Supporting Information

Base-mediated synthesis of ring-fluorinated imidazo[1,2-*a*]pyridines *via* sequential C–F substitutions

Qiuyun Li,*[a] Tianyu Du,[a] Fan Zhang,[a] Xue Feng,[a] Wei Wang,[a] Zhongfei Han,[a] Yannan Zhu,[a] Kelu Yan,*[c] Wen-Juan Hao[b] and Bo Jiang*[b]

[a]Faculty of Chemistry and Chemical Engineering, Yancheng Institute of Technology, Yancheng 224051, P. R. China;

[b]School of Chemistry & Materials Science, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, P. R. China;

[c]Key Laboratory of Life-Organic Analysis of Shandong Province, School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, P. R. China.

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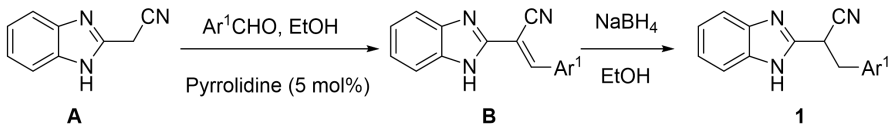
1. General Information

All the solvents were used without further purification. 1C,3N-Dinucleophiles **1**,[1-2] *β*-CF_3-1,3-enynes **2**[3-6] were prepared following literature procedures. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) were recorded on a NMR spectrometer with DMSO-d_6 or $CDCl_3$ as solvent. Chemical shifts of ^{1}H, ^{13}C, and ^{19}F NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.43 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200−300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm and 365 nm). High-resolution mass spectrometry (HRMS) was done on a FTICR-mass spectrometer (0.3 mm thickness). Column chromatography was performed on silica gel (200–300 mesh) using petroleum ether (PE)/ethyl acetate as eluent.

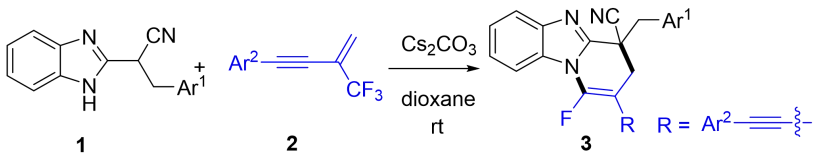
2. Experimental procedures

General Procedure for the Synthesis of 1[1-2]



To a solution of 2-benzimidazoleacetonitrile **A** (0.78 g, 5 mmol) and benzaldehyde (5.25 mmol) in ethanol (10 mL) was added pyrrolidine (17.8 mg, 0.25 mmol) at room temperature, and the mixture was stirred overnight. After completion, the solvent was removed partly at reduced pressure. Then, Methyl tert-Butyl ether (30 mL) was added to the slurry followed by filtering. The filtered solid **B** was used for next reaction without further purification. To a solution of compound **B** in ethanol (10 mL) was added $NaBH_4$ (378 mg, 10 mmol) slowly at 0 ℃. The reaction mixture was allowed to warm up to room temperature and stirred until completion of the reaction (monitored by TLC). After completion, the reduction of the double bond was quenched with saturated aqueous NH_4Cl (10 mL) and ethyl acetate (30 mL) was added. The organic phase was separated and aqueous phase was extracted with ethyl acetate (3×20 mL). Combined the organic layer, which was washed by brine (3×30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The obtained solid was used as 1C,3Nbisnucleophile **1** after recrystallization.

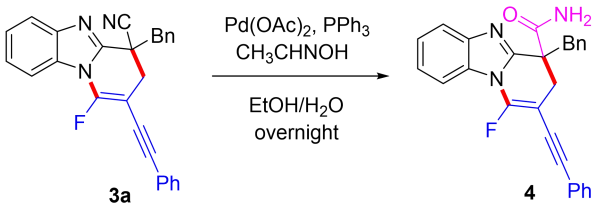
General Procedure for the Synthesis of 3



1 2 3

A mixture of **1** (0.25 mmol, 1.0 equiv), **2** (0.3 mmol, 1.2 equiv), Cs_2CO_3 (0.5 mmol, 2.0 equiv) was weighed in a sealed Schlenk tube equipped with a stir bar. 1,4-dioxane (2.5 mL) was added and the mixture was stirred at rt for 18 h. The solvent was evaporated under reduced pressure and the residue was purified by a silica gel column using PE/ ethyl acetate (10/1) as eluent to give pure product **3**.

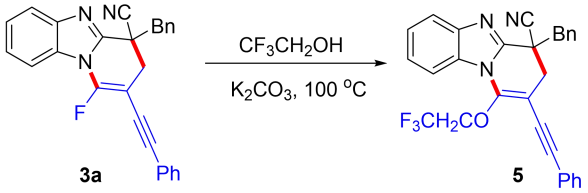
General Procedure for the Synthesis of 4 [1,7]



3a 4

The mixture of **3a** (0.2 mmol, 80.6 mg), acetaldehyde oxime (1.6 mmol, 94.4 mg), diacetoxypalladium (0.02 mmol, 4.5 mg), and triphenylphosphine (0.04 mmol, 10.5 mg) were dissolved in EtOH/H_2O (1.6 mL/0.4 mL) and stirred at 75 °C overnight. After completion, the mixture was cooled down to room temperature and then directly subjected to silica gel column chromatography (petroleum ether / ethyl acetate as eluent) to afford **4**.

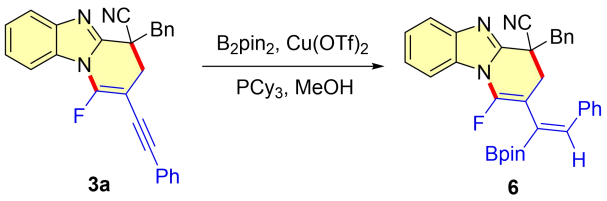
General Procedure for the Synthesis of 5 [8]



3a 5

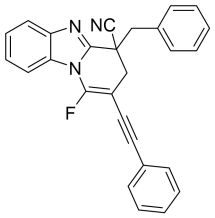
A mixture of **3a** (0.2 mmol, 80.6 mg), K_2CO_3 (0.4 mmol, 55.2 mg, 2.0 equiv) were weighted in a Schlenk tube. Dry TFE (2.0 mL) was added and the resulting mixture was stirred at 100 °C for overnight. The reaction was cooled to room temperature and purification was performed by flash column chromatography on silica gel with petroleum ether/EtOAc to give the final product **5**.

General Procedure for the Synthesis of 6 [9]

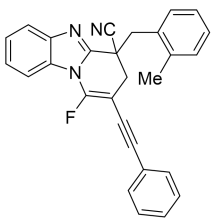


To a 25 mL Schlenk tube, was added B_2pin_2 (0.6 mmol, 152.4 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), PCy_3 (0.02 mmol, 5.6 mg) and NaO^{t}Bu (0.06 mmol, 5.8 mg). Subsequently, the MeOH (0.6 mmol, 24.0 μL), **3a** (0.2 mmol, 80.6 mg), and THF (1.0 mL) were added under nitrogen atmosphere. The Schlenk tube was sealed and stirred at 20 °C for 12 h. Then, the reaction mixture was concentrated to dryness.The crude product was purified by silica gel chromatography to afford the product **6**.

3. Experimental Data

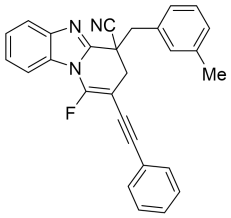


4-Benzyl-1-fluoro-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3a): light yellow solid (79.6 mg, 79% yield). M.p. 123–124 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, J = 6.5 Hz, 1H), 7.77 (d, J = 5.8 Hz, 1H), 7.48 (t, J = 23.4 Hz, 12H), 3.76 (d, J = 13.6 Hz, 1H), 3.38 (d, J = 13.7 Hz, 1H), 3.06 (dd, J = 15.7, 4.1 Hz, 1H), 2.93 (d, J = 15.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9 (d, J = 273.7 Hz), 146.8, 142.3, 132.9, 131.5, 130.8 (d, J = 3.0 Hz), 130.6, 128.9, 128.5, 128.4, 125.8, 124.7, 122.4, 121.1, 118.0, 112.5 (d, J = 8.1 Hz), 97.0 (d, J = 6.1 Hz), 80.3 (d, J = 2.0 Hz), 80.1 (d, J = 12.1 Hz), 41.2, 39.4, 34.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.44. **HRMS (ESI)** calcd for $C_{27}H_{19}FN_3$ $[M+H]^+$ 404.1563, found 404.1553.

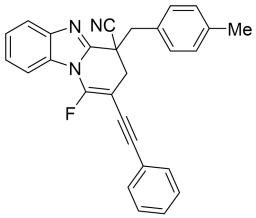


1-Fluoro-4-(2-methylbenzyl)-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3b): light yellow solid (67.8 mg, 65% yield). M.p. 145–146 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 5.8 Hz, 1H), 7.62–7.34 (m, 8H), 7.34–7.22 (m, 3H), 3.92 (d, J = 14.2 Hz, 1H), 3.40 (d, J = 14.2 Hz, 1H), 3.15 (dd, J

= 16.0, 5.4 Hz, 1H), 3.03 (dd, *J* = 16.0, 5.3 Hz, 1H), 2.50 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.0 (d, *J* = 272.7 Hz), 147.0, 142.3, 137.7, 131.5, 131.4, 131.3, 131.2, 130.8 (d, *J* = 4.0 Hz), 128.9, 128.5, 128.3, 126.3, 125.8, 124.7, 122.4, 121.1, 118.4, 112.5 (d, *J* = 7.1 Hz), 97.0 (d, *J* = 6.1 Hz), 80.4 (d, *J* = 2.0 Hz), 80.2 (d, *J* = 12.1 Hz), 39.4, 37.6, 34.5, 20.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.49. **HRMS (ESI)** calcd for $C_{28}H_{21}FN_3^+$ $[M+H]^+$ 418.1720, found 418.1720.

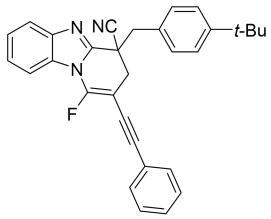


1-Fluoro-4-(3-methylbenzyl)-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3c): light yellow solid (74.0 mg, 71% yield). M.p. 91–92 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 5.9 Hz, 1H), 7.77 (d, *J* = 3.2 Hz, 1H), 7.60 – 7.39 (m, 7H), 7.37 – 7.20 (m, 4H), 3.69 (d, *J* = 13.8 Hz, 1H), 3.32 (d, *J* = 13.7 Hz, 1H), 3.06 (dd, *J* = 16.0, 4.6 Hz, 1H), 2.91 (dd, *J* = 15.9, 4.6 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9 (d, *J* = 273.7 Hz), 147.0, 142.4, 138.6 132.8, 131.5, 131.4, 130.8 (d, *J* = 4.0 Hz), 129.1, 128.9, 128.8, 128.5, 127.6, 125.7, 124.6, 122.4, 121.1, 118.1, 112.5 (d, *J* = 8.1 Hz), 96.9 (d, *J* = 6.1 Hz), 80.4 (d, *J* = 2.1 Hz), 80.1 (d, *J* = 12.1 Hz), 41.2, 39.4, 33.9, 21.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.48. **HRMS (ESI)** calcd for $C_{28}H_{21}FN_3^+$ $[M+H]^+$ 418.1720, found 418.1729.

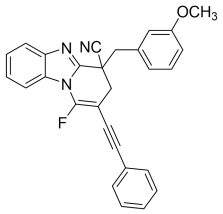


1-Fluoro-4-(4-methylbenzyl)-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3d): light yellow solid (79.2 mg, 76% yield). M.p. 82–83 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 7.1 Hz, 1H), 7.77 (d, *J* = 5.3 Hz, 1H), 7.56 (s, 2H), 7.52 – 7.39 (m, 5H), 7.31 (dd, *J* = 37.0, 7.4 Hz, 4H), 3.71 (d, *J* = 13.8 Hz, 1H), 3.32 (d, *J* = 13.8 Hz, 1H), 3.04 (dd, *J* = 16.0, 5.1 Hz, 1H), 2.92 (dd, *J* = 16.0, 5.1 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.0 (d, *J* = 272.7 Hz), 147.0, 142.4, 138.1, 131.5, 130.8 (d, *J* = 3.1 Hz), 130.5, 129.9, 129.6, 128.9, 128.5, 125.7, 124.6, 122.5, 121.1, 118.1, 112.5 (d, *J* = 7.1 Hz), 96.9 (d, *J* = 6.1 Hz), 80.4 (d, *J* = 2.0 Hz), 80.1 (d, *J* = 12.0 Hz), 40.8, 39.5, 33.9, 21.2.

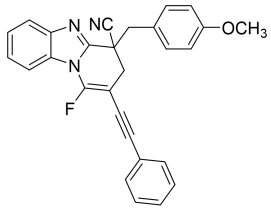
^{19}F NMR (376 MHz, $CDCl_3$) δ –106.45. **HRMS (ESI)** calcd for $C_{28}H_{21}FN_3^+$ $[M+H]^+$ 418.1720, found 418.1723.



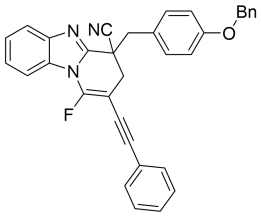
4-(4-(Tert-butyl)benzyl)-1-fluoro-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3e): light yellow solid (89.5 mg, 78% yield). M.p. 161–162 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (d, J = 7.0 Hz, 1H), 7.71 (d, J = 3.8 Hz, 1H), 7.39 (dt, J = 21.3, 20.6 Hz, 11H), 3.66 (d, J = 13.8 Hz, 1H), 3.31 (d, J = 13.8 Hz, 1H), 3.01 (dd, J = 16.1, 4.9 Hz, 1H), 2.89 (dd, J = 15.9, 5.0 Hz, 1H), 1.34 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.0 (d, J = 273.7 Hz), 151.3, 147.0, 142.4, 131.5, 130.8, 130.3, 129.8, 128.9, 128.5, 125.8 (d, J = 12.9 Hz), 124.6, 122.5, 121.1, 118.2, 112.5 (d, J = 7.8 Hz), 96.9 (d, J = 6.1 Hz), 80.4 (d, J = 2.0 Hz), 80.1 (d, J = 12.2 Hz), 40.8, 39.4, 34.7, 33.9, 31.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.50. **HRMS (ESI)** calcd for $C_{31}H_{27}FN_3^+$ $[M+H]^+$ 460.2189, found 460.2176.



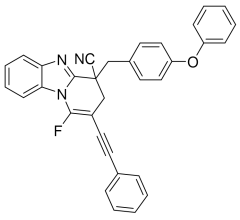
1-Fluoro-4-(3-methoxybenzyl)-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3f): light yellow solid (67.1 mg, 62% yield). M.p. 144–145 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, J = 5.9 Hz, 1H), 7.76 (s, 1H), 7.41 (ddd, J = 24.4, 23.7, 18.9 Hz, 8H), 7.12 – 6.87 (m, 3H), 3.82 (s, 3H), 3.71 (d, J = 13.8 Hz, 1H), 3.35 (d, J = 13.7 Hz, 1H), 3.07 (d, J = 16.1 Hz, 1H), 2.94 (d, J = 15.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.9, 150.0 (d, J = 273.7 Hz), 146.9, 142.3, 134.3, 131.5, 130.8 (d, J = 3.0 Hz), 129.9, 128.9, 128.5, 125.8, 124.7, 122.87, 122.47, 121.1, 118.1, 115.8, 114.2, 112.5 (d, J = 8.1 Hz), 97.0 (d, J = 6.1 Hz), 80.4, 80.1 (d, J = 12.1 Hz), 55.2, 41.3, 39.4, 33.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.45. **HRMS (ESI)** calcd for $C_{28}H_{21}FN_3O^+$ $[M+H]^+$ 434.1669, found 434.1682.



1-Fluoro-4-(4-methoxybenzyl)-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3g): light yellow solid (79.0 mg, 73% yield). M.p. 81–82 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, J = 6.9 Hz, 1H), 7.76 (d, J = 5.1 Hz, 1H), 7.61–7.33 (m, 9H), 6.97 (d, J = 7.6 Hz, 2H), 3.87 (s, 3H), 3.68 (d, J = 13.9 Hz, 1H), 3.32 (d, J = 13.9 Hz, 1H), 3.05 (dd, J = 16.0, 4.7 Hz, 1H), 2.91 (dd, J = 15.8, 4.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.7, 149.9 (d, J = 272.7 Hz), 147.0, 142.3, 131.7, 131.5, 130.8 (d, J = 3.0 Hz), 128.9, 128.5, 125.7, 124.9, 124.6, 122.5, 121.1, 118.2, 114.3, 112.5 (d, J = 7.1 Hz), 97.0 (d, J = 6.1 Hz), 80.4, 80.1 (d, J = 12.1 Hz), 55.3, 40.5, 39.6, 33.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.46. **HRMS (ESI)** calcd for $C_{28}H_{21}FN_3O^+$ $[M+H]^+$ 434.1669, found 434.1680.

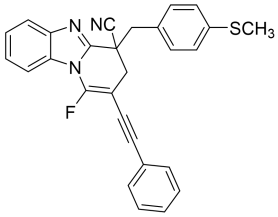


4-(4-(Benzyloxy)benzyl)-1-fluoro-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3h): light yellow solid (111.9 mg, 88% yield), M.p. 140–141 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, J = 7.4 Hz, 1H), 7.77 (d, J = 5.3 Hz, 1H), 7.63 – 7.33 (m, 14H), 7.06 (d, J = 7.8 Hz, 2H), 5.13 (s, 2H), 3.68 (d, J = 13.9 Hz, 1H), 3.32 (d, J = 14.0 Hz, 1H), 3.06 (dd, J = 16.0, 5.3 Hz, 1H), 2.92 (dd, J = 16.0, 5.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.9, 149.9 (d, J = 272.7 Hz), 148.6, 146.9, 142.4, 136.8, 131.8, 131.5, 130.8 (d, J = 4.0 Hz), 128.9, 128.6 (d, J = 14.0 Hz), 128.1, 127.6, 125.7, 125.2, 124.7, 122.5, 121.1, 118.2, 115.2, 112.5 (d, J = 8.1 Hz), 97.0 (d, J = 6.1 Hz), 80.4 (d, J = 2.0 Hz), 80.1 (d, J = 12.1 Hz), 70.1, 40.5, 39.6, 33.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.44. **HRMS (ESI)** calcd for $C_{34}H_{24}FN_3O^+$ $[M+H]^+$ 510.1982, found 510.1988.

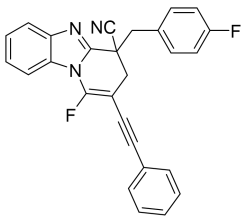


1-Fluoro-4-(4-phenoxybenzyl)-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3i): light yellow solid (92.8 mg, 75% yield), M.p. 159–160 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (d, J = 6.7 Hz, 1H), 7.76 (d, J = 5.8 Hz, 1H), 7.54 (s, 2H), 7.52 – 7.30 (m, 8H), 7.12 (ddd, J = 41.3, 19.5, 7.9 Hz, 6H), 3.70 (d, J = 13.8 Hz, 1H), 3.37 (d, J = 13.8 Hz, 1H), 3.10 (dd, J = 15.9, 5.1 Hz, 1H), 2.95 (dd, J = 16.0, 4.9 Hz, 1H). **^{13}C NMR**

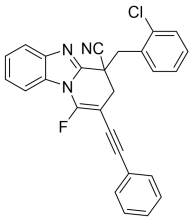
(101 MHz, $CDCl_3$) δ 157.8, 156.68, 149.9 (d, J = 272.7 Hz), 146.6, 142.3, 134.8, 131.6, 130.8 (d, J = 3.0 Hz), 130.2, 129.9, 128.9, 128.5, 125.8, 125.2, 124.7, 123.6, 122.4, 121.1, 120.7, 119.2, 118.4, 118.0, 112.5 (d, J = 8.1 Hz), 97.1 (d, J = 6.1 Hz), 80.2 (d, J = 2.0 Hz), 80.1 (d, J = 12.1 Hz),, 41.1, 39.3, 34.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.42. **HRMS (ESI)** calcd for $C_{33}H_{22}FN_3O^+$ $[M+H]^+$ 496.1825, found 496.1812.



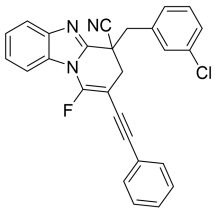
1-Fluoro-4-(4-(methylthio)benzyl)-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3j): light yellow solid (83.1 mg, 74% yield), M.p. 90–91 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, J = 6.3 Hz, 1H), 7.80 – 7.72 (m, 1H), 7.55 (d, J = 2.7 Hz, 2H), 7.51 – 7.40 (m, 5H), 7.37 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 3.69 (d, J = 13.9 Hz, 1H), 3.31 (d, J = 13.9 Hz, 1H), 3.03 (dd, J = 16.0, 4.8 Hz, 1H), 2.89 (dd, J = 16.0, 4.8 Hz, 1H), 2.54 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9 (d, J = 273.7 Hz), 146.8, 142.3, 139.0, 131.5, 131.0, 130.8 (d, J = 4.0 Hz), 129.4, 129.0, 128.6, 126.6, 125.8, 124.7, 122.4, 121.1, 118.0, 112.5 (d, J = 8.1 Hz), 97.0 (d, J = 6.1 Hz), 80.4 (d, J = 2.0 Hz), 80.0 (d, J = 12.1 Hz), 40.6, 39.4, 33.9, 31.7, 22.7, 15.6, 14.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.34. **HRMS (ESI)** calcd for $C_{28}H_{20}FN_3S^+$ $[M+H]^+$ 450.1440, found 450.1428.



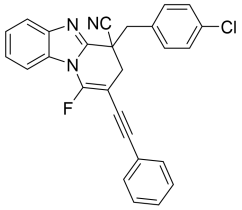
1-Fluoro-4-(4-fluorobenzyl)-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3k): light yellow solid (84.2 mg, 80% yield), M.p. 89–90 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, J = 6.6 Hz, 1H), 7.77 (d, J = 3.9 Hz, 1H), 7.66 – 7.36 (m, 9H), 7.13 (t, J = 8.0 Hz, 2H), 3.71 (d, J = 13.9 Hz, 1H), 3.36 (d, J = 14.0 Hz, 1H), 3.07 (dd, J = 16.1, 4.6 Hz, 1H), 2.90 (dd, J = 15.9, 4.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.8 (d, J = 248.5 Hz), 149.9 (d, J = 272.7 Hz), 132.2 (d, J = 8.1 Hz), 131.5, 130.8 (d, J = 3.0 Hz), 129.0, 128.7 (d, J = 3.0 Hz), 128.6, 125.8, 124.7, 122.3, 121.1, 117.9, 116.0, 115.8, 112.5 (d, J = 8.1 Hz), 97.1 (d, J = 6.1 Hz), 80.2 (d, J = 2.0 Hz), 80.0 (d, J = 12.1 Hz), 40.4, 39.5, 34.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.29, –113.53. **HRMS(ESI)** calcd for $C_{27}H_{18}F_2N_3^+$ $[M+H]^+$ 422.1469, found 422.1467.



4-(2-Chlorobenzyl)-1-fluoro-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3l): light yellow solid (92.9 mg, 85% yield), M.p. 83–84 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (d, J = 6.8 Hz, 1H), 7.76 (d, J = 6.4 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.56 (d, J = 1.7 Hz, 2H), 7.52 – 7.32 (m, 8H), 4.02 (d, J = 14.0 Hz, 1H), 3.70 (d, J = 14.0 Hz, 1H), 3.15 (d, J = 3.4 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9 (d, J = 272.7 Hz), 146.1, 142.4, 135.2, 132.6, 131.5, 131.3, 130.8 (d, J = 3.0 Hz), 130.0, 129.7, 128.9, 128.5, 127.4, 125.8, 124.6, 122.5, 121.1, 118.1, 112.5 (d, J = 8.1 Hz), 96.9 (d, J = 6.1 Hz), 80.5, 80.4, 39.6, 37.5, 34.7. **^{19}FNMR (376 MHz, $CDCl_3$)** δ –106.76. **HRMS(ESI)** calcd for $C_{27}H_{18}ClFN_3^+$ $[M+H]^+$ 438.1173, found 438.1182.

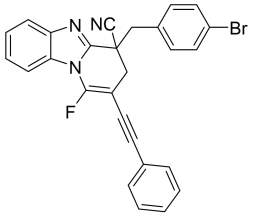


4-(3-Chlorobenzyl)-1-fluoro-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3m): light yellow solid (71.0 mg, 65% yield), M.p. 171–172 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, J = 6.8 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.52 (d, J = 3.0 Hz, 2H), 7.39 (tdd, J = 23.0, 15.2, 7.6 Hz, 9H), 3.65 (d, J = 13.8 Hz, 1H), 3.30 (d, J = 13.9 Hz, 1H), 3.02 (dd, J = 15.9, 4.7 Hz, 1H), 2.85 (dd, J = 15.9, 4.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9 (d, J = 272.7 Hz), 146.5, 142.3, 134.9, 134.7, 131.6, 130.8 (d, J = 3.0 Hz), 130.7, 130.2, 129.0, 128.7, 128.6, 128.5, 125.9, 124.8, 122.3, 121.1, 117.8, 112.5 (d, J = 7.1 Hz), 97.3 (d, J = 6.1 Hz), 80.1 (d, J = 2.0 Hz), 80.0 (d, J = 12.1 Hz), 40.7, 39.2, 34.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.24. **HRMS (ESI)** calcd for $C_{27}H_{18}ClFN_3^+$ $[M+H]^+$ 438.1173, found 438.1165.

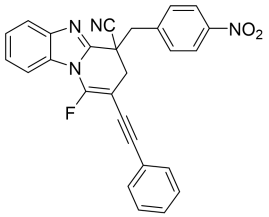


4-(4-Chlorobenzyl)-1-fluoro-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3n): light yellow solid (86.3 mg, 79% yield), M.p. 98–99 °C. **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 6.7 Hz, 1H), 7.71 (d, J = 5.6 Hz, 1H), 7.57 – 7.28 (m, 11H), 3.67 (d, J = 13.9 Hz, 1H), 3.30 (d, J = 13.9 Hz, 1H), 3.01 (dd, J = 16.1, 4.8 Hz, 1H), 2.84 (dd, J = 16.1, 4.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9 (d, J = 272.7 Hz), 148.5, 146.4, 142.2, 134.6, 131.9, 131.4 (d, J = 13.3 Hz), 130.8 (d, J = 3.0 Hz), 129.1 (d, J = 13.5 Hz), 128.6, 125.9, 124.8, 122.3, 121.1, 117.8, 112.5 (d, J = 7.1 Hz), 97.2 (d, J = 7.1 Hz), 80.1, 80.0 (d, J = 12.1 Hz), 40.5, 39.3, 34.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.26. **HRMS (ESI)** calcd for $C_{27}H_{18}ClFN_3^+$ $[M+H]^+$ 438.1173, found 438.1186.

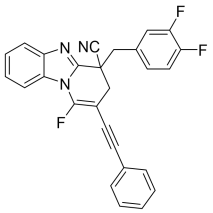


4-(4-Bromobenzyl)-1-fluoro-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3o): light yellow solid (79.4 mg, 66% yield), M.p. 190–191 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (d, J = 6.8 Hz, 1H), 7.76 (d, J = 5.8 Hz, 1H), 7.57 (d, J = 7.5 Hz, 4H), 7.52 – 7.38 (m, 5H), 7.32 (d, J = 7.4 Hz, 2H), 3.69 (d, J = 13.9 Hz, 1H), 3.33 (d, J = 13.9 Hz, 1H), 3.05 (dd, J = 15.9, 4.5 Hz, 1H), 2.88 (dd, J = 16.0, 4.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9 (d, J = 272.7 Hz), 146.46, 142.3, 132.2, 132.1, 131.9, 131.5, 130.8 (d, J = 3.0 Hz), 129.0, 128.6, 125.9, 124.8, 122.7, 122.3, 121.1, 117.8, 112.5 (d, J = 8.1 Hz), 97.2 (d, J = 6.1 Hz), 80.2 (d, J = 3.0 Hz), 80.1 (d, J = 12.1 Hz), 40.5, 39.2, 34.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.20. **HRMS (ESI)** calcd for $C_{27}H_{18}BrFN_3^+$ $[M+H]^+$ 482.0668, found 482.0657.

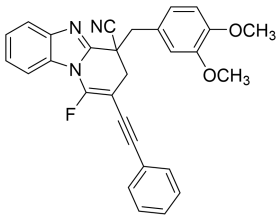


1-Fluoro-4-(4-nitrobenzyl)-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3p): light yellow solid (90.7 mg, 81% yield), M.p. 212–213 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23 (d, J = 7.8 Hz, 2H), 7.84 (d, J = 7.4 Hz, 1H), 7.72 (d, J = 6.7 Hz, 1H), 7.61 – 7.31 (m, 9H), 3.79 (d, J = 13.8 Hz, 1H), 3.45 (d, J = 13.8 Hz, 1H), 3.05 (dd, J = 15.9, 5.0 Hz, 1H), 2.86 (dd, J = 15.9, 5.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9 (d, J = 273.7 Hz), 148.0, 145.8, 142.2, 140.3, 131.5 (d, J = 7.1 Hz), 130.8 (d, J = 3.0 Hz), 129.1, 128.6, 126.1, 124.9, 124.0, 122.2, 121.2, 117.5, 112.6 (d, J = 7.1 Hz), 97.4 (d, J =

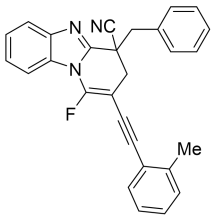
6.1 Hz), 80.0 (d, *J* = 2.0 Hz), 79.8, 40.8, 39.2, 34.5. **^{19}F NMR (376 MHz, CDCl$_3$)** δ –105.95. **HRMS (ESI)** calcd for $C_{27}H_{21}FNO_2^+$ $[M+H]^+$ 449.1414, found 449.1424.



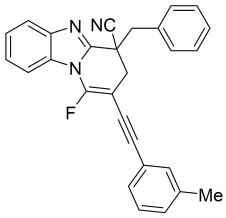
4-(3,4-Difluorobenzyl)-1-fluoro-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3q): light yellow solid (82.3 mg, 75% yield), M.p. 179–180 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.90 (d, *J* = 7.1 Hz, 1H), 7.76 (d, *J* = 6.4 Hz, 1H), 7.62 – 7.35 (m, 7H), 7.34 – 7.14 (m, 3H), 3.68 (d, *J* = 14.0 Hz, 1H), 3.34 (d, *J* = 14.0 Hz, 1H), 3.08 (dd, *J* = 15.9, 5.0 Hz, 1H), 2.89 (dd, *J* = 16.0, 5.1 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 151.8–151.5 (m), 149.9 (d, *J* = 273.7 Hz), 149.3–149.0 (m), 148.6, 146.2, 142.2, 131.5, 130.8 (d, *J* = 3.0 Hz), 129.9–129.8, 129.1, 128.6, 126.9–126.8, 125.9, 124.8, 122.2, 121.1, 119.6 (d, *J* = 18.2 Hz), 117.9, 117.7, 112.5 (d, *J* = 8.1 Hz), 97.3 (d, *J* = 6.2 Hz), 80.0 (dd, *J* = 18.6, 7.4 Hz), 40.2, 39.3, 34.1. **^{19}F NMR (376 MHz, CDCl$_3$)** δ –106.11, –136.25, –137.80. **HRMS (ESI)** calcd for $C_{27}H_{17}F_3N_3^+$ $[M+H]^+$ 440.1375, found 440.1386.



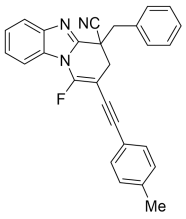
4-(3,4-Dimethoxybenzyl)-1-fluoro-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3r): light yellow solid (83.3 mg, 72% yield), M.p. 182–183 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.84 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 4.5 Hz, 1H), 7.56 – 7.28 (m, 7H), 6.89 (dd, *J* = 28.1, 9.5 Hz, 3H), 3.87 (s, 3H), 3.77 (s, 3H), 3.53 (d, *J* = 13.9 Hz, 1H), 3.23 (d, *J* = 13.9 Hz, 1H), 3.02 (dd, *J* = 16.0, 5.0 Hz, 1H), 2.86 (dd, *J* = 16.0, 5.0 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 149.9 (d, *J* = 273.7 Hz), 149.0 (d, *J* = 3.0 Hz), 148.6, 147.0, 142.3, 131.4, 130.7 (d, *J* = 4.0 Hz), 129.0, 128.6, 125.7, 125.2, 124.7, 122.9, 122.4, 121.0, 118.3, 113.4, 112.5 (d, *J* = 8.1 Hz), 111.3, 96.9 (d, *J* = 7.1 Hz), 80.5 (d, *J* = 2.0 Hz), 79.9 (d, *J* = 12.1 Hz), 56.0, 55.9, 41.2, 39.7, 33.6. **^{19}F NMR (376 MHz, CDCl$_3$)** δ –106.41. **HRMS (ESI)** calcd for $C_{29}H_{23}FN_3O_2^+$ $[M+H]^+$ 464.1774, found 464.1764.



4-Benzyl-1-fluoro-2-(*o*-tolylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3s): light yellow solid (71.9 mg, 69% yield), M.p. 145–146 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 5.8 Hz, 1H), 7.62 – 7.34 (m, 8H), 7.34 – 7.22 (m, 3H), 3.92 (d, J = 14.2 Hz, 1H), 3.40 (d, J = 14.2 Hz, 1H), 3.15 (dd, J = 16.0, 5.4 Hz, 1H), 3.03 (dd, J = 16.0, 5.3 Hz, 1H), 2.50 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.7 (d, J = 272.7 Hz), 147.0 142.3, 132.9, 131.7, 130.8 (d, J = 3.0 Hz), 130.6, 129.7, 129.0, 128.9, 128.4, 125.7 (d, J = 8.1 Hz), 124.7, 122.3, 121.1, 118.4, 112.5 (d, J = 7.1 Hz), 97.0 (d, J = 7.1 Hz), 84.2 (d, J = 2.0 Hz), 80.2 (d, J = 12.1 Hz), 39.4, 37.6, 34.5, 20.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.49. **HRMS (ESI)** calcd for $C_{28}H_{21}FN_3^+$ $[M+H]^+$ 418.1720, found 418.1729.

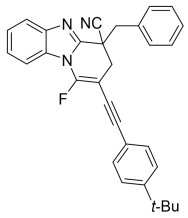


4-Benzyl-1-fluoro-2-(*m*-tolylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3t): light yellow solid (74.0 mg, 71% yield), M.p. 91–92 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, J = 5.9 Hz, 1H), 7.77 (d, J = 3.2 Hz, 1H), 7.60 – 7.39 (m, 7H), 7.37 – 7.20 (m, 4H), 3.69 (d, J = 13.8 Hz, 1H), 3.32 (d, J = 13.7 Hz, 1H), 3.06 (dd, J = 16.0, 4.6 Hz, 1H), 2.91 (dd, J = 15.9, 4.6 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9 (d, J = 272.7 Hz), 147.0, 142.4, 138.6, 132.9, 132.0, 130.8 (d, J = 3.0 Hz), 130.6, 129.8, 128.9, 128.6, 128.4, 128.3, 125.7, 124.6, 122.2, 121.1, 118.1, 112.5 (d, J = 8.1 Hz), 97.2 (d, J = 6.1 Hz), 80.1 (d, J = 2.0 Hz), 80.0 (d, J = 12.1 Hz), 41.2, 39.4, 33.9, 21.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.48. **HRMS (ESI)** calcd for $C_{28}H_{21}FN_3^+$ $[M+H]^+$ 418.1720, found 418.1710.

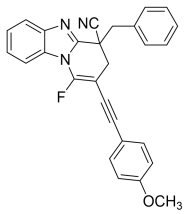


4-Benzyl-1-fluoro-2-(*p*-tolylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3u): light yellow solid (84.4 mg, 81% yield), M.p. 92–93 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, J = 7.1 Hz, 1H), 7.77 (d, J = 5.3 Hz, 1H), 7.56 (s, 2H), 7.52 – 7.39

(m, 5H), 7.31 (dd, *J* = 37.0, 7.4 Hz, 4H), 3.71 (d, *J* = 13.8 Hz, 1H), 3.32 (d, *J* = 13.8 Hz, 1H), 3.04 (dd, *J* = 16.0, 5.1 Hz, 1H), 2.92 (dd, *J* = 16.0, 5.1 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.7 (d, *J* = 272.7 Hz), 147.0, 142.4, 138.1, 131.5, 130.8 (d, *J* = 4.0 Hz), 130.5, 129.9, 129.6, 128.9, 128.5, 125.7, 124.6, 122.5, 121.1, 118.1, 112.5 (d, *J* = 8.1 Hz), 97.2 (d, *J* = 6.1 Hz), 80.2 (d, *J* = 12.1 Hz), 79.7 (d, *J* = 2.0 Hz), 40.8, 39.5, 33.9, 21.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.45. **HRMS (ESI)** calcd for $C_{28}H_{21}FN_3^+$ $[M+H]^+$ 418.1720, found 418.1728.

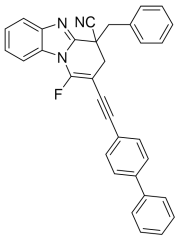


4-Benzyl-2-((4-(tert-butyl)phenyl)ethynyl)-1-fluoro-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3v): light yellow solid (90.7 mg, 79% yield). M.p. 140–141 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 6.5 Hz, 1H), 7.77 (d, *J* = 5.8 Hz, 1H), 7.57 – 7.34 (m, 11H), 3.73 (d, *J* = 13.8 Hz, 1H), 3.37 (d, *J* = 13.8 Hz, 1H), 3.06 (dd, *J* = 16.1, 5.1 Hz, 1H), 2.92 (dd, *J* = 16.0, 5.2 Hz, 1H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.4, 149.7 (d, *J* = 272.7 Hz), 146.9, 142.3, 132.9, 131.3, 130.8 (d, *J* = 16.9 Hz), 130.6, 128.9, 128.3, 125.6 (d, *J* = 16.9 Hz), 124.6, 121.1, 119.4, 118.1, 112.5 (d, *J* = 7.1 Hz), 97.2 (d, *J* = 6.1 Hz), 80.3 (d, *J* = 12.1 Hz), 79.7 (d, *J* = 2.0 Hz), 41.2, 39.5, 34.9, 34.0, 31.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.86. **HRMS (ESI)** calcd for $C_{31}H_{27}FN_3^+$ $[M+H]^+$ 460.2189, found 460.2198.

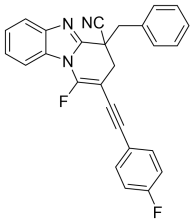


4-Benzyl-1-fluoro-2-((4-methoxyphenyl)ethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3w): light yellow solid (79.0 mg, 73% yield). M.p. 148–149 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 6.2 Hz, 1H), 7.76 (d, *J* = 5.5 Hz, 1H), 7.59 – 7.36 (m, 9H), 6.94 (d, *J* = 7.9 Hz, 2H), 3.89 (s, 3H), 3.74 (d, *J* = 13.8 Hz, 1H), 3.36 (d, *J* = 13.8 Hz, 1H), 3.03 (dd, *J* = 16.0, 4.7 Hz, 1H), 2.89 (dd, *J* = 16.0, 4.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.1, 149.5 (d, *J* = 272.7 Hz), 146.8, 142.3, 133.0 (d, *J* = 4.0 Hz), 130.8 (d, *J* = 3.0 Hz), 130.6, 128.9, 128.3, 125.7, 124.6, 121.1, 118.1, 114.5, 114.2, 112.5 (d, *J* = 8.1 Hz), 97.1 (d, *J* = 6.1 Hz), 80.4 (d, *J* = 12.1 Hz), 79.1 (d, *J* = 2.0 Hz), 55.40, 41.2, 39.4, 34.1. **^{19}F NMR**

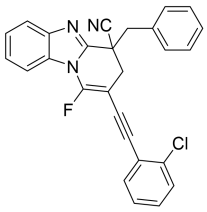
(376 MHz, $CDCl_3$) δ –107.33. **HRMS (ESI)** calcd for $C_{28}H_{21}FN_3O^+$ $[M+H]^+$ 434.1669, found 434.1674.



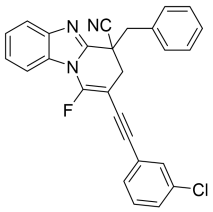
2-([1,1'-Biphenyl]-4-ylethynyl)-4-benzyl-1-fluoro-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3x): light yellow solid (100.6 mg, 84% yield). M.p. 98–99 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, J = 6.8 Hz, 1H), 7.78 (d, J = 4.7 Hz, 1H), 7.75 – 7.36 (m, 16H), 3.76 (d, J = 13.8 Hz, 1H), 3.38 (d, J = 13.8 Hz, 1H), 3.07 (dd, J = 16.0, 4.0 Hz, 1H), 2.93 (dd, J = 15.9, 4.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9 (d, J = 273.7 Hz), 146.9, 142.4, 141.6, 140.2, 133.0, 131.9, 130.8 (d, J = 3.0 Hz), 130.6 (m), 129.0 (d, J = 3.0 Hz), 128.4, 127.9, 127.1 (d, J = 11.1 Hz), 125.8, 124.9, 121.3, 121.1, 118.1, 112.5 (d, J = 8.1 Hz), 97.0 (d, J = 6.1 Hz), 81.1 (d, J = 2.0 Hz), 80.1 (d, J = 12.1 Hz), 41.2, 39.4, 34.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.34. **HRMS (ESI)** calcd for $C_{33}H_{23}FN_3^+$ $[M+H]^+$ 480.1876, found 480.1886.



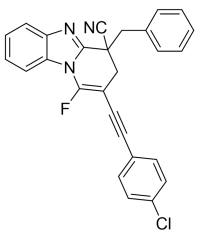
4-Benzyl-1-fluoro-2-((4-fluorophenyl)ethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3y): light yellow solid (75.8 mg, 72% yield). M.p. 165–166 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 5.2 Hz, 1H), 7.64 – 7.39 (m, 9H), 7.12 (t, J = 8.3 Hz, 2H), 3.77 (d, J = 13.8 Hz, 1H), 3.37 (d, J = 13.8 Hz, 1H), 3.03 (dd, J = 16.1, 5.3 Hz, 1H), 2.91 (dd, J = 16.1, 5.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9 (d, J = 251.5 Hz), 150.0 (d, J = 272.7 Hz), 146.8, 142.3, 133.4 (d, J = 8.1 Hz), 132.9, 130.8 (d, J = 3.0 Hz), 130.6, 128.9, 128.4, 125.8, 124.7, 121.1, 118.5 (d, J = 3.0 Hz), 118.0, 116.0, 115.8, 112.5 (d, J = 8.1 Hz), 95.8 (d, J = 6.1 Hz), 80.1, 79.9 (d, J = 12.1 Hz), 41.2, 39.3, 34.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.34, –109.64 . **HRMS (ESI)** calcd for $C_{27}H_{18}F_2N_3^+$ $[M+H]^+$ 422.1469, found 422.1470.



4-Benzyl-2-((2-chlorophenyl)ethynyl)-1-fluoro-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3z): light yellow solid (73.2 mg, 67% yield). M.p. 154–155 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, J = 6.1 Hz, 1H), 7.77 (d, J = 3.3 Hz, 1H), 7.51 (dt, J = 16.6, 7.9 Hz, 9H), 7.39 – 7.23 (m, 2H), 3.66 (d, J = 13.7 Hz, 1H), 3.37 (d, J = 13.7 Hz, 1H), 3.09 (dd, J = 16.0, 4.6 Hz, 1H), 2.96 (dd, J = 16.0, 4.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.2 (d, J = 273.7 Hz), 147.0, 142.4, 135.8, 133.1, 132.8, 130.7 (d, J = 4.0 Hz), 130.7, 129.9, 129.5, 128.9, 128.4, 126.7, 125.8, 124.8, 122.5, 121.1, 118.0, 112.5 (d, J = 8.1 Hz), 93.6 (d, J = 7.1 Hz), 85.5 (d, J = 2.0 Hz), 79.7 (d, J = 12.1 Hz), 41.3, 39.6, 33.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –105.22. **HRMS (ESI)** calcd for $C_{27}H_{18}ClFN_3^+$ $[M+H]^+$ 438.1173, found 438.1171.

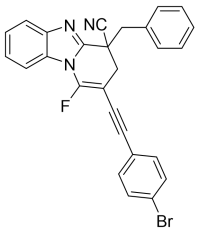


4-Benzyl-2-((3-chlorophenyl)ethynyl)-1-fluoro-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3aa): Light yellow solid (77.6 mg, 71% yield). M.p. 140–141 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, J = 6.4 Hz, 1H), 7.76 (d, J = 5.6 Hz, 1H), 7.56 – 7.32 (m, 11H), 3.78 (d, J = 13.7 Hz, 1H), 3.38 (d, J = 13.8 Hz, 1H), 3.03 (dd, J = 15.9, 4.3 Hz, 1H), 2.91 (dd, J = 15.7, 4.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.3 (d, J = 273.7 Hz), 146.8, 142.3, 134.4, 132.9, 131.3, 130.8 (d, J = 3.0 Hz), 130.6, 129.7, 129.6, 129.1, 128.9, 128.4, 125.9, 124.8, 124.1, 121.2, 118.0, 112.5 (d, J = 7.1 Hz), 95.4 (d, J = 6.1 Hz), 81.5 (d, J = 3.0 Hz), 79.7 (d, J = 12.1 Hz), 41.2, 39.3, 33.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –105.50. **HRMS (ESI)** calcd for $C_{27}H_{18}ClFN_3^+$ $[M+H]^+$ 438.1173, found 438.1163.

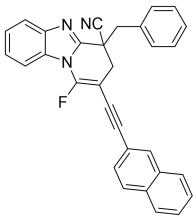


4-Benzyl-2-((4-chlorophenyl)ethynyl)-1-fluoro-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3ab): Light yellow solid (86.3 mg, 79% yield). M.p.174–175 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 6.9 Hz, 1H), 7.76 (d, J = 5.7 Hz, 1H), 7.54 – 7.33 (m, 11H), 3.77 (d, J = 13.8 Hz, 1H), 3.37 (d, J = 13.8 Hz, 1H), 3.03 (dd, J = 16.0, 5.3 Hz, 1H), 2.91 (dd, J = 16.0, 5.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.2 (d, J = 272.7 Hz), 146.8, 142.3, 135.0, 132.9, 132.7, 130.8 (d, J = 4.0 Hz), 130.6, 128.9 (d, J = 3.0 Hz), 128.5, 125.8, 124.7, 121.1, 120.9, 118.0, 112.5 (d, J = 8.1 Hz), 95.7 (d, J = 7.1 Hz), 81.4 (d, J = 2.0 Hz), 79.8 (d, J = 12.1 Hz), 41.2, 39.3, 34.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –105.89. **HRMS (ESI)** calcd for $C_{27}H_{18}ClFN_3^+$ $[M+H]^+$ 438.1173, found 438.1163.

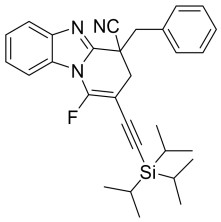


4-**Benzyl-2-((4-bromophenyl)ethynyl)-1-fluoro-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3ac)**: Light yellow solid (92.6 mg, 77% yield). M.p. 199–200 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (d, J = 6.6 Hz, 1H), 7.70 (d, J = 5.7 Hz, 1H), 7.50 (d, J = 7.7 Hz, 2H), 7.46 – 7.30 (m, 9H), 3.72 (d, J = 13.8 Hz, 1H), 3.32 (d, J = 13.9 Hz, 1H), 2.97 (dd, J = 15.9, 5.0 Hz, 1H), 2.85 (dd, J = 15.9, 4.9 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-D_6)** δ 150.2 (d, J = 273.7 Hz), 146.8, 142.3, 132.9 (d, J = 6.1 Hz), 131.8, 130.8 (d, J = 3.0 Hz), 130.6, 128.9, 128.4, 125.8, 124.8, 123.2, 121.4, 121.2, 118.0, 112.5 (d, J = 8.1 Hz), 95.8 (d, J = 6.1 Hz), 81.5 (d, J = 2.0 Hz), 79.8 (d, J = 12.1 Hz), 41.2, 39.3, 33.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –105.80. **HRMS (ESI)** calcd for $C_{27}H_{18}BrFN_3^+$ $[M+H]^+$ 482.0668, found 482.0658.

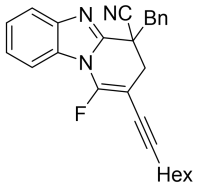


4-Benzyl-1-fluoro-2-(naphthalen-2-ylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3ad): Light yellow solid (82.7 mg, 73% yield). M.p. 129–130 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (s, 1H), 7.85 (dd, J = 21.0, 6.8 Hz, 4H), 7.73 (d, J = 6.1 Hz, 1H), 7.59 – 7.48 (m, 3H), 7.48 – 7.31 (m, 7H), 3.72 (d, J = 13.8 Hz, 1H), 3.34 (d, J = 13.8 Hz, 1H), 3.03 (d, J = 16.0 Hz, 1H), 2.90 (d, J = 16.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.0 (d, J = 272.7 Hz), 146.9, 142.39, 133.0 (d, J = 10.1 Hz), 131.6, 130.8 (d, J = 3.0 Hz), 130.6, 128.9, 128.4, 128.3, 128.0, 127.9 (d, J = 3.0 Hz), 127.1, 126.8, 125.8, 124.7, 121.1, 119.7, 118.1, 112.5 (d, J = 7.1 Hz), 97.5 (d, J = 6.1 Hz), 80.7, 80.2 (d, J = 12.1 Hz), 41.2, 39.4,

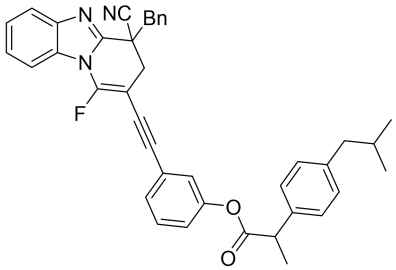
34.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –106.28. **HRMS (ESI)** calcd for $C_{31}H_{21}FN_3^+$ $[M+H]^+$ 454.1720, found 454.1708.



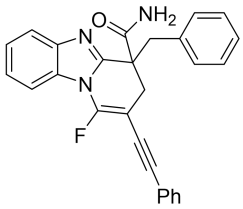
5-**Benzyl-1-fluoro-2-((triisopropylsilyl)ethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3ae)**: Light yellow solid (76.1 mg, 63% yield). M.p. 137 – 138 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 – 7.84 (m, 1H), 7.74 (d, J = 4.4 Hz, 1H), 7.44 (s, 7H), 3.52 (d, J = 13.7 Hz, 1H), 3.31 (d, J = 13.7 Hz, 1H), 3.04 (dd, J = 16.1, 5.1 Hz, 1H), 2.84 (dd, J = 16.1, 5.2 Hz, 1H), 1.21 (s, 21H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.9 (d, J = 272.7 Hz), 147.2, 142.32, 132.8, 130.7 (d, J = 3.0 Hz), 130.6, 128.9, 128.4, 125.7, 124.6, 121.1, 118.0, 112.5 (d, J = 8.1 Hz), 100.1 (d, J = 6.1 Hz), 97.1 (d, J = 2.0 Hz), 79.9 (d, J = 12.1 Hz), 41.2, 39.7, 33.2, 18.7, 11.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –105.98. **HRMS (ESI)** calcd for $C_{30}H_{35}FN_3Si^+$ $[M+H]^+$ 484.2584, found 484.2597.



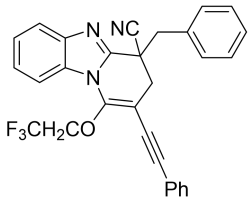
4-**Benzyl-1-fluoro-2-(3-oxooct-1-yn-1-yl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (3af)**: white solid (60.6 mg, 57% yield). M.p. 114 – 115 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, J = 7.4 Hz, 1H), 7.67 (d, J = 4.5 Hz, 1H), 7.39 (d, J = 7.6 Hz, 7H), 3.63 (d, J = 13.8 Hz, 1H), 3.26 (d, J = 13.8 Hz, 1H), 2.94 – 2.82 (m, 1H), 2.80 – 2.68 (m, 1H), 2.51 – 2.33 (m, 2H), 1.68 – 1.54 (m, 2H), 1.42 (dd, J = 27.8, 21.0 Hz, 6H), 0.99 – 0.84 (t, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.7 (d, J = 270.7 Hz), 146.8, 142.3, 132.8, 130.8 (d, J = 4.0 Hz), 130.6, 128.8, 128.3, 125.6, 124.4, 121.0, 118.1, 112.4 (d, J = 8.1 Hz), 98.9 (d, J = 6.1 Hz), 80.5 (d, J = 12.1 Hz), 71.5 (d, J = 2.0 Hz), 41.1, 39.4, 34.1, 31.4, 28.6 (d, J = 8.1 Hz), 22.6, 19.8, 14.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –109.18. **HRMS (ESI)** calcd for $C_{27}H_{27}FN_3^+$ $[M+H]^+$ 412.1289, found 412.2181.



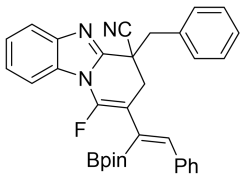
3-((4-Benzyl-4-cyano-1-fluoro-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridin-2-yl)ethynyl)phenyl 2-(4-isobutylphenyl)propanoate (3ag): white solid (116.9 mg, 77% yield). M.p. 243 – 244 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (d, J = 7.3 Hz, 1H), 7.71 (d, J = 5.5 Hz, 1H), 7.50 – 7.28 (m, 11H), 7.18 (d, J = 7.5 Hz, 1H), 7.03 (s, 1H), 4.06 – 3.86 (m, 1H), 3.70 (d, J = 13.8 Hz, 1H), 3.31 (d, J = 13.8 Hz, 1H), 3.06 – 2.90 (m, 2H), 2.91 – 2.78 (m, 1H), 2.50 (d, J = 7.1 Hz, 1H), 1.97 – 1.81 (m, 1H), 1.63 (d, J = 7.1 Hz, 3H), 0.94 (d, J = 6.5 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.0, 150.8, 150.2 (d, J = 273.7 Hz), 146.9, 142.3, 141.0, 137.1, 132.9, 130.8 (d, J = 3.0 Hz), 130.6, 129.6, 128.9, 128.4, 127.3, 125.8, 124.7, 124.5, 123.6, 122.3, 121.1, 118.0, 112.5 (d, J = 8.1 Hz), 95.9 (d, J = 6.1 Hz), 81.1 (d, J = 2.0 Hz), 79.8 (d, J = 12.1 Hz), 45.3, 45.1, 41.2, 39.4, 33.9, 30.3, 22.5, 18.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –105.83. **HRMS (ESI)** calcd for $C_{40}H_{34}FN_3O_2^+$ $[M+H]^+$ 608.2713, found 608.2703.



4-Benzyl-1-fluoro-2-(phenylethynyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carboxamide (4): white solid (54.7 mg, 65% yield). M.p. 293 – 294 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.81 (t, J = 4.0 Hz, 1H), 7.66 (d, J = 3.5 Hz, 1H), 7.51 (dd, J = 24.8, 5.0 Hz, 4H), 7.38 (dd, J = 10.2, 6.1 Hz, 5H), 7.24 (t, J = 10.3 Hz, 5H), 3.51 (d, J = 7.7 Hz, 3H), 3.03 (dd, J = 15.8, 5.6 Hz, 1H), 2.72 (dd, J = 15.8, 5.2 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-d_6)** δ 171.5, 152.5, 149.7 (d, J = 269.7 Hz), 142.5, 136.4, 131.5, 130.8 (d, J = 4.0 Hz), 129.3 (d, J = 4.0 Hz), 128.4, 127.4, 125.2, 124.2, 122.5, 120.5, 112.7 (d, J = 7.1 Hz), 95.6 (d, J = 6.1 Hz), 82.7 (d, J = 2.0 Hz), 81.9 (d, J = 9.1 Hz), 49.7, 41.0, 32.8. **^{19}F NMR (376 MHz, DMSO-d_6)** δ –109.03. **HRMS (ESI)** calcd for $C_{27}H_{25}FN_3O^+$ $[M+H]^+$ 422.1669, found 422.1660.



4-Benzyl-2-(phenylethynyl)-1-(2,2,2-trifluoroethoxy)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (5): white solid (49.3 mg, 51% yield). M.p. 105 – 106 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, J = 7.7 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 12.7 Hz, 12H), 5.08 – 4.72 (m, 2H), 3.72 (d, J = 13.8 Hz, 1H), 3.33 (d, J = 13.8 Hz, 1H), 2.92 (dd, J = 53.3, 15.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.8, 147.2, 142.4, 133.2, 131.5, 131.1, 130.6, 129.0, 128.9, 128.7, 128.2, 125.0 (d, J = 125.2 Hz), 124.3, 122.3, 120.9, 118.4, 113.3, 97.9, 83.8, 82.7, 69.4 (dd, J = 36.4 Hz; J = 72.7 Hz), 41.3, 39.3, 35.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –73.62. **HRMS (ESI)** calcd for $C_{29}H_{20}F_3N_3O^+$ $[M+H]^+$ 484.1637, found 484.1630.



(E)-4-Benzyl-1-fluoro-2-(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (6): white solid (71.2 mg, 67% yield). M.p. 87 – 88 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (d, J = 3.9 Hz, 1H), 7.69 (s, 1H), 7.50 (s, 1H), 7.40 (ddd, J = 36.3, 18.7, 8.4 Hz, 12H), 3.71 (d, J = 13.6 Hz, 1H), 3.39 (d, J = 13.7 Hz, 1H), 2.96 (dd, J = 16.3, 5.0 Hz, 1H), 2.61 (dd, J = 16.2, 5.2 Hz, 1H), 1.38 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.6, 146.4, 143.1 (d, J = 263.6 Hz), 142.3, 137.1, 133.7, 131.1 (d, J = 3.0 Hz), 130.6, 128.8, 128.7, 128.6 (dd, J = 5.1 Hz), 127.9, 125.0, 123.9, 120.8, 118.7, 112.6 (d, J = 8.1 Hz), 95.0 (d, J = 13.1 Hz), 84.3, 40.9, 39.8, 34.5 (d, J = 3.0 Hz), 24.9, 24.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –111.4. **HRMS (ESI)** calcd for $C_{33}H_{32}BFN_3O_2^+$ $[M+H]^+$ 532.2572, found 532.2563.

6. X-ray crystal data of 3j

The crystal of **3j** for X-ray diffraction study has been obtained through the dissolving of compound in PE-DCM, followed by slow evaporation of the solvent at room temperature. The crystal was kept at 298(2) K during data collection.

Table S1 Crystal data and structure refinement for **3j**

Crystallized from	PE/DCM(1:1)
Empirical formula	$C_{28}H_{20}FN_3S$
Formula weight [g mol^{-1}]	449.53
Temperature [K]	296(2)
Crystal system	Monoclinic
Space group	P2(1)/n
a/Å	12.1973(15)

b/Å	8.1592(10)
c/Å	22.874(3)
α/°	90
β/°	92.147(2)
γ/°	90
V[Å^3]	2274.9(5)
Z	4
ρ[g/cm^3]	1.313
μ [mm^{-1}]	0.172
F(000)	936
Radiation	MoKα(0.71073)
2Θ range for data collection/°	1.86 to 27.90
Reflections collected	13636
Independent reflections	5324 [$R_{(int)}$ = 0.0439]
Data/restraints/parameters	5324 / 0 / 299
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1= 0.0528, wR_2= 0.1395
Final R indexes [all data]	R_1 = 0.0733, wR_2 = 0.1570
Largest diff. peak/hole / e Å^{-3}	0.319/-0.324

Crystal structure determination of **3j**

Crystal Data for $C_{28}H_{20}FN_3S$ (M =449.53 g/mol): monoclinic, space group P2(1), a = 12.1973(15) Å, b = 8.1592(10) Å, c = 22.874(3) Å, α = 90°, β = 92.147(2)°, γ = 90°, V = 2274.9(5) Å3, Z = 4, T = 296(2) K, μ(Mo Kα) = 0.172 mm-1, Dcalc = 1.313 g/cm^3, 13636 reflections measured (1.86° ≤ 2Θ ≤ 27.90°), 5324 unique (Rint = 0.0439) which were used in all calculations. The final R_1 was 0.0528 (I > 2σ(I)) and wR_2 was 0.1570 (all data).

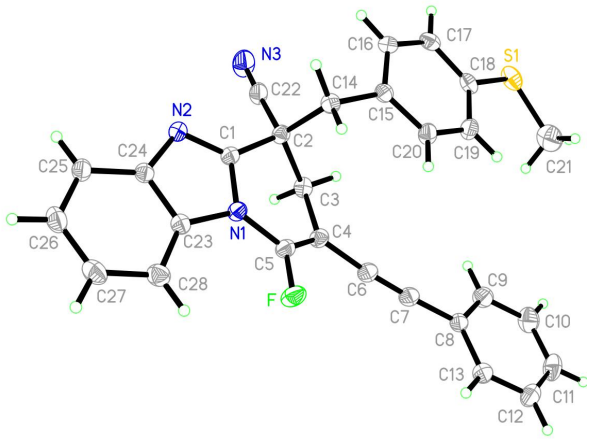
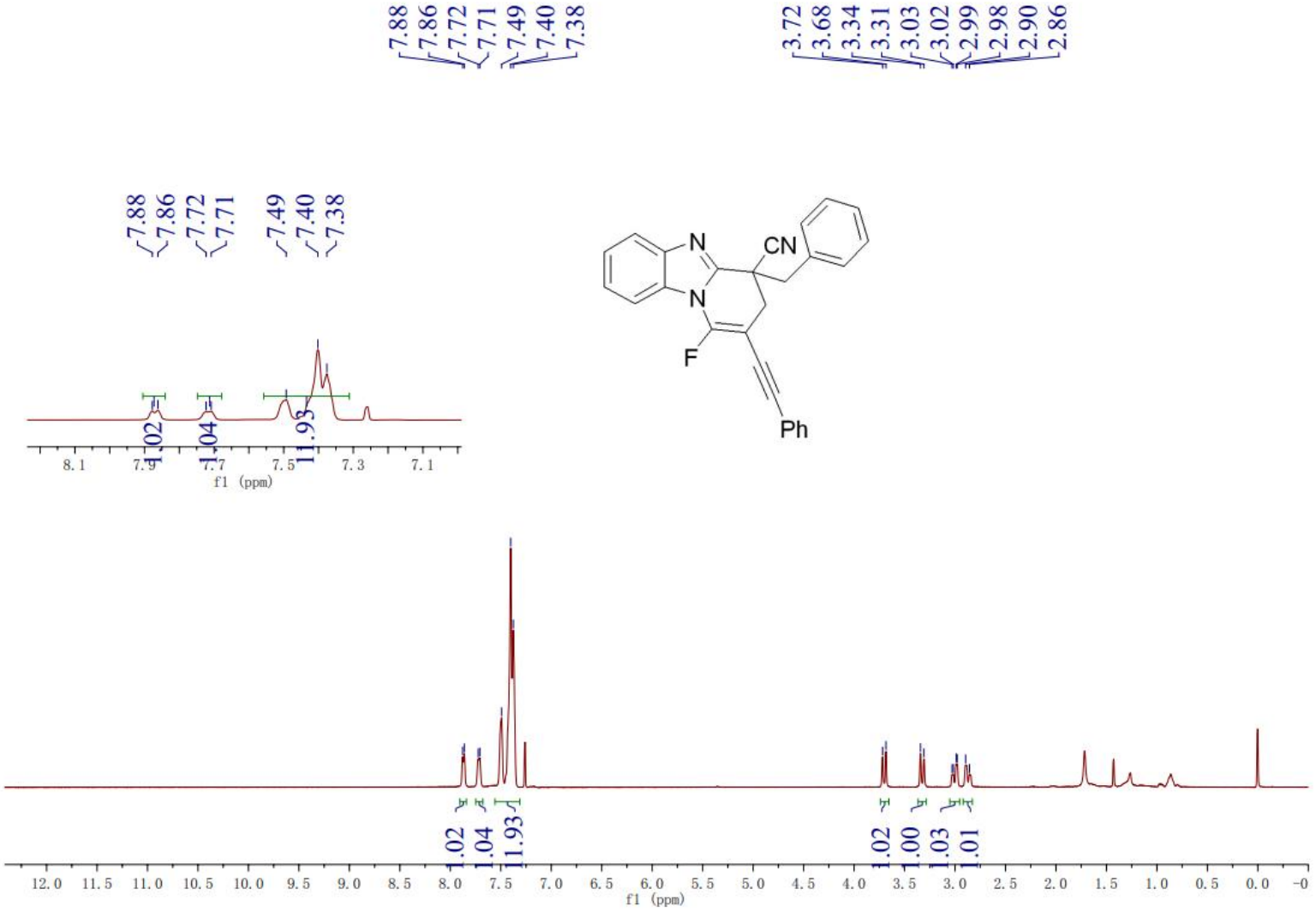


Figure S1. X-ray crystal structure of **3j**

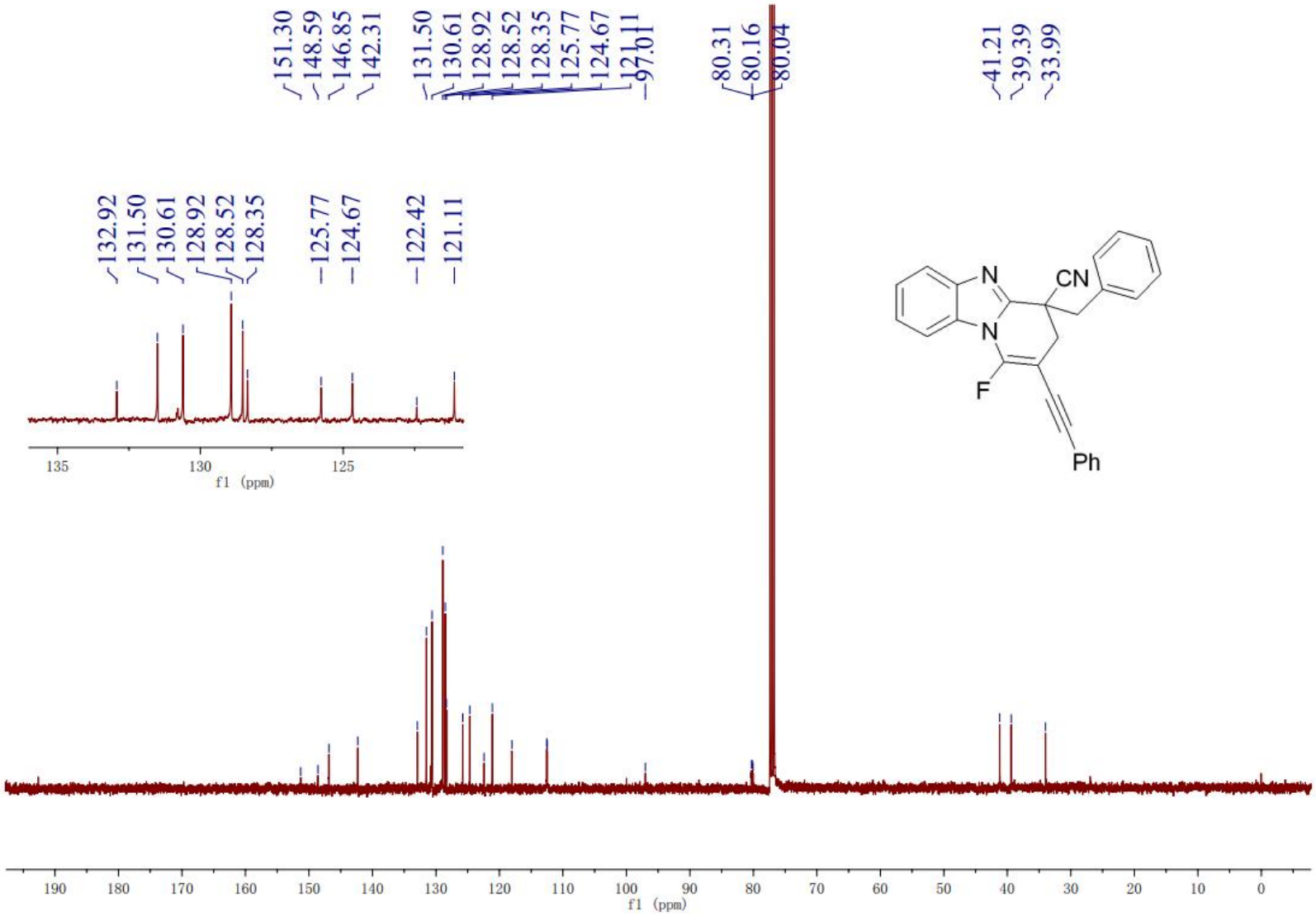
CCDC:2395285 **(3j)**

7. Copies of ^{1}H, ^{13}C, and ^{19}F NMR Spectra for Compounds

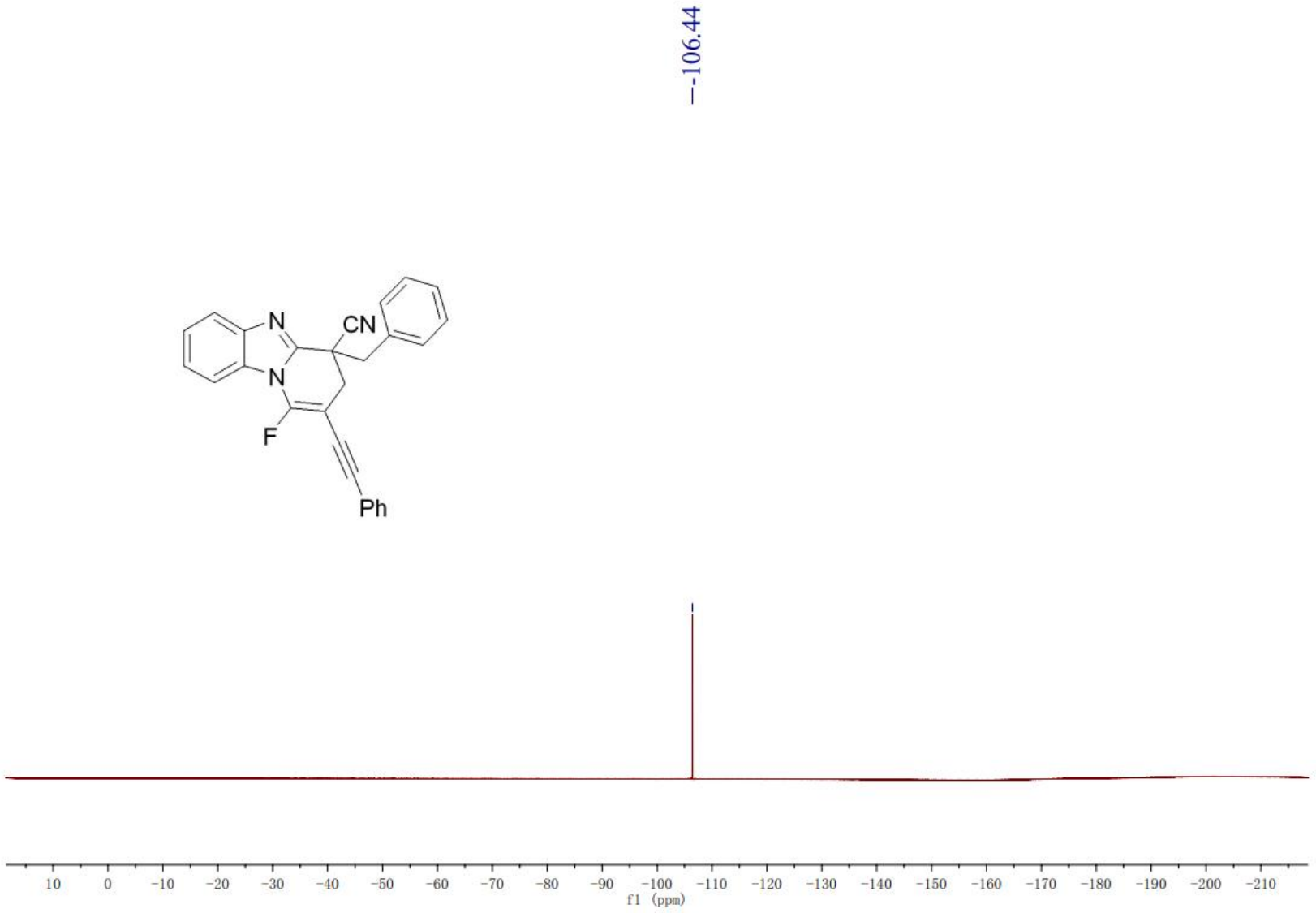
^{1}H NMR spectrum of **3a**



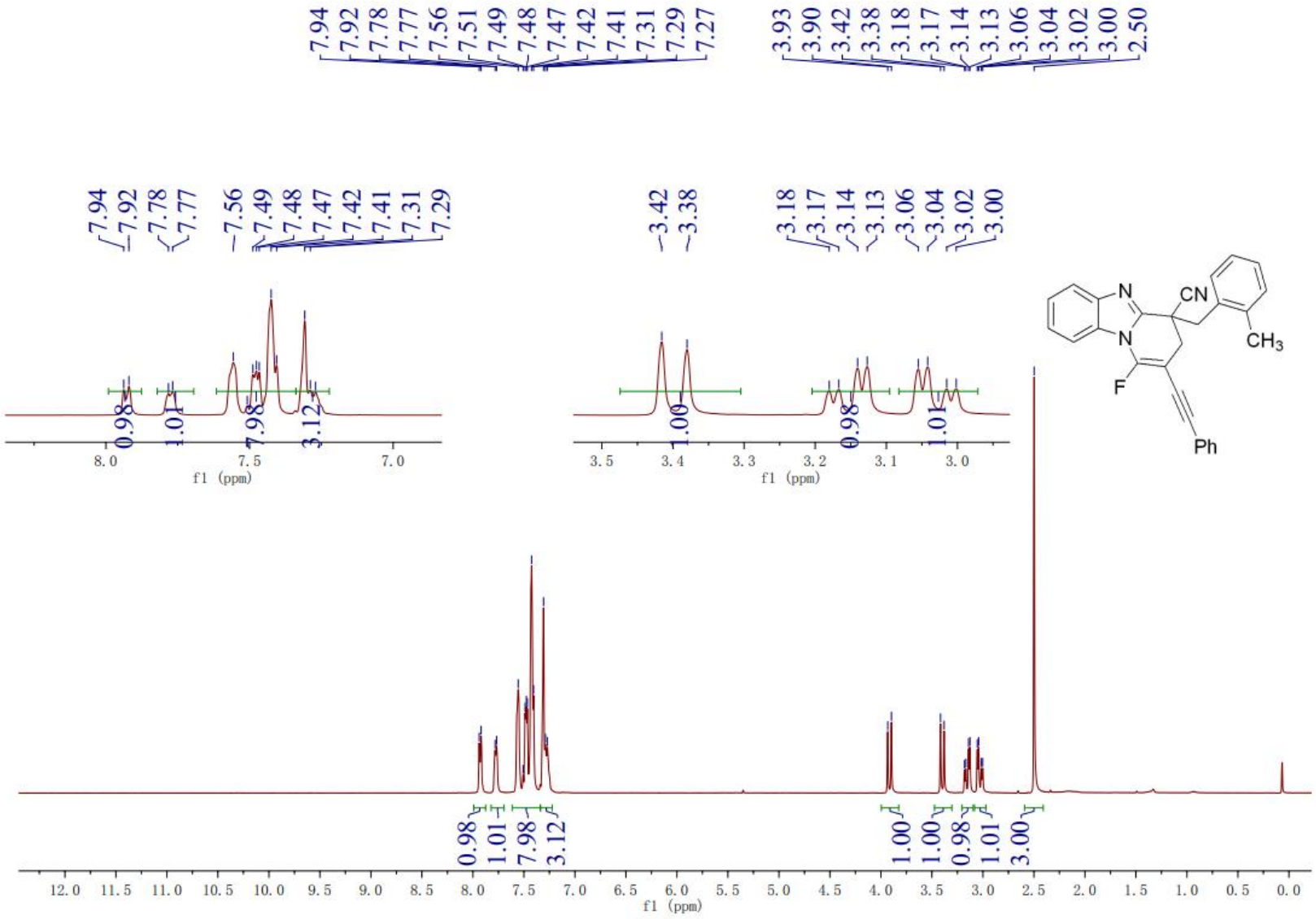
^{13}C NMR spectrum of **3a**



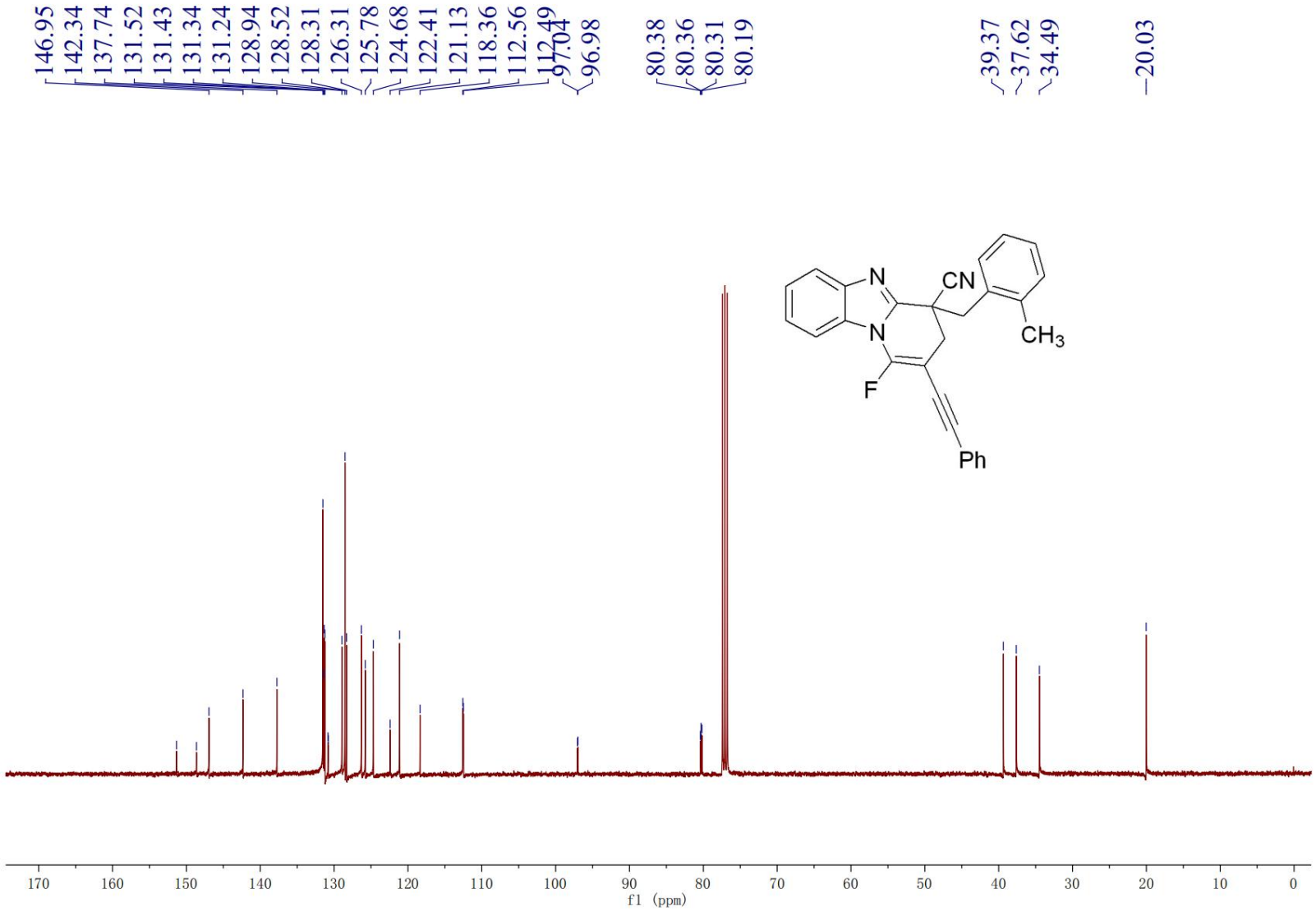
^{19}F NMR spectrum of **3a**



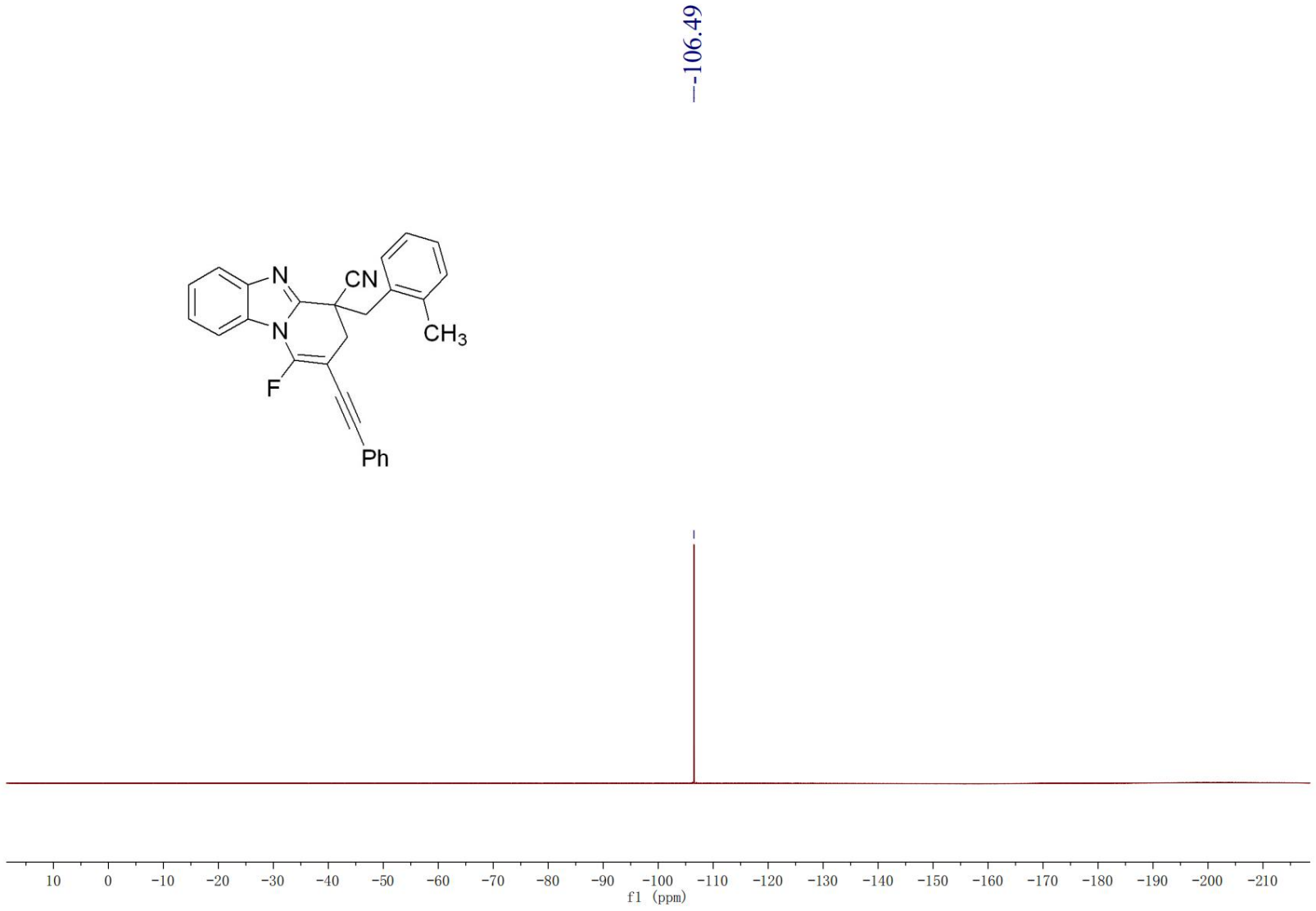
^{1}H NMR spectrum of **3b**



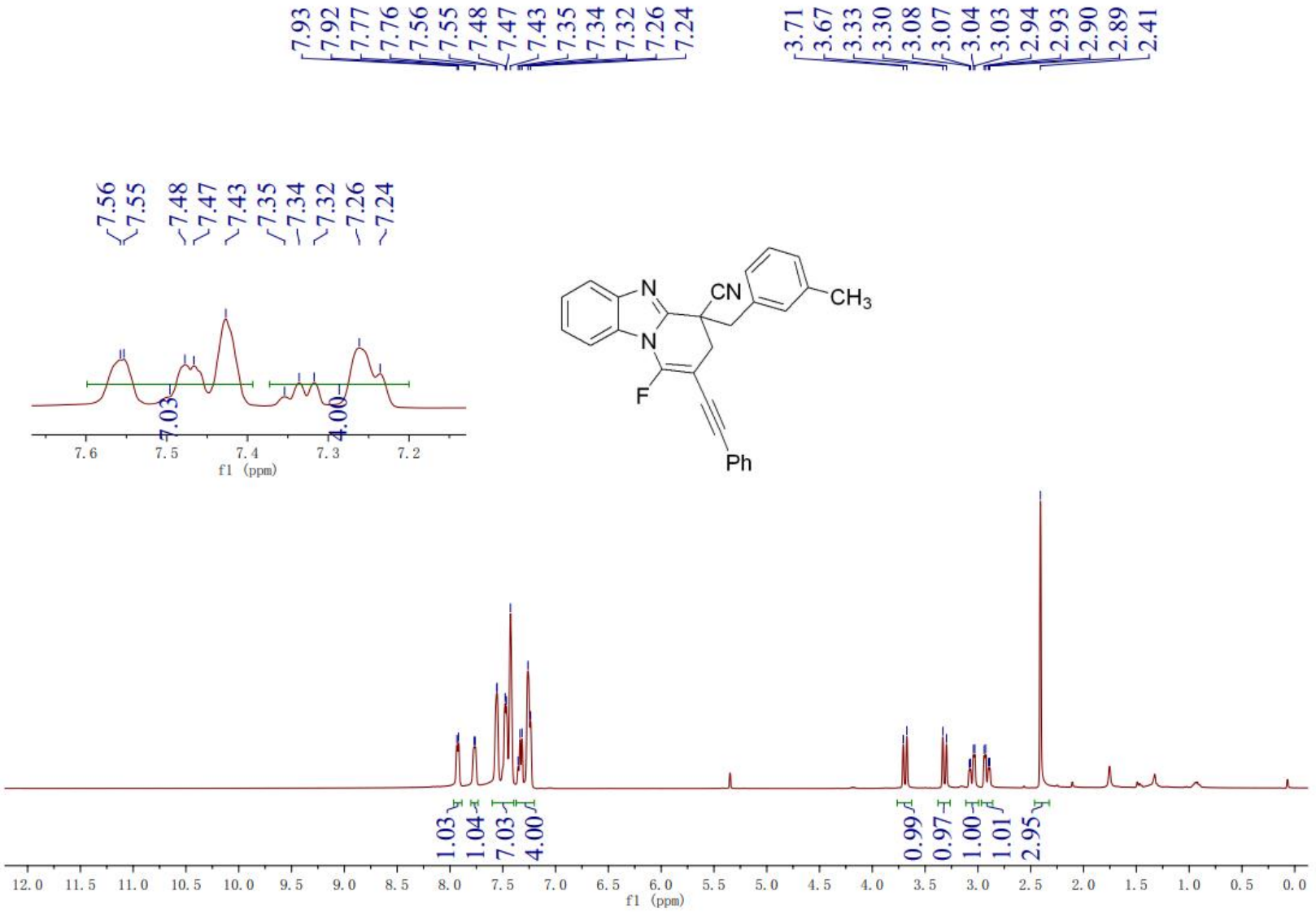
^{13}C NMR spectrum of **3b**



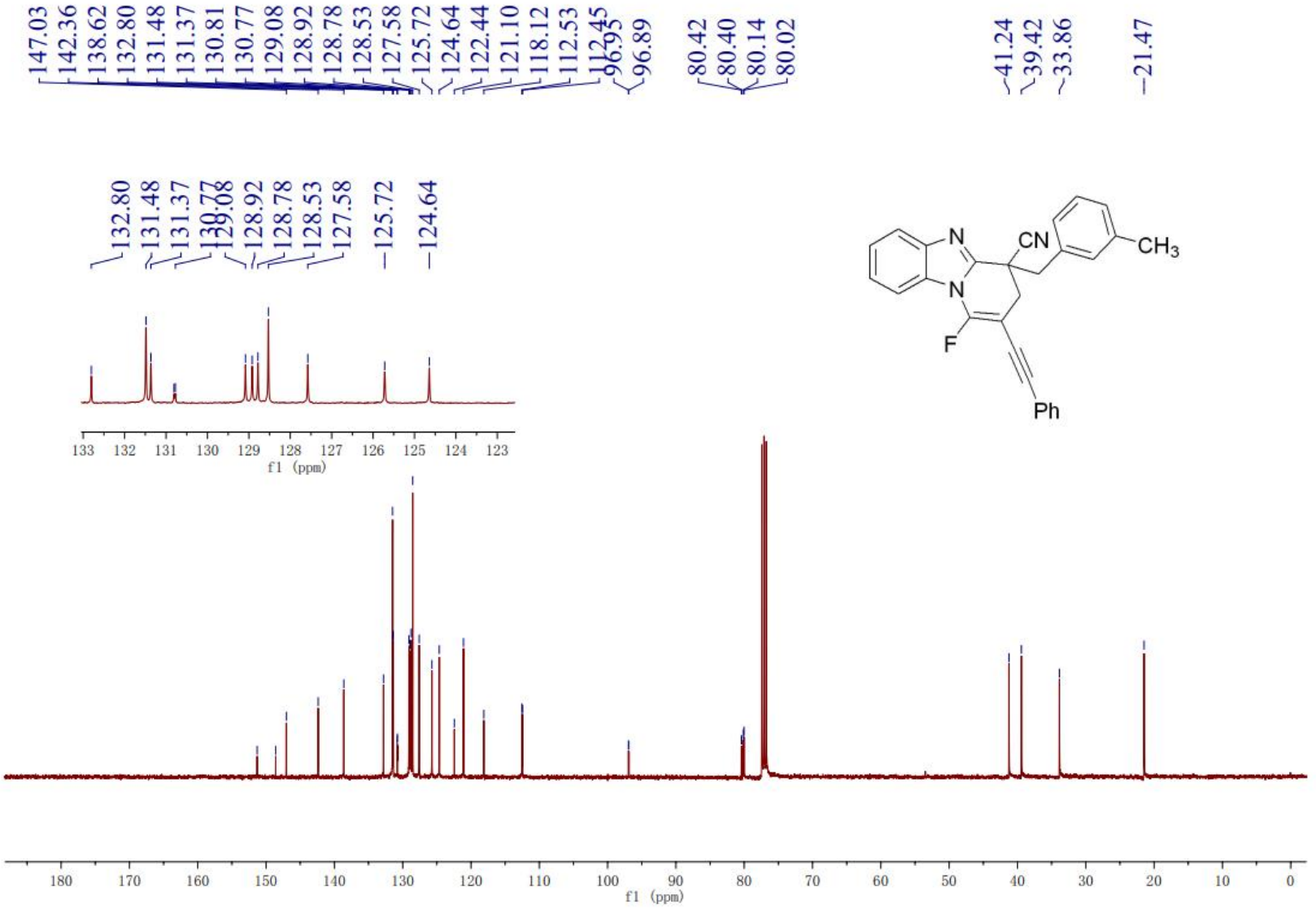
^{19}F NMR spectrum of **3b**



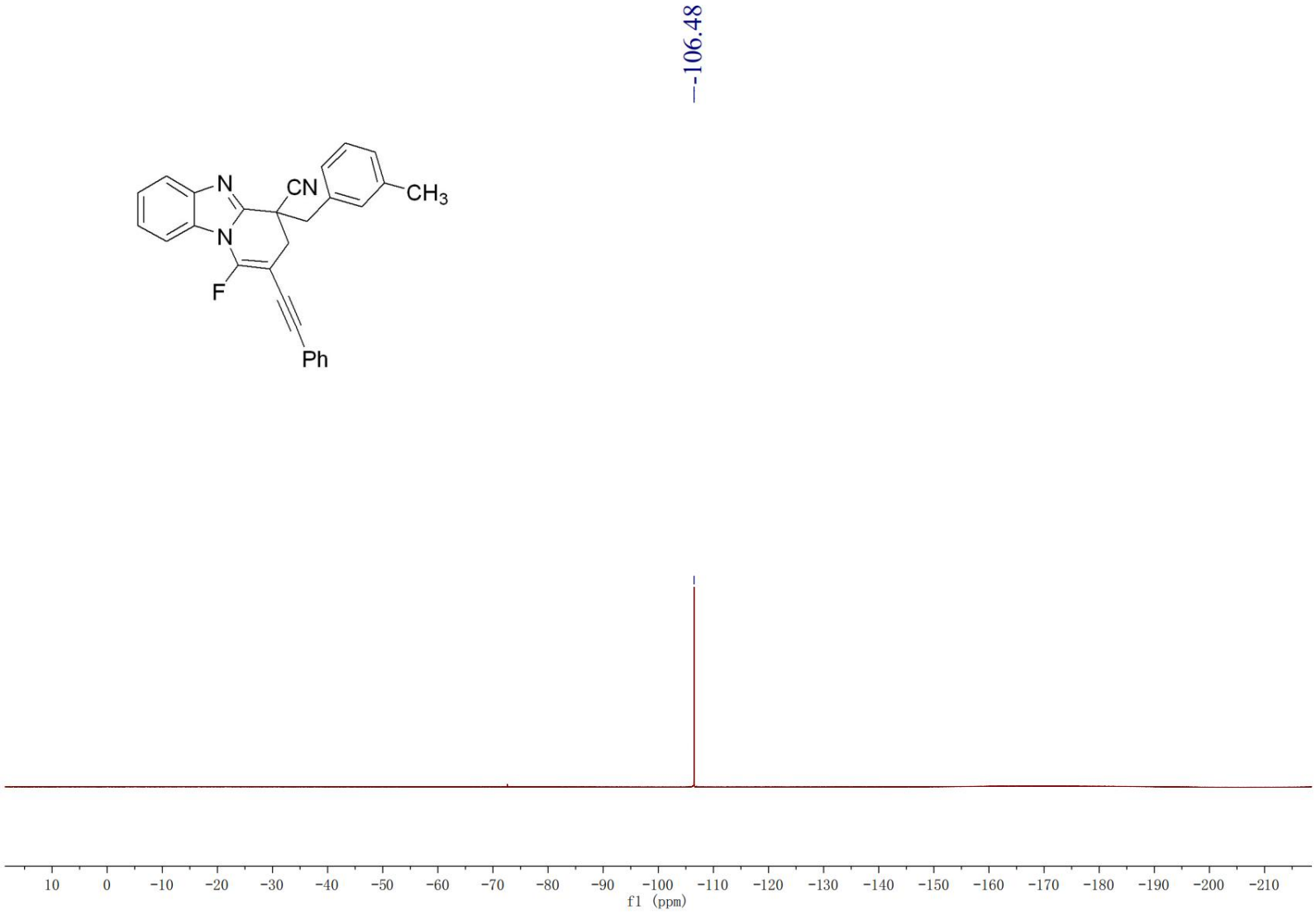
^{1}H NMR spectrum of **3c**



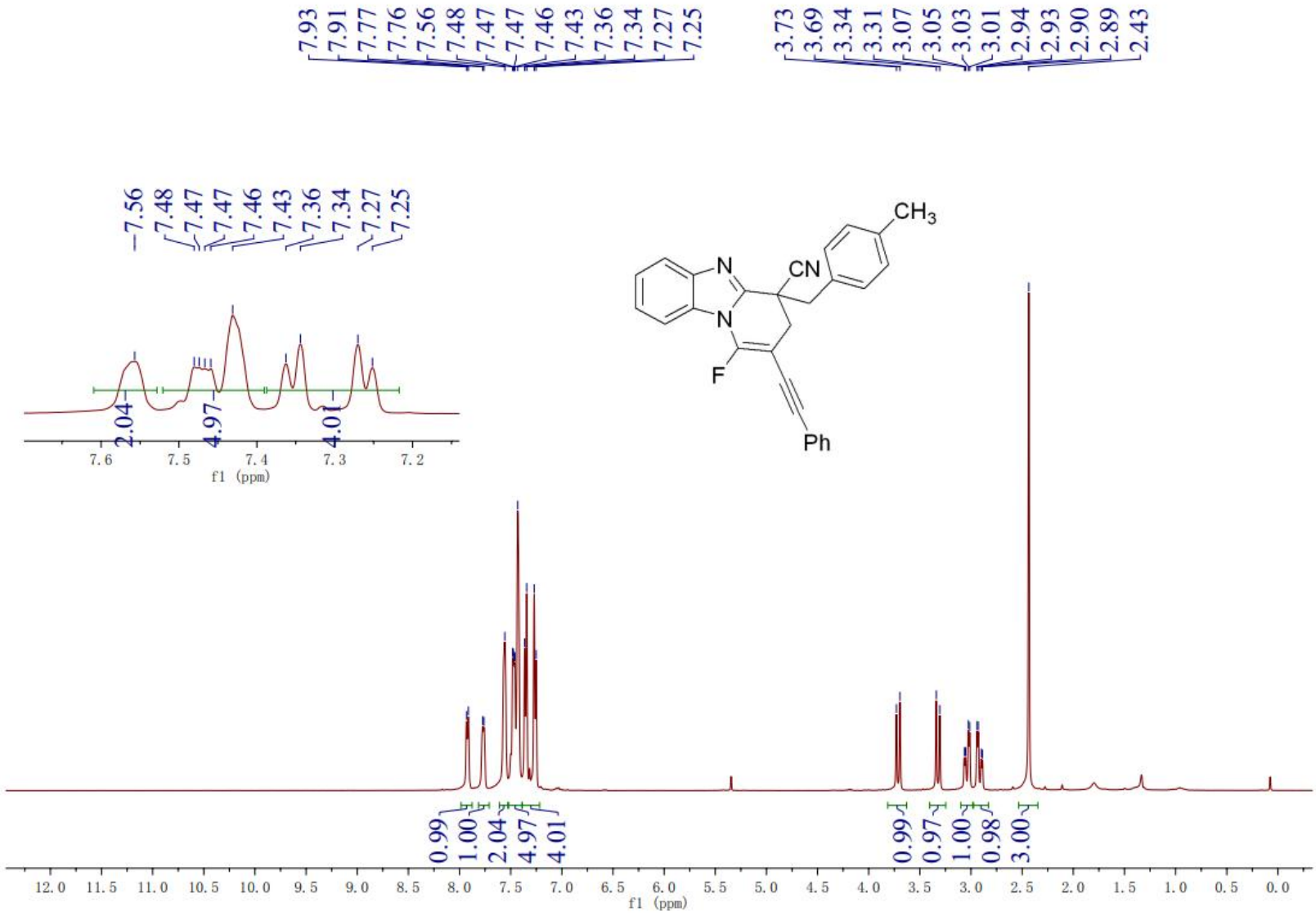
^{13}C NMR spectrum of **3c**



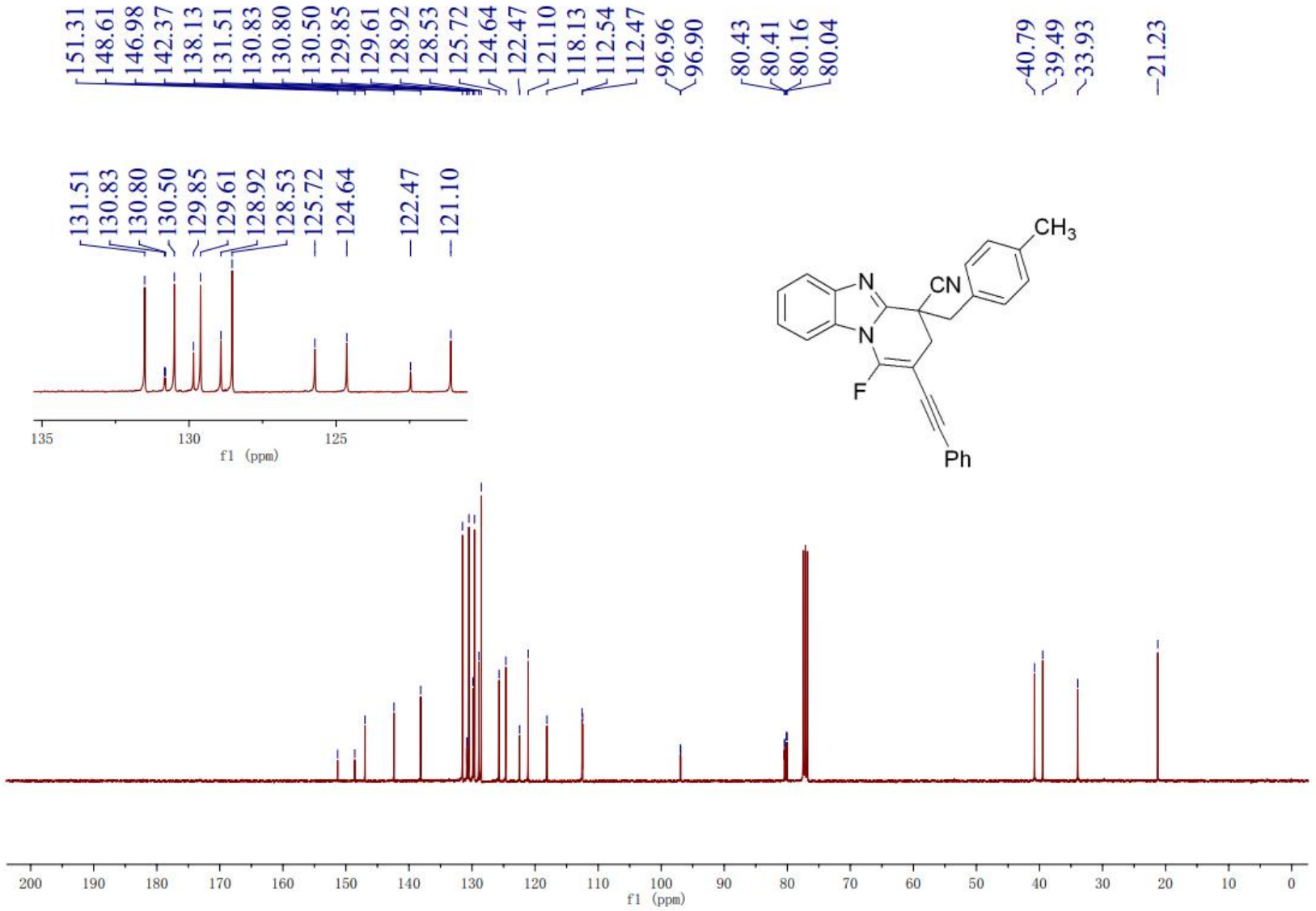
^{19}F NMR spectrum of **3c**



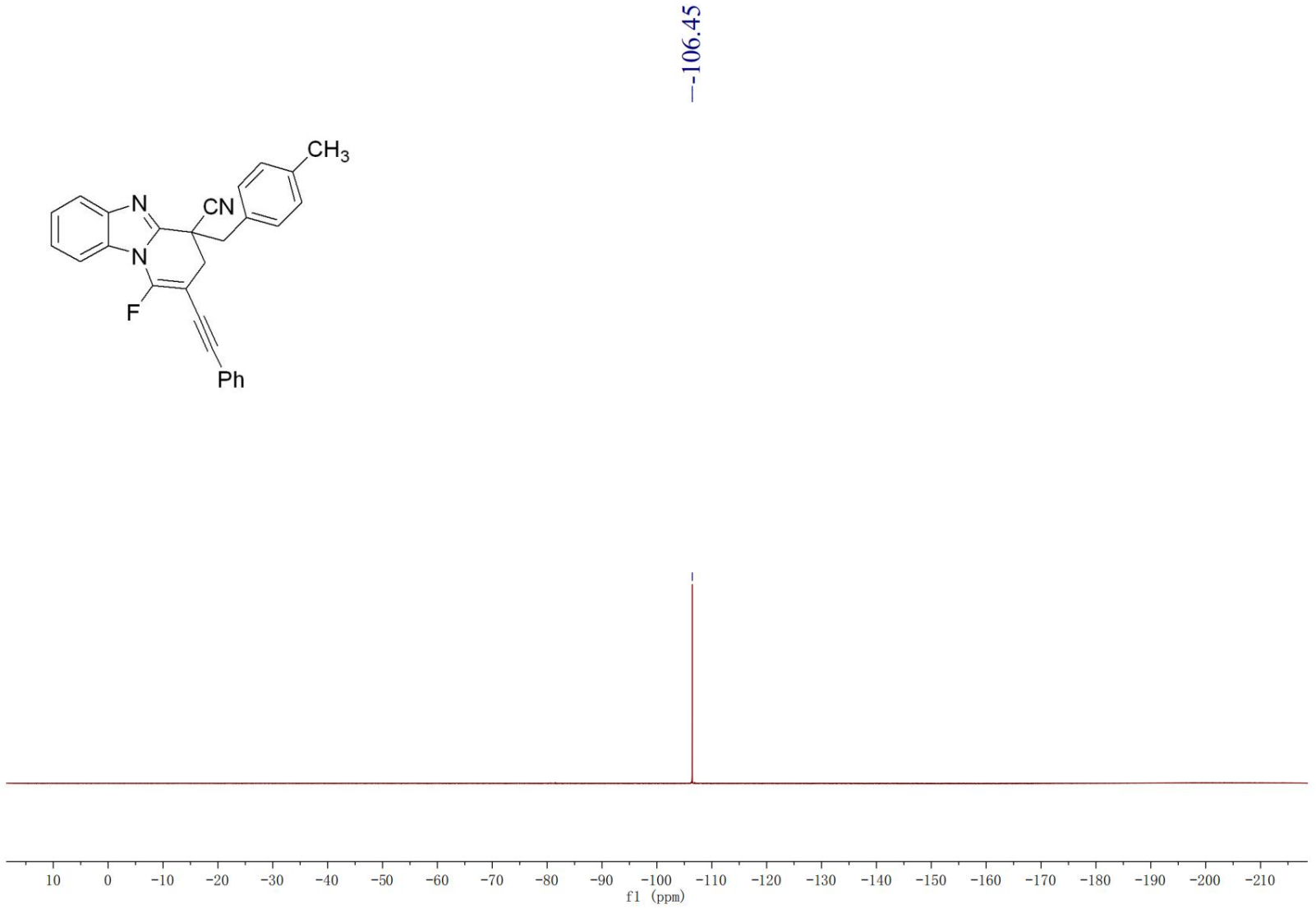
^{1}H NMR spectrum of **3d**



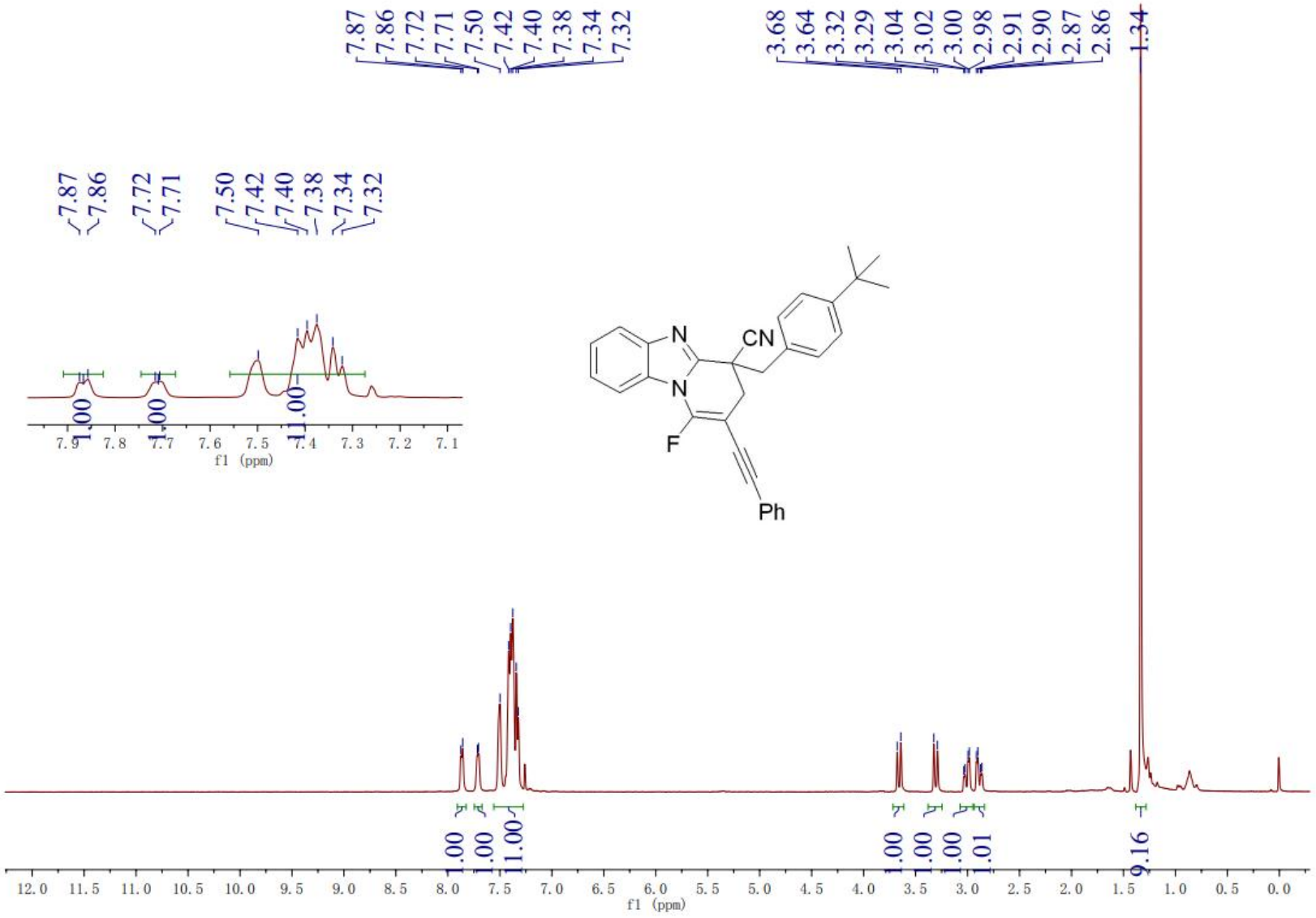
^{13}C NMR spectrum of **3d**



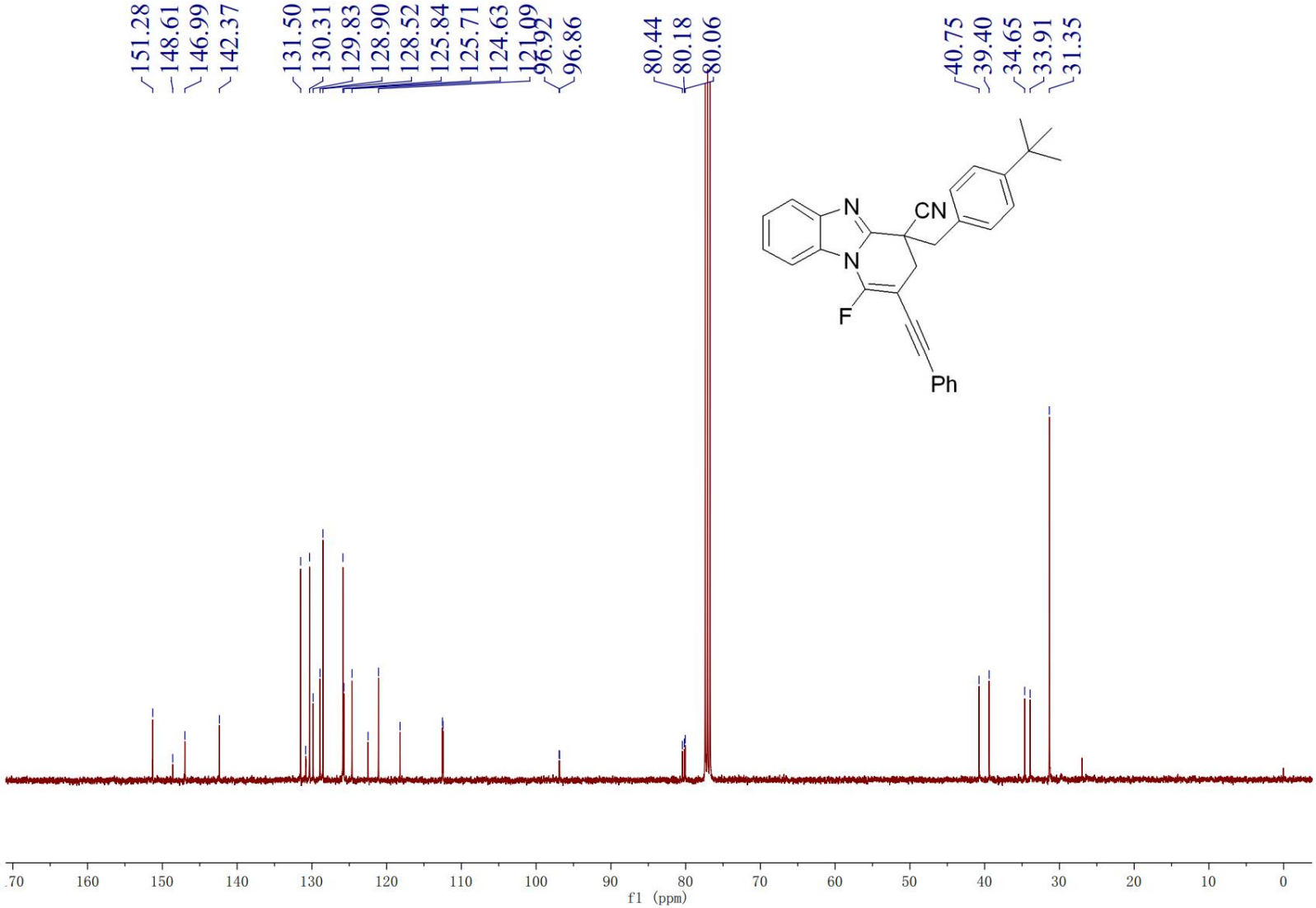
^{19}F NMR spectrum of **3d**



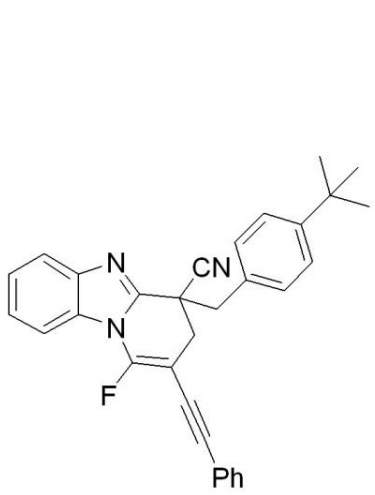
^{1}H NMR spectrum of **3e**



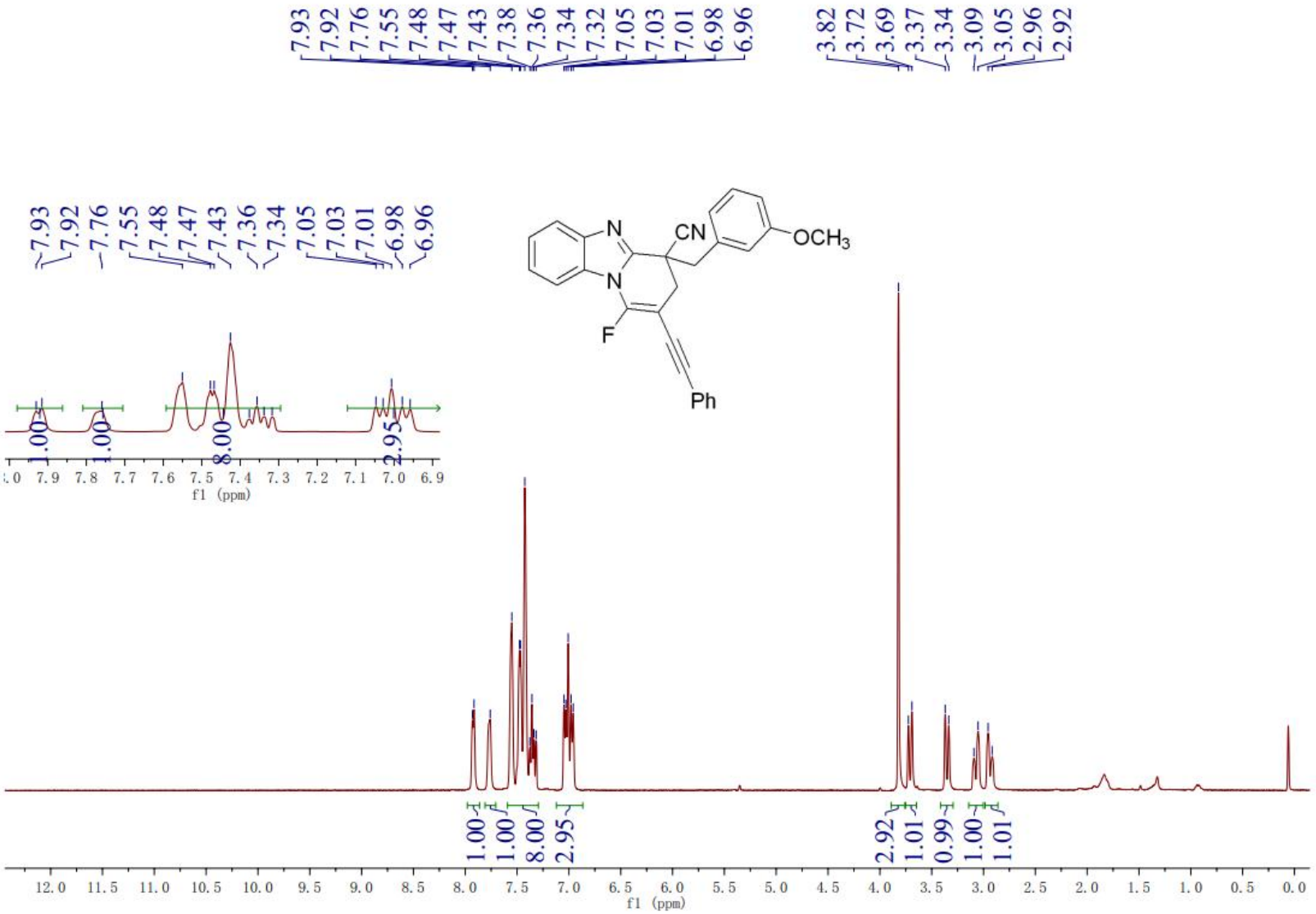
^{13}C NMR spectrum of **3e**



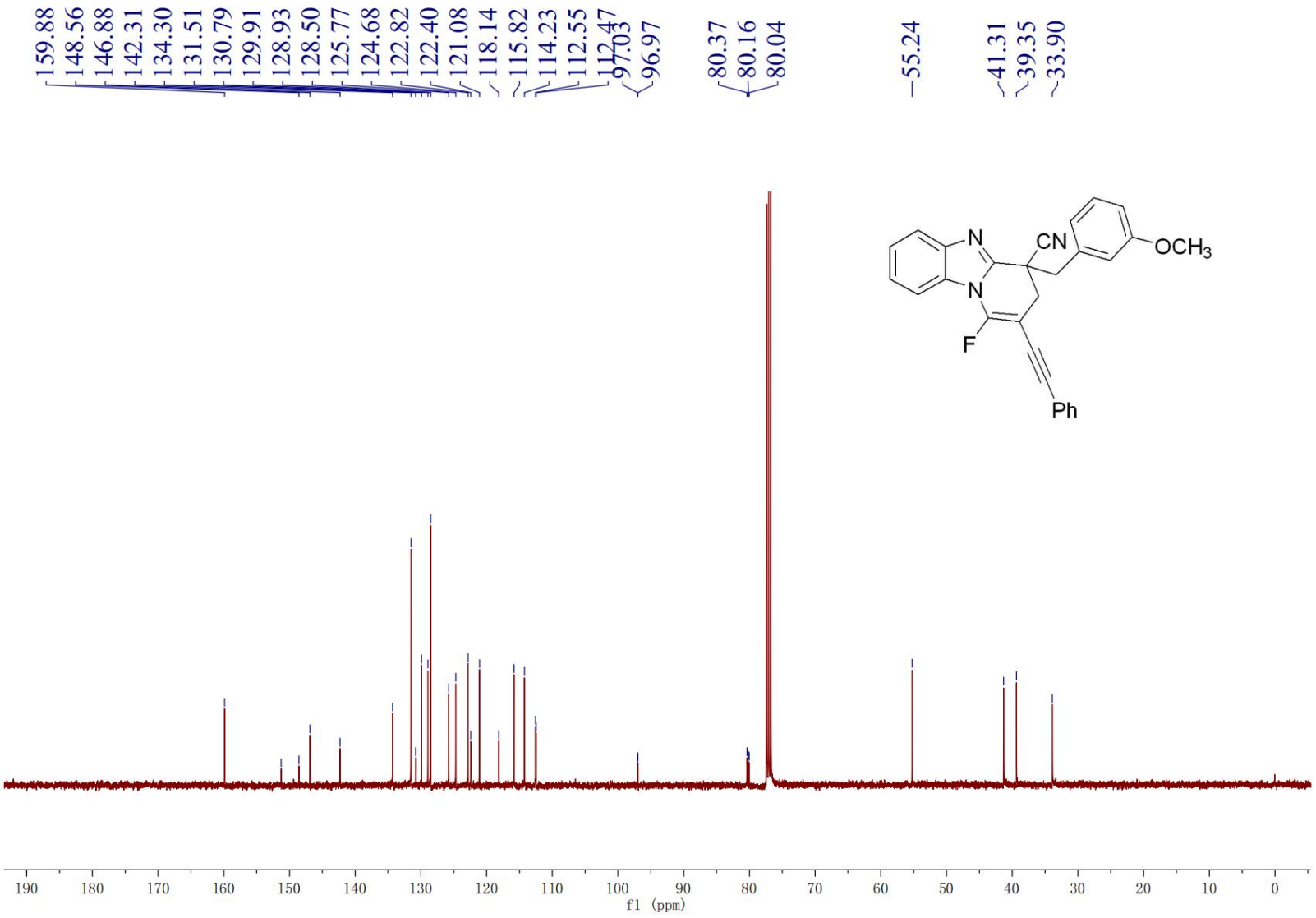
^{19}F NMR spectrum of **3e**



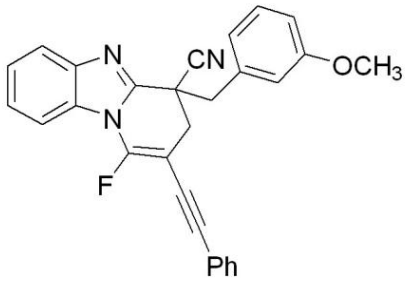
^{1}H NMR spectrum of **3f**



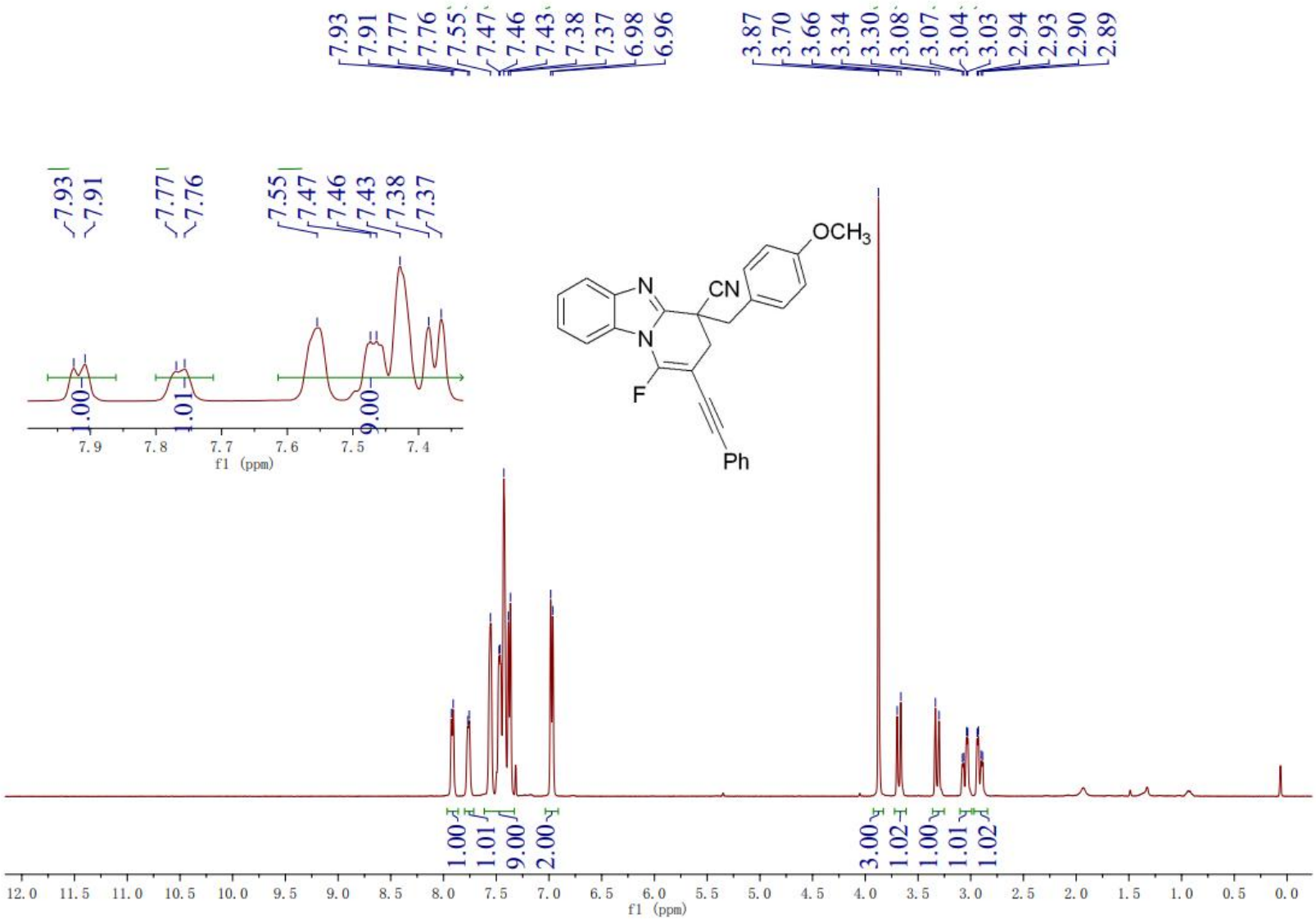
^{13}C NMR spectrum of **3f**



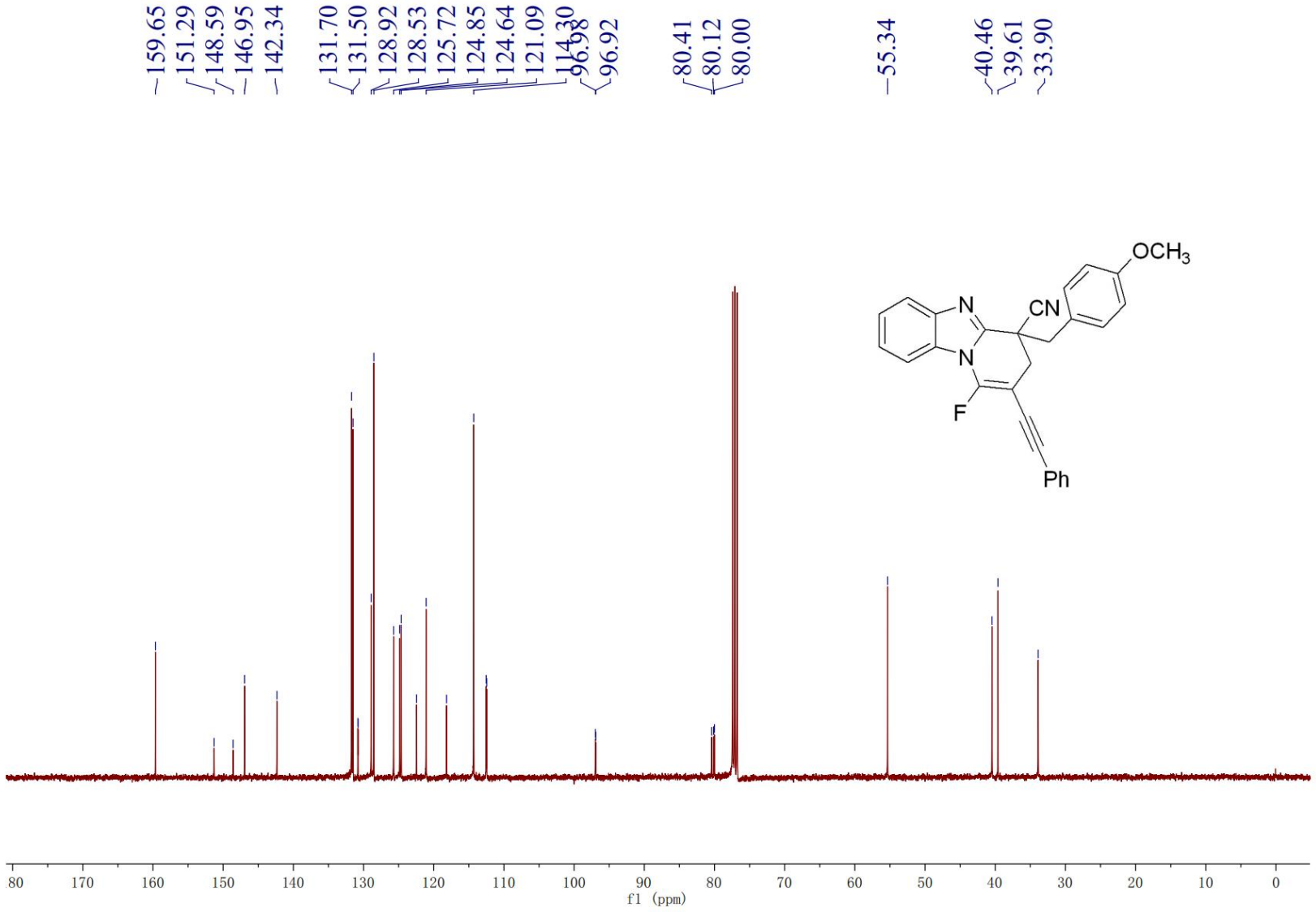
^{19}F NMR spectrum of **3f**



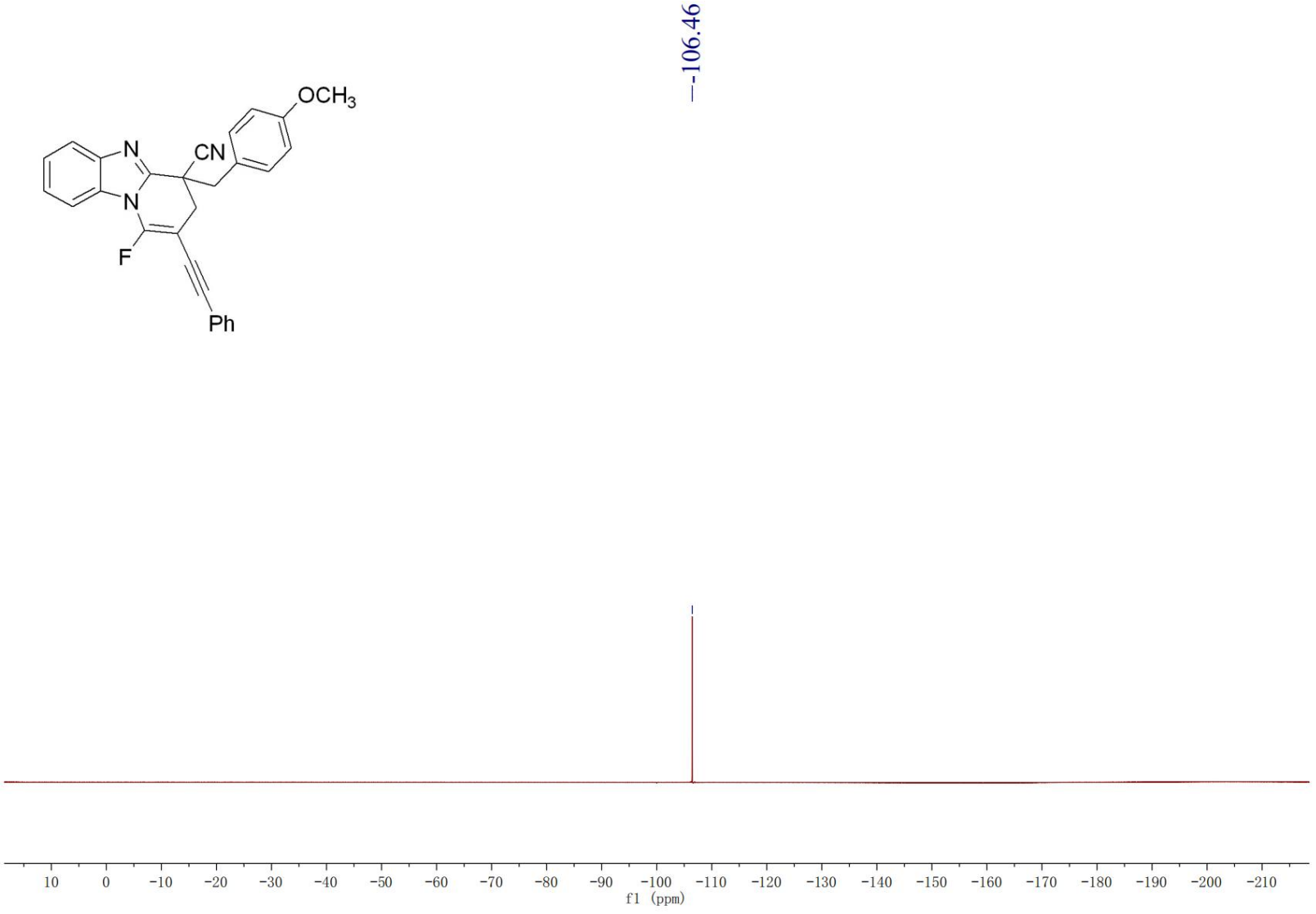
^{1}H NMR spectrum of **3g**



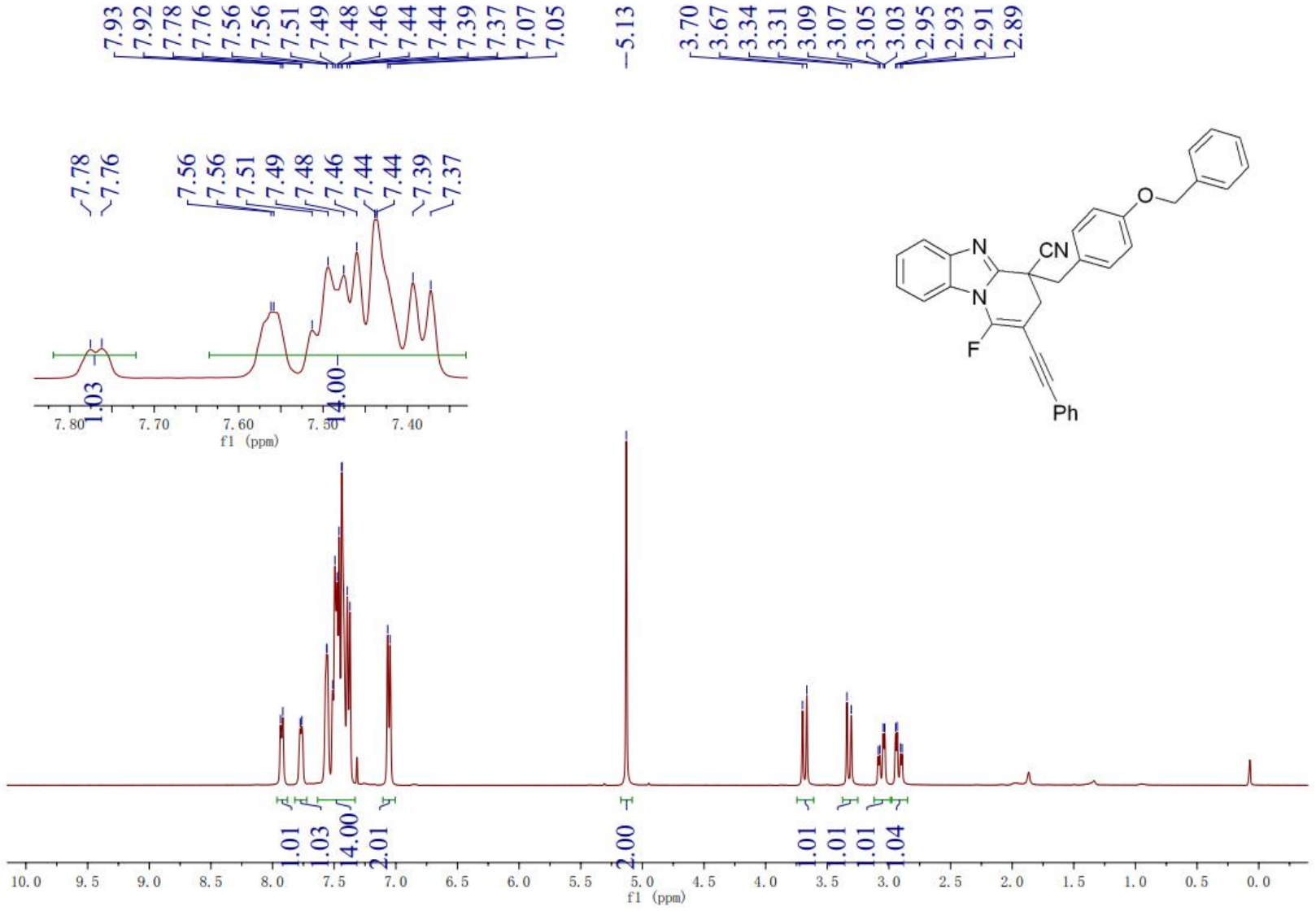
^{13}C NMR spectrum of **3g**



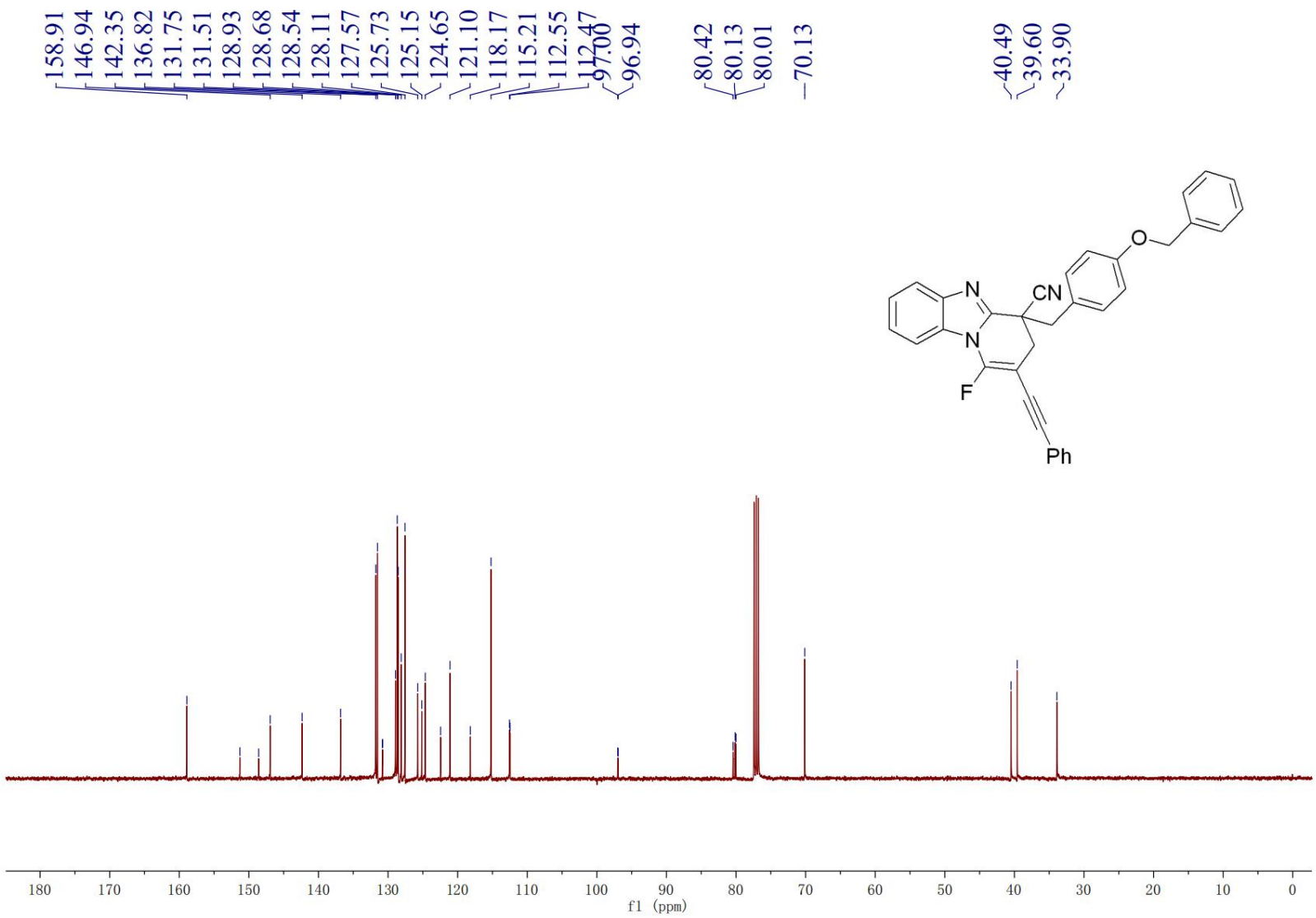
^{19}F NMR spectrum of **3g**



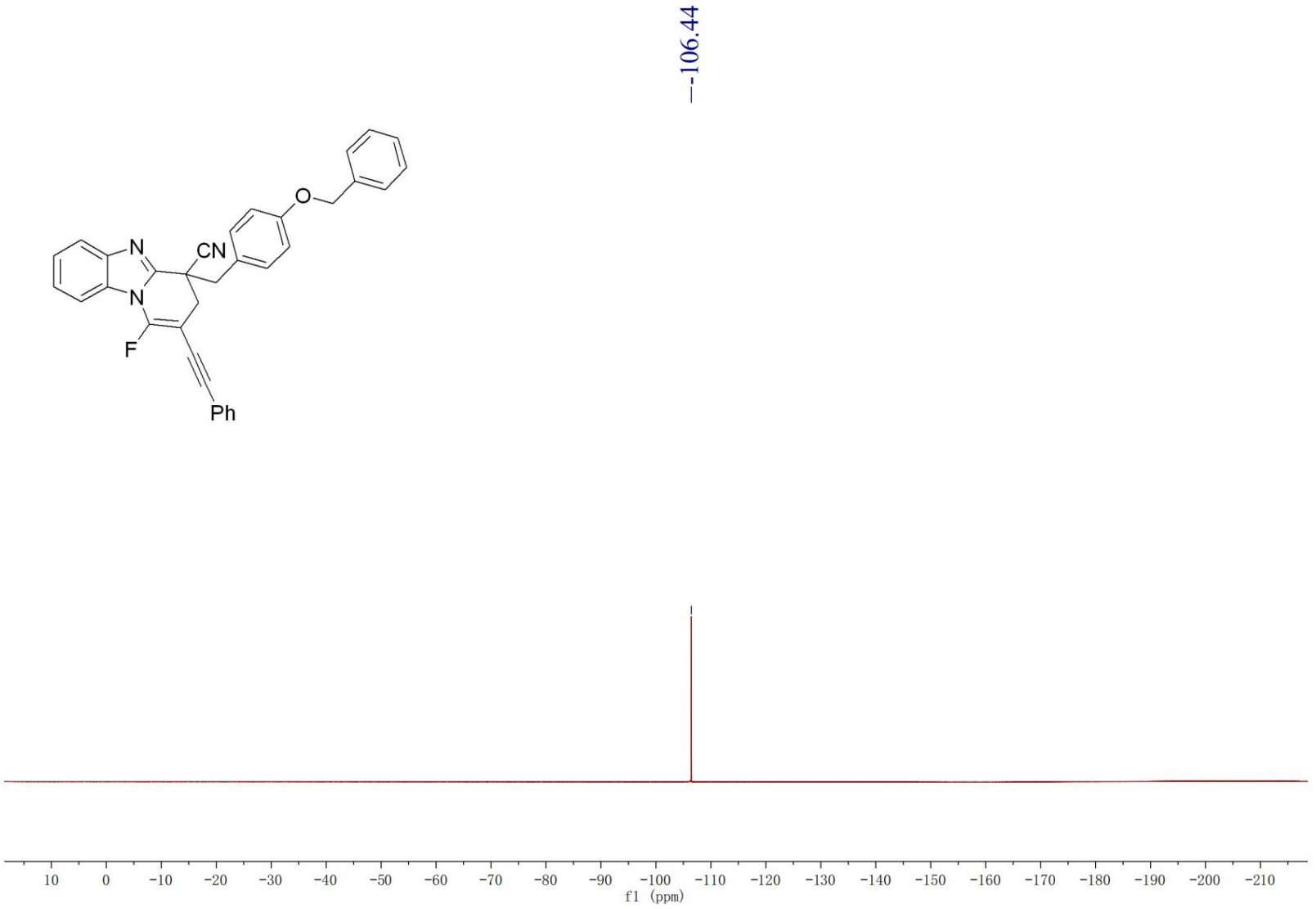
^{1}H NMR spectrum of **3h**



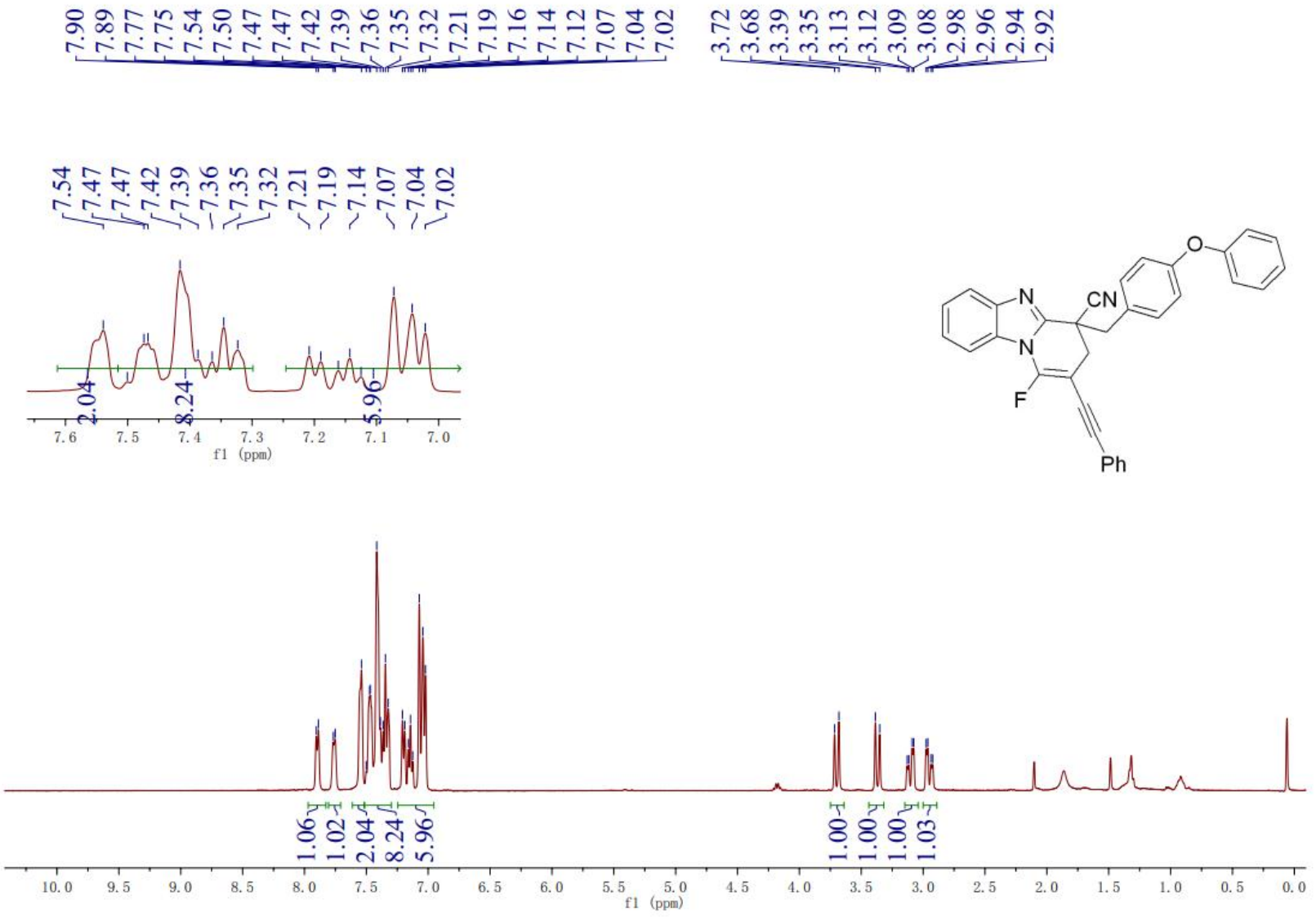
^{13}C NMR spectrum of **3h**



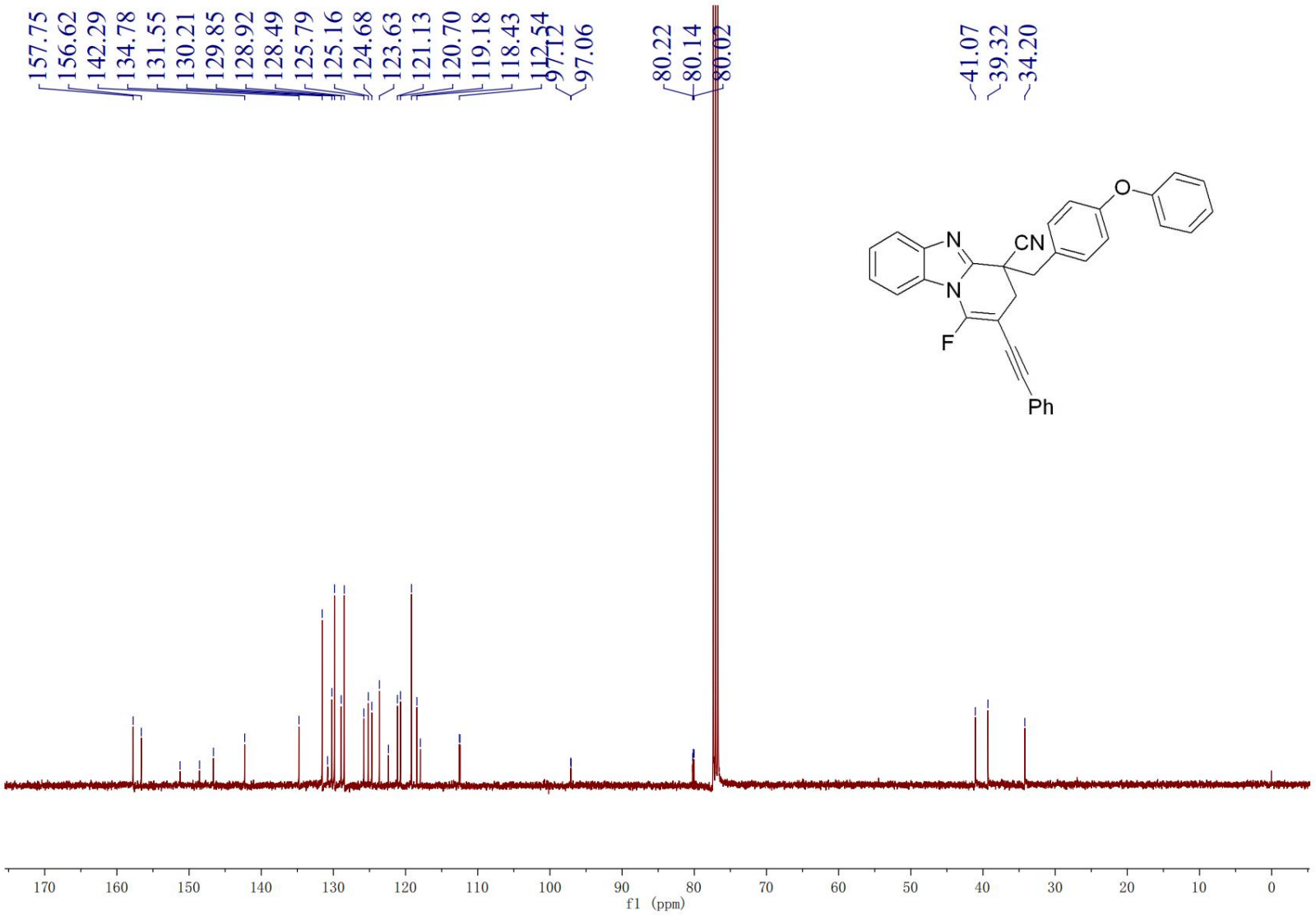
^{19}F NMR spectrum of **3h**



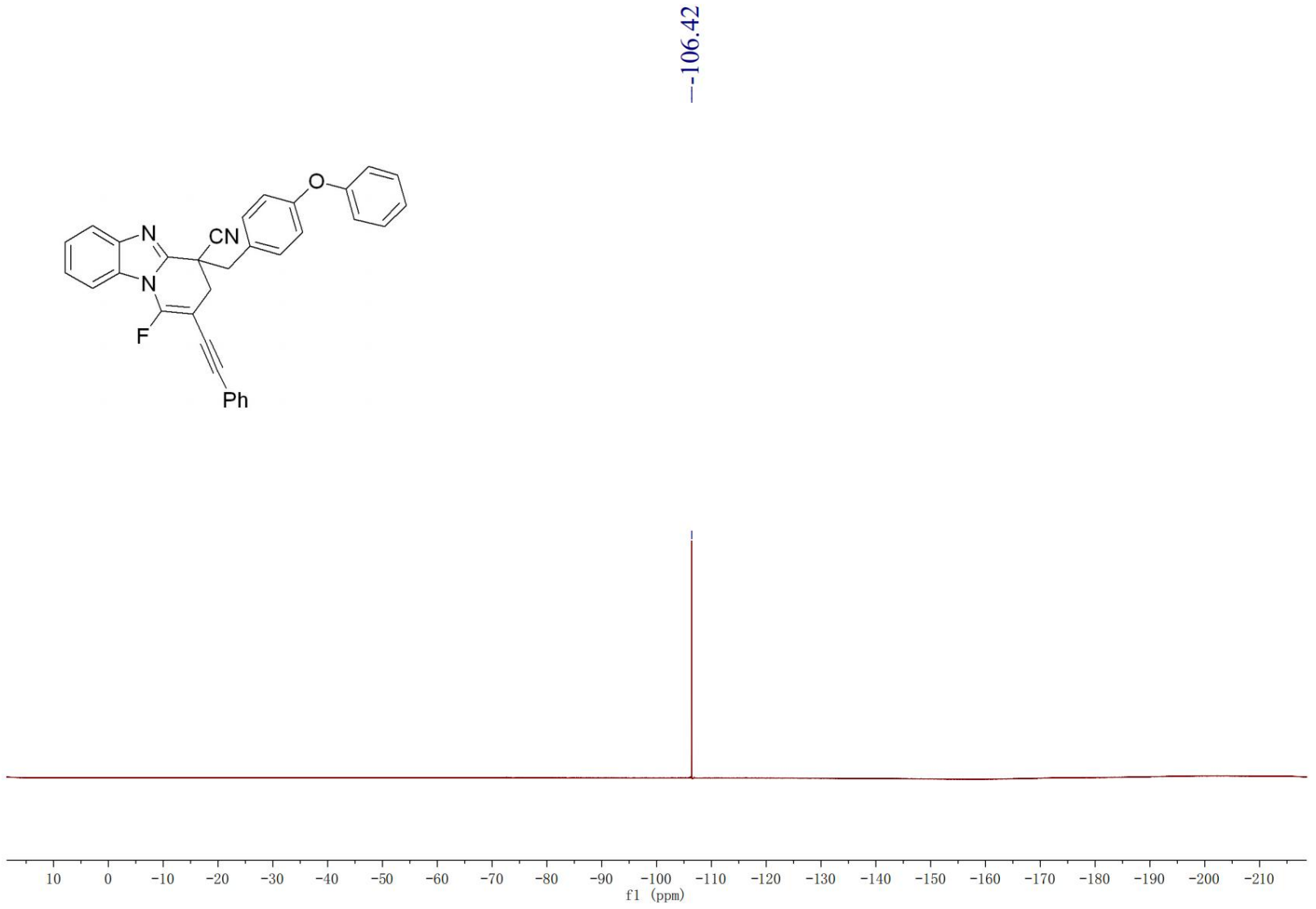
^{1}H NMR spectrum of **3i**



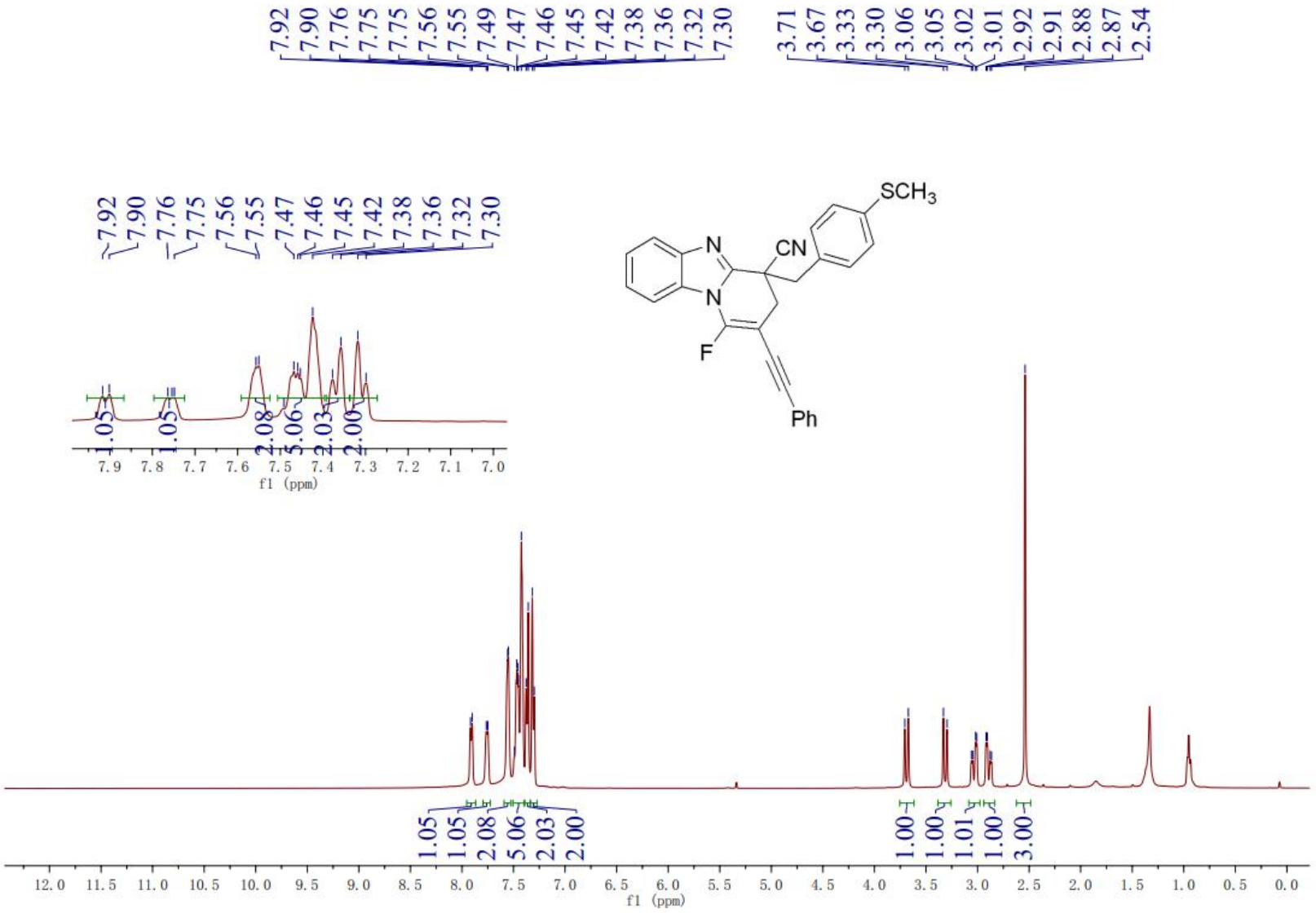
^{13}C NMR spectrum of **3i**



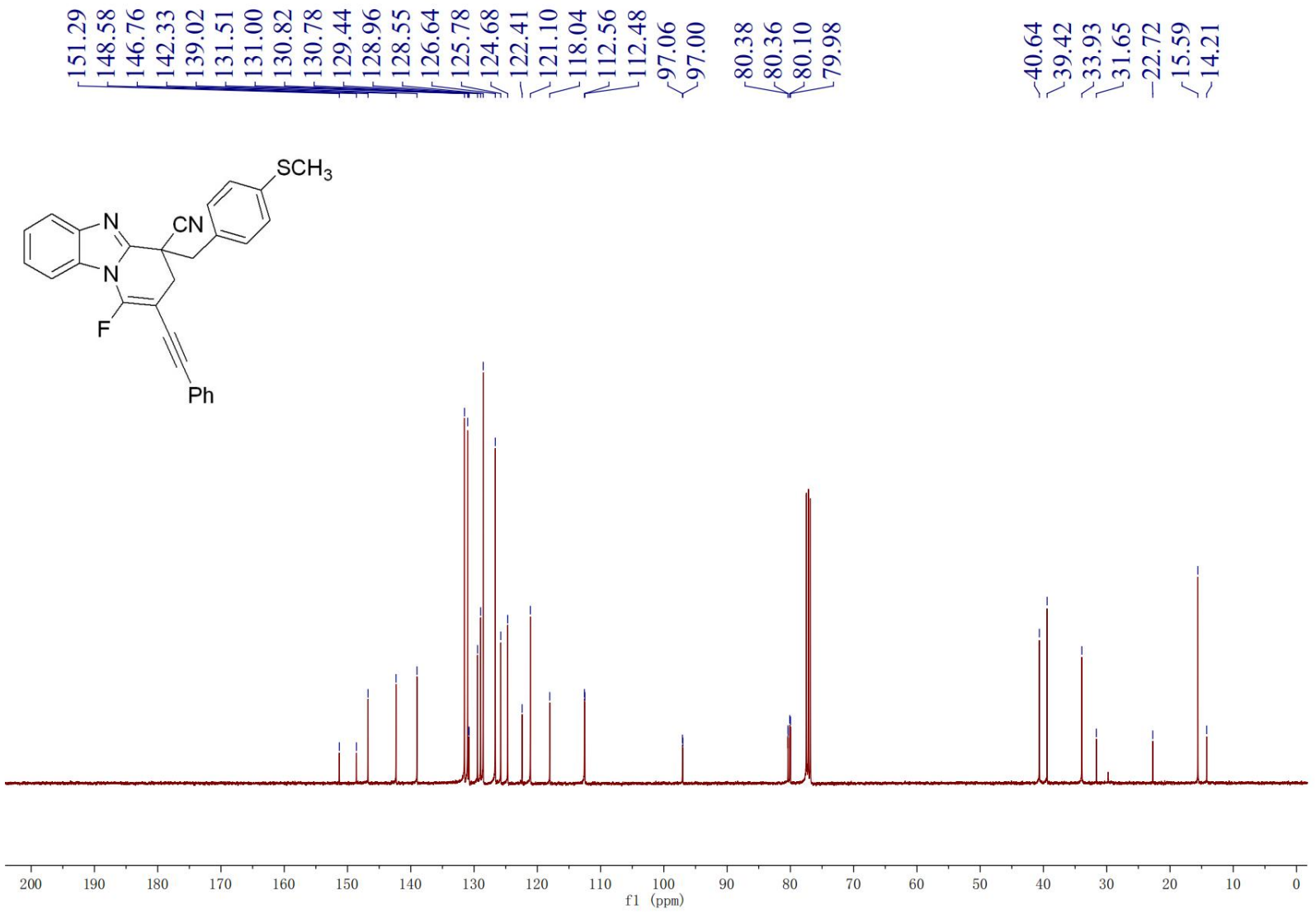
^{19}F NMR spectrum of **3i**



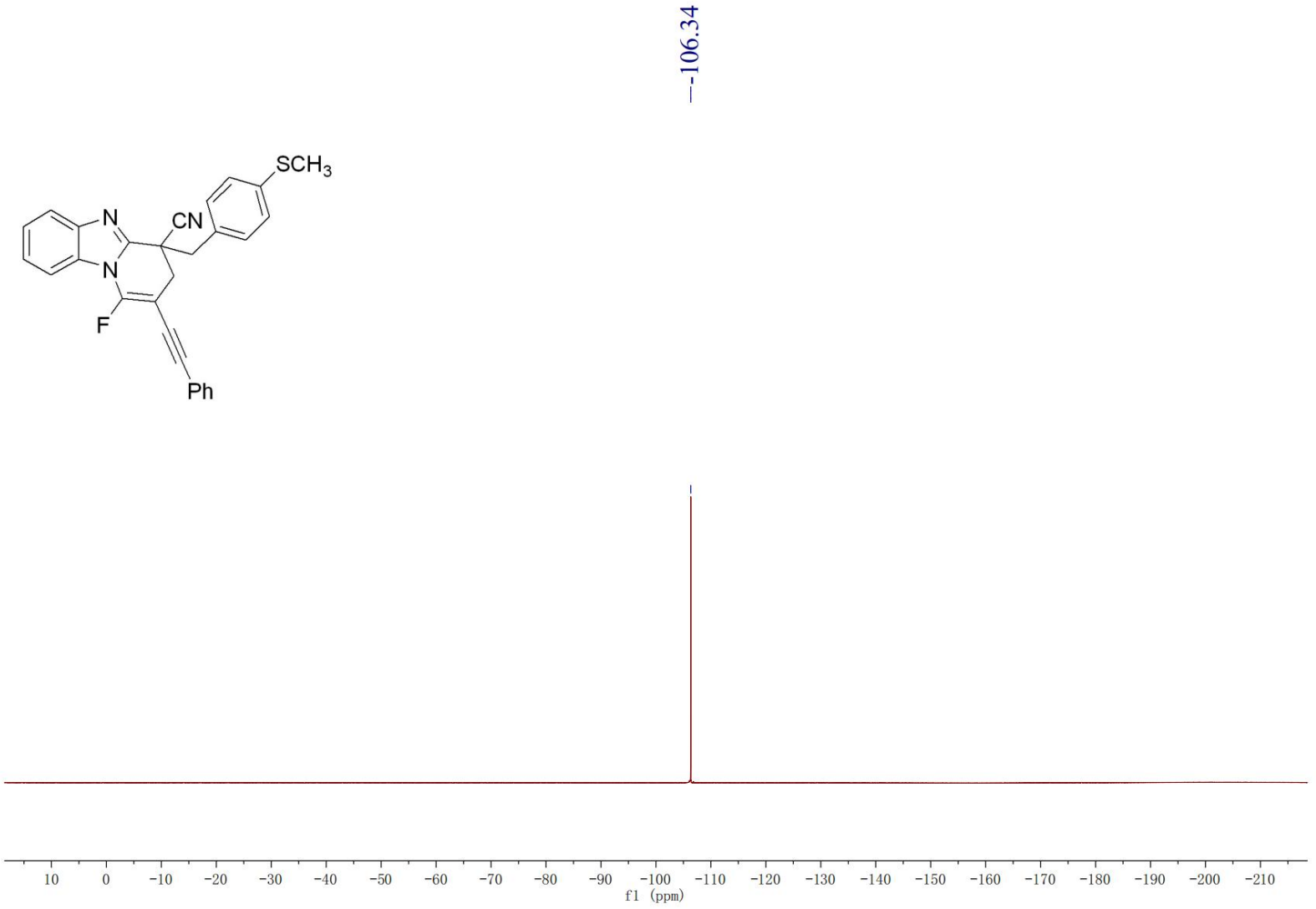
^{1}H NMR spectrum of **3j**



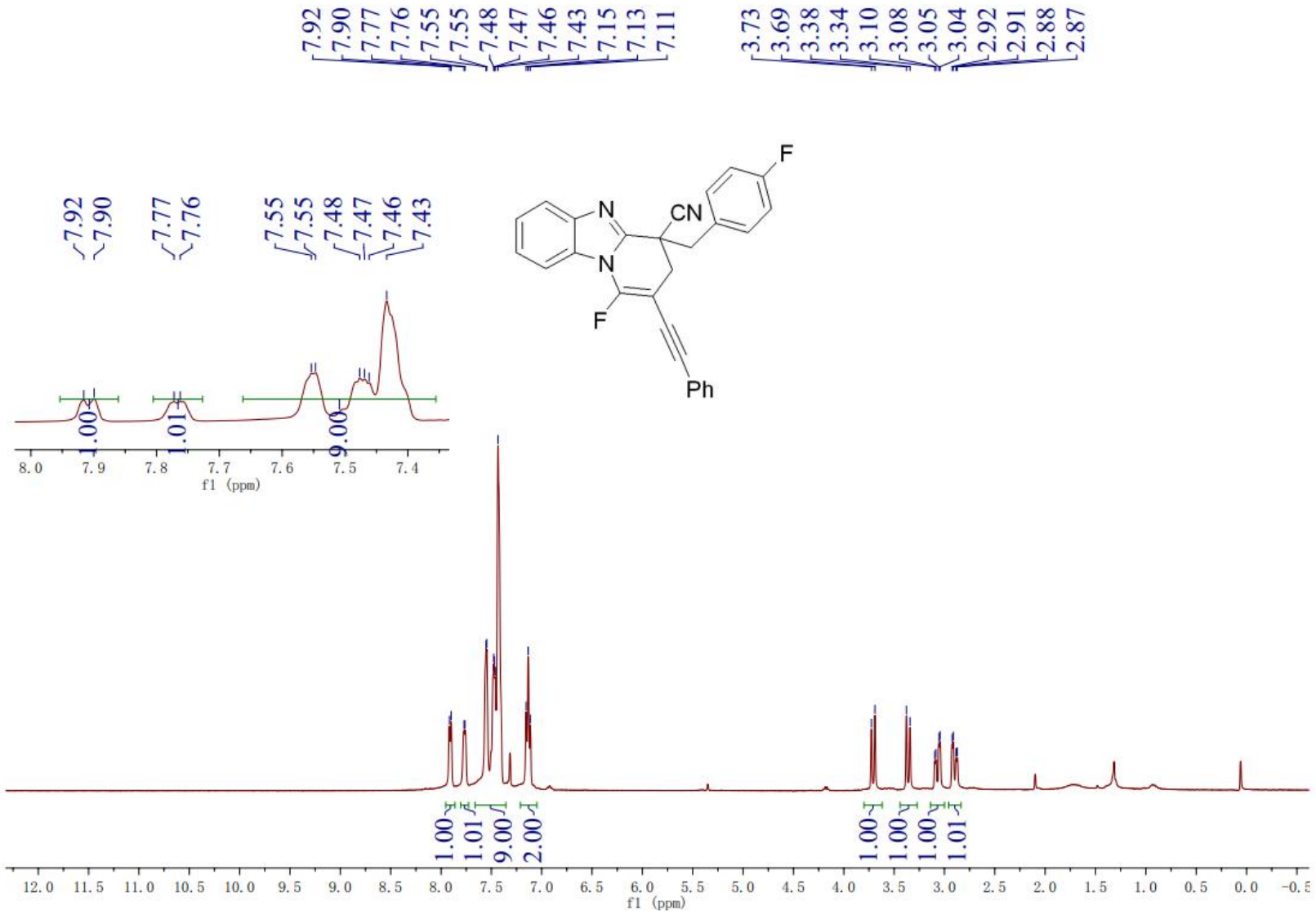
^{13}C NMR spectrum of **3j**



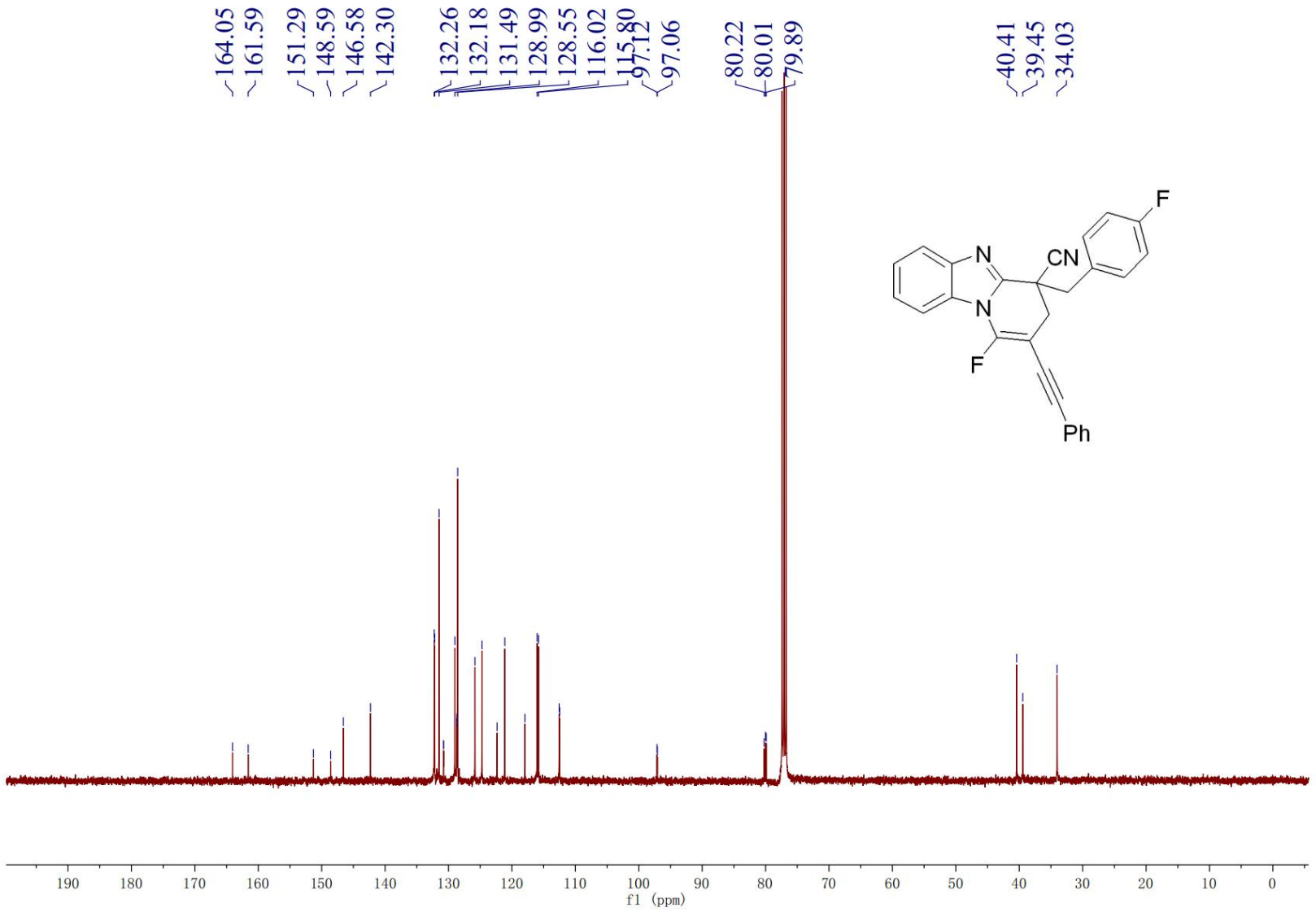
^{19}F NMR spectrum of **3j**



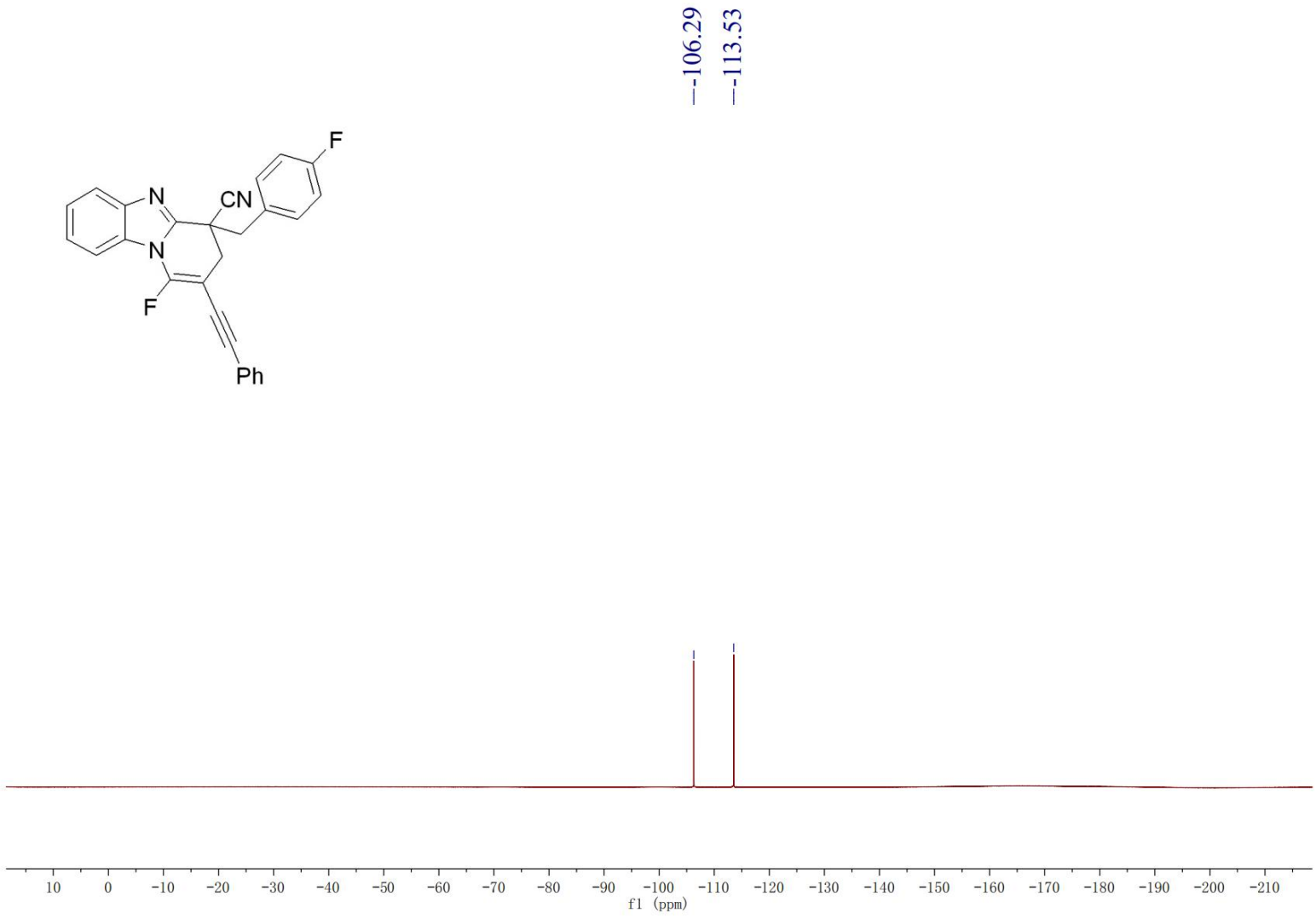
^{1}H NMR spectrum of **3k**



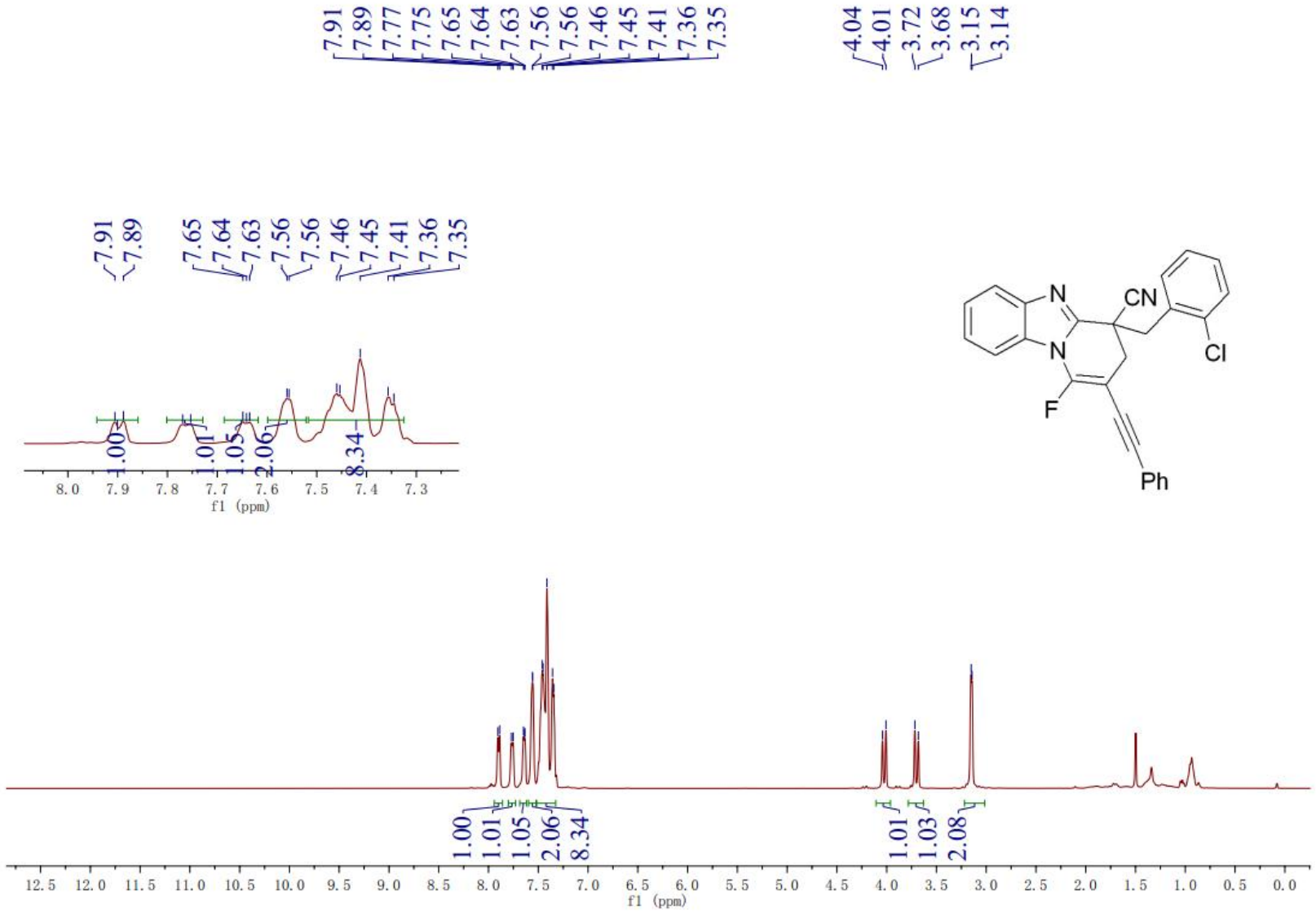
^{13}C NMR spectrum of **3k**



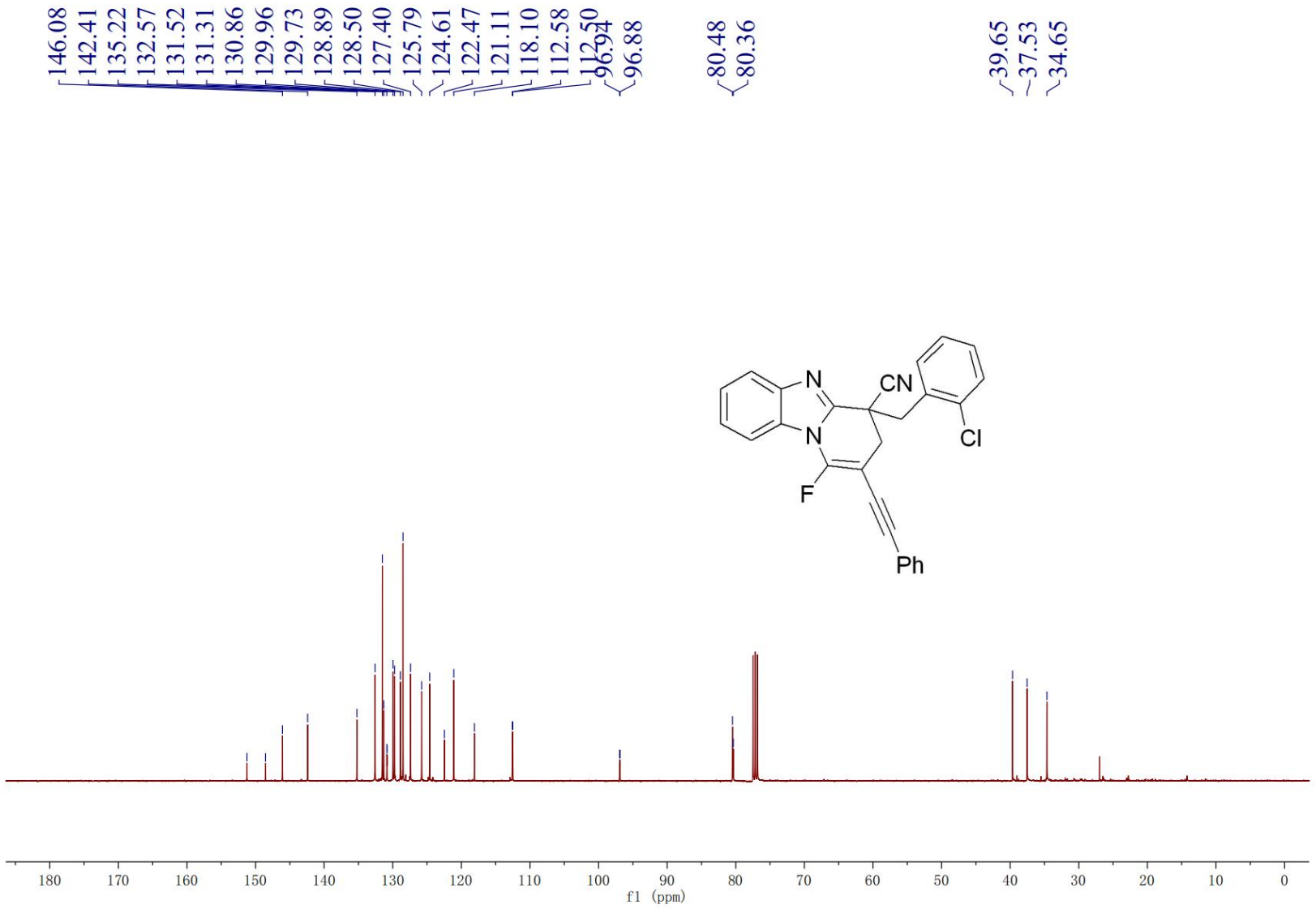
^{19}F NMR spectrum of **3k**



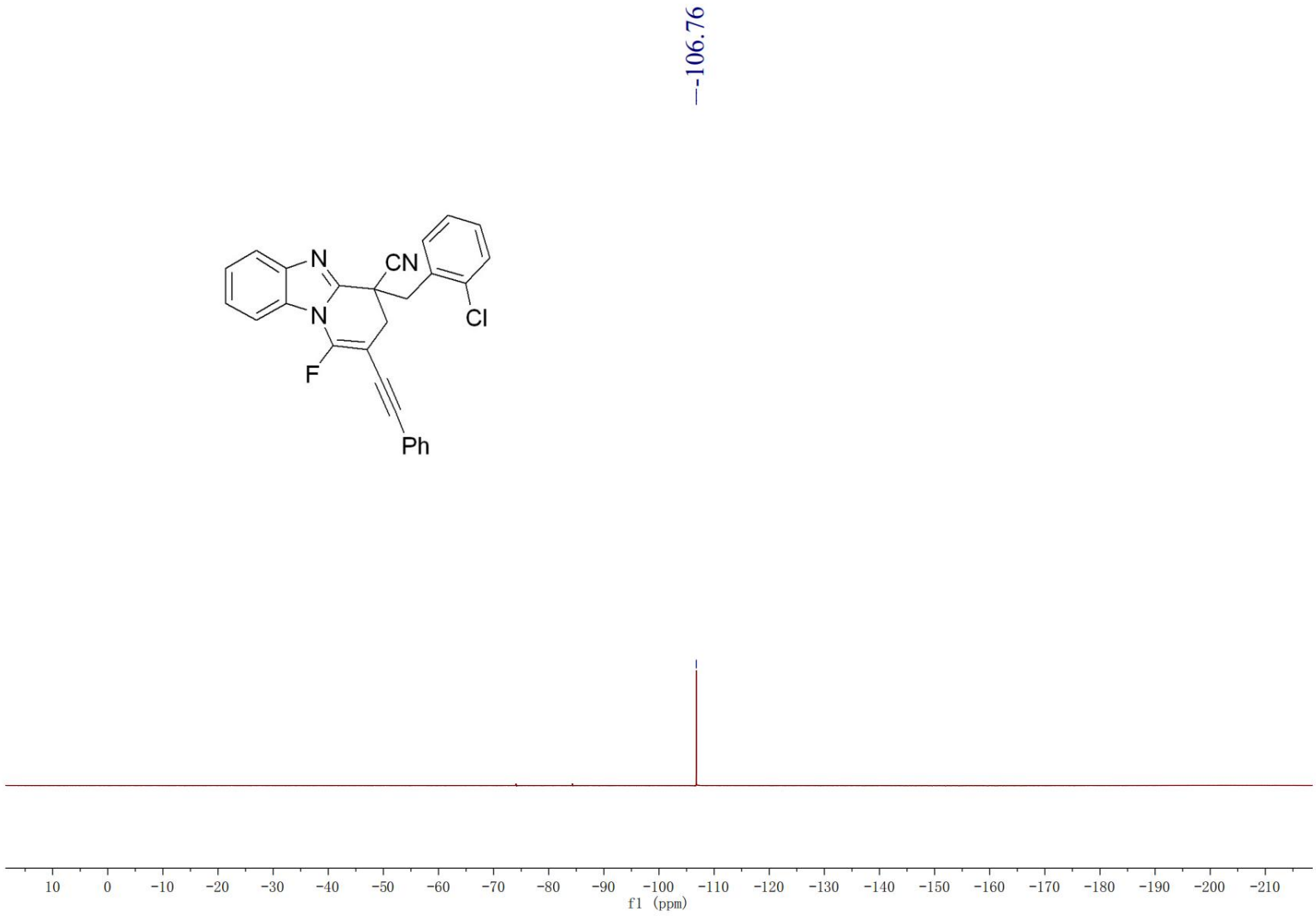
^{1}H NMR spectrum of **3l**



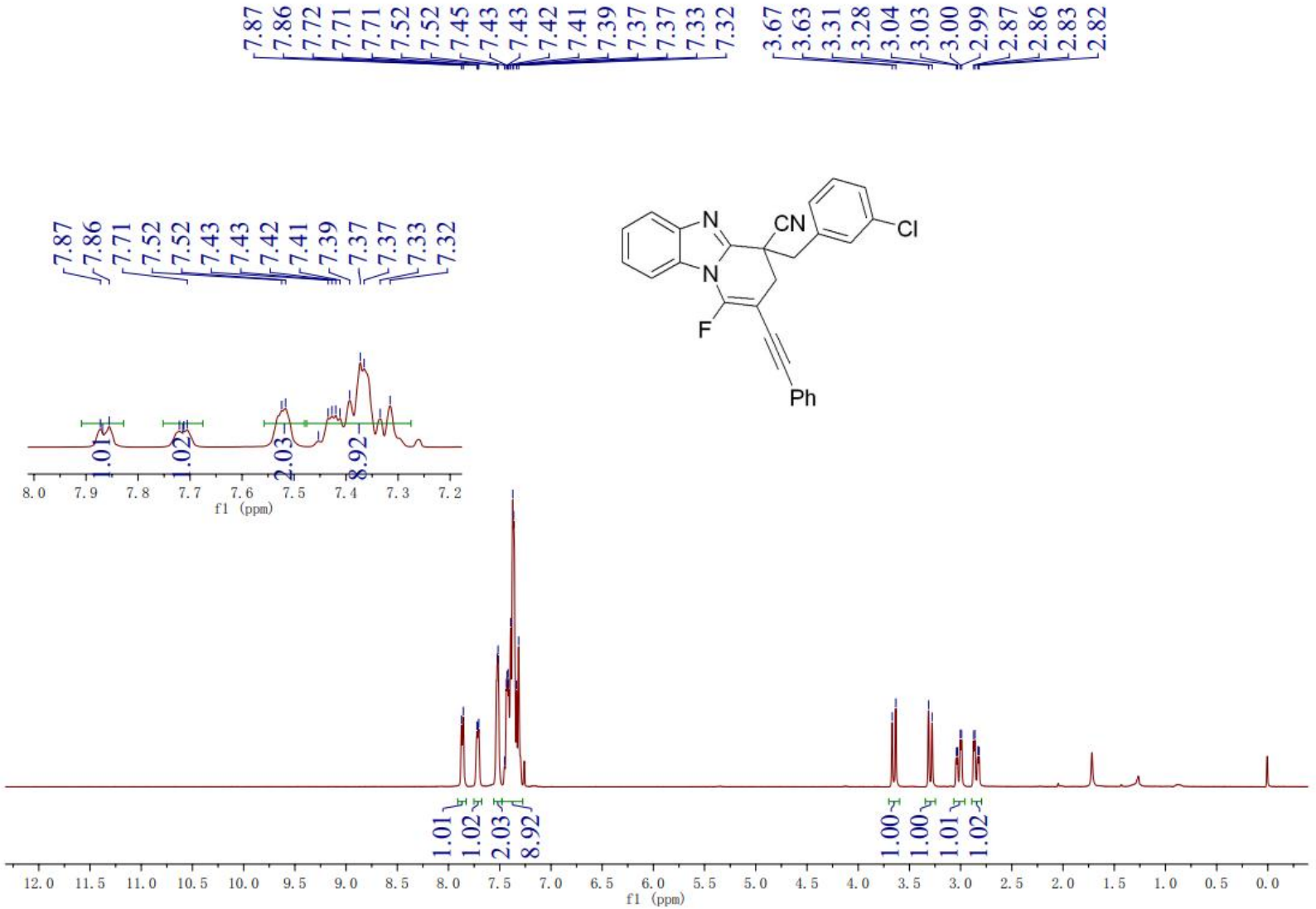
^{13}C NMR spectrum of **3l**



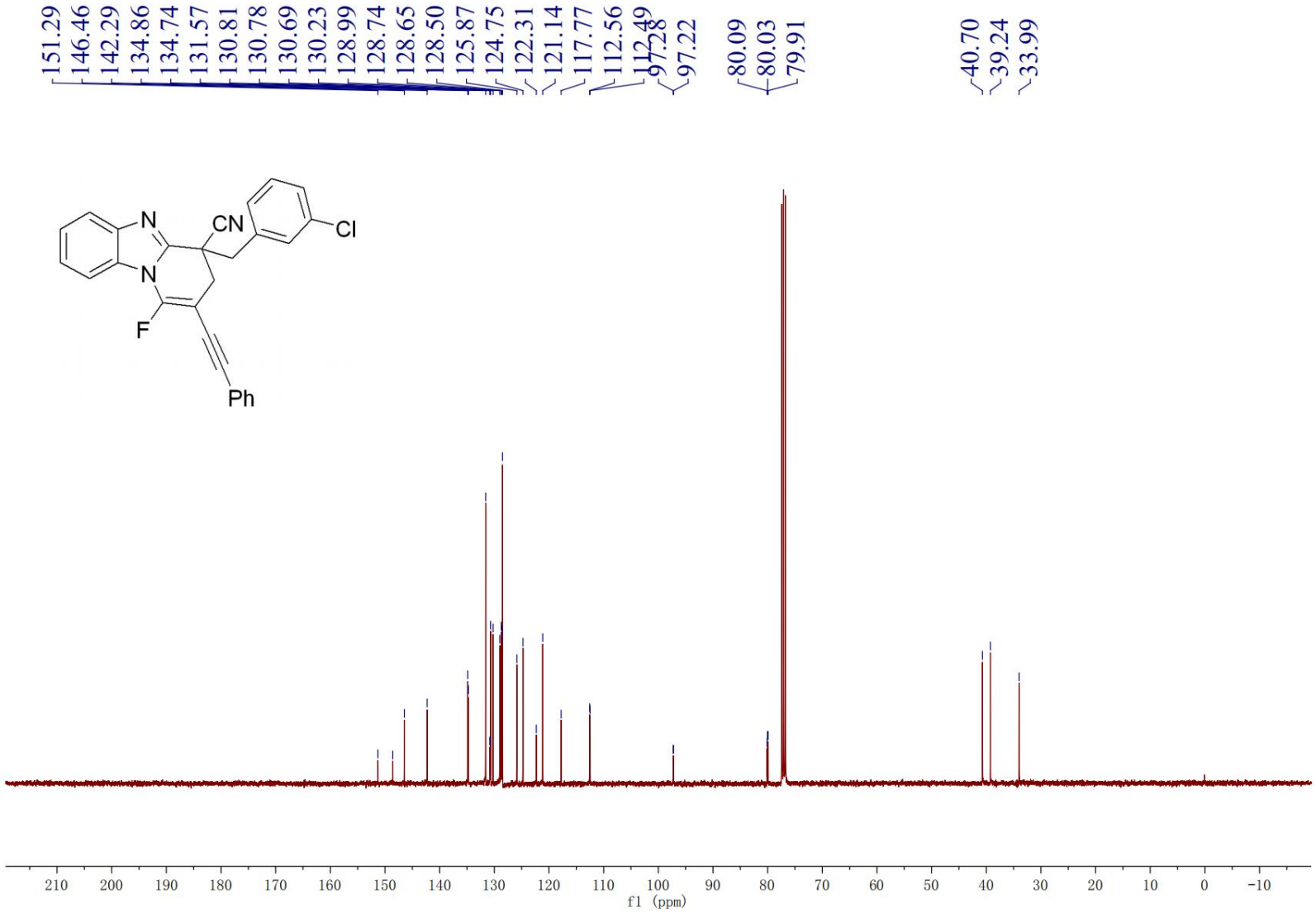
^{19}F NMR spectrum of **3l**



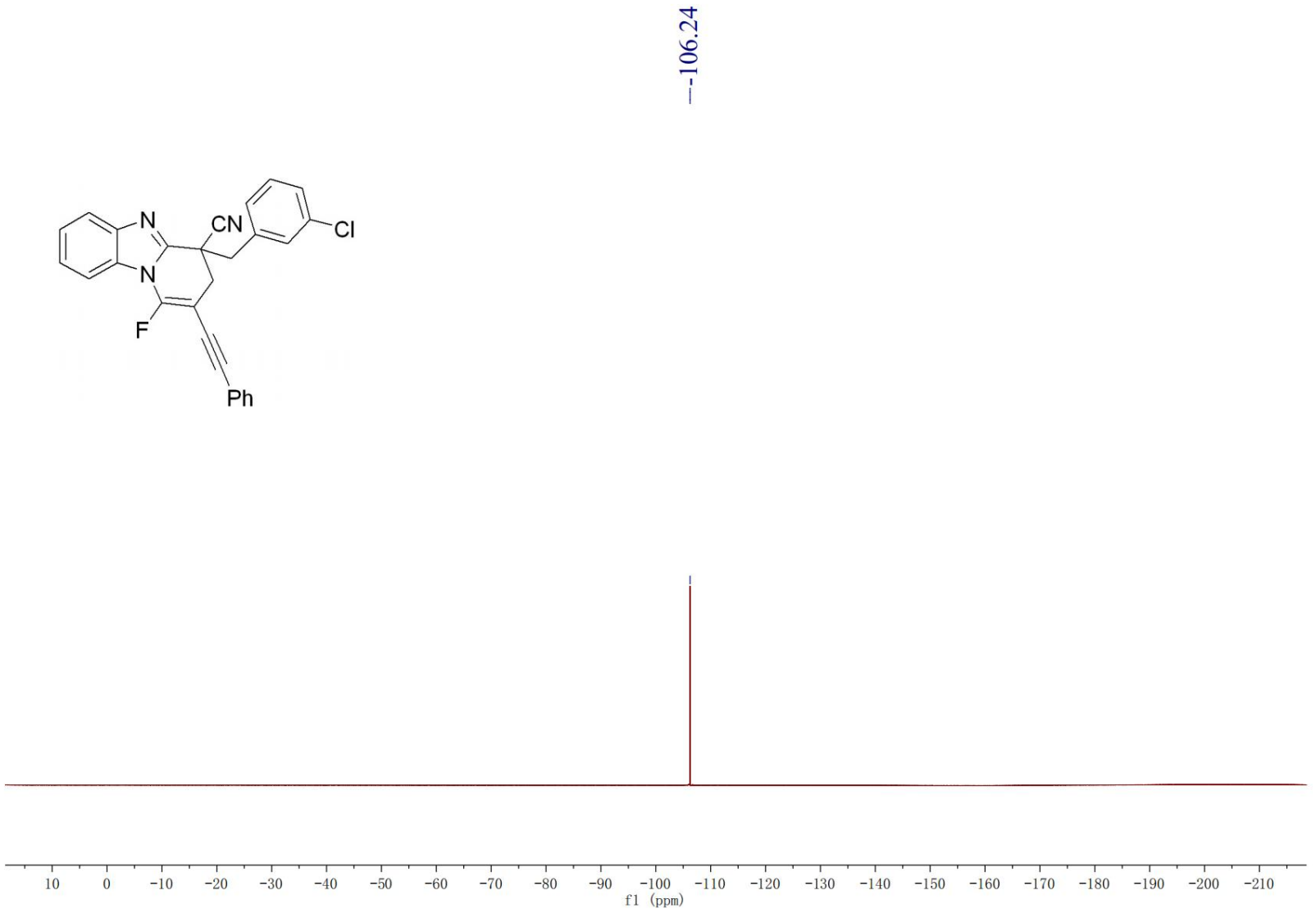
^{1}H NMR spectrum of **3m**



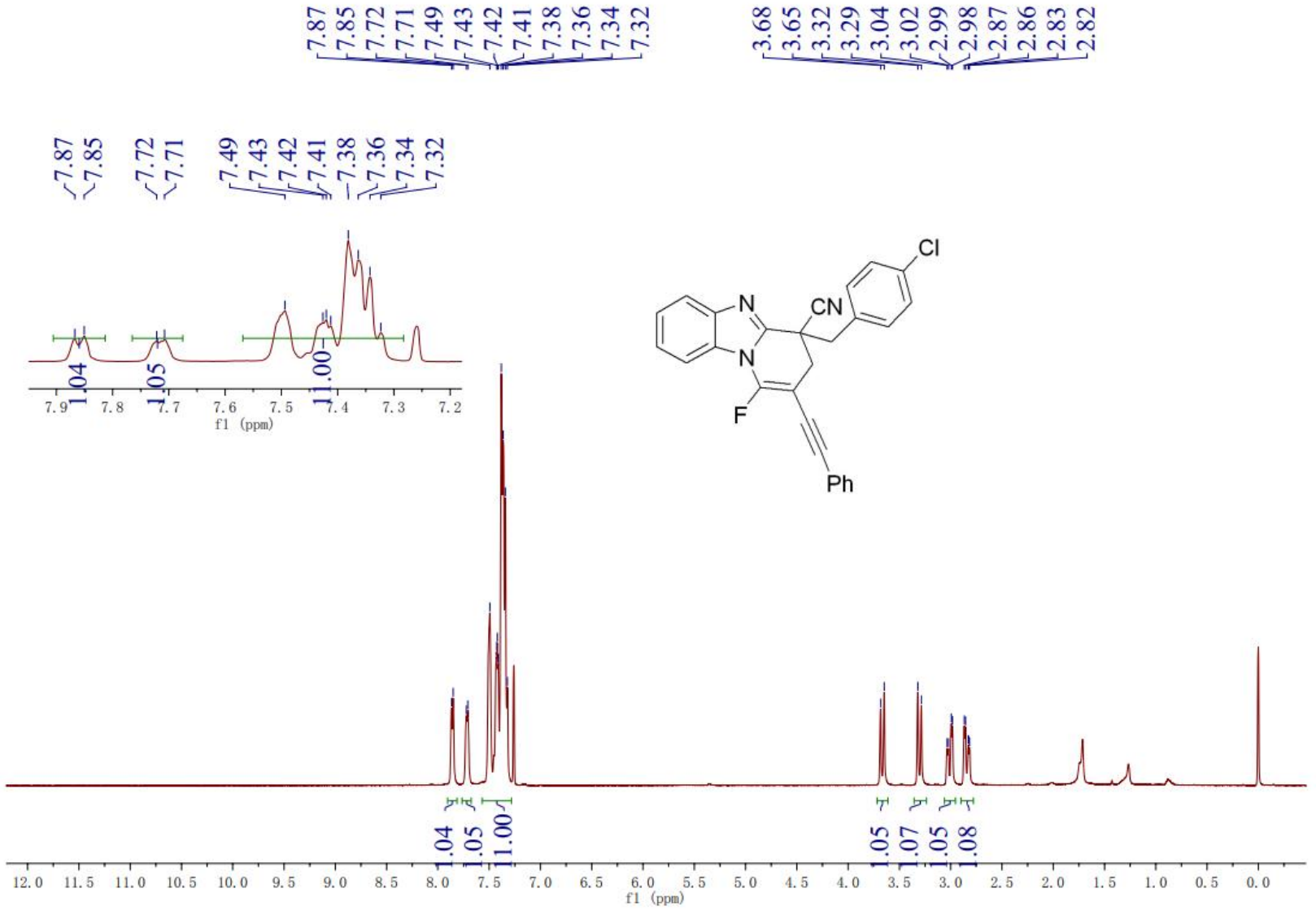
^{13}C NMR spectrum of **3m**



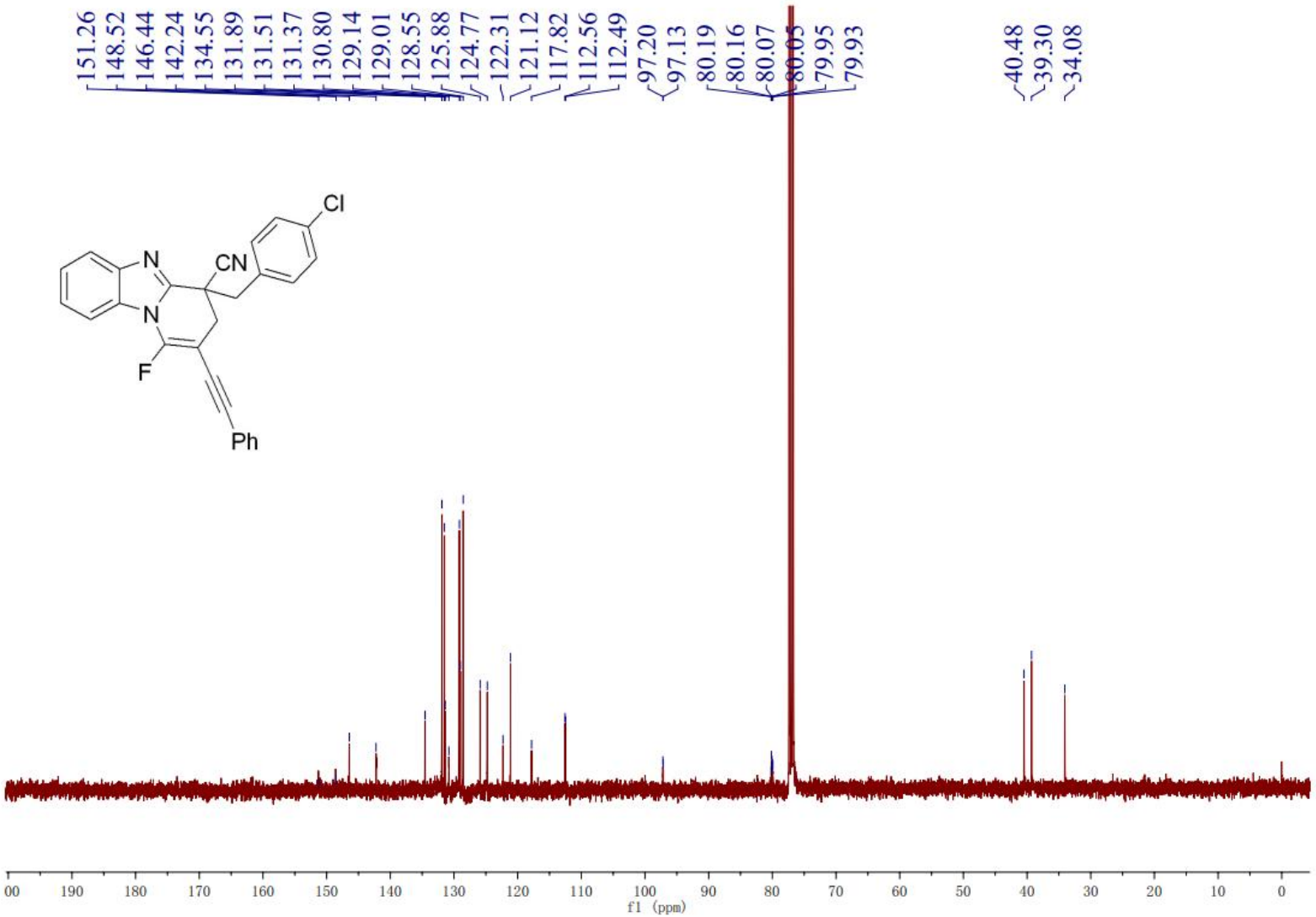
^{19}F NMR spectrum of **3m**



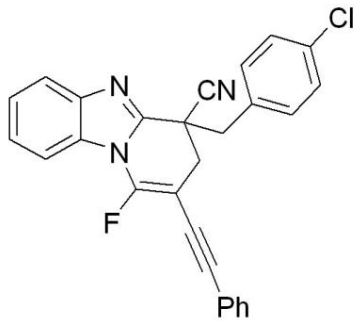
^{1}H NMR spectrum of **3n**



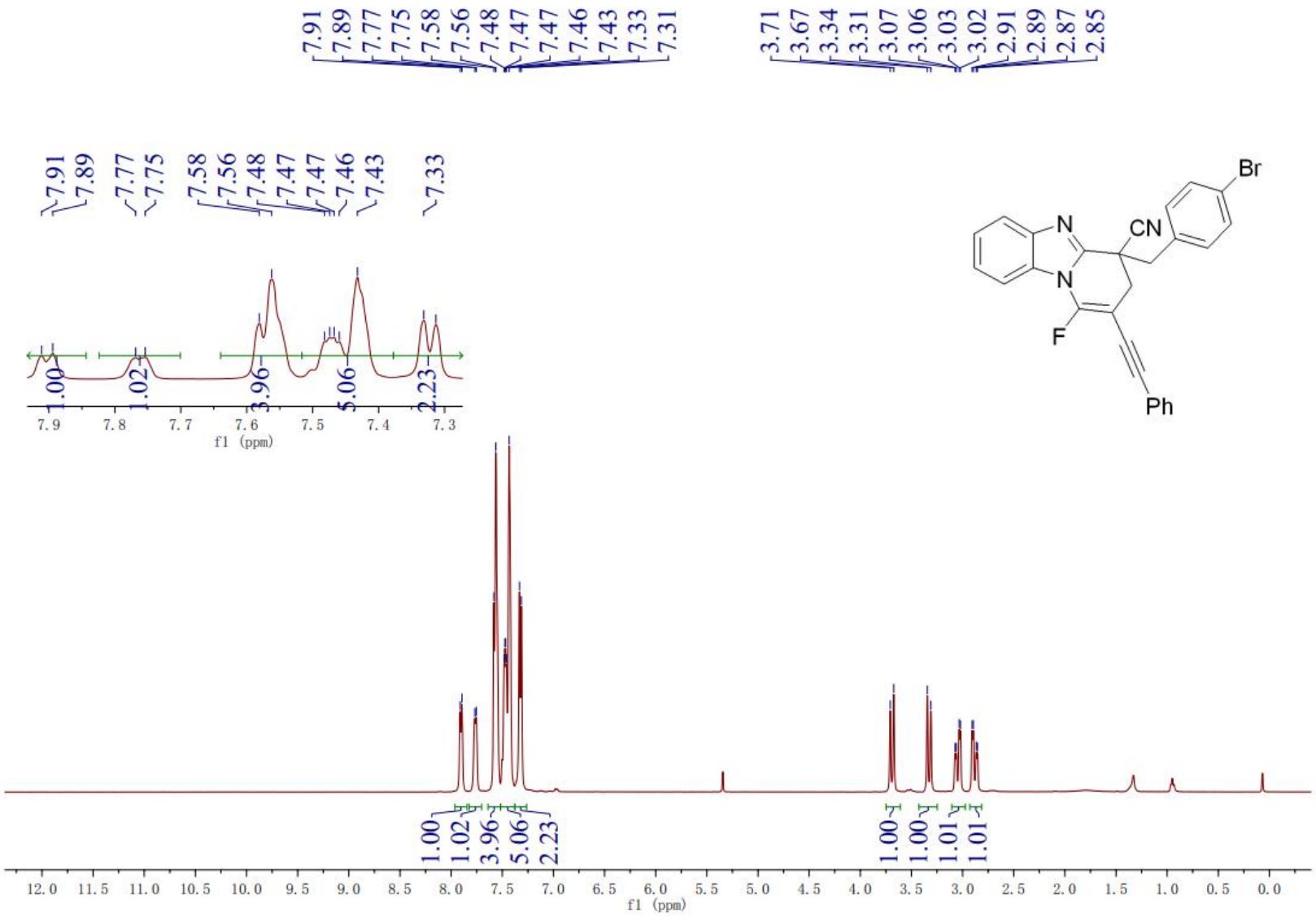
^{13}C NMR spectrum of **3n**



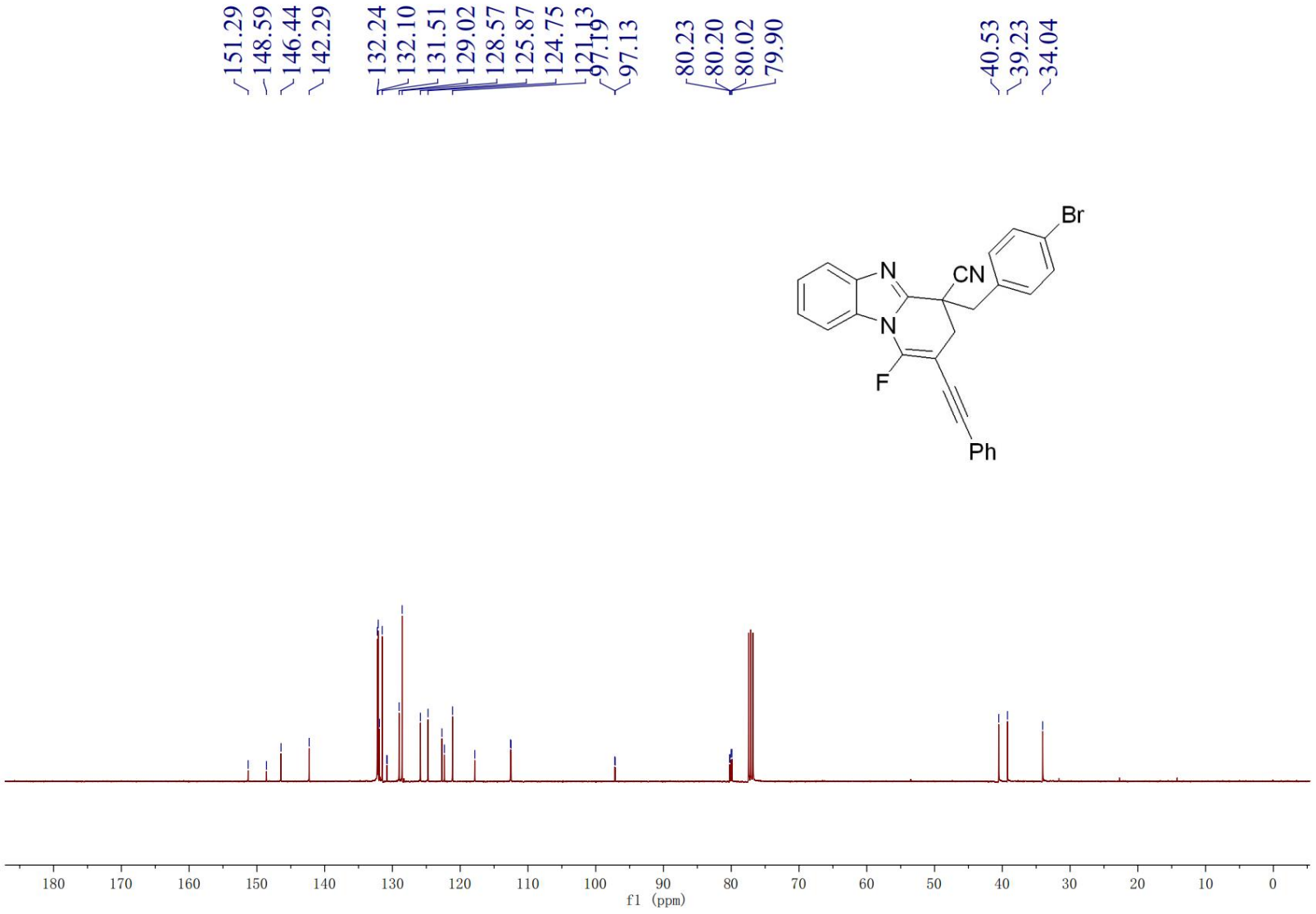
^{19}F NMR spectrum of **3n**



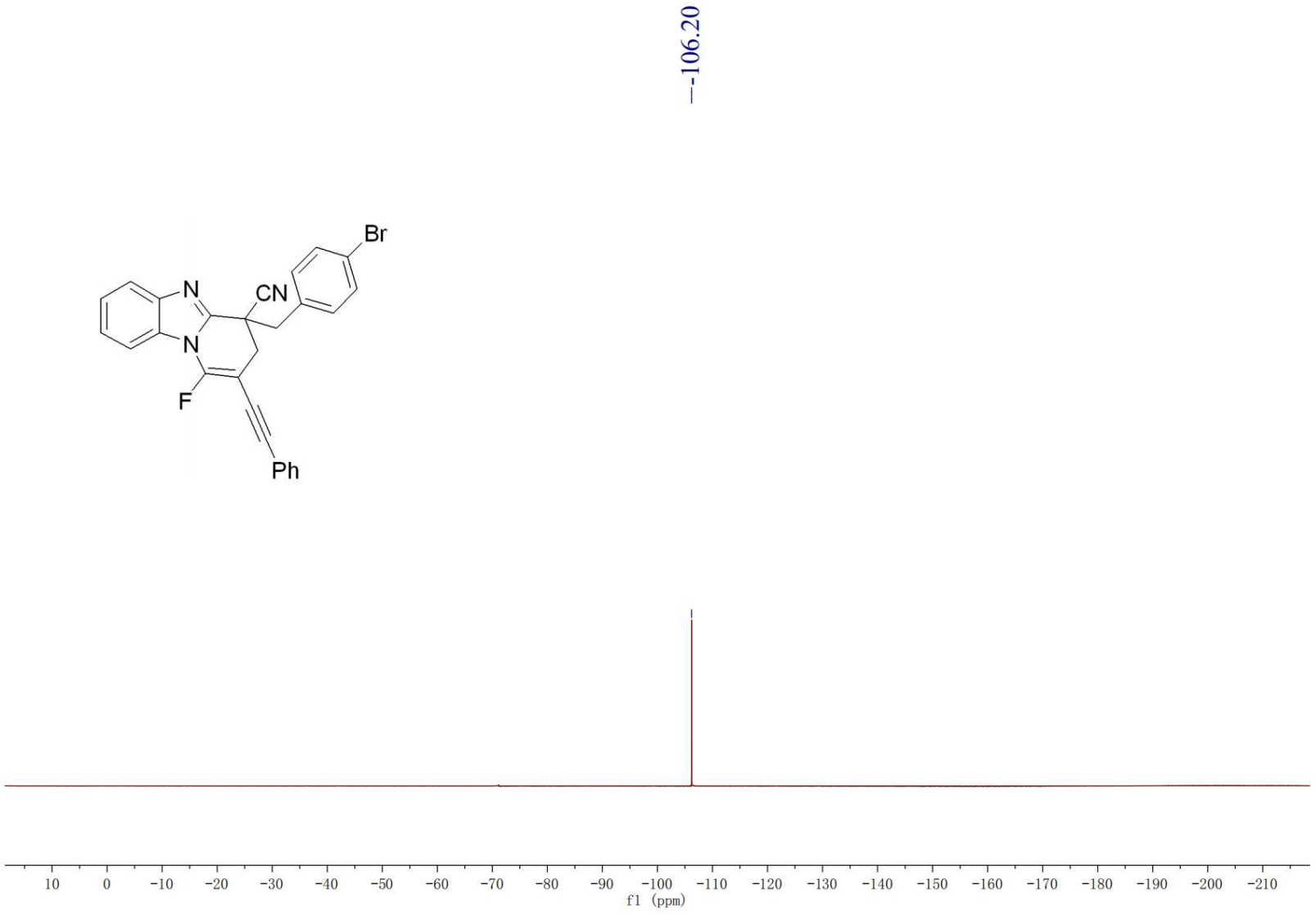
^{1}H NMR spectrum of **3o**



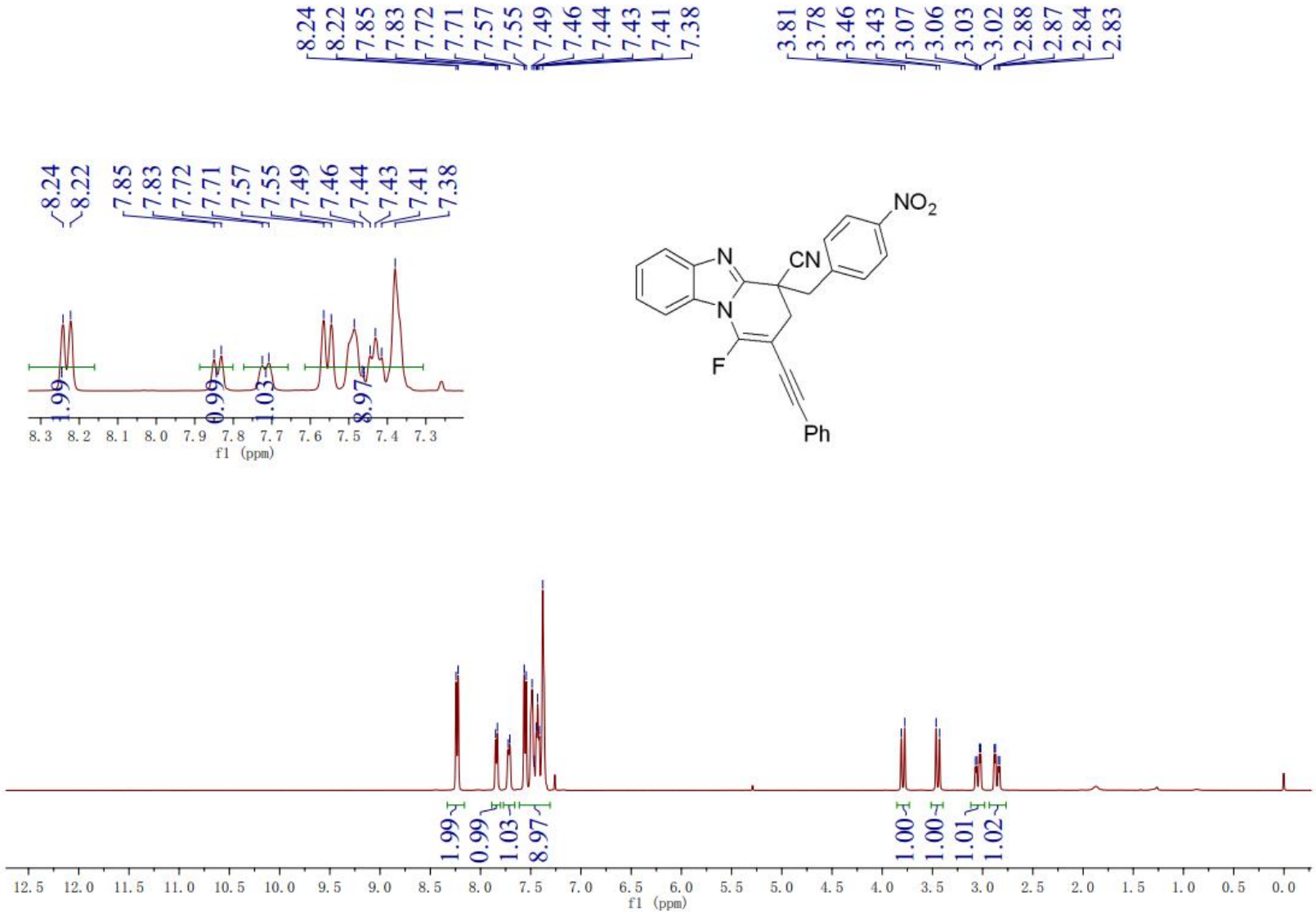
^{13}C NMR spectrum of **3o**



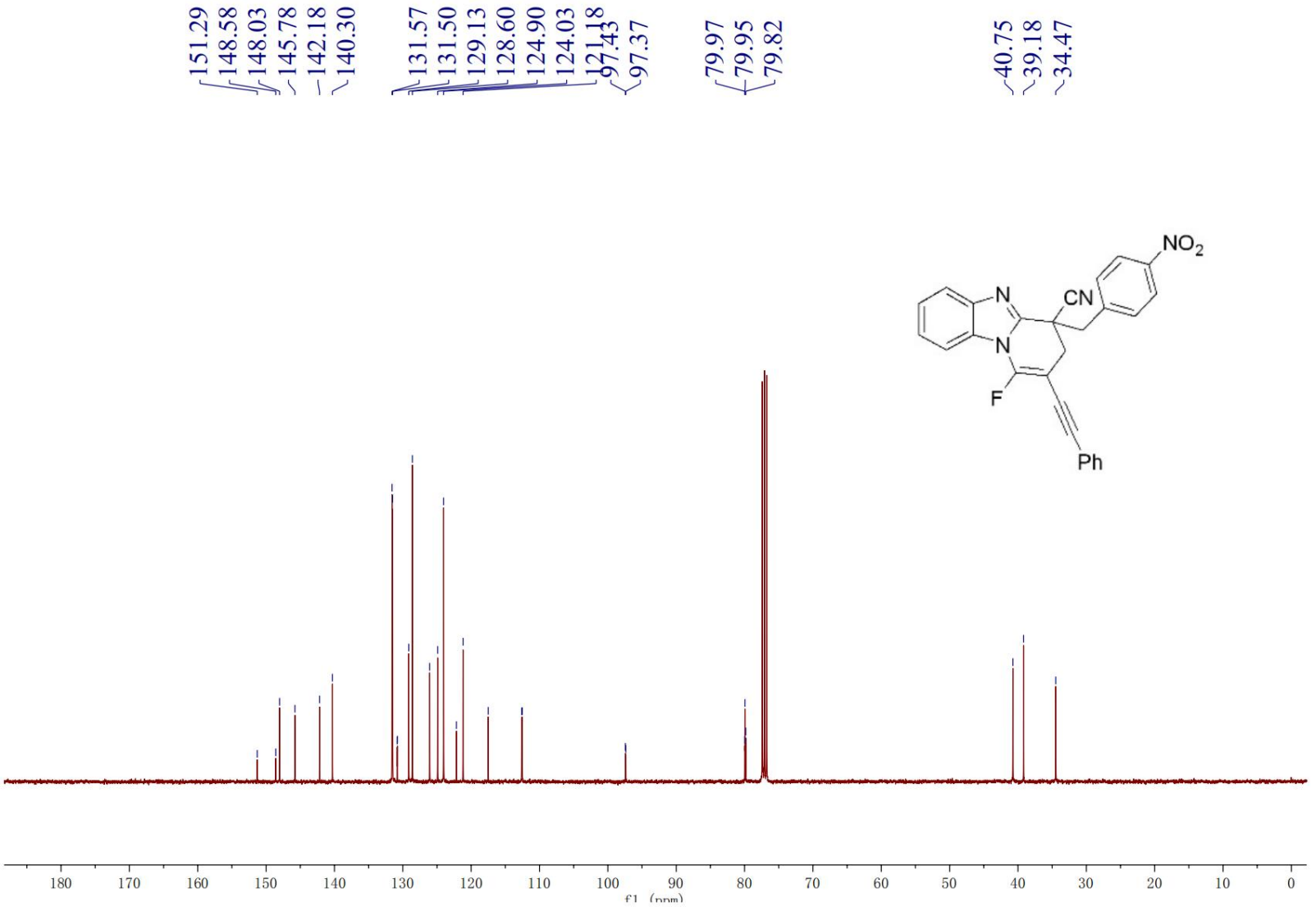
^{19}F NMR spectrum of **3o**



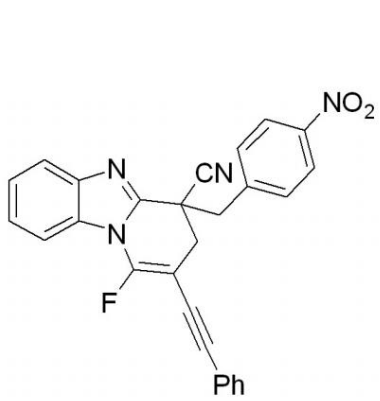
^{1}H NMR spectrum of **3p**



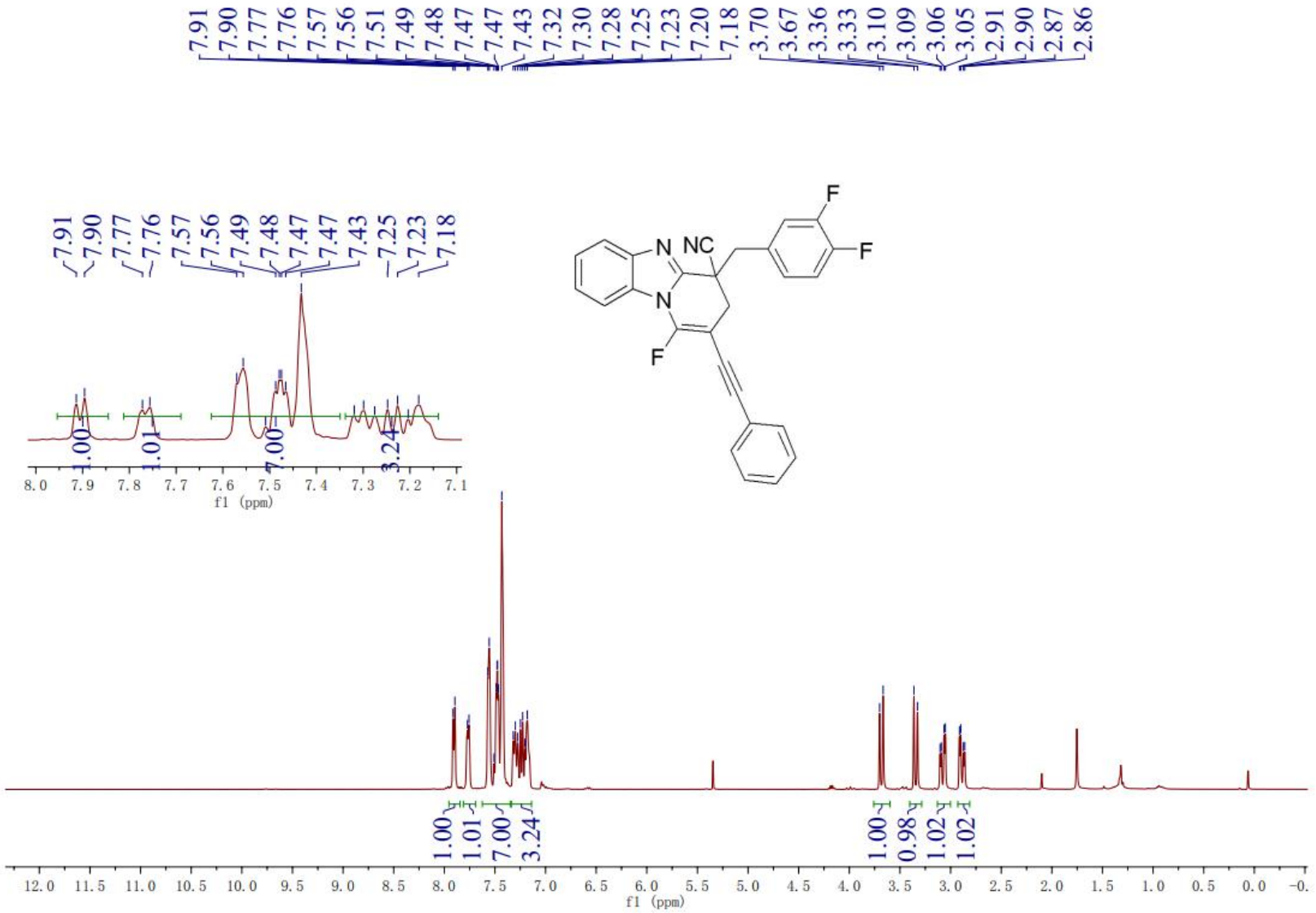
^{13}C NMR spectrum of **3p**



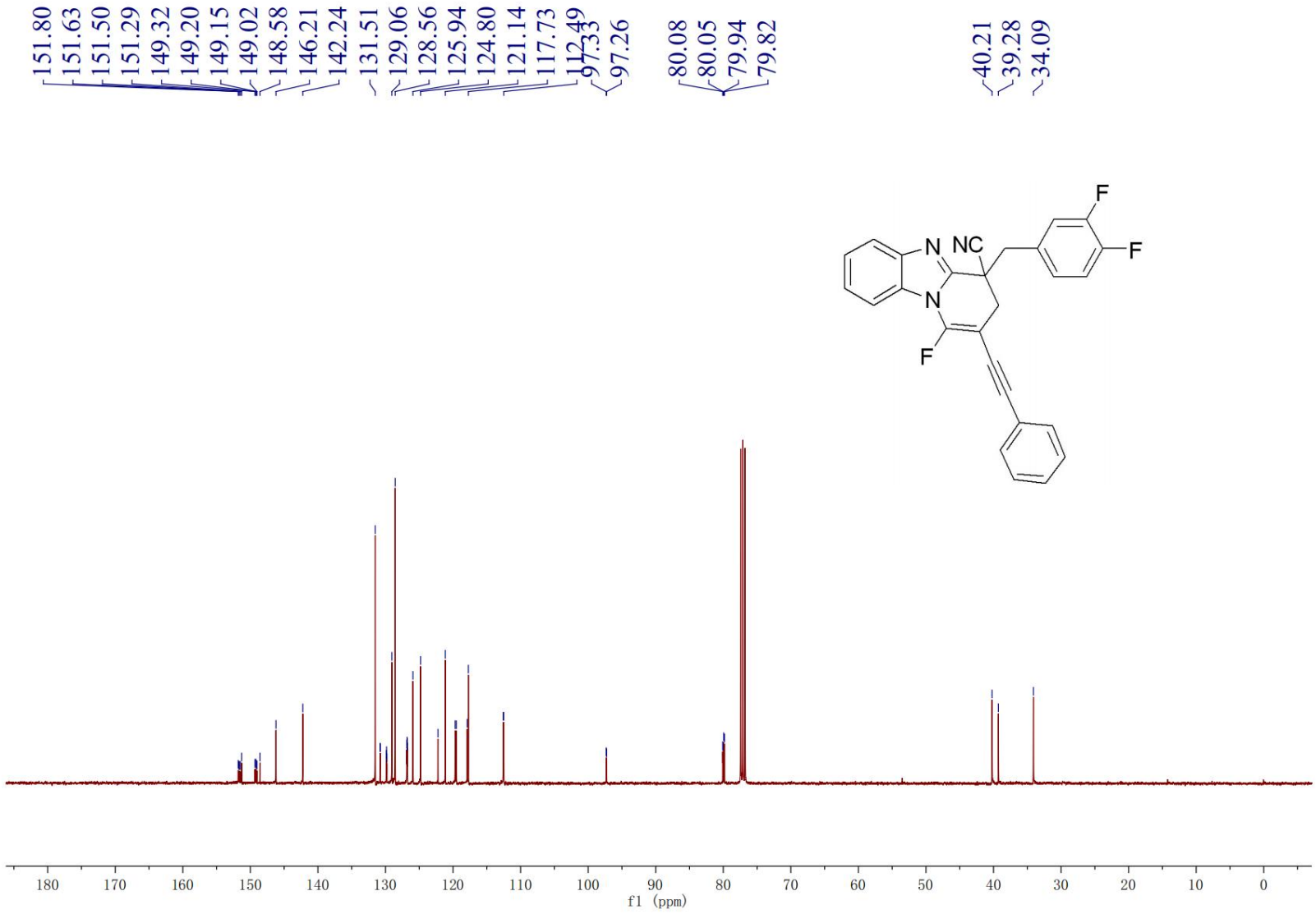
^{19}F NMR spectrum of **3p**



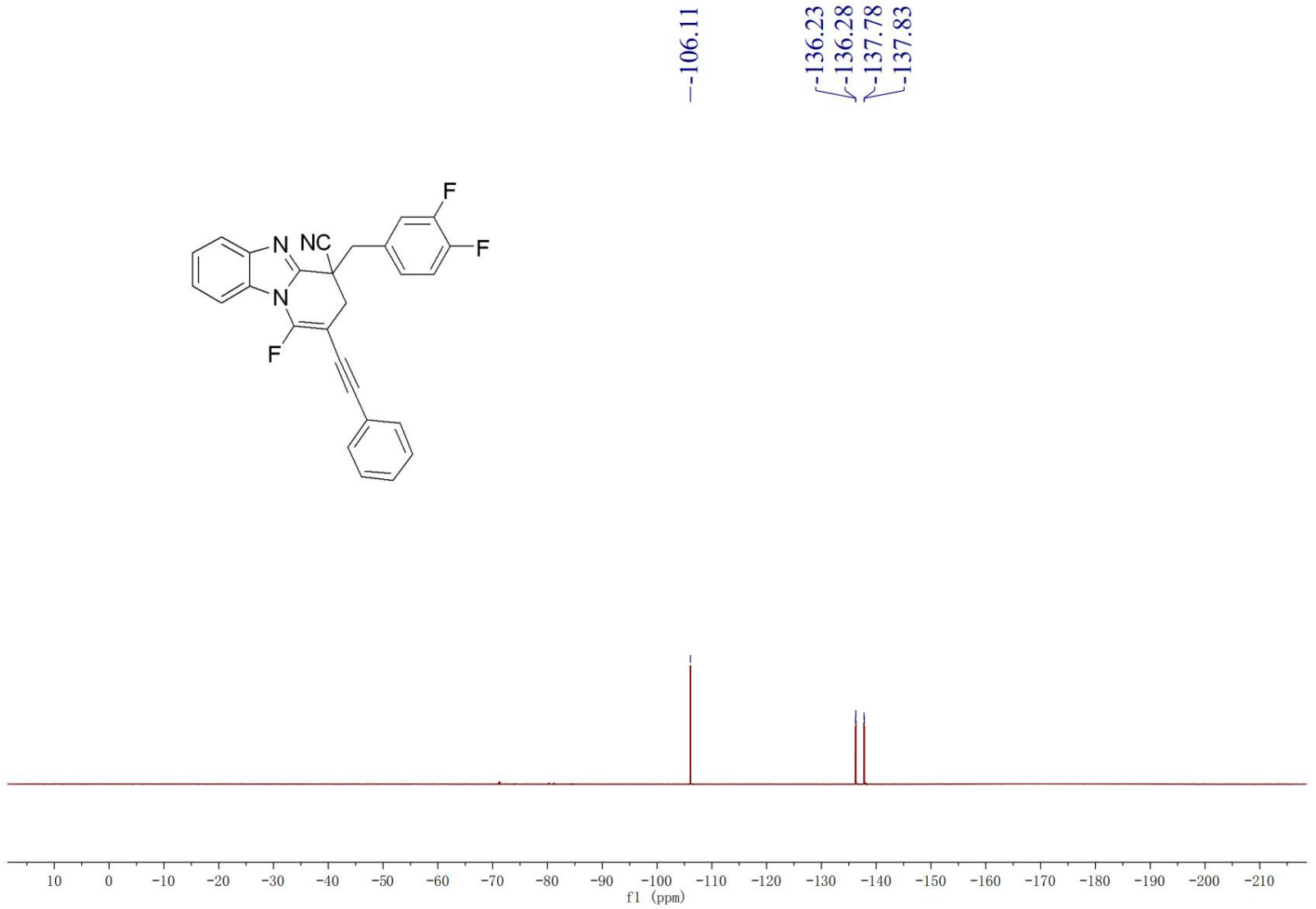
^{1}H NMR spectrum of **3q**



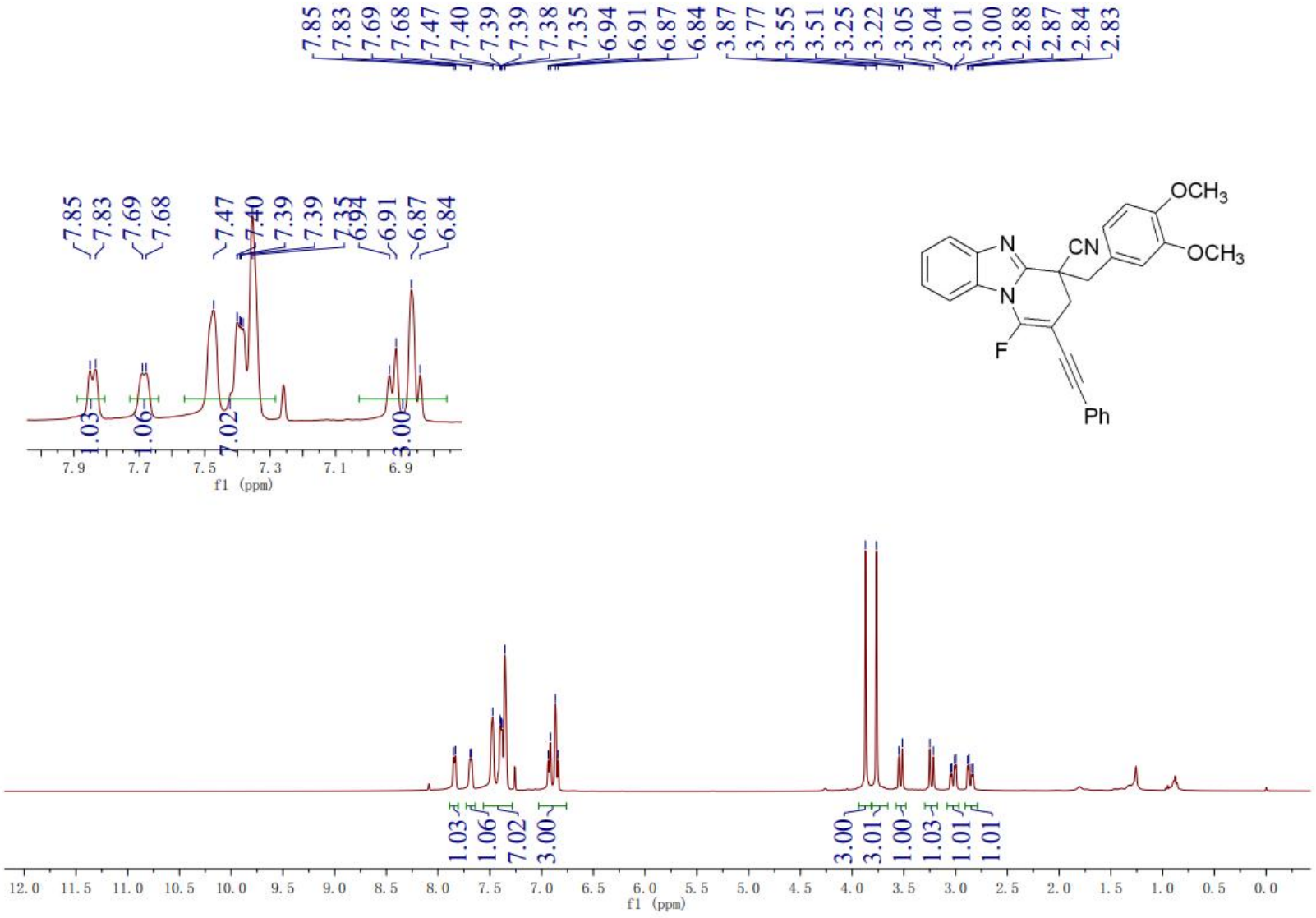
^{13}C NMR spectrum of **3q**



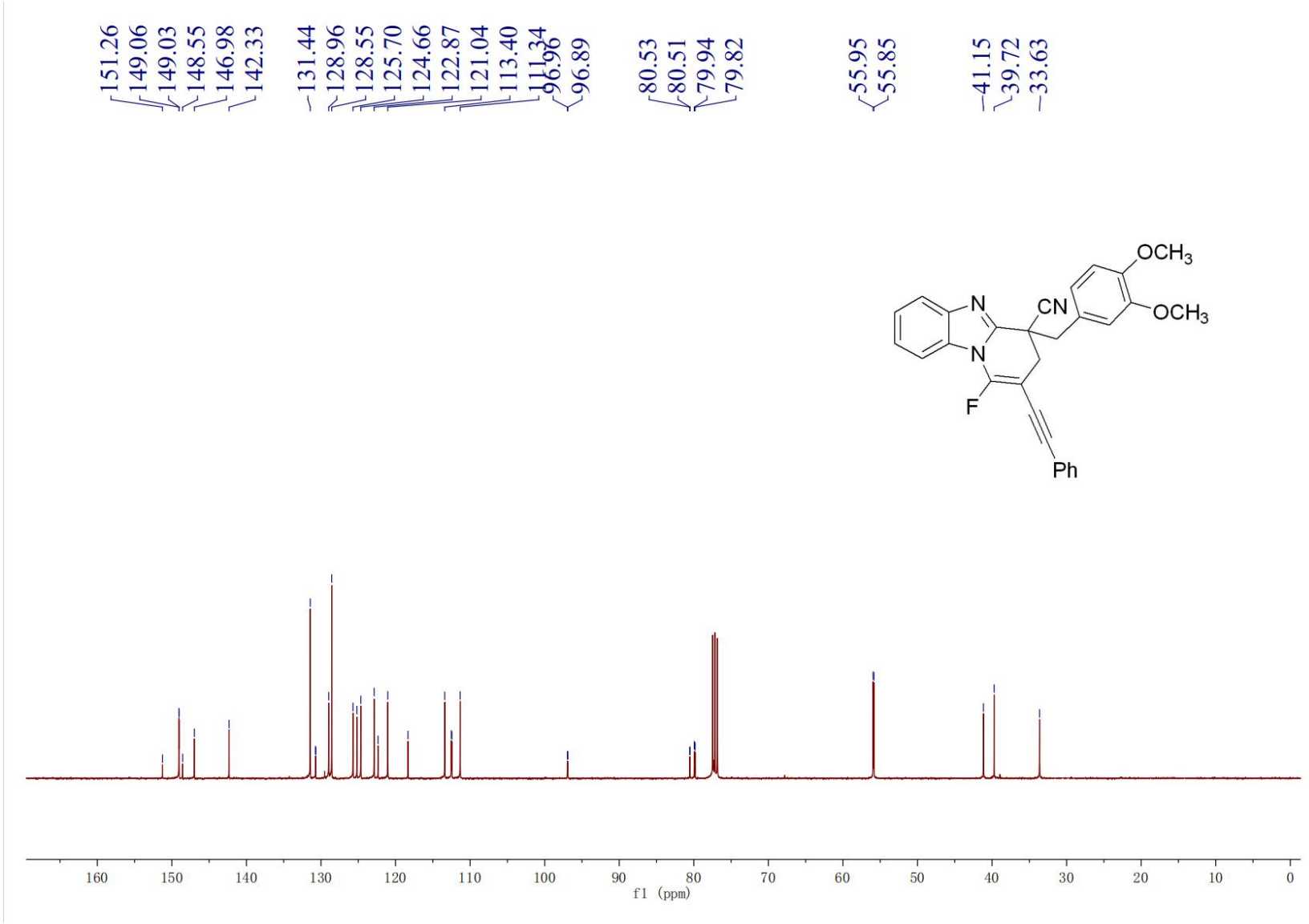
^{19}F NMR spectrum of **3q**



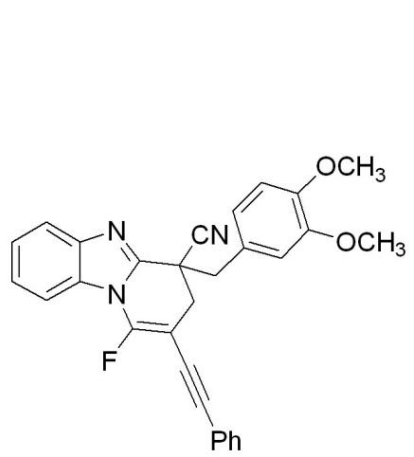
^{1}H NMR spectrum of **3r**



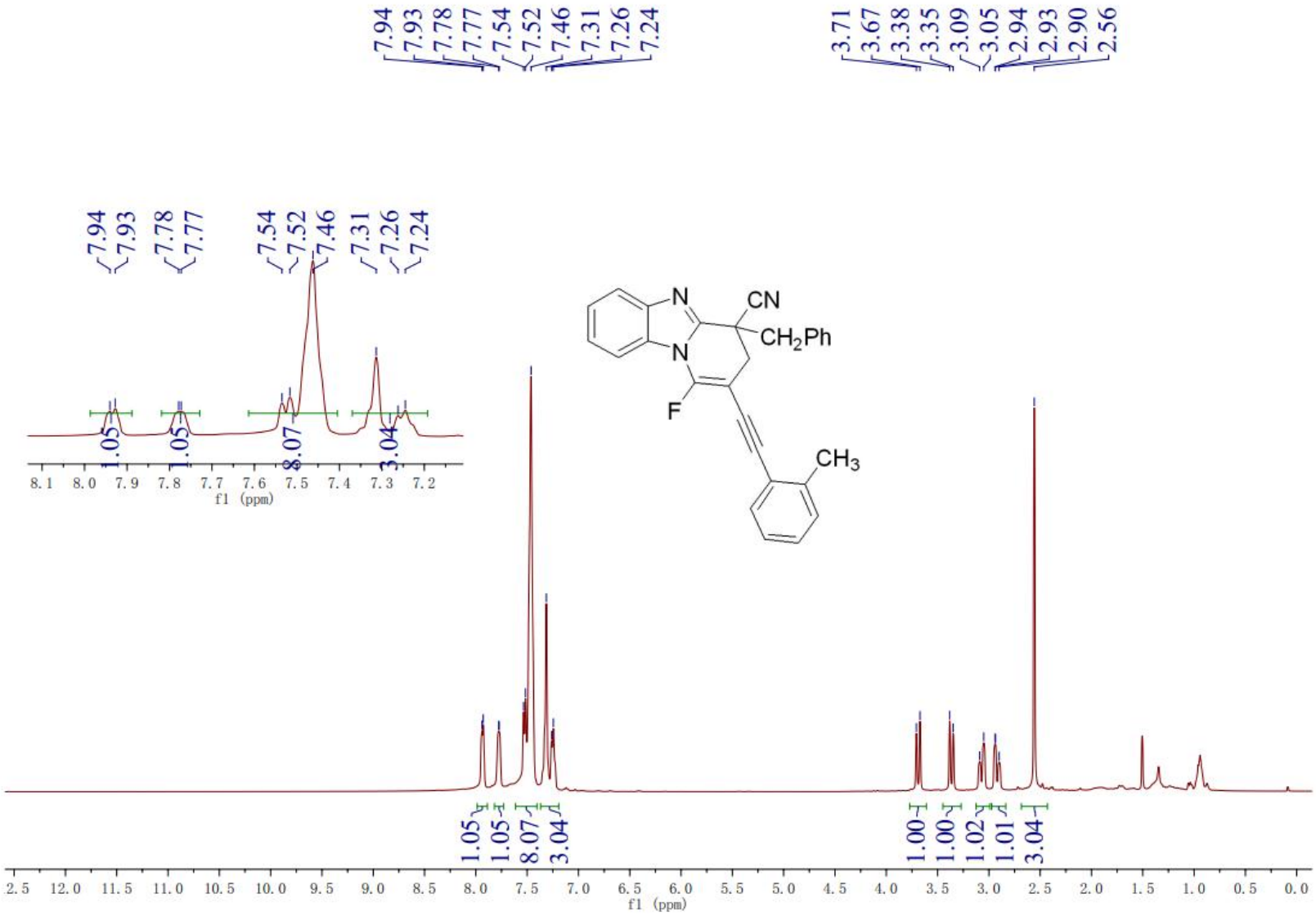
^{13}C NMR spectrum of **3r**



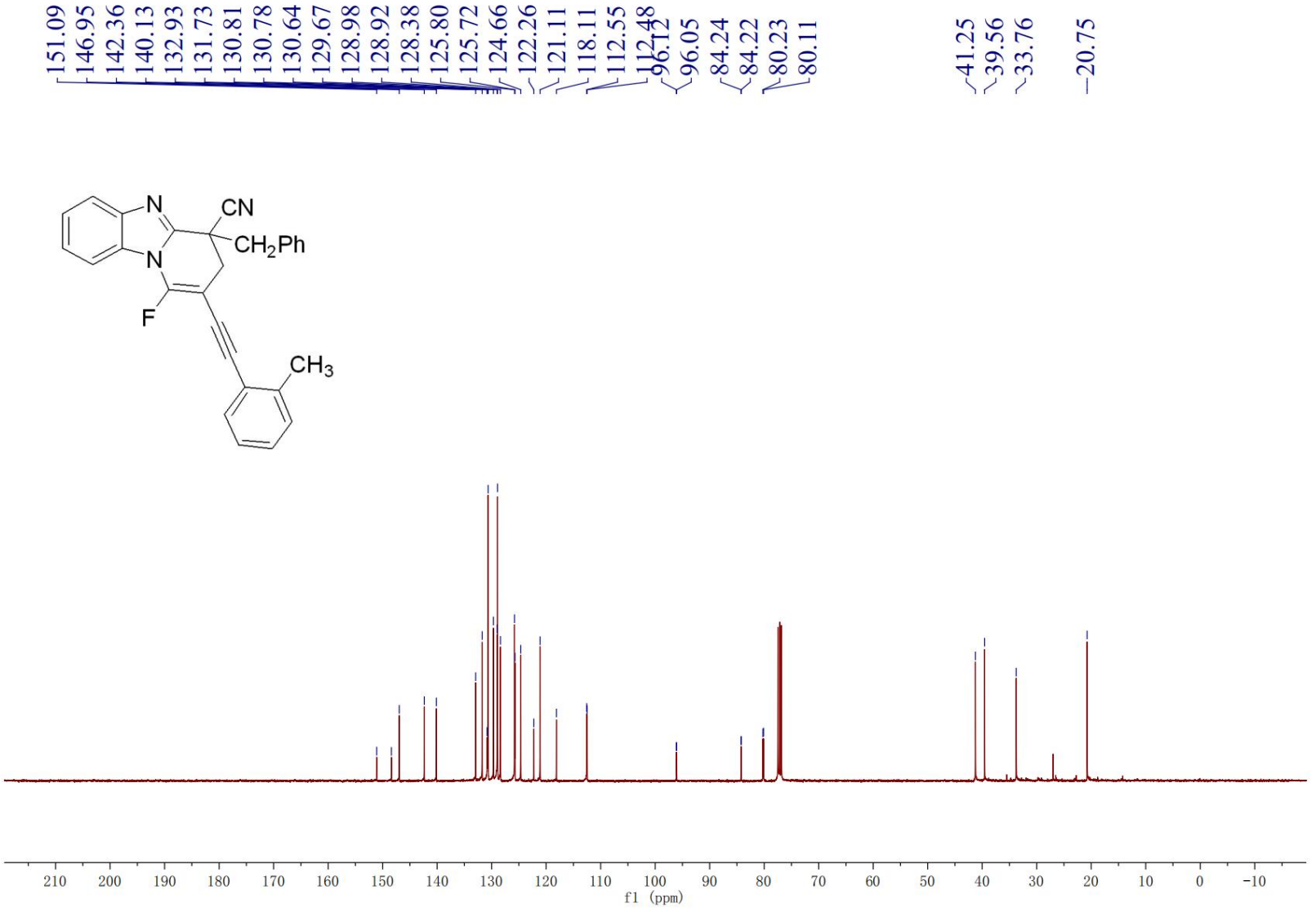
^{19}F NMR spectrum of **3r**



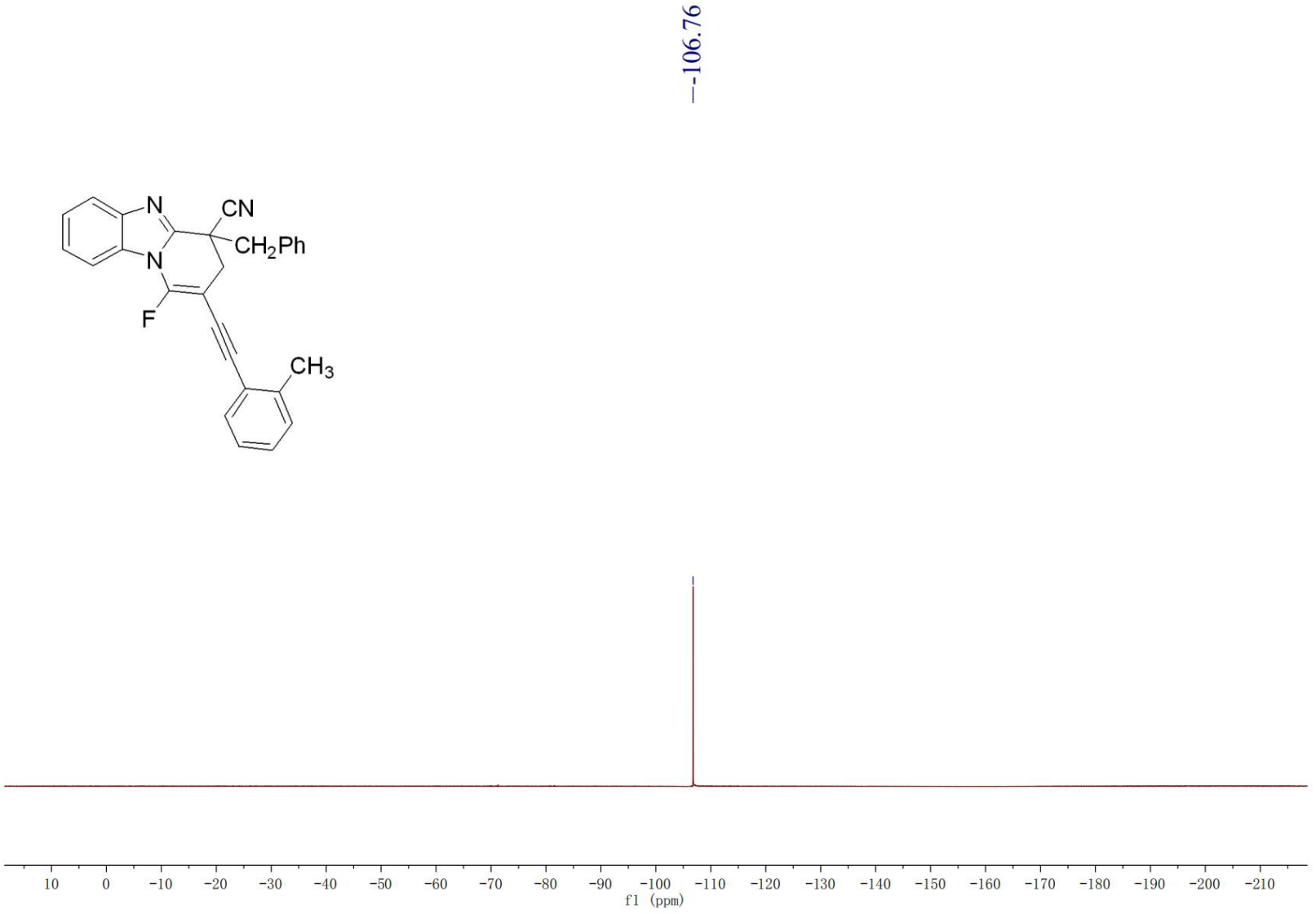
^{1}H NMR spectrum of **3s**



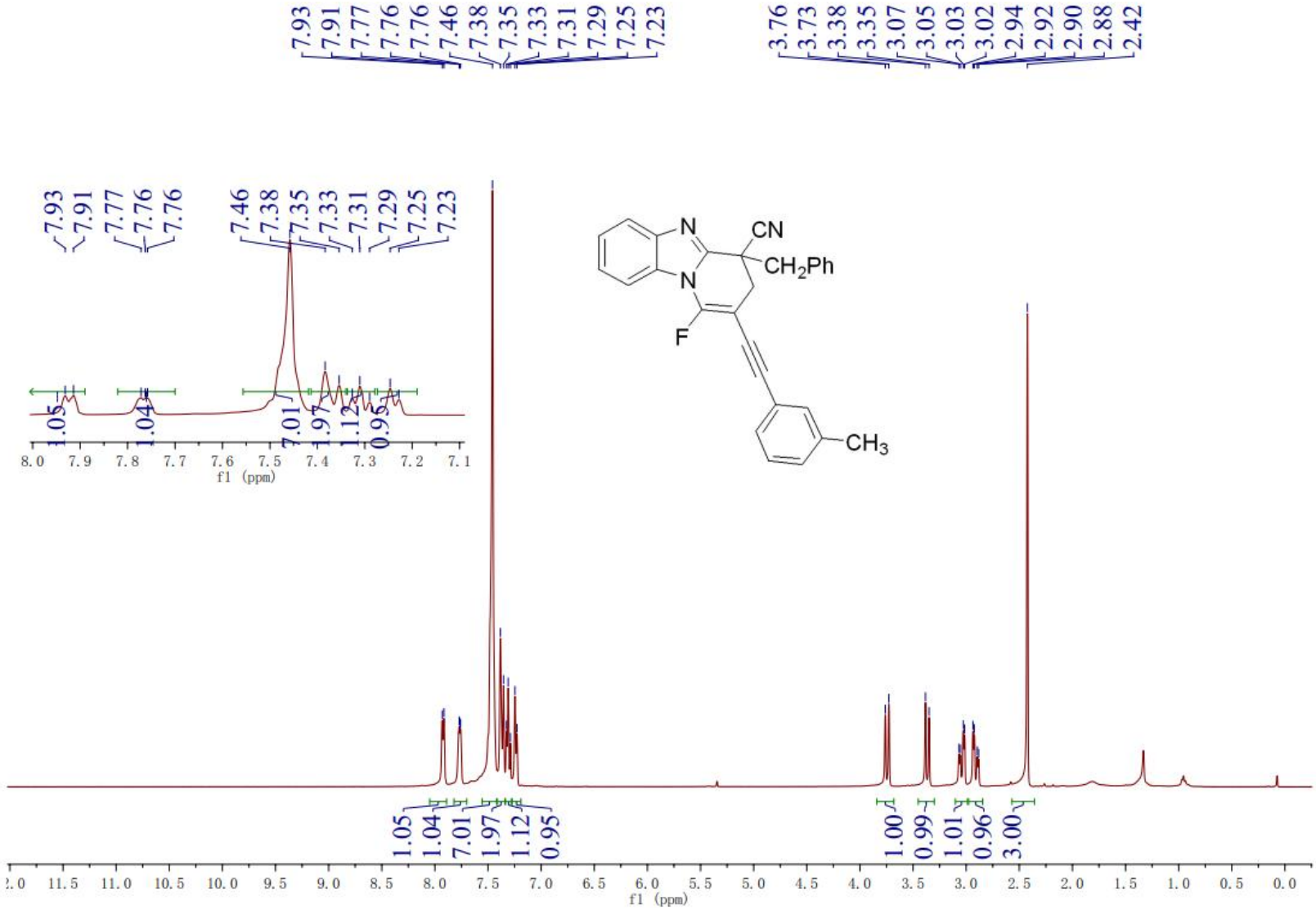
^{13}C NMR spectrum of **3s**



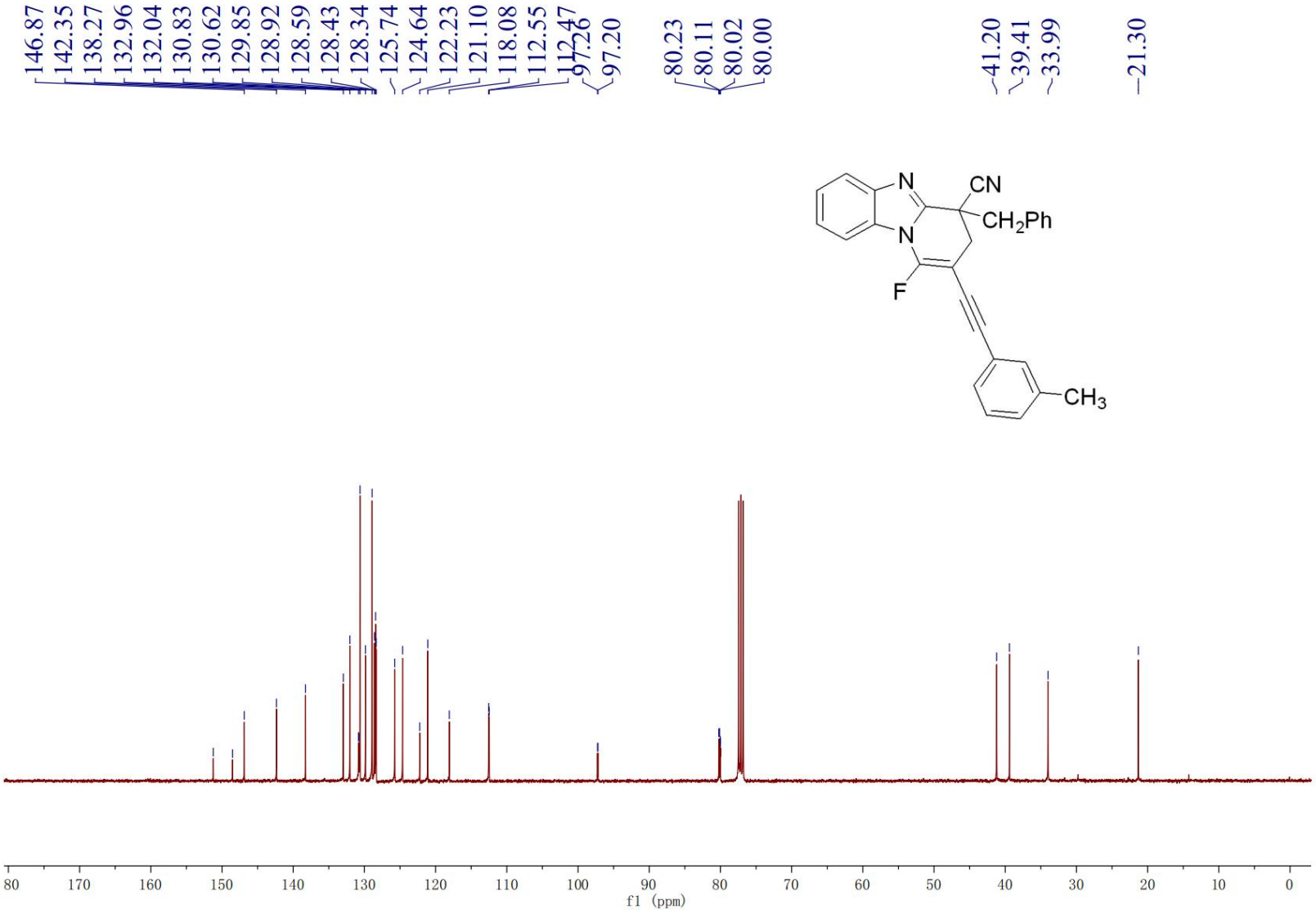
^{19}F NMR spectrum of **3s**



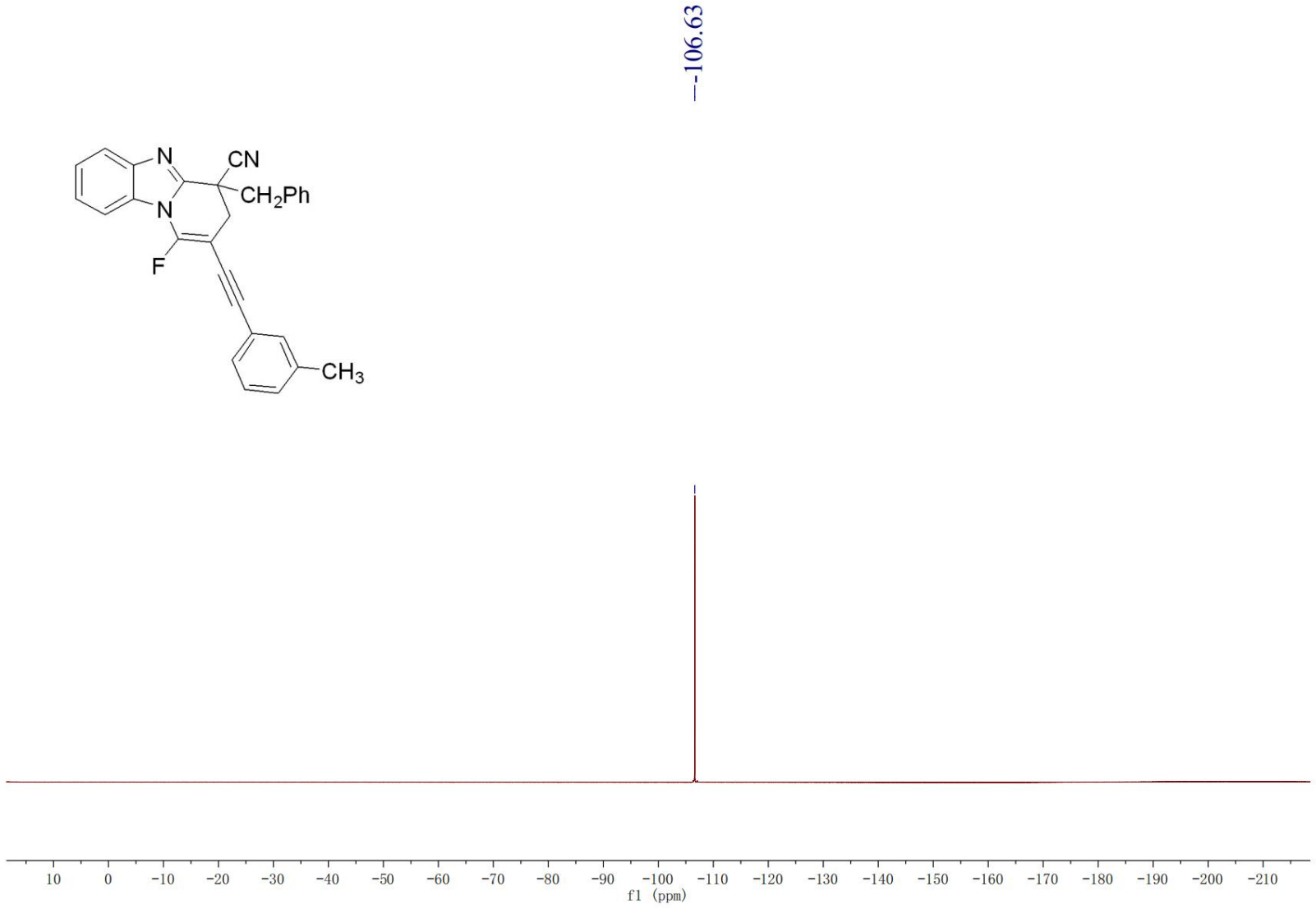
^{1}H NMR spectrum of **3t**



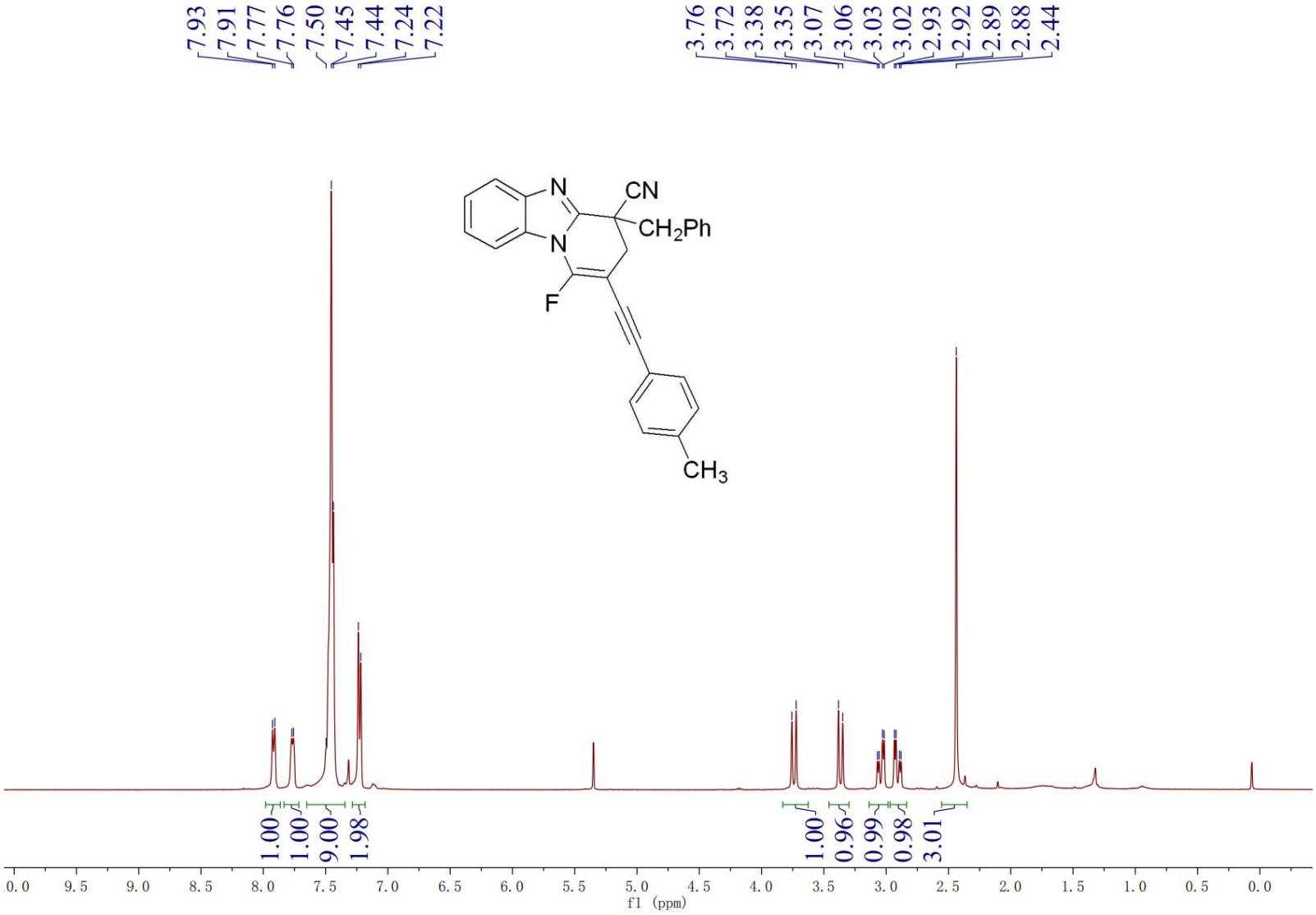
^{13}C NMR spectrum of **3t**



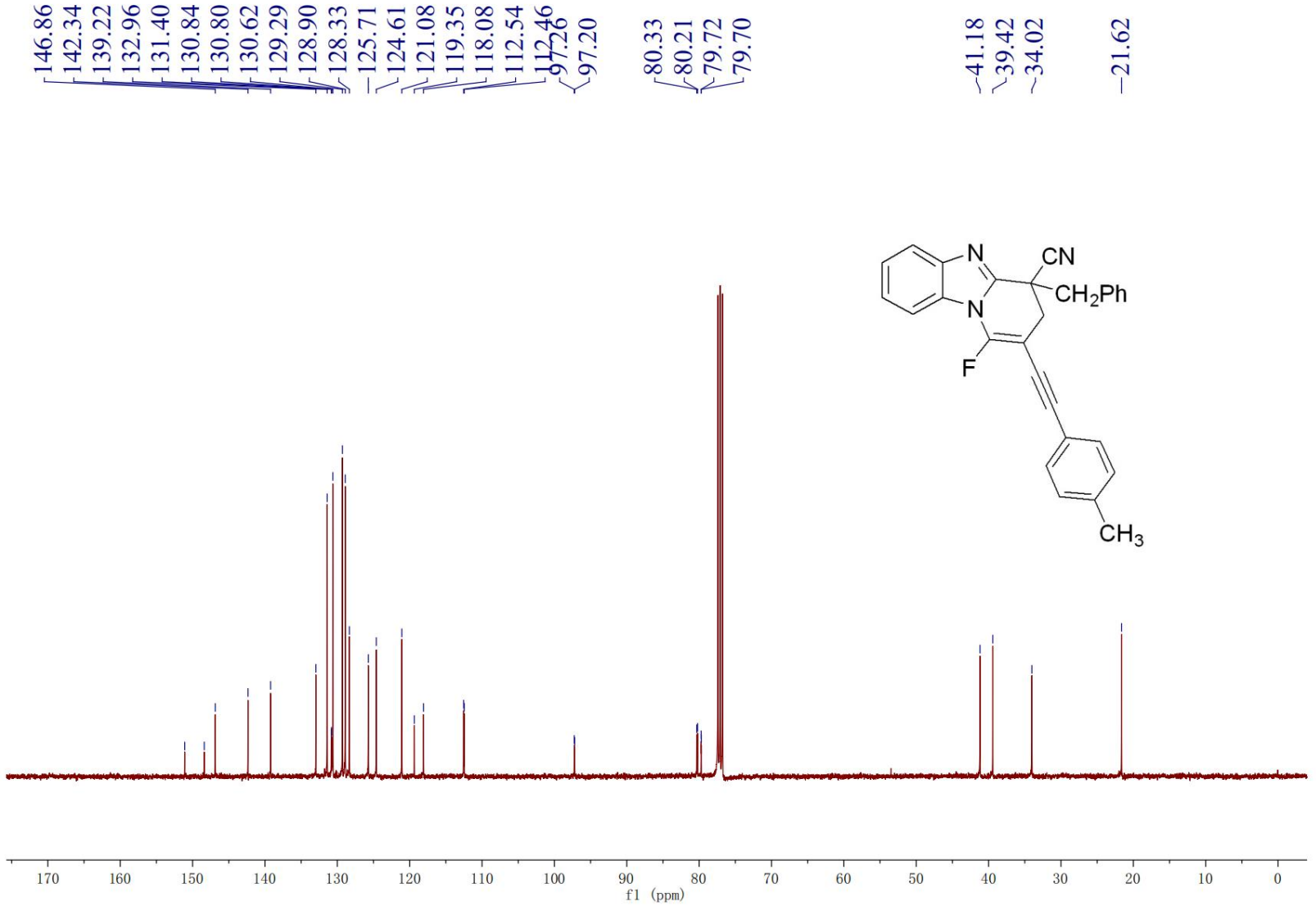
^{19}F NMR spectrum of **3t**



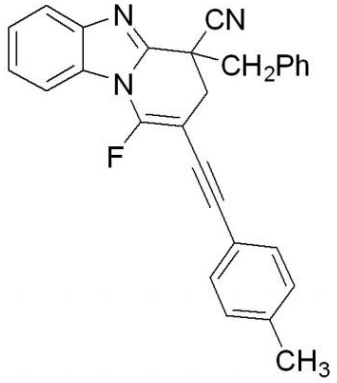
^{1}H NMR spectrum of **3u**



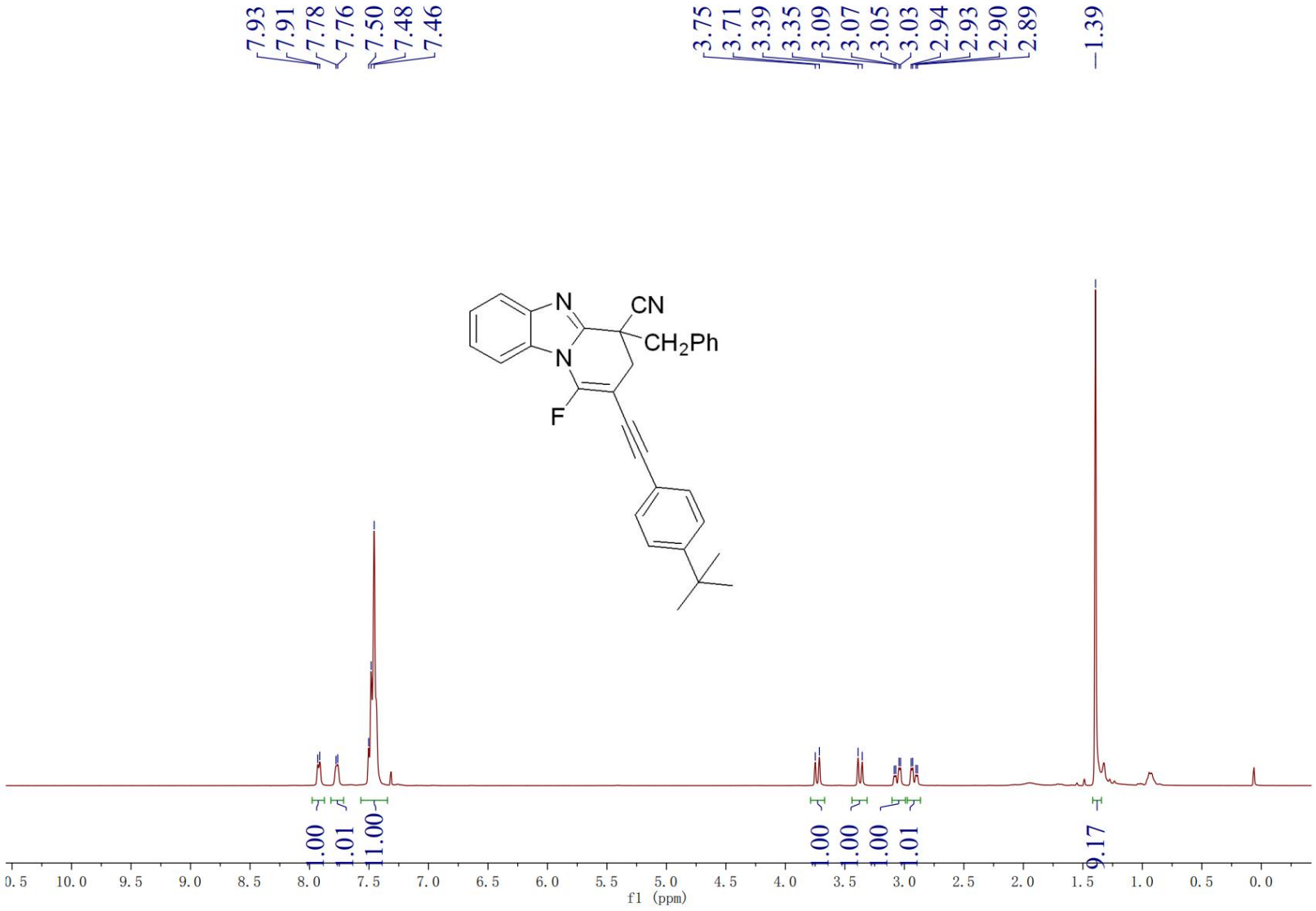
^{13}C NMR spectrum of **3u**



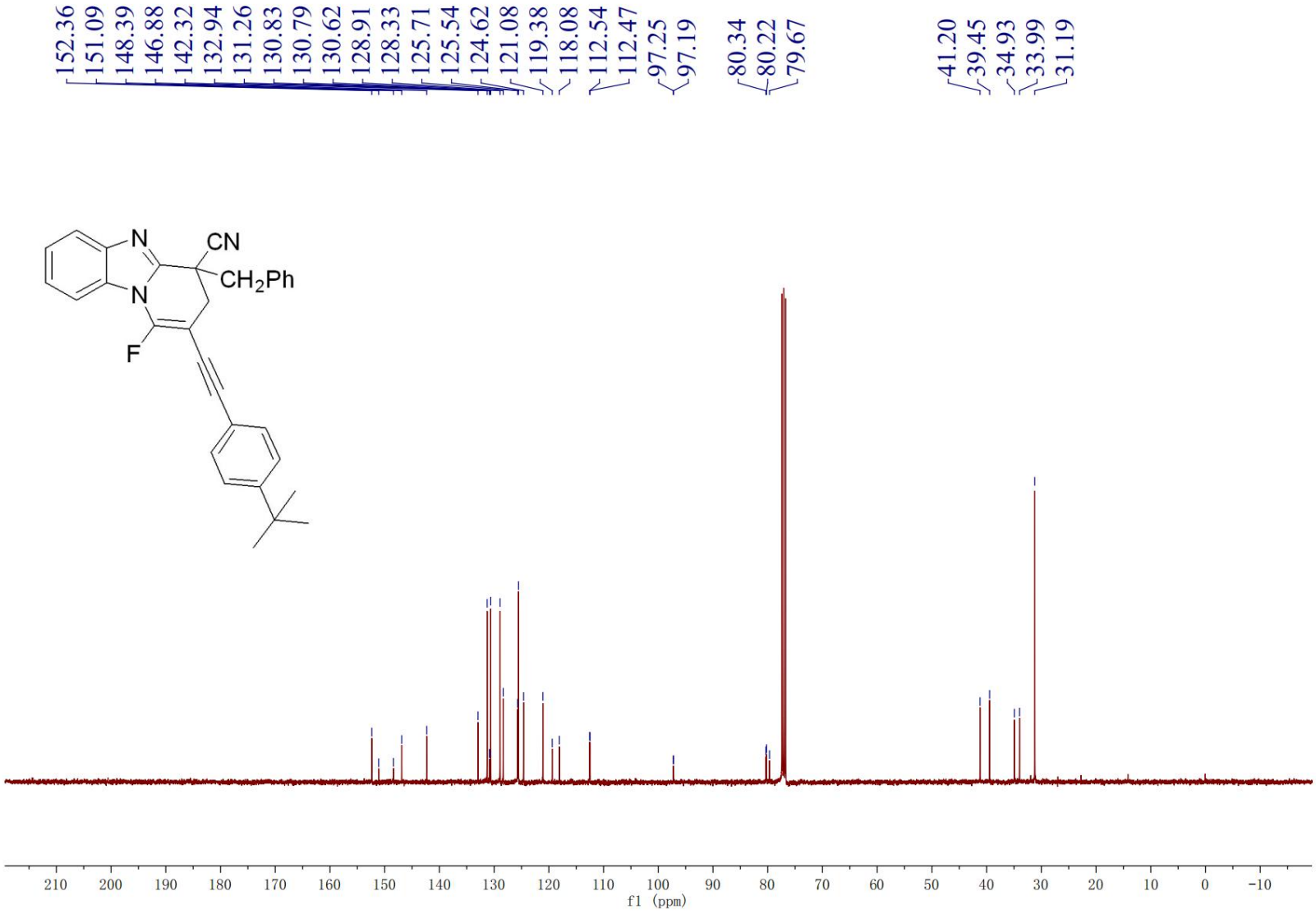
^{19}F NMR spectrum of **3u**



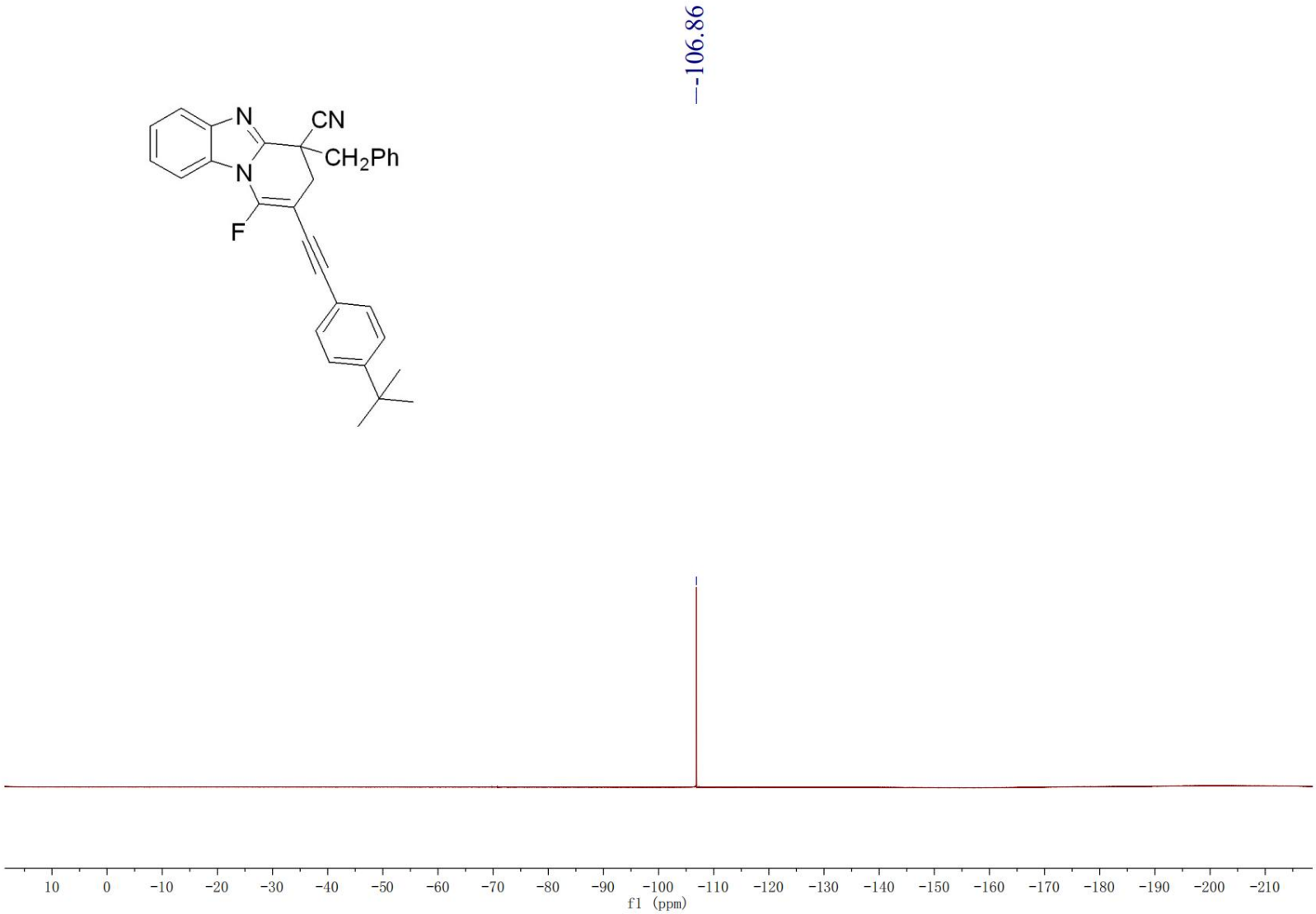
^{1}H NMR spectrum of **3v**



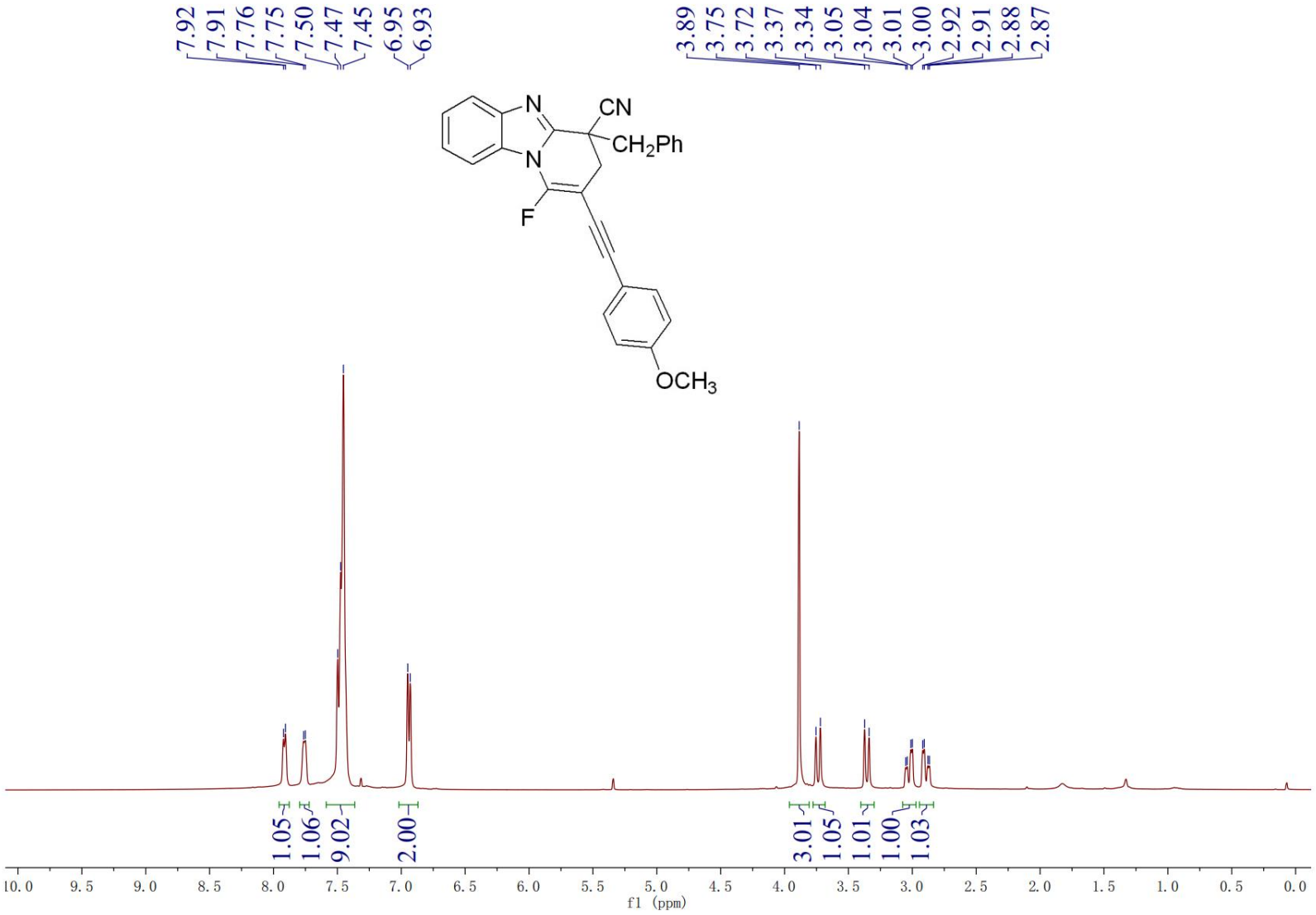
^{13}C NMR spectrum of **3v**



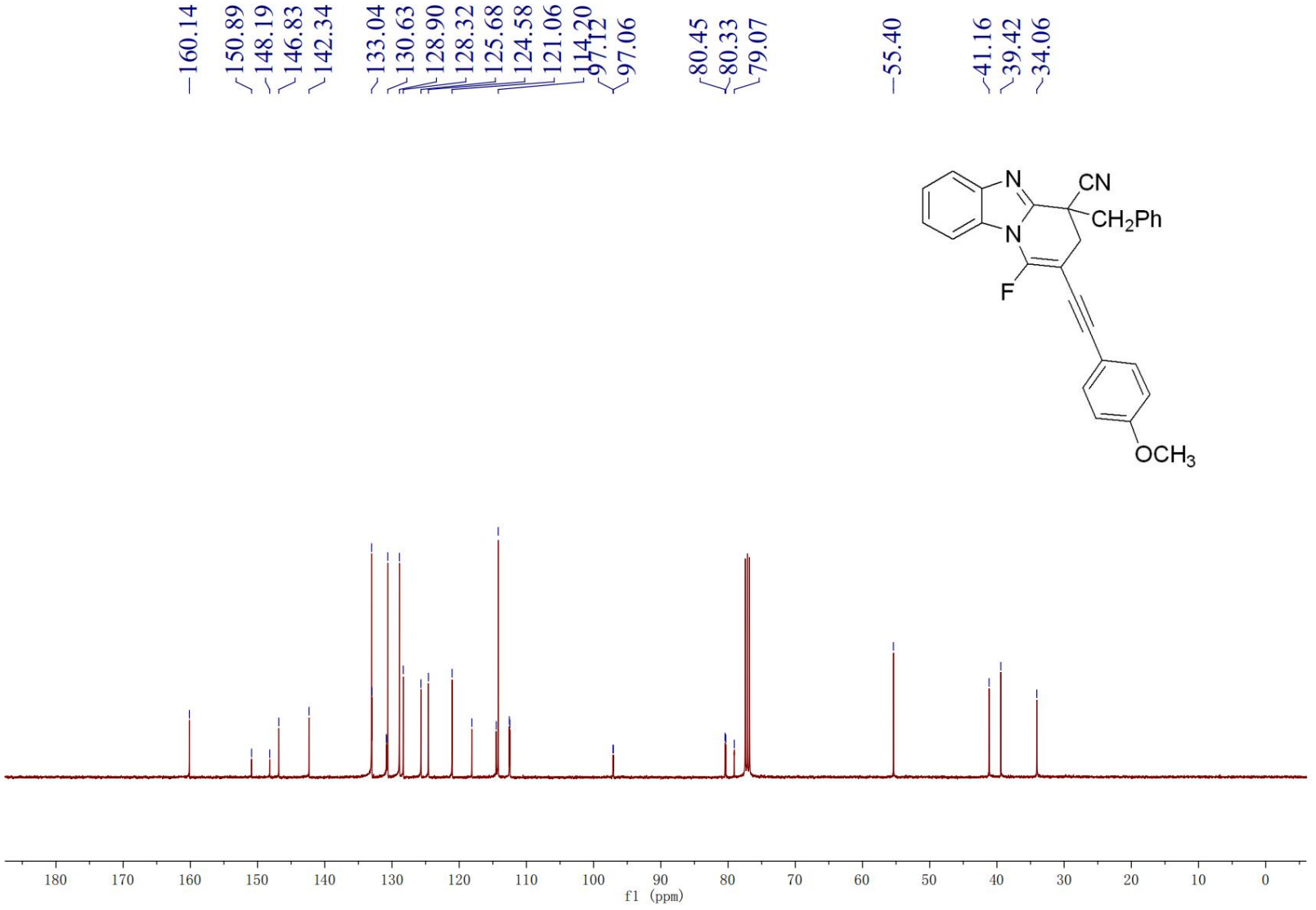
^{19}F NMR spectrum of **3v**



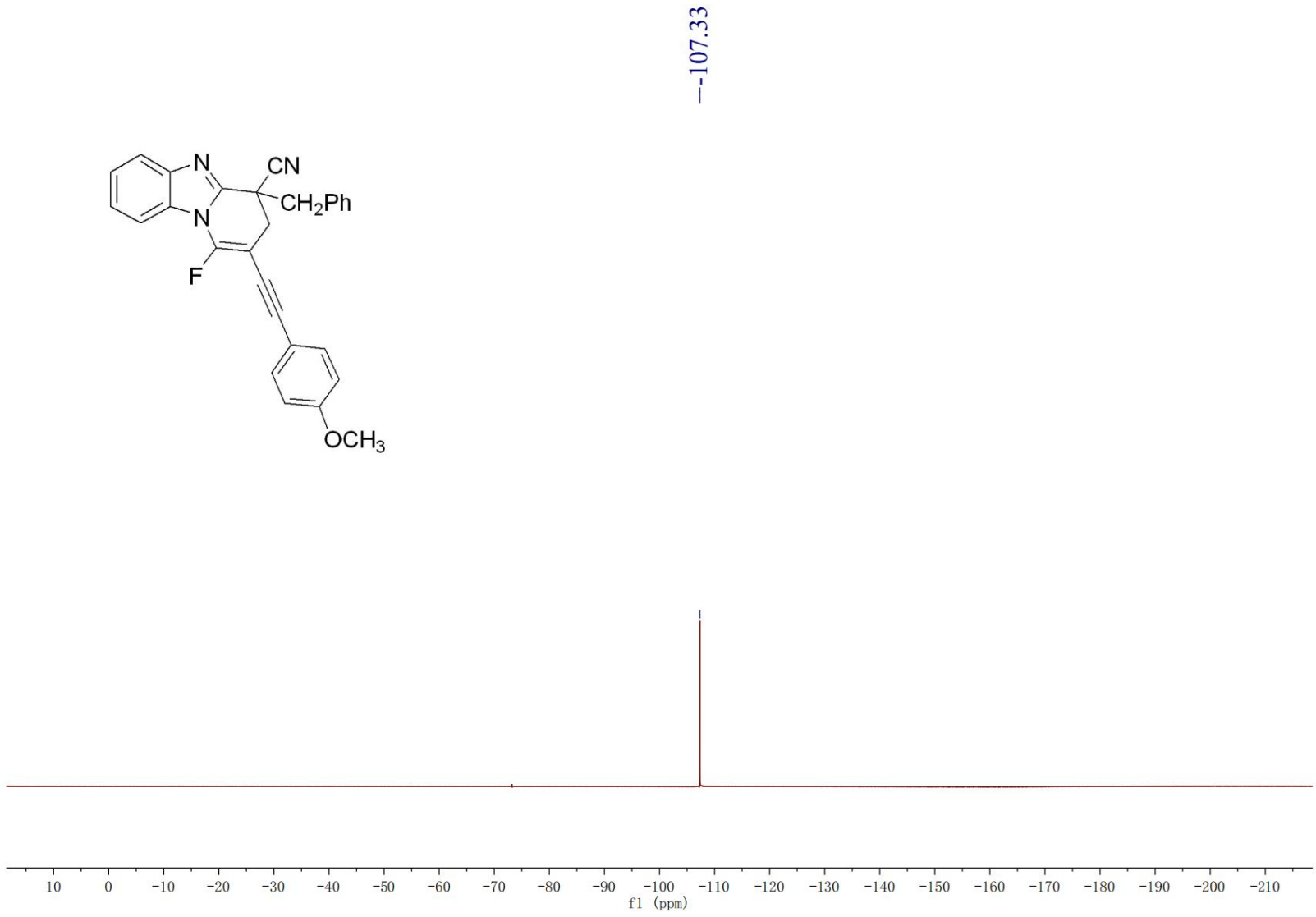
^{1}H NMR spectrum of **3w**



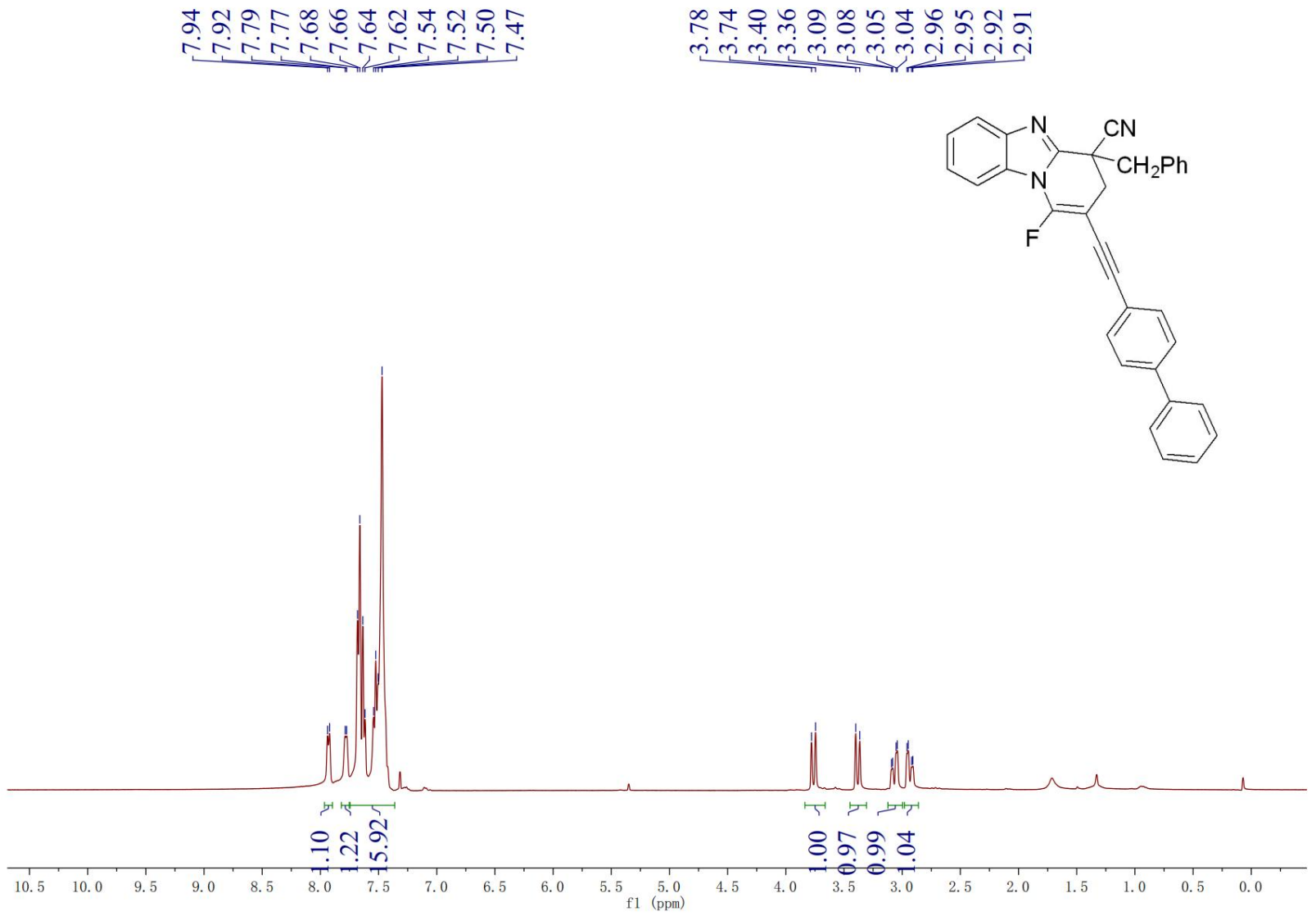
^{13}C NMR spectrum of **3w**



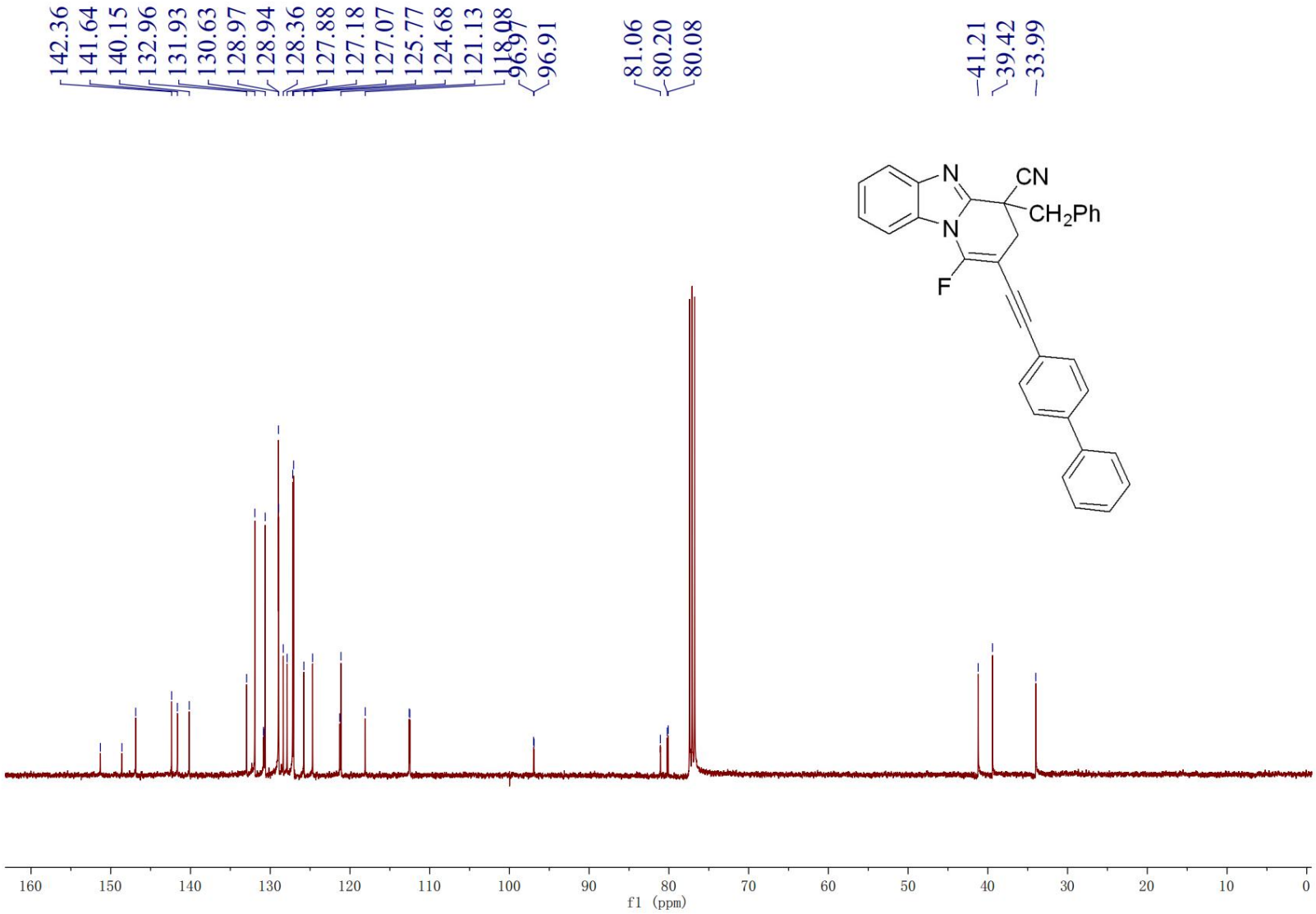
^{19}F NMR spectrum of **3w**



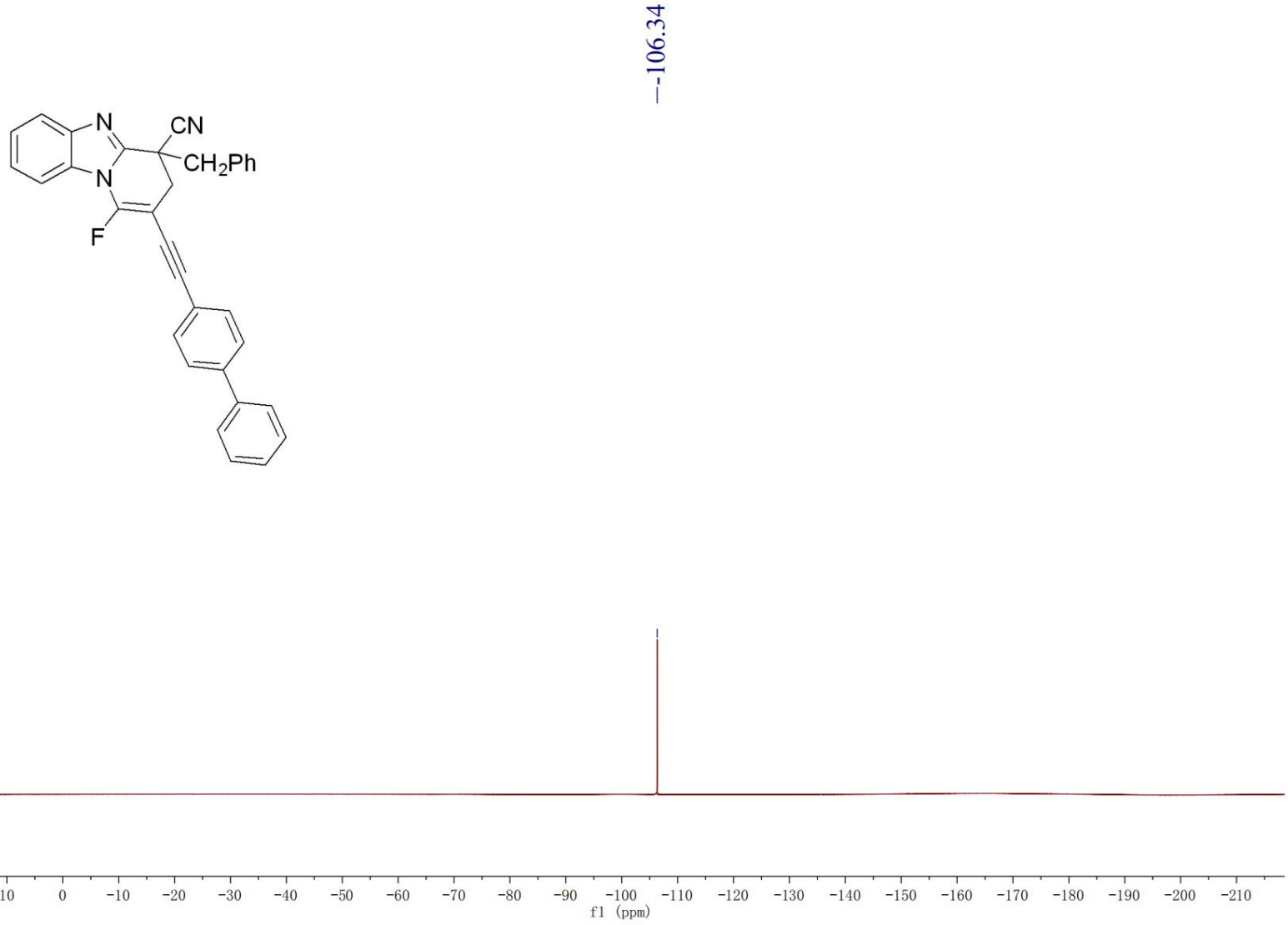
^{1}H NMR spectrum of **3x**



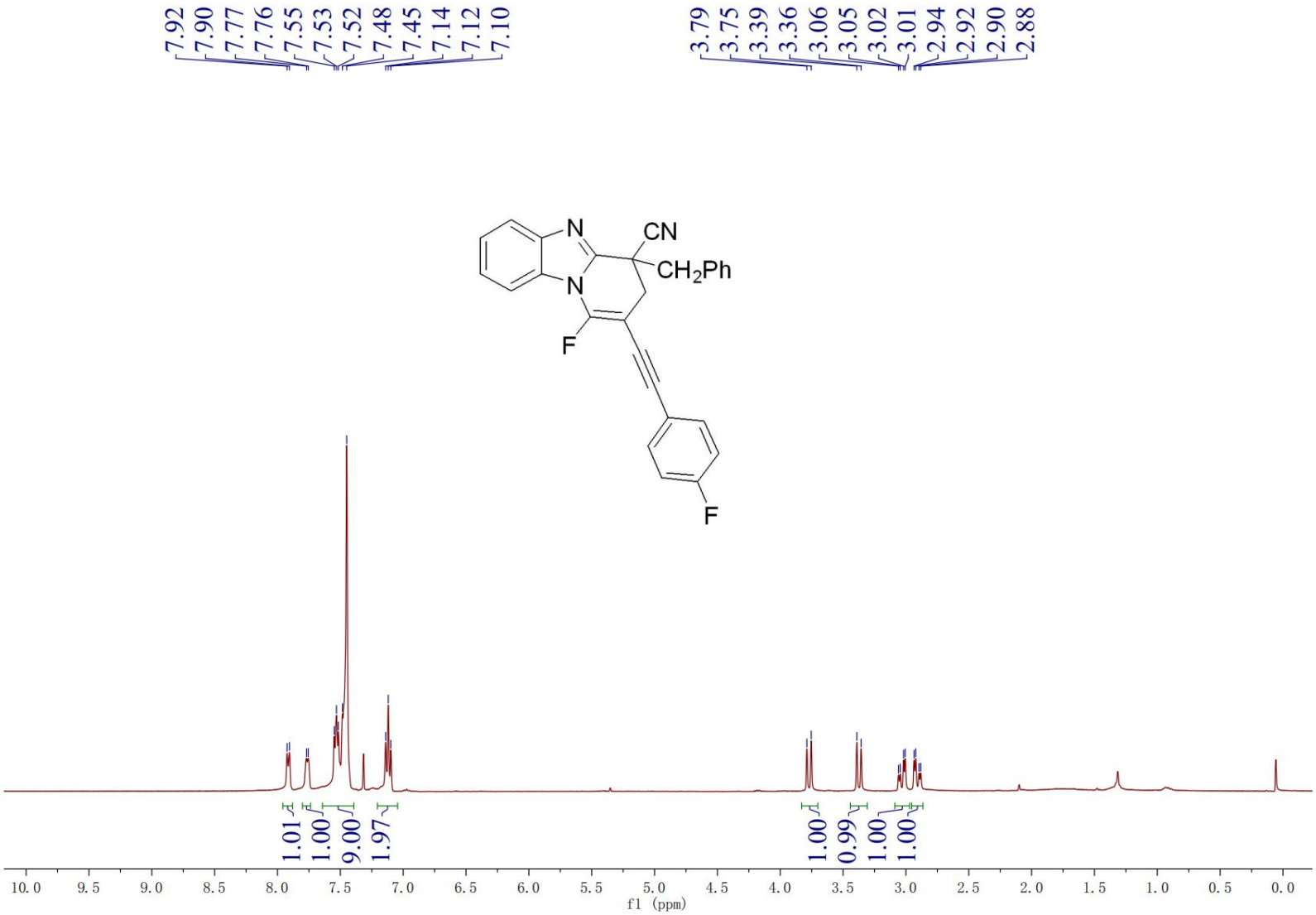
^{13}C NMR spectrum of **3x**



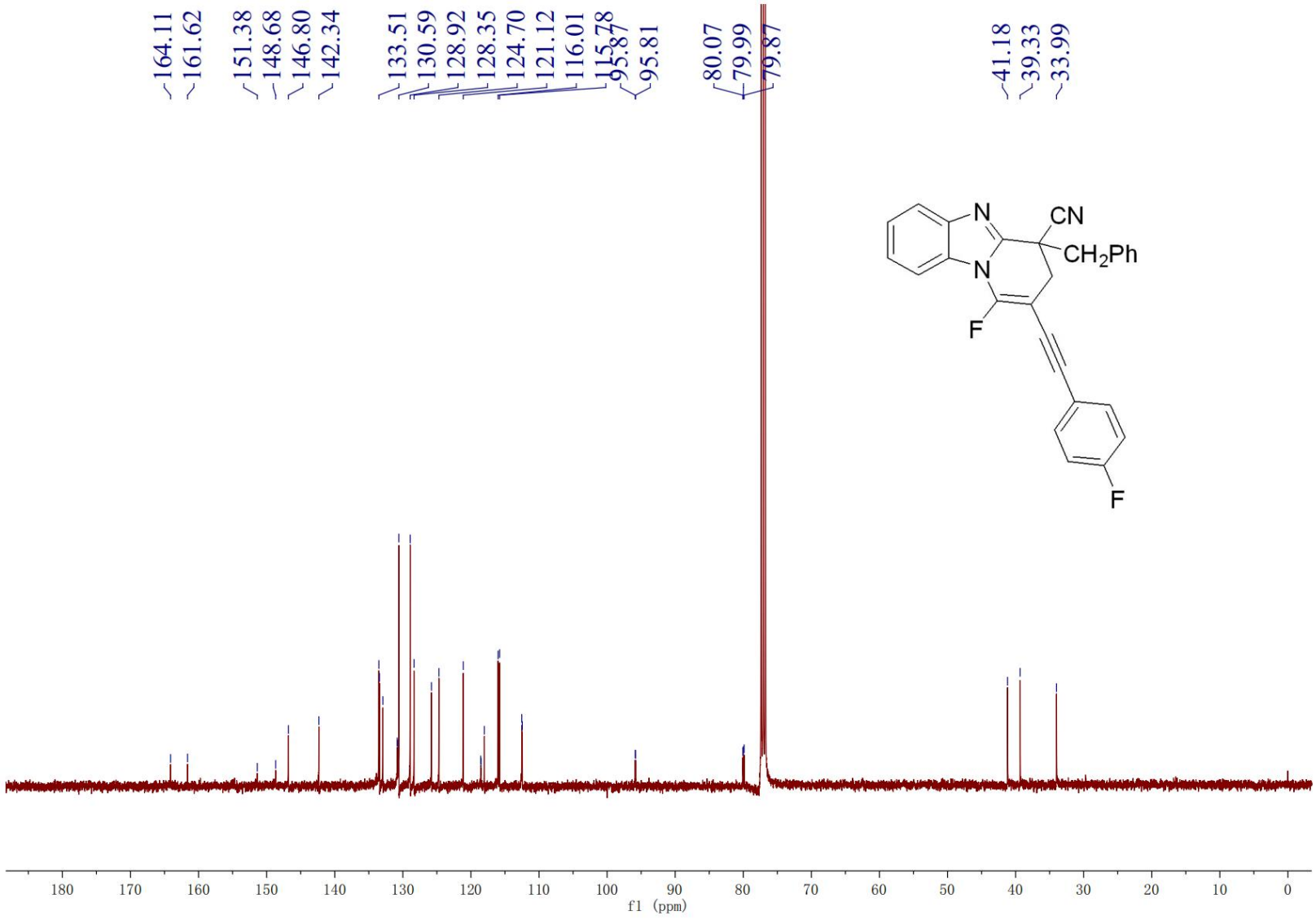
^{19}F NMR spectrum of **3x**



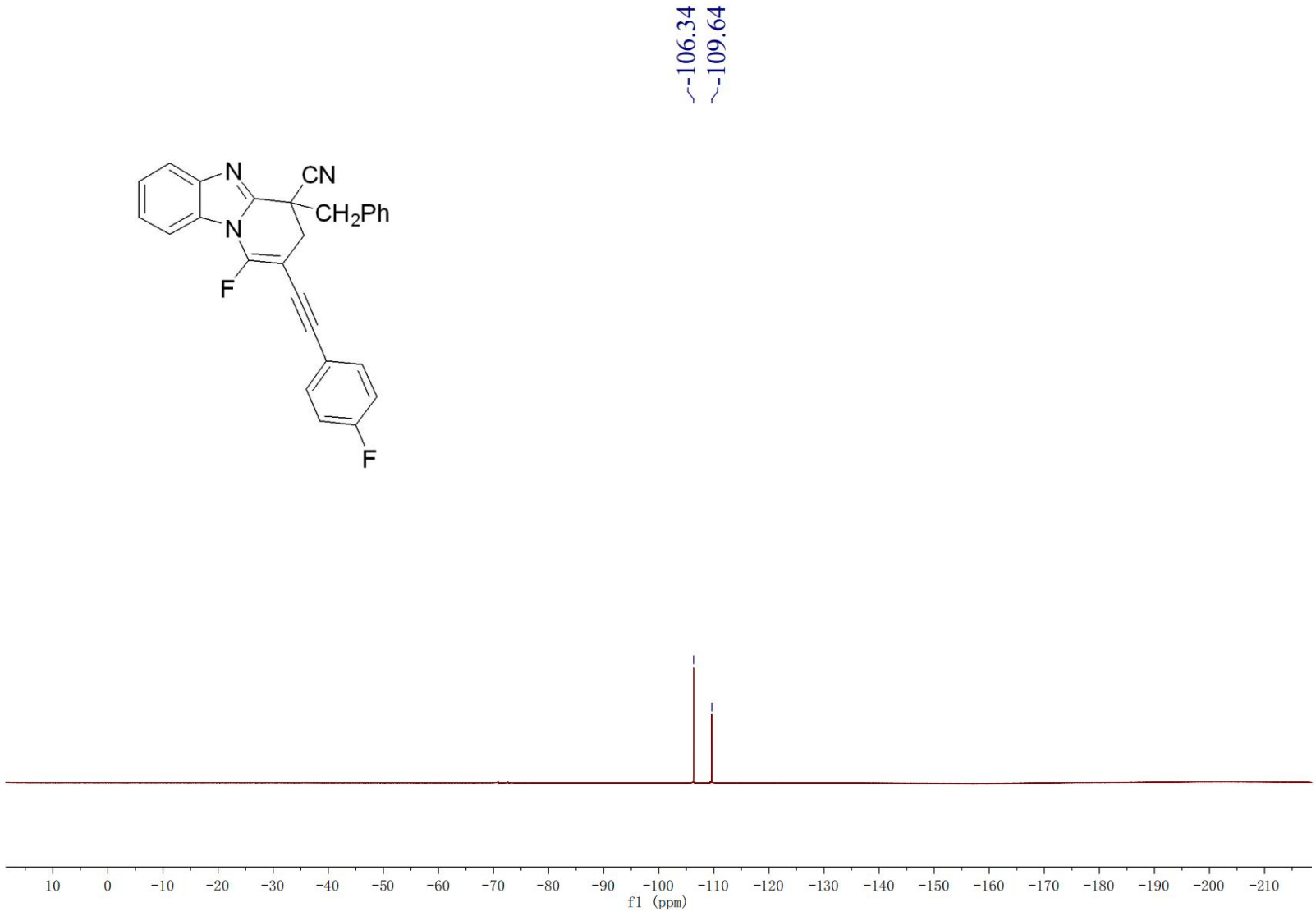
^{1}H NMR spectrum of **3y**



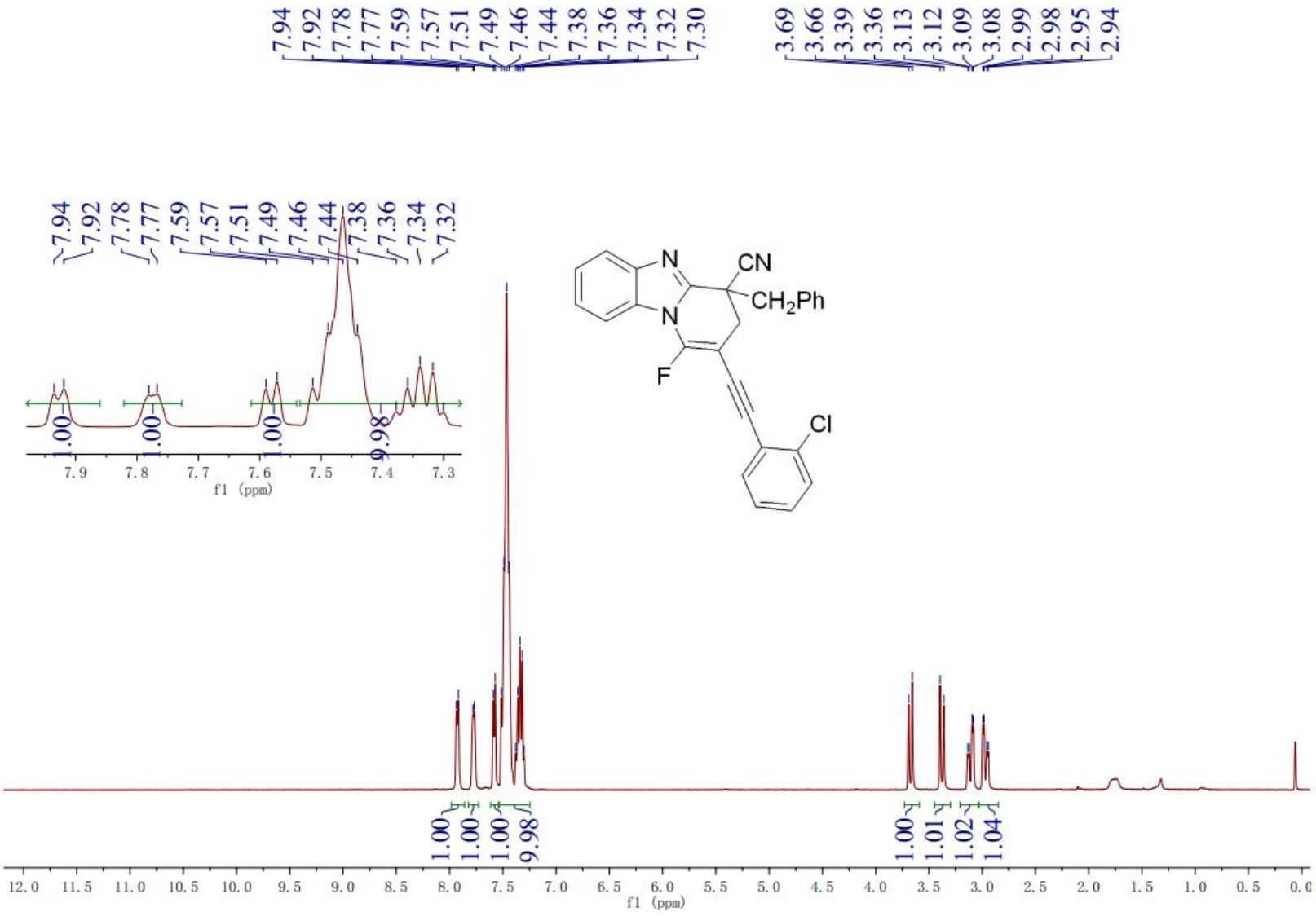
^{13}C NMR spectrum of **3y**



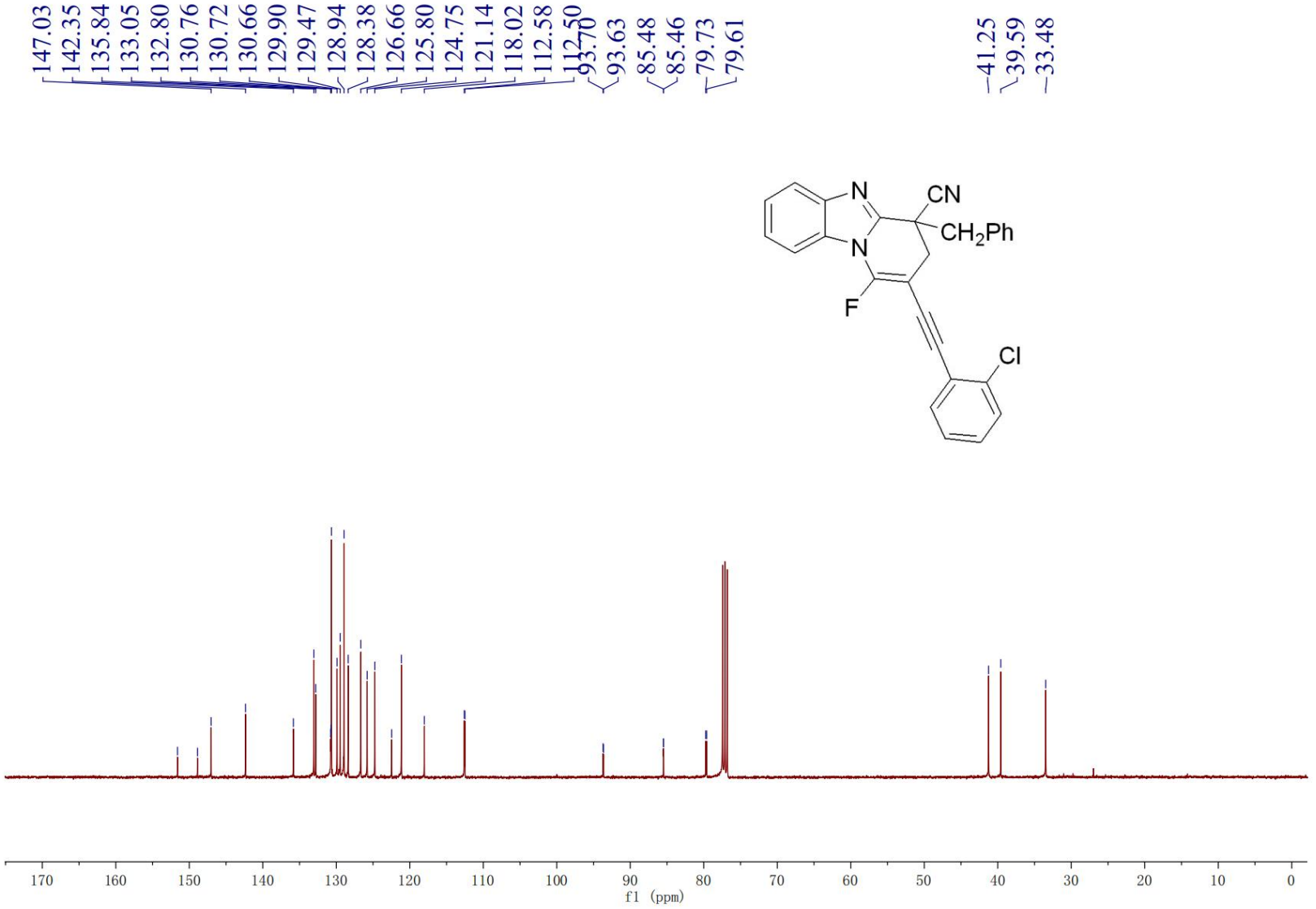
^{19}F NMR spectrum of **3y**



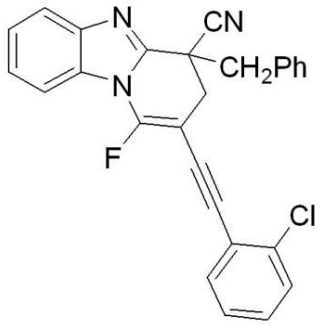
^{1}H NMR spectrum of **3z**



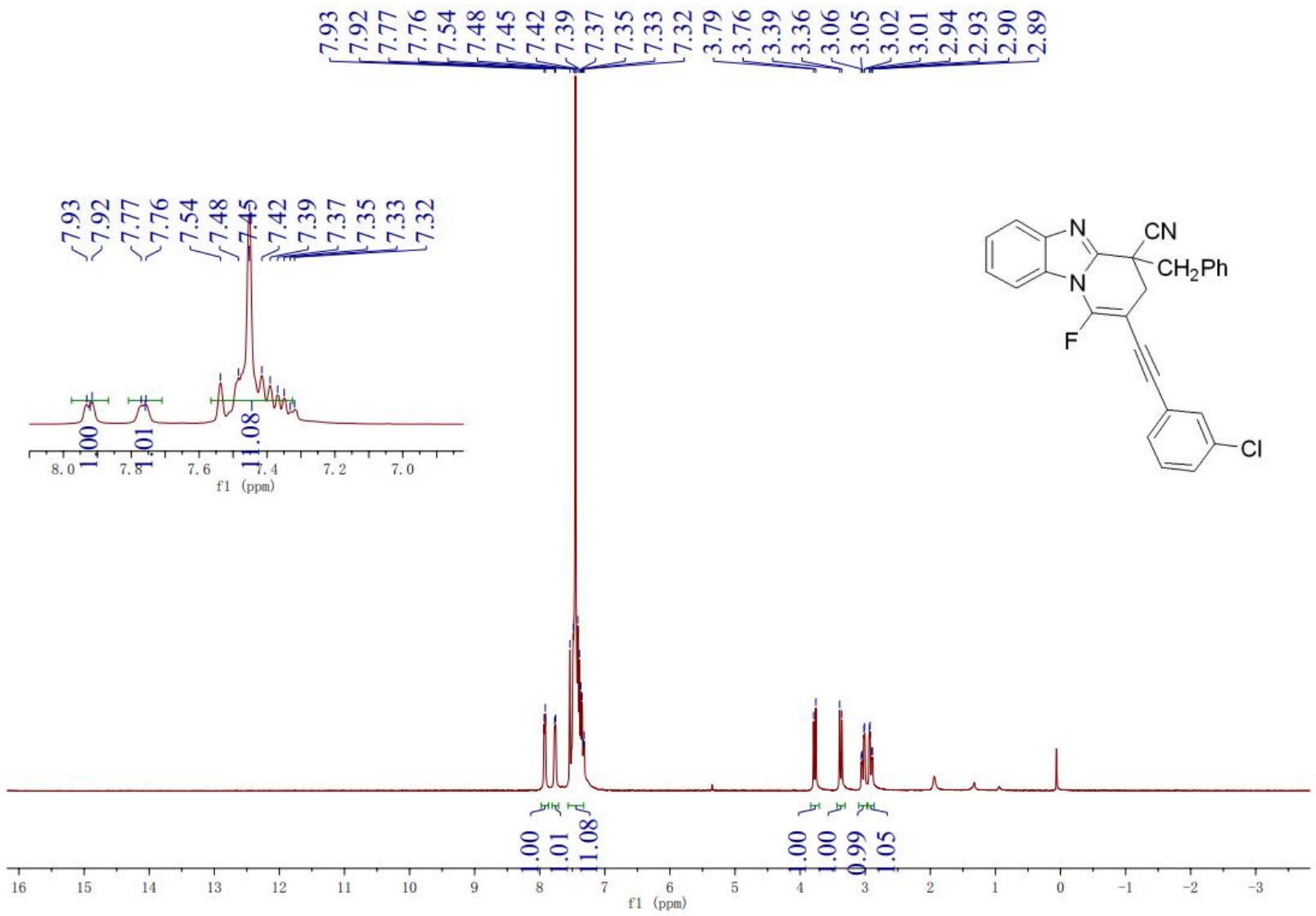
^{13}C NMR spectrum of **3z**



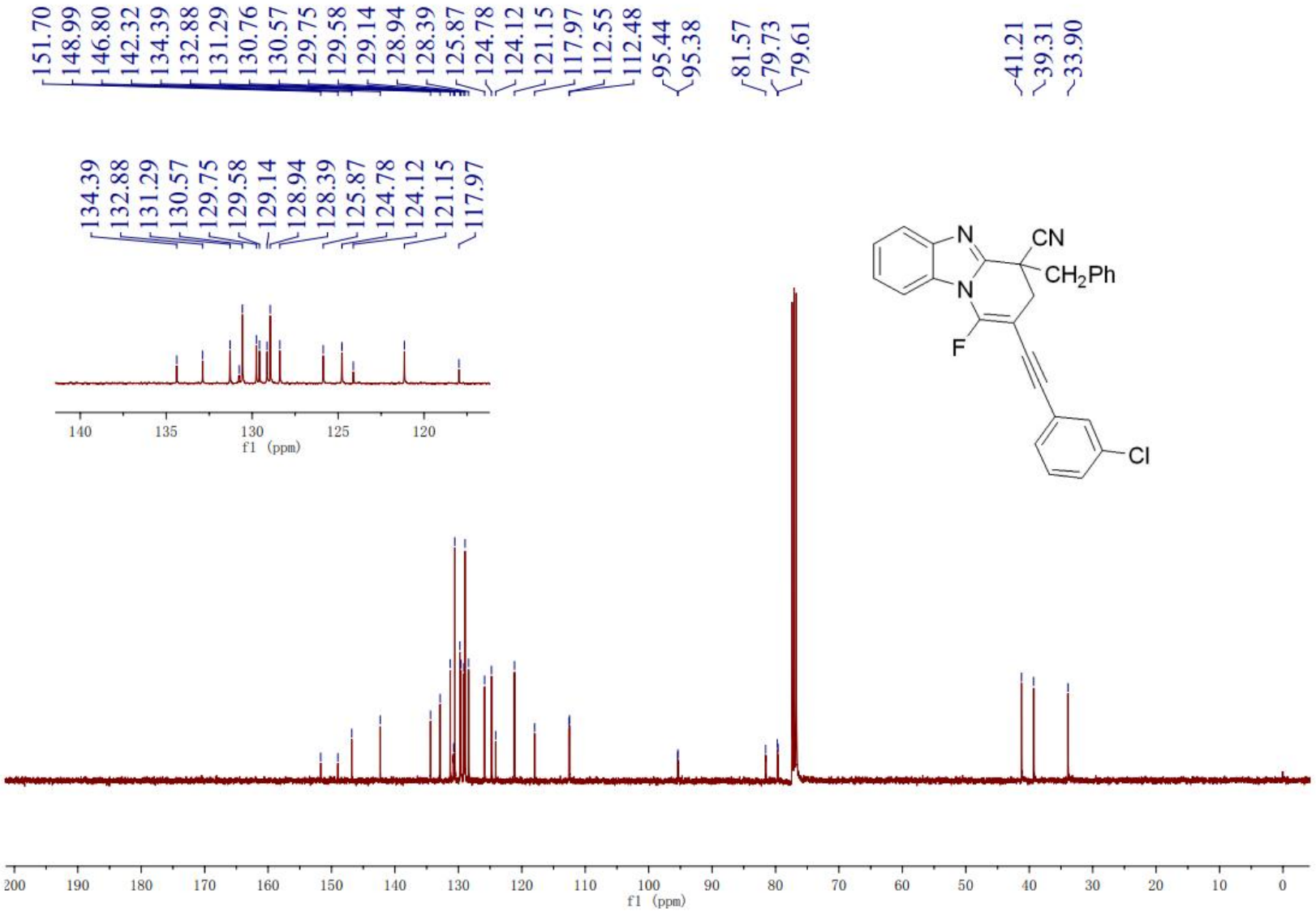
^{19}F NMR spectrum of **3z**



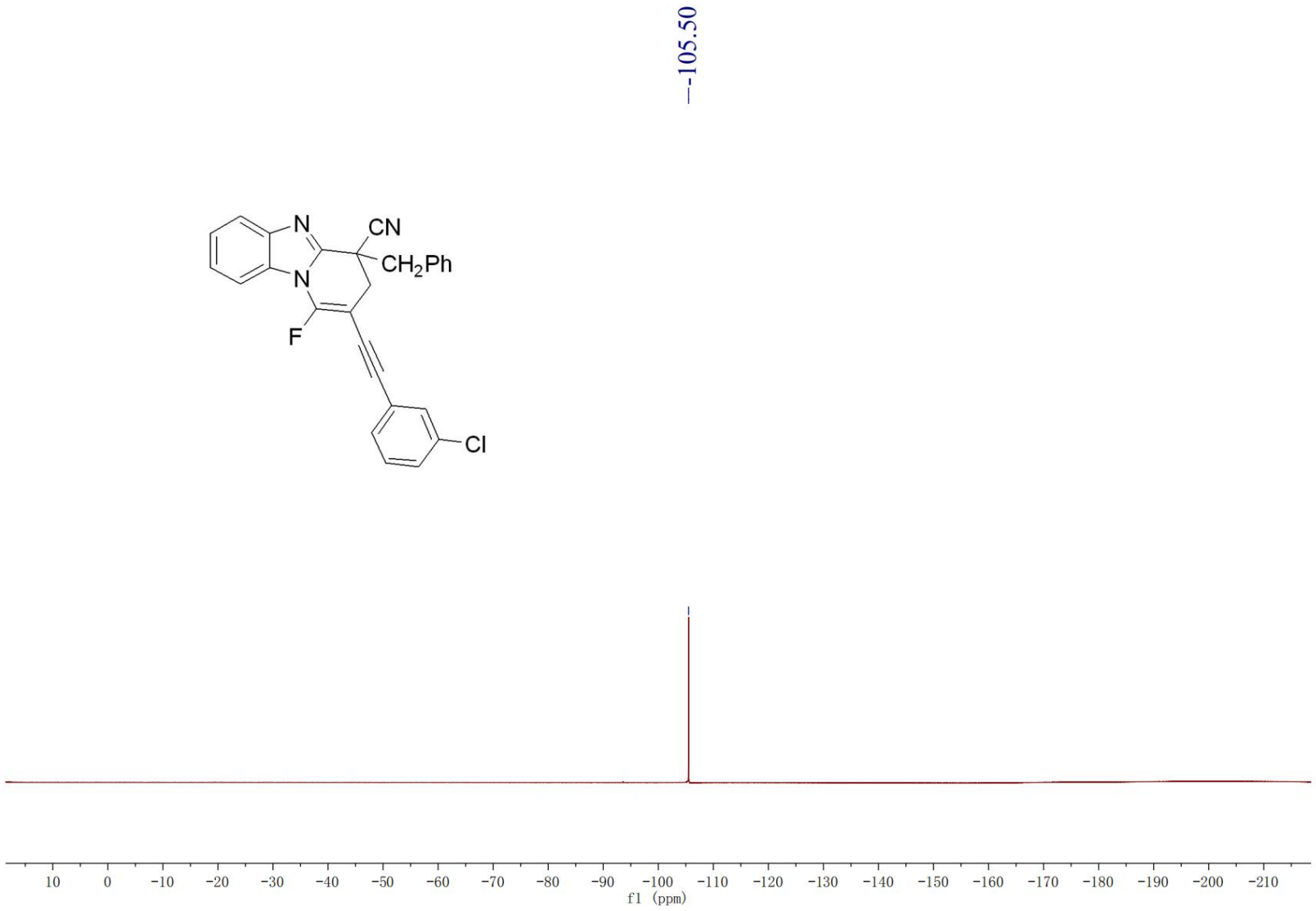
^{1}H NMR spectrum of **3aa**



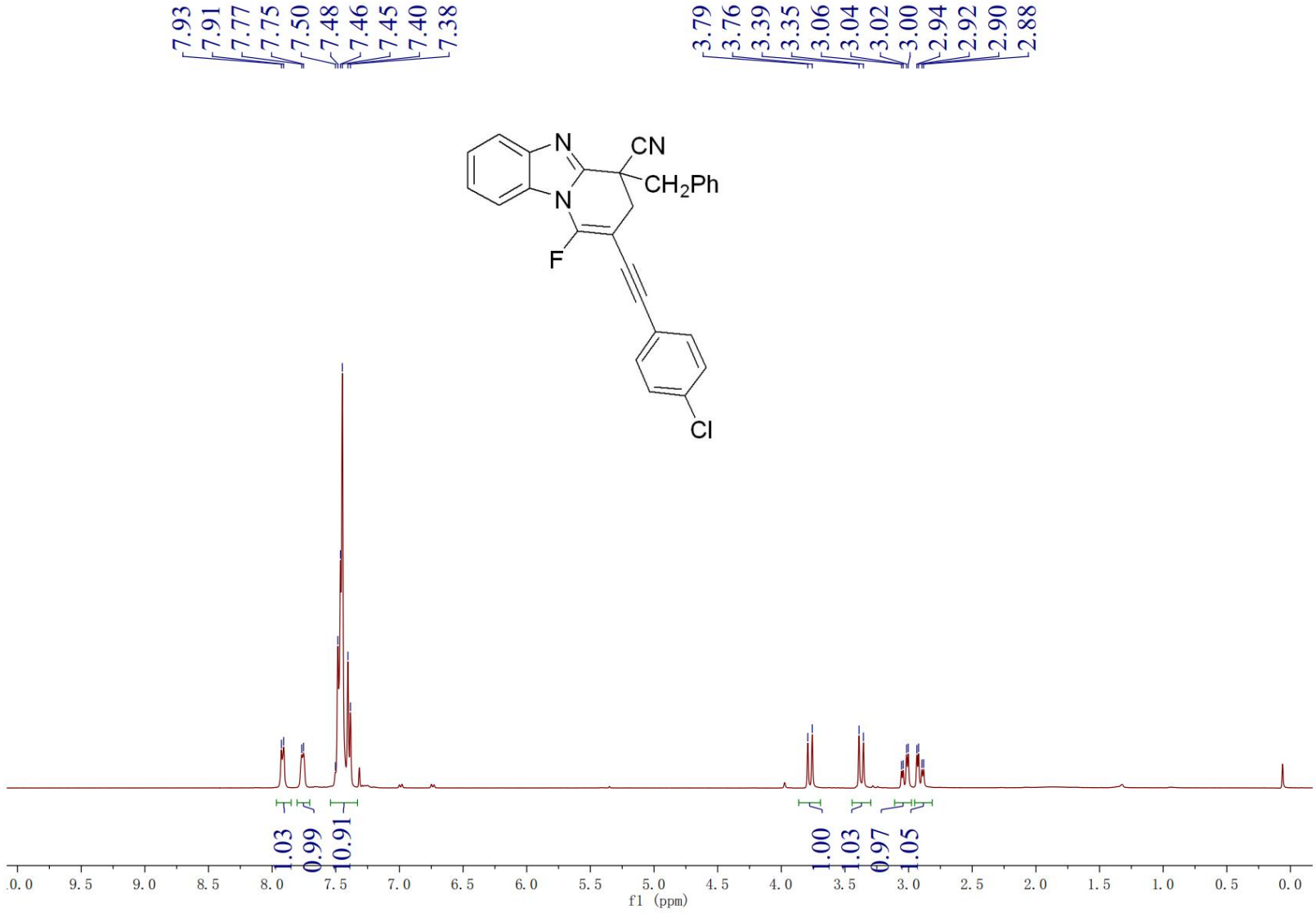
^{13}C NMR spectrum of **3aa**



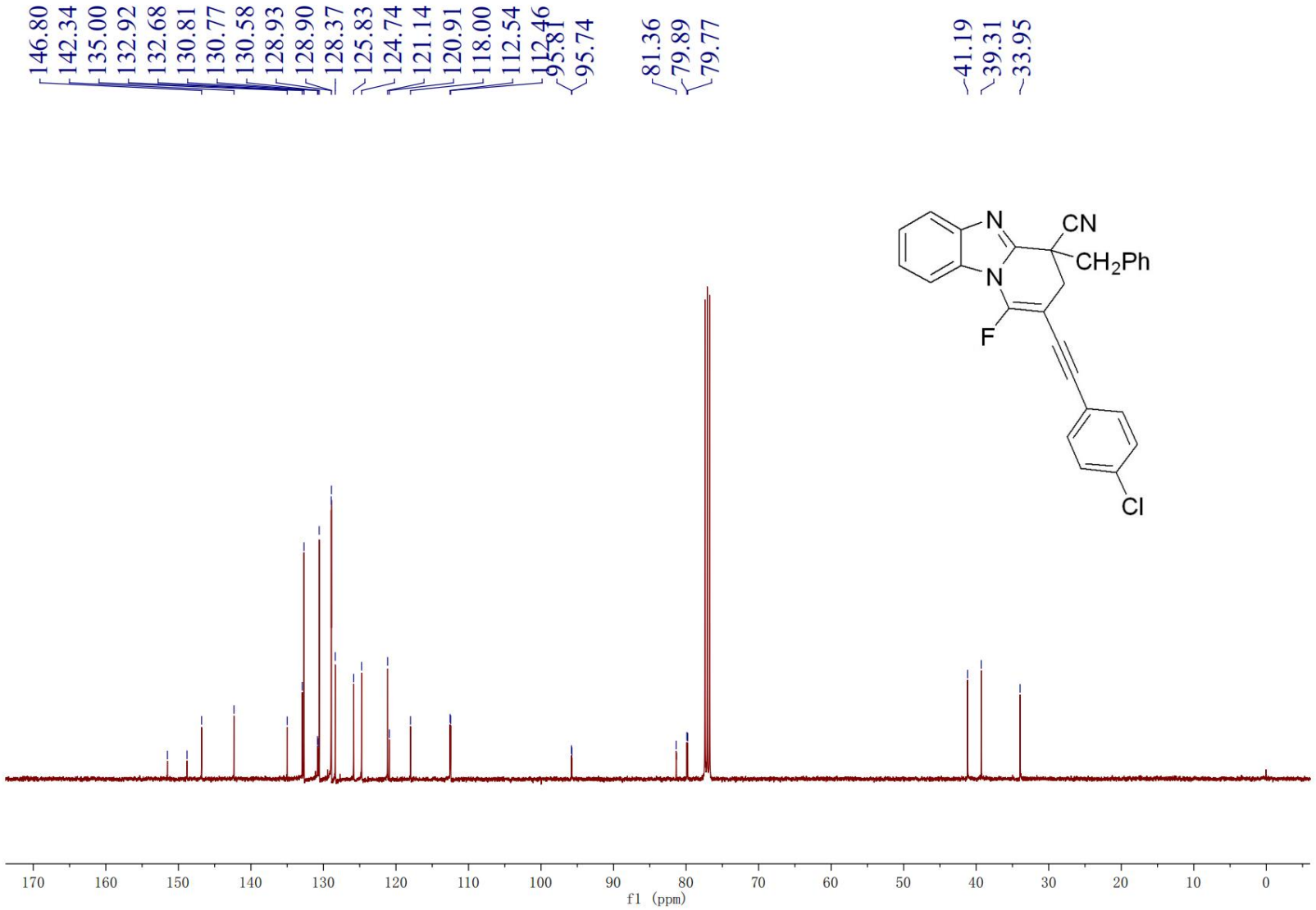
^{19}F NMR spectrum of **3aa**



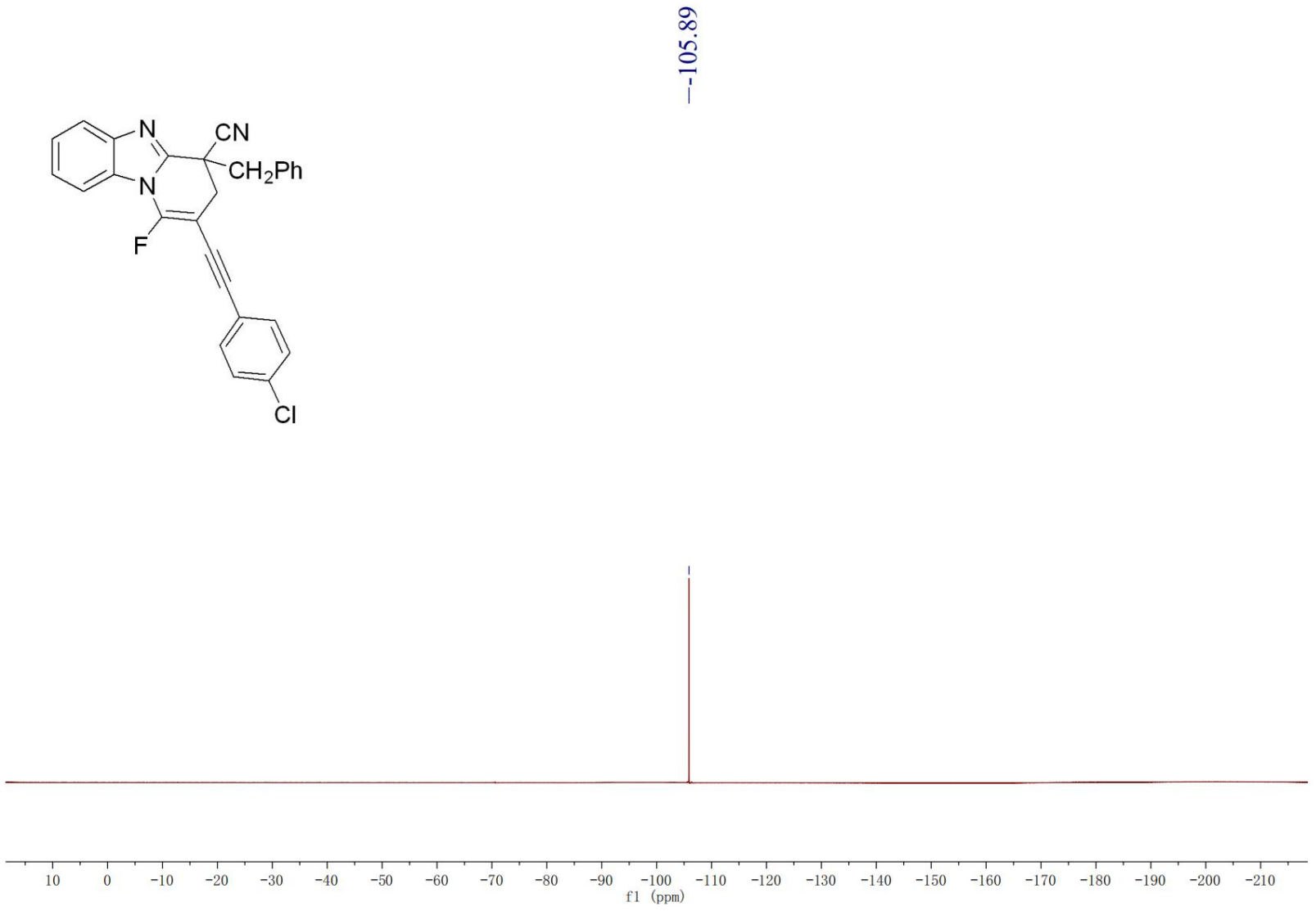
^{1}H NMR spectrum of **3ab**



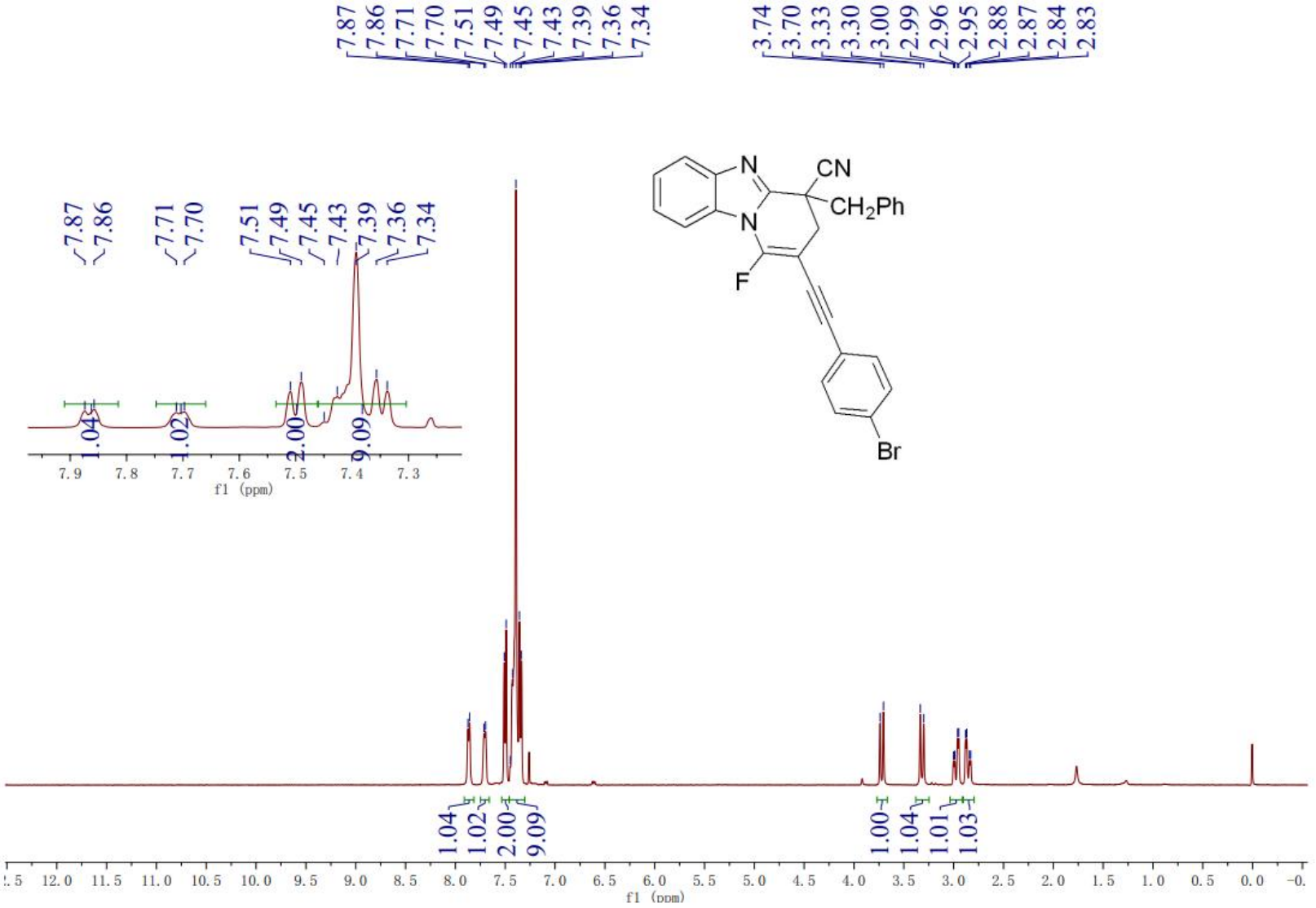
^{13}C NMR spectrum of **3ab**



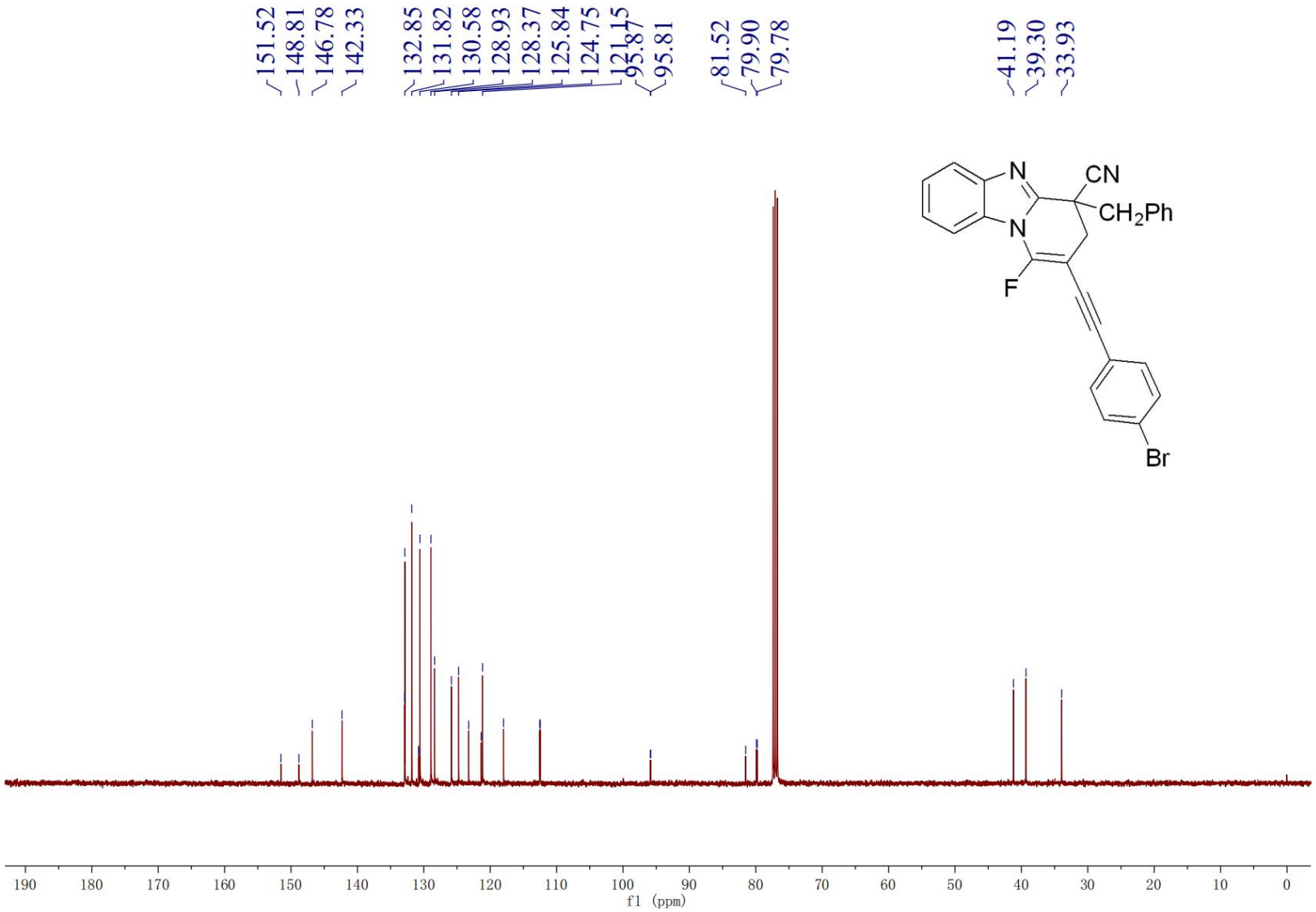
^{19}F NMR spectrum of **3ab**



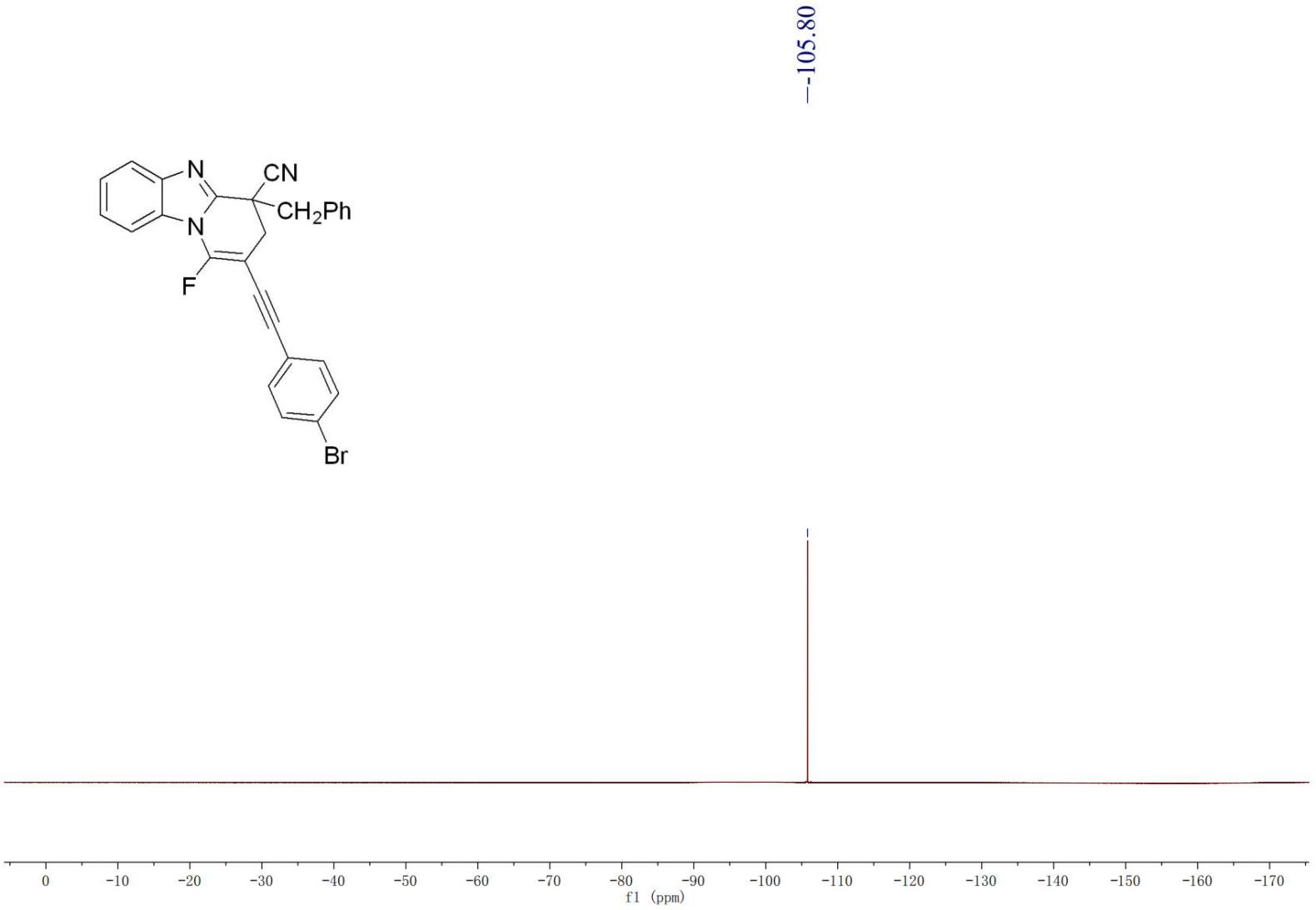
^{1}H NMR spectrum of **3ac**



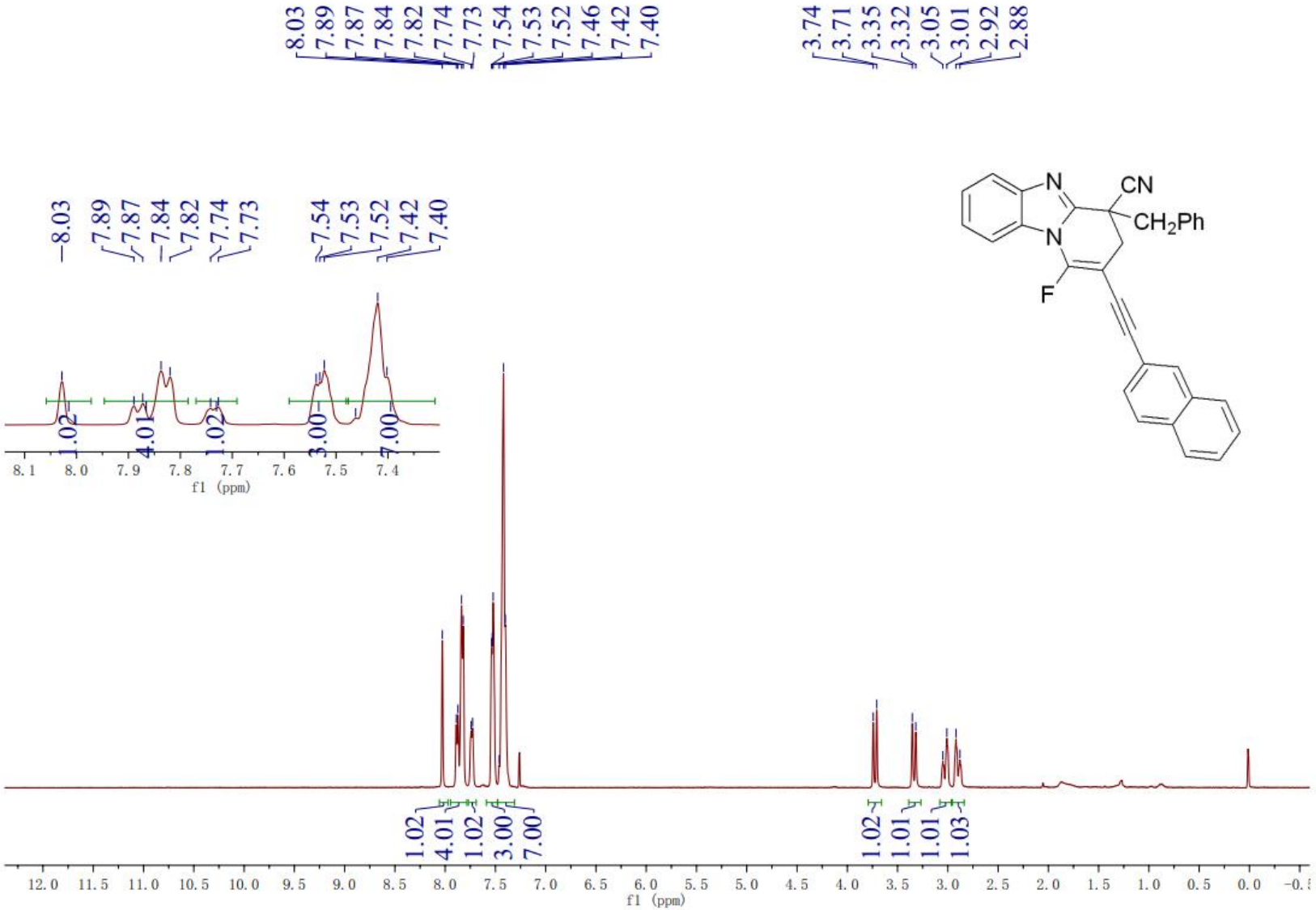
^{13}C NMR spectrum of **3ac**



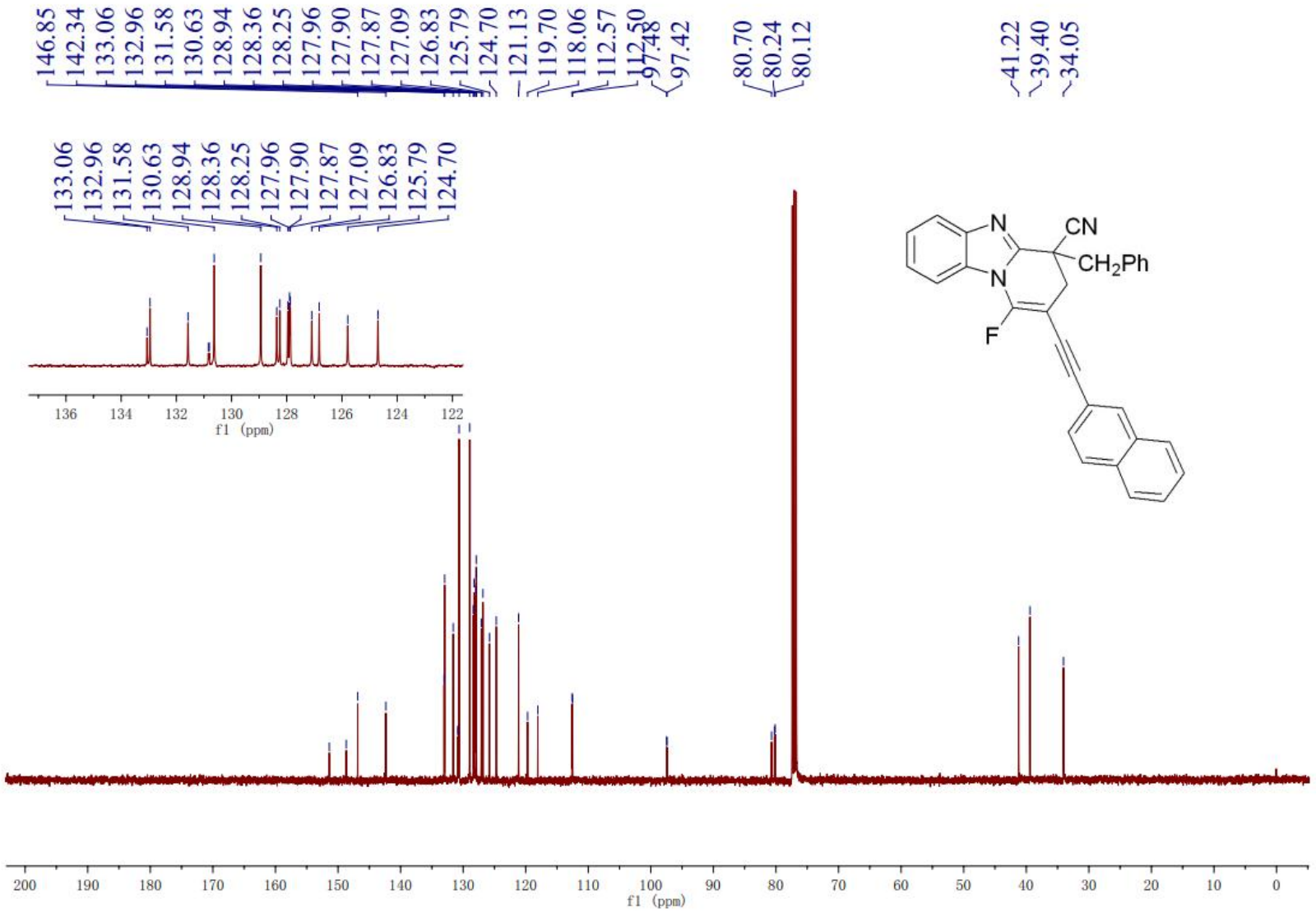
^{19}F NMR spectrum of **3ac**



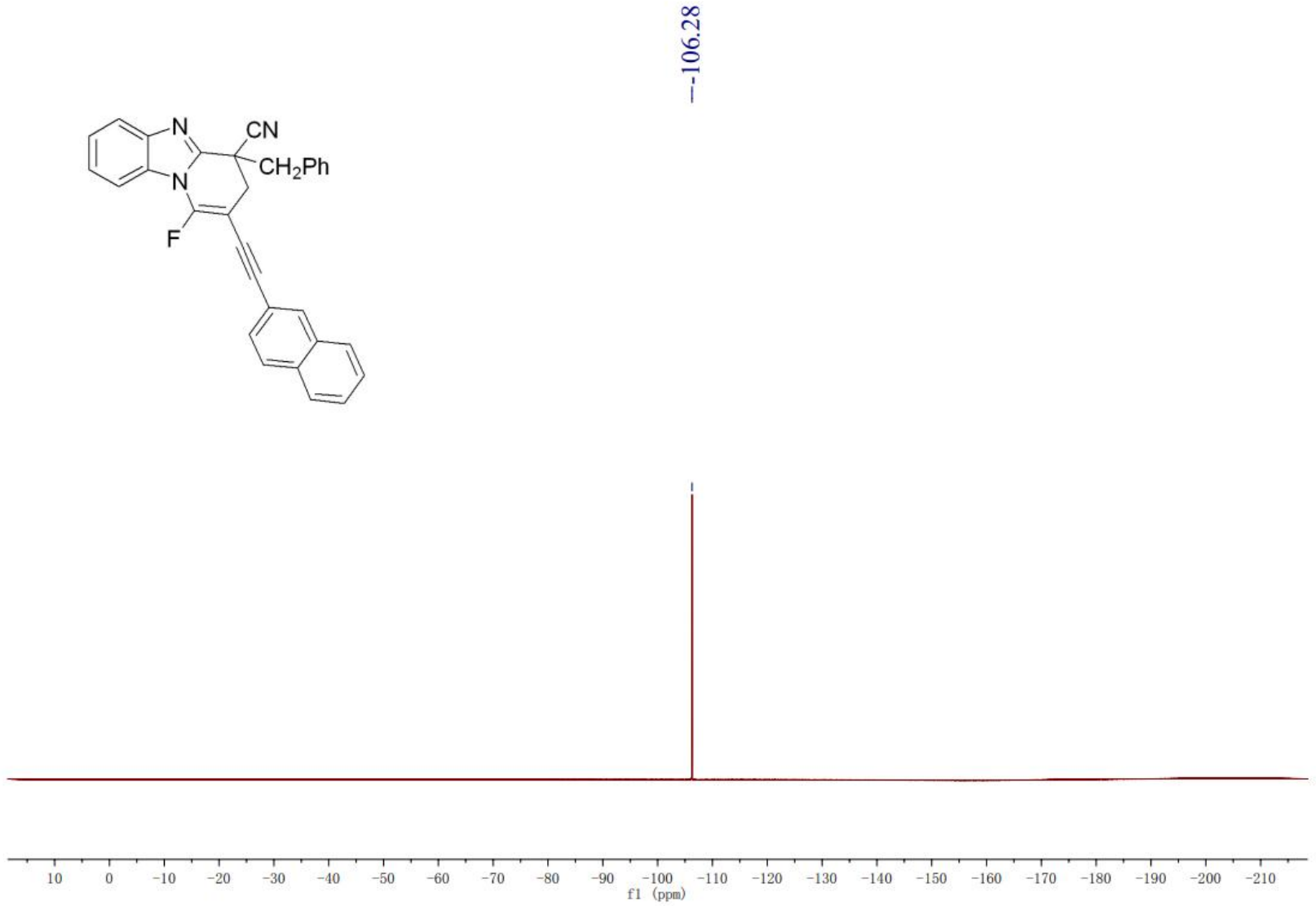
^{1}H NMR spectrum of **3ad**



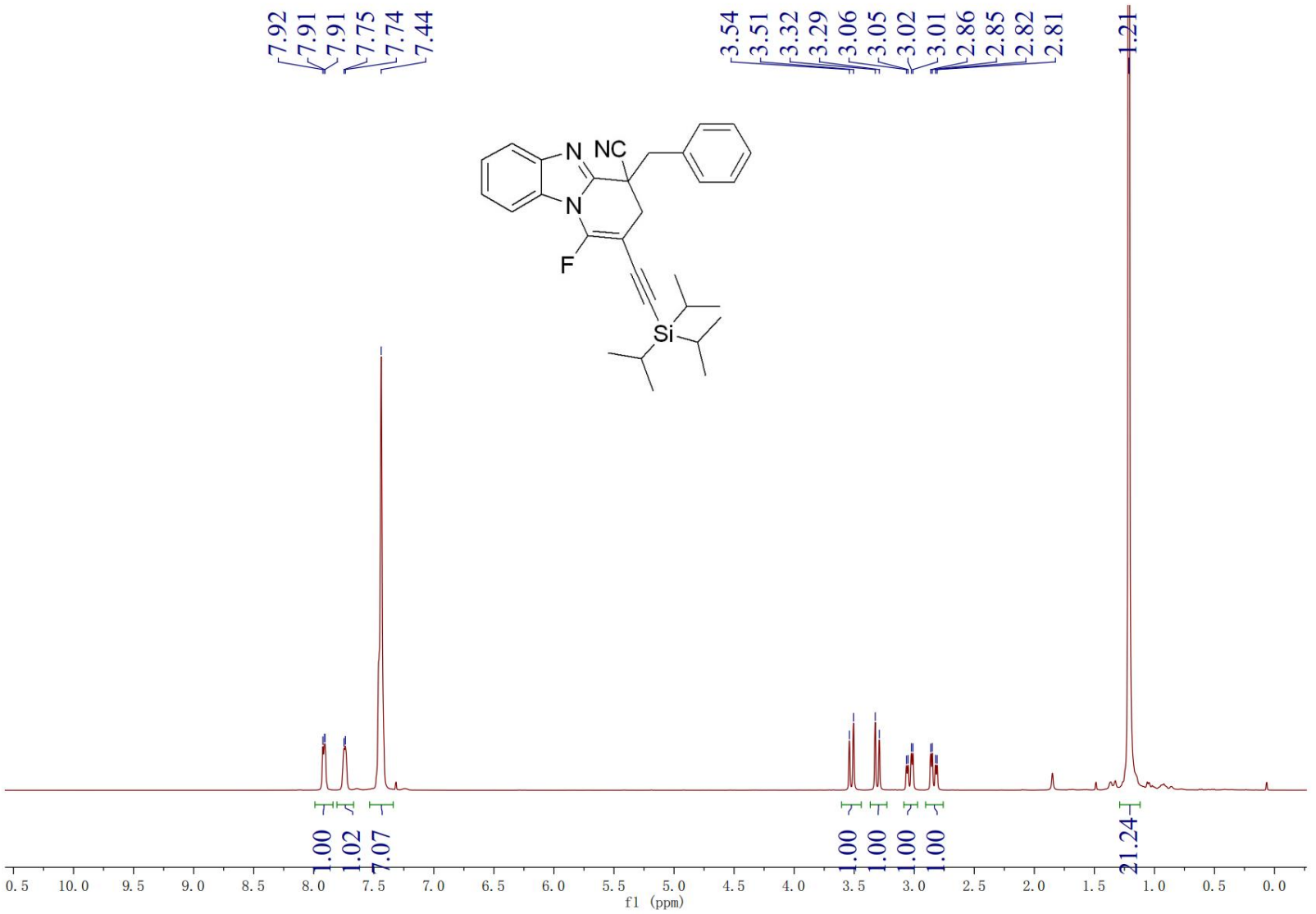
^{13}C NMR spectrum of **3ad**



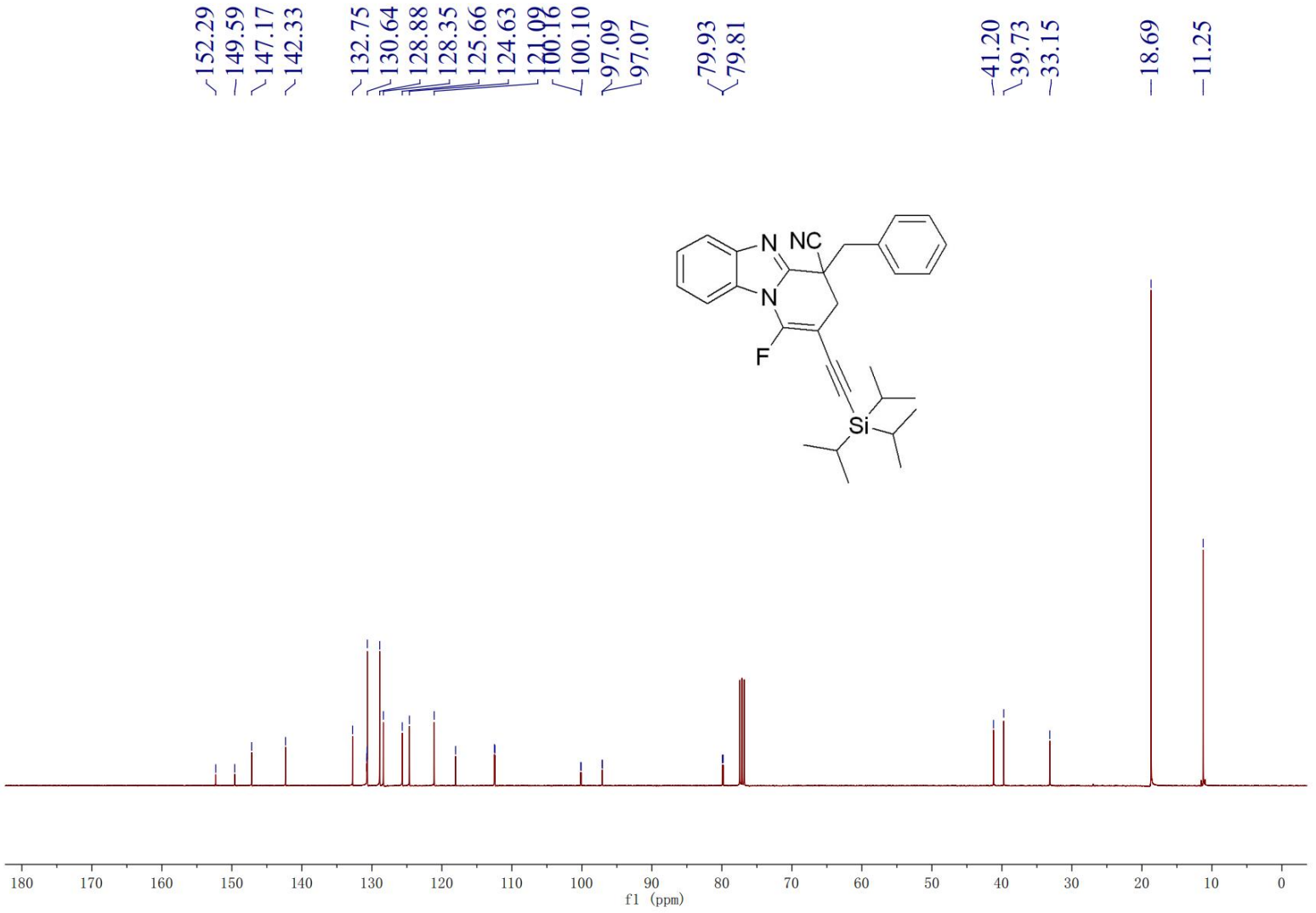
^{19}F NMR spectrum of **3ad**



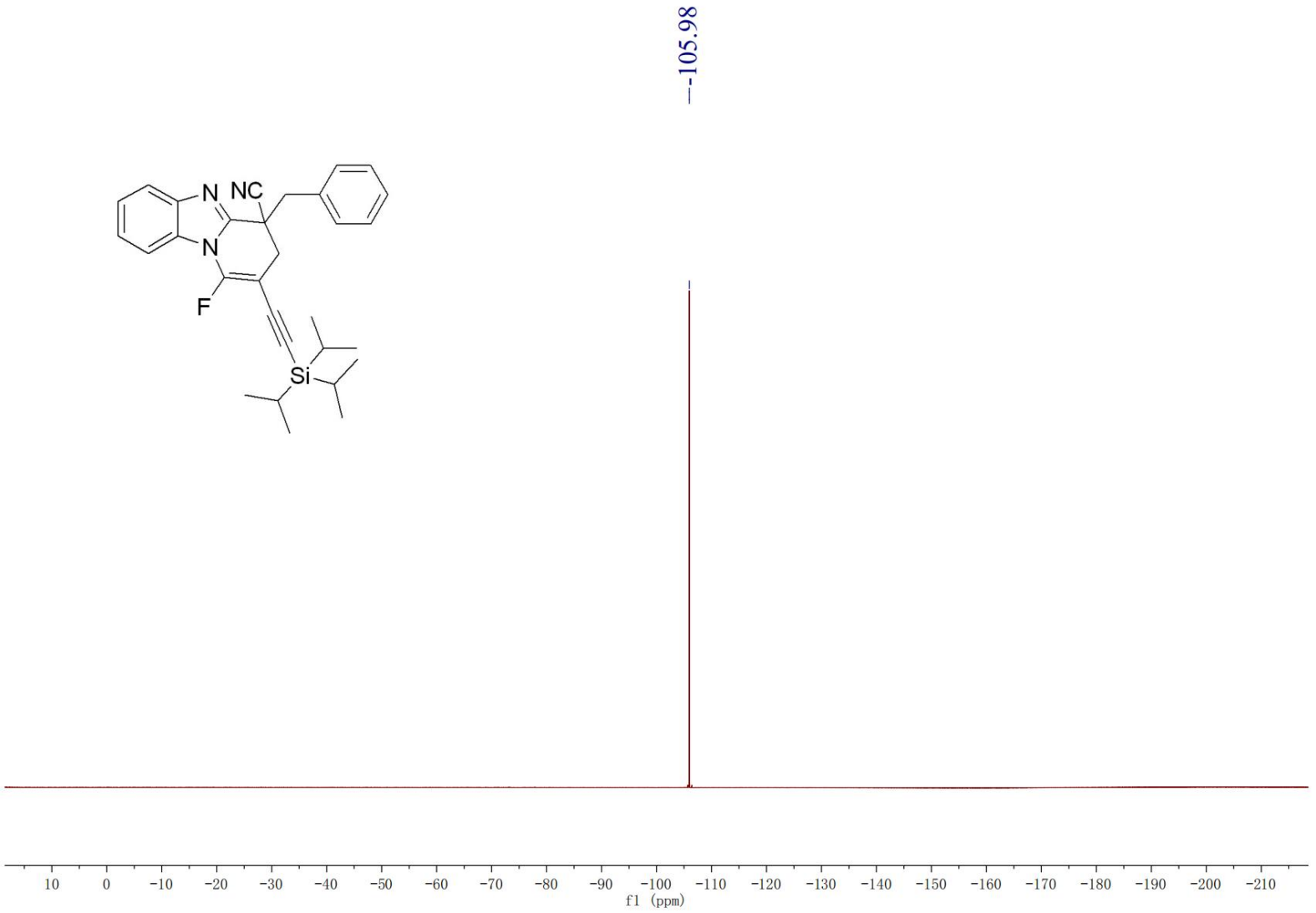
^{1}H NMR spectrum of **3ae**



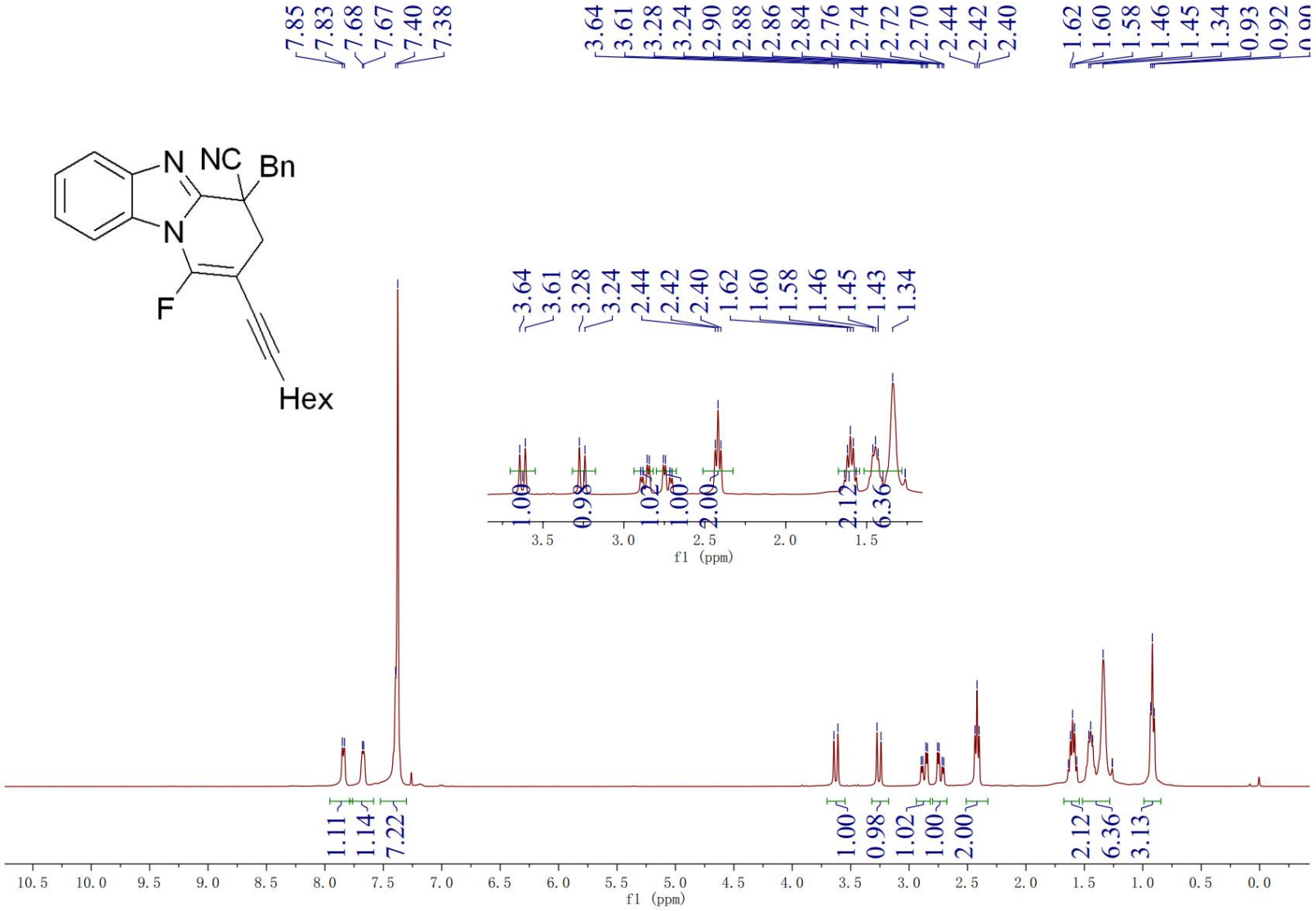
^{13}C NMR spectrum of **3ae**



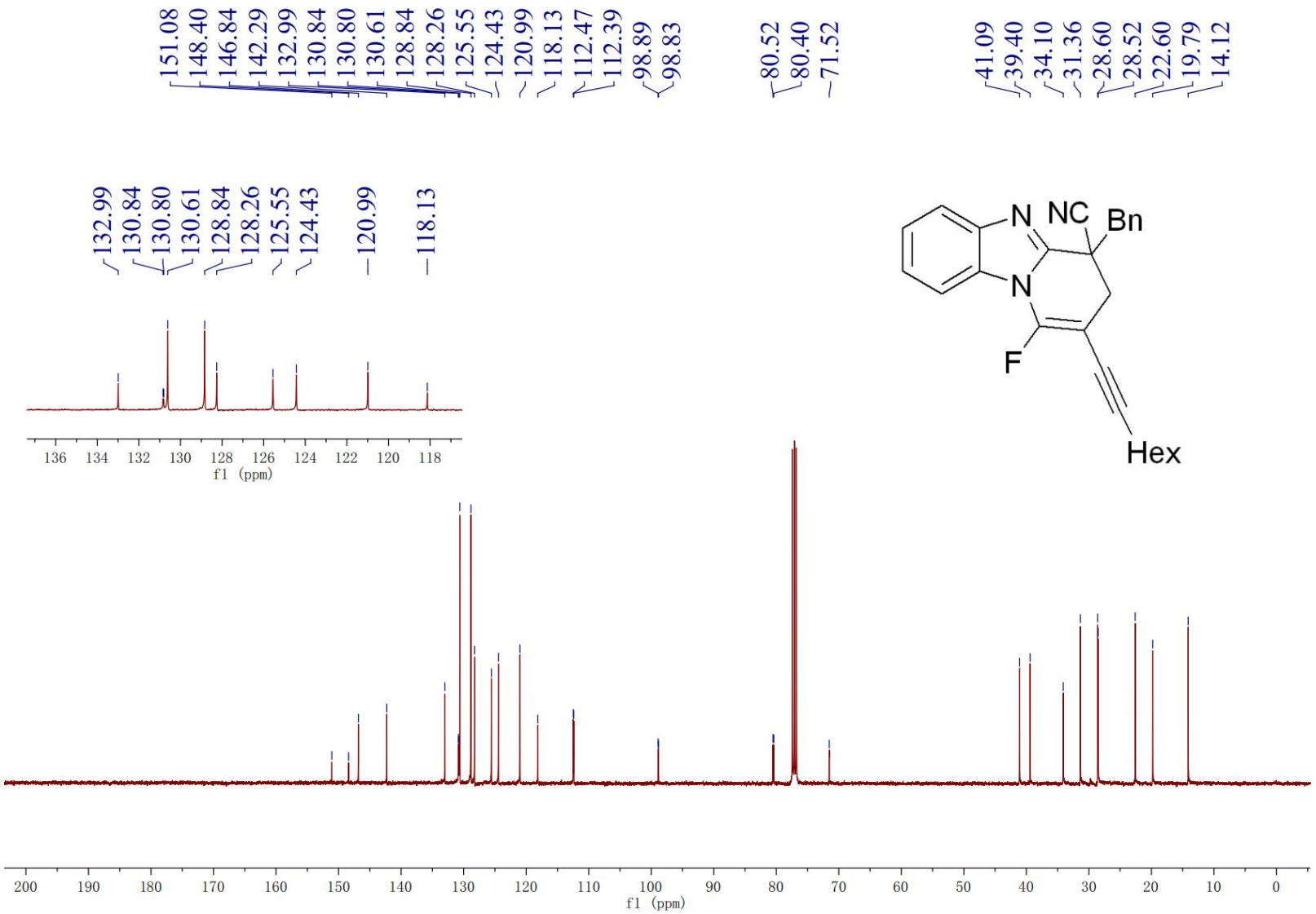
^{19}F NMR spectrum of **3ae**



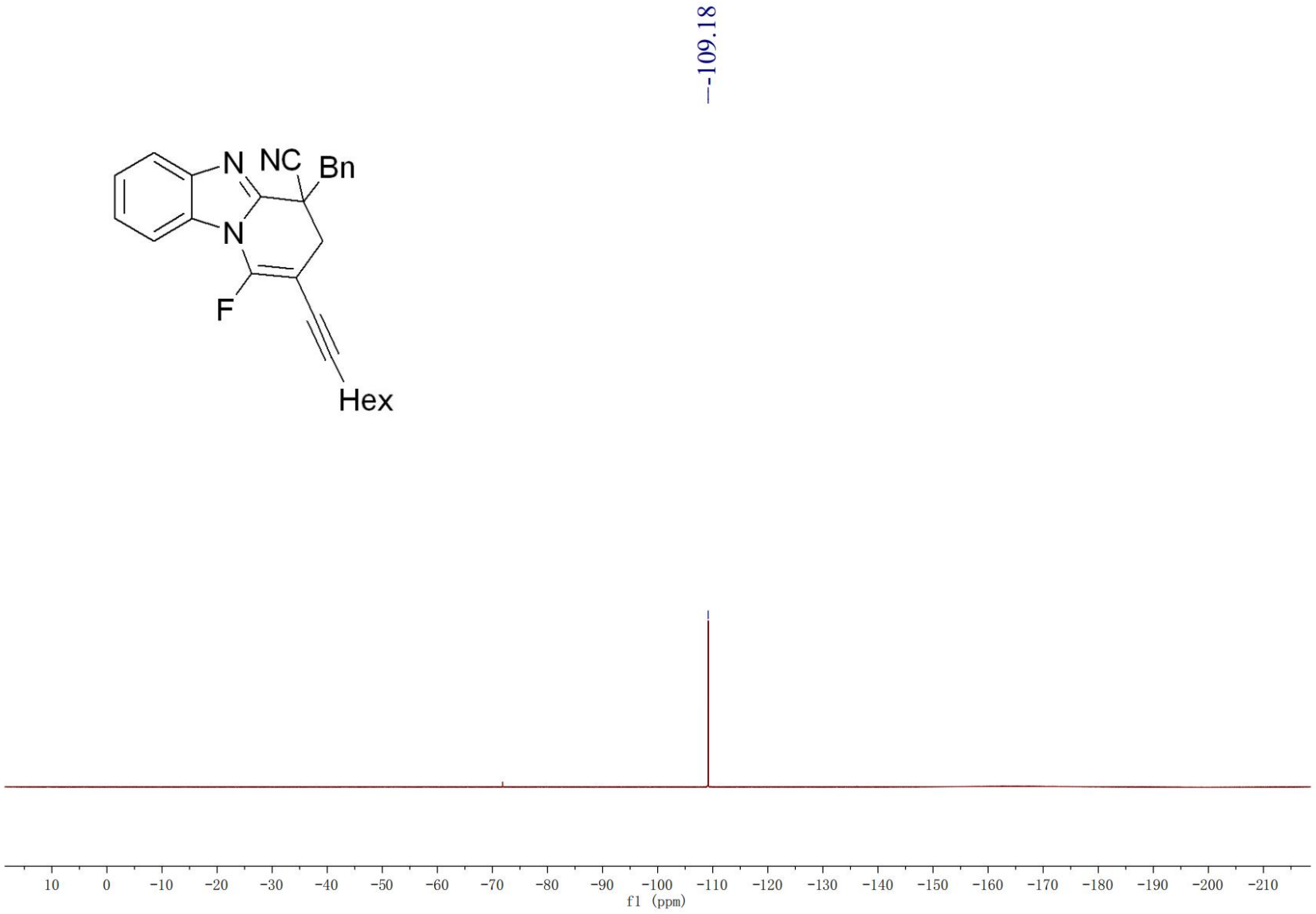
^{1}H NMR spectrum of **3af**



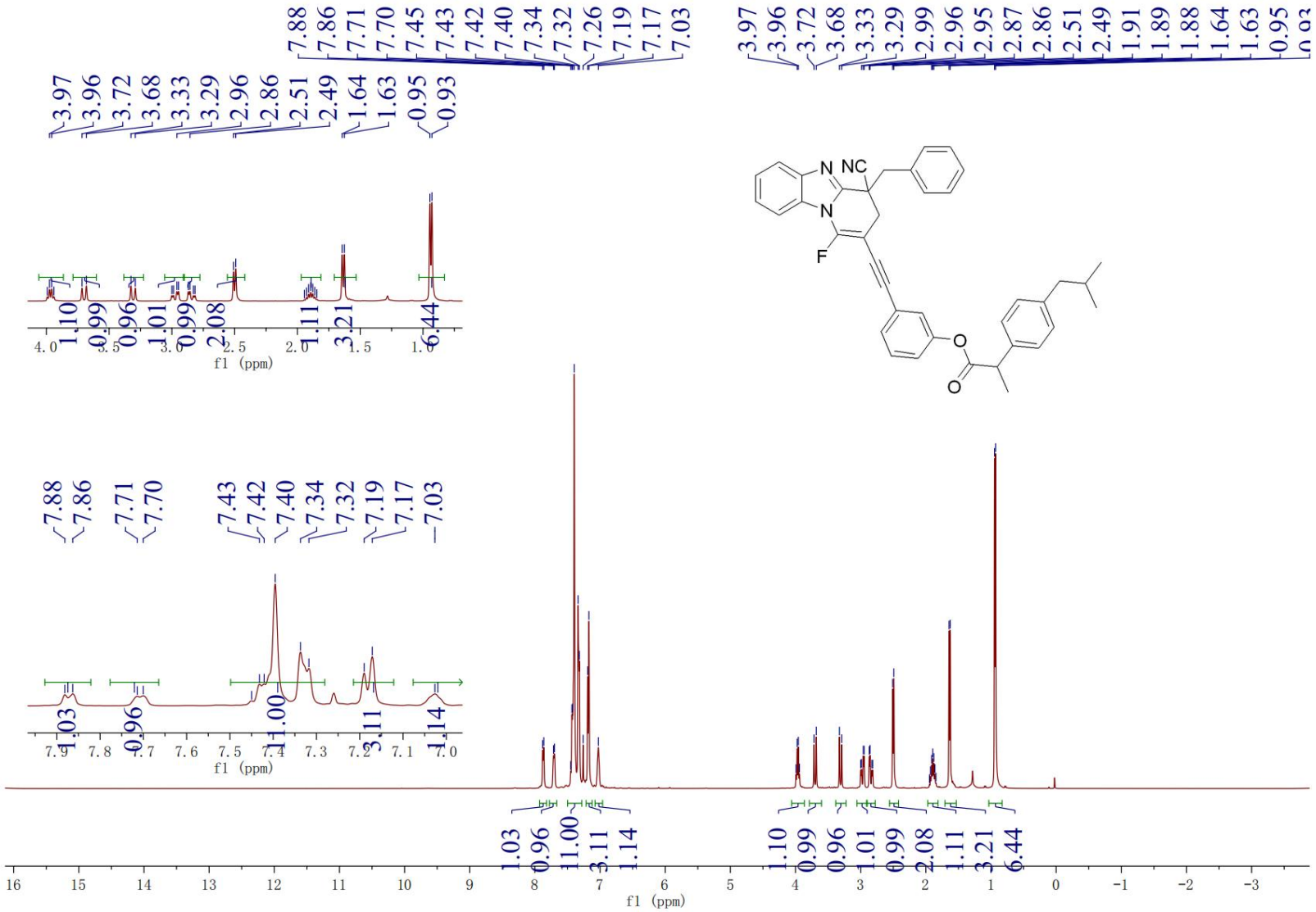
^{13}C NMR spectrum of **3af**



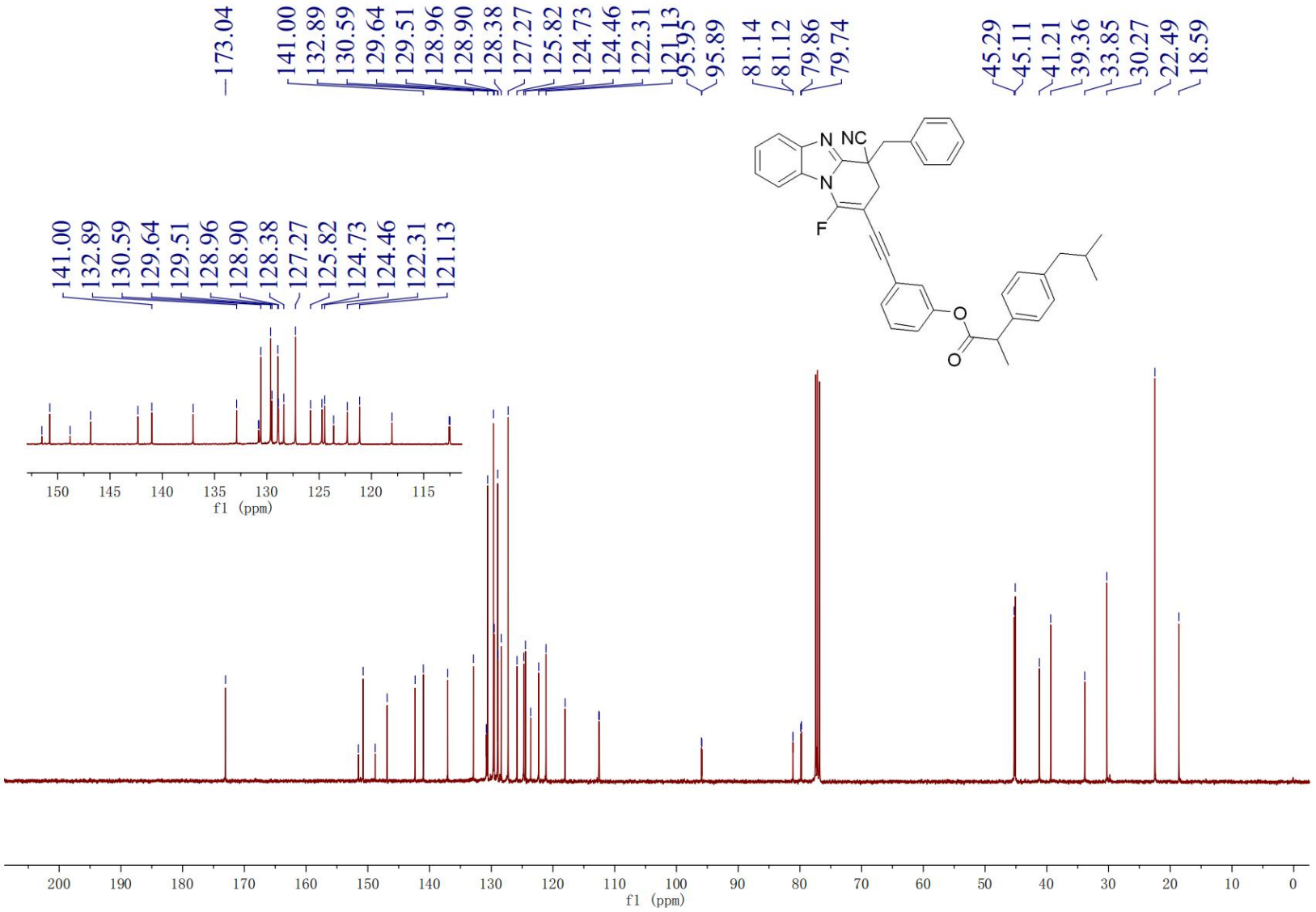
^{19}F NMR spectrum of **3af**



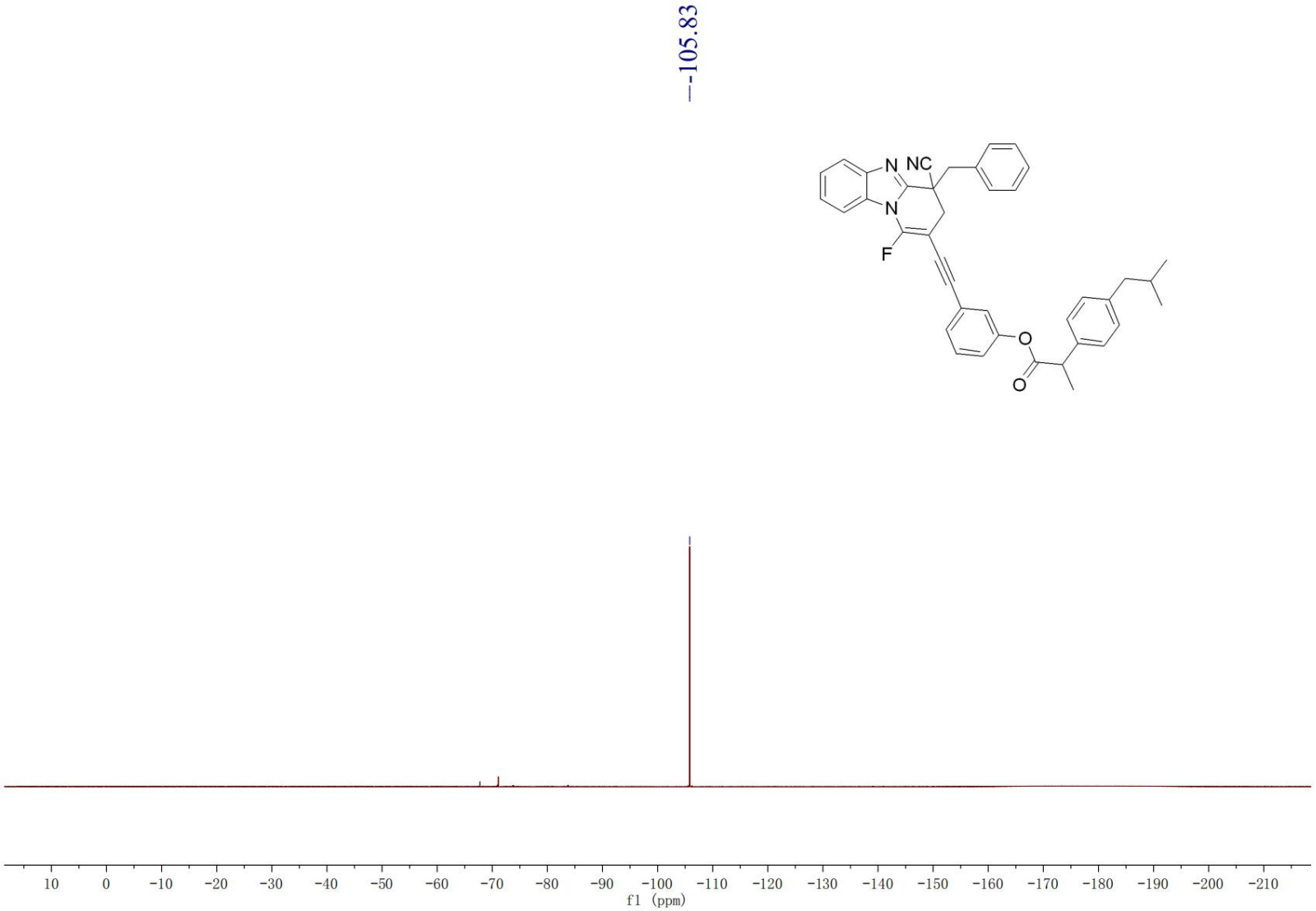
^{1}H NMR spectrum of **3ag**



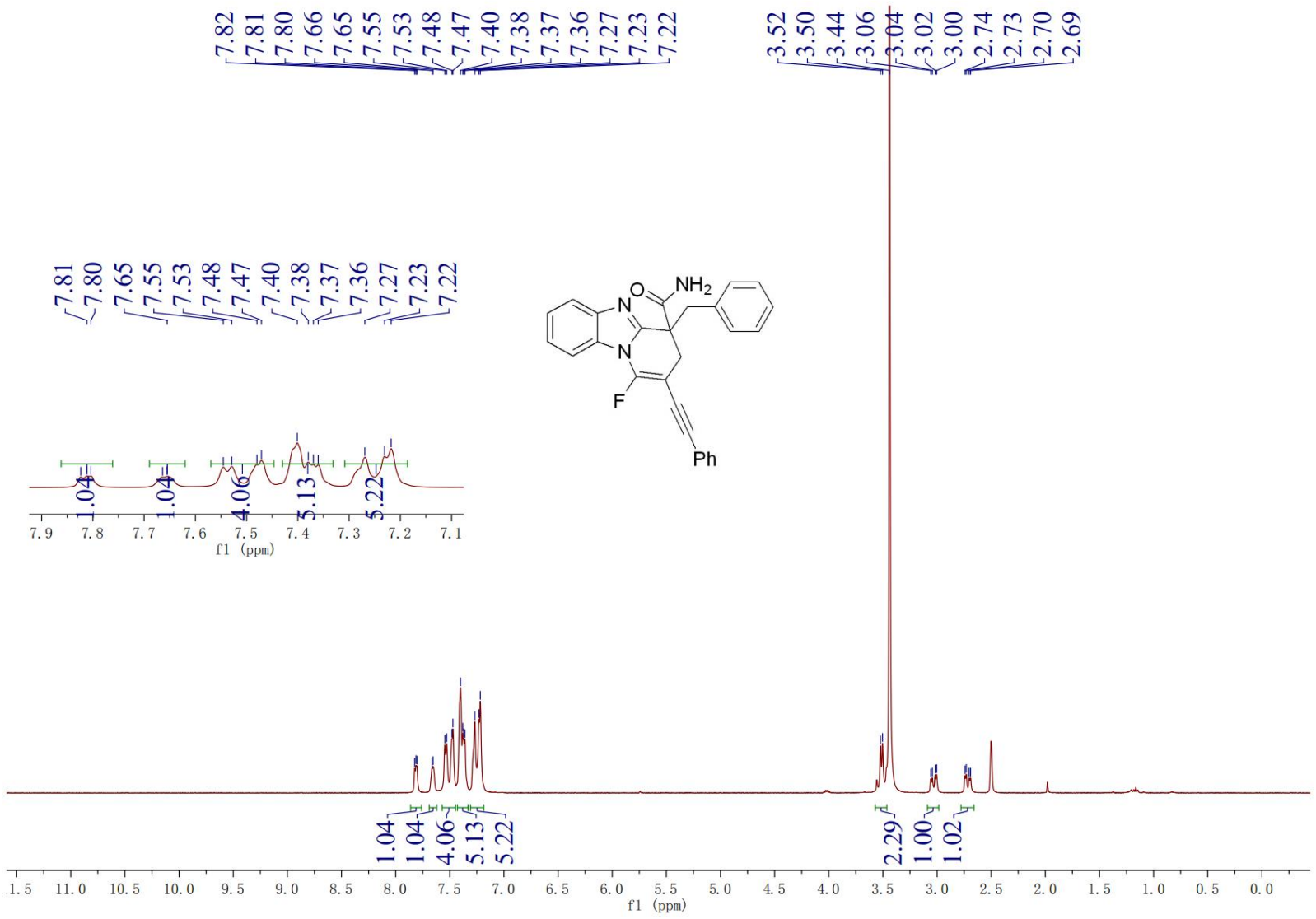
^{13}C NMR spectrum of **3ag**



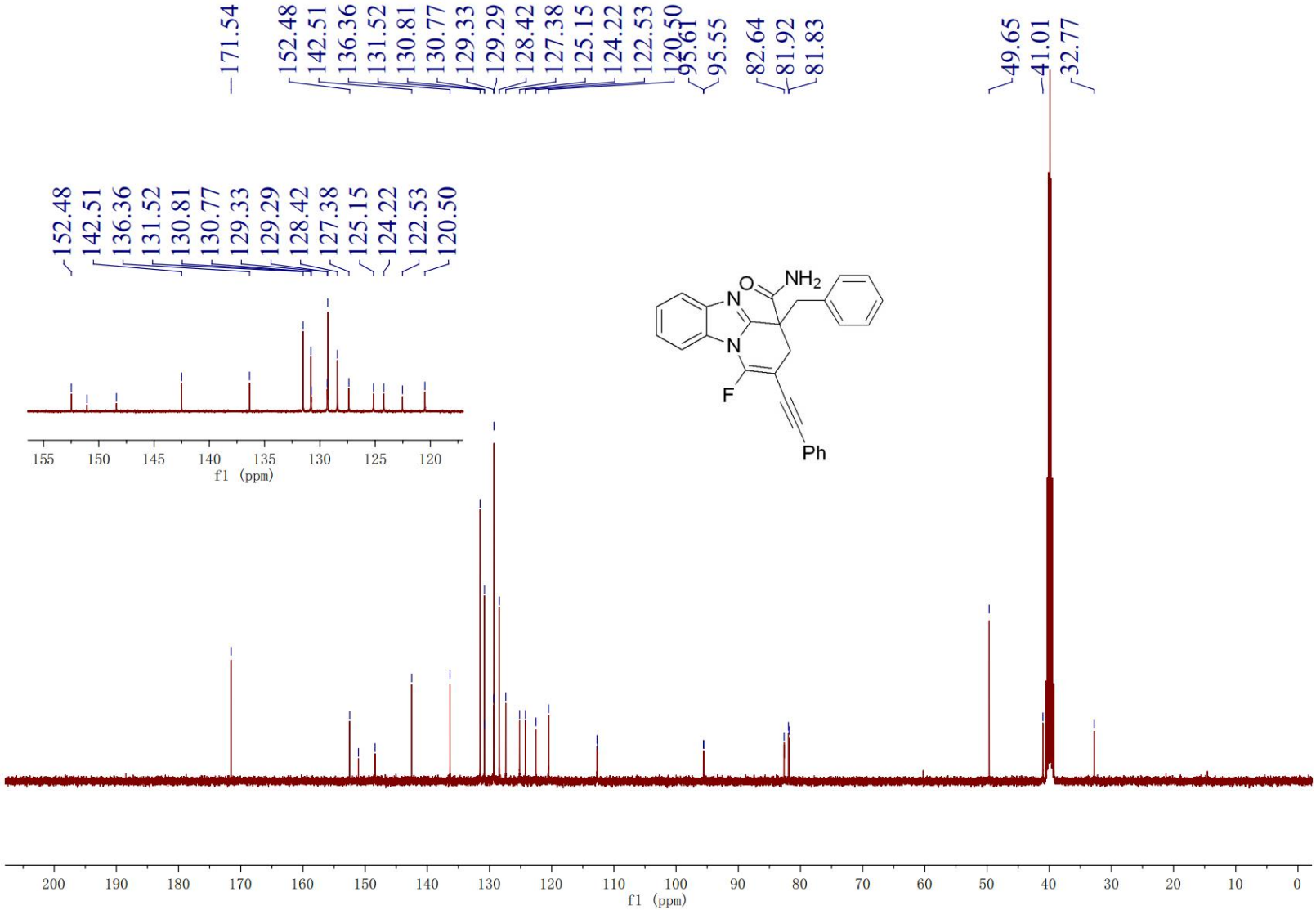
^{19}F NMR spectrum of **3ag**



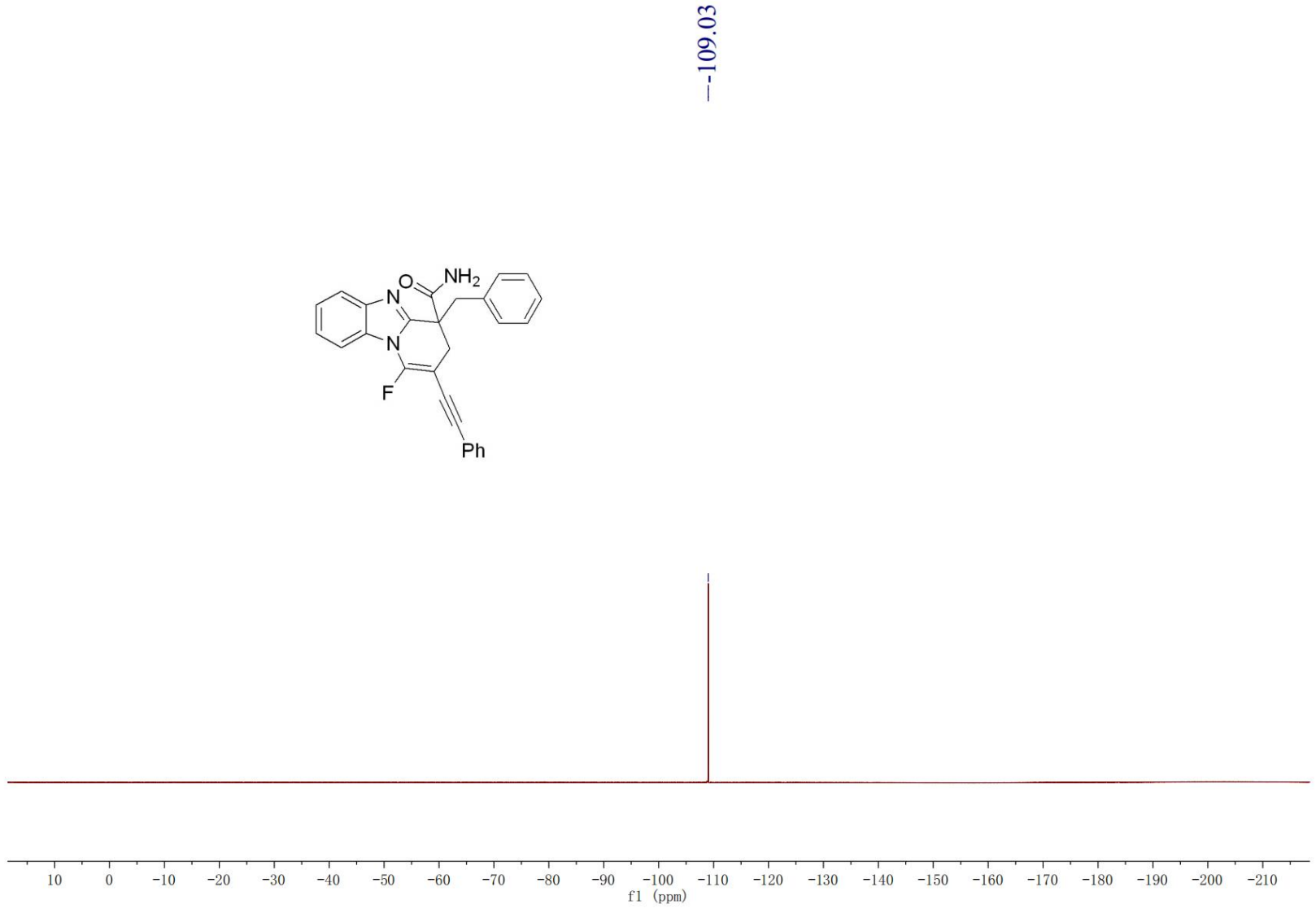
^{1}H NMR spectrum of **4**



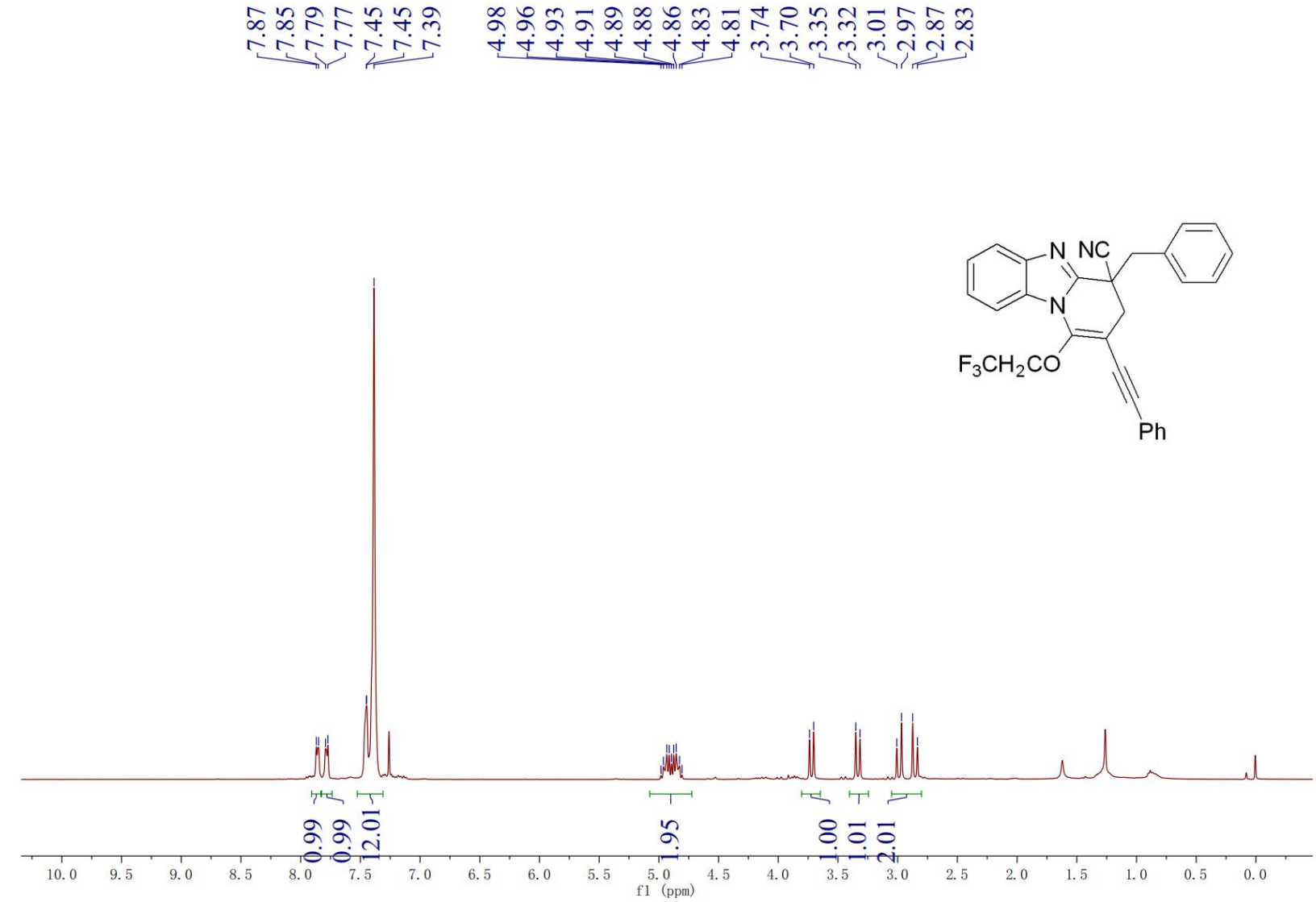
^{13}C NMR spectrum of **4**



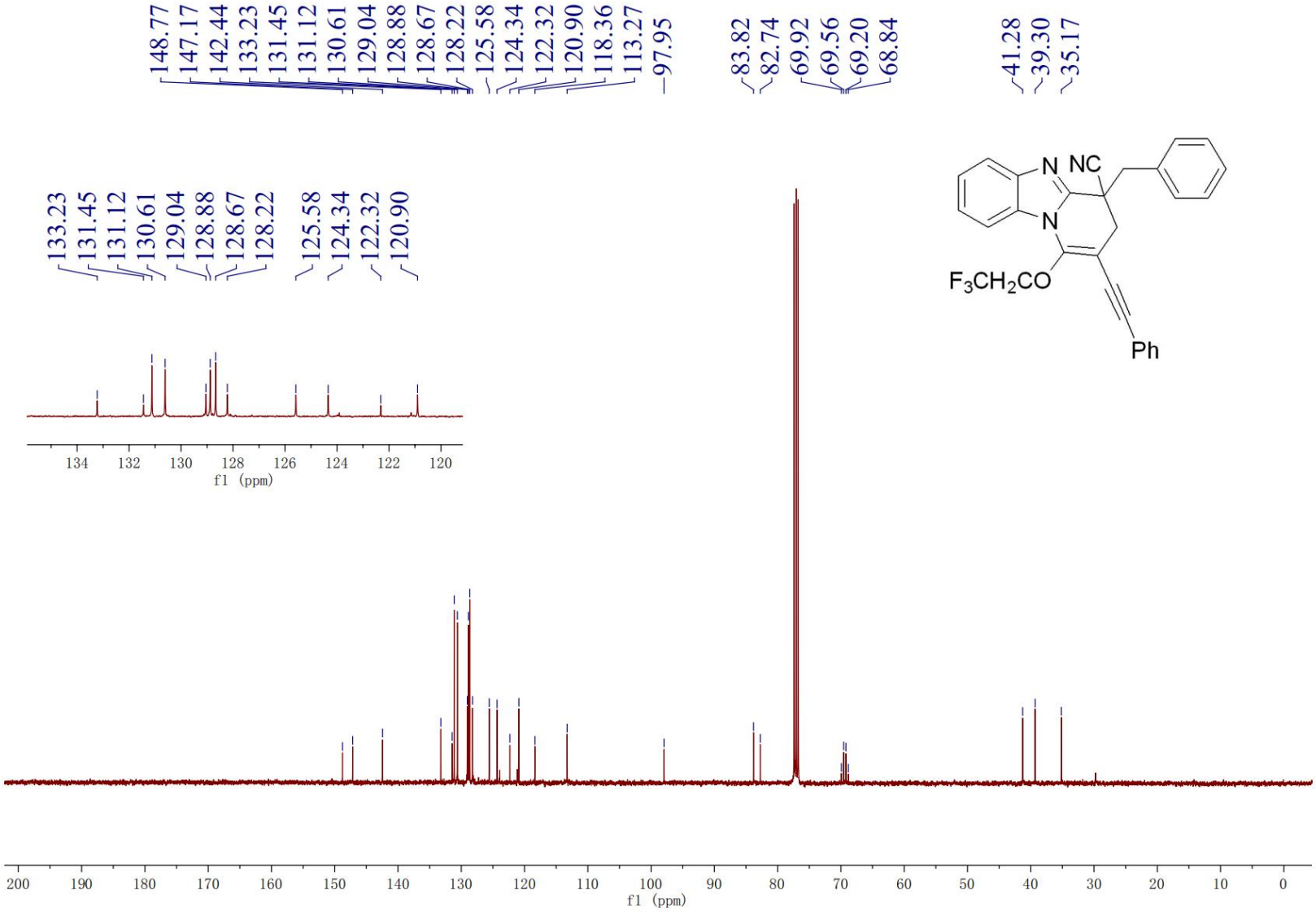
^{19}F NMR spectrum of **4**



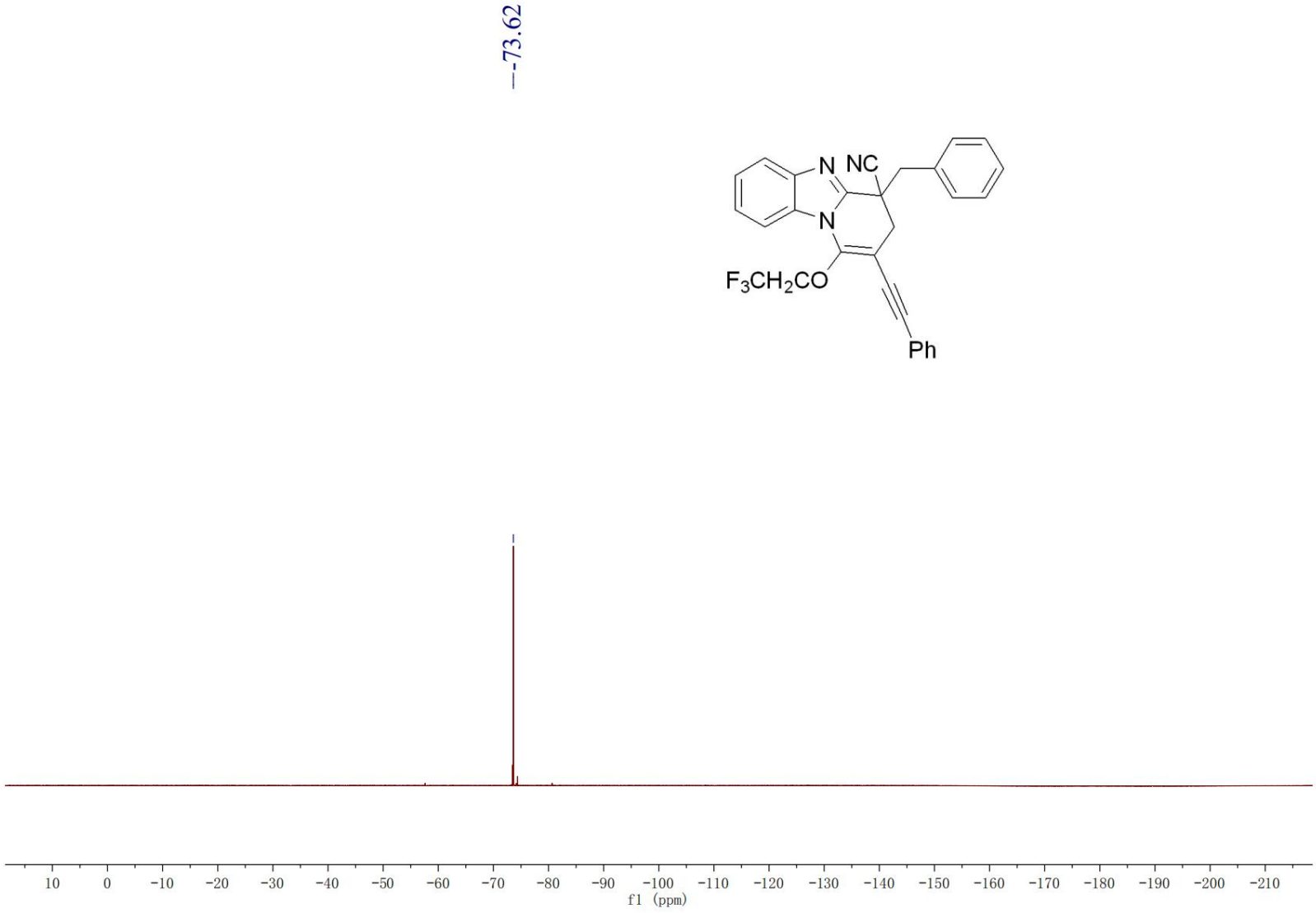
^{1}H NMR spectrum of **5**



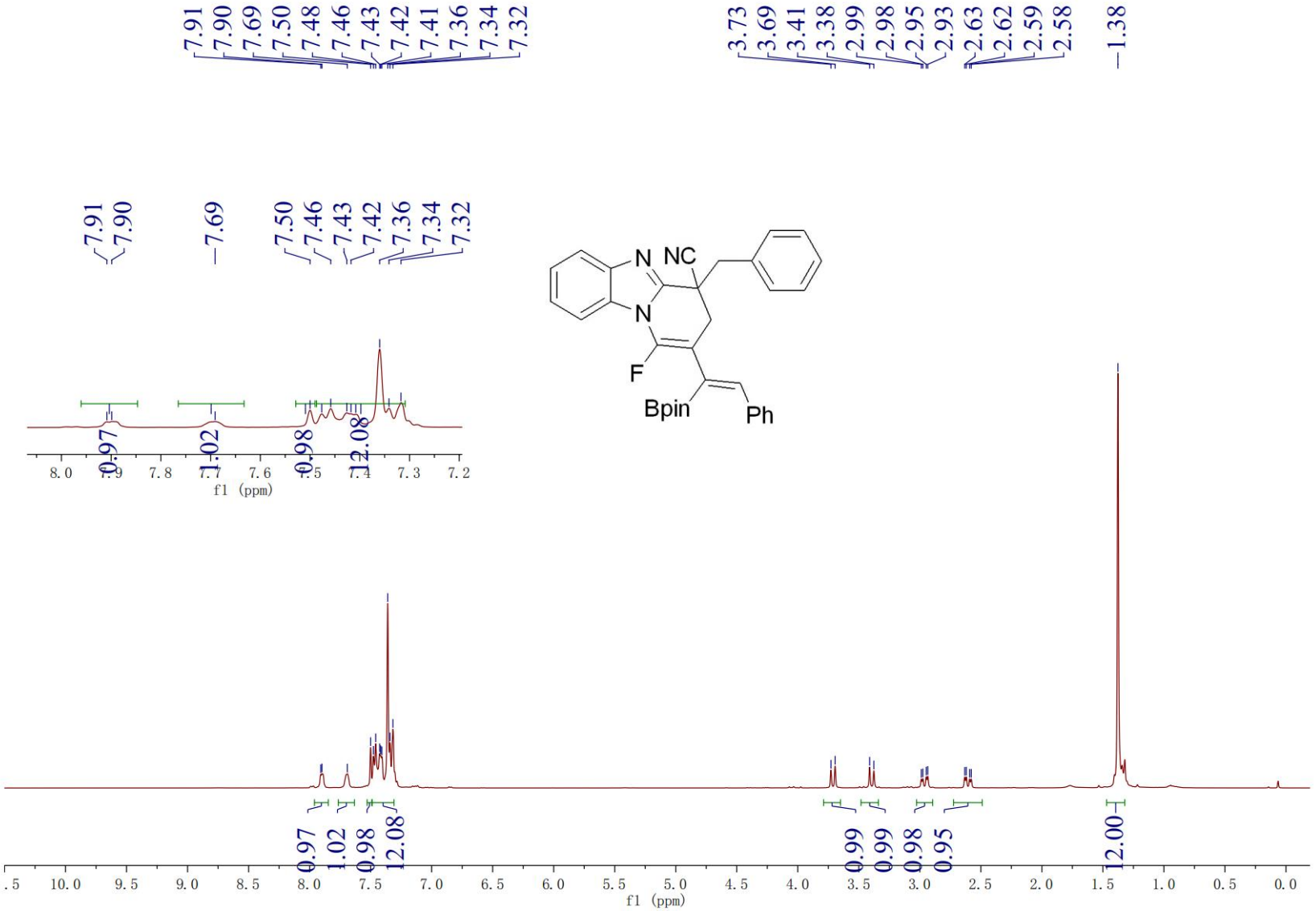
^{13}C NMR spectrum of **5**



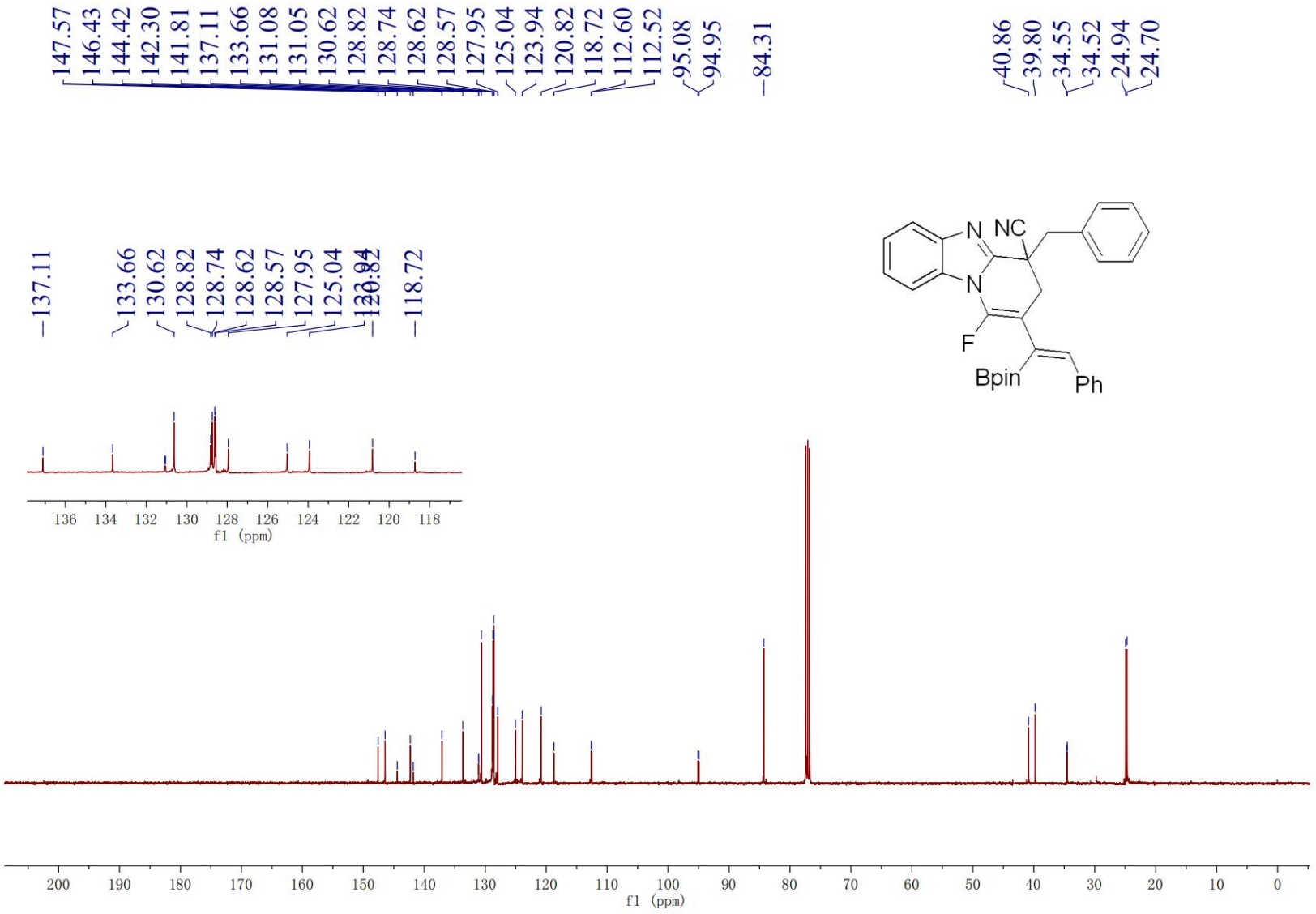
^{19}F NMR spectrum of **5**



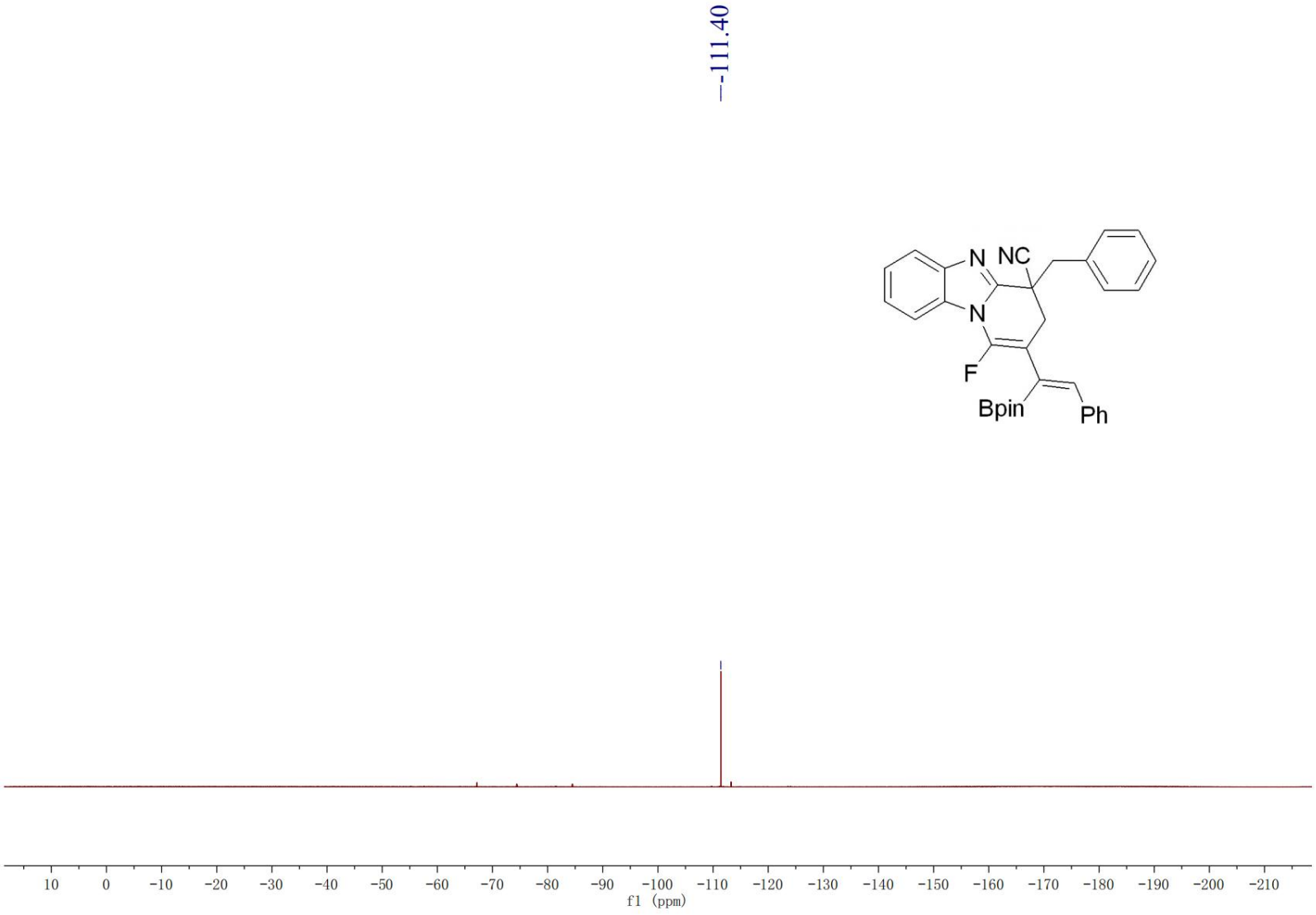
^{1}H NMR spectrum of **6**



^{13}C NMR spectrum of **6**



^{19}F NMR spectrum of **6**



8. References

[1] Ni, C.; Pan, S.; Yuan, C.; Qin, S. *J. Org. Chem*. **2023**, *88*, 8937–8945.

[2] Ni, C.; Liang, Z.; Xu, X.; Yu, F.; Zhang, D.; Chen, C. *J. Org. Chem*. **2024**, *89*, 4784−4791.

[3] Zeng, Q.; Huang, X.; Liu, M.; Yu, Z.; Xiao, Y. *Org. Lett*. **2022**, *24*, 8186–8191.

[4] Jin, S.; Li, S.-J.; Ma, X.; Su, J.; Chen, H.; Lan, Y.; Song, Q. *Angew. Chem., Int. Ed*. **2021**, *60*, 881–888.

[5] Zhang, J.; Ma, Z.-G.; Tian, Y.; Li, W.; Gao, W.-C.; Chang, H.-H. *J. Org. Chem*., 2022, **87**, 15086–15100.

[6] Yang, C.; Liu, Z.-L.; Dai, D.-T.; Li, Q.; Ma, W.-W.; Zhao, M.; Xu, Y.-H. *Org. Lett.,* 2020, **22**, 1360−1367.

[7] Kim, E. S.; Kim, H. S.; Kim, J. N. *Tetrahedron Lett.* **2009**, *50*, 2973−2975.

[8] Dong, Z.; Zhang, H.; Wang, B.; Li, B. *Org. Lett*., **2023**, *25*, 4770-4775.

[9] Zhang, J.; Ma, Z.-G.; Tian, Y.; Li, W.; Gao, W.-C.; Chang, H.-H. *J. Org. Chem*. **2022**, *87*, 15086–15100.