

Supporting Information

Copper/Iron Controlled Regioselective 1,2- Carboazidation of 1,3-Dienes with Acetonitrile and Azidotrimethylsilane

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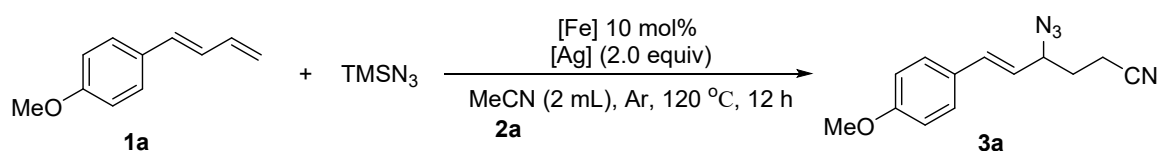
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(A) Typical experimental procedure

(a) General Information

The ^1H and ^{13}C NMR spectra were recorded in CDCl_3 solvents on a NMR spectrometer using TMS as the internal standard. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry.

General procedure for synthesis of compound **3a**.

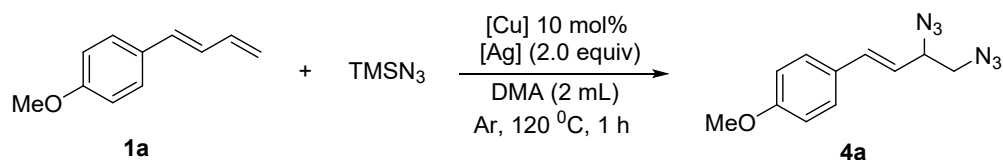


To a Schlenk tube were added substrates **1a** (0.2 mmol), TMSN_3 (0.4 mmol, 2.0 equiv), FeCl_2 (0.02 mmol, 10 mol%), Ag_2CO_3 (0.4 mmol, 2.0 equiv) and MeCN (2 mL), the tube was then charged with Ar. The mixture was stirred at 120 °C until complete consumption of starting material as monitored by TLC (about 12 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product.

One millimol reaction: To a Schlenk tube were added substrates **1a** (1 mmol), TMSN_3 (2 mmol, 2.0 equiv), FeCl_2 (0.1 mmol, 10 mol%), Ag_2CO_3 (2 mmol, 2.0 equiv) and MeCN (10 mL), the tube was then charged with Ar. The mixture was stirred at 120 °C until complete consumption of starting material as monitored by TLC (about 12 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and

the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product **3a** (76%, 183.9 mg).

General procedure for synthesis of compound 4a.

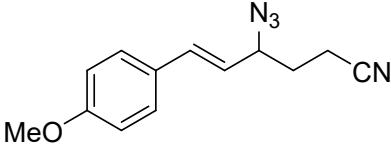


To a Schlenk tube were added substrates **1a** (0.2 mmol), TMSN₃ (0.6 mmol, 3.0 equiv), CuSCN (0.02 mmol, 10 mol%), Ag₂CO₃ (0.4 mmol, 2.0 equiv) and DMA (2 mL), the tube was then charged with Ar. The mixture was stirred at 120 °C until complete consumption of starting material as monitored by TLC (about 1 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product.

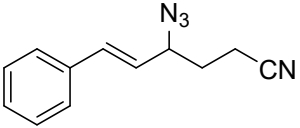
One millimol reaction: To a Schlenk tube were added substrates **1a** (1 mmol), TMSN₃ (3 mmol, 3.0 equiv), CuSCN (0.1 mmol, 10 mol%), Ag₂CO₃ (2 mmol, 2.0 equiv) and DMA (10 mL), the tube was then charged with Ar. The mixture was stirred at 120 °C until complete consumption of starting material as monitored by TLC (about 1 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product **4a** (95%, 231.8 mg).

(B) Analytical data

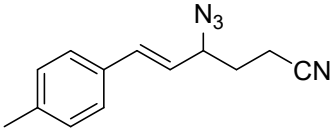
(E)-4-azido-6-(4-methoxyphenyl)hex-5-enitrile (3a):

 36.8 mg, 76% yield; Colorless liquid; ¹H NMR (500 MHz, CDCl₃) δ 7.34 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 16.0 Hz, 1H), 5.95 – 5.89 (m, 1H), 4.15 (q, *J* = 7.5 Hz, 1H), 3.79 (s, 3H), 2.45 - 2.41 (m, 2H), 1.90 - 1.86 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 159.8, 134.5, 127.9, 127.8, 122.2, 118.8, 114.0, 63.1, 55.1, 30.3, 13.8. HRMS *m/z* (ESI) calcd for C₁₃H₁₅N₄O([M+H]⁺) 243.1240, found 243.1240.

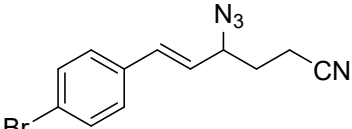
(E)-1-(hept-1-en-6-yn-1-yl)-4-methoxybenzene (3b):

 29.3 mg, 69% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 6.11 – 6.05 (m, 1H), 4.24 – 4.19 (m, 1H), 2.52 – 2.43 (m, 2H), 1.95 – 1.90 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 135.3, 135.1, 128.7, 128.6, 126.8, 124.7, 118.7, 63.0, 30.4, 14.0. HRMS *m/z* (ESI) calcd. for C₁₂H₁₃N₄([M+H]⁺) 213.1135, found 213.1135.

(E)-4-azido-6-(p-tolyl)hex-5-enitrile (3c):

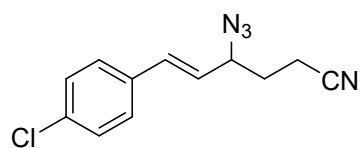
 28.9 mg, 64% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.68 (d, *J* = 15.5 Hz, 1H), 6.05 – 5.99 (m, 1H), 4.23 – 4.17 (m, 1H), 2.50 – 2.45 (m, 2H), 2.36 (s, 3H), 1.95 – 1.89 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 138.7, 135.1, 132.5, 129.4, 126.7, 123.6, 118.8, 63.1, 30.5, 21.3, 14.0. HRMS *m/z* (ESI) calcd for C₁₃H₁₅N₄([M+H]⁺) 227.1291, found 227.1291.

(E)-4-azido-6-(4-bromophenyl)hex-5-enitrile (3d):

 31.3 mg, 54% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.19 (m, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.03 – 5.97 (m, 1H), 4.17 – 4.11 (m, 1H), 2.46 – 2.37 (m, 2H), 1.88 – 1.83 (m, 2H). ¹³C NMR (125

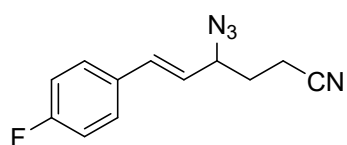
MHz, Chloroform-*d*) δ 134.2 , 133.8 , 131.9 , 128.3 , 125.5 , 122.5 , 118.7 , 62.9 , 30.4 , 13.9. HRMS *m/z* (ESI) calcd. for C₁₂H₁₂BrN₄([M+H]⁺)291.0240, found 291.0240.

(*E*)-4-azido-6-(4-chlorophenyl)hex-5-enitrile (3e):



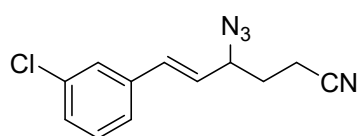
36.4 mg, 74% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 4H), 6.67 (d, *J* = 15.5 Hz, 1H), 6.09 – 6.03 (m, 1H), 4.24 – 4.19 (m, 1H), 2.53 – 2.44 (m, 2H), 1.95 – 1.90 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 134.3 , 133.8 , 133.7 , 128.9 , 128.0 , 125.4 , 118.7 , 62.9 , 30.4 , 13.9. HRMS *m/z* (ESI) calcd. for C₁₂H₁₂CIN₄ ([M+H]⁺) 247.0745, found 247.0745.

(*E*)-4-azido-6-(4-fluorophenyl)hex-5-enitrile (3f):



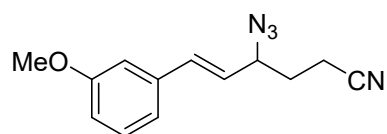
33.6 mg, 73% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.32 (t, *J* = 7.0 Hz, 2H), 6.97 (t, *J* = 8.5 Hz, 2H), 6.61 (d, *J* = 16.0 Hz, 1H), 5.96 – 5.90 (m, 1H), 4.17 – 4.11 (m, 1H), 2.46 – 2.37 (m, 2H), 1.88 – 1.83 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 163.9, 161.9, 134.0, 131.5, 131.4, 128.5, 128.4, 124.5, 124.5, 118.7, 115.8, 115.7, 63.0, 30.4, 14.0. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -112.59. HRMS *m/z* (ESI) calcd. for C₁₂H₁₂FN₄([M+H]⁺) 231.1041, found 231.1042.

(*E*)-4-azido-6-(3-chlorophenyl)hex-5-enitrile (3g):



36.4 mg, 74% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.40 (s, 1H), 7.27 (s, 3H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.12 – 6.06 (m, *J* = 16.0, 8.0 Hz, 1H), 4.24 – 4.18 (m, 1H), 2.50 – 2.45 (m, 2H), 1.94 – 1.89 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 137.1 , 134.6 , 133.5 , 129.9 , 128.4 , 126.5 , 126.3 , 125.0 , 118.6 , 62.7 , 30.2 , 13.8. HRMS *m/z* (ESI) calcd. for C₁₂H₁₂CIN₄([M+H]⁺) 247.0745, found 247.0745.

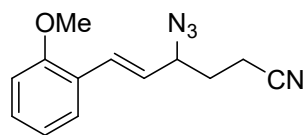
(*E*)-4-azido-6-(3-methoxyphenyl)hex-5-enitrile (3h):



27.1 mg, 56% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 5.0 Hz, 1H), 7.01 (d, *J* = 7.0 Hz, 1H), 6.94 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 15.5 Hz, 1H), 6.10 – 6.04 (m, 1H), 4.24 – 4.18 (m, 1H), 3.83 (s, 3H),

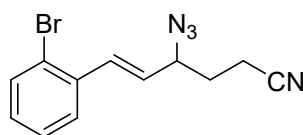
2.53 – 2.43 (m, 2H), 1.95 – 1.90 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 159.9, 136.7, 135.0, 129.7, 125.0, 119.4, 118.7, 114.2, 112.1, 63.0, 55.3, 30.4, 14.0. HRMS *m/z* (ESI) calcd. for C₁₃H₁₅N₄O([M+H]⁺) 243.1240, found 243.1236.

(*E*)-4-azido-6-(2-methoxyphenyl)hex-5-enitrile (3i):



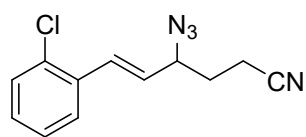
40.2 mg, 83% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.01 (d, *J* = 16.0 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.14 – 6.08 (m, 1H), 4.20 – 4.17 (m, 1H), 3.86 (s, 3H), 2.50 – 2.44 (m, 2H), 1.95 – 1.90 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 157.0, 130.3, 129.7, 127.3, 125.1, 124.2, 120.6, 118.8, 111.0, 63.5, 55.4, 30.5, 13.9. HRMS *m/z* (ESI) calcd. for C₁₃H₁₅N₄O([M+H]⁺) 243.1240, found 243.1240.

(*E*)-4-azido-6-(2-bromophenyl)hex-5-enitrile (3j):



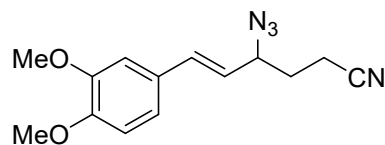
45.2 mg, 78% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 16.0 Hz, 1H), 5.98 – 5.92 (m, 1H), 4.23 – 4.17 (m, 1H), 2.43 (t, *J* = 7.5 Hz, 2H), 1.93 – 1.84 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 135.5, 133.9, 133.1, 129.8, 127.7, 127.6, 127.3, 123.8, 118.7, 62.7, 30.3, 13.9. HRMS *m/z* (ESI) calcd. for C₁₂H₁₂BrN₄([M+H]⁺) 291.0240, 291.0252.

(*E*)-4-azido-6-(2-chlorophenyl)hex-5-enitrile (3k):



28.1 mg, 57% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.56 – 7.51 (m, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.09 (d, *J* = 16.0 Hz, 1H), 6.09 – 6.03 (m, 1H), 4.28 – 4.23 (m, 1H), 2.49 (t, *J* = 6.5 Hz, 2H), 1.97 – 1.92 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 133.5, 133.3, 131.2, 129.8, 129.5, 127.5, 127.0, 126.9, 118.7, 62.7, 30.3, 13.8. HRMS *m/z* (ESI) calcd for C₁₂H₁₂ClN₄([M+H]⁺) 247.0745, found 247.0744.

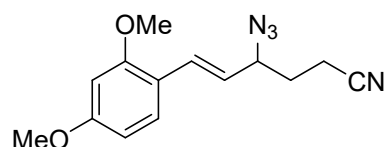
(*E*)-4-azido-6-(3,4-dimethoxyphenyl)hex-5-enitrile (3l):



35.5 mg, 65% yield; Light red liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 6.97 (d, *J* = 9.0 Hz, 2H), 6.84

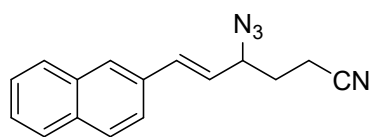
(d, $J = 8.0$ Hz, 1H), 6.64 (d, $J = 15.5$ Hz, 1H), 5.97 – 5.92 (m, 1H), 4.22 – 4.17 (m, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 2.49 – 2.45 (m, 2H), 1.95 – 1.89 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 149.5, 149.0, 134.8, 128.2, 122.5, 120.2, 118.8, 111.0, 108.9, 63.1, 55.8, 55.8, 30.4, 13.9. HRMS m/z (ESI) calcd. for $\text{C}_{14}\text{H}_{17}\text{N}_4\text{O}_2([\text{M}+\text{H}]^+)$ 273.1346, found 273.1346.

(*E*)-4-azido-6-(2,4-dimethoxyphenyl)hex-5-enitrile (3m):



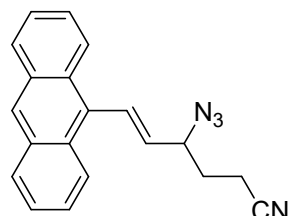
34.8 mg, 64% yield; Light yellow liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.35 (d, $J = 8.0$ Hz, 1H), 6.91 (d, $J = 16.0$ Hz, 1H), 6.48 (d, $J = 8.5$ Hz, 1H), 6.45 (s, 1H), 6.03 – 5.97 (m, 1H), 4.20 – 4.14 (m, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.48 – 2.44 (m, 2H), 1.94 – 1.89 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.2, 158.3, 130.1, 128.2, 122.7, 118.9, 117.3, 104.9, 98.4, 63.9, 55.4, 55.4, 30.6, 14.0. HRMS m/z (ESI) calcd. for $\text{C}_{14}\text{H}_{17}\text{N}_4\text{O}_2([\text{M}+\text{H}]^+)$ 273.1346, found 273.1344.

(*E*)-4-azido-6-(naphthalen-2-yl)hex-5-enitrile (3n):



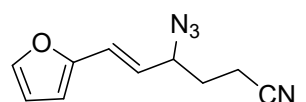
38.3 mg, 73% yield; Light yellow solid; mp 105.3-109.5 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, $J = 5.5$ Hz, 3H), 7.69 (s, 1H), 7.50 (d, $J = 8.5$ Hz, 1H), 7.39 (d, $J = 4.0$ Hz, 2H), 6.77 (d, $J = 15.5$ Hz, 1H), 6.12 – 6.07 (m, 1H), 4.19 – 4.14 (m, 1H), 2.43 – 2.35 (m, 2H), 1.88 – 1.83 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 135.1, 133.4, 133.4, 132.7, 128.4, 128.1, 127.7, 127.3, 126.5, 126.4, 125.0, 123.3, 118.8, 63.1, 30.4, 14.0. HRMS m/z (ESI) calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_4([\text{M}+\text{H}]^+)$ 263.1291, found 263.1291.

(*E*)-6-(anthracen-9-yl)-4-azidohex-5-enitrile (3o):



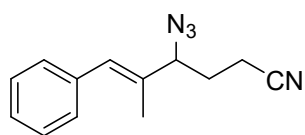
41.8 mg, 67% yield; Light yellow liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.21 (d, $J = 8.5$ Hz, 2H), 8.02 (d, $J = 8.0$ Hz, 2H), 7.53 (s, 1H), 7.49 (d, $J = 10.5$ Hz, 4H), 6.01 – 5.95 (m, 1H), 4.59 – 4.54 (m, 1H), 2.67 – 2.57 (m, 2H), 2.15 – 2.03 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 133.7, 131.4, 131.3, 130.4, 129.3, 128.8, 127.2, 126.0, 125.3, 118.7, 63.4, 30.5, 14.2. HRMS m/z (ESI) calcd. for $\text{C}_{20}\text{H}_{17}\text{N}_4([\text{M}+\text{H}]^+)$ 313.1448, found 313.1449.

(E)-4-azido-6-(furan-2-yl)hex-5-enitrile (3p):



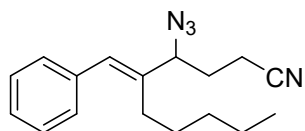
26.7 mg, 66% yield; Gray liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 6.52 (d, $J = 18.5$ Hz, 1H), 6.38 (d, $J = 27.5$ Hz, 2H), 6.04 – 5.98 (m, 1H), 4.21 – 4.15 (m, $J = 8.0$ Hz, 1H), 2.52 – 2.42 (m, 2H), 1.94 – 1.89 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 150.9, 142.8, 122.9, 122.9, 118.7, 111.6, 110.1, 62.7, 30.4, 13.9. HRMS m/z (ESI) calcd. for $\text{C}_{10}\text{H}_{11}\text{N}_4\text{O}([\text{M}+\text{H}]^+)$ 203.0927, found 203.0924.

(E)-4-azido-5-methyl-6-phenylhex-5-enitrile (3q):



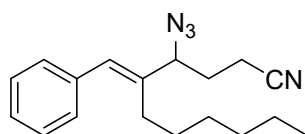
34.8 mg, 77% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.36 (t, $J = 7.5$ Hz, 2H), 7.31 – 7.26 (m, 3H), 6.61 (s, 1H), 4.19 – 4.15 (m, 1H), 2.47 – 2.43 (m, 2H), 1.96 – 1.90 (m, 2H), 1.90 – 1.87 (m, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 136.1, 133.4, 130.6, 129.0, 128.2, 127.2, 118.7, 68.9, 28.5, 14.2, 13.3. HRMS m/z (ESI) calcd. for $\text{C}_{13}\text{H}_{15}\text{N}_4([\text{M}+\text{H}]^+)$ 227.1291, found 227.1290.

(E)-4-azido-5-benzylidenedecanenitrile (3r):

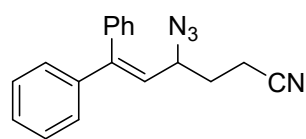


42.8 mg, 76% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.28 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 3H), 6.52 (s, 1H), 4.07 (t, $J = 6.5$ Hz, 1H), 2.42 (t, $J = 7.5$ Hz, 2H), 2.25 – 2.11 (m, 2H), 1.92 – 1.86 (m, 2H), 1.47 – 1.38 (m, 2H), 1.23 – 1.18 (m, 4H), 0.80 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 138.6, 136.3, 130.2, 128.7, 128.4, 127.2, 118.9, 67.0, 32.0, 29.31, 28.7, 28.4, 22.2, 14.4, 13.9. HRMS m/z (ESI) calcd. for $\text{C}_{17}\text{H}_{23}\text{N}_4([\text{M}+\text{H}]^+)$ 283.1917, found 283.1906.

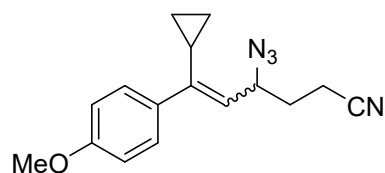
(E)-4-azido-5-benzylideneundecanenitrile (3s):



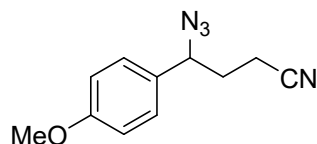
42.0 mg, 74% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.28 (d, $J = 7.5$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 3H), 6.52 (s, 1H), 4.07 (t, $J = 6.5$ Hz, 1H), 2.42 (t, $J = 7.5$ Hz, 2H), 2.24 – 2.12 (m, 2H), 1.92 – 1.86 (m, 2H), 1.47 – 1.35 (m, 2H), 1.25-1.18 (m, 6H), 0.80 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 138.6, 136.3, 130.2, 128.7, 128.4, 127.2, 118.9, 67.0, 31.4, 29.5, 29.3, 28.9, 28.7, 22.5, 14.4, 14.0. HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{25}\text{N}_4([\text{M}+\text{H}]^+)$ 285.1822, found 285.1821.

4-azido-6,6-diphenylhex-5-enitrile (3t):

46.7 mg, 81% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.42 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.0 Hz, 1H), 7.29 (d, *J* = 4.5 Hz, 5H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.00 (d, *J* = 10.0 Hz, 1H), 4.18 – 4.12 (m, *J* = 8.0 Hz, 1H), 2.43 – 2.30 (m, 2H), 1.91-1.86 – 5.92 (m, *J* = 7.5 Hz, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 148.1, 140.3, 138.0, 129.5, 128.7, 128.4, 128.3, 128.0, 127.4, 123.6, 118.7, 59.2, 30.8, 13.9. HRMS *m/z* (ESI) calcd. for C₁₈H₁₇N₄([M+H]⁺) 289.1448, found 289.1455.

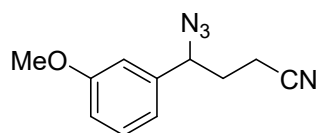
(*E*)-4-azido-6-cyclopropyl-6-(4-methoxyphenyl)hex-5-enitrile (3u):

40.6 mg, 72% yield; Reddish liquid; *E/Z*=3:1; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.17 (d, *J* = 8.0 Hz, 0.56), 6.92 (d, *J* = 7.5 Hz, 1.44H), 6.81 (d, *J* = 8.0 Hz, 1.44H), 6.76 (d, *J* = 8.0 Hz, 0.56H), 5.41 (d, *J* = 9.5 Hz, 0.28H), 5.29 (d, *J* = 9.5 Hz, 0.72H), 4.82 – 4.76 (m, 0.28H), 3.87 – 3.82 (m, 0.72H), 3.72 (s, 3H), 2.44 – 2.36 (m, 0.56H), 2.27 – 2.17 (m, 1.44H), 1.85 – 1.76 (m, 0.56H), 1.74 – 1.66 (m, 1.44H), 1.65 – 1.62 (m, 0.28H), 1.60 – 1.53 (m, 0.72H), 0.87 – 0.79 (m, 0.56H), 0.65 – 0.61 (m, 1.44H), 0.42 – 0.30 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 159.0, 158.9, 150.4, 148.0, 132.5, 129.7, 129.1, 128.7, 124.5, 120.5, 118.9, 118.8, 113.6, 113.2, 58.8, 57.7, 55.1, 55.1, 30.7, 30.6, 18.5, 14.0, 13.7, 11.8, 7.3, 6.7, 5.9, 5.3. HRMS *m/z* (ESI) calcd. for C₁₆H₁₉N₄O([M+H]⁺) 283.1553, found 283.1548.

4-azido-4-(4-methoxyphenyl)butanenitrile (3v):

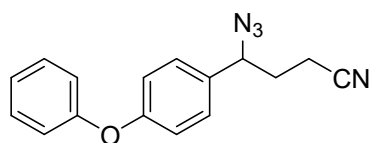
30.3 mg, 70% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 4.59 – 4.55 (m, 1H), 3.82 (s, 3H), 2.47 – 2.33 (m, 2H), 2.11 – 1.97 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 159.9, 129.5, 128.1, 118.7, 114.5, 63.9, 55.3, 31.9, 14.3, 62.7, 30.2, 13.8. HRMS *m/z* (ESI) calcd. for C₁₁H₁₃N₄O ([M+H]⁺) 217.1084, found 217.1086.

4-azido-4-(3-methoxyphenyl)butanenitrile (3w):



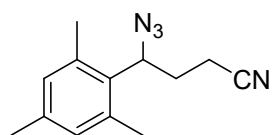
26.4 mg, 61% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.28 – 7.24 (m, 1H), 6.83 (d, $J = 6.5$ Hz, 2H), 6.78 (s, 1H), 4.53 (t, $J = 7.0$ Hz, 1H), 3.76 (s, 3H), 2.44 – 2.37 (m, 1H), 2.33 – 2.25 (m, 1H), 2.04 – 1.92 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.1, 139.2, 130.3, 119.0, 118.7, 114.2, 112.5, 64.2, 55.3, 31.9, 14.2. HRMS m/z (ESI) calcd. for $\text{C}_{11}\text{H}_{13}\text{N}_4\text{O}$ ($[\text{M}+\text{H}]^+$) 217.1084, found 217.1087.

4-azido-4-(4-phenoxyphenyl)butanenitrile (3x):



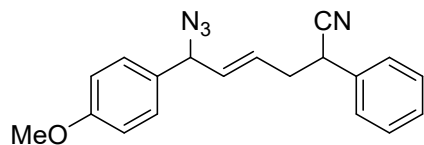
45.1 mg, 81% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.27 (m, 2H), 7.20 (d, $J = 6.0$ Hz, 2H), 7.07 (t, $J = 7.5$ Hz, 1H), 6.97 – 6.93 (m, 4H), 4.53 (t, $J = 7.0$ Hz, 1H), 2.44 – 2.27 (m, 2H), 2.06 – 1.89 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 158.0, 156.4, 132.1, 129.9, 128.3, 123.8, 119.4, 118.9, 118.6, 63.8, 31.9, 14.3. HRMS m/z (ESI) calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_4\text{O}$ ($[\text{M}+\text{H}]^+$) 279.1240, found 279.1240.

4-azido-4-mesitylbutanenitrile (3y):



25.6 mg, 56% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 6.81 (s, 2H), 5.14 – 5.09 (m, 1H), 2.47 – 2.37 (m, 2H), 2.34 (s, 6H), 2.19 (s, 3H), 2.16 – 2.11 (m, 1H), 1.90 – 1.82 (m, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 138.0, 136.4, 130.6, 118.9, 60.4, 29.4, 20.8, 20.6, 15.0. HRMS m/z (ESI) calcd. for $\text{C}_{13}\text{H}_{17}\text{N}_4$ ($[\text{M}+\text{H}]^+$) 229.1448, found 229.1456.

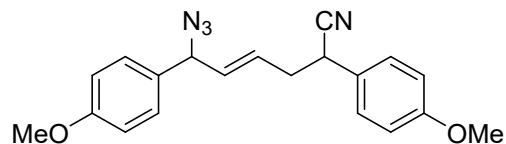
(E)-6-azido-6-(4-methoxyphenyl)-2-phenylhex-4-enitrile (5a):



45.8 mg, 72% yield; Light yellow liquid; dr= 3:2; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.24 (m, 7H), 6.79 (d, $J = 8.5$ Hz, 2H), 6.59 – 6.49 (m, 1H), 5.90 – 5.83 (m, 1H), 4.24 (d, $J = 12.0$ Hz, 0.6H), 3.99 – 3.95 (m, 0.6H), 3.92 – 3.86 (m, 0.4H), 3.83 (d, $J = 8.0$ Hz, 0.4H), 3.73 (s, 3H), 2.24 – 2.17 (m, 0.4H), 2.09 – 2.03 (m, 0.6H), 2.00 – 1.91 (m, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.0, 159.9, 135.0, 135.0, 134.6, 134.5, 129.3, 129.3, 128.5, 128.3, 128.1, 128.0, 128.0,

127.9, 127.5, 127.2, 122.4, 122.2, 120.4, 120.0, 114.1, 62.5, 61.9, 55.3, 41.0, 40.2, 34.3, 33.8. HRMS m/z (ESI) calcd. for $C_{19}H_{19}N_4O$ ($[M+H]^+$) 319.1553, found 319.1549.

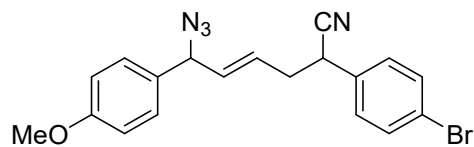
(E)-6-azido-2,6-bis(4-methoxyphenyl)hex-4-enitrile (5b):



47.3 mg, 68% yield; Light yellow liquid; dr= 1:1; 1H NMR (500 MHz, Chloroform-*d*) δ 7.33 (d, $J = 8.5$ Hz, 2H), 7.24 (d, $J = 6.5$ Hz,

2H), 6.93 – 6.86 (m, 4H), 6.65 – 6.55 (m, 1H), 5.97 – 5.90 (m, 1H), 4.31 – 4.25 (m, 0.5H), 4.00 – 3.96 (m, 0.5H), 3.93 (t, $J = 8.0$ Hz, 0.5H), 3.86 (t, $J = 8.0$ Hz, 0.5H), 3.81 (s, 6H), 2.29 – 2.22 (m, 0.5H), 2.15 – 2.08 (m, 0.5H), 2.04 – 1.96 (m, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.0, 159.9, 159.6, 159.5, 134.8, 134.6, 128.7, 128.4, 128.1, 128.0, 128.0, 126.9, 126.3, 122.5, 122.3, 120.6, 120.3, 114.7, 114.6, 114.1, 62.5, 61.8, 55.3, 55.3, 41.0, 40.2, 33.5, 33.0. HRMS m/z (ESI) calcd. for $C_{20}H_{21}N_4O_2$ ($[M+H]^+$) 349.1659, found 349.1658.

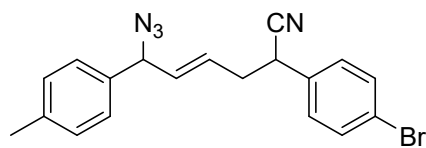
(E)-6-azido-2-(4-bromophenyl)-6-(4-methoxyphenyl)hex-4-enitrile (5c):



51.5 mg, 65% yield; Light yellow liquid; dr= 7:3; 1H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d, $J = 9.0$ Hz, 2H), 7.33 (d, $J = 7.0$ Hz, 2H),

7.22 (d, $J = 8.0$ Hz, 2H), 6.88 (d, $J = 8.0$ Hz, 2H), 6.67 – 6.58 (m, 1H), 5.97 – 5.89 (m, 1H), 4.32 (t, $J = 9.0$ Hz, 0.7H), 4.05 – 4.01 (m, 0.7H), 3.98 – 3.92 (m, 0.3H), 3.89 (t, $J = 8.0$ Hz, 0.3H), 3.82 (s, 3H), 2.31 – 2.24 (m, 0.3H), 2.14 – 2.08 (m, 0.7H), 2.05 – 1.95 (m, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.0, 135.3, 134.8, 134.1, 132.5, 132.5, 129.2, 128.9, 128.1, 128.1, 127.9, 122.7, 122.5, 122.2, 121.9, 119.5, 114.2, 62.5, 61.7, 55.3, 41.0, 40.1, 33.9, 33.4. HRMS m/z (ESI) calcd. for $C_{19}H_{18}BrN_4O$ ($[M+H]^+$) 397.0659, found 397.0655.

(E)-6-azido-2-(4-bromophenyl)-6-(p-tolyl)hex-4-enitrile (5d):

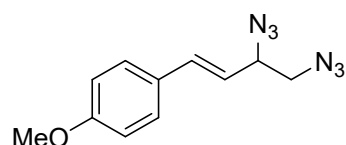


41.0 mg, 54% yield; Light yellow liquid; dr= 11:9; 1H NMR (500 MHz, Chloroform-*d*) δ 7.45 (t, $J = 9.5$ Hz, 2H), 7.23 – 7.19 (m, 2H), 7.17 – 7.12 (m,

2H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.61 – 6.52 (m, 1H), 5.97 – 5.90 (m, 1H), 4.25 (t, $J = 10.0$ Hz, 0.55H), 3.96 – 3.93 (m, 0.55H), 3.90 – 3.84 (m, 0.45H), 3.80 (t, $J = 7.5$

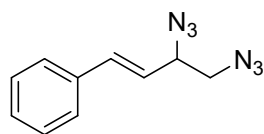
Hz, 0.45H), 2.27 (s, 3H), 2.22 – 2.16 (m, 0.45H), 2.06 – 2.00 (m, 0.55H), 1.97 – 1.87 (m, 1H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 138.8, 138.7, 135.6, 135.2, 134.0, 133.5, 132.5, 132.4, 129.4, 129.2, 128.9, 126.7, 126.7, 123.5, 123.2, 122.7, 122.4, 119.8, 119.5, 62.3, 61.6, 40.8, 40.0, 33.9, 33.3, 21.2. HRMS *m/z* (ESI) calcd. for C₁₉H₁₈BrN₄([M+H]⁺) 381.0709, found 381.0707.

(*E*)-1-(3,4-diazidobut-1-en-1-yl)-4-methoxybenzene (4a):



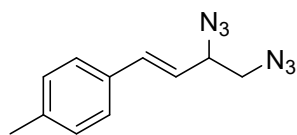
46.4 mg, 95% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.66 (d, *J* = 15.5 Hz, 1H), 6.00 – 5.95 (m, 1H), 4.25 – 4.20 (m, 1H), 3.81 (s, 3H), 3.37 (t, *J* = 6.0 Hz, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 159.9, 135.1, 128.1, 120.5, 114.1, 64.1, 55.3, 54.6. HRMS *m/z* (ESI) calcd. for C₁₁H₁₃N₆O ([M+H]⁺) 245.1145, found 245.1145.

(*E*)-(3,4-diazidobut-1-en-1-yl)benzene (4b):



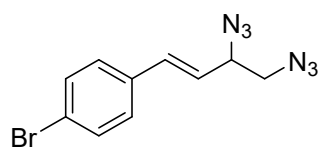
39.0 mg, 91% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.0 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.08 – 6.02 (m, 1H), 4.22 – 4.16 (m, 1H), 3.36 – 3.28 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 135.5, 135.3, 128.7, 128.6, 126.8, 122.9, 63.9, 54.5. HRMS *m/z* (ESI) calcd. for C₁₀H₁₁N₆([M+H]⁺) 215.1040, found 215.1041.

(*E*)-1-(3,4-diazidobut-1-en-1-yl)-4-methylbenzene (4c):



42.4 mg, 93% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.01 – 5.96 (m, 1H), 4.18 – 4.13 (m, 1H), 3.29 (t, *J* = 6.0 Hz, 2H), 2.27 (s, 3H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 138.6, 135.5, 132.5, 129.4, 126.7, 121.8, 64.0, 54.5, 21.2. HRMS *m/z* (ESI) calcd for C₁₁H₁₃N₆ ([M+H]⁺) 229.1196, found 229.1197.

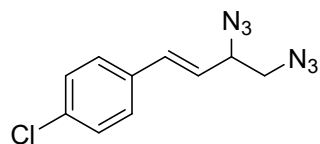
(*E*)-1-bromo-4-(3,4-diazidobut-1-en-1-yl)benzene (4d):



50.2 mg, 86% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.05 – 5.99 (m, 1H), 4.18

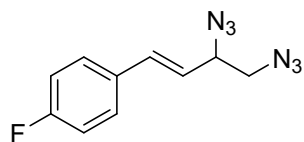
– 4.12 (m, 1H), 3.34 – 3.26 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 134.2 , 134.1 , 131.8 , 128.2 , 123.8 , 122.4 , 63.6 , 54.3. HRMS *m/z* (ESI) calcd. for C₁₀H₁₀BrN₆([M+H]⁺)293.0145, found 293.0145.

(E)-1-chloro-4-(3,4-diazidobut-1-en-1-yl)benzene (4e):



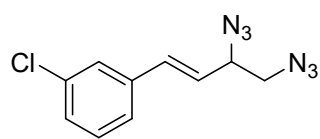
41.2 mg, 83% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 4H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.12 – 6.07 (m, 1H), 4.28 – 4.21 (m, 1H), 3.42 – 3.36 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 134.3 , 134.1 , 133.8 , 128.9 , 128.0 , 123.7 , 63.7 , 54.4. HRMS *m/z* (ESI) calcd. for C₁₀H₁₀ClN₆ ([M+H]⁺) 249.0650, found 249.0652.

(E)-1-(3,4-diazidobut-1-en-1-yl)-4-fluorobenzene (4f):



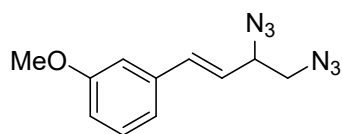
41.8 mg, 90% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.31 (t, *J* = 7.0 Hz, 2H), 6.96 (t, *J* = 8.5 Hz, 2H), 6.62 (d, *J* = 15.5 Hz, 1H), 5.97 (m, 1H), 4.19 – 4.15 (m, 1H), 3.36 – 3.28 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 163.9, 161.9, 134.3, 131.6, 131.5, 128.5, 128.4, 122.8, 122.7, 115.8, 115.6, 77.3, 63.8, 54.5. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -112.61. HRMS *m/z* (ESI) calcd. for C₁₀H₁₀FN₆([M+H]⁺) 233.0945, found 233.0945.

(E)-1-chloro-3-(3,4-diazidobut-1-en-1-yl)benzene (4g):



38.7 mg, 78% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 7.27 (s, 3H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.16 – 6.10 (m, 1H), 4.27 – 4.22 (m, 1H), 3.43 – 3.36 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 137.2 , 134.7 , 134.0 , 130.0 , 128.5 , 126.6 , 125.0 , 124.6 , 63.6 , 54.4. HRMS *m/z* (ESI) calcd. for C₁₀H₁₀ClN₆([M+H]⁺) 249.0650, found 249.0649.

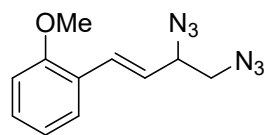
(E)-1-(3,4-diazidobut-1-en-1-yl)-3-methoxybenzene (4h):



40.0 mg, 82% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.86 (s, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.06 – 6.01 (m, 1H), 4.20 – 4.14 (m, 1H), 3.75 (s, 3H), 3.35 – 3.27 (m,

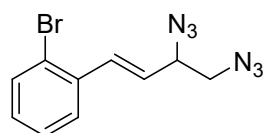
2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 159.8, 136.8, 135.4, 129.7, 123.3, 119.4, 114.2, 112.1, 63.8, 55.2, 54.5. HRMS m/z (ESI) calcd. for $\text{C}_{11}\text{H}_{13}\text{N}_6\text{O}([\text{M}+\text{H}]^+)$ 245.1145, found 245.1151.

(*E*)-1-(3,4-diazidobut-1-en-1-yl)-2-methoxybenzene (4i):



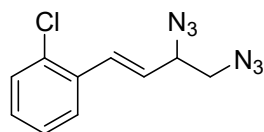
43.5 mg, 89% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.44 (d, $J = 9.5$ Hz, 1H), 7.29 – 7.26 (m, 1H), 7.04 (d, $J = 16.0$ Hz, 1H), 6.94 (t, $J = 7.5$ Hz, 1H), 6.89 (d, $J = 8.0$ Hz, 1H), 6.19 – 6.13 (m, 1H), 4.28 – 4.24 (m, 1H), 3.86 (s, 3H), 3.42 – 3.36 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 157.1, 130.7, 129.7, 127.3, 124.3, 123.4, 120.7, 111.0, 64.5, 55.5, 54.7. HRMS m/z (ESI) calcd. for $\text{C}_{11}\text{H}_{13}\text{N}_6\text{O}([\text{M}+\text{H}]^+)$ 245.1145, found 245.1145.

(*E*)-1-chloro-3-(3,4-diazidobut-1-en-1-yl)benzene (4j):



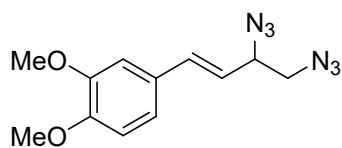
53.7 mg, 92% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, $J = 8.0$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.29 (t, $J = 7.5$ Hz, 1H), 7.16 (t, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 15.5$ Hz, 1H), 5.10 – 5.04 (m, 1H), 4.33 – 4.28 (m, 1H), 3.46 – 3.37 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 135.42, 134.30, 133.04, 129.79, 127.61, 127.27, 125.95, 123.85, 63.53, 54.40. HRMS m/z (ESI) calcd. for $\text{C}_{10}\text{H}_{10}\text{BrN}_6([\text{M}+\text{H}]^+)$ 293.0145, found 293.0151.

(*E*)-1-chloro-2-(3,4-diazidobut-1-en-1-yl)benzene (4k):



42.7 mg, 86% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.44 (m, 1H), 7.33 – 7.27 (m, 1H), 7.18 – 7.15 (m, 2H), 7.04 (d, $J = 16.0$ Hz, 1H), 6.01 – 6.01 (m, 1H), 4.26 – 4.20 (m, 1H), 3.39 – 3.30 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 133.6, 133.4, 131.7, 129.8, 129.6, 127.1, 127.0, 125.8, 63.7, 54.4. HRMS m/z (ESI) calcd for $\text{C}_{10}\text{H}_{10}\text{ClN}_6([\text{M}+\text{H}]^+)$ 249.0650, found 249.0649.

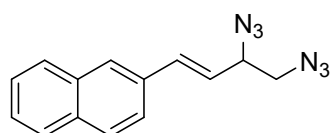
(*E*)-4-(3,4-diazidobut-1-en-1-yl)-1,2-dimethoxybenzene (4l):



47.7 mg, 87% yield; Light yellow solid; mp 74.5-79.2 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 6.87 (t, $J = 4.0$ Hz, 2H), 6.74 (d, $J = 6.5$ Hz, 1H), 6.57 (d, $J = 15.5$ Hz, 1H),

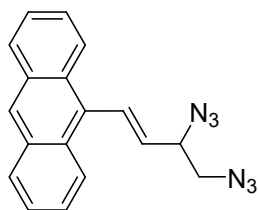
5.93 – 5.87 (m, 1H), 4.17 – 4.12 (m, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.33 – 3.24 (m, 2H).¹³C NMR (125 MHz, Chloroform-*d*) δ 149.5, 149.0, 135.1, 128.2, 120.6, 120.2, 110.9, 108.8, 63.9, 55.7, 55.7, 54.4. HRMS *m/z* (ESI) calcd. for C₁₂H₁₅N₆O₂([M+H]⁺) 275.1251, found 275.1253.

(*E*)-2-(3,4-diazidobut-1-en-1-yl)naphthalene (4m):



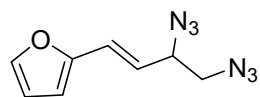
47.0 mg, 89% yield; white solid; mp 75.2-89.6 °C; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.0 Hz, 3H), 7.66 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 4.0 Hz, 2H), 6.76 (d, *J* = 15.5 Hz, 1H), 6.15 – 6.09 (m, 1H), 4.20 – 4.15 (m, 1H), 3.33 – 3.26 (m, 2H).¹³C NMR (125 MHz, Chloroform-*d*) δ 135.5, 133.4, 132.7, 128.4, 128.1, 127.7, 127.3, 126.5, 126.4, 123.3, 123.2, 63.9, 54.5. HRMS *m/z* (ESI) calcd. for C₁₄H₁₃N₆([M+H]⁺) 265.1196, found 265.1185.

(*E*)-9-(3,4-diazidobut-1-en-1-yl)anthracene (4n):



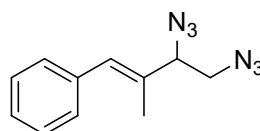
54.0 mg, 86% yield; Reddish liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.46 – 7.39 (m, 4H), 7.32 (d, *J* = 16.0 Hz, 1H), 5.87 – 5.82 (m, 1H), 4.43 – 4.38 (m, 1H), 3.44 (t, *J* = 4.5 Hz, 2H).¹³C NMR (125 MHz, Chloroform-*d*) δ 131.8, 131.6, 131.2, 130.5, 129.1, 128.7, 127.1, 125.8, 125.3, 125.1, 64.0, 54.4. HRMS *m/z* (ESI) calcd. for C₁₈H₁₅N₆([M+H]⁺) 315.1353, found 315.1359.

(*E*)-2-(3,4-diazidobut-1-en-1-yl)furan (4o):



34.7 mg, 85% yield; Grey liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 6.53 (d, *J* = 15.5 Hz, 1H), 6.40 (s, 1H), 6.35 (s, 1H), 6.08 – 6.02 (m, 1H), 4.24 – 4.19 (m, 1H), 3.41 – 3.36 (m, 2H).¹³C NMR (125 MHz, Chloroform-*d*) δ 151.0, 142.8, 123.2, 121.3, 111.5, 110.1, 63.6, 54.5. HRMS *m/z* (ESI) calcd. for C₈H₉N₆O([M+H]⁺) 205.0832, found 205.0835.

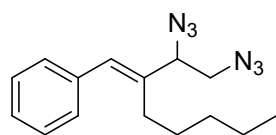
(*E*)-(3,4-diazido-2-methylbut-1-en-1-yl)benzene (4p):



42.0 mg, 92% yield; Colorless liquid; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.26 (m, 3H), 6.63 (s, 1H), 4.25 – 4.18 (m, 1H), 3.41 – 3.39 (m, 2H), 1.90 (d,

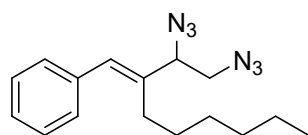
$J = 1.5$ Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 136.2 , 132.4 , 131.0 , 129.0 , 128.3 , 127.3 , 69.5 , 53.0 , 13.9. HRMS m/z (ESI) calcd. for $\text{C}_{11}\text{H}_{13}\text{N}_6$ ($[\text{M}+\text{H}]^+$) 229.1196, found 229.1197.

(E)-(2-(1,2-diazidoethyl)hept-1-en-1-yl)benzene (4q):



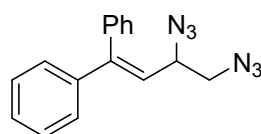
50.6 mg, 89% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.28 (t, $J = 8.0$ Hz, 2H), 7.19 (t, $J = 8.0$ Hz, 3H), 6.54 (s, 1H), 4.11 (t, $J = 6.5$ Hz, 1H), 3.33 (d, $J = 6.5$ Hz, 2H), 2.27 – 2.06 (m, 2H), 1.44 – 1.41 (m, 2H), 1.23 – 1.20 (m, 4H), 0.80 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 137.5, 136.4, 130.3, 128.6, 128.3, 127.2, 67.4, 53.9, 31.9, 29.2, 28.3, 22.2, 13.9. HRMS m/z (ESI) calcd. for $\text{C}_{15}\text{H}_{21}\text{N}_6$ ($[\text{M}+\text{H}]^+$) 285.1822, found 285.1826.

(E)-(2-(1,2-diazidoethyl)oct-1-en-1-yl)benzene (4r):



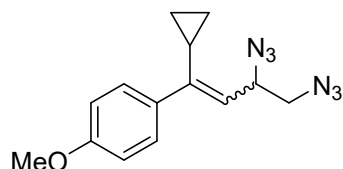
53.6 mg, 90% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.35 (t, $J = 7.5$ Hz, 2H), 7.26 (t, $J = 7.5$ Hz, 3H), 6.62 (s, 1H), 4.19 (t, $J = 6.5$ Hz, 1H), 3.41 (d, $J = 6.5$ Hz, 2H), 2.35 – 2.14 (m, 2H), 1.53 – 1.45 (m, 2H), 1.32 – 1.23 (m, 6H), 0.87 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 137.5, 136.4, 130.4, 128.7, 128.7, 128.3, 127.2, 67.4, 53.9, 31.4, 29.4, 29.2, 28.6, 22.5, 14.0. HRMS m/z (ESI) calcd. for $\text{C}_{16}\text{H}_{23}\text{N}_6$ ($[\text{M}+\text{H}]^+$) 299.1979, found 299.1984.

(3,4-diazidobut-1-ene-1,1-diyl)dibenzene (4s):



52.8 mg, 91% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.32 (m, 3H), 7.21 (m, 5H), 7.11 (d, $J = 7.5$ Hz, 2H), 5.97 (d, $J = 10.0$ Hz, 1H), 4.17 – 4.12 (m, 1H), 3.26 (d, $J = 6.0$ Hz, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 148.77, 140.41, 138.13, 129.48, 128.68, 128.41, 128.33, 128.03, 127.48, 121.76, 60.11, 54.56. HRMS m/z (ESI) calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_6$ ($[\text{M}+\text{H}]^+$) 291.1353, found 291.1346.

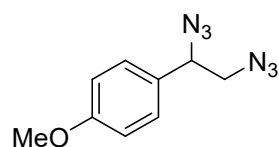
(E)-1-(3,4-diazido-1-cyclopropylbut-1-en-1-yl)-4-methoxybenzene (4t):



46.0 mg, 81% yield; Colorless liquid; $E/Z=6:1$; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.18 (d, $J = 5.5$ Hz,

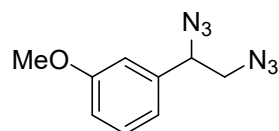
0.3H), 6.94 (d, $J = 7.5$ Hz, 1.7H), 6.82 (d, $J = 7.5$ Hz, 1.7H), 6.78 (d, $J = 10.0$ Hz, 0.3H), 5.47 (d, $J = 9.5$ Hz, 0.15H), 5.36 (d, $J = 9.5$ Hz, 0.85H), 4.84 – 4.79 (m, 0.15H), 3.97 – 3.92 (m, 0.85H), 3.75 (s, 3.51H), 3.31 (t, $J = 4.0$ Hz, 0.3H), 3.13 (t, $J = 3.5$ Hz, 1.7H), 1.73 – 1.69 (m, 0.15H), 1.62 – 1.55 (m, 0.85H), 0.85 – 0.80 (m, 0.3H), 0.69 – 0.62 (m, 1.7H), 0.44 – 0.33 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 159.0, 151.2, 129.8, 129.4, 128.8, 122.7, 118.7, 113.8, 113.3, 59.8, 58.9, 55.2, 54.6, 18.7, 12.0, 6.8, 6.0, 5.5. HRMS m/z (ESI) calcd. for $\text{C}_{14}\text{H}_{17}\text{N}_6\text{O}([\text{M}+\text{H}]^+)$ 285.1458, found 285.1455.

1-(1,2-diazidoethyl)-4-methoxybenzene (4u):



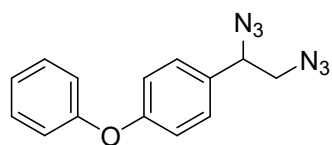
37.5 mg, 86% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.18 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 4.56 – 4.53 (m, 1H), 3.74 (s, 3H), 3.43 – 3.31 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.0, 129.80, 128.2, 114.4, 65.0, 55.8, 55.3. HRMS m/z (ESI) calcd. for $\text{C}_9\text{H}_{11}\text{N}_6\text{O}([\text{M}+\text{H}]^+)$ 219.0989, found 219.0989.

1-(1,2-diazidoethyl)-3-methoxybenzene (4v):



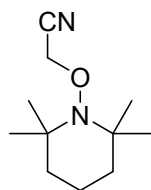
27.5 mg, 63% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.25 (t, $J = 8.0$ Hz, 1H), 6.84 (d, $J = 8.0$ Hz, 2H), 6.80 (s, 1H), 4.59 – 4.54 (m, 1H), 3.76 (s, 3H), 3.45 – 3.34 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.1, 137.8, 130.2, 119.1, 114.3, 112.6, 65.5, 55.9, 55.3. HRMS m/z (ESI) calcd. for $\text{C}_9\text{H}_{11}\text{N}_6\text{O}([\text{M}+\text{H}]^+)$ 219.0989, found 219.0981.

1-(1,2-diazidoethyl)-4-phenoxybenzene (4w):



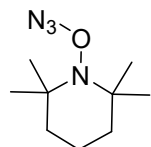
45.9 mg, 82% yield; Colorless liquid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.28 (t, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.07 (t, $J = 7.5$ Hz, 1H), 6.95 (d, $J = 7.0$ Hz, 4H), 4.59 – 4.56 (m, 1H), 3.45 – 3.34 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 158.1, 156.5, 130.8, 129.9, 128.4, 123.8, 119.4, 118.9, 65.0, 55.9. HRMS m/z (ESI) calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_6\text{O}([\text{M}+\text{H}]^+)$ 281.1145, found 281.1155.

2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acetonitrile:



Colorless liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.45 (s, 2H), 1.51 – 1.45 (m, m 1H), 1.38 (d, $J = 16.5$ Hz, 4H), 1.28 – 1.24 (m, 1H), 1.13 (s, 6H), 1.03 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 115.9, 62.5, 60.2, 39.5, 32.9, 19.8, 16.8. LRMS (EI, 70eV) m/z (%): 196 (4), 181 (75), 156 (100), 109 (52); HRMS m/z (ESI) calcd for $\text{C}_{11}\text{H}_{21}\text{N}_2\text{O}([\text{M}+\text{H}]^+)$ 197.1648, found 197.1645.

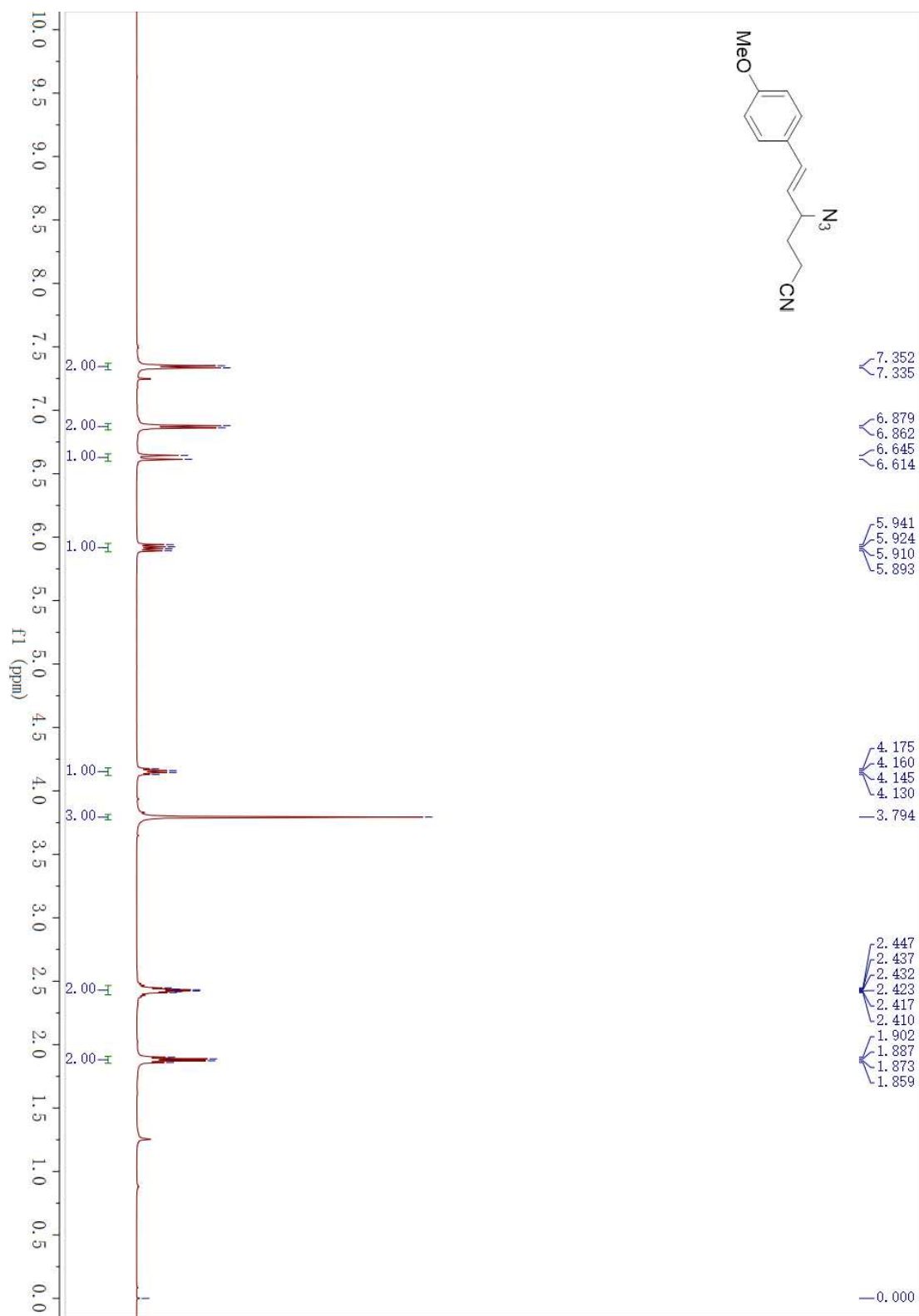
1-(azidooxy)-2,2,6,6-tetramethylpiperidine:

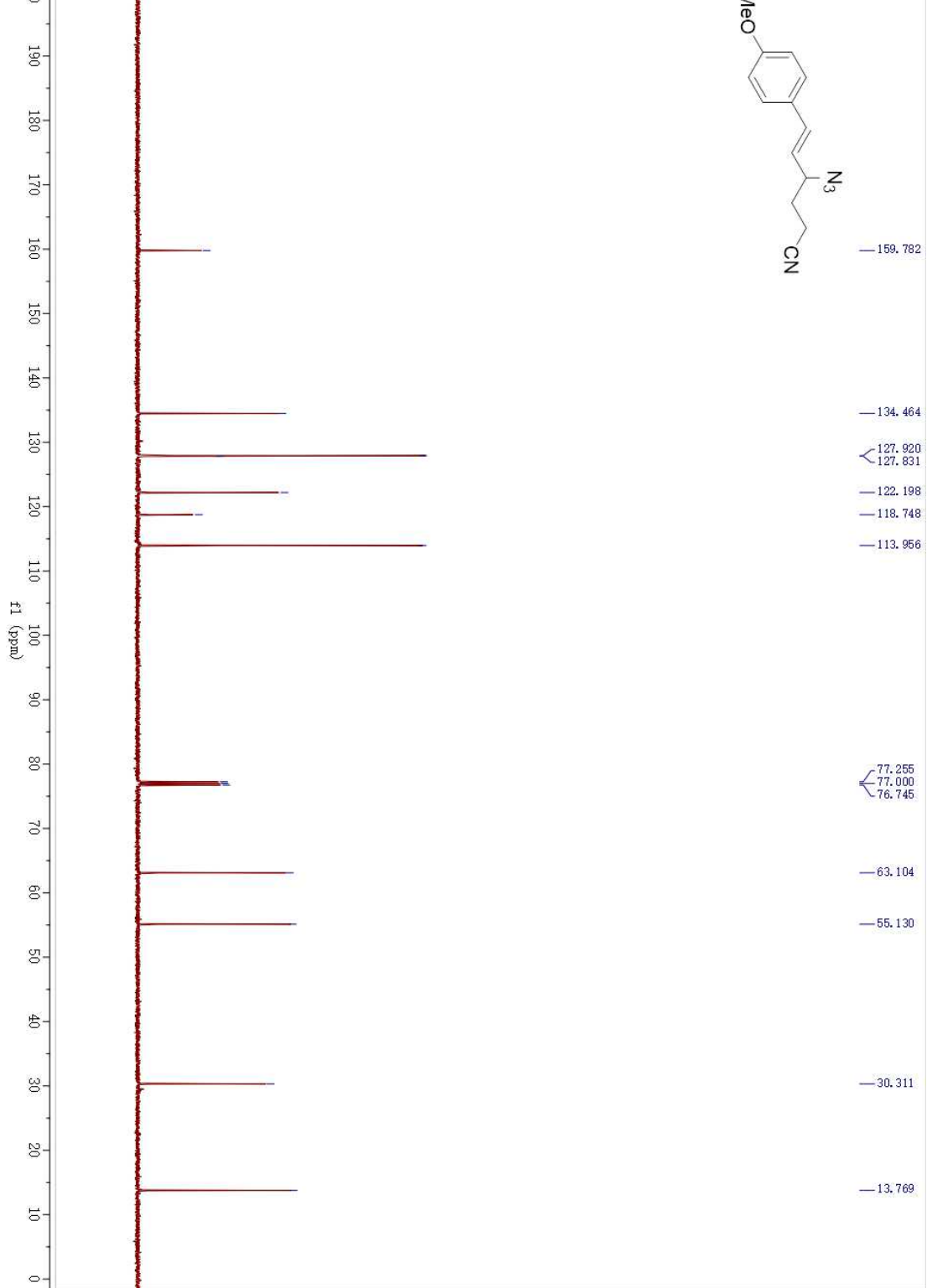
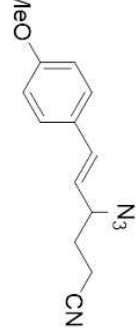


Colorless liquid; LRMS (EI, 70eV) m/z (%): 198 (5), 142 (84), 133 (100), 87 (73); HRMS m/z (ESI) calcd for $\text{C}_9\text{H}_{19}\text{N}_4\text{O}([\text{M}+\text{H}]^+)$ 199.1553, found 199.1559.

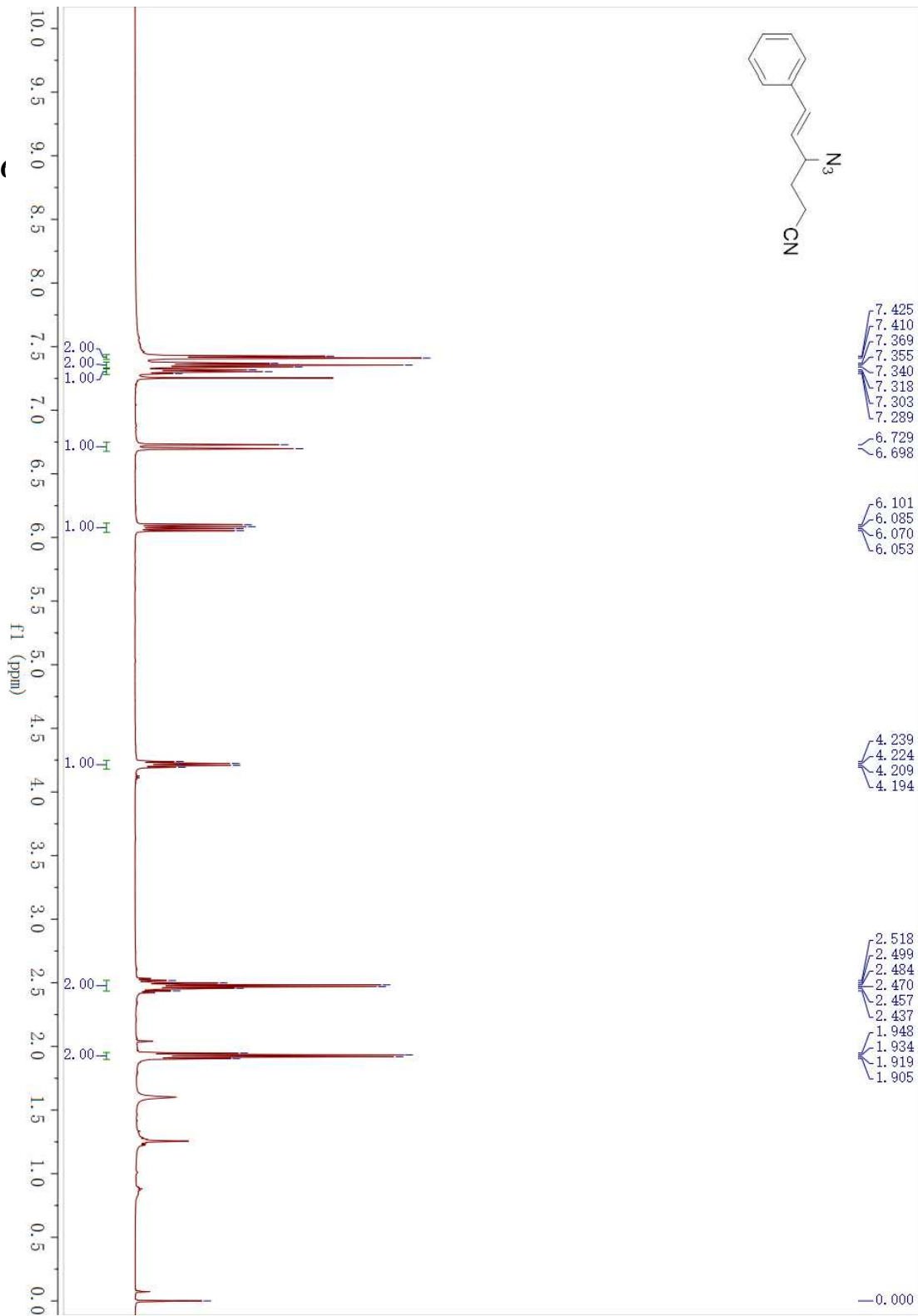
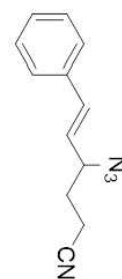
(C) Spectra

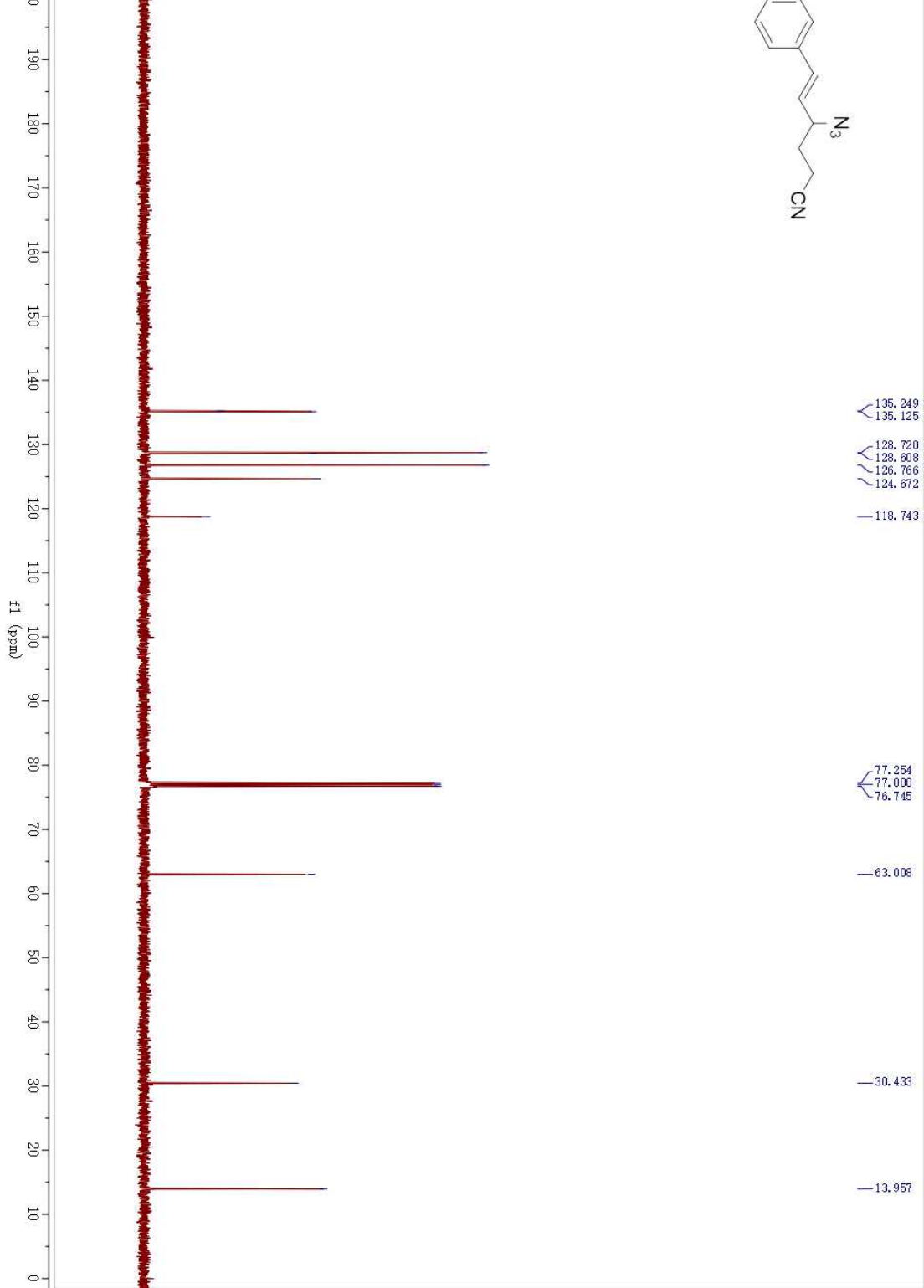
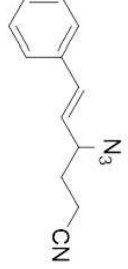
(E)-4-azido-6-(4-methoxyphenyl)hex-5-enitrile (3a):



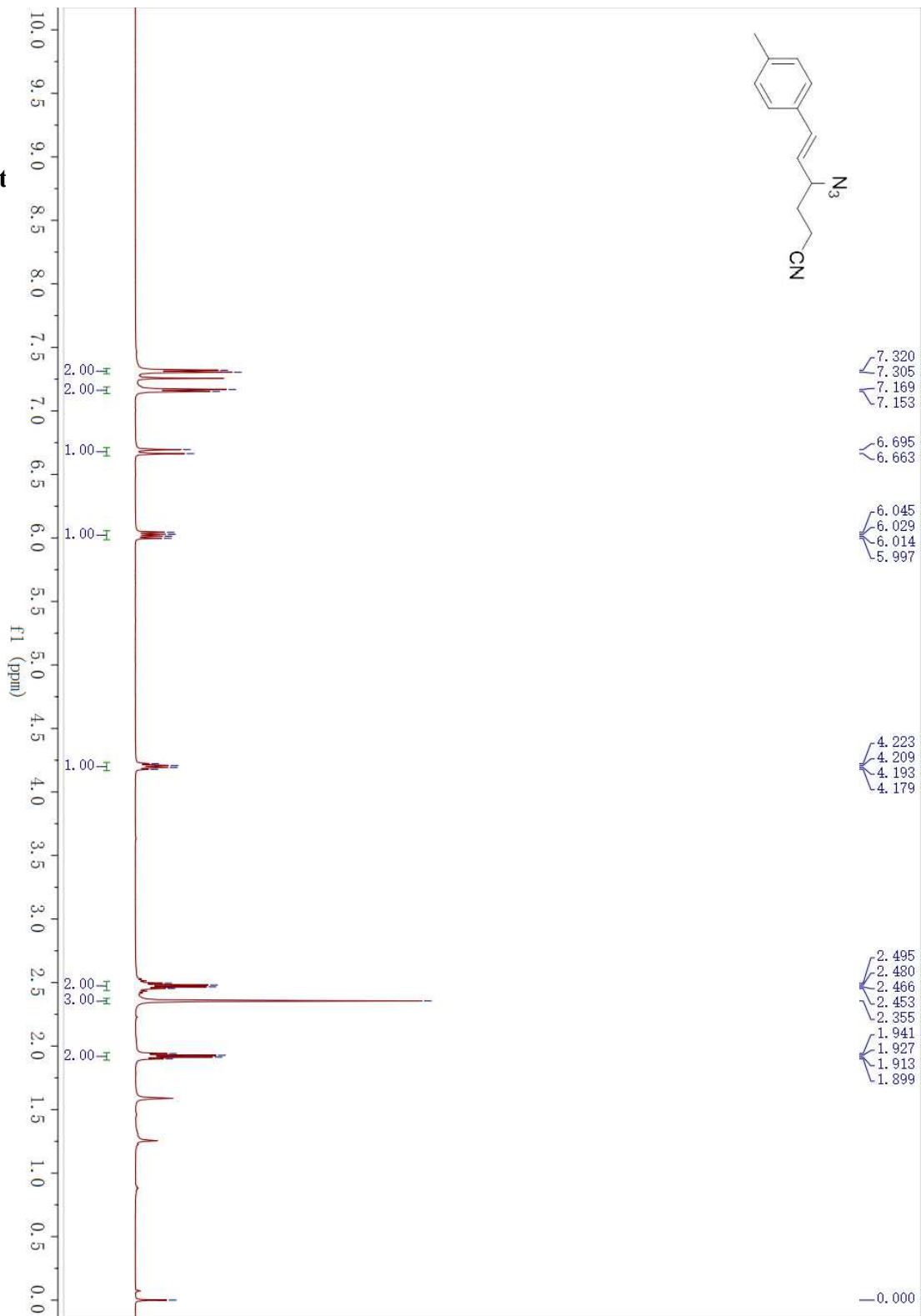


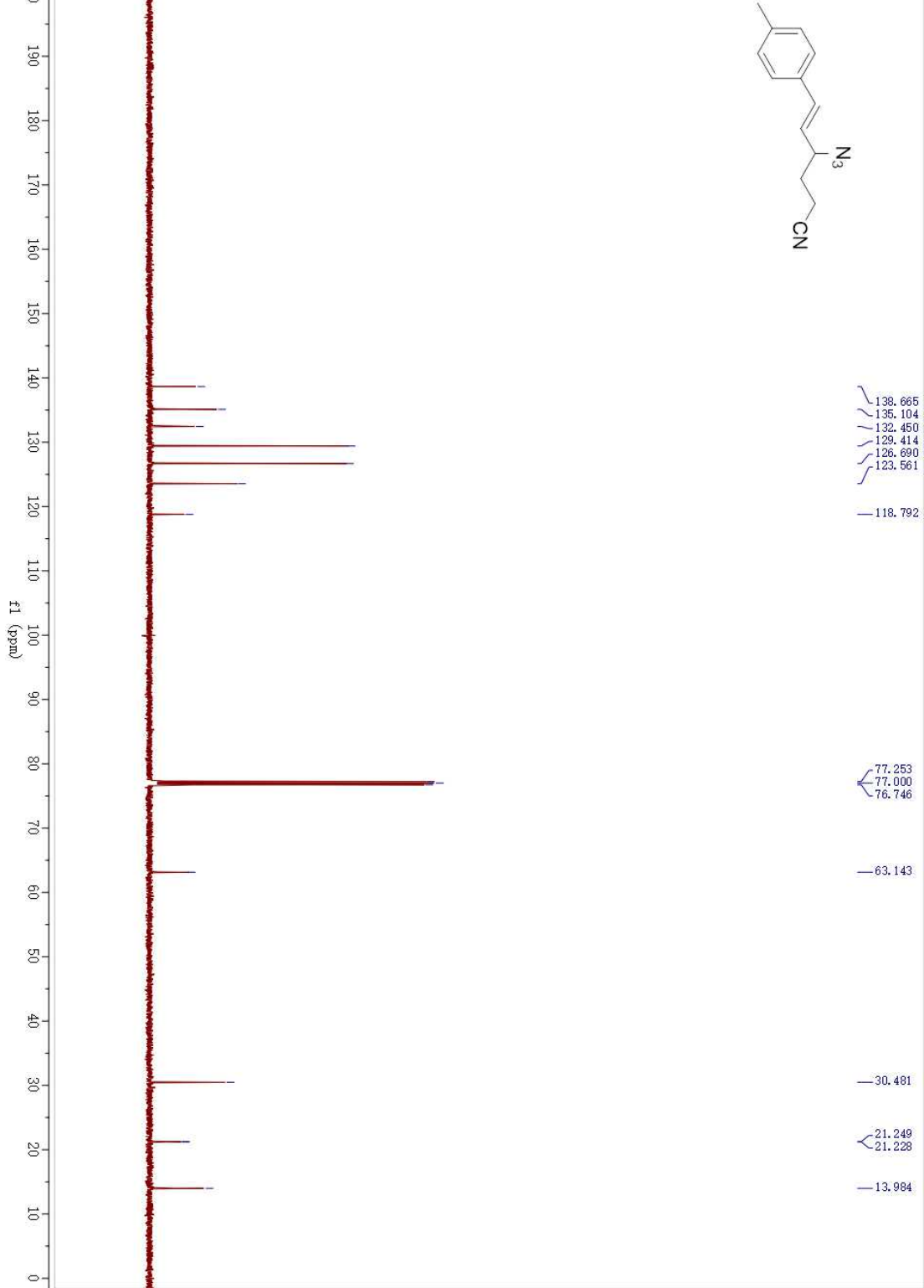
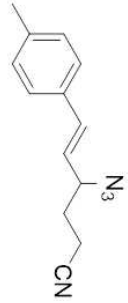
(E)-1-(hept-1-en-1-yl)-4-phenylbut-3-yn-1-amine



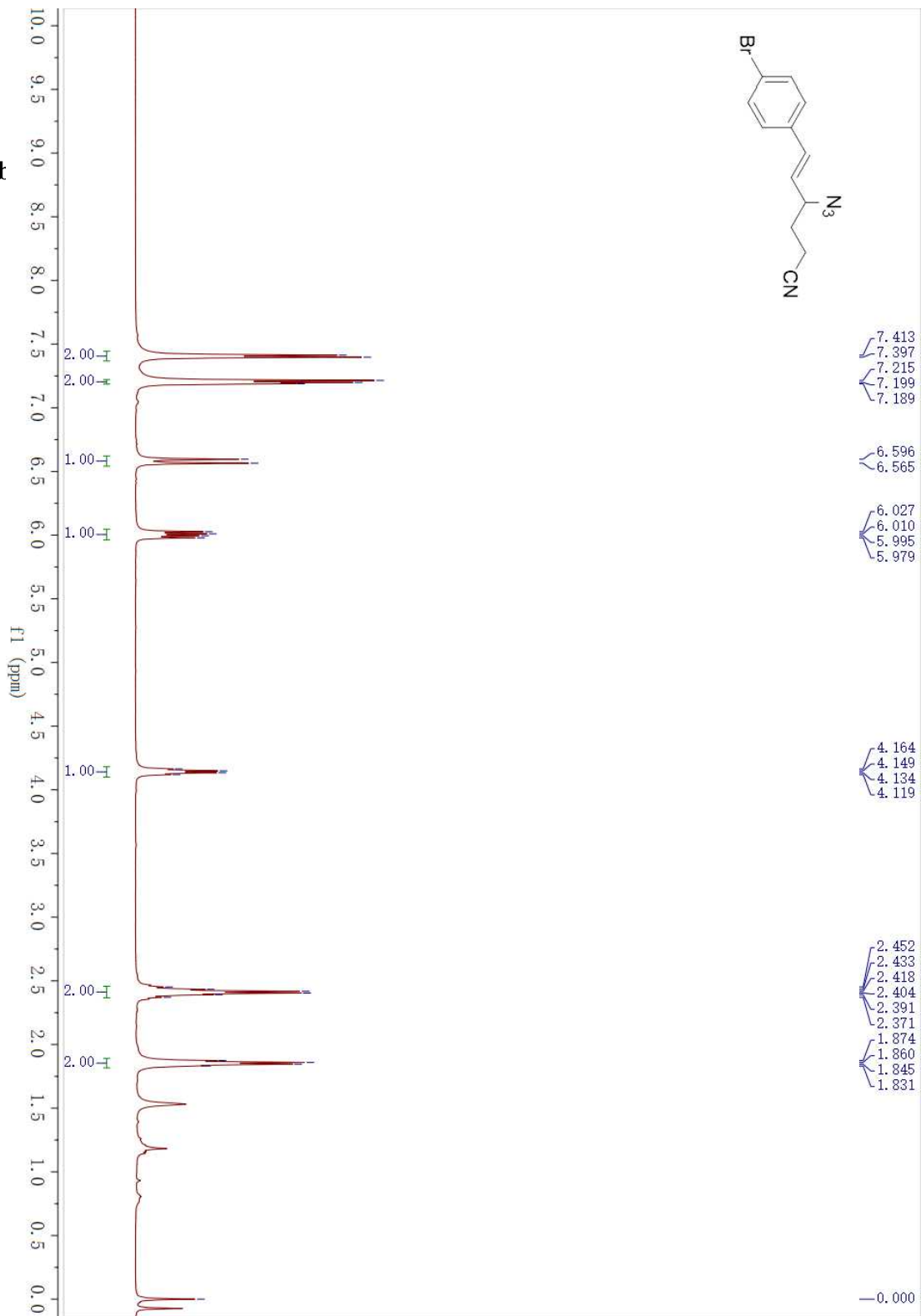


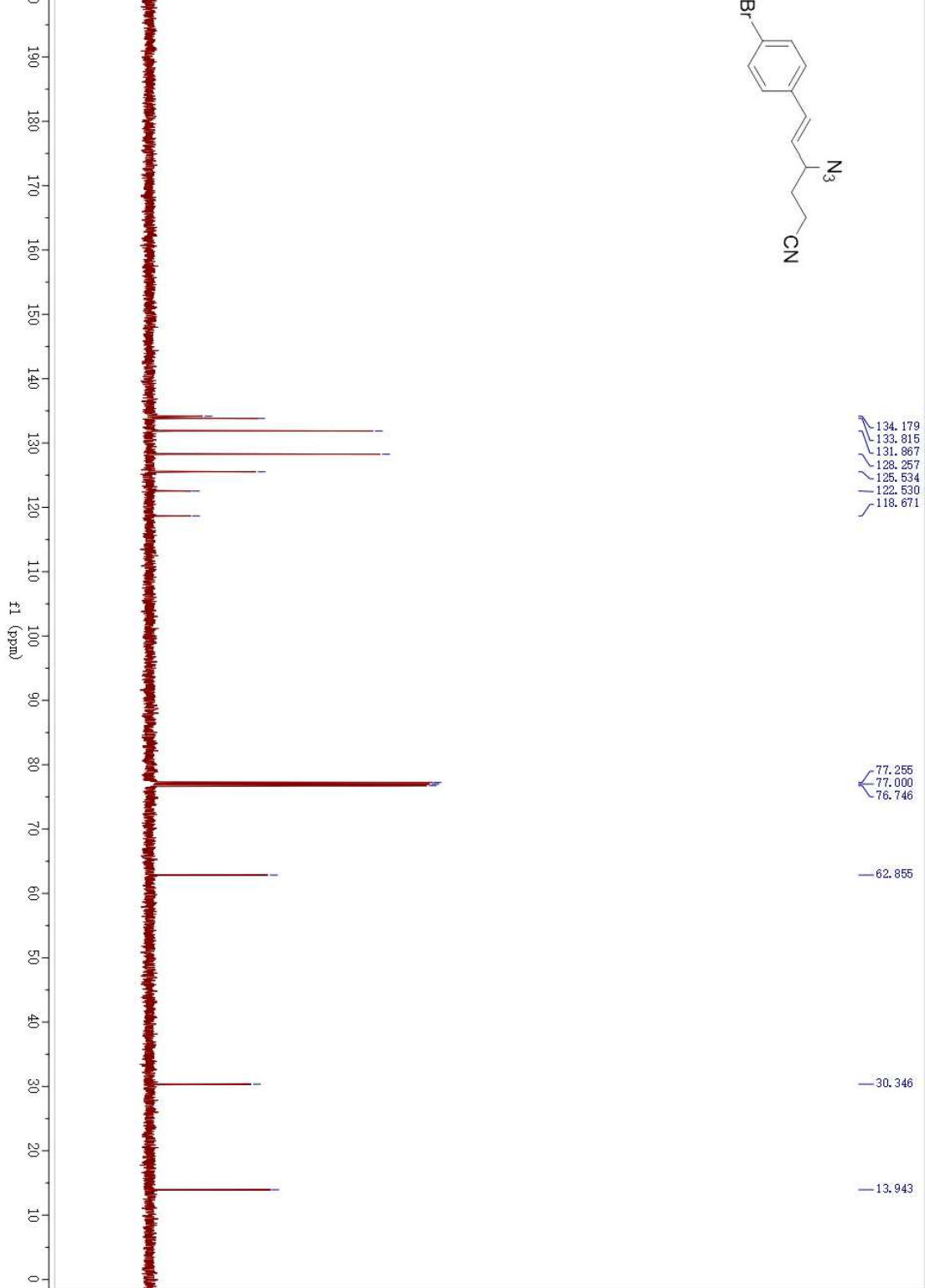
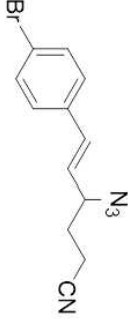
(E)-4-azido-6-(p-t



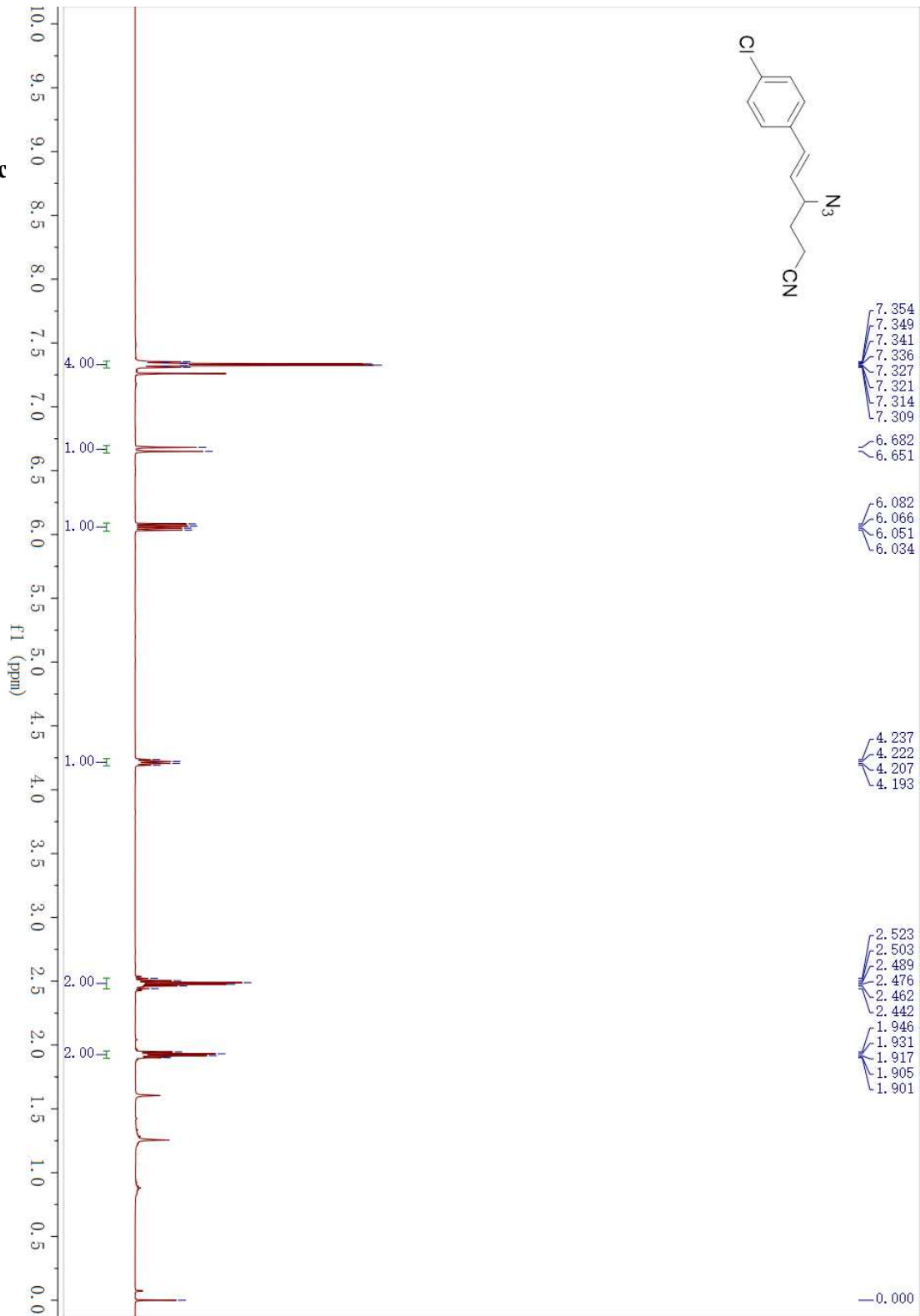


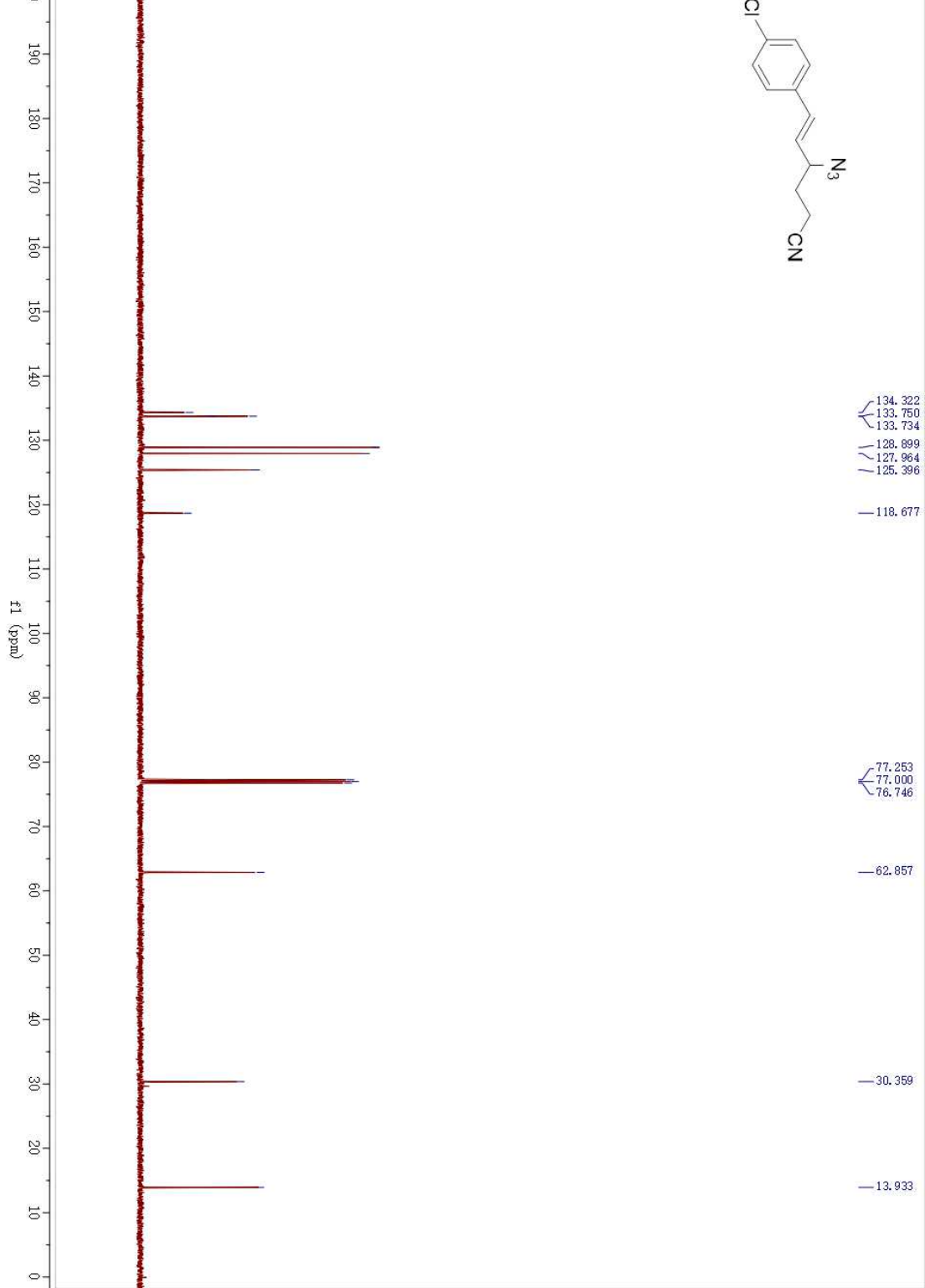
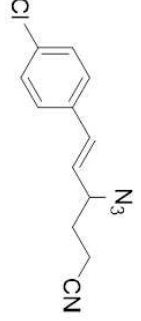
(E)-4-azido-6-(4-t



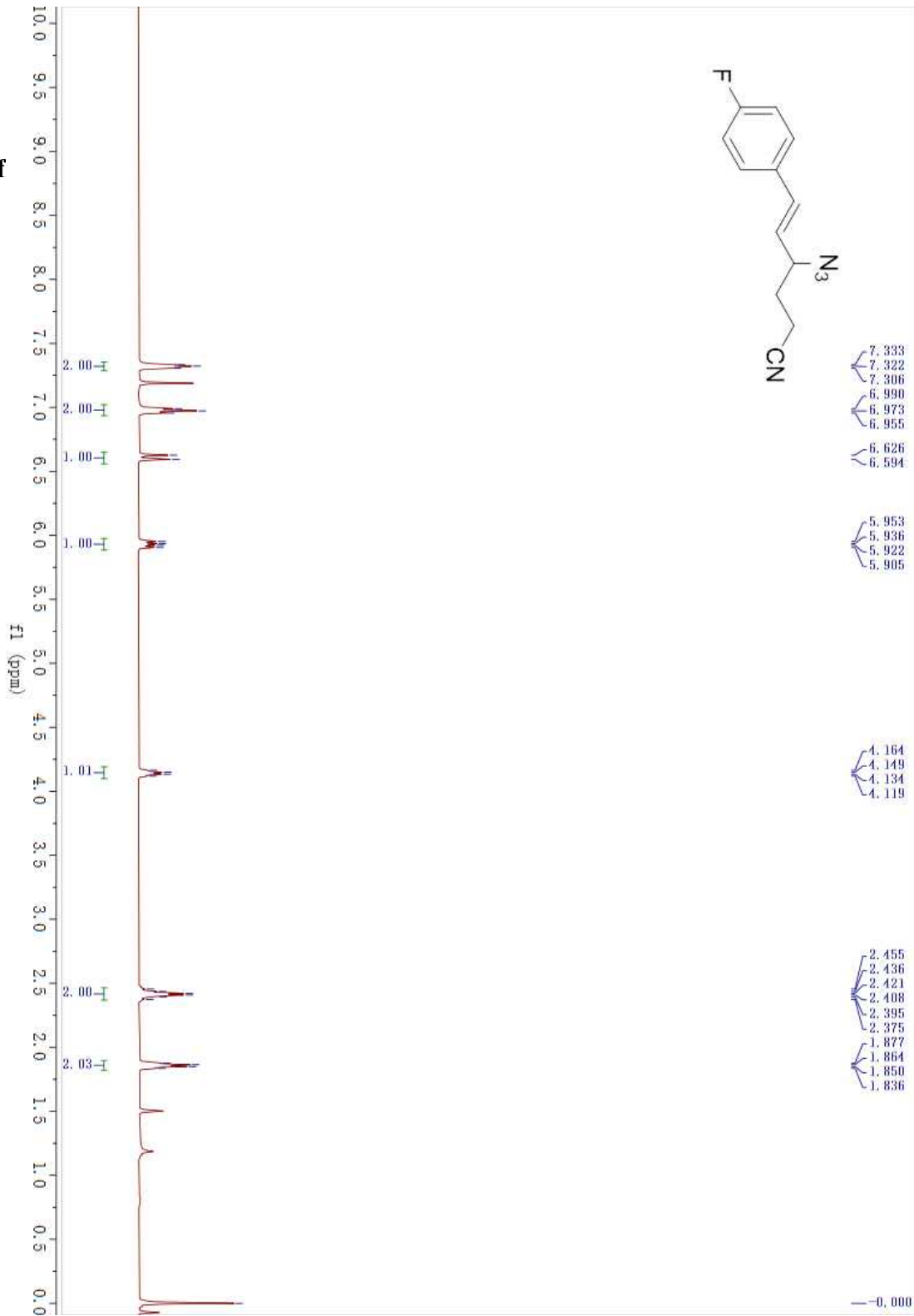


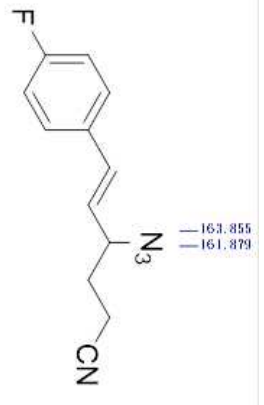
(E)-4-azido-6-(4-c





(E)-4-azido-6-(4-f





163.855
161.879

133.930
131.462
131.437
128.466
128.461
124.497
124.478

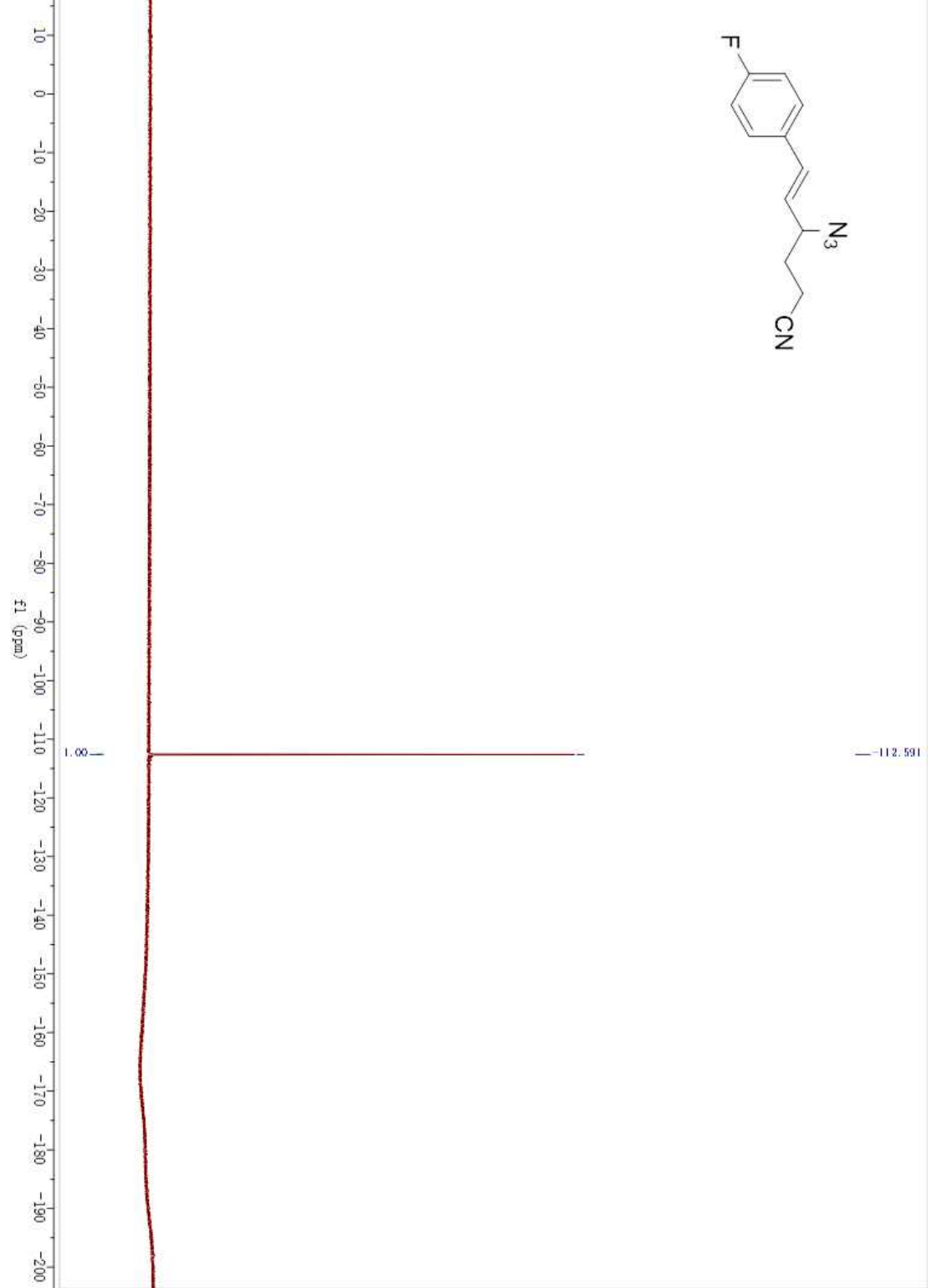
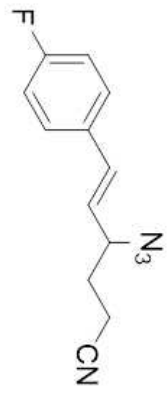
77.254
77.000
76.746

62.973

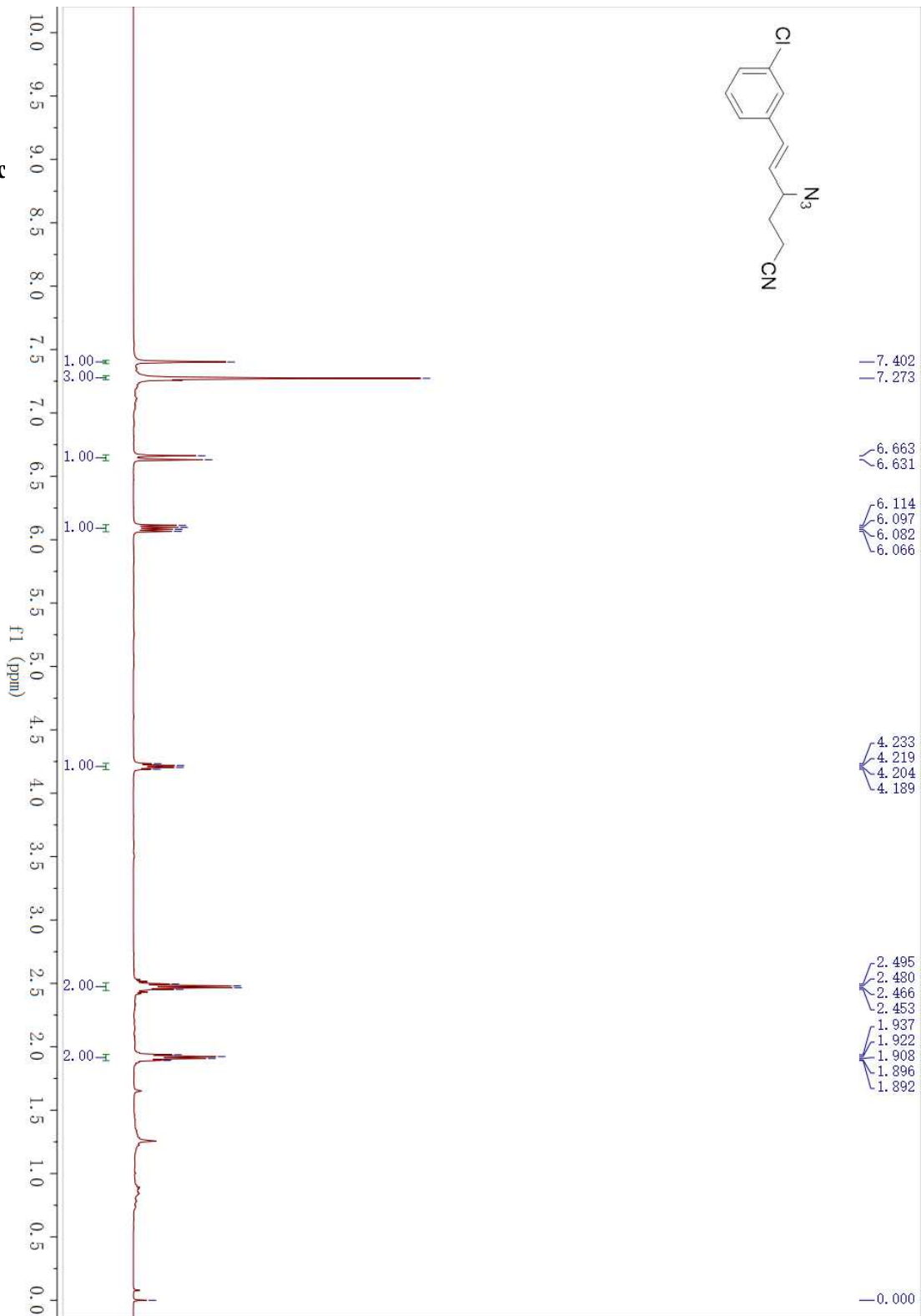
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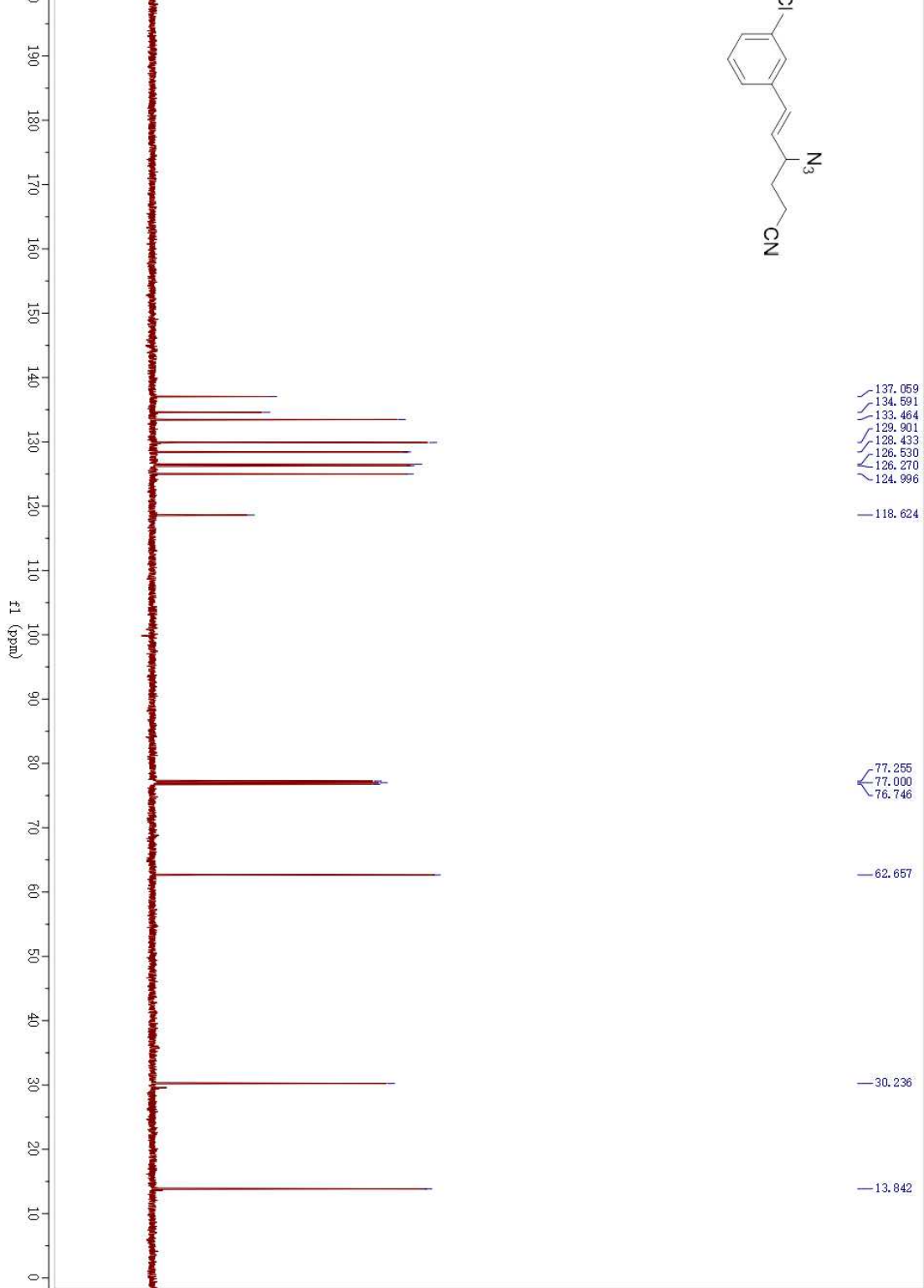
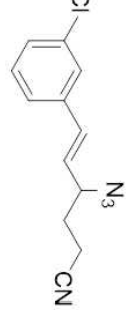
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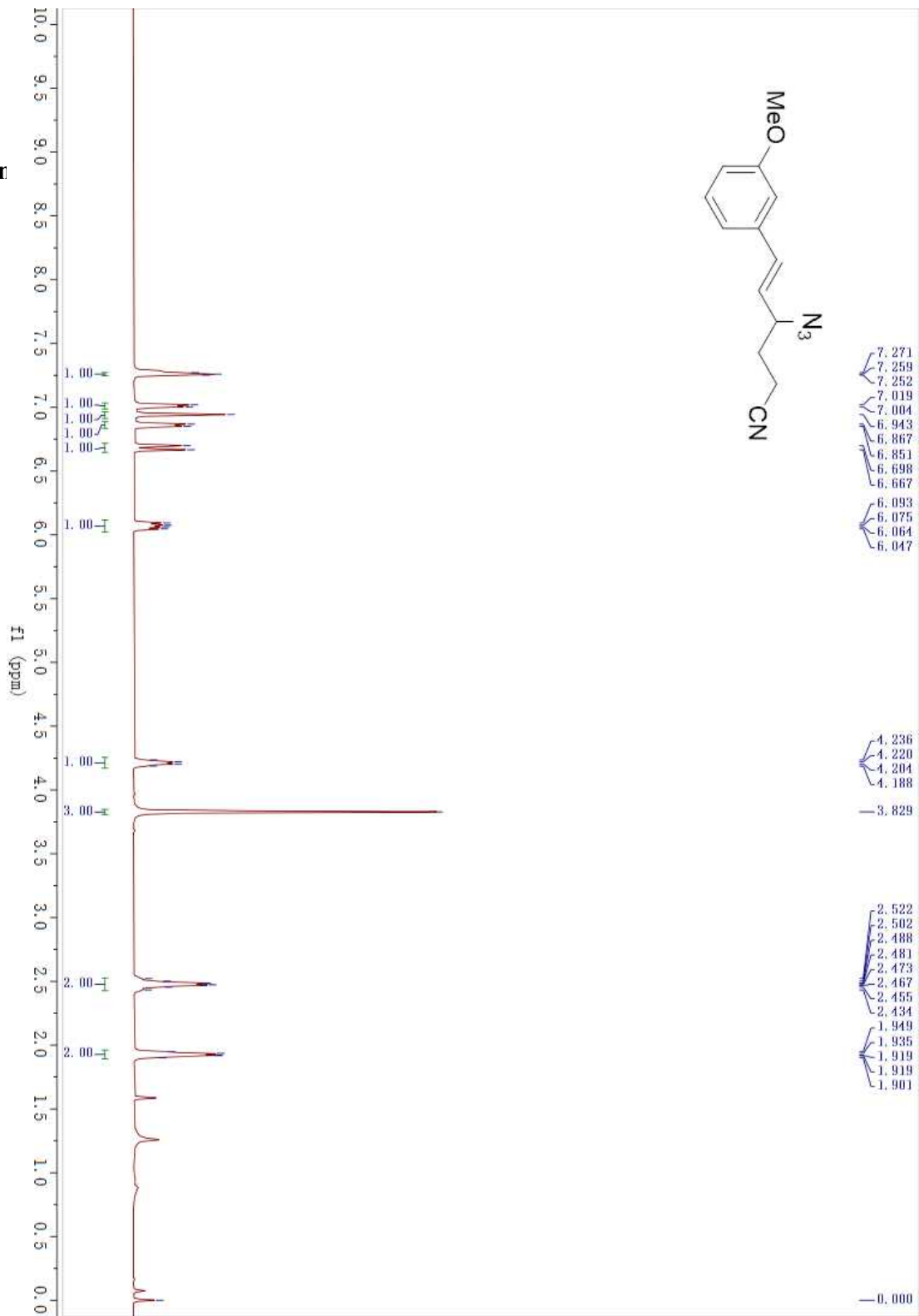


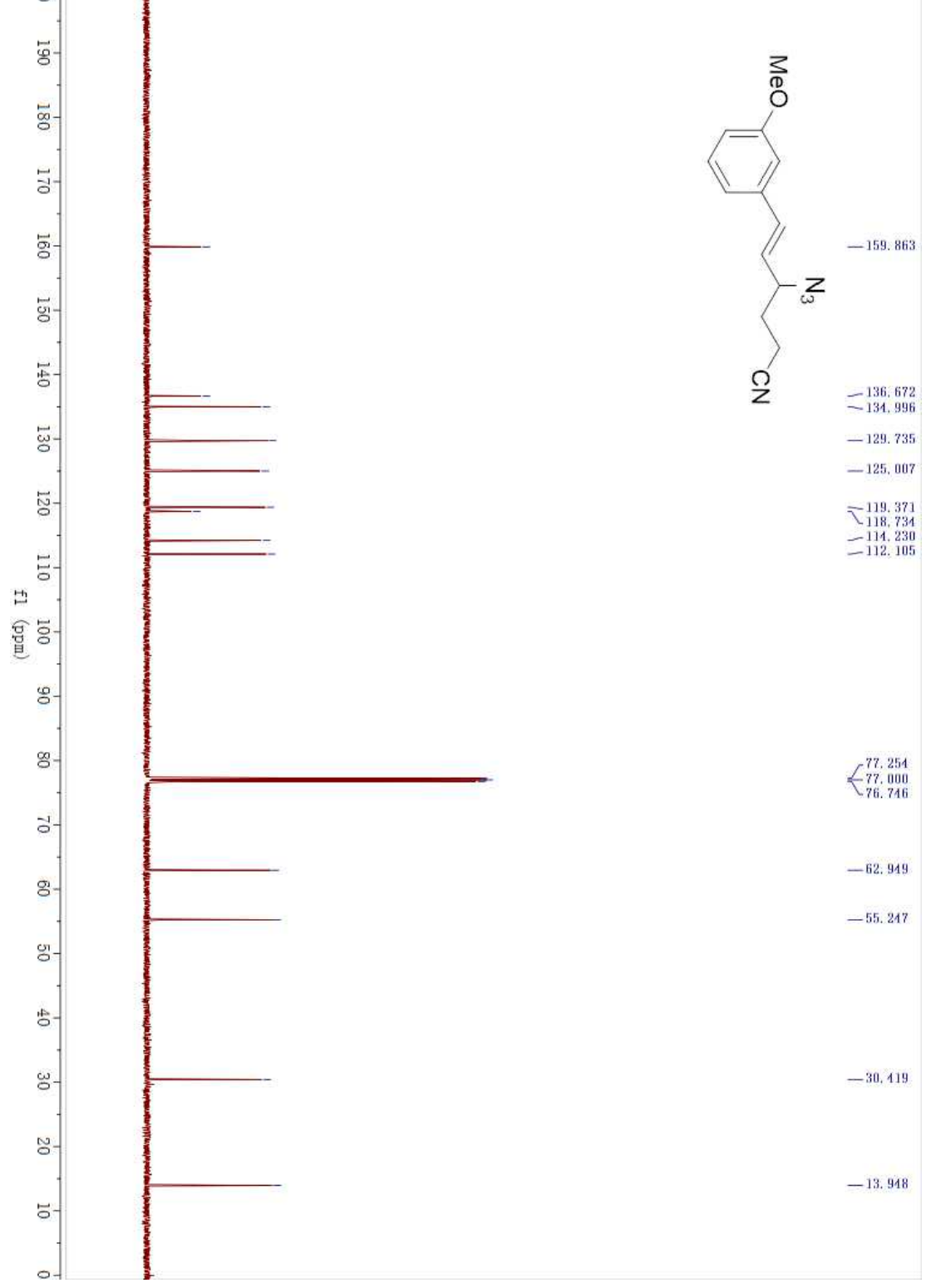
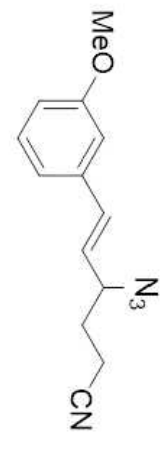
(E)-4-azido-6-(3-c



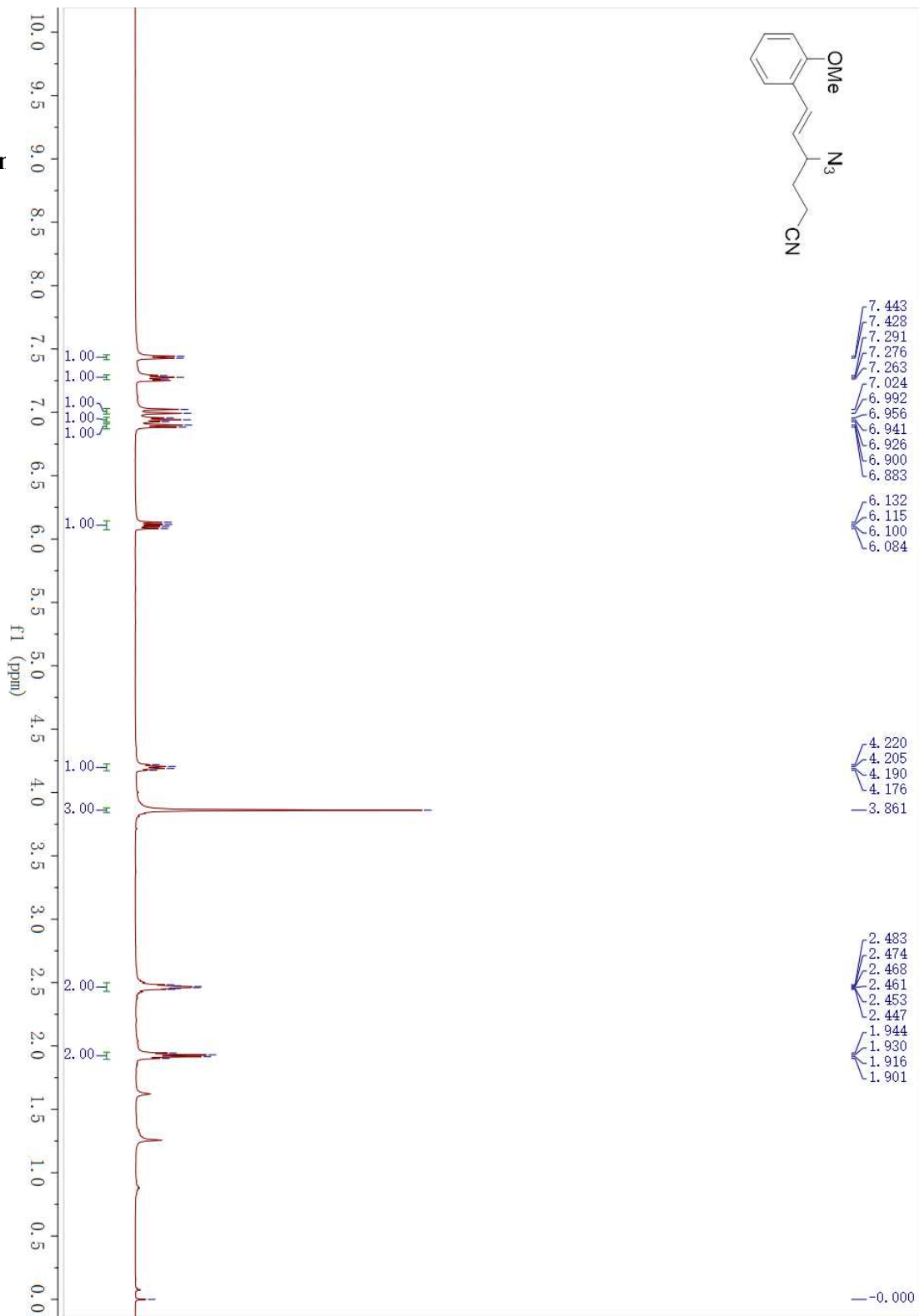


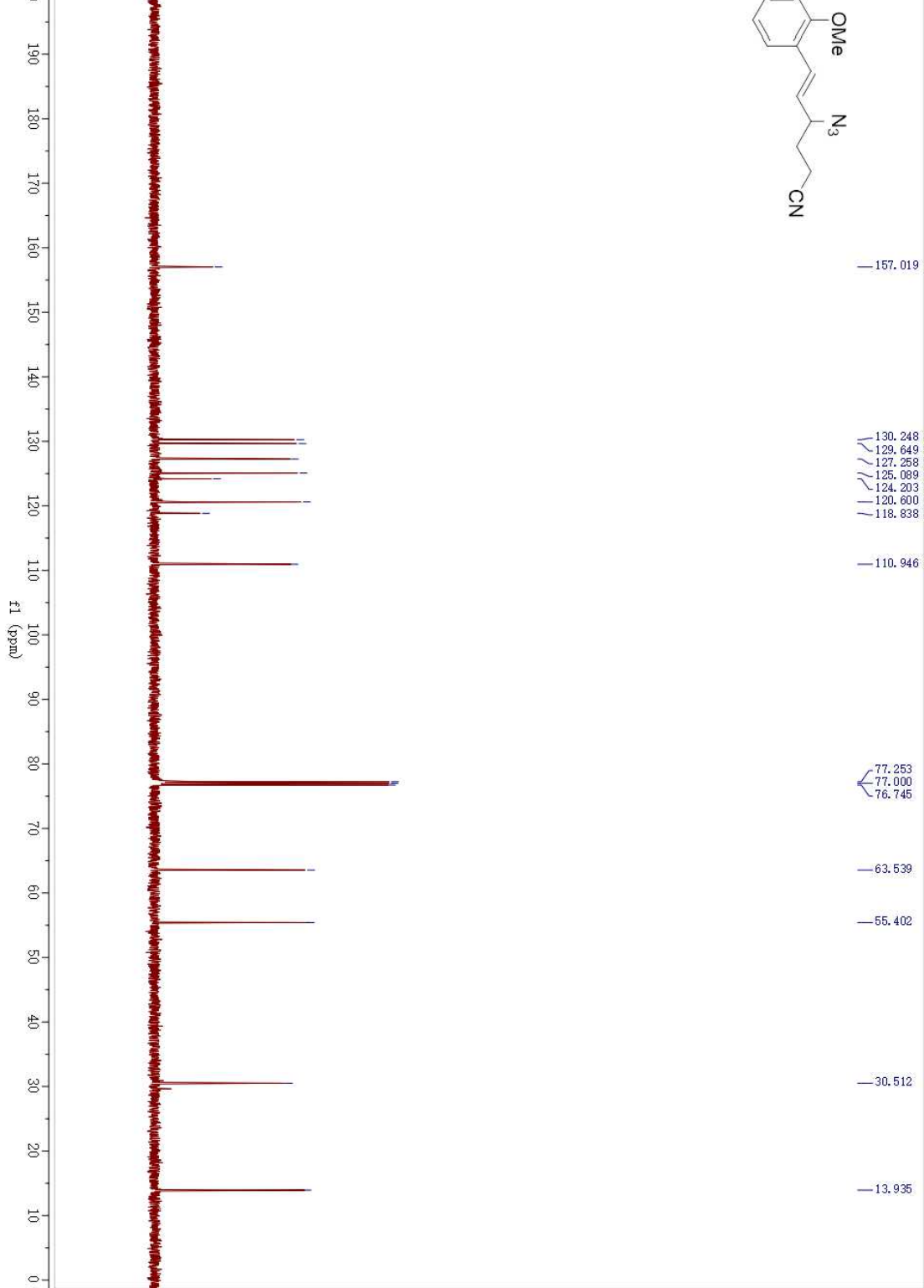
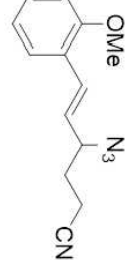
(E)-4-azido-6-(3-methoxyphenyl)-6-cyano-1-butene

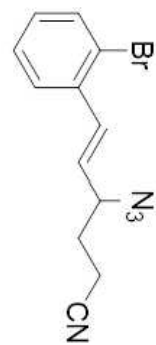




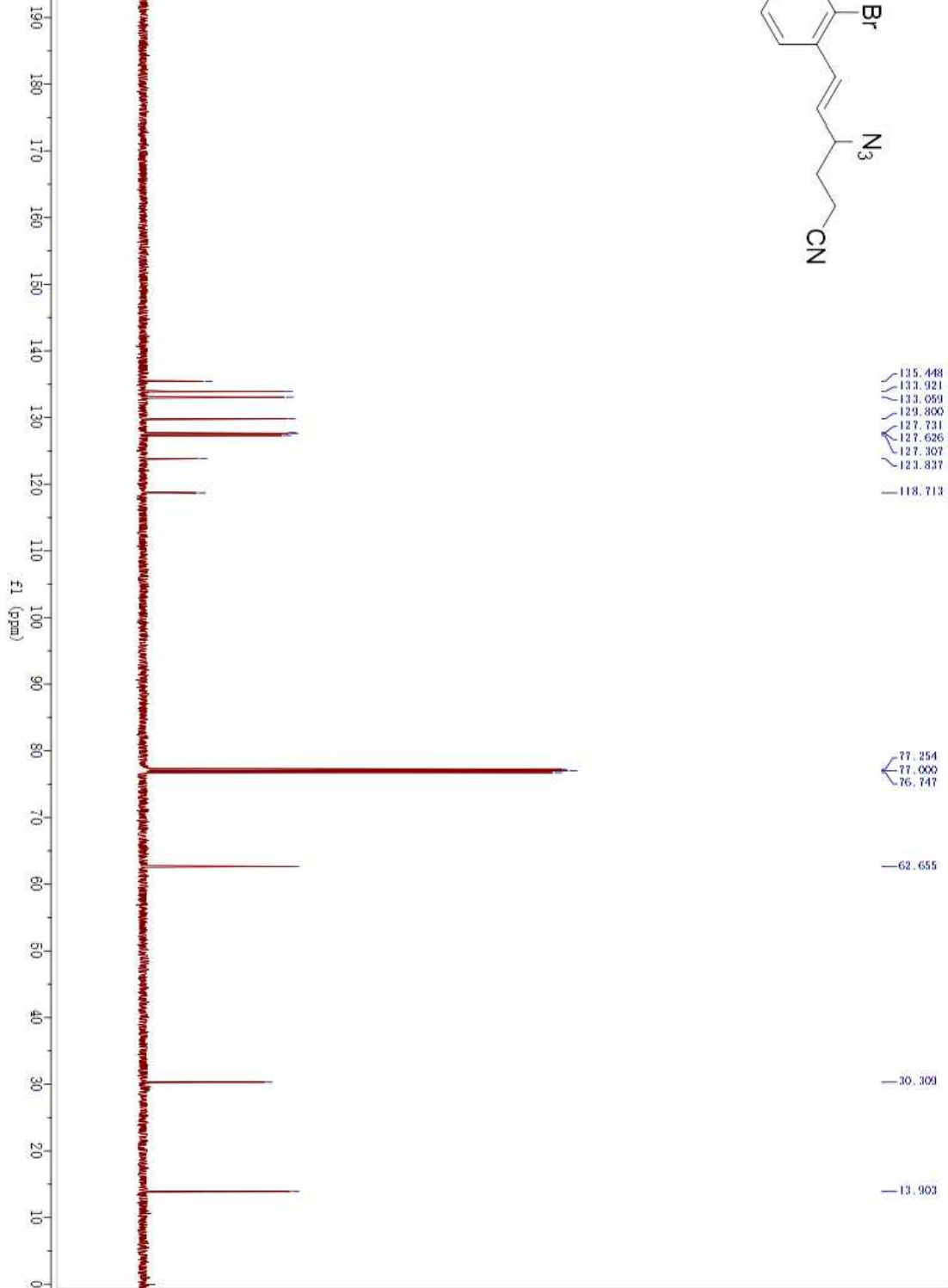
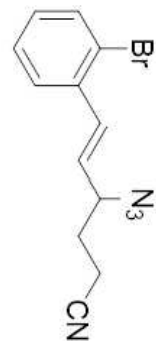
(E)-4-azido-6-(2-methoxyphenyl)hexanenitrile



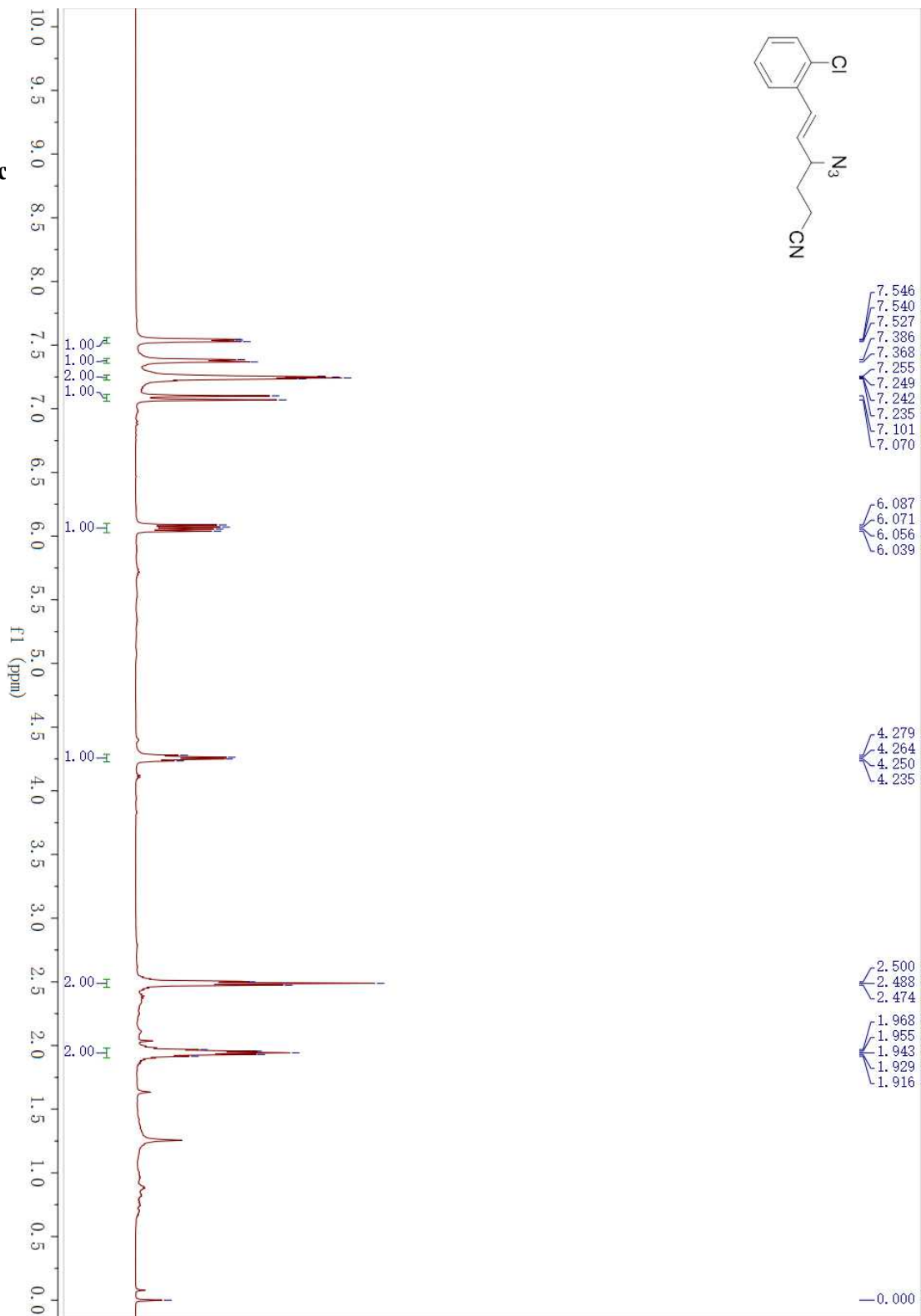


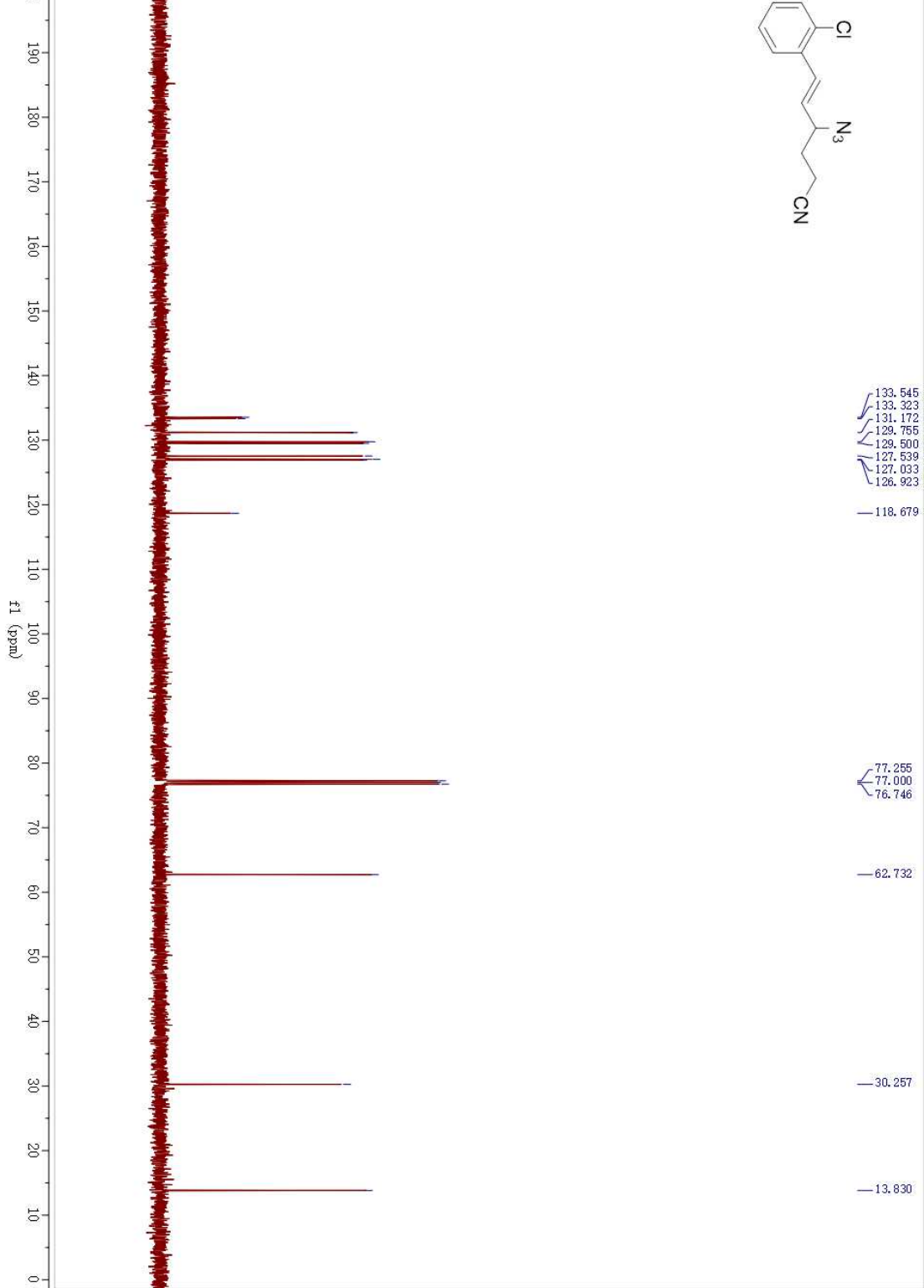
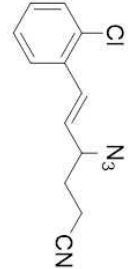


(E)-4-azido-6-(2-t

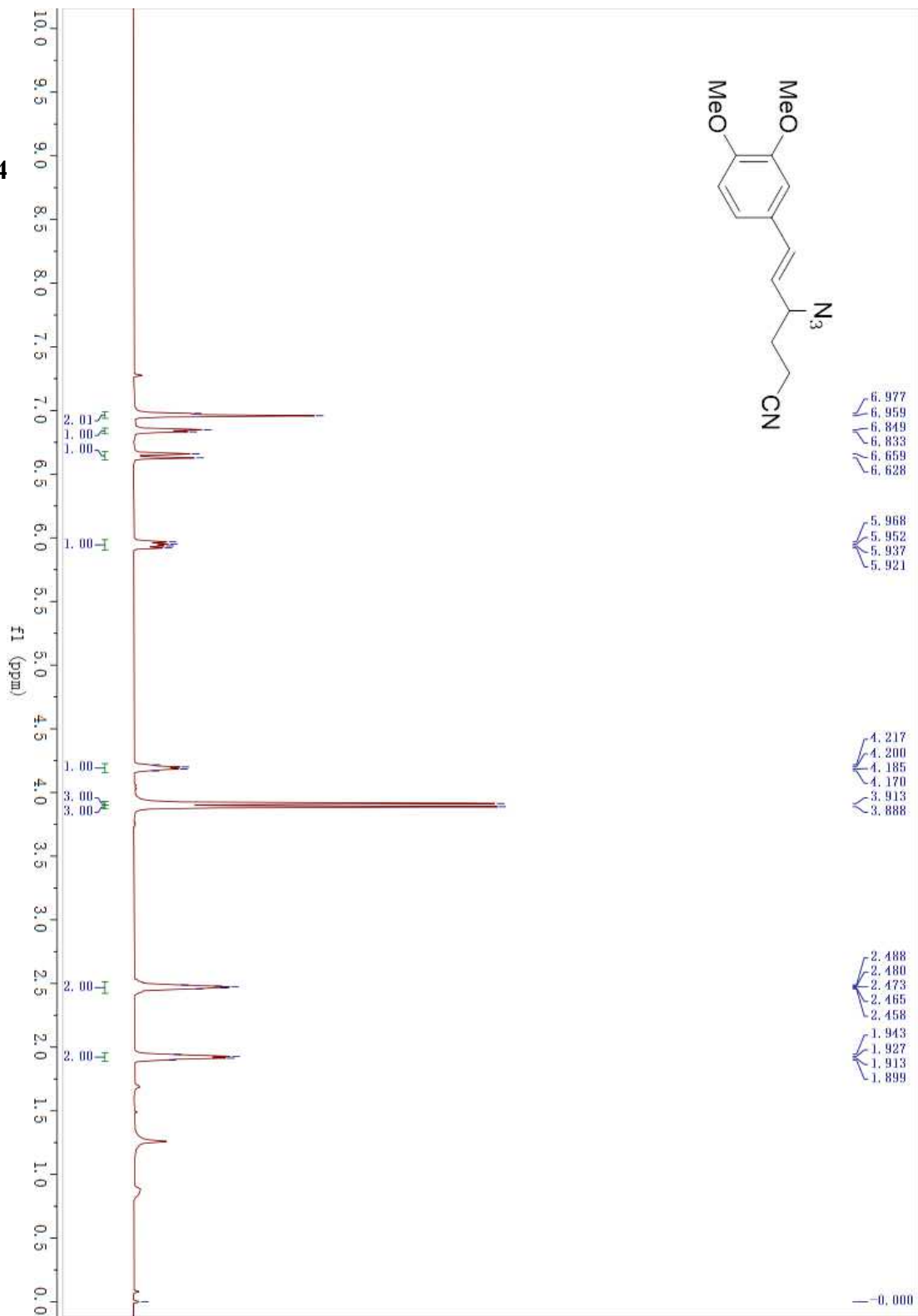


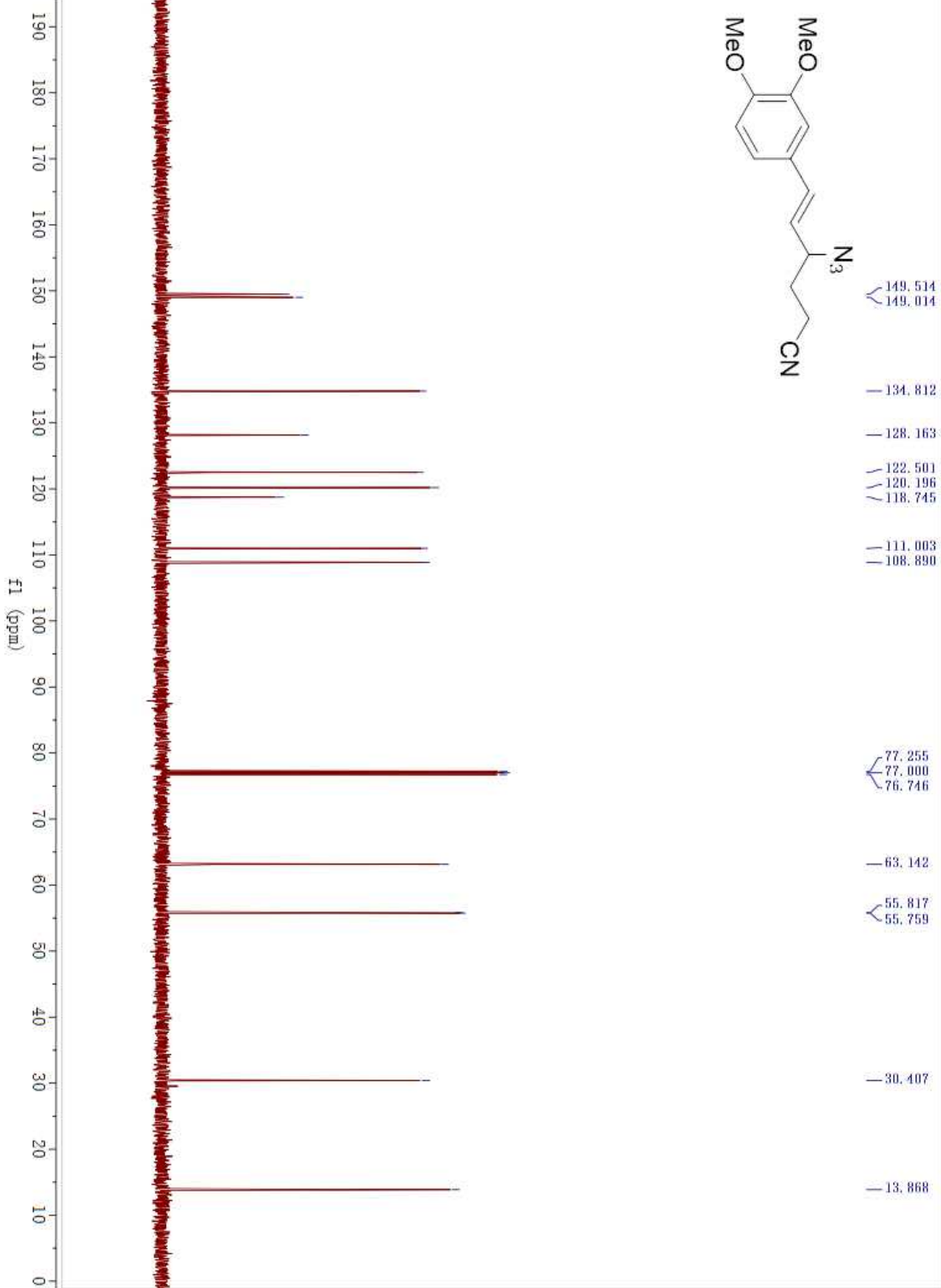
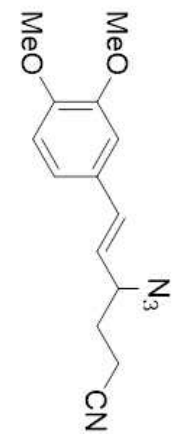
(E)-4-azido-6-(2-c



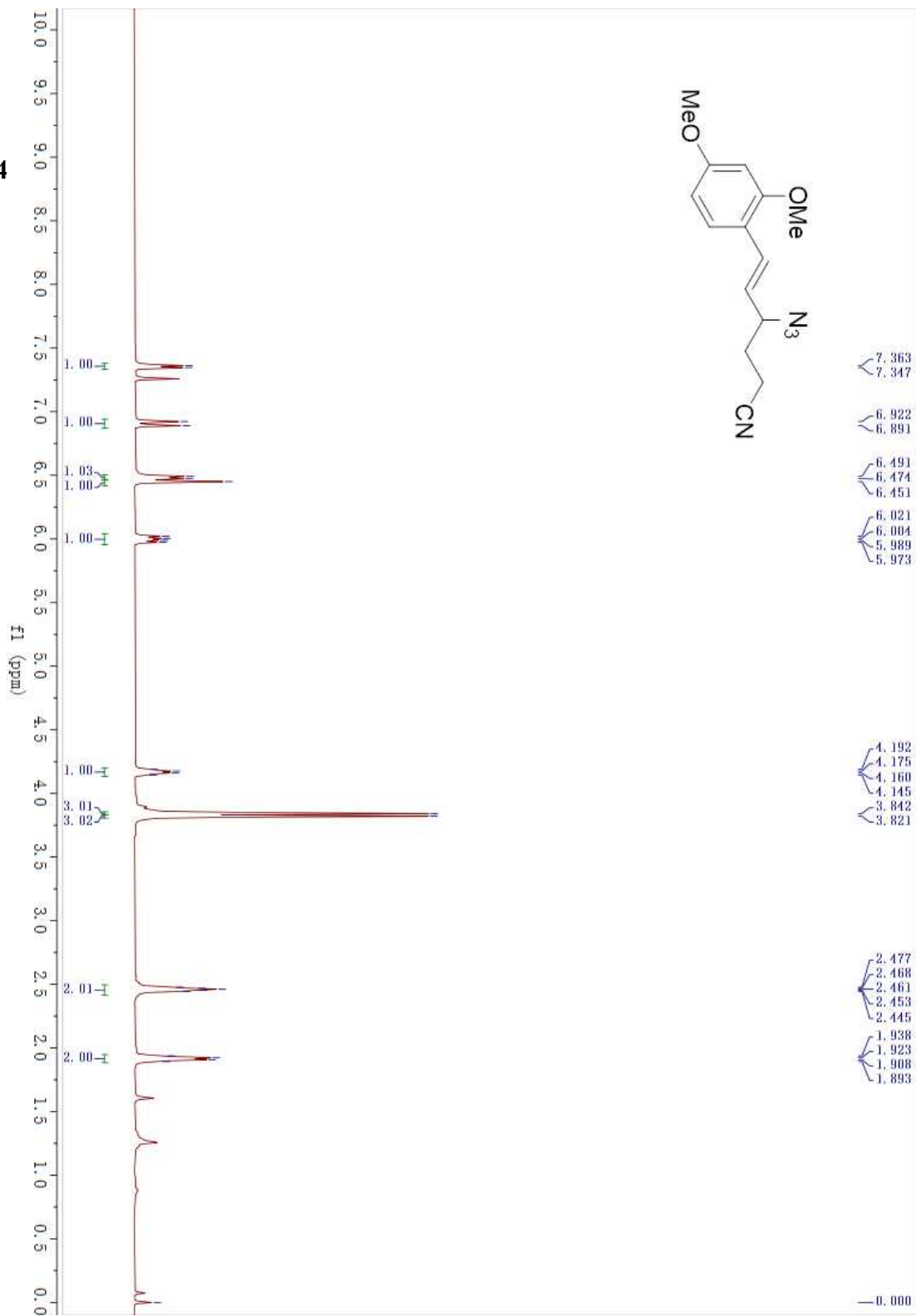


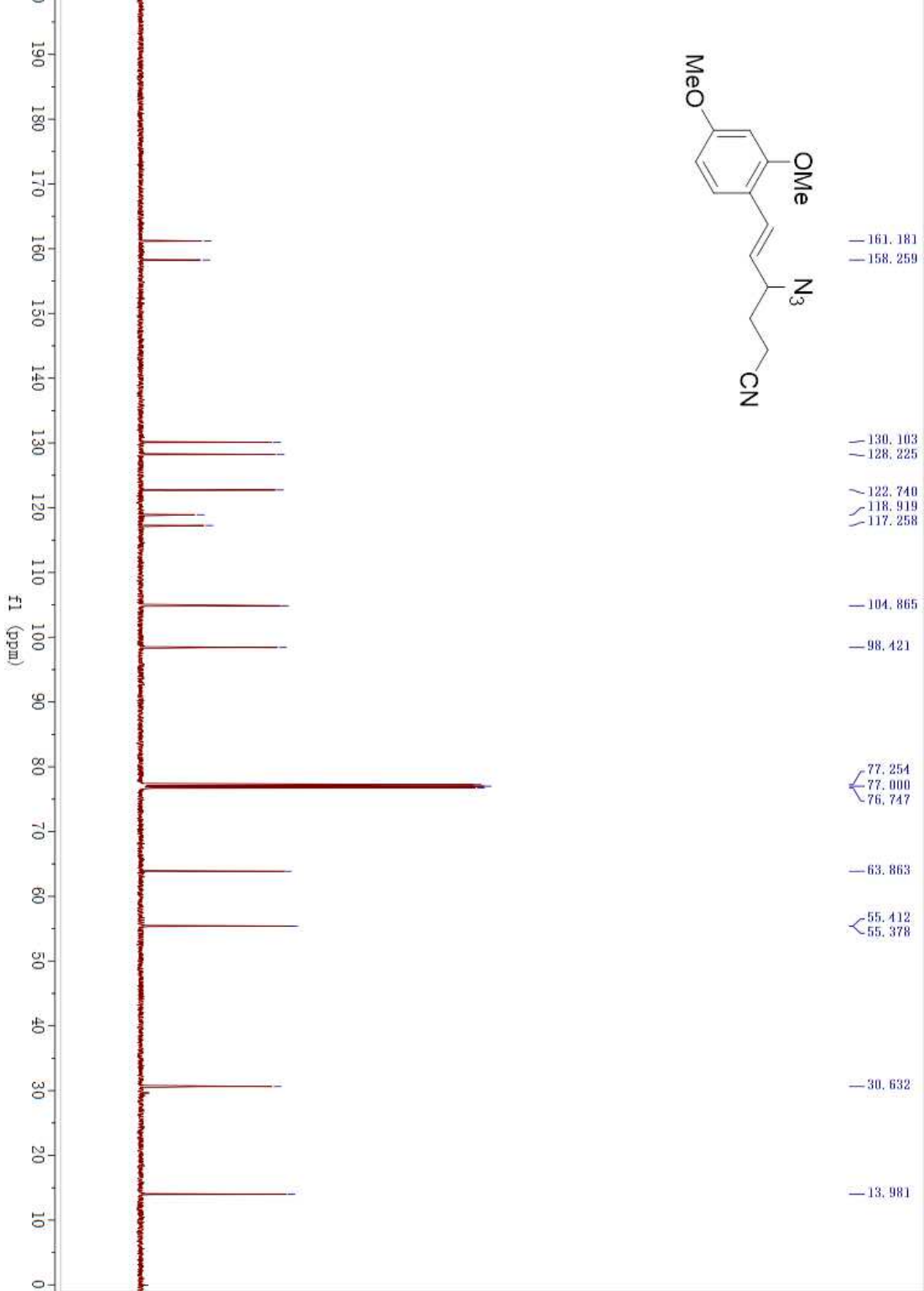
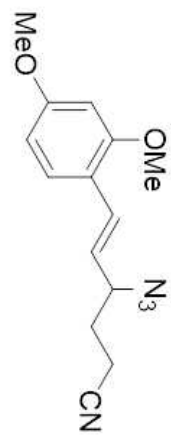
(E)-4-azido-6-(3,4



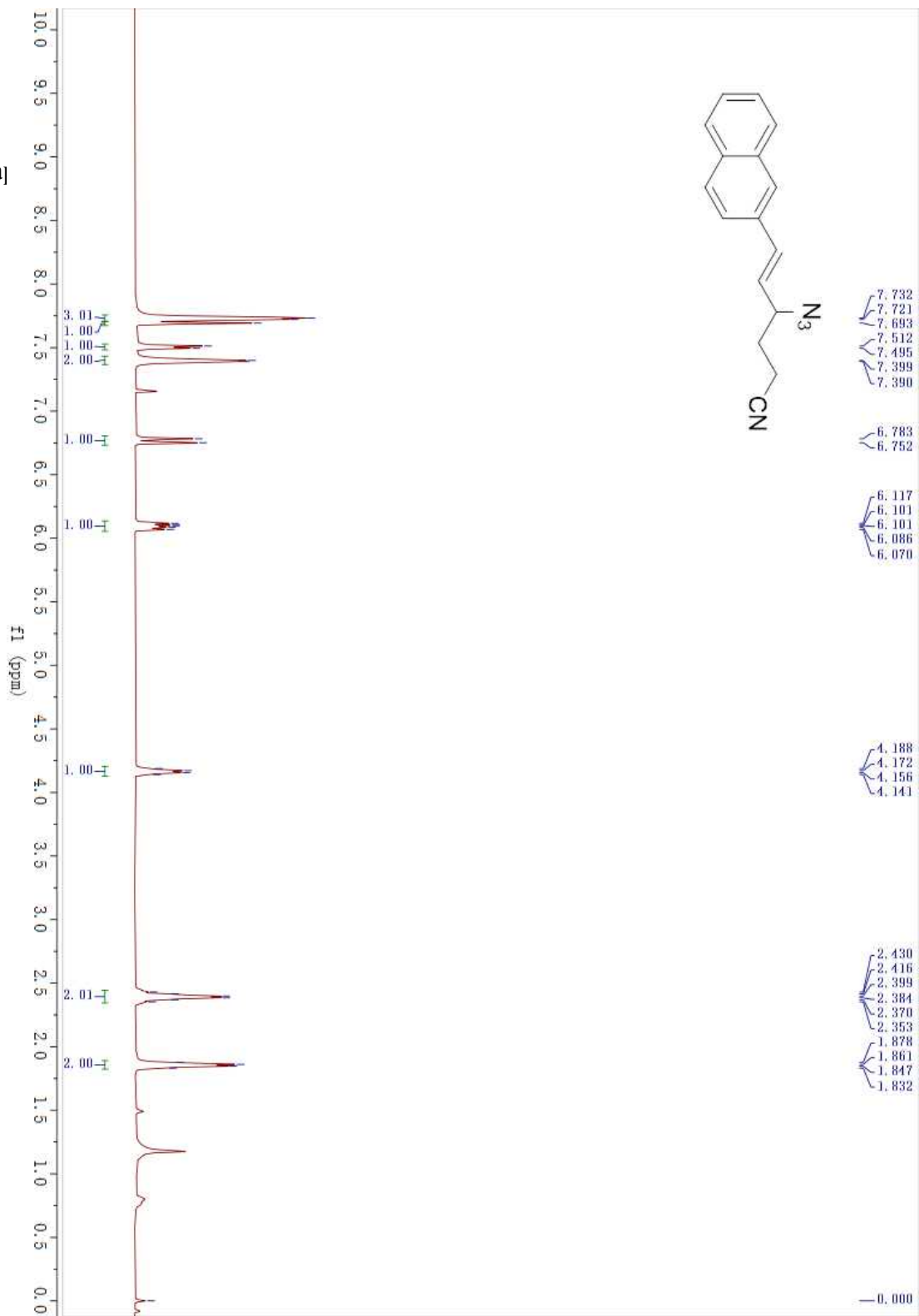


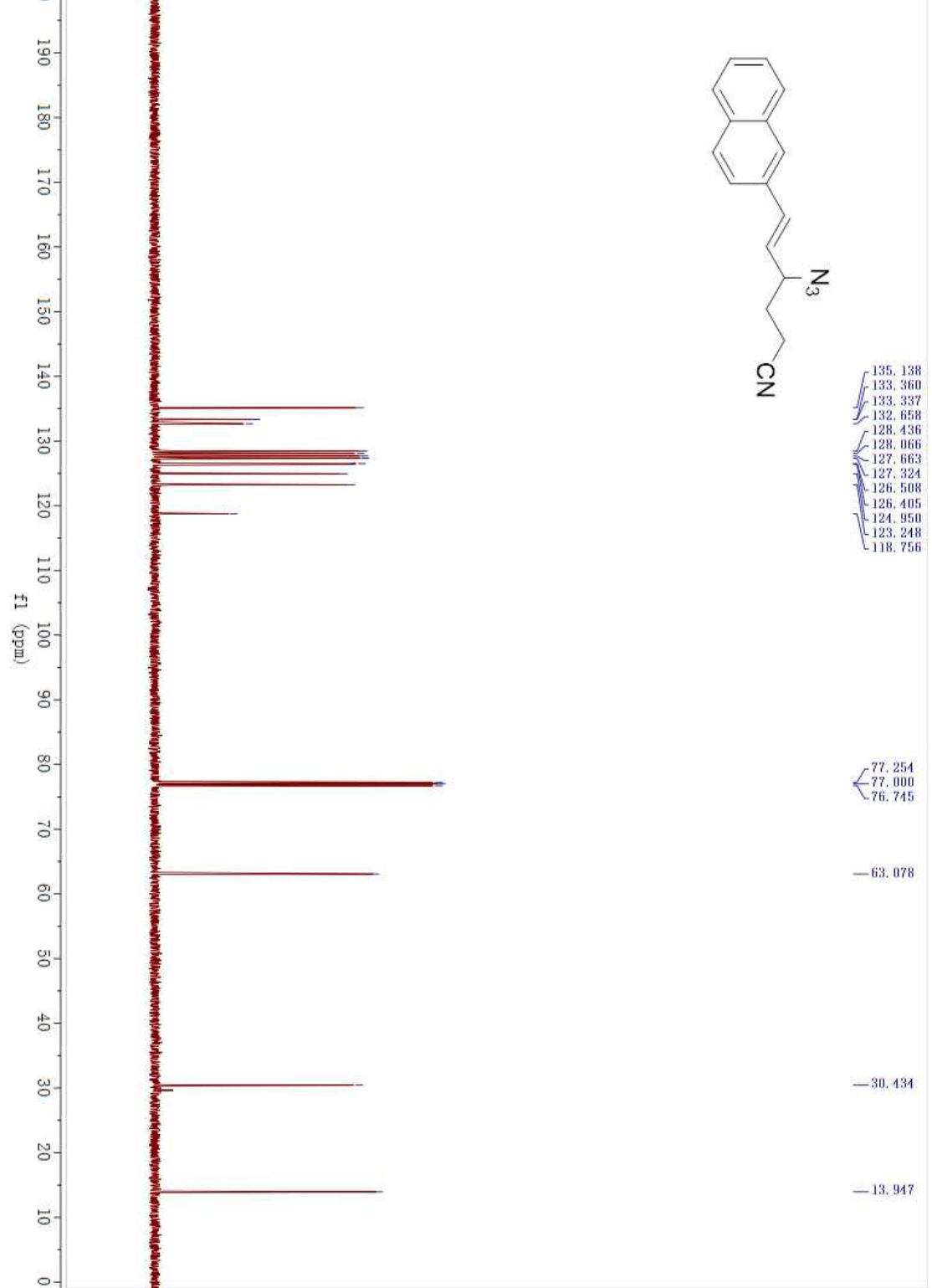
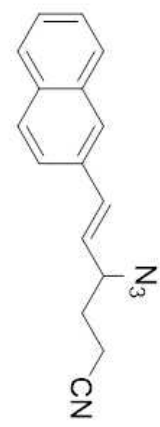
(E)-4-azido-6-(2,4



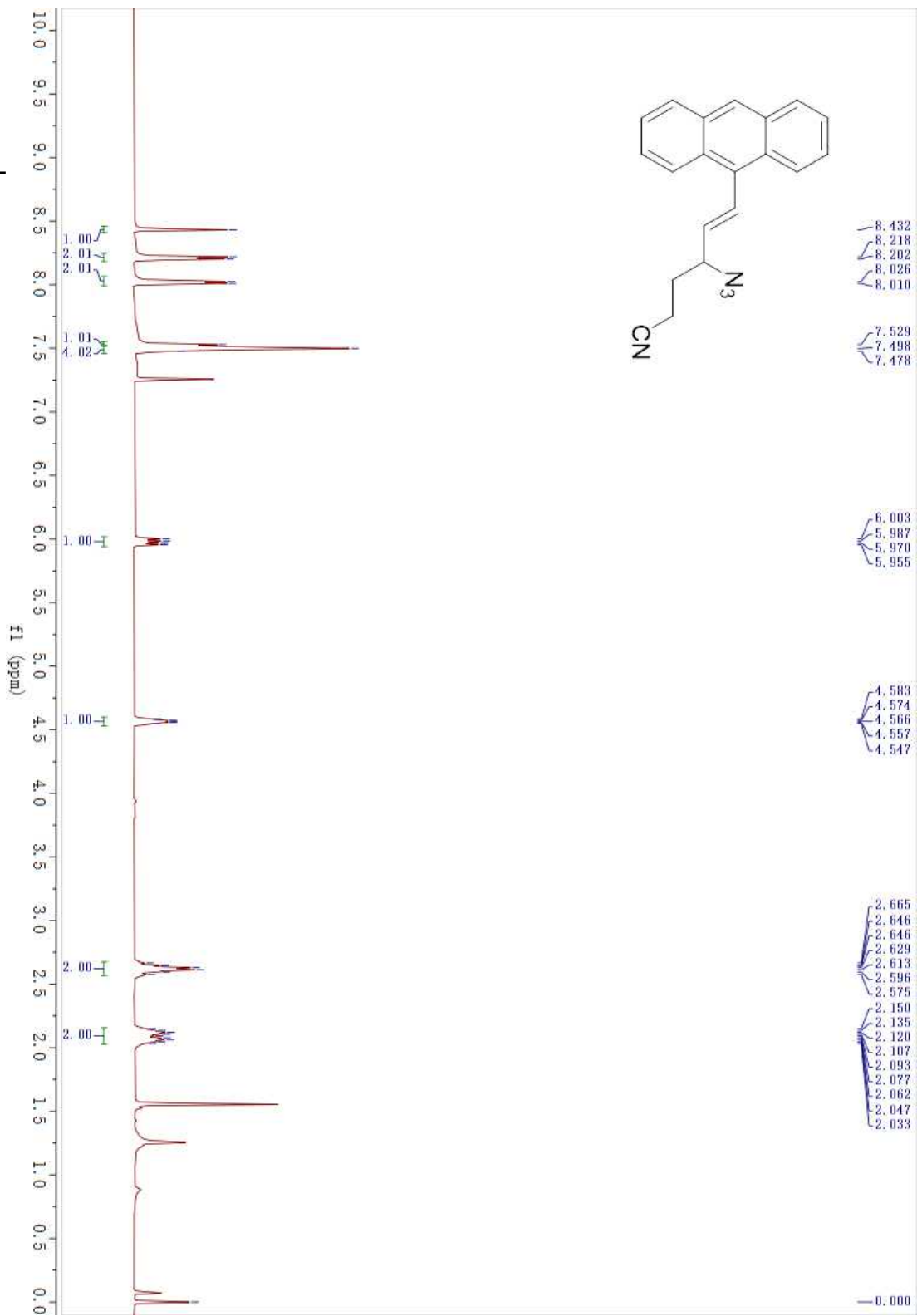


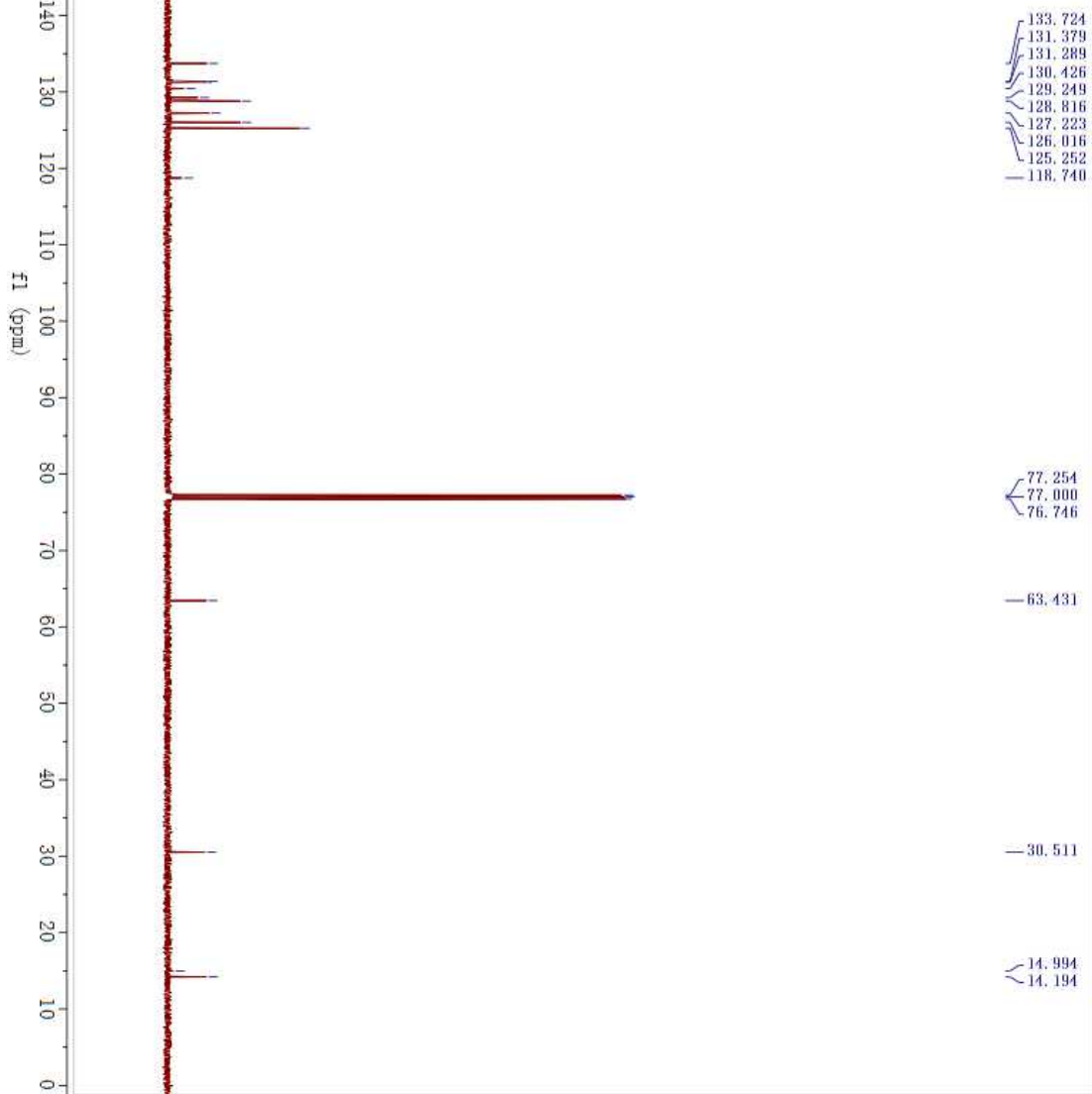
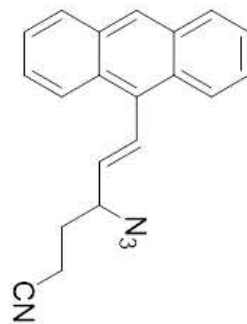
(E)-4-azido-6-(naphthalen-2-yl)hexanenitrile



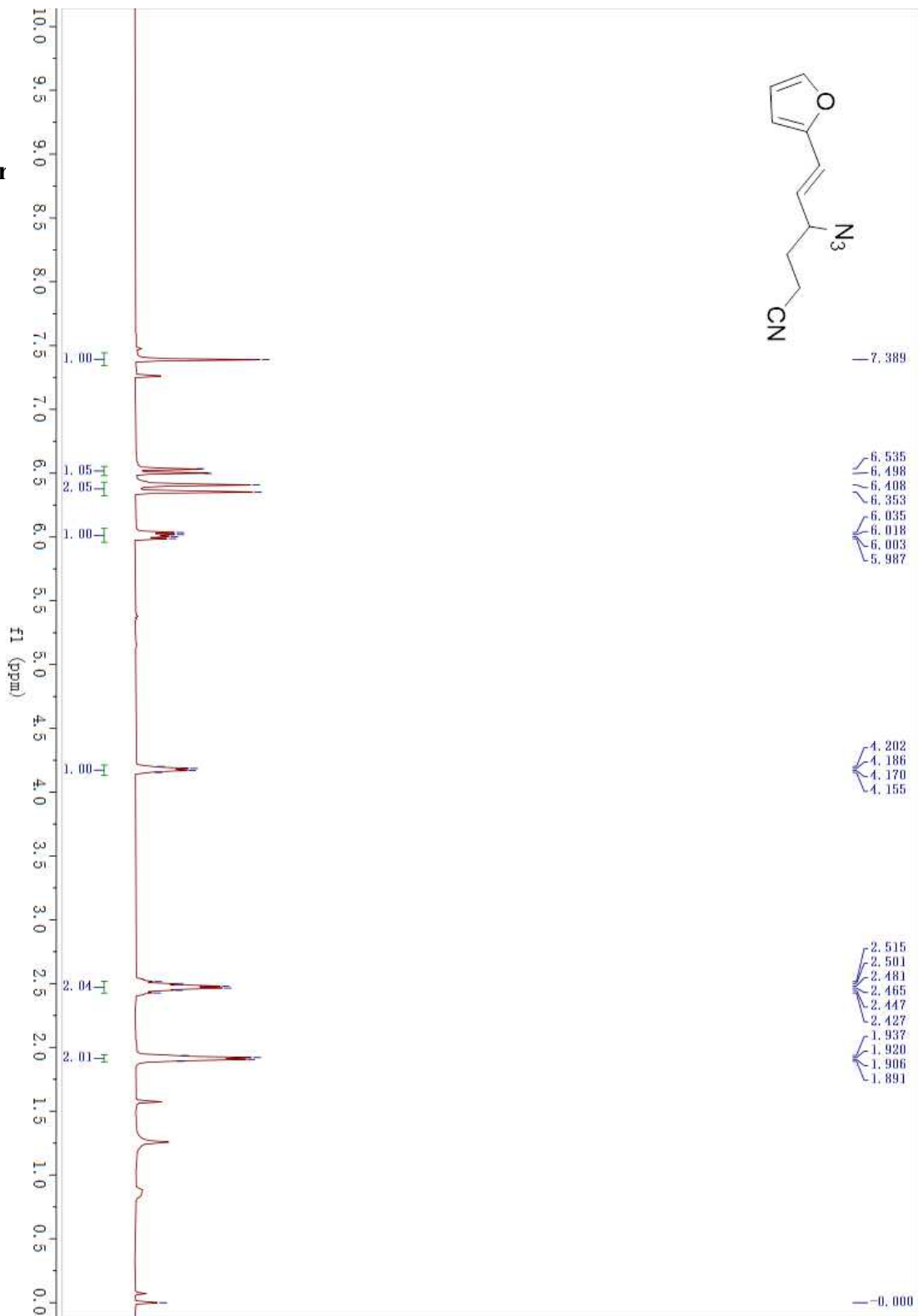


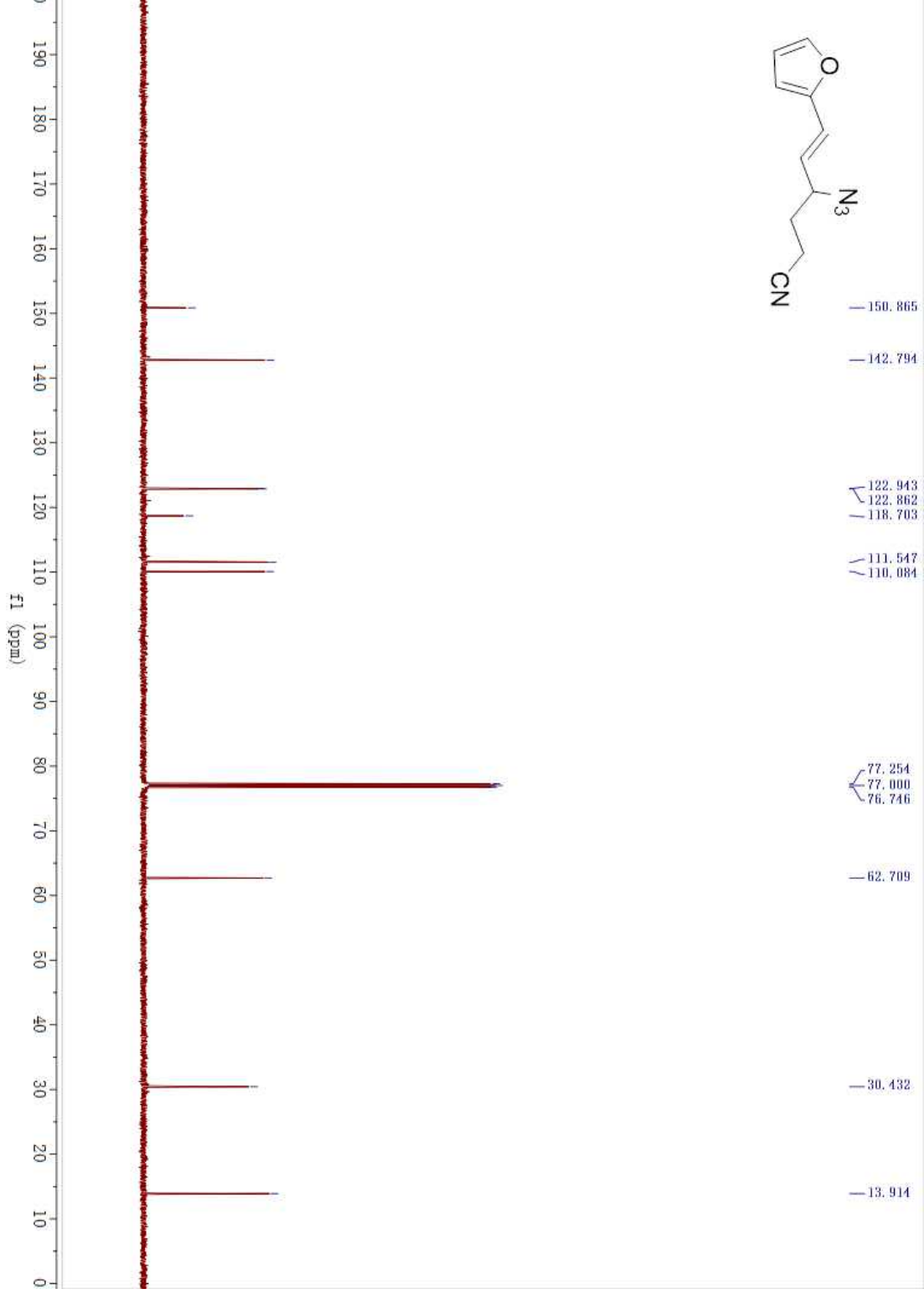
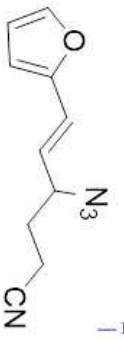
(E)-6-(anthracen-



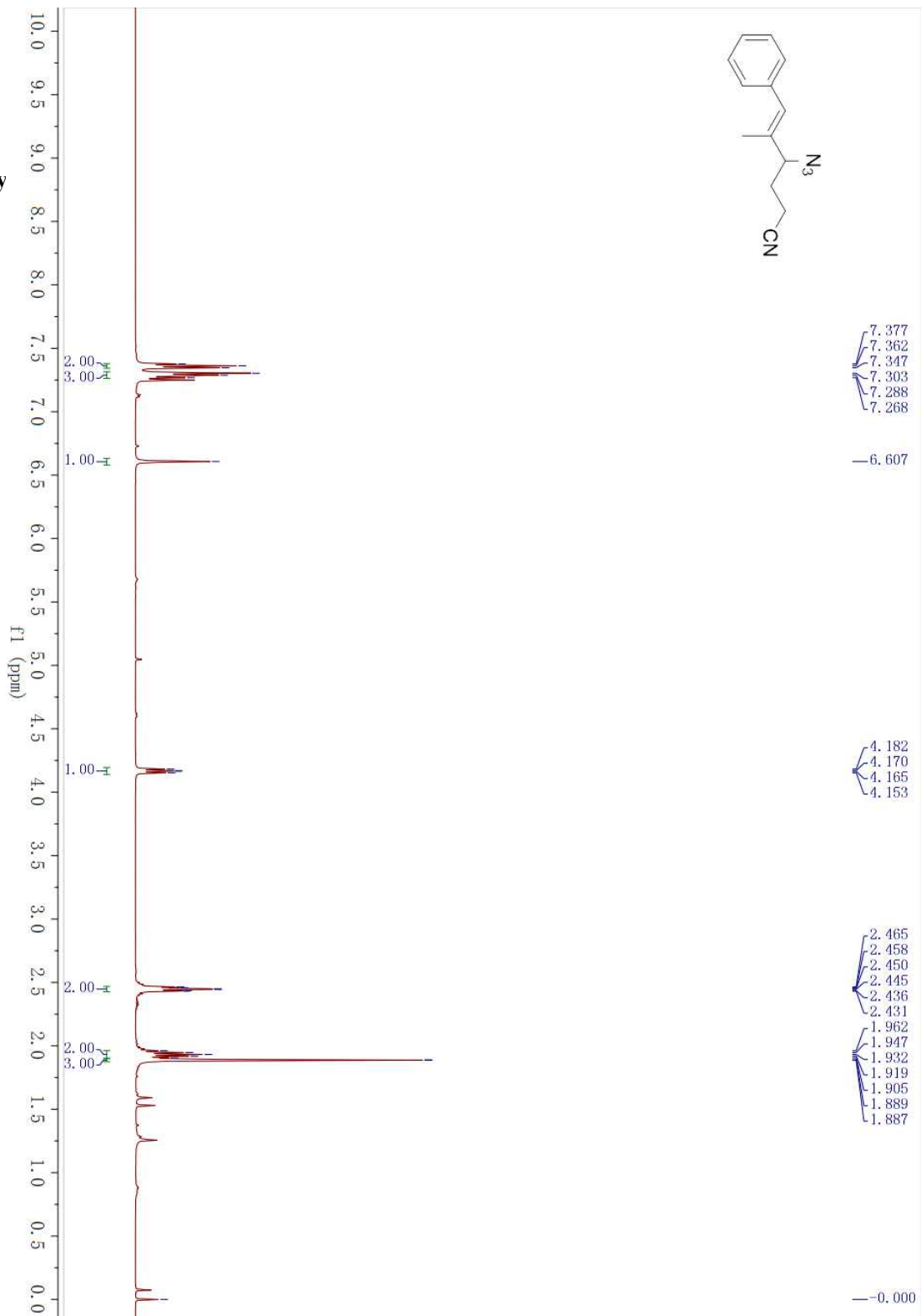
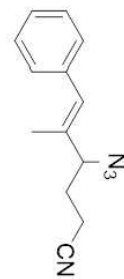


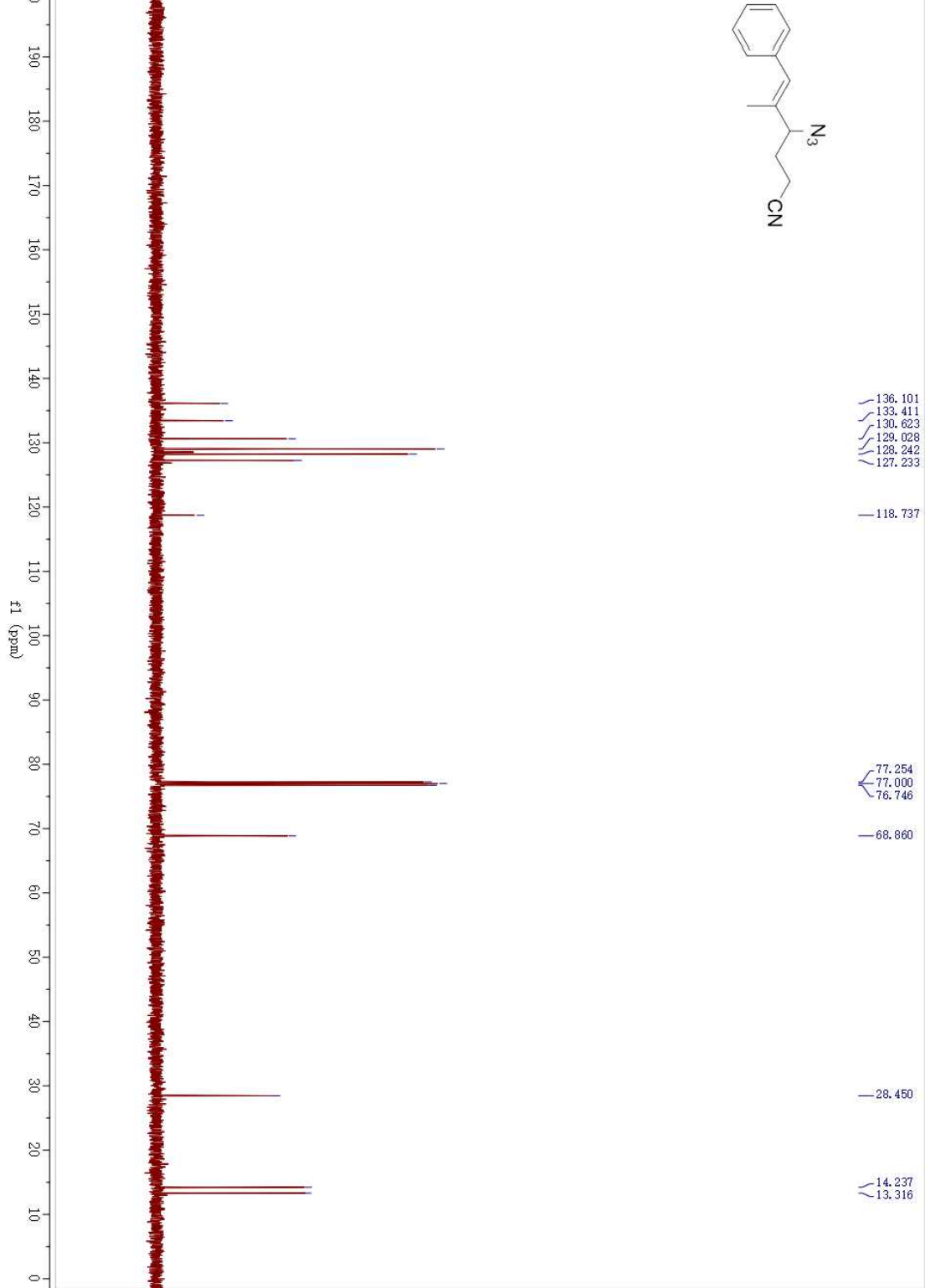
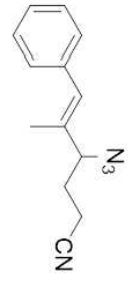
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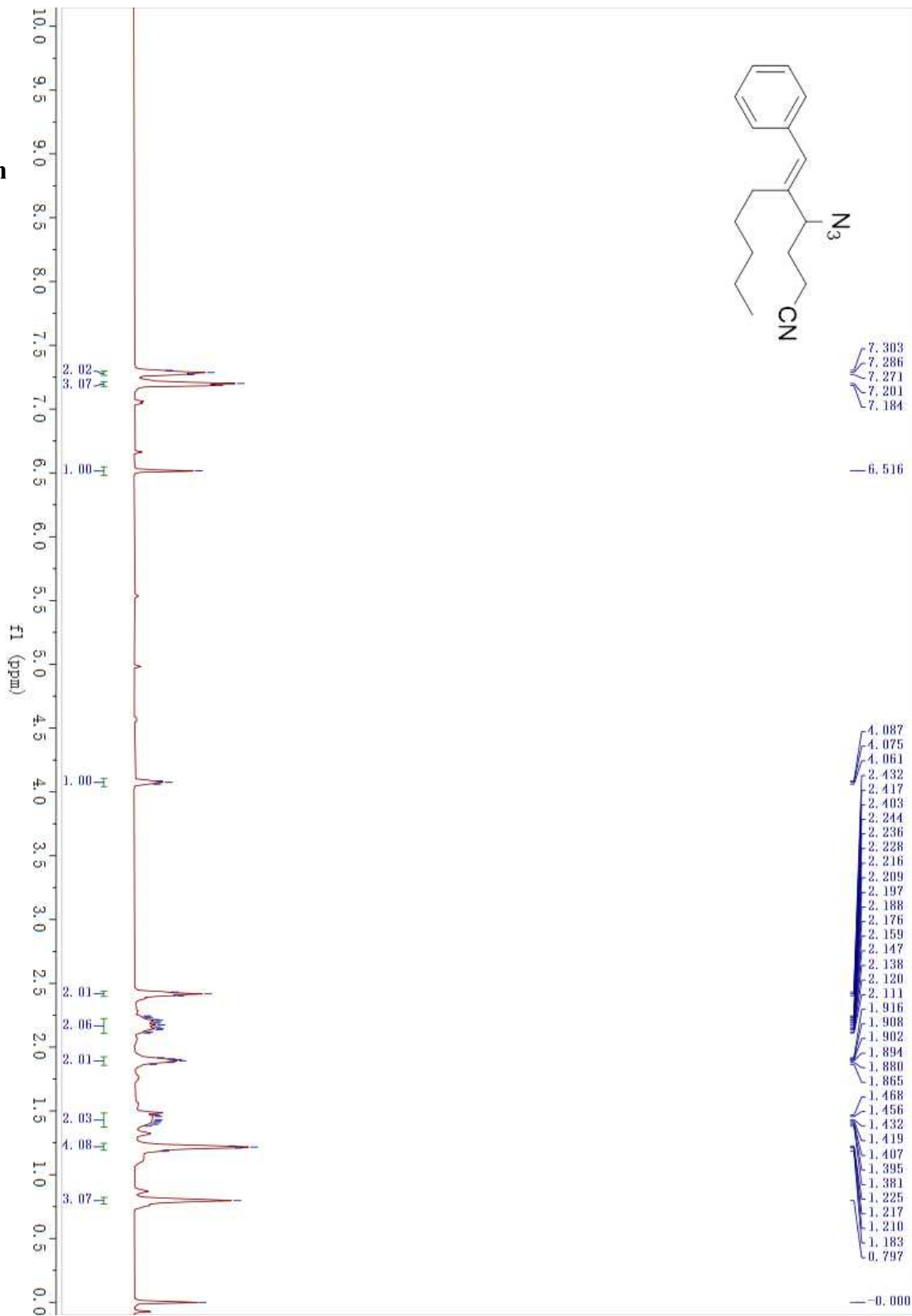


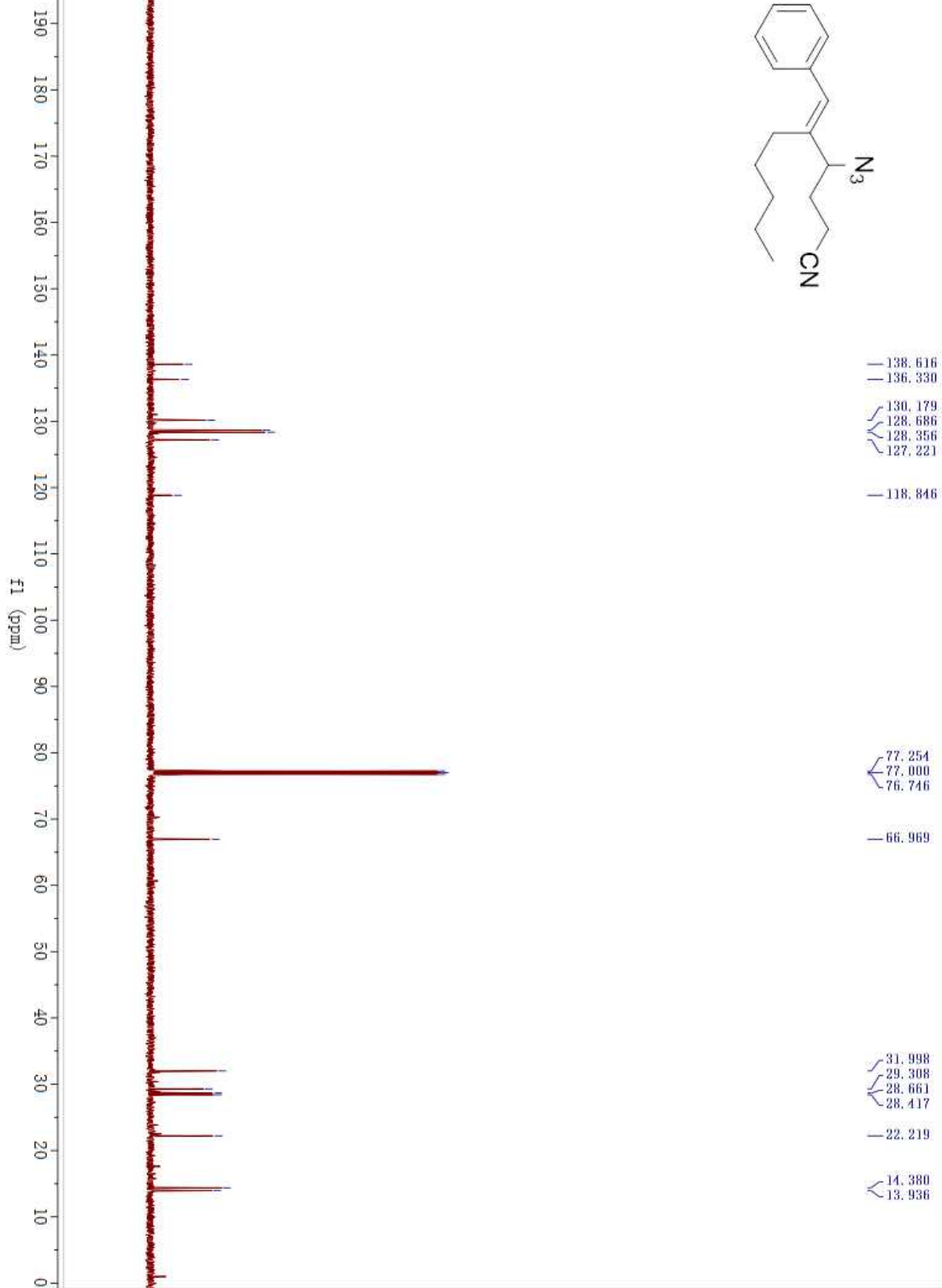
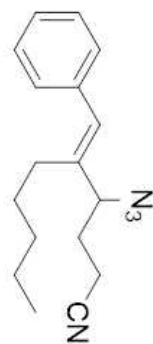
(E)-4-azido-5-methy



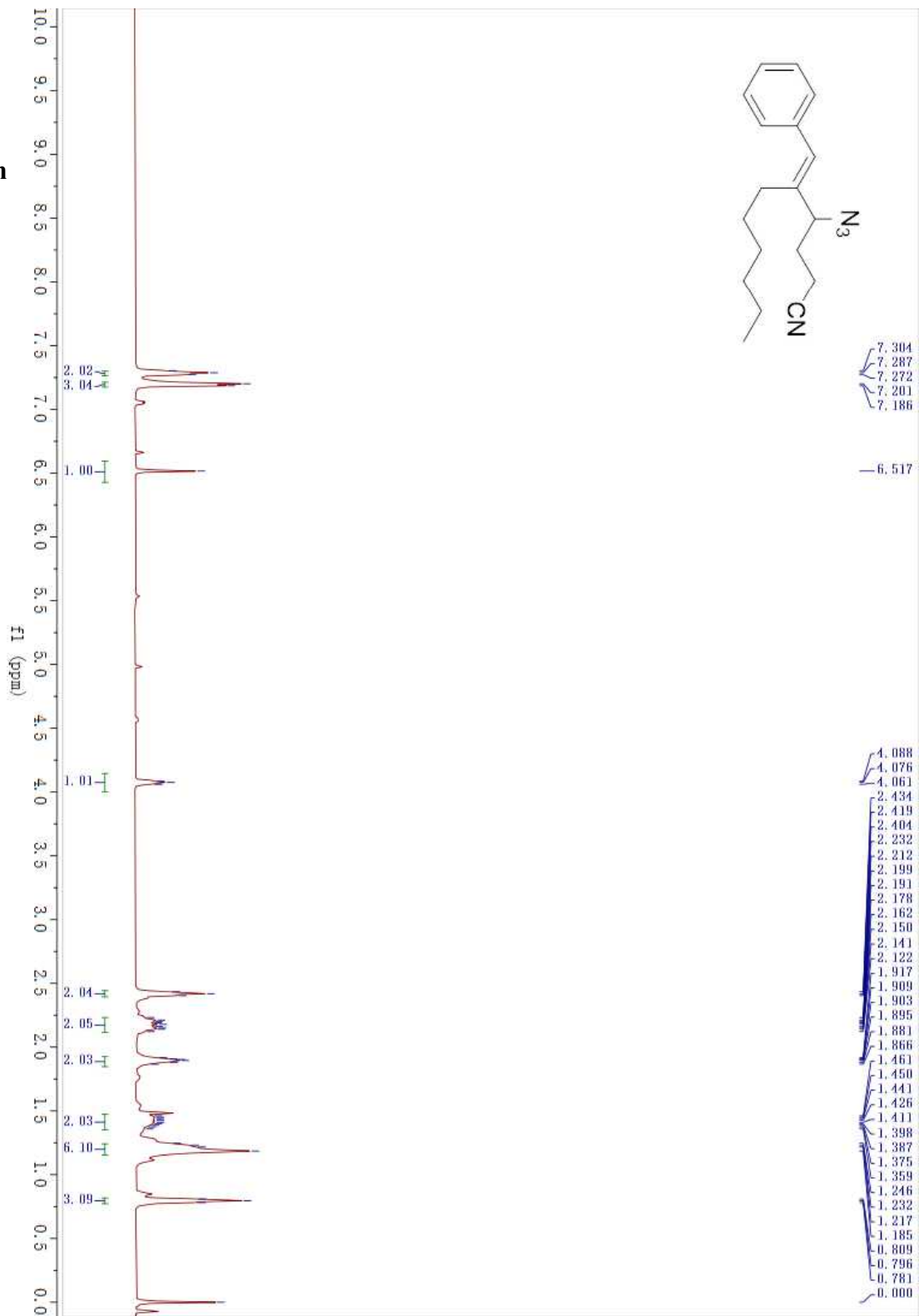


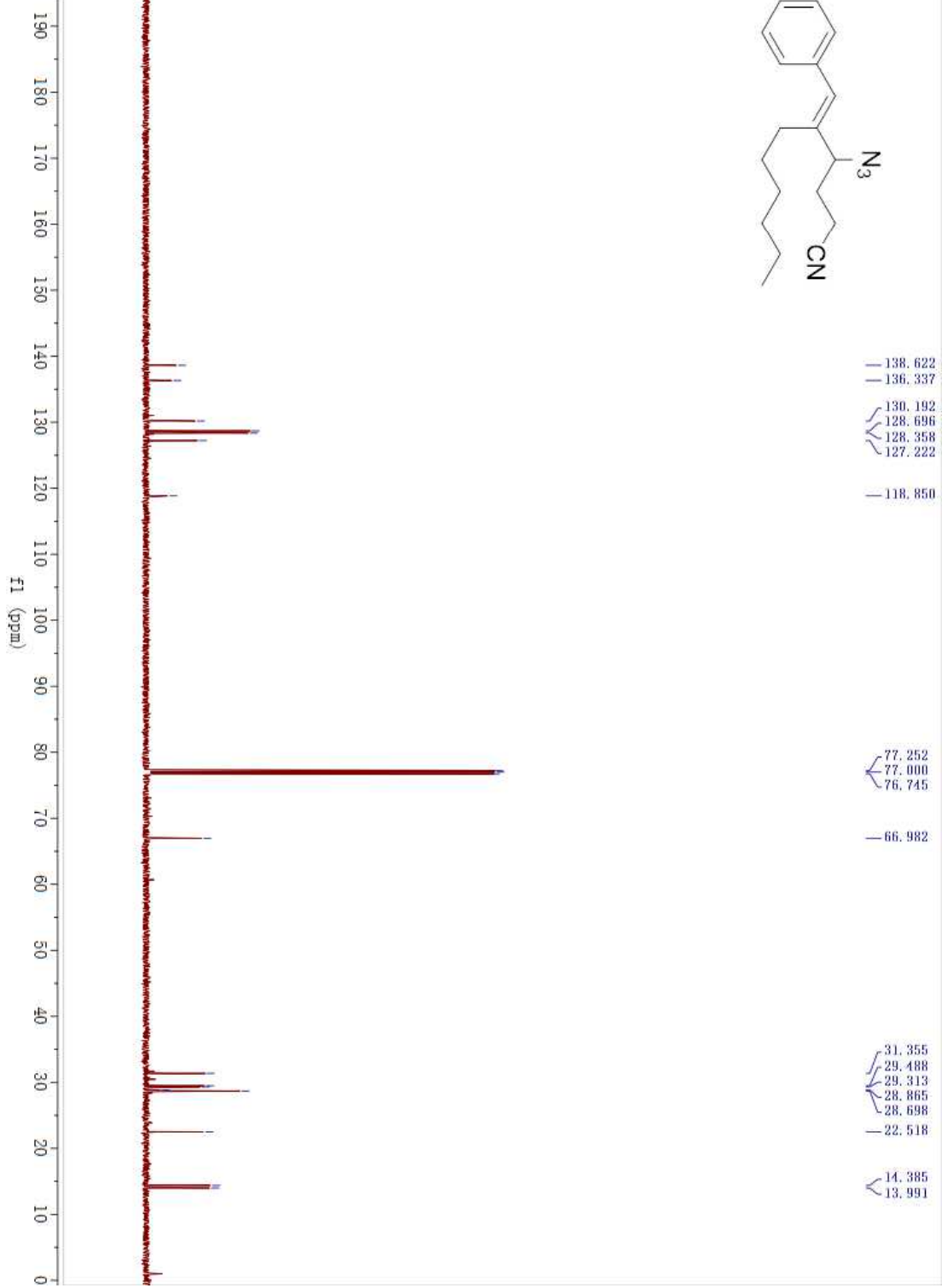
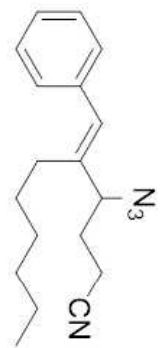
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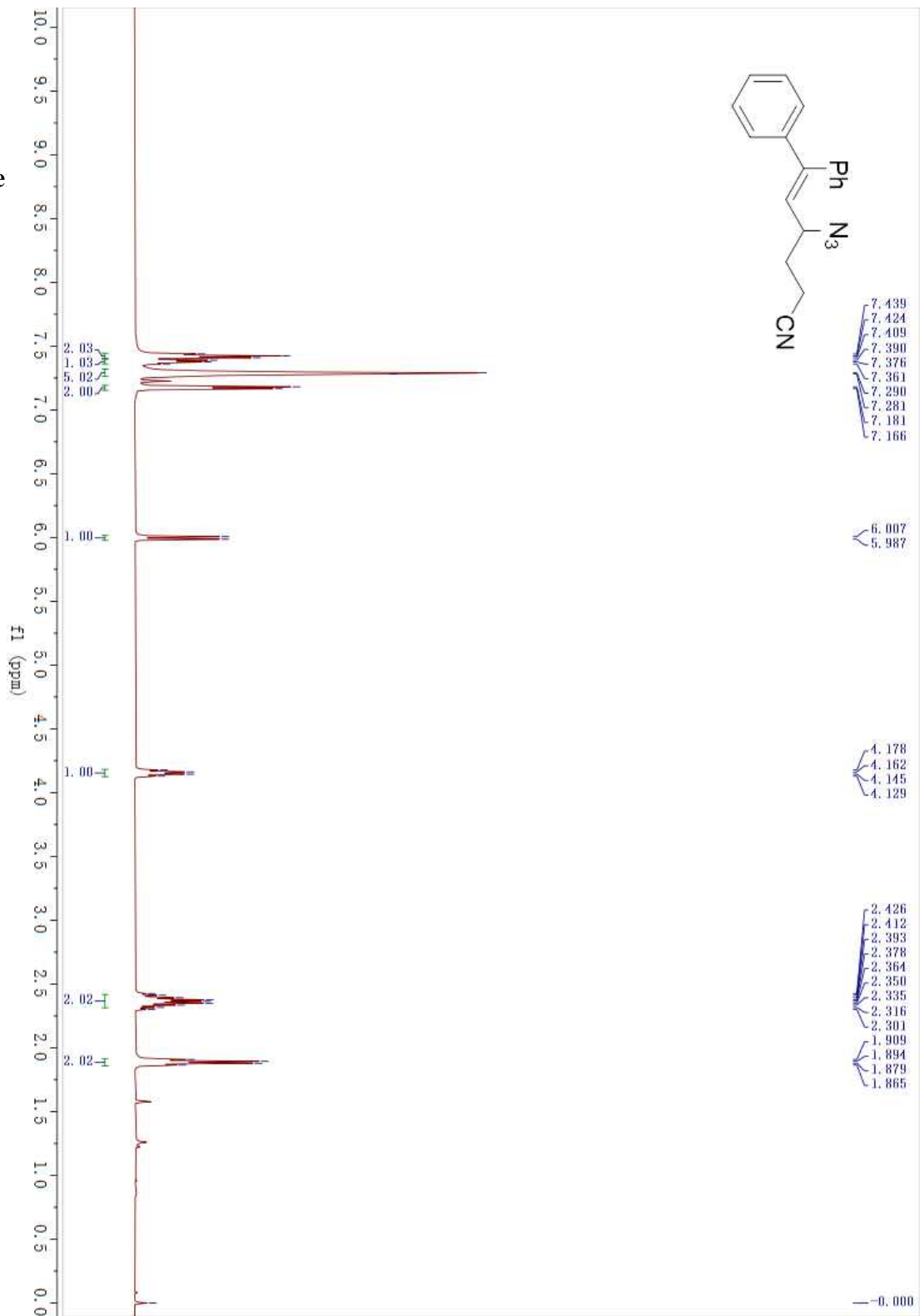


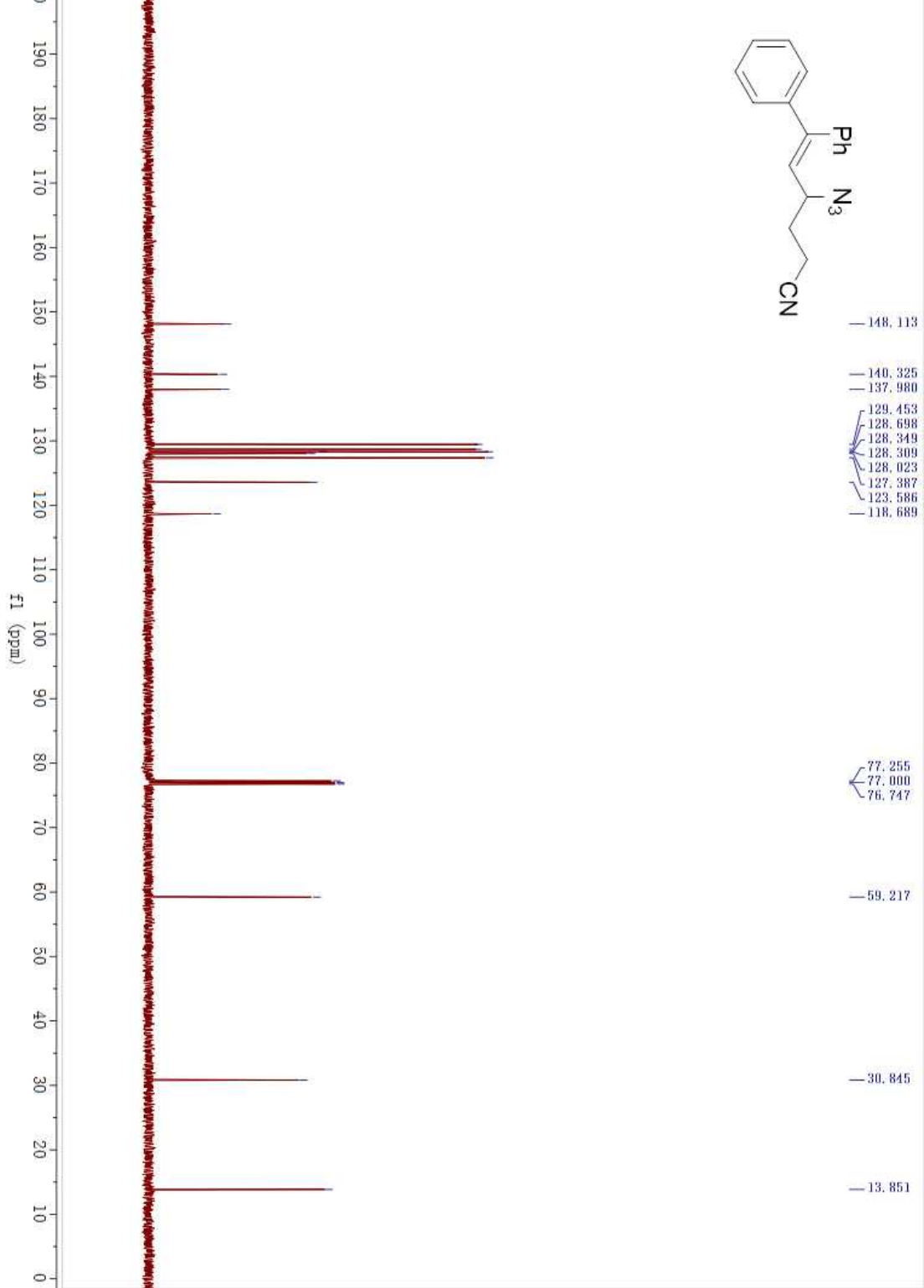
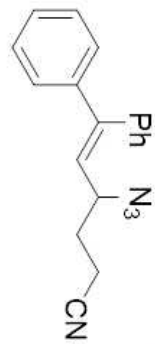
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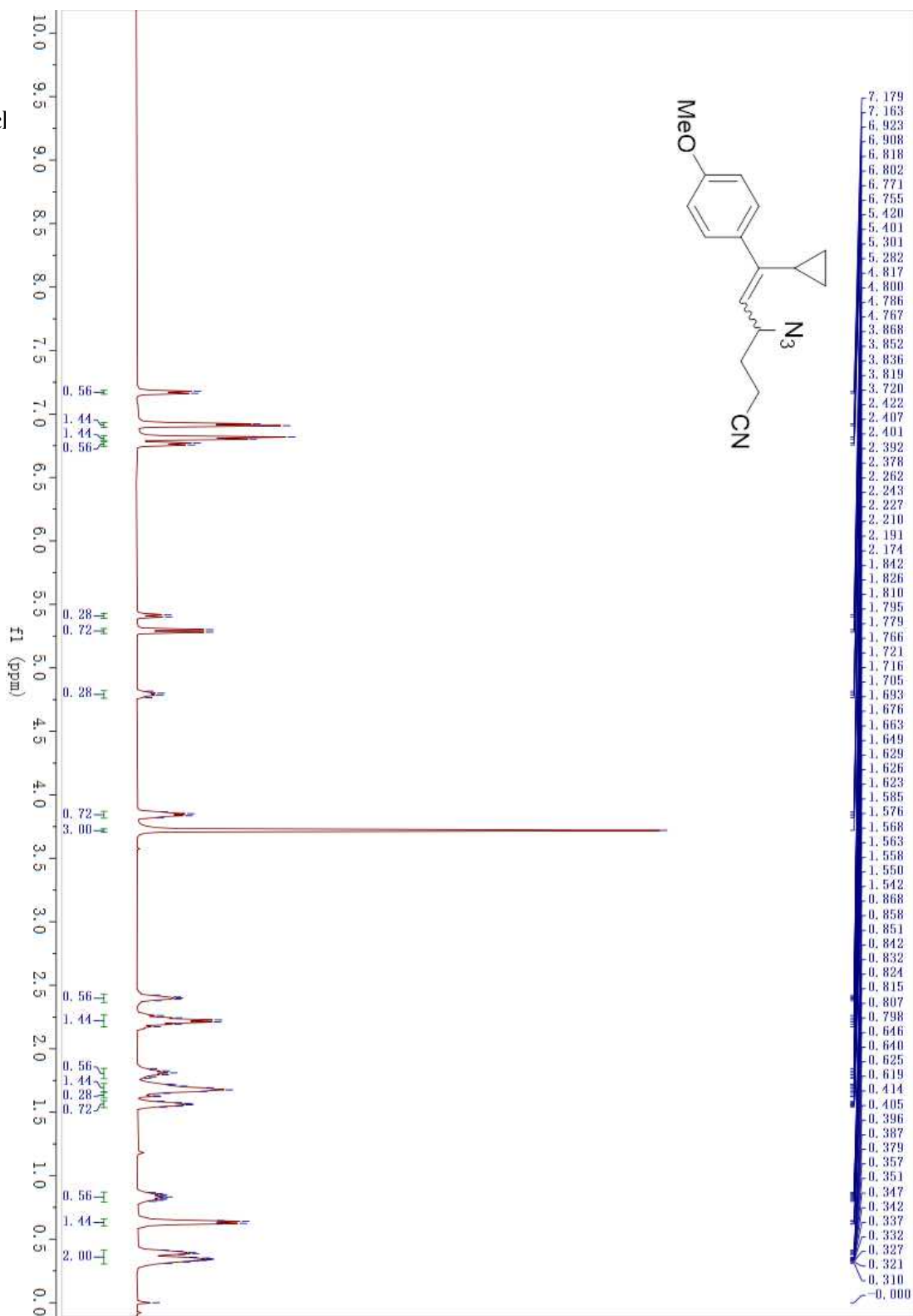


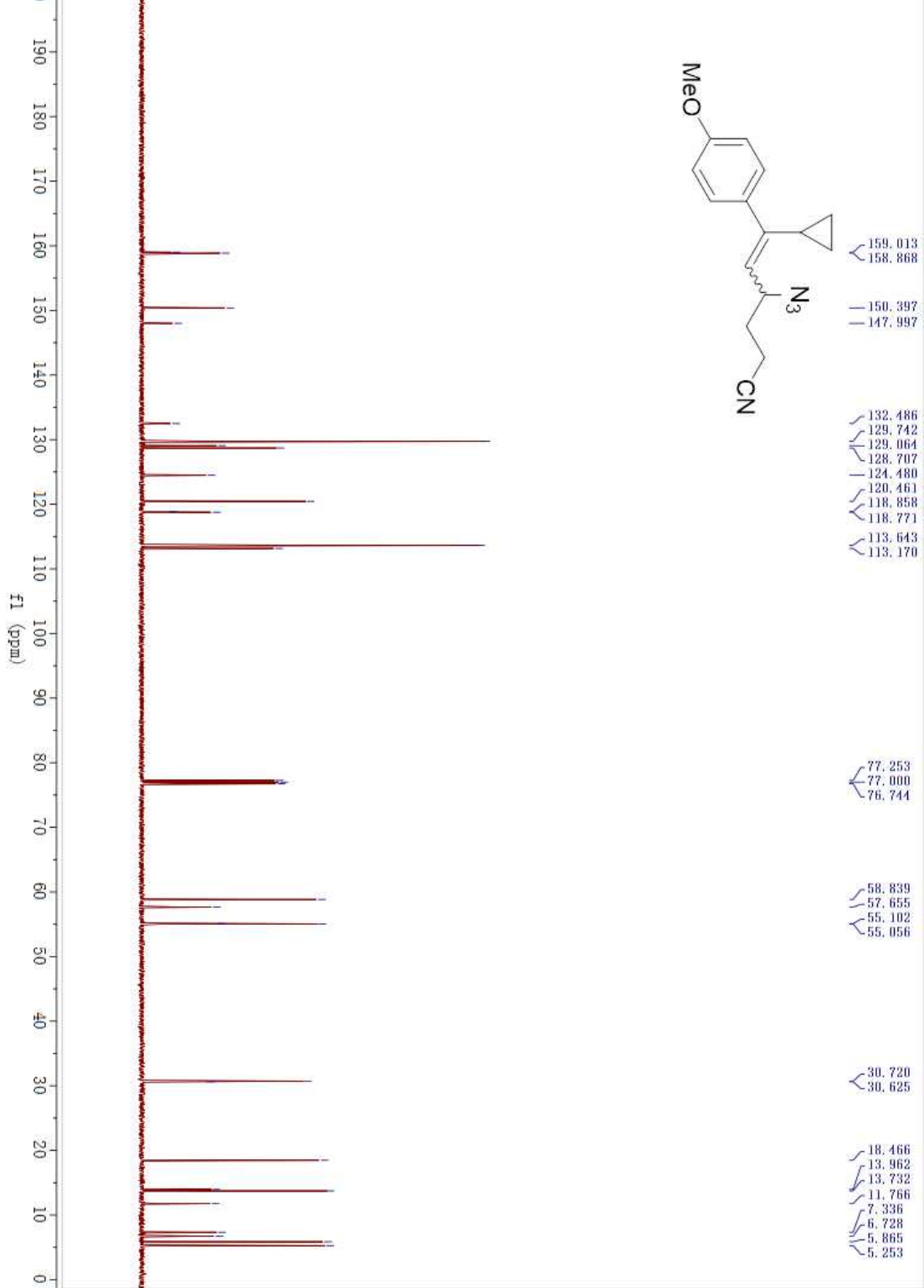
4-azido-6,6-diphe



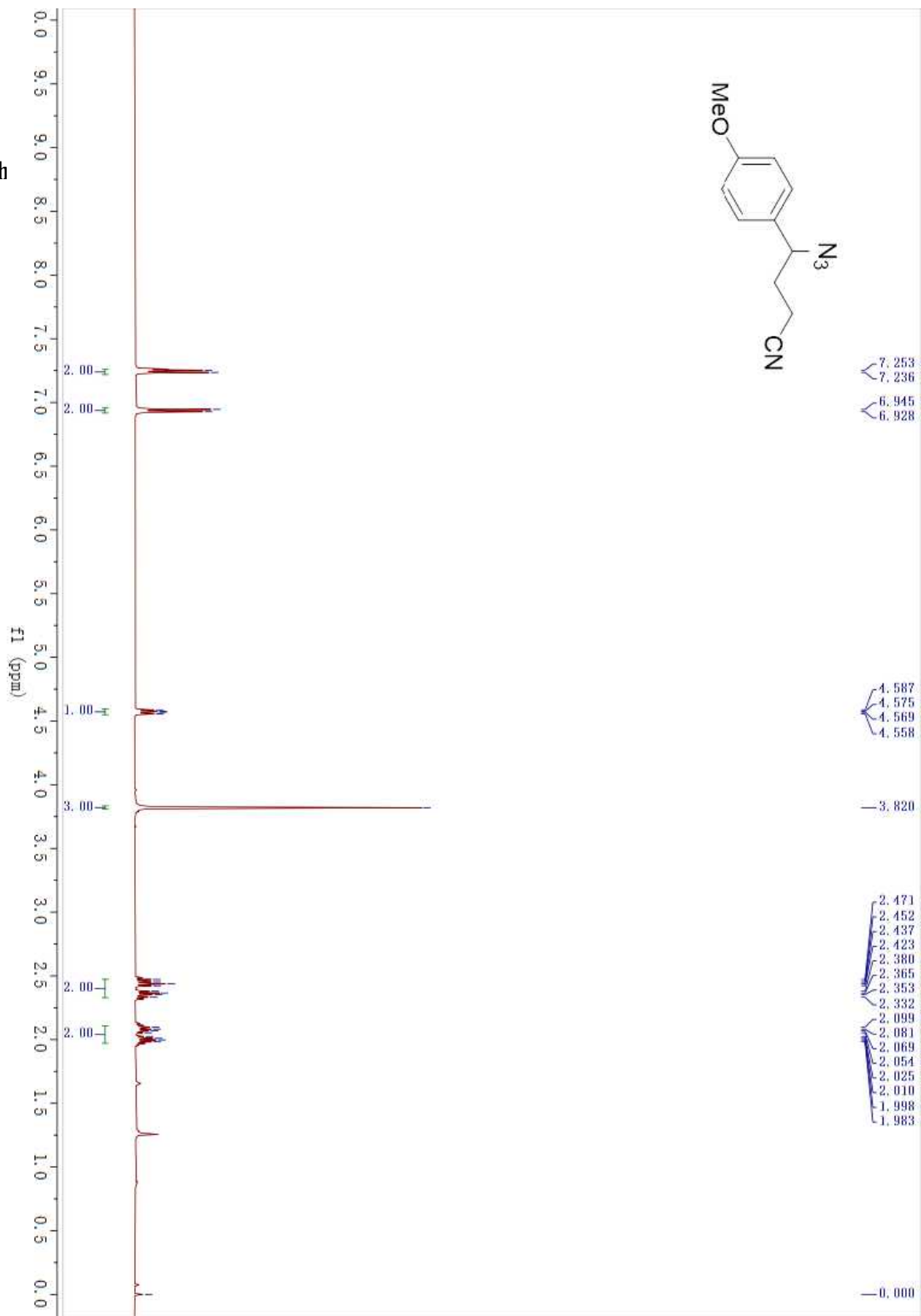


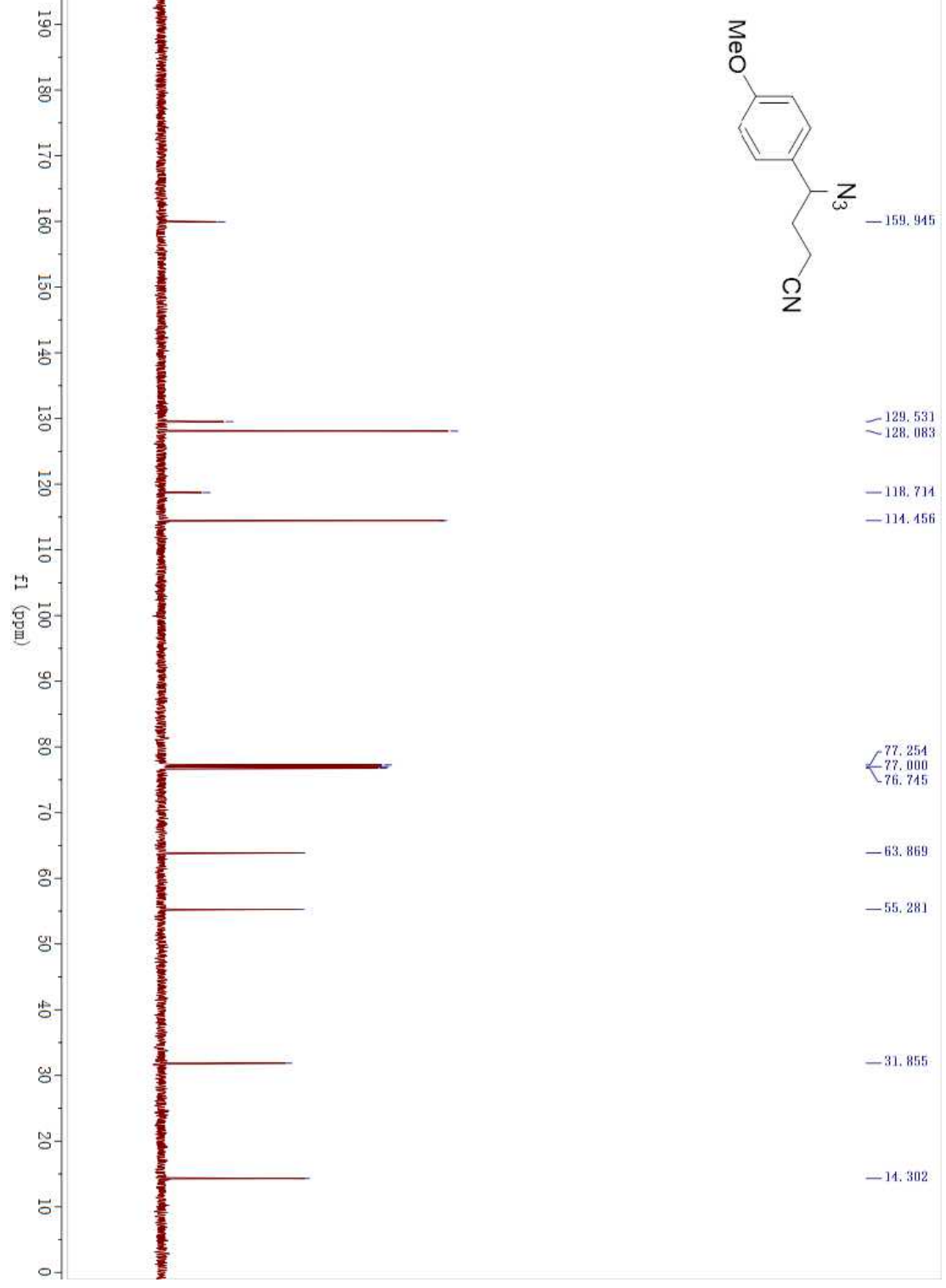
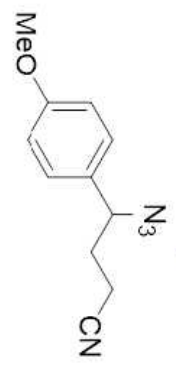
(E)-4-azido-6-cycl



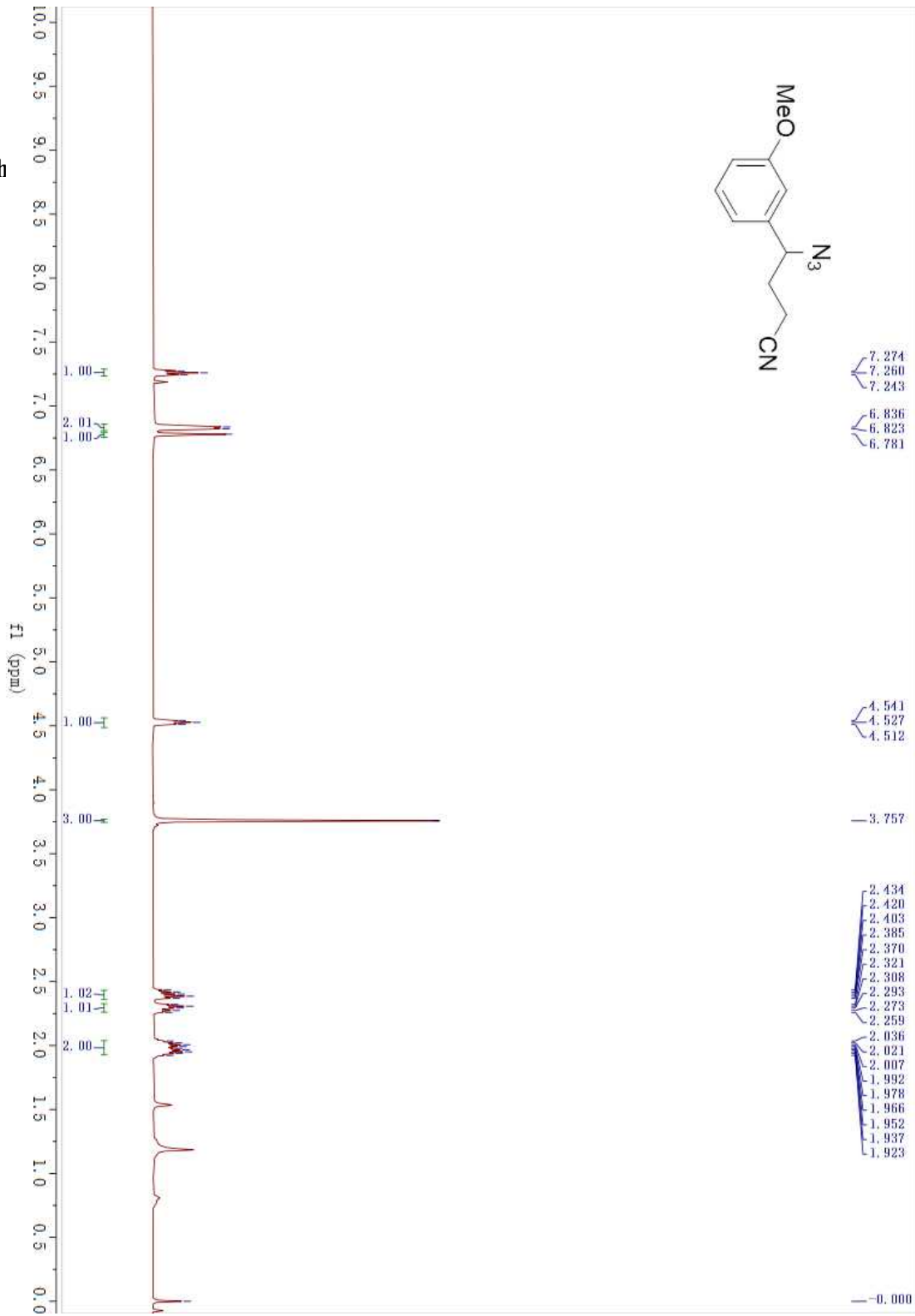


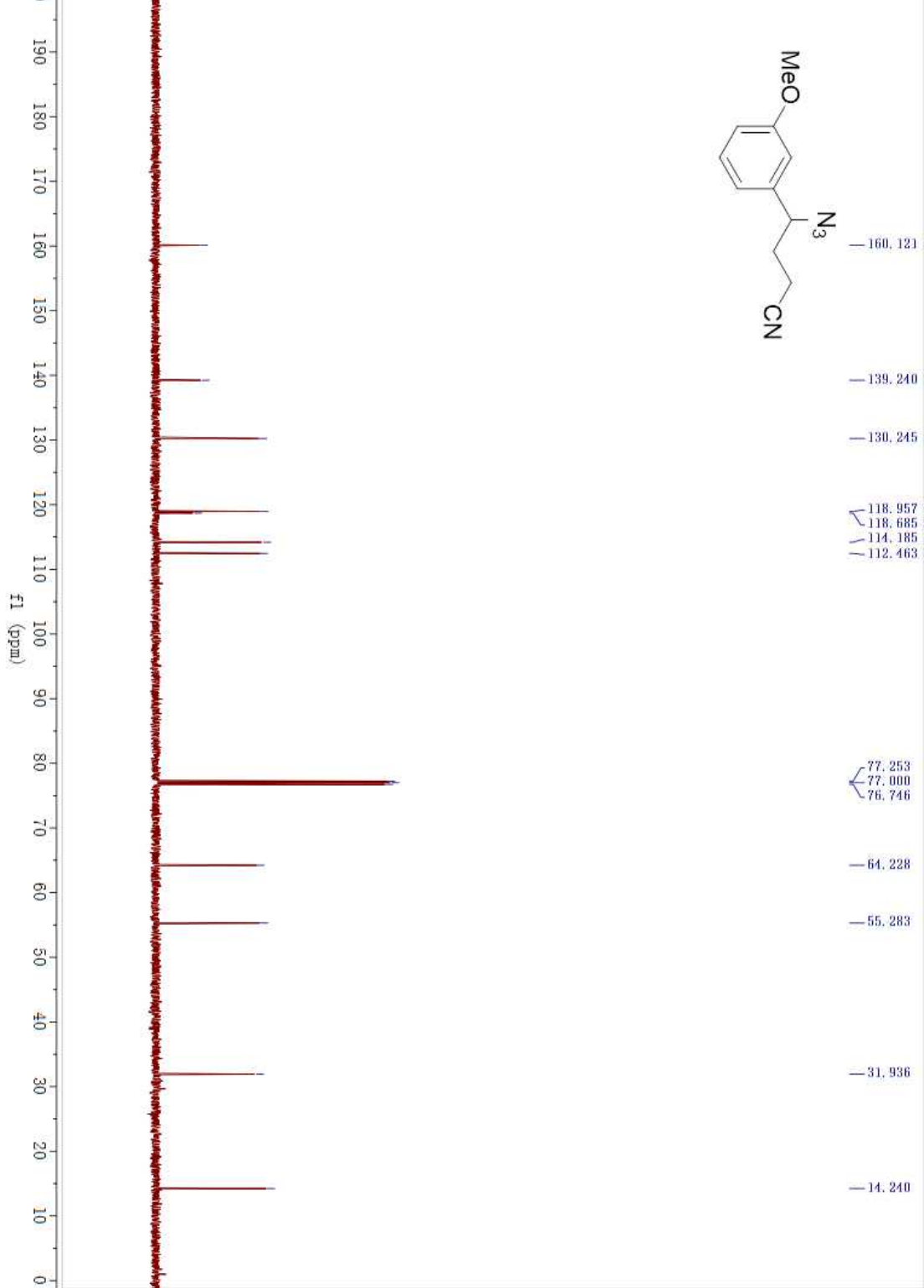
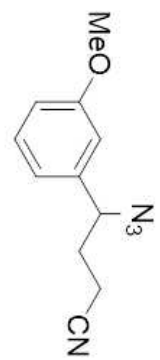
4-azido-4-(4-meth



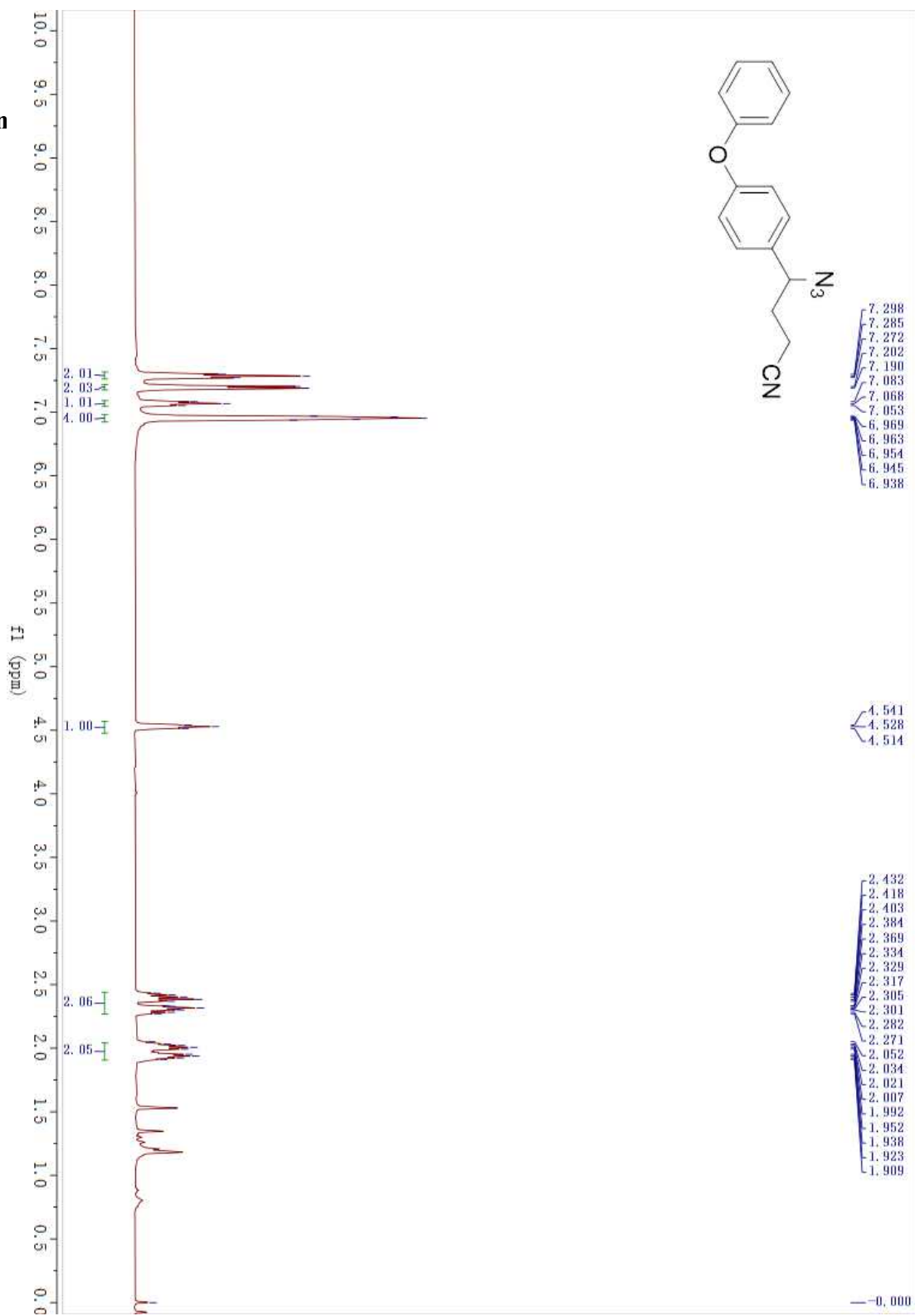


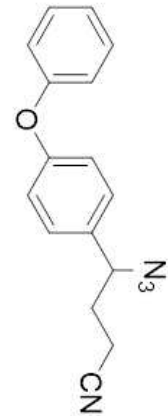
4-azido-4-(3-meth



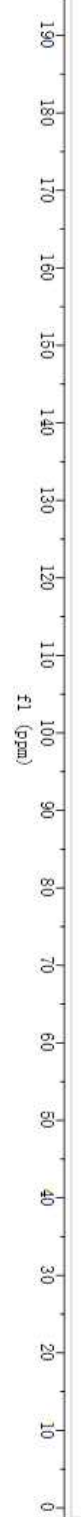


4-azido-4-(4-phen

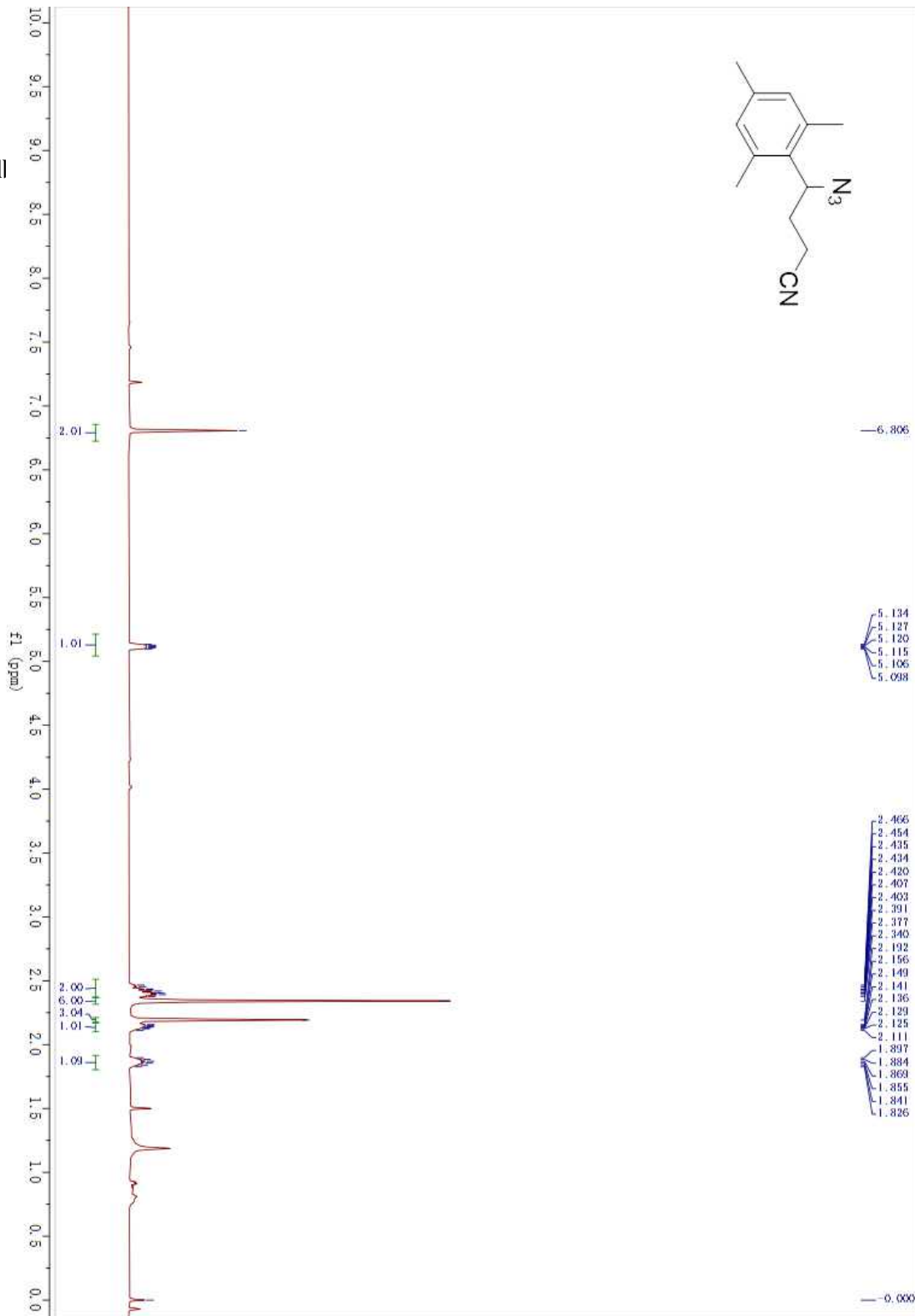
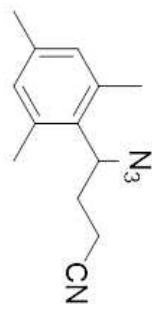


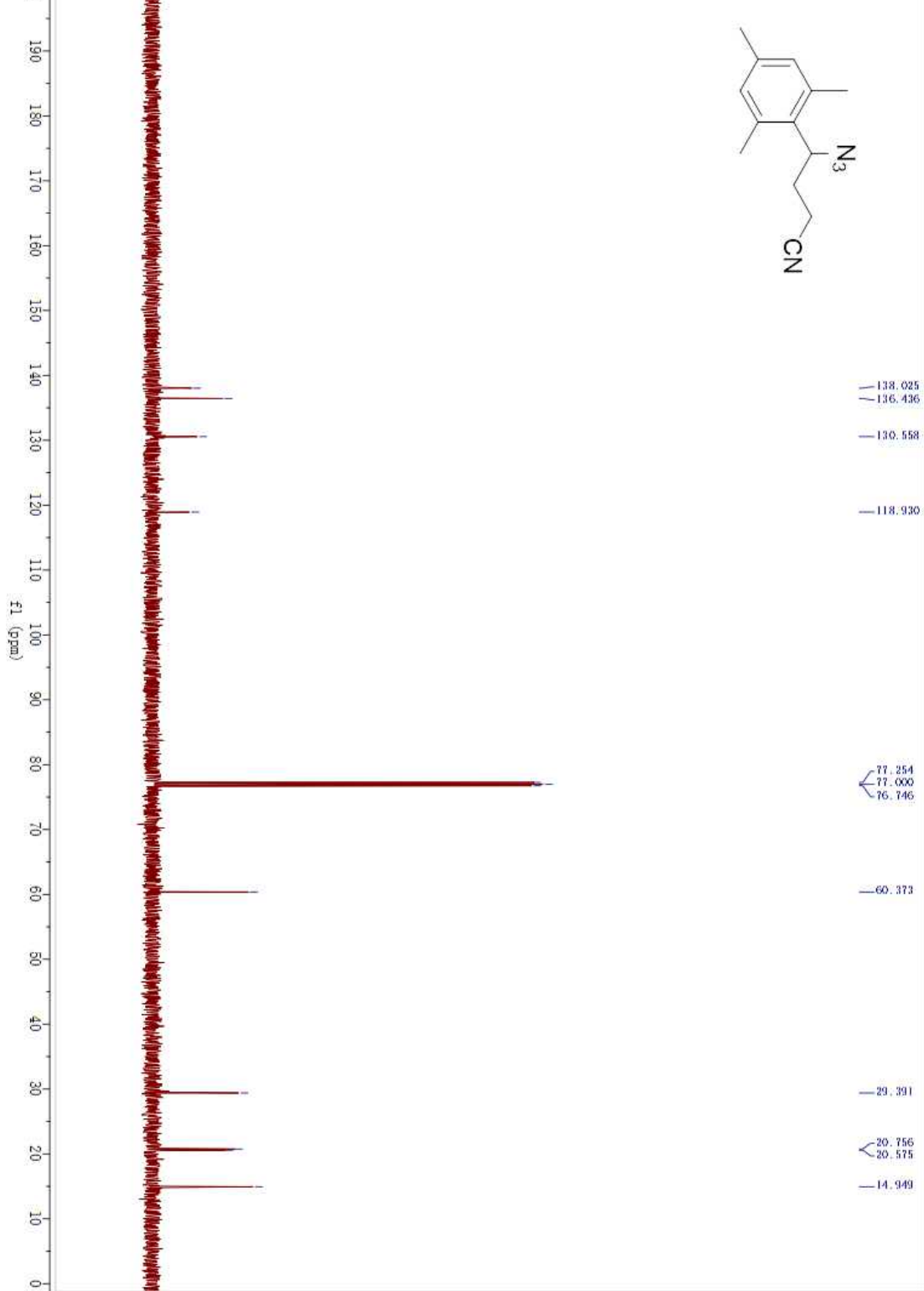
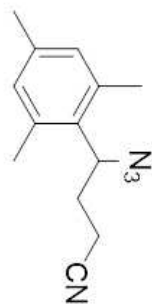


- 158.014
- 156.383
- 132.082
- 129.856
- 128.256
- 123.831
- 119.363
- 118.850
- 118.634
- 77.254
- 77.000
- 76.745
- 63.797
- 31.932
- 14.283

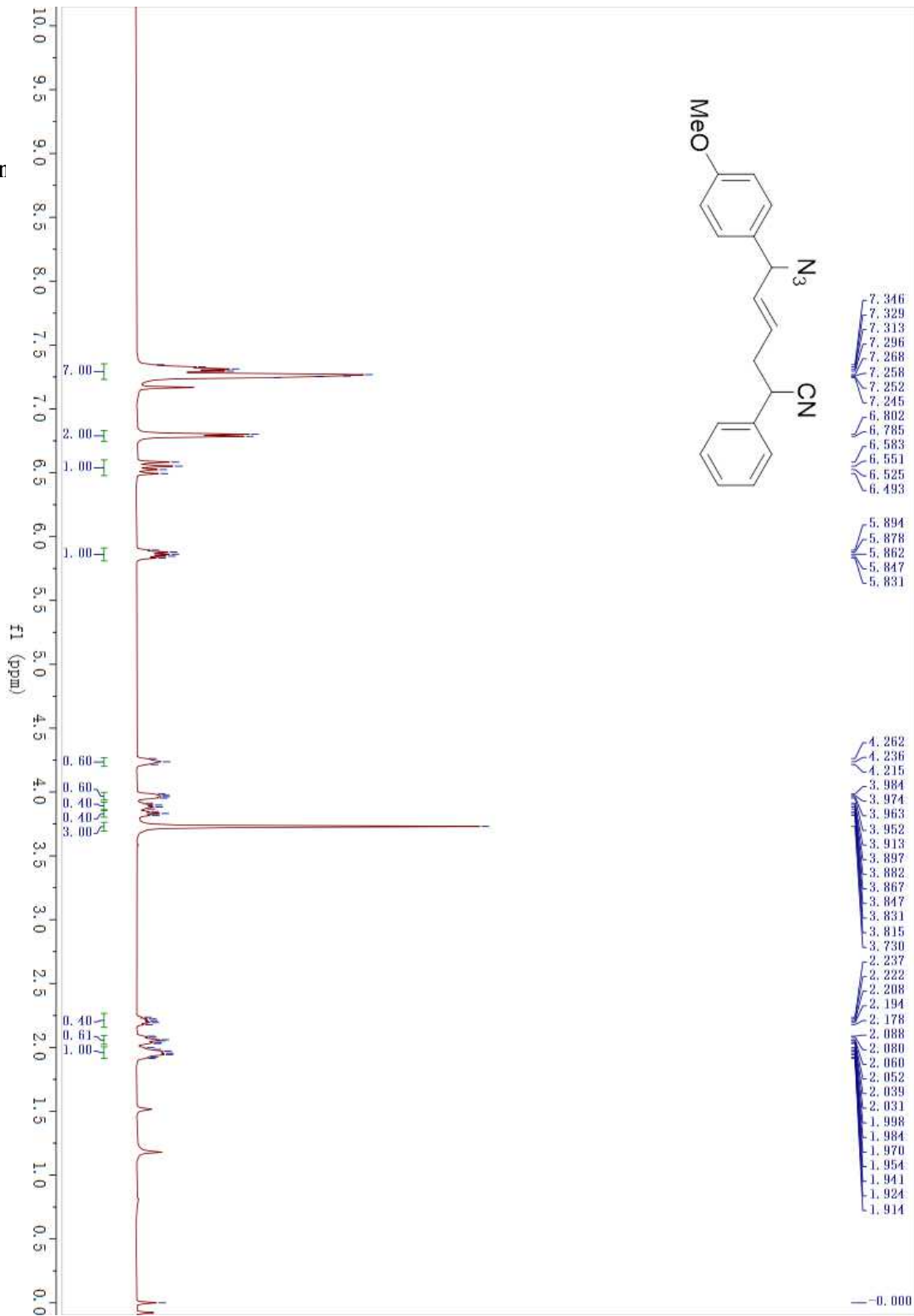


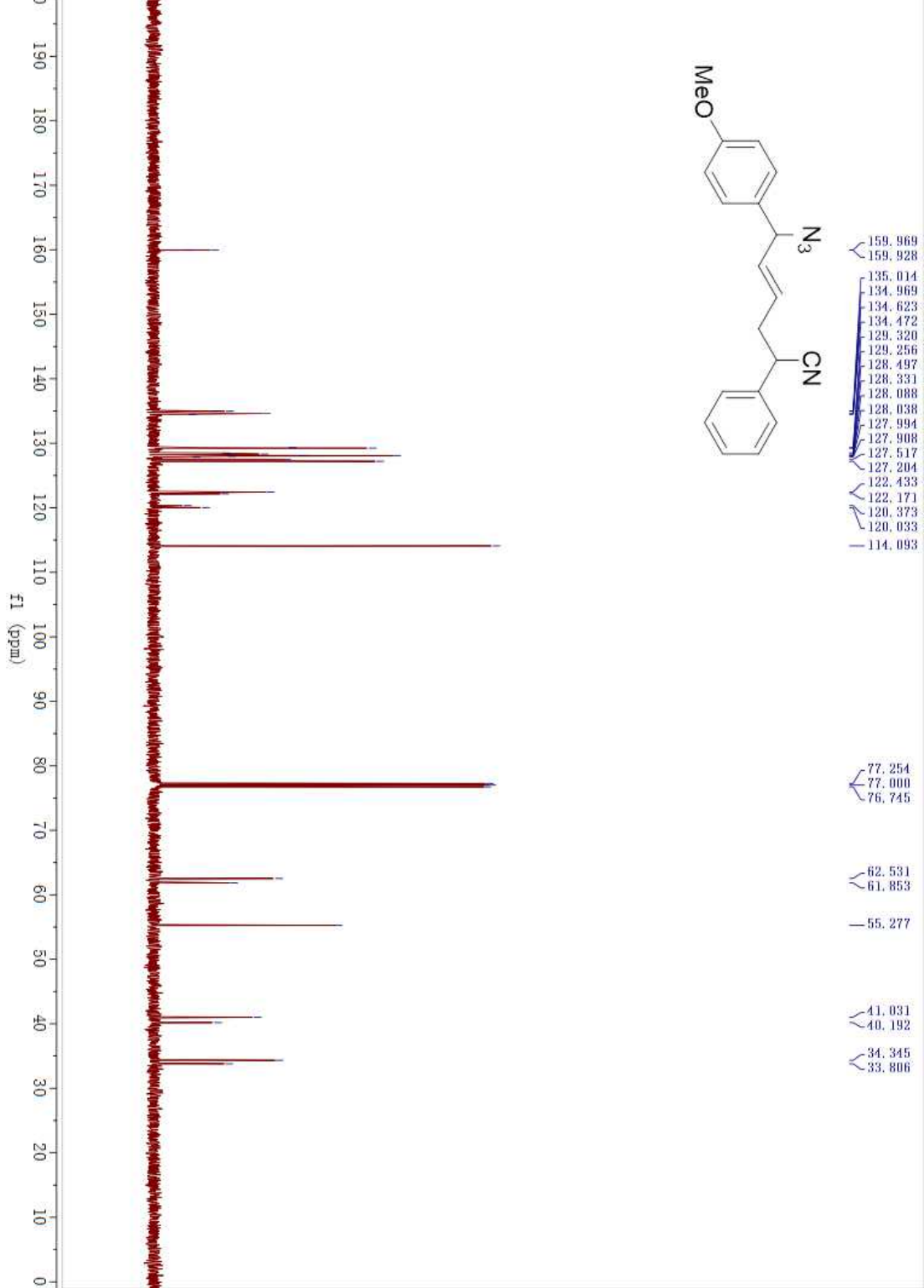
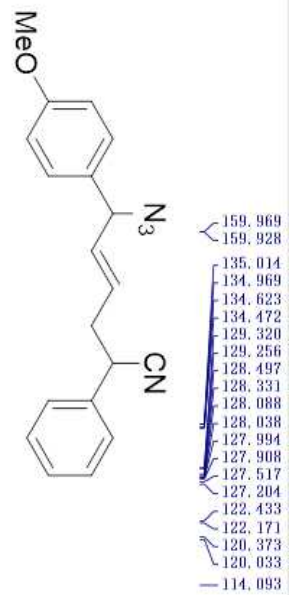
4-azido-4-mesityll



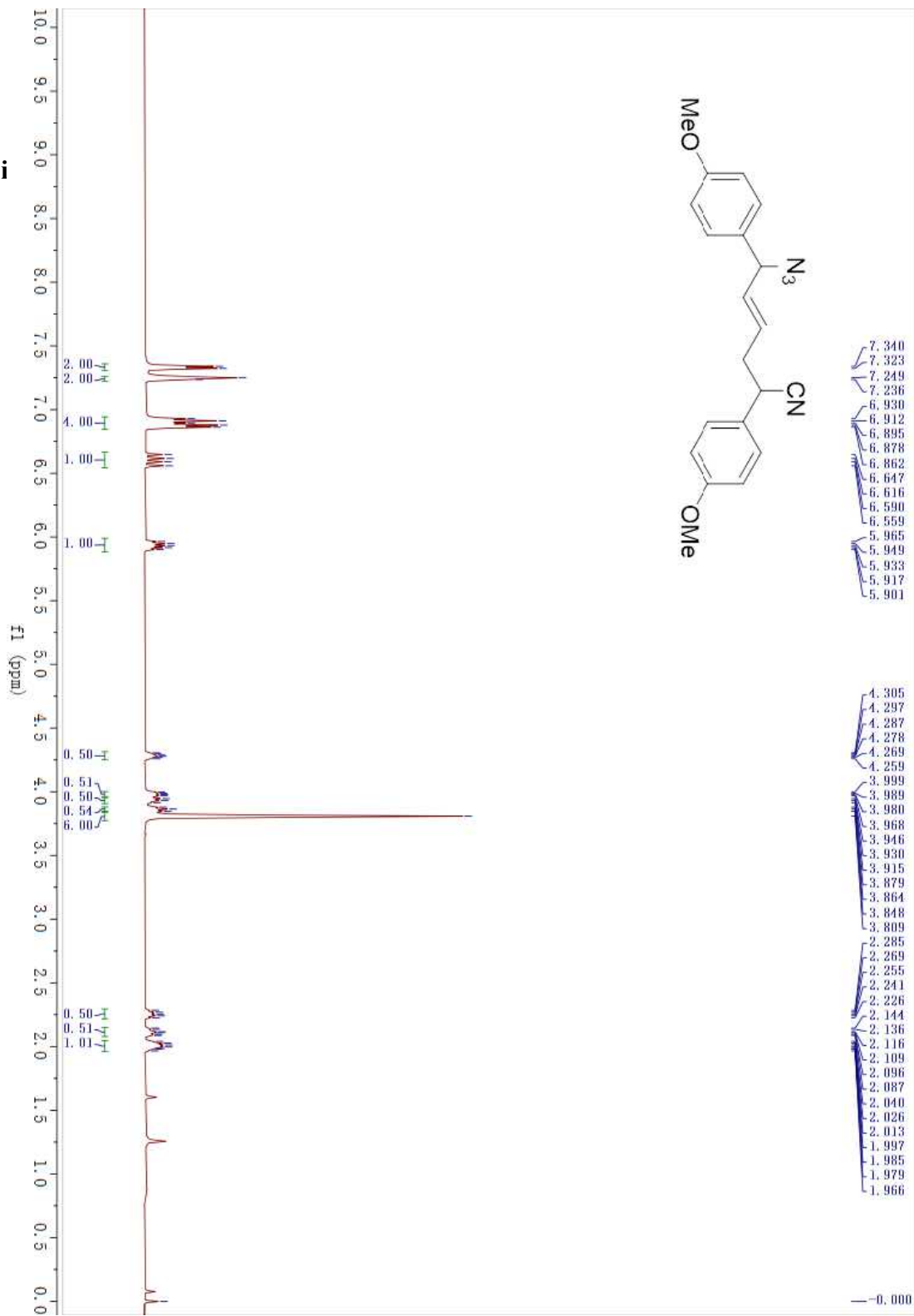


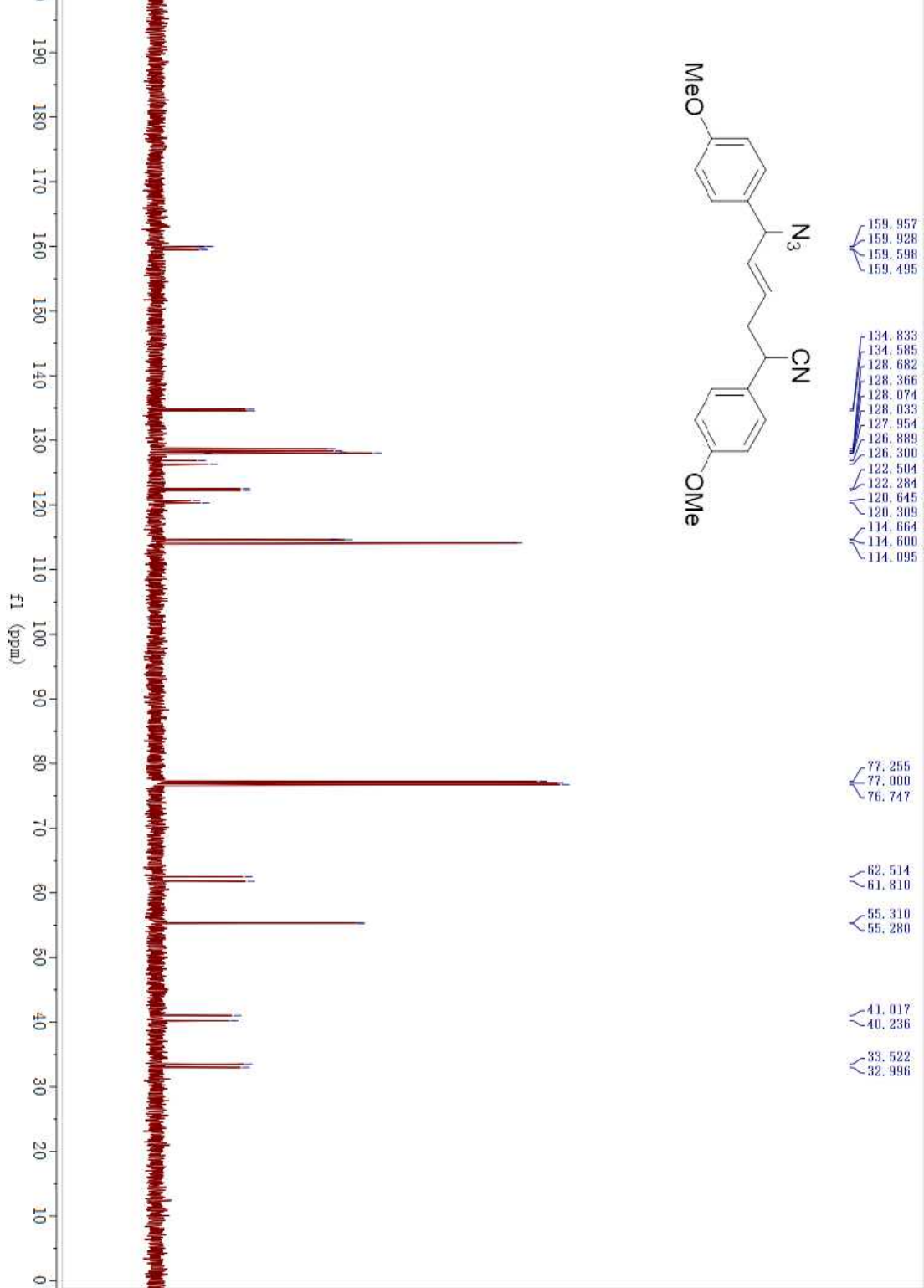
(E)-6-azido-6-(4-*r*



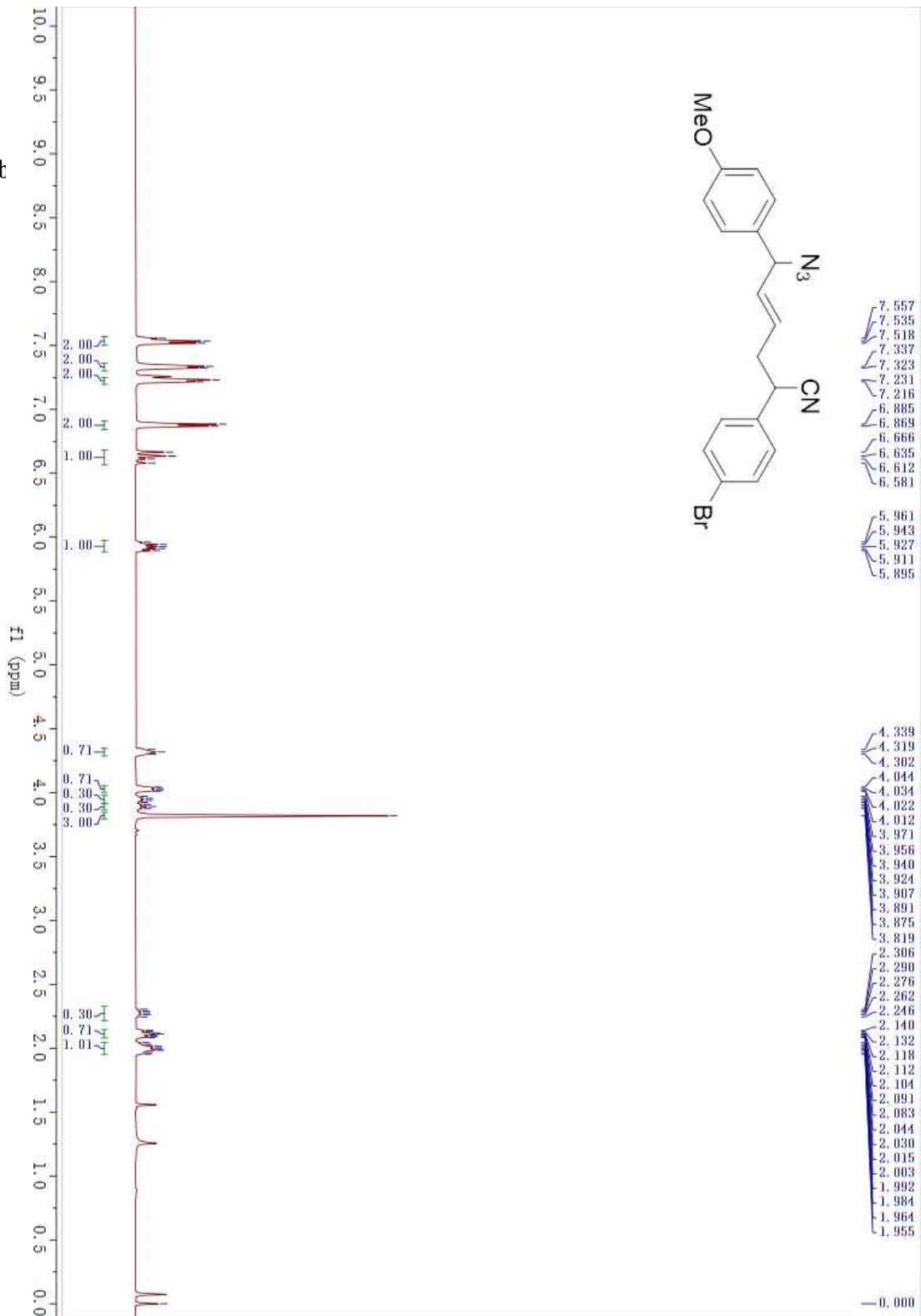


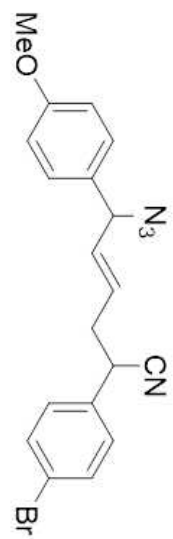
(E)-6-azido-2,6-bi





(E)-6-azido-2-(4-t

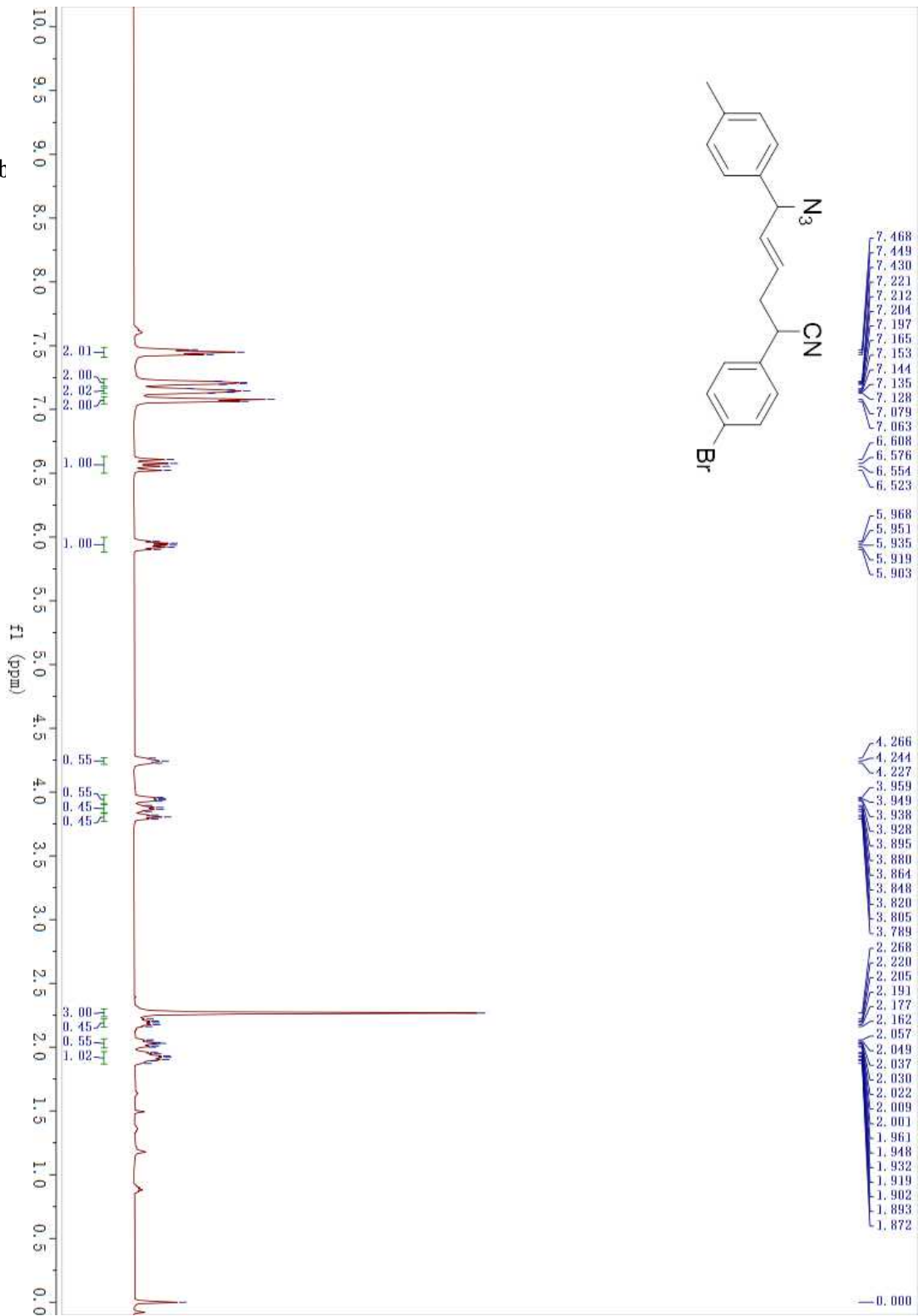


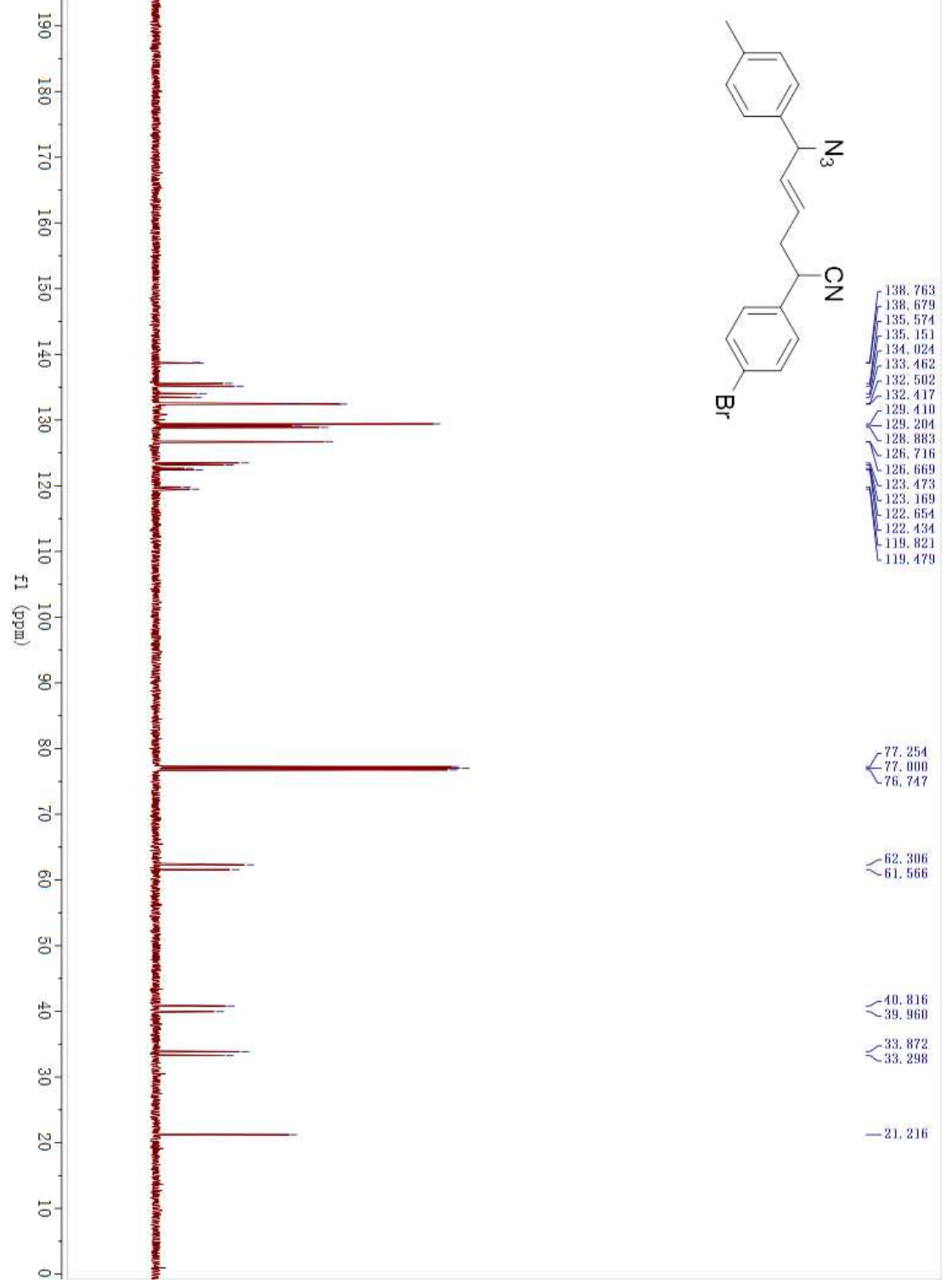
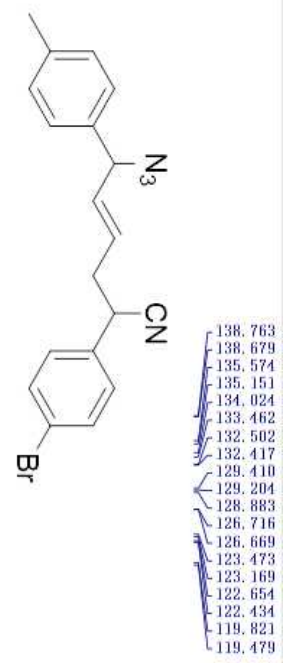


- 160.020
- 135.259
- 134.826
- 134.073
- 133.524
- 132.539
- 132.457
- 129.235
- 128.914
- 128.139
- 128.083
- 127.918
- 122.685
- 122.468
- 122.233
- 121.899
- 119.528
- 114.148
- 77.255
- 77.000
- 76.746
- 62.469
- 61.732
- 55.321
- 40.947
- 40.075
- 33.930
- 33.355

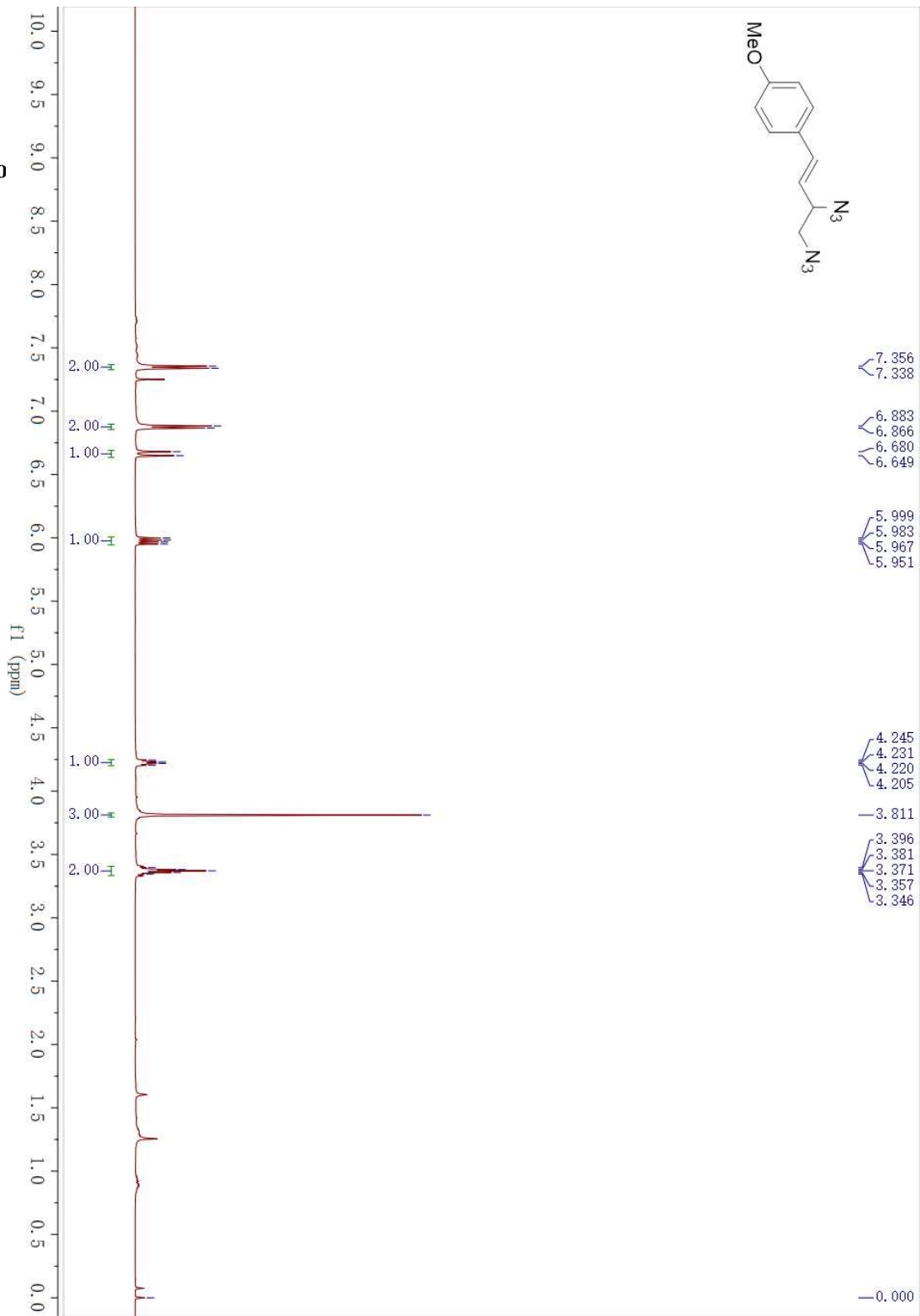


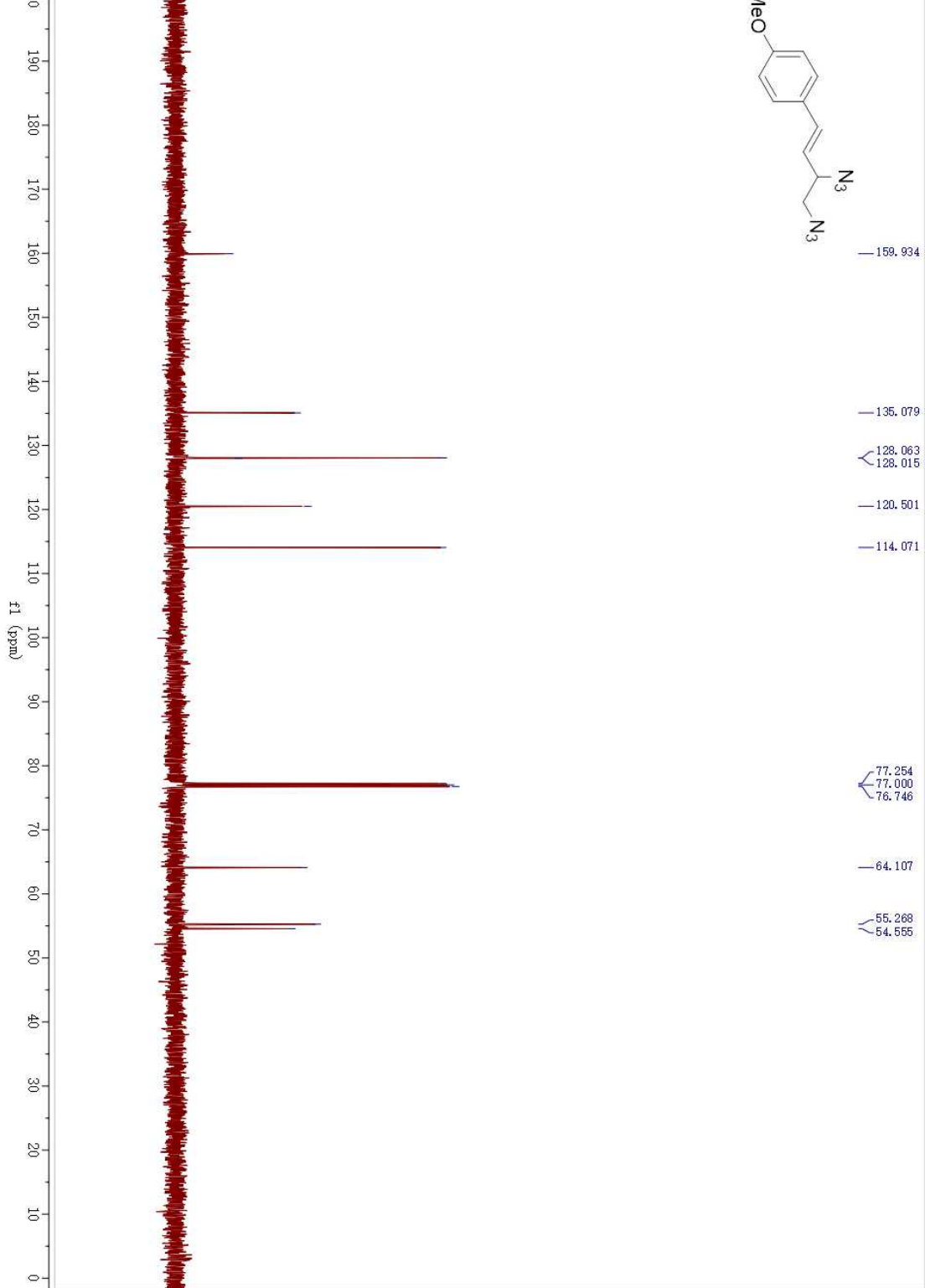
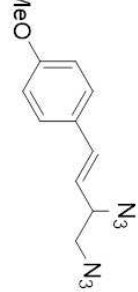
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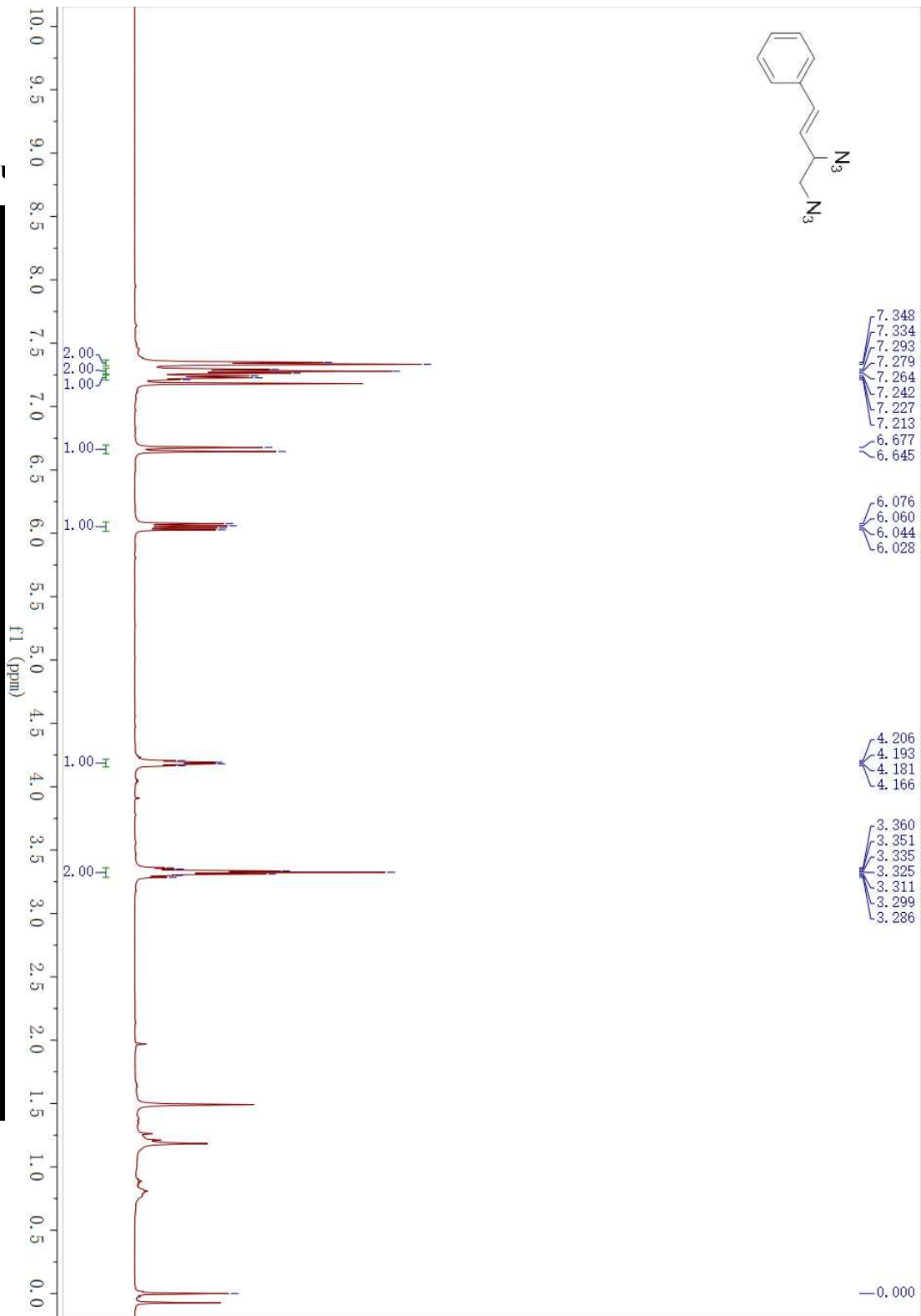
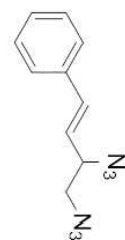


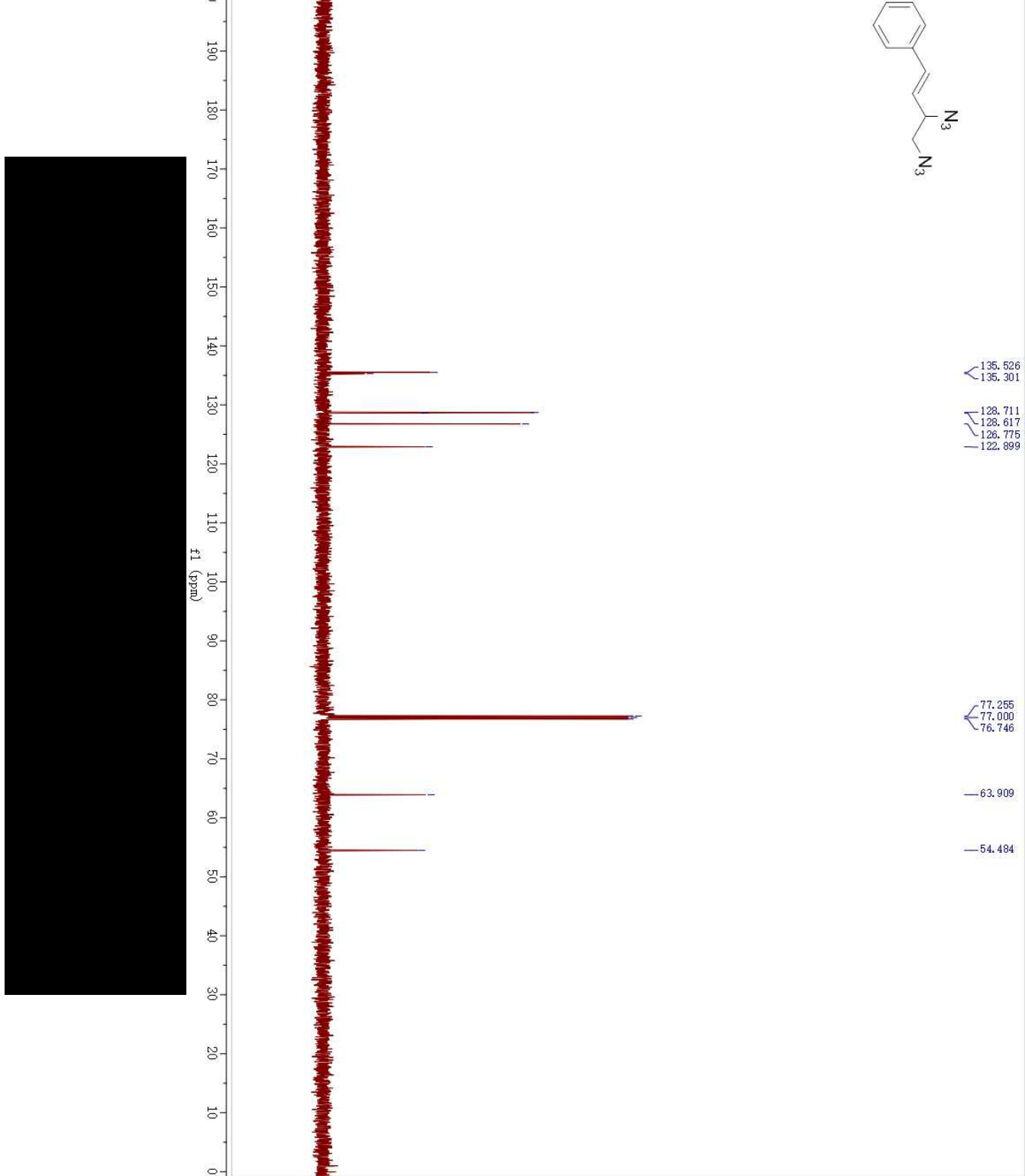
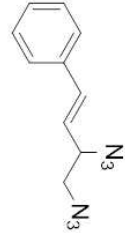
(E)-1-(3,4-diazido



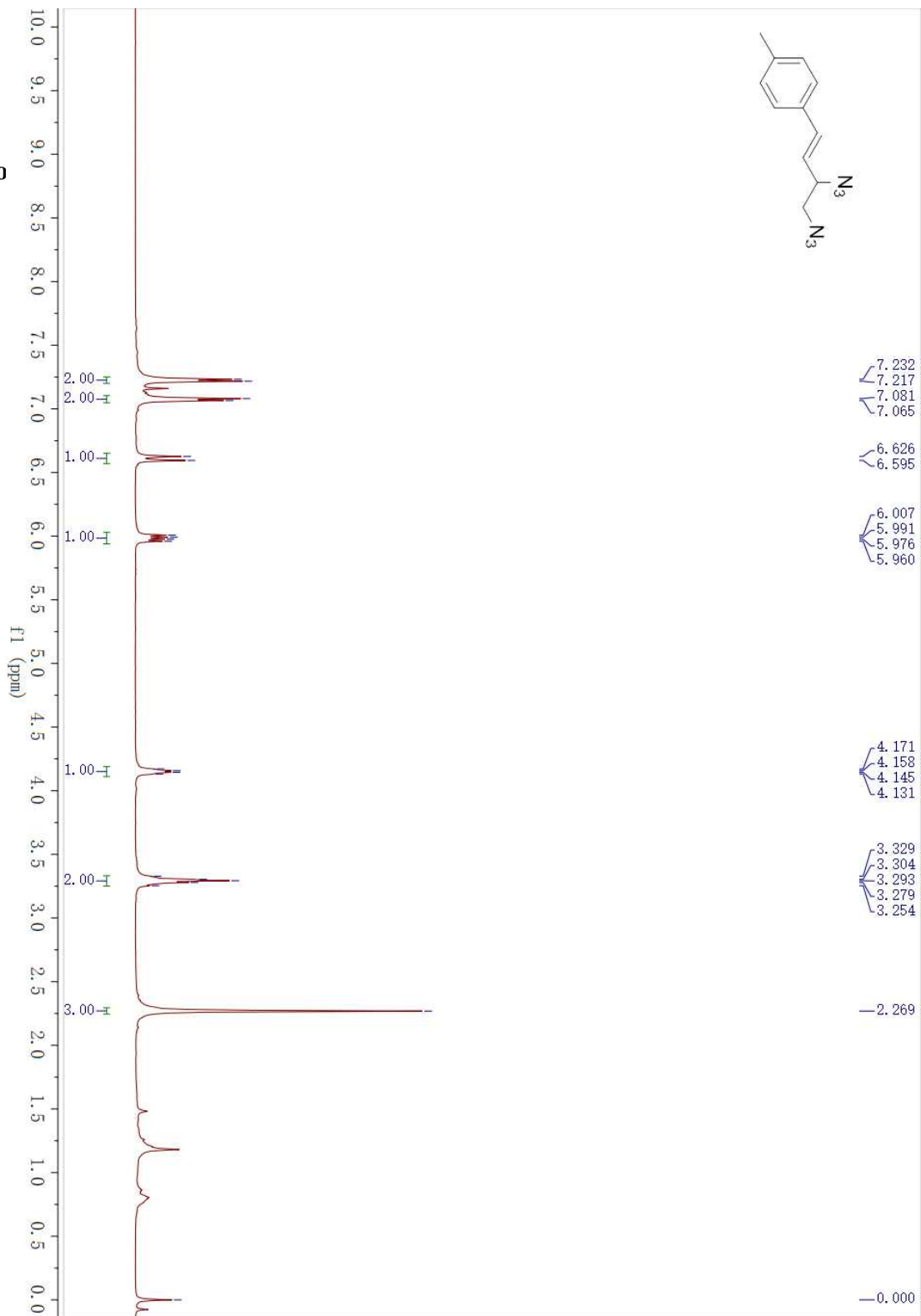


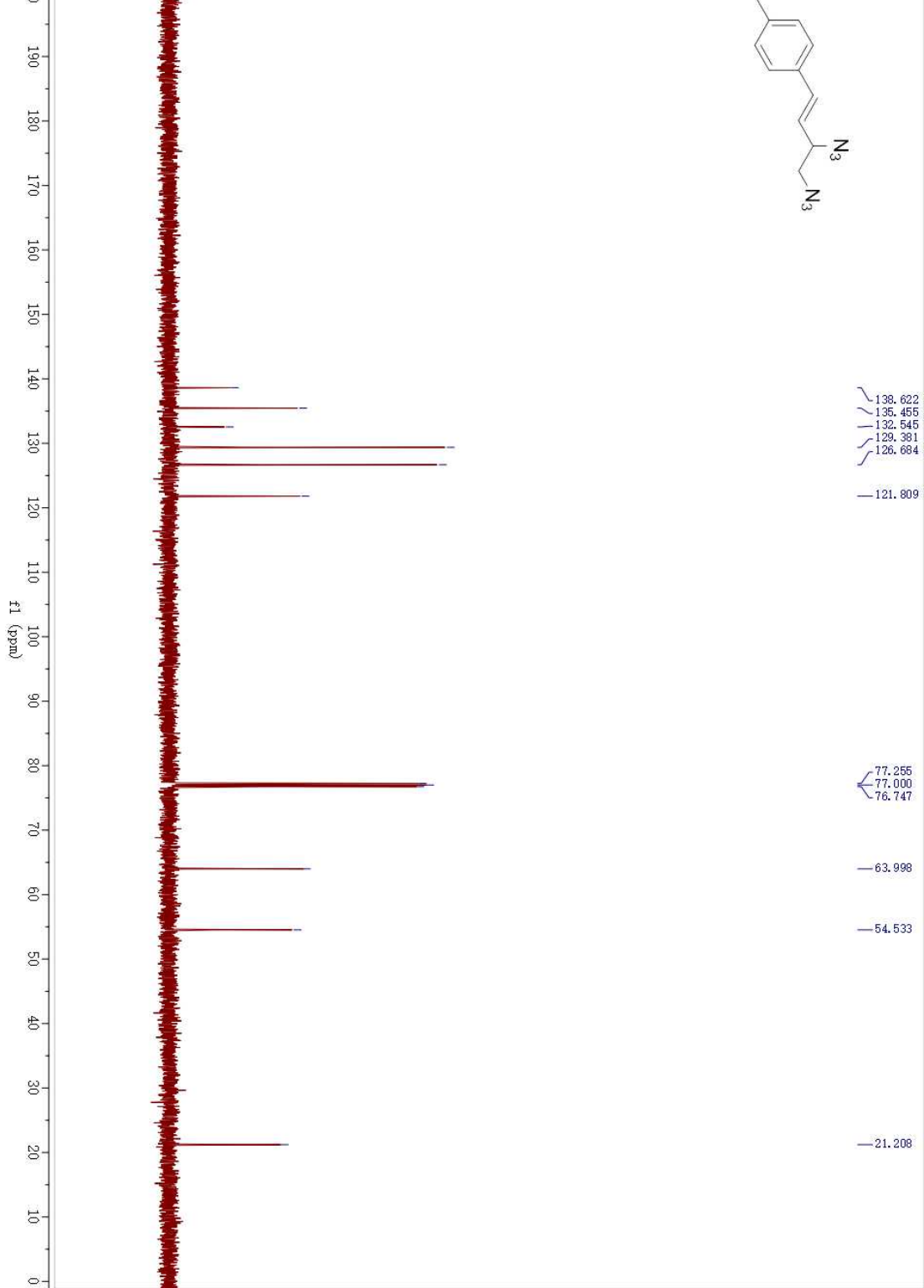
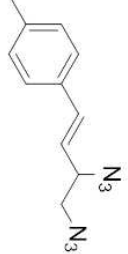
(E)-(3,4-diazidobut-1-en-1-yl)benzene



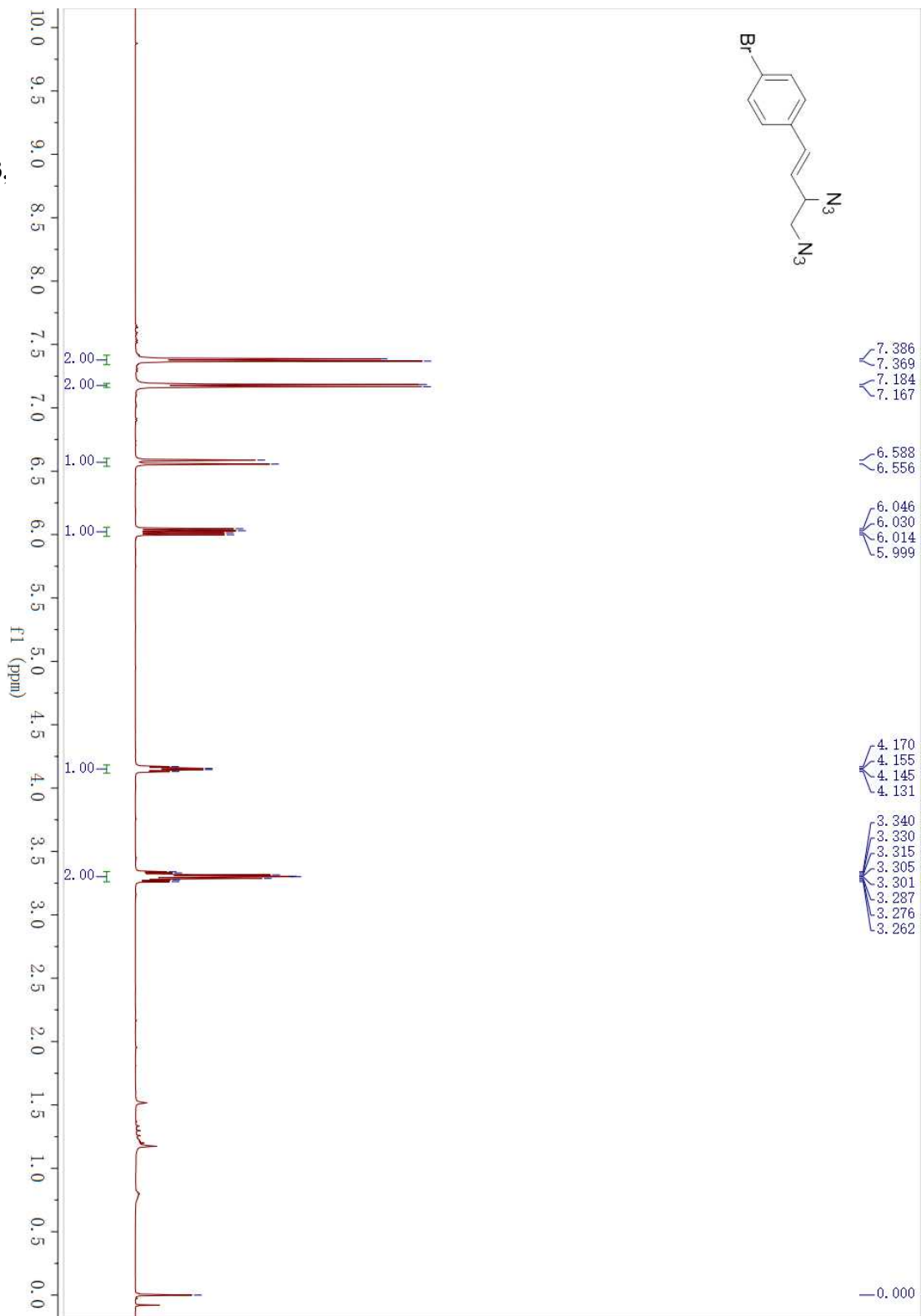


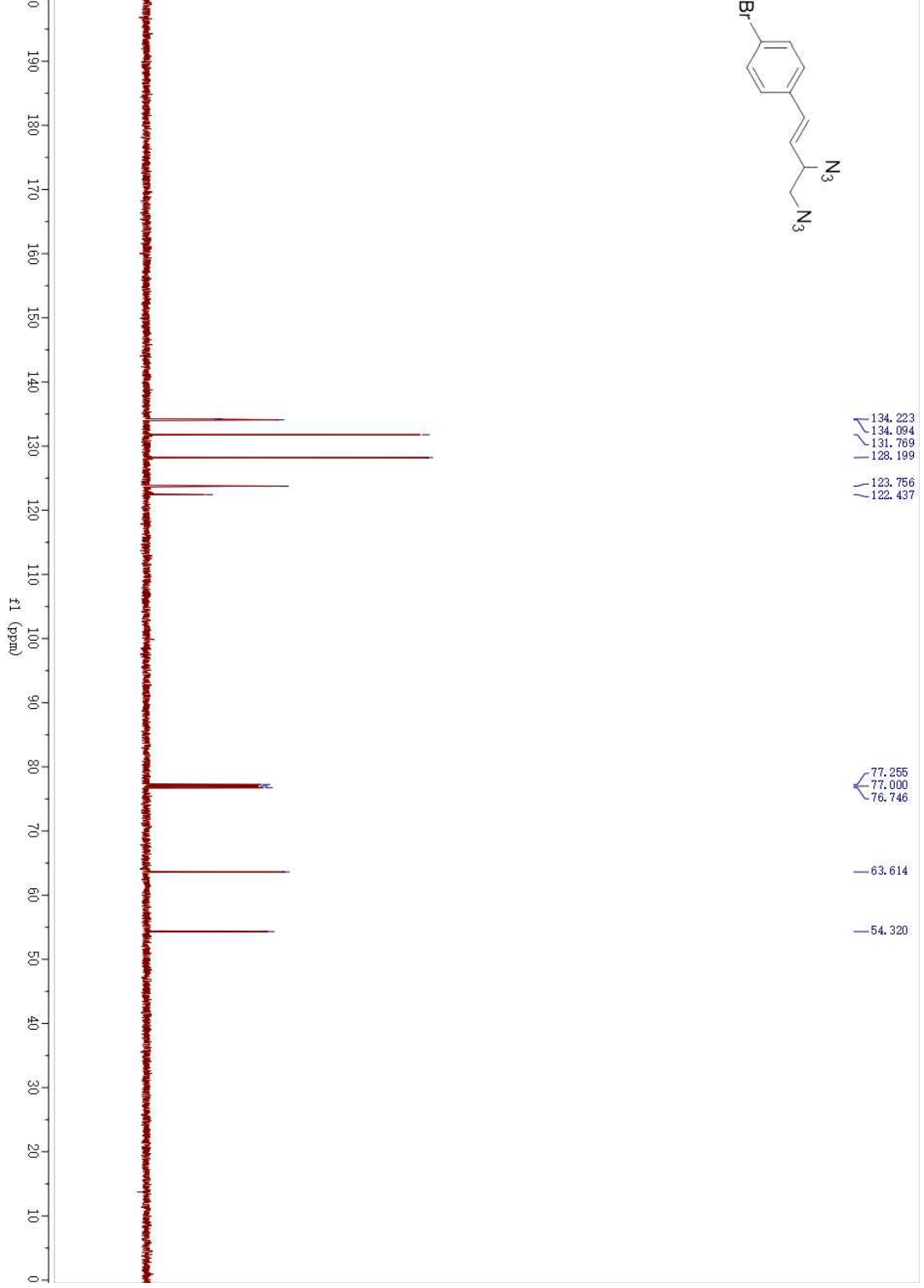
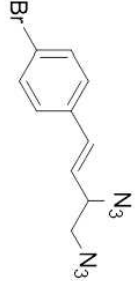
(E)-1-(3,4-diazido



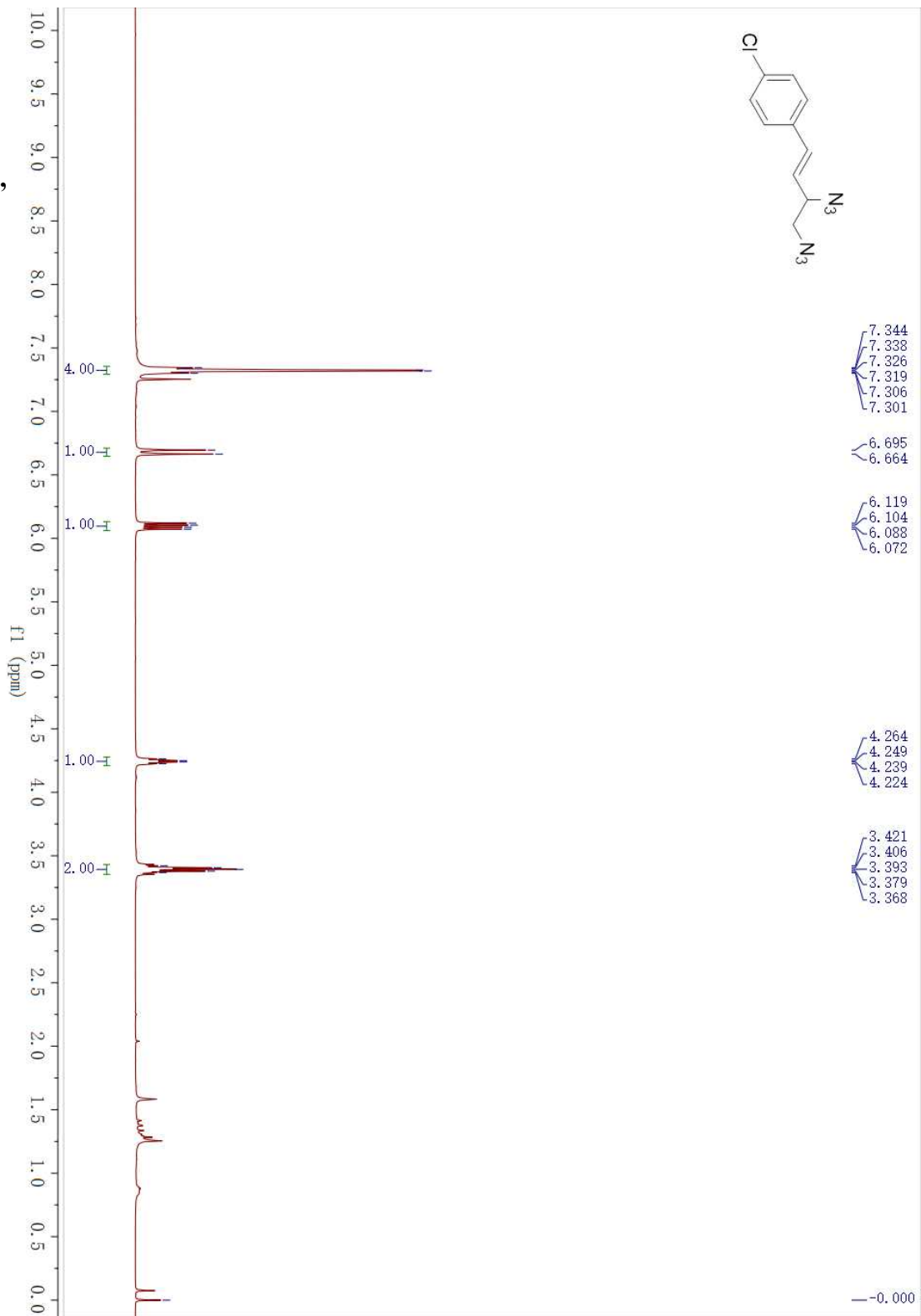


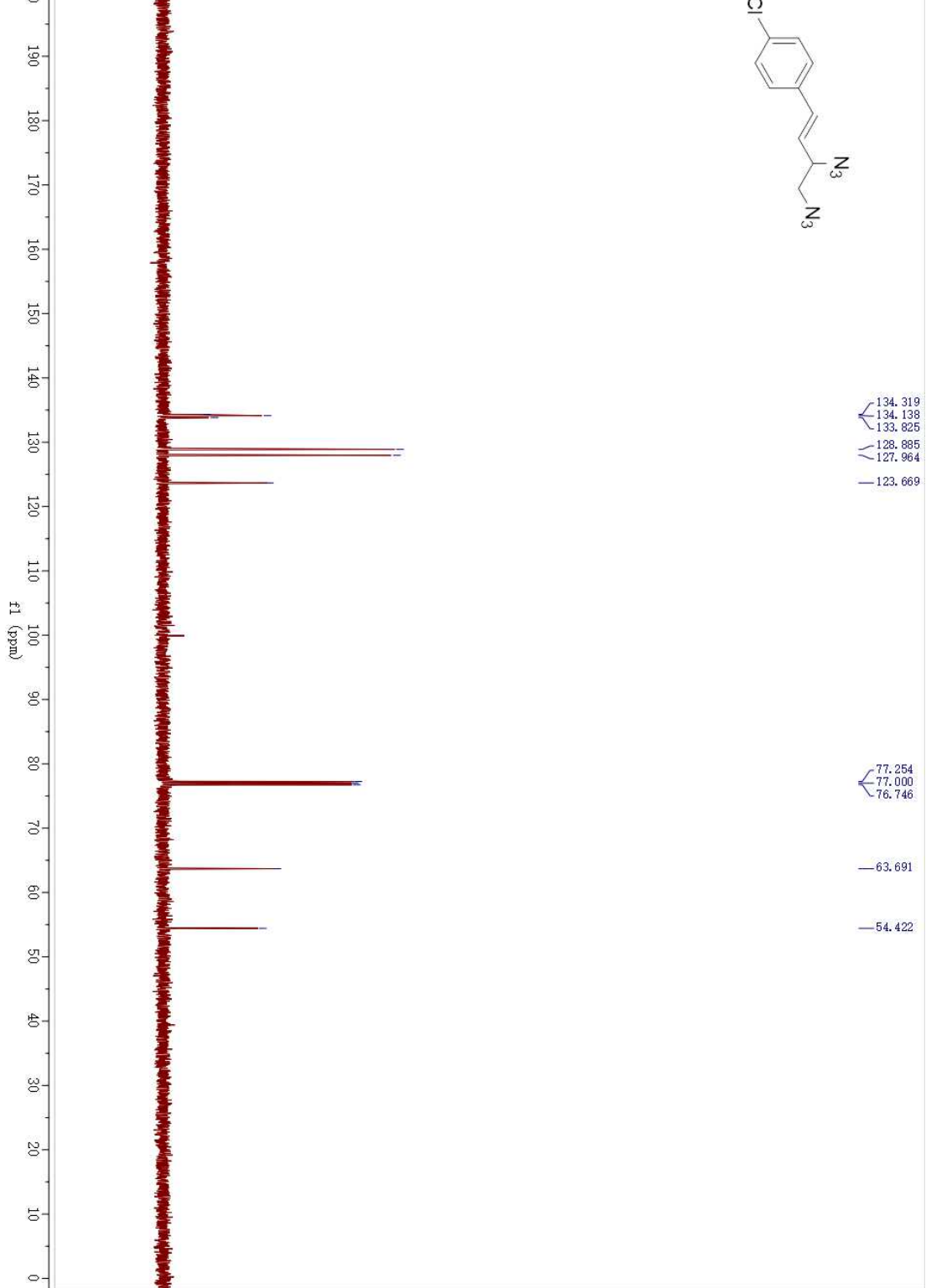
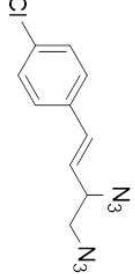
(E)-1-bromo-4-(3-



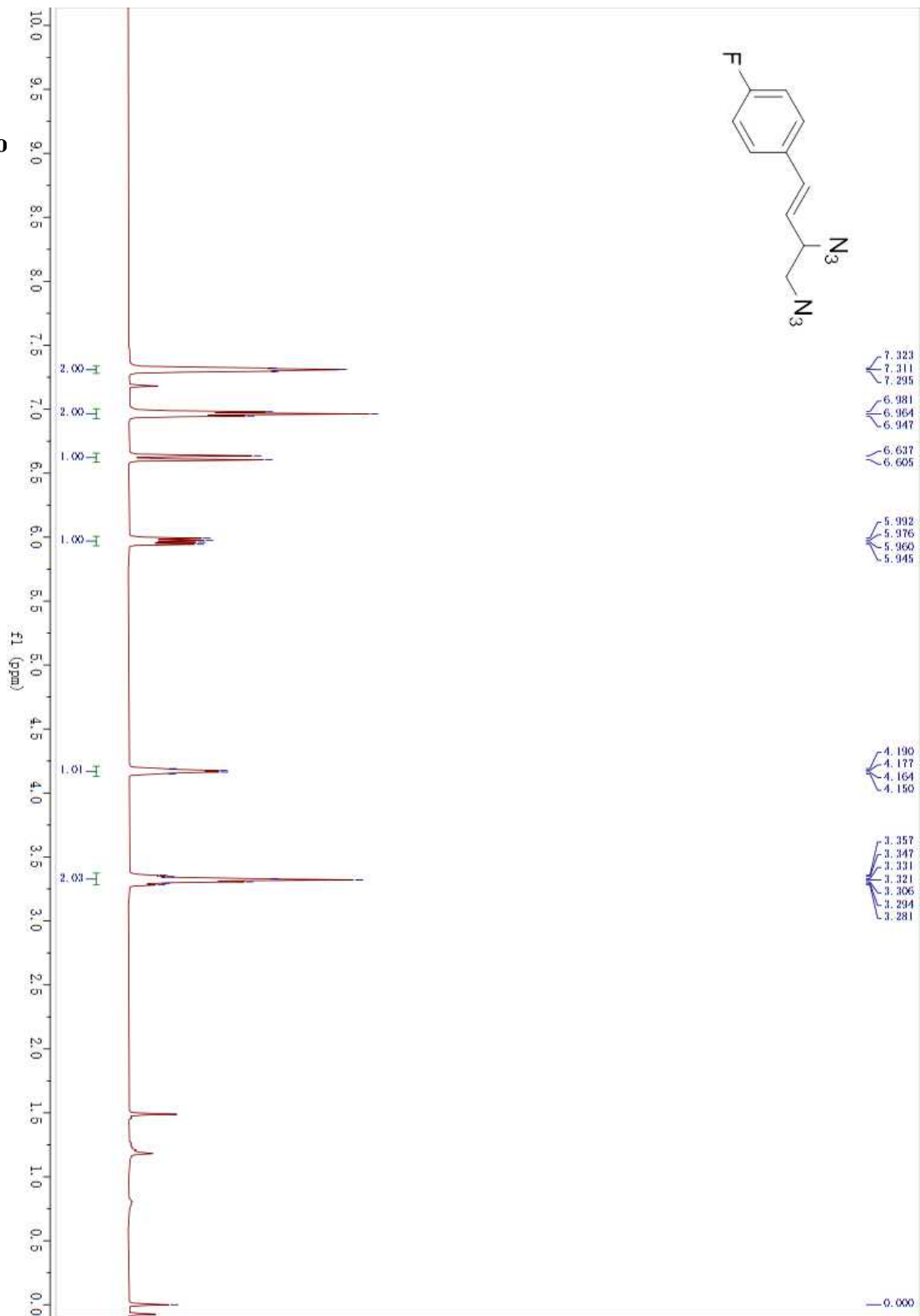


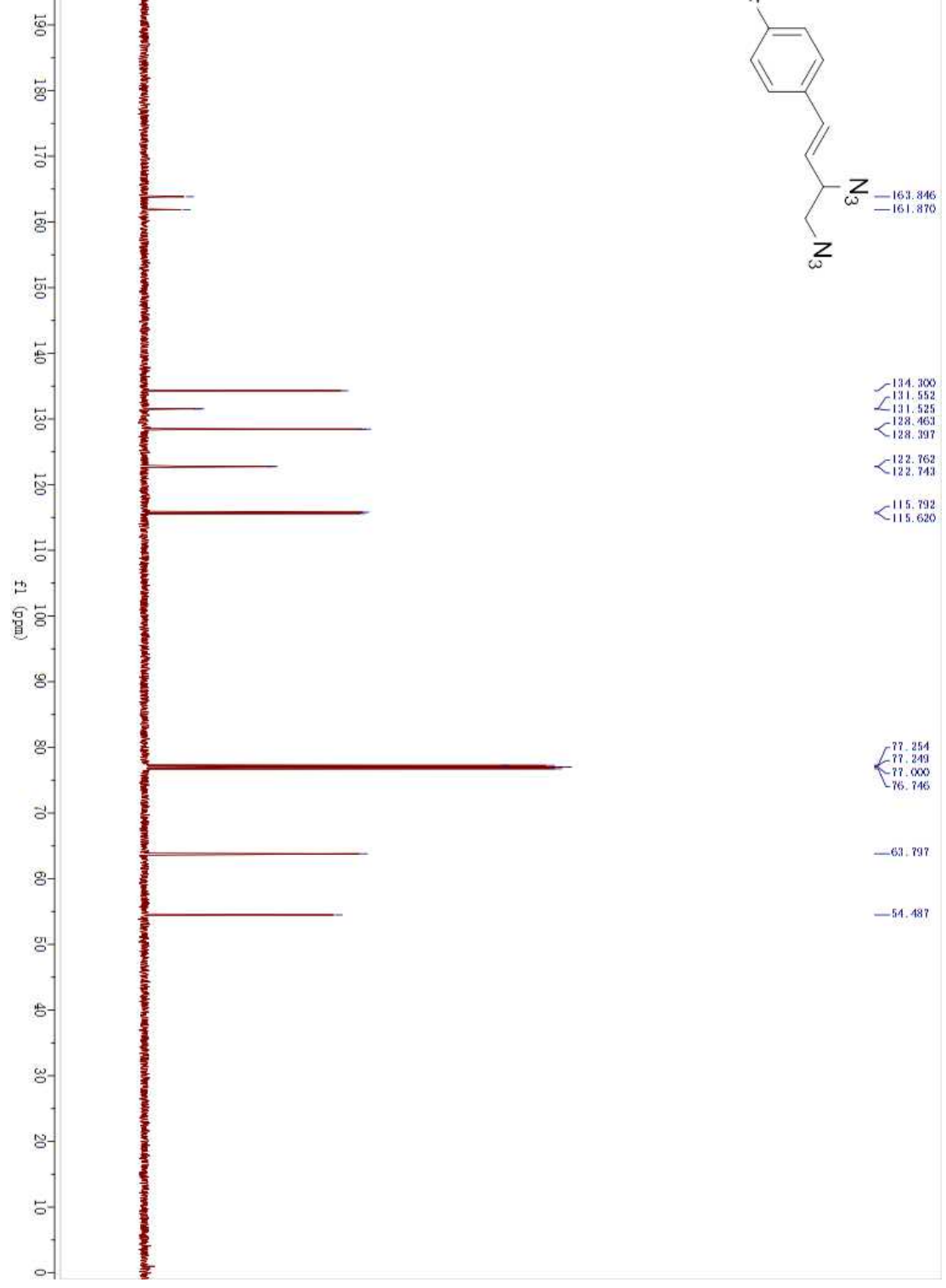
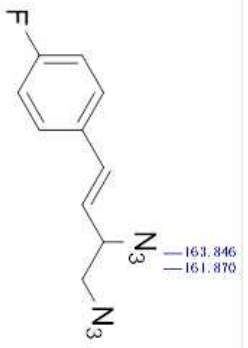
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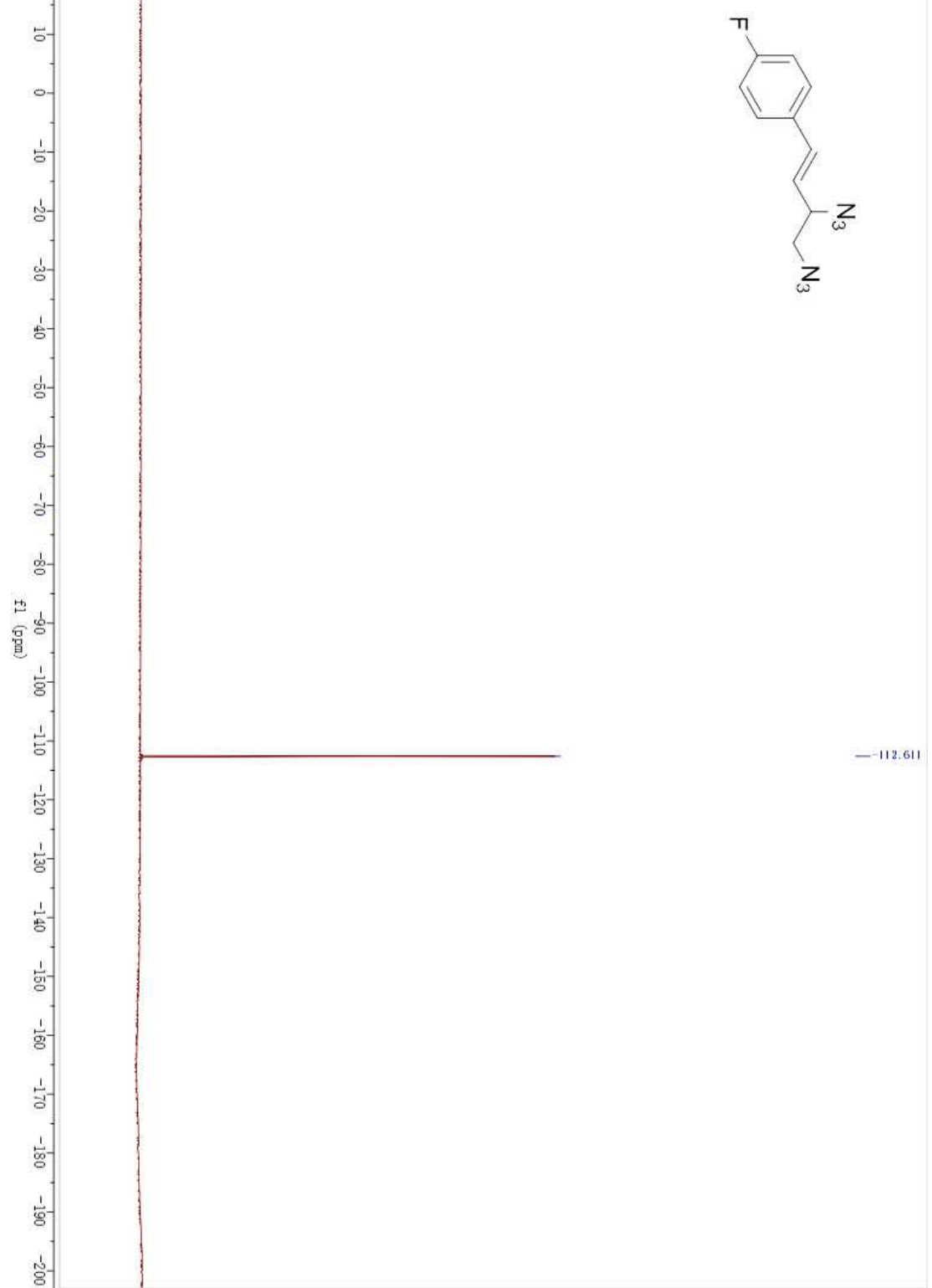
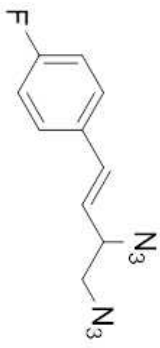


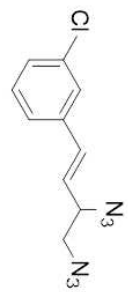


(E)-1-(3,4-diazido

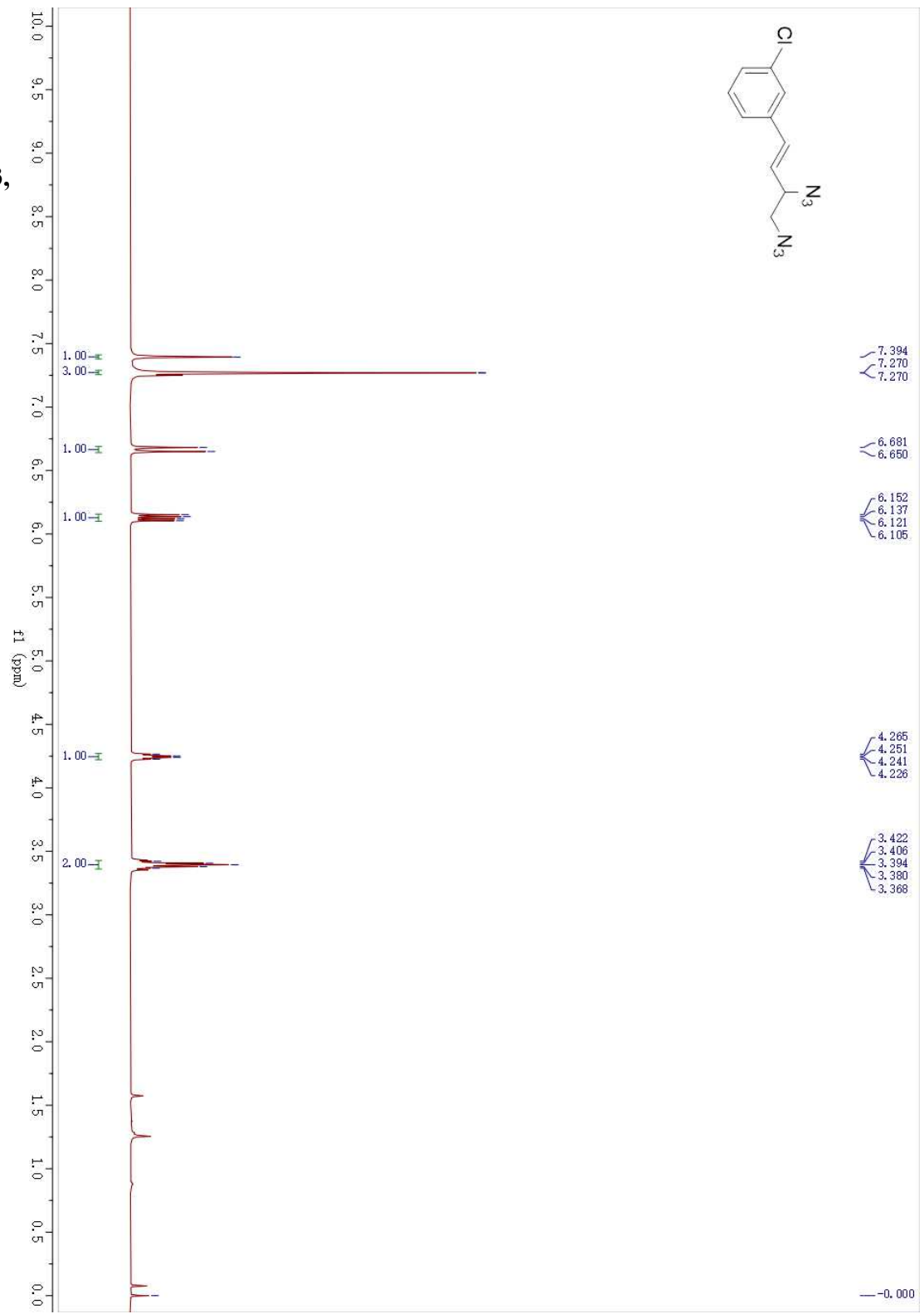


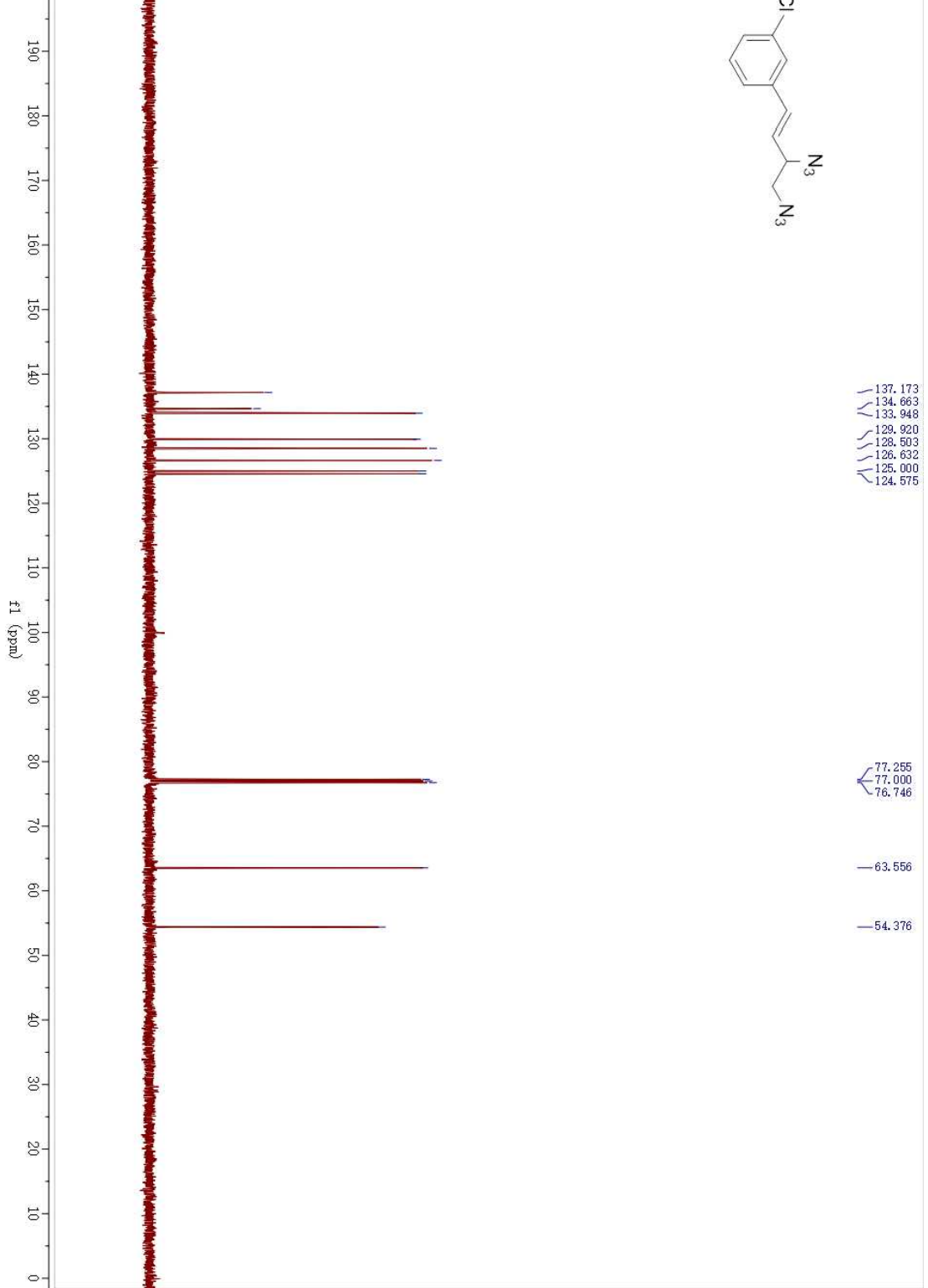
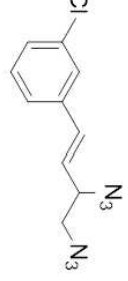




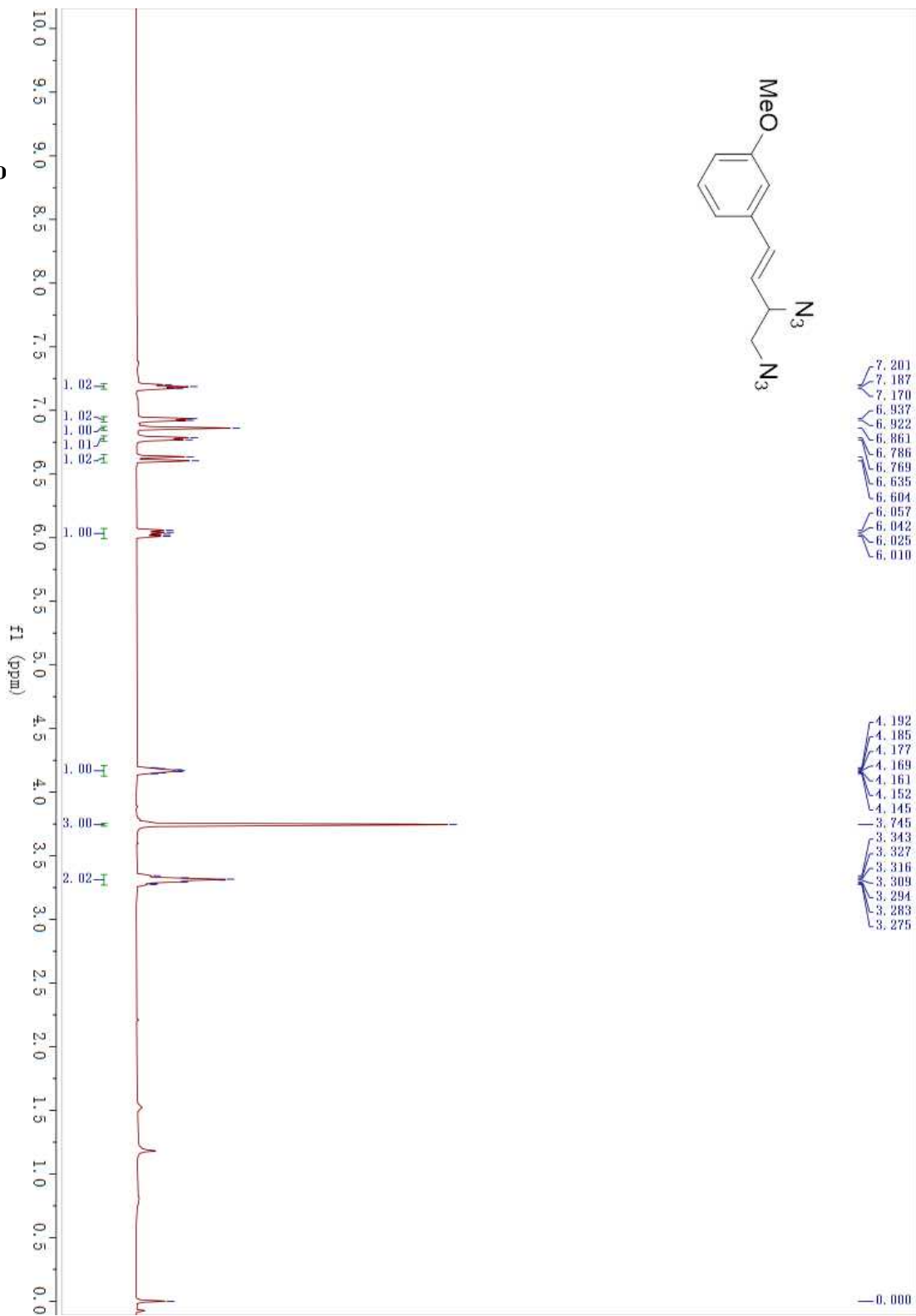


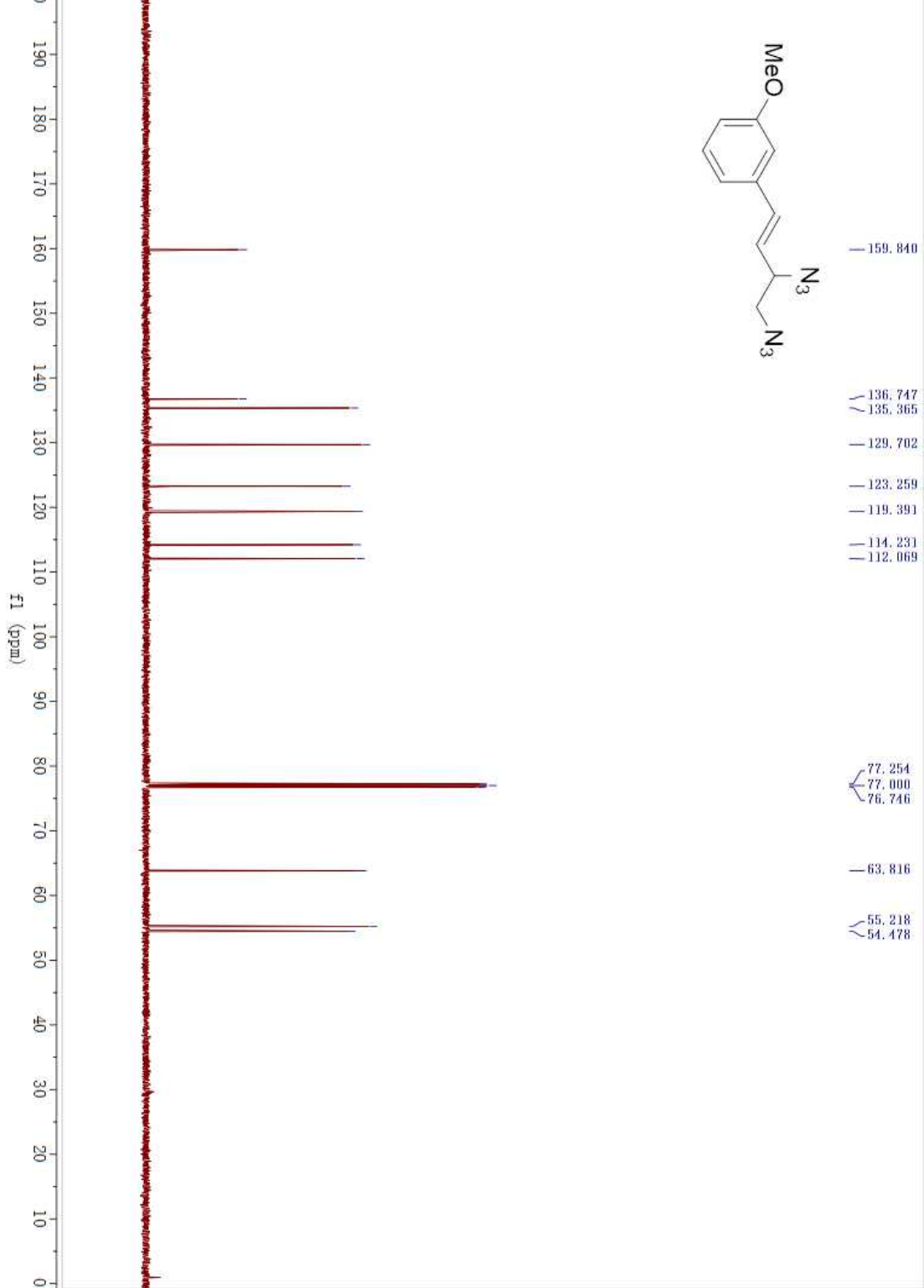
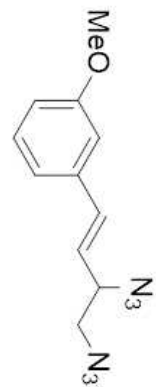
(E)-1-chloro-3-(3,3,3-triazol-1-yl)prop-1-ene



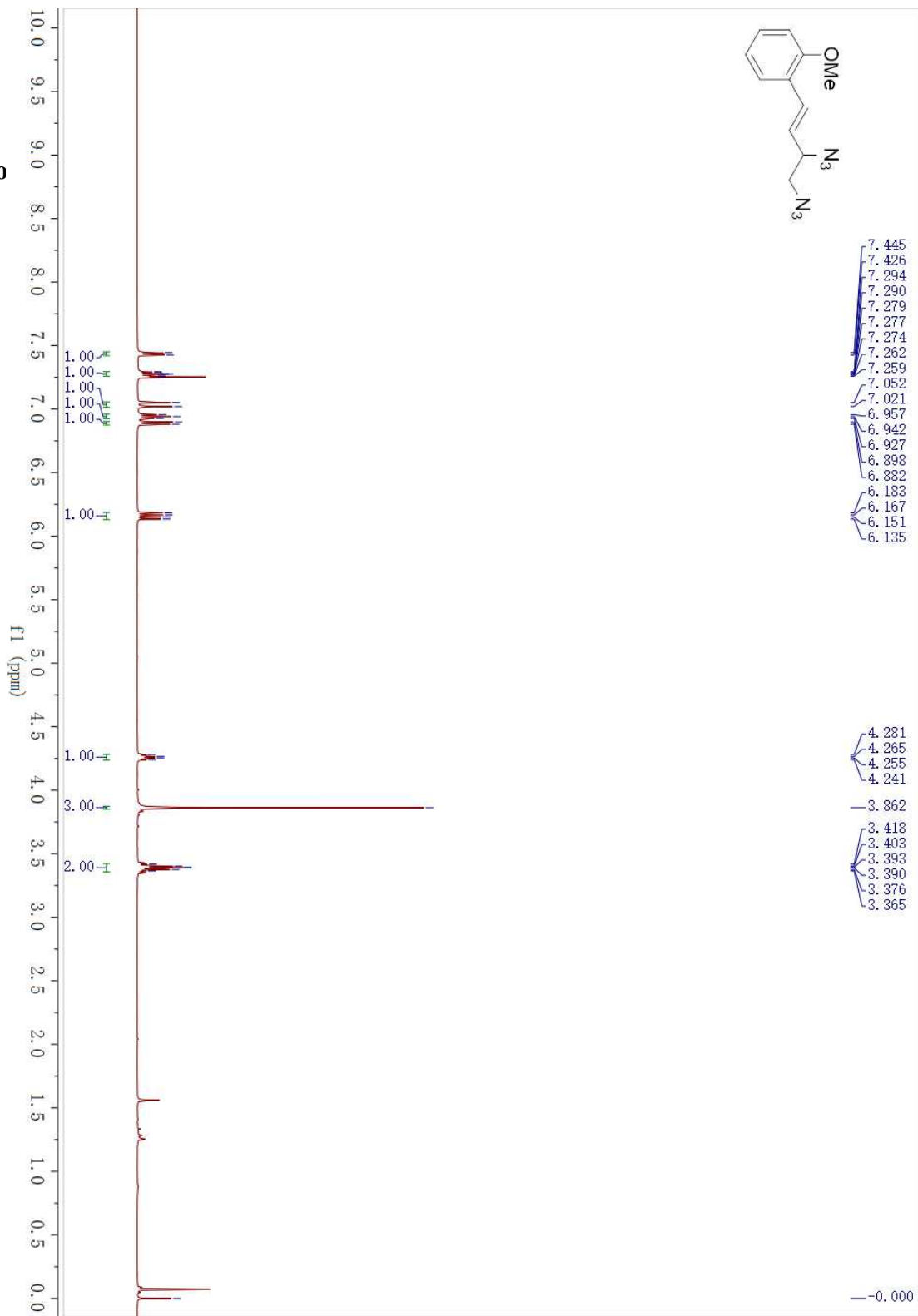


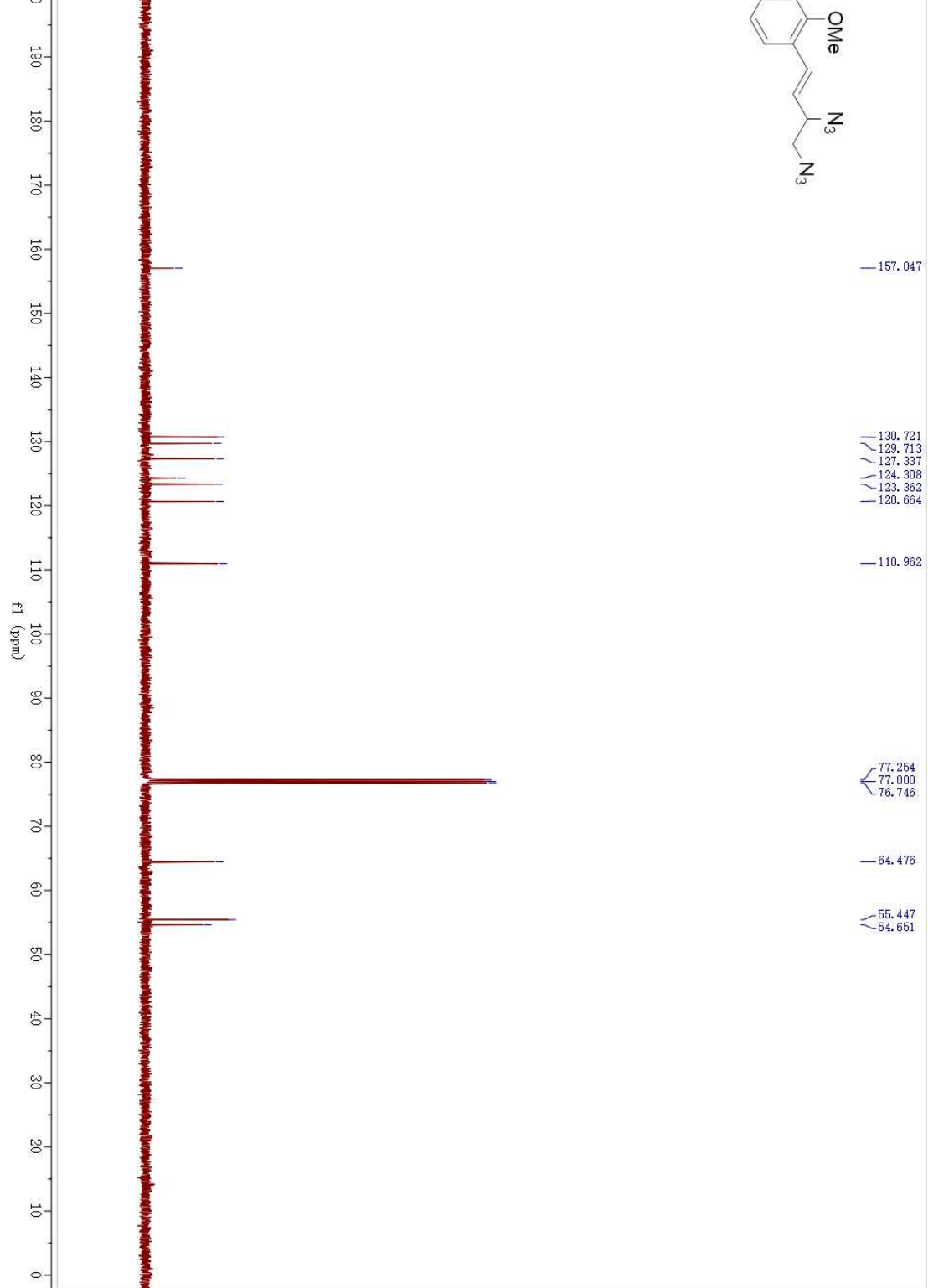
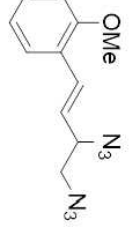
(E)-1-(3,4-diazido

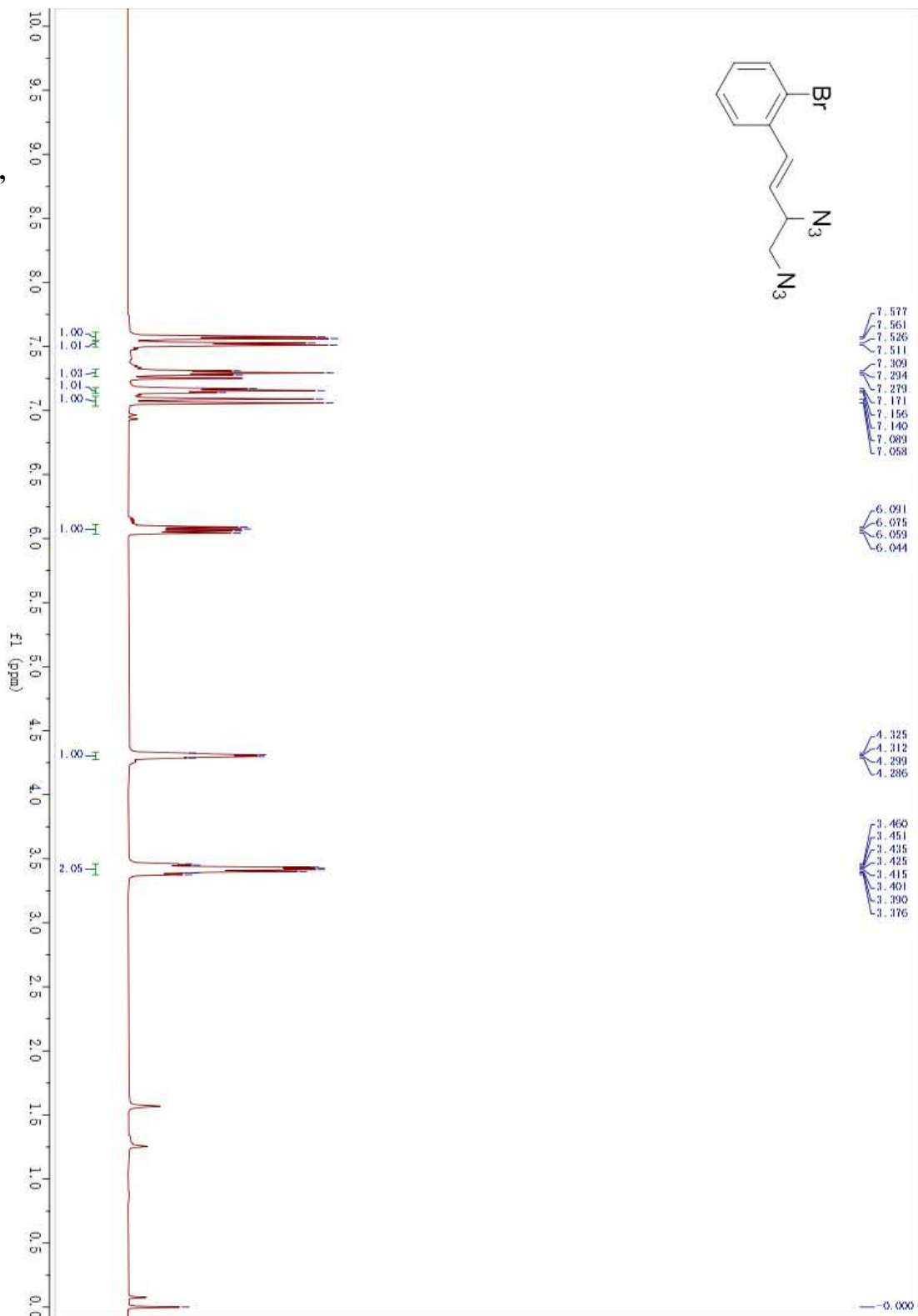
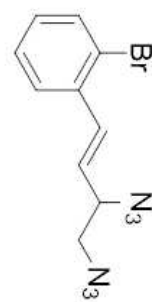




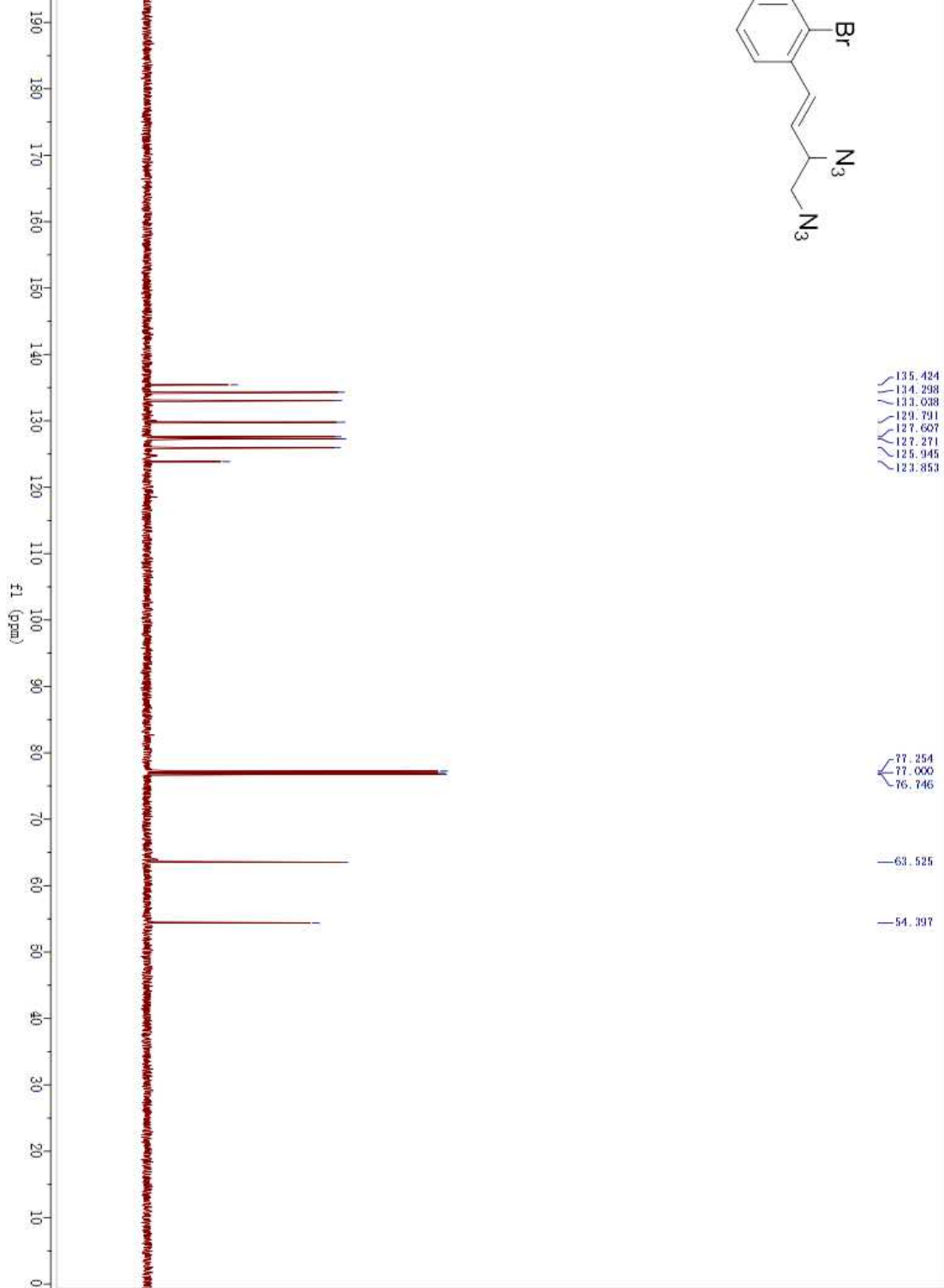
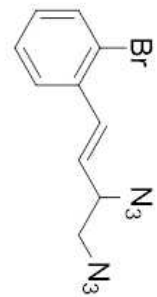
(E)-1-(3,4-diazido

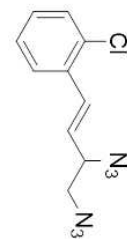




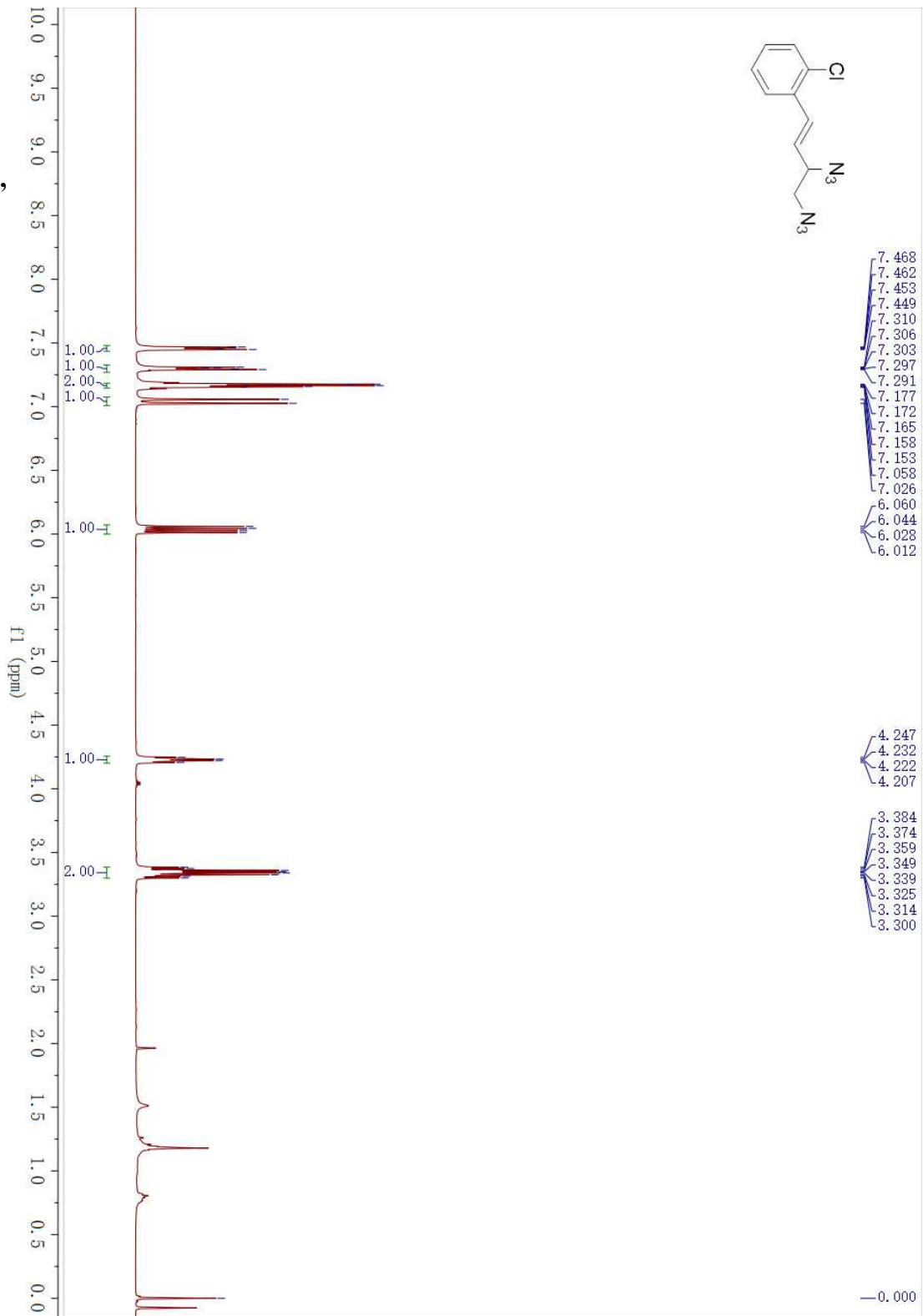


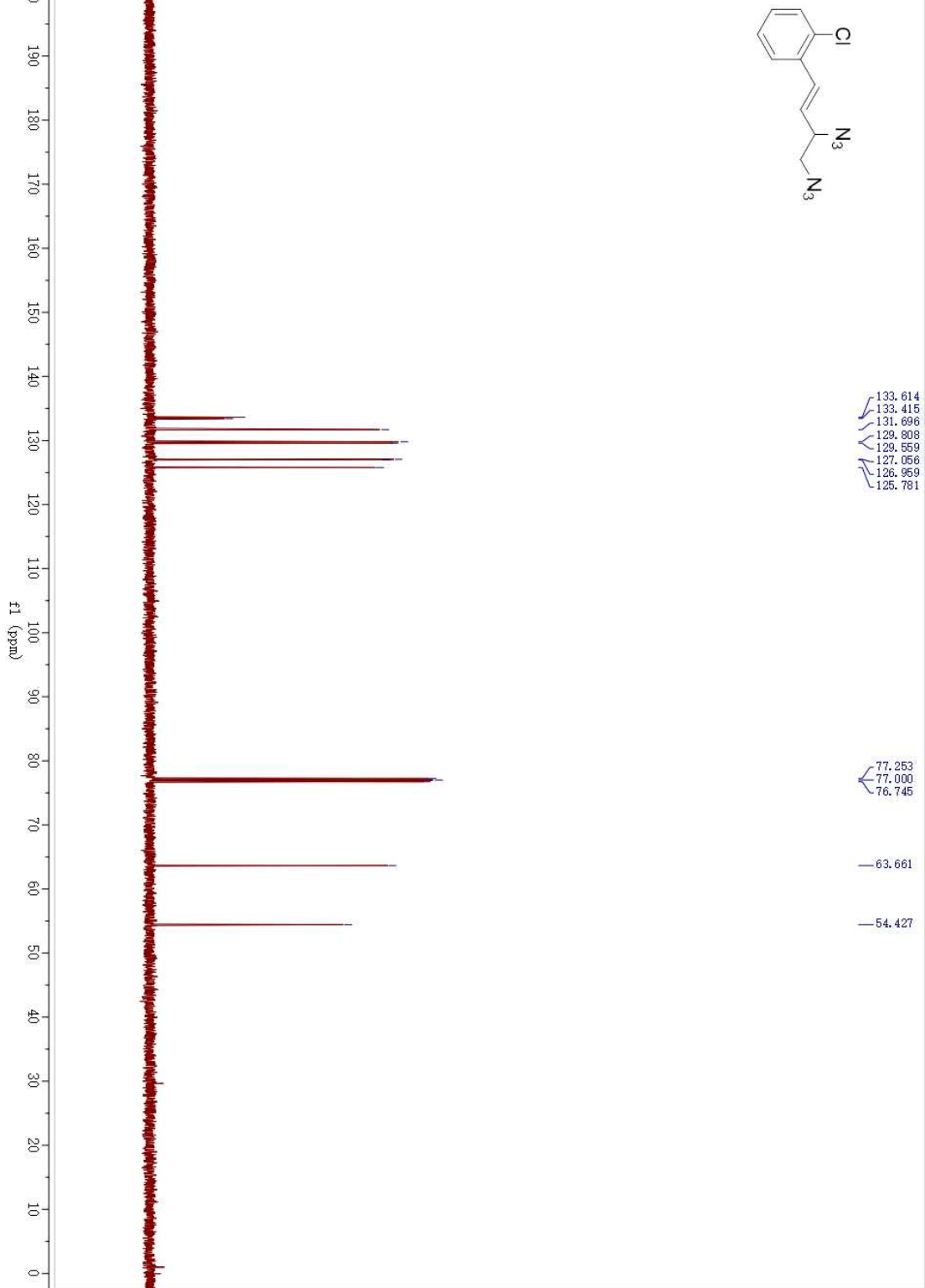
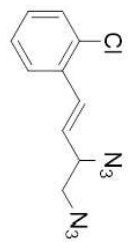
(E)-1-bromo-3-(3-



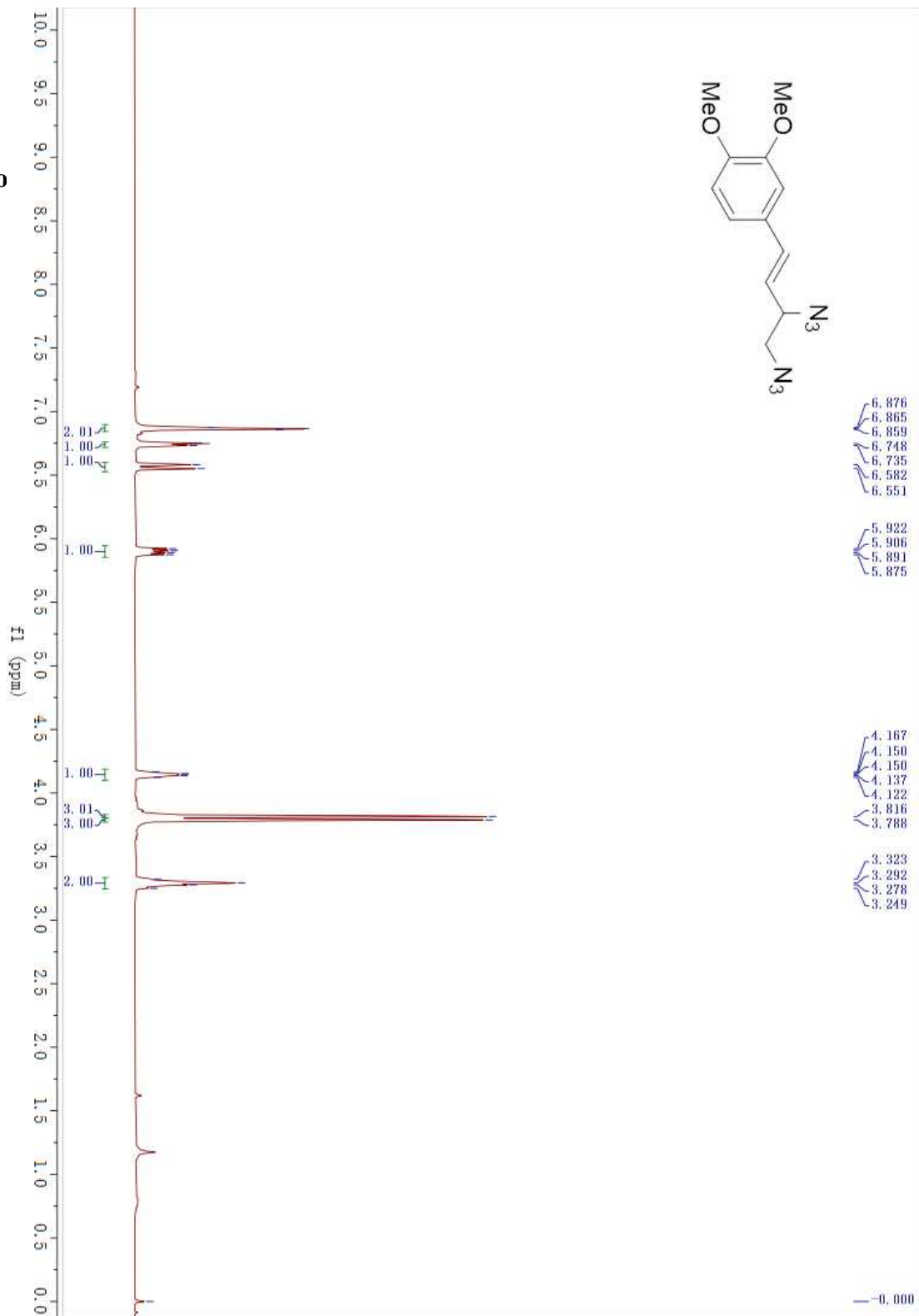


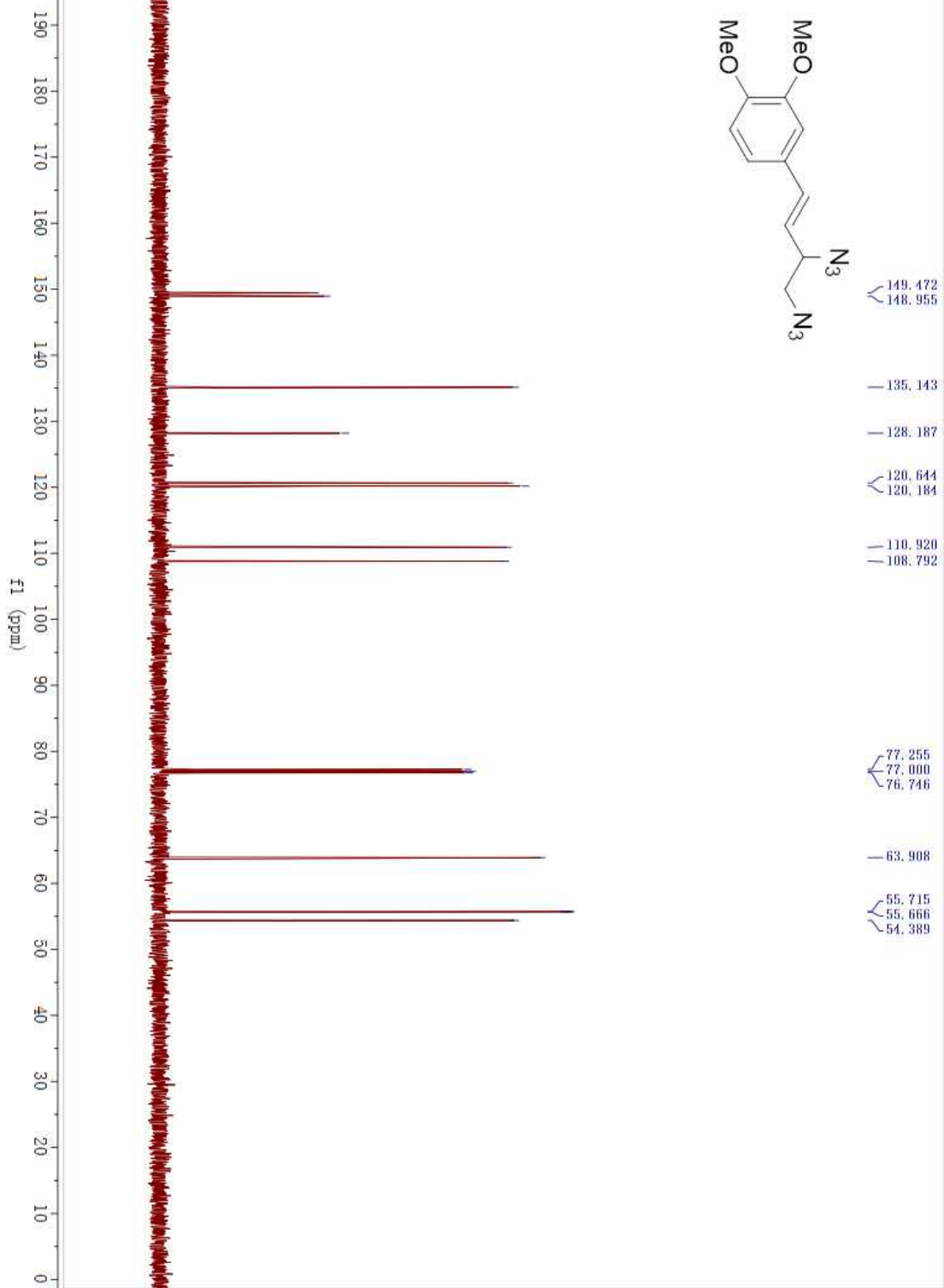
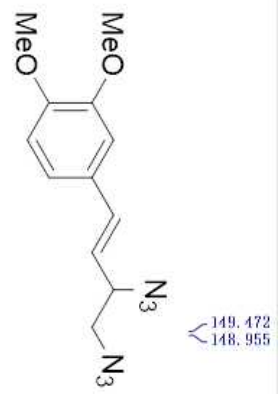
(E)-1-chloro-2-(3,



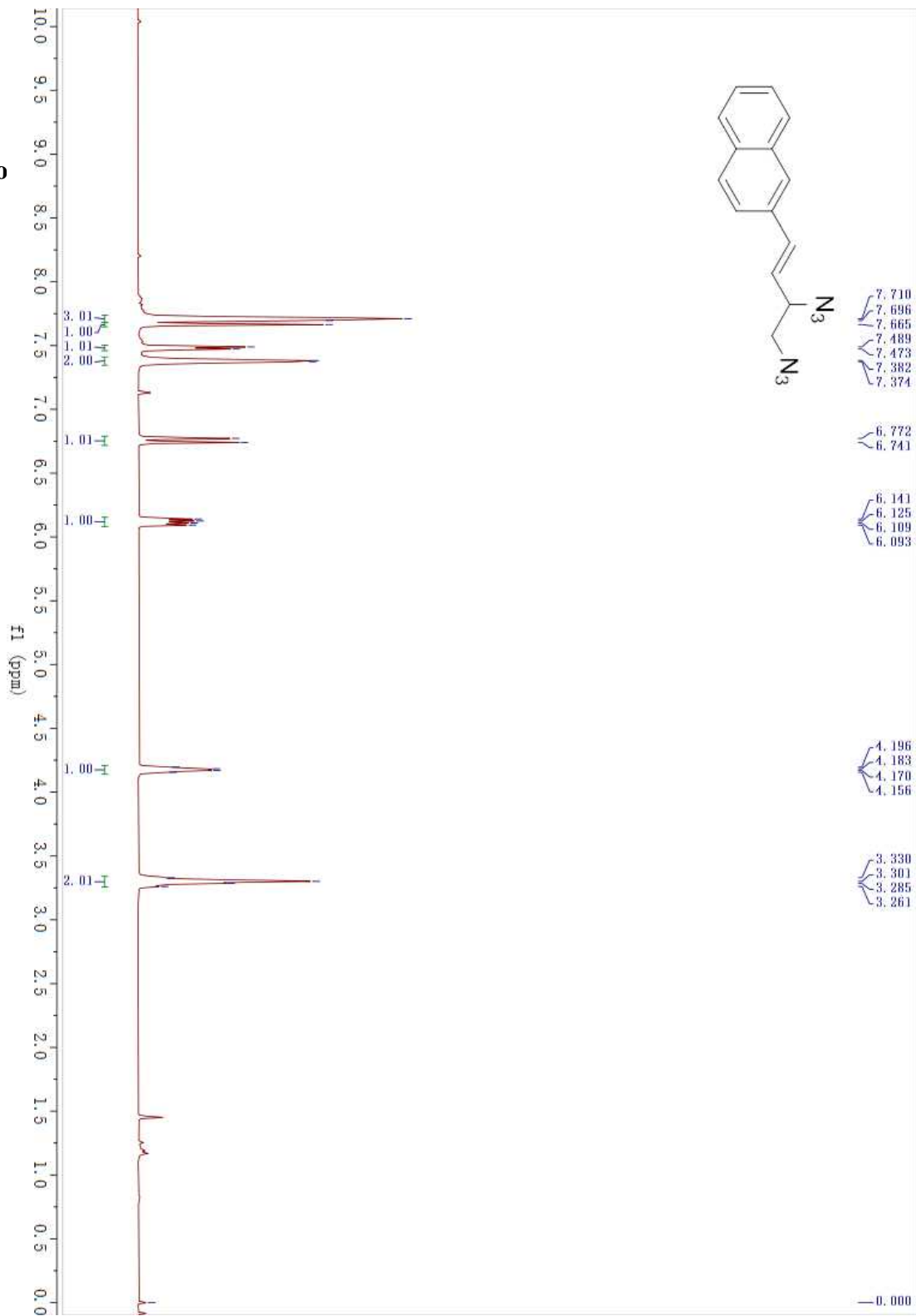


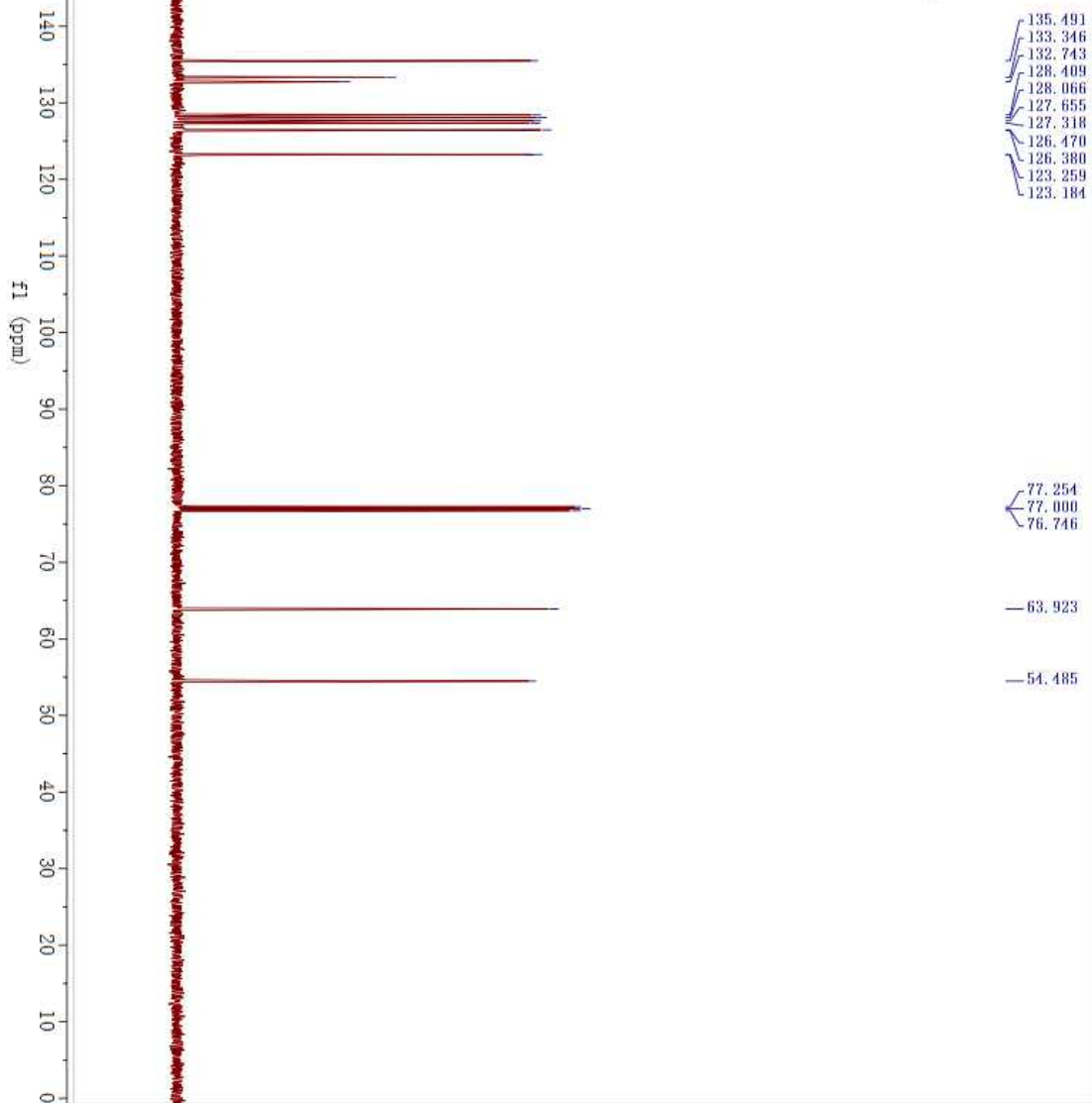
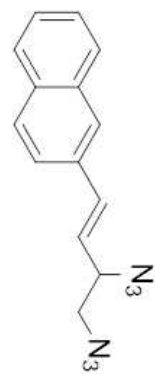
(E)-4-(3,4-diazido



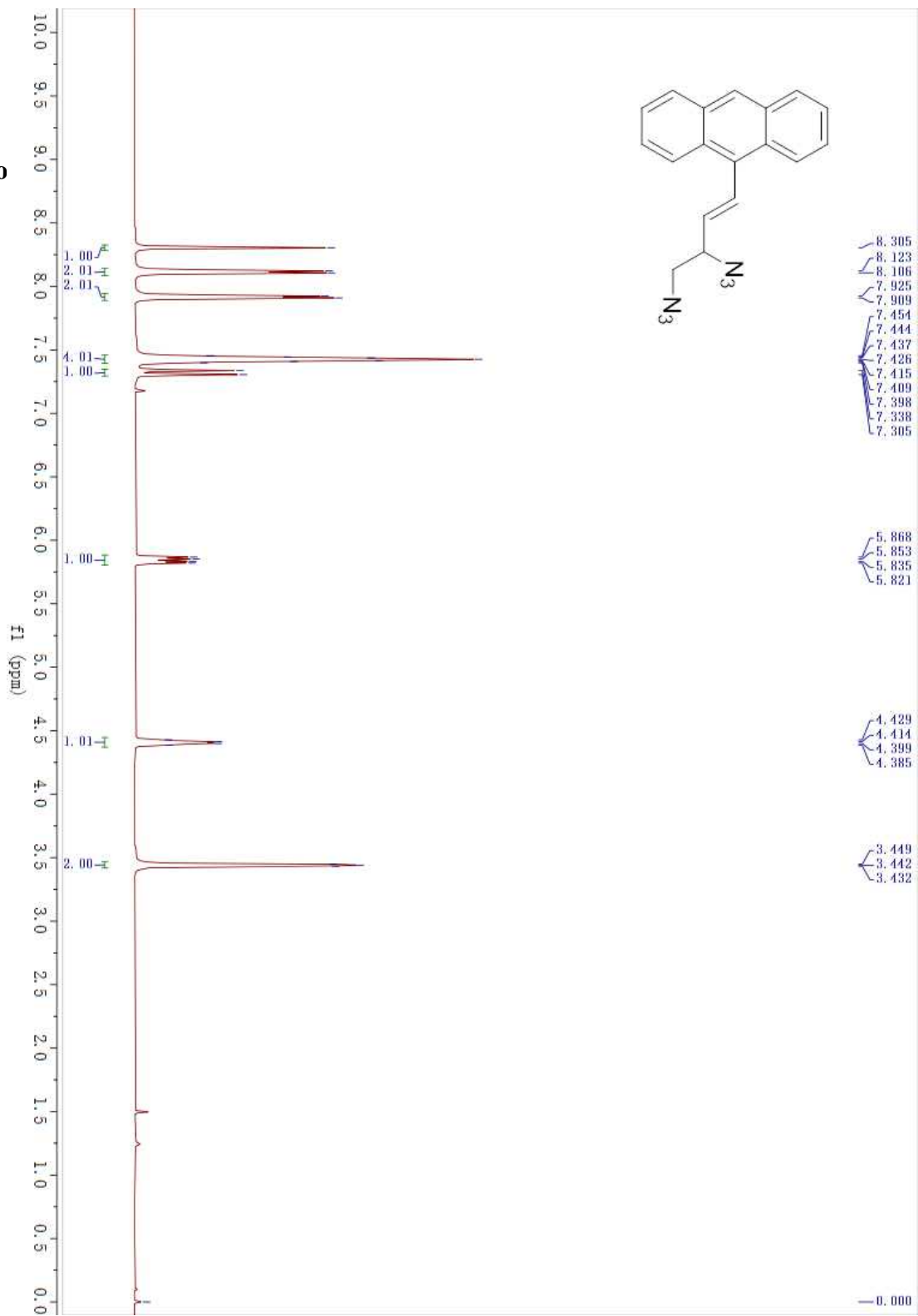


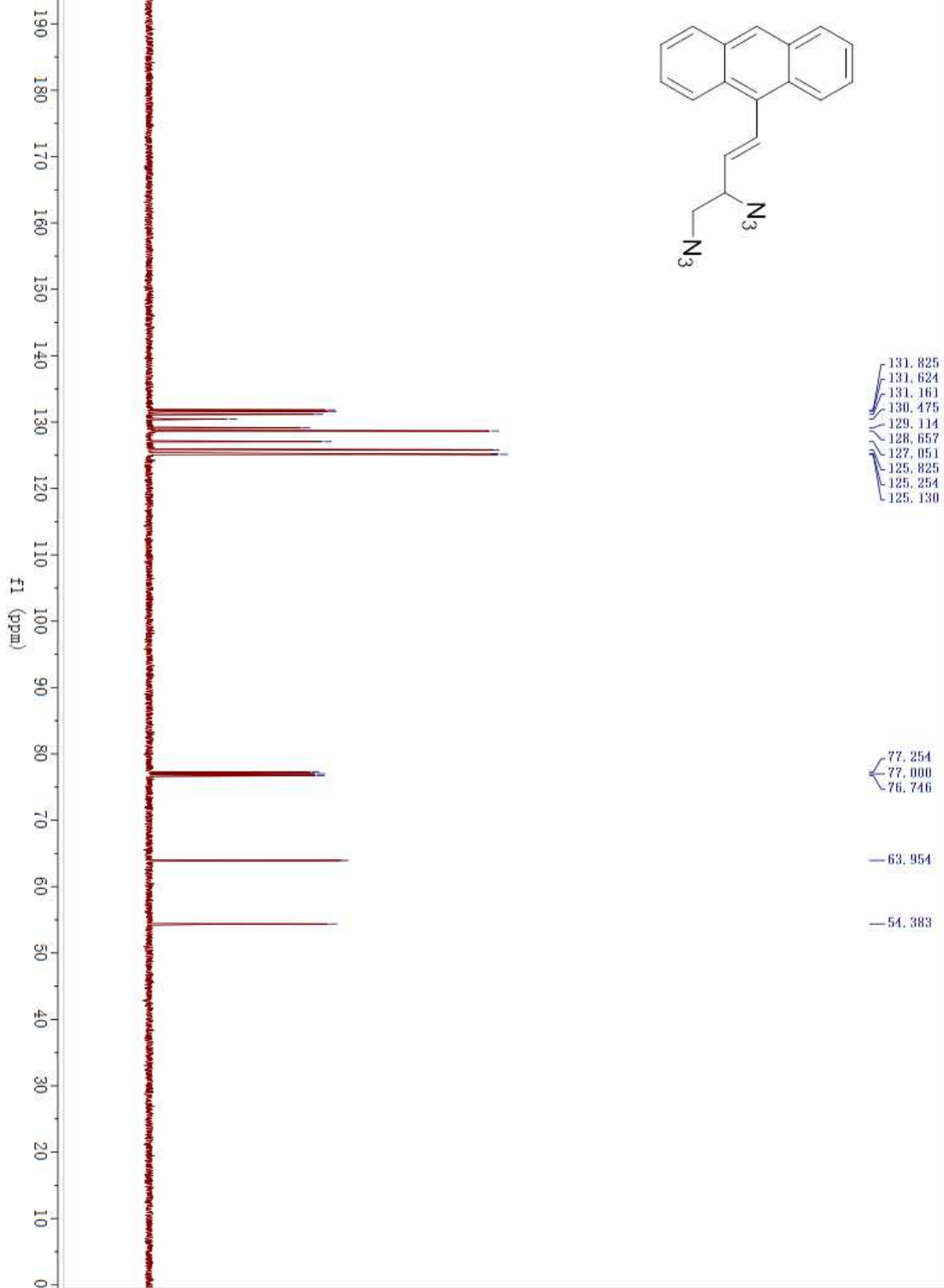
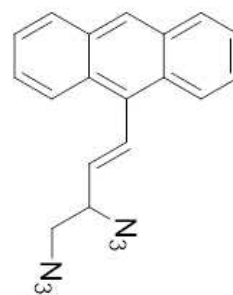
(E)-2-(3,4-diazido



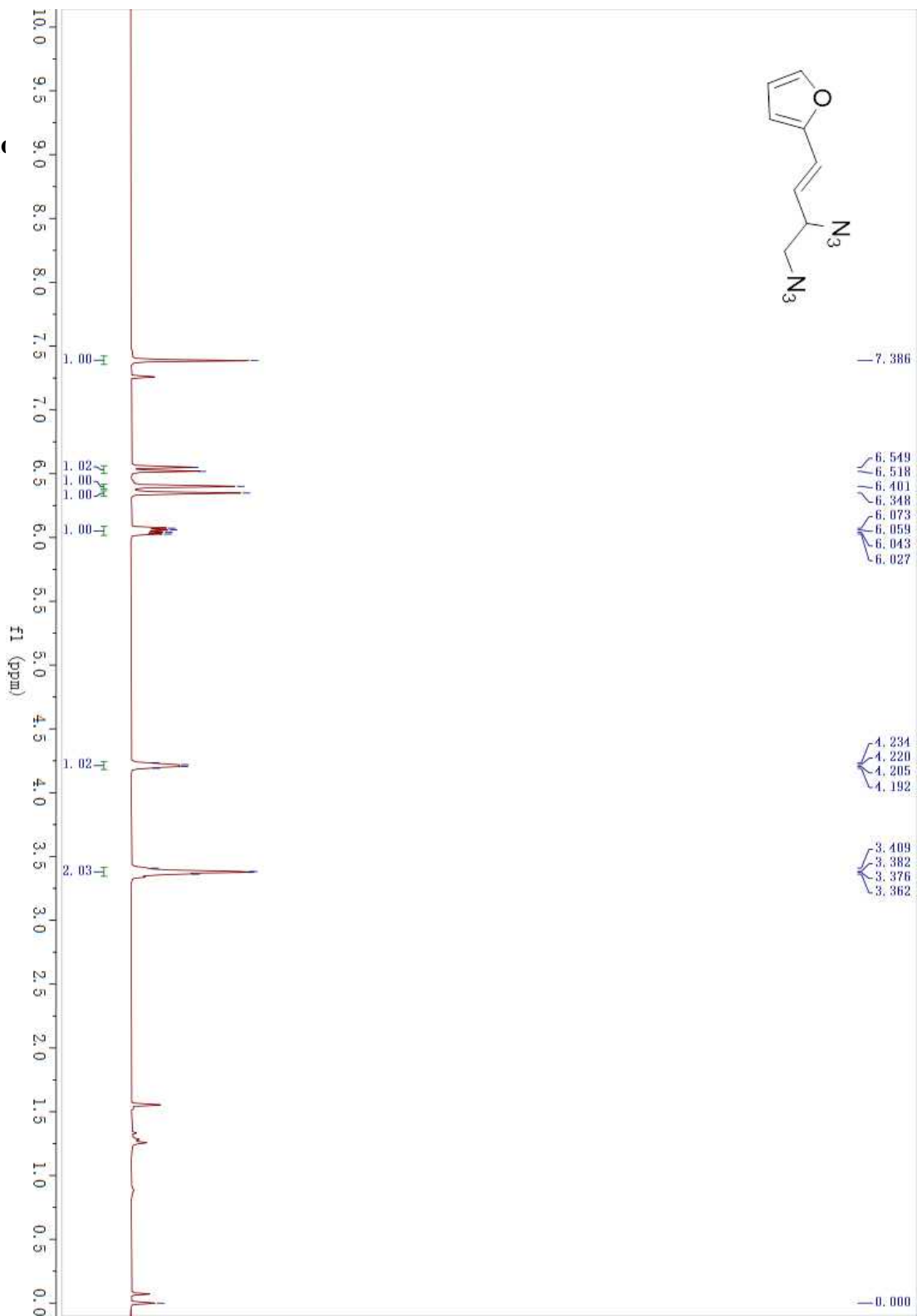


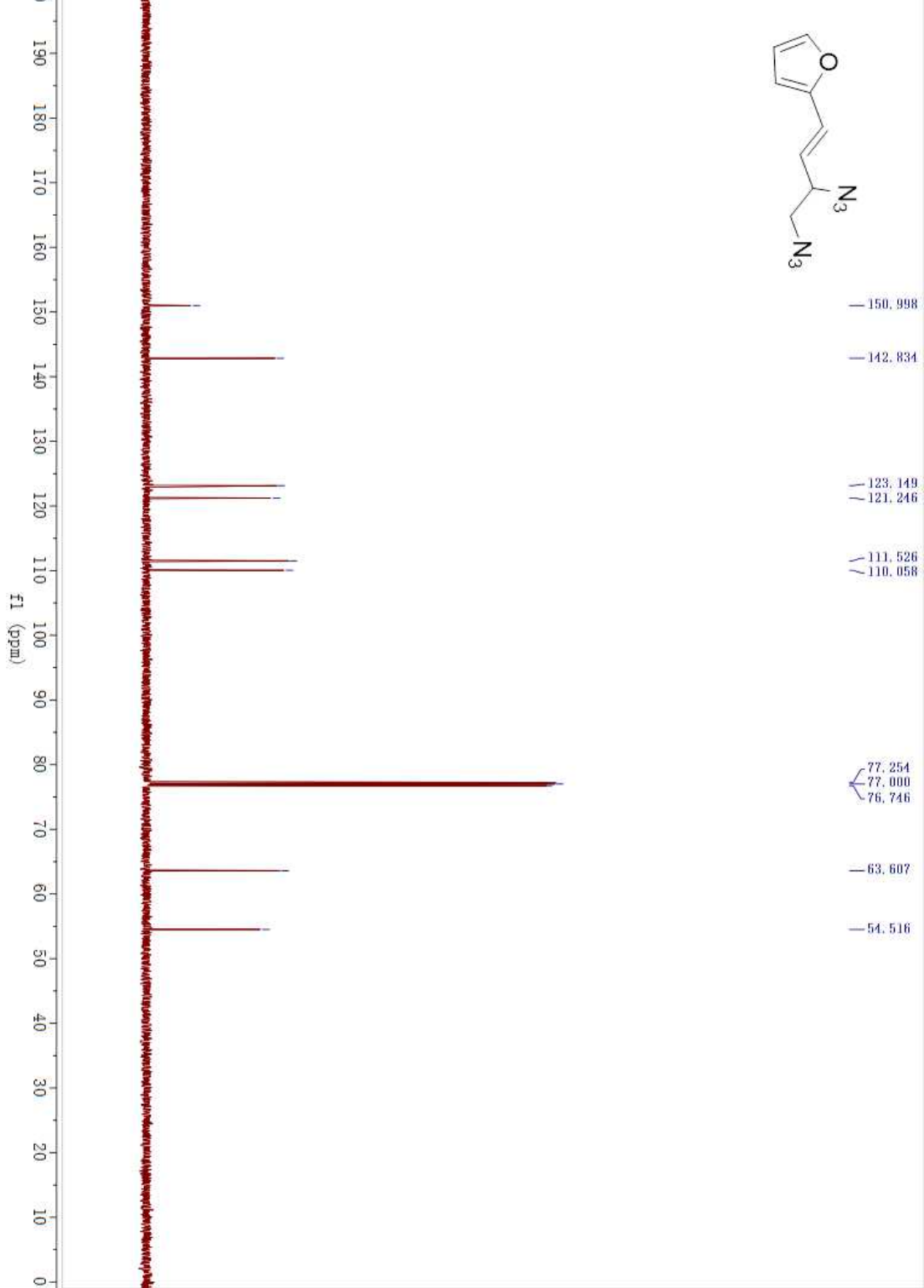
(E)-9-(3,4-diazido



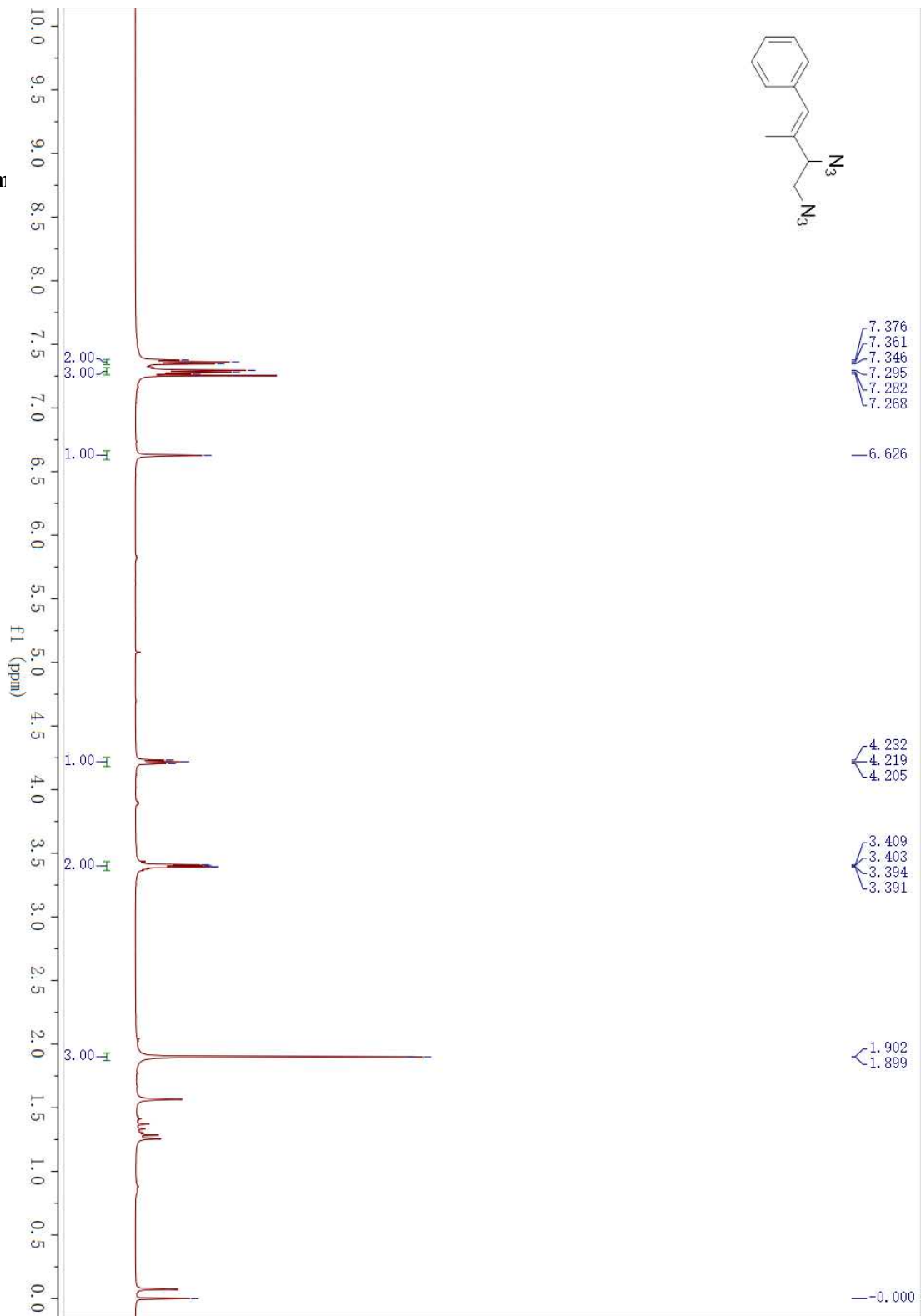


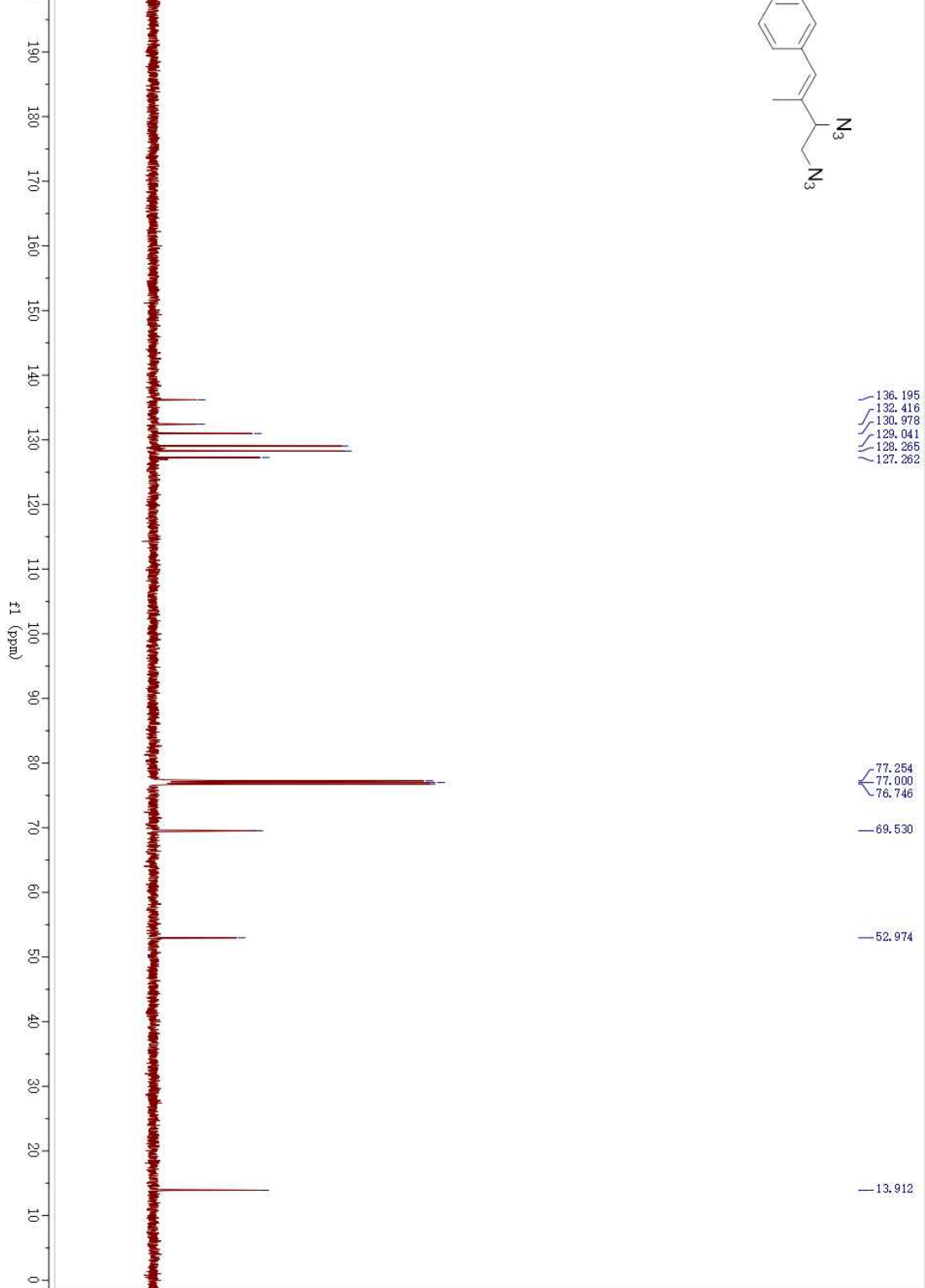
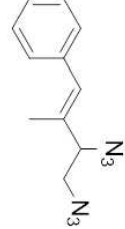
(E)-2-(3,4-diazidoprop-1-en-1-yl)furan



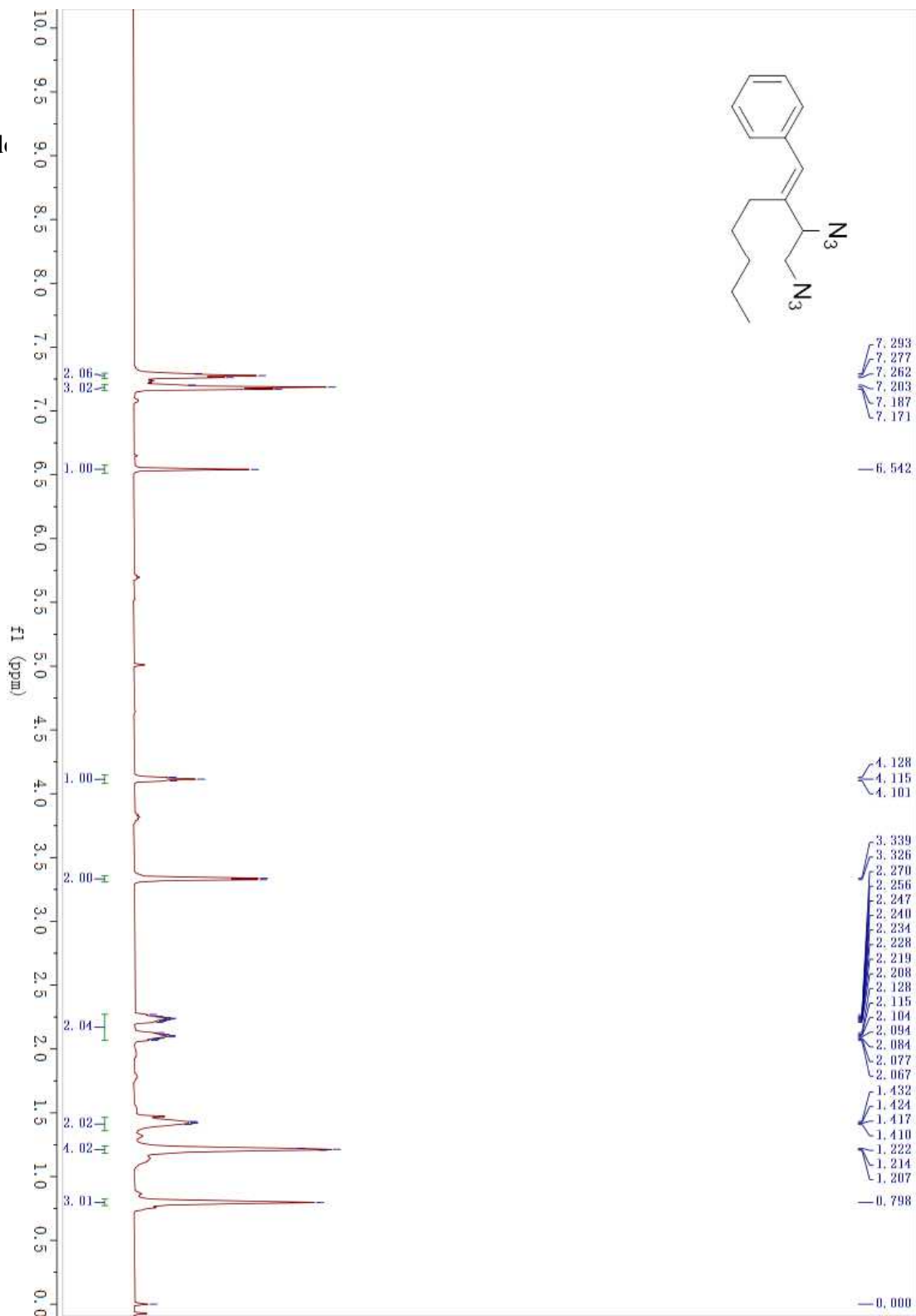


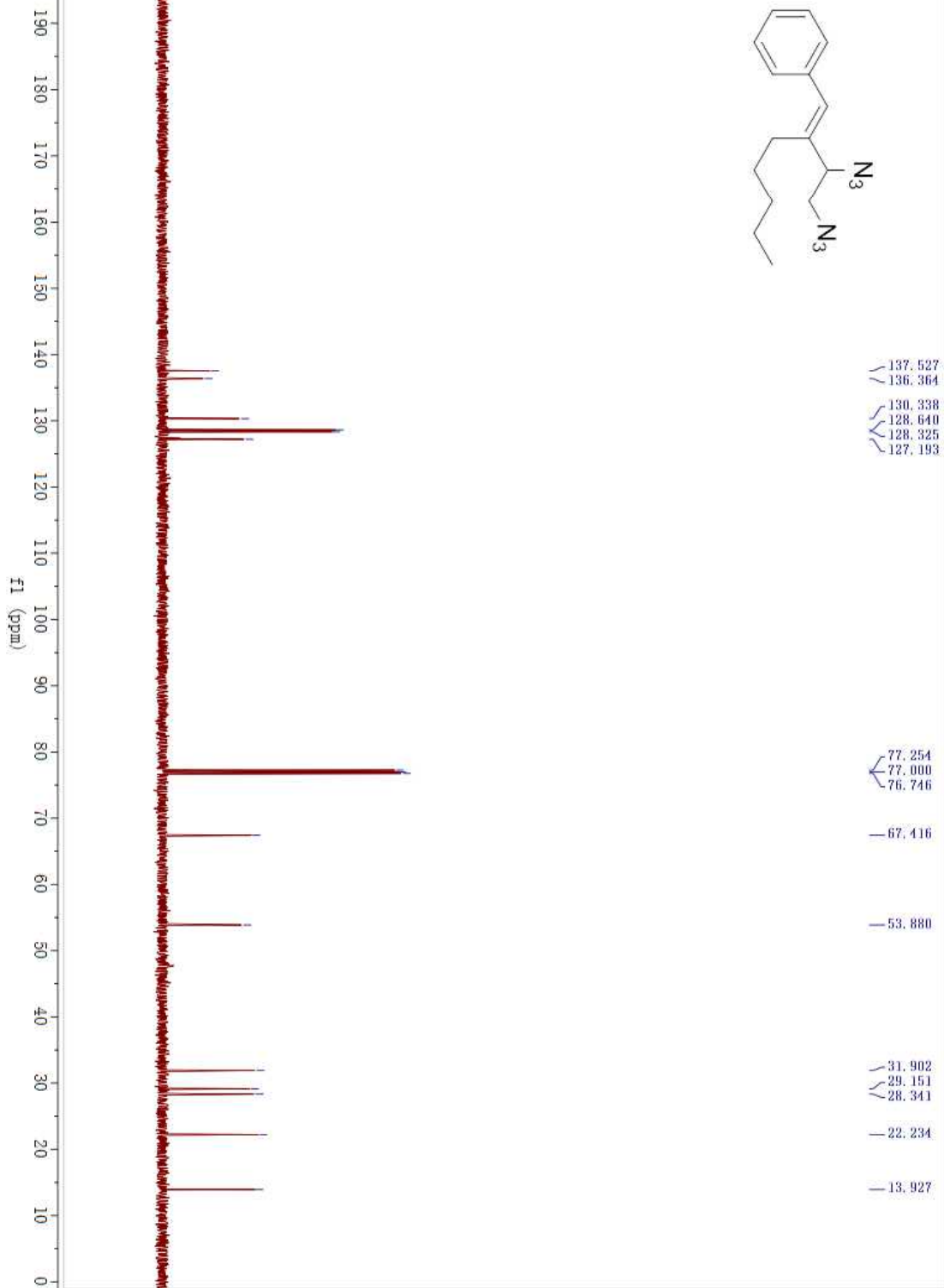
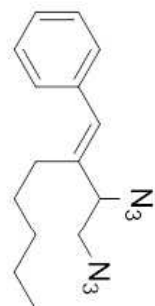
(E)-(3,4-diazido-2-m



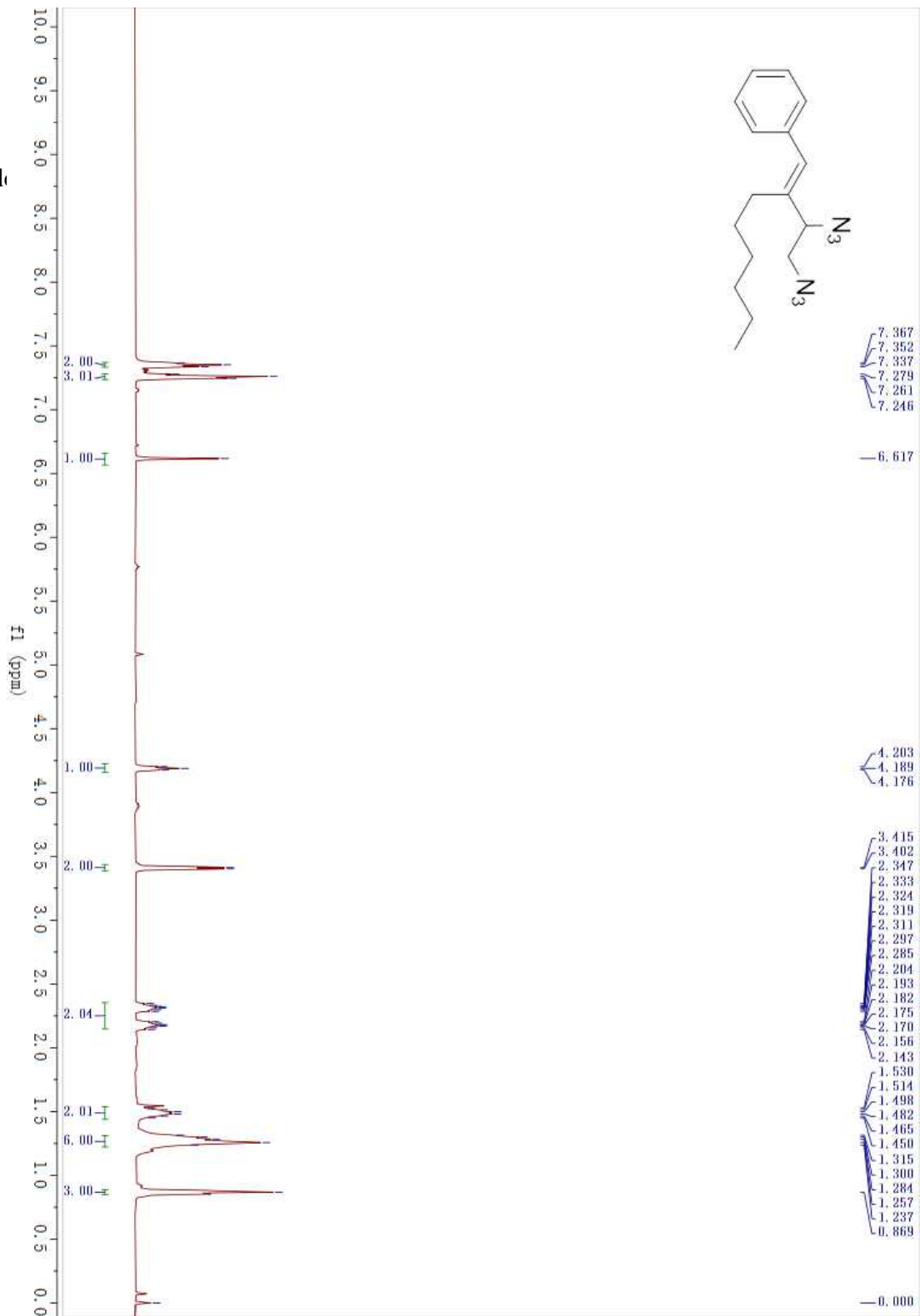


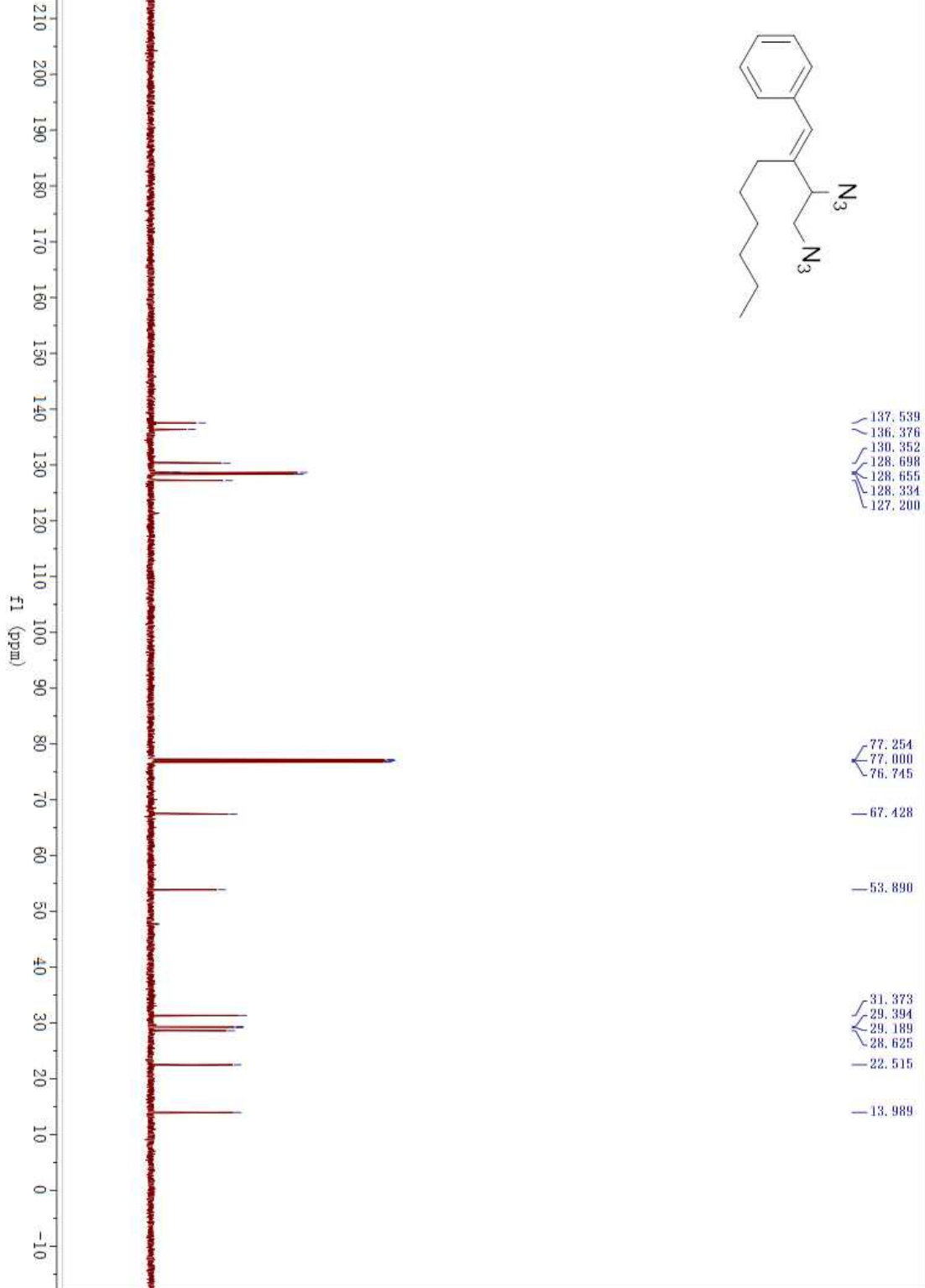
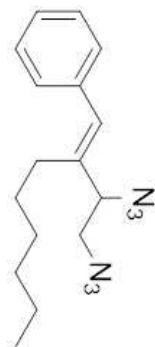
(E)-2-(1,2-diazid



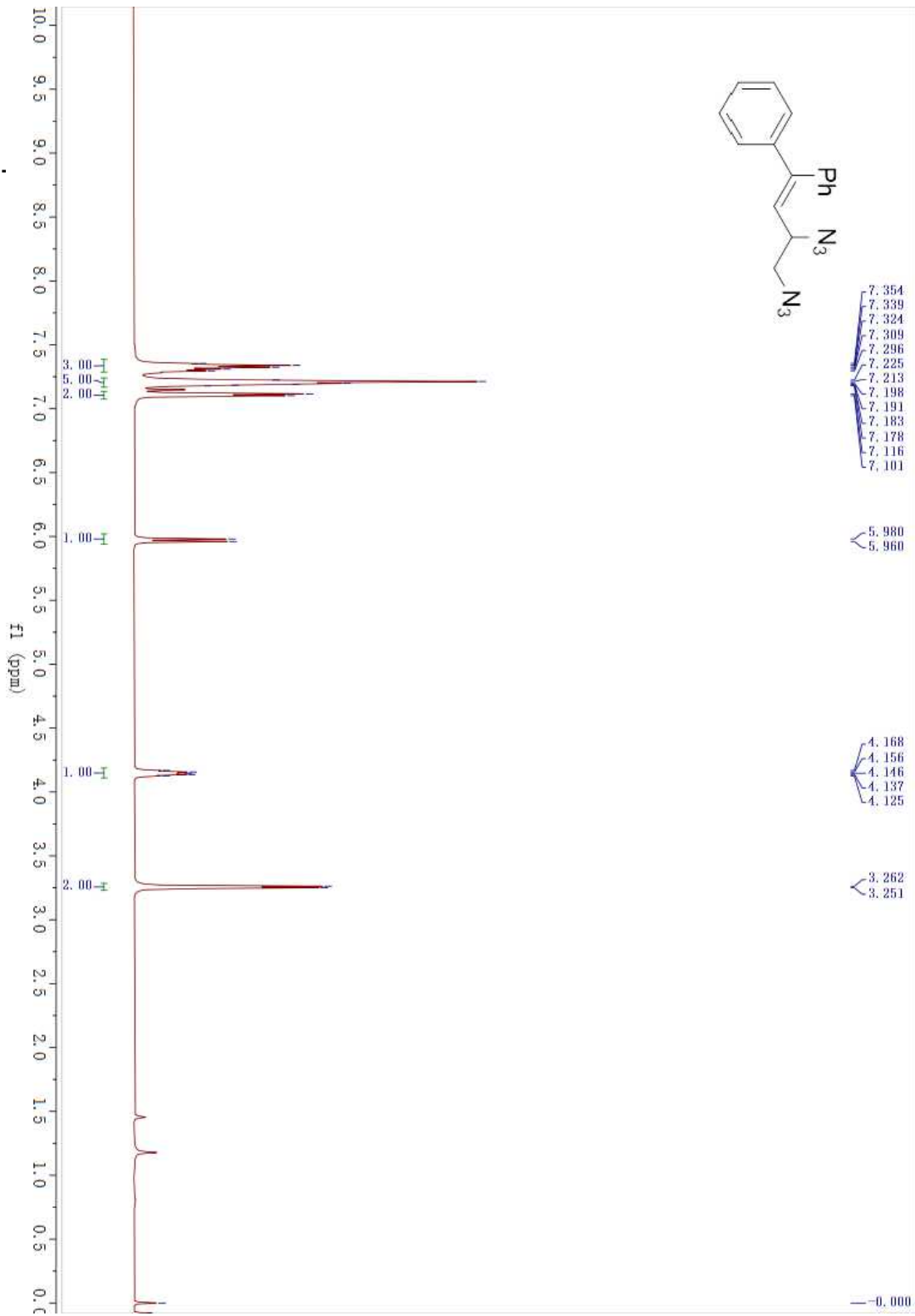


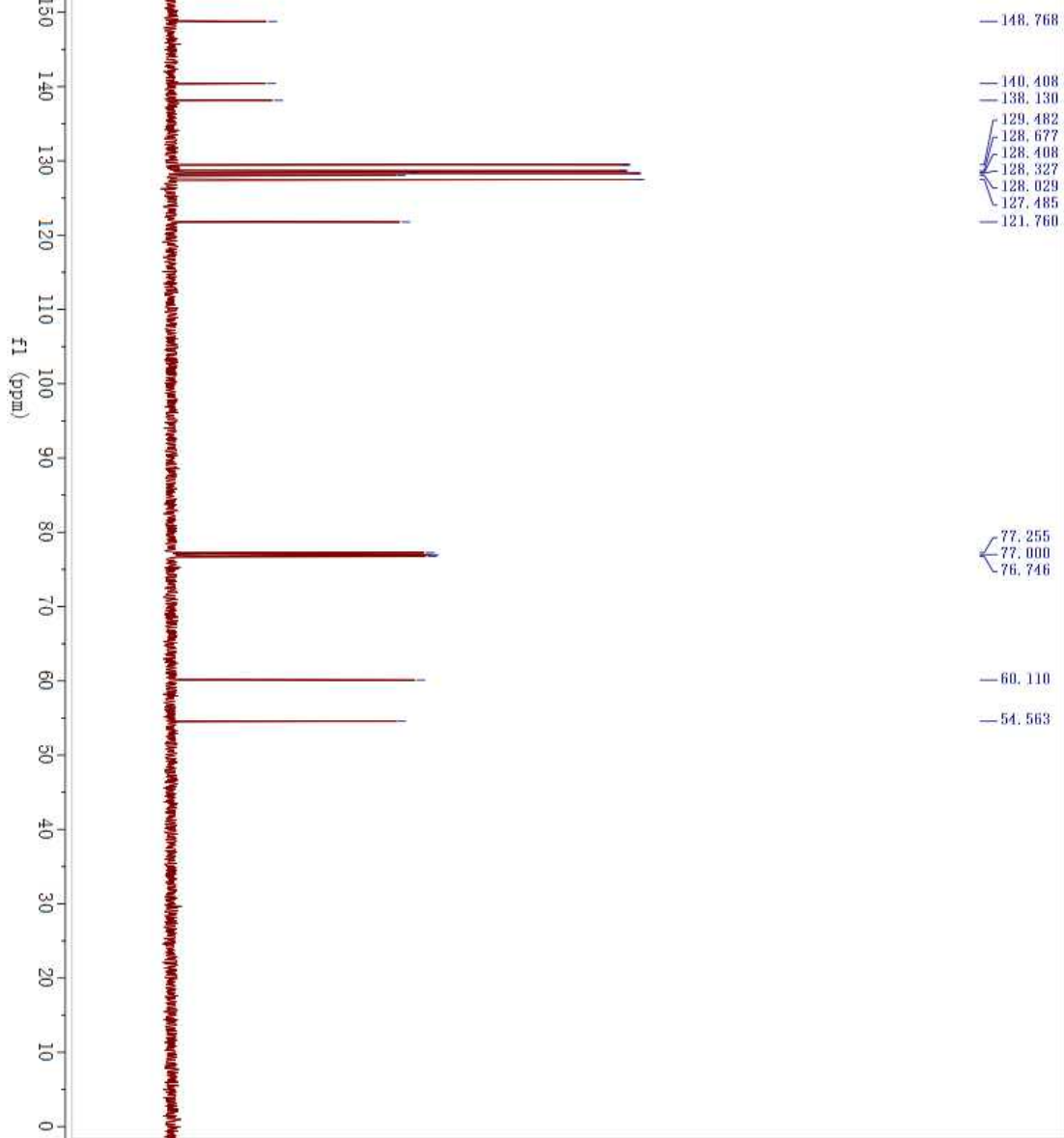
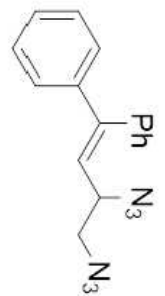
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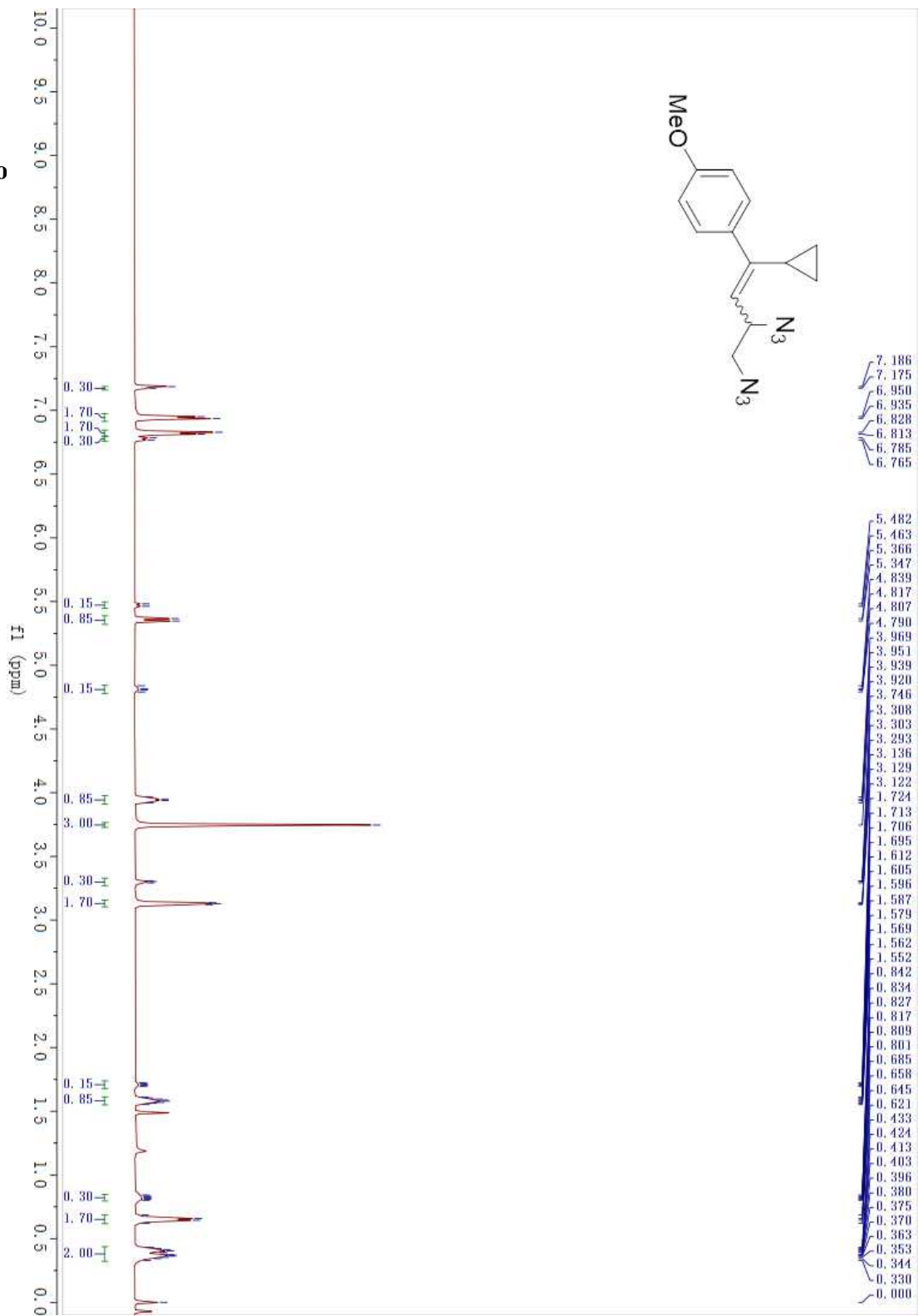


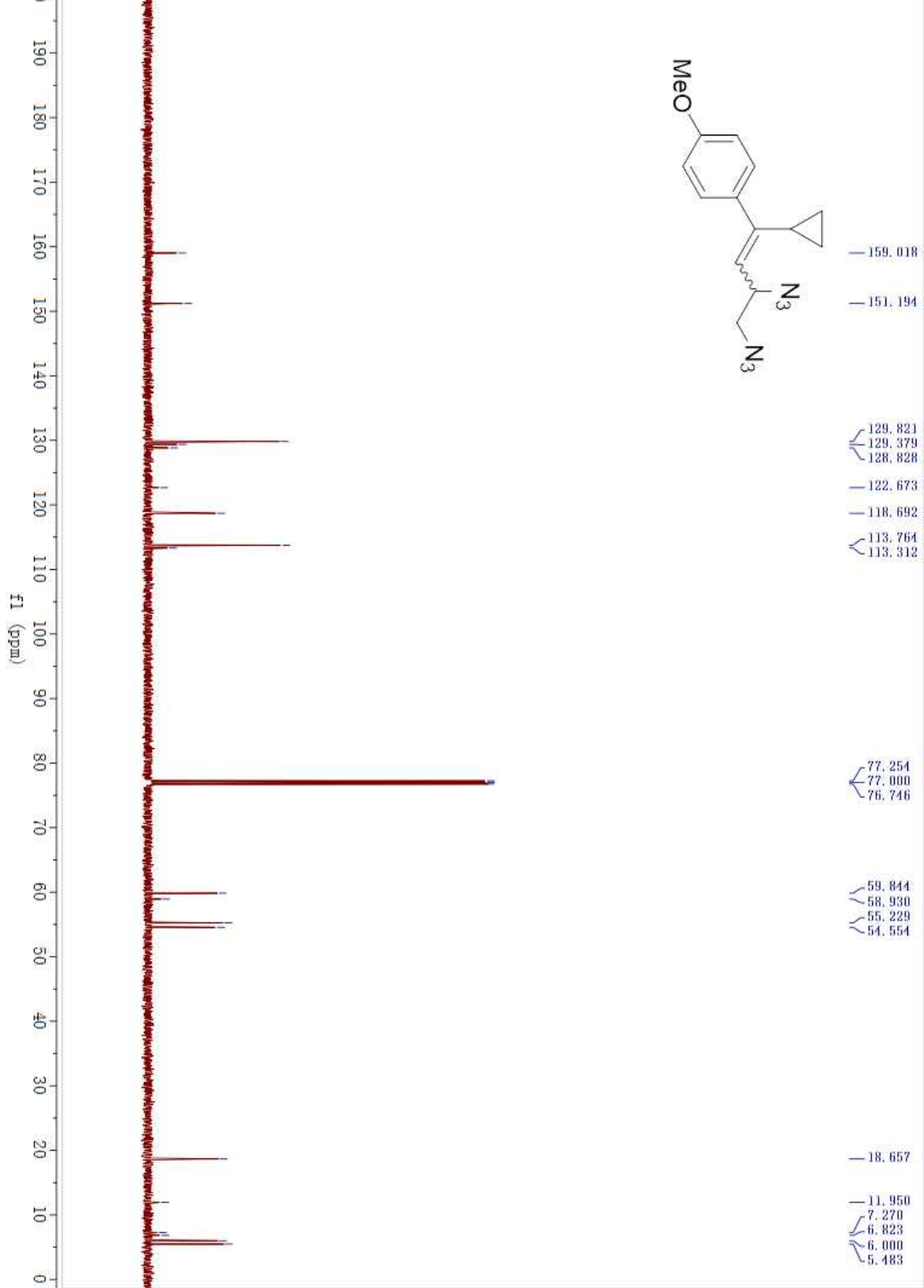
(3,4-diazidobut-1-



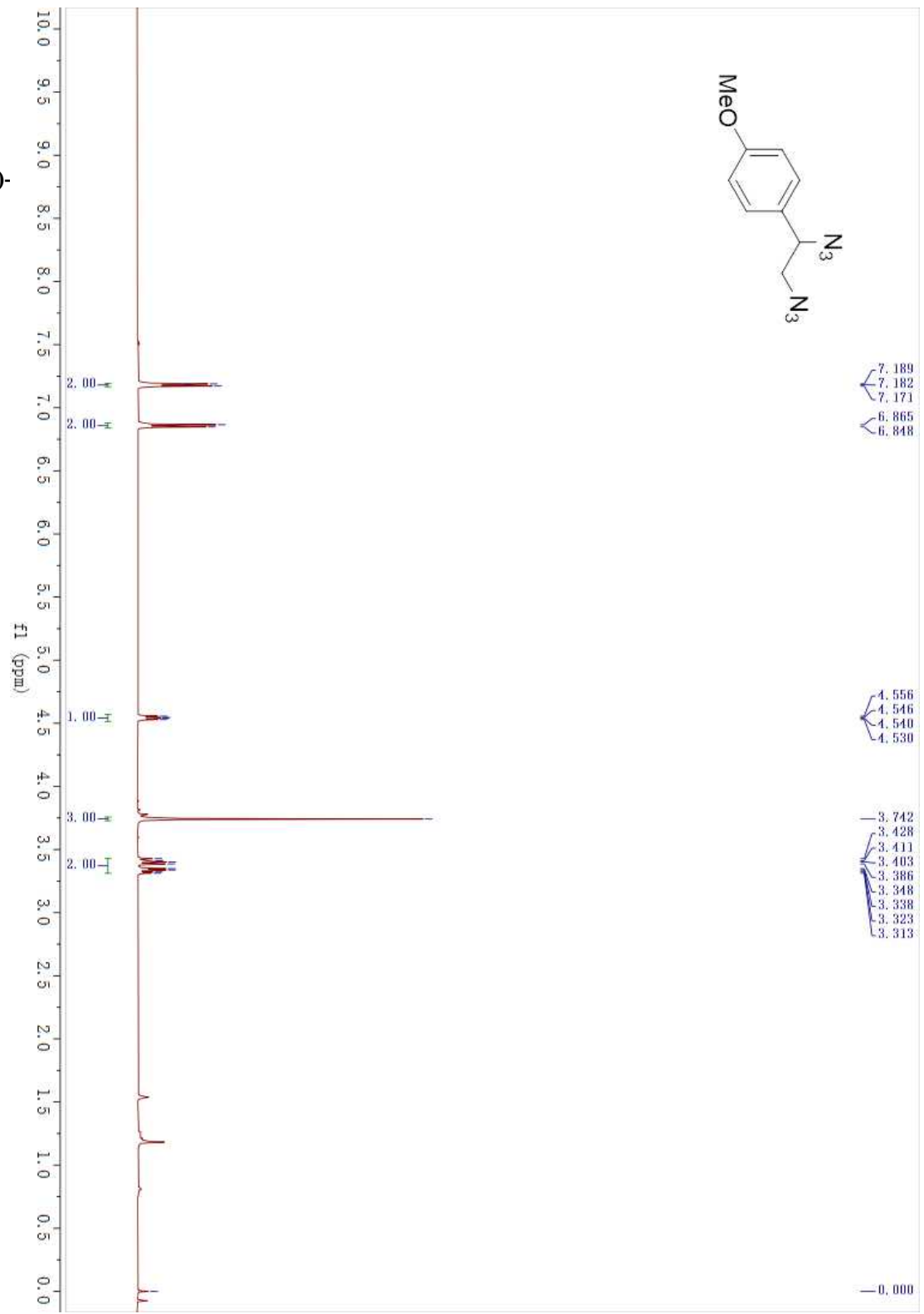
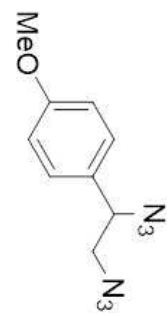


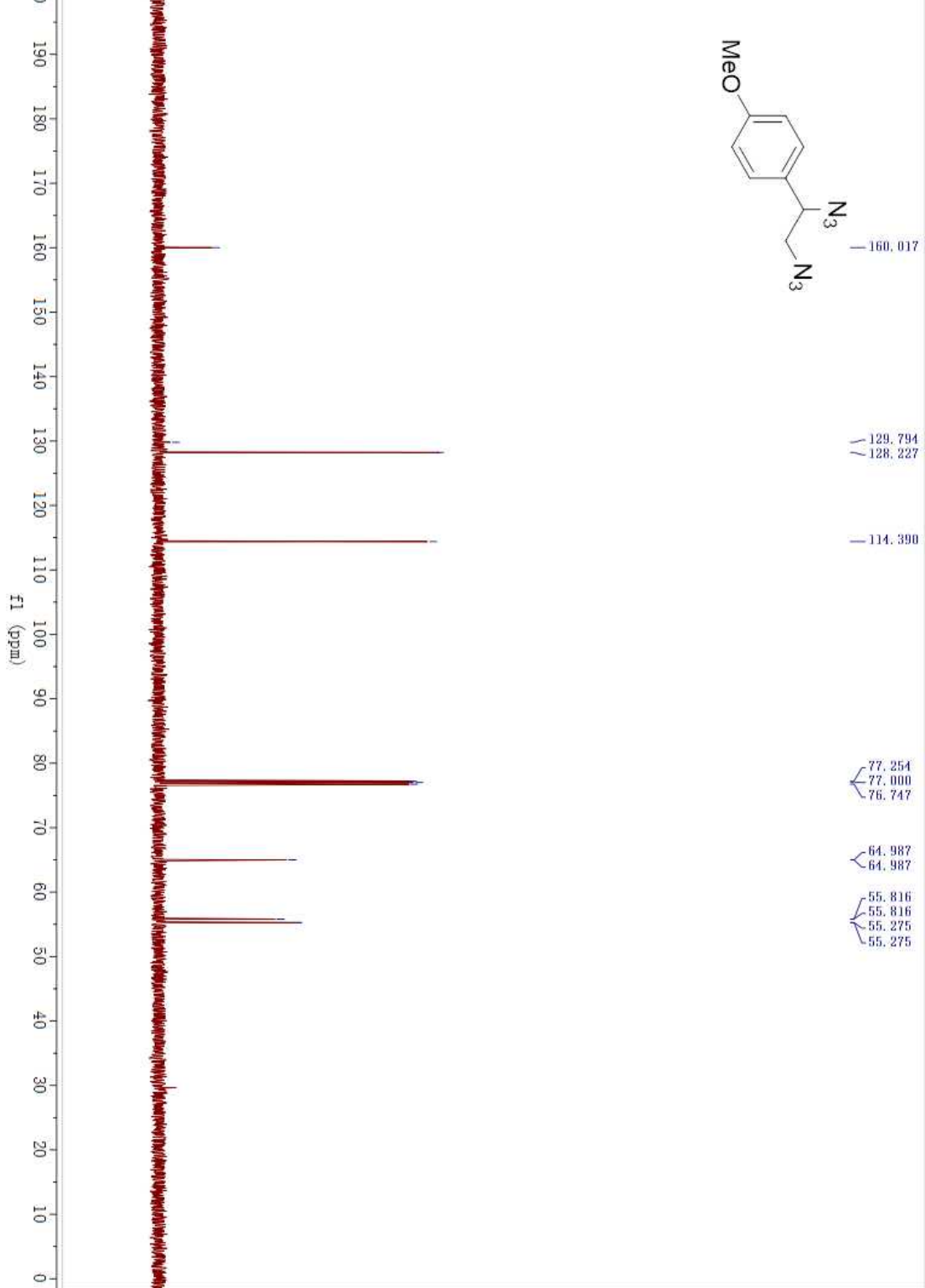
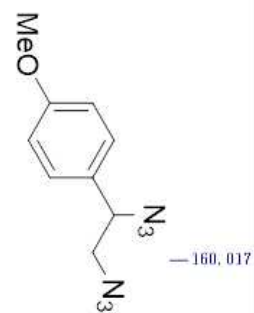
(E)-1-(3,4-diazido



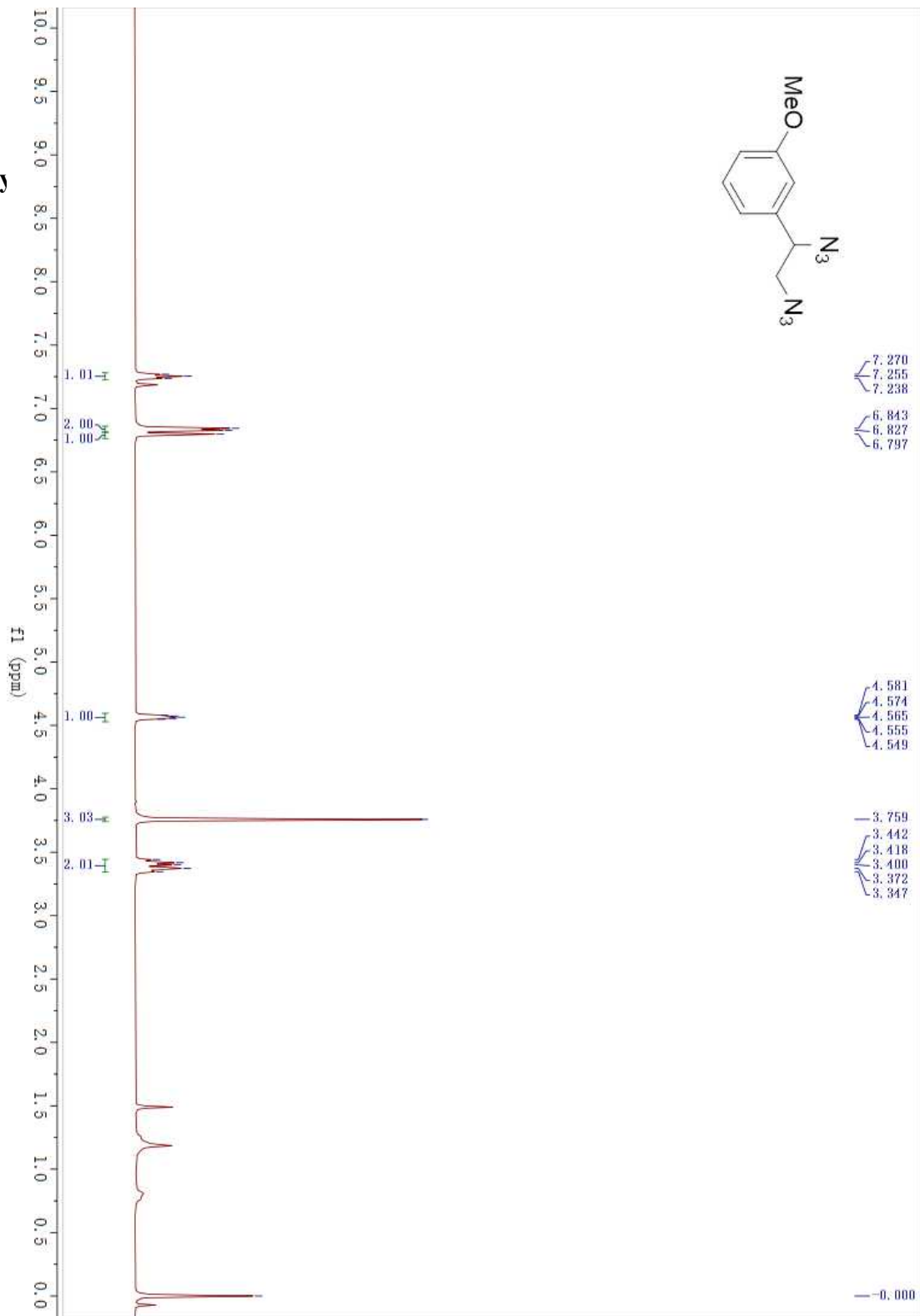


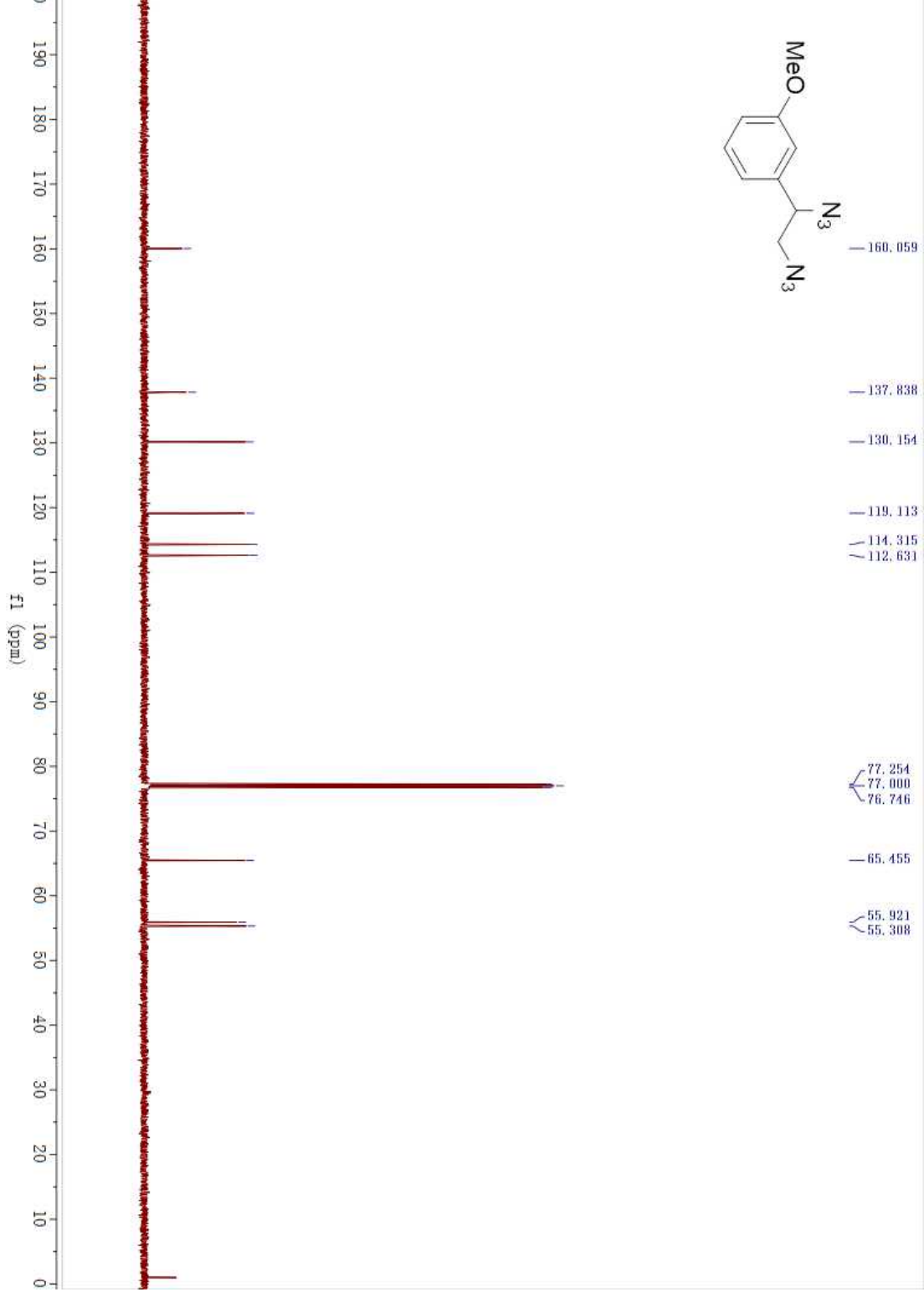
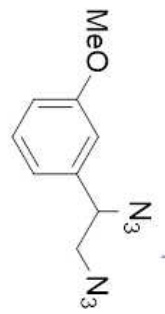
1-(1,2-diazidoethyl)-



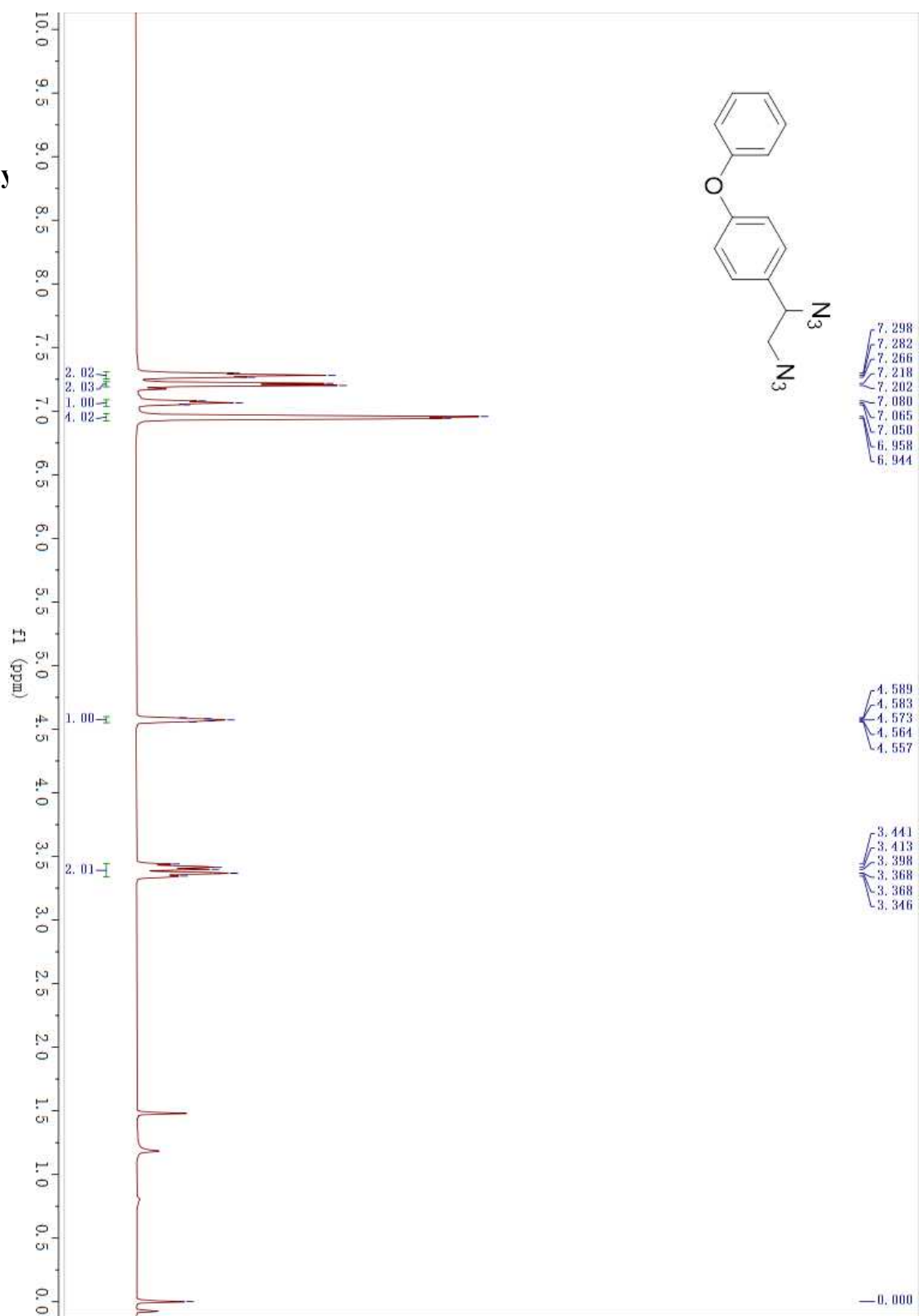


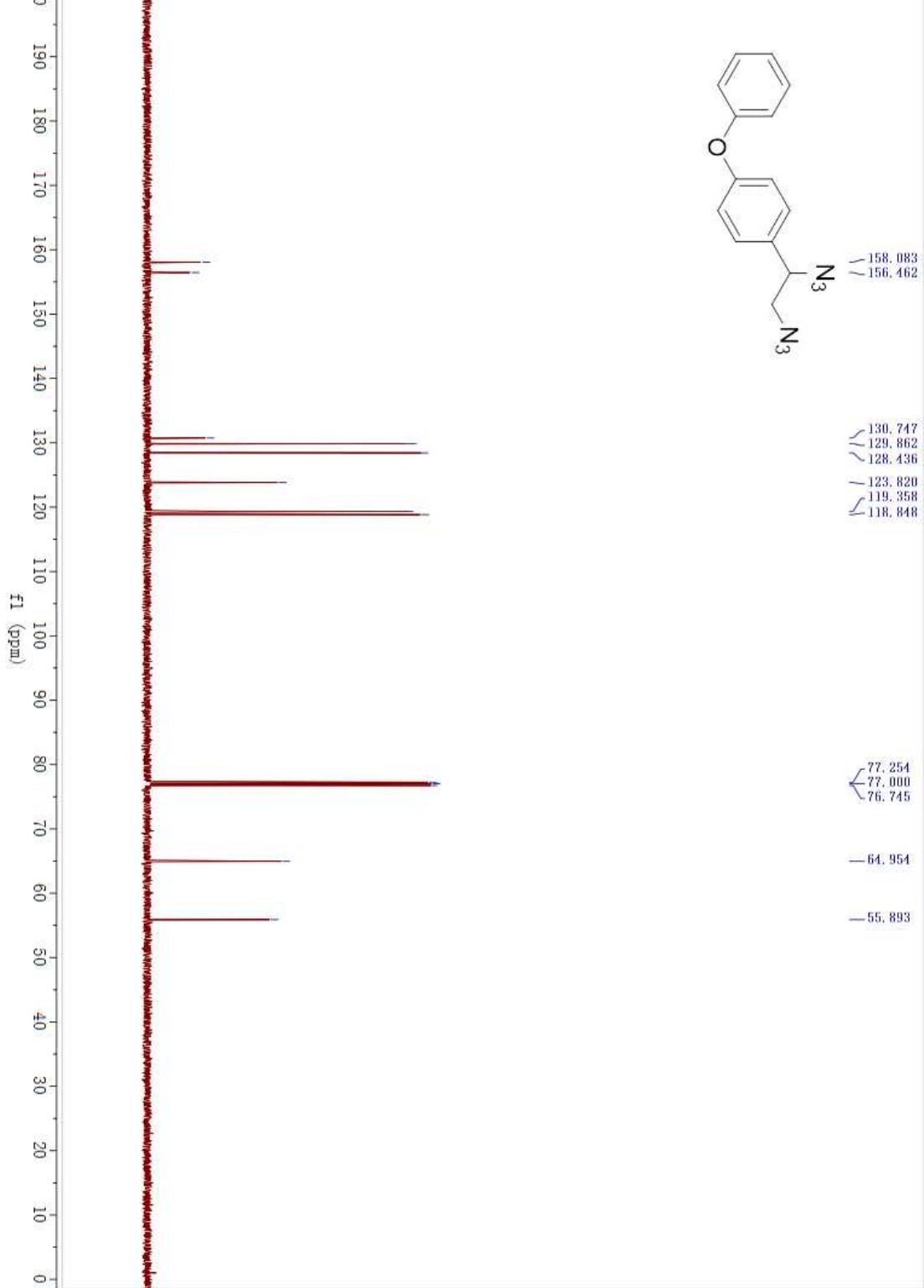
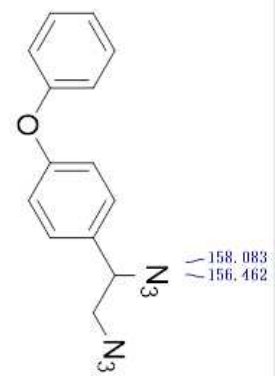
1-(1,2-diaziidoethy





1-(1,2-diazidoethy





2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acetonitrile

