

Step-controlled Povarov-type Reaction with 1,2-Dihydroquinolines as Precursors of Dienophiles: Direct Synthesis of Spiro-cyclic Bi-tetrahydroquinolines and Functionalized 1,2-Dihydroquinolines

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General information

All reactions that required anhydrous conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents from Alfa Aesar and Adamas-beta were used as received. The solvents were dried by distillation over the appropriate drying reagents.

Melting points were measured on a Meltemp melting point apparatus and were not corrected. ^1H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 , $\delta = 7.26$). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (101 Hz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl_3 , $\delta = 77.0$).

1. General procedural for the preparation of spiro bi-tetrahydroquinole 3

A reaction tube was charged with the 1,2-DHQ **1** (0.2 mmol, 1 eq.), imine **2** (0.2 mmol, 1 eq.), anhydrous toluene (2 mL), InCl_3 (0.01 mmol, 0.05eq). The system was stirred under a nitrogen atmosphere at 40 °C for 18 h. Then the products were obtained by purification with flash silica gel chromatography eluted with petroleum: ethyl acetate (5:1).

2. General procedural for the preparation of functionalized 1,2-DHQ 4

A reaction tube was charged with the 1,2-DHQ **1** (0.2 mmol, 1 eq.), imine **2** (0.2 mmol, 1 eq.), anhydrous toluene (2 mL), TsOH (0.02 mmol, 0.1eq). The system was stirred under a nitrogen atmosphere at 40 °C for 24 h. Then the products were obtained by purification with flash silica gel chromatography eluted with petroleum: ethyl acetate (10:1).

3. NMR experiment for exploring the reaction process

0.1 mmol dihydroquinoline **1a**, 0.1 mmol TsOH were dissolved in 0.5 mL $\text{DMSO-}d_6$. After analyzed with NMR, a drop of D_2O was added and the mixture was analyzed again with NMR. The NMR Results were depicted in Figure S1.

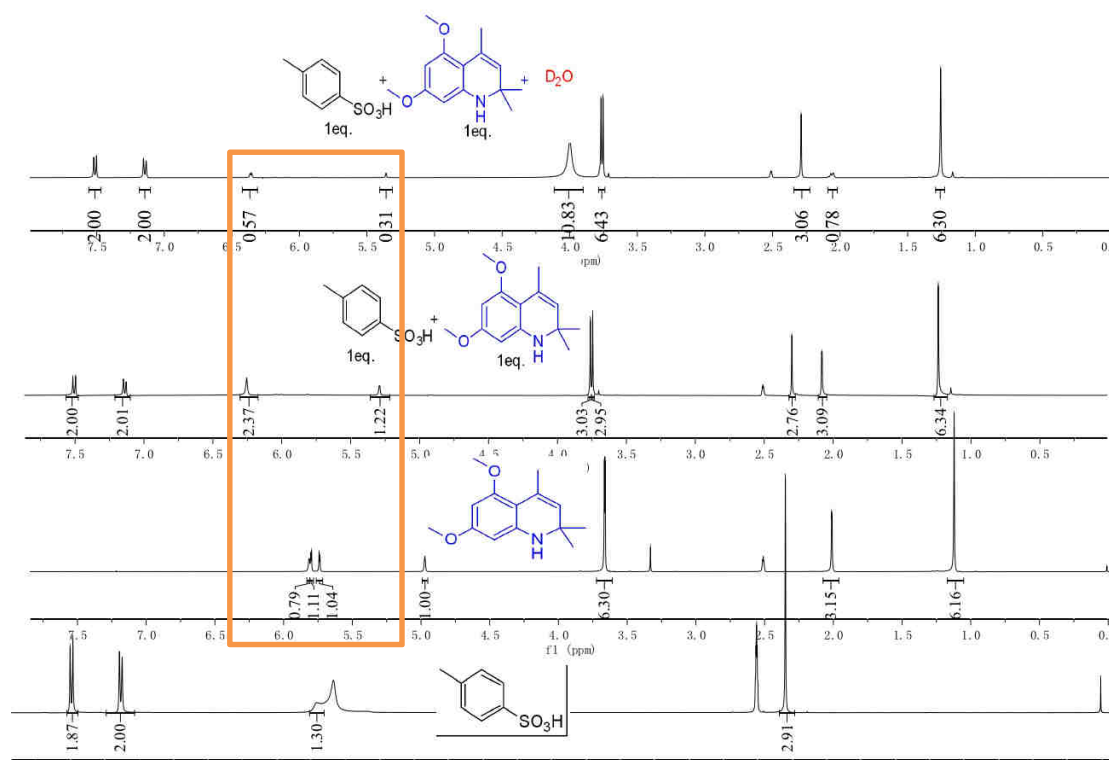
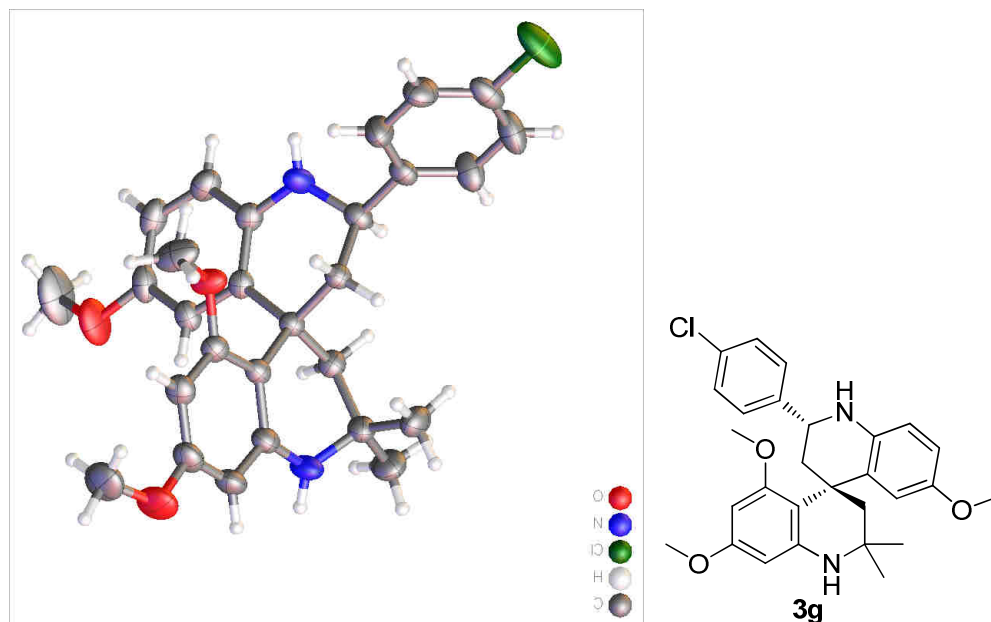


Figure S1 NMR results for the exploration of the reaction process.

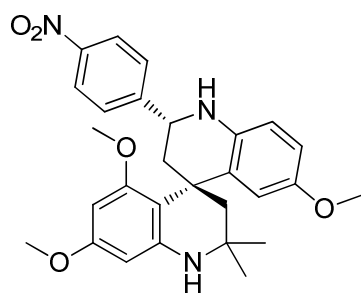
The results revealed that the signal of the aromatic hydrogen and the alkene hydrogen of **1j** moved to the lower field after the addition of equal equivalent of TsOH. This indicated that the electro density of the phenyl ring was decreased, which might be ascribed to the electrophilic substitution of the phenyl ring. Then the D₂O exchange experiment revealed that both the phenyl hydrogen and the alkene hydrogen, even the 4-CH₃ hydrogen were deuterated. These explained that the reactions could easily occur at phenyl ring, the alkene as well as the 4-CH₃.

4. X-ray single crystal data for **3g** (CCDC 1512451)



Chemical formula	C ₂₈ H ₃₁ ClN ₂ O ₃
Formula weight	408.52
Space group	P -1
Z	2
a/Å	7.8118(3)
b/Å	8.2779(3)
c/Å	20.3825(8)
α/°	100.537(3)
β/°	93.304(3)
γ/°	102.748(3)
Volume/Å³	1257.26(9)
ρ_{calc}/cm³	1.265
Temperature/K	292 K

5. Characterization of selected substrates and products.



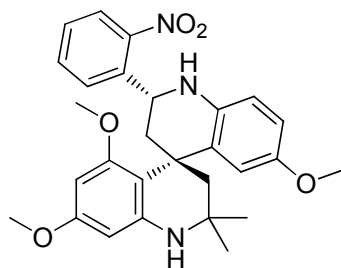
3a

Yellow solid (90.9 mg, 93%); M.p. 213–215 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 6.60 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.55 (d, *J* = 8.5 Hz, 1H), 6.42 (d, *J* = 2.1 Hz, 1H), 5.84 (s, 1H), 5.78 (s, 1H), 4.71 (t, *J* = 16.1 Hz, 1H), 3.76 (s, 3H), 3.65 (d, *J* = 9.5 Hz, 3H), 3.39 (s, 3H), 2.72 (dd, *J* = 23.8, 11.2 Hz, 1H), 2.35 (d, *J* = 14.1 Hz, 1H), 2.16 (dd, *J* = 24.3, 13.0 Hz, 2H), 1.36 (s, 3H), 1.28 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 159.74, 152.67, 152.49, 147.20, 146.33, 137.84, 134.19, 127.59, 123.88, 114.93, 113.10, 112.02, 109.20, 92.63, 91.06, 55.89, 55.44, 55.03, 53.21, 52.23, 49.64, 41.40, 38.91, 32.29, 28.72;

HRMS (ESI): calcd. For C₂₈H₃₁N₃NaO₅ (M+Na): 512.2155; found: 512.2146.



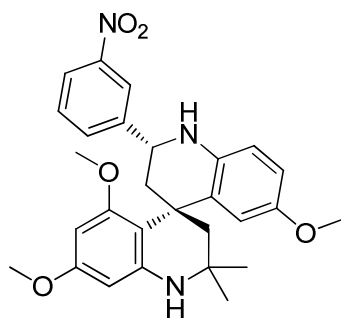
3b

Yellow solid (86.1 mg, 88%); M.p. 208–209 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 6.54 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.47 (d, *J* = 8.6 Hz, 1H), 6.38 (d, *J* = 2.7 Hz, 1H), 5.81 (d, *J* = 2.1 Hz, 1H), 5.75 (d, *J* = 2.2 Hz, 1H), 5.02 (d, *J* = 9.5 Hz, 1H), 3.73 (s, 4H), 3.60 (s, 3H), 3.35 (s, 3H), 2.71 (t, *J* = 12.2 Hz, 1H), 2.44 (dd, *J* = 17.6, 8.0 Hz, 2H), 2.08 (d, *J* = 14.1 Hz, 1H), 1.38 (s, 3H), 1.26 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 159.79, 159.65, 152.59, 149.00, 146.65, 139.78, 138.49, 134.80, 133.20, 129.60, 127.80, 123.88, 114.93, 113.33, 111.94, 110.19, 92.73, 91.29, 55.89, 55.47, 54.99, 51.75, 49.76, 48.42, 40.36, 39.17, 32.36, 27.65;

HRMS (ESI): calcd. For C₂₈H₃₁N₃NaO₅ (M+Na): 512.2155; found: 512.2142.



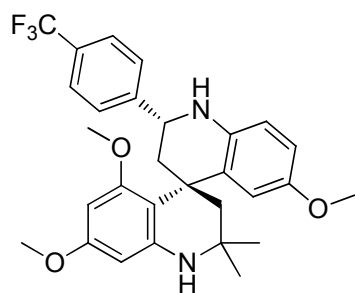
3c

Yellow solid (73.4 mg, 75%); M.p. 218–219 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 1H), 8.15 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.9 Hz, 1H), 6.60 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 6.42 (d, *J* = 2.7 Hz, 1H), 5.84 (d, *J* = 2.4 Hz, 1H), 5.78 (d, *J* = 2.3 Hz, 1H), 4.68 (dd, *J* = 11.9, 2.3 Hz, 1H), 3.76 (s, 3H), 3.64 (s, 3H), 3.40 (s, 3H), 2.77 (t, *J* = 12.6 Hz, 1H), 2.36 (d, *J* = 14.2 Hz, 1H), 2.26 – 2.10 (m, 2H), 1.36 (s, 3H), 1.29 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 159.77, 159.74, 152.53, 148.50, 147.28, 146.34, 137.93, 134.22, 133.11, 129.48, 122.45, 121.84, 114.96, 113.14, 112.04, 109.36, 92.66, 91.07, 55.90, 55.44, 55.01, 53.06, 52.35, 49.64, 41.44, 38.92, 32.32, 28.71;

HRMS (ESI): calcd. For C₂₈H₃₁N₃NaO₅ (M+Na): 512.2155; found: 512.2149.



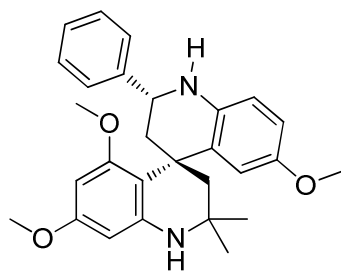
3d

Yellow oil (78.8 mg, 77%); M.p. 229–231 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.63 (s, 4H), 6.60 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.53 (d, *J* = 8.6 Hz, 1H), 6.43 (d, *J* = 2.7 Hz, 1H), 5.85 (d, *J* = 2.3 Hz, 1H), 5.78 (d, *J* = 2.3 Hz, 1H), 4.64 (dd, *J* = 11.8, 2.0 Hz, 1H), 3.77 (d, *J* = 5.3 Hz, 4H), 3.65 (d, *J* = 9.0 Hz, 3H), 3.40 (s, 3H), 2.76 (s, 1H), 2.36 (s, 1H), 2.24 – 2.04 (m, 2H), 1.36 (s, 3H), 1.29 (d, *J* = 4.9 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 159.80, 159.68, 152.35, 149.08, 146.32, 138.23, 134.22, 129.71 (q, *J* = 32.32), 127.17, 125.52 (q, *J* = 4.04), 114.79, 113.20, 111.97, 109.52, 92.64, 91.07, 55.91, 55.42, 55.01, 53.27, 52.27, 49.67, 41.35, 38.96, 32.31, 28.69;

HRMS (ESI): calcd. For C₂₉H₃₂F₃N₂O₃ (M+H): 513.2355; found: 513.2346.



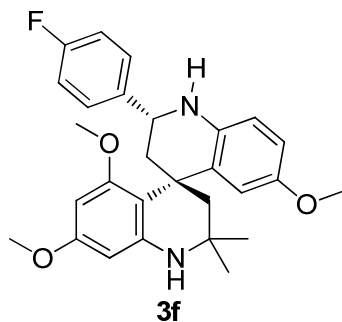
3e

Colorless oil (55.1 mg, 62%); M.p. 211–212 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 6.55 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.47 (d, *J* = 8.5 Hz, 1H), 6.40 (s, 1H), 5.82 (s, 1H), 5.74 (s, 1H), 4.54 (d, *J* = 11.7 Hz, 1H), 3.74 (s, 4H), 3.61 (s, 3H), 3.37 (s, 3H), 2.76 (t, *J* = 12.6 Hz, 1H), 2.36 (d, *J* = 14.1 Hz, 1H), 2.18 (d, *J* = 13.3 Hz, 1H), 2.11 (d, *J* = 14.0 Hz, 1H), 1.33 (s, 3H), 1.25 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 159.89, 159.61, 152.17, 146.27, 144.89, 138.67, 134.20, 128.53, 127.36, 126.85, 116.47, 114.86, 114.60, 113.32, 111.98, 110.01, 92.69, 91.13, 55.99, 55.41, 54.99, 53.50, 52.24, 49.69, 41.20, 39.04, 32.32, 28.71;

HRMS (ESI): calcd. For C₂₈H₃₃N₂O₃ (M+H): 445.2443; found: 445.2446.

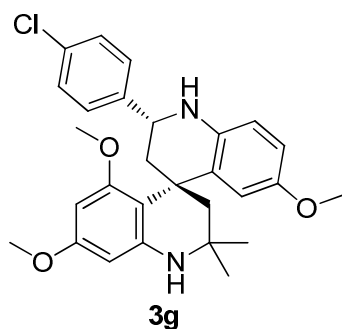


Yellow solid (62.8 mg, 68%); M.p. 204–206 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.46 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.06 (t, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 1H), 6.68 (d, *J* = 8.9 Hz, 1H), 6.58 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.50 (d, *J* = 8.6 Hz, 1H), 6.42 (d, *J* = 2.7 Hz, 1H), 5.85 (d, *J* = 2.3 Hz, 1H), 5.78 (d, *J* = 2.3 Hz, 1H), 4.64 – 4.47 (m, 1H), 3.77 (s, 1H), 3.76 (s, 3H), 3.63 (s, 3H), 3.39 (s, 3H), 2.74 (t, *J* = 12.6 Hz, 1H), 2.36 (d, *J* = 14.1 Hz, 1H), 2.25 – 2.08 (m, 2H), 1.35 (s, 3H), 1.27 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 163.28 (d, *J* = 245.43), 159.81, 159.60, 152.19, 146.31, 140.62 (d, *J* = 3.03), 138.58, 134.24, 128.40 (d, *J* = 8.08), 116.44, 115.40 (d, *J* = 21.21), 114.80, 113.22, 111.90, 109.85, 92.59, 91.07, 55.93, 55.75, 55.45, 55.02, 52.81, 52.35, 49.66, 41.33, 39.00, 32.40, 28.69;

HRMS (ESI): calcd. For C₂₈H₃₂FN₂O₃ (M+H): 463.2378; found: 463.2360.

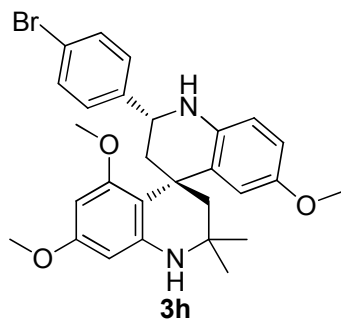


Off-white solid (78.4 mg, 82%); M.p. 221–225 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.57 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.50 (d, *J* = 8.6 Hz, 1H), 6.41 (d, *J* = 2.7 Hz, 1H), 5.84 (d, *J* = 2.3 Hz, 1H), 5.77 (d, *J* = 2.3 Hz, 1H), 4.53 (dd, *J* = 11.9, 2.2 Hz, 1H), 3.77 (d, *J* = 4.7 Hz, 3H), 3.63 (s, 3H), 3.38 (s, 3H), 2.72 (t, *J* = 12.7 Hz, 1H), 2.42 – 2.29 (m, 1H), 2.25 – 2.05 (m, 2H), 1.34 (s, 3H), 1.27 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 159.82, 159.64, 152.26, 146.30, 143.45, 138.43, 134.19, 132.87, 128.64, 128.19, 116.44, 114.83, 114.65, 113.23, 111.95, 109.74, 92.63, 91.09, 55.94, 55.42, 55.00, 52.93, 52.28, 49.64, 41.30, 38.98, 32.34, 28.71;

HRMS (ESI): calcd. For C₂₈H₃₂ClN₂O₃ (M+H): 479.2112; found: 479.2105.

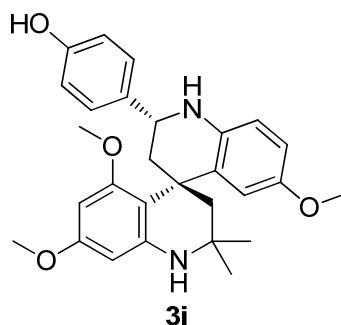


Yellow solid (72.0 mg, 69%); M.p. 219–222 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 6.58 (d, *J* = 2.7 Hz, 1H), 6.52 (d, *J* = 8.6 Hz, 1H), 6.44 (d, *J* = 2.6 Hz, 1H), 5.86 (d, *J* = 2.1 Hz, 1H), 5.79 (d, *J* = 2.1 Hz, 1H), 4.66 – 4.49 (m, 1H), 3.78 (d, *J* = 11.5 Hz, 3H), 3.70 – 3.59 (m, 3H), 3.45 – 3.34 (m, 3H), 2.75 (t, *J* = 12.6 Hz, 1H), 2.37 (d, *J* = 14.1 Hz, 1H), 2.21 – 2.07 (m, 2H), 1.36 (s, 3H), 1.28 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 159.84, 159.66, 152.29, 146.34, 144.03, 138.41, 134.22, 131.62, 128.62, 120.95, 114.75, 113.26, 111.98, 109.72, 92.70, 91.11, 55.95, 55.45, 55.02, 53.02, 52.31, 49.66, 41.34, 39.00, 32.35, 28.74;

HRMS (ESI): calcd. For C₂₈H₃₂BrN₂O₃ (M+H): 523.1468; found: 523.1463.

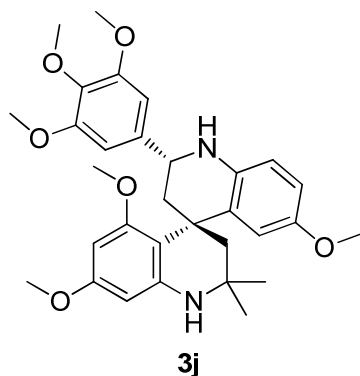


Off-white solid (46.0 mg, 50%); M.p. 205–208 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.58 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.50 (d, *J* = 8.6 Hz, 1H), 6.42 (d, *J* = 2.7 Hz, 1H), 5.85 (d, *J* = 2.3 Hz, 1H), 5.77 (d, *J* = 2.3 Hz, 1H), 4.54 (dd, *J* = 11.9, 2.1 Hz, 1H), 3.76 (s, 4H), 3.63 (s, 3H), 3.39 (s, 3H), 2.73 (t, *J* = 12.6 Hz, 1H), 2.35 (d, *J* = 14.1 Hz, 1H), 2.25 – 2.04 (m, 2H), 1.34 (s, 3H), 1.27 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 159.82, 159.64, 152.26, 146.32, 143.46, 138.45, 134.20, 132.87, 128.65, 128.20, 114.67, 113.24, 111.96, 109.74, 92.64, 91.09, 55.94, 55.43, 55.01, 52.94, 52.29, 49.64, 41.32, 38.98, 32.35, 28.72;

HRMS (ESI): calcd. For C₂₈H₃₂N₂NaO₄ (M+Na): 483.2260; found: 483.2265.

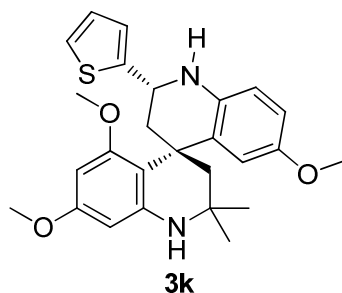


Yellow solid (71.8 mg, 95%); M.p. 245–247 °C;

¹H NMR (400 MHz, CDCl₃) δ 6.71 (s, 2H), 6.58 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.51 (d, *J* = 8.5 Hz, 1H), 6.41 (t, *J* = 7.0 Hz, 1H), 5.85 (d, *J* = 2.3 Hz, 1H), 5.77 (d, *J* = 2.4 Hz, 1H), 4.48 (dd, *J* = 11.7, 2.0 Hz, 1H), 3.91 (s, 6H), 3.86 (s, 3H), 3.76 (s, 3H), 3.63 (s, 3H), 3.40 (s, 3H), 2.75 (t, *J* = 12.5 Hz, 1H), 2.36 (d, *J* = 14.1 Hz, 1H), 2.25 – 2.02 (m, 2H), 1.36 (s, 3H), 1.27 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 159.83, 159.61, 153.32, 152.20, 146.33, 140.72, 138.58, 137.09, 134.27, 114.71, 113.26, 111.89, 109.82, 103.59, 92.60, 91.06, 60.88, 56.20, 55.94, 55.42, 55.02, 53.71, 52.38, 49.67, 41.15, 39.02, 32.35, 28.79;

HRMS (ESI): calcd. For C₃₁H₃₉N₂O₆ (M+H): 535.2178; found: 535.2170.

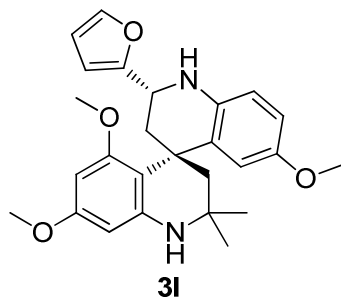


Colorless oil (58.5 mg, 65%);

¹H NMR (600 MHz, CDCl₃) δ 7.26 – 7.19 (m, 1H), 7.05 (d, *J* = 3.1 Hz, 1H), 6.97 (dd, *J* = 4.9, 3.6 Hz, 1H), 6.61 – 6.53 (m, 1H), 6.48 (d, *J* = 8.6 Hz, 1H), 6.39 (d, *J* = 2.7 Hz, 1H), 5.83 (d, *J* = 2.1 Hz, 1H), 5.75 (d, *J* = 2.0 Hz, 1H), 4.86 (dd, *J* = 11.8, 2.2 Hz, 1H), 3.74 (s, 4H), 3.60 (s, 3H), 3.37 (s, 3H), 2.85 (t, *J* = 12.6 Hz, 1H), 2.36 – 2.25 (m, 2H), 2.09 (d, *J* = 14.3 Hz, 1H), 1.33 (s, 3H), 1.24 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 159.87, 159.69, 152.46, 149.14, 146.33, 138.06, 134.44, 126.47, 123.98, 123.23, 114.91, 113.20, 111.94, 109.68, 92.63, 91.02, 55.90, 55.39, 55.00, 52.33, 49.63, 49.10, 41.91, 39.01, 32.35, 28.63;

HRMS (ESI): calcd. For C₂₆H₃₁N₂O₃S (M+H): 451.2010; found: 451.2014.

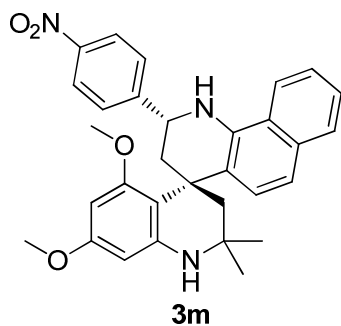


Colorless oil (69.4 mg, 80%);

¹H NMR (400 MHz, CDCl₃) δ 7.47 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 6.59 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.51 (d, *J* = 8.6 Hz, 1H), 6.43 (d, *J* = 2.7 Hz, 1H), 5.86 (d, *J* = 2.2 Hz, 1H), 5.79 (d, *J* = 2.3 Hz, 1H), 4.55 (dd, *J* = 11.8, 1.8 Hz, 1H), 3.77 (s, 3H), 3.64 (s, 3H), 3.40 (s, 3H), 2.75 (t, *J* = 12.6 Hz, 1H), 2.37 (d, *J* = 14.1 Hz, 1H), 2.23 – 2.07 (m, 2H), 1.35 (s, 3H), 1.28 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 163.31, 160.87, 159.84, 159.63, 152.23, 146.35, 140.66, 140.63, 138.60, 134.28, 128.43, 128.35, 115.42, 115.21, 114.69, 113.26, 111.93, 109.88, 92.65, 91.11, 55.94, 55.46, 55.02, 52.83, 52.37, 49.67, 41.37, 39.03, 32.39, 29.75, 28.70;

HRMS (ESI): calcd. For C₂₆H₃₀N₂NaO₄ (M+Na): 457.2103; found: 457.2110.

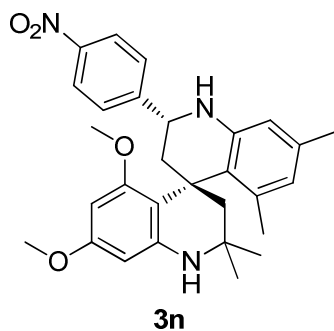


Yellow solid (66.2 mg, 65%); m.p. 169-171 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.7 Hz, 2H), 7.77 (dt, *J* = 15.0, 4.5 Hz, 4H), 7.50 – 7.36 (m, 2H), 7.15 (d, *J* = 8.6 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 5.84 (s, 2H), 4.86 (d, *J* = 10.0 Hz, 1H), 4.72 (s, 1H), 3.78 (s, 4H), 3.23 (s, 3H), 2.92 (t, *J* = 12.7 Hz, 1H), 2.35 (t, *J* = 14.8 Hz, 2H), 2.27 – 2.18 (m, 1H), 1.42 (s, 3H), 1.31 (s, 4H);

¹³C NMR (101 MHz, CDCl₃) δ 159.94, 159.84, 152.60, 147.39, 146.60, 137.39, 132.55, 128.51, 127.76, 126.64, 126.55, 124.82, 124.79, 124.04, 122.91, 119.51, 117.99, 109.08, 92.75, 90.96, 55.44, 55.03, 53.31, 52.23, 49.68, 41.13, 38.86, 32.30, 28.79;

HRMS (ESI): calcd. For C₃₁H₃₁N₃NaO₄ (M+Na): 532.1405; found: 532.1398.

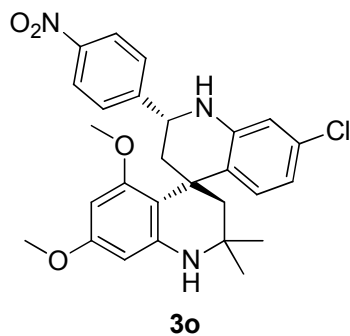


Yellow solid (58.4 mg, 60%); M.p. 200–203 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 7.1 Hz, 2H), 5.87 (d, *J* = 2.4 Hz, 1H), 5.77 (d, *J* = 2.4 Hz, 1H), 4.68 (dd, *J* = 11.7, 1.6 Hz, 1H), 4.03 (s, 1H), 3.76 (s, 3H), 3.42 (s, 3H), 2.72 (t, *J* = 12.3 Hz, 1H), 2.31 – 2.24 (m, 2H), 2.21 (d, *J* = 9.2 Hz, 3H), 2.13 (d, *J* = 13.8 Hz, 1H), 1.80 (s, 3H), 1.43 (s, 3H), 1.34 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 159.71, 159.55, 152.61, 147.24, 145.65, 144.47, 136.36, 135.09, 127.53, 127.47, 124.00, 123.90, 113.93, 110.16, 92.83, 90.96, 55.90, 55.03, 52.56, 49.43, 48.71, 43.20, 37.57, 33.25, 29.63, 20.77, 20.25;

HRMS (ESI): calcd. For C₂₉H₃₄N₃O₄ (M+H): 488.2544; found: 488.2529.

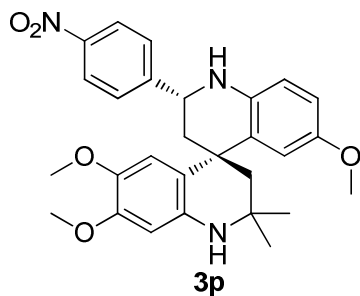


Off-white solid (46.3 mg, 50%); m.p. 181–183 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 2.0 Hz, 1H), 6.53 (dd, *J* = 8.3, 2.0 Hz, 1H), 5.85 (d, *J* = 2.3 Hz, 1H), 5.78 (d, *J* = 2.4 Hz, 1H), 4.72 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.12 (s, 1H), 3.77 (d, *J* = 5.2 Hz, 3H), 3.42 (s, 3H), 2.73 (t, *J* = 12.7 Hz, 1H), 2.32 (dd, *J* = 17.4, 8.8 Hz, 1H), 2.16 (dd, *J* = 13.4, 3.0 Hz, 1H), 2.11 – 1.95 (m, 1H), 1.35 (s, 3H), 1.27 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 159.89, 159.63, 151.94, 147.39, 146.44, 144.30, 131.02, 130.93, 128.75, 127.47, 124.01, 118.00, 113.53, 108.25, 92.66, 90.84, 55.32, 55.02, 53.03, 52.00, 49.64, 41.28, 38.25, 31.93, 28.97;

HRMS (ESI): calcd. For C₂₇H₂₈ClN₃NaO₄ (M+Na): 516.1666; found: 516.1653.

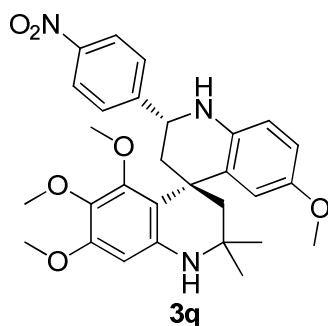


Yellow solid (68.5 mg, 70%); M.p. 221–223 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 6.68 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.59 (d, *J* = 8.6 Hz, 1H), 6.46 – 6.36 (m, 2H), 6.14 (s, 1H), 4.80 (dd, *J* = 11.8, 2.5 Hz, 1H), 3.97 (s, 1H), 3.84 (s, 3H), 3.67 (s, 3H), 3.63 (s, 3H), 2.43 (dd, *J* = 13.6, 2.7 Hz, 1H), 2.34 (d, *J* = 14.1 Hz, 1H), 2.14 (dd, *J* = 20.3, 8.9 Hz, 2H), 1.37 (s, 3H), 1.28 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 152.47, 152.16, 148.87, 147.38, 142.03, 138.89, 137.97, 132.15, 127.37, 124.00, 118.49, 115.50, 115.07, 113.75, 113.32, 99.99, 99.58, 56.92, 55.89, 55.71, 53.35, 50.62, 50.17, 46.34, 40.52, 31.88, 29.87;

HRMS (ESI): calcd. For C₂₈H₃₂N₃O₅ (M+H): 490.2340; found: 490.2344.

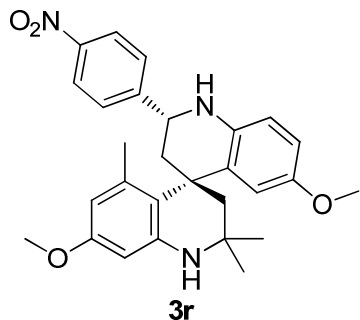


Yellow solid (70.6 mg, 68%); M.p. 233–235 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.29 (s, 1H), 6.59 (d, *J* = 2.1 Hz, 2H), 6.44 (d, *J* = 1.4 Hz, 1H), 5.88 (s, 1H), 4.71 – 4.58 (m, 1H), 3.81 (s, 3H), 3.70 (s, 3H), 3.63 (s, 3H), 3.14 (s, 3H), 2.79 (t, *J* = 12.4 Hz, 1H), 2.33 (d, *J* = 14.2 Hz, 1H), 2.22 (dd, *J* = 13.3, 2.2 Hz, 1H), 2.16 (s, 1H), 1.33 (s, 3H), 1.28 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 153.05, 152.95, 152.64, 152.33, 147.27, 141.05, 138.26, 134.96, 134.61, 127.71, 123.86, 115.49, 114.11, 114.00, 112.47, 94.03, 60.51, 58.98, 55.94, 55.58, 53.26, 52.98, 49.73, 42.32, 39.37, 32.48, 28.28;

HRMS (ESI): calcd. For C₂₉H₃₄N₃O₆ (M+H): 520.2442; found: 520.2441.

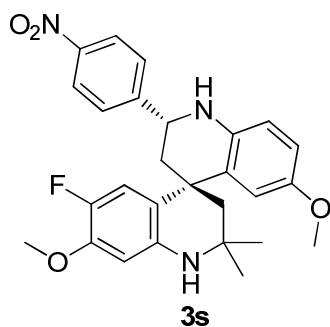


Gray solid (71.0 mg, 75%); M.p. 188–189 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 6.58 (dt, *J* = 18.9, 5.6 Hz, 2H), 6.42 (d, *J* = 2.6 Hz, 1H), 6.04 (s, 2H), 4.68 (dd, *J* = 11.9, 2.4 Hz, 1H), 3.63 (s, 3H), 3.38 (s, 3H), 2.76 (t, *J* = 12.6 Hz, 1H), 2.35 (d, *J* = 14.2 Hz, 1H), 2.26 – 2.11 (m, 5H), 1.35 (s, 3H), 1.28 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 158.67, 152.54, 147.27, 145.60, 137.87, 134.15, 127.60, 123.87, 114.90, 113.35, 111.97, 109.40, 104.08, 55.92, 55.43, 53.20, 52.31, 49.54, 41.38, 39.06, 32.29, 28.69, 21.41;

HRMS (ESI): calcd. For C₂₈H₃₁N₃NaO₄ (M+Na): 496.2207; found: 496.2195.

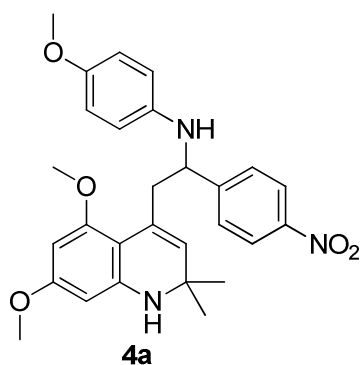


Yellow solid (57.2 mg, 60%); M.p. 211–212 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.6 Hz, 3H), 7.66 (d, *J* = 8.6 Hz, 3H), 6.71 – 6.63 (m, 2H), 6.58 (d, *J* = 8.6 Hz, 1H), 6.38 (d, *J* = 2.7 Hz, 1H), 6.14 (d, *J* = 7.6 Hz, 1H), 4.74 (d, *J* = 9.6 Hz, 1H), 3.84 (s, 3H), 3.66 (s, 3H), 2.42 (dd, *J* = 13.6, 2.6 Hz, 1H), 2.33 (d, *J* = 14.2 Hz, 1H), 2.17 (d, *J* = 14.2 Hz, 1H), 2.13 – 2.02 (m, 1H), 1.36 (s, 3H), 1.28 (s, 4H);

¹³C NMR (101 MHz, CDCl₃) δ 169.38, 161.40, 152.47, 151.92, 147.41, 138.02, 131.83, 127.43, 124.00, 116.35, 116.16, 115.58, 115.30, 115.27, 113.50, 100.24, 56.12, 55.81, 53.28, 50.52, 50.30, 46.44, 40.34, 31.94, 29.72;

HRMS (ESI): calcd. For C₂₇H₂₉FN₃O₄ (M+H): 478.1528; found: 478.1520.

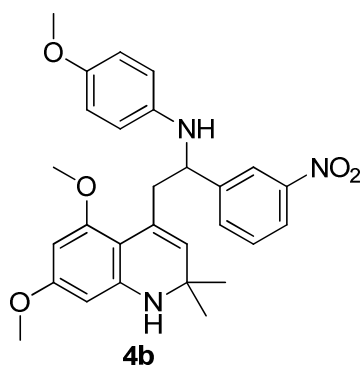


Yellow solid (83.1 mg, 85%); M.p. 182-185 °C;

¹H NMR (600 MHz, CDCl₃) δ 8.15 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 6.32 (d, *J* = 8.8 Hz, 2H), 5.85 (s, 1H), 5.74 (d, *J* = 1.9 Hz, 1H), 5.02 (s, 1H), 4.38 – 4.31 (m, 1H), 3.80 (s, 4H), 3.74 (s, 3H), 3.66 (s, 3H), 3.11 (dd, *J* = 13.1, 5.5 Hz, 1H), 2.77 (dd, *J* = 13.0, 8.2 Hz, 1H), 1.27 (s, 3H), 1.12 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 160.83, 158.14, 153.29, 152.22, 147.02, 146.89, 141.68, 130.02, 128.90, 127.35, 123.66, 114.88, 114.68, 102.49, 92.28, 89.33, 57.90, 55.69, 55.25, 55.07, 50.84, 45.49, 30.19, 29.13;

HRMS (ESI): calcd. For C₂₈H₃₁N₃NaO₅ (M+Na): 512.2156; found: 512.2146.

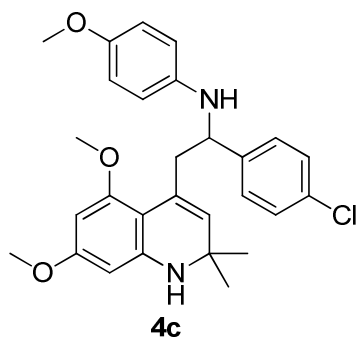


Yellow solid (48.5 mg, 70%); M.p. 176-178 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.09 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 8.9 Hz, 2H), 6.37 (d, *J* = 8.9 Hz, 2H), 5.88 (d, *J* = 2.2 Hz, 1H), 5.75 (d, *J* = 2.3 Hz, 1H), 5.05 (s, 1H), 4.37 (dd, *J* = 8.1, 5.5 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 4H), 3.68 (s, 3H), 3.17 (dd, *J* = 12.9, 5.3 Hz, 1H), 2.77 (dd, *J* = 13.0, 8.3 Hz, 1H), 1.29 (s, 3H), 1.14 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 160.80, 158.13, 152.18, 148.50, 147.70, 146.99, 141.69, 132.65, 129.92, 129.22, 129.05, 121.75, 114.91, 114.66, 102.45, 92.22, 89.31, 57.76, 55.70, 55.25, 55.10, 50.80, 45.76, 30.25, 29.11;

HRMS (ESI): calcd. For C₂₈H₃₁N₃NaO₅ (M+Na): 512.2156; found: 512.2148.

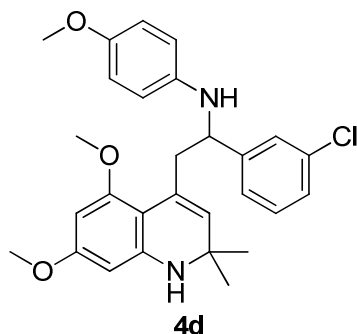


Off-white solid (62.1 mg, 65%); M.p. 162–165 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.25 (m, 4H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.37 (d, *J* = 8.9 Hz, 2H), 5.87 (d, *J* = 2.2 Hz, 1H), 5.74 (d, *J* = 2.2 Hz, 1H), 5.09 (s, 1H), 4.23 (dd, *J* = 8.7, 5.0 Hz, 1H), 4.06 (dd, *J* = 72.8, 14.6 Hz, 1H), 3.83 (d, *J* = 9.2 Hz, 3H), 3.77 (s, 3H), 3.69 (d, *J* = 7.2 Hz, 3H), 3.19 (dd, *J* = 13.1, 4.8 Hz, 1H), 2.65 (dd, *J* = 13.1, 8.8 Hz, 1H), 1.31 (s, 3H), 1.17 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 160.65, 158.18, 151.90, 146.94, 143.91, 142.24, 131.98, 129.70, 129.40, 128.47, 127.82, 114.90, 114.55, 102.66, 92.17, 89.24, 57.51, 55.72, 55.19, 55.07, 50.85, 45.88, 30.46, 29.05;

HRMS (ESI): calcd. For C₂₈H₃₁ClN₂NaO₃ (M+Na): 501.1923; found: 501.1928.

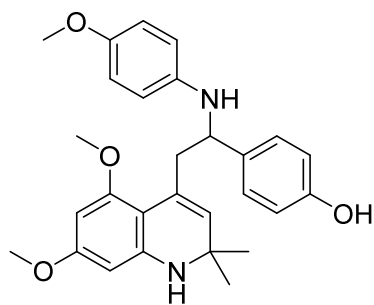


Off-white solid (76.5 mg, 80%); M.p. 154–157 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.27 (m, 4H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 8.8 Hz, 2H), 5.88 (d, *J* = 2.1 Hz, 1H), 5.75 (d, *J* = 2.1 Hz, 1H), 5.10 (s, 1H), 4.24 (dd, *J* = 8.6, 5.0 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.69 (s, 3H), 3.20 (dd, *J* = 13.1, 4.9 Hz, 1H), 2.66 (dd, *J* = 13.1, 8.8 Hz, 1H), 1.32 (s, 3H), 1.18 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 160.68, 158.20, 156.74, 151.95, 146.98, 143.91, 142.24, 132.01, 129.74, 129.41, 129.05, 128.50, 127.87, 122.27, 114.96, 114.58, 114.47, 102.67, 92.20, 89.26, 57.57, 55.73, 55.21, 55.08, 50.86, 45.89, 30.47, 29.76, 29.06;

HRMS (ESI): calcd. For C₂₈H₃₁ClN₂NaO₃ (M+Na): 501.1923; found: 501.1927.



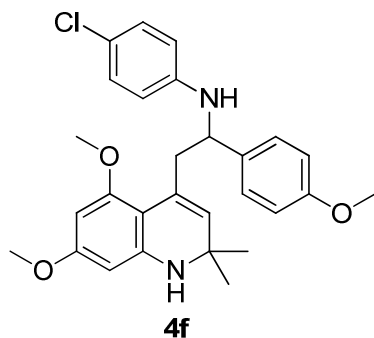
4e

Yellow solid (49.7 mg, 54%); M.p. 147–149 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.27 (m, 4H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.37 (d, *J* = 8.9 Hz, 2H), 5.87 (d, *J* = 2.2 Hz, 1H), 5.74 (d, *J* = 2.3 Hz, 1H), 5.10 (s, 1H), 4.23 (dd, *J* = 8.7, 5.0 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 4H), 3.68 (s, 3H), 3.19 (dd, *J* = 13.1, 4.9 Hz, 1H), 2.65 (dd, *J* = 13.1, 8.8 Hz, 1H), 1.31 (s, 3H), 1.17 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 160.65, 158.18, 151.91, 146.95, 143.92, 142.25, 131.98, 129.71, 129.40, 128.48, 127.83, 114.91, 114.56, 102.66, 92.18, 89.25, 57.52, 55.72, 55.19, 55.07, 50.86, 45.89, 30.46, 29.05;

HRMS (ESI): calcd. For C₂₈H₃₂N₂NaO₄ (M+Na): 483.2261; found: 483.2266.



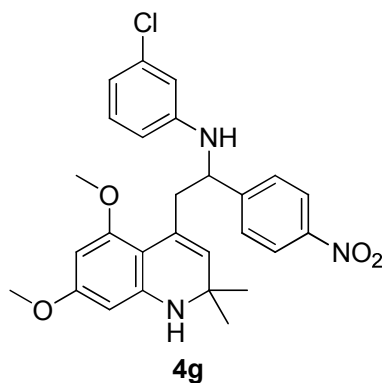
4f

Off-white solid (84.1 mg, 88%); M.p. 155–157 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 8.8 Hz, 2H), 5.89 (d, *J* = 2.2 Hz, 1H), 5.78 (d, *J* = 2.2 Hz, 1H), 5.04 (s, 1H), 4.50 (s, 1H), 4.41 (t, *J* = 6.1 Hz, 1H), 3.83 (s, 4H), 3.77 (s, 3H), 3.16 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.81 (dd, *J* = 13.0, 8.2 Hz, 1H), 1.29 (s, 3H), 1.15 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 160.88, 158.07, 152.38, 147.06, 146.98, 145.94, 130.14, 128.87, 128.73, 127.24, 123.79, 114.68, 102.34, 92.31, 89.36, 77.46, 77.14, 76.82, 57.25, 55.29, 55.11, 50.86, 45.30, 30.16, 29.08;

HRMS (ESI): calcd. For C₂₈H₃₂ClN₂O₃ (M+H): 479.2102; found: 479.2208.

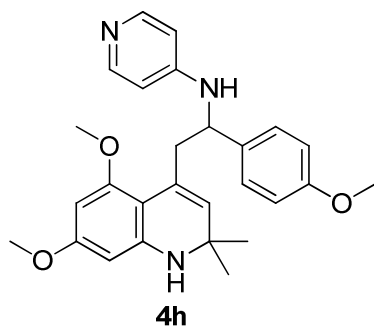


Yellow solid (88.8 mg, 90%); M.p. 192–193 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.61 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.37 (t, *J* = 2.0 Hz, 1H), 6.26 (dd, *J* = 8.1, 1.9 Hz, 1H), 5.90 (d, *J* = 2.2 Hz, 1H), 5.78 (d, *J* = 2.3 Hz, 1H), 5.04 (s, 1H), 4.57 (d, *J* = 2.8 Hz, 1H), 4.44 (dd, *J* = 10.7, 5.5 Hz, 1H), 3.16 (dd, *J* = 13.1, 5.6 Hz, 1H), 2.82 (dd, *J* = 13.1, 8.2 Hz, 1H), 1.29 (s, 3H), 1.15 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 160.90, 158.06, 152.16, 148.49, 147.05, 147.02, 134.70, 130.16, 130.06, 128.68, 127.21, 123.82, 117.59, 113.38, 111.81, 102.35, 92.35, 89.38, 57.02, 55.32, 55.12, 50.86, 45.27, 30.16, 29.09;

HRMS (ESI): calcd. For C₂₇H₂₉ClN₃O₄ (M+H): 494.1830; found: 494.1833.

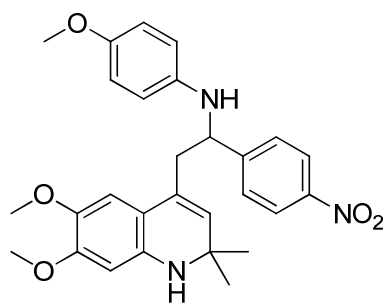


White solid (40.0 mg, 45%); M.p. 162–164 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, *J* = 5.9 Hz, 2H), 7.35 – 7.23 (m, 3H), 6.71 – 6.55 (m, 2H), 6.40 – 6.28 (m, 2H), 5.87 (d, *J* = 2.3 Hz, 1H), 5.75 (d, *J* = 2.3 Hz, 1H), 5.06 (s, 1H), 4.24 (dd, *J* = 8.4, 5.3 Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 3.68 (s, 3H), 3.16 (dd, *J* = 13.0, 5.2 Hz, 1H), 2.71 (dd, *J* = 13.1, 8.5 Hz, 1H), 1.30 (s, 3H), 1.17 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 160.75, 158.14, 154.59, 152.11, 149.72, 146.99, 141.79, 137.51, 129.97, 128.96, 121.88, 114.84, 114.62, 102.45, 92.21, 89.29, 58.97, 57.34, 56.79, 55.70, 55.22, 55.08, 54.50, 50.86, 46.78, 45.20, 30.31, 29.71, 29.09;

HRMS (ESI): calcd. For C₂₇H₃₂N₃O₃ (M+H): 446.2440; found: 446.2446.



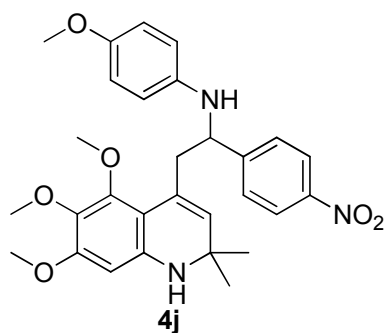
4i

Yellow solid (89.0 mg, 91%); M.p. 188–190 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 6.75 (s, 1H), 6.67 (d, *J* = 8.9 Hz, 2H), 6.38 (d, *J* = 8.9 Hz, 2H), 6.12 (s, 1H), 5.12 (s, 1H), 4.54 (dd, *J* = 7.8, 6.1 Hz, 1H), 3.86 (d, *J* = 7.9 Hz, 3H), 3.82 (s, 3H), 3.69 (s, 3H), 2.75 (qd, *J* = 14.3, 7.0 Hz, 2H), 1.28 (s, 3H), 1.20 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 152.53, 152.37, 150.46, 147.17, 141.14, 140.95, 138.95, 128.91, 128.13, 127.33, 123.99, 114.95, 114.78, 111.72, 109.13, 98.59, 57.51, 57.24, 55.80, 55.69, 51.76, 41.68, 30.55, 30.23;

HRMS (ESI): calcd. For C₂₈H₃₁N₃NaO₅ (M+Na): 512.2156; found: 512.2141.



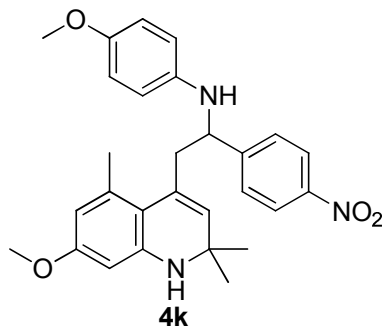
4j

Yellow solid (96.5 mg, 93%); M.p. 202–203 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.33 (d, *J* = 8.9 Hz, 2H), 5.90 (s, 1H), 5.20 (s, 1H), 4.42 (dd, *J* = 9.0, 4.6 Hz, 1H), 3.88 (s, 3H), 3.82 (d, *J* = 6.3 Hz, 6H), 3.67 (s, 3H), 3.14 (dd, *J* = 13.2, 4.3 Hz, 1H), 2.63 (dd, *J* = 13.3, 9.1 Hz, 1H), 1.32 (s, 3H), 1.16 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 153.84, 153.40, 152.15, 151.55, 146.91, 141.73, 141.56, 134.45, 131.40, 128.86, 127.31, 123.82, 116.45, 114.87, 114.63, 106.02, 94.21, 61.35, 61.27, 57.50, 55.69, 50.97, 44.91, 30.33, 28.73;

HRMS (ESI): calcd. For C₂₉H₃₃N₃NaO₆ (M+Na): 542.2262; found: 542.2253.



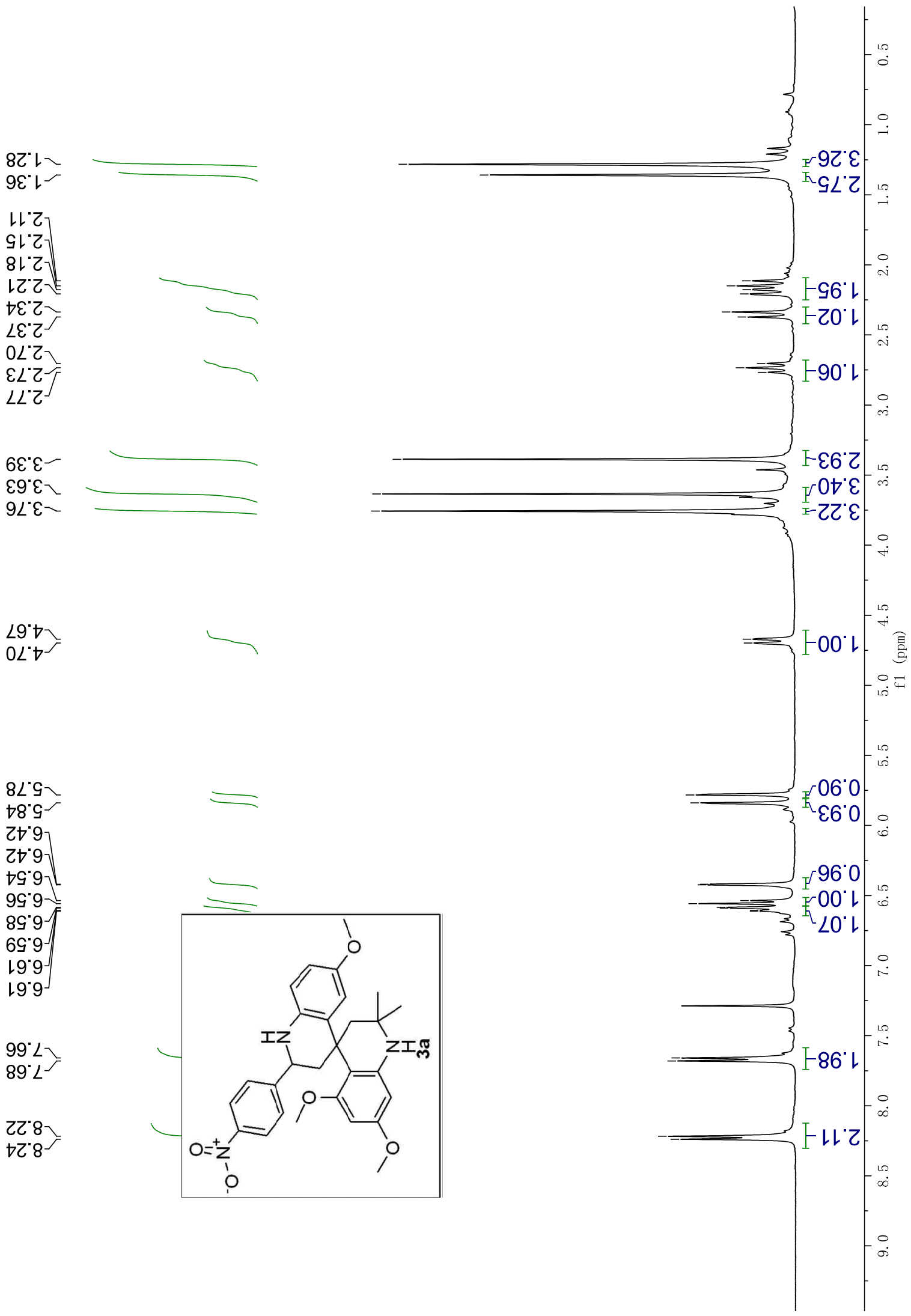
Gray solid (85.1 mg, 90%); M.p. 157–159 °C;

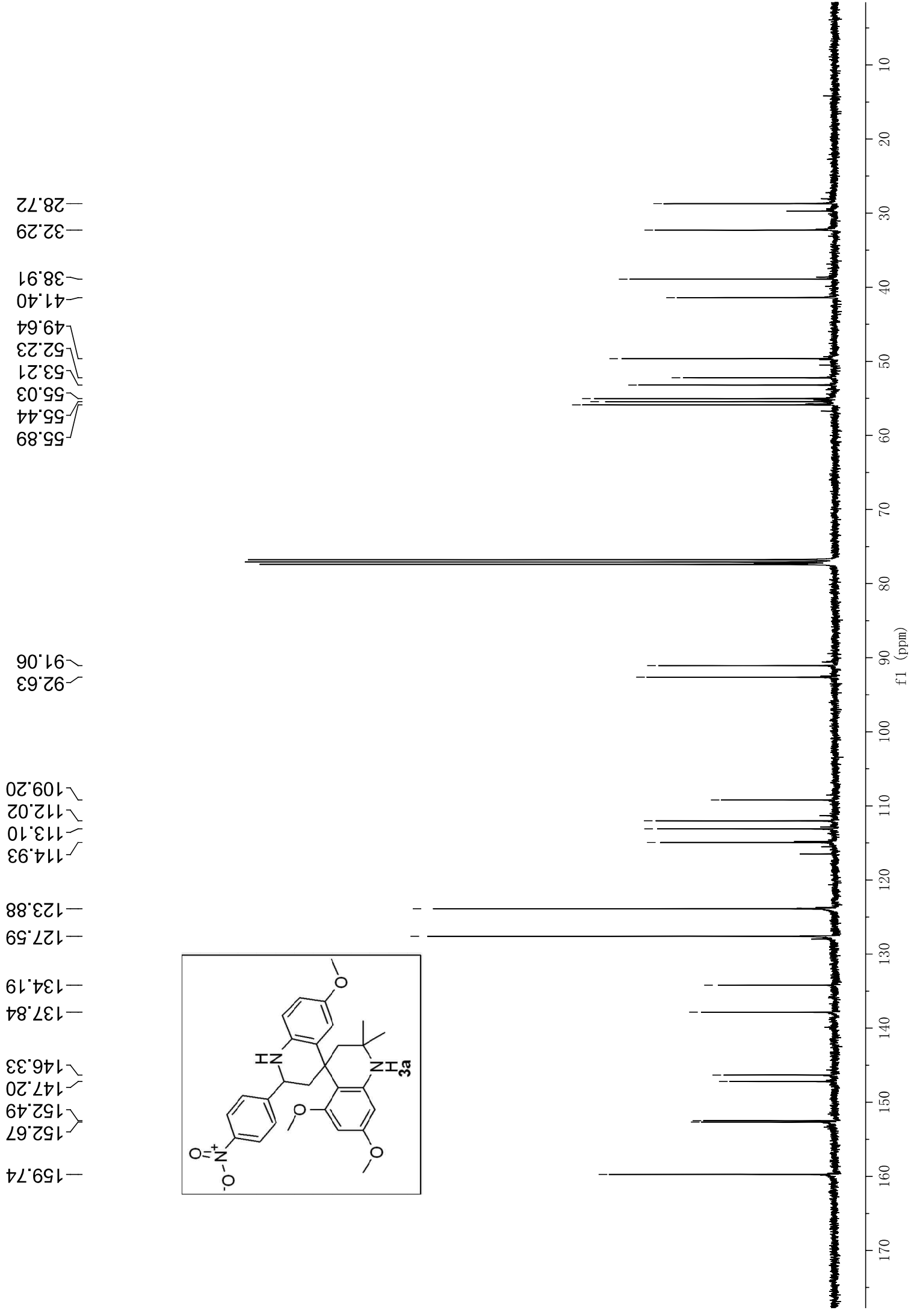
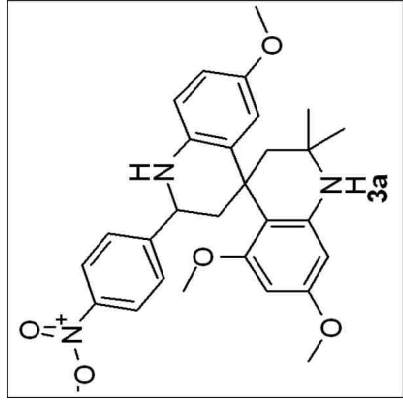
¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 6.70 – 6.58 (m, 2H), 6.42 – 6.28 (m, 2H), 6.08 (s, 1H), 6.03 (s, 1H), 5.11 (s, 1H), 4.38 (dd, *J* = 8.0, 5.6 Hz, 1H), 4.27 – 4.13 (m, 1H), 3.83 (s, 3H), 3.68 (s, 4H), 3.16 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.80 (dd, *J* = 13.0, 8.2 Hz, 1H), 2.23 (s, 3H), 1.29 (s, 3H), 1.15 (s, 3H);

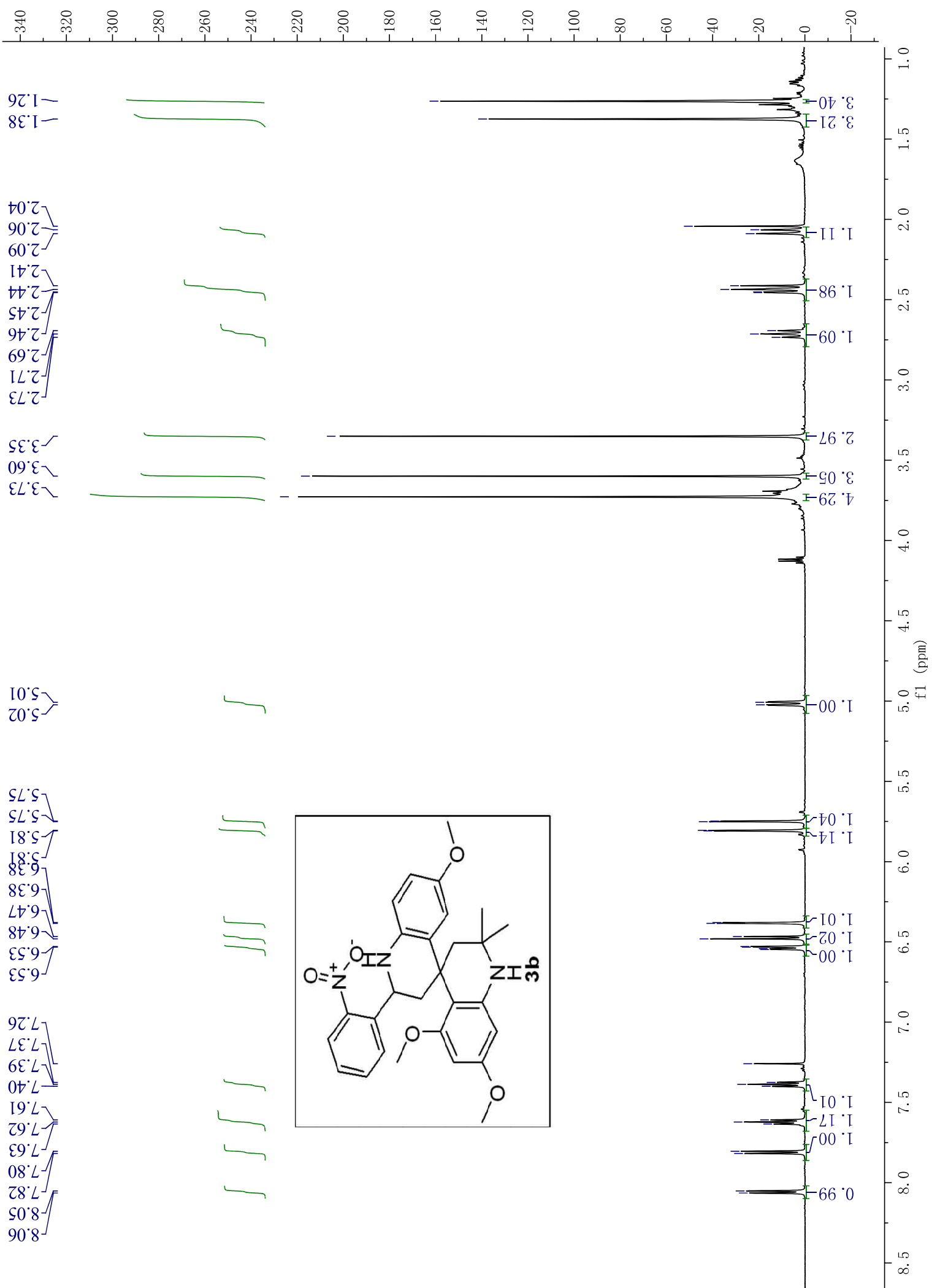
¹³C NMR (101 MHz, CDCl₃) δ 156.89, 153.24, 152.17, 146.86, 145.96, 141.62, 139.44, 131.69, 129.02, 127.33, 123.67, 114.87, 114.63, 108.63, 106.28, 102.26, 57.87, 55.69, 55.22, 50.77, 45.53, 30.19, 29.09, 21.66;

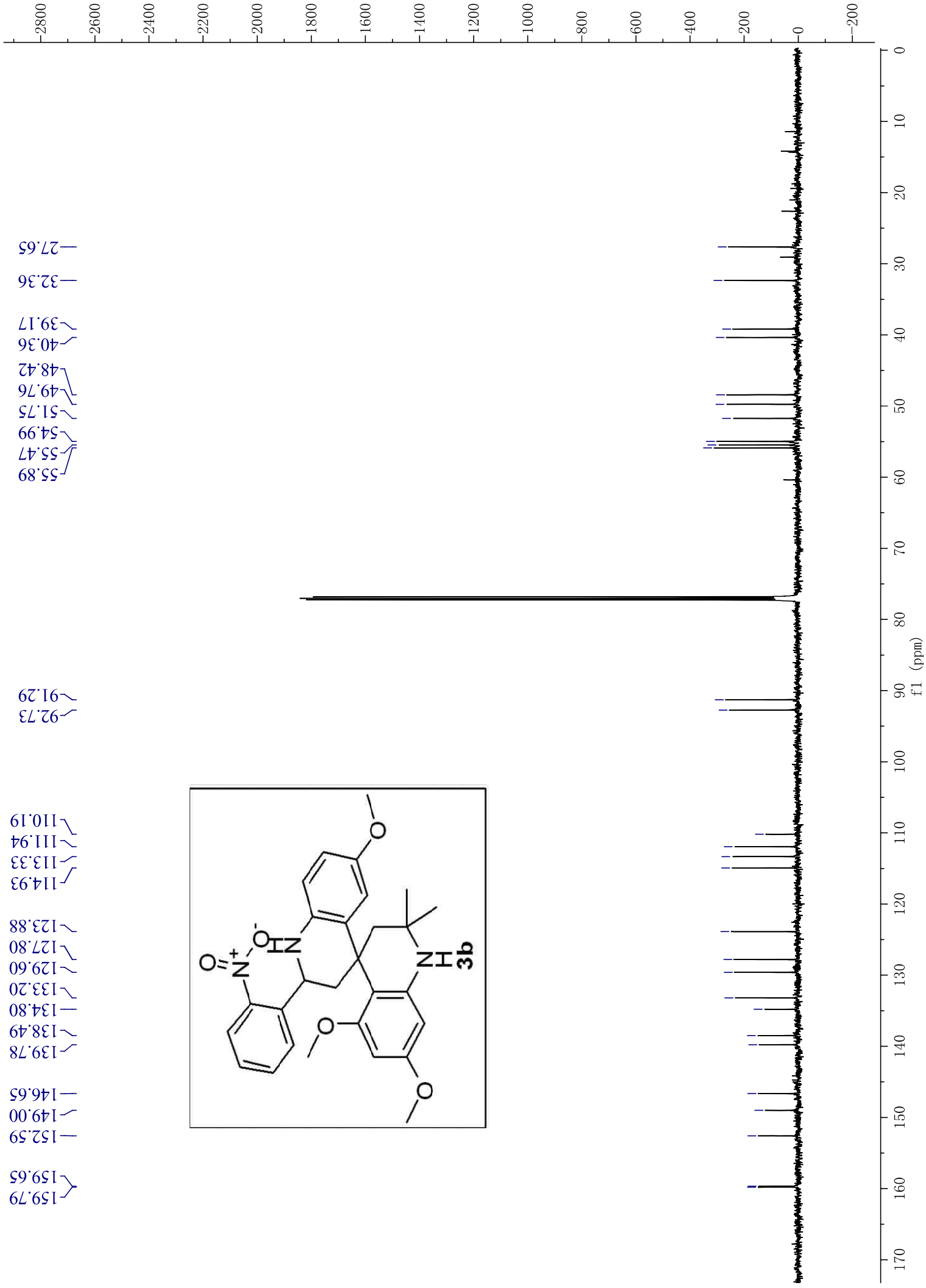
HRMS (ESI): calcd. For C₂₈H₃₁N₃NaO₄ (M+Na): 496.2207; found: 496.2197.

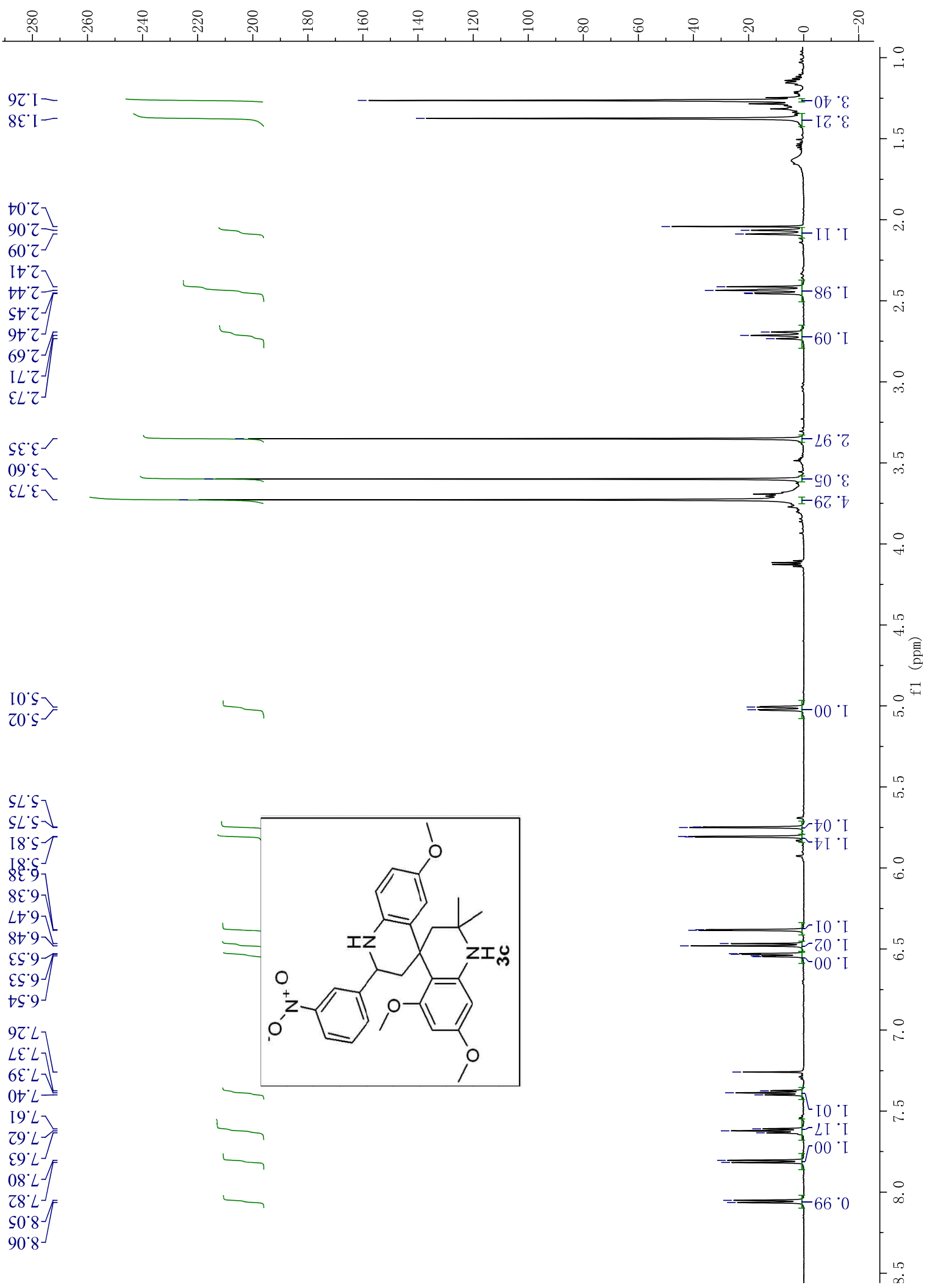
6. NMR spectrums

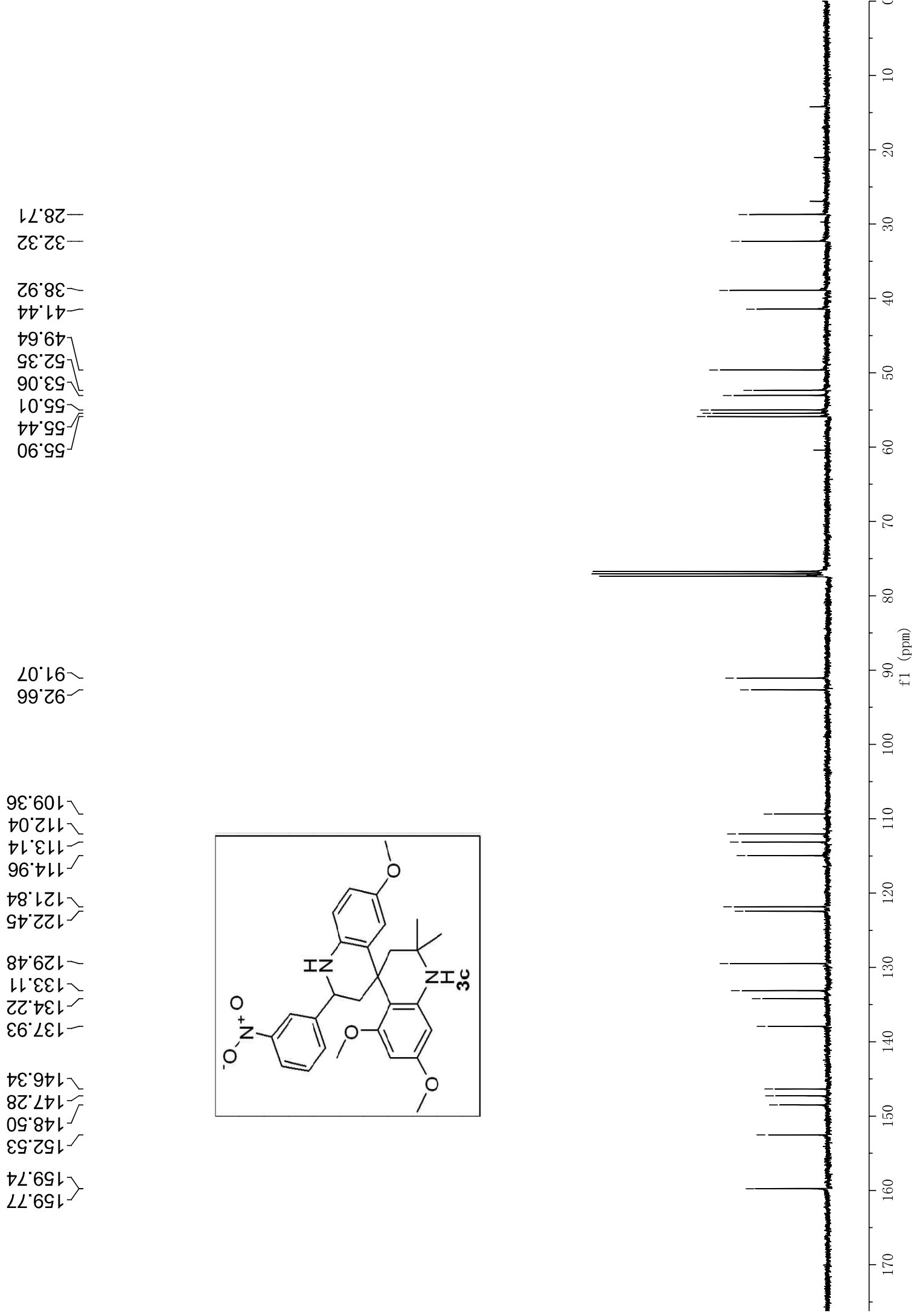


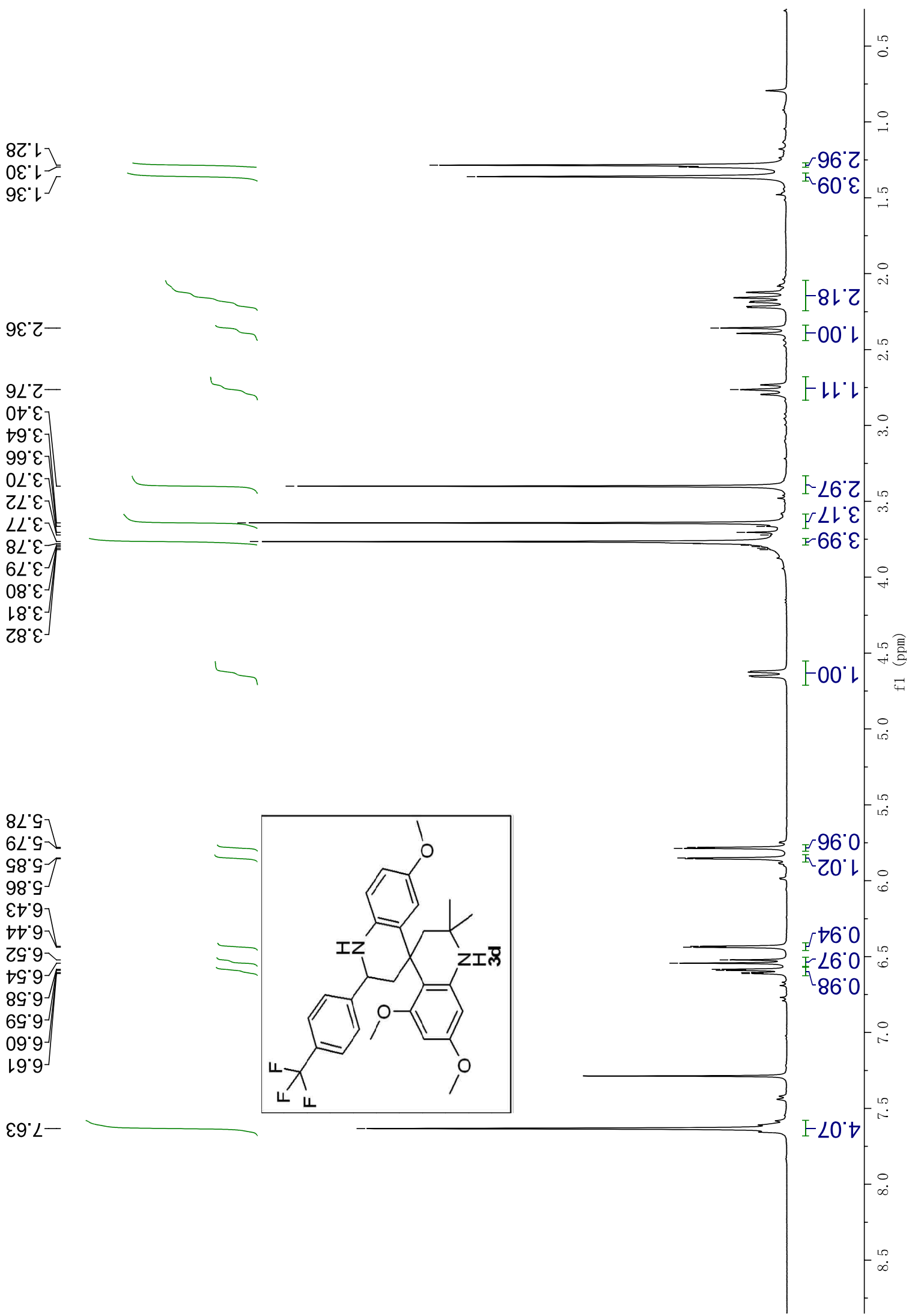








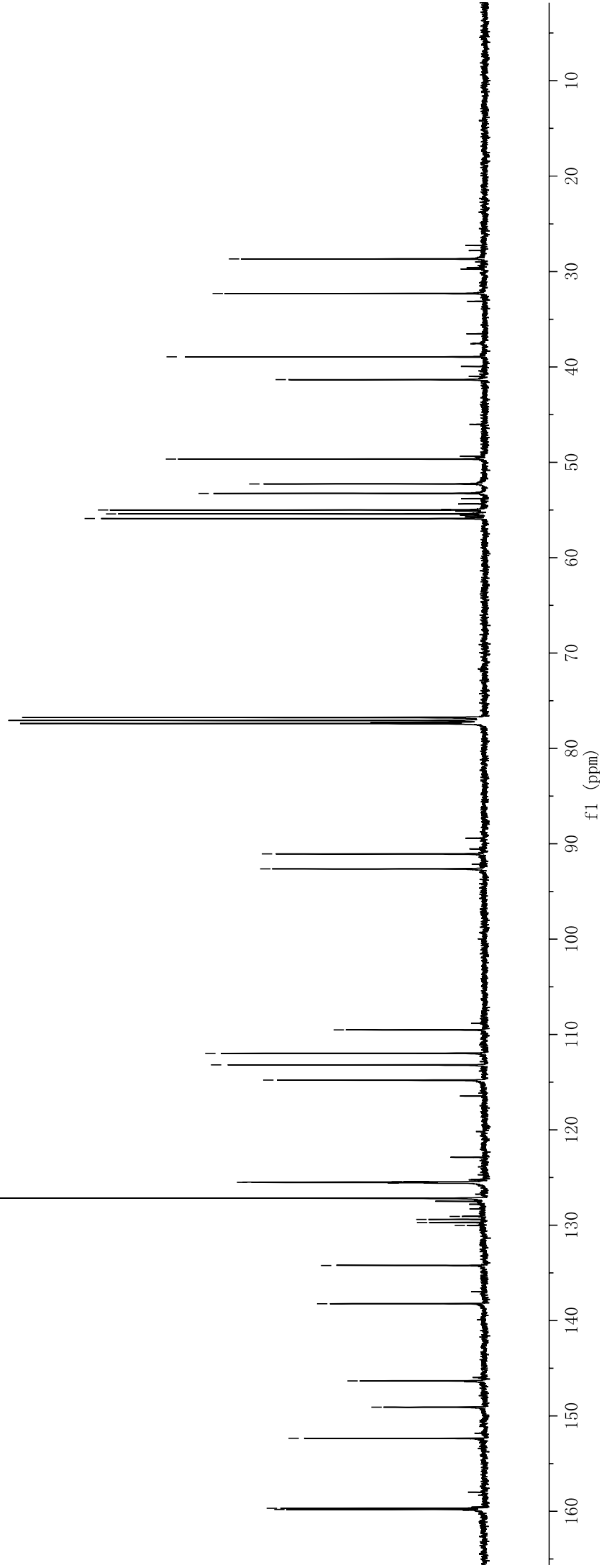
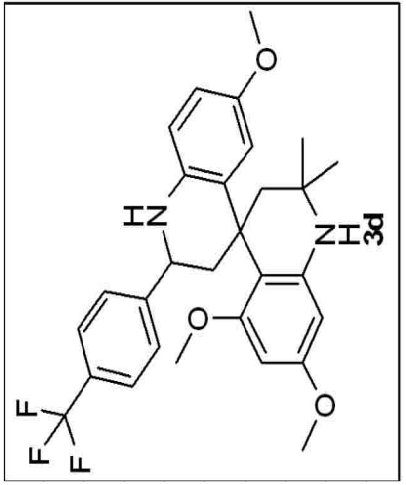


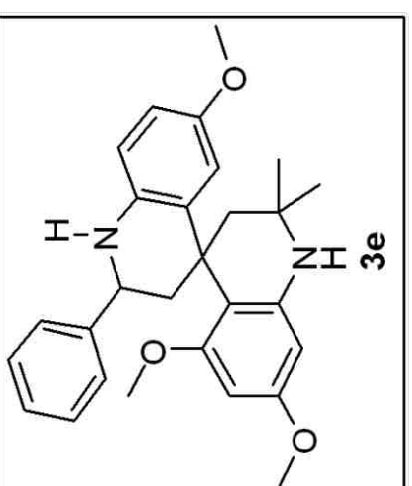
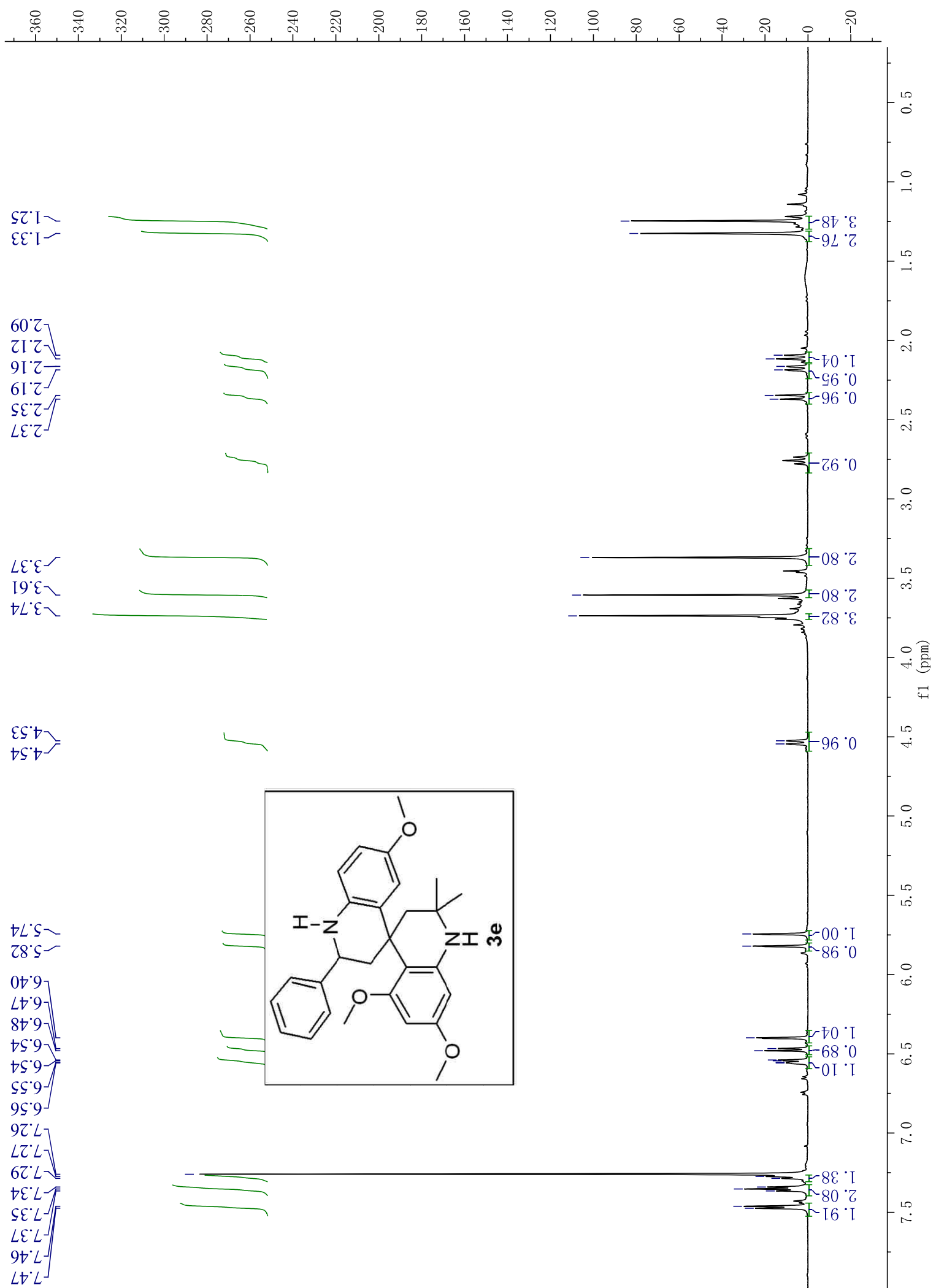


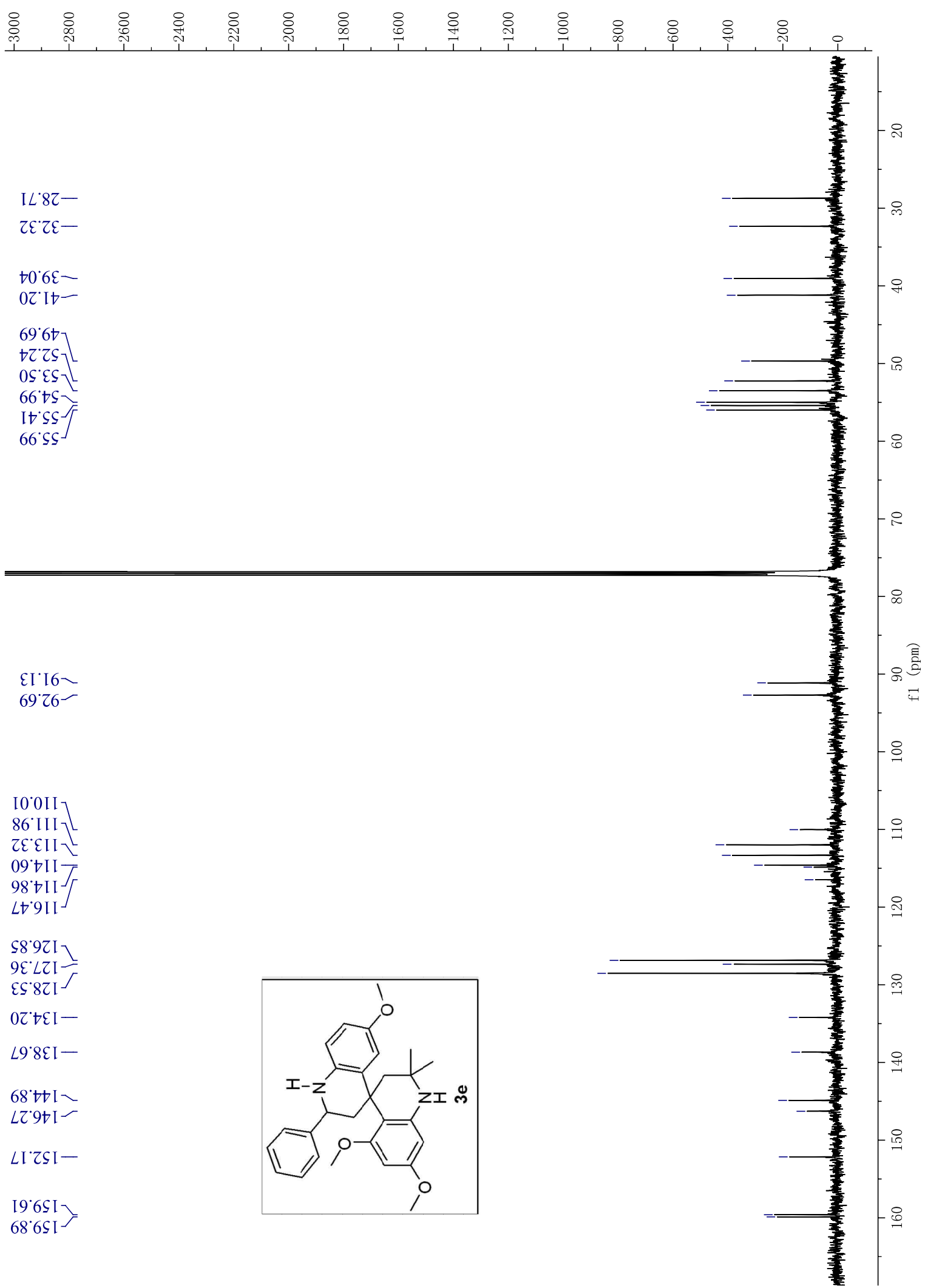
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32.31
38.96
41.35
49.67
52.27
53.27
55.01
55.42
55.91

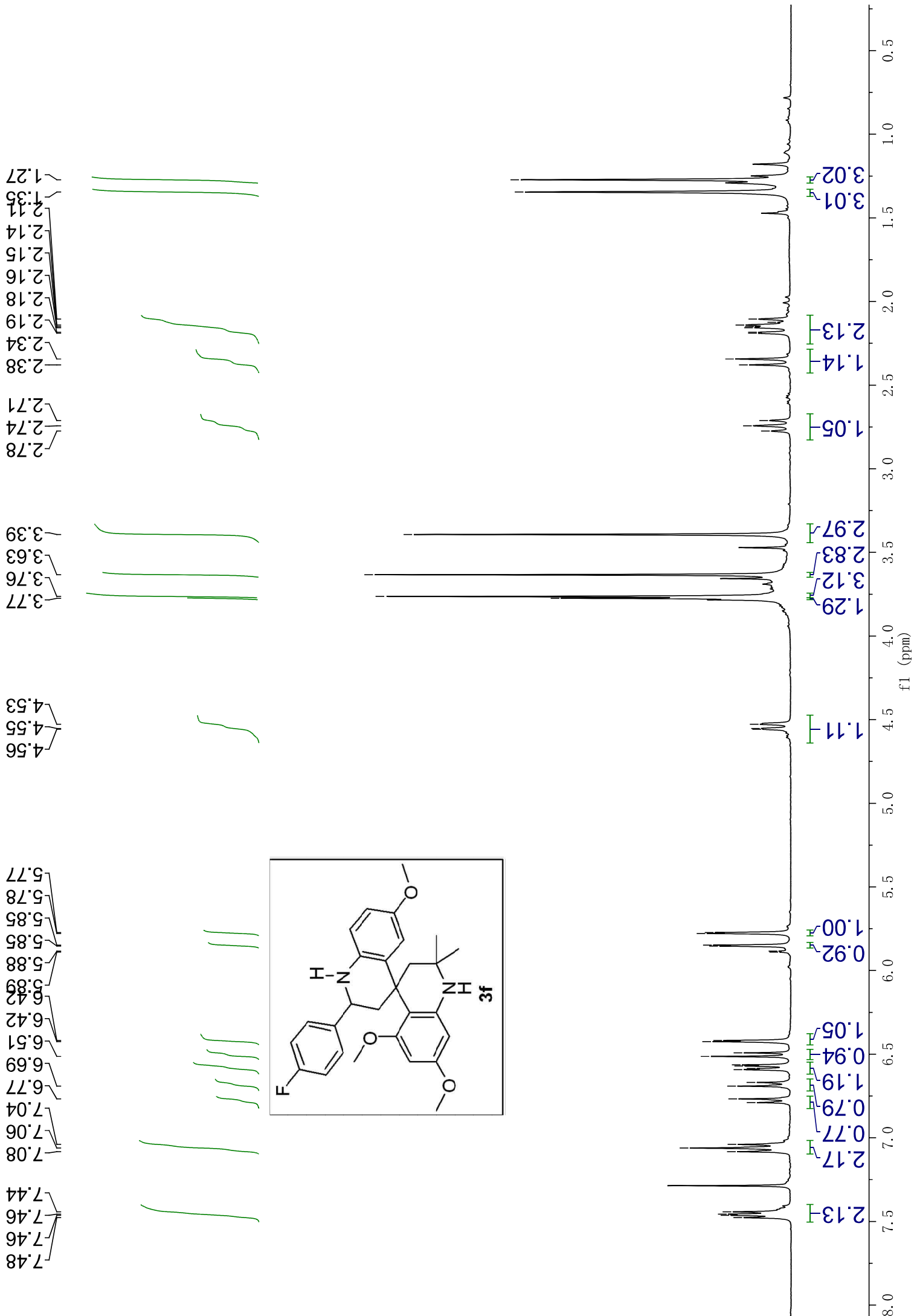
91.07
92.64

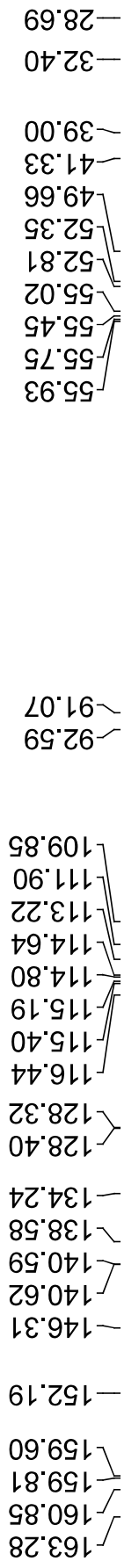
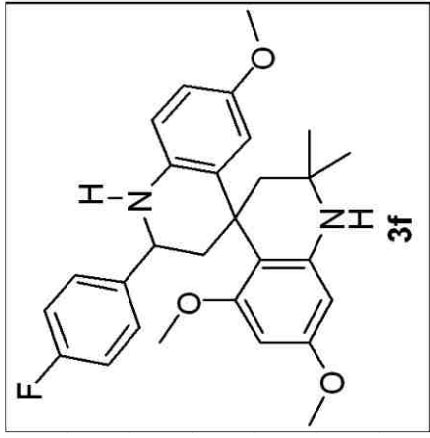
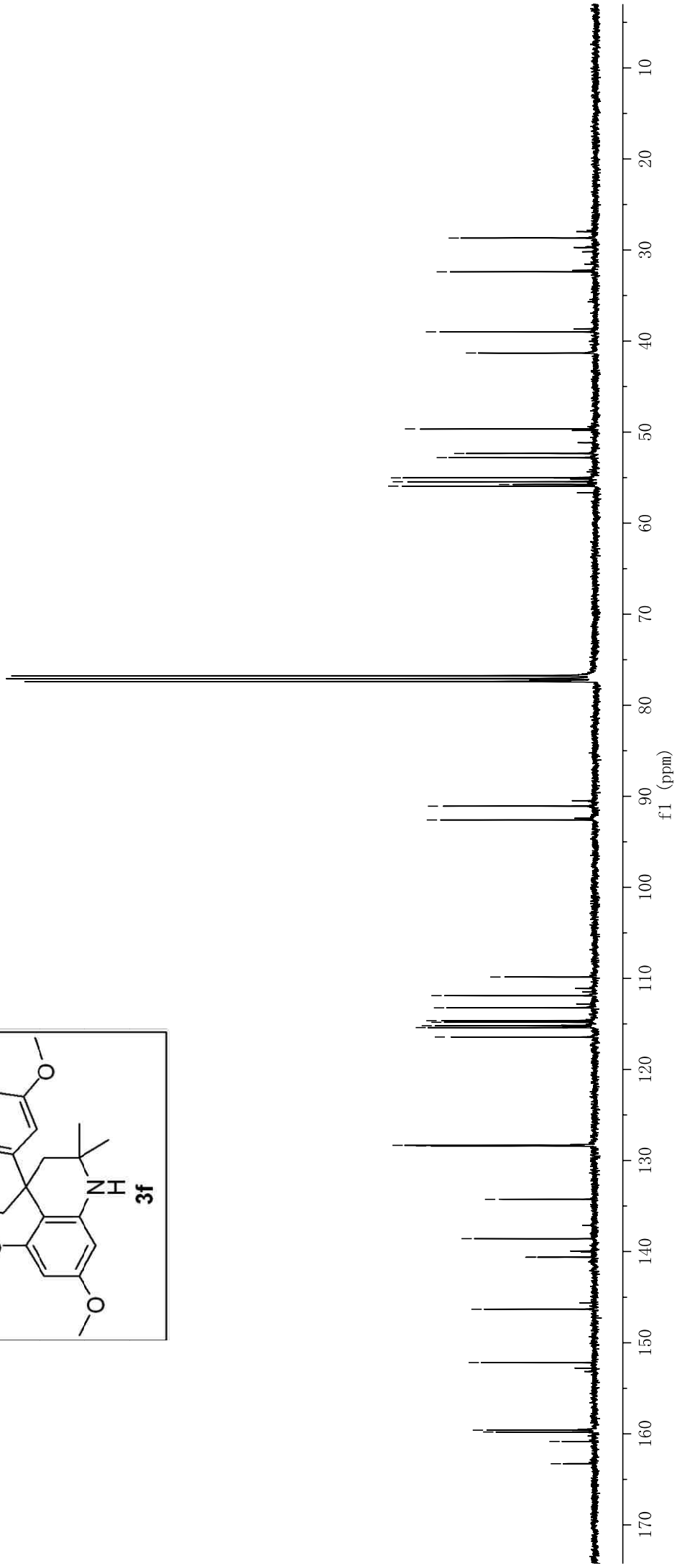
109.52
111.97
113.20
114.79
125.44
125.48
125.52
127.17
129.07
129.39
129.71
134.22
138.23
146.32
149.08
152.35
159.68
159.80

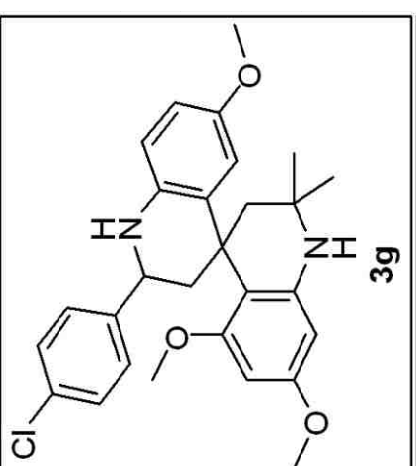
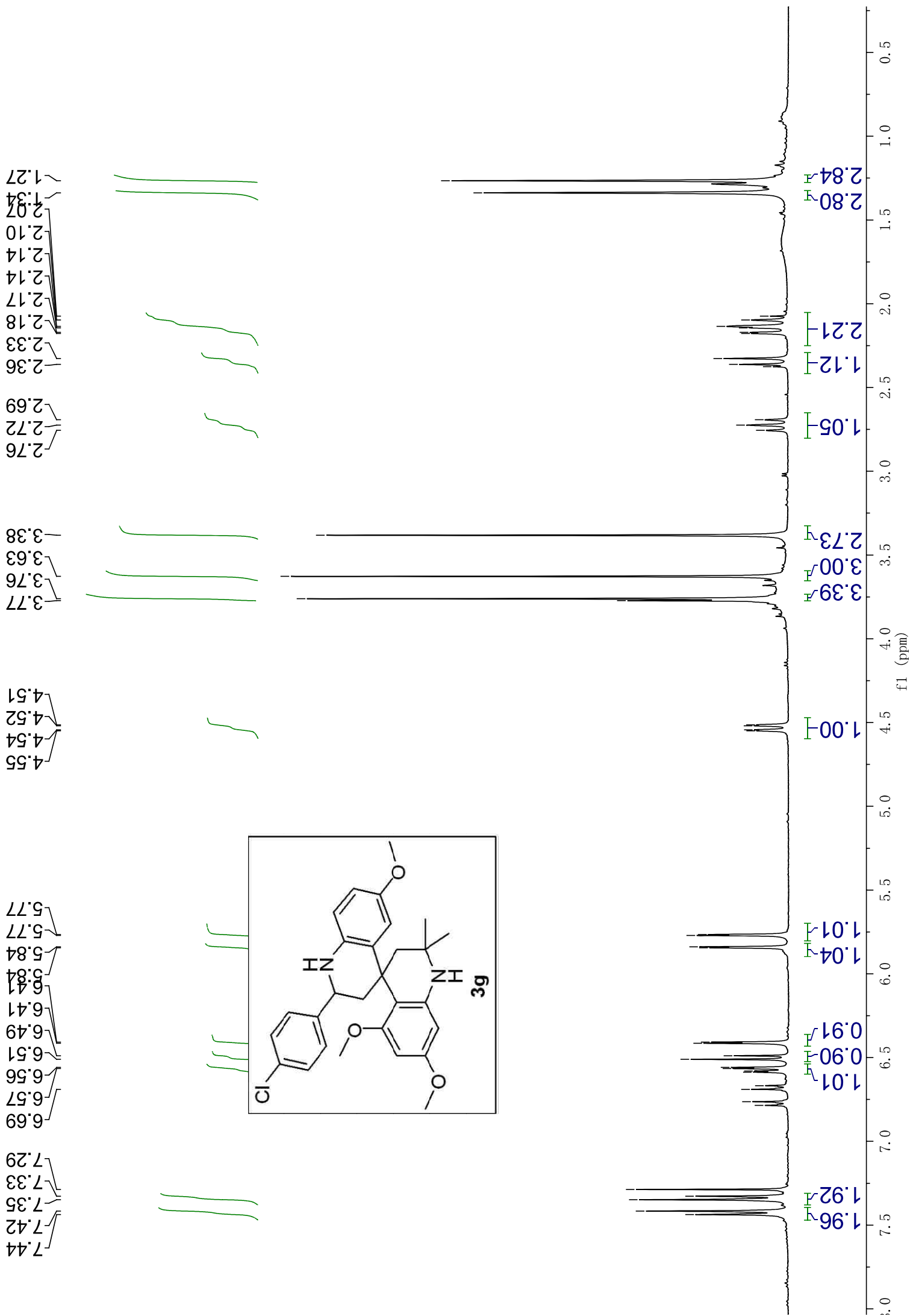


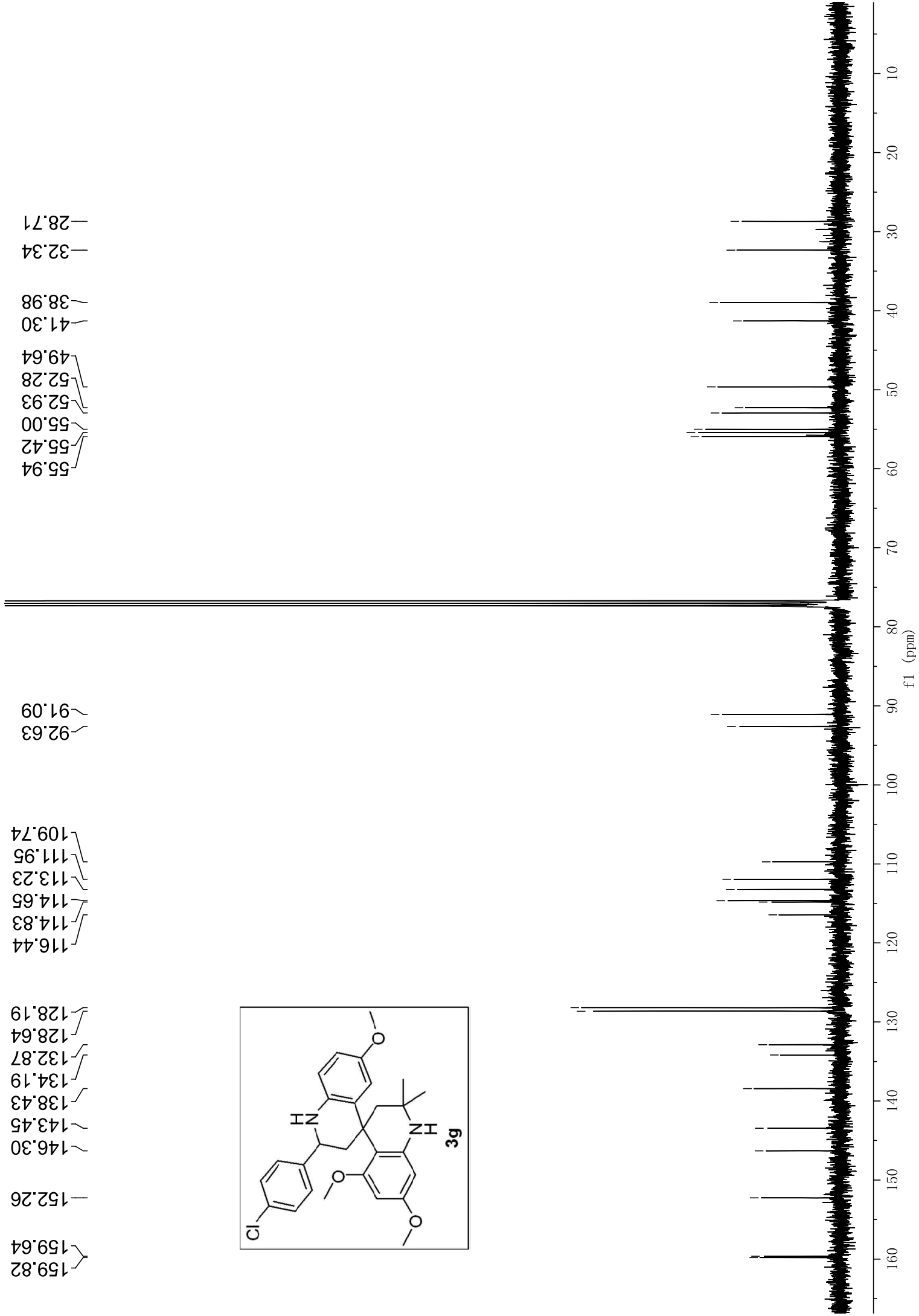


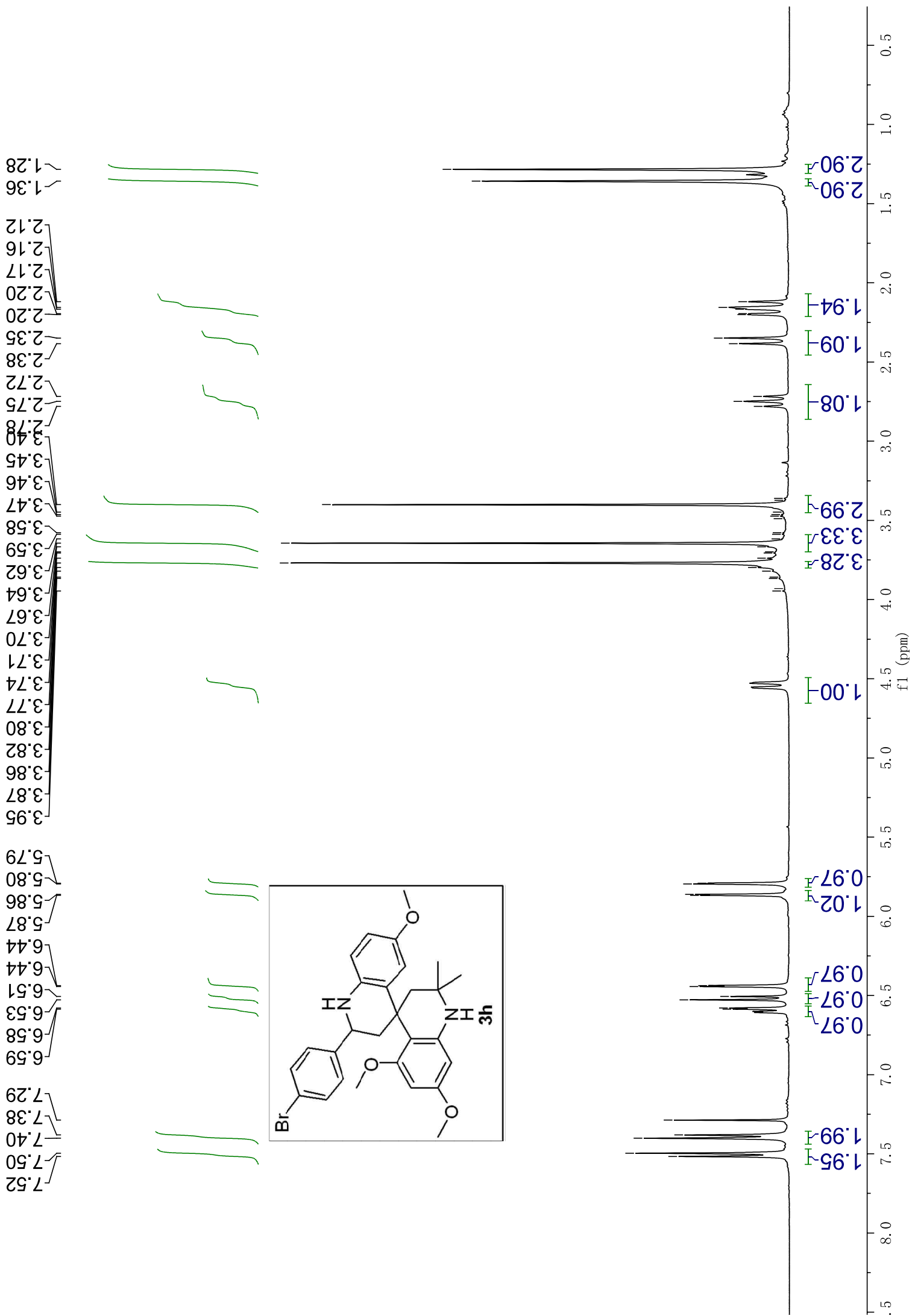


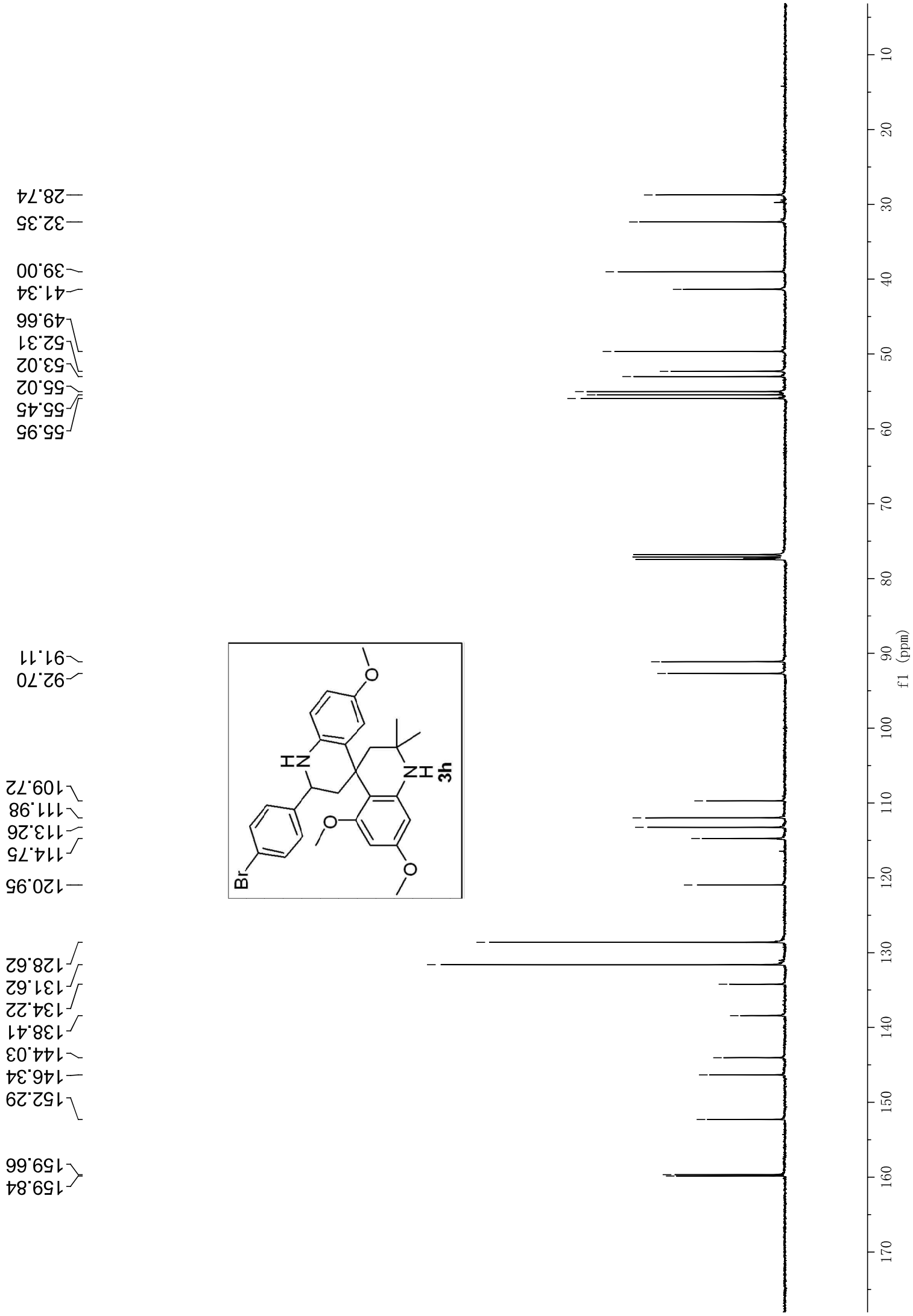


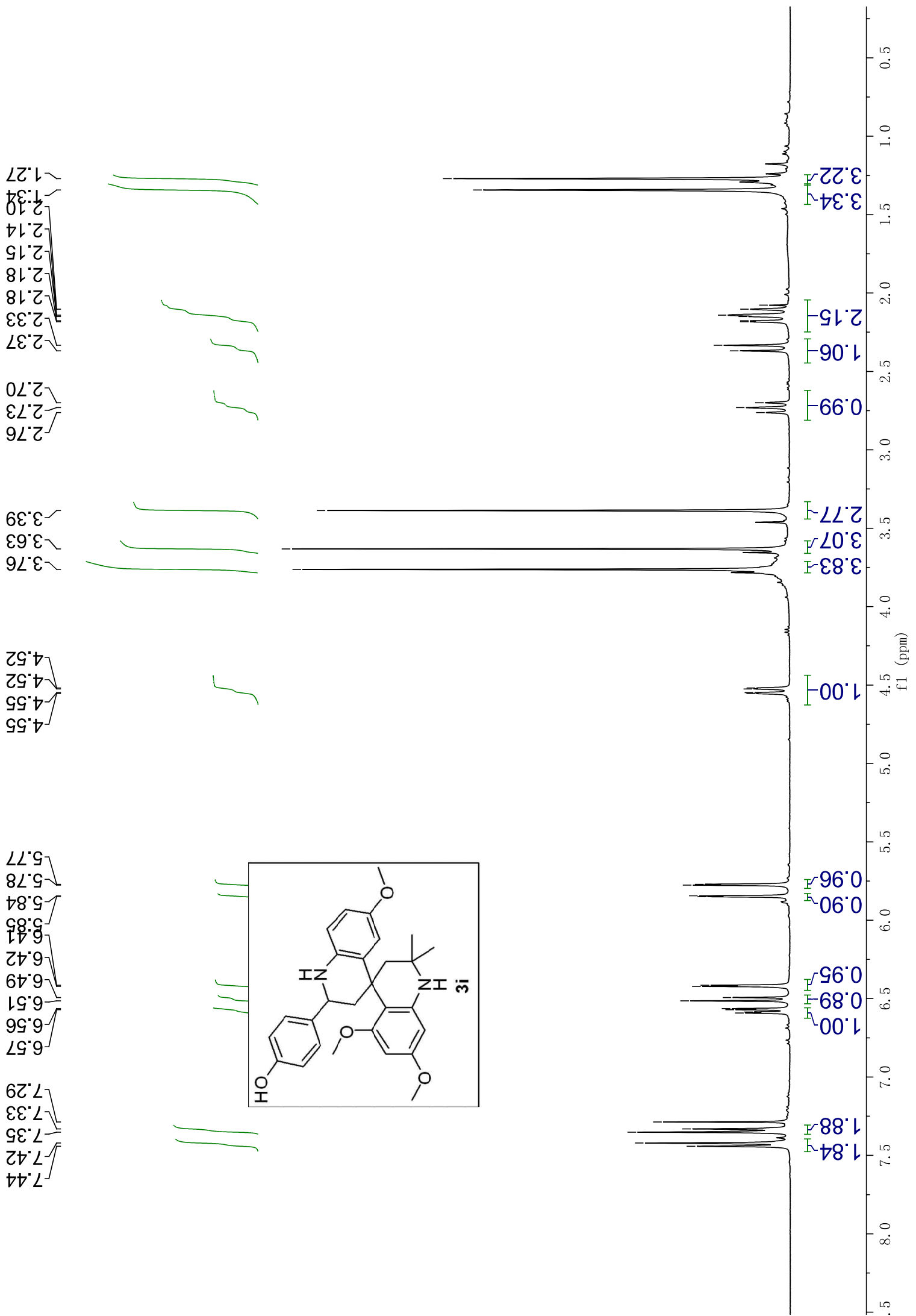


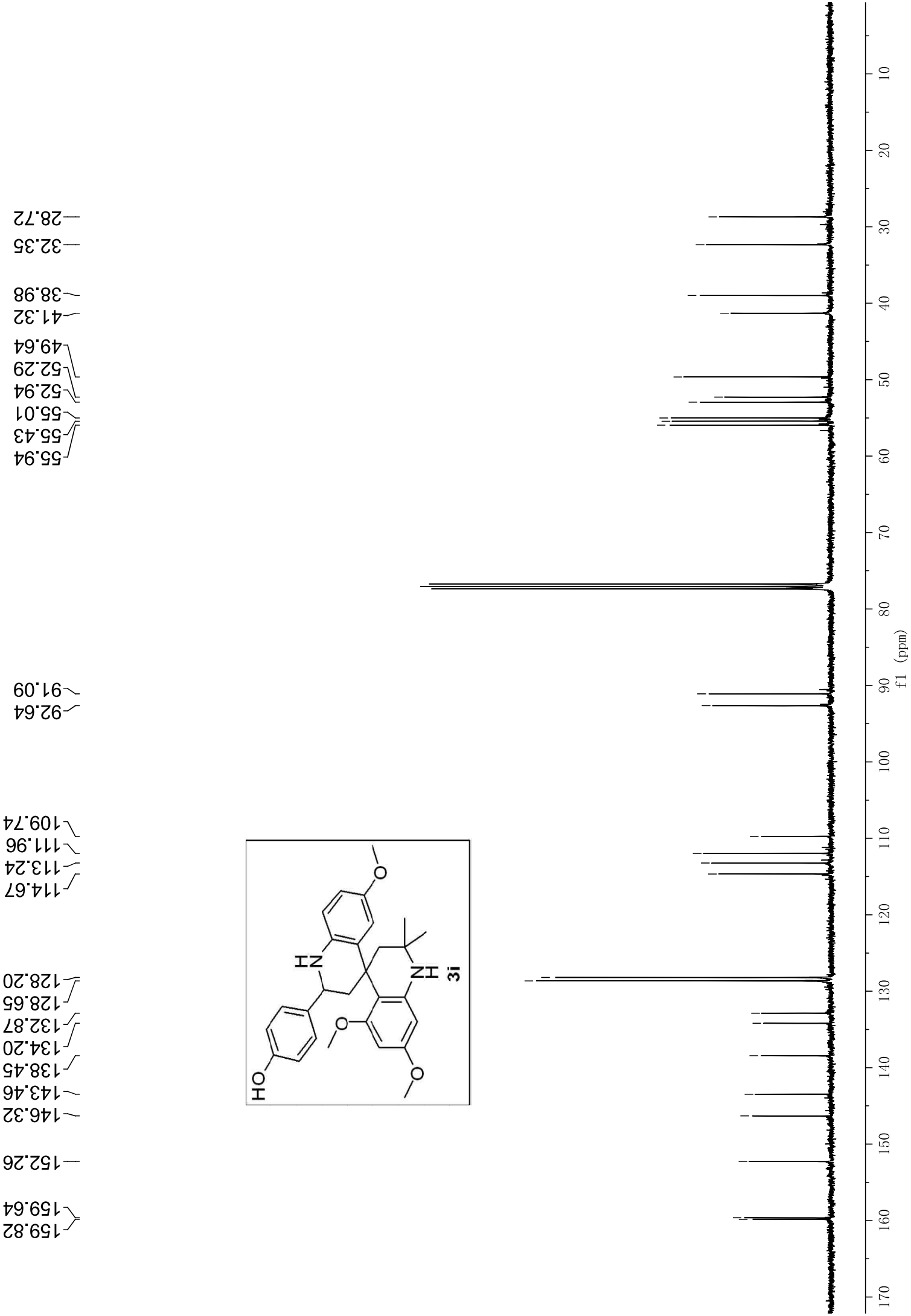


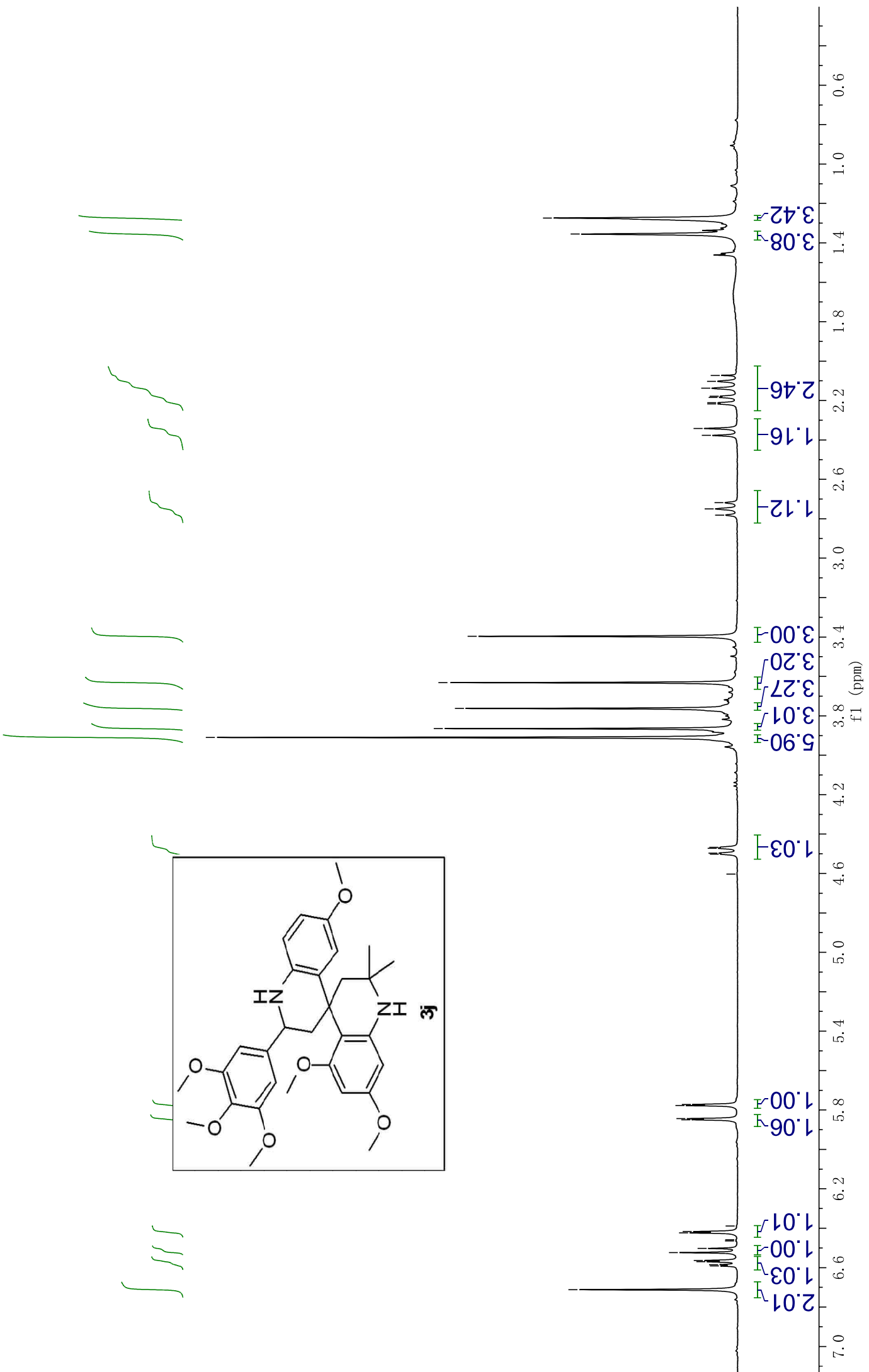












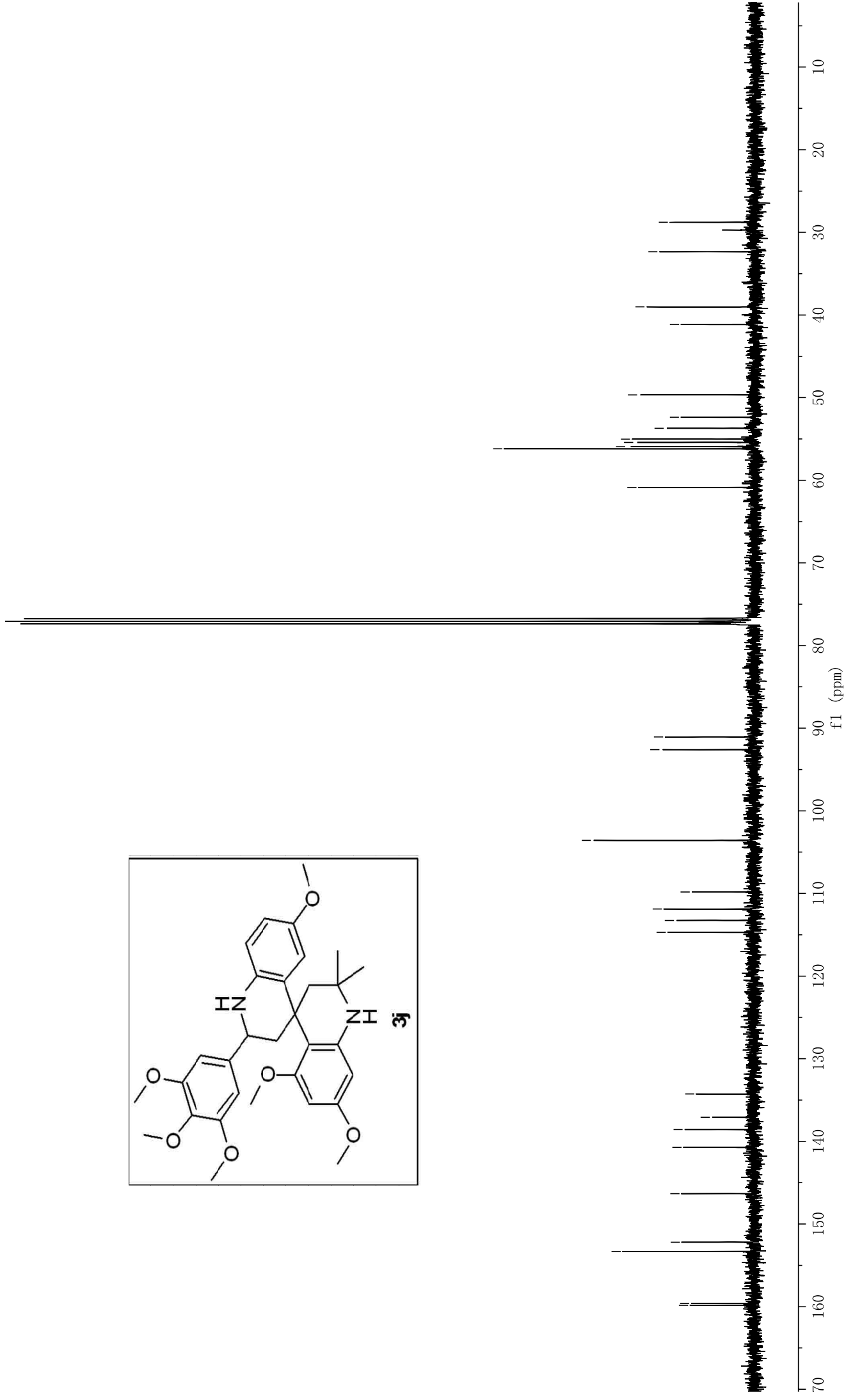
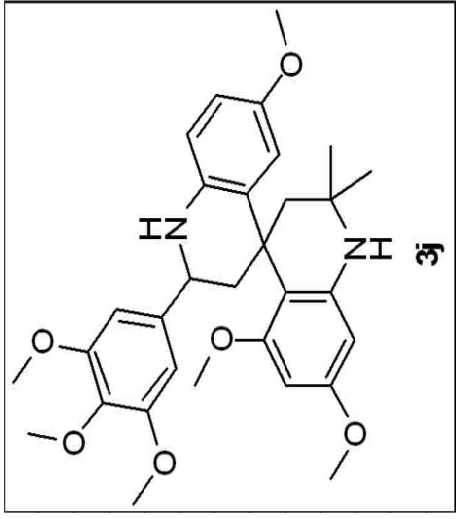
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 56.20
 55.94
 55.42
 55.02
 53.71
 52.38
 49.67
 41.15
 39.02
 32.35
 28.79

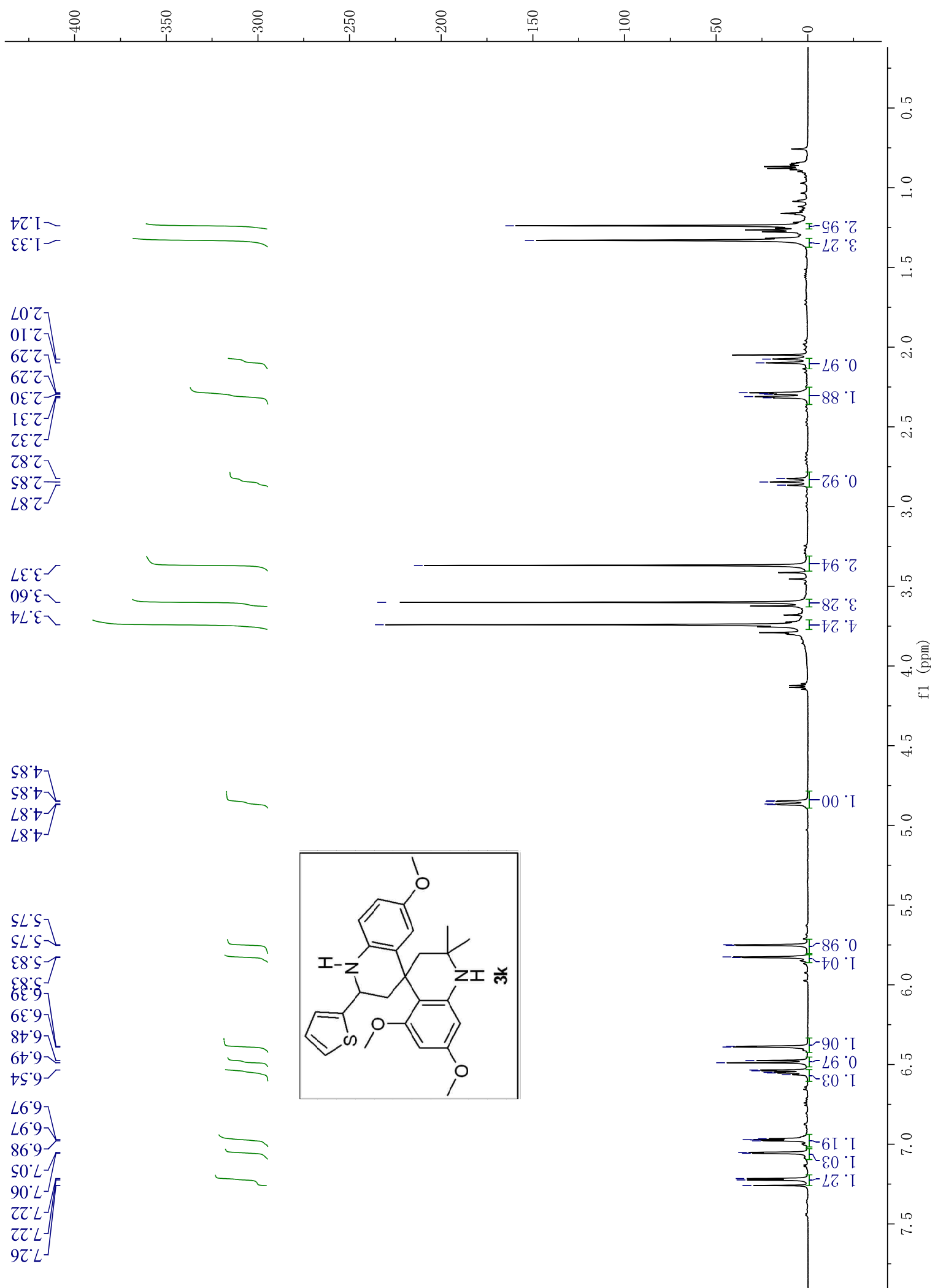
92.60
 91.06

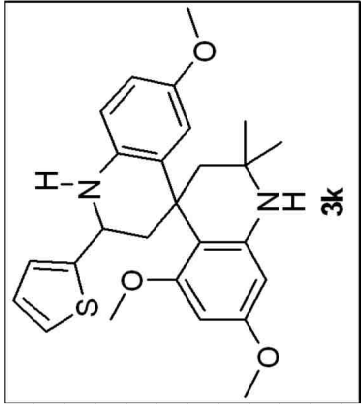
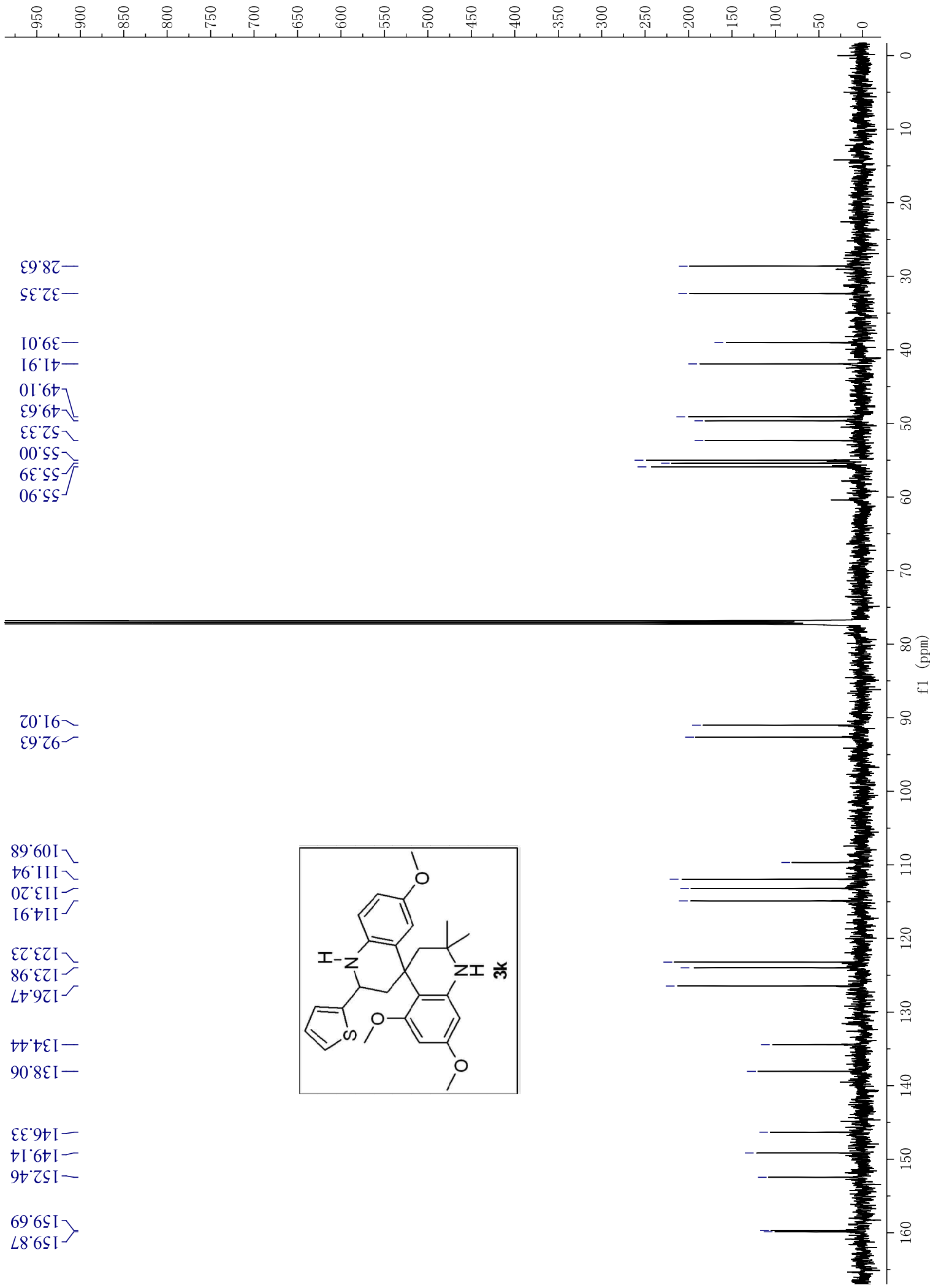
103.59
 109.82
 111.89
 113.26
 114.71

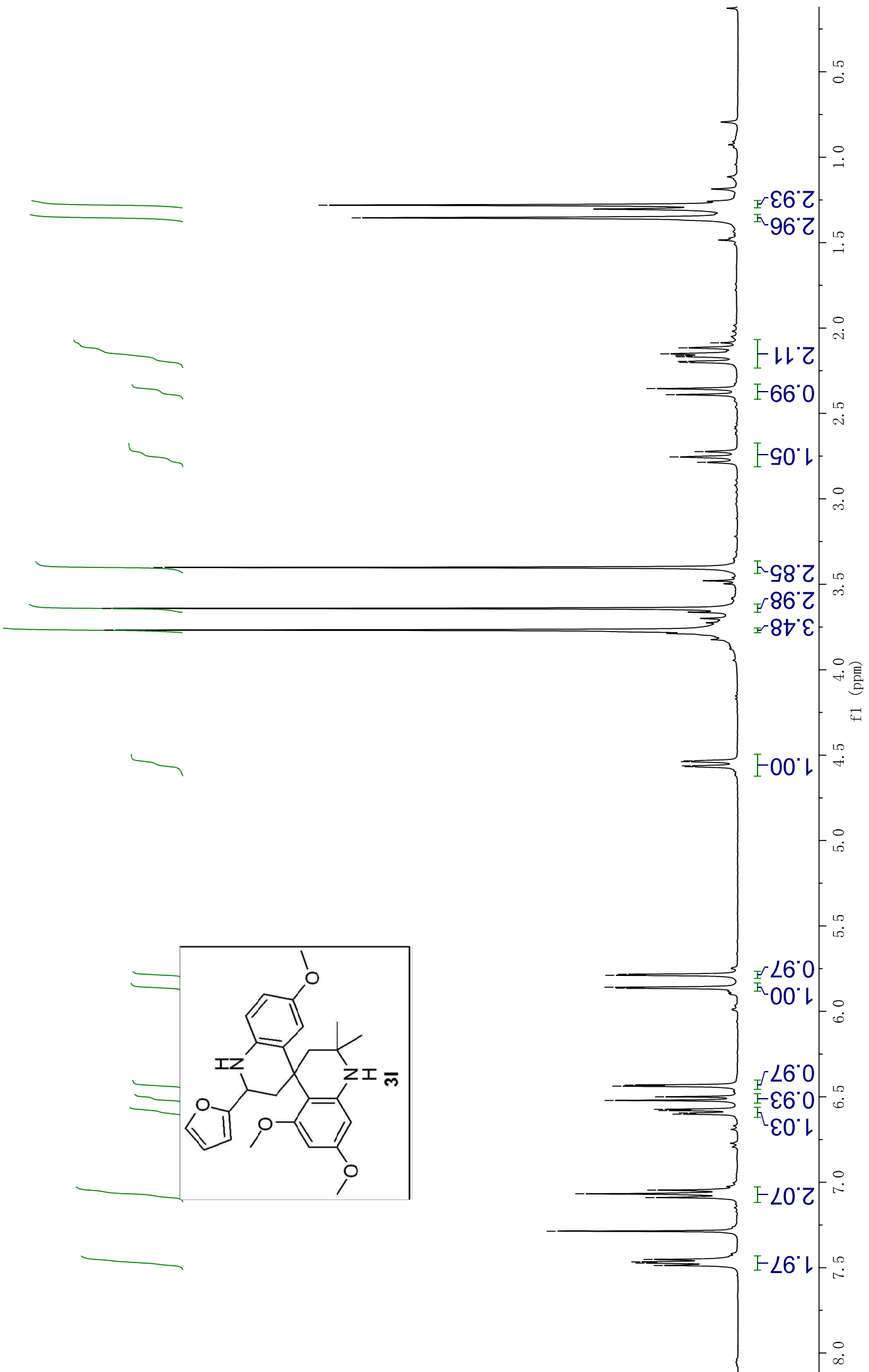
146.33
 140.72
 138.58
 137.09
 134.27

159.83
 159.61
 153.32
 152.20



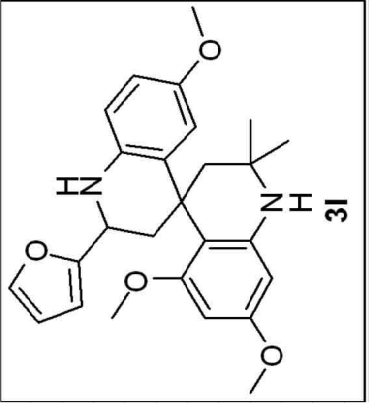
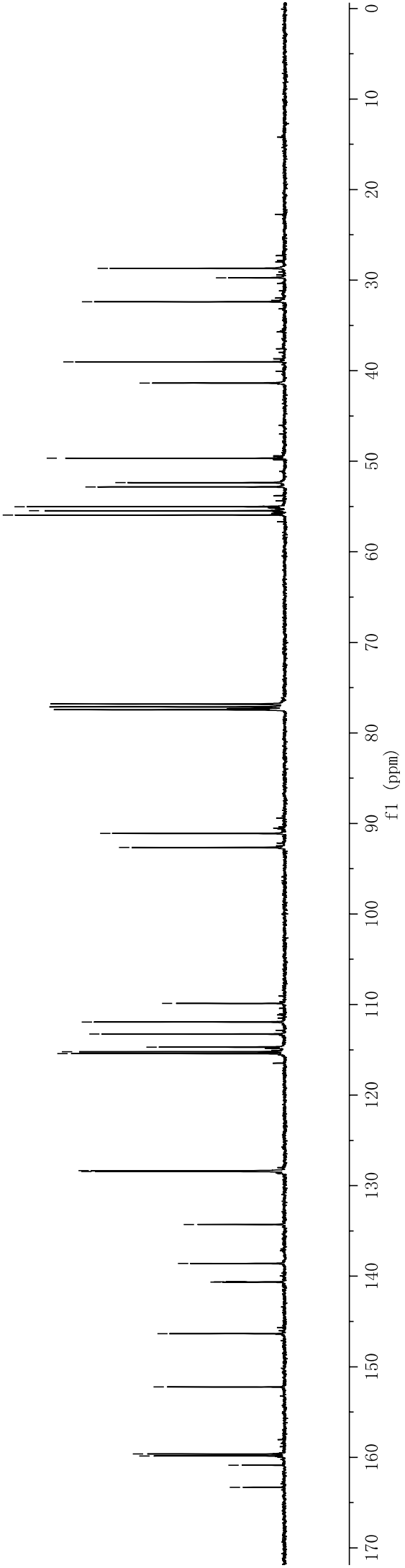




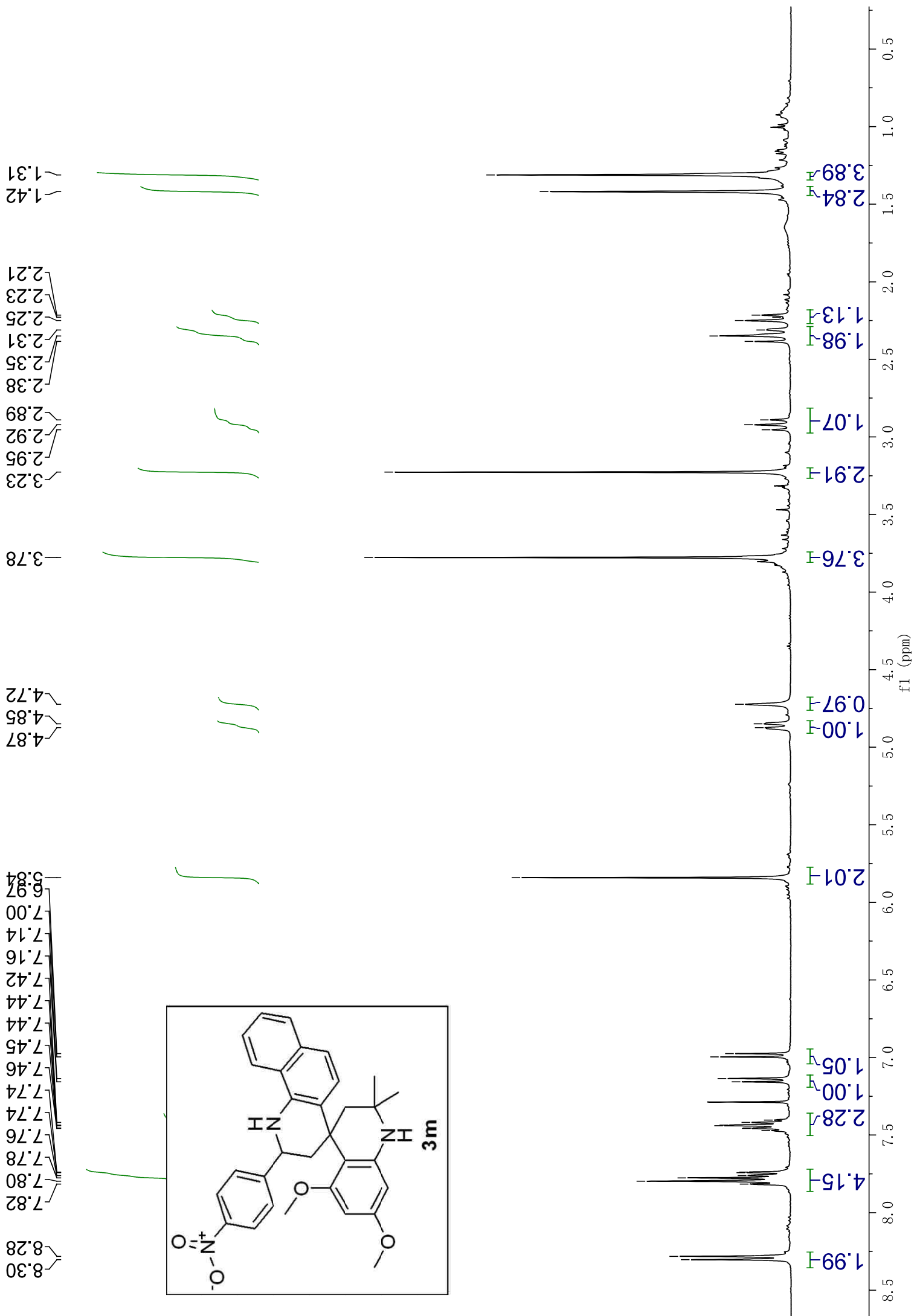


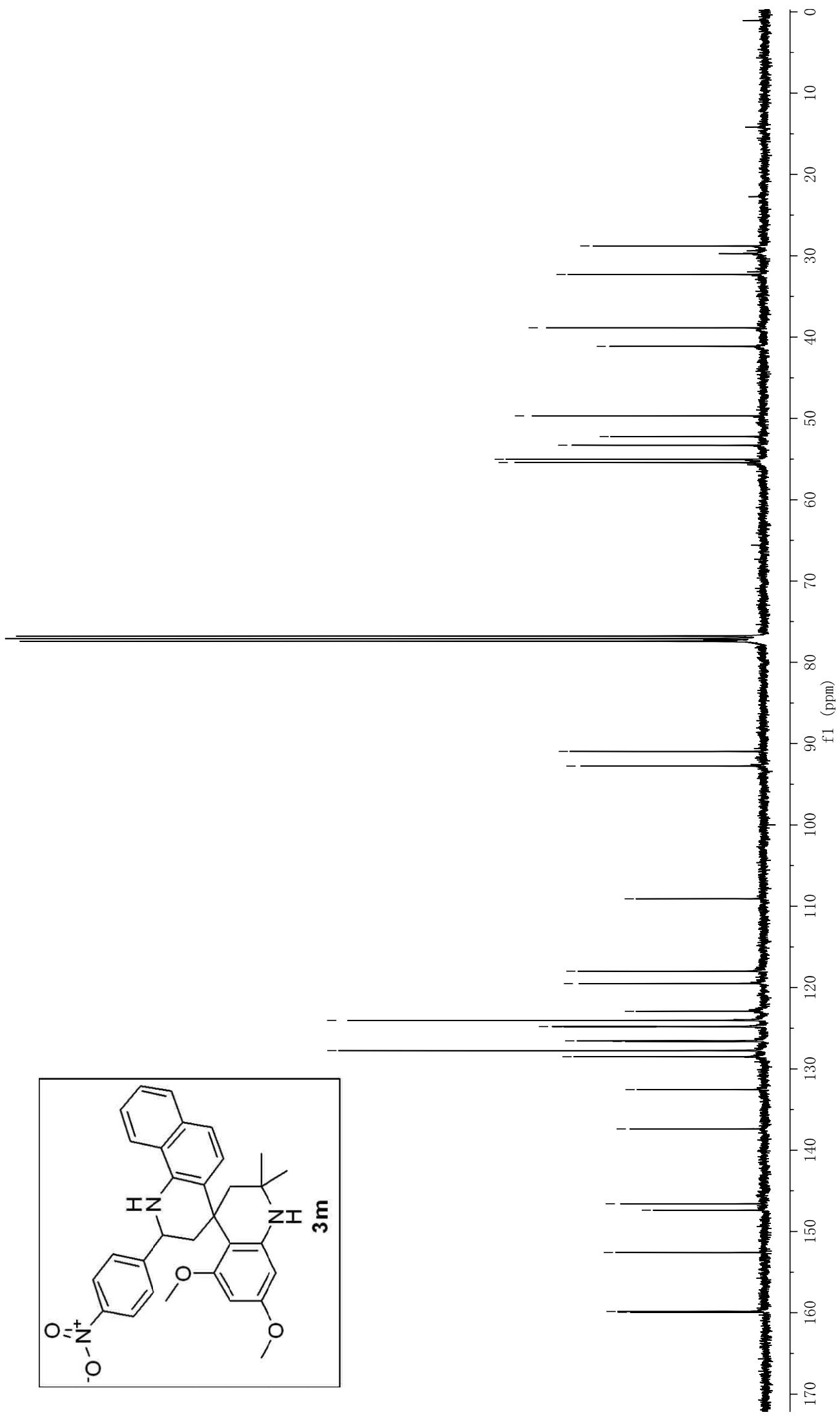
Peak list (ppm):

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163.31
160.87
159.84
159.63
152.23
146.35
140.66
140.63
138.60
134.28
128.43
128.35
115.42
115.21
114.69
113.26
111.93
109.88
92.65
91.11
55.94
55.46
55.02
52.83
52.37
49.67
41.37
39.03
32.39
29.75
28.70



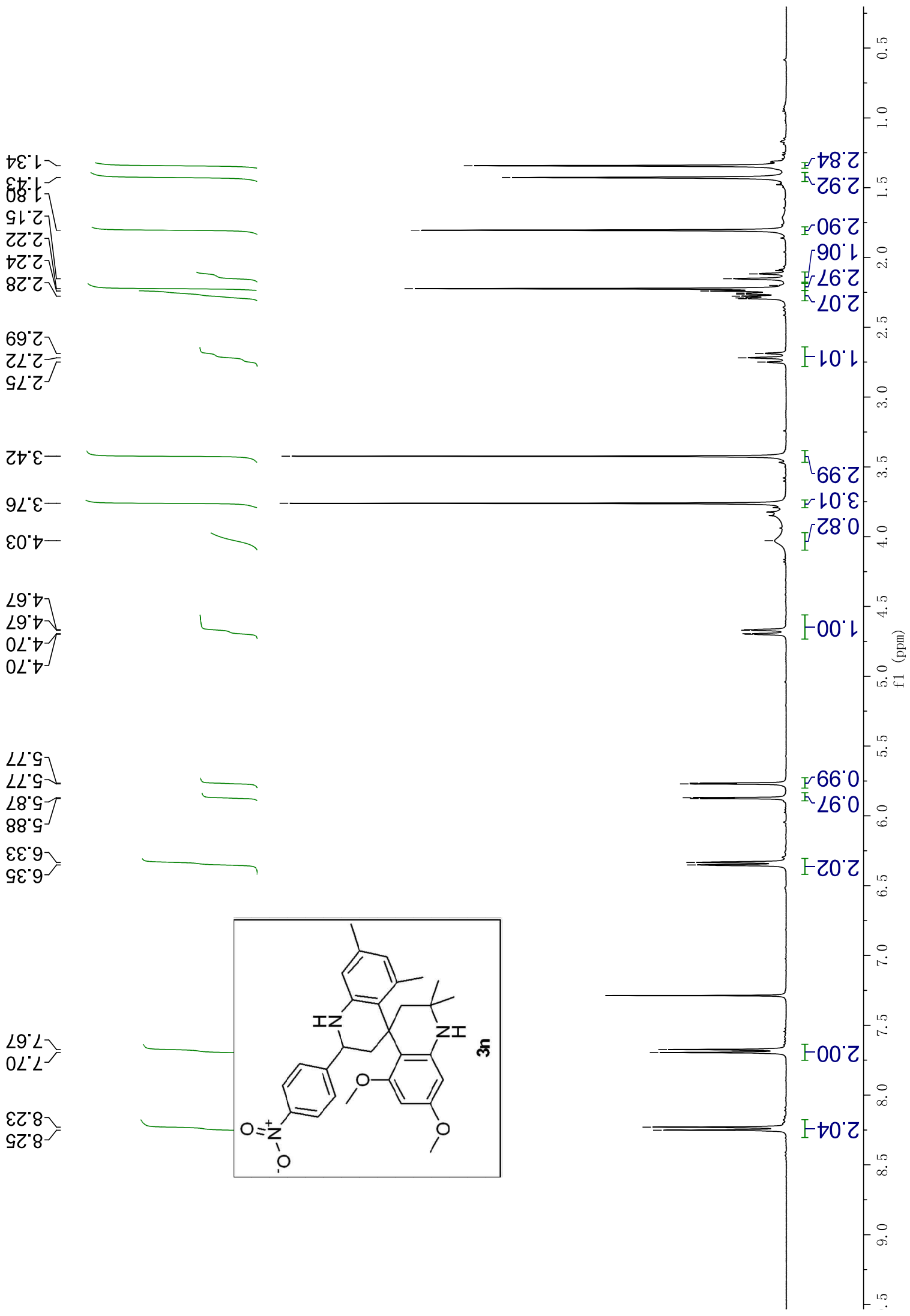


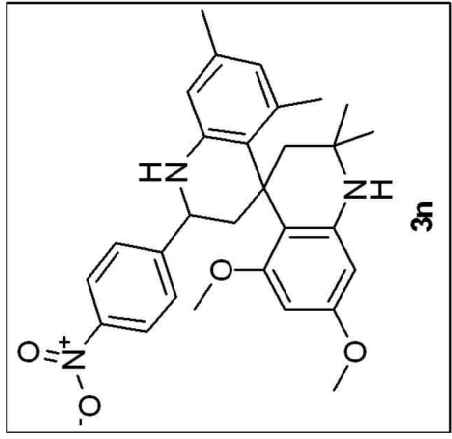
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55.03
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52.23
49.68
41.13
38.86
32.30
28.79

92.75
90.96

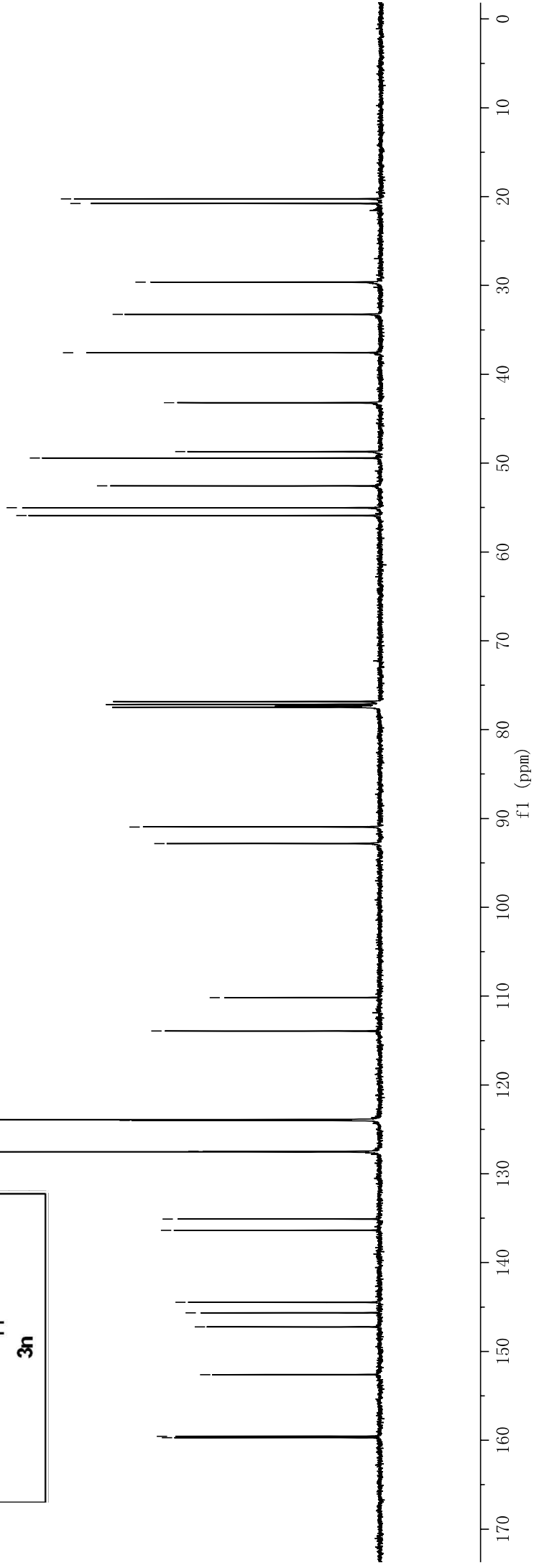
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124.79
124.82
126.55
126.64
127.76
128.51
137.39

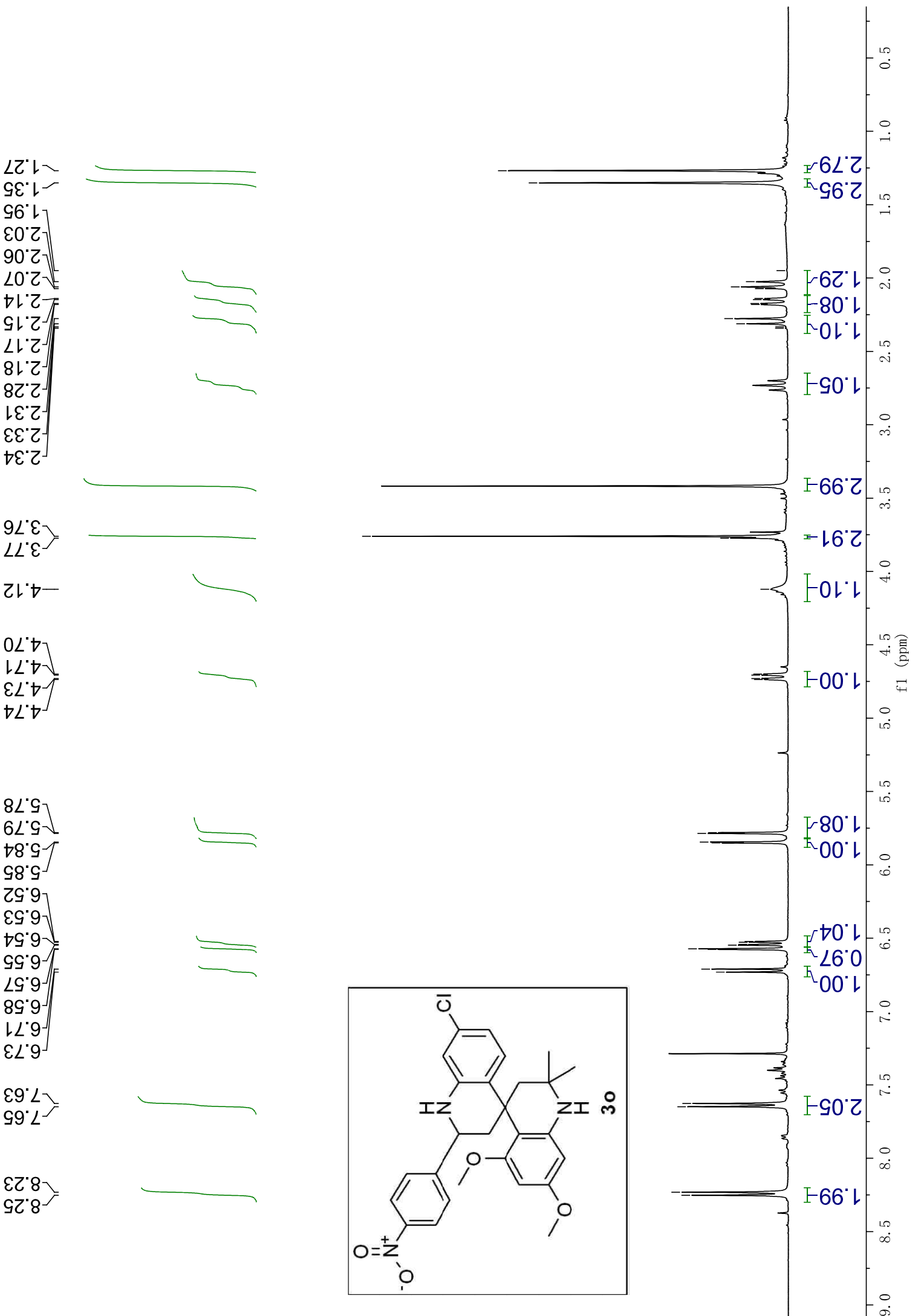
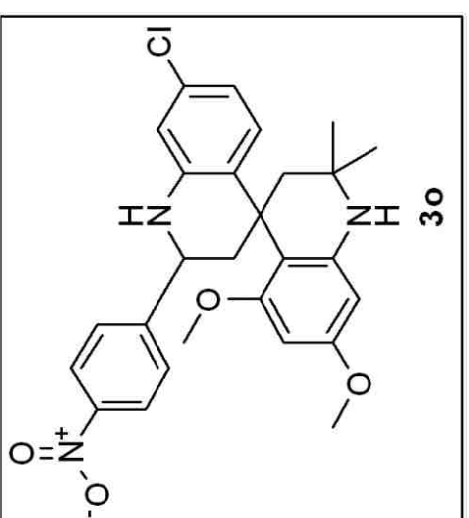
146.60
147.39
152.60
159.84
159.94

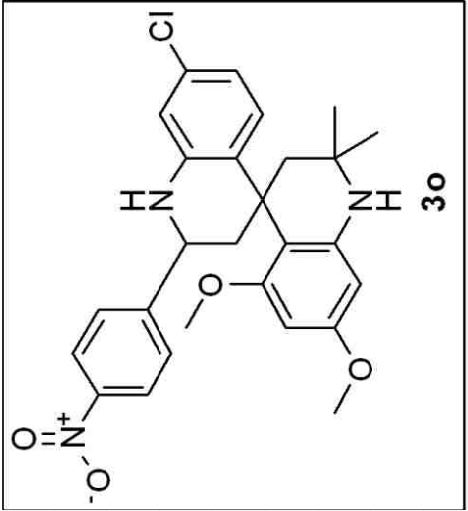
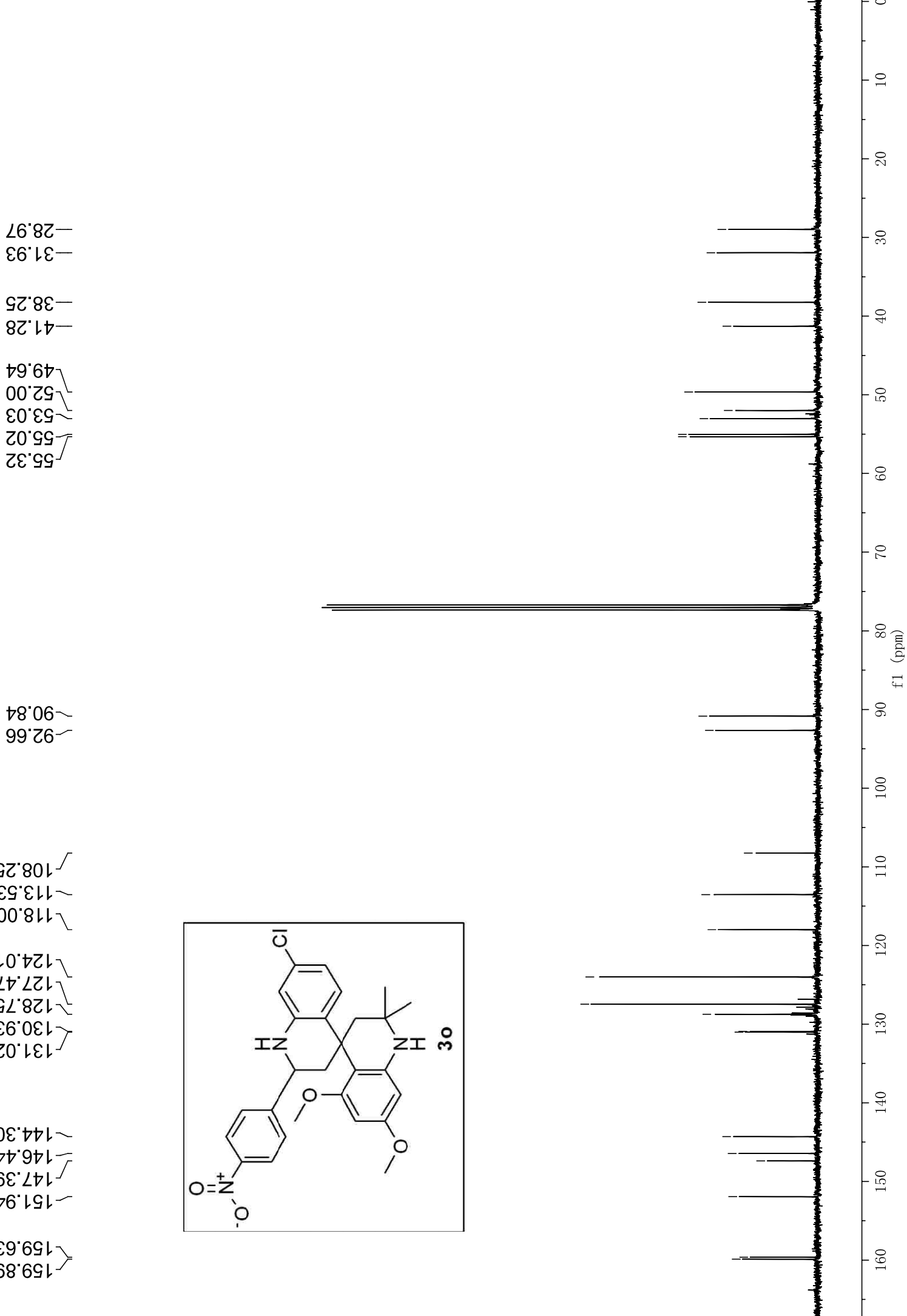


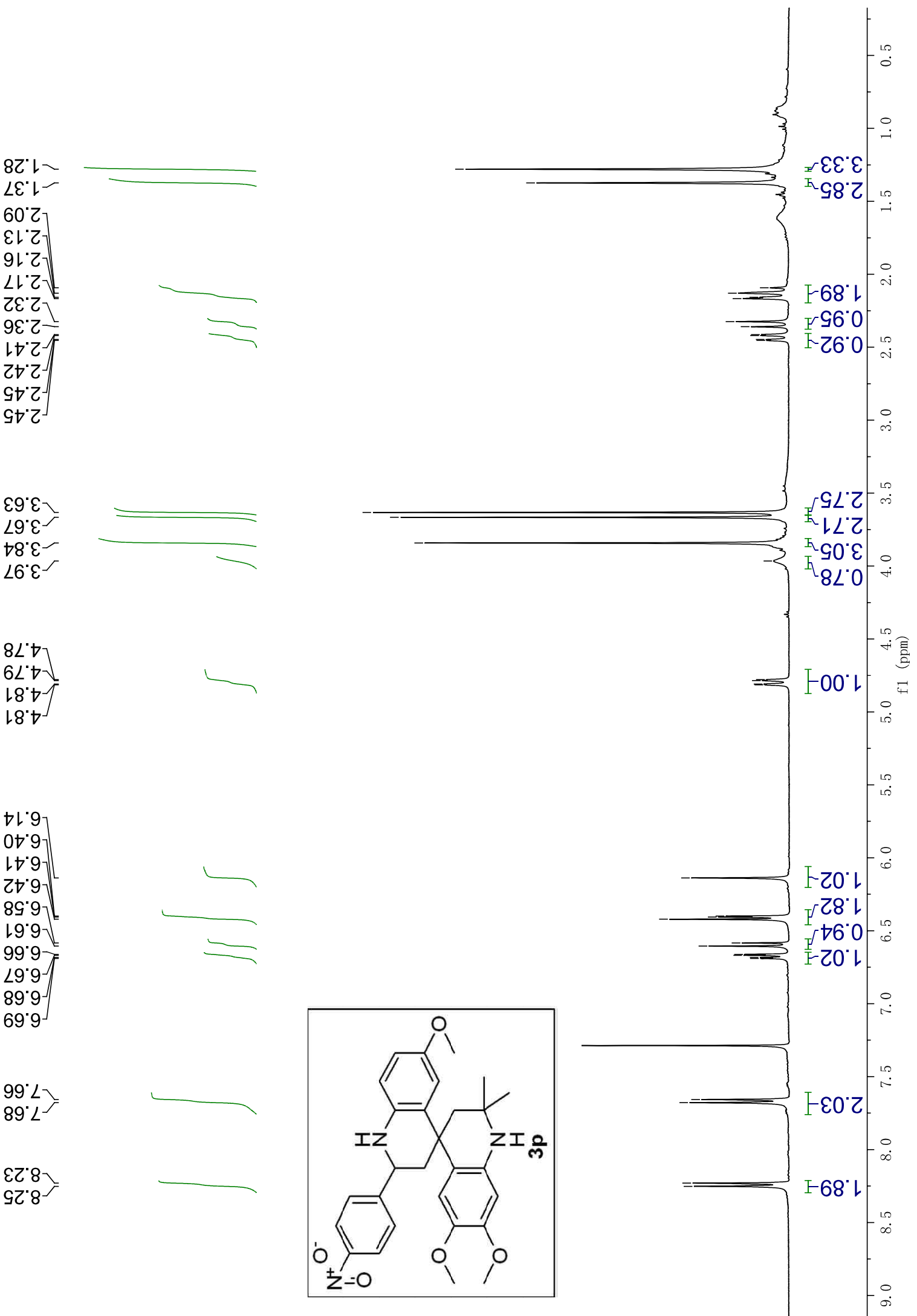
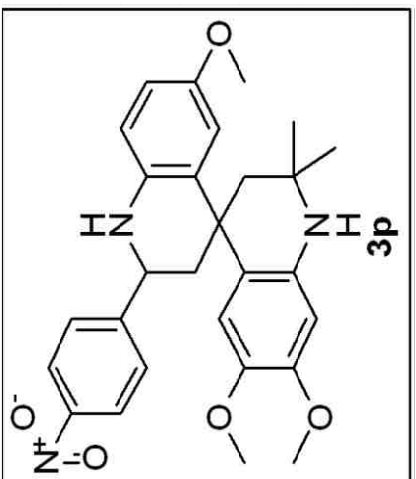


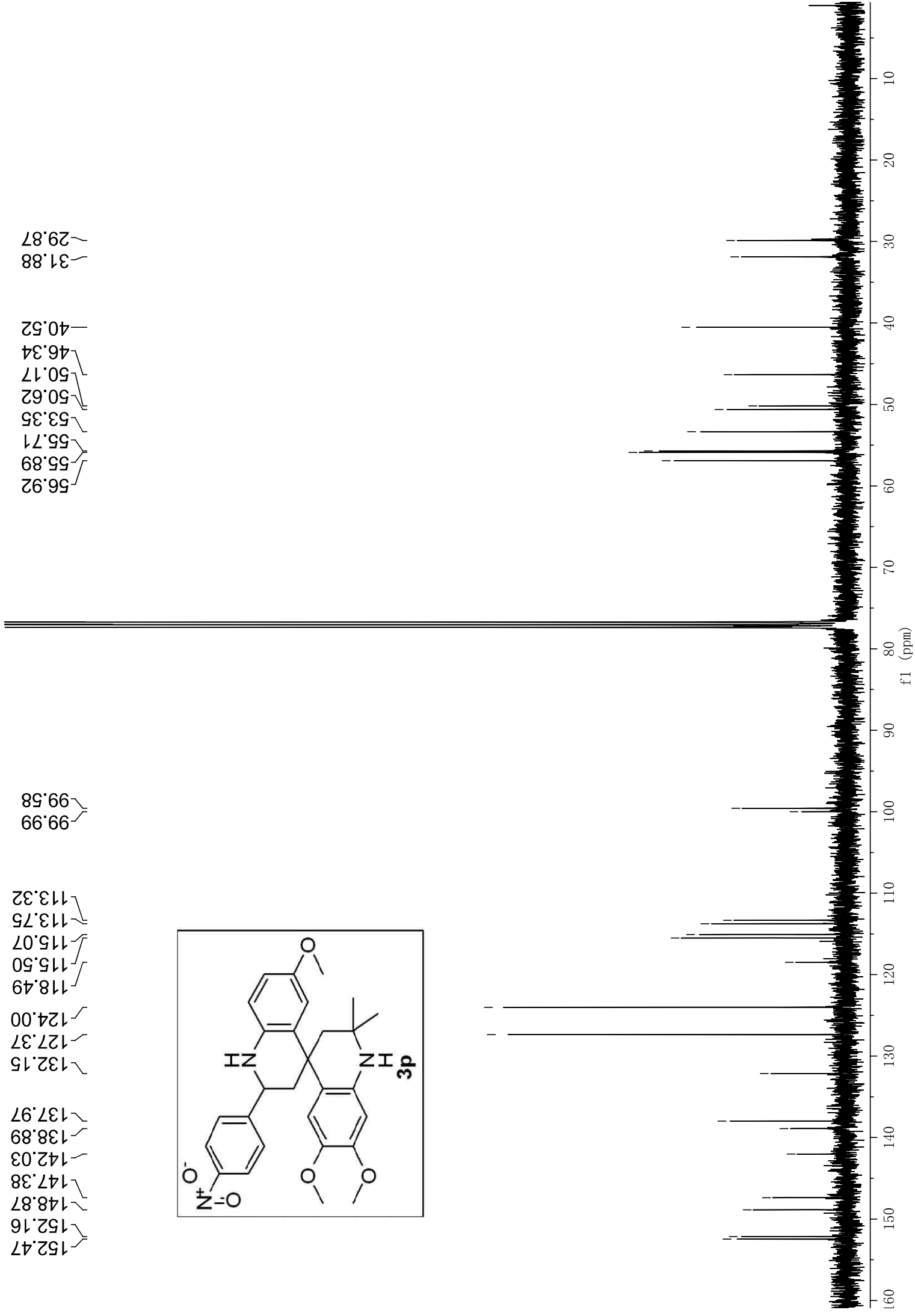
δ 159.71, 159.55, 152.61, 147.24, 145.65, 144.47, 136.36, 135.09, 127.53, 127.47, 124.00, 123.90, 113.93, 110.16, 92.83, 90.96, 55.90, 55.03, 52.56, 49.43, 48.71, 43.20, 37.57, 33.25, 29.63, 20.77, 20.25

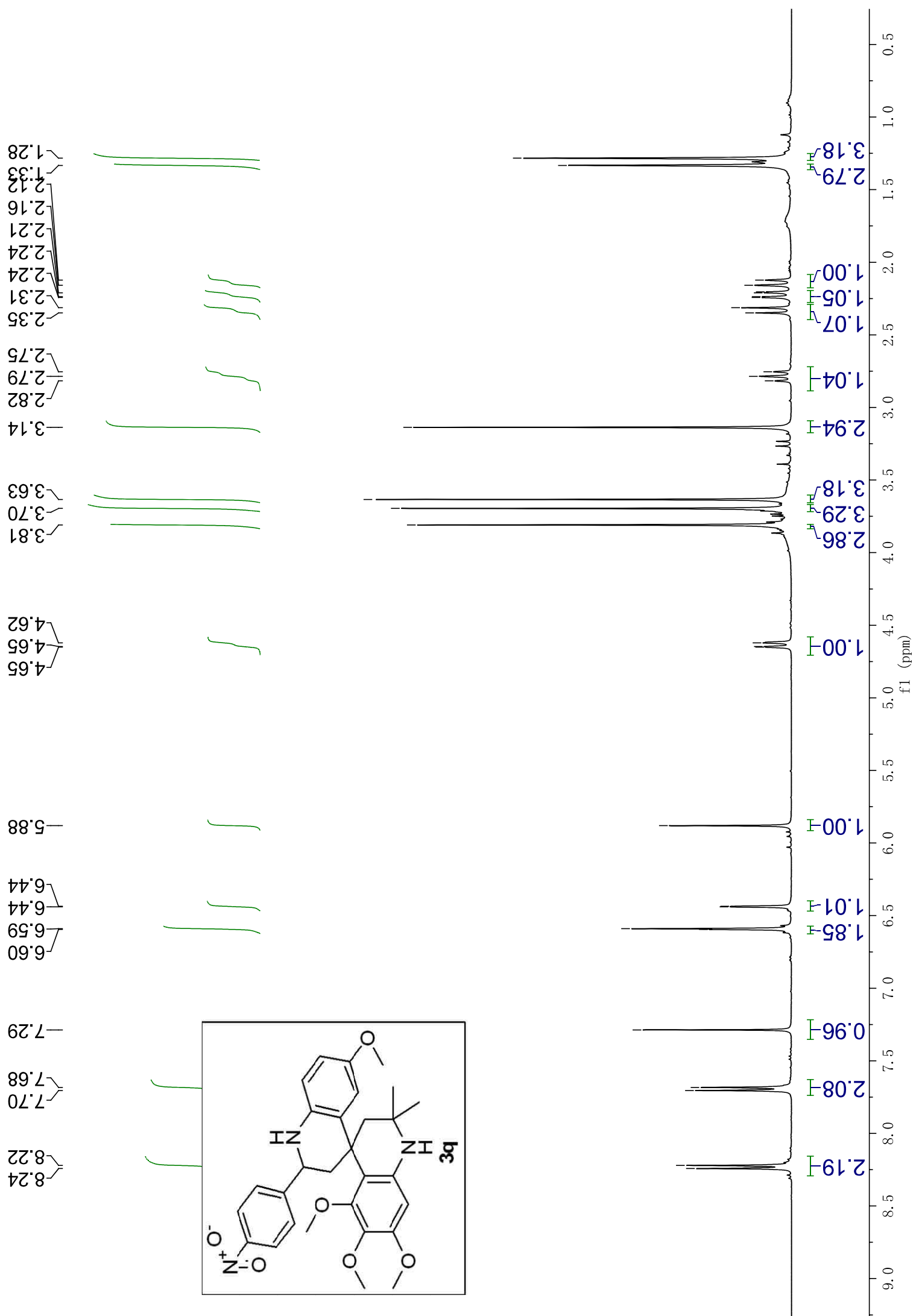




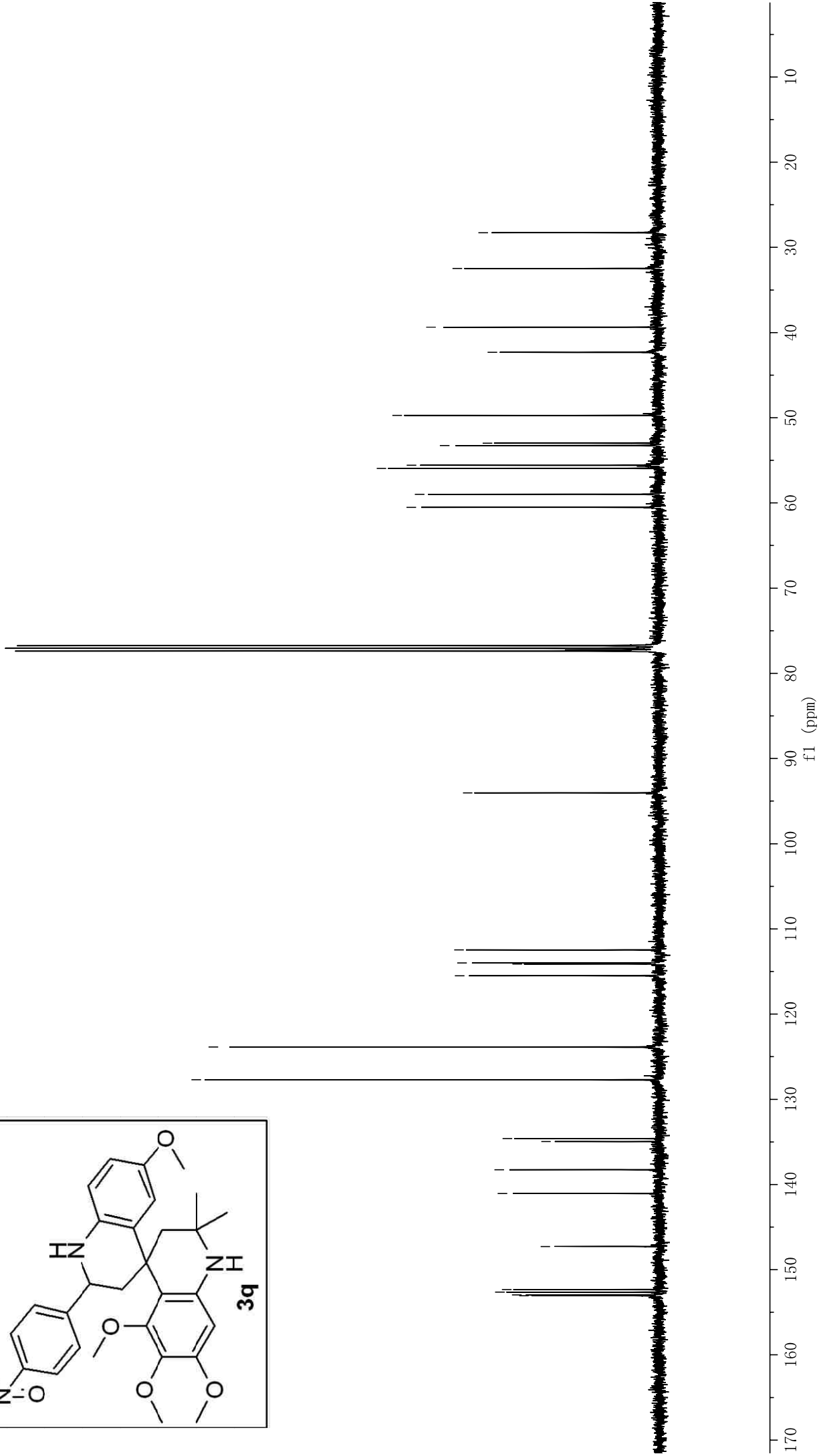
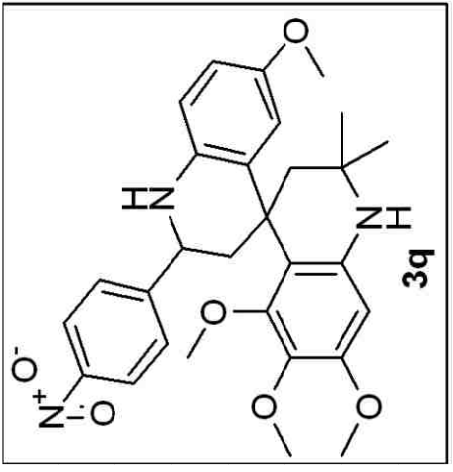


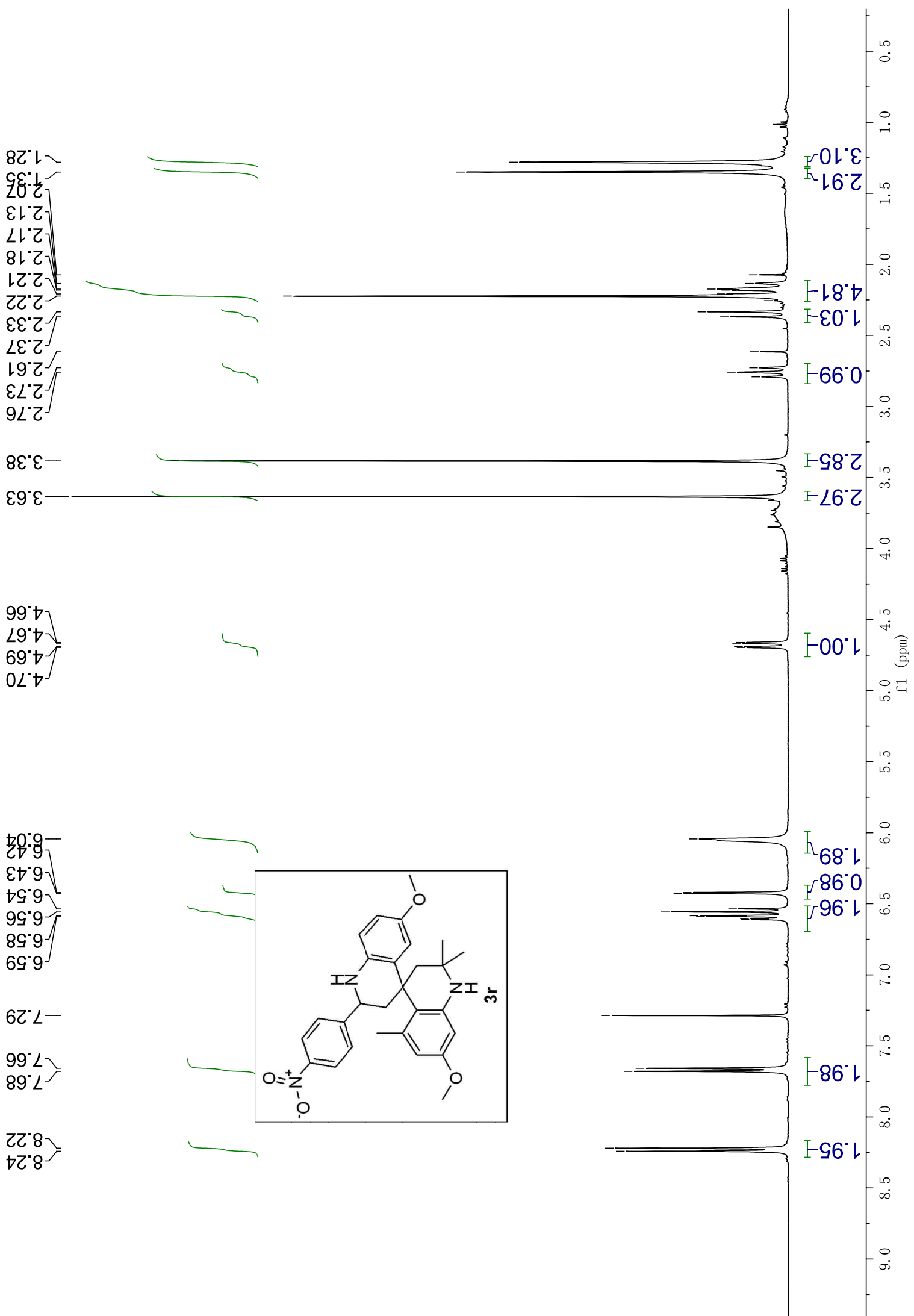


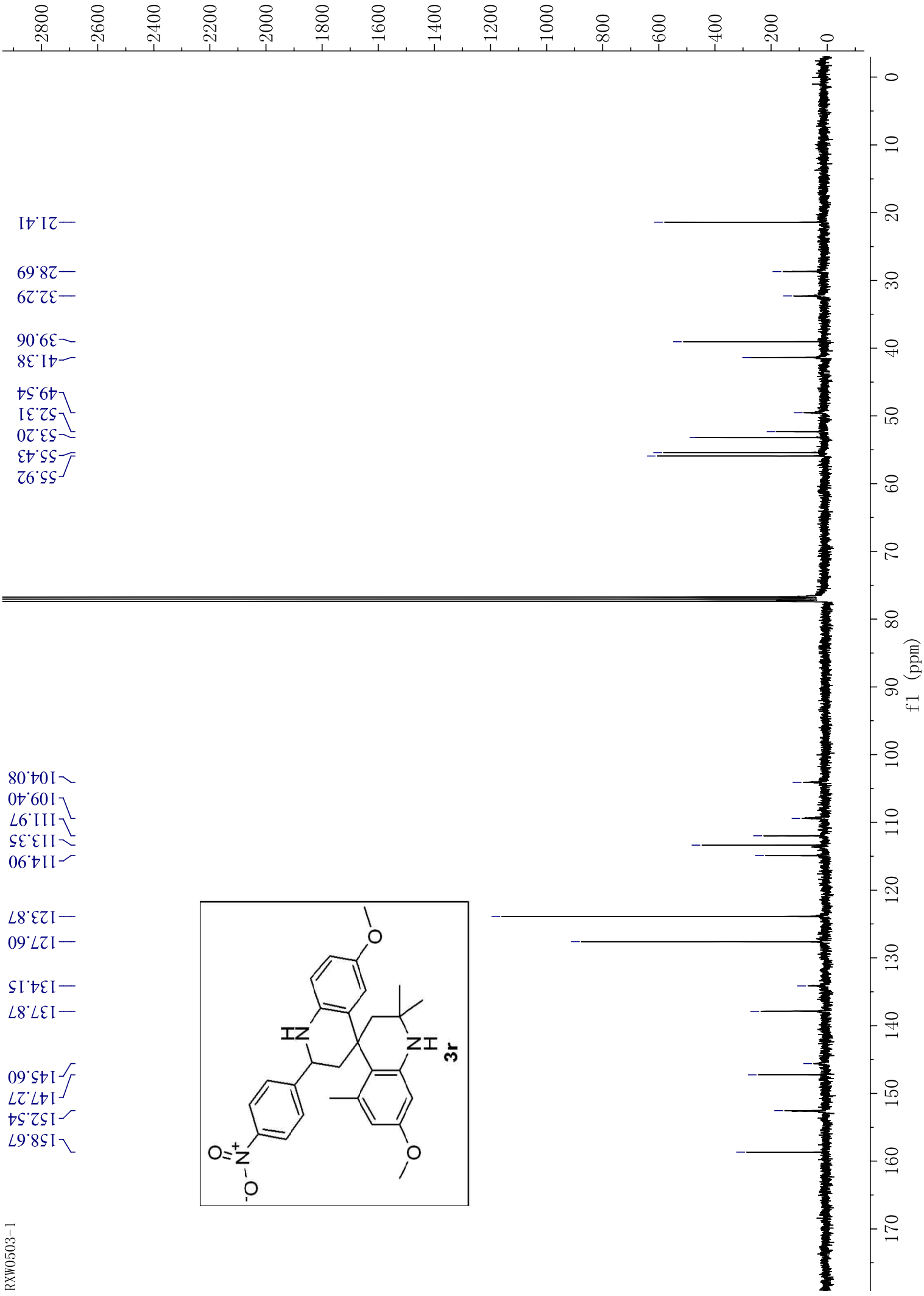


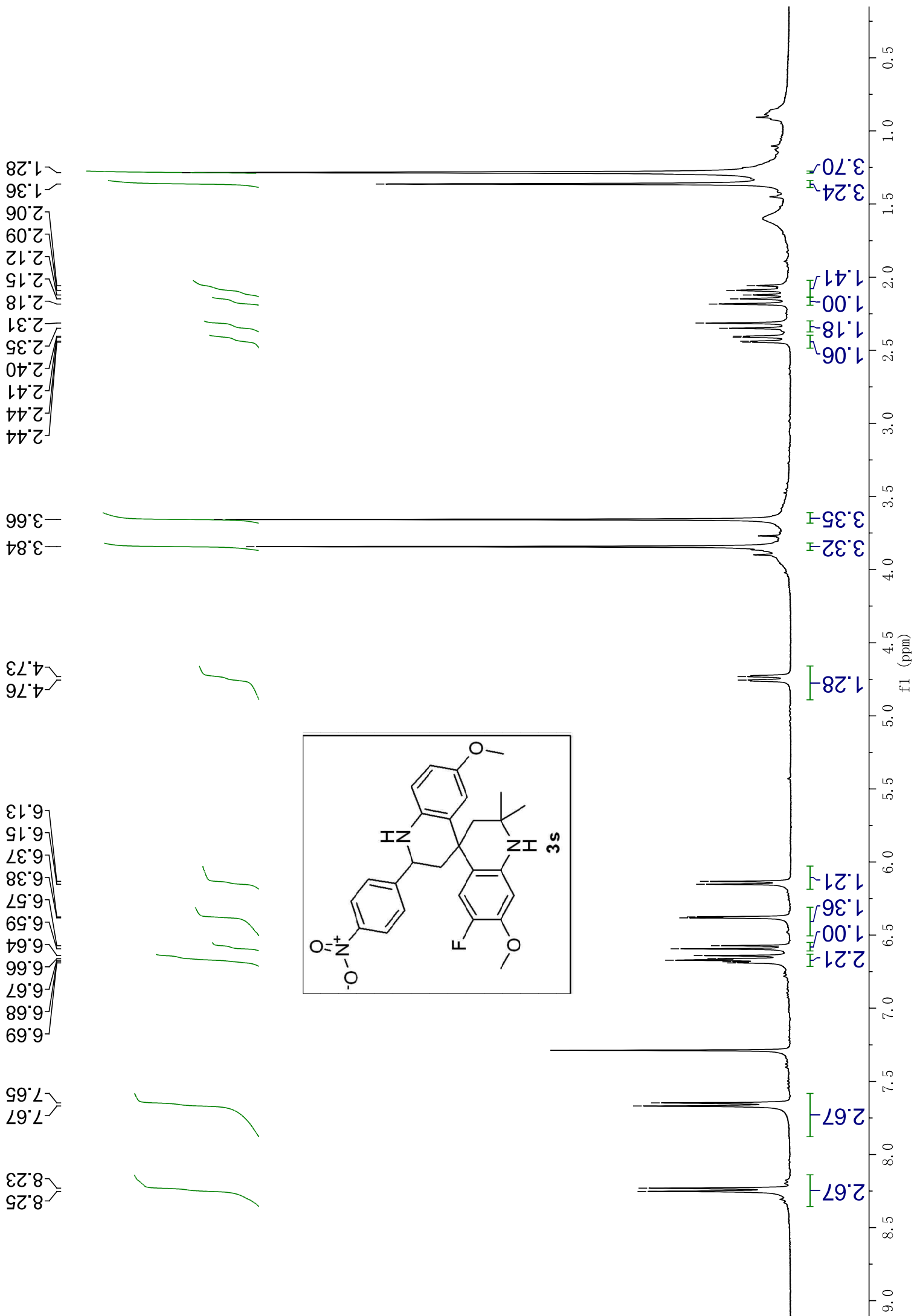


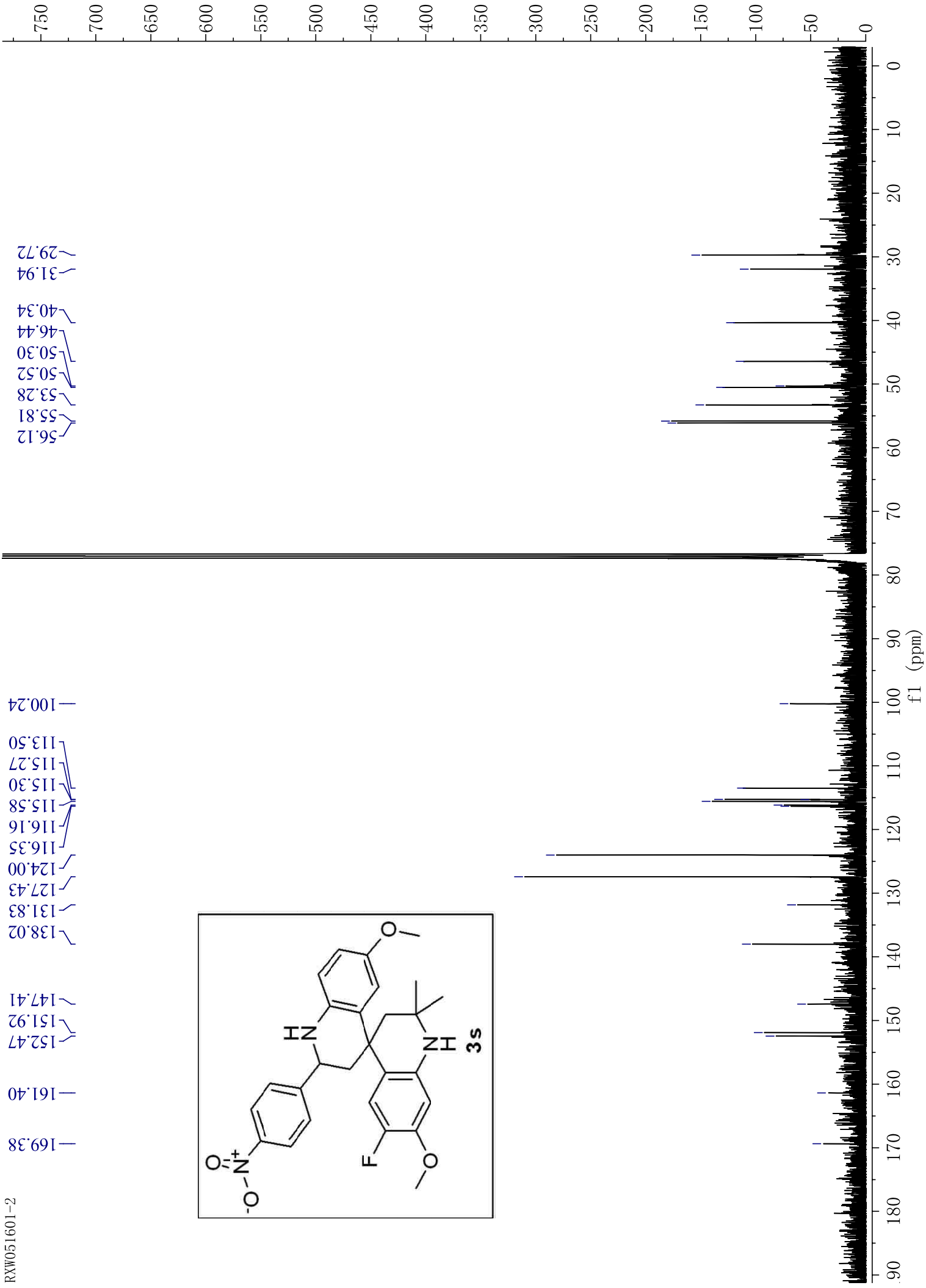
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 32.48
 28.28

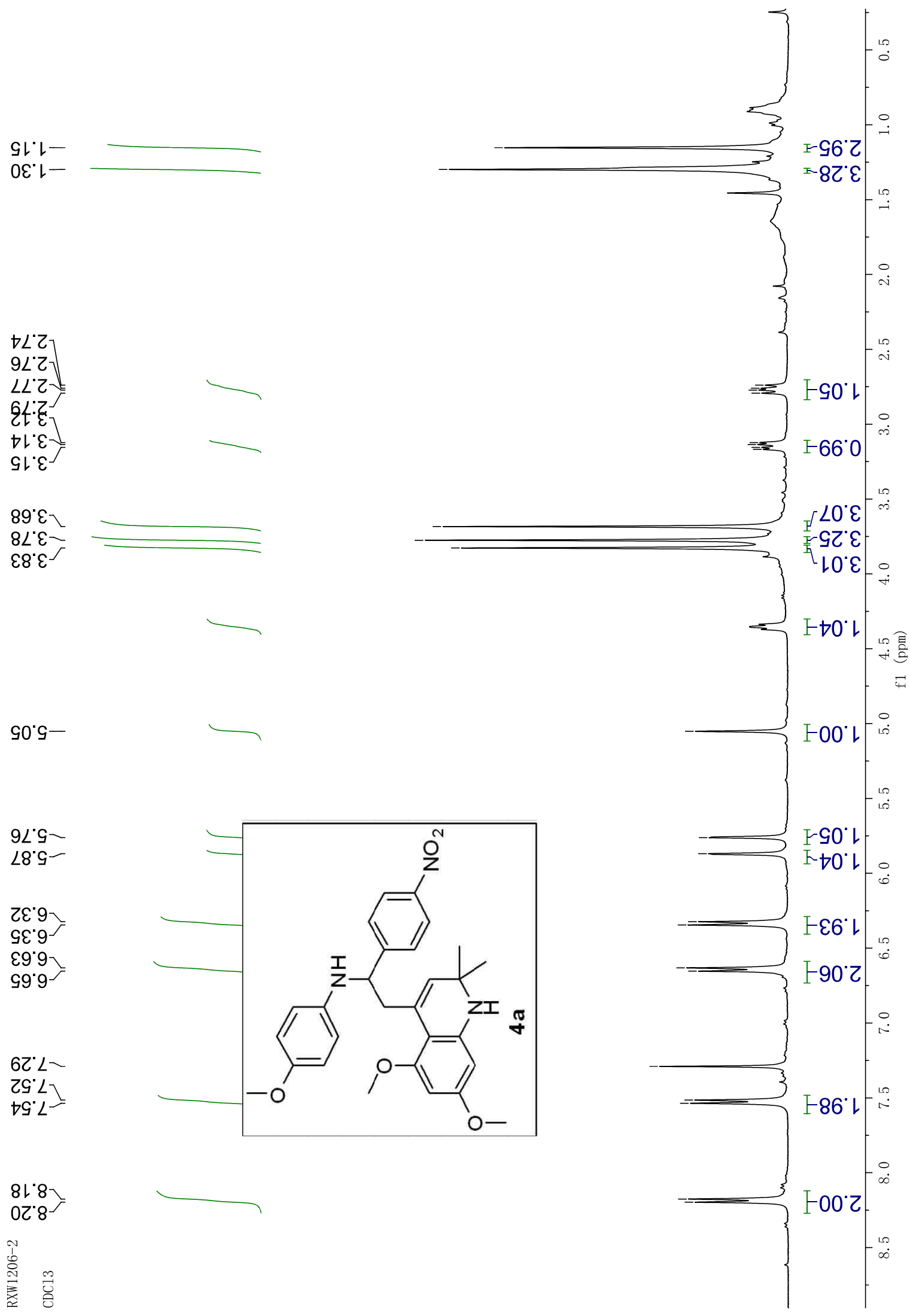


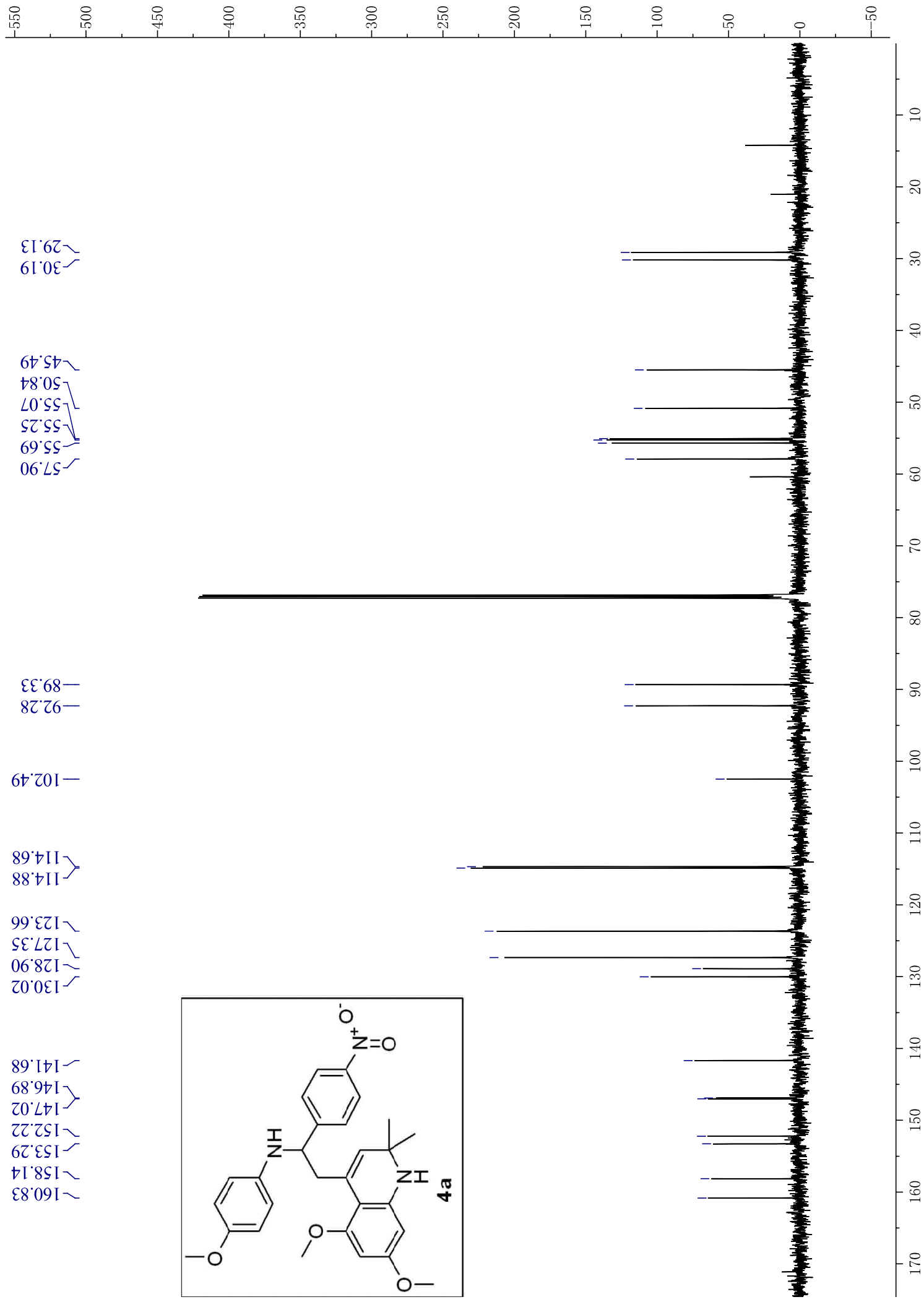


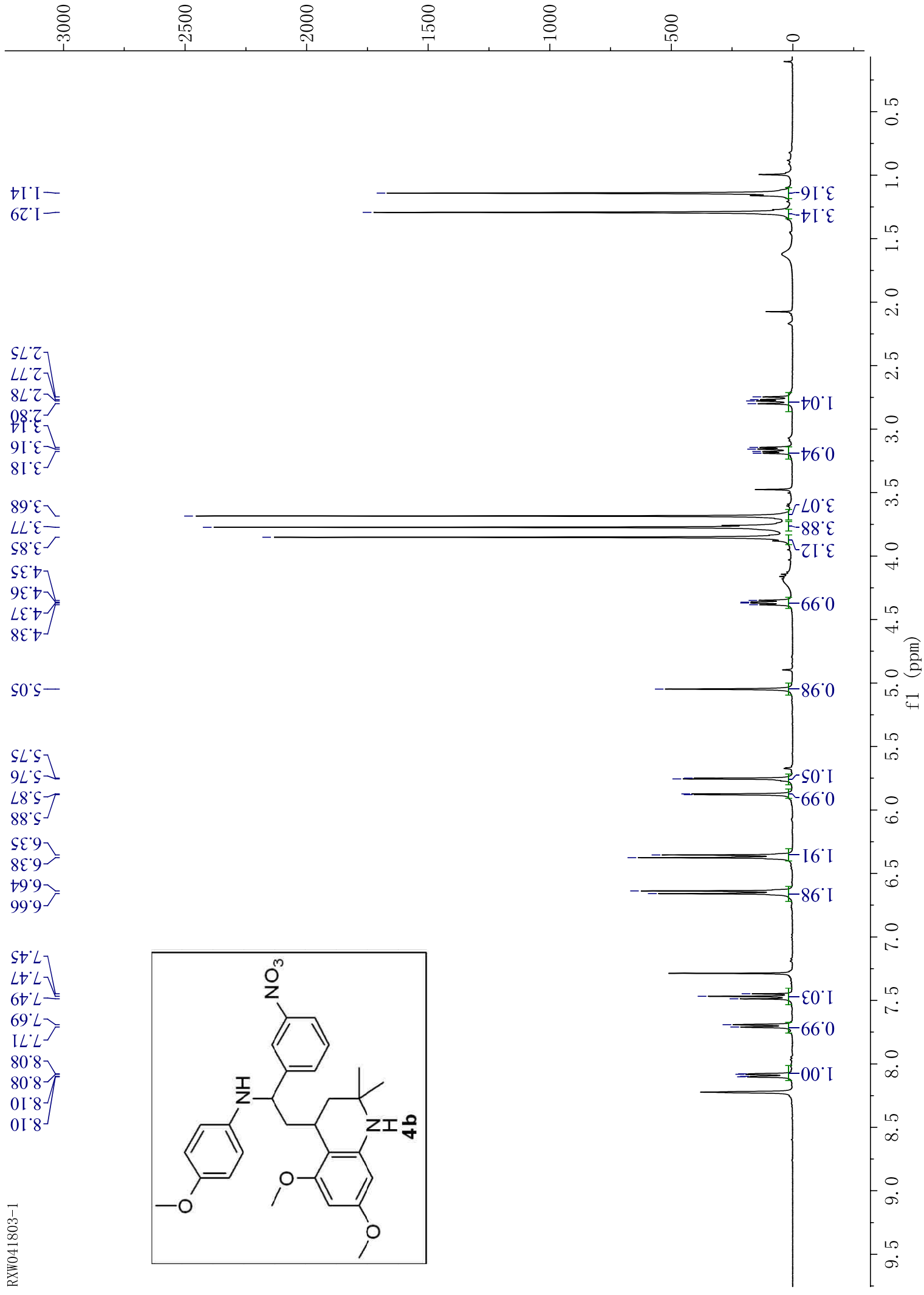


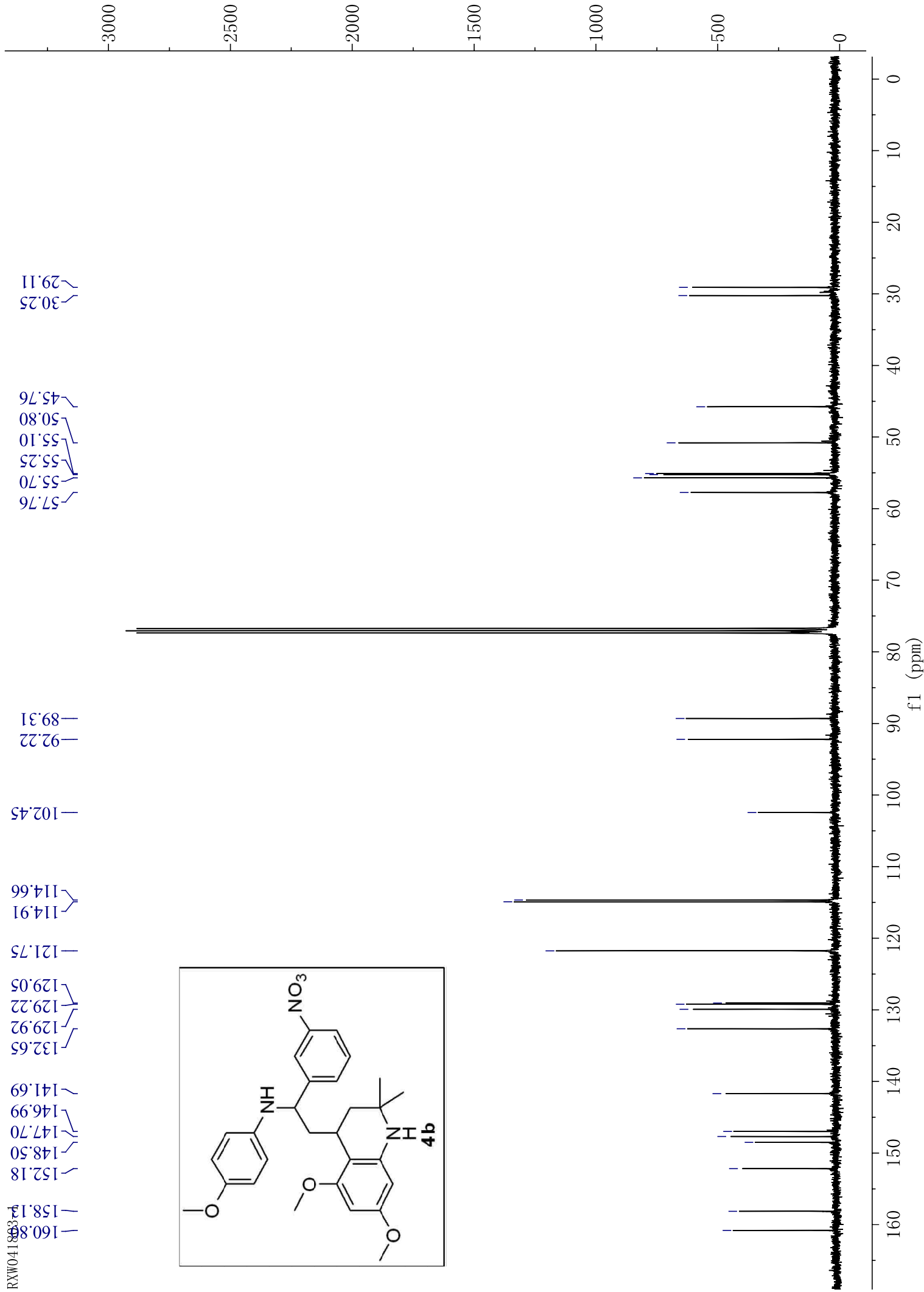


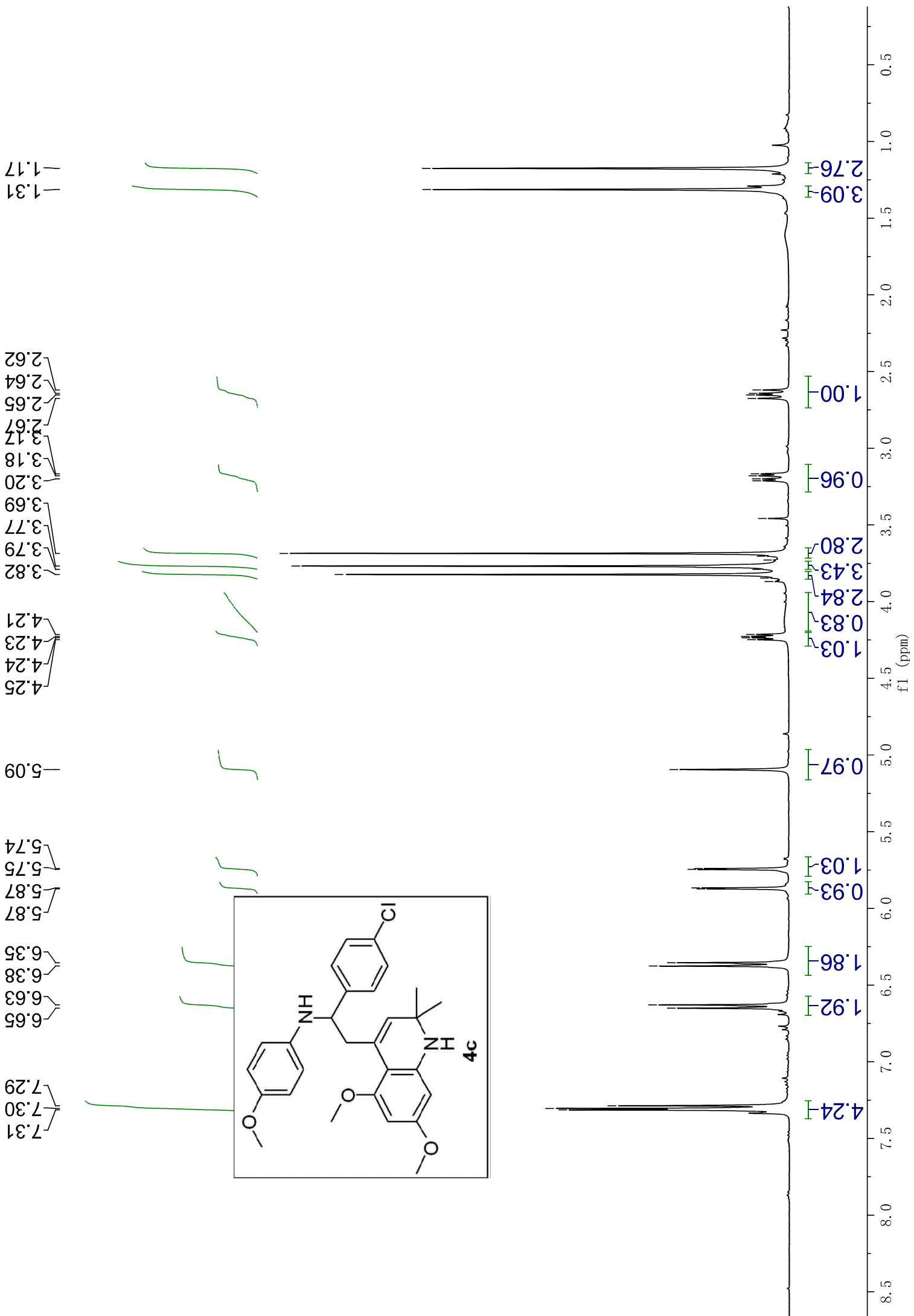


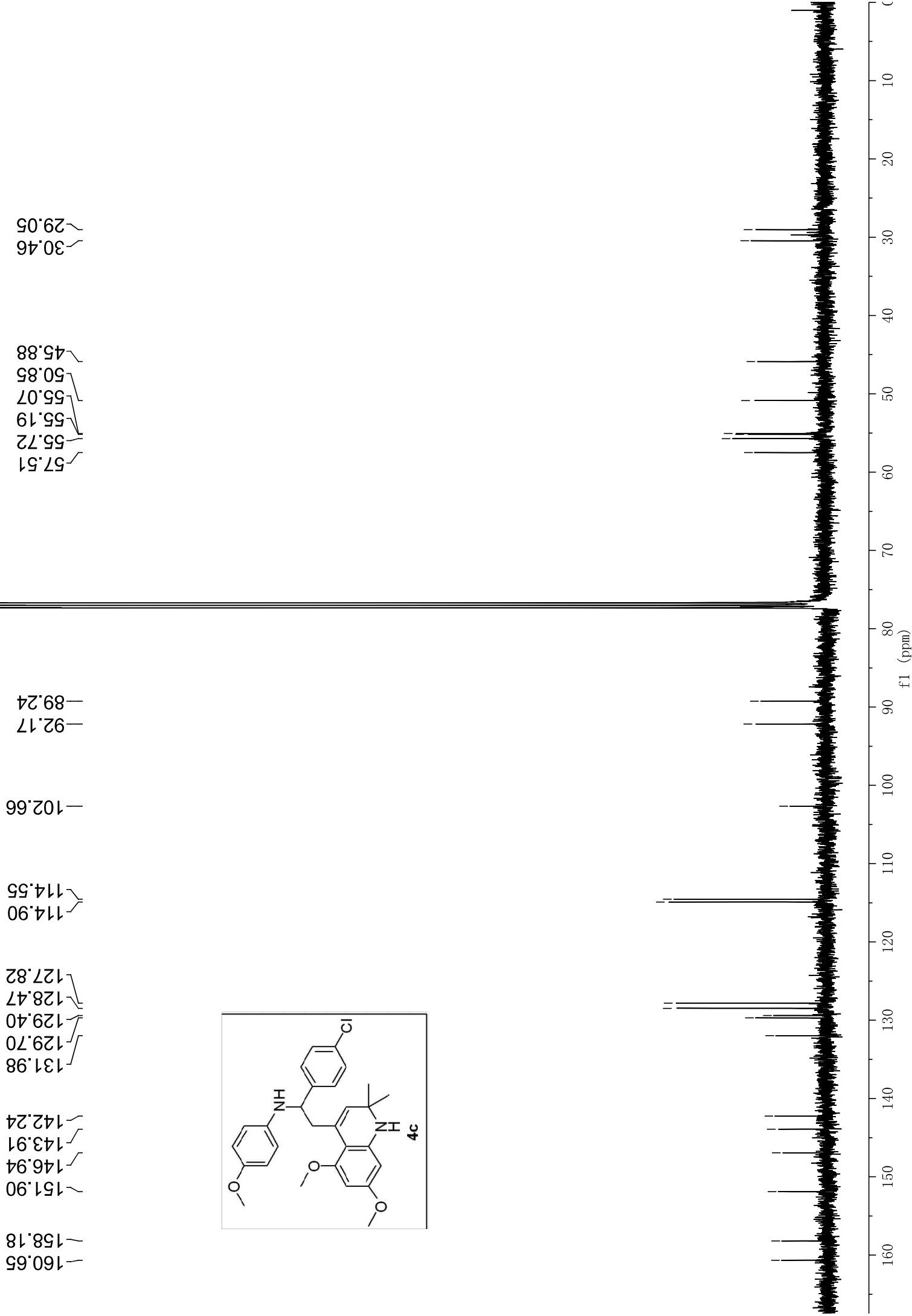


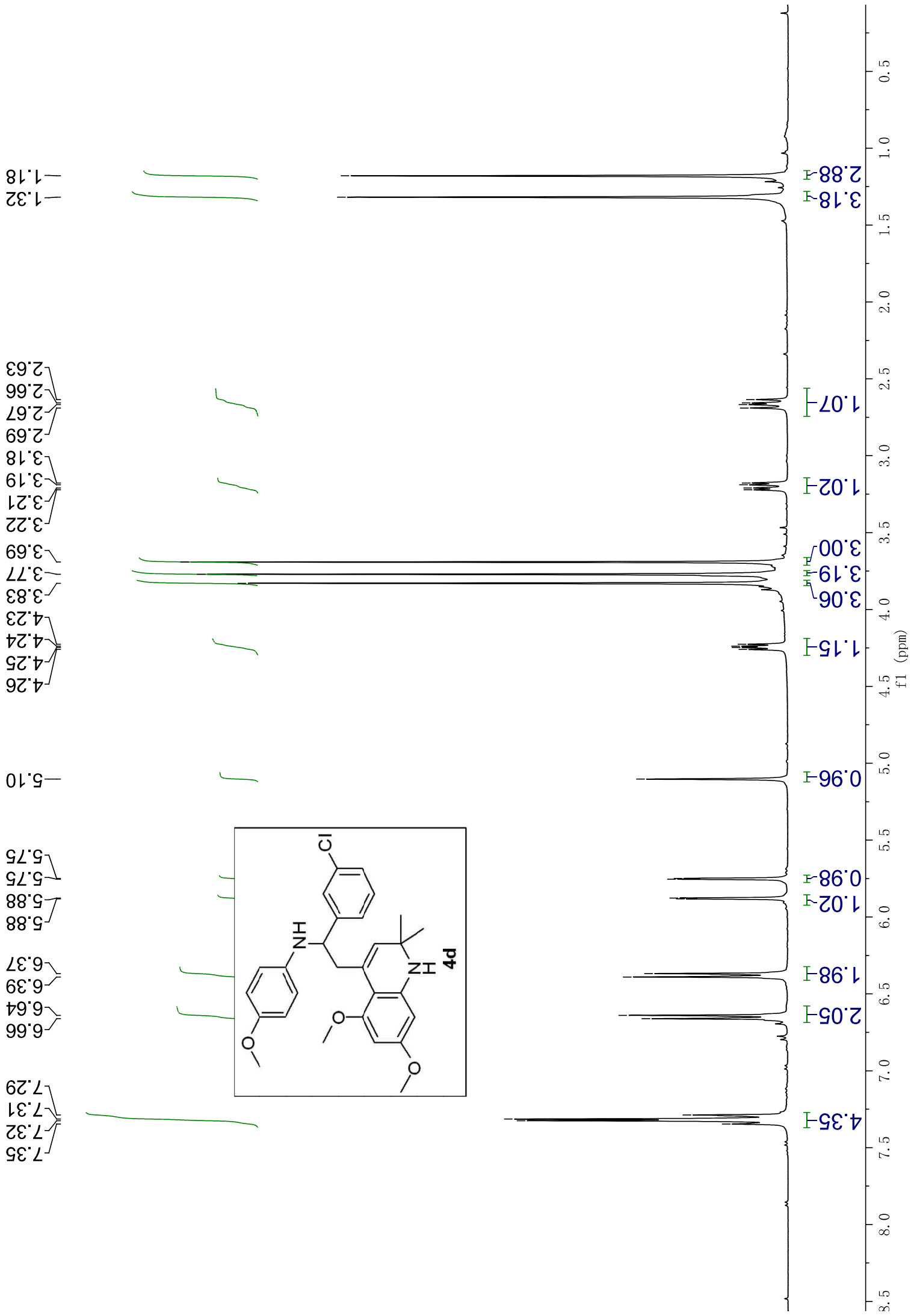


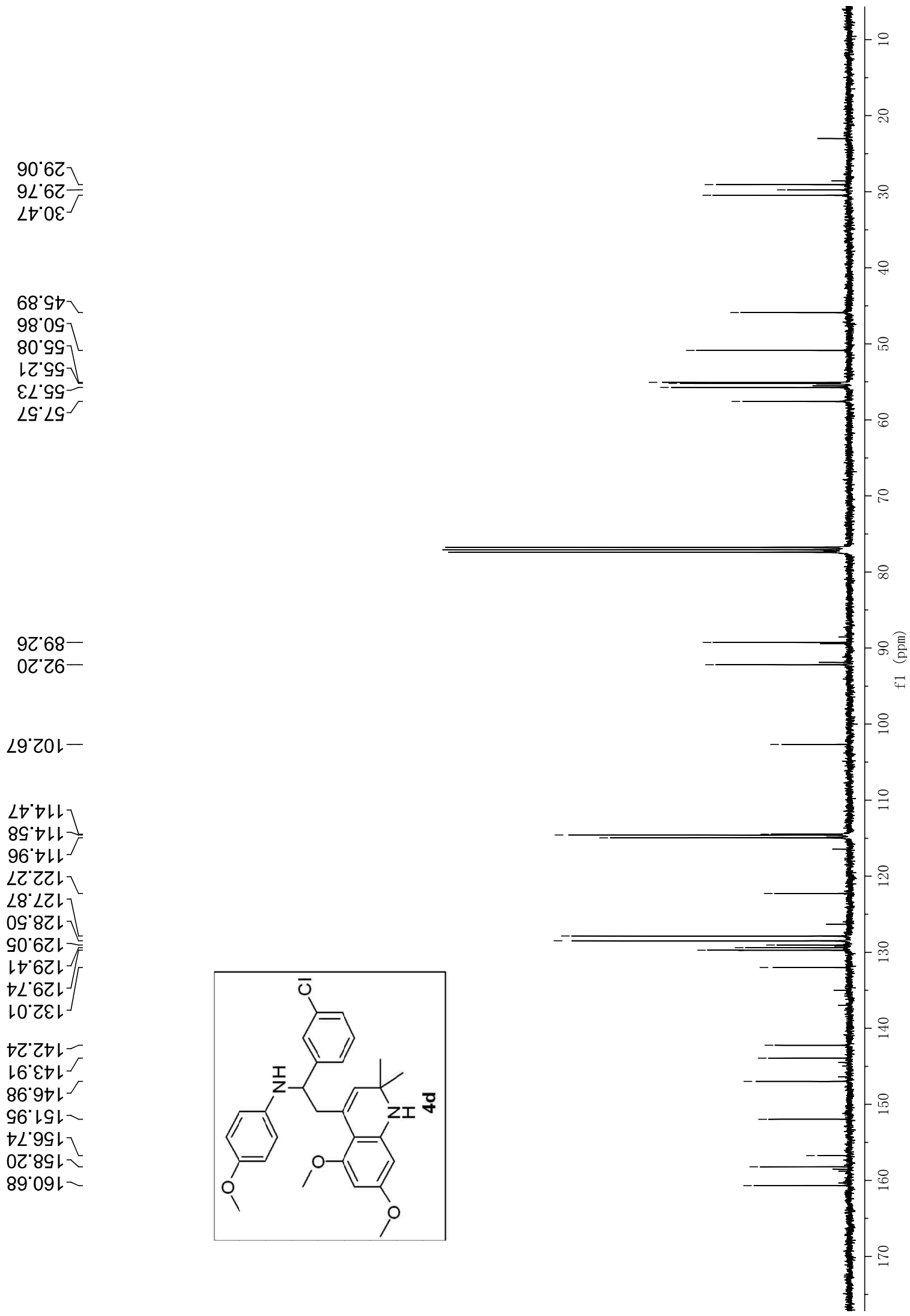












30.47
29.76
29.06

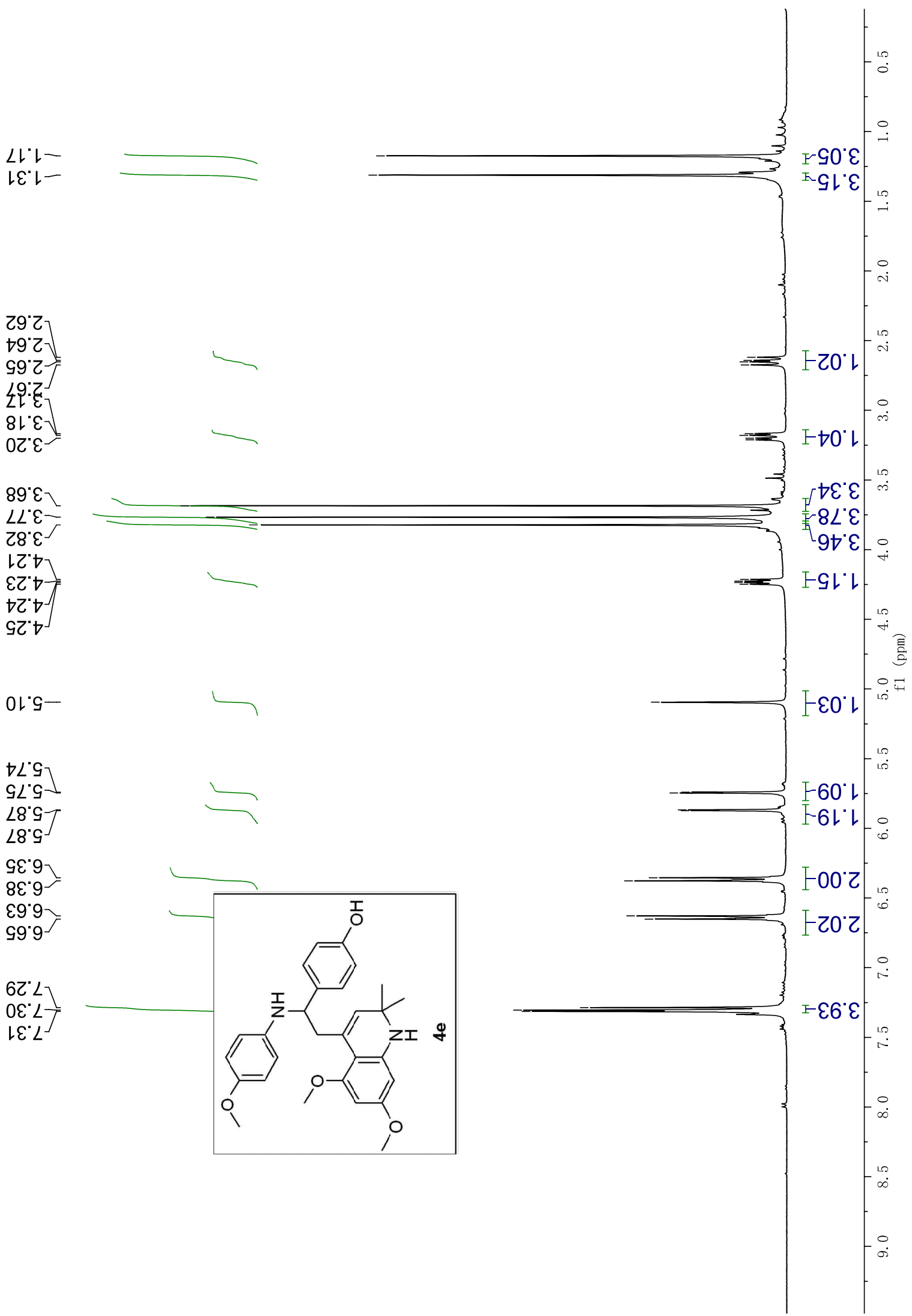
45.89
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55.08
55.21
55.73
57.57

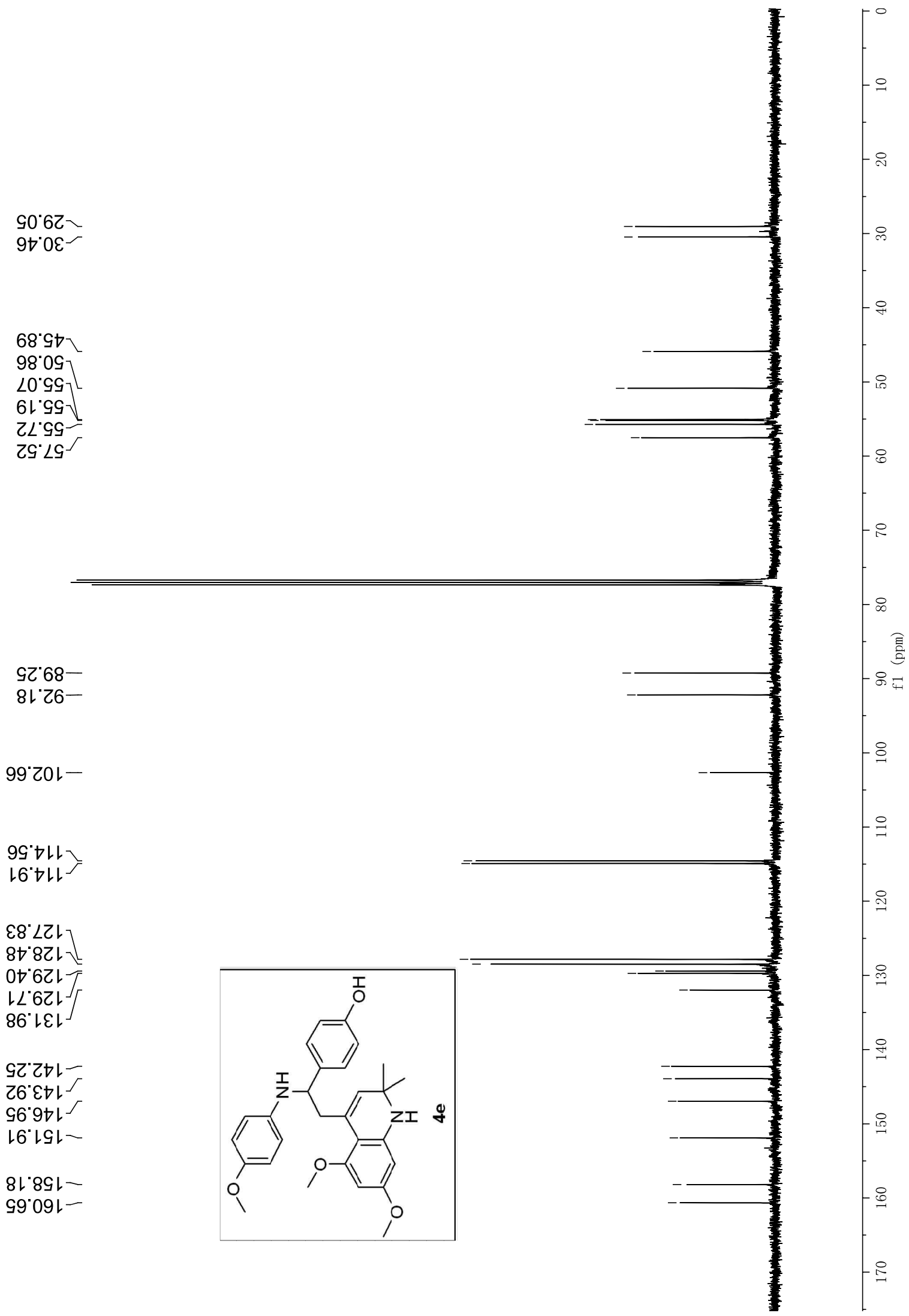
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92.20

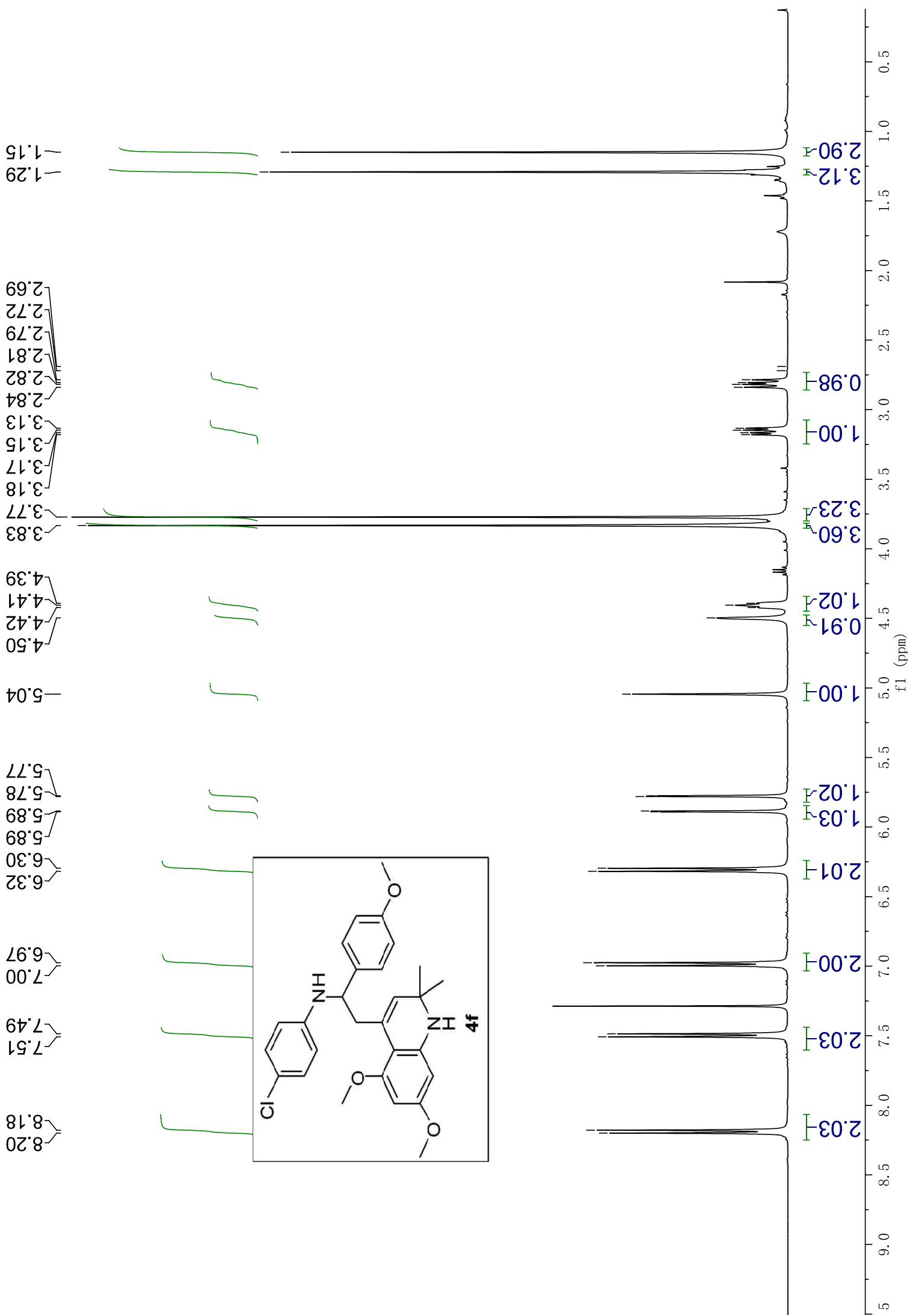
102.67

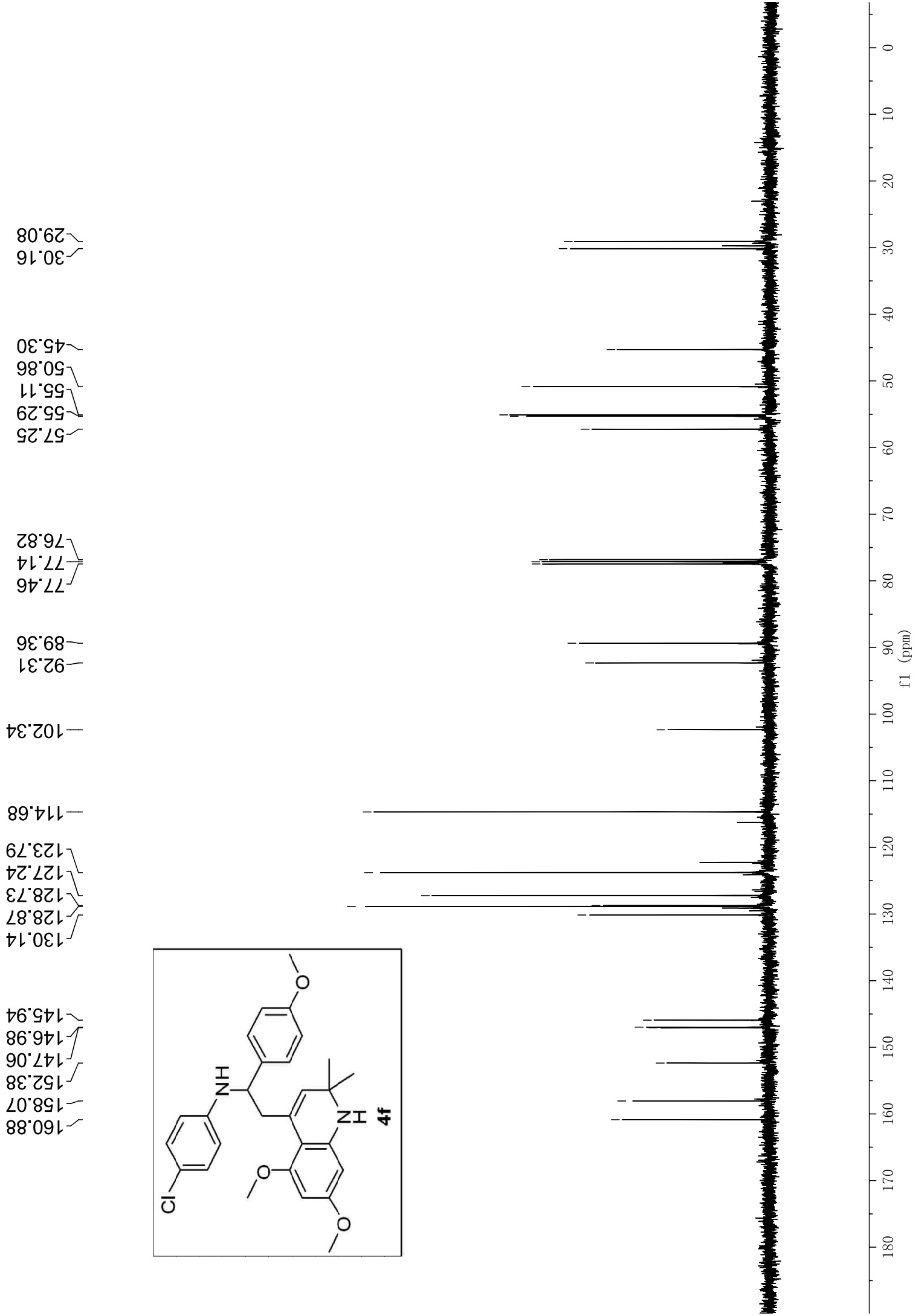
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132.01

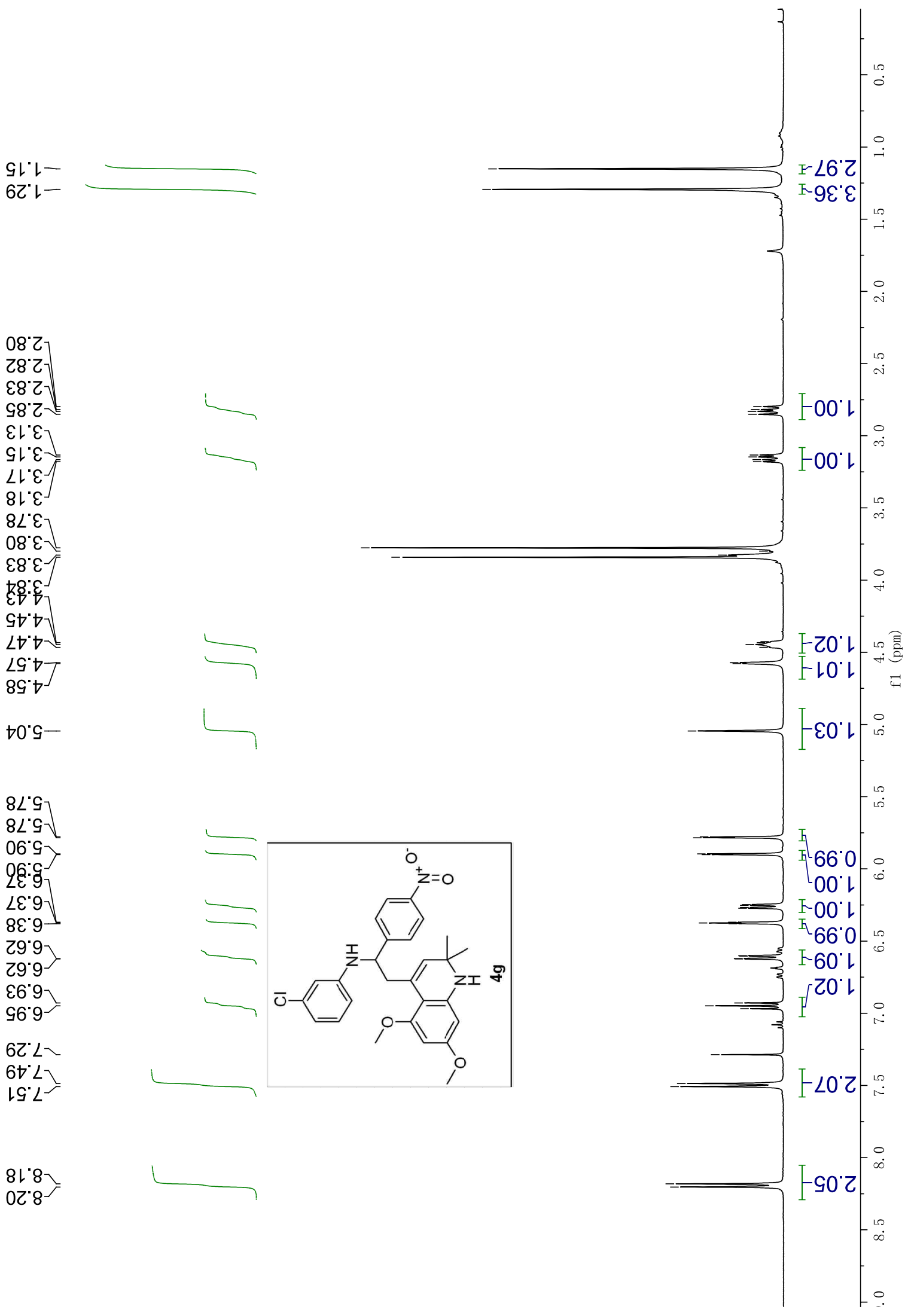
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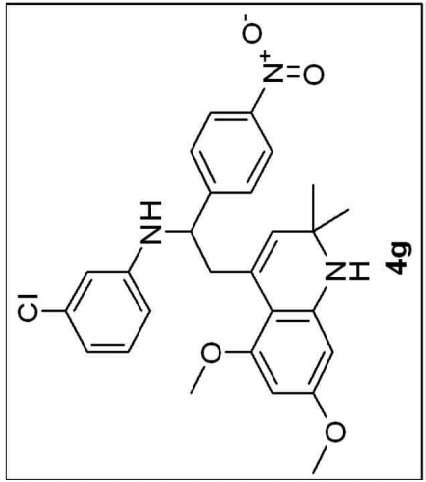








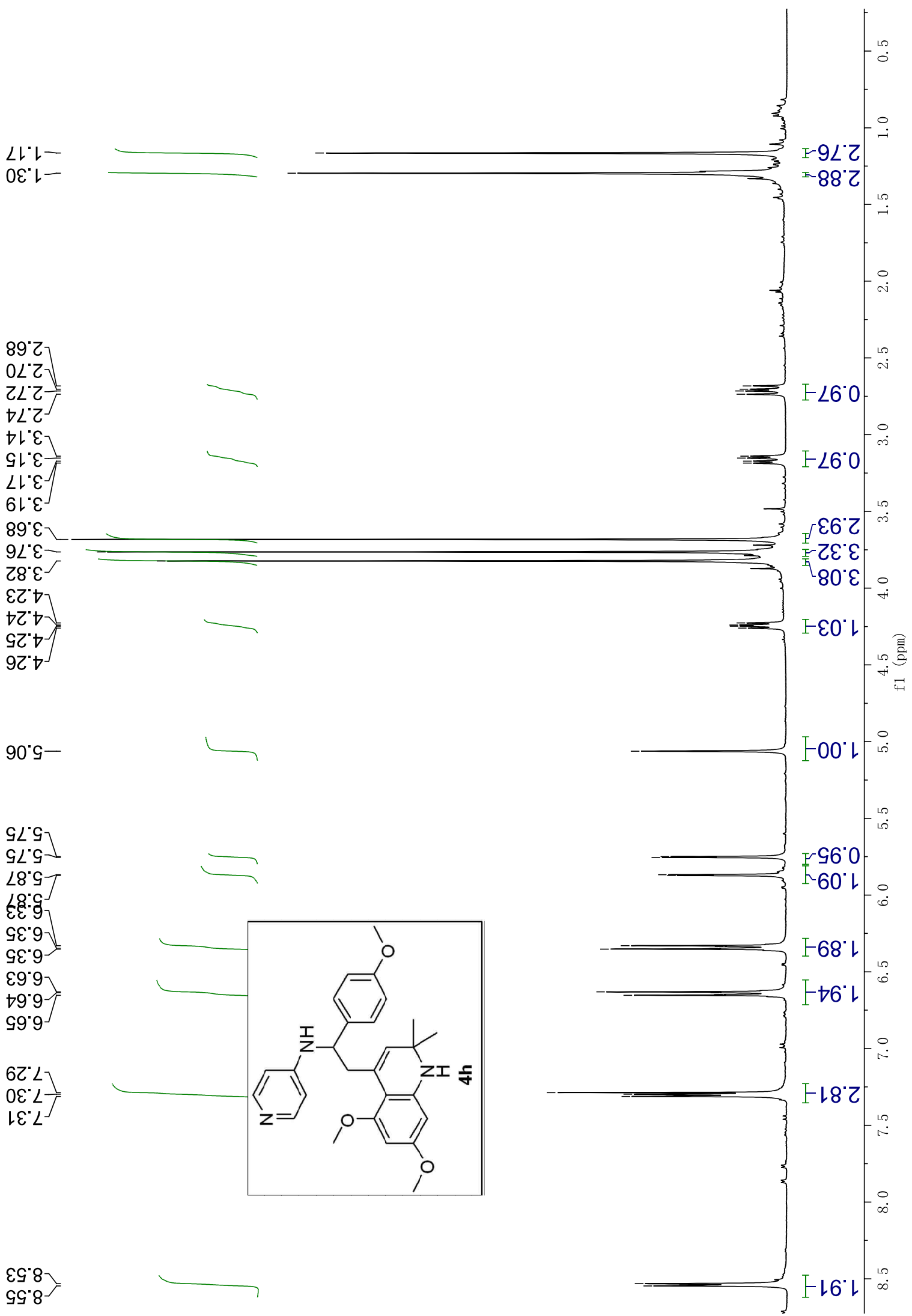


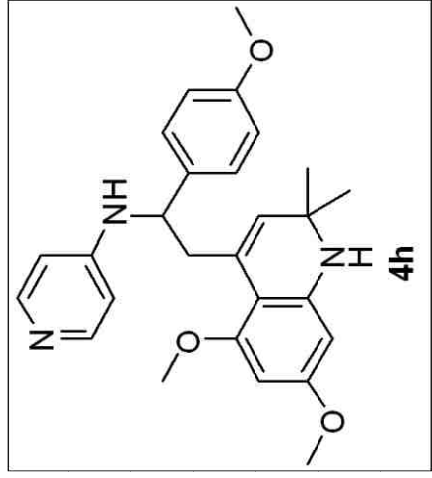
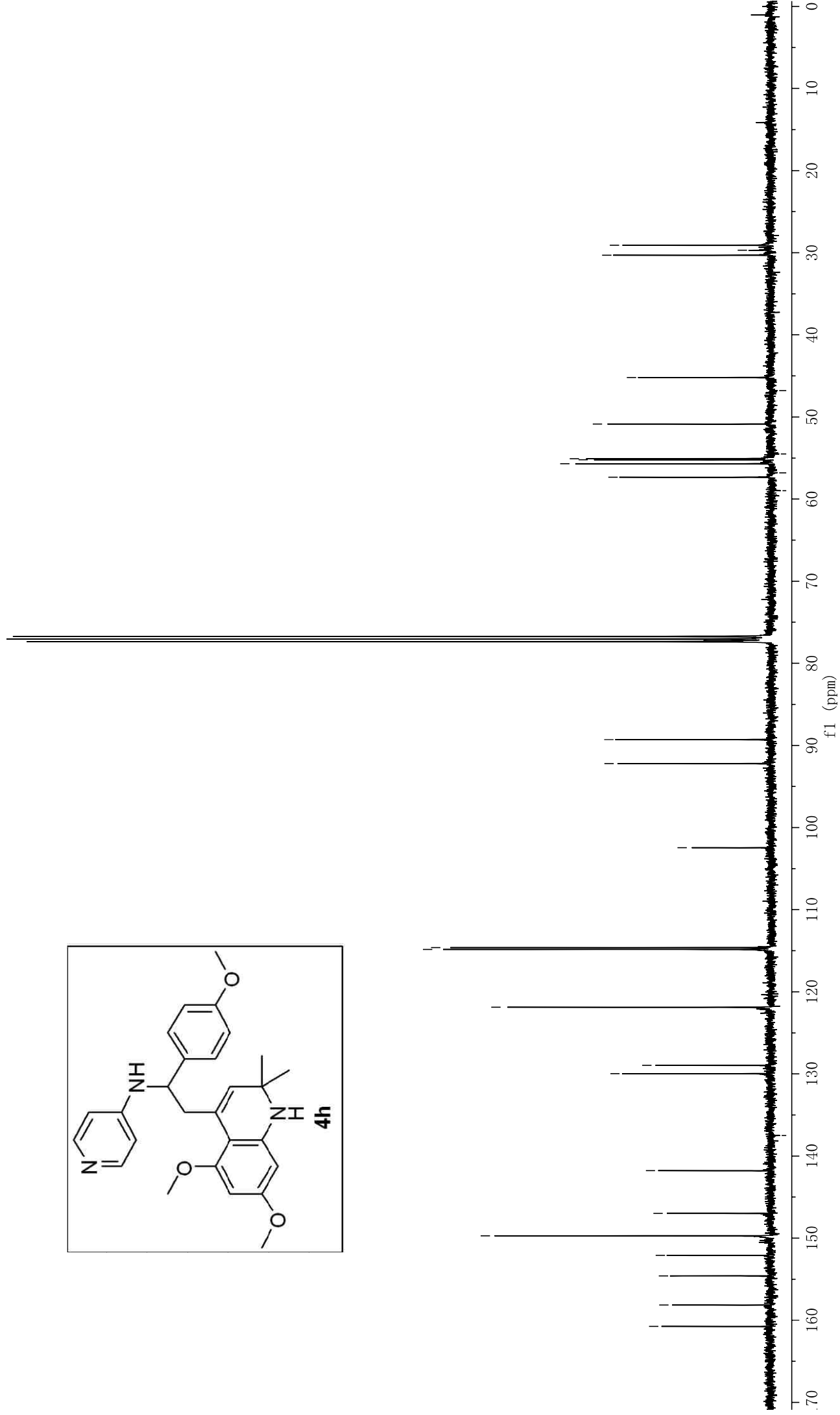


160.90
 158.06
 152.16
 148.49
 147.05
 147.02
 134.70
 130.16
 130.06
 128.68
 127.21
 123.82
 117.59
 113.38
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 102.35
 92.35
 89.38
 57.02
 55.32
 55.12
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 45.27
 30.16
 29.09

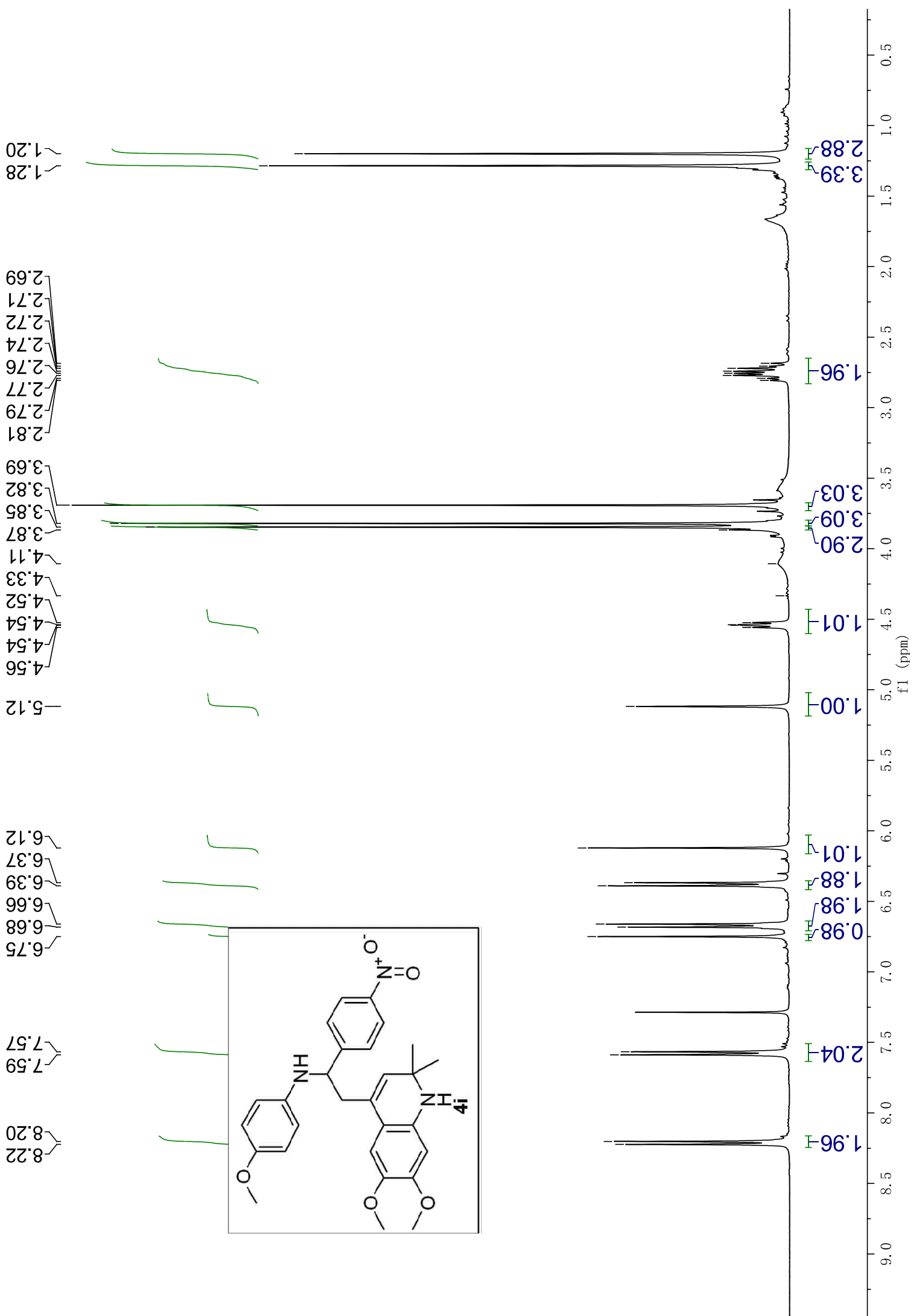
f1 (ppm)

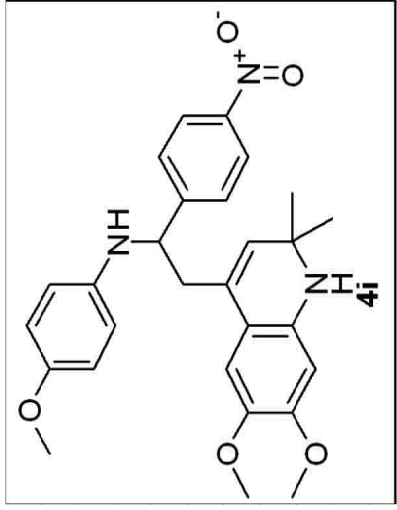
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158.14
154.59
152.11
149.72
146.99
141.79
137.51
129.97
128.96
121.88
114.84
114.62
102.45
92.21
89.29
58.97
57.34
56.79
55.70
55.22
55.08
54.50
50.86
46.78
45.20
30.31
29.71
29.09





152.53
 152.37
 150.46
 147.17
 141.14
 140.95
 138.95
 128.91
 128.13
 127.33
 123.99
 114.95
 114.78
 111.72
 109.13
 98.59
 57.51
 57.24
 55.80
 55.69
 51.76
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 30.23

f1 (ppm)

0

10

20

30

40

50

60

70

80

90

100

110

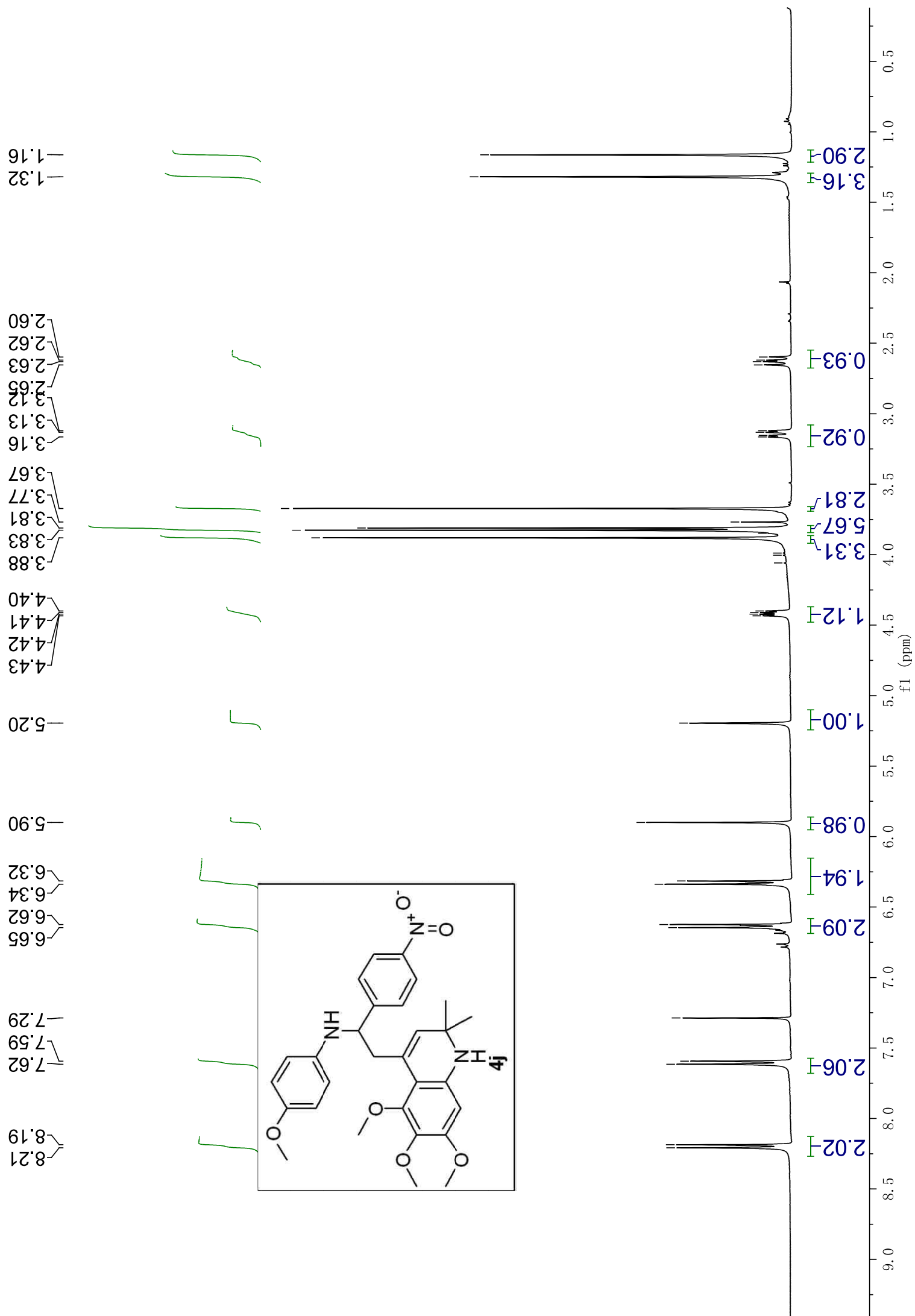
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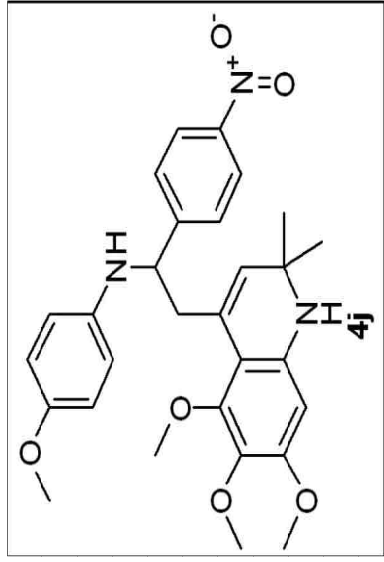
130

140

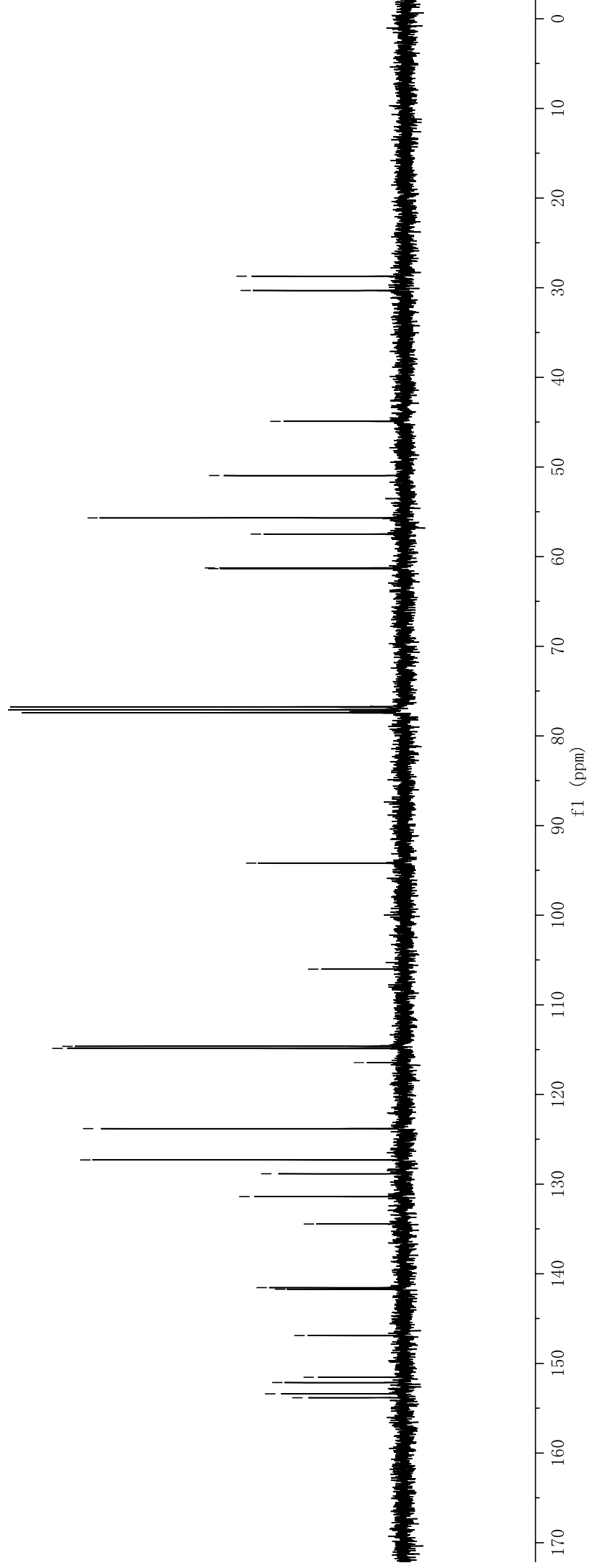
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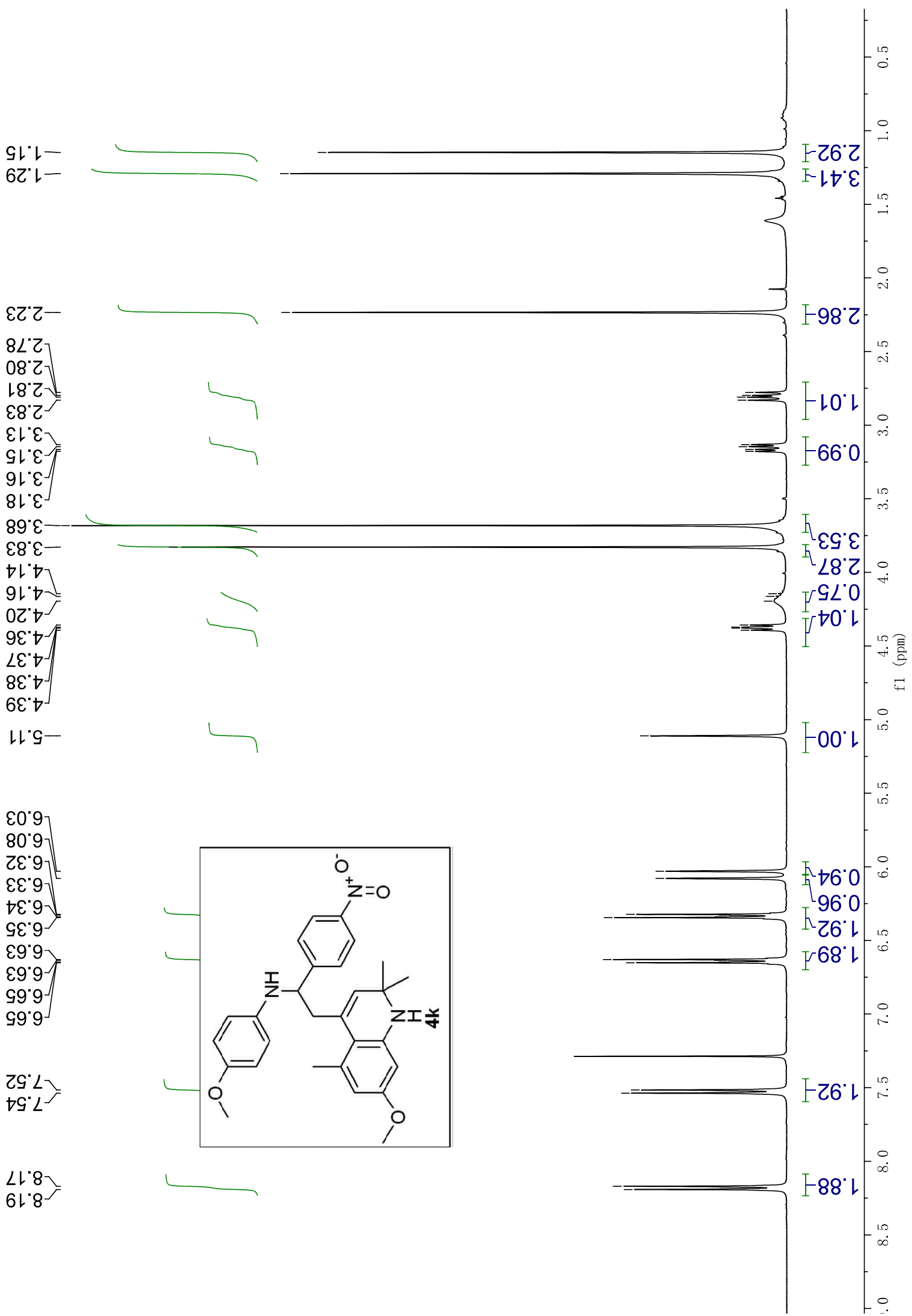
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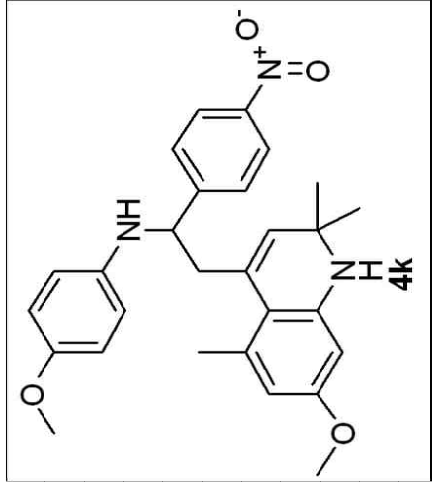




153.84
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 152.15
 151.55
 146.91
 141.73
 141.56
 134.45
 131.40
 128.86
 127.31
 123.82
 116.45
 114.87
 114.63
 106.02
 94.21
 61.35
 61.27
 57.50
 55.69
 50.97
 44.91
 30.33
 28.73







156.89
 153.24
 152.17
 146.86
 145.96
 141.62
 139.44
 131.69
 129.02
 127.33
 123.67
 114.87
 114.63
 108.63
 106.28
 102.26
 57.87
 55.69
 55.22
 50.77
 45.53
 30.19
 29.09
 21.66

f1 (ppm)

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