

# Supporting information

## Pyridine hydrochloride Catalyzed Thiolation of Alkenes: Divergent Synthesis of Allyl and Vinyl Sulfides

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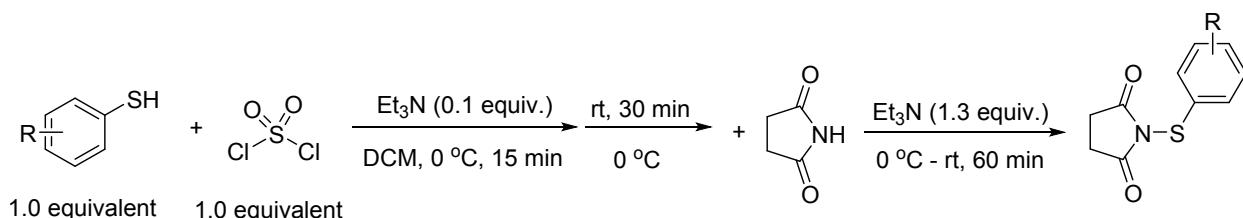
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## 1. General

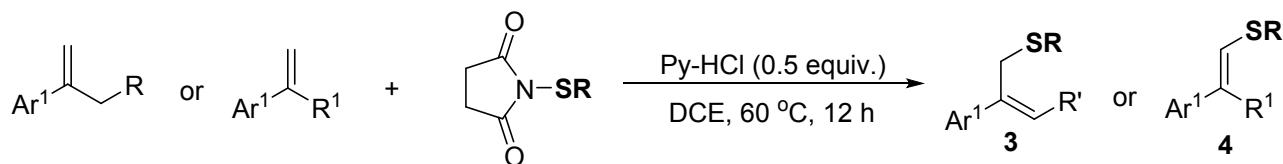
Commercial reagents and solvents were obtained from the commercial providers and used without further purification. The products were purified using a commercial flash chromatography system or a regular glass column. TLC was developed on silica gel 60 F254 glass plates.  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in  $\delta$  (ppm) values ( $^1\text{H}$  and  $^{13}\text{C}$  NMR relative to  $\text{CHCl}_3$ ,  $\delta$  7.26 ppm for  $^1\text{H}$  NMR and  $\delta$  77.0 ppm for  $^{13}\text{C}$  NMR). Or alternatively,  $^1\text{H}$  NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad). Coupling constants ( $J$ ), are reported in Hertz (Hz). GC analyses were performed using a Shimadzu GC-2010-ultra gas chromatography–mass spectrometry instrument equipped with a Shimadzu AOC-20s autosampler.

## 2. General procedure for the preparation of *N*-thiosuccinimides



Sulfuryl chloride (1.0 equivalent) was added dropwise to a solution of thiol (1.0 equivalent) and triethylamine (0.1 equivalents) in dichloromethane (1M) at 0 °C. After stirring for 15 minutes, the mixture was warmed to room temperature and stirred for 30 minutes and then cooled to 0 °C. The resulting solution was transferred dropwise via cannula to a solution of succinimide (1.0 equivalent) in dichloromethane (1M) and triethylamine (1.3 equivalents) at 0 °C, and the mixture was then warmed to room temperature over 1 hour. The solution was diluted with water and extracted with an equal volume of dichloromethane before being dried over sodium sulfate. Evaporation of the solvent gave a crude product that was purified by using flash column chromatography.<sup>[1]</sup>

## 3. General procedure for the thiolation of alkenes



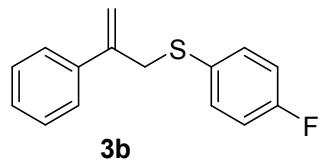
An oven-dried glass vial was charged with *N*-thiosuccinimides (0.24 mmol), Py-HCl (0.10 mmol), and

alkene (0.20 mmol). Then, DCE (2 mL) was added, and the mixture was heated to 60°C and stirred for 12 h under air. After completion of the reaction, water was added to quench the reaction; the resulting aqueous mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude product was further purified by silica gel column chromatography.

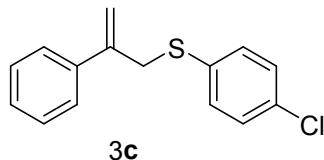
#### 4. Characterization data of the products



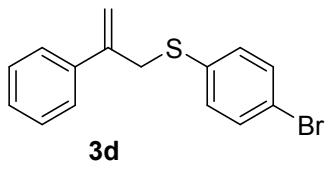
**(2-phenylallyl)(*p*-tolyl)sulfane (3a).** Colorless oil (43 mg, 91%)<sup>[2]</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 7.0 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 5.38 (s, 1H), 5.13 (s, 1H), 3.94 (s, 2H), 2.33 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 143.28, 139.56, 136.71, 132.32, 131.26, 129.63, 128.42, 127.87, 126.32, 115.56, 40.23, 21.12.



**(4-fluorophenyl)(2-phenylallyl)sulfane (3b).** Colorless oil (42 mg, 87%)<sup>[2]</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.45 (d, *J* = 7.4 Hz, 2H), 7.38–7.31 (m, 5H), 6.99 (t, *J* = 8.6 Hz, 2H), 5.35 (s, 1H), 5.04 (s, 1H), 3.91 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 162.16 (d, *J* = 246.1 Hz), 143.13, 139.30, 133.95 (d, *J* = 8.1 Hz), 130.65, 128.45, 127.95, 126.32, 115.85 (d, *J* = 39.8 Hz), 115.84, 40.89.



**(4-chlorophenyl)(2-phenylallyl)sulfane (3c).** Colorless oil (46 mg, 90%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.43 (m, 2H), 7.38 – 7.34 (m, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 0.9 Hz, 4H), 5.38 (s, 1H), 5.14 (s, 1H), 3.94 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 142.91, 139.30, 134.51, 132.62, 132.01, 128.94, 128.45, 127.99, 126.28, 115.87, 39.80. HRMS (EI) Calculated for C<sub>15</sub>H<sub>13</sub>ClS (M<sup>+</sup>) 260.0426, found 260.0422.



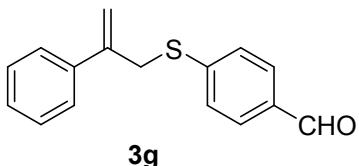
**(4-bromophenyl)(2-phenylallyl)sulfane (3d).** Colorless oil (57 mg, 94%)<sup>[3]</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.45 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.32 (m, 5H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.41 (s, 1H), 5.17 (s, 1H), 3.96 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 142.83, 139.28, 135.26, 132.08, 131.88, 128.49, 128.03, 126.29, 120.51, 115.94, 39.56.



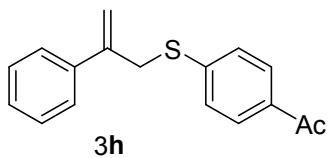
**(4-iodophenyl)(2-phenylallyl)sulfane (3e).** Colorless oil (60 mg, 85%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.58 (m, 2H), 7.47 – 7.44 (m, 2H), 7.40 – 7.36 (m, 2H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.09 – 7.05 (m, 2H), 5.42 (s, 1H), 5.21 (d, *J* = 0.9 Hz, 1H), 3.97 (d, *J* = 1.0 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 142.81, 139.30, 137.76, 136.25, 131.97, 128.46, 128.00, 126.26, 115.92, 91.44, 39.27. HRMS (EI) Calculated for C<sub>15</sub>H<sub>13</sub>IS (M<sup>+</sup>) 351.9783, found 351.9789.



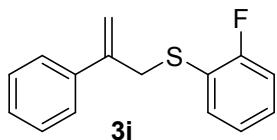
**(4-methoxyphenyl)(2-phenylallyl)sulfane (3f).** Colorless oil (40 mg, 79%)<sup>[2]</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.44 – 7.31 (m, 6H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.34 (s, 1H), 5.00 (s, 1H), 3.88 (s, 2H), 3.82 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 159.24, 143.41, 139.49, 134.54, 132.71, 128.38, 127.81, 126.35, 115.48, 114.40, 55.33, 41.62.



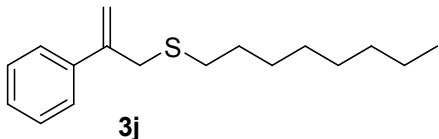
**4-((2-phenylallyl)thio)benzaldehyde (3g).** Colorless oil (41 mg, 82%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.93 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 4H), 7.35 – 7.31 (m, 1H), 5.50 (s, 1H), 5.39 (s, 1H), 4.09 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 191.32, 146.14, 142.14, 139.20, 133.53, 130.00, 128.55, 128.20, 127.28, 126.19, 116.34, 37.28. HRMS (EI) Calculated for C<sub>16</sub>H<sub>14</sub>OS (M<sup>+</sup>) 254.0765, found 254.0761.



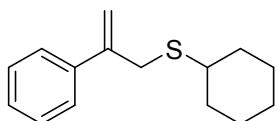
**1-(4-((2-phenylallyl)thio)phenyl)ethan-1-one (3h).** Colorless oil (46 mg, 86%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.4$  Hz, 2H), 7.45 (d,  $J = 7.2$  Hz, 2H), 7.36 (t,  $J = 7.3$  Hz, 2H), 7.34–7.31 (m, 3H), 5.48 (s, 1H), 5.36 (s, 1H), 4.07 (s, 2H), 2.57 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  197.26, 144.03, 142.34, 139.28, 134.23, 128.73, 128.53, 128.14, 127.36, 126.21, 116.21, 37.53, 26.51. HRMS (EI) Calculated for  $\text{C}_{17}\text{H}_{16}\text{OS} (\text{M}^+)$  268.0922, found 268.0920.



**(2-fluorophenyl)(2-phenylallyl)sulfane (3i).** Colorless oil (40 mg, 85%)<sup>[2]</sup>.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.44 (m, 2H), 7.39 – 7.35 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 7.10 – 7.05 (m, 2H), 5.35 (d,  $J = 0.9$  Hz, 1H), 5.14 (d,  $J = 0.9$  Hz, 1H), 3.99 (d,  $J = 0.9$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  162.03 (d,  $J = 246.1$  Hz), 143.14, 139.34, 133.89 (d,  $J = 1.6$  Hz), 129.11 (d,  $J = 8.0$  Hz), 128.38, 127.89, 126.30, 124.31 (d,  $J = 3.7$  Hz), 122.34 (d,  $J = 17.7$  Hz), 115.80, 115.62 (d,  $J = 37.7$  Hz), 38.78 (d,  $J = 2.8$  Hz).

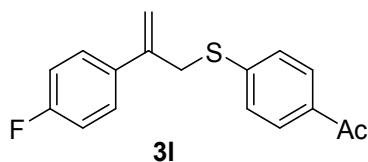


**octyl(2-phenylallyl)sulfane (3j).** Colorless oil (40 mg, 76%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 – 7.49 (m, 2H), 7.39 – 7.35 (m, 2H), 7.33 – 7.32 (m, 1H), 5.46 (d,  $J = 1.1$  Hz, 1H), 5.23 (d,  $J = 1.0$  Hz, 1H), 3.62 (d,  $J = 0.8$  Hz, 2H), 2.53 – 2.45 (m, 2H), 1.61 – 1.57 (m, 2H), 1.40 – 1.35 (m, 2H), 1.33 – 1.28 (m, 8H), 0.91 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  143.87, 139.52, 128.34, 127.80, 126.32, 114.74, 36.57, 31.84, 31.45, 29.22, 29.21, 28.96, 22.68, 14.12. HRMS (EI) Calculated for  $\text{C}_{17}\text{H}_{26}\text{S} (\text{M}^+)$  262.1755, found 262.1760.

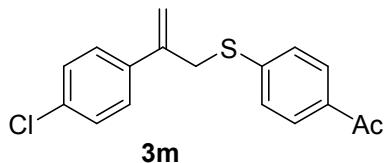


**3k**

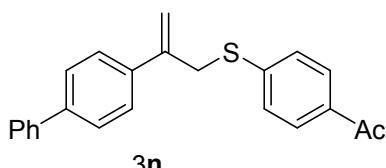
**Cyclohexyl(2-phenylallyl)sulfane (**3k**).** Colorless oil (37 mg, 81%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 – 7.43 (m, 2H), 7.39 – 7.25 (m, 3H), 5.42 (s, 1H), 5.25 (s, 1H), 3.62 (s, 2H), 2.71 – 2.59 (m, 1H), 1.95 (d,  $J = 10.4$  Hz, 2H), 1.80 – 1.70 (m, 2H), 1.64 – 1.57 (m, 1H), 1.30 (td,  $J = 20.4, 9.9$  Hz, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.54, 139.83, 128.30, 127.73, 126.30, 114.56, 43.27, 34.99, 33.44, 26.08, 25.89. HRMS (EI) Calculated for  $\text{C}_{15}\text{H}_{20}\text{S}$  ( $\text{M}^+$ ) 232.1278, found 232.1276.



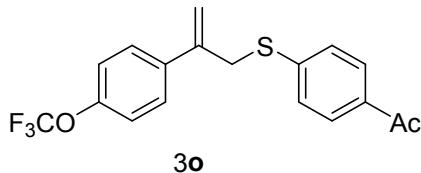
**1-((4-((2-(4-fluorophenyl)allyl)thio)phenyl)ethan-1-one (**3l**).** Colorless oil (50 mg, 88%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.3$  Hz, 2H), 7.43 (dd,  $J = 8.5, 5.4$  Hz, 2H), 7.34 (d,  $J = 8.3$  Hz, 2H), 7.06 (t,  $J = 8.6$  Hz, 2H), 5.43 (s, 1H), 5.35 (s, 1H), 4.06 (s, 2H), 2.59 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.15, 162.63 (d,  $J = 246.0$  Hz), 143.67, 141.53, 135.33 (d,  $J = 3.4$  Hz), 134.45, 128.72, 127.93 (d,  $J = 8.0$  Hz), 127.63, 116.19, 115.37 (d,  $J = 21.2$  Hz), 37.87, 26.44. HRMS (EI) Calculated for  $\text{C}_{17}\text{H}_{15}\text{FOS}$  ( $\text{M}^+$ ) 286.0828, found 286.0820.



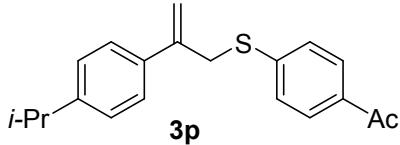
**1-((4-((2-(4-chlorophenyl)allyl)thio)phenyl)ethan-1-one (**3m**).** Colorless oil (58 mg, 96%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.5$  Hz, 2H), 7.39 – 7.34 (m, 2H), 7.34 – 7.29 (m, 4H), 5.44 (s, 1H), 5.34 (s, 1H), 4.03 (s, 2H), 2.57 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.13, 143.51, 141.48, 137.67, 134.51, 133.98, 128.73, 128.66, 127.73, 127.56, 116.70, 37.71, 26.45. HRMS (EI) Calculated for  $\text{C}_{17}\text{H}_{15}\text{ClOS}$  ( $\text{M}^+$ ) 302.0532, found 302.0537.



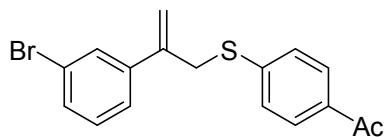
**1-(4-((2-([1, 1'-biphenyl]-4-yl)allyl)thio)phenyl)ethan-1-one (3n).** Colorless oil (55 mg, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.59 (dd, *J* = 7.6, 4.7 Hz, 4H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 3H), 5.53 (s, 1H), 5.37 (s, 1H), 4.09 (s, 2H), 2.55 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.25, 143.99, 141.85, 140.93, 140.49, 138.03, 134.28, 128.86, 128.76, 127.50, 127.44, 127.20, 127.03, 126.60, 116.17, 37.52, 26.51. HRMS (EI) Calculated for C<sub>23</sub>H<sub>20</sub>OS (M<sup>+</sup>) 344.1235, found 344.1231.



**1-(4-((2-(4-(trifluoromethoxy)phenyl)allyl)thio)phenyl)ethan-1-one (3o).** Colorless oil (55 mg, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 5.45 (s, 1H), 5.36 (s, 1H), 4.04 (s, 2H), 2.57 (s, 3H). <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -57.80 (s). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.12, 148.98 (d, *J* = 1.8 Hz), 143.44, 141.36, 137.95, 134.55, 128.74, 127.76, 127.69, 121.30 (d, *J* = 258.5 Hz), 120.85, 117.03, 37.77, 26.43. HRMS (EI) Calculated for C<sub>18</sub>H<sub>15</sub>F<sub>3</sub>O<sub>2</sub>S (M<sup>+</sup>) 352.0745, found 352.0740.

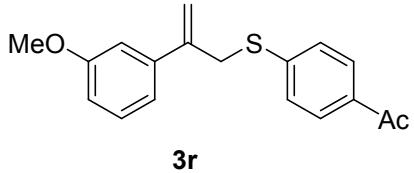


**1-(4-((2-(4-isopropylphenyl)allyl)thio)phenyl)ethan-1-one (3p).** Colorless oil (59 mg, 95%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.47 (s, 1H), 5.32 (s, 1H), 4.06 (s, 2H), 2.96 - 2.89 (m, 1H), 2.57 (s, 3H), 1.27 (d, *J* = 6.9 Hz, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.23, 148.94, 144.22, 142.03, 136.66, 134.16, 128.71, 127.24, 126.58, 126.07, 115.39, 37.47, 33.82, 26.49, 23.94. HRMS (EI) Calculated for C<sub>20</sub>H<sub>22</sub>OS (M<sup>+</sup>) 310.1391, found 310.1390.

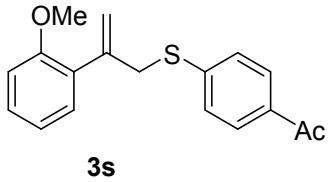


**1-(4-((2-(3-bromophenyl)allyl)thio)phenyl)ethan-1-one (3q).** Colorless oil (42 mg, 81%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.58 (s, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.4 Hz,

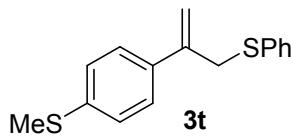
2H), 7.25 (t,  $J$  = 7.9 Hz, 1H), 5.48 (s, 1H), 5.39 (s, 1H), 4.04 (s, 2H), 2.60 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  197.24, 143.43, 141.46, 141.36, 134.48, 131.05, 130.02, 129.38, 128.76, 127.75, 124.88, 122.70, 117.36, 37.57, 26.51. HRMS (EI) Calculated for  $\text{C}_{17}\text{H}_{15}\text{BrOS} (\text{M}^+)$  346.0027, found 346.0020.



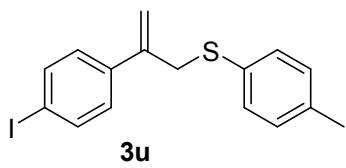
**1-(4-((2-(3-methoxyphenyl)allyl)thio)phenyl)ethan-1-one (3r).** Colorless oil (50 mg, 84%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J$  = 8.4 Hz, 2H), 7.32 (d,  $J$  = 8.4 Hz, 2H), 7.28 (t,  $J$  = 8.0 Hz, 1H), 7.03 (d,  $J$  = 7.7 Hz, 1H), 6.99 – 6.96 (m, 1H), 6.88 – 6.86 (m, 1H), 5.47 (s, 1H), 5.35 (s, 1H), 4.04 (s, 2H), 3.82 (s, 3H), 2.57 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  197.25, 159.66, 144.00, 142.30, 140.85, 134.25, 129.52, 128.72, 127.39, 118.68, 116.36, 113.22, 112.35, 55.28, 37.59, 26.49. HRMS (EI) Calculated for  $\text{C}_{18}\text{H}_{18}\text{O}_2\text{S} (\text{M}^+)$  298.1028, found 298.1022.



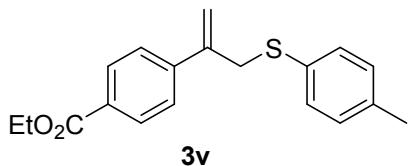
**1-(4-((2-(2-methoxyphenyl)allyl)thio)phenyl)ethan-1-one (3s).** Colorless oil (45 mg, 76%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J$  = 8.5 Hz, 2H), 7.32 (d,  $J$  = 8.5 Hz, 2H), 7.31 – 7.28 (m, 1H), 7.12 – 7.11 (m, 1H), 6.99 – 6.88 (m, 2H), 5.43 (d,  $J$  = 1.2 Hz, 1H), 5.19 (s, 1H), 4.10 (s, 2H), 3.84 (s, 3H), 2.56 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  197.31, 156.51, 144.63, 143.44, 133.84, 130.53, 129.82, 129.26, 128.57, 127.01, 120.74, 117.46, 110.59, 55.42, 37.65, 26.47. HRMS (EI) Calculated for  $\text{C}_{18}\text{H}_{18}\text{O}_2\text{S} (\text{M}^+)$  298.1028, found 298.1022.



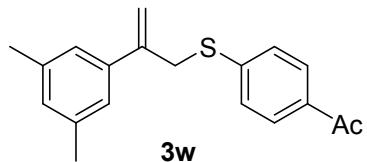
**Methyl(4-(3-(phenylthio)prop-1-en-2-yl)phenyl)sulfane (3t).** Colorless oil (38 mg, 70%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.44 (m, 2H), 7.40 – 7.28 (m, 5H), 6.87 – 6.81 (m, 2H), 5.32 (d,  $J$  = 0.9 Hz, 1H), 4.99 (d,  $J$  = 0.8 Hz, 1H), 3.86 (s, 2H), 3.80 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.24, 142.47, 138.52, 133.43, 127.32, 126.75, 125.31, 125.08, 114.39, 113.39, 54.28, 40.58. HRMS (EI) Calculated for  $\text{C}_{16}\text{H}_{16}\text{S}_2 (\text{M}^+)$  272.0693, found 272.0690.



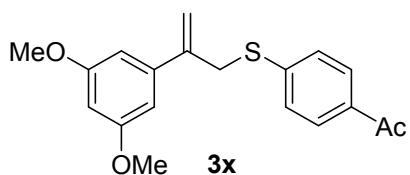
**(2-(4-iodophenyl)allyl)(p-tolyl)sulfane (3u).** Colorless oil (62 mg, 86%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 – 7.64 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.16 (m, 2H), 7.08 (d,  $J$  = 7.9 Hz, 2H), 5.33 (d,  $J$  = 0.5 Hz, 1H), 5.09 (d,  $J$  = 0.7 Hz, 1H), 3.87 (d,  $J$  = 0.8 Hz, 2H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.50, 139.04, 137.45, 136.96, 131.90, 131.54, 129.64, 128.22, 116.09, 93.41, 40.16, 21.09. HRMS (EI) Calculated for  $\text{C}_{16}\text{H}_{15}\text{IS} (\text{M}^+)$  365.9939, found 365.9936.



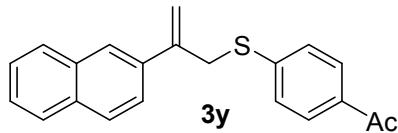
**Ethyl 4-(3-(p-tolylthio)prop-1-en-2-yl)benzoate (3v).** Colorless oil (39 mg, 63%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J$  = 8.5 Hz, 2H), 7.49 (d,  $J$  = 8.5 Hz, 2H), 7.22 (d,  $J$  = 8.1 Hz, 2H), 7.08 (d,  $J$  = 7.9 Hz, 2H), 5.42 (s, 1H), 5.17 (s, 1H), 4.38 (q,  $J$  = 7.1 Hz, 2H), 3.92 (s, 2H), 2.31 (s, 3H), 1.39 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.37, 143.97, 142.78, 136.98, 131.88, 131.59, 129.76, 129.65, 126.28, 117.19, 60.93, 40.19, 21.07, 14.36. HRMS (EI) Calculated for  $\text{C}_{19}\text{H}_{20}\text{O}_2\text{S} (\text{M}^+)$  312.1184, found 312.1188.



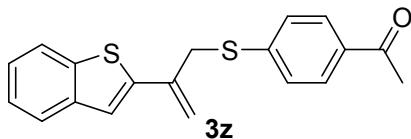
**1-(4-((2-(3,5-dimethylphenyl)allyl)thio)phenyl)ethan-1-one (3w).** Colorless oil (54 mg, 91%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J$  = 8.4 Hz, 2H), 7.35 (d,  $J$  = 8.4 Hz, 2H), 7.08 (s, 2H), 6.99 (s, 1H), 5.47 (s, 1H), 5.35 (s, 1H), 4.07 (s, 2H), 2.60 (s, 3H), 2.35 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.17, 144.27, 142.69, 139.41, 137.98, 134.23, 129.81, 128.68, 127.31, 124.09, 115.71, 37.63, 26.43, 21.39. HRMS (EI) Calculated for  $\text{C}_{19}\text{H}_{20}\text{OS} (\text{M}^+)$  296.1235, found 296.1233.



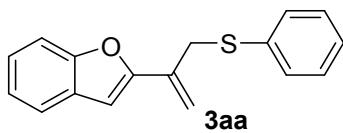
**1-(4-((2-(3, 5-dimethoxyphenyl)allyl)thio)phenyl)ethan-1-one (3x).** Colorless oil (56 mg, 86%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 2.2 Hz, 2H), 6.44 - 6.43 (m, 1H), 5.46 (s, 1H), 5.34 (s, 1H), 4.02 (s, 2H), 3.80 (s, 6H), 2.57 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.25, 160.79, 143.99, 142.47, 141.60, 134.26, 128.72, 127.41, 116.43, 104.74, 99.75, 55.39, 37.62, 26.49. HRMS (EI) Calculated for C<sub>19</sub>H<sub>20</sub>O<sub>3</sub>S (M<sup>+</sup>) 328.1133, found 328.1137.



**1-(4-((2-(naphthalen-2-yl)allyl)thio)phenyl)ethan-1-one (3y).** Colorless oil (50 mg, 79%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 - 7.81 (m, 6H), 7.59 - 7.57 (m, 1H), 7.50 - 7.44 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.61 (s, 1H), 5.45 (s, 1H), 4.17 (s, 2H), 2.55 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.16, 143.98, 142.36, 136.49, 134.37, 133.29, 133.08, 128.73, 128.28, 128.15, 127.61, 127.57, 126.39, 126.26, 125.14, 124.34, 116.61, 37.71, 26.45. HRMS (EI) Calculated for C<sub>21</sub>H<sub>18</sub>OS (M<sup>+</sup>) 318.1078, found 318.1071.

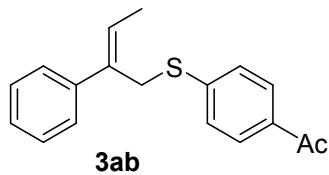


**1-(4-((2-(benzo[b]thiophen-2-yl)allyl)thio)phenyl)ethan-1-one (3z).** Colorless oil (44 mg, 68%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.80 - 7.75 (m, 1H), 7.74 - 7.71 (m, 1H), 7.38 - 7.35 (m, 3H), 7.35 - 7.31 (m, 2H), 5.64 (s, 1H), 5.37 (s, 1H), 4.10 (s, 2H), 2.57 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.26, 143.49, 142.83, 140.10, 139.01, 136.34, 134.52, 128.82, 127.70, 125.06, 124.57, 123.84, 122.11, 121.19, 116.95, 37.13, 26.53. HRMS (EI) Calculated for C<sub>19</sub>H<sub>16</sub>OS<sub>2</sub> (M<sup>+</sup>) 324.0643, found 324.0640.

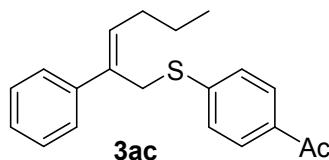


**1-(4-((2-(benzofuran-2-yl)allyl)thio)phenyl)ethan-1-one (3aa).** Colorless oil (32 mg, 60%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.31 - 7.26 (m, 3H), 7.24 - 7.20 (m, 2H), 6.81 (s, 1H), 5.87 (s, 1H), 5.25 (s, 1H), 3.93 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.80, 135.91, 133.18, 130.73,

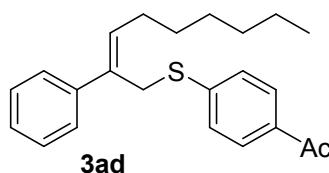
128.92, 126.79, 124.78, 122.86, 121.18, 115.60, 111.04, 103.58, 37.46. HRMS (EI) Calculated for C<sub>17</sub>H<sub>14</sub>OS (M<sup>+</sup>) 266.0765, found 266.0761.



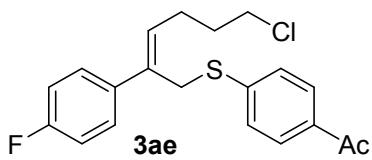
**(Z)-1-(4-((2-phenylbut-2-en-1-yl)thio)phenyl)ethan-1-one (3ab).** Colorless oil (48 mg, 86%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.29 (m, 5H), 6.06 (q, *J* = 7.0 Hz, 1H), 4.11 (s, 2H), 2.60 (s, 3H), 1.89 (d, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.27, 145.02, 141.50, 134.44, 134.11, 128.70, 128.44, 128.15, 127.23, 123.20, 126.04, 32.64, 26.50, 14.59. HRMS (EI) Calculated for C<sub>18</sub>H<sub>18</sub>OS (M<sup>+</sup>) 282.1078, found 282.1070.



**(Z)-1-(4-((2-phenylhex-2-en-1-yl)thio)phenyl)ethan-1-one (3ac).** Colorless oil (57 mg, 92%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 4H), 7.28 (s, 1H), 5.98 (t, *J* = 7.4 Hz, 1H), 4.11 (s, 2H), 2.60 (s, 3H), 2.26 (q, *J* = 7.4 Hz, 2H), 1.54 - 1.51 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.24, 145.14, 141.55, 134.16, 133.47, 128.71, 128.43, 127.25, 127.06, 127.00, 126.14, 32.88, 31.04, 26.50, 22.80, 13.96. HRMS (EI) Calculated for C<sub>20</sub>H<sub>22</sub>OS (M<sup>+</sup>) 310.1391, found 310.1398.

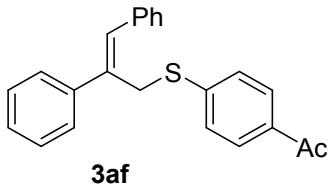


**(Z)-1-(4-((2-phenylnon-2-en-1-yl)thio)phenyl)ethan-1-one (3ad).** Colorless oil (62 mg, 88%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 8.4 Hz, 4H), 7.27 - 7.26 (m, 1H), 5.95 (t, *J* = 7.4 Hz, 1H), 4.08 (s, 2H), 2.58 (s, 3H), 2.24 (q, *J* = 7.4 Hz, 2H), 1.48 - 1.43 (m, 2H), 1.37 - 1.26 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.25, 145.13, 141.55, 134.41, 134.07, 133.25, 128.70, 128.42, 127.26, 127.11, 126.13, 32.90, 31.76, 29.57, 29.10, 29.05, 26.49, 22.65, 14.13. HRMS (EI) Calculated for C<sub>23</sub>H<sub>28</sub>OS (M<sup>+</sup>) 352.1861, found 352.1866.

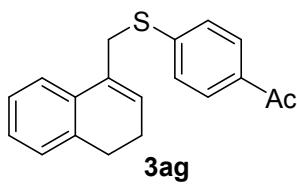


**(Z)-1-((6-chloro-2-(4-fluorophenyl)hex-2-en-1-yl)thio)phenyl)ethan-1-one (3ae).** Colorless oil (55 mg, 76%).

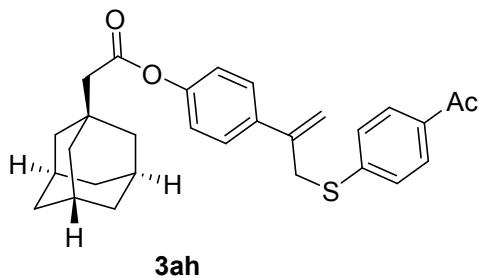
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.43 - 7.40 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 5.90 (t, *J* = 7.3 Hz, 1H), 4.06 (d, *J* = 3.6 Hz, 2H), 3.62 (t, *J* = 6.7 Hz, 2H), 2.72 (q, *J* = 6.9 Hz, 2H), 2.60 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.20, 162.38 (d, *J* = 246.1 Hz), 144.02, 137.08, 135.75, 134.49, 128.89, 128.80, 127.94 (d, *J* = 8.0 Hz), 127.59, 115.37 (d, *J* = 21.1 Hz), 43.81, 33.31, 32.04, 26.52. HRMS (EI) Calculated for C<sub>20</sub>H<sub>20</sub>ClFOS (M<sup>+</sup>) 362.0907, found 362.0903.



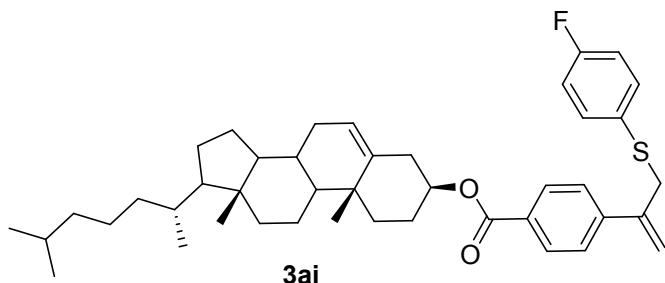
**(Z)-1-((2,3-diphenylallyl)thio)phenyl)ethan-1-one (3af).** Colorless oil (62 mg, 91%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.41 - 7.38 (m, 4H), 7.35 - 7.29 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.00 (s, 1H), 4.30 (s, 2H), 2.57 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.22, 144.43, 140.85, 136.91, 135.53, 134.10, 132.07, 128.81, 128.73, 128.64, 128.63, 128.00, 127.55, 126.90, 126.51, 33.58, 26.50. HRMS (EI) Calculated for C<sub>23</sub>H<sub>20</sub>OS (M<sup>+</sup>) 344.1235, found 344.1231.



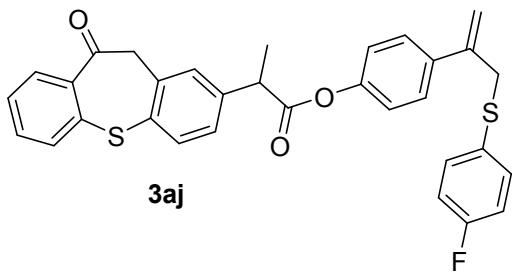
**(4-fluorophenyl)(2-phenylallyl)sulfane (3ag).** Colorless oil (48 mg, 82%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 8.3 Hz, 3H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.21 - 7.15 (m, 2H), 6.13 - 6.12 (m, 1H), 4.04 (s, 2H), 2.75 (t, *J* = 8.0 Hz, 2H), 2.57 (s, 3H), 2.30 - 2.27 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.28, 144.57, 136.59, 134.15, 133.28, 130.81, 129.30, 128.70, 127.83, 127.36, 127.31, 126.52, 122.85, 35.46, 27.96, 26.50, 23.25. HRMS (EI) Calculated for C<sub>19</sub>H<sub>18</sub>OS (M<sup>+</sup>) 294.1078, found 294.1073.



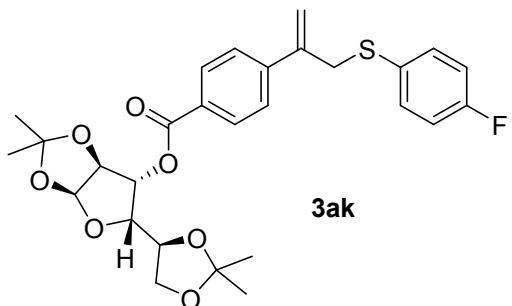
**4-((3-((4-acetylphenyl)thio)prop-1-en-2-yl)phenyl 2-((3r,5r,7r)-adamantan-1-yl)acetate (3ah).** Colorless oil (70 mg, 76%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.4$  Hz, 2H), 7.44 (d,  $J = 8.6$  Hz, 2H), 7.31 (d,  $J = 8.4$  Hz, 2H), 7.08 (d,  $J = 8.6$  Hz, 2H), 5.44 (s, 1H), 5.34 (s, 1H), 4.04 (s, 2H), 2.57 (s, 3H), 2.31 (s, 2H), 2.02 (s, 3H), 1.74 (d,  $J = 8.4$  Hz, 9H), 1.68 - 1.66 (m, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  170.17, 150.51, 143.79, 141.57, 136.82, 134.33, 128.74, 127.51, 127.25, 121.74, 116.37, 48.76, 42.49, 37.63, 36.72, 33.29, 28.63, 26.49. HRMS (ESI) Calculated for  $\text{C}_{29}\text{H}_{33}\text{O}_3\text{S}$  ( $\text{M}+\text{H}$ ) 461.2145, found 461.2141.



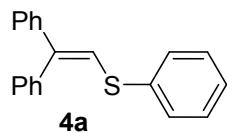
**(3S, 10R, 13R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((3-((4-fluorophenyl)thio)prop-1-en-2-yl)benzoate (3ai).** Colorless oil (67 mg, 51%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 8.4$  Hz, 2H), 7.50 (d,  $J = 8.4$  Hz, 2H), 7.34 – 7.28 (m, 2H), 7.00 (t,  $J = 8.6$  Hz, 2H), 5.49 – 5.40 (m, 2H), 5.11 (s, 1H), 4.93 – 4.85 (m, 1H), 3.92 (s, 2H), 2.49 (d,  $J = 7.7$  Hz, 2H), 2.08 – 1.99 (m, 3H), 1.98 – 1.92 (m, 1H), 1.91 – 1.82 (m, 1H), 1.81 – 1.72 (m, 1H), 1.58 – 1.34 (m, 8H), 1.31 – 1.08 (m, 12H), 1.07 – 0.99 (m, 3H), 0.95 (d,  $J = 6.5$  Hz, 3H), 0.90 – 0.88 (m, 6H), 0.71 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.72, 162.28 (d,  $J = 246.1$  Hz), 143.56, 142.53, 139.66, 134.23 (d,  $J = 8.4$  Hz), 130.19 (d,  $J = 4.2$  Hz), 129.71, 126.24, 122.83, 117.36, 115.98 (d,  $J = 36.4$  Hz), 74.64, 56.71, 56.15, 50.06, 42.34, 40.80, 39.76, 39.54, 38.24, 37.05, 36.68, 36.20, 35.82, 31.96, 31.90, 28.26, 28.04, 27.91, 24.32, 23.85, 22.84, 22.58, 21.07, 19.41, 18.74, 11.89. HRMS (ESI) Calculated for  $\text{C}_{43}\text{H}_{57}\text{FO}_2\text{SNa}$  ( $\text{M}+\text{Na}$ ) 679.3956, found 679.3949.



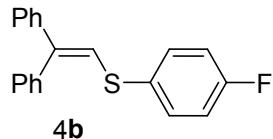
**4-((3-((4-fluorophenyl)thio)prop-1-en-2-yl)phenyl 2-(10-oxo-10, 11-dihydrodibenzo[b, f]thiepin- 2-yl)propanoate (3aj).** Colorless oil (75 mg, 70%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 - 8.21 (m, 1H), 7.65 (d,  $J$  = 8.0 Hz, 1H), 7.61 (d,  $J$  = 7.9 Hz, 1H), 7.49 (d,  $J$  = 1.5 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.39 (d,  $J$  = 8.6 Hz, 2H), 7.34 – 7.25 (m, 5H), 6.99 – 6.95 (m, 4H), 5.28 (s, 1H), 5.00 (s, 1H), 4.40 (s, 2H), 3.97 (q,  $J$  = 7.1 Hz, 1H), 3.85 (s, 2H), 1.61 (d,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  191.30, 172.39, 162.19 (d,  $J$  = 246.1 Hz), 150.32, 142.19 (d,  $J$  = 11.1 Hz), 140.12, 138.20, 137.05, 136.17, 134.04 (d,  $J$  = 8.1 Hz), 133.61, 132.60, 131.72, 131.57, 130.88, 130.44, 128.72, 127.35, 127.04, 126.91, 126.36, 121.40, 121.21, 116.00 (s), 115.92 (d,  $J$  = 22.6 Hz), 51.09, 45.33, 40.90, 18.55. HRMS (ESI) Calculated for  $\text{C}_{32}\text{H}_{26}\text{FO}_3\text{S}_2$  ( $\text{M}+\text{H}$ ) 540.1302, found 541.1299.



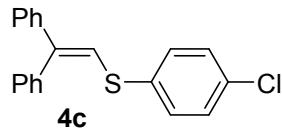
**(3aS, 5S, 6R, 6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydropyran-6-yl 4-((3-((4-fluorophenyl)thio)prop-1-en-2-yl)benzoate (3ak).** Colorless oil (48 mg, 46%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J$  = 8.3 Hz, 2H), 7.50 (d,  $J$  = 8.4 Hz, 2H), 7.31 – 7.29 (m, 2H), 6.98 (t,  $J$  = 8.6 Hz, 2H), 5.95 (d,  $J$  = 3.6 Hz, 1H), 5.50 (d,  $J$  = 2.7 Hz, 1H), 5.41 (s, 1H), 5.10 (s, 1H), 4.63 (d,  $J$  = 3.6 Hz, 1H), 4.39 – 4.35 (m, 1H), 4.33 (dd,  $J$  = 7.9, 2.8 Hz, 1H), 4.11 (dt,  $J$  = 8.5, 3.2 Hz, 2H), 3.90 (s, 2H), 1.60 (s, 3H), 1.42 (s, 4H), 1.33 (s, 3H), 1.28 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.92, 143.36 (d,  $J$  = 8.3 Hz), 134.31 (d,  $J$  = 305.0 Hz), 129.90, 126.50, 117.80, 116.02 (d,  $J$  = 22.6 Hz), 112.42, 109.45, 105.15, 83.40, 79.96, 76.65, 72.60, 67.26, 40.80, 26.87, 26.76, 26.23, 25.25. HRMS (EI) Calculated for  $\text{C}_{28}\text{H}_{31}\text{FO}_7\text{S}$  ( $\text{M}^+$ ) 530.1762, found 530.1761.



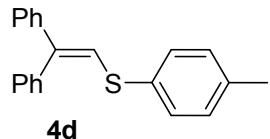
**(2, 2-diphenylvinyl)(phenyl)sulfane (4a).** Colorless oil (50 mg, 88%)<sup>[4]</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 – 7.43 (m, 4H), 7.41 – 7.26 (m, 11H), 6.88 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.52, 141.15, 139.24, 136.55, 129.80, 129.58, 129.15, 128.42, 128.35, 127.84, 127.33, 127.24, 126.82, 124.14.



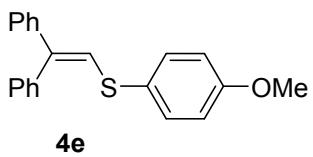
**(2, 2-diphenylvinyl)(4-fluorophenyl)sulfane (4b).** Colorless oil (55 mg, 91%)<sup>[5]</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.41 (m, 4H), 7.37 (t, *J* = 7.7 Hz, 3H), 7.32 – 7.24 (m, 5H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.77 (s, 1H). <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -114.35 – -115.00 (m). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.17 (d, *J* = 246.2 Hz), 141.37, 140.93, 139.10, 132.10 (d, *J* = 8.1 Hz), 131.56 (d, *J* = 3.3 Hz), 129.75, 128.45, 128.36, 127.90, 127.38, 127.21, 124.65, 116.29 (d, *J* = 22.1 Hz).



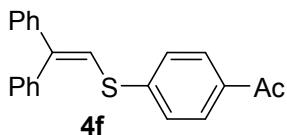
**(4-chlorophenyl)(2, 2-diphenylvinyl)sulfane (4c).** Colorless oil (54 mg, 85%)<sup>[5]</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.40 (m, 2H), 7.39 – 7.31 (m, 5H), 7.30 – 7.23 (m, 7H), 6.77 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.06, 141.29, 139.04, 135.13, 132.87, 130.75, 129.70, 129.26, 128.42, 128.36, 127.94, 127.50, 127.23, 123.21.



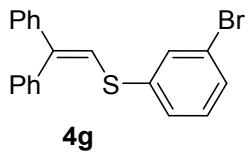
**(2, 2-diphenylvinyl)(p-tolyl)sulfane (4d).** Colorless oil (55 mg, 92%)<sup>[5]</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.43 – 7.40 (m, 2H), 7.37 – 7.32 (m, 5H), 7.29 – 7.22 (m, 5H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 2.33 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.60, 140.28, 139.30, 137.00, 132.89, 130.13, 129.89, 129.80, 128.37, 128.27, 127.71, 127.17, 125.25, 21.01.



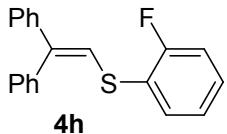
**(2, 2-diphenylvinyl)(4-methoxyphenyl)sulfane (4e).** Colorless oil (51 mg, 81%)<sup>[5]</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 – 7.36 (m, 7H), 7.27 (s, 1H), 7.26 – 7.20 (m, 4H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.77 (s, 1H), 3.82 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.32, 141.57, 139.31, 139.27, 132.57, 129.80, 128.339, 128.27, 127.71, 127.13, 127.08, 126.56, 114.82, 55.41.



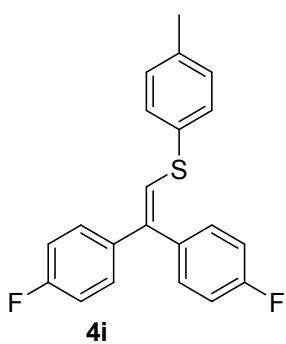
**1-(4-((2, 2-diphenylvinyl)thio)phenyl)ethan-1-one (4f).** Colorless oil (50 mg, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.28 (m, 12H), 6.89 (s, 1H), 2.59 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.08, 144.25, 143.63, 141.16, 138.91, 134.84, 129.70, 128.99, 128.45, 128.12, 127.84, 127.58, 127.37, 120.52, 26.50. HRMS (EI) Calculated for C<sub>22</sub>H<sub>18</sub>OS 330.1078 (M<sup>+</sup>), found 330.1077.



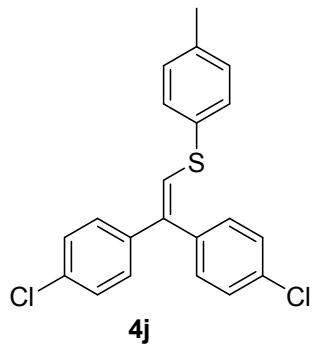
**(3-bromophenyl)(2, 2-diphenylvinyl)sulfane (4g).** Colorless oil (60 mg, 82%)<sup>[5]</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (s, 1H), 7.46 – 7.26 (m, 12H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.81 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.78, 141.22, 138.99, 131.62, 130.39, 129.72, 128.45, 128.41, 128.01, 127.69, 129.64, 127.31, 123.02, 122.25.



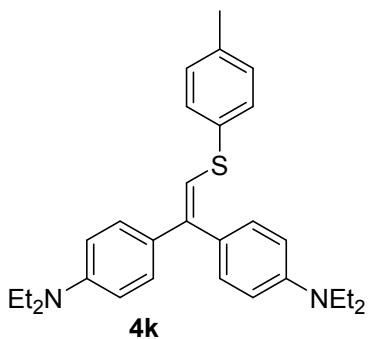
**(2, 2-diphenylvinyl)(2-fluorophenyl)sulfane (4h).** Colorless oil (52 mg, 86%)<sup>[5]</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 – 7.41 (m, 3H), 7.41 – 7.35 (m, 3H), 7.32 – 7.24 (m, 6H), 7.16 – 7.07 (m, 2H), 6.76 (s, 1H). <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -109.60 – -109.66 (m). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.85 (d, *J* = 247.4 Hz), 142.05, 141.38, 138.95, 131.93 (d, *J* = 1.4 Hz), 129.79, 128.93 (d, *J* = 7.8 Hz), 128.46, 128.33, 127.93, 127.46, 127.26, 124.73 (d, *J* = 3.8 Hz), 123.40 (d, *J* = 17.2 Hz), 122.57 (d, *J* = 1.9 Hz), 116.92 (d, *J* = 22.2 Hz).



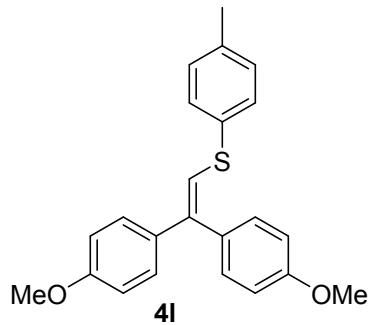
**(2, 2-bis(4-fluorophenyl)vinyl)(p-tolyl)sulfane (4i).** Colorless oil (54 mg, 81%)<sup>[6]</sup>.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  -7.37 – 7.28 (m, 4H), 7.21 – 7.07 (m, 6H), 7.00 – 6.92 (m, 2H), 6.73 (s, 1H), 2.34 (s, 3H).  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.53 – -113.65 (m), -114.89 – -114.99 (m).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  162.26 (d,  $J$ =247.6 Hz), 162.21 (d,  $J$ =246.1 Hz), 138.08, 137.68 (d,  $J$ =3.2 Hz), 137.31, 134.98 (d,  $J$ =3.4 Hz), 132.40, 131.53 (d,  $J$ =8.1 Hz), 130.24, 130.00, 128.75 (d,  $J$ =7.9 Hz), 125.48, 115.49 (d,  $J$ =19.4 Hz), 115.26 (d,  $J$ =21.1 Hz), 21.09.



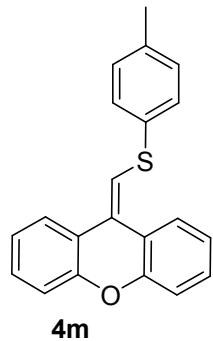
**(2, 2-bis(4-chlorophenyl)vinyl)(p-tolyl)sulfane (4j).** Colorless oil (66 mg, 90%)<sup>[7]</sup>.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 2H), 7.25 – 7.21 (m, 2H), 7.18 – 7.10 (m, 4H), 6.80 (s, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  139.68, 137.53, 137.41, 137.21, 133.78, 133.20, 132.10, 131.15, 130.41, 130.05, 128.81, 128.55, 128.34, 126.89, 21.11.



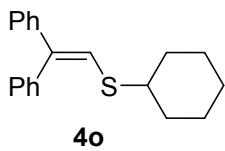
**4, 4'-(2-(p-tolylthio)ethene-1,1-diyl)bis(N, N-diethylaniline) (4k).** Colorless oil (74 mg, 84%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 8.1$  Hz, 2H), 7.25 - 7.16 (m, 4H), 7.10 (d,  $J = 8.0$  Hz, 2H), 6.67 (d,  $J = 8.8$  Hz, 2H), 6.58 (d,  $J = 8.8$  Hz, 2H), 6.46 (s, 1H), 3.40 - 3.31 (m, 8H), 2.32 (s, 3H), 1.17 (dt,  $J = 13.7, 7.0$  Hz, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.25, 147.10, 142.81, 135.85, 134.61, 131.07, 129.77, 129.65, 129.05, 128.77, 126.40, 116.99, 111.23, 110.85, 44.37, 44.26, 21.03, 12.76, 12.66. HRMS (EI) Calculated for  $\text{C}_{29}\text{H}_{36}\text{N}_2\text{S}$  ( $\text{M}^+$ ) 444.2599, found 444.2590.



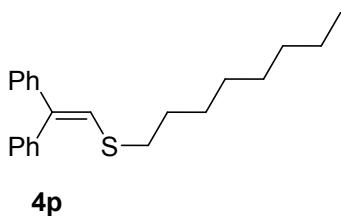
**(2, 2-bis(4-methoxyphenyl)vinyl)(p-tolyl)sulfane (4l).** Colorless oil (63 mg, 87%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 - 7.18 (m, 4H), 7.13 - 7.08 (m, 2H), 7.05 (d,  $J = 8.0$  Hz, 2H), 6.89 - 6.83 (m, 2H), 6.76 - 6.71 (m, 2H), 6.56 (s, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 2.26 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  159.07, 159.01, 140.20, 136.71, 134.72, 133.30, 131.78, 131.07, 129.86, 129.77, 128.51, 122.07, 113.69, 113.66, 55.33, 55.26, 21.08. HRMS (EI) Calculated for  $\text{C}_{23}\text{H}_{22}\text{O}_2\text{S}$  ( $\text{M}^+$ ) 362.1341, found 362.1344.



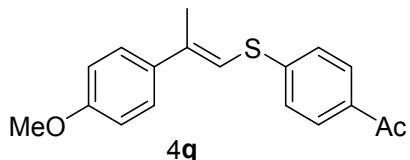
**(4-fluorophenyl)(2-phenylallyl)sulfane (4m).** Colorless oil (52 mg, 84%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 7.8$  Hz, 1H), 7.45 (d,  $J = 7.9$  Hz, 1H), 7.37 (d,  $J = 8.1$  Hz, 2H), 7.34 - 7.29 (m, 1H), 7.24 - 7.04 (m, 7H), 6.63 (s, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  152.09, 150.64, 137.61, 133.10, 130.54, 130.01, 129.02, 128.35, 128.00, 124.63, 124.61, 123.77, 123.30, 122.75, 121.98, 119.78, 116.68, 116.31, 21.12. HRMS (EI) Calculated for  $\text{C}_{21}\text{H}_{16}\text{OS}$  ( $\text{M}^+$ ) 316.0922, found 316.0928.



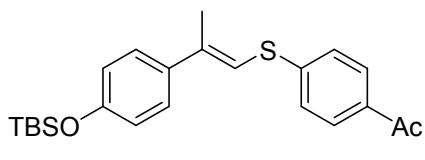
**Cyclohexyl(2,2-diphenylvinyl)sulfane (4o).** Colorless oil (43 mg, 74%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 - 7.28 (m, 2H), 7.26 – 7.17 (m, 5H), 7.15 - 7.12 (m, 3H), 6.59 (s, 1H), 2.87 - 2.80 (m, 1H), 2.00 - 1.96 (m, 2H), 1.73 - 1.70 (m, 2H), 1.60 – 1.51 (m, 1H), 1.39 – 1.15 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.28, 139.76, 138.26, 129.80, 128.25, 128.22, 127.37, 127.06, 126.74, 124.74, 46.84, 33.86, 26.09, 25.64. HRMS (EI) Calculated for  $\text{C}_{20}\text{H}_{22}\text{S}$  ( $\text{M}^+$ ) 294.1442, found 294.1447.



**(2, 2-diphenylvinyl)(octyl)sulfane (4p).** Colorless oil (45 mg, 70%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.37 (m, 2H), 7.35 – 7.26 (m, 5H), 7.23 (t,  $J = 7.0$  Hz, 3H), 6.60 (s, 1H), 2.77 (t,  $J = 7.4$  Hz, 2H), 1.74 – 1.64 (m, 2H), 1.43–1.38 (m, 2H), 1.38 – 1.29 (m, 8H), 0.90 (t,  $J = 6.7$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.06, 139.68, 138.39, 129.76, 128.29, 128.24, 127.43, 127.03, 126.79, 126.43, 34.98, 31.82, 30.38, 29.18, 28.67, 22.66, 14.10. HRMS (EI) Calculated for  $\text{C}_{22}\text{H}_{28}\text{S}$  ( $\text{M}^+$ ) 324.1912, found 324.1918.

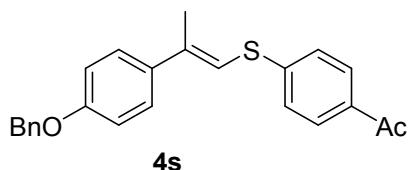


**(E)-1-((2-(4-methoxyphenyl)prop-1-en-1-yl)thio)phenylethan-1-one (4q).** Colorless oil (50 mg, 84%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.4$  Hz, 2H), 7.41 - 7.38 (m, 4H), 6.90 (d,  $J = 8.7$  Hz, 2H), 6.49 (s, 1H), 3.83 (s, 3H), 2.57 (s, 3H), 2.27 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.09, 159.47, 144.20, 141.63, 134.39, 133.97, 128.91, 126.83, 115.54, 113.91, 113.57, 55.36, 26.45, 18.04. HRMS (EI) Calculated for  $\text{C}_{18}\text{H}_{18}\text{O}_2\text{S}$  ( $\text{M}^+$ ) 298.1028, found 298.1031.



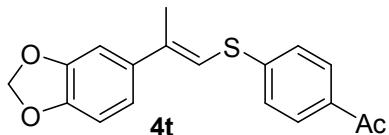
**4r**

**(E)-1-(4-((2-(4-((tert-butyldimethylsilyl)oxy)phenyl)prop-1-en-1-yl)thio)phenyl)ethan-1-one (4r).** Colorless oil (61 mg, 77%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.4$  Hz, 2H), 7.41 (d,  $J = 8.4$  Hz, 2H), 7.36 (d,  $J = 8.6$  Hz, 2H), 6.85 (d,  $J = 8.6$  Hz, 2H), 6.51 (s, 1H), 2.60 (s, 3H), 2.28 (s, 3H), 1.02 (s, 9H), 0.24 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  197.19, 155.65, 144.24, 141.68, 134.44, 134.31, 128.92, 126.82, 126.75, 120.03, 115.53, 26.51, 25.69, 18.26, 18.03, -4.36. HRMS (EI) Calculated for  $\text{C}_{23}\text{H}_{30}\text{O}_2\text{SSi}$  ( $\text{M}^+$ ) 398.1730, found 398.1726.

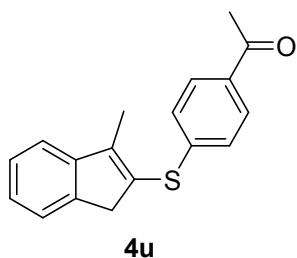


**4s**

**(E)-1-(4-((2-(4-(benzyloxy)phenyl)prop-1-en-1-yl)thio)phenyl)ethan-1-one (4s).** Colorless oil (51 mg, 69%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.6$  Hz, 2H), 7.46 – 7.34 (m, 9H), 6.98 (d,  $J = 8.8$  Hz, 2H), 6.49 (s, 1H), 5.10 (s, 2H), 2.58 (s, 3H), 2.27 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  197.21, 158.62, 144.19, 141.52, 136.83, 134.34, 134.18, 128.94, 128.66, 128.08, 127.48, 126.86, 126.83, 115.65, 114.83, 70.10, 26.52, 18.05. HRMS (EI) Calculated for  $\text{C}_{24}\text{H}_{22}\text{O}_2\text{S}$  ( $\text{M}^+$ ) 374.1341, found 374.1340.



**(E)-1-(4-((2-(benzo[d][1,3]dioxol-5-yl)prop-1-en-1-yl)thio)phenyl)ethan-1-one (4t).** Colorless oil (50 mg, 81%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.5$  Hz, 2H), 7.38 (d,  $J = 8.5$  Hz, 2H), 6.96 – 6.91 (m, 2H), 6.80 (d,  $J = 7.9$  Hz, 1H), 6.47 (d,  $J = 0.7$  Hz, 1H), 5.97 (s, 2H), 2.57 (s, 3H), 2.24 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.07, 147.92, 147.37, 143.88, 141.18, 135.83, 134.50, 128.93, 126.97, 119.39, 116.52, 108.20, 106.16, 101.23, 26.46, 18.26. HRMS (EI) Calculated for  $\text{C}_{18}\text{H}_{16}\text{O}_3\text{S}$  ( $\text{M}^+$ ) 312.0808, found 312.0815.



**1-((1*H*-inden-3-yl)methyl)thio)phenyl ethan-1-one (**4u**).** Colorless oil (46 mg, 83%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.44 (t, *J* = 6.9 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 3.56 (d, *J* = 1.9 Hz, 2H), 2.58 (s, 3H), 2.31 (t, *J* = 2.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.19, 147.86, 145.04, 144.59, 143.51, 134.27, 128.97, 128.93, 126.99, 126.68, 126.04, 123.57, 119.75, 42.37, 26.50, 11.87. HRMS (EI) Calculated for C<sub>18</sub>H<sub>16</sub>OS (M<sup>+</sup>) 280.0919, found 280.0916.

## 5. X-ray Crystallographic Analysis of product **3ab**

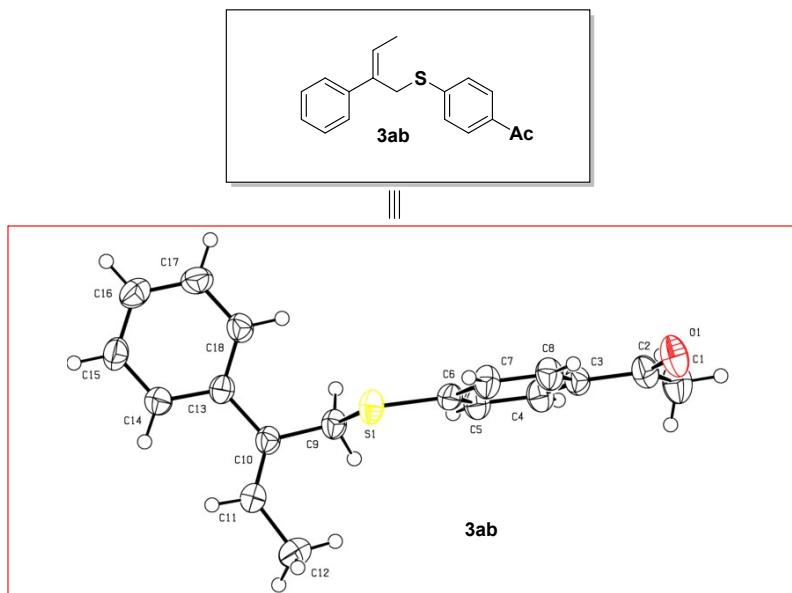
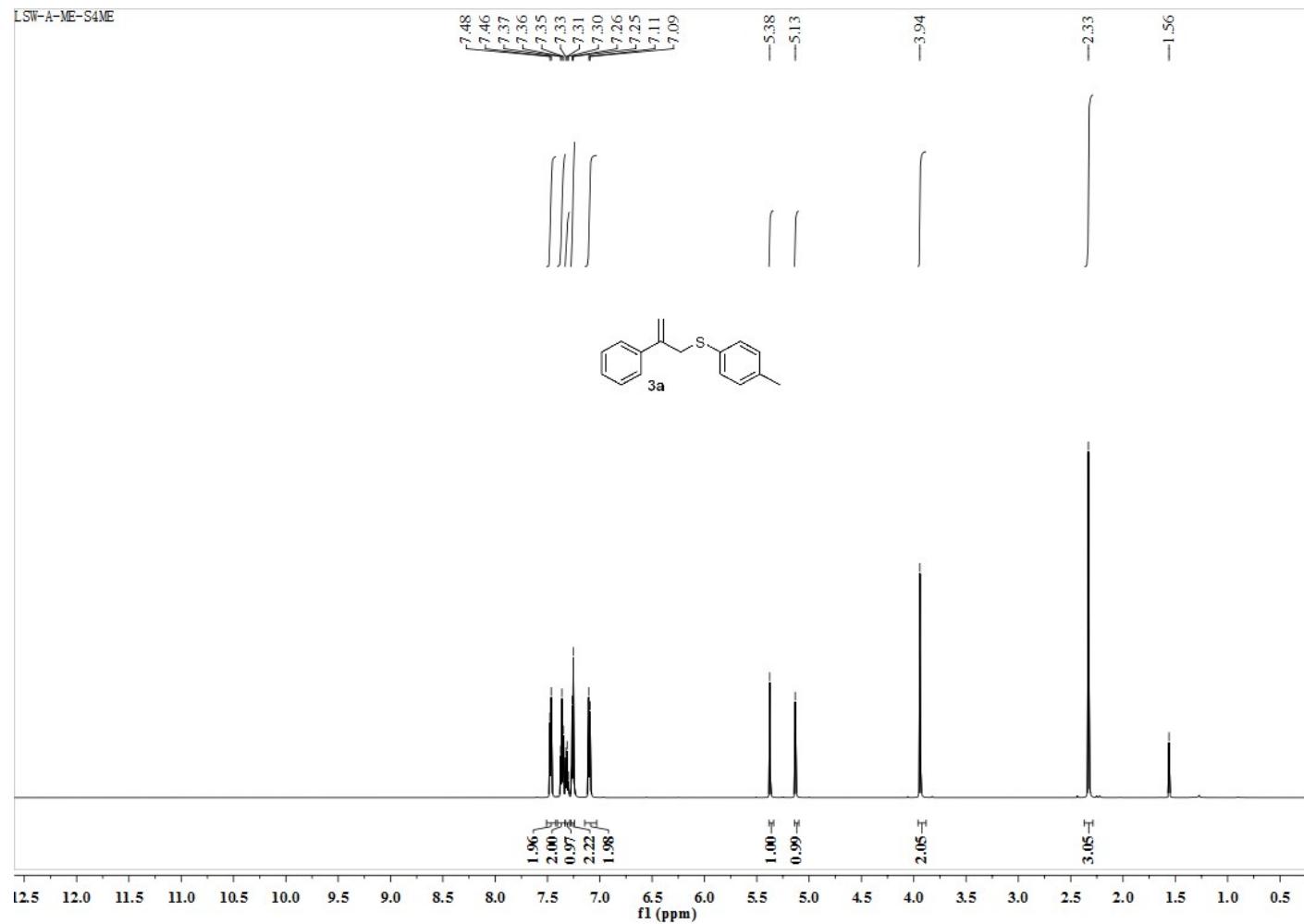


Table 1. Crystal data and structure refinement for 20200822LI\_ZNZ6233\_0m\_a.

Identification code	20200822li_znz6233_0m_a
Empirical formula	C <sub>18</sub> H <sub>18</sub> OS
Formula weight	282.38
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	P 1 21/c 1	
Unit cell dimensions	$a = 8.5247(14) \text{ \AA}$	$\alpha = 90^\circ.$
	$b = 21.621(3) \text{ \AA}$	$\beta = 115.939(4)^\circ.$
	$c = 9.2060(14) \text{ \AA}$	$\gamma = 90^\circ.$
Volume	$1525.8(4) \text{ \AA}^3$	
Z	4	
Density (calculated)	$1.229 \text{ Mg/m}^3$	
Absorption coefficient	$0.205 \text{ mm}^{-1}$	
F(000)	600	
Crystal size	$0.12 \times 0.11 \times 0.08 \text{ mm}^3$	
Theta range for data collection	2.635 to $27.530^\circ.$	
Index ranges	$-8 \leq h \leq 11, -28 \leq k \leq 27, -11 \leq l \leq 11$	
Reflections collected	13345	
Independent reflections	3504 [ $R(\text{int}) = 0.0543$ ]	
Completeness to theta = $25.242^\circ$	100.0 %	
Absorption correction	None	
Max. and min. transmission	0.7456 and 0.6277	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	3504 / 0 / 183	
Goodness-of-fit on $F^2$	1.026	
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0557, wR_2 = 0.1161$	
R indices (all data)	$R_1 = 0.1000, wR_2 = 0.1409$	
Extinction coefficient	n/a	
Largest diff. peak and hole	$0.211 \text{ and } -0.277 \text{ e.\AA}^{-3}$	

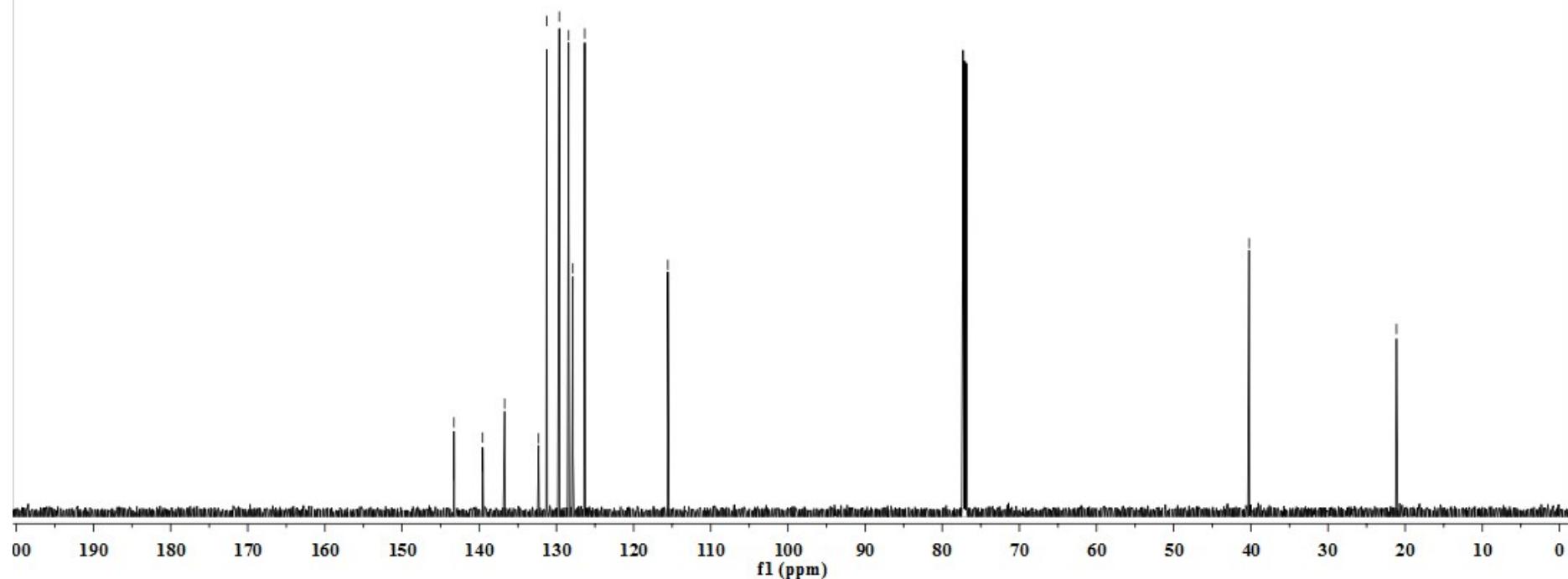
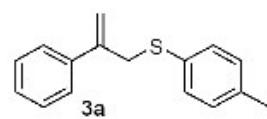
## 6. Copies of NMR Spectra



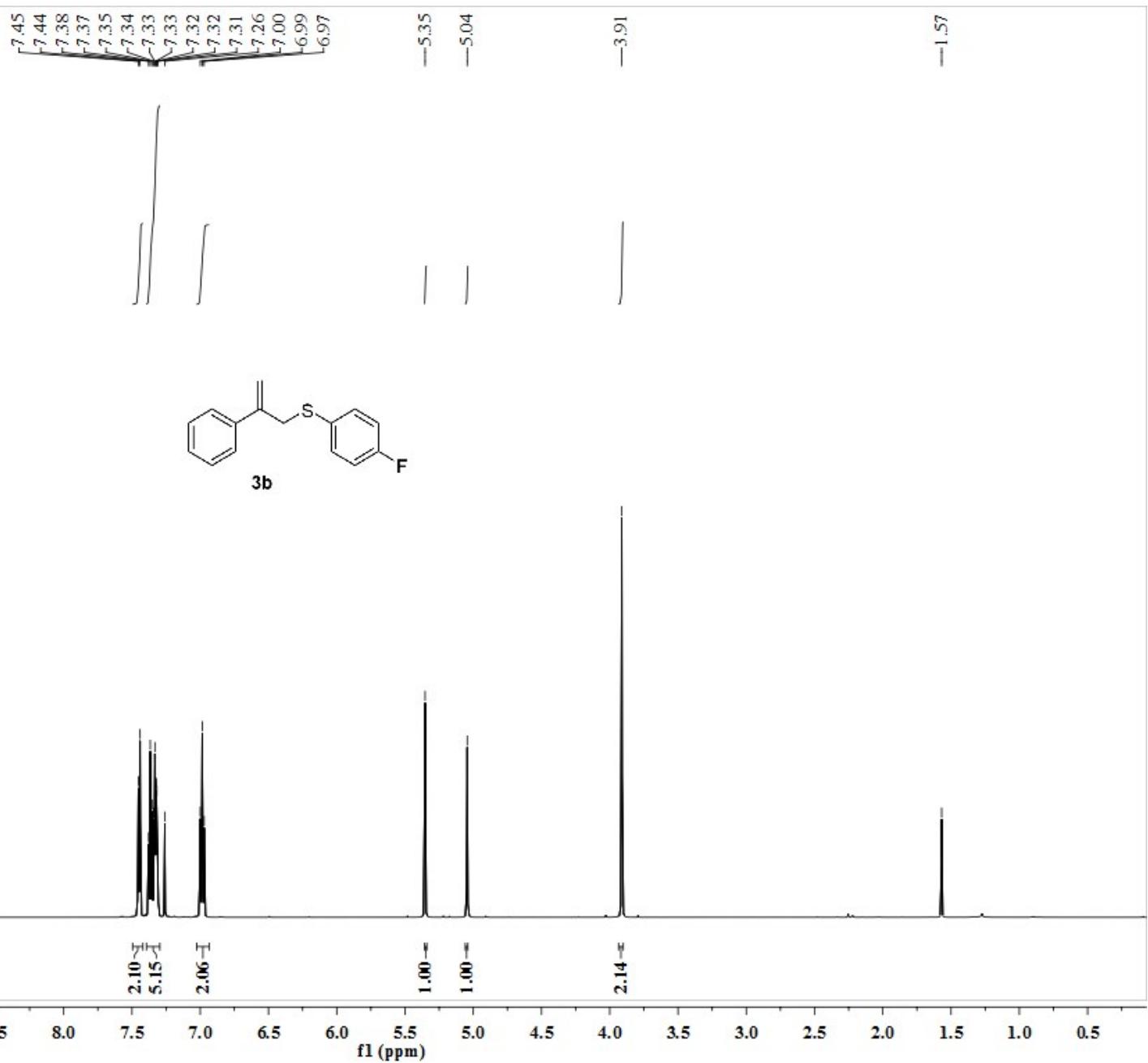
LSW-A-ME-S4ME

143.28  
139.56  
136.71  
132.32  
131.26  
129.63  
128.42  
127.87  
126.32  
-115.56

-40.23  
-21.12

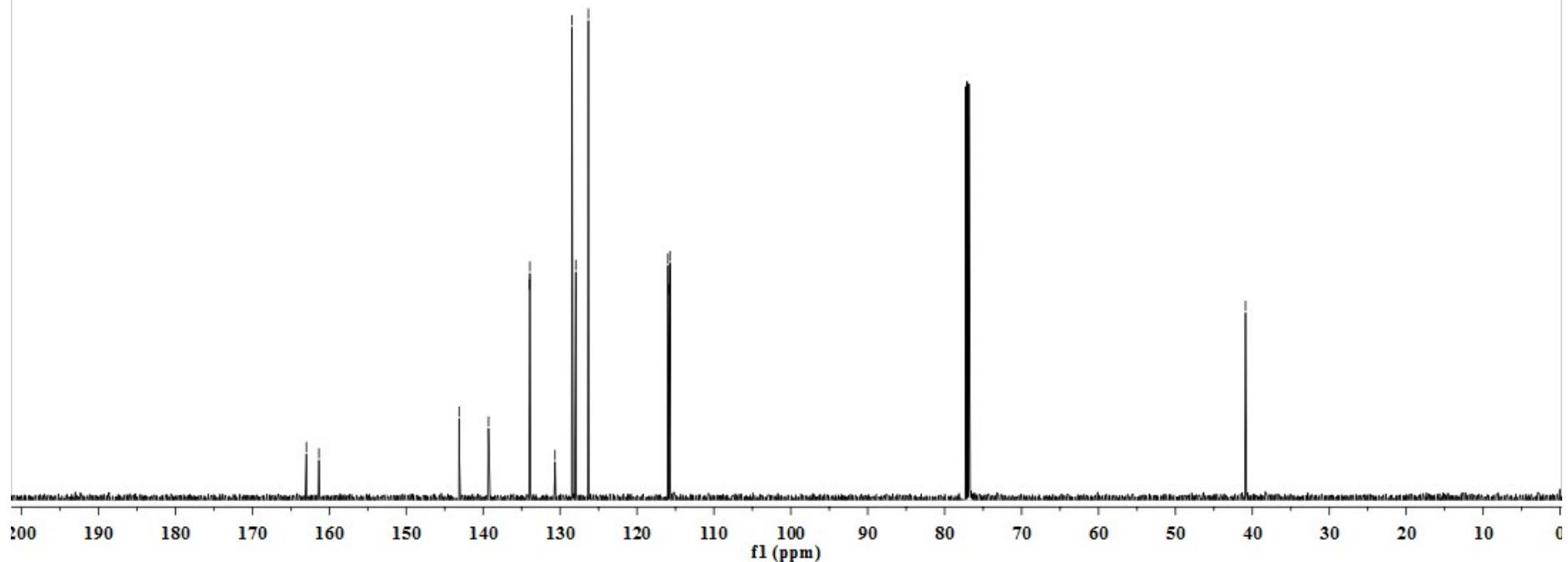
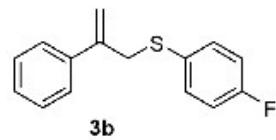


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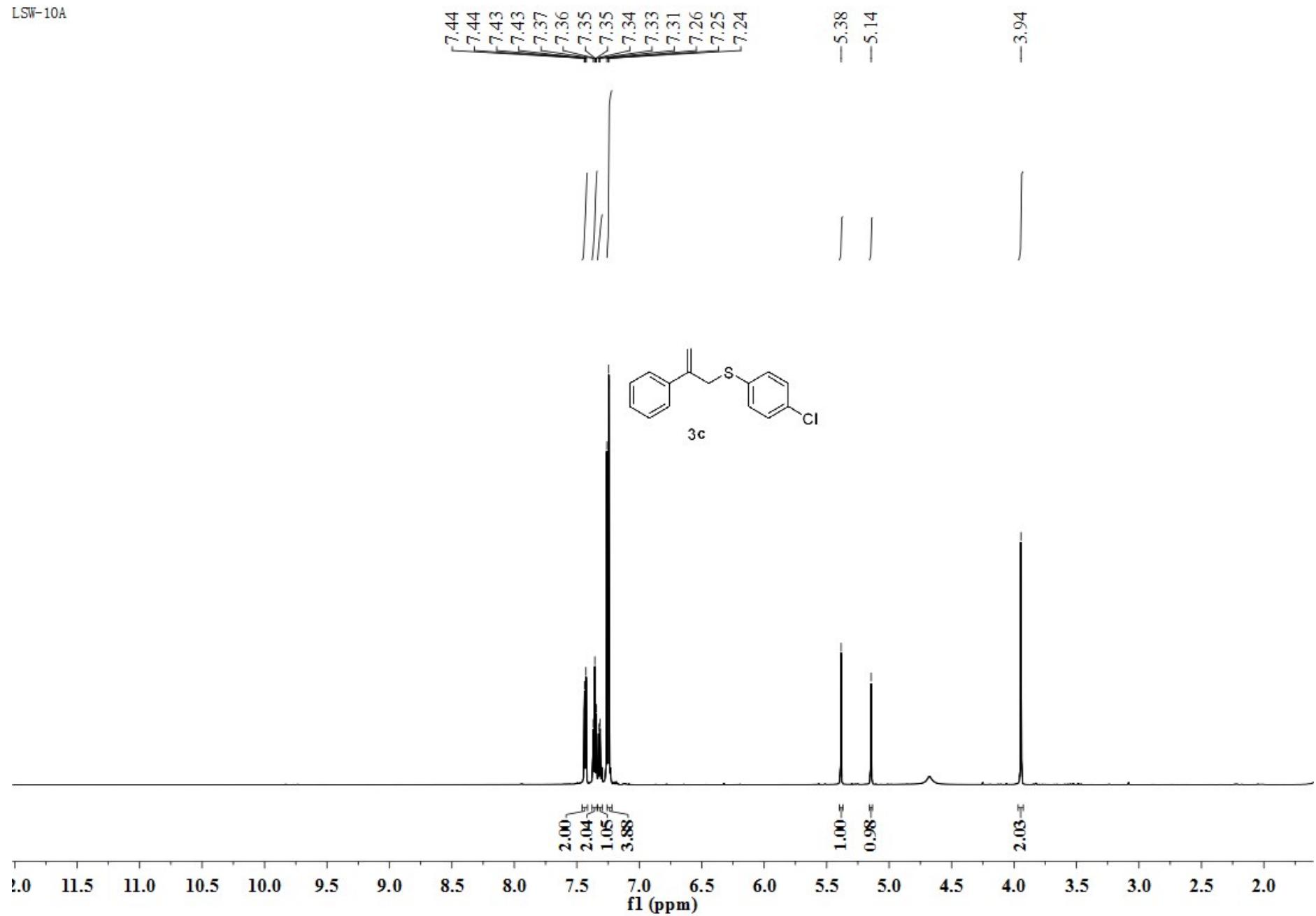


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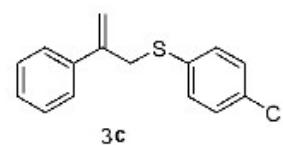
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>139.30  
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>133.92  
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>128.45  
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>126.32  
<115.98  
<115.84  
<115.72  
—40.89



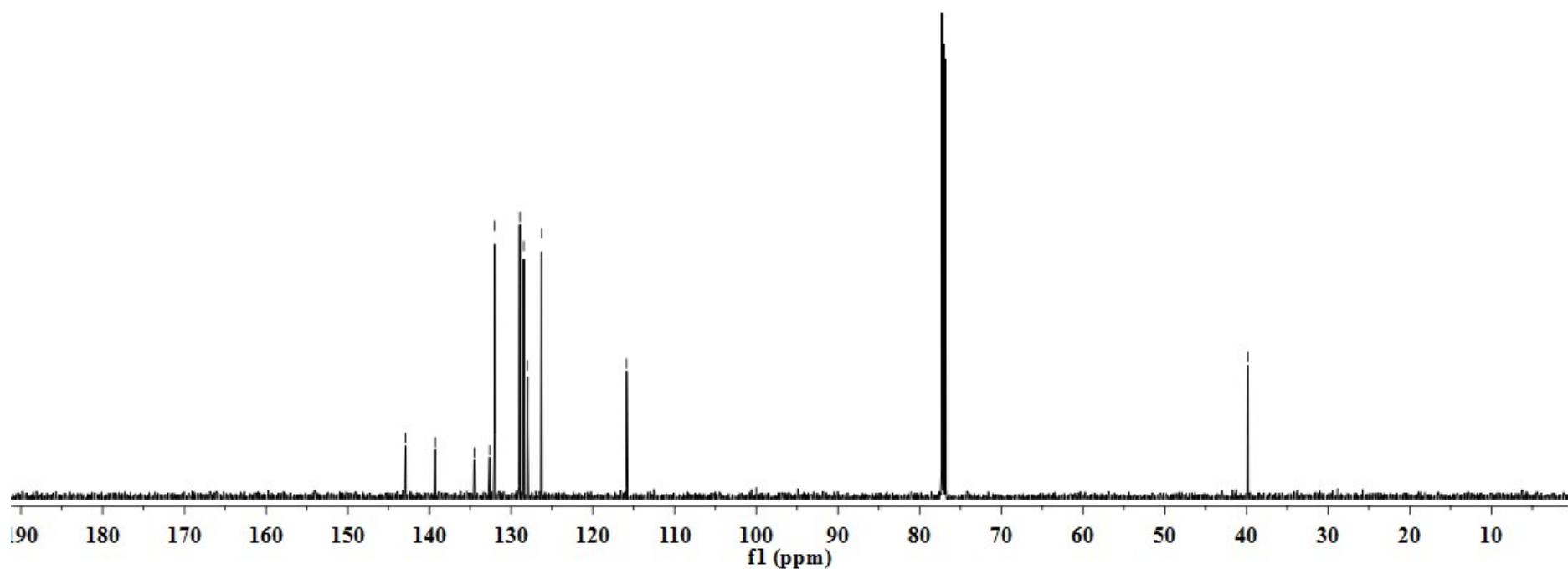
LSW-10A



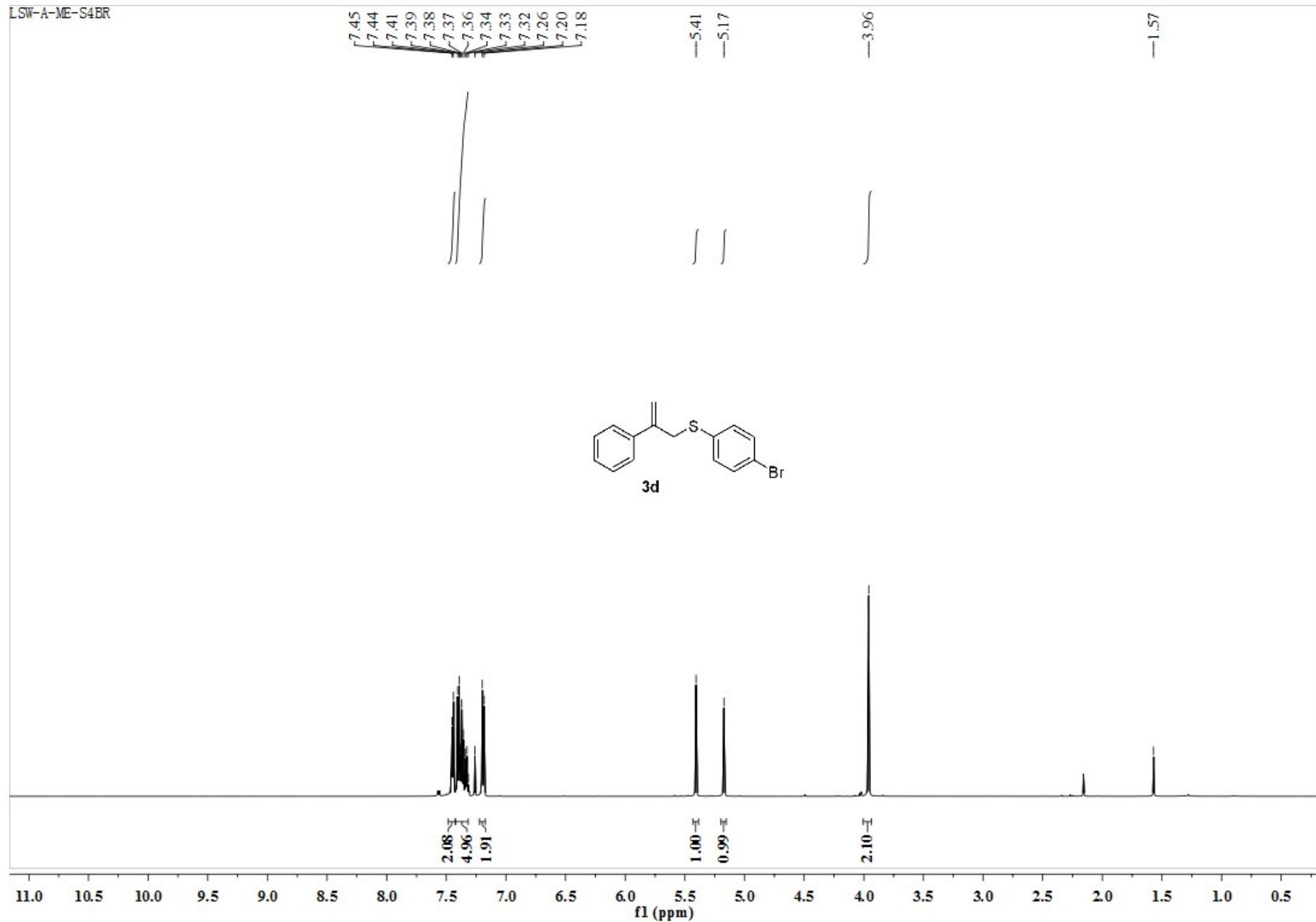
LSW-10-A



3c

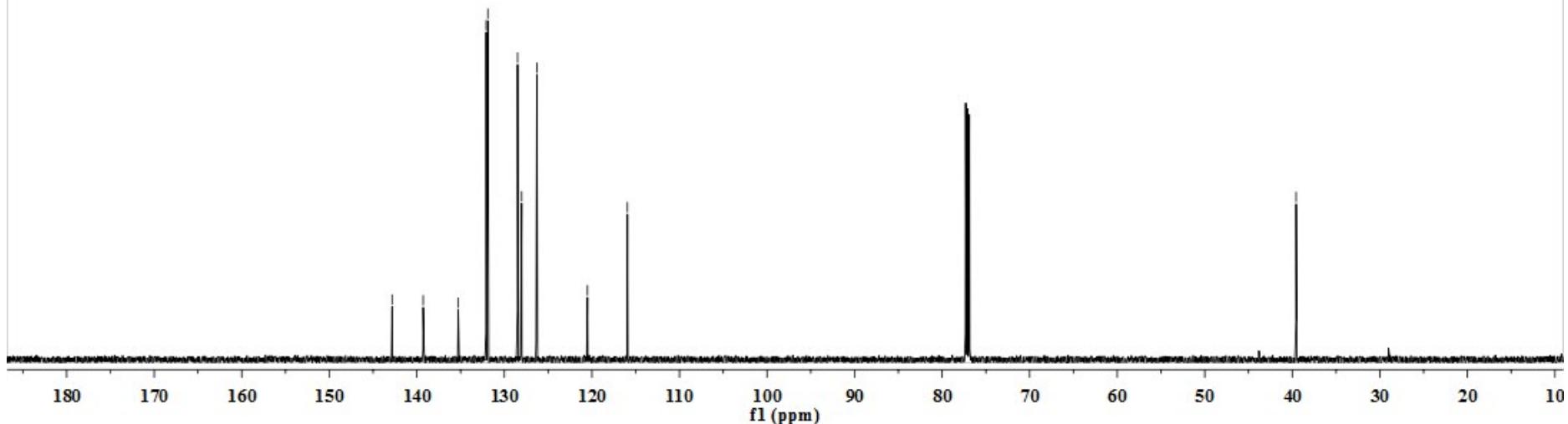
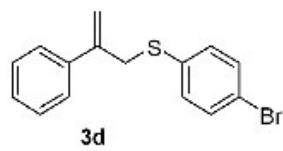


LSW-A-ME-S4BR

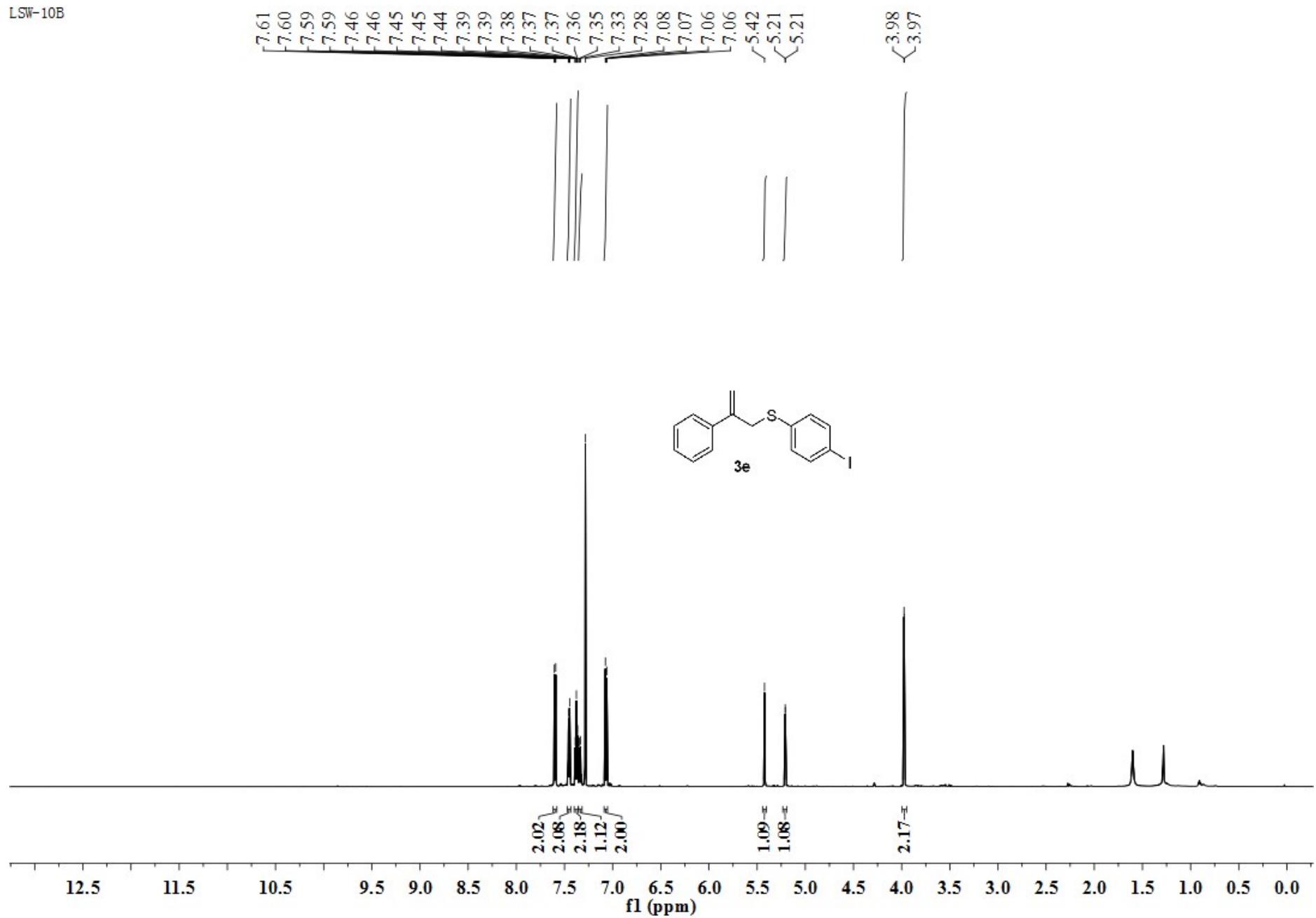


LSW-A-ME-S4BR

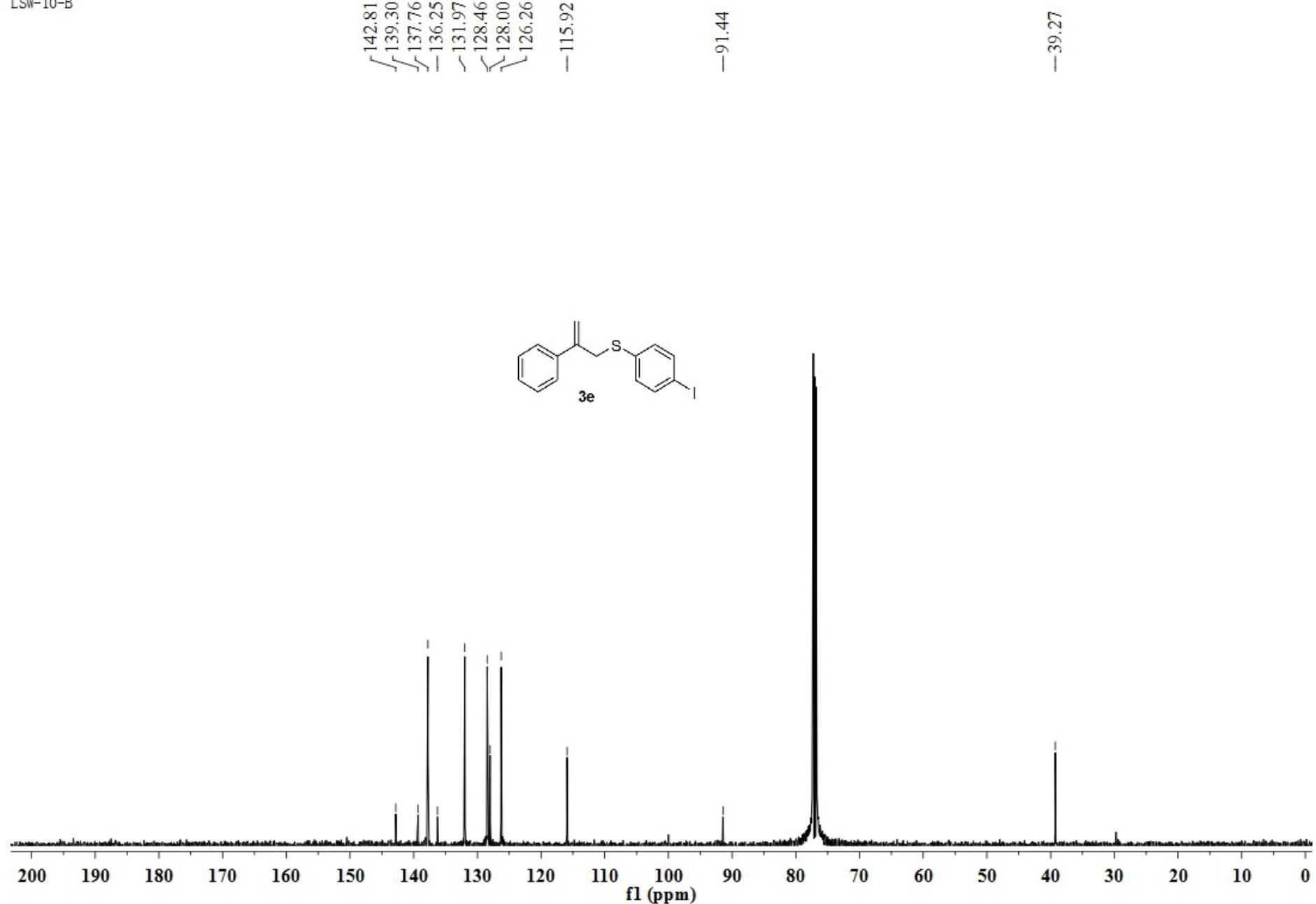
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-126.29  
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-115.94  
-39.56



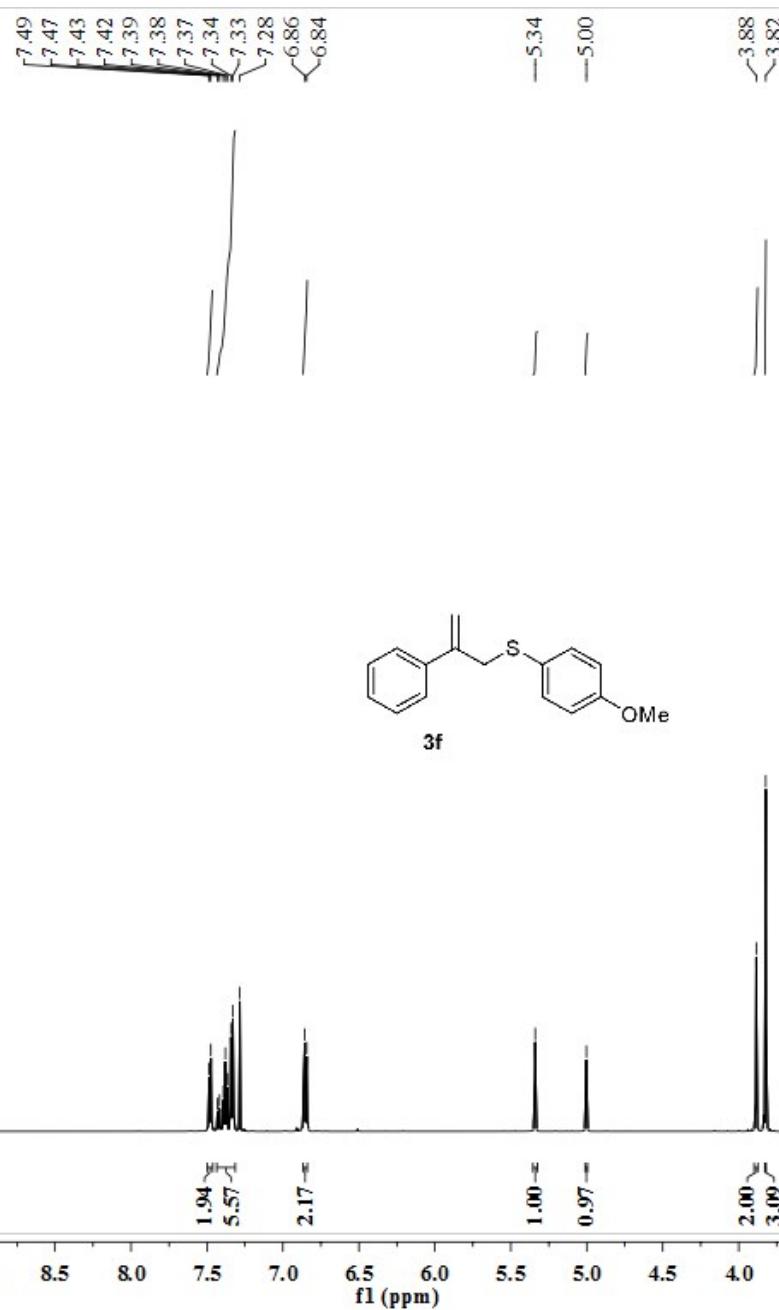
LSW-10B



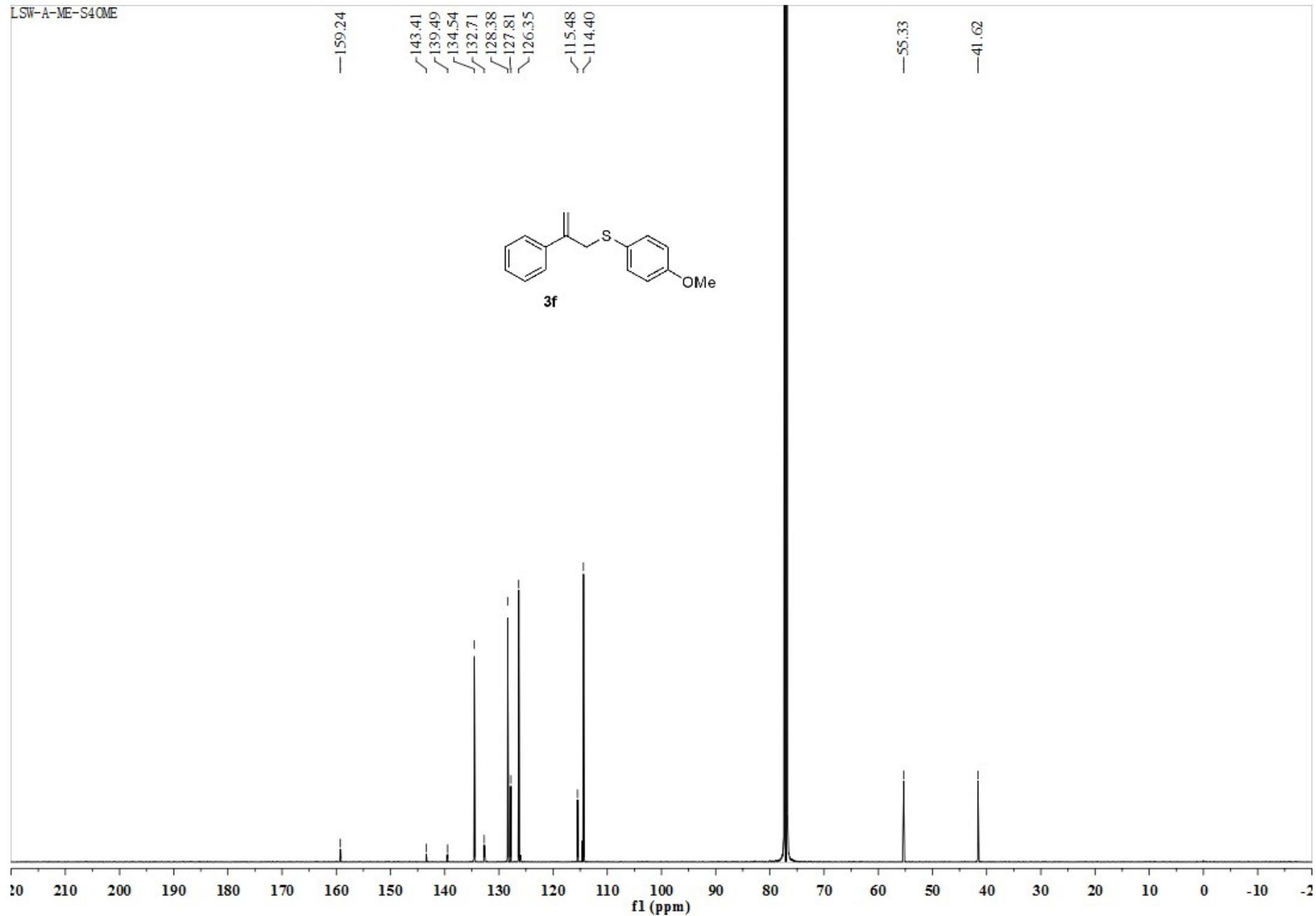
LSW-10-B



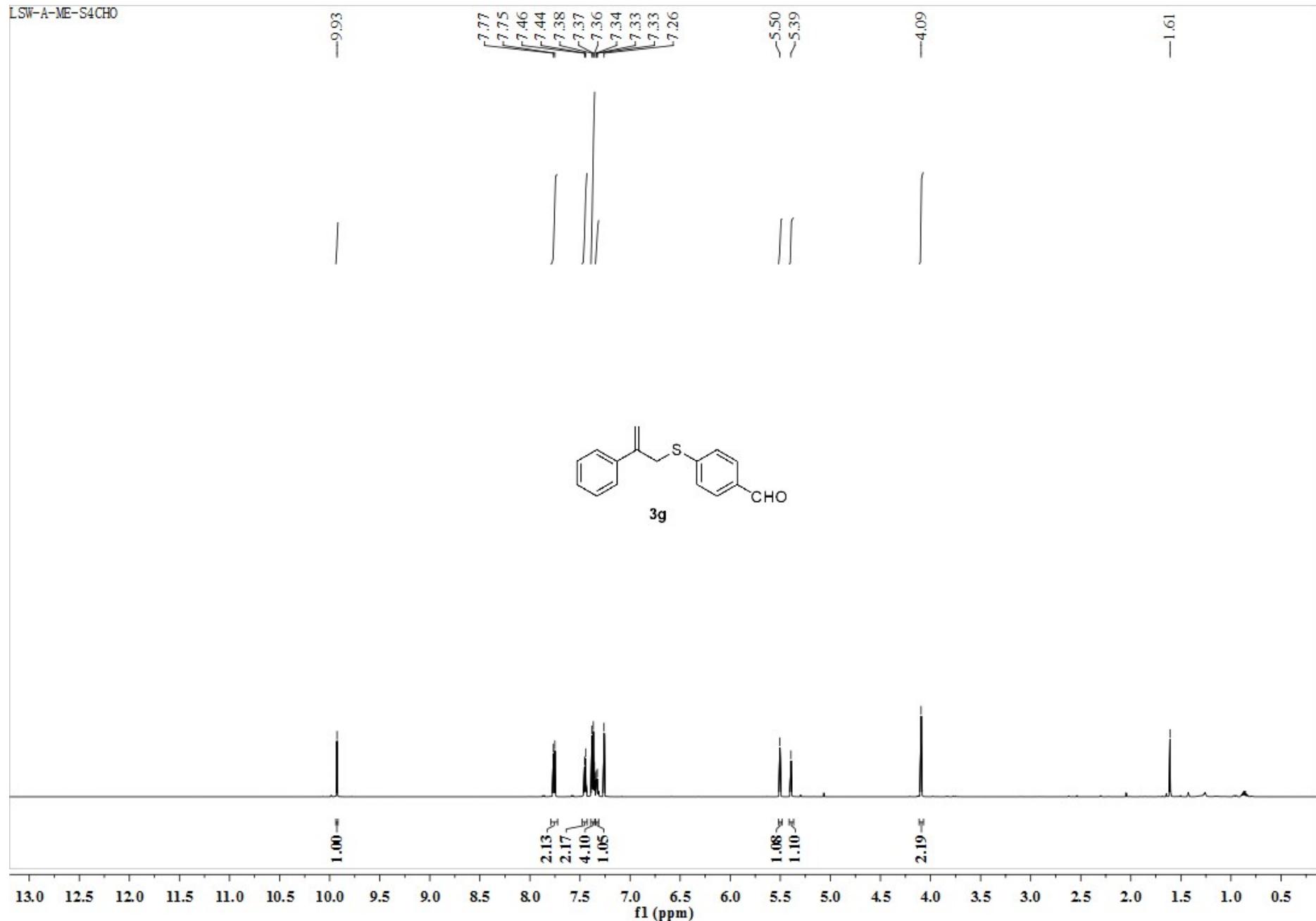
LSW-A-ME-S4OME



LSW-A-ME-S4OME



LSW-A-ME-S4CHO



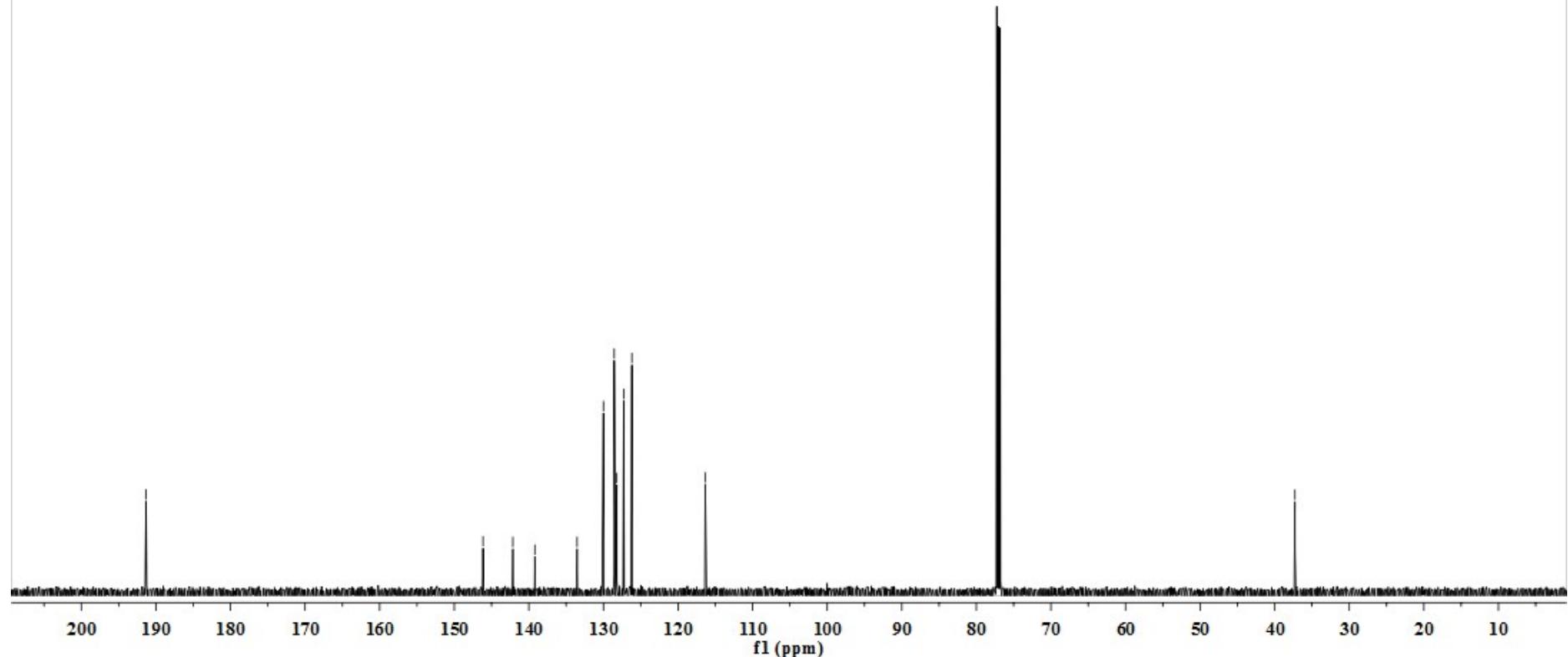
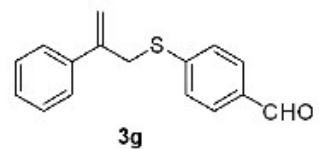
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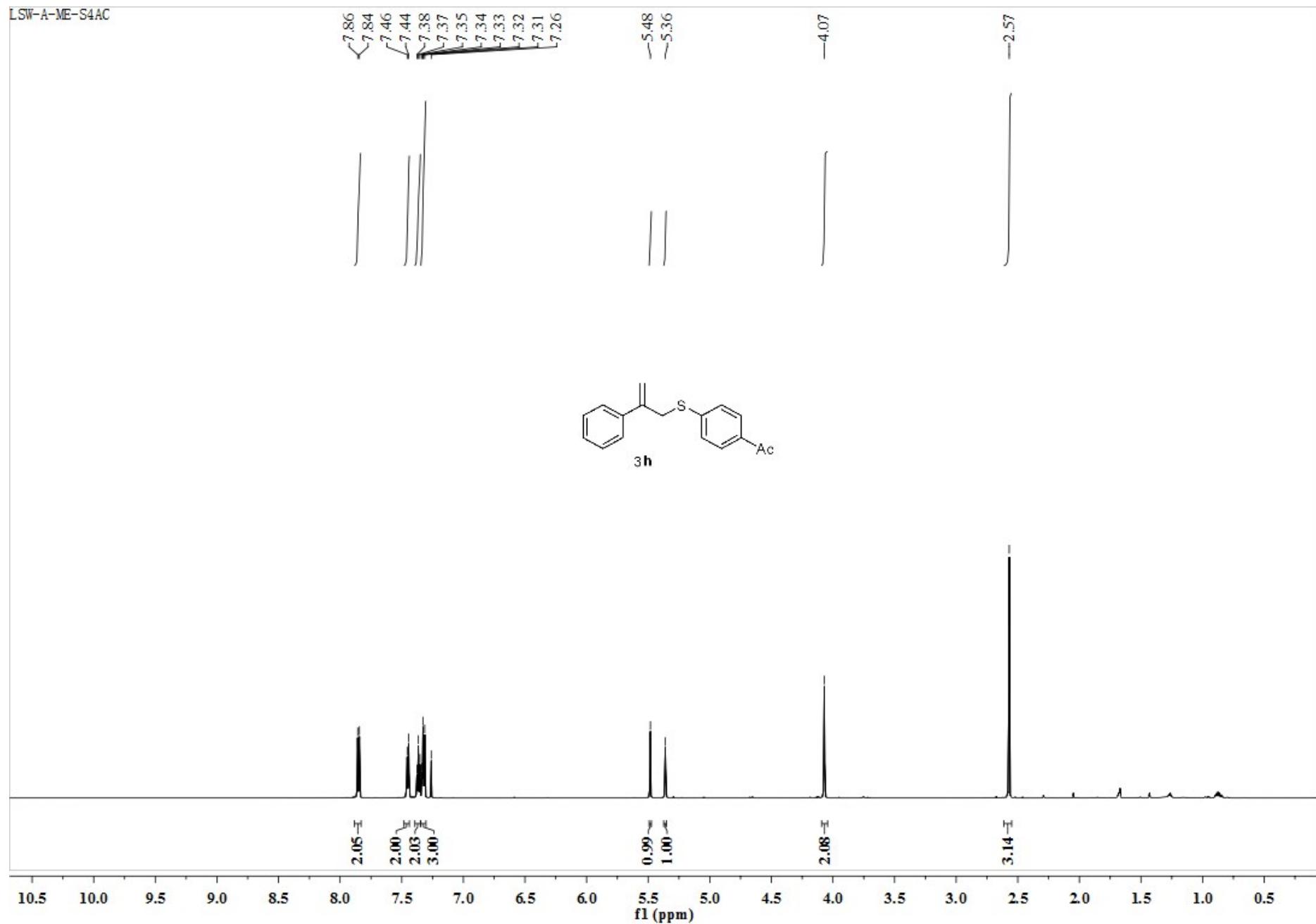
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-126.19

-116.34

-37.28



LSW-A-ME-S4AC

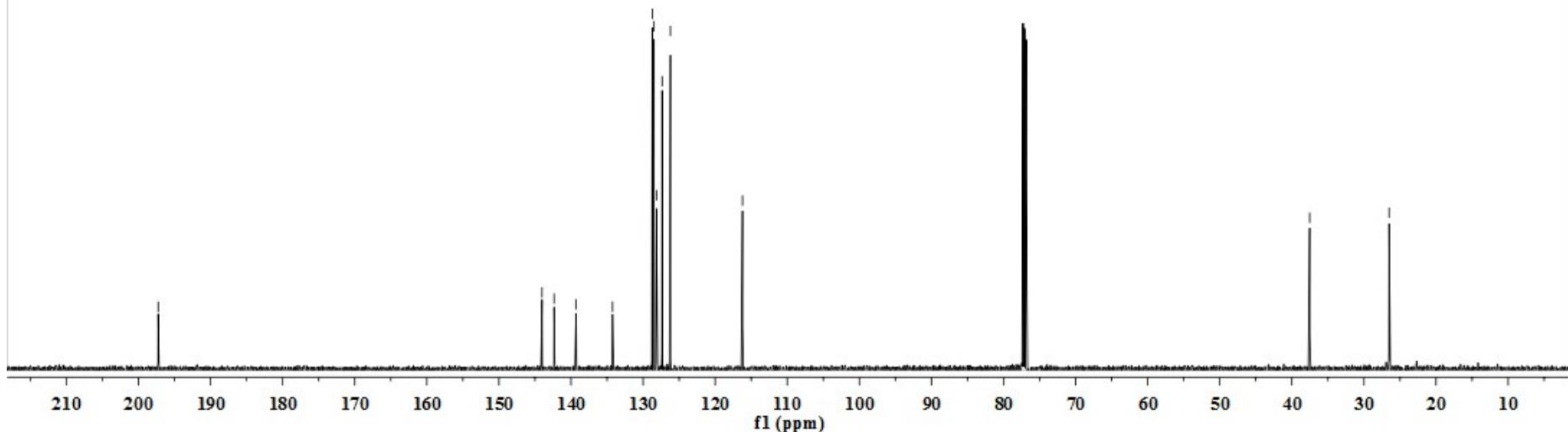
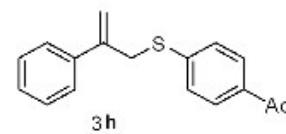


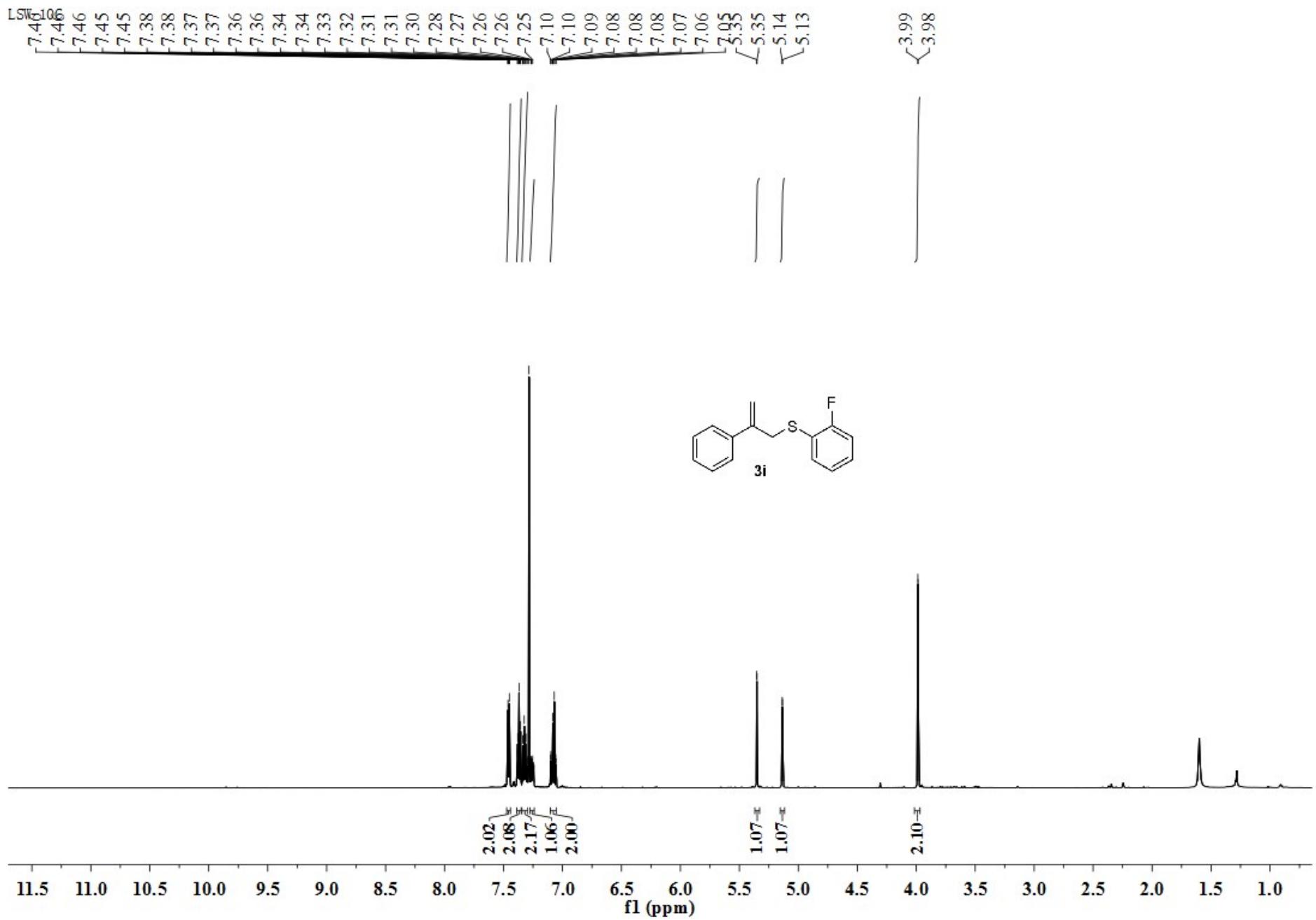
LSW-A-ME-S4AC

-197.26

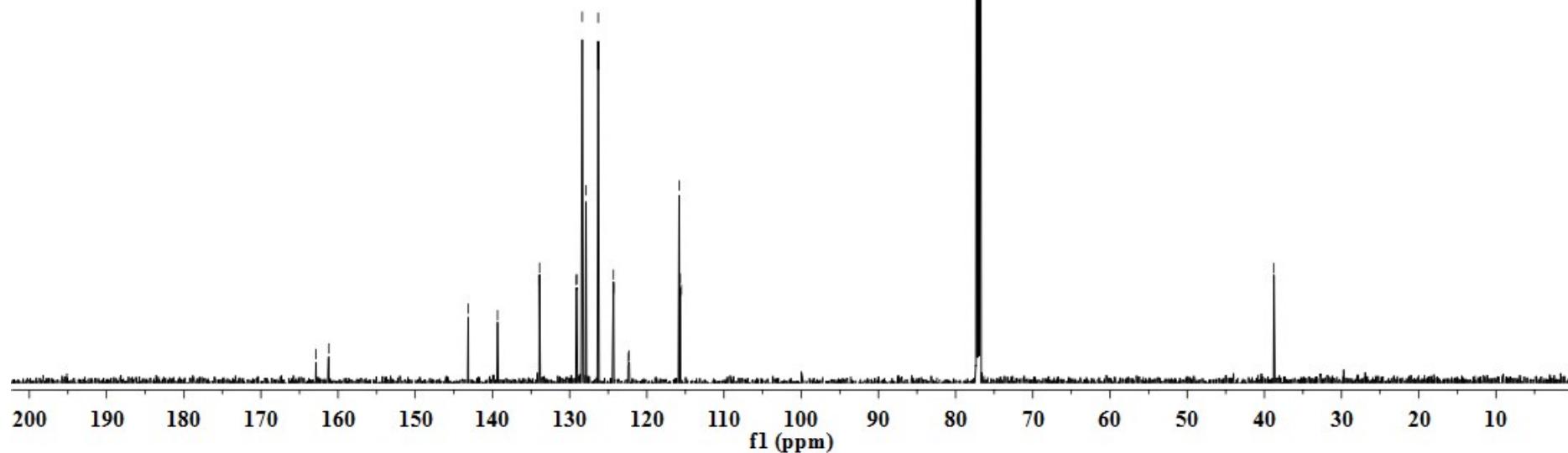
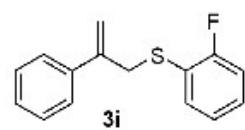
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-126.21  
-116.21

-37.53  
-26.51

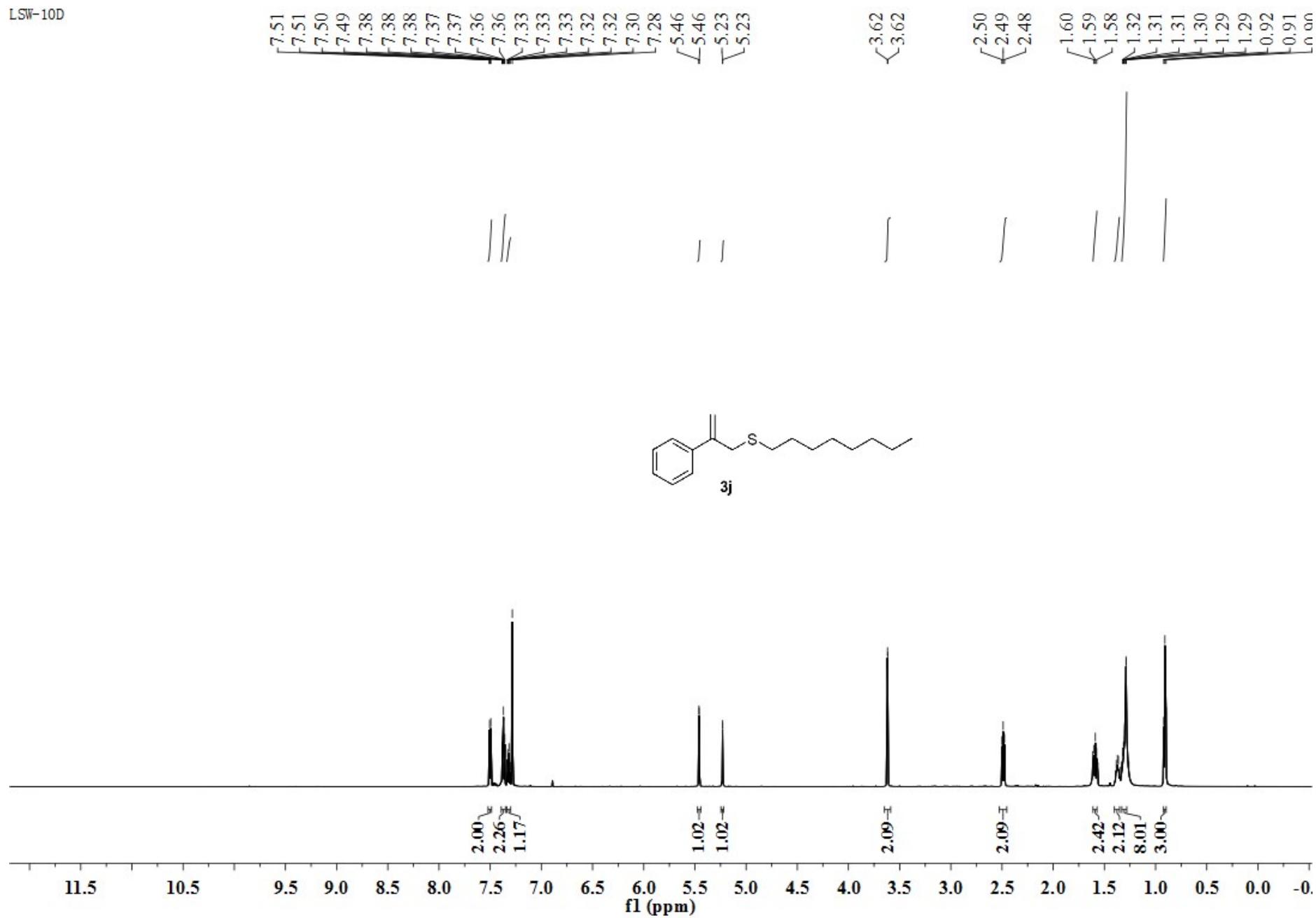




LSW-10-C

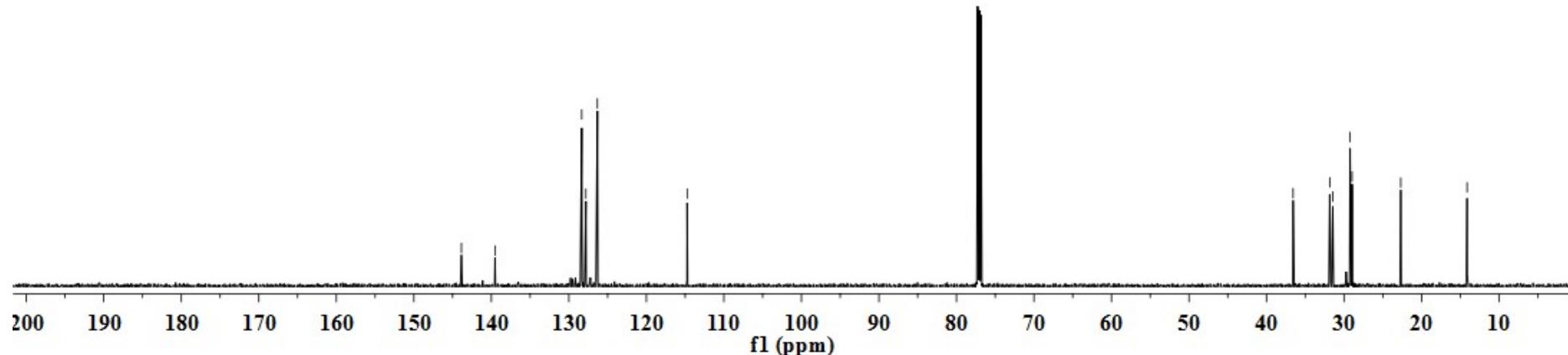
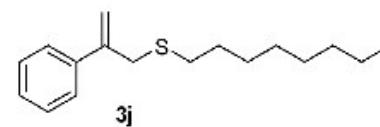


LSW-10D

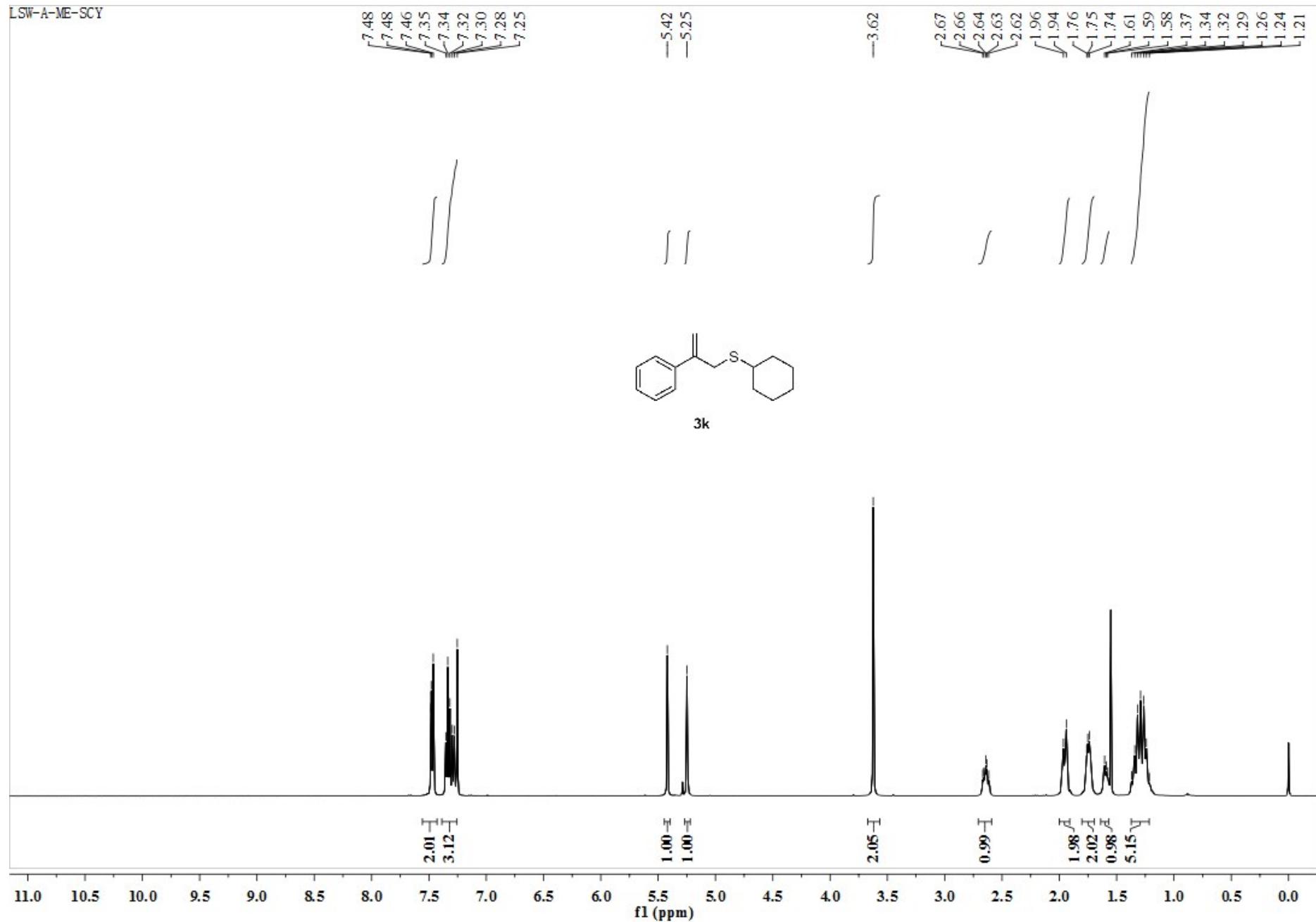


LSW-10-D

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128.34  
127.80  
126.32  
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36.57  
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31.45  
29.22  
29.21  
28.96  
22.68  
-14.12

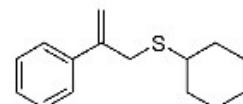


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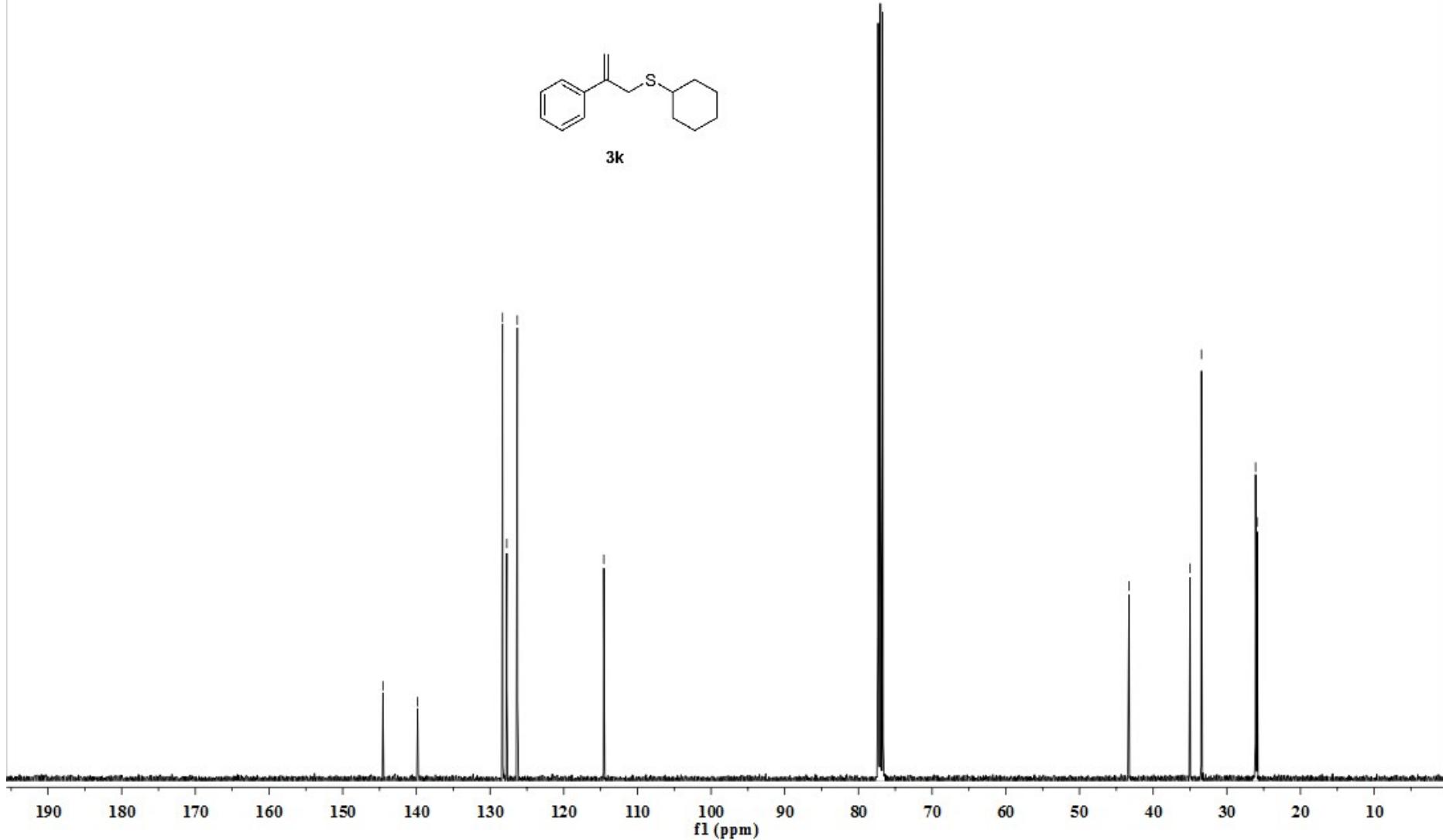


LSW-A-ME-SCY

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✓127.73  
✓126.30  
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-34.99  
-33.44  
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✓25.89

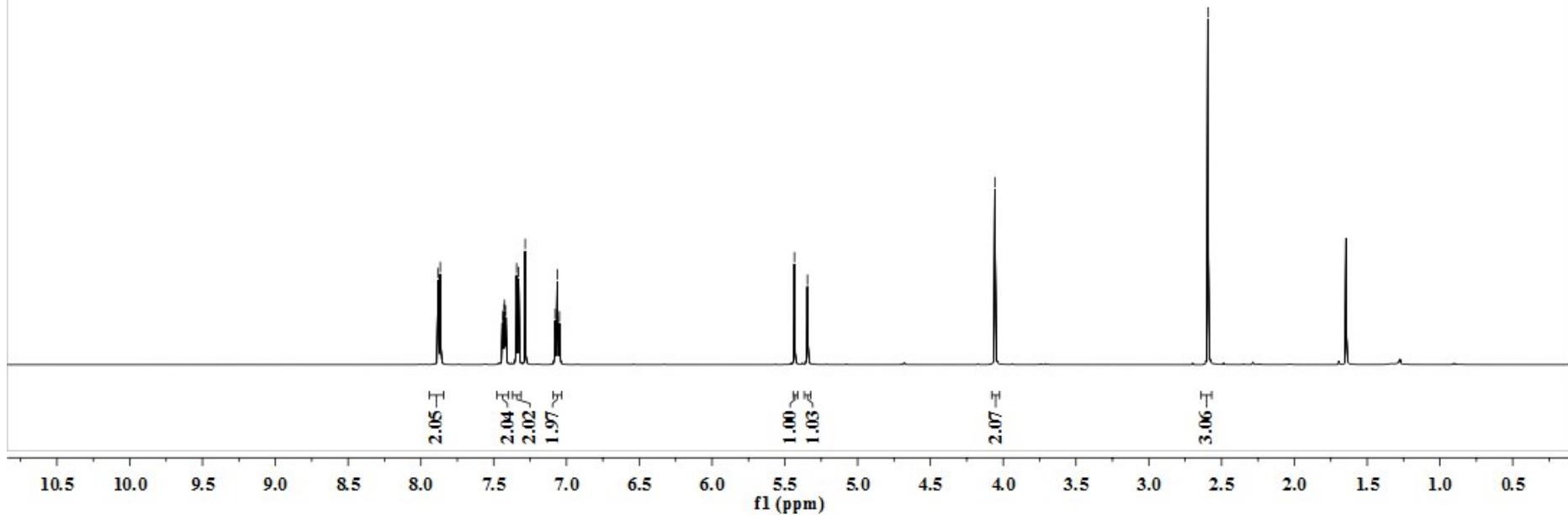
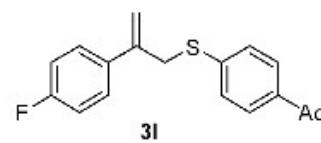


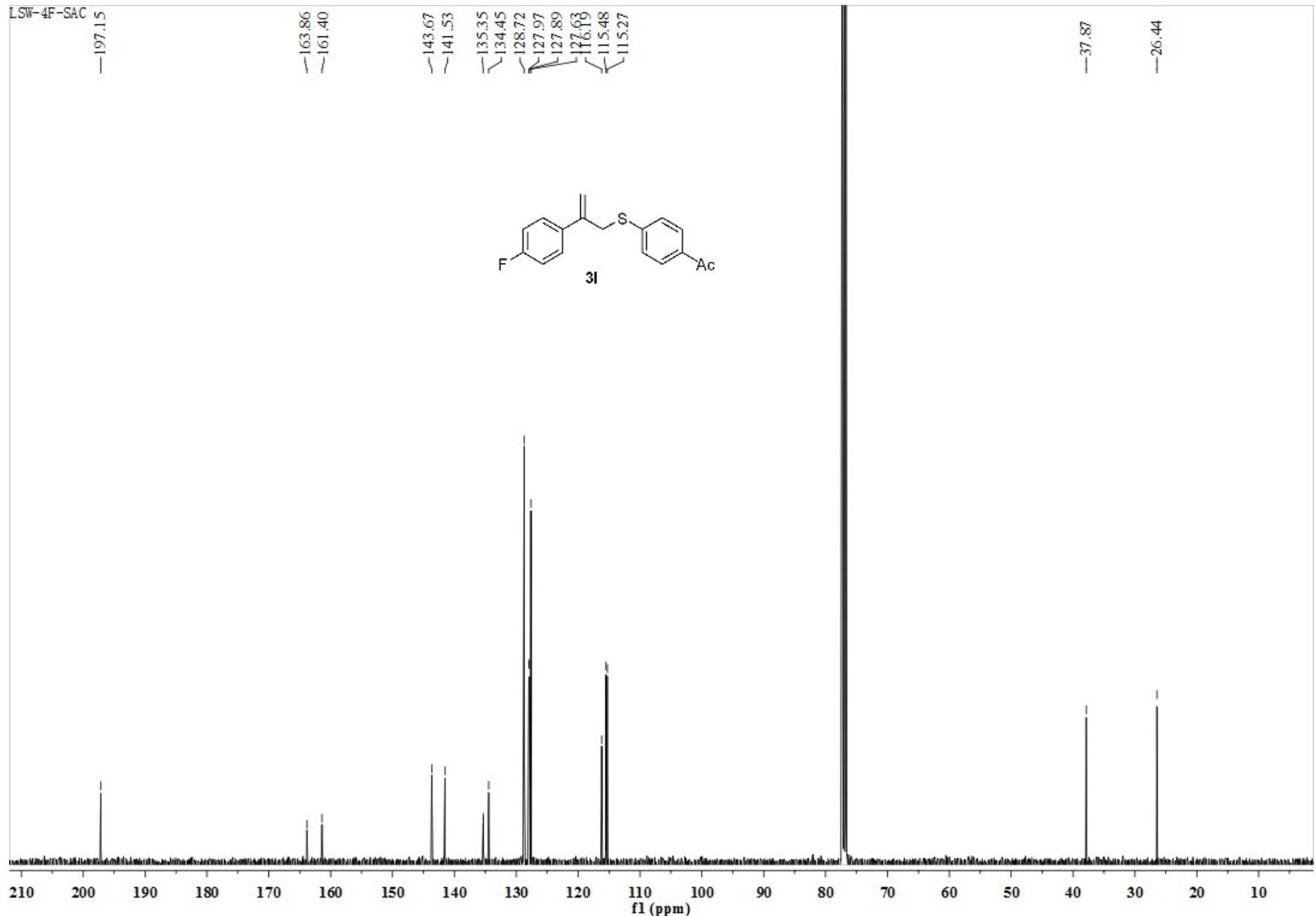
**3k**



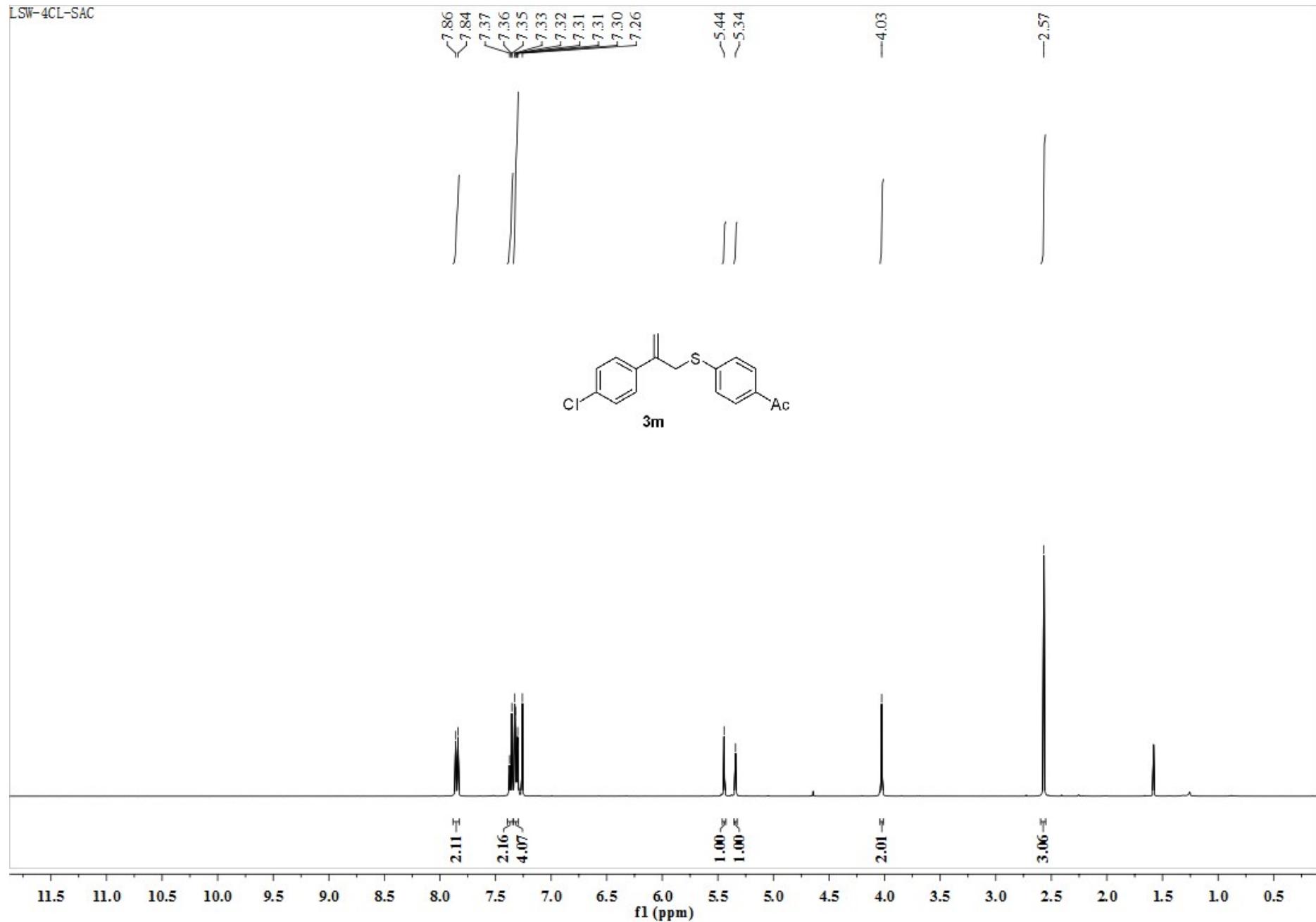
LSW-4F-A-ME-S4AC

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7.44  
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7.43  
7.42  
7.34  
7.33  
7.28  
7.08  
7.06  
7.05  
5.43  
5.35  
-4.06  
-2.59





LSW-4CL-SAC

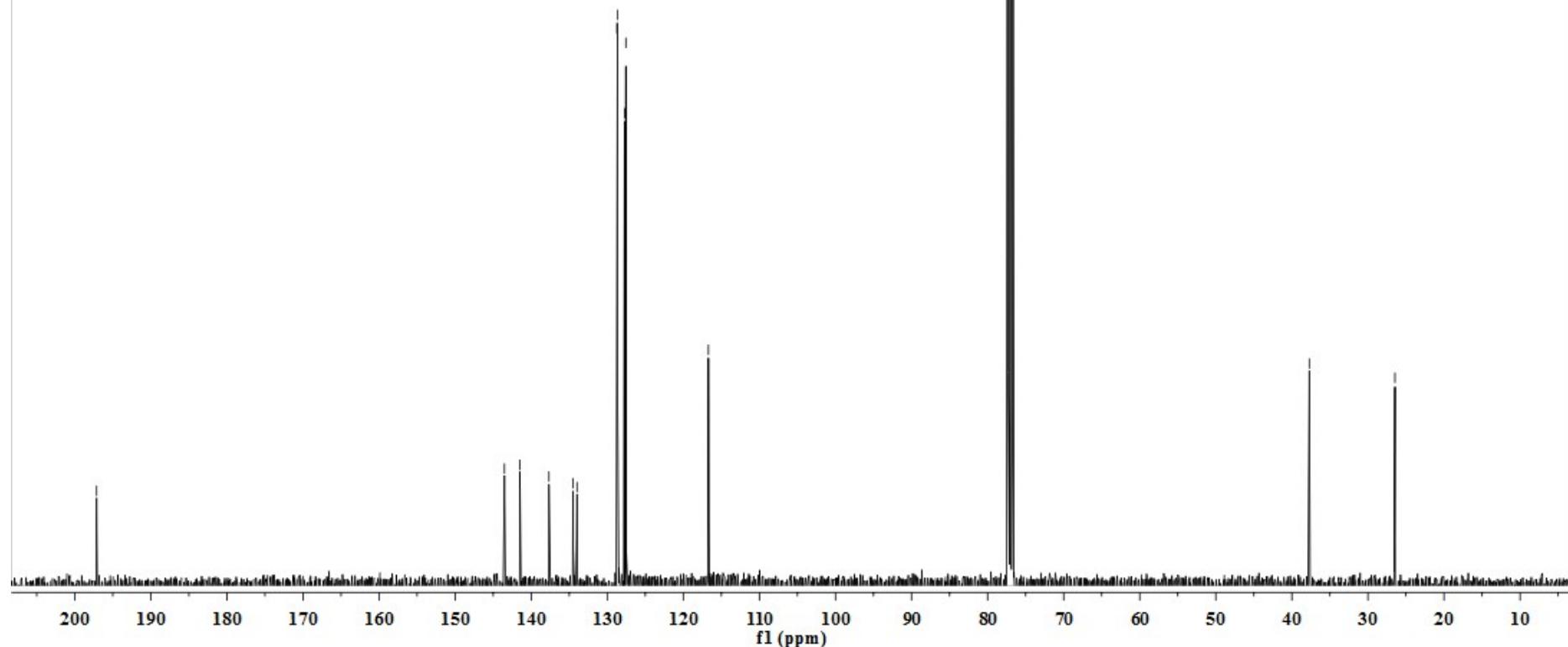
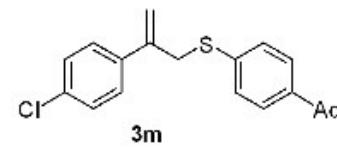


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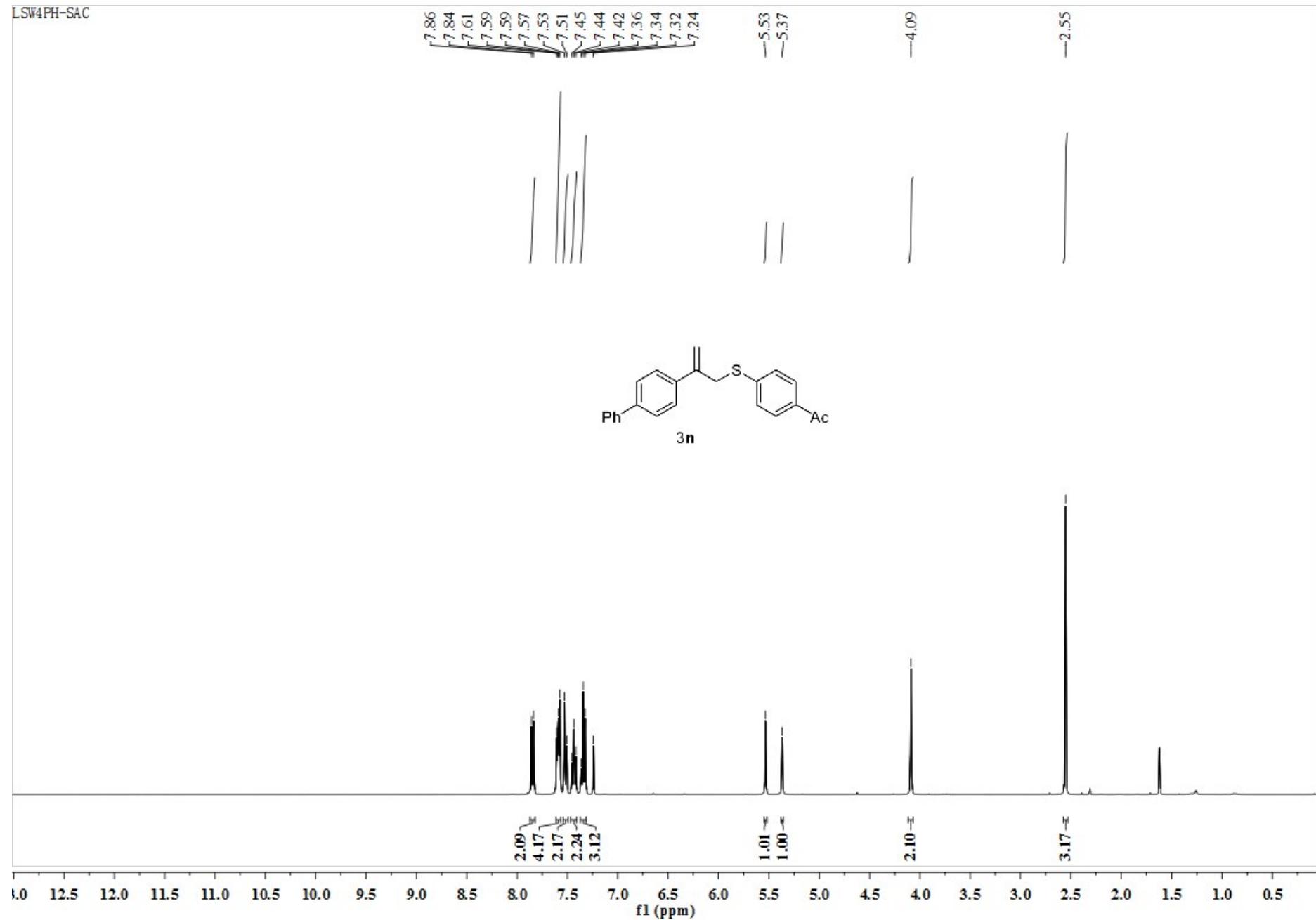
—197.1

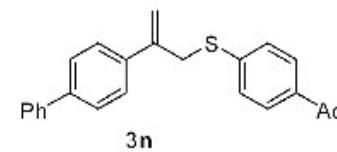
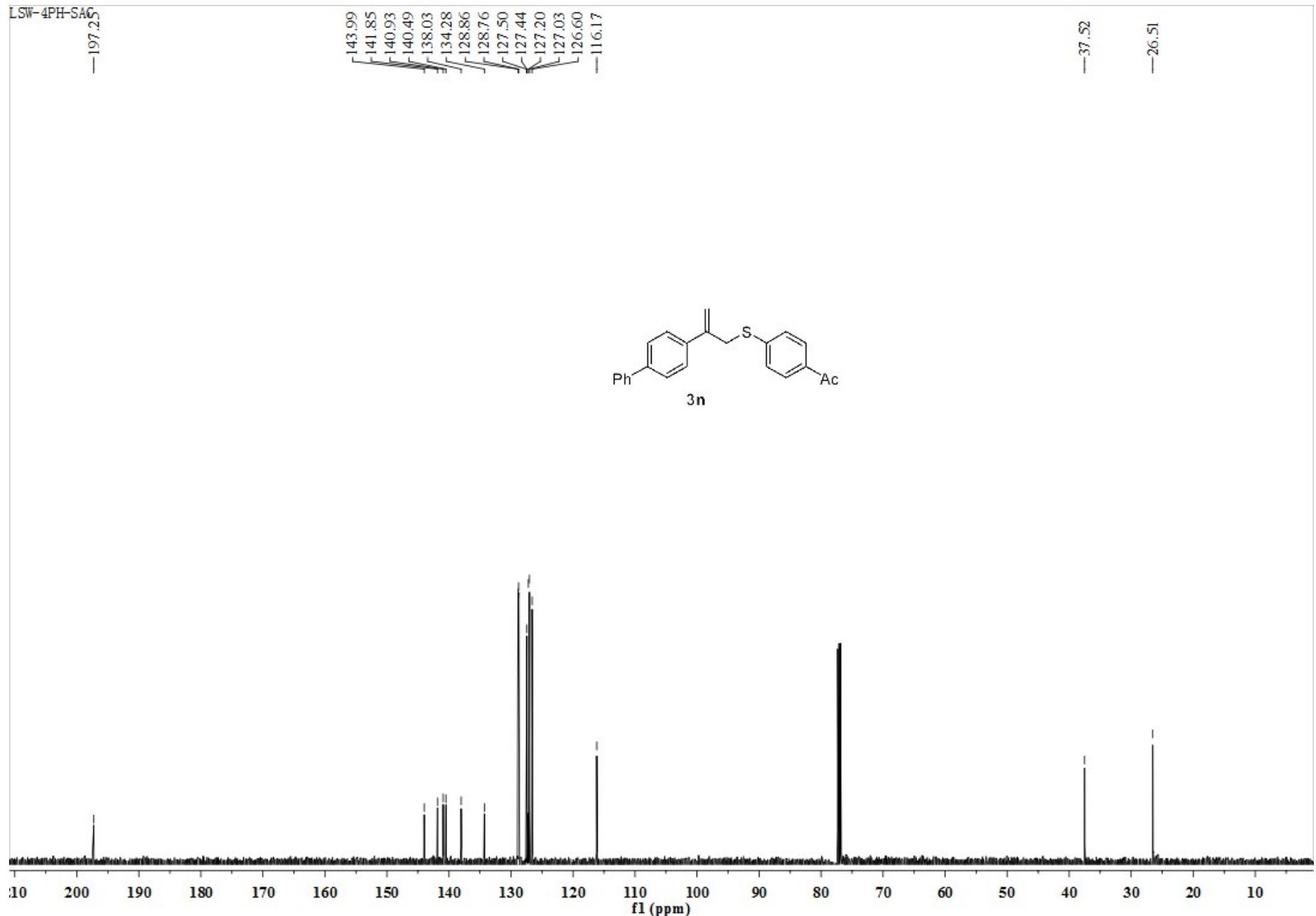
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—116.70

—37.71  
—26.45



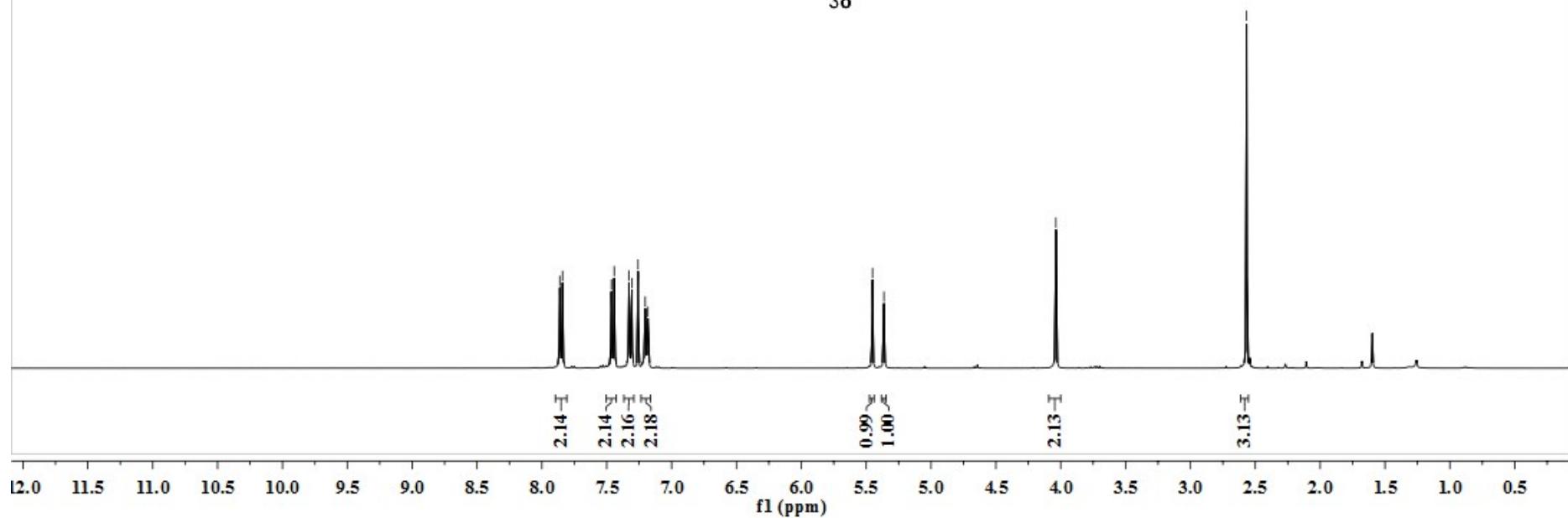
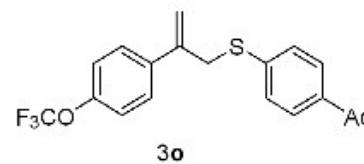
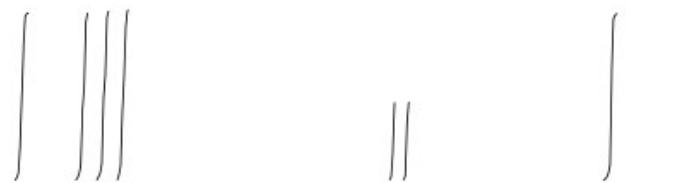
LSW4PH-SAC





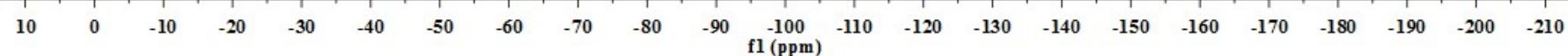
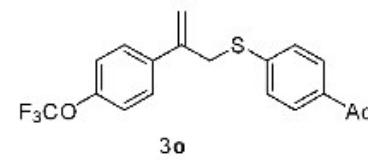
LSW-40CF<sub>3</sub>-SAC

7.86  
7.84  
7.46  
7.44  
7.33  
7.31  
7.26  
7.20  
7.18  
5.45  
~5.36  
4.04  
—2.57



LSW-40CF3-SAC

-57.80



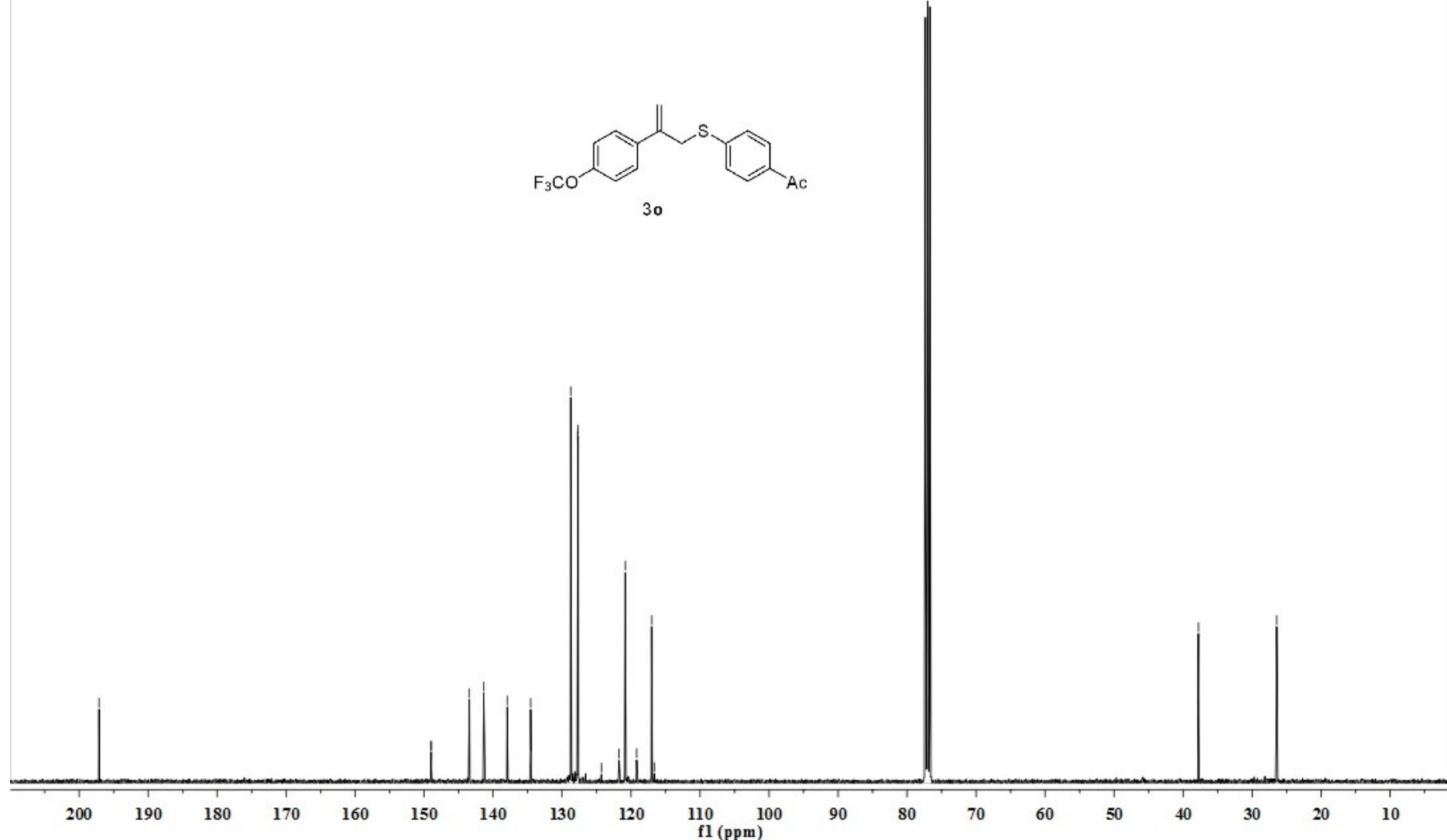
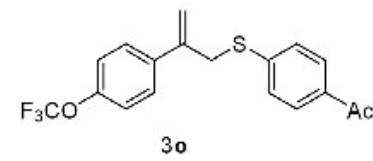
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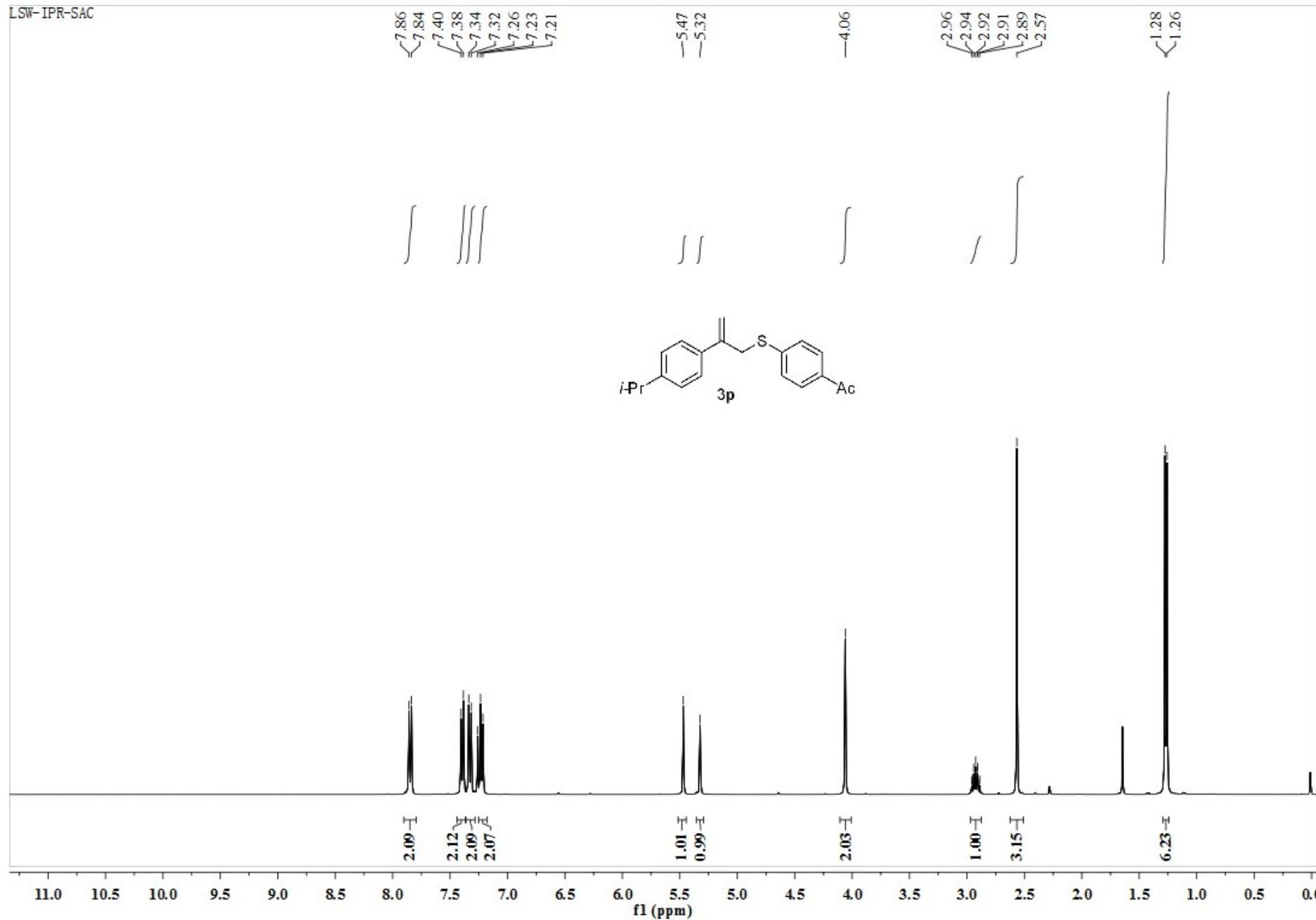
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-37.77

-26.43

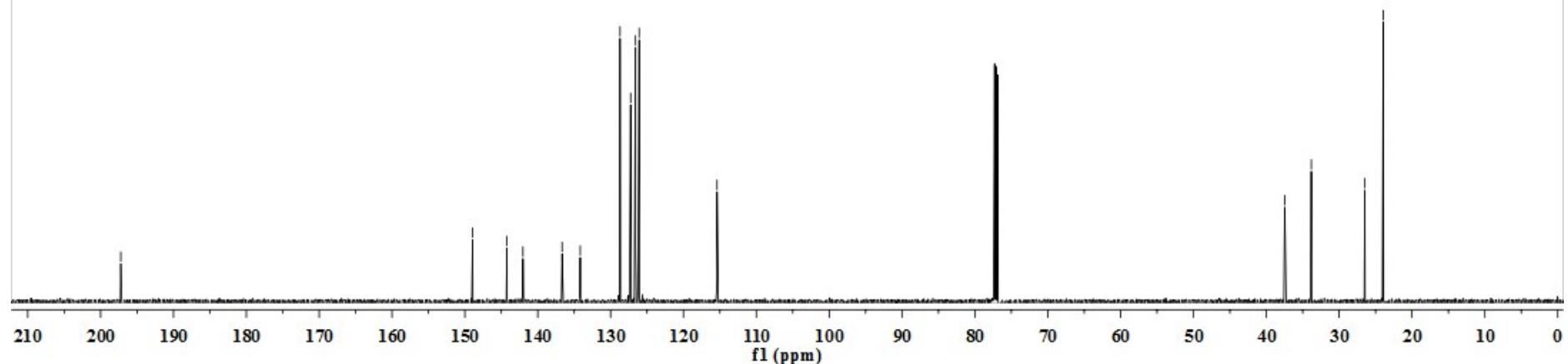
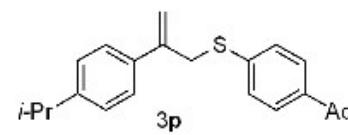


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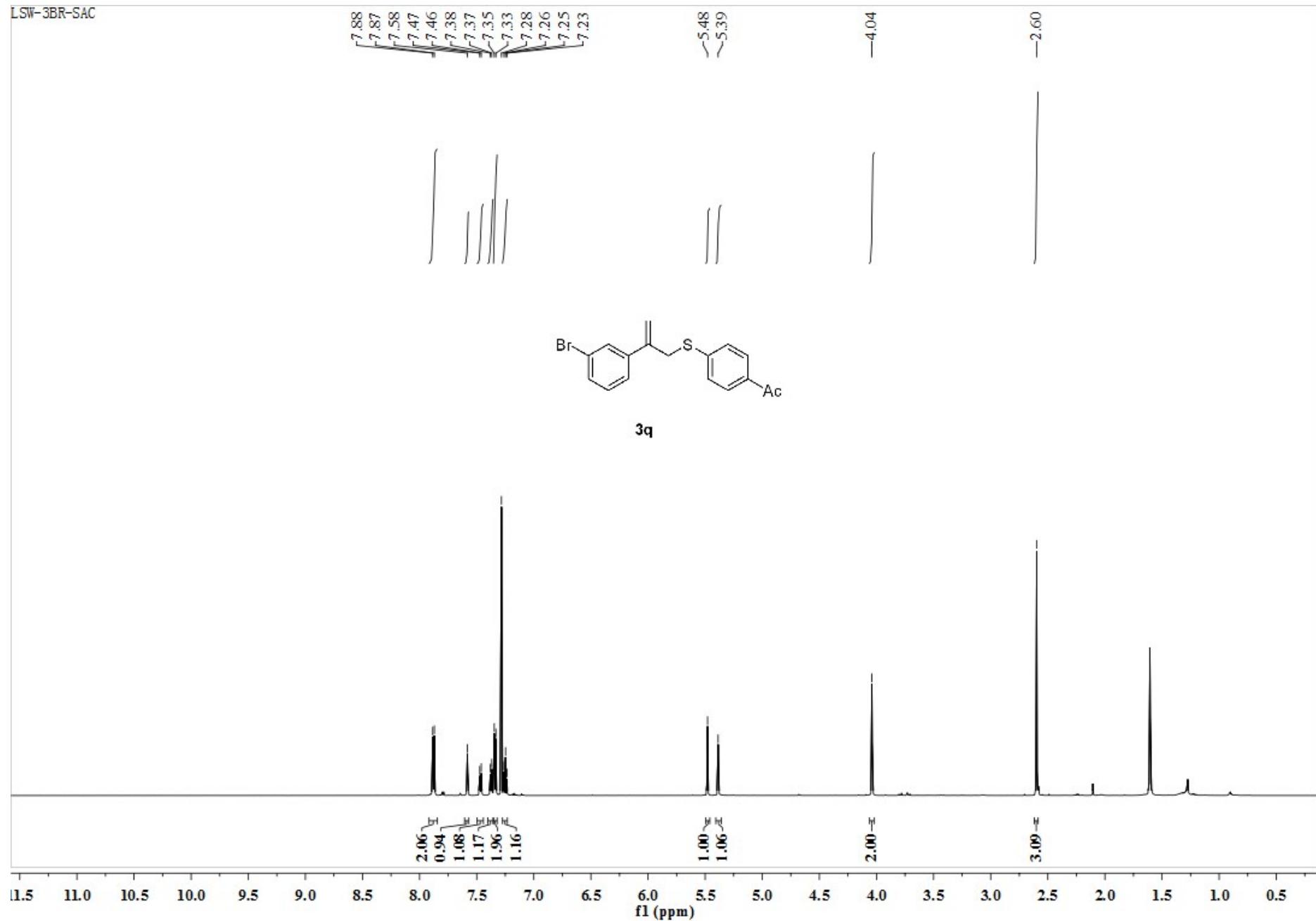


LSW-IPR-SAC  
—197.23

—148.94  
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—136.66  
—134.16  
—128.71  
—127.24  
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—23.94



LSW-3BR-SAC



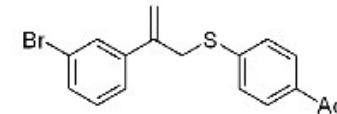
LSW-3BB-SAC-4

-197.28

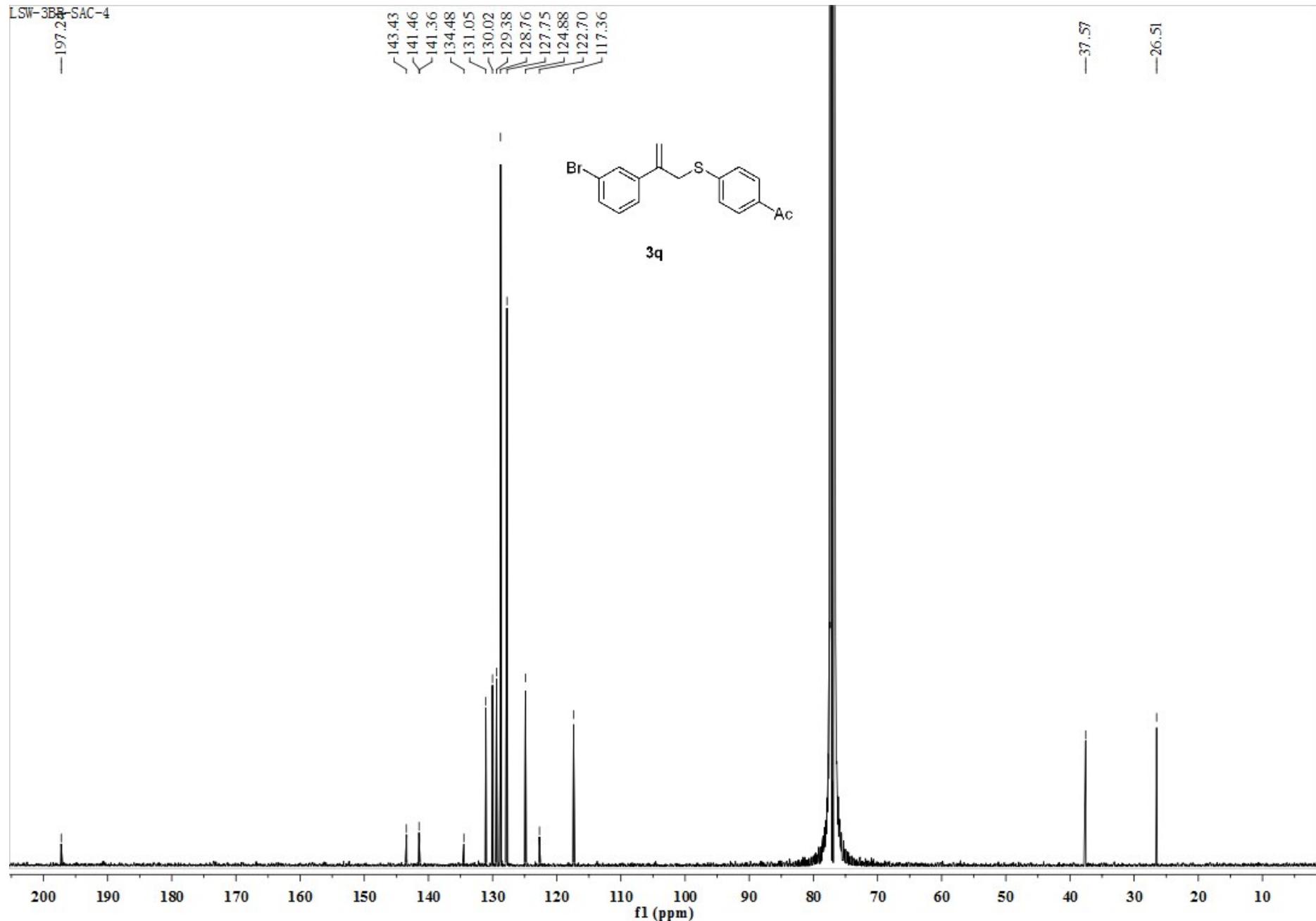
-143.43  
-141.46  
-141.36  
-134.48  
-131.05  
-130.02  
-129.38  
-128.76  
-127.75  
-124.88  
-122.70  
-117.36

-37.57

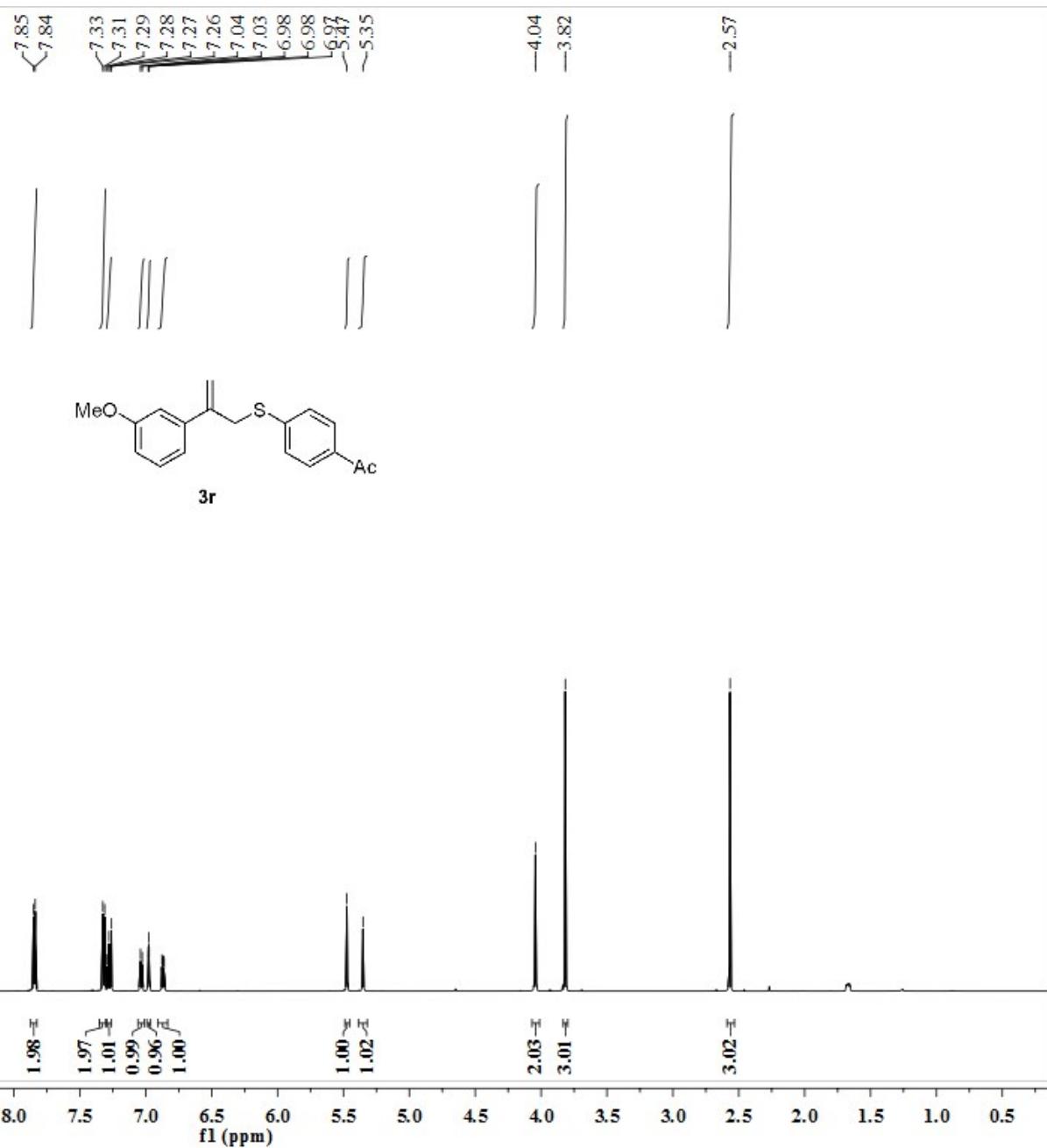
-26.51



3q

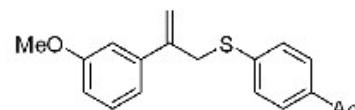


LSW-3-OME-SAC

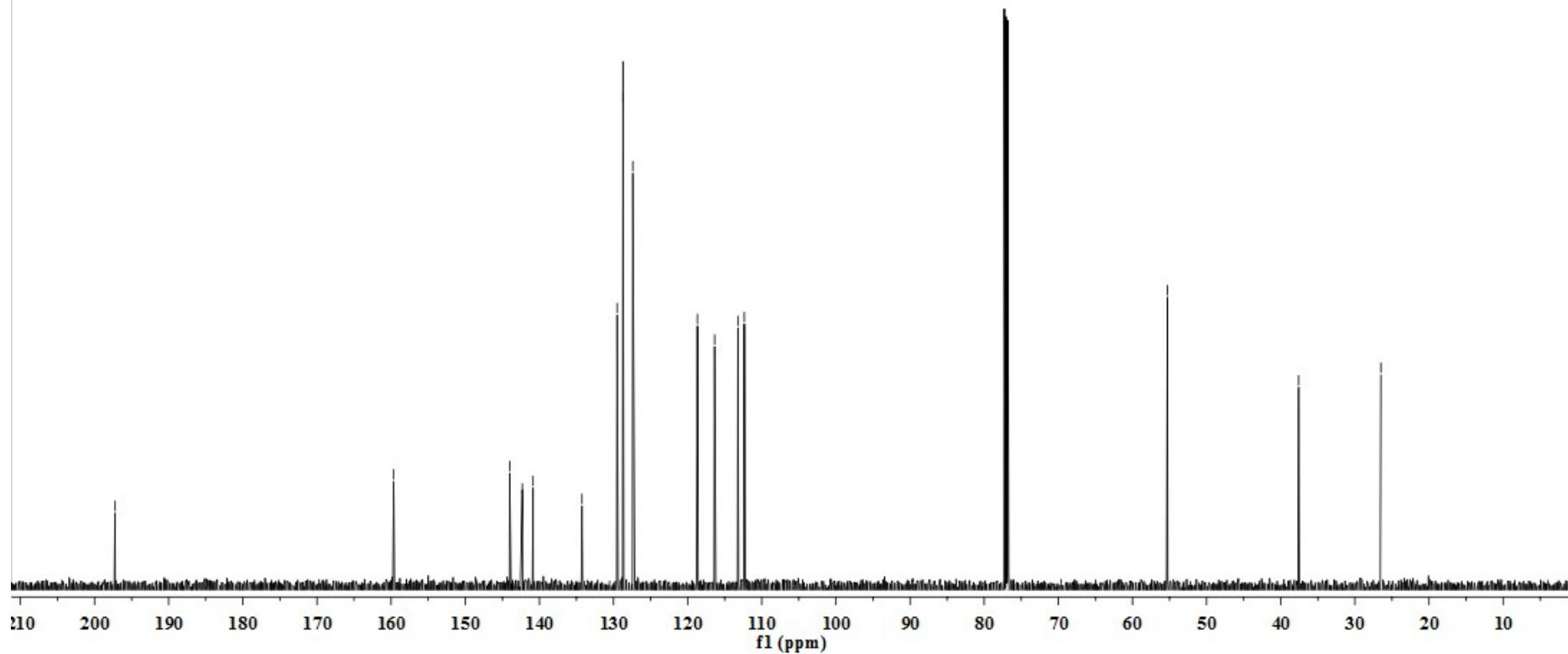


LSW-3-OME-SAC  
—197.28

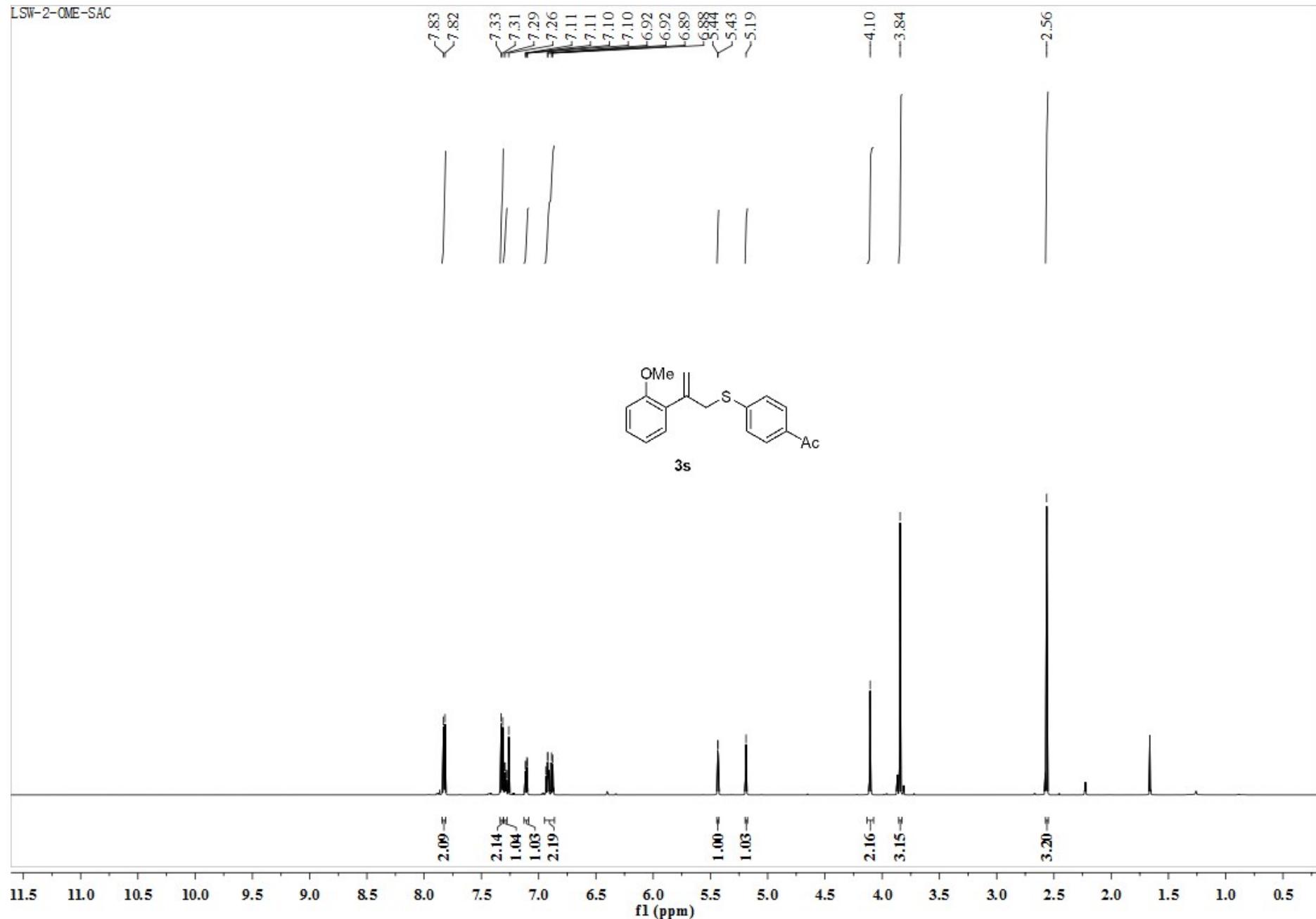
—159.66  
✓—144.00  
✓—142.30  
✓—140.85  
✓—134.25  
✓—129.52  
✓—128.72  
✓—127.39  
✓—118.68  
✓—116.36  
✓—113.22  
✓—112.35  
—55.28  
—37.59  
—26.49

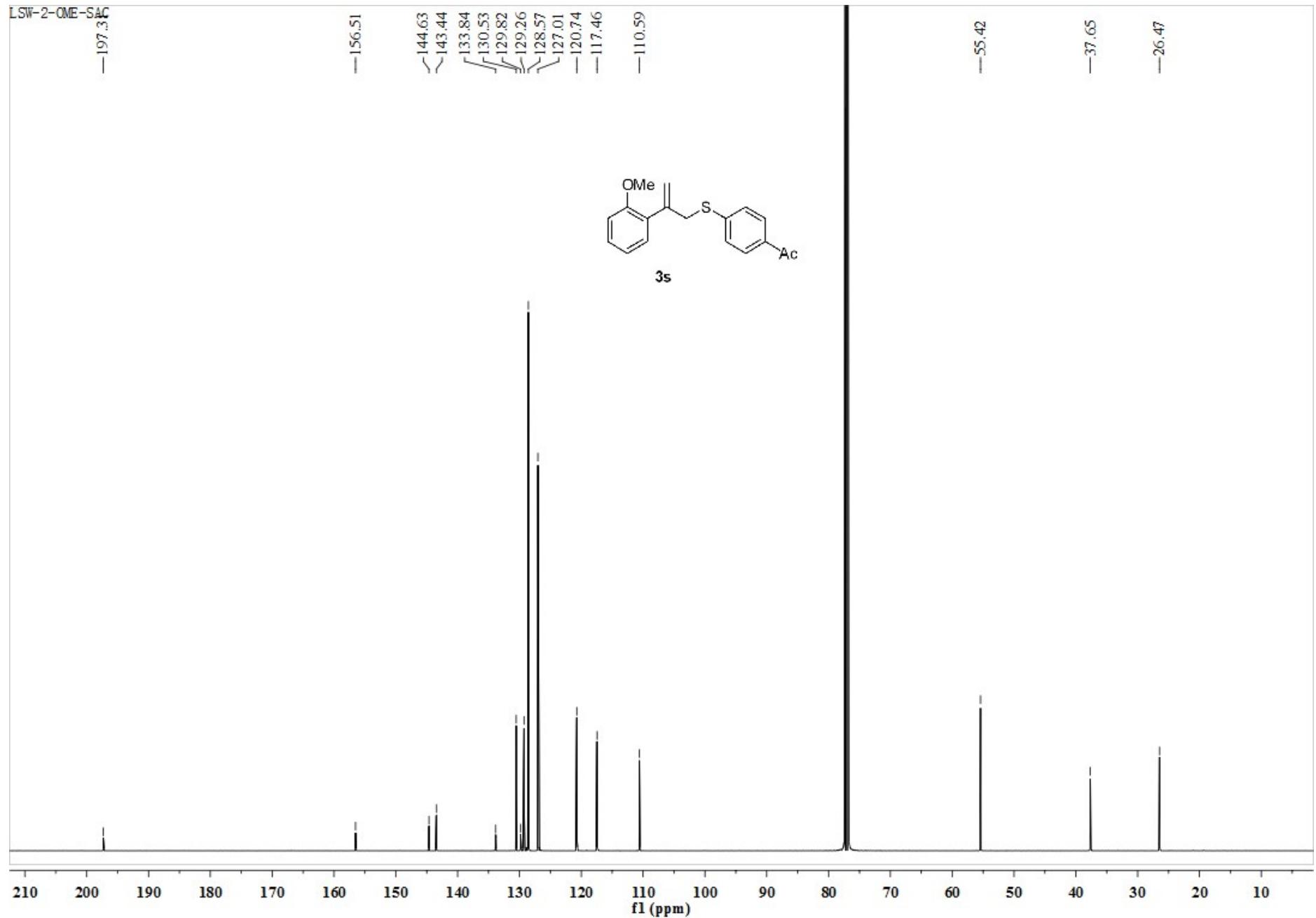


**3r**



LSW-2-OME-SAC





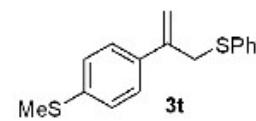
LSW-SME-STOL

7.47  
7.47  
7.45  
7.38  
7.37  
7.37  
7.36  
7.35  
7.34  
7.33  
7.32  
7.32  
7.31  
7.31  
7.26  
6.84  
6.83  
6.82  
6.82

5.32  
5.32  
5.00  
4.99

3.86  
3.80

-1.55



12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

1.98

5.08

1.99

1.02

1.00

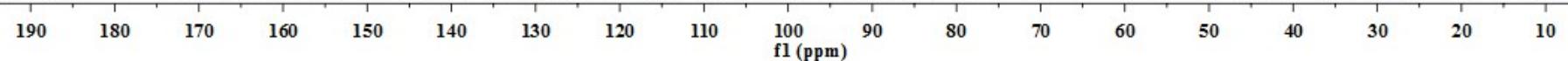
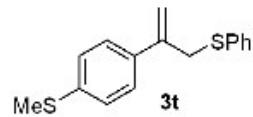
2.07

3.10

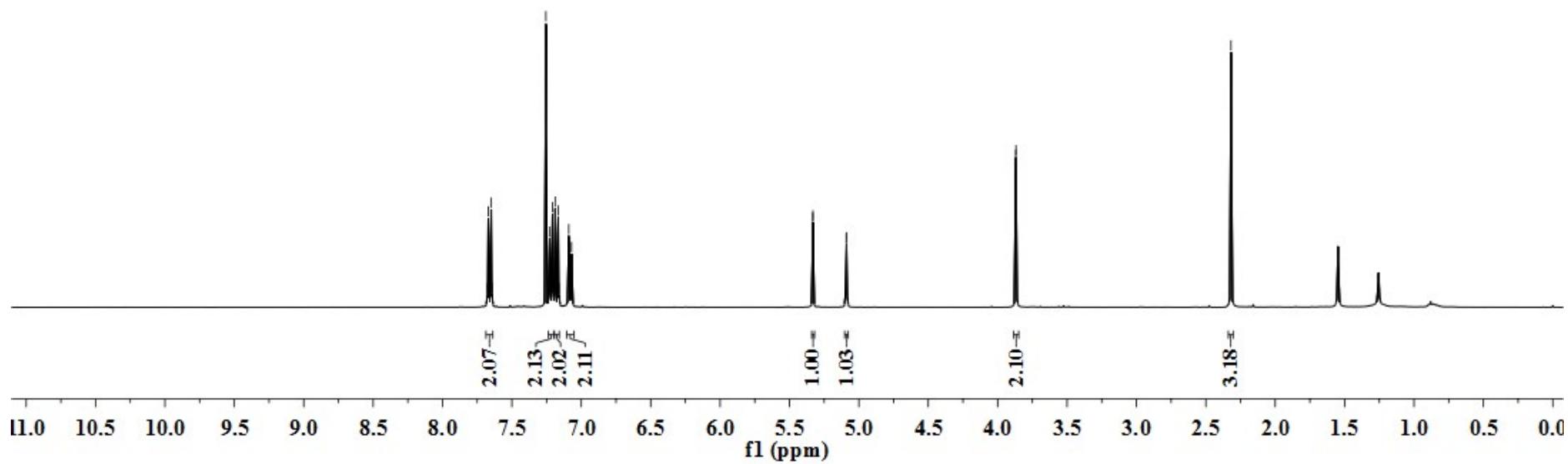
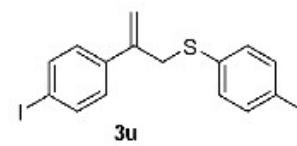
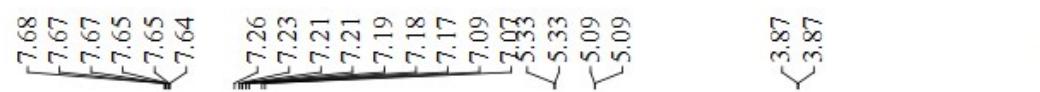
f1 (ppm)

LSW-SME-SPH

-158.24  
-142.47  
-138.52  
-133.43  
-127.32  
-126.75  
-125.31  
-125.08  
-114.39  
-113.39  
-54.28  
-40.88

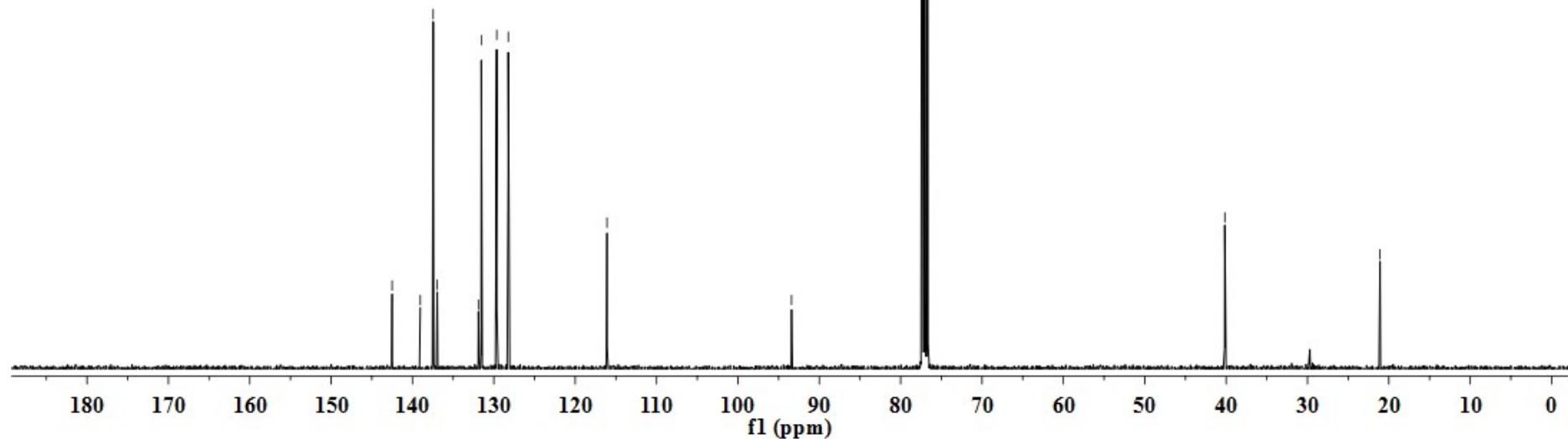
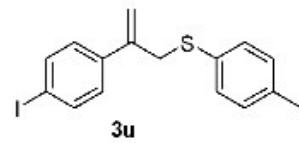


LSW-4I-STOL

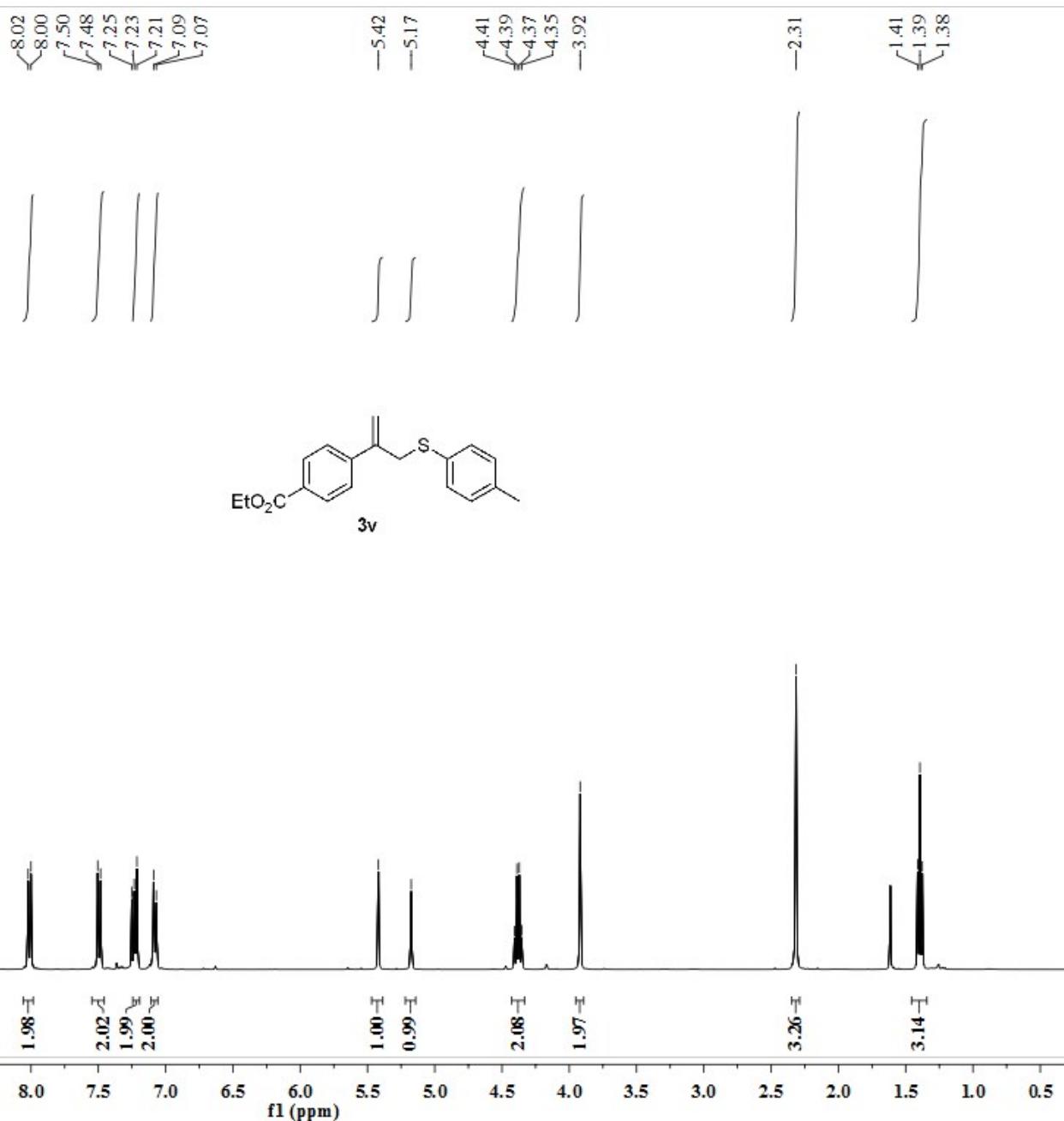


LSW-4I-STOL

142.50  
139.04  
137.45  
136.96  
131.90  
131.54  
129.64  
128.22  
-116.09  
-93.41  
-40.16  
-21.09



LSW-4C02ME-SME



LSW-4C02ET-SME

-166.37

>143.97  
>-142.78  
>136.98  
∫-131.88  
∫-131.59  
<-129.76  
<-129.65  
>-126.28

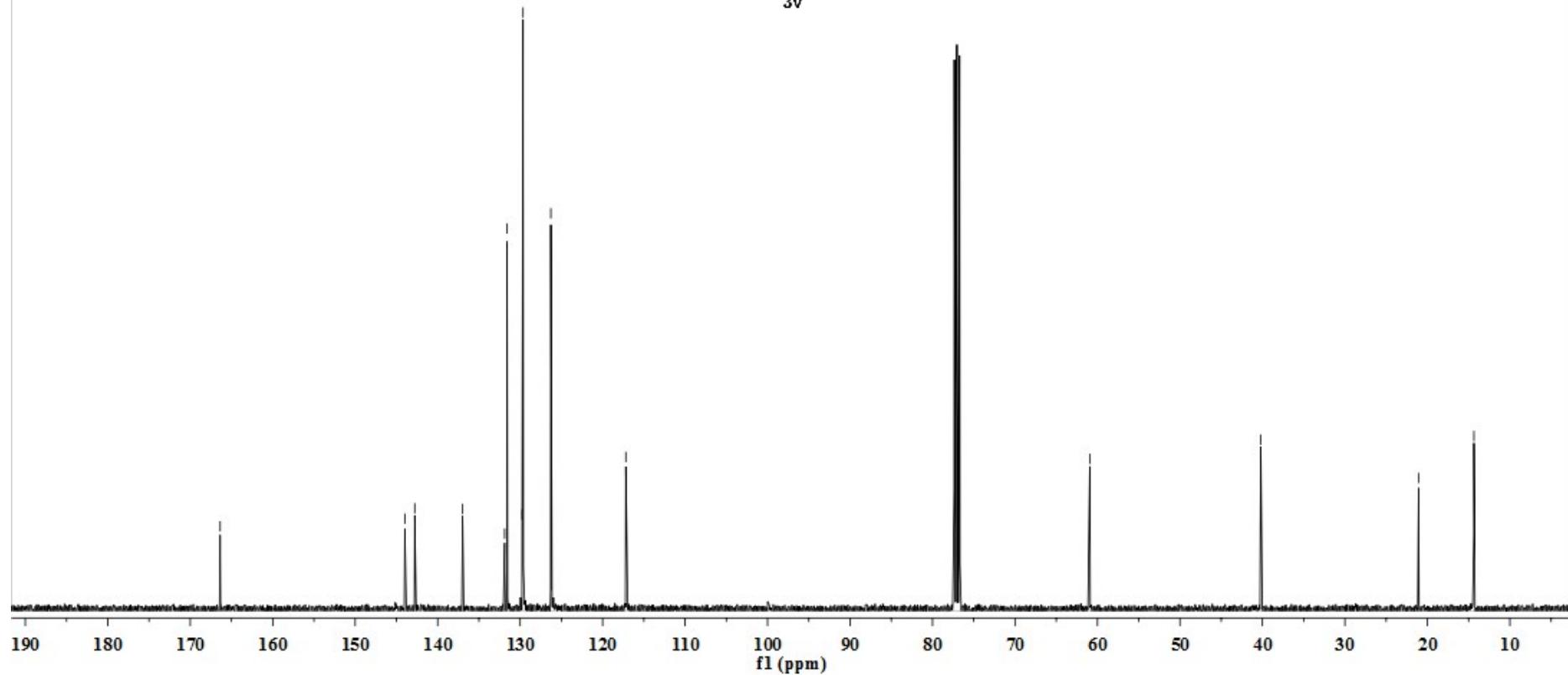
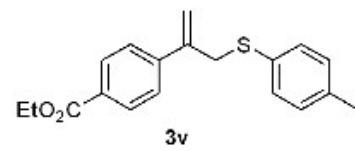
-117.19

-60.93

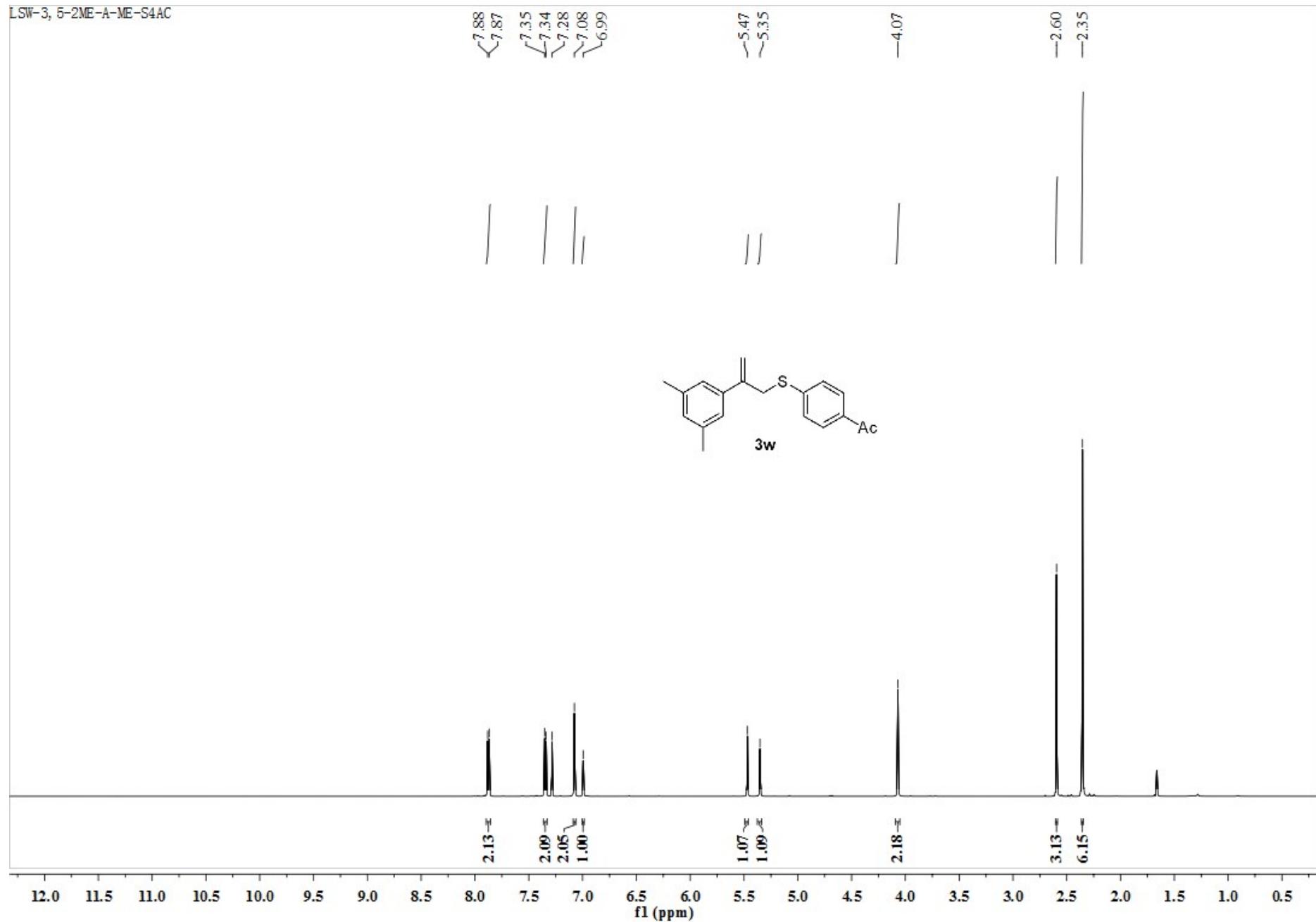
-40.19

-21.07

-14.36



LSW-3, 5-2ME-A-ME-S4AC



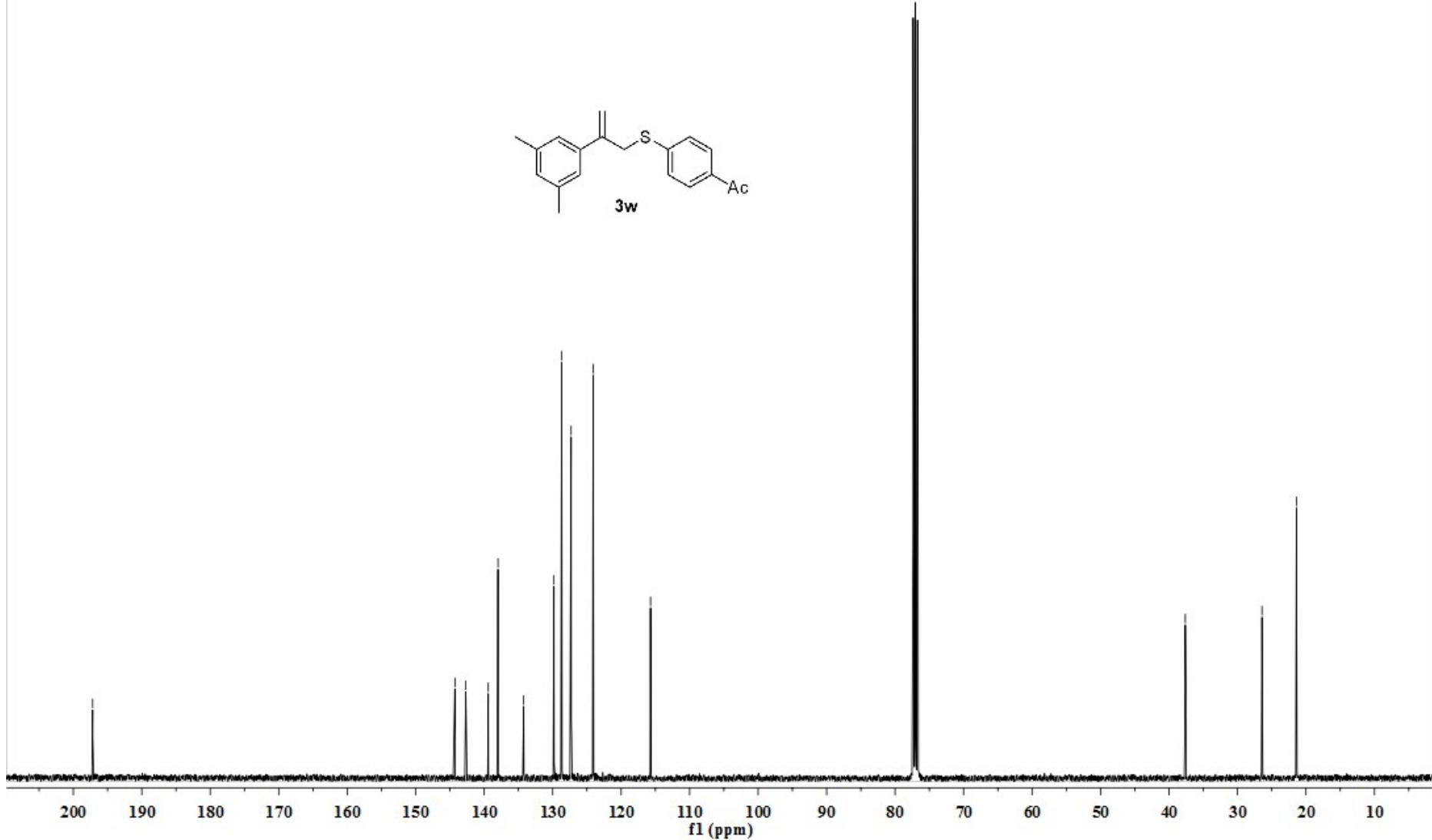
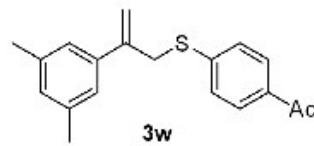
LSW-3, 5-2ME-SAC

-197.1

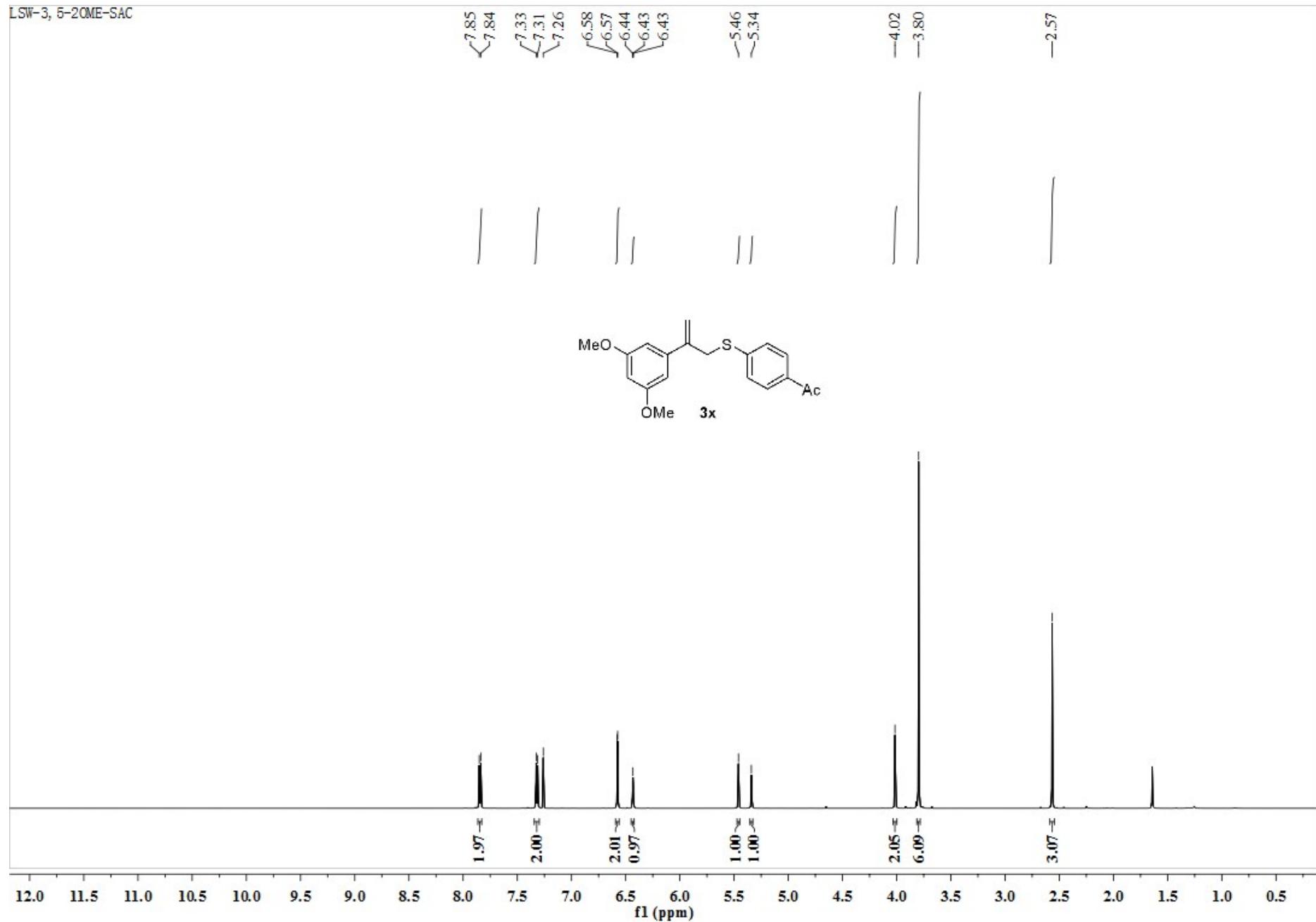
✓-144.27  
✓-142.69  
✓-139.41  
✓-137.98  
-134.23  
✓-129.81  
✓-128.68  
✓-127.31  
✓-124.09

-115.71

-37.63  
-26.43  
-21.39



LSW-3, 5-20ME-SAC



LSW-3, 5-2QME-SAC

-197.2

-160.79

>143.99  
>142.47  
>141.60

>-134.26  
>-128.72  
>-127.41

-116.43

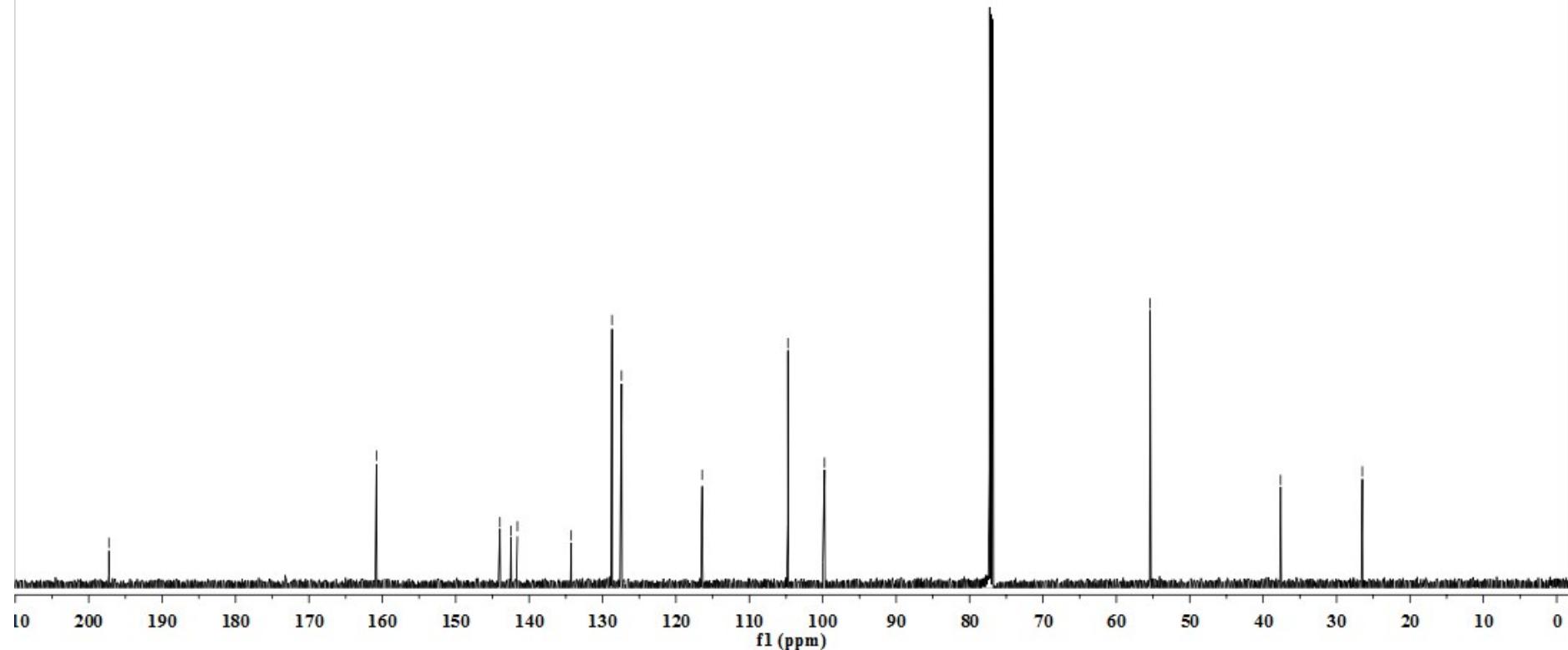
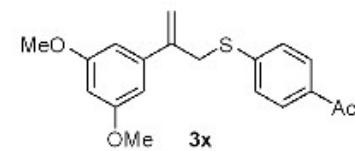
-104.74

-99.75

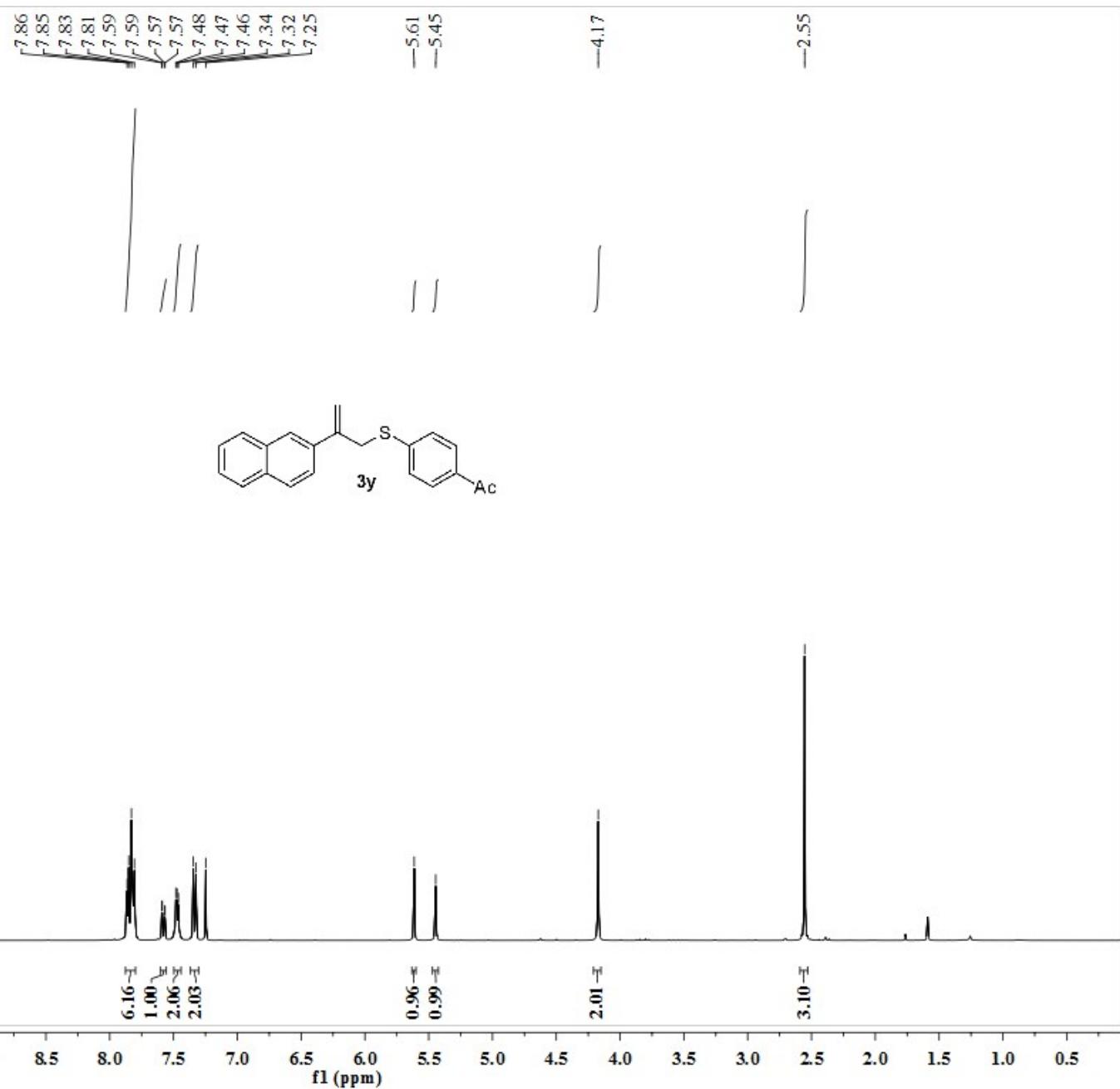
-55.39

-37.62

-26.49



LSW-NAI-SAC



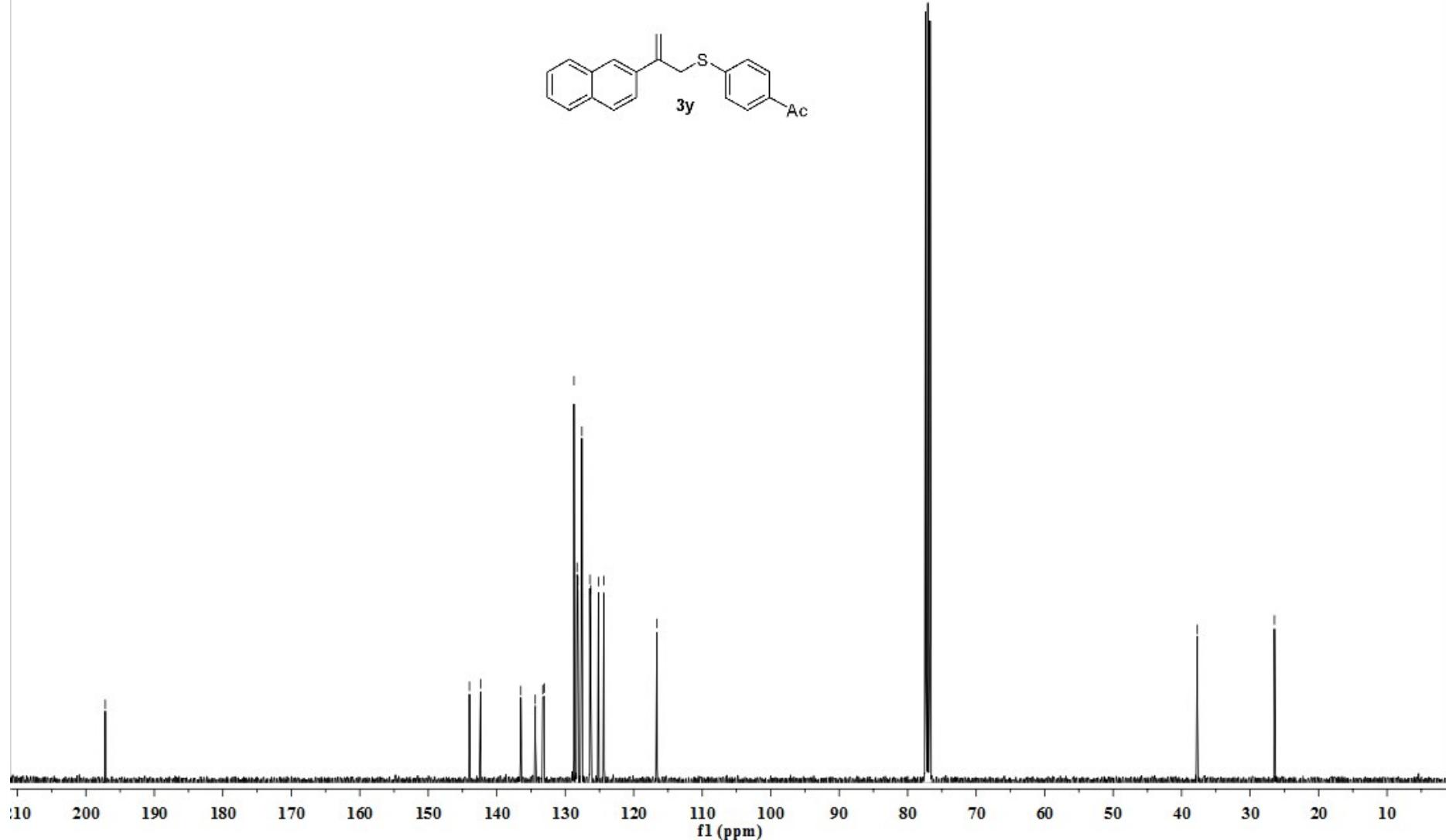
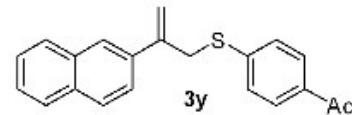
LSW-NAI-SAC<sub>1</sub>

—197.1

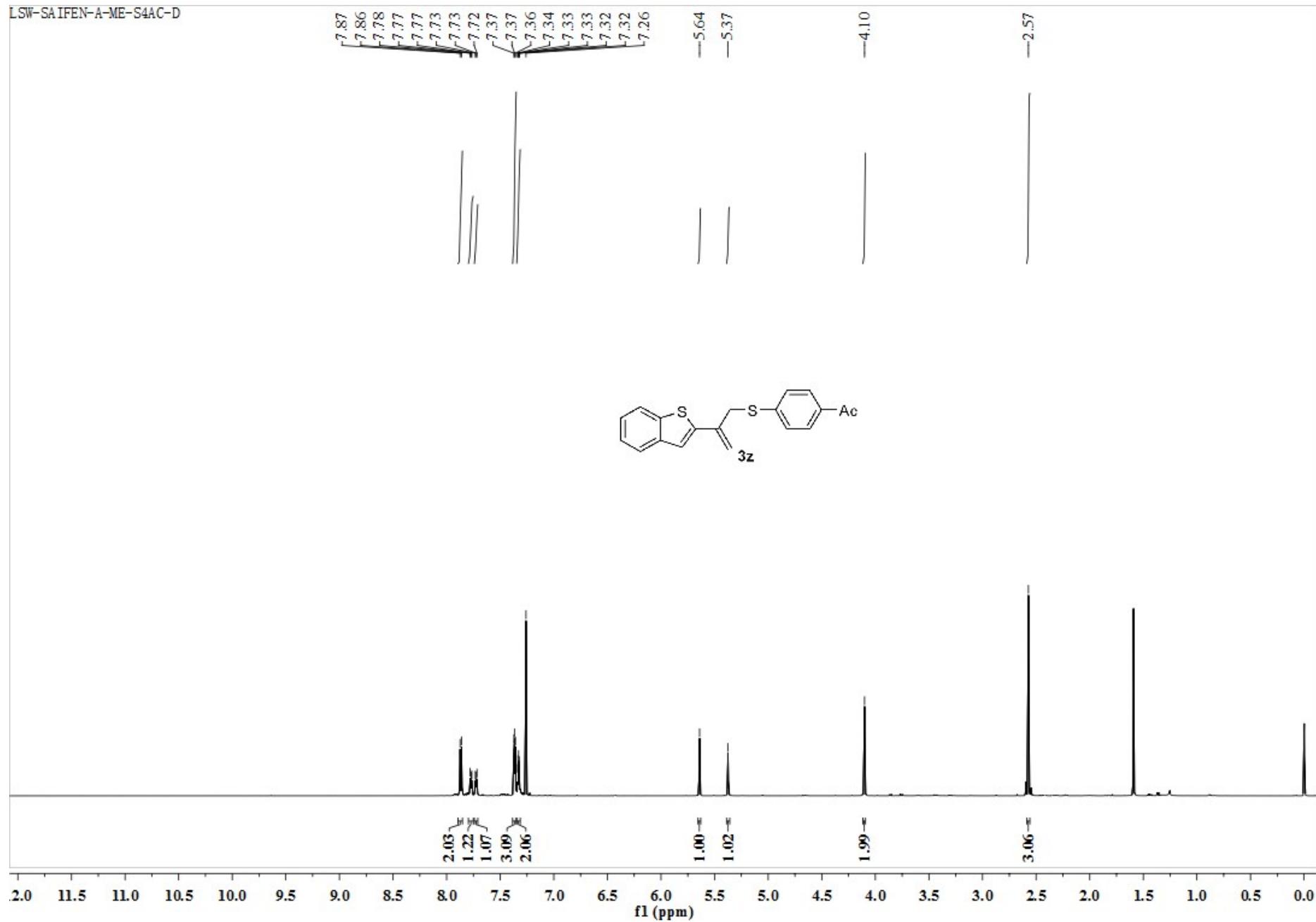
—143.98  
—142.36  
—136.49  
—134.37  
—133.29  
—133.08  
—128.73  
—128.28  
—128.15  
—127.61  
—127.57  
—126.39  
—126.26  
—125.14  
—124.34  
—116.61

—37.71

—26.45



LSW-SAIFEN-A-ME-S4AC-D



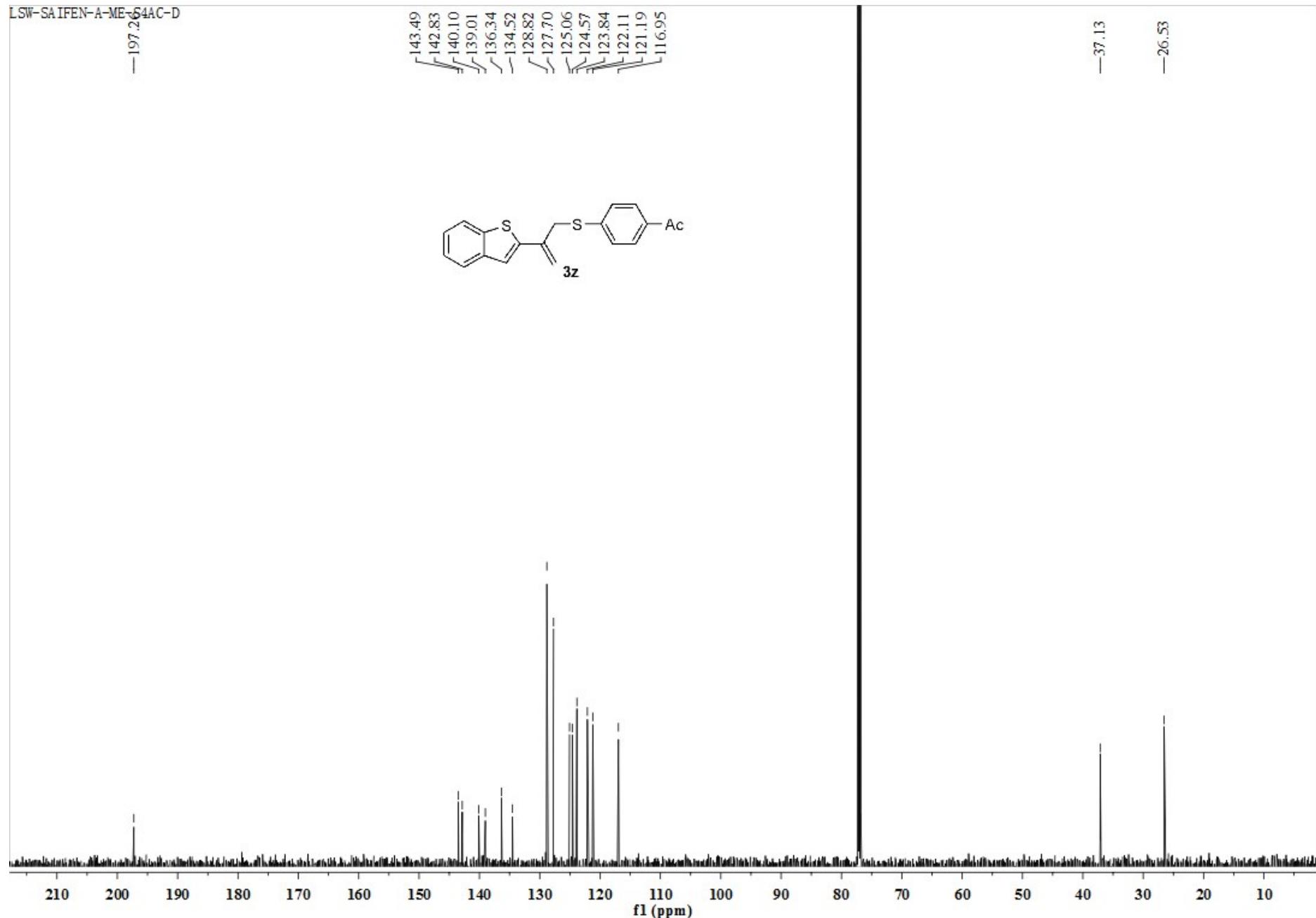
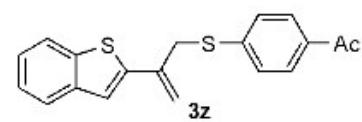
LSW-SAIFEN-A-ME-S4AC-D

-197.23

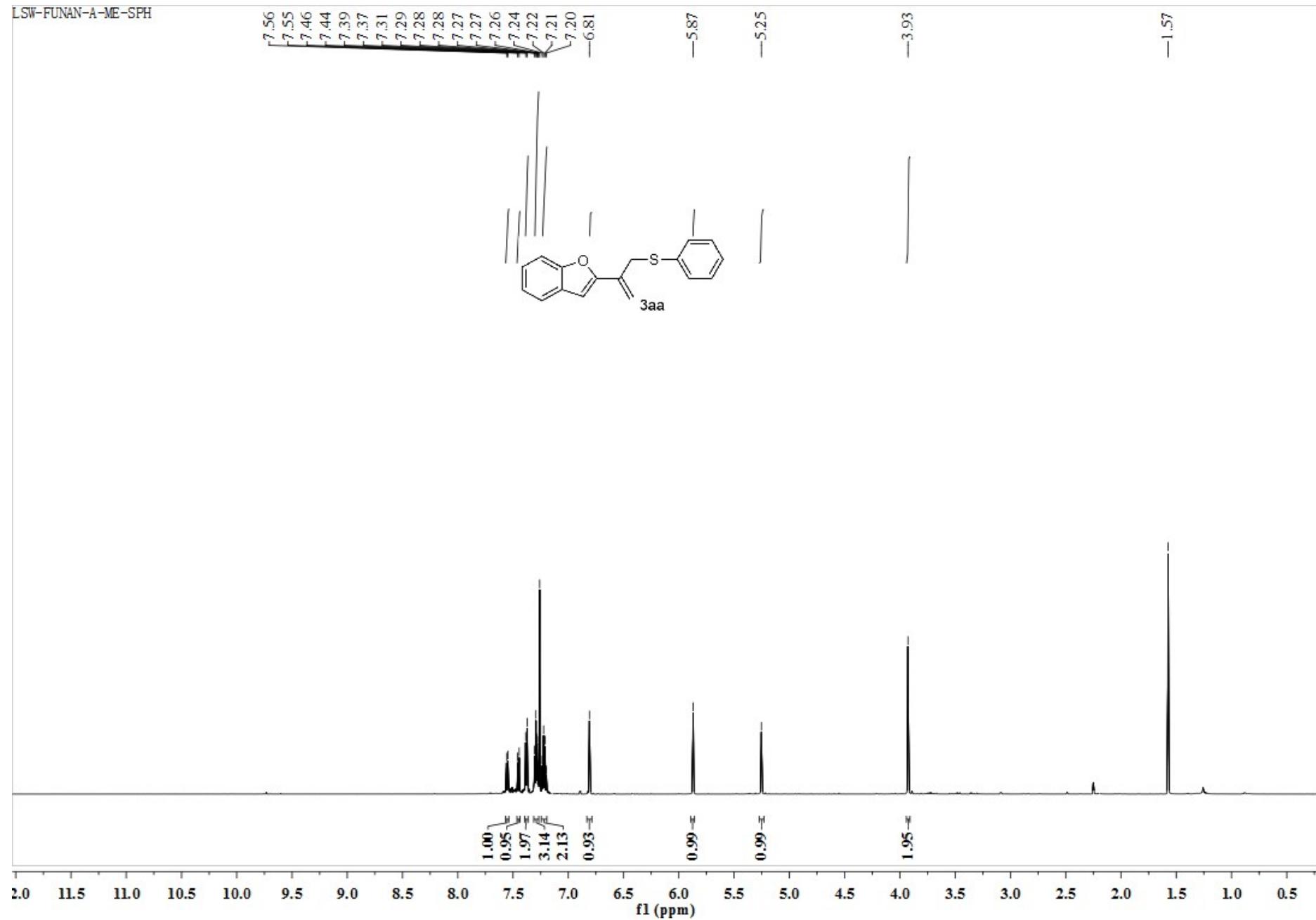
143.49  
142.83  
140.10  
139.01  
136.34  
134.52  
128.82  
127.70  
125.06  
124.57  
123.84  
122.11  
121.19  
116.95

-37.13

-26.53

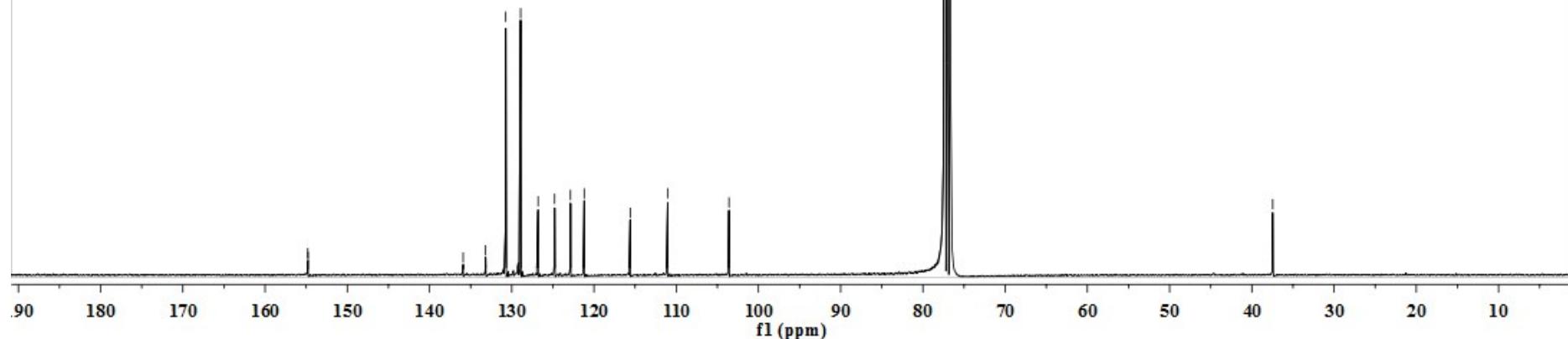
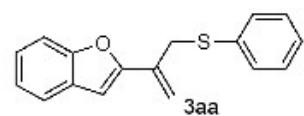


LSW-FUNAN-A-ME-SPH



LSW-FUNAN-SPH

-154.80  
-154.77  
-135.91  
-133.18  
-130.73  
-128.92  
-126.79  
-124.78  
-122.86  
-121.18  
-115.60  
-111.04  
-103.58  
-37.46



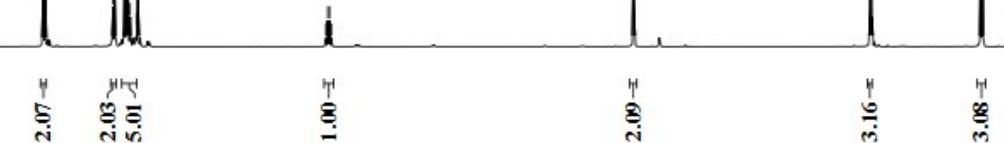
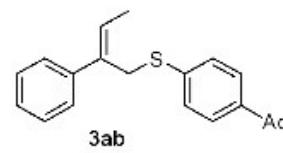
LSW-ET-SAC



—4.11

—2.60

1.89  
1.88



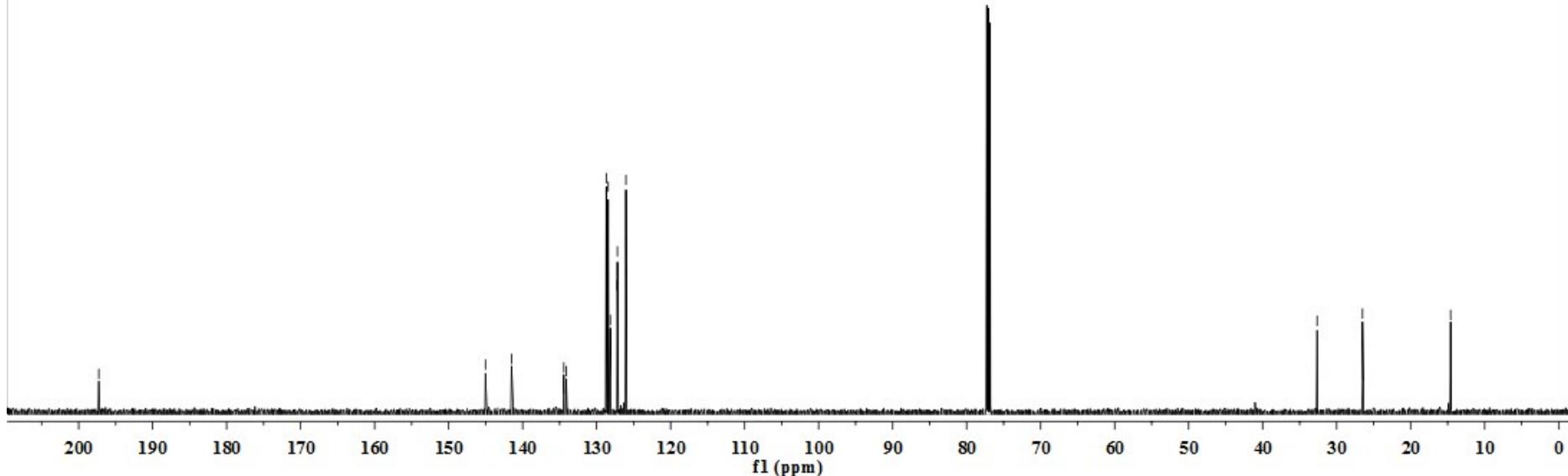
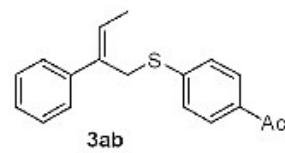
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

f1 (ppm)

LSW-ET-SAC  
—197.2<sup>y</sup>

—145.02  
—141.50  
∫134.44  
∫134.11  
∫128.70  
∫128.44  
—128.15  
—127.23  
—127.20  
—126.04

—32.64  
—26.50  
—14.59



LSW-PHDING-SAC

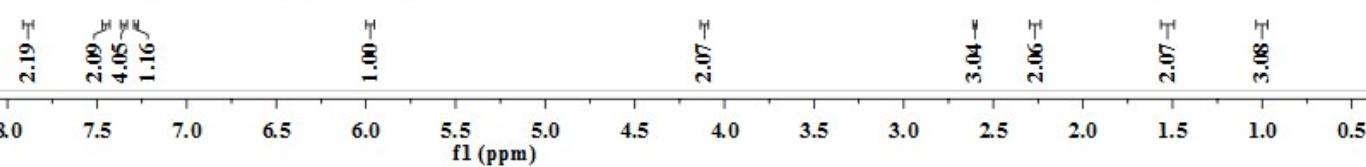
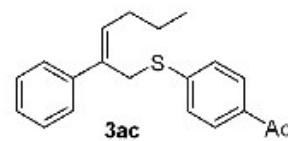
7.89  
7.88  
7.46  
7.45  
7.36  
7.35  
7.34  
7.28

5.99  
5.98  
5.96

4.11

2.60

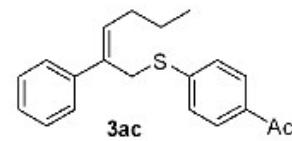
2.27  
2.26  
2.24  
1.69  
1.54  
1.53  
1.52  
1.51  
1.01  
0.99  
0.98



LSW-PHDING-SAC

-197.24

-145.14  
-141.55  
-134.16  
-134.07  
-133.47  
-128.71  
-128.43  
-127.25  
-127.06  
-127.00  
-126.14



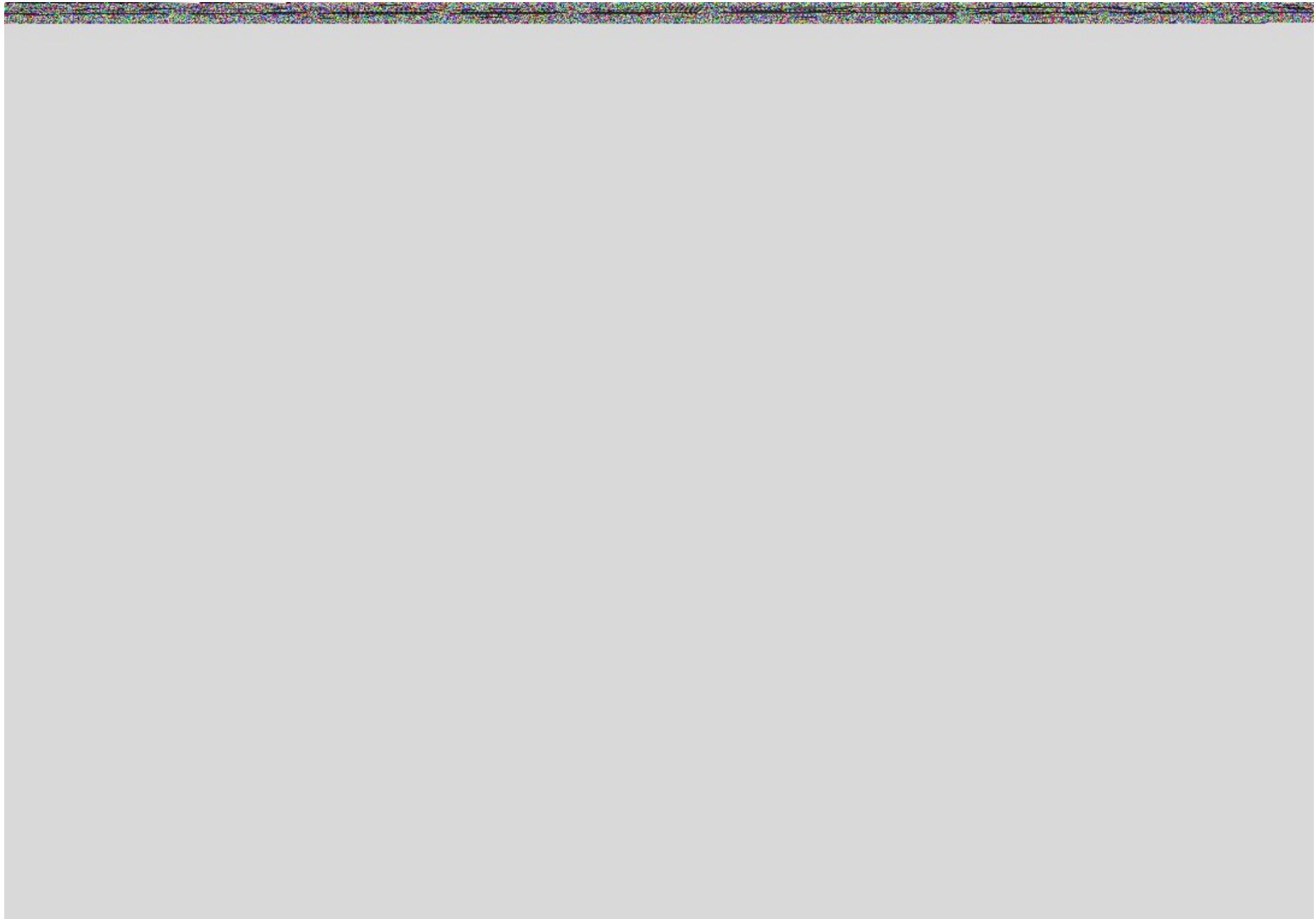
3ac

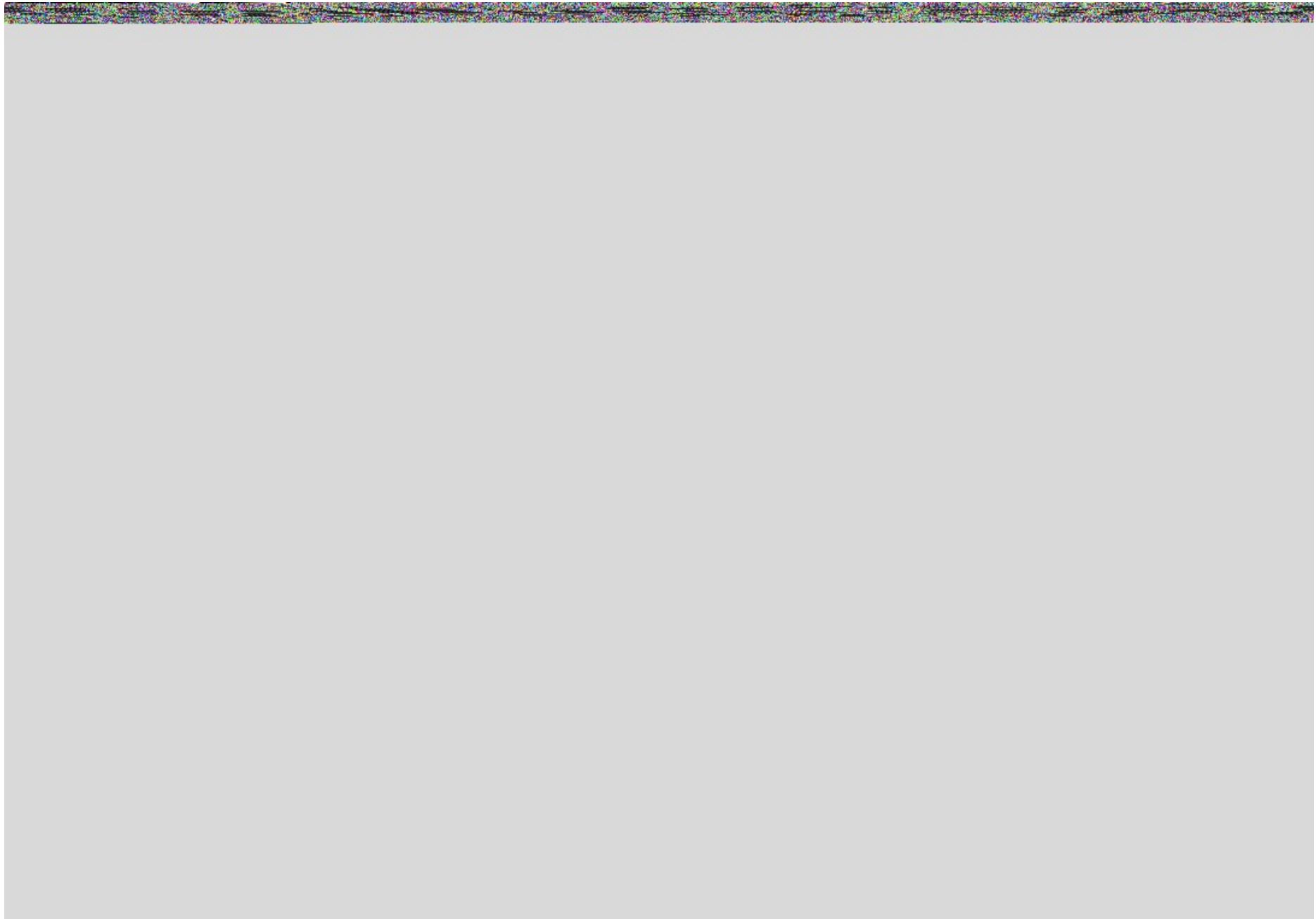
>32.88  
>31.04  
>26.50  
>22.80

-13.96

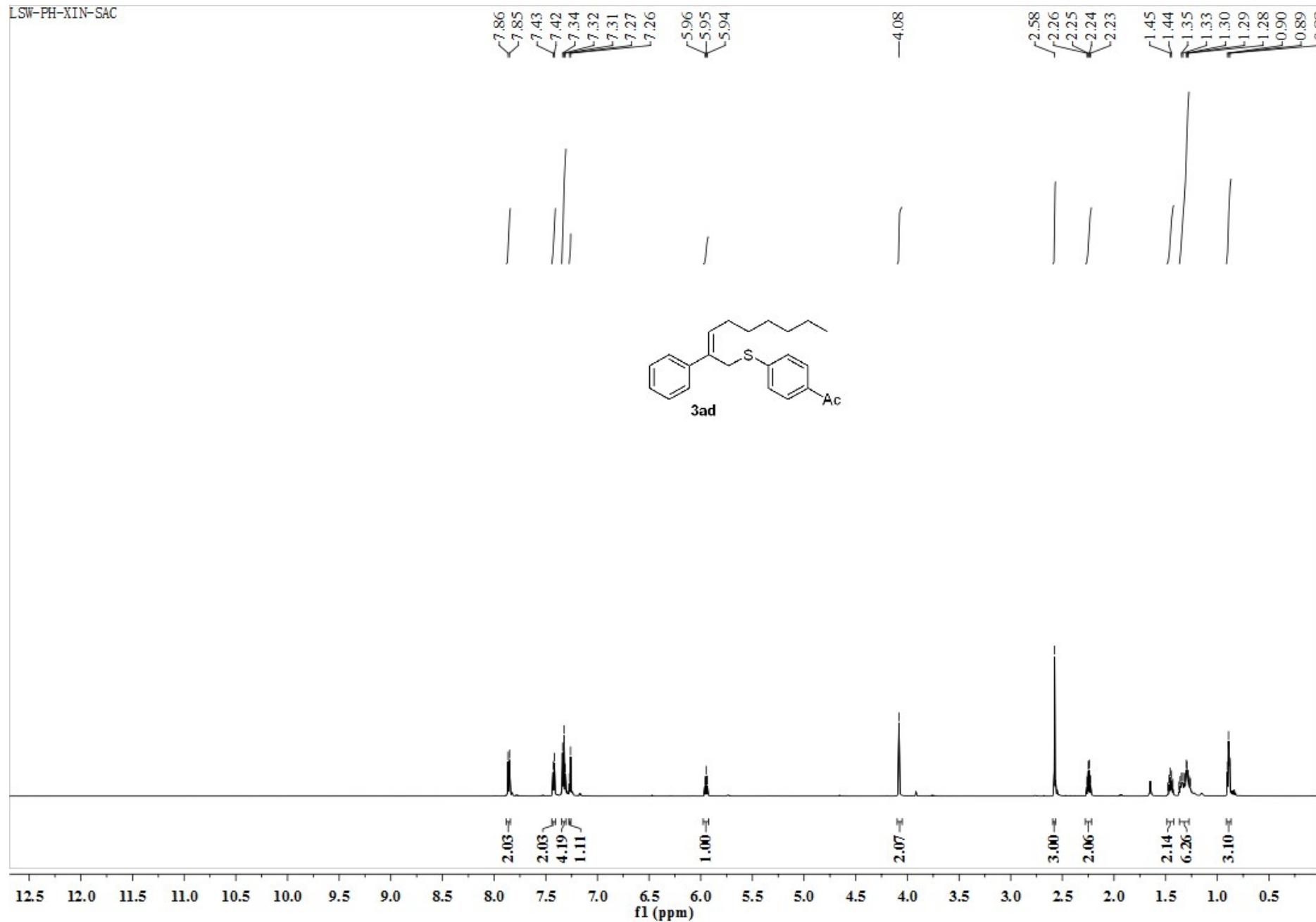
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)





LSW-PH-XIN-SAC

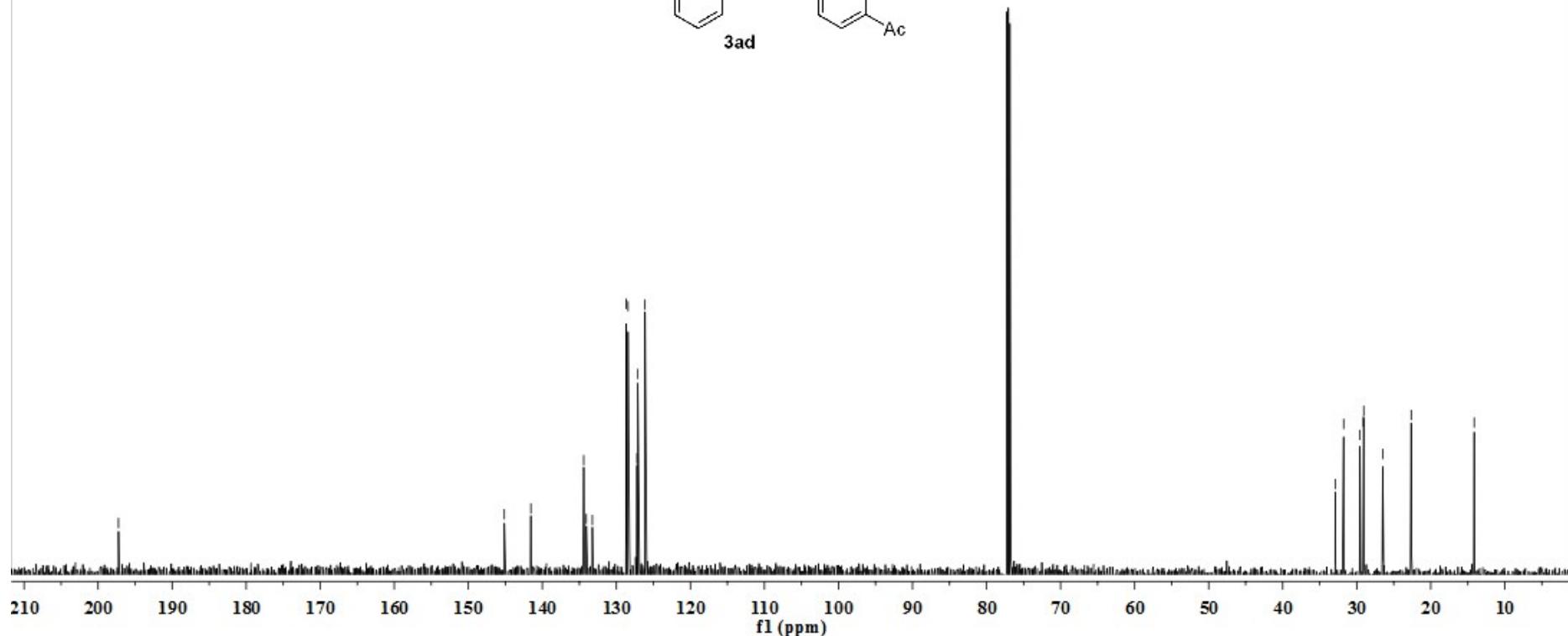
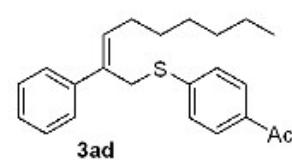


LSW-PH-XIN-SAC

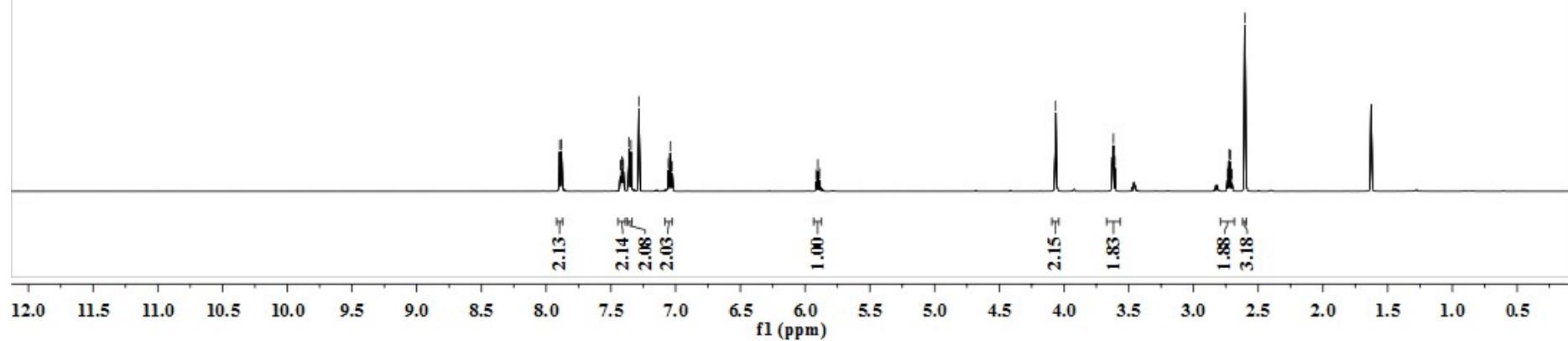
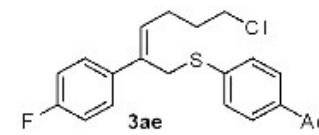
-197.2

-145.13  
-141.55  
-134.41  
-134.07  
-133.25  
-128.70  
-128.42  
-127.22  
-127.11  
-126.13

-32.90  
-31.76  
-29.57  
-29.10  
-29.05  
-26.49  
-22.65  
-14.13



LSW-4CL-4F-SAC-1



LSW-4F4CL-SA6

-197.26

-163.20

-161.57

-144.02

-135.75

-134.49

-128.89

-128.80

-127.97

-127.92

-127.59

-125.24

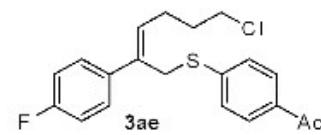
-115.30

-43.81

-33.31

-32.04

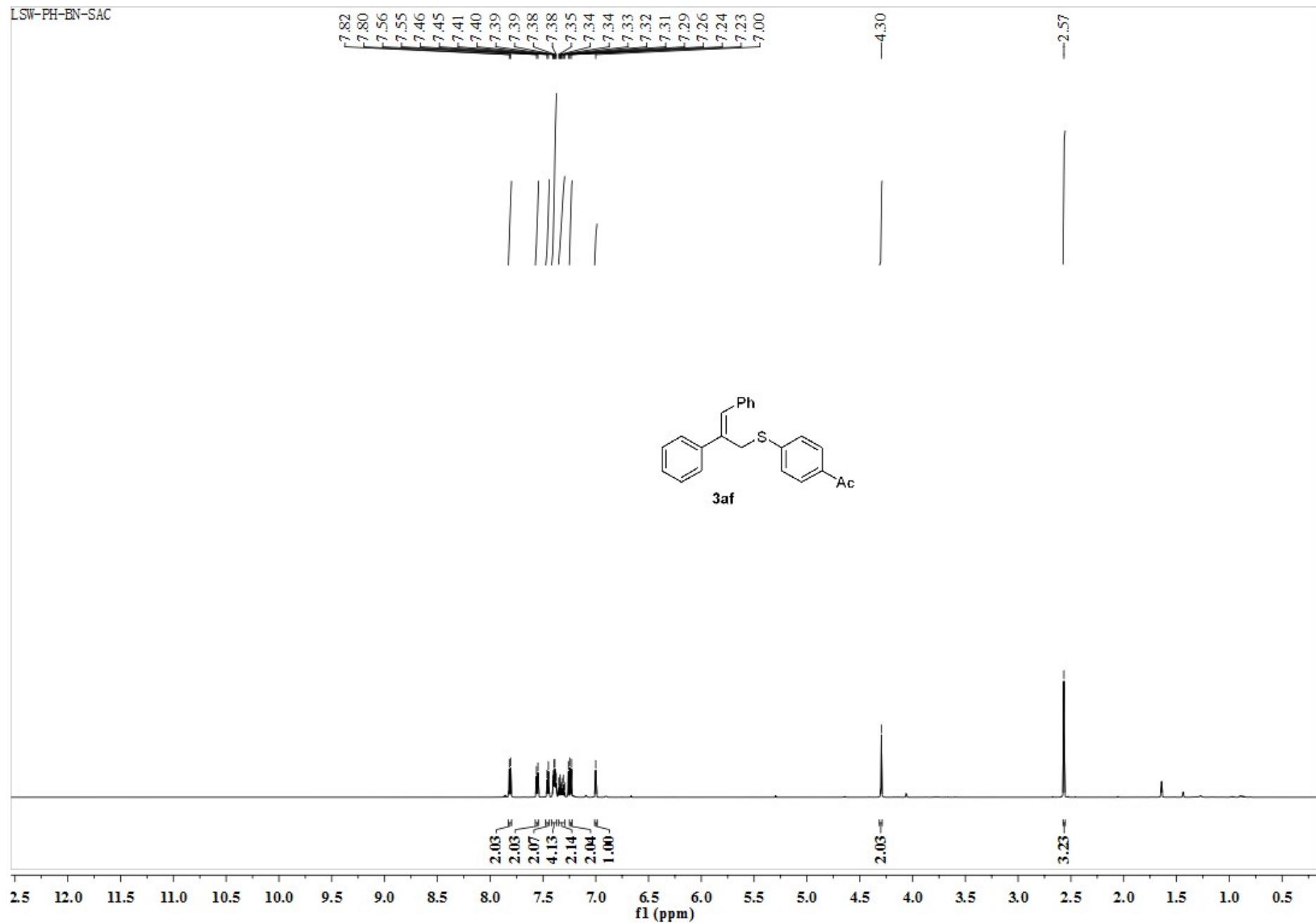
-26.52



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

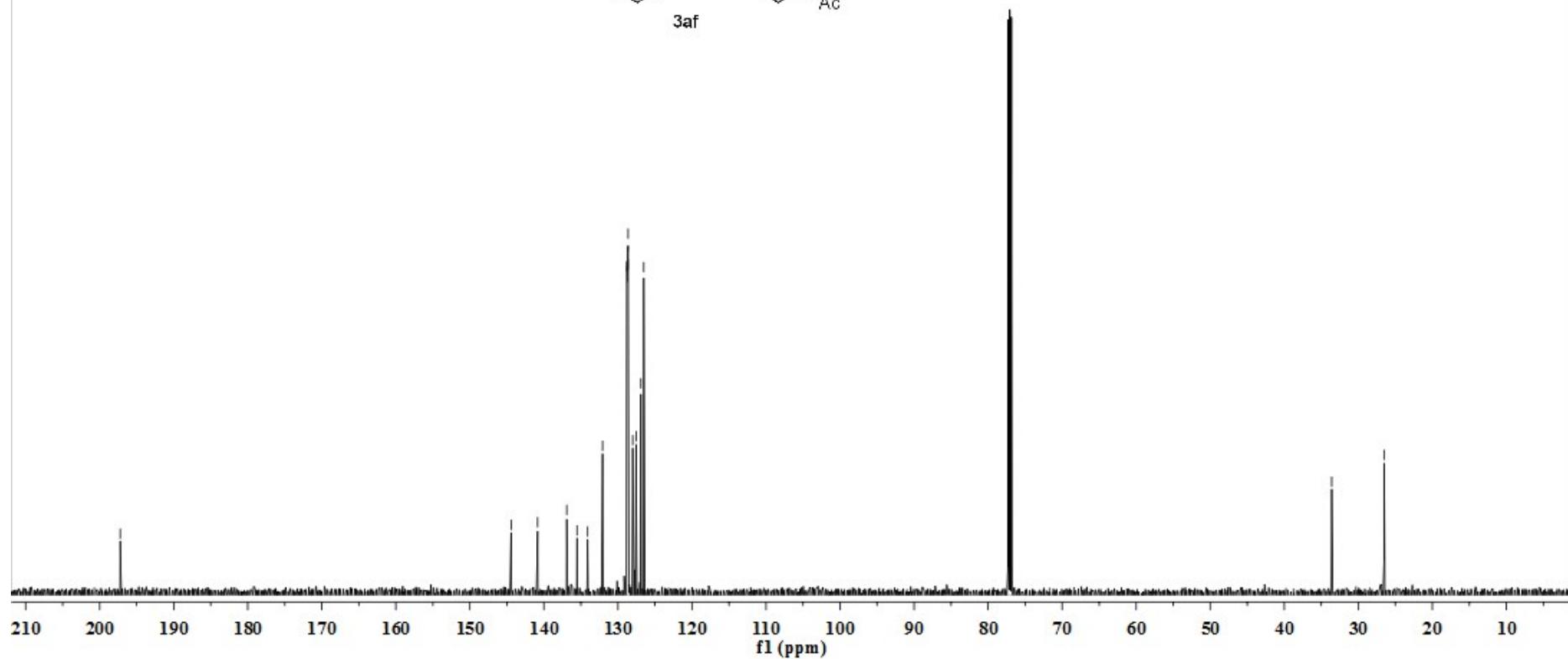
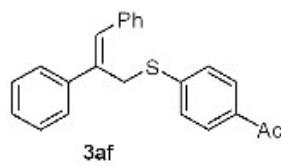
f1 (ppm)

LSW-PH-BN-SAC

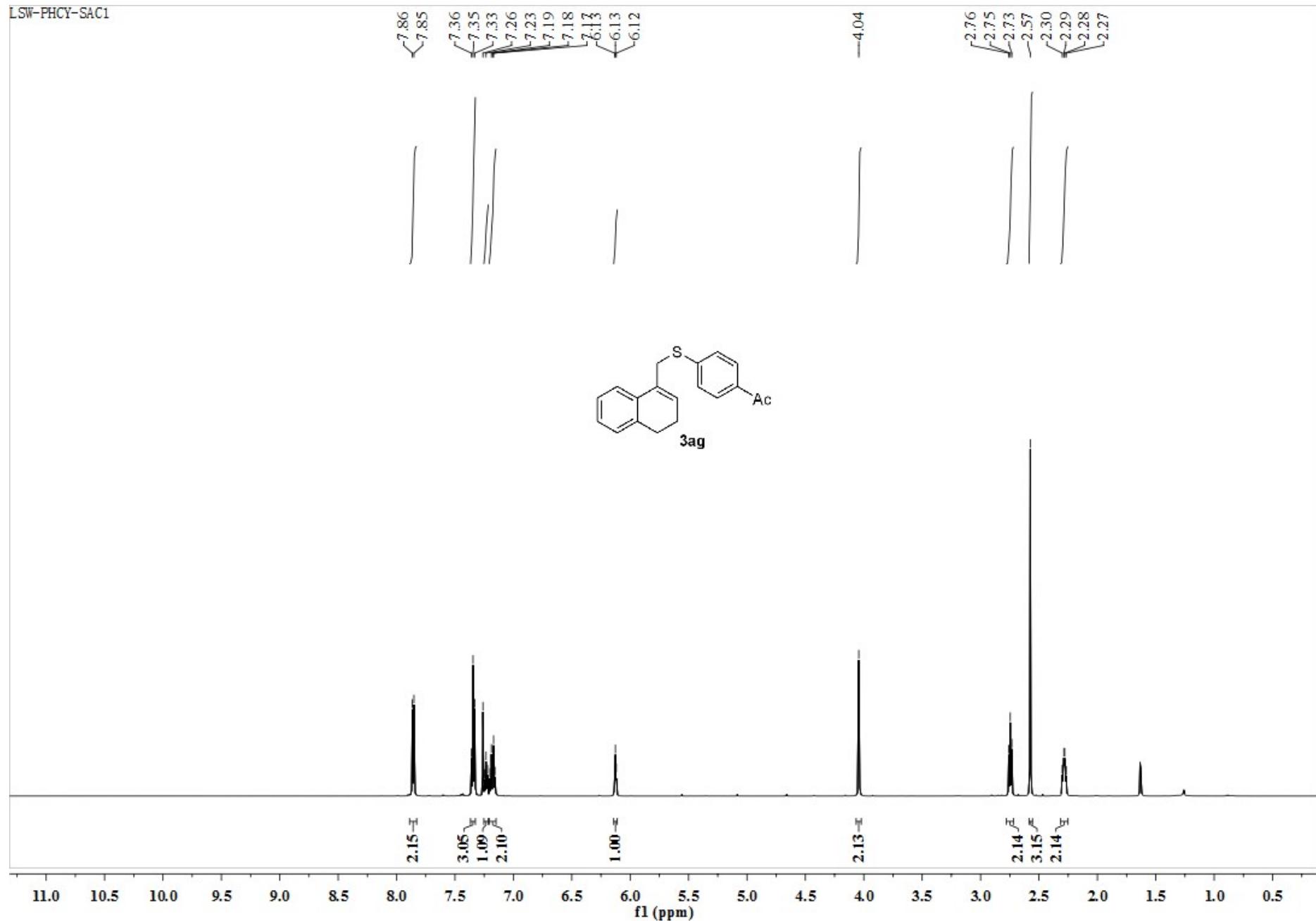


LSW-PH-BN-SAC  
—197.28

—144.43  
—140.85  
—136.91  
—135.53  
—134.10  
—132.07  
—128.81  
—128.73  
—128.64  
—128.63  
—128.00  
—127.55  
—126.90  
—126.51  
—33.88  
—26.50



LSW-PHCY-SAC1

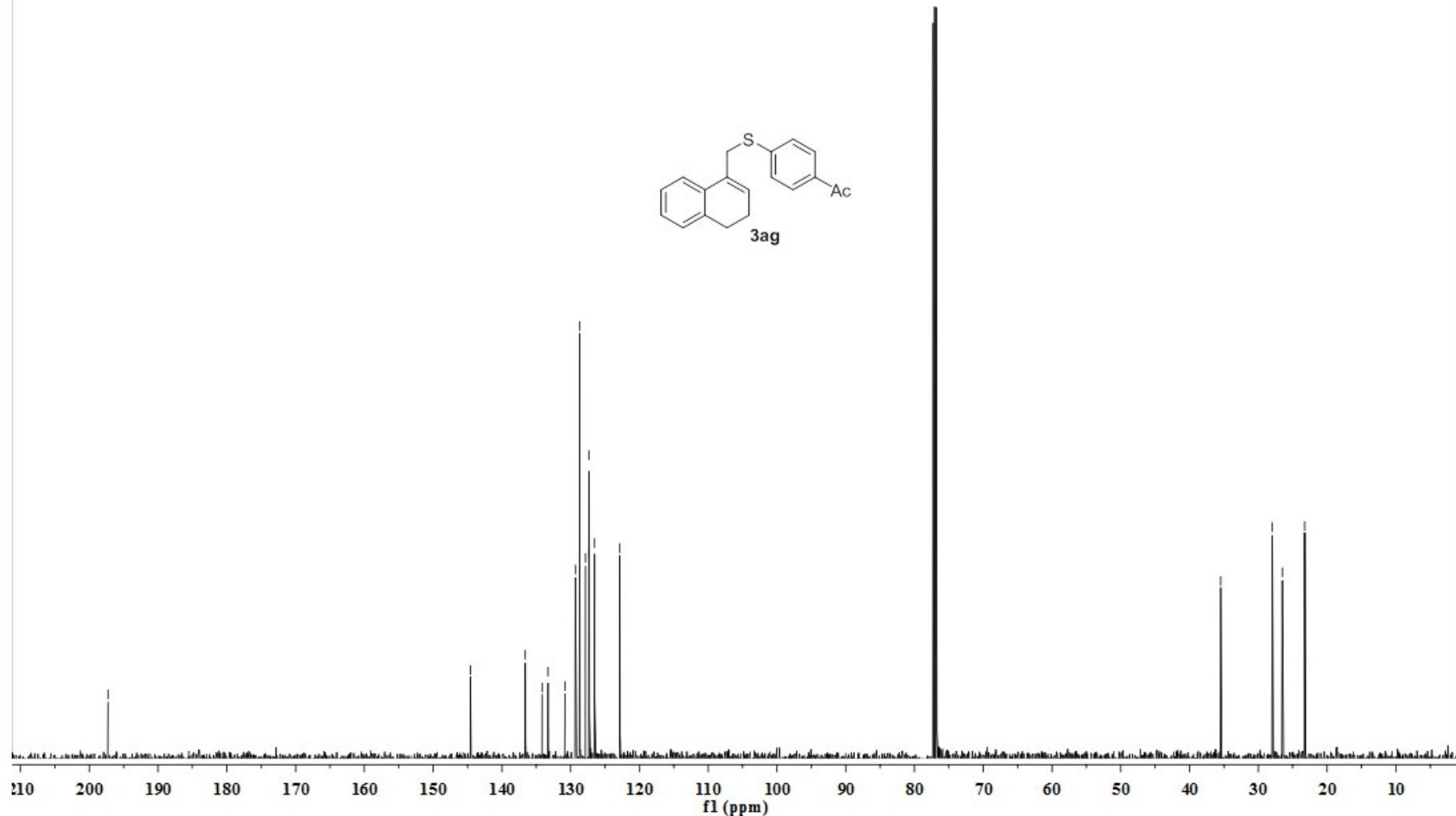
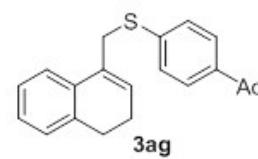


LSW-PHCY-SAG1

-197.26

-144.57  
-136.59  
-134.15  
-133.28  
-130.81  
-129.30  
-128.70  
-127.83  
-127.36  
-127.31  
-126.52  
-122.85

-35.46  
>27.96  
>26.50  
>23.25



LSW-JIN-SAC

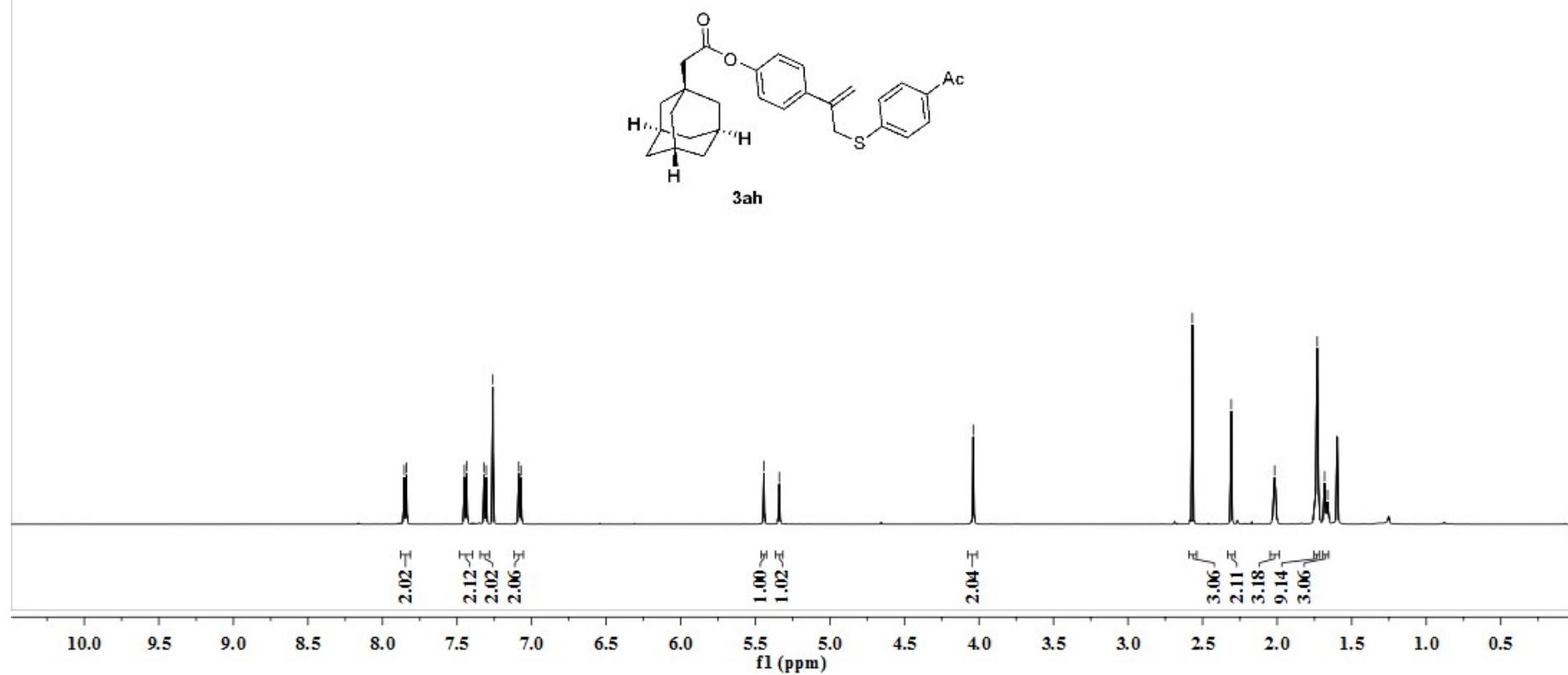


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ʃ ʃ ʃ ʃ



LSW-JIN-SAC

-197.26

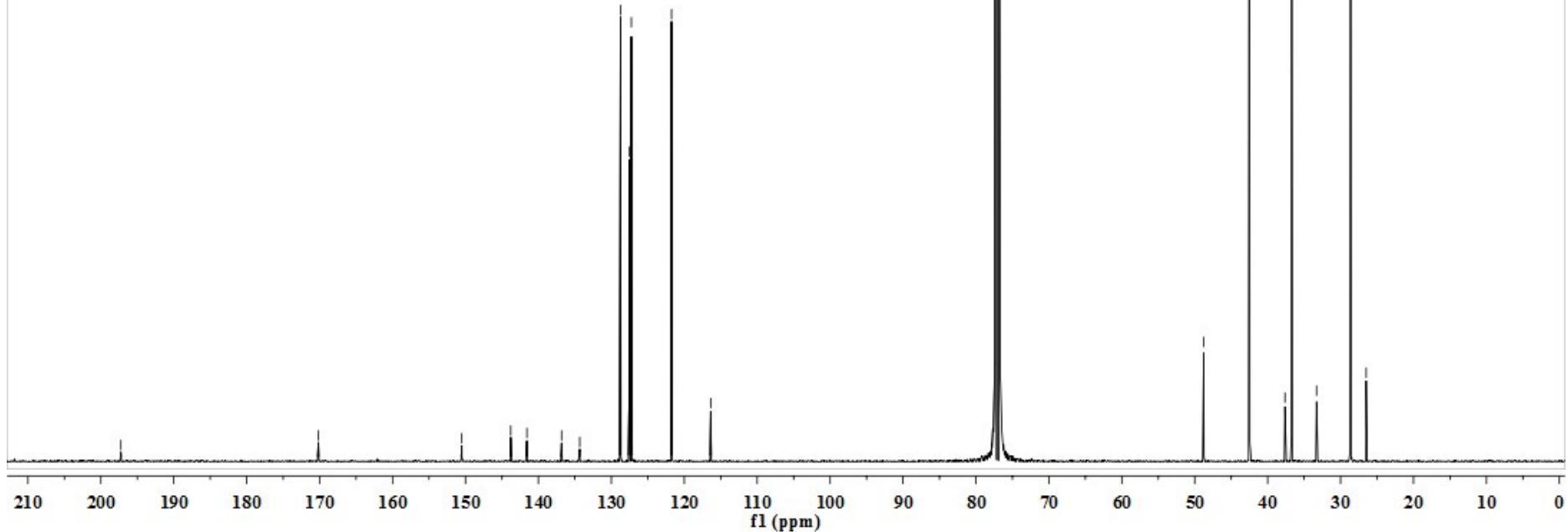
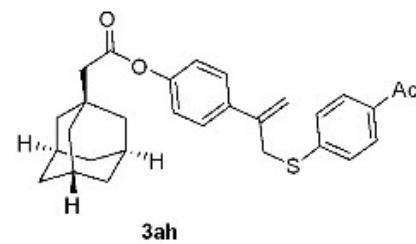
-170.17

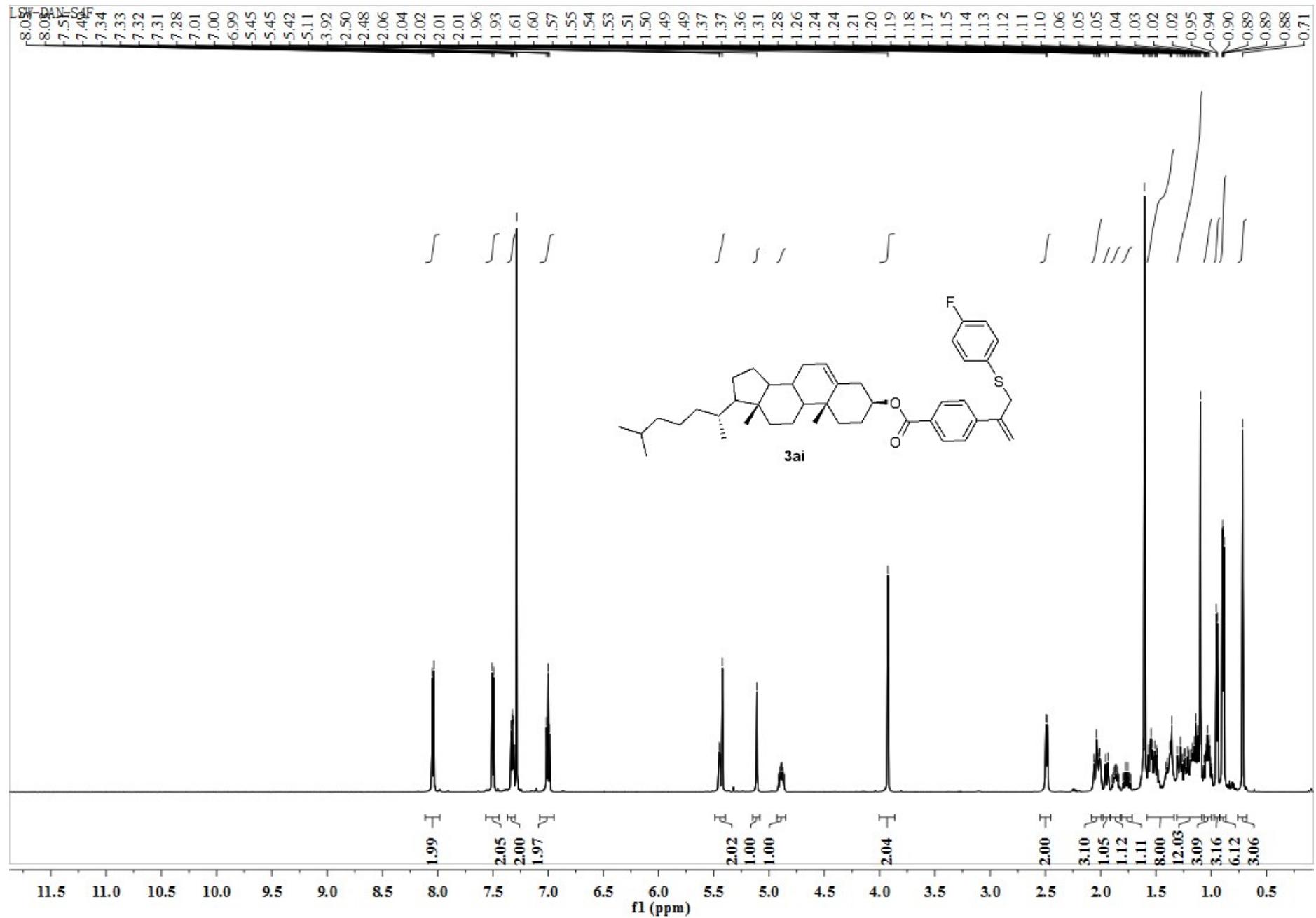
-150.51

-143.79  
-141.57  
-136.82  
-134.33  
-128.74  
-127.51  
-127.25  
-121.74  
-116.37

-48.76

-42.49  
-37.63  
-36.72  
-33.29  
-28.63  
-26.49





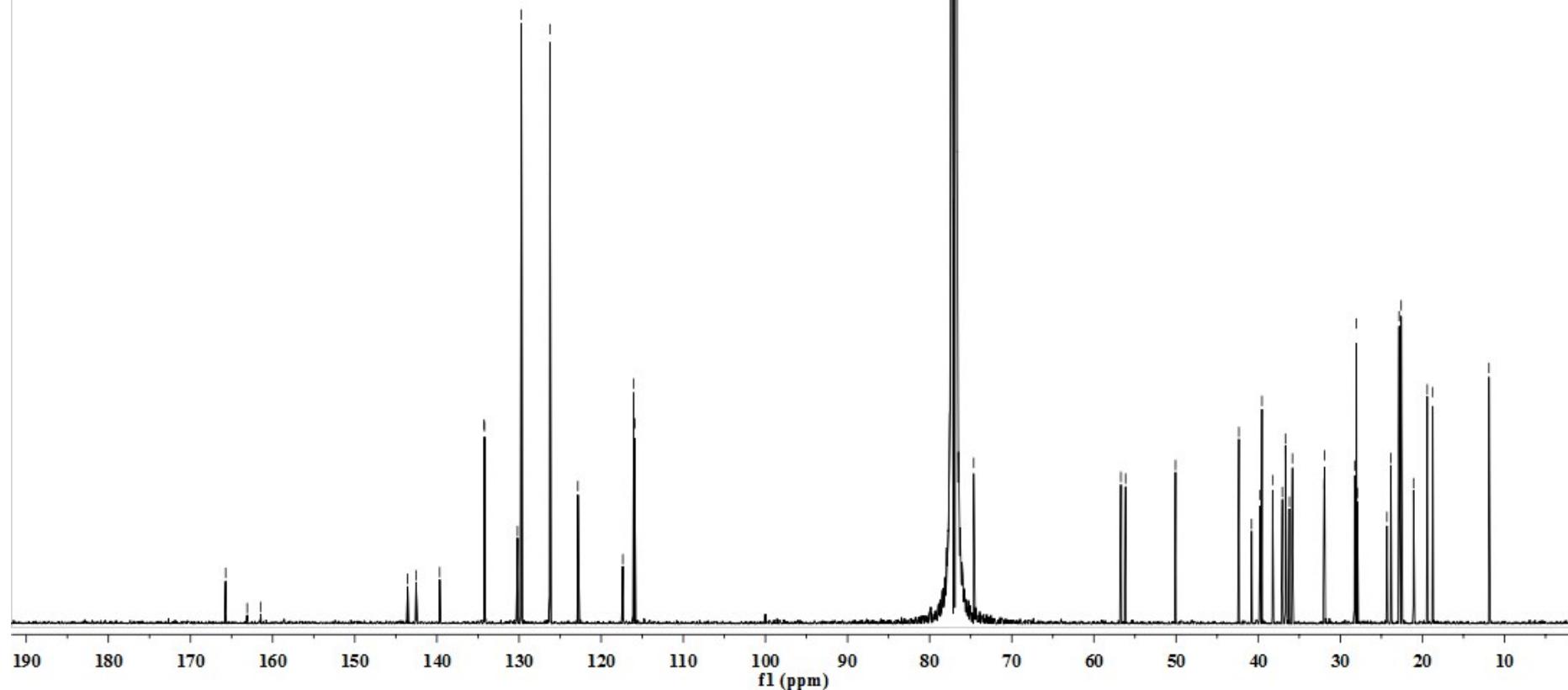
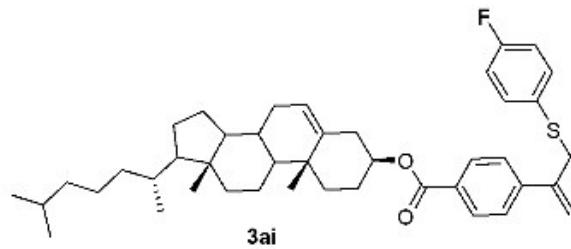
LSW-DAN-S4F

-165.72  
-163.10  
-161.46

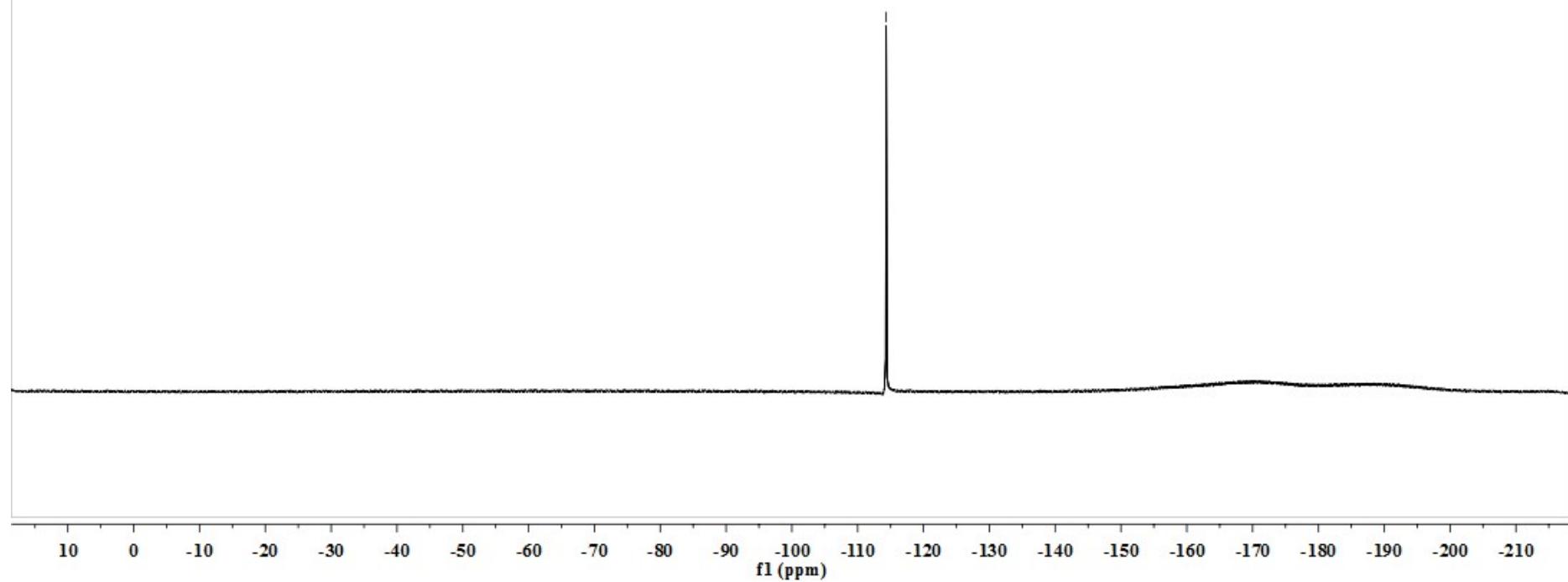
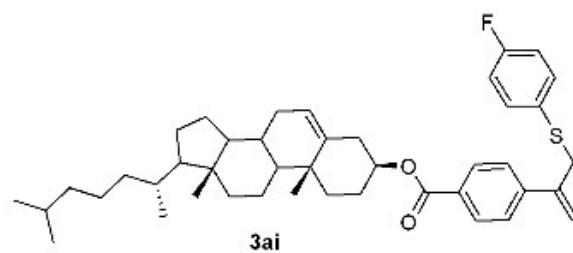
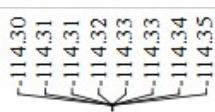
-143.56  
-142.53  
-139.66  
-134.26  
-134.20  
-130.21  
-130.18  
-129.71  
-126.24  
-122.83  
-117.36  
-116.05  
-115.91

-74.64

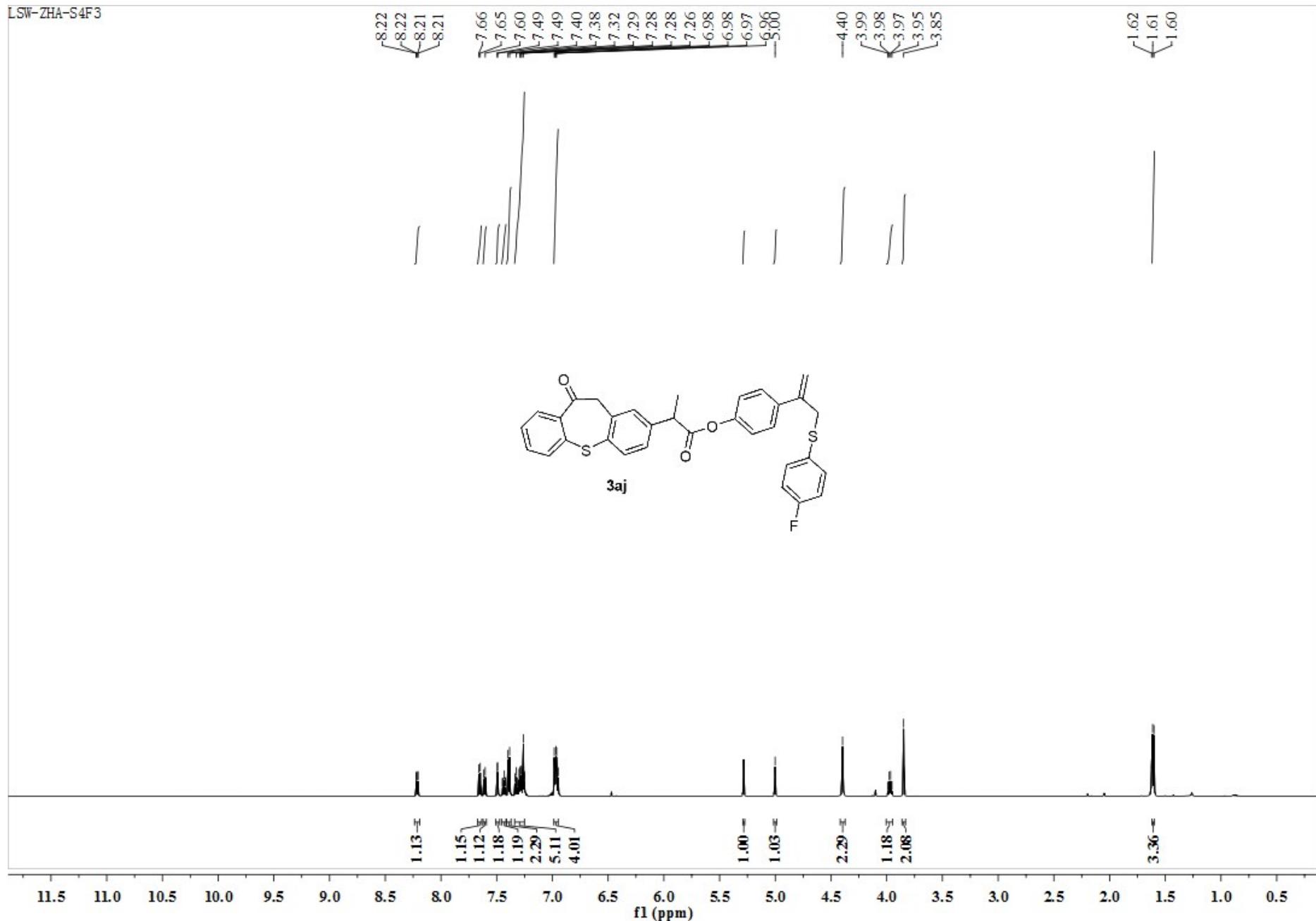
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-18.89

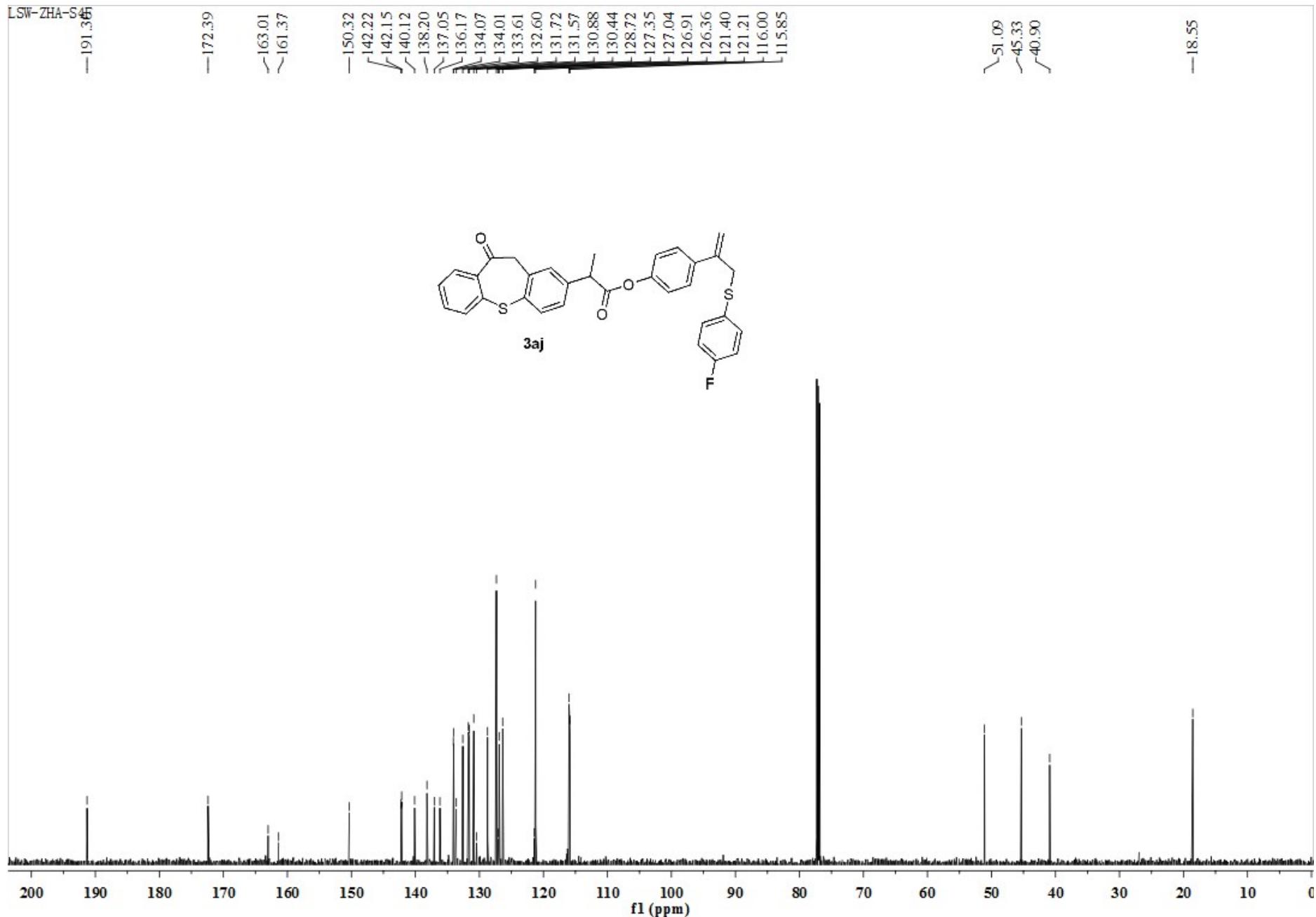


LSW-DAN-S4F

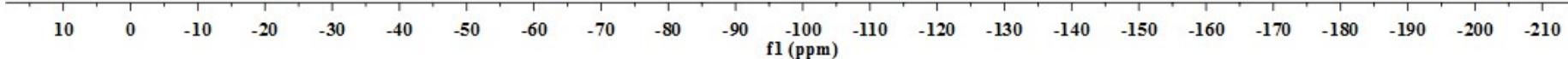
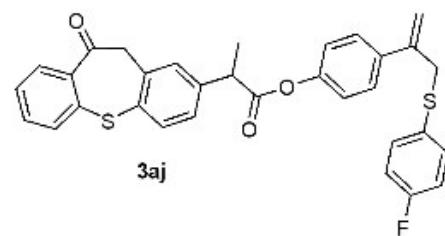


LSW-ZHA-S4F3

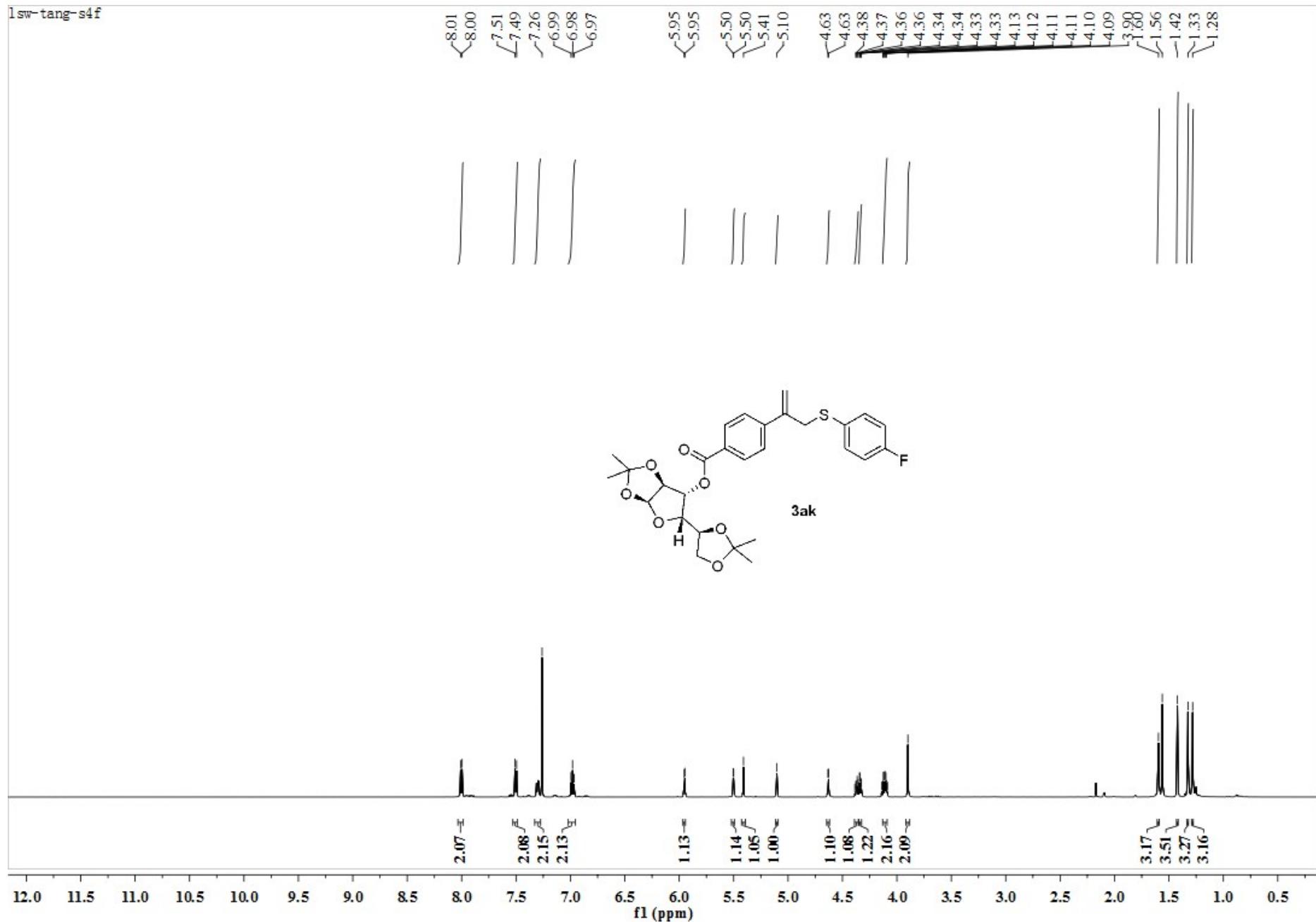




LSW-ZHA-S4F



lsw-tang-s4f



lsw-tang-s4f

-164.92

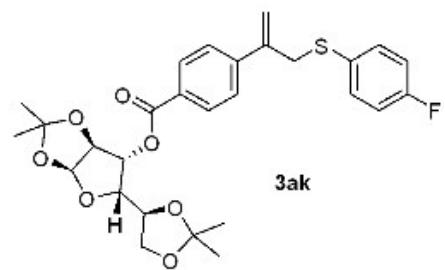
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134.28  
129.90  
128.79  
126.50

-117.80  
116.09  
115.95  
112.42  
109.45  
105.15

83.40  
79.96  
76.65  
72.60  
67.26

-40.80

26.87  
26.76  
26.23  
25.25

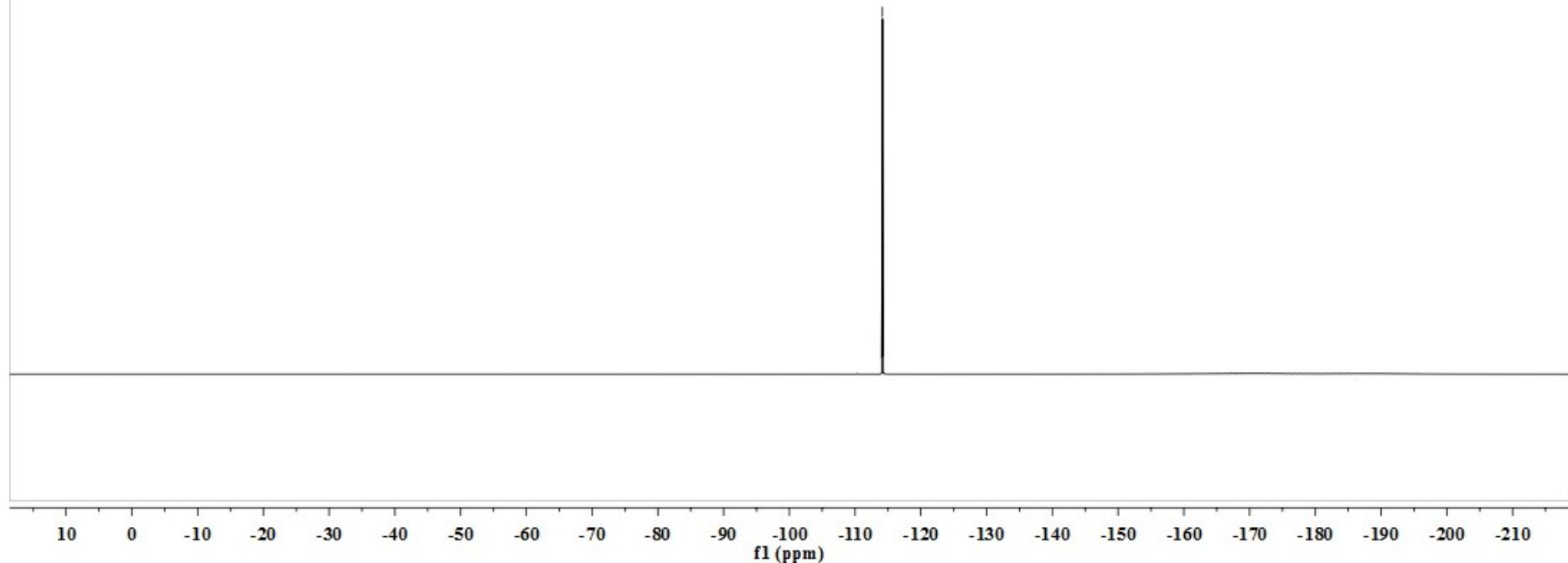
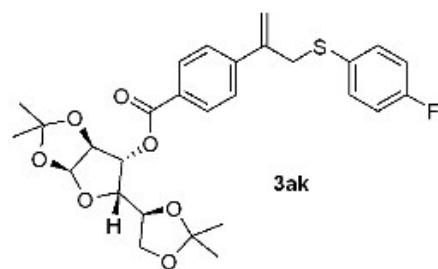


3ak

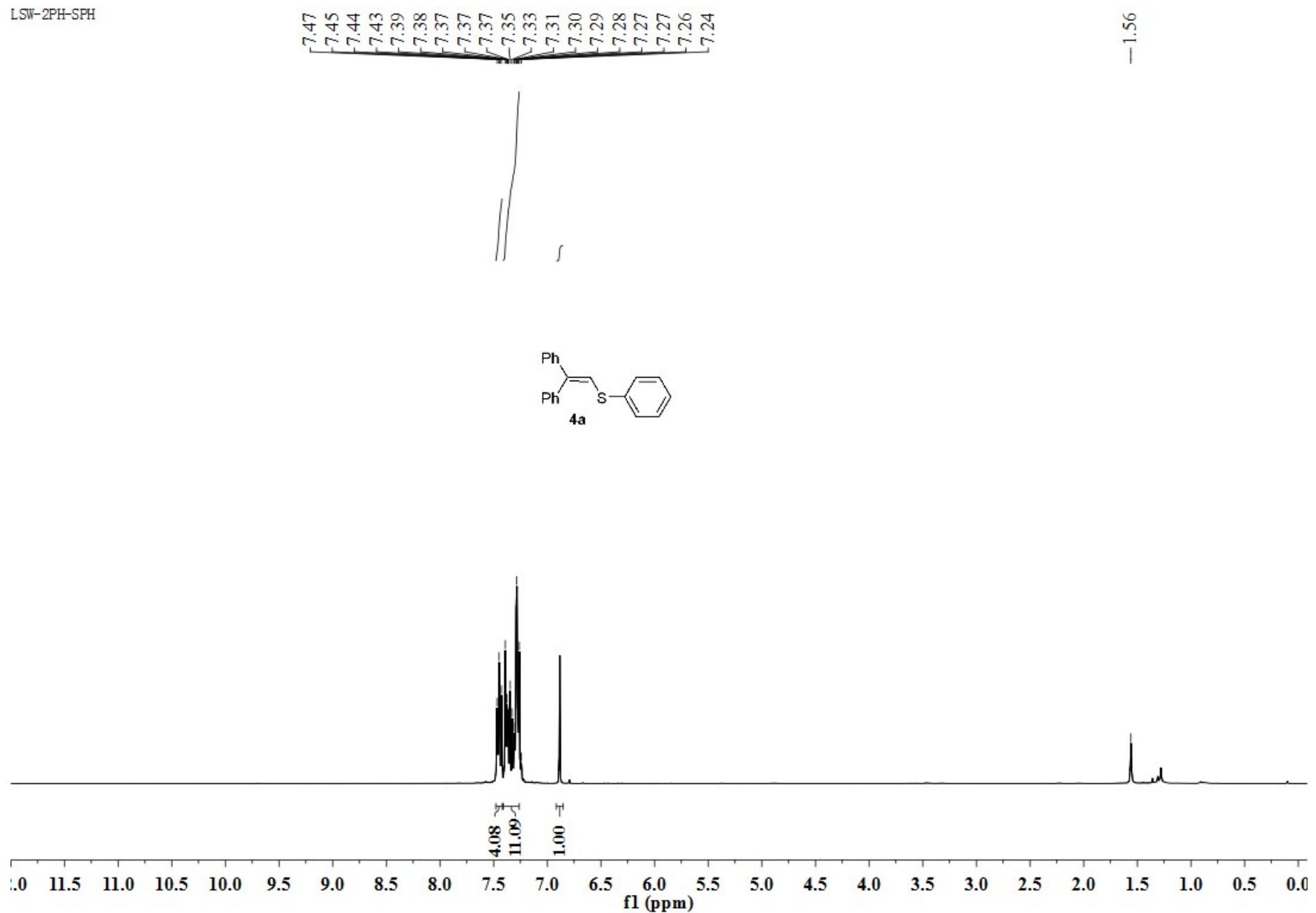
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

f1 (ppm)

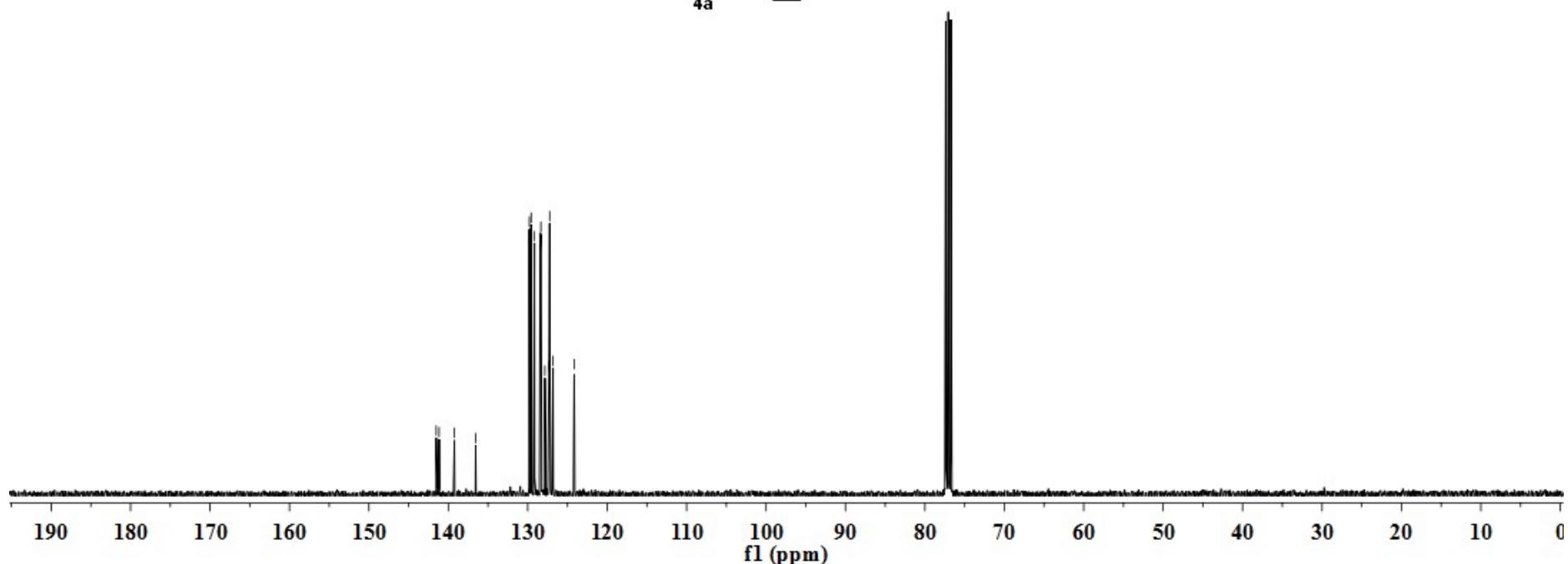
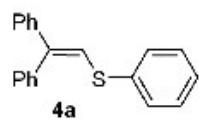
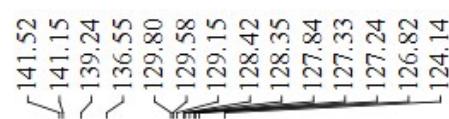
lsw-tang-s4f



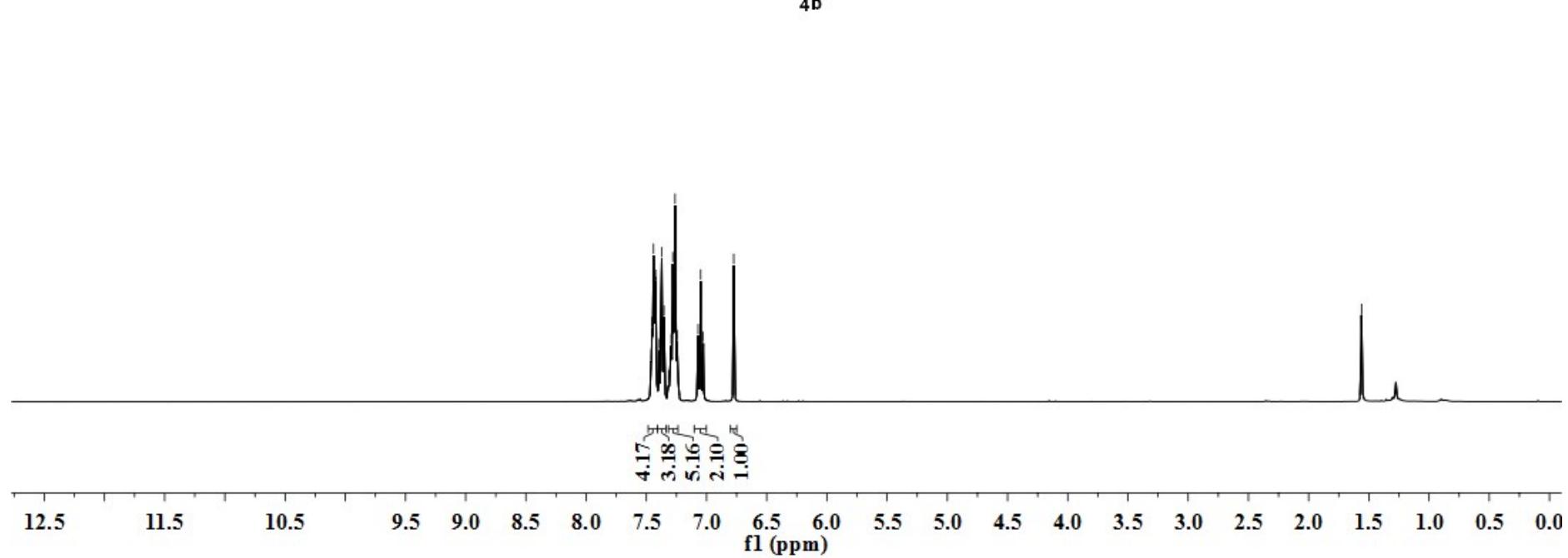
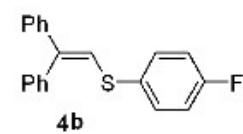
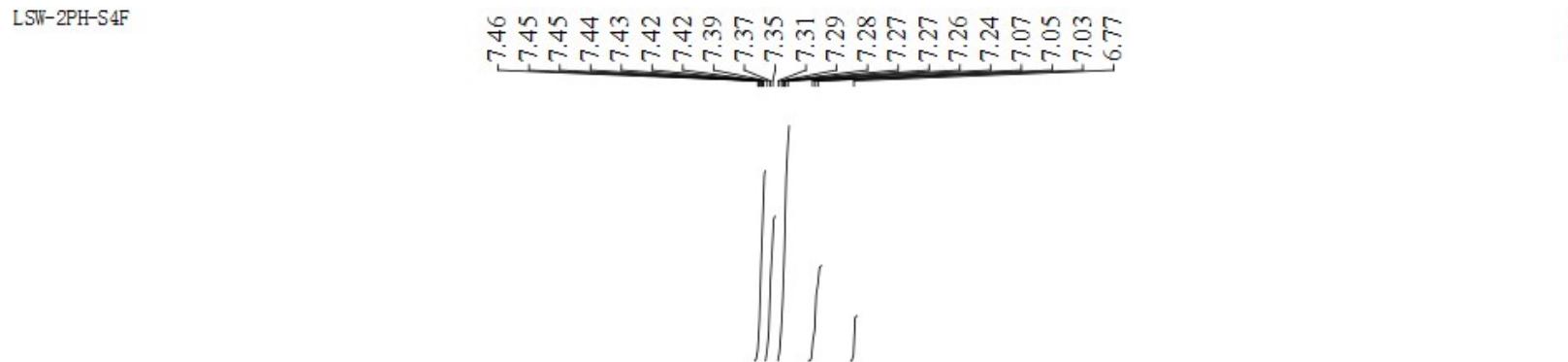
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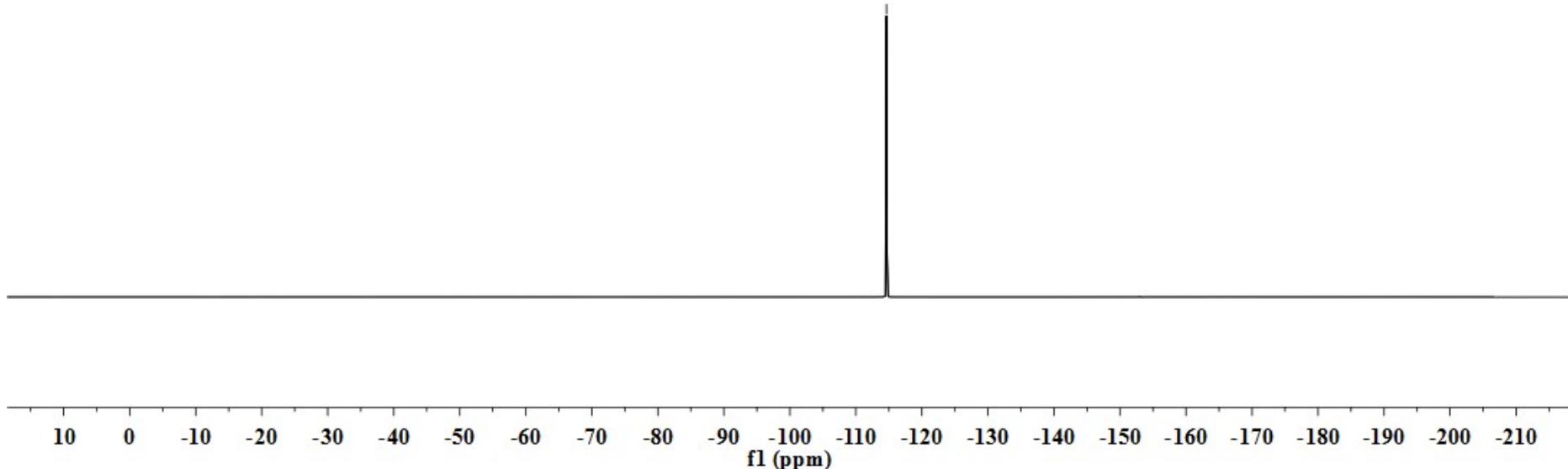
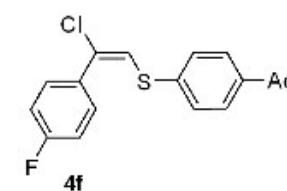
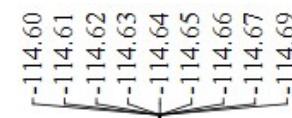
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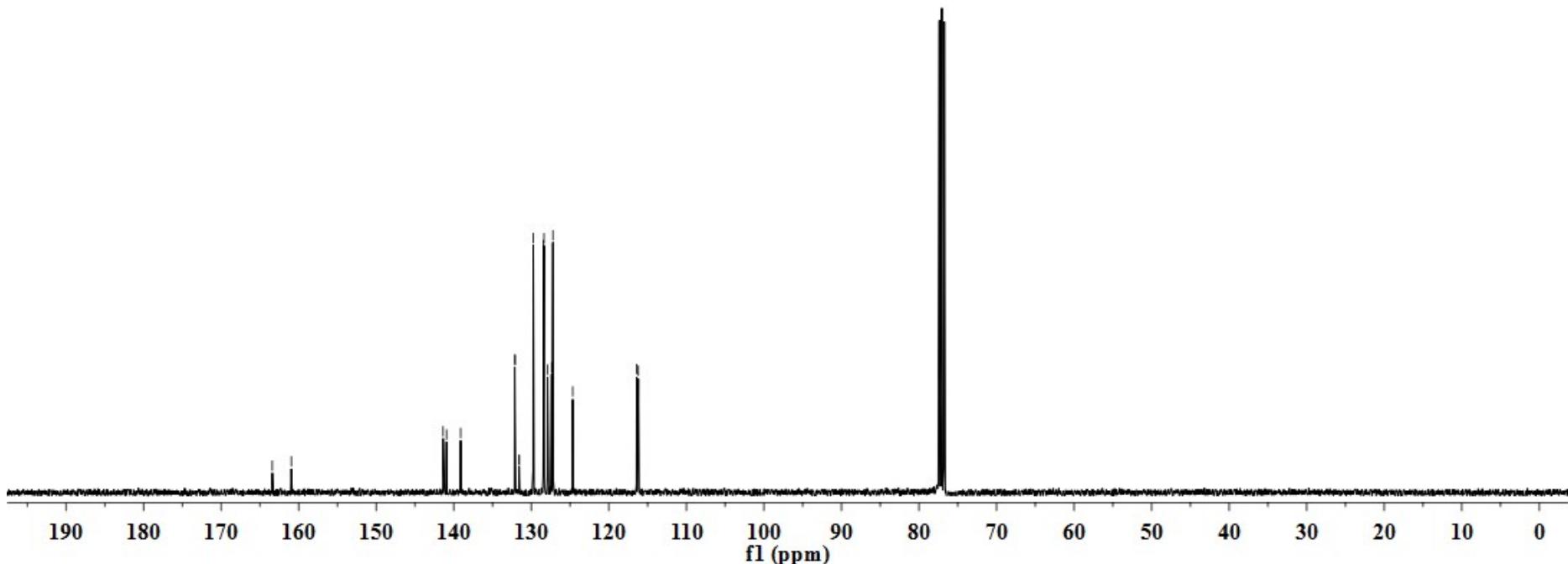
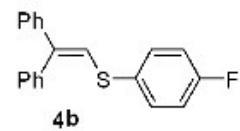
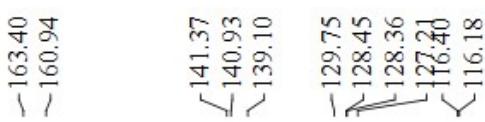
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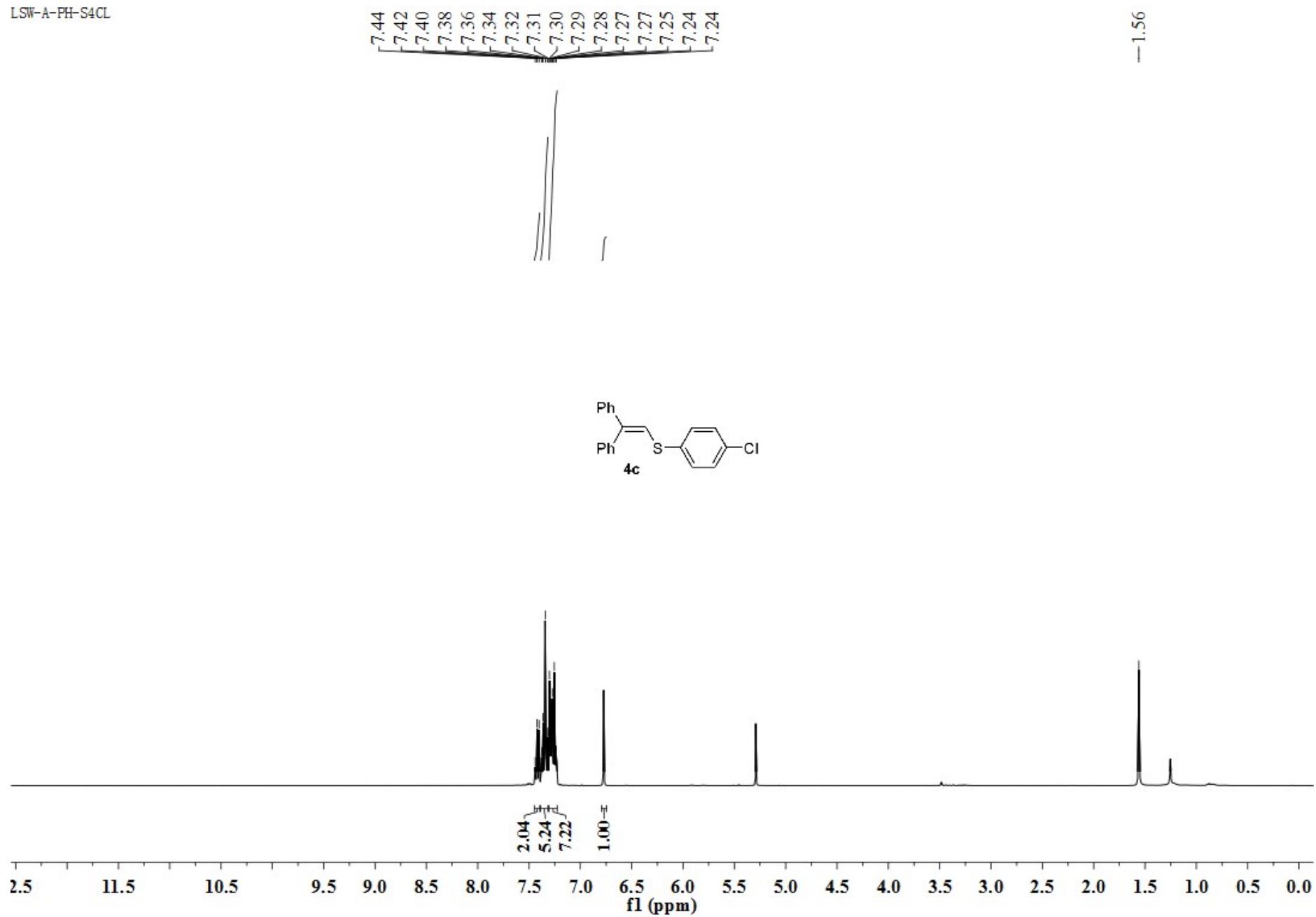
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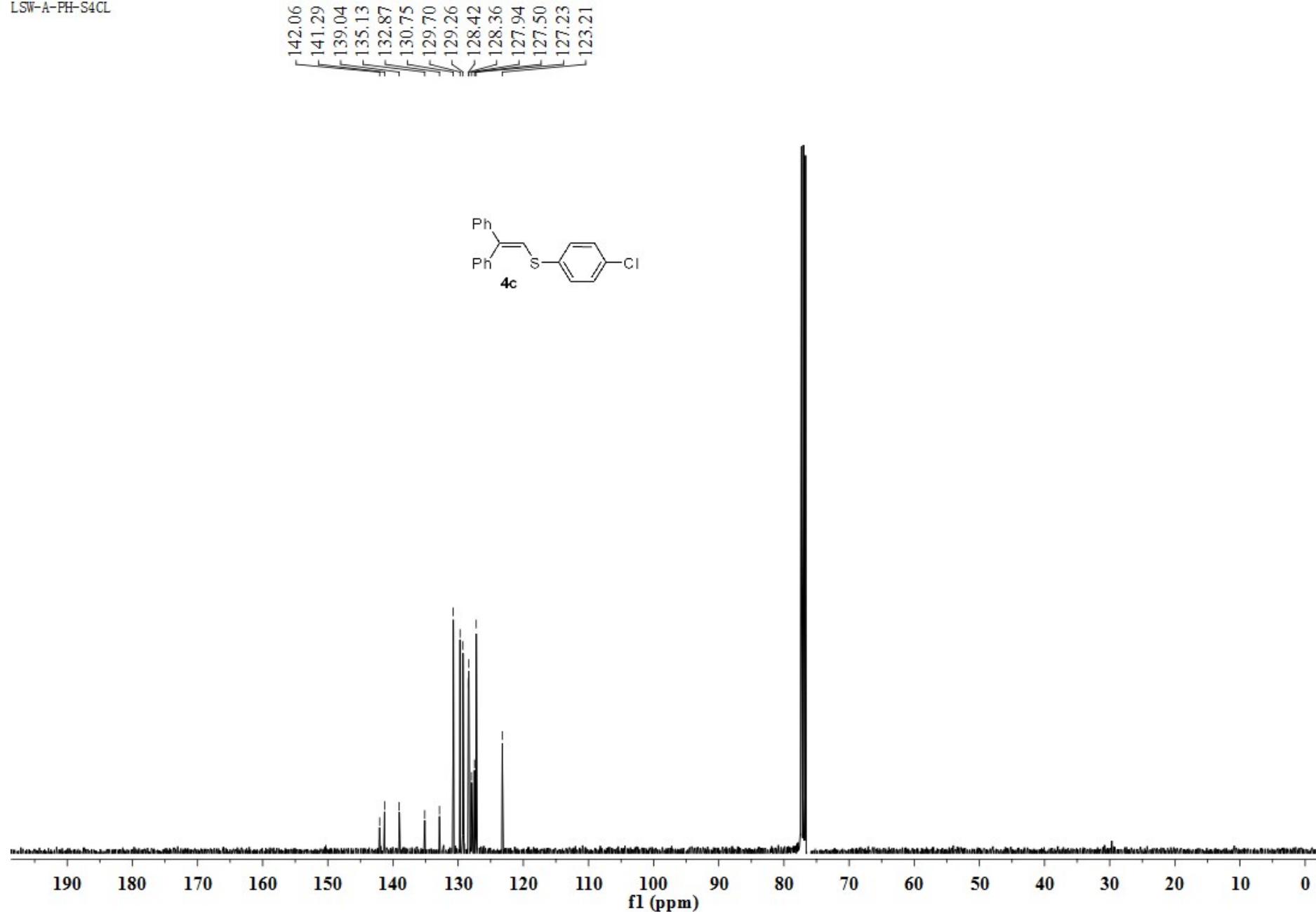
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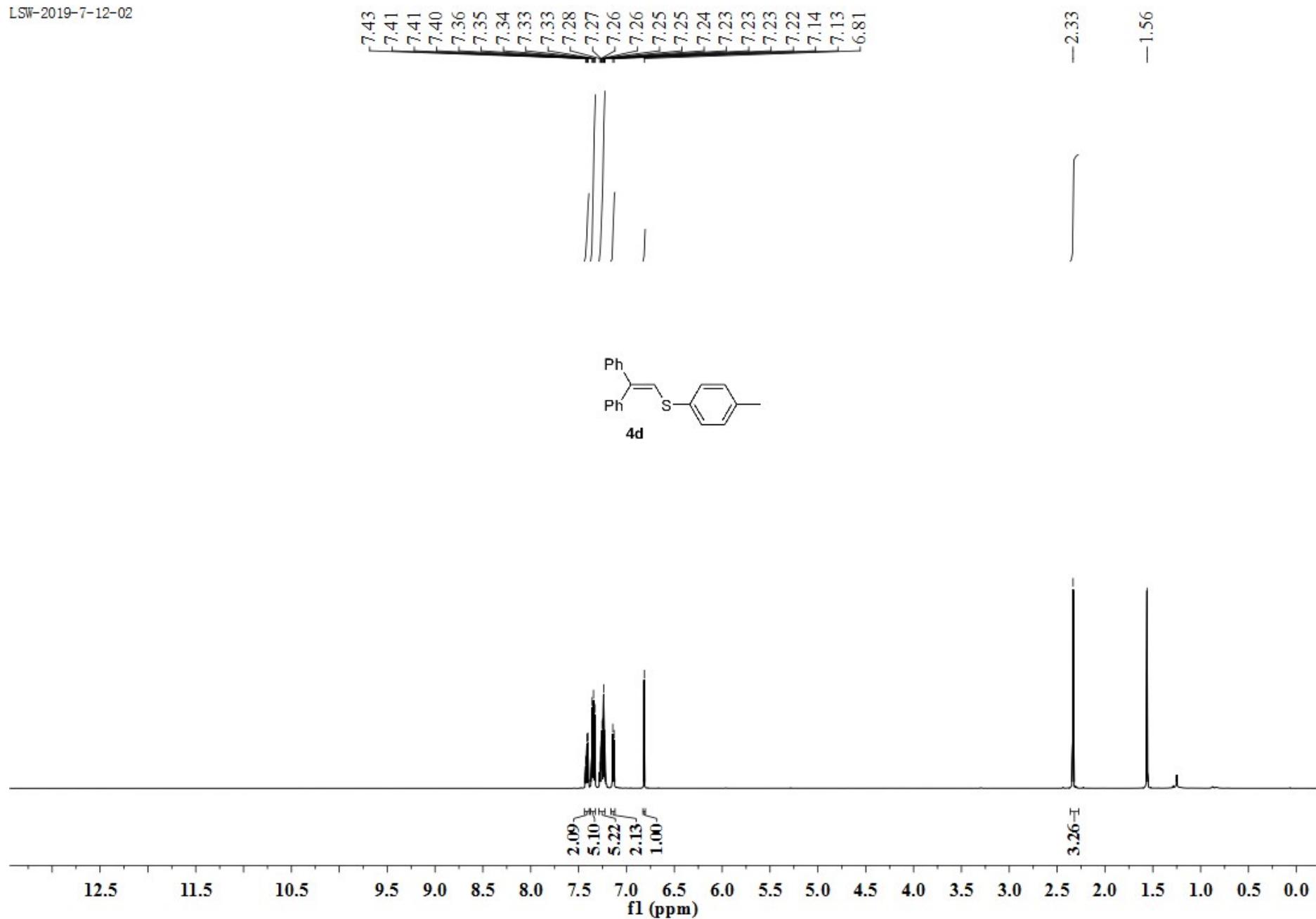
LSW-A-PH-S4CL



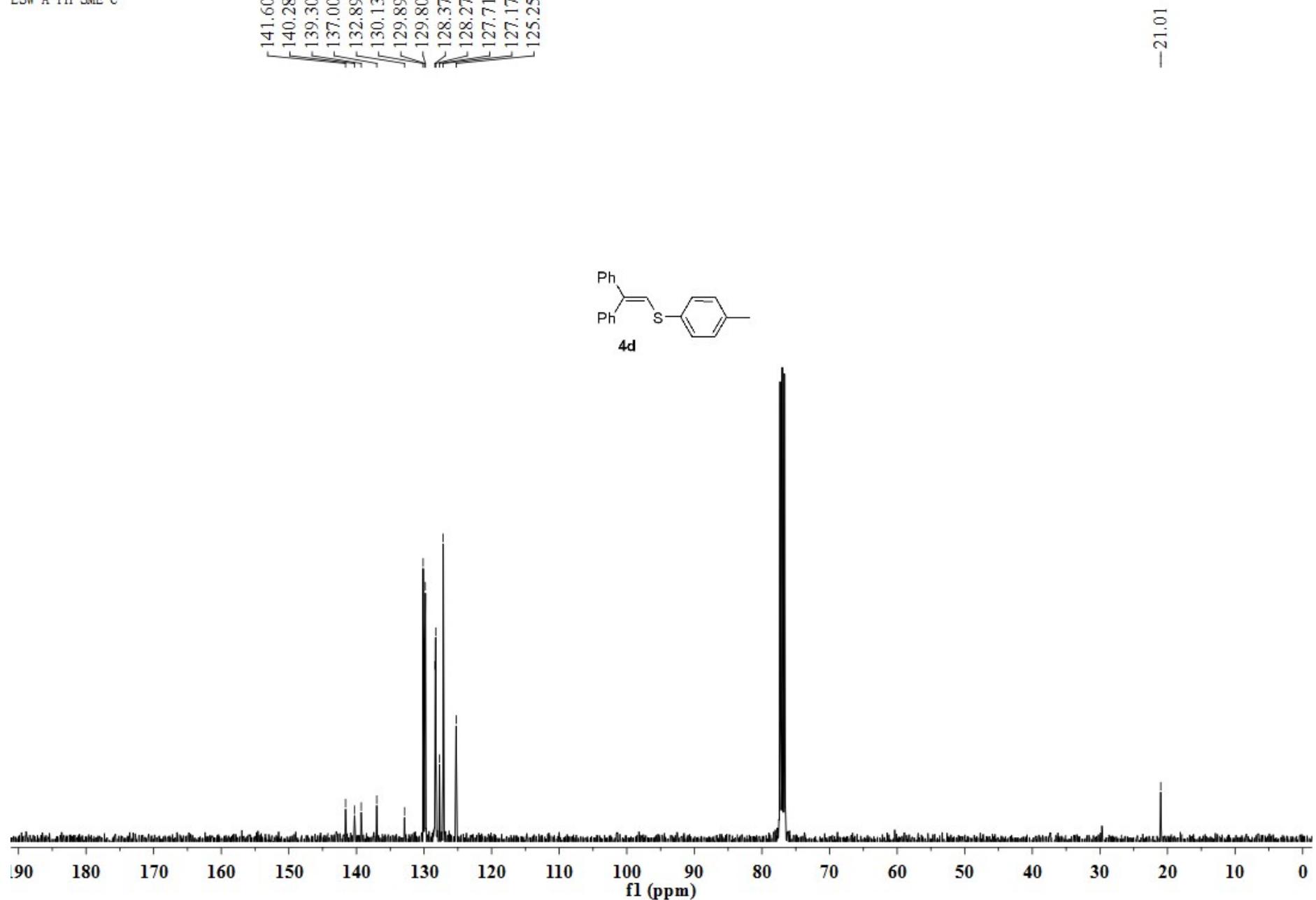
LSW-A-PH-S4CL



LSW-2019-7-12-02



LSW-A-PH-SME-C

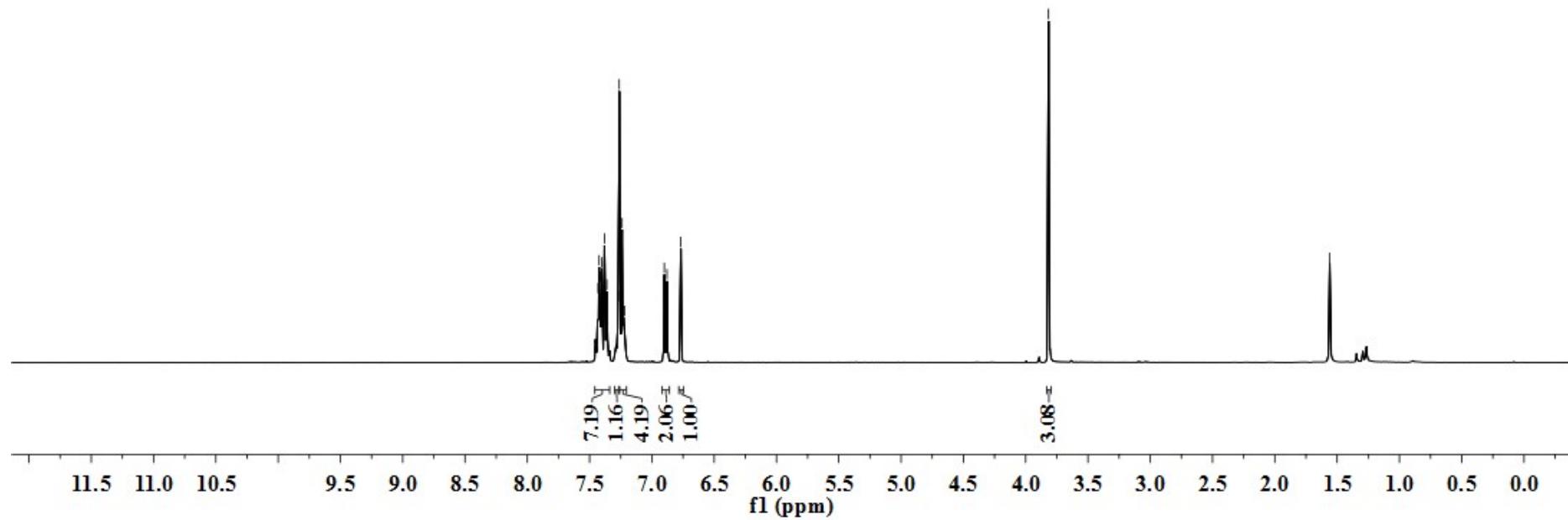
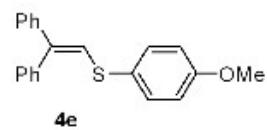


LSW-2PH-SOME-01

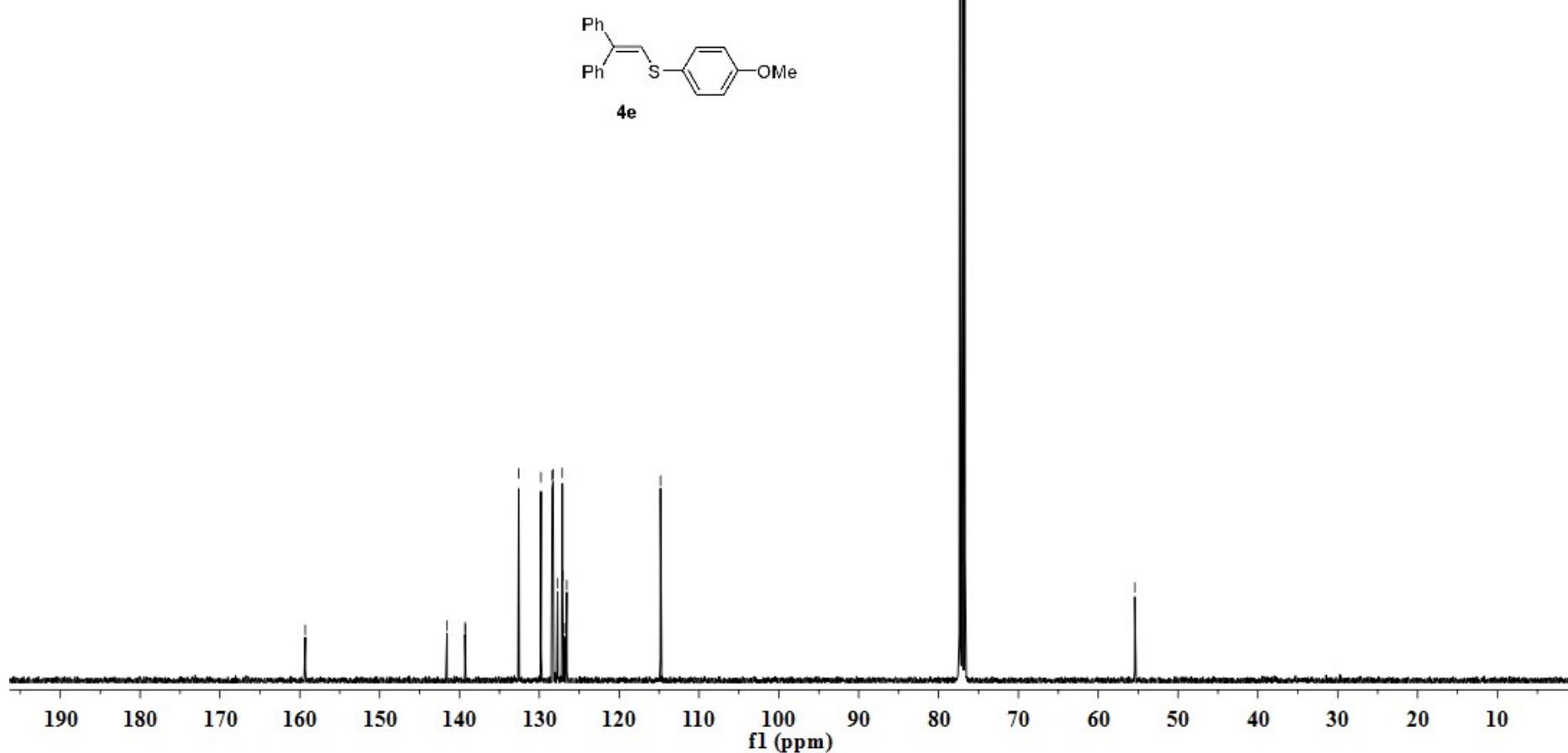
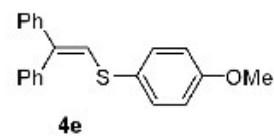


—3.82

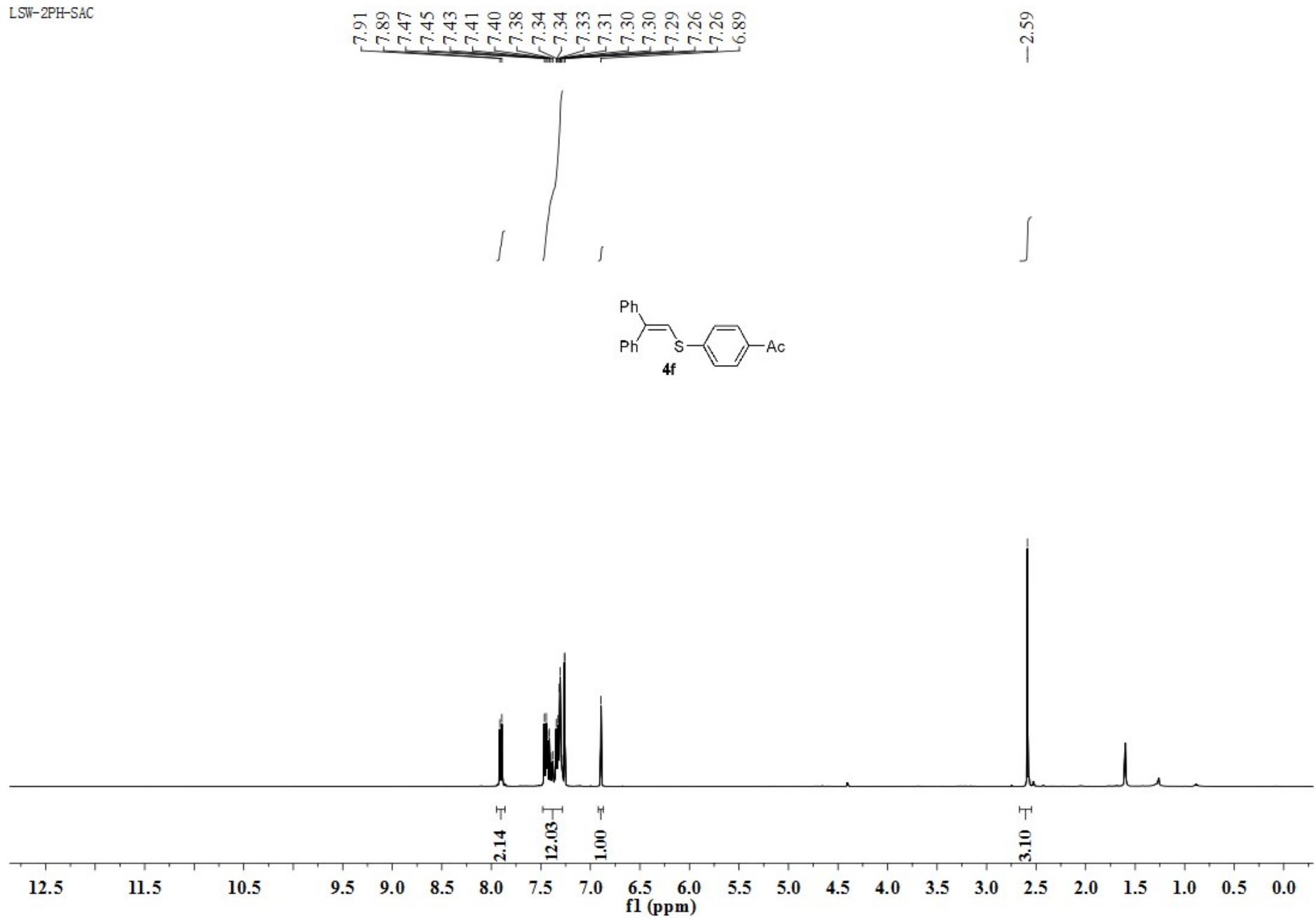
—1.56



LSW-2PH-SOME-C



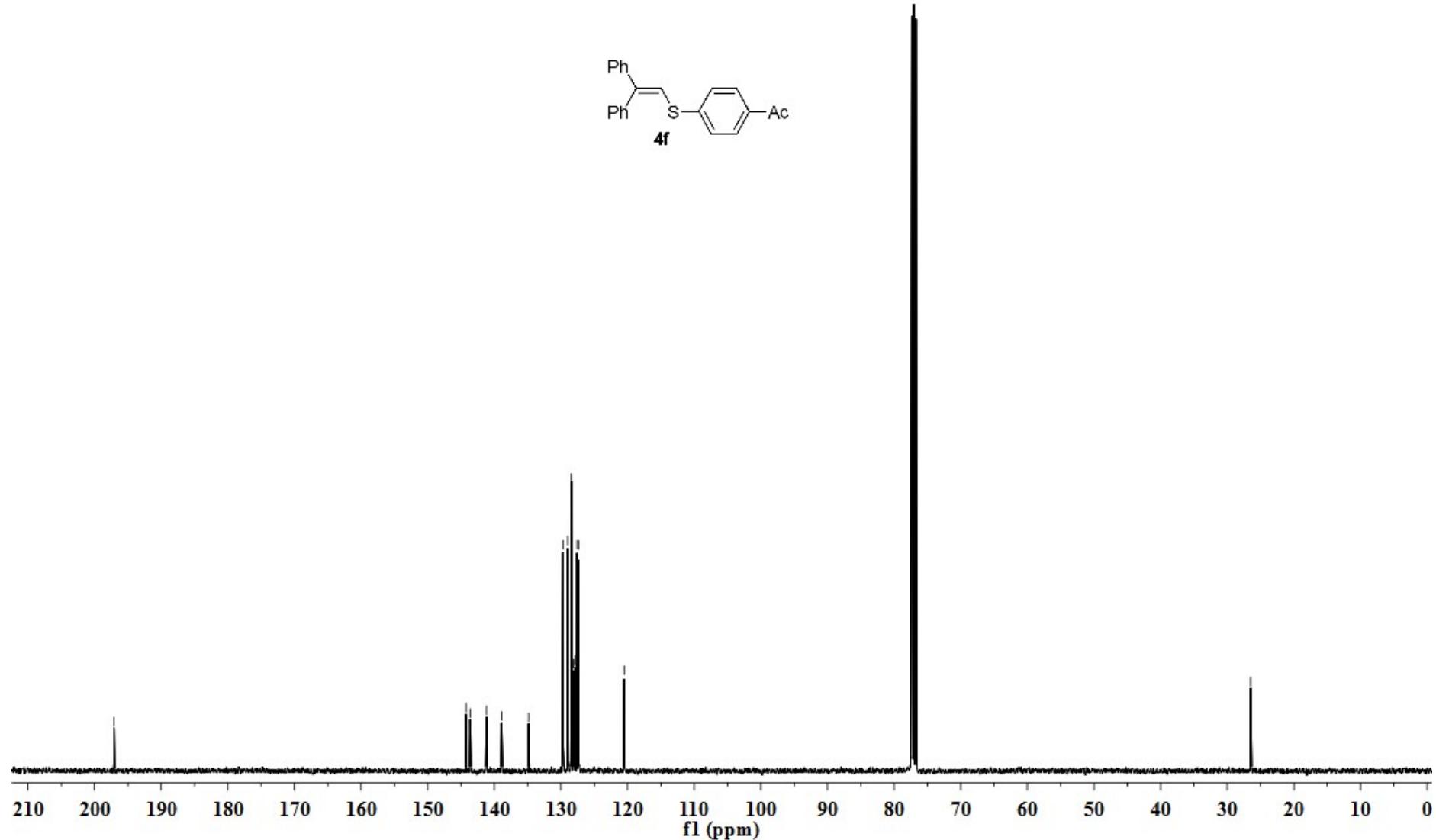
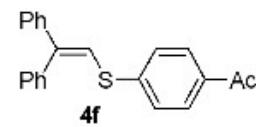
LSW-2PH-SAC



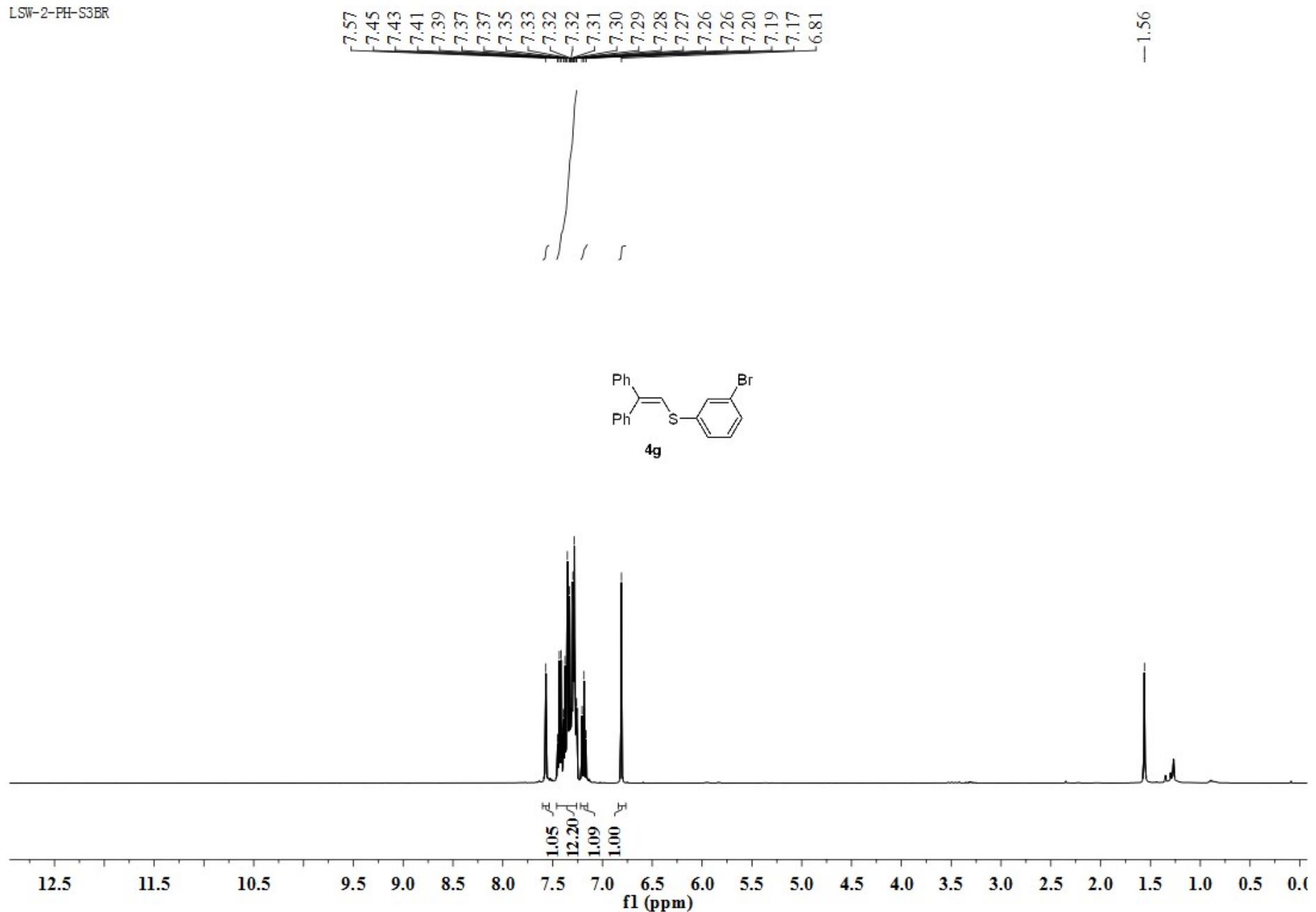
LSW-2PH-SAC<sup>6</sup>  
— 197.08

144.25  
143.63  
141.16  
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128.45  
128.12  
127.84  
127.58  
127.37  
120.52

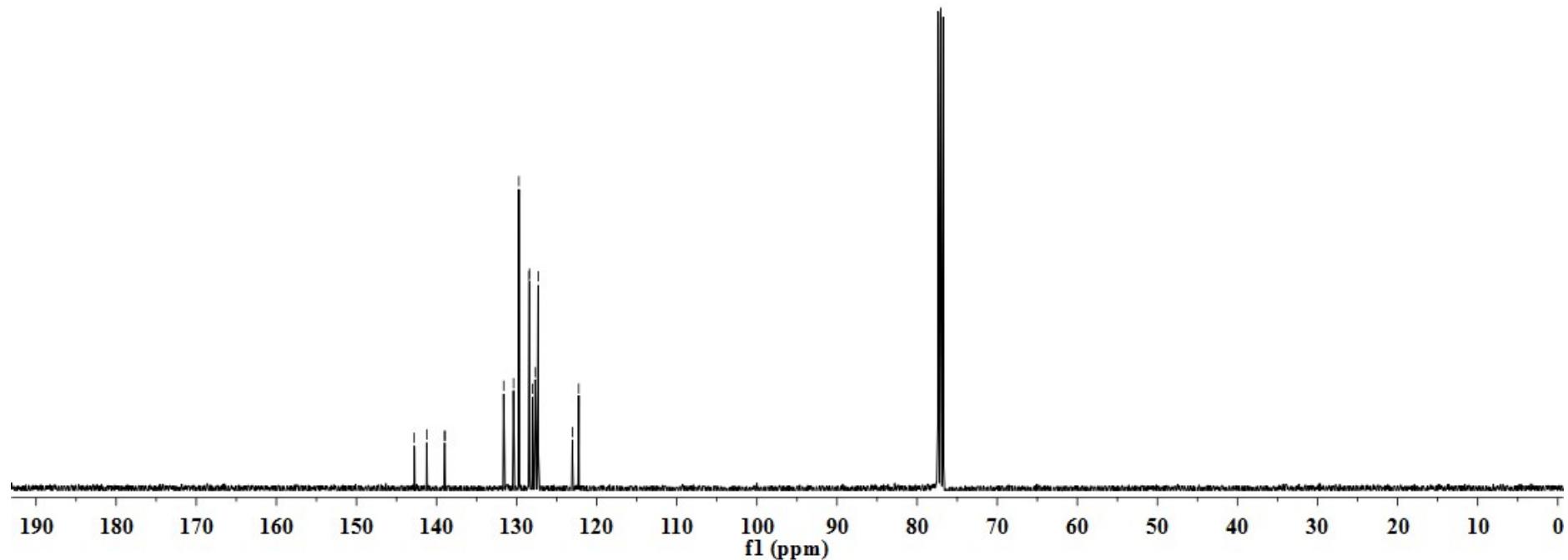
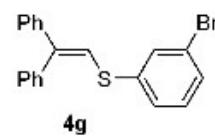
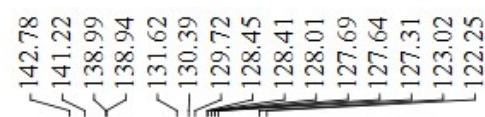
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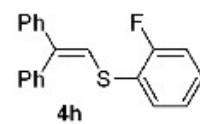
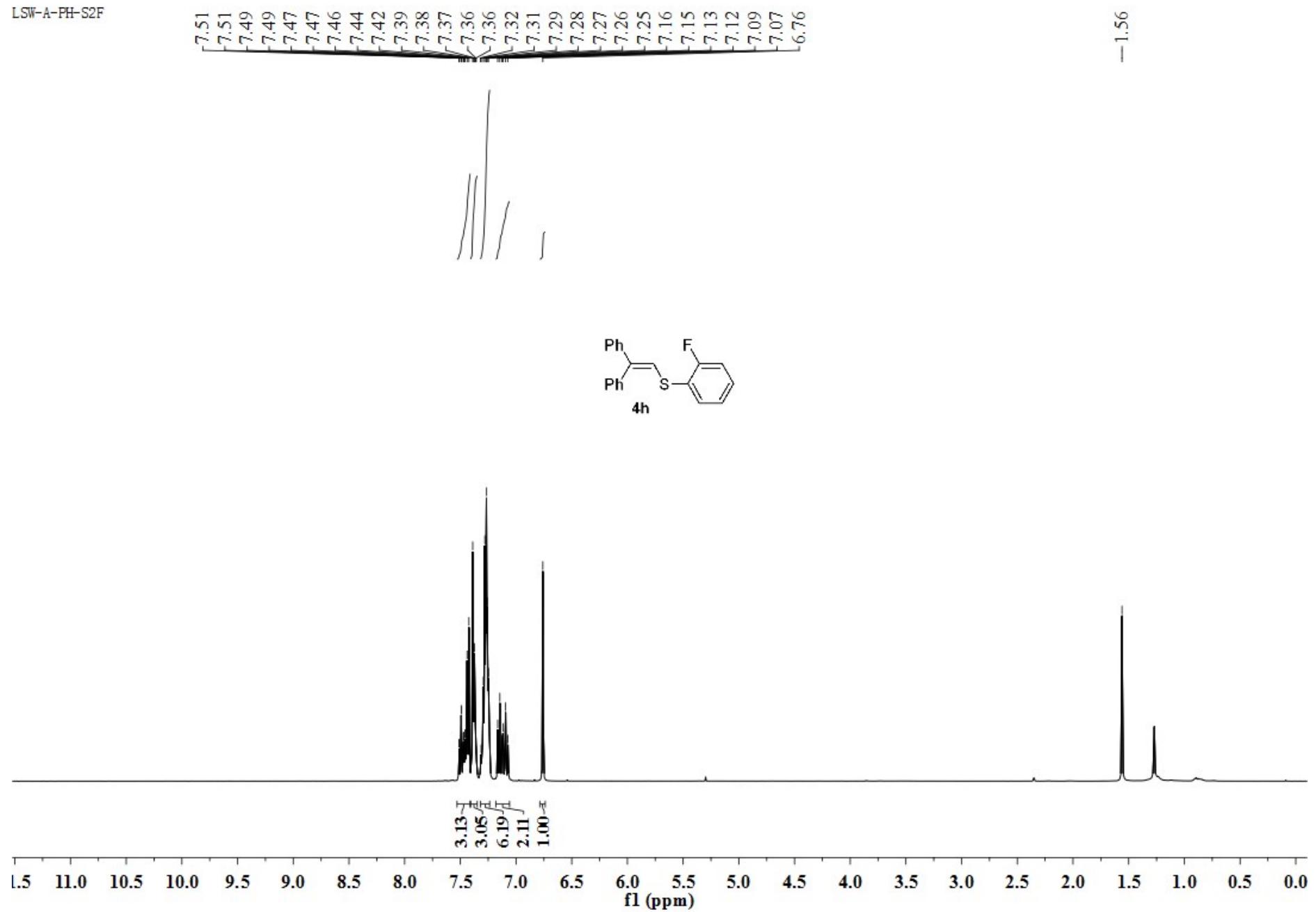
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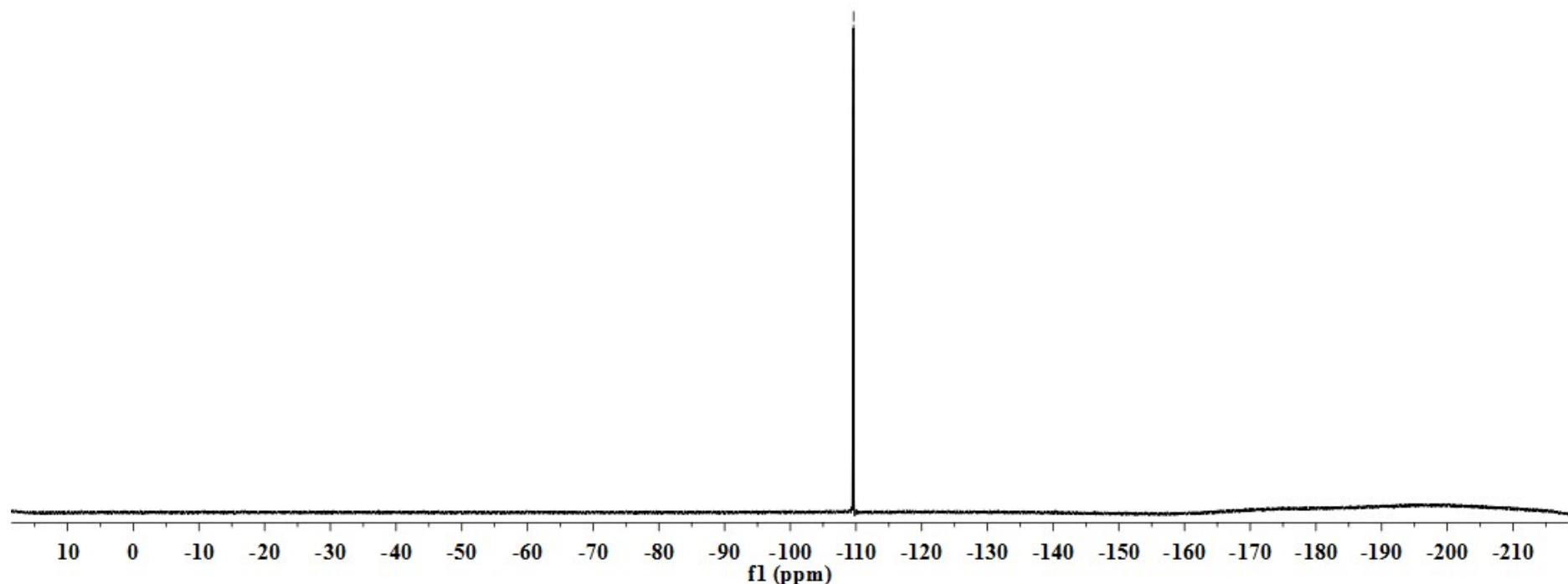
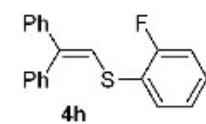
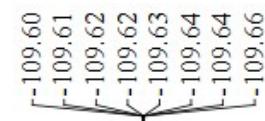
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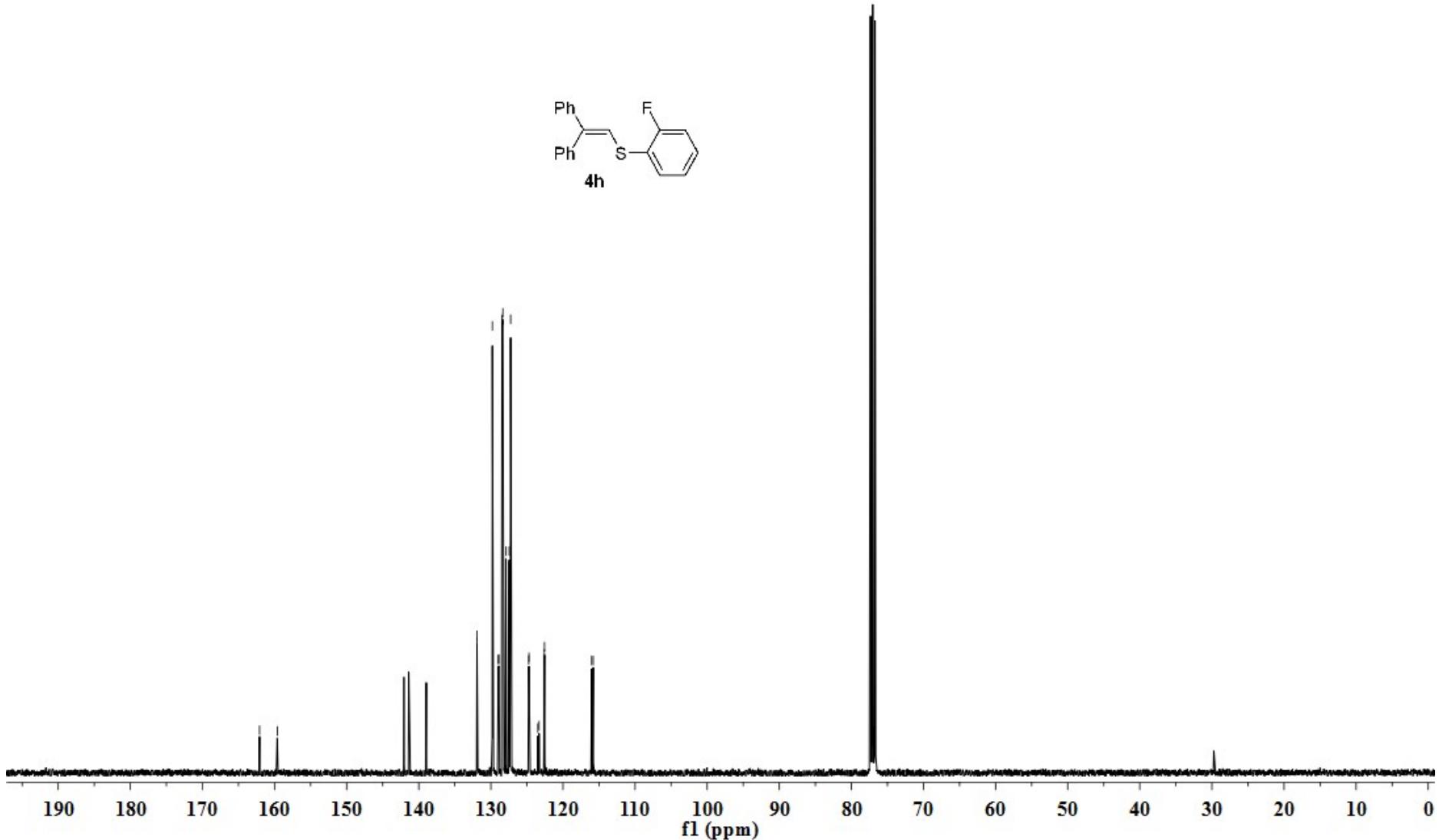
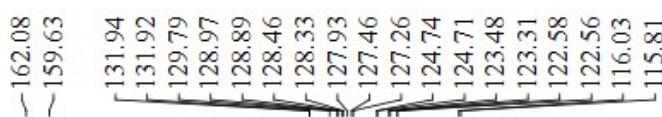
LSW-A-PH-S2F



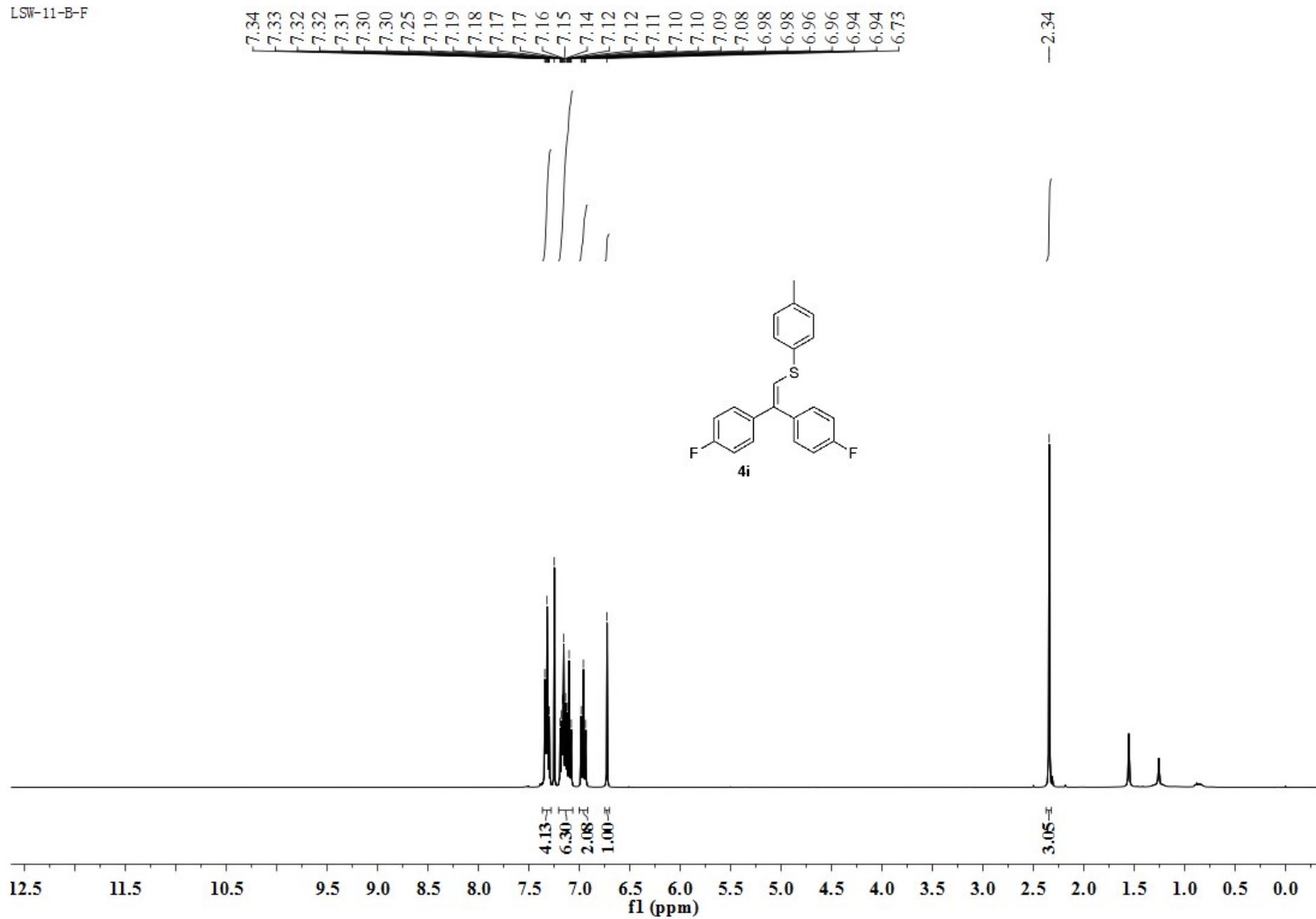
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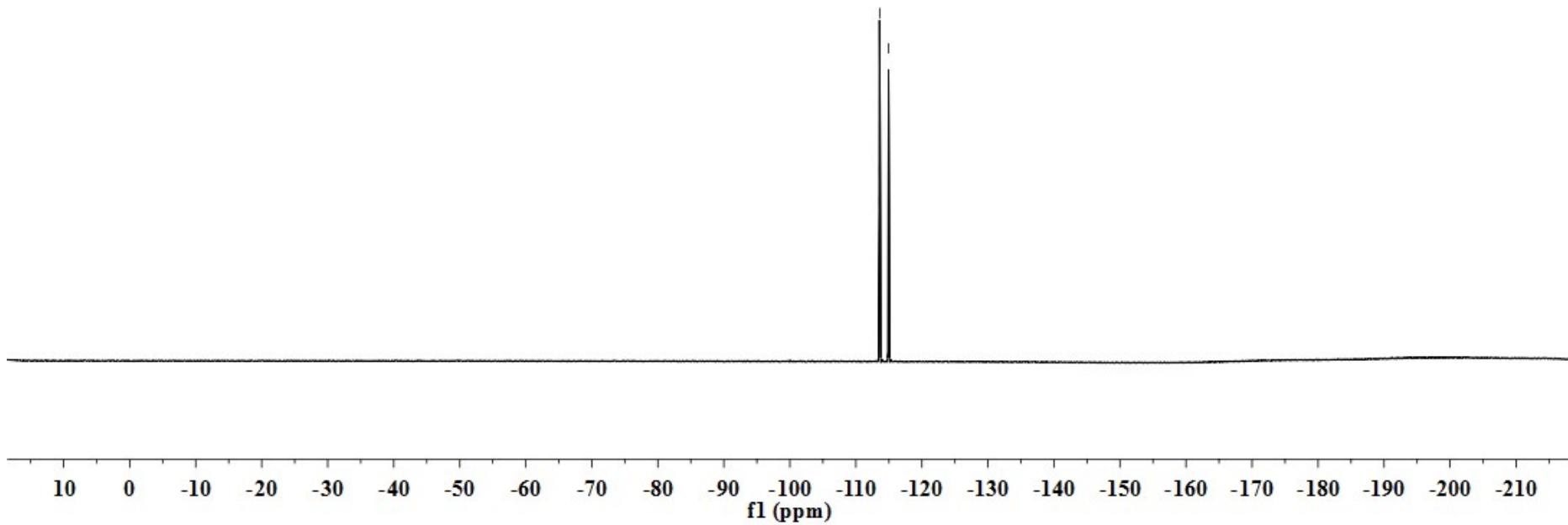
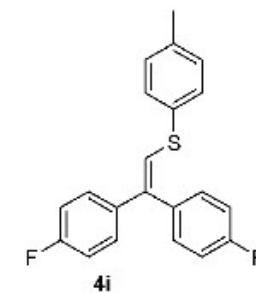
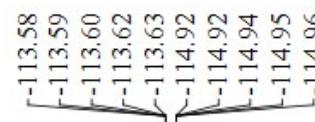
LSW-2PH-S2F-C



LSW-11-B-F



LSW-11-B-F

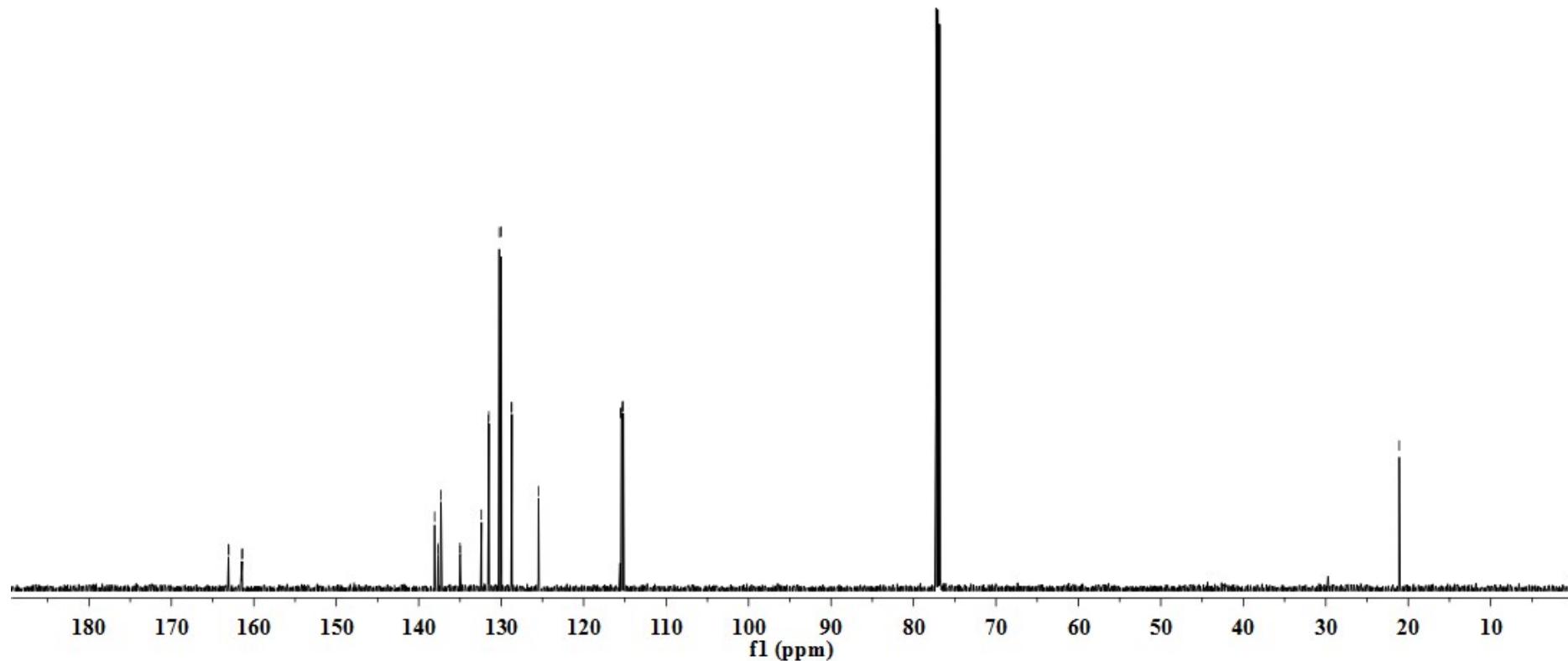
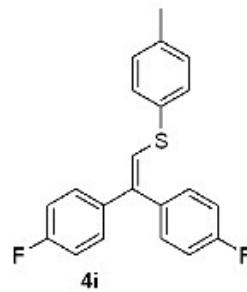


LSW-11-B

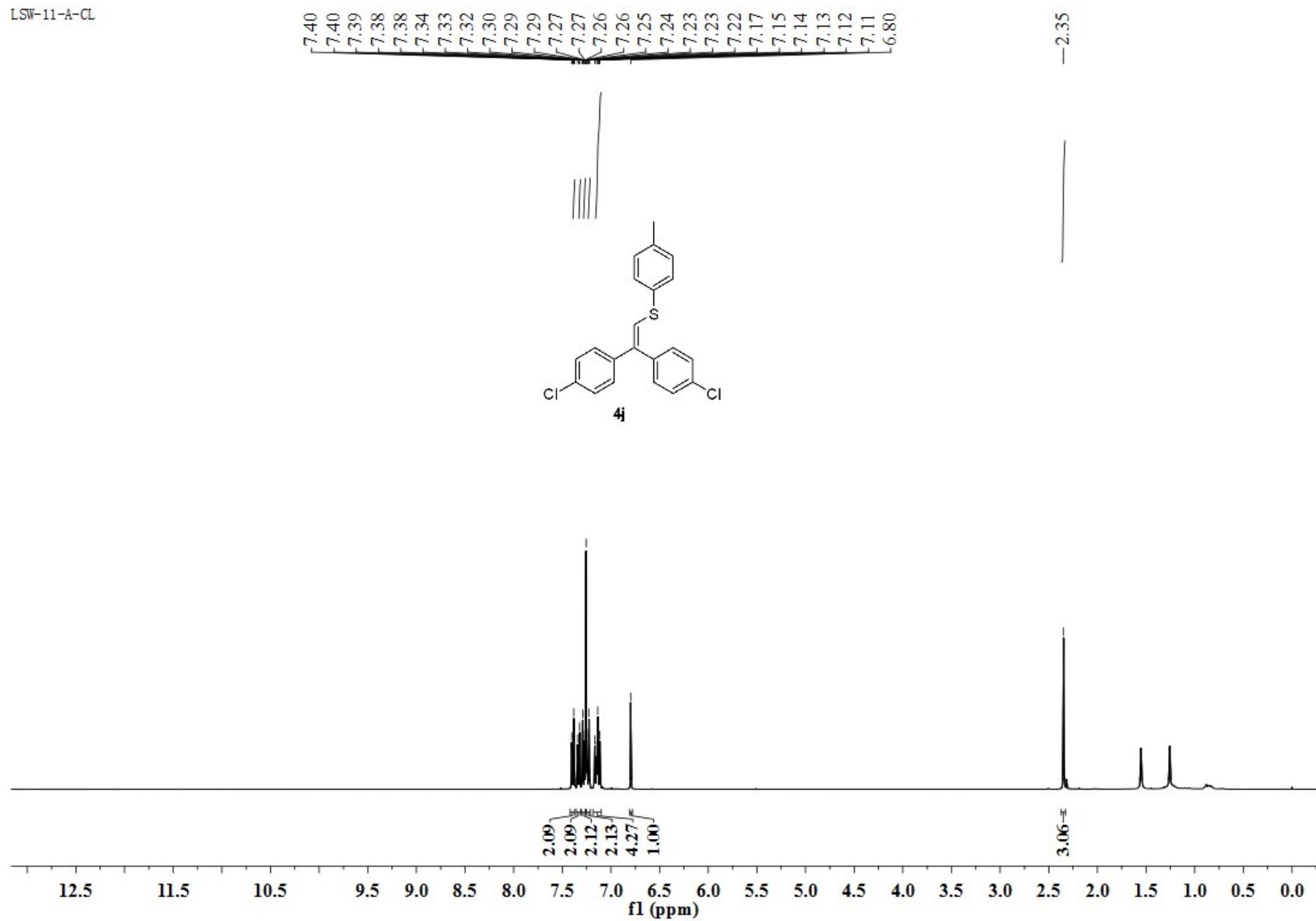
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161.44  
161.40

138.08  
137.31  
132.40  
131.55  
131.50  
130.24  
130.00  
128.77  
128.72  
125.48  
115.57  
115.42  
115.33  
115.19

-21.09



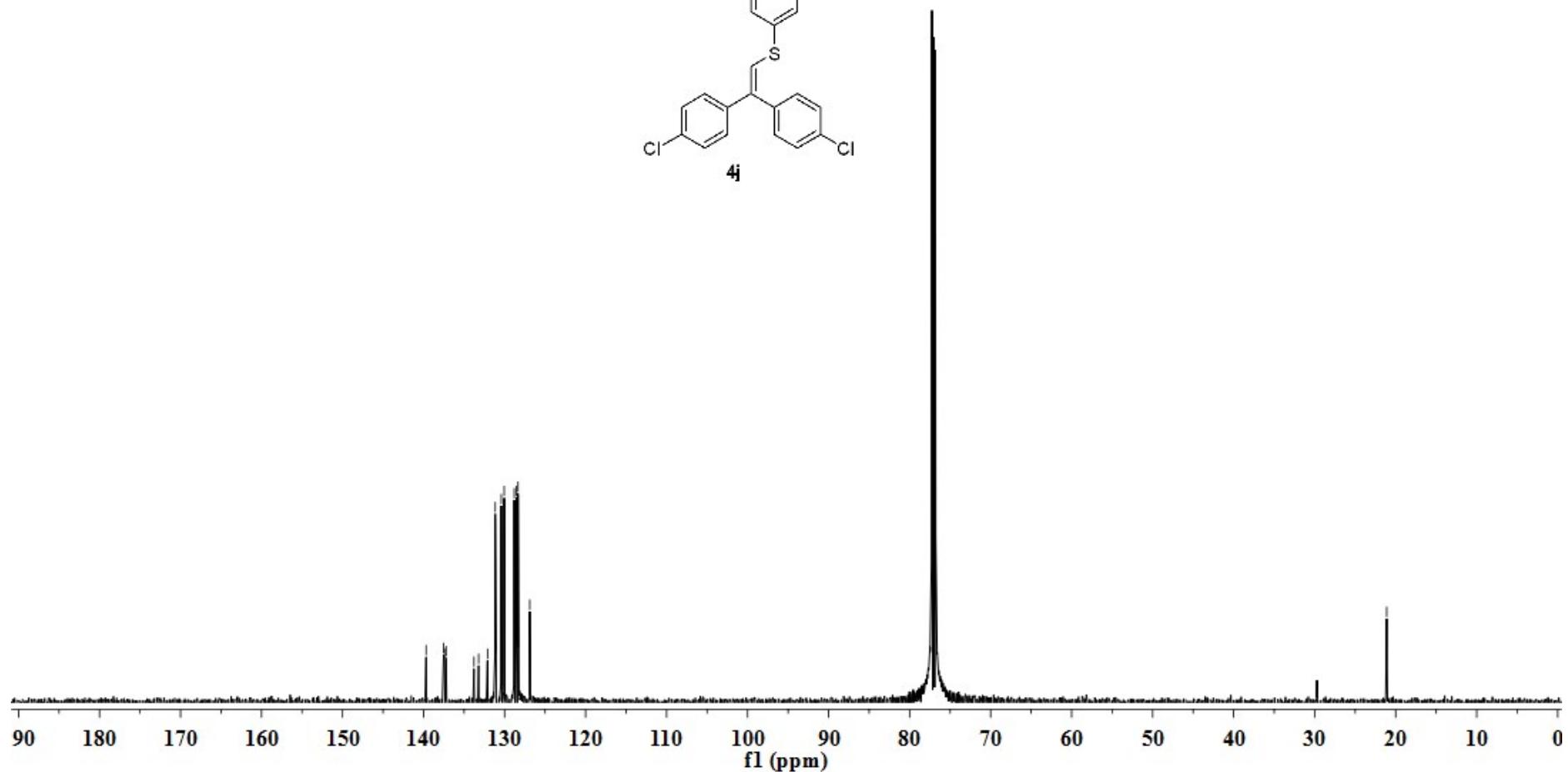
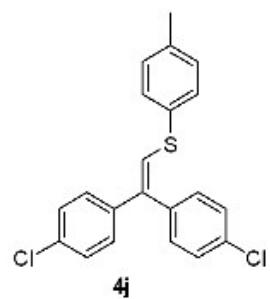
LSW-11-A-CL



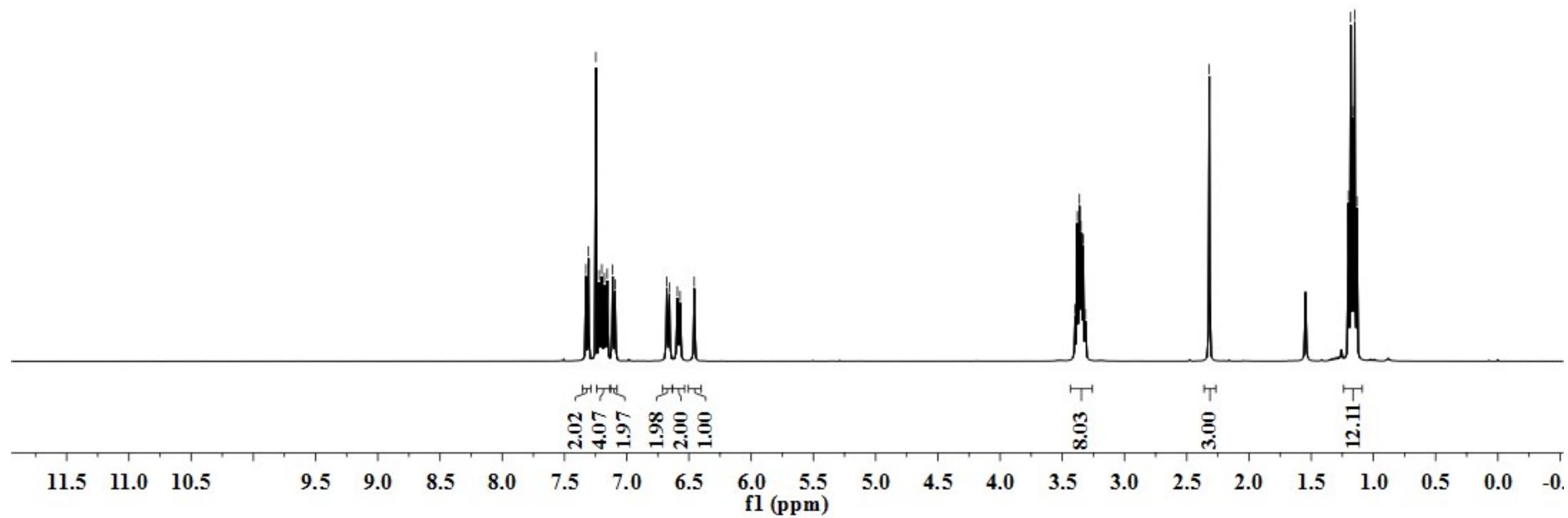
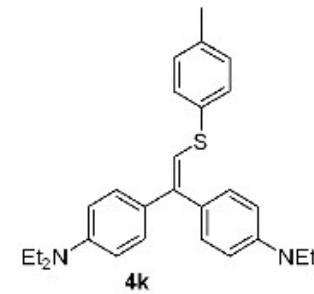
LSW-11-A

139.68  
137.53  
137.41  
137.21  
133.78  
133.20  
132.10  
131.15  
130.41  
130.05  
128.81  
128.55  
128.34  
126.89

-21.11

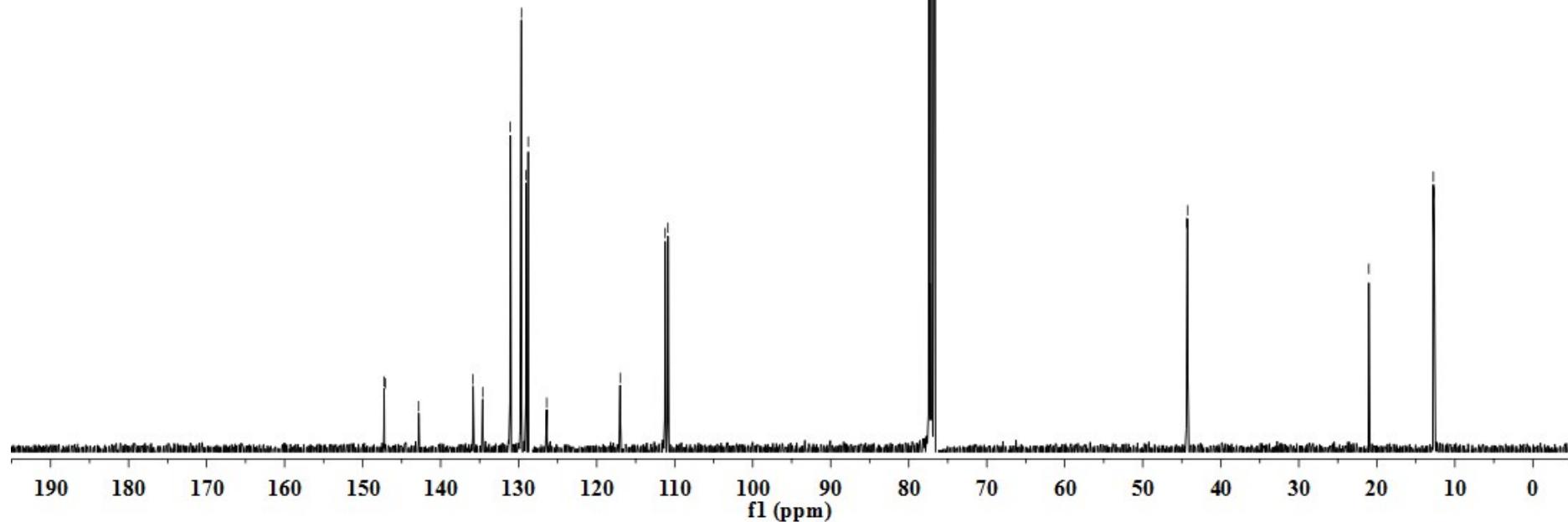
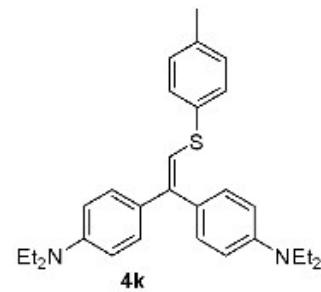


LSW-ET<sub>2</sub>N

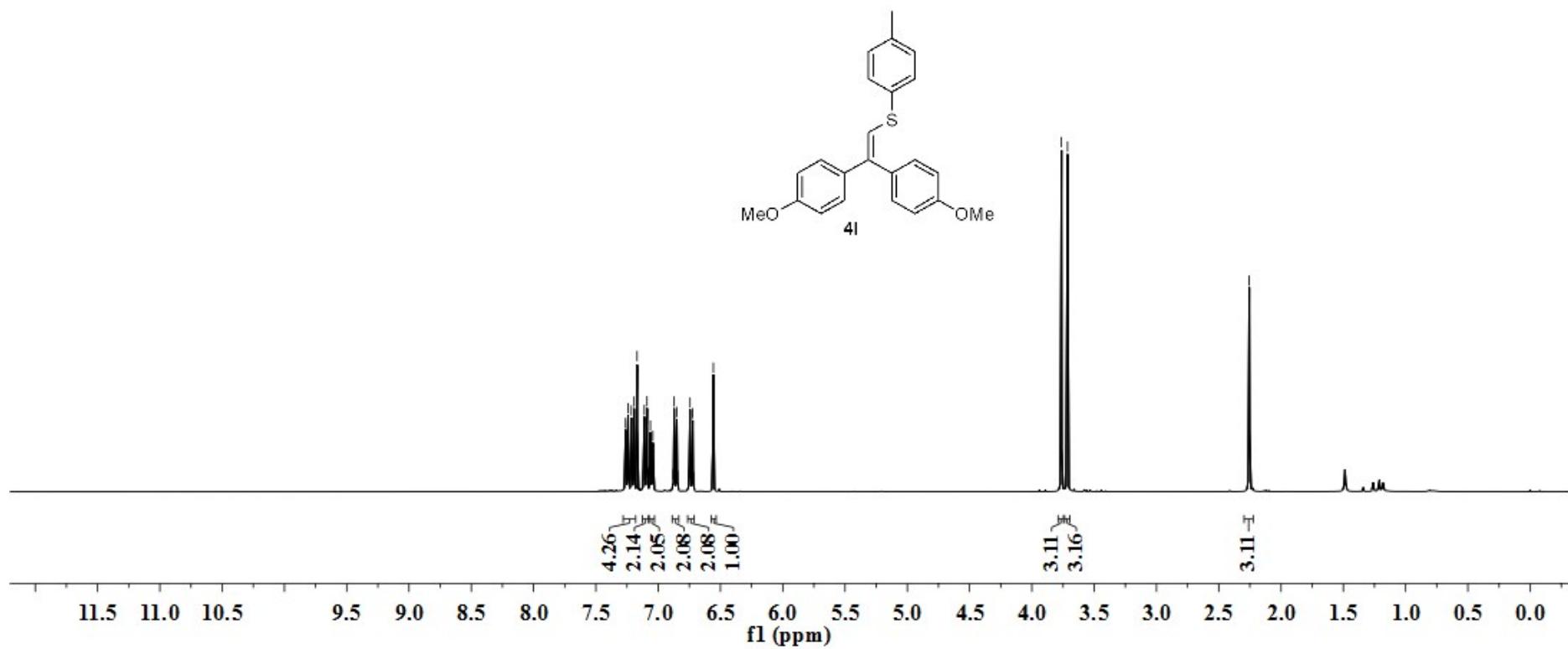
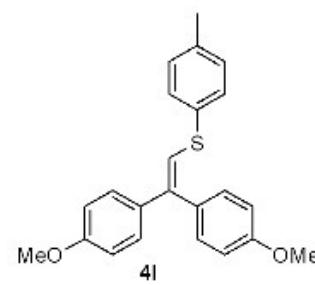
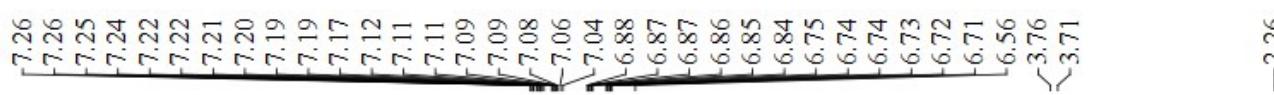


LSW-ET2N

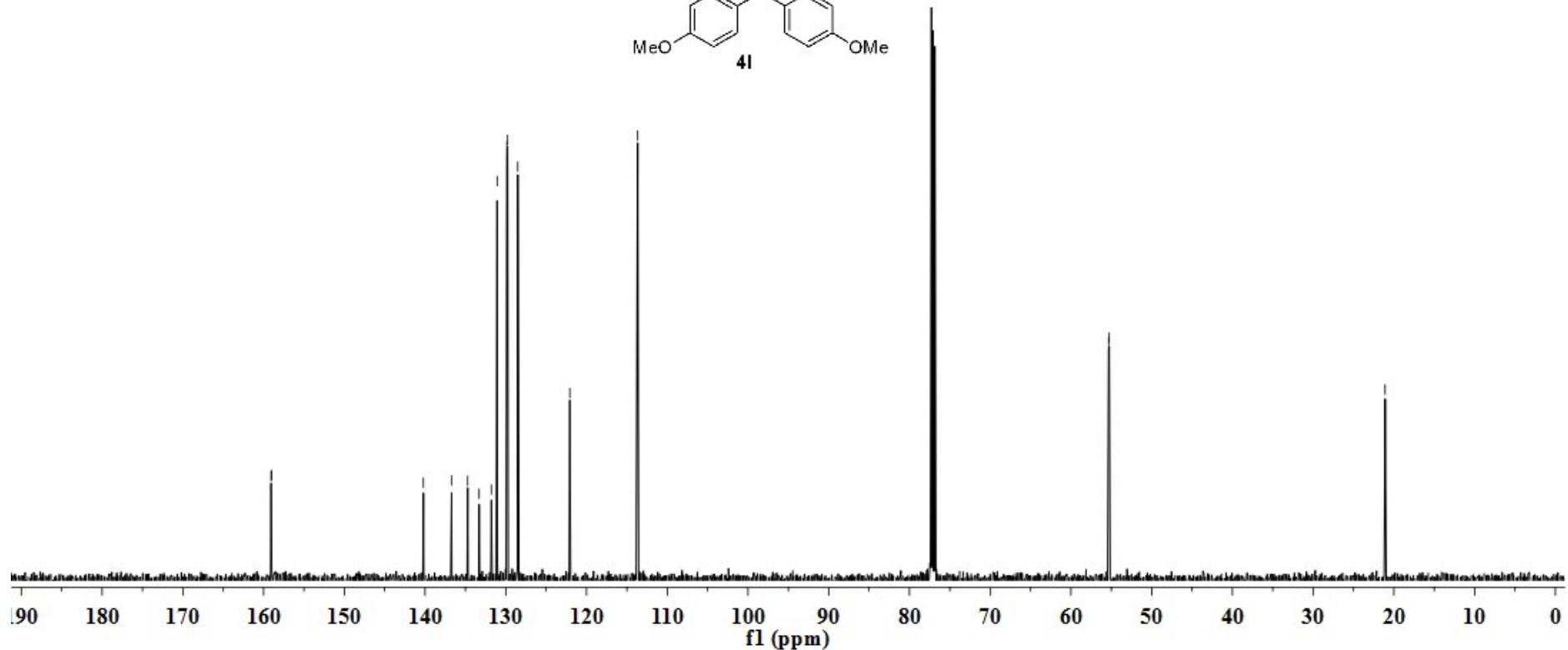
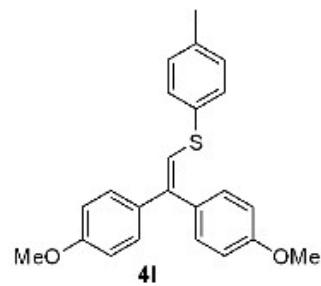
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>147.10  
>142.81  
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<129.05  
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<128.59  
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<12.66



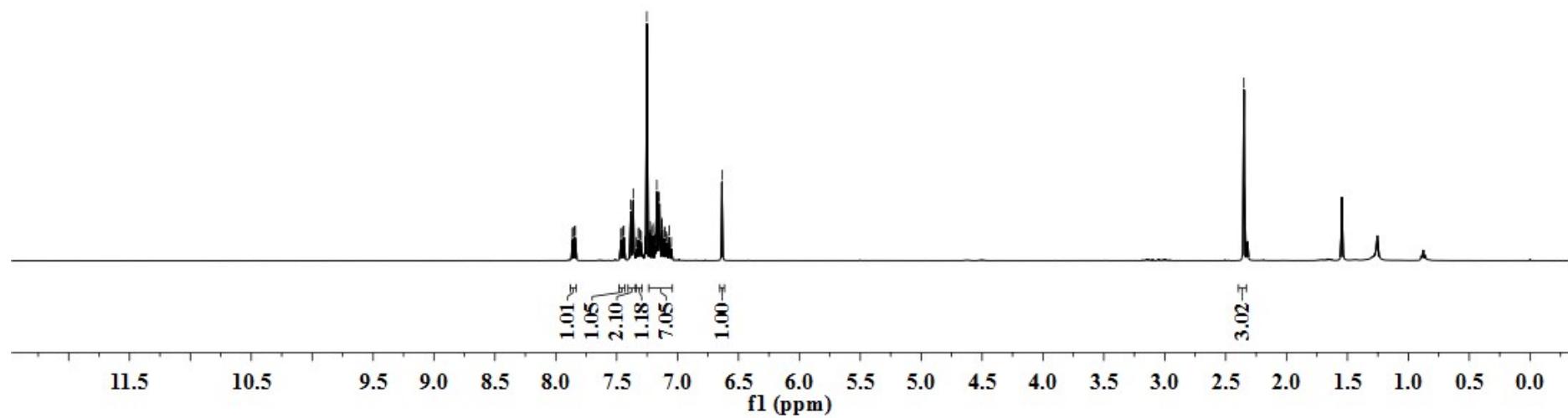
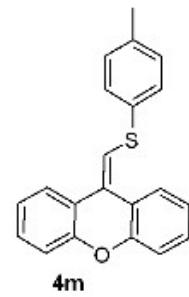
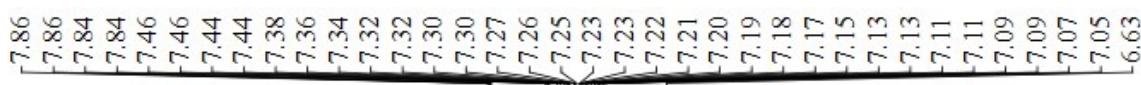
LSW-11-C-OME



LSW-11-C

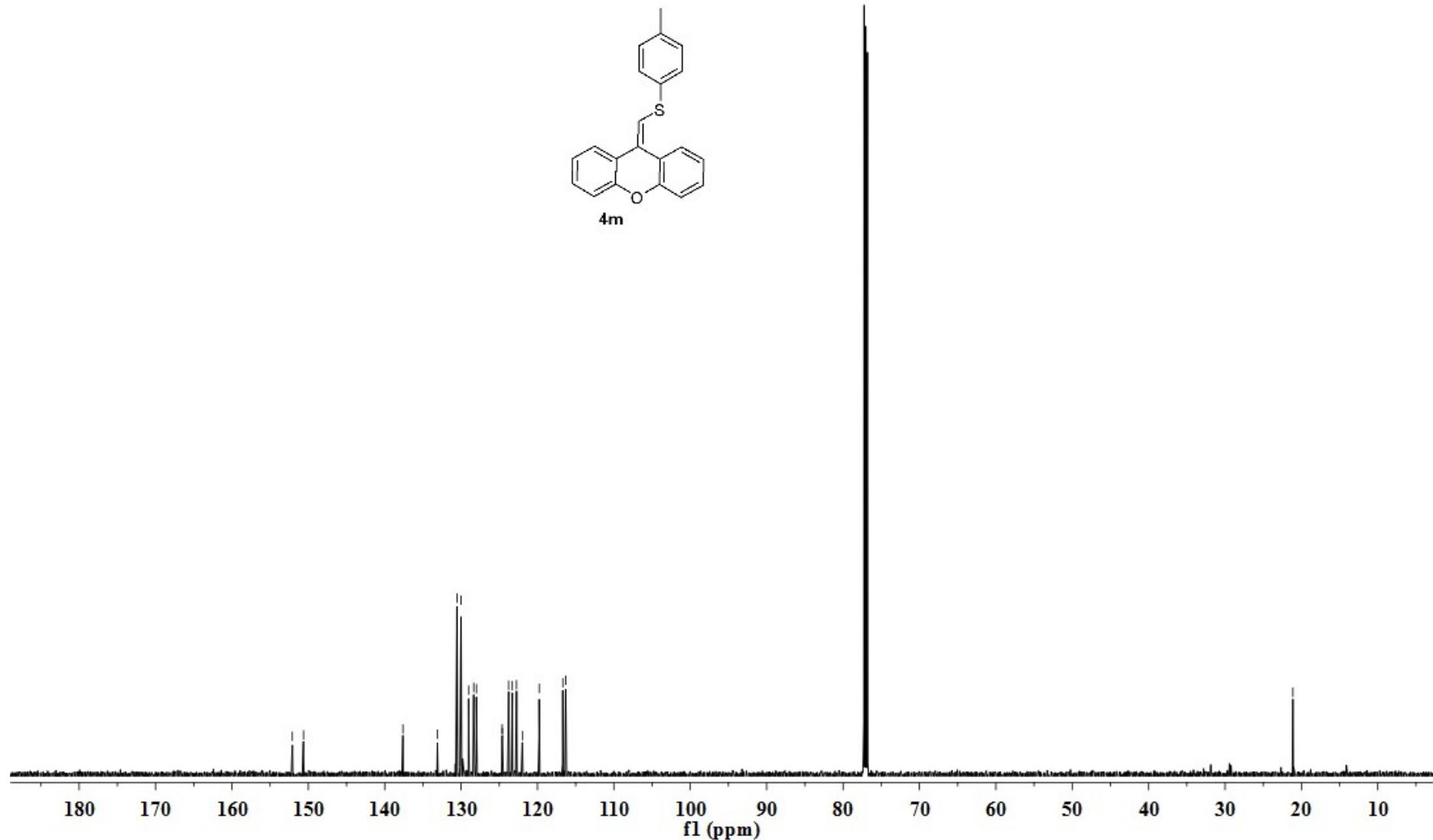
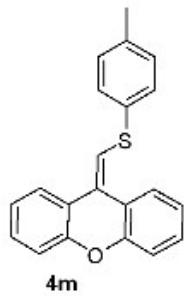


LSW-ZHAN-STOL

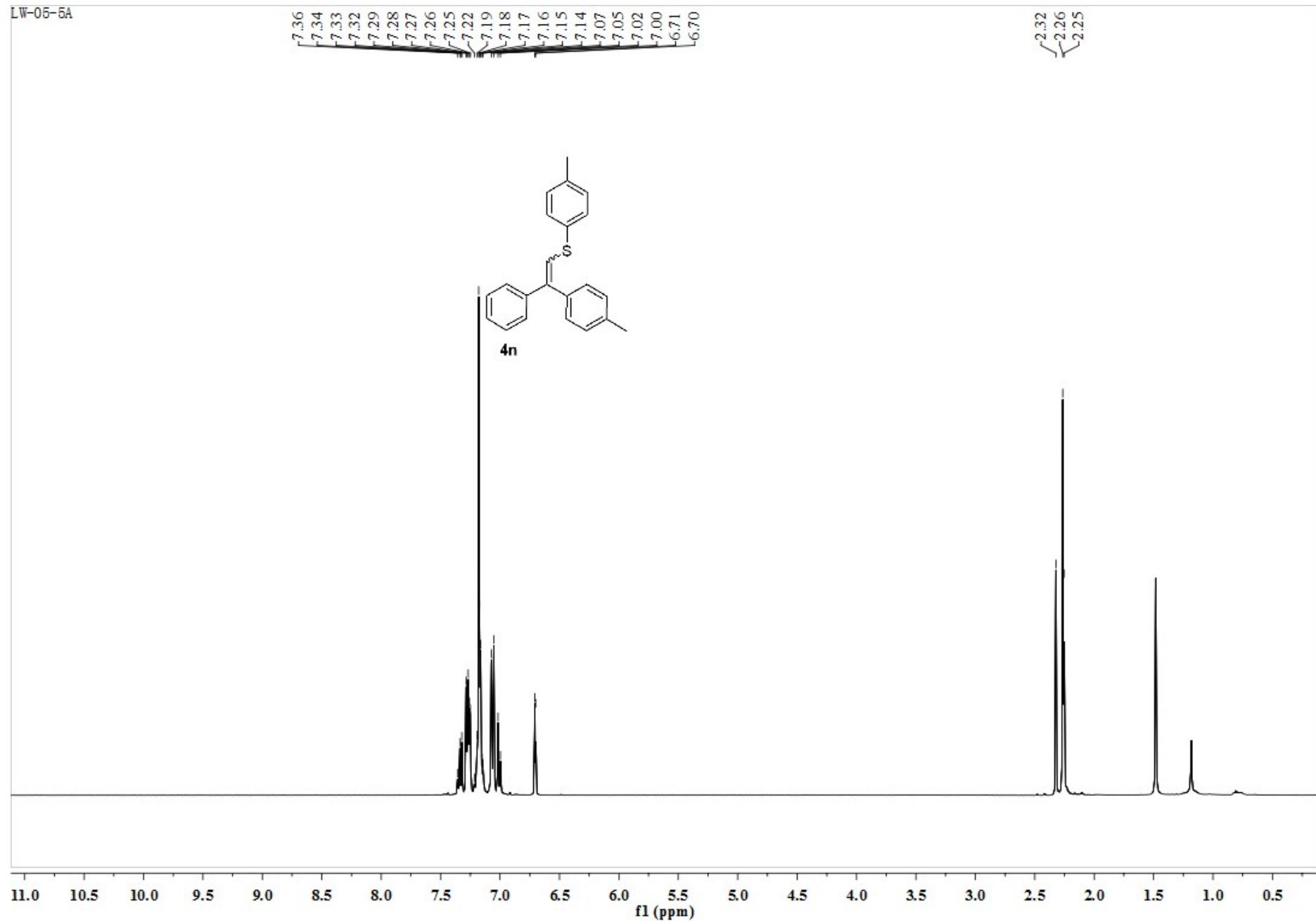


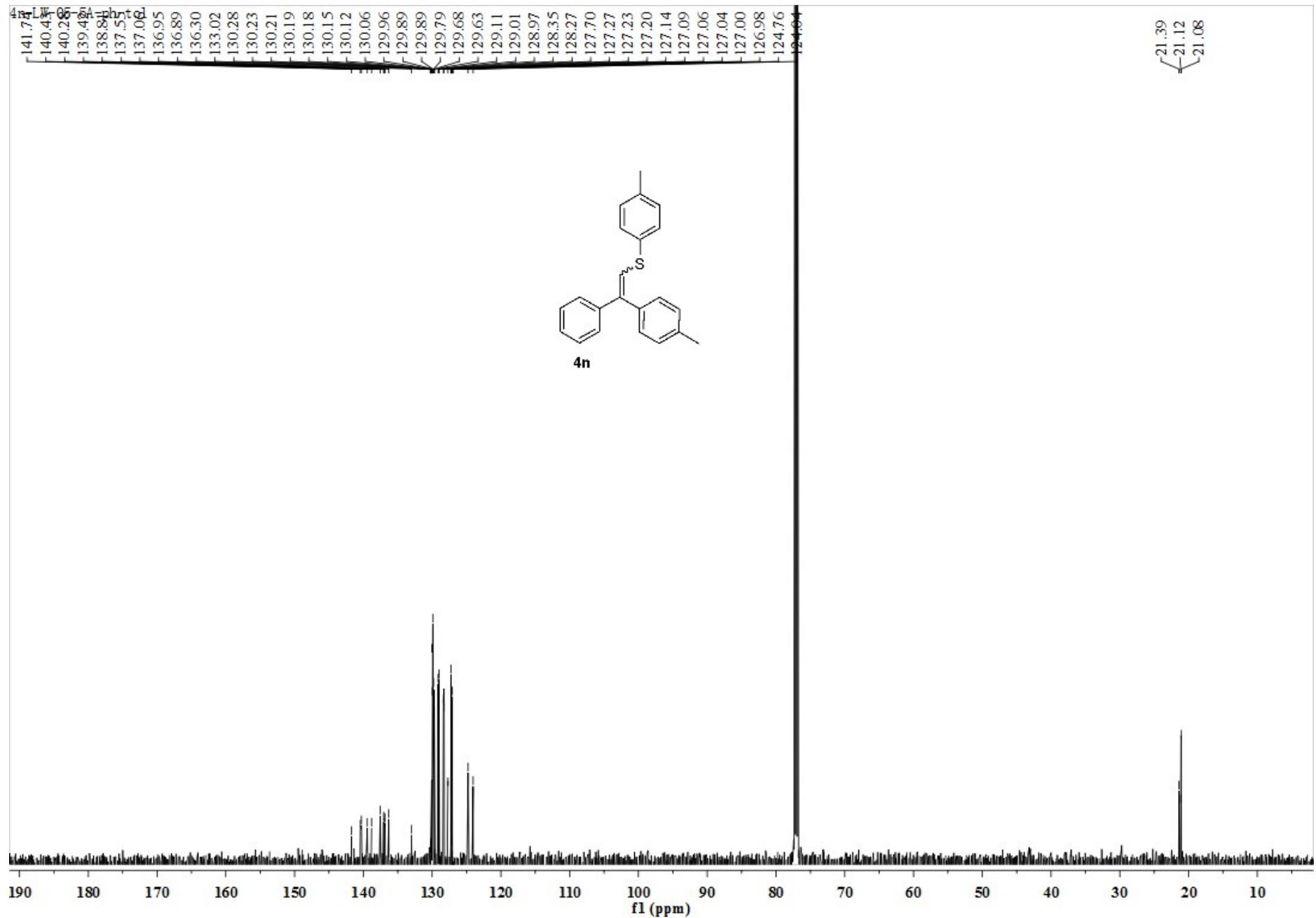
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150.64  
137.61  
133.10  
130.54  
130.01  
129.02  
128.35  
128.00  
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124.61  
123.77  
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121.98  
119.78  
116.68  
116.31

-21.12

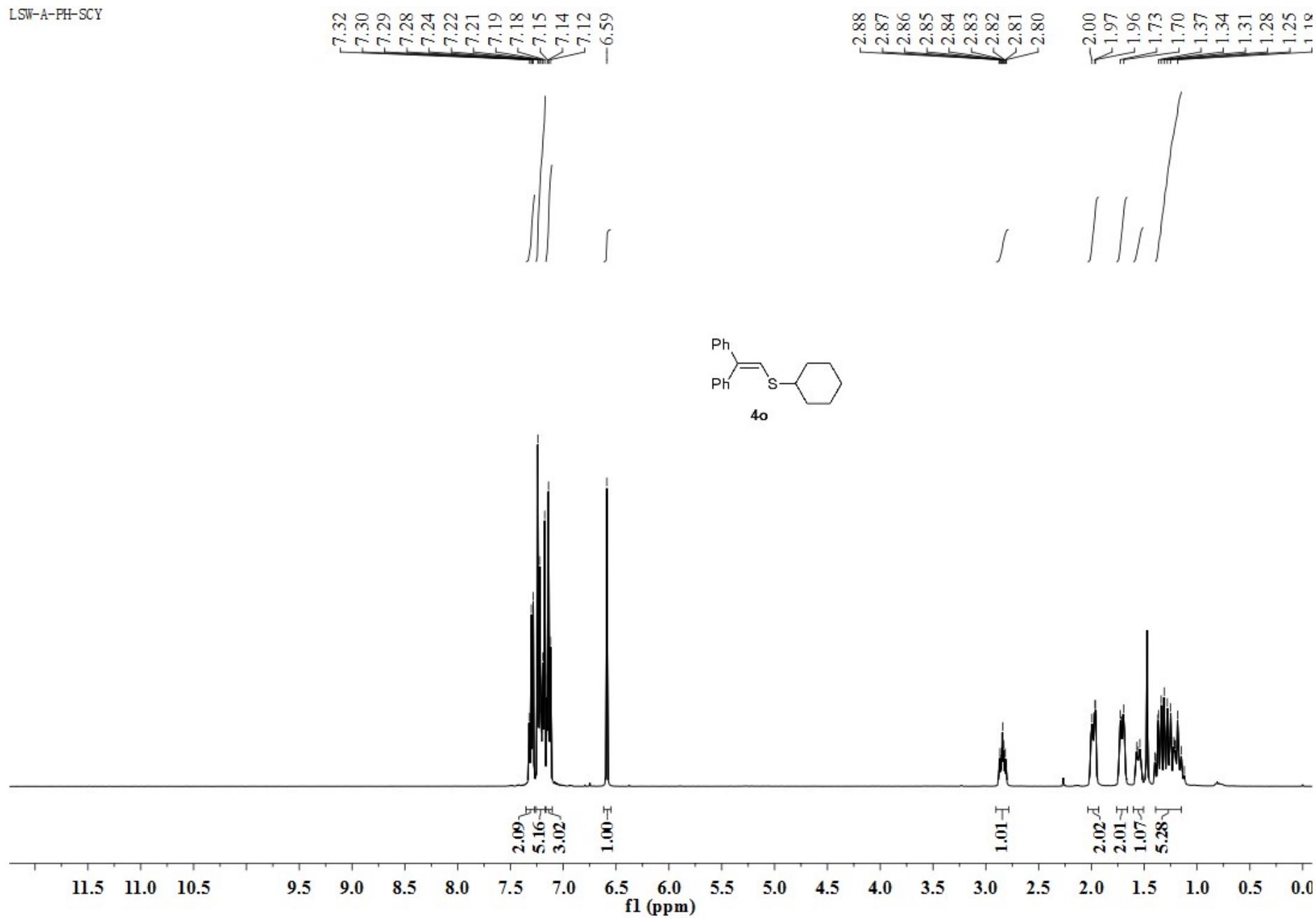


LW-05-5A





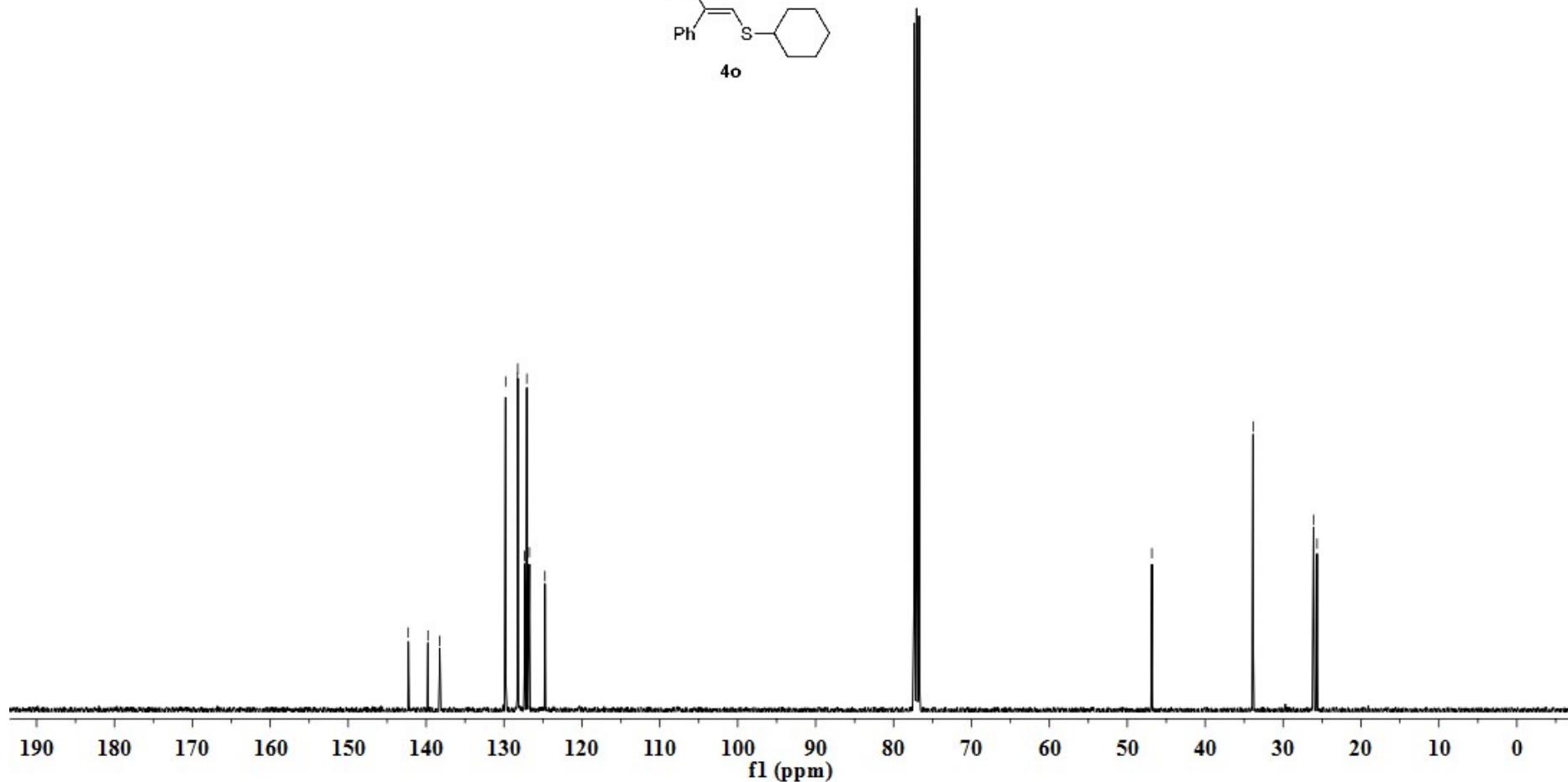
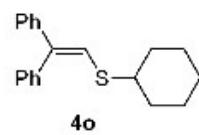
LSW-A-PH-SCY



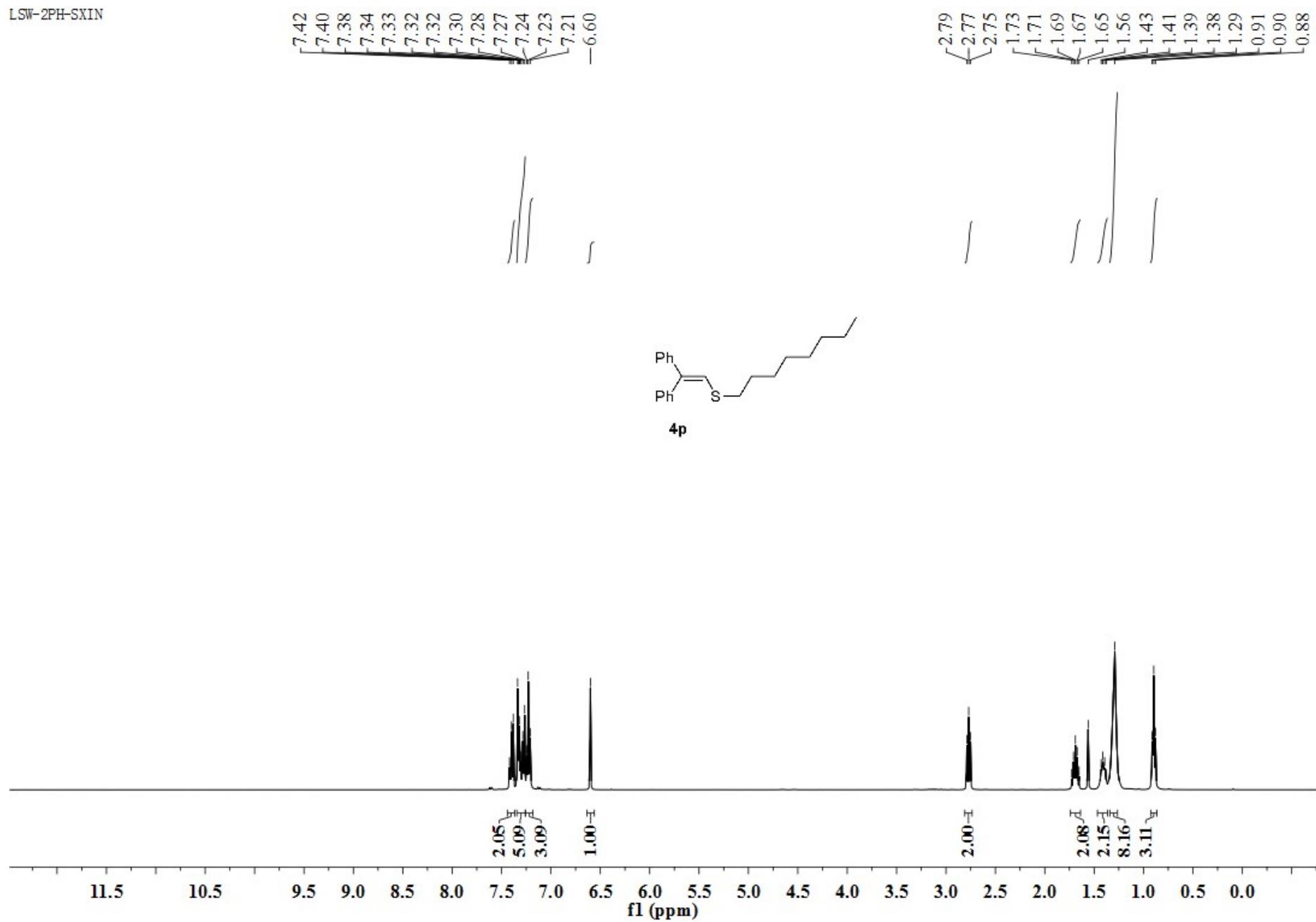
LSW-2PH-SCY-C

142.28  
139.76  
138.26  
129.80  
128.25  
128.22  
127.37  
127.06  
126.74  
124.74

—46.84  
—33.86  
—26.09  
—25.64



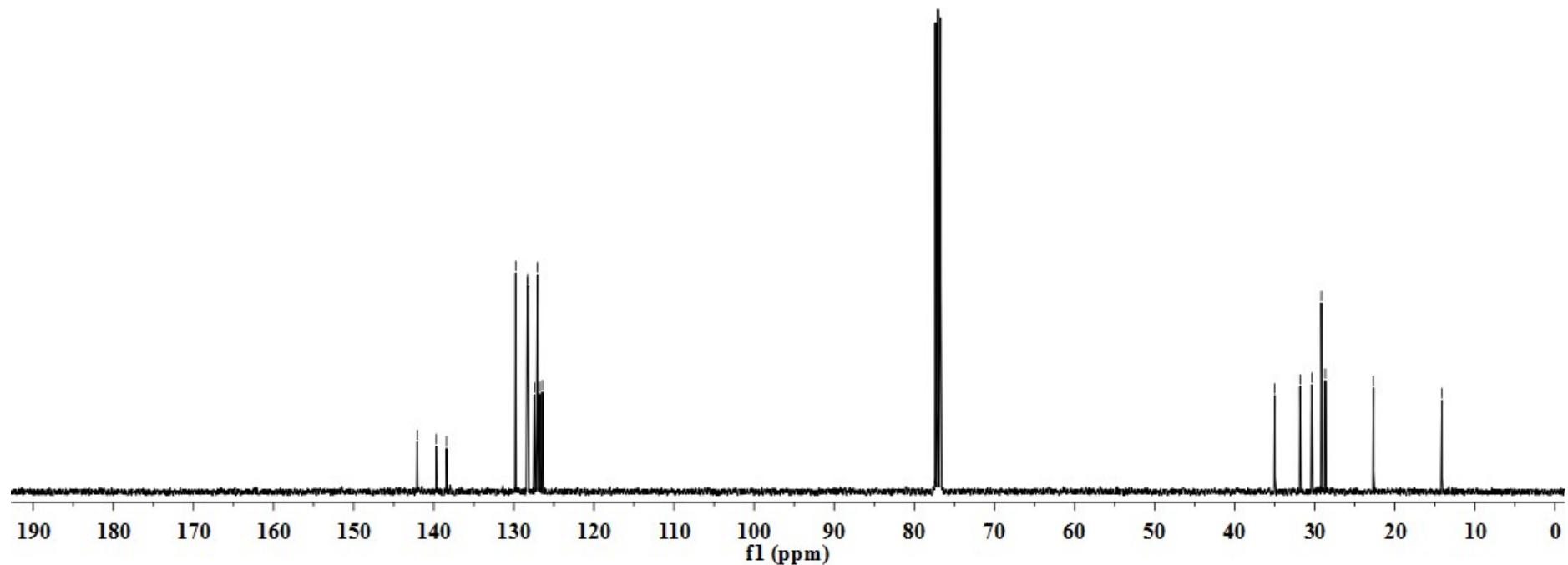
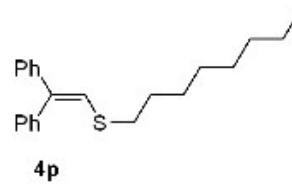
LSW-2PH-SXIN



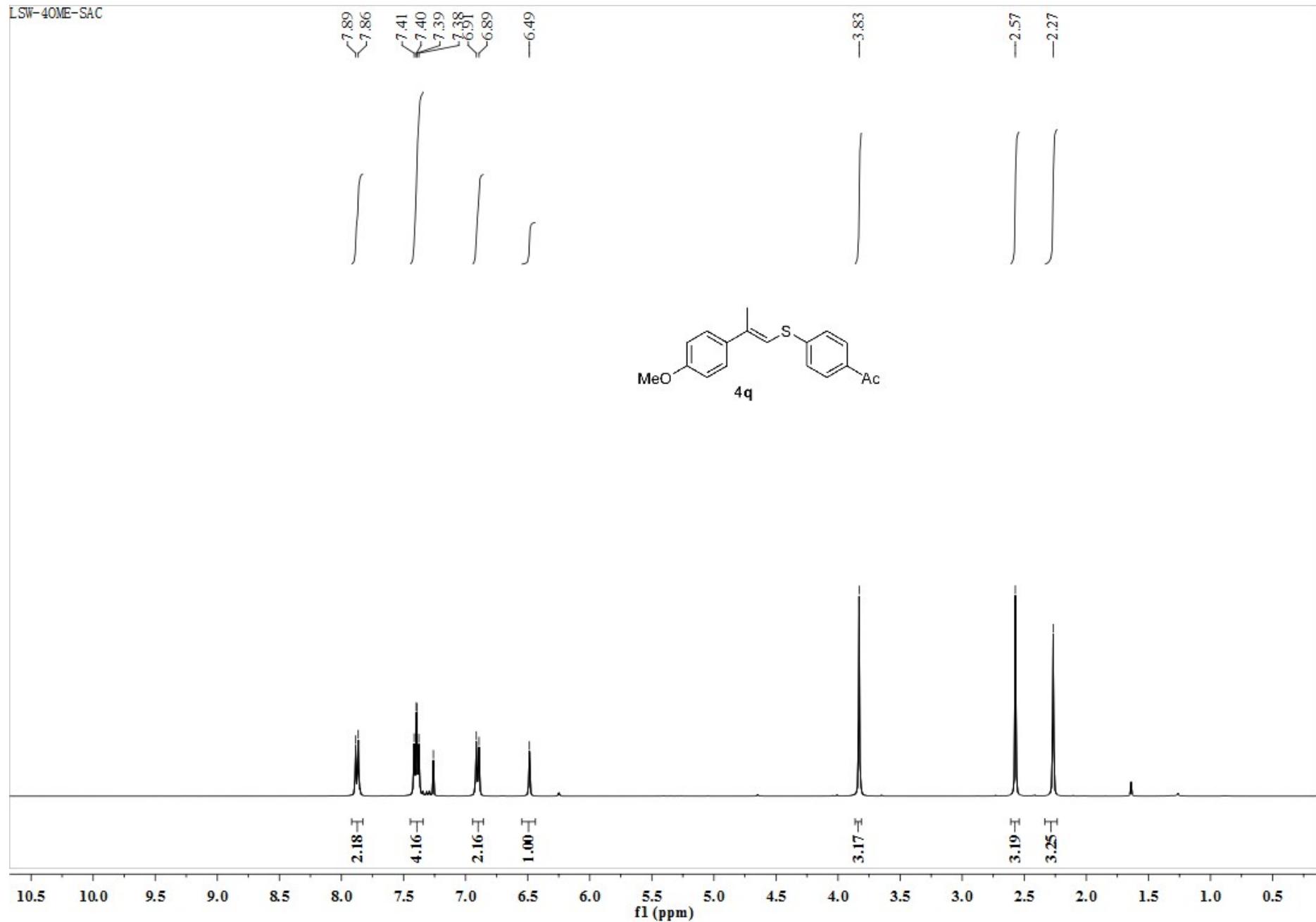
LSW-2PH-SXIN

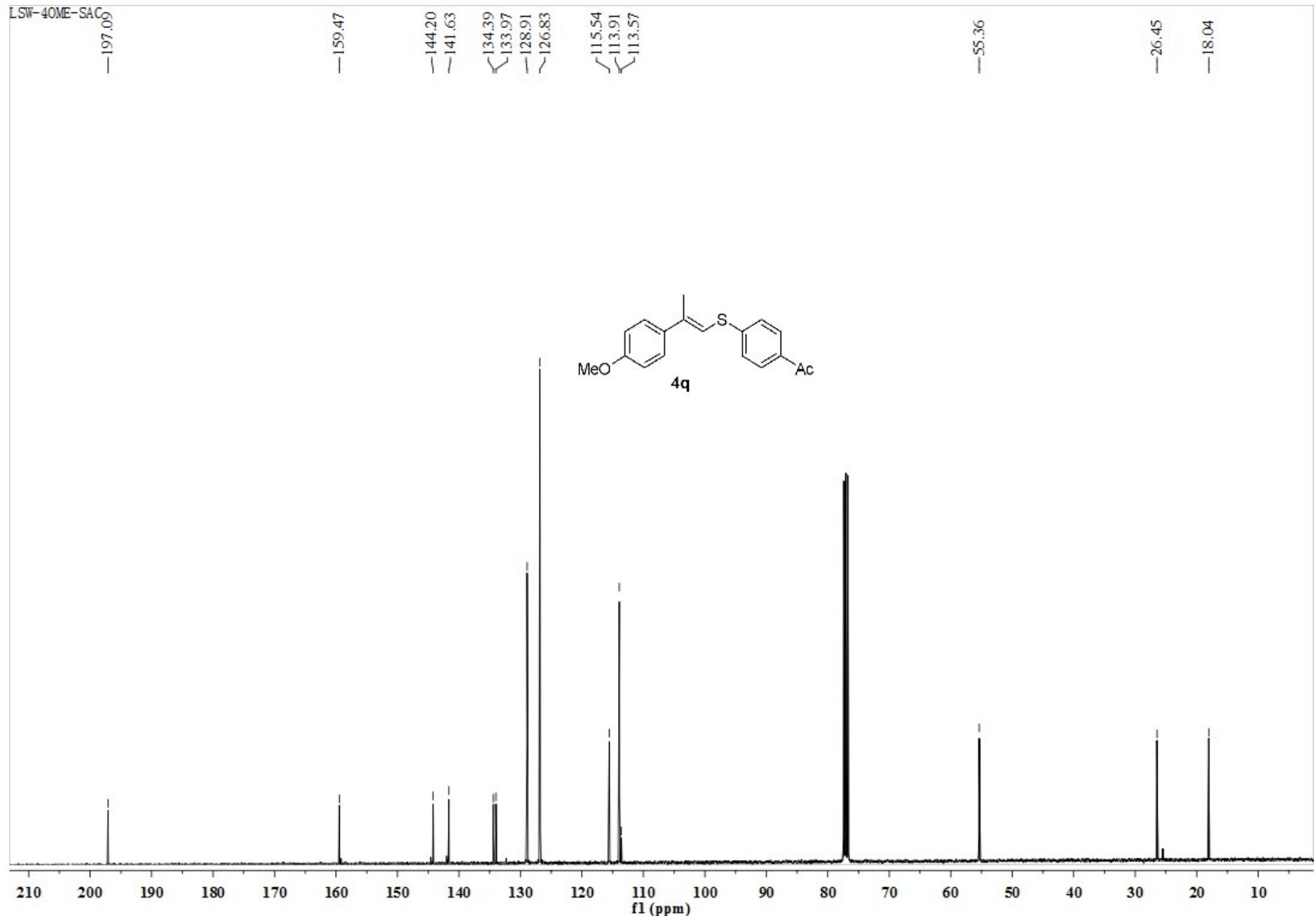
142.06  
139.68  
138.39  
129.76  
128.29  
128.24  
127.43  
127.03  
126.79  
126.43

34.98  
31.82  
30.38  
29.18  
28.67  
22.66  
-14.10



LSW-4OME-SAC



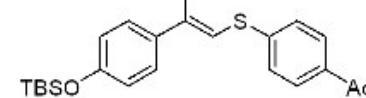


LSW-OTBS-SAC-U

7.91  
7.89  
7.42  
7.37  
7.35  
7.28  
6.86  
6.85  
6.51

-2.60  
-2.28  
-1.02  
-0.24

|      ||      |    |



4r

2.08<sup>—x</sup>  
1.99<sup>—x</sup>  
2.17<sup>—x</sup>  
2.14<sup>—x</sup>  
1.00<sup>—x</sup>

3.19<sup>—x</sup>  
3.21<sup>—x</sup>  
9.07<sup>—x</sup>  
6.19<sup>—x</sup>

1.0    11.5    11.0    10.0    9.5    9.0    8.5    8.0    7.5    7.0    6.5    6.0    5.5    5.0    4.5    4.0    3.5    3.0    2.5    2.0    1.5    1.0    0.5    0.0

f1 (ppm)

LSW-OTBS-SAG-U

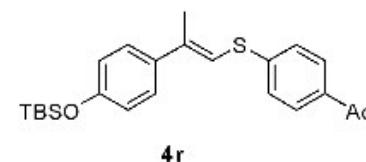
-197.1

-155.65

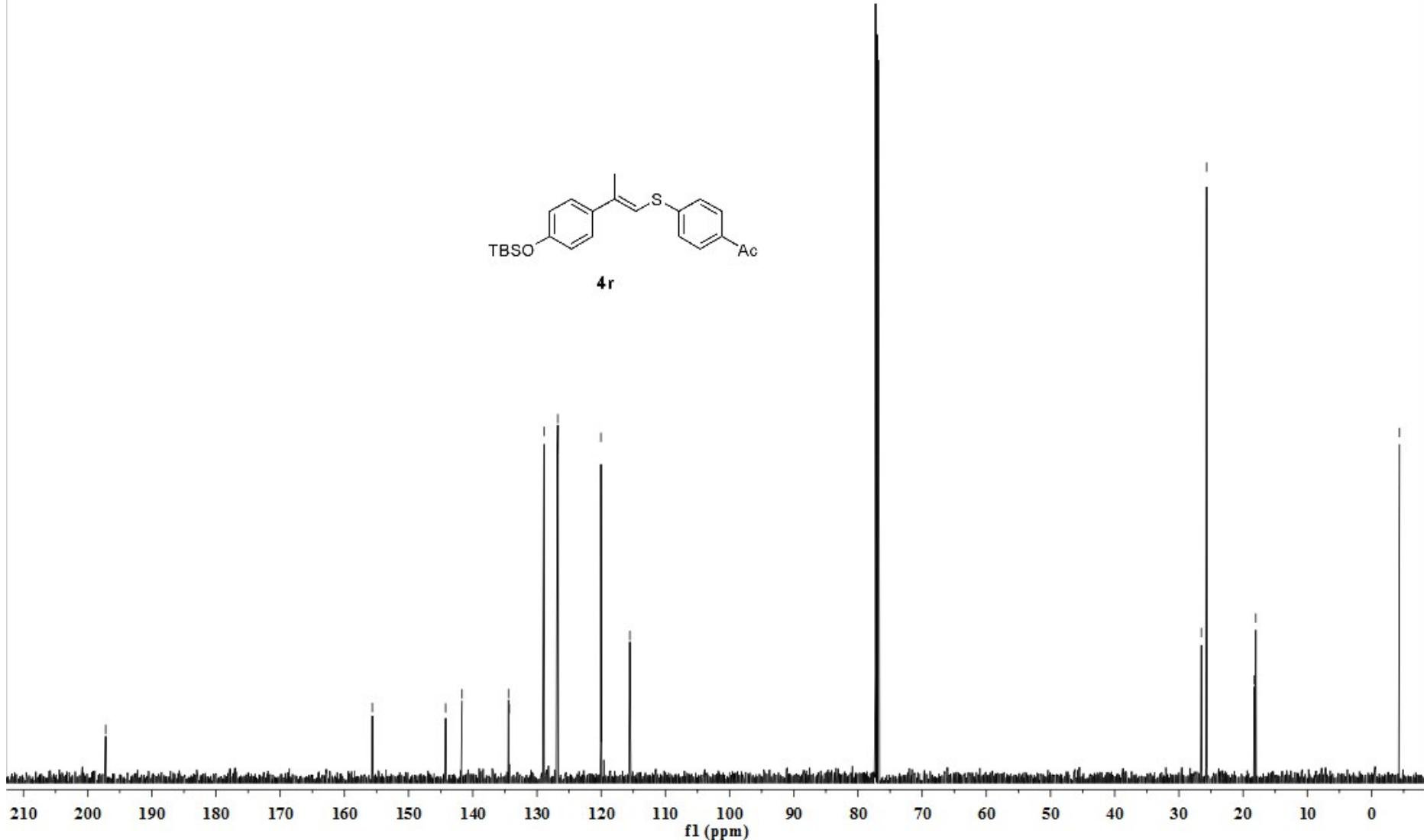
-144.24  
-141.68  
-134.44  
<-134.31  
>-128.92  
<-126.82  
<-126.75  
-120.03  
-115.53

<-26.51  
<-25.69  
<-18.26  
<-18.03

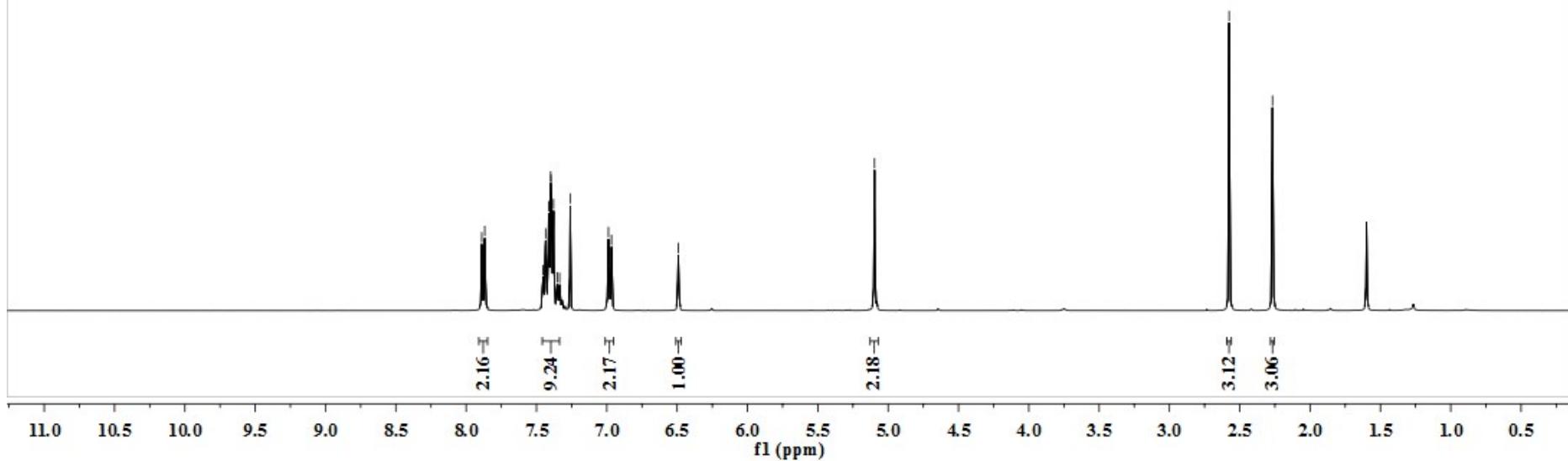
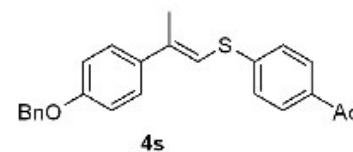
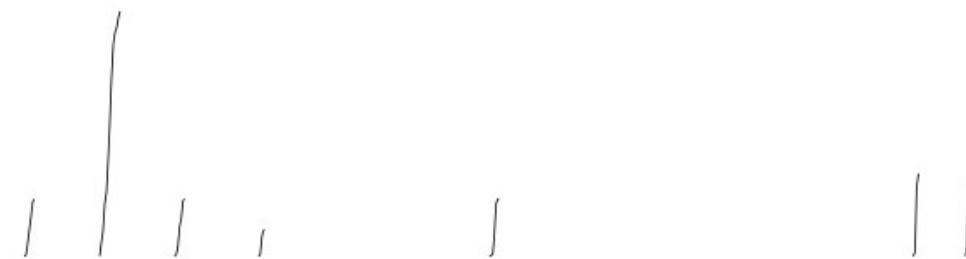
-4.36

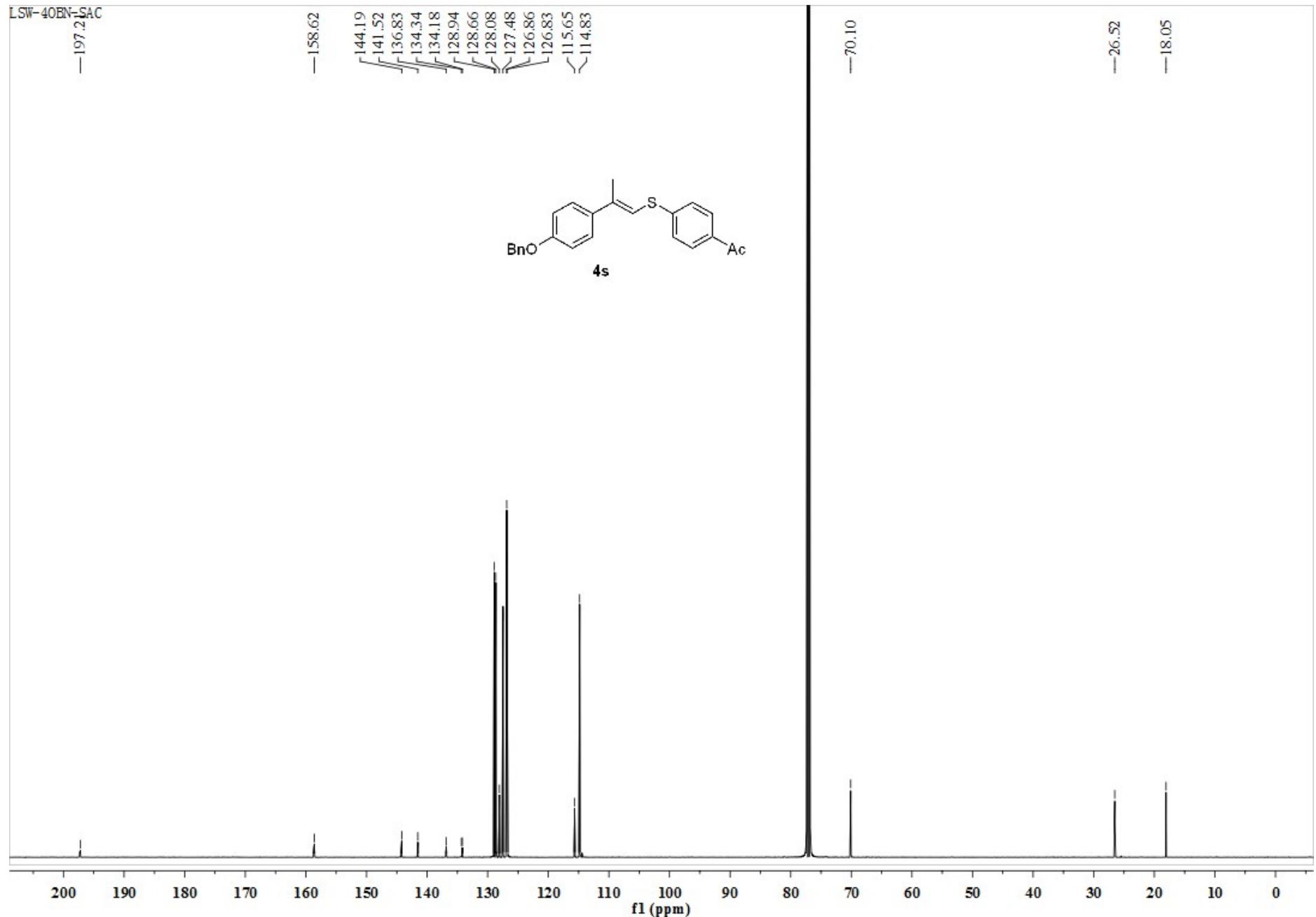


**4r**



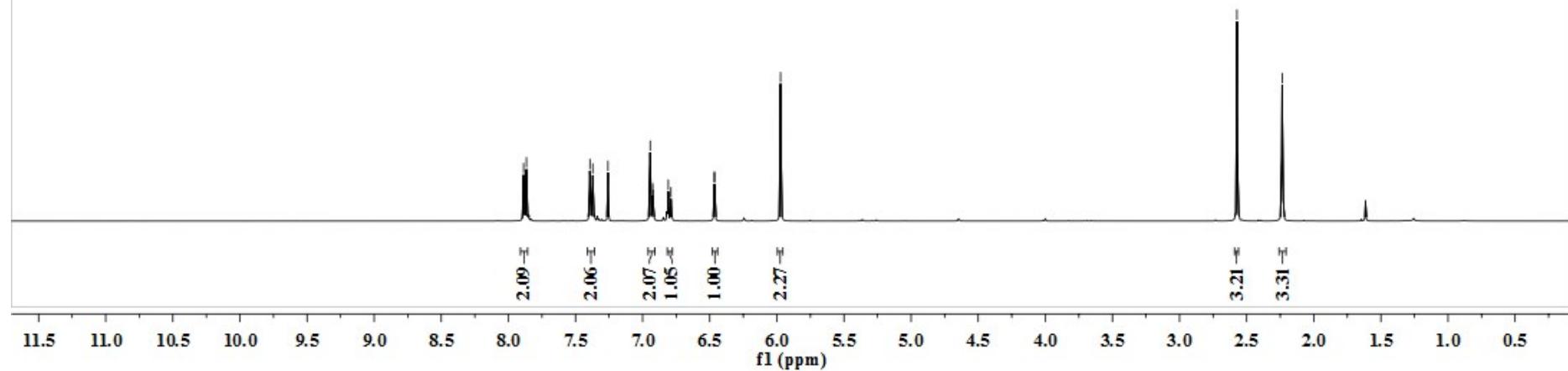
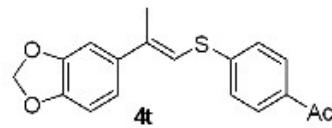
LSW-OBN-SAC





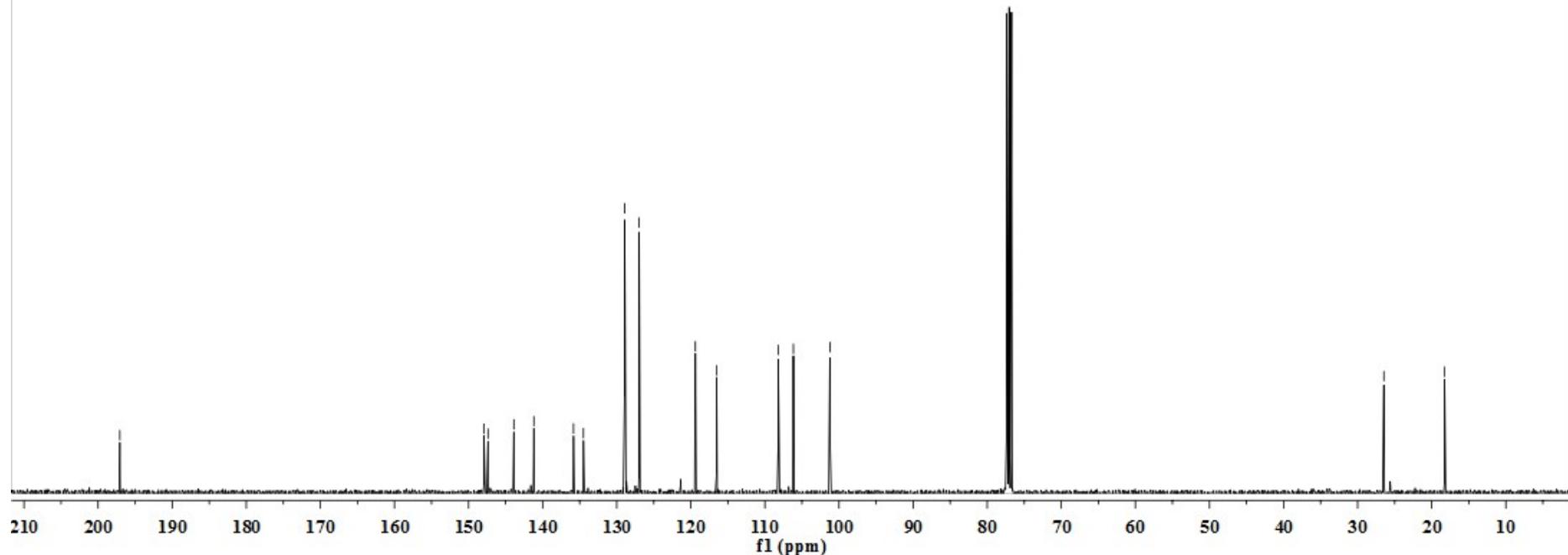
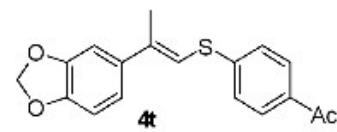
LSW-20CH2-SAC

7.89  
7.87  
7.39  
7.37  
7.26  
6.94  
6.92  
6.81  
6.79  
6.47  
6.46  
—2.57  
—2.24

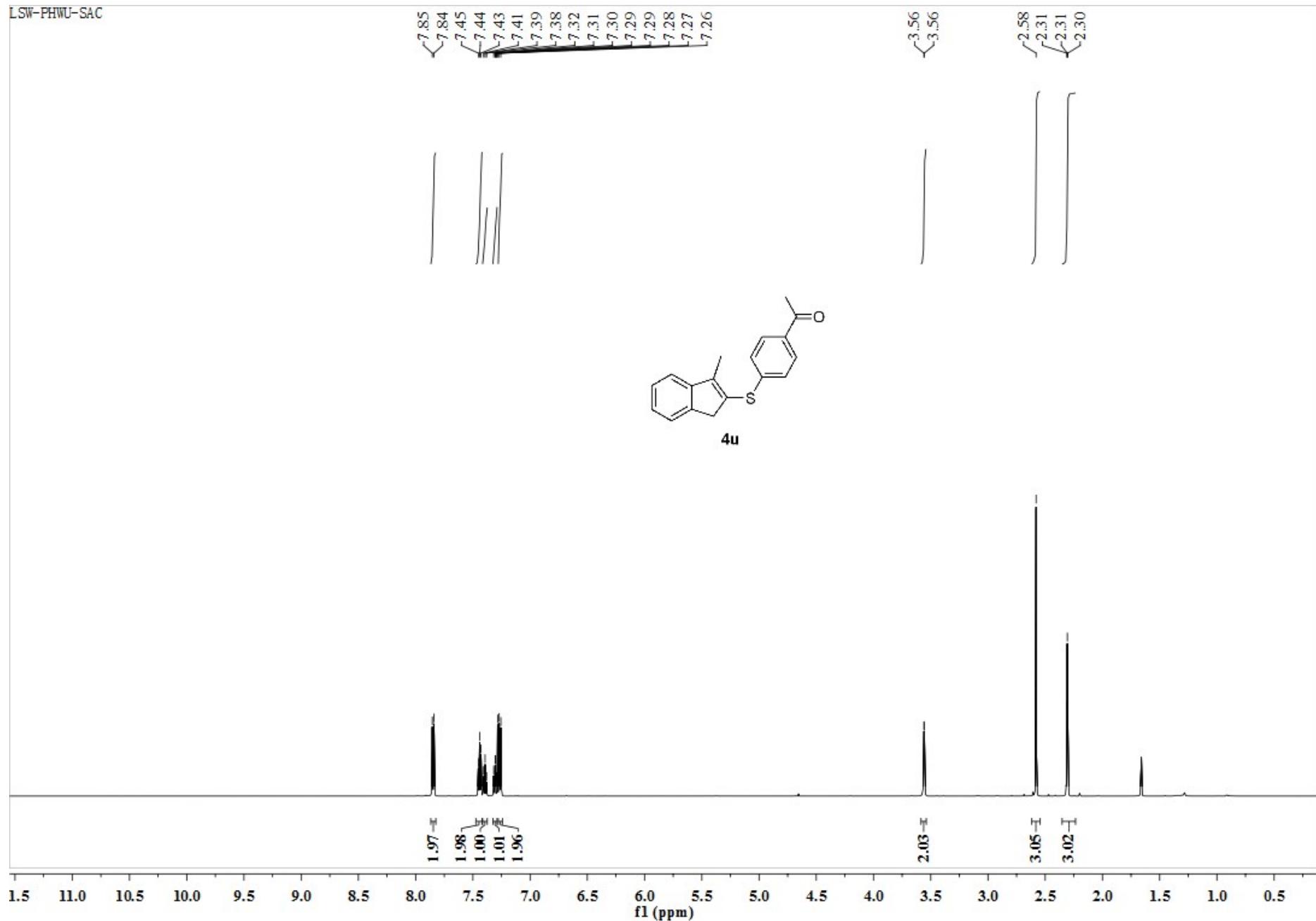


LSW-20CH<sub>2</sub>-SAC  
—197.04

—147.92  
—147.37  
—143.88  
—141.18  
—135.83  
—134.50  
—128.93  
—126.97  
—119.39  
—116.52  
—108.20  
—106.16  
—101.23  
—26.46  
—18.26



LSW-PHWU-SAC



LSW-PHWU-S4C

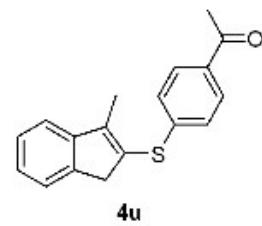
-197.11

147.86  
145.04  
144.59  
143.51  
134.27  
128.97  
128.93  
126.99  
126.68  
126.04  
123.57  
119.75

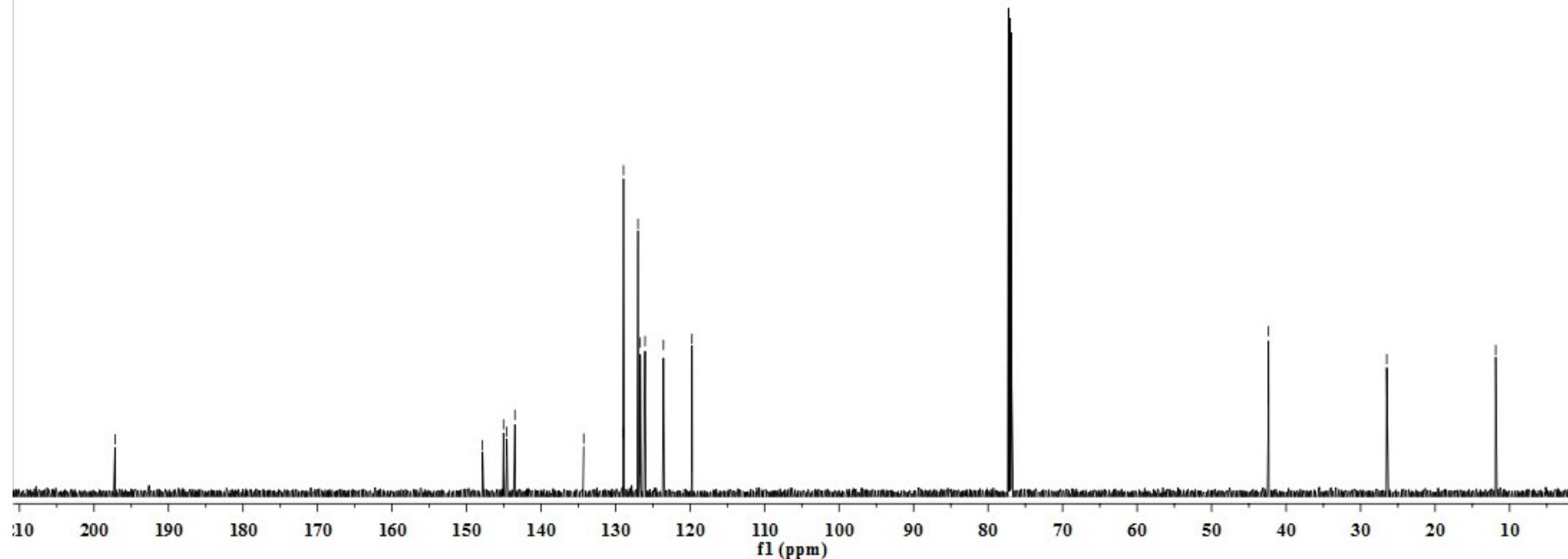
-42.37

-26.50

-11.87



**4u**



## 7. References

- [1] C. J. Nalbandian, E. M. Miller, S. T. Toenjes, J. L. Gustafson, *Chemical Communications* **2017**, *53*, 1494-1497.
- [2] C. Li, J. Li, C. Tan, W. Wu, H. Jiang, *Organic Chemistry Frontiers* **2018**, *5*, 3158-3162.
- [3] X. Zhang, C. Gao, X. Xie, Y. Liu, S. Ding, *European Journal of Organic Chemistry* **2020**, *2020*, 556-560.
- [4] K. Wang, J. Hou, C. Zhang, K. Cheng, R. Bai, Y. Xie, *Advanced Synthesis & Catalysis* **2020**, *362*, 2947-2952.
- [5] B.-W. Wang, K. Jiang, J.-X. Li, S.-H. Luo, Z.-Y. Wang, H.-F. Jiang, *Angewandte Chemie International Edition* **2020**, *59*, 2338-2343.
- [6] J. Zhang, E. Wang, Y. Zhou, L. Zhang, M. Chen, X. Lin, *Organic Chemistry Frontiers* **2020**, *7*, 1490-1494.
- [7] S. Ni, L. Zhang, W. Zhang, H. Mei, J. Han, Y. Pan, *The Journal of Organic Chemistry* **2016**, *81*, 9470-9475.