

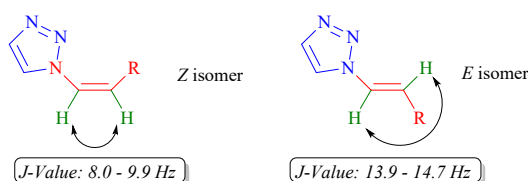
## Supporting Information

Synthesis of vinyl-1,2,3-triazole derivatives under transition metal-free promoted  
Menghan Cui,<sup>a</sup> Changhui Su,<sup>c</sup> Rong Wang,<sup>a</sup> Qing Yang<sup>b</sup> and Chunxiang Kuang<sup>\*a</sup>

### 1. General Comments

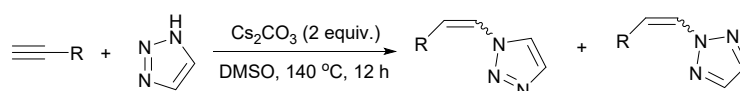
Unless indicated, all reagents were obtained from commercial sources and used without further purification. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra were recorded on a Bruker 600 MHz NMR with tetramethylsilane as internal standard and deuterated chloroform (CDCl<sub>3</sub>) as the solvent. Chemical shifts (δ) were recorded, referenced to the residual proton resonance of CDCl<sub>3</sub> (7.26), to the carbon resonance of CDCl<sub>3</sub> (77.16). Coupling constants (J) were reported in Hertz (Hz). The abbreviations m, q, t, d, s were indicate multiplet, quartet, triplet, doublet, singlet. HRMS (ESI) were recorded on a Themofisher MicroTOFII instrument by CH<sub>3</sub>CN as solvent. The reaction progress was monitored by Thin layer chromatography (TLC). Column chromatography was performed with silica gel (200-300 meshes).

The Z and E stereoselectivity in the product was characterized by the coupling constant of the styryl protons in <sup>1</sup>H NMR spectroscopy. The J-value of the two styryl protons in products between 8.0–9.5 Hz which supports the Z-stereoselectivity in the products; however, products with coupling constant between 14.6–16.7 Hz conforms the E-stereoselectivity in the addition products.

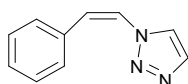


### 2. Experimental Section

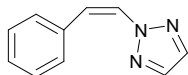
#### 2.1 General procedure for triazolization of terminal alkynes



A mixture of terminal alkynes (1a-1p) (0.5 mmol), 1H-1,2,3-Triazole (2a) (1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1mmol) in DMSO (1.5 ml) as stirred at 140 °C for 12 h in sealed tube. The mixture was extracted with ethyl acetate and washed with water (20 ml\*3) three times. The combined organic layer dried by anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The resulting residue was purified by by column chromatography (silica gel, eluent: PE/EtOAc) to afford product 3aa-3pa and 4aa-4pa.

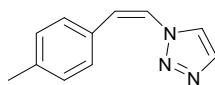


**(Z)-1-styryl-1H-1,2,3-triazole (3aa):** <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ = 7.51 (s, 1H), 7.32 (s, 1H), 7.24 (dd, *J*=1.8, 5.2, 3H), 7.20 (d, *J*=9.6, 1H), 7.07 – 7.03 (m, 2H), 6.50 (d, *J*=9.6, 1H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ = 133.48, 133.08, 128.95, 128.77, 128.49, 124.07, 123.41, 123.30. HRMS (ESI) Exact mass calculated for C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>[M+H]<sup>+</sup>: 172.0869; found: 172.0840.

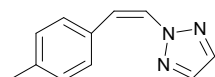


**(Z)-2-styryl-1H-1,2,3-triazole (4aa):** <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ = 7.68 (s, 2H), 7.31 – 7.26

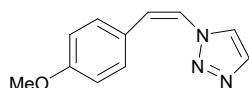
(m, 5H), 7.14 (d,  $J=10.0$ , 1H), 6.42 (d,  $J=10.0$ , 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  = 135.06, 133.53, 129.39, 128.28, 128.07, 125.10, 122.78. HRMS (ESI) Exact mass calculated for  $\text{C}_{10}\text{H}_9\text{N}_3[\text{M}+\text{H}]^+$ : 172.0869; found: 172.0841.



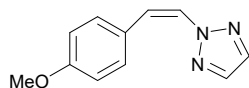
**(Z)-1-(4-methylstyryl)-1H-1,2,3-triazole (3ba):**  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.61 (s, 1H), 7.44 (s, 1H), 7.22 (d,  $J=9.5$  Hz, 1H), 7.12 (d,  $J=7.9$  Hz, 2H), 7.00 (d,  $J=8.0$  Hz, 2H), 6.54 (d,  $J=9.5$  Hz, 1H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  138.83, 133.41, 130.06, 129.60, 128.41, 124.38, 123.42, 122.73, 21.30. HRMS (ESI) Exact mass calculated for  $\text{C}_{11}\text{H}_{11}\text{N}_3[\text{M}+\text{H}]^+$ : 186.1026; found: 186.1032.



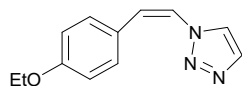
**(Z)-2-(4-methylstyryl)-1H-1,2,3-triazole (4ba):**  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.70 (s, 2H), 7.19 (d,  $J=8.1$  Hz, 2H), 7.09 (dd,  $J=9.0, 3.8$  Hz, 3H), 6.40 (d,  $J=9.9$  Hz, 1H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  = 138.29, 134.92, 130.50, 129.30, 128.79, 124.46, 124.46, 123.10, 21.37. HRMS (ESI) Exact mass calculated for  $\text{C}_{11}\text{H}_{11}\text{N}_3[\text{M}+\text{H}]^+$ : 186.1026; found: 186.1025.



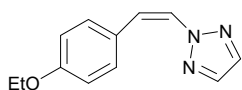
**(Z)-1-(4-methoxystyryl)-1H-1,2,3-triazole (3ca):**  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.64 (s, 1H), 7.49 (s, 1H), 7.15 (d,  $J=9.4$  Hz, 1H), 7.02 (d,  $J=8.6$  Hz, 2H), 6.83 (d,  $J=8.8$  Hz, 2H), 6.53 (d,  $J=9.4$  Hz, 1H), 3.80 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  = 159.89, 133.48, 130.02, 125.16, 124.84, 123.52, 121.83, 114.28, 55.29. HRMS (ESI) Exact mass calculated for  $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}[\text{M}+\text{H}]^+$ : 202.0975; found: 202.0980.



**(Z)-2-(4-methoxystyryl)-1H-1,2,3-triazole (4ca):**  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.71 (s, 2H), 7.26 (d,  $J=4.1$  Hz, 2H), 7.04 (d,  $J=9.9$  Hz, 1H), 6.82 (d,  $J=8.8$  Hz, 2H), 6.37 (d,  $J=9.9$  Hz, 1H), 3.80 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  = 159.60, 159.60, 134.87, 130.94, 125.79, 123.55, 123.01, 113.51, 55.23. HRMS (ESI) Exact mass calculated for  $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}[\text{M}+\text{H}]^+$ : 202.0975; found: 202.0977.

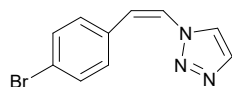


**(Z)-1-(4-ethoxystyryl)-1H-1,2,3-triazole (3da):**  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.64 (s, 1H), 7.49 (s, 1H), 7.14 (d,  $J=9.4$  Hz, 1H), 7.00 (d,  $J=8.7$  Hz, 2H), 6.81 (d,  $J=8.8$  Hz, 2H), 6.52 (d,  $J=9.4$  Hz, 1H), 4.02 (q,  $J=7.0$  Hz, 2H), 1.41 (t,  $J=7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  = 159.29, 133.46, 130.01, 124.88, 123.52, 121.74, 114.76, 63.50, 14.75. HRMS (ESI) Exact mass calculated for  $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}[\text{M}+\text{H}]^+$ : 216.1131; found: 216.1137.

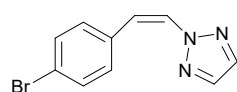


**(Z)-2-(4-ethoxystyryl)-1H-1,2,3-triazole (4da):**  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  = 7.71 (s, 2H),

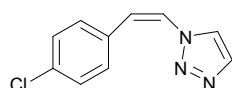
7.24 (d,  $J=8.7$ , 2H), 7.03 (d,  $J=9.9$ , 1H), 6.80 (d,  $J=8.8$ , 2H), 6.36 (d,  $J=9.9$ , 1H), 4.03 (q,  $J=7.0$ , 2H), 1.40 (t,  $J=7.0$ , 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  = 159.03, 134.87, 130.95, 125.60, 123.44, 123.18, 63.40, 14.82. HRMS (ESI) Exact mass calculated for  $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}[\text{M}+\text{H}]^+$ : 216.1131; found: 216.1132.



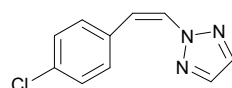
**(Z)-1-(4-bromostyryl)-1H-1,2,3-triazole (3ea)**:  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.64 (s, 1H), 7.46 (d,  $J = 8.4$  Hz, 2H), 7.42 (s, 1H), 7.28 (d,  $J = 9.5$  Hz, 1H), 7.01 (d,  $J = 8.3$  Hz, 2H), 6.51 (d,  $J = 9.6$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  133.68, 132.14, 131.90, 130.15, 123.71, 123.38, 123.18, 122.94. HRMS (ESI) Exact mass calculated for  $\text{C}_{10}\text{H}_9\text{BrN}_3$   $[\text{M}+\text{H}]^+$ : 249.9979; found: 249.9973.



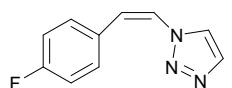
**(Z)-2-(4-bromostyryl)-2H-1,2,3-triazole (4ea)**:  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.70 (s, 2H), 7.42 (d,  $J = 8.5$  Hz, 2H), 7.22 (d,  $J = 8.4$  Hz, 2H), 7.17 (d,  $J = 10.1$  Hz, 1H), 6.31 (d,  $J = 10.1$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  = 135.21, 132.48, 131.19, 131.02, 125.56, 122.26, 120.73. HRMS (ESI) Exact mass calculated for  $\text{C}_{10}\text{H}_9\text{BrN}_3$   $[\text{M}+\text{H}]^+$ : 249.9979; found: 249.9974.



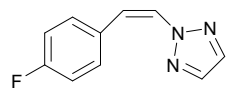
**(Z)-1-(4-chlorostyryl)-1H-1,2,3-triazole (3fa)**:  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.64 (s, 1H), 7.42 (s, 1H), 7.30 (d,  $J = 8.4$  Hz, 2H), 7.28 (d,  $J = 9.6$  Hz, 1H), 7.07 (d,  $J = 8.4$  Hz, 2H), 6.54 (d,  $J = 9.6$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  134.75, 133.67, 131.43, 129.90, 129.19, 123.69, 123.37, 123.20. HRMS (ESI) Exact mass calculated for  $\text{C}_{10}\text{H}_8\text{ClN}_3$   $[\text{M}+\text{H}]^+$ : 206.0480; found: 206.0482.



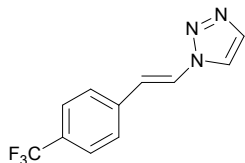
**(Z)-2-(4-chlorostyryl)-2H-1,2,3-triazole (4fa)**:  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.70 (s, 2H), 7.27 (t,  $J = 2.6$  Hz, 4H), 7.16 (d,  $J = 10.1$  Hz, 1H), 6.34 (d,  $J = 10.1$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  135.21, 133.99, 132.00, 130.76, 128.24, 125.51, 120.77. HRMS (ESI) Exact mass calculated for  $\text{C}_{10}\text{H}_8\text{ClN}_3$   $[\text{M}+\text{H}]^+$ : 206.0480; found: 206.0483.



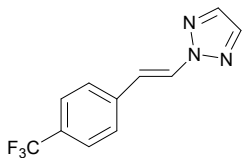
**(Z)-1-(4-fluorostyryl)-1H-1,2,3-triazole (3ga)**:  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.57 (s, 1H), 7.34 (s, 1H), 7.18 (d,  $J = 9.5$  Hz, 1H), 7.03 (dd,  $J = 8.3, 5.5$  Hz, 2H), 6.94 (t,  $J = 8.6$  Hz, 2H), 6.48 (d,  $J = 9.5$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  = 162.48, 160.82, 132.59, 129.43 (d,  $J=8.2$ ), 127.95 (d,  $J=3.5$ ), 122.53, 122.27 (d,  $J=18.7$ ), 115.01 (d,  $J=21.7$ ).  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta$  = -111.61. HRMS (ESI) Exact mass calculated for  $\text{C}_{10}\text{H}_8\text{FN}_3$   $[\text{M}+\text{H}]^+$ : 190.0775; found: 190.0773.



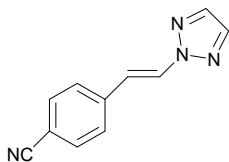
**(Z)-2-(4-fluorostyryl)-2H-1,2,3-triazole (4ga):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.70 (s, 2H), 7.32 (dd,  $J = 8.5, 5.5$  Hz, 2H), 7.13 (d,  $J = 10.0$  Hz, 1H), 6.99 (t,  $J = 8.7$  Hz, 2H), 6.36 (d,  $J = 10.0$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta = 163.26, 161.62, 135.09, 131.29$  (d,  $J=8.2$ ), 129.52 (d,  $J=3.4$ ), 124.97, 121.27.  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta = -112.75$ . HRMS (ESI) Exact mass calculated for  $\text{C}_{10}\text{H}_8\text{FN}_3$   $[\text{M}+\text{H}]^+$ : 190.0775; found: 190.0774.



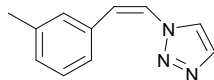
**(E)-1-(4-(trifluoromethyl) styryl)-1H-1,2,3-triazole (3ha):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.91 (s, 1H), 7.86 (d,  $J = 14.7$  Hz, 1H), 7.82 (s, 1H), 7.66 (d,  $J = 8.2$  Hz, 2H), 7.59 (d,  $J = 8.1$  Hz, 2H), 7.25 (d,  $J = 14.7$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta = 134.32, 130.55$  (q,  $J=32.7$ ), 126.90, 126.02 (q,  $J=3.7$ ), 124.72, 121.27, 120.27.  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta = -62.71$ . HRMS (ESI) Exact mass calculated for  $\text{C}_{11}\text{H}_8\text{F}_3\text{N}_3$   $[\text{M}+\text{H}]^+$ : 240.0743; found: 240.0752.



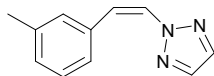
**(E)-2-(4-(trifluoromethyl) styryl)-2H-1,2,3-triazole (4ha):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.85 (d,  $J = 14.5$  Hz, 1H), 7.78 (s, 2H), 7.63 (d,  $J = 8.2$  Hz, 2H), 7.57 (d,  $J = 8.2$  Hz, 2H), 7.44 (d,  $J = 14.5$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta = 137.84, 135.87, 129.96$  (q,  $J=32.6$ ), 128.01, 126.75, 125.87 (q,  $J=3.8$ ), 124.94, 123.13, 118.75.  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta = -62.62$ . HRMS (ESI) Exact mass calculated for  $\text{C}_{11}\text{H}_8\text{F}_3\text{N}_3$   $[\text{M}+\text{H}]^+$ : 240.0743; found: 240.0781.



**(E)-4-(2-(2H-1,2,3-triazol-2-yl) vinyl) benzonitrile (4ia):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.86 (d,  $J = 14.5$  Hz, 1H), 7.80 (s, 2H), 7.67 (d,  $J = 8.3$  Hz, 2H), 7.57 (d,  $J = 8.2$  Hz, 2H), 7.42 (d,  $J = 14.5$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  138.98, 136.16, 132.70, 128.77, 127.02, 118.70, 118.32, 111.42. HRMS (ESI) Exact mass calculated for  $\text{C}_{11}\text{H}_8\text{N}_4$   $[\text{M}+\text{H}]^+$ : 197.0822; found: 197.0831.

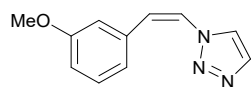


**(Z)-1-(3-methylstyryl)-1H-1,2,3-triazole (3ja):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.59 (s, 1H), 7.41 (s, 1H), 7.27 (d,  $J = 9.6$  Hz, 1H), 7.21 (t,  $J = 7.6$  Hz, 1H), 7.13 (d,  $J = 7.6$  Hz, 1H), 6.95 (s, 1H), 6.92 (d,  $J = 7.6$  Hz, 1H), 6.55 (d,  $J = 9.6$  Hz, 1H), 2.30 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  138.70, 133.39, 133.05, 129.48, 129.08, 128.83, 125.43, 123.96, 123.36, 123.22, 21.33. HRMS (ESI) Exact mass calculated for  $\text{C}_{11}\text{H}_{11}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 186.1026; found: 186.1030.

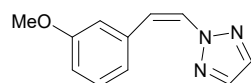


**(Z)-2-(3-methylstyryl)-2H-1,2,3-triazole (4ja):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.69 (s, 2H), 7.17 (t,  $J = 7.8$  Hz, 1H), 7.12 (d,  $J = 9.9$  Hz, 1H), 7.08 (d,  $J = 14.8$  Hz, 3H), 6.41 (d,  $J = 9.9$  Hz, 1H), 2.30 (s,

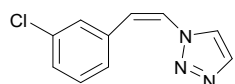
3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  137.57, 134.95, 133.37, 130.02, 129.07, 127.91, 126.35, 124.96, 123.24, 21.42. HRMS (ESI) Exact mass calculated for  $\text{C}_{11}\text{H}_{11}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 186.1026; found: 186.1029.



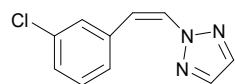
**(Z)-1-(3-methoxystyryl)-1H-1,2,3-triazole (3ka):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.61 (s, 1H), 7.43 (s, 1H), 7.29 (d,  $J = 9.6$  Hz, 1H), 7.25 (t,  $J = 7.9$  Hz, 1H), 6.87 (d,  $J = 8.3$  Hz, 1H), 6.74 (d,  $J = 7.5$  Hz, 1H), 6.64 (s, 1H), 6.56 (d,  $J = 9.6$  Hz, 1H), 3.73 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  159.89, 134.37, 133.45, 130.04, 123.79, 123.46, 120.83, 114.65, 113.46, 55.22. HRMS (ESI) Exact mass calculated for  $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$ : 202.0975; found: 202.0981.



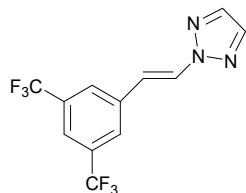
**(Z)-2-(3-methoxystyryl)-2H-1,2,3-triazole (4ka):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.70 (s, 2H), 7.21 (t,  $J = 7.9$  Hz, 1H), 7.14 (d,  $J = 10.0$  Hz, 1H), 6.90 – 6.86 (m, 2H), 6.85 – 6.82 (m, 1H), 6.41 (d,  $J = 10.0$  Hz, 1H), 3.74 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  159.17, 135.05, 134.70, 129.02, 125.23, 122.84, 122.01, 114.51, 114.29, 55.15. HRMS (ESI) Exact mass calculated for  $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$ : 202.0975; found: 202.0983.



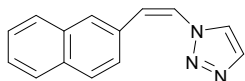
**(Z)-1-(3-chlorostyryl)-1H-1,2,3-triazole (3la):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  = 7.64 (s, 1H), 7.41 (s, 1H), 7.32 (d,  $J = 9.6$ , 1H), 7.29 (d,  $J = 13.3$ , 1H), 7.26 (d,  $J = 8.1$ , 1H), 7.16 (s, 1H), 7.01 (d,  $J = 7.5$ , 1H), 6.52 (d,  $J = 9.6$ , 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  134.88, 133.69, 130.24, 128.88, 128.60, 126.56, 124.27, 123.26, 122.33. HRMS (ESI) Exact mass calculated for  $\text{C}_{10}\text{H}_8\text{ClN}_3$   $[\text{M}+\text{H}]^+$ : 206.4080; found: 206.4086.



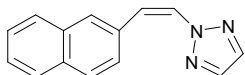
**(Z)-2-(3-chlorostyryl)-2H-1,2,3-triazole (4la):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.70 (s, 2H), 7.35 (s, 1H), 7.26 – 7.22 (m, 2H), 7.22 – 7.21 (m, 1H), 7.18 (d,  $J = 10.1$  Hz, 1H), 6.32 (d,  $J = 10.1$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  = 135.40, 135.30, 133.86, 129.41, 129.20, 128.20, 127.57, 126.01, 120.29. HRMS (ESI) Exact mass calculated for  $\text{C}_{10}\text{H}_8\text{ClN}_3$   $[\text{M}+\text{H}]^+$ : 206.4080; found: 206.4083.



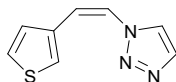
**(E)-2-(3,5-bis(trifluoromethyl)styryl)-2H-1,2,3-triazole (4ma):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.91 (d,  $J = 14.5$  Hz, 1H), 7.89 (s, 2H), 7.80 (s, 3H), 7.47 (d,  $J = 14.5$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  = 136.65, 136.30, 132.42 (q,  $J = 33.6$ ), 129.04, 126.33 (q,  $J = 3.6$ ), 124.10, 122.29, 121.52 (p,  $J = 3.8$ ), 117.21.  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta$  = -63.17. HRMS (ESI) Exact mass calculated for  $\text{C}_{12}\text{H}_7\text{F}_6\text{N}_3$   $[\text{M}+\text{H}]^+$ : 308.0617; found: 308.0619.



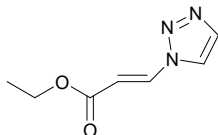
**(Z)-1-(2-(naphthalen-2-yl)vinyl)-1H-1,2,3-triazole (3na):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.82 – 7.79 (m, 1H), 7.76 (t,  $J = 8.5$  Hz, 2H), 7.66 (s, 1H), 7.57 (s, 1H), 7.52 – 7.47 (m, 2H), 7.41 (s, 1H), 7.34 (d,  $J = 9.6$  Hz, 1H), 7.12 (d,  $J = 8.5$  Hz, 1H), 6.71 (d,  $J = 9.6$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta = 133.47, 133.17, 133.02, 130.42, 128.63, 128.26, 128.07, 127.71, 126.88, 126.66, 125.53, 124.02, 123.48, 123.44$ . HRMS (ESI) Exact mass calculated for  $\text{C}_{14}\text{H}_{11}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 222.1027; found: 222.1026.



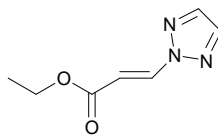
**(Z)-2-(2-(naphthalen-2-yl)vinyl)-1H-1,2,3-triazole (4na):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.84 (s, 1H), 7.78 (td,  $J = 9.3, 3.7$  Hz, 2H), 7.73 – 7.69 (m, 3H), 7.46 (q,  $J = 5.0, 3.8$  Hz, 2H), 7.31 (d,  $J = 8.5$  Hz, 1H), 7.22 (d,  $J = 9.9$  Hz, 1H), 6.59 (d,  $J = 9.9$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta = 135.10, 133.01, 131.07, 129.03, 128.21, 127.60, 127.36, 126.78, 126.39, 126.12, 125.28, 122.74$ . HRMS (ESI) Exact mass calculated for  $\text{C}_{14}\text{H}_{11}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 222.1027; found: 222.1042.



**(Z)-1-(2-(thiophen-3-yl)vinyl)-1H-1,2,3-triazole (3oa):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.73 (s, 1H), 7.58 (s, 1H), 7.27 (s, 1H), 7.23 (s, 1H), 7.11 (d,  $J = 9.3$  Hz, 1H), 6.65 (d,  $J = 4.7$  Hz, 1H), 6.59 (d,  $J = 9.2$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  133.68, 133.44, 127.17, 126.48, 126.40, 123.80, 121.86, 120.78. HRMS (ESI) Exact mass calculated for  $\text{C}_8\text{H}_7\text{N}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 178.0433; found: 178.0440.

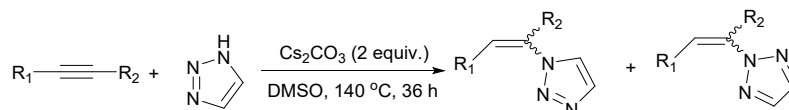


**ethyl (E)-3-(1H-1,2,3-triazol-1-yl)acrylate (3pa):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  8.27 (d,  $J = 14.4$  Hz, 1H), 7.89 (s, 1H), 7.82 (s, 1H), 6.55 (d,  $J = 14.4$  Hz, 1H), 4.31 (q,  $J = 7.1$  Hz, 2H), 1.36 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  165.14, 136.01, 134.80, 122.30, 110.97, 61.32, 14.21. HRMS (ESI) Exact mass calculated for  $\text{C}_7\text{H}_{10}\text{N}_3\text{O}_2$   $[\text{M}+\text{H}]^+$ : 168.0768; found: 168.0752.

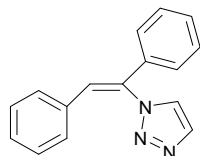


**ethyl (E)-3-(2H-1,2,3-triazol-2-yl)acrylate (4pa):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  8.27 (d,  $J = 14.4$  Hz, 1H), 7.86 (d,  $J = 54.2$  Hz, 2H), 6.55 (d,  $J = 14.4$  Hz, 1H), 4.31 (q,  $J = 7.1$  Hz, 2H), 1.35 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  165.13, 136.01, 134.79, 122.33, 110.94, 61.29, 14.21. HRMS (ESI) Exact mass calculated for  $\text{C}_7\text{H}_{10}\text{N}_3\text{O}_2$   $[\text{M}+\text{H}]^+$ : 168.0768; found: 168.0727.

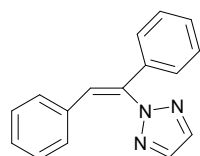
## 2-2. General procedure for triazolation of internal alkynes



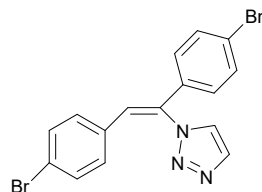
A mixture of internal alkynes (1q-1s) (0.5 mmol), 1H-1,2,3-Triazole (2) (1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1mmol) in DMSO (1.5 ml) as stirred at 140 °C for 36 h in sealed tube. The mixture was extracted with ethyl acetate and washed with water (20 ml\*3) three times. The combined organic layer dried by anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The resulting residue was purified by column chromatography (silica gel, eluent: PE/EtOAc) to afford product 5qa-5sa and 5qa'-5ra'.



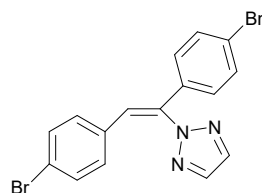
**(Z)-1-(1,2-diphenylvinyl)-1H-1,2,3-triazole (5qa):** <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.56 (s, 1H), 7.38 – 7.36 (m, 3H), 7.21 (t, *J* = 5.9 Hz, 6H), 6.78 (d, *J* = 7.6 Hz, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ = 136.43, 134.77, 134.20, 133.23, 129.41, 128.90, 128.83, 128.74, 126.90, 125.78, 125.70. HRMS (ESI) Exact mass calculated for C<sub>16</sub>H<sub>14</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 248.1182; found: 248.1194.



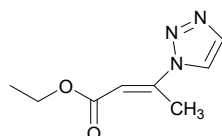
**(Z)-2-(1,2-diphenylvinyl)-2H-1,2,3-triazole (5qa'):** <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ = 7.86 (s, 2H), 7.40 – 7.33 (m, 3H), 7.19 (dd, *J* = 7.5, 15.3, 6H), 6.72 (d, *J* = 6.8, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ = 138.07, 136.81, 135.53, 129.12, 128.75, 128.71, 128.48, 128.45, 127.13, 125.99. HRMS (ESI) Exact mass calculated for C<sub>16</sub>H<sub>14</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 248.1182; found: 248.1177.



**(Z)-1-(1,2-bis(4-bromophenyl)vinyl)-1H-1,2,3-triazole (5ra):** <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ = 7.87 (s, 1H), 7.54 (s, 1H), 7.51 (d, *J* = 8.6, 2H), 7.34 (d, *J* = 8.5, 2H), 7.12 (s, 1H), 7.06 (d, *J* = 8.6, 2H), 6.62 (d, *J* = 8.5, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ = 135.10, 134.49, 134.40, 132.16, 132.03, 131.85, 130.16, 127.24, 126.07, 125.60, 123.94, 123.32. HRMS (ESI) Exact mass calculated for C<sub>16</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 403.9392; found: 403.9384.

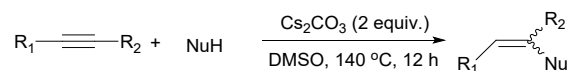


**(Z)-2-(1,2-bis(4-bromophenyl)vinyl)-2H-1,2,3-triazole (5ra'):** <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ = 7.86 (s, 2H), 7.49 (d, *J* = 8.6, 2H), 7.33 (d, *J* = 7.5, 2H), 7.08 (s, 1H), 7.03 (d, *J* = 7.5, 2H), 6.57 (d, *J* = 7.8, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ = 137.69, 135.88, 135.50, 132.48, 131.96, 131.71, 130.20, 127.59, 126.19, 123.61, 122.88. HRMS (ESI) Exact mass calculated for C<sub>16</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 403.9392; found: 403.9387.

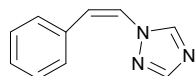


**ethyl (E)-3-(1H-1,2,3-triazol-1-yl) but-2-enoate (5sa):** <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ = 7.89 (s, 1H), 7.79 (s, 1H), 6.52 (s, 1H), 4.25 (q, *J*=7.1, 2H), 2.85 (s, 3H), 1.33 (t, *J*=7.1, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ = 165.66, 147.36, 121.26, 109.66, 60.75, 15.83, 14.23. HRMS (ESI) Exact mass calculated for C<sub>8</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 181.0851; found: 181.0866.

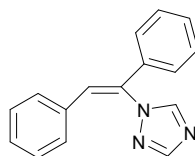
### 2-3. General procedure for alkenylation of Triazole.



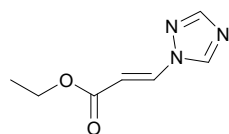
A mixture of alkynes (1a - 1q and 1p) (0.5 mmol), NuH (2b and 2c) (1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1mmol) in DMSO (1.5 ml) as stirred at 140 °C for 36 h in sealed tube. The mixture was extracted with ethyl acetate and washed with water (20 ml\*3) three times. The combined organic layer dried by anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The resulting residue was purified by column chromatography (silica gel, eluent: PE/EtOAc) to afford product 5ab - 5qb - 5pc and 5pb..



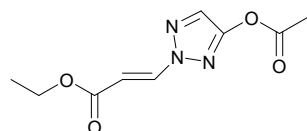
**(Z)-1-styryl-1H-1,2,4-triazole (5ab):** <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.92 (s, 1H), 7.32 (q, *J* = 7.3, 6.7 Hz, 3H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 9.5 Hz, 1H), 6.55 (d, *J* = 9.5 Hz, 1H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ = 151.81, 143.29, 133.20, 129.05, 128.71, 128.35, 124.44, 123.28. HRMS (ESI) Exact mass calculated for C<sub>10</sub>H<sub>10</sub>N<sub>3</sub>[M+H]<sup>+</sup>: 172.0869; found: 172.0862.



**(Z)-1-(1,2-diphenylvinyl)-1H-1,2,4-triazole (5qb):** <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ = 8.21 (s, 1H), 8.03 (s, 1H), 7.42 - 7.36 (m, 3H), 7.28 - 7.20 (m, 5H), 7.16 (s, 1H), 6.85 (dd, *J*=3.1, 6.3, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ = 152.89, 145.23, 136.17, 134.81, 133.45, 129.47, 128.89, 128.87, 128.75, 128.57, 126.73, 125.89. HRMS (ESI) Exact mass calculated for C<sub>16</sub>H<sub>14</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 248.1182; found: 248.1190.



**ethyl (E)-3-(1H-1,2,4-triazol-1-yl) acrylate (5pb):** <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 8.08 (s, 1H), 8.04 (d, *J* = 13.9 Hz, 1H), 6.61 (d, *J* = 13.8 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ = 165.63, 153.58, 144.57, 135.04, 110.40, 61.09, 14.22. HRMS (ESI) Exact mass calculated for C<sub>7</sub>H<sub>10</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 168.0768; found: 168.0773.



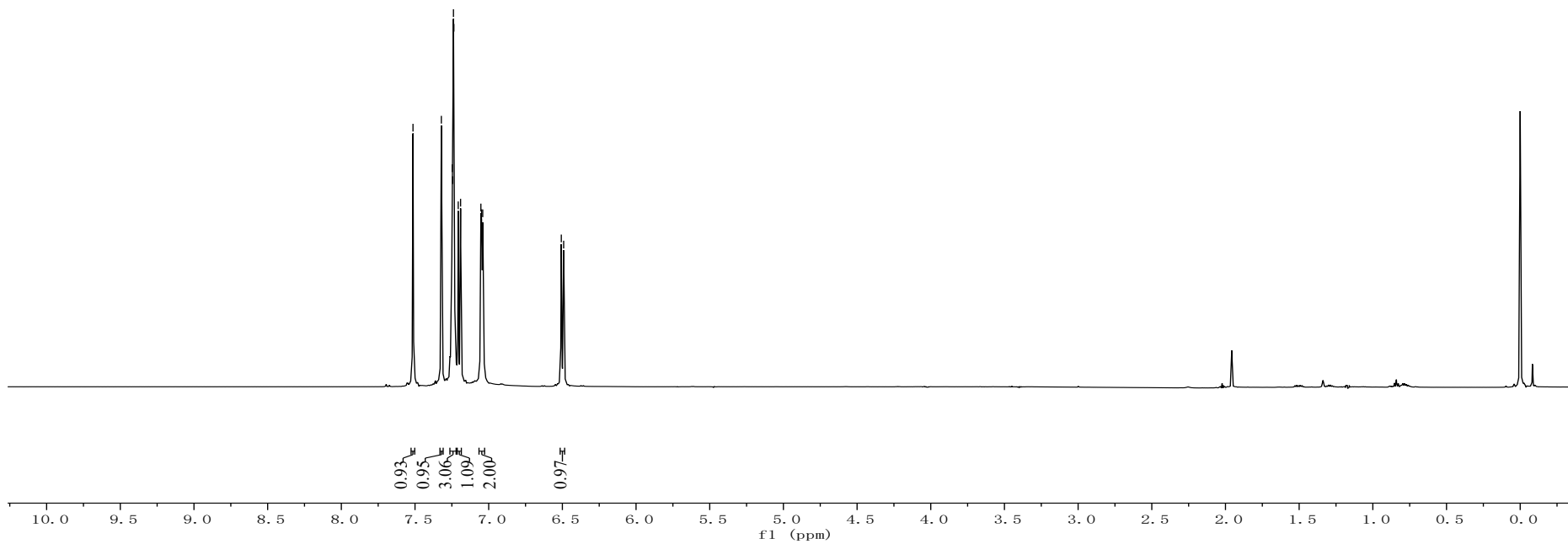
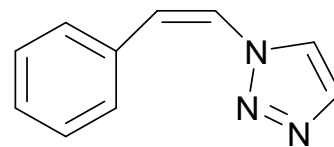
**ethyl (E)-3-(4-acetoxy-2H-1,2,3-triazol-2-yl) acrylate (5pc):** <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 8.19 (d, *J* = 14.1 Hz, 1H), 6.82 (d, *J* = 14.1 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ = 165.08, 160.27, 142.26, 139.10, 138.76, 112.66, 61.23, 52.78, 14.20. HRMS (ESI) Exact mass calculated for C<sub>9</sub>H<sub>12</sub>N<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 226.0822;

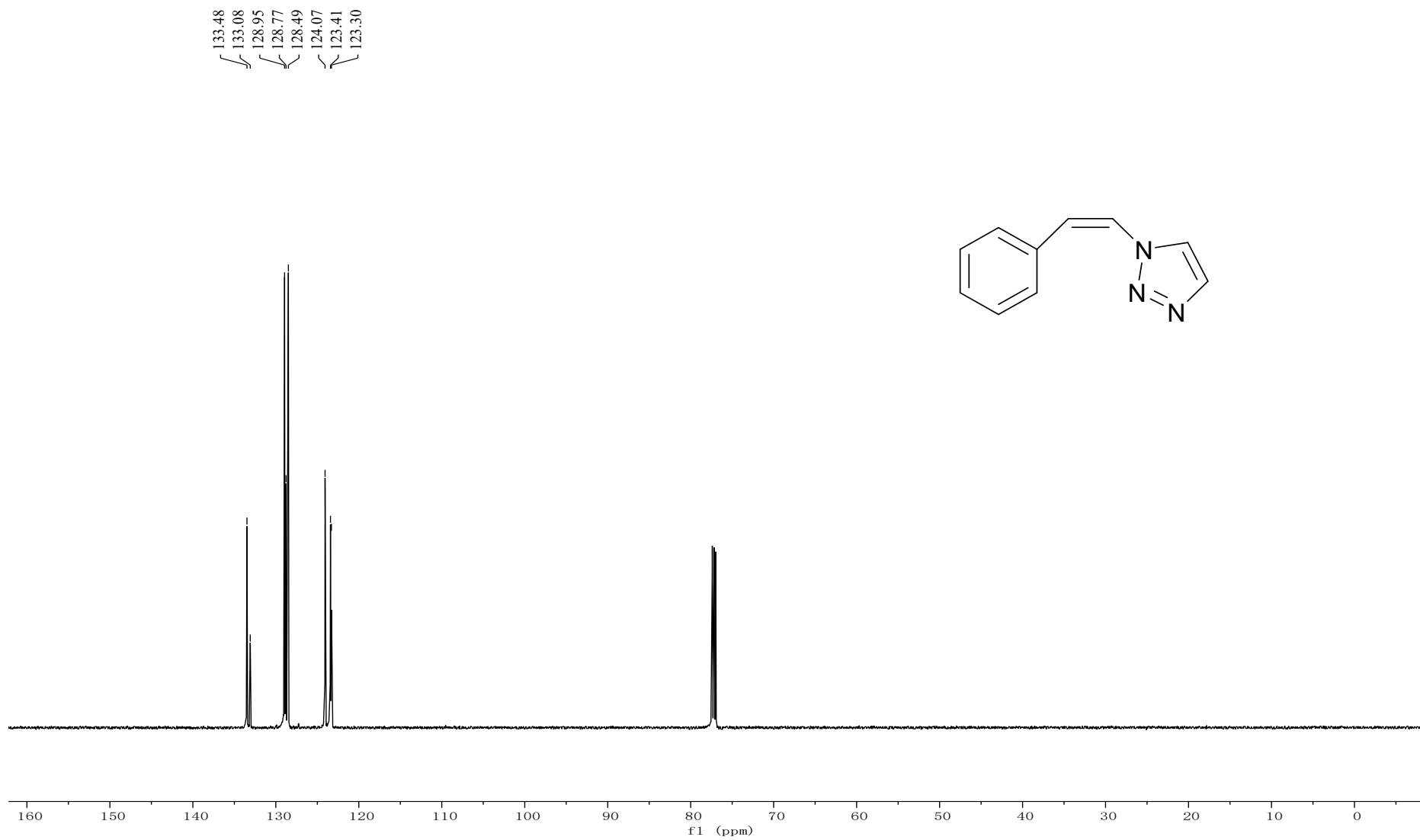


found: 226.0838.

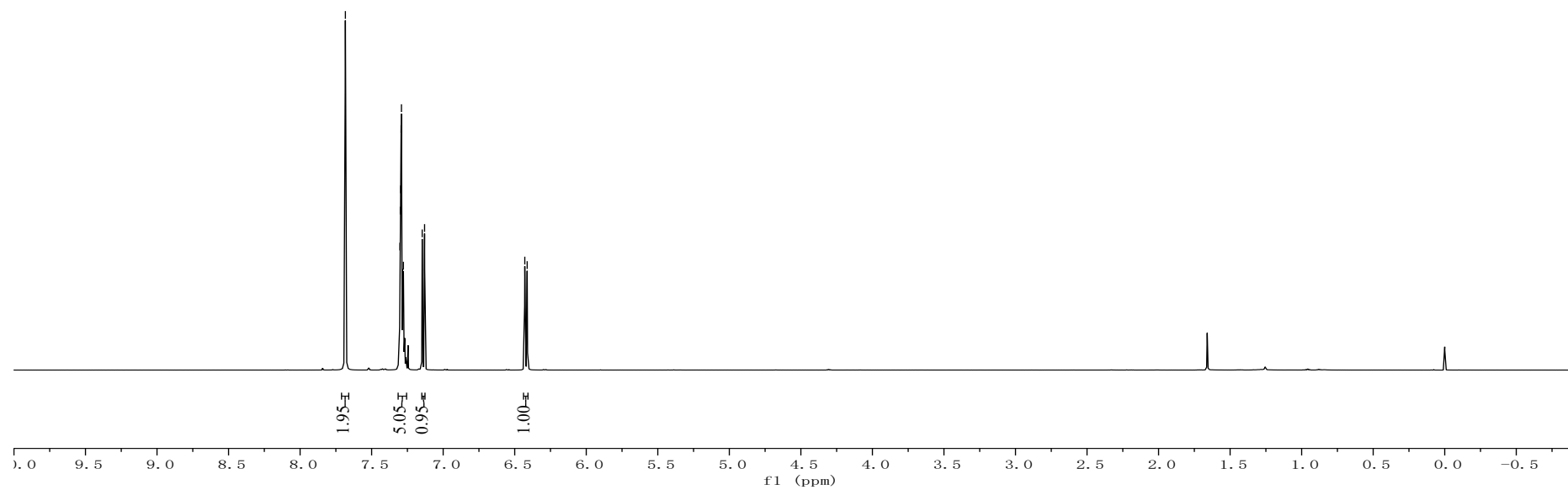
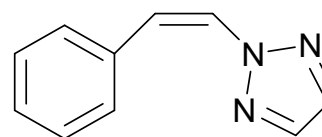
**3. Copies of  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR Spectra**

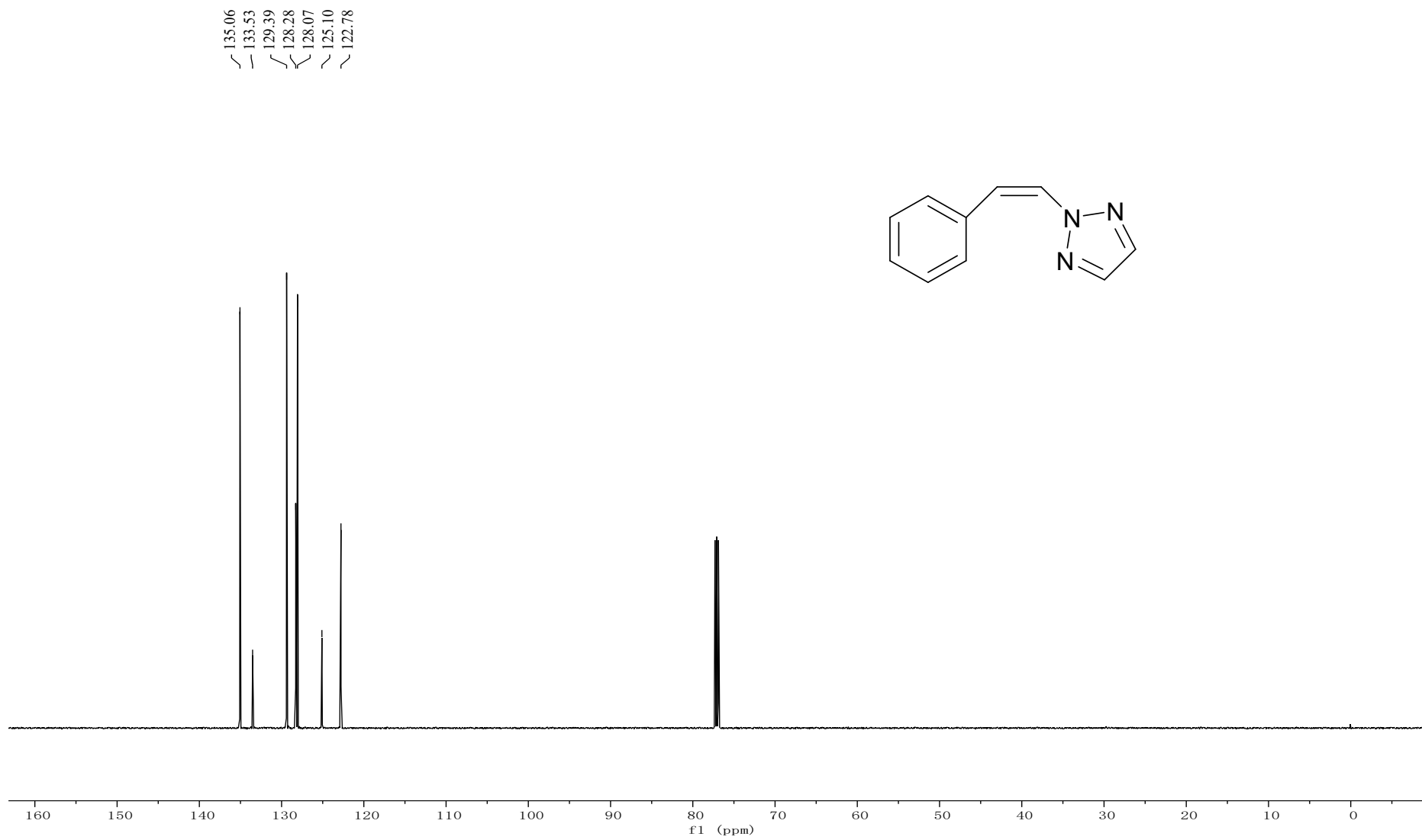
7.51  
7.32  
7.25  
7.24  
7.24  
7.21  
7.19  
7.05  
7.05  
7.04  
6.51  
6.49

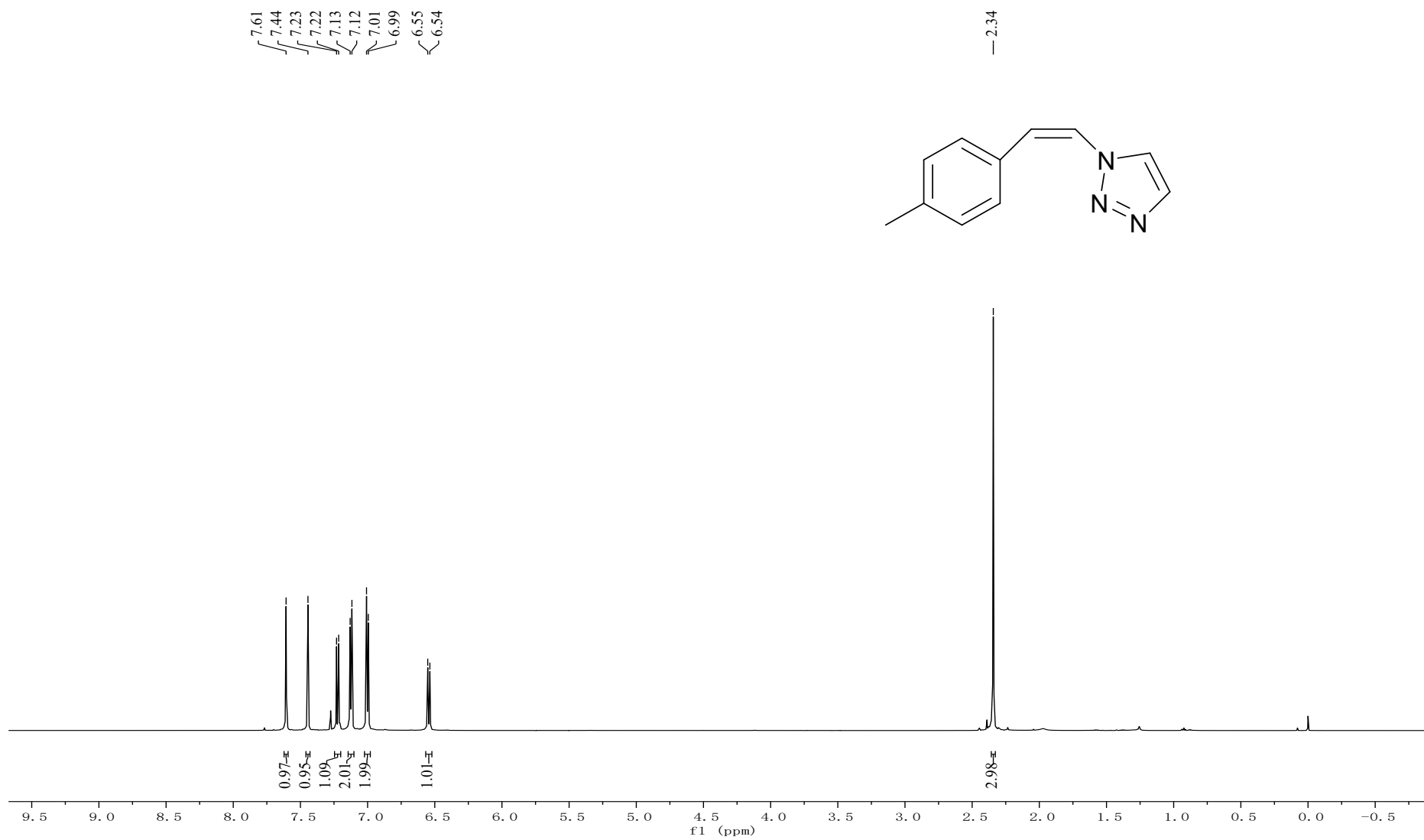


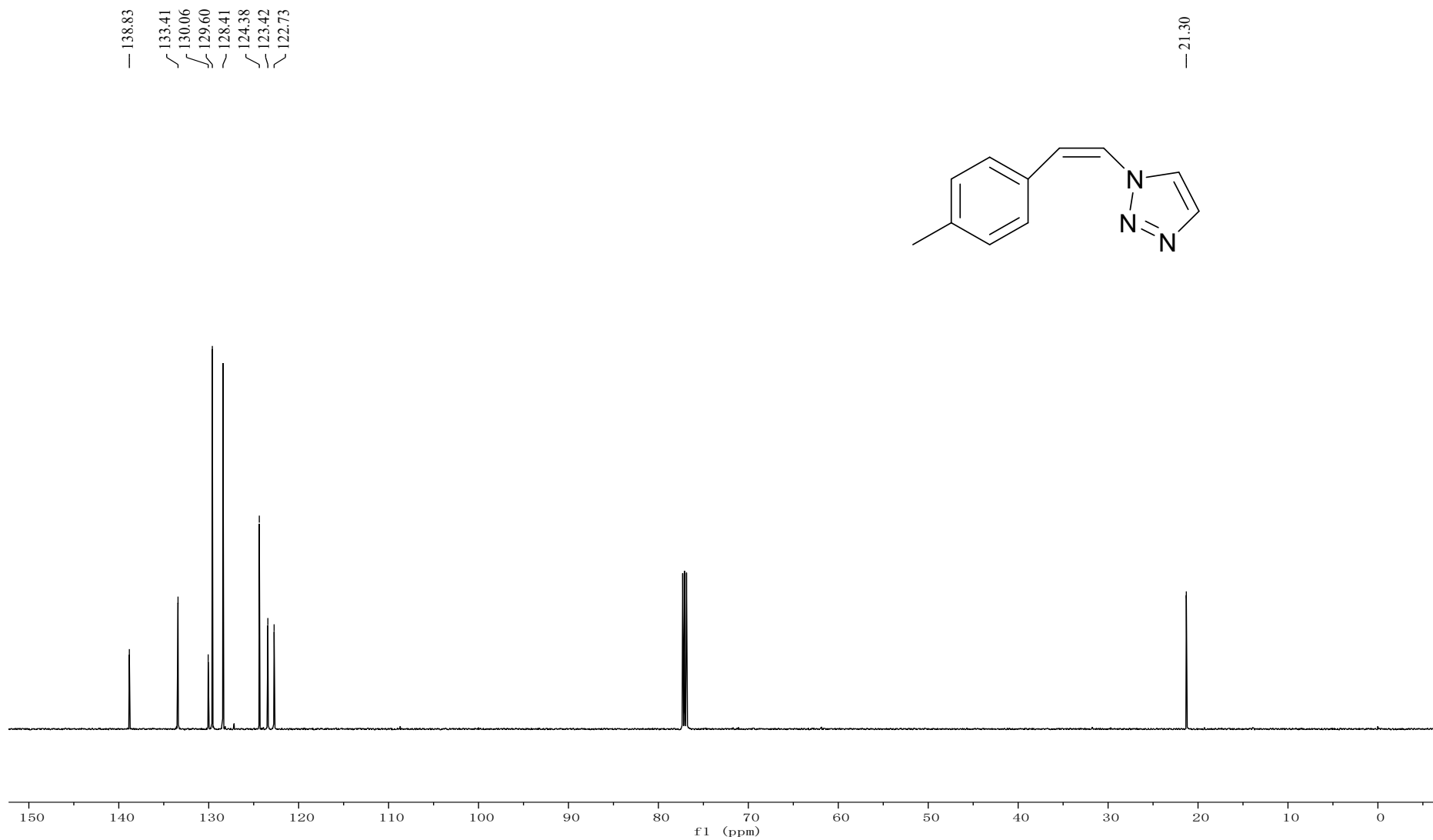


7.68  
7.30  
7.30  
7.30  
7.29  
7.29  
7.28  
7.28  
7.15  
7.13  
6.43  
6.41



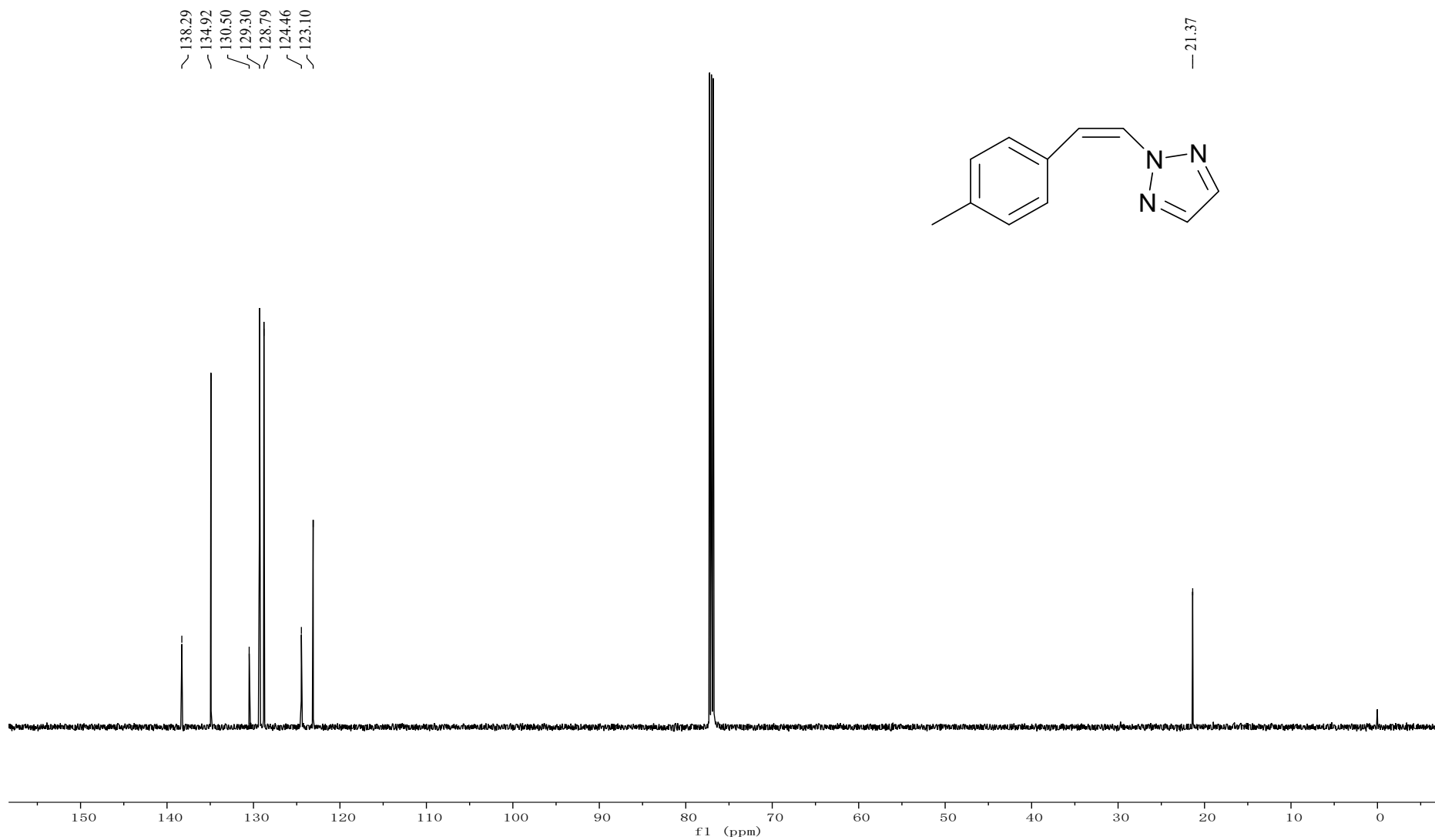


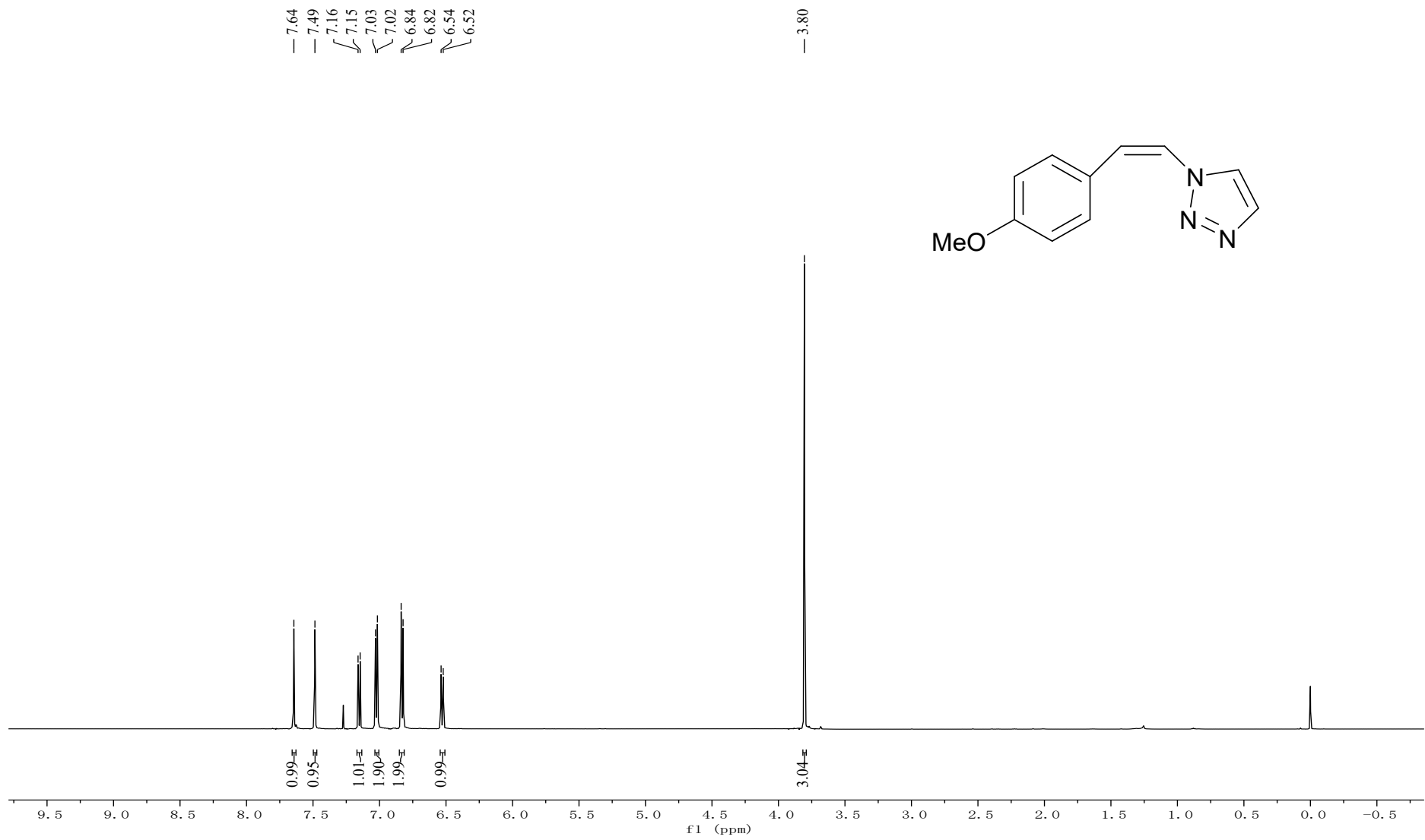


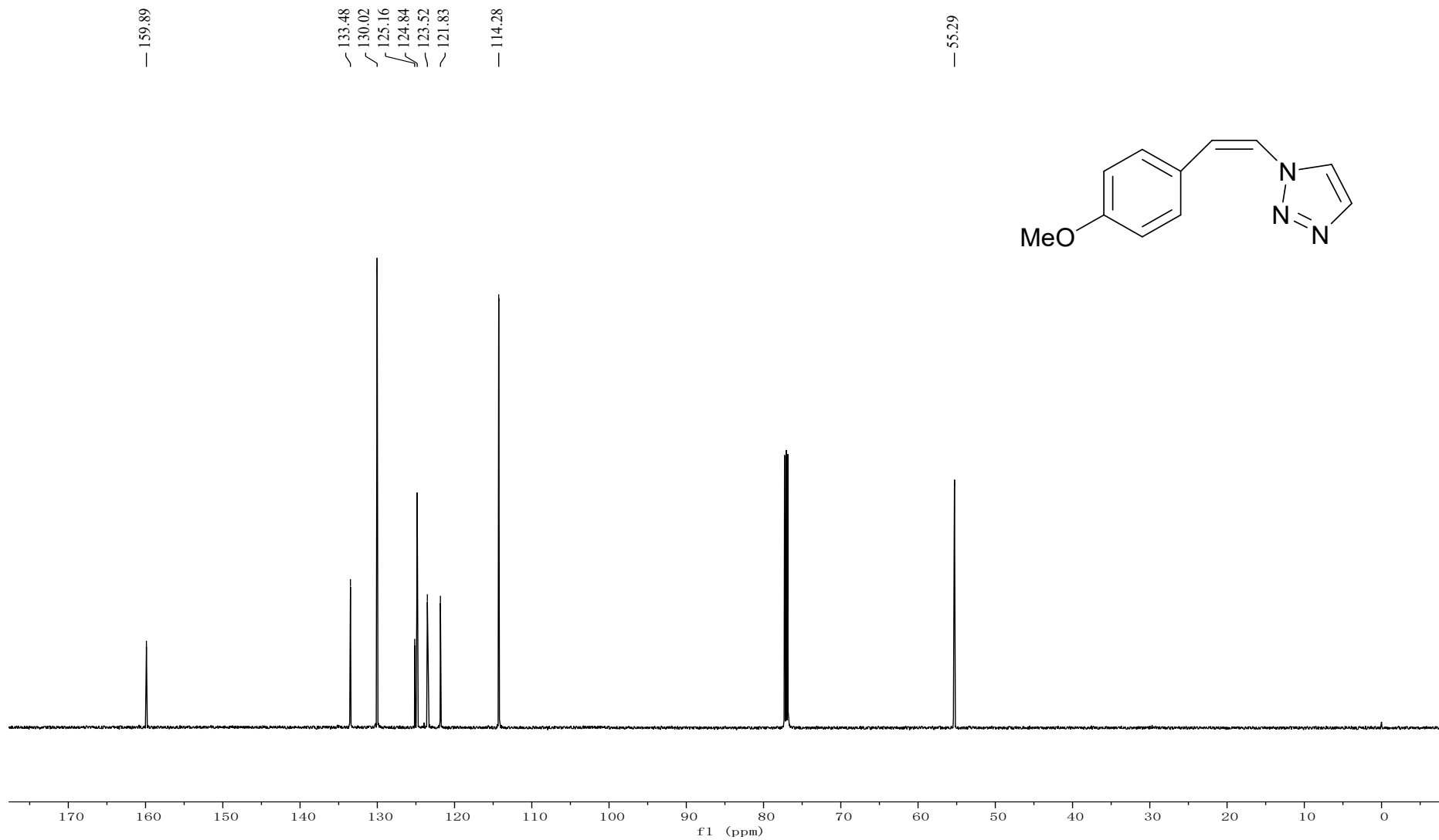


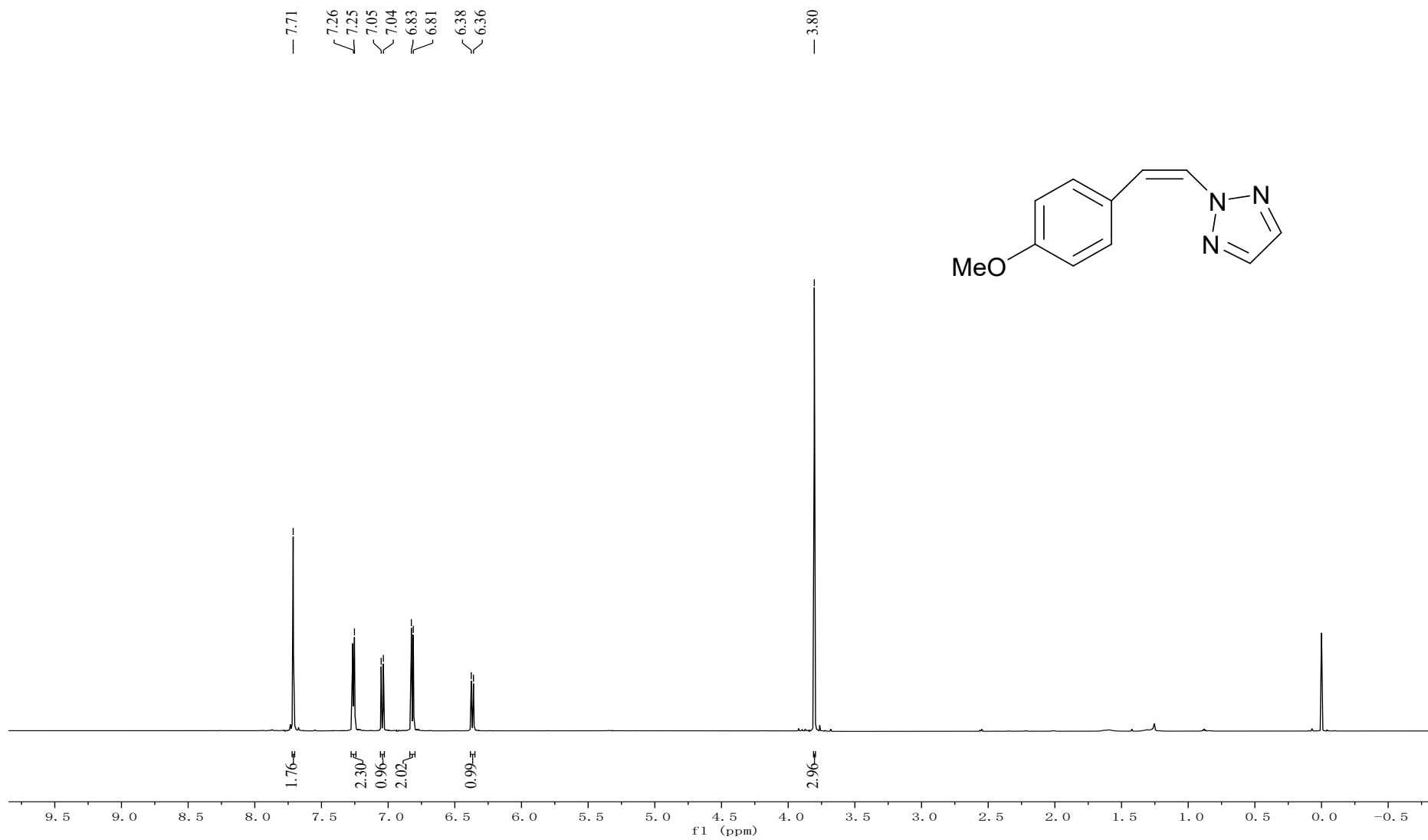


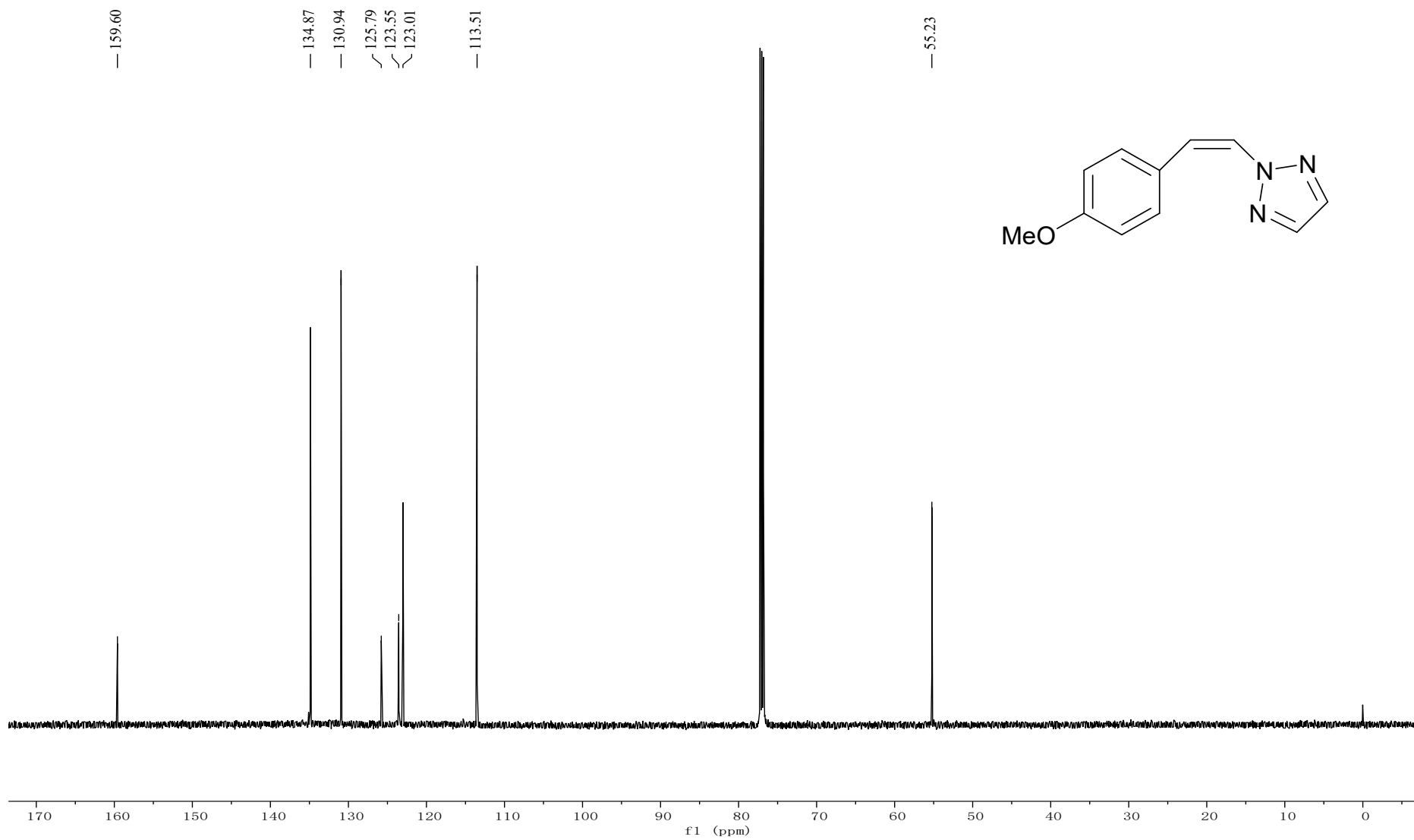


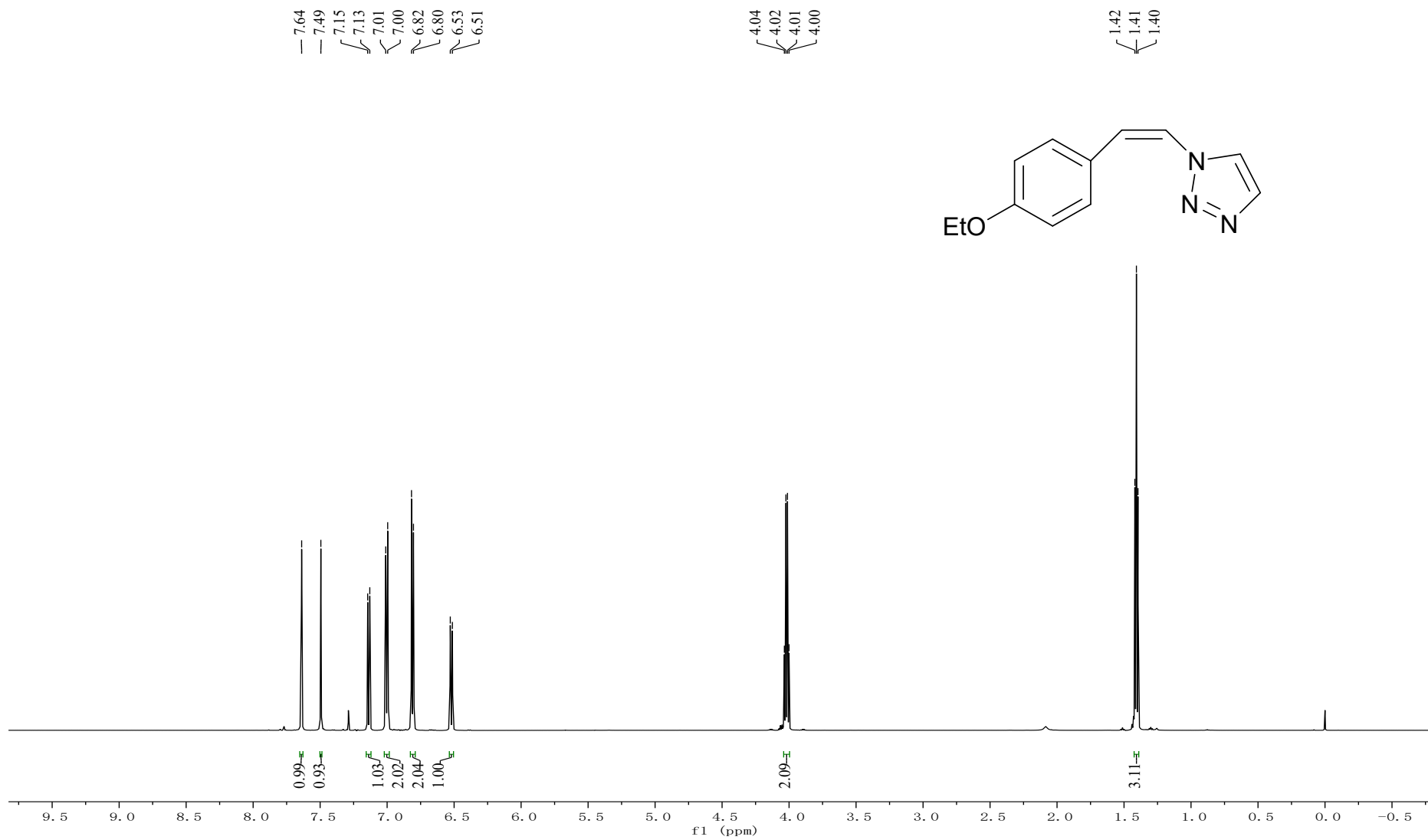


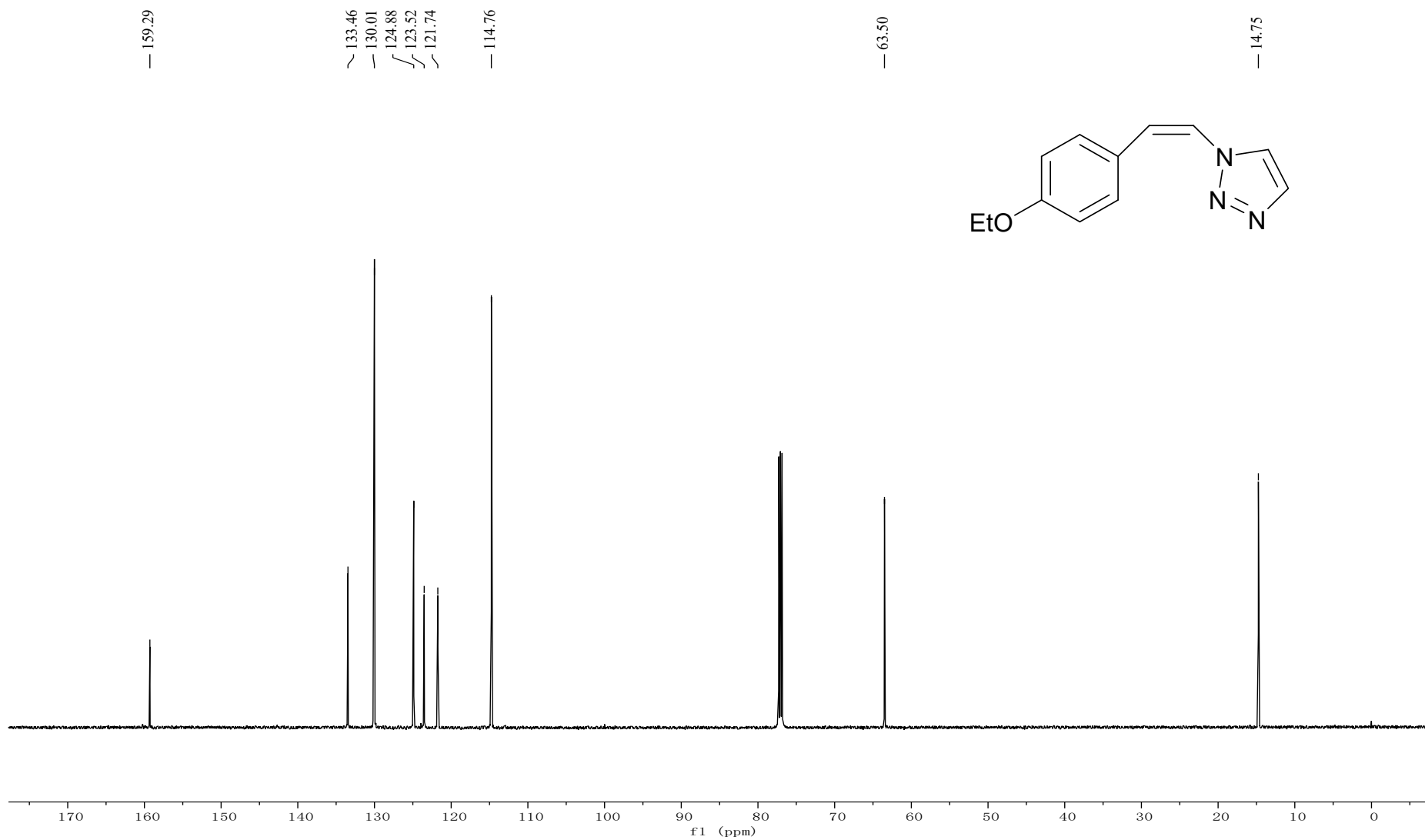


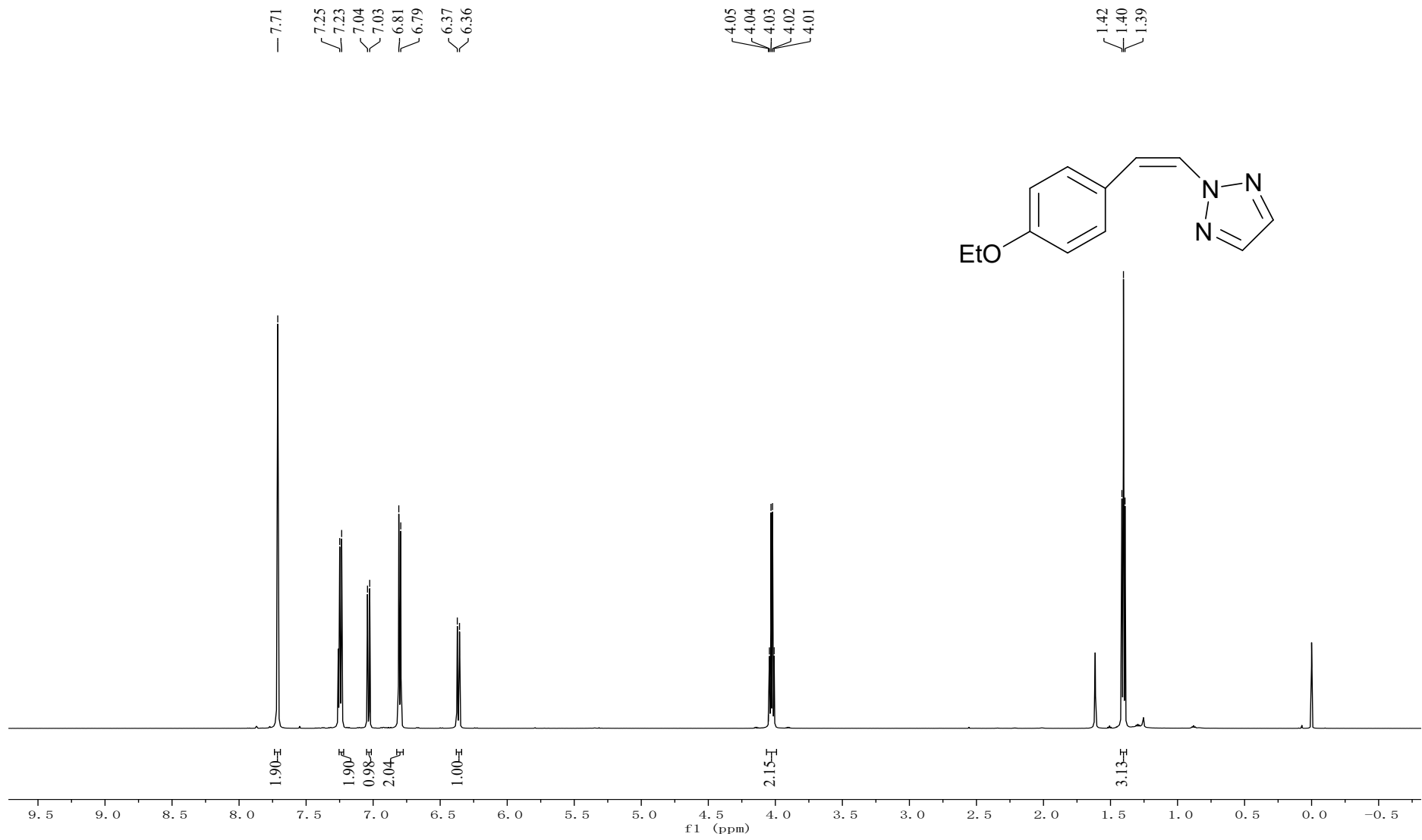




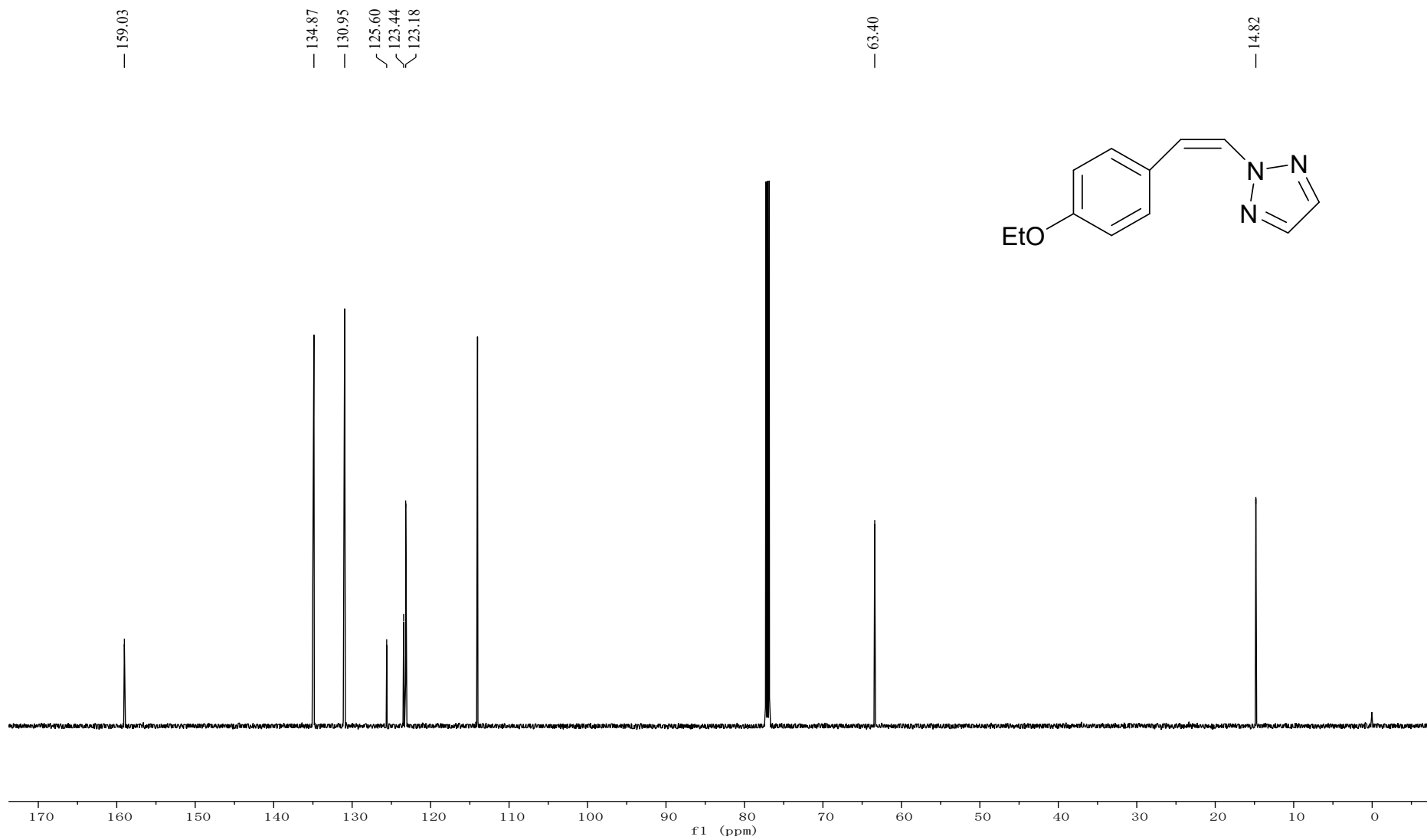


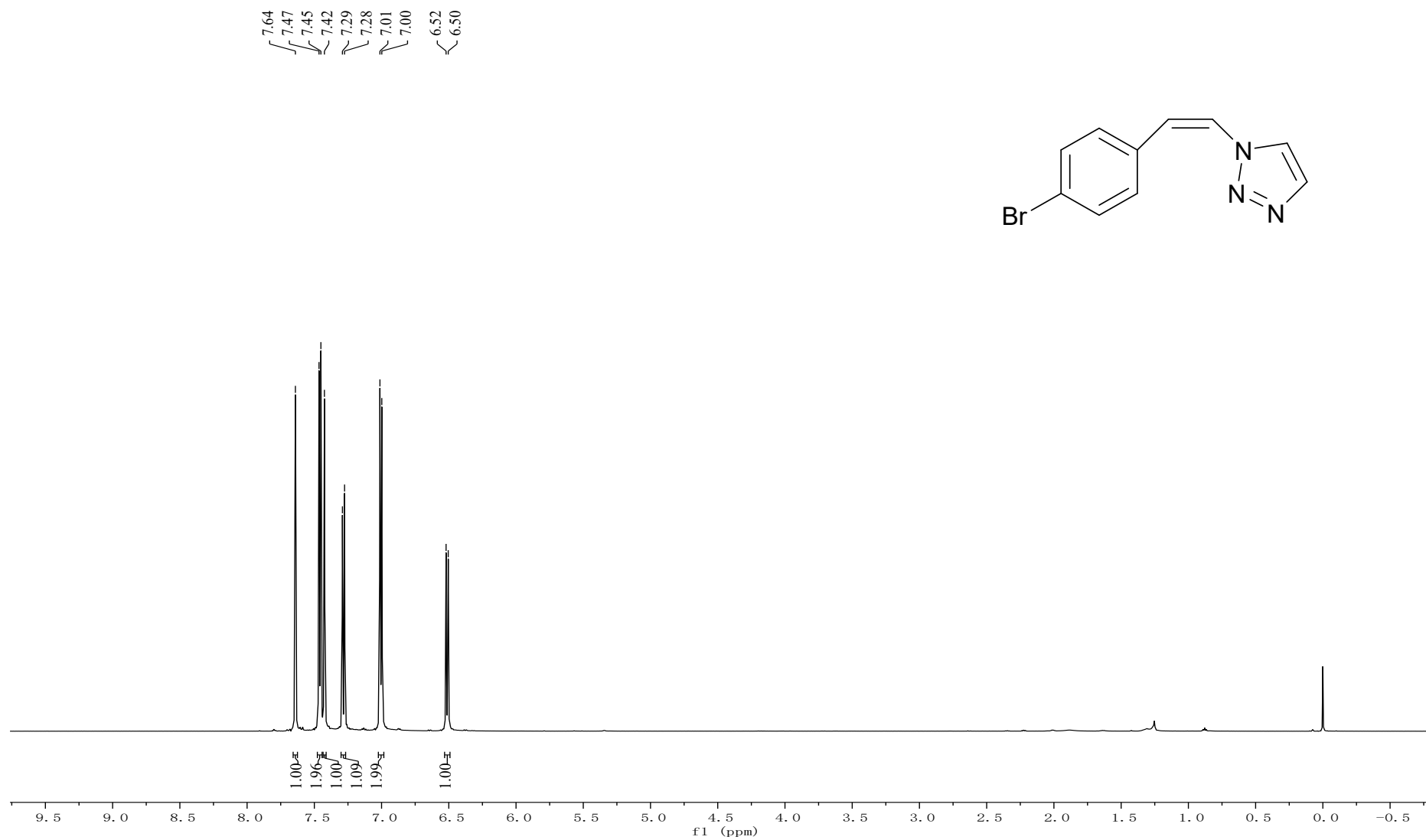
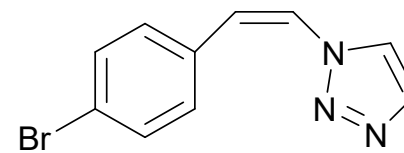




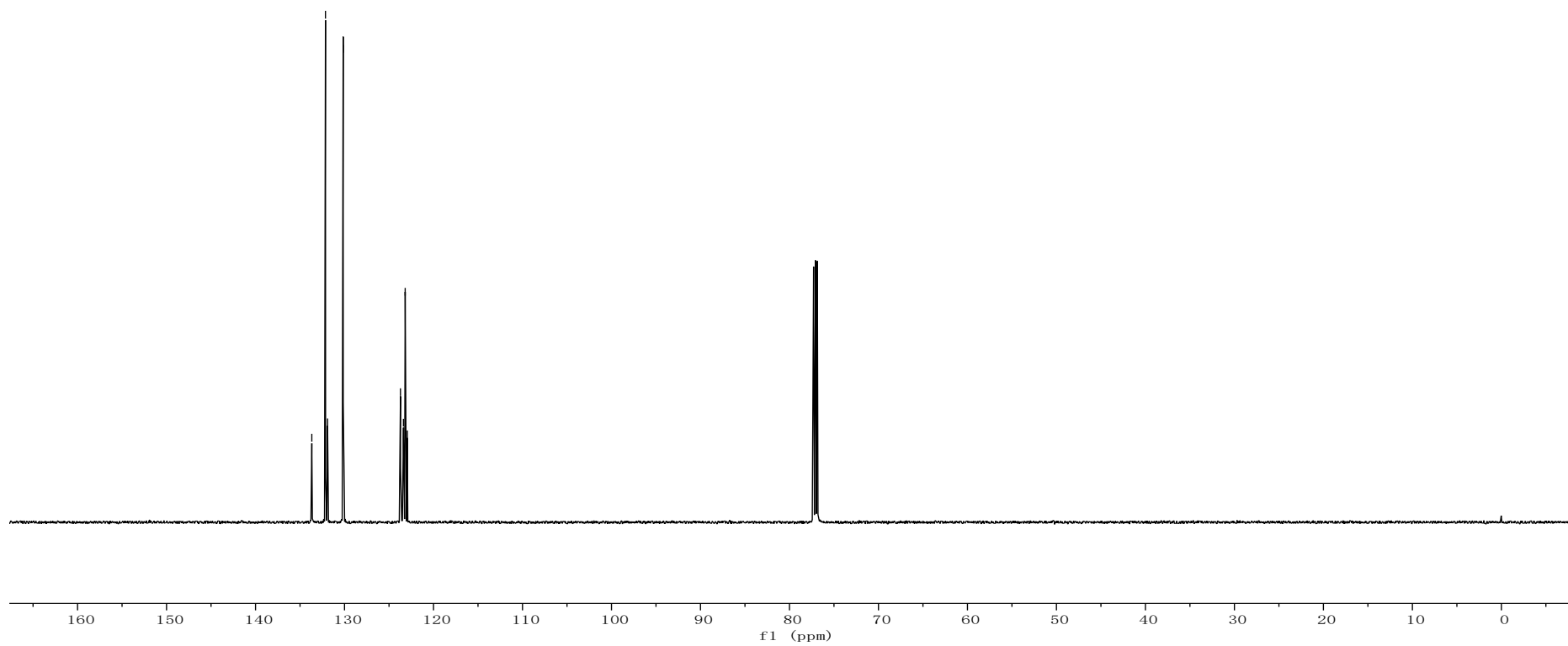
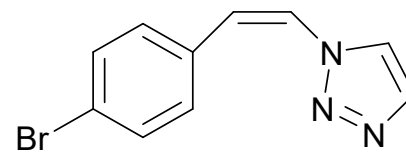


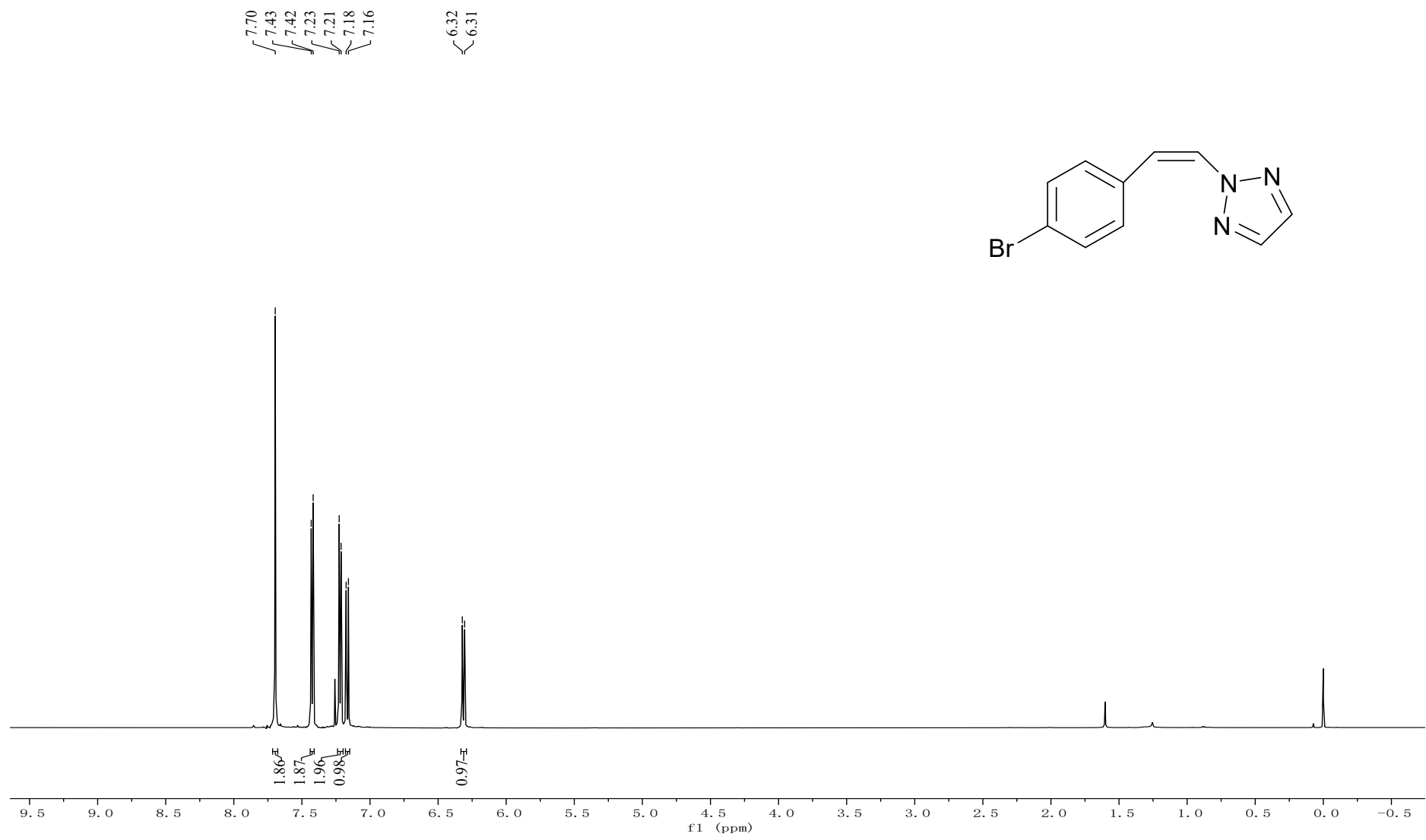
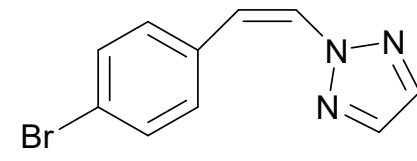




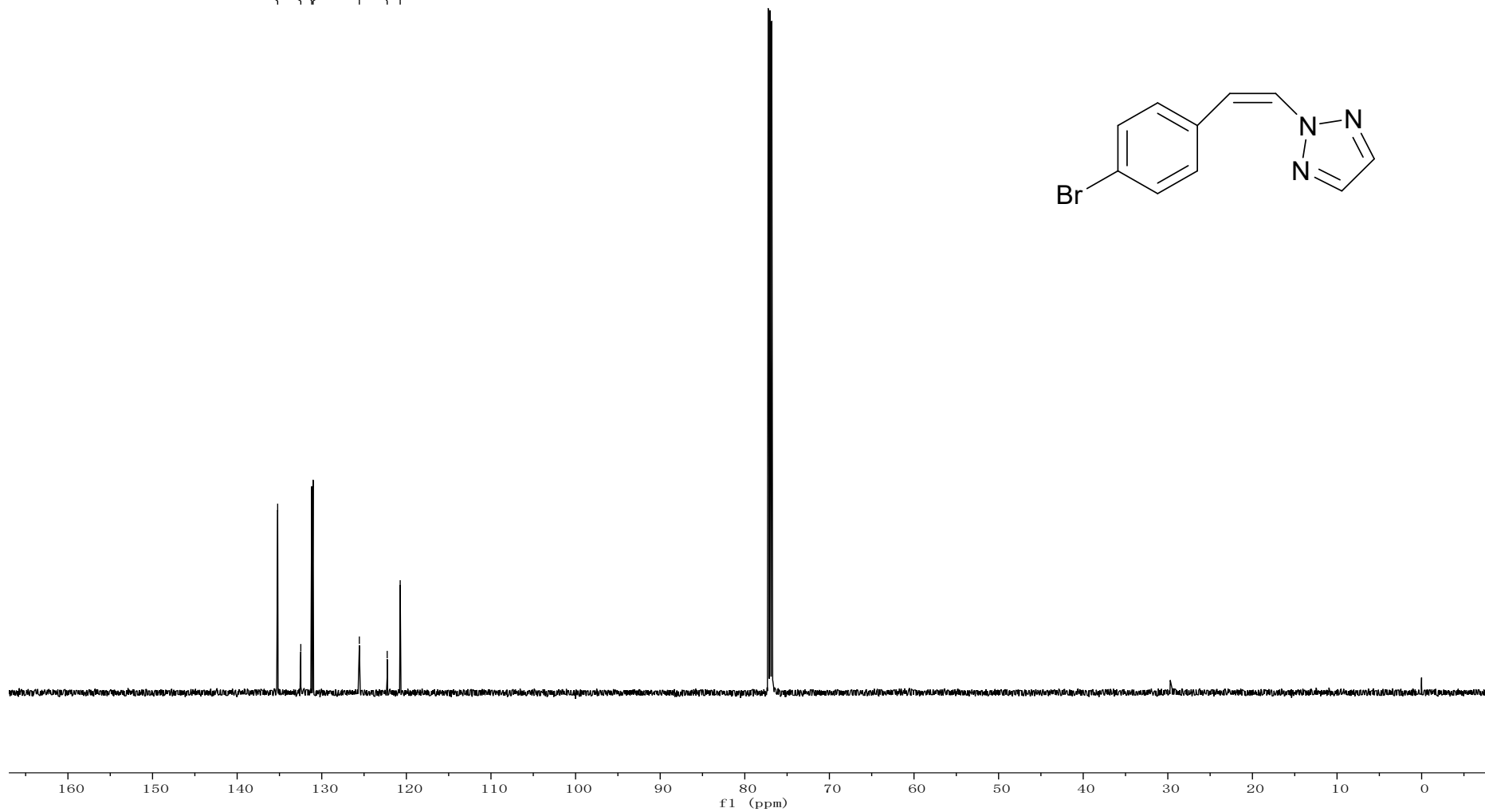
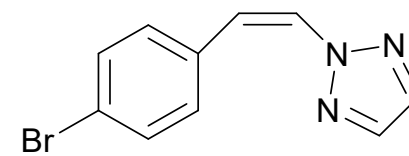


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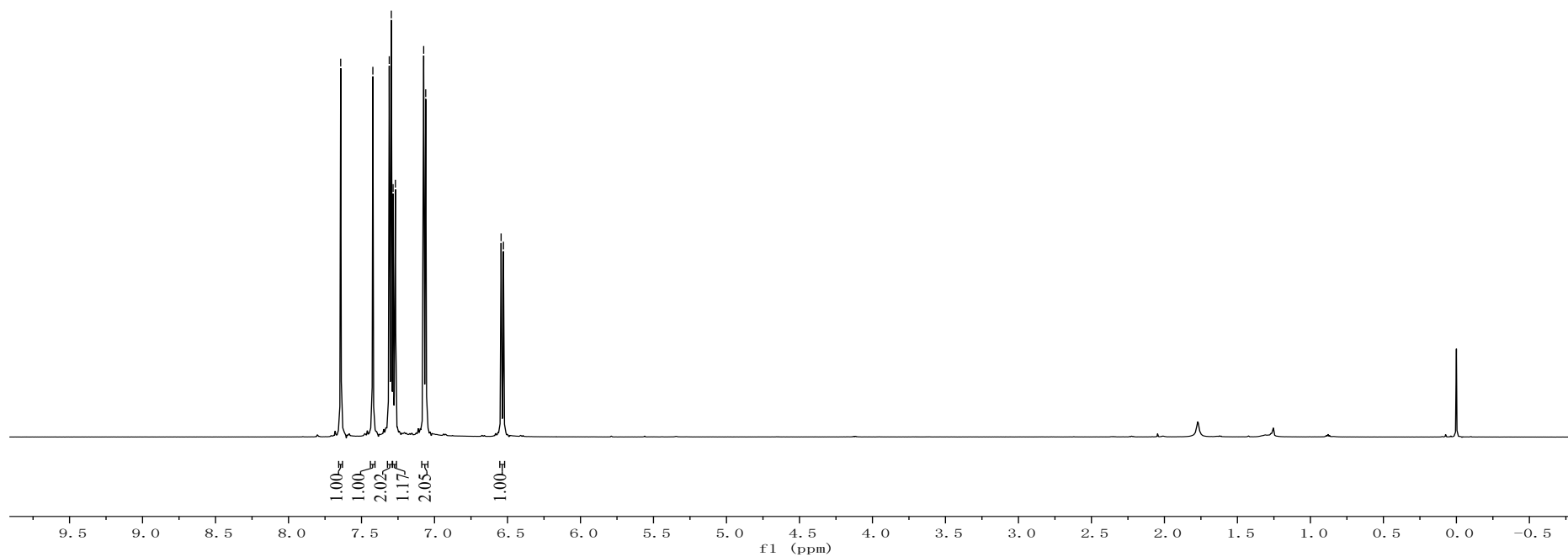
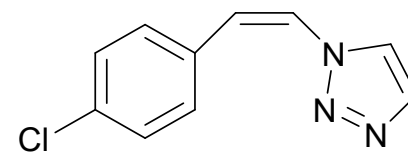




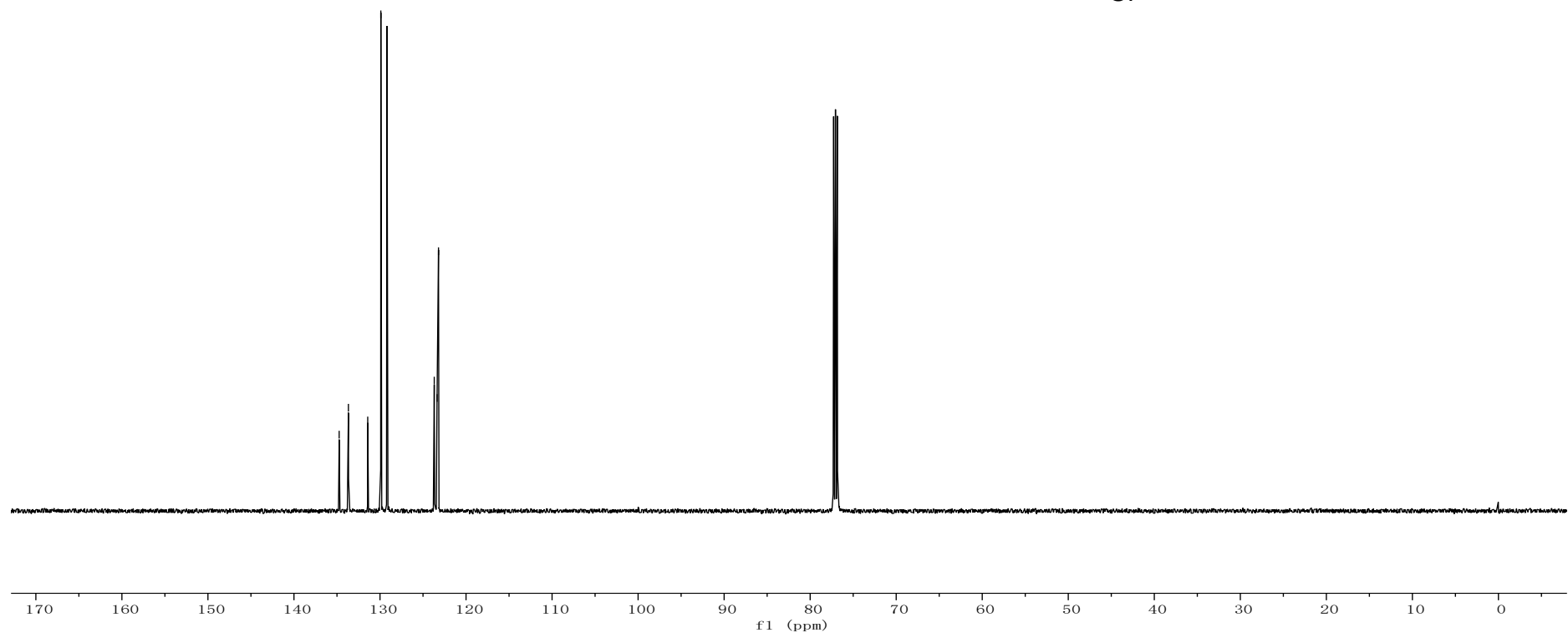
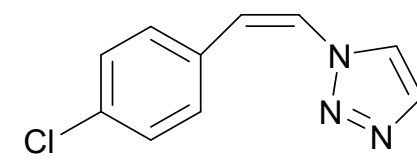
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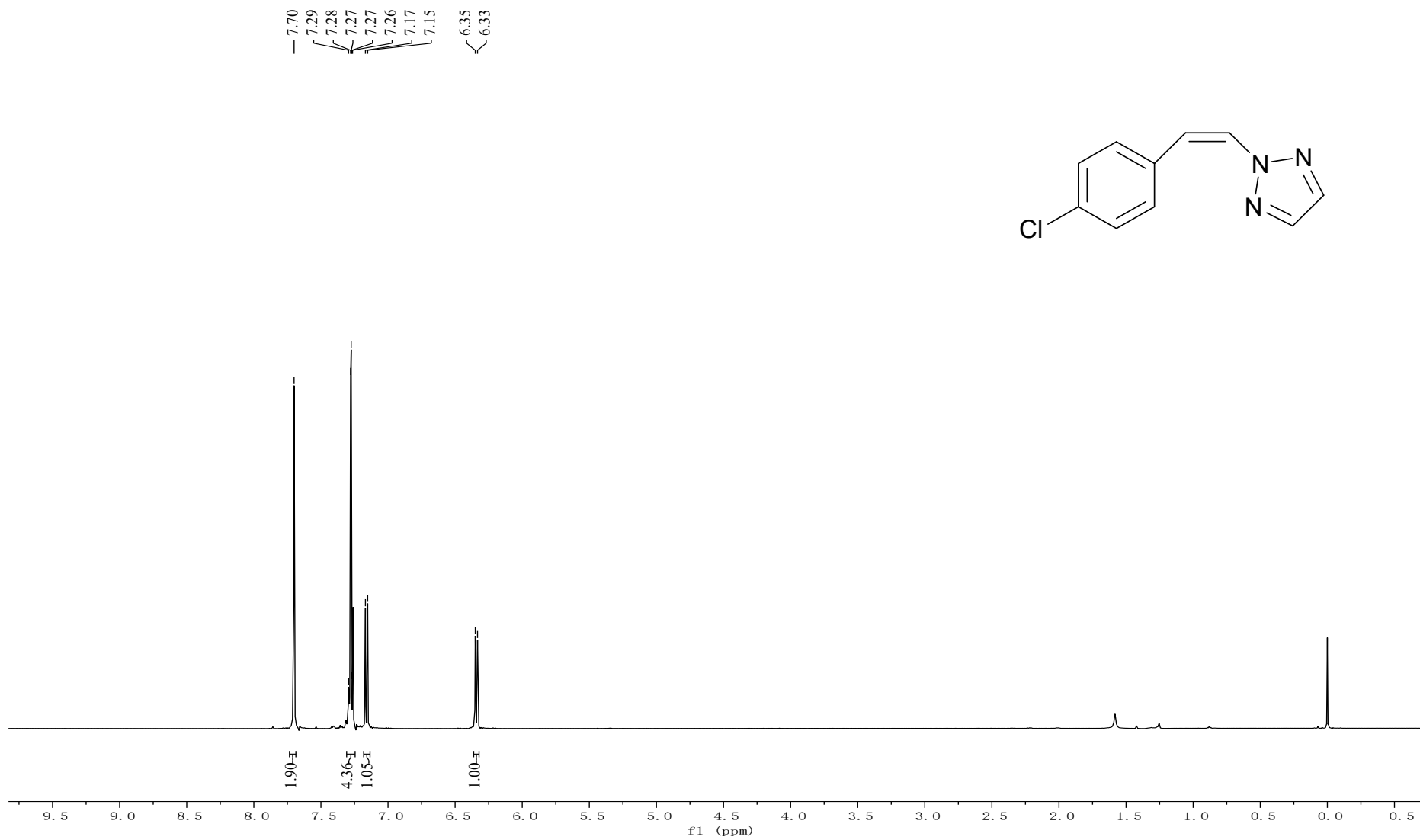
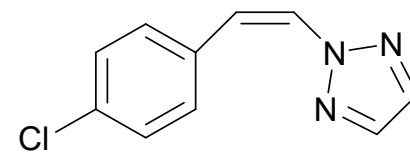


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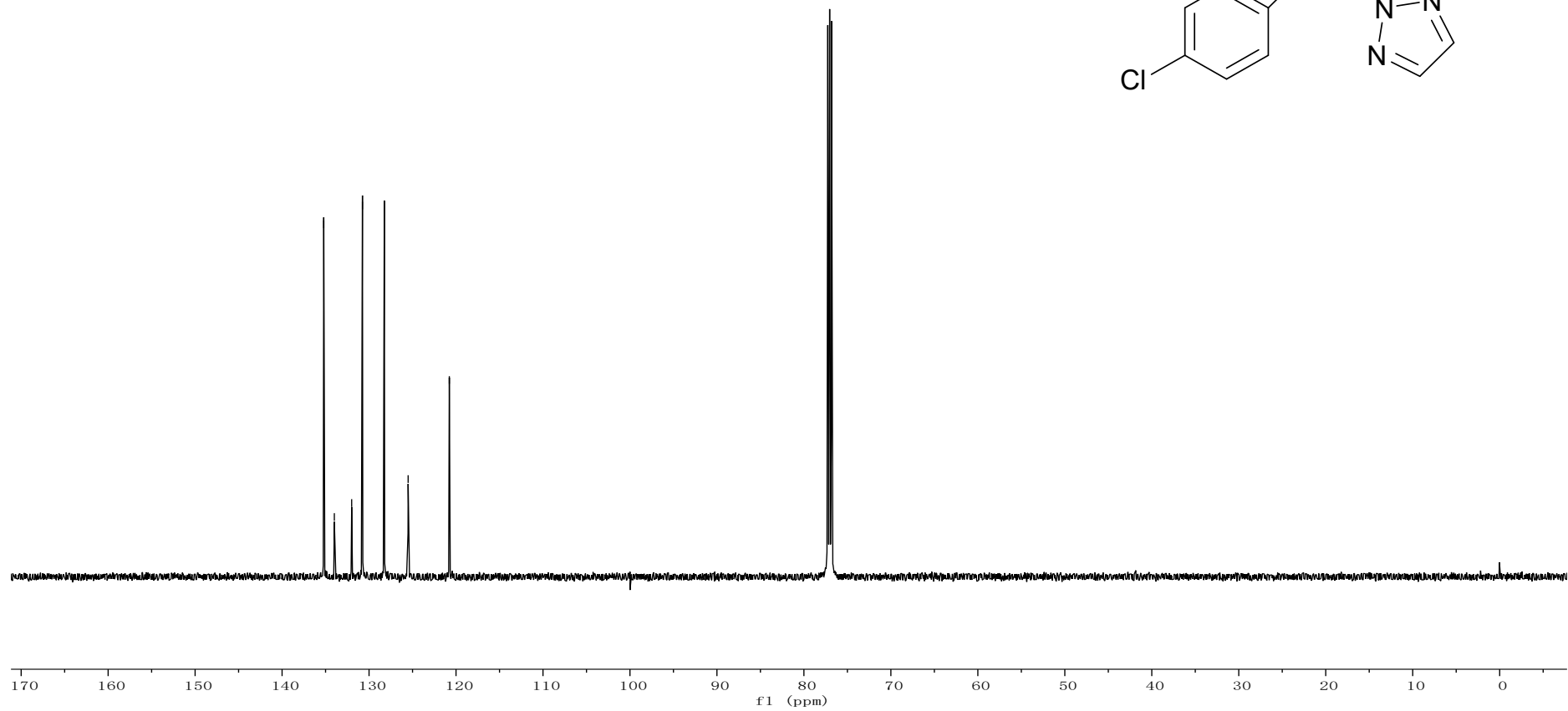
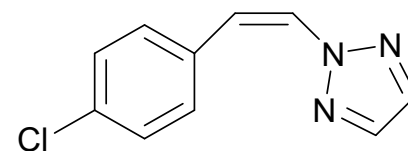
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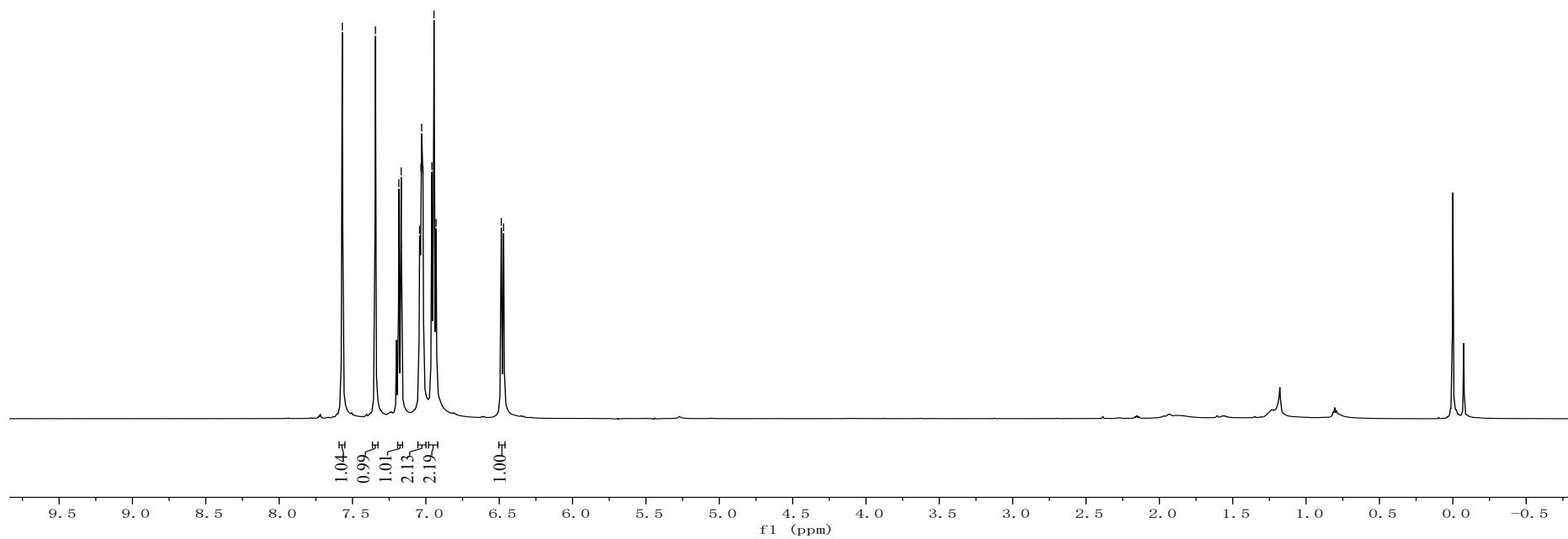
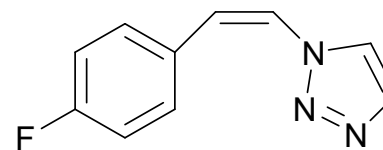


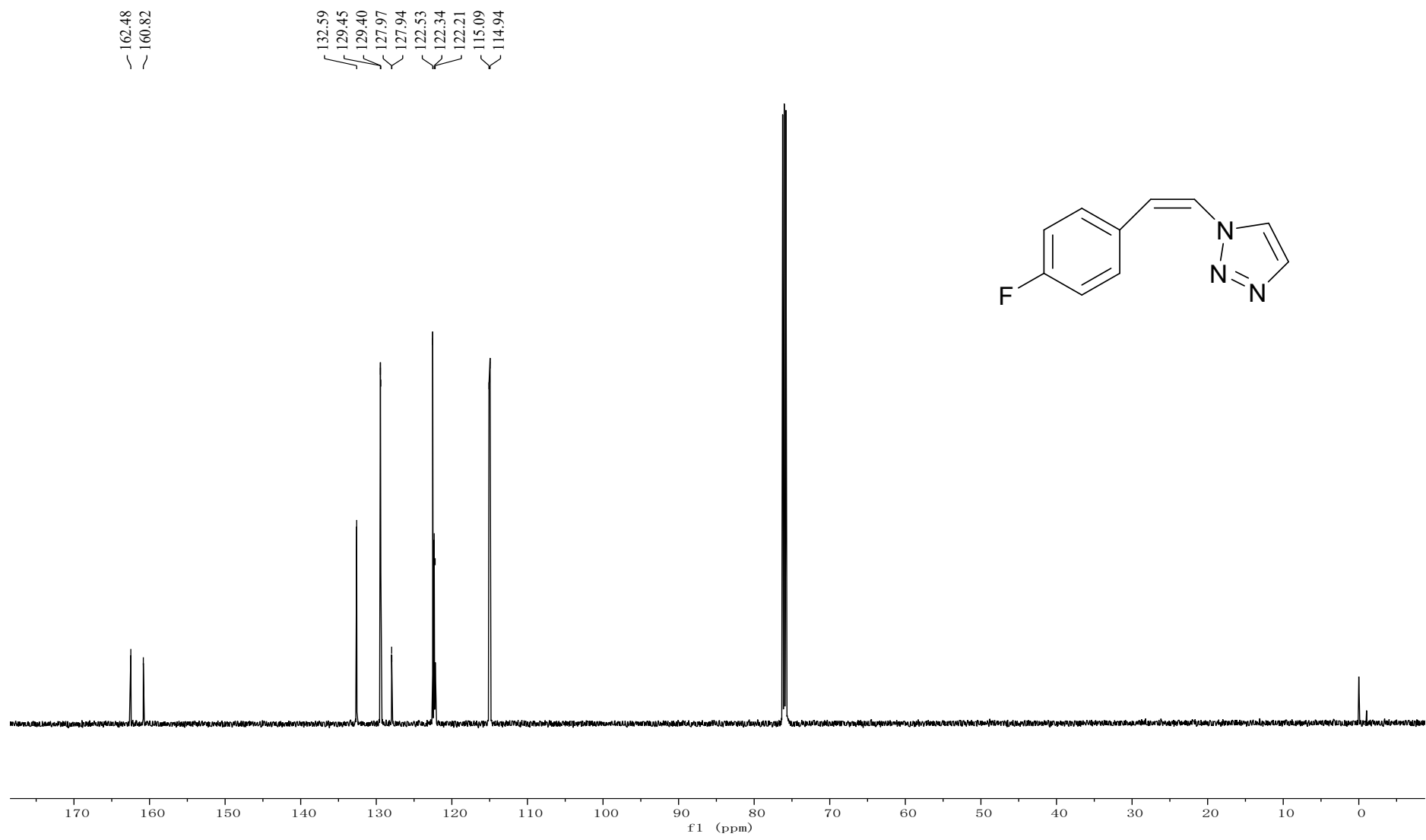


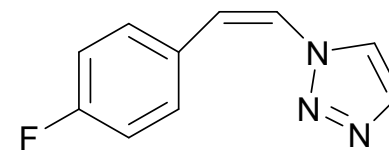
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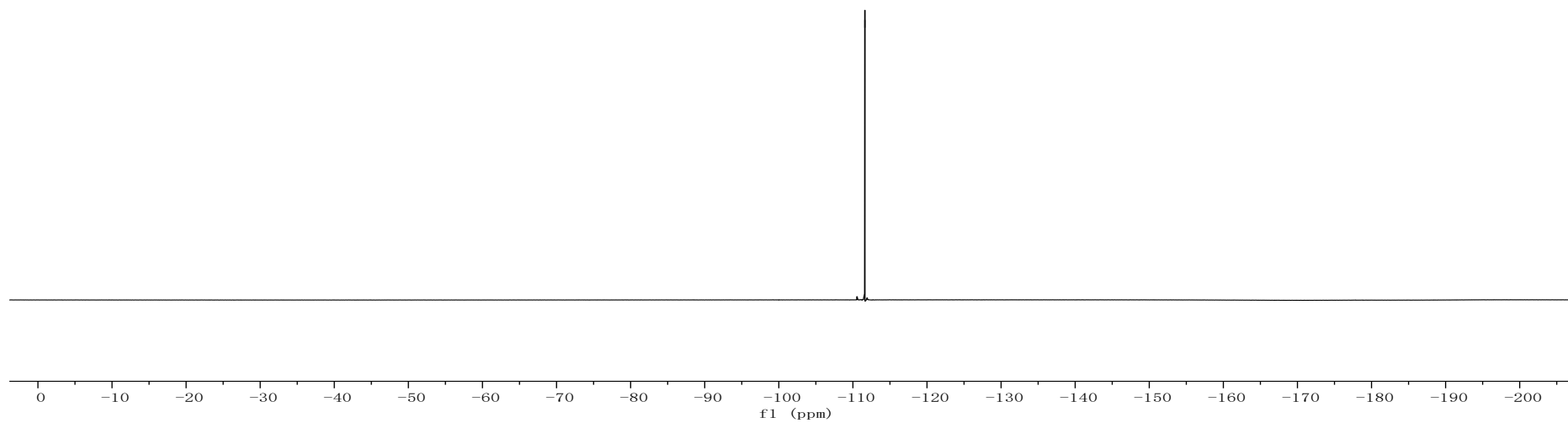
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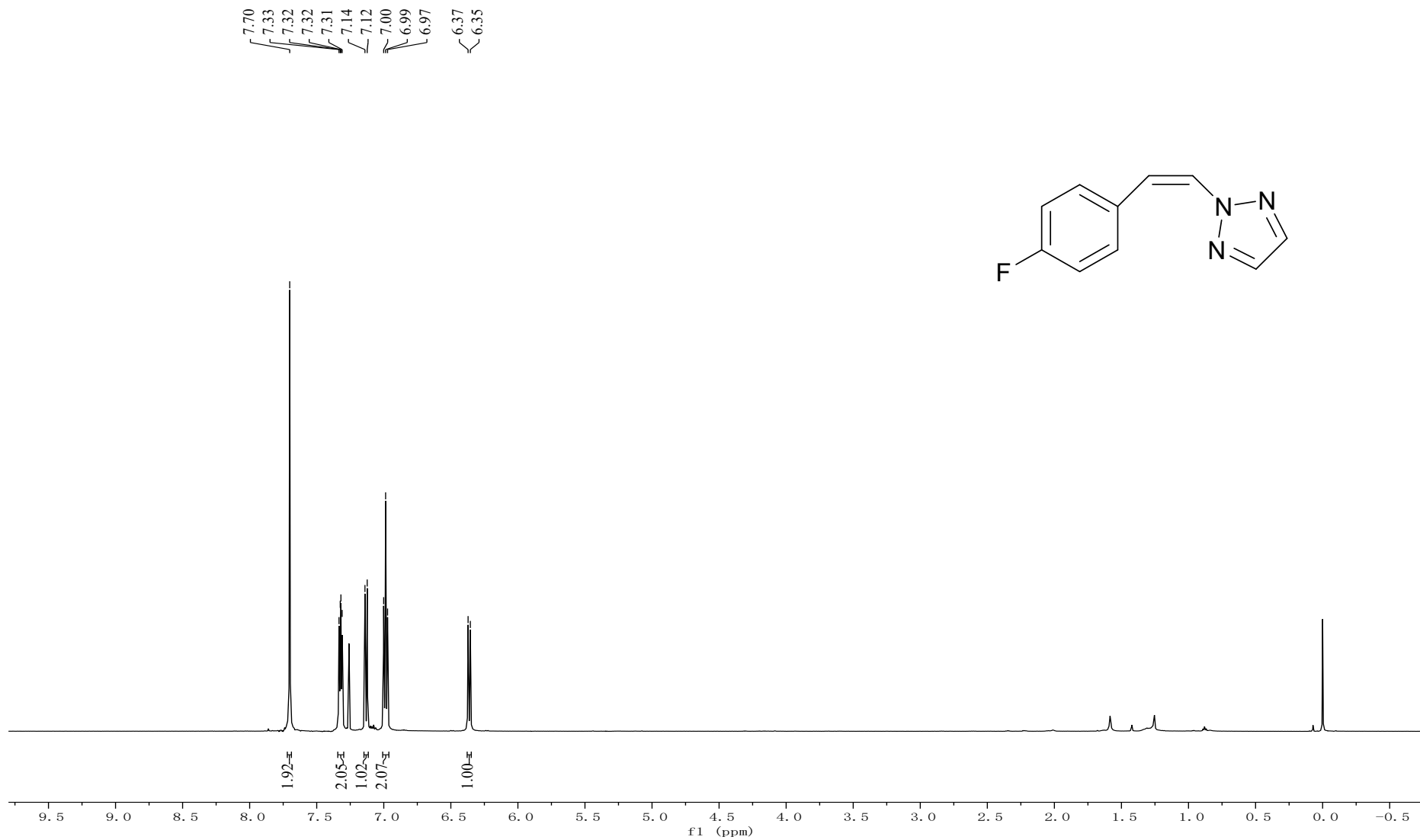


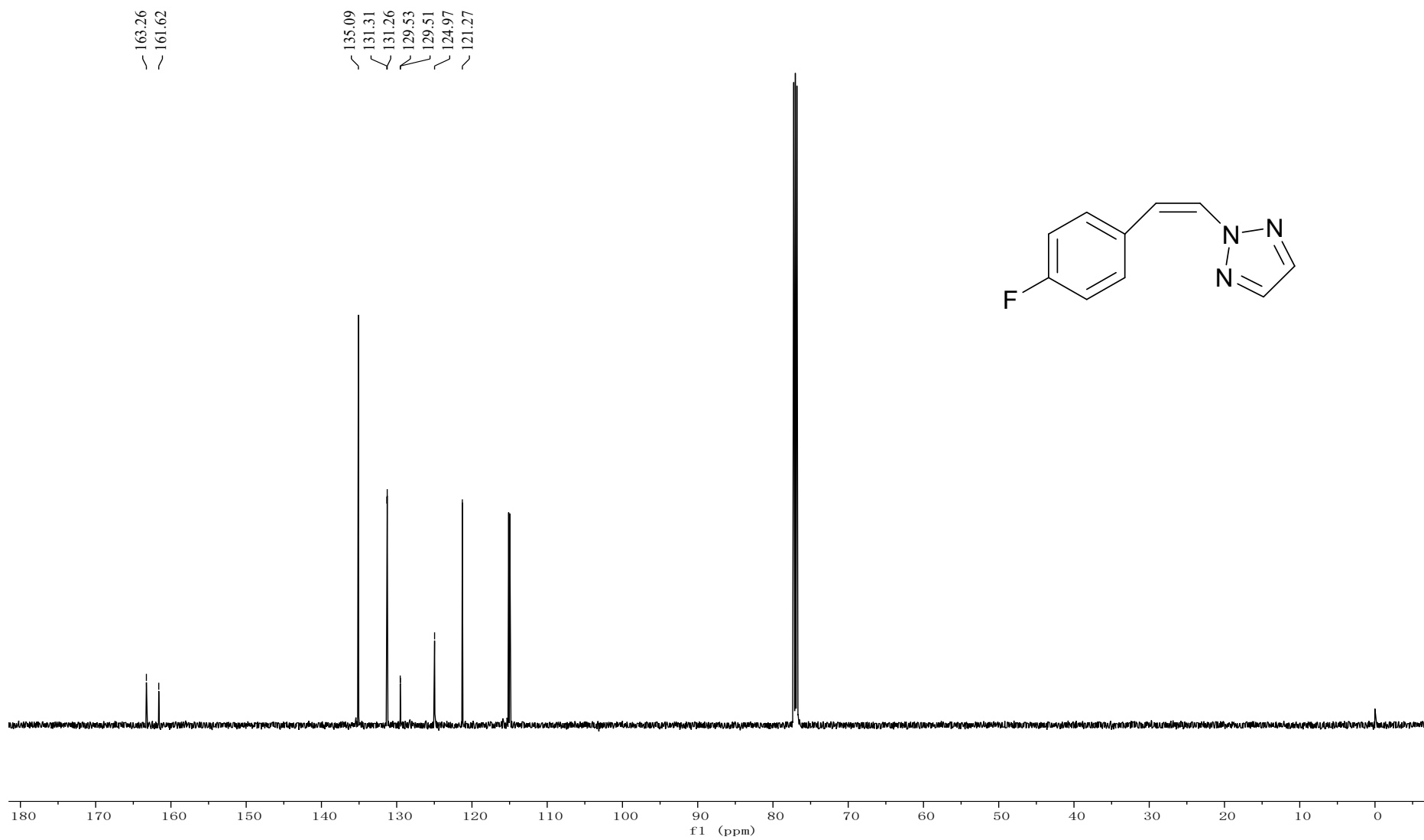


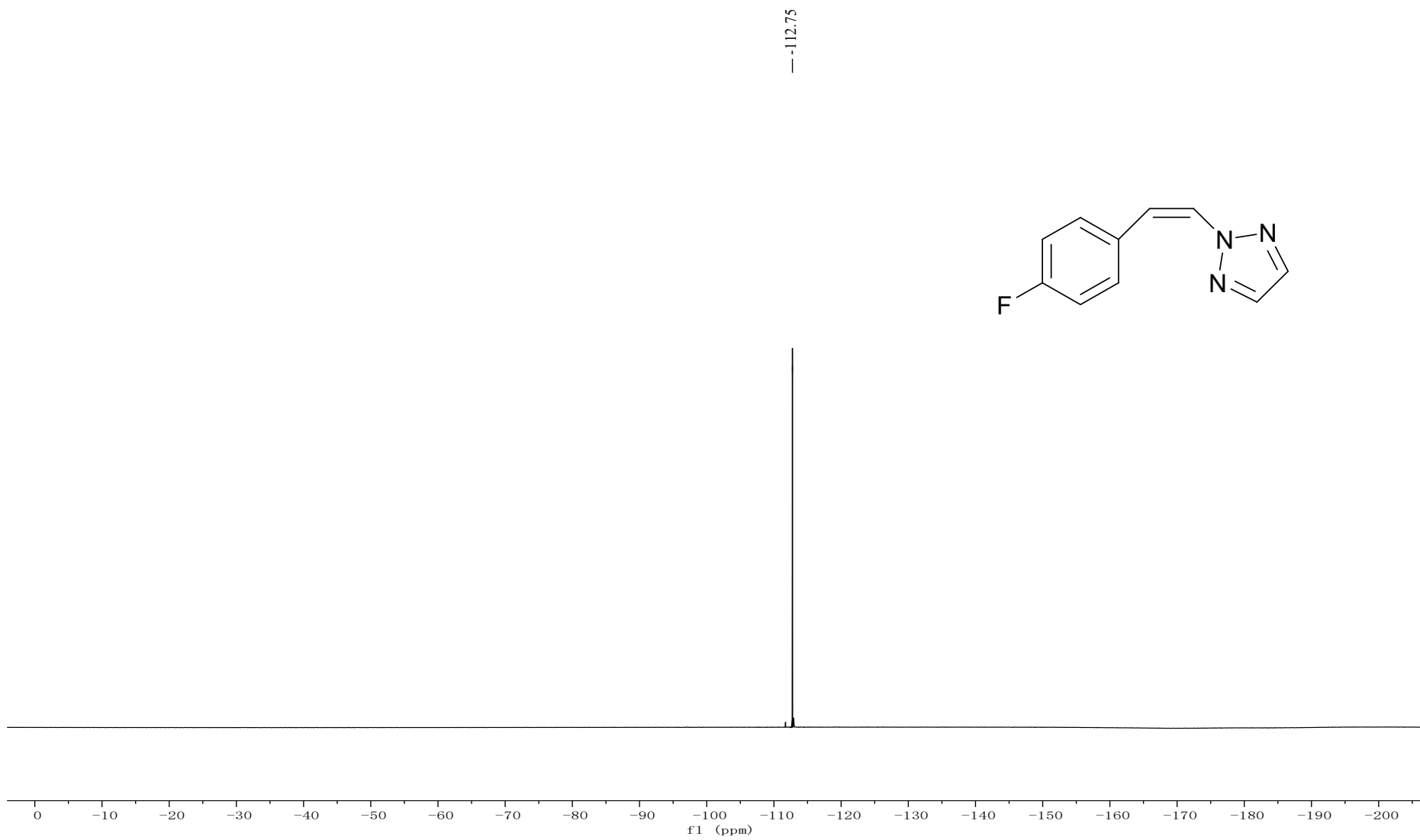


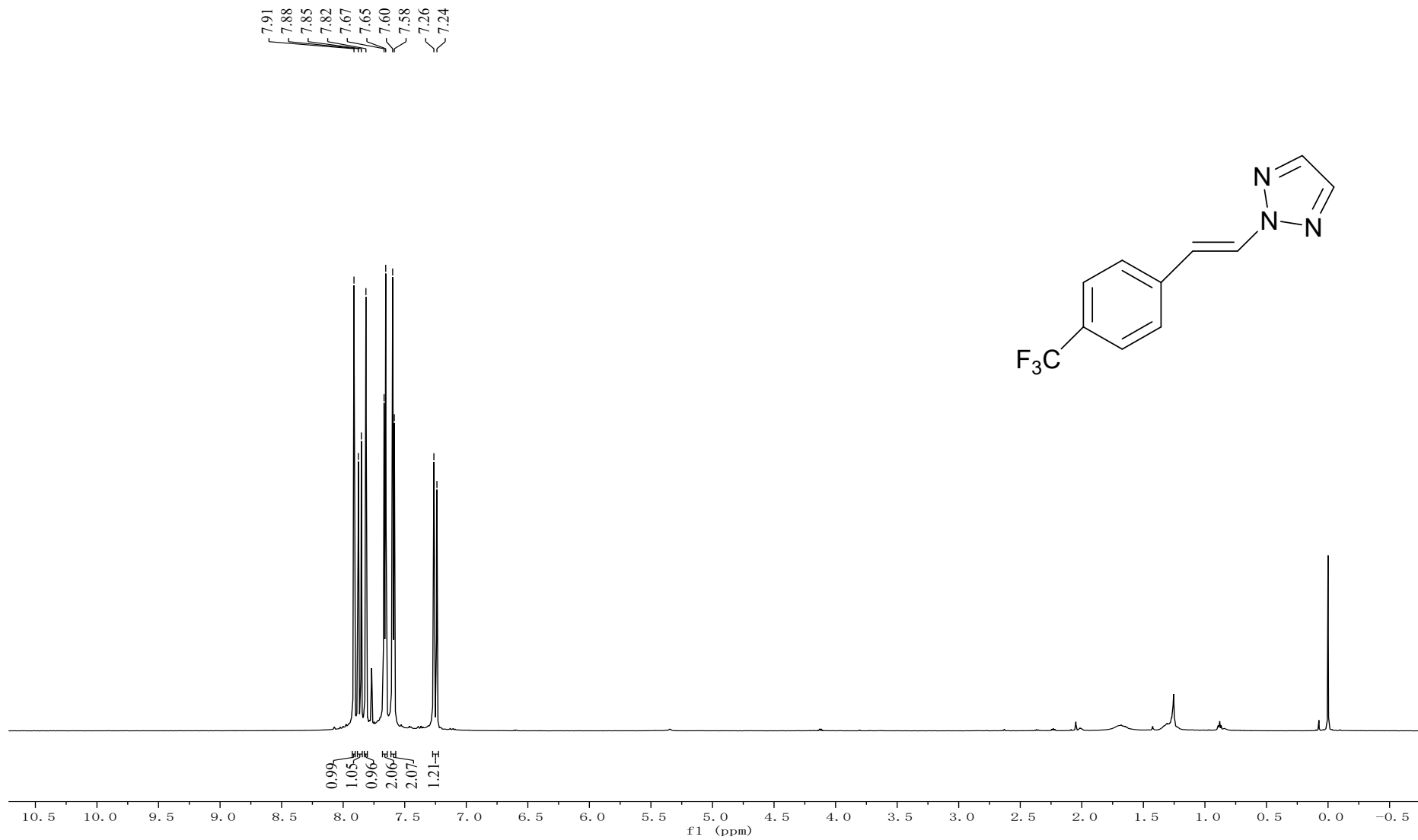
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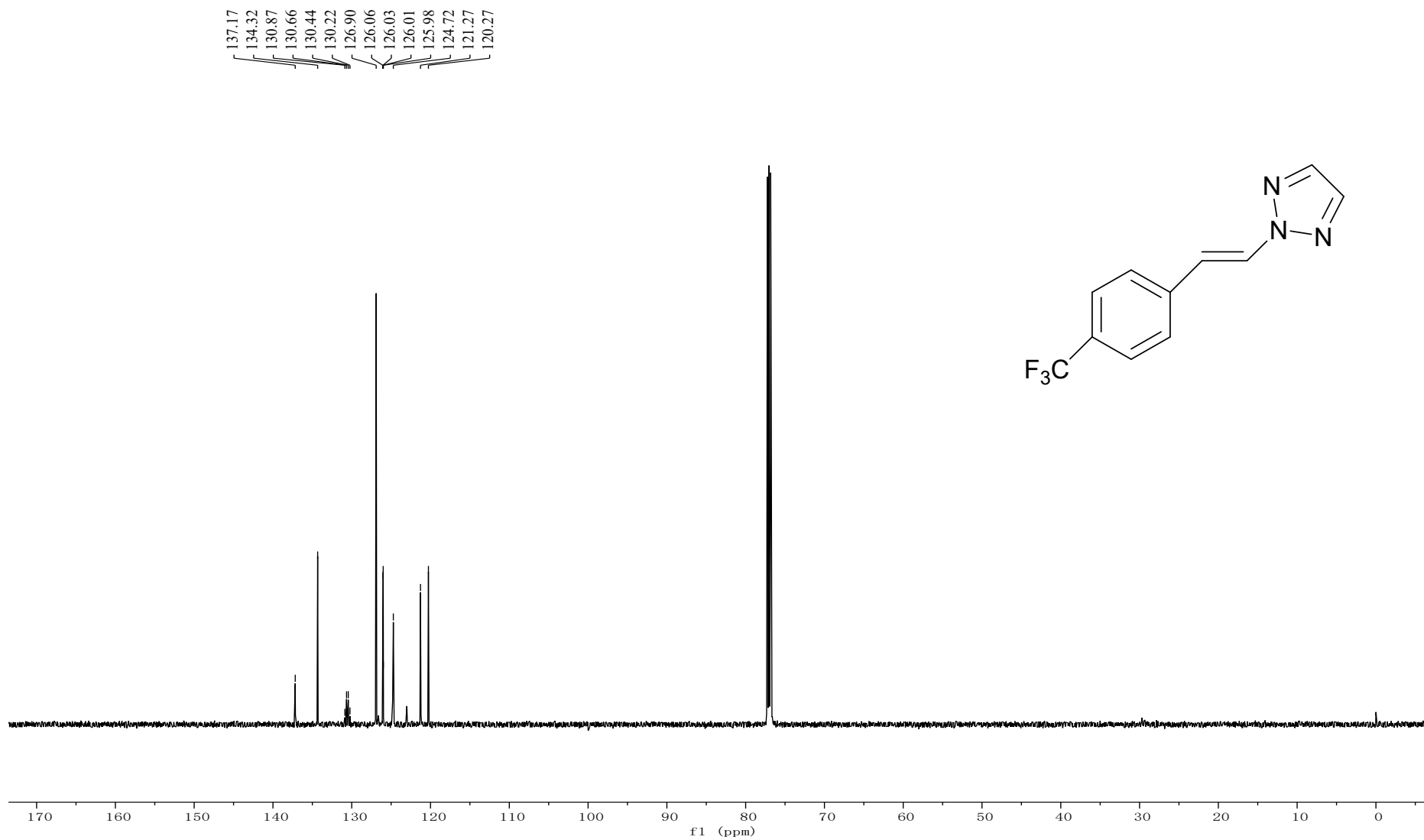


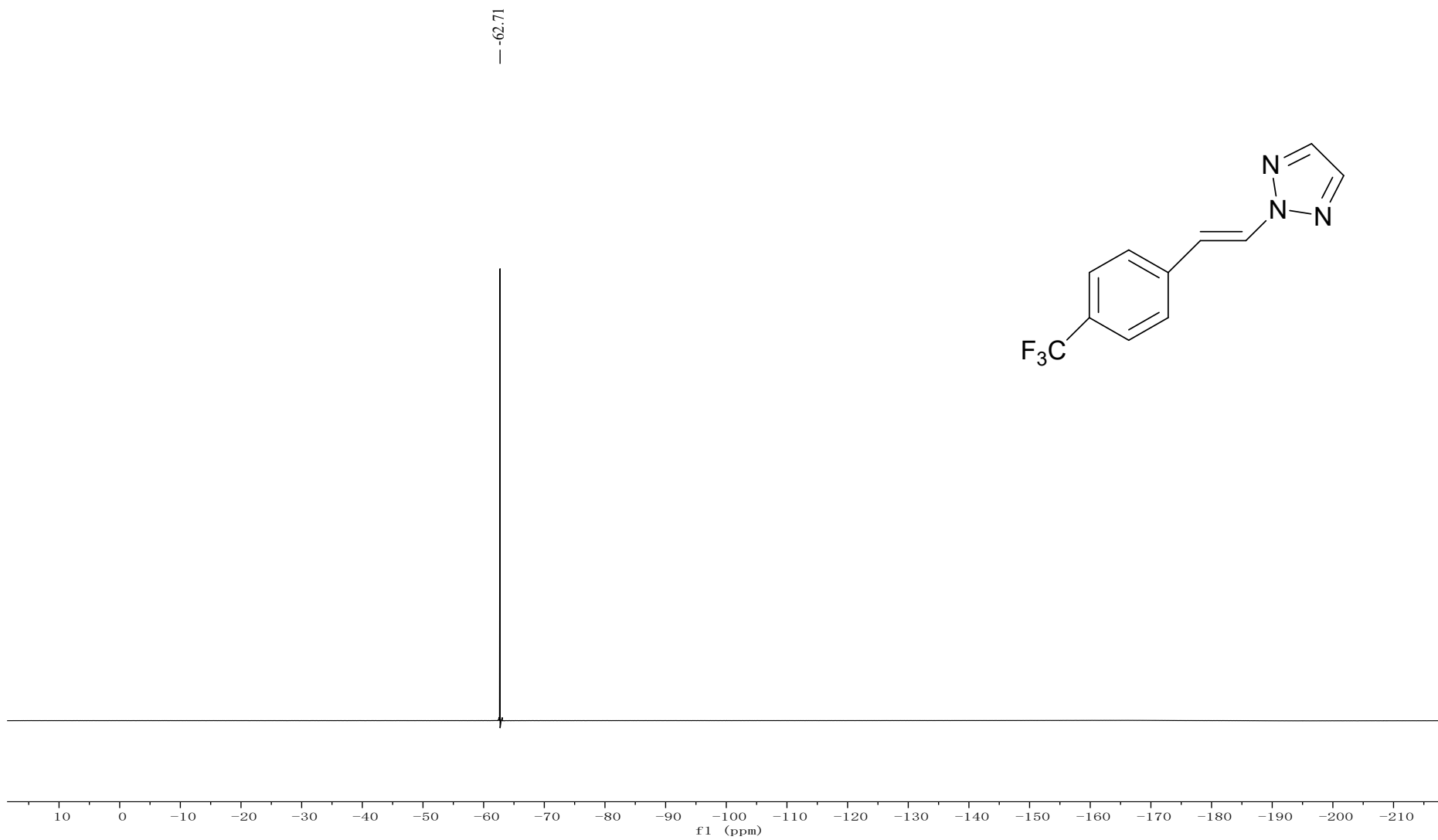


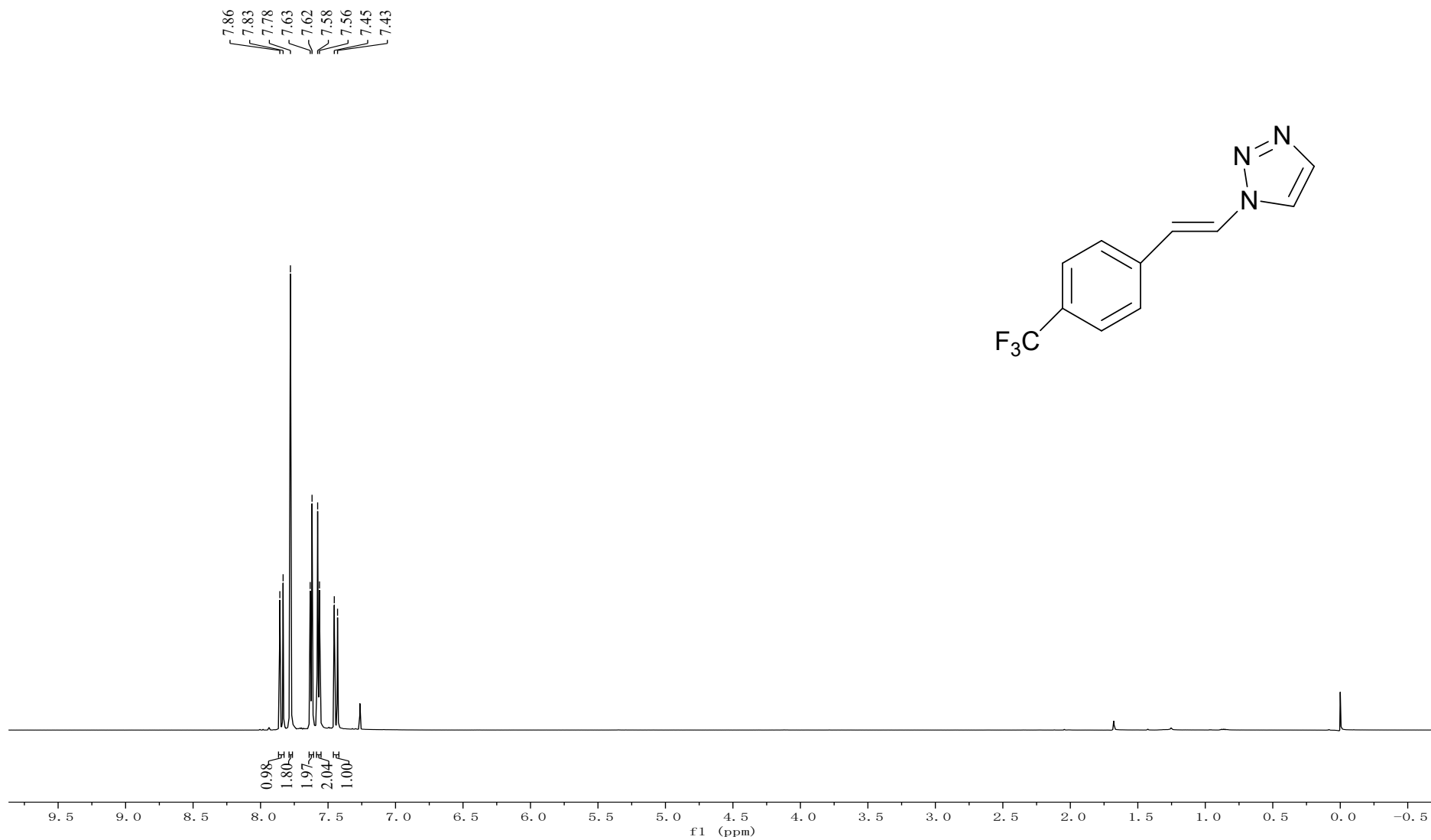


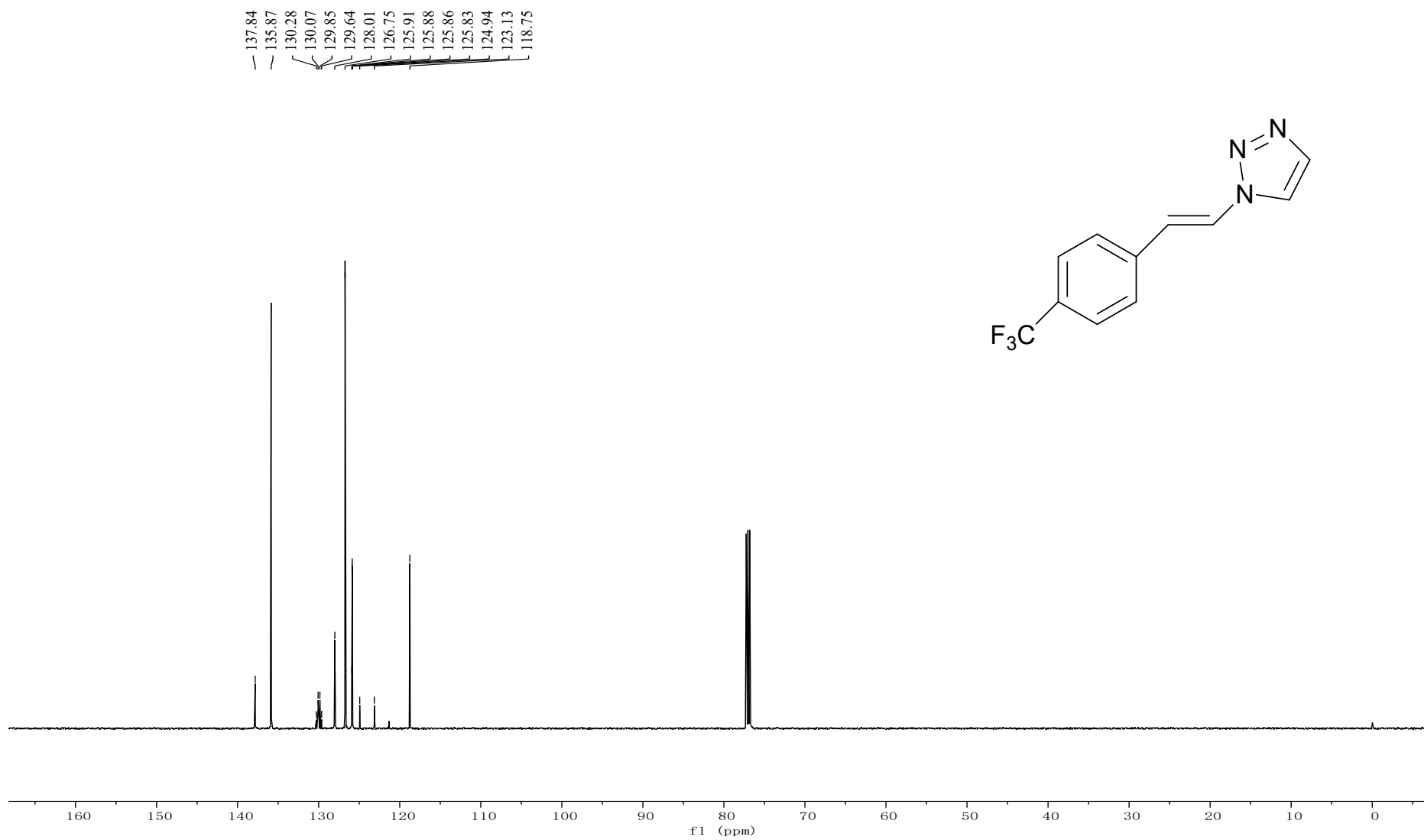


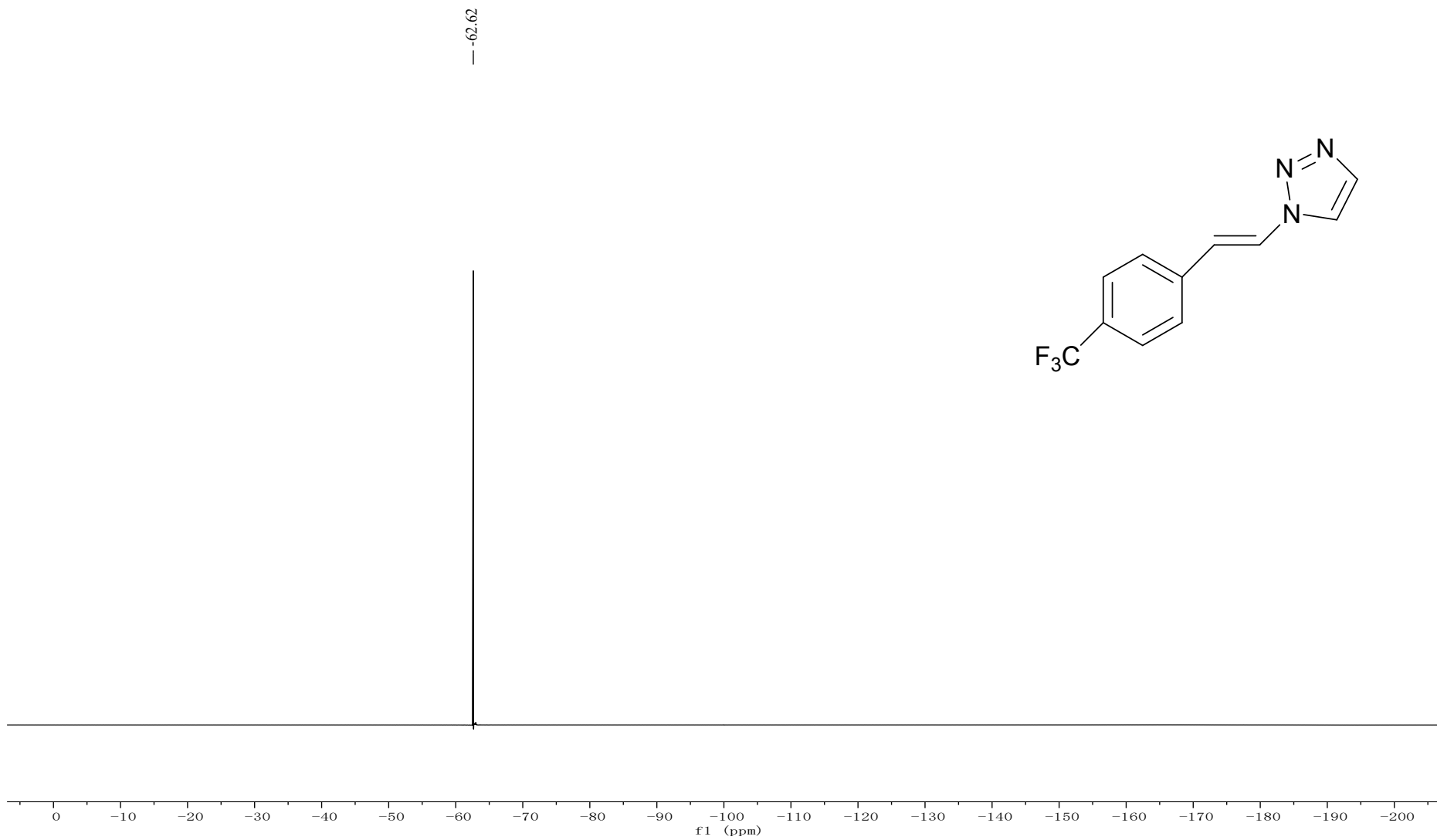


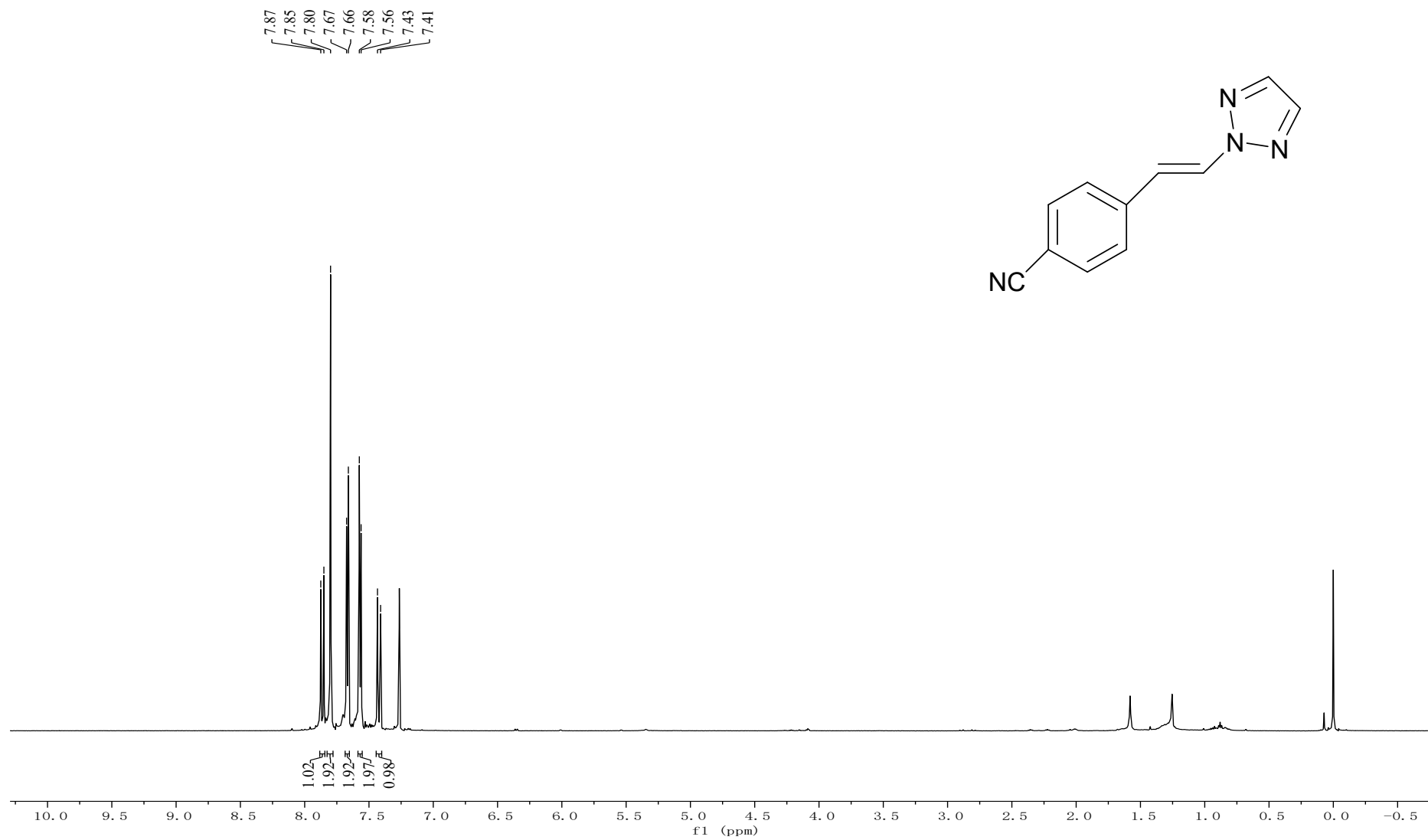


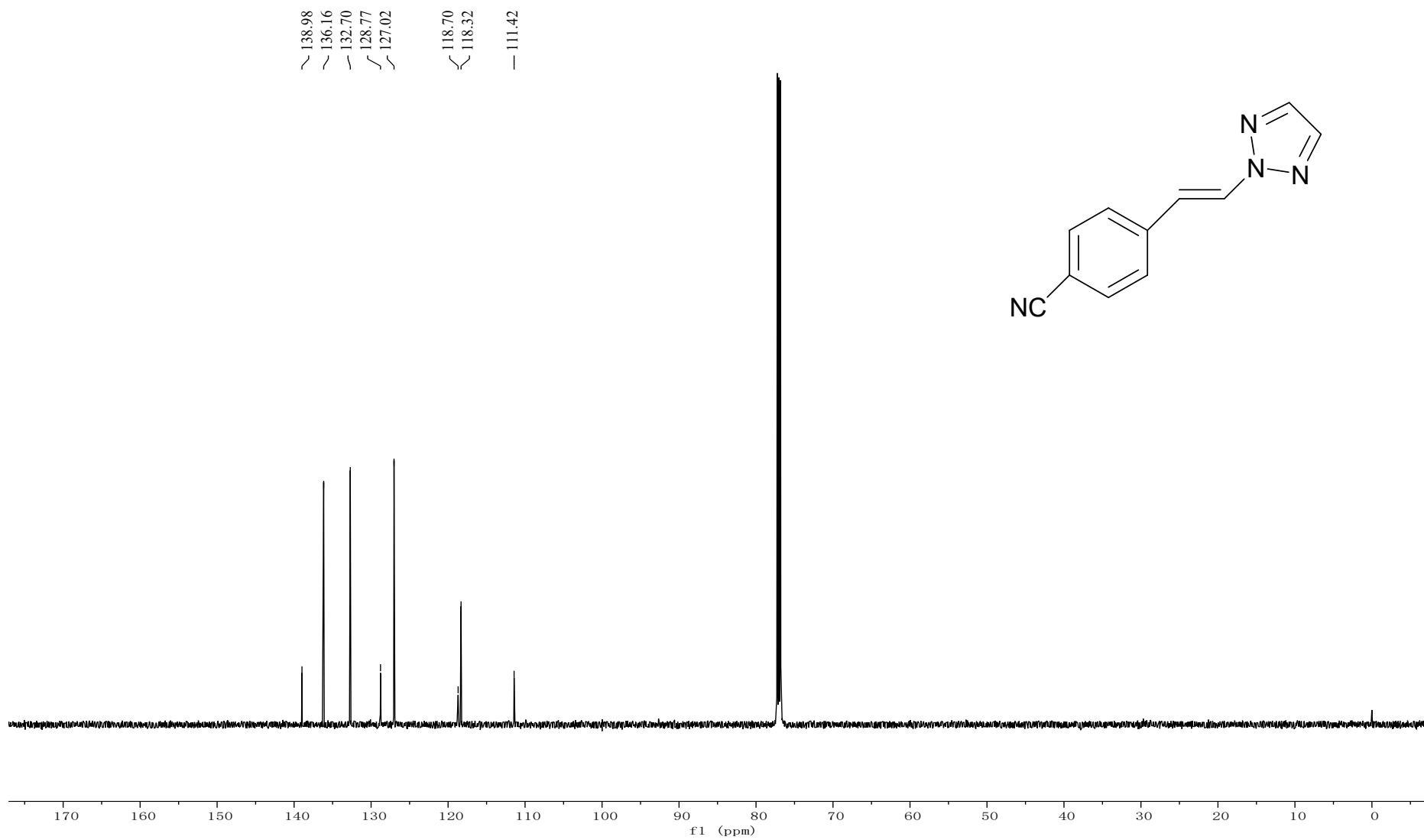


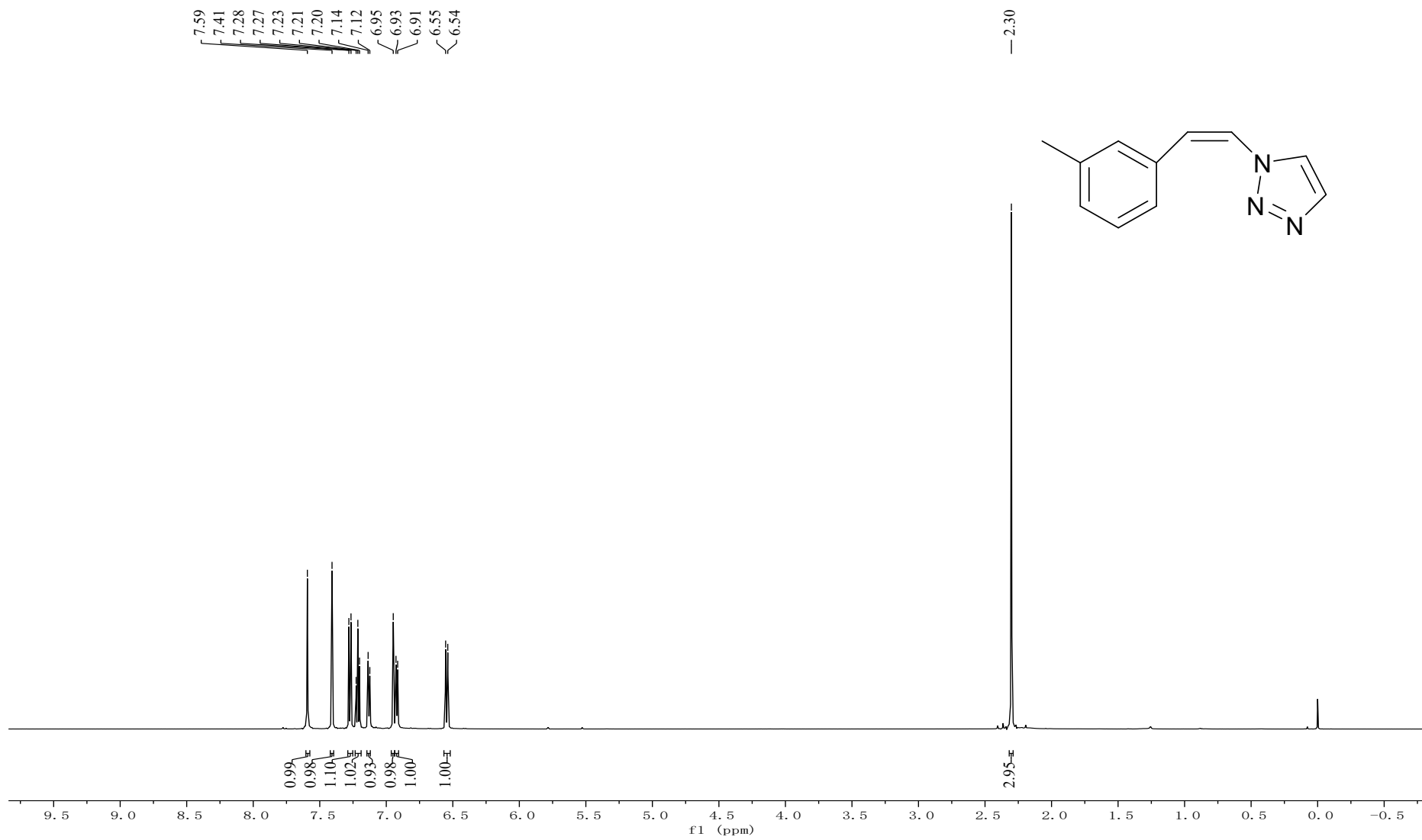




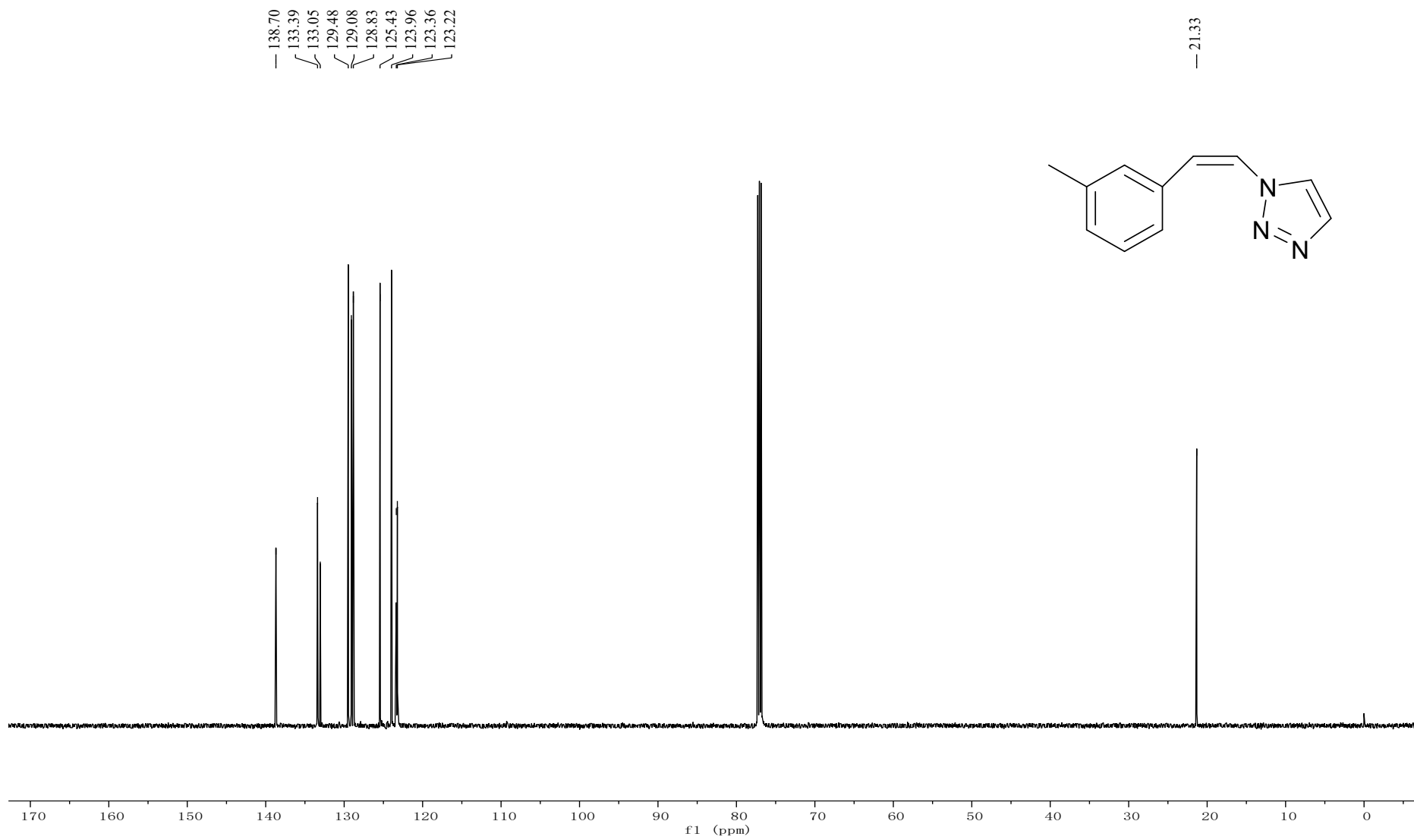


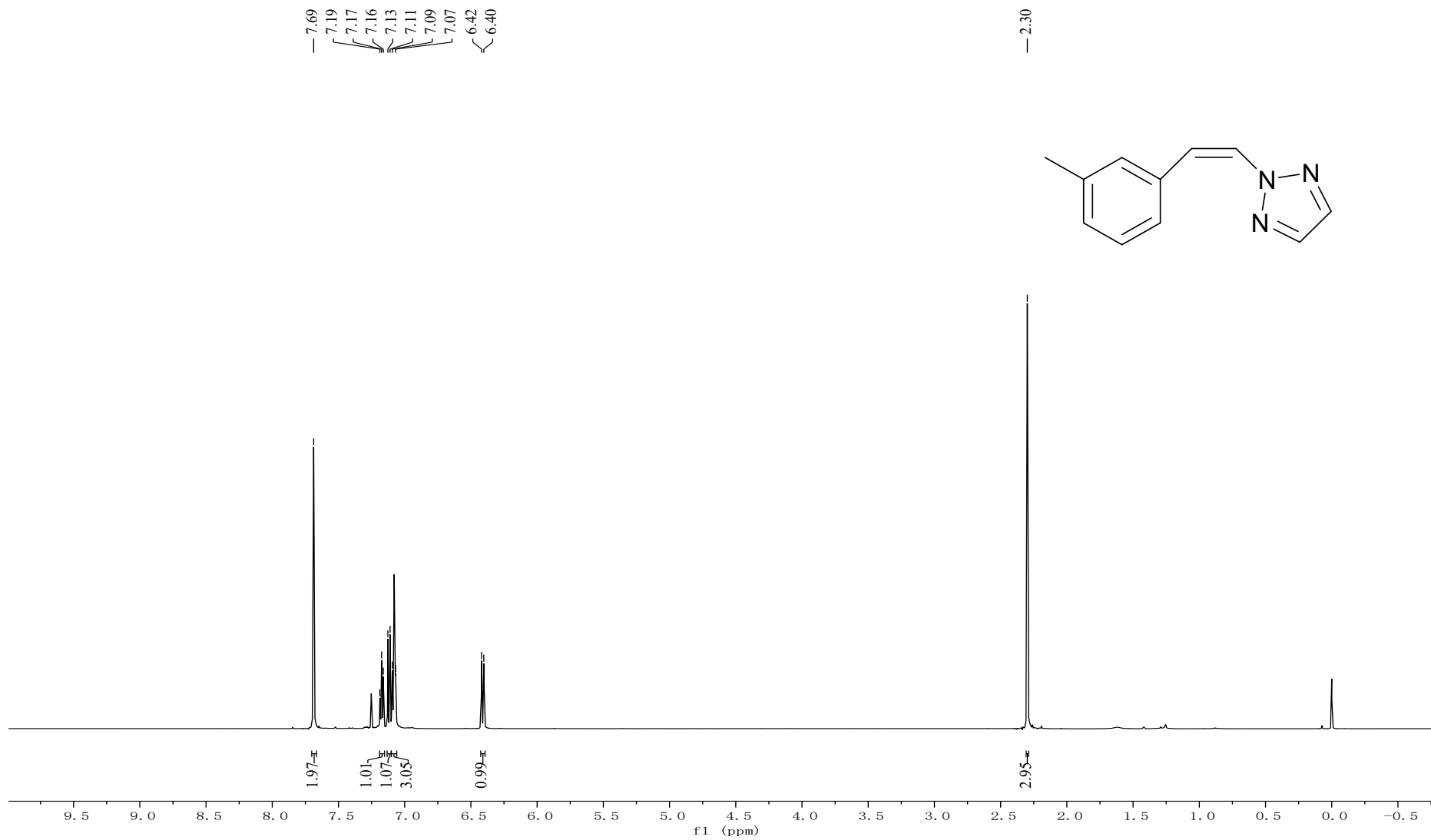


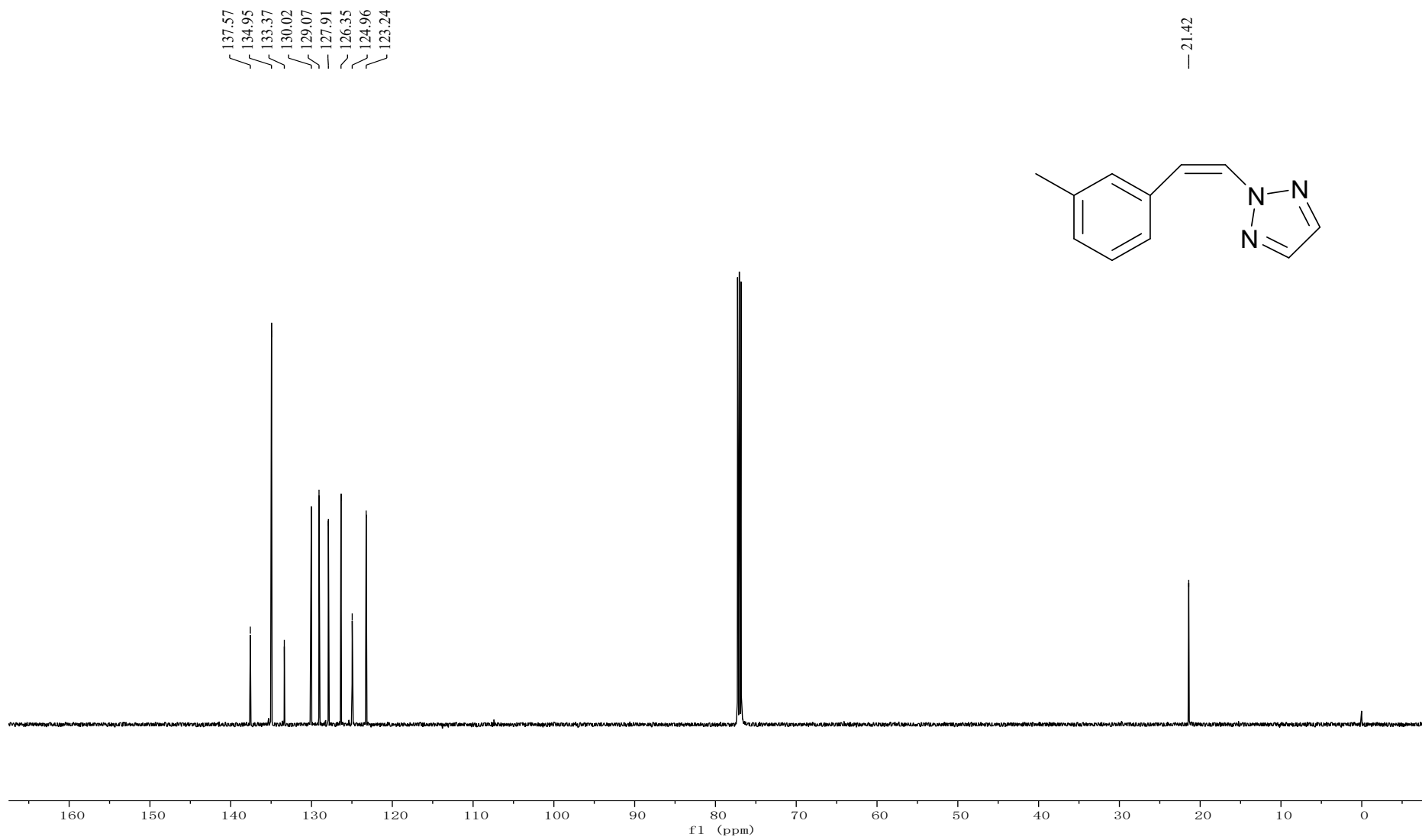


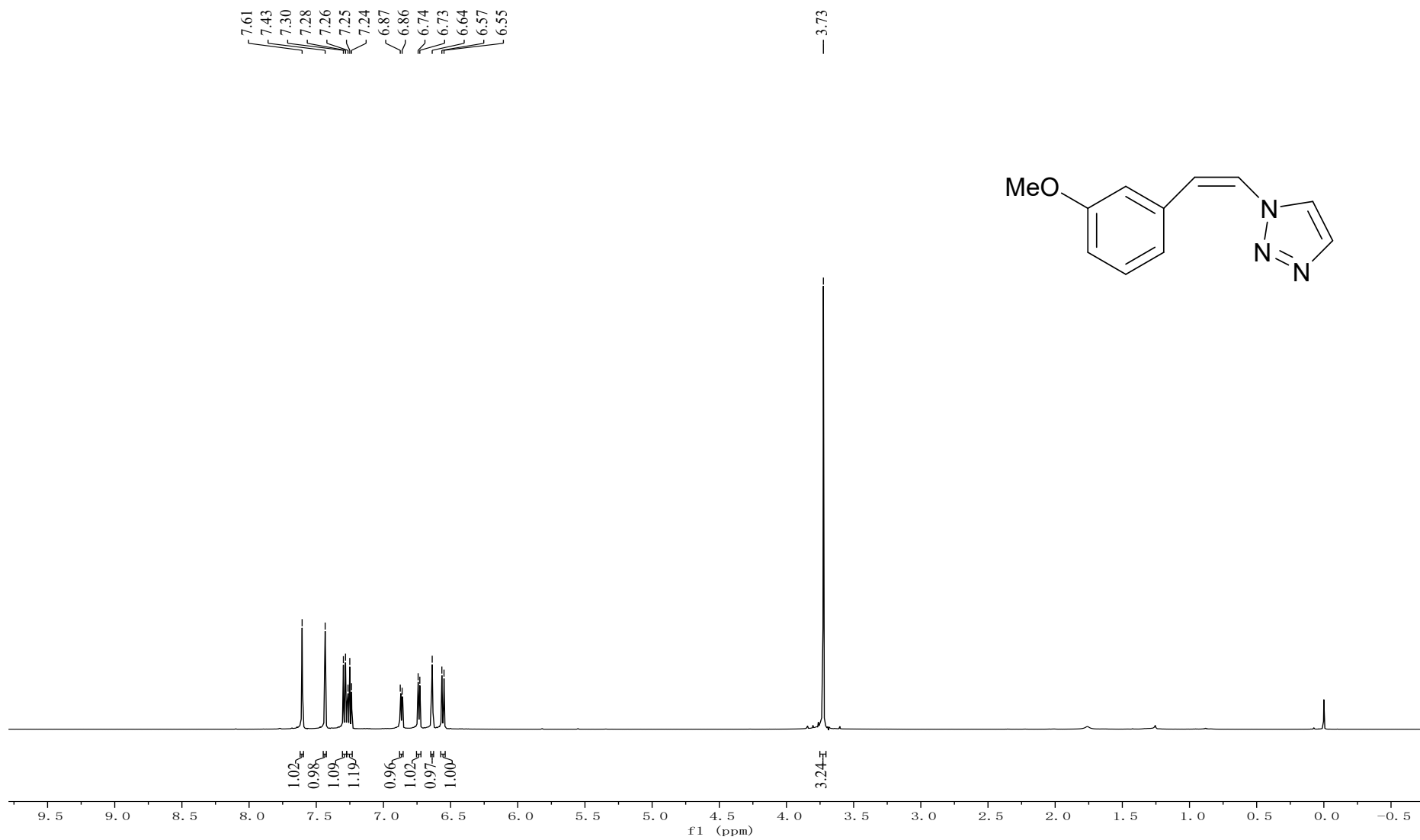


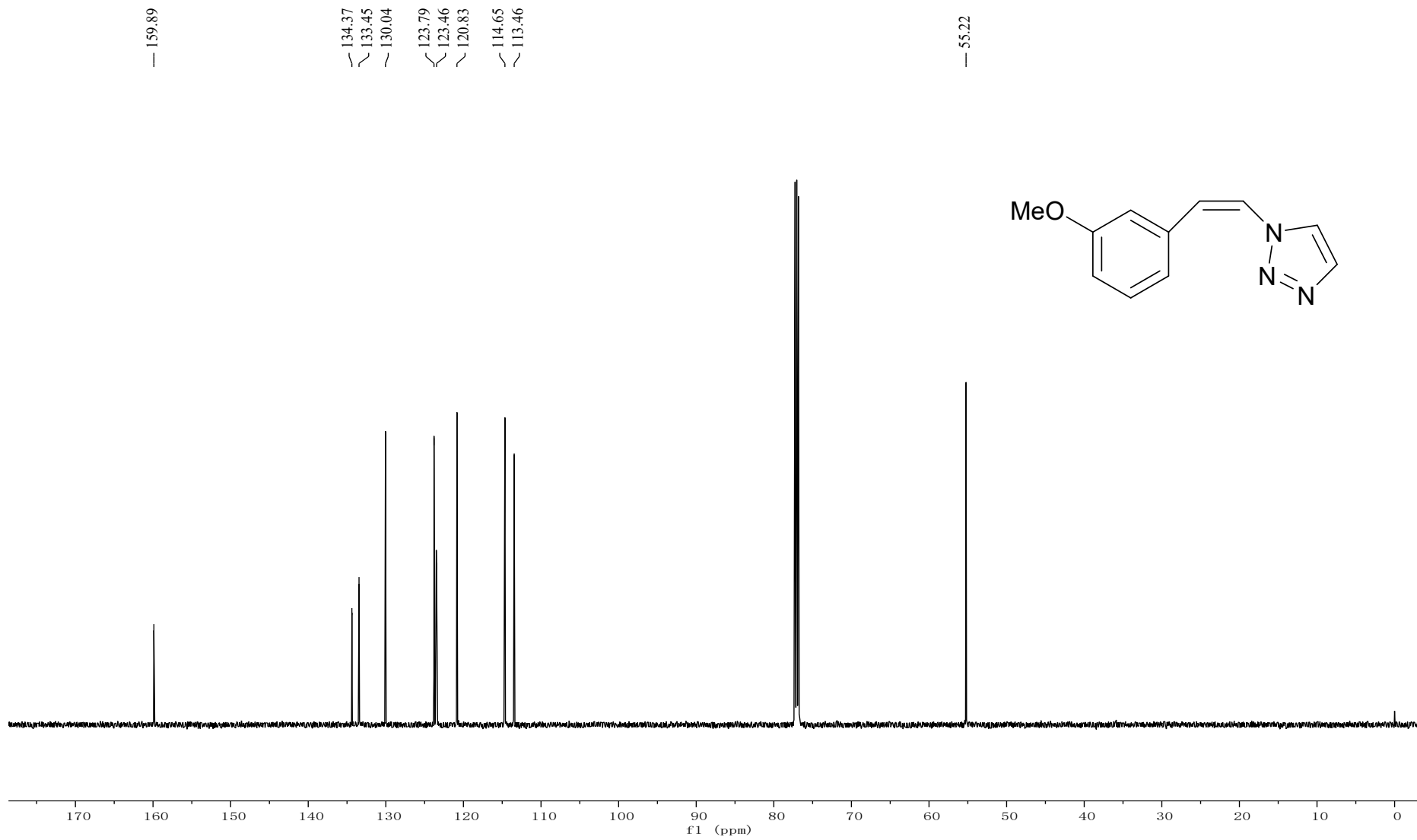


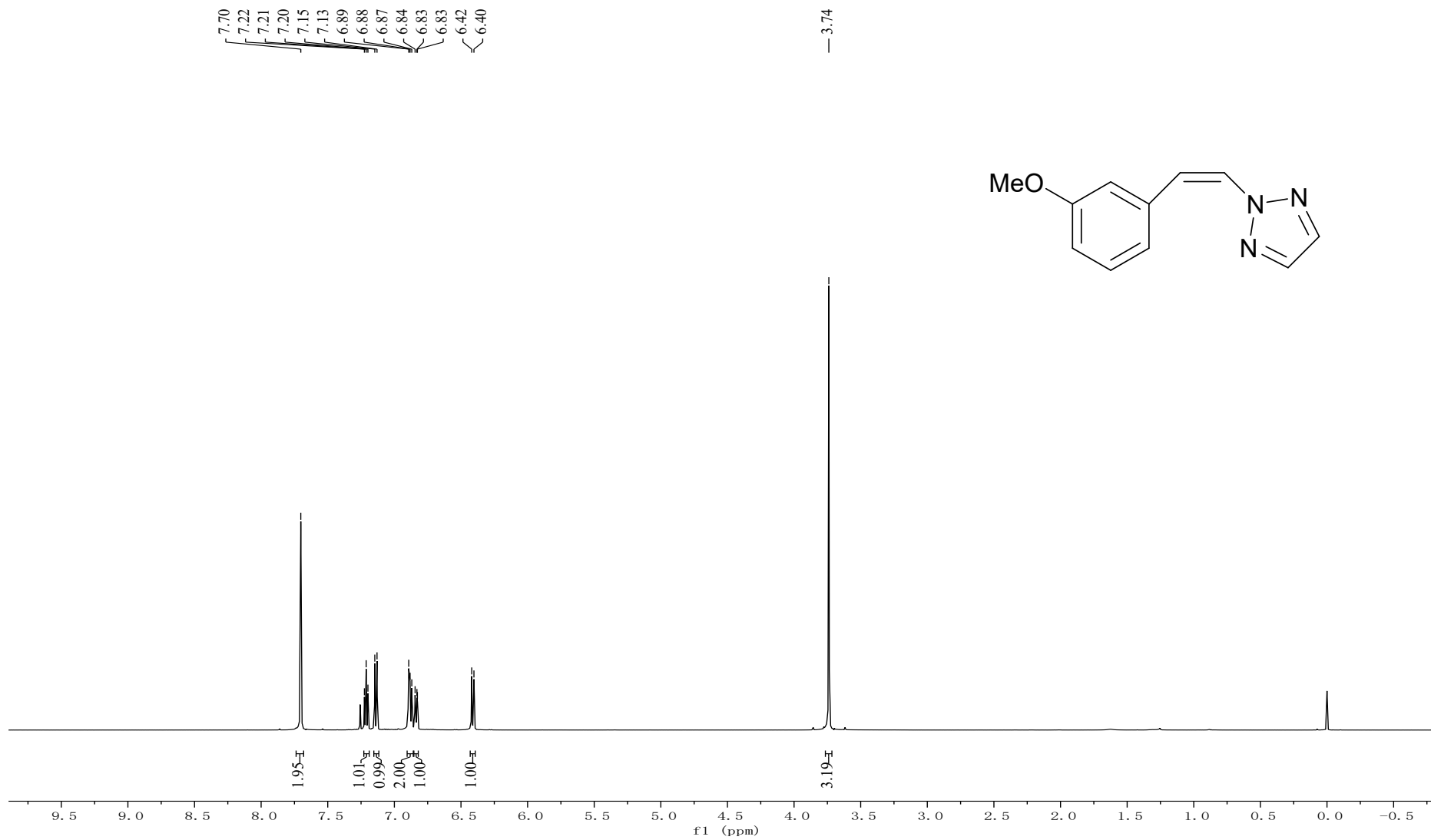




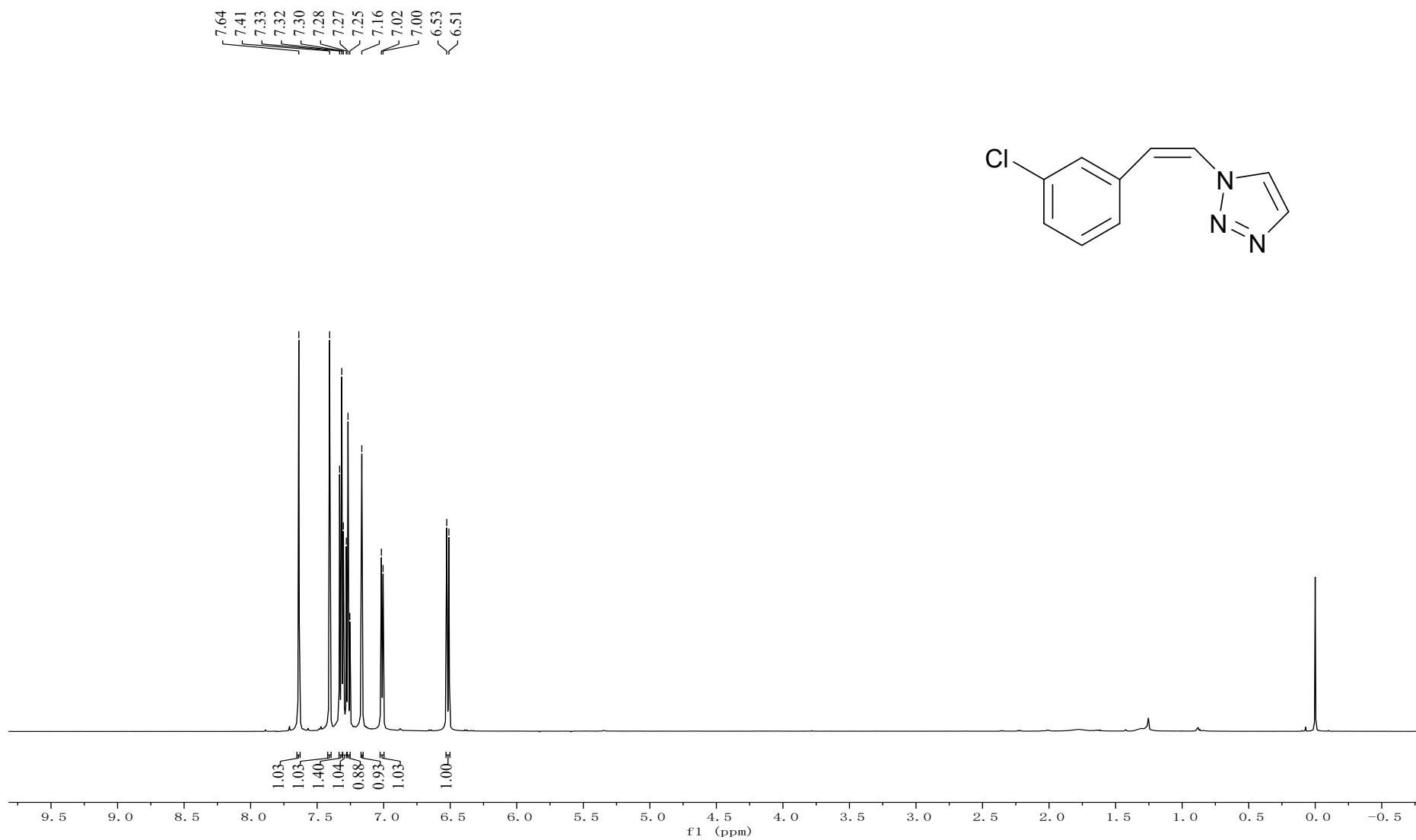
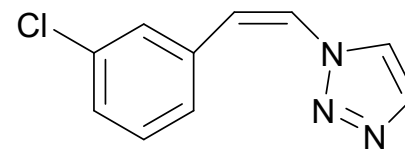




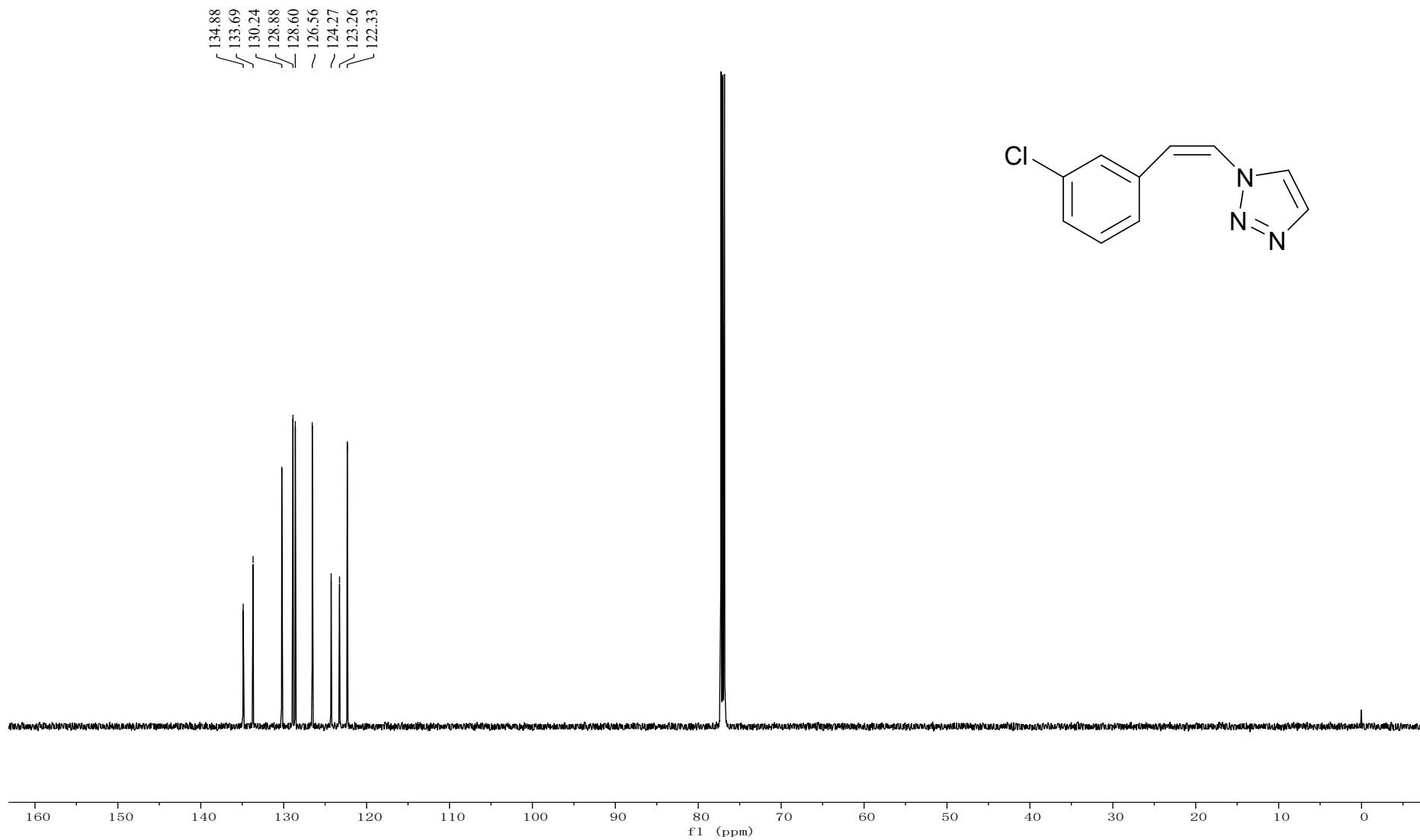


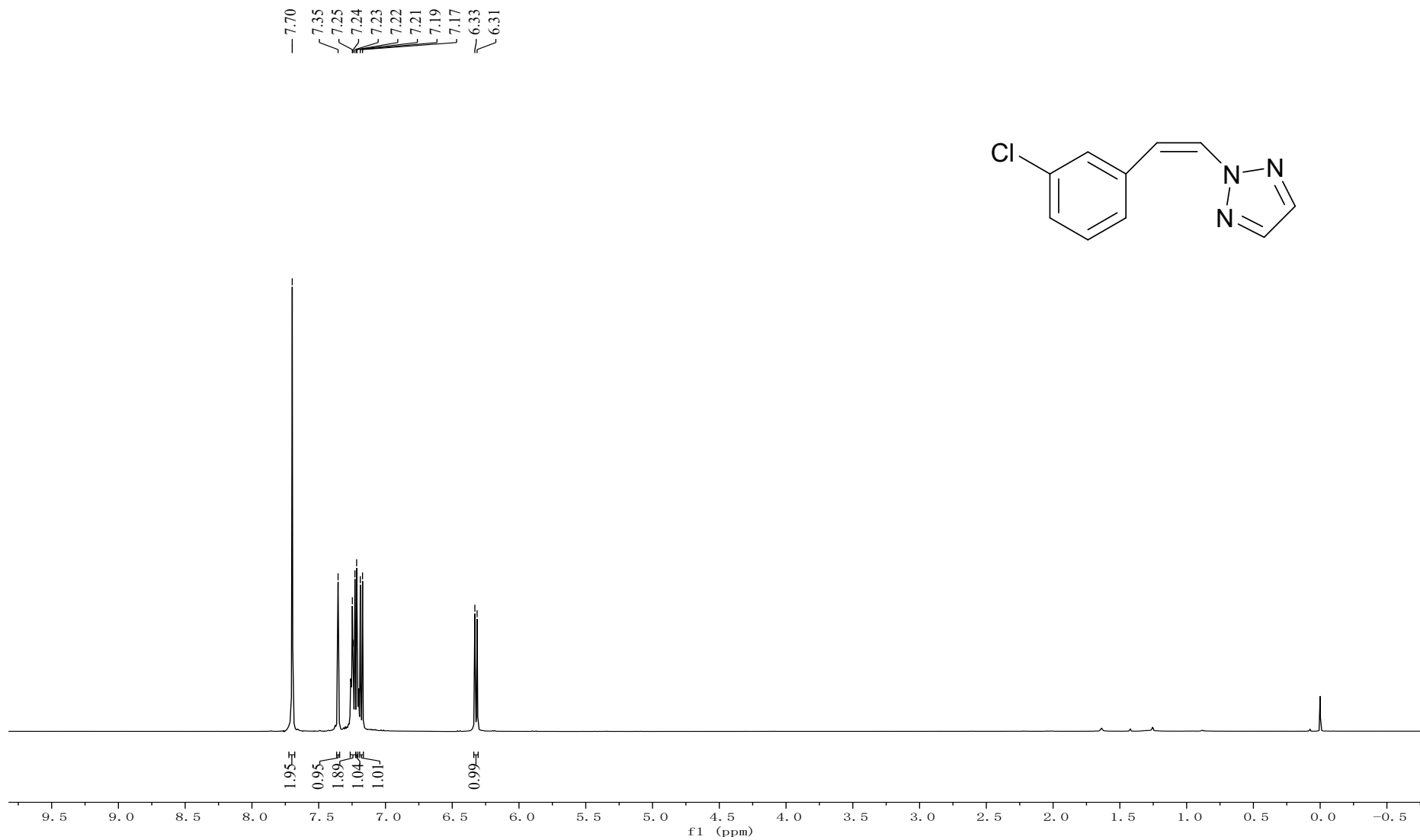


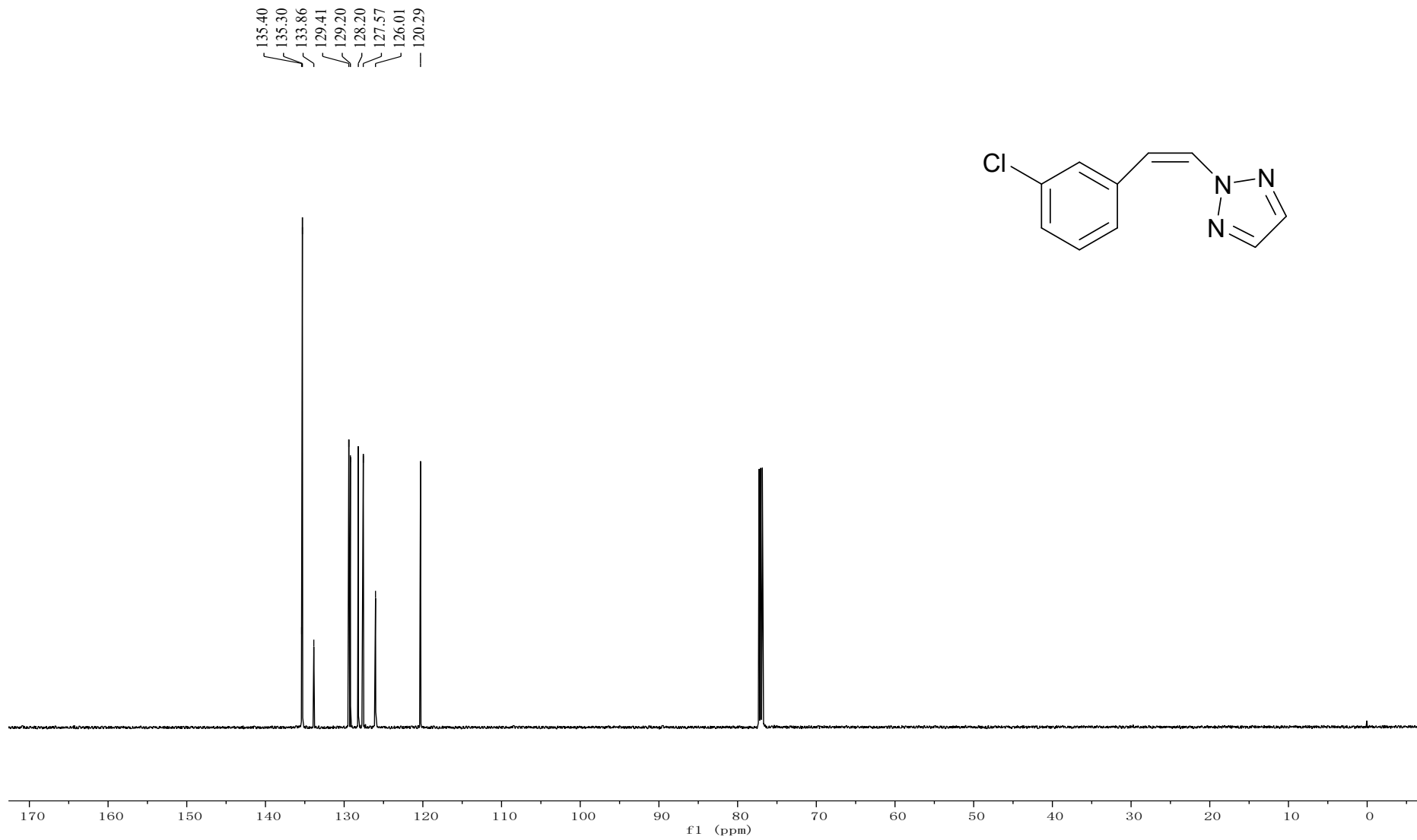


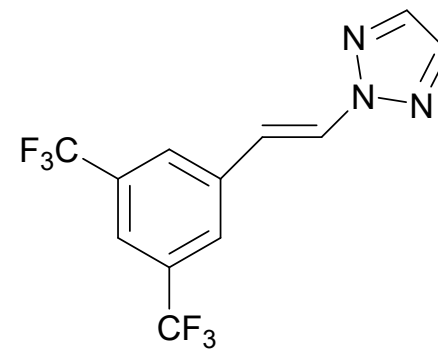
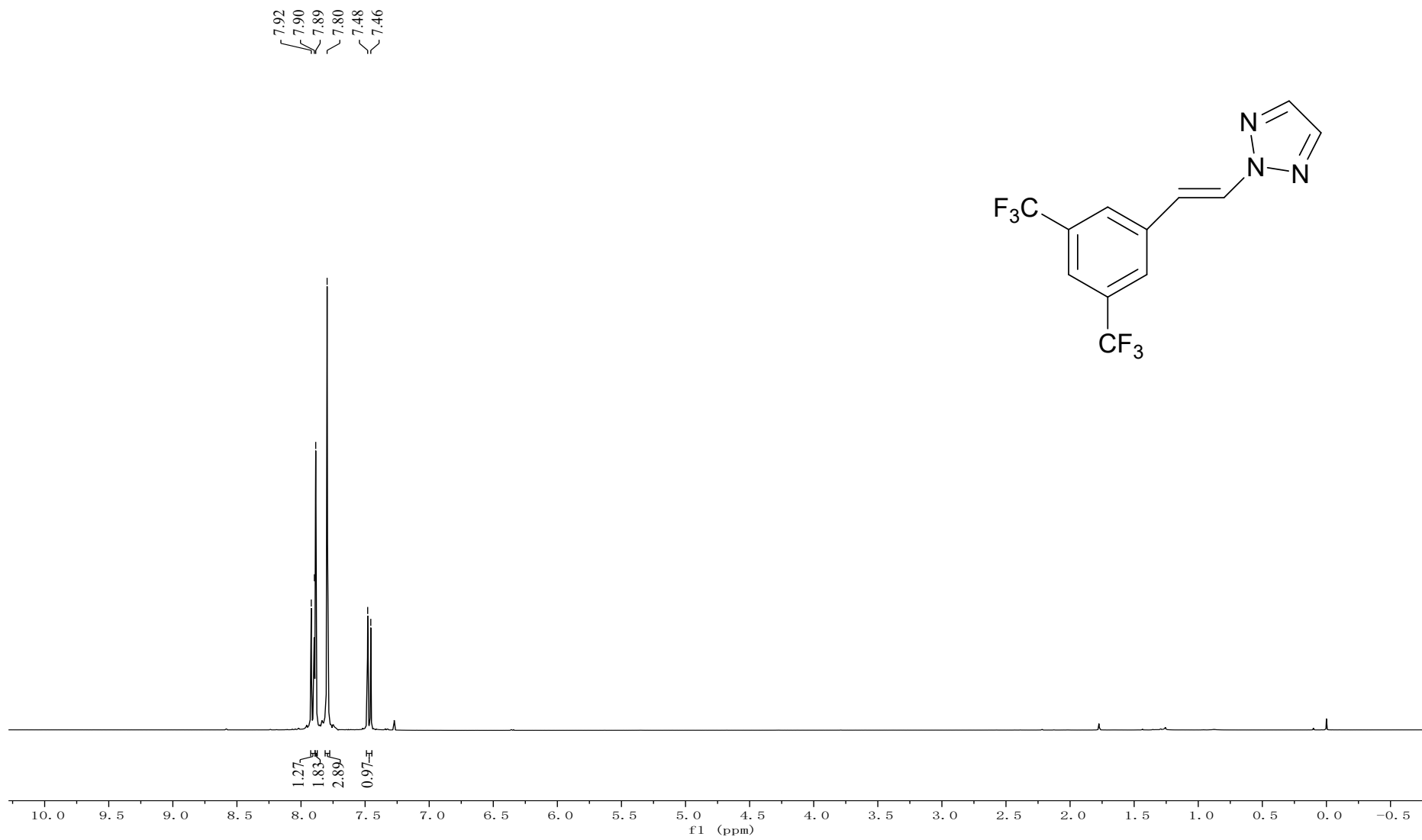


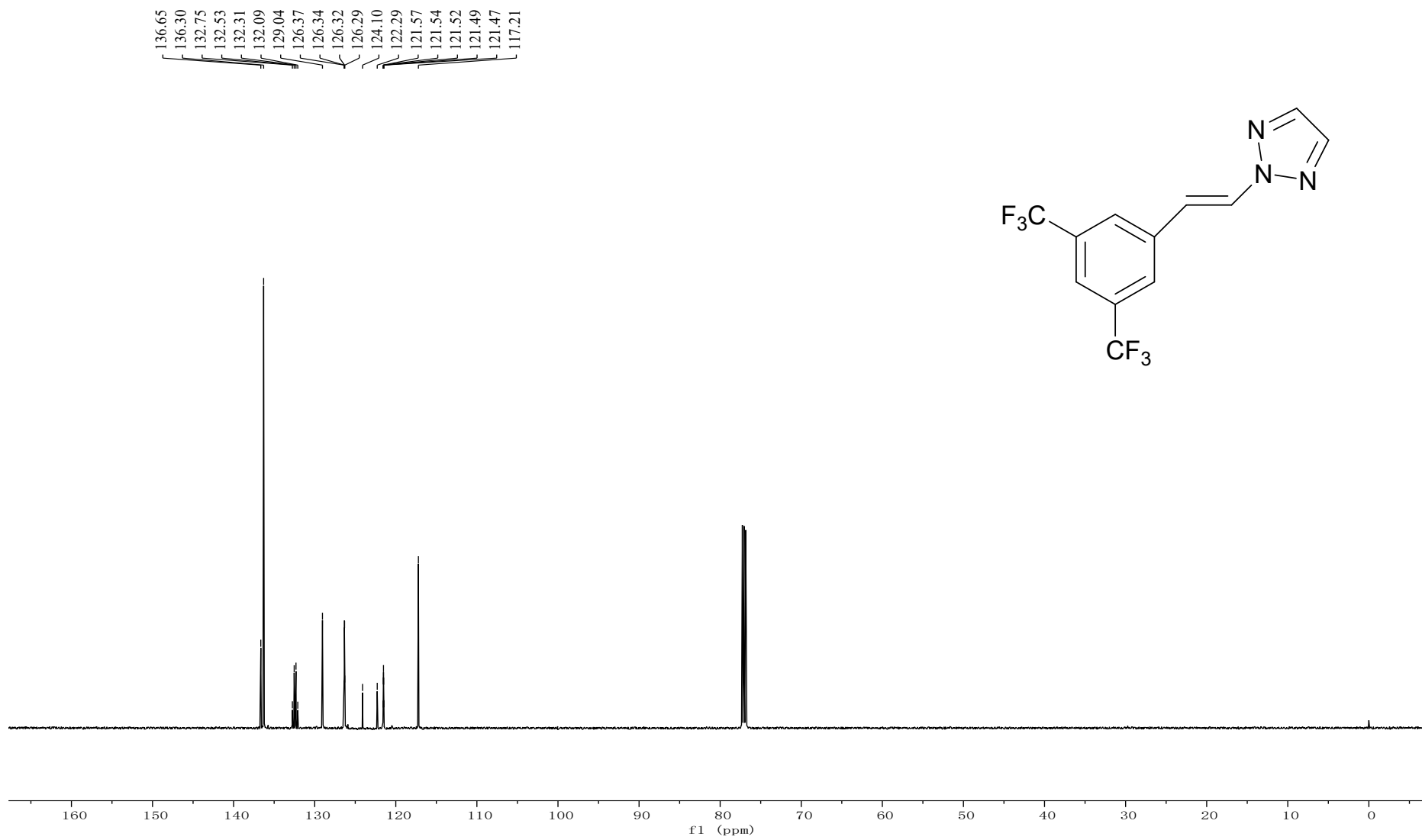


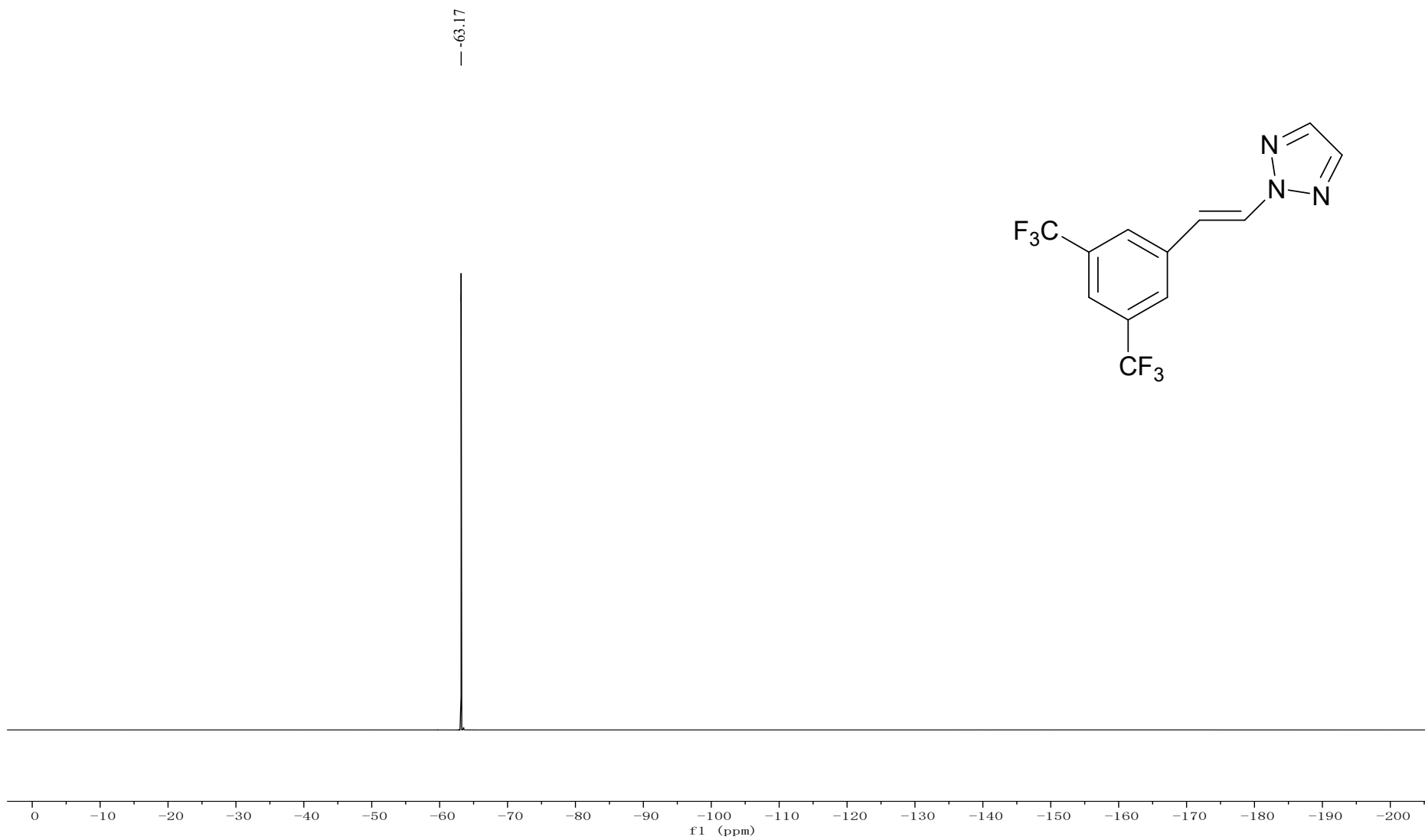




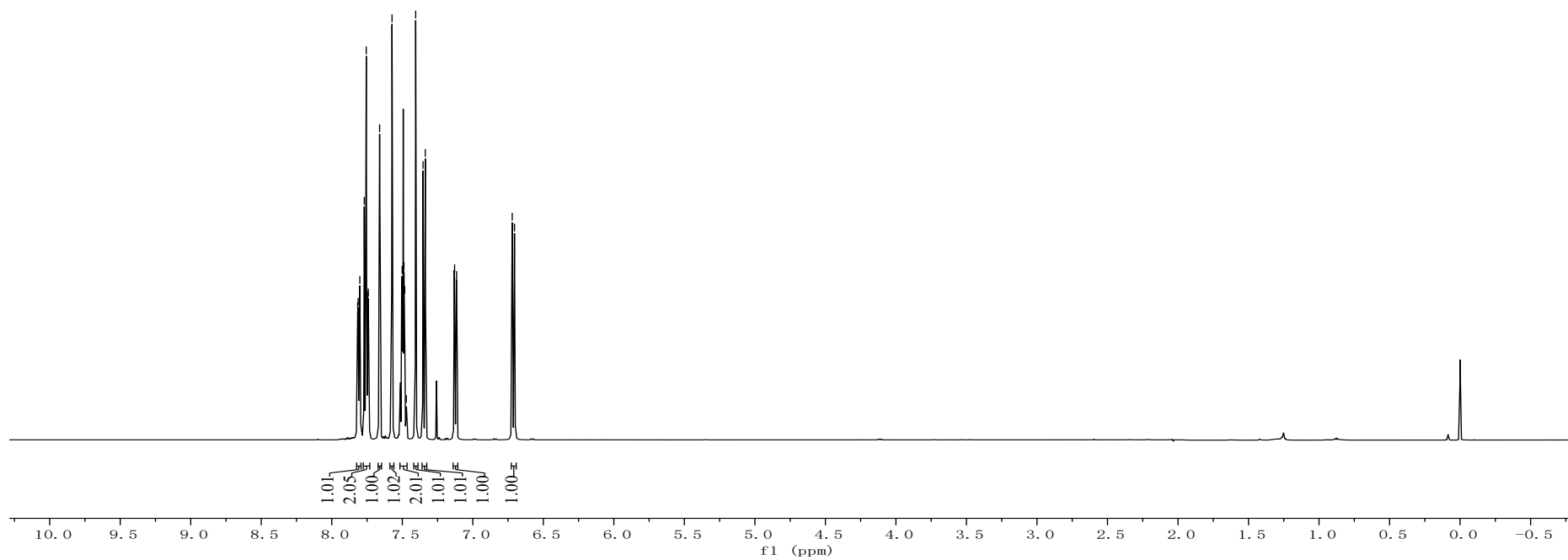
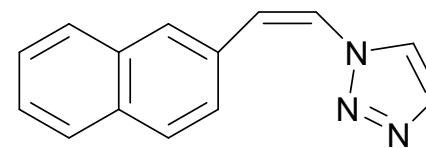




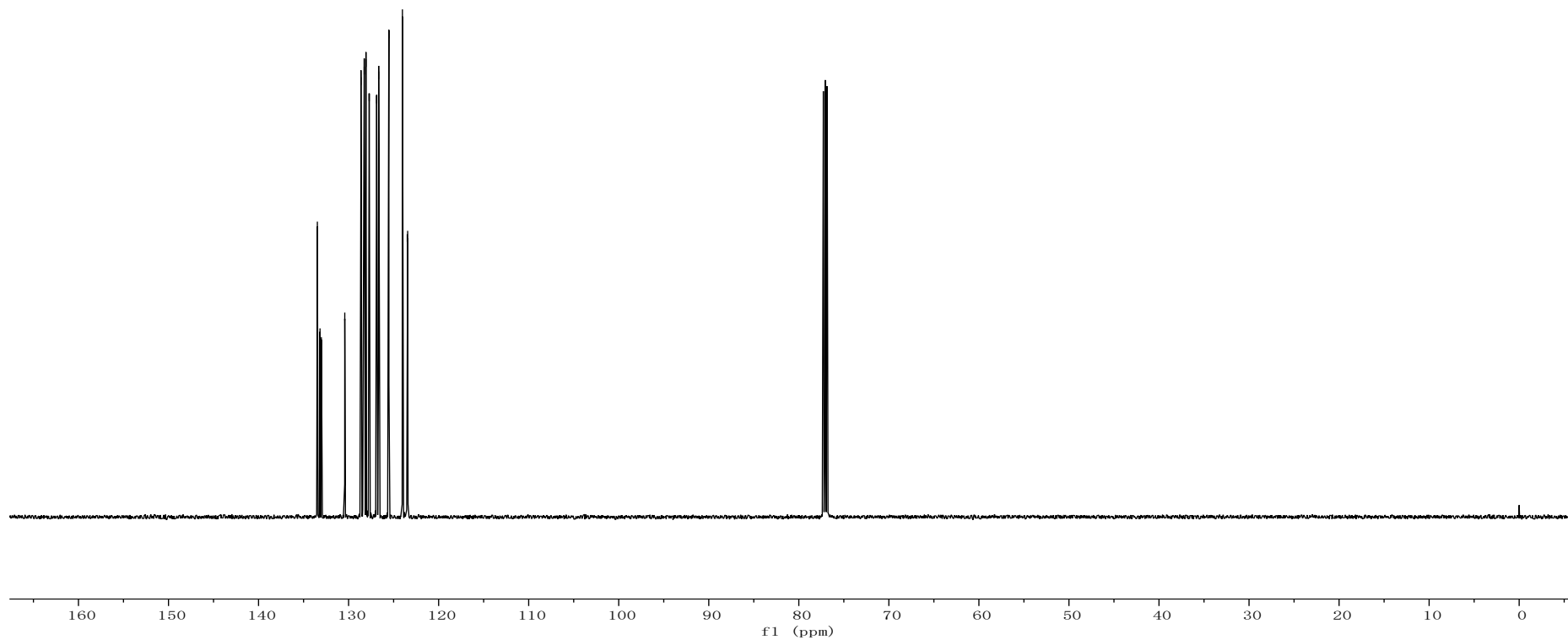
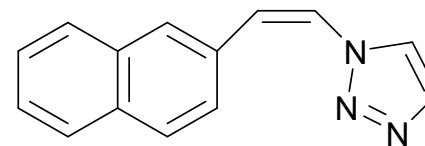




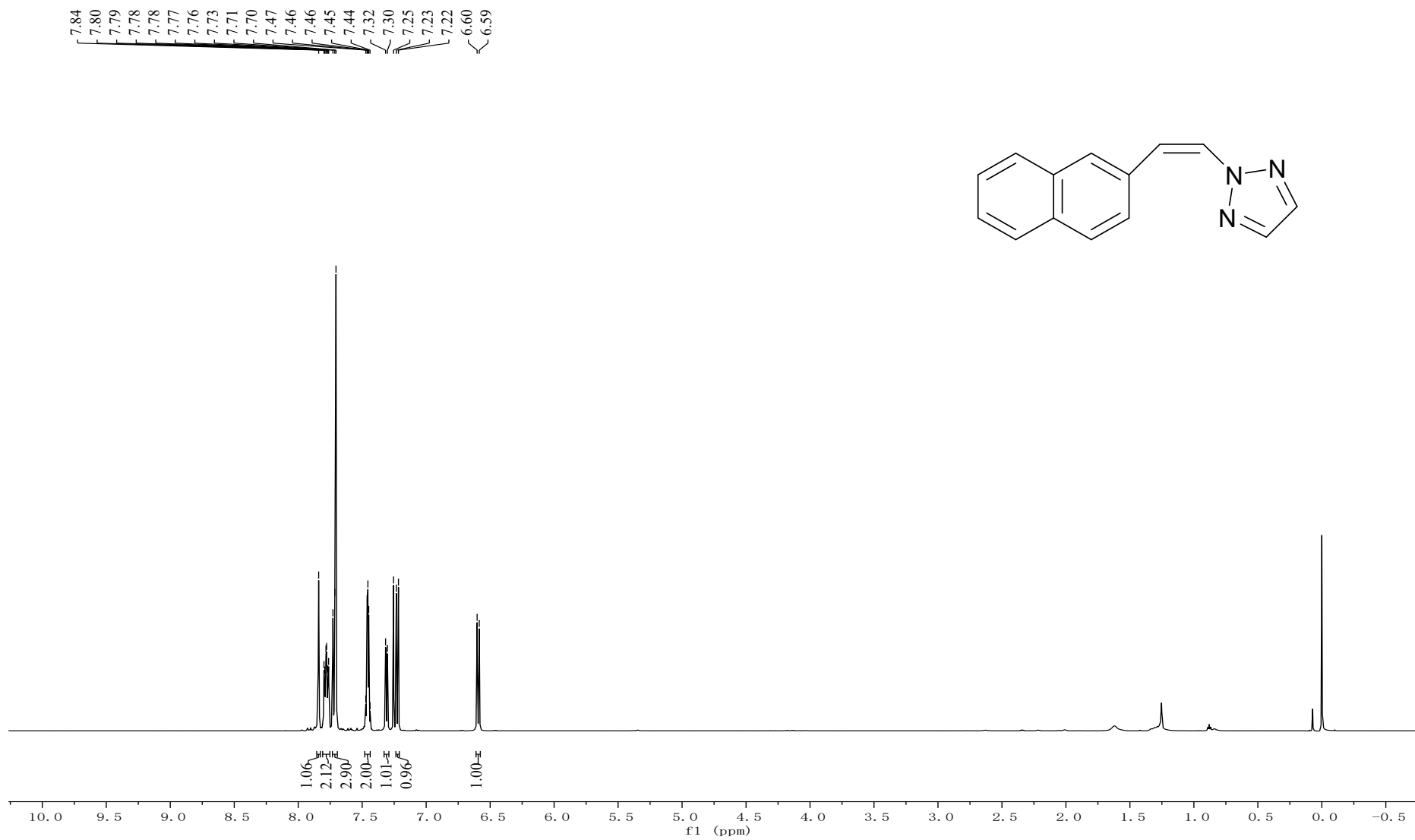
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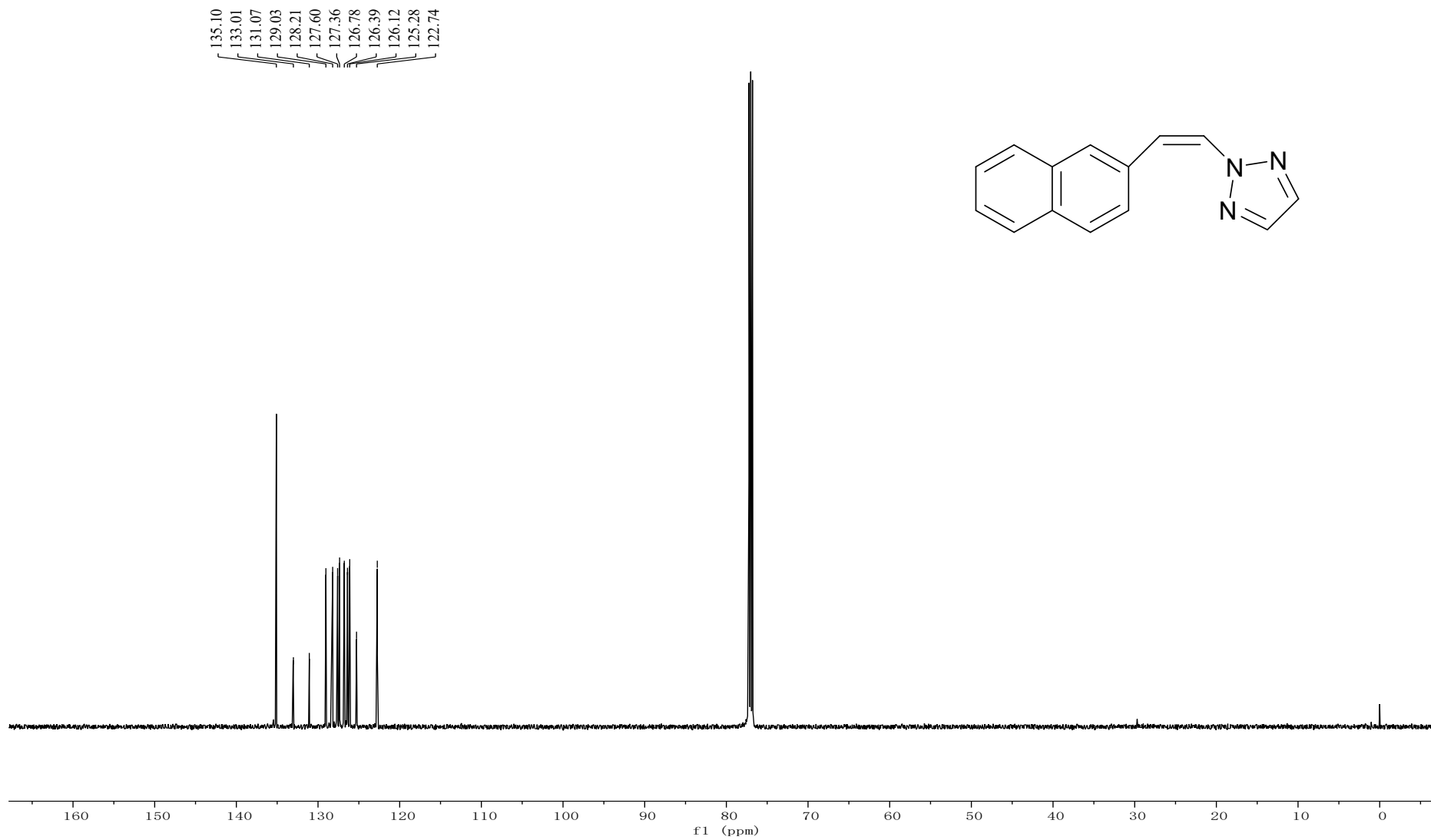


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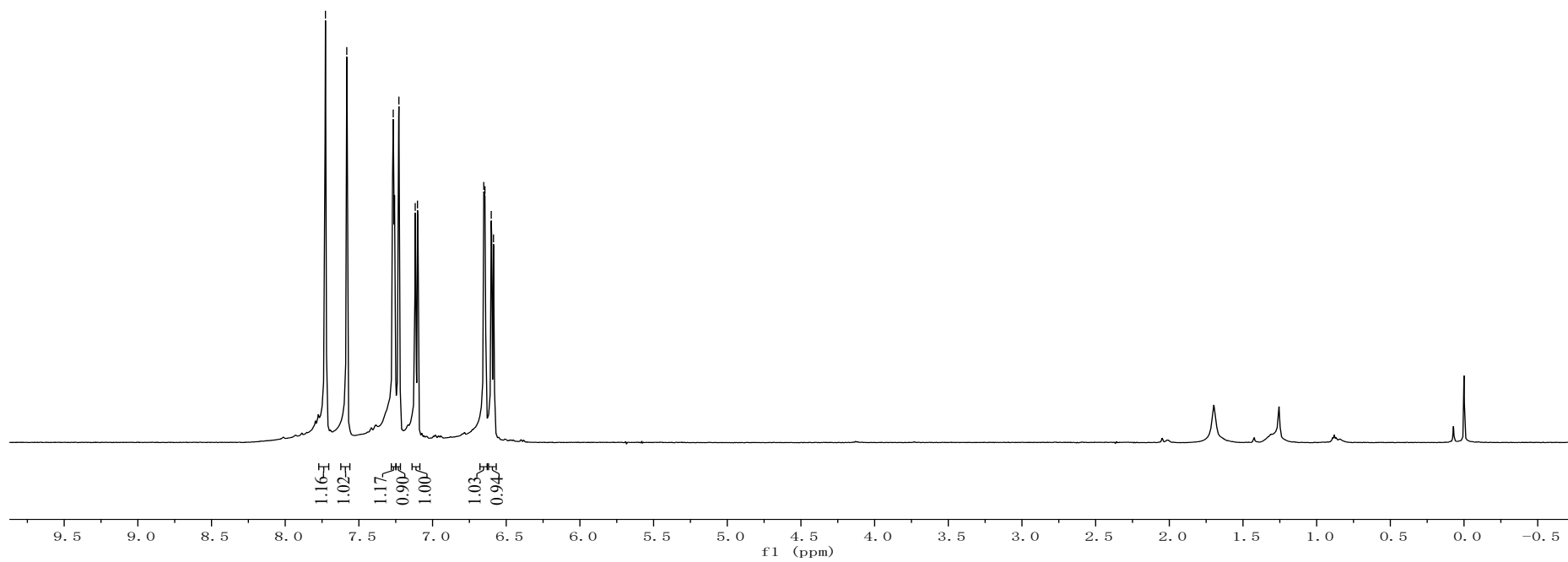
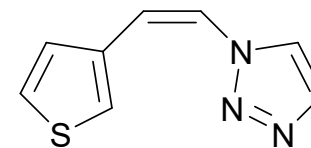


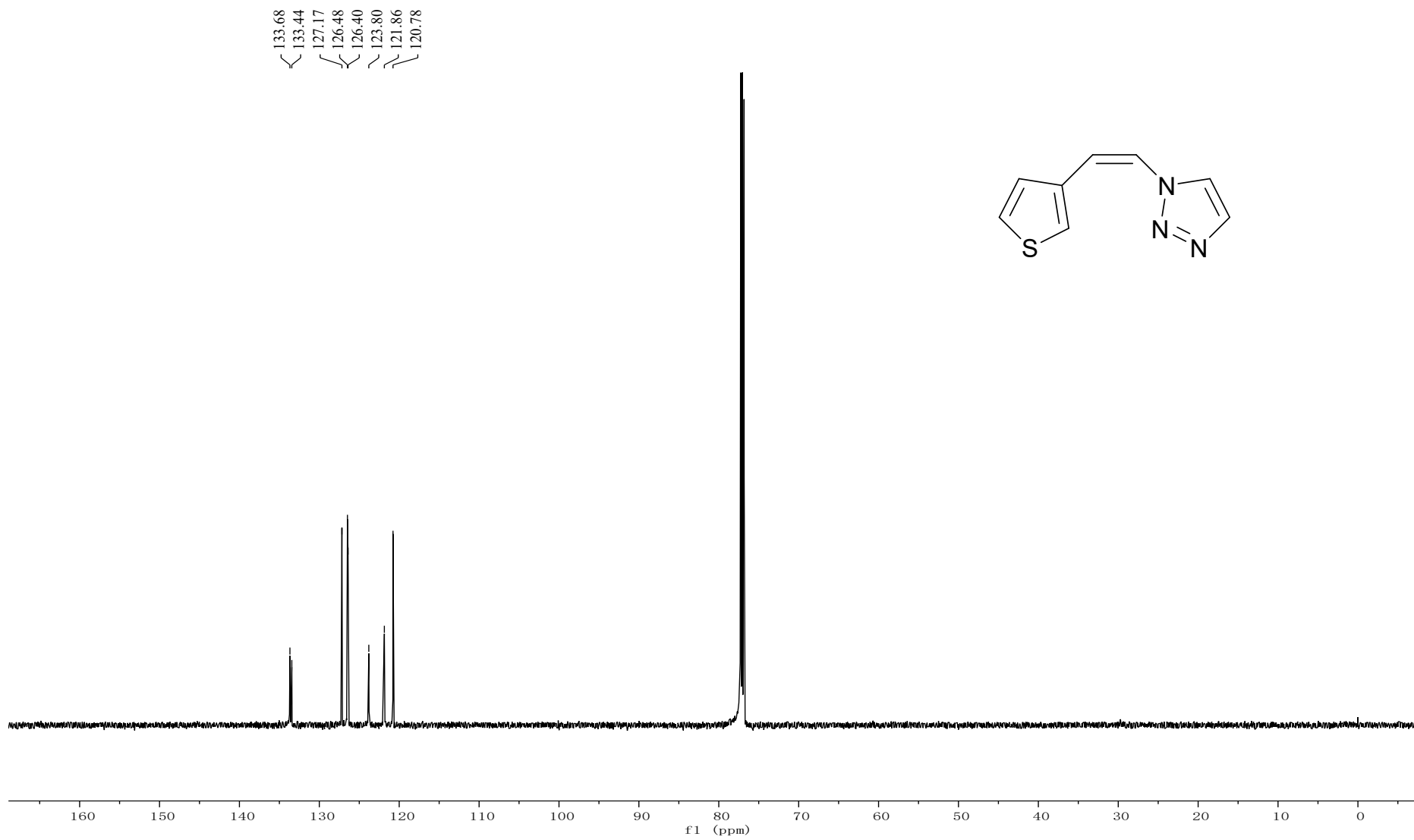


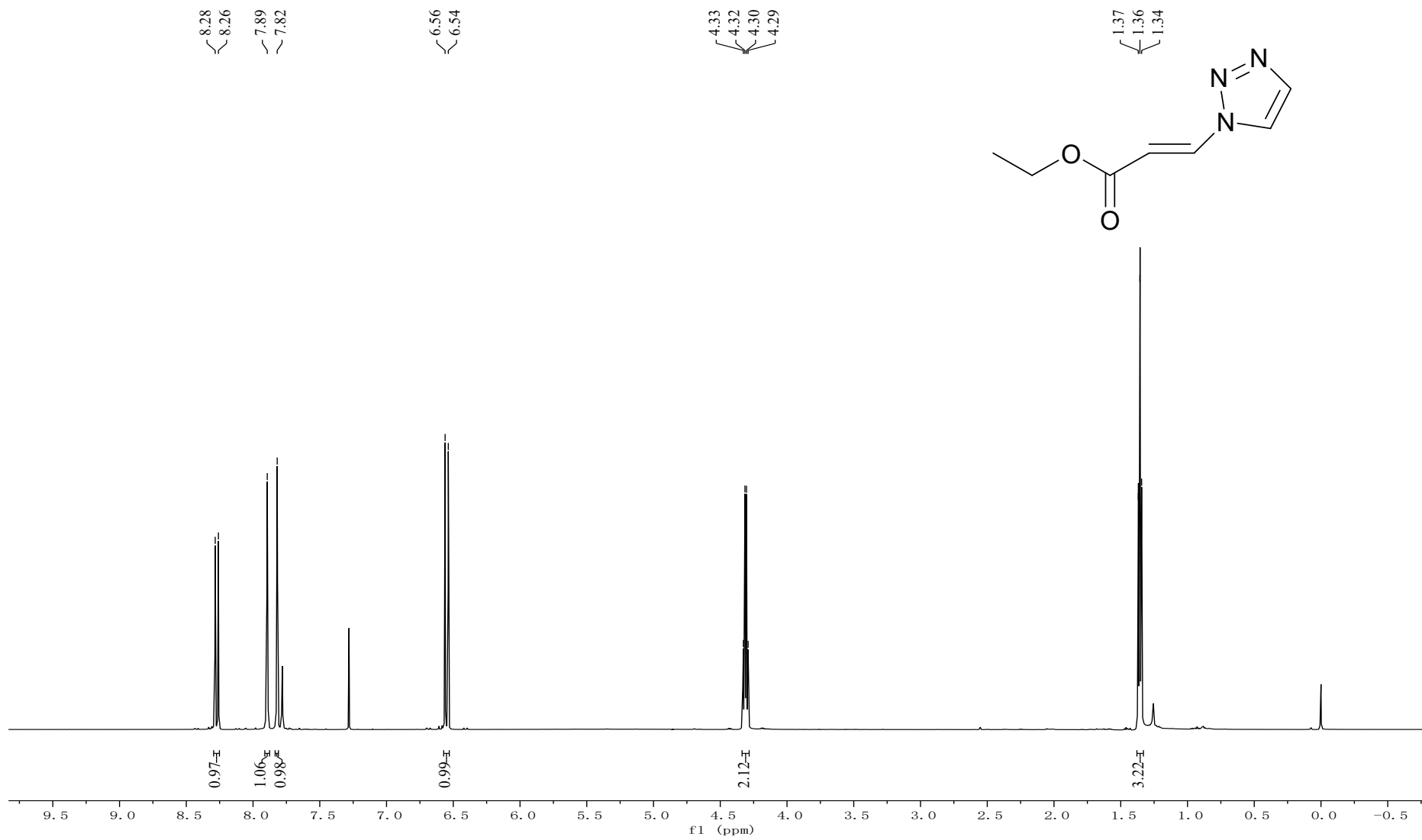


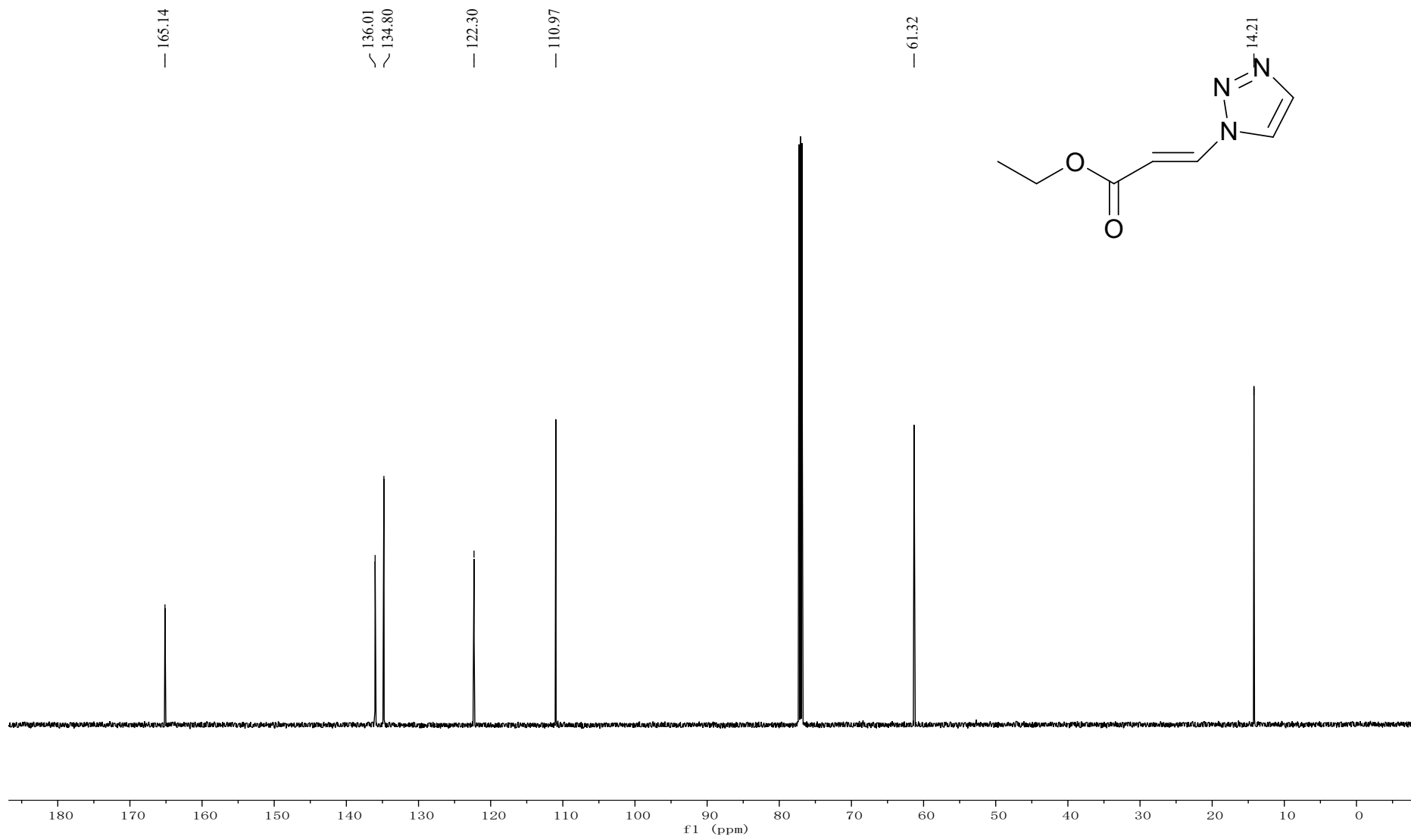


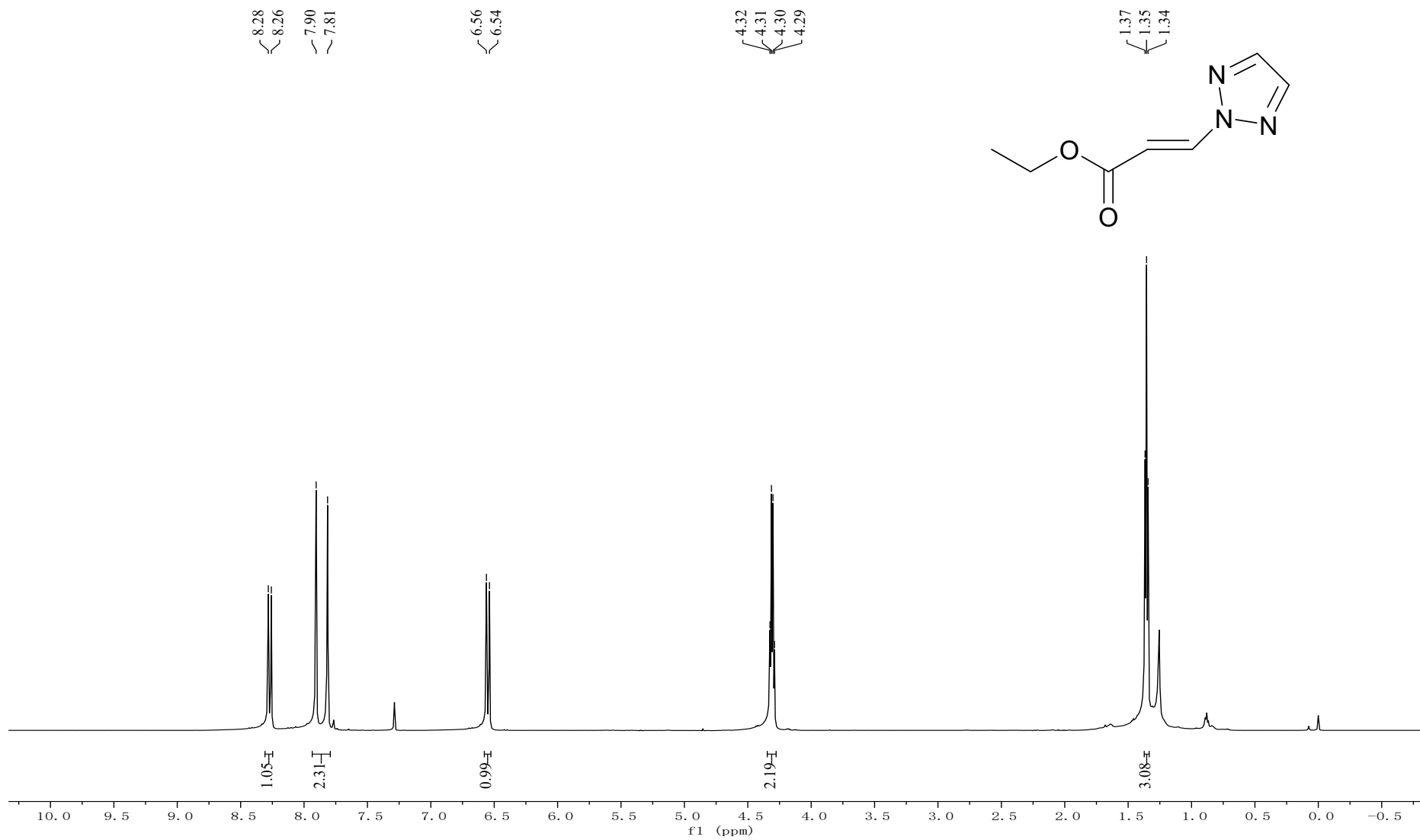
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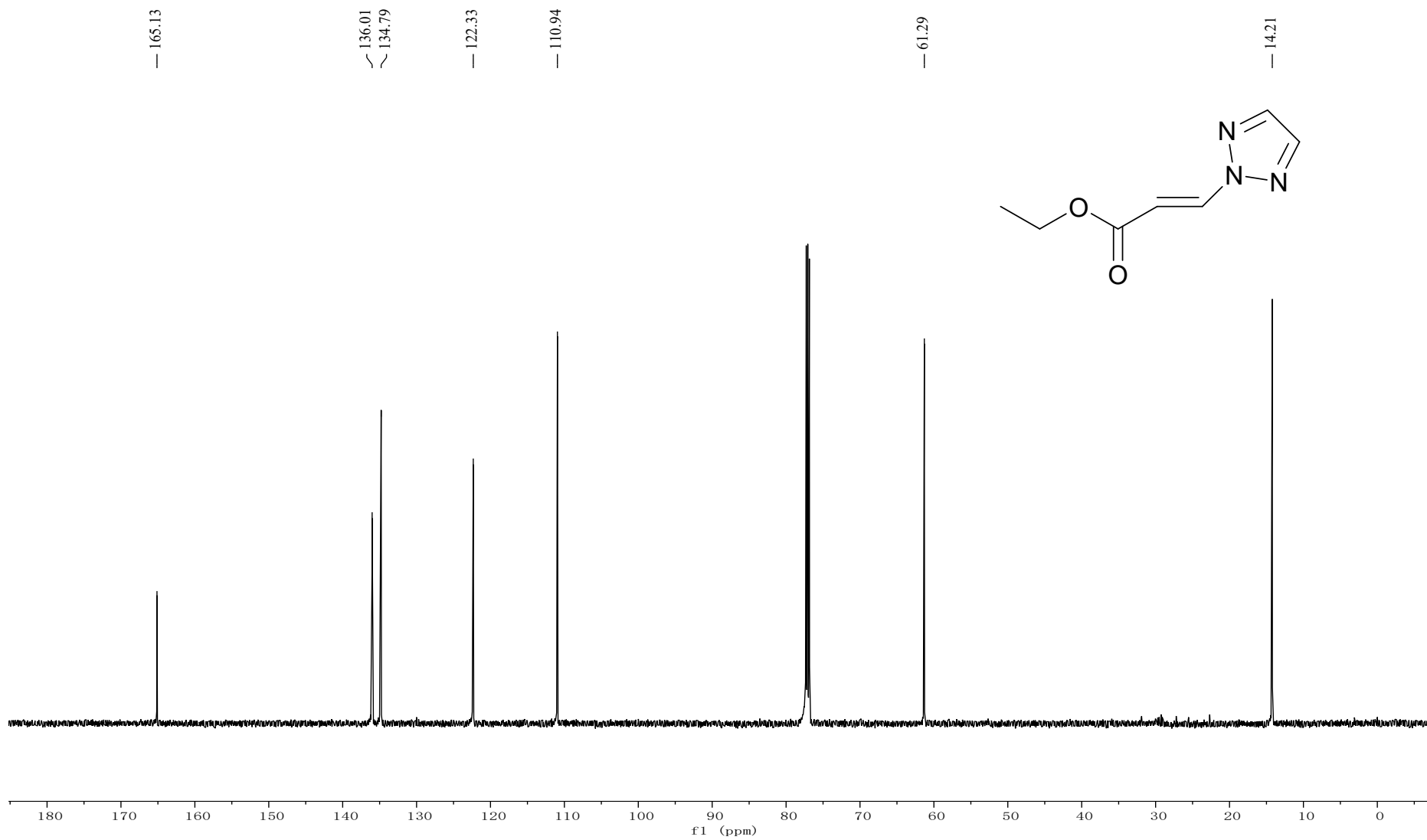




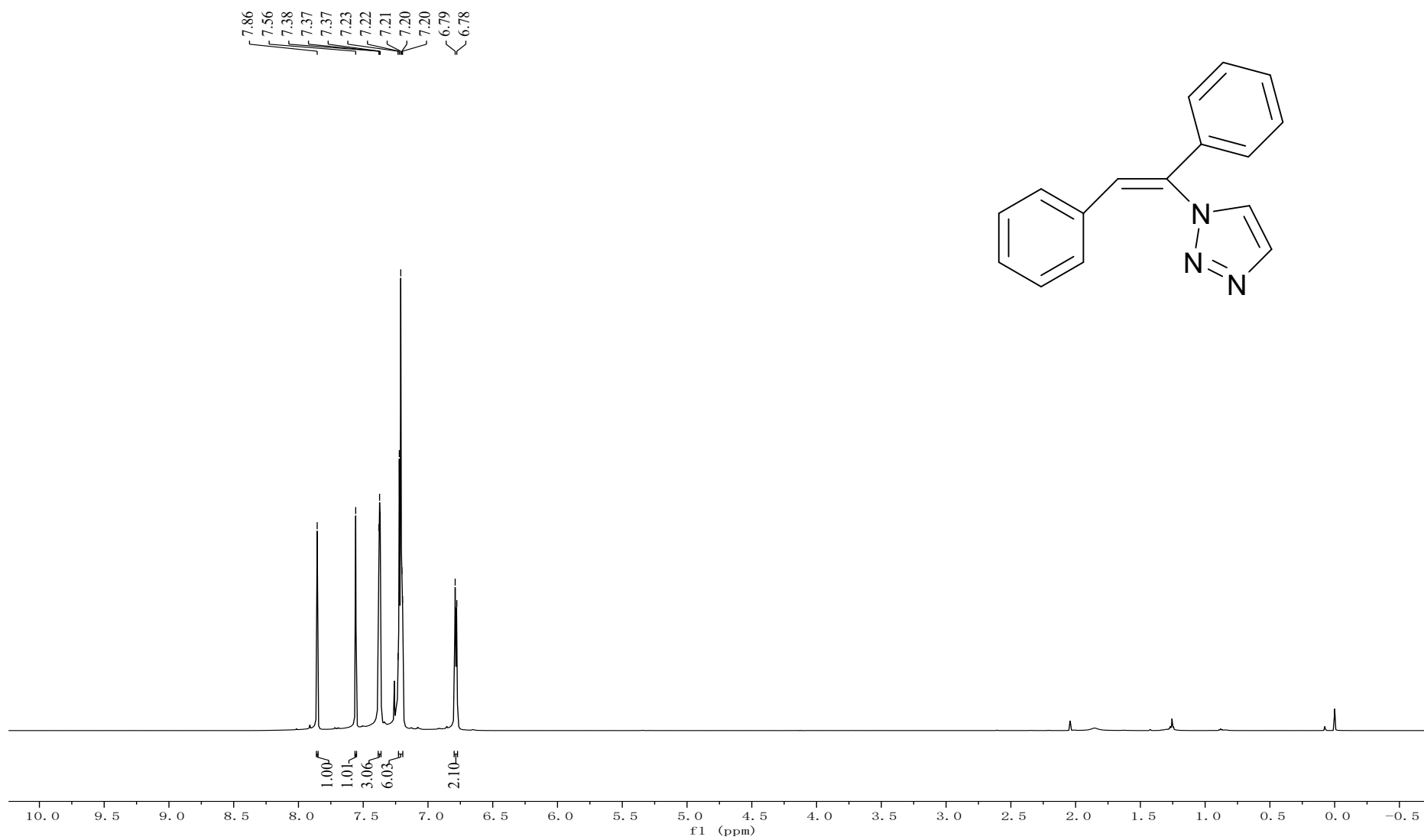


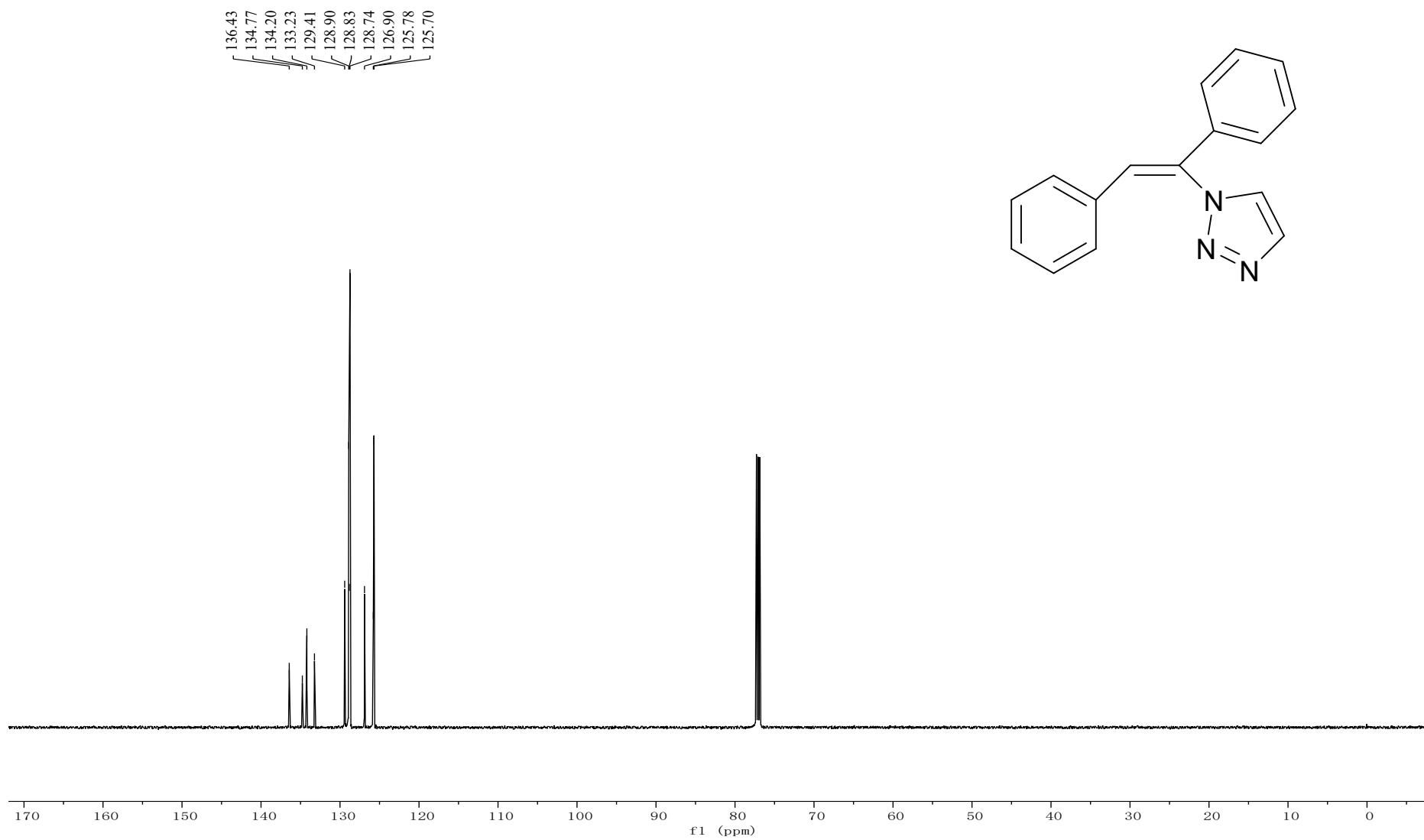


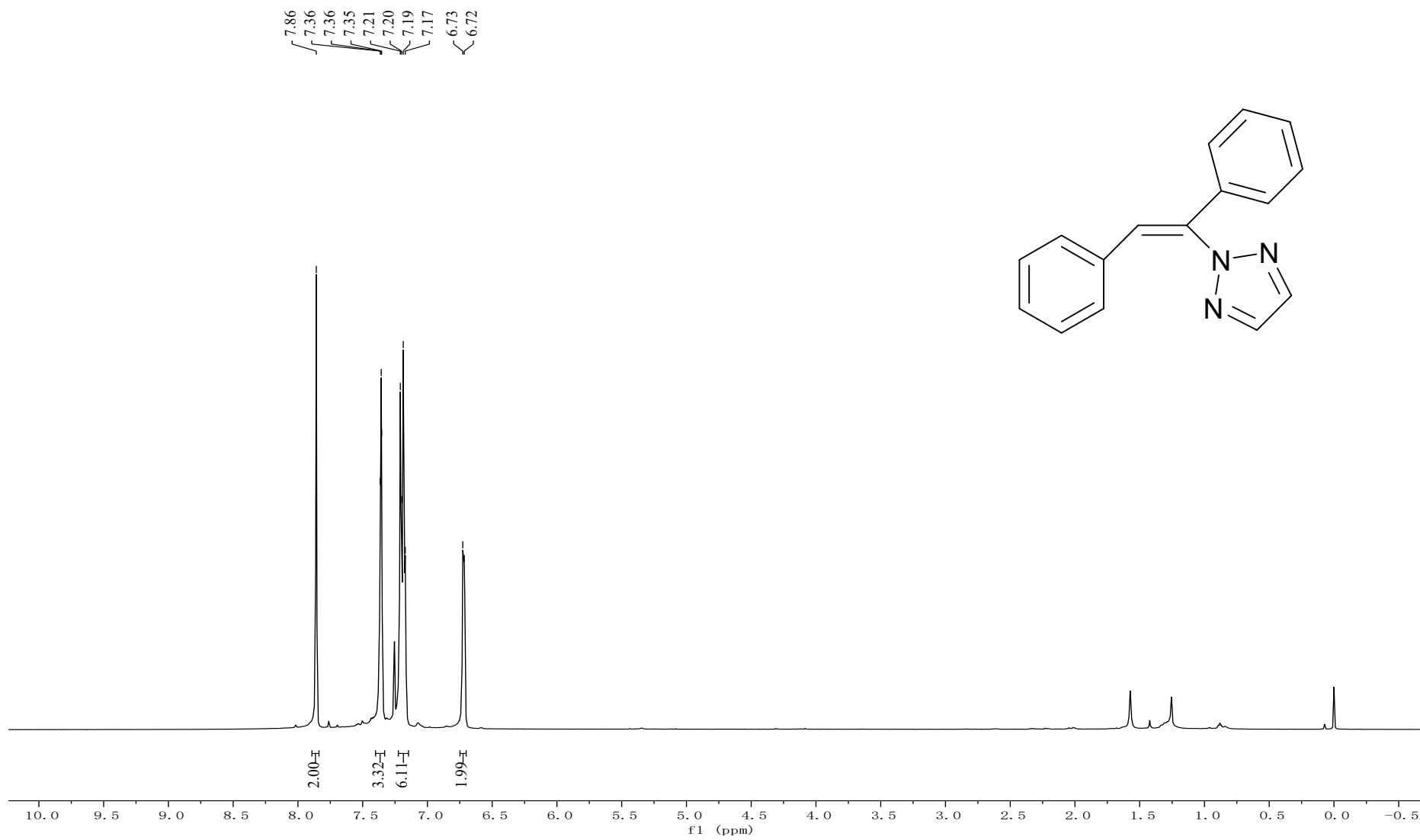


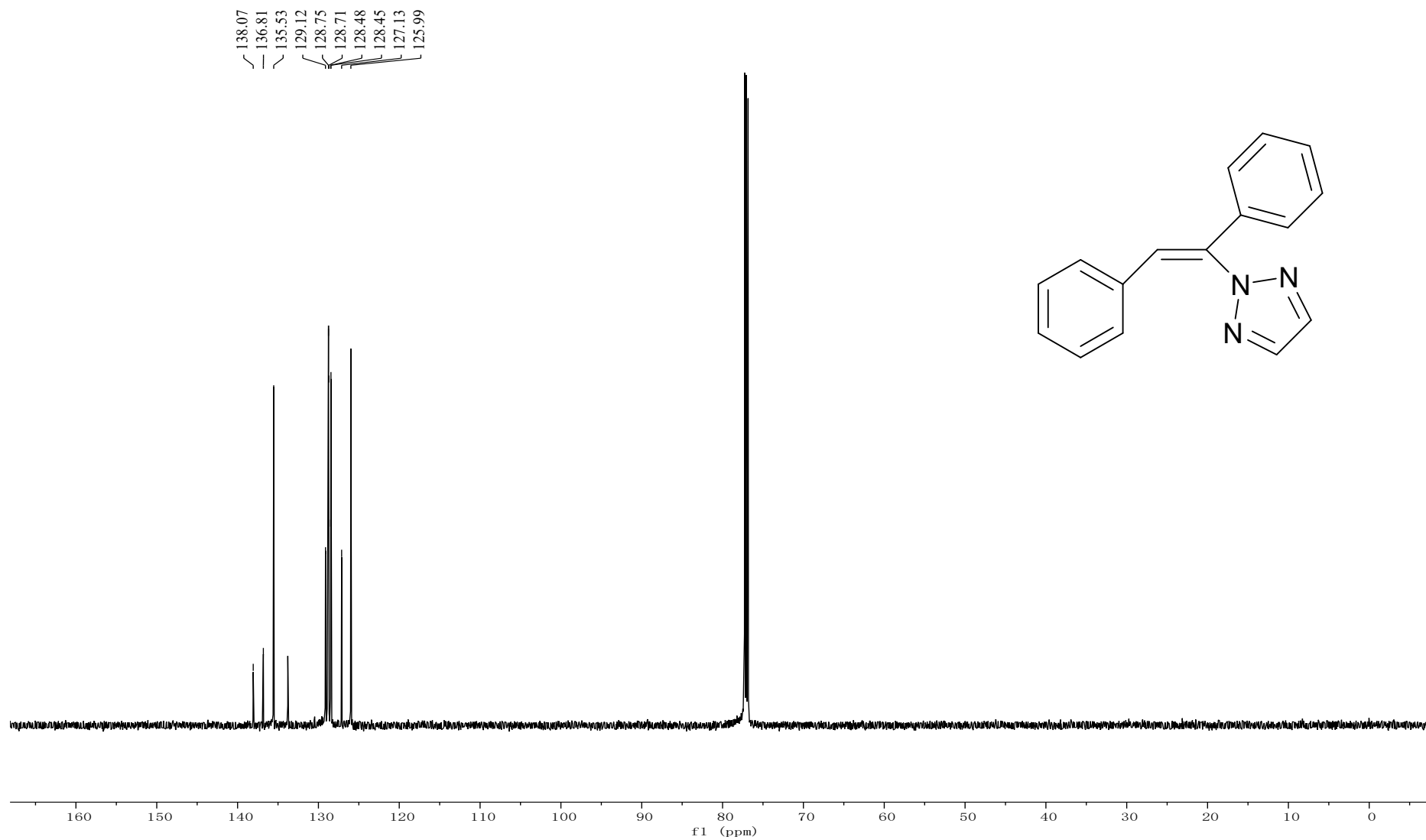


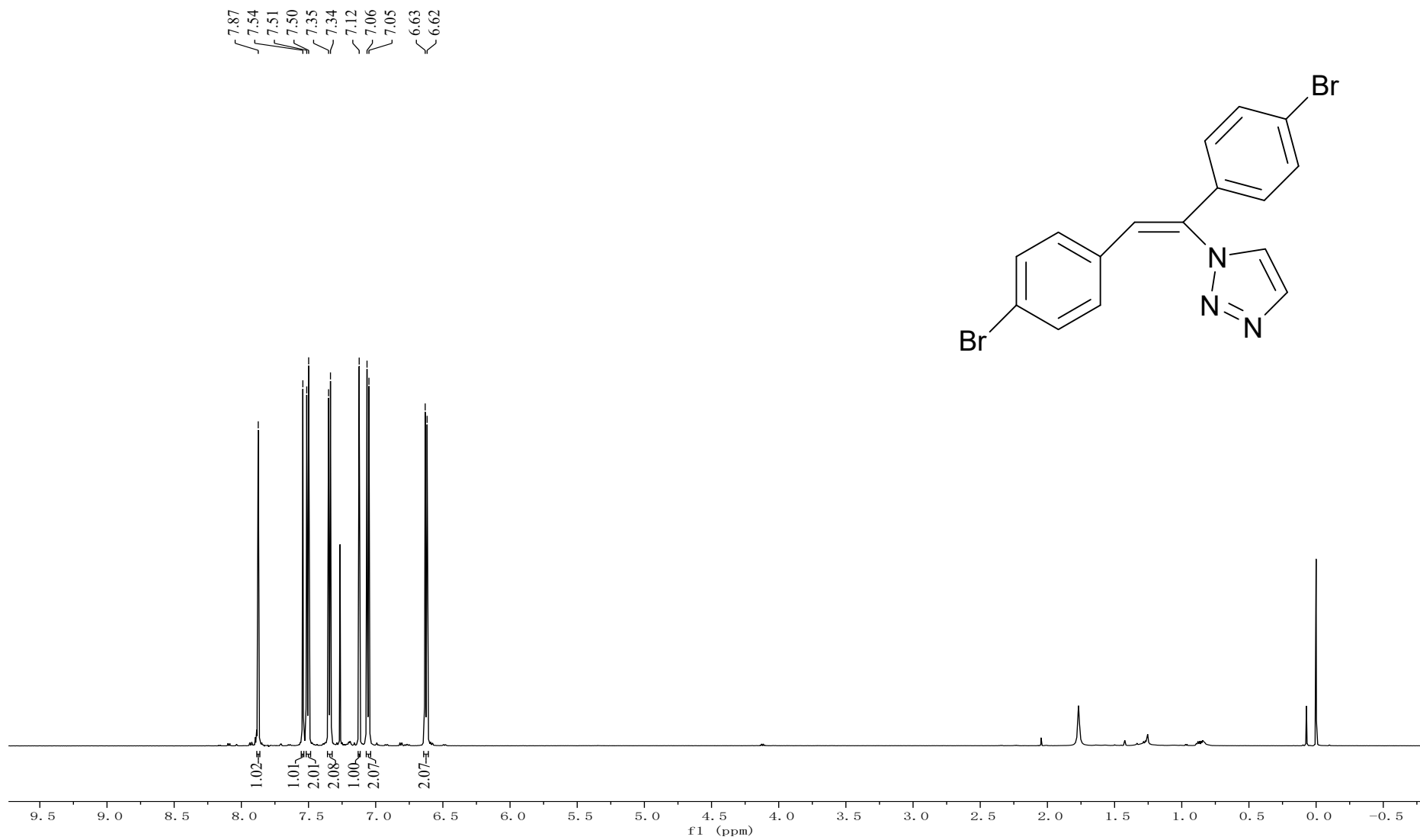


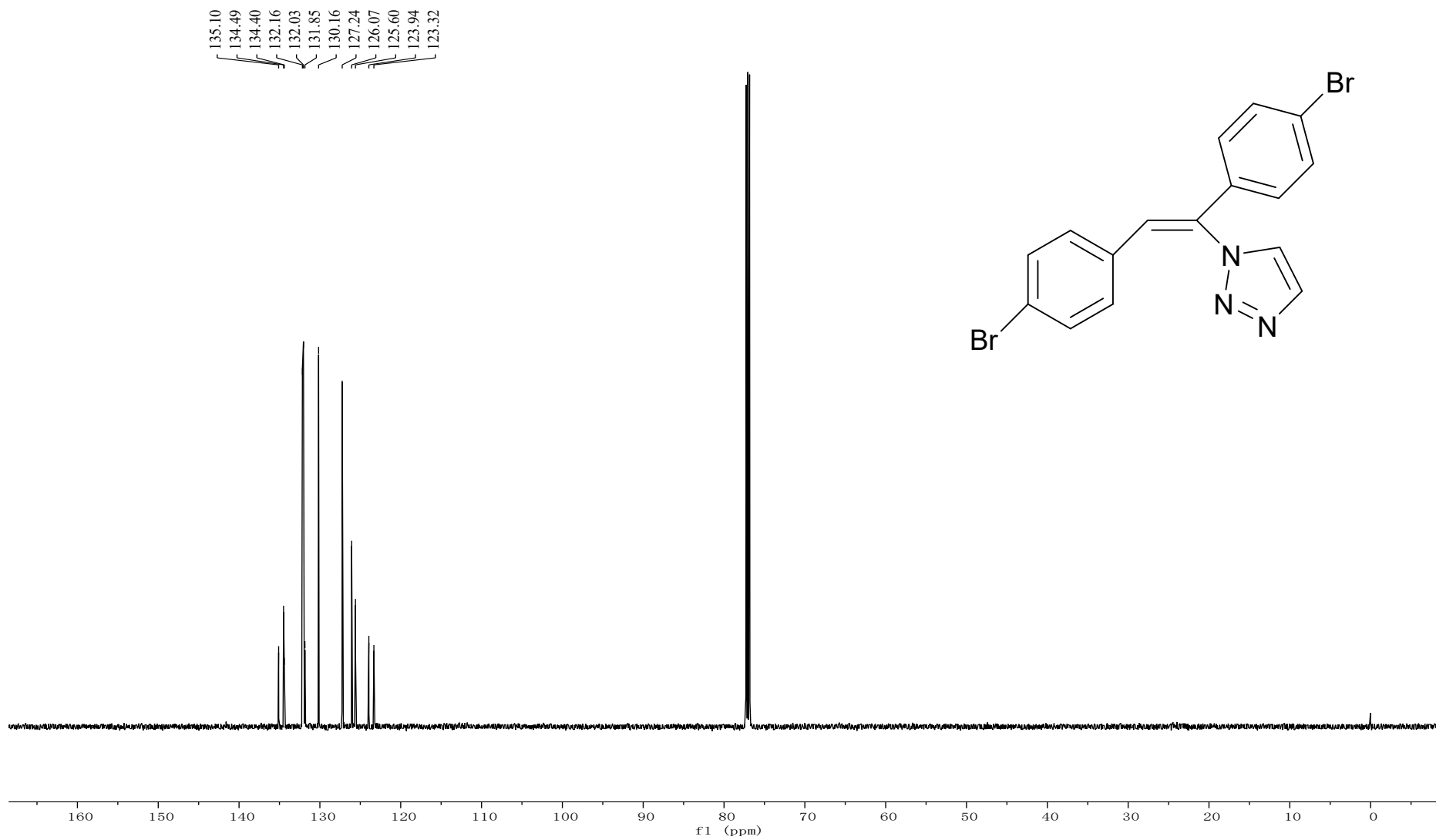


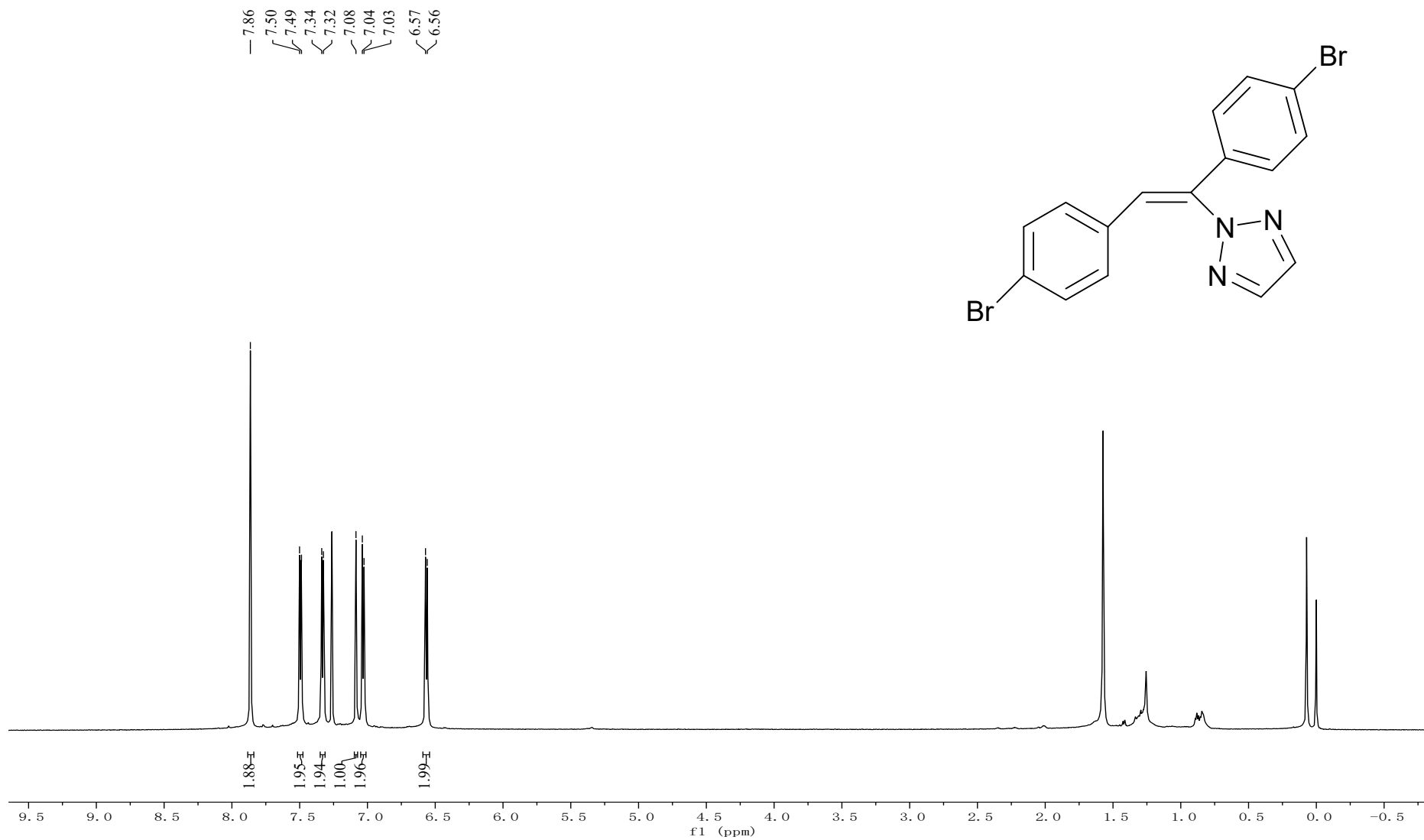


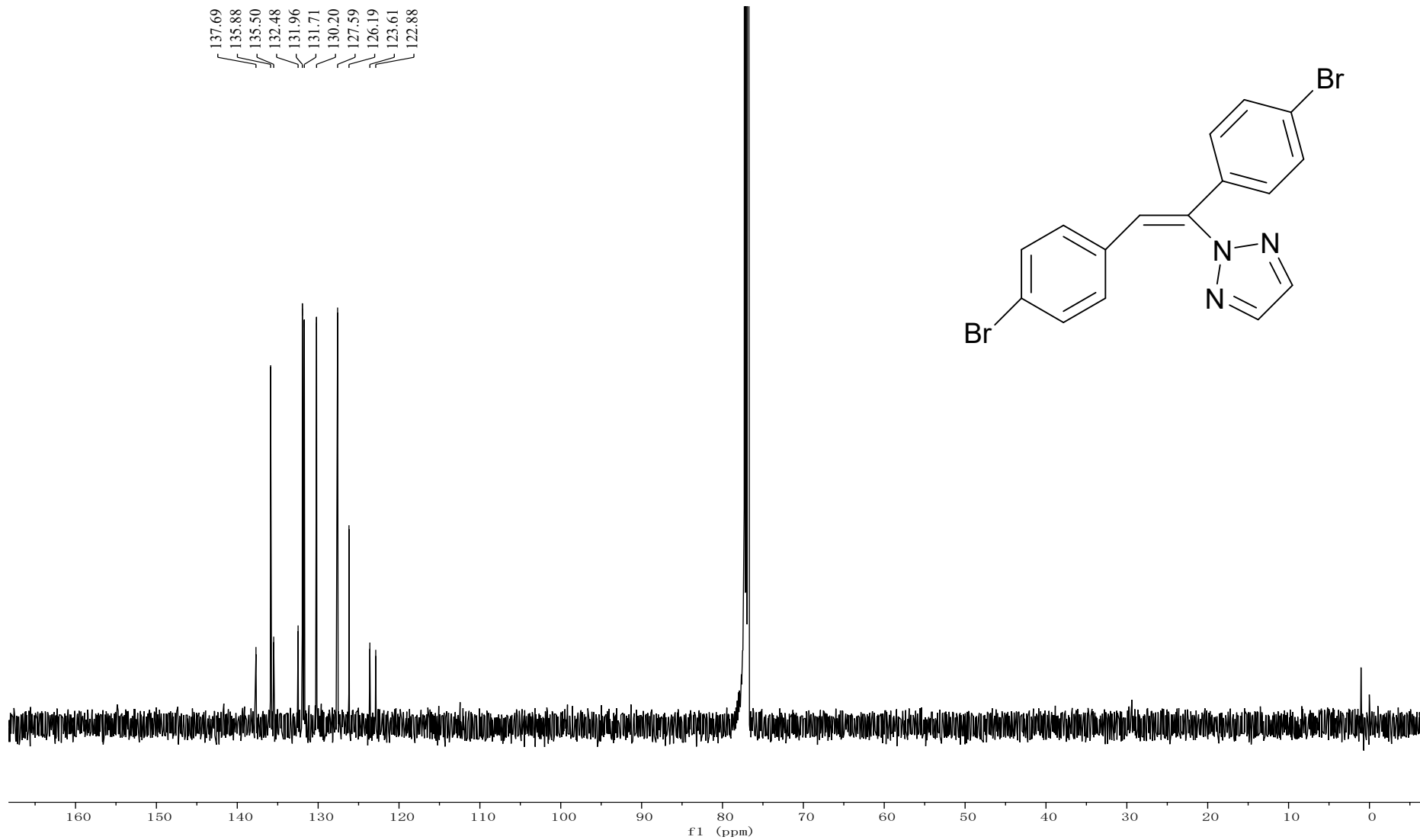




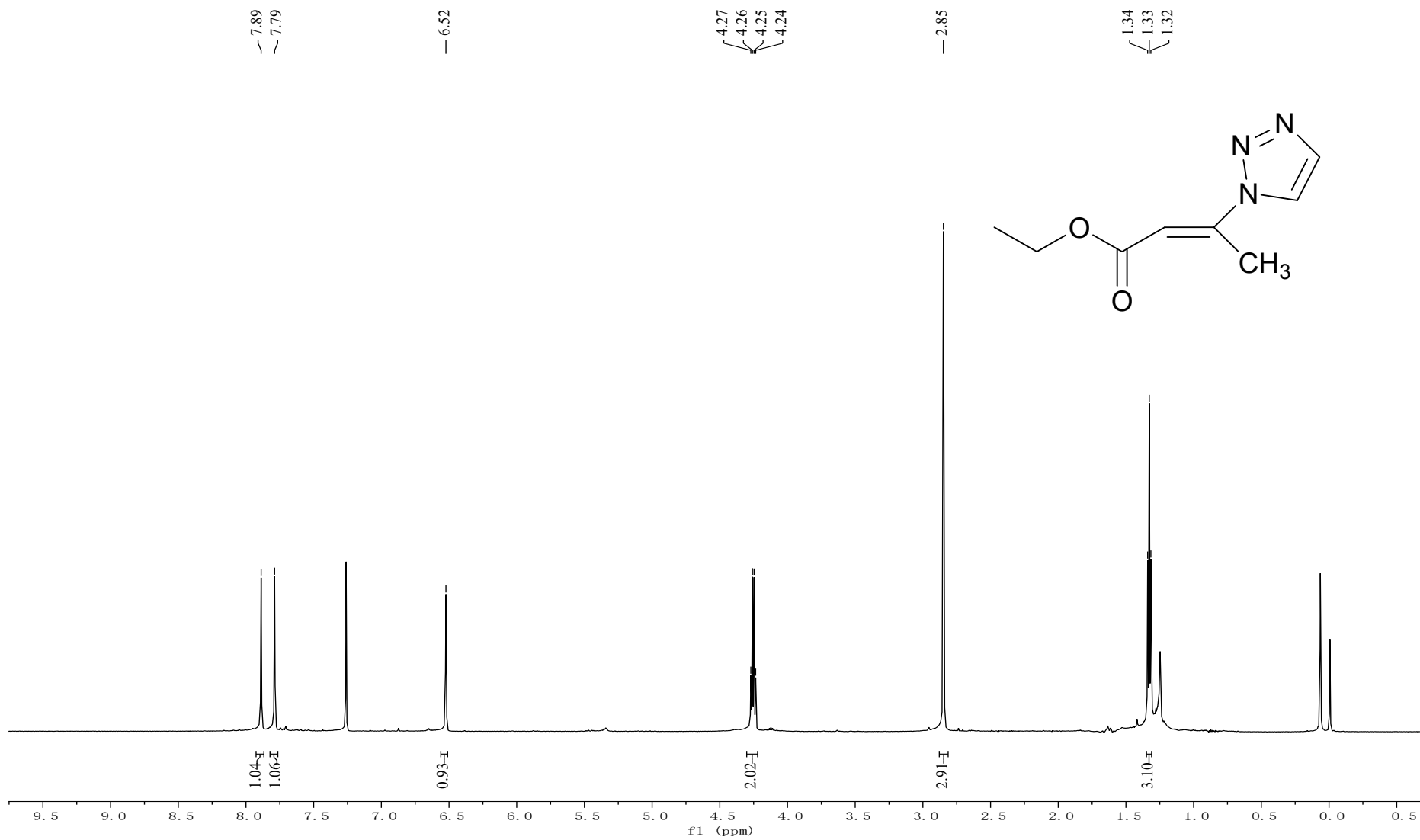


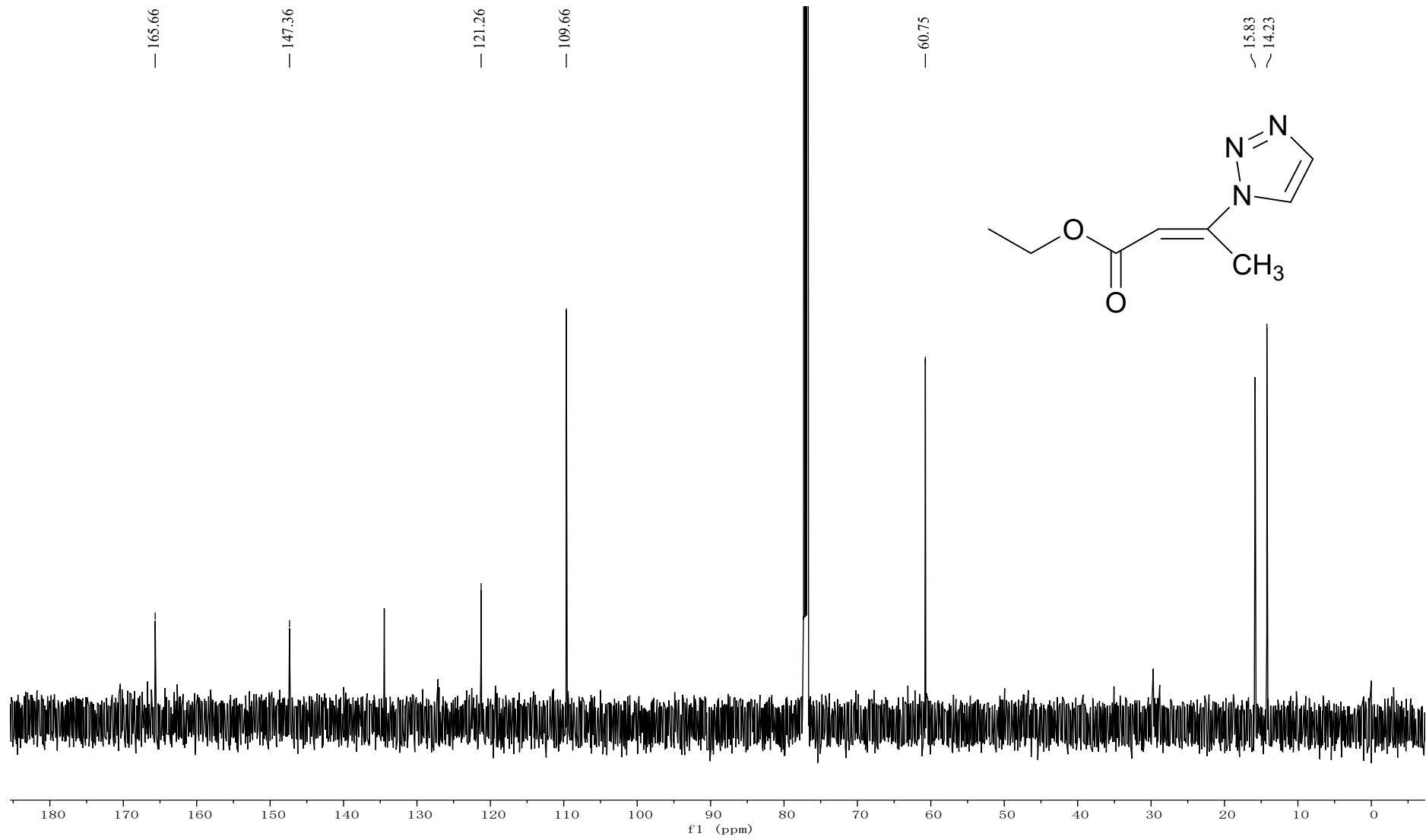


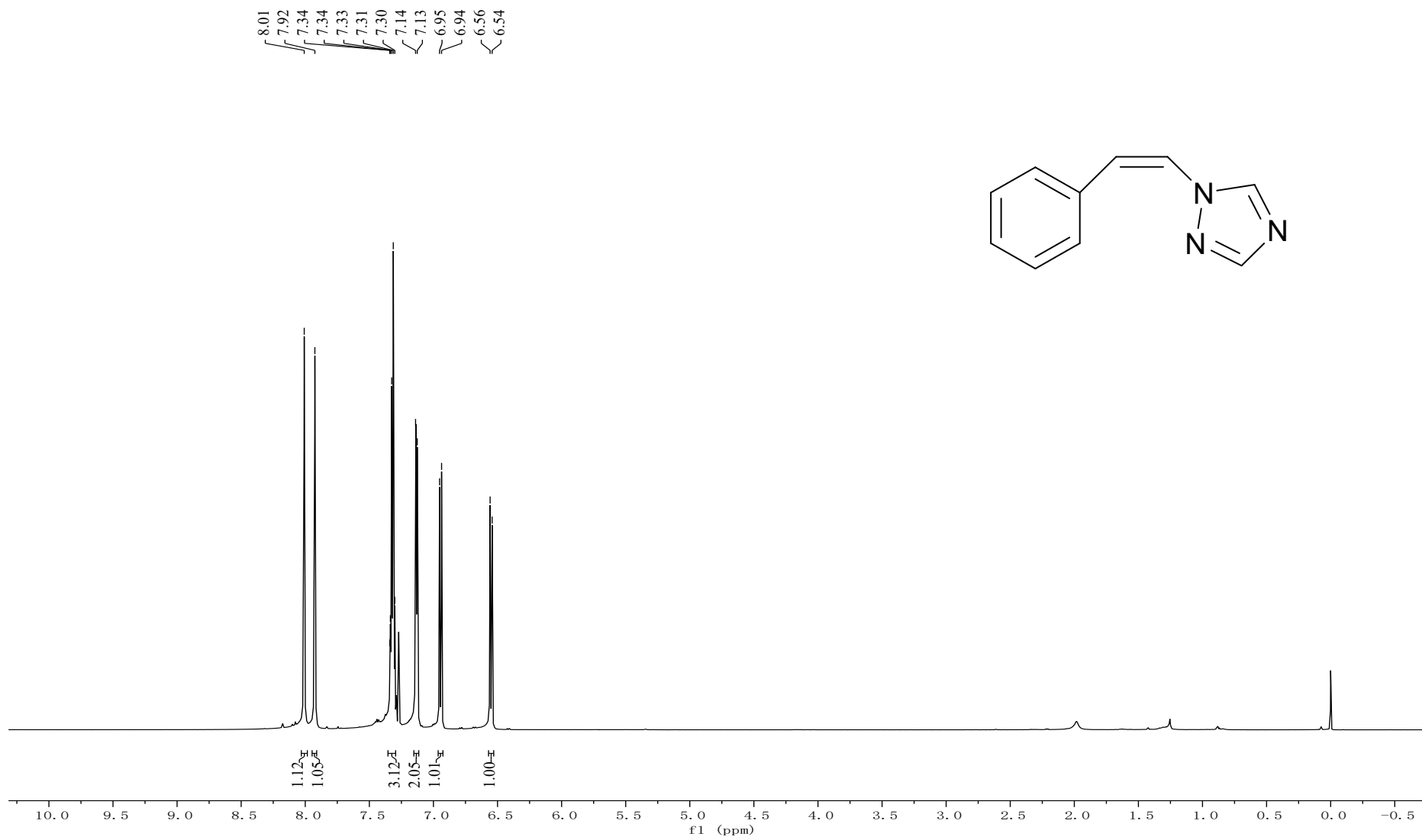




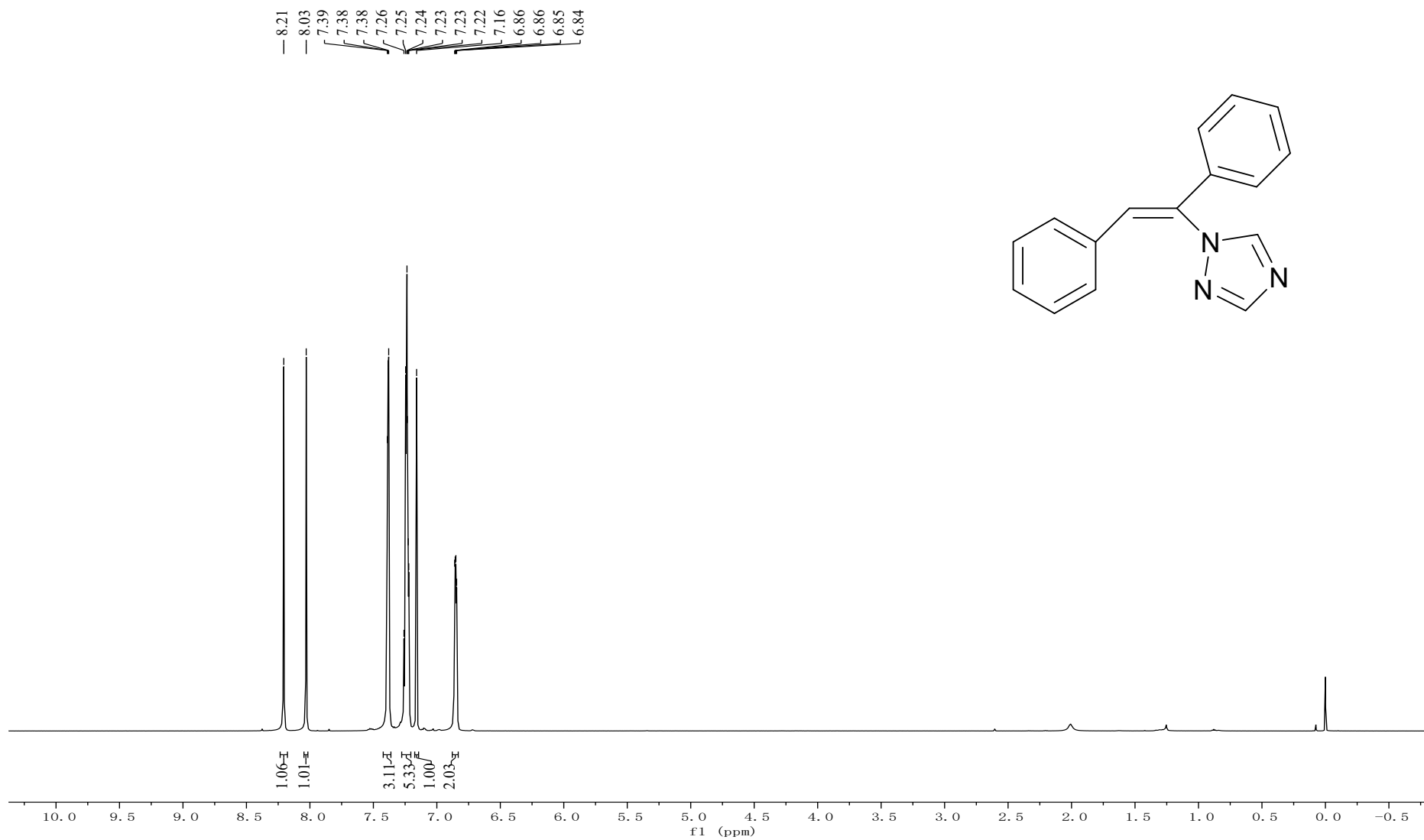


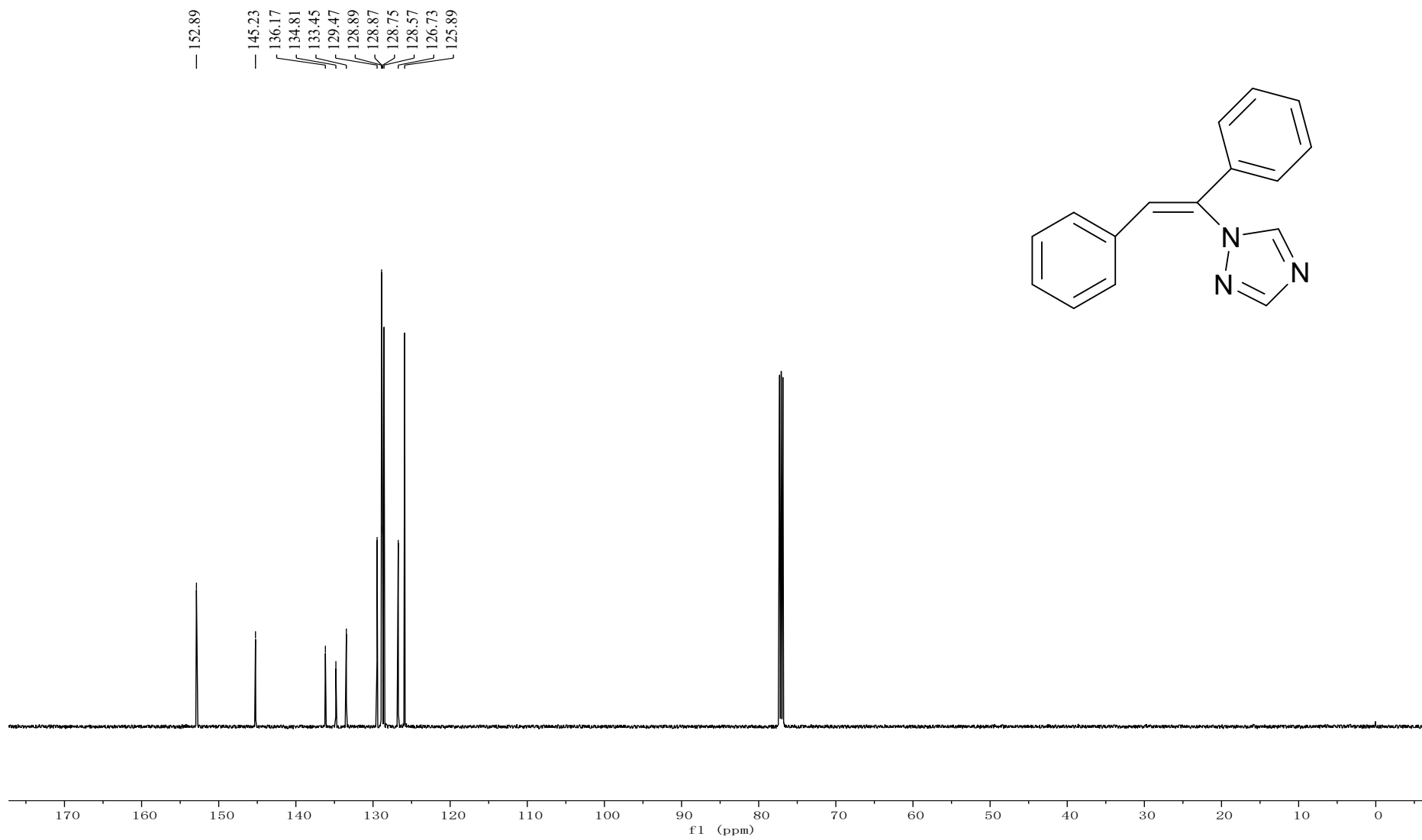


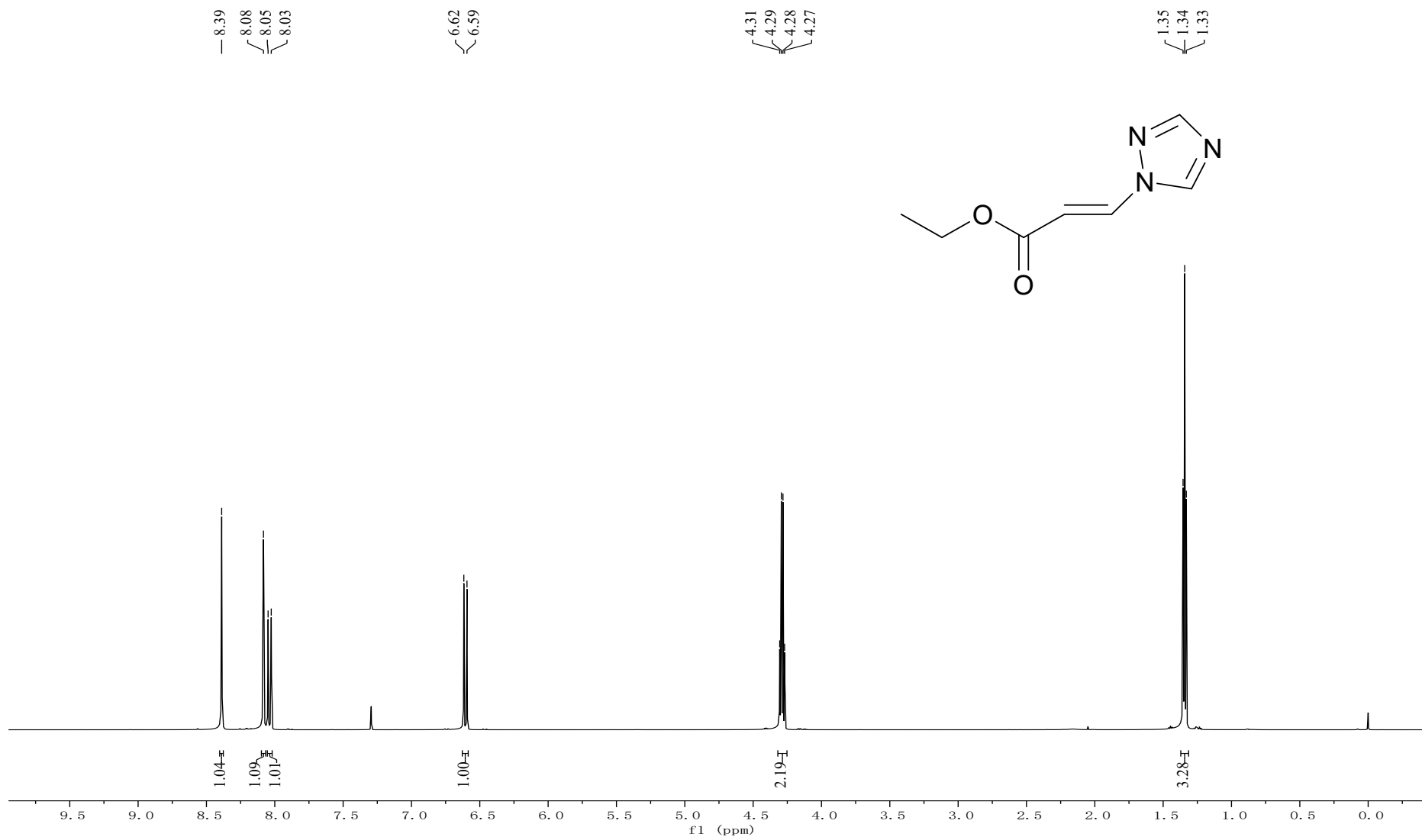


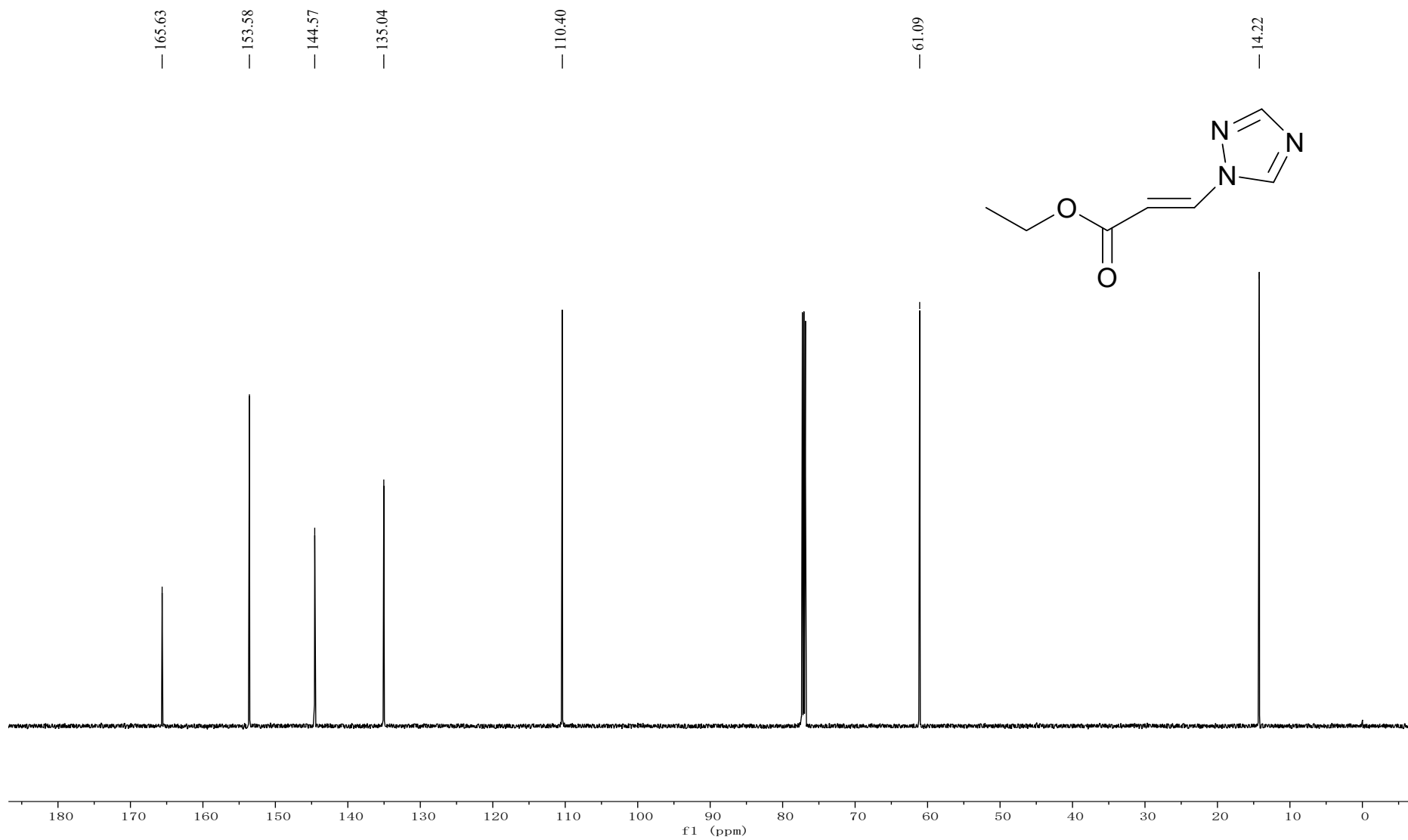




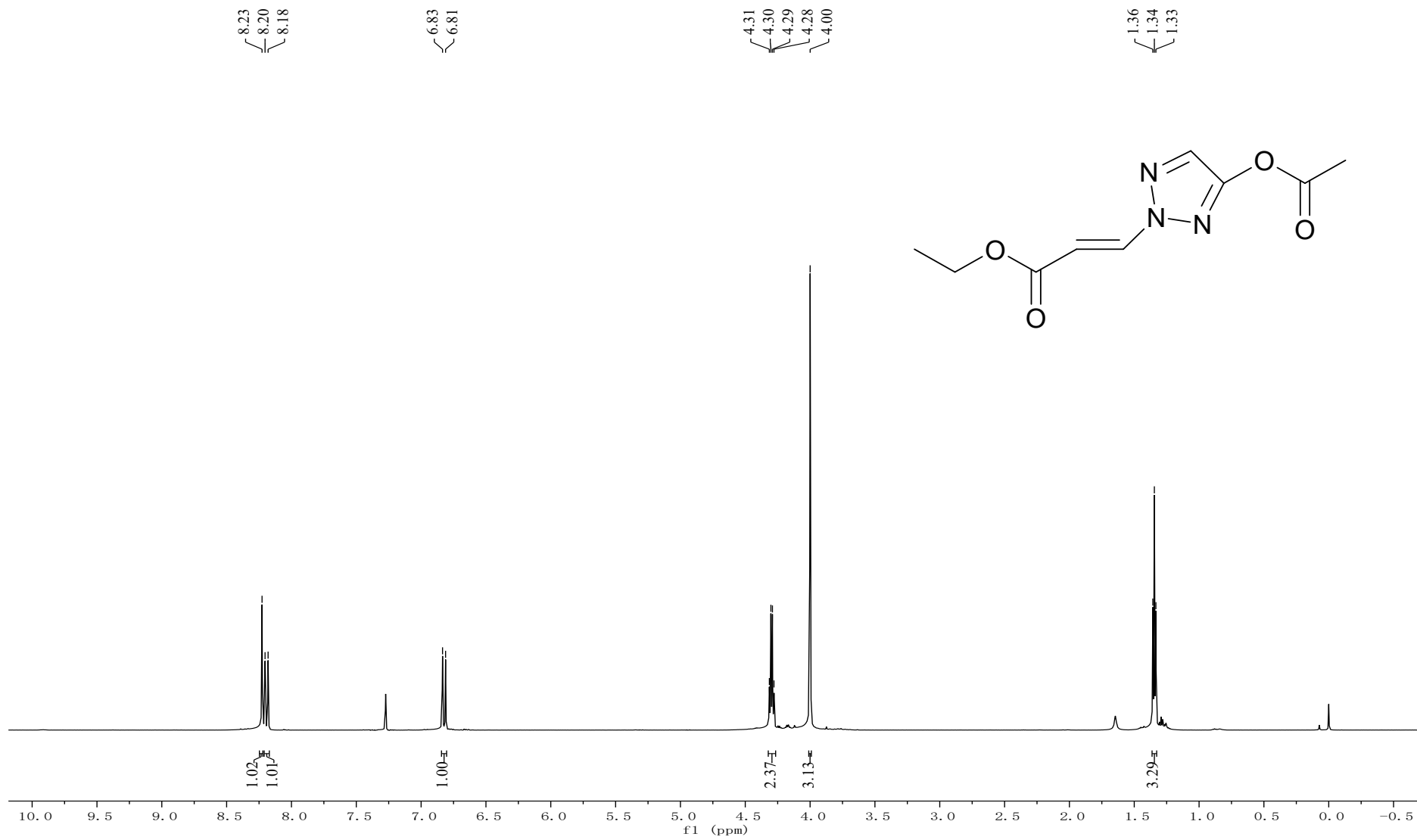




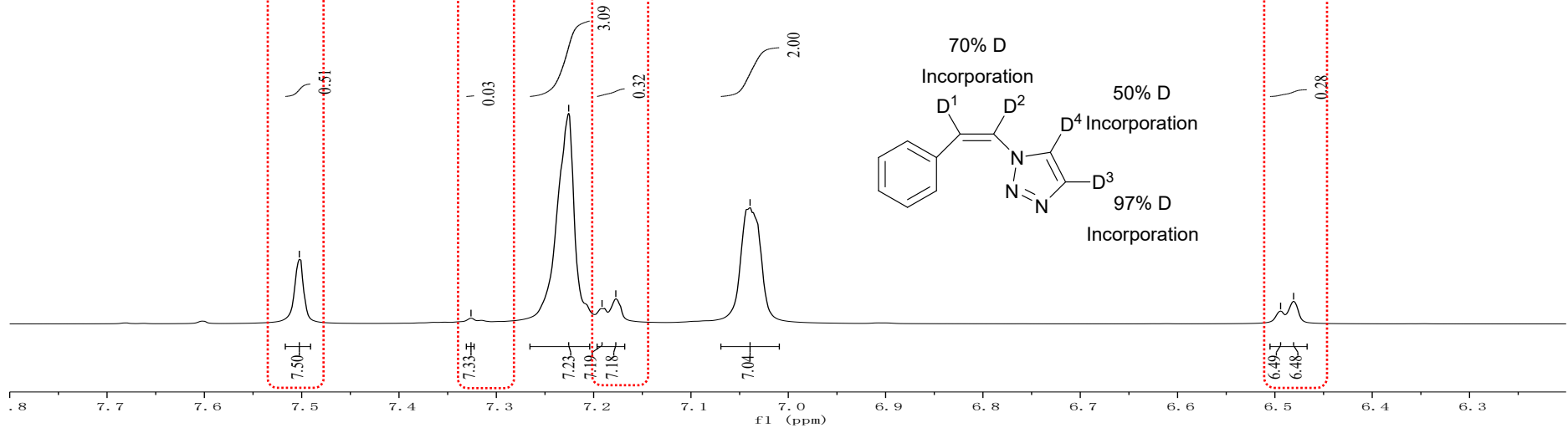
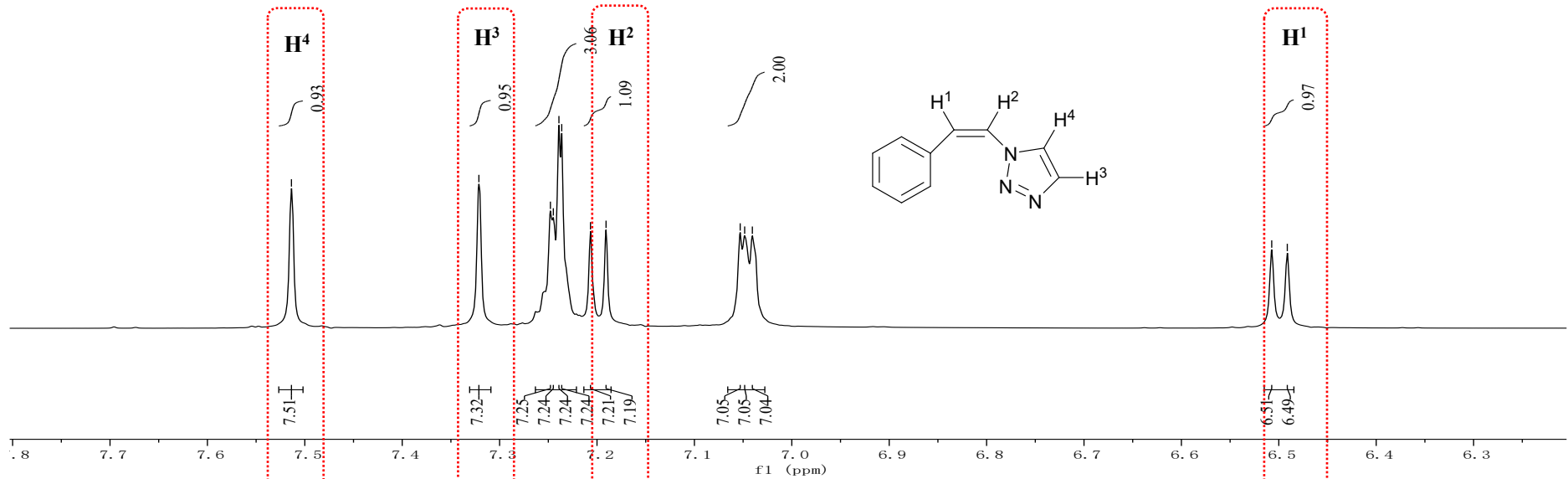


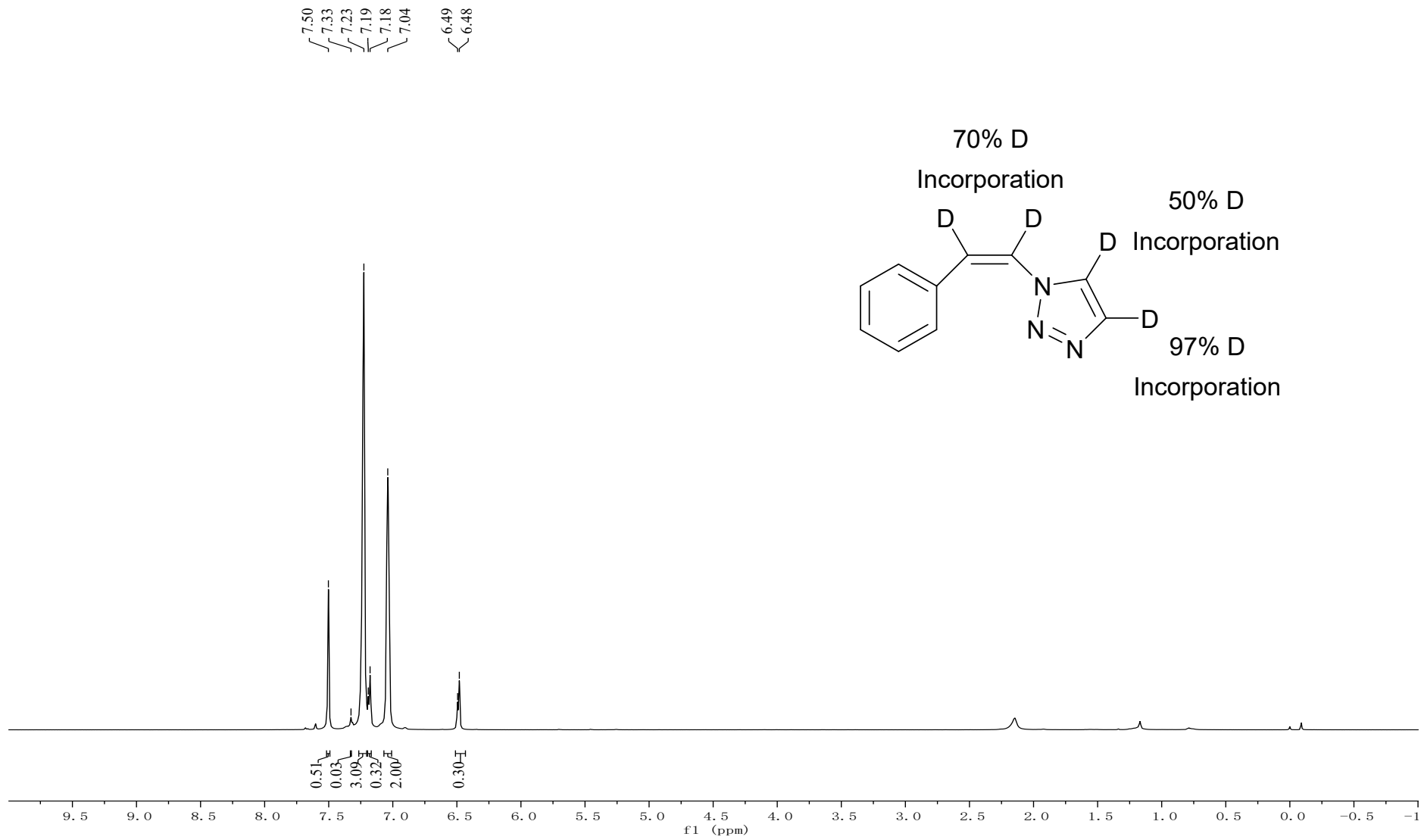












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128.49  
124.02  
123.75  
123.29  
123.19

