Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Ruthenium-catalyzed Decarboxylative C-S Cross-Coupling of carbonothioate: Synthesis of allyl(Aryl)sulfide

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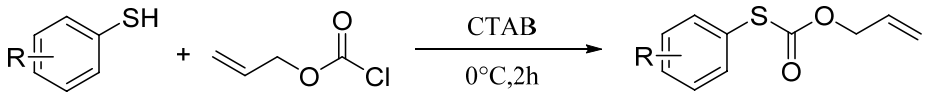
GENERAL. Ethyl acetate (ACS grade), petroleum ether (ACS grade) and dichloromethane (ACS grade) were obtained commercially and used without further purification. Anhydrous 1,2-dichloroethane (HPLC grade) was purified by distillation over calcium hydride. Tetrahydrofuran was distilled over sodium/ benzophenone. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Silicycle precoated silica gel plates. Flash column chromatography was performed over Silicycle silica gel (300-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer using tetramethylsilane (TMS) as internal standards. Infrared spectra were recorded with a Nicolet 5700 spectrometer and are reported in reciprocal centimeter (cm^{-1}). HRESI-MS data were measured on a Synapt G2-Si instrument.

PROCEDURE FOR THE SYNTHESIS

1. Preparation of unsubstituted allyl carbonothioates

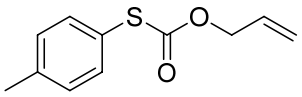


3 **4** **1**

1a-1l was prepared according to the literature procedure[1].

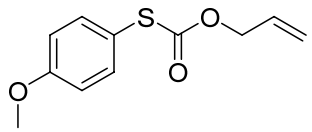
The thiophenol **3** (5 mmol) and tetra-*n*-butyl ammonium chloride hydrate (0.035 mmol) were dissolved in dichloromethane (10 mL) and 4M sodium hydroxide (2mL) at 0 °C. Allyl chloroformate **4** (6 mmol) was slowly added and the reaction mixture was stirred for 2 hr. After 2 hr, the two layers were separated and the organic layer was washed with 2M sodium hydroxide (5 mL) and dried over $MgSO_4$. A yellow oil remained after evaporation of the solvent under reduced pressure. This oil was purified by flash column chromatography using ethyl acetate and petroleum ether as an eluent.

O-allyl S-(p-tolyl) carbonothioate (1a)



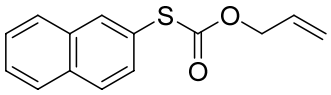
Purified by flash column chromatography (petroleum ether/ethyl acetate, 20/1) to afford **1a** (0.91g, 88%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J*=7.8 Hz, 2H), 7.20 (d, *J*=7.8 Hz, 2H), 6.00 – 5.85 (m, 1H), 5.40 – 5.23 (m, 2H), 4.71 (d, *J*=5.8 Hz, 2H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.90, 139.97, 134.89, 131.37, 130.01, 124.10, 119.28, 68.20,21.33; **IR** (film) *v*: 2939, 1722, 1448, 1132, 937, 812 cm^{-1}; **HRMS** (ESI) calcd for $C_{11}H_{12}O_2S$ ($[M+Na]^+$): 231.0486; found: 231.0487.

O-allyl S-(4-methoxyphenyl) carbonothioate (1b)



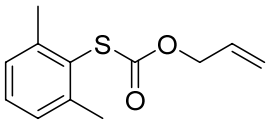
Purified by flash column chromatography (petroleum ether) to afford **1b** (1.0g, 91%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 2H), 6.96 – 6.85 (m, 2H), 5.97 – 5.84 (m, 1H), 5.39 – 5.22 (m, 2H), 4.70 (dt, *J*=5.8, 1.3 Hz, 2H), 3.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.25, 160.88, 136.67, 131.40, 119.25, 118.27, 114.83, 68.17, 55.37; **IR** (film) *v*: 2945, 2839, 1724, 1593, 1456, 1249, 831 cm^{-1}; **HRMS** (ESI) calcd for $C_{11}H_{12}O_3S$ ($[M+Na]^+$): 247.0405; found: 247.0403.

O-allyl S-(naphthalen-2-yl) carbonothioate (1c)



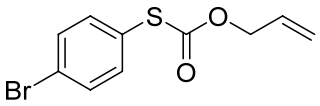
Purified by flash column chromatography (petroleum ether) to afford **1c** (1.07g, 88%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.87 – 7.80 (m, 3H), 7.58 – 7.50 (m, 3H), 6.01 – 5.84 (m, 1H), 5.38 – 5.26 (m, 2H), 4.75 – 4.69 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.58, 134.70, 133.45, 133.41, 131.32, 131.21, 128.88, 128.02, 127.79, 127.30, 126.67, 124.90, 119.41, 68.34; **IR** (film) *v*: 3053, 2922, 1624, 1587, 1425, 1226, 920, 812, 742 cm^{-1}; **HRMS** (ESI) calcd for $C_{14}H_{12}O_2S$ ($[M+Na]^+$): 267.0456; found: 267.0455.

O-allyl S-(2,6-dimethylphenyl) carbonothioate (1d)



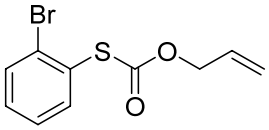
Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford **1d** (0.91 g, 82%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 2H), 7.16 – 7.14 (m,1H), 5.96 – 5.88 (m,1H), 5.41 – 5.20 (m, 2H), 4.70 (d, *J*=5.6 Hz, 2H), 2.45 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.41, 143.33, 131.46, 130.08, 128.34, 126.81, 119.02, 68.01, 21.91; **IR** (film) *v*: 2954, 1722, 1460, 1136, 937, 773 cm^{-1}; **HRMS** (ESI) calcd for $C_{12}H_{14}O_2S$ ($[M+H+Na]^+$): 246.0690; found: 246.0692.

O-allyl S-(4-bromophenyl) carbonothioate (1e)



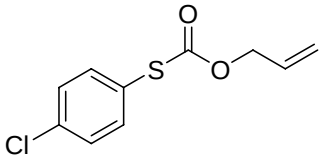
Purified by flash column chromatography (petroleum ether) to afford **1e** (1.22g, 89%) as pale yellow oil. **^{1}H NMR** (400 MHz, CDCl3) δ 7.52 (d, J=8.4 Hz, 2H), 7.39 (d, J=8.4 Hz, 2H), 5.95 – 5.87 (m, 1H), 5.37 – 5.28 (m, 2H), 4.73 – 4.71 (m, 2H); **^{13}C NMR** (101 MHz, CDCl3) δ 168.80, 136.26, 132.40, 131.14, 126.79, 124.34, 119.58, 68.52; **IR** (film) *v*: 3086, 2947, 1726, 1471, 1132, 939, 819 cm^{-1}; **HRMS** (ESI) calcd for $C_{10}H_9BrO_2S$ ($[M+Na]^+$): 294.9404; found: 294.9402.

O-allyl S-(2-bromophenyl) carbonothioate (1f)



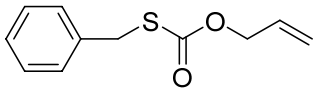
Purified by flash column chromatography (petroleum ether) to afford **1f** (1.13g, 87%) as pale yellow oil. **^{1}H NMR** (400 MHz, CDCl3) δ 7.73 – 7.65 (m, 2H), 7.35 – 7.24 (m, 2H), 6.00 – 5.86 (m, 1H), 5.41 – 5.24 (m, 2H), 4.74 (d, J=5.9 Hz, 1H); **^{13}C NMR** (101 MHz, CDCl3) δ 167.86, 137.34, 133.62, 131.36, 131.17, 129.94, 129.34, 128.02, 119.40, 68.54; **IR** (film) *v*: 3086, 2949, 1728, 1450, 1267, 1141, 1022, 939, 754 cm^{-1}; **HRMS** (ESI) calcd for $C_{10}H_9BrO_2S$ ($[M+Na]^+$): 294.9404; found: 294.9406.

O-allyl S-(4-chlorophenyl) carbonothioate (1g)



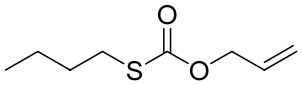
Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford **1g** (1.04g, 90%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.40 – 7.34 (m, 2H), 5.98 – 5.88 (m, 1H), 5.41 – 5.25 (m, 2H), 4.72 (dt, *J*=5.9, 1.3 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.97, 136.10, 136.06, 131.14, 129.44, 126.15, 119.56, 68.50; **IR** (film) *v*: 3086, 2947, 1726, 1475, 1136, 939, 825 cm^{-1}; **HRMS** (ESI) calcd for $C_{10}H_9ClO_2S$ ($[M+Na]^+$): 250.9909; found: 250.9906.

O-allyl S-benzyl carbonothioate (1h)



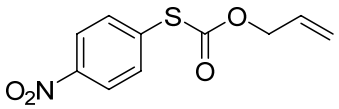
Purified by flash column chromatography (petroleum ether) to afford **1h** (0.87g, 83%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 5H), 5.99 – 5.83 (m, 1H), 5.42 – 5.21 (m, 2H), 4.71 (d, *J*=5.8, 1.4 Hz, 2H), 4.11 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.56, 137.13, 131.45, 128.86, 128.64, 127.46, 119.17, 67.97, 35.41; **IR** (film) *v*: 2927, 1710, 1452, 1136, 935, 704 cm^{-1}; **HRMS** (ESI) calcd for $C_{11}H_{12}O_2S$ ($[M+Na]^+$): 231.0456; found: 231.0453.

O-allyl S-butyl carbonothioate (1i)



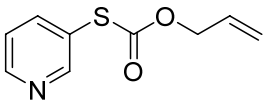
Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford **1i** (0.79g, 90%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.99 – 5.86 (m, 1H), 5.39 – 5.22 (m, 2H), 4.71 – 4.69 (m, 2H), 2.87 (t, *J*=7.4 Hz, 2H), 1.69-1.56 (m, 2H), 1.44 – 1.39 (m, 2H), 0.93 (t, *J*=7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.12, 131.60, 118.94, 67.63, 31.80, 30.73, 21.80, 13.54; **IR** (film) *v*: 2960, 2873, 1712, 1458, 1138, 935 cm^{-1}; **HRMS** (ESI) calcd for $C_8H_{14}O_2S$ ($[M+Na]^+$): 197.0612; found: 197.0615.

O-allyl S-(4-nitrophenyl) carbonothioate (1j)



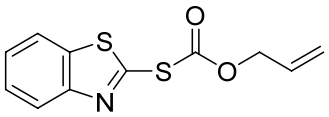
Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford **1j** (1.04g, 87%) as pale yellow solid. Mp: 68-70 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J*=8.9 Hz, 2H), 7.73 (d, *J*=8.9 Hz, 2H), 5.96 – 5.89 (m,1H), 5.56 – 5.18 (m, 2H), 4.77 (d, *J*=5.9 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.38, 148.16, 136.35, 134.61, 130.82, 123.94, 120.00, 68.97; **IR** (film) *v*: 3097, 1720, 1512, 1344, 1161, 943, 846 cm^{-1}; **HRMS** (ESI) calcd for $C_{10}H_9NO_4S$ ($[M+Na]^+$): 262.0150; found: 262.0153.

O-allyl S-(pyridin-3-yl) carbonothioate (1k)



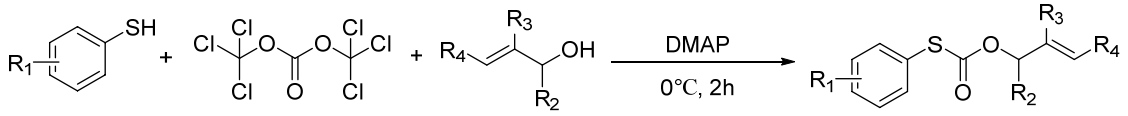
Purified by flash column chromatography (petroleum ether/ethyl acetate, 10/1) to afford **1k** (0.85g, 86%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 – 8.56 (m, 1H), 7.77 – 7.69 (m, 2H), 7.29 – 7.25 (m, 1H), 6.00 – 5.87 (m, 1H), 5.39 – 5.27 (m, 2H), 4.76 (d, *J*= 5.9 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.25, 151.71, 150.16, 137.26, 131.10, 129.38, 123.46, 119.55, 68.42; **IR** (film) *v*: 2949, 1724, 1570, 1450, 1145, 941, 767 cm^{-1}; **HRMS** (ESI) calcd for $C_9H_9NO_2S$ ($[M+H]^+$): 196.0432; found: 196.0431.

O-allyl S-(benzo[d]thiazol-2-yl) carbonothioate (1l)



Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford **1l** (1.08g, 86%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08–7.95 (m, 1H), 7.94–7.82 (m, 1H), 7.52 – 7.40 (m, 2H), 6.02 – 5.92 (m, 1H), 5.48–5.31 (m, 2H), 4.84 (dt, *J*=6.0, 1.3 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.00, 157.78, 152.08, 136.51, 130.52, 126.41, 125.62, 123.08, 121.14, 120.41, 69.44; **IR** (film) *v*: 3062, 1728, 1419, 1147, 1001, 1147, 759 cm^{-1}; **HRMS** (ESI) calcd for $C_{11}H_9NO_2S_2$ ($[M+H]^+$): 252.0153; found: 252.0152.

2. Preparation of substituted allyl carbonothioates

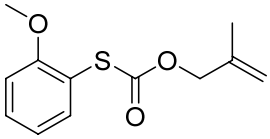


3 **5** **1**

1m-1t was prepared according to the literature procedure[2].

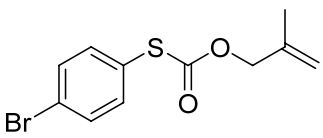
To a solution of a substituted thiophenol **3** (5 mmol) and triphosgene (1.8 mmol) in dry dichloromethane (30 mL) was added 4-dimethylaminopyridine (DMAP) (5 mmol) dropwise at 0 °C. The resulting mixture was stirred for 30 min at that temperature, and then an allylic alcohol **5** (5 mmol) and DMAP (6 mmol) were sequentially added. After stirring for 2 h, the reaction mixture was quenched by adding H_2O (20 mL). The organic phase was separated, dried over Na_2SO_4, concentrated in vacuo, and the residue was purified by flash chromatography. The following compounds were synthesized:

S-(2-methoxyphenyl) O-(2-methylallyl) carbonothioate (1m)



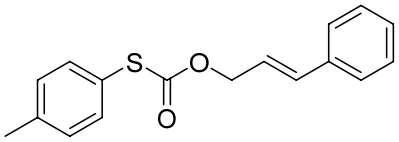
Purified by flash column chromatography (petroleum ether/ethyl acetate, 80/1) to afford **1m** as pale yellow oil (0.83g, 70%). **^{1}H NMR** (400 MHz, CDCl3) δ 7.51 (dd, J = 8.2, 1.6 Hz, 1H), 7.41 (dd, J = 8.2, 1.6 Hz, 1H), 7.01 – 6.93 (m, 2H), 4.99 (s, 1H), 4.94 (s, 1H), 4.62 (s, 2H), 3.88 (d, J = 8.6 Hz, 3H), 1.75 (s, 3H); **^{13}C NMR** (101 MHz, CDCl3) δ 168.84, 159.63, 139.33, 137.06, 131.92, 121.02, 115.87, 113.77, 111.56, 70.75, 56.00, 19.36; **IR** (film) *v*: 2939, 1726, 1479, 1277, 1139, 1069, 1024, 754 cm^{-1}; **HRMS** (ESI) calcd for $C_{12}H_{14}O_3S$ ($[M+Na]^+$): 261.0561; found: 261.0563.

S-(4-bromophenyl) O-(2-methylallyl) carbonothioate (1n)



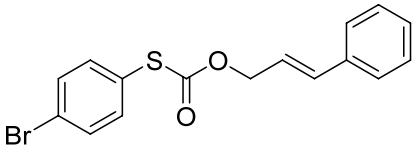
Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford **1n** as pale yellow oil (1.06g, 74%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 4.99 (d, *J* = 6.1 Hz, 1H), 4.97 (s, 1H), 4.64 (s, 2H), 1.76 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.83, 139.03, 136.28, 132.40, 126.86, 124.33, 114.31, 71.21, 19.39; **IR** (film) *v*: 2976, 2941, 1726, 1472, 1387, 1138, 1090, 912, 817 cm^{-1}; **HRMS** (ESI) calcd for $C_{11}H_{11}B_rO_2S$ ($[M+Na]^+$): 308.9561; found: 308.9560.

O-cinnamyl S-(p-tolyl) carbonothioate (1o)



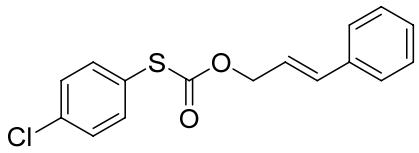
Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford **1o** as pale yellow oil(0.97g, 68%). Mp: 83-85 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.15 (m, 9H), 6.64 (d, *J* = 15.7 Hz, 1H), 6.38 – 6.16 (m, 1H), 4.85 (d, *J* = 5.6 Hz, 2H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.01, 140.00, 136.04, 135.31, 134.97, 130.07, 128.67, 128.31, 126.78, 124.26, 122.29, 68.26, 21.38; **IR** (film) *v*: 2941, 1726, 1472, 1386, 1138, 1069, 912, 817 cm^{-1}; **HRMS** (ESI) calcd for $C_{17}H_{16}O_2S$ ($[M+Na]^+$): 307.0769; found: 307.0766.

S-(4-bromophenyl) O-cinnamyl carbonothioate (1p)



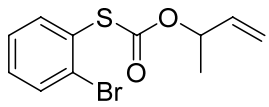
Purified by flash column chromatography (petroleum ether) to afford **1p** as white solid (1.12g, 64%). Mp: 86-89 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H), 7.41 – 7.25 (m, 7H), 6.66 (d, *J* = 15.8 Hz, 1H), 6.38 – 6.19 (m, 1H), 4.88 (d, *J* = 6.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.92, 136.31, 135.88, 135.64, 132.43, 128.68, 128.39, 126.77, 124.38, 121.94, 68.60; **IR** (film) *v*: 2853, 1717, 1472, 1163, 1092, 923, 819, 740 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{13}BrO_2S$ ($[M+Na]^+$): 370.9717; found: 370.9716.

S-(4-chlorophenyl) O-cinnamylcarbonothioate (1q)



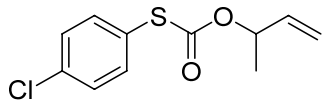
Purified by flash column chromatography (petroleum ether) to afford **1q** as white solid(1.01g, 66%). Mp: 83-85 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.46 (m, 2H), 7.43 – 7.23 (m, 7H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.32 – 6.26 (m, 1H), 4.88 (d, *J* = 6.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.08, 136.12, 135.89, 135.63, 129.48, 128.68, 128.39, 126.78, 126.22, 121.96, 68.59; **IR** (film) *v*: 2920, 1737, 1468, 1383, 1087, 970, 808, 756 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{13}ClO_2S$ ($[M+Na]^+$): 327.0222; found: 327.0220.

S-(2-bromophenyl) O-(but-3-en-2-yl) carbonothioate (1r)



Purified by flash column chromatography (petroleum ether/ethyl acetate, 80/1) to afford **1r** as pale yellow oil(1.05g, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.63 (m, 2H), 7.37 – 7.23 (m, 2H), 5.93 – 5.79 (m, 1H), 5.46 – 5.40 (m, 1H), 5.30 – 5.26 (m, 1H), 5.20 – 5.17 (m, 1H), 1.38 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.27, 137.31, 136.67, 133.58, 131.25, 127.97, 116.97, 75.73, 20.00; **IR** (film) *v*: 2984, 1730, 1449, 1429, 1149, 1022, 845, 752 cm^{-1}; **HRMS** (ESI) calcd for $C_{11}H_{11}BrO_2S$ ($[M+Na]^+$): 308.9561; found: 308.9563.

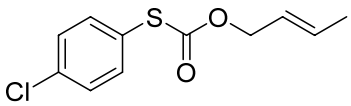
O-(but-3-en-2-yl) S-(4-chlorophenyl) carbonothioate (1s)



Purified by flash column chromatography (petroleum ether/ethyl acetate, 80/1) to afford **1s** as pale yellow oil(0.89g, 73%). **^{1}H NMR** (400 MHz, CD Cl_3) δ 7.46 (t, *J* =8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 5.89 – 5.81 (m, 1H), 5.45 – 5.39 (m, 1H), 5.30 – 5.17 (m, 2H), 1.38 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.39, 136.64, 136.05, 129.39,

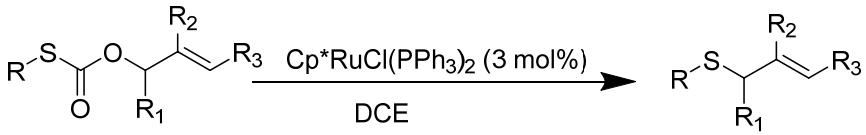
126.42, 117.11, 75.69, 19.98; **IR** (film) ν: 2985, 1726, 1477, 1150, 1094, 1037, 847, 819 cm^{-1}; **HRMS** (ESI) calcd for $C_{11}H_{11}ClO_2S$ ([M+Na]$^+$): 265.0066; found: 265.0069.

(E)-O-(but-2-en-1-yl) S-(4-chlorophenyl) carbonothioate (1t)



Purified by flash column chromatography (petroleum ether/ethyl acetate, 80/1) to afford **1t** as pale yellow oil(0.91g, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.37 (, *J* = 8.3 Hz, 2H), 5.90 – 5.76 (m, 1H), 5.67 – 5.54 (m, 1H), 4.65 (d, *J* = 6.7 Hz, 2H), 1.73 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.96, 136.05, 133.14, 129.41, 126.36, 124.19, 68.79, 17.82. **IR** (film) ν: 2945, 1724, 1477, 1136, 1092, 1015, 966, 821 cm^{-1}; **HRMS** (ESI) calcd for $C_{11}H_{11}ClO_2S$ ([M+Na]+): 265.0066; found: 265.0067.

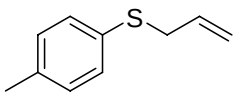
3. General procedure for ruthenium-catalyzed decarboxylative allylic etherification



1 **2**

To a 2 dram septum-capped vial were added sequentially **1** (0.3 mmol), Cp*RuCl$(PPh_3)_2$ (0.009 mmol, 3 mol%) and 3 mL of dry DCE, and the resulting homogenous solution was stirred at 50 °C until **1** disappeared on TLC. After complete reaction, the solvent was removed under reduced pressure, and the crude product was purified through flash chromatography on silica gel to afford target compounds **2** series as following.

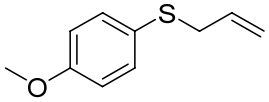
allyl(p-tolyl)sulfane (2a)



Purified by flash column chromatography (petroleum ether) to afford **2a** (47.3mg, 96%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J*=8.0 Hz, 2H), 7.09 (d, *J*=8.0

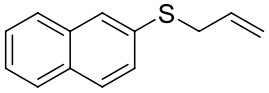
Hz, 2H), 5.91 – 5.81 (m, 1H), 5.13 – 4.98 (m, 1H), 5.07 – 5.02 (m, 1H), 3.50 (d, *J*=6.9 Hz, 2H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.43, 133.84, 132.03, 130.70, 129.58, 117.42, 37.91, 21.04. **IR** (film) *v*: 3018, 2920, 1636, 1492, 1224, 987, 918, 804 cm^{-1}.

allyl(4-methoxyphenyl)sulfane (2b)



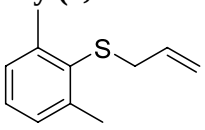
Purified by flash column chromatography (petroleum ether/ethyl acetate,60/1) to afford **2b** (52.0mg, 94%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 1H), 6.85 – 6.81 (m, 1H), 5.93 – 5.77 (m, 1H), 5.06 – 4.93 (m, 2H), 3.79 (s, 3H), 3.43 (d, *J* = 7.1, 1.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.08, 134.04, 133.91, 125.81, 117.26, 114.41, 55.30, 39.35; **IR** (film) *v*: 2922, 1573, 1461, 1205, 1125, 809, 742 cm^{-1}.

allyl(naphthalen-2-yl)sulfane (2c)



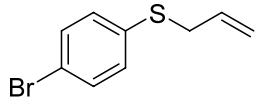
Purified by flash column chromatography (petroleum ether) to afford **2c** (57.7mg, 96%)as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 4H), 7.48 – 7.41 (m, 3H), 5.99 – 5.86 (m, 1H), 5.20-5.05 (m, 2H), 3.65 (d, *J* = 6.8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.71, 133.48, 133.44, 131.86, 128.28, 127.78, 127.72, 127.71, 127.13, 126.49, 125.71, 117.84, 37.07; **IR** (film) *v*: 3053, 2922, 1624, 1587, 1425, 1226, 920, 812, 742 cm^{-1}.

allyl(2,6-dimethylphenyl)sulfane (2d)



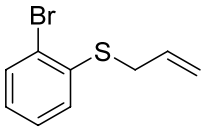
Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford **2 d** (47.1mg, 88%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 – 10 (m, 3H), 5. 88 – 5.77 (m, 1H), 4.95-4.82 (m, 2H), 3.28 (d, *J*=7.3 Hz, 2H), 2.53 (s, 6H); **^{13}C NMR** (10 1 MHz, $CDCl_3$) δ 143.32, 134.03, 132.86, 128.24, 116.80, 38.37, 22.16; **IR** (film) *v*: 2953, 2920, 1635, 1460, 1224, 916, 769 cm^{-1}.

allyl(4-bromophenyl)sulfane (2e)



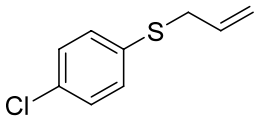
Purified by flash column chromatography (petroleum ether) to afford **2e** (61.9mg, 90%)as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 5.88 – 5.79 (m, 1H), 5.14 – 5.07 (m, 2H), 3.53 – 3.51 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.07, 133.18, 131.82, 131.44, 120.15, 117.99, 37.24; **IR** (film) *v*: 2922, 1473, 1226, 1091, 920, 808 cm^{-1}.

allyl(2-bromophenyl)sulfane (2f)



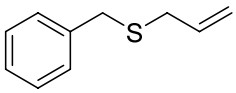
Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford **2 f** (59.1mg, 86%) as pale yellow oil.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.30 – 7. 23 (m, 2H), 7.03 (s, 1H), 5.99 – 5.82 (m, 1H), 5.33 – 5.05 (m, 2H), 3.60 (d, *J* = 6.7 Hz, 2 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.41, 132.96, 132.59, 128.91, 127.60, 126.82, 123. 89, 118.48, 36.16; **IR** (film) *v*: 2922, 1573, 1448, 1109, 921, 742 cm^{-1}.

allyl(4-chlorophenyl)sulfane (2g)：



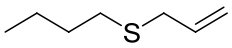
Purified by flash column chromatography (petroleum ether) to afford **2g** (48.7mg, 89%) as pale yellow oil. 1H NMR (400 MHz, CDCl3) δ 7.30 – 7.17 (m, 4H), 5.89 – 5.79 (m, 1 H), 5.18 - 5.01 (m, 2H), 3.51 (d, *J*=6.8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.34, 133.25, 132.30, 131.34, 128.91, 117.94, 37.45; **IR** (film) *v*: 3082, 2922, 1635, 1475, 1095, 814, 731 cm^{-1}.

allyl(benzyl)sulfane (2h)



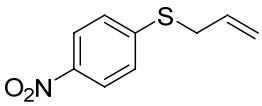
Purified by flash column chromatography (petroleum ether) to afford **2h** (45.2mg, 91%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 5.88 – 5.71 (m, 1H), 5.18 – 5.04 (m, 2H), 3.66 (s, 2H), 3.03 (d, *J* = 7.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.32, 134.21, 129.02, 128.47, 126.93, 117.30, 34.94, 34.09; **IR** (film) *v*: 2924, 1726, 1454, 1271, 916, 769 cm^{-1}.

allyl(butyl)sulfane (2i)



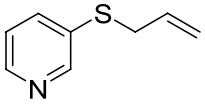
Purified by flash column chromatography (petroleum ether) to afford **2i** (34.0 mg, 87%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.85 – 5.74 (m, 1H), 5.14 – 5.08 (m, 1H), 5.06 (d, *J* =1.2 Hz, 1H), 3.14 – 3.10 (m, 2H), 2.46 (t, *J* =8.0 Hz, 2H), 1.61-1.48 (m, 2H), 1.46-1.32 (m, 2H), 0.91 (t, *J*=7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.59, 116.64, 34.76, 31.42, 30.38, 21.99, 13.70; **IR** (film) *v*: 3358, 2922, 2852, 1656, 1462 cm^{-1}.

allyl(4-nitrophenyl)sulfane (2j)



Purified by flash column chromatography (petroleum ether/ethyl acetate,40/1) to afford **2 j** (48.6 mg, 83%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J*=8.9 Hz, 2 H), 7.35 (d, *J*=8.9 Hz, 2H), 5.94 – 5.84 (m, 1H), 5.35 – 5.30 (m, 1H), 5.23 – 5.20 (m, 1H), 3.68 (d, *J*=6.9 Hz 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.82, 145.22, 131.95, 126.80, 1 23.87, 119.05, 35.21; **IR** (film) *v*: 2920, 1640, 1512, 1336, 1087, 842, cm^{-1}.

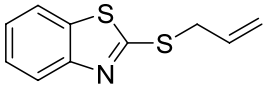
3-(allylthio)pyridine (2k)



Purified by flash column chromatography (petroleum ether/ethyl acetate,10/1) to afford **2k** (42.8mg,86%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 – 8.42 (m, 1H),

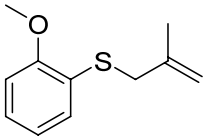
7.52 – 7.41 (m, 1H), 7.18 – 7.16 (m, 1H), 7.03 – 6.92 (m, 1H), 6.05 – 5.88 (m, 1H), 5.31 – 5.26 (m, 1H), 5.12 – 5.09 (m, 1H), 3.85 – 3.83 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.58, 149.43, 135.93, 133.84, 122.28, 119.50, 117.51, 33.05; **IR** (film) *v*: 2942, 1491, 1224, 987, 913, 803, 765 cm^{-1}.

2-(allylthio)benzo[d]thiazole (2l)



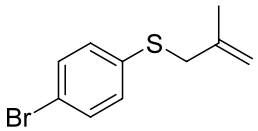
Purified by flash column chromatography (petroleum ether) to afford **2l** (53.90 mg, 87%) as pale yellow oil. **^{1}H NMR** (400 MH z,$CDCl_3$) δ 7.88 (dd, *J*=8.0, 1.2 Hz, 1H), 7.75 (dd, *J*=8.0, 1.2 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.34-7.22 (m, 1H), 6.08 – 5.97 (m, 1H), 5.41 – 5. 36 (m, 1H), 5.22 – 5.19 (m, 1H), 4.00 (dt, *J*=7.0, 1.2 Hz, 2H); **^{13}C NMR** (101 MHz, CDC l_3) δ 166.18, 153.21, 135.33, 132.32, 126.05, 124.28, 121.59, 120.97, 119.17, 36.26; **IR** (f ilm) *v*: 3062, 2922, 1460, 1236, 995, 756 cm^{-1}.

(2-methoxyphenyl)(2-methylallyl)sulfane (2m)



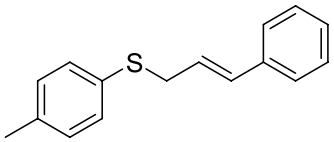
Purified by flash column chromatography (petroleum ether/ethyl acetate, 80/1) to afford **2m** (53.1mg, 91%)as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 1H), 7.23 – 7.15 (m, 1H), 6.93 – 6.82 (m, 2H), 4.79 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.51 (s, 2H), 1.85 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.75, 140.95, 130.87, 127.56, 124.22, 120.89, 113.75, 110.46, 55.74, 40.11, 21.29; **IR** (film) *v*: 2954, 2924, 2854, 1579, 1471, 1244, 1026, 894, 748 cm^{-1}; IR (film) *v*: 2954, 2924, 2854, 1579, 1471, 1244, 1026, 894, 748 cm^{-1}.

(4-bromophenyl)(2-methylallyl)sulfane (2n)



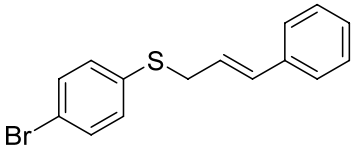
Purified by flash column chromatography (petroleum ether) to afford **2n** (68.6mg, 94%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.81 (d, *J* = 5.2 Hz, 2H), 3.49 (s, 2H), 1.84 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.12, 140.39, 135.57, 131.7 8, 131.63, 120.16, 114.34, 41.99, 21.07. IR (film) *v*: 3078, 2972, 2918, 1647, 1566, 1471, 1091, 1006, 898, 810, 771; **IR** (film) *v*: 2972, 2918, 1647, 1566, 1471, 1091, 1006, 898, 810 cm^{-1}.

cinnamyl(p-tolyl)sulfane (2o)



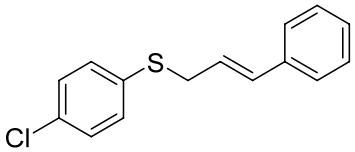
Purified by flash column chromatography (petroleum ether) to afford **2o** (67.1mg, 93%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.17 (m, 7H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.29 – 6.17 (m, 1H), 3.65 (d, *J* = 7.0 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.87, 136.67, 132.60, 131.96, 131.16, 129.66, 128.53, 127.53, 126.36, 125.41, 37.88, 21.07; **IR** (film) *v*: 3026, 2922, 1701, 1678, 1490, 1450, 1122, 966, 806, 750, 696 cm^{-1}.

(4-bromophenyl)(cinnamyl)sulfane (2p)



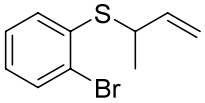
Purified by flash column chromatography (petroleum ether) to afford **2p** (78.4mg, 89%) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 77.41 – 7.36 (m, 2H), 7.34 – 7.28 (m, 4H), 7.26 – 7.20 (m, 3H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.27 – 6.16 (m, 1H), 3.68 (d, *J* = 7.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.55, 135.02, 133.13, 131.90, 131.86, 128.59, 127.73, 126.37, 124.62, 120.41, 37.20; **IR** (film) *v*: 2920, 1468, 1383, 1213, 1088, 970, 808 cm^{-1}.

(4-chlorophenyl)(cinnamyl)sulfane (2q)



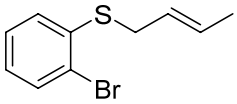
Purified by flash column chromatography (petroleum ether) to afford **2q** (68.9 mg, 87%) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.17 (m, 9H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.28 – 6.14 (m, 1H), 3.67 (d, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.57, 134.27, 133.08, 132.56, 131.80, 128.99, 128.58, 127.72, 126.36, 124.69, 37.43; **IR** (film) *v*: 2922, 1475, 1389, 1221, 1097, 968, 810, 756 cm^{-1}.

(2-bromophenyl)(but-3-en-2-yl)sulfane (2r-1)



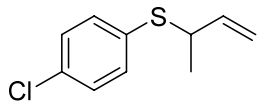
Purified by flash column chromatography (petroleum ether) to afford **2r-1** (32.5mg, 45%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 1H), 7.31 – 7.17 (m, 3H), 5.89 – 5.75 (m, 1H), 5.08 – 4.93 (m, 2H), 3.91 (p, *J* = 7.0 Hz, 1H), 1.44 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.32, 132.89, 129.97, 128.54, 127.58, 126.56, 124.98, 115.31, 35.43, 17.79; **IR** (film) *v*: 2920, 2852, 1573, 1446, 1220, 1020, 962, 744 cm^{-1}.

(2-bromophenyl)(but-2-en-1-yl)sulfane (2r-2)



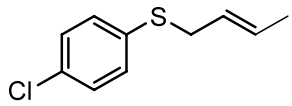
Purified by flash column chromatography (petroleum ether) to afford **2r-2** (32.8 mg, 45%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 2H), 7.10 – 6.97 (m, 2H), 5.73 – 5.61 (m, 1H), 5.59 – 5.48 (m, 1H), 3.62 – 3.51 (m, 2H), 1.66 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.01, 136.50, 133.08, 132.60, 127.86, 127.50, 123.59, 115.31, 45.39, 20.03; **IR** (film) *v*: 2920, 2852, 1573, 1446, 1220, 1020, 962, 744 cm^{-1}.

but-3-en-2-yl(4-chlorophenyl)sulfane (2s-1)



Purified by flash column chromatography (petroleum ether) to afford **2s-1** (27.1mg, 45.5%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.23 (m, 4H), 5.85 – 5.70 (m, 1H), 4.95 – 4.88 (m, 2H), 3.74 – 3.67 (m, 1H), 1.38 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.16, 131.13, 129.37, 128.84, 128.83, 114.95, 46.71, 20.04; **IR** (film) *v*: 2966, 2992, 1475, 1386, 1220, 1095, 962, 920, 815 cm^{-1}.

(E)-but-2-en-1-yl(4-chlorophenyl)sulfane (2s-2)



Purified by flash column chromatography (petroleum ether) to afford **2s-2** (27.1mg, 45.5%) as pale yellow oil.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 5.64 – 5.42 (m, 2H), 3.56 – 3.42 (m, 2H), 1.65 (d, *J* = 5.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.60, 134.16, 131.13, 128.83, 125.81, 114.95, 36.67, 17.72; **IR** (film) *v*: 2966, 2992, 1475, 1386, 1220, 1095, 962, 920, 815 cm^{-1}.

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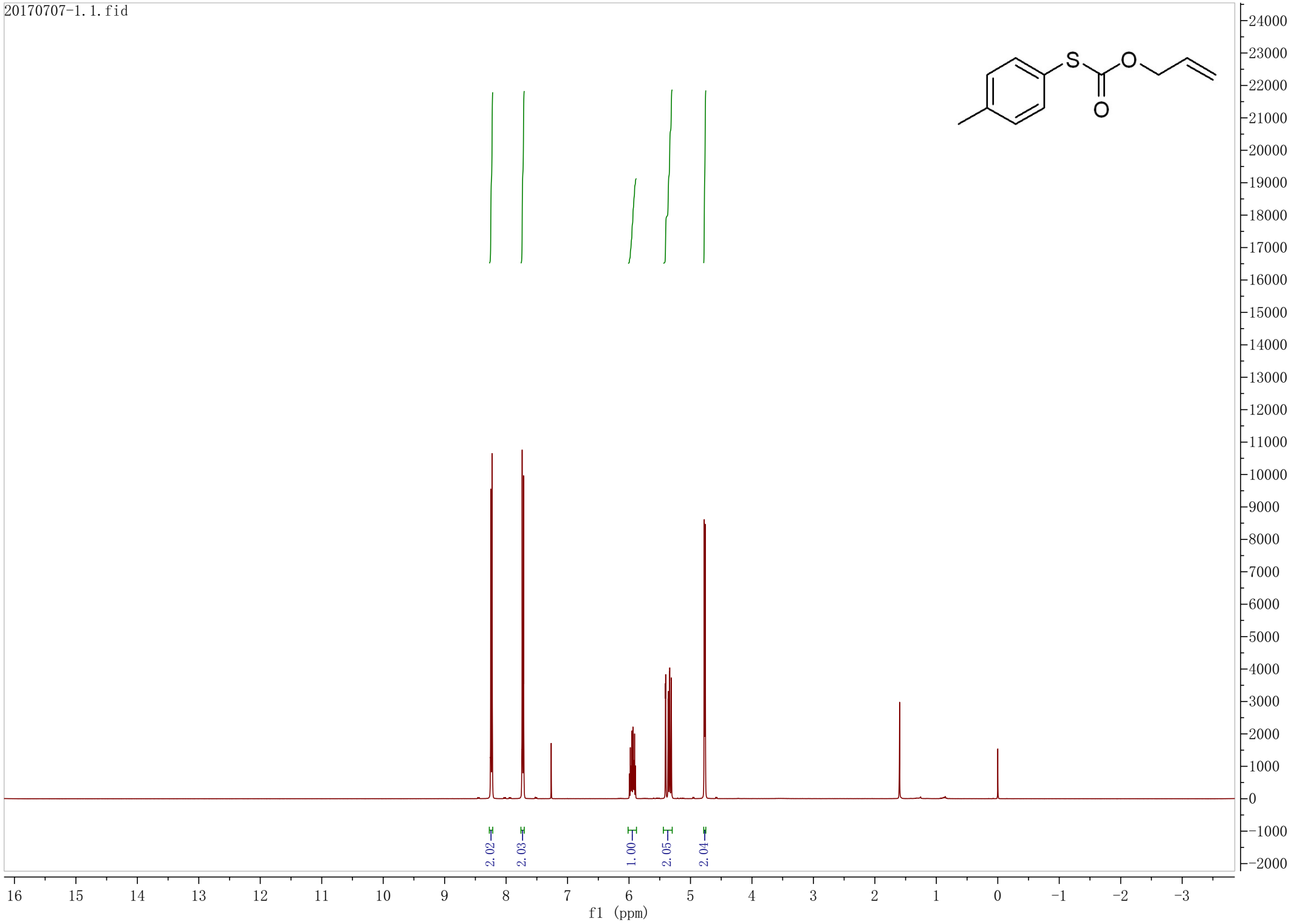
1. Breen G F. Enzymatic resolution of a secondary amine using novel acylating reagents[J]. Tetrahedron A symmetry, 2004, 15(9):1427-1430.
2. Kim D, Reddy S, Singh O V, et al. Ir(I) - Catalyzed Enantioselective Decarboxylative Allylic Etherifica tion: A General Method for the Asymmetric Synthesis of Aryl Allyl Ethers[J]. Organic Letters, 2013, 15 (3):512-515.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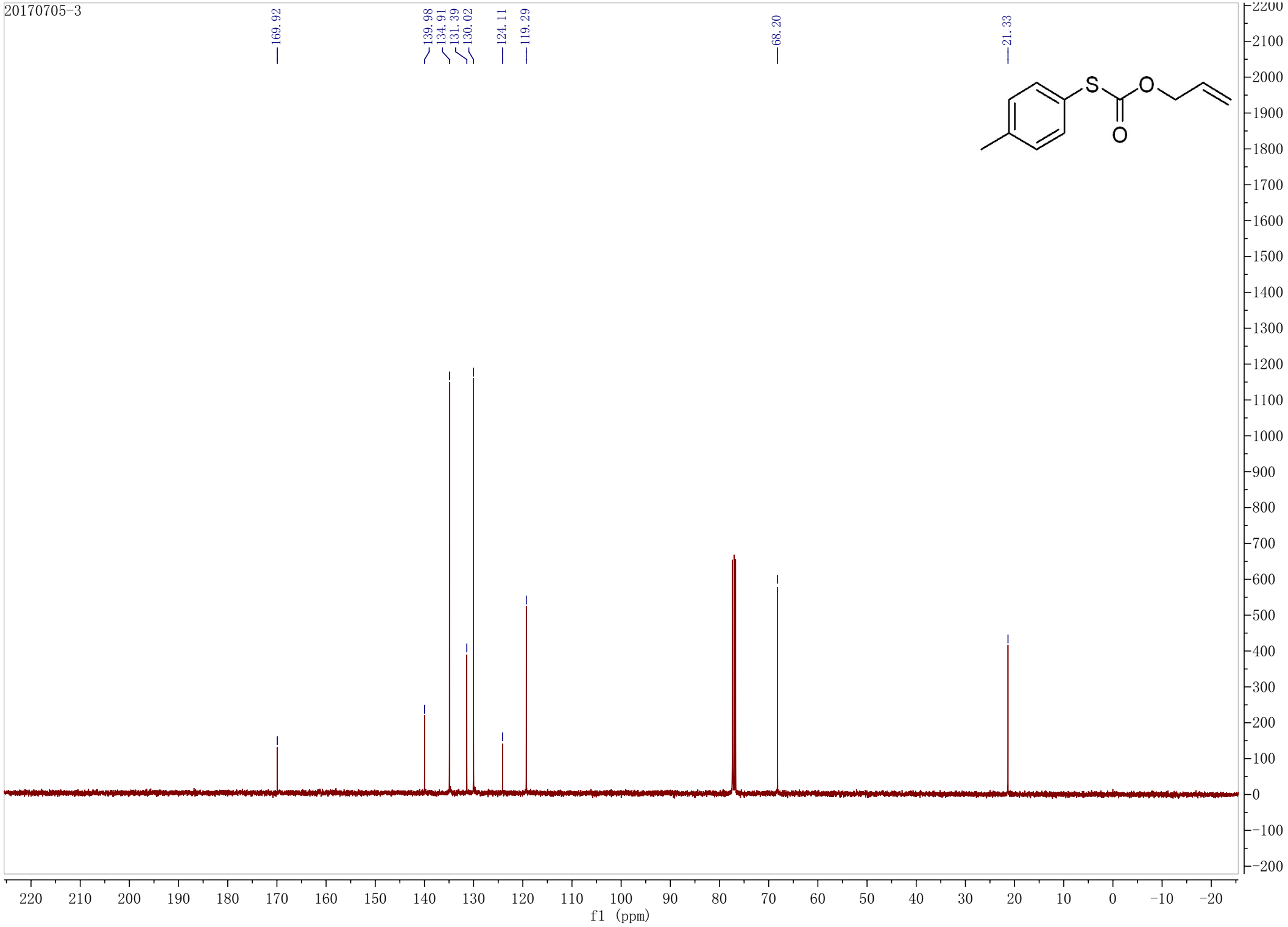
2.05
2.04
f1 (ppm)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124.11
119.29
68.20
21.33
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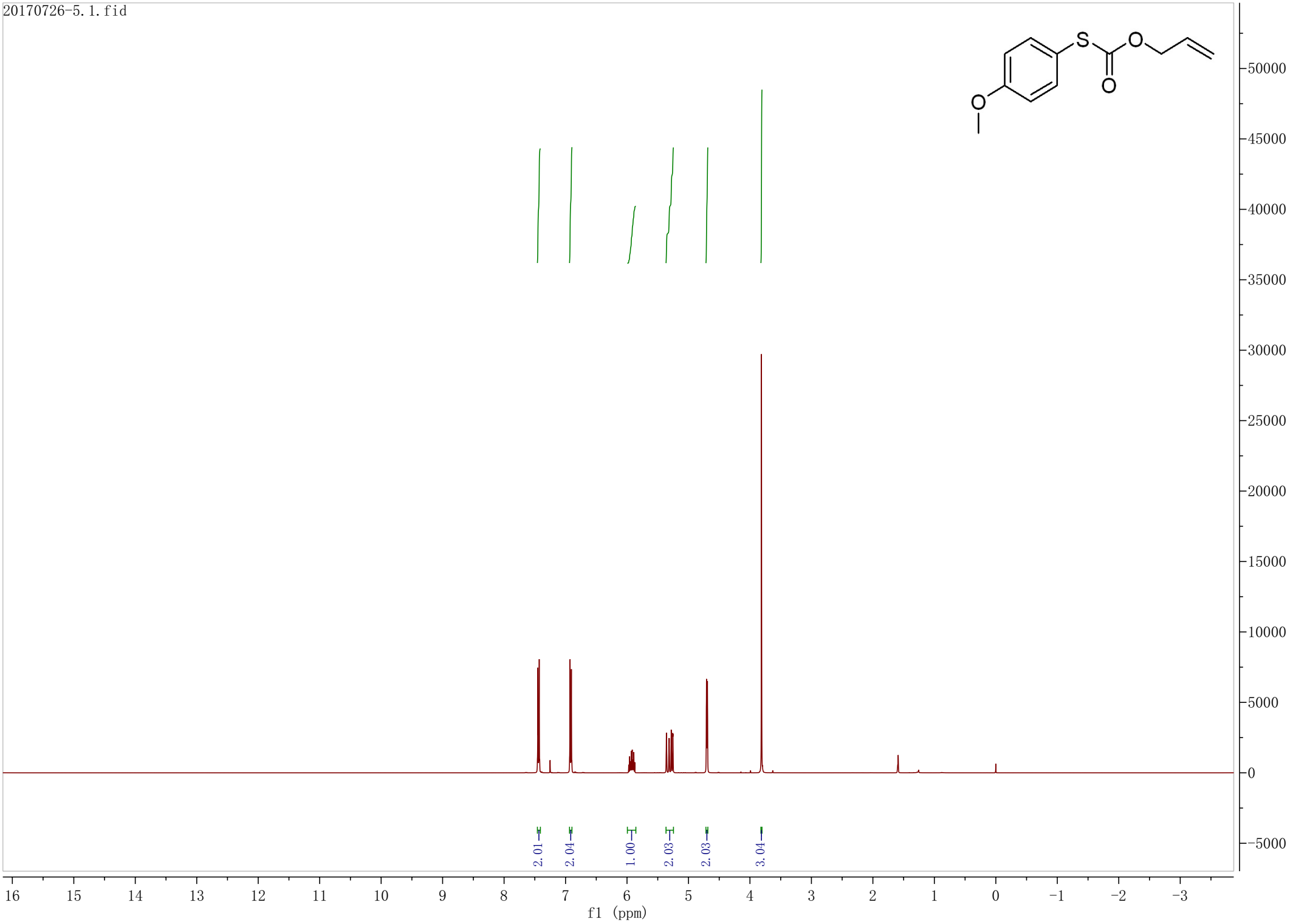
O
O
f1 (ppm)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2.04
1.00
2.03
2.03
3.04
16
15
14
13
12
11
10
9
8
7
6
5
4
3
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1
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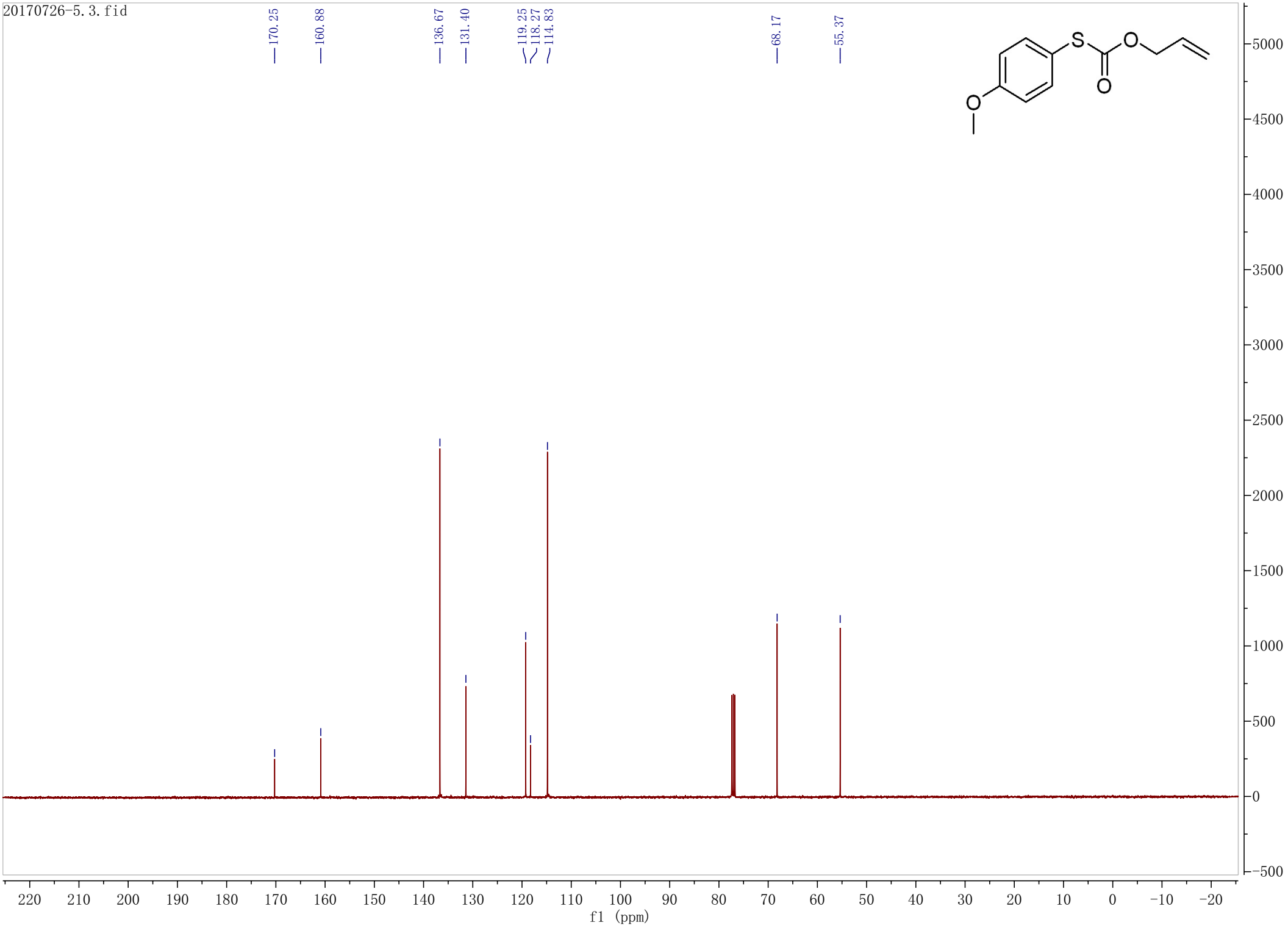
-1
-2
-3
f1 (ppm)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500
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200
190
180
170
160
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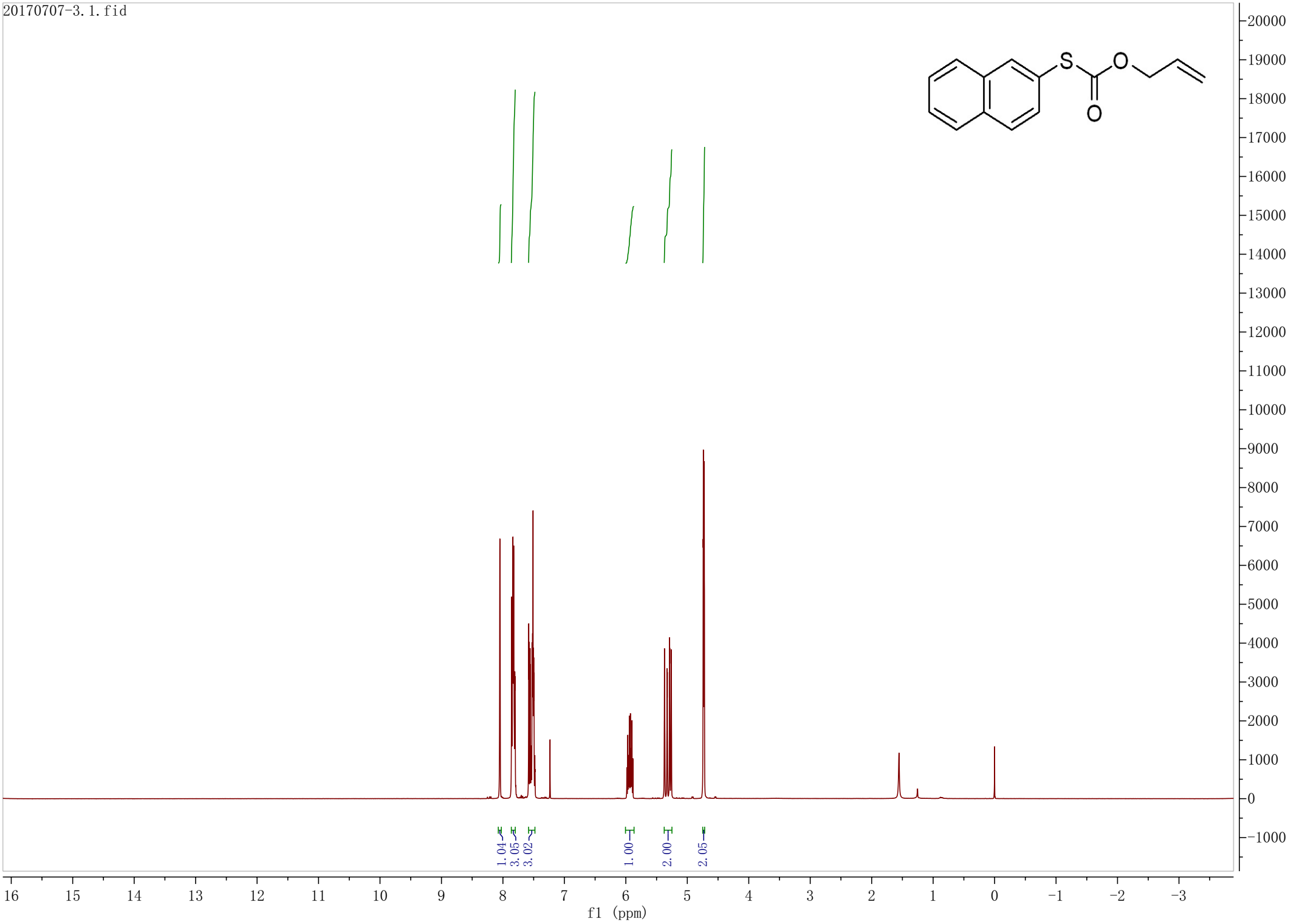
f1 (ppm)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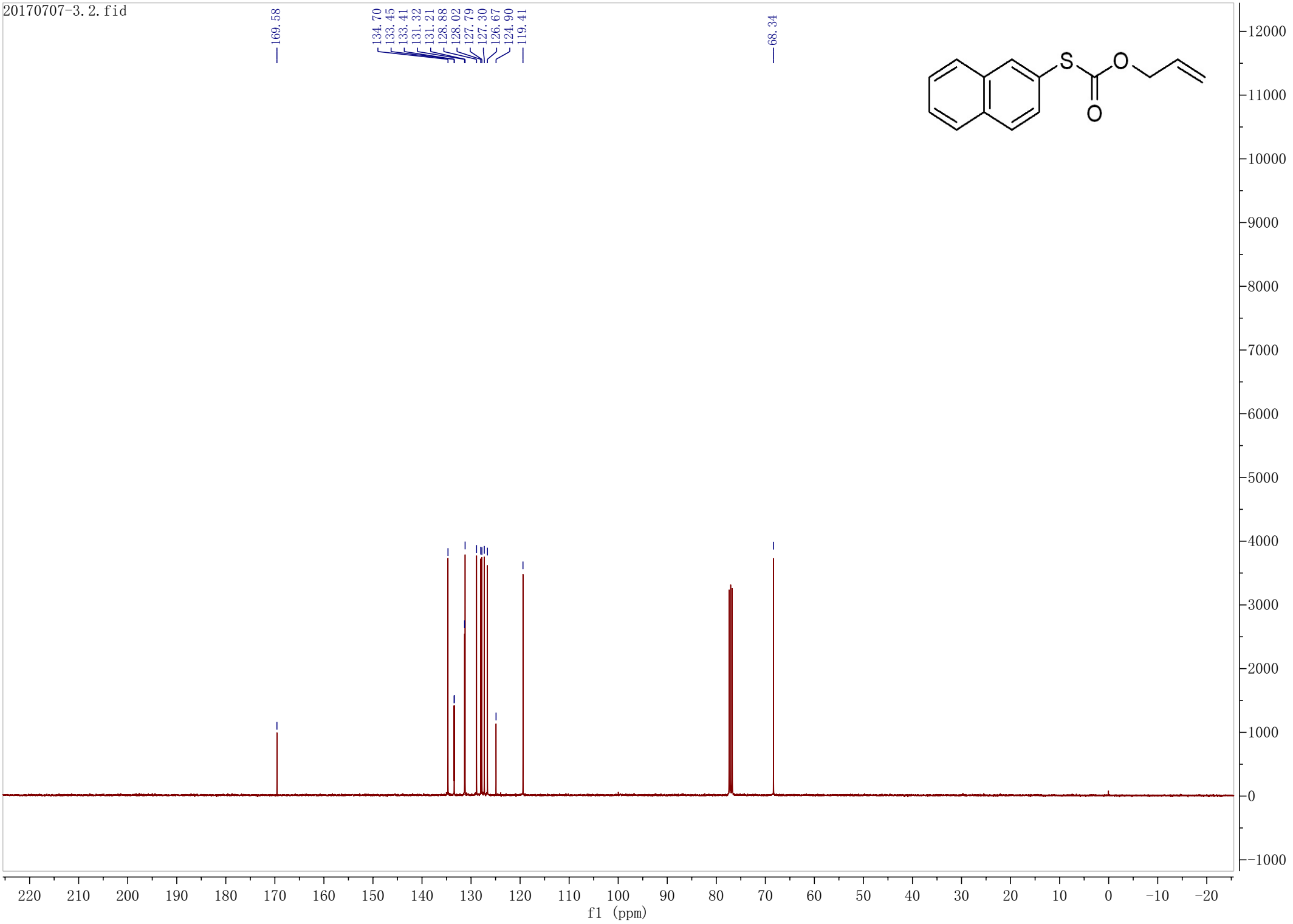
1.00
2.00
2.05
f1 (ppm)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128.02
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119.41
68.34
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9000
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7000
6000
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1000
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190
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170
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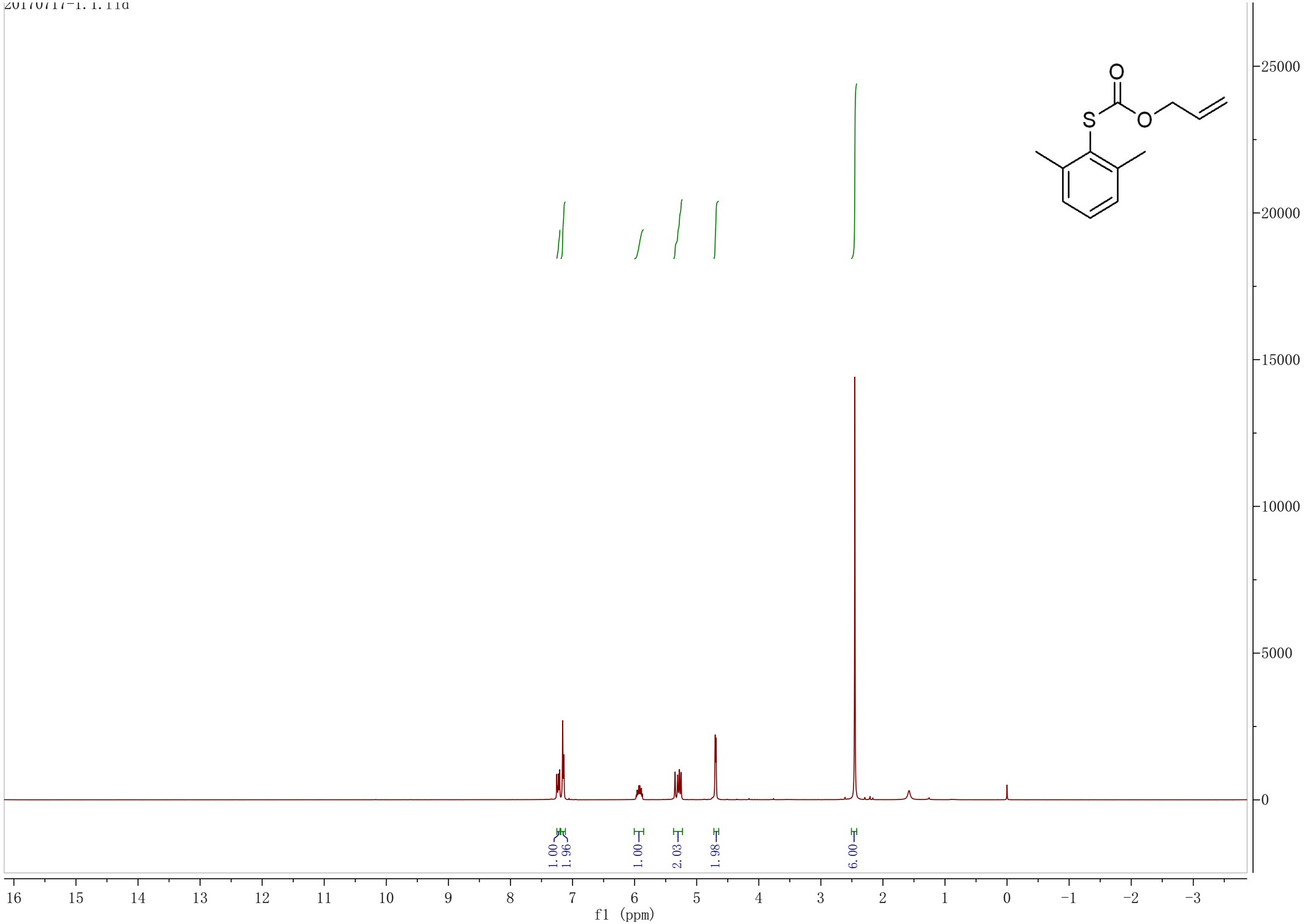
f1 (ppm)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6.00
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9
8
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6
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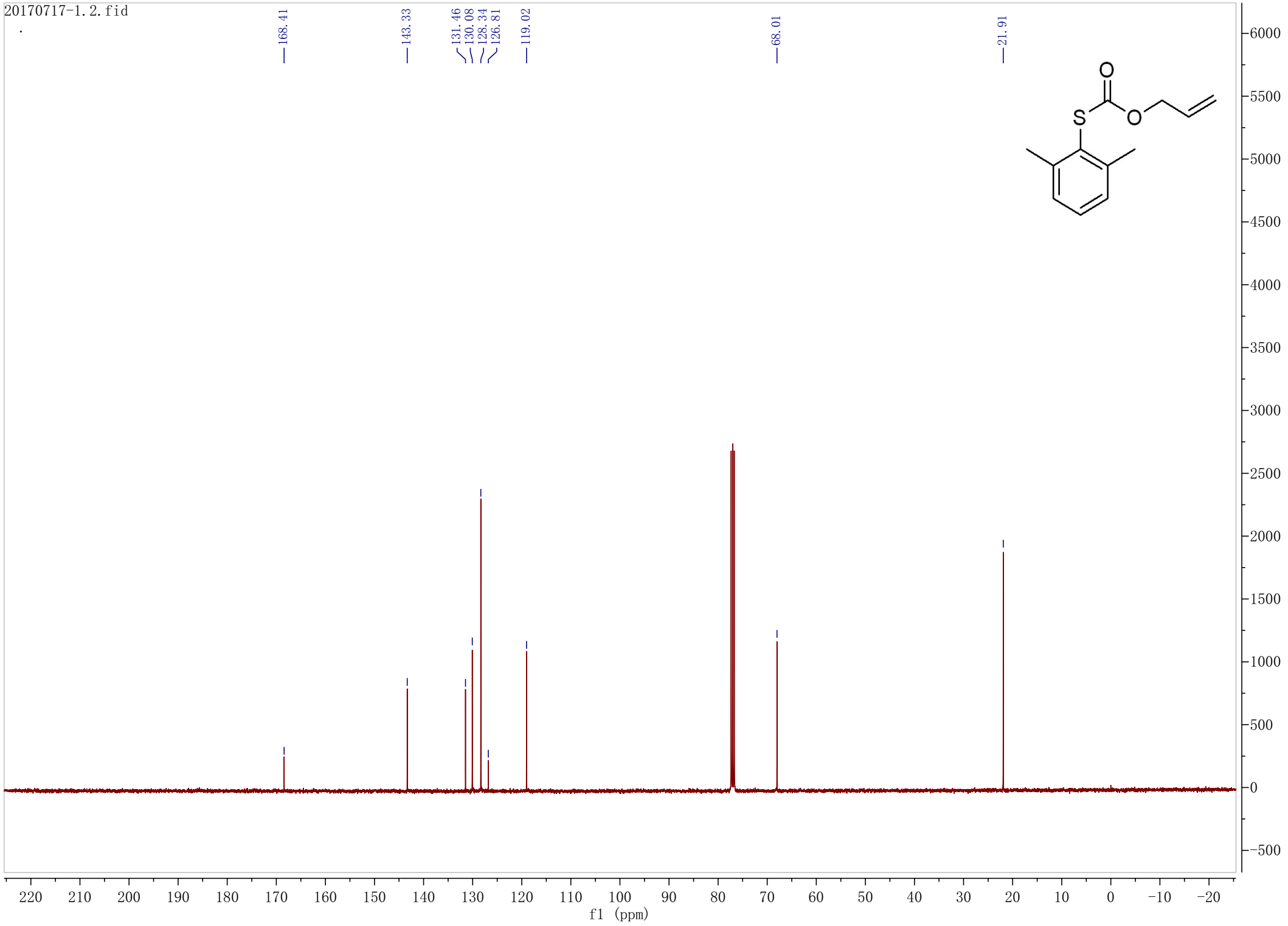
f1 (ppm)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128.34
126.81
119.02
68.01
21.91
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5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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200
190
180
170
160
150
140
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100
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80
70
60
50
40
30
20
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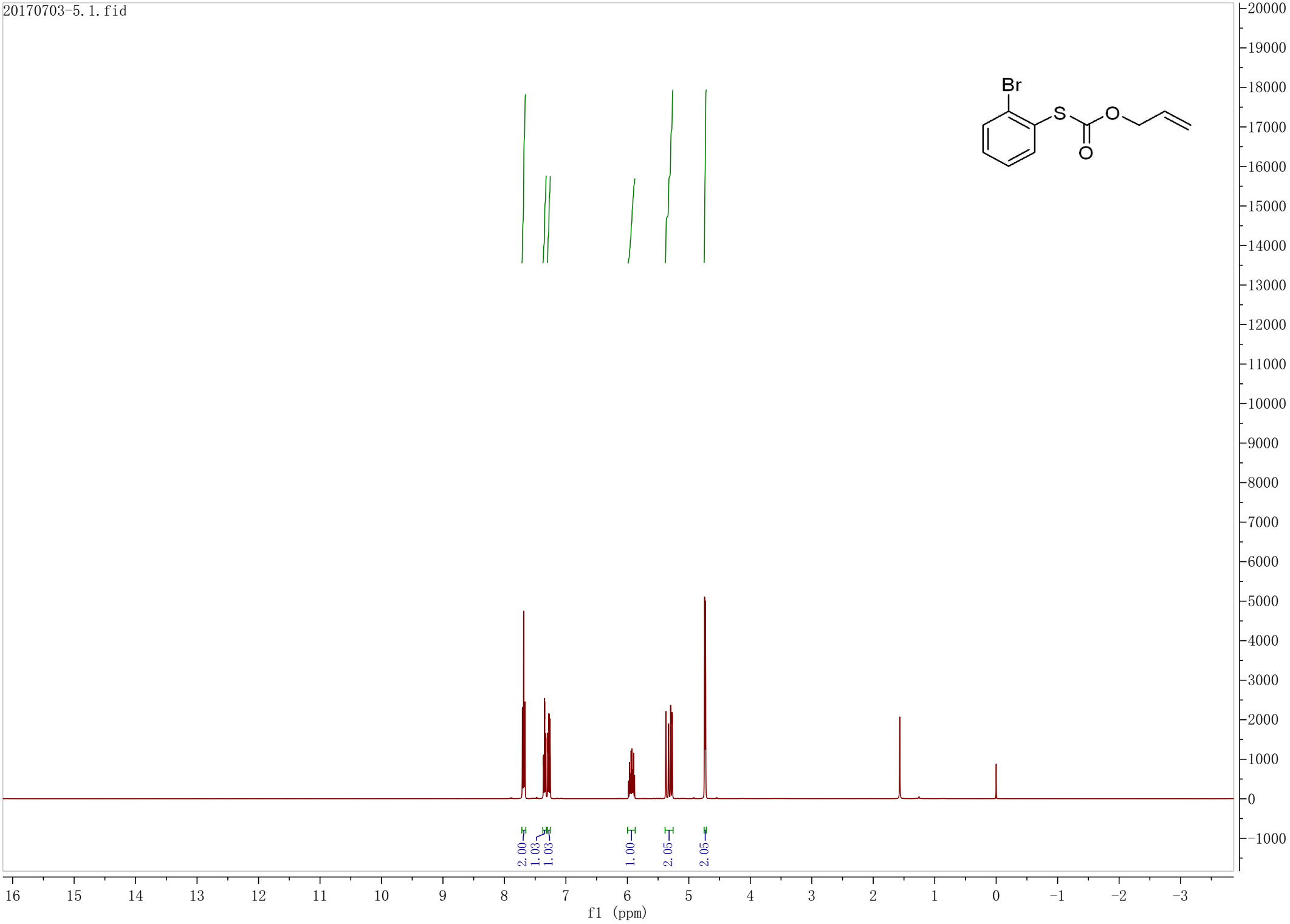
f1 (ppm)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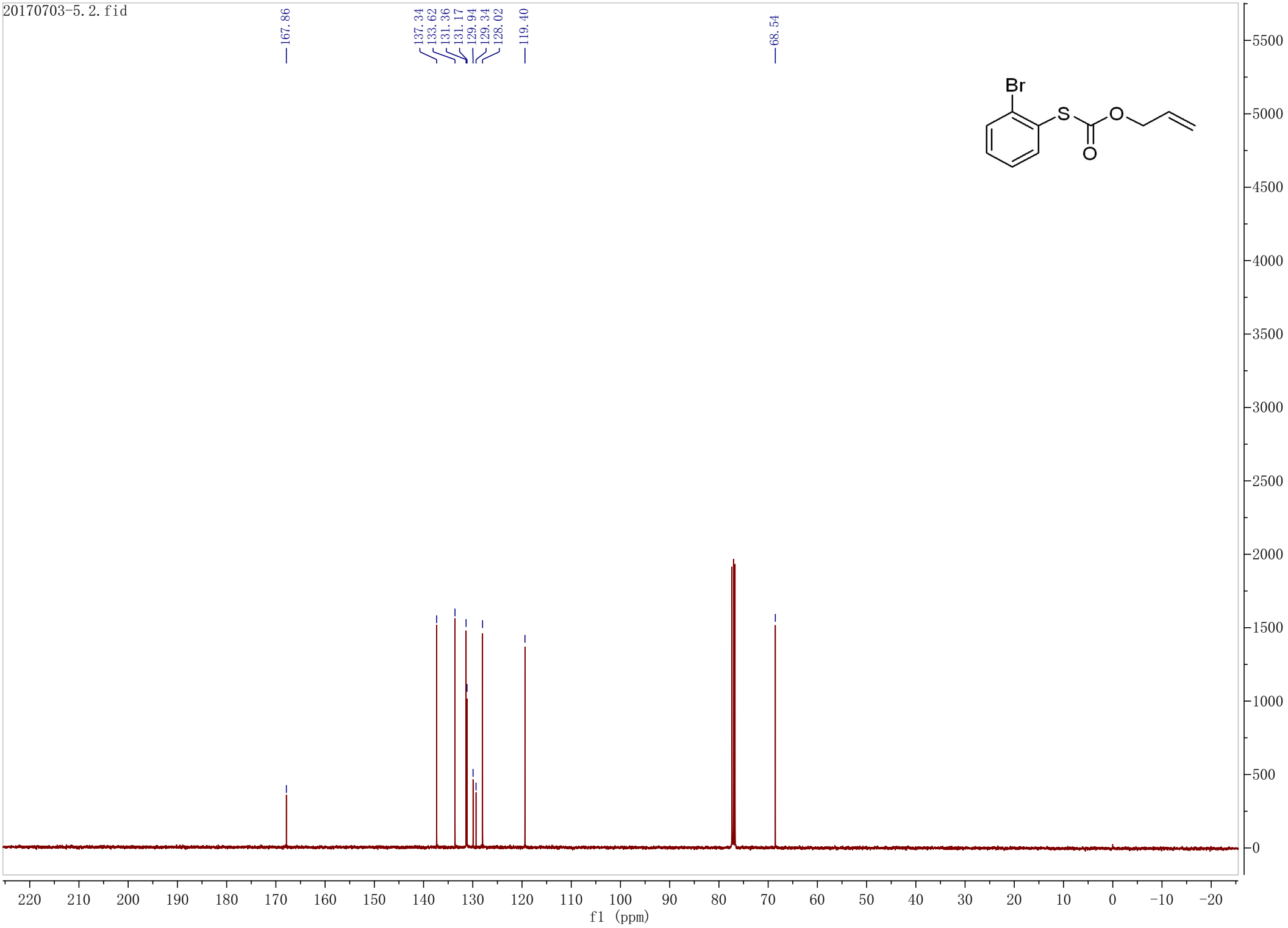
1.00
2.05
2.05
f1 (ppm)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128.02
119.40
68.54
Br
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O
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2500
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1500
1000
500
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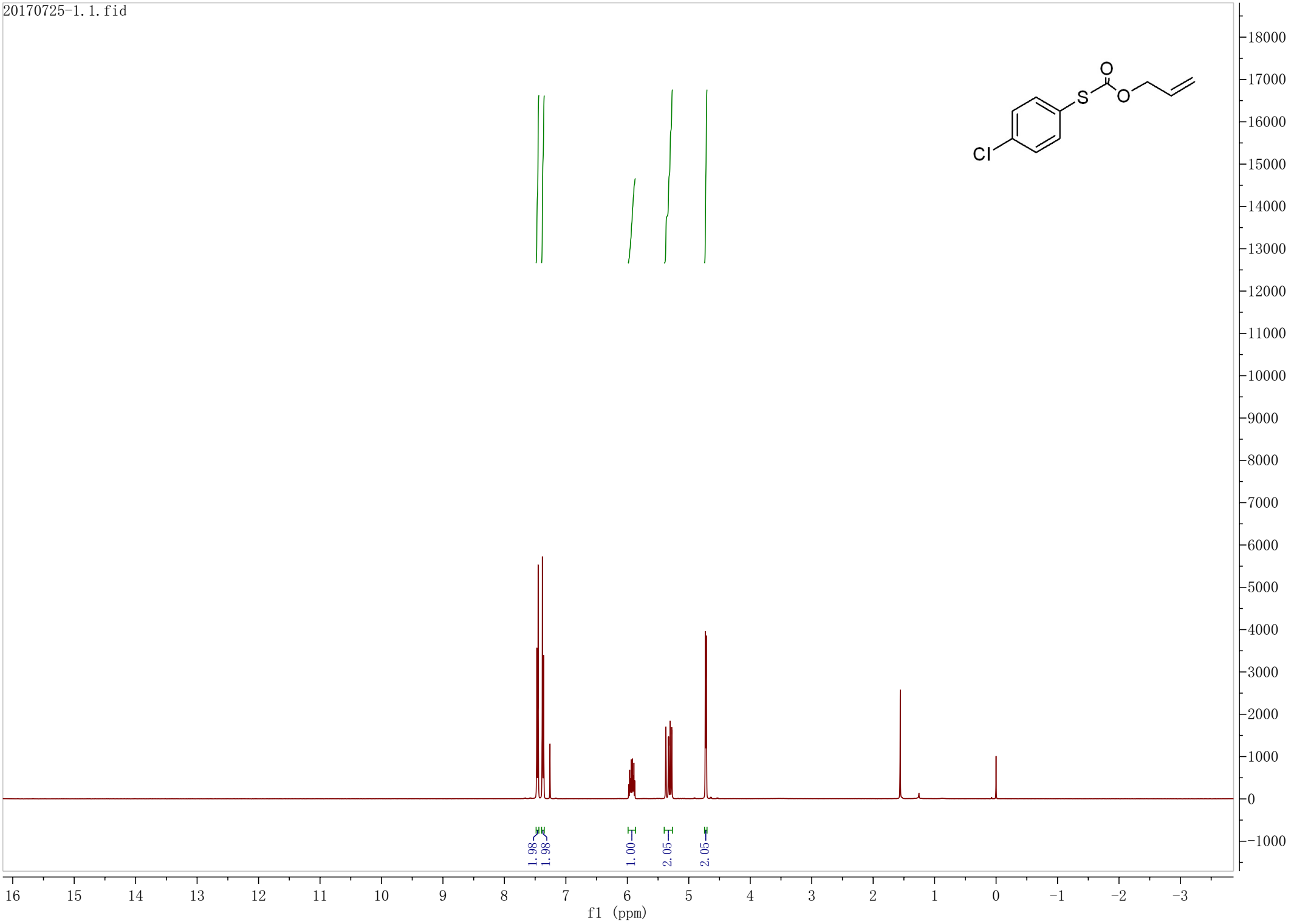
f1 (ppm)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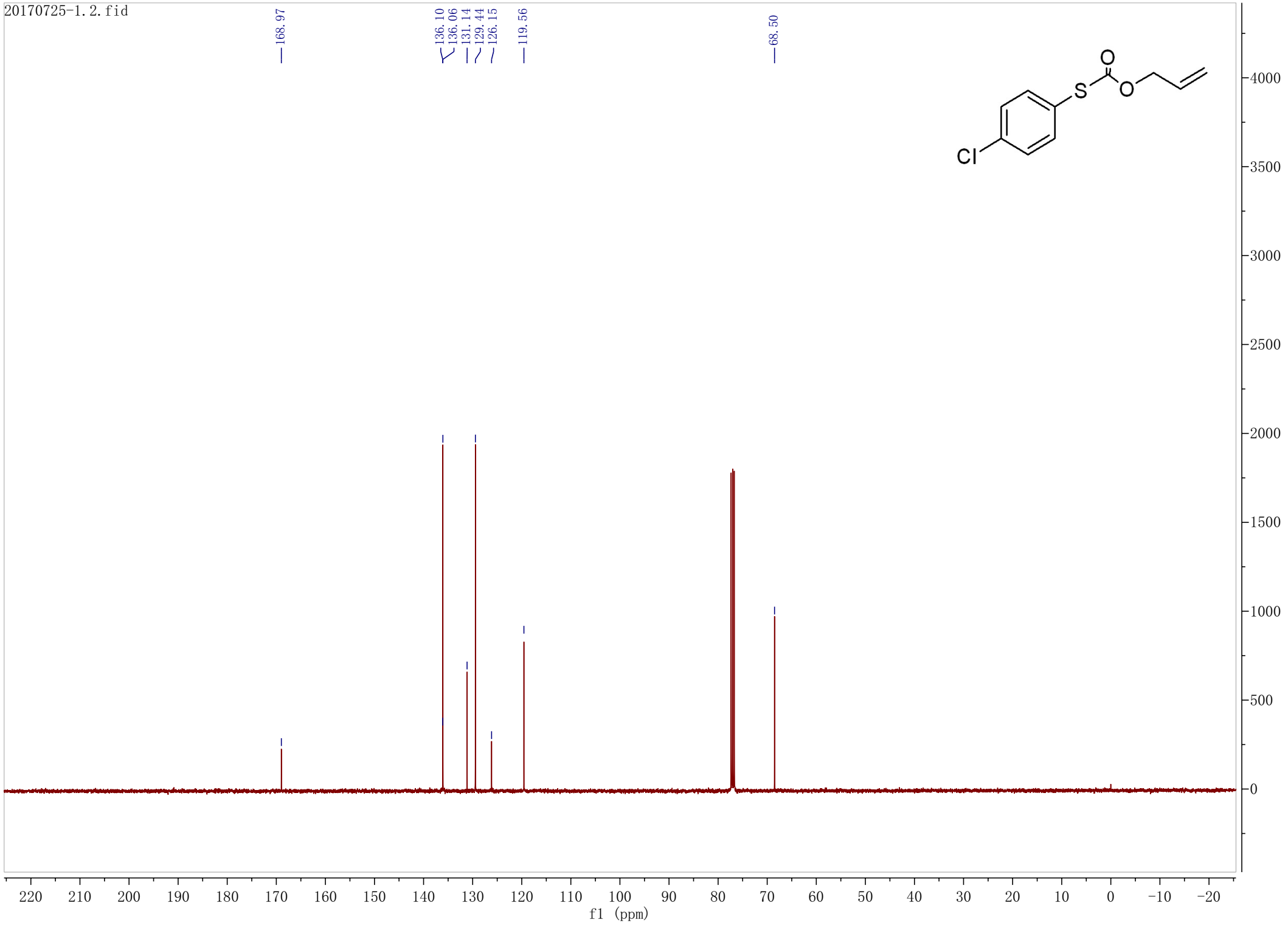
f1 (ppm)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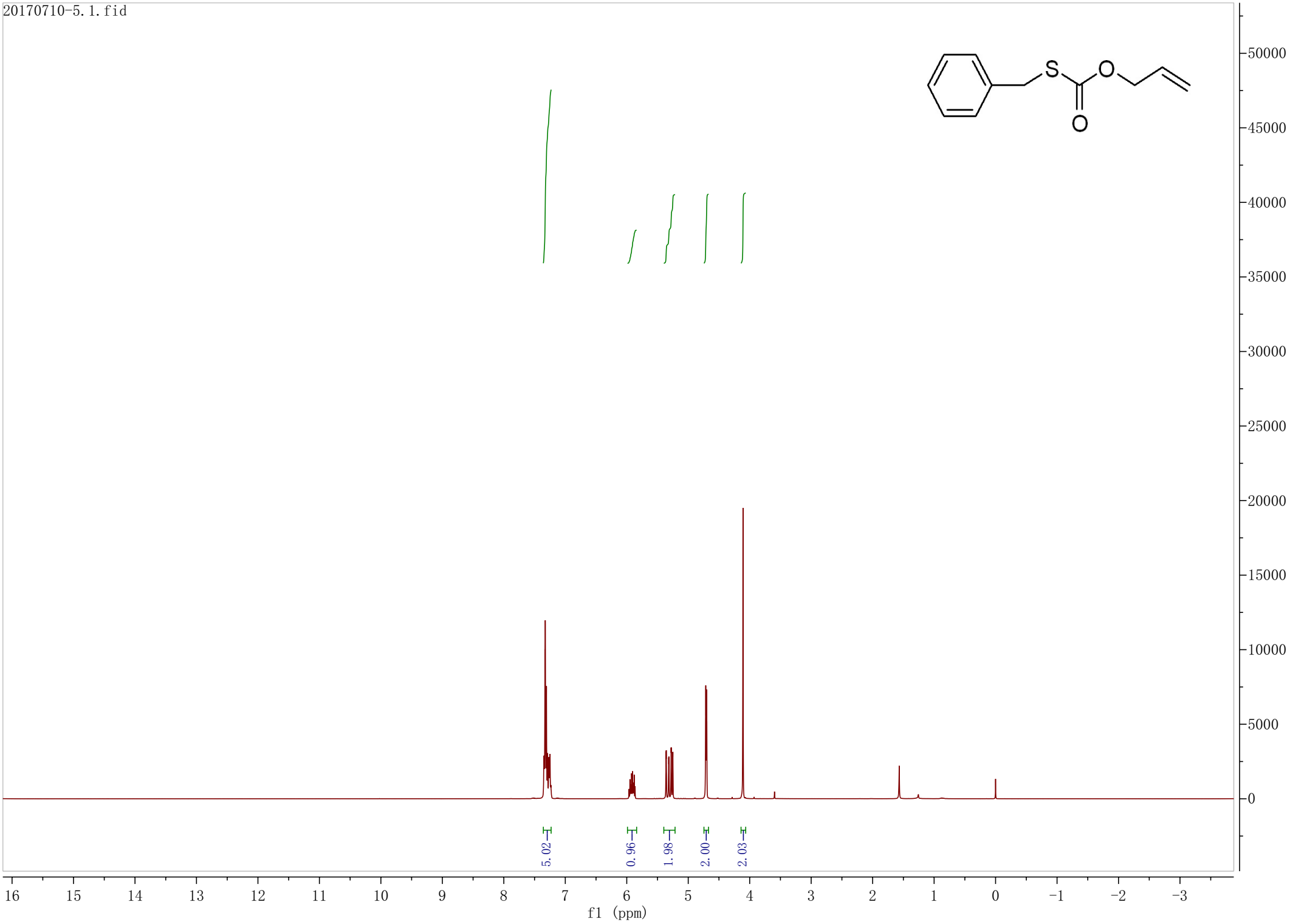
f1 (ppm)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2.00
2.03
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15
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5
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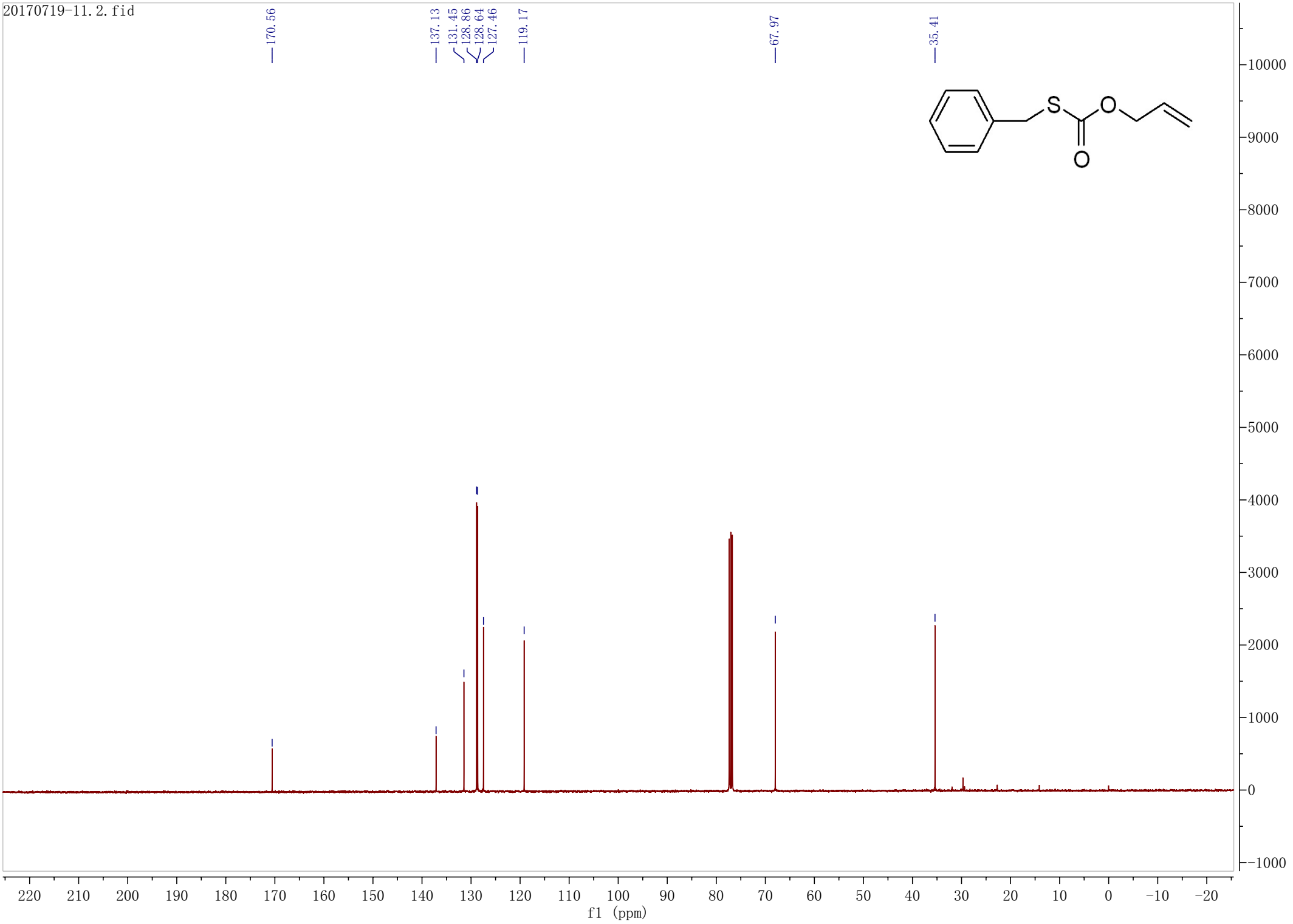
f1 (ppm)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127.46
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6000
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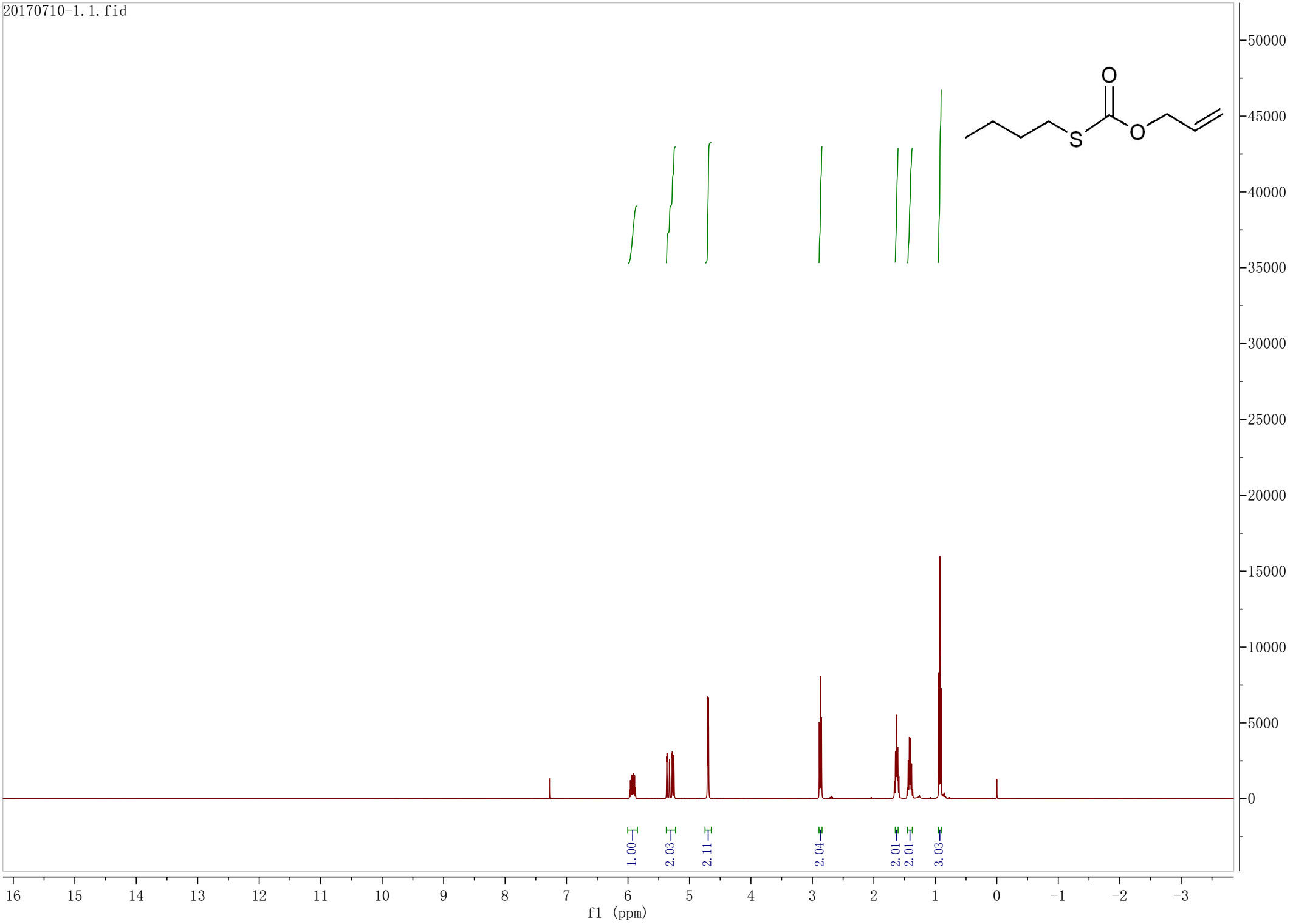
f1 (ppm)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2.03
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2.04
2.01
2.01
3.03
16
15
14
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9
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7
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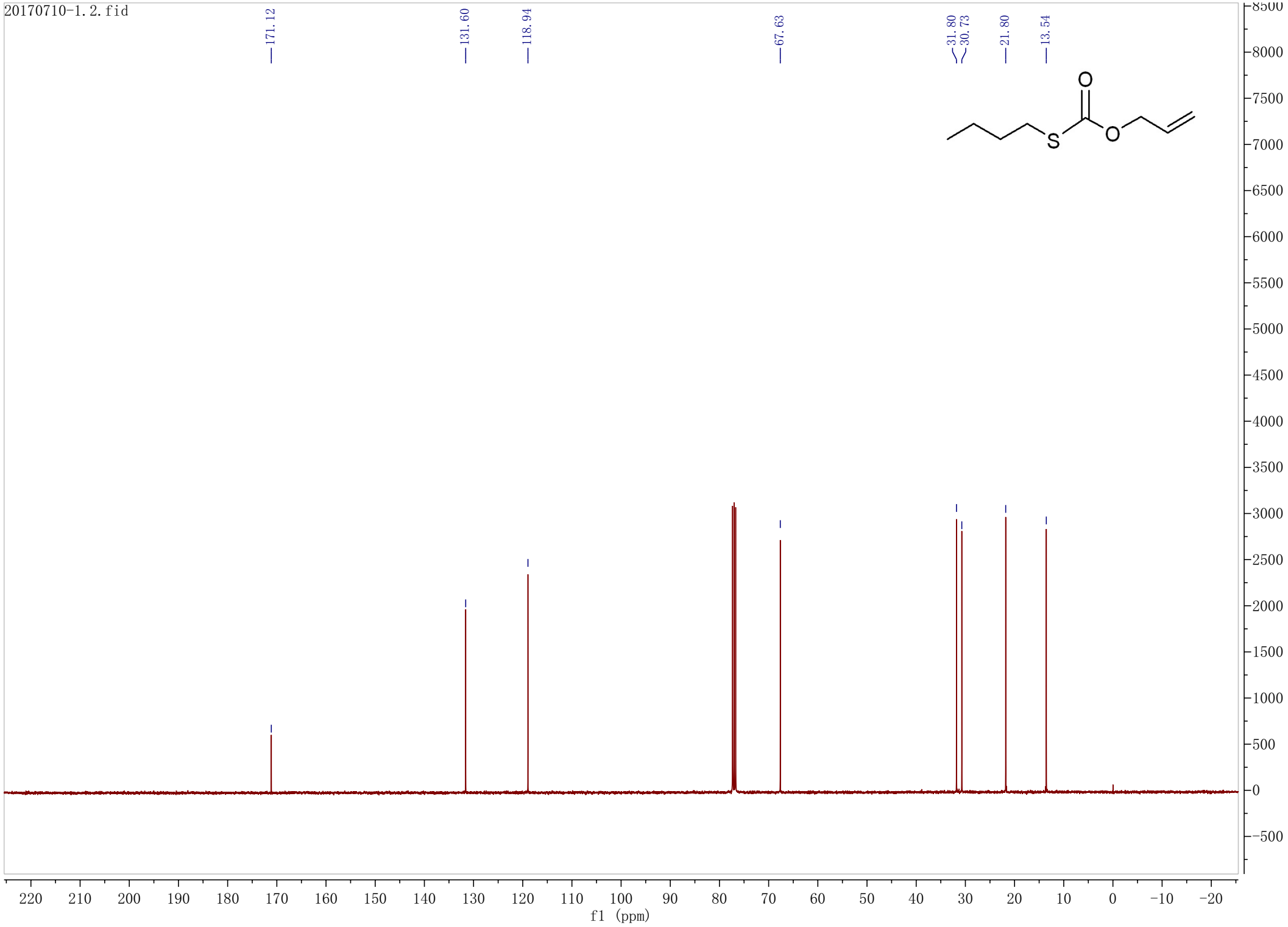
f1 (ppm)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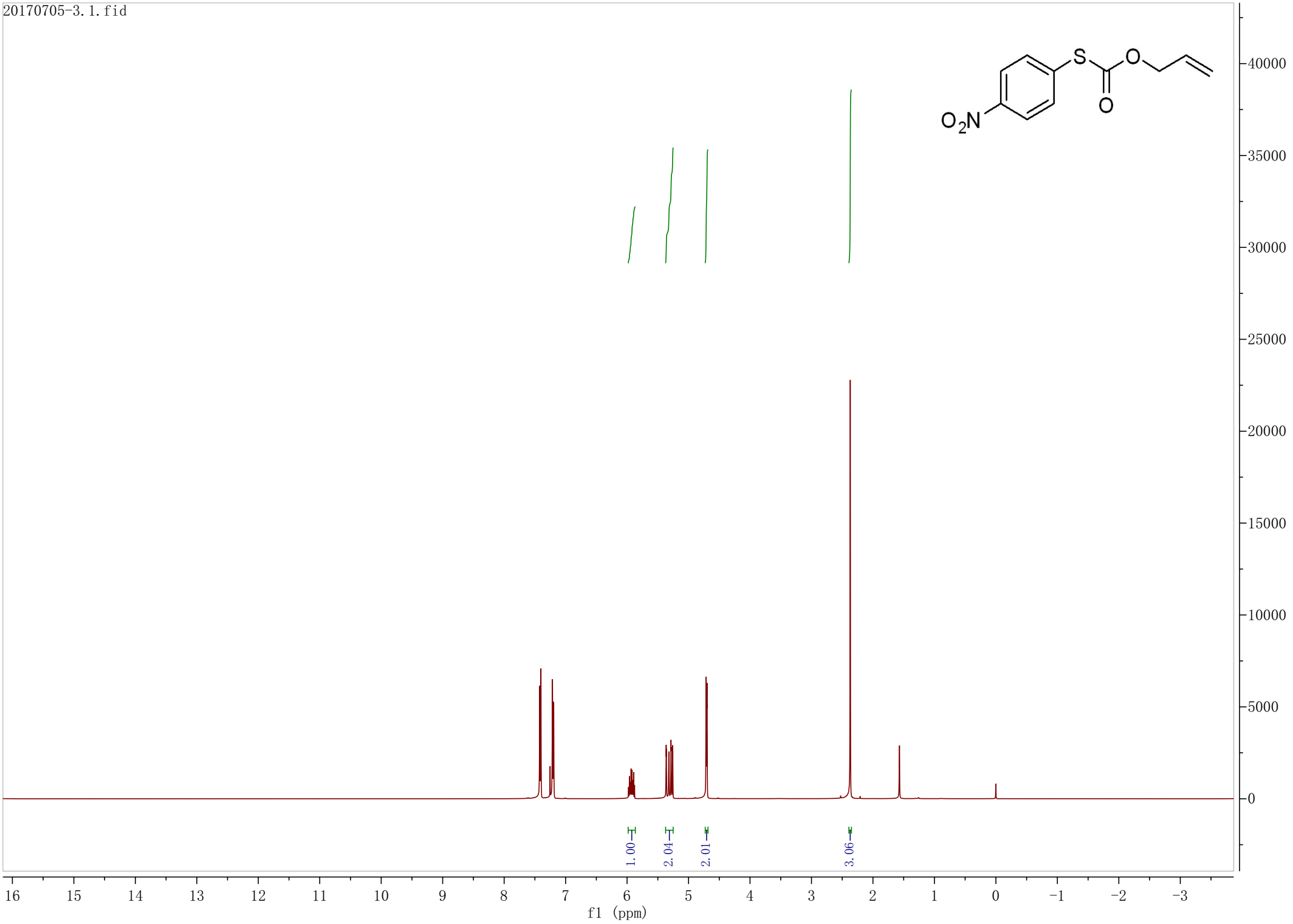
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2.01
3.06
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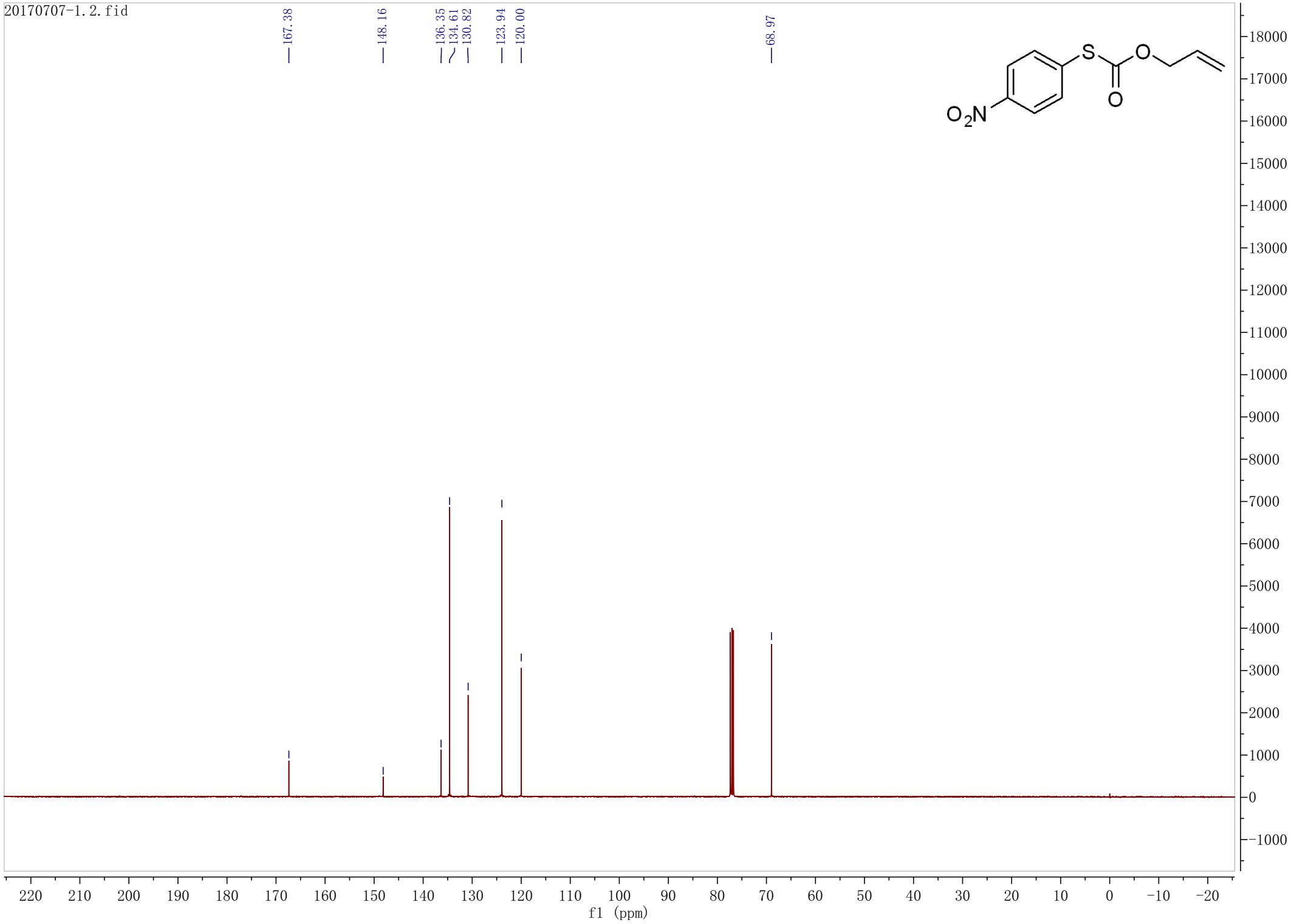
−1
−2
−3
f1 (ppm)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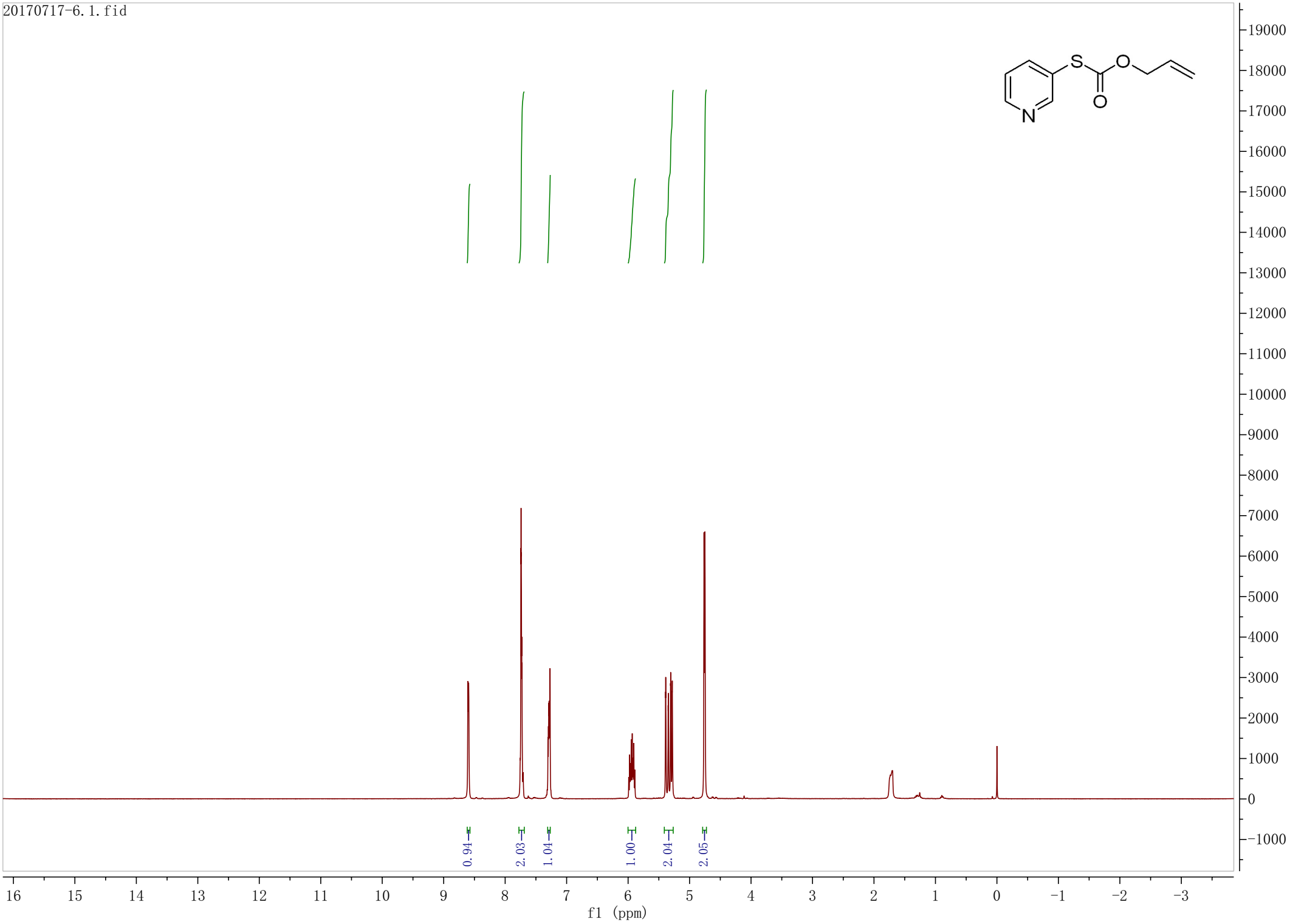
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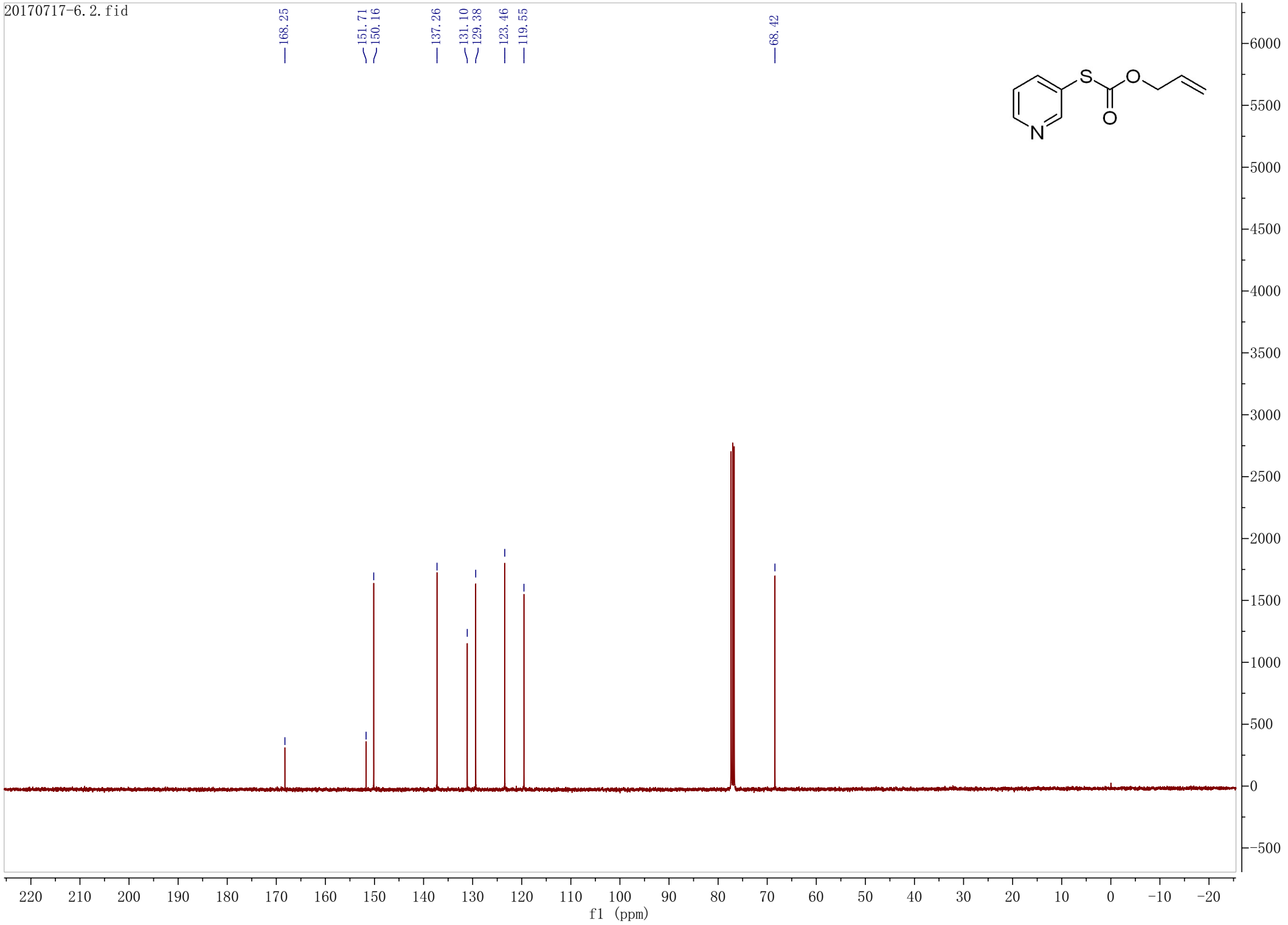
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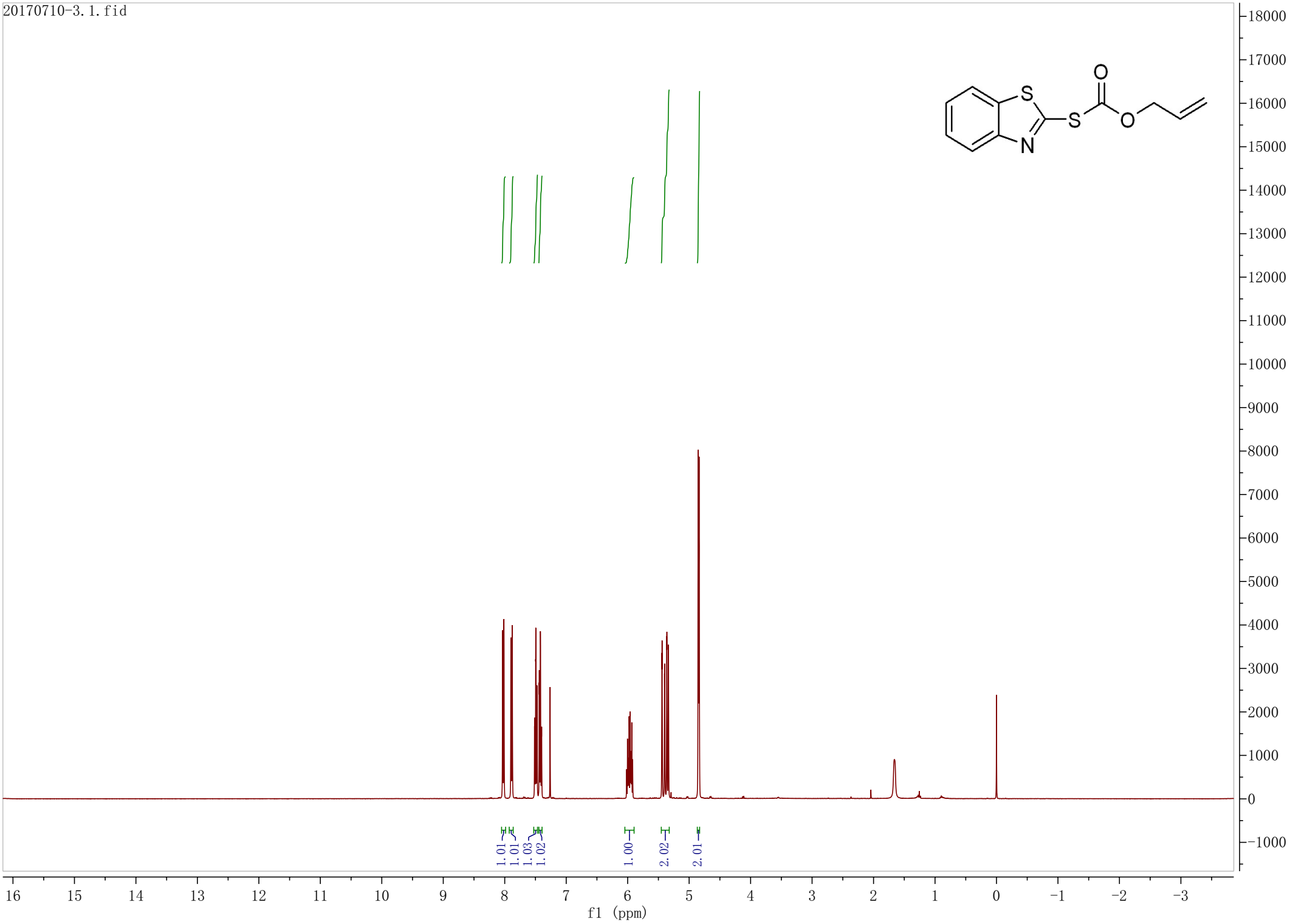
f1 (ppm)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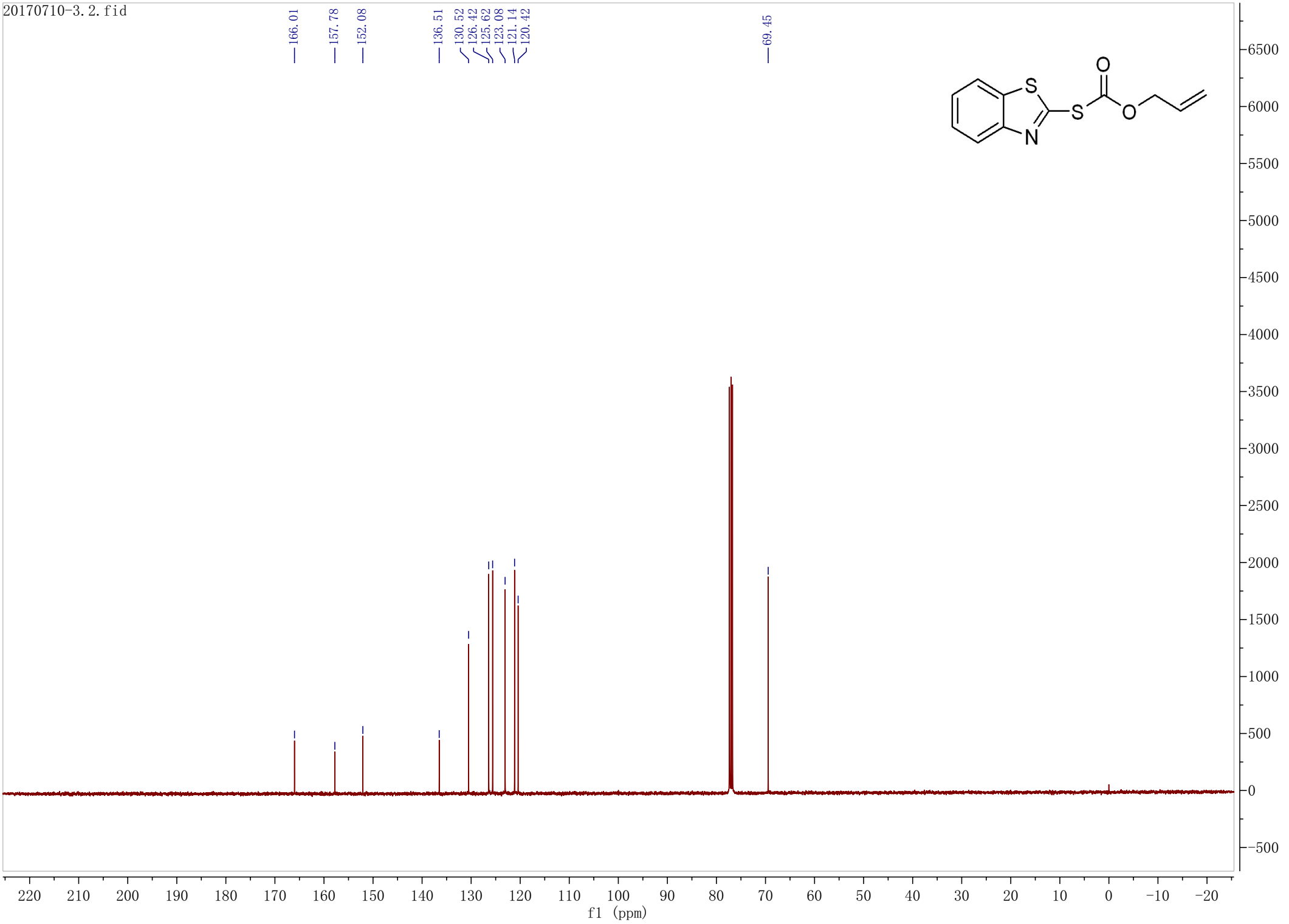
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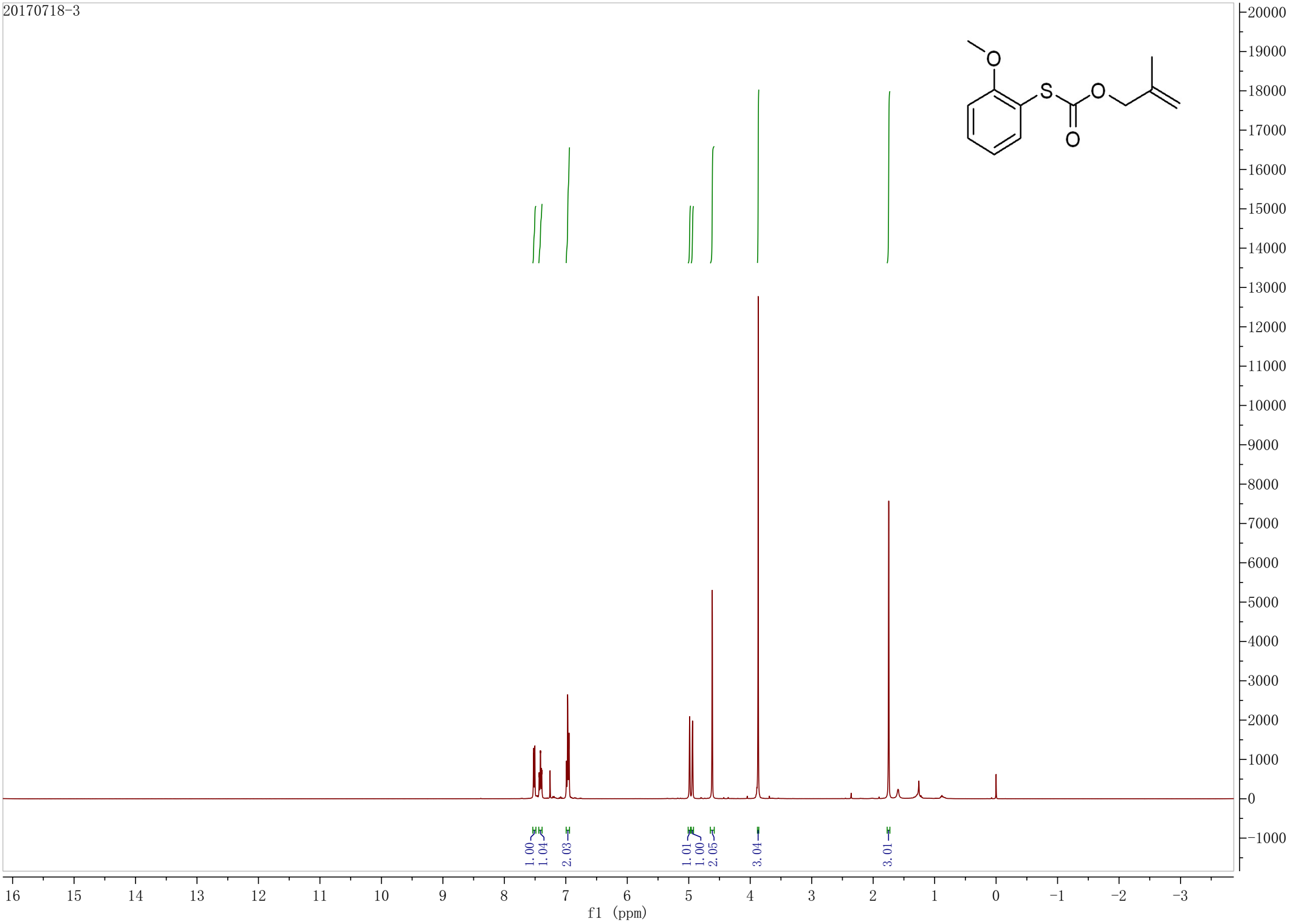
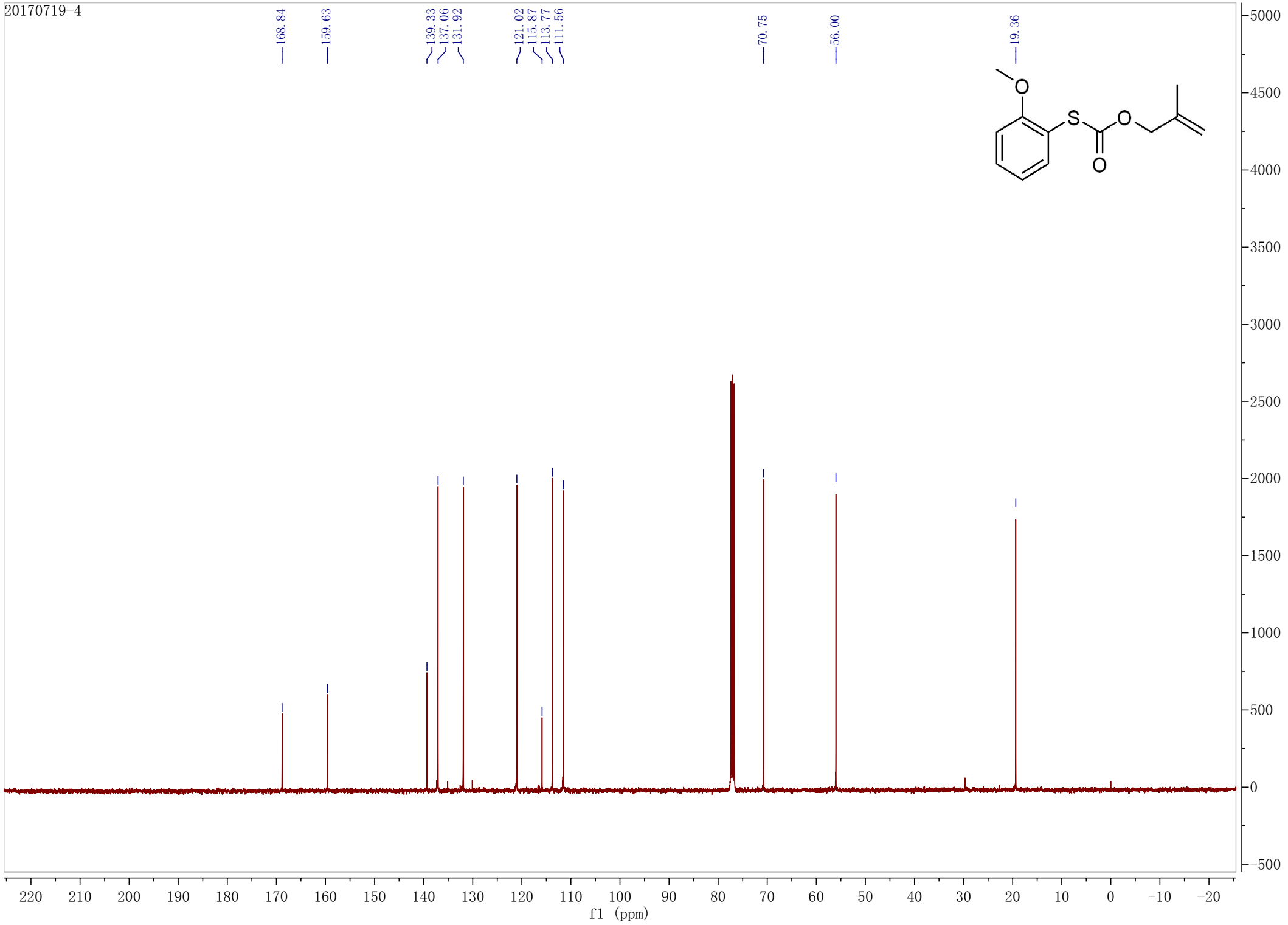
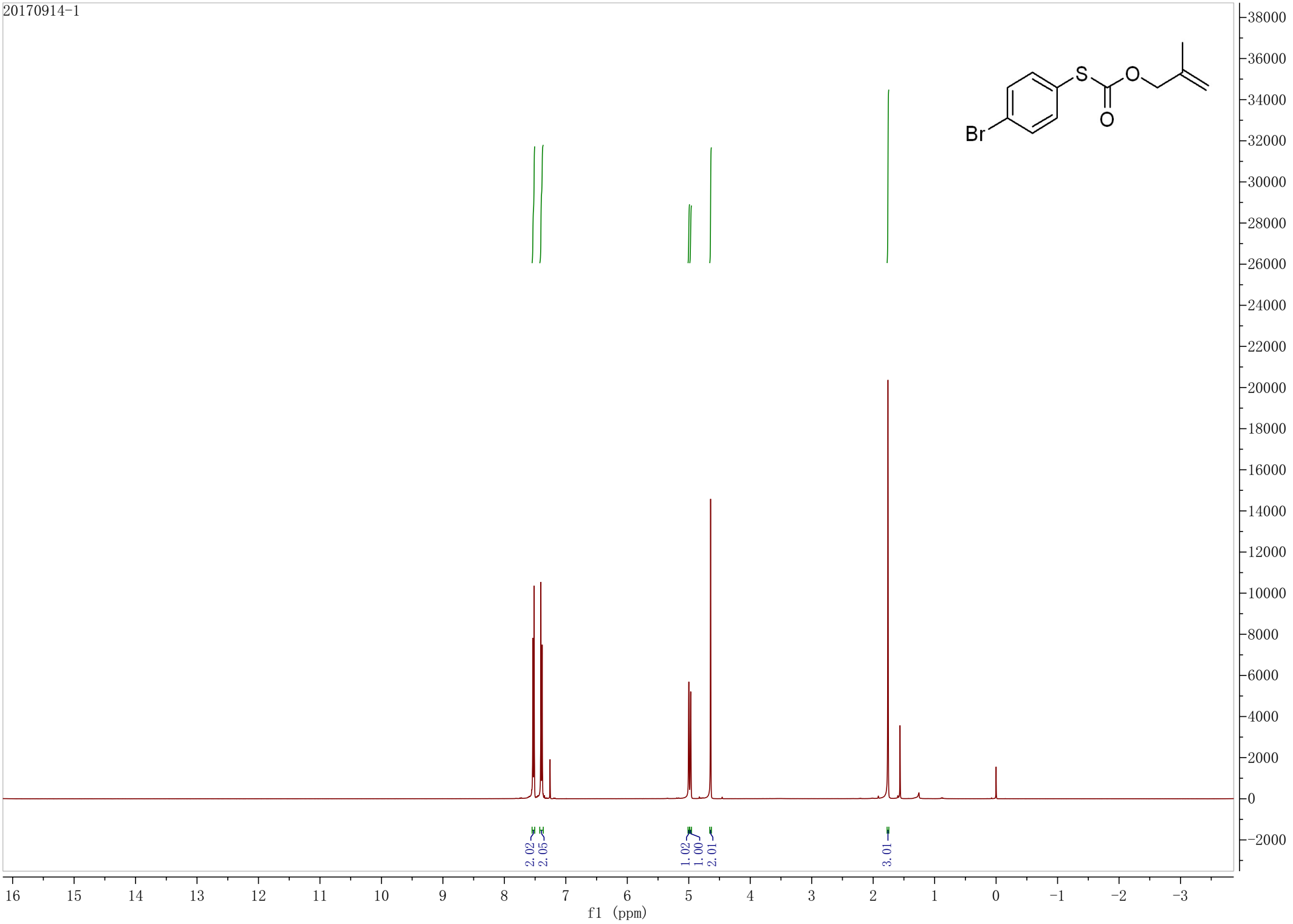
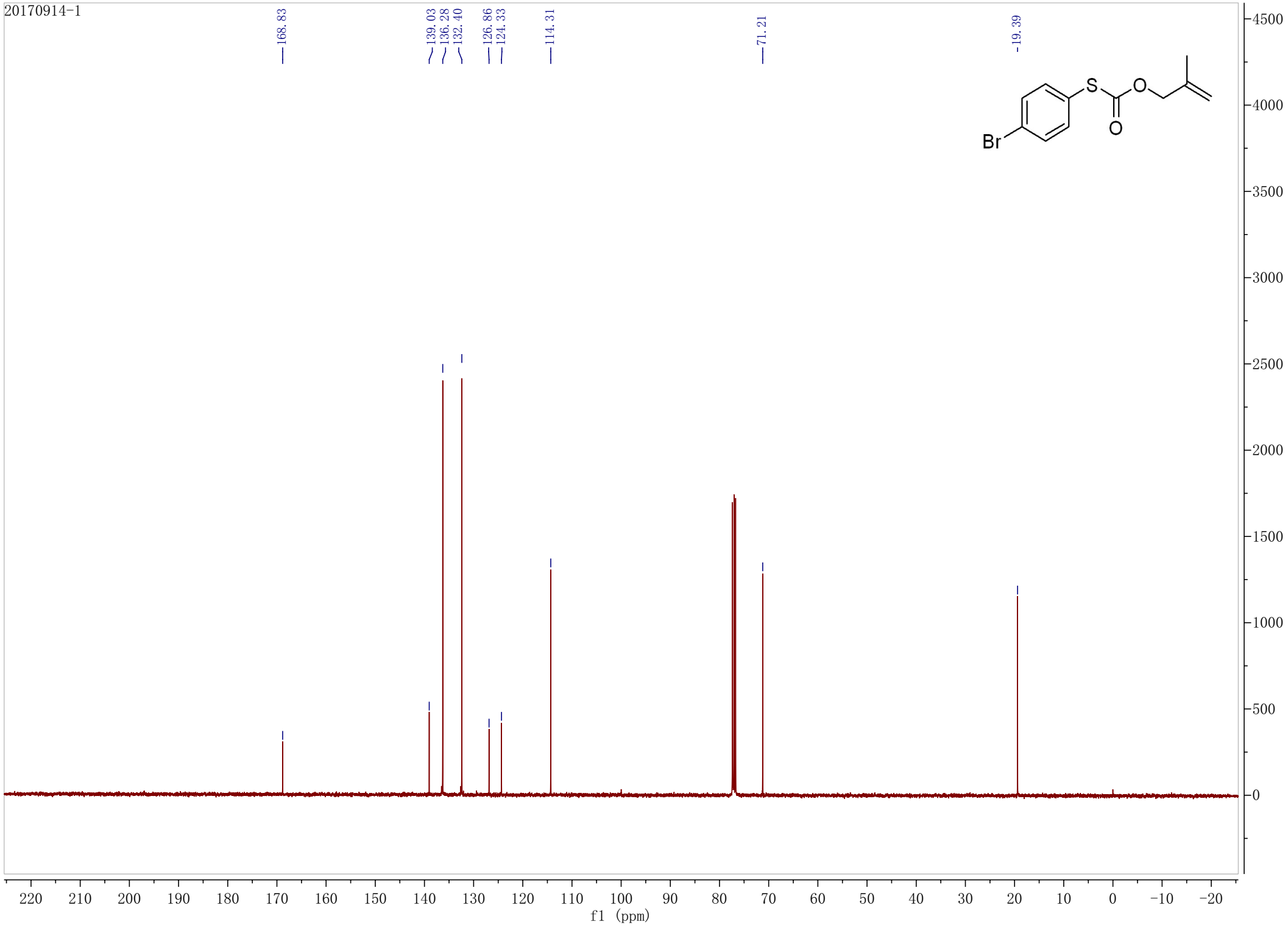
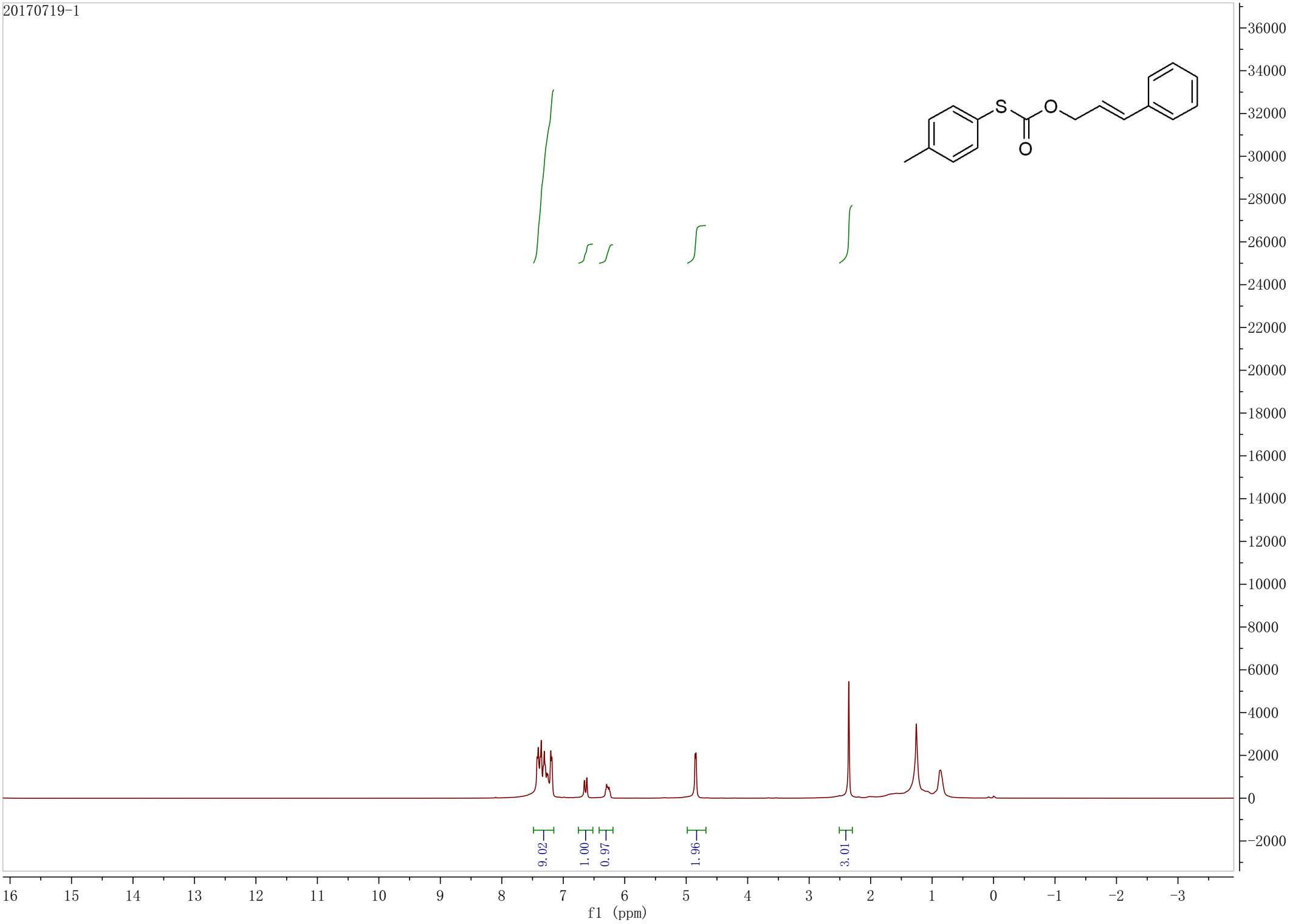
-10
-20
f1 (ppm)

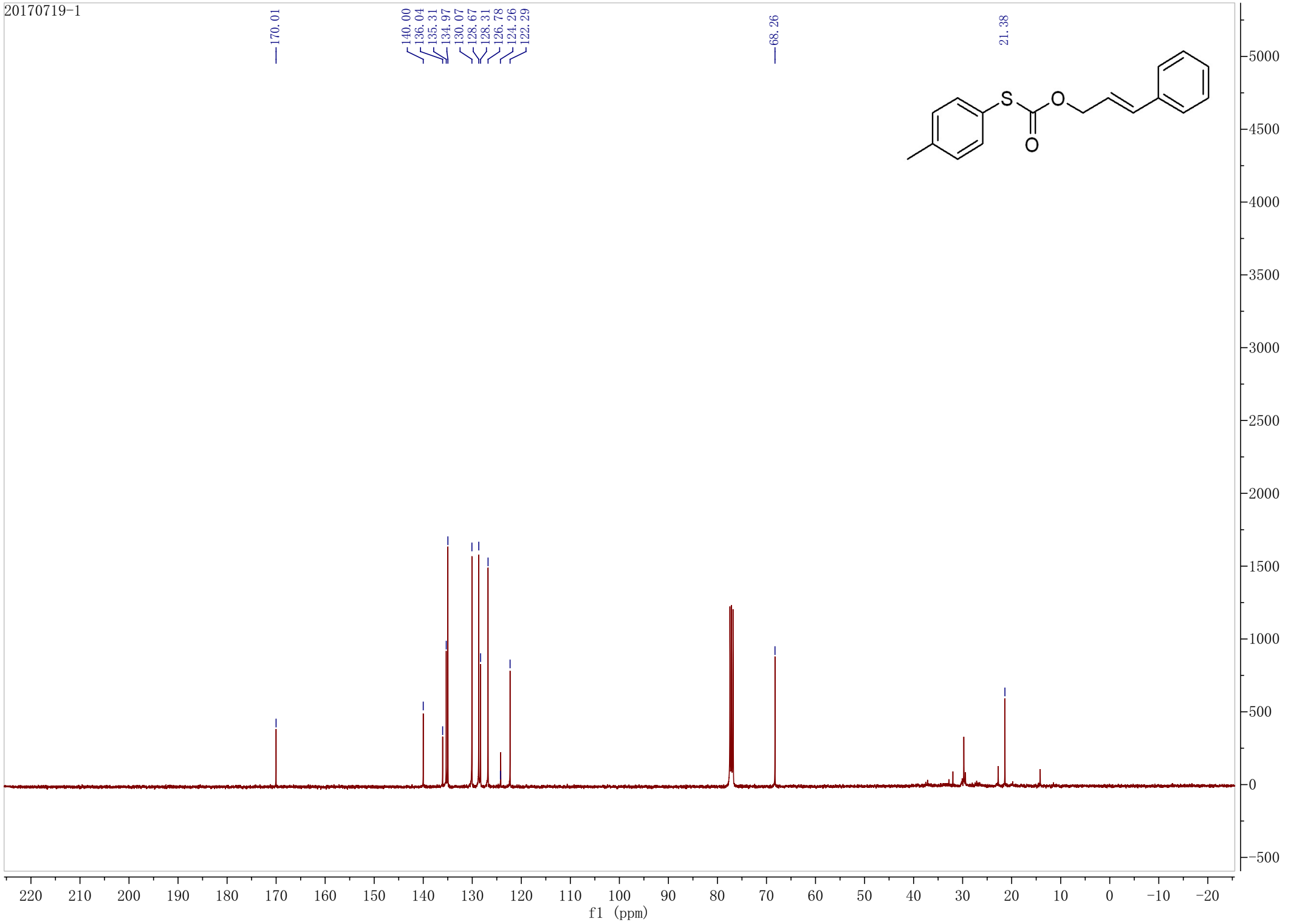

20170718-3
O
S
O
O
1.00
1.04
2.03
1.01
1.00
2.05
3.04
3.01
f1 (ppm)

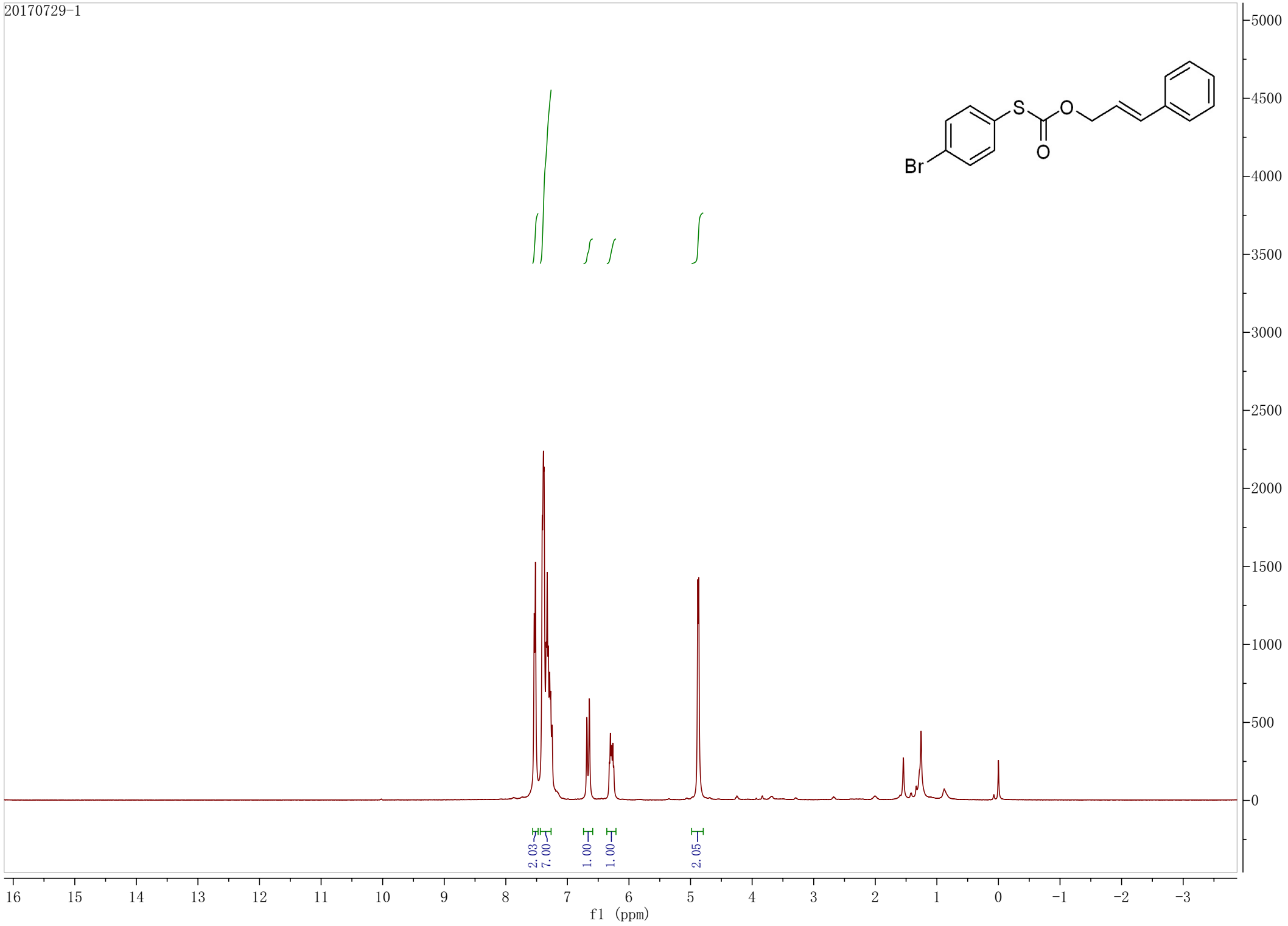

20170719-4
168.84
159.63
139.33
137.06
131.92
121.02
115.87
113.77
111.56
70.75
56.00
19.36
O
S
O
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

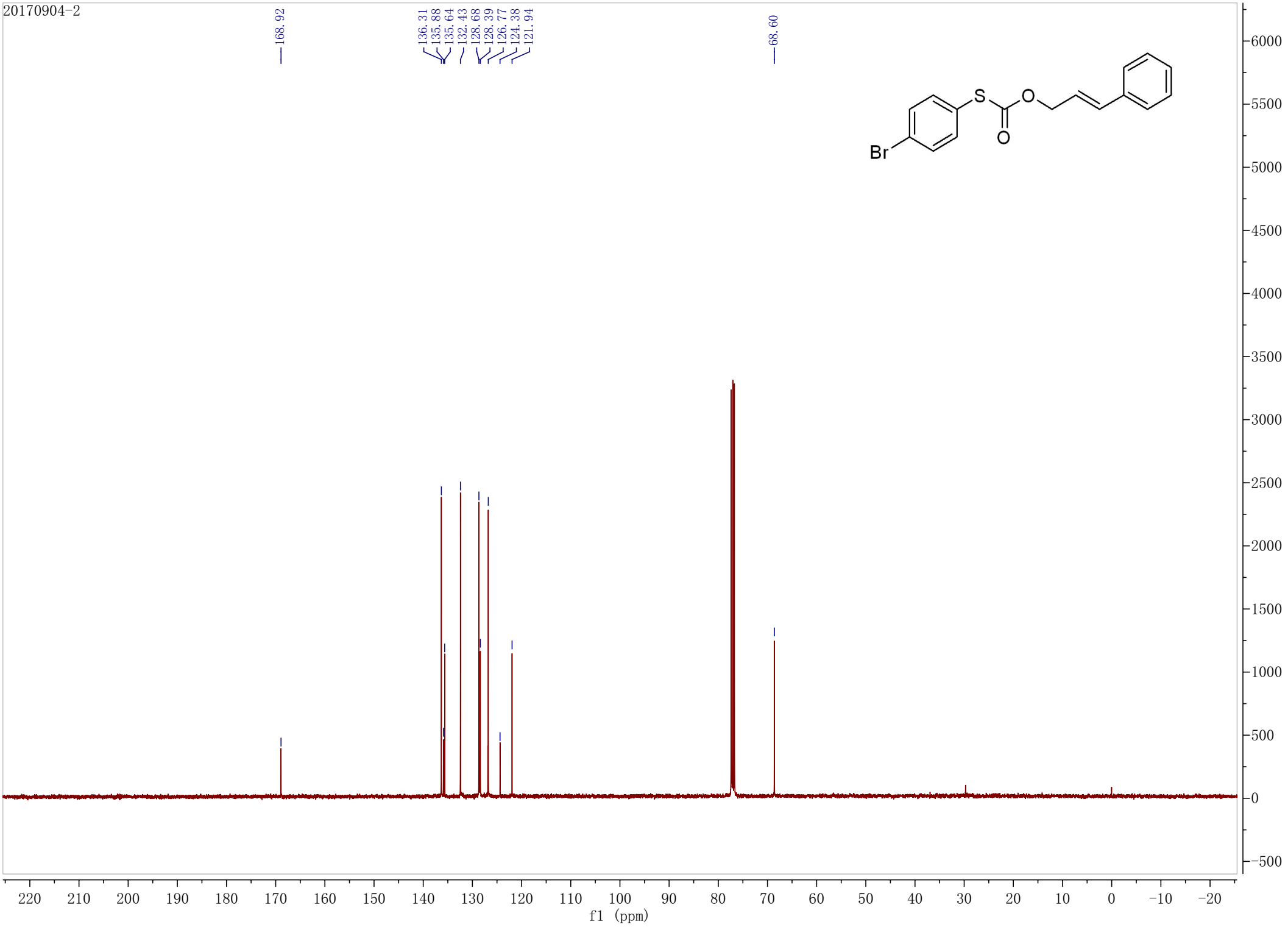

20170914-1
Br
S
O
O
2.02
2.05
1.02
1.00
2.01
3.01
f1 (ppm)

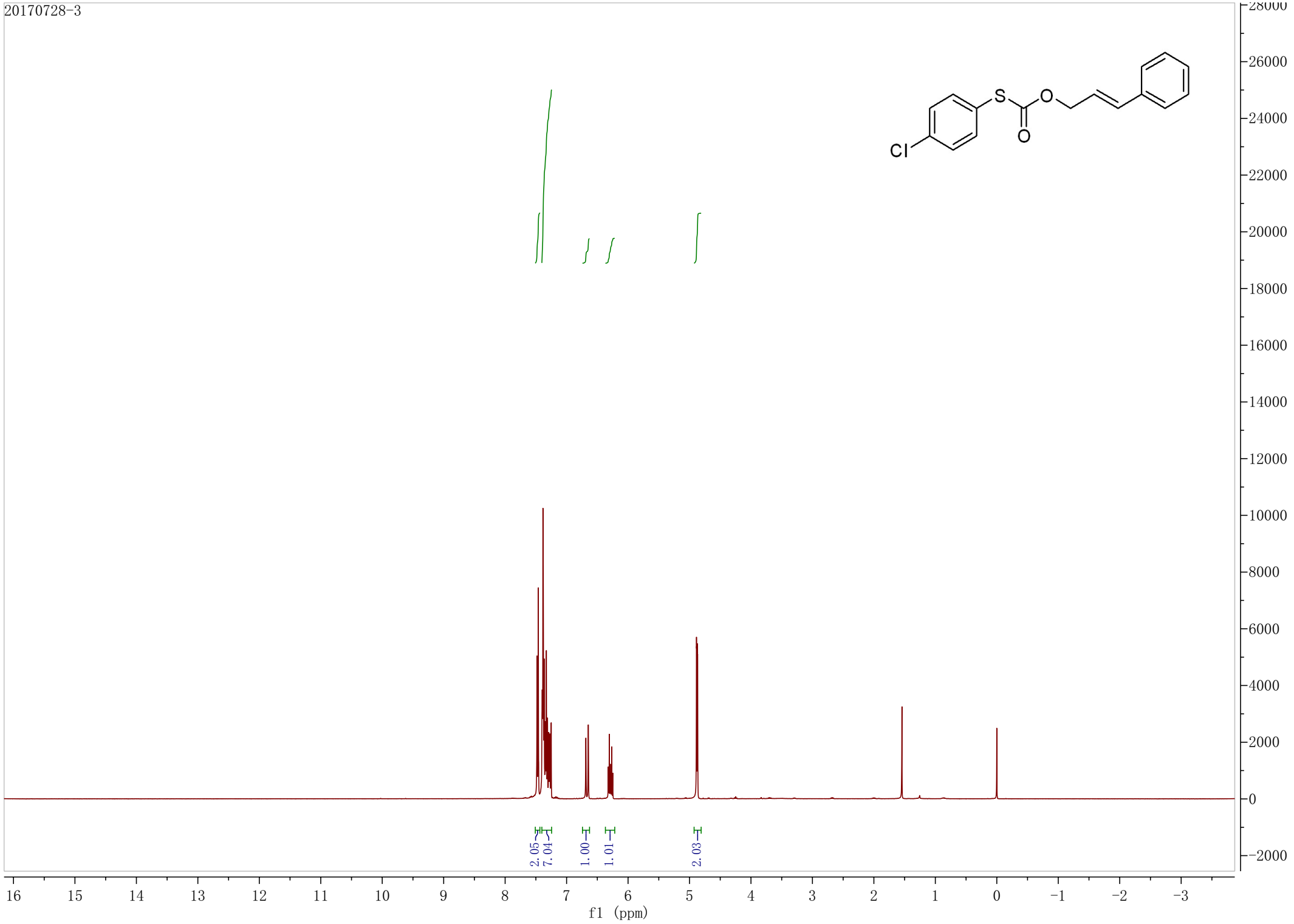

20170914-1
168.83
139.03
136.28
132.40
126.86
124.33
114.31
71.21
19.39
Br
S
O
O
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

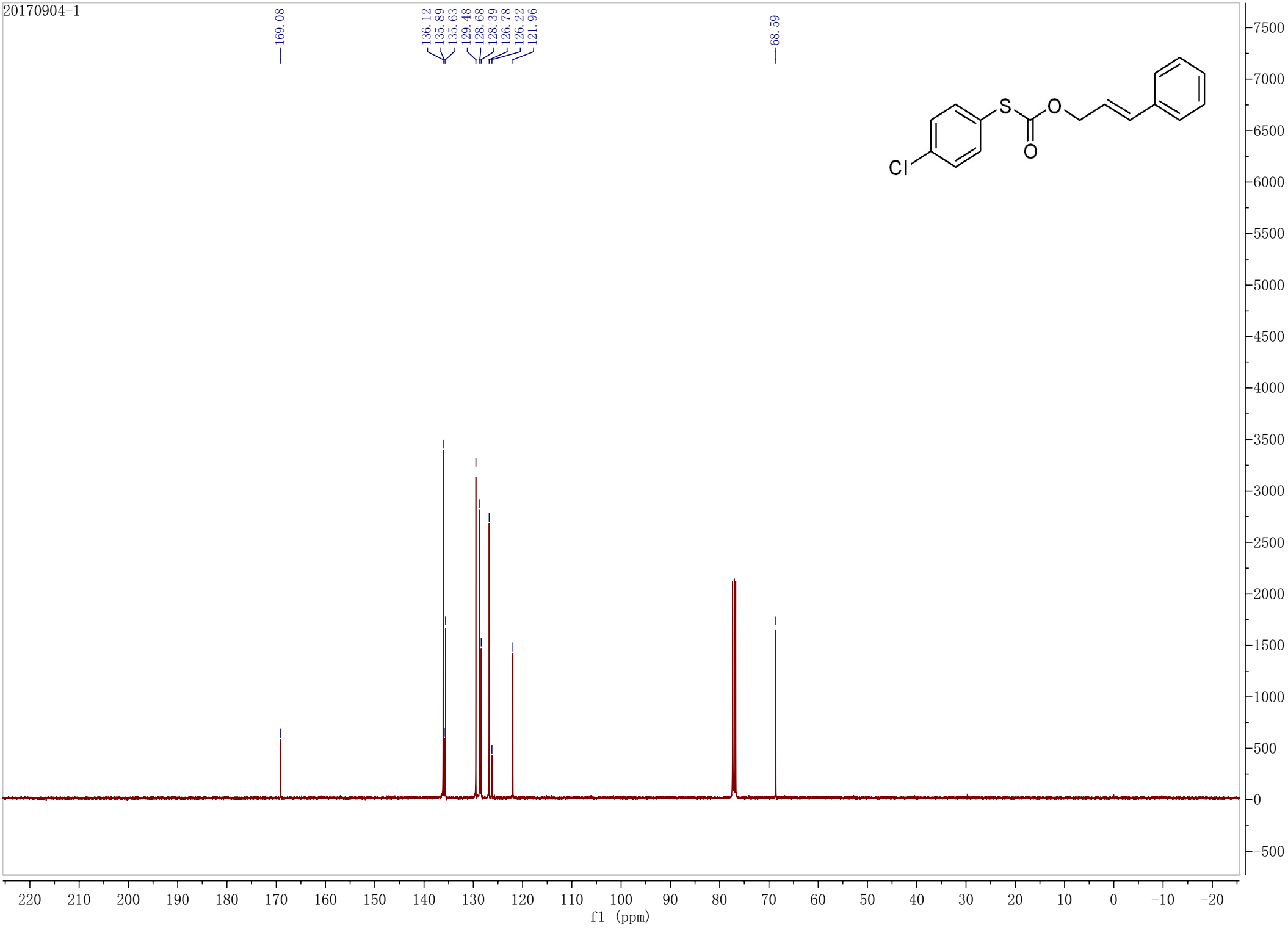

20170719-1
S
O
O
9.02
1.00
0.97
1.96
3.01
f1 (ppm)

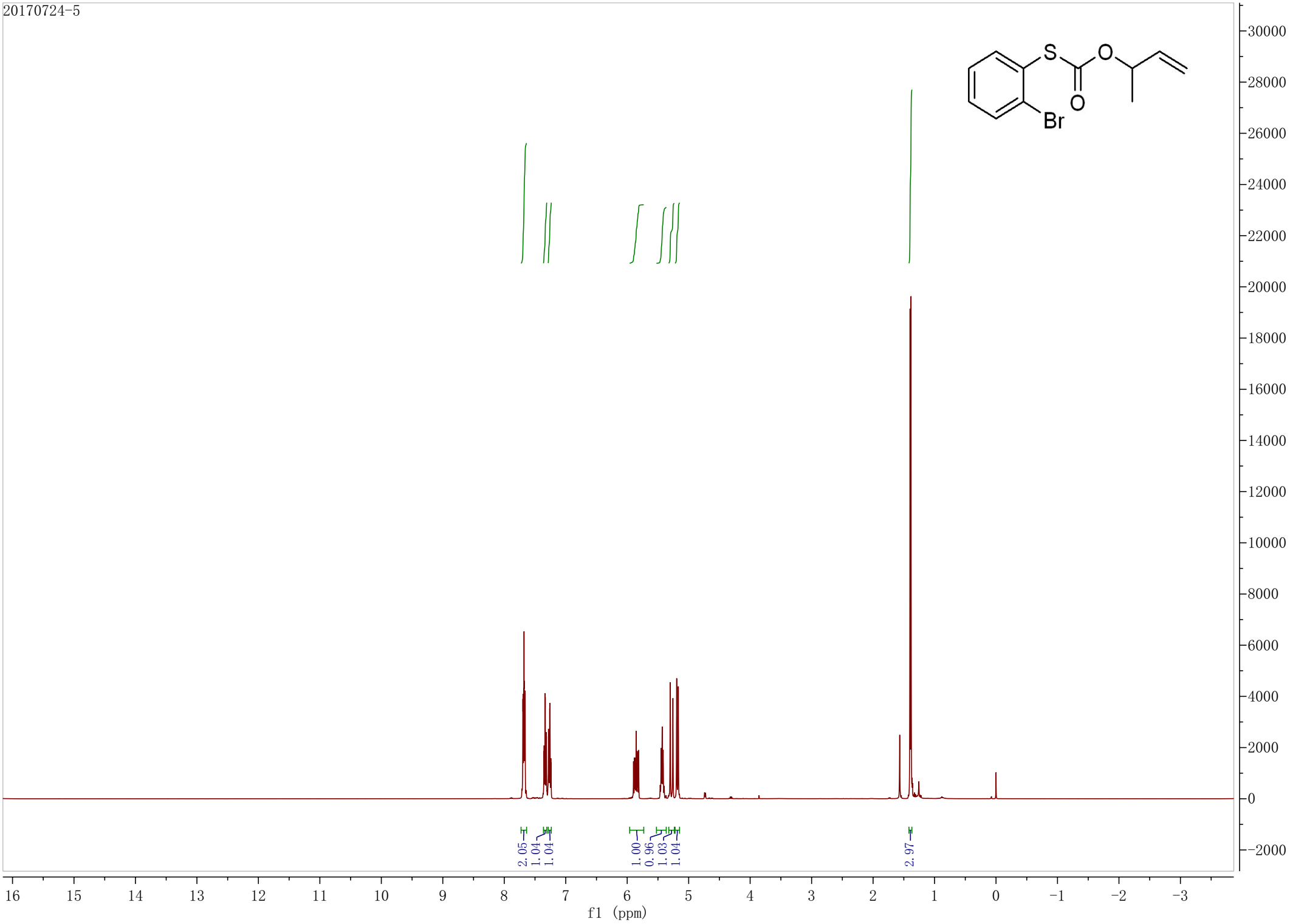

20170719-1
170.01
140.00
136.04
135.31
134.97
130.07
128.67
128.31
126.78
124.26
122.29
68.26
21.38
S
O
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

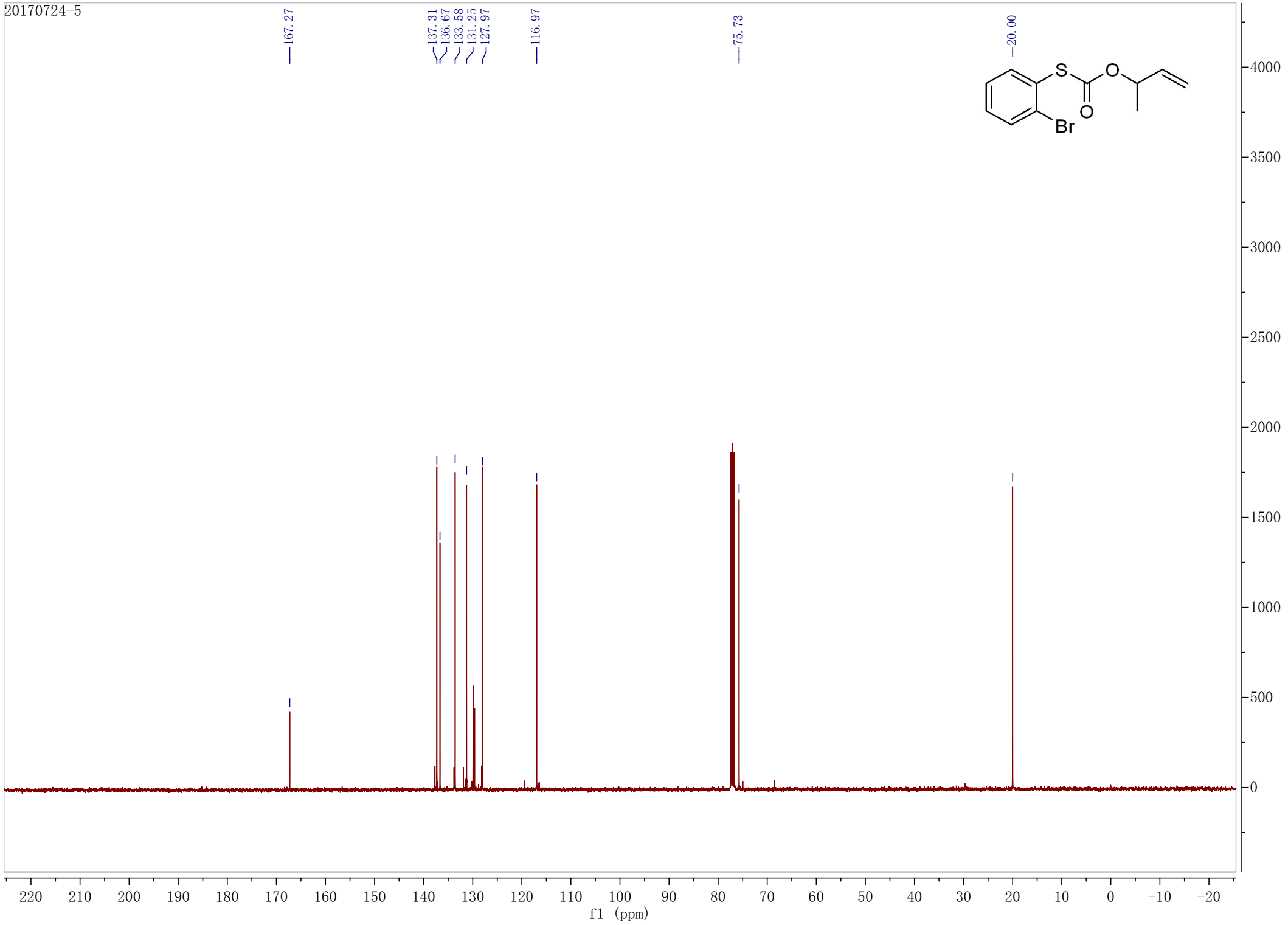

20170729-1
Br
S
O
O
2.03
7.00
1.00
1.00
2.05
f1 (ppm)

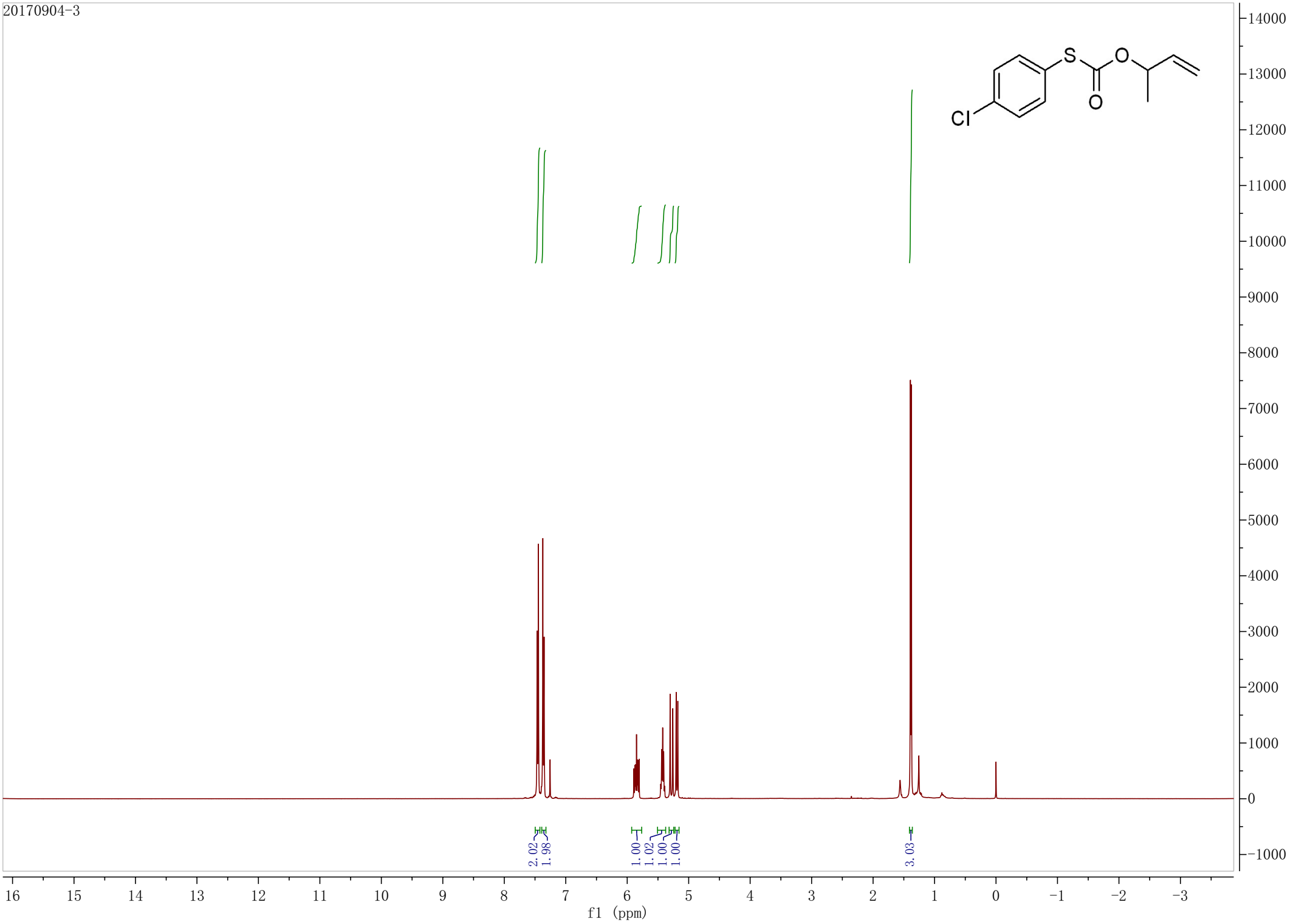

20170904-2
168.92
136.31
135.88
135.64
132.43
128.68
128.39
126.77
124.38
121.94
68.60
Br
S
O
O
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

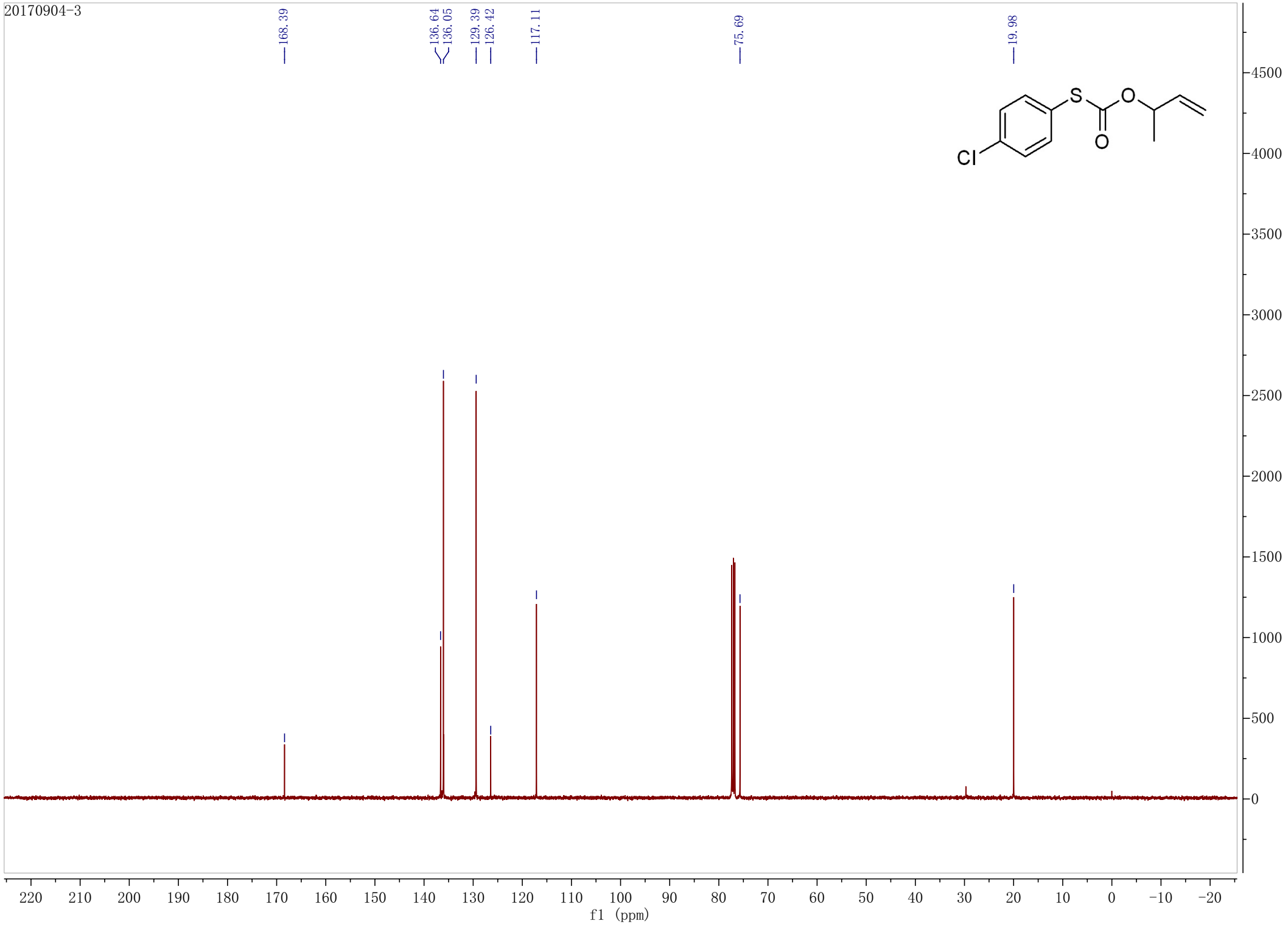

20170728-3
S
O
O
Cl
2.05
7.04
1.00
1.01
2.03
f1 (ppm)

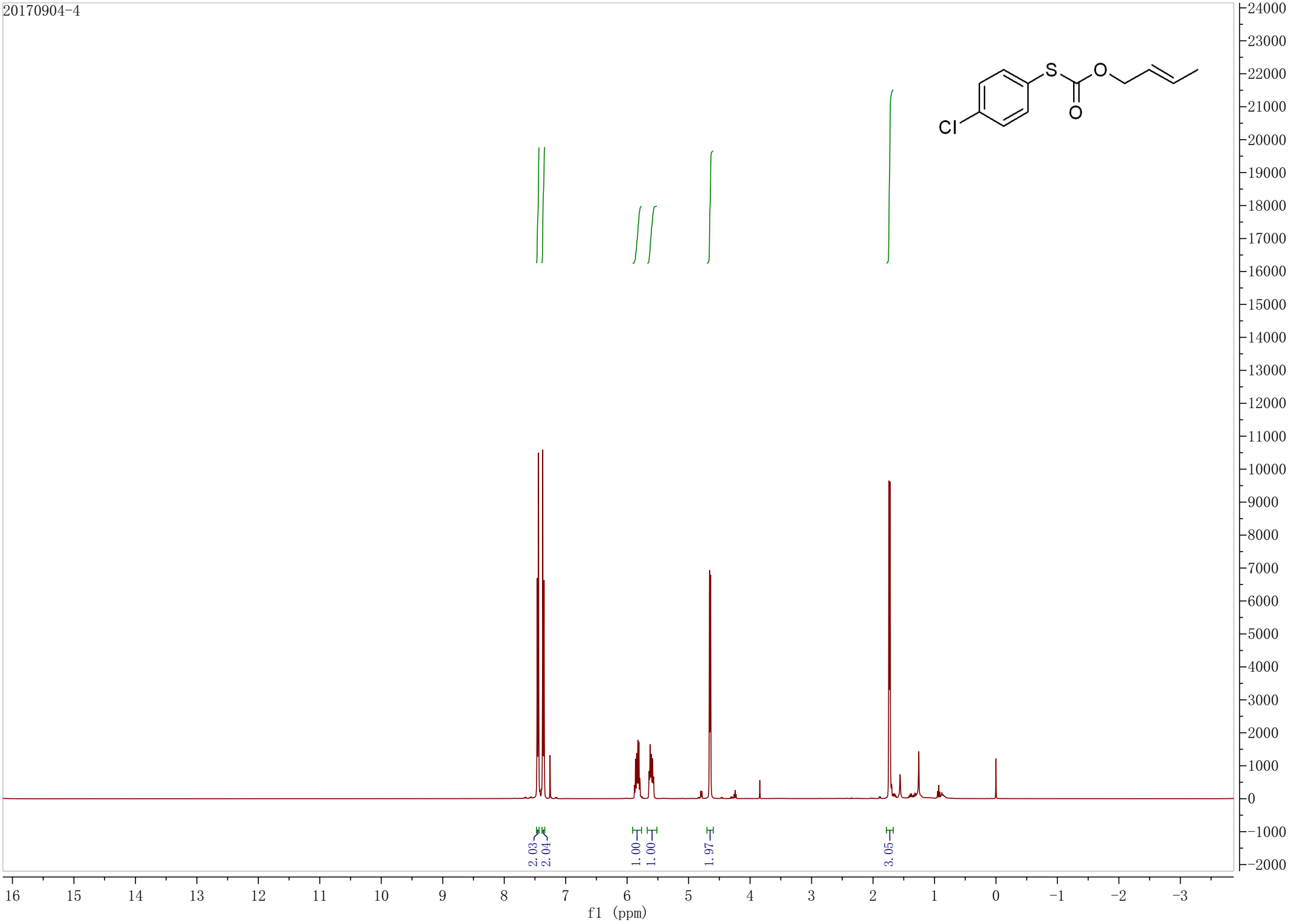

20170904-1
169.08
136.12
135.89
135.63
129.48
128.68
128.39
126.78
126.22
121.96
68.59
S
O
O
Cl
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

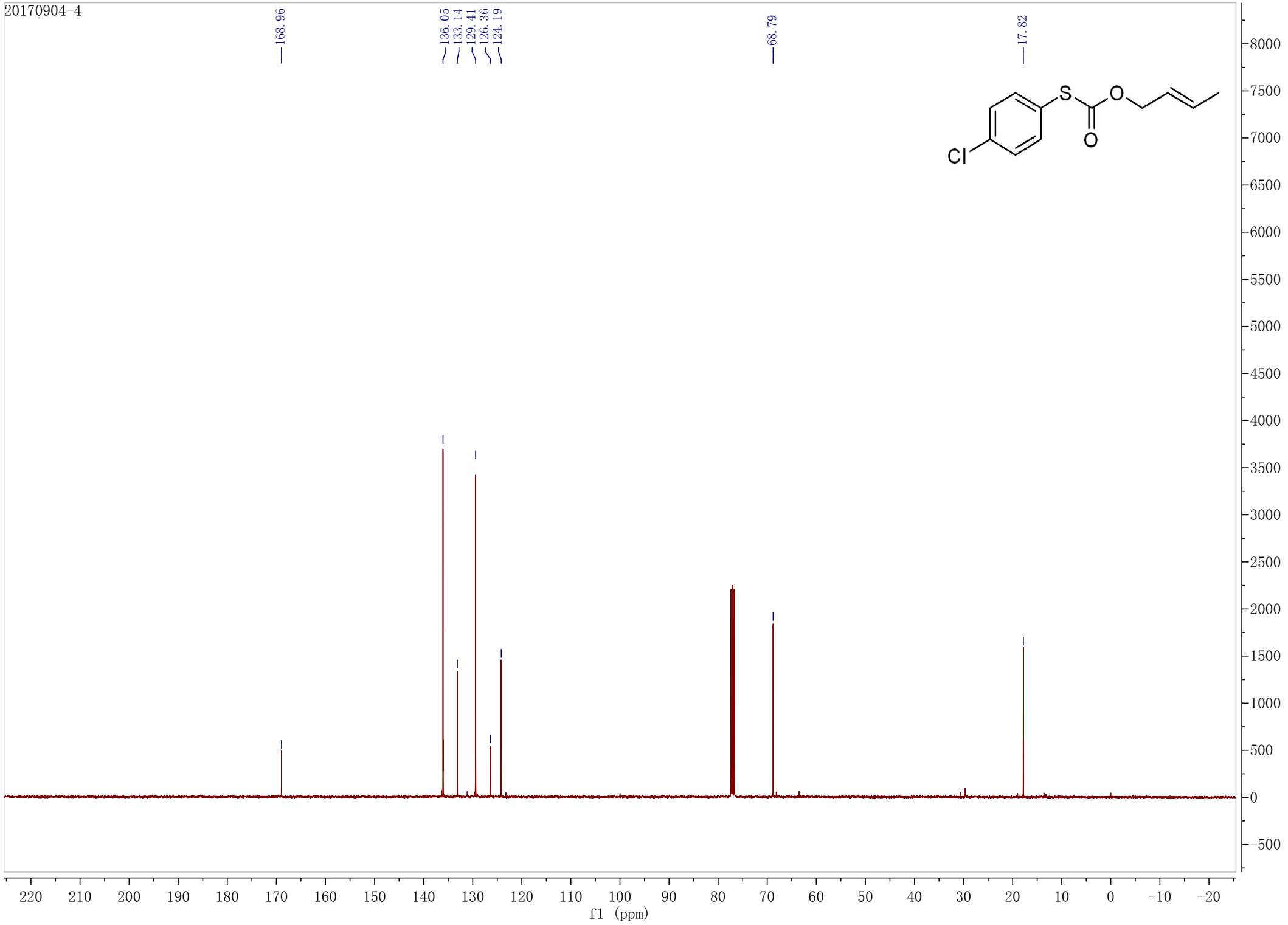

20170724-5
S
O
O
Br
2.05
1.04
1.04
1.00
0.96
1.03
1.04
2.97
f1 (ppm)

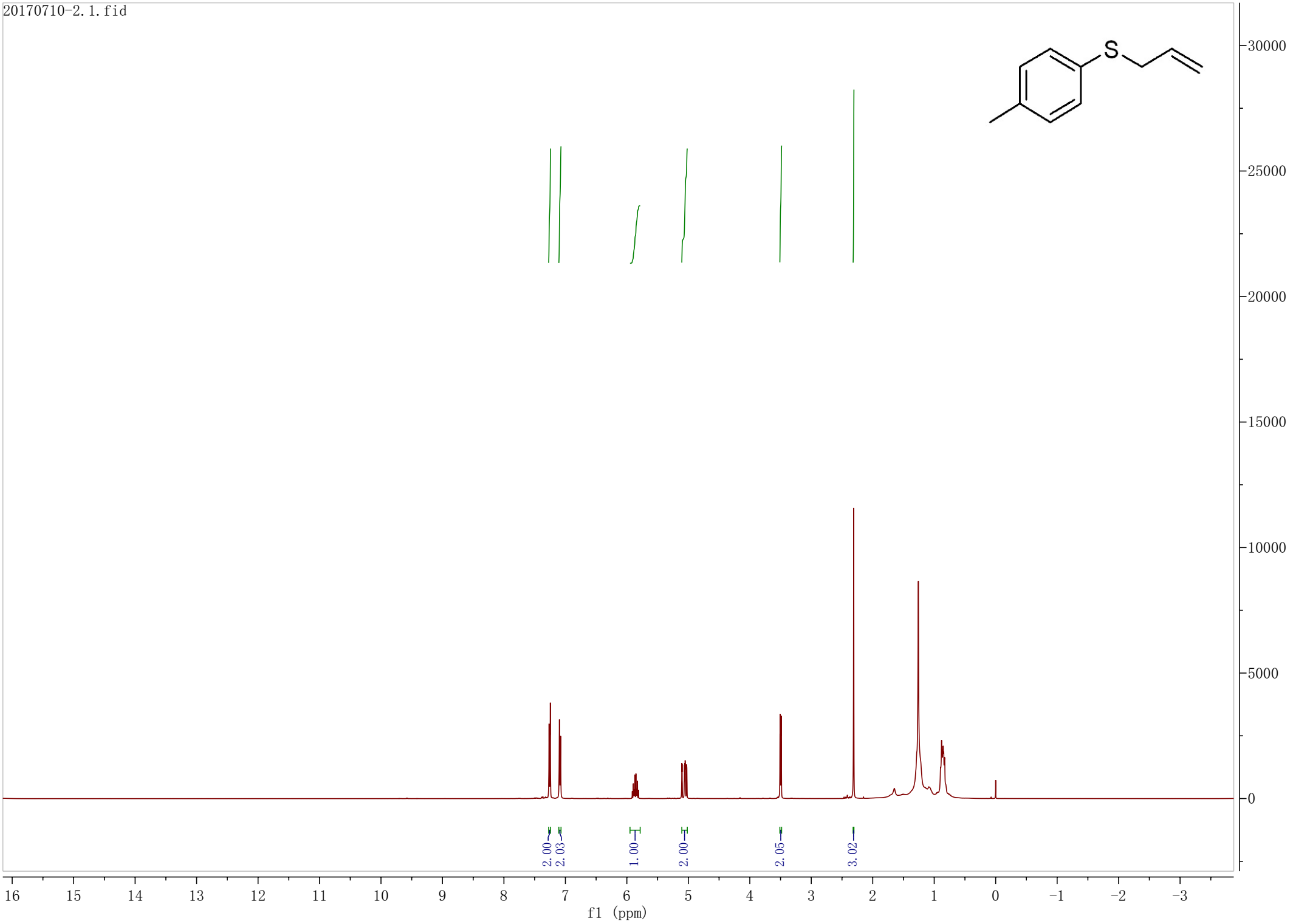

20170724-5
167.27
137.31
136.67
133.58
131.25
127.97
116.97
75.73
20.00
S
O
O
Br
4000
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

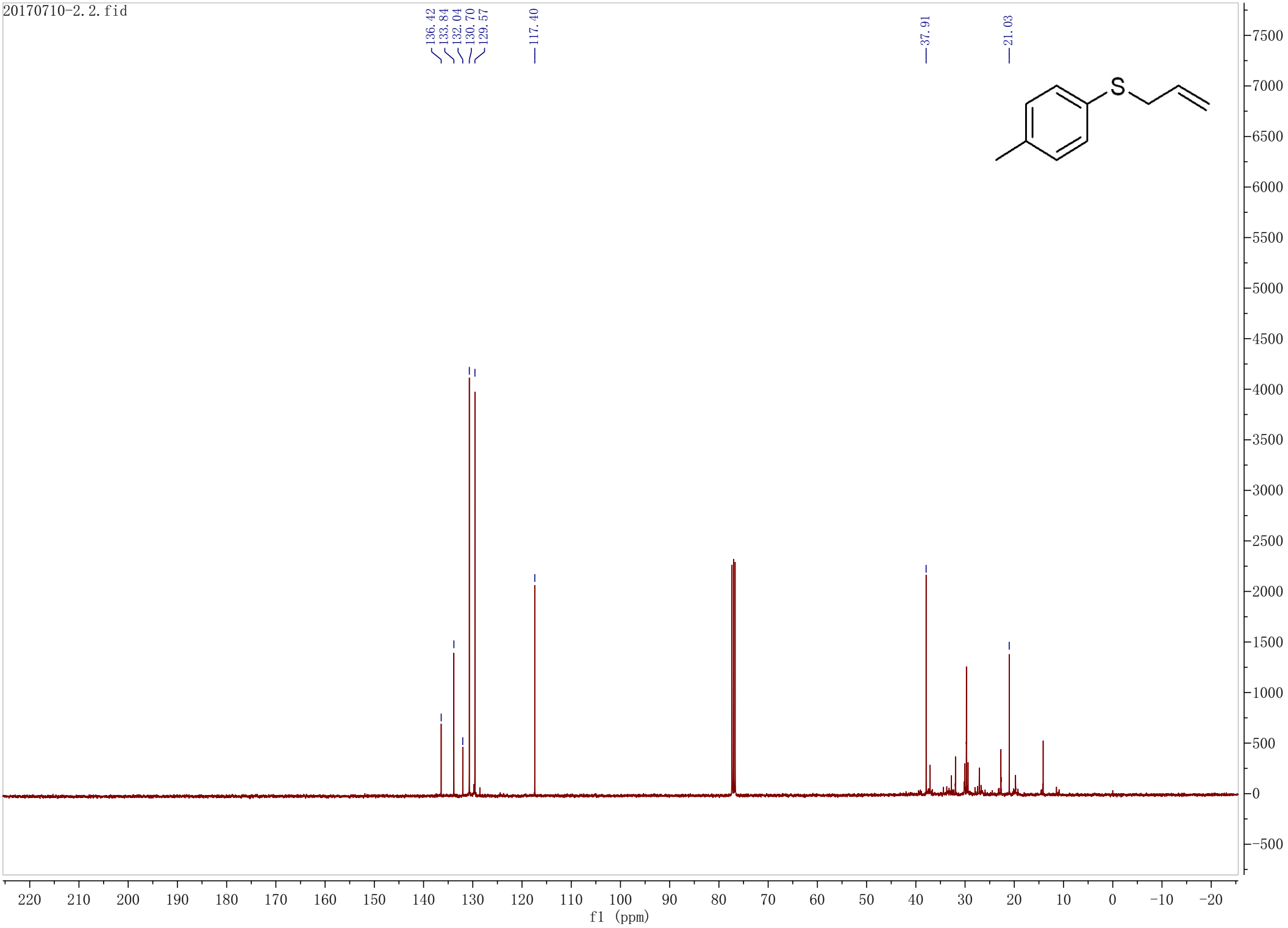

20170904-3
S
O
O
Cl
2.02
1.98
1.00
1.02
1.00
1.00
3.03
f1 (ppm)

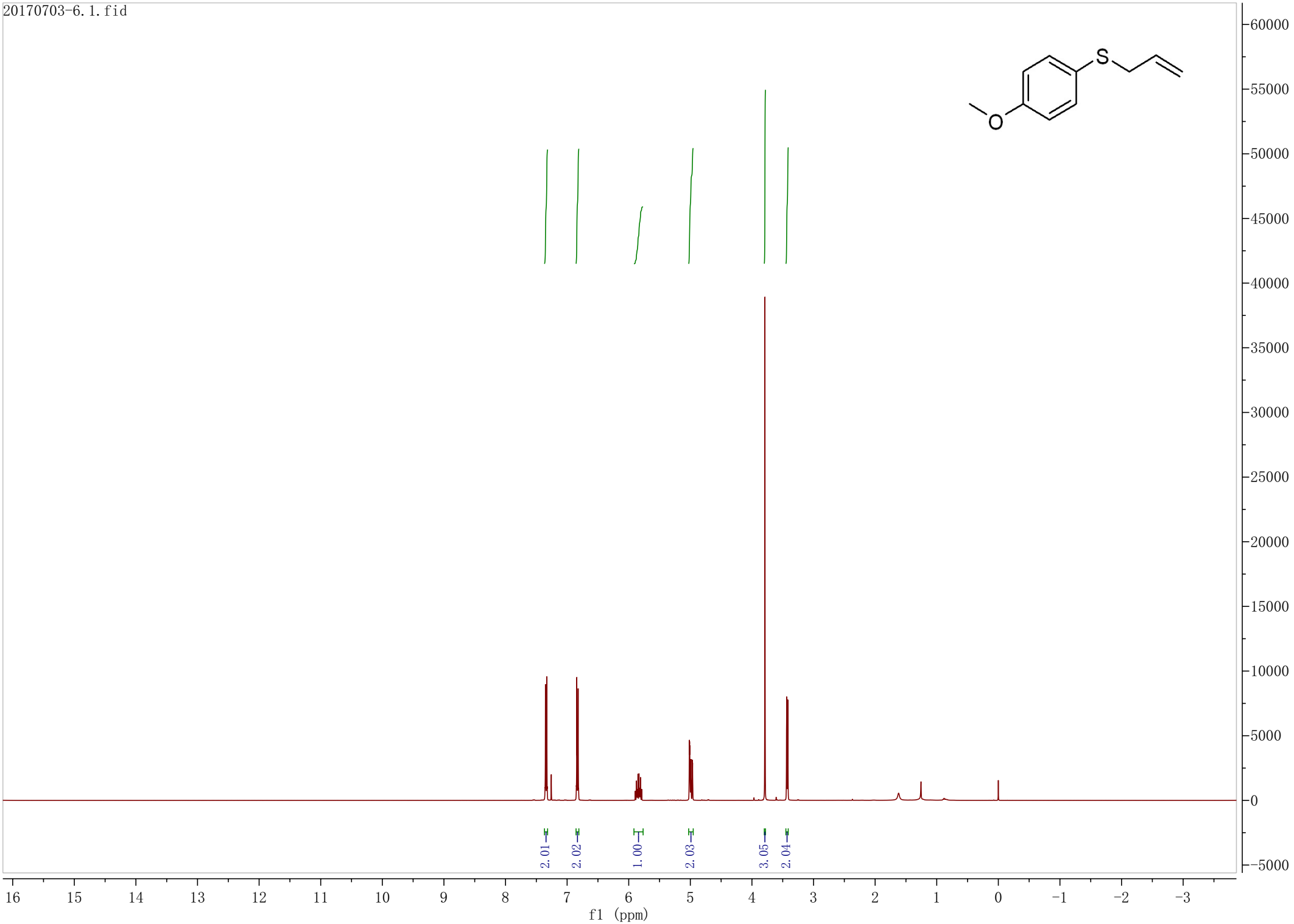

20170904-3
168.39
136.64
136.05
129.39
126.42
117.11
75.69
19.98
S
O
O
Cl
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

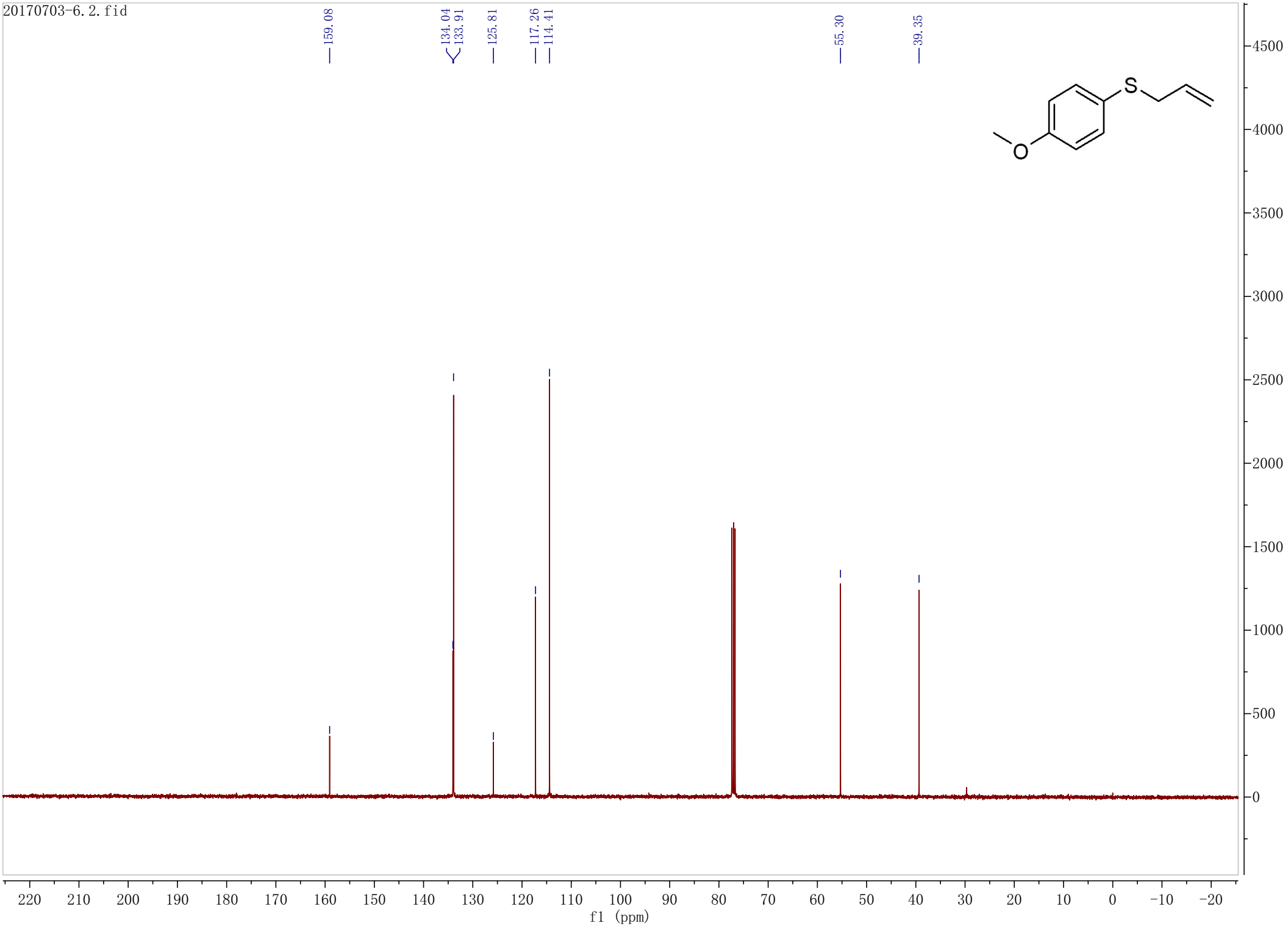

20170904-4
Cl
S
O
O
2.03
2.04
1.00
1.00
1.97
3.05
f1 (ppm)

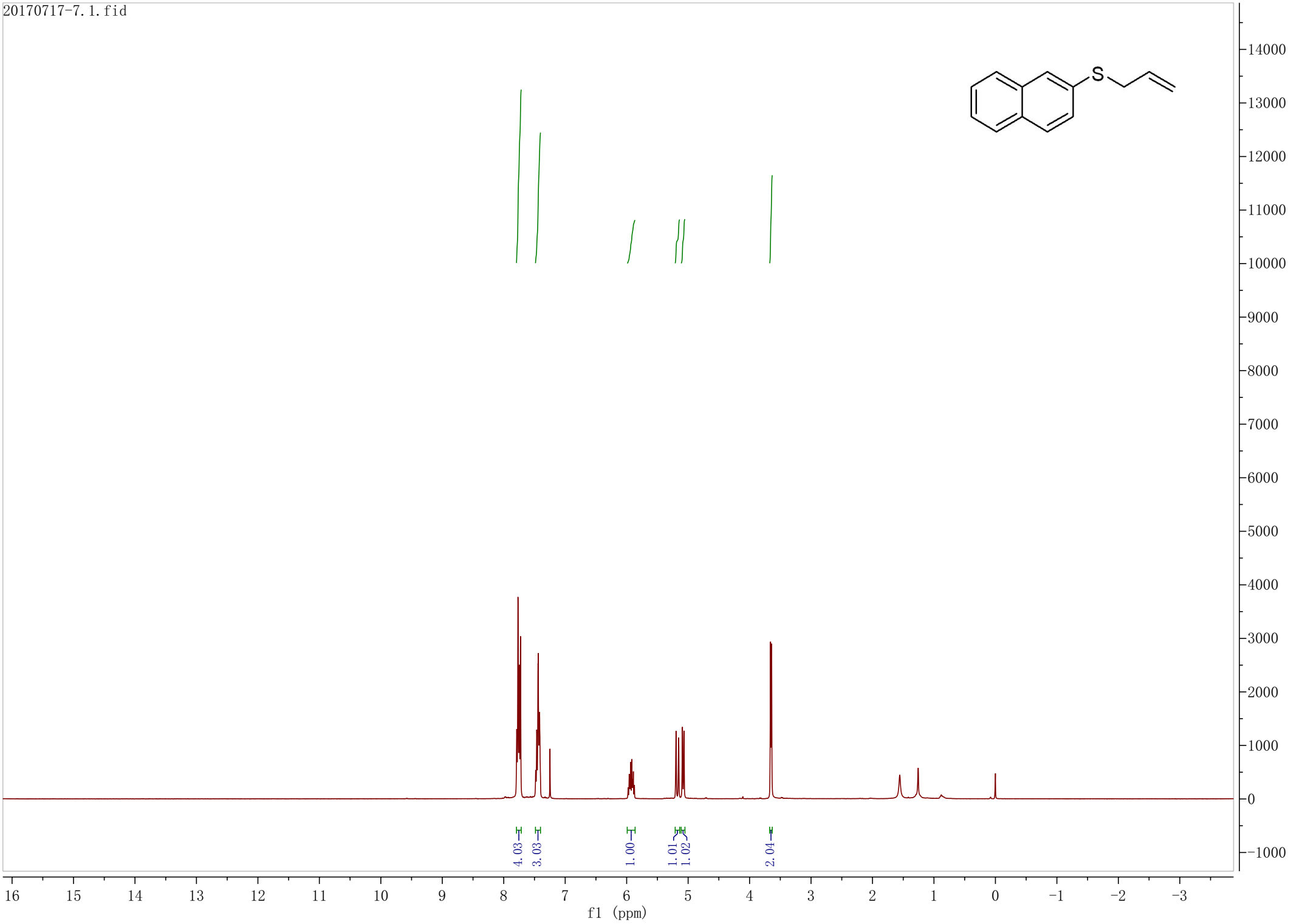

20170904-4
168.96
136.05
133.14
129.41
126.36
124.19
68.79
17.82
S
O
O
Cl
f1 (ppm)

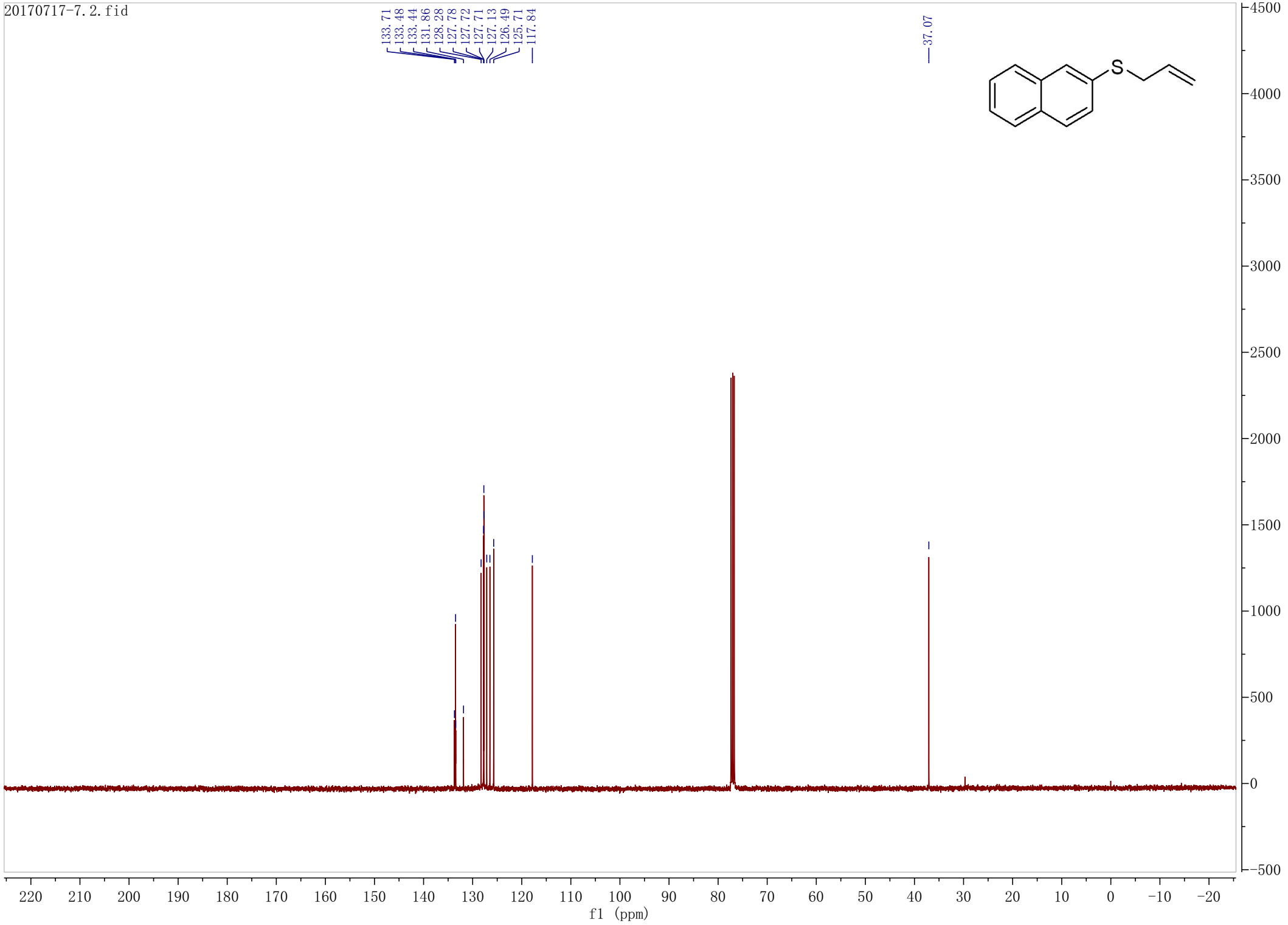

20170710-2.1.fid
S
30000
25000
20000
15000
10000
5000
0
2.00
2.03
1.00
2.00
2.05
3.02
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

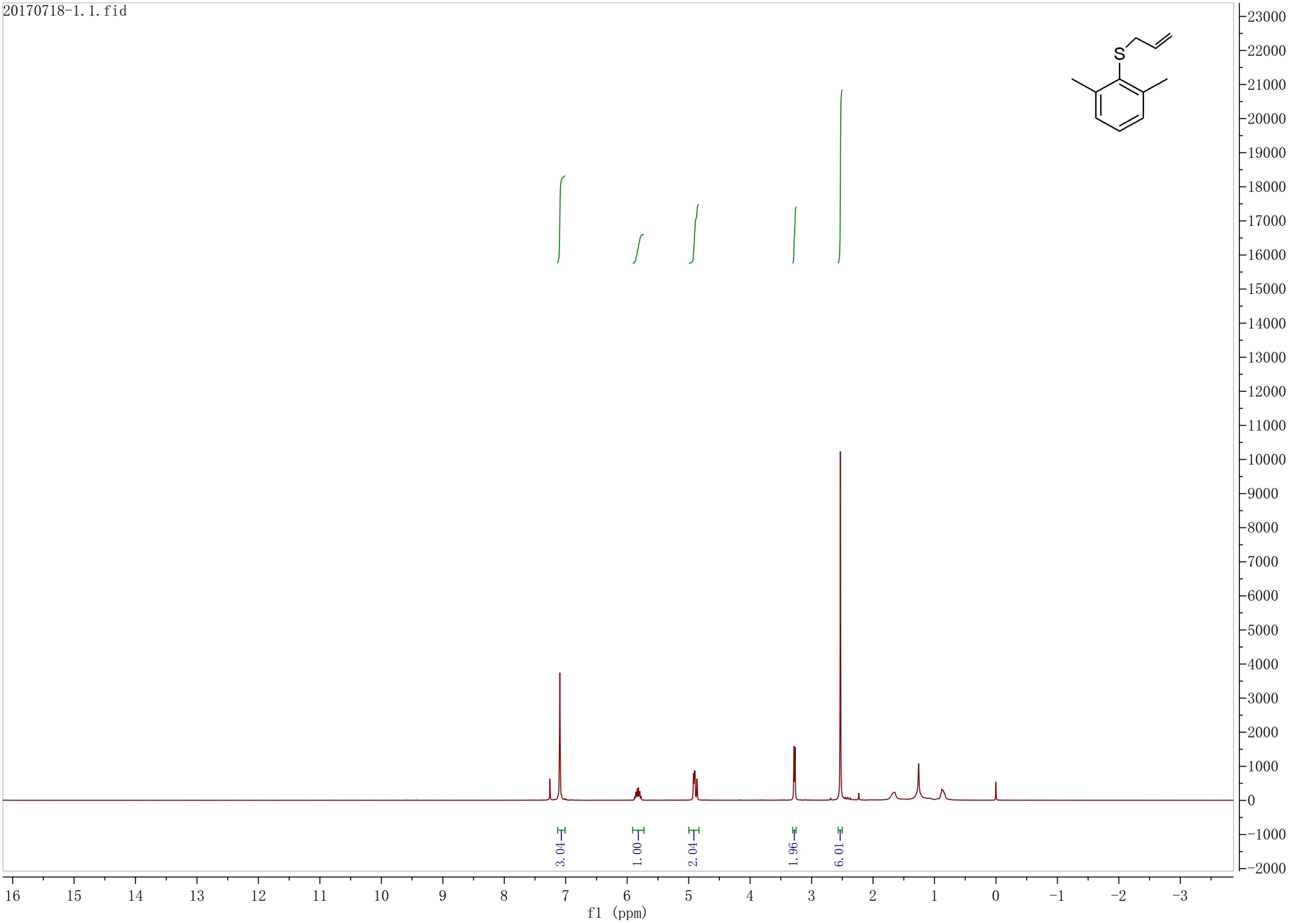

20170710-2.2.fid
136.42
133.84
132.04
130.70
129.57
117.40
37.91
21.03
S
f1 (ppm)

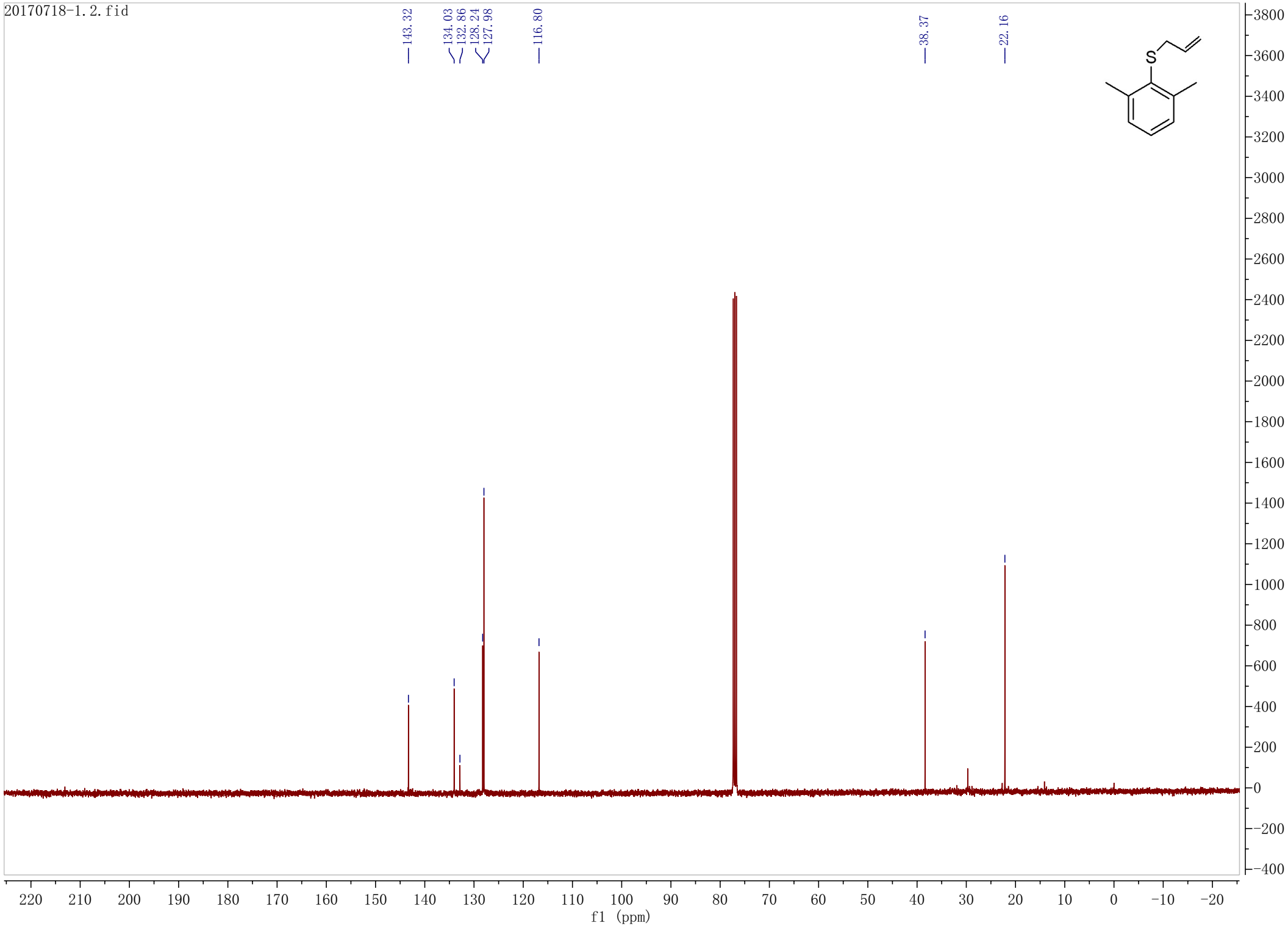

20170703-6.1.fid
S
O
2.01
2.02
1.00
2.03
3.05
2.04
f1 (ppm)

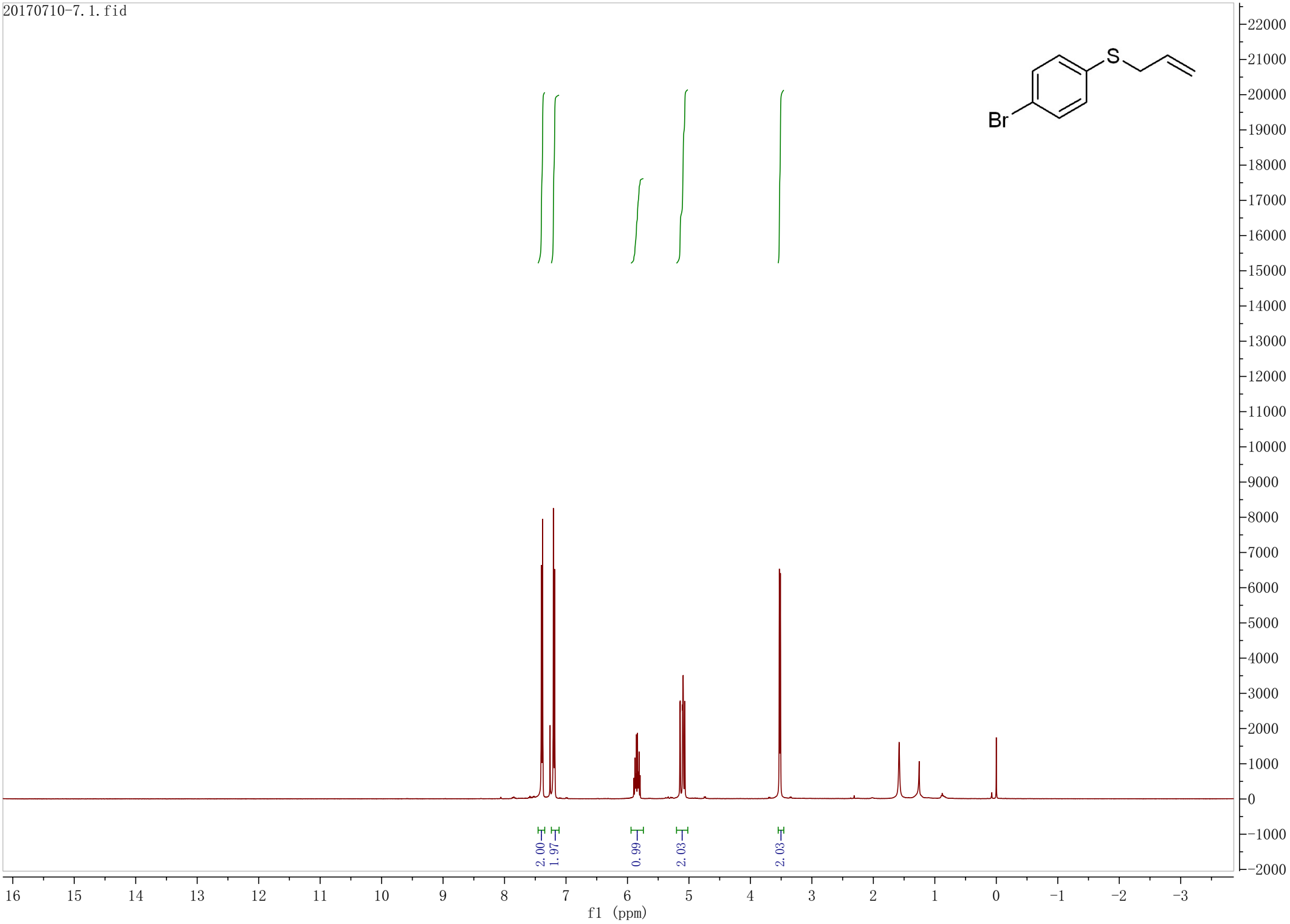

20170703-6.2.fid
159.08
134.04
133.91
125.81
117.26
114.41
55.30
39.35
S
O
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

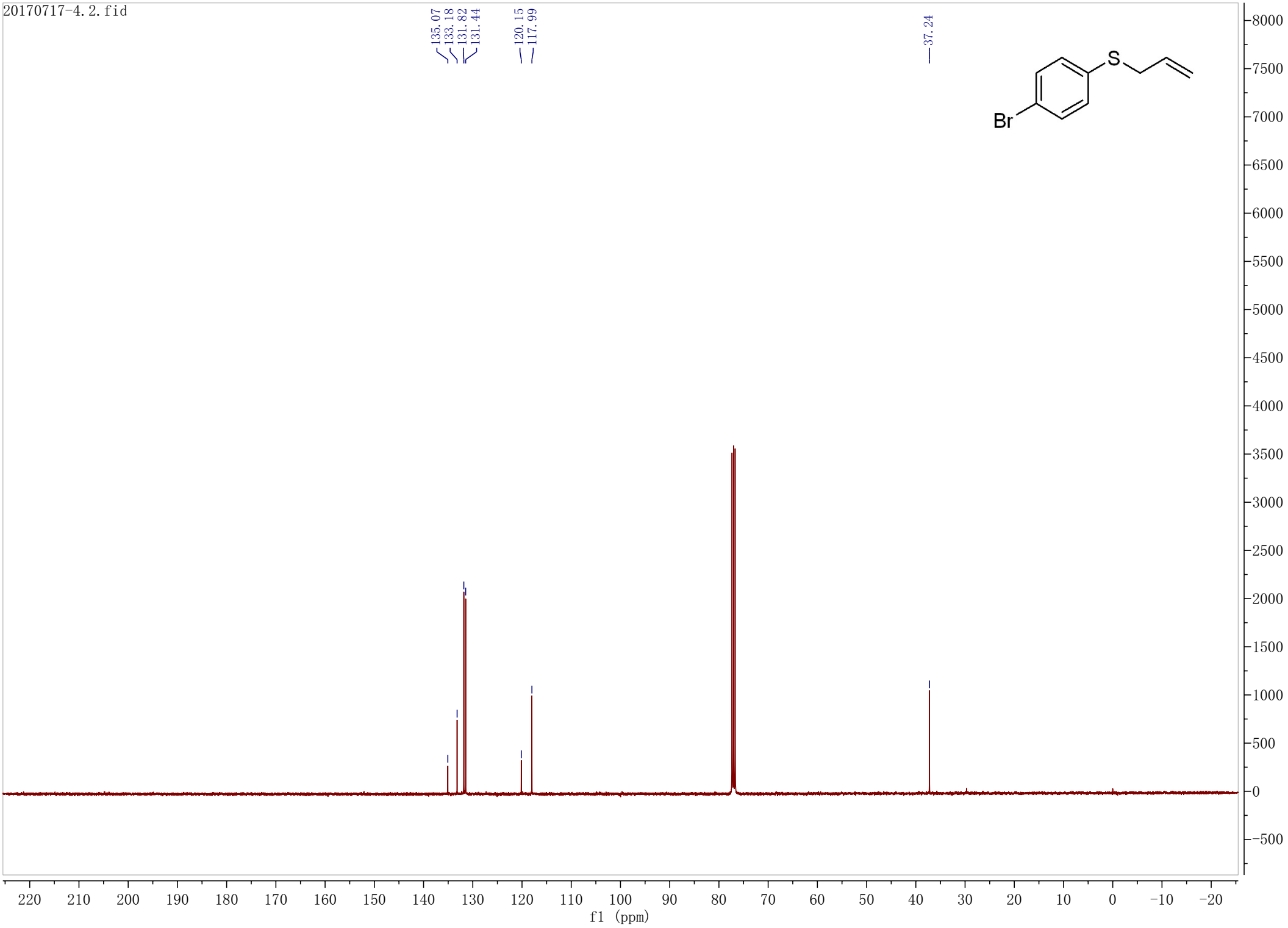

20170717-7.1.fid
S
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
4.03
3.03
1.00
1.01
1.02
2.04
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

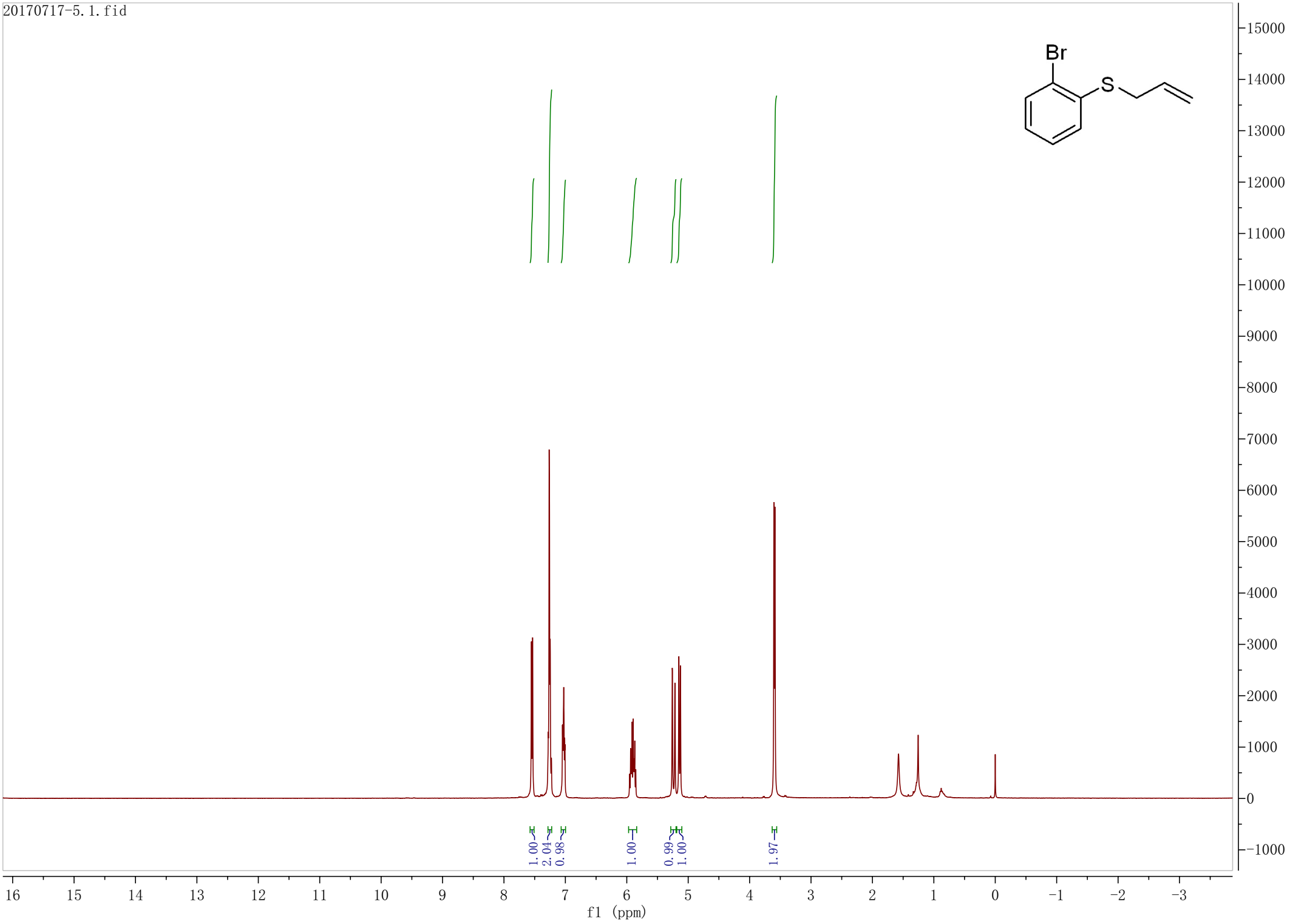

20170717-7.2.fid
133.71
133.48
133.44
131.86
128.28
127.78
127.72
127.71
127.13
126.49
125.71
117.84
37.07
S
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

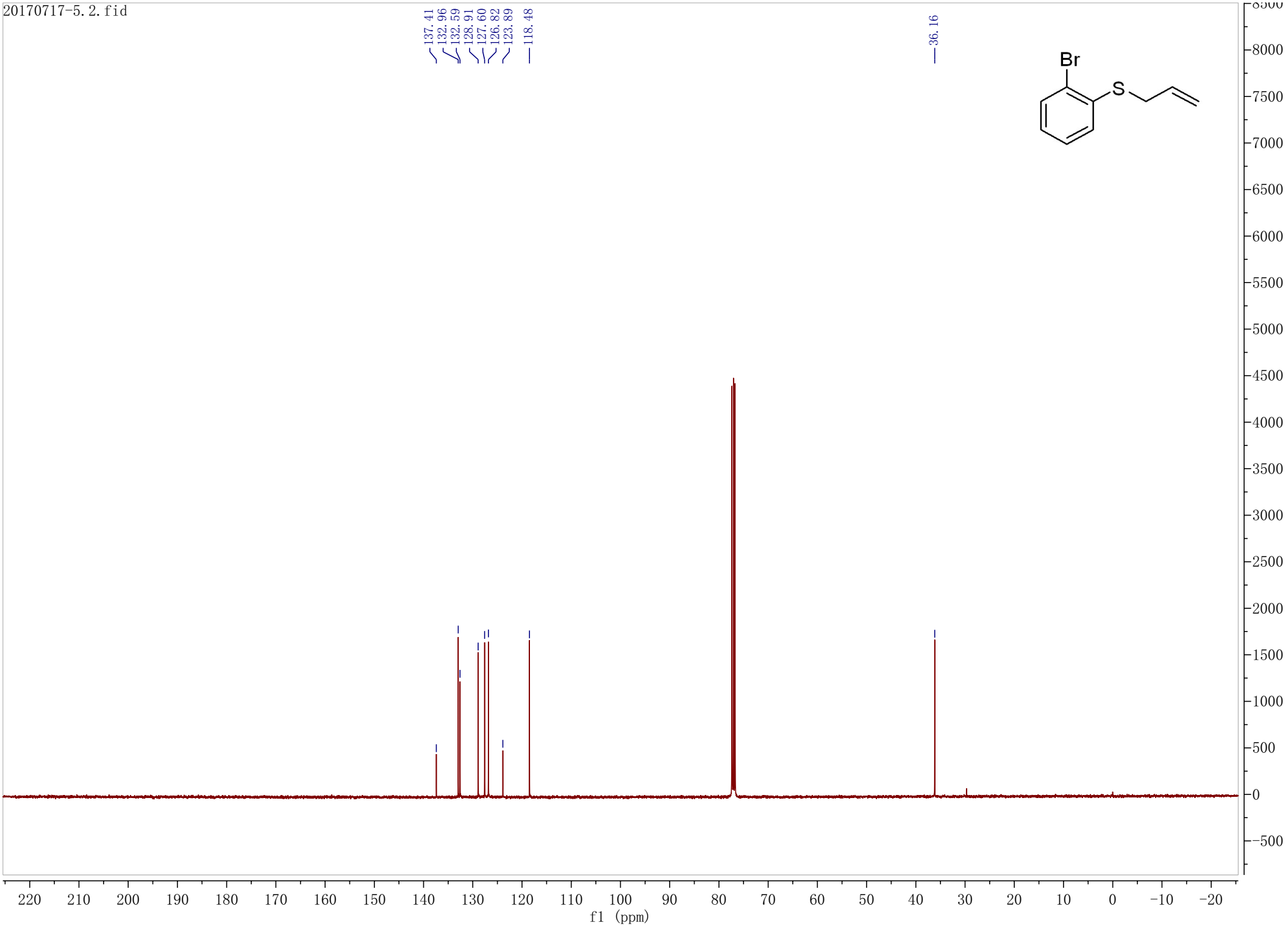

20170718-1.1.fid
S
3.04
1.00
2.04
1.96
6.01
f1 (ppm)

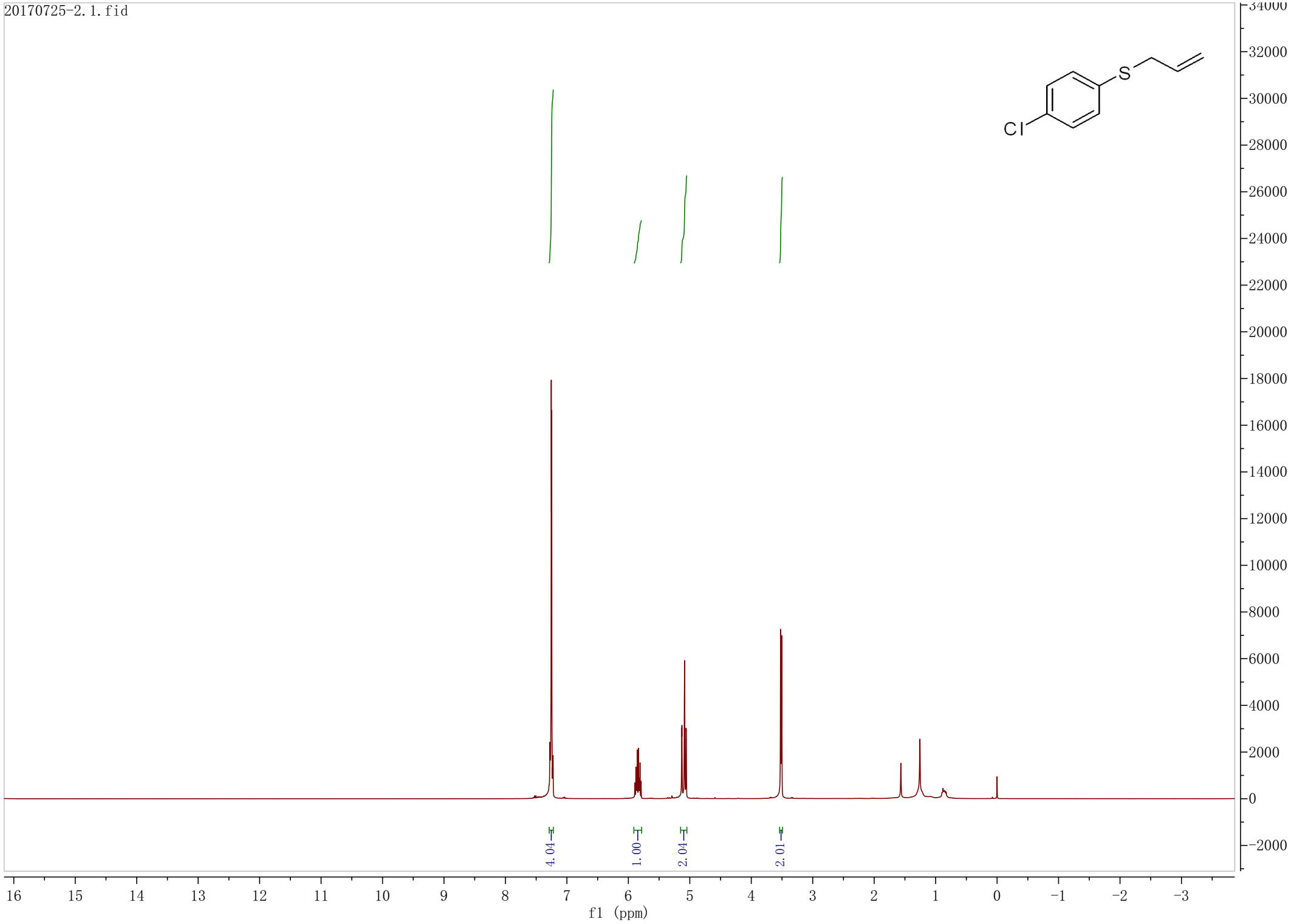

20170718-1.2.fid
143.32
134.03
132.86
128.24
127.98
116.80
38.37
22.16
S
f1 (ppm)

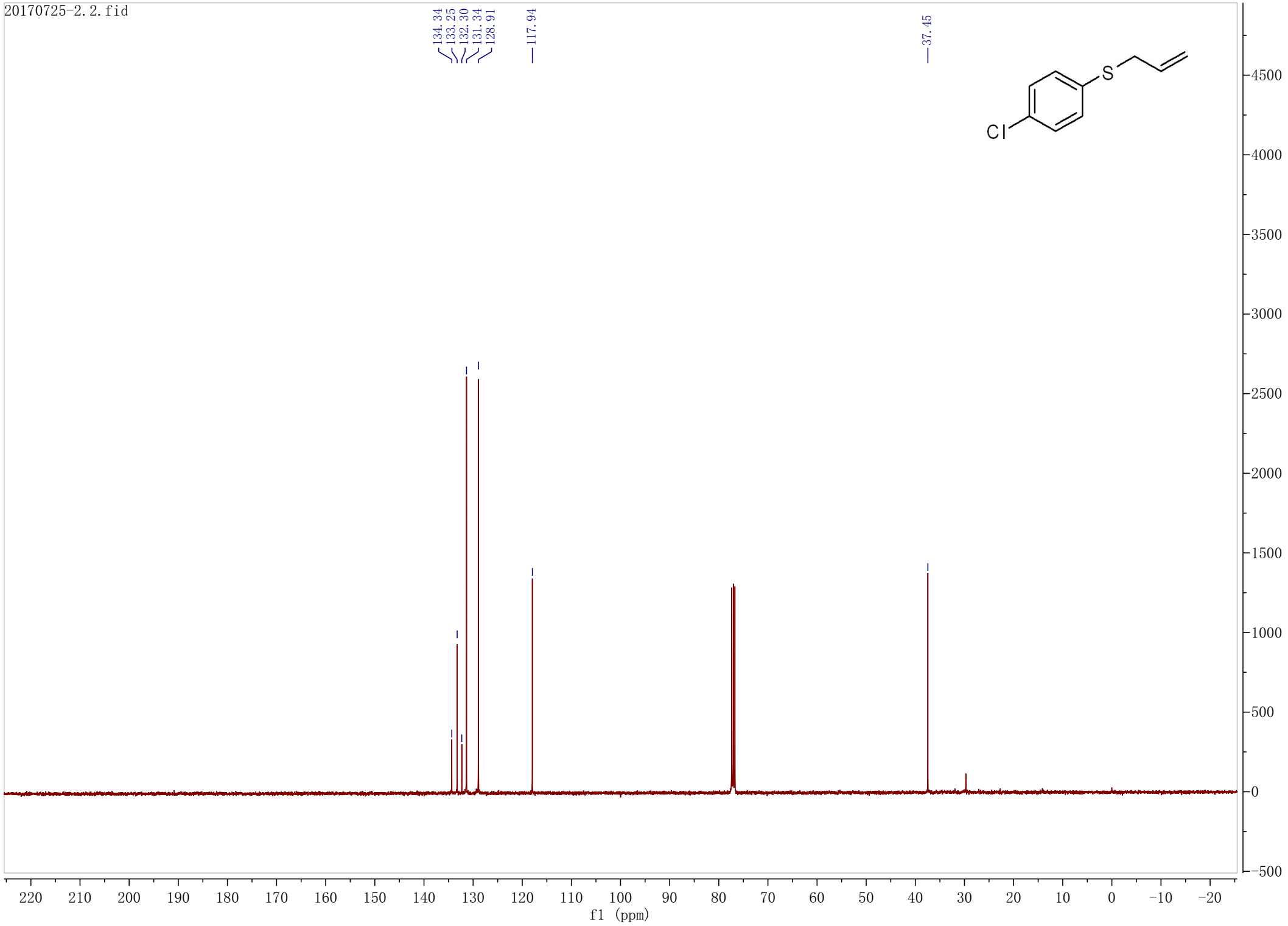

20170710-7.1.fid
S
Br
2.00
1.97
0.99
2.03
2.03
f1 (ppm)

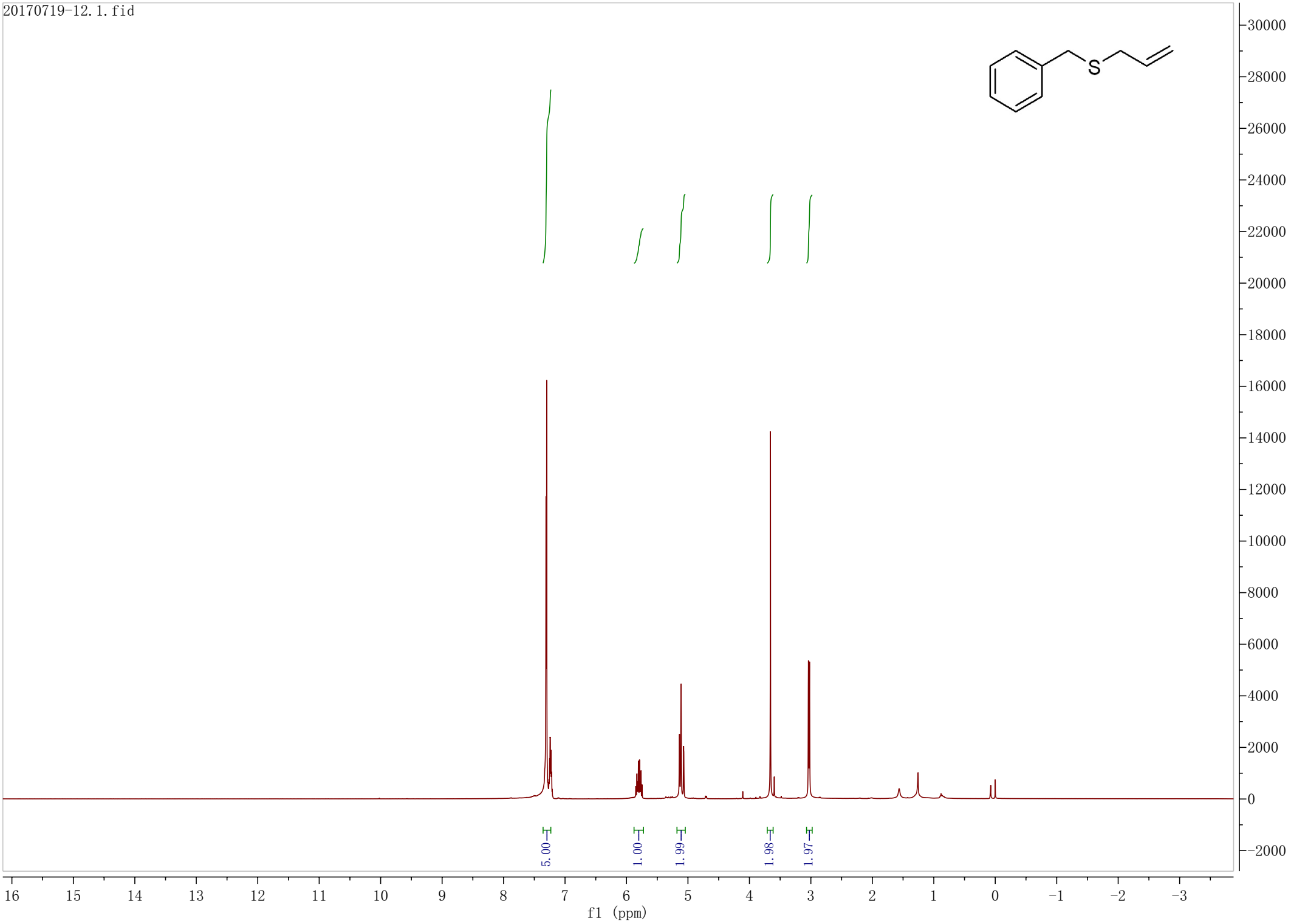

20170717-4.2.fid
135.07
133.18
131.82
131.44
120.15
117.99
37.24
S
Br
f1 (ppm)

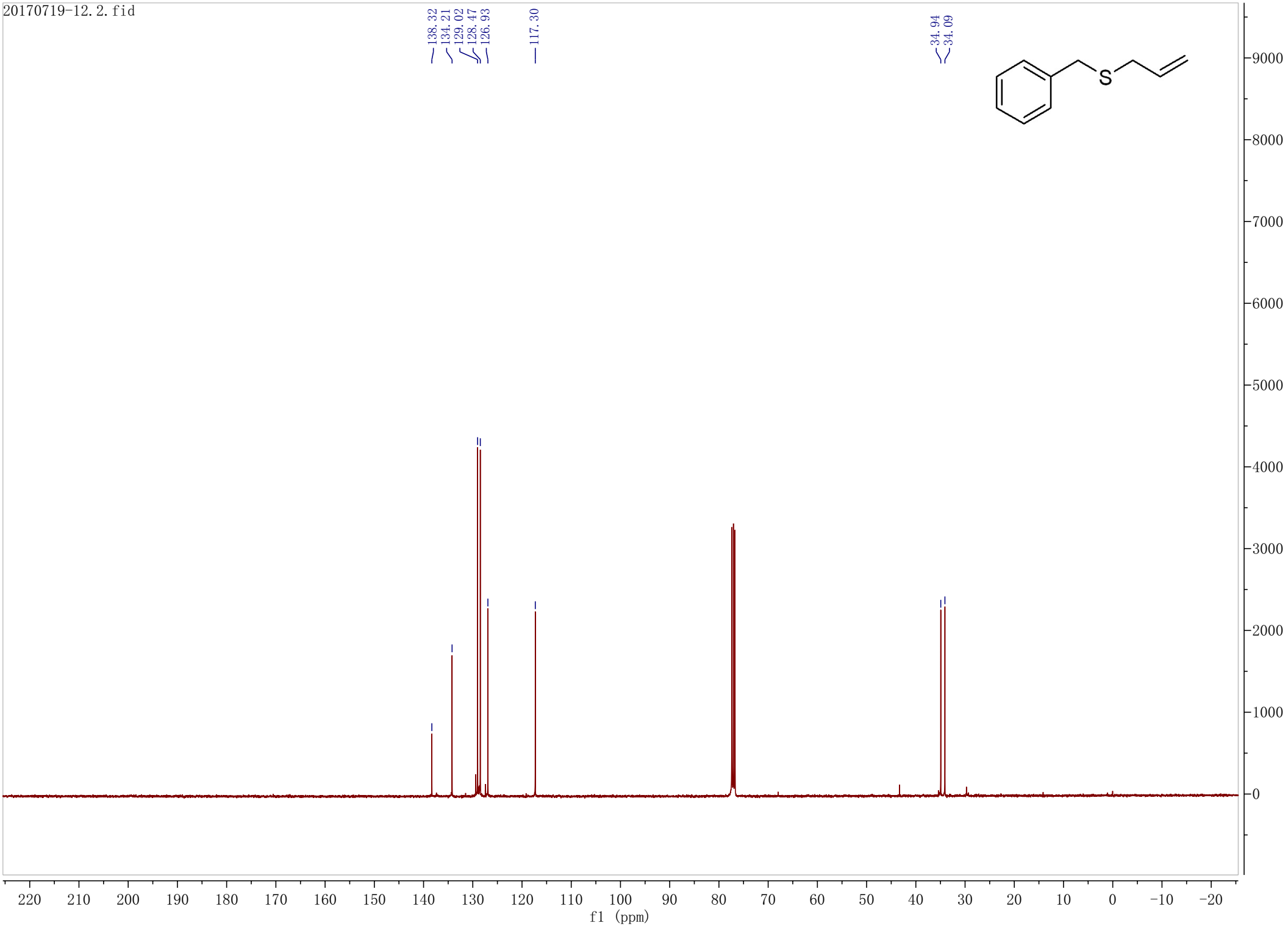

20170717-5.1.fid
Br
S
1.00
2.04
0.98
1.00
0.99
1.00
1.97
f1 (ppm)

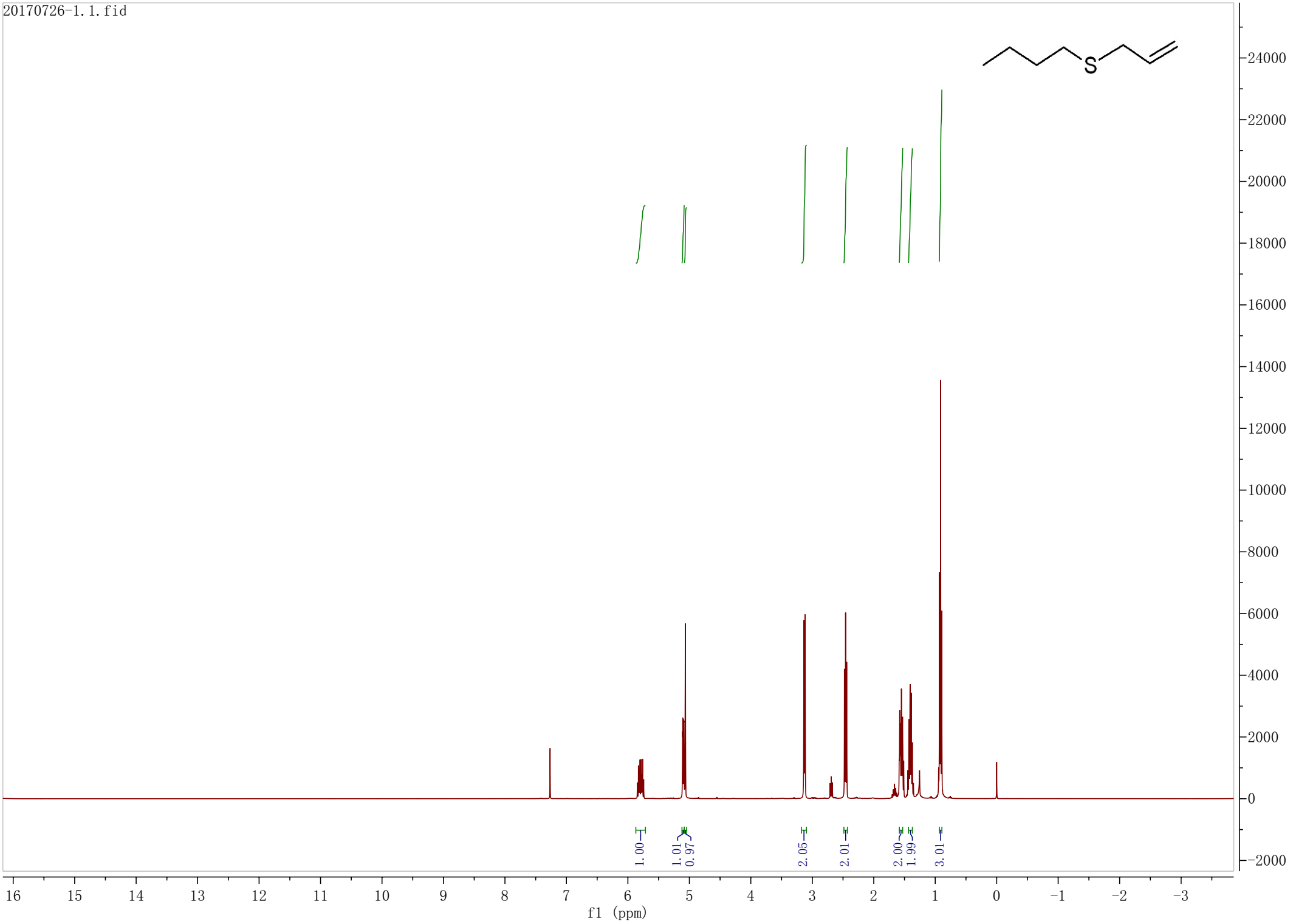

20170717-5.2.fid
137.41
132.96
132.59
128.91
127.60
126.82
123.89
118.48
36.16
Br
S
f1 (ppm)

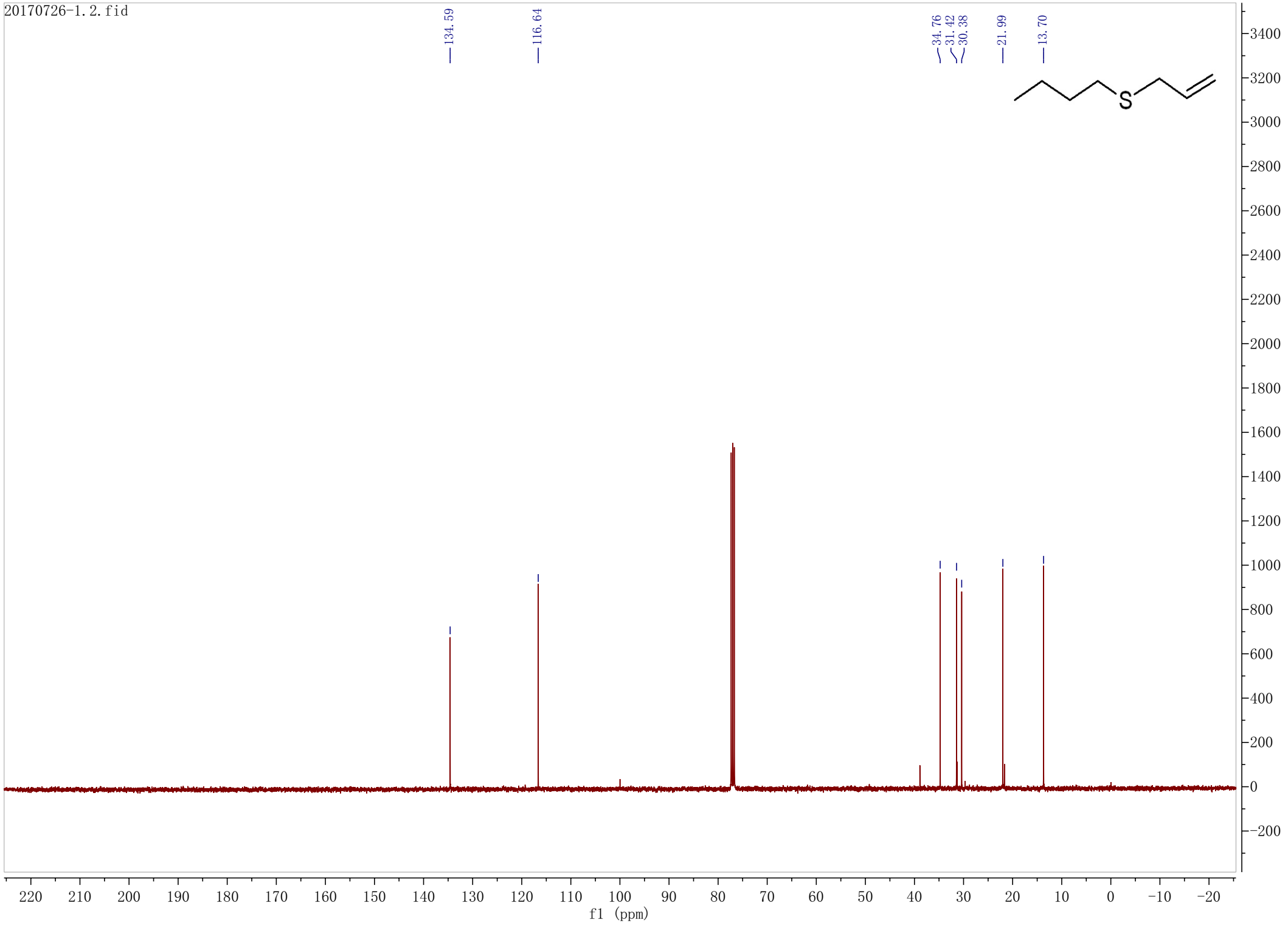

20170725-2.1.fid
Cl
S
4.04
1.00
2.04
2.01
f1 (ppm)

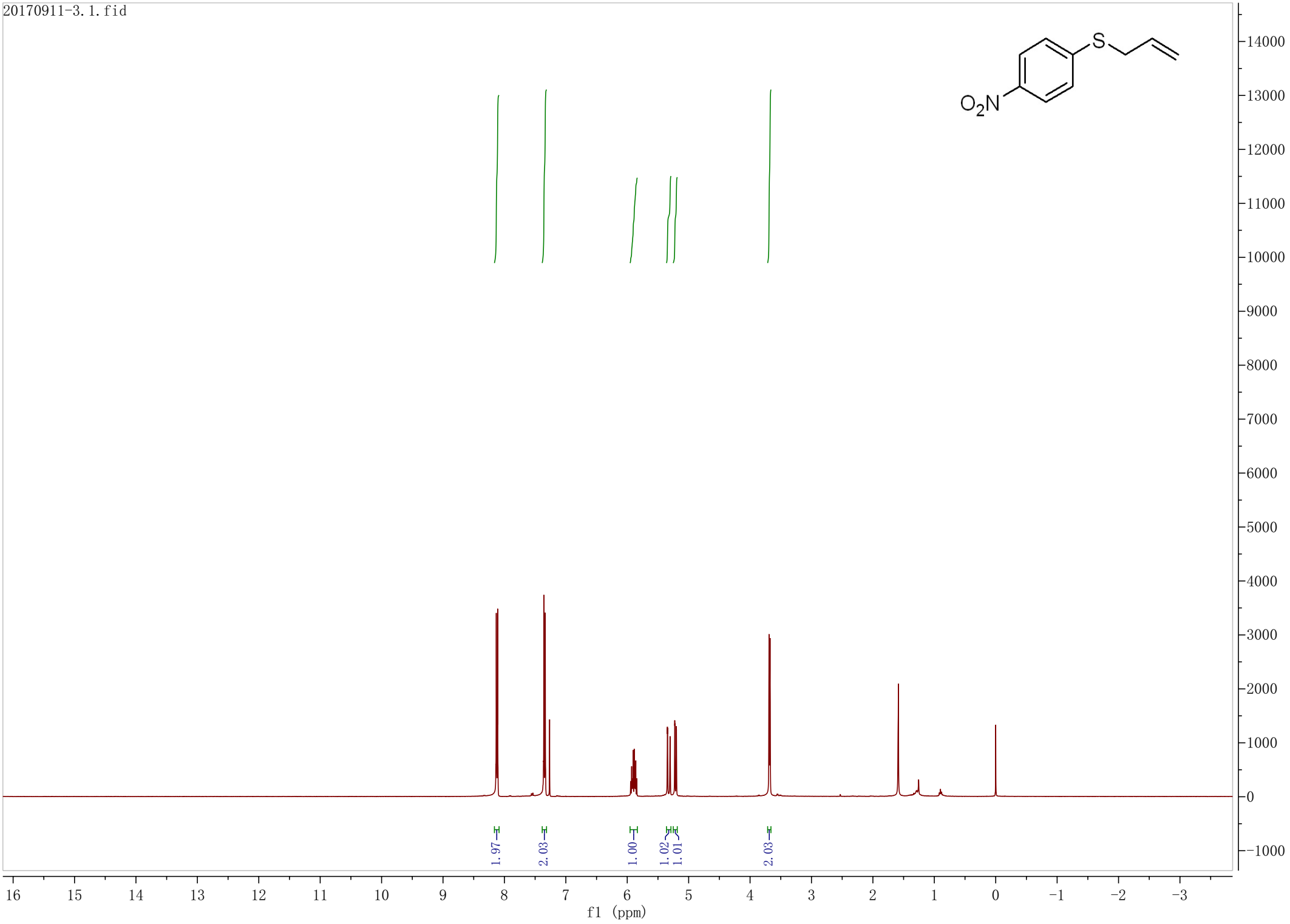

20170725-2.2.fid
134.34
133.25
132.30
131.34
128.91
117.94
37.45
S
Cl
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

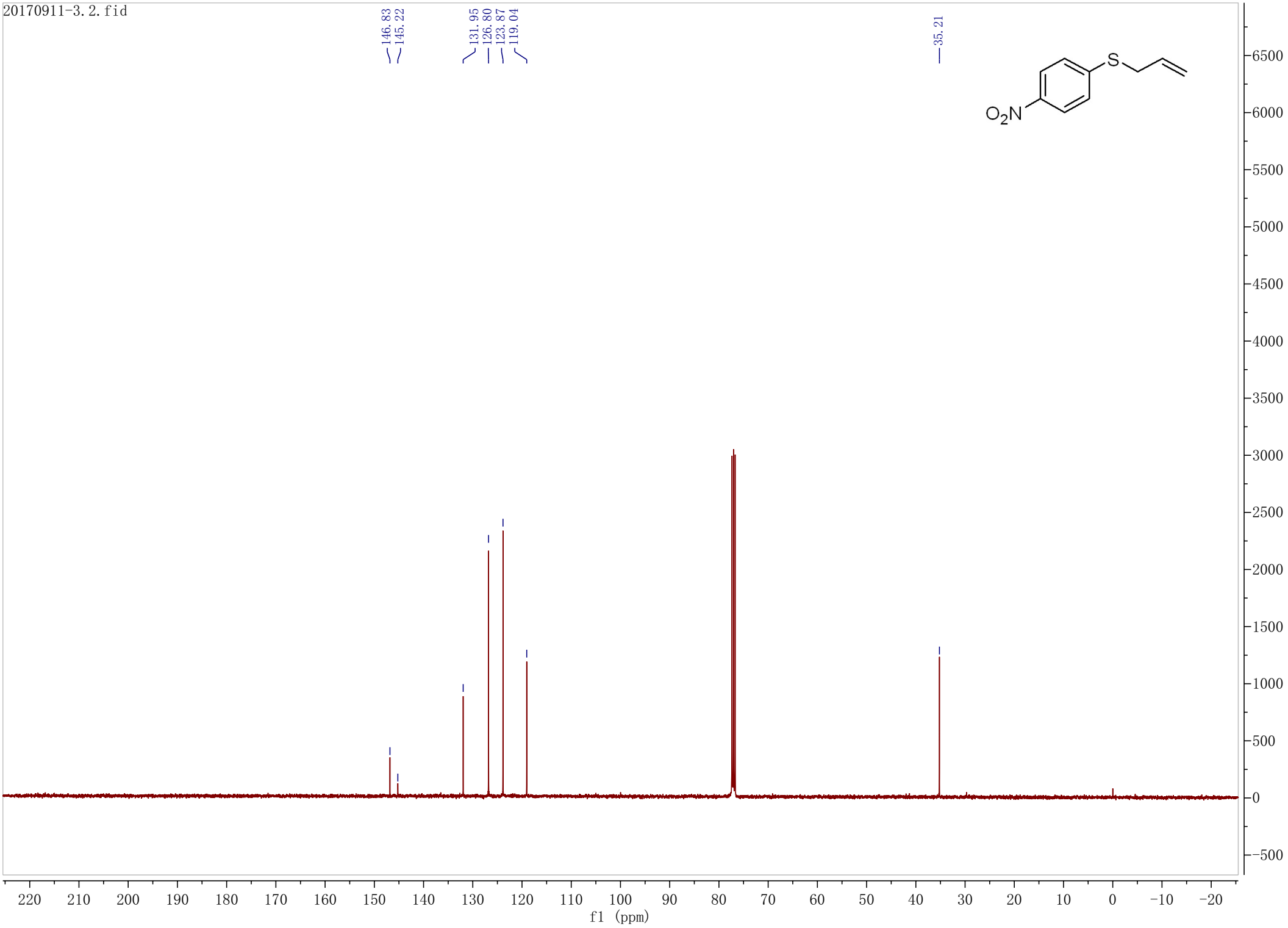

20170719-12.1.fid
S
5.00
1.00
1.99
1.98
1.97
f1 (ppm)

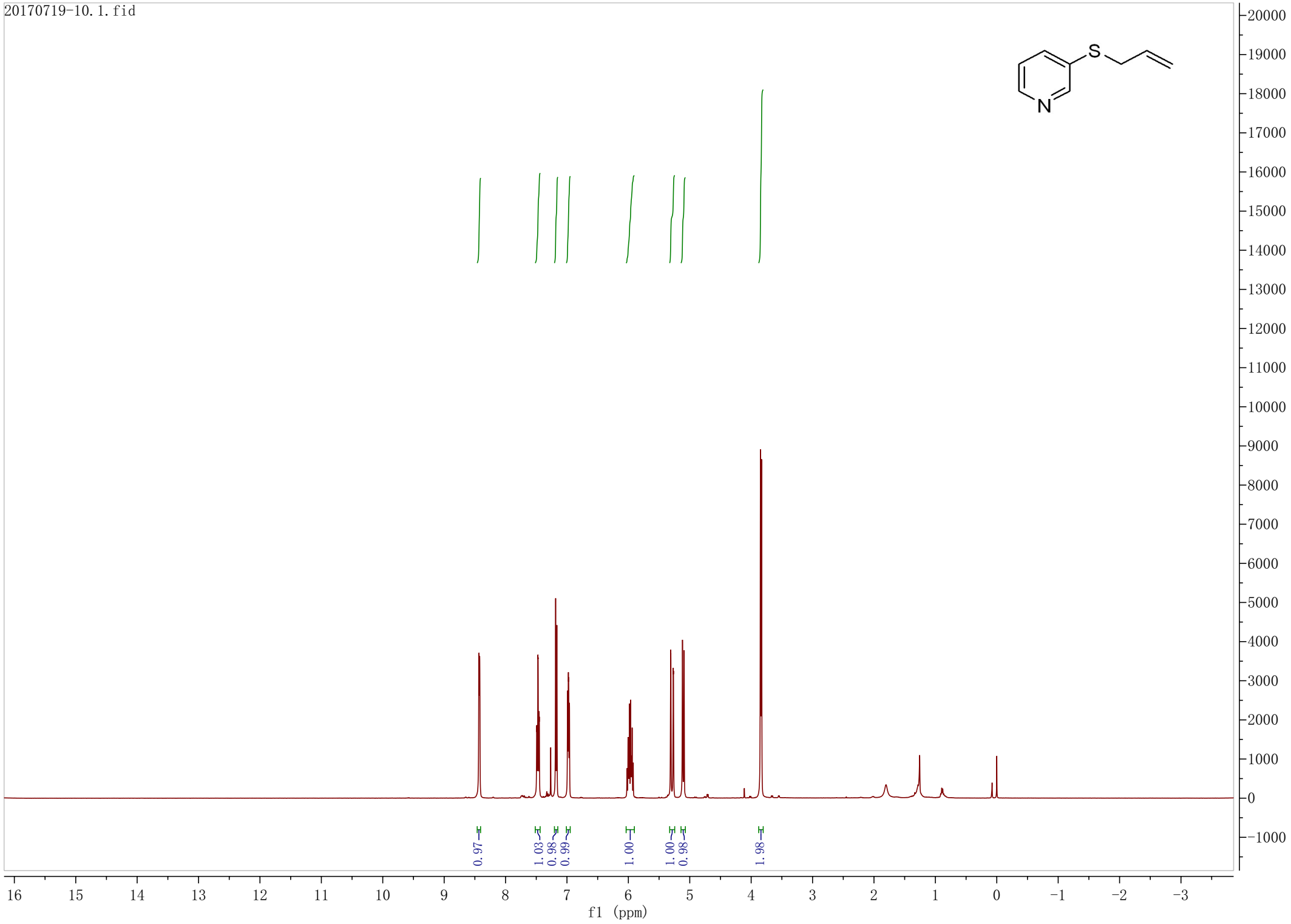

20170719-12.2.fid
138.32
134.21
129.02
128.47
126.93
117.30
34.94
34.09
S
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

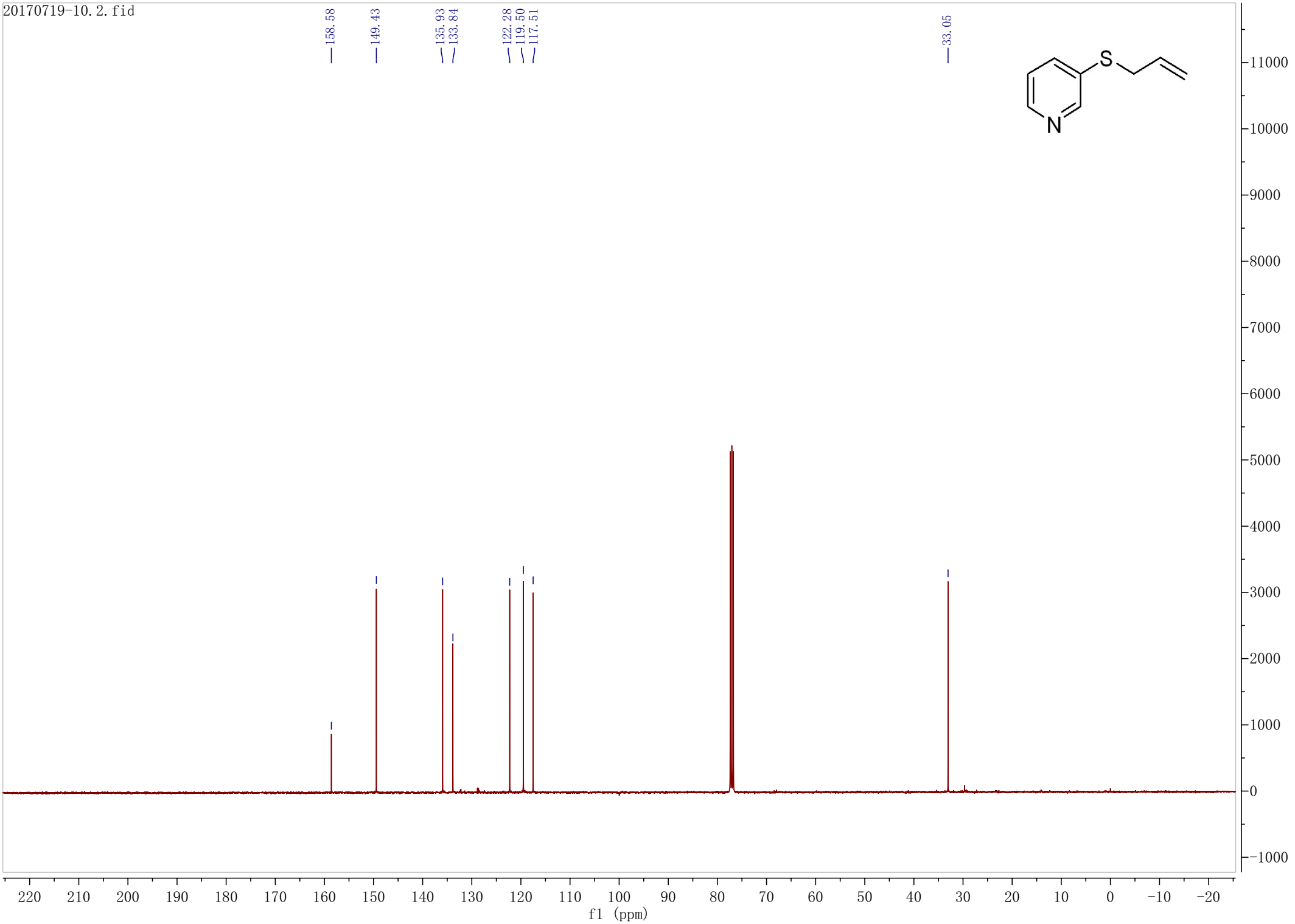

20170726-1.1.fid
S
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.00
1.01
0.97
2.05
2.01
2.00
1.99
3.01
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

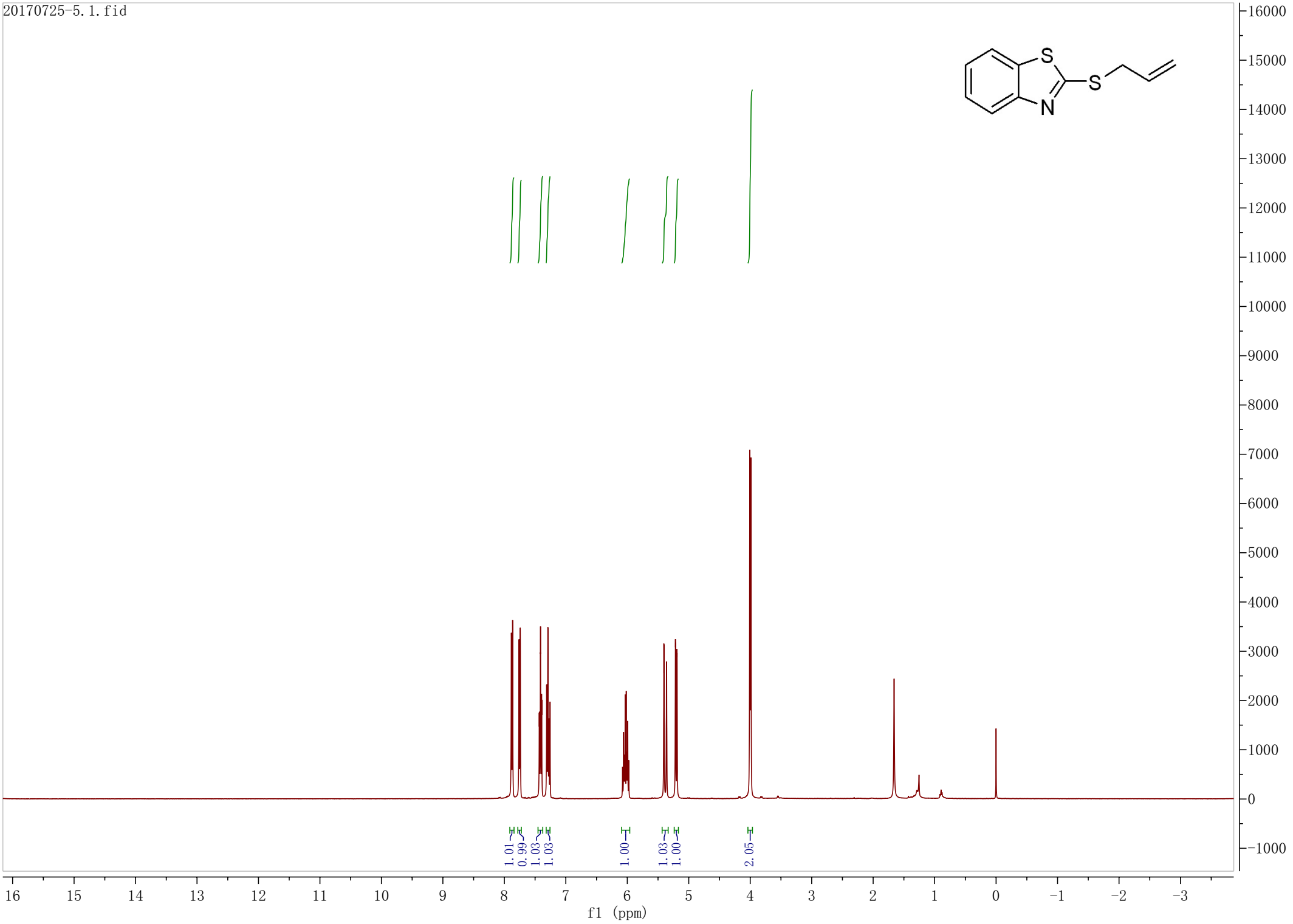

20170726-1.2.fid
134.59
116.64
34.76
31.42
30.38
21.99
13.70
S
f1 (ppm)

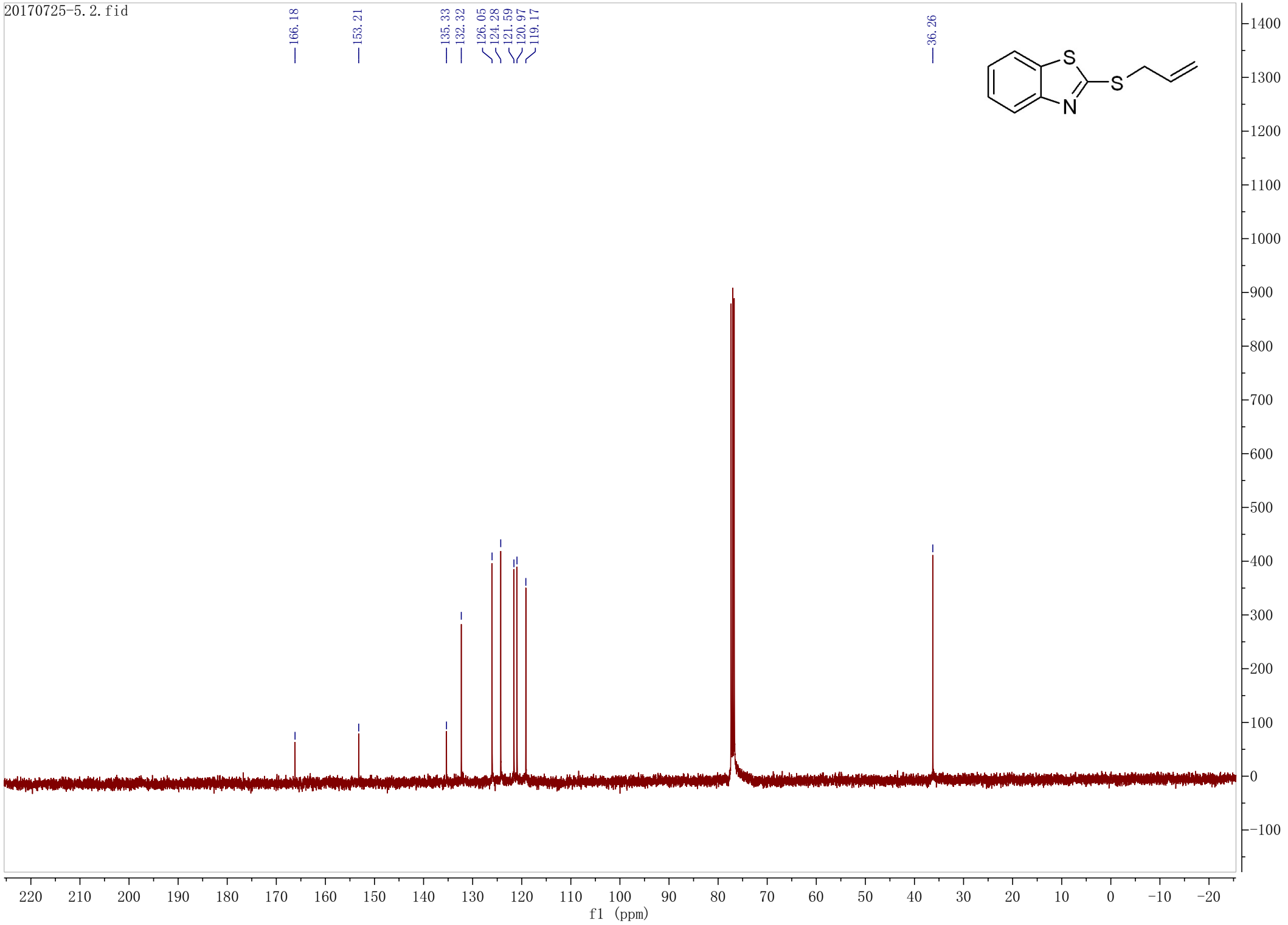

20170911-3.1.fid
S
O_2N
1.97
2.03
1.00
1.02
1.01
2.03
f1 (ppm)

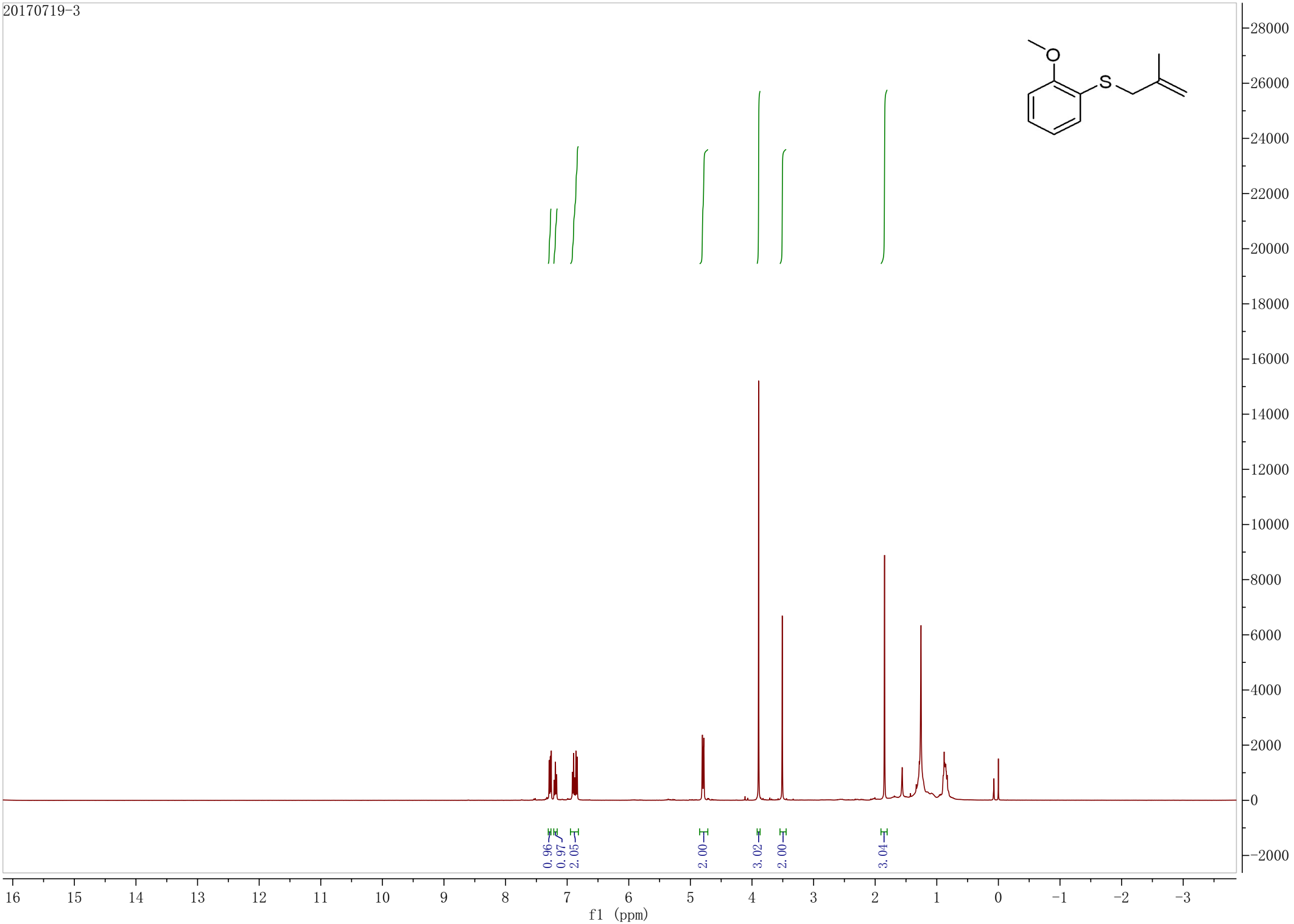

20170911-3.2.fid
146.83
145.22
131.95
126.80
123.87
119.04
35.21
S
O2N
f1 (ppm)

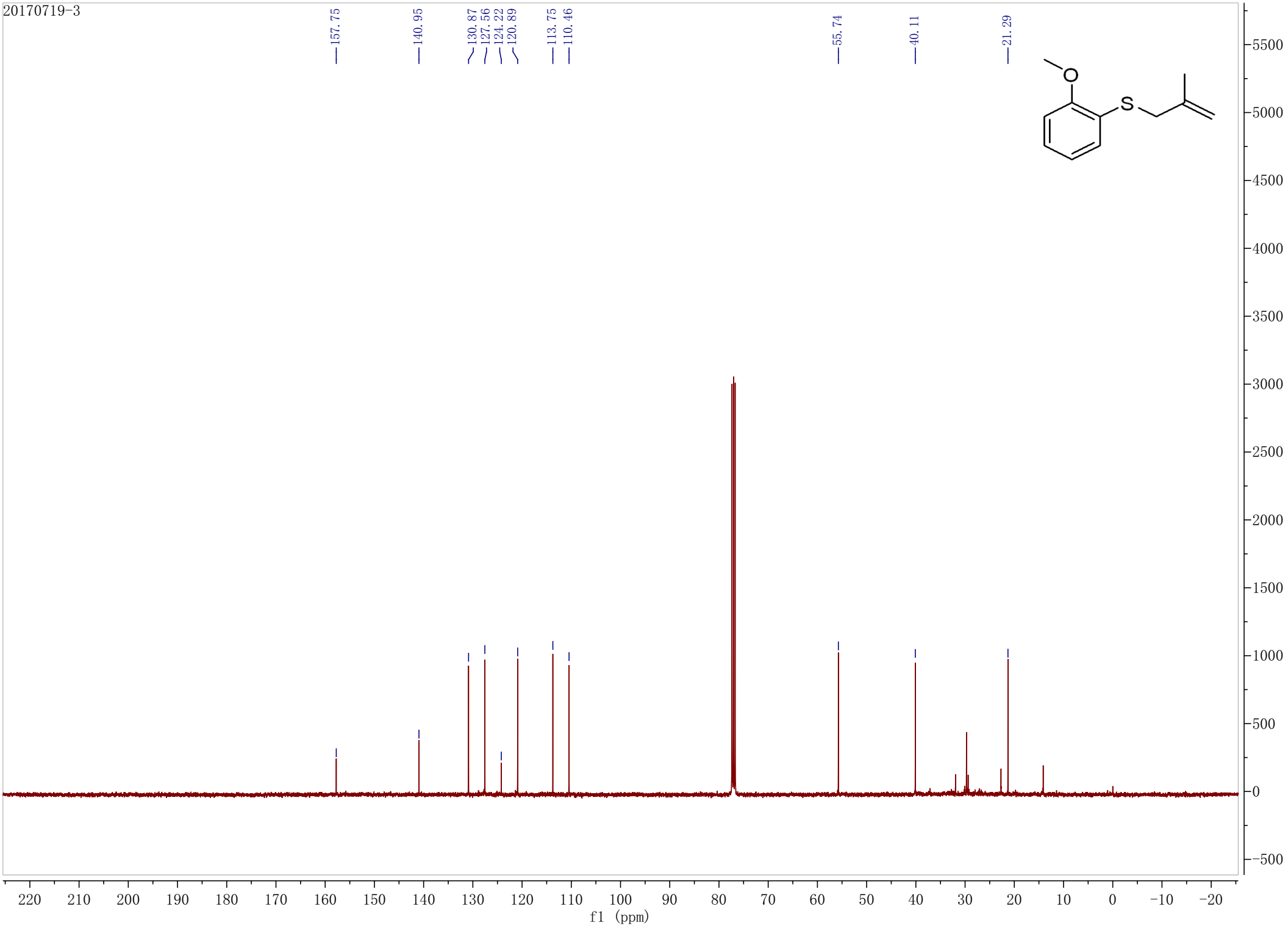

20170719-10.1.fid
S
N
0.97
1.03
0.98
0.99
1.00
1.00
0.98
1.98
f1 (ppm)

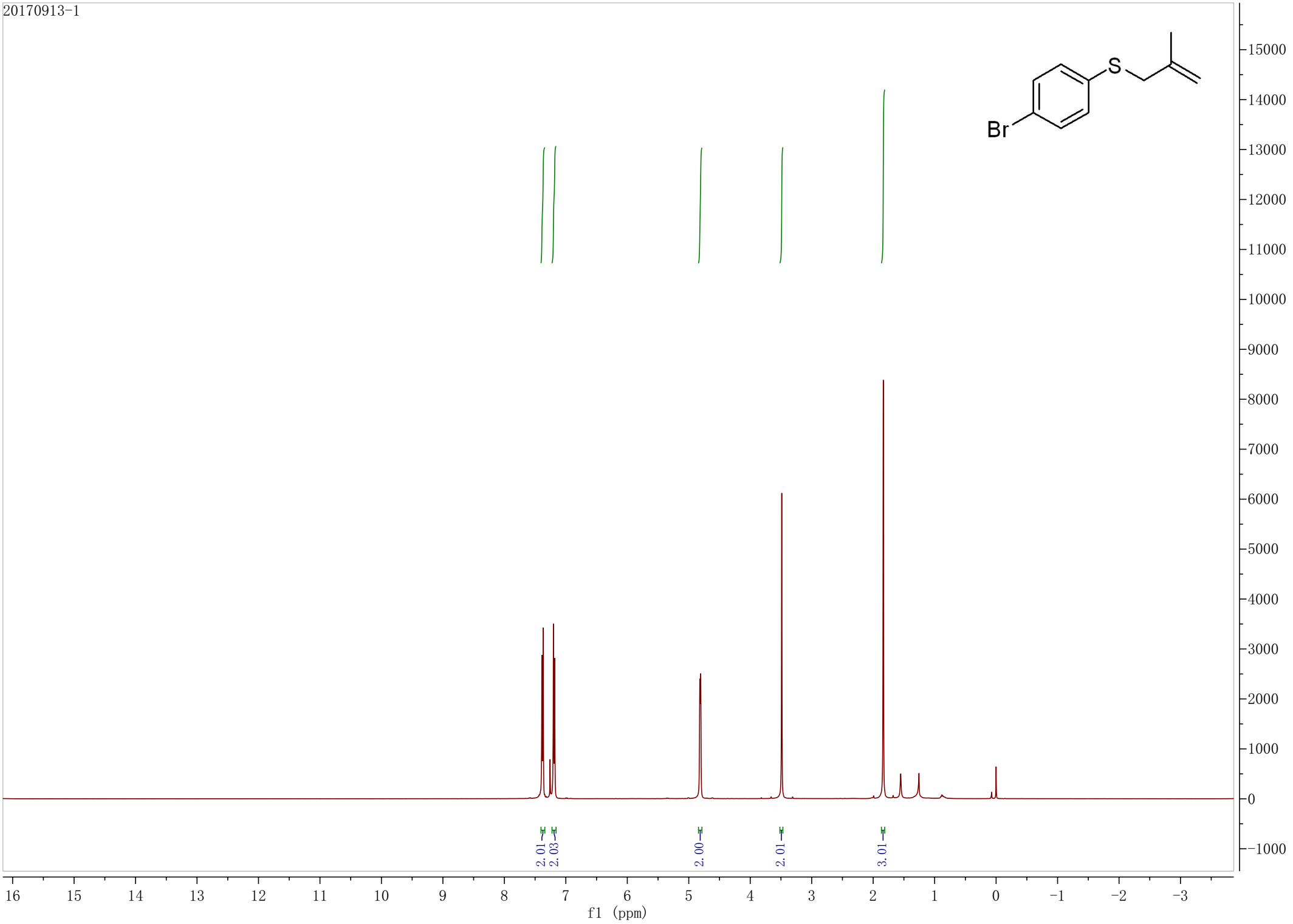

20170719-10.2.fid
158.58
149.43
135.93
133.84
122.28
119.50
117.51
33.05
S
N
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

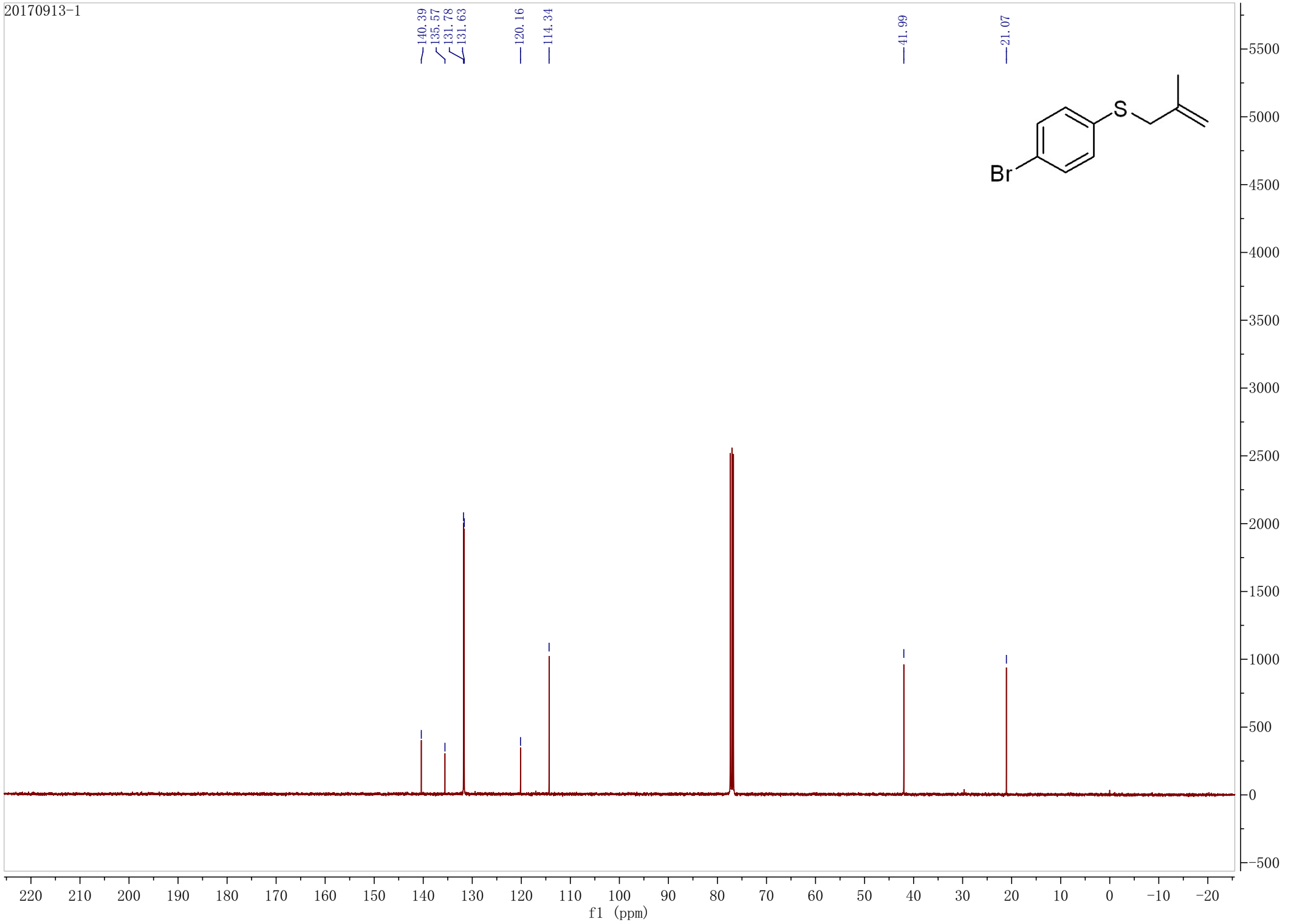

20170725-5.1.fid
S
S
N
1.01
0.99
1.03
1.03
1.00
1.03
1.00
2.05
f1 (ppm)

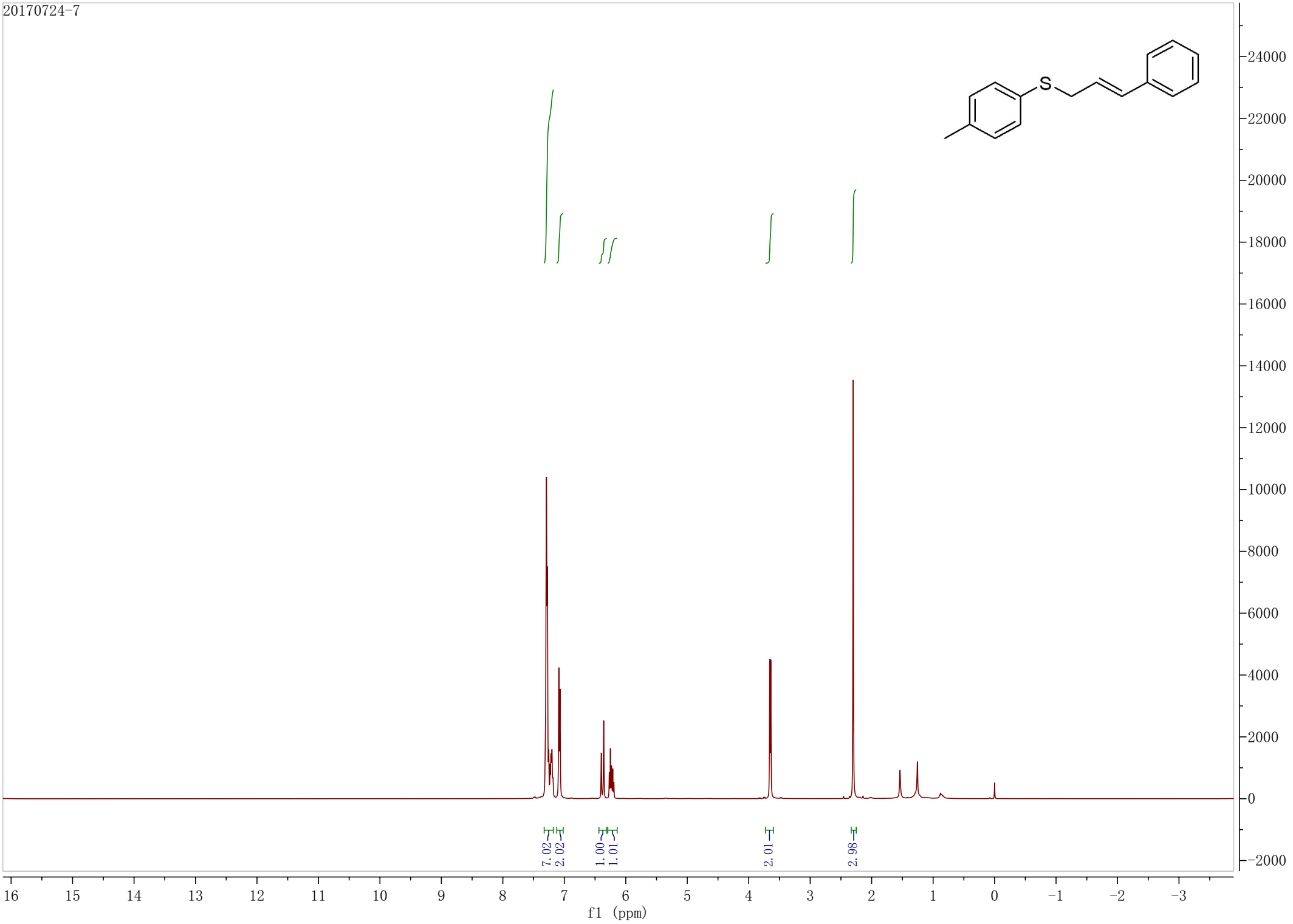

20170725-5.2.fid
166.18
153.21
135.33
132.32
126.05
124.28
121.59
120.97
119.17
36.26
S
S
N
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

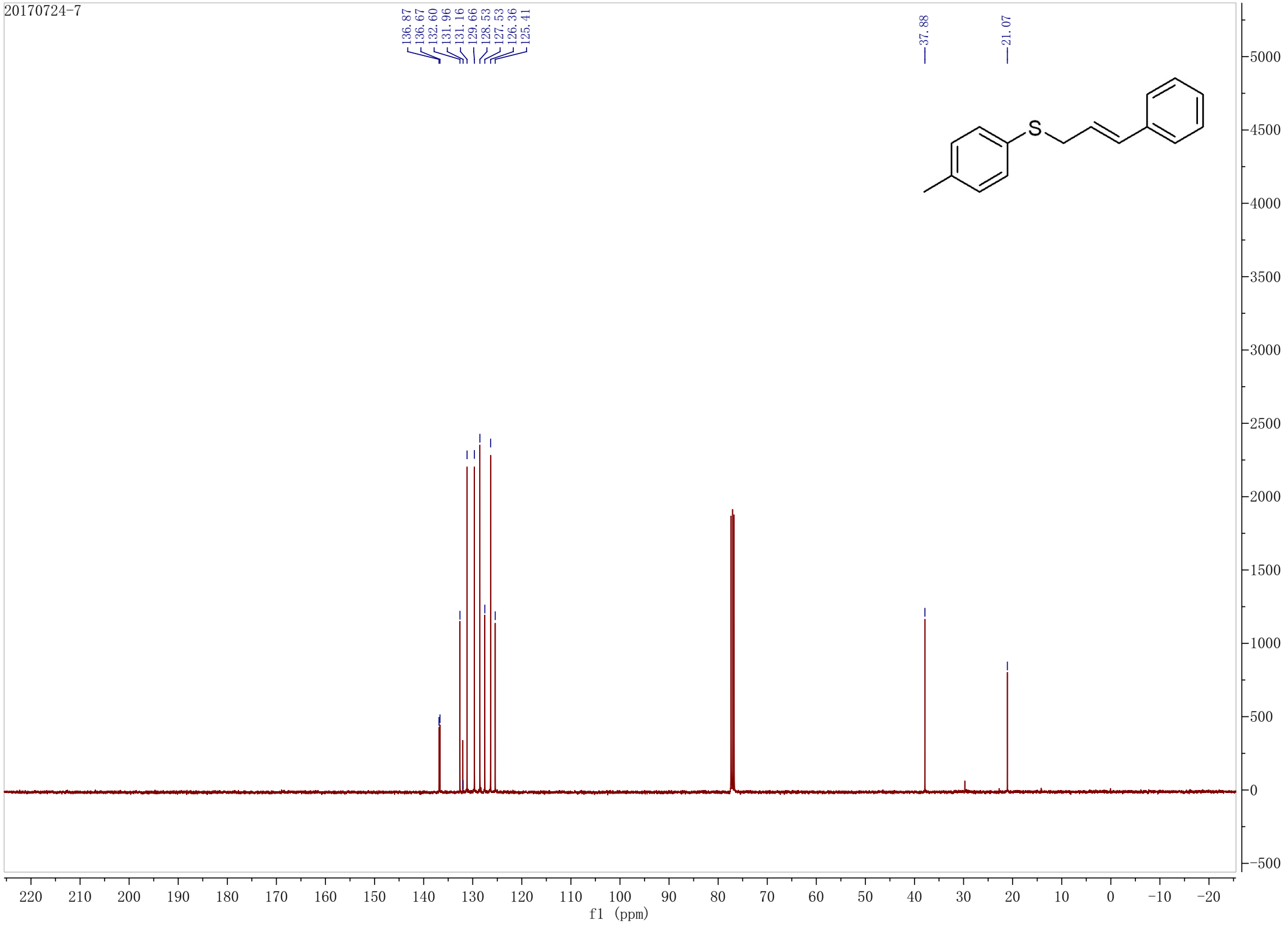

20170719-3
O
S
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
0.96
0.97
2.05
2.00
3.02
2.00
3.04
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

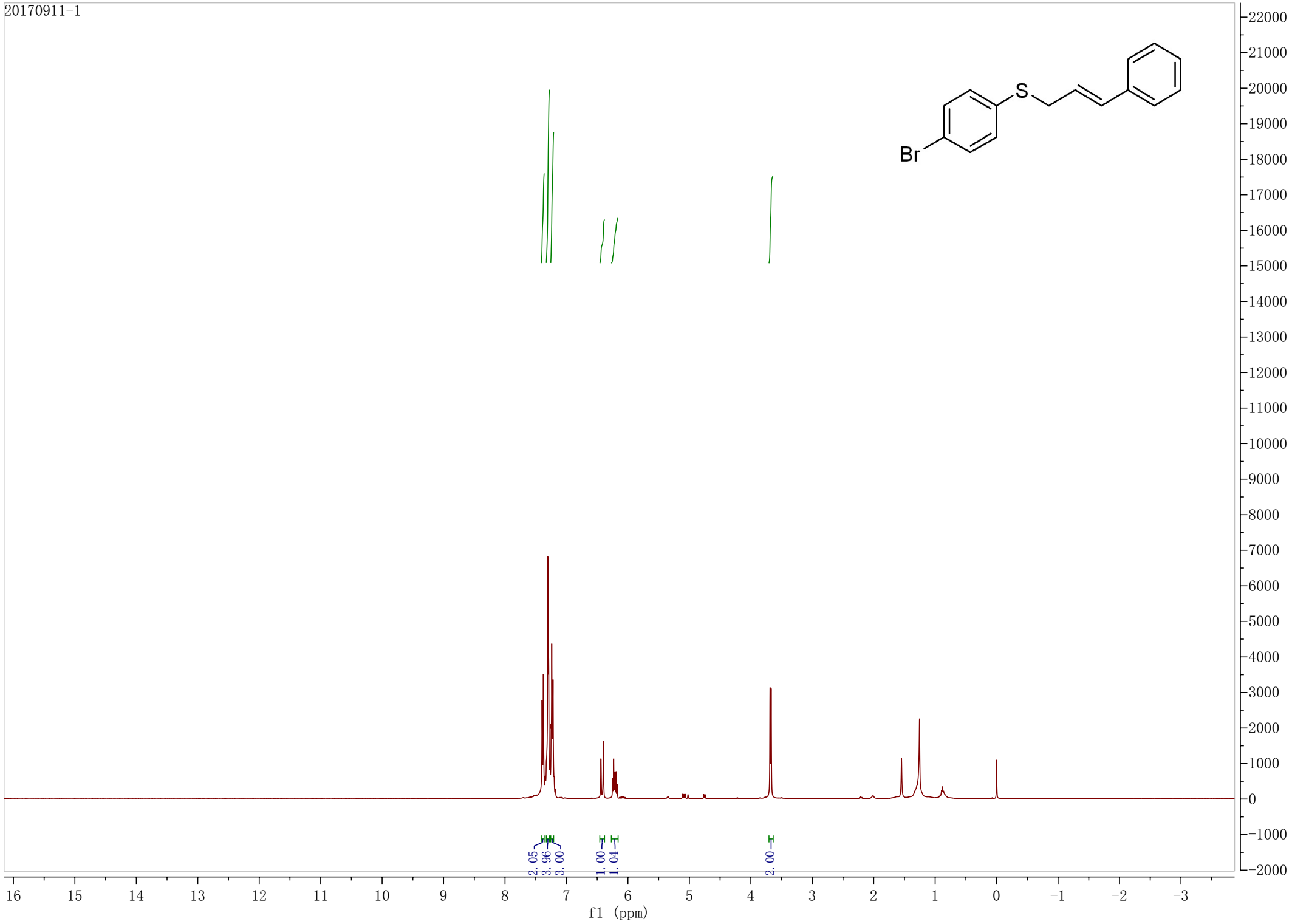

20170719-3
157.75
140.95
130.87
127.56
124.22
120.89
113.75
110.46
55.74
40.11
21.29
O
S
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

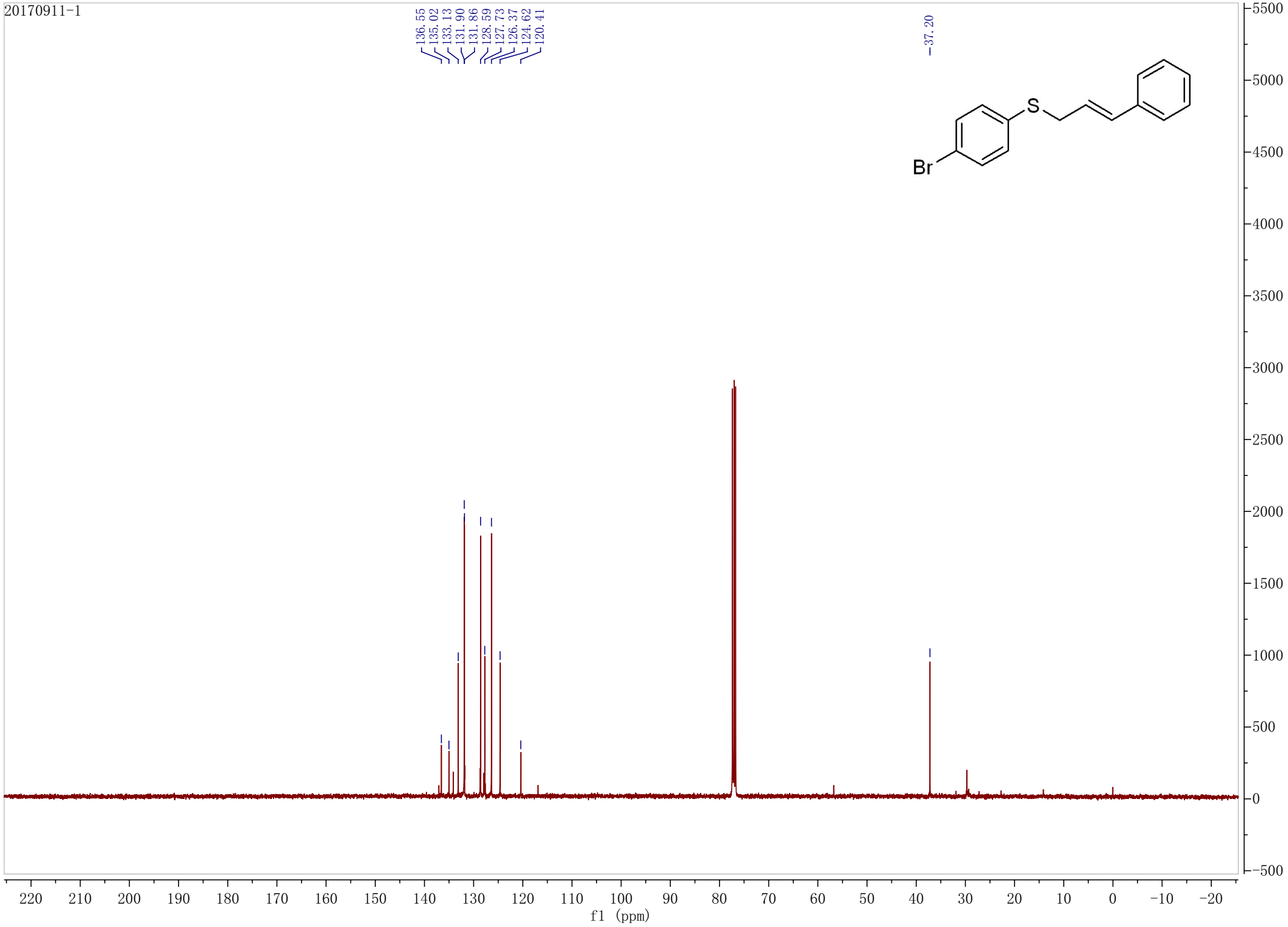

20170913-1
Br
S
2.01
2.03
2.00
2.01
3.01
f1 (ppm)

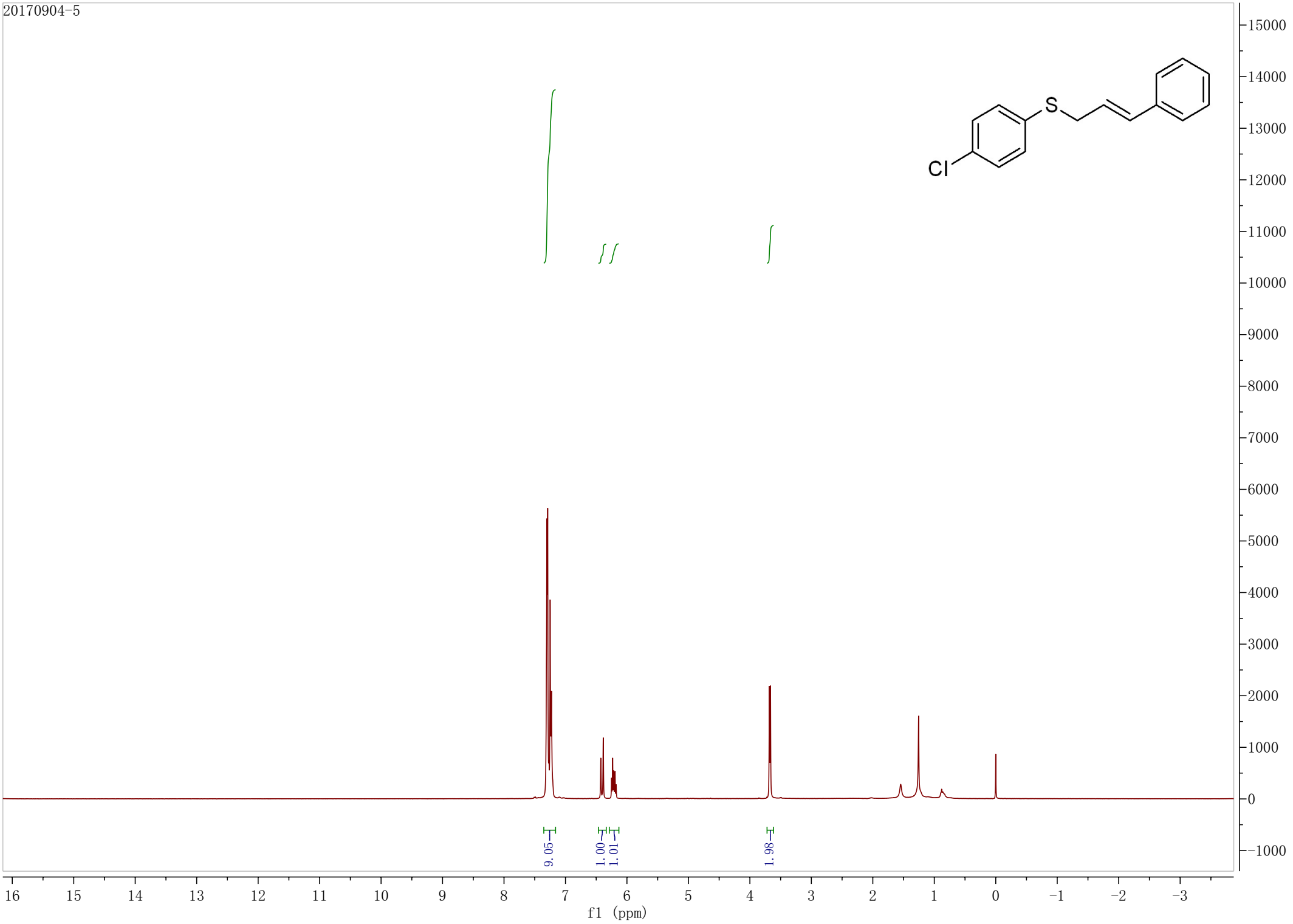

20170913-1
140.39
135.57
131.78
131.63
120.16
114.34
41.99
21.07
S
Br
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

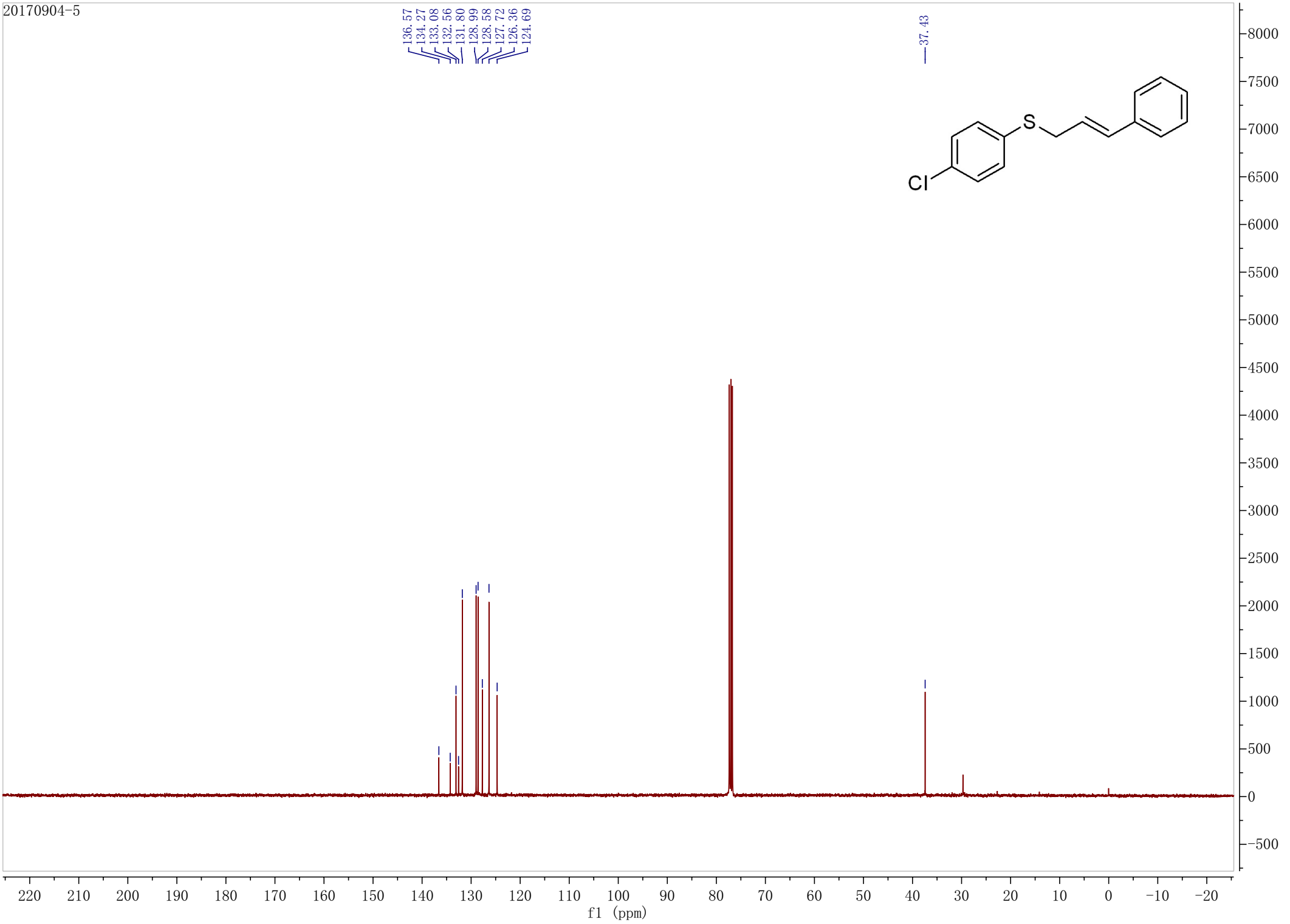

20170724-7
S
7.02
2.02
1.00
1.01
2.01
2.98
f1 (ppm)

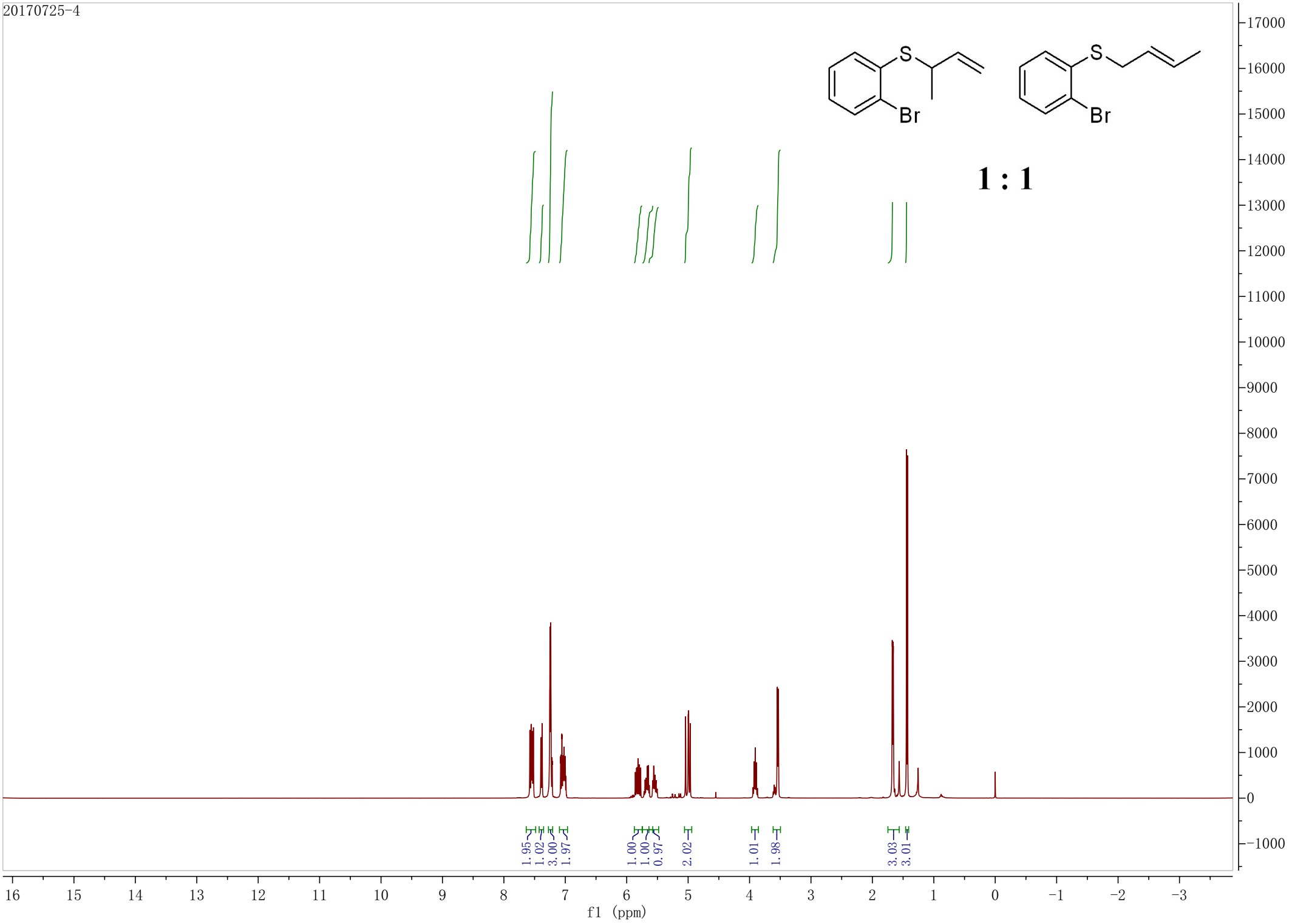

20170724-7
136.87
136.67
132.60
131.96
131.16
129.66
128.53
127.53
126.36
125.41
37.88
21.07
S
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

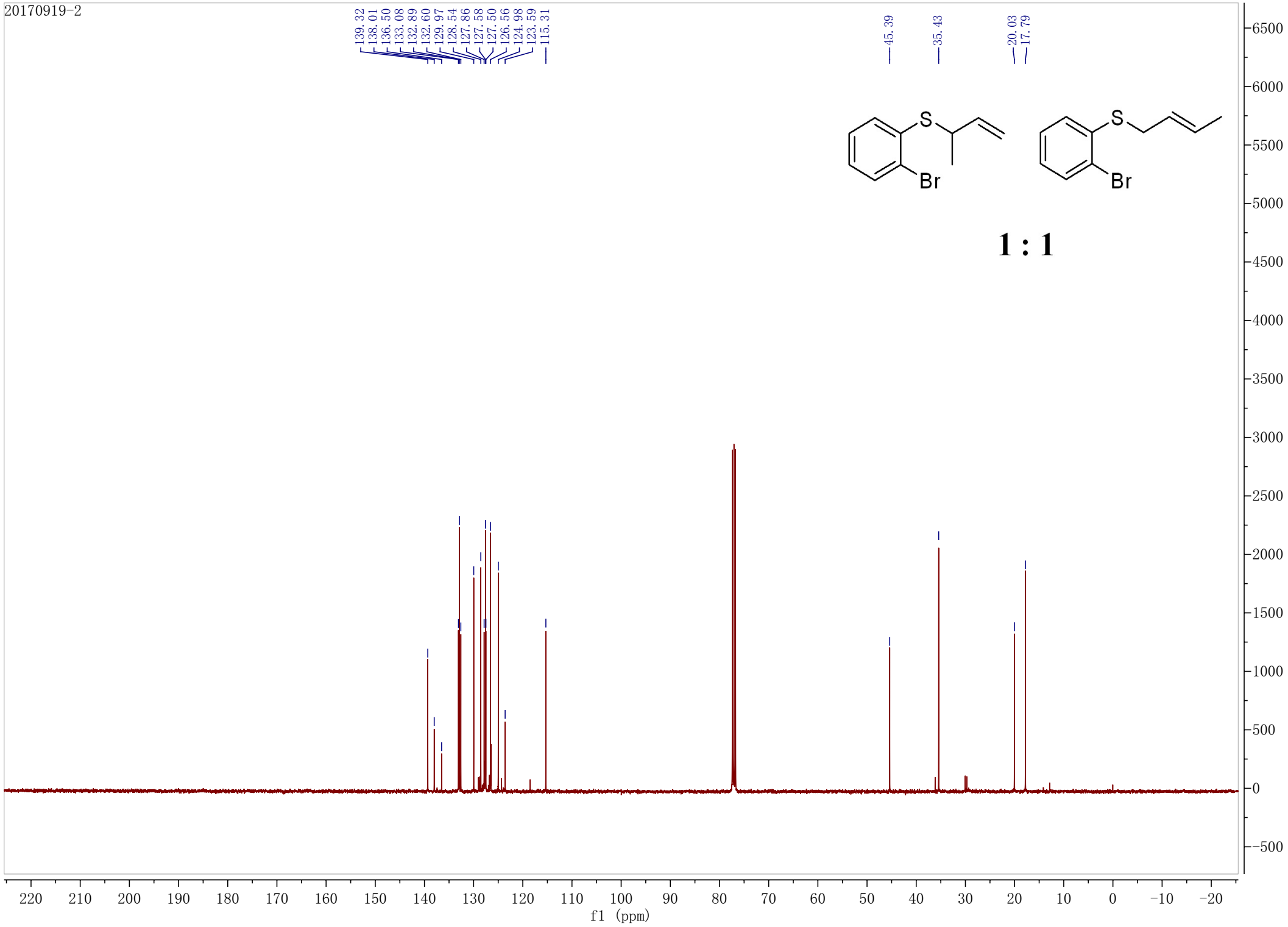

20170911-1
Br
S
2.05
3.96
3.00
1.00
1.04
2.00
f1 (ppm)

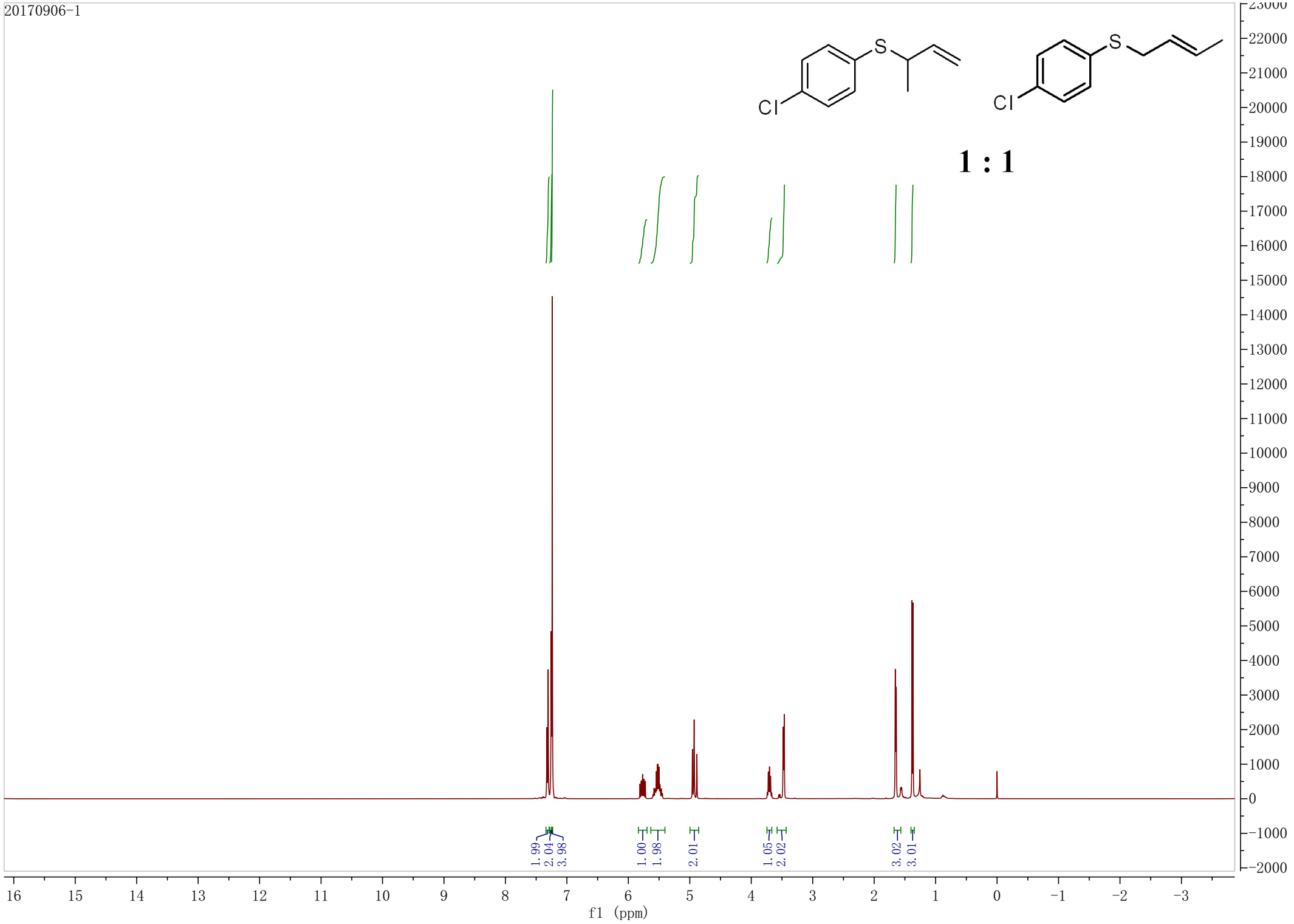

20170911-1
136.55
135.02
133.13
131.90
131.86
128.59
127.73
126.37
124.62
120.41
37.20
S
Br
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

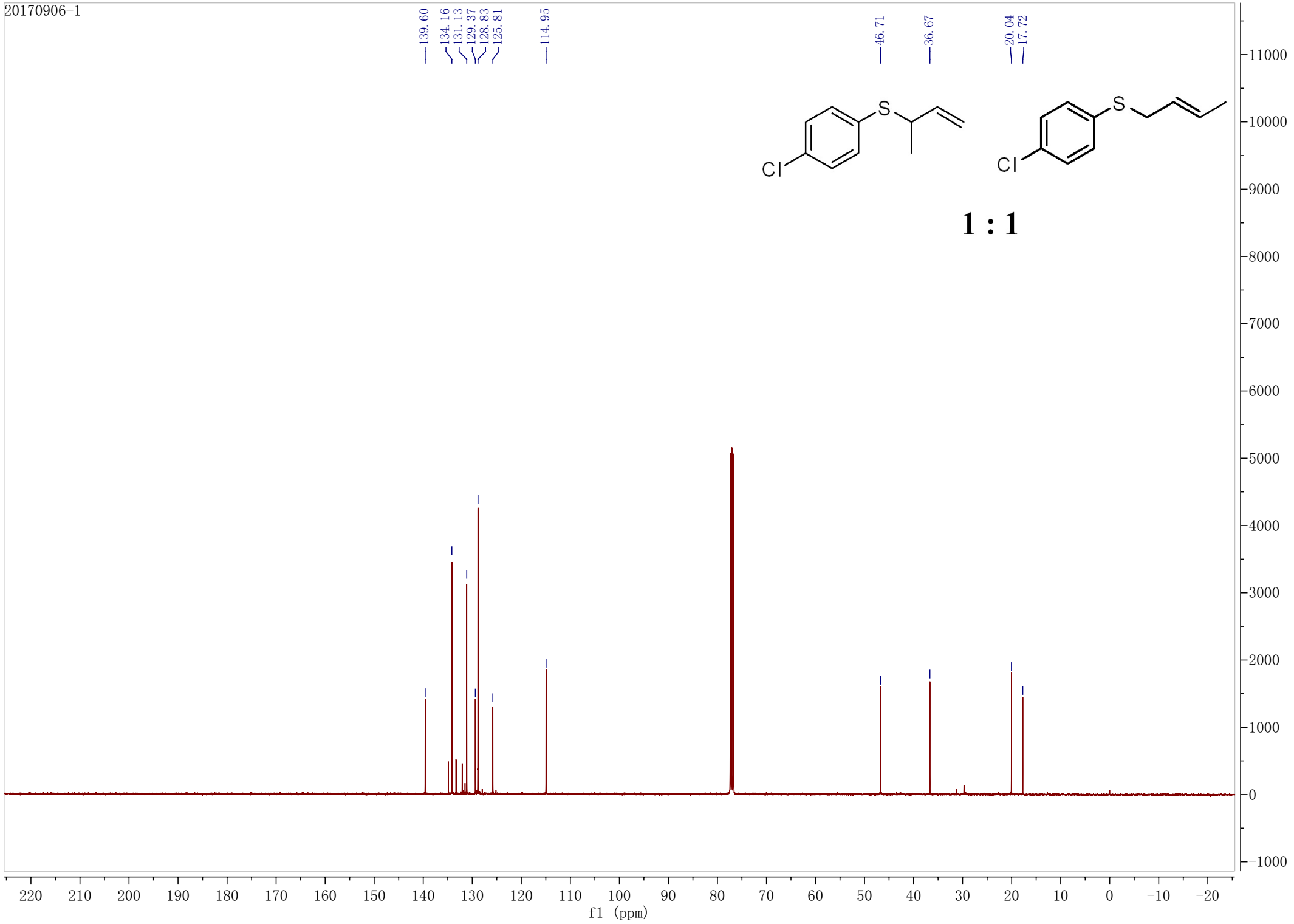

20170904-5
S
Cl
9.05
1.00
1.01
1.98
f1 (ppm)


20170904-5
136.57
134.27
133.08
132.56
131.80
128.99
128.58
127.72
126.36
124.69
37.43
S
Cl
f1 (ppm)


20170725-4
S
Br
S
Br
1 : 1
1.95
1.02
3.00
1.97
1.00
1.00
0.97
2.02
1.01
1.98
3.03
3.01
f1 (ppm)


20170919-2
139.32
138.01
136.50
133.08
132.89
132.60
129.97
128.54
127.86
127.58
127.50
126.56
124.98
123.59
115.31
45.39
35.43
20.03
17.79
S
Br
S
Br
1 : 1
f1 (ppm)


20170906-1
S
Cl
S
Cl
1 : 1
1.99
2.04
3.98
1.00
1.98
2.01
1.05
2.02
3.02
3.01
f1 (ppm)


20170906-1
139.60
134.16
131.13
129.37
128.83
125.81
114.95
46.71
36.67
20.04
17.72
S
Cl
S
Cl
1 : 1
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)