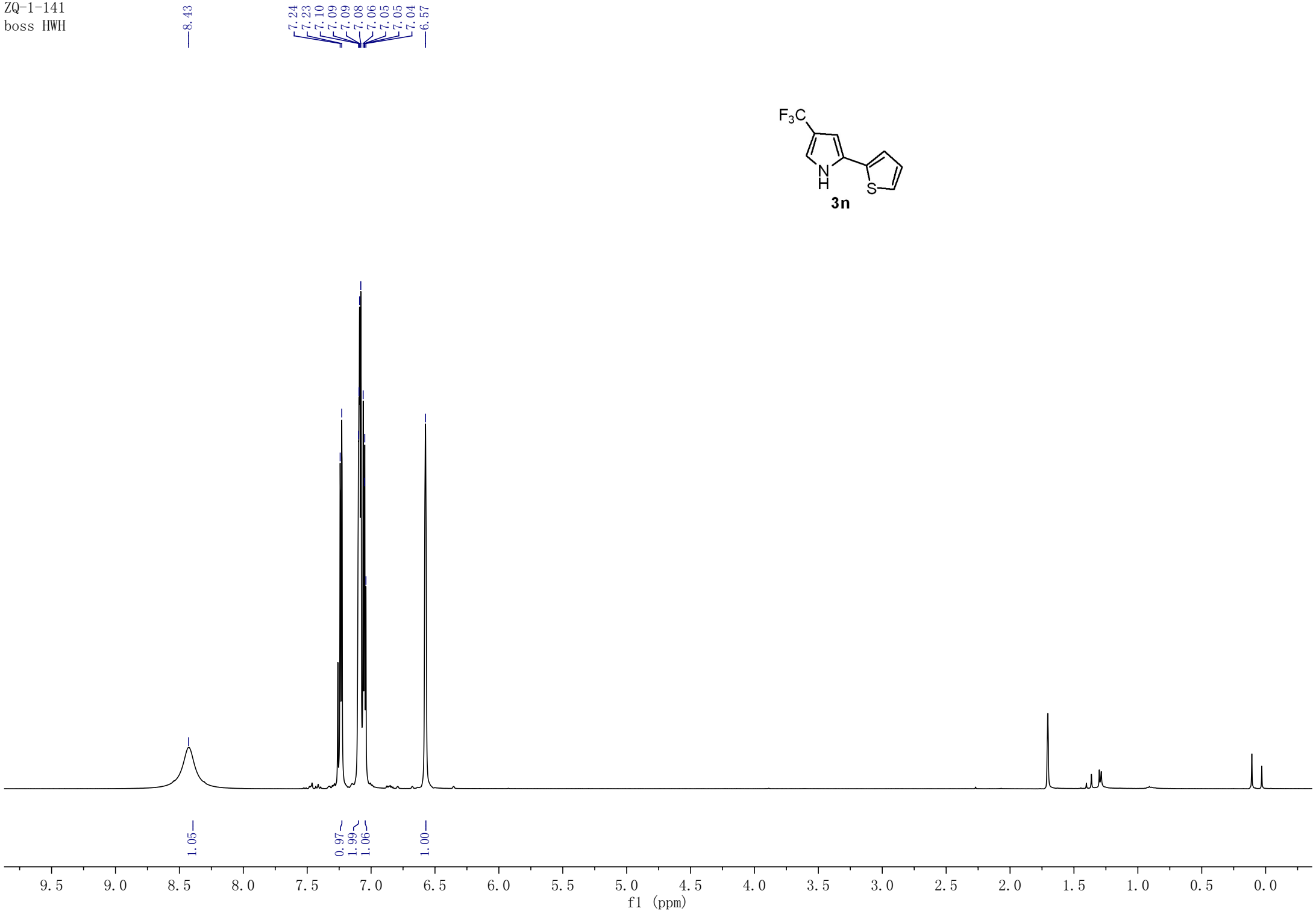


zq-1-113
zq-1-113



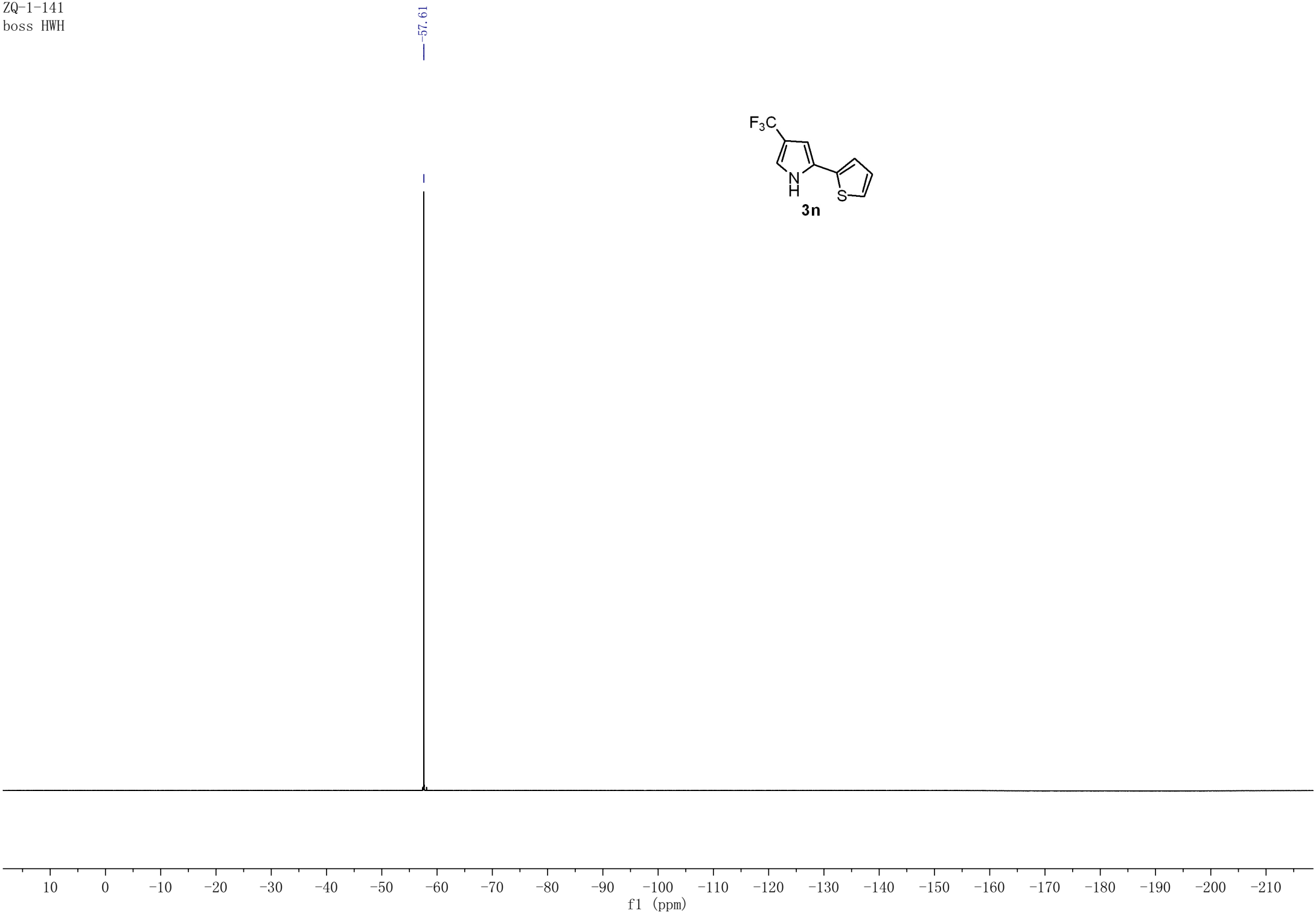

zq-1-113
zq-1-113
133.93
131.77
131.37
129.96
128.57
128.55
127.89
126.79
126.77
126.23
125.33
125.24
125.16
122.60
119.96
117.86
117.81
117.76
117.71
116.68
116.31
115.94
115.58
106.77
106.75
106.72
106.70
77.32
77.00
76.68
F3C
N
H
3m
f1 (ppm)
f1 (ppm)

ZQ-1-141
boss HWH

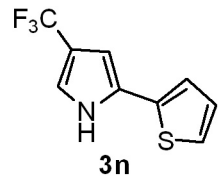


ZQ-1-141
boss HWH

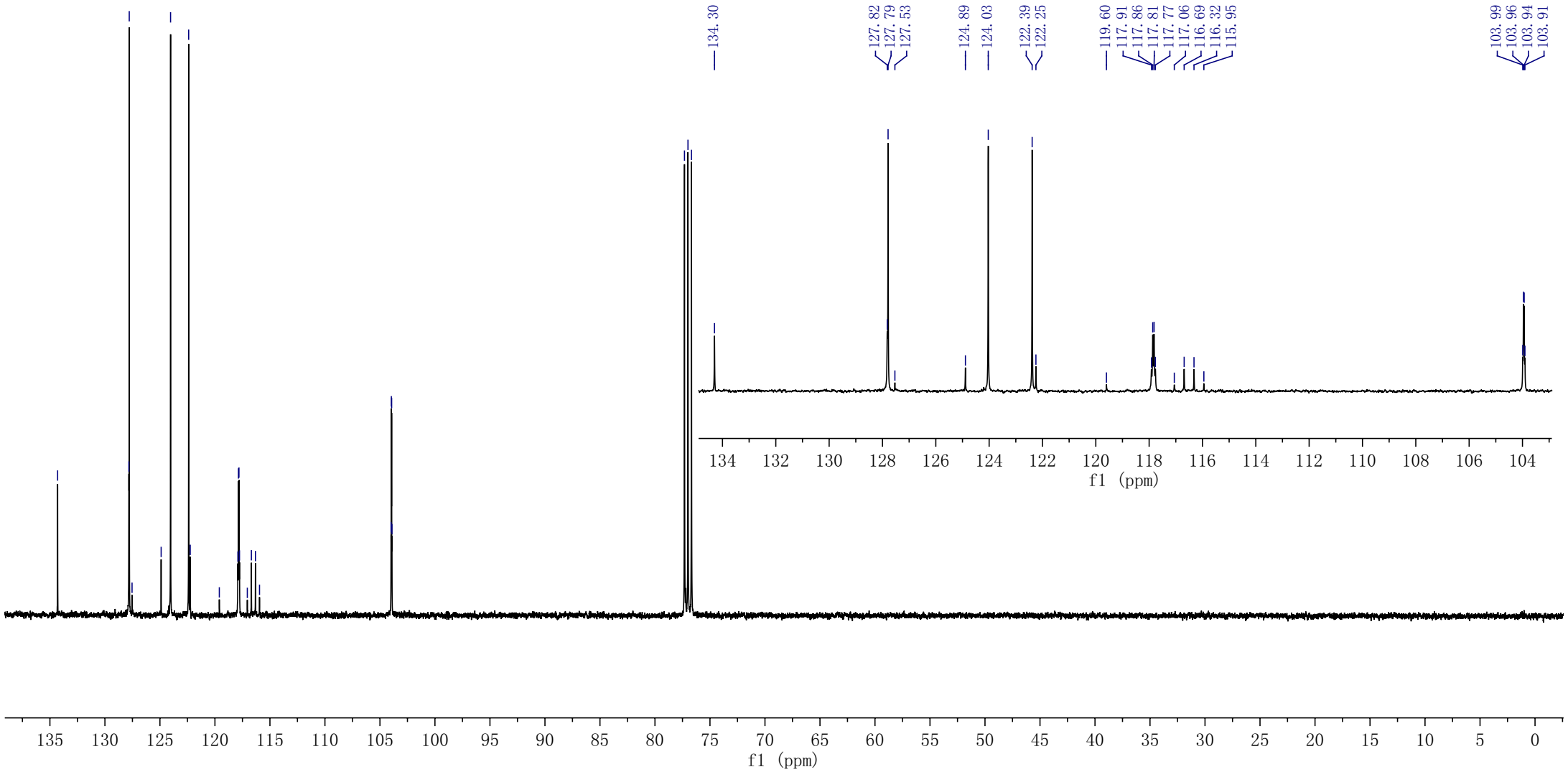
3n



ZQ-1-141
boss HWH

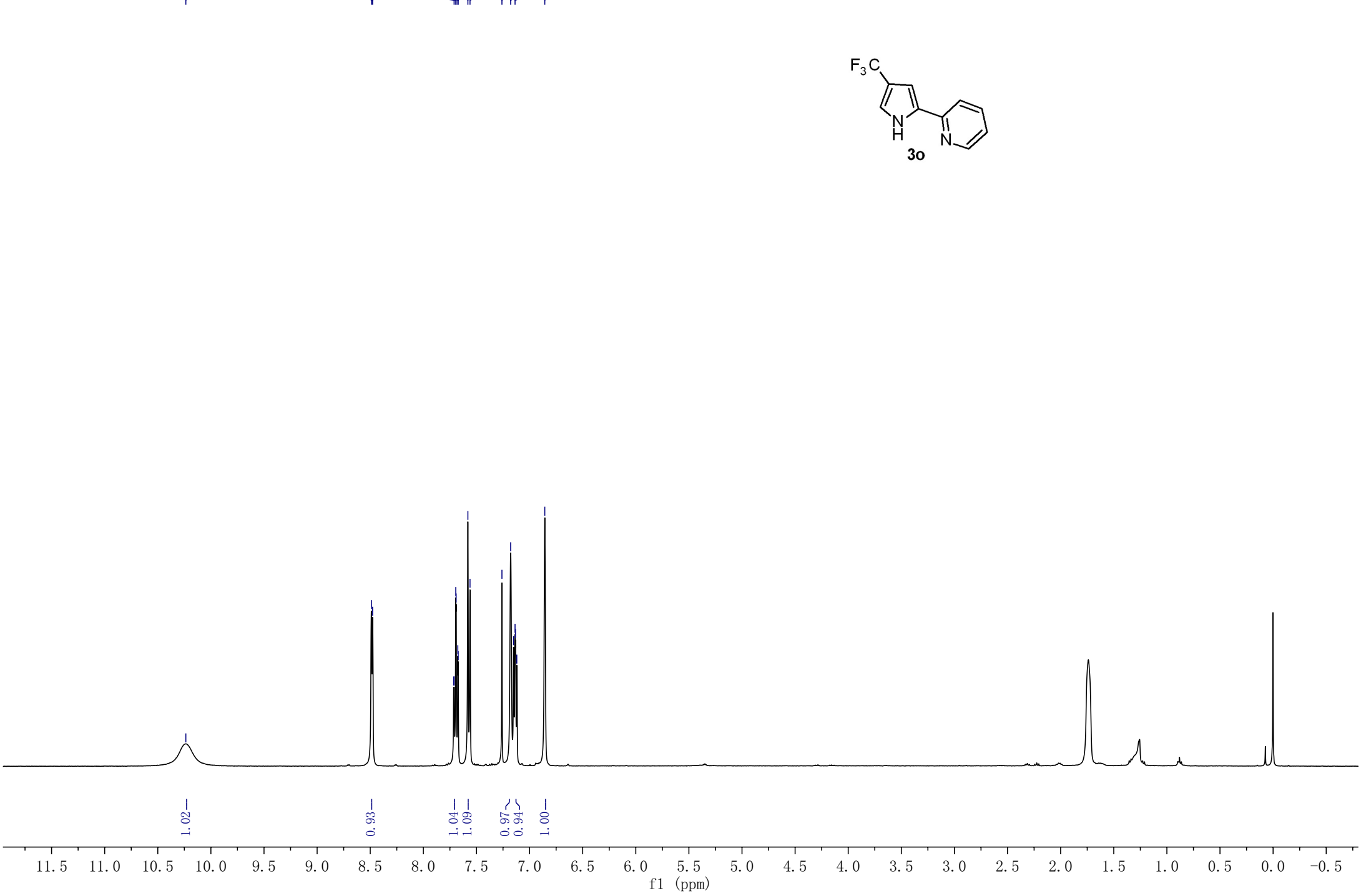


3n



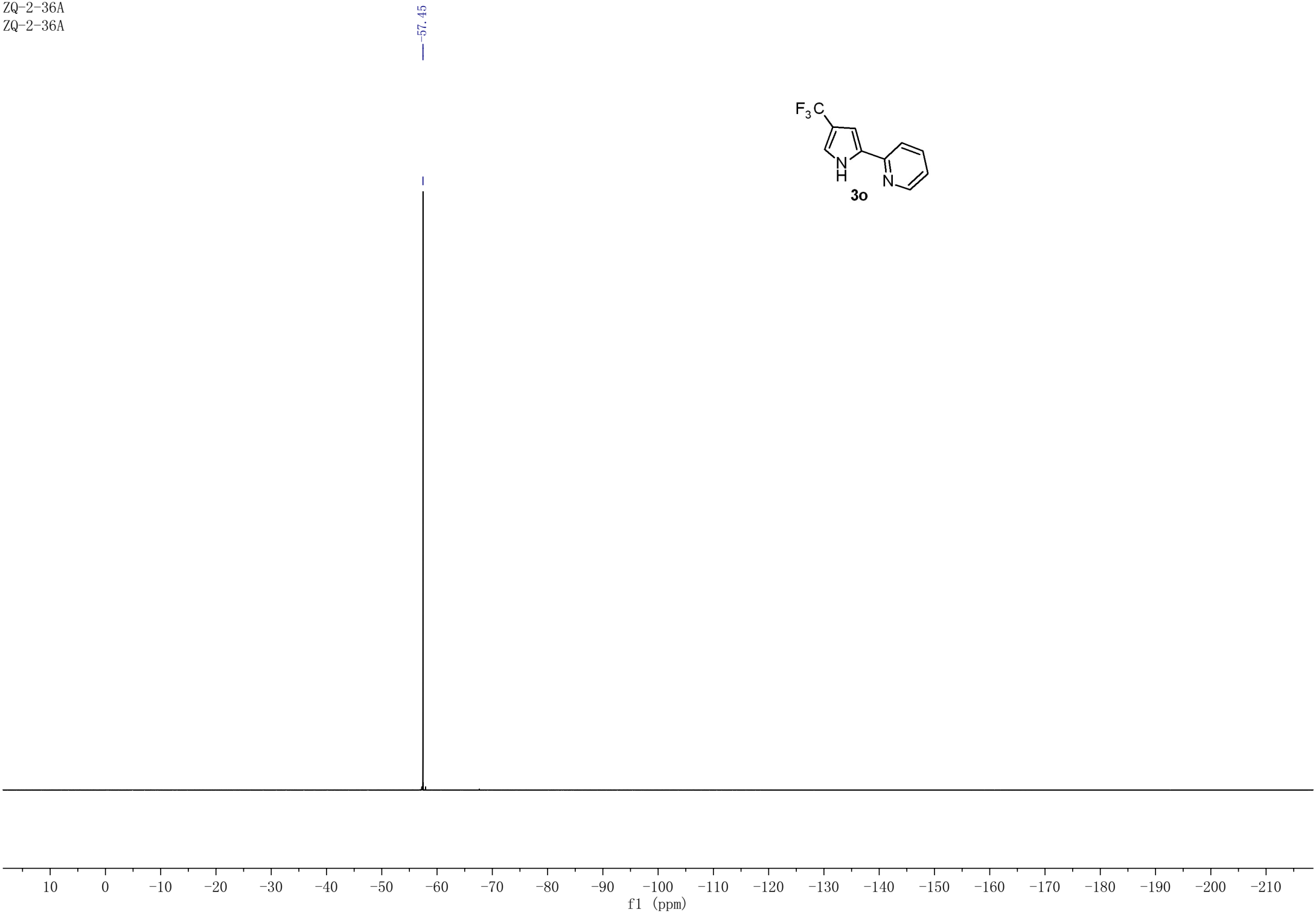
ZQ-2-36 A H
ZQ-2-36 A H

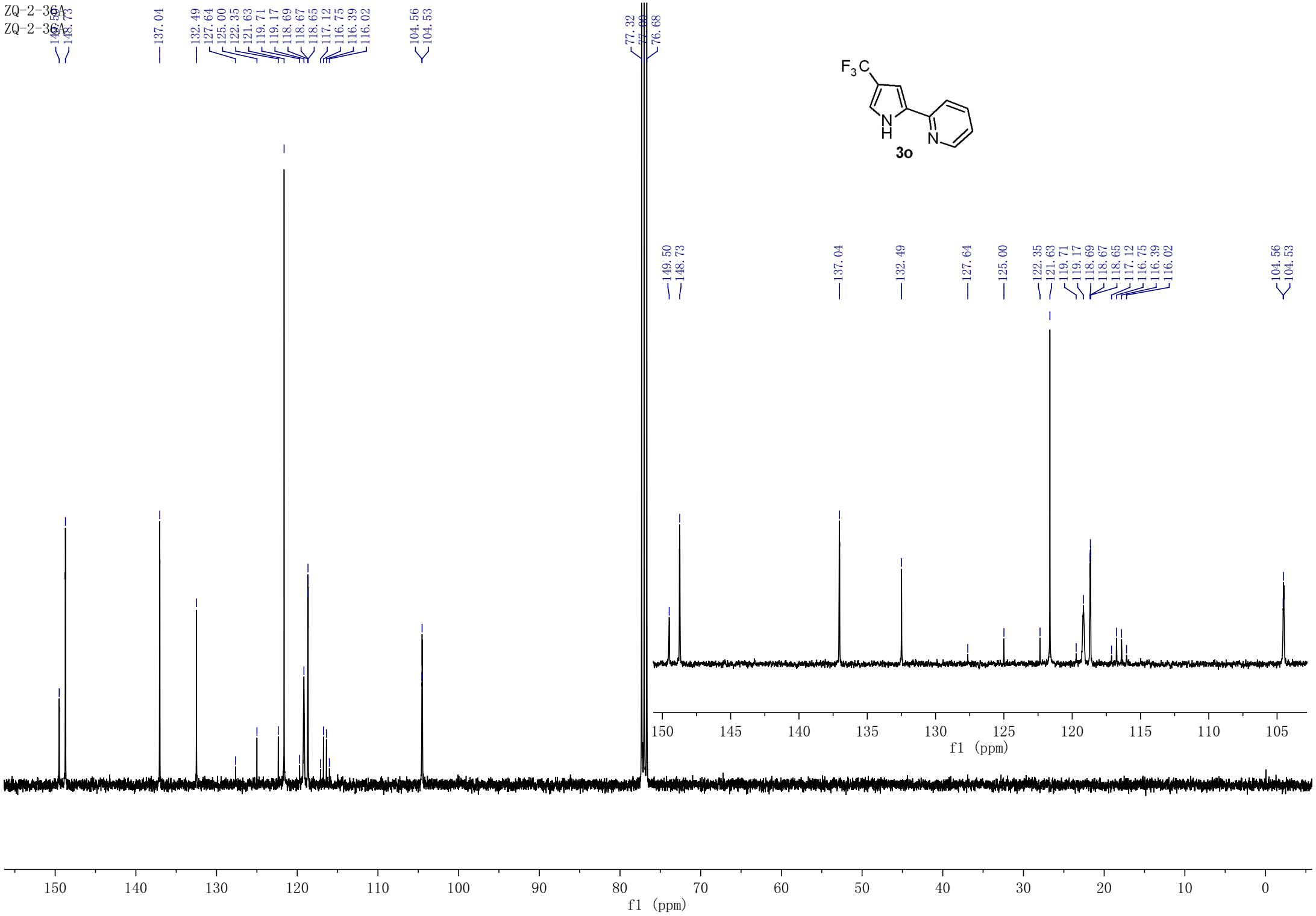
3o



ZQ-2-36A
ZQ-2-36A

3o




ZQ-2-36A
ZQ-2-36A
149.50
148.73
137.04
132.49
127.64
125.00
122.35
121.63
119.71
119.17
118.69
118.67
118.65
117.12
116.75
116.39
116.02
104.56
104.53
77.32
77.00
76.68
F3C
N
H
N
3o
f1 (ppm)
f1 (ppm)

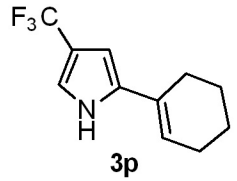
zq-2-32
zq-2-32

8.33

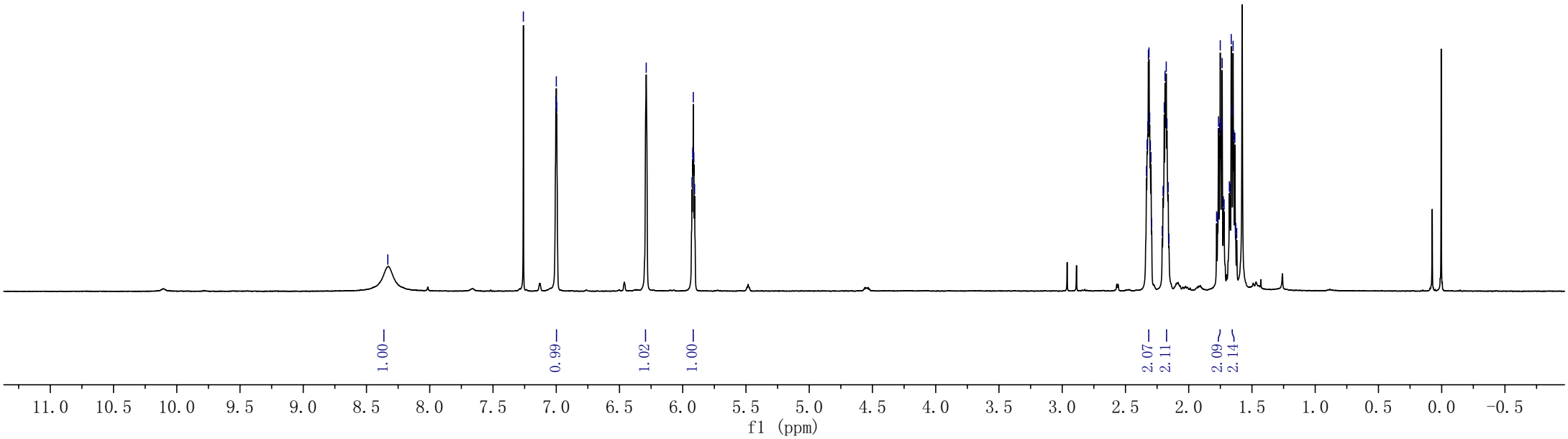
7.26 7.00 7.00 7.00

6.29 5.93 5.92 5.92 5.91 5.91

2.33 2.33 2.32 2.32 2.31 2.31 2.30 2.30 2.29 2.21 2.20 2.19 2.19 2.18 2.17 2.16 2.16 1.78 1.77 1.76 1.76 1.75 1.74 1.74 1.73 1.72 1.68 1.67 1.66 1.66 1.65 1.64 1.64 1.63 1.62

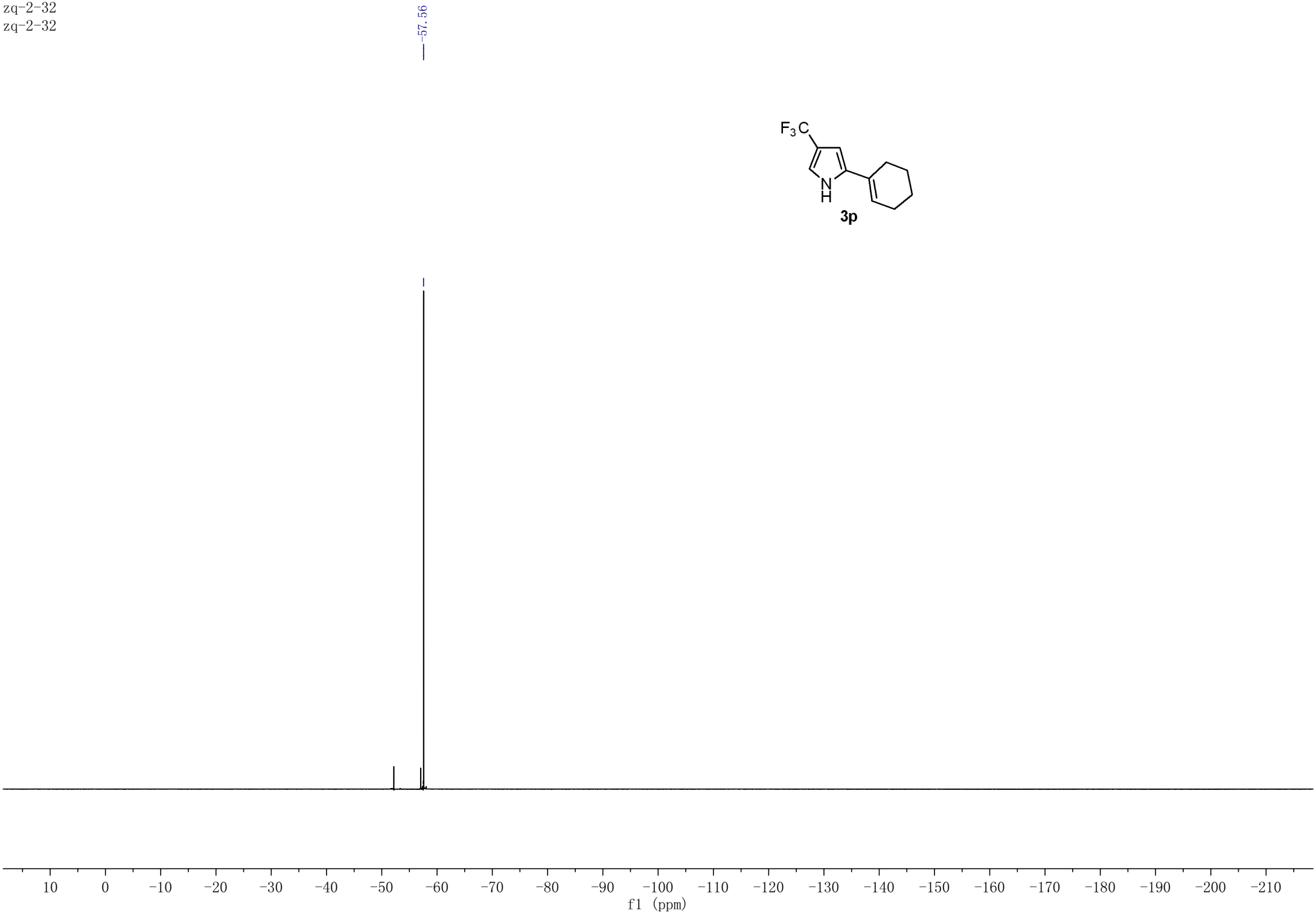


3p



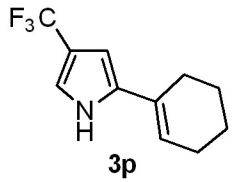
zq-2-32
zq-2-32

3p

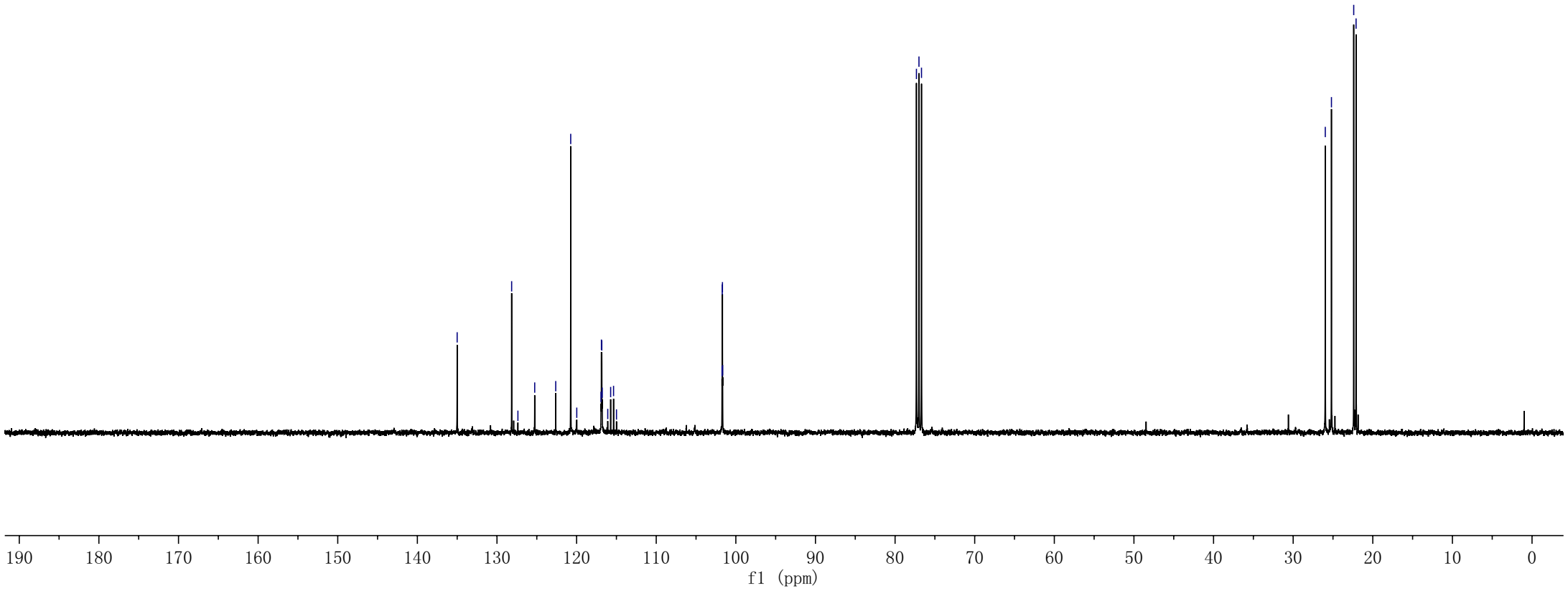


zq-2-32
zq-2-32

135.00
128.16
127.37
125.26
122.62
120.74
119.98
116.93
116.88
116.83
116.78
116.09
115.72
115.36
114.99
101.74
101.71
101.68
101.66
77.32
77.00
76.68
25.97
25.19
22.40
22.10

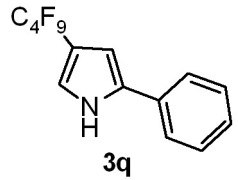


3p



zq-2-18
zq-2-18

8.69
7.49
7.49
7.47
7.47
7.43
7.41
7.39
7.31
7.30
7.28
7.14
7.14
7.14
7.13
6.66



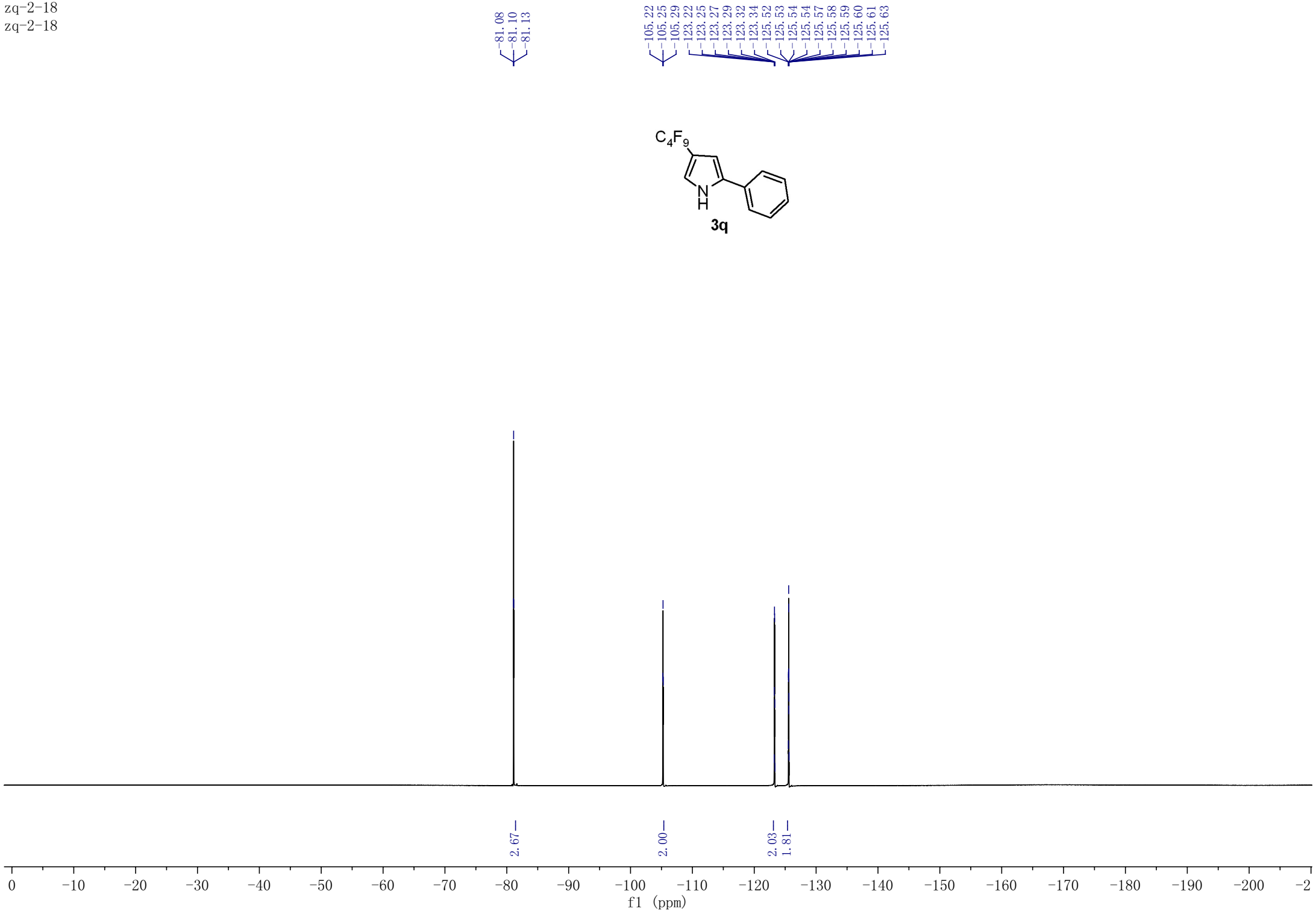
3q

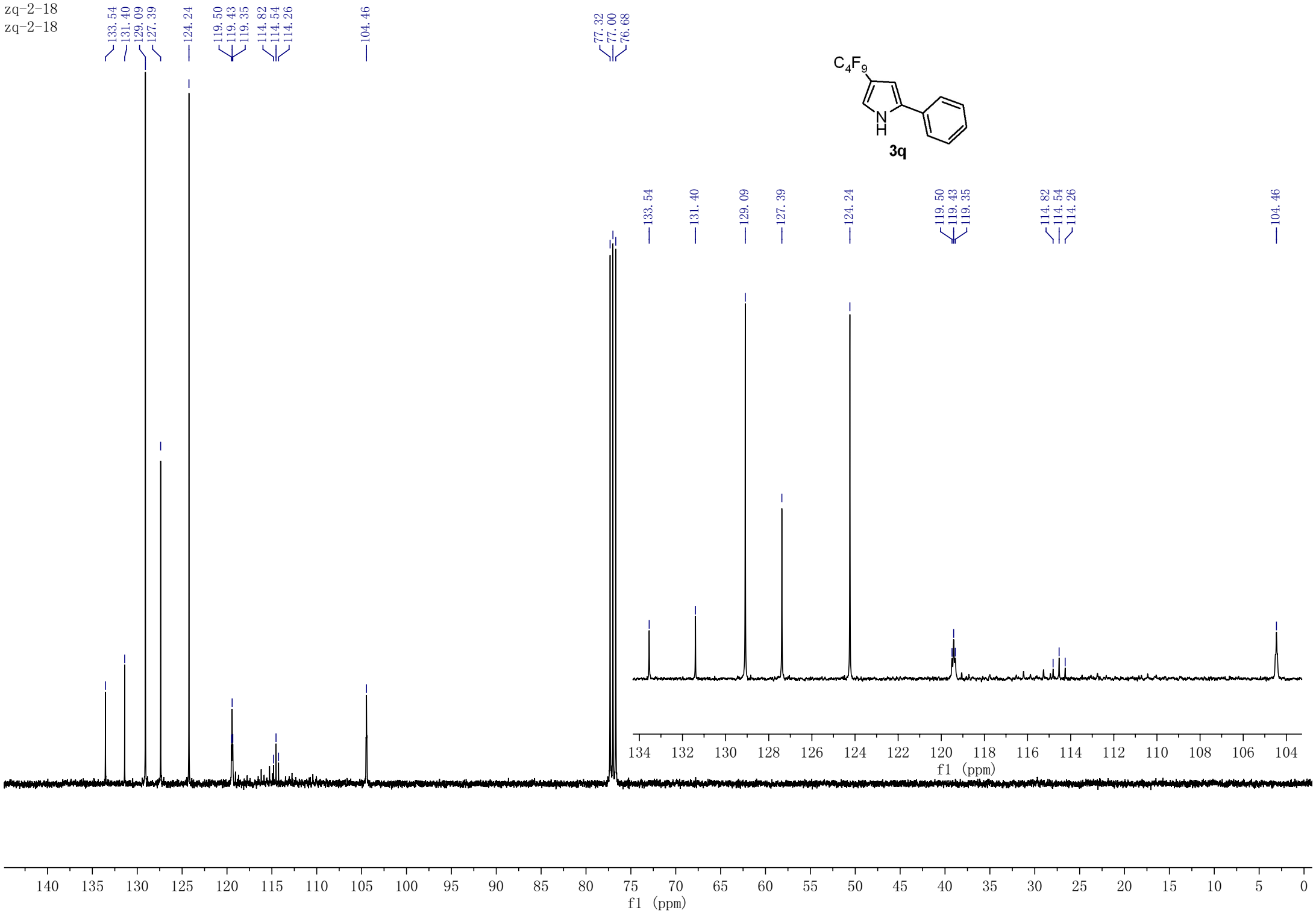
1.07
2.01
2.00
1.00
0.99
1.00

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.

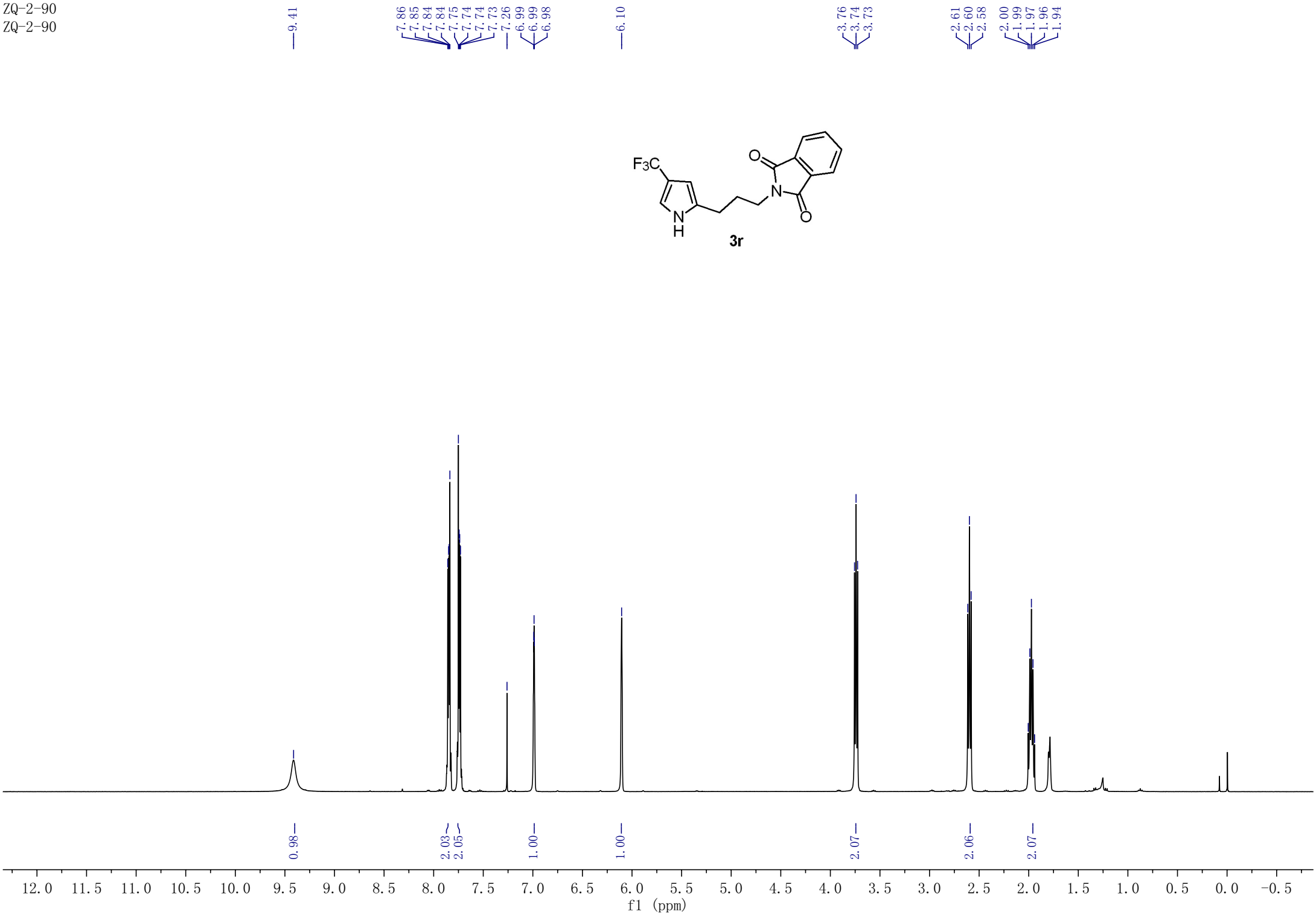
f1 (ppm)

zq-2-18
zq-2-18


-81.08
-81.10
-81.13
-105.22
-105.25
-105.29
-123.22
-123.25
-123.27
-123.29
-123.32
-123.34
-125.52
-125.53
-125.54
-125.57
-125.58
-125.59
-125.60
-125.61
-125.63
C4F9
N
H
3q
2.67
2.00
2.03
1.81
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)

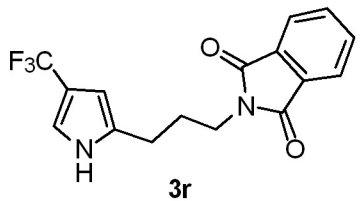

zq-2-18
zq-2-18
133.54
131.40
129.09
127.39
124.24
119.50
119.43
119.35
114.82
114.54
114.26
104.46
77.32
77.00
76.68
C_4F_9
N
H
3q
f1 (ppm)

ZQ-2-90
ZQ-2-90


9.41
7.86
7.85
7.84
7.84
7.75
7.74
7.74
7.73
7.26
6.99
6.99
6.98
6.10
3.76
3.74
3.73
2.61
2.60
2.58
2.00
1.99
1.97
1.96
1.94
F3C
N
H
O
N
O
3r
0.98
2.03
2.05
1.00
1.00
2.07
2.06
2.07
12.0 11.5 11.0 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 -0.5
f1 (ppm)

zq-2-90
zq-2-90

-57.16

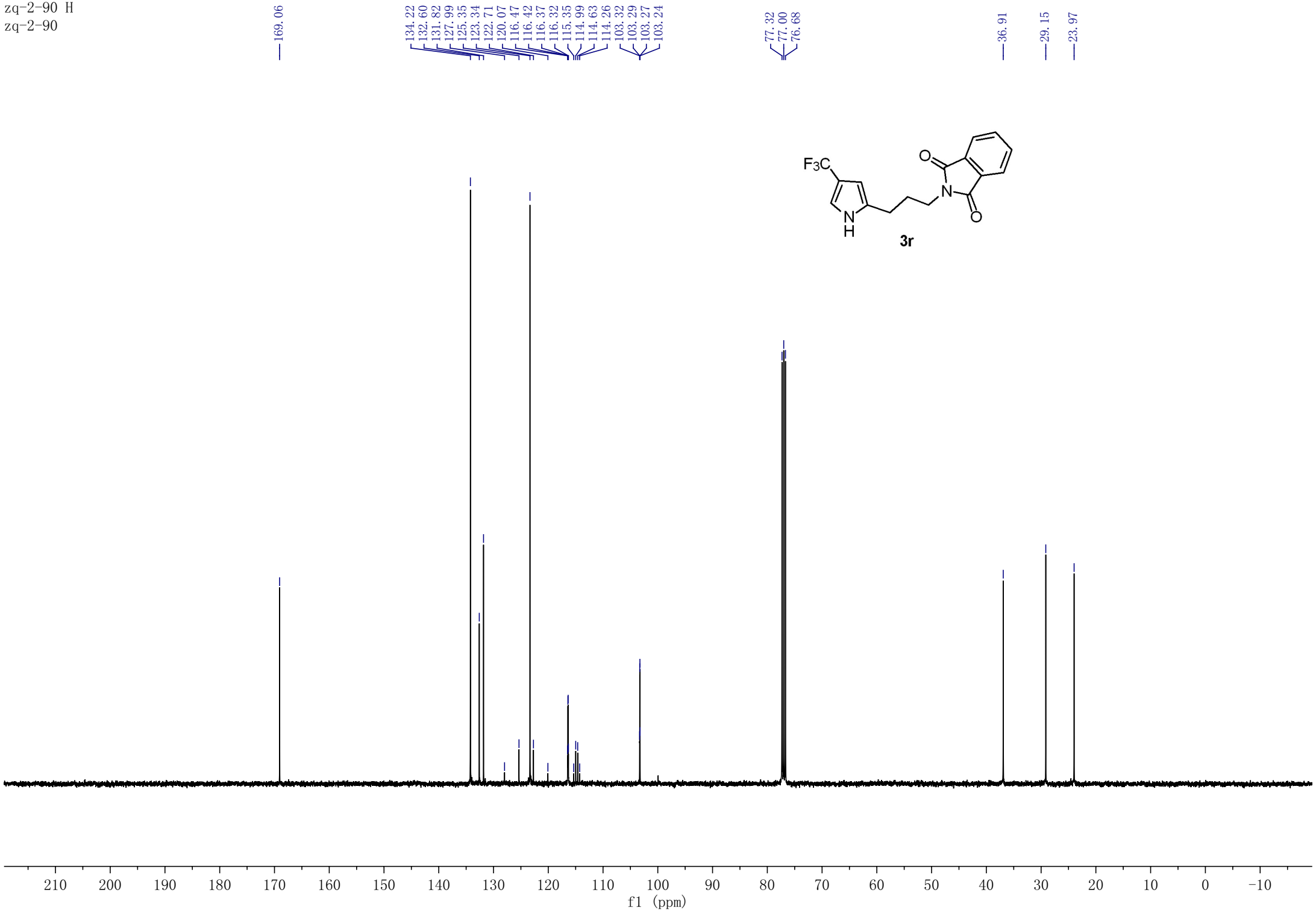


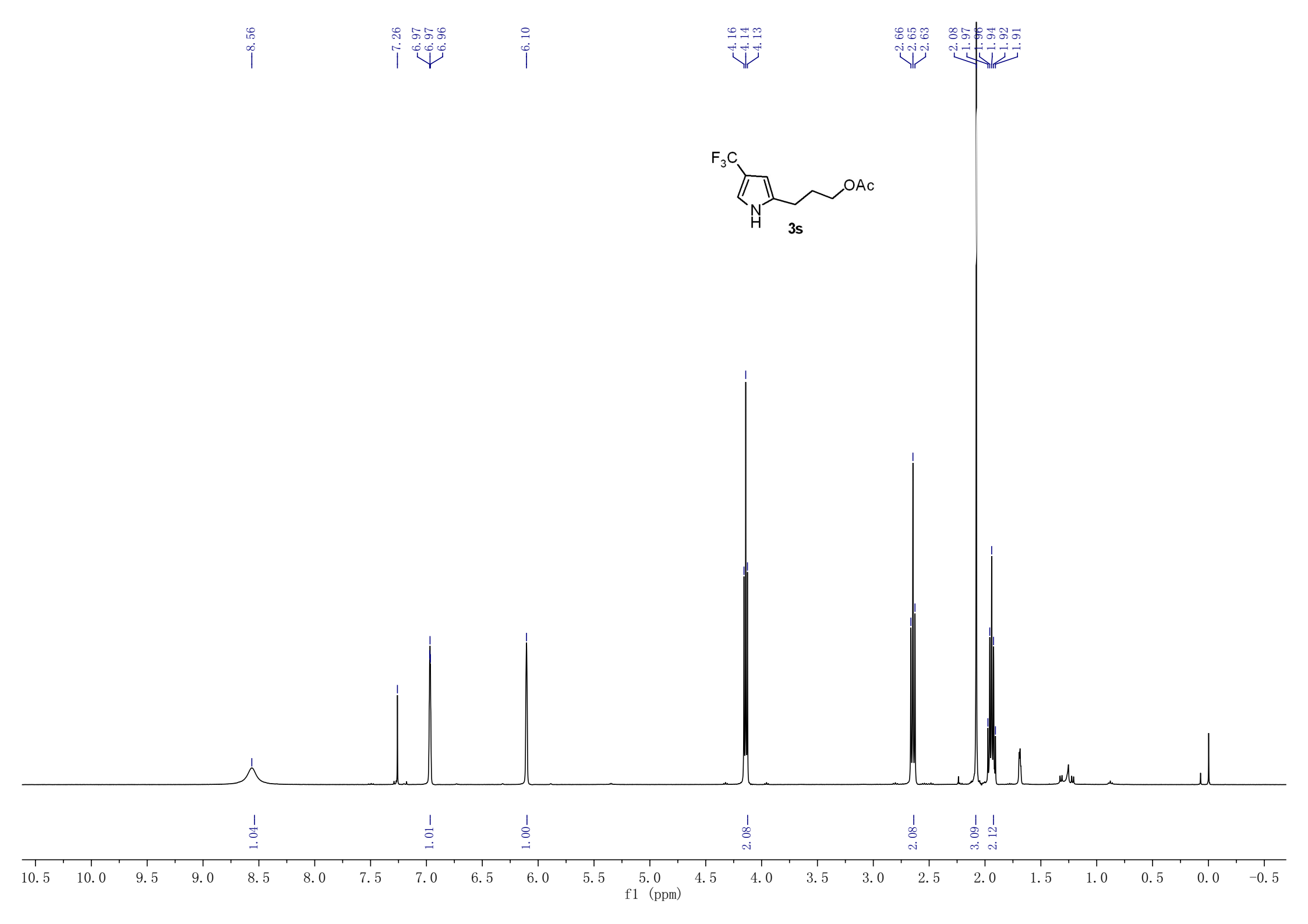
3r

10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210

f1 (ppm)

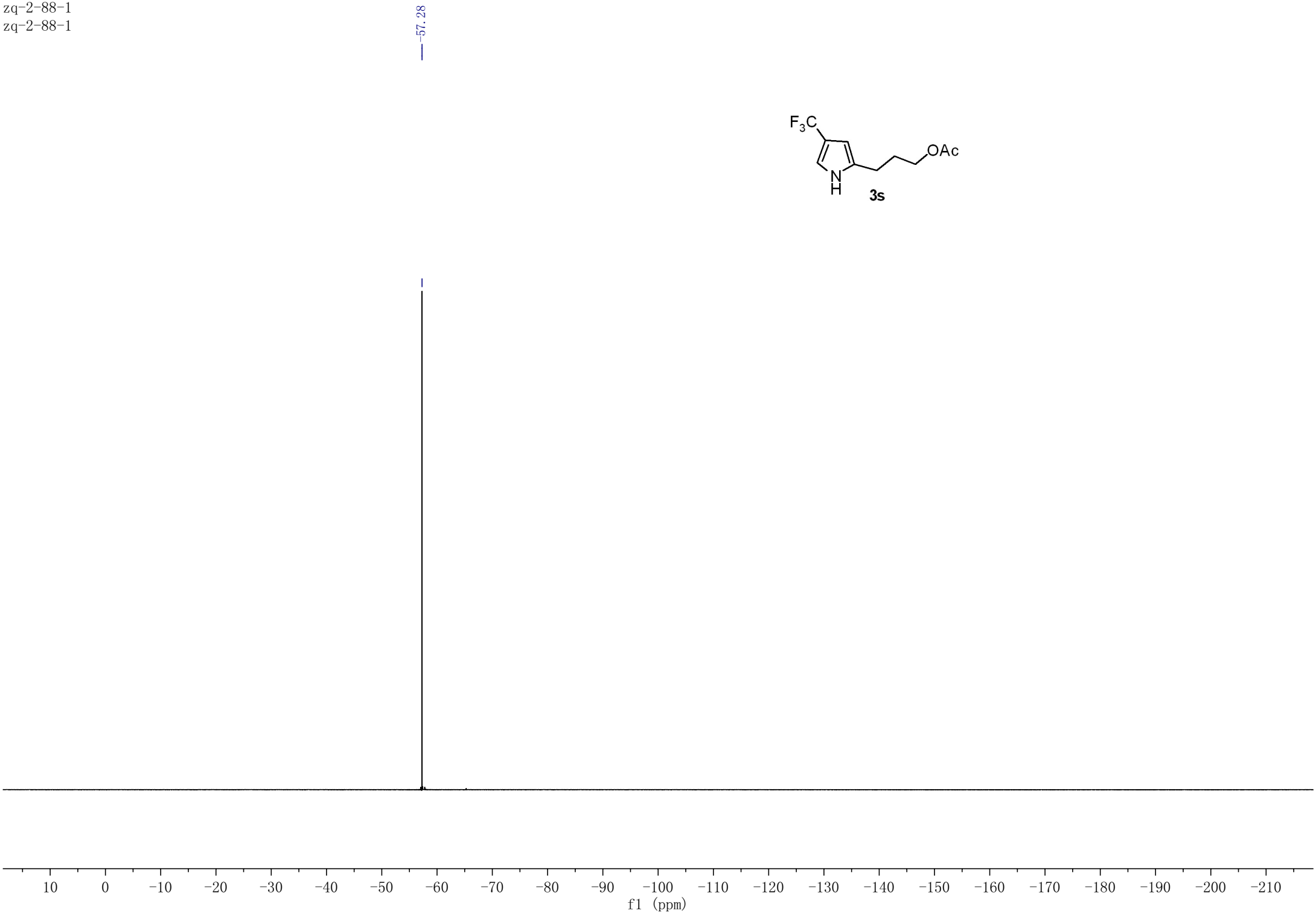
zq-2-90 H
zq-2-90

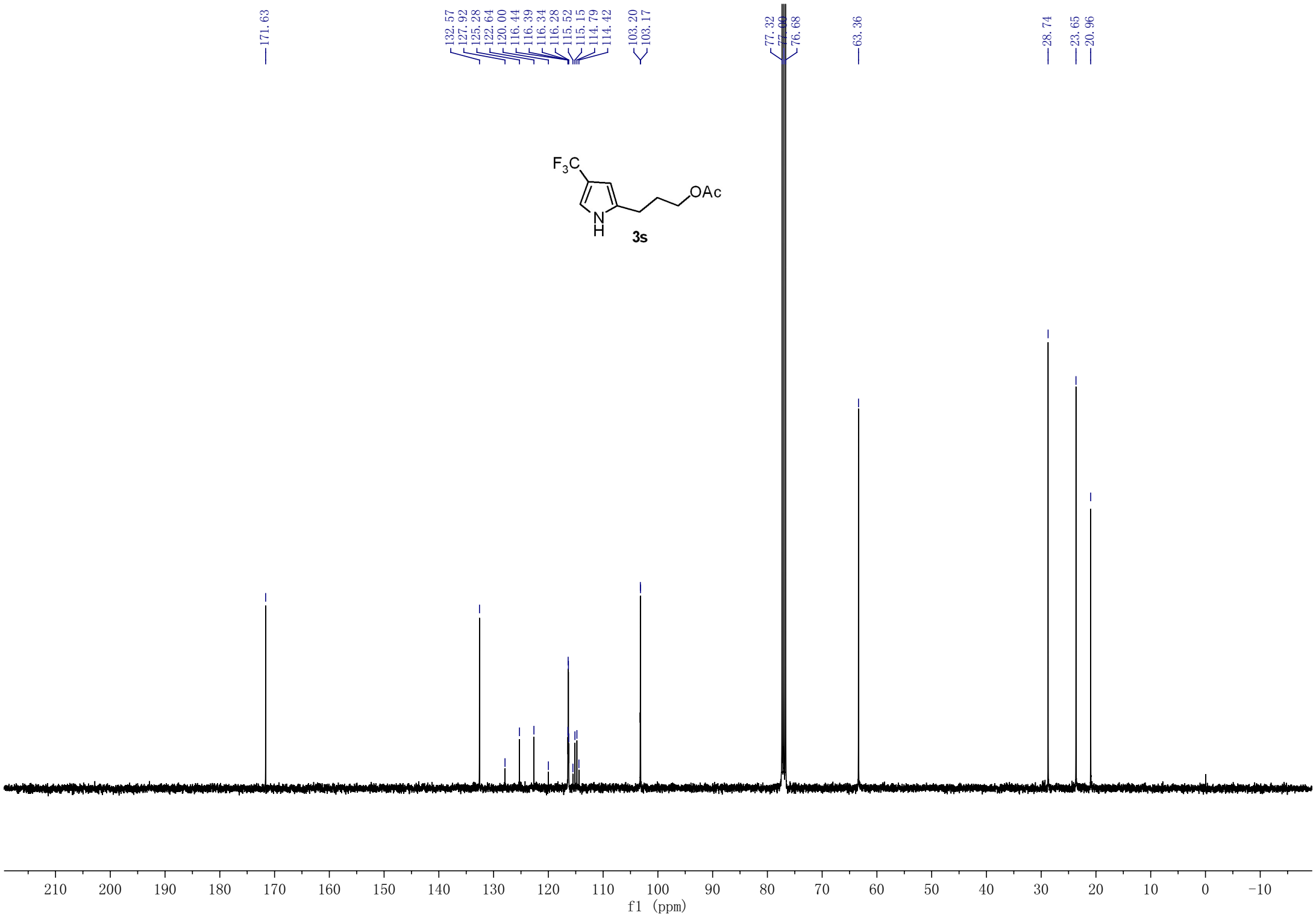



8.56
7.26
6.97
6.97
6.96
6.10
4.16
4.14
4.13
2.66
2.65
2.63
2.08
1.97
1.96
1.94
1.92
1.91
F3C
OAc
N
H
3s
1.04
1.01
1.00
2.08
2.08
3.09
2.12
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

zq-2-88-1
zq-2-88-1

3s



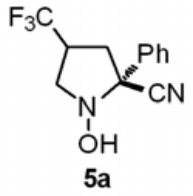

171.63
132.57
127.92
125.28
122.64
120.00
116.44
116.39
116.34
116.28
115.52
115.15
114.79
114.42
103.20
103.17
77.32
77.00
76.68
63.36
28.74
23.65
20.96
F3C
OAc
N
H
3s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

ZQ-2-105a
ZQ-2-105a

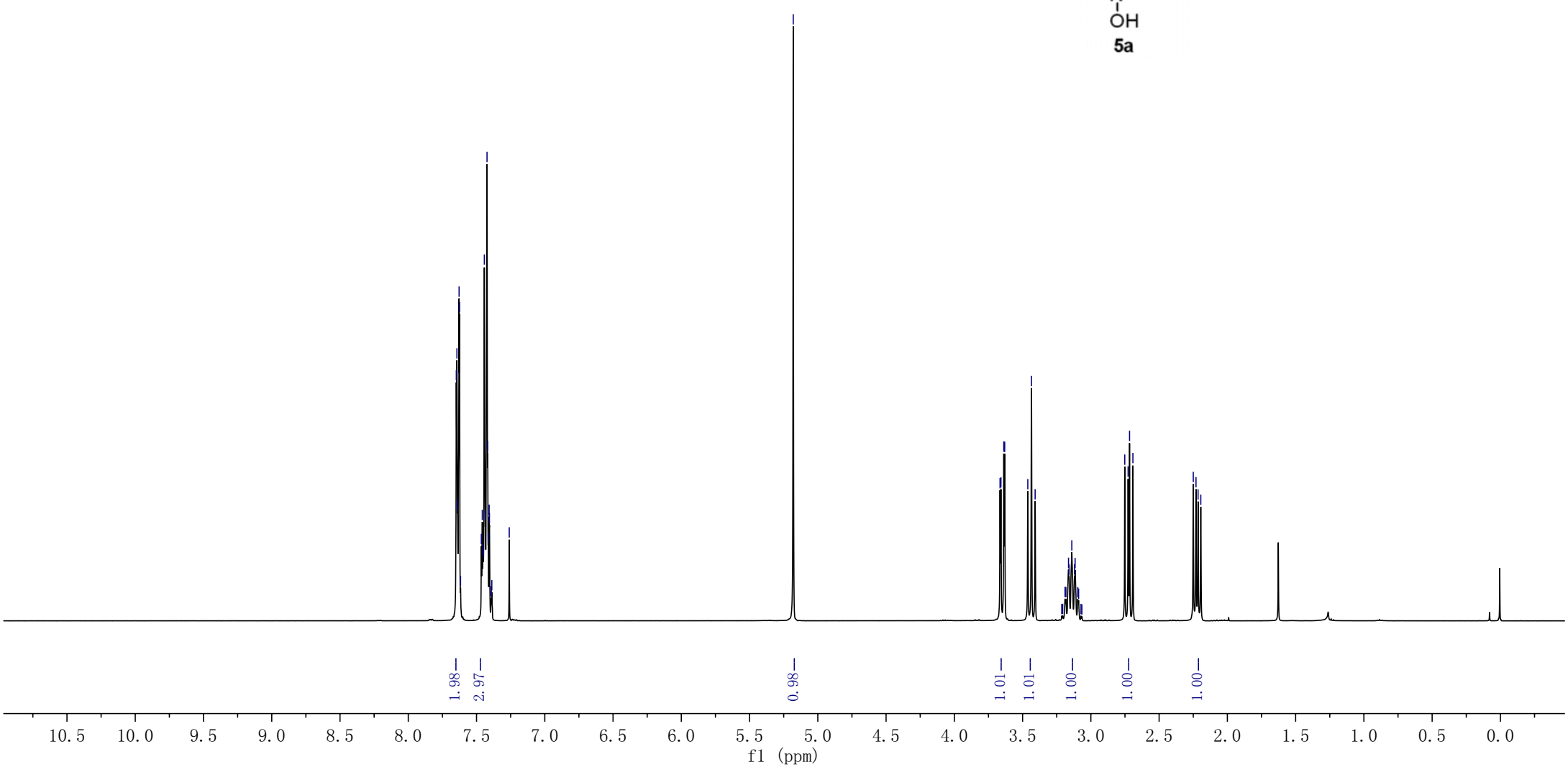
7.65 7.64 7.64 7.63 7.62 7.62 7.46 7.46 7.45 7.45 7.44 7.43 7.42 7.42 7.41 7.41 7.41 7.39 7.39 7.26

5.18

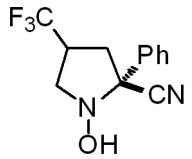
3.67 3.66 3.64 3.63 3.46 3.44 3.41 3.21 3.21 3.19 3.18 3.16 3.16 3.14 3.12 3.12 3.10 3.09 2.73 2.72 2.69 2.25 2.23 2.21 2.19



5a



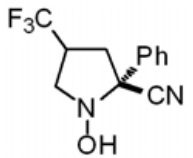
ZQ-2-105a
ZQ-2-105a



5a

ZQ-2-105a
ZQ-2-105a

135.03
130.77
129.50
129.11
128.02
126.21
125.26
122.51
117.14
77.32
77.00
76.68
72.69
53.34
53.32
37.85
37.82
37.80
37.10
36.80
36.50
36.20



5a

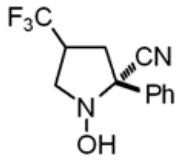
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

zq-2-105b
zq-2-105b

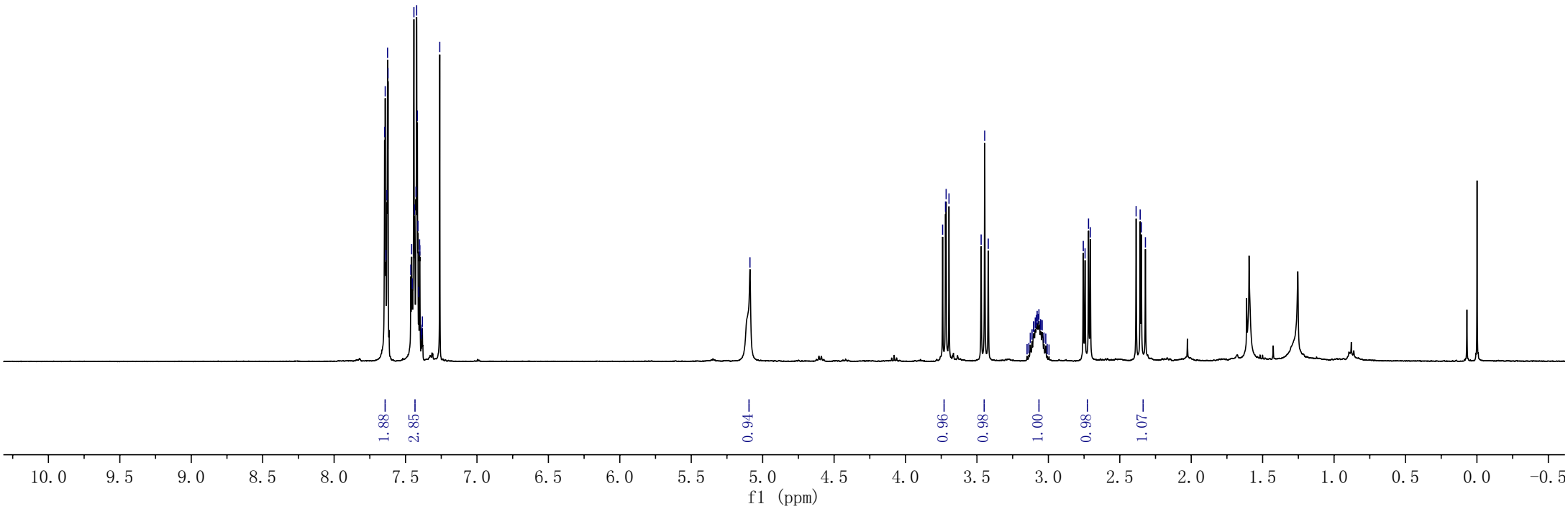
7.65 7.64 7.64 7.63 7.63 7.62 7.46 7.46 7.45 7.44 7.44 7.43 7.42 7.42 7.41 7.40 7.40 7.39 7.38 7.26

5.09

3.74 3.72 3.72 3.70 3.47 3.45 3.08 3.07 3.07 2.76 2.72 2.71 2.39 2.36 2.35 2.32

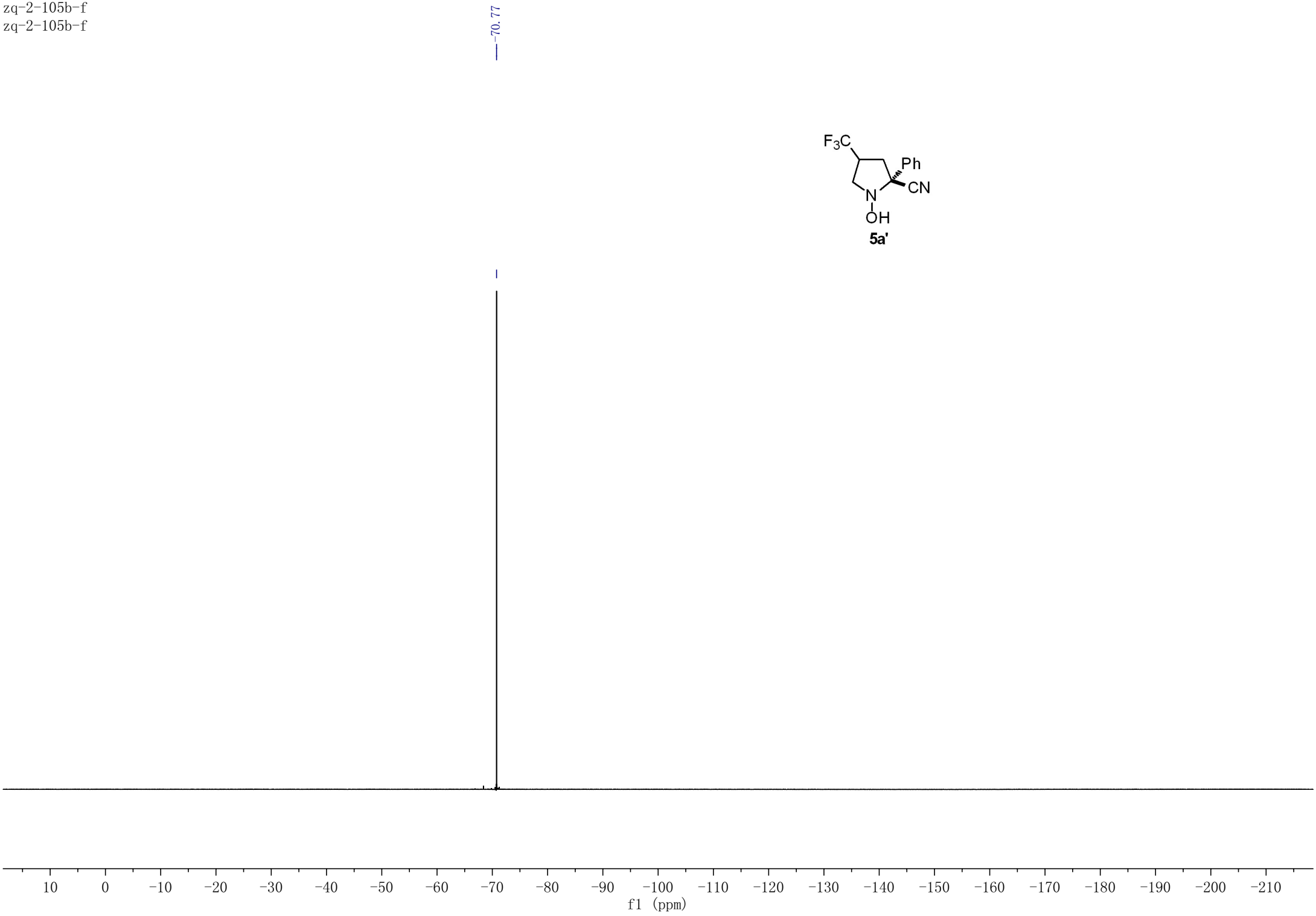


5a'



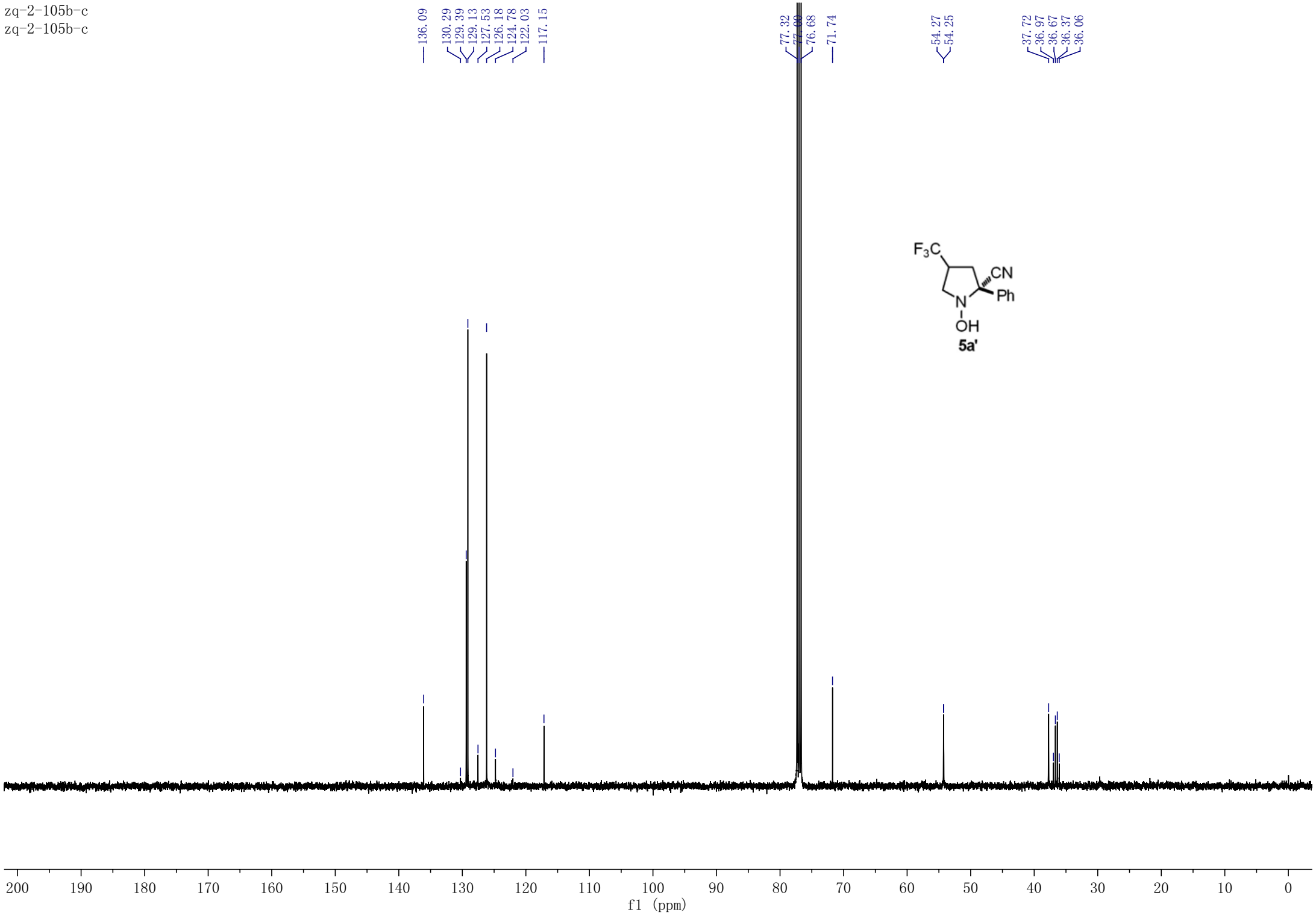
zq-2-105b-f
zq-2-105b-f

5a'

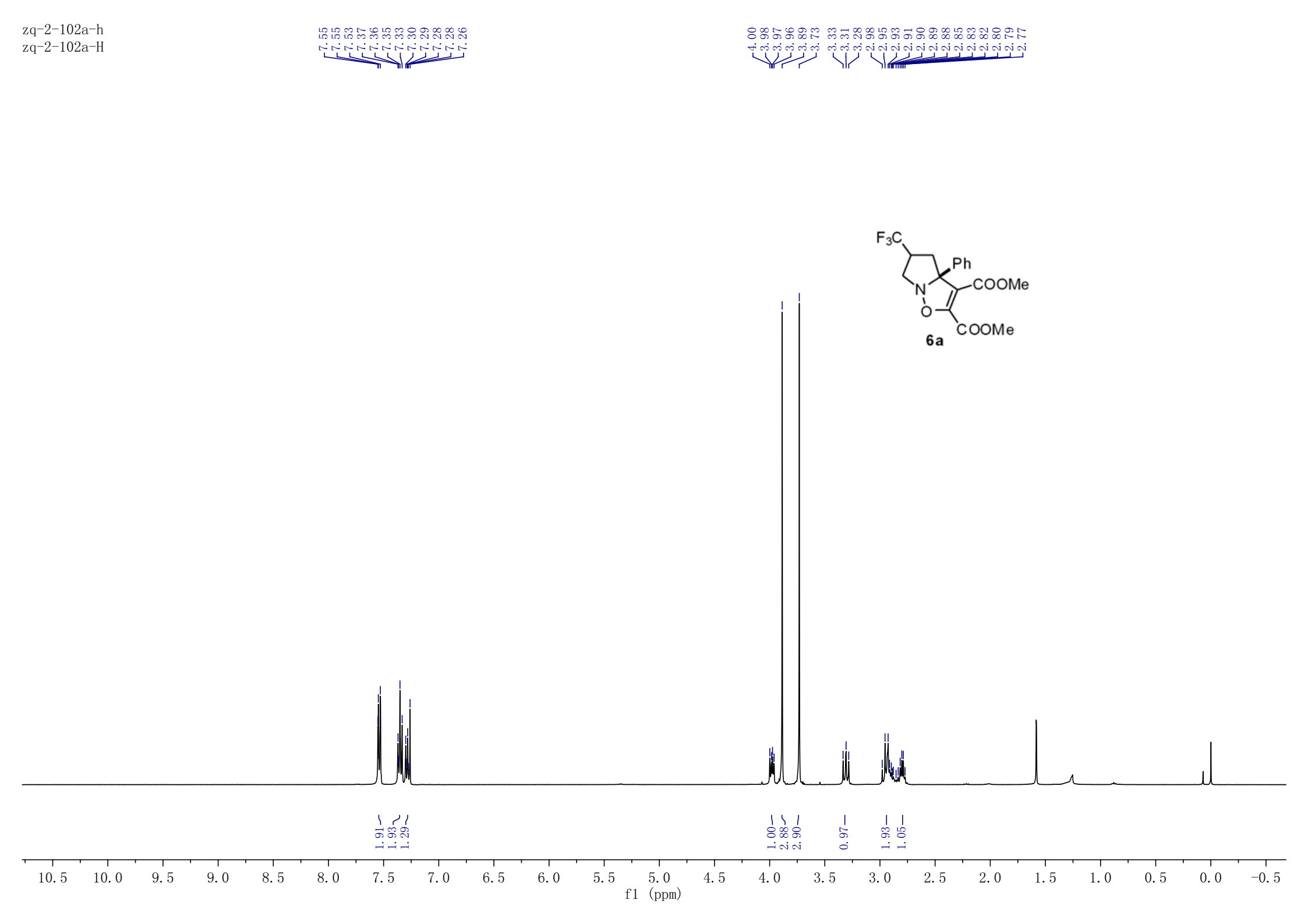


zq-2-105b-c

zq-2-105b-c

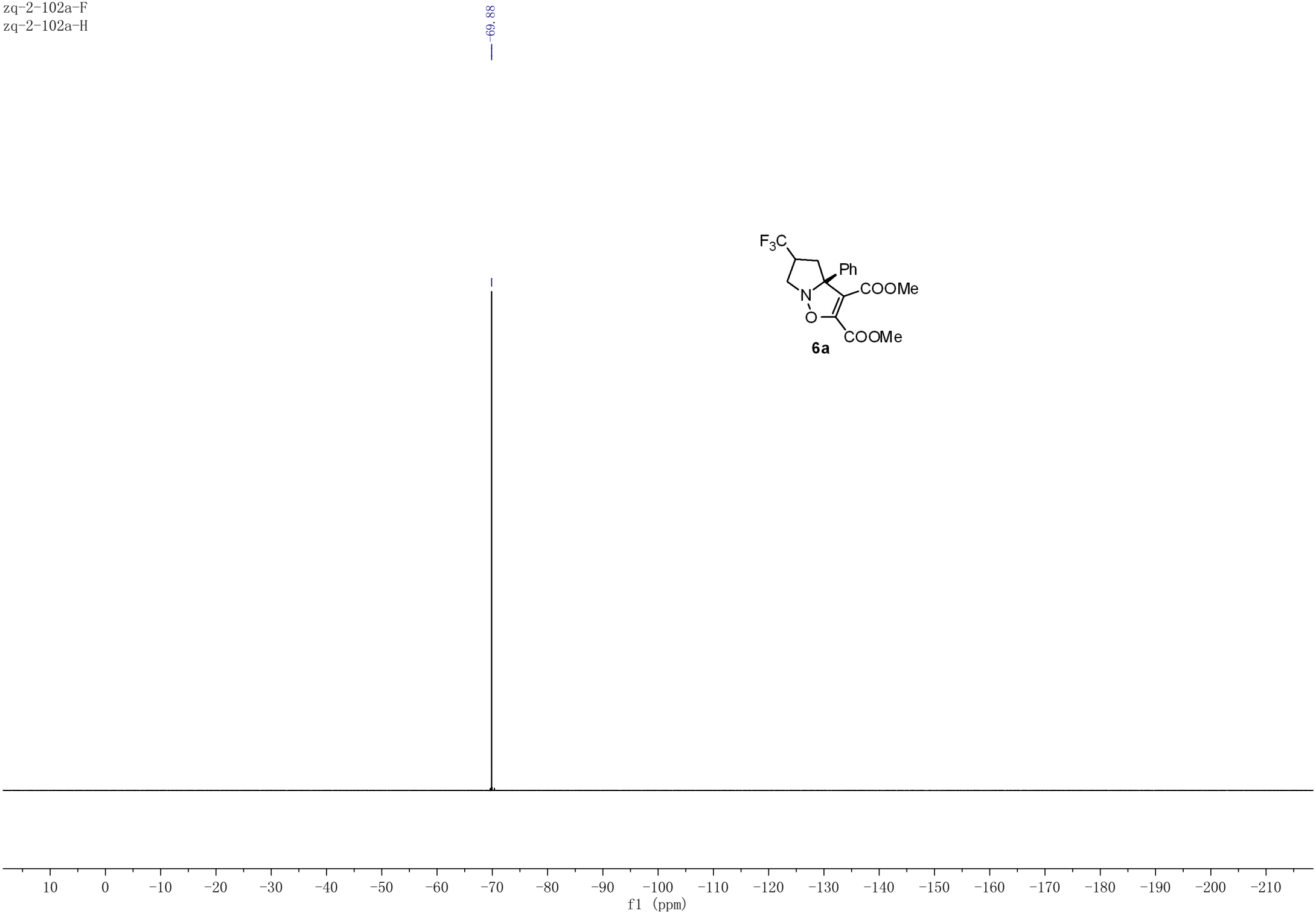


zq-2-102a-h
zq-2-102a-H

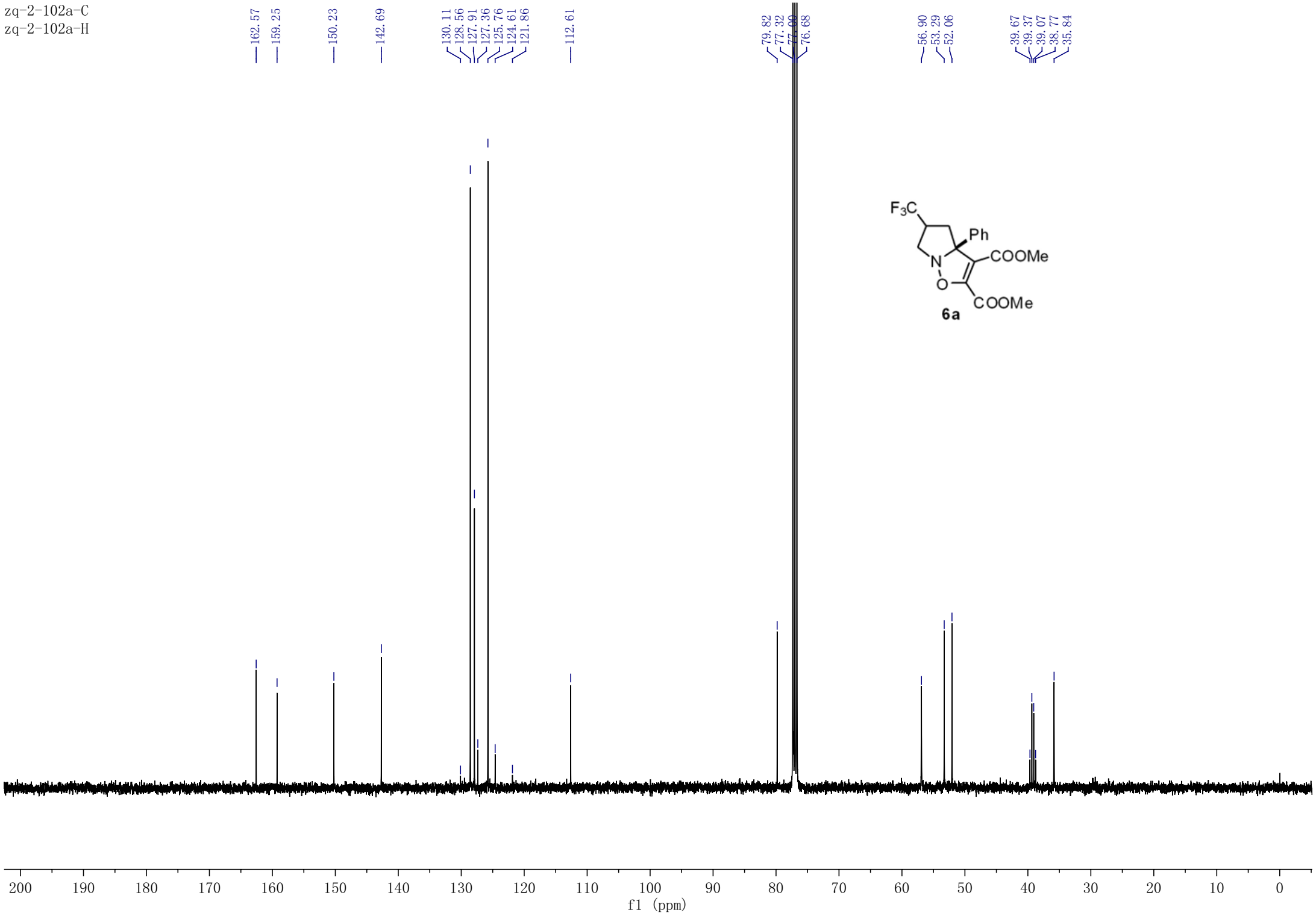


zq-2-102a-F
zq-2-102a-H

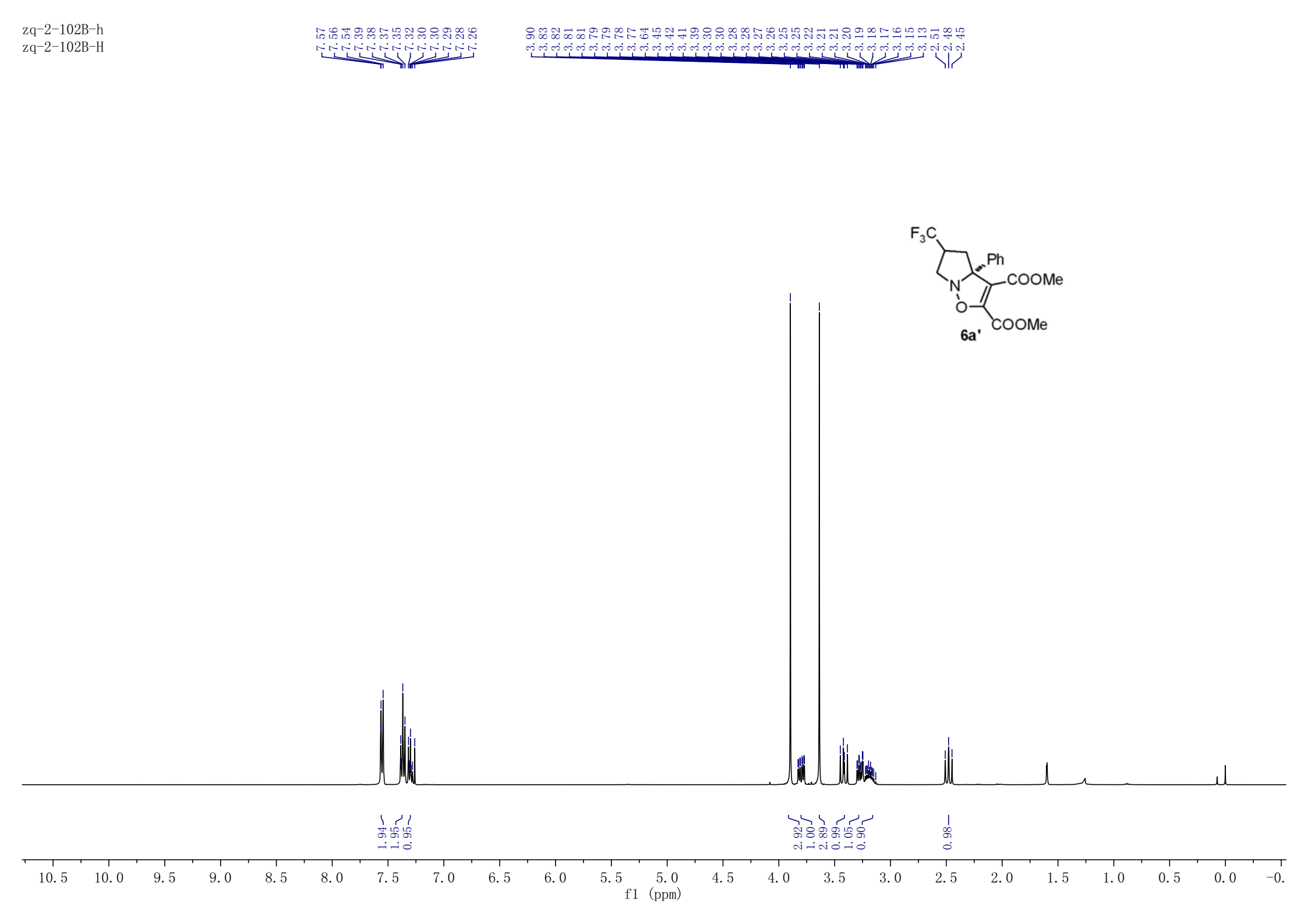
6a



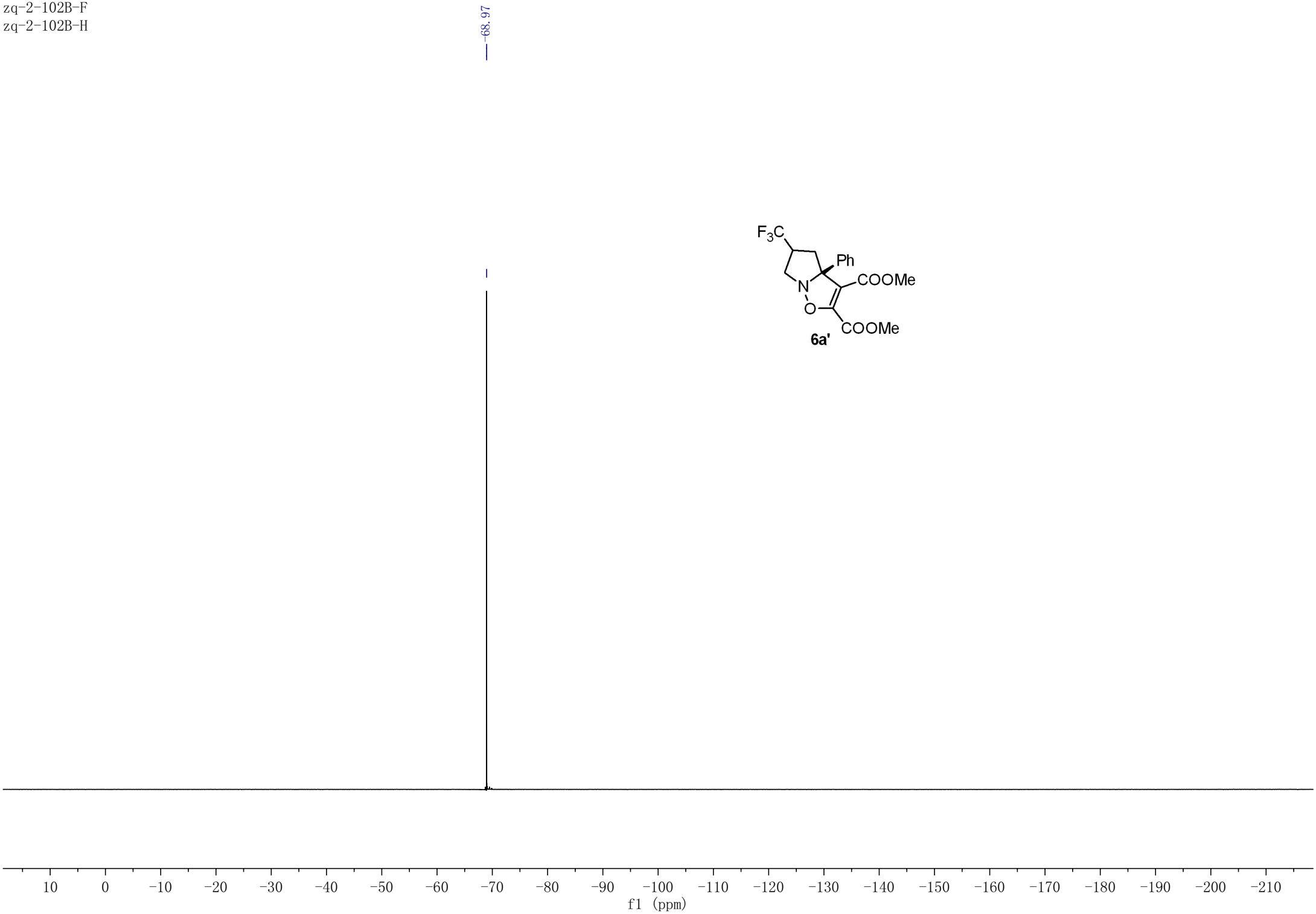
zq-2-102a-C
zq-2-102a-H



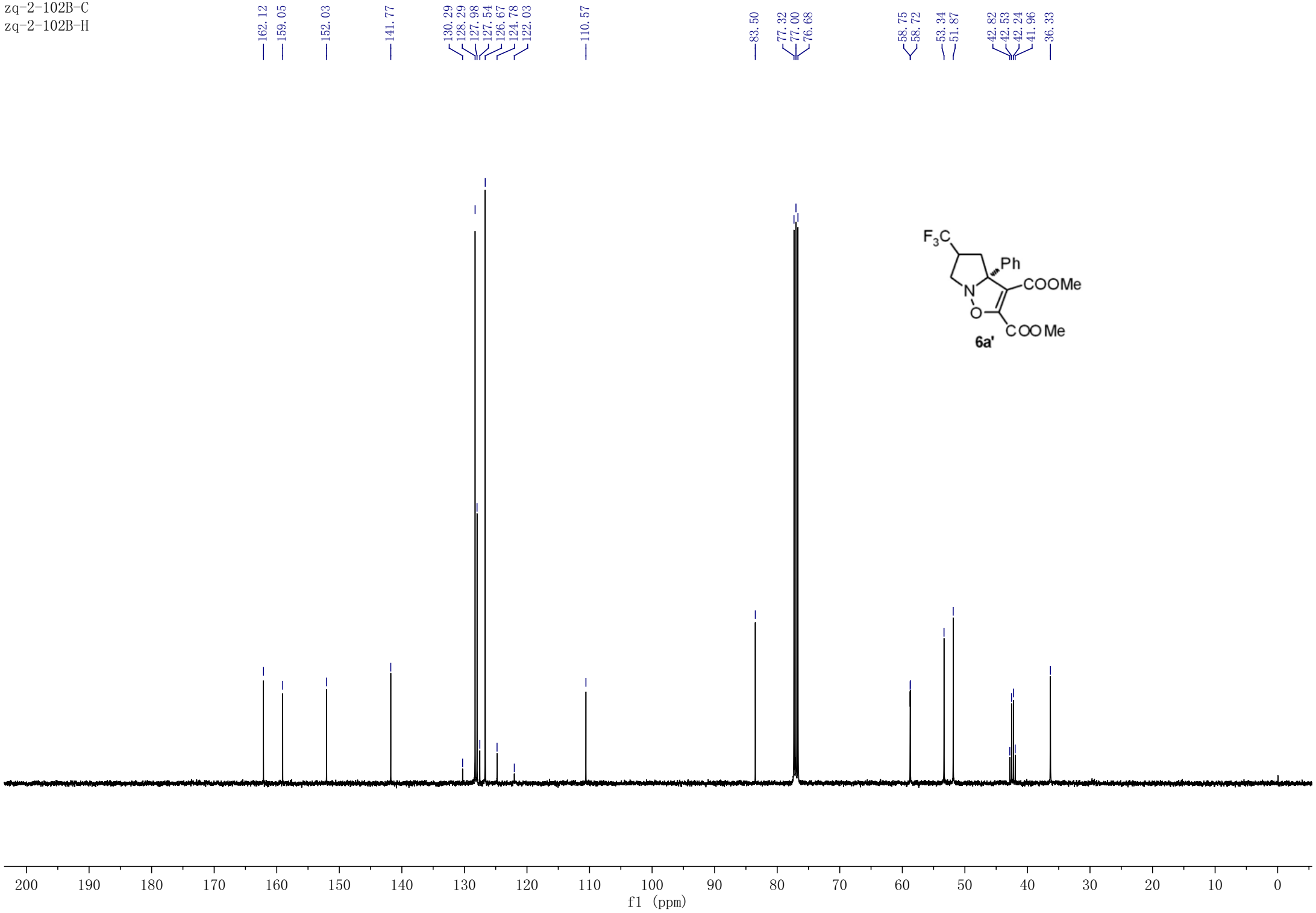
zq-2-102B-h
zq-2-102B-H



zq-2-102B-F
zq-2-102B-H



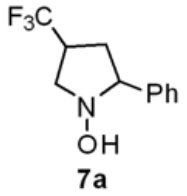
zq-2-102B-C
zq-2-102B-H



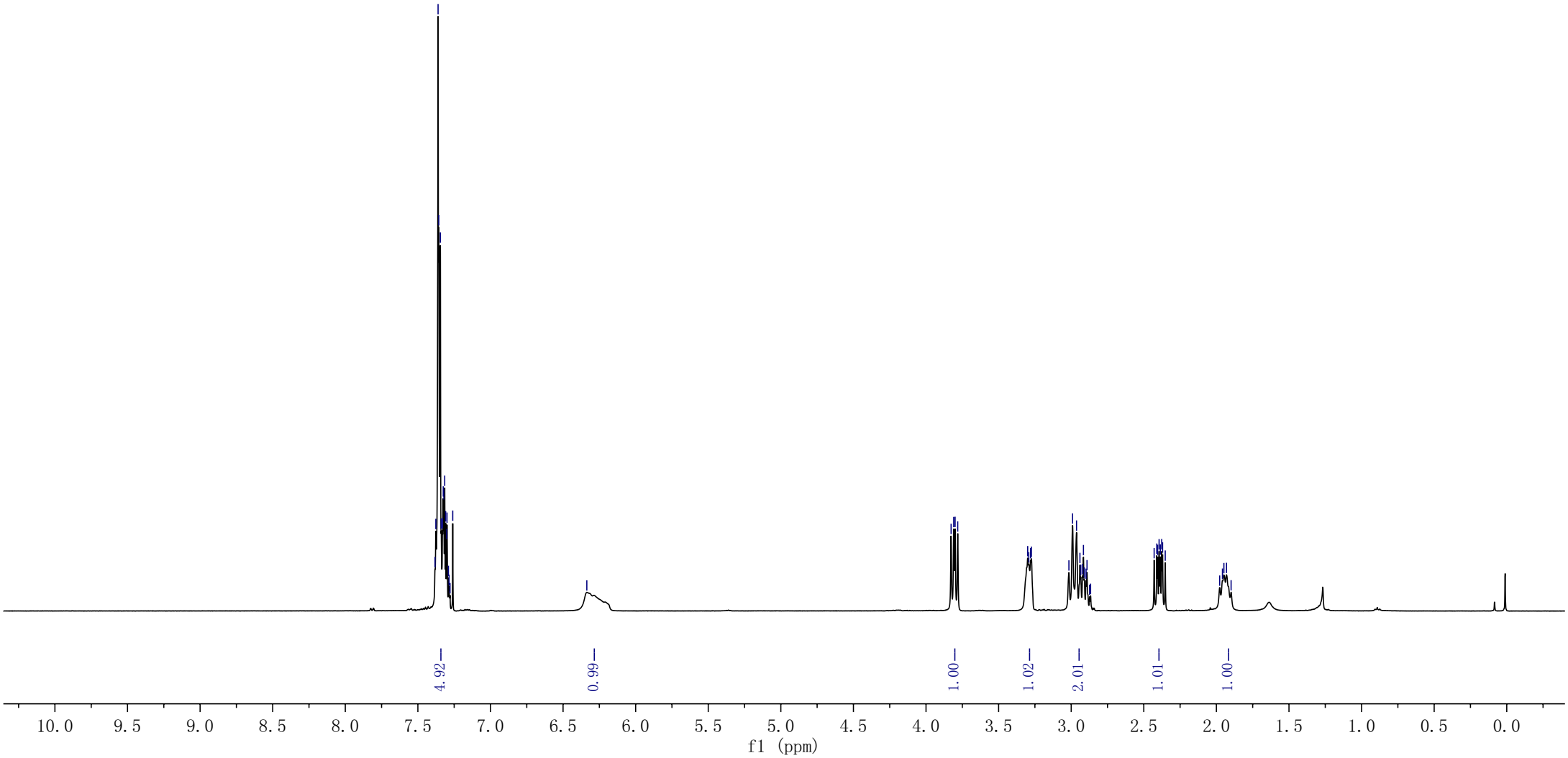
zq-2-106a
zq-2-106a

7.38 7.38 7.36 7.36 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.28 7.26 6.34

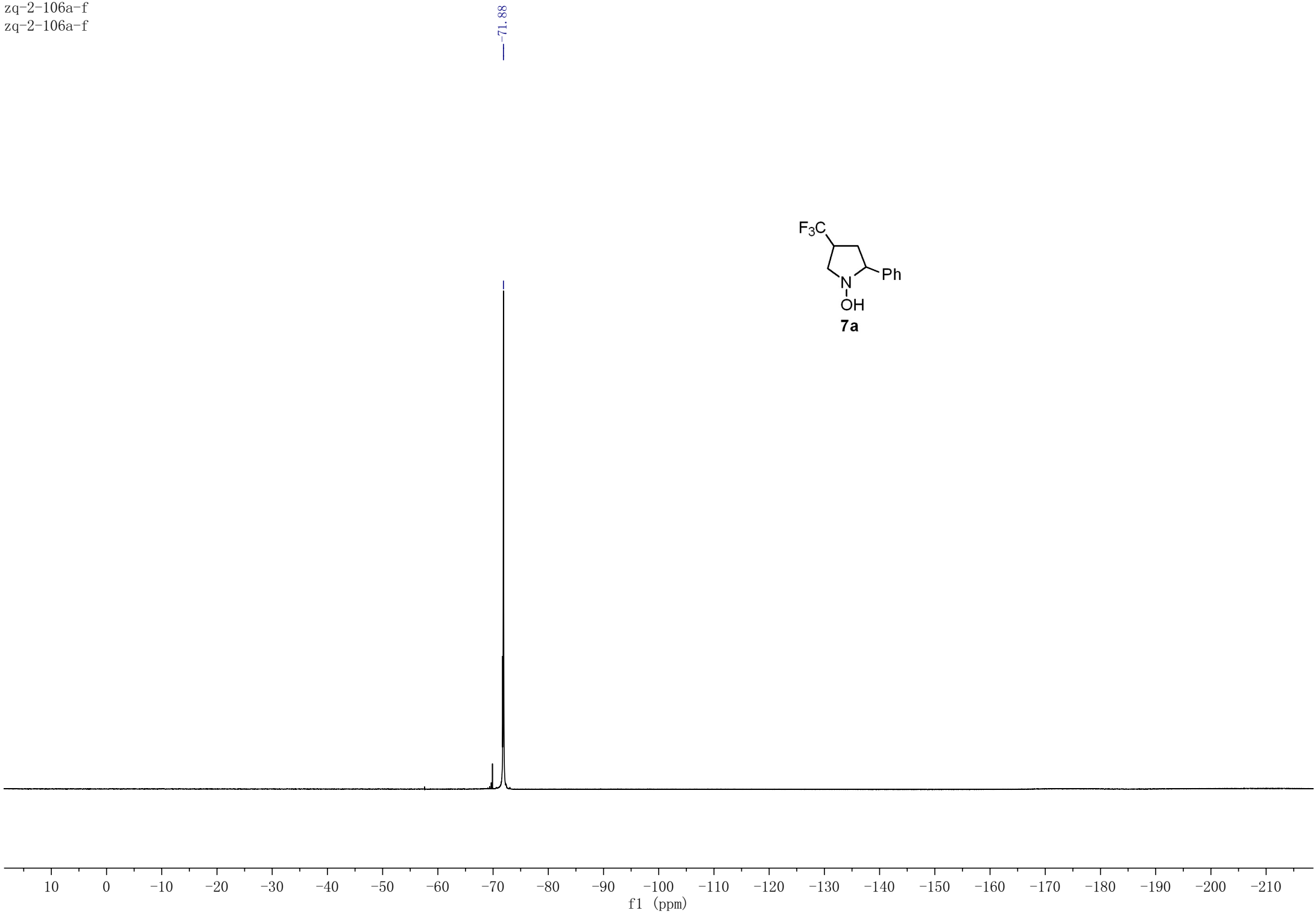
3.83 3.81 3.80 3.78 3.30 3.29 3.28 3.27 2.99 2.96 2.94 2.92 2.41 2.39 2.38 2.37 1.98 1.96 1.95 1.93 1.90



7a

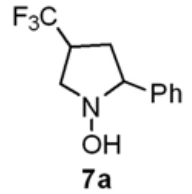


zq-2-106a-f
zq-2-106a-f

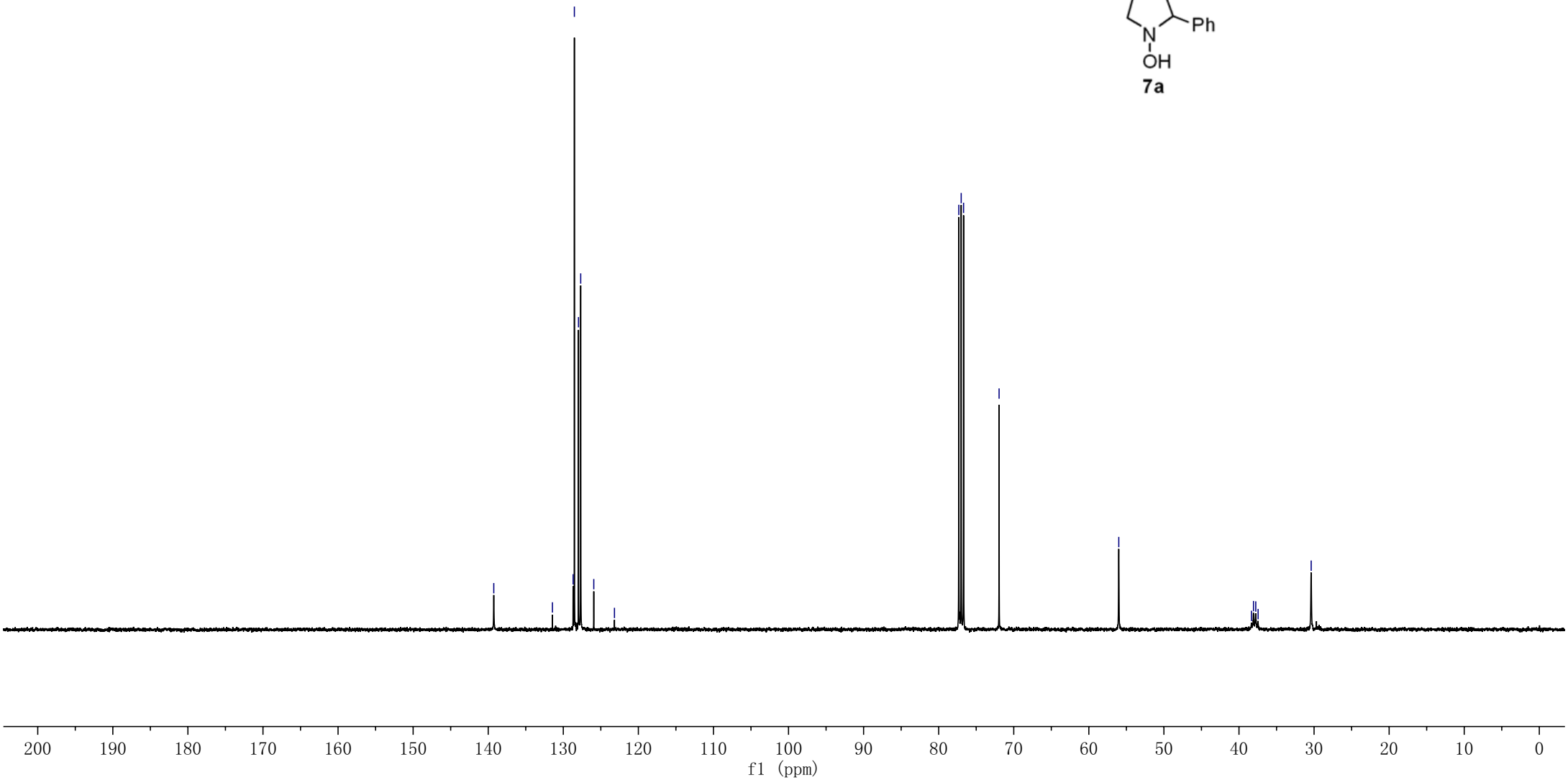


zq-2-106a-c
zq-2-106a-c

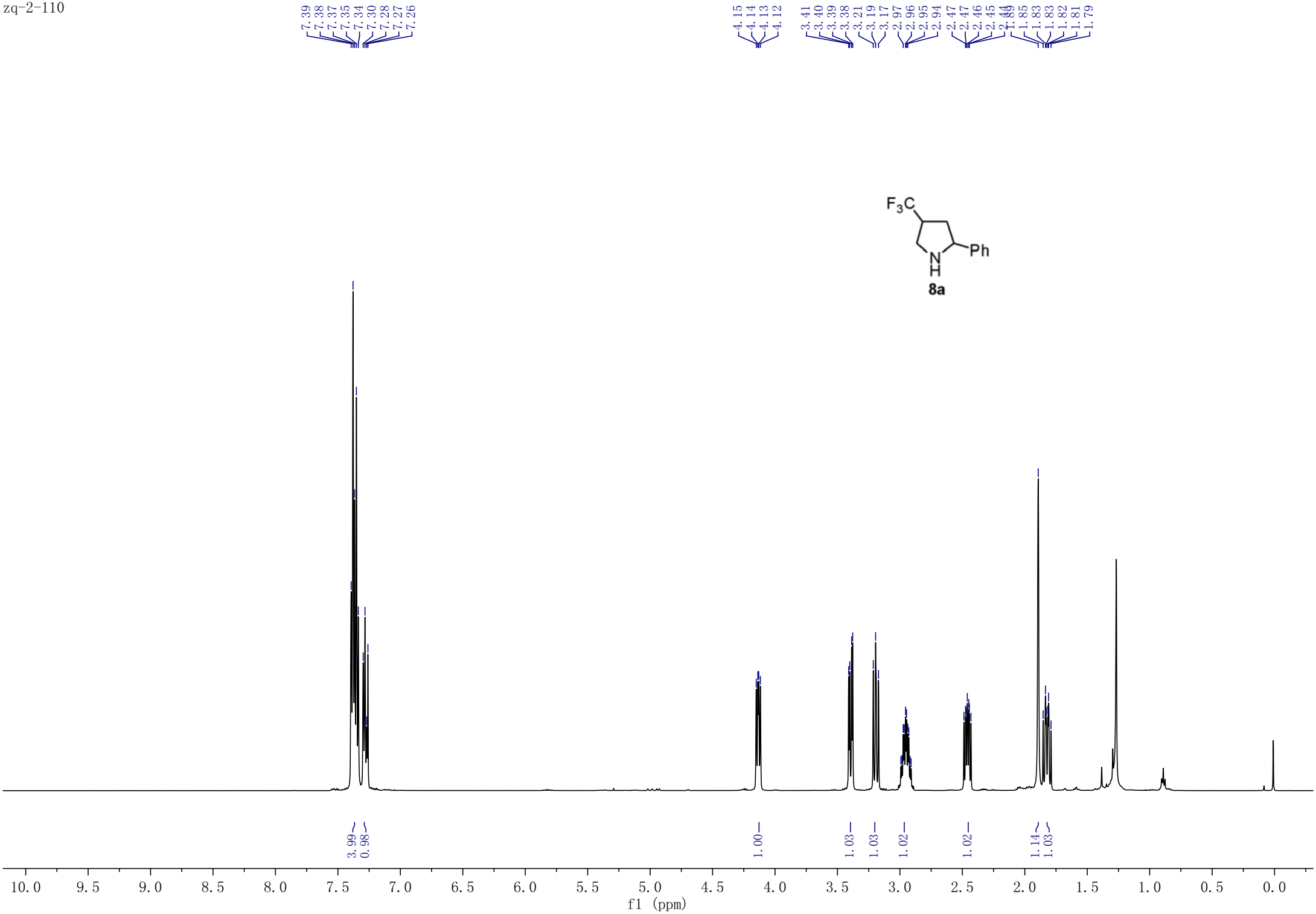
139.26
131.45
128.69
128.52
127.98
127.68
125.94
123.18
77.32
77.00
76.68
71.95
56.01
38.34
38.07
37.77
37.45
30.38



7a

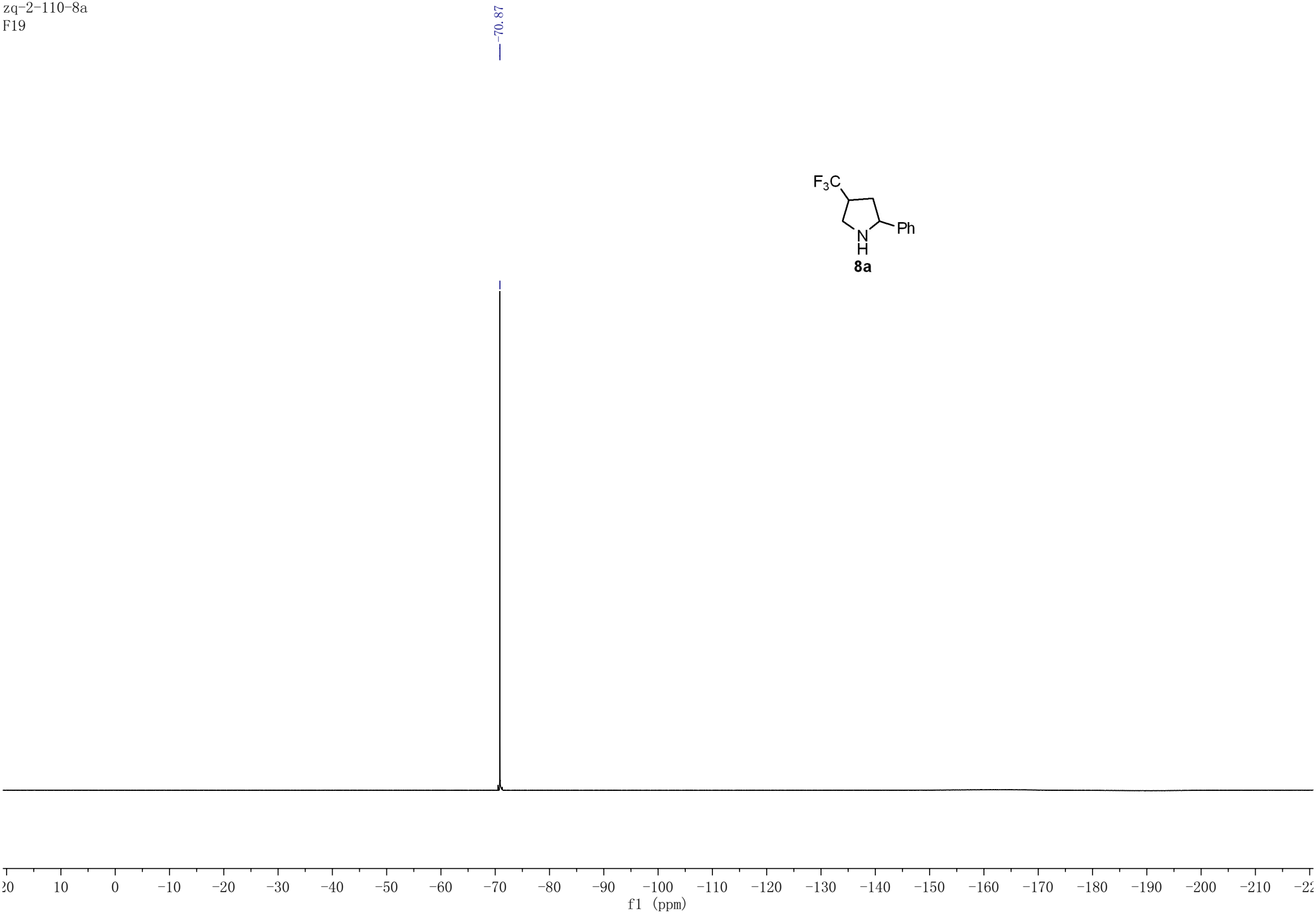


zq-2-110


7.39
7.38
7.37
7.35
7.34
7.30
7.28
7.27
7.26
4.15
4.14
4.13
4.12
3.41
3.40
3.39
3.38
3.21
3.19
3.17
2.97
2.96
2.95
2.94
2.47
2.47
2.46
2.45
2.44
1.89
1.85
1.83
1.83
1.82
1.81
1.79
F3C
Ph
N
H
8a
3.99
0.98
1.00
1.03
1.03
1.02
1.02
1.14
1.03
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)

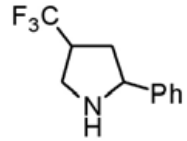
zq-2-110-8a
F19

8a

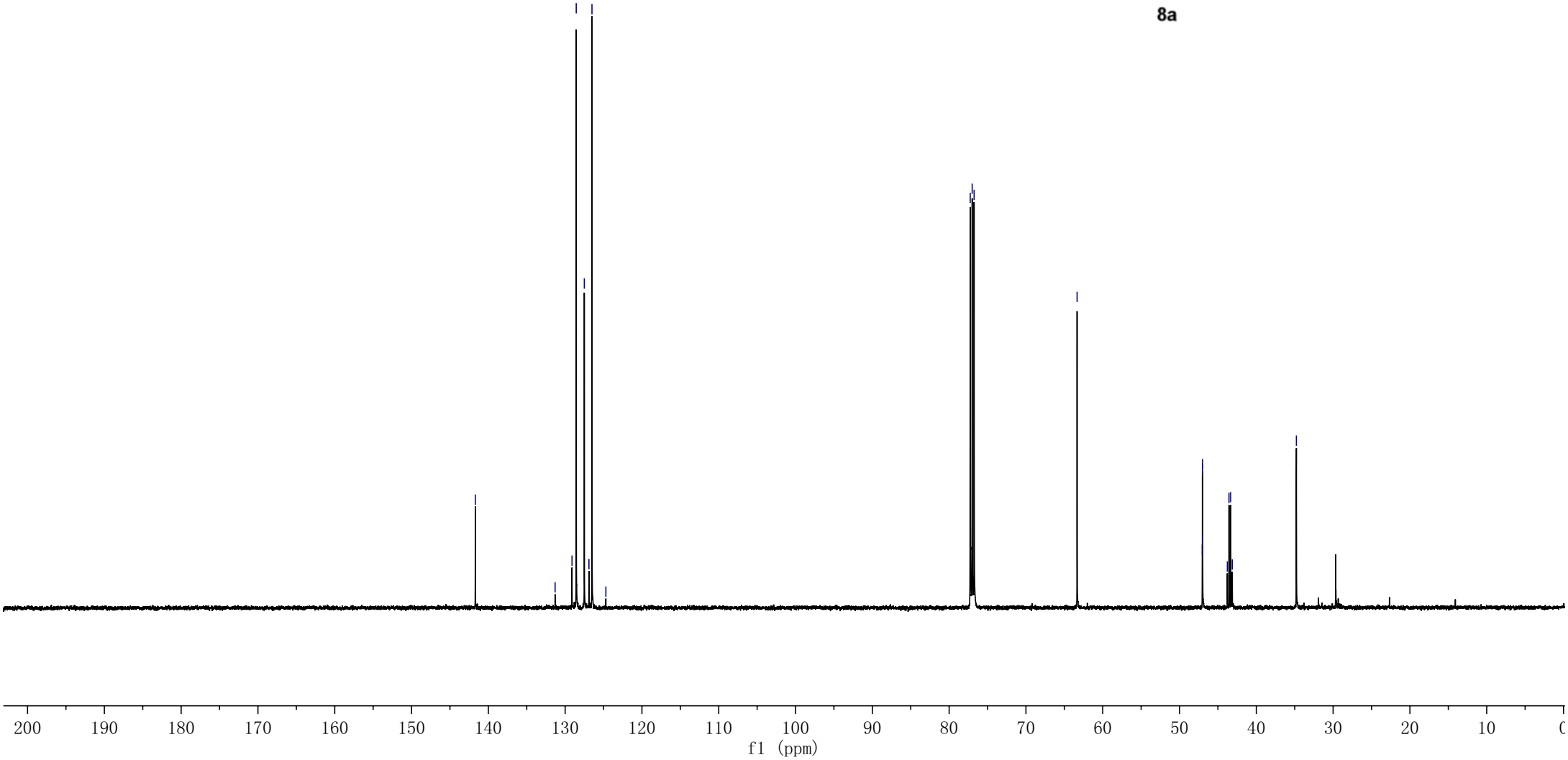


zq-2-110

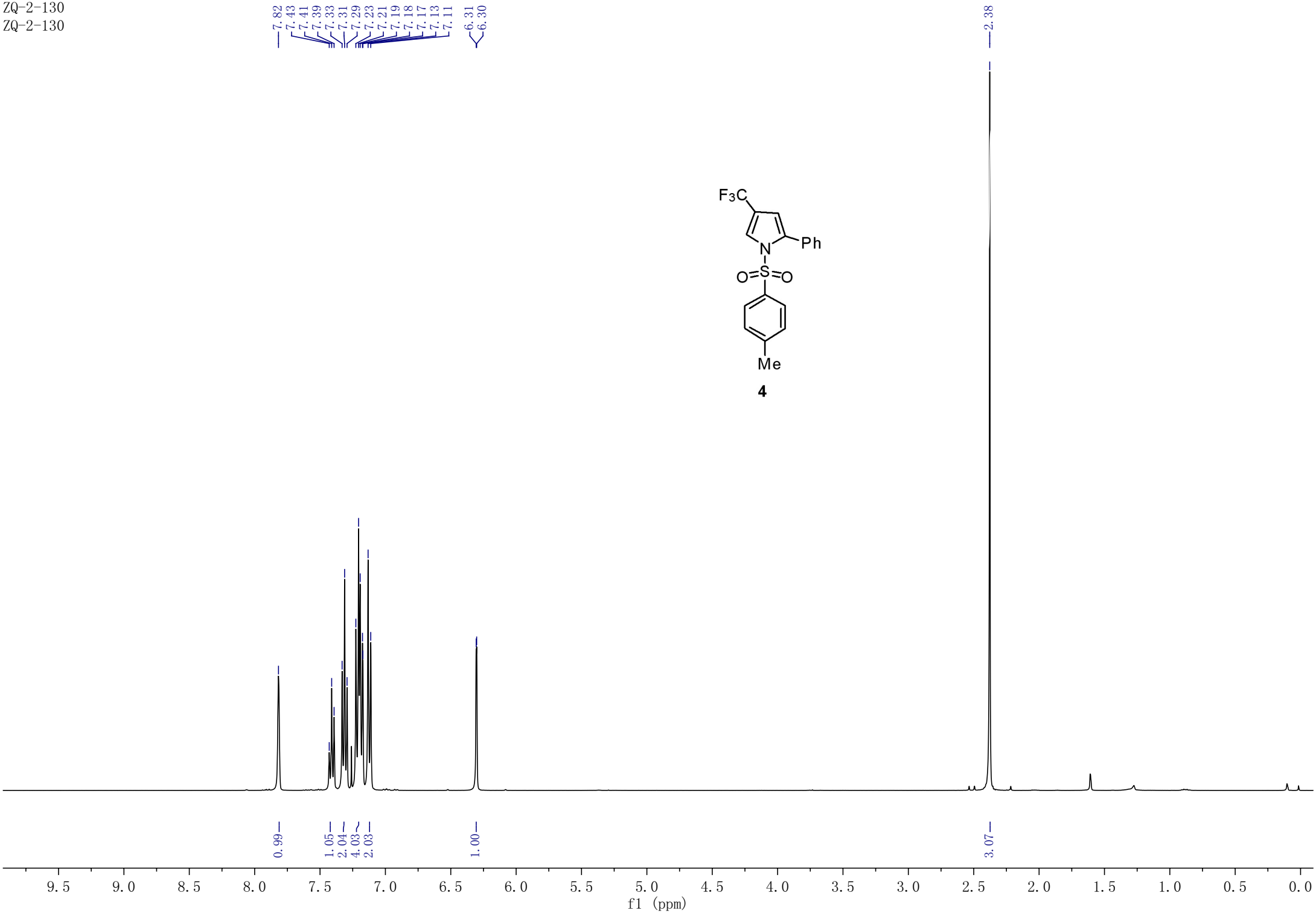
141.69
131.31
129.10
128.56
127.50
126.90
126.51
124.70
77.25
77.00
76.75
63.34
47.04
47.02
47.00
46.98
43.77
43.56
43.34
43.13
34.78



8a

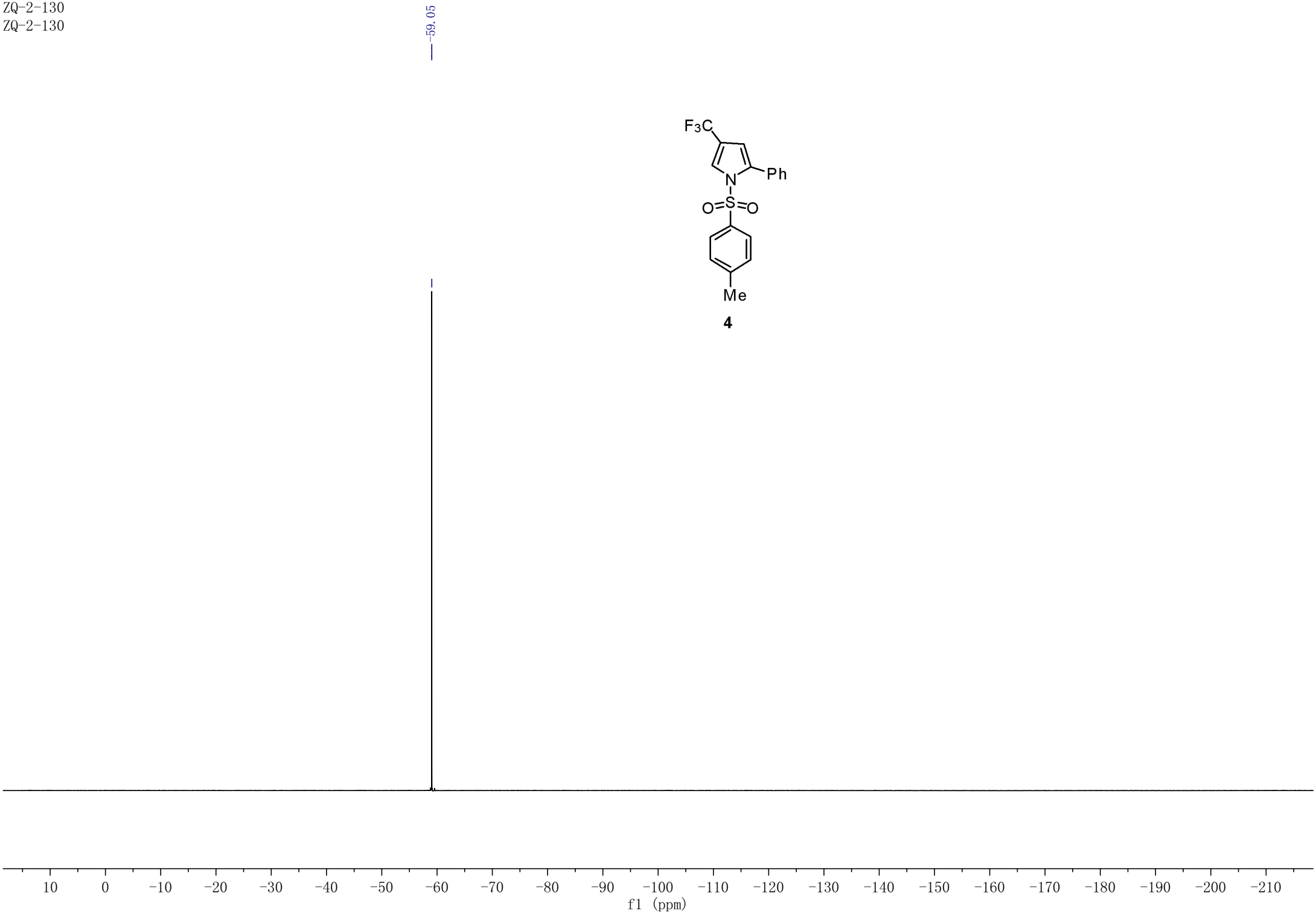


ZQ-2-130
ZQ-2-130



ZQ-2-130
ZQ-2-130

4



ZQ-2-130
ZQ-2-130