

## Supporting Information

### Copper-catalyzed direct sulfenoamination of saturated ketones via *in situ* formed enaminones

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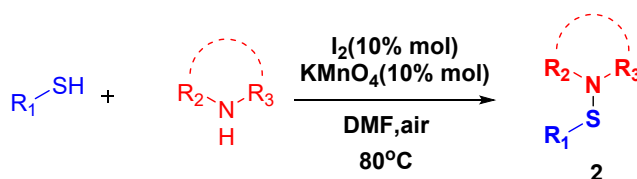
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## 1 General Information

All reagents used in the experiments were obtained from commercial sources and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. All NMR spectra were recorded on Bruker AVANCE 400 for  $^1\text{H}$  and  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$ . The NMR chemical shift was reported in ppm relative to 7.26 / 77.23 ppm of  $\text{CDCl}_3$  as the standards of  $^1\text{H}$  and  $^{13}\text{C}$  NMR, respectively. The HRMS of products were tested on electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer. IR was tested on Bruker ALPHA. Besides, melting point was tested on micro melting point apparatus.



## 2 General procedure for the synthesis of sulfenamides 2

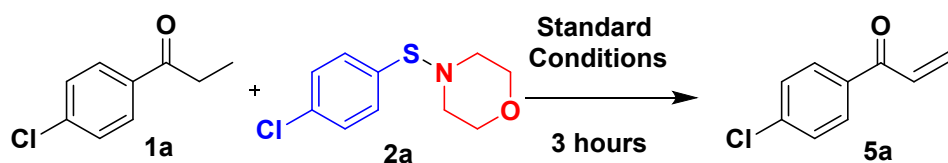
Sulfenamides **2** were synthesized according to the reported literatures.<sup>1,2</sup>

General method: A mixture of  $\text{I}_2$  (50.8 mg, 0.20 mmol),  $\text{KMnO}_4$  (32 mg, 0.20 mmol), amine (2.0 mmol), thiophenol (2.0 mmol) and DMF (10 mL) was stirred at  $80^\circ\text{C}$  under air for 12 h. After completion of reaction (monitored by TLC), the mixture was washed with water and extracted with ethyl acetate then dried over  $\text{Na}_2\text{SO}_4$ . The organic layer was then evaporated under reduced pressure and the residue was separated by column chromatography on silica gel (200-300) with petroleum ether/ethyl acetate to get the desired product **2**.

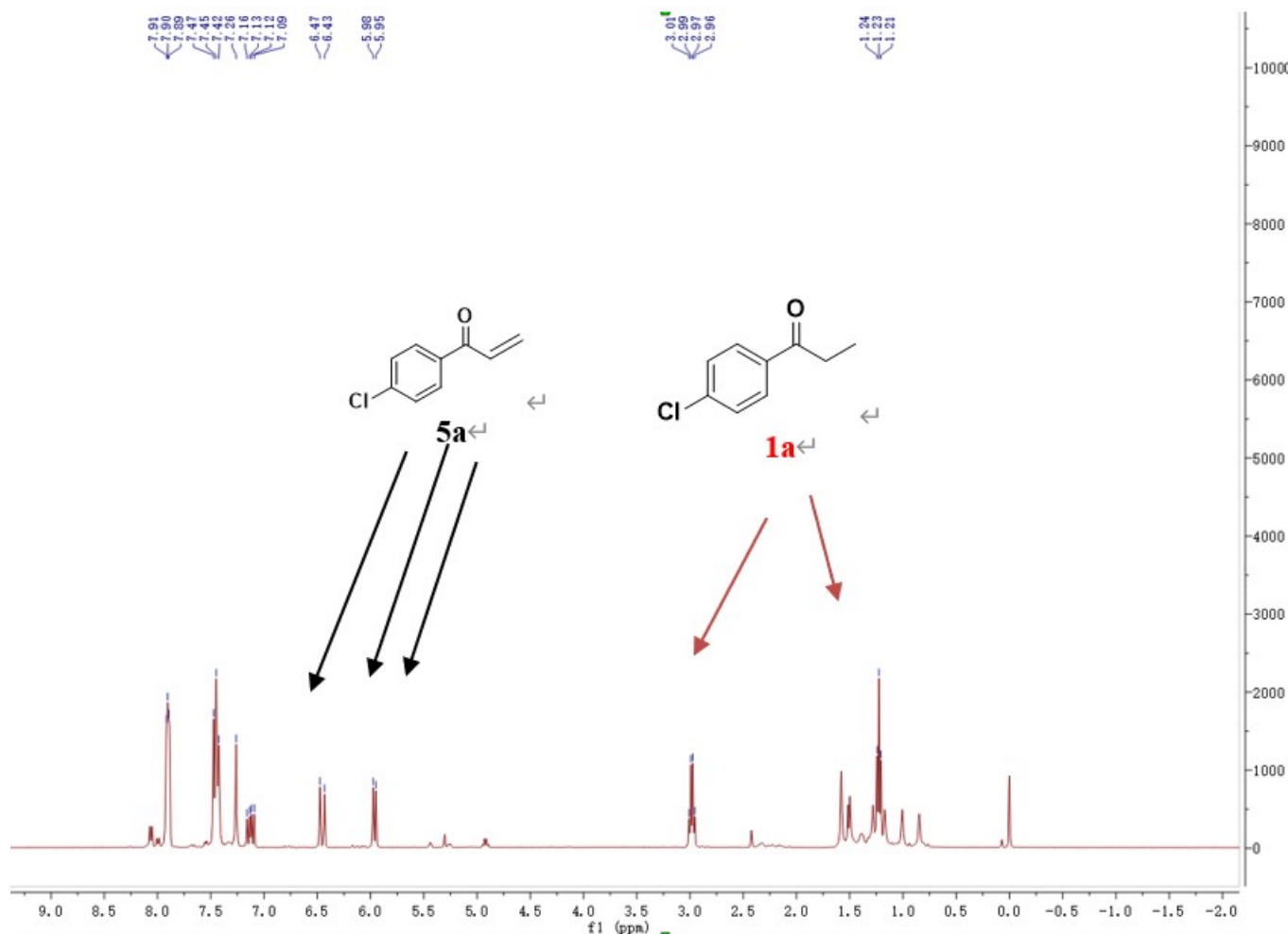
### Reference

1. Liu, S.; Qi, Z.; Zhang, Z.; Qian, B., Iodine/Manganese Dual Catalysis for Oxidative Dehydrogenation Coupling of Amines with Thiols. *Org. Lett.* **2019**, 21, 7722-7725.
2. Taniguchi, N., Copper-Catalyzed Formation of Sulfur-Nitrogen Bonds by Dehydrocoupling of Thiols with Amines. *Eur. J. Org. Chem.* **2010**, 2010, 2670-2673.

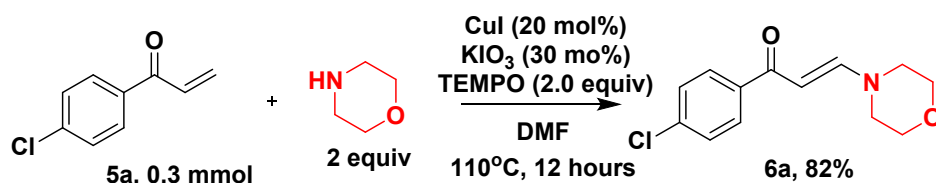
### 3 Control experiment of 5a



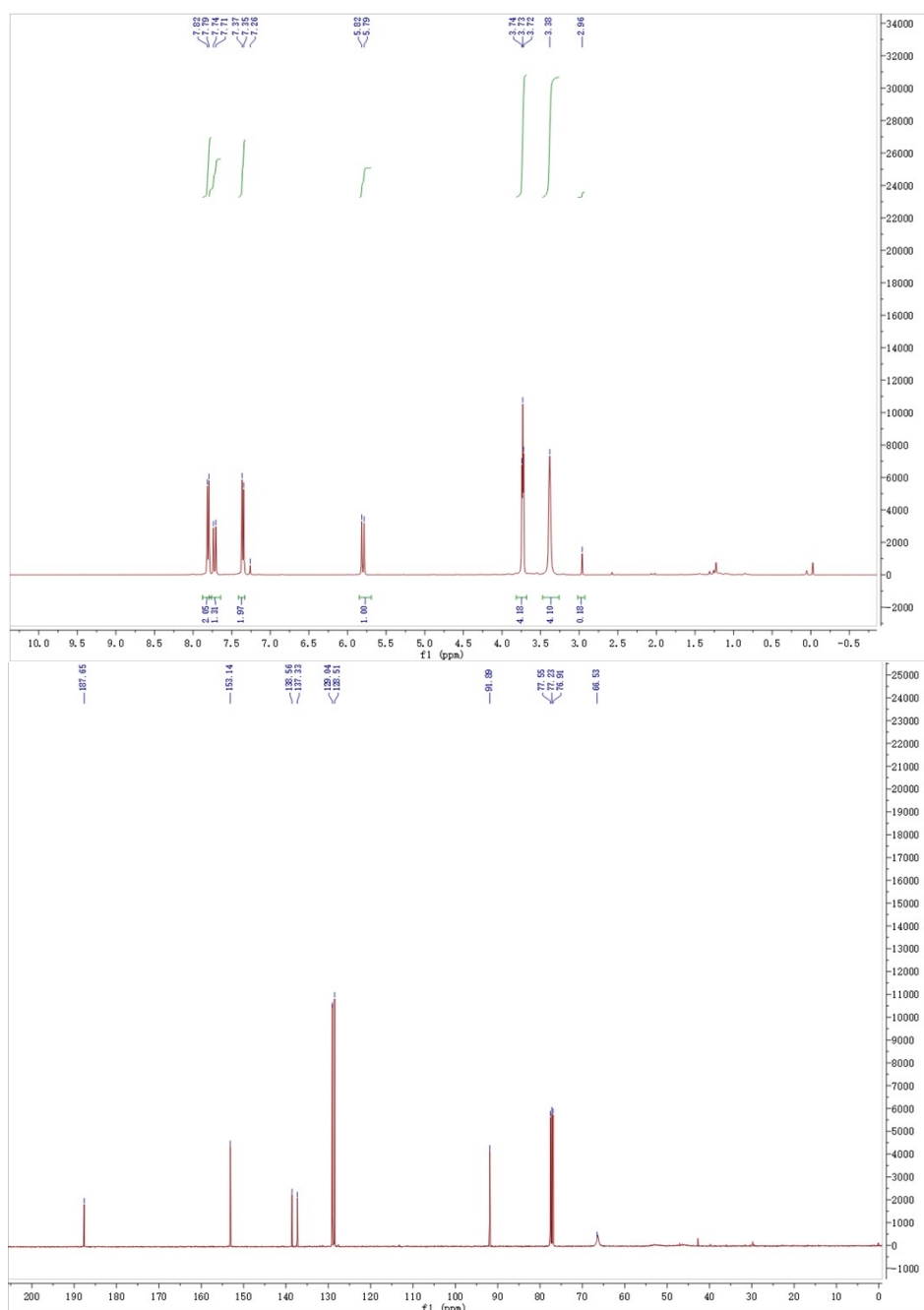
A mixture of sulfenamide (0.3 mmol), 1-(4-chlorophenyl)propan-1-one **1a** (2.0 equiv), CuI (20 mol%), KIO<sub>3</sub> (30 mol%), TEMPO (2.0 equiv) and DMF (1.5 mL) was stirred at 110°C in heating mantle under air atmosphere for 3 hours. After cooling to room temperature, the mixture was washed with water and extracted with ethyl acetate then dried over Na<sub>2</sub>SO<sub>4</sub>. The organic layer was then evaporated under reduced pressure and the residue was separated by column chromatography on silica gel (200-300) with petroleum ether/ethyl acetate (20:1) to get the mixture products with small polarity. The mixture was then measured on the H-NMR. The formation of 1-(4-chlorophenyl)prop-2-en-1-one **5a** was confirmed via  $\alpha,\beta$ -desaturation of saturated ketone **1a**.



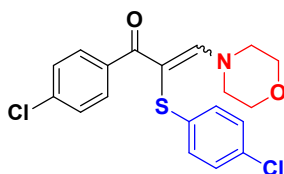
## 4 Control experiment of 6a



A mixture of 1-(4-chlorophenyl)prop-2-en-1-one **5a** (0.3 mmol), morpholine (0.6 mmol), CuI (20 mol%), KIO<sub>3</sub> (30 mol%), TEMPO (2.0 equiv) and DMF (1.5 mL) was stirred at 110°C in heating mantle under air atmosphere for 12 hours. After cooling to room temperature, the mixture was washed with water and extracted with ethyl acetate then dried over Na<sub>2</sub>SO<sub>4</sub>. The organic layer was then evaporated under reduced pressure and the residue was separated by column chromatography on silica gel (200-300) with petroleum ether/ethyl acetate (2:1) to get the desired product **6a** (61.7 mg, 82%).

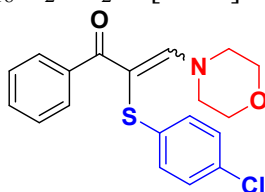


## 5 Characterization of products



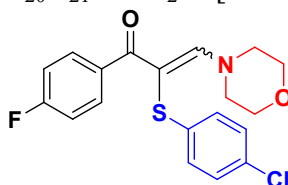
### 1-(4-chlorophenyl)-2-((4-chlorophenyl)thio)-3-morpholinoprop-2-en-1-one (3a)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **3a** was isolated as a white solid (m.p. 145°C) (94.3 mg, 80%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.95 (s, 1H), 7.40 (d,  $J = 8.0$  Hz, 2H), 7.27 (d,  $J = 8.0$  Hz, 2H), 7.21 (d,  $J = 8.0$  Hz, 2H), 7.02 (d,  $J = 8.0$  Hz, 2H), 3.84 (s, 4H), 3.63 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  195.1, 156.1, 139.1, 137.7, 136.2, 131.0, 129.5, 129.4, 128.2, 126.4, 93.9, 67.0, 51.6 (brs); IR (KBr):  $\nu_{\text{max}}$  3012, 2964, 2908, 2863, 1627, 1546, 1469, 1304, 1236, 1086, 1006, 905, 849, 805, 756, 612, 487, 442; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{NO}_2\text{S}^+$   $[\text{M}+\text{H}]^+$  394.0430, found 394.0410.



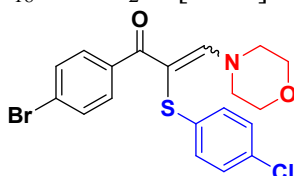
### 2-((4-chlorophenyl)thio)-3-morpholino-1-(p-tolyl)prop-2-en-1-one (3b)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **3b** was isolated as a white solid (m.p. 118-119°C) (60.4 mg, 54%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.88 (s, 1H), 7.40 (d,  $J = 8.0$  Hz, 2H), 7.21 (d,  $J = 8.0$  Hz, 2H), 7.13 (d,  $J = 8.0$  Hz, 2H), 7.06 (d,  $J = 8.0$  Hz, 2H), 3.82 (s, 4H), 3.62 (s, 4H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  195.9, 156.2, 140.6, 137.9, 137.8, 130.8, 129.3, 128.7, 128.4, 126.6, 94.9, 67.0, 51.7 (brs), 21.7; IR (KBr):  $\nu_{\text{max}}$  2956, 2924, 2852, 1618, 1546, 1469, 1441, 1312, 1264, 1107, 1091, 950, 901, 825, 744, 495; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{20}\text{H}_{21}\text{ClNO}_2\text{S}^+$   $[\text{M}+\text{H}]^+$  373.0976, found 374.0965.



### 2-((4-chlorophenyl)thio)-1-(4-fluorophenyl)-3-morpholinoprop-2-en-1-one (3c)

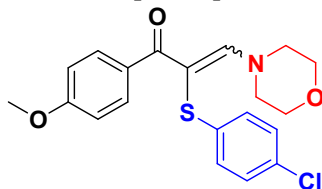
Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **3c** was isolated as a white solid (m.p. 139-141°C) (83.7 mg, 74%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.94 (s, 1H), 7.49 (t,  $J = 8.0$  Hz, 2H), 7.21 (d,  $J = 8.0$  Hz, 2H), 7.03 (d,  $J = 8.0$  Hz, 2H), 6.98 (d,  $J = 8.0$  Hz, 2H), 3.85 (s, 4H), 3.64 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  195.0, 163.9 (d,  $J = 248.4$  Hz), 156.0, 137.7, 136.6 (d,  $J = 3.2$  Hz), 131.0, 130.5 (d,  $J = 8.6$  Hz), 129.4, 126.5, 114.9 (d,  $J = 21.5$  Hz), 94.0, 67.0, 51.8 (brs);  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -109.9-110.0 (m, 1F); IR (KBr):  $\nu_{\text{max}}$  2960, 2920, 2852, 1627, 1594, 1546, 1469, 1308, 1220, 1086, 1006, 905, 808, 623, 487; HRMS(ESI,  $m/z$ ) calcd. For  $\text{C}_{19}\text{H}_{18}\text{ClFNO}_2\text{S}^+$   $[\text{M}+\text{H}]^+$  378.0725, found 378.0707.



### 1-(4-bromophenyl)-2-((4-chlorophenyl)thio)-3-morpholinoprop-2-en-1-one (3d)

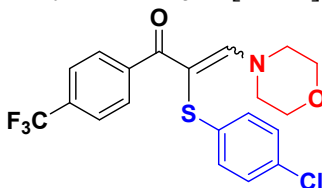
Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **3d** was isolated as a white solid (m.p. 142-144°C) (91.8 mg, 70%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.95 (s, 1H), 7.44 (d,  $J = 8.0$  Hz, 2H), 7.33 (d,  $J = 8.0$  Hz, 2H), 7.21 (d,  $J = 8.0$  Hz, 2H), 7.02 (d,  $J = 8.0$  Hz, 2H), 3.84 (s, 4H), 3.63 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  195.1, 156.1, 137.7, 137.1, 131.1, 131.0, 129.7, 129.4, 126.4, 124.6, 93.8, 67.0, 51.7 (brs); IR (KBr):  $\nu_{\text{max}}$  3012, 2960, 2912, 2859, 1627, 1551, 1469, 1389, 1308, 1240, 1086, 1006, 905, 805, 756, 612,

487; HRMS(ESI,  $m/z$ ) calcd. for  $C_{19}H_{18}BrClNO_2S^+$   $[M+H]^+$  437.9925, found 437.9911.



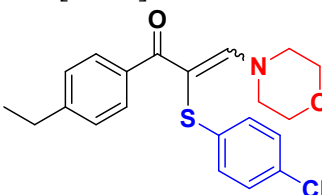
**2-((4-chlorophenyl)thio)-1-(4-methoxyphenyl)-3-morpholinoprop-2-en-1-one (3e)**

Eluent in chromatography: petroleum ether/ethyl acetate 1:1, **3e** was isolated as a pale yellow solid (m.p. 137-139°C) (66.5 mg, 57%);  $^1H$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.85 (s, 1H), 7.52 (d,  $J = 8.0$  Hz, 2H), 7.20 (d,  $J = 8.0$  Hz, 2H), 7.05 (d,  $J = 8.0$  Hz, 2H), 6.83 (d,  $J = 8.0$  Hz, 2H), 3.80 (m, 7H), 3.60 (s, 4H);  $^{13}C$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  194.9, 161.5, 155.8, 137.9, 132.8, 130.7, 130.6, 129.3, 126.5, 113.2, 94.5, 67.0, 55.5, 51.6 (brs); IR (KBr):  $\nu_{max}$  2908, 2848, 1622, 1599, 1546, 1401, 1308, 1244, 1163, 1083, 1026, 909, 837, 808, 761, 623, 487; HRMS(ESI,  $m/z$ ) calcd. for  $C_{20}H_{21}ClNO_3S^+$   $[M+H]^+$  390.0925, found 390.0907.



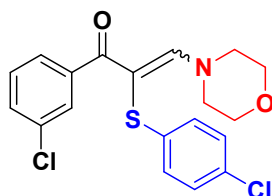
**2-((4-chlorophenyl)thio)-3-morpholino-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (3f)**

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **3f** was isolated as a white solid (m.p. 139-140°C) (94.8 mg, 74%);  $^1H$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.02 (s, 1H), 7.55 (d,  $J = 8.0$  Hz, 2H), 7.51 (d,  $J = 8.0$  Hz, 2H), 7.23 (d,  $J = 8.0$  Hz, 2H), 7.02 (d,  $J = 8.0$  Hz, 2H), 3.87 (s, 4H), 3.65 (s, 4H);  $^{13}C$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  195.3, 156.2, 144.4, 137.6, 131.6 (q,  $J = 32.3$  Hz), 131.1, 129.5, 128.0, 126.4, 125.0 (q,  $J = 3.4$  Hz), 124.1 (q,  $J = 270.6$  Hz), 93.5, 67.0, 51.6 (brs);  $^{19}F$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -62.75 (s, 3F); IR (KBr):  $\nu_{max}$  2973, 2920, 2852, 1627, 1551, 1312, 1163, 1111, 905, 853, 817, 769, 668, 612, 469; HRMS(ESI,  $m/z$ ) calcd. for  $C_{20}H_{18}ClF_3NO_2S^+$   $[M+H]^+$  428.0693 found, 428.0676.



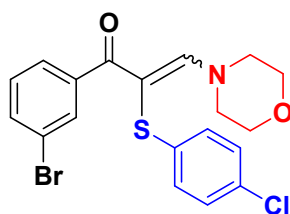
**2-((4-chlorophenyl)thio)-1-(4-ethylphenyl)-3-morpholinoprop-2-en-1-one (3g)**

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **3g** was isolated as a white solid (m.p. 109-111°C) (74.3 mg, 64%);  $^1H$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.87 (s, 1H), 7.43 (d,  $J = 8.0$  Hz, 2H), 7.21 (d,  $J = 8.0$  Hz, 2H), 7.16 (d,  $J = 8.0$  Hz, 2H), 7.06 (d,  $J = 8.0$  Hz, 2H), 3.83 (s, 4H), 3.62 (s, 4H), 2.65 (q,  $J = 8.0$  Hz, 2H), 1.23 (t,  $J = 8.0$  Hz, 3H);  $^{13}C$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  195.8, 156.2, 146.9, 137.9, 130.8, 129.3, 128.5, 127.5, 126.6, 95.0, 67.0, 51.7 (brs), 29.0, 15.5; IR (KBr):  $\nu_{max}$  2956, 2924, 2852, 1627, 1554, 1474, 1308, 1086, 954, 905, 813, 756, 720, 620, 491; HRMS(ESI,  $m/z$ ) calcd. for  $C_{21}H_{23}ClNO_2S^+$   $[M+H]^+$  388.1133 found, 388.1113.



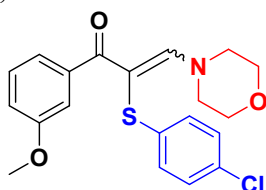
**1-(3-chlorophenyl)-2-((4-chlorophenyl)thio)-3-morpholinoprop-2-en-1-one (3h)**

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **3h** was isolated as a white solid (m.p. 112-114°C) (83.7 mg, 71%);  $^1H$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.94 (s, 1H), 7.42 (s, 1H), 7.34 (d,  $J = 8.0$  Hz, 1H), 7.30 (d,  $J = 8.0$  Hz, 1H), 7.29-7.21 (m, 3H), 7.03 (d,  $J = 8.0$  Hz, 2H), 3.86 (s, 4H), 3.64 (s, 4H);  $^{13}C$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  194.7, 156.3, 142.6, 137.6, 134.0, 131.1, 130.1, 129.4, 129.3, 128.1, 126.5, 126.0, 94.1, 67.0, 51.7 (brs). IR (KBr):  $\nu_{max}$  3053, 2964, 2912, 2852, 1627, 1538, 1474, 1304, 1115, 1026, 930, 817, 752, 680, 612, 491; HRMS(ESI,  $m/z$ ) calcd. for  $C_{19}H_{18}Cl_2NO_2S^+$   $[M+H]^+$  394.0430 found, 394.0430.



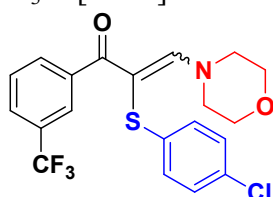
### 1-(3-bromophenyl)-2-((4-chlorophenyl)thio)-3-morpholinoprop-2-en-1-one (3i)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **3i** was isolated as a White solid (m.p.92-94°C) (91.8 mg, 70%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.56 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 4H), 3.64 (s, 4H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 194.6, 156.3, 142.8, 137.6, 133.0, 131.0, 130.9, 129.5, 129.4, 126.5, 126.4, 122.1, 94.0, 67.0, 51.8 (brs); IR (KBr):  $\nu_{\max}$  3049, 2964, 2900, 2852, 1622, 1534, 1474, 1304, 1232, 1115, 1091, 1006, 909, 817, 748, 668, 612, 487; HRMS(ESI, *m/z*) calcd. for C<sub>19</sub>H<sub>18</sub>BrClNO<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 437.9925 found, 437.9931.



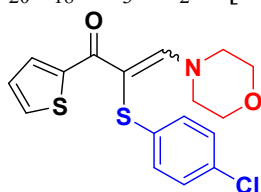
### 2-((4-chlorophenyl)thio)-1-(3-methoxyphenyl)-3-morpholinoprop-2-en-1-one (3j)

Eluent in chromatography: petroleum ether/ethyl acetate 1:1, **3j** was isolated as a pale yellow solid (m.p.110-112°C) (67.7 mg, 58%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.27-7.21 (m, 3H), 7.08-7.03 (m, 3H), 6.99 (s, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 4H), 3.72 (s, 3H), 3.62 (s, 4H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 195.6, 159.2, 156.5, 142.2, 137.8, 130.8, 129.3, 129.0, 126.5, 120.4, 116.3, 112.9, 94.7, 67.0, 55.4, 51.7 (brs); IR (KBr):  $\nu_{\max}$  3069, 2960, 2924, 2859, 1618, 1542, 1469, 1308, 1224, 1086, 958, 849, 744, 498; HRMS(ESI, *m/z*) calcd. for C<sub>20</sub>H<sub>21</sub>ClNO<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup> 390.0925 found, 390.0929.



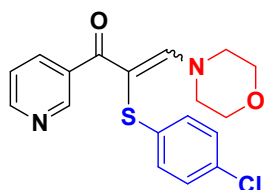
### 2-((4-chlorophenyl)thio)-3-morpholino-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one (3k)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **3k** was isolated as a yellow oily liquid (67.9 mg, 53%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.68 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 4H), 3.65 (s, 4H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 194.9, 156.2, 141.5, 137.5, 131.1, 131.0, 130.2 (q, *J* = 32.3 Hz), 129.4, 128.4, 126.6 (q, *J* = 3.4 Hz), 126.4, 124.9 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 270.8 Hz), 93.4, 67.0, 51.8 (brs); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -62.72 (s, 3F); IR (KBr):  $\nu_{\max}$  3072, 2966, 2924, 2856, 1633, 1561, 1473, 1337, 1122, 814, 751, 696, 485; HRMS(ESI, *m/z*) calcd. for C<sub>20</sub>H<sub>18</sub>ClF<sub>3</sub>NO<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 428.0693 found, 428.0698.



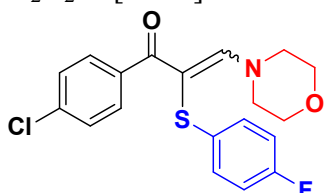
### 2-((4-chlorophenyl)thio)-3-morpholino-1-(thiophen-2-yl)prop-2-en-1-one (3l)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **3l** was isolated as a pale yellow solid (m.p.134-136°C) (59.1 mg, 54%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.86 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 8.0 Hz, 1H), 3.85 (s, 4H), 3.63 (s, 4H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 185.1, 156.0, 142.9, 137.8, 133.1, 132.2, 131.0, 129.4, 127.0, 126.3, 92.1, 67.0, 51.8 (brs); IR (KBr):  $\nu_{\max}$  3080, 3009, 2971, 2924, 2844, 1578, 1443, 1278, 1110, 1025, 857, 819, 717, 485; HRMS(ESI, *m/z*) calcd. for C<sub>17</sub>H<sub>17</sub>ClNO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup> 366.0384 found, 366.0371.



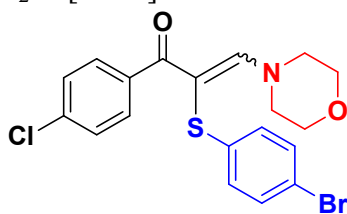
### 2-((4-chlorophenyl)thio)-3-morpholino-1-(pyridin-3-yl)prop-2-en-1-one (3m)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **3m** was isolated as a yellow oily liquid (37.8 mg, 35%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.67 (s, 1H), 8.55 (s, 1H), 8.05 (s, 1H), 7.74 (d,  $J = 8.0$  Hz, 1H), 7.21-7.17 (m, 3H), 6.99 (d,  $J = 8.0$  Hz, 2H), 3.87 (s, 3H), 3.65 (s, 3H), 3.28 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  194.0, 158.4, 156.1, 150.6, 150.4, 148.6, 148.6, 137.4, 135.6, 131.2, 129.5, 129.3, 126.3, 126.2, 123.0, 93.5, 67.0, 51.8 (brs); IR (KBr):  $\nu_{\text{max}}$  2920, 2856, 1624, 1582, 1473, 1300, 1100, 1025, 814, 705, 485; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{18}\text{H}_{18}\text{ClN}_2\text{O}_2\text{S}^+$   $[\text{M}+\text{H}]^+$  361.0772 found, 366.0762.



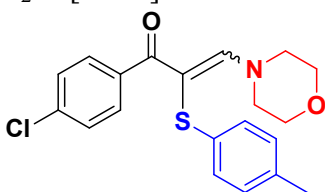
### 1-(4-chlorophenyl)-2-((4-fluorophenyl)thio)-3-morpholinoprop-2-en-1-one (4a)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4a** was isolated as a pale yellow solid (m.p. 144-146°C) (79.2 mg, 70%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.91 (s, 1H), 7.41 (d,  $J = 8.0$  Hz, 2H), 7.28 (d,  $J = 8.0$  Hz, 2H), 7.06 (t,  $J = 8.0$  Hz, 2H), 6.96 (t,  $J = 8.0$  Hz, 2H), 3.86 (s, 4H), 3.63 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  195.1, 161.1 (d,  $J = 243$  Hz), 155.9, 139.1, 136.1, 134.0, 129.6, 128.1, 127.0 (d,  $J = 7.7$  Hz), 116.4 (d,  $J = 21.9$  Hz), 94.9, 67.0, 51.7 (brs);  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -117.69-117.76 (m, 1F); IR (KBr):  $\nu_{\text{max}}$  2971, 2920, 2869, 1620, 1536, 1486, 1303, 1219, 1106, 907, 823, 755, 675, 620, 502; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{19}\text{H}_{18}\text{ClFNO}_2\text{S}^+$   $[\text{M}+\text{H}]^+$  378.0725 found, 378.0735.



### 2-((4-bromophenyl)thio)-1-(4-chlorophenyl)-3-morpholinoprop-2-en-1-one (4b)

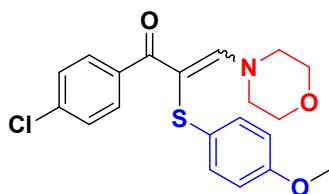
Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4b** was isolated as a white solid (m.p. 161-162°C) (94.4 mg, 72%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.96 (s, 1H), 7.41 (d,  $J = 8.0$  Hz, 2H), 7.36 (d,  $J = 8.0$  Hz, 2H), 7.28 (d,  $J = 8.0$  Hz, 2H), 6.97 (d,  $J = 8.0$  Hz, 2H), 3.85 (s, 4H), 3.64 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  195.1, 156.1, 139.0, 138.4, 136.2, 132.3, 129.5, 128.2, 126.7, 118.8, 93.7, 67.0, 51.6 (brs); IR (KBr):  $\nu_{\text{max}}$  3012, 2960, 2912, 2855, 1627, 1546, 1465, 1308, 1095, 1002, 905, 801, 756, 612, 483; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{19}\text{H}_{18}\text{BrClNO}_2\text{S}^+$   $[\text{M}+\text{H}]^+$  437.9925 found, 437.9931.



### 1-(4-chlorophenyl)-3-morpholino-2-(*p*-tolylthio)prop-2-en-1-one (4c)

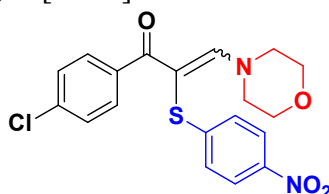
Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4c** was isolated as a white solid (m.p. 149-150°C) (69.4 mg, 62%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.96 (s, 1H), 7.41 (d,  $J = 8.0$  Hz, 2H), 7.25 (d,  $J = 8.0$  Hz, 2H), 7.06 (d,  $J = 8.0$  Hz, 2H), 6.98 (d,  $J = 8.0$  Hz, 2H), 3.85 (s, 4H), 3.60 (s, 4H), 2.28 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  195.4, 155.8, 139.3, 135.9, 135.4, 135.0, 130.1, 129.6, 128.0, 125.2, 94.5, 67.0, 51.5 (brs), 21.1; IR (KBr):  $\nu_{\text{max}}$  2916, 2852, 1627, 1546, 1401, 1308, 1095, 1015, 905, 845, 805, 756, 620, 491; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{20}\text{H}_{21}\text{ClNO}_2\text{S}^+$   $[\text{M}+\text{H}]^+$  374.0976 found, 374.0980.





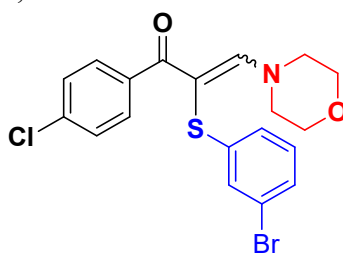
#### 1-(4-chlorophenyl)-2-((4-methoxyphenyl)thio)-3-morpholinoprop-2-en-1-one (4d)

Eluent in chromatography: petroleum ether/ethyl acetate 1:1, **4d** was isolated as a white solid (m.p.98-100°C) (77.0 mg, 66%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 4H), 3.77 (s, 3H), 3.62 (s, 4H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 195.4, 157.9, 155.6, 139.4, 136.0, 129.7, 129.6, 128.0, 127.1, 115.1, 95.6, 67.0, 55.5, 51.7 (brs); IR (KBr):  $\nu_{\max}$  2968, 2855, 1622, 1546, 1308, 1236, 1095, 905, 813, 756, 612, 446; HRMS(ESI, *m/z*) calcd. for C<sub>20</sub>H<sub>21</sub>ClNO<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup> 390.0925 found, 390.0928.



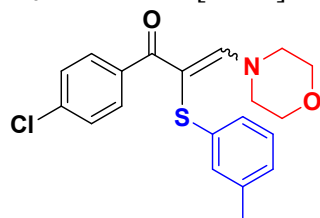
#### 1-(4-chlorophenyl)-3-morpholino-2-((4-nitrophenyl)thio)prop-2-en-1-one (4e)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4e** was isolated as a yellow oily liquid (114.7 mg, 77%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.96 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.82 (s, 4H), 3.65 (s, 4H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 194.3, 156.7, 148.8, 145.3, 138.6, 136.5, 129.6, 128.4, 124.9, 124.5, 92.4, 66.9, 51.6 (brs); IR (KBr):  $\nu_{\max}$  2962, 2920, 2856, 1578, 1334, 1110, 903, 852, 730, 465; HRMS(ESI, *m/z*) calcd. for C<sub>19</sub>H<sub>18</sub>ClN<sub>2</sub>O<sub>4</sub>S<sup>+</sup> [M+H]<sup>+</sup> 405.0670 found, 405.0659.



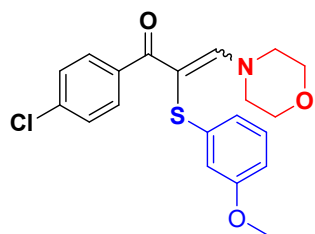
#### 2-((3-bromophenyl)thio)-1-(4-chlorophenyl)-3-morpholinoprop-2-en-1-one (4f)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4f** was isolated as a white solid (m.p.103-105°C) (107.5 mg, 82%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23-7.21 (m, 2H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 4H), 3.64 (s, 4H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 195.0, 156.2, 141.5, 139.0, 136.3, 130.7, 129.6, 128.3, 128.2, 127.6, 123.7, 123.5, 93.3, 67.0, 52.1 (brs); IR (KBr):  $\nu_{\max}$  2958, 2920, 2844, 1624, 1549, 1452, 1303, 1093, 903, 836, 773, 680, 447; HRMS(ESI, *m/z*) calcd. for C<sub>19</sub>H<sub>18</sub>BrClNO<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 437.9925 found, 437.9933.



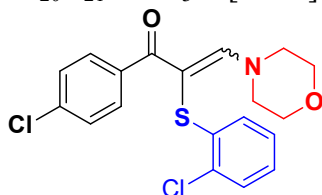
#### 1-(4-chlorophenyl)-3-morpholino-2-(m-tolylthio)prop-2-en-1-one (4g)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4g** was isolated as a pale yellow solid (m.p.116-117°C) (88.4 mg, 79%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.90 (m, 3H), 3.85 (s, 4H), 3.59 (s, 4H), 2.29 (s, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 195.3, 155.8, 139.3, 139.0, 138.7, 135.9, 129.5, 129.1, 128.0, 126.1, 125.6, 122.1, 94.0, 67.0, 51.6 (brs), 21.6; IR (KBr):  $\nu_{\max}$  3041, 2977, 2896, 2855, 1614, 1534, 1437, 1304, 1176, 1107, 1034, 970, 905, 849, 773, 688, 616, 446; HRMS(ESI, *m/z*) calcd. for C<sub>20</sub>H<sub>21</sub>ClNO<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 374.0976 found, 374.0982.



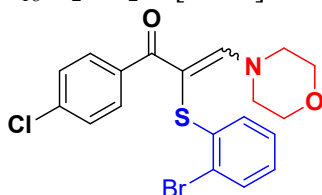
#### 1-(4-chlorophenyl)-2-((3-methoxyphenyl)thio)-3-morpholinoprop-2-en-1-one (4h)

Eluent in chromatography: petroleum ether/ethyl acetate 1:1, **4h** was isolated as a pale yellow solid (m.p. 85-87°C) (88.7 mg, 76%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.71-6.65 (m, 3H), 3.86 (s, 4H), 3.77 (s, 3H), 3.62 (s, 4H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 195.3, 160.4, 156.0, 140.5, 139.3, 136.1, 130.2, 129.6, 128.1, 117.5, 110.9, 110.7, 93.9, 67.1, 55.5, 51.6 (brs); IR (KBr):  $\nu_{\max}$  2958, 2920, 2853, 1591, 1477, 1308, 1232, 1110, 1029, 907, 836, 751, 675, 447; HRMS(ESI, *m/z*) calcd. for C<sub>20</sub>H<sub>21</sub>ClNO<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup> 390.0925 found, 390.0927.



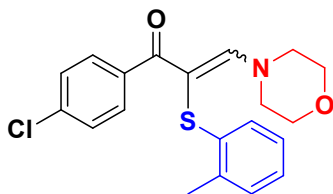
#### 1-(4-chlorophenyl)-2-((2-chlorophenyl)thio)-3-morpholinoprop-2-en-1-one (4i)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4i** was isolated as a pale yellow solid (m.p. 166-167°C) (103.8 mg, 88%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 3H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.09-7.03 (m, 2H), 3.82 (s, 4H), 3.60 (s, 4H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 194.9, 156.2, 138.9, 137.6, 136.2, 130.6, 130.0, 129.6, 128.1, 127.4, 126.1, 93.0, 67.0, 51.6 (brs); IR (KBr):  $\nu_{\max}$  2968, 2900, 2848, 1627, 1551, 1450, 1312, 1095, 1030, 954, 905, 849, 744, 676, 616, 483; HRMS(ESI, *m/z*) calcd. for C<sub>19</sub>H<sub>18</sub>Cl<sub>2</sub>NO<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 394.0430 found, 394.0434.



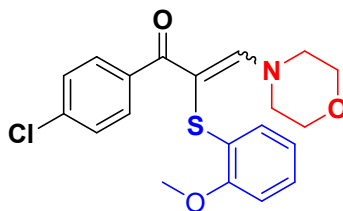
#### 2-((2-bromophenyl)thio)-1-(4-chlorophenyl)-3-morpholinoprop-2-en-1-one (4j)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4j** was isolated as a pale yellow solid (m.p. 127-129°C) (120.6 mg, 92%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.44-7.43 (m, 3H), 7.28-7.22 (m, 3H), 7.07-6.94 (m, 2H), 3.80 (s, 4H), 3.59 (s, 4H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 194.9, 156.2, 139.5, 138.8, 136.2, 133.2, 129.6, 128.1, 128.0, 126.3, 126.2, 120.2, 93.8, 67.0, 51.8 (brs); IR (KBr):  $\nu_{\max}$  3059, 2971, 2899, 2849, 1629, 1552, 1443, 1316, 1088, 1013, 954, 903, 848, 743, 675, 612, 477; HRMS(ESI, *m/z*) calcd. for C<sub>19</sub>H<sub>18</sub>BrClNO<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 437.9925 found, 437.9926.



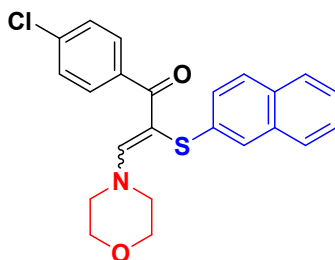
#### 1-(4-chlorophenyl)-3-morpholino-2-(o-tolylthio)prop-2-en-1-one (4k)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4k** was isolated as a pale yellow solid (m.p. 159-161°C) (95.1 mg, 85%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.09-7.00 (m, 3H), 3.82 (s, 4H), 3.59 (s, 4H), 2.21 (s, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 195.3, 156.0, 139.2, 137.6, 135.9, 134.4, 130.4, 129.5, 128.0, 126.8, 124.9, 124.4, 93.6, 67.0, 51.6 (brs), 19.8; IR (KBr):  $\nu_{\max}$  3065, 2964, 2908, 2848, 1627, 1551, 1441, 1316, 1272, 1095, 950, 901, 853, 741, 672, 616, 474; HRMS(ESI, *m/z*) calcd. for C<sub>20</sub>H<sub>21</sub>ClNO<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 374.0976 found, 374.0983.



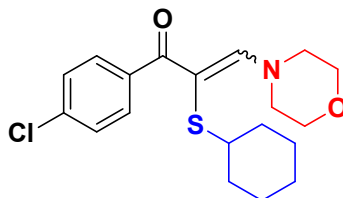
#### 1-(4-chlorophenyl)-2-((2-methoxyphenyl)thio)-3-morpholinoprop-2-en-1-one (4l)

Eluent in chromatography: petroleum ether/ethyl acetate 1:1, **4l** was isolated as a yellow oily liquid (86.4 mg, 74%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.02 (s, 1H), 7.43 (d,  $J = 8.0$  Hz, 2H), 7.25 (d,  $J = 8.0$  Hz, 2H), 7.09 (t,  $J = 8.0$  Hz, 1H), 7.02 (d,  $J = 8.0$  Hz, 1H), 6.92 (t,  $J = 8.0$  Hz, 1H), 6.80 (d,  $J = 8.0$  Hz, 1H), 3.83-3.81 (m, 7H), 3.60 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  195.5, 156.1, 155.5, 139.2, 136.0, 129.6, 128.0, 127.0, 126.0, 125.5, 121.5, 110.8, 92.7, 67.1, 56.0, 51.8 (brs); IR (KBr):  $\nu_{\text{max}}$  2962, 2920, 2853, 1578, 1473, 1232, 1093, 1013, 903, 832, 751, 468; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{20}\text{H}_{21}\text{ClNO}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  390.0925 found, 390.0930.



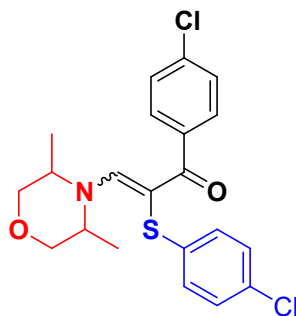
#### 1-(4-chlorophenyl)-3-morpholino-2-(naphthalen-1-ylthio)prop-2-en-1-one (4m)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4m** was isolated as a yellow oily liquid (70.0 mg, 57%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.10 (s, 1H), 7.77-7.69 (m, 3H), 7.48-7.38 (m, 5H), 7.25-7.21 (m, 3H), 3.86-3.67 (m, 4H), 3.57 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  195.4, 156.1, 139.2, 136.6, 136.0, 134.1, 131.5, 129.5, 129.0, 128.0, 127.9, 126.9, 126.9, 125.4, 123.8, 122.5, 93.5, 67.0, 51.7 (brs); IR (KBr):  $\nu_{\text{max}}$  3051, 2966, 2916, 2853, 1578, 1439, 1303, 1093, 1013, 903, 814, 730, 468; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{23}\text{H}_{21}\text{ClNO}_2\text{S}^+$   $[\text{M}+\text{H}]^+$  410.0976 found, 410.0957.



#### 1-(4-chlorophenyl)-2-(cyclohexylthio)-3-morpholinoprop-2-en-1-one (4n)

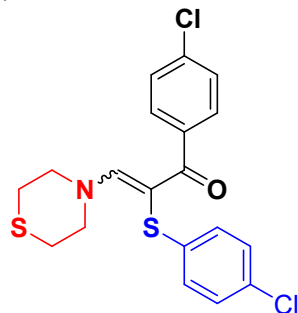
Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4n** was isolated as a yellow oily liquid (44.9 mg, 41%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.50-7.47 (m, 3H), 7.33 (d,  $J = 8.0$  Hz, 2H), 3.94 (s, 4H), 3.74 (s, 4H), 2.67 (s, 1H), 1.83-1.57 (m, 4H), 1.20 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  195.4, 155.9, 139.9, 135.9, 130.3, 128.2, 98.7, 66.9, 51.8 (brs), 47.4, 33.2, 26.3, 26.0; IR (KBr):  $\nu_{\text{max}}$  2928, 2853, 1629, 1578, 1401, 1283, 1088, 1013, 903, 836, 755, 616, 570, 477; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{19}\text{H}_{25}\text{ClNO}_2\text{S}^+$   $[\text{M}+\text{H}]^+$  366.1289 found, 366.1274.



#### 1-(4-chlorophenyl)-2-((4-chlorophenyl)thio)-3-(3,5-dimethylmorpholino)prop-2-en-1-one (4o)

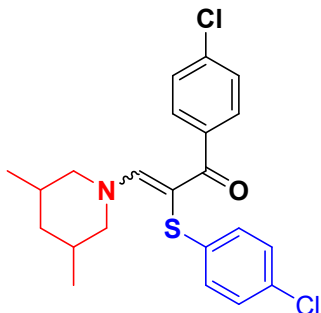
Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4o** was isolated as a White solid (m.p.159-161°C) (88.4 mg, 70%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.95 (s, 1H), 7.41 (d,  $J = 8.0$  Hz, 2H), 7.28 (d,  $J = 8.0$  Hz, 2H), 7.22 (d,  $J = 8.0$  Hz, 2H), 7.04 (d,  $J = 8.0$  Hz, 2H), 4.33 (bs, 2H), 3.48 (s, 2H), 2.84 (s, 2H), 1.09 (d,

$J = 8.0$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  195.1, 155.6, 139.2, 137.7, 136.1, 131.0, 129.5, 129.4, 128.2, 126.5, 93.6, 72.3, 57.4 (brs), 18.6; IR (KBr):  $\nu_{\text{max}}$  2964, 2904, 2855, 1627, 1546, 1469, 1301, 1091, 1010, 898, 845, 756, 487; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{21}\text{H}_{22}\text{Cl}_2\text{NO}_2\text{S}^+$   $[\text{M}+\text{H}]^+$  422.0743 found, 422.0725.



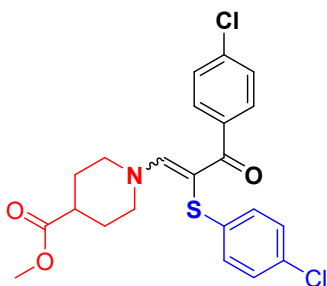
#### 1-(4-chlorophenyl)-2-((4-chlorophenyl)thio)-3-thiomorpholinoprop-2-en-1-one (**4p**)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4p** was isolated as a pale yellow solid (m.p. 139-142°C) (42.9mg, 35%);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.93 (s, 1H), 7.40 (d,  $J = 8.0$  Hz, 2H), 7.27 (d,  $J = 8.0$  Hz, 2H), 7.21 (d,  $J = 8.0$  Hz, 2H), 7.01 (d,  $J = 8.0$  Hz, 2H), 4.06 (s, 4H), 2.63 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  195.2, 156.2, 139.1, 137.6, 136.2, 131.0, 129.6, 129.4, 128.2, 126.5, 94.2, 54.9 (brs), 28.3; IR (KBr):  $\nu_{\text{max}}$  3000, 2912, 1624, 1545, 1468, 1321, 1088, 1009, 954, 891, 755, 477; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{NOS}_2^+$   $[\text{M}+\text{H}]^+$  410.0201 found, 410.0190.



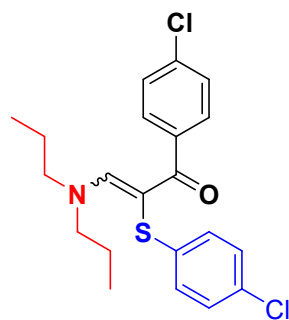
#### 1-(4-chlorophenyl)-2-((4-chlorophenyl)thio)-3-(3,5-dimethylpiperidin-1-yl)prop-2-en-1-one (**4q**)

Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4q** was isolated as a white solid (m.p. 161-162°C) (84.2 mg, 67%);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.01 (s, 1H), 7.40 (d,  $J = 8.0$  Hz, 2H), 7.27 (d,  $J = 8.0$  Hz, 2H), 7.20 (d,  $J = 8.0$  Hz, 2H), 7.05 (d,  $J = 8.0$  Hz, 2H), 4.20-3.50 (m, 2H), 2.56 (bs, 2H), 1.82-1.30 (m, 3H), 0.80 (m, 7H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  195.0, 155.9, 139.5, 138.3, 135.6, 130.5, 129.3, 129.0, 127.9, 126.2, 92.3, 53.3 (brs), 41.8, 32.5, 18.7; IR (KBr):  $\nu_{\text{max}}$  2949, 2903, 1624, 1545, 1468, 1316, 1088, 1009, 907, 848, 755, 477; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{NOS}^+$   $[\text{M}+\text{H}]^+$  420.0950 found, 420.0934.



#### Methyl-1-(3-(4-chlorophenyl)-2-((4-chlorophenyl)thio)-3-oxoprop-1-en-1-yl)piperidine-4-carboxylate (**4r**)

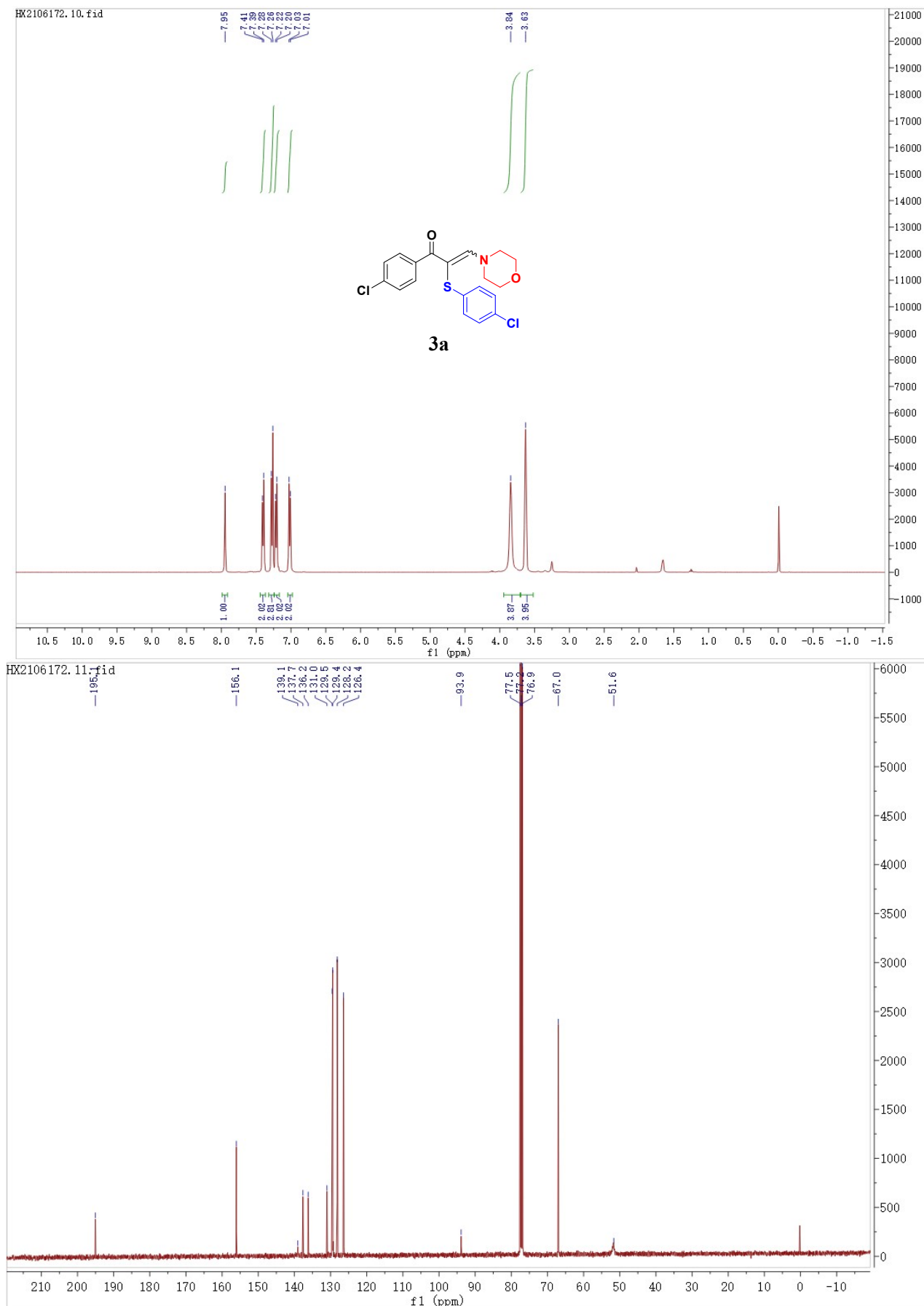
Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4r** was isolated as a yellow oily liquid (67.4 mg, 50%);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.96 (s, 1H), 7.39 (d,  $J = 8.0$  Hz, 2H), 7.27 (d,  $J = 8.0$  Hz, 2H), 7.20 (d,  $J = 8.0$  Hz, 2H), 7.03 (d,  $J = 8.0$  Hz, 2H), 4.29 (bs, 2H), 3.68 (s, 3H), 3.35 (t,  $J = 12.0$  Hz, 2H), 2.56 (t,  $J = 12.0$  Hz, 1H), 1.93 (d,  $J = 12.0$  Hz, 2H), 1.72 (d,  $J = 12.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  194.9, 173.9, 156.3, 139.2, 137.9, 135.8, 130.6, 129.3, 129.1, 127.9, 126.3, 93.3, 52.1, 50.6 (brs), 40.0, 28.5; IR (KBr):  $\nu_{\text{max}}$  2949, 1730, 1578, 1473, 1283, 1088, 1038, 907, 814, 730, 481; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{22}\text{H}_{22}\text{Cl}_2\text{NO}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  450.0692 found, 450.0676.

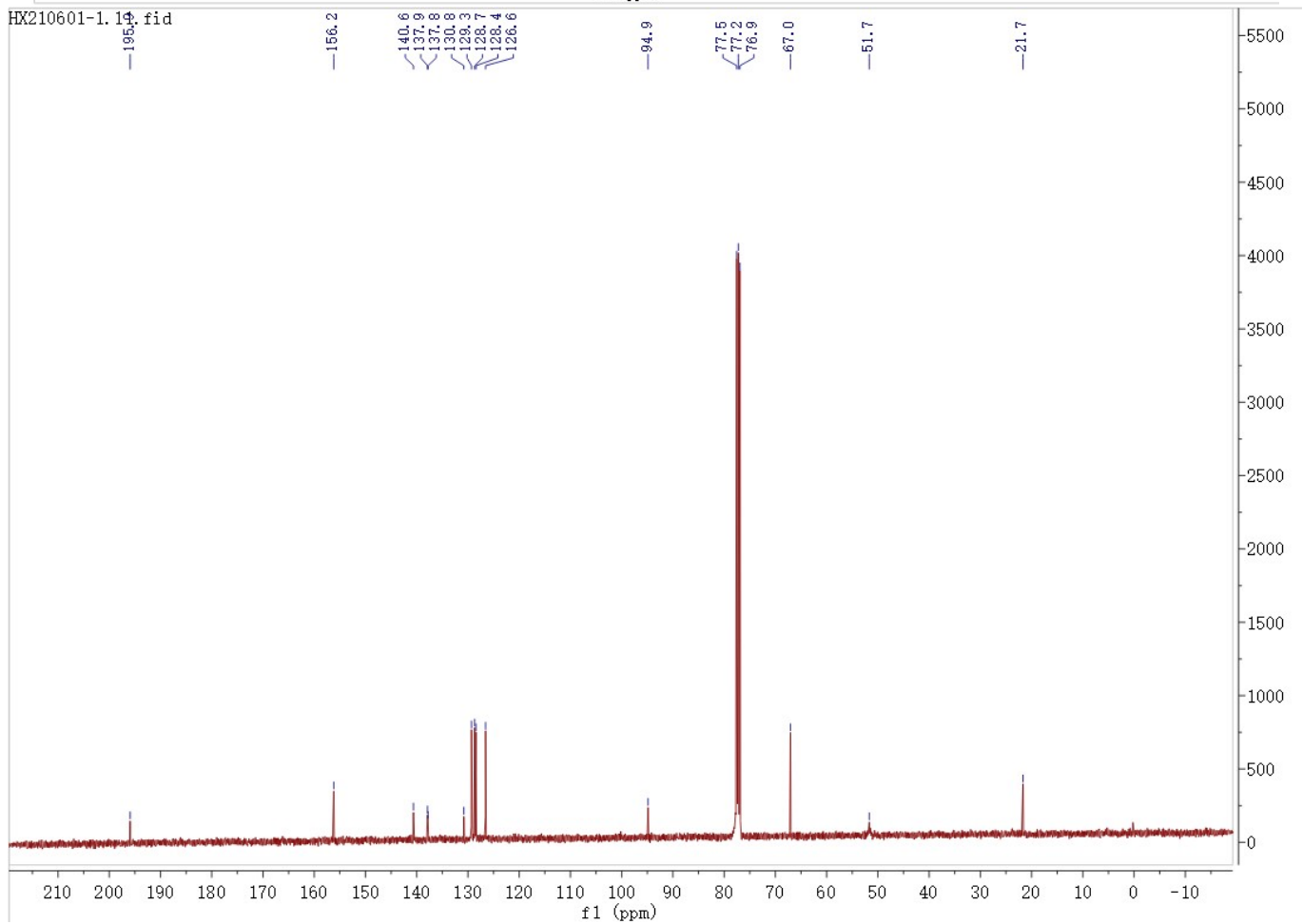
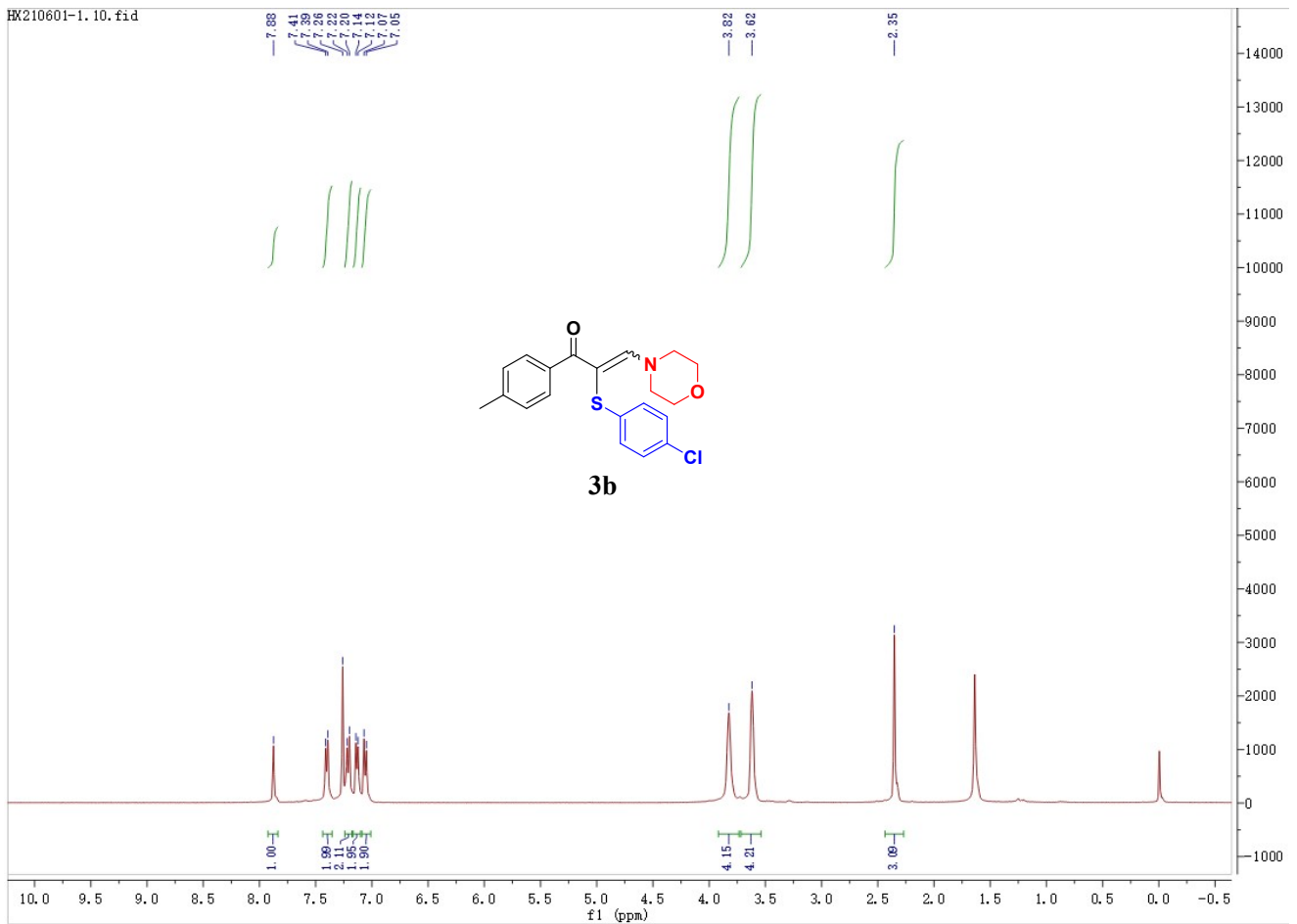


**1-(4-chlorophenyl)-2-((4-chlorophenyl)thio)-3-(dipropylamino)prop-2-en-1-one (4s)**

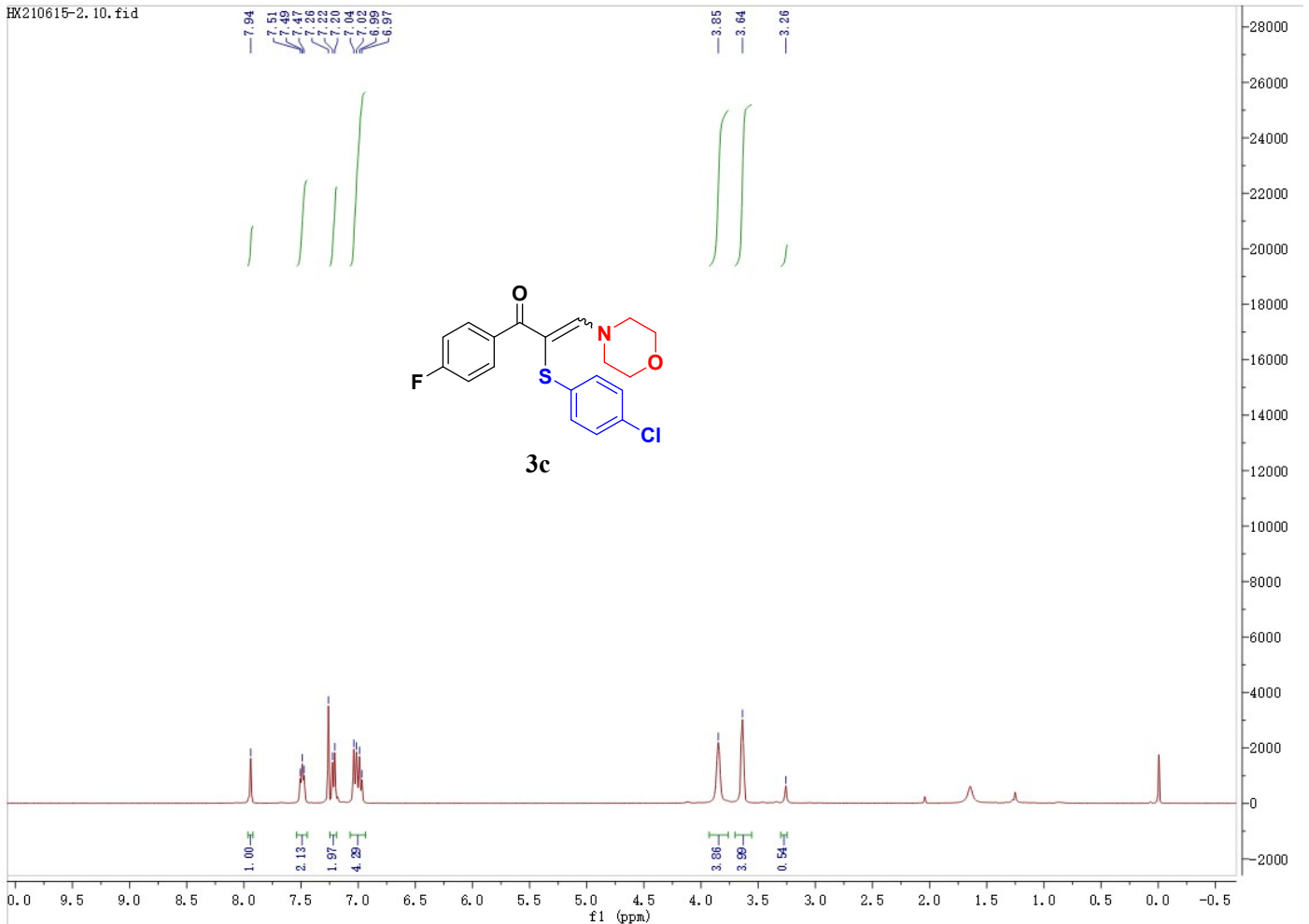
Eluent in chromatography: petroleum ether/ethyl acetate 2:1, **4s** was isolated as a white solid (m.p.89-91°C) (52.5 mg, 43%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.98 (s, 1H), 7.40 (d,  $J = 8.0$  Hz, 2H), 7.27 (d,  $J = 8.0$  Hz, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 7.01 (d,  $J = 8.0$  Hz, 2H), 3.60 (bs, 2H), 3.26 (bs, 2H), 1.62 (s, 4H), 0.86 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  195.1, 157.2, 139.8, 139.2, 135.8, 130.5, 129.5, 129.2, 128.1, 126.1, 93.0, 50.5 (brs), 22.6, 11.0; IR (KBr):  $\nu_{\text{max}}$  2966, 1624, 1582, 1401, 1088, 1009, 814, 755, 608, 481; HRMS(ESI,  $m/z$ ) calcd. for  $\text{C}_{21}\text{H}_{24}\text{Cl}_2\text{NOS}^+ [\text{M}+\text{H}]^+$  408.0950 found, 408.0931.

## 6 NMR Spectra of products

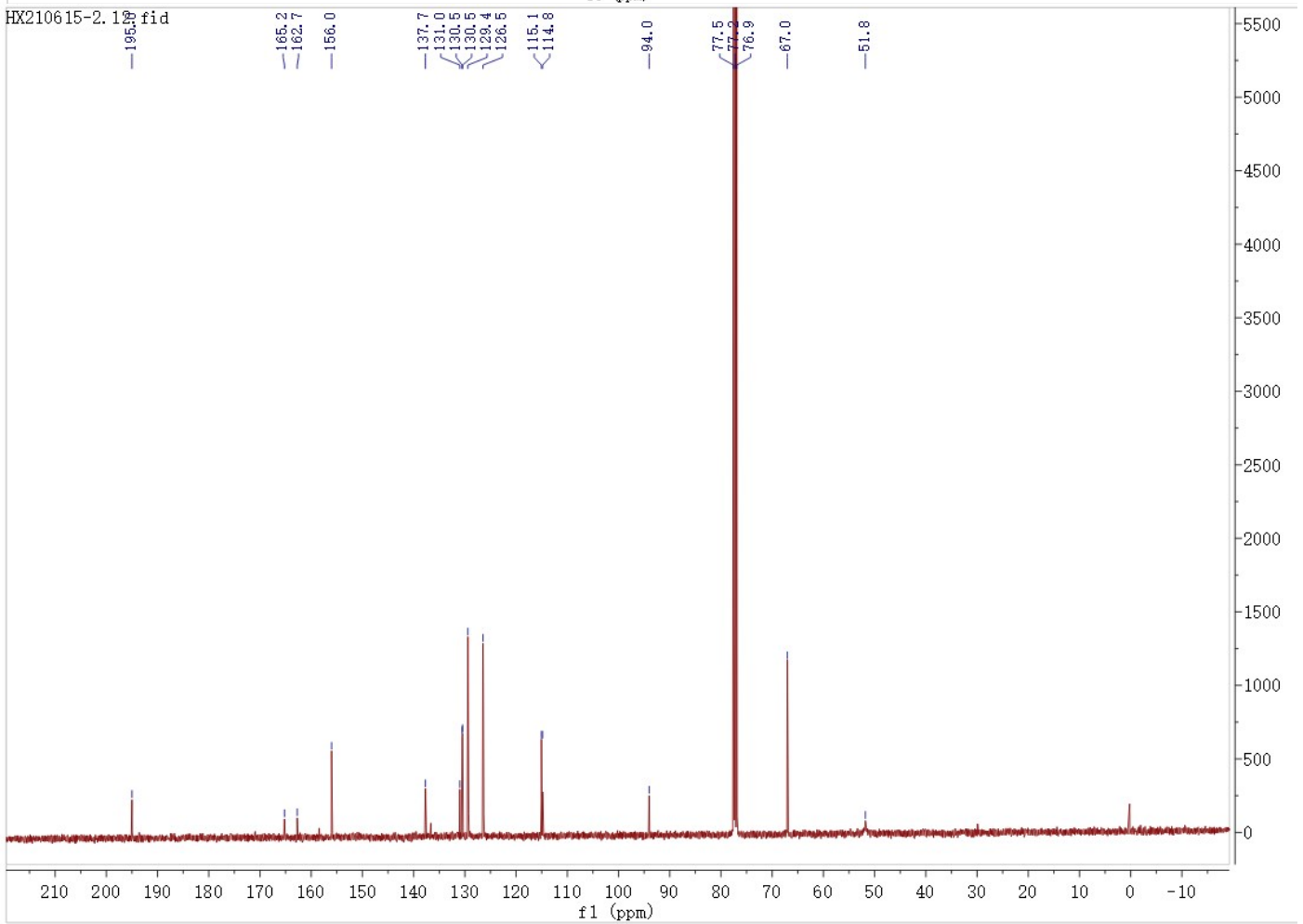




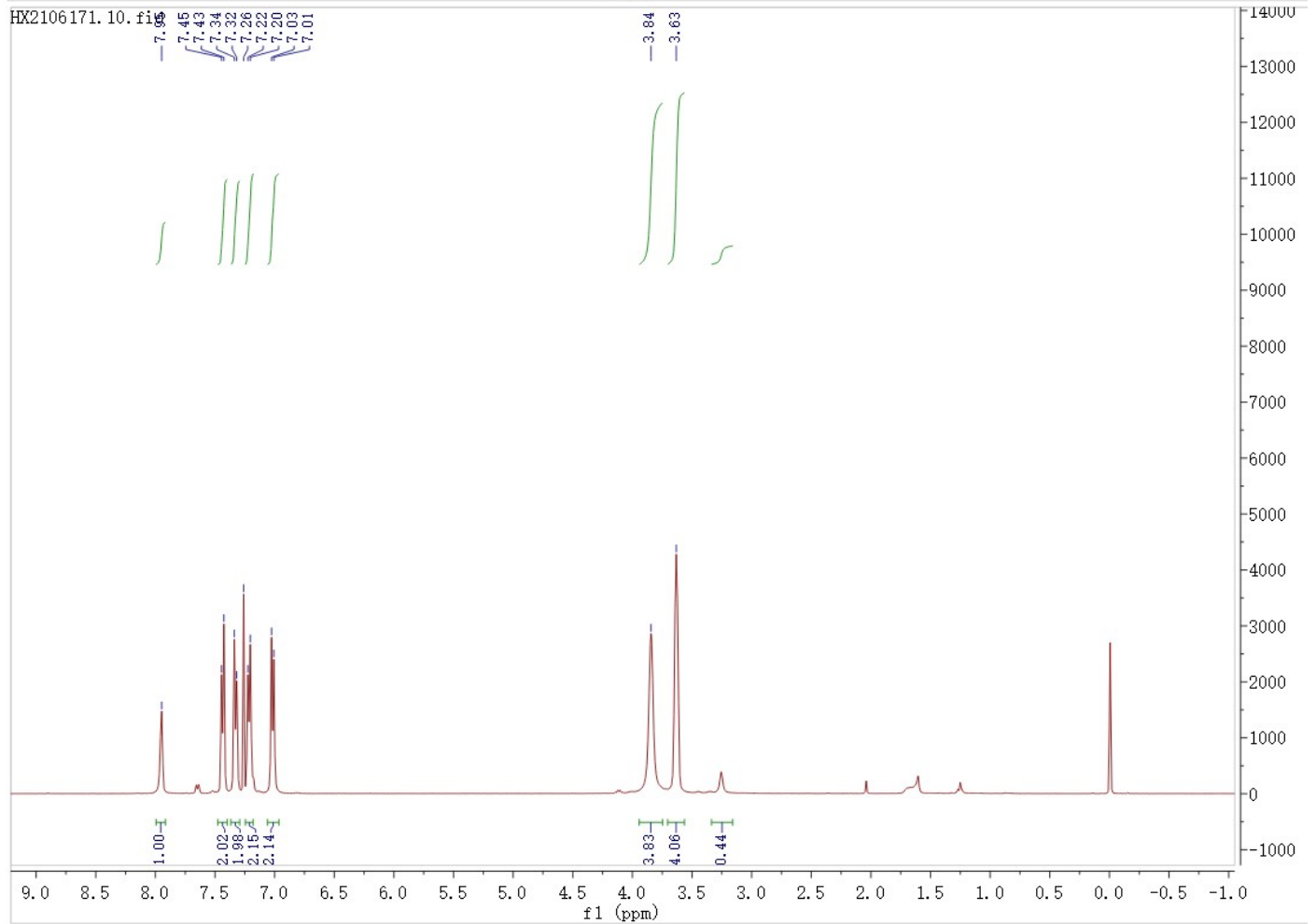
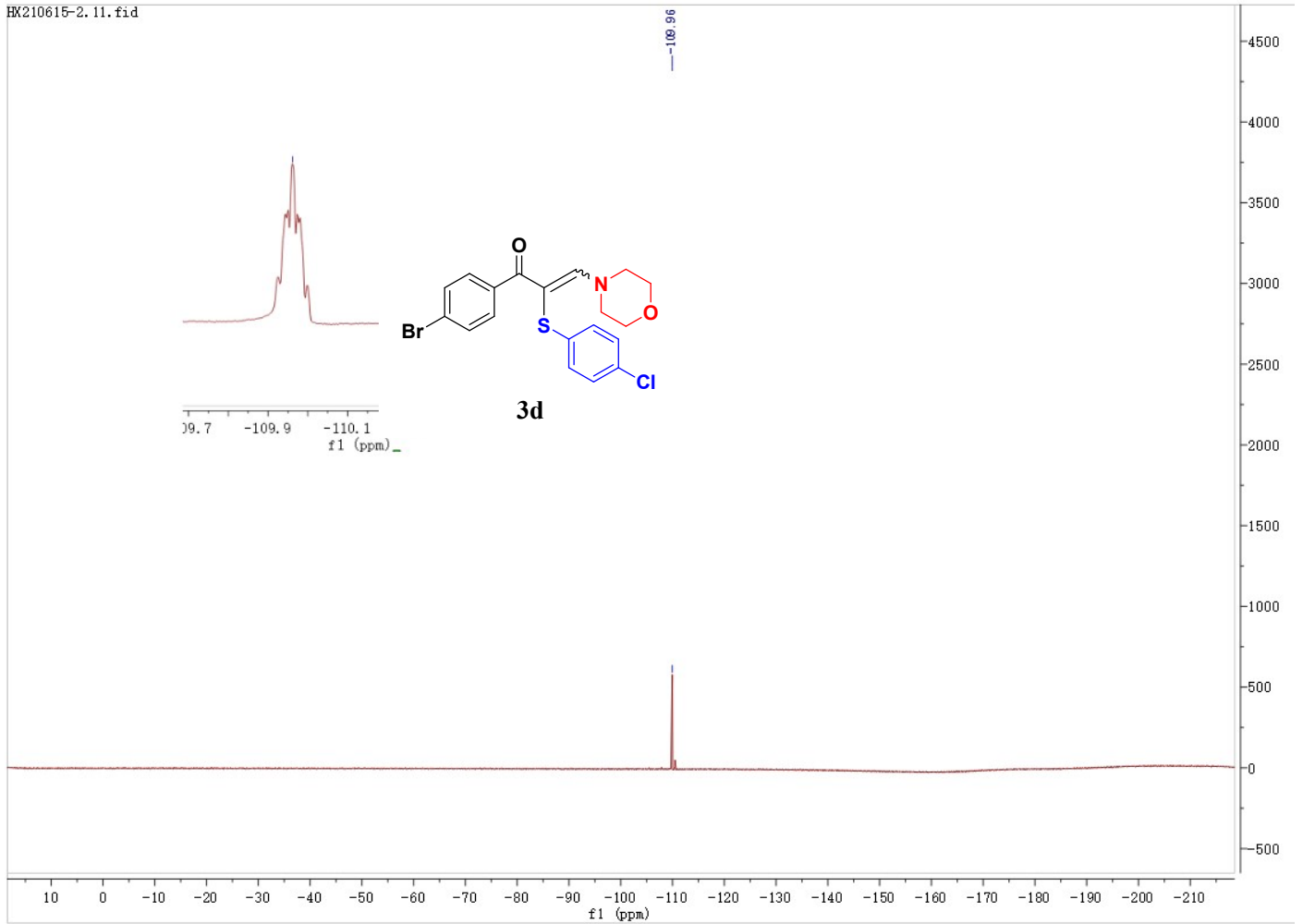
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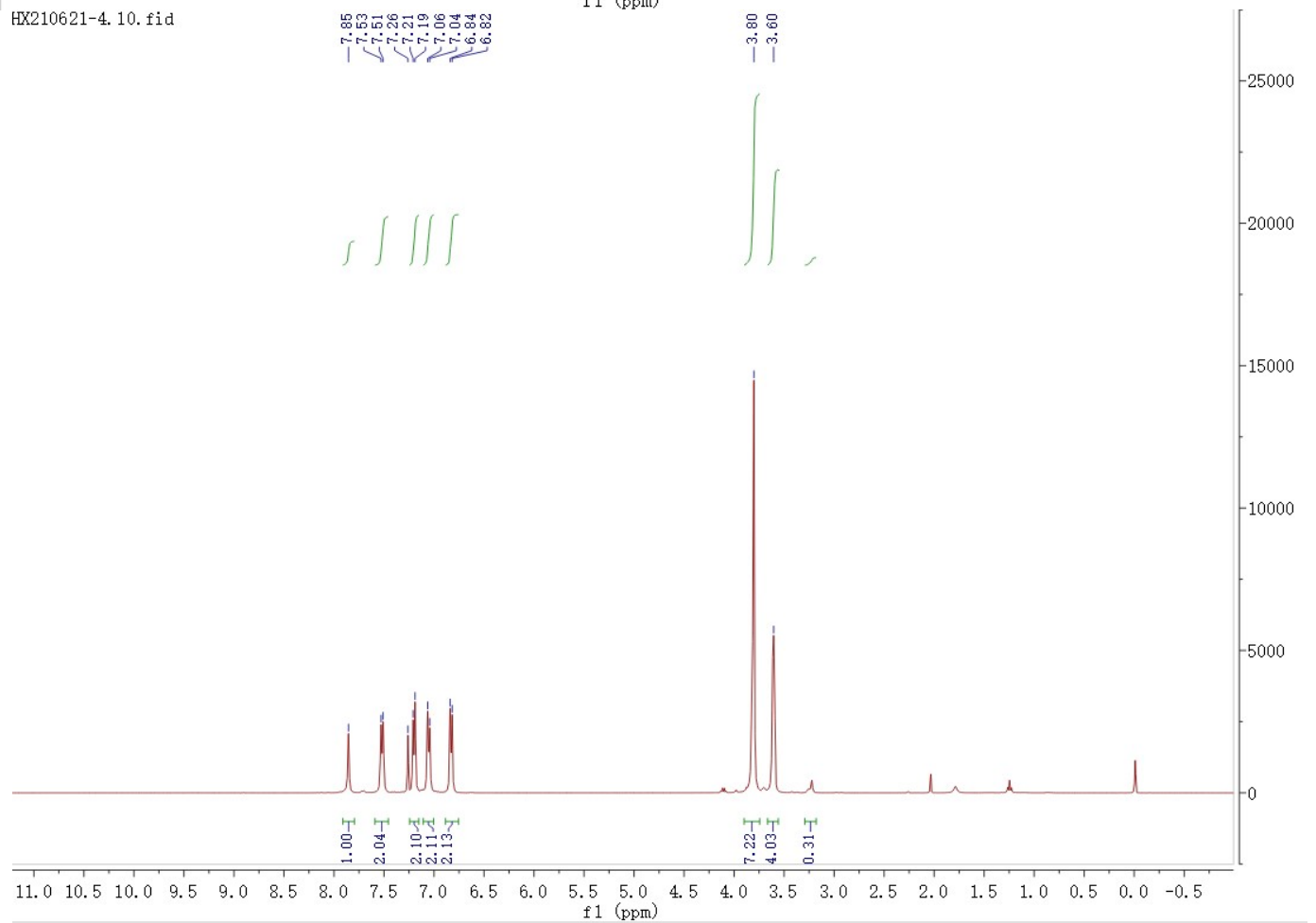
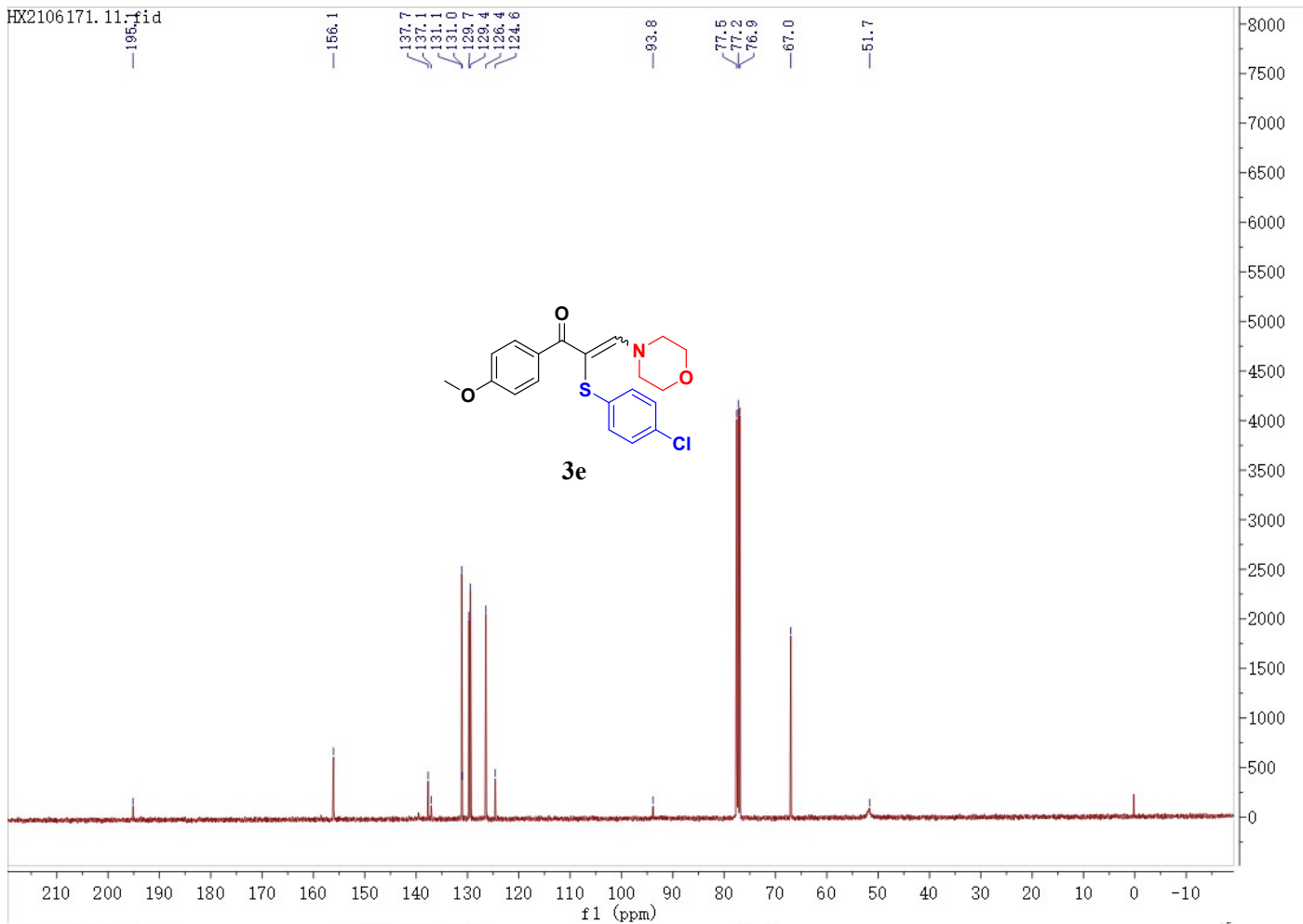


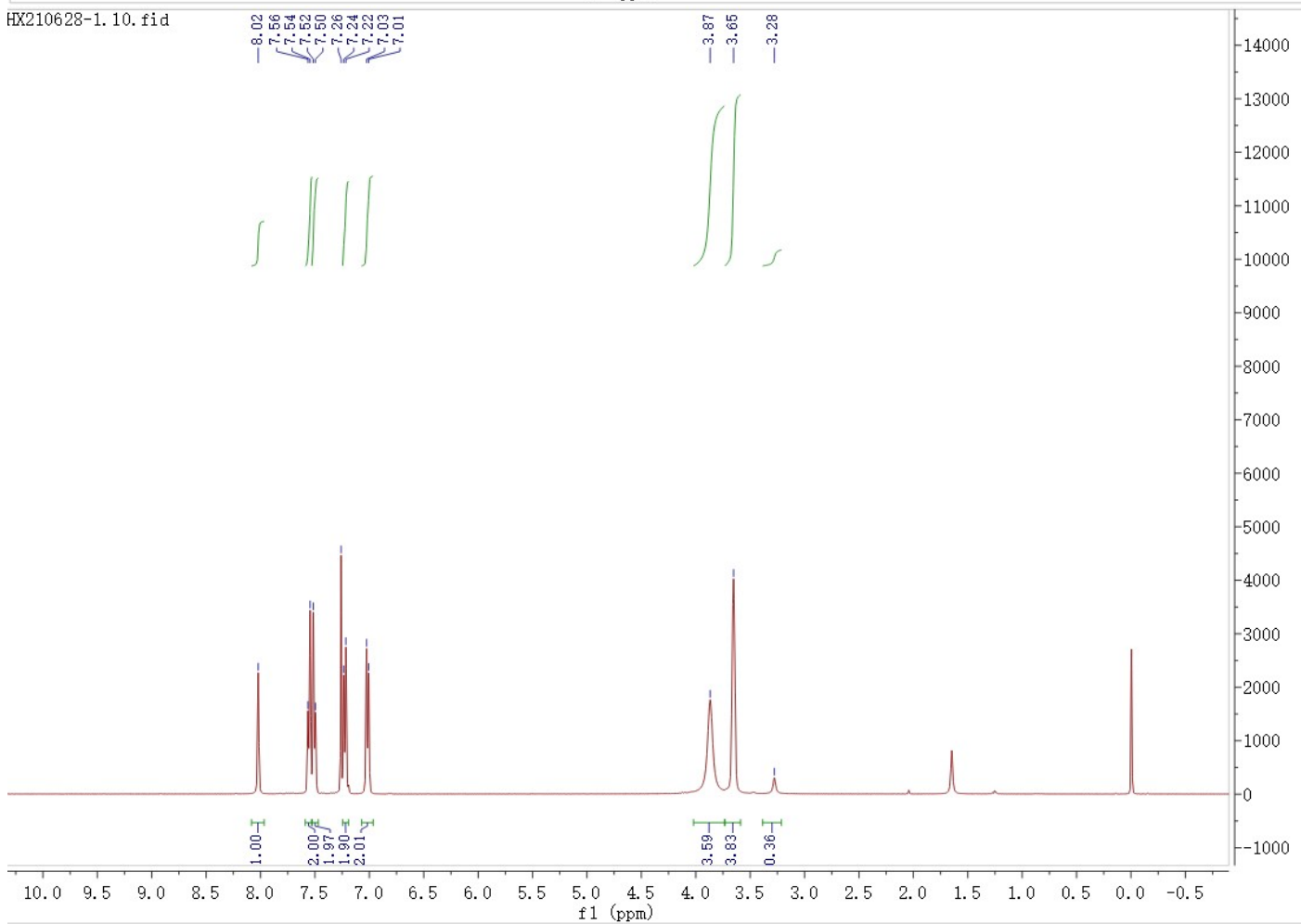
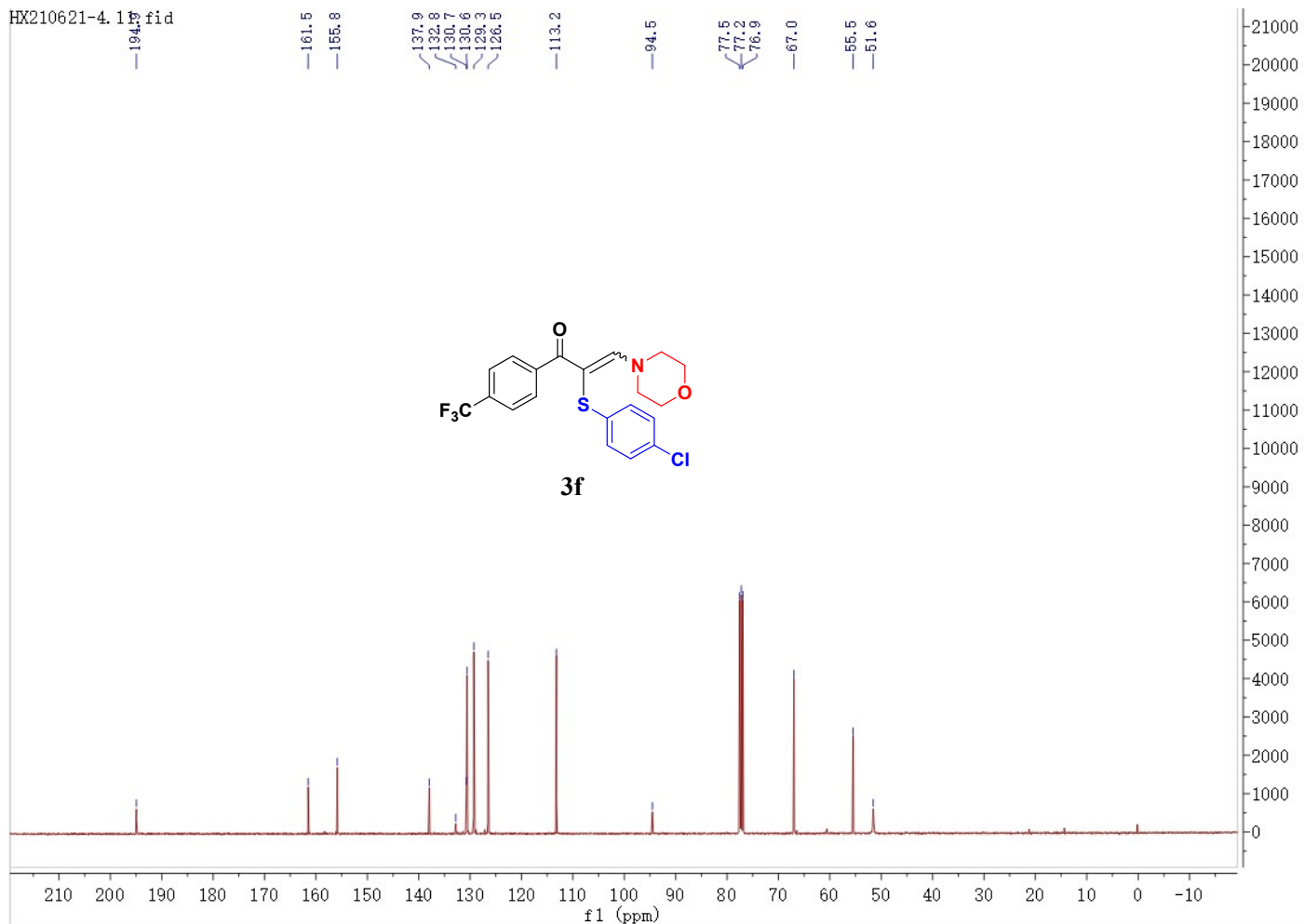
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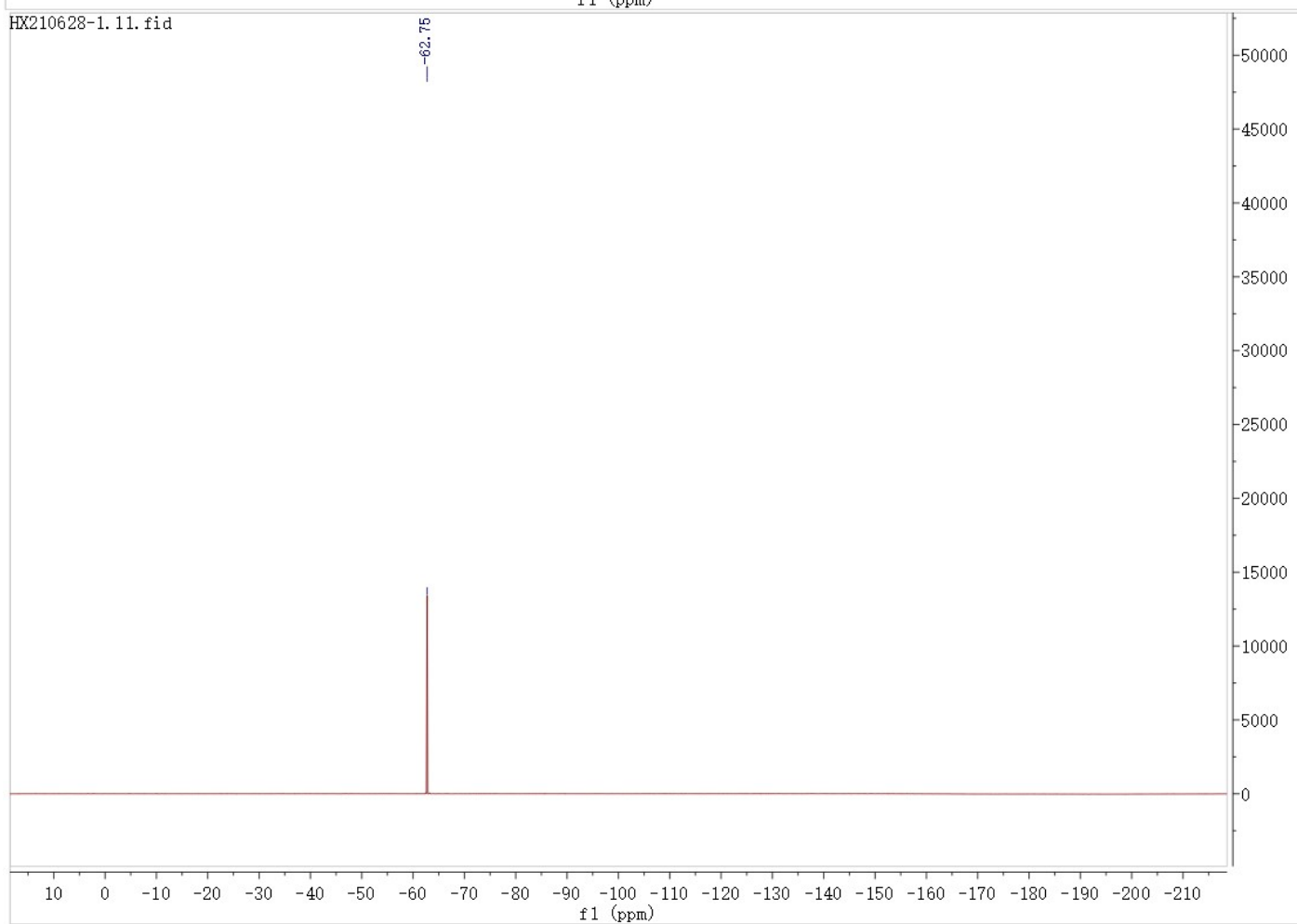
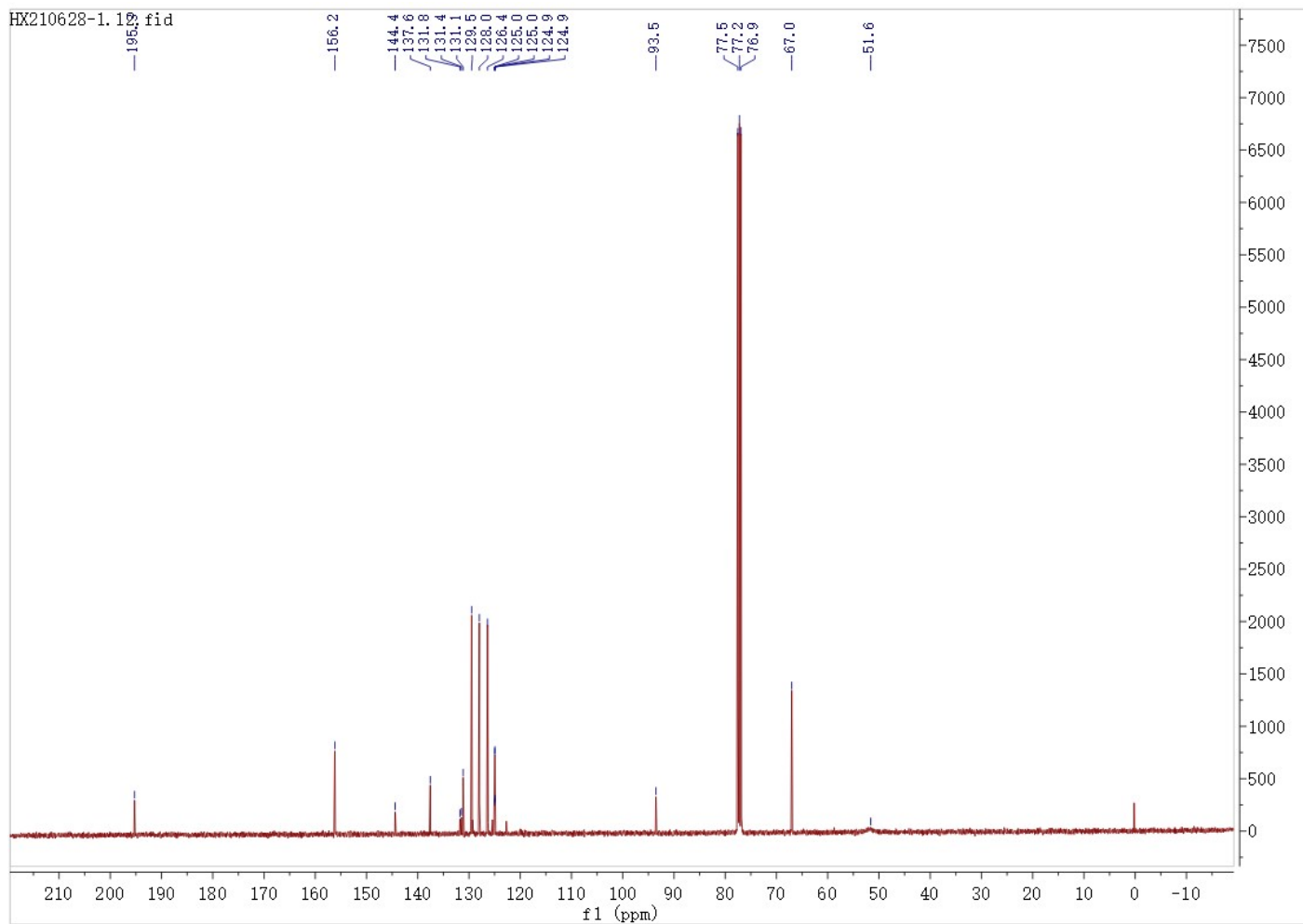






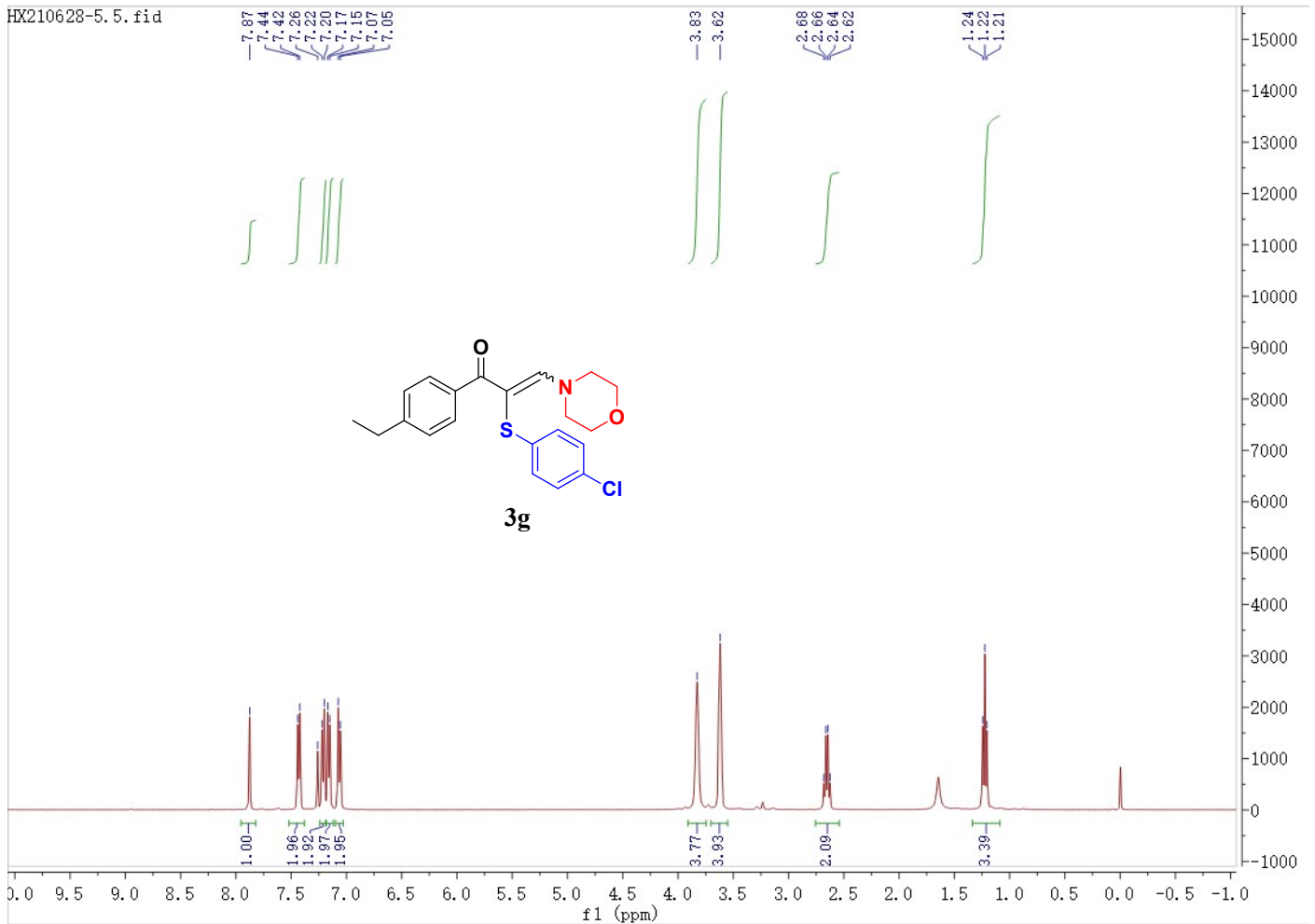




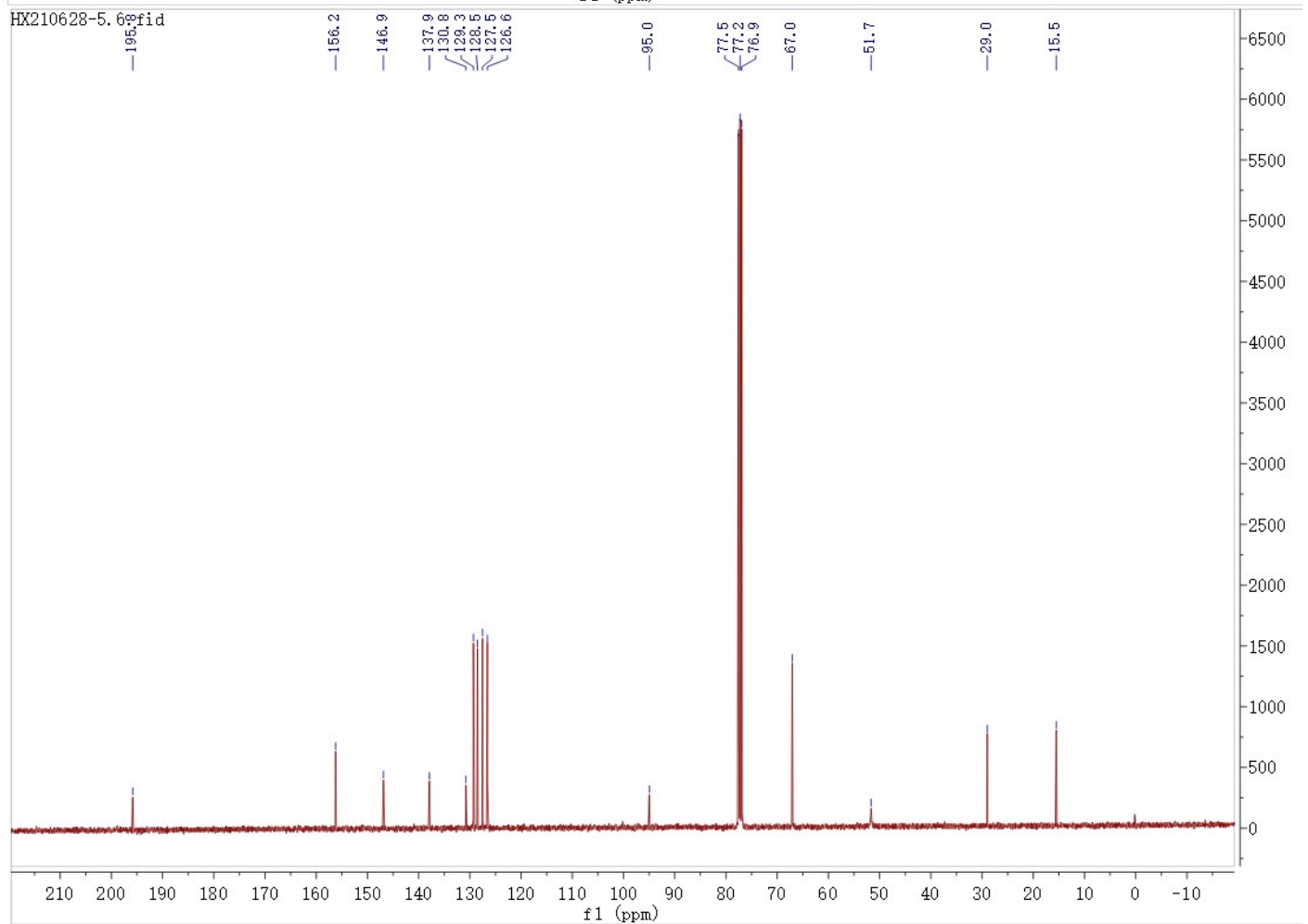




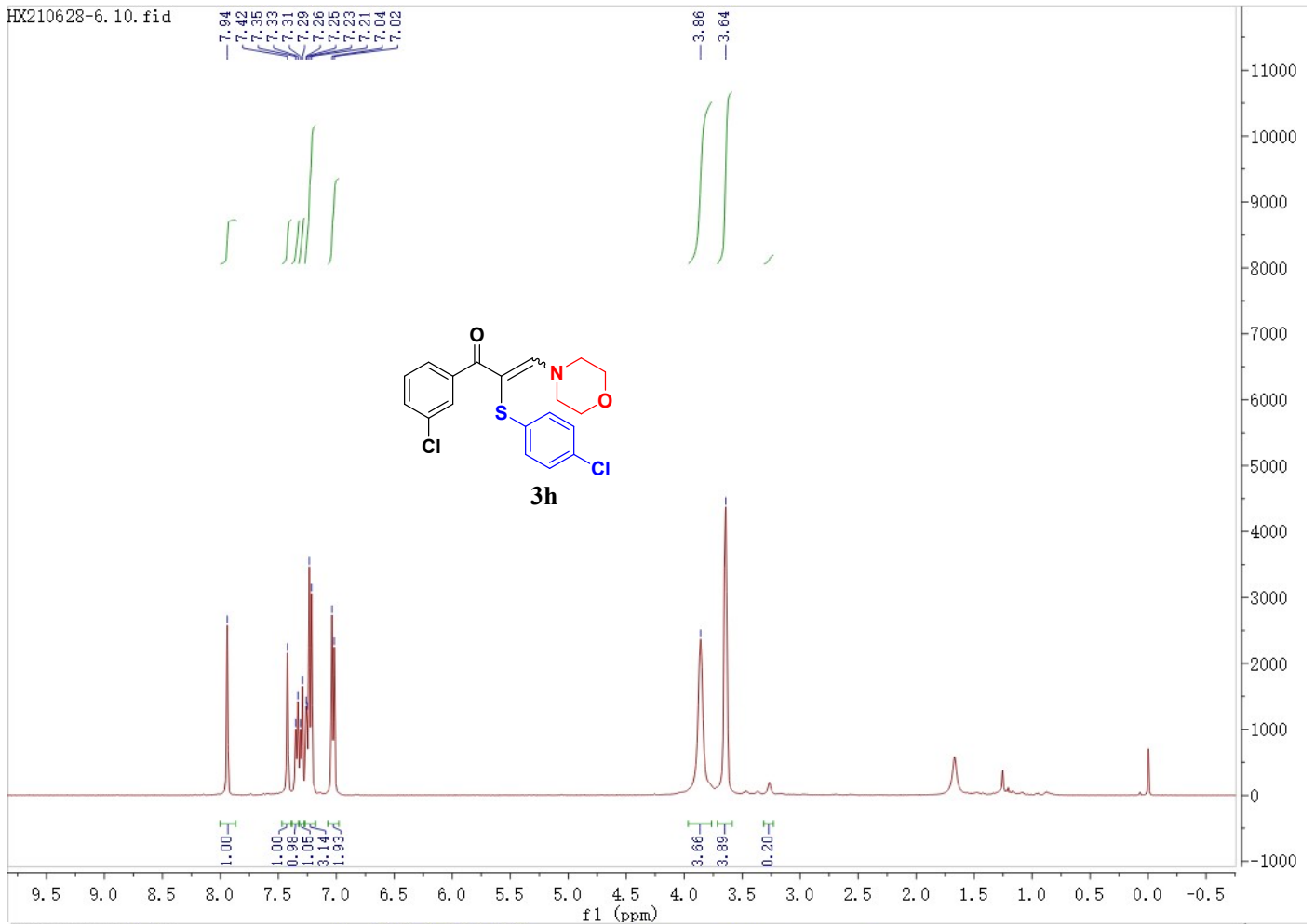
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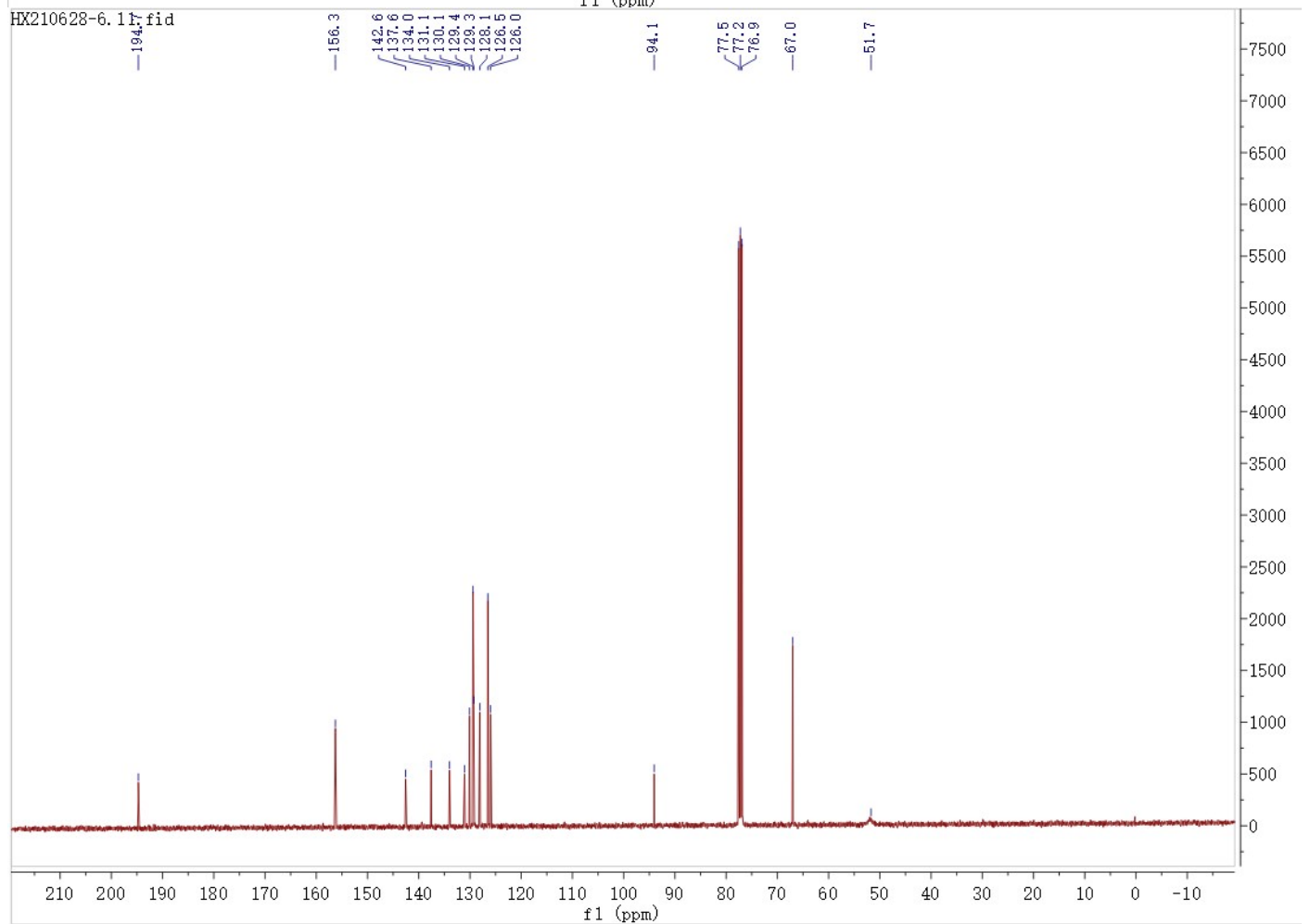
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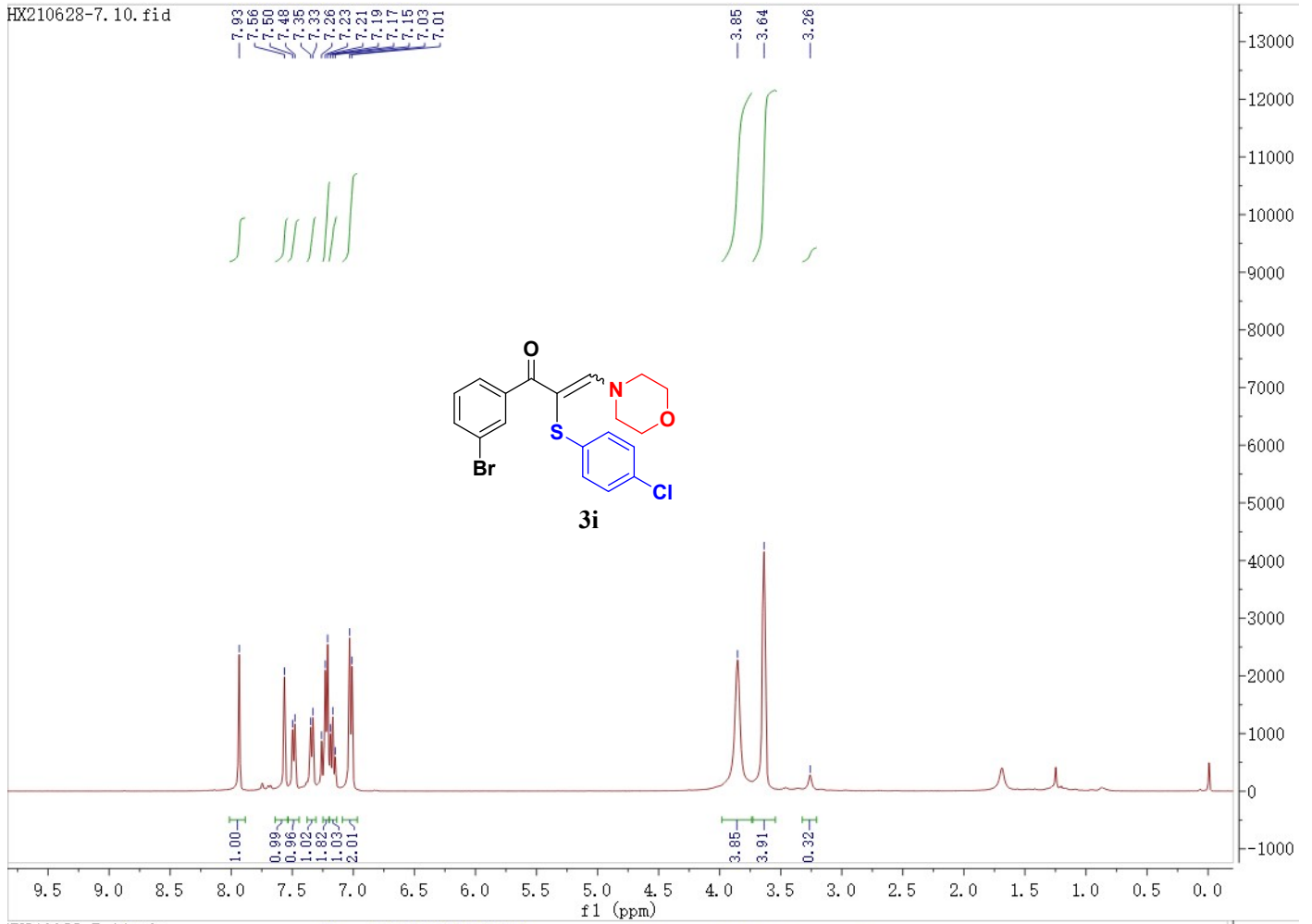
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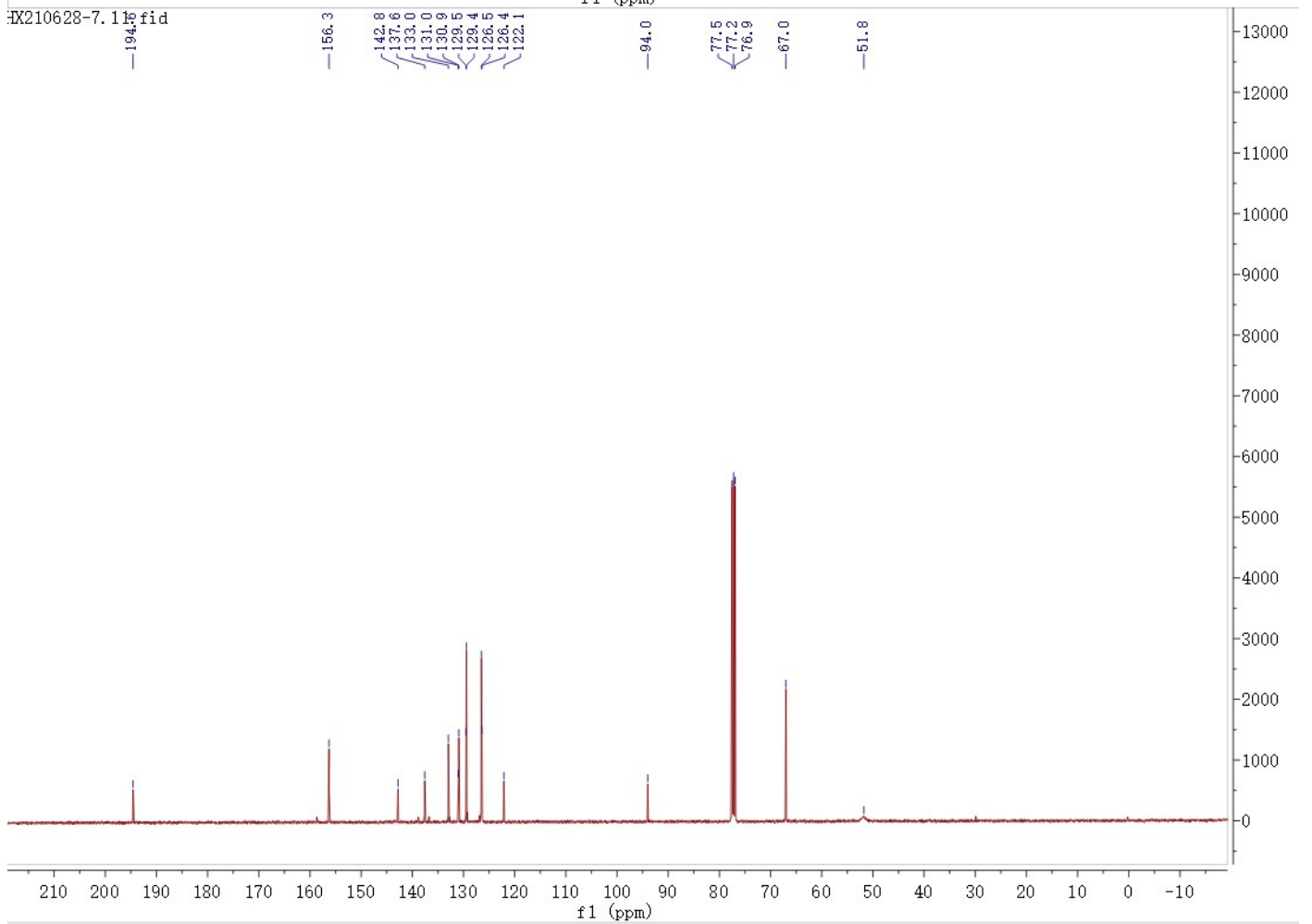
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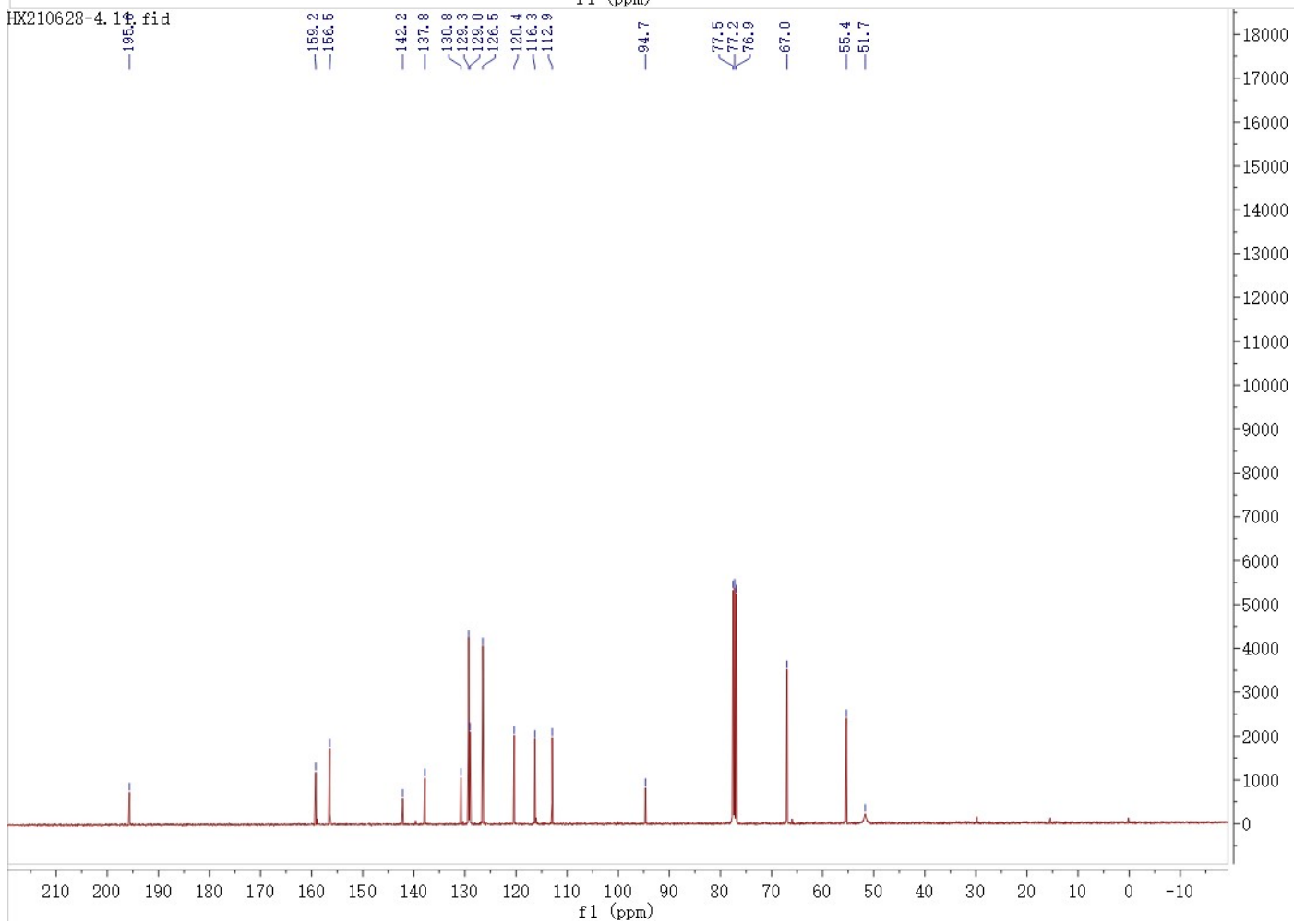
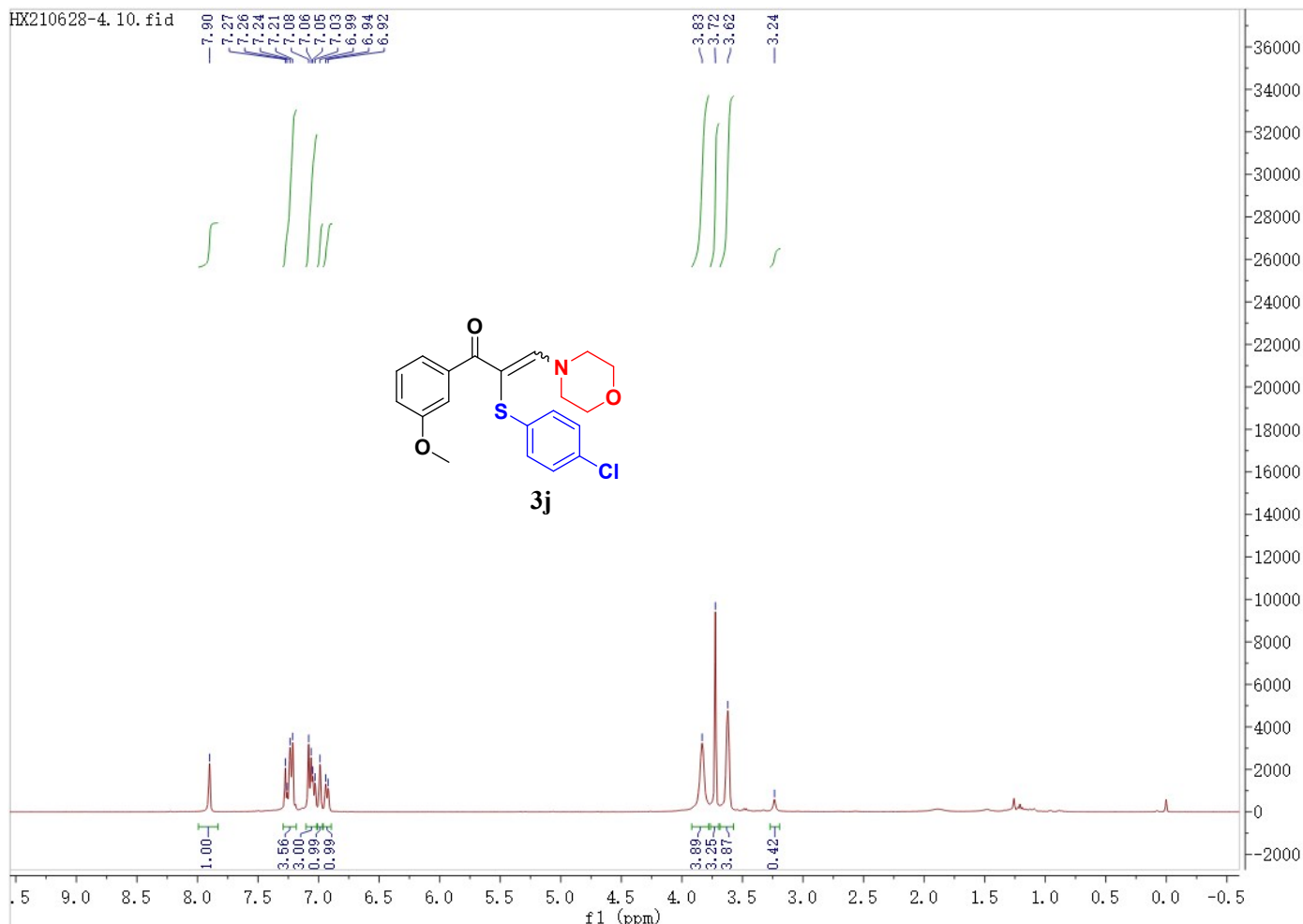
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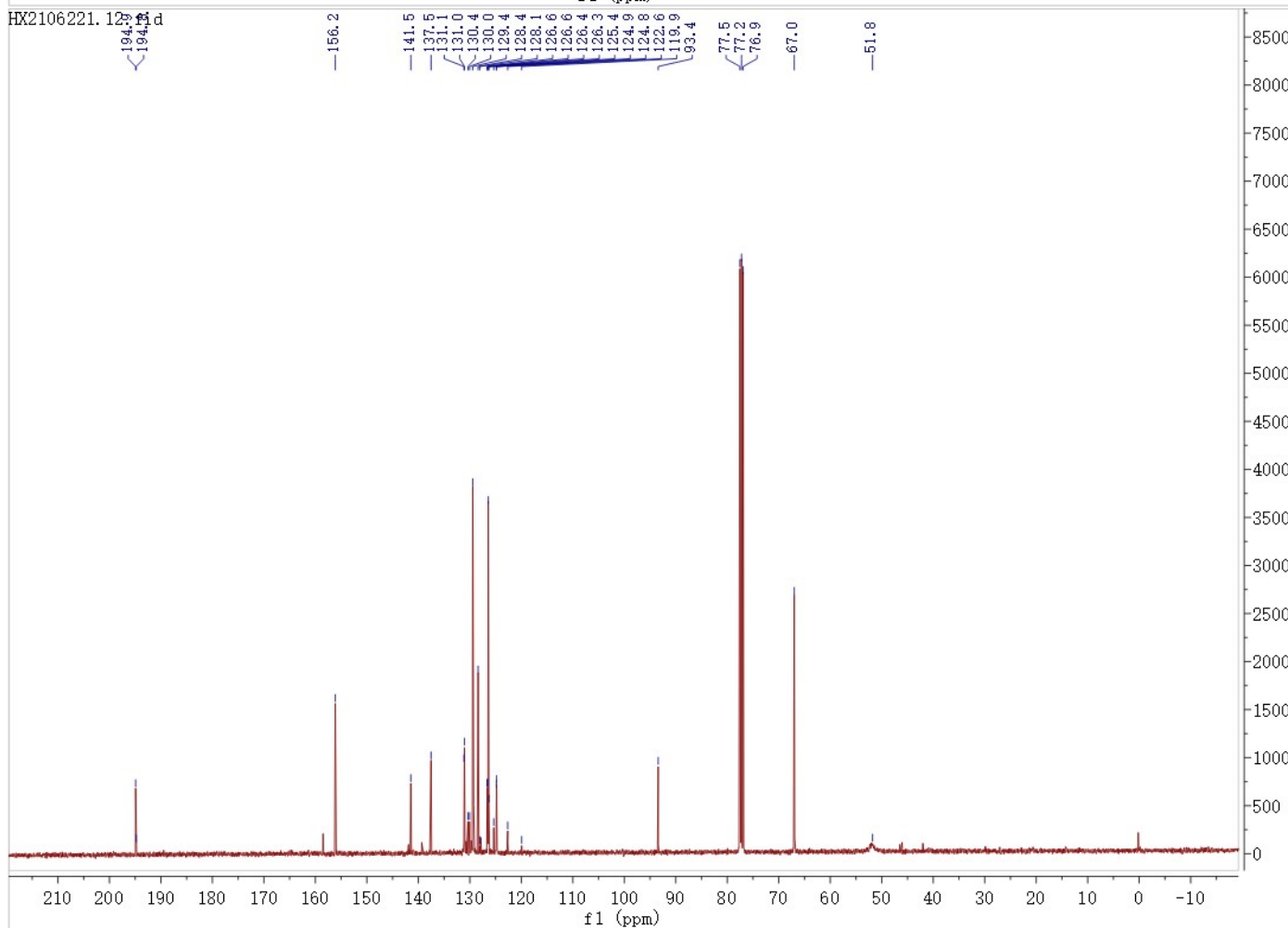
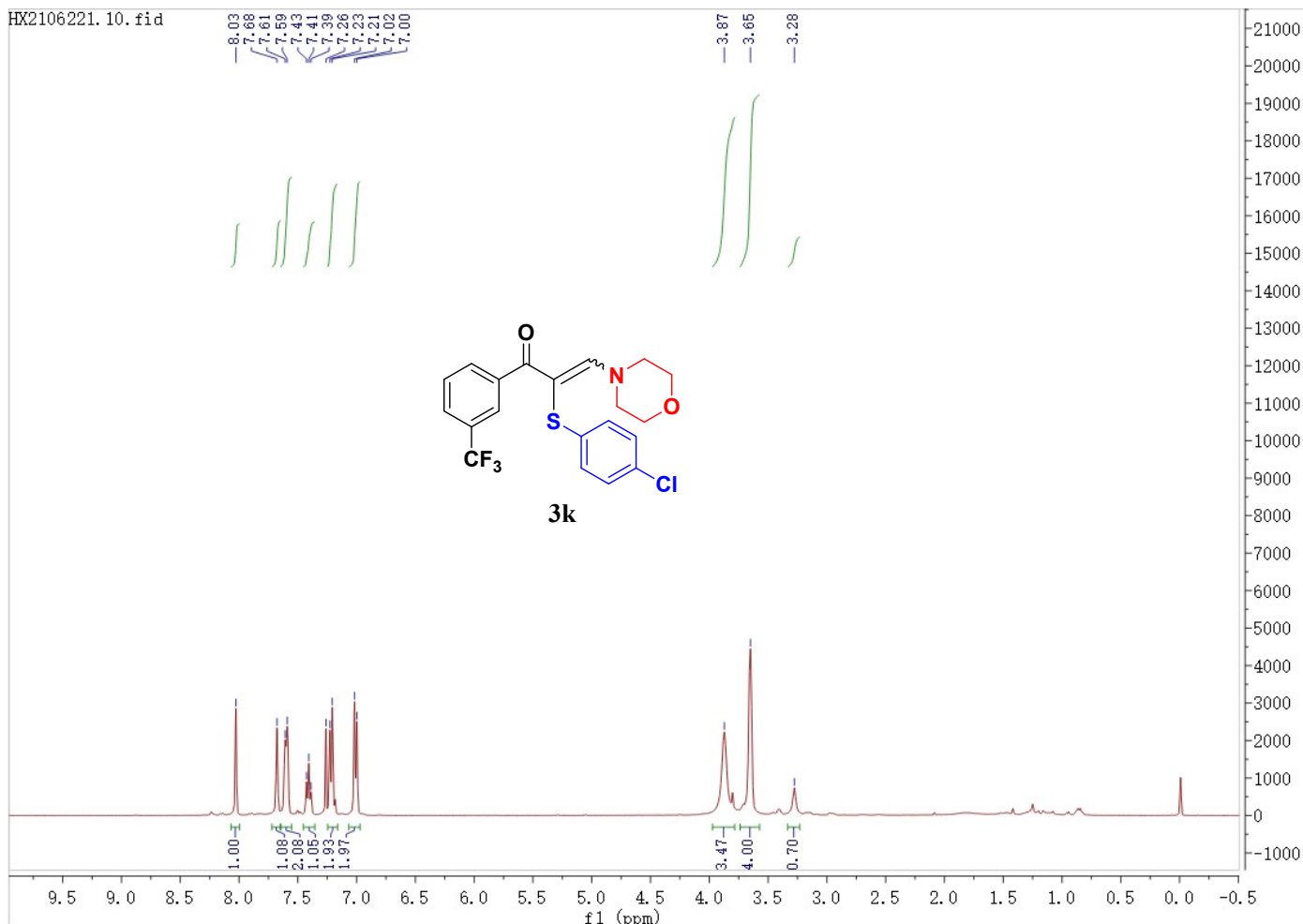


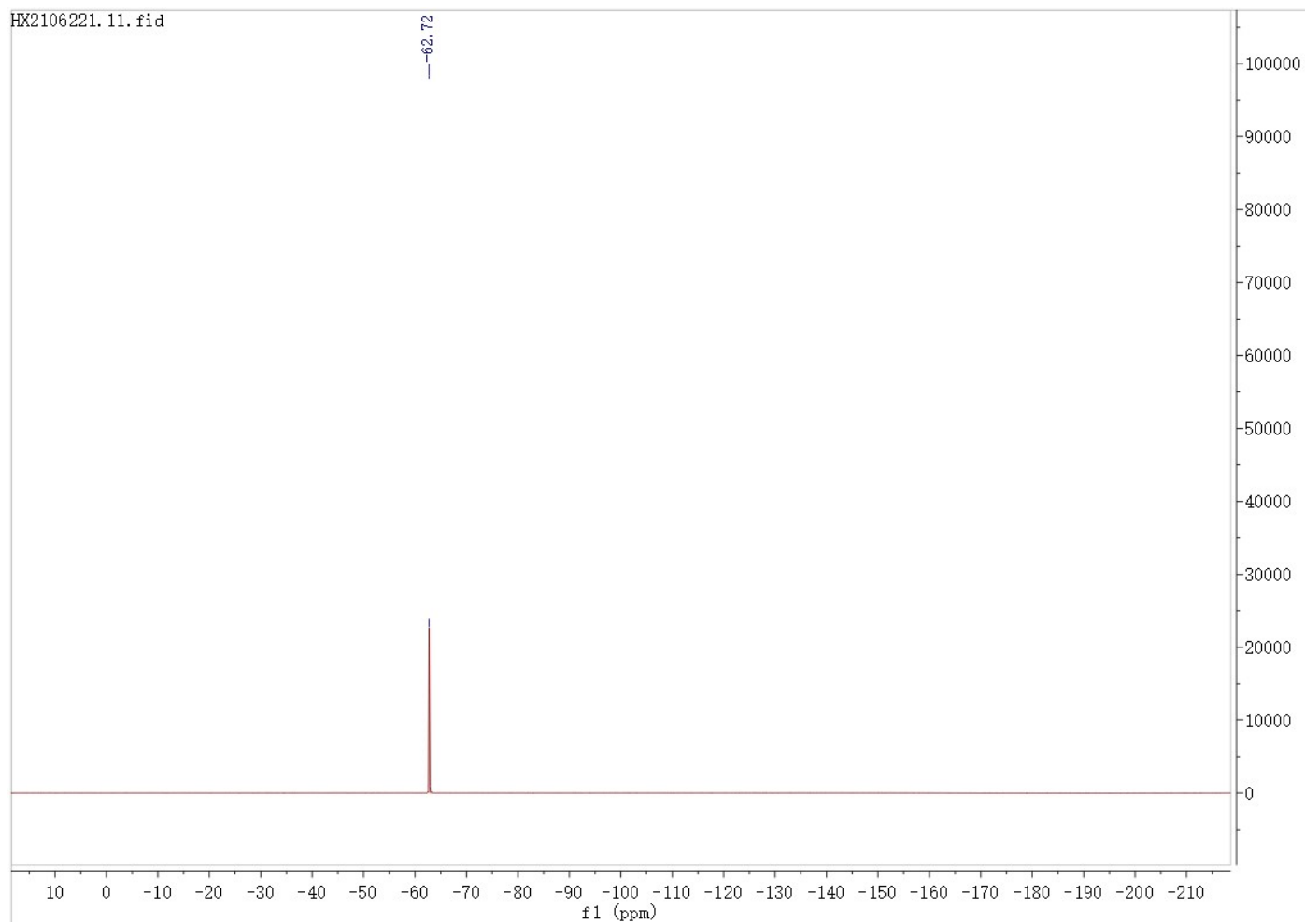
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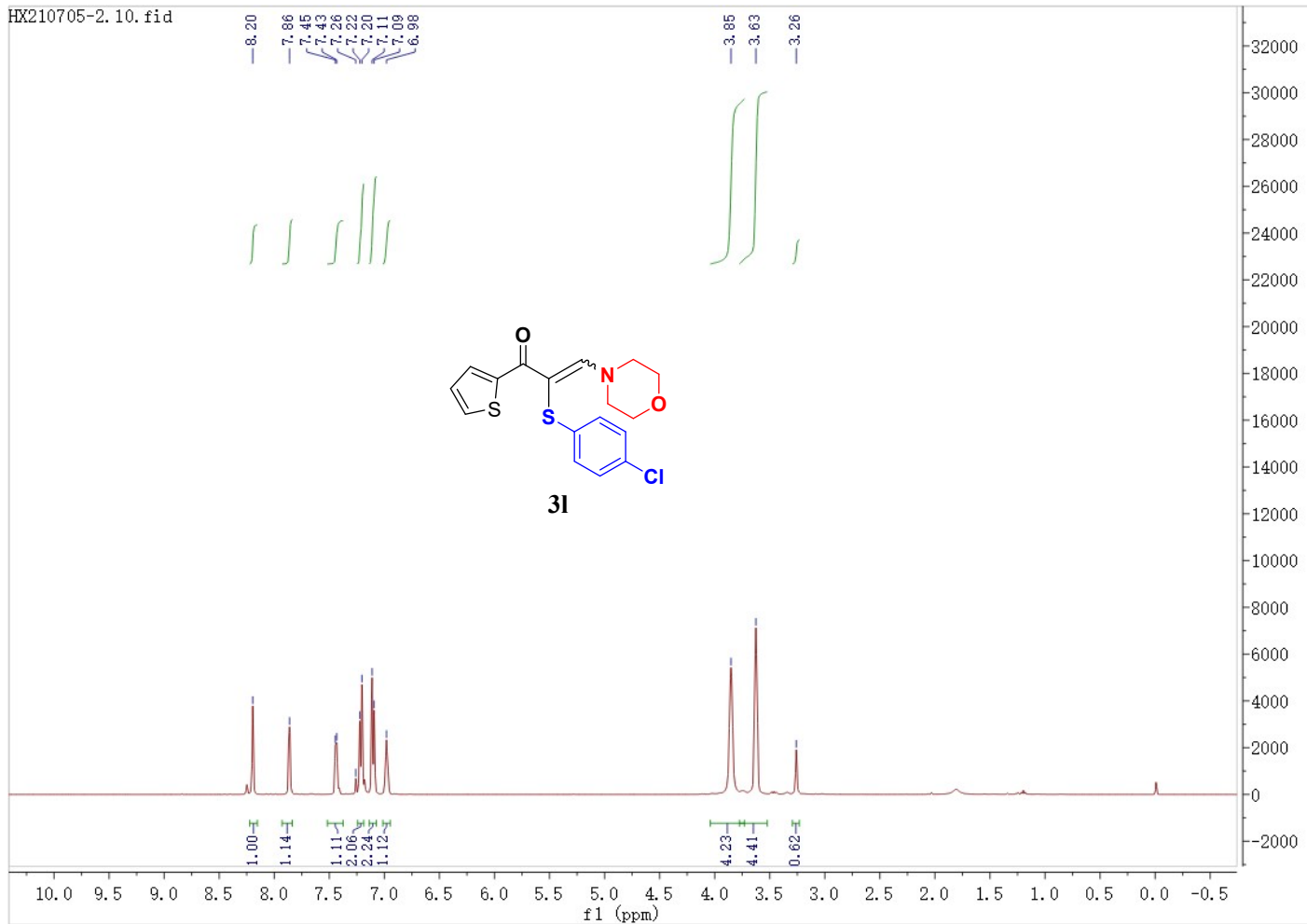




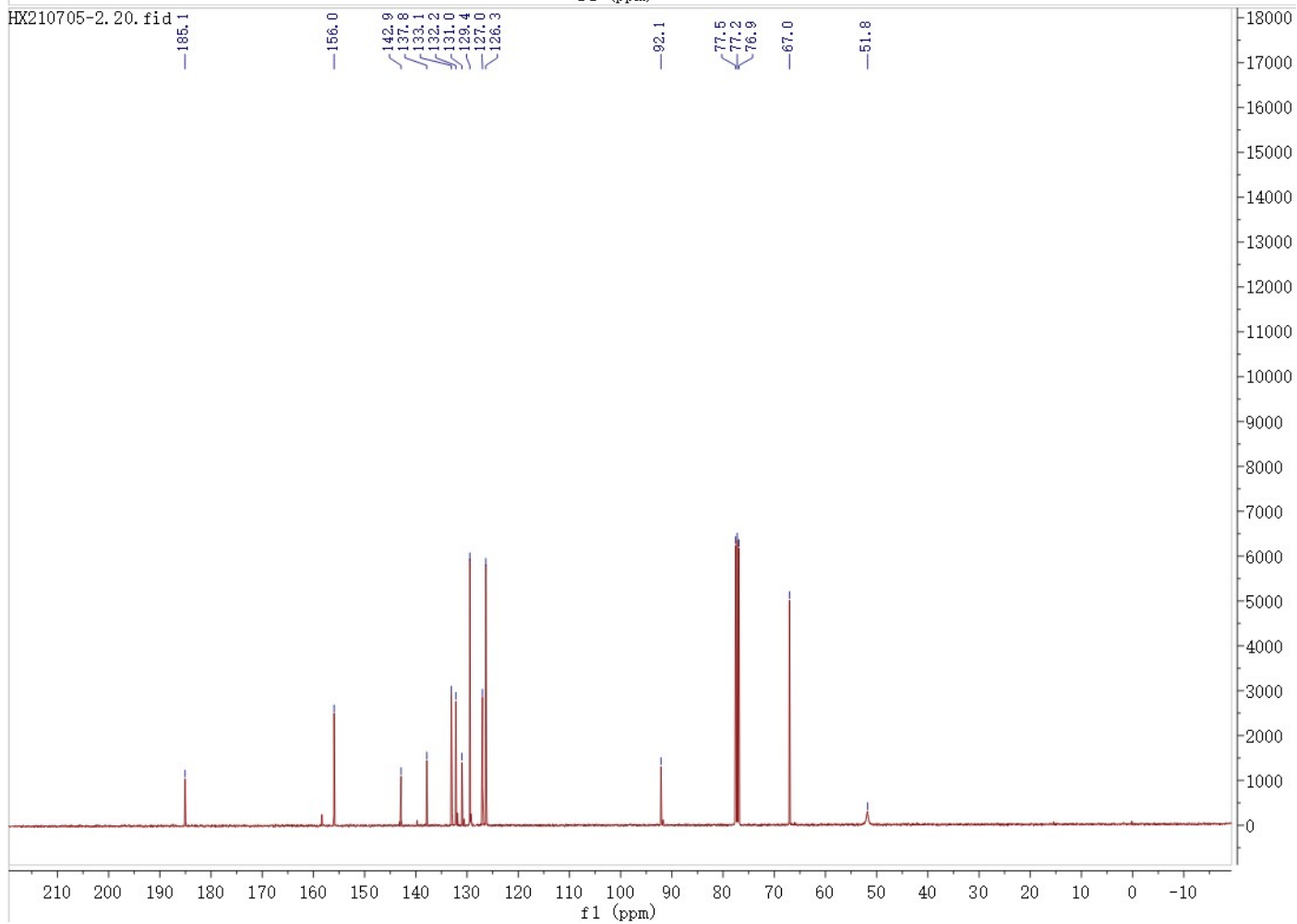


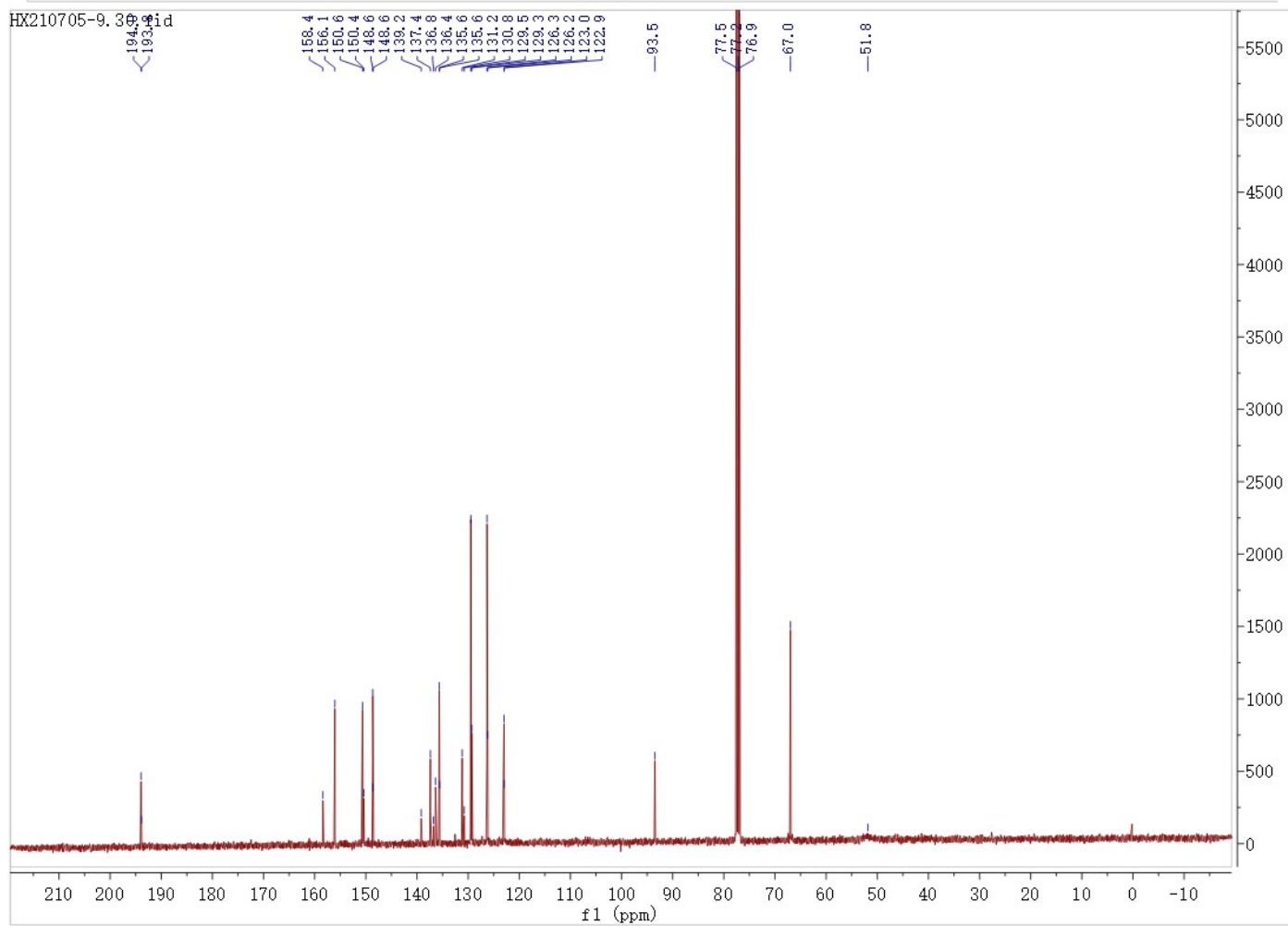
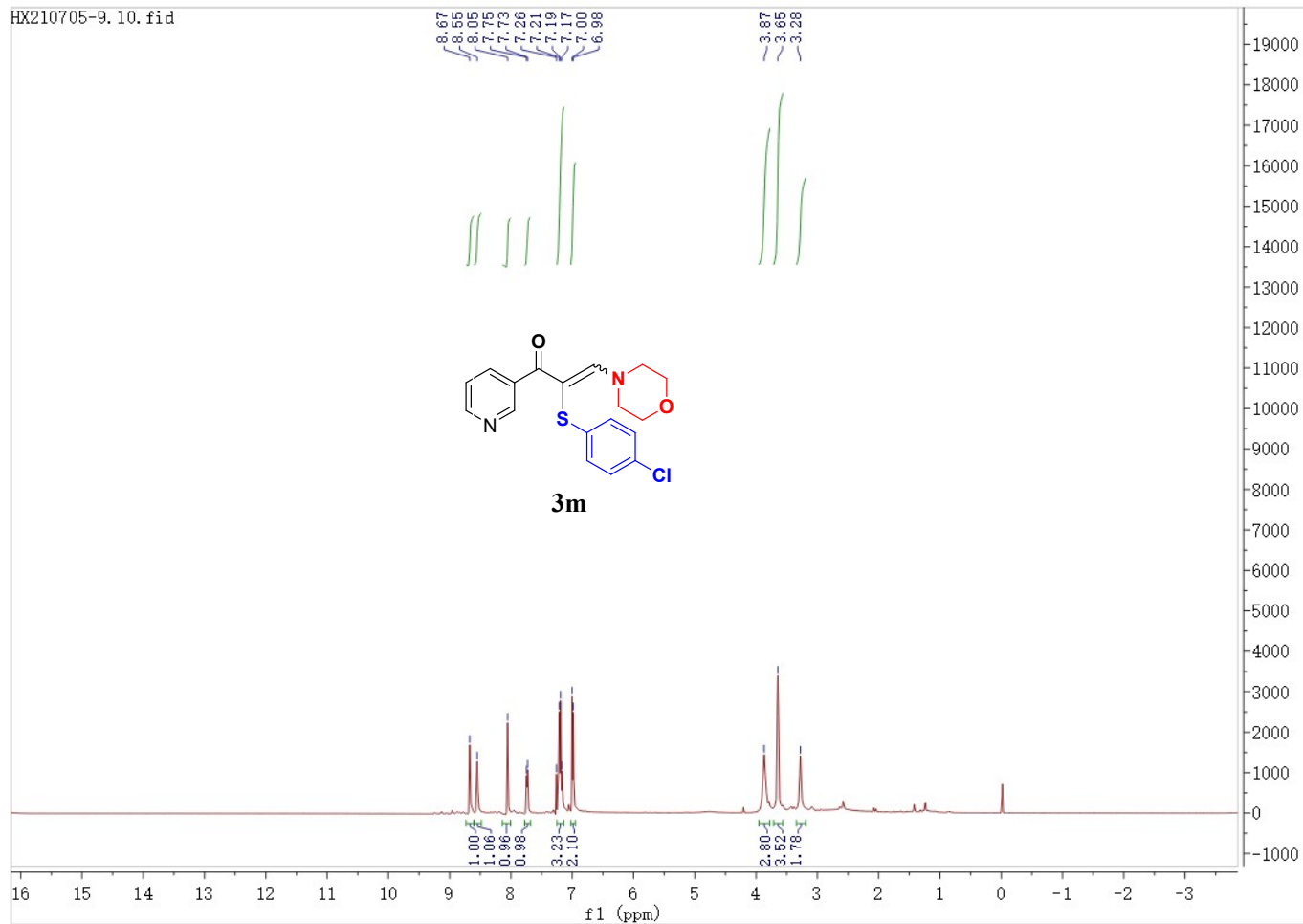


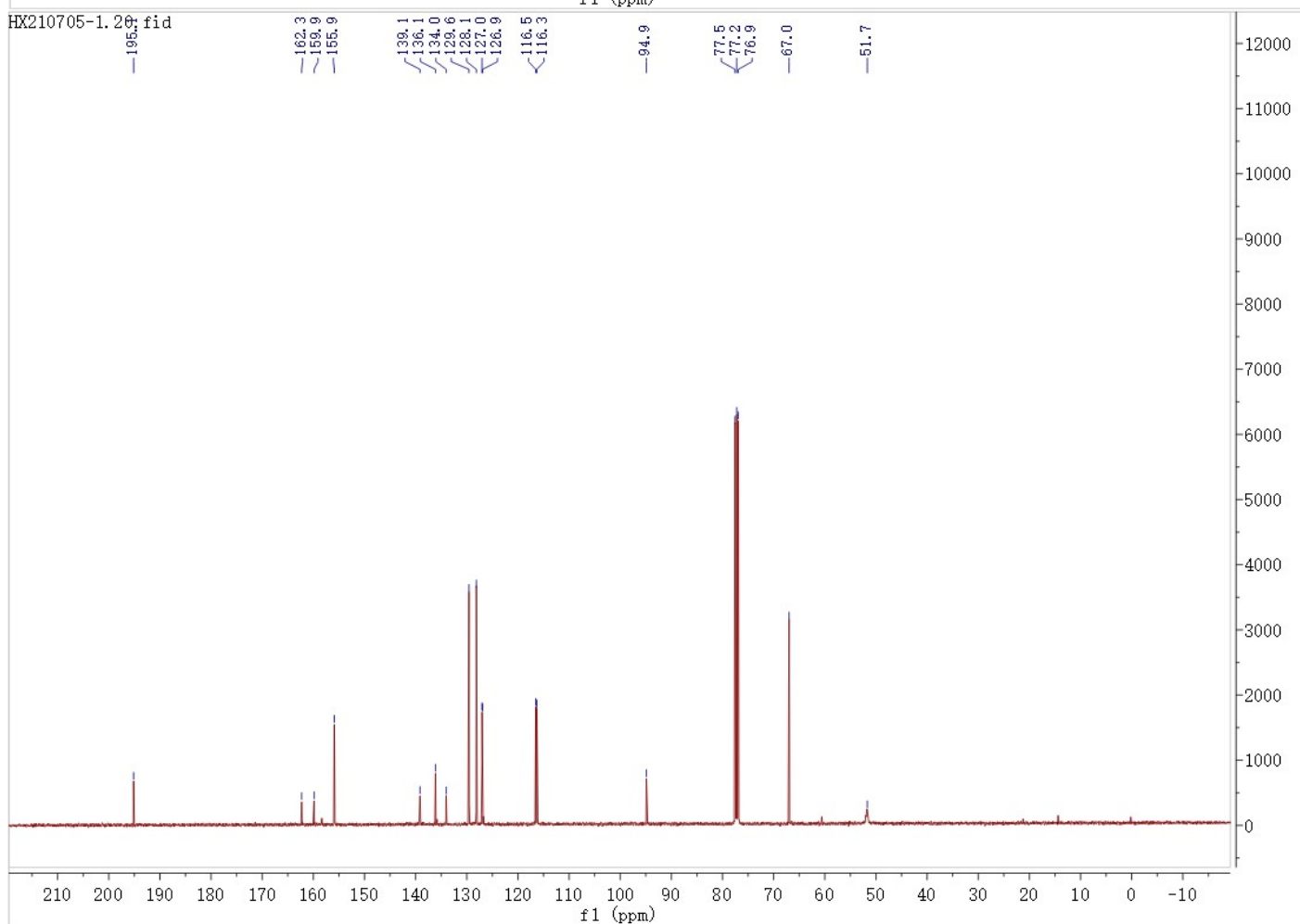
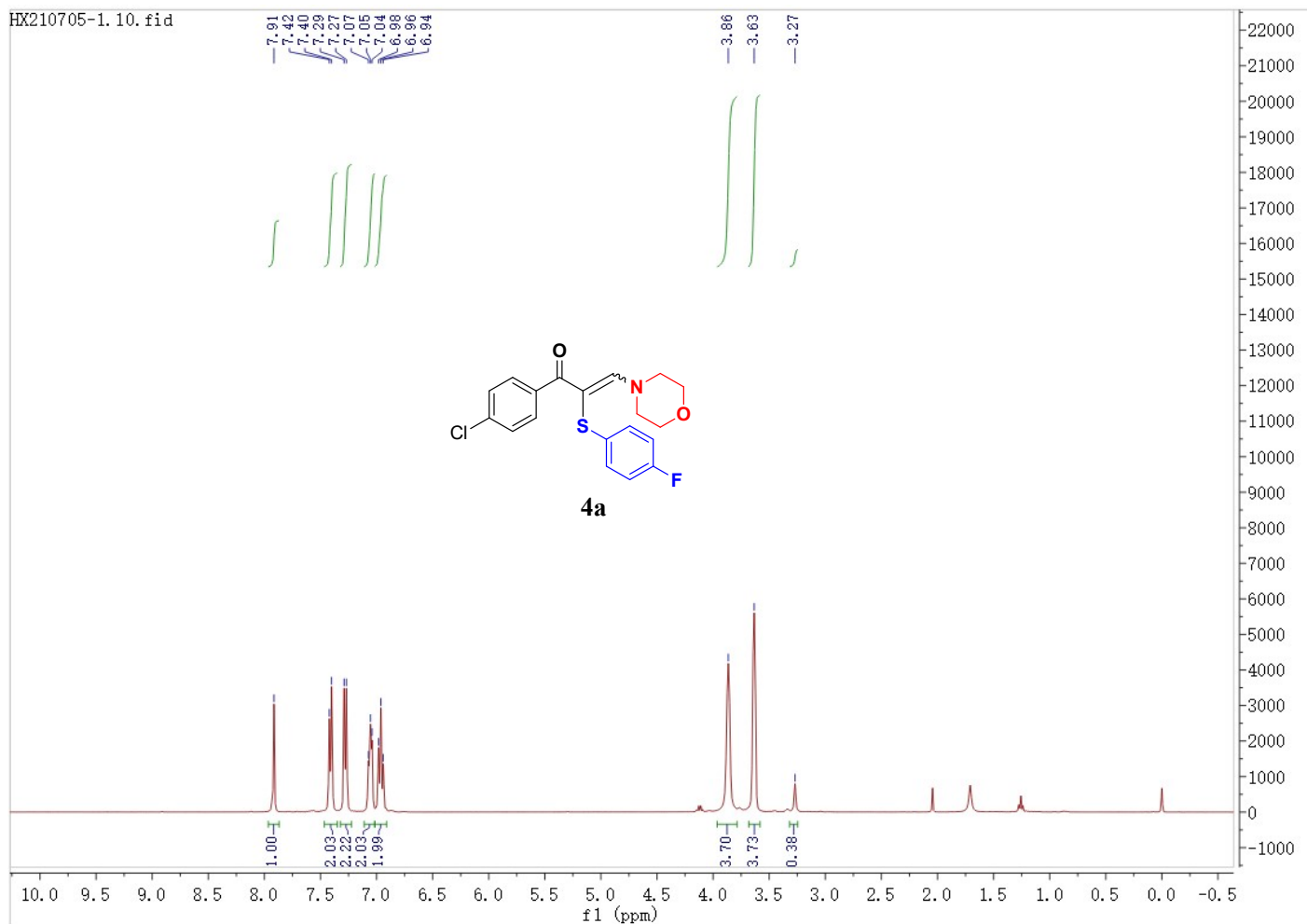
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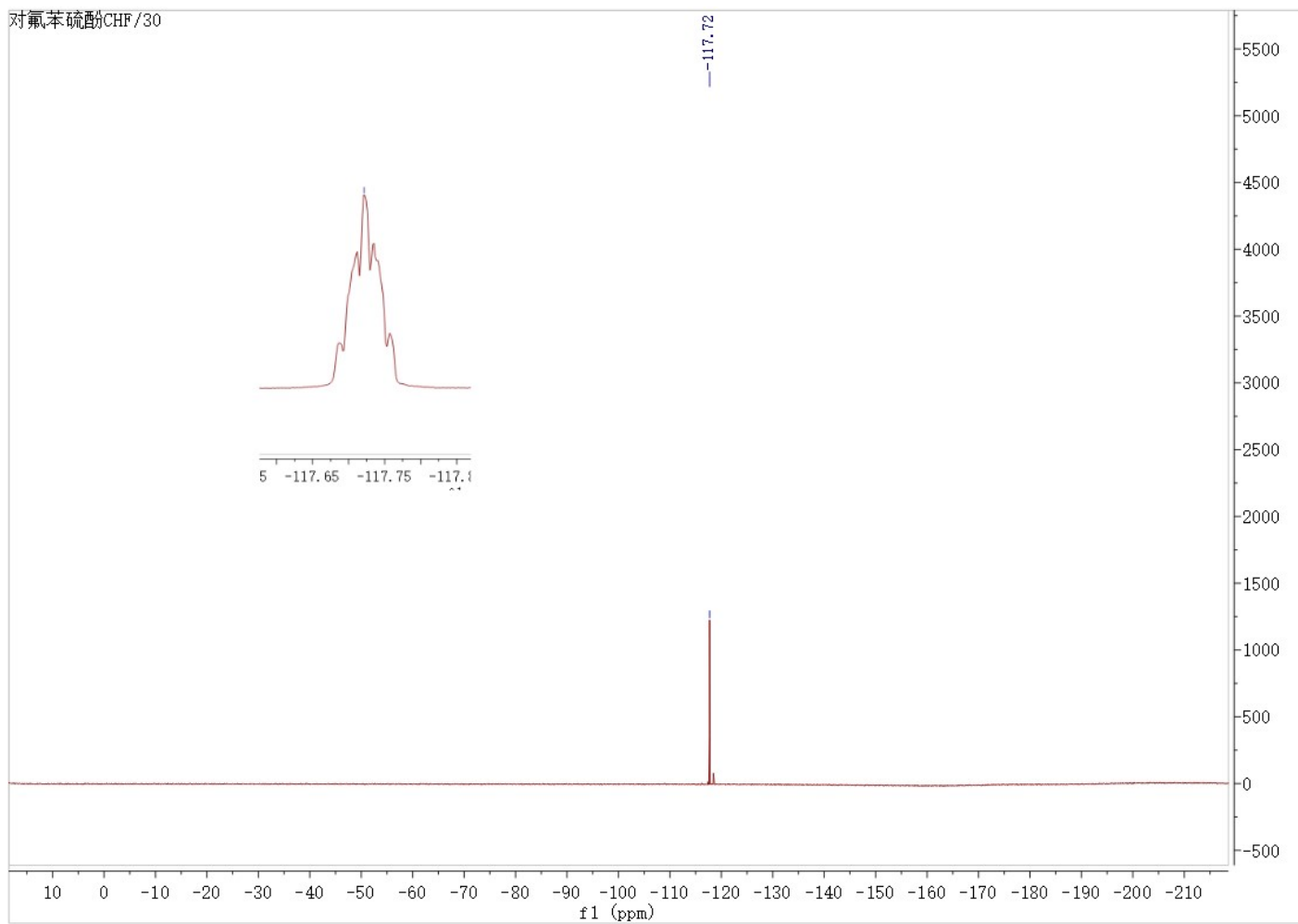


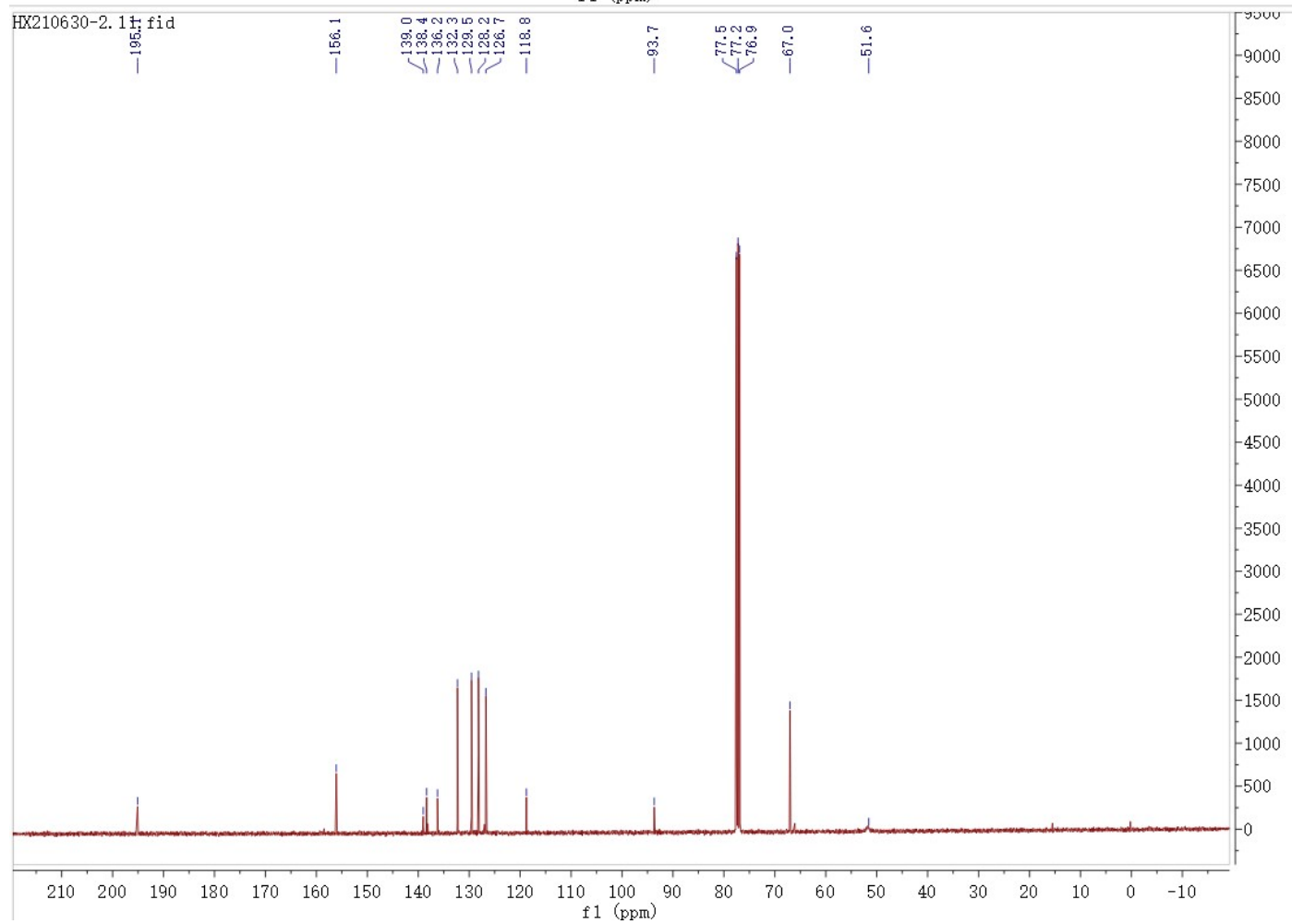
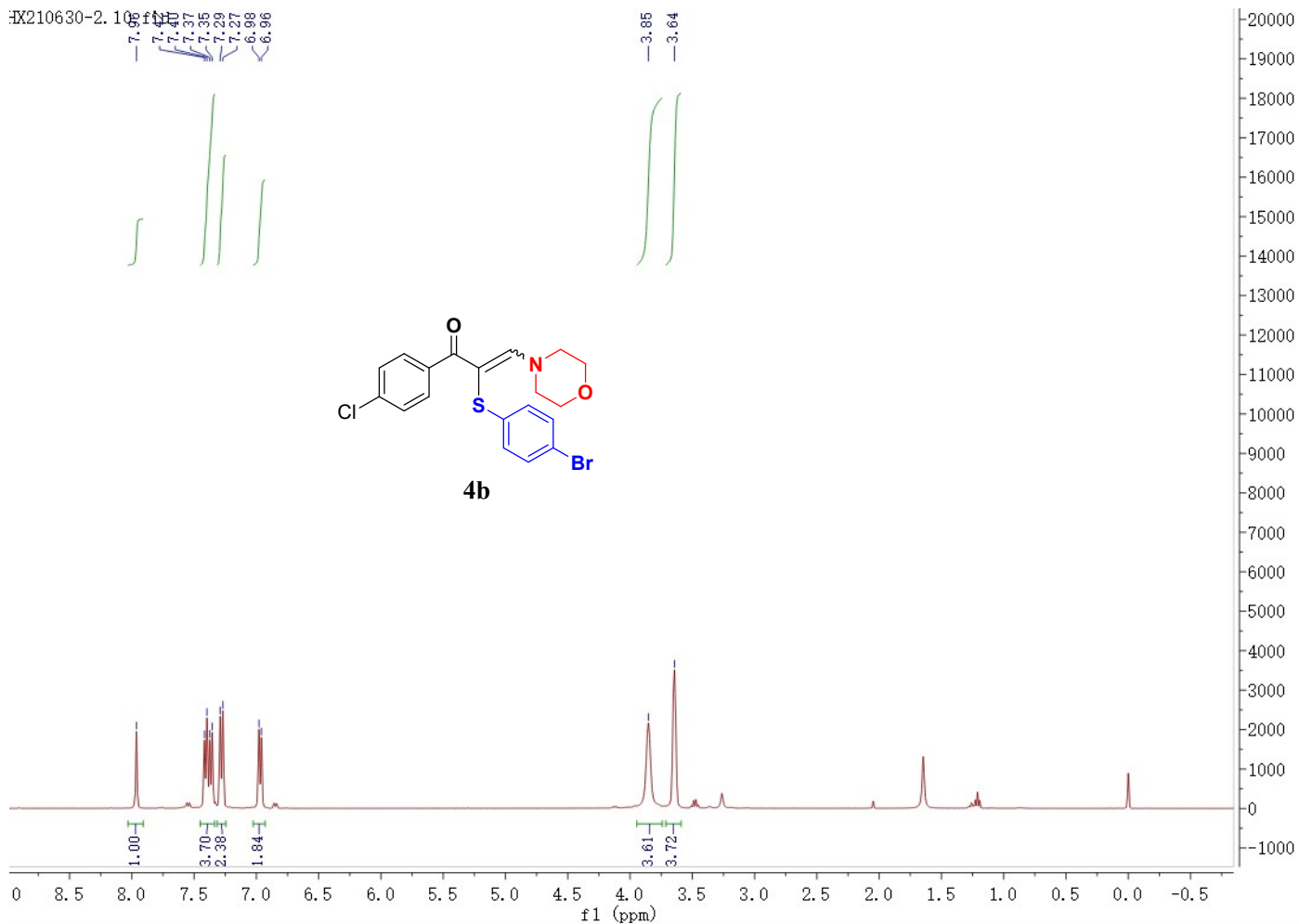
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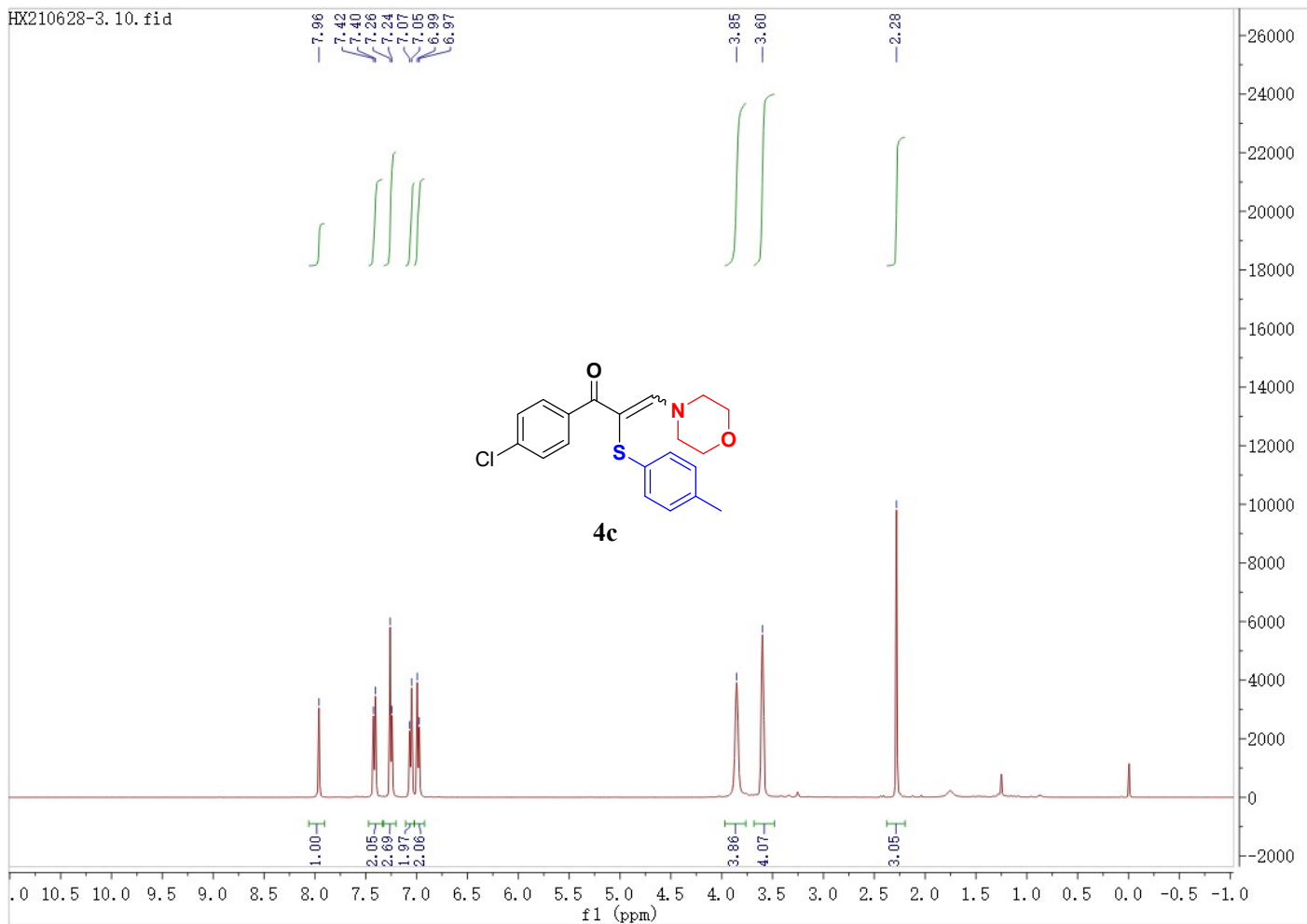




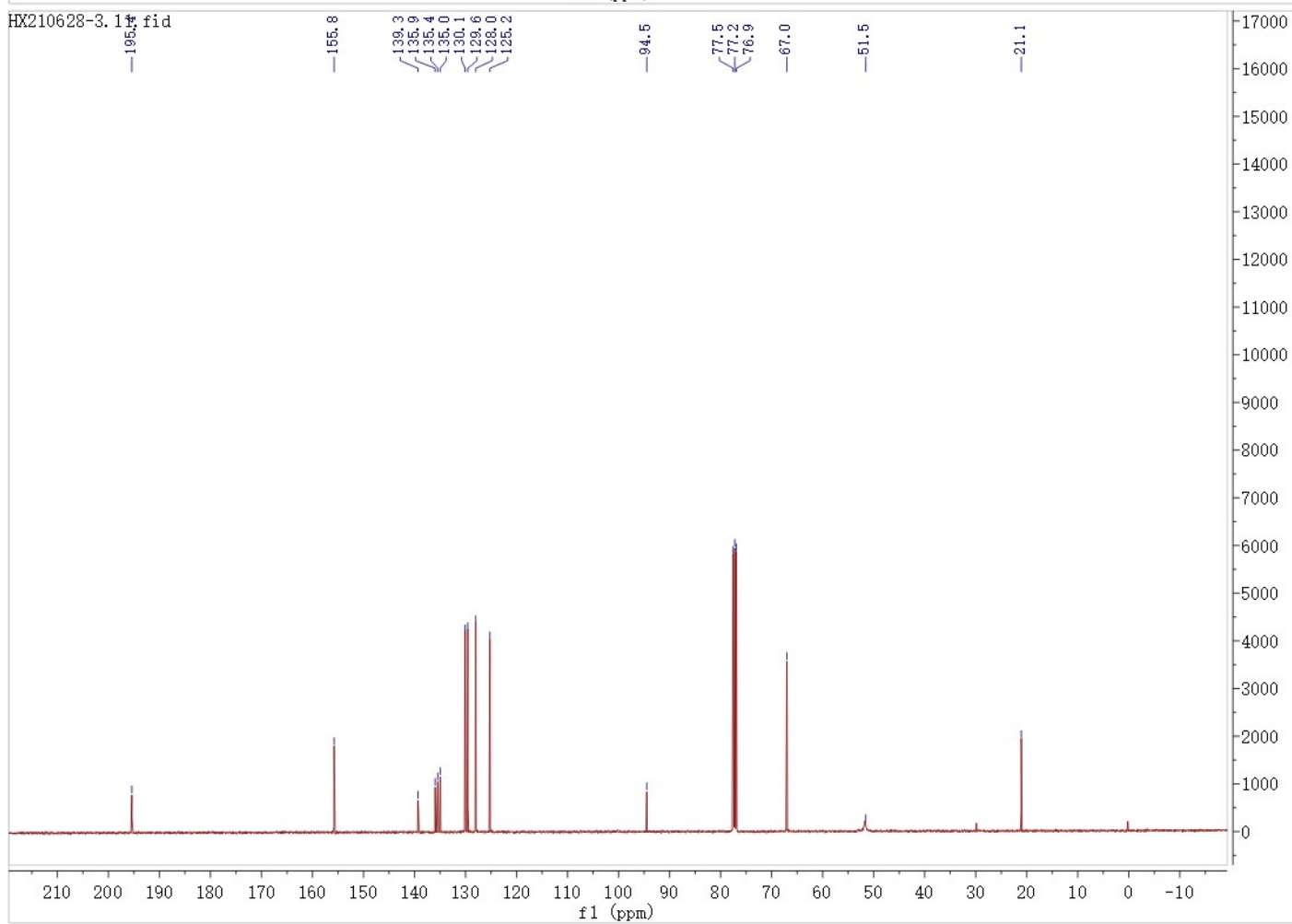


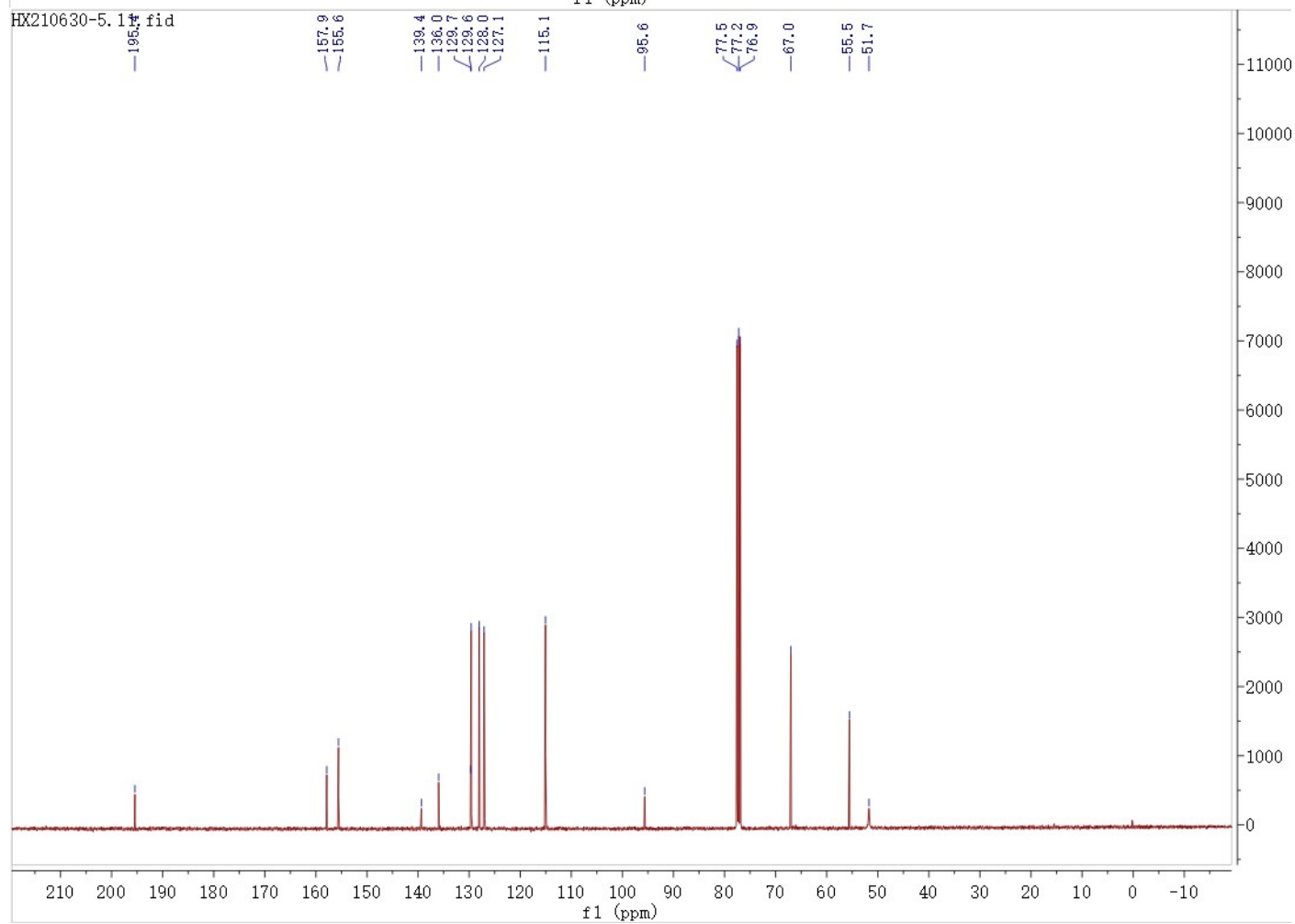
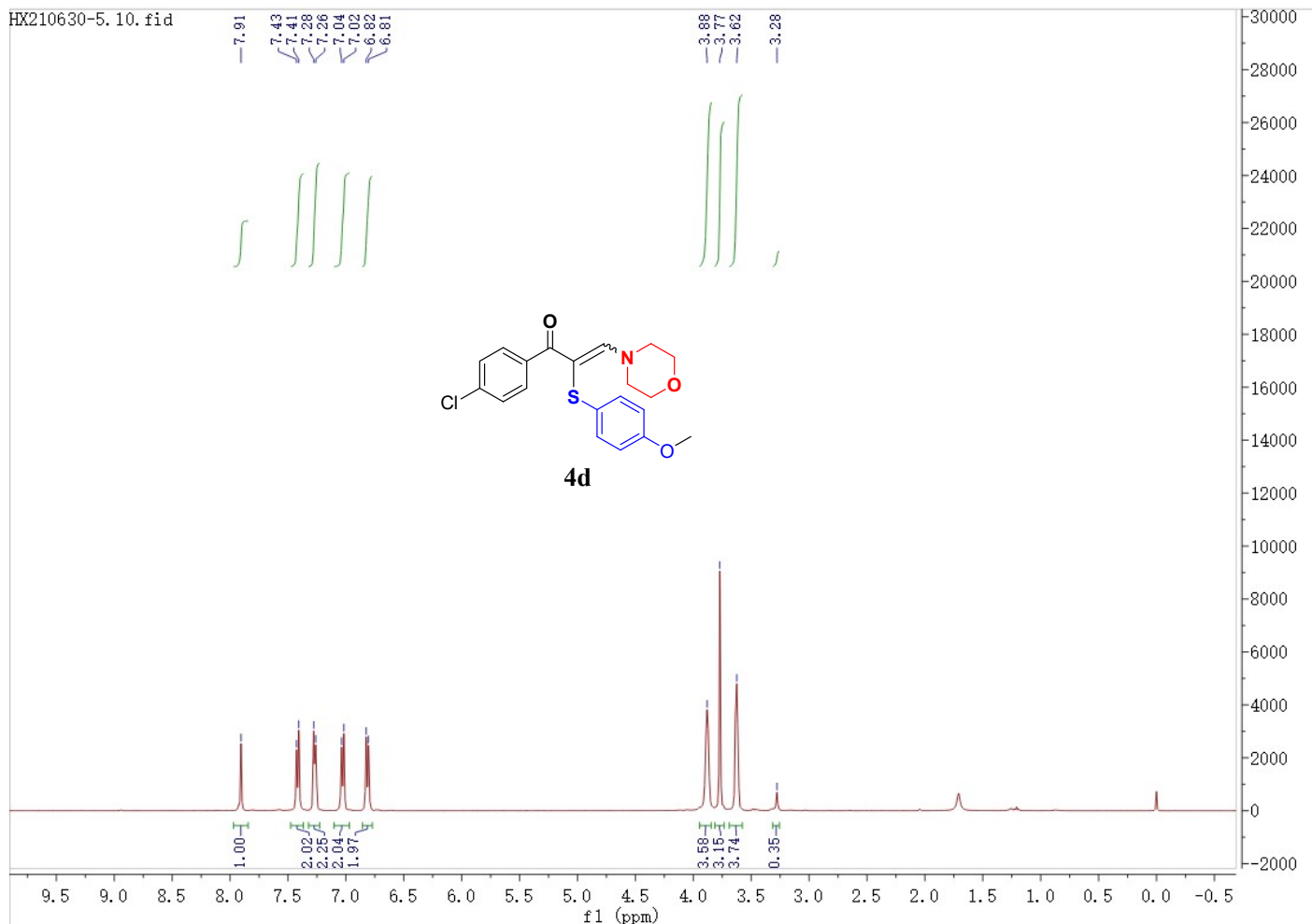


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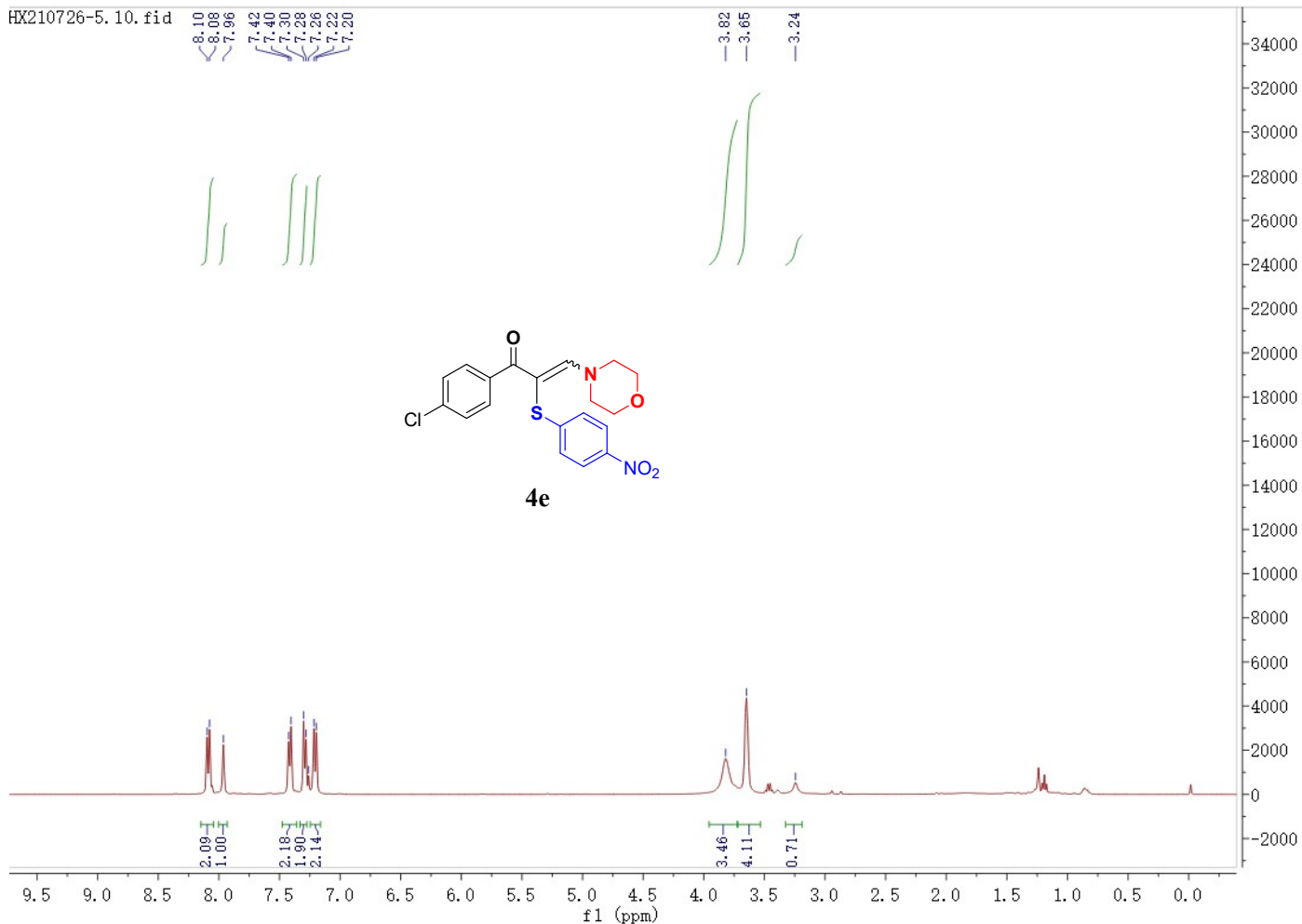


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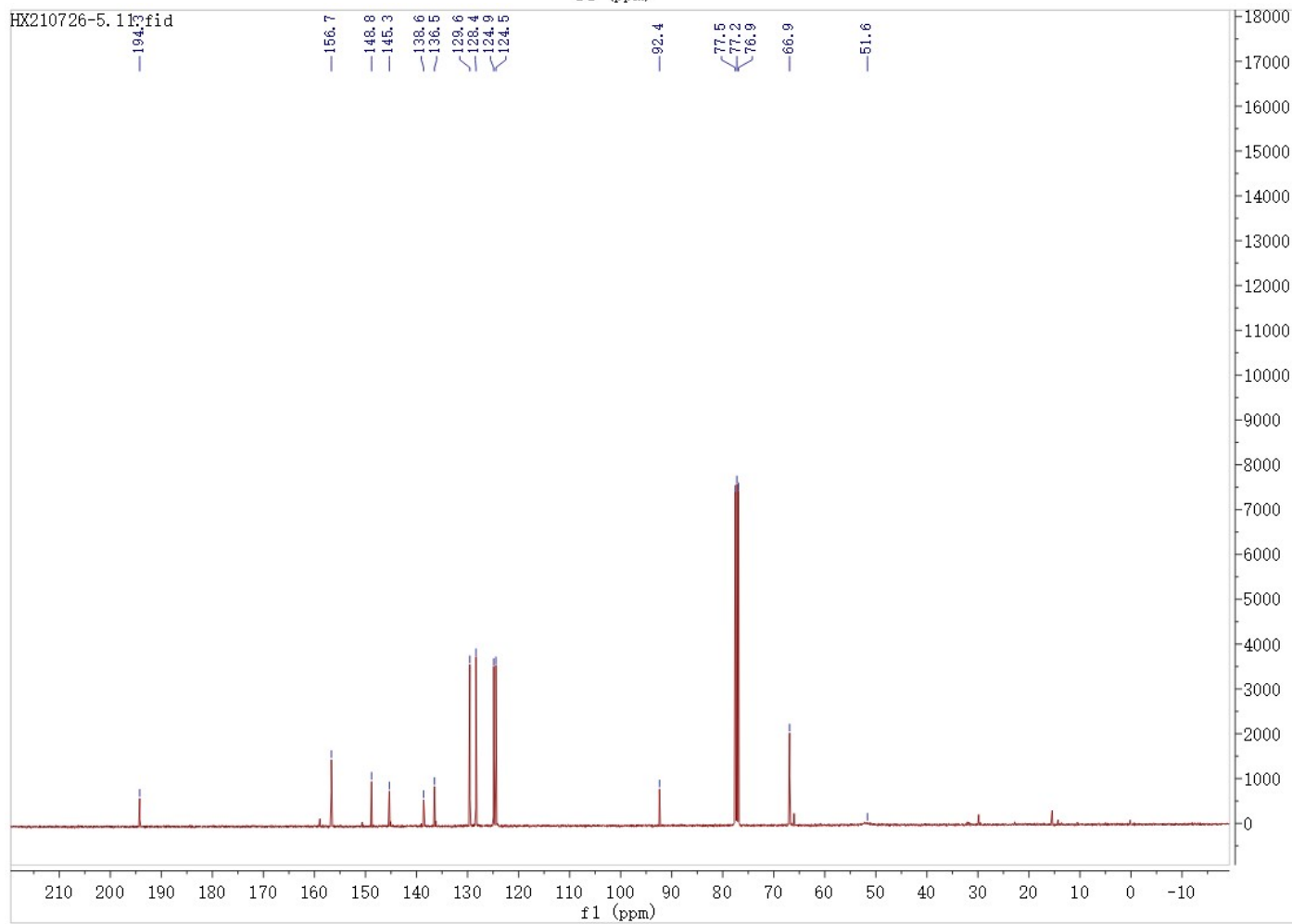




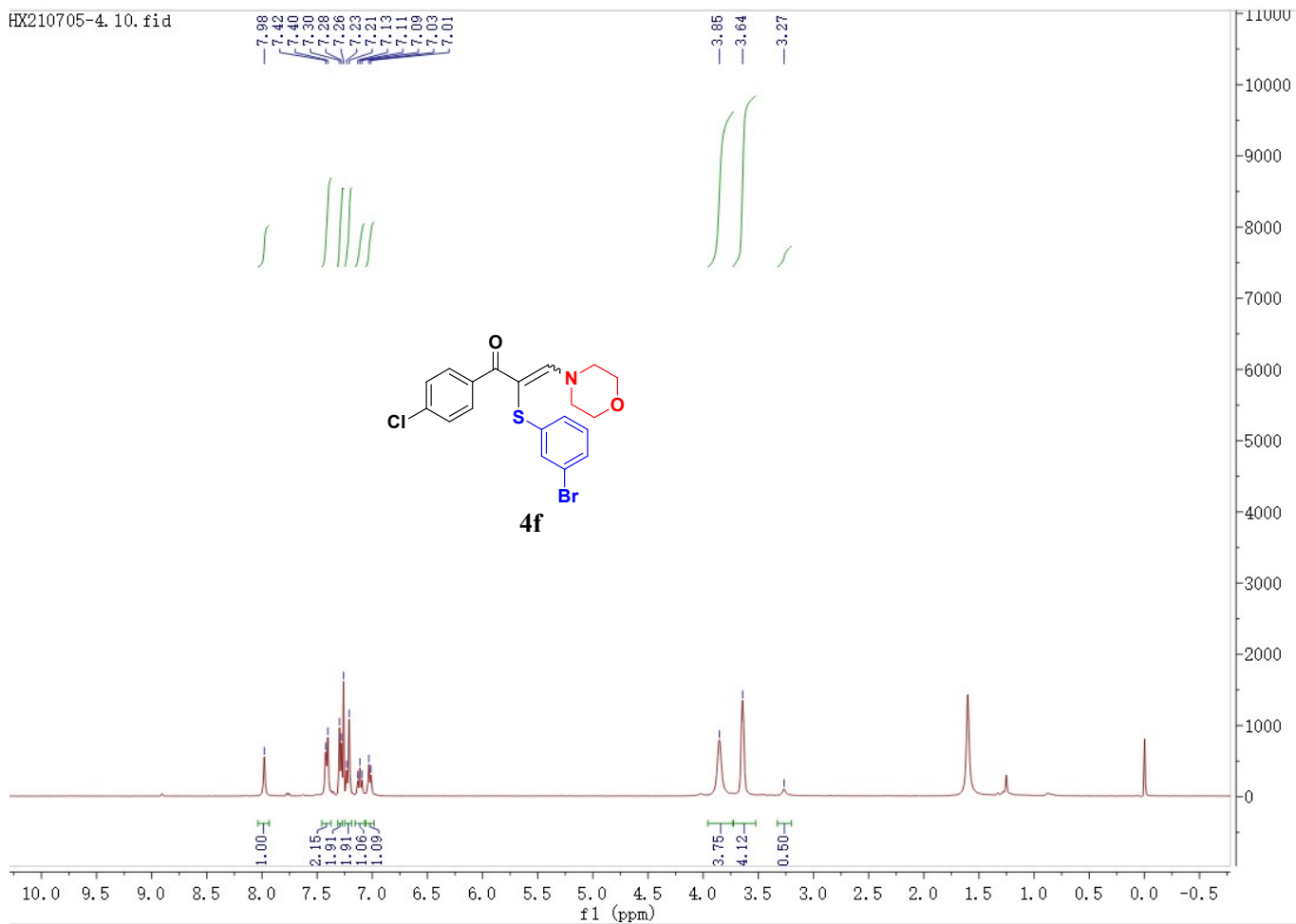
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