

Supporting Information

***t*-BuOLi promoted regioselective *N*-thiolation of indoles with *N*-arylthio phthalimide**

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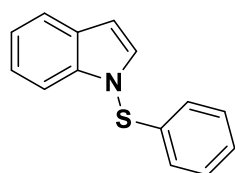
General information and materials:

All commercially available reagents and solvents were used without further purification unless otherwise stated. Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 UltraShield spectrometer (400 MHz for ^1H and 101 MHz for ^{13}C) in chloroform- d or DMSO- d_6 . Data are reported as follows: chemical shifts (δ) reported in parts per million (ppm), multiplicity, coupling constants (J) reported in Hertz (Hz) and integration. Analytical thin-layer chromatography (TLC) was carried out on precoated plates (silica gel 60 F254), and spots were visualized under ultraviolet light. Gas chromatography (GC) was performed on Agilent 7890A. Gas chromatography-mass spectrometry (GC-MS) was performed on Agilent 7890A/5975C. High-resolution mass spectra (HR-MS) were recorded under electron impact (EI-TOF) (70 eV) condition using a MicroMass GCT CA 055 instrument.

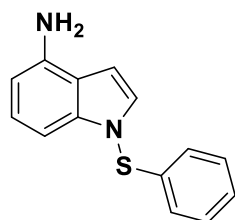
General procedure for product synthesis:

A mixture of indole 1 (0.3 mmol), N-phenylthiophthalimide 2 (0.33 mmol), t-BuOLi (0.3 mmol), and acetonitrile (1.5 mL) was added into a 5.0 mL glass tube and was stirred at room temperature for 1 h. When the reaction was complete, the reaction mixture was quenched with water and the resulting mixture was extracted three times with ethyl acetate. The combined organic layer was washed two times with a little amount of water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was evaporated under vacuum and the residue was purified by flash column chromatography on silica gel (eluting with petroleum ether–ethyl acetate) to provide the desired product 3.

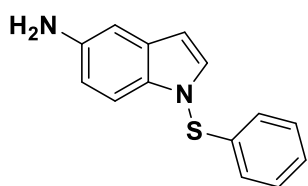
Characterization of product 3



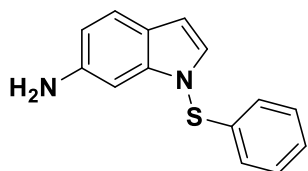
1-(Phenylthio)-1*H*-indole (3a): 64.2 mg (95%), white solid; m.p. 43.3 – 44.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (t, $J = 7.8$ Hz, 2H), 7.29 – 7.15 (m, 5H), 7.14 – 7.07 (m, 1H), 6.92 – 6.88 (m, 2H), 6.65 (d, $J = 3.2$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 140.3, 139.0, 134.3, 129.6, 129.3, 126.8, 123.9, 123.3, 121.3, 121.2, 111.3, 105.9 ppm; HRMS (EI-TOF) calcd for $\text{C}_{14}\text{H}_{12}\text{NS}$ [M^+] m/z 225.0612, found 225.0614.



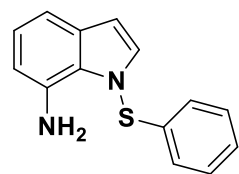
1-(phenylthio)-1*H*-indol-4-amine (3b): 62.0 mg (86%), brown oil; ^1H NMR (400 MHz, DMSO- d_6) δ 7.36 – 7.26 (m, 3H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.00 – 6.90 (m, 3H), 6.88 – 6.84 (m, 1H), 6.75 (d, $J = 8.0$ Hz, 1H), 6.32 (d, $J = 7.5$ Hz, 1H), 5.48 (s, 2H) ppm; ^{13}C NMR (101 MHz, DMSO- d_6) δ 142.62, 141.36, 139.11, 131.90, 129.86, 127.47, 124.89, 124.51, 117.92, 104.64, 104.40, 99.18 ppm; HRMS (EI-TOF) calcd for $\text{C}_{14}\text{H}_{12}\text{NS}$ [M^+] m/z 240.0721, found 240.0724.



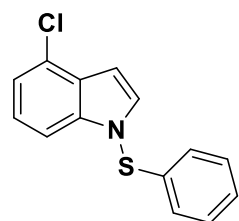
1-(phenylthio)-1*H*-indol-5-amine (3c): 56.9 mg (79%) brown oil; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.38 – 7.30 (m, 3H), 7.29 – 7.21 (m, 1H), 7.07 – 7.01 (m, 2H), 6.93 – 6.83 (m, 2H), 6.59 (d, $J = 3.3$ Hz, 1H), 6.48 (dd, $J = 6.5, 2.2$ Hz, 1H), 5.49 (s, 2H) ppm; ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 143.98, 139.39, 135.01, 133.03, 130.77, 129.86, 127.44, 124.40, 113.49, 111.38, 105.41, 104.57 ppm; HRMS (EI-TOF) calcd for $\text{C}_{14}\text{H}_{12}\text{NS}$ [M^+] m/z 240.0721, found 240.0724.



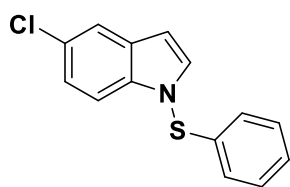
1-(phenylthio)-1*H*-indol-6-amine (3d): 49.7 mg (69%), pale yellow oil; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.34 – 7.29 (m, 2H), 7.27 (d, $J = 8.3$ Hz, 1H), 7.23 – 7.16 (m, 1H), 7.13 (d, $J = 3.3$ Hz, 1H), 6.93 – 6.88 (m, 1H), 6.71 (s, 1H), 6.53 – 6.48 (m, 2H), 5.04 (s, 2H) ppm; ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 146.42, 141.86, 139.35, 131.54, 129.88, 127.17, 123.78, 121.75, 120.50, 111.63, 106.40, 94.88 ppm; HRMS (EI-TOF) calcd for $\text{C}_{14}\text{H}_{12}\text{NS}$ [M^+] m/z 240.0721, found 240.0724.



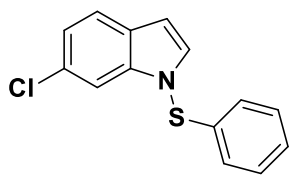
1-(phenylthio)-1*H*-indol-7-amine (3e): 67.4mg (93%) brown oil; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.41 – 7.20 (m, 4H), 7.04 (d, $J = 7.9$ Hz, 2H), 6.94 – 6.83 (m, 2H), 6.62 – 6.56 (m, 1H), 6.49 (dd, $J = 6.5, 2.1$ Hz, 1H), 5.49 (s, 2H) ppm; ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 139.59, 136.20, 135.50, 131.32, 129.45, 127.50, 125.98, 124.63, 122.52, 109.71, 109.09, 106.68 ppm; HRMS (EI-TOF) calcd for $\text{C}_{14}\text{H}_{12}\text{NS}$ [M^+] m/z 240.0721, found 240.0724.



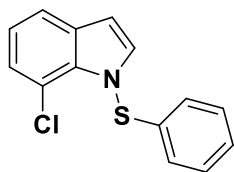
4-chloro-1-(phenylthio)-1*H*-indole (3f): 46.8 mg (60%) colorless oil; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.74 (d, $J = 3.4$ Hz, 1H), 7.61–7.58 (m, 1H), 7.36 (t, $J = 7.7$ Hz, 2H), 7.31 – 7.25 (m, 3H), 7.13 – 7.09 (m, 2H), 6.78 (dd, $J = 3.5, 1.0$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 140.97, 137.77, 136.60, 130.04 (d, $J = 8.4$ Hz), 128.33, 127.73, 125.82, 124.58, 121.42, 110.63, 104.05 ppm; HRMS (EI-TOF) calcd for $\text{C}_{14}\text{H}_{10}\text{ClNS}$ [M^+] m/z 259.0222, found 259.0224.



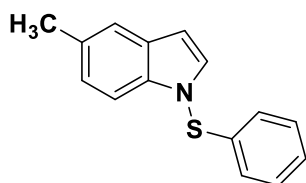
5-chloro-1-(phenylthio)-1*H*-indole (3g): 58.4 mg (75%) white solid; m.p. 43.3 – 44.6 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.71 (d, $J = 2.1$ Hz, 1H), 7.66 (d, $J = 3.4$ Hz, 1H), 7.57 (d, $J = 8.6$ Hz, 1H), 7.33 (dd, $J = 8.4, 7.0$ Hz, 2H), 7.29 – 7.20 (m, 2H), 7.10 – 7.00 (m, 2H), 6.72 (dd, $J = 3.3, 0.9$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 138.64, 137.99, 137.07, 130.99, 130.06, 128.20, 126.42, 125.57, 123.61, 120.92, 112.97, 105.94 ppm; HRMS (EI-TOF) calcd for $\text{C}_{14}\text{H}_{10}\text{ClNS}$ [M^+] m/z 259.0222, found 259.0224.



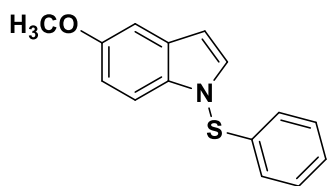
6-chloro-1-(phenylthio)-1*H*-indole (3h): 52.2 mg (67%) colorless oil; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.67 (d, $J = 8.3$ Hz, 1H), 7.63 (d, $J = 3.3$ Hz, 1H), 7.60 (s, 1H), 7.37 – 7.31 (m, 2H), 7.28 – 7.23 (m, 1H), 7.20 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.12 – 7.06 (m, 2H), 6.78 (dd, $J = 3.3, 0.9$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 140.68, 137.89, 136.37, 130.07, 128.61, 128.57, 128.21, 127.71, 125.58, 123.11, 122.18, 111.08, 106.40 ppm; HRMS (EI-TOF) calcd for $\text{C}_{14}\text{H}_{10}\text{ClNS}$ [M^+] m/z 259.0222, found 259.0224.



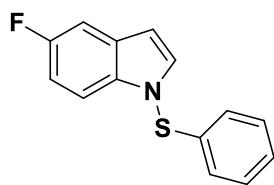
7-chloro-1-(phenylthio)-1*H*-indole (3i): 20.3 mg (26%) colorless oil; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.64 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.58 (d, $J = 3.3$ Hz, 1H), 7.38 – 7.32 (m, 2H), 7.29 – 7.21 (m, 2H), 7.16 (t, $J = 7.7$ Hz, 1H), 7.06 – 6.99 (m, 2H), 6.83 (d, $J = 3.3$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 140.13, 139.04, 133.84, 133.17, 129.97, 127.70, 125.51, 124.52, 123.01, 121.06, 117.66, 106.93 ppm; HRMS (EI-TOF) calcd for $\text{C}_{14}\text{H}_{10}\text{ClNS}$ [M^+] m/z 259.0222, found 259.0224.



5-methyl-1-(phenylthio)-1*H*-indole (3j): 67.5 mg (94%) white solid; m.p. 66.5 – 68.0 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.48 (d, $J = 3.3$ Hz, 1H), 7.43 (d, $J = 9.0$ Hz, 2H), 7.30 (t, $J = 7.2$ Hz, 2H), 7.20 (t, $J = 7.5$ Hz, 1H), 7.06 (dd, $J = 8.3, 1.8$ Hz, 1H), 6.97 (dd, $J = 8.6, 1.5$ Hz, 2H), 6.64 (dd, $J = 3.3, 1.0$ Hz, 1H), 2.38 (s, 3H) ppm; ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 138.76, 138.37, 135.36, 130.56, 130.00, 129.94, 127.72, 125.13, 124.79, 121.33, 110.99, 105.95, 21.47 ppm; HRMS (EI-TOF) calcd for $\text{C}_{15}\text{H}_{13}\text{NS}$ [M^+] m/z 239.0769, found 239.0771.

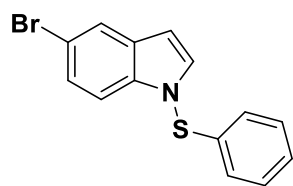


5-methoxy-1-(phenylthio)-1*H*-indole (3k): 75.8 mg (99%) yellow oil; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.50 (d, $J = 3.3$ Hz, 1H), 7.43 (d, $J = 8.9$ Hz, 1H), 7.31 (dd, $J = 8.4, 7.1$ Hz, 2H), 7.25 – 7.18 (m, 1H), 7.15 (d, $J = 2.4$ Hz, 1H), 7.02 – 6.93 (m, 2H), 6.87 (dd, $J = 8.9, 2.5$ Hz, 1H), 6.65 (dd, $J = 3.3, 0.9$ Hz, 1H), 3.76 (s, 3H) ppm; ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 155.40, 138.80, 135.95, 134.79, 130.37, 129.95, 127.75, 124.82, 113.25, 112.01, 106.18, 103.68, 55.90 ppm; HRMS (EI-TOF) calcd for $\text{C}_{15}\text{H}_{13}\text{NOS}$ [M^+] m/z 255.0718, found 255.0721.

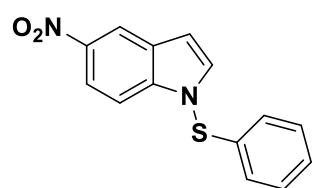


5-fluoro-1-(phenylthio)-1*H*-indole (3l): 64.2 mg (88%) white solid; m.p. 68.0 – 70.0 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.66 (d, $J = 3.2$ Hz, 1H), 7.56 (q, $J = 4.4$ Hz, 1H), 7.44 (dd, $J = 9.5, 2.5$ Hz, 1H), 7.37 – 7.31 (m, 2H), 7.28 – 7.21 (m, 1H), 7.14 – 7.02 (m, 3H), 6.73 (dd, $J = 3.3, 0.9$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 158.8 (d, $J = 235.2$ Hz), 138.2, 137.3, 136.6, 130.3 (d, $J = 10.4$ Hz), 129.9, 128.1, 125.4, 112.5 (d, $J = 9.9$ Hz), 111.6 (d, $J = 26.2$ Hz), 106.6 (d, $J = 24.1$

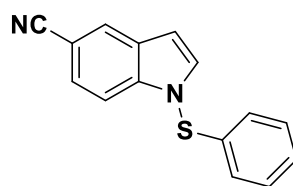
Hz), 106.3 (d, $J = 4.2$ Hz) ppm; HRMS (EI-TOF) calcd for $C_{14}H_{10}FNS$ [M^+] m/z 243.0518, found 243.0520.



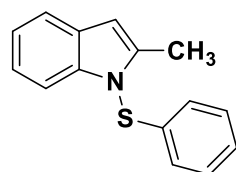
5-bromo-1-(phenylthio)-1*H*-indole (3m): 62.0 mg (68%) white solid; m.p. 55.2 – 57.3 °C; 1H NMR (400 MHz, $DMSO-d_6$) δ 7.85 (d, $J = 1.9$ Hz, 1H), 7.64 (d, $J = 3.3$ Hz, 1H), 7.53 (d, $J = 8.7$ Hz, 1H), 7.40 – 7.29 (m, 3H), 7.27 – 7.21 (m, 1H), 7.07 – 7.02 (m, 2H), 6.72 (dd, $J = 3.3, 0.9$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, $DMSO-d_6$) δ 138.91, 137.93, 136.87, 131.63, 130.04, 128.19, 126.18, 125.54, 123.92, 114.34, 113.40, 105.81 ppm; HRMS (EI-TOF) calcd for $C_{14}H_{10}BrNS$ [M^+] m/z 302.9717, found 302.9719.



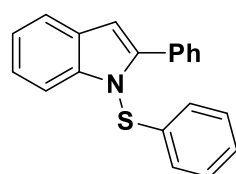
5-nitro-1-(phenylthio)-1*H*-indole (3n): 41.4 mg (51%) pale yellow oil; 1H NMR (400 MHz, $DMSO-d_6$) δ 8.62 (t, $J = 1.8$ Hz, 1H), 8.12 (dt, $J = 9.2, 1.8$ Hz, 1H), 7.88 – 7.81 (m, 1H), 7.78 (d, $J = 9.0$ Hz, 1H), 7.35 (t, $J = 7.4$ Hz, 2H), 7.27 (t, $J = 6.6$ Hz, 1H), 7.16 (d, $J = 7.9$ Hz, 2H), 6.98 (d, $J = 3.3$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, $DMSO-d_6$) δ 143.35, 142.98, 138.78, 137.13, 130.17, 129.36, 128.75, 126.51, 118.88, 118.38, 112.17, 108.08 ppm; HRMS (EI-TOF) calcd for $C_{14}H_{10}N_2O_2S$ [M^+] m/z 270.0463, found 270.0465.



1-(phenylthio)-1*H*-indole-5-carbonitrile (3o): 33.8 mg (45%) white solid; m.p. 61.4 – 62.3 °C; 1H NMR (400 MHz, $DMSO-d_6$) δ 8.21 (d, $J = 1.6$ Hz, 1H), 7.83 (d, $J = 3.3$ Hz, 1H), 7.78 (d, $J = 8.5$ Hz, 1H), 7.64 (dd, $J = 8.5, 1.6$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 2H), 7.29 (t, $J = 7.3$ Hz, 1H), 7.16 (dd, $J = 7.2, 1.5$ Hz, 2H), 6.89 (dd, $J = 3.4, 0.9$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, $DMSO-d_6$) δ 142.01, 137.82, 137.29, 130.12, 129.69, 128.59, 127.03, 126.57, 126.30, 120.44, 112.74, 106.72, 104.15 ppm; HRMS (EI-TOF) calcd for $C_{15}H_{10}N_2S$ [M^+] m/z 250.0565, found 250.0567.

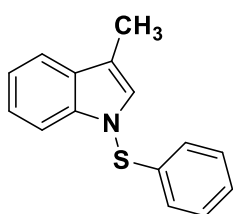


2-methyl-1-(phenylthio)-1*H*-indole (3p): 66.0 mg (92%) white solid; m.p. 47.5 – 49.9 °C; 1H NMR (400 MHz, $DMSO-d_6$) δ 7.54 (d, $J = 7.5$ Hz, 1H), 7.49 (d, $J = 7.8$ Hz, 1H), 7.35 – 7.28 (m, 2H), 7.25 – 7.10 (m, 3H), 6.87 (d, $J = 8.3$ Hz, 2H), 6.58 (d, $J = 1.6$ Hz, 1H), 2.43 (s, 3H) ppm; ^{13}C NMR (101 MHz, $DMSO-d_6$) δ 141.32, 140.77, 138.82, 130.04, 129.50, 127.32, 123.79, 122.68, 121.90, 120.51, 111.16, 104.33, 13.12 ppm; HRMS (EI-TOF) calcd for $C_{15}H_{13}NS$ [M^+] m/z 239.0769, found 239.0771.

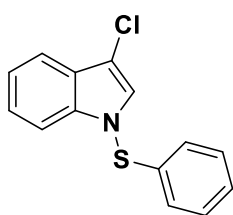


2-phenyl-1-(phenylthio)-1*H*-indole (3r): 70.0 mg (77%) yellow oil; 1H NMR (400 MHz, $DMSO-d_6$) δ 7.67 (d, $J = 6.9$ Hz, 1H), 7.63 – 7.58 (m, 3H), 7.47 – 7.39 (m, 3H), 7.30 – 7.18 (m, 4H), 7.14 – 7.08 (m, 1H), 6.95 (s, 1H), 6.77 (d, $J = 7.6$ Hz, 2H) ppm; ^{13}C NMR (101 MHz, $DMSO-d_6$) δ 144.86, 141.95, 138.95, 131.70, 129.9, 129.8,

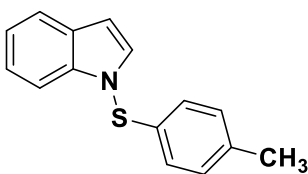
129.56, 128.9, 128.8, 127.21, 123.97, 123.64, 122.56, 121.42, 112.21, 106.55 ppm; HRMS (EI-TOF) calcd for C₂₀H₁₅NS [M⁺] *m/z* 301.0925, found 301.0928.



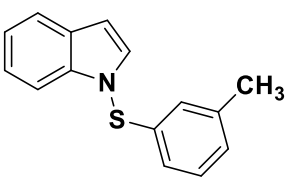
3-methyl-1-(phenylthio)-1*H*-indole (3s): 46.7 mg (65%) colorless oil; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.13 (m, 6H), 6.98 (dd, *J* = 8.3, 1.3 Hz, 2H), 2.27 (s, 3H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 139.87, 138.39, 131.50, 129.88, 129.38, 127.13, 124.28, 123.13, 120.72, 119.19, 114.30, 110.62, 9.39 ppm; HRMS (EI-TOF) calcd for C₁₅H₁₃NS [M⁺] *m/z* 239.0769, found 239.0771.



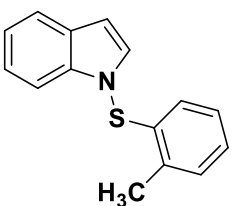
3-chloro-1-(phenylthio)-1*H*-indole (3t): 44.4 mg (57%) colorless oil; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.87 (s, 1H), 7.68 – 7.63 (m, 1H), 7.59 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.39 – 7.24 (m, 5H), 7.18 – 7.13 (m, 2H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 139.39, 137.61, 131.55, 130.06, 128.50, 127.00, 126.28, 125.00, 122.56, 118.60, 111.96, 108.00 ppm; HRMS (EI-TOF) calcd for C₁₄H₁₀ClNS [M⁺] *m/z* 259.0222, found 259.0224.



1-(*p*-tolylthio)-1*H*-indole (3u): 62.4 mg (87%) white solid; m.p. 62.0 – 64.5 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.61 (t, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 3.3 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.18–7.11 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 3.3 Hz, 1H), 2.23 (s, 3H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 140.00, 138.25, 135.27, 134.55, 130.55, 129.73, 126.96, 123.50, 121.57, 111.36, 106.01, 21.08 ppm; HRMS (EI-TOF) calcd for C₁₅H₁₃NS [M⁺] *m/z* 239.0769, found 239.0771.

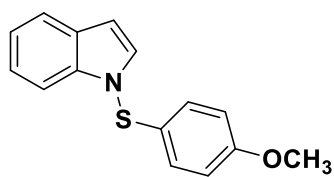


1-(*m*-tolylthio)-1*H*-indole (3u'): 64.6 mg (90%) white solid; m.p. 72.0 – 74.0 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.66 – 7.61 (m, 1H), 7.59 – 7.53 (m, 2H), 7.28 – 7.23 (m, 1H), 7.22 – 7.13 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.95 (s, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.73 (dd, *J* = 3.3, 0.9 Hz, 1H), 2.21 (s, 3H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 140.06, 139.48, 138.27, 135.37, 129.87, 129.72, 128.76, 125.67, 123.61, 122.48, 121.67, 121.61, 111.31, 106.20, 21.41 ppm; HRMS (EI-TOF) calcd for C₁₅H₁₃NS [M⁺] *m/z* 239.0769, found 239.0771.

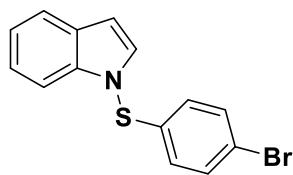


1-(*o*-tolylthio)-1*H*-indole (3u''): 58.1 mg (81%) white solid; m.p. 67.0 – 68.8 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.27 – 7.22 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 3.3 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 2.38 (s, 3H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 140.00, 137.69, 135.27, 132.98, 131.07, 129.80, 127.49, 127.13, 123.70, 123.24, 121.78, 121.70, 111.29, 106.55, 19.00

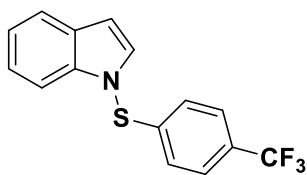
ppm; HRMS (EI-TOF) calcd for C₁₅H₁₃NS [M⁺] *m/z* 239.0769, found 239.0771.



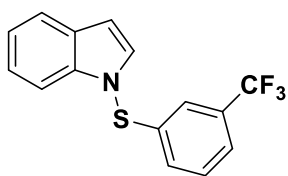
1-((4-methoxyphenyl)thio)-1*H*-indole (3v): (78%) white solid; m.p. 58.0 – 60.0 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 3.3 Hz, 1H), 3.70 (s, 3H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 160.66, 139.87, 135.06, 132.39, 129.70, 127.74, 123.32, 121.42 (d, *J* = 10.8 Hz), 115.52, 111.51, 105.62, 55.85 ppm; HRMS (EI-TOF) calcd for C₁₅H₁₃NOS [M⁺] *m/z* 255.0718, found 255.0721.



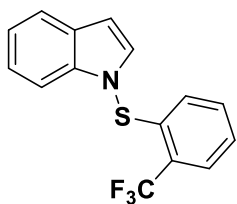
1-((4-bromophenyl)thio)-1*H*-indole (3w): 68.4 mg (75%) white solid; m.p. 96.0 – 97.5 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.29 – 7.22 (m, 1H), 7.20 – 7.14 (m, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 3.3 Hz, 1H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 139.86, 138.25, 135.15, 132.82, 129.80, 126.85, 123.80, 121.89, 121.72, 120.77, 111.22, 106.61 ppm; HRMS (EI-TOF) calcd for C₁₄H₁₀BrNS [M⁺] *m/z* 302.9717, found 302.9719.



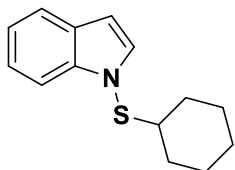
1-((4-(trifluoromethyl)phenyl)thio)-1*H*-indole (3x): 63.4 mg (72%) white solid; m.p. 85.0 – 87.0 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.67 (t, *J* = 7.9 Hz, 3H), 7.58 – 7.55 (m, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 3.2 Hz, 1H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 144.98, 139.77, 135.03, 129.83, 127.44 (q, *J* = 31.3 Hz), 126.81 (q, *J* = 3.6 Hz), 124.50 (q, *J* = 272.7 Hz), 123.95, 123.42, 122.06, 121.79, 111.09, 107.01 ppm; HRMS (EI-TOF) calcd for C₁₅H₁₀F₃NS [M⁺] *m/z* 293.0486, found 293.0490.



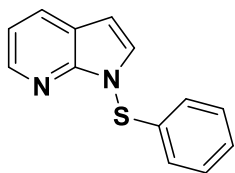
1-((3-(trifluoromethyl)phenyl)thio)-1*H*-indole (3x'): 66.9 mg (76%) white solid; m.p. 81.5 – 83.0 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 3.4 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.36 (s, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 3.3 Hz, 1H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 141.01, 139.81, 135.10, 131.08, 130.6 (q, *J* = 32.3 Hz), 129.82, 127.90, 124.16 (q, *J* = 273.7 Hz), 124.11 (q, *J* = 4.0 Hz), 123.9, 122.02, 121.77, 120.52 (q, *J* = 4.0 Hz), 111.14, 106.91 ppm; HRMS (EI-TOF) calcd for C₁₅H₁₀F₃NS [M⁺] *m/z* 293.0486, found 293.0490.



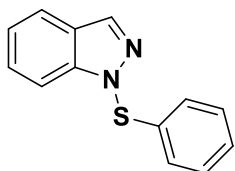
1-((2-(trifluoromethyl)phenyl)thio)-1*H*-indole (3x''): 57.2 mg (65%) white solid; m.p. 75.8 – 77.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.67 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.20 (m, 5H), 6.80 (d, *J* = 4.0 Hz, 1H), 6.34 (d, *J* = 4.0 Hz, 1H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 140.00, 139.43, 134.09, 132.65, 129.84, 126.94 (q, *J* = 5.0 Hz), 126.02, 124.52 (q, *J* = 32.3 Hz), 124.10 (q, *J* = 274.7 Hz), 123.93, 123.73, 121.85, 121.39, 111.27, 106.92 ppm; HRMS (EI-TOF) calcd for C₁₅H₁₀F₃NS [M⁺] *m/z* 293.0486, found 293.0490.



1-(cyclohexylthio)-1*H*-indole (3z): 52.7 mg (76%) colorless oil; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.61 (dd, *J* = 11.0, 8.0 Hz, 2H), 7.35 (d, *J* = 3.3 Hz, 1H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 3.3 Hz, 1H), 3.17 (ddq, *J* = 10.7, 7.5, 3.6 Hz, 1H), 1.87 – 1.75 (m, 2H), 1.74 – 1.63 (m, 2H), 1.58 – 1.49 (m, 1H), 1.32 – 1.18 (m, 4H), 1.16 – 1.04 (m, 1H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 141.17, 136.47, 129.40, 123.03, 121.25, 121.03, 111.64, 104.76, 50.72, 31.53, 25.58, 25.49 ppm; MS (GC-MS): *m/z* 231.1 (M⁺).

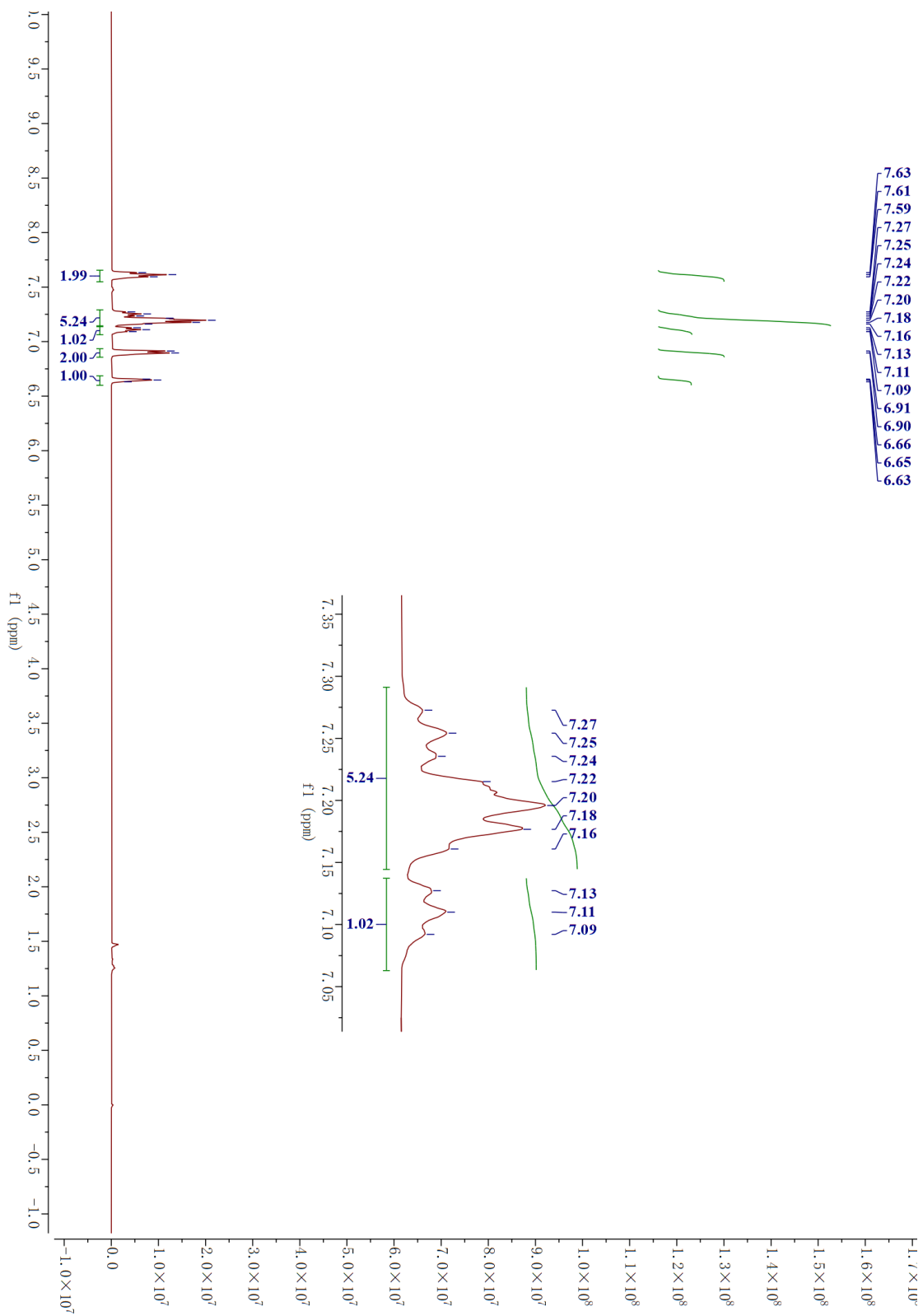
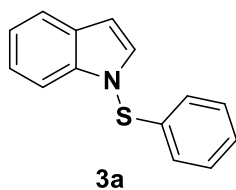


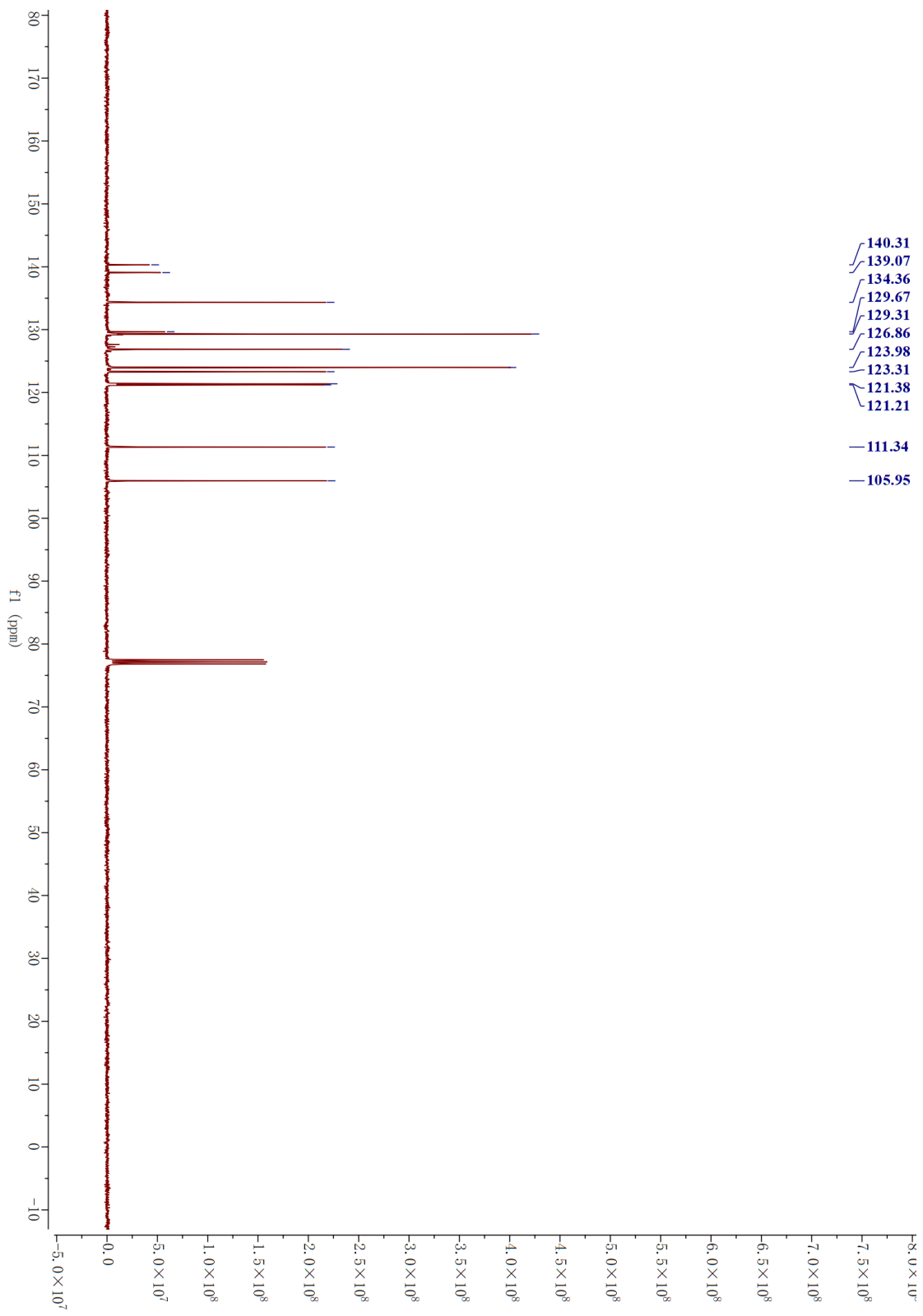
1-(phenylthio)-1*H*-pyrrolo[2,3-*b*]pyridine (3ac): 39.0 mg (57%) white solid; m.p. 112.5 – 114.0 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.35 (d, *J* = 4.7 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 3.7 Hz, 1H), 7.37 – 7.18 (m, 4H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.77 (d, *J* = 3.7 Hz, 1H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 150.33, 144.51, 138.82, 135.71, 130.04, 129.86, 127.75, 125.22, 121.70, 118.14, 104.57 ppm; HRMS (EI-TOF) calcd for C₁₃H₁₀N₂S [M⁺] *m/z* 226.0565, found 226.0568.

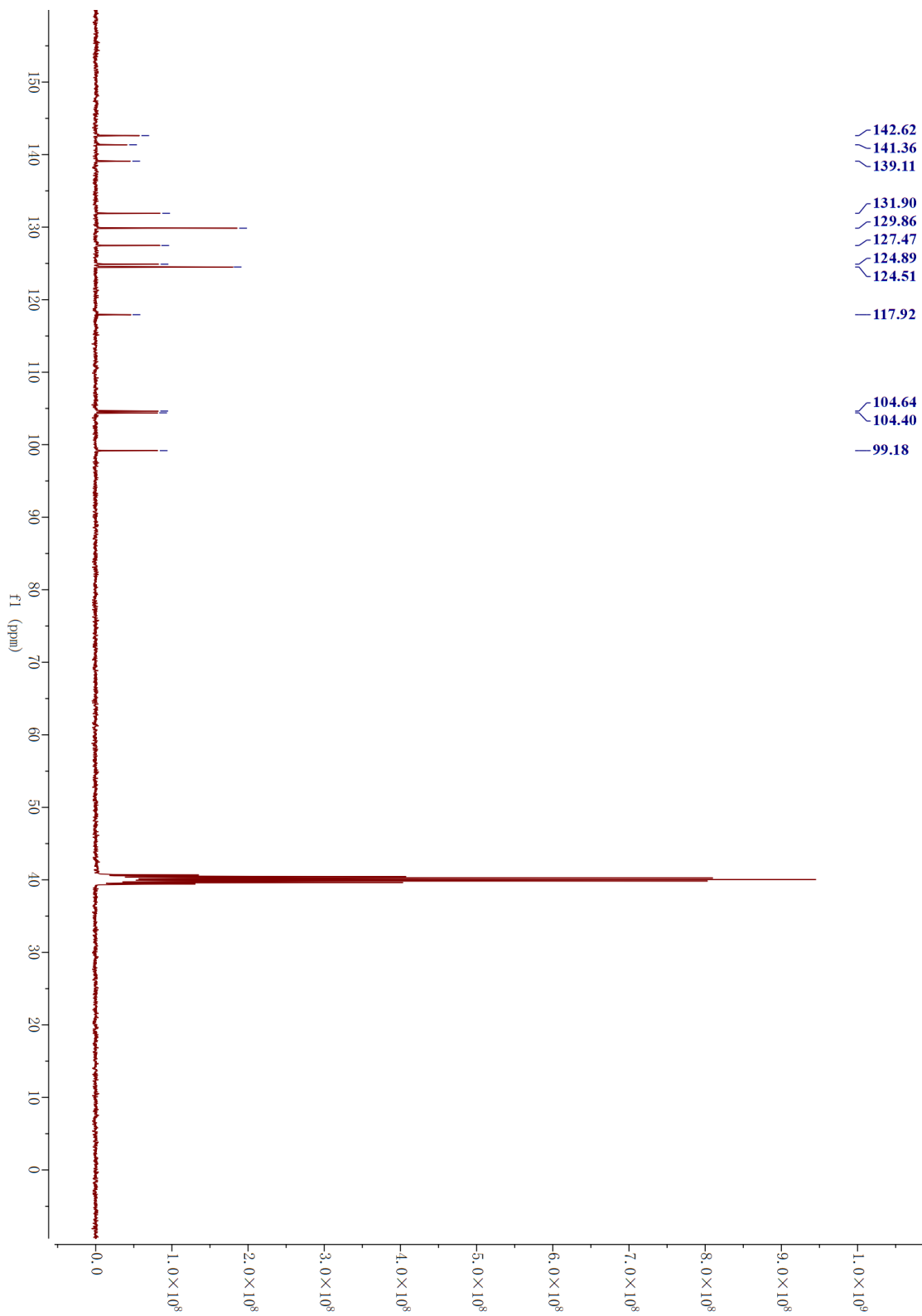


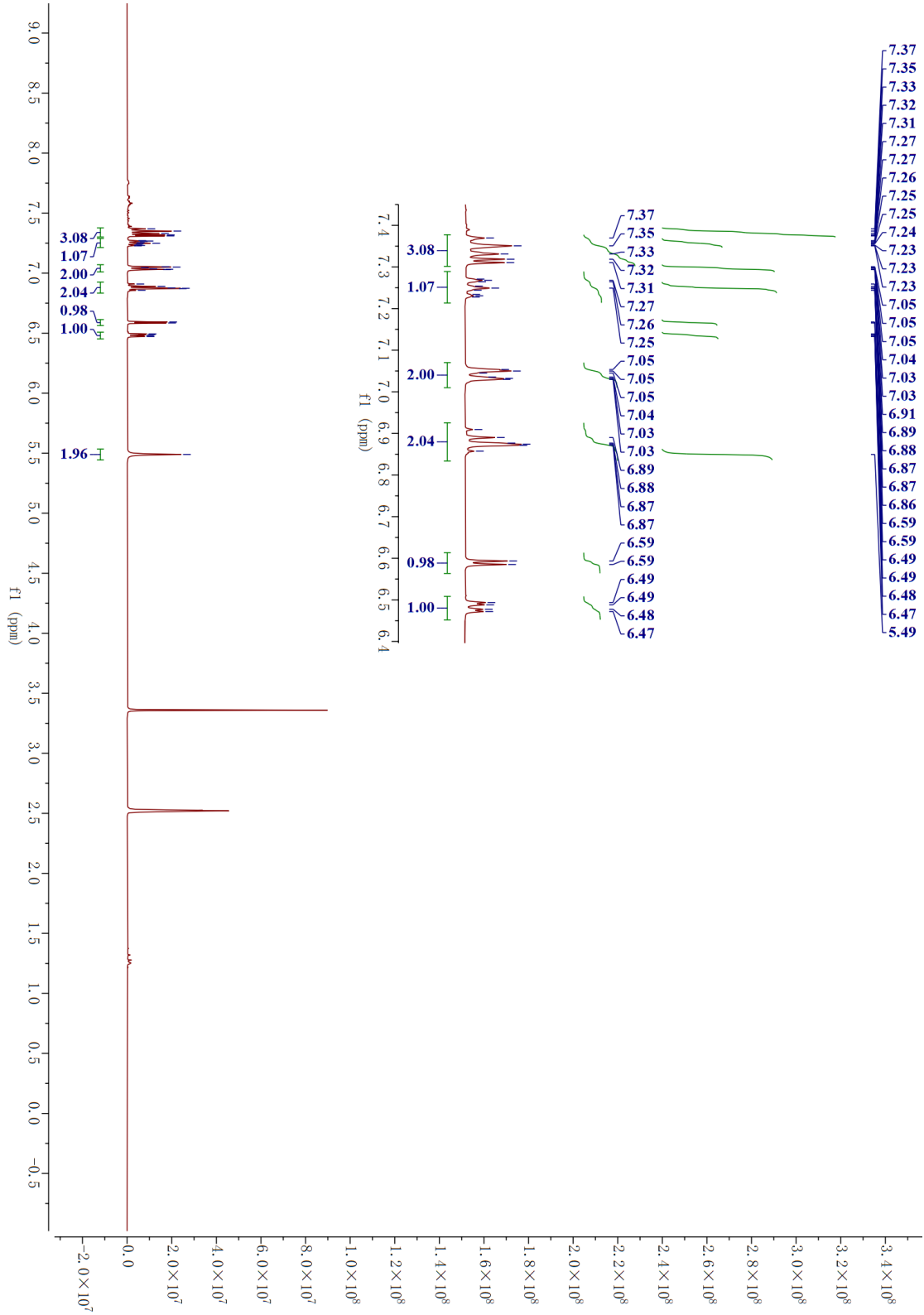
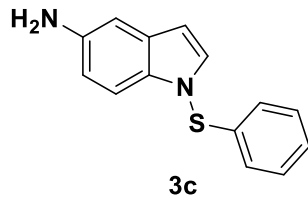
1-(phenylthio)-1*H*-indazole (3ad): 54.5 mg (80%) white solid; m.p. 93.3 – 95.7 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.44 (d, *J* = 3.4 Hz, 1H), 7.86 (dd, *J* = 8.0, 3.2 Hz, 1H), 7.70 (dd, *J* = 8.4, 3.2 Hz, 1H), 7.48 – 7.57 (m, 1H), 7.20 – 7.37 (m, 4H), 7.11 (dd, *J* = 8.0, 3.2 Hz, 2H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 145.02, 139.74, 137.71, 130.02, 128.71, 128.50, 126.38, 125.31, 122.96, 122.17, 111.00 ppm; HRMS (EI-TOF) calcd for C₁₃H₁₀N₂S [M⁺] *m/z* 226.0565, found 226.0567.

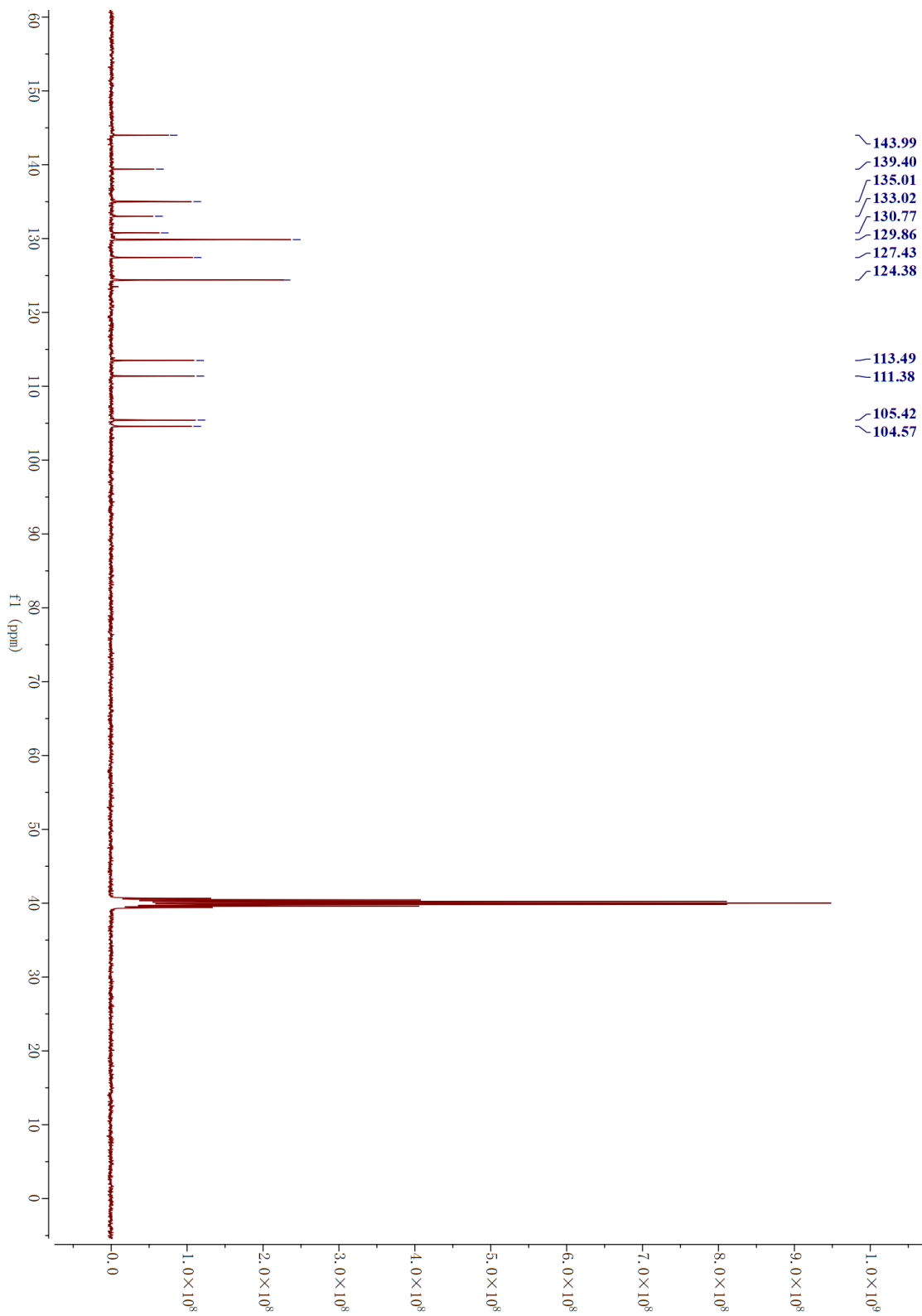
Copies of ^1H , ^{13}C NMR spectrum of products

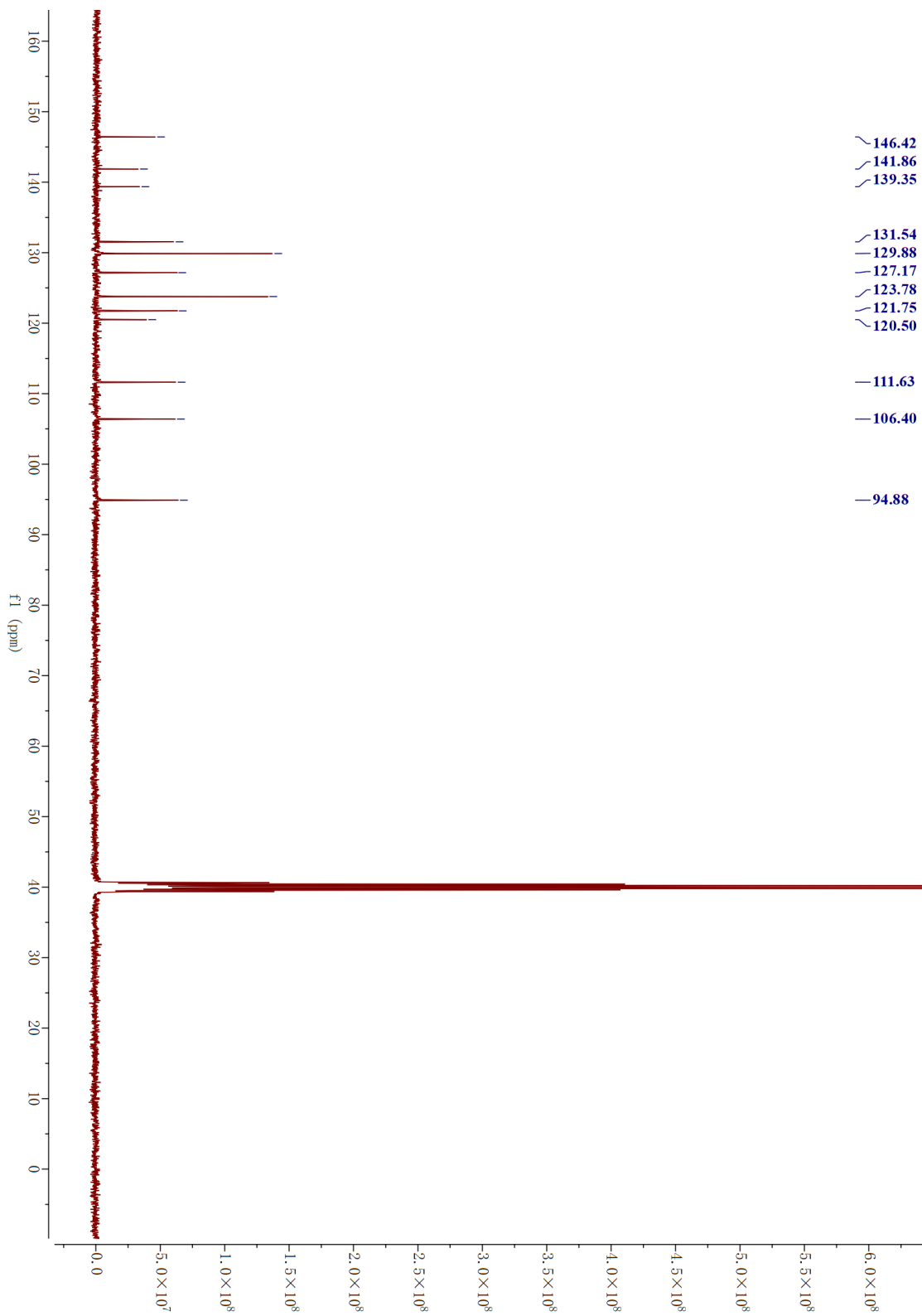


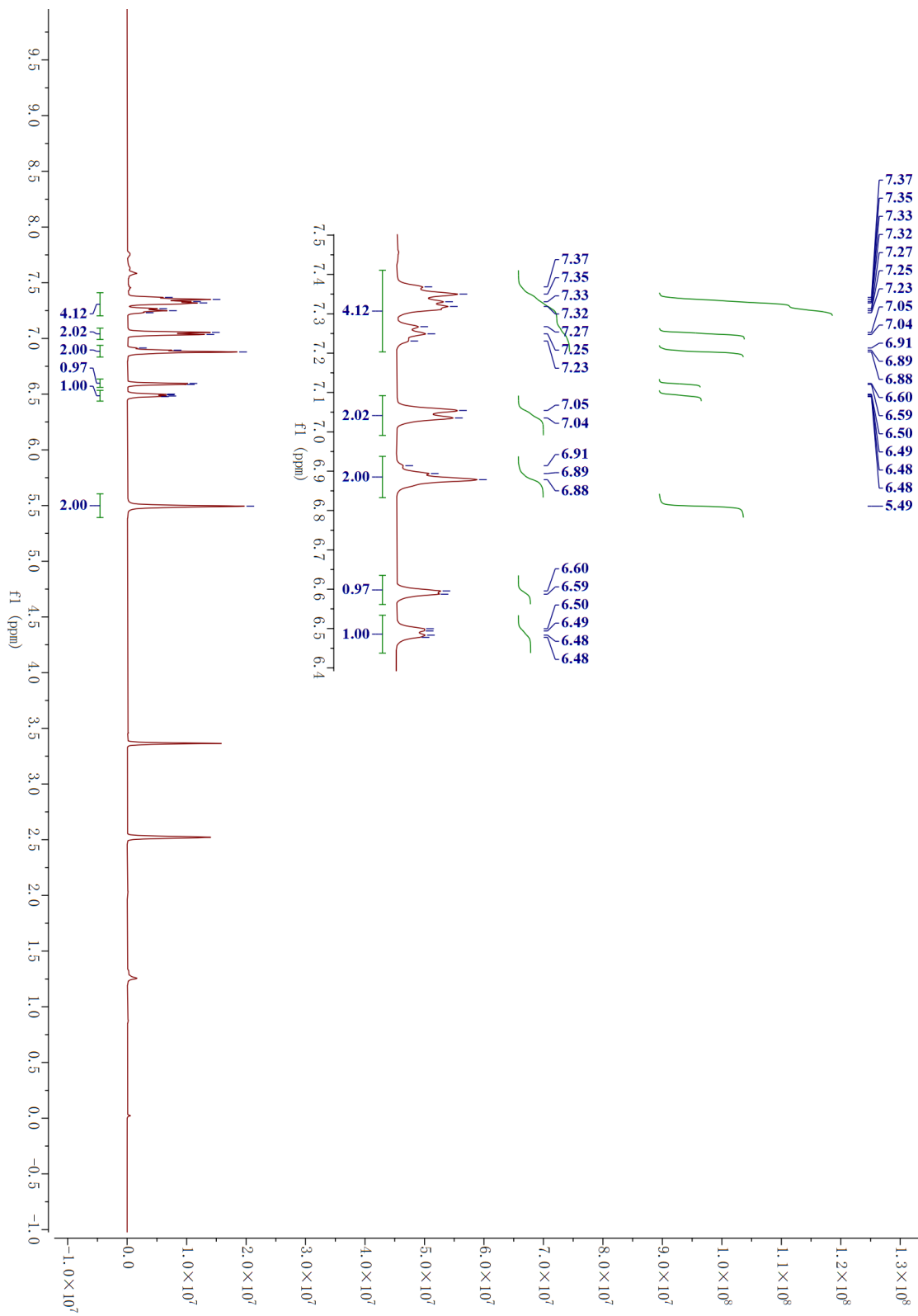
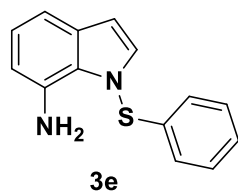


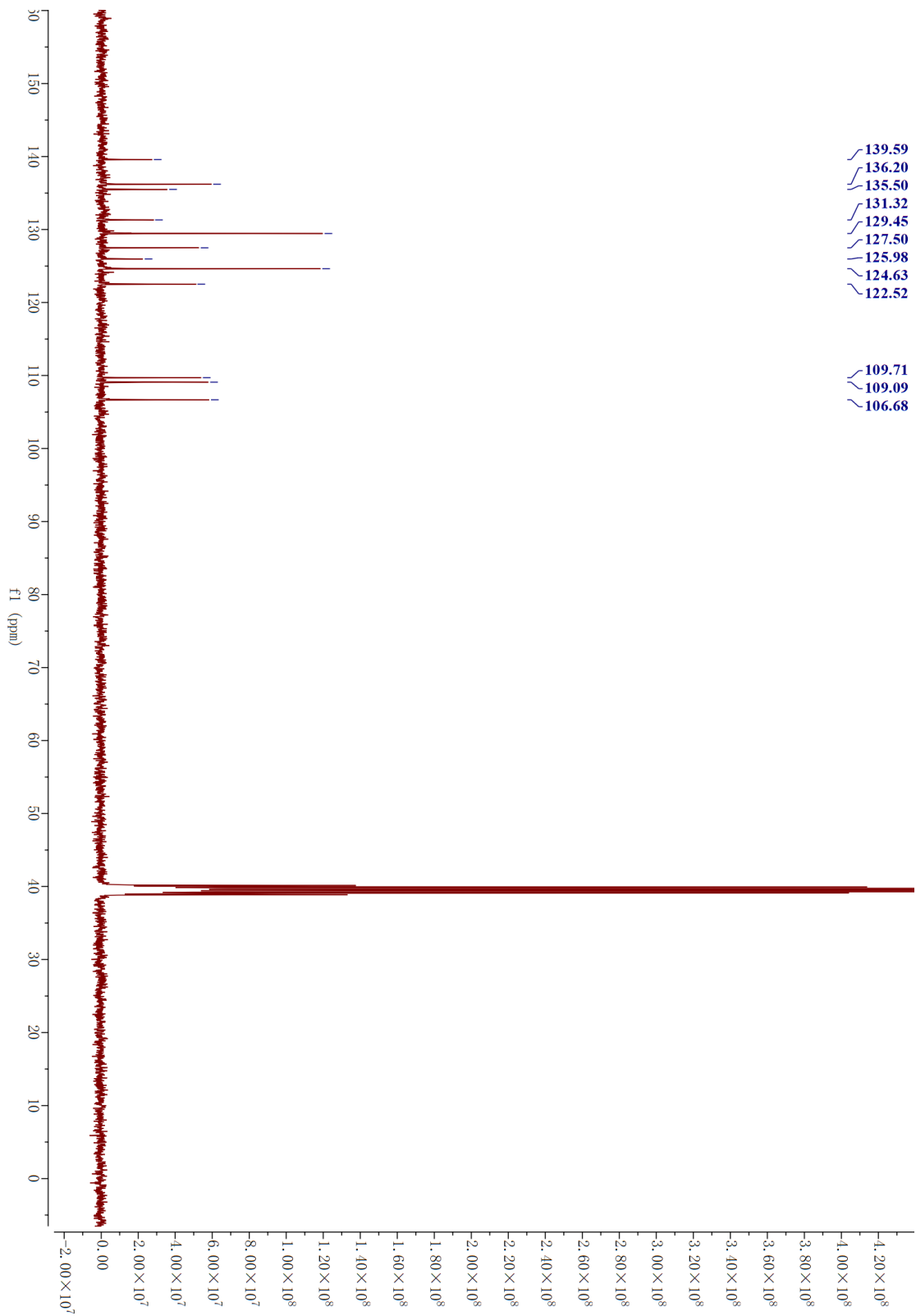


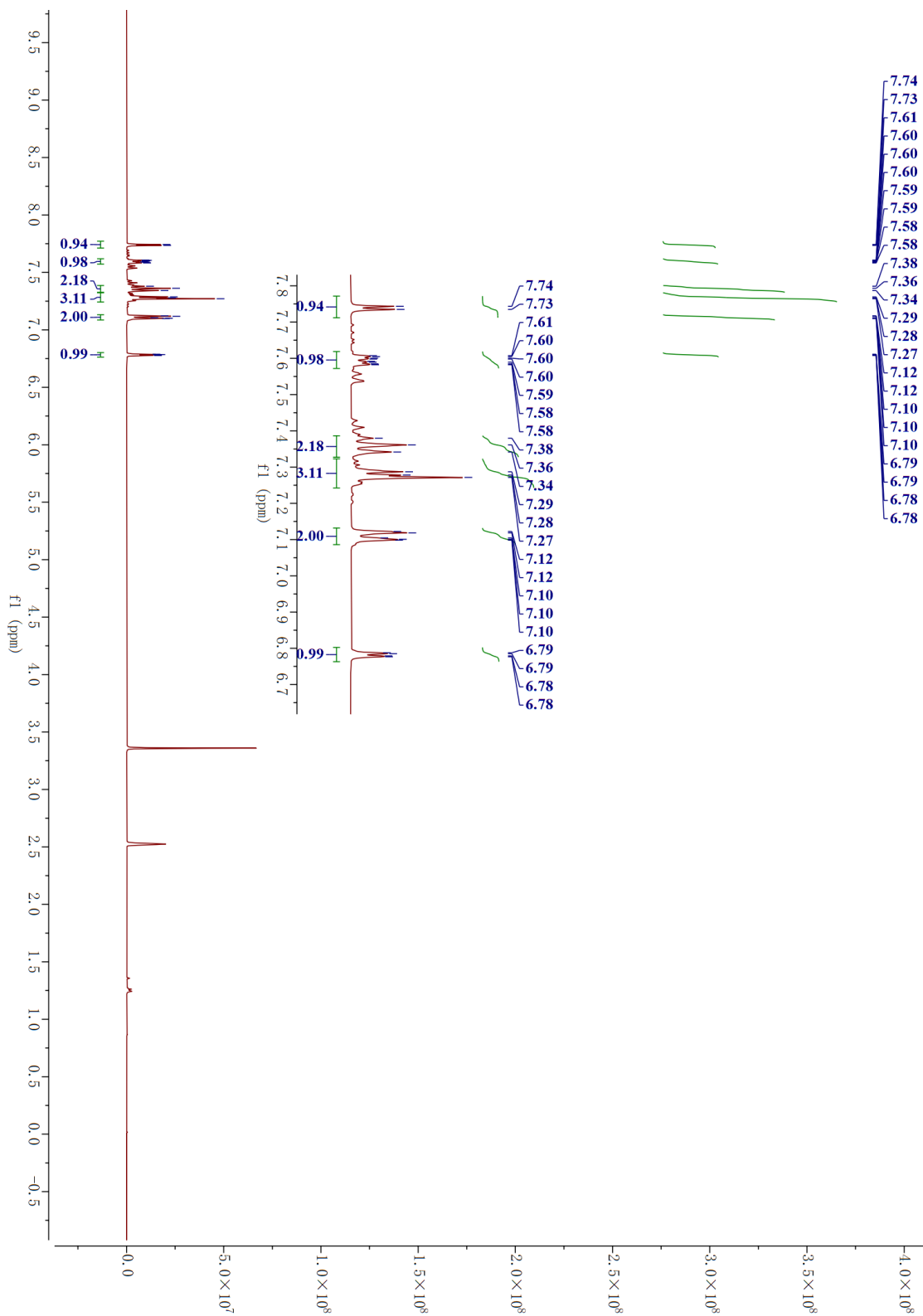
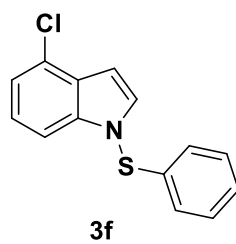


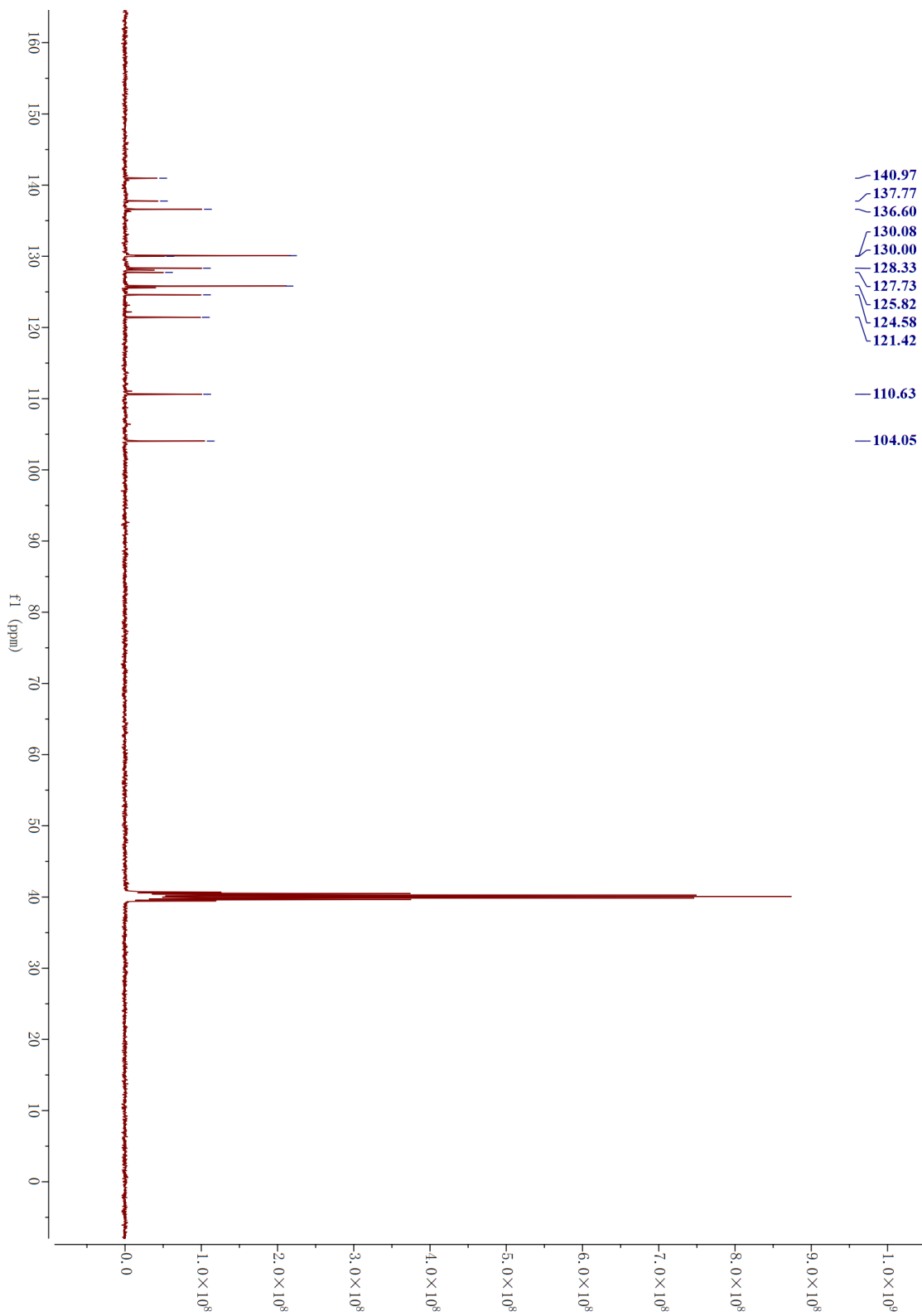


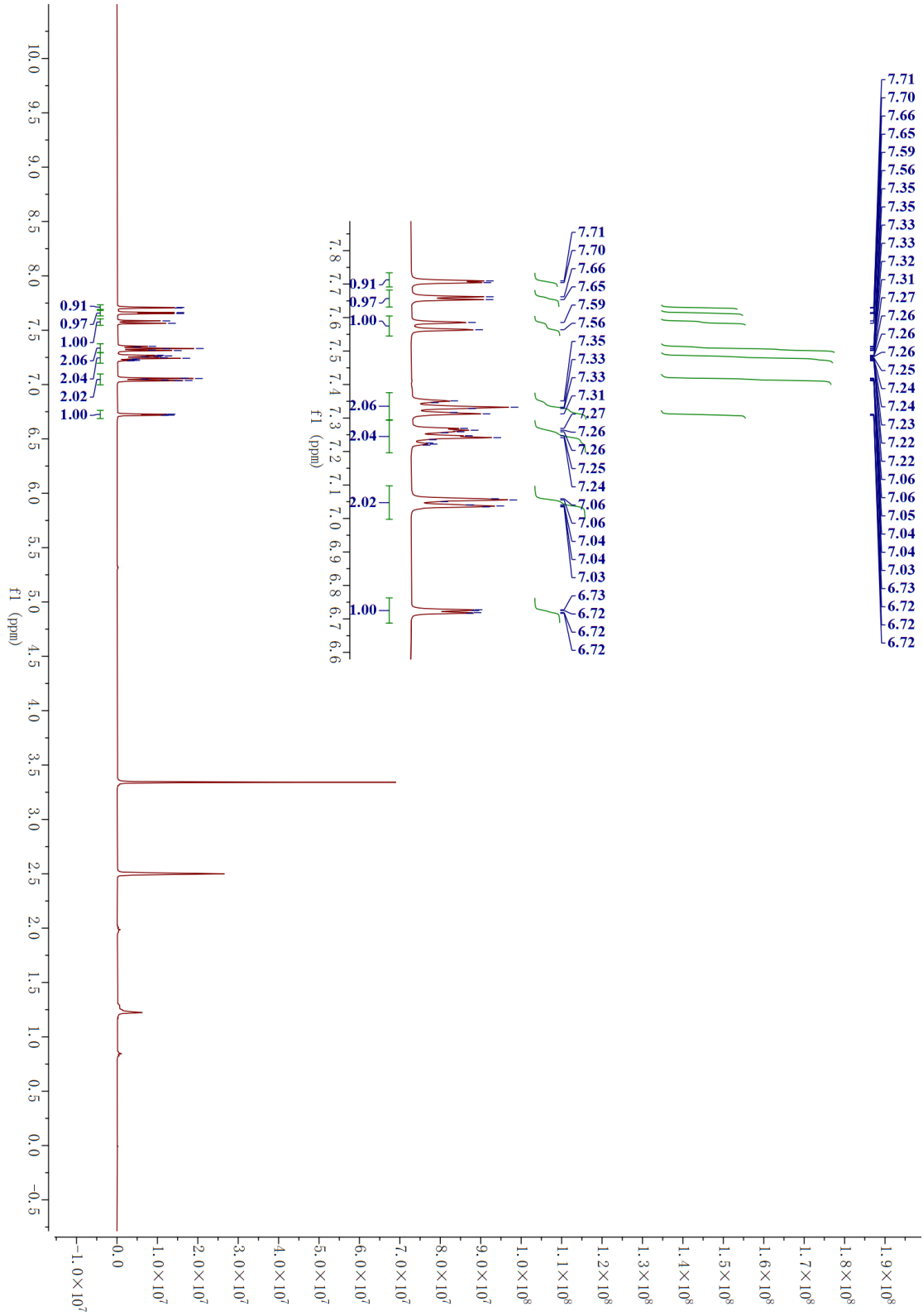
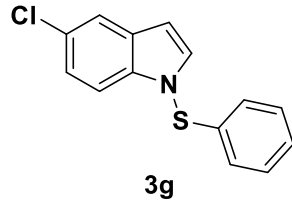


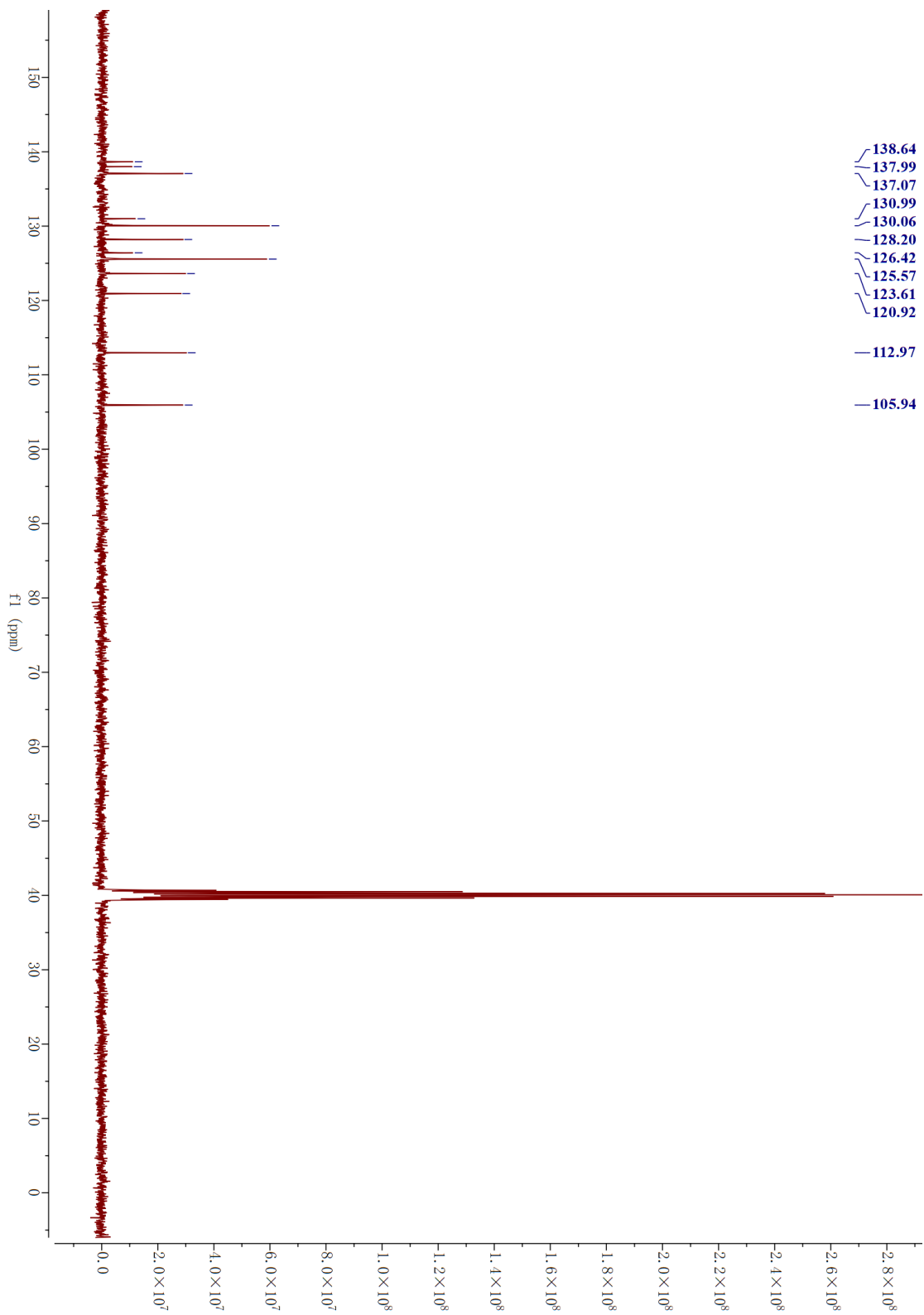


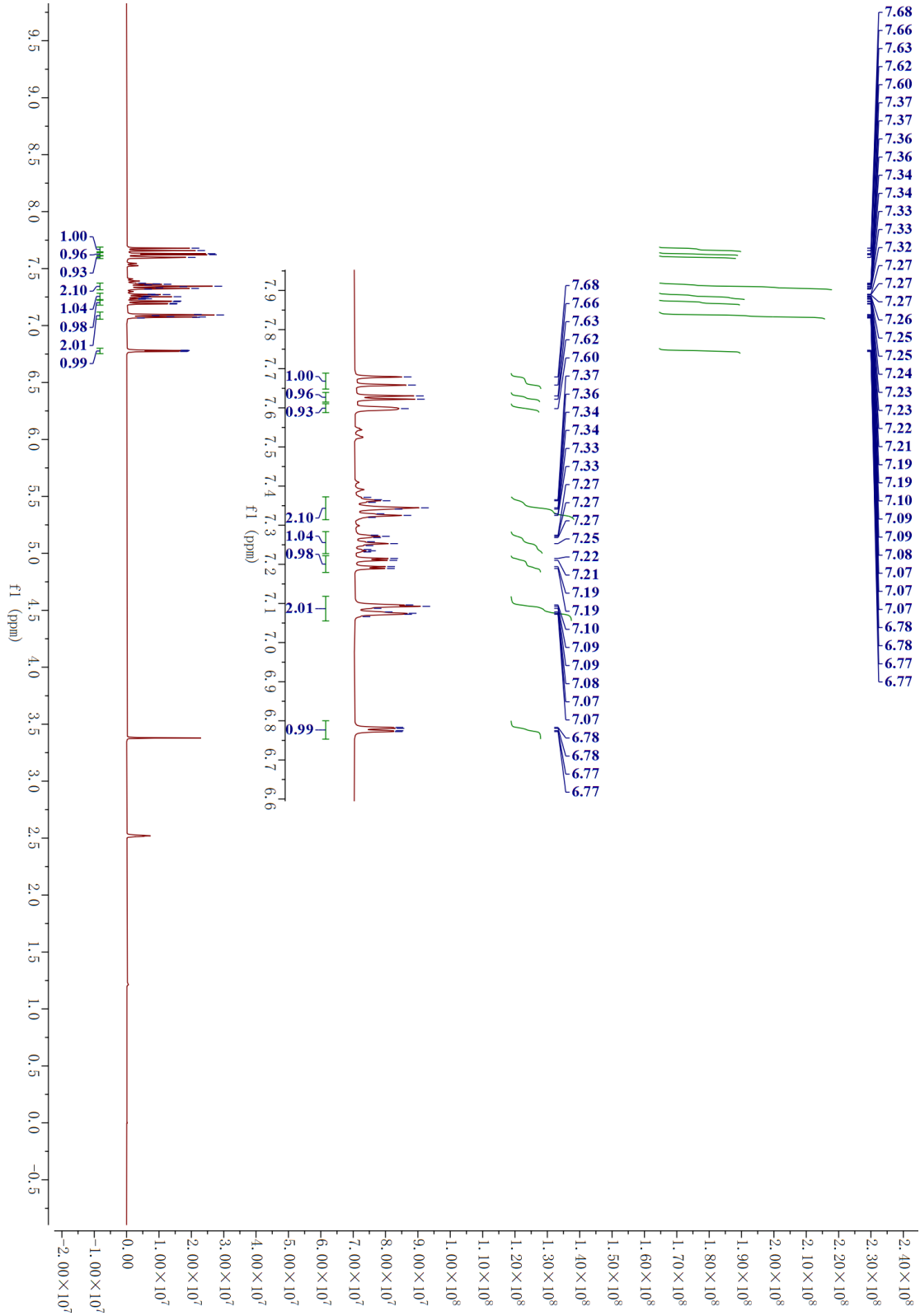
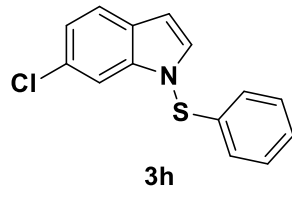


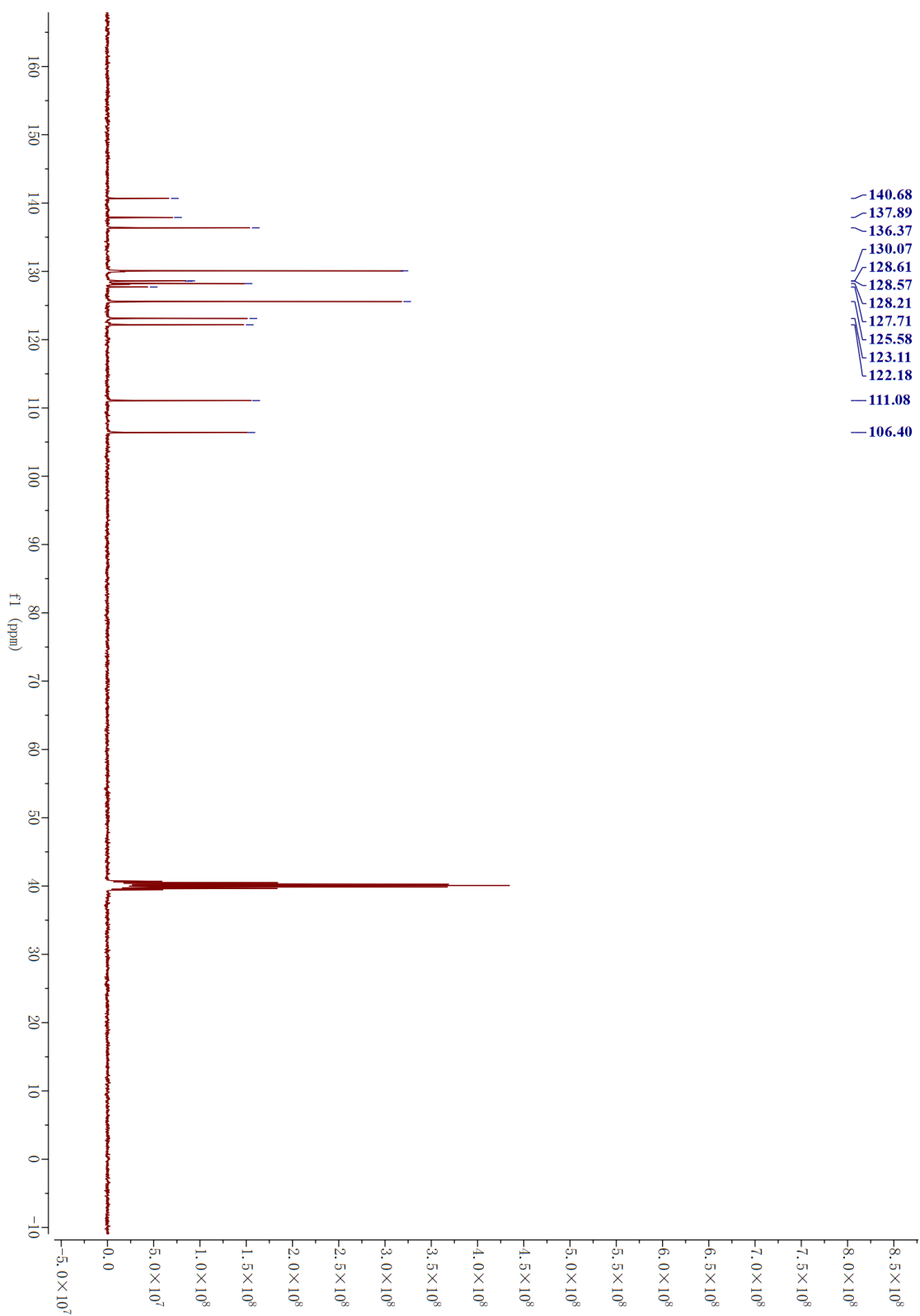


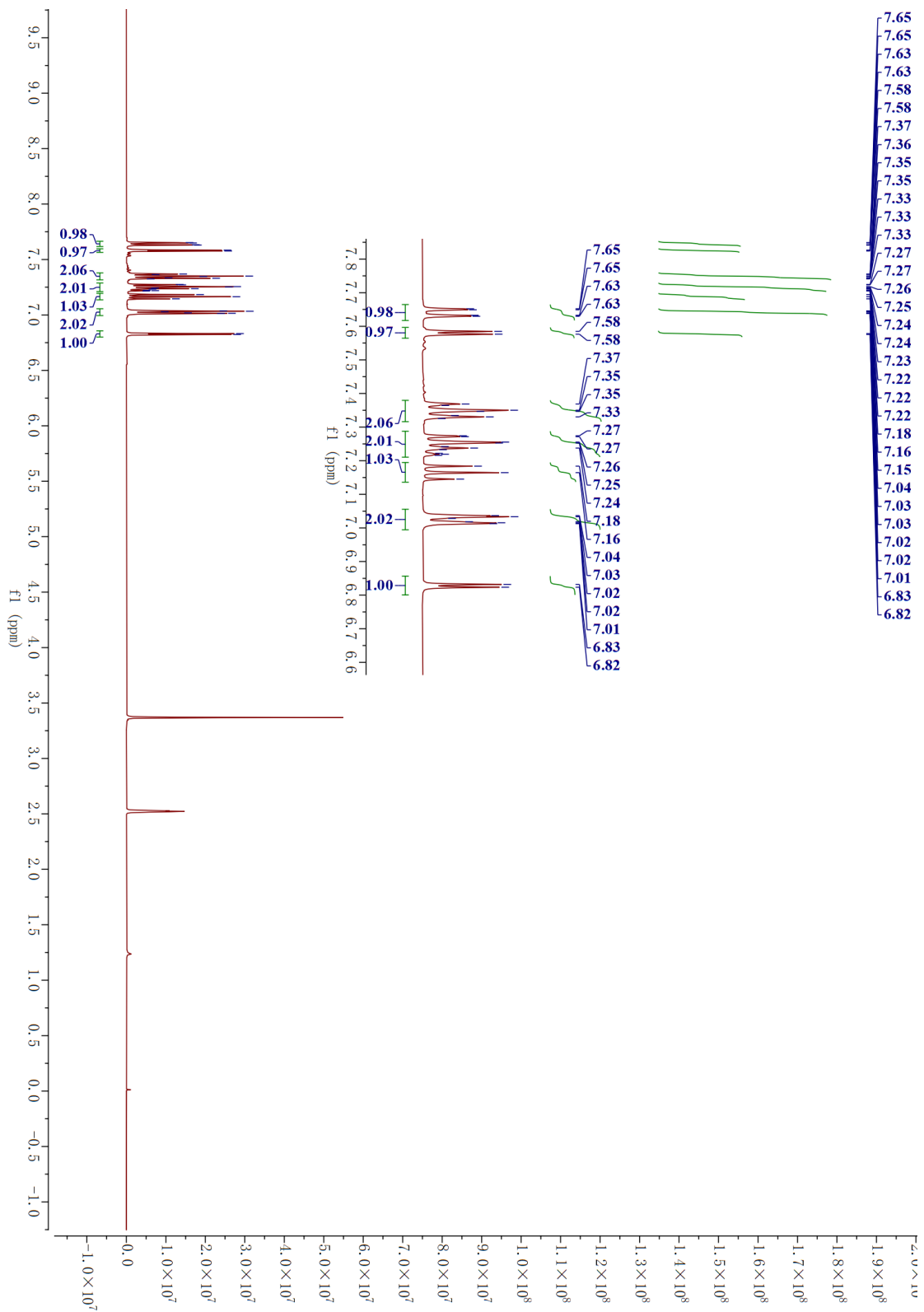
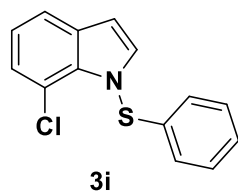


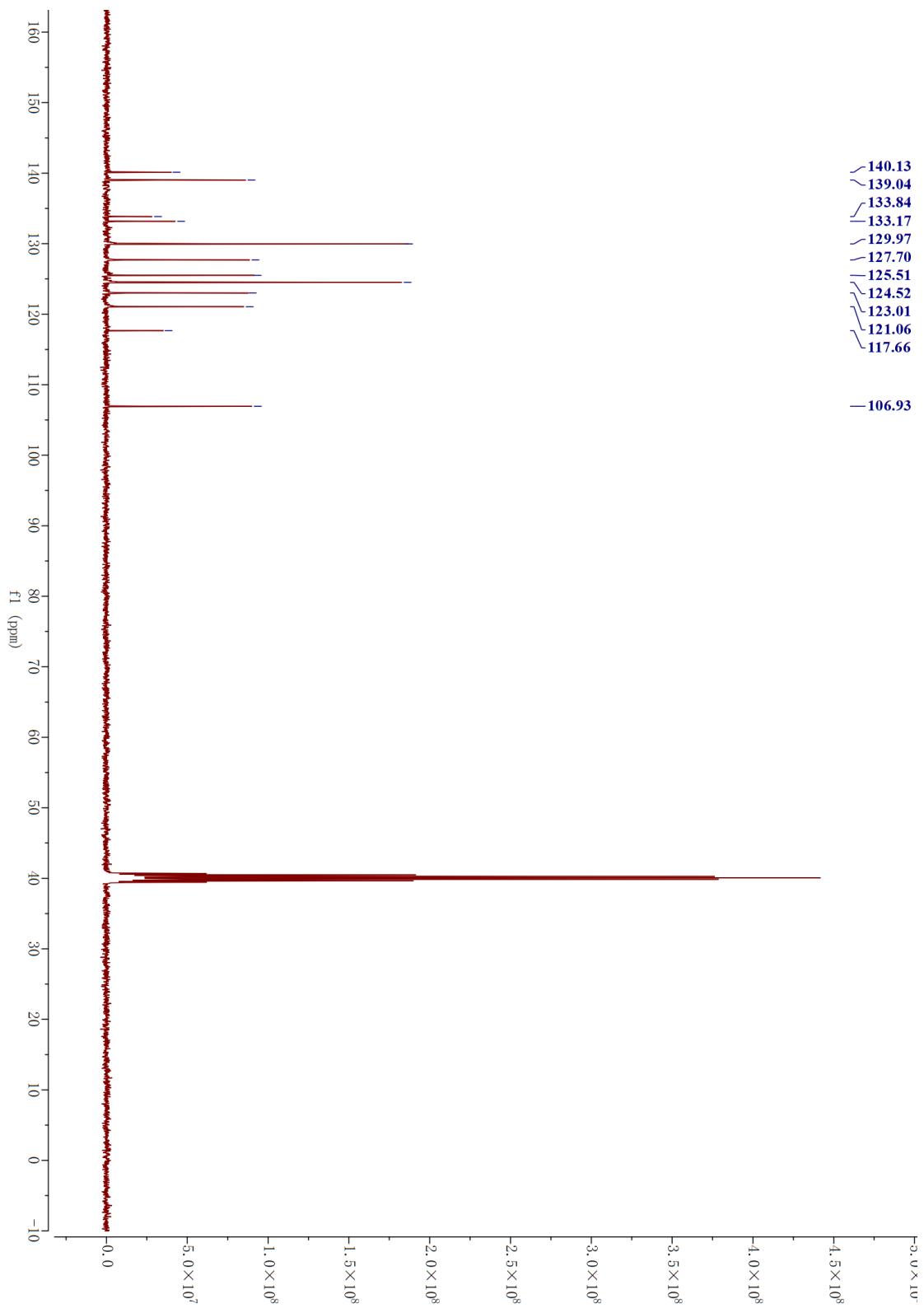


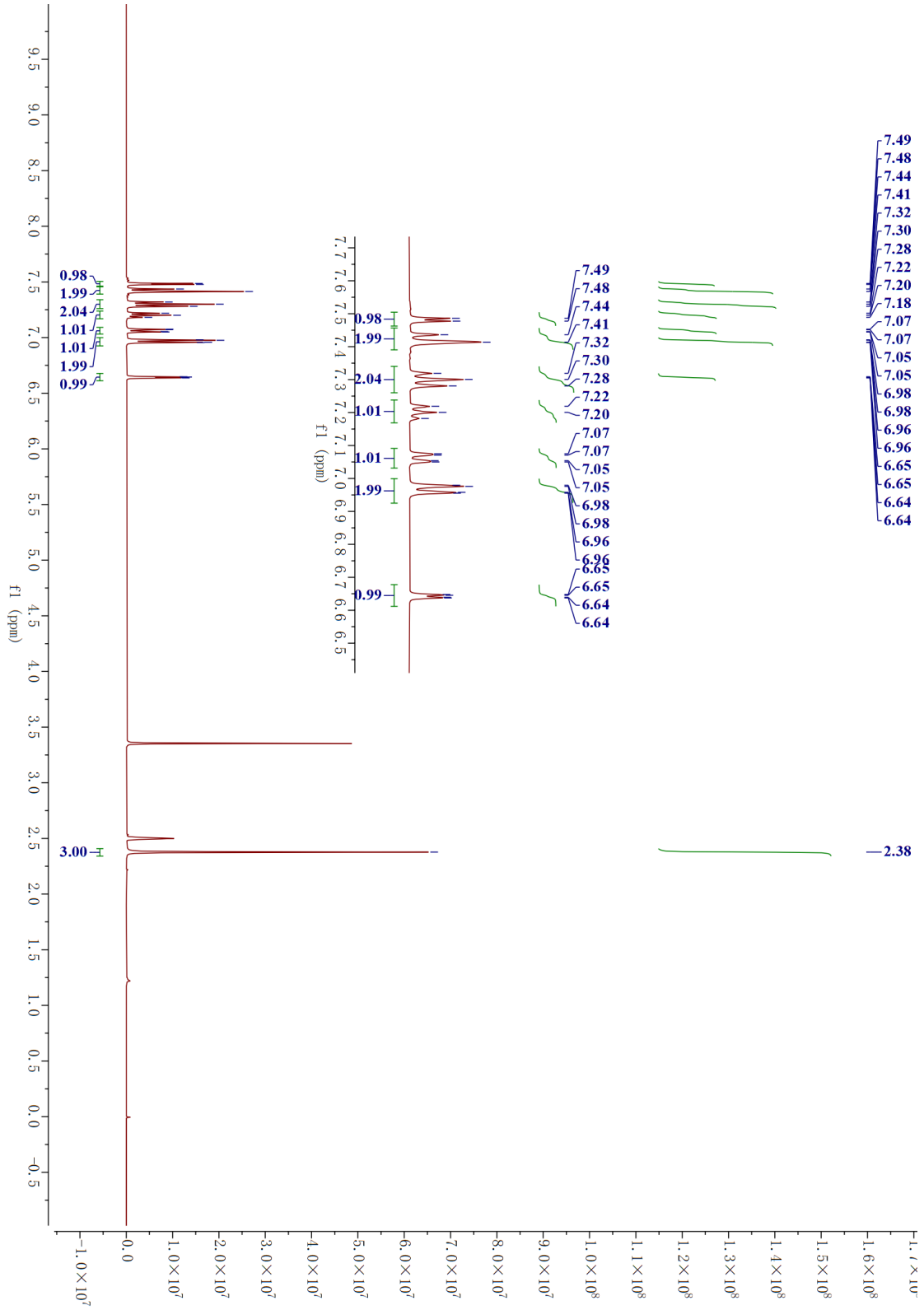
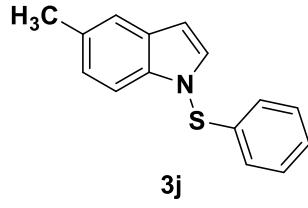


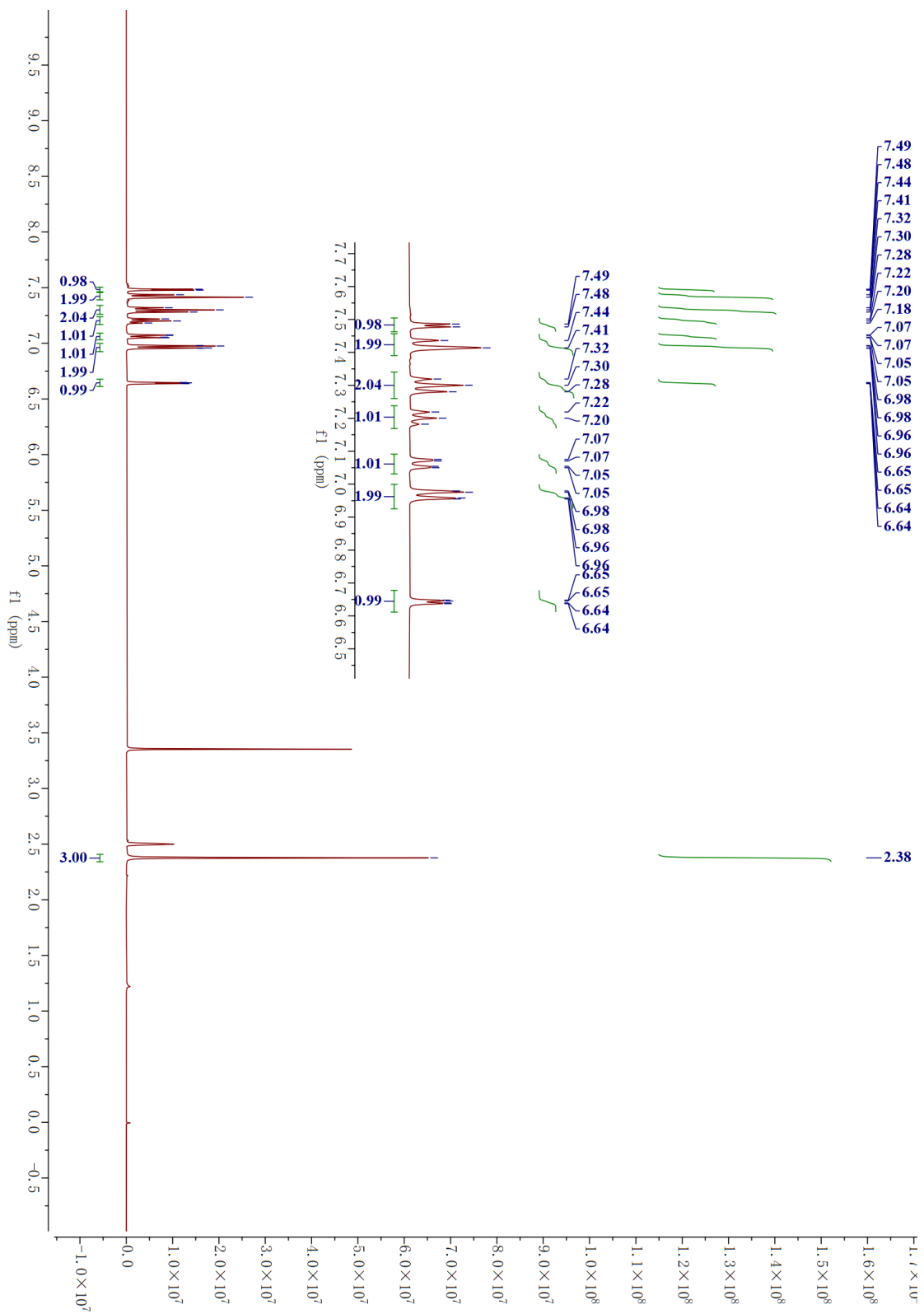


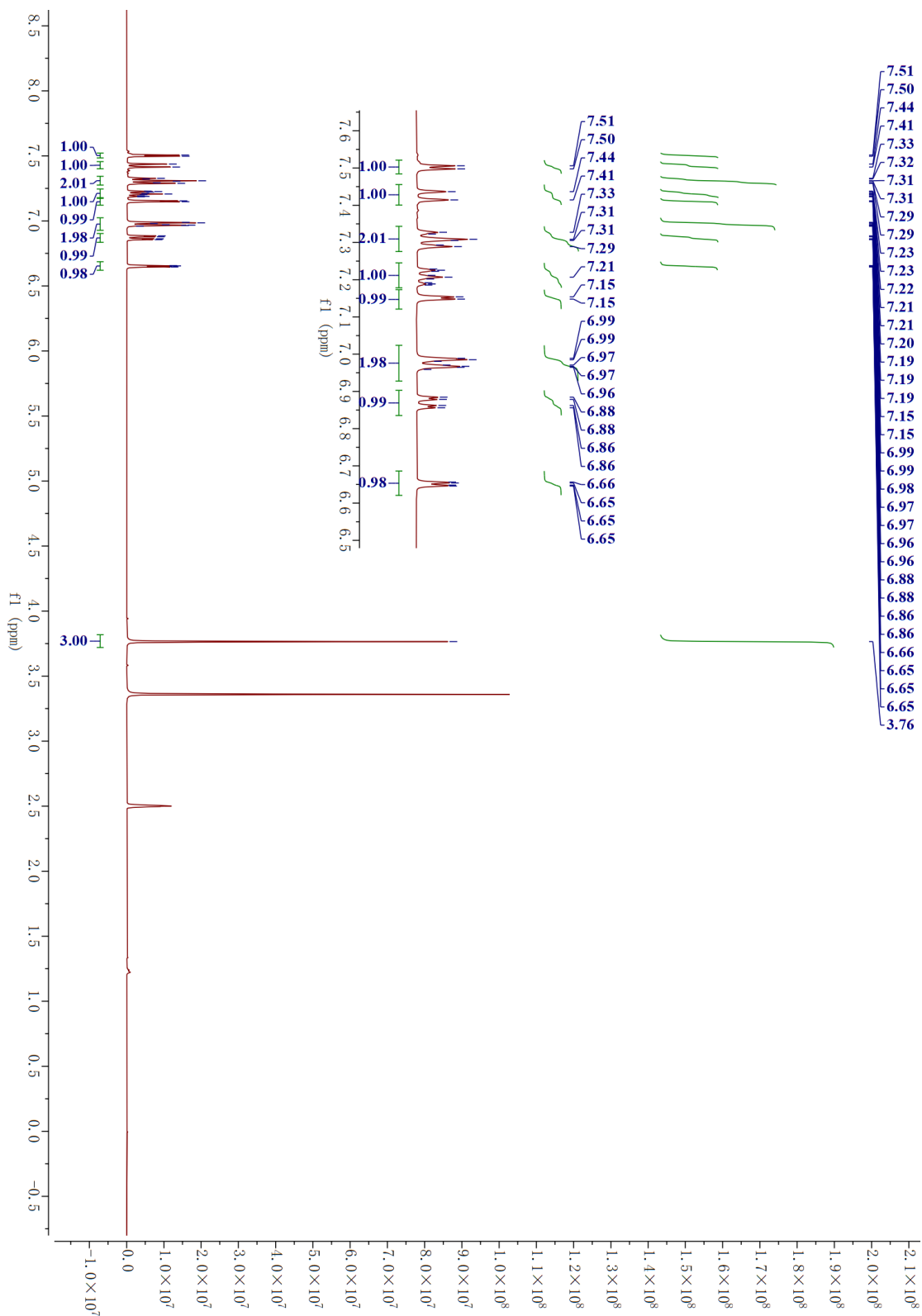
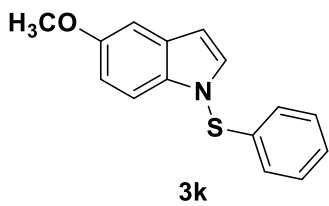


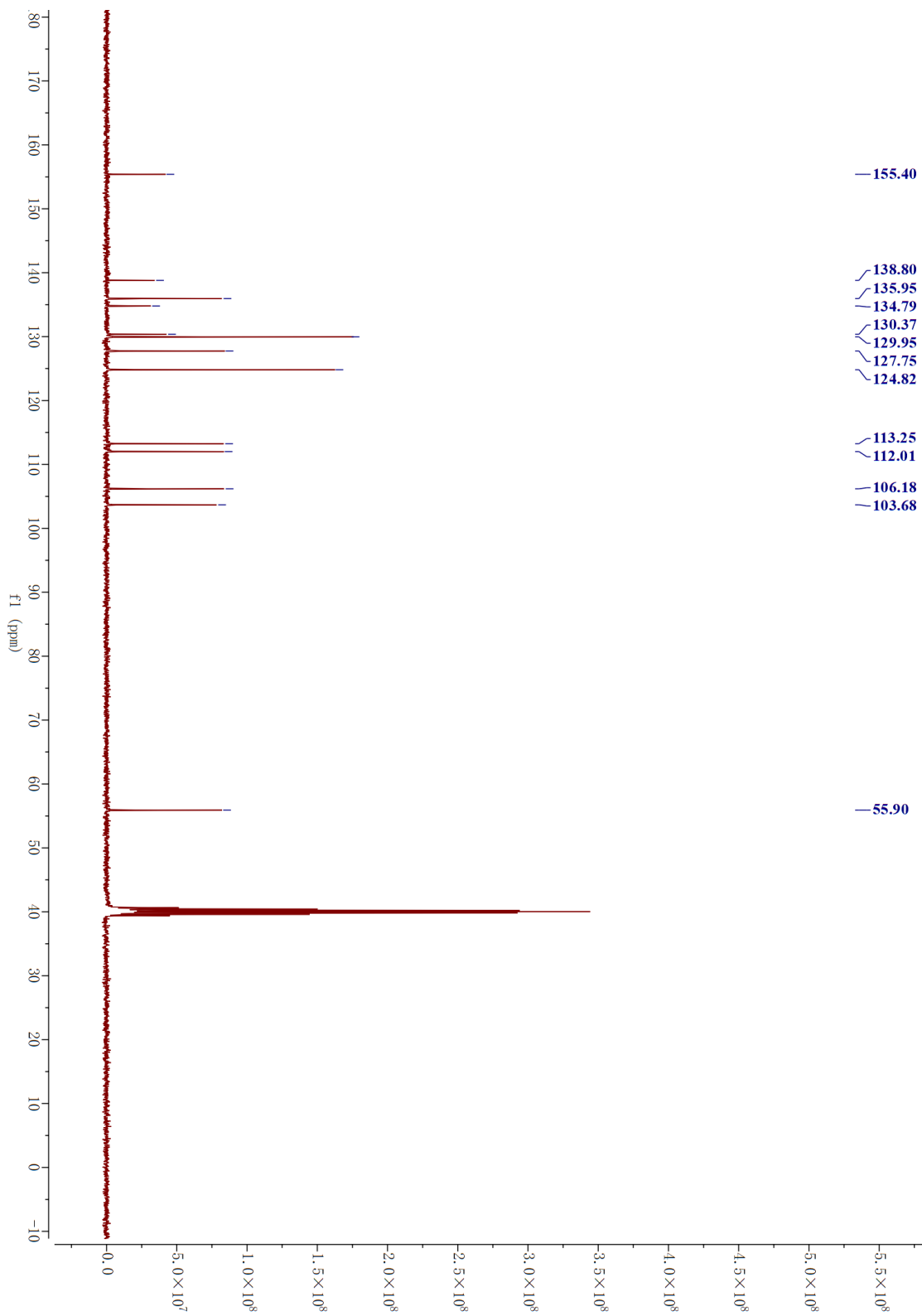


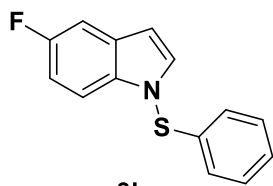




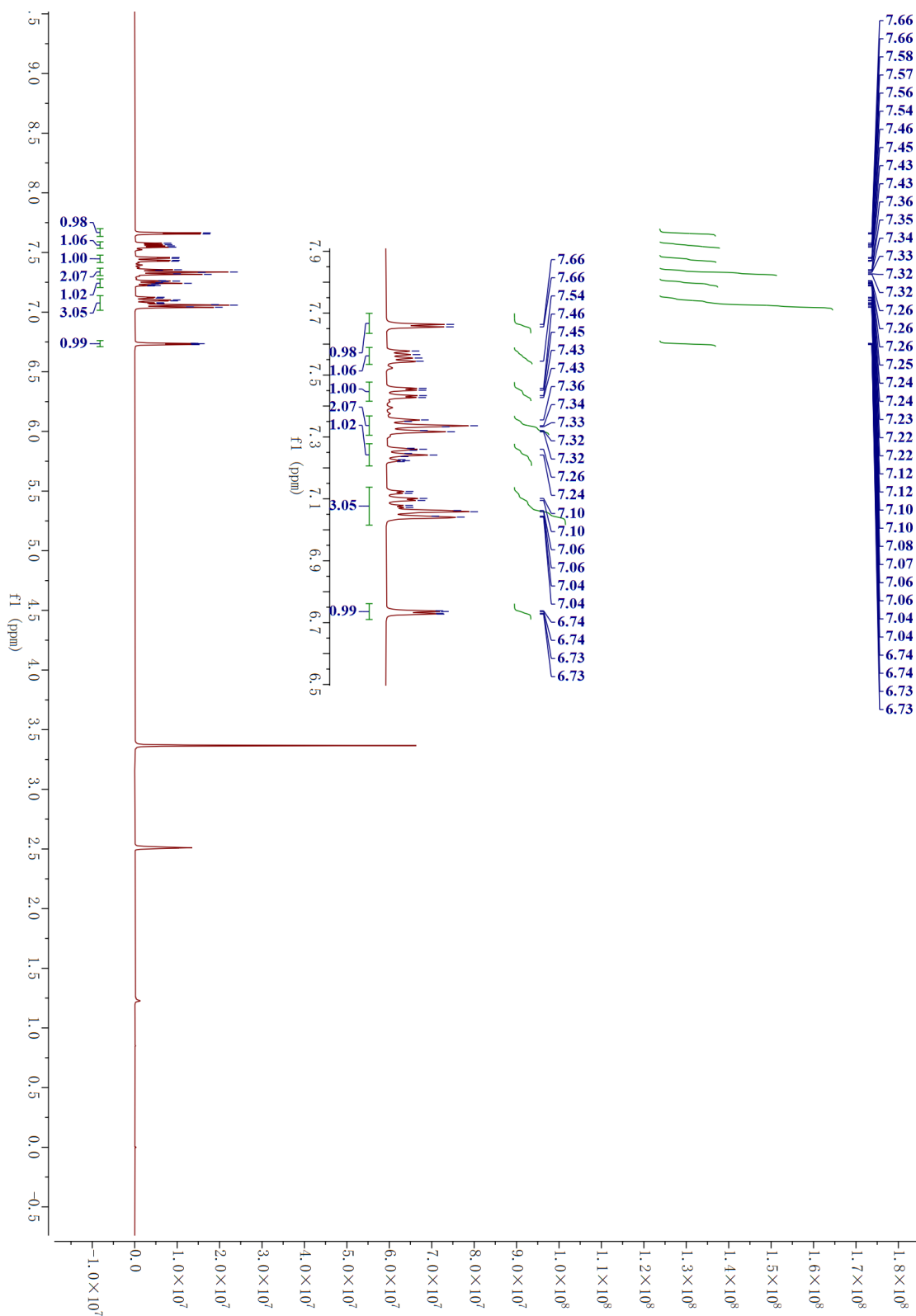


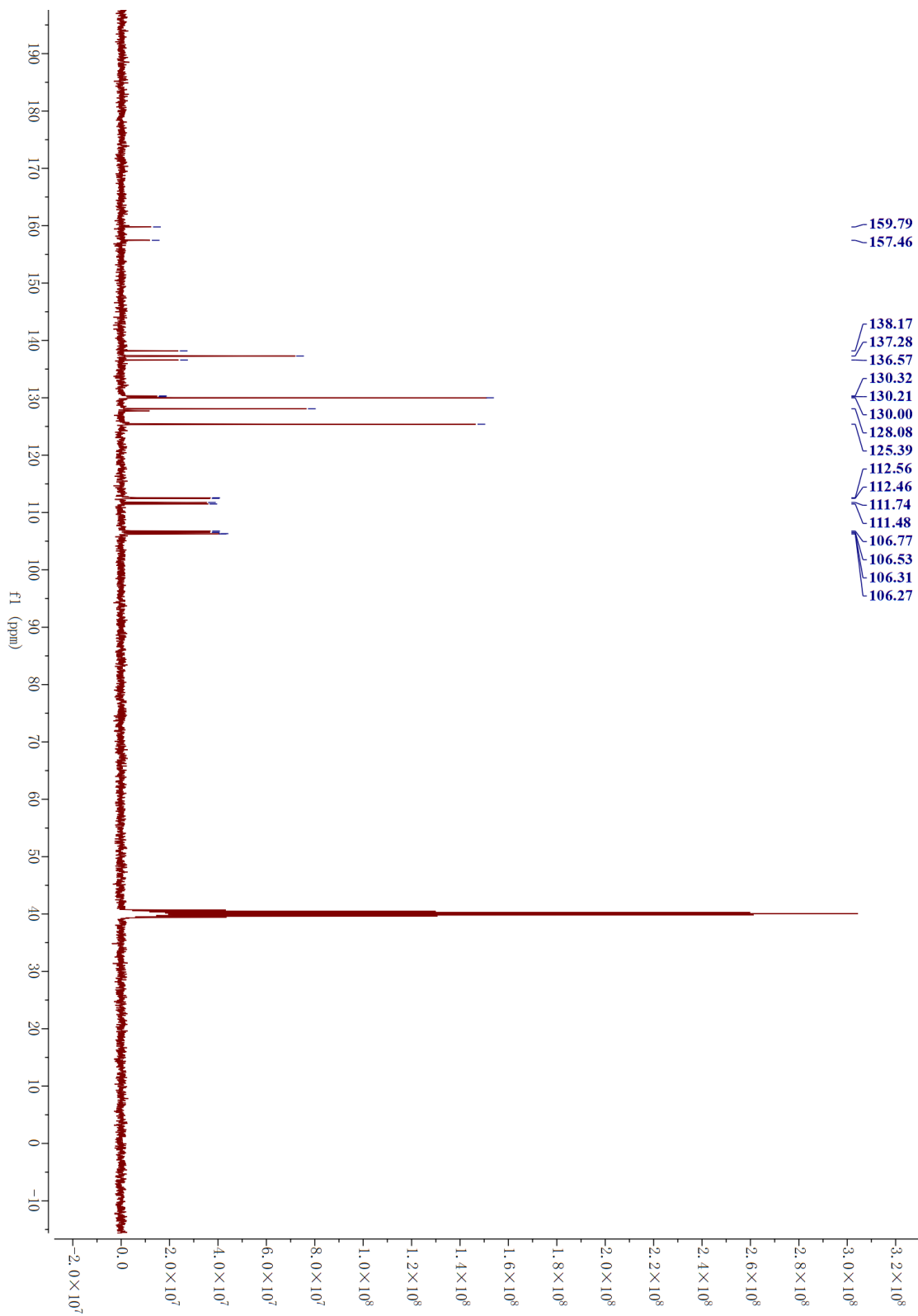


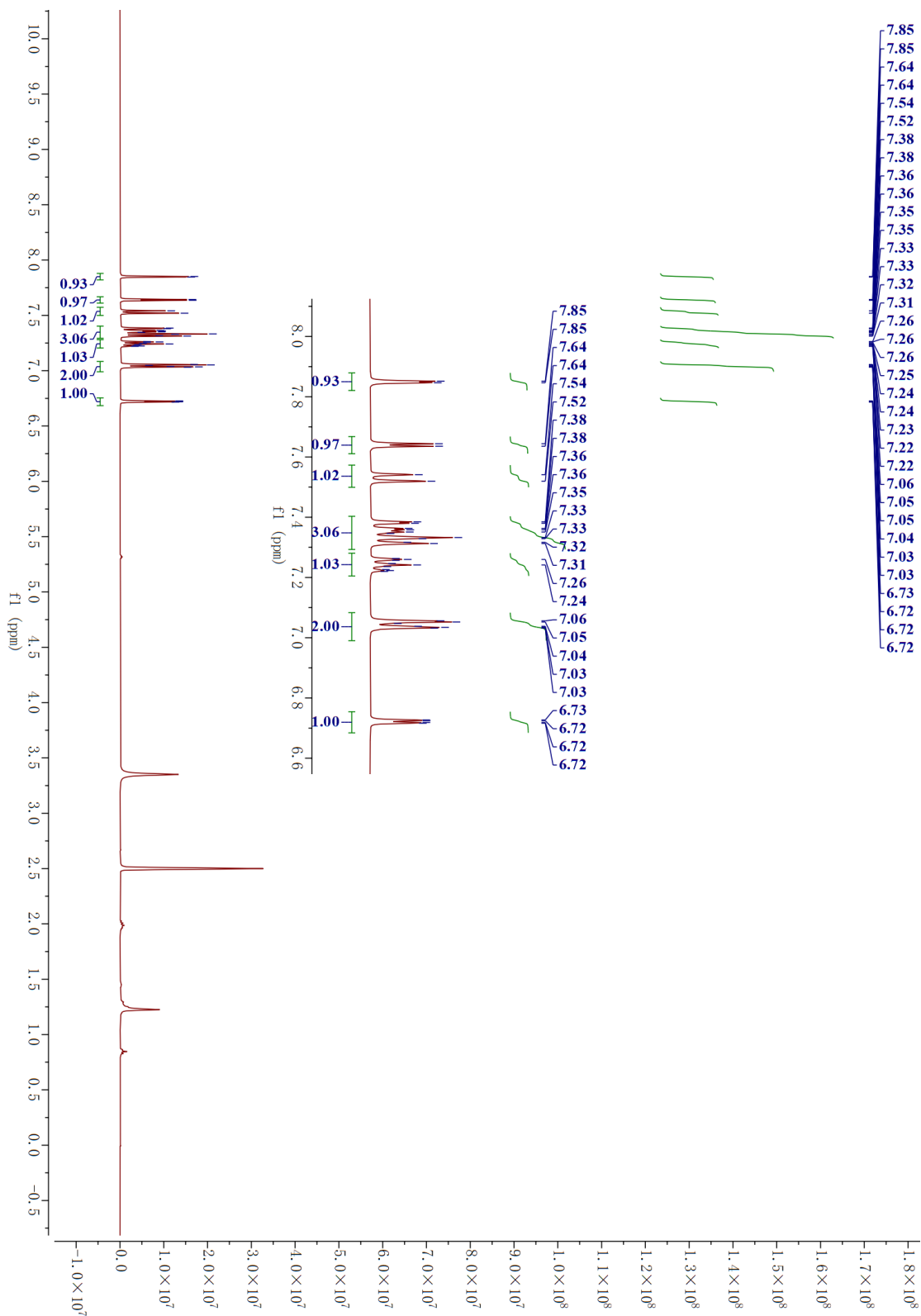
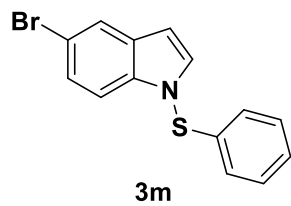


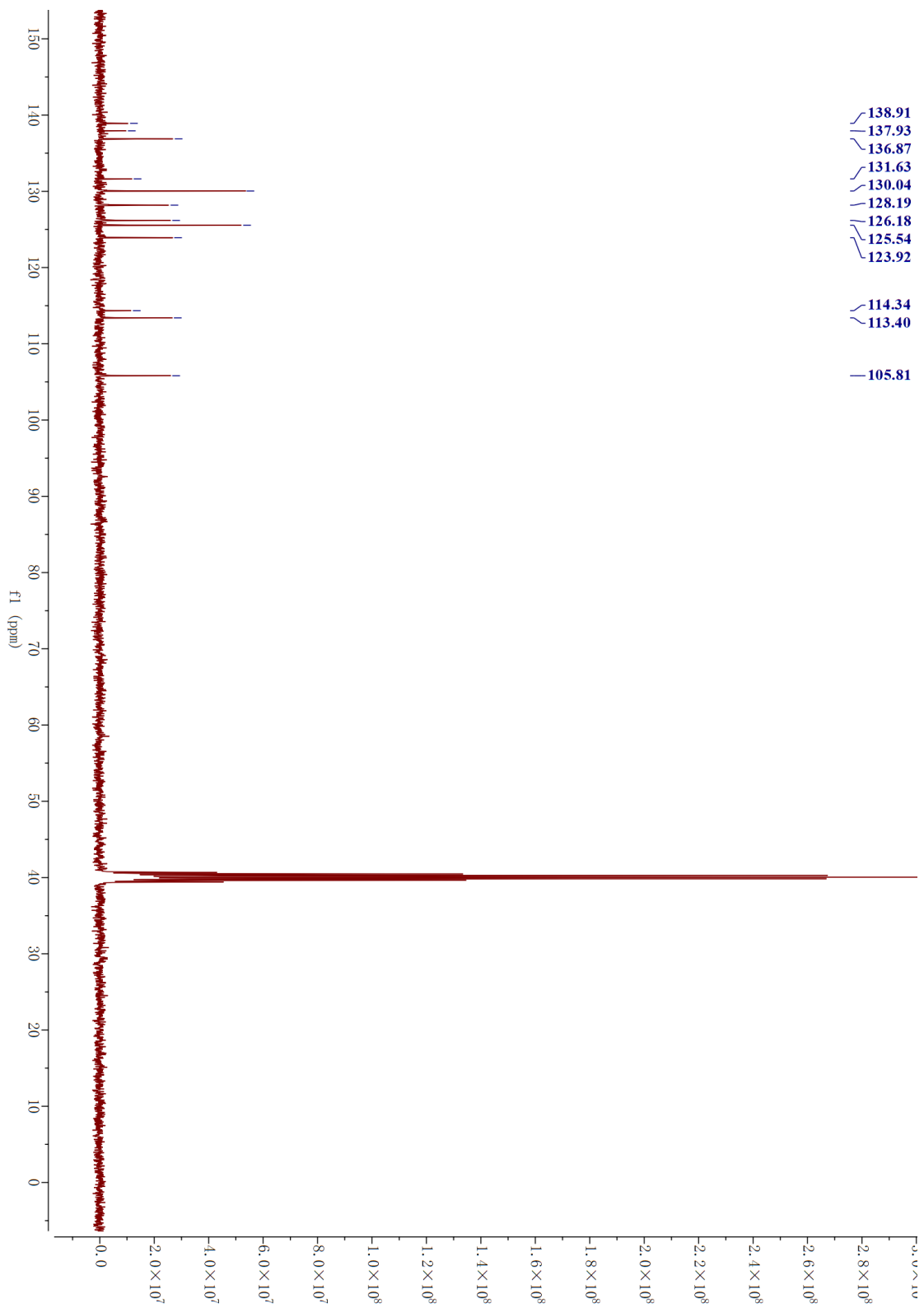


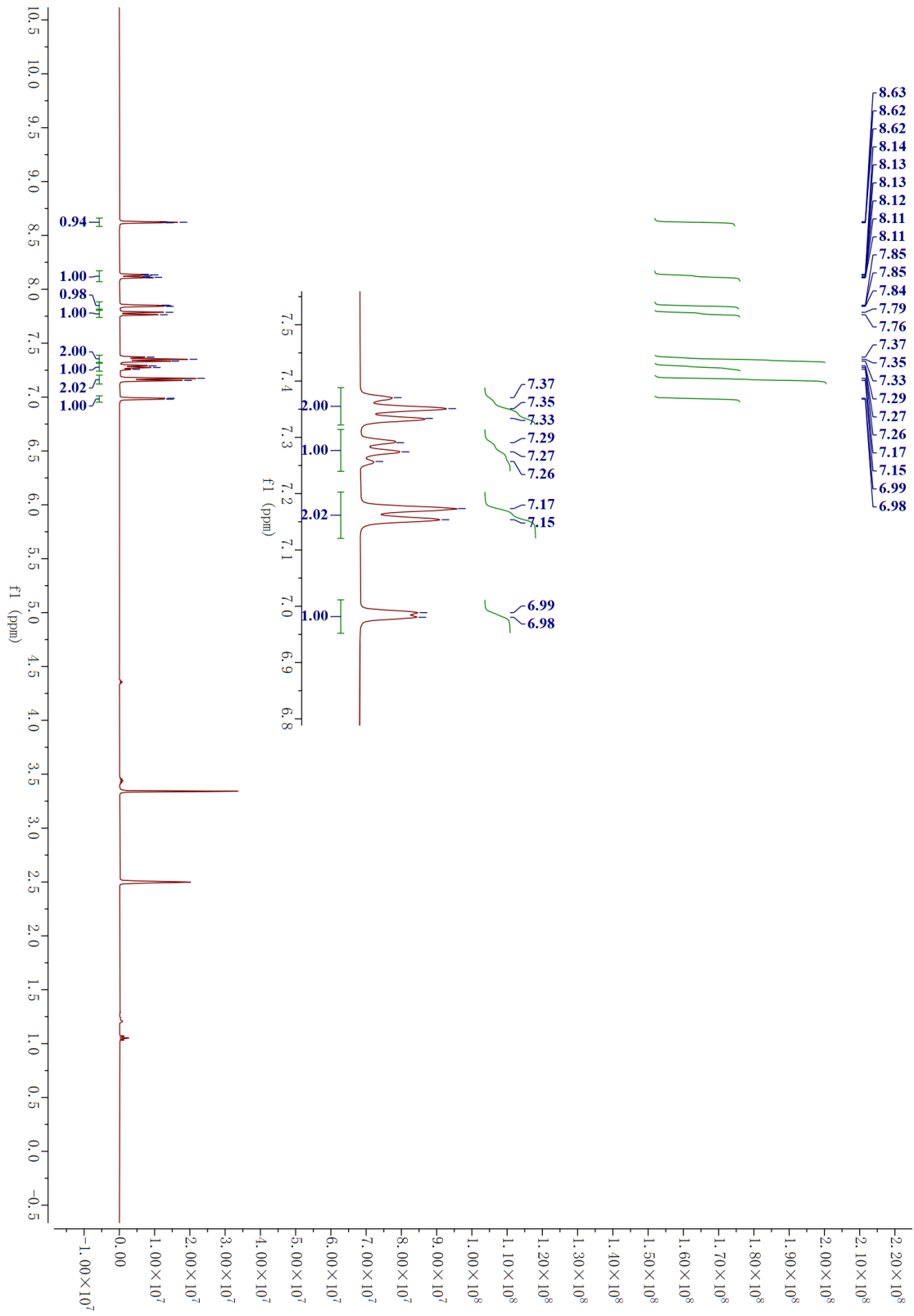
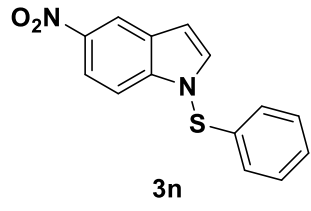
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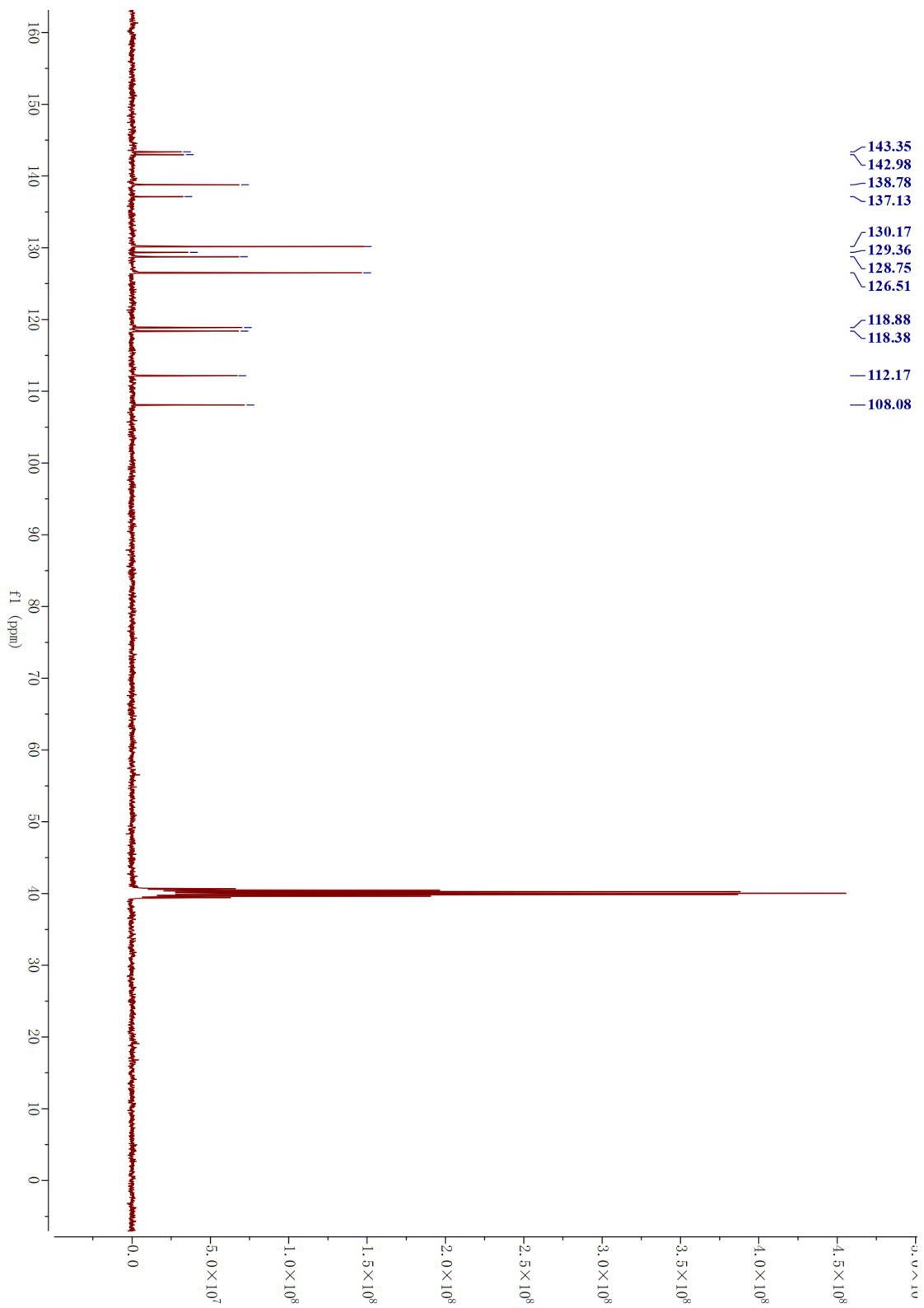


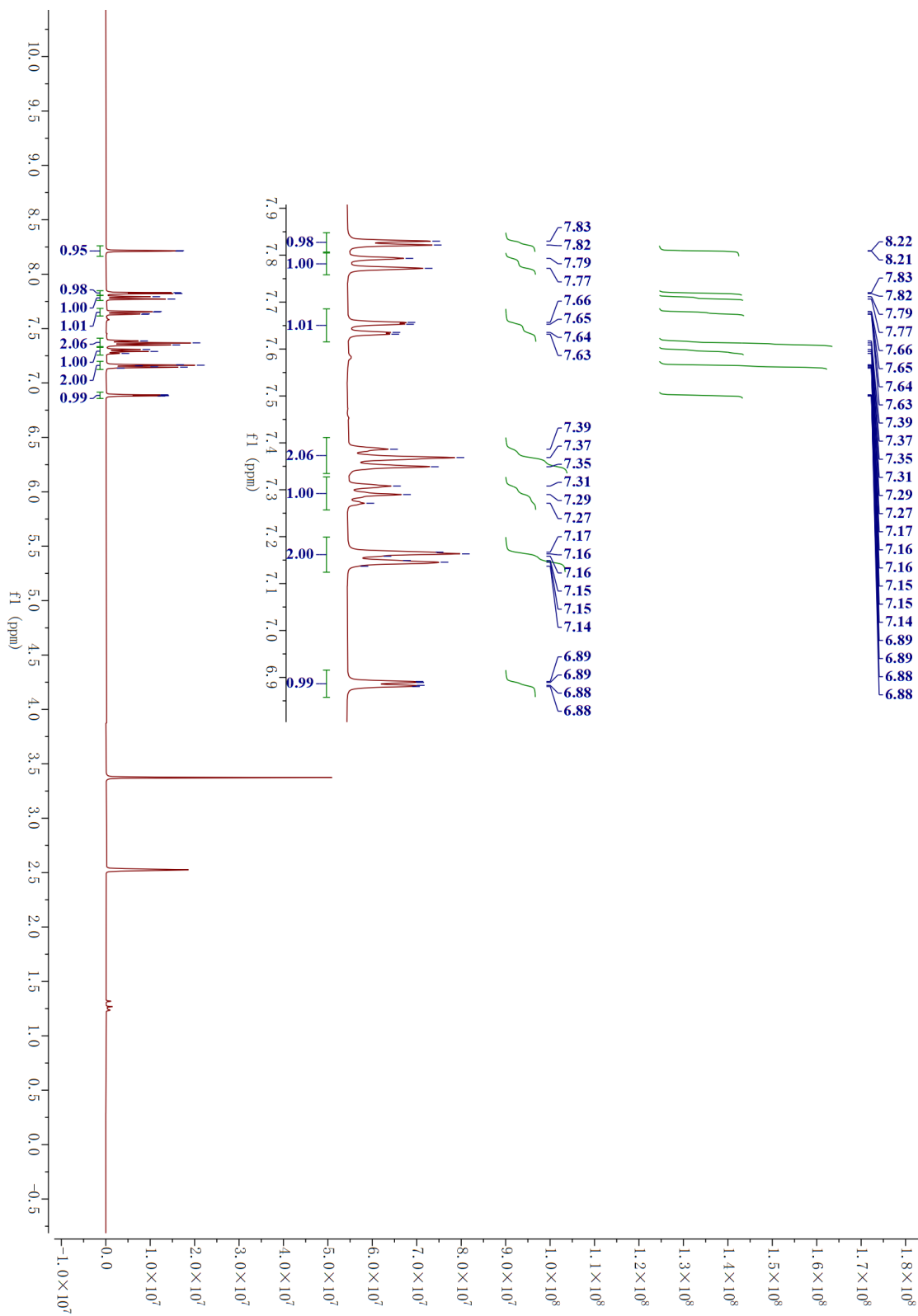
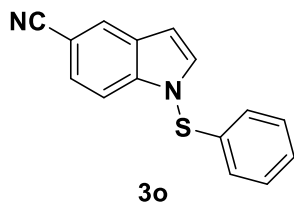


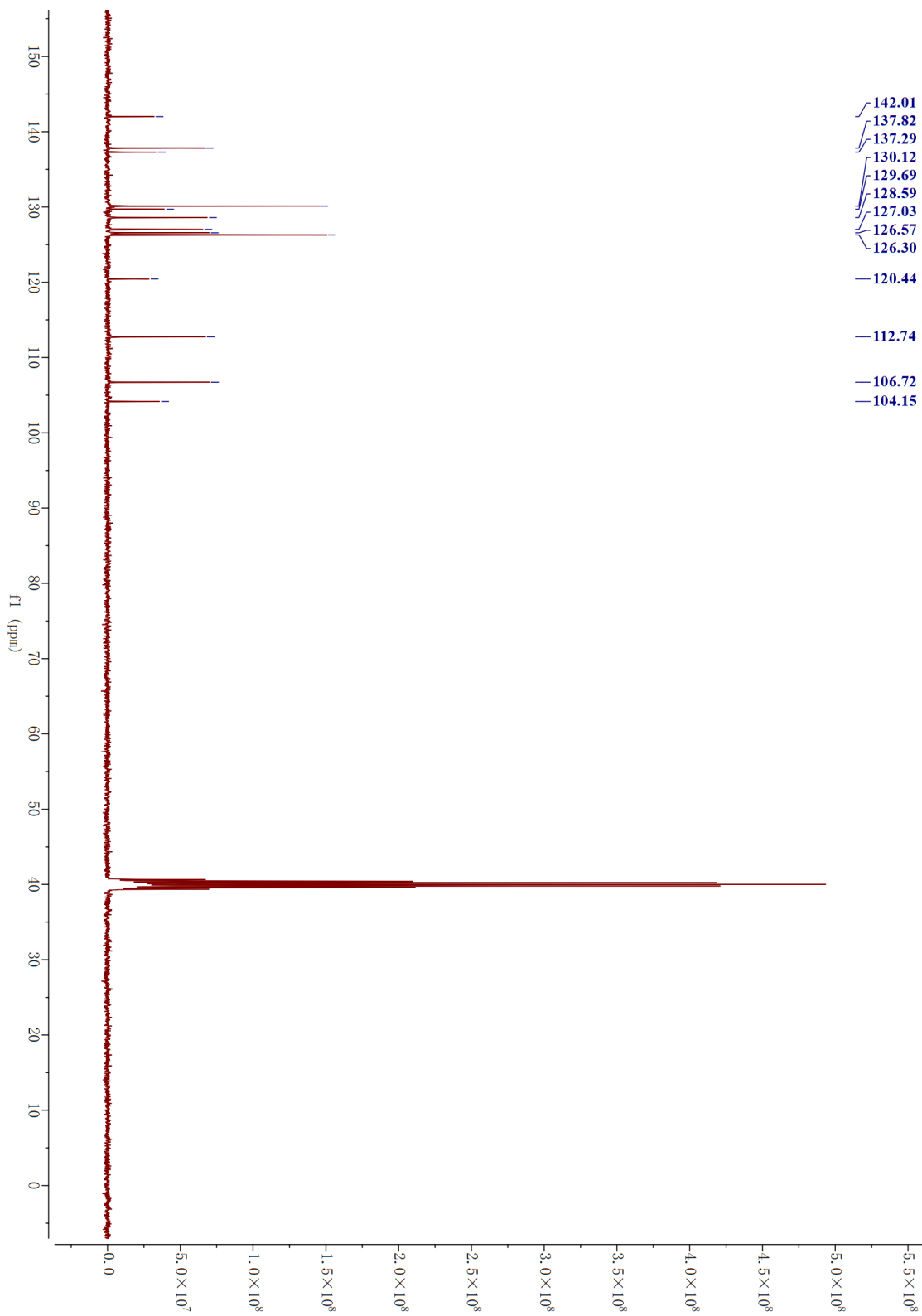


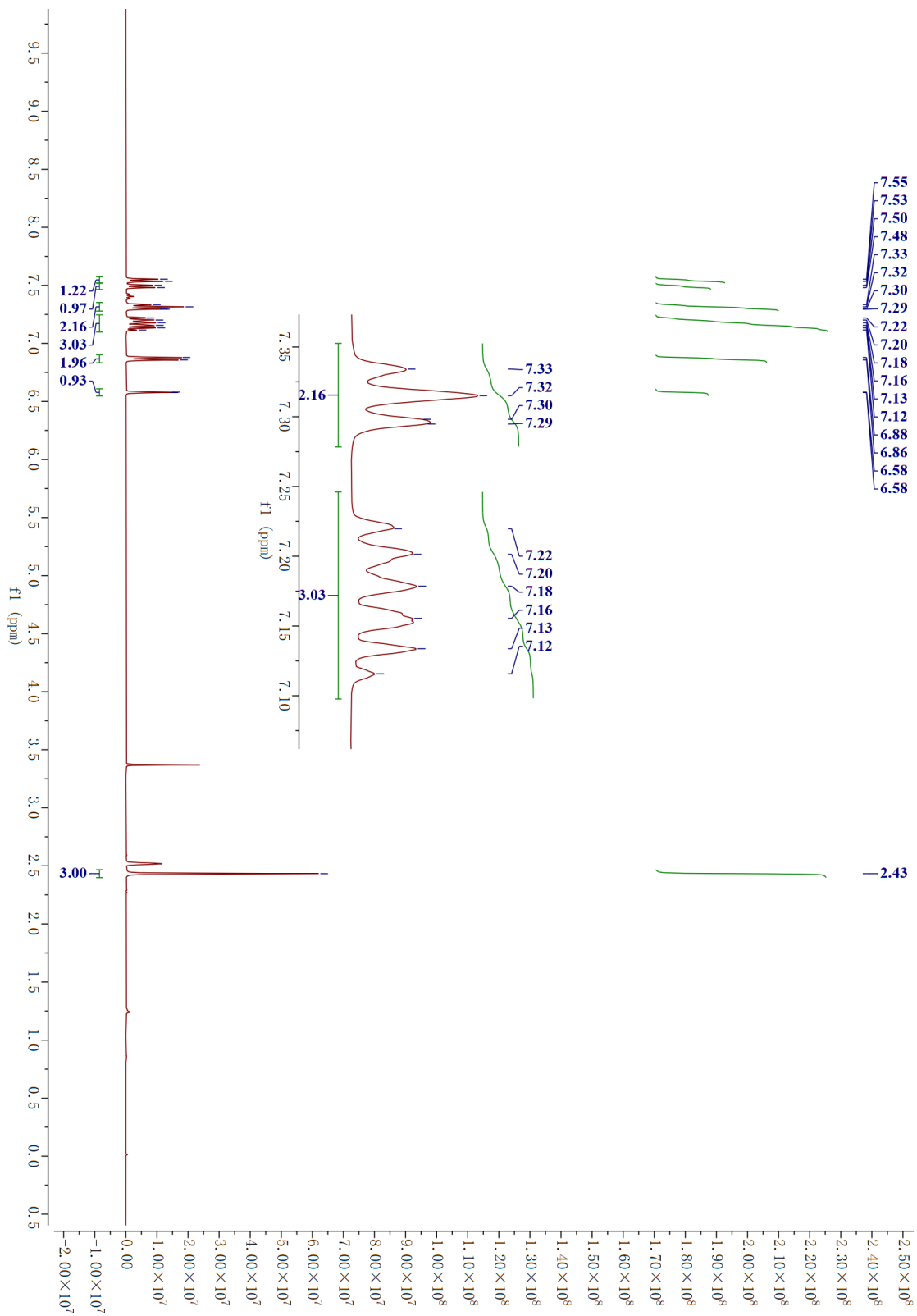
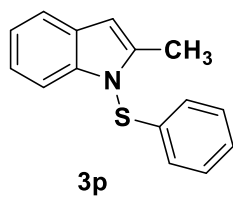


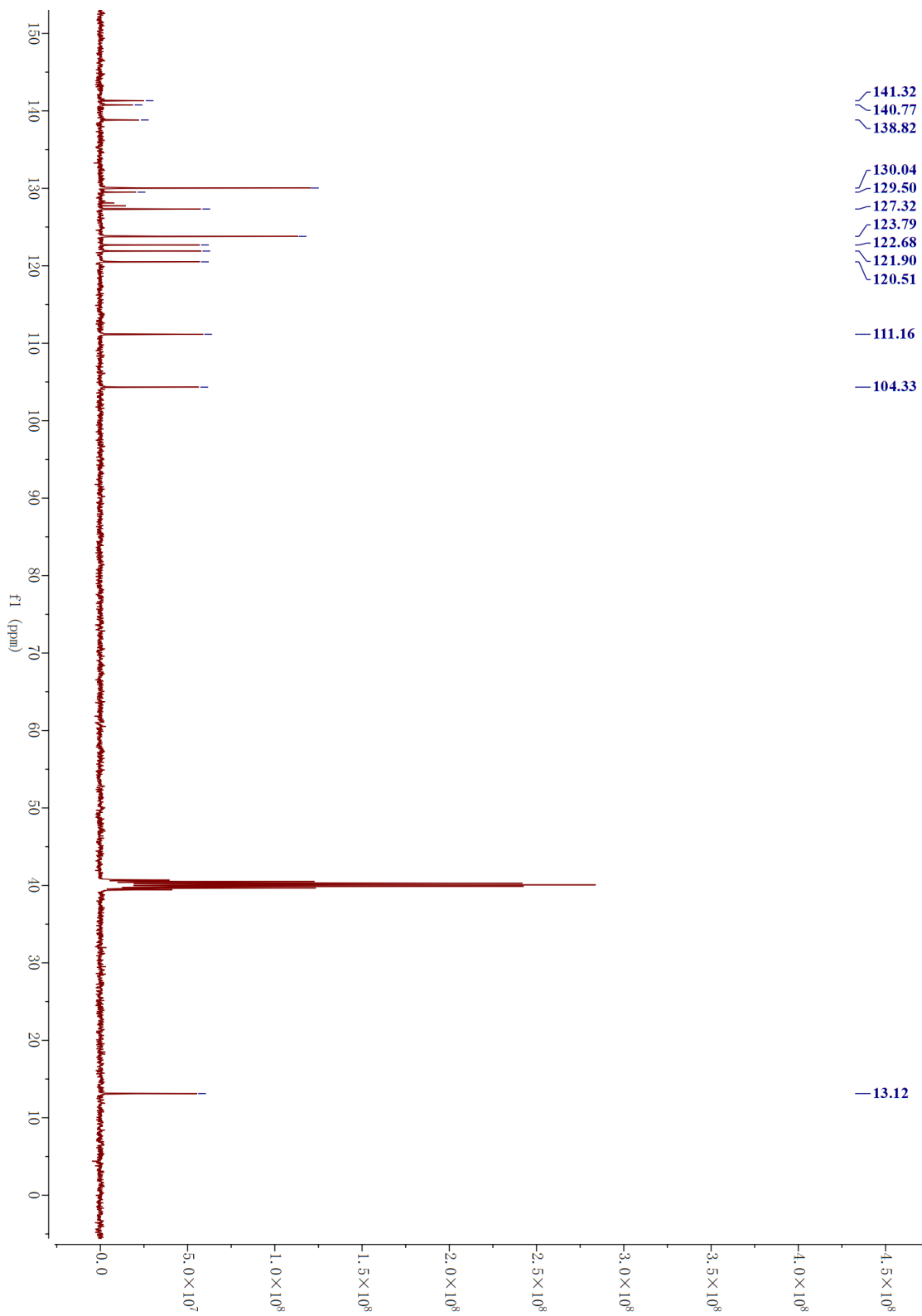


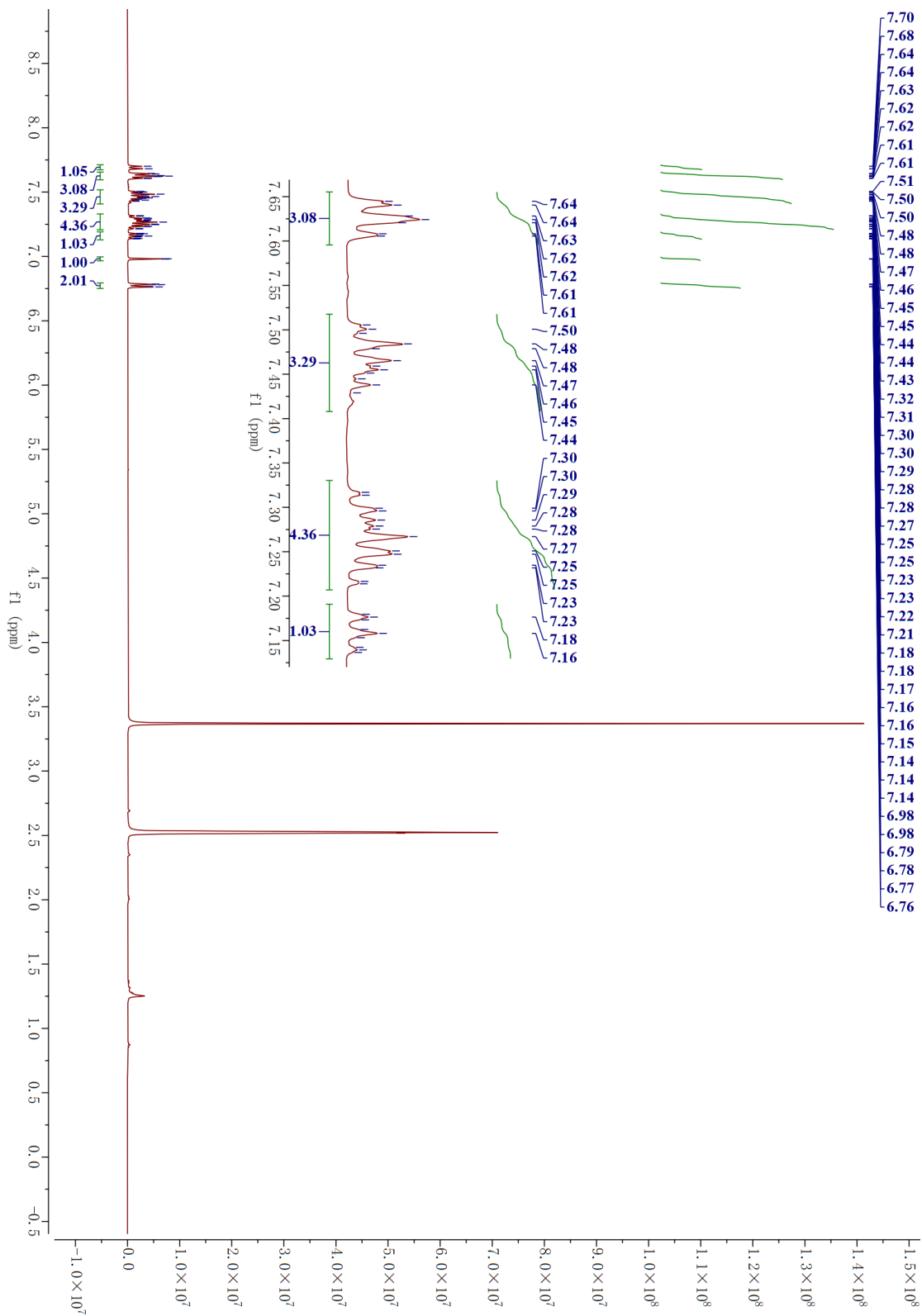
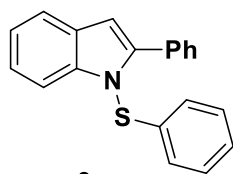


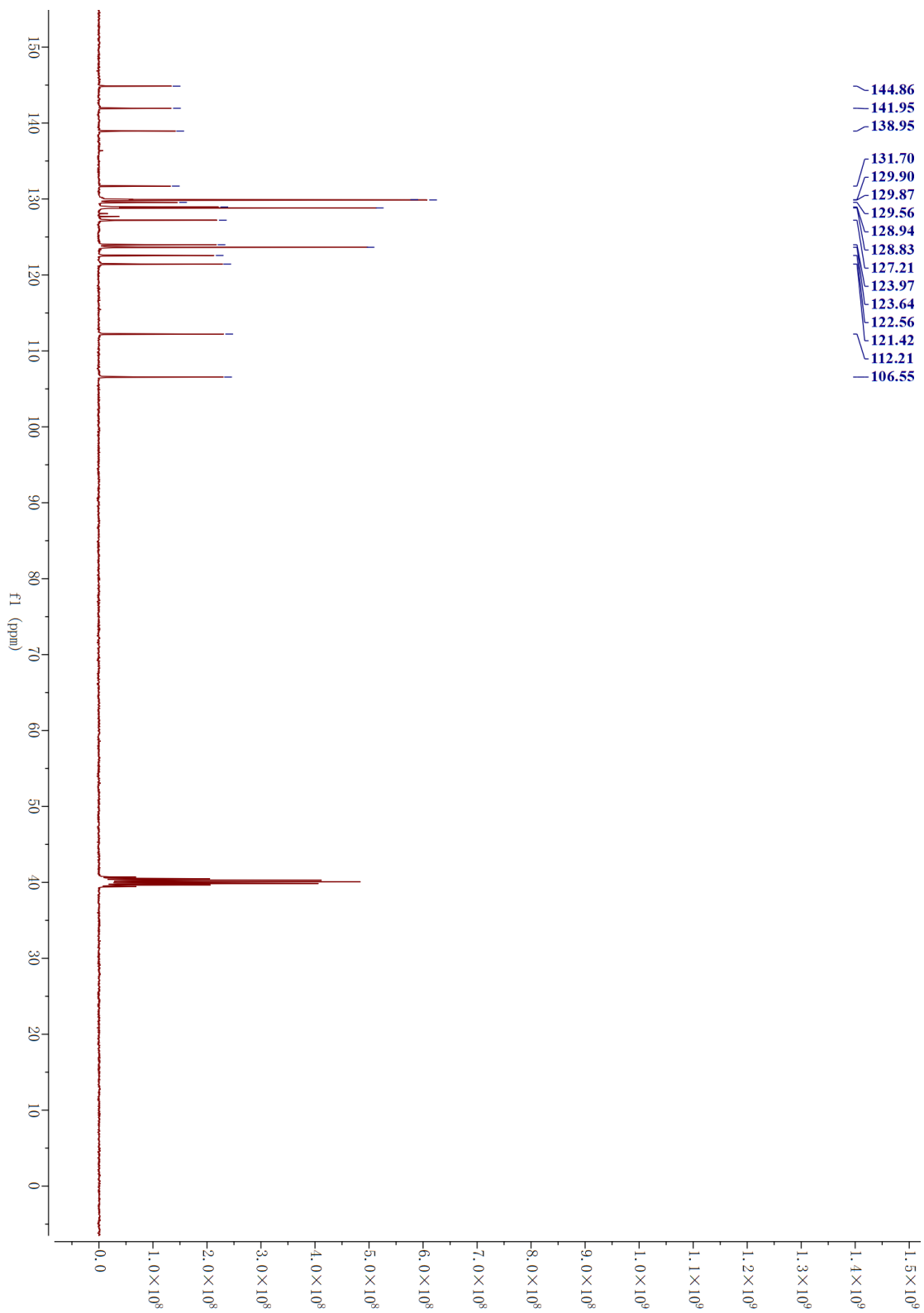


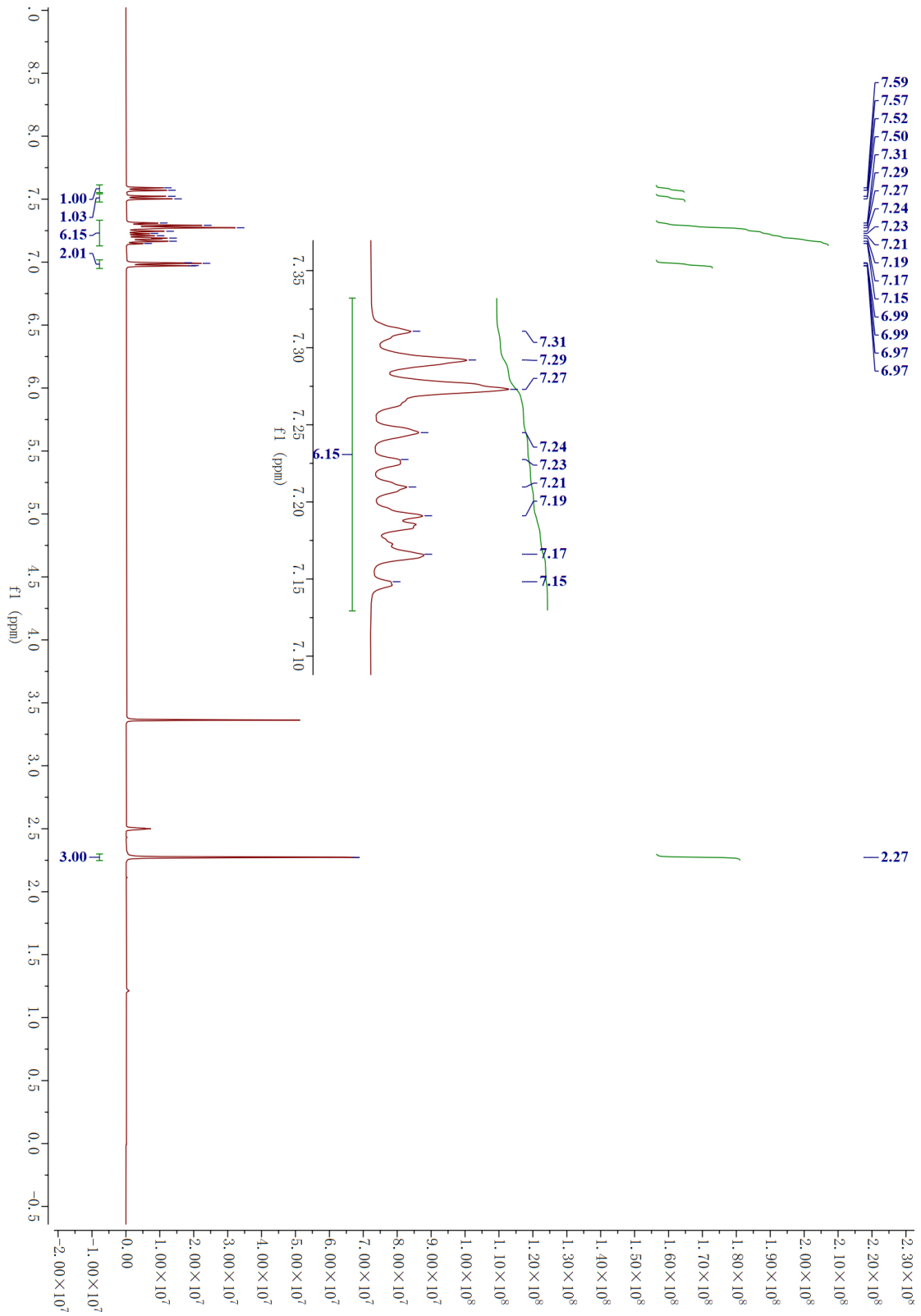
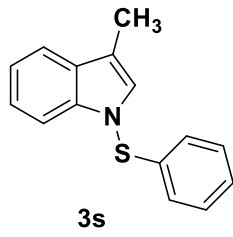


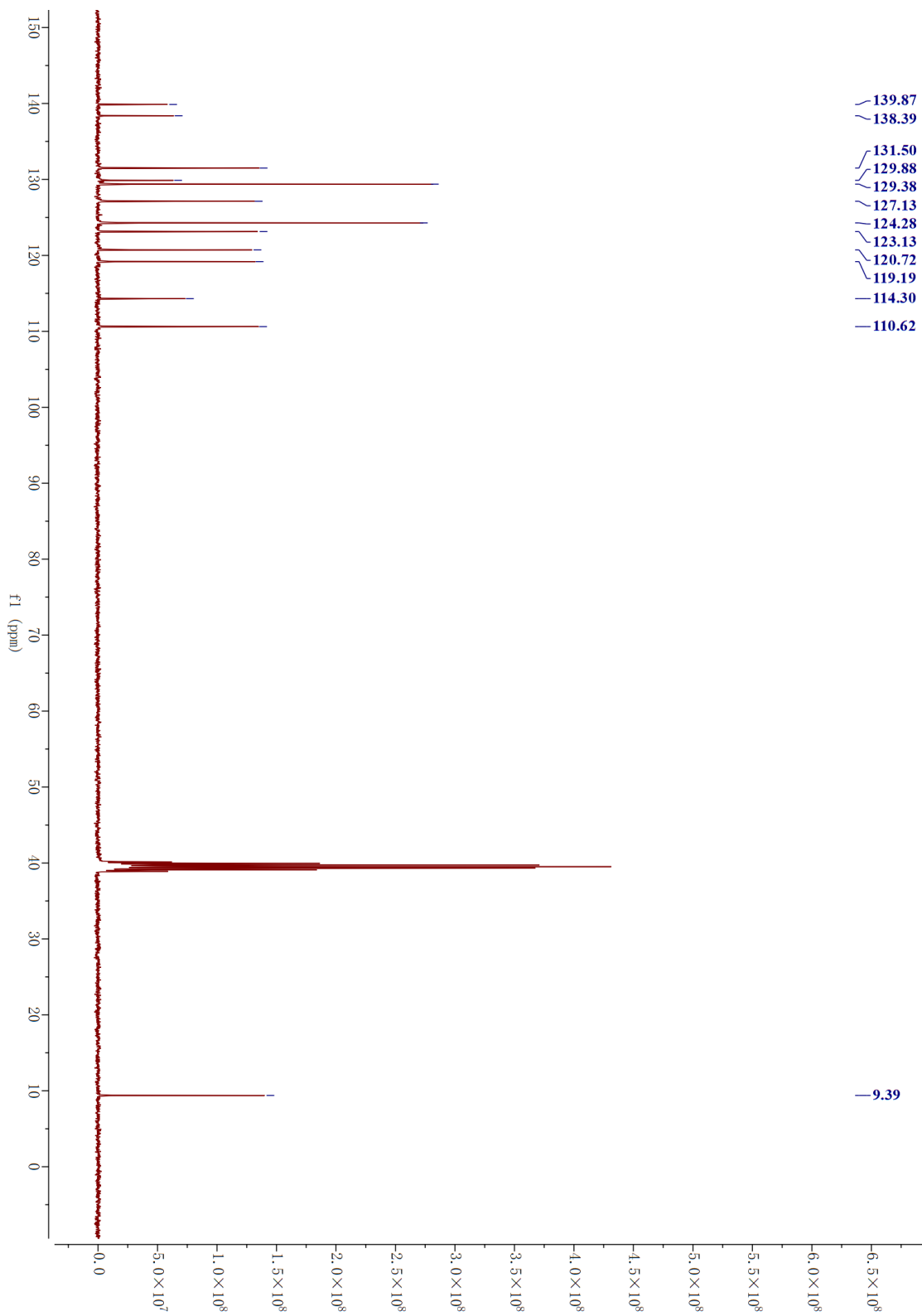


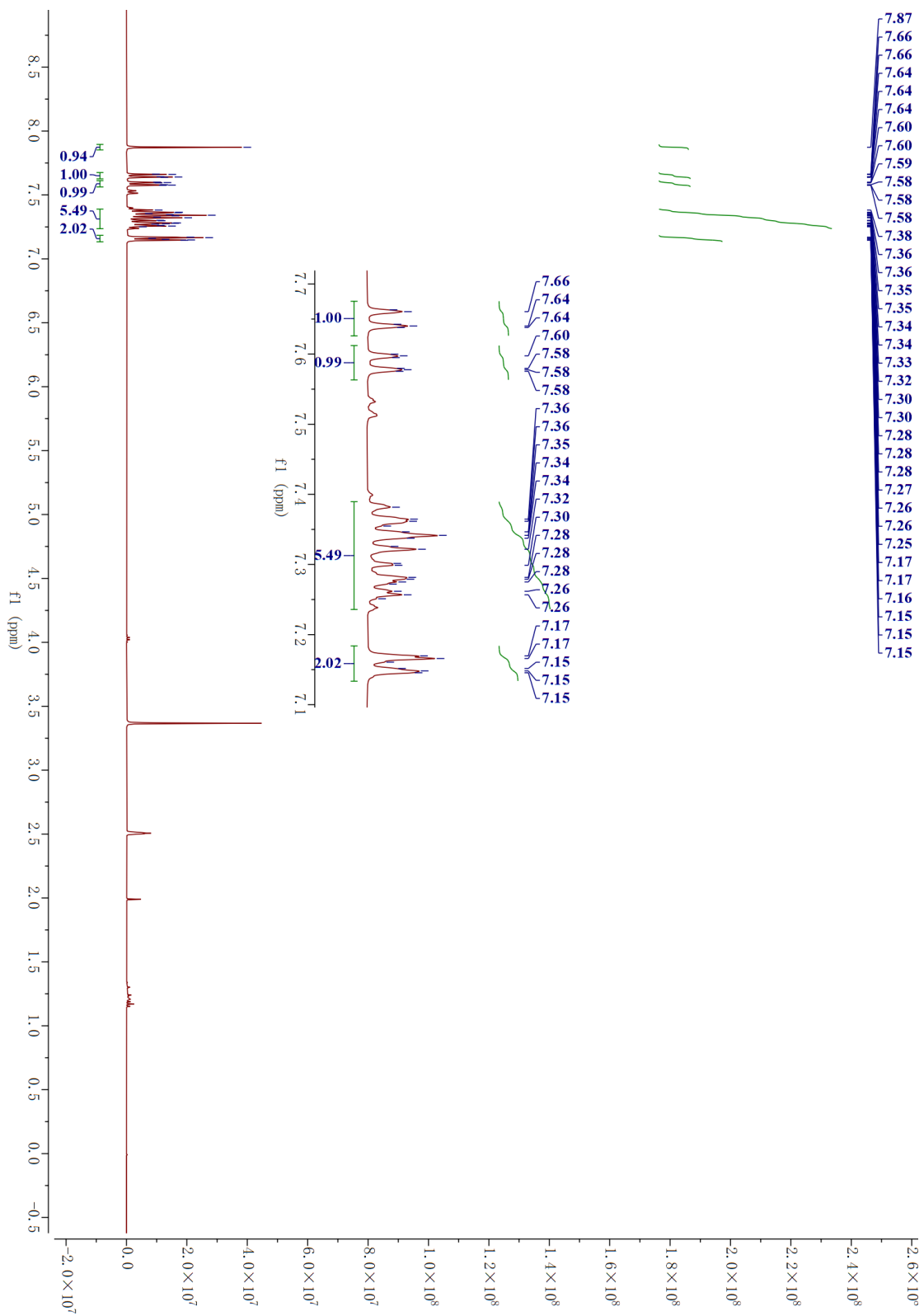
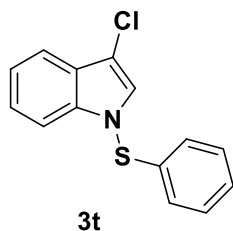


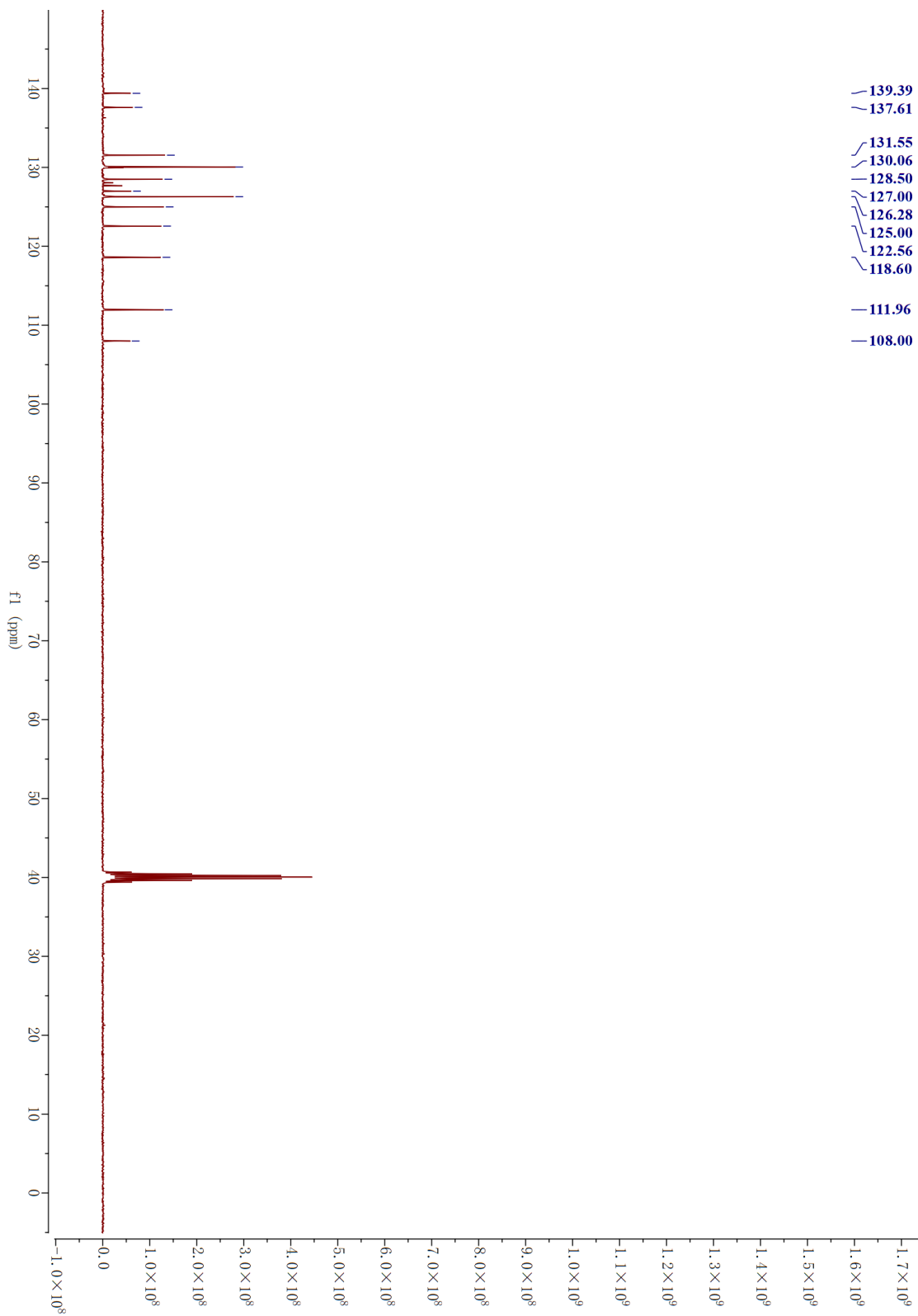


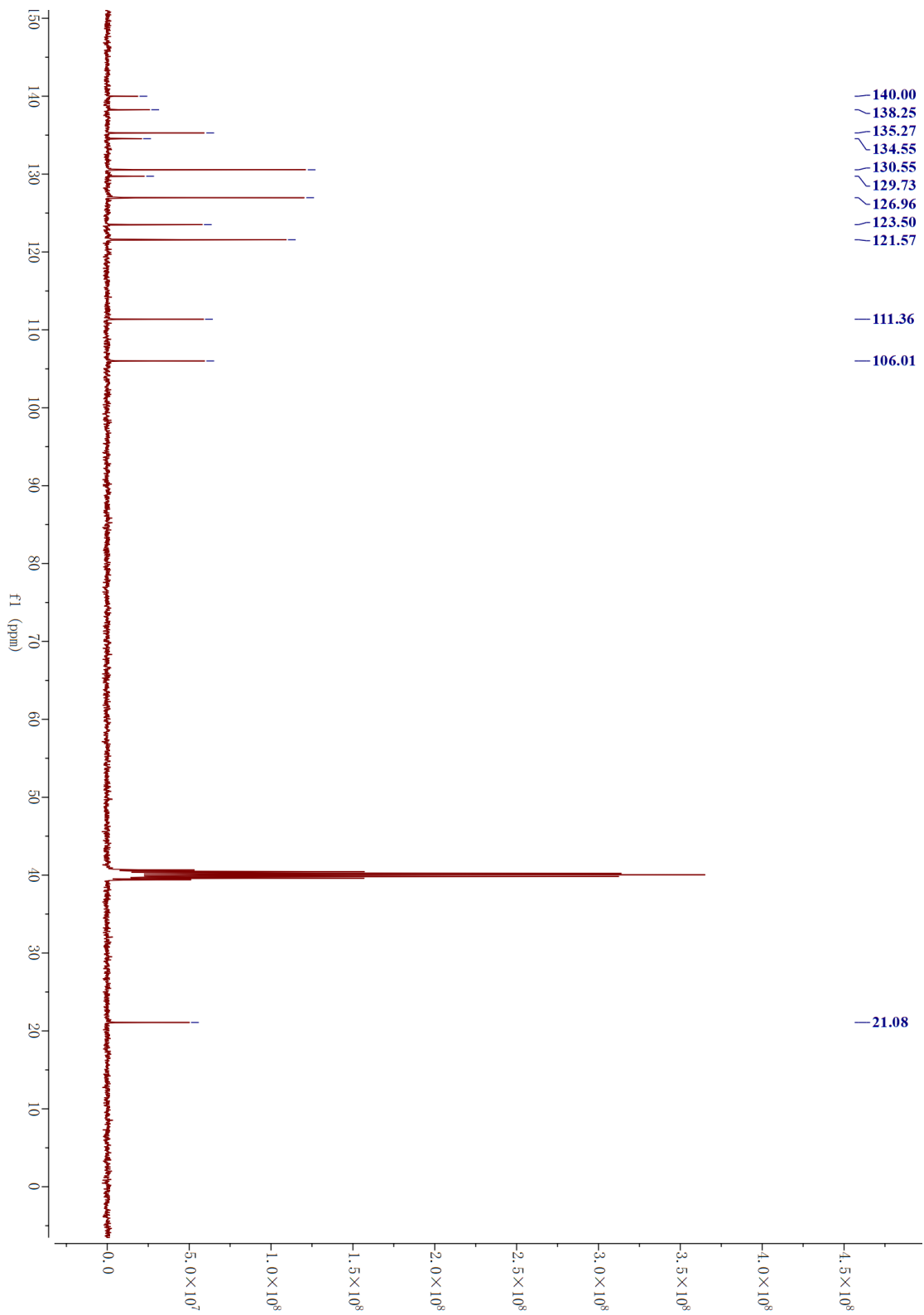


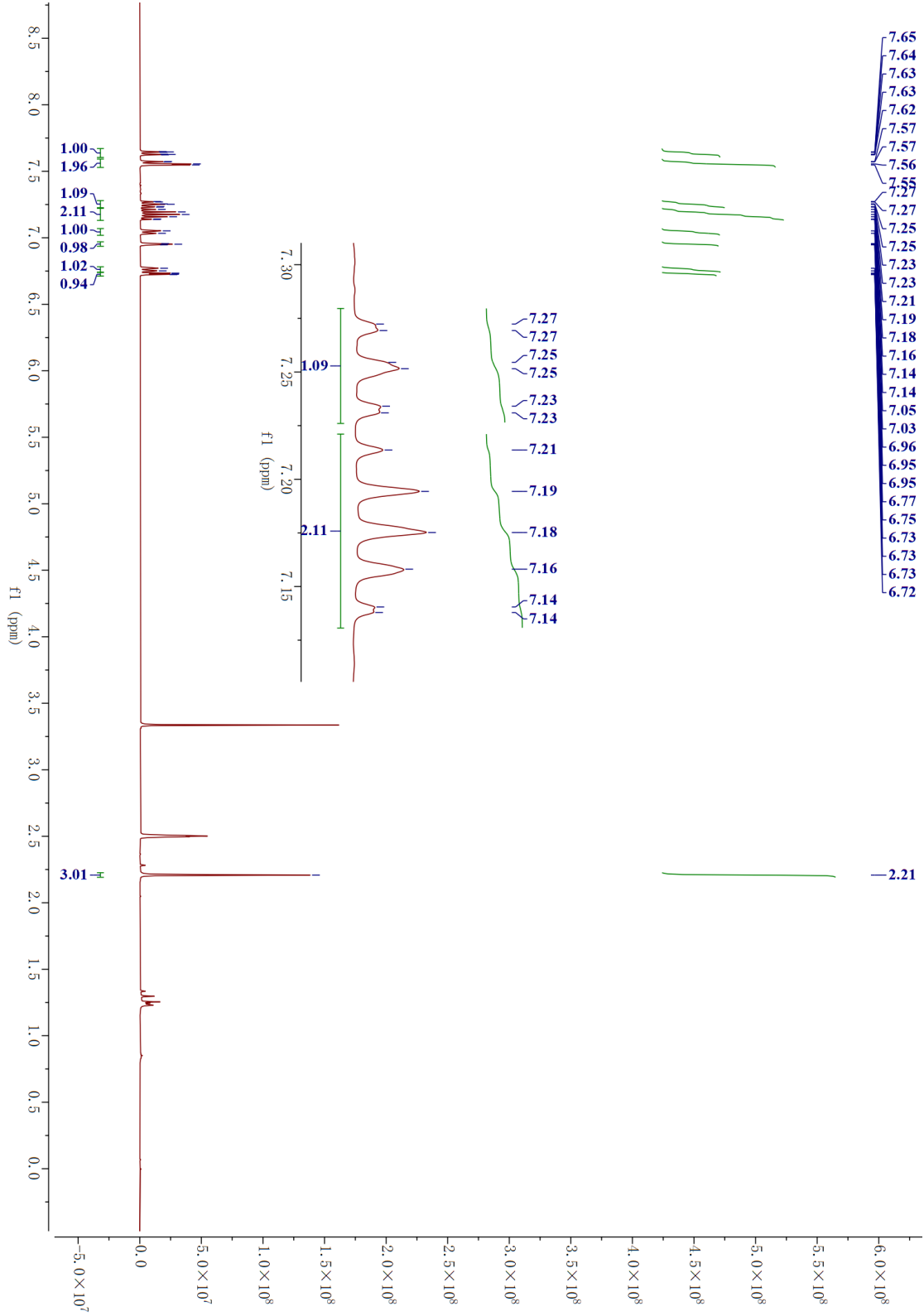
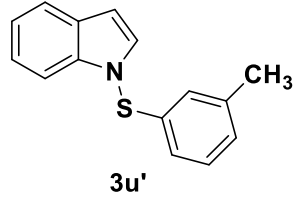


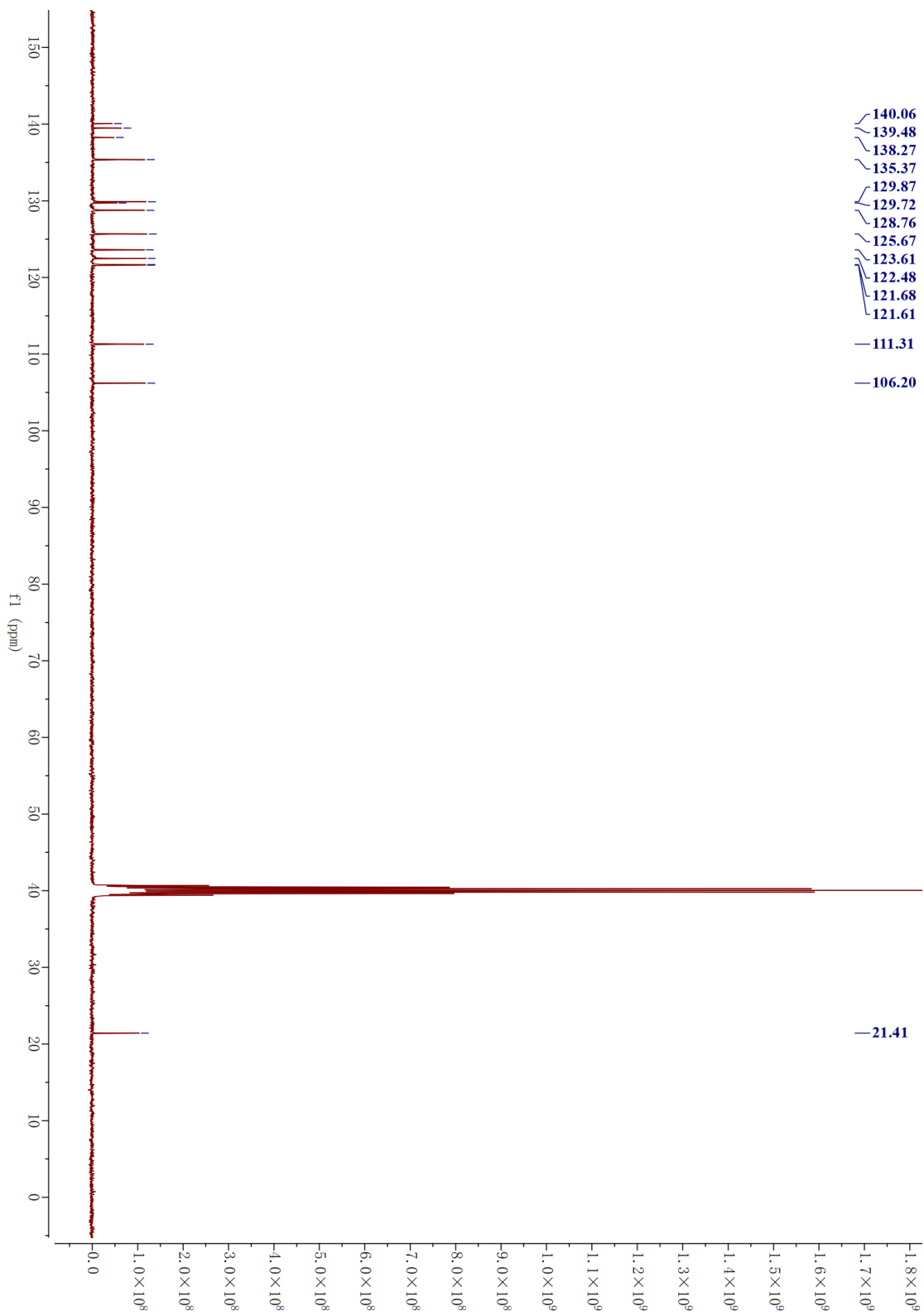


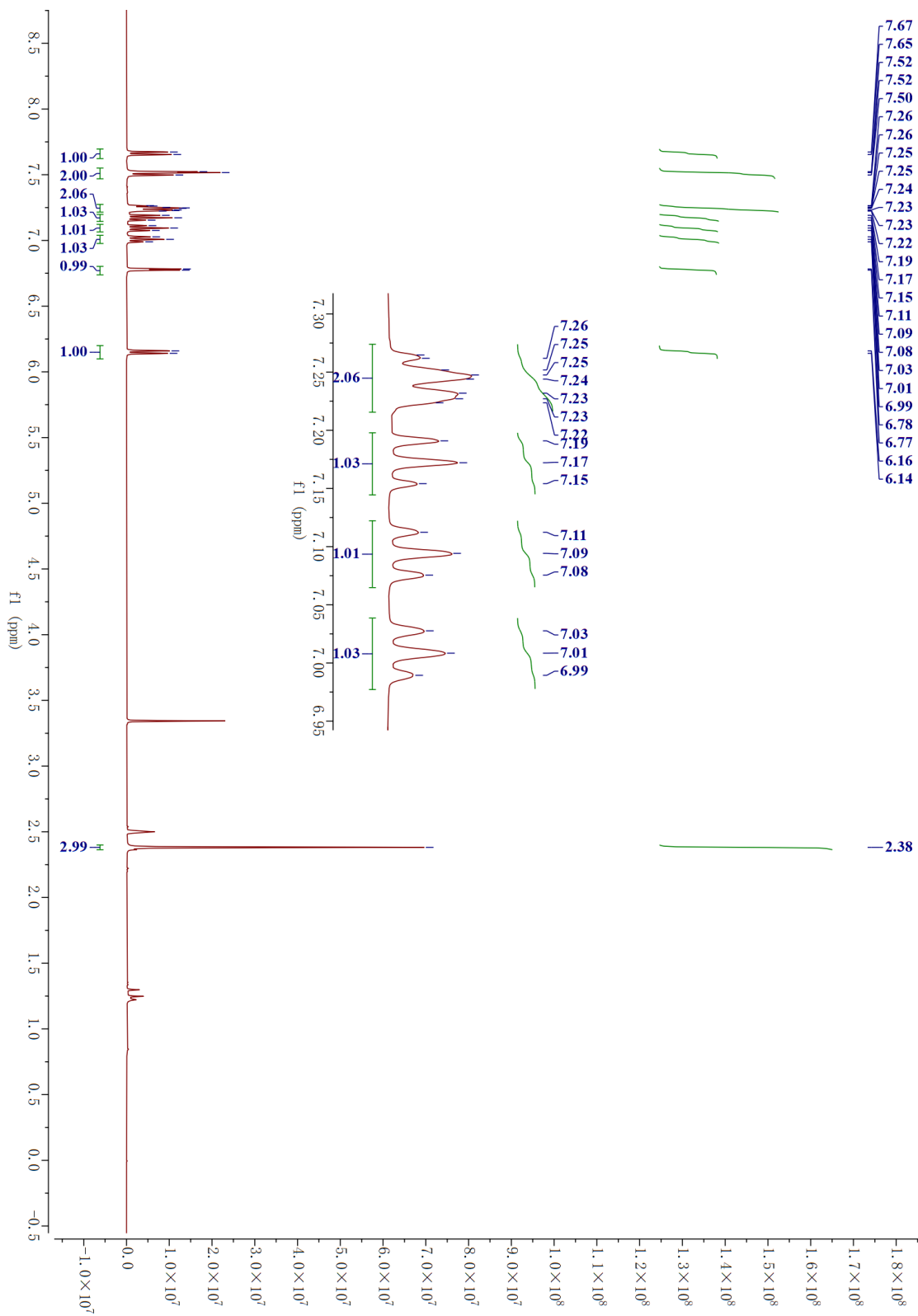
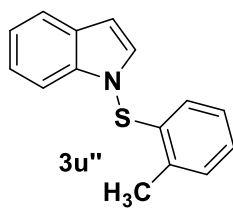


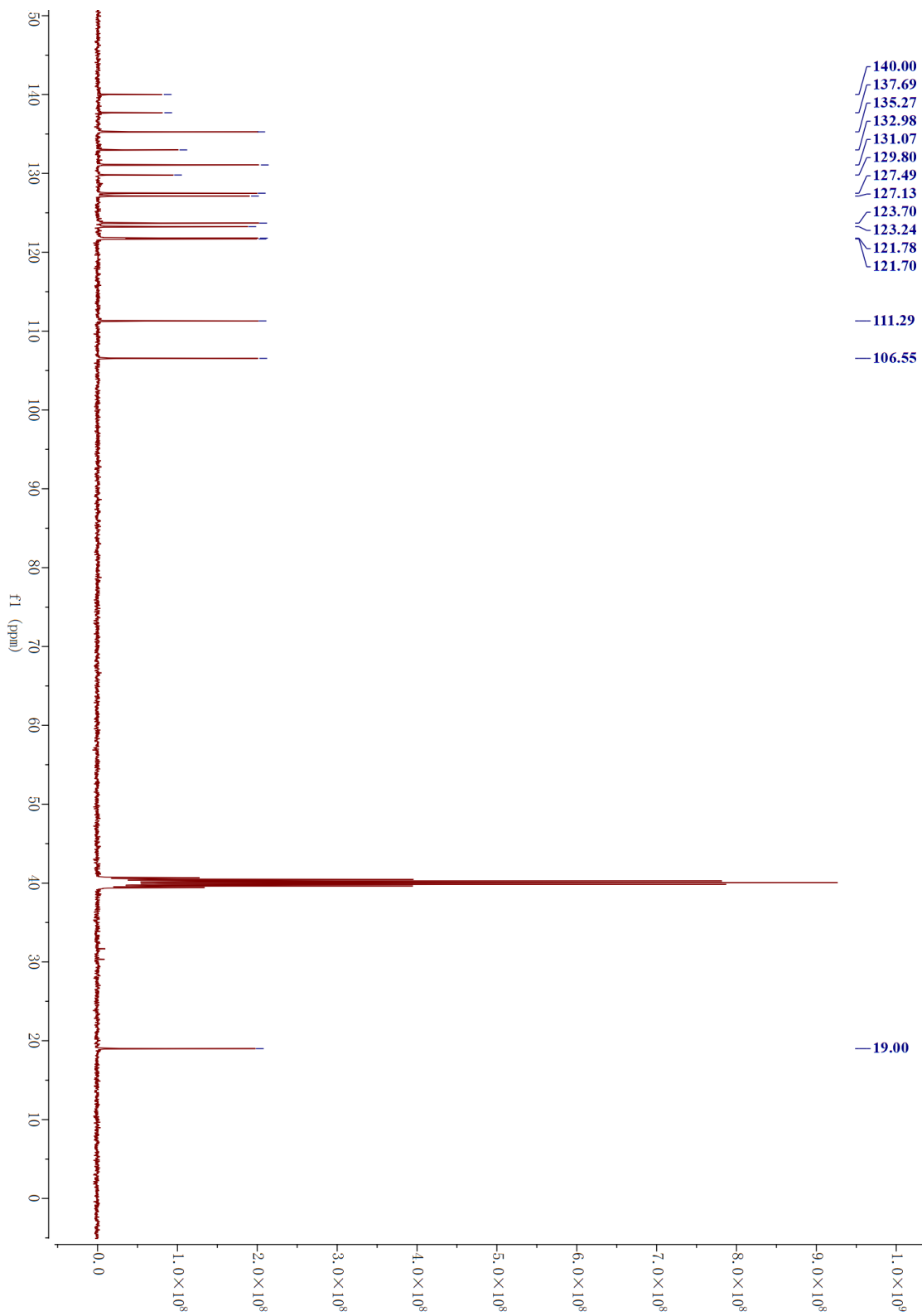


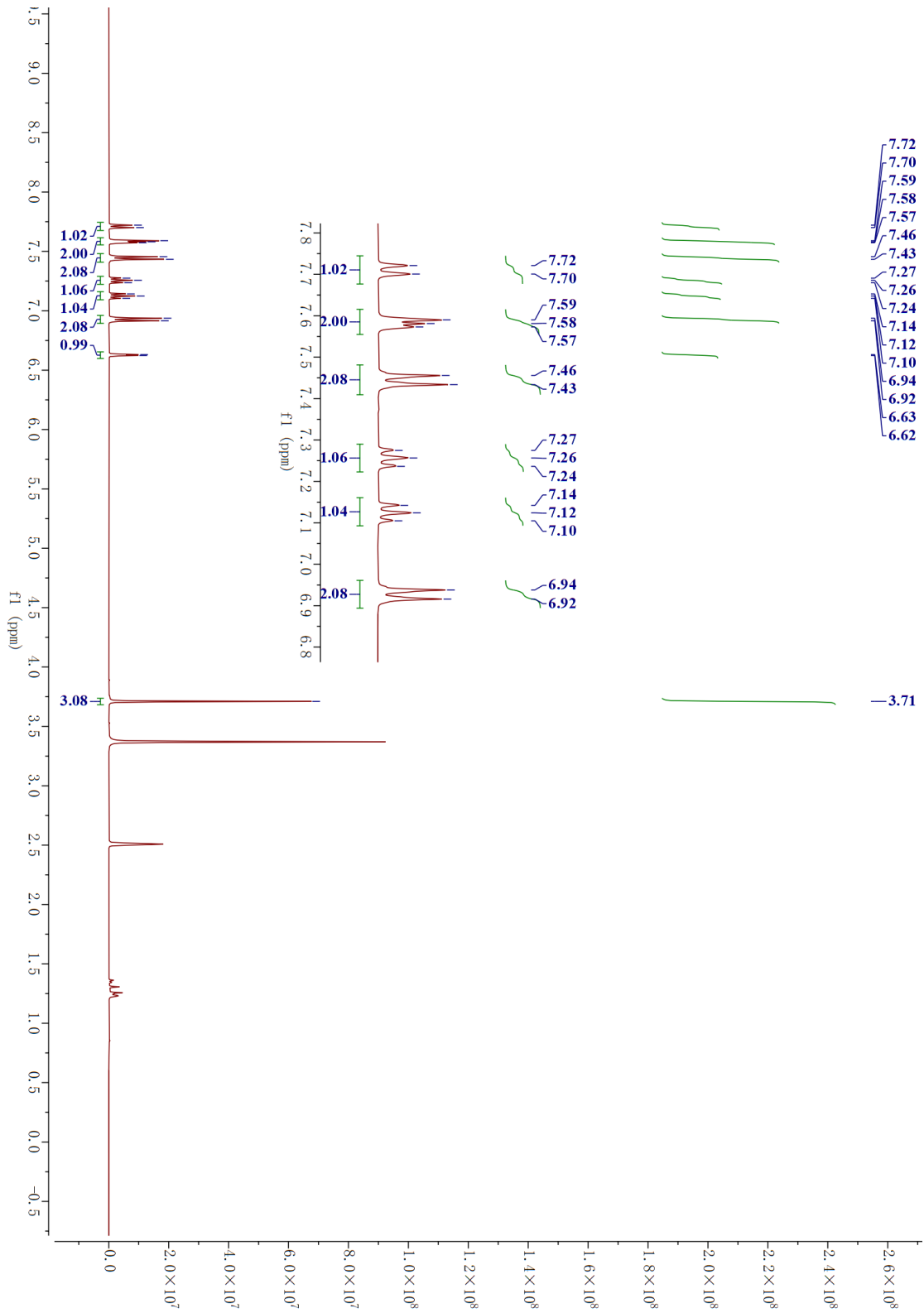
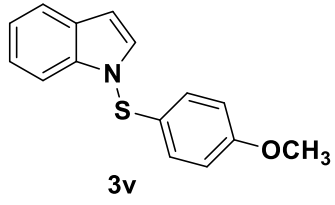


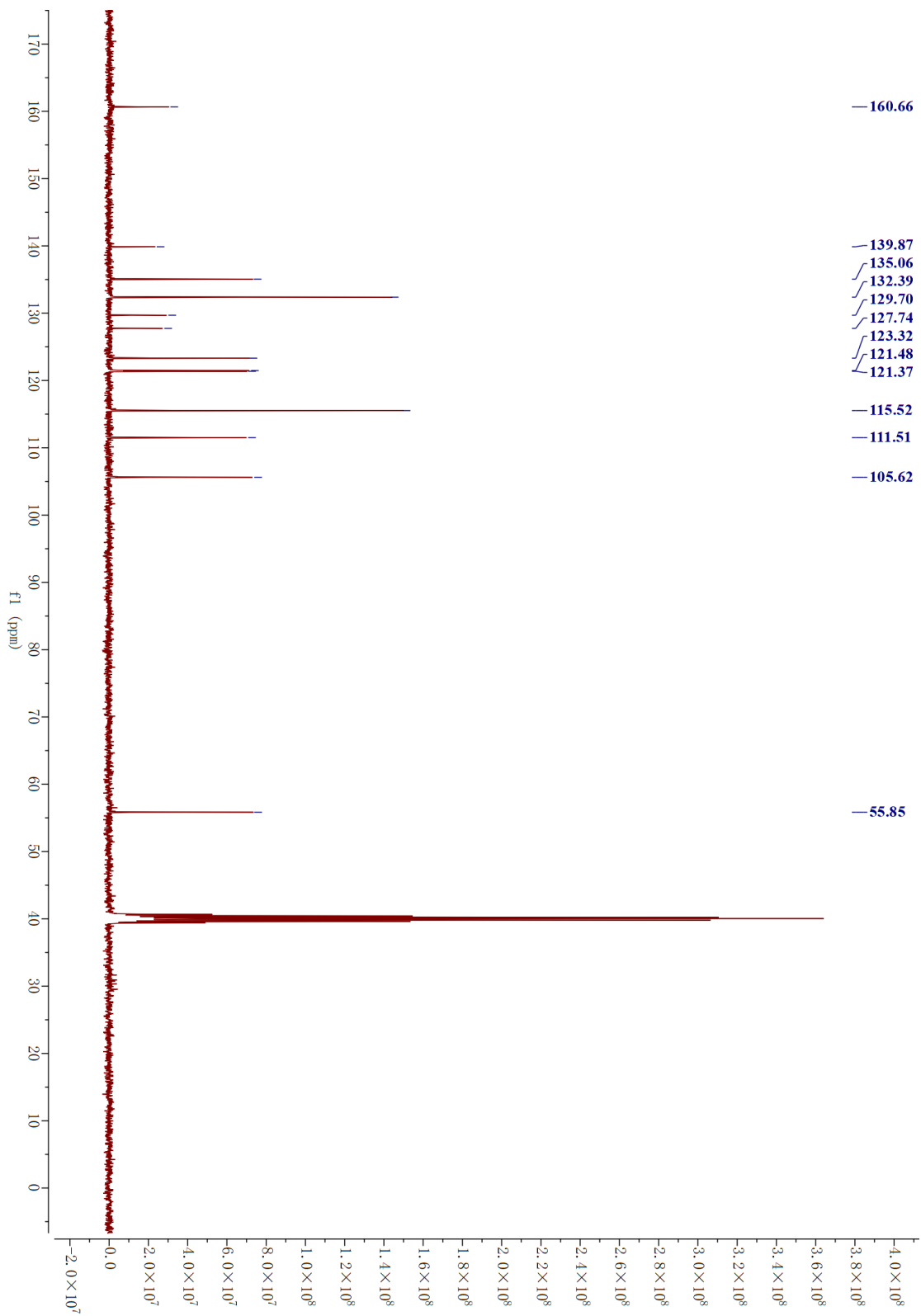


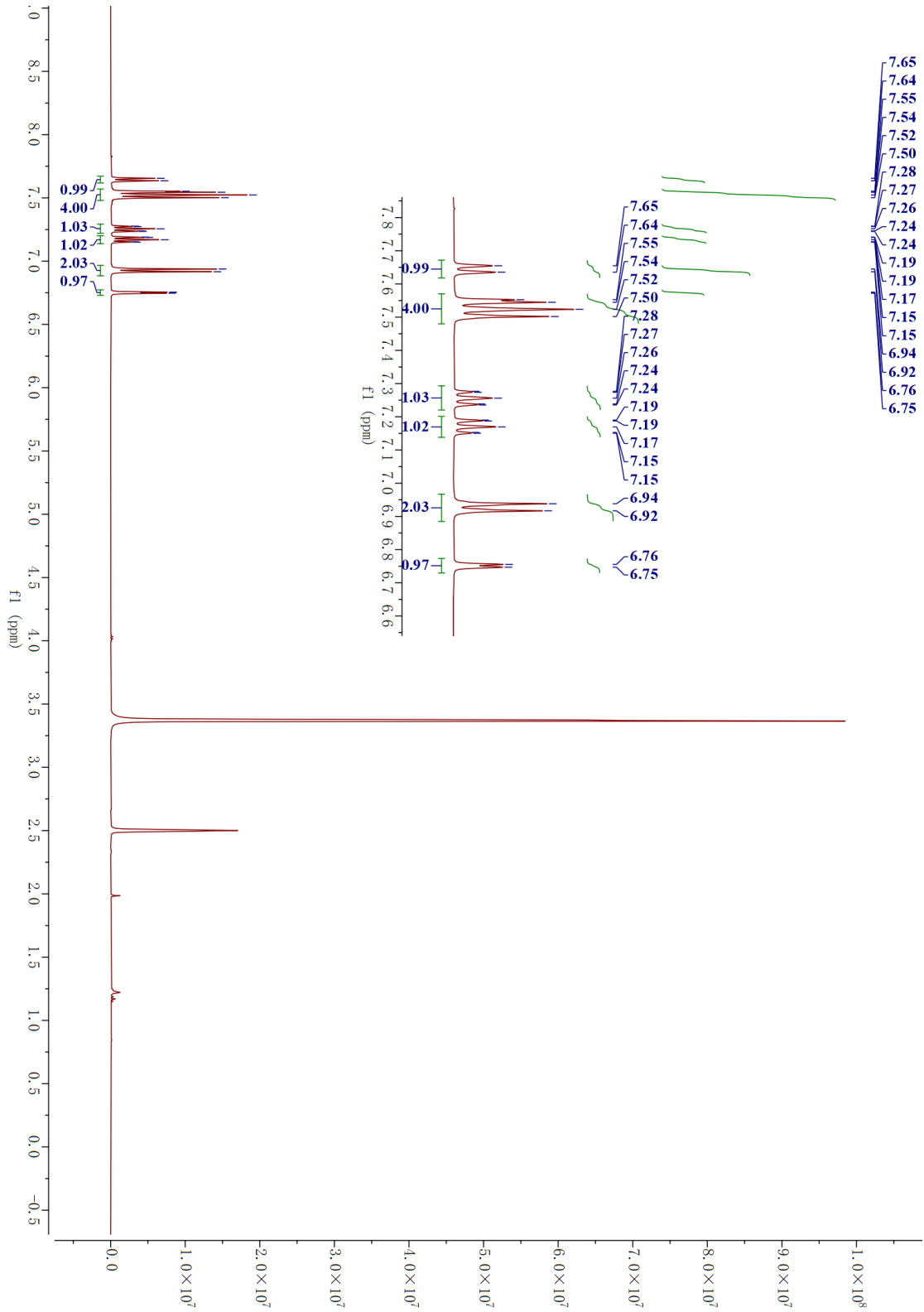
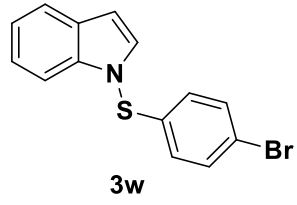


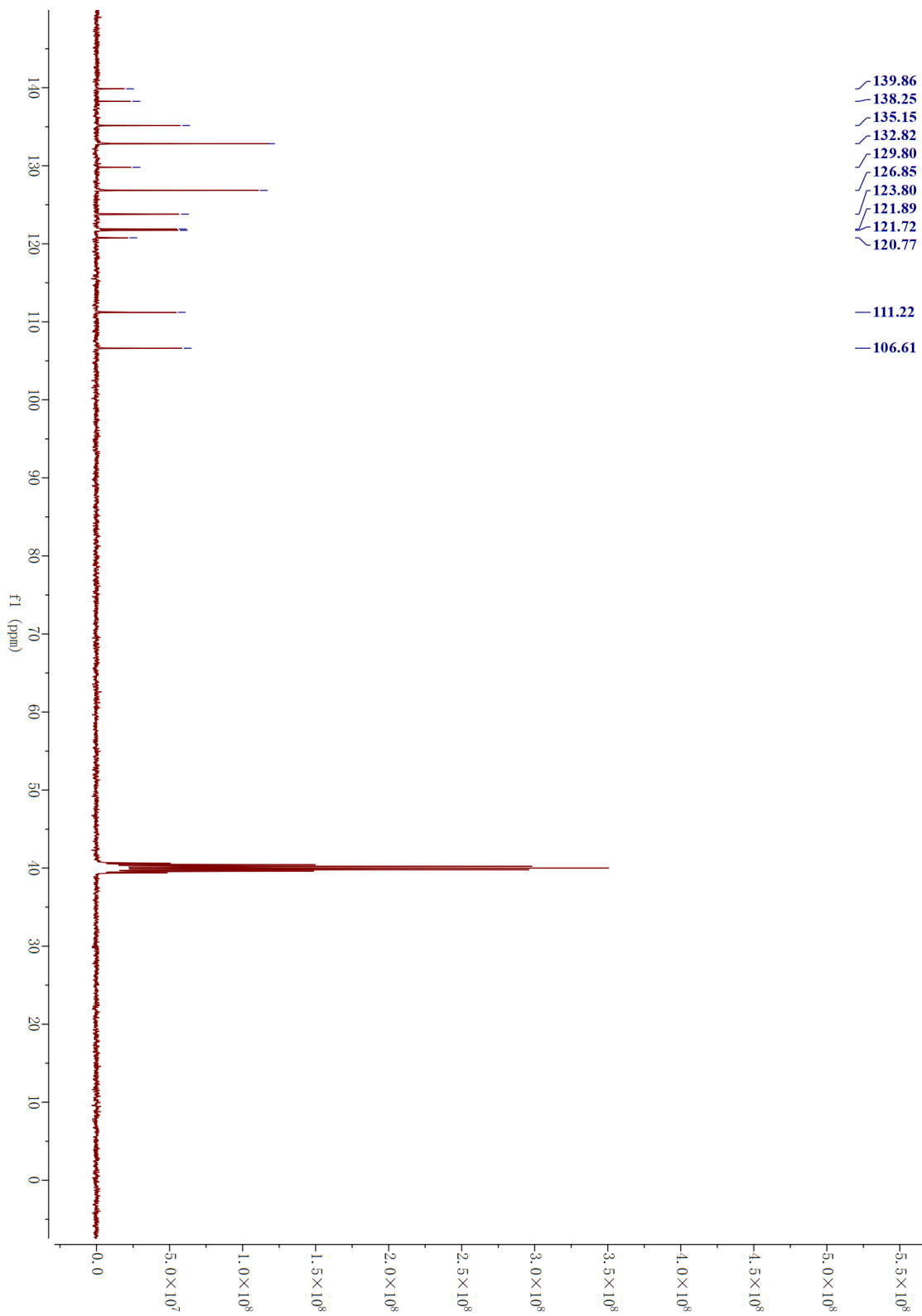


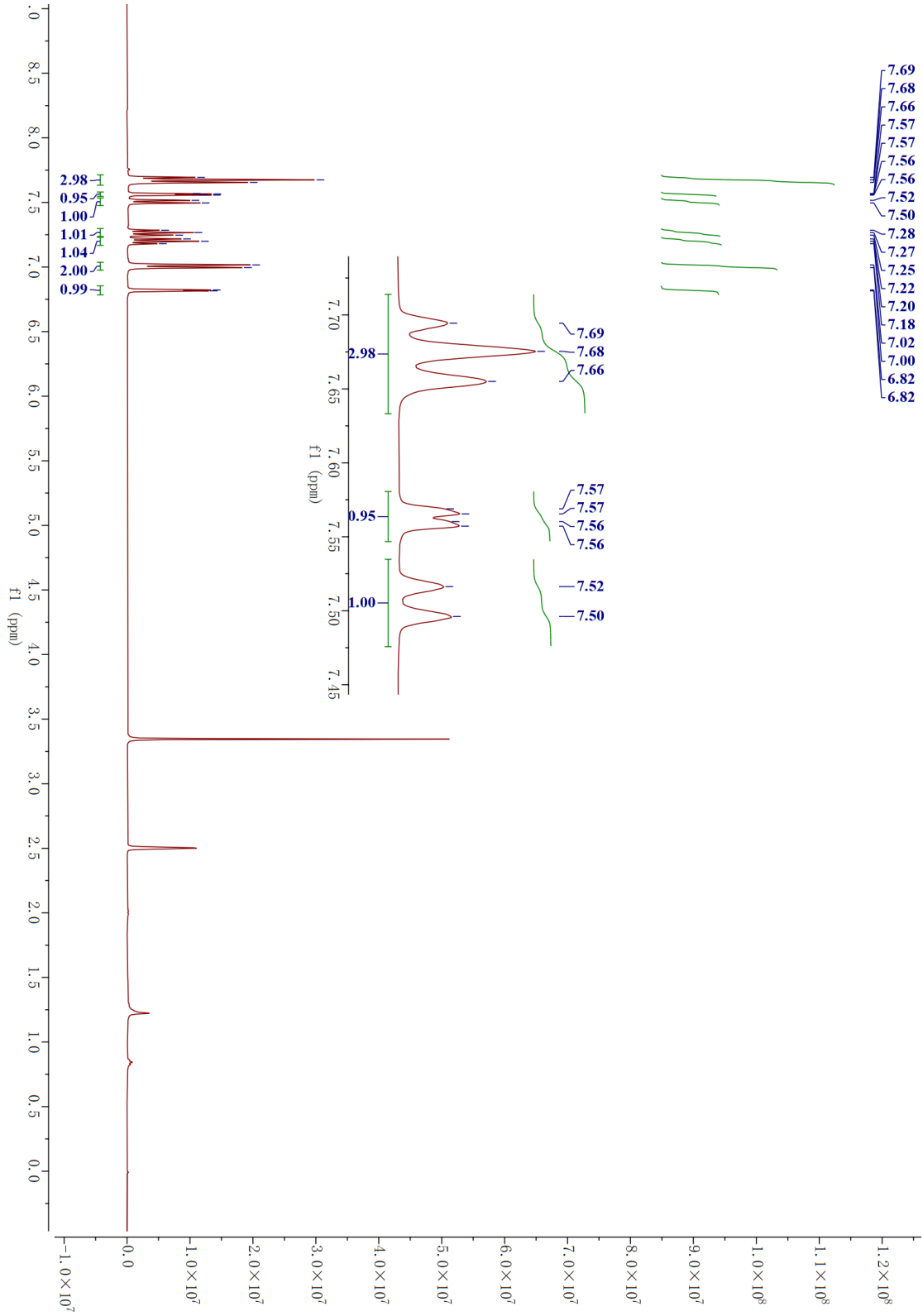
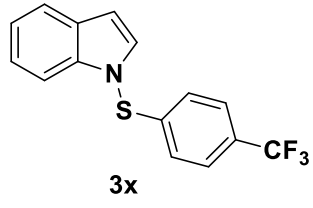


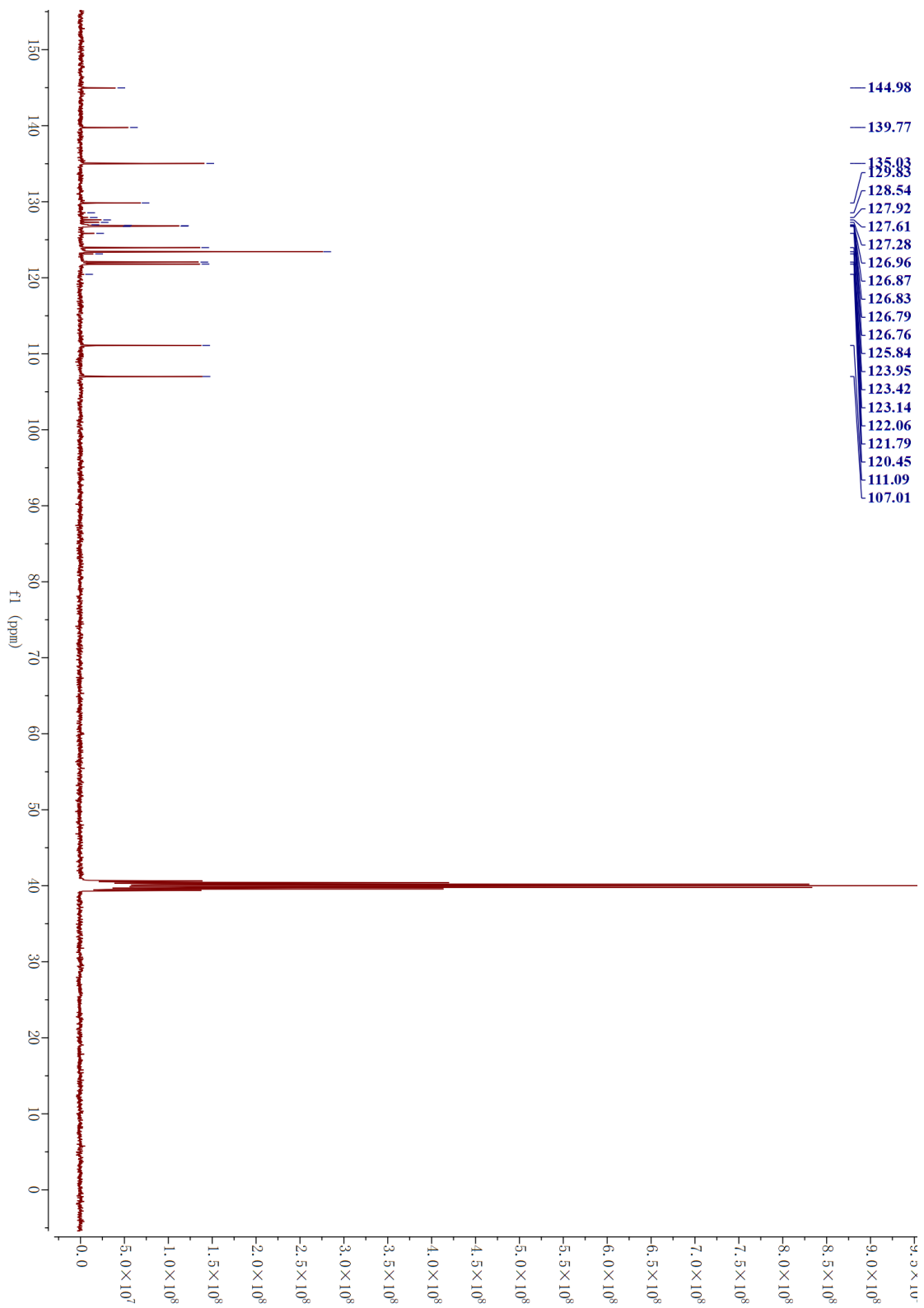


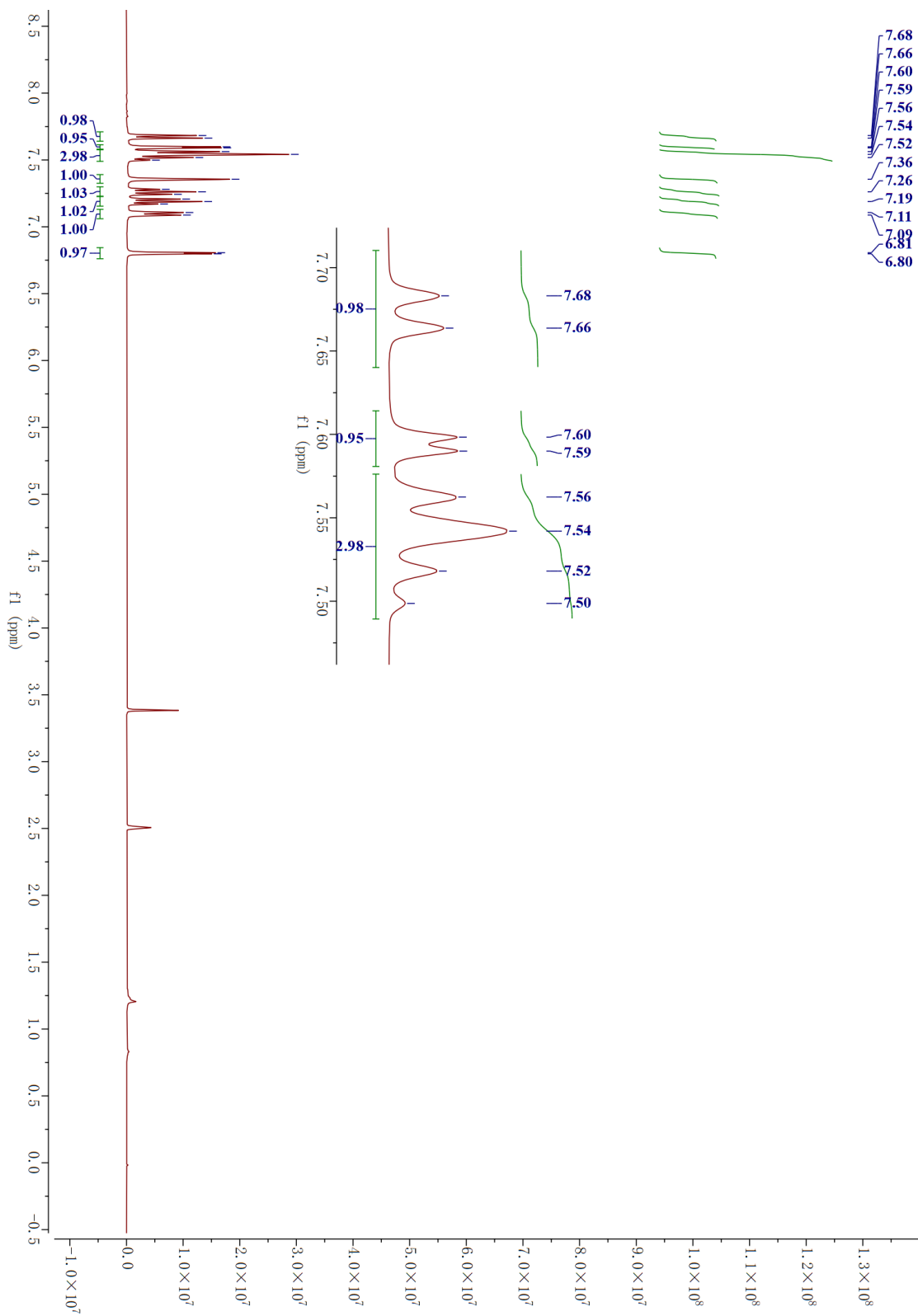
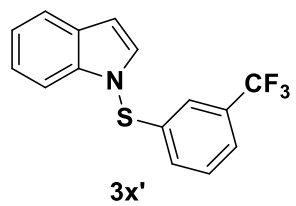


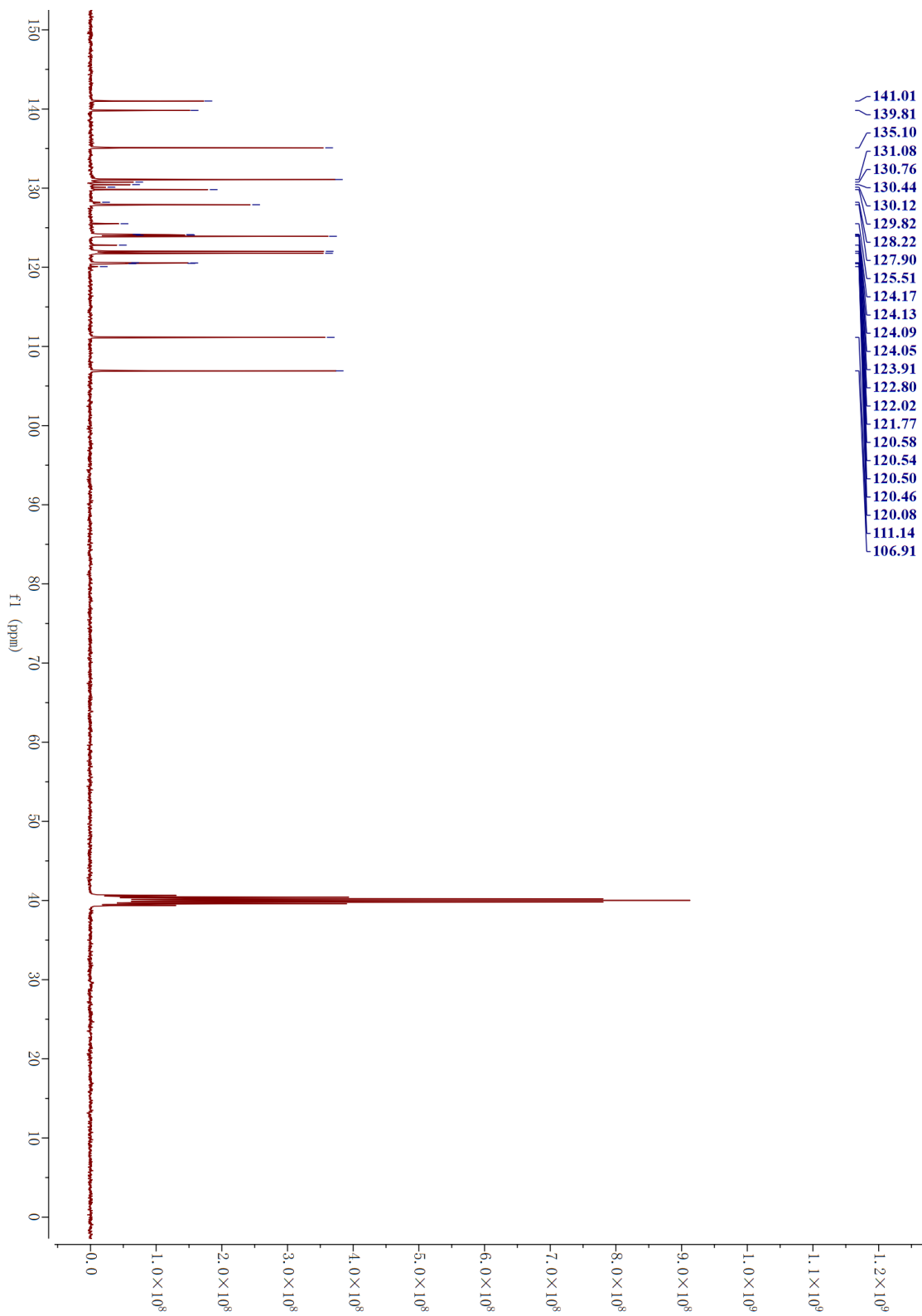


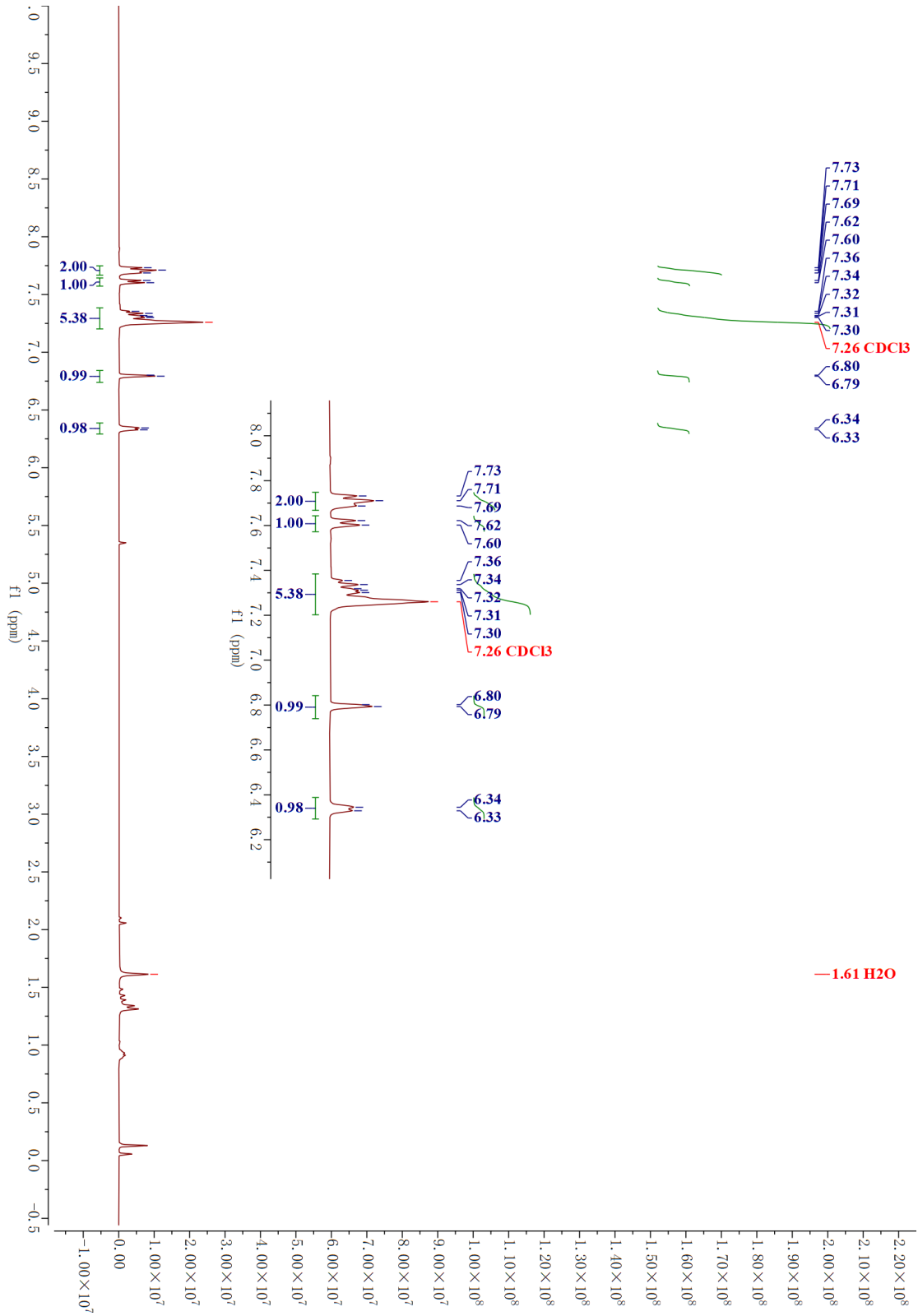
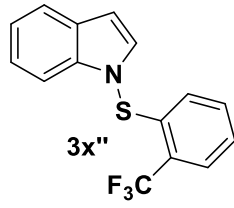


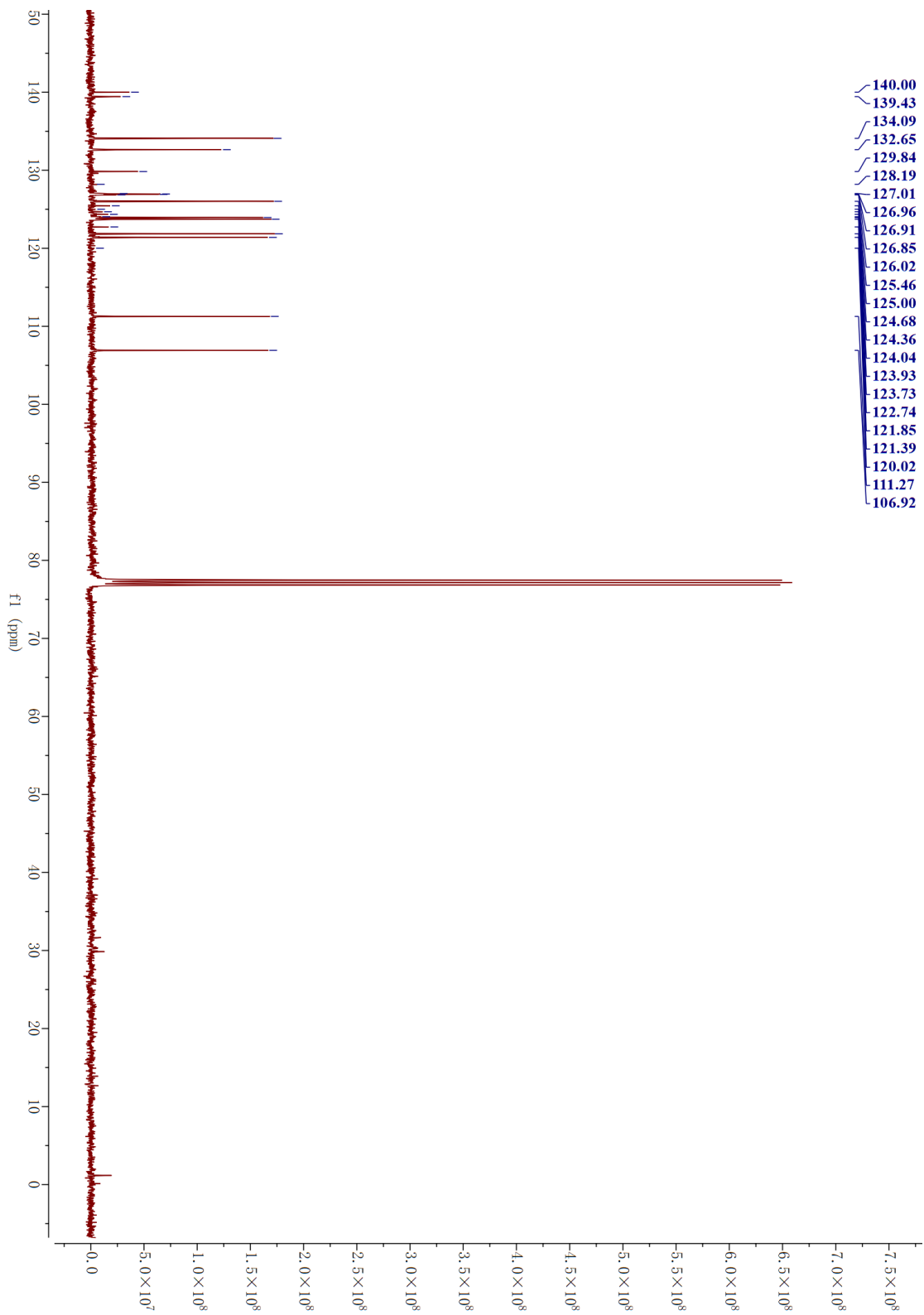


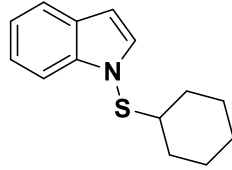












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