Supporting Information

Base-Promoted Intermolecular Cyclization of Substituted 3-Aryl-3-chloropropenals with Tetrahydro-β-carboline: A Method for the Synthesis of Indolizino[8,7-b]indole Compounds

Kairong Chen[1], Miao Yang[1], Shuang Chen[1], Yanchuan Gong[2], Junnan Xu[1], Meixiang Ye[1], Jie Zhang[1*], and Liang Guo[1*]

1.School of Chemistry and Chemical Engineering/ State Key Laboratory Incubation Base for Green Processing of Chemical Engineering, Shihezi University, Shihezi 832003, China

2. Xinjiang Huashidan Pharmaceutical Research Co. Ltd., 175 He Nan East Road, Urumqi 830011, China

E-mail: zhangjie-xj@163.com (J. Zhang), guoliang_xj@163.com (L. Guo).

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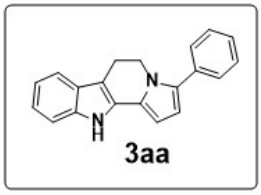
1.Experimental Section

General Information：The progress of the reaction was monitored by thin-layer chromatography (TLC) using commercially available silica gel plates (GF254). Developed plates were visualized under ultraviolet light at 254 nm. Flash column chromatography was performed using 200–300 mesh silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in parts per million (ppm) downfield units from tetramethylsilane (TMS), and all coupling constants are reported in Hertz. The description of the signals includes the following: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, td = triplet of doublet, and m = multiplet. High-resolution mass spectrometry (HRMS) data were obtained using an ESI-Q-TOF mass spectrometer.

General procedure for the synthesis of substrate 2: Phosphorus oxychloride (5.10 g, 33.29 mmol) was added dropwise over 15 minutes to an ice-cooled, stirred solution of anhydrous N,N-dimethylformamide (DMF, 10 mL). After 30 minutes, the appropriate acetophenone derivative (8.32 mmol) dissolved in 5 mL of DMF was added dropwise to the $POCl_3$/DMF complex. The reaction mixture was stirred at 0 °C for 20 minutes and then heated at 70 °C for 2 hours. The mixture was then cooled to room temperature and finally poured into a 20% aqueous NaOAc solution (20 mL). The resulting mixture was extracted with ethyl acetate (3 × 15 mL). The organic phase was washed with water (3 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (95:0.5) as the eluent to afford the desired compounds **General procedure for the synthesis of substrate 3**: Compound **1** (36 mmol) and compound **2** (9 mmol) were placed in a 100 mL thick-walled eggplant-shaped flask. Triethylamine (TEA, 22.5 mmol) and 40 mL of DMF solvent were added, and the mixture was thoroughly stirred. The reaction was heated to 120 °C under argon protection and refluxed for approximately 16 hours. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion, the reaction mixture was cooled to room temperature and poured into 100 mL of water. The resulting mixture was extracted with ethyl acetate (3 × 200 mL), and the organic phase was washed with saturated brine (3 × 200 mL), dried over anhydrous Na_2SO_4, and filtered to remove solid impurities. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography using a gradient elution (petroleum ether/ethyl acetate from 40:1 to 10:1 by volume) to afford the desired compounds **3**.

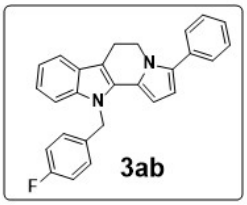
Characterization data



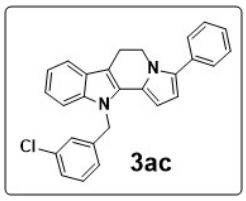
3aa

3-Phenyl-5,6,11-trihydroindolizino[8,7-b]indole (**3aa**): light yellow solid, yield 60.1%. m.p. 204.1~205.6℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.50 (dd, J = 6.8, 2.0 Hz, 1H), 7.48 – 7.41 (m, 4H), 7.38 – 7.31 (m, 2H), 7.18 – 7.09 (m, 2H), 6.37 (d, J = 3.8 Hz, 1H), 6.30 (d, J = 3.8 Hz, 1H), 4.24 (t, J = 6.8 Hz, 2H), 3.11 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.54, 135.45, 132.93, 129.21, 128.60, 128.51, 127.06, 127.04, 125.75, 121.52, 119.98, 117.89, 110.93, 109.27, 105.70, 102.42, 43.69, 21.42.

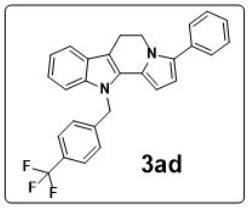
HRMS (ESI) m/z calcd for $C_{20}H_{17}N_2^+$ $(M+H)^+$ 285.1386, found 285.1386.



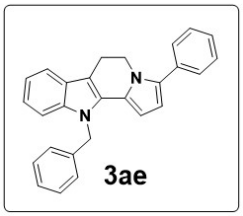
11-(4-Fluorobenzyl)-3-phenyl-5,6-dihydroindolizino[8,7-b]indole (**3ab**): light yellow solid, yield 54.4%. m.p. 203.1~204.9℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 1H), 7.43 (d, J = 4.4 Hz, 4H), 7.34 (dq, J = 8.8, 4.0 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.17 – 7.09 (m, 4H), 6.99 (t, J = 8.8 Hz, 2H), 6.23 (d, J = 3.8 Hz, 1H), 6.20 (d, J = 3.8 Hz, 1H), 5.55 (s, 2H), 4.24 (t, J = 6.8 Hz, 2H), 3.14 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.02 (d, J = 245.4 Hz), 137.65, 135.41, 133.44 (d, J = 3.0 Hz), 132.78, 130.72, 128.77, 128.49, 127.65 (d, J = 8.0 Hz), 127.16, 126.38, 124.66, 121.43, 119.99, 118.04, 115.76 (d, J = 21.6 Hz), 109.33, 109.18, 105.83, 104.32, 47.05, 43.47, 21.56. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.47. HRMS (ESI) m/z calcd for $C_{27}H_{22}FN_2^+$ $(M+H)^+$ 393.1762, found 393.1754.



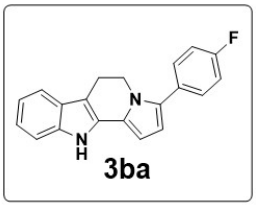
11-(3-Chlorobenzyl)-3-phenyl-5,6-dihydroindolizino[8,7-b]indole (**3ac**): light yellow solid, yield 52.7%. m.p. 146.2~147.3℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 6.2, 2.8 Hz, 1H), 7.44 (d, J = 4.4 Hz, 4H), 7.34 (q, J = 4.4 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.16 (dd, J = 9.6, 5.2 Hz, 3H), 7.04 – 6.98 (m, 1H), 6.23 (d, J = 3.8 Hz, 1H), 6.17 (d, J = 3.8 Hz, 1H), 5.55 (s, 2H), 4.25 (t, J = 6.8 Hz, 2H), 3.15 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.97, 137.70, 135.44, 134.87, 132.77, 130.77, 130.21, 128.78, 128.49, 127.60, 127.17, 126.43, 126.13, 124.56, 124.22, 121.51, 120.09, 118.08, 109.28, 109.23, 105.93, 104.32, 47.24, 43.46, 21.55. HRMS (ESI) m/z calcd for $C_{27}H_{22}ClN_2^+$ $(M+H)^+$ 409.1466, found 409.1459.



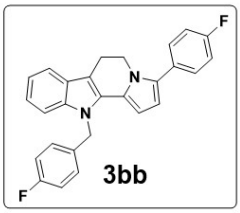
11-(4-(Trifluoromethyl)benzyl)-3-phenyl-5,6-dihydroindolizino[8,7-b]indole (**3ad**): light yellow solid, yield 52.0%. m.p. 180.2~181.4℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 3H), 7.43 (d, J = 4.4 Hz, 4H), 7.34 (dt, J = 8.8, 4.2 Hz, 1H), 7.26 (d, J = 7.2 Hz, 2H), 7.21 – 7.18 (m, 1H), 7.15 (td, J = 7.2, 6.4, 3.6 Hz, 2H), 6.22 (d, J = 3.8 Hz, 1H), 6.14 (d, J = 3.8 Hz, 1H), 5.63 (s, 2H), 4.25 (t, J = 6.8 Hz, 2H), 3.15 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.90, 137.63, 135.53, 132.71, 130.71, 129.68 (q, J = 32.4 Hz), 128.78, 128.51, 127.22, 126.46, 126.37, 125.90 (q, J = 3.7 Hz), 124.50, 124.05 (q, J = 272.1 Hz), 121.58, 120.18, 118.15, 109.21, 109.17, 106.05, 104.23, 47.34, 43.47, 21.56. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.50. HRMS (ESI) m/z calcd for $C_{28}H_{22}F_3N_2^+$ $(M+H)^+$ 443.1730, found 443.1723.



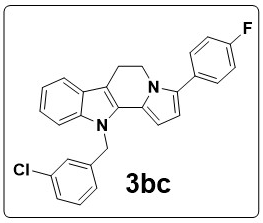
11-Benzyl-3-phenyl-5,6-dihydroindolizino[8,7-b]indole (**3ae**): light yellow solid, yield 53.2%. m.p. 180.3~182.1℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 1H), 7.43 (d, J = 4.4 Hz, 4H), 7.37 – 7.33 (m, 1H), 7.32 – 7.27 (m, 2H), 7.25 – 7.22 (m, 2H), 7.19 – 7.11 (m, 4H), 6.22 (s, 2H), 5.59 (s, 2H), 4.25 (t, J = 6.8 Hz, 2H), 3.14 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.81, 137.79, 135.31, 132.86, 130.88, 128.85, 128.77, 128.47, 127.24, 127.10, 126.33, 126.03, 124.79, 121.33, 119.87, 117.95, 109.47, 109.19, 105.67, 104.46, 47.69, 43.49, 21.59. HRMS (ESI) m/z calcd for $C_{27}H_{23}N_2^+$ $(M+H)^+$ 375.1856, found 375.1853.



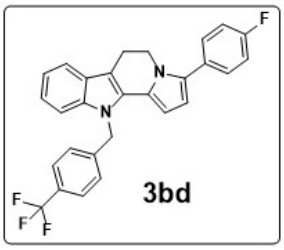
3-(4-Fluorophenyl)-5,6,11-trihydroindolizino[8,7-b]indole (**3ba**): light yellow solid, yield 54.9%. m.p. 216.4~217.7℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.50 (d, J = 6.8 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.35 (d, J = 7.0 Hz, 1H), 7.18 – 7.08 (m, 4H), 6.35 (d, J = 3.8 Hz, 1H), 6.25 (d, J = 3.8 Hz, 1H), 4.17 (t, J = 6.8 Hz, 2H), 3.10 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.06 (d, J = 246.9 Hz), 136.53, 134.34, 130.29 (d, J = 8.0 Hz), 129.10, 129.03 (d, J = 3.4 Hz), 127.02, 125.70, 121.60, 120.01, 117.91, 115.50 (d, J = 21.5 Hz), 110.95, 109.23, 105.65, 102.34, 43.57, 21.39. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.91. HRMS (ESI) m/z calcd for $C_{20}H_{16}FN_2^+$ $(M+H)^+$ 303.1292, found 303.1285.



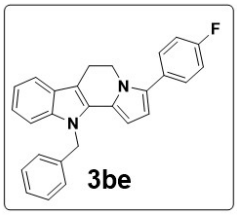
11-(4-Fluorobenzyl)-3-(4-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (**3bb**): light yellow solid, yield 56.8%. m.p. 187.8~189.6℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 1H), 7.42 – 7.35 (m, 2H), 7.24 – 7.20 (m, 1H), 7.16 (dd, J = 6.0, 3.2 Hz, 2H), 7.13 (d, J = 4.4 Hz, 2H), 7.11 (dd, J = 5.6, 3.4 Hz, 2H), 7.03 – 6.95 (m, 2H), 6.18 (s, 2H), 5.55 (s, 2H), 4.19 (t, J = 6.8 Hz, 2H), 3.14 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.13 (d, J = 247.0 Hz), 162.03 (d, J = 245.4 Hz), 137.65, 134.29, 133.40 (d, J = 3.0 Hz), 130.61, 130.46 (d, J = 8.0 Hz), 128.89 (d, J = 3.3 Hz), 127.63 (d, J = 8.0 Hz), 126.34, 124.63, 121.50, 120.03, 118.06, 115.76 (d, J = 21.6 Hz), 115.49 (d, J = 21.6 Hz), 109.34, 109.15, 105.79, 104.24, 47.04, 43.37, 21.54. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.70, -115.42. HRMS (ESI) m/z calcd for $C_{27}H_{21}F_2N_2^+$ $(M+H)^+$ 411.1667, found 411.1670.



11-(3-Chlorobenzyl)-3-(4-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (**3bc**): light yellow solid, yield 52.8%. m.p. 184.5~185.1℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 1H), 7.42 – 7.36 (m, 2H), 7.30 – 7.16 (m, 3H), 7.16 (d, J = 2.4 Hz, 2H), 7.16 – 7.09 (m, 3H), 7.03 – 6.97 (m, 1H), 6.19 (d, J = 3.8 Hz, 1H), 6.16 (d, J = 3.8 Hz, 1H), 5.54 (s, 2H), 4.19 (t, J = 6.8 Hz, 2H), 3.15 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.14 (d, J = 247.2 Hz), 139.93, 137.70, 134.88, 134.33, 130.65, 130.47 (d, J = 8.0 Hz), 130.21, 128.88 (d, J = 3.3 Hz), 127.62, 126.39, 126.11, 124.53, 124.20, 121.59, 120.12, 118.10, 115.50 (d, J = 21.6 Hz), 109.29, 109.20, 105.88, 104.24, 47.23, 43.36, 21.53. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.70. HRMS (ESI) m/z calcd for $C_{27}H_{21}ClFN_2^+$ $(M+H)^+$ 427.1372, found 427.1373.

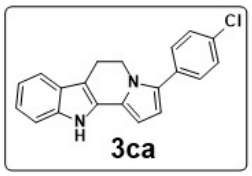


11-(4-(Trifluoromethyl)benzyl)-3-(4-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**bd**): light yellow solid, yield 49.5%. m.p. 171.5~172.8℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 3H), 7.42 – 7.35 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.22 – 7.18 (m, 1H), 7.18 – 7.14 (m, 2H), 7.14 – 7.08 (m, 2H), 6.18 (d, J = 3.8 Hz, 1H), 6.12 (d, J = 3.8 Hz, 1H), 5.63 (s, 2H), 4.20 (t, J = 6.8 Hz, 2H), 3.15 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.16 (d, J = 247.2 Hz), 141.87, 137.64, 134.42, 130.60, 130.48 (d, J = 8.0 Hz), 129.71 (q, J = 32.5 Hz), 128.82 (d, J = 3.4 Hz), 126.42, 126.35, 125.91 (q, J = 3.8 Hz), 124.48, 124.04 (q, J = 272.0 Hz), 121.66, 120.22, 118.17, 115.52 (d, J = 21.6 Hz), 109.19, 106.01, 104.15, 47.34, 43.37, 21.53. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.51, -114.62. HRMS (ESI) m/z calcd for $C_{28}H_{21}F_4N_2^+$ $(M+H)^+$ 461.1635, found 461.1628.



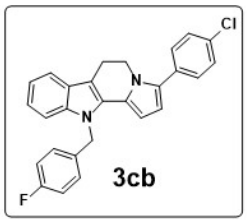
11-Benzyl-3-(4-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**be**): light yellow solid, yield 54.0%. m.p. 192.2~193.8℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 1H), 7.38 (dd, J = 8.6, 5.4 Hz, 2H), 7.30 (dd, J = 8.0, 6.4 Hz, 2H), 7.25 (d, J = 4.8 Hz, 1H), 7.24 (d, J = 3.2 Hz, 1H), 7.15 (dt, J = 5.4, 1.6 Hz, 4H), 7.13 – 7.09 (m, 2H), 6.20 (d, J = 3.8 Hz, 1H), 6.17 (d, J = 3.8 Hz, 1H), 5.58 (s, 2H), 4.19 (t, J = 6.8 Hz, 2H), 3.14 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.10 (d, J = 247.1 Hz), 137.81, 137.75, 134.19, 130.76, 130.45 (d, J = 8.0 Hz), 128.96 (d, J = 3.4 Hz), 128.85, 127.26, 126.28, 126.01, 124.75, 121.40,

119.91, 117.97, 115.47 (d, J = 21.5 Hz), 109.48, 109.15, 105.62, 104.37, 47.68, 43.38, 21.56. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.82. HRMS (ESI) m/z calcd for $C_{27}H_{22}FN_2^+$ $(M+H)^+$ 393.1762, found 393.1761.



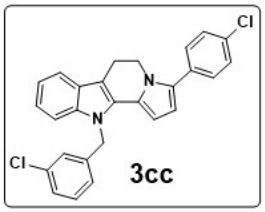
3ca

3-(4-Chlorophenyl)-5,6,11-trihydroindolizino[8,7-b]indole (3**ca**): light yellow solid, yield 56.8%. m.p. 207.3~209.2℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.52 – 7.48 (m, 1H), 7.40 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.35 – 7.33 (m, 1H), 7.14 (pd, J = 7.2, 1.4 Hz, 2H), 6.35 (d, J = 3.8 Hz, 1H), 6.28 (d, J = 3.8 Hz, 1H), 4.19 (t, J = 6.8 Hz, 2H), 3.11 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.55, 134.15, 132.95, 131.35, 129.72, 128.99, 128.73, 126.98, 126.12, 121.68, 120.05, 117.95, 110.96, 109.61, 105.81, 102.53, 43.69, 21.39. HRMS (ESI) m/z calcd for $C_{20}H_{16}ClN_2^+$ $(M+H)^+$ 319.0996, found 319.0988.



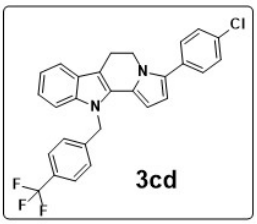
3cb

11-(4-Fluorobenzyl)-3-(4-chlorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**cb**): light yellow solid, yield 52.4%. m.p. 172.3~174.1℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 1H), 7.40 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.15 (dd, J = 6.0, 3.2 Hz, 2H), 7.11 (dd, J = 8.4, 5.4 Hz, 2H), 6.98 (t, J = 8.6 Hz, 2H), 6.21 (d, J = 3.8 Hz, 1H), 6.18 (d, J = 3.8 Hz, 1H), 5.54 (s, 2H), 4.21 (t, J = 6.8 Hz, 2H), 3.14 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.03 (d, J = 245.6 Hz), 137.68, 134.10, 133.37 (d, J = 3.2 Hz), 133.11, 131.21, 130.50, 129.89, 128.72, 127.62 (d, J = 8.1 Hz), 126.31, 125.05, 121.58, 120.06, 118.10, 115.77 (d, J = 21.6 Hz), 109.51, 109.36, 105.95, 104.41, 47.04, 43.47, 21.54. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.39. HRMS (ESI) m/z calcd for $C_{27}H_{21}ClFN_2^+$ $(M+H)^+$ 427.1372, found 427.1367.

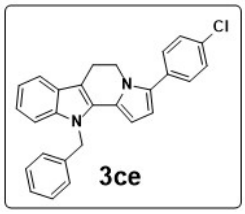


3cc

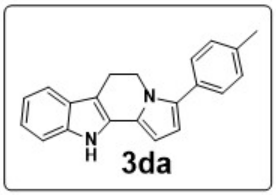
11-(3-Chlorobenzyl)-3-(4-chlorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**cc**): light yellow solid, yield 56.2%. m.p. 221.8~223.8℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 1H), 7.40 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 7.24 – 7.22 (m, 2H), 7.21 – 7.13 (m, 4H), 7.02 – 6.97 (m, 1H), 6.21 (d, J = 3.8 Hz, 1H), 6.16 (d, J = 3.8 Hz, 1H), 5.54 (s, 2H), 4.21 (t, J = 6.8 Hz, 2H), 3.15 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.90, 137.73, 134.89, 134.14, 133.13, 131.20, 130.54, 130.22, 129.90, 128.72, 127.63, 126.36, 126.10, 124.95, 124.18, 121.67, 120.15, 118.14, 109.55, 109.31, 106.04, 104.40, 47.23, 43.46, 21.53. HRMS (ESI) m/z calcd for $C_{27}H_{21}Cl_2N_2^+$ $(M+H)^+$ 443.1076, found 443.1082.



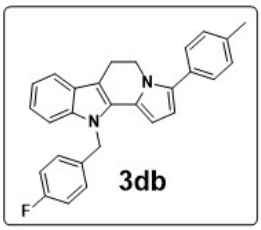
11-(4-(Trifluoromethyl)benzyl)-3-(4-chlorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**cd**): light yellow solid, yield 48.4%. m.p. 178.2~179.2℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 3H), 7.43 – 7.38 (m, 2H), 7.37 – 7.32 (m, 2H), 7.24 (d, J = 7.4 Hz, 2H), 7.22 – 7.13 (m, 3H), 6.20 (d, J = 3.8 Hz, 1H), 6.13 (d, J = 3.8 Hz, 1H), 5.63 (s, 2H), 4.21 (t, J = 6.8 Hz, 2H), 3.16 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.83, 137.66, 134.22, 133.19, 131.14, 130.49, 129.90, 129.72 (q, J = 32.3 Hz), 128.74, 126.39, 126.34, 125.92 (q, J = 3.8 Hz), 124.88, 124.03 (q, J = 272.0 Hz), 121.74, 120.25, 118.21, 109.53, 109.21, 106.17, 104.31, 47.34, 43.47, 21.53. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.52. HRMS (ESI) m/z calcd for $C_{28}H_{21}ClF_3N_2^+$ $(M+H)^+$ 477.1340, found 477.1343.



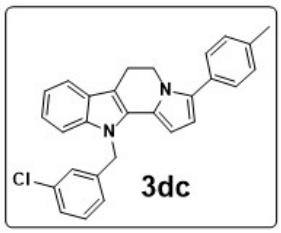
11-Benzyl-3-(4-chlorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**ce**): light yellow solid, yield 51.9%. m.p. 227.3~228.7℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 7.30 (dd, J = 8.0, 6.4 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.17 – 7.12 (m, 4H), 6.20 (s, 2H), 5.58 (s, 2H), 4.20 (t, J = 6.8 Hz, 2H), 3.15 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.84, 137.72, 133.99, 133.05, 131.28, 130.65, 129.88, 128.86, 128.70, 127.27, 126.25, 126.00, 125.17, 121.48, 119.94, 118.01, 109.51, 109.50, 105.78, 104.54, 47.68, 43.49, 21.56. HRMS (ESI) m/z calcd for $C_{27}H_{22}ClN_2^+$ $(M+H)^+$ 409.1466, found 409.1459.



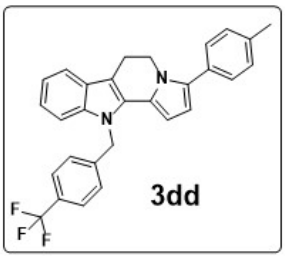
3-(*p*-Tolyl)-5,6,11-trihydroindolizino[8,7-b]indole (3**da**): light yellow solid, yield 52.7%. m.p. 200.1~201.3℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.49 (dd, J = 6.6, 2.0 Hz, 1H), 7.36 (d, J = 2.0 Hz, 1H), 7.34 (d, J = 1.8 Hz, 2H), 7.25 (d, J = 4.8 Hz, 2H), 7.13 (tt, J = 7.2, 5.6 Hz, 2H), 6.35 (d, J = 3.8 Hz, 1H), 6.26 (d, J = 3.8 Hz, 1H), 4.22 (t, J = 6.8 Hz, 2H), 3.10 (t, J = 6.8 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.90, 136.52, 135.49, 130.03, 129.29, 129.21, 128.56, 127.09, 125.46, 121.45, 119.95, 117.85, 110.90, 108.90, 105.57, 102.32, 43.60, 21.41, 21.22. HRMS (ESI) m/z calcd for $C_{21}H_{19}N_2^+$ $(M+H)^+$ 299.1543, found 299.1543.



11-(4-Fluorobenzyl)-3-(p-tolyl)-5,6-dihydroindolizino[8,7-b]indole (3**db**): light yellow solid, yield 55.6%. m.p. 167.6~169.0℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.25 – 7.19 (m, 3H), 7.16 – 7.09 (m, 4H), 7.02 – 6.94 (m, 2H), 6.19 (d, J = 1.2 Hz, 2H), 5.54 (s, 2H), 4.22 (t, J = 6.8 Hz, 2H), 3.13 (t, J = 6.8 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.02 (d, J = 245.4 Hz), 137.63, 137.04, 135.45, 133.47 (d, J = 3.1 Hz), 130.80, 129.88, 129.19, 128.72, 127.65 (d, J = 8.1 Hz), 126.41, 124.39, 121.35, 119.96, 118.00, 115.74 (d, J = 21.6 Hz), 109.31, 108.83, 105.70, 104.25, 47.04, 43.38, 21.54, 21.22. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.51. HRMS (ESI) m/z calcd for $C_{28}H_{24}FN_2^+$ $(M+H)^+$ 407.1918, found 407.1912.

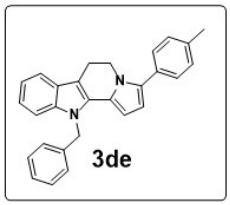


11-(3-Chlorobenzyl)-3-(*p*-tolyl)-5,6-dihydroindolizino[8,7-b]indole (3**dc**): light yellow solid, yield 52.9%. m.p. 172.1~173.1℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.25 (s, 1H), 7.24 – 7.21 (m, 3H), 7.21 – 7.17 (m, 2H), 7.17 – 7.12 (m, 2H), 7.03 – 6.97 (m, 1H), 6.19 (d, J = 3.8 Hz, 1H), 6.16 (d, J = 3.8 Hz, 1H), 5.55 (s, 2H), 4.23 (t, J = 6.8 Hz, 2H), 3.13 (t, J = 6.8 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.99, 137.68, 137.05, 135.49, 134.86, 130.85, 130.20, 129.87, 129.19, 128.73, 127.58, 126.46, 126.13, 124.29, 124.22, 121.44, 120.06, 118.03, 109.26, 108.87, 105.79, 104.24, 47.23, 43.38, 21.54, 21.23. HRMS (ESI) m/z calcd for $C_{28}H_{24}ClN_2^+$ $(M+H)^+$ 423.1622, found 423.1623.

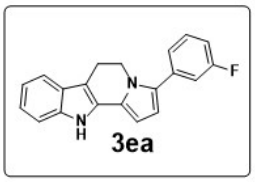


11-(4-(Trifluoromethyl)benzyl)-3-(p-tolyl)-5,6-dihydroindolizino[8,7-b]indole (3**dd**): light yellow solid, yield 49.0%. m.p. 146.0~146.8℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.6 Hz, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.24 (dd, J = 5.2, 2.8 Hz, 4H), 7.21 – 7.13 (m, 3H), 6.18 (d, J = 3.8 Hz, 1H), 6.12 (d, J = 3.8 Hz, 1H), 5.63 (s, 2H), 4.23 (t, J = 6.8 Hz, 2H), 3.14 (t, J = 6.8 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.93, 137.61, 137.11, 135.58, 130.79, 129.81, 129.66 (q, J = 32.2 Hz), 129.21, 128.73, 126.49, 126.38, 125.90 (q, J = 3.7 Hz), 124.23, 124.05 (q, J = 272.2 Hz), 121.51, 120.16, 118.11, 109.15, 108.86, 105.92,

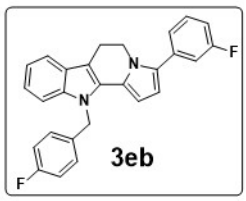
104.15, 47.33, 43.38, 21.54, 21.22. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.50. HRMS (ESI) m/z calcd for $C_{29}H_{24}F_3N_2^+$ $(M+H)^+$ 457.1886, found 457.1886.



11-Benzyl-3-(*p*-tolyl)-5,6-dihydroindolizino[8,7-b]indole (3**de**): light yellow solid, yield 55.8%. m.p. 194.2~195.7℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 7.6 Hz, 2H), 7.24 (d, J = 8.0 Hz, 4H), 7.16 (d, J = 8.6 Hz, 3H), 7.14 – 7.10 (m, 1H), 6.20 (d, J = 3.8, 1.2 Hz, 1H), 6.18 (d, J = 3.8, 1.2 Hz, 1H), 5.59 (s, 2H), 4.23 (t, J = 6.8 Hz, 2H), 3.13 (t, J = 6.8 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.81, 137.78, 136.97, 135.35, 130.96, 129.96, 129.17, 128.84, 128.72, 127.23, 126.35, 126.03, 124.51, 121.25, 119.84, 117.91, 109.44, 108.83, 105.54, 104.38, 47.68, 43.40, 21.57, 21.22. HRMS (ESI) m/z calcd for $C_{28}H_{25}N_2^+$ $(M+H)^+$ 389.2012, found 389.2021.

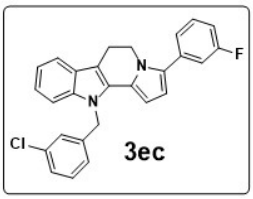


3-(3-Fluorophenyl)-5,6,11-trihydroindolizino[8,7-b]indole (3**ea**): light yellow solid, yield 52.1%. m.p. 174.7~175.8℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.50 (dd, J = 6.8, 2.0 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.35 – 7.32 (m, 1H), 7.24 – 7.20 (m, 1H), 7.18 – 7.15 (m, 1H), 7.15 – 7.09 (m, 2H), 7.06 – 6.98 (m, 1H), 6.35 (d, J = 3.8 Hz, 1H), 6.31 (d, J = 3.8 Hz, 1H), 4.22 (t, J = 6.8 Hz, 2H), 3.11 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.80 (d, J = 246.0 Hz), 136.56, 134.99 (d, J = 8.3 Hz), 134.12 (d, J = 2.5 Hz), 130.01 (d, J = 8.6 Hz), 128.94, 126.97, 126.32, 124.11 (d, J = 2.8 Hz), 121.71, 120.05, 117.98, 115.23 (d, J = 22.0 Hz), 113.79 (d, J = 21.2 Hz), 110.97, 109.92, 105.92, 102.55, 43.76, 21.39. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.80. HRMS (ESI) m/z calcd for $C_{20}H_{16}FN_2^+$ $(M+H)^+$ 303.1292, found 303.1289.

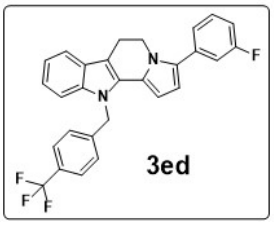


11-(4-Fluorobenzyl)-3-(3-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**eb**): light yellow solid, yield 50.5%. m.p. 179.2~180.3℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 1H), 7.39 (td, J = 8.0, 6.0 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.17 (d, J = 4.0 Hz, 1H), 7.15 (d, J = 2.8 Hz, 1H), 7.13 (d, J = 5.6 Hz, 1H), 7.12 – 7.08 (m, 2H), 7.06 – 7.02 (m, 1H), 7.02 – 6.96 (m, 2H), 6.24 (d, J = 3.8 Hz, 1H), 6.19 (d, J = 3.8 Hz, 1H), 5.55 (s, 2H), 4.25 (t, J = 6.8 Hz, 2H), 3.15 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.75 (d, J = 246.1 Hz), 162.04 (d, J = 245.5 Hz), 137.70, 134.84 (d, J = 8.1 Hz), 134.06 (d, J = 2.5 Hz), 133.37 (d, J = 3.1 Hz), 130.46, 130.00 (d, J = 8.7 Hz), 127.62 (d, J = 8.1 Hz), 126.30, 125.23, 124.31 (d, J = 2.8 Hz), 121.61, 120.07, 118.13, 115.78 (d, J = 21.5 Hz), 115.43 (d, J = 22.0 Hz), 113.93 (d, J = 21.1 Hz), 109.80,

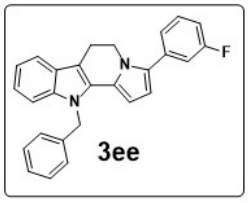
109.37, 106.05, 104.43, 47.05, 43.55, 21.54. HRMS (ESI) m/z calcd for $C_{27}H_{21}F_2N_2^+$ $(M+H)^+$ 411.1667, found 411.1662.



11-(3-Chlorobenzyl)-3-(3-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**ec**): light yellow solid, yield 54.6%. m.p. 160.2~161.3℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 1H), 7.39 (td, J = 8.0, 6.0 Hz, 1H), 7.26 – 7.19 (m, 4H), 7.19 – 7.10 (m, 4H), 7.06 – 6.96 (m, 2H), 6.24 (d, J = 3.8 Hz, 1H), 6.16 (d, J = 3.8 Hz, 1H), 5.54 (s, 2H), 4.24 (t, J = 6.8 Hz, 2H), 3.16 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.75 (d, J = 246.2 Hz), 139.90, 137.75, 134.89, 134.84 (d, J = 8.3 Hz), 134.09 (d, J = 2.3 Hz), 130.50, 130.22, 130.00 (d, J = 8.7 Hz), 127.64, 126.35, 126.11, 125.12, 124.31 (d, J = 2.8 Hz), 124.18, 121.70, 120.16, 118.17, 115.44 (d, J = 22.0 Hz), 113.94 (d, J = 21.2 Hz), 109.85, 109.32, 106.14, 104.42, 47.23, 43.53, 21.53. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.77. HRMS (ESI) m/z calcd for $C_{27}H_{21}ClFN_2^+$ $(M+H)^+$ 427.1372, found 427.1369.

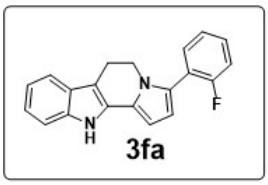


11-(4-(Trifluoromethyl)benzyl)-3-(3-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**ed**): light yellow solid, yield 55.9%. m.p. 156.9~158.5℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 3H), 7.39 (td, J = 8.0, 6.0 Hz, 1H), 7.25 (d, J = 2.8 Hz, 2H), 7.22 – 7.15 (m, 4H), 7.12 (ddd, J = 10.0, 2.6, 1.6 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.23 (d, J = 3.8 Hz, 1H), 6.13 (d, J = 3.8 Hz, 1H), 5.63 (s, 2H), 4.25 (t, J = 6.8 Hz, 2H), 3.17 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.76 (d, J = 246.1 Hz), 141.83, 137.68, 134.77 (d, J = 8.2 Hz), 134.18 (d, J = 2.4 Hz), 130.44, 130.02 (d, J = 8.7 Hz), 129.73 (q, J = 32.4 Hz), 126.38, 126.34, 125.92 (q, J = 3.7 Hz), 125.06, 124.32 (d, J = 2.9 Hz), 124.04 (q, J = 270.3 Hz), 121.77, 120.26, 118.24, 115.45 (d, J = 22.0 Hz), 114.00 (d, J = 21.0 Hz), 109.83, 109.22, 106.27, 104.33, 47.35, 43.54, 21.53. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.51, -112.74. HRMS (ESI) m/z calcd for $C_{28}H_{21}F_4N_2^+$ $(M+H)^+$ 461.1635, found 461.1631.



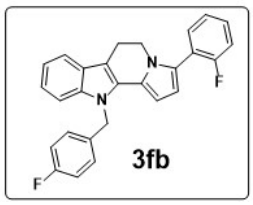
11-Benzyl-3-(3-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**ee**): light yellow solid, yield 56.6%. m.p. 141.8~143.5℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 1H), 7.38 (td, J = 8.0, 6.0 Hz, 1H), 7.30 (dd, J = 8.0, 6.4 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.20 (dt, J = 7.6, 1.2 Hz, 1H), 7.15 (d, J = 2.8 Hz, 2H), 7.14 –

7.10 (m, 3H), 7.05 – 6.99 (m, 1H), 6.23 (d, J = 3.8 Hz, 1H), 6.20 (d, J = 3.8 Hz, 1H), 5.58 (s, 2H), 4.25 (t, J = 6.8 Hz, 2H), 3.16 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.75 (d, J = 246.1 Hz), 137.85, 137.71, 134.91 (d, J = 8.4 Hz), 133.96 (d, J = 2.5 Hz), 130.60, 129.97 (d, J = 8.7 Hz), 128.86, 127.28, 126.24, 125.99, 125.35, 124.29 (d, J = 2.8 Hz), 121.51, 119.94, 118.04, 115.41 (d, J = 21.9 Hz), 113.86 (d, J = 21.2 Hz), 109.81, 109.50, 105.88, 104.56, 47.69, 43.56, 21.56. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.82. HRMS (ESI) m/z calcd for $C_{27}H_{22}FN_2^+$ $(M+H)^+$ 393.1762, found 393.1754.



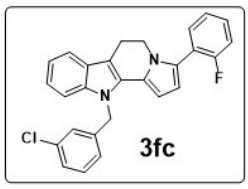
3fa

3-(2-Fluorophenyl)-5,6,11-trihydroindolizino[8,7-b]indole (3**fa**): light yellow solid, yield 57.6%. m.p. 186.1~187.6℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.50 (dd, J = 7.0, 1.8 Hz, 1H), 7.42 (td, J = 7.6, 1.8 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.24 – 7.16 (m, 2H), 7.16 – 7.09 (m, 2H), 6.39 (d, J = 3.8 Hz, 1H), 6.31 (d, J = 3.8 Hz, 1H), 4.08 (td, J = 6.8, 1.4 Hz, 2H), 3.10 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.89 (d, J = 247.1 Hz), 136.54, 131.78 (d, J = 2.9 Hz), 129.37 (d, J = 8.1 Hz), 129.07, 128.94, 127.04, 126.04, 124.25 (d, J = 3.7 Hz), 121.58, 120.83 (d, J = 15.0 Hz), 119.98, 117.96, 115.89 (d, J = 22.3 Hz), 110.94, 110.44, 105.92, 102.36, 43.83 (d, J = 4.3 Hz), 21.28. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.52. HRMS (ESI) m/z calcd for $C_{20}H_{16}FN_2^+$ $(M+H)^+$ 303.1292, found 303.1286.



3fb

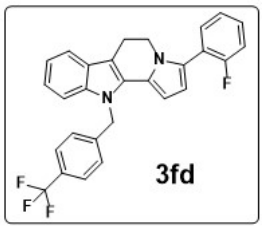
11-(4-Fluorobenzyl)-3-(2-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**fb**): light yellow solid, yield 55.3%. m.p. 187.7~189.6℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 1H), 7.42 – 7.32 (m, 2H), 7.24 – 7.16 (m, 3H), 7.16 – 7.09 (m, 4H), 7.03 – 6.96 (m, 2H), 6.24 (d, J = 3.8 Hz, 1H), 6.21 (d, J = 3.8 Hz, 1H), 5.55 (s, 2H), 4.09 (td, J = 6.8 Hz, 2H), 3.13 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.03 (d, J = 245.4 Hz), 159.96 (d, J = 247.1 Hz), 137.64, 133.44 (d, J = 3.0 Hz), 131.83 (d, J = 2.9 Hz), 130.60, 129.52 (d, J = 8.1 Hz), 128.97, 127.66 (d, J = 8.1 Hz), 126.37, 125.02, 124.26 (d, J = 3.5 Hz), 121.49, 120.73 (d, J = 15.1 Hz), 119.99, 118.11, 115.87 (d, J = 22.4 Hz), 115.76 (d, J = 21.6 Hz), 110.31, 109.34, 106.01, 104.24, 47.06, 43.71 (d, J = 4.3 Hz), 21.41. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.39, -115.48. HRMS (ESI) m/z calcd for $C_{27}H_{21}F_2N_2^+$ $(M+H)^+$ 411.1667, found 411.1666.



3fc

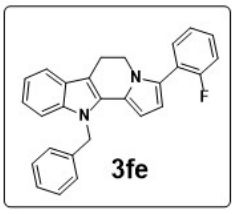
11-(3-Chlorobenzyl)-3-(2-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**fc**): light yellow solid, yield 54.2%. m.p. 176.6~178.1℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 1H), 7.41 – 7.32 (m, 2H),

7.23 (dd, *J* = 5.2, 3.8 Hz, 3H), 7.21 – 7.20 (m, 1H), 7.18 (d, *J* = 4.4 Hz, 2H), 7.16 – 7.13 (m, 2H), 7.03 – 6.97 (m, 1H), 6.24 (d, *J* = 3.8 Hz, 1H), 6.19 (d, *J* = 3.8 Hz, 1H), 5.54 (s, 2H), 4.09 (td, *J* = 6.8, 1.5 Hz, 2H), 3.13 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.95 (d, *J* = 247.2 Hz), 139.97, 137.69, 134.86, 131.83 (d, *J* = 2.9 Hz), 130.63, 130.21, 129.52 (d, *J* = 8.1 Hz), 128.99, 127.59, 126.41, 126.12, 124.91, 124.25 (d, *J* = 3.3 Hz), 124.22, 121.57, 120.70 (d, *J* = 15.1 Hz), 120.08, 118.14, 115.86 (d, *J* = 22.2 Hz), 110.35, 109.28, 106.10, 104.24, 47.24, 43.69 (d, *J* = 4.3 Hz), 21.39. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.36. HRMS (ESI) m/z calcd for $C_{27}H_{21}ClFN_2^+$ $(M+H)^+$ 427.1372, found 427.1370.



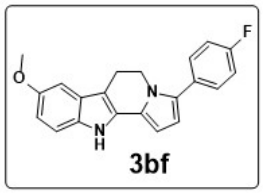
3fd

11-(4-(Trifluoromethyl)benzyl)-3-(2-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**fd**): light yellow solid, yield 50.2%. m.p. 197.0~198.8℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 3H), 7.41 – 7.33 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.19 – 7.13 (m, 3H), 6.23 (d, *J* = 3.8 Hz, 1H), 6.15 (d, *J* = 3.8 Hz, 1H), 5.63 (s, 2H), 4.09 (td, *J* = 6.8, 1.6 Hz, 2H), 3.14 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.96 (d, *J* = 247.1 Hz), 141.90, 137.62, 131.83 (d, *J* = 3.0 Hz), 130.58, 129.69 (q, *J* = 32.5 Hz), 129.59 (d, *J* = 8.2 Hz), 129.10, 126.44, 126.38, 125.91 (q, *J* = 3.8 Hz), 124.86, 124.28 (d, *J* = 3.5 Hz), 124.05 (q, *J* = 272.2 Hz), 121.64, 120.66 (d, *J* = 15.1 Hz), 120.18, 118.22, 115.88 (d, *J* = 22.2 Hz), 110.33, 109.18, 106.23, 104.14, 47.35, 43.70 (d, *J* = 4.4 Hz), 21.40. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.50, -113.40. HRMS (ESI) m/z calcd for $C_{28}H_{21}F_4N_2^+$ $(M+H)^+$ 461.1635, found 461.1639.



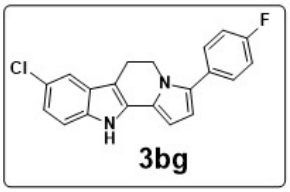
3fe

11-Benzyl-3-(2-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3**fe**): light yellow solid, yield 57.3%. m.p. 190.5~191.3℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 1H), 7.41 – 7.33 (m, 2H), 7.33 – 7.30 (m, 1H), 7.30 – 7.25 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.16 (m, 2H), 7.15 – 7.11 (m, 3H), 6.23 (s, 2H), 5.59 (s, 2H), 4.09 (td, *J* = 6.8, 1.5 Hz, 2H), 3.14 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.95 (d, *J* = 247.1 Hz), 137.80, 137.79, 131.83 (d, *J* = 3.0 Hz), 130.75, 129.46 (d, *J* = 8.1 Hz), 128.85, 127.25, 126.31, 126.03, 125.14, 124.23 (d, *J* = 3.6 Hz), 121.38, 120.79 (d, *J* = 15.1 Hz), 119.87, 118.02, 115.86 (d, *J* = 22.3 Hz), 110.31, 109.48, 105.84, 104.38, 47.70, 43.72 (d, *J* = 4.3 Hz), 21.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.37. HRMS (ESI) m/z calcd for $C_{27}H_{22}FN_2^+$ $(M+H)^+$ 393.1762, found 393.1758.



3bf

3-(4-Fluorophenyl)-8-methoxy-5,6,11-trihydroindolizino[8,7-b]indole (3**bf**): light yellow solid, yield 47.6%. m.p. 198.6~200.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.41 (dd, J = 8.6, 5.6 Hz, 2H), 7.24 (d, J = 9.2 Hz, 1H), 7.13 (t, J = 8.8 Hz, 2H), 6.95 (d, J = 2.4 Hz, 1H), 6.80 (dd, J = 8.8, 2.4 Hz, 1H), 6.33 (d, J = 3.8 Hz, 1H), 6.24 (d, J = 3.8 Hz, 1H), 4.17 (t, J = 6.8 Hz, 2H), 3.87 (s, 3H), 3.08 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.06 (d, J = 246.9 Hz), 154.49, 134.28, 131.62, 130.29 (d, J = 8.0 Hz), 129.94, 129.05 (d, J = 3.3 Hz), 127.46, 125.78, 115.50 (d, J = 21.5 Hz), 111.58, 111.30, 109.25, 105.55, 102.26, 100.19, 55.91, 43.58, 21.44. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.94. HRMS (ESI) m/z calcd for $C_{21}H_{18}FN_2O^+$ $(M+H)^+$ 333.1398, found 333.1399.



3bg

3-(4-Fluorophenyl)-8-chloro-5,6,11-trihydroindolizino[8,7-b]indole (3**bg**): light yellow solid, yield 52.0%. m.p. 208.1~209.8°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.44 (d, J = 2.0 Hz, 1H), 7.40 (dd, J = 8.8, 5.6 Hz, 2H), 7.25 (d, J = 5.6 Hz, 1H), 7.13 (t, J = 8.8 Hz, 2H), 7.08 (dd, J = 8.6, 2.0 Hz, 1H), 6.37 (d, J = 3.8 Hz, 1H), 6.25 (d, J = 3.8 Hz, 1H), 4.17 (t, J = 6.8 Hz, 2H), 3.06 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.14 (d, J = 247.1 Hz), 134.85, 134.75, 130.50, 130.33 (d, J = 8.0 Hz), 128.85 (d, J = 3.3 Hz), 128.18, 125.74, 125.11, 121.62, 117.42, 115.55 (d, J = 21.5 Hz), 111.77, 109.39, 105.15, 102.92, 43.47, 21.26. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.65. HRMS (ESI) m/z calcd for $C_{20}H_{15}ClFN_2^+$ $(M+H)^+$ 337.0902, found 337.0891.

2. Crystallographic data and molecular structure

(1). 11-(4-Fluorobenzyl)-3-(4-fluorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3bb)

X-ray structure determination was obtained via slow evaporation of compound **3bb** in $CHCl_3$ at room temperature.

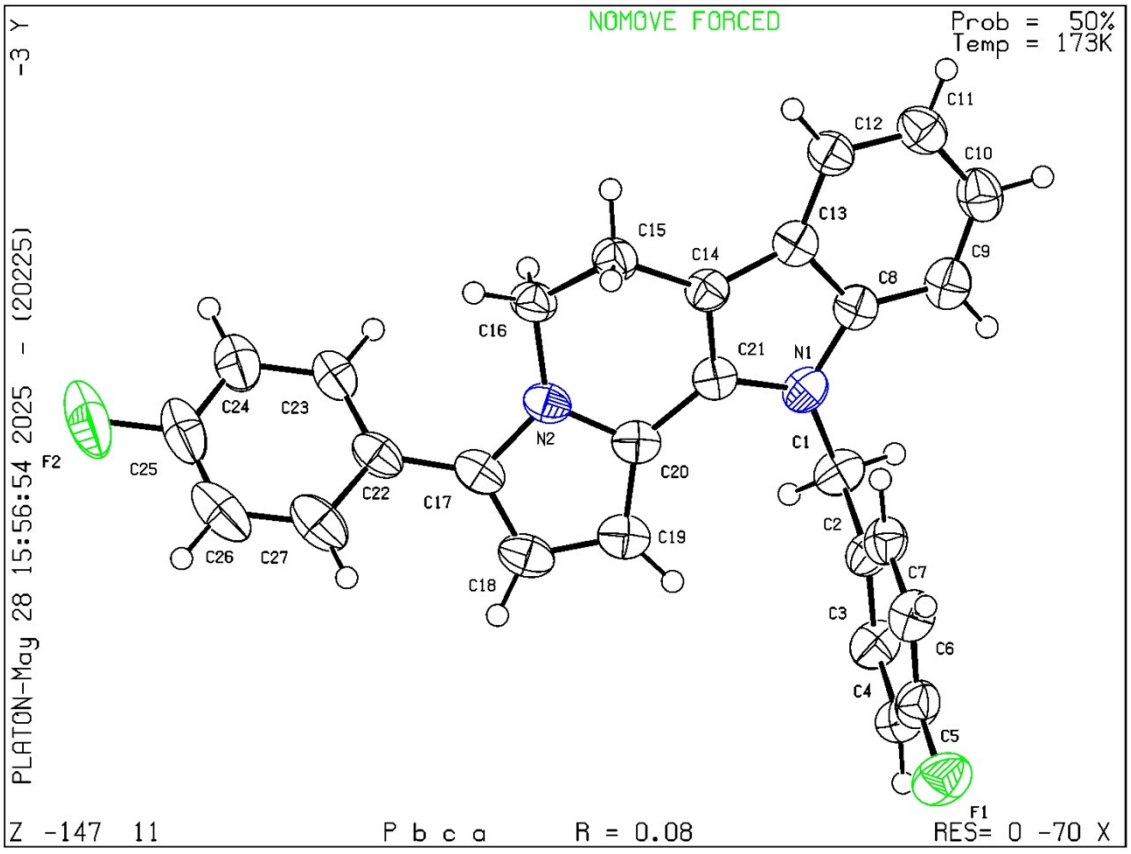


Figure S1. X-ray crystal structure of **3bb;**

Table S1. Crystal data and structure refinement for compound **3bb (CCDC: 2498971)**

Bond precision:	C-C = 0.0049 A	Wavelength=1.54178	
Cell:	a=14.6398(13)	b=9.8340(9)	c=27.715(3)
	alpha=90	beta=90	gamma=90
Temperature:	173 K		

	Calculated	Reported
Volume	3990.1(7)	3990.1(6)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C27 H20 F2 N2	C27 H20 F2 N2
Sum formula	C27 H20 F2 N2	C27 H20 F2 N2
Mr	410.45	410.45
Dx,g cm-3	1.367	1.367
Z	8	8
Mu (mm-1)	0.758	0.758
F000	1712.0	1712.0
F000'	1717.29	
h,k,lmax	18,12,34	18,12,33
Nref	3925	3867
Tmin,Tmax	0.879,0.899	0.635,0.754
Tmin'	0.879	

Correction method= # Reported T Limits: Tmin=0.635 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 0.985 Theta(max)= 72.077

R(reflections)= 0.0750(2504) wR2(reflections)= 0.1940(3867)

S = 1.057 Npar= 281

(2). 11-Benzyl-3-(4-chlorophenyl)-5,6-dihydroindolizino[8,7-b]indole (3ce)

X-ray structure determination was obtained via slow evaporation of compound **3ce** in $CHCl_3$ at room temperature.

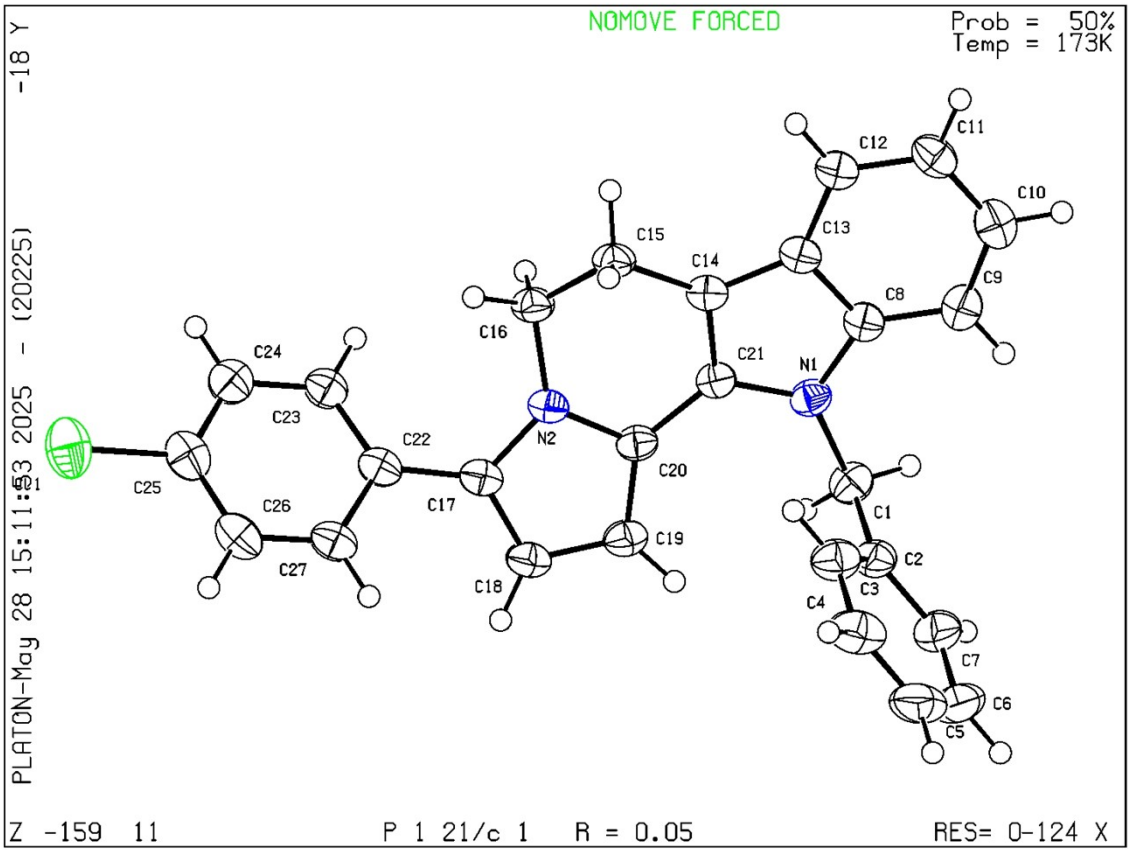


Figure S2. X-ray crystal structure of **3ce;**

Table S2. Crystal data and structure refinement for compound **3ce (CCDC: 2498970)**

Bond precision:	C-C = 0.0032 A	Wavelength=1.54178	
Cell:	a=13.8440(6)	b=11.6532(5)	c=12.5453(6)
	alpha=90	beta=99.307(3)	gamma=90
Temperature:	173 K		

	Calculated	Reported
Volume	1997.25(16)	1997.25(16)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C27 H21 Cl N2	C27 H21 Cl N2
Sum formula	C27 H21 Cl N2	C27 H21 Cl N2
Mr	408.91	408.91
Dx,g cm-3	1.360	1.360
Z	4	4
Mu (mm-1)	1.808	1.808
F000	856.0	856.0
F000'	859.54	
h,k,lmax	17,14,15	17,14,15
Nref	3939	3886
Tmin,Tmax	0.758,0.776	0.567,0.754
Tmin'	0.688	

Correction method= # Reported T Limits: Tmin=0.567 Tmax=0.754
AbsCorr = MULTI-SCAN

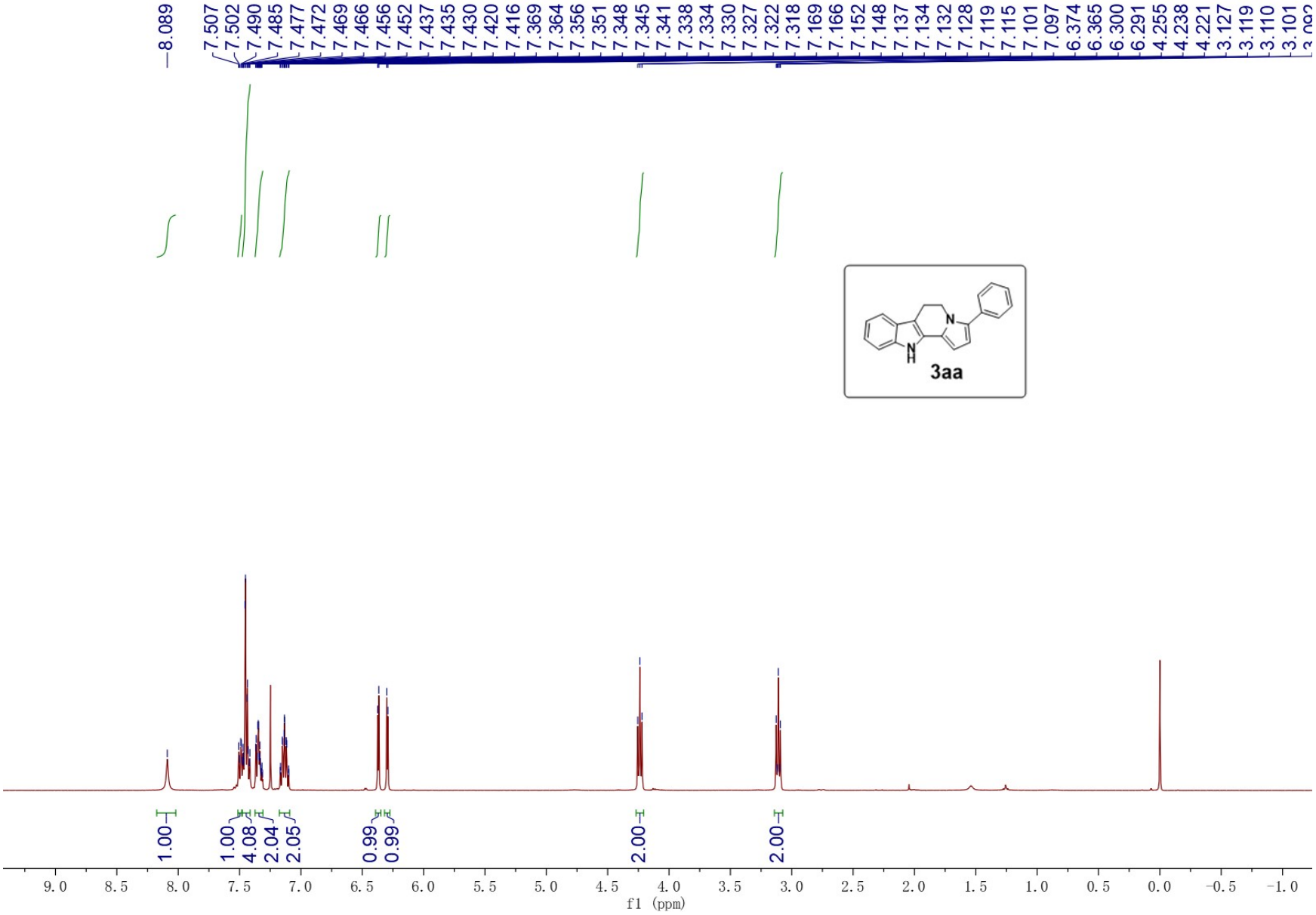
Data completeness= 0.987 Theta(max)= 72.182

R(reflections)= 0.0505(3208) wR2(reflections)= 0.1381(3886)

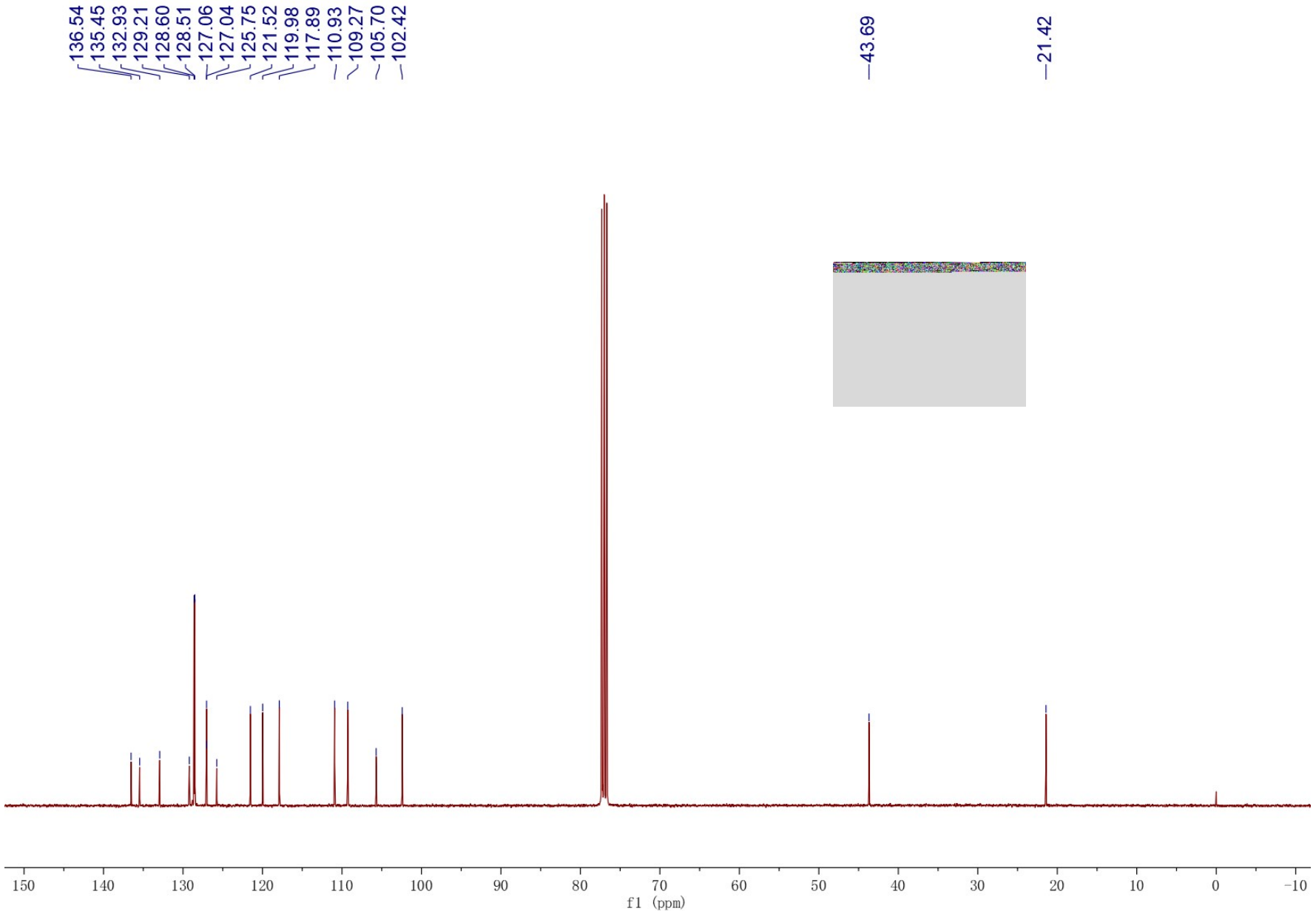
S = 1.081 Npar= 272

3. ^{1}H and ^{13}C NMR and ^{19}F NMR Spectra

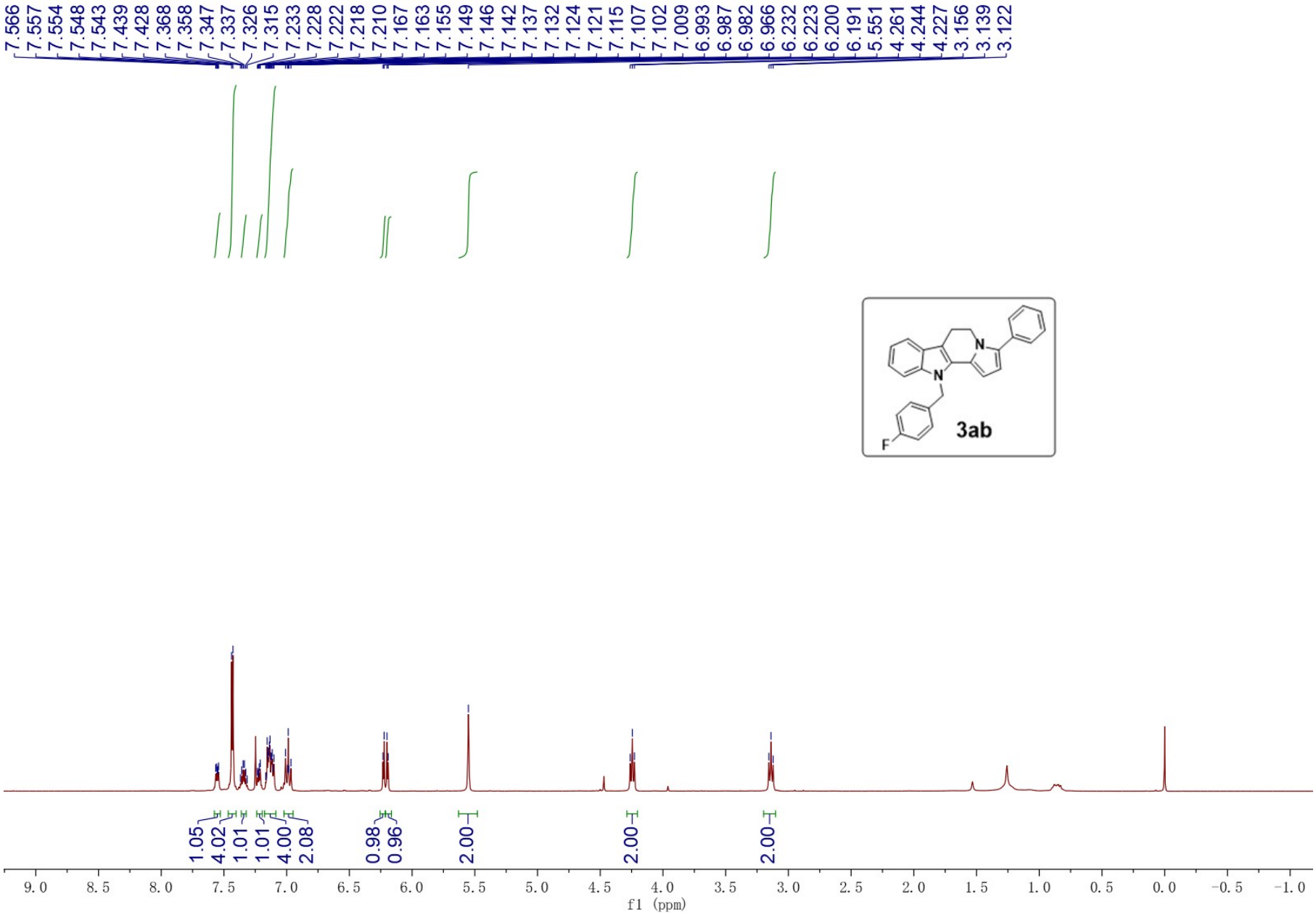
^{1}H NMR of 3aa (400 MHz, $CDCl_3$)



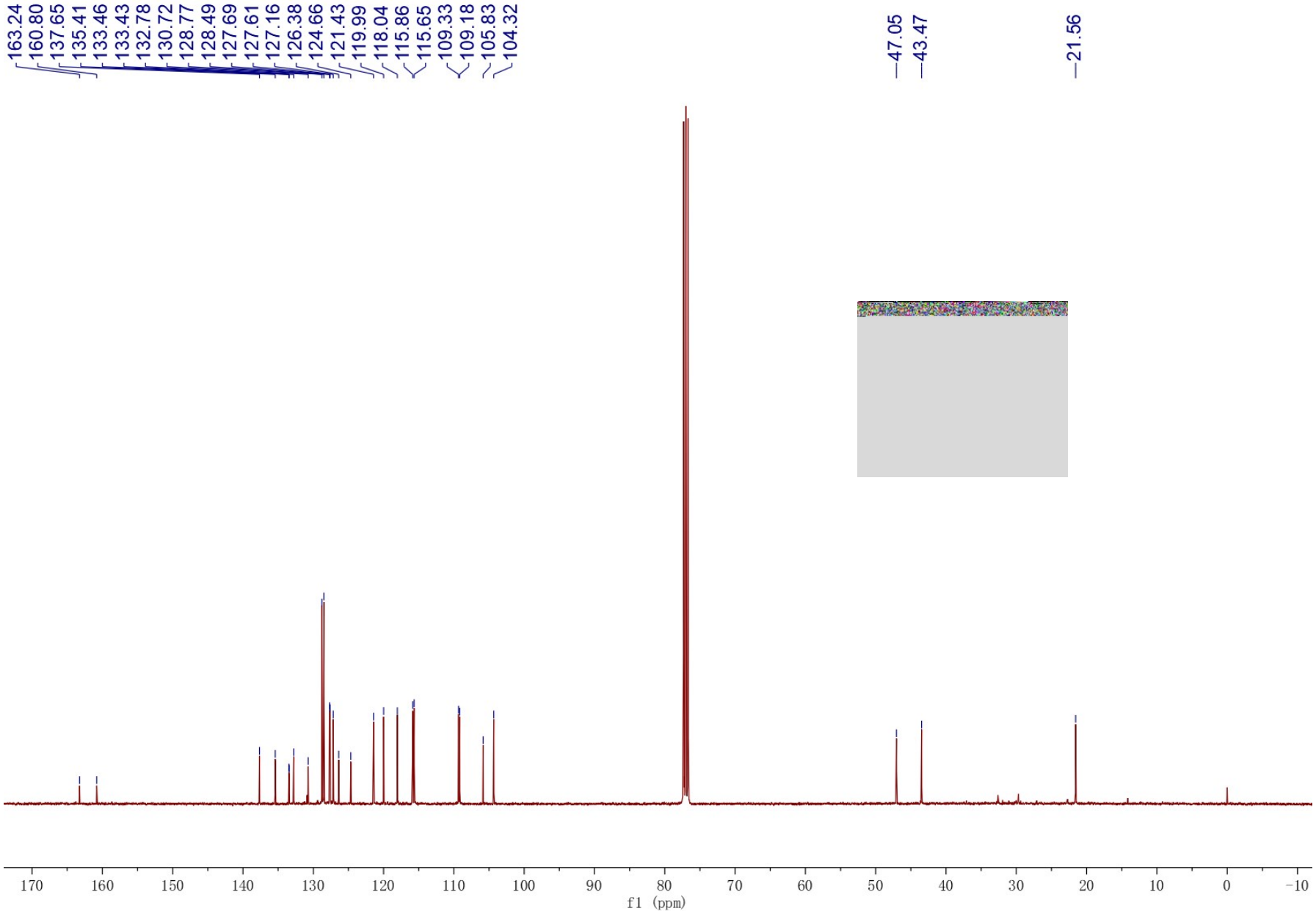
^{13}C NMR of 3aa (100 MHz, $CDCl_3$)



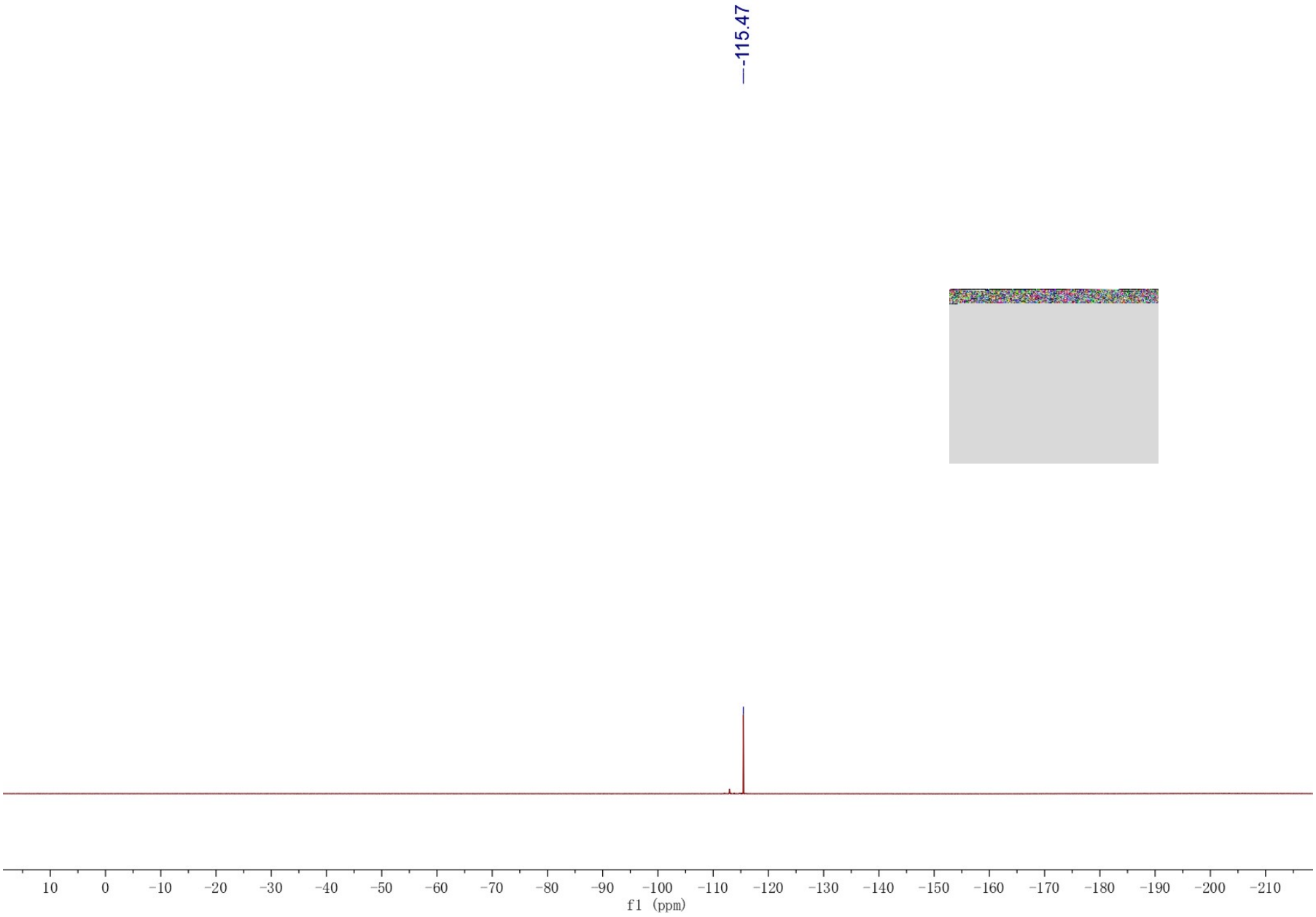
^{1}H NMR of 3ab (400 MHz, $CDCl_3$)



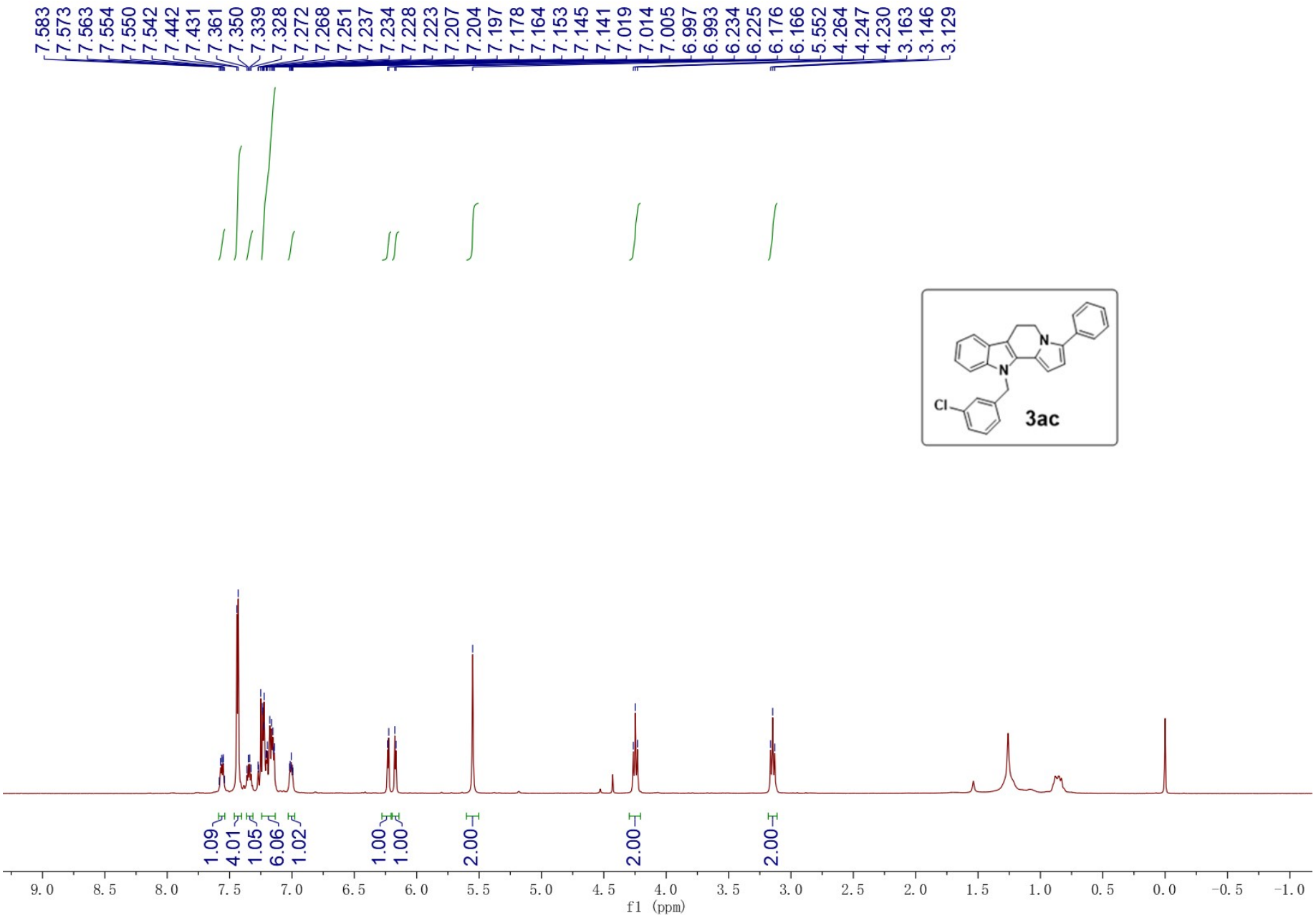
^{13}C NMR of 3ab (100 MHz, $CDCl_3$)



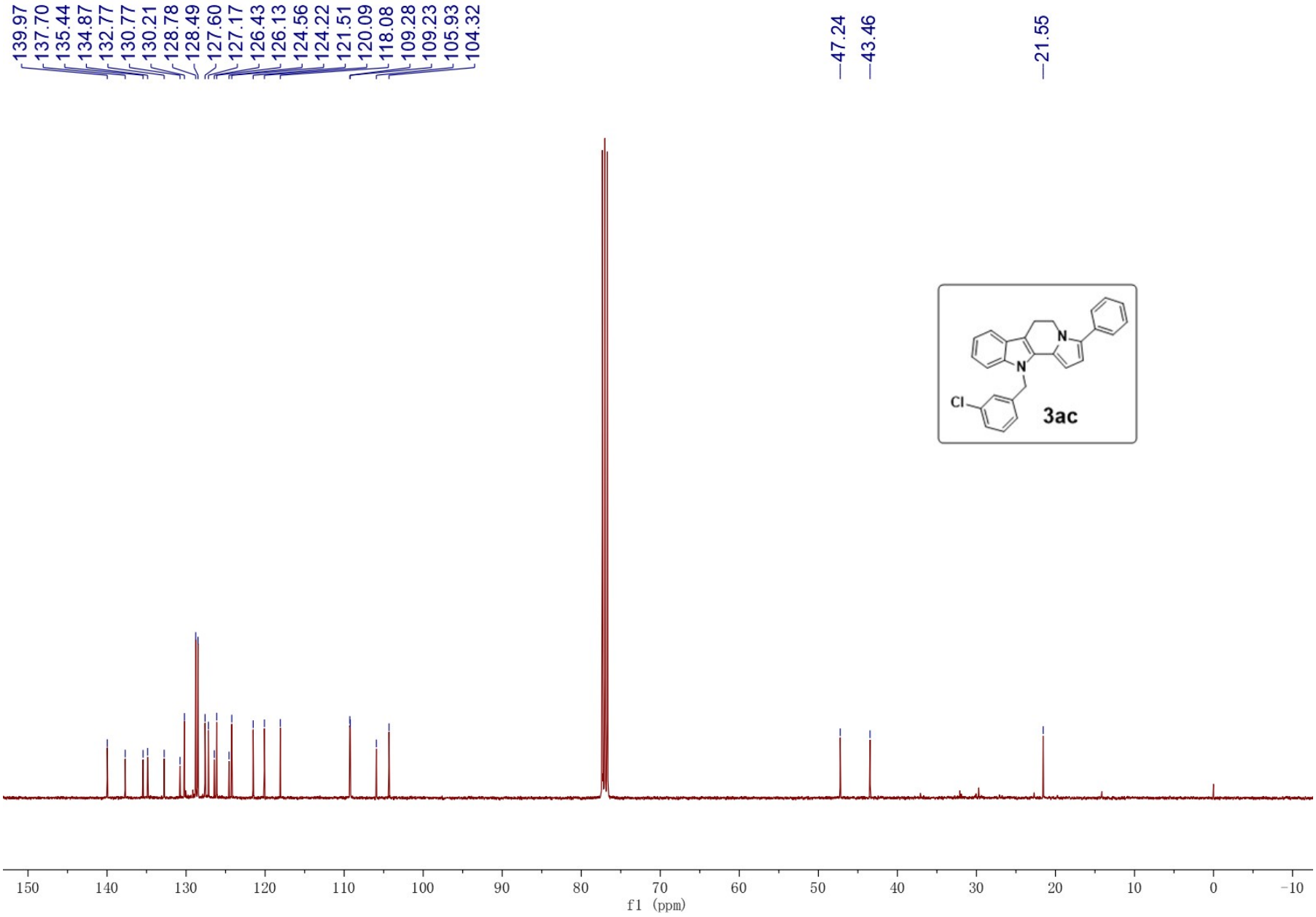
^{19}F NMR of 3ab (376 MHz, $CDCl_3$)



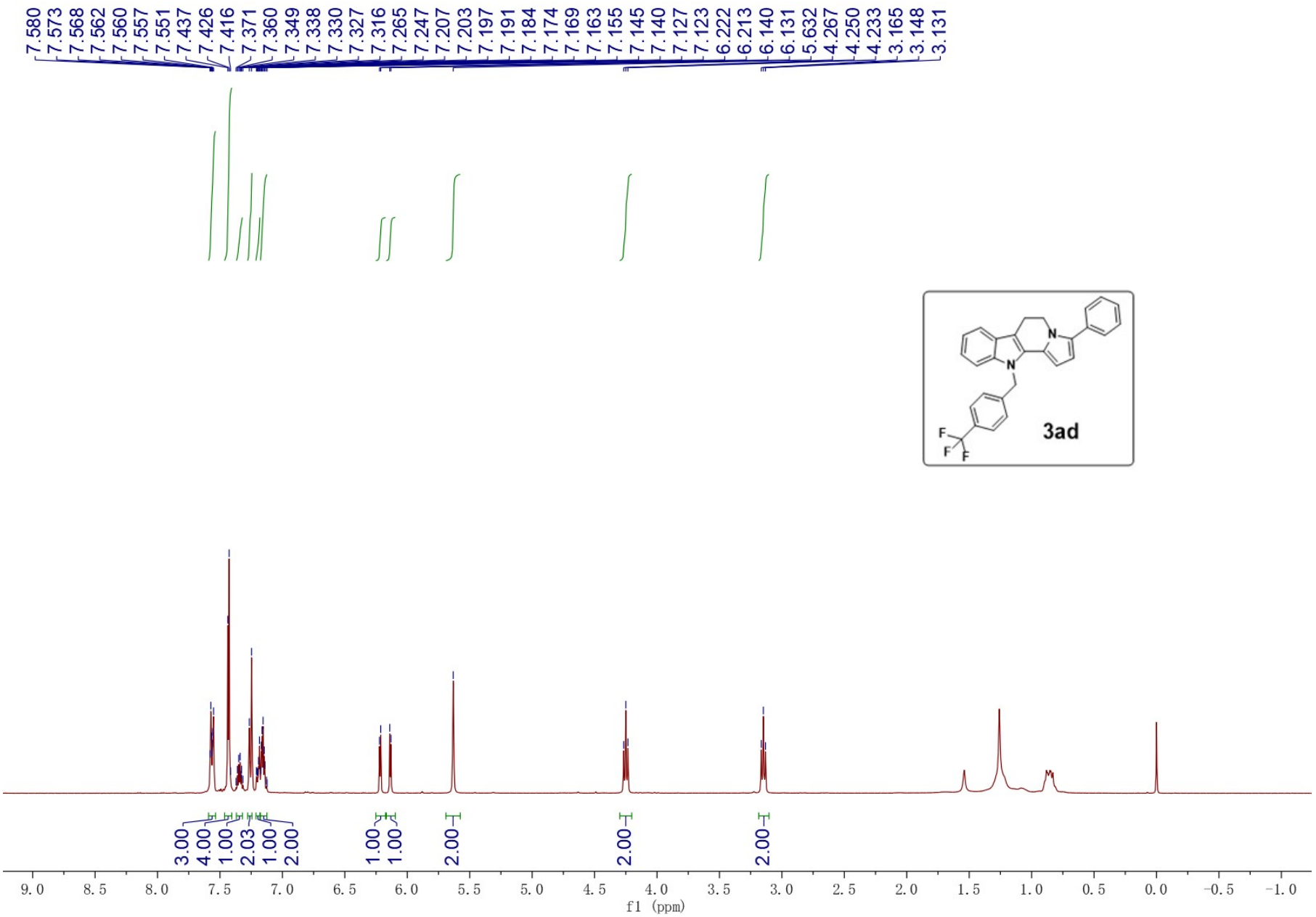
^{1}H NMR of 3ac (400 MHz, $CDCl_3$)



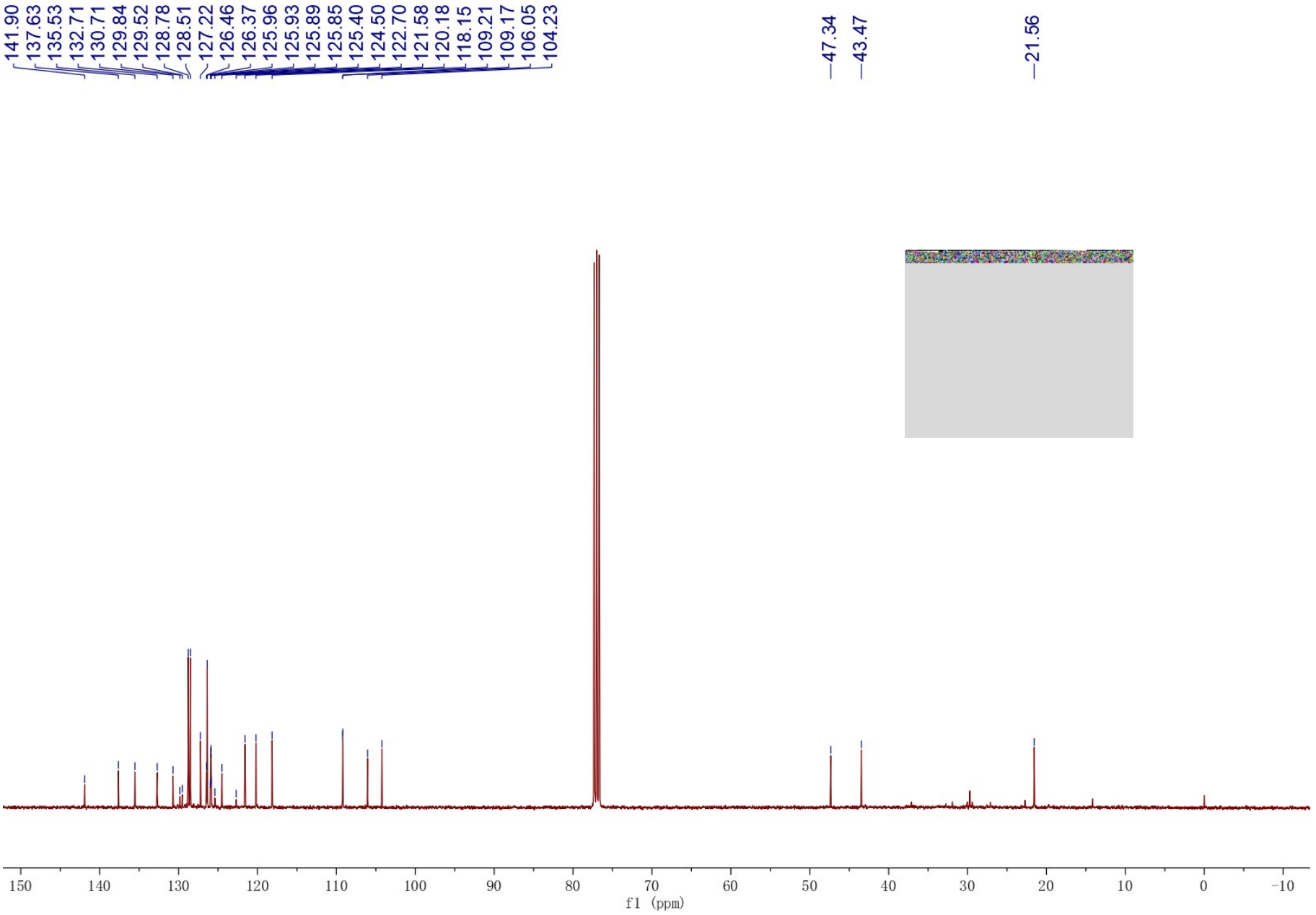
^{13}C NMR of 3ac (100 MHz, $CDCl_3$)



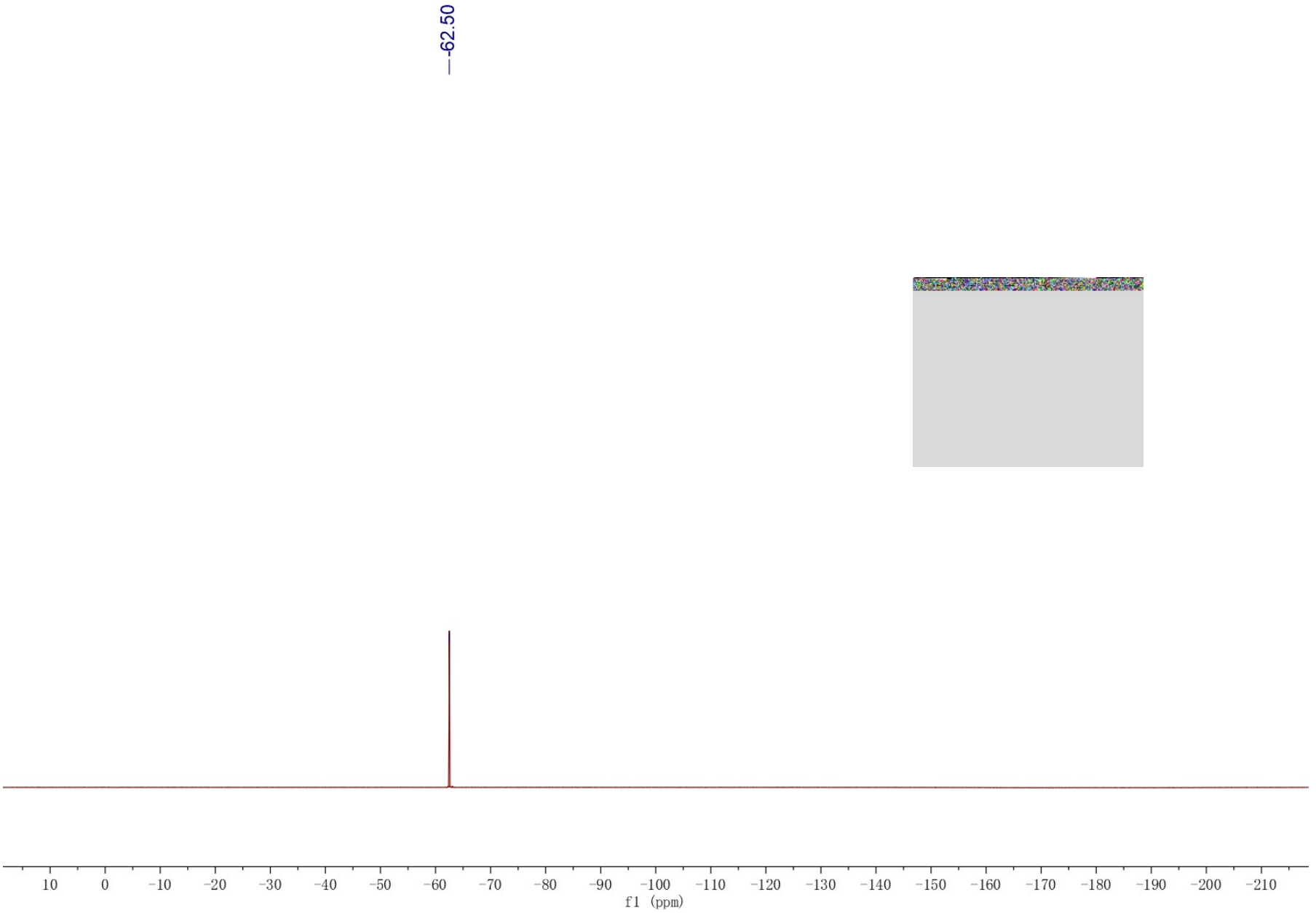
^{1}H NMR of 3ad (400 MHz, $CDCl_3$)



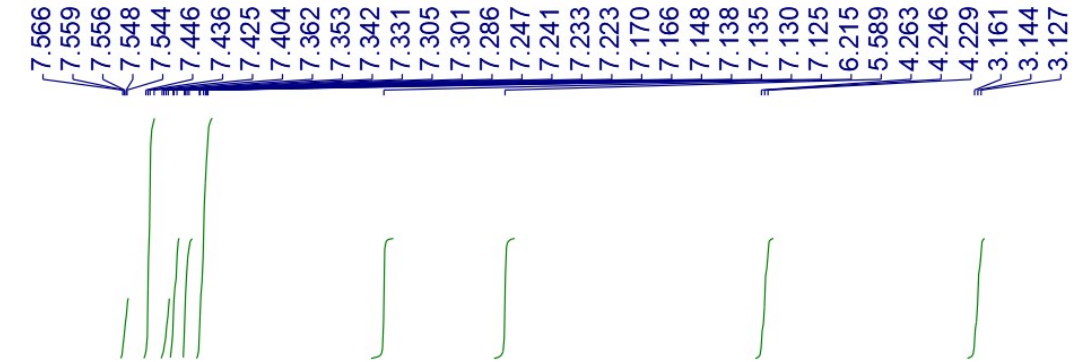
^{13}C NMR of 3ad (100 MHz, $CDCl_3$)

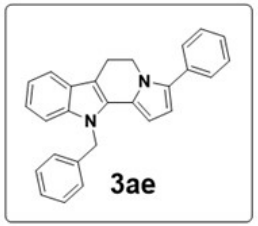


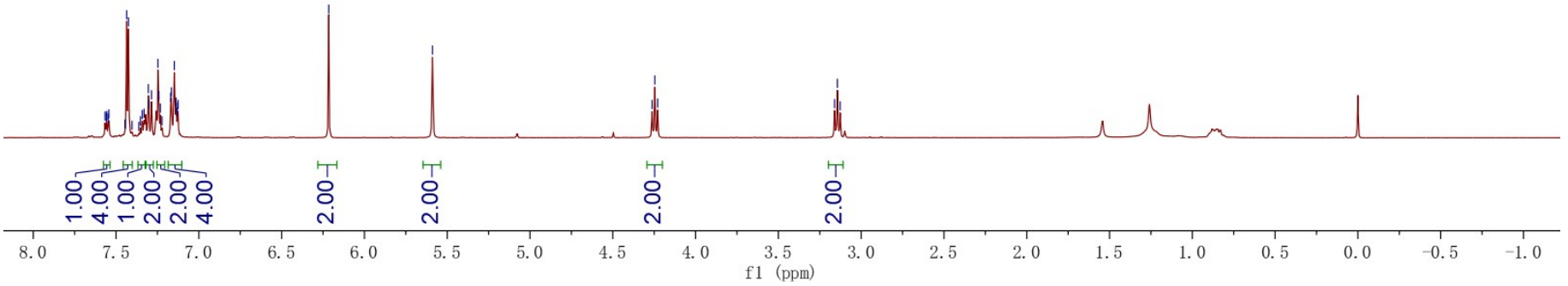
^{19}F NMR of 3ad (376 MHz, $CDCl_3$)



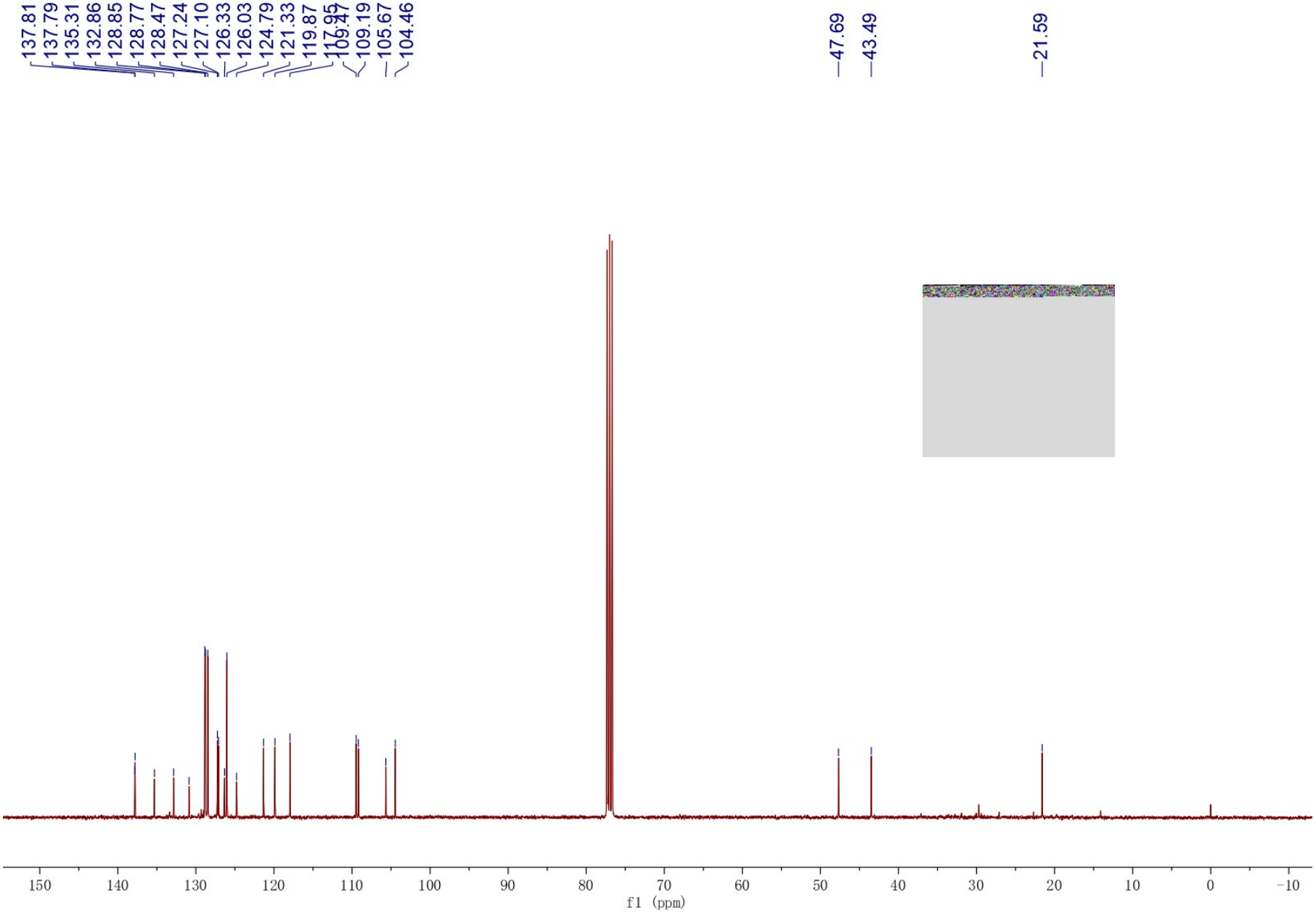
^{1}H NMR of 3ae (400 MHz, $CDCl_3$)



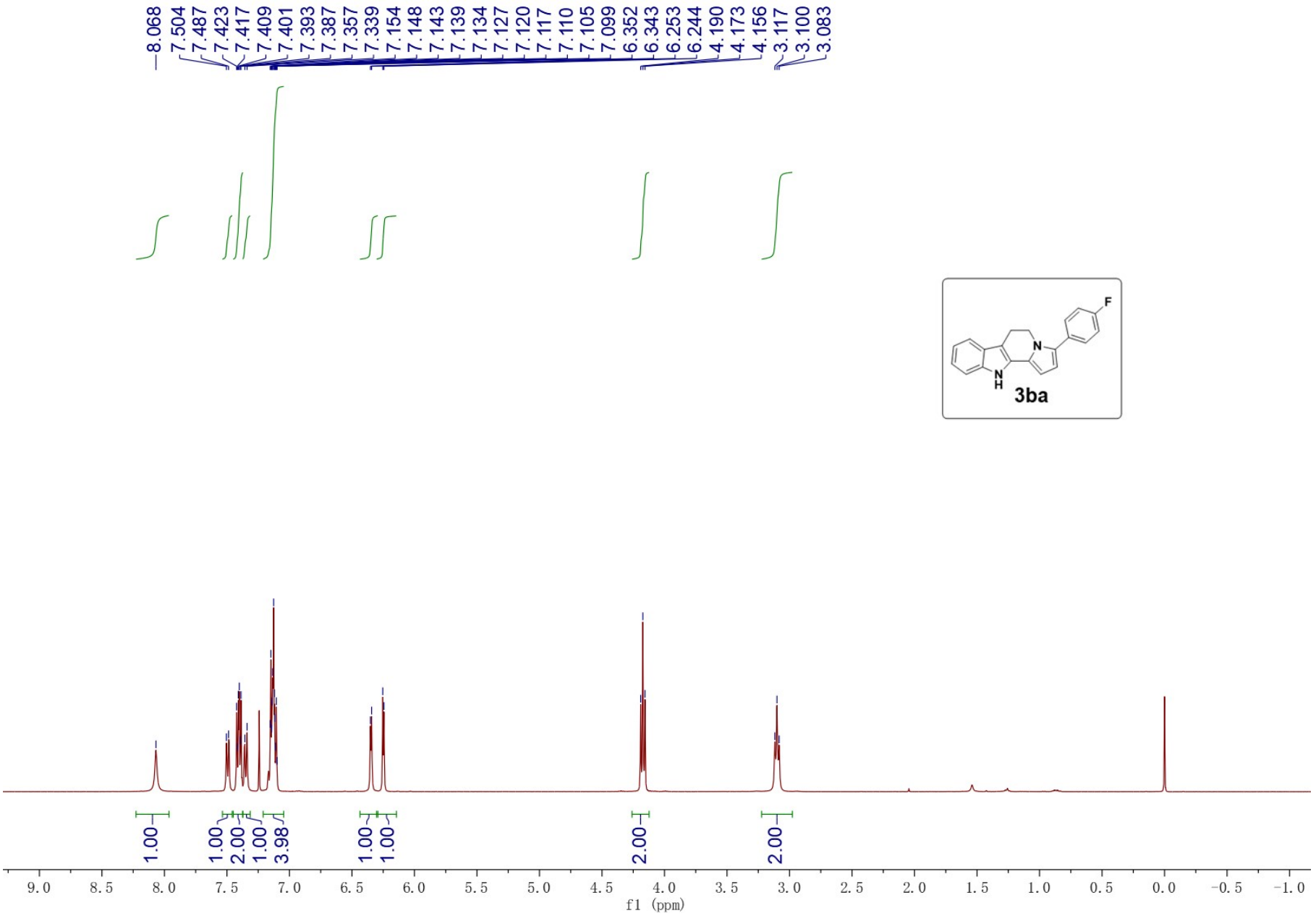




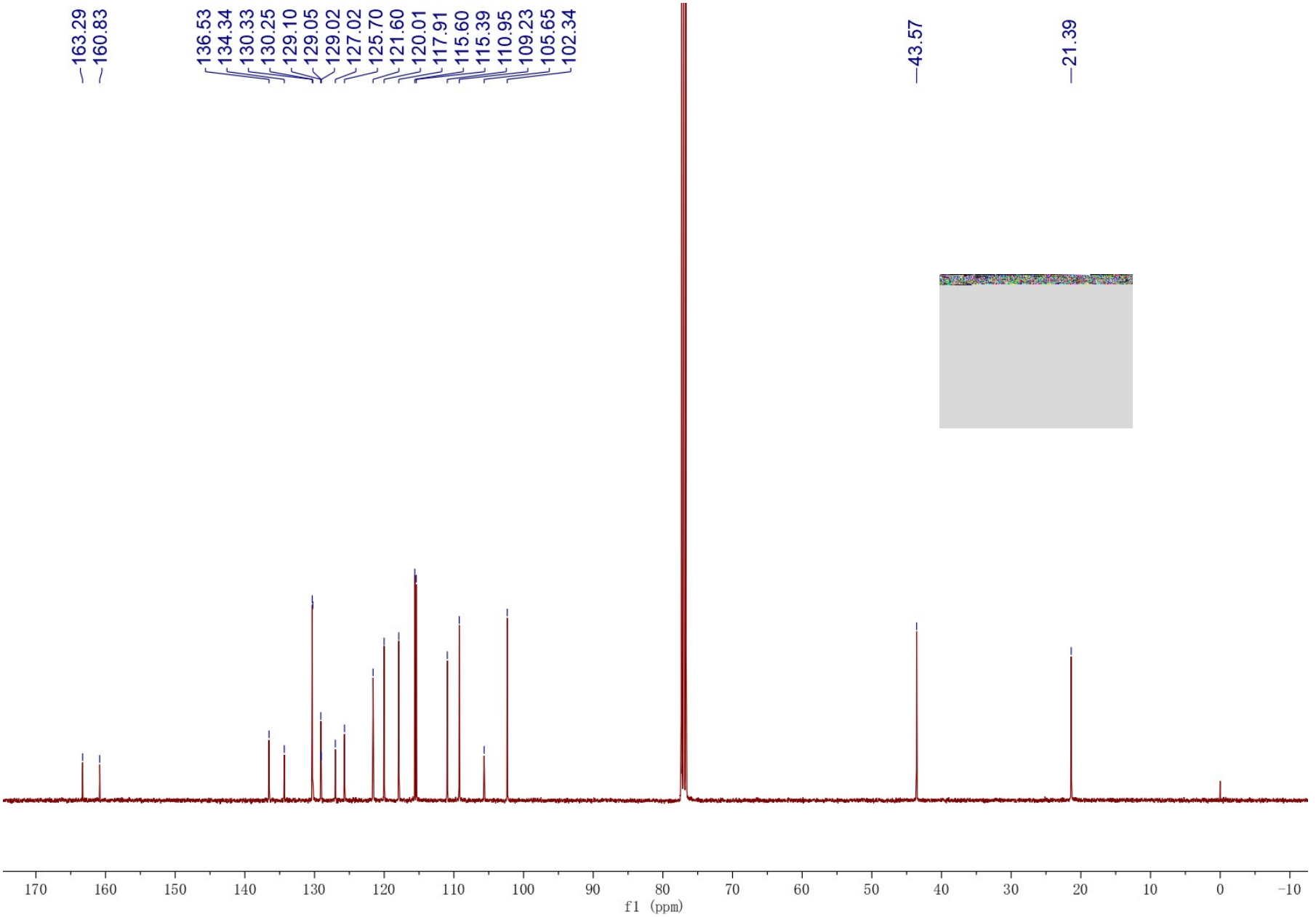
^{13}C NMR of 3ae (100 MHz, $CDCl_3$)



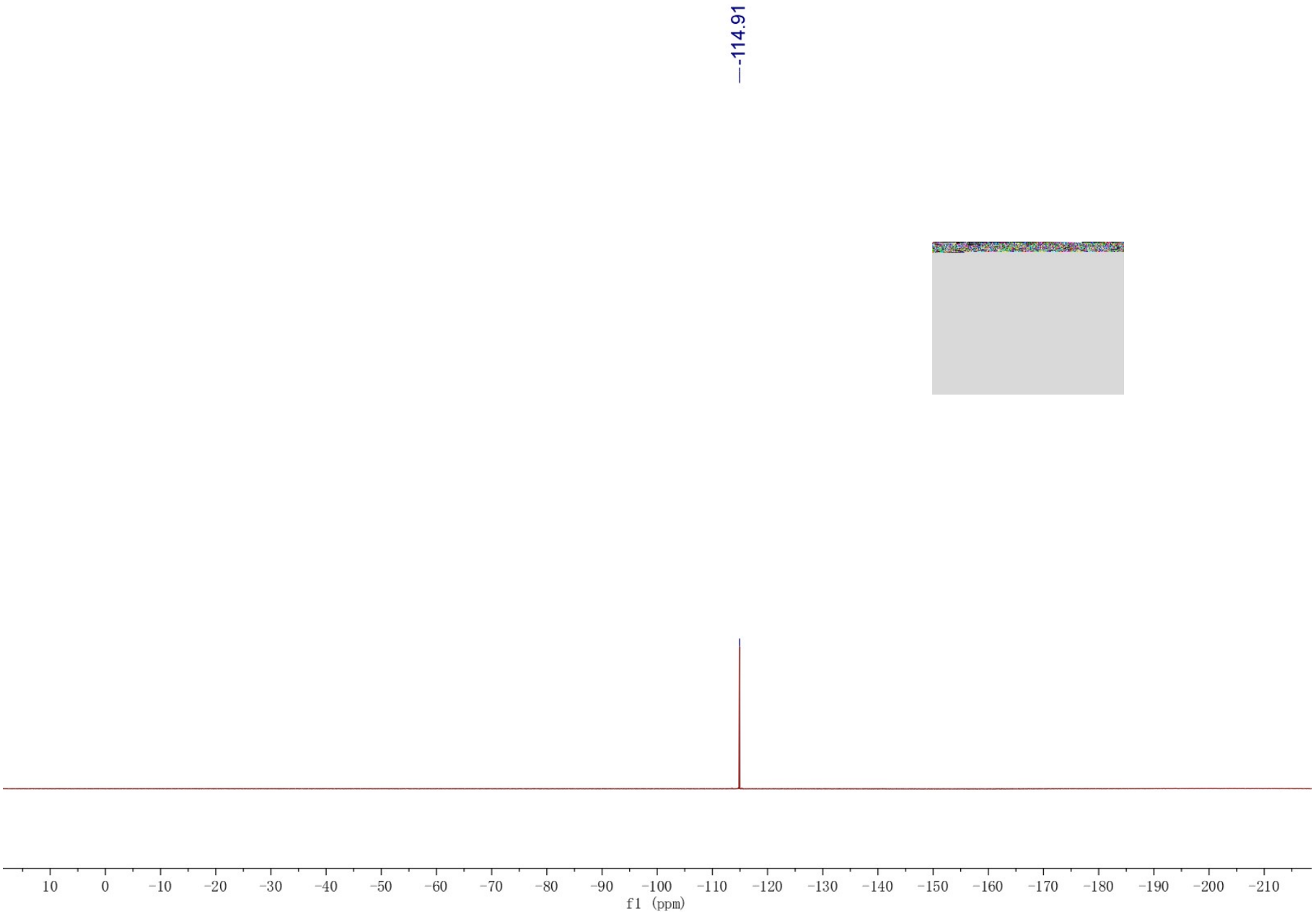
^{1}H NMR of 3ba (400 MHz, $CDCl_3$)



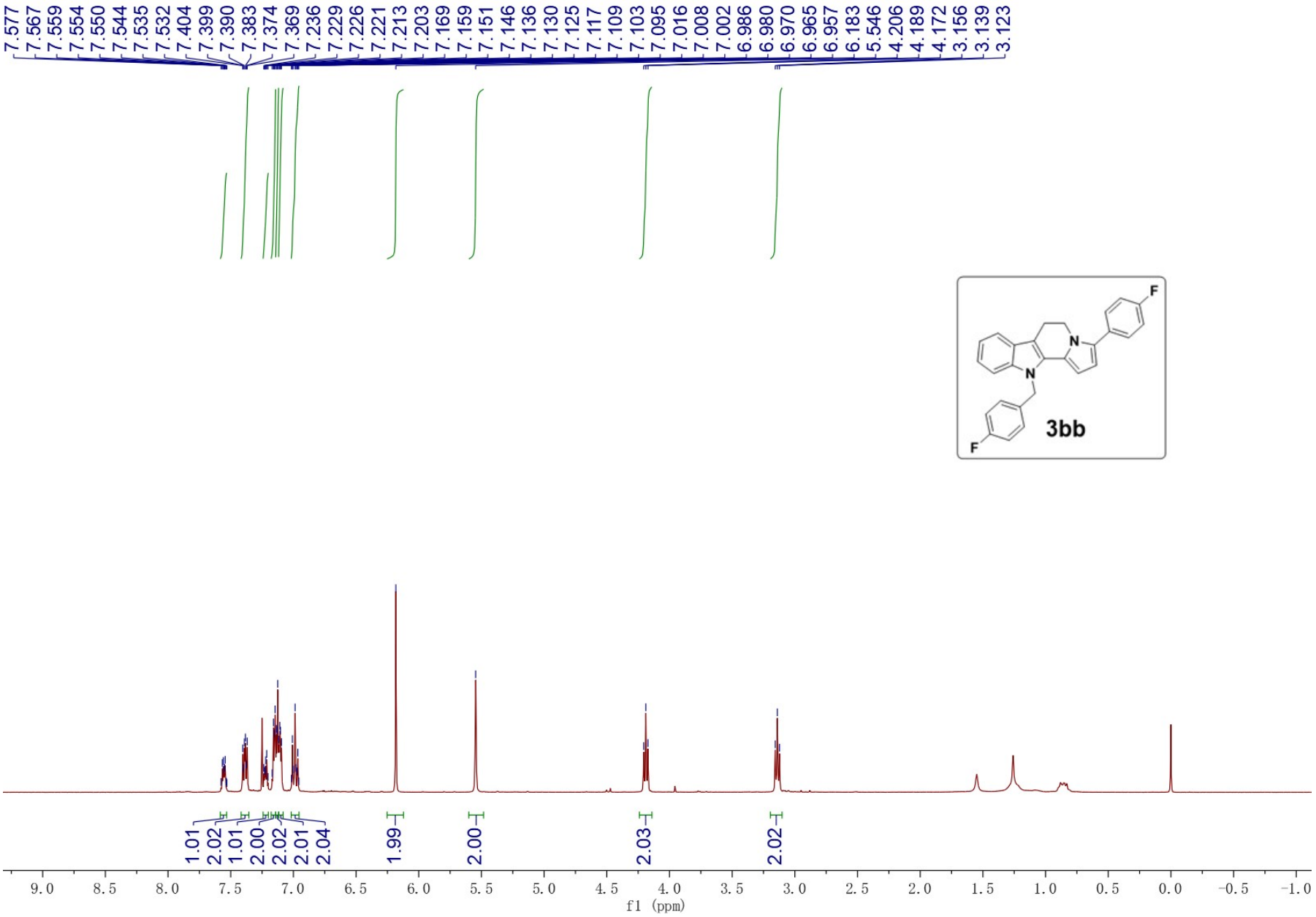
^{13}C NMR of 3ba (100 MHz, $CDCl_3$)



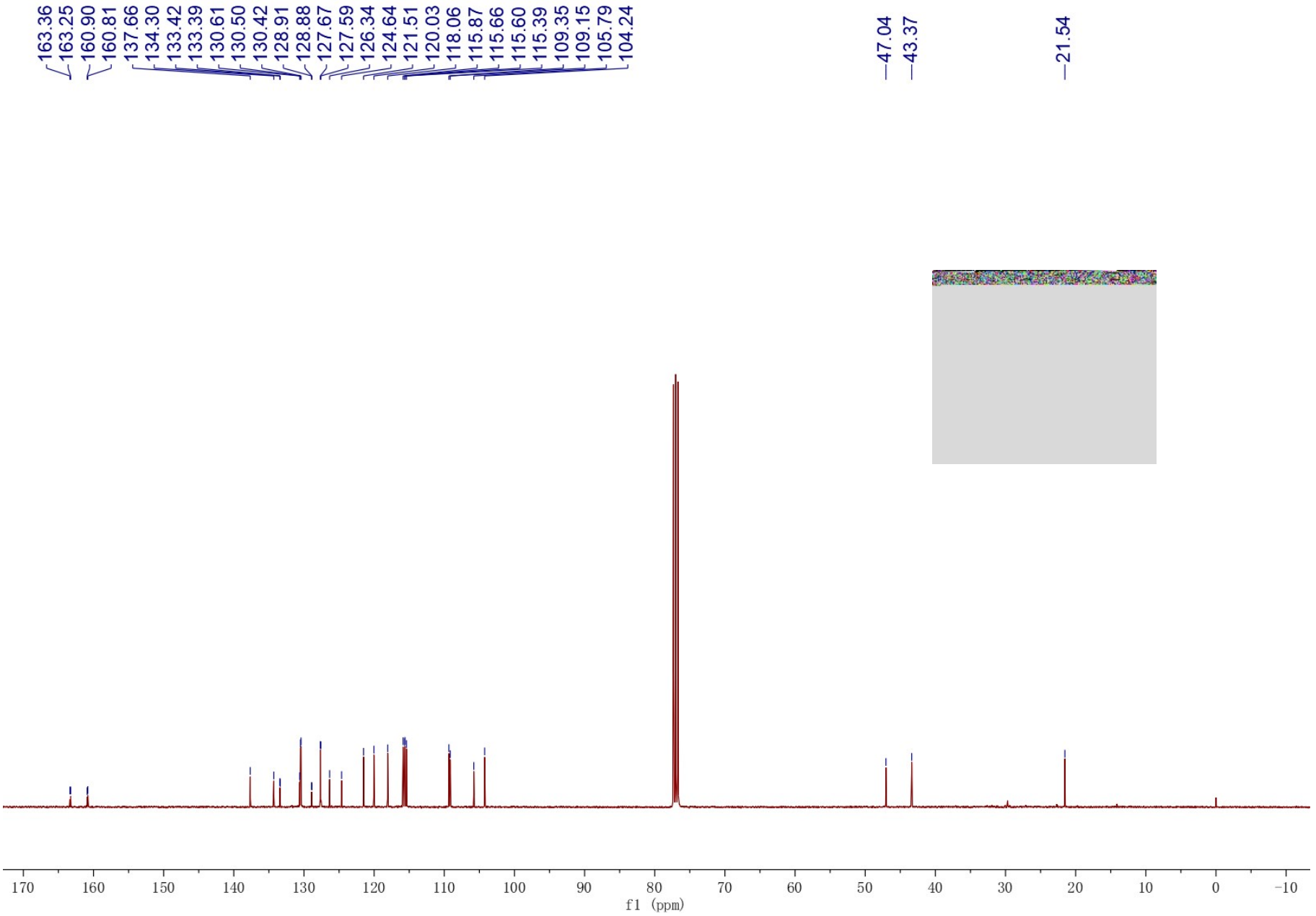
^{19}F NMR of 3ba (376 MHz, $CDCl_3$)



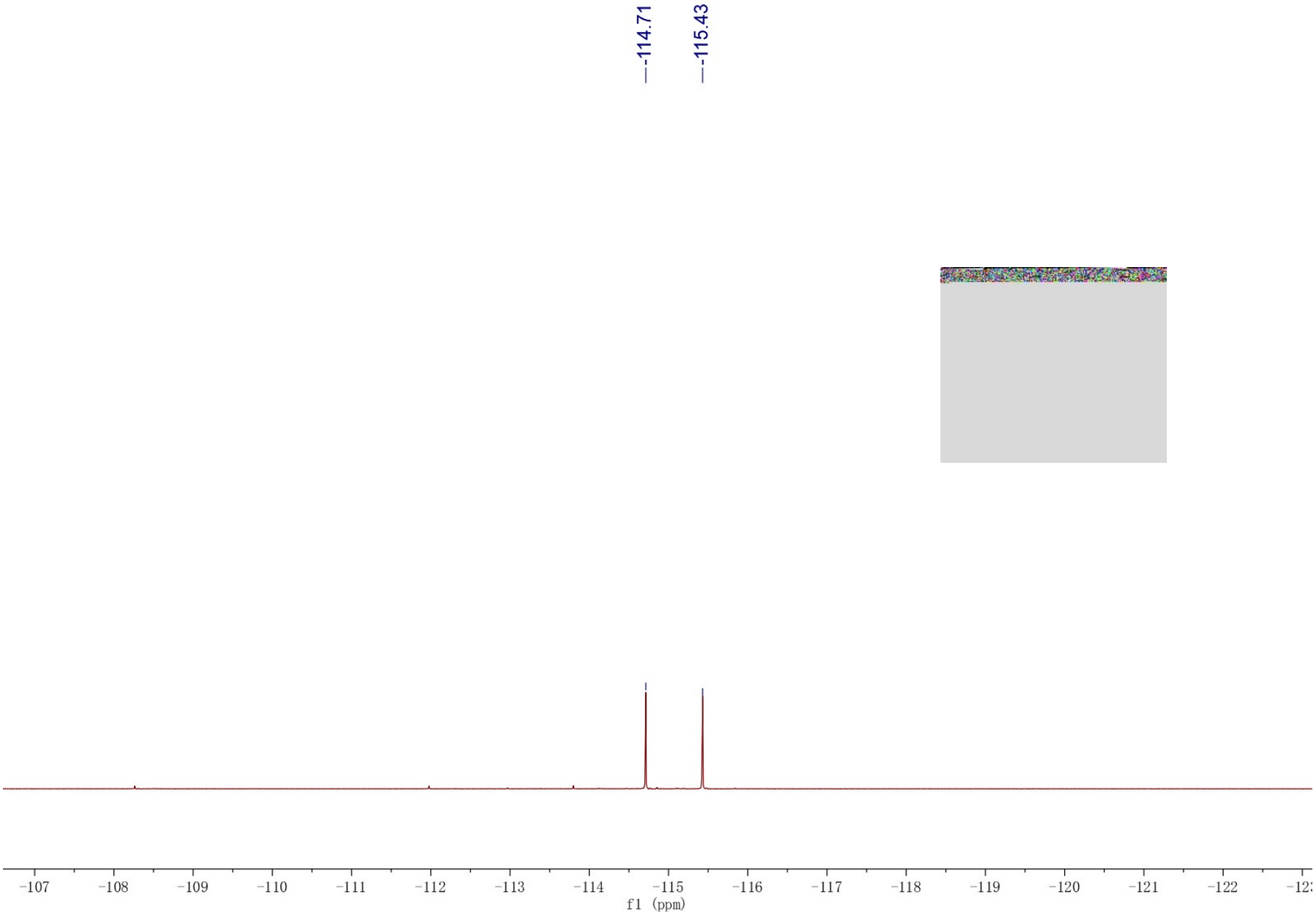
^{1}H NMR of 3bb (400 MHz, $CDCl_3$)



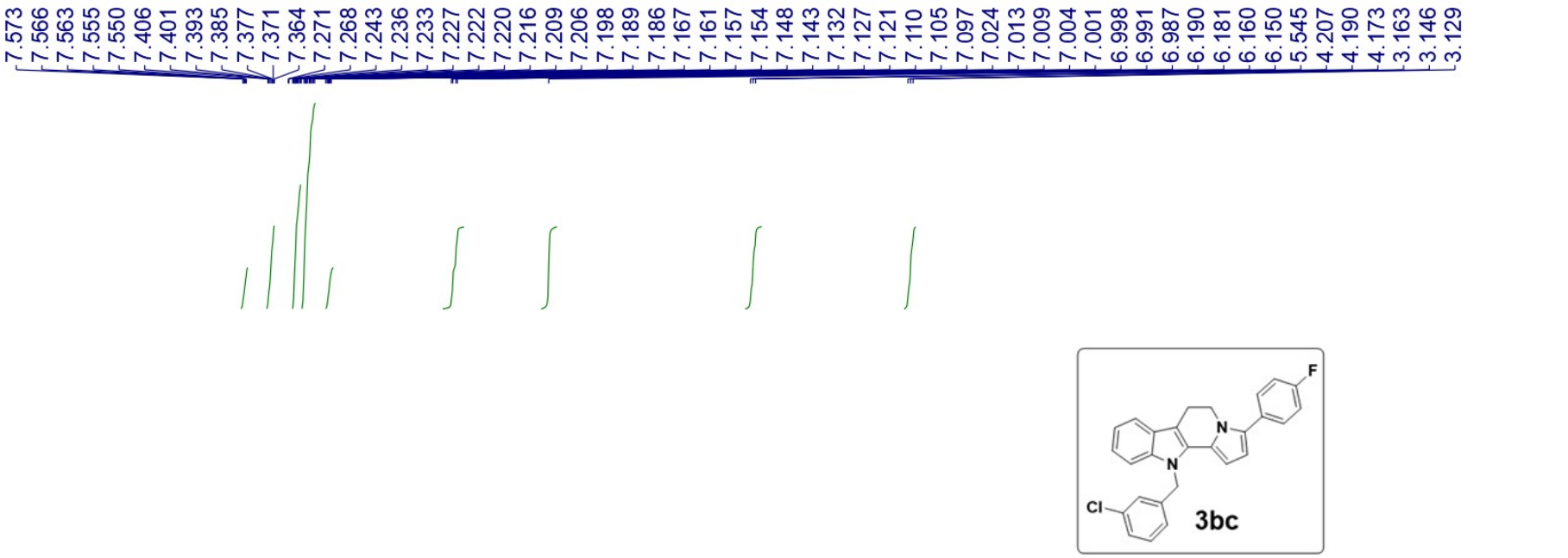
^{13}C NMR of 3bb (100 MHz, $CDCl_3$)

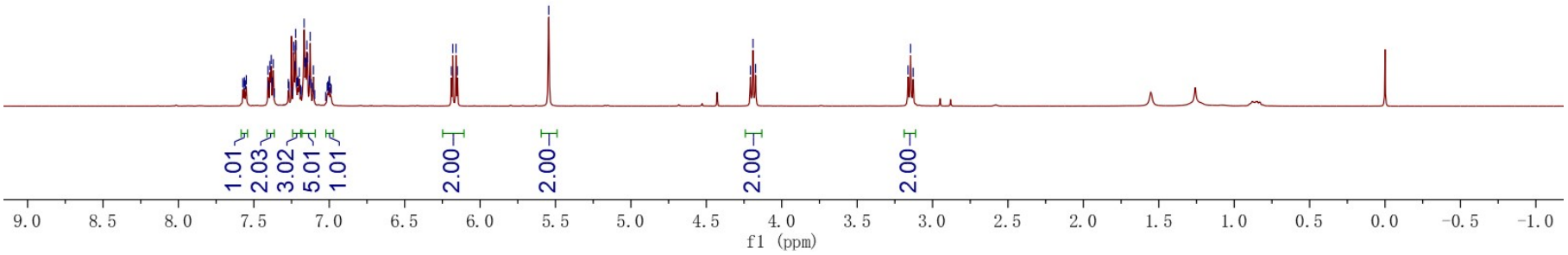


^{19}F NMR of 3bb (376 MHz, $CDCl_3$)

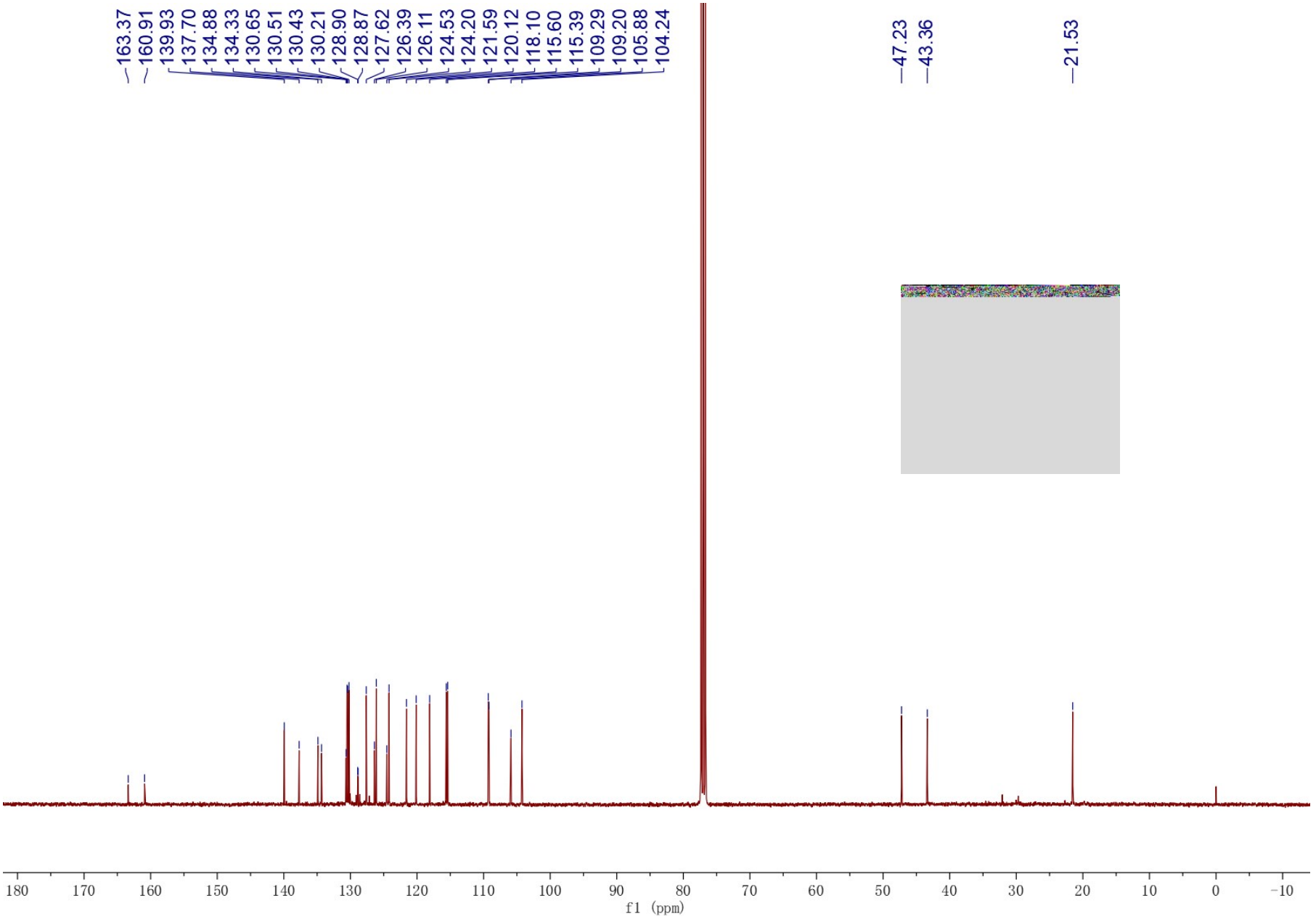


^{1}H NMR of 3bc (400 MHz, $CDCl_3$)

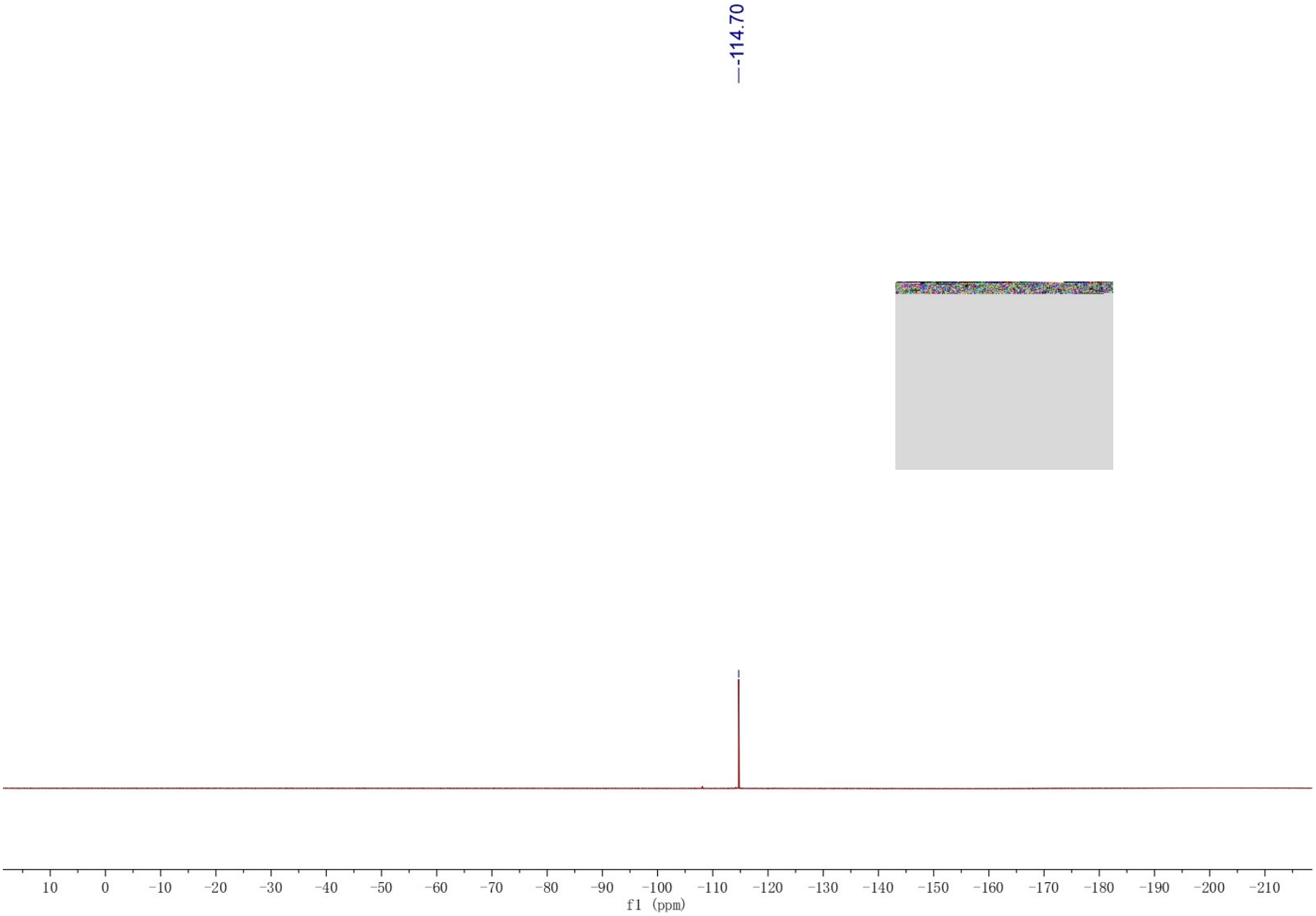




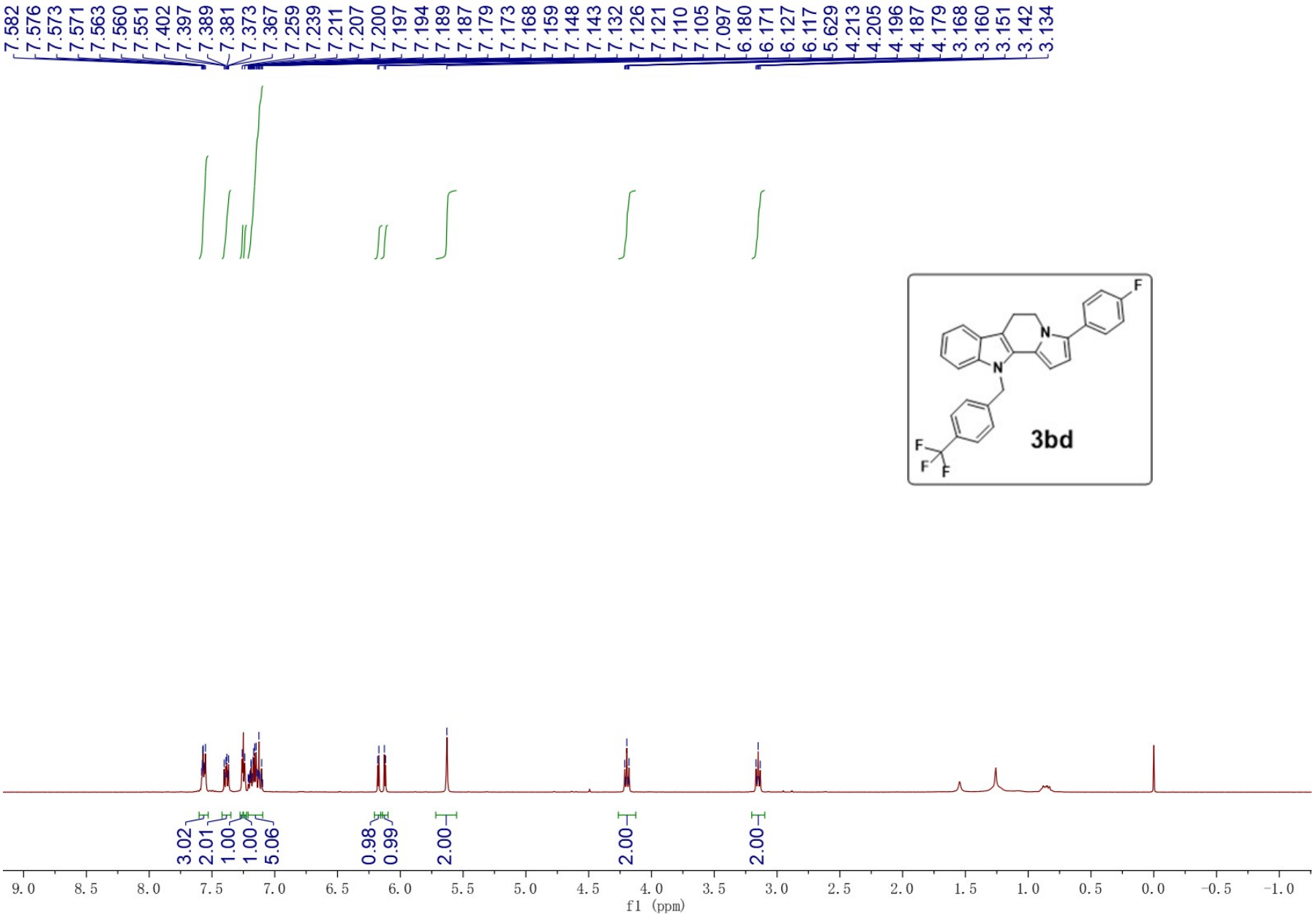
^{13}C NMR of 3bc (100 MHz, $CDCl_3$)



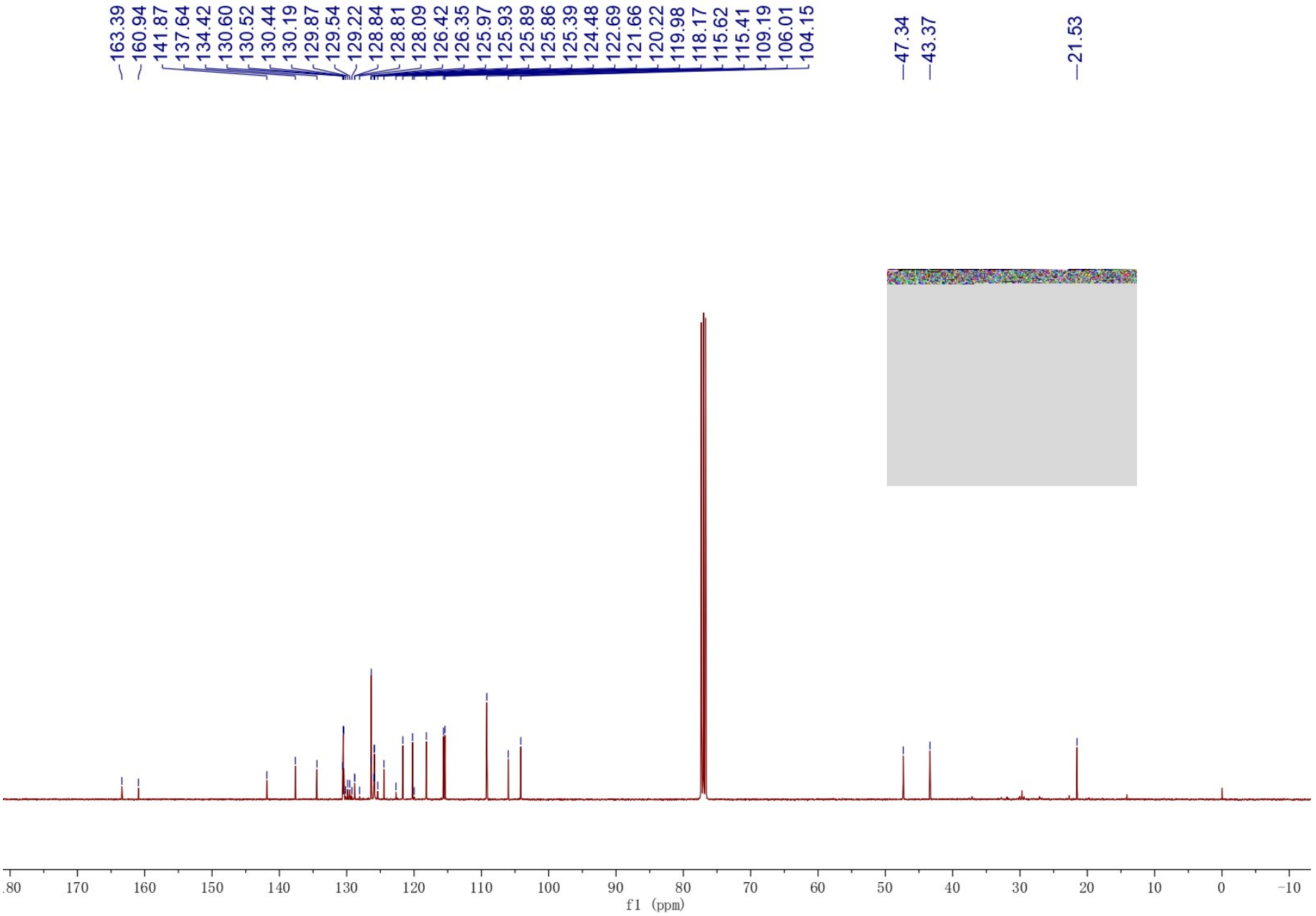
^{19}F NMR of 3bc (376 MHz, $CDCl_3$)



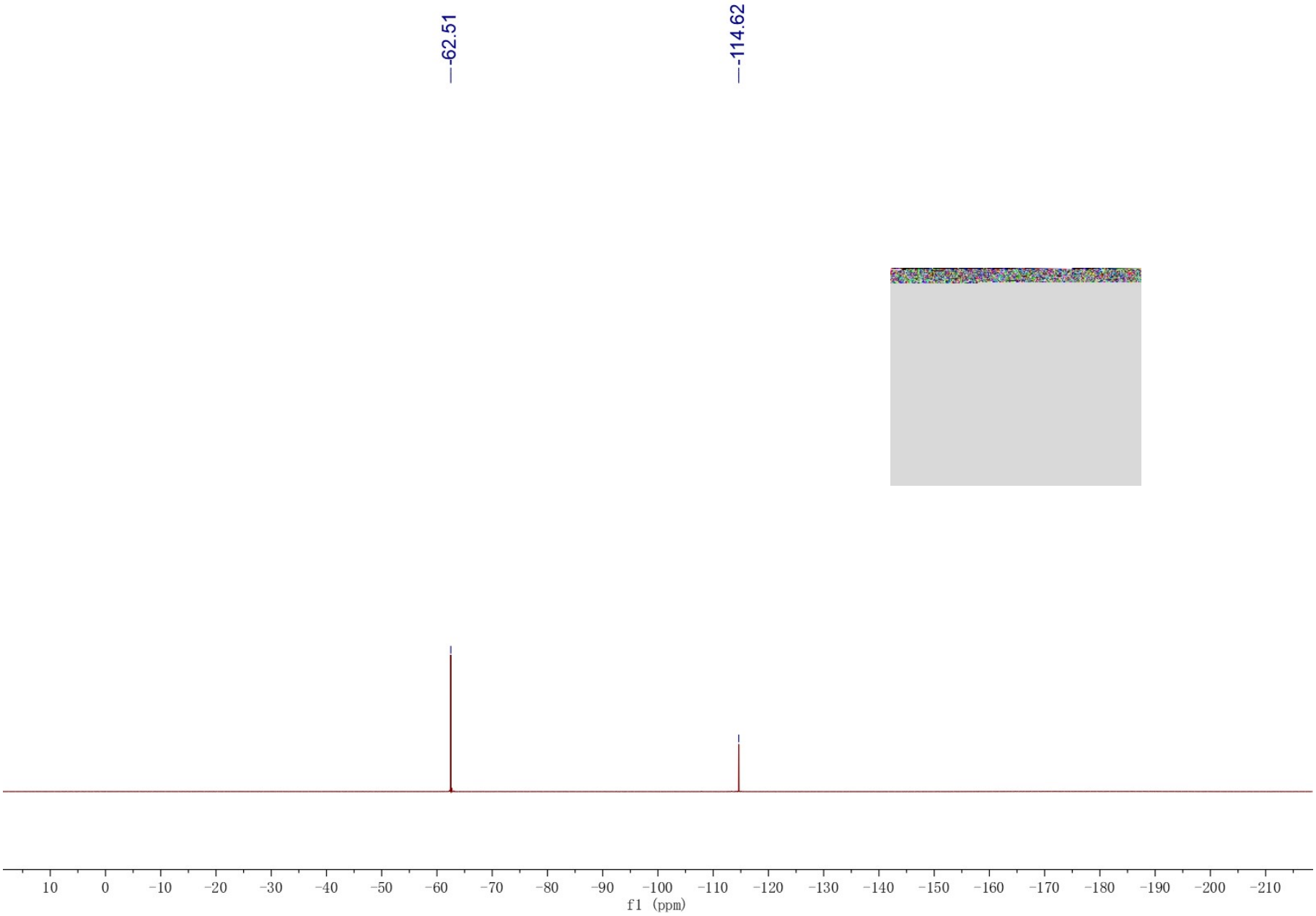
^{1}H NMR of 3bd (400 MHz, $CDCl_3$)



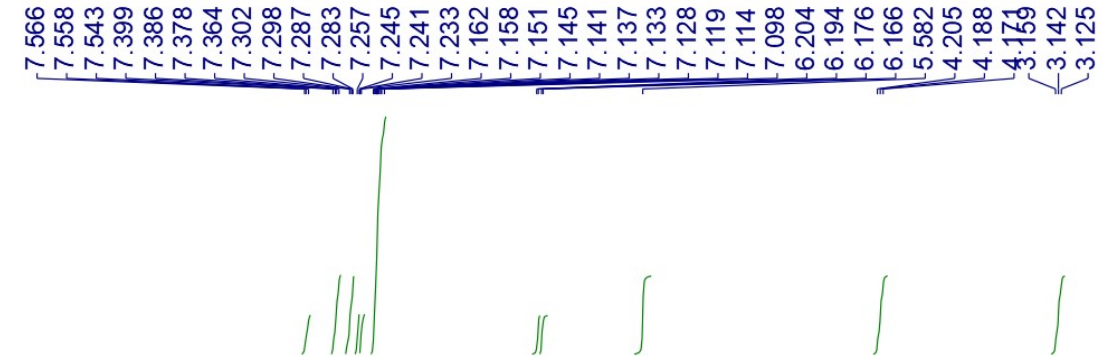
^{13}C NMR of 3bd (100 MHz, $CDCl_3$)

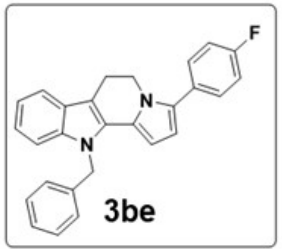


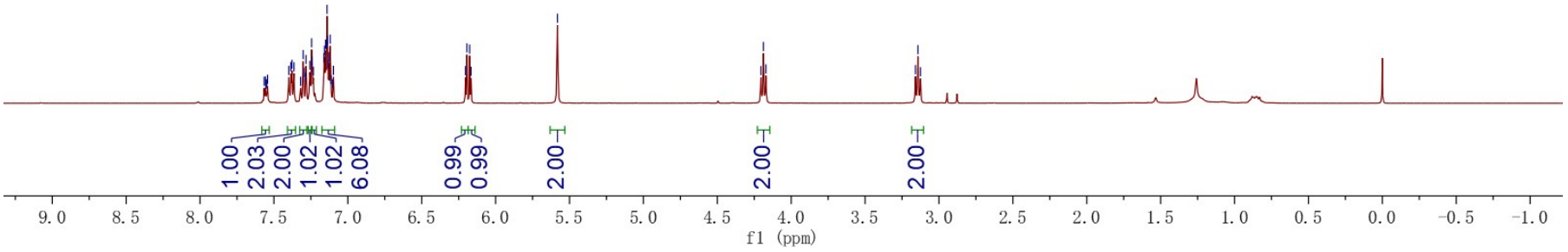
^{19}F NMR of 3bd (376 MHz, $CDCl_3$)



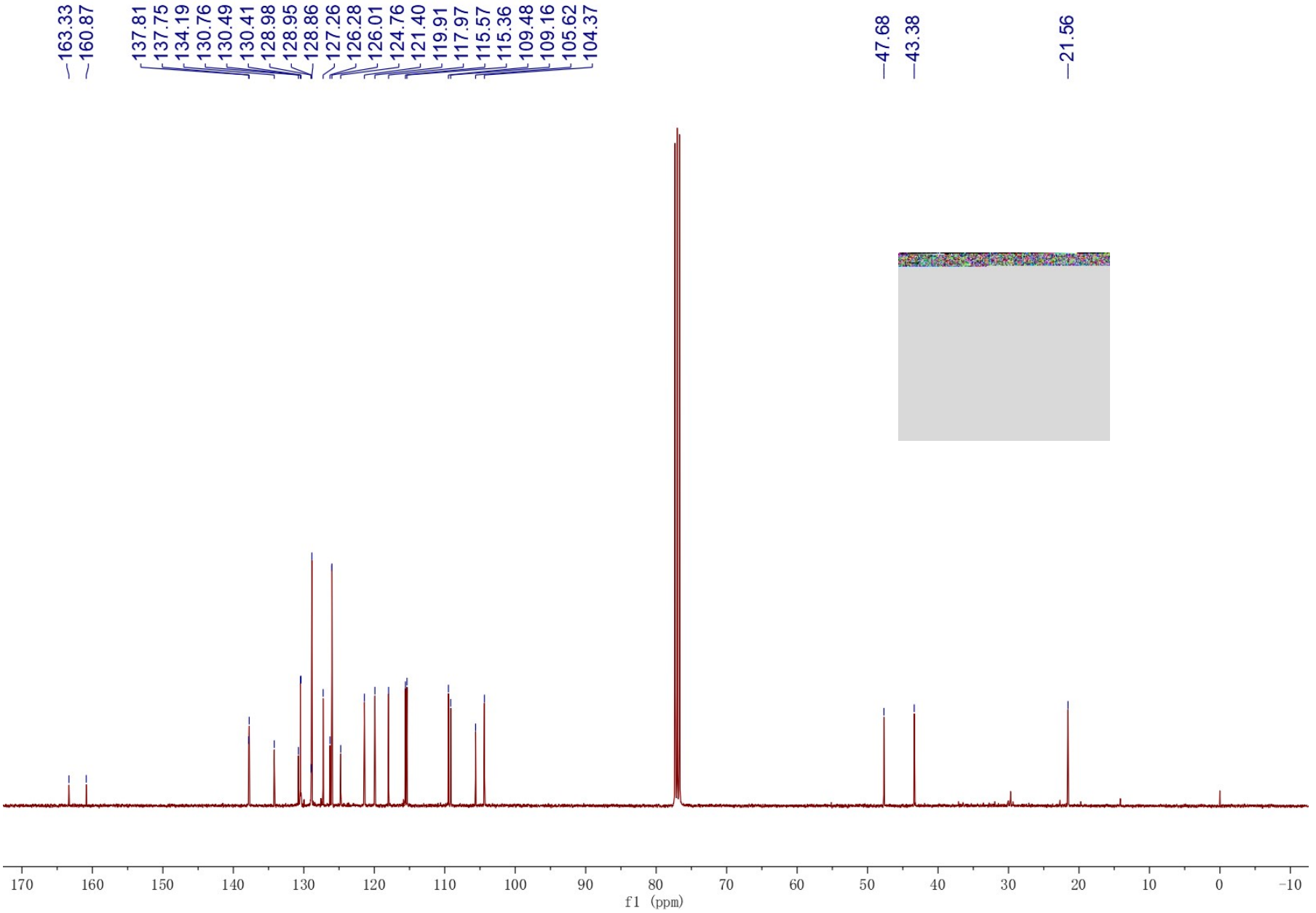
^{1}H NMR of 3be (400 MHz, $CDCl_3$)



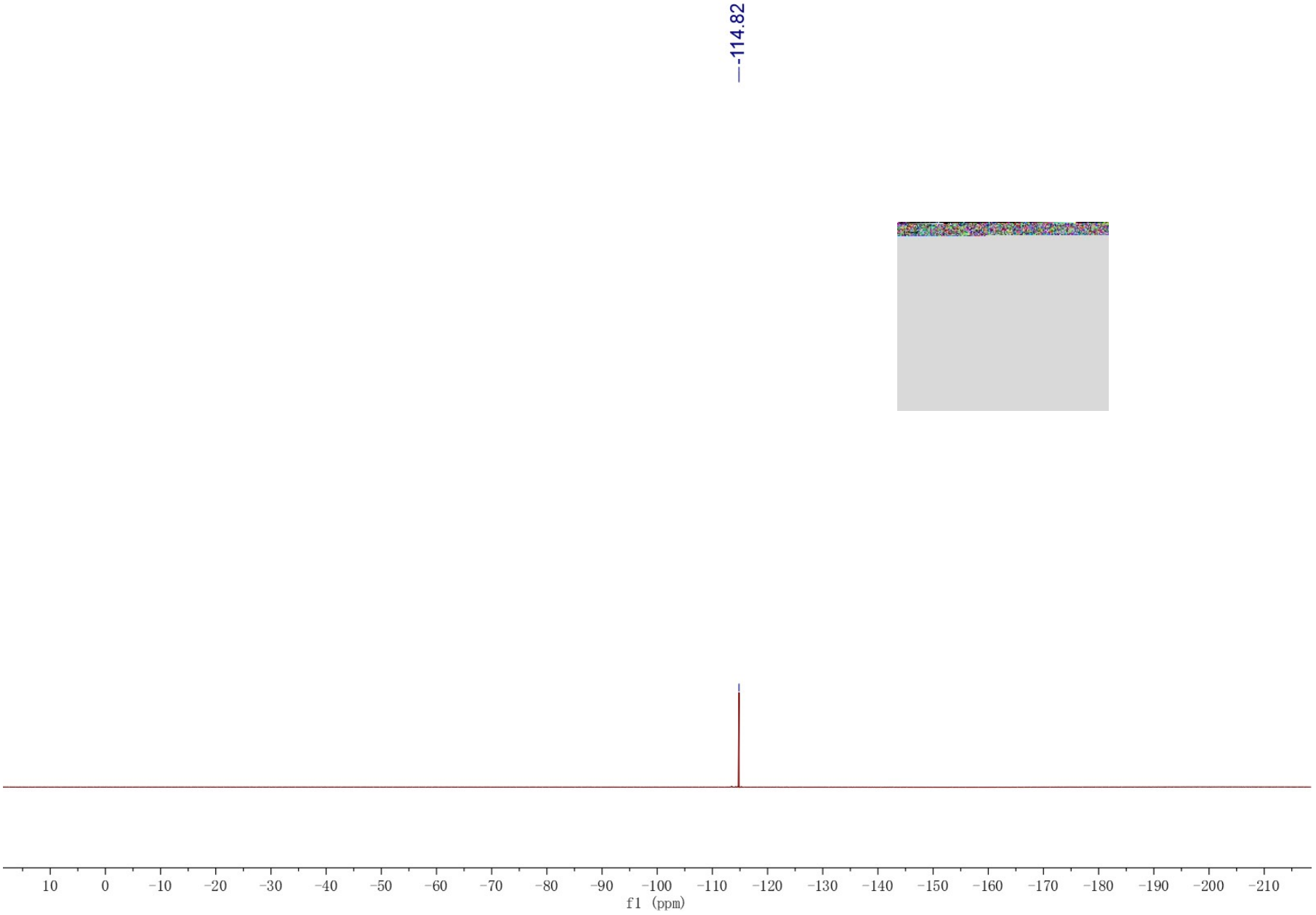




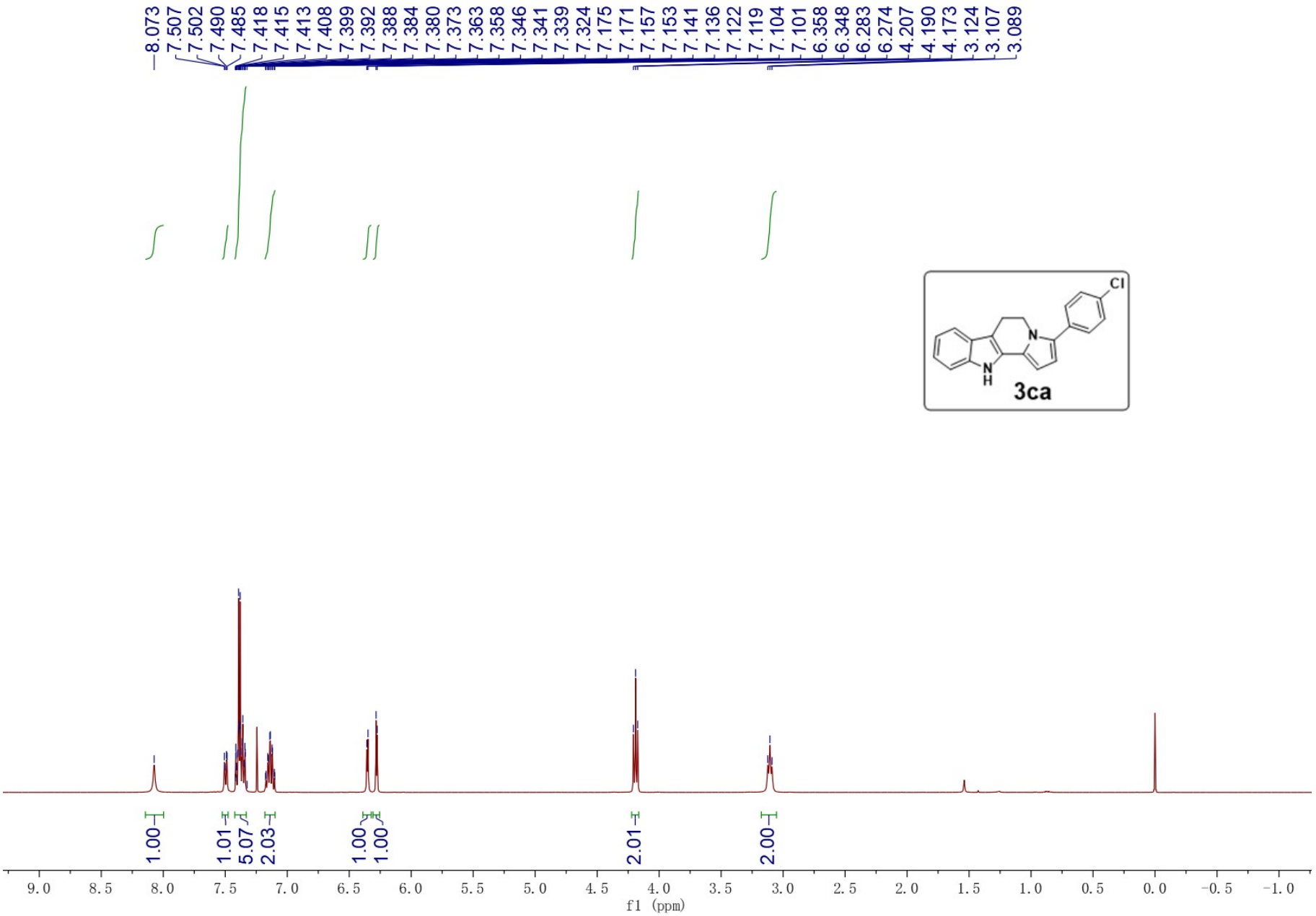
^{13}C NMR of 3be (100 MHz, $CDCl_3$)



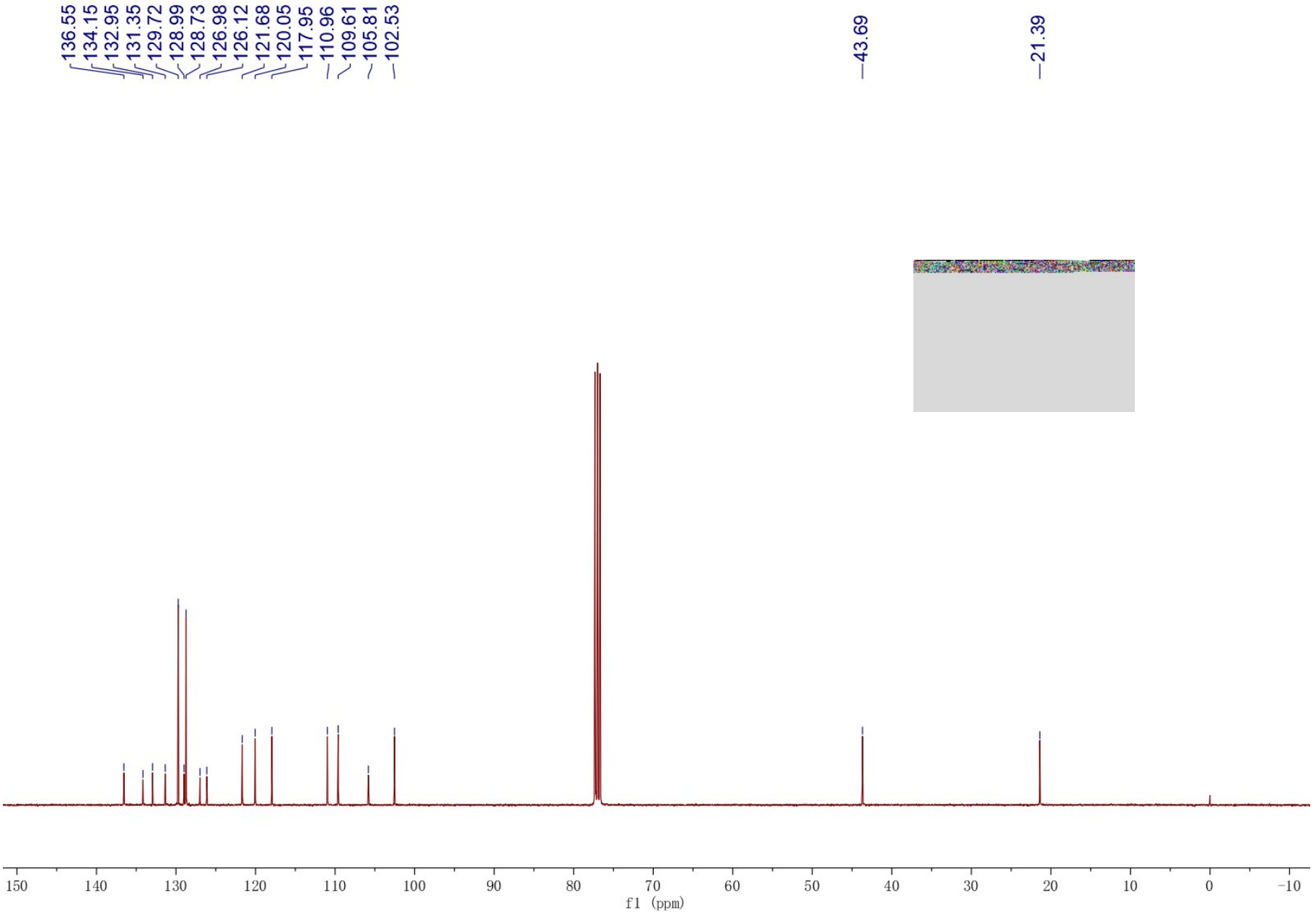
^{19}F NMR of 3be (376 MHz, $CDCl_3$)



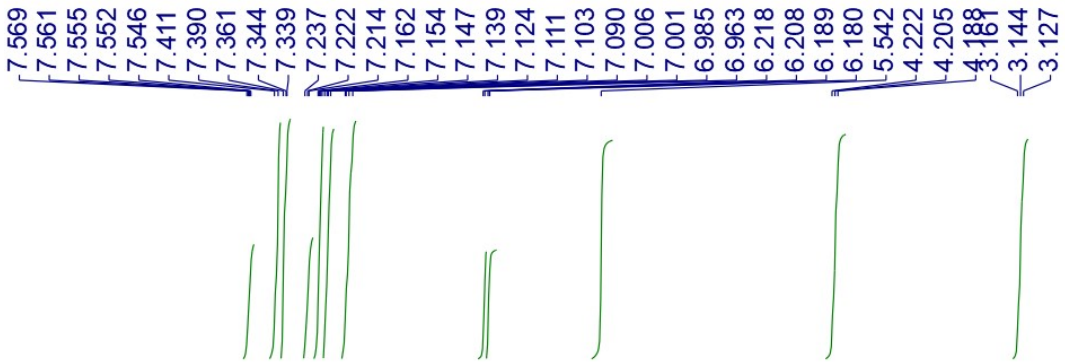
^{1}H NMR of 3ca (400 MHz, $CDCl_3$)

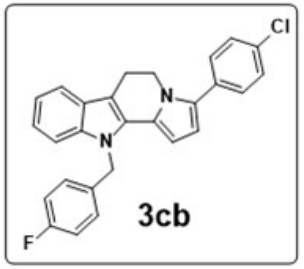


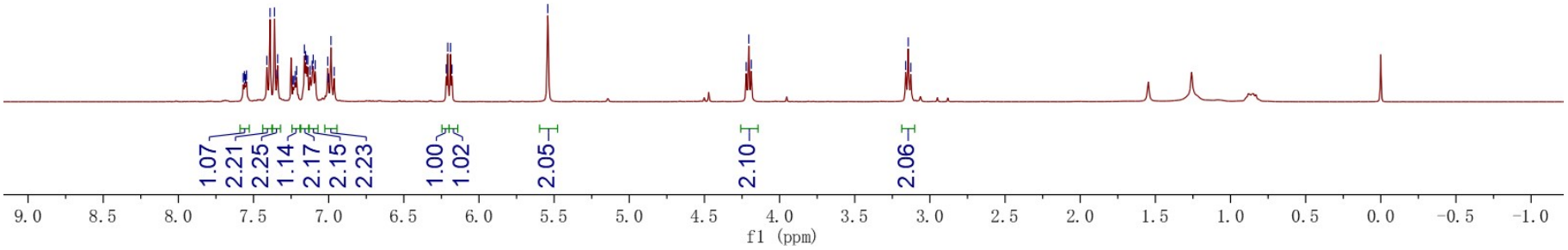
^{13}C NMR of 3ca (100 MHz, $CDCl_3$)



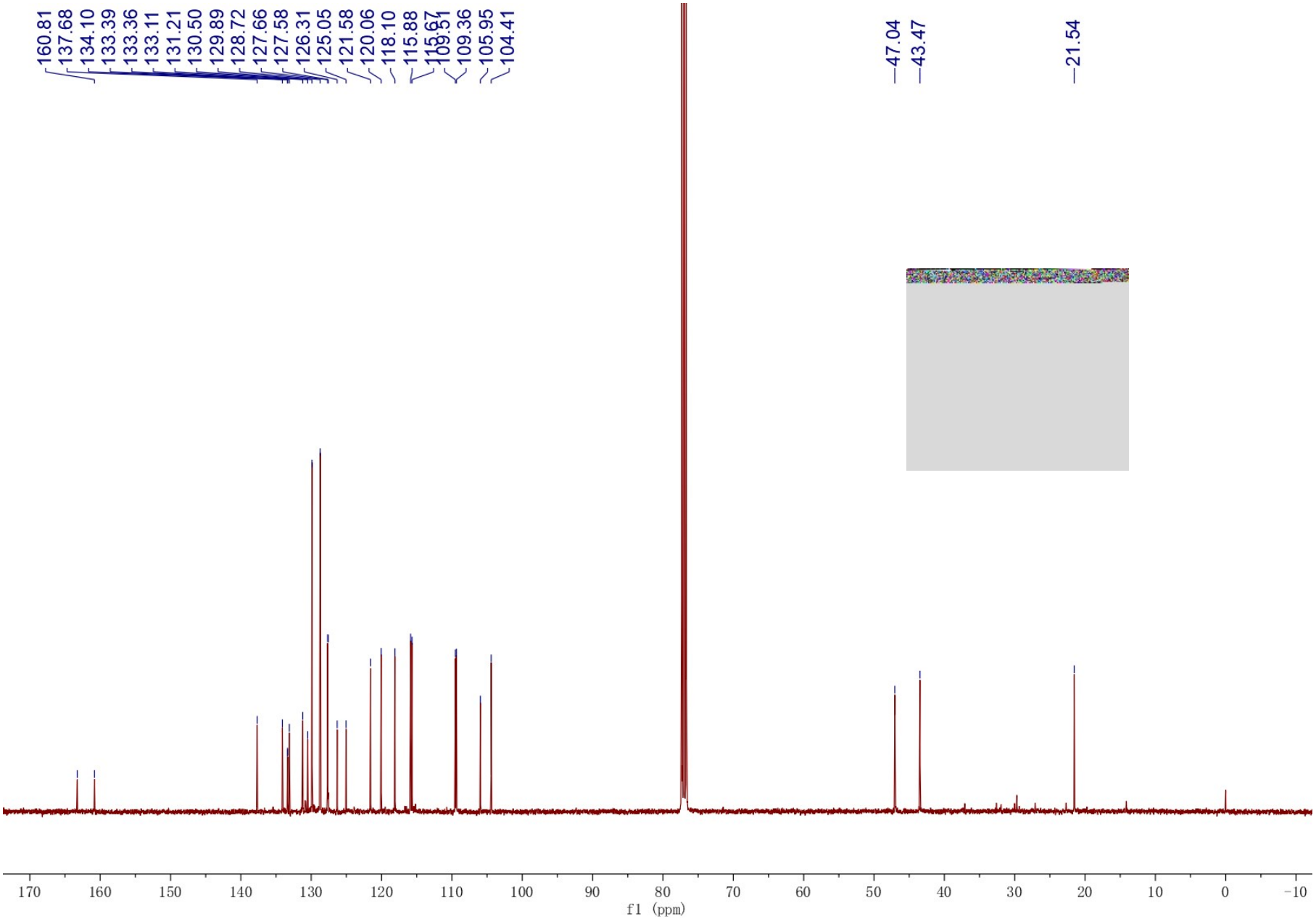
^{1}H NMR of 3cb (400 MHz, $CDCl_3$)



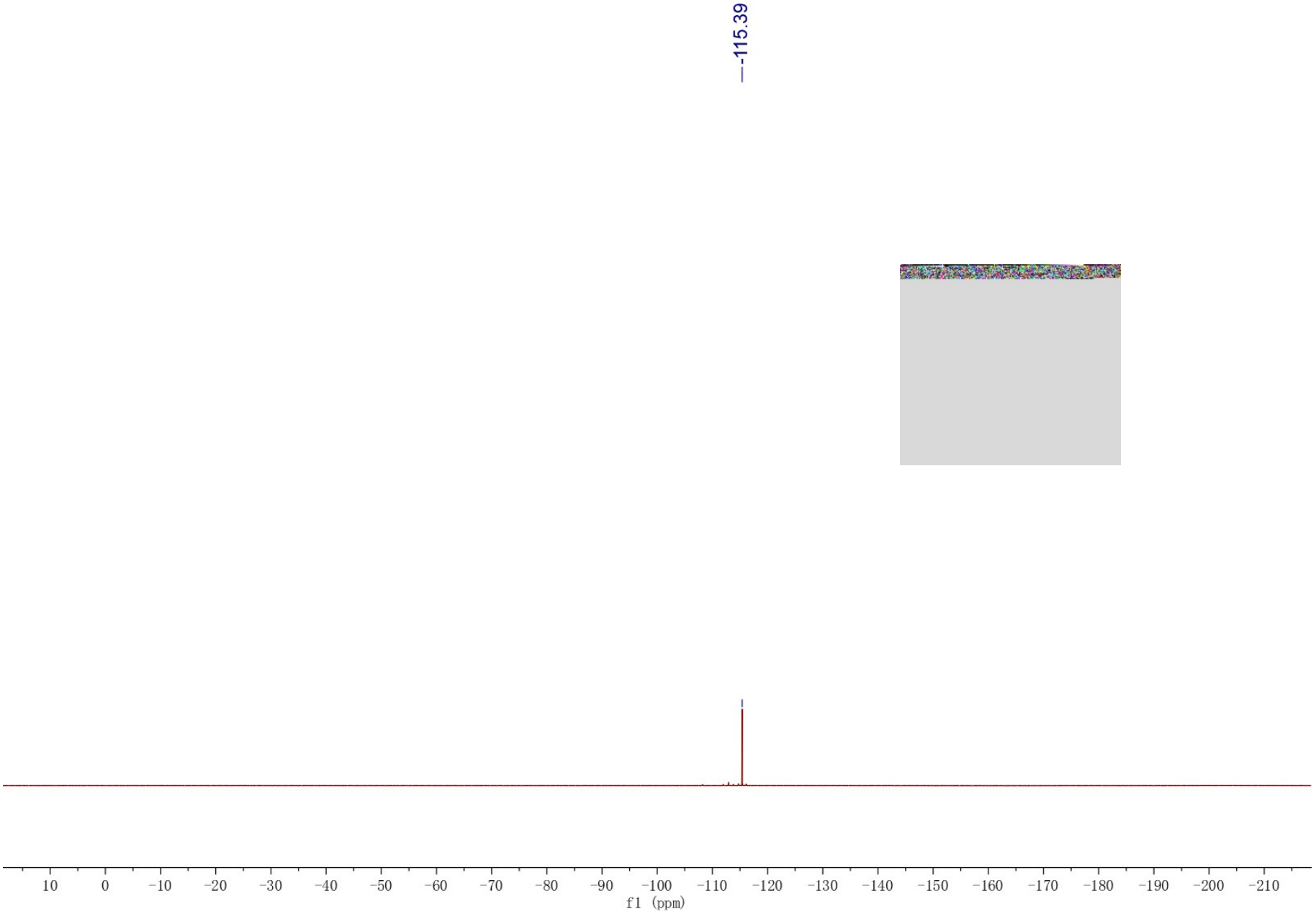




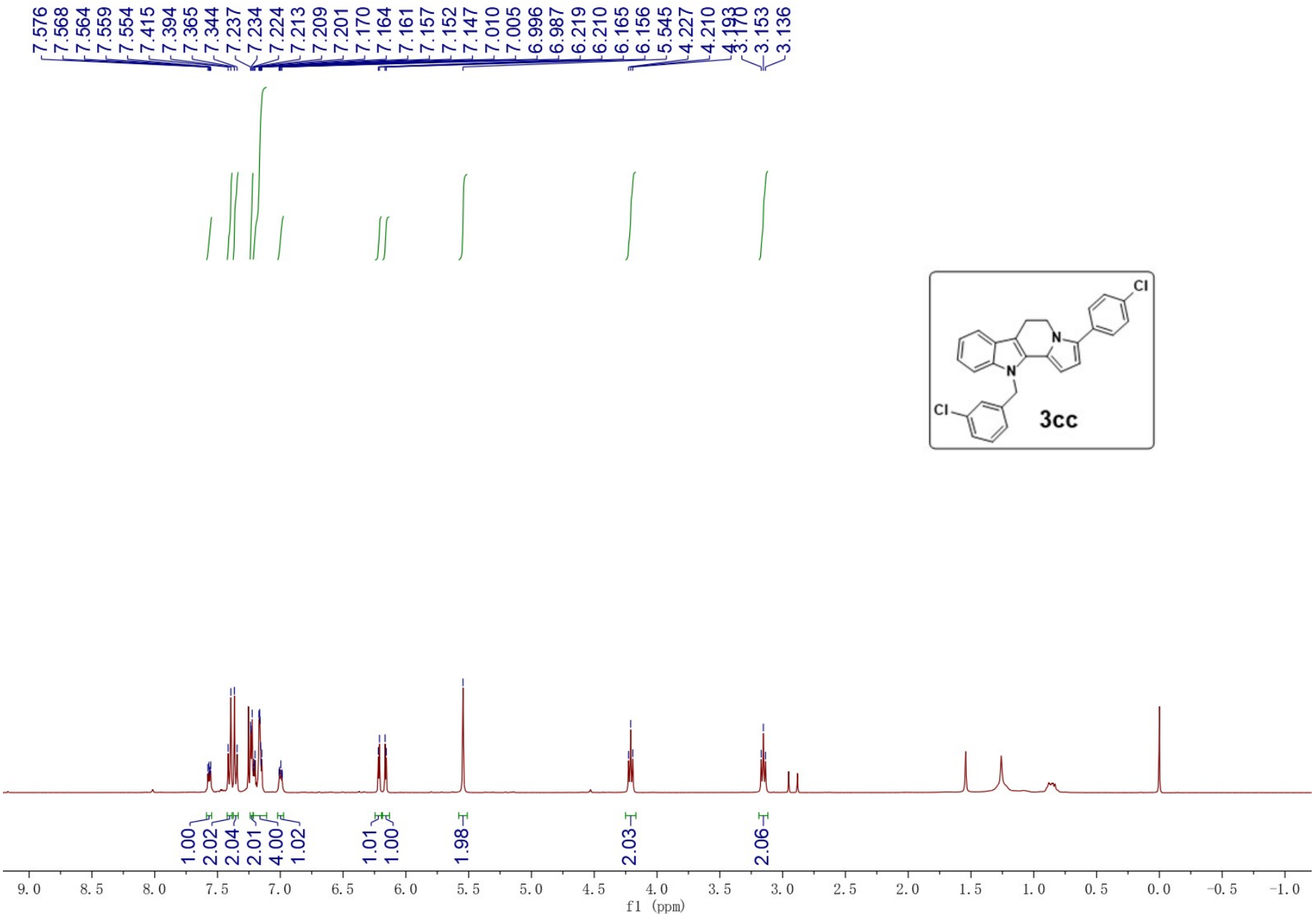
^{13}C NMR of 3cb (100 MHz, $CDCl_3$)



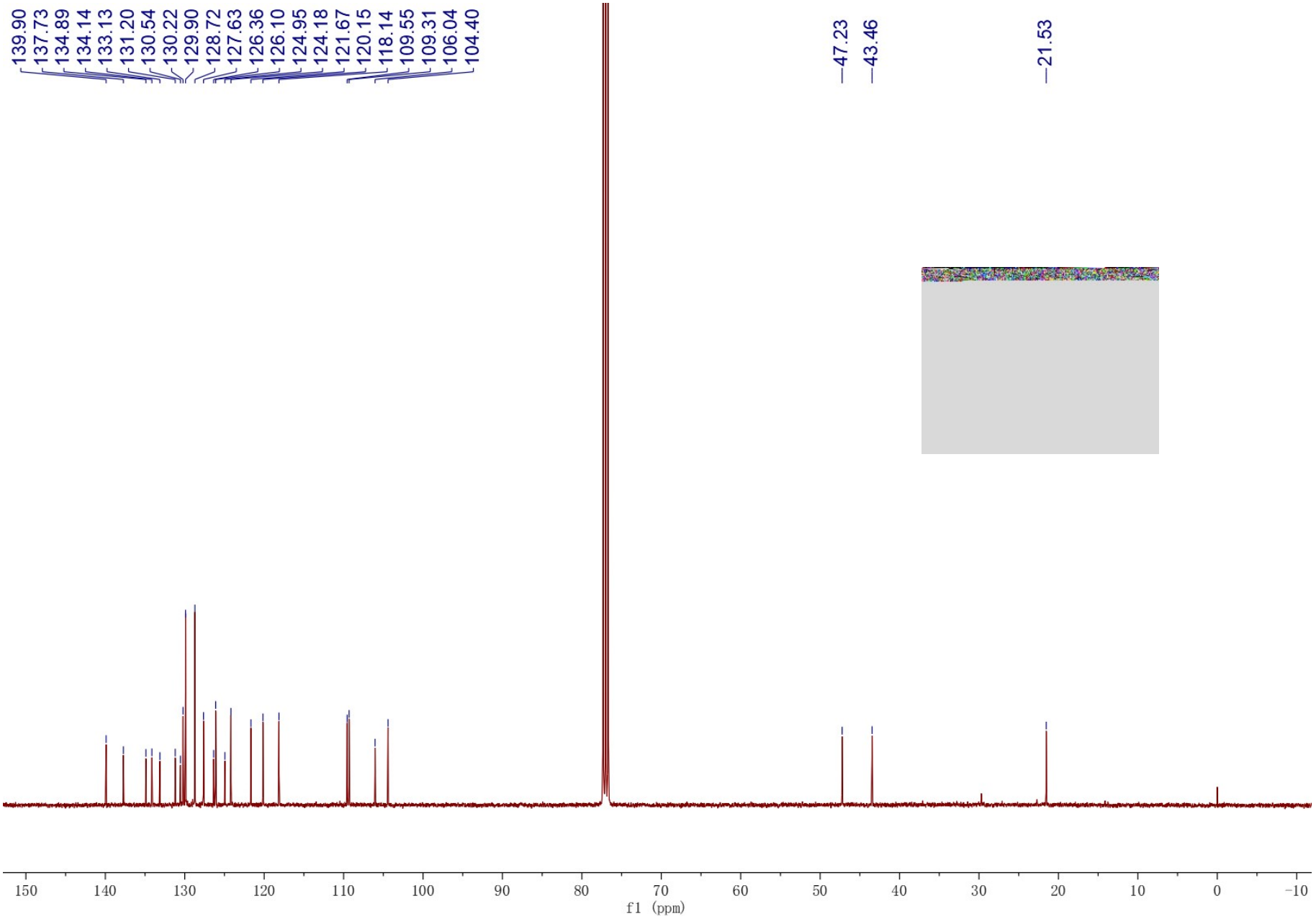
^{19}F NMR of 3cb (376 MHz, $CDCl_3$)



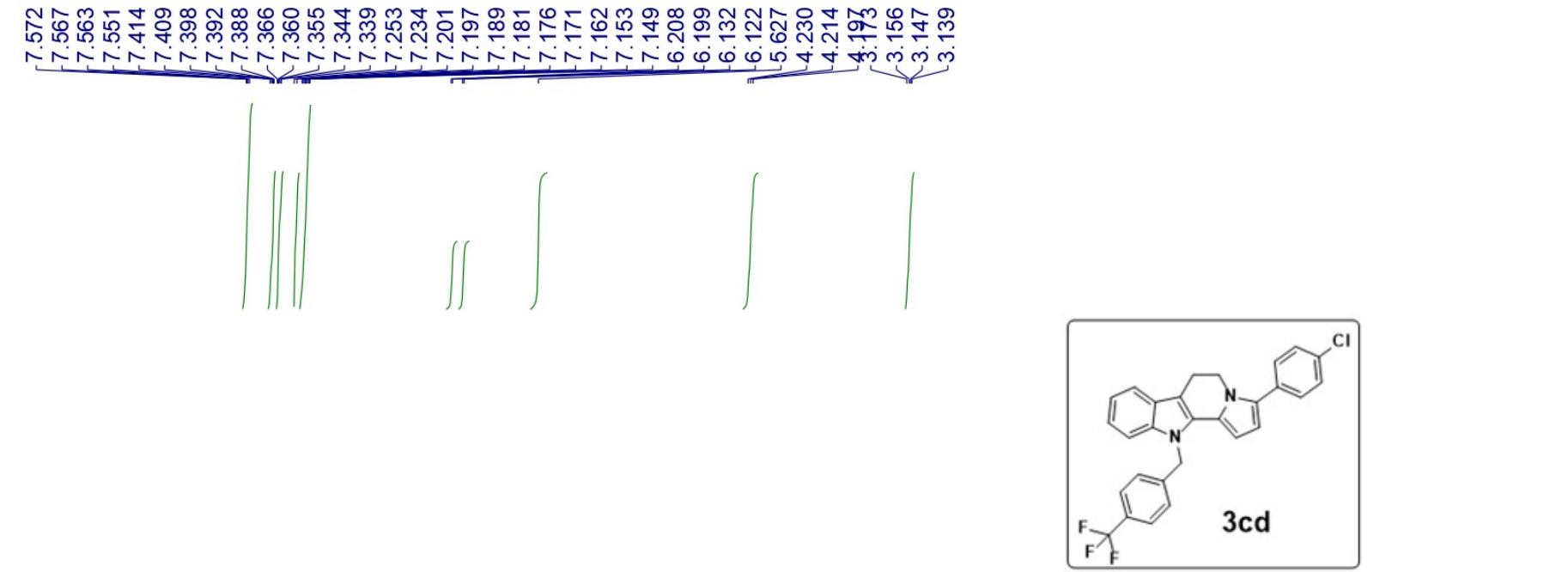
^{1}H NMR of 3cc (400 MHz, $CDCl_3$)



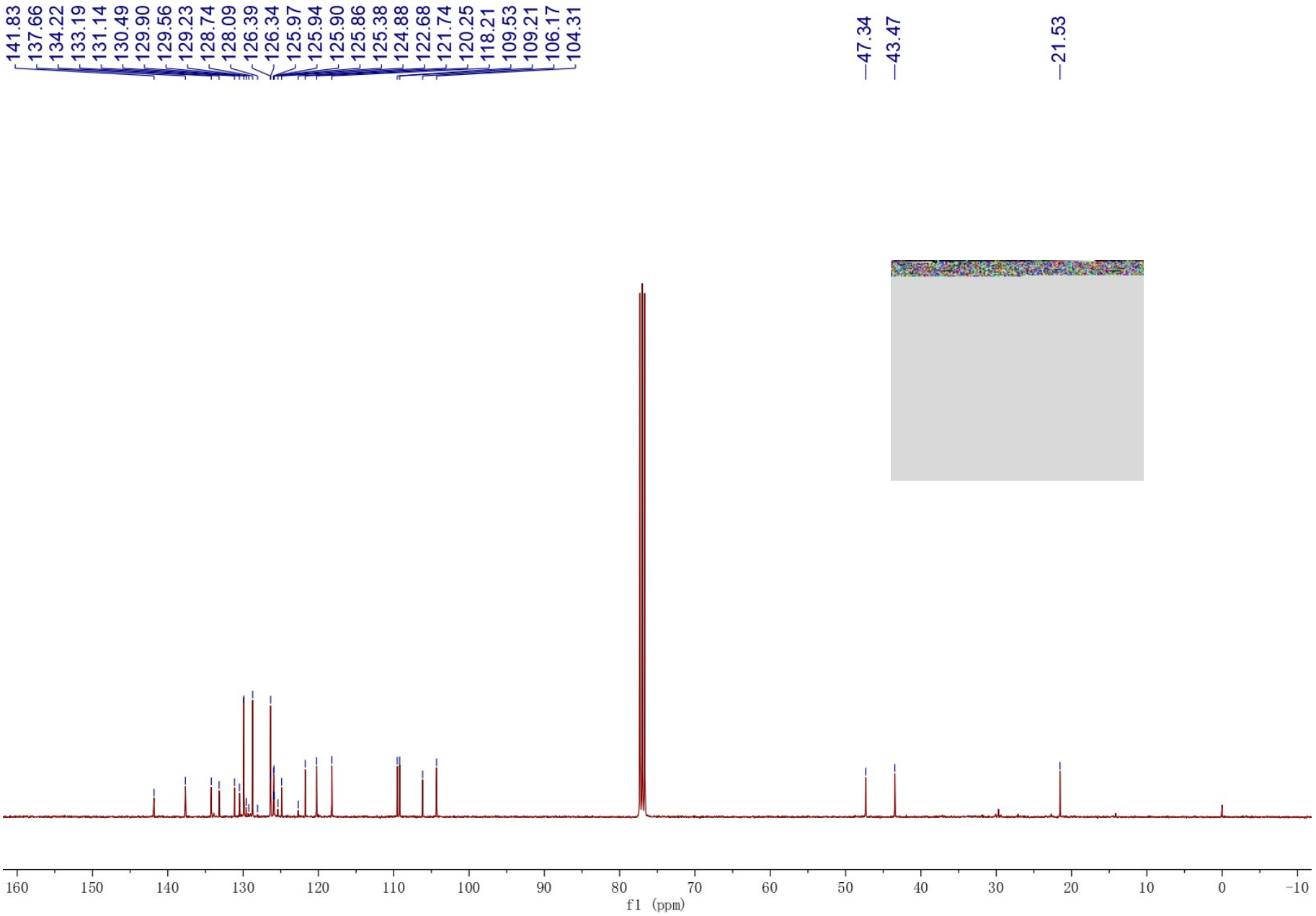
^{13}C NMR of 3cc (100 MHz, $CDCl_3$)



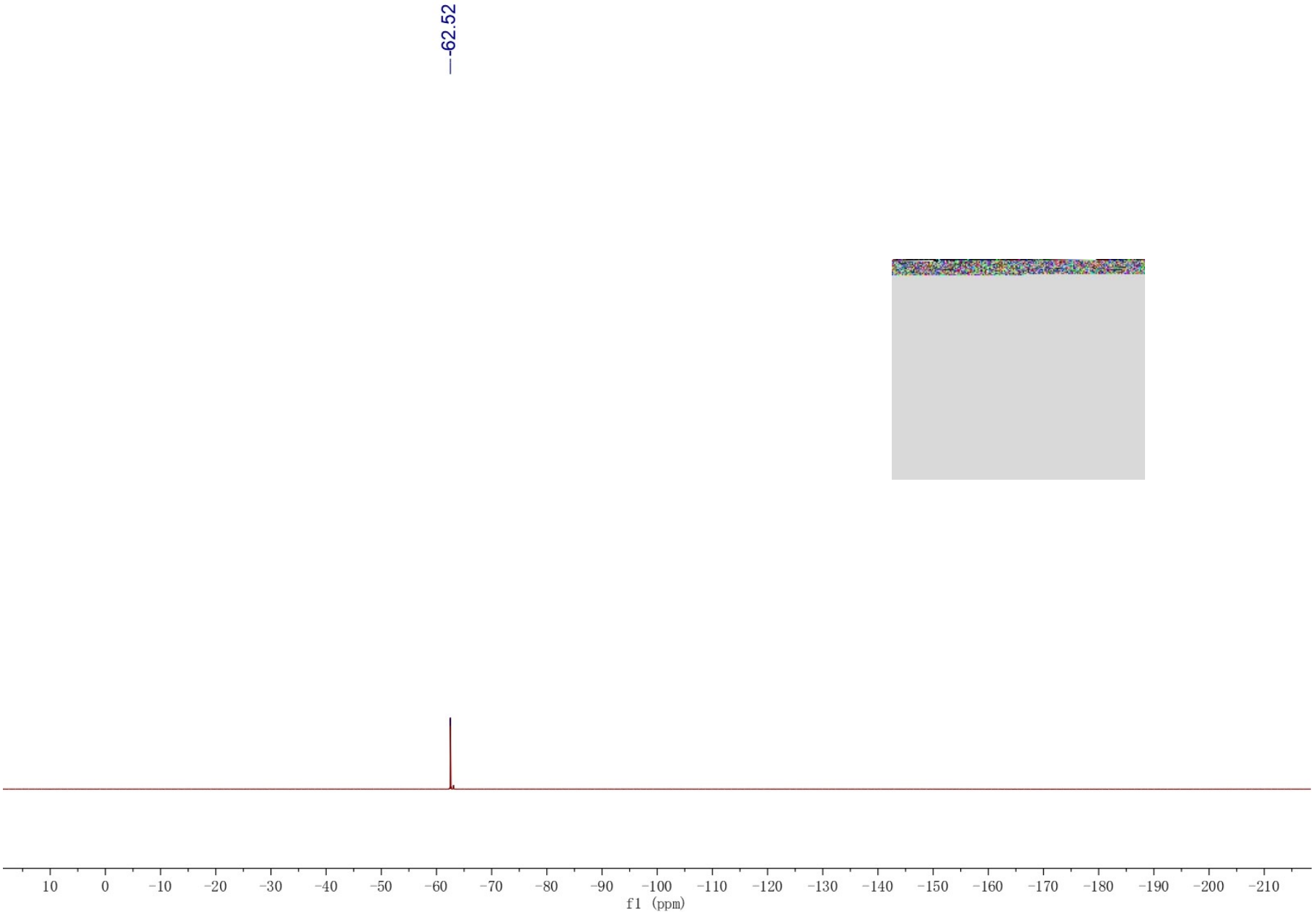
^{1}H NMR of 3cd (400 MHz, $CDCl_3$)



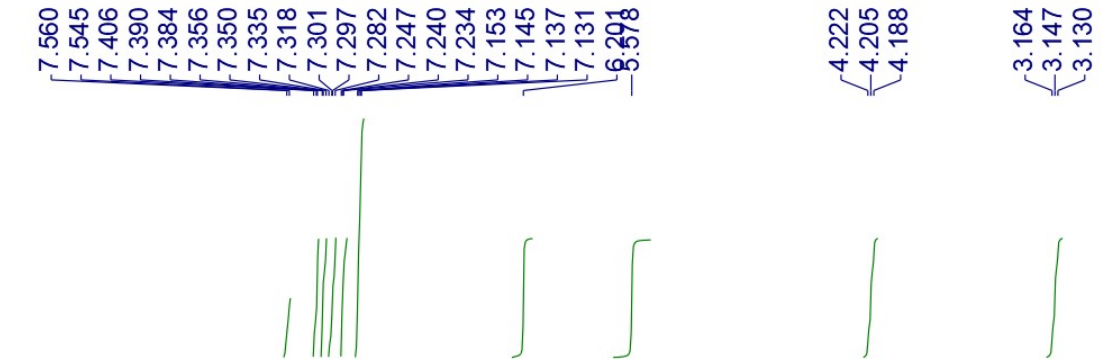
^{13}C NMR of 3cd (100 MHz, $CDCl_3$)

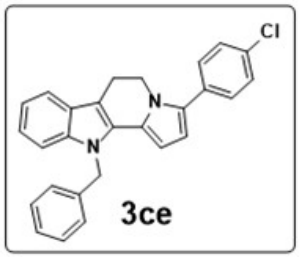


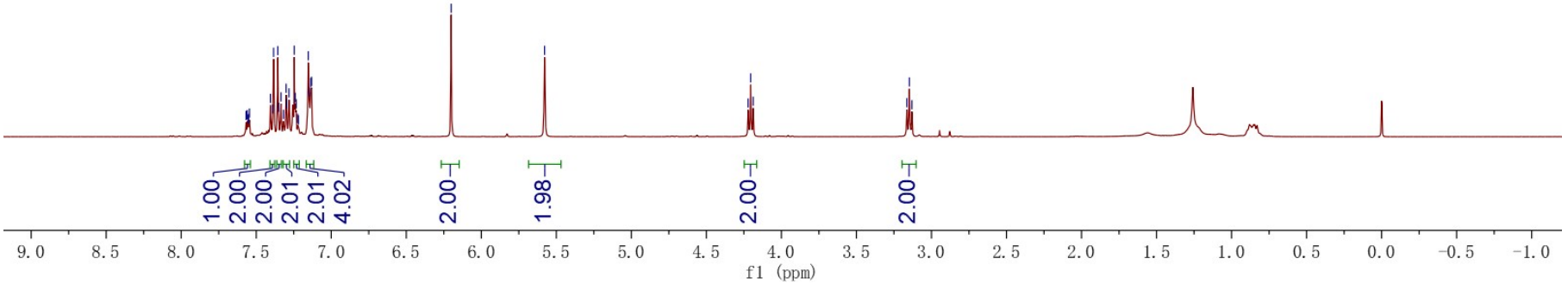
^{19}F NMR of 3cd (376 MHz, $CDCl_3$)



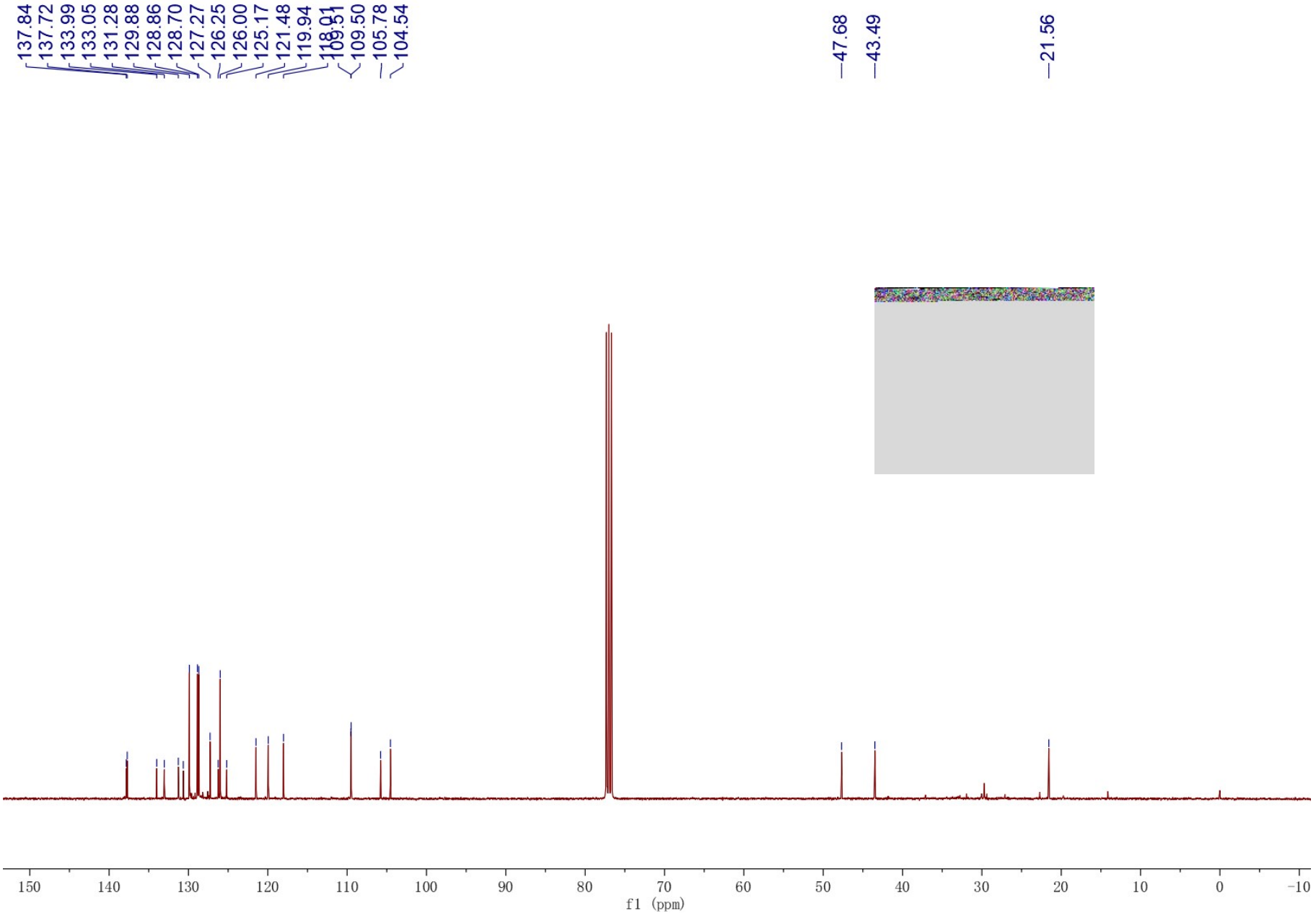
^{1}H NMR of 3ce (400 MHz, $CDCl_3$)



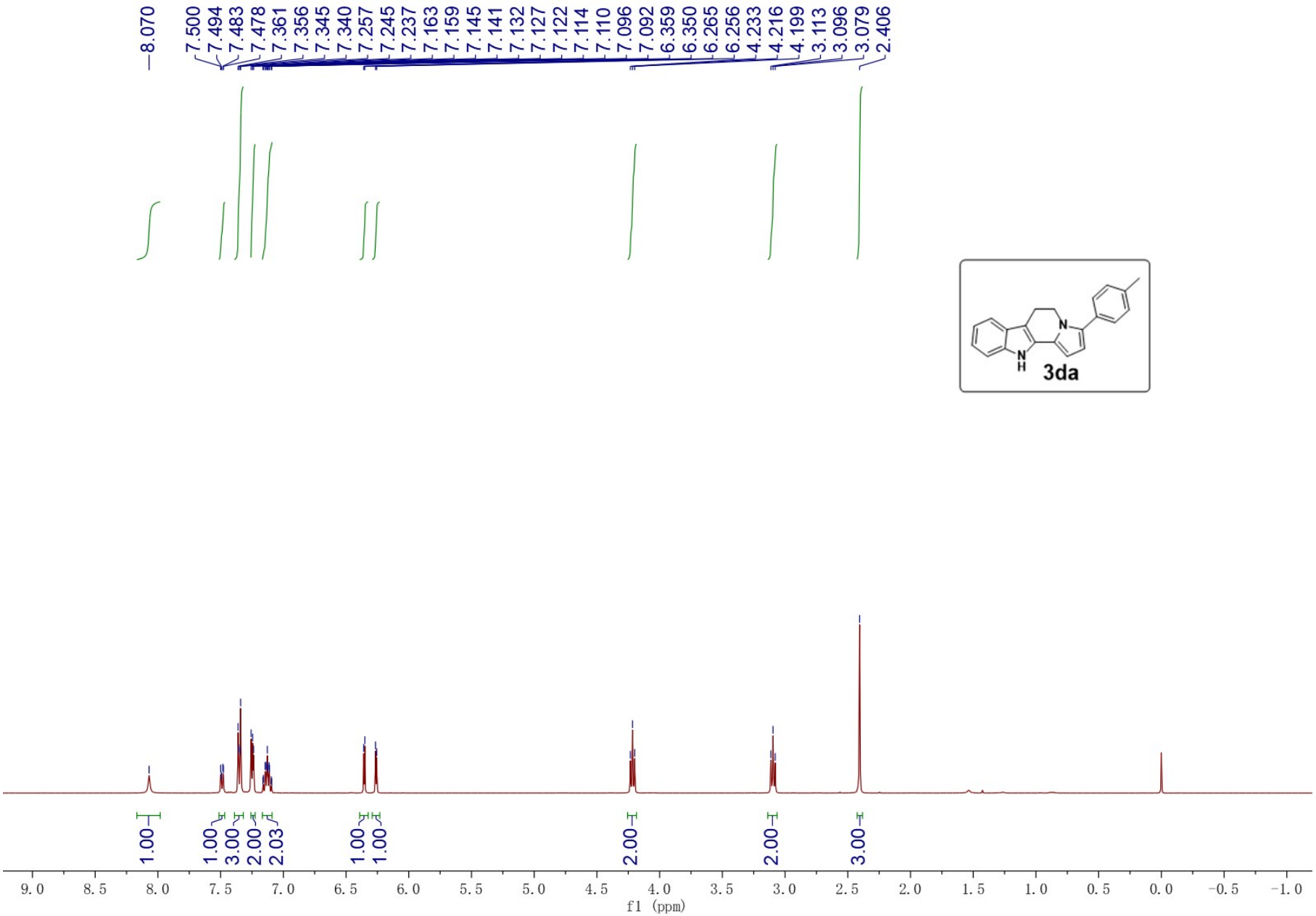




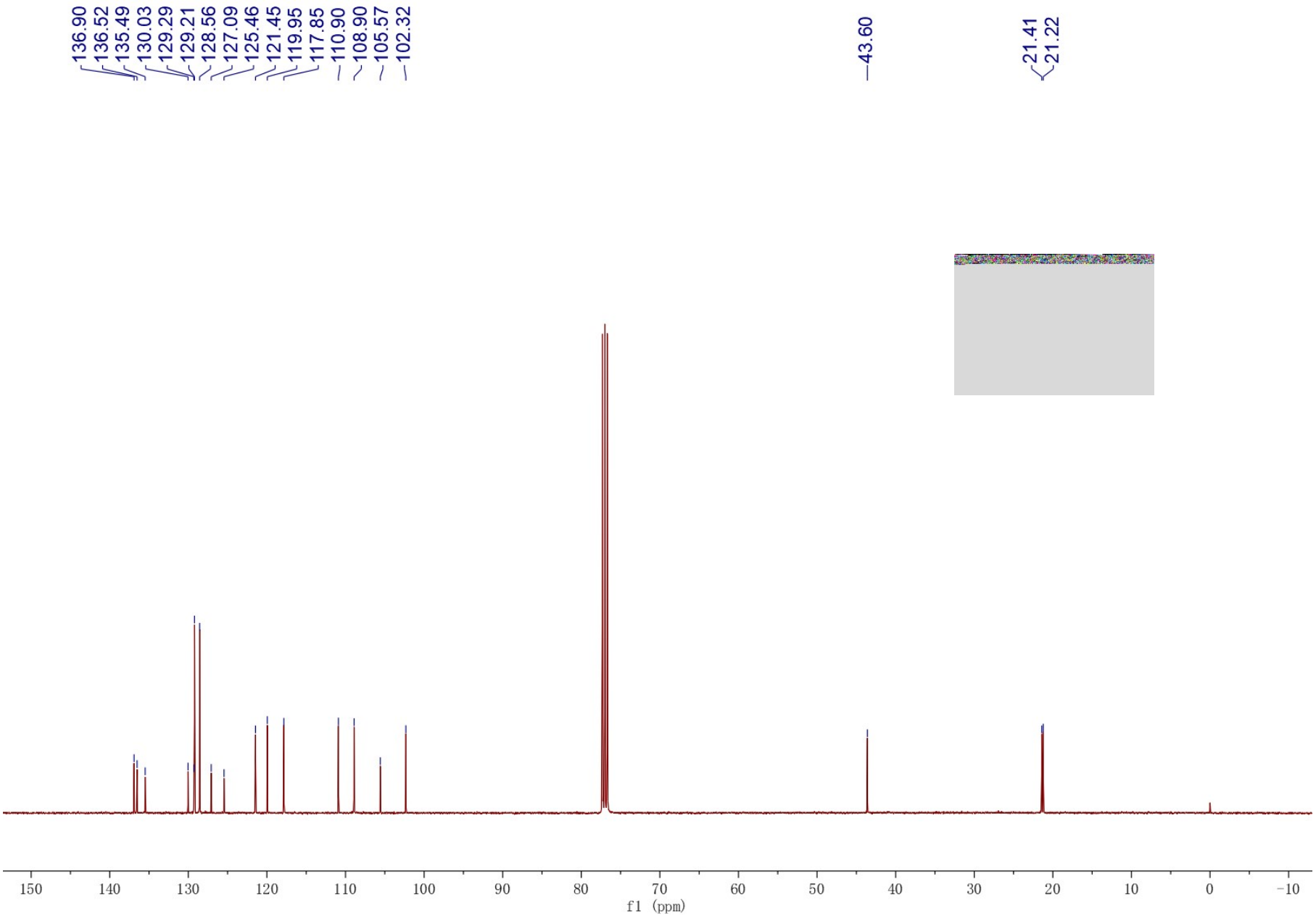
^{13}C NMR of 3ce (100 MHz, $CDCl_3$)



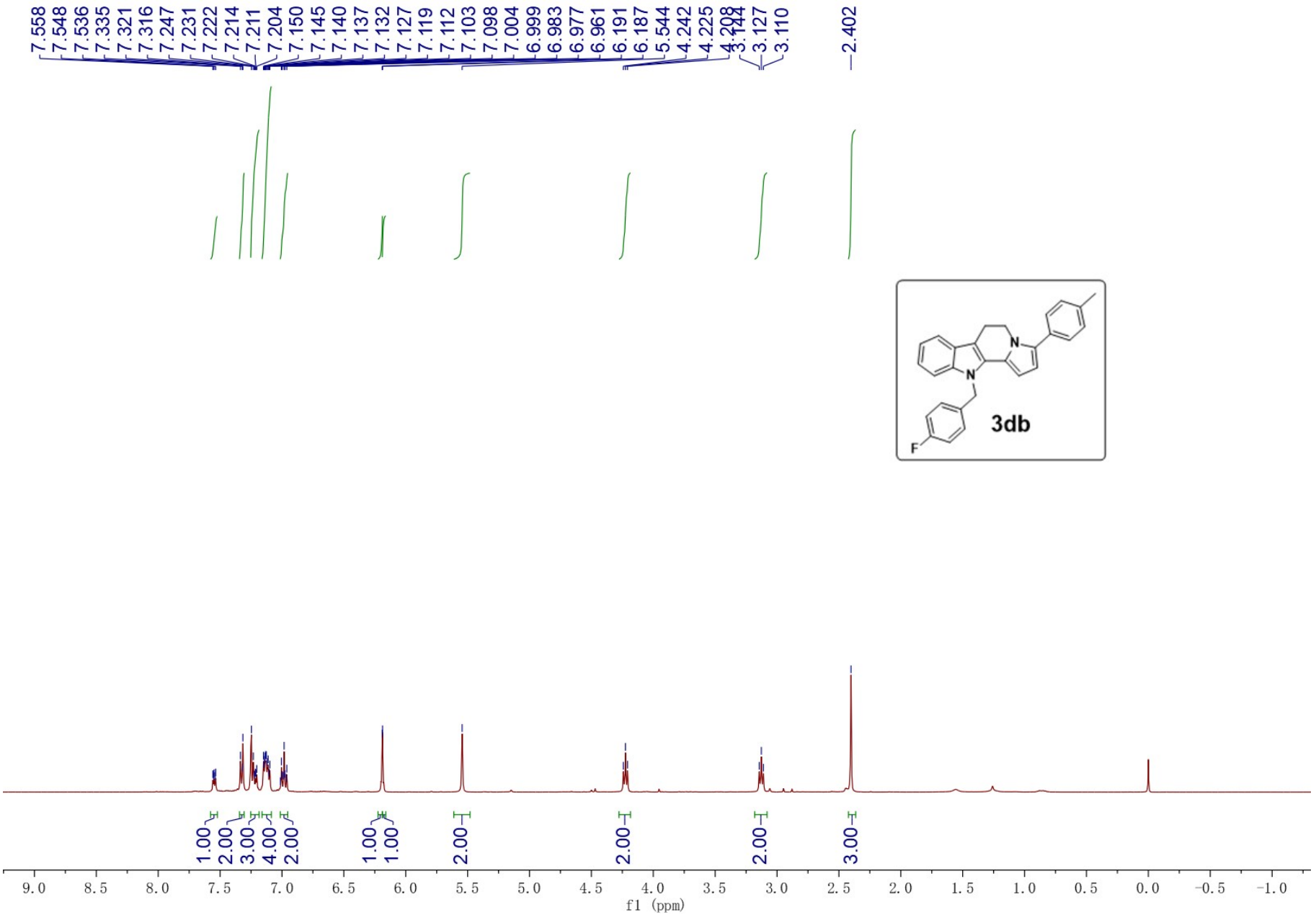
^{1}H NMR of 3da (400 MHz, $CDCl_3$)



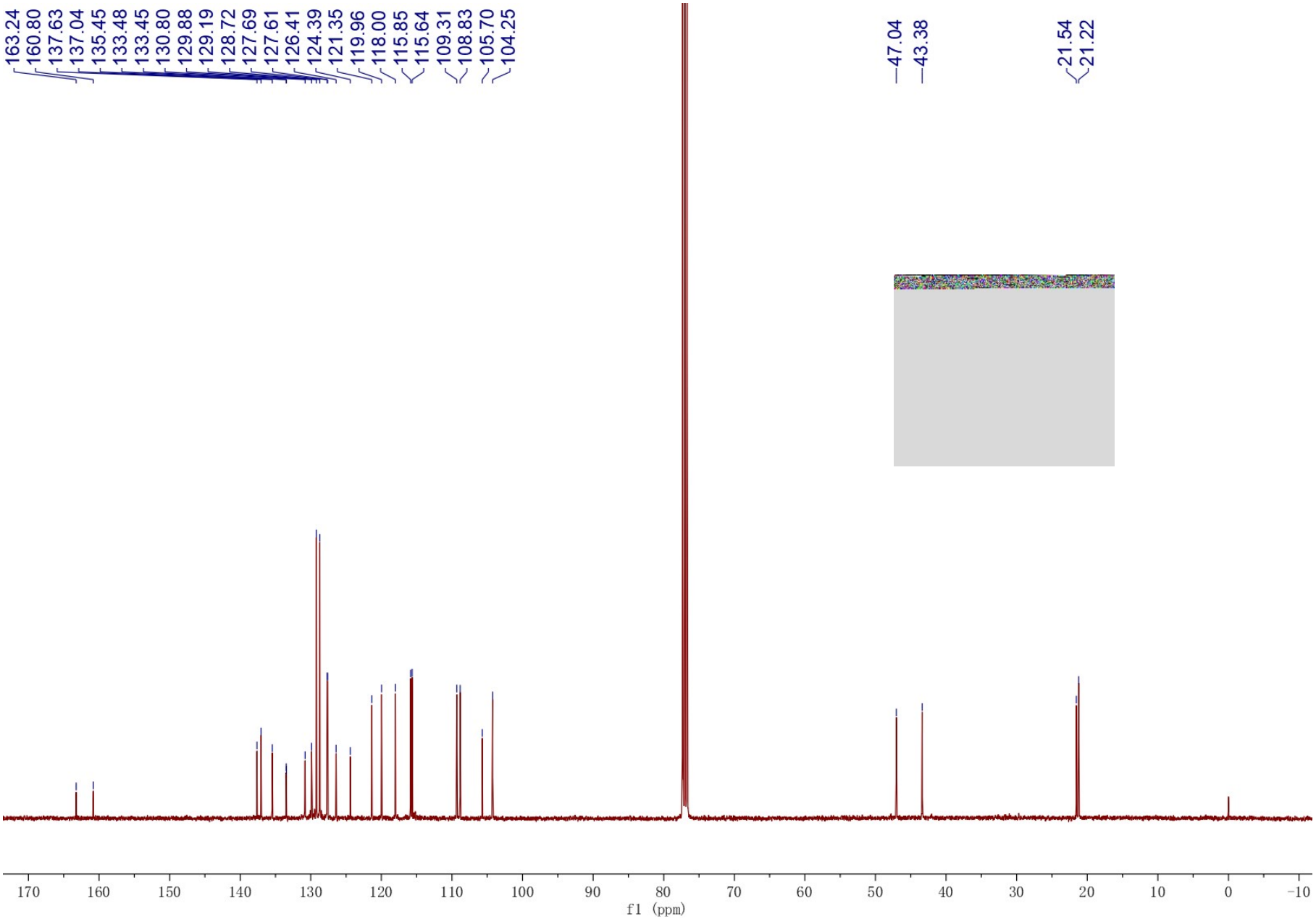
^{13}C NMR of 3da (100 MHz, $CDCl_3$)



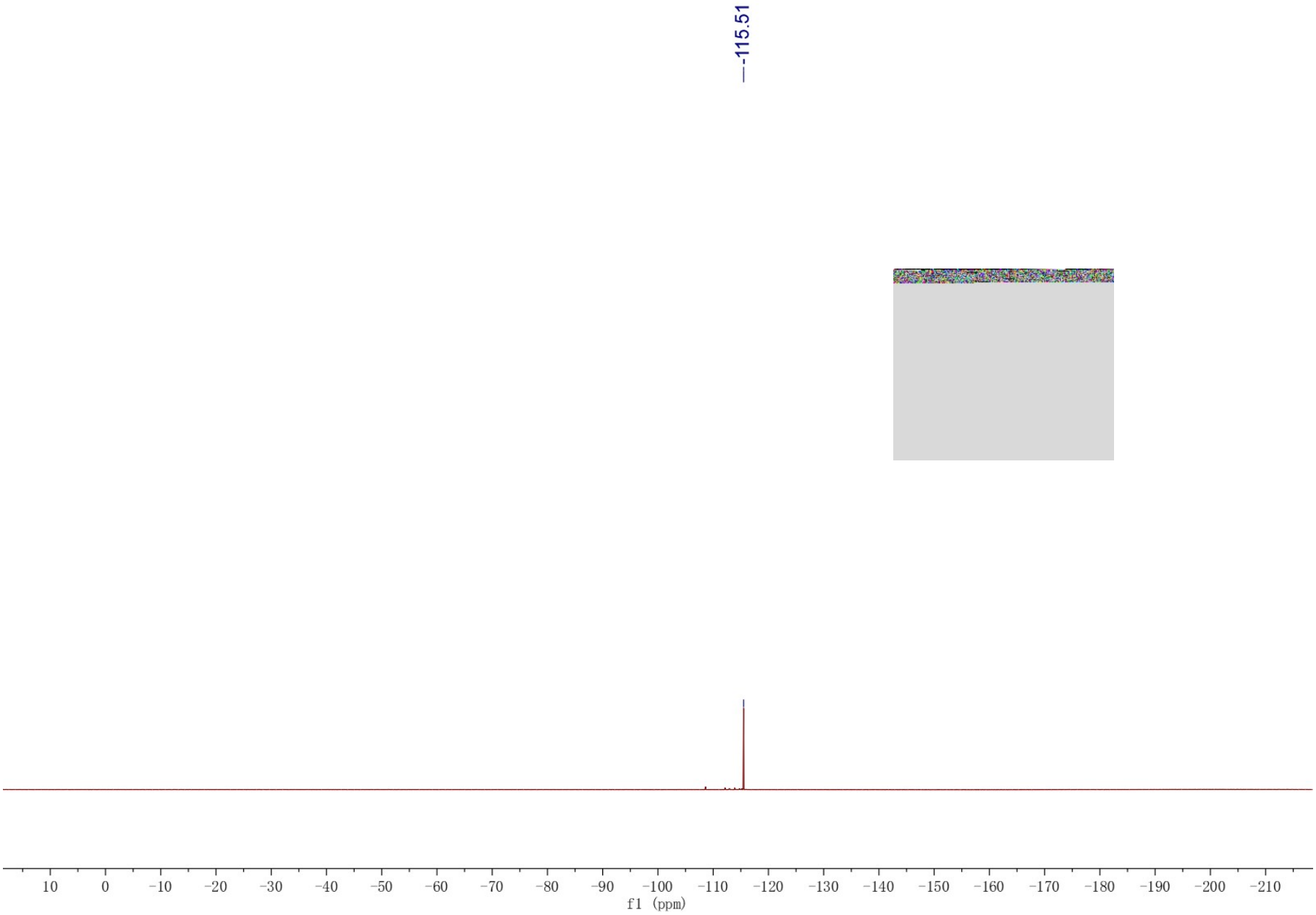
^{1}H NMR of 3db (400 MHz, $CDCl_3$)



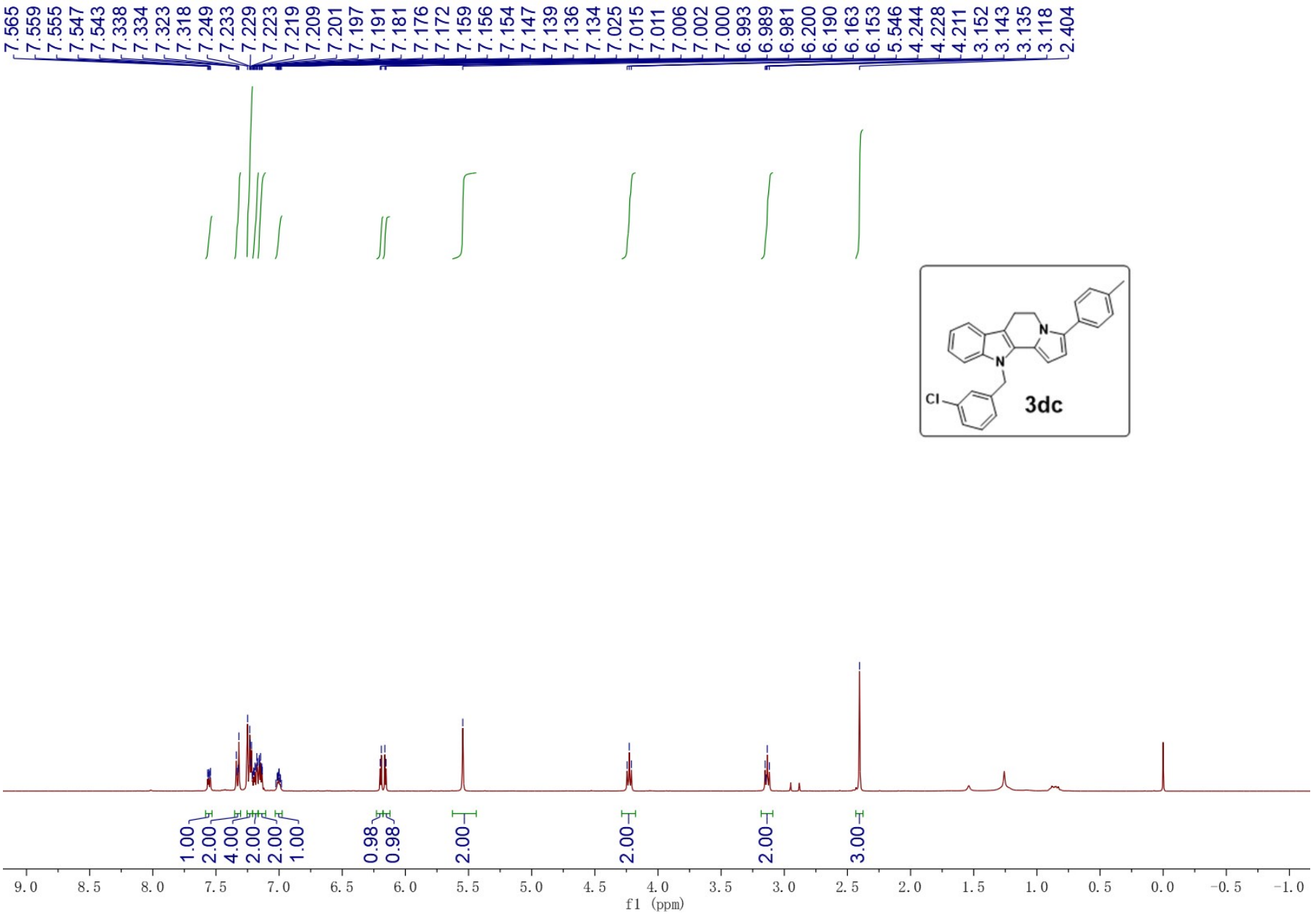
^{13}C NMR of 3db (100 MHz, $CDCl_3$)



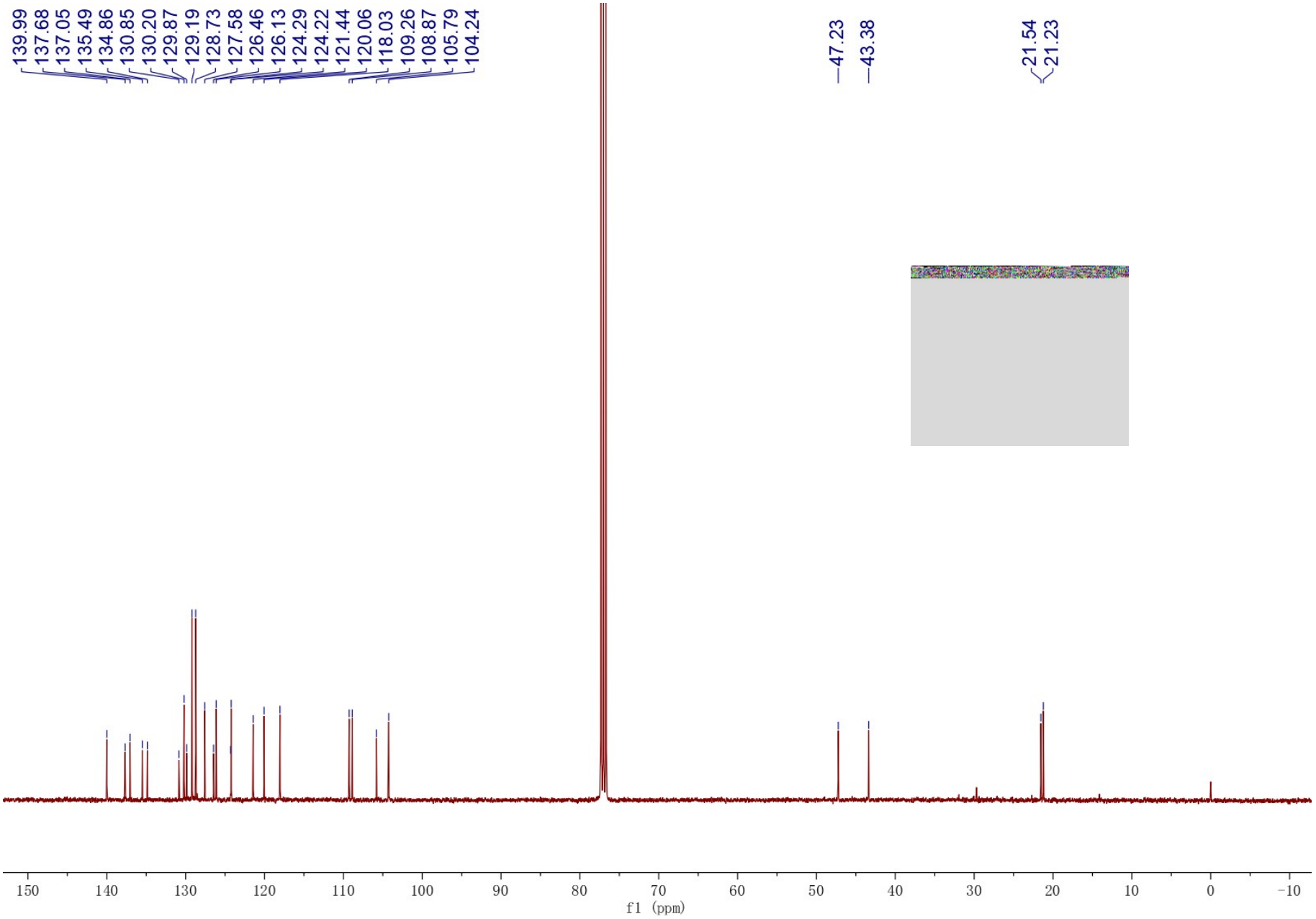
^{19}F NMR of 3db (376 MHz, $CDCl_3$)



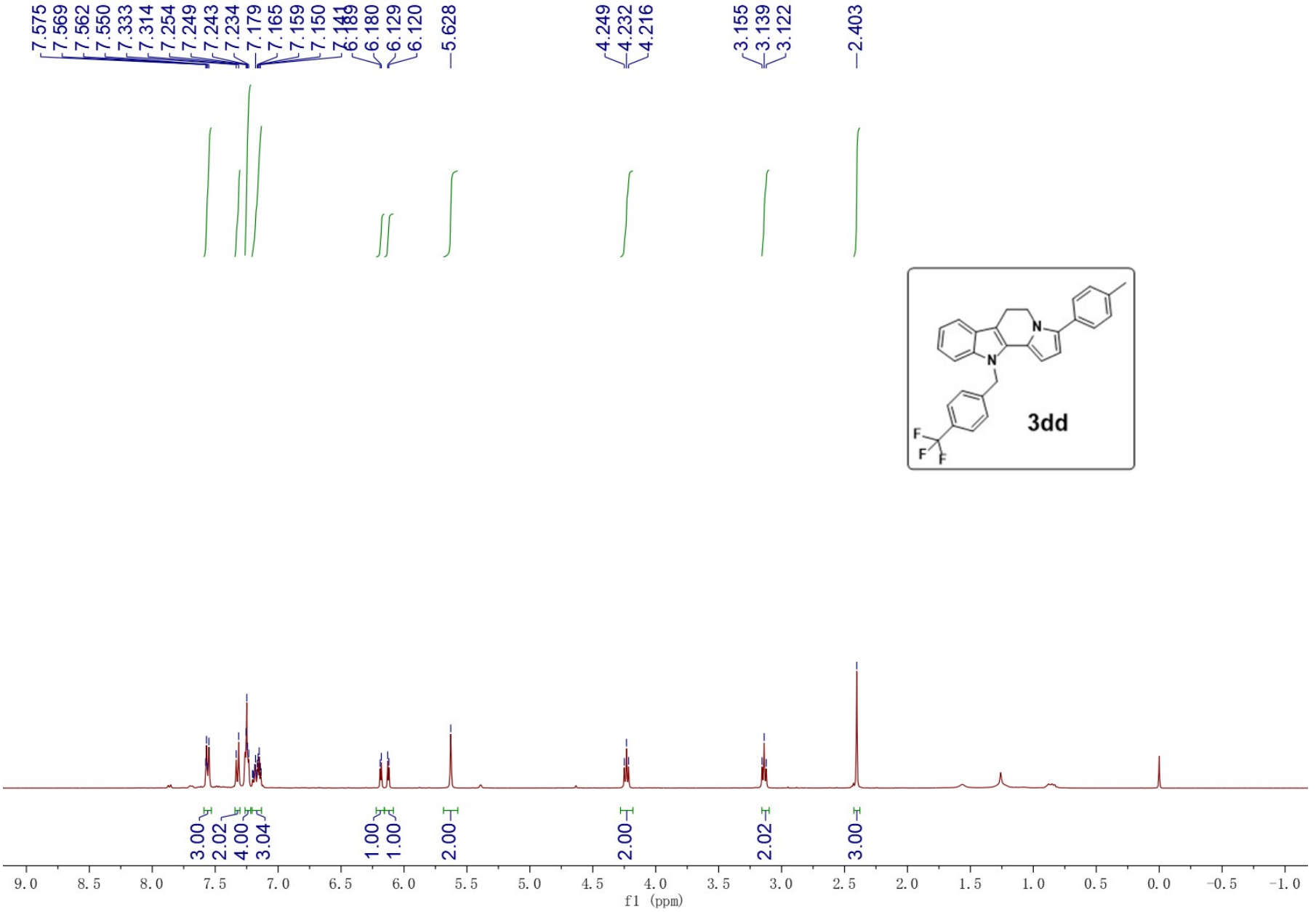
^{1}H NMR of 3dc (400 MHz, $CDCl_3$)



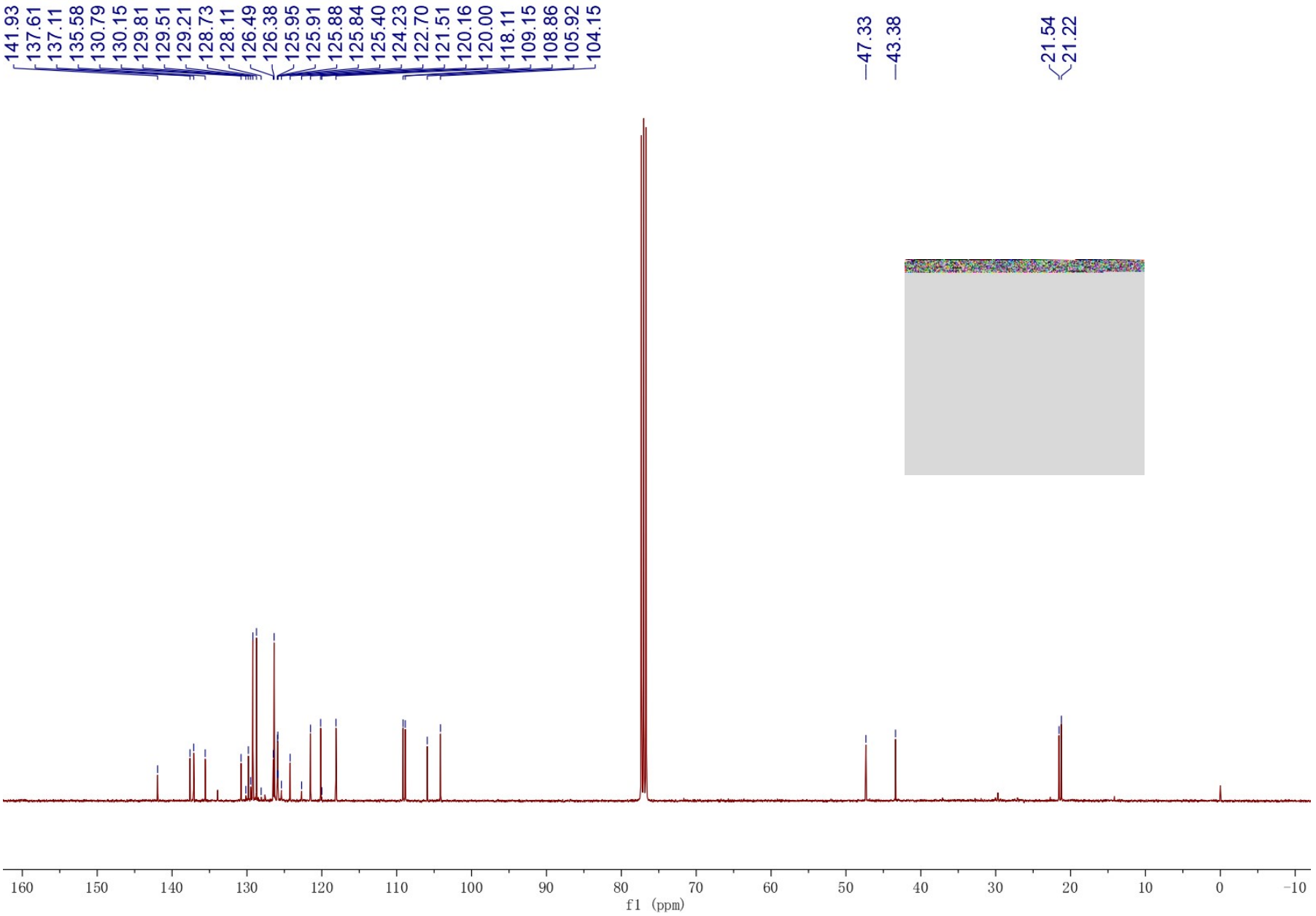
^{13}C NMR of 3dc (100 MHz, $CDCl_3$)



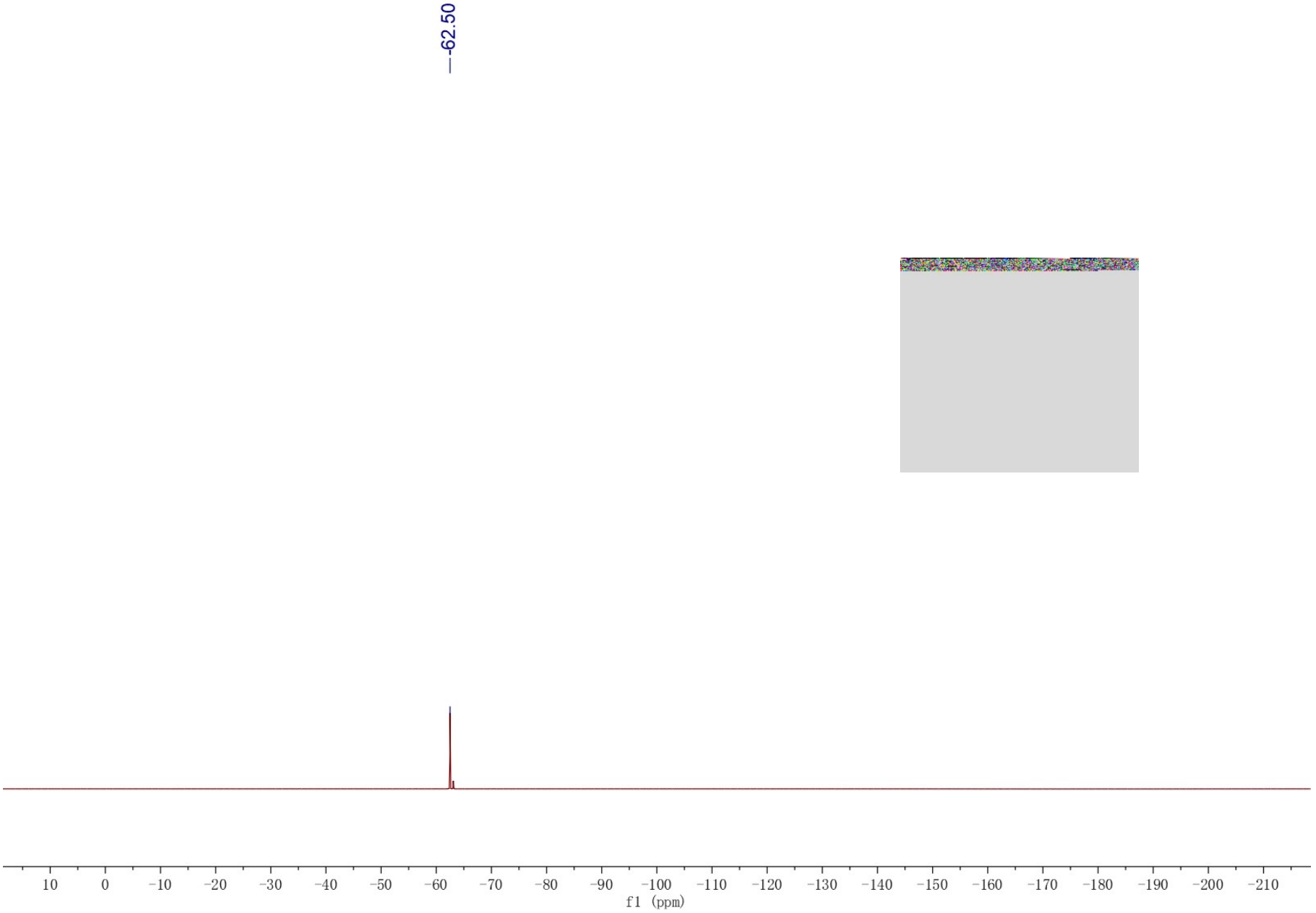
^{1}H NMR of 3dd (400 MHz, $CDCl_3$)



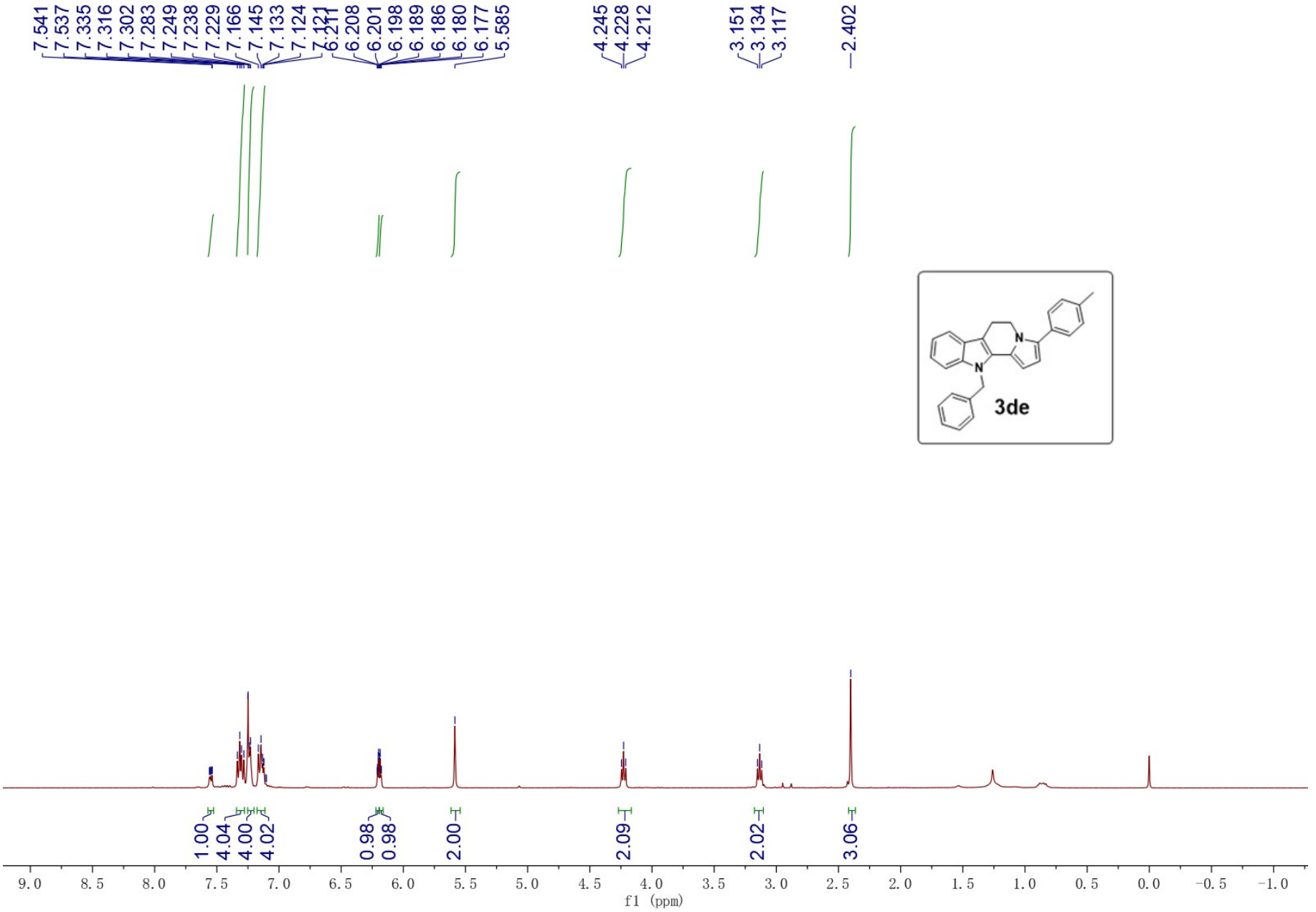
^{13}C NMR of 3dd (100 MHz, $CDCl_3$)



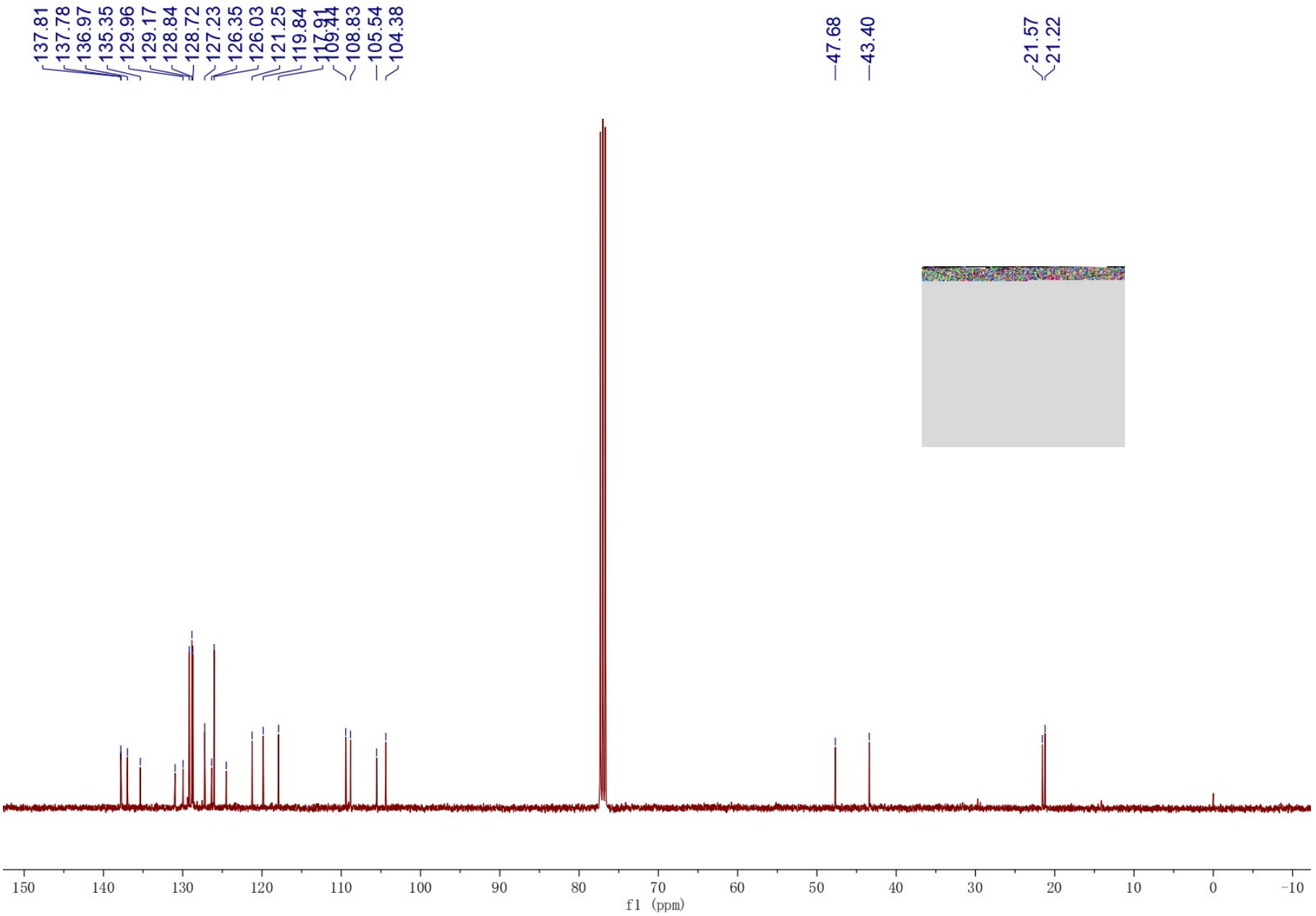
^{19}F NMR of 3dd (376 MHz, $CDCl_3$)



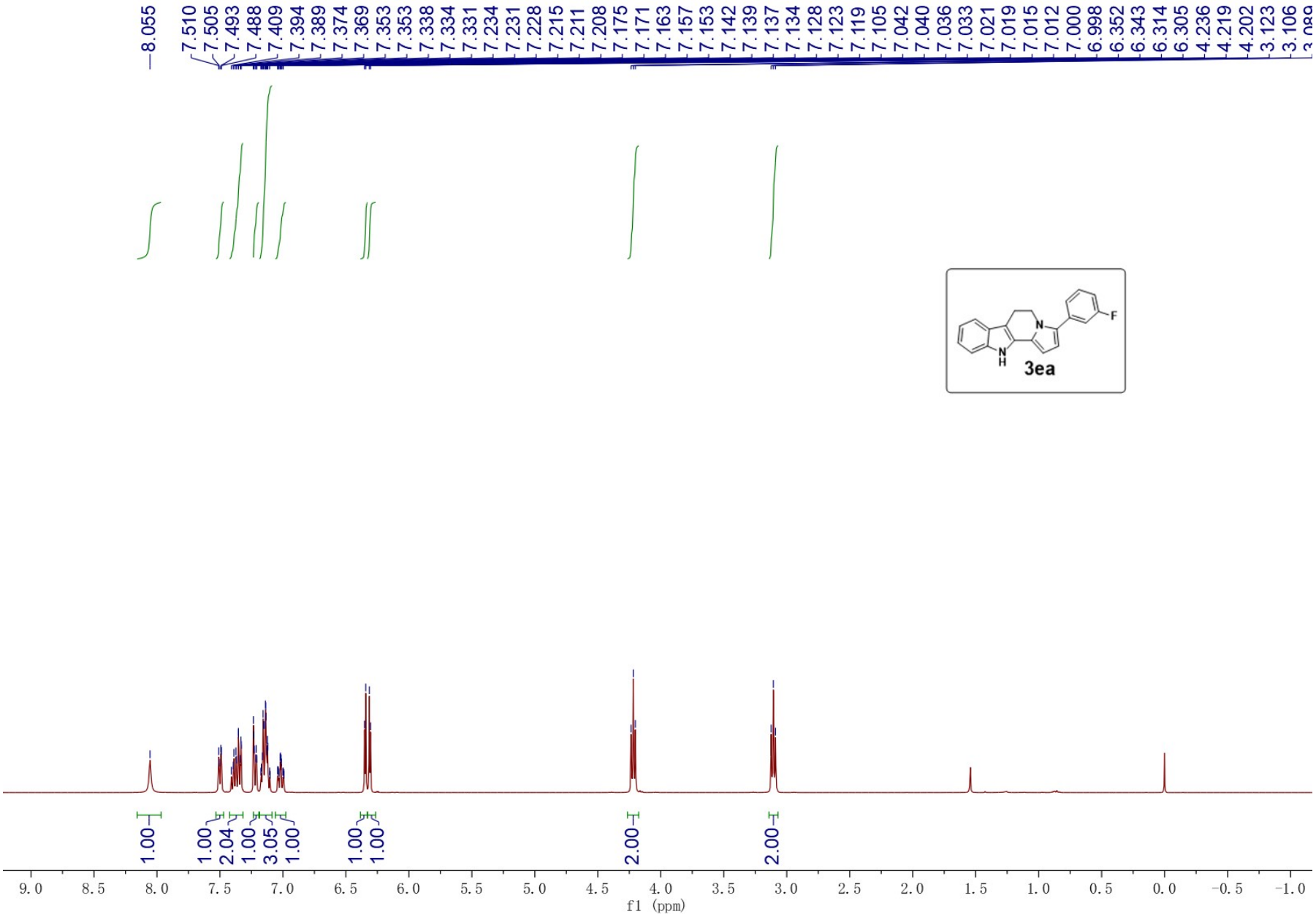
^{1}H NMR of 3de (400 MHz, $CDCl_3$)



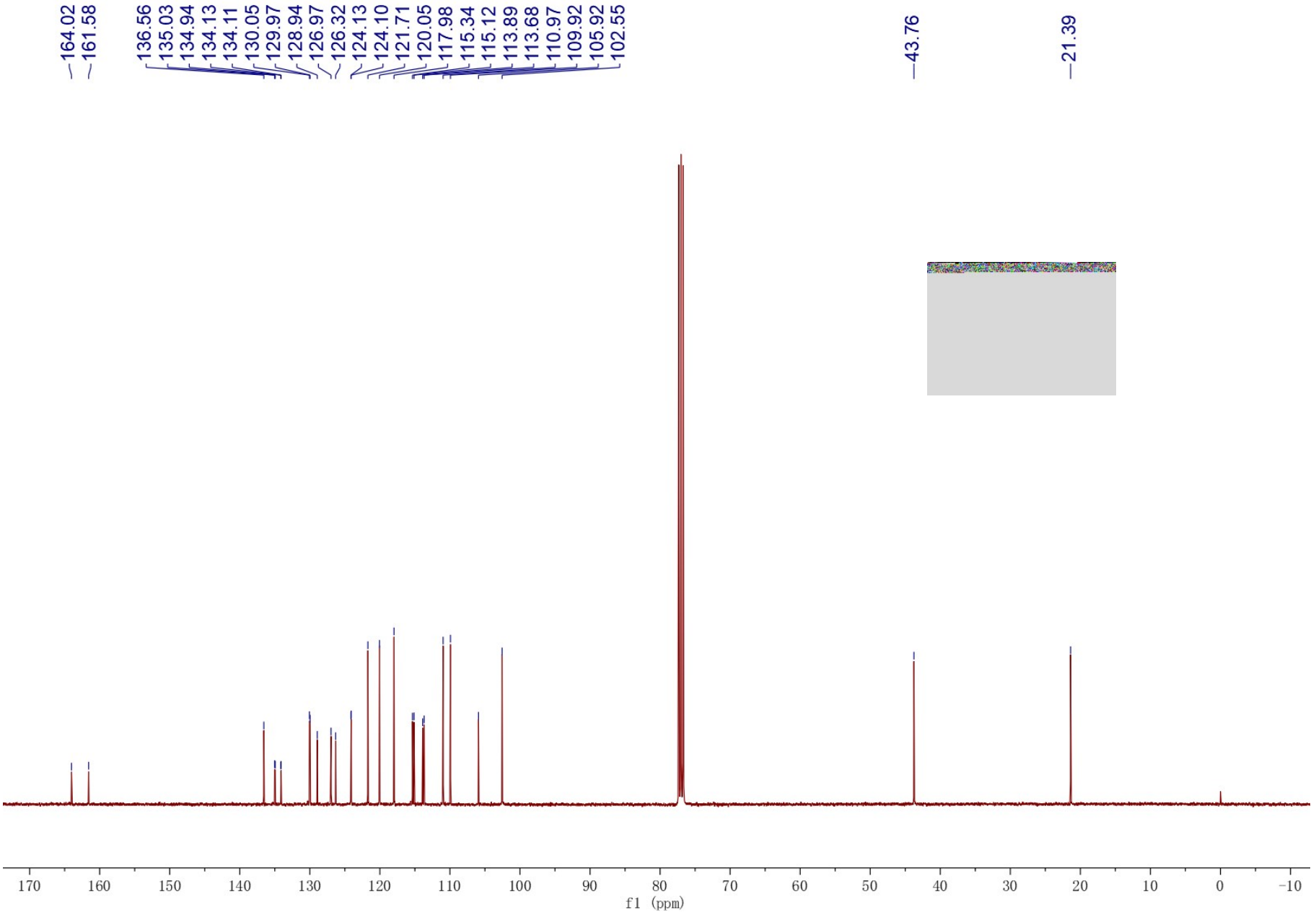
^{13}C NMR of 3de (100 MHz, $CDCl_3$)



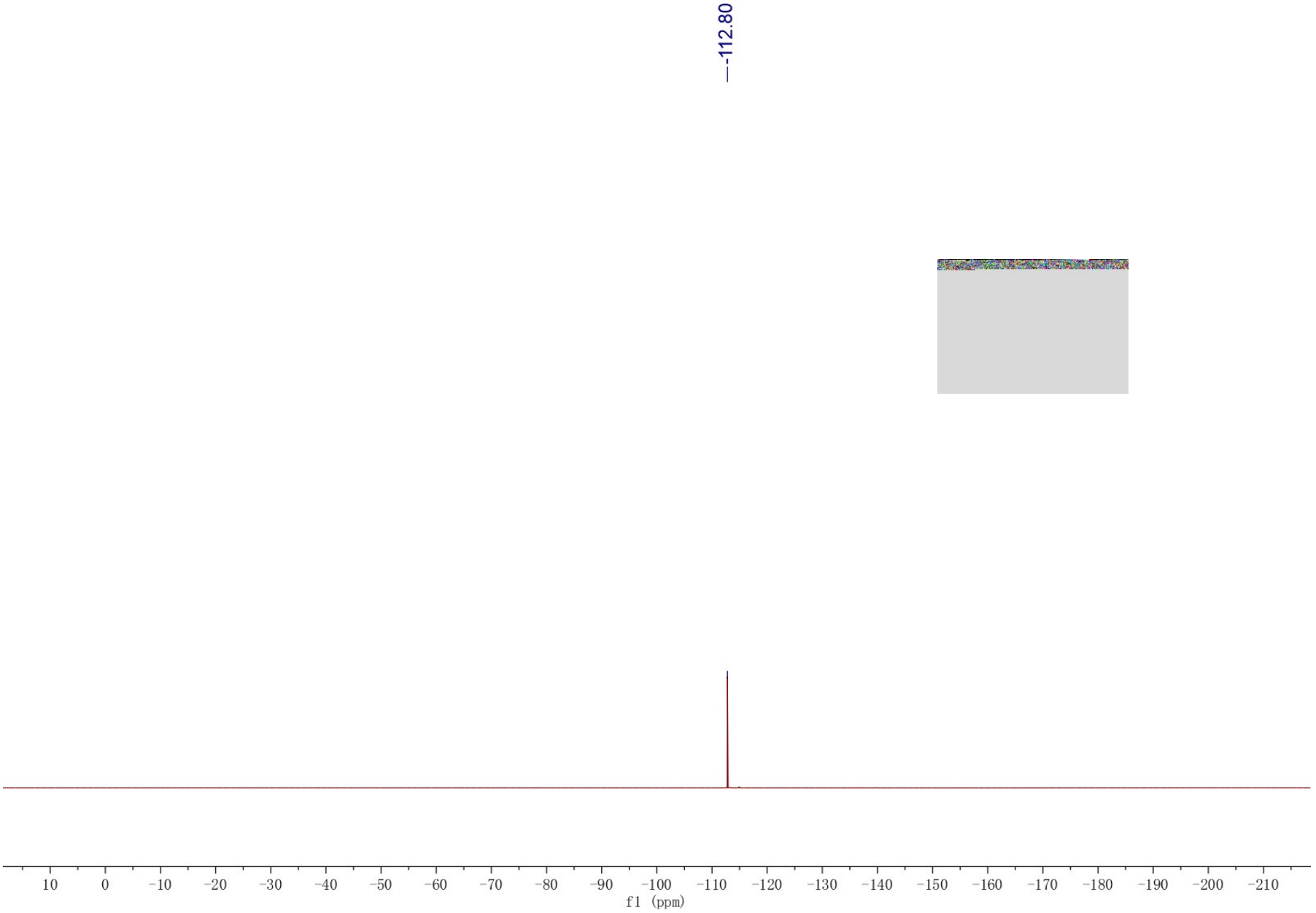
^{1}H NMR of 3ea (400 MHz, $CDCl_3$)



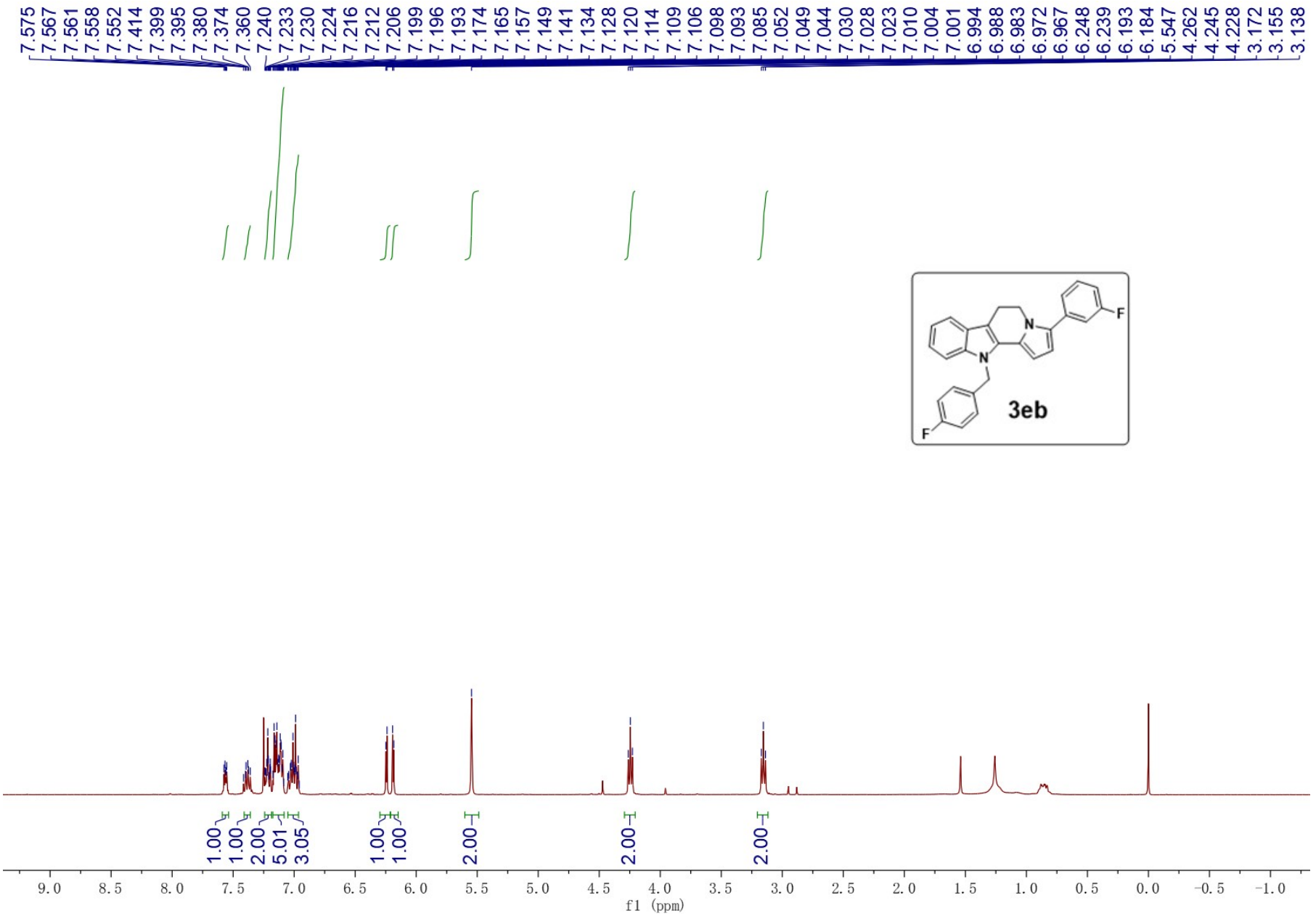
^{13}C NMR of 3ea (100 MHz, $CDCl_3$)



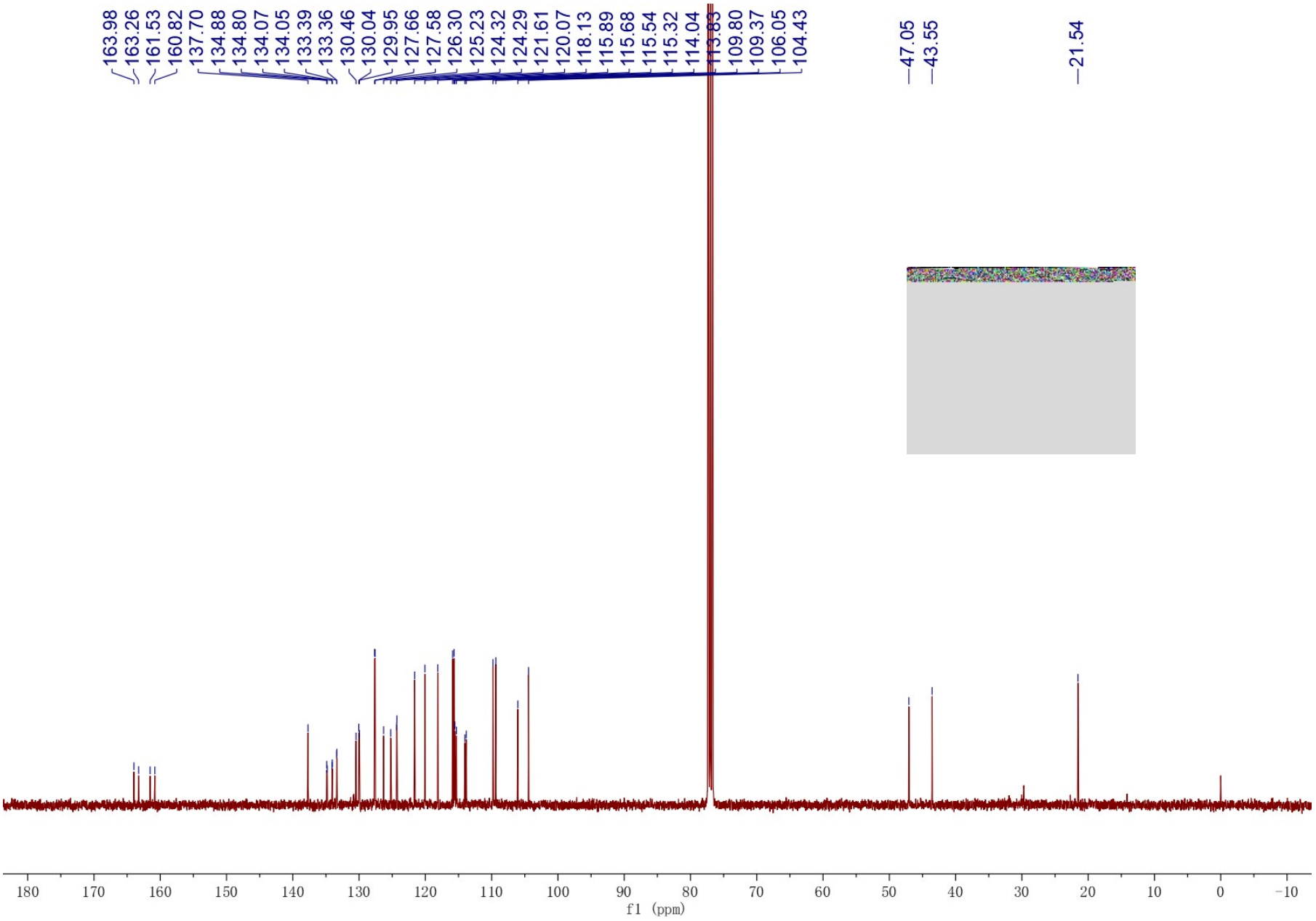
^{19}F NMR of 3ea (376 MHz, $CDCl_3$)



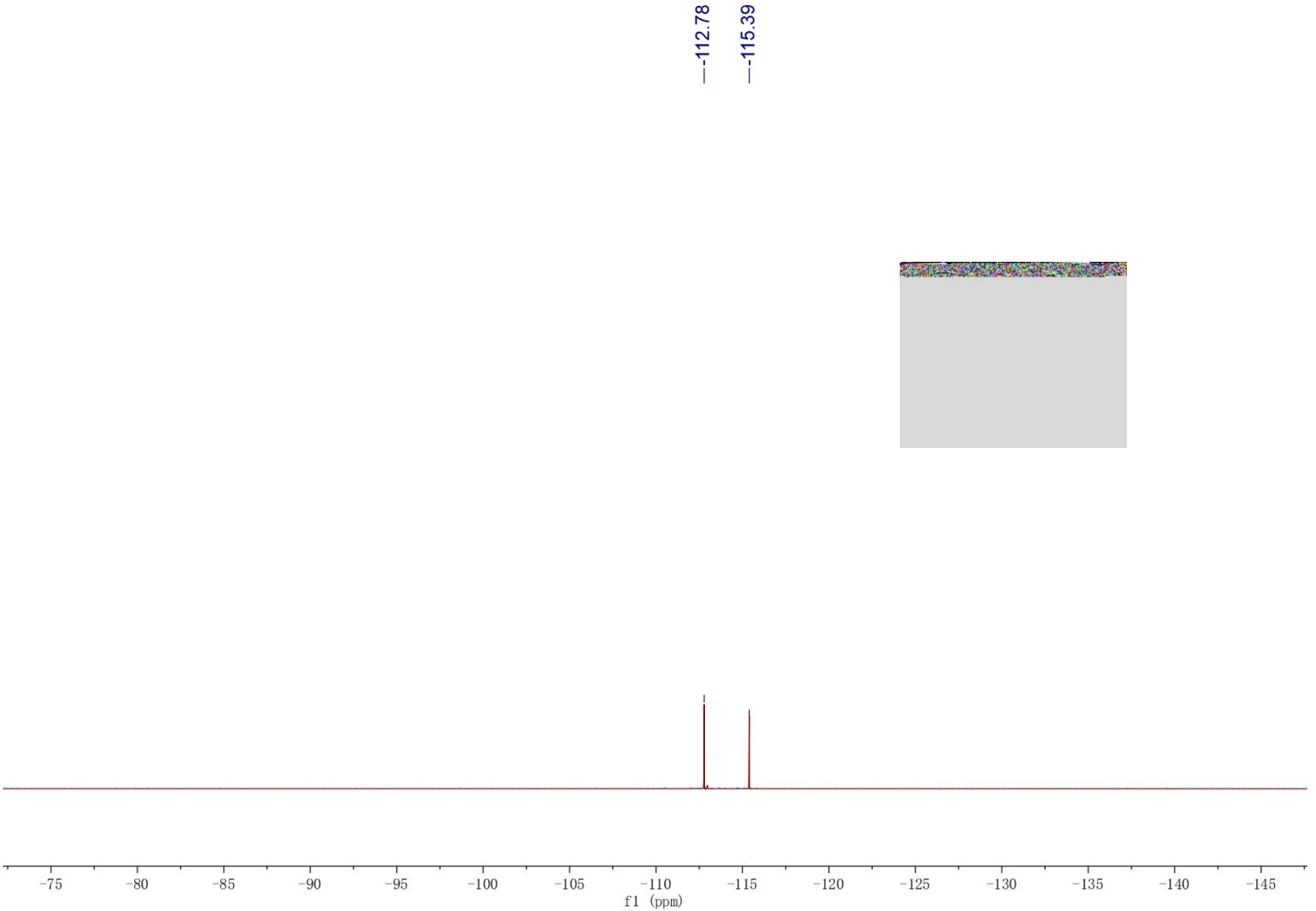
^{1}H NMR of 3eb (400 MHz, $CDCl_3$)



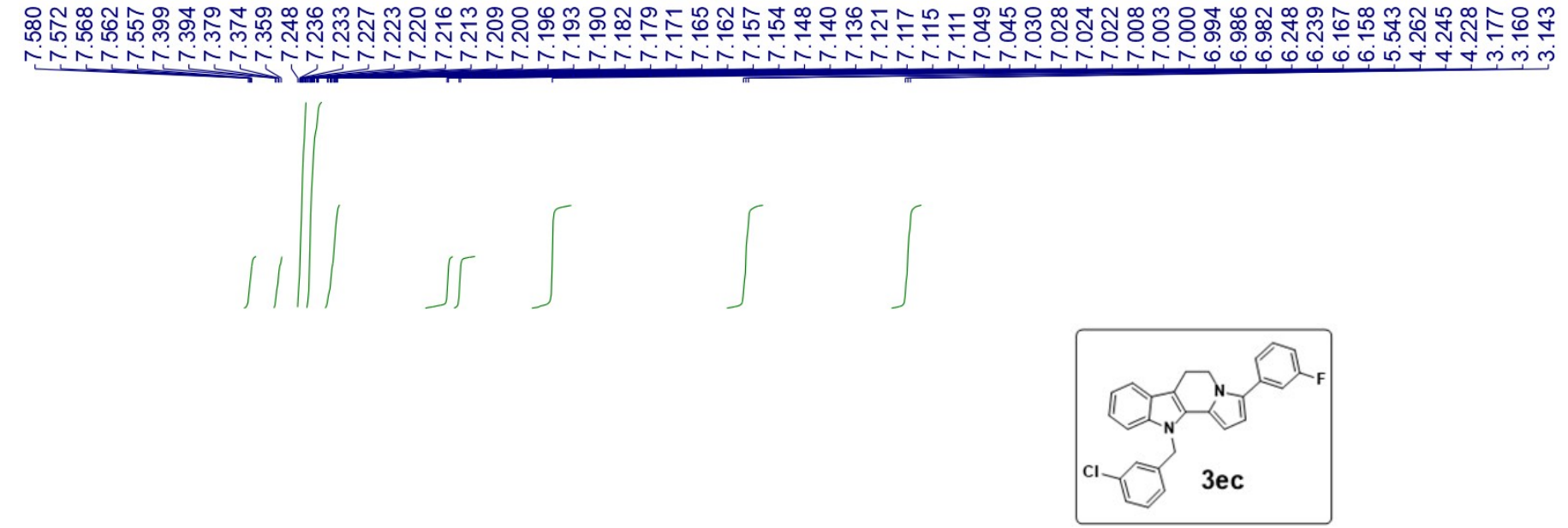
^{13}C NMR of 3eb (100 MHz, $CDCl_3$)

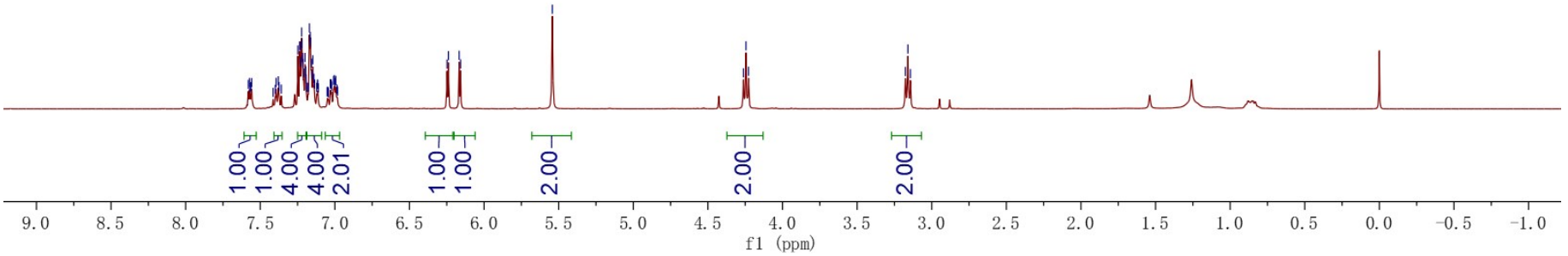


^{19}F NMR of 3eb (376 MHz, $CDCl_3$)

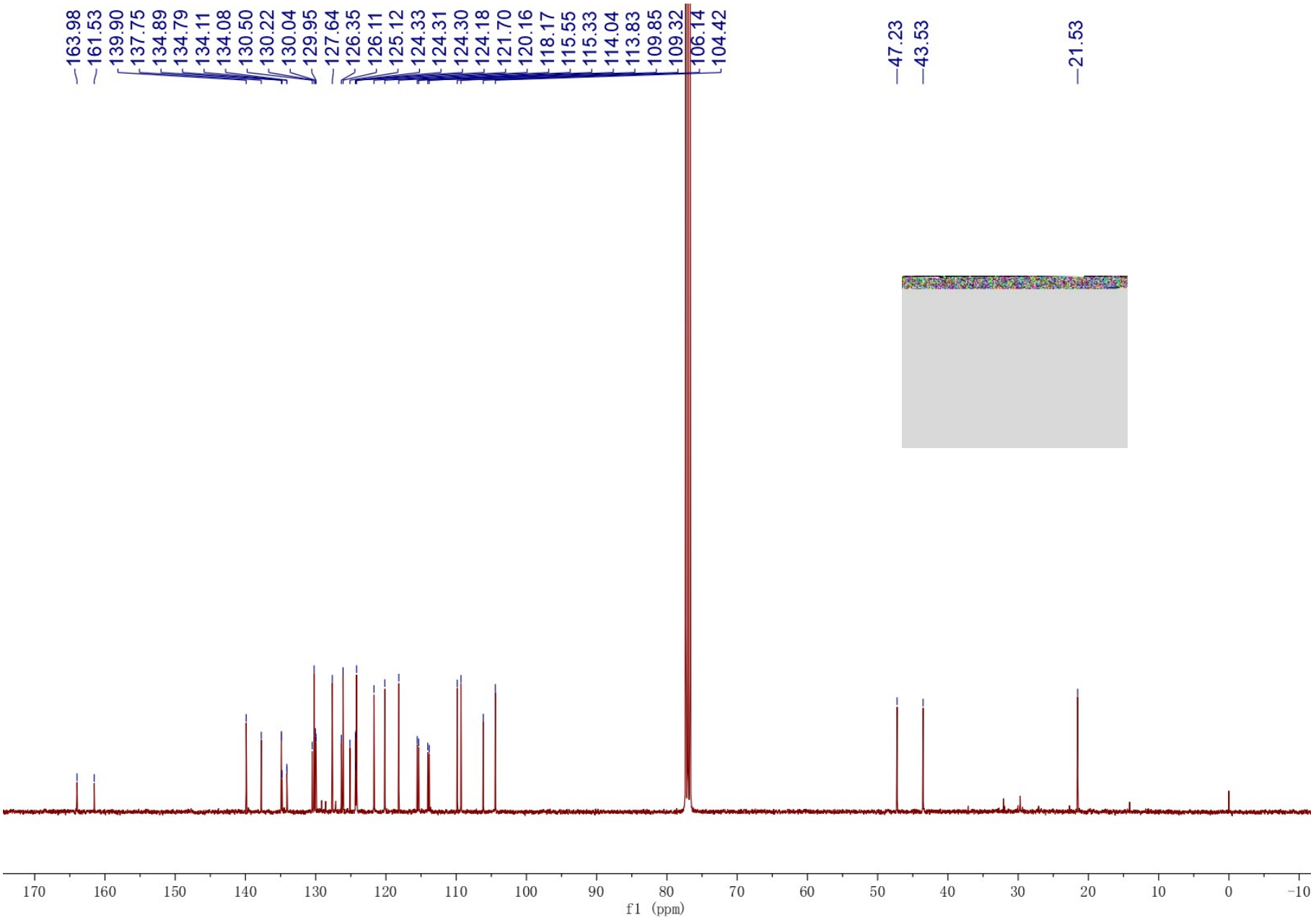


^{1}H NMR of 3ec (400 MHz, $CDCl_3$)

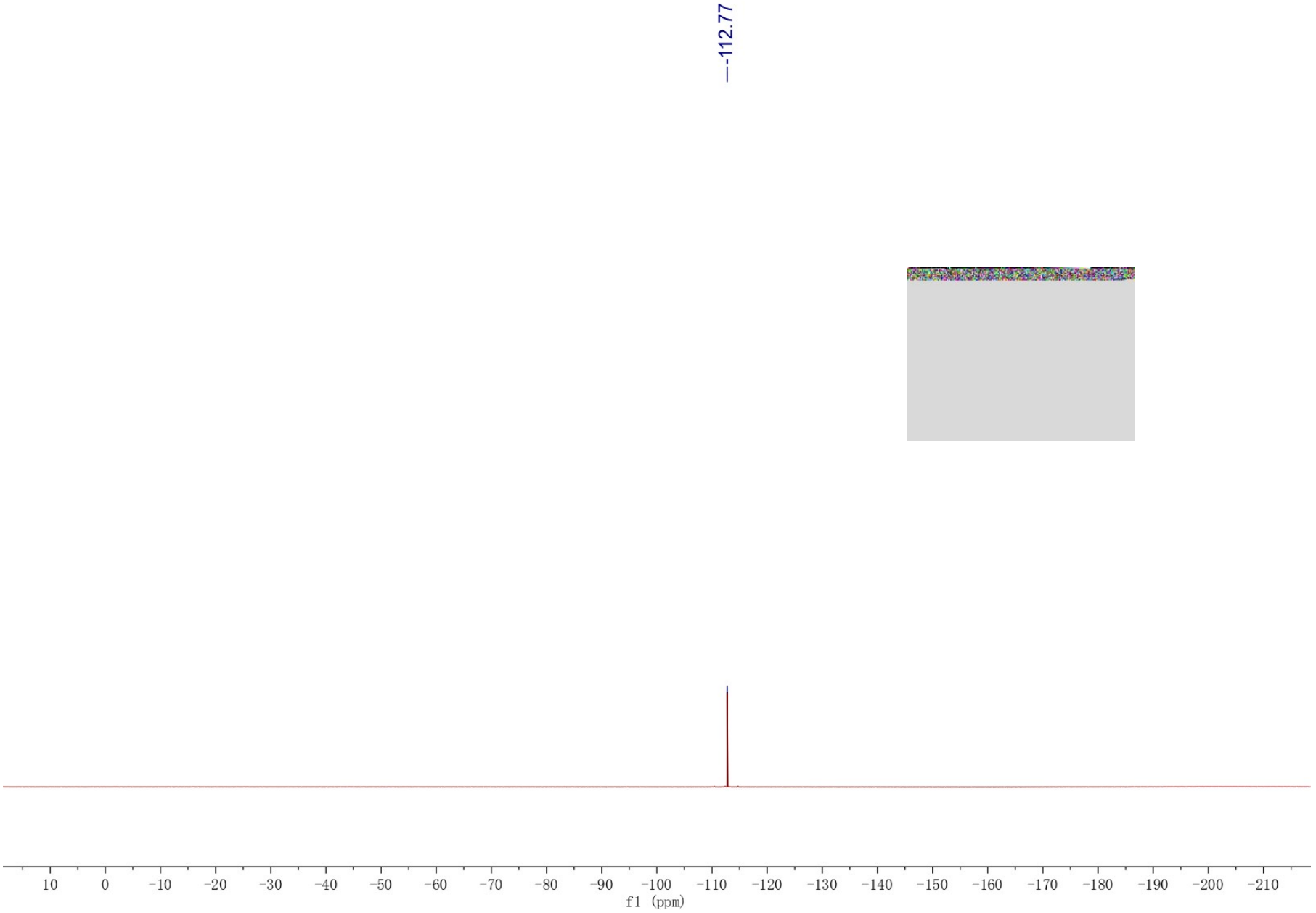




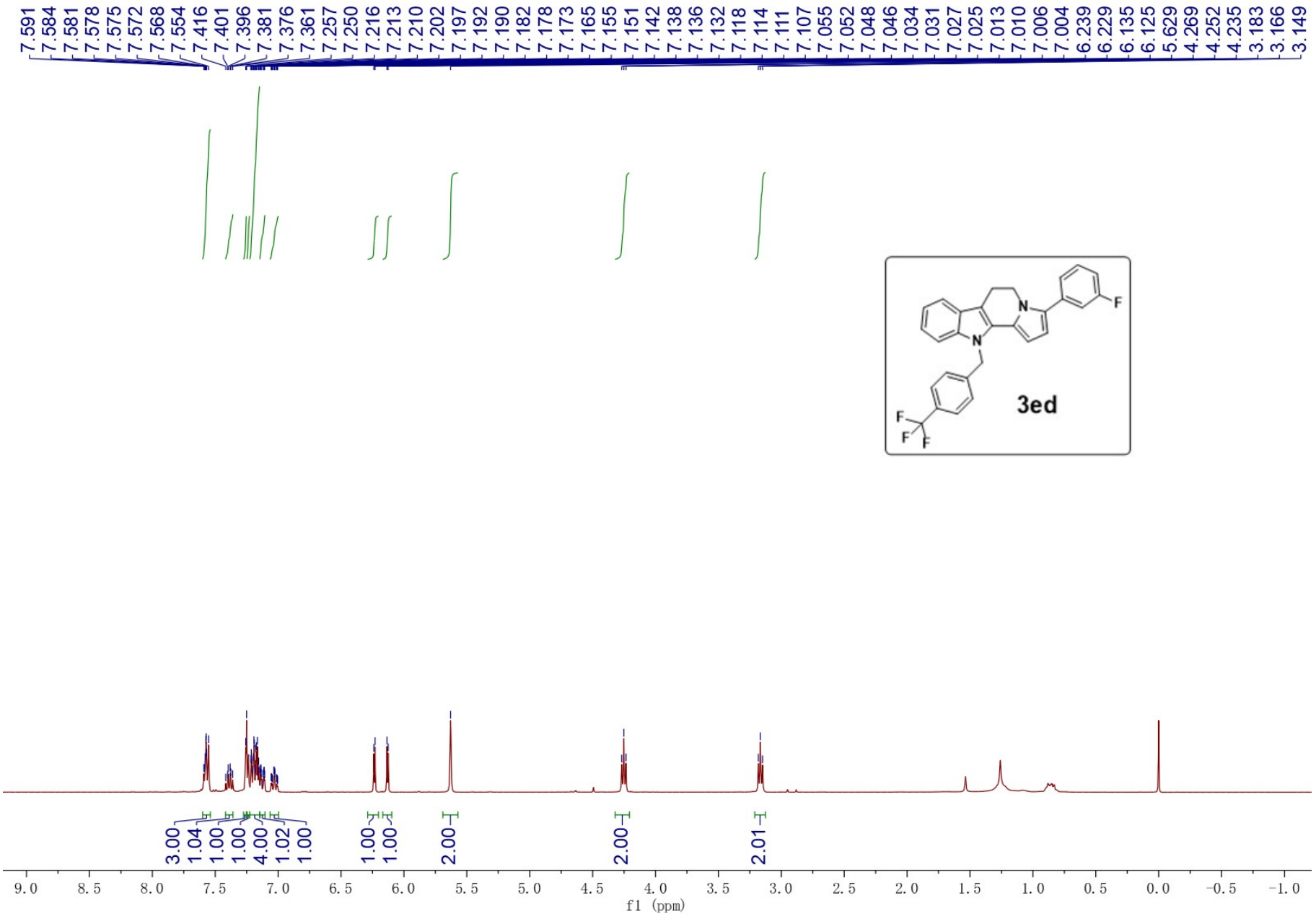
^{13}C NMR of 3ec (100 MHz, $CDCl_3$)



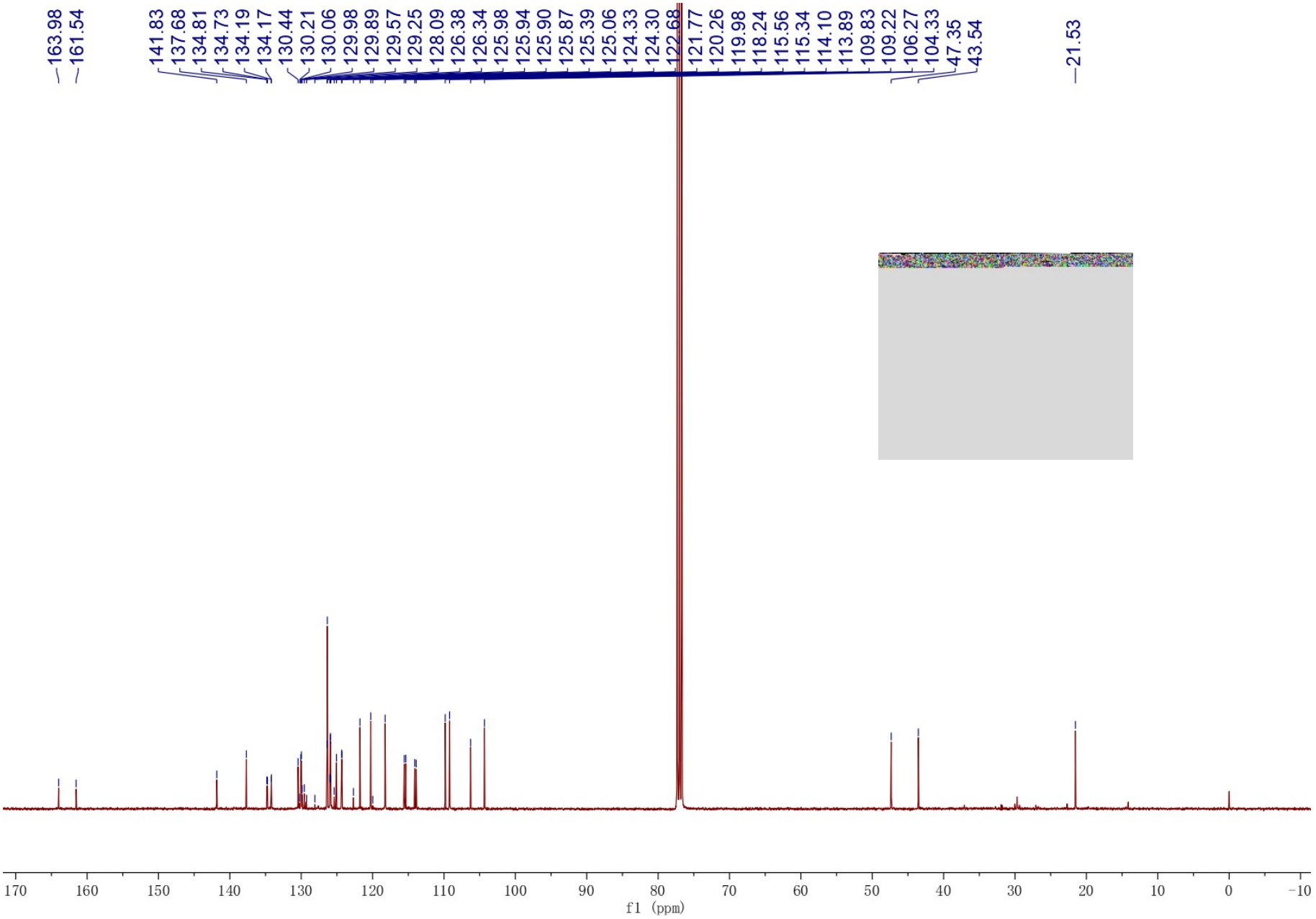
^{19}F NMR of 3ec (376 MHz, $CDCl_3$)



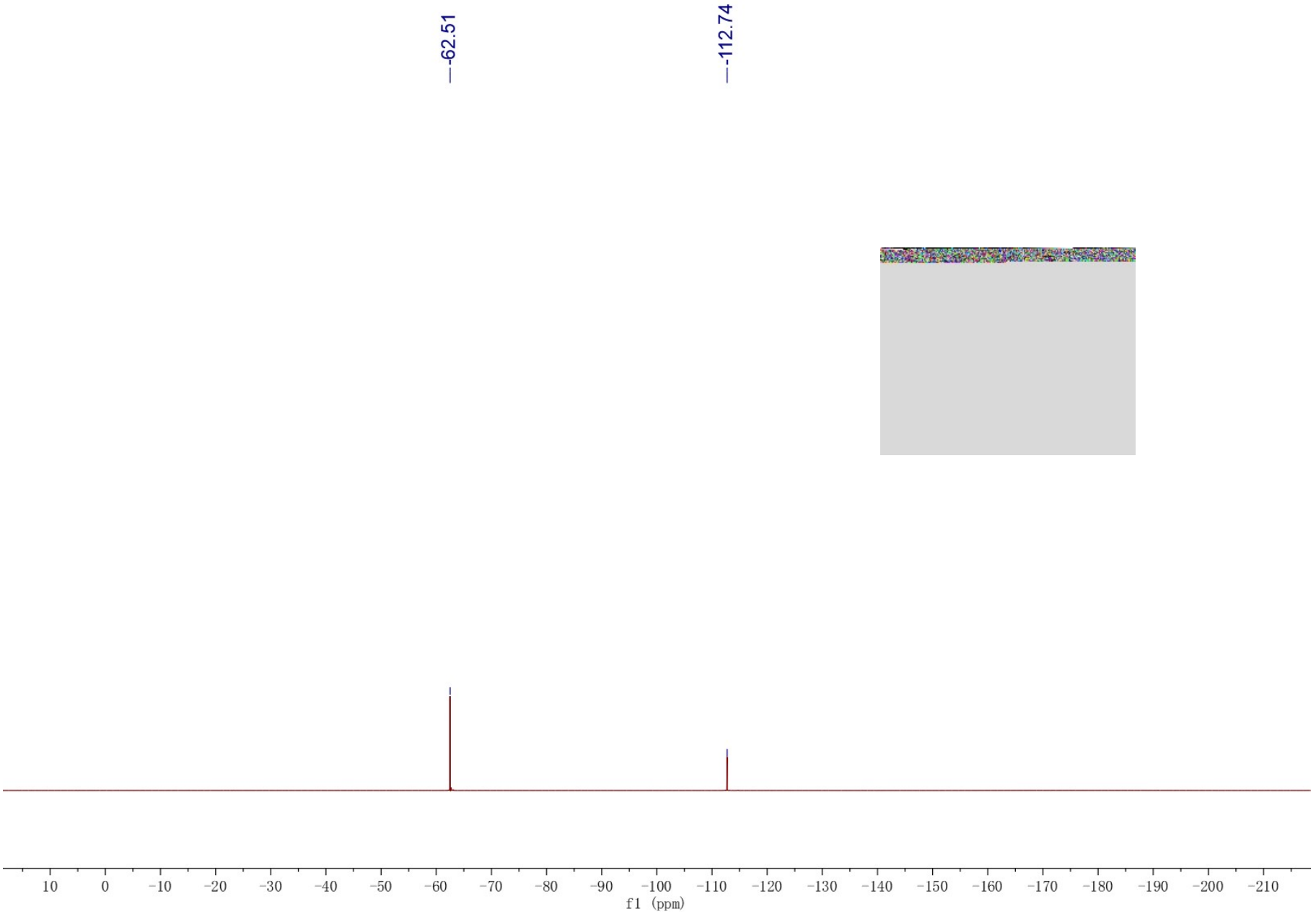
^{1}H NMR of 3ed (400 MHz, $CDCl_3$)



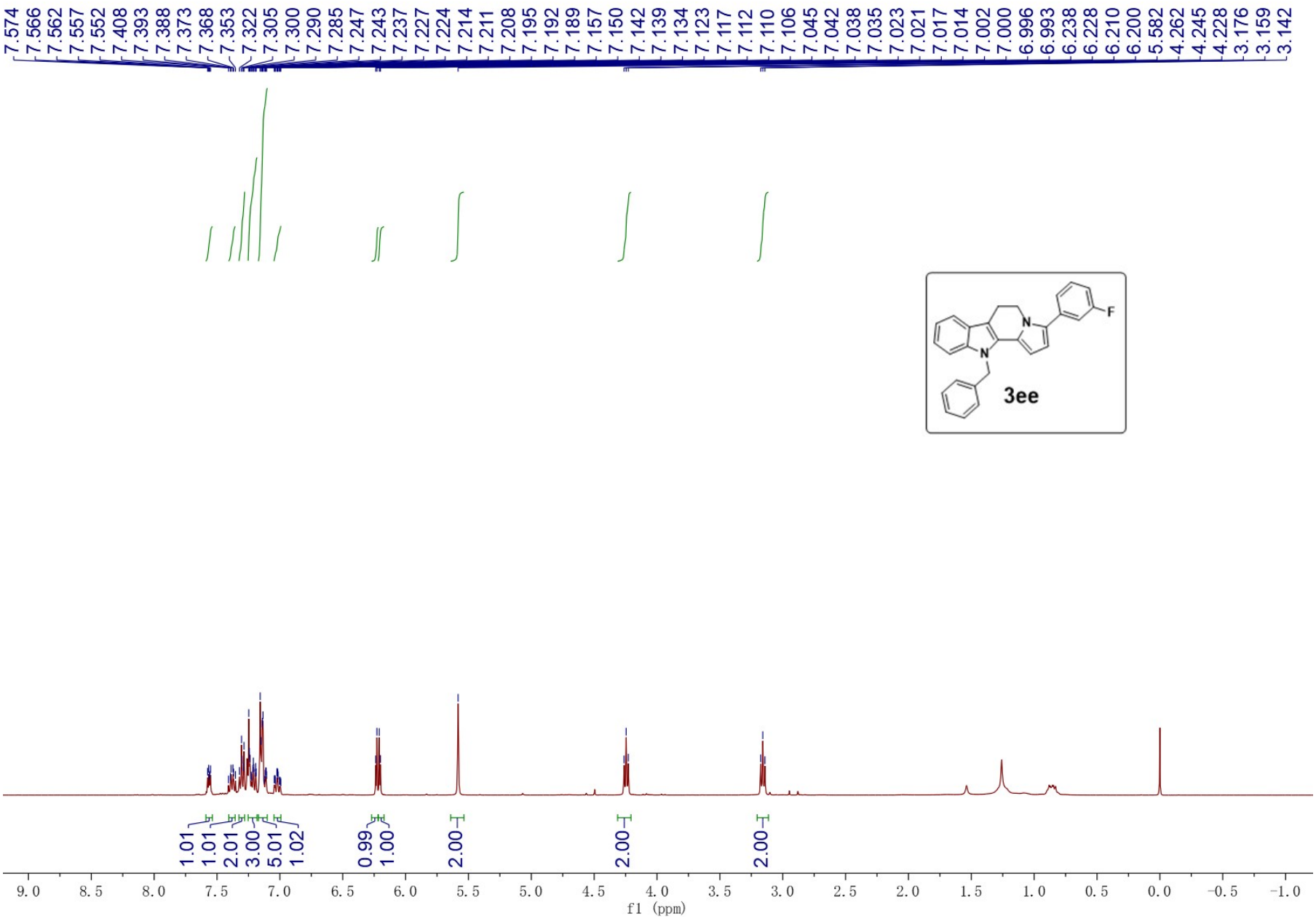
^{13}C NMR of 3ed (100 MHz, $CDCl_3$)



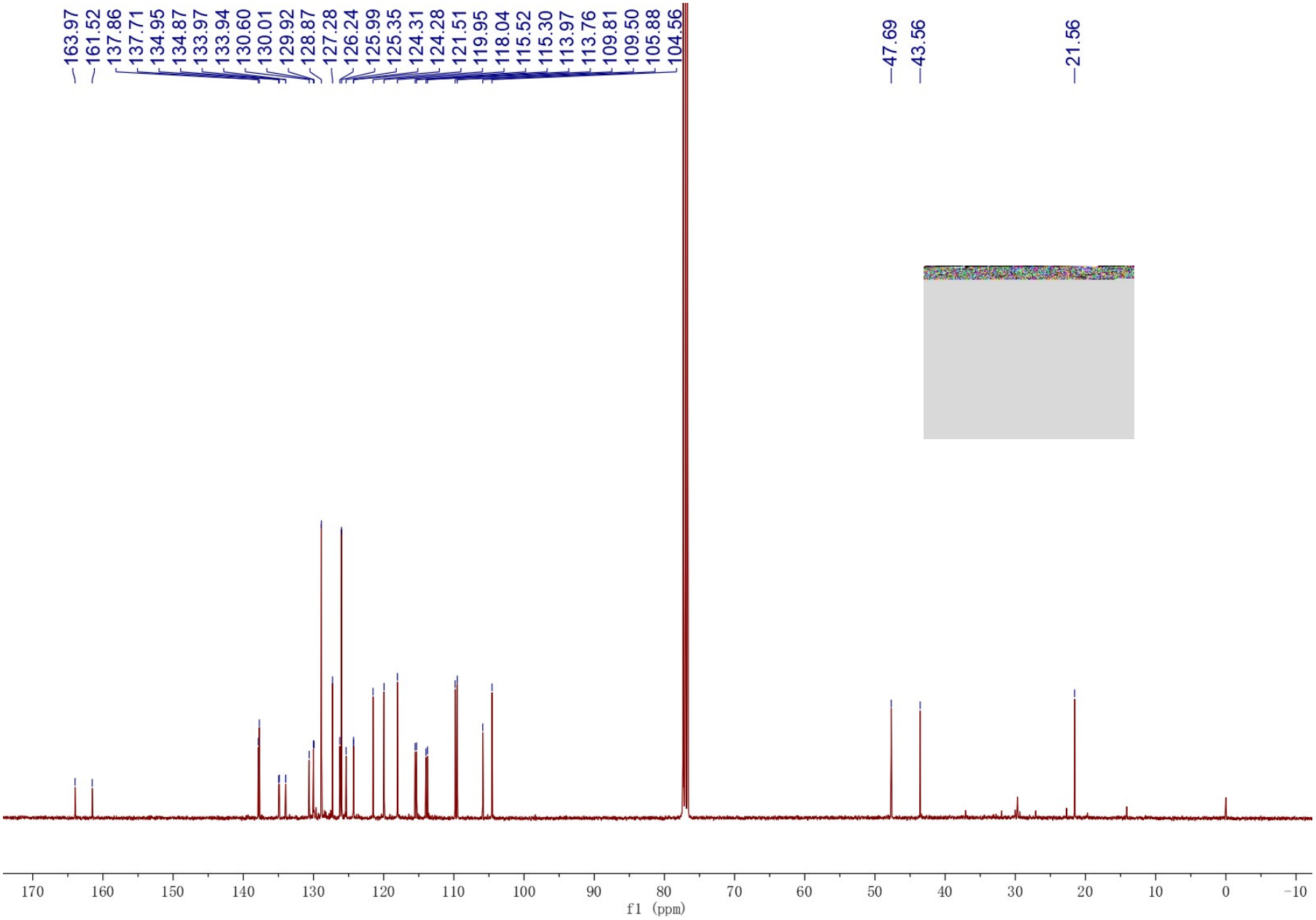
^{19}F NMR of 3ed (376 MHz, $CDCl_3$)



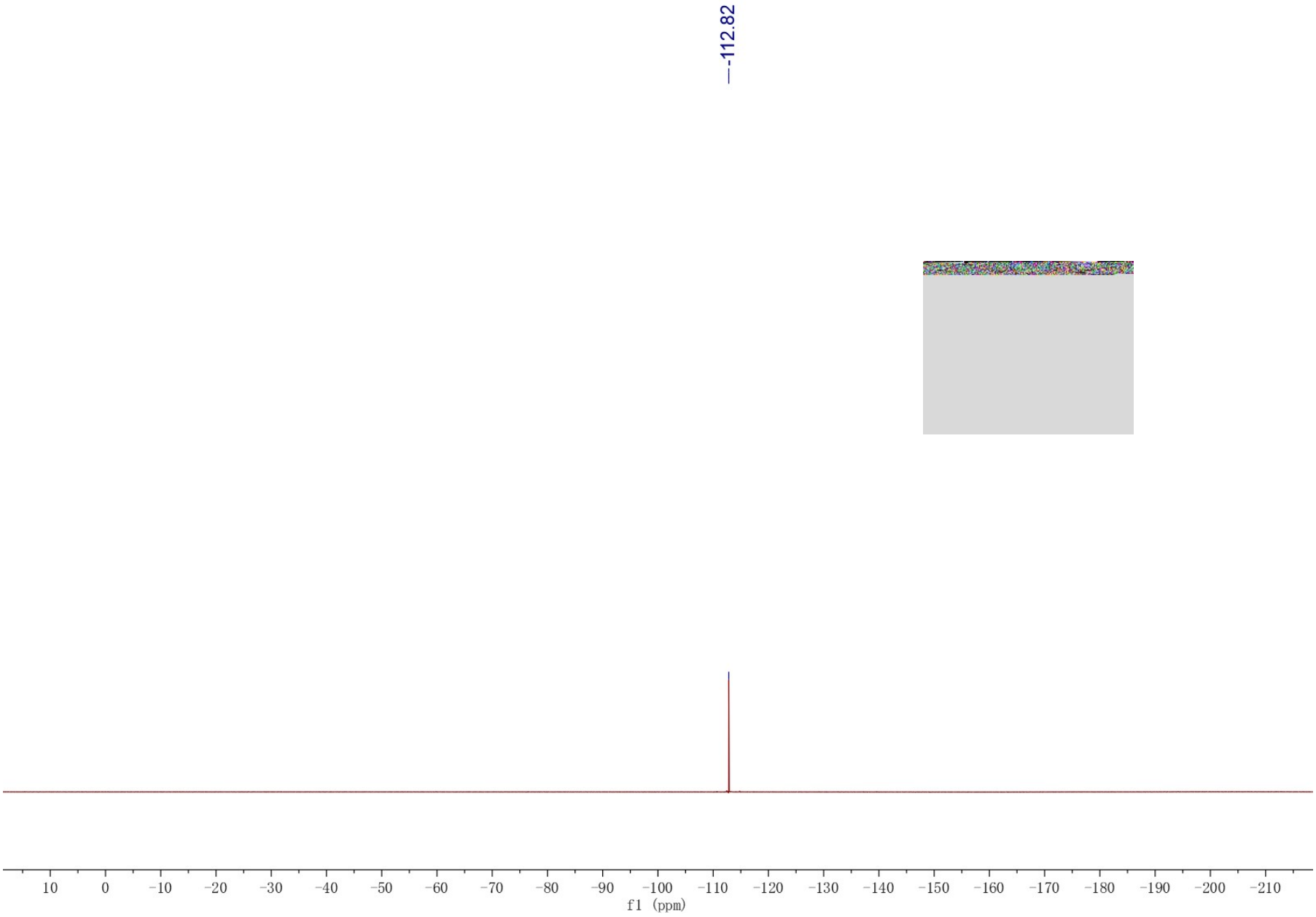
^{1}H NMR of 3ee (400 MHz, $CDCl_3$)



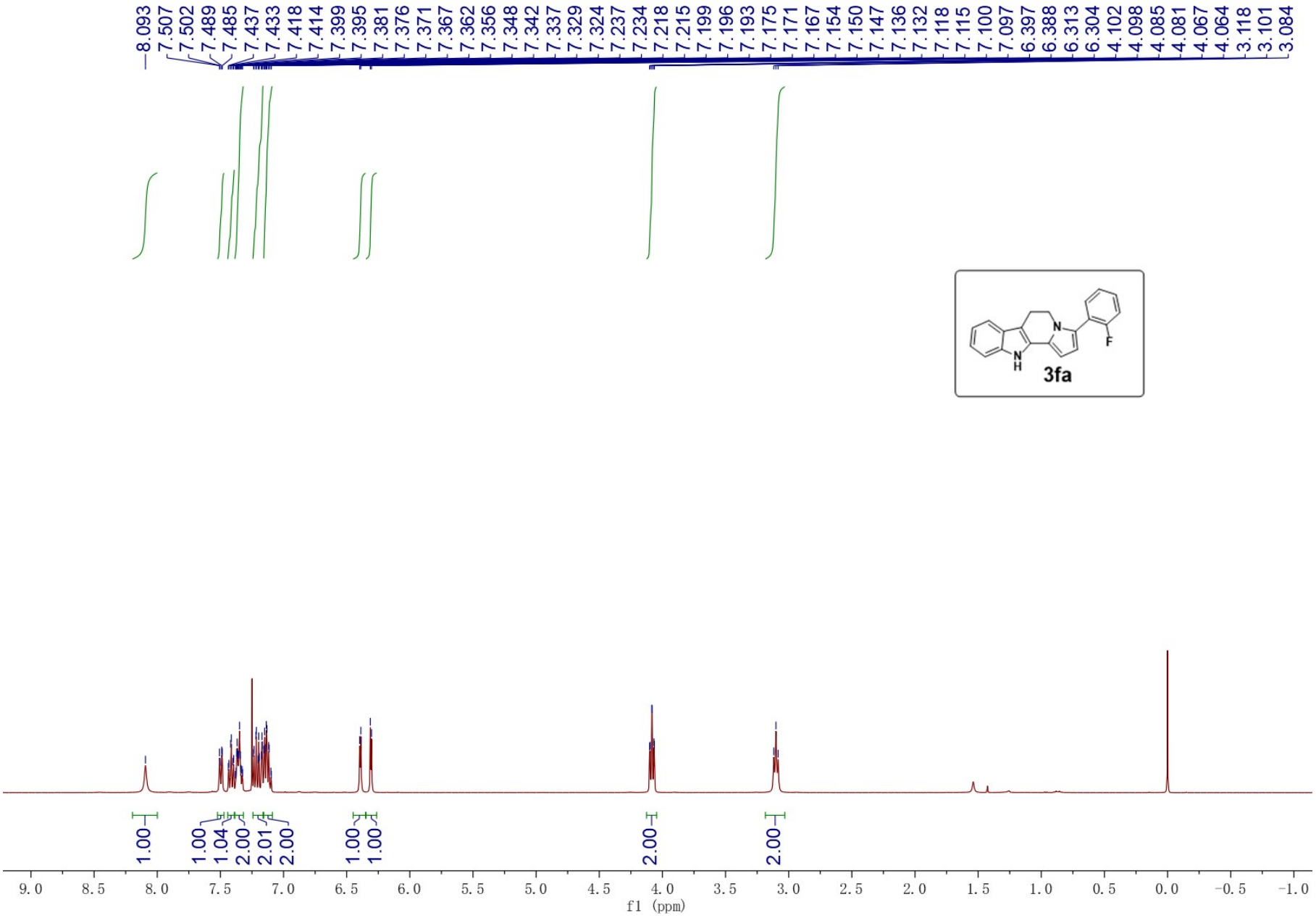
^{13}C NMR of 3ee (100 MHz, $CDCl_3$)



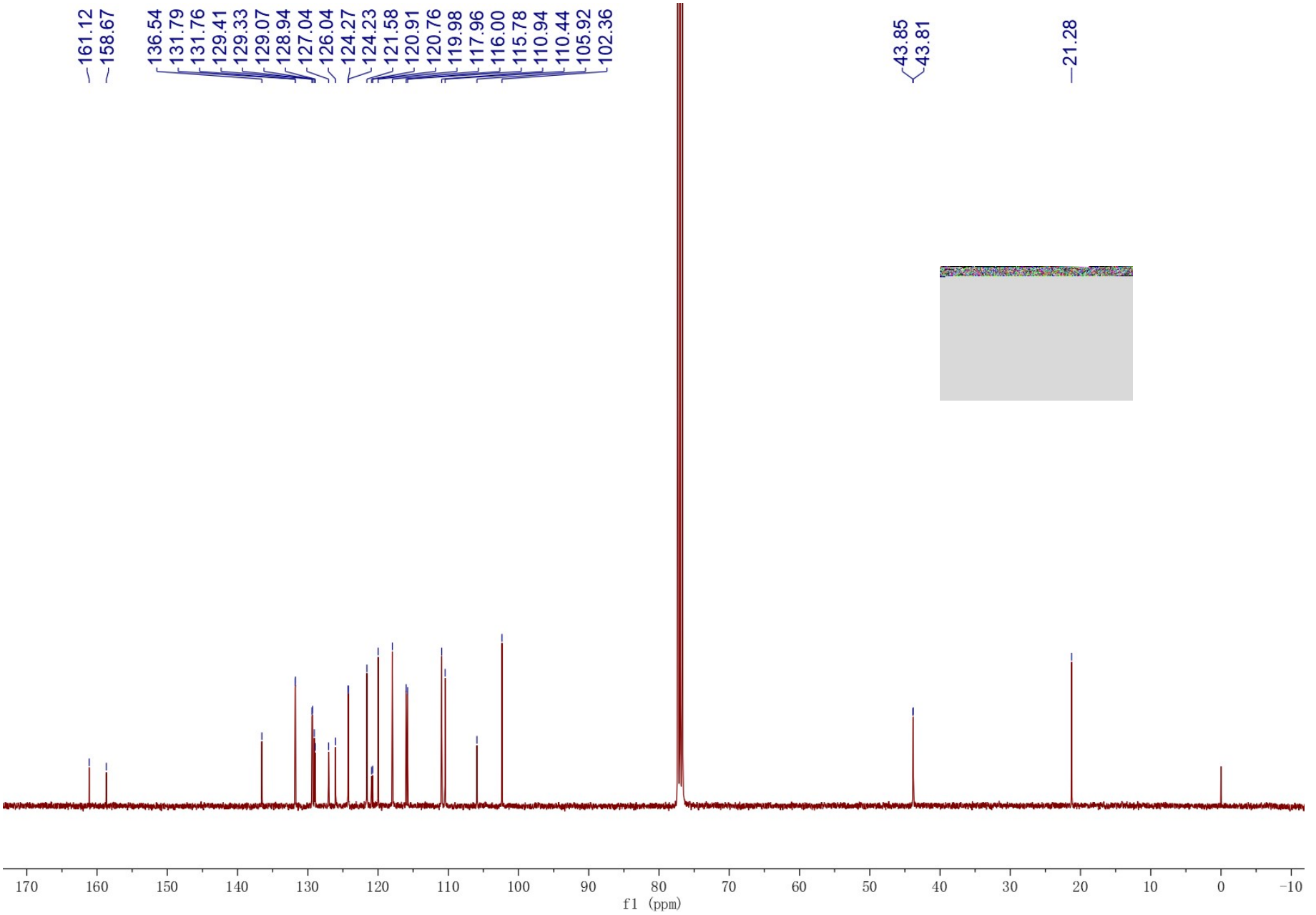
^{19}F NMR of 3ee (376 MHz, $CDCl_3$)



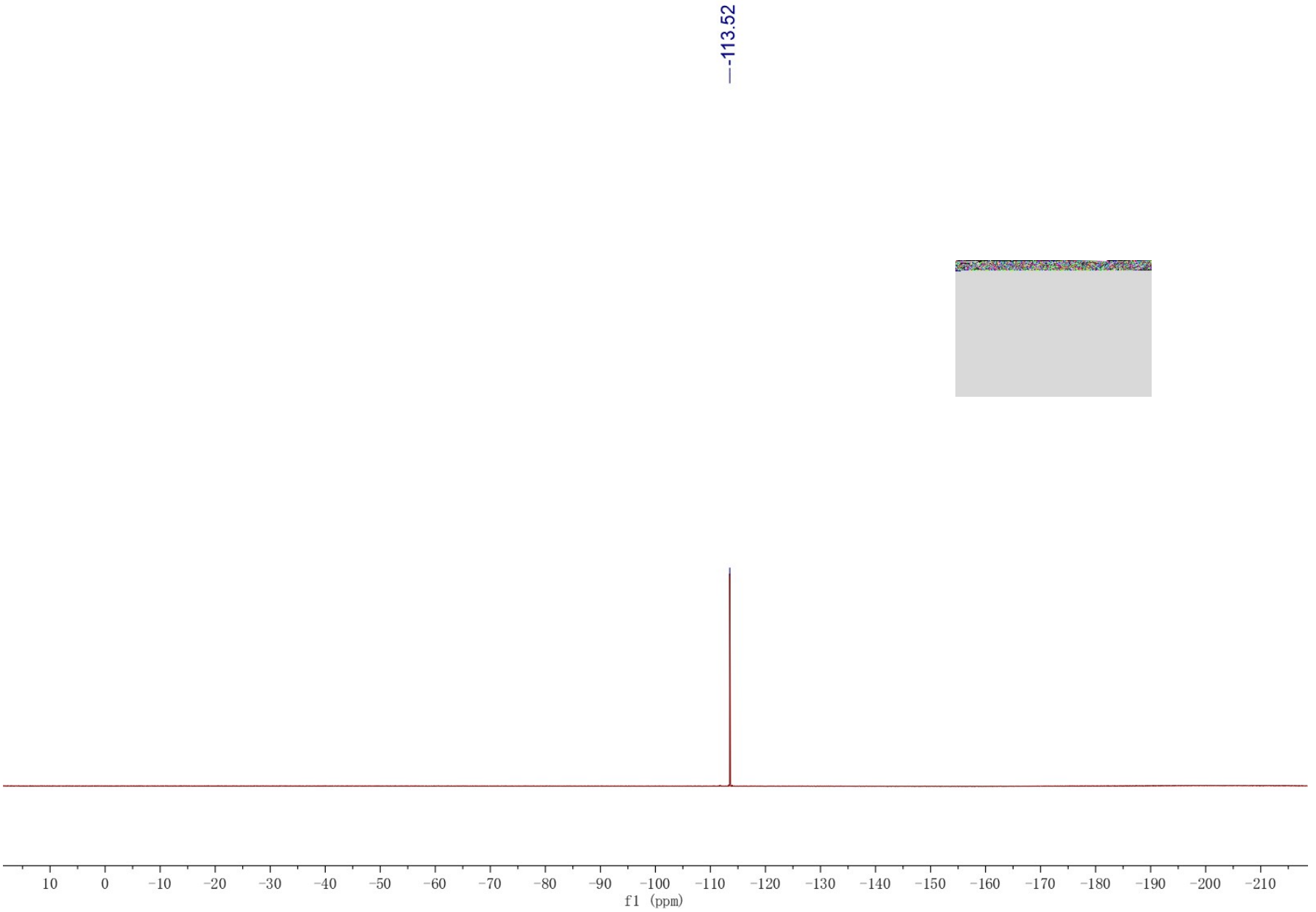
^{1}H NMR of 3fa (400 MHz, $CDCl_3$)



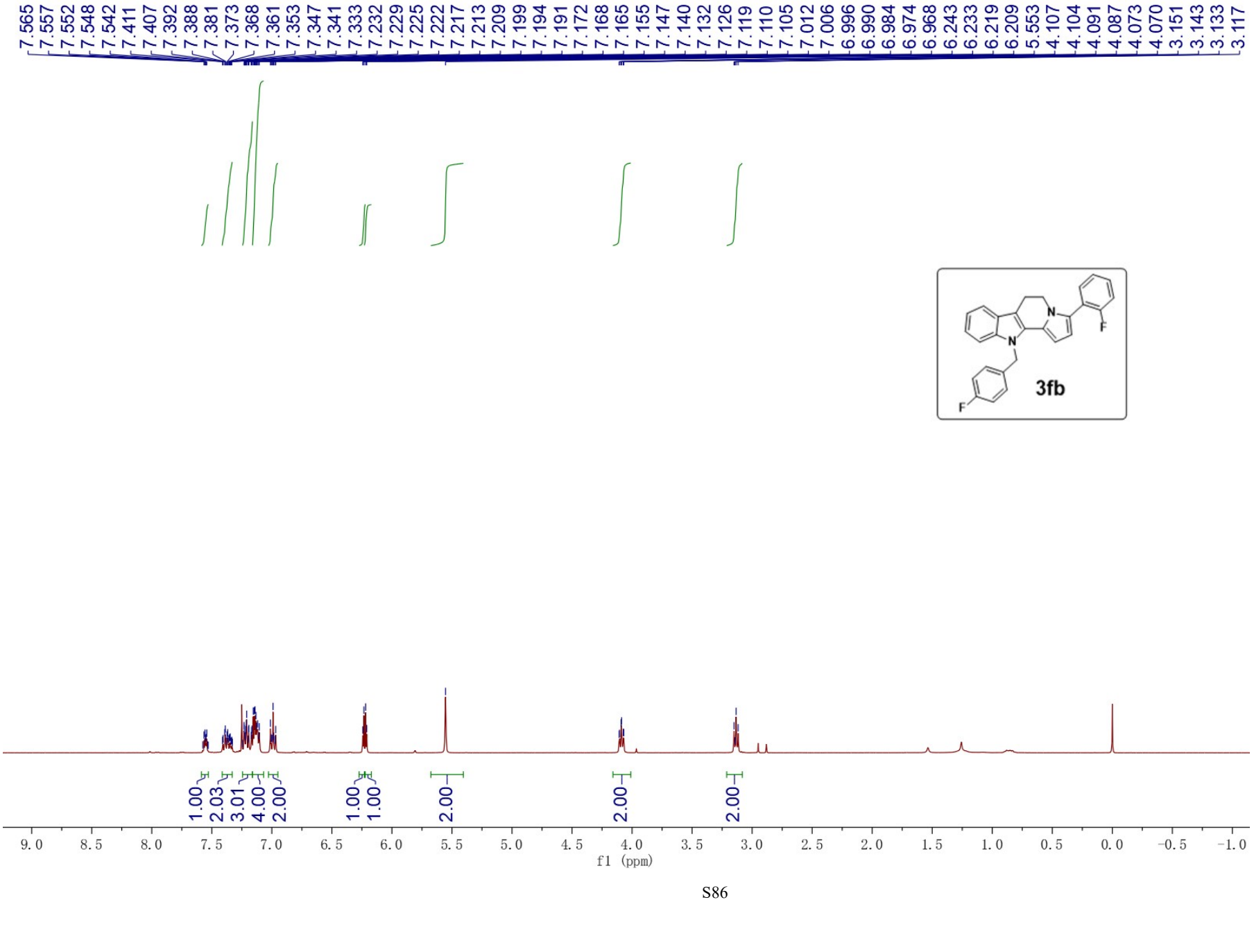
^{13}C NMR of 3fa (100 MHz, $CDCl_3$)



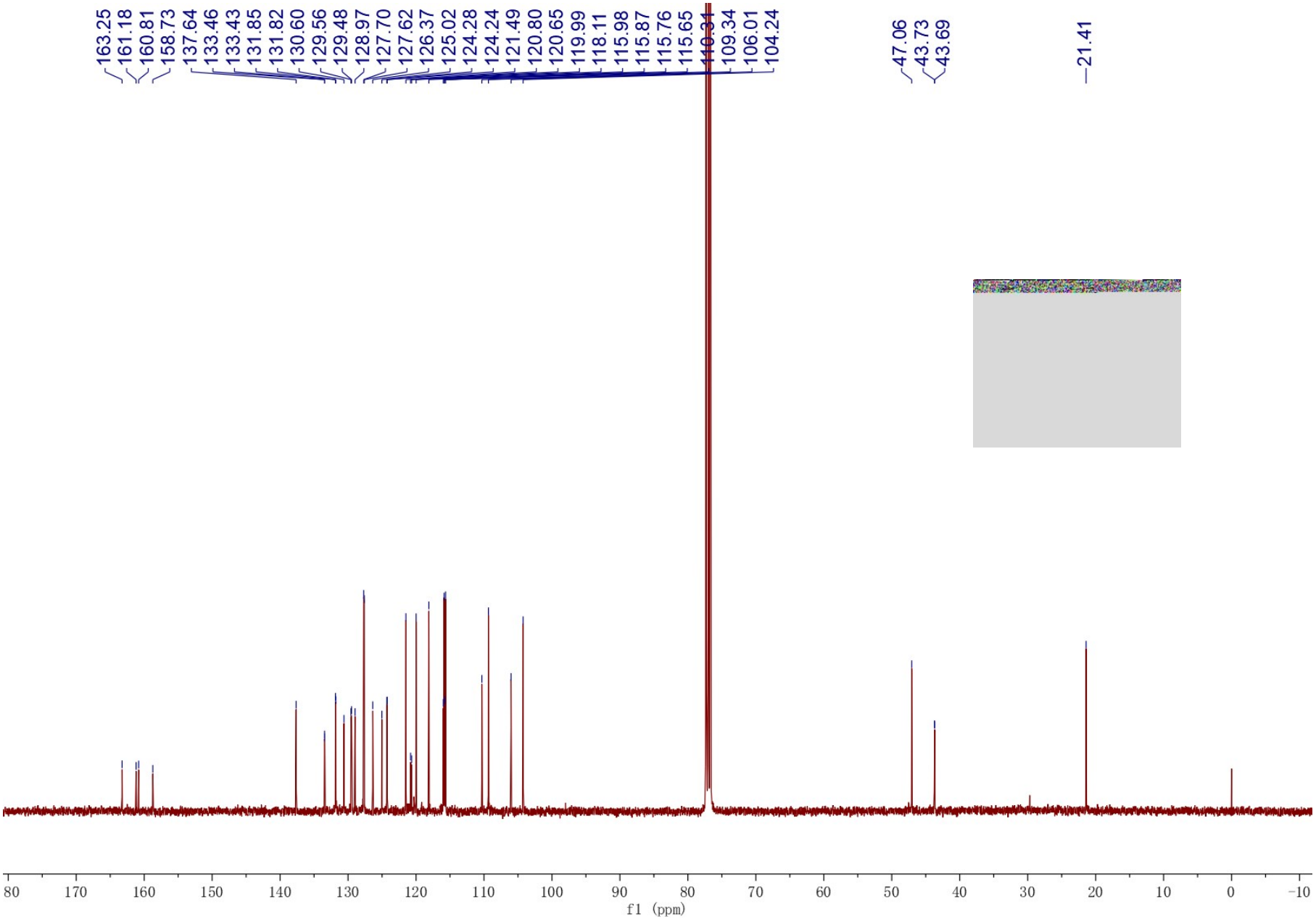
^{19}F NMR of 3fa (376 MHz, $CDCl_3$)



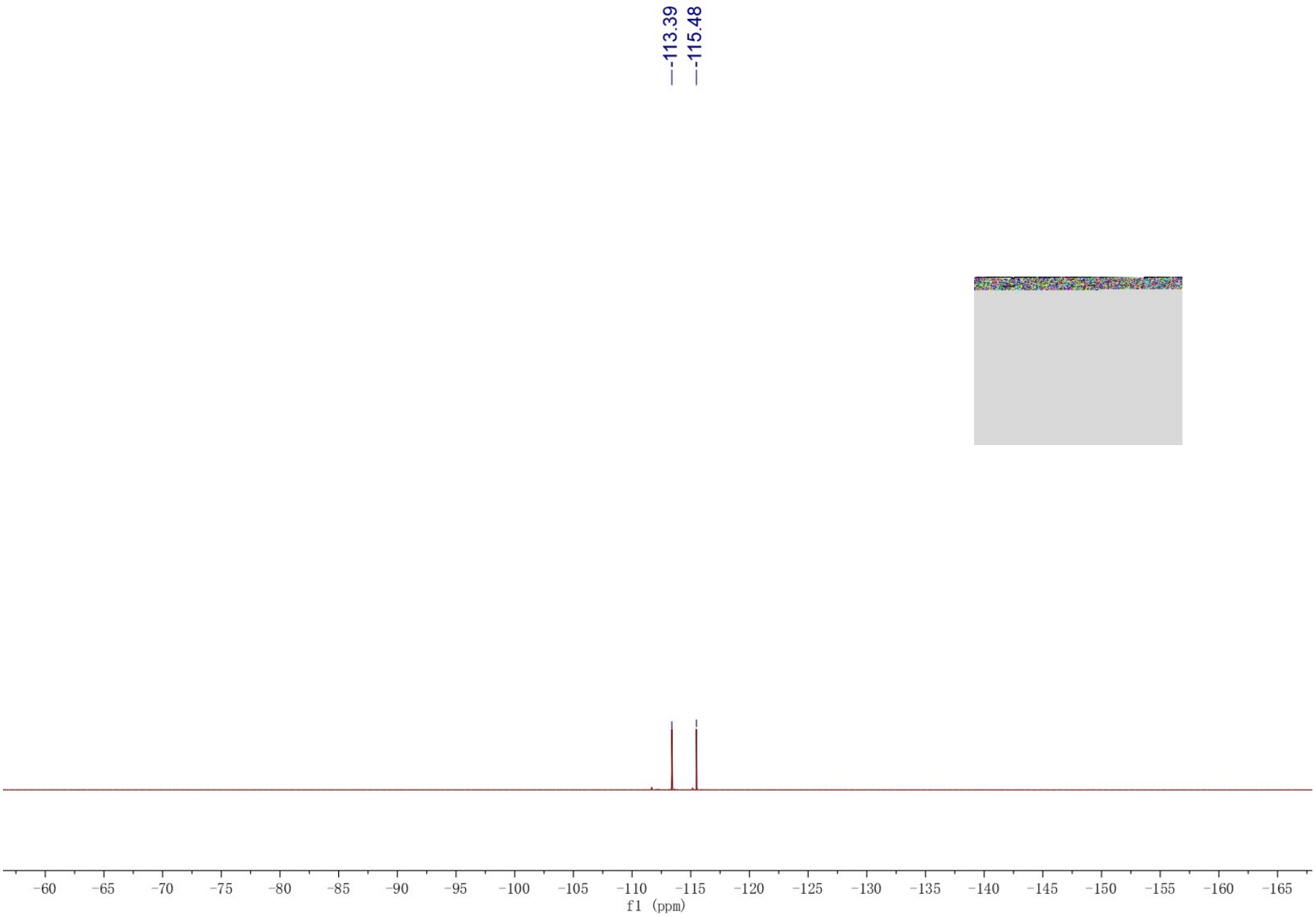
^{1}H NMR of 3fb (400 MHz, $CDCl_3$)



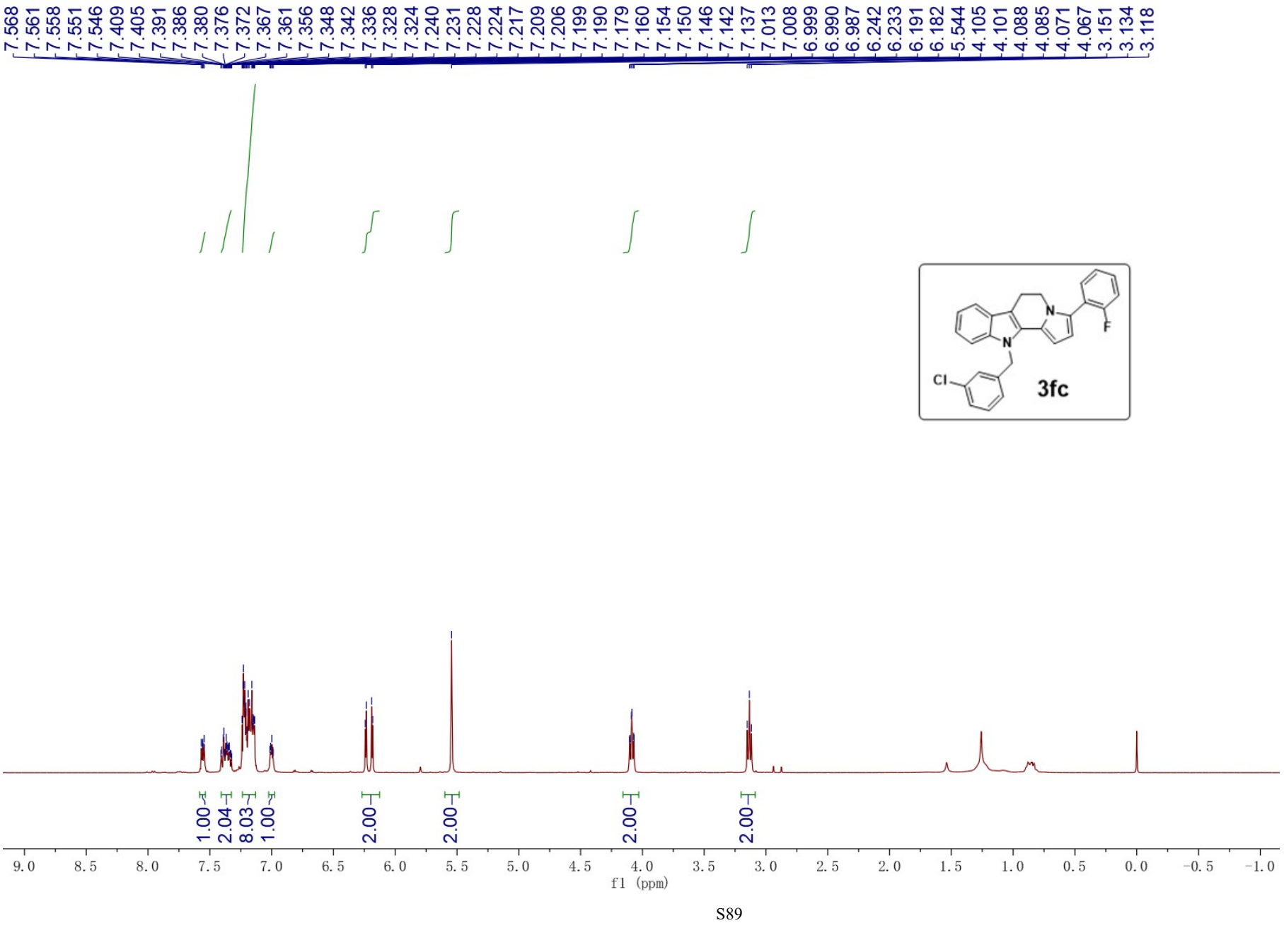
^{13}C NMR of 3fb (100 MHz, $CDCl_3$)



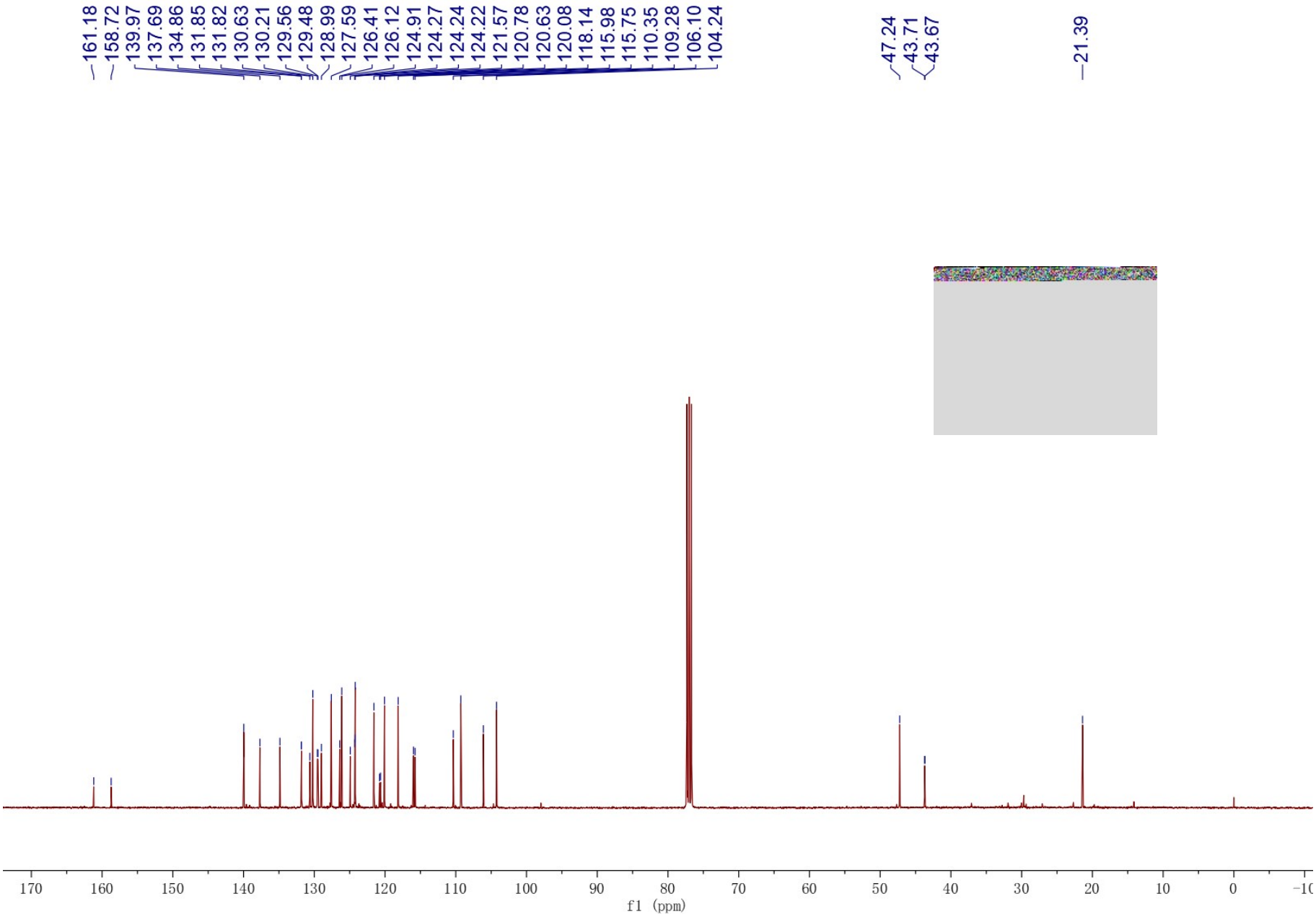
^{19}F NMR of 3fb (376 MHz, $CDCl_3$)



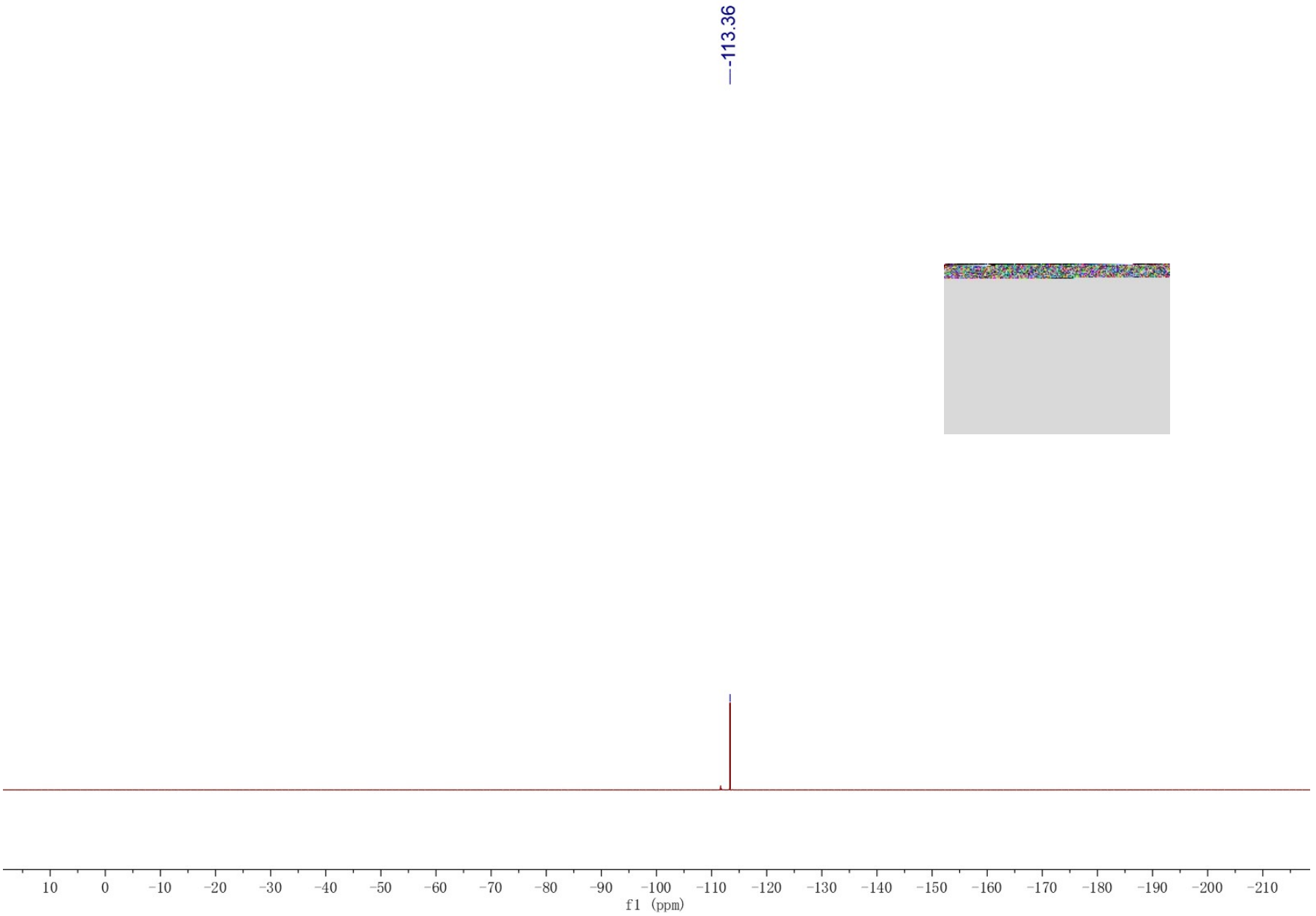
^{1}H NMR of 3fc (400 MHz, $CDCl_3$)



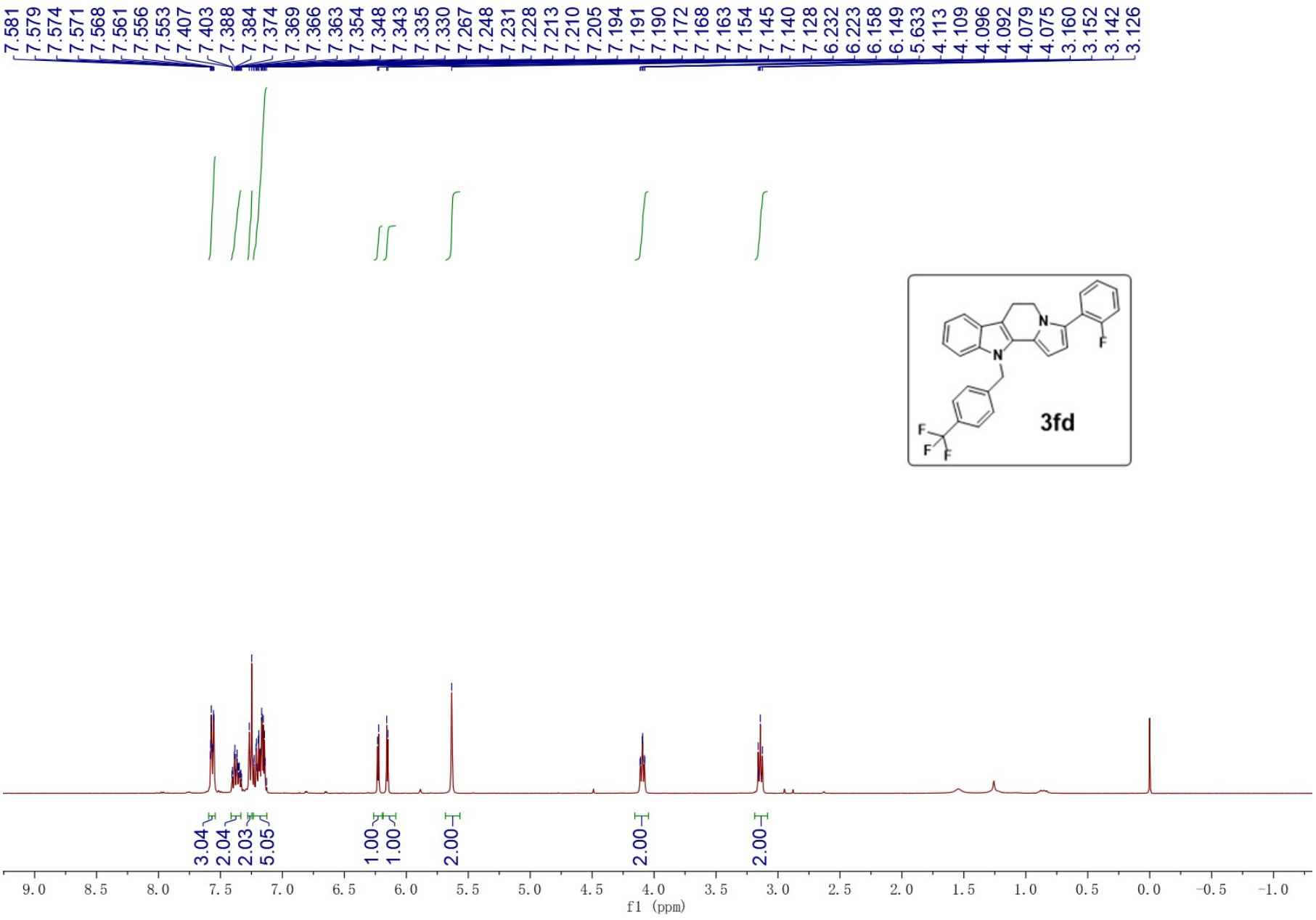
^{13}C NMR of 3fc (100 MHz, $CDCl_3$)



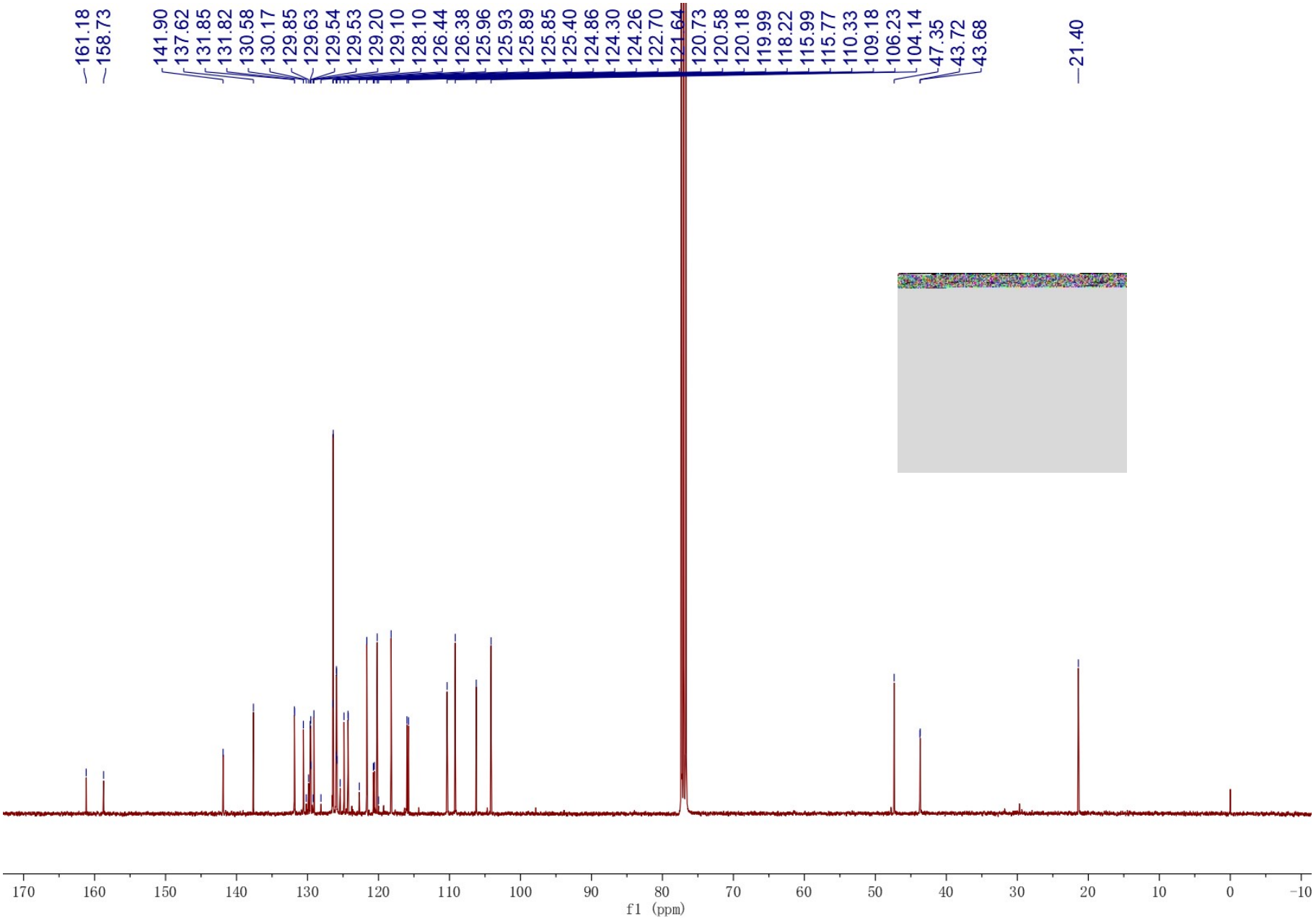
^{19}F NMR of 3fc (376 MHz, $CDCl_3$)



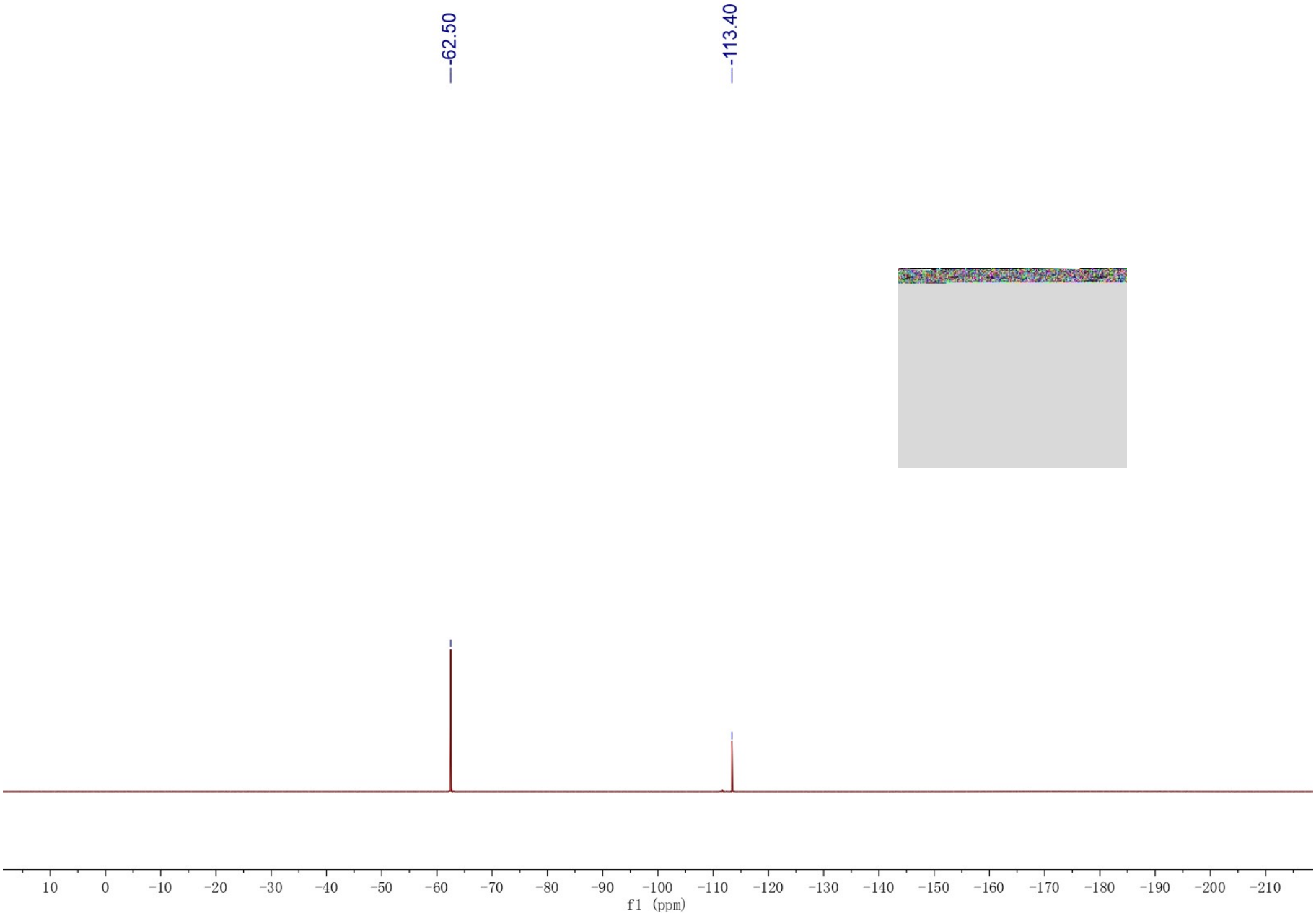
^{1}H NMR of 3fd (400 MHz, $CDCl_3$)



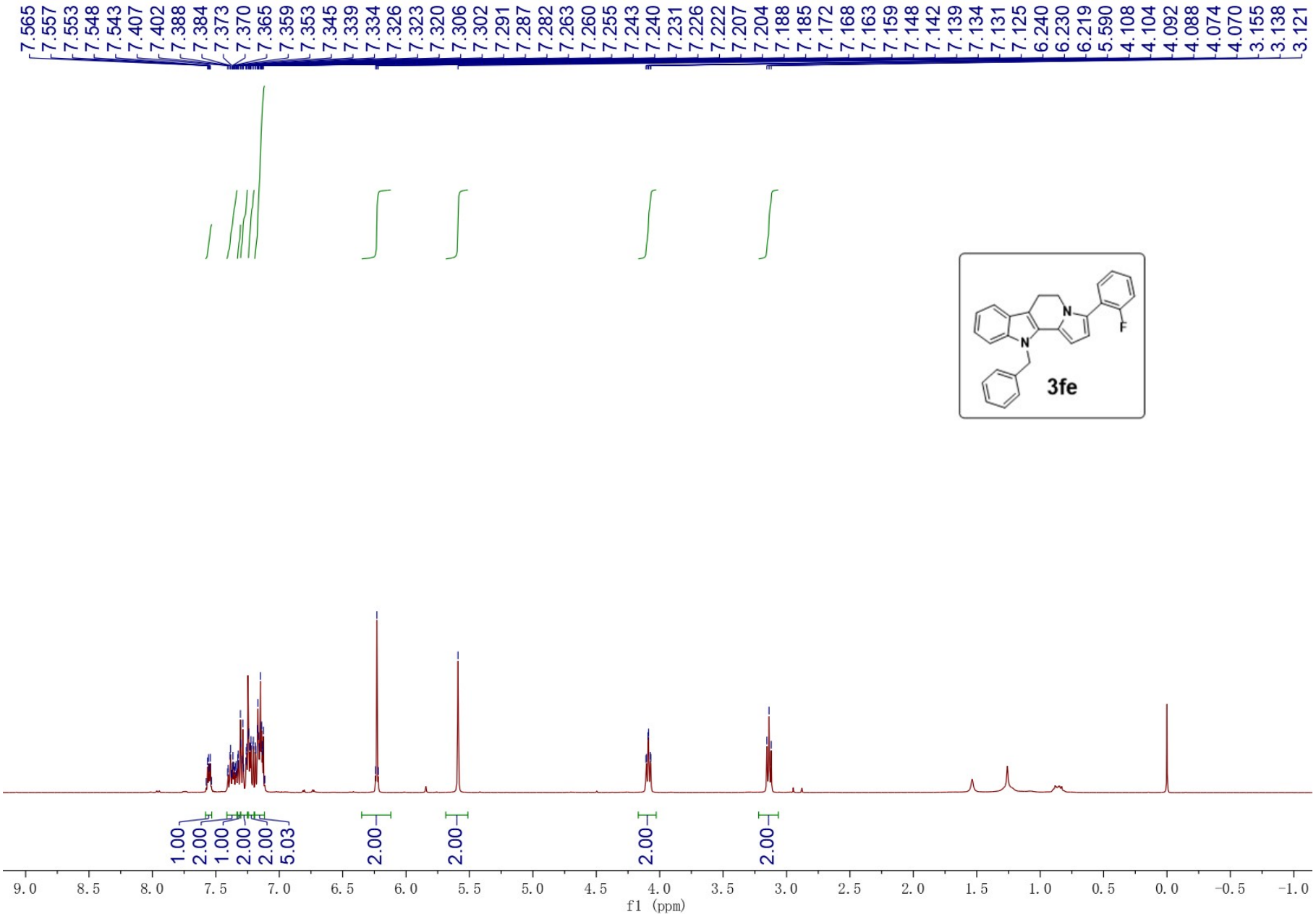
^{13}C NMR of 3fd (100 MHz, $CDCl_3$)



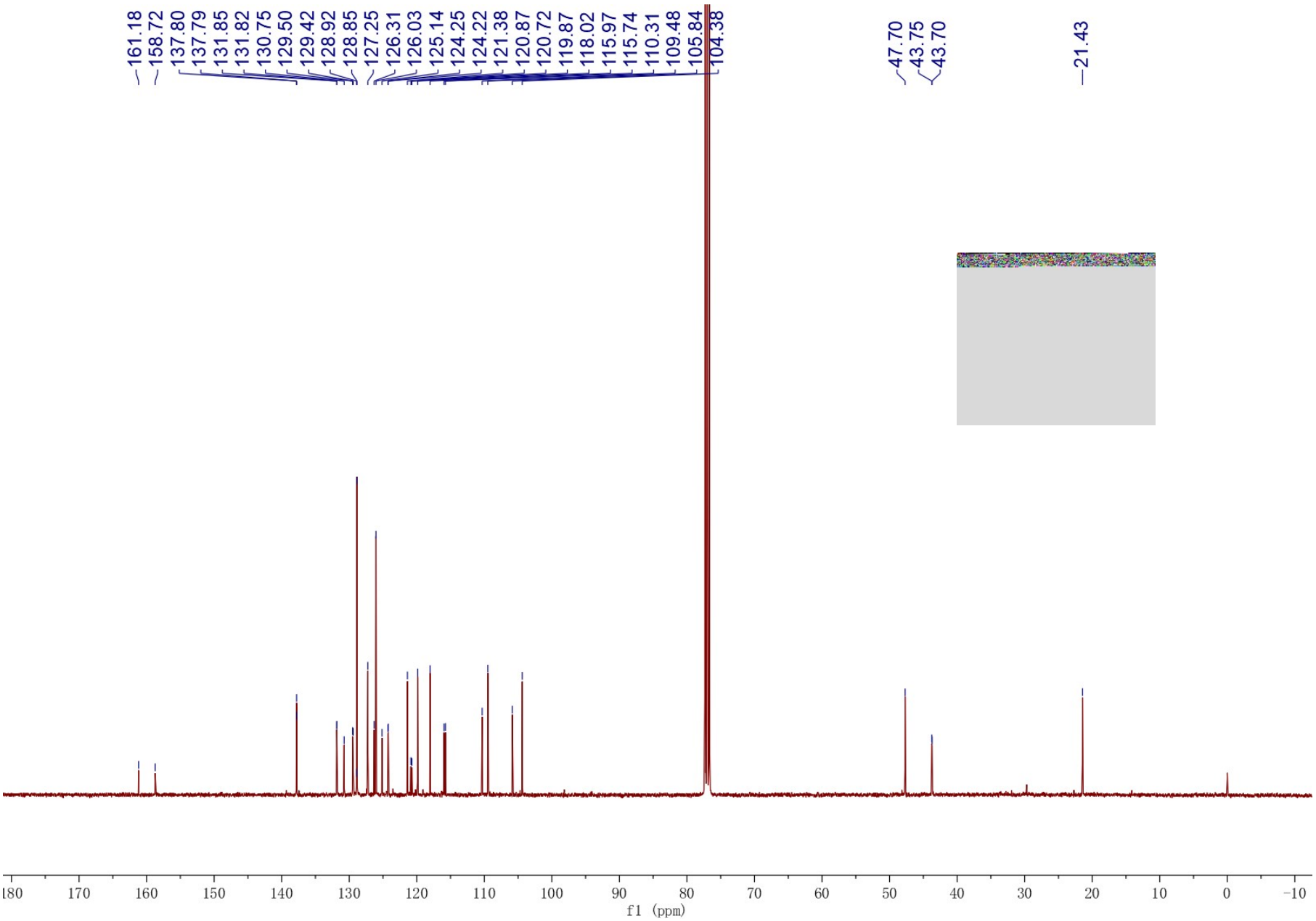
^{19}F NMR of 3fd (376 MHz, $CDCl_3$)



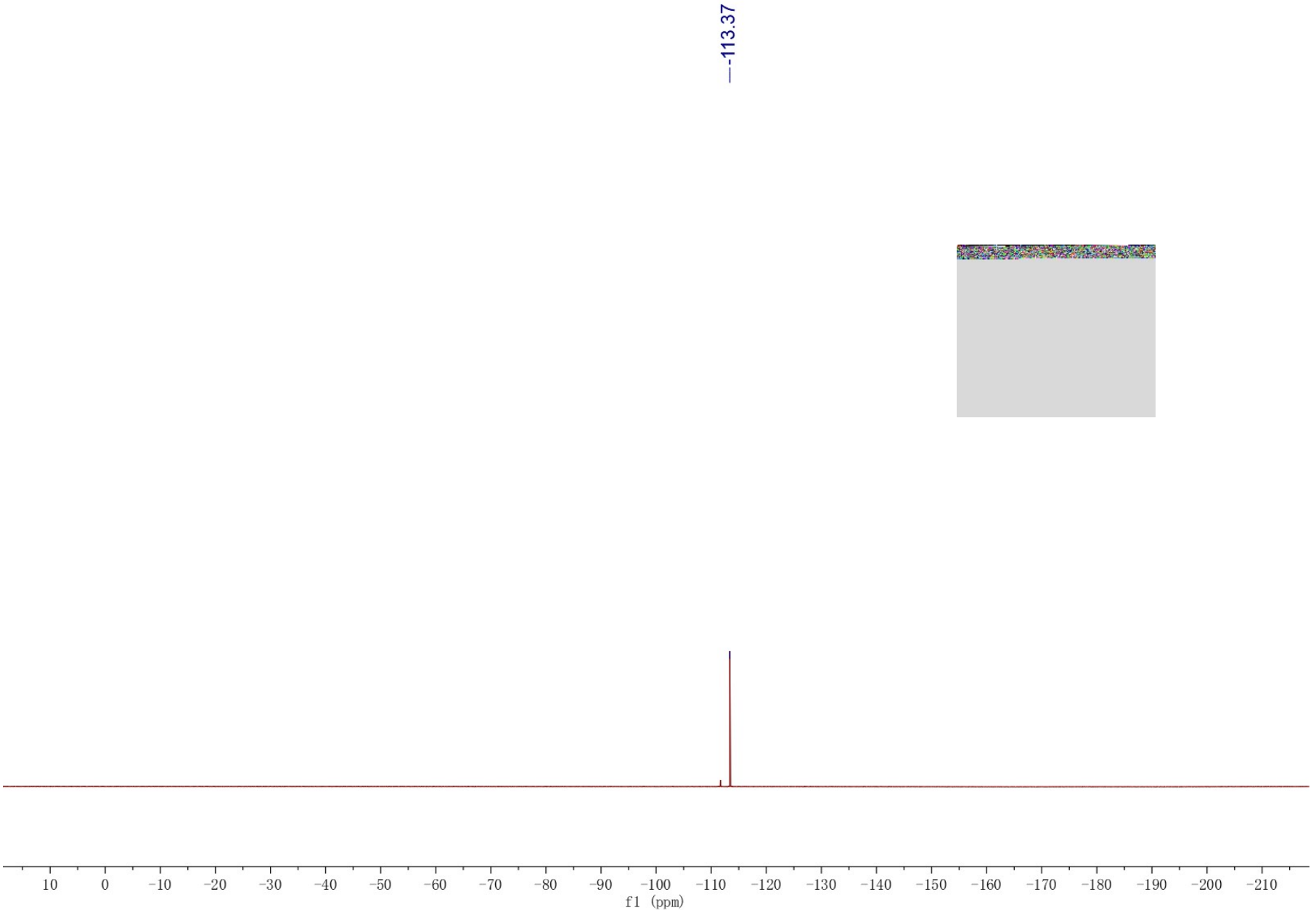
^{1}H NMR of 3fe (400 MHz, $CDCl_3$)



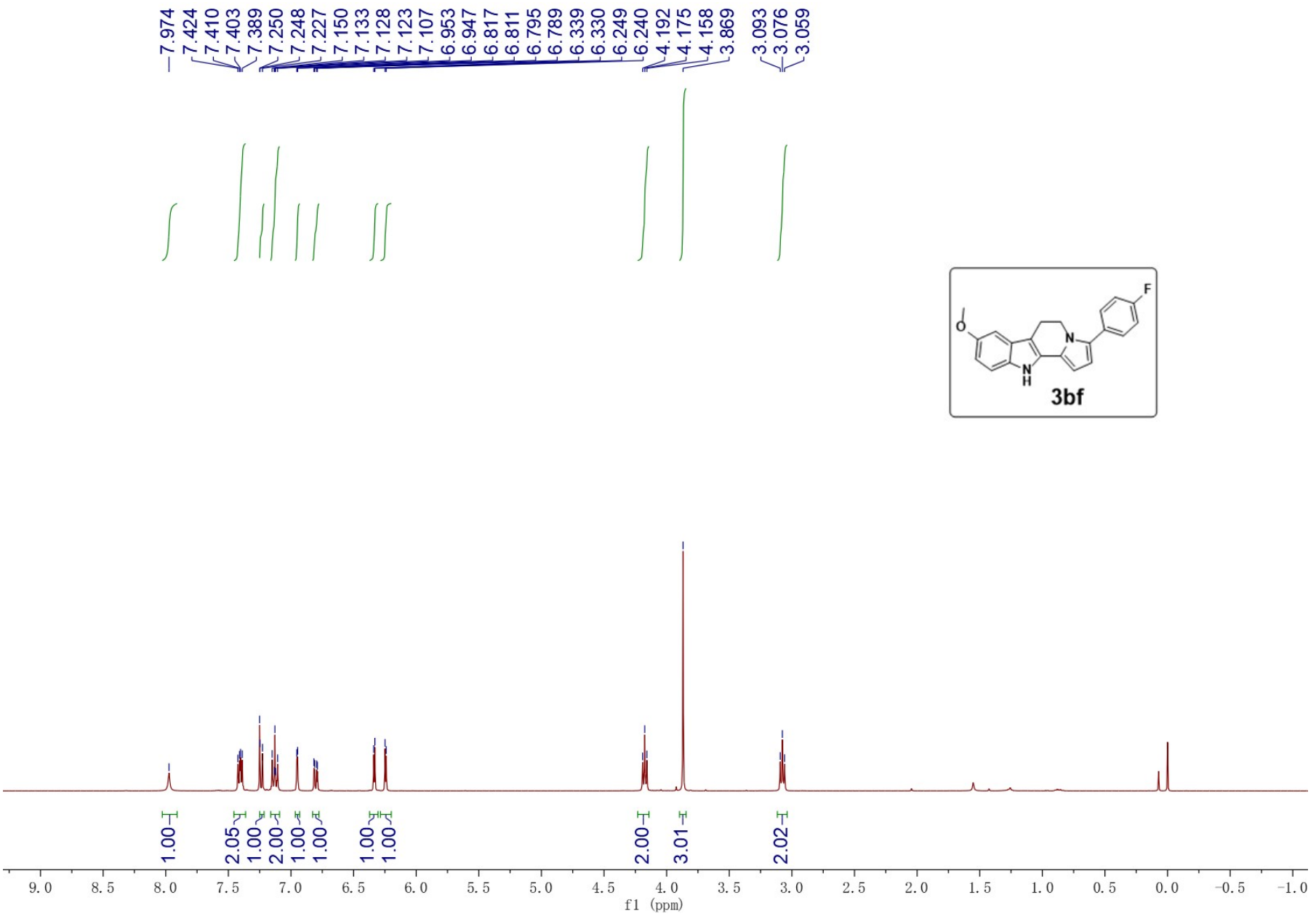
^{13}C NMR of 3fe (100 MHz, $CDCl_3$)



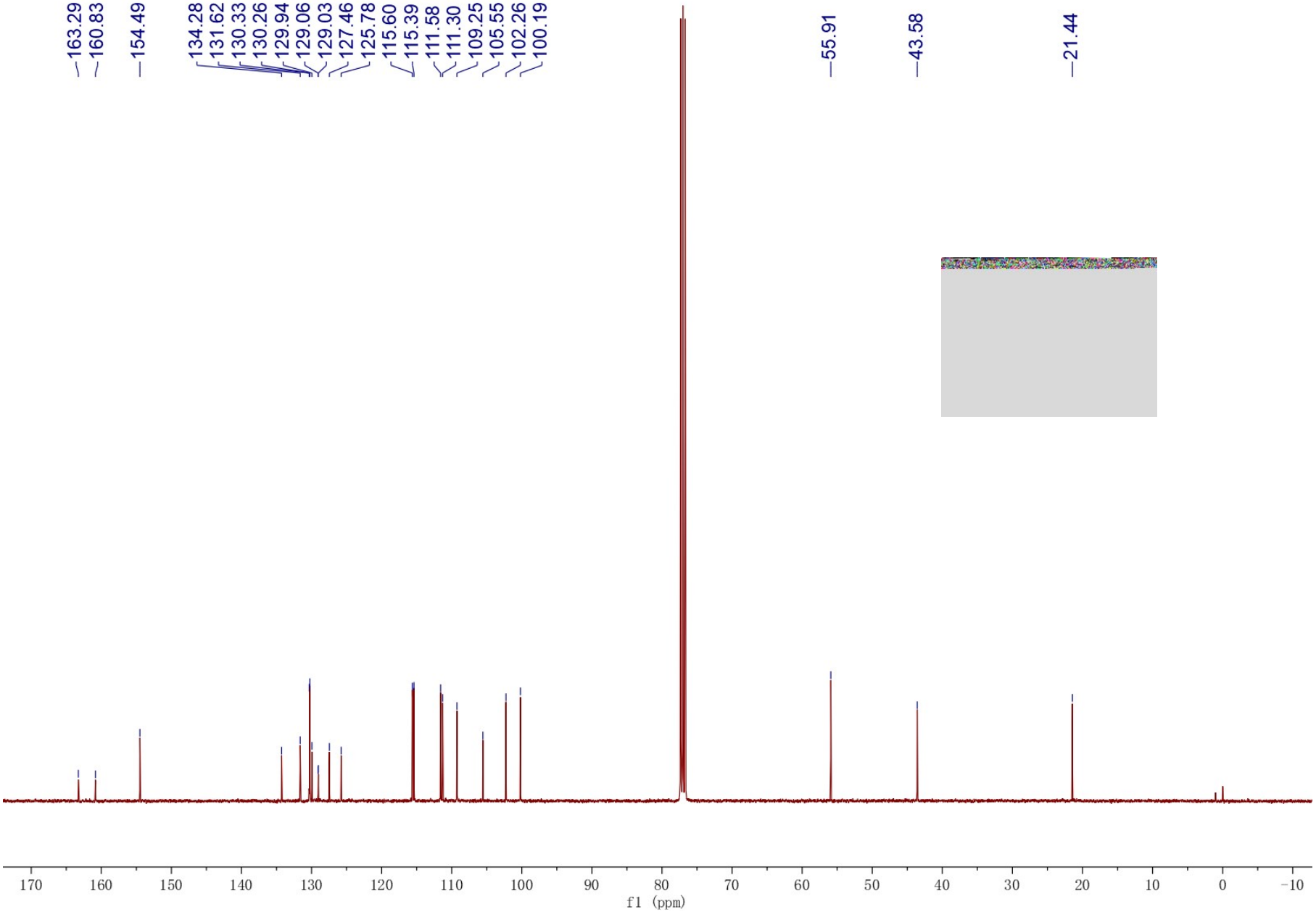
^{19}F NMR of 3fe (376 MHz, $CDCl_3$)



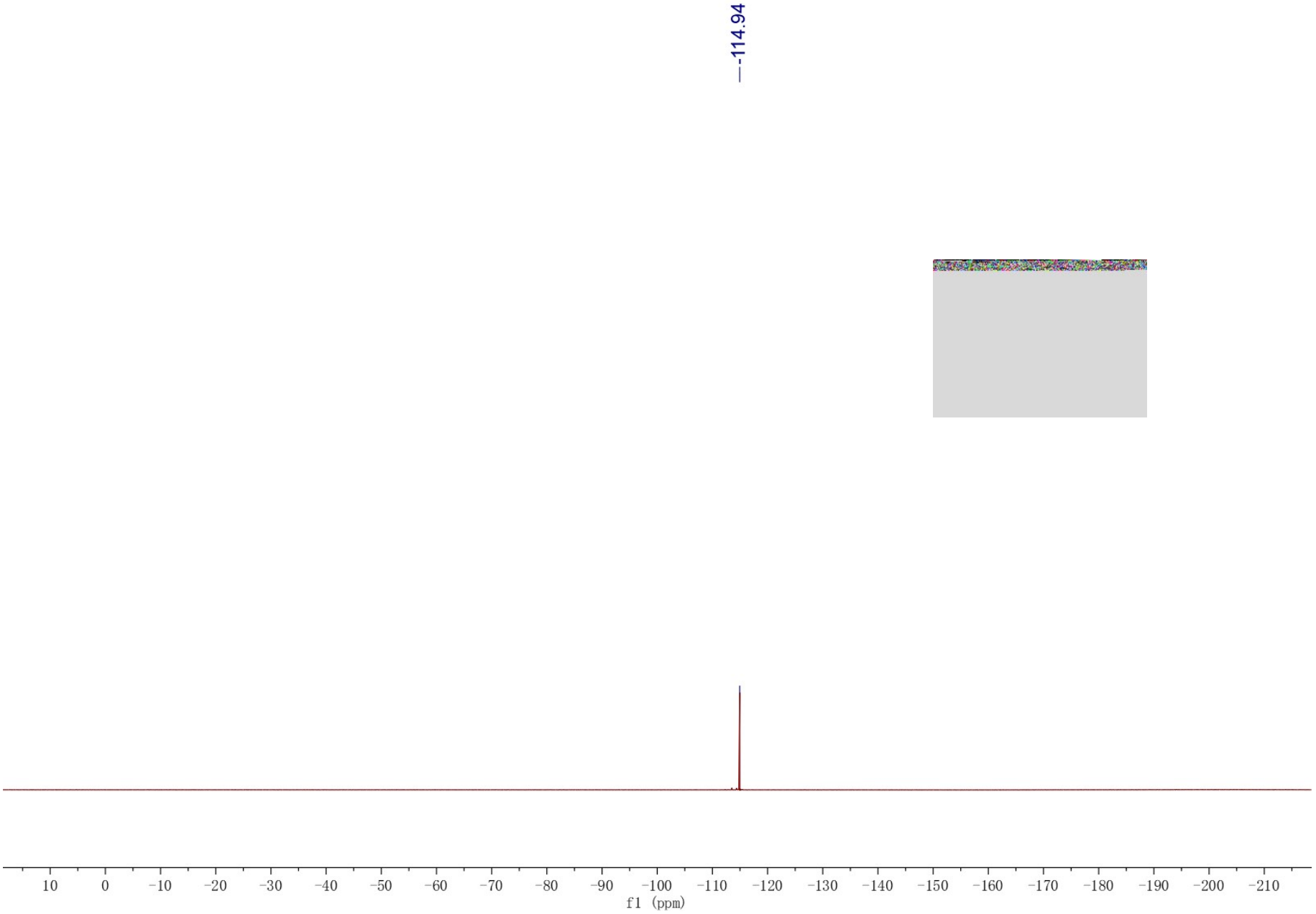
^{1}H NMR of 3bf (400 MHz, $CDCl_3$)



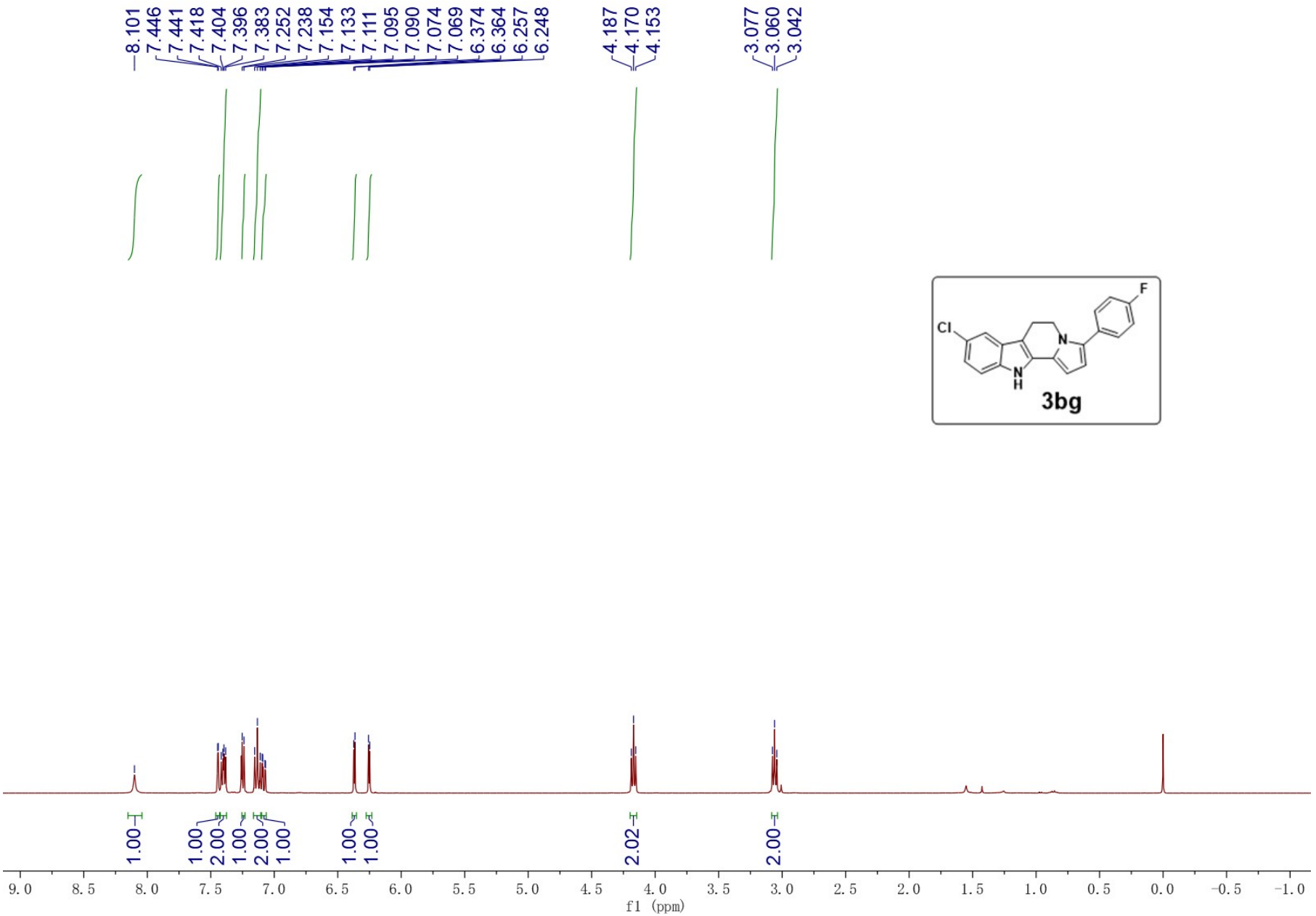
^{13}C NMR of 3bf (100 MHz, $CDCl_3$)



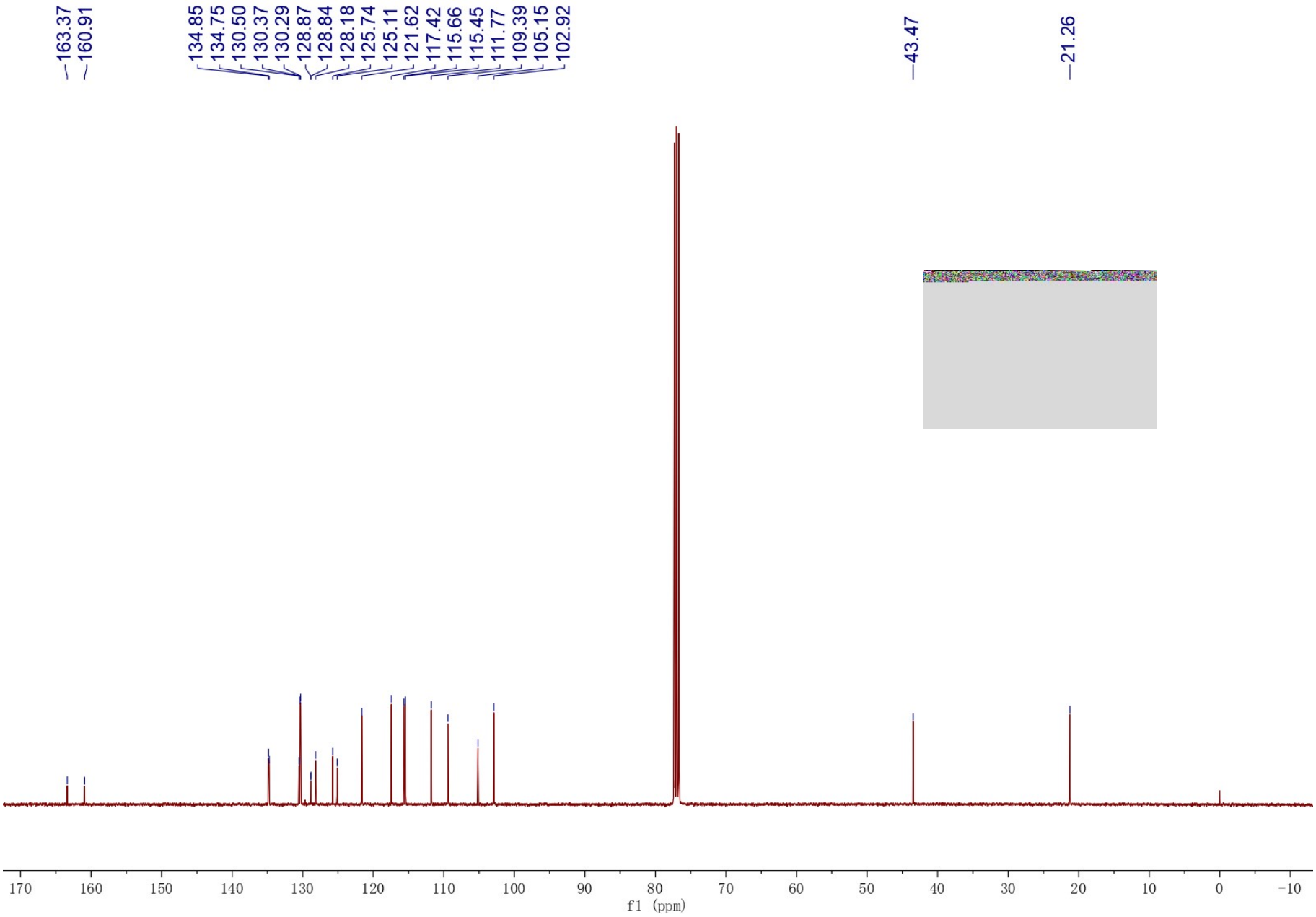
^{19}F NMR of 3bf (376 MHz, $CDCl_3$)



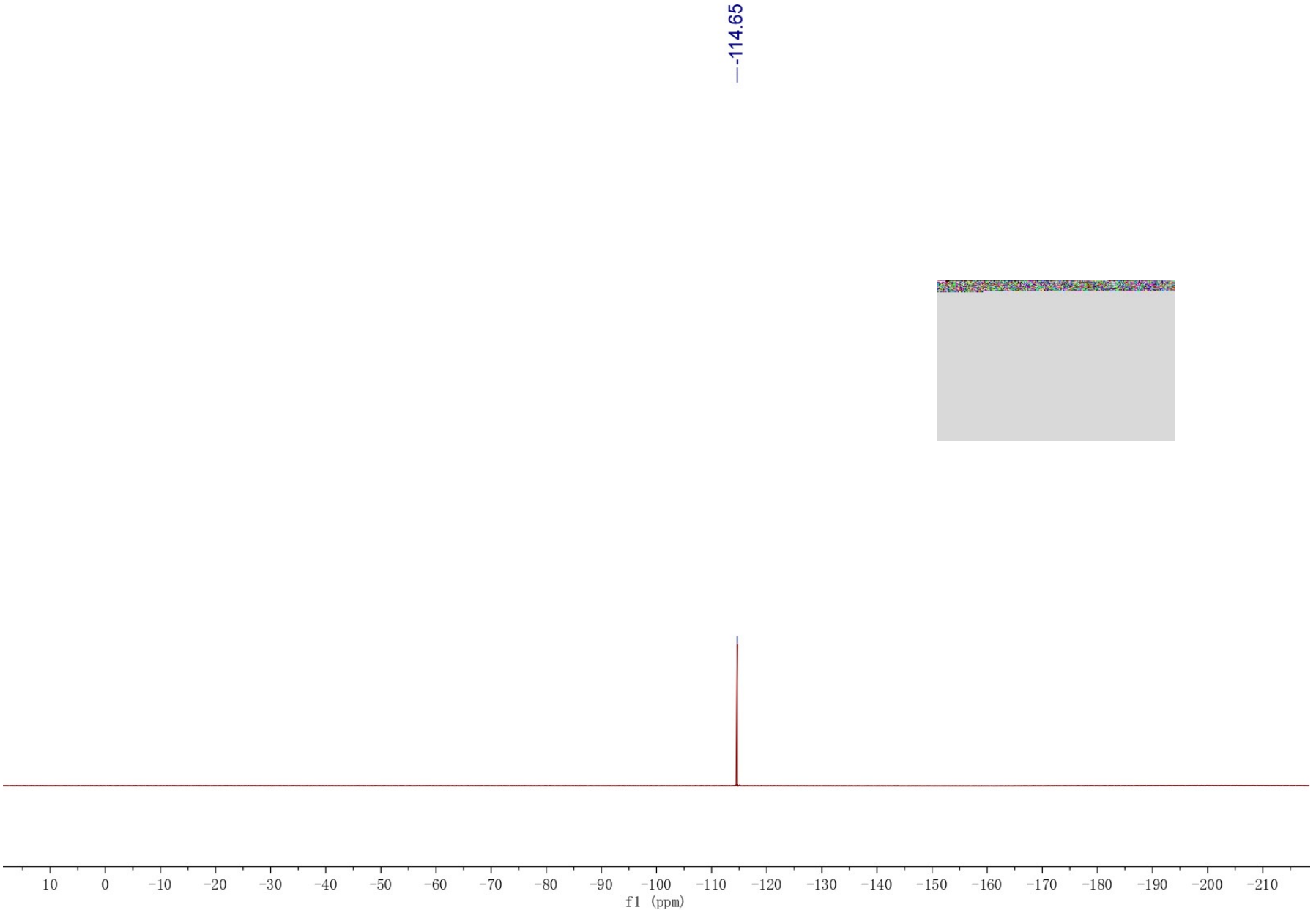
^{1}H NMR of 3bg (400 MHz, $CDCl_3$)



^{13}C NMR of 3bg (100 MHz, $CDCl_3$)

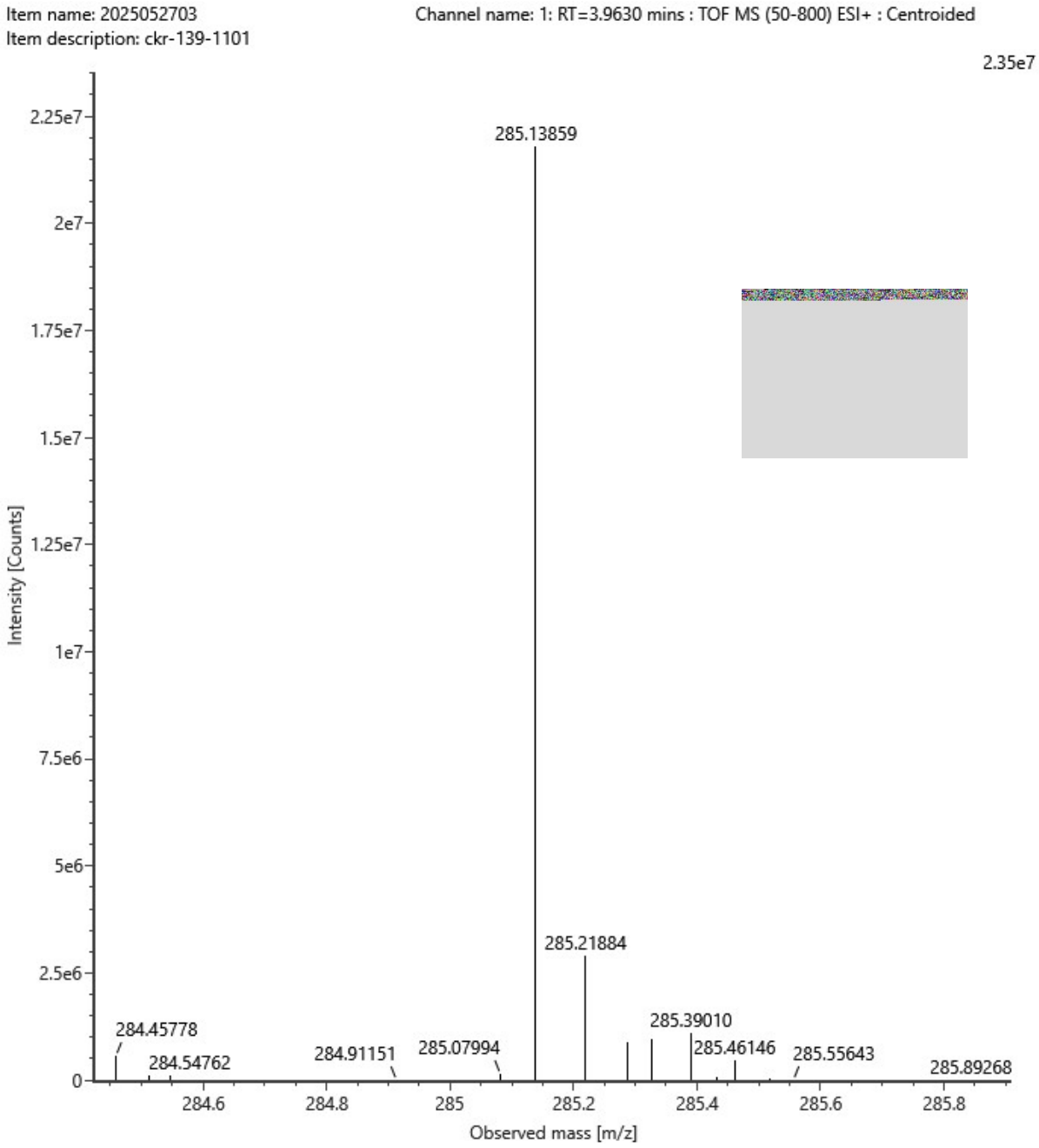


^{19}F NMR of 3bg (376 MHz, $CDCl_3$)

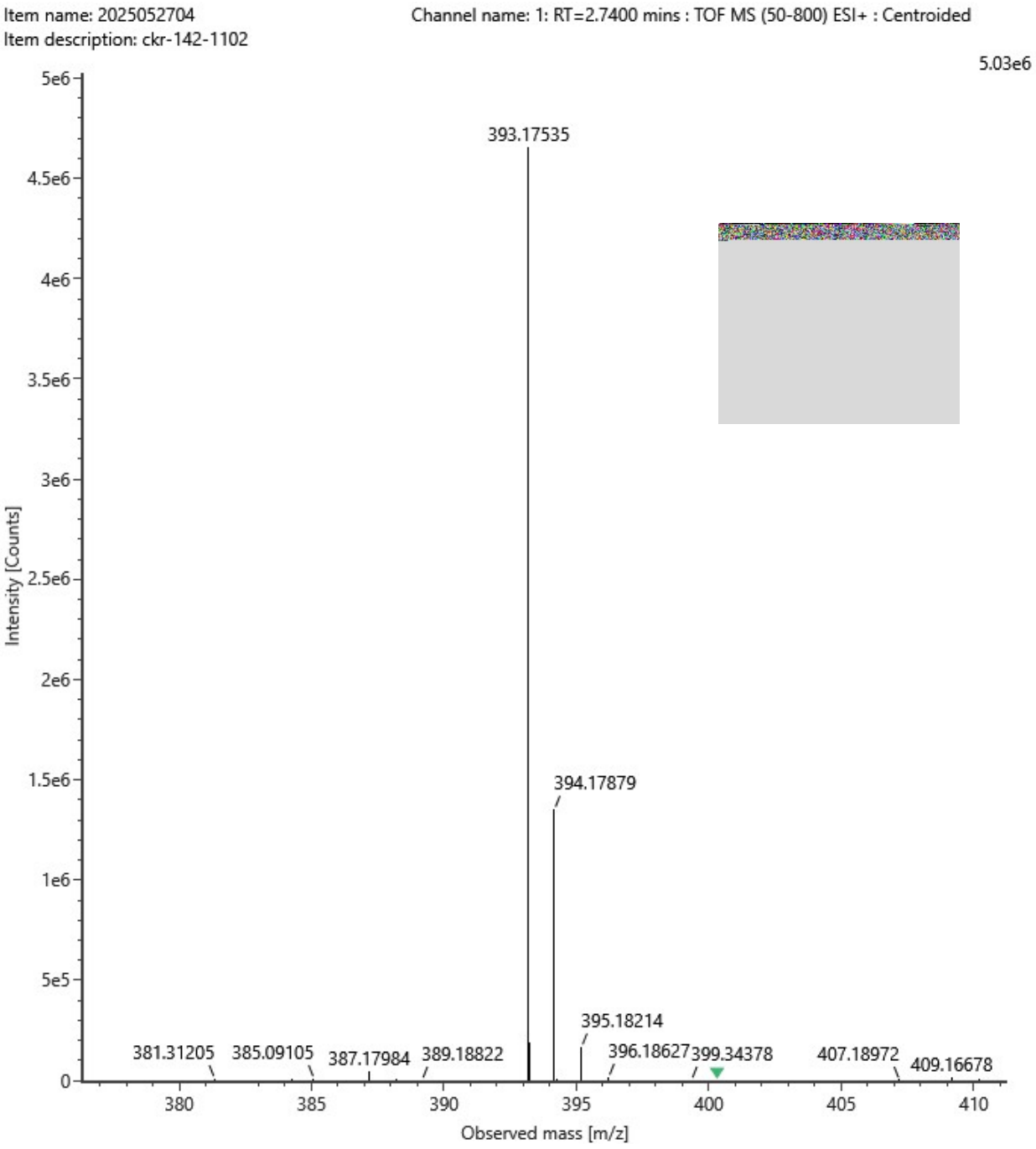


High-Resolution Mass Spectrometry (HRMS) Spectrum

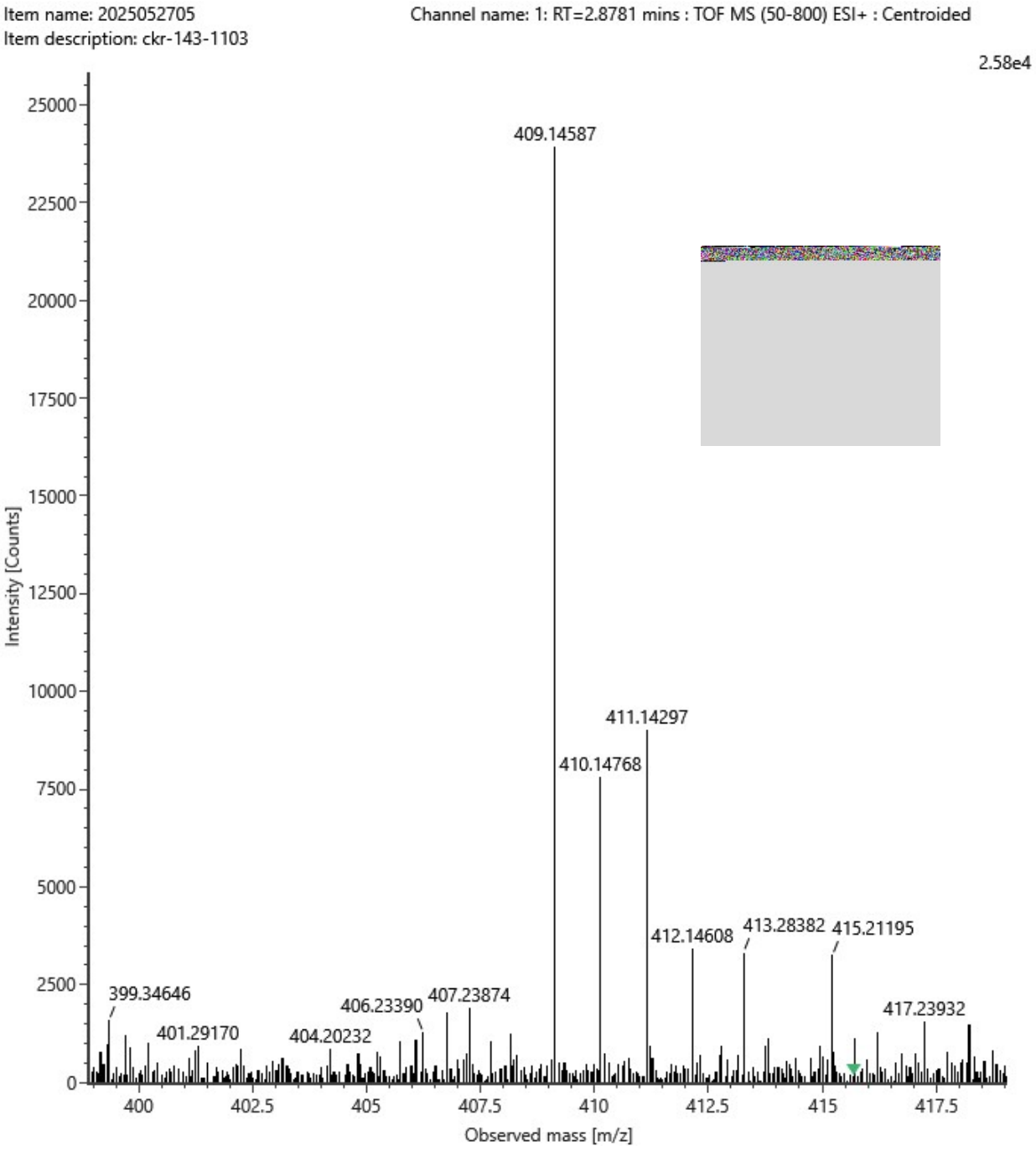
3aa. HRMS（ESI）m/z calcd for $C_{20}H_{17}N_2^+$ $(M+H)^+$ 285.1386, found 285.1386;



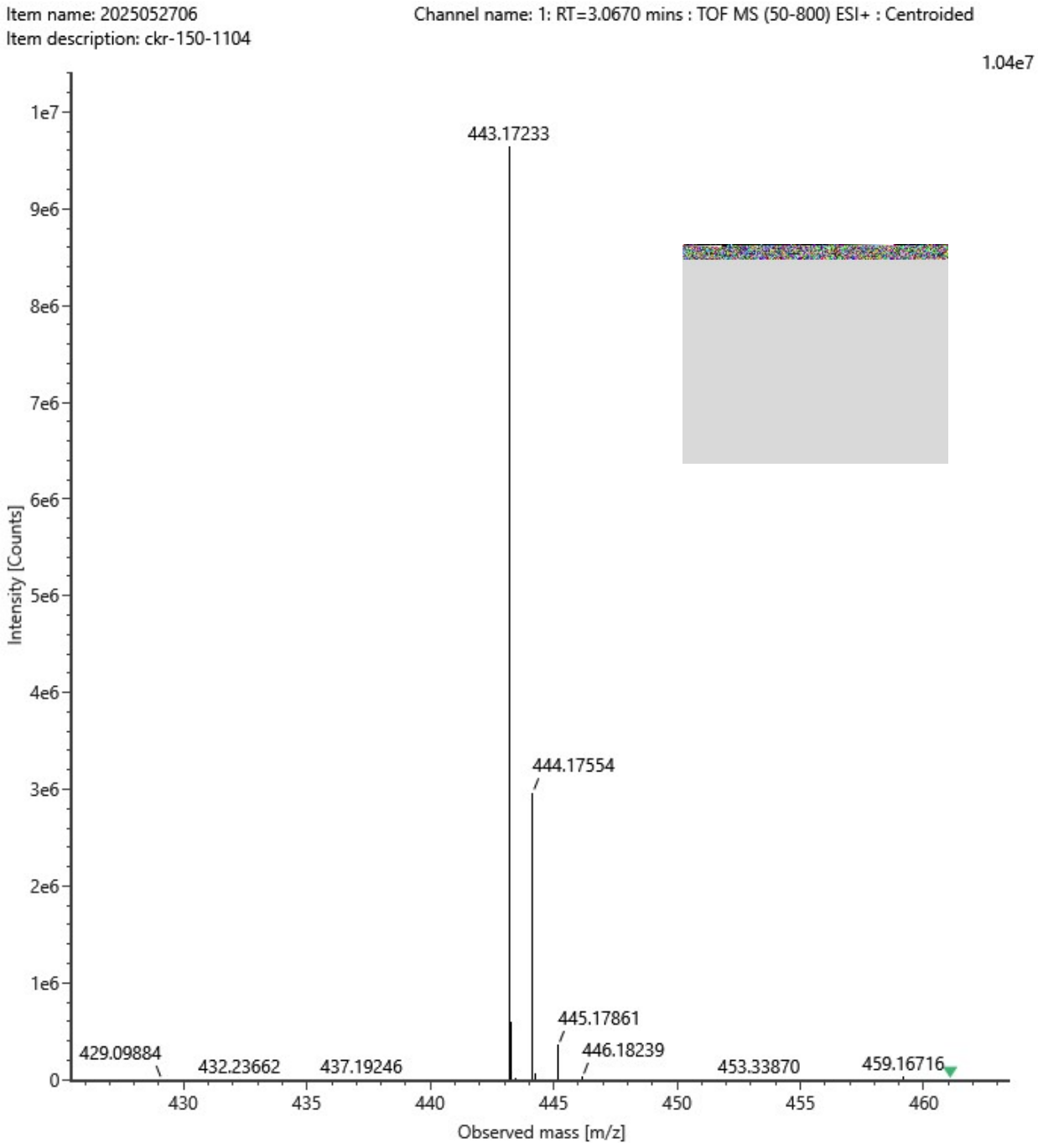
3ab. HRMS（ESI）m/z calcd for $C_{27}H_{22}FN_2^+$ $(M+H)^+$ 393.1762, found 393.1754;



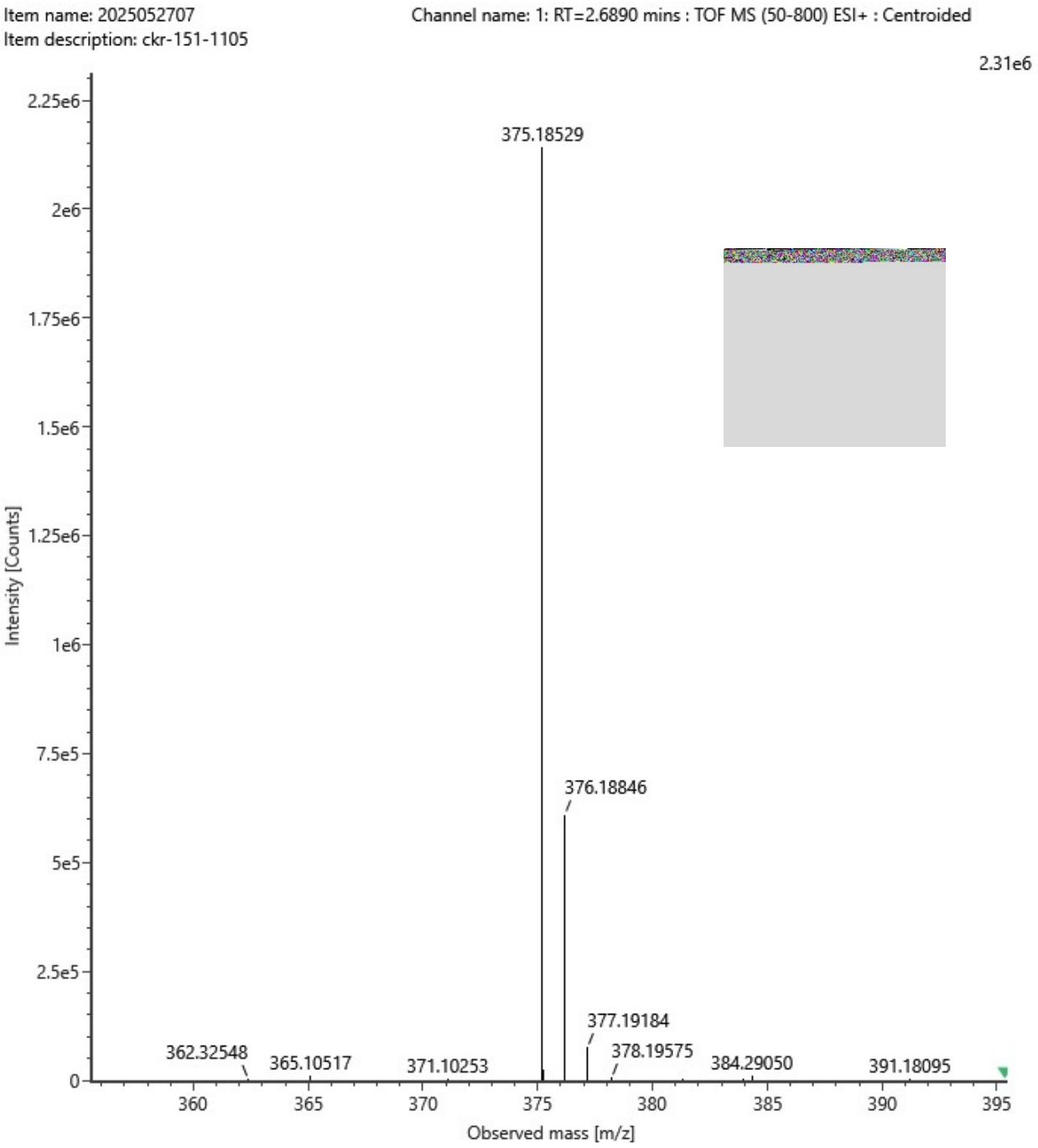
3ac. HRMS（ESI）m/z calcd for $C_{27}H_{22}ClN_2^+$ $(M+H)^+$ 409.1466, found 409.1459;



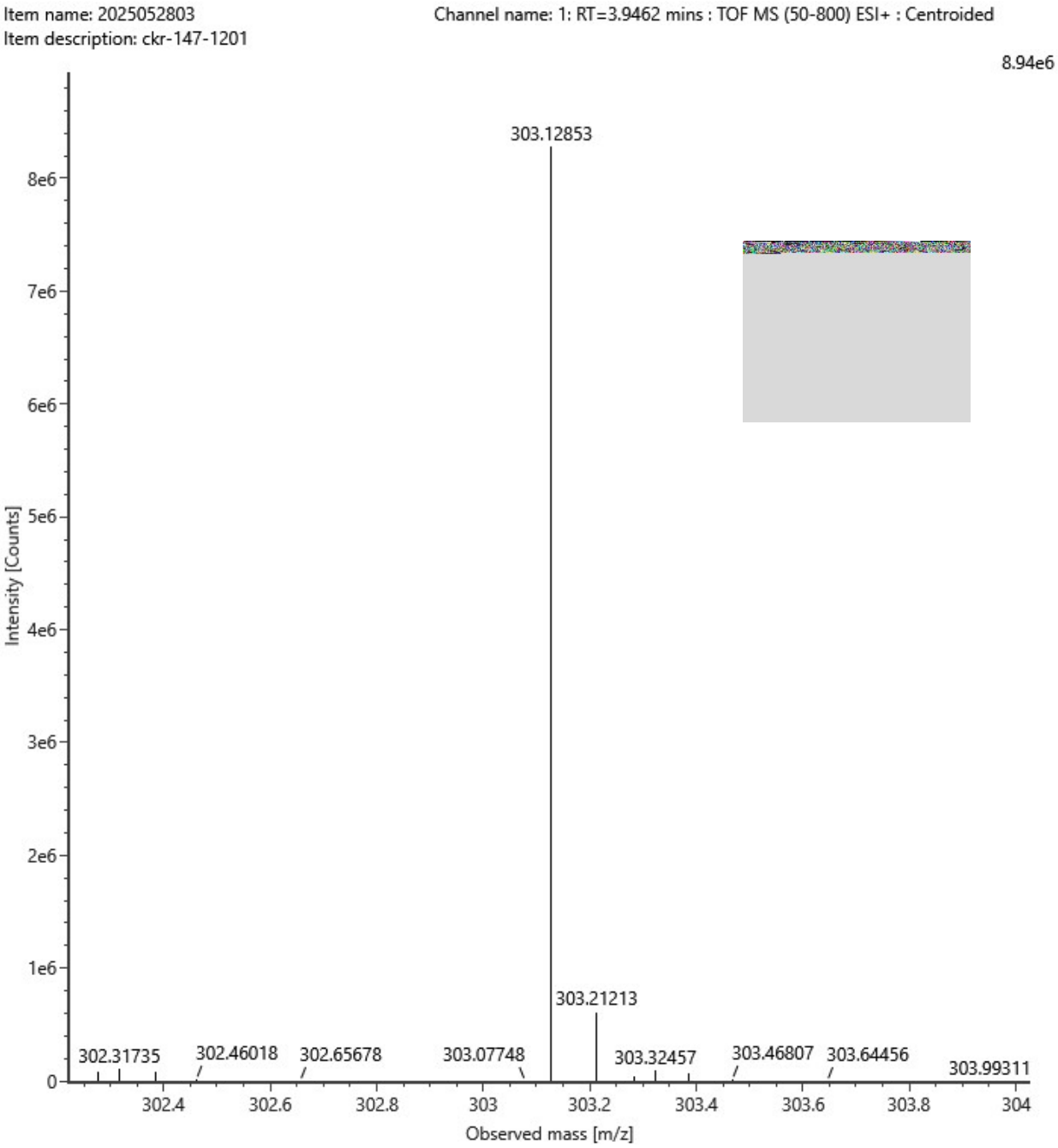
3ad. HRMS（ESI）m/z calcd for $C_{28}H_{22}F_3N_2^+$ $(M+H)^+$ 443.1730, found 443.1723



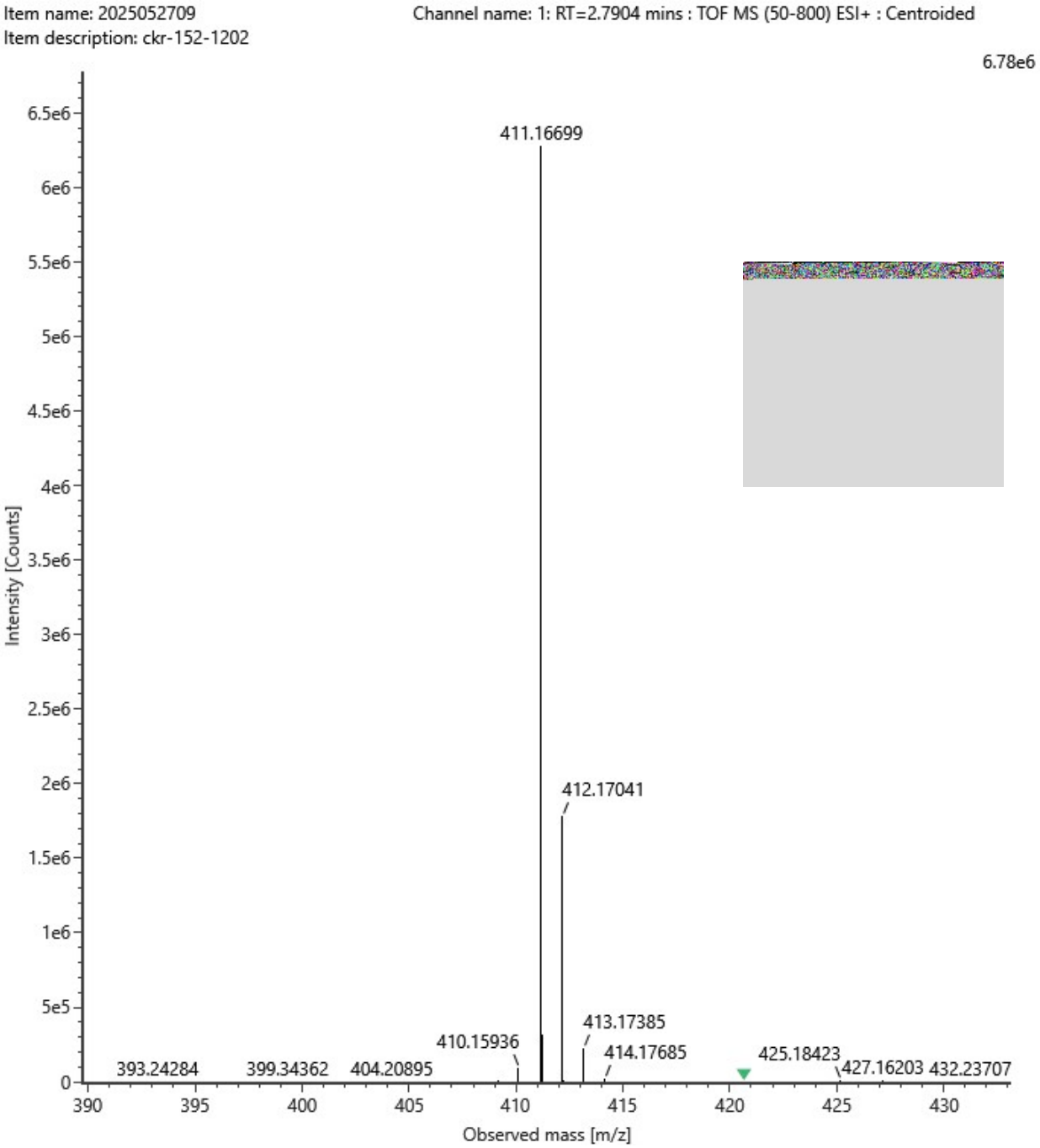
3ae. HRMS（ESI）m/z calcd for $C_{27}H_{23}N_2^+$ $(M+H)^+$ 375.1856, found 375.1853;



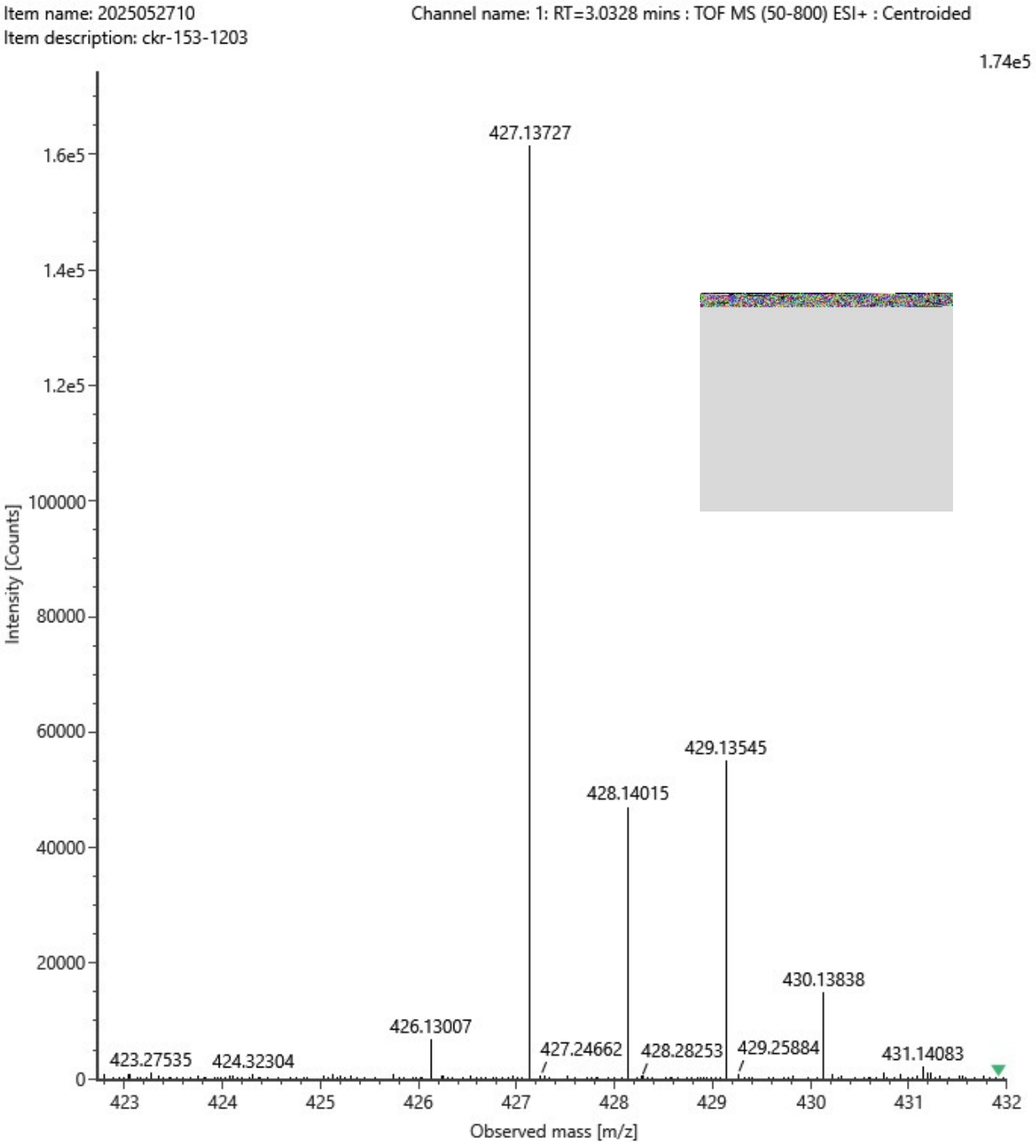
3ba. HRMS（ESI）m/z calcd for $C_{20}H_{16}FN_2^+$ $(M+H)^+$ 303.1292, found 303.1285;



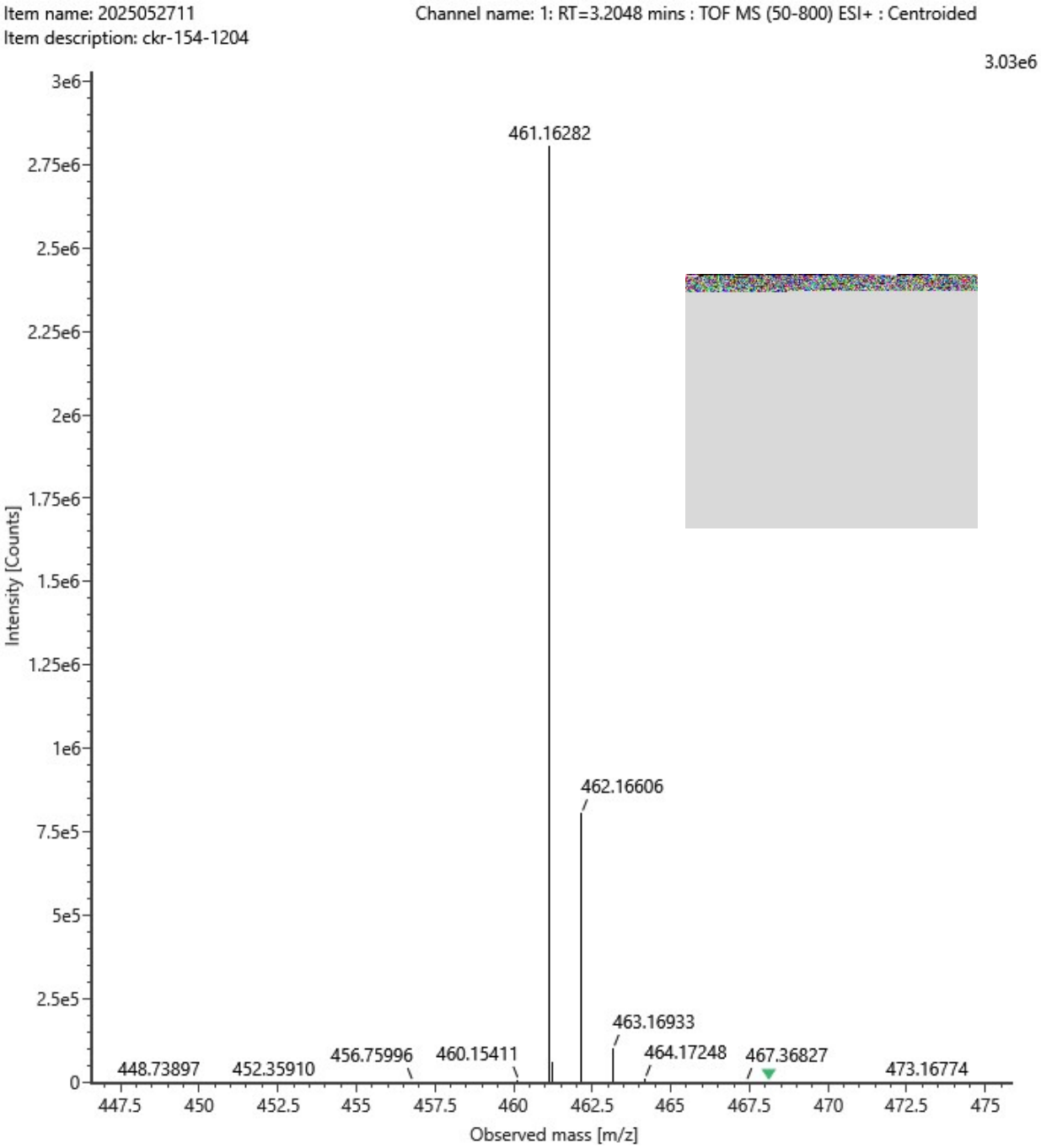
3bb. HRMS（ESI）m/z calcd for $C_{27}H_{21}F_2N_2^+$ $(M+H)^+$ 411.1667, found 411.1670;



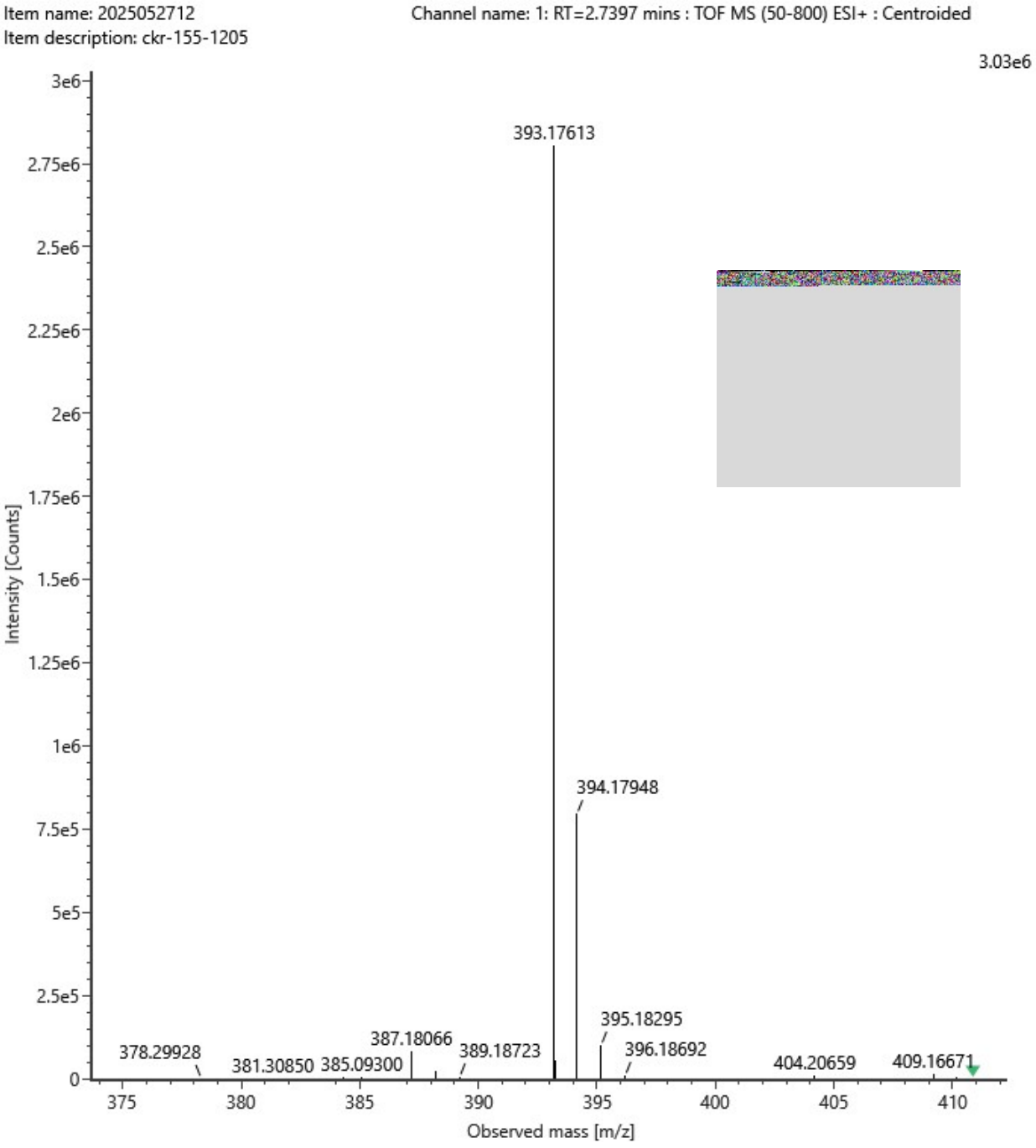
3bc. HRMS（ESI）m/z calcd for $C_{27}H_{21}ClFN_2^+$ $(M+H)^+$ 427.1372, found 427.1373;



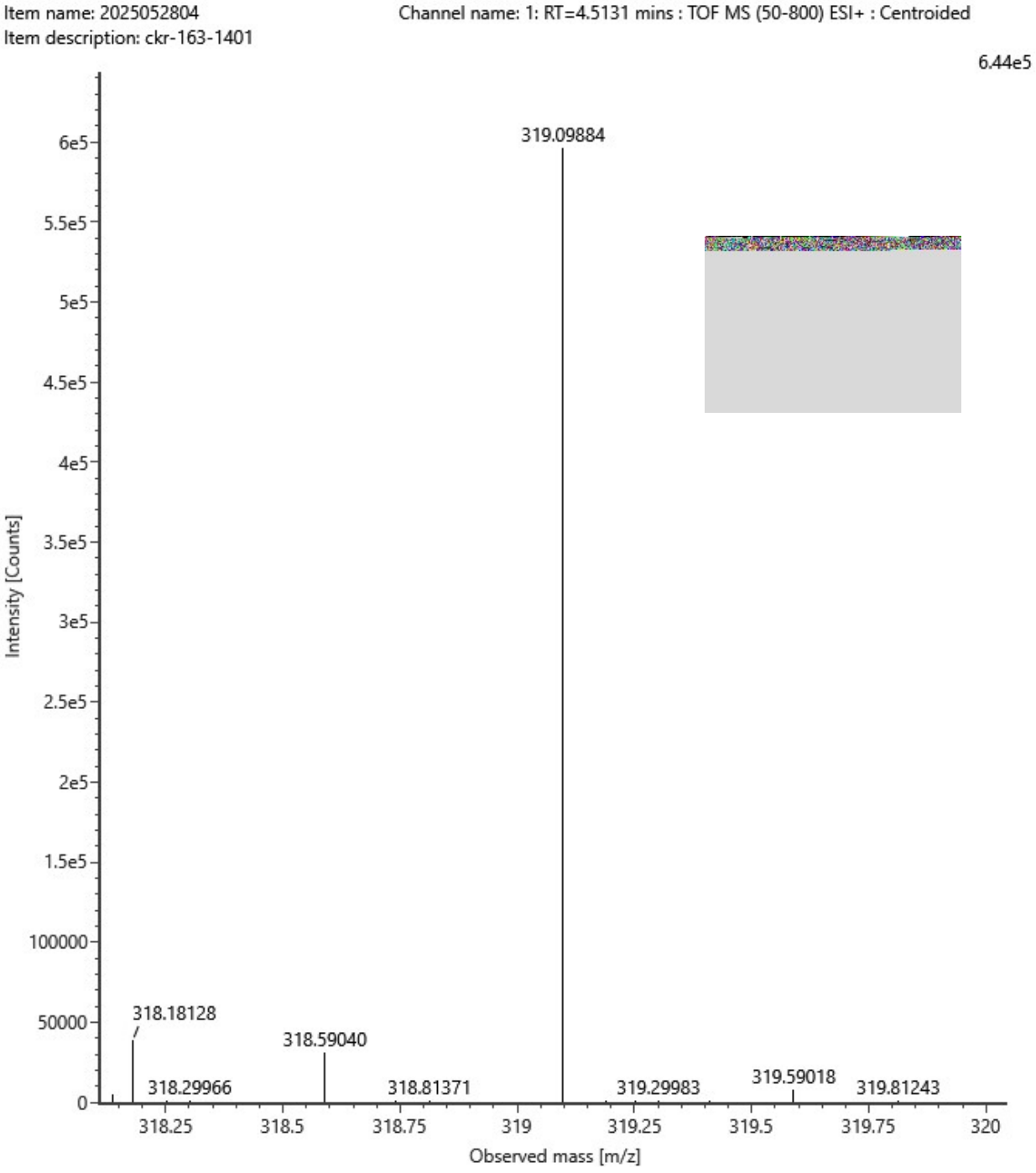
3bd. HRMS（ESI）m/z calcd for $C_{28}H_{21}F_4N_2^+$ $(M+H)^+$ 461.1635, found 461.1628;



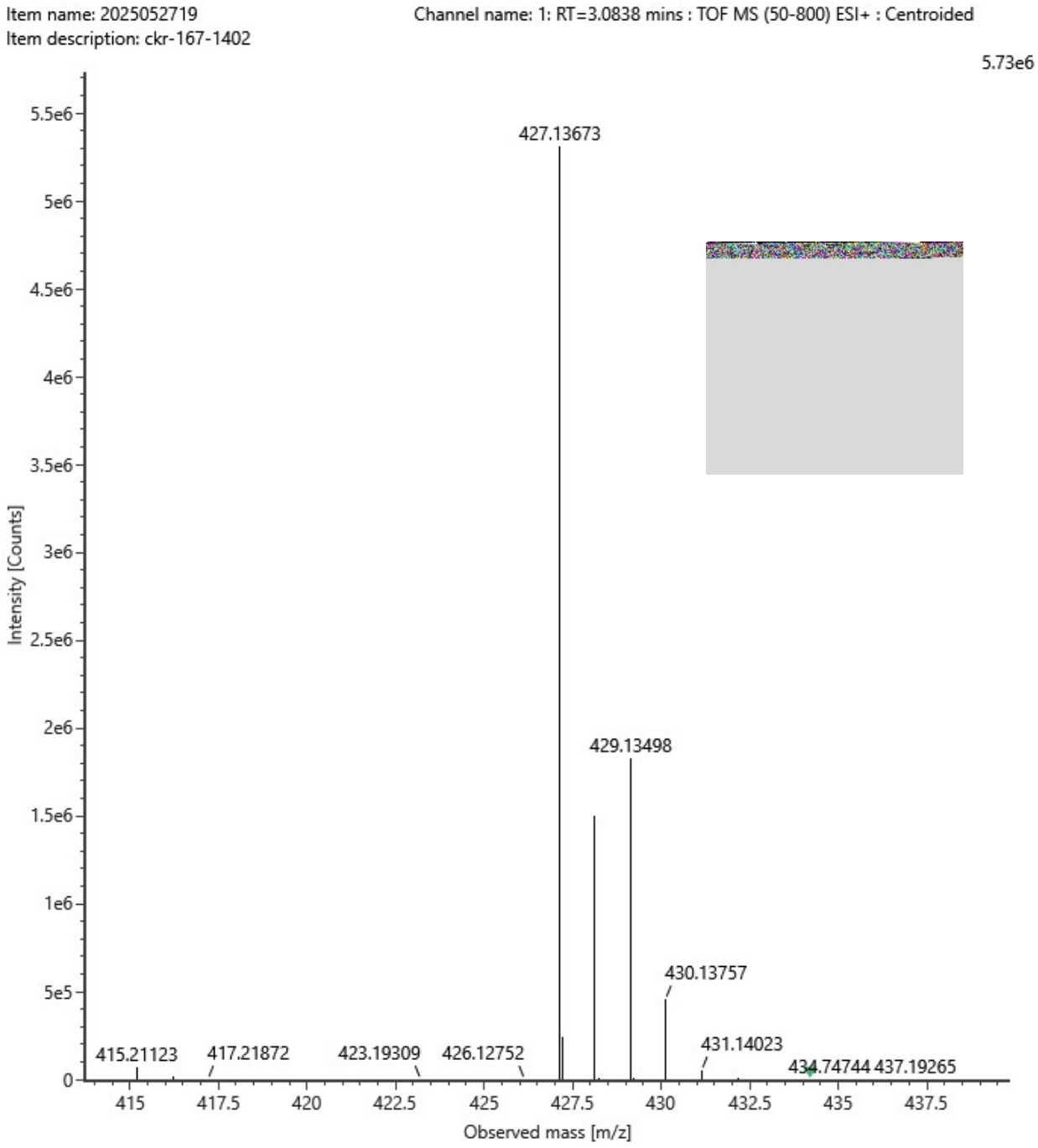
3be. HRMS（ESI）m/z calcd for $C_{27}H_{22}FN_2^+$ $(M+H)^+$ 393.1762, found 393.1761;



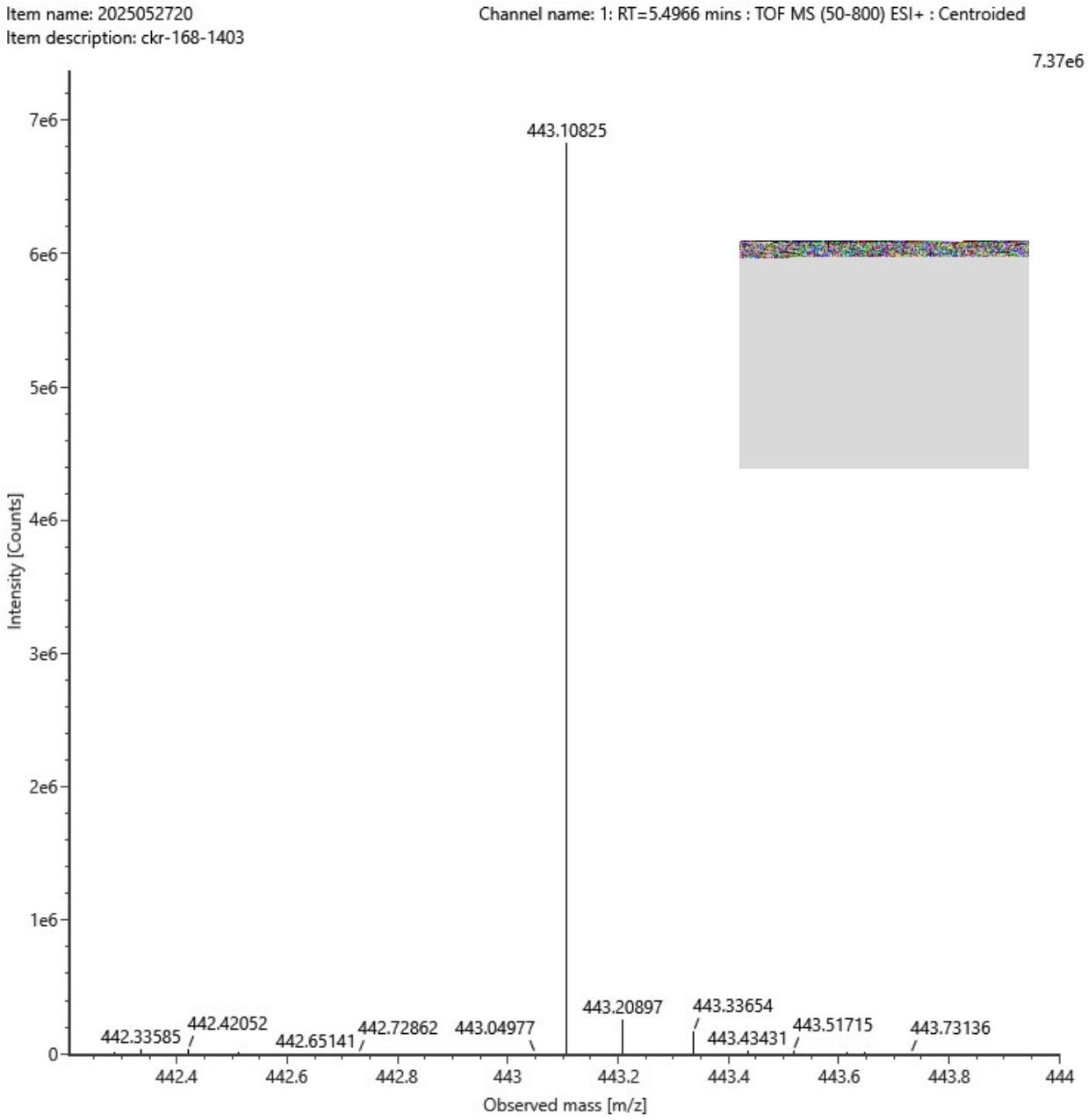
3ca. HRMS（ESI）m/z calcd for $C_{20}H_{16}ClN_2^+$ $(M+H)^+$ 319.0996, found 319.0988;



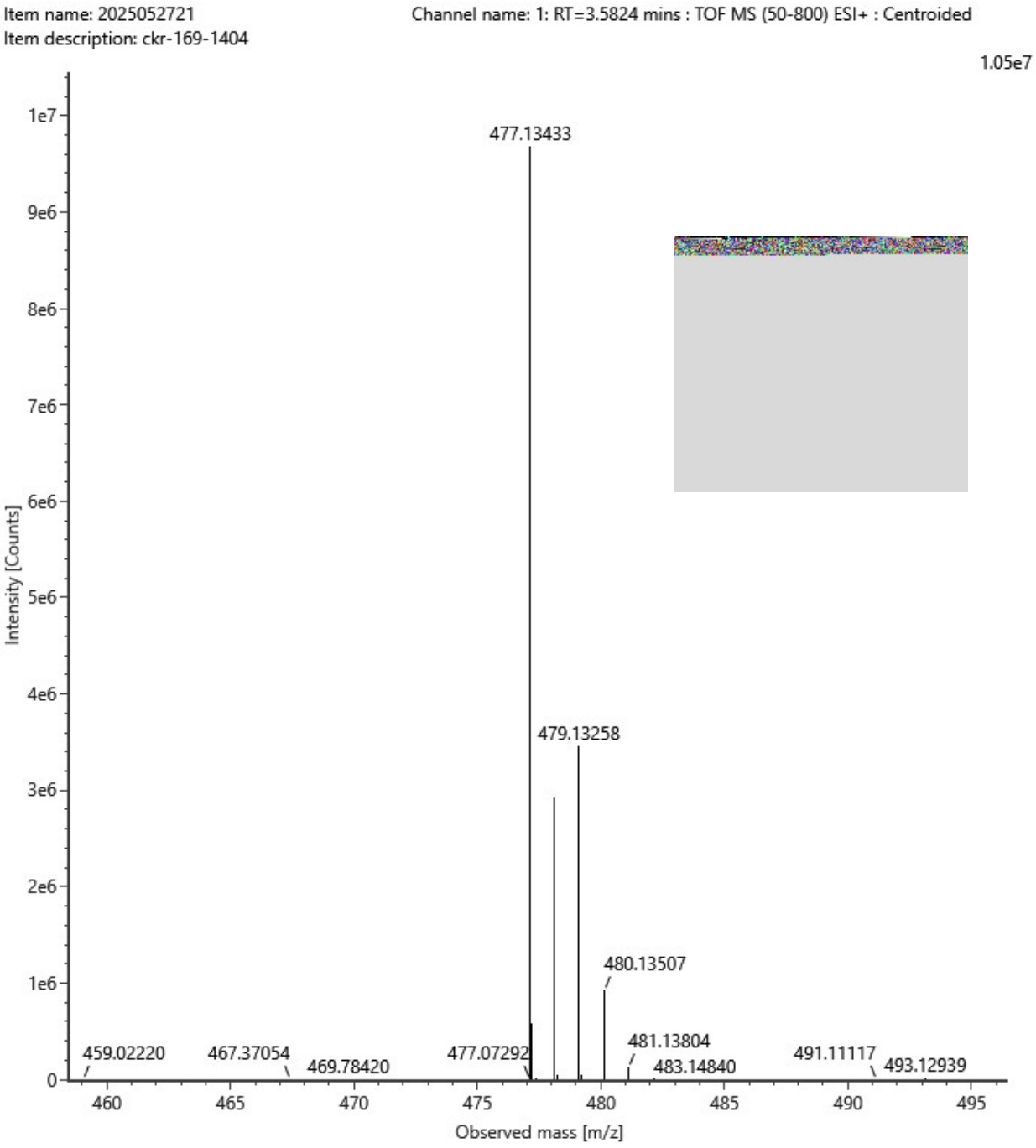
3cb. HRMS（ESI）m/z calcd for $C_{27}H_{21}ClFN_2^+$ $(M+H)^+$ 427.1372, found 427.1367;



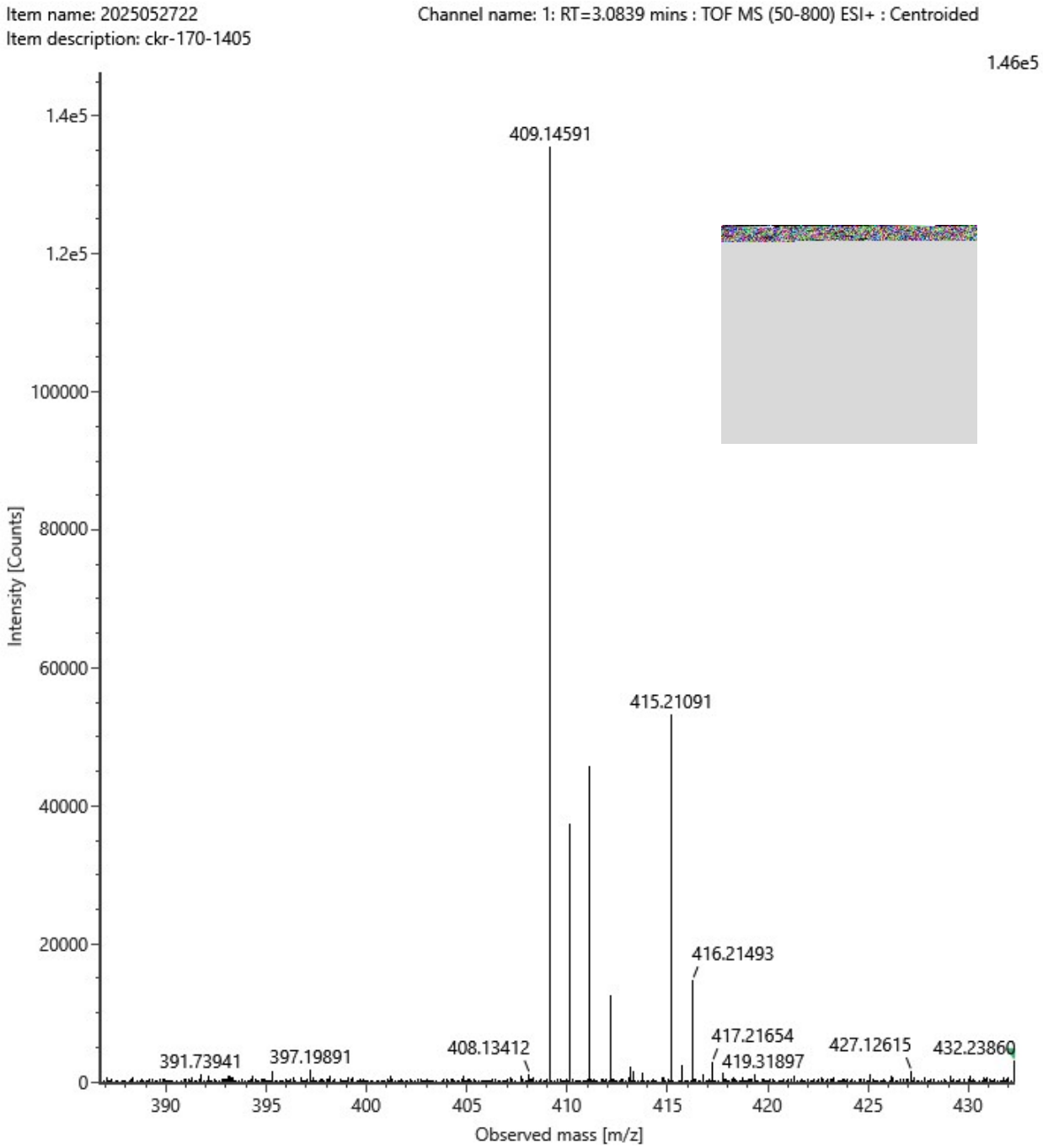
3cc. HRMS（ESI）m/z calcd for $C_{27}H_{21}Cl_2N_2^+$ $(M+H)^+$ 443.1076, found 443.1082;



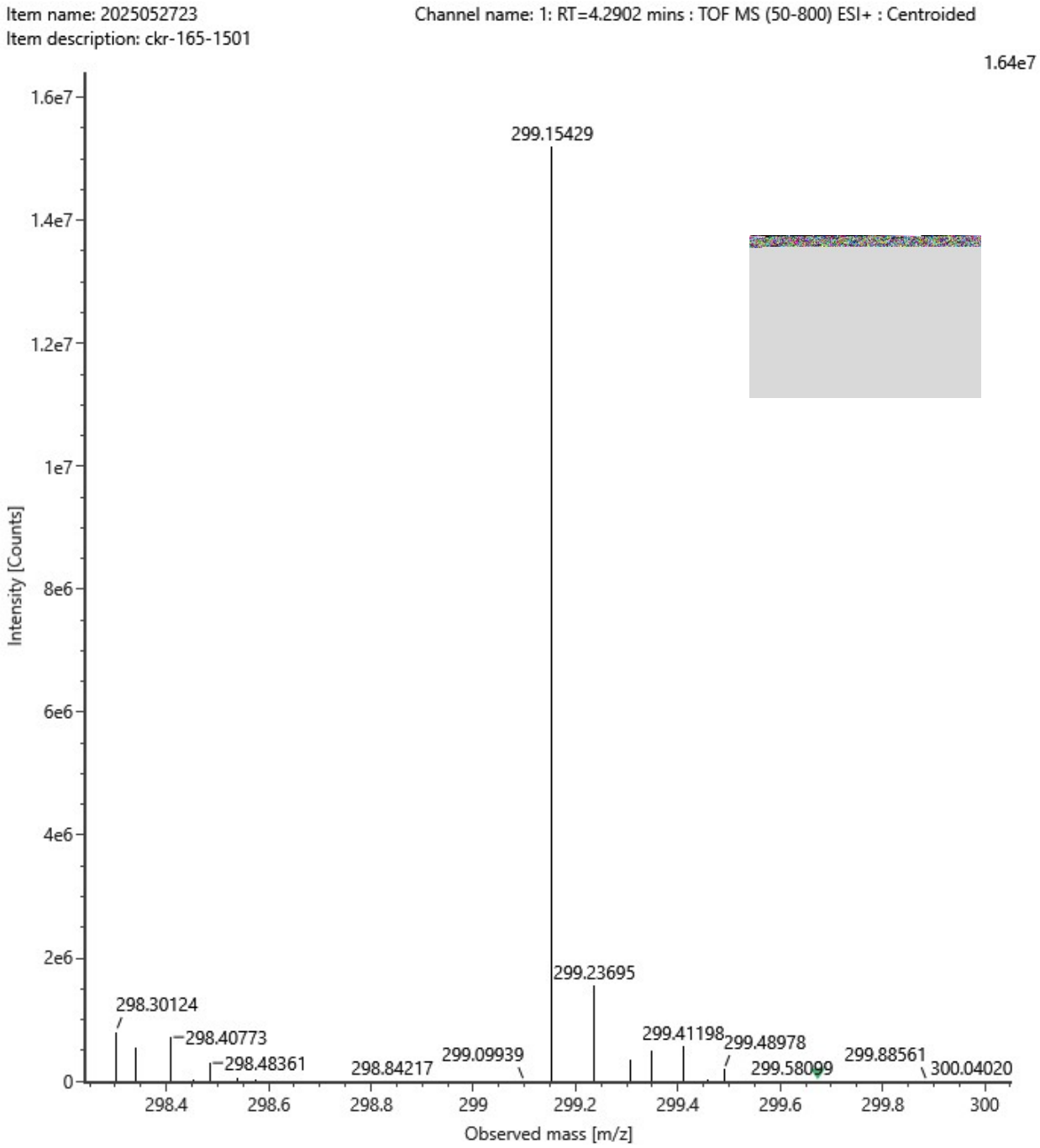
3cd. HRMS（ESI）m/z calcd for $C_{28}H_{21}ClF_3N_2^+$ $(M+H)^+$ 477.1340, found 477.1343;



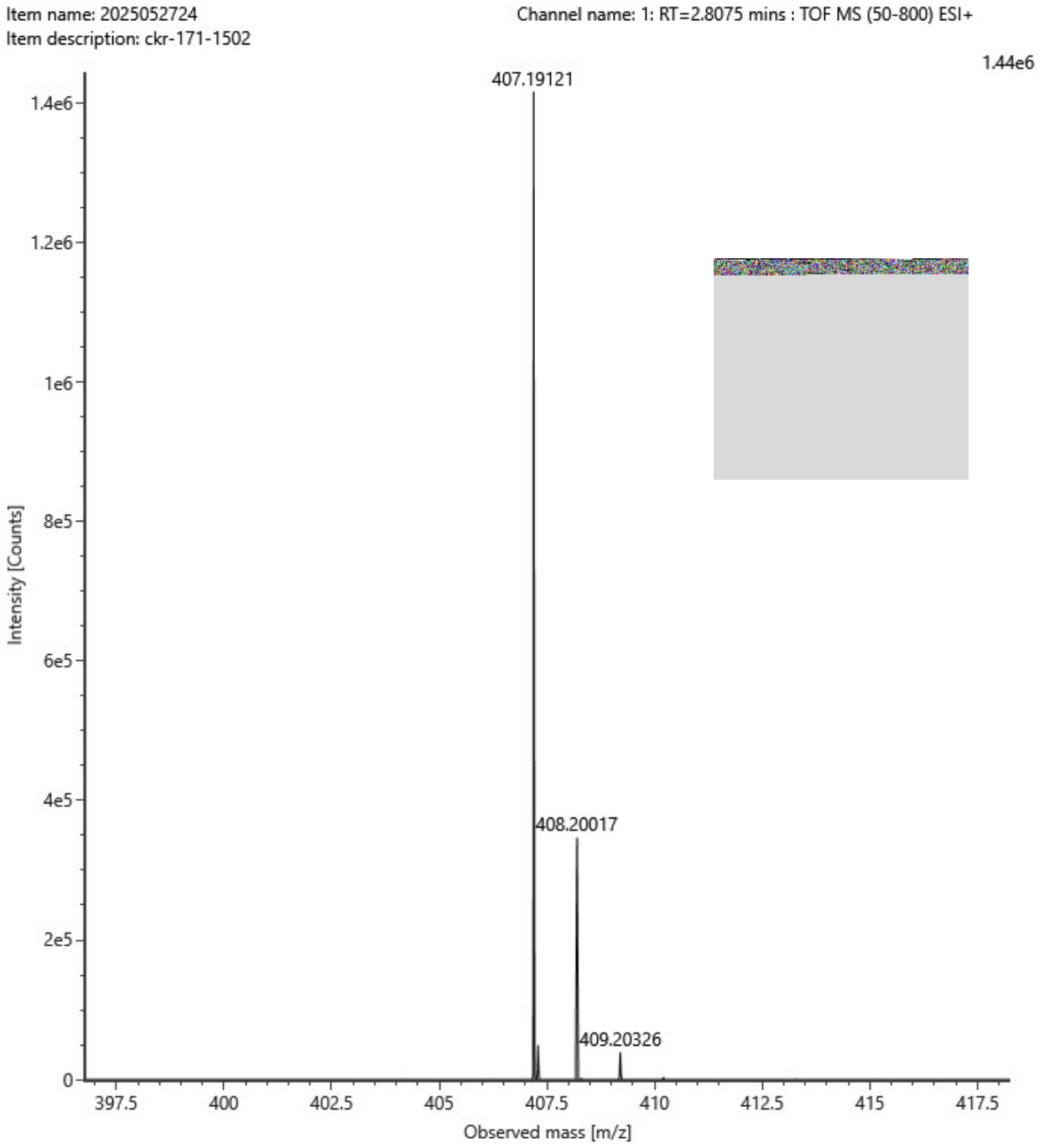
3ce. HRMS（ESI）m/z calcd for $C_{27}H_{22}ClN_2^+$ $(M+H)^+$ 409.1466, found 409.1459;



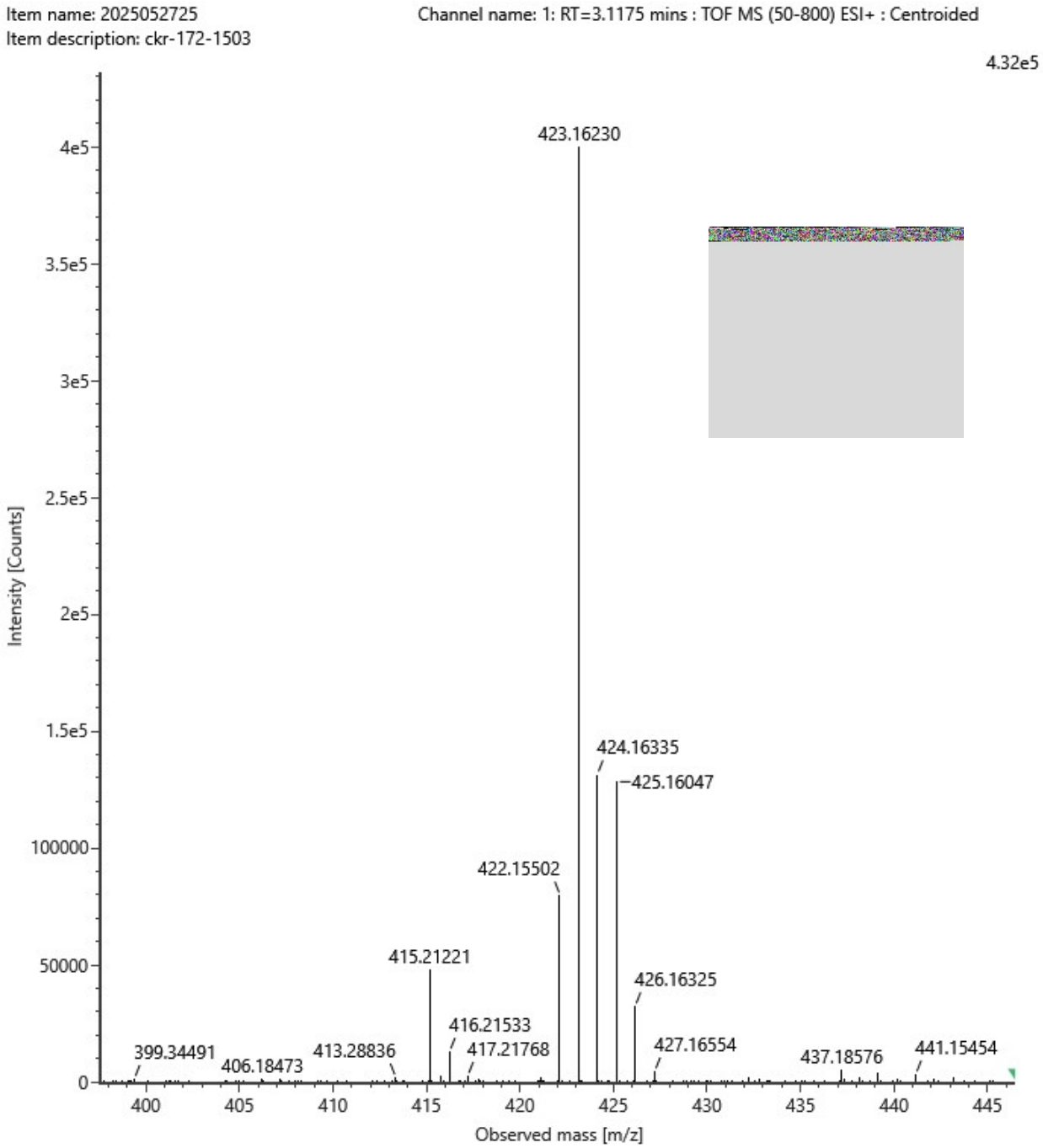
3da. HRMS（ESI）m/z calcd for $C_{21}H_{19}N_2^+$ $(M+H)^+$ 299.1543, found 299.1543;



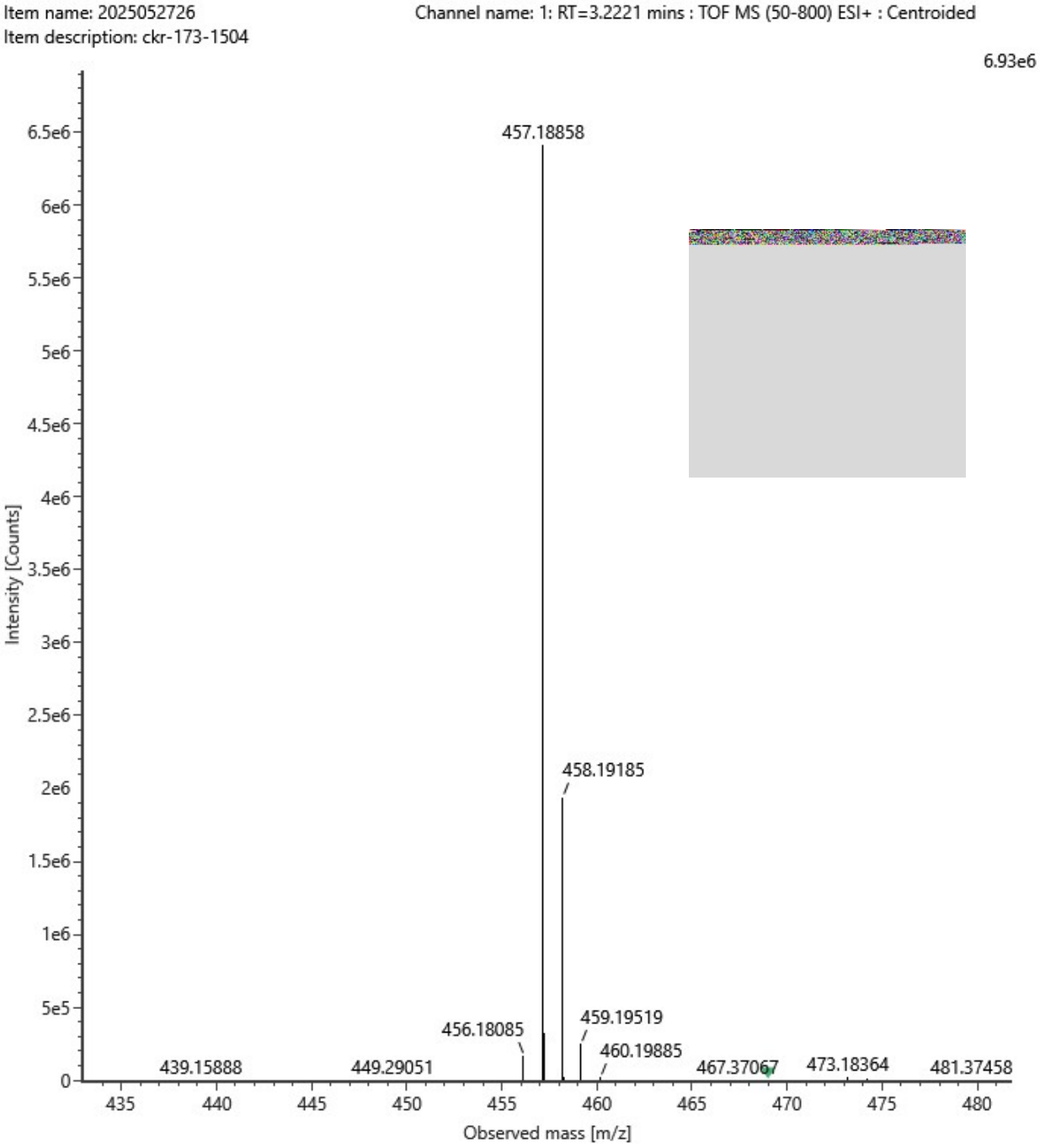
3db. HRMS（ESI）m/z calcd for $C_{28}H_{24}FN_2^+$ $(M+H)^+$ 407.1918, found 407.1912;



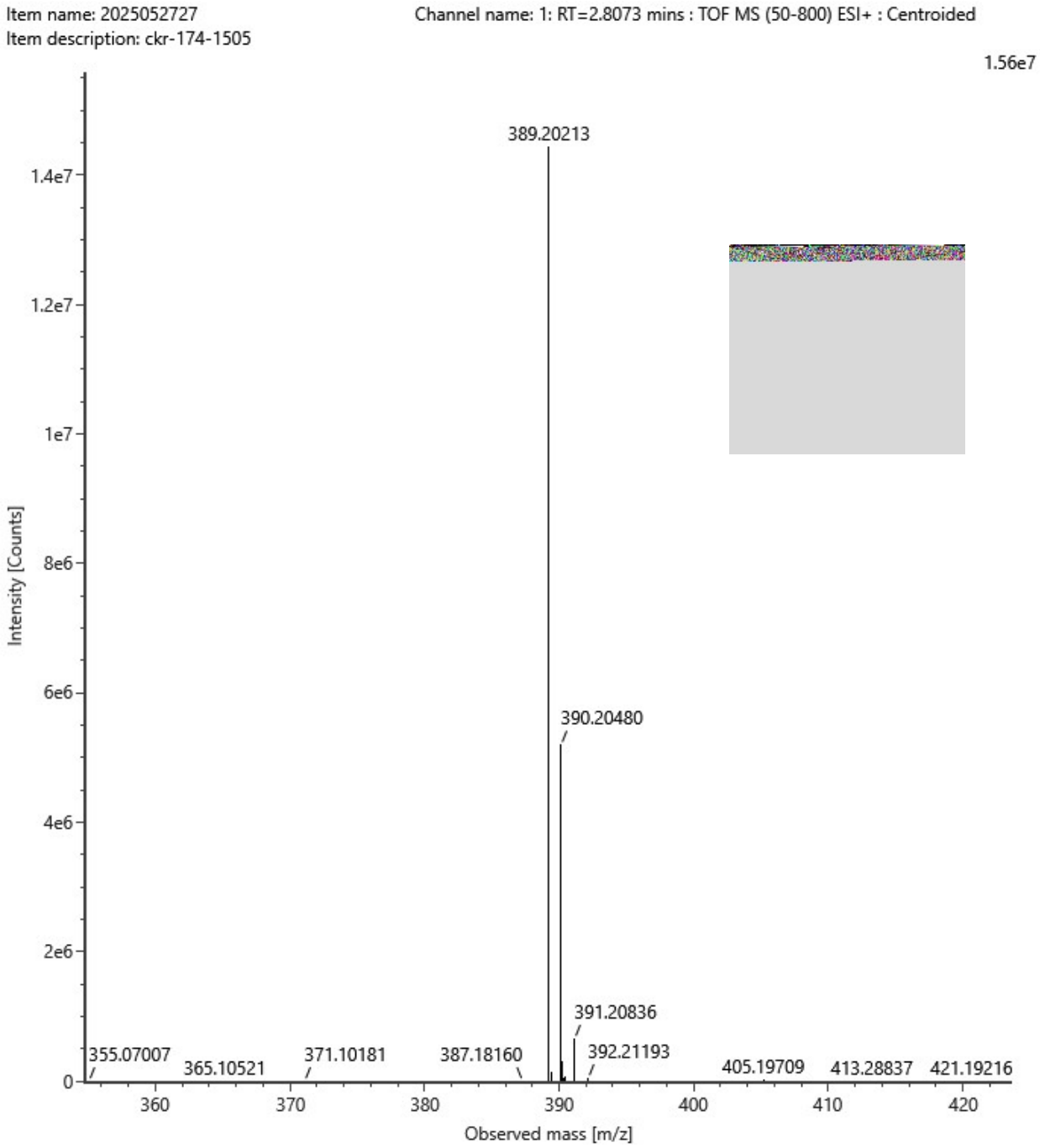
3dc. HRMS（ESI）m/z calcd for $C_{28}H_{24}ClN_2^+$ $(M+H)^+$ 423.1622, found 423.1623;



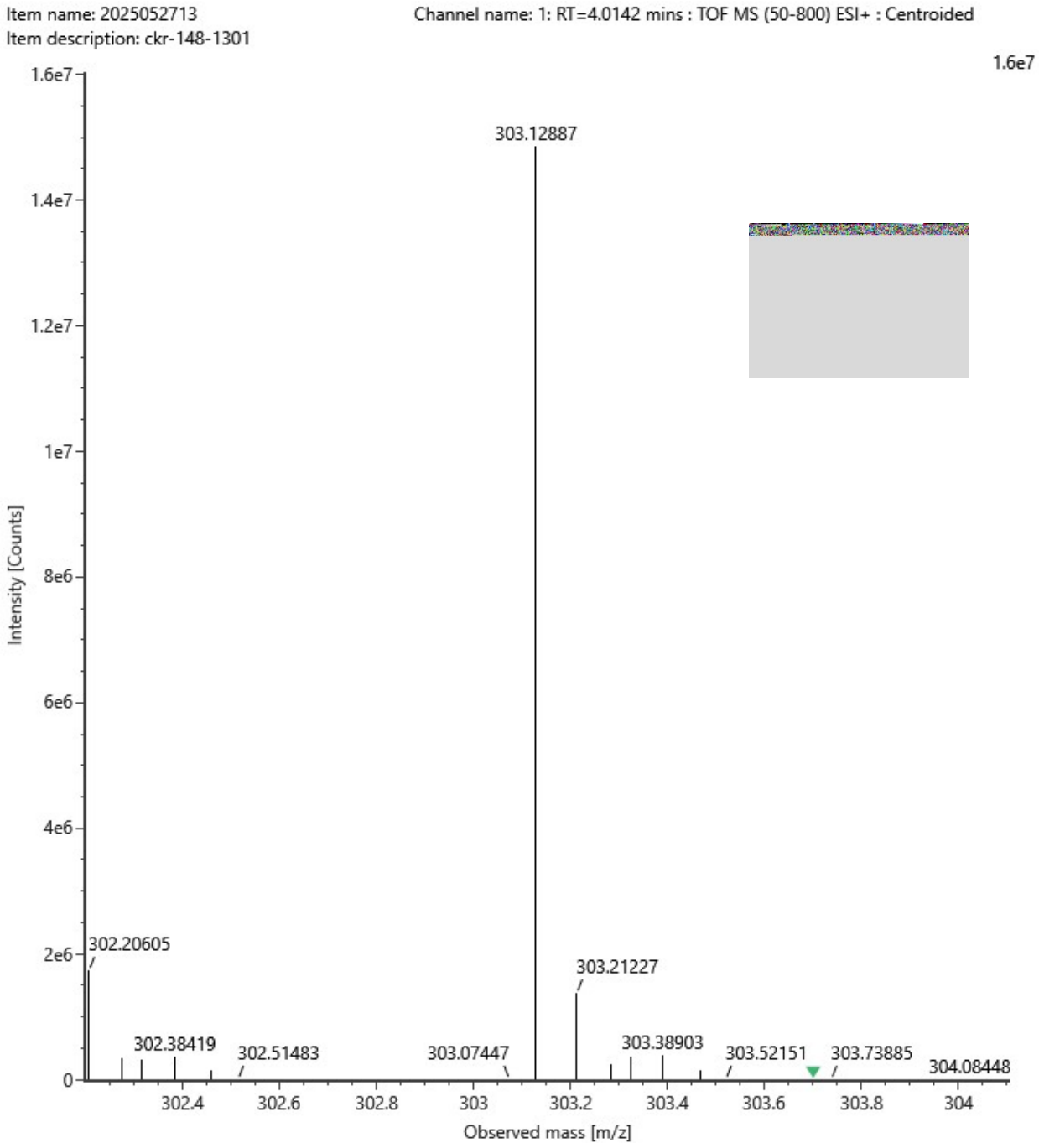
3dd. HRMS（ESI）m/z calcd for $C_{29}H_{24}F_3N_2^+$ $(M+H)^+$ 457.1886, found 457.1886;



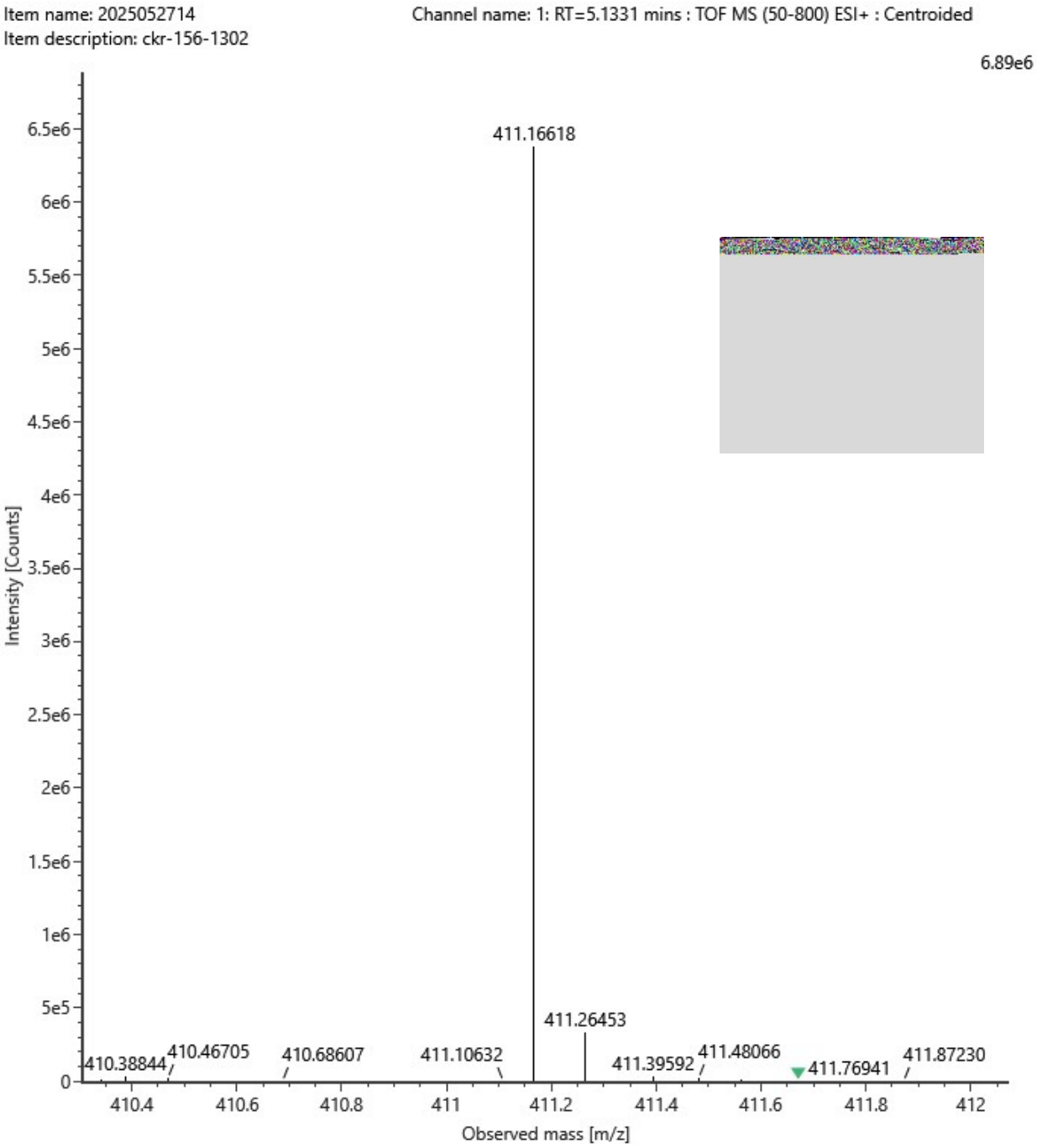
3de. HRMS（ESI）m/z calcd for $C_{28}H_{25}N_2^+$ $(M+H)^+$ 389.2012, found 389.2021;



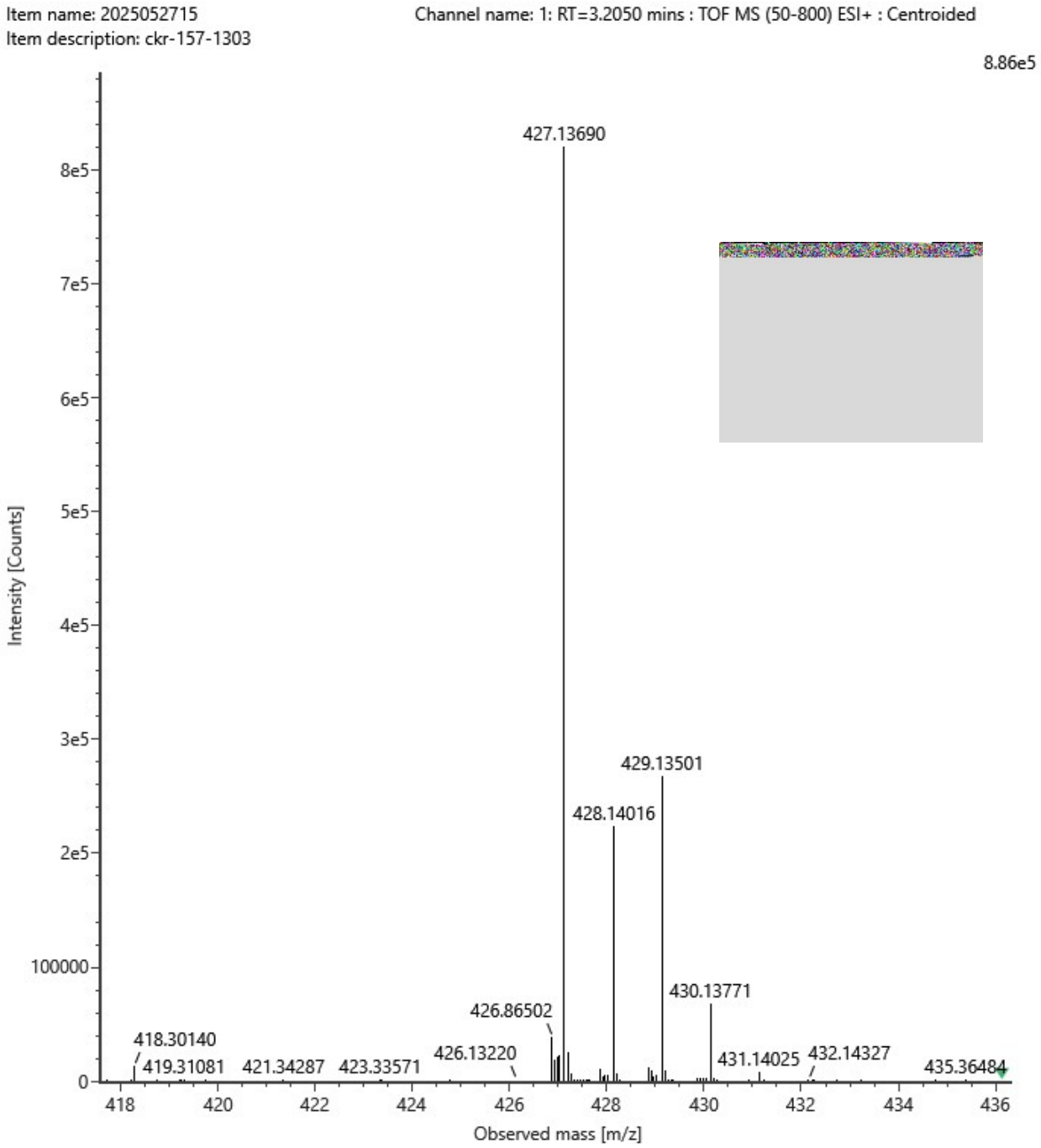
3ea. HRMS（ESI）m/z calcd for $C_{20}H_{16}FN_2^+$ $(M+H)^+$ 303.1292, found 303.1289;



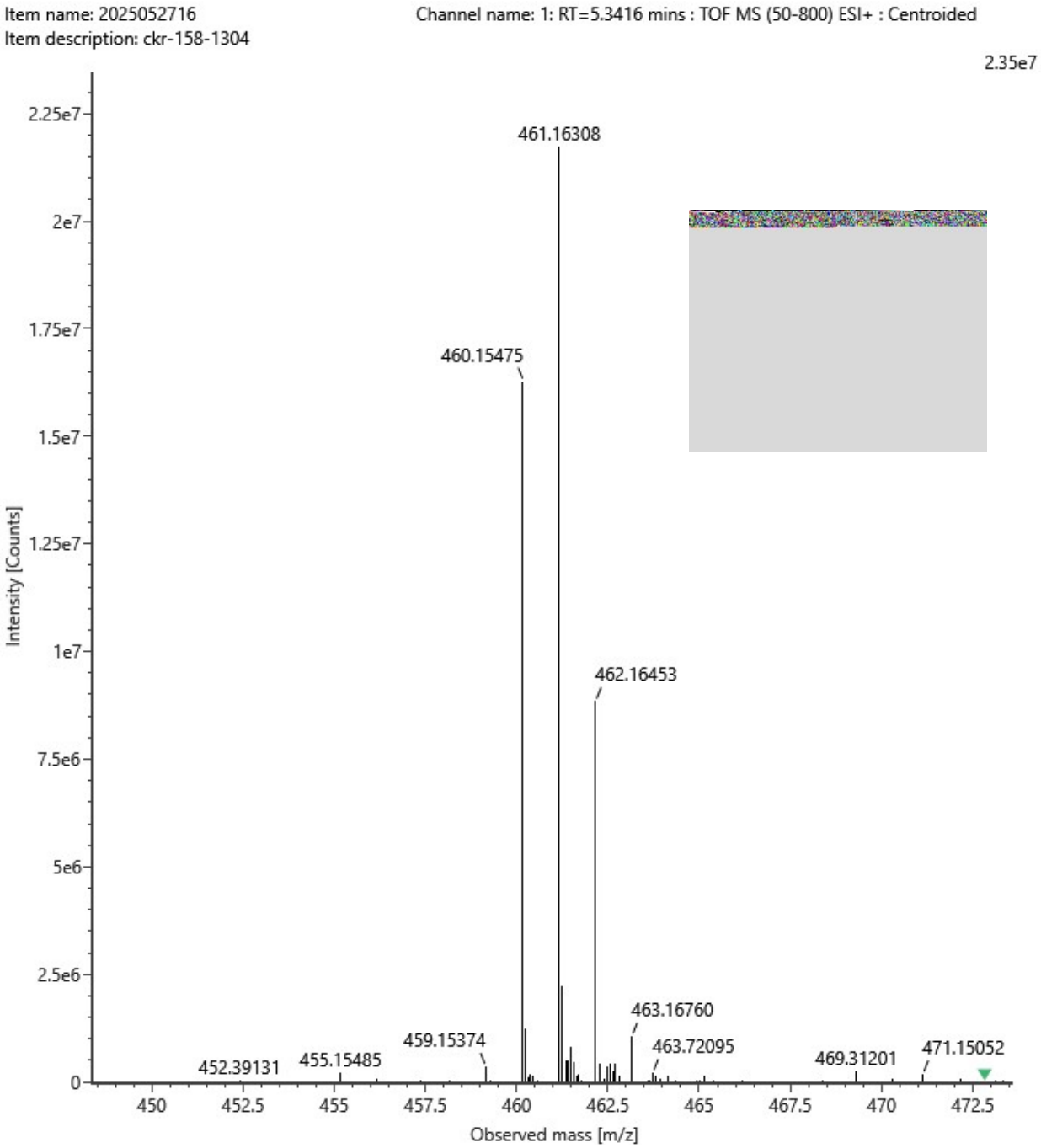
3eb. HRMS（ESI）m/z calcd for $C_{27}H_{21}F_2N_2^+$ $(M+H)^+$ 411.1667, found 411.1662;



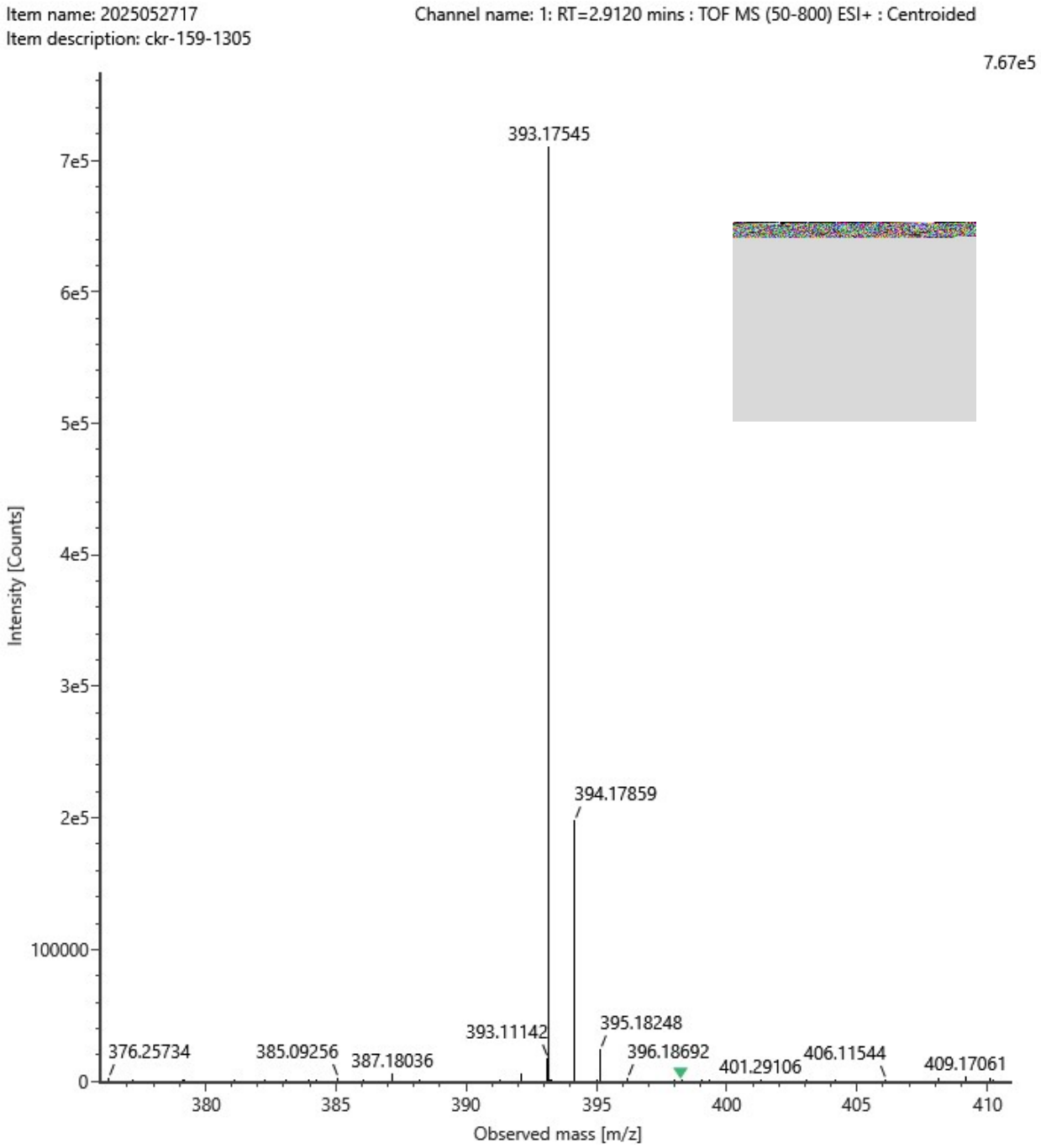
3ec. HRMS（ESI）m/z calcd for $C_{27}H_{21}ClFN_2^+$ $(M+H)^+$ 427.1372, found 427.1369;



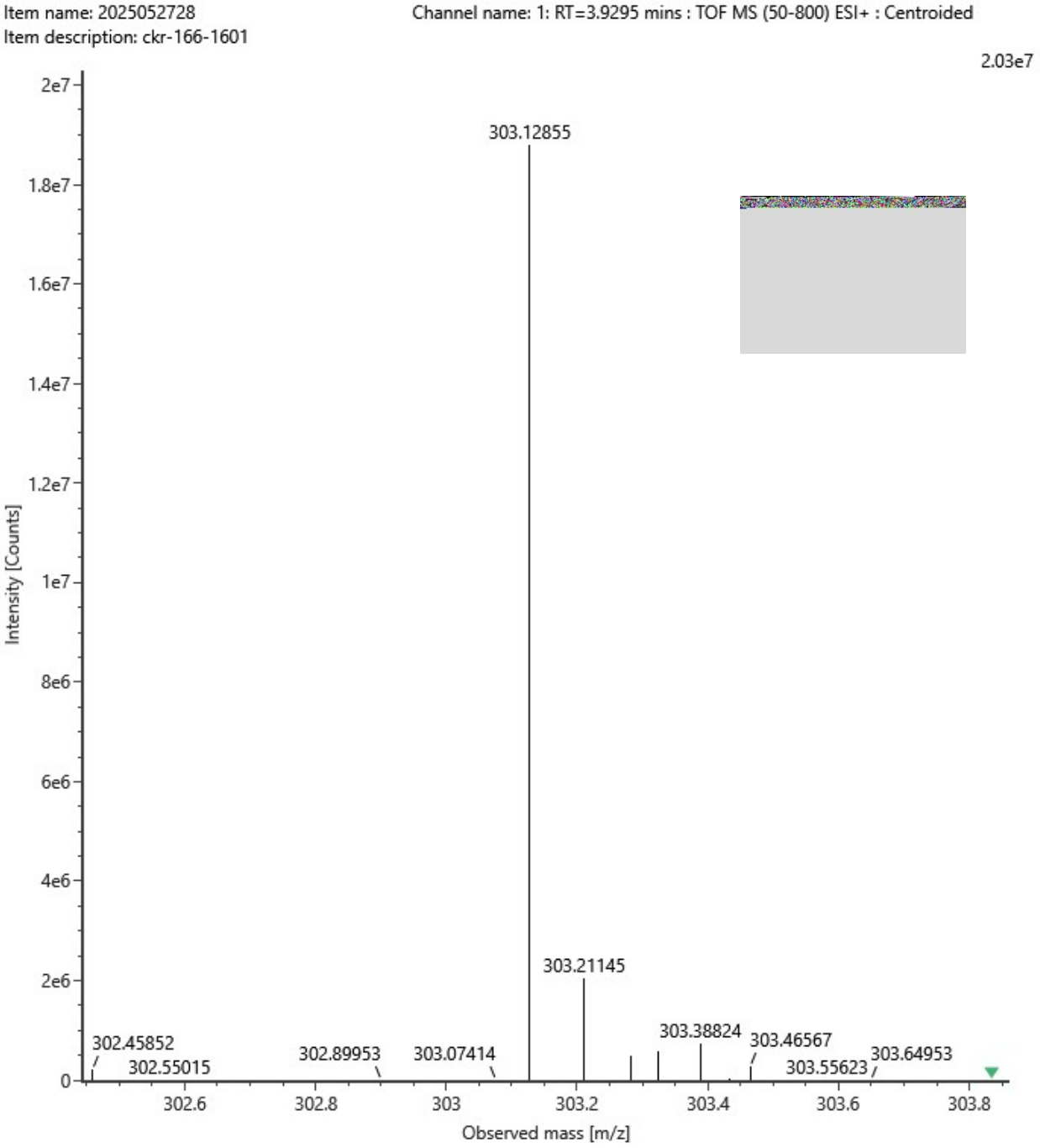
3ed. HRMS（ESI）m/z calcd for $C_{28}H_{21}F_4N_2^+$ $(M+H)^+$ 461.1635, found 461.1631;



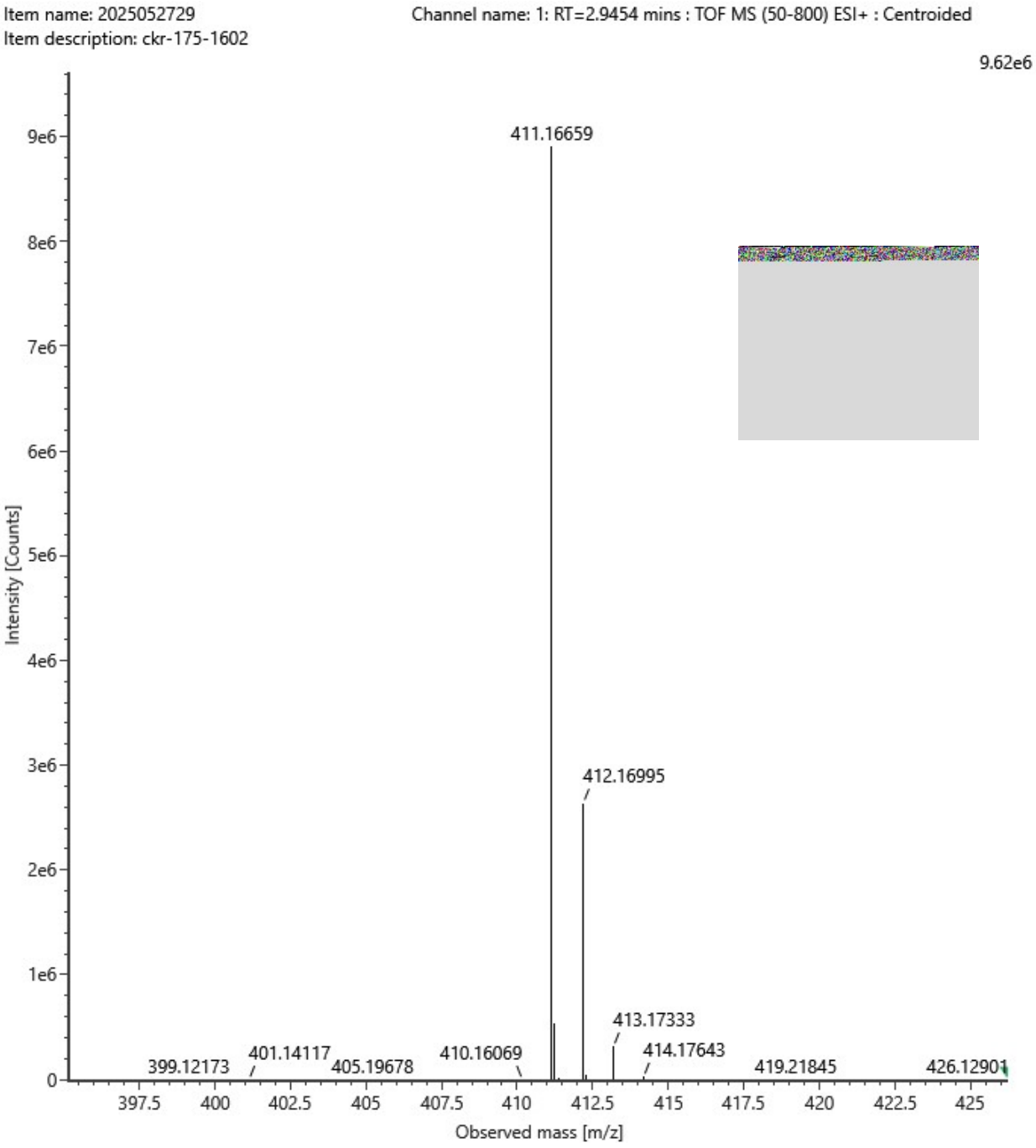
3ee. HRMS（ESI）m/z calcd for $C_{27}H_{22}FN_2^+$ $(M+H)^+$ 393.1762, found 393.1754;



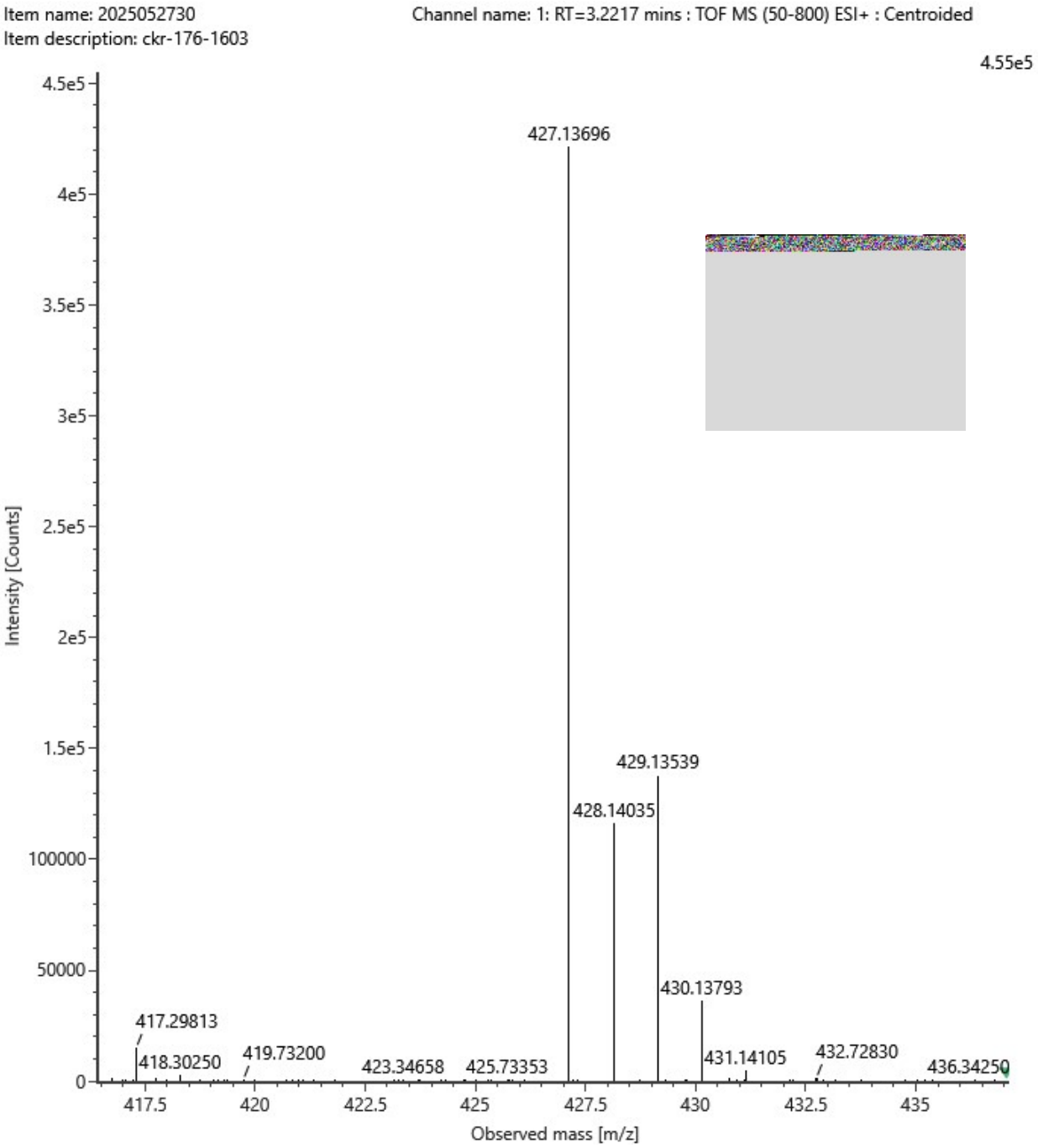
3fa. HRMS（ESI）m/z calcd for $C_{20}H_{16}FN_2^+$ $(M+H)^+$ 303.1292, found 303.1286;



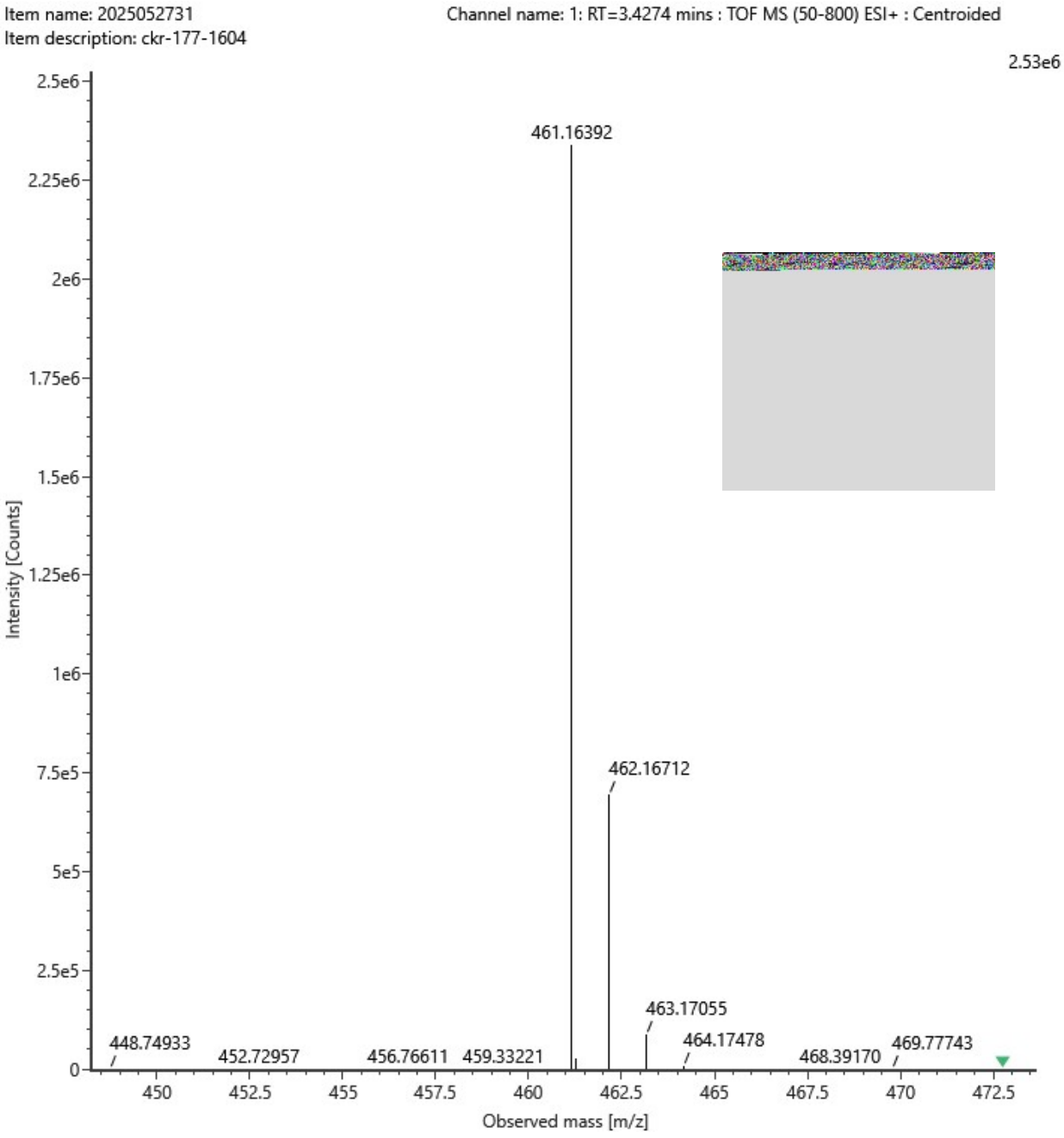
3fb. HRMS（ESI）m/z calcd for $C_{27}H_{21}F_2N_2^+$ $(M+H)^+$ 411.1667, found 411.1666;



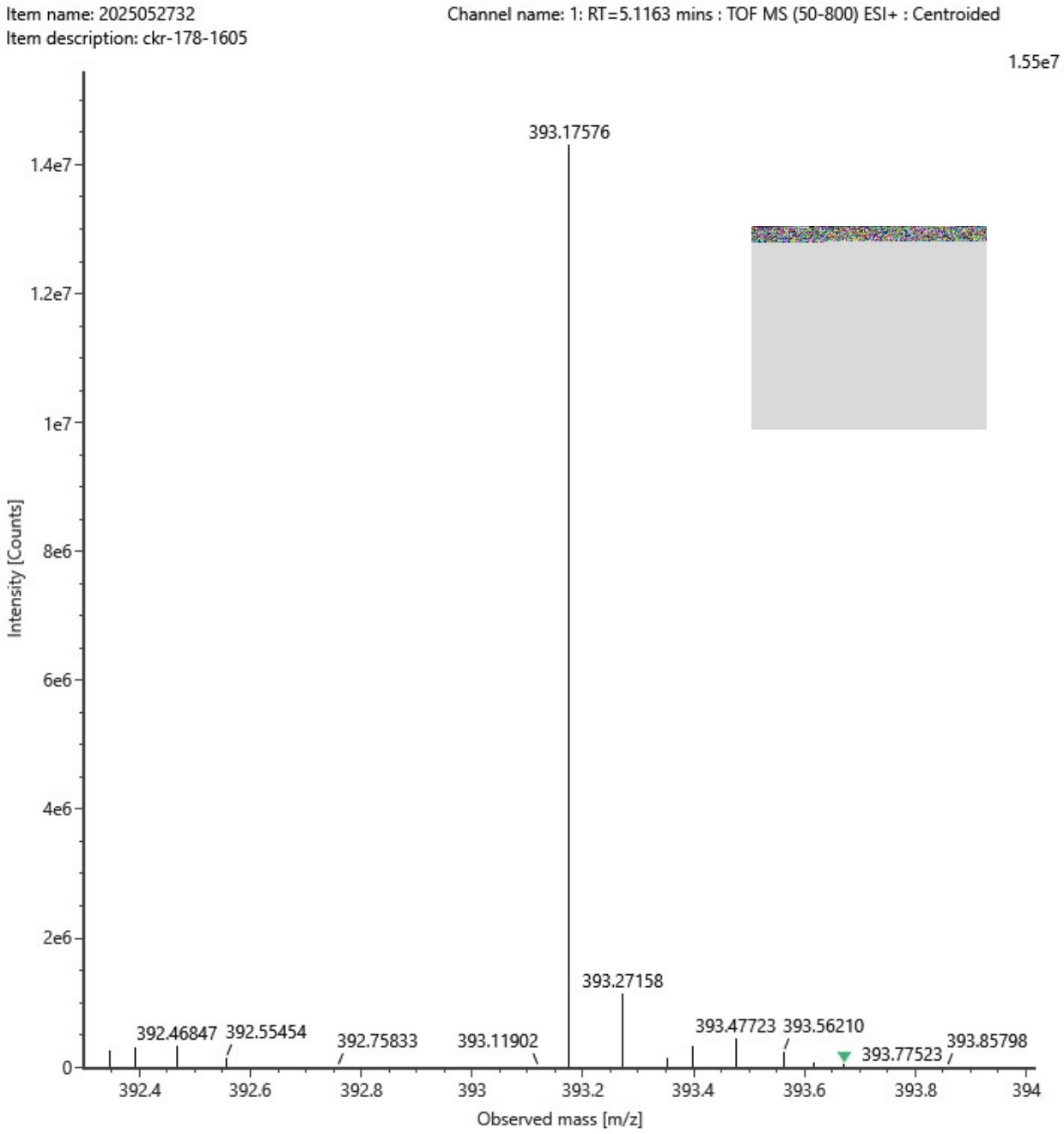
3fc. HRMS（ESI）m/z calcd for $C_{27}H_{21}ClFN_2^+$ $(M+H)^+$ 427.1372, found 427.1370;



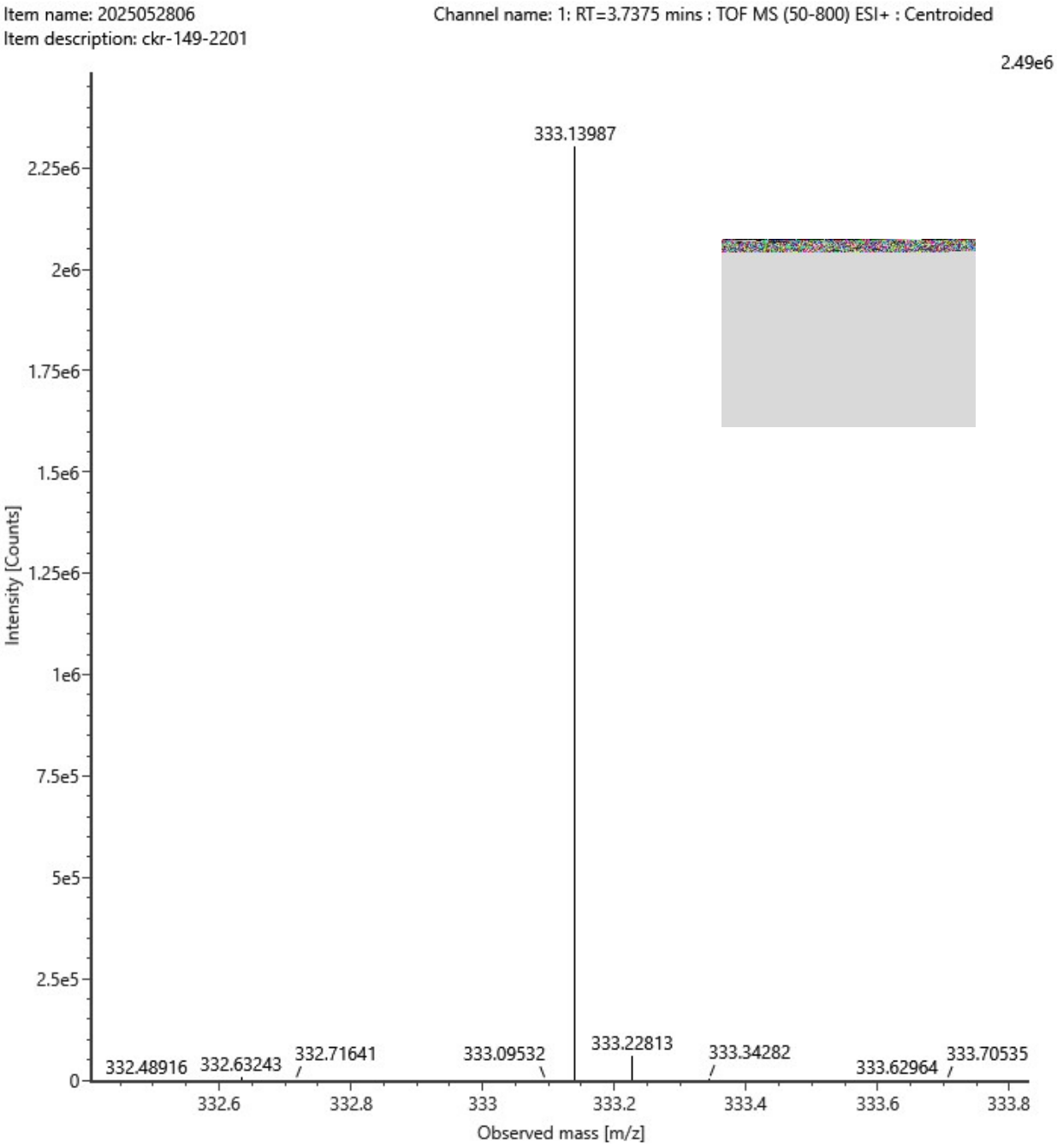
3fd. HRMS（ESI）m/z calcd for $C_{28}H_{21}F_4N_2^+$ $(M+H)^+$ 461.1635, found 461.1639;



3fe. HRMS（ESI）m/z calcd for $C_{27}H_{22}FN_2^+$ $(M+H)^+$ 393.1762, found 393.1758;



3bf. HRMS（ESI）m/z calcd for $C_{21}H_{18}FN_2O^+$ $(M+H)^+$ 333.1398, found 333.1399;



3bg. HRMS（ESI）m/z calcd for $C_{20}H_{15}ClFN_2^+$ $(M+H)^+$ 337.0902, found 337.0891;