

# Photoredox $\beta$ -thiol- $\alpha$ -carbonylation of enones accompanied by unexpected $Csp^2$ -C(CO) Cleavage

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## 1. General Information

Unless otherwise noted, all reactions were carried out in reaction tube (5 mL from Synware) equipped with a Teflon-coated magnetic stir bar. All commercially available reagents were used without further purification. Blue LED (3Wx3) marked 450-460 nm, White LED (23W) marked 375-820 nm, Green LED (3Wx3) marked 520-560 nm was used for photo-catalysis equipped with a dark box. Analytical thin layer chromatography (TLC) was performed using Silica Gel 60 F25 plates (Qingdao, 0.25 mm thick). Ammonium phosphomolybdate hydrate chromogenic agent was used to identify aldehyde product. GC-MS data were recorded on an Agilent Technologies 7890A GC system coupled with Agilent Technologies 5975C mass spectrometer using HP-5MS column (30 m x 0.250 mm, 0.25  $\mu$ ) purchased from Agilent Technologies.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained in  $\text{CDCl}_3$  or DMSO using 400 MHz, 500 MHz Varian NMR spectrometer. Chemical shifts in  $^1\text{H}$  NMR spectra are reported in parts per million (ppm) on the  $\delta$  scale from an internal standard of residual  $\text{CDCl}_3$  (7.27 ppm) or the central peak of  $\text{DMSO}-d_6$  (2.50 ppm).

## 2. General procedures

### a) General procedure for preparation of enones

A solution of acetophenone (50 mmol), alcohol (15 mL), 10 % sodium hydroxide (25 mL) are introduced into 100 mL three-neck flasks, supplied with an effective stirrer. The bottle is cooled in ice bath. After the stirrer started, benzaldehyde (5 mol) is then added at once, warm to room temperature and stir for 1.5 hour. Upon completion, the flask was cooled in a freezing bath, yellow solid products appears. Then solids were separated out by filtration, washed with water, cold alcohol. The crude product is purified by recrystallization with alcohol.

### b) General procedure for photoredox oxidative C-C bond cleavage of $\alpha,\beta$ -unsaturated enones

A 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with thiophenol (0.4 mmol), benzalacetophenone (0.2 mmol), MeCN (4 mL). With the rubber septum fitted to the vial, the vessel was degassed using a vent needle for ca. 30 sec and charged with an oxygen balloon. Next, fac-Ir(ppy)<sub>3</sub> (2.4 mg, 0.004 mmol, pre-dissolved in  $\text{CH}_3\text{CN}$ ) was added via syringe. The top of the vial was wrapped in Parafilm® and the mixture was stirred vigorously under irradiation of Blue LEDs for 4 h. After completion, stirring was stopped and septum was opened.  $\text{NaBH}_4$  (0.6 mmol) was slowly added in portion and further stirred for extra 30 min. The mixture was then concentrated in vacuo and the crude material was further purified via

column chromatography (petroleum ether/ ethyl acetate from 1/20 to 1/10).

**c) Procedures for the preparation of 5**

A 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), benzalacetophenone (41.6 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane. With the rubber septum fitted to the vial, the vessel was degassed using a vent needle for ca. 30 sec and charged with an oxygen balloon. Next, *fac*-Ir(ppy)<sub>3</sub> (2.4 mg, pre-dissolved in CH<sub>3</sub>CN) was added via syringe. The top of the vial was wrapped in Parafilm® and the mixture was stirred vigorously under irradiation of Blue LEDs. After completion, stirring was stopped and septum was opened. 2,4-Dinitrophenylhydrazine (40 mg, 0.2 mmol) was added and further stirred for extra 30 min. Yellow precipitates were then collected and washed with Et<sub>2</sub>O (1 mLx3) to afford compound 1-(2-((4-chlorophenyl)thio)-2-phenylethylidene)-2-(2,4-dinitrophenyl)hydrazine **5**, yellow solid, 85.6 mg, 92% yield. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 11.02 (s, 1H), 9.12 (d, *J* = 2.6 Hz, 1H), 8.31 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.79-7.54 (m, 2H), 7.41 (dd, *J* = 14.5, 6.2 Hz, 6H), 7.28 (d, *J* = 8.9 Hz, 4H), 5.08 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.2, 144.8, 138.4, 135.9, 134.8, 134.6, 131.5, 130.0, 129.4, 129.3, 129.3, 128.7, 128.0, 123.3, 116.5, 55.0. HRMS (ESI) *m/z* M+Na<sup>+</sup> calcd for C<sub>20</sub>H<sub>15</sub>ClN<sub>4</sub>O<sub>4</sub>SNa<sup>+</sup> 465.0395, found 465.0390.

**d) Procedures for the preparation of 6**

A 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), benzalacetophenone (41.6 mg, 0.2 mmol), 4 mL dichloromethane. With the rubber septum fitted to the vial, the vessel was degassed using a vent needle for ca. 30 sec and charged with an oxygen balloon. Next, *fac*-Ir(ppy)<sub>3</sub> (2.4 mg, pre-dissolved in CH<sub>3</sub>CN) was added via syringe. The top of the vial was wrapped in Parafilm® and the mixture was stirred vigorously under irradiation of Blue LEDs. After completion, stirring was stopped and septum was opened. MeMgCl (0.6 mmol, dissolved in THF) was added dropwise and further stirred for extra 2h. The mixture was then quenched with sat. NH<sub>4</sub>Cl solution and extracted with EtOAc (3 mL x3). The extractions were then concentrated in vacuo and the crude material was further purified via column chromatography (EA/PE from 1/10 to 1/5) to give product **6** as a mixture (dr = 1/1).

Mixture of two isomers. colorless oil: 19.5 mg, 70% yield. <sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.41-7.22 (m, 5H), 7.19-7.09 (m, 4H), 4.19-3.93 (m, 2H), 1.24 -1.12 (m, 1H). <sup>13</sup>C NMR (101 MHz,

CDCl<sub>3</sub>)  $\delta$  139.5, 138.1, 134.1, 133.8, 133.5, 133.0, 132.4, 129.1, 129.0, 128.9, 128.6, 128.6, 128.5, 128.3, 127.8, 127.7, 125.4, 69.9, 69.7, 63.9, 61.8, 20.5. HRMS (ESI)  $m/z$  M+O+H<sup>+</sup> calcd for C<sub>15</sub>H<sub>16</sub>ClO<sub>2</sub>S<sup>+</sup> 295.0554, found 295.0558.

**e) Procedures for the synthesis of 7**

A 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with thiophenol (0.4 mmol), benzalacetophenone (0.2 mmol), MeCN (4 mL). With the rubber septum fitted to the vial, the vessel was degassed using a vent needle for ca. 30 sec and charged with an oxygen balloon. Next, fac-Ir(ppy)<sub>3</sub> (2.4 mg, 0.004 mmol, pre-dissolved in CH<sub>3</sub>CN) was added via syringe. The top of the vial was wrapped in Parafilm® and the mixture was stirred vigorously under irradiation of Blue LEDs for 4 h. After completion, stirring was stopped and septum was opened. NaBH<sub>4</sub> (0.6 mmol) was slowly added in portion and further stirred for extra 30 min. Without isolation, the reaction tube was charged with nitrogen, Et<sub>3</sub>N (0.3 mmol) and DCM (2 mL) was sequentially added. After that methacryloyl chloride (0.3 mmol) was then added dropwise at 0 °C, the mixture was allowed to warm to room temperature and stirred at room temperature for 12 h. Reaction was monitored by TLC. Unupon completion, reaction mixture was diluted with 3 mL DCM, washed with water (3 mLx3), the collected organic mixture was then concentrated in vacuo and the crude material could pass through a short silica gel column to yield pure product 2-((4-chlorophenyl)thio)-2-phenylethyl methacrylate **7** as pale yellow oil: 51 mg, 73% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.18 (ddt,  $J$  = 19.2, 8.7, 5.3 Hz, 10H), 5.89 (dd,  $J$  = 1.5, 1.0 Hz, 1H), 5.52-5.34 (m, 1H), 4.47 -4.31 (m, 3H), 1.77 (dd,  $J$  = 1.4, 1.0 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  167.2, 138.1, 135.8, 133.9, 133.8, 132.2, 129.1, 128.7, 128.0, 127.9, 127.9, 126.0, 66.6, 51.7, 18.2. HRMS (ESI)  $m/z$  M+O+H<sup>+</sup> calcd for C<sub>18</sub>H<sub>18</sub>ClO<sub>3</sub>S<sup>+</sup> 349.0660, found 349.0658.

**f) Procedure for the preparation of 8**

In a 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with **4a** (52.8 mg, 0.2 mmol), PPh<sub>3</sub> (58.2 mg, 0.21 mmol), CBr<sub>4</sub> (79 mg, 0.25 mmol), DCM (2 mL). The mixture was stirred at room temperature for 4 h. The mixture was then concentrated in vacuo and the crude material was further purified via column chromatography (EA/PE from 1/20 to 1/10) to yield 2-((4-chlorophenyl)thio)-1-phenylethan-1-ol **8** as a pale yellow oil: 41.7 mg, 79% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.23 (m, 9H), 4.65 (dd,  $J$  = 9.1, 3.5 Hz, 1H), 3.20 (dd,  $J$  = 13.8, 3.7 Hz, 1H), 3.03 (dd,  $J$  = 13.7, 9.2 Hz, 1H), 2.73 (s, 1H); <sup>13</sup>C NMR (75 MHz,

CDCl<sub>3</sub>)  $\delta$  142.1, 133.6, 132.9, 131.5, 129.3, 128.6, 128.1, 125.9, 71.9, 44.1. HRMS (ESI)  $m/z$  calcd for C<sub>14</sub>H<sub>13</sub>ClOSNa<sup>+</sup> (M+Na)<sup>+</sup> 287.0268, found 287.0274.

**g) Procedure for the synthesis of 9**

In a 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with **4a** (52.8 mg, 0.2 mmol), PPh<sub>3</sub> (58.2 mg, 0.21 mmol), CBr<sub>4</sub> (79 mg, 0.25 mmol), 4-ClPhNH<sub>2</sub> (25.5 mg, 0.2 mmol), DCM (2 mL). The mixture was stirred at room temperature for 8 h. The mixture was then concentrated in vacuo and the crude material was further purified via column chromatography (EA/PE from 1/20 to 1/10) to yield 4-*N*-(2-((4-chlorophenyl)thio)-1-phenylethyl)aniline **9** as yellow oil, 51 mg, 75% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.52 – 7.31 (m, 9H), 7.21 (t,  $J$ =7.9 Hz, 2H), 6.81 (t,  $J$ =7.3Hz, 1H), 6.62 (d,  $J$ =8.3 Hz, 2H), 4.61 (s, 1H), 4.52 (dd,  $J$ =9.0, 4.5 Hz, 1H), 3.45 (dd,  $J$ =13.4, 4.5 Hz, 1H), 3.25 (dd,  $J$ =13.4, 9.0 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 147.1, 142.3, 133.7, 133.1, 132.0, 129.4, 129.3, 129.0, 127.8, 126.5, 118.2, 113.9, 57.2, 42.9. HRMS (ESI)  $m/z$  calcd for C<sub>20</sub>H<sub>19</sub>ClNS<sup>+</sup> (M+H)<sup>+</sup> 340.0921, found 349.0932.

**h) Procedure for the synthesis of PPAR modulator analogue 10**

A solution of 5-bromothiophene-2-carbaldehyde (950 mg, 5 mmol), alcohol (5 mL), 10% sodium hydroxide (2.5 mL) are introduced into 25 mL three-neck flasks, supplied with an effective stirrer. The bottle is cooled in ice bath. After the stirrer started, benzaldehyde (530 mg, 5 mmol) is then added at once, warm to room temperature for 1.5 hour. Unupon completion, the flask was cooled in a freezing bath, and yellow solid products appeared. Then solids were separated out by filtration, washed with water, cold alcohol. The crude product was purified by recrystallization with alcohol yielding the enone (1.17g, 80%).

A 5 mL reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum was sequentially charged with 4-chlorothiophenol (57.8 mg, 0.4 mmol), enone (58.4 mg, 0.2 mmol), MeCN (4 mL). With the rubber septum fitted to the vial, the vessel was degassed using a vent needle for ca. 30 sec and charged with an Oxygen balloon. Next, *fac*-Ir(ppy)<sub>3</sub> (0.004 mmol, pre-dissolved in CH<sub>3</sub>CN) was added via syringe. The top of the vial was wrapped in Parafilm® and the mixture was stirred vigorously under irradiation of LEDs. After completion, stirring was stopped. NaBH<sub>4</sub> (0.5 mmol) was slowly added in portion and further stir for extra 30 min. The mixture was then passed through celite and concentrated in vacuo. Without isolation, the mixture was charged to another reaction tube, Pd(PPh<sub>3</sub>)Cl<sub>2</sub> (3 mg, 0.004 mmol), benzenboric acid (36.7 mg, 0.3 mmol), DMF (2 mL)

was then added. The resulting mixture was stirred at 80 °C in argon for 2 h. After that reaction solution was diluted with water (5 mL) and extracted with EtOAc (5 mLx3), the combining organic layer was concentrated and obtaining crude material was further purified via column chromatography (EA/PE from 1/10 to 1/4) to give 2-((4-chlorophenyl)thio)-2-(5-phenylthiophen-2-yl)ethan-1-ol **9a** as a yellow oil, 42 mg, 61% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.41-7.24 (m, 7H), 7.12 (d, *J* = 3.5 Hz, 1H), 6.83 (d, *J* = 3.5 Hz, 1H), 4.53 (t, *J* = 6.4 Hz, 1H), 4.14- 3.72 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 141.2, 134.6, 134.4, 134.2, 134.0, 131.3, 129.2, 128.9, 127.7, 127.2, 127.0, 125.7, 122.6, 65.2, 52.2. HRMS (ESI) *m/z* M+O+H<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>ClO<sub>2</sub>S<sub>2</sub><sup>+</sup> 363.0275, found 363.0274.

### 3. Reported data for products

For known compounds **4a**, **4d**, and **3u**, NMR data were given and in accordance with literature results. For other compounds, NMR and HRMS data were given. It is noteworthy that compounds **4c** and **9** showed [M+H<sup>+</sup>] peak, compounds **5** and **8** showed [M+Na<sup>+</sup>] peak, compound **4e** showed both [M+Na<sup>+</sup>], [M+O+H<sup>+</sup>] and [M+O+Na<sup>+</sup>] peak, and the HRMS data of other products was obtained with [M+O+H<sup>+</sup>] or [M+O+Na<sup>+</sup>] peak. The abnormal MS results (exact mass plus oxygen plus H<sup>+</sup> or Na<sup>+</sup>) of these compounds may be due to the oxidation of sulfide to sulfoxide during HRMS process. We also retested the HNMR of the recovered samples with abnormal HRMS data, but the NMR spectra were same to the previous ones, which indicated that the products are stable under air.

*2-((4-chlorophenyl)thio)-2-phenylethan-1-ol* **4a** The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), benzalacetophenone (41.6 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a colorless oil (45 mg, 85% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.46-7.17 (m, 9H), 4.30 (t, *J* = 6.9 Hz, 1H), 4.04-3.76 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 138.5, 134.0, 133.8, 132.1, 129.1, 128.8, 128.1, 128.0, 65.2, 56.3. GC-MS(EI):264*m/z*. The analytic data is in accordance with literature.<sup>1</sup>

*2-phenyl-2-(*m*-tolylthio)ethan-1-ol* **4b** The title compound was obtained according to the general procedure b using the following amounts and conditions: 3-methylbenzenethiol (50.0 mg, 0.4 mmol), benzalacetophenone (41.6 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl

acetate=1/10) to provide the desired compound as a colorless oil (37 mg, 76 % yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.30-7.17 (m, 5H), 7.13-7.00 (m, 3H), 6.97 (d, *J* = 3.8 Hz, 1H), 4.23 (t, *J* = 6.8 Hz, 1H), 3.96-3.72 (m, 2H), 2.21 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.1, 138.8, 133.5, 133.2, 129.5, 128.8, 128.7, 128.5, 128.1, 127.8, 65.3, 56.0, 21.2. HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>SNa 283.0763 (M+O+Na<sup>+</sup>), found 283.0765.

*methyl (3-((2-hydroxy-1-phenylethyl)thio)benzoate 4c* The title compound was obtained according to the general procedure b using the following amounts and conditions: methyl 2-mercaptobenzoate (67.2 mg, 0.4 mmol), benzalacetophenone (41.6 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a colorless oil (35.7 mg, 62% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.46 (s, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.44-7.13 (m, 8H), 7.39-7.12 (m, 6H), 4.49 (t, *J* = 6.6 Hz, 1H), 4.49 (t, *J* = 6.6 Hz, 1H), 3.95 (d, *J* = 7.9 Hz, 2H), 3.94 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 167.5, 138.8, 138.2, 132.2, 130.9, 130.4, 129.5, 128.9, 128.2, 127.9, 125.6, 65.9, 54.8, 52.4. HRMS (ESI) *m/z* calcd for C<sub>16</sub>H<sub>17</sub>O<sub>3</sub>S (M+H)<sup>+</sup> 289.0893, found 289.0896.

*2-phenyl-2-(p-tolylthio)ethan-1-ol 4d* The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-methylbenzenethiol (50.0 mg, 0.4 mmol), benzalacetophenone (41.6 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a colorless oil (33 mg, 68% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.18 (m, 7H), 6.97 (d, *J* = 7.9 Hz, 2H), 4.15 (t, *J* = 6.9 Hz, 1H), 3.93-3.67 (m, 2H), 2.22 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.1, 138.0, 133.3, 129.8, 128.7, 128.1, 127.8, 65.1, 56.5, 21.1. GC-MS (EI): 244*m/z*. The analytic data is in accordance with literature.<sup>1</sup>

*2-((4-(tert-butyl)phenyl)thio)-2-phenylethan-1-ol 4e* The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-methylbenzenethiol (66.4 mg, 0.4 mmol), benzalacetophenone (41.6 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/5) to provide the desired compound as a colorless oil (46 mg, 80% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.21 (d, *J* = 7.6 Hz, 8H), 4.18 (t, *J* = 6.8 Hz, 1H), 3.93-3.66 (m, 2H), 1.20 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 151.1, 139.2, 132.7, 130.2, 128.7, 128.1, 127.8, 126, 65.3, 56.2, 31.2. HRMS (ESI) *m/z* calcd for C<sub>18</sub>H<sub>22</sub>OSNa (M+Na)<sup>+</sup> 309.1289, found 309.1280; for

$C_{18}H_{22}O_2SNa$  (M+O+Na)<sup>+</sup> 325.1238, found 325.1229; for  $C_{18}H_{23}O_2$  (M+O+H)<sup>+</sup>: 303.1419, found 303.1412.

3-(butylthio)-1,3-diphenylpropan-1-one **3f'** The title compound was obtained according to the general procedure b using the following amounts and conditions: butane-1-thiol (36 mg, 0.4 mmol), benzalacetophenone (41.6 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a colorless oil (14.9 mg, 25% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 – 7.90 (m, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.50 – 7.39 (m, 4H), 7.39 – 7.20 (m, 3H), 4.60 (t, *J* = 7.1 Hz, 1H), 3.57 (dd, *J* = 7.1, 1.1 Hz, 2H), 2.45 – 2.29 (m, 2H), 1.62 – 1.43 (m, 2H), 1.35 (dt, *J* = 15.1, 6.4 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.0, 142.3, 136.8, 133.3, 128.6, 128.5, 128.1, 127.9, 127.2, 45.5, 44.3, 31.3, 31.2, 22.0, 13.7. HRMS (ESI) *m/z* calcd for C<sub>21</sub>H<sub>25</sub>OS (M+H)<sup>+</sup> 299.1464, found 299.1470.

3-(cyclohexylthio)-1,3-diphenylpropan-1-one **3g'** The title compound was obtained according to the general procedure b using the following amounts and conditions: cyclohexanethiol (46.4 mg, 0.4 mmol), benzalacetophenone (41.6 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a colorless oil (19.4 mg, 30% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.92 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.61 – 7.51 (m, 1H), 7.45 (ddd, *J* = 7.1, 4.9, 2.0 Hz, 4H), 7.38 – 7.27 (m, 2H), 7.23 (dt, *J* = 9.5, 4.3 Hz, 1H), 4.68 (t, *J* = 7.1 Hz, 1H), 3.54 (dd, *J* = 7.1, 1.1 Hz, 2H), 2.55 – 2.38 (m, 1H), 2.13 – 1.91 (m, 1H), 1.87 – 1.46 (m, 5H), 1.46 – 1.05 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.12, 142.92, 136.87, 133.21, 128.62, 128.52, 128.13, 127.78, 127.11, 45.91, 43.17, 42.82, 33.64, 33.23, 26.00, 25.82, 25.79. HRMS (ESI) *m/z* calcd for C<sub>21</sub>H<sub>25</sub>OS (M+H)<sup>+</sup> 325.1621, found 325.1624.

2-(4-fluorophenyl)-2-(*p*-tolylthio)ethan-1-ol **4i** The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), 3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (42.6 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a colorless oil (41.7 mg, 74% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.30-7.13 (m, 6H), 7.10- 6.89 (m, 2H), 4.26 (t, *J* = 6.8 Hz, 1H), 3.99-3.73 (m, 2H), 2.60 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 162.2(<sup>1</sup>*J*<sub>C-F</sub>=245Hz), 134.6,



134.6, 134.5, 134.1, 134.0, 131.9, 129.8 ( $^3J_{\text{C-F}} = 8\text{Hz}$ ), 129.2, 115.7 ( $^2J_{\text{C-F}} = 21\text{Hz}$ ), 65.1, 55.4. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{13}\text{ClFO}_2\text{S}$  ( $\text{M}+\text{O}+\text{H}$ ) $^+$  299.0303, found 299.0305.

*2-(4-methylphenyl)-2-(p-tolylthio)ethan-1-ol* **4j** The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), 3-(4-methylphenyl)-1-phenylprop-2-en-1-one (44.4 mg, 0.2 mmol), *fac*-Ir(ppy) $_3$  (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a colorless oil (45.6 mg, 82% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 6.93 (m, 8H), 4.29 (t,  $J = 6.9$  Hz, 1H), 3.99 – 3.78 (m, 2H), 2.36 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  137.7, 135.6, 133.8, 133.6, 129.5, 129.1, 128.0, 65.3, 55.9, 21.2. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{16}\text{ClO}_2\text{S}$  ( $\text{M}+\text{O}+\text{H}$ ) $^+$  295.0554 found 295.0558.

*2-(4-(tert-butyl)phenyl)-2-((4-chlorophenyl)thio)ethan-1-ol* **4k** The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), 3-(4-(tert-butyl)phenyl)-1-phenylprop-2-en-1-one (52.8 mg, 0.2 mmol), *fac*-Ir(ppy) $_3$  (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a colorless oil (51 mg, 80% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.2-7.09 (m, 5H), 6.77 (ddd,  $J = 12.3, 7.5, 1.0$  Hz, 3H), 4.17 (t,  $J = 6.9$  Hz, 1H), 3.83 (t,  $J = 6.7$  Hz, 2H), 3.71 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 140.1, 133.8, 133.8, 132.2, 129.8, 129.1, 120.3, 113.7, 113.4, 65.3, 56.3, 55.3. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{22}\text{ClO}_2\text{S}$  ( $\text{M}+\text{O}+\text{H}$ ) $^+$  337.1024, found 337.1021.

*2-(4-chlorophenyl)-2-((4-chlorophenyl)thio)ethan-1-ol* **4l** The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), 3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (48.4 mg, 0.2 mmol), *fac*-Ir(ppy) $_3$  (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a colorless oil (50 mg, 84% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta = 7.55$ -6.98 (m, 8H), 4.25 (t,  $J=6.8$ , 1H), 3.98-3.77 (m, 2H), 2.28 (s, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = 137.3, 134.2, 134.1, 133.7, 131.7, 129.4, 129.2, 128.9, 65.0, 55.7$ . HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{13}\text{Cl}_2\text{O}_2\text{S}$  ( $\text{M}+\text{O}+\text{H}$ ) $^+$  315.0008, found 315.0012.

*2-(4-chlorophenyl)-2-((4-chlorophenyl)thio)ethan-1-ol* **4m** The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-

chlorobenzenethiol (57.6 mg, 0.4 mmol), 3-(3-methylphenyl)-1-phenylprop-2-en-1-one (44.4 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a colorless oil (47.8 mg, 86% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.29-7.18 (m, 5H), 7.11 – 6.99 (m, 3H), 6.97 (d, *J* = 3.8 Hz, 1H), 4.23 (t, *J* = 6.8 Hz, 1H), 3.93-3.73 (m, 2H), 2.21 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.1, 138.8, 133.5, 133.2, 129.5, 128.8, 128.7, 128.5, 128.1, 127.8, 65.3, 56.0, 21.2. HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>16</sub>ClO<sub>2</sub>S (M+O+H)<sup>+</sup> 295.0554 found 295.0557.

*2-(3-chlorophenyl)-2-((4-chlorophenyl)thio)ethan-1-ol* **4n** The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), 3-(3-chlorophenyl)-1-phenylprop-2-en-1-one (48.4 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a colorless oil (47.4 mg, 79% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.34-7.10 (m, 8H), 4.23 (t, *J* = 6.8 Hz, 1H), 3.86 (dd, *J* = 6.8, 2.0 Hz, 2H), 2.76 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 141.0, 134.6, 134.16, 131.8, 130.0, 129.2, 128.3, 128.1, 126.4, 64.9, 55.7. HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>13</sub>Cl<sub>2</sub>O<sub>2</sub>S (M+O+H)<sup>+</sup> 315.0008, found 315.0006.

*2-(2-chlorophenyl)-2-((4-chlorophenyl)thio)ethan-1-ol* **4o** The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), 3-(2-chlorophenyl)-1-phenylprop-2-en-1-one (48.4 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a colorless oil (49 mg, 83% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.38 (dd, *J* = 9.0, 5.6 Hz, 2H), 7.31-7.13 (m, 6H), 4.94- 4.76 (m, 1H), 3.93 (dd, *J* = 11.4, 6.6 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 136.1, 134.0, 134.0, 133.8, 131.9, 129.9, 129.1, 128.9, 128.9, 127.2, 64.2, 52.2. HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>13</sub>Cl<sub>2</sub>O<sub>2</sub>S (M+O+H)<sup>+</sup> 315.0008, found 315.0008.

*2-(4-bromophenyl)-2-(*p*-tolylthio)ethan-1-ol* **4p** The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), 3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one (63.2 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a yellow oil (47.2

mg, 69% yield). Yield was obtained when charging 3-(4-bromophenyl)-1-phenylprop-2-en-1-one as substrate (57.2 mg, 0.2 mmol). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.15 (s, 4H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.15 (t, *J* = 6.8 Hz, 1H), 3.80 (d, *J* = 6.7 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 137.8, 134.2, 131.9, 131.6, 129.8, 129.2, 128.6, 121.8, 64.9, 55.9. HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>13</sub>BrClO<sub>2</sub>S (M+O+H)<sup>+</sup> 358.9503, found 358.9505.

*3-(1-((4-chlorophenyl)thio)-2-hydroxyethyl)benzonitrile 4q* The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), 3-(3-(2-methoxyphenyl)-3-oxoprop-1-en-1-yl)benzonitrile (52.6 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a yellow oil (44.0 mg, 76% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.61-7.50 (m, 3H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.22 (s, 4H), 4.27 (t, *J* = 6.5 Hz, 1H), 3.93 (d, *J* = 6.5 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 140.8, 134.6, 134.4, 132.5, 131.7, 131.4, 131.1, 129.5, 129.3, 118.3, 113.0, 64.7, 55.8. HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>13</sub>ClNO<sub>2</sub>S (M+O+H)<sup>+</sup> 306.0350, found 306.0352.

*2-((4-chlorophenyl)thio)-2-(naphthalen-2-yl)ethan-1-ol 4r* The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), 3-(naphthalen-2-yl)-1-phenylprop-2-en-1-one (51.6 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a yellow oil (43.0 mg, 68% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.81 (dd, *J* = 16.0, 11.5 Hz, 4H), 7.47 (dd, *J* = 8.7, 6.7 Hz, 4H), 7.21 (dd, *J* = 20.7, 7.9 Hz, 4H), 4.43 (t, *J* = 6.9 Hz, 1H), 4.00 (t, *J* = 5.9 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 135.7, 134.1, 133.8, 133.3, 133.0, 132.0, 129.1, 128.7, 127.9, 127.7, 127.1, 126.4, 126.3, 125.8, 65.3, 56.5. HRMS (ESI) *m/z* calcd for C<sub>18</sub>H<sub>16</sub>ClO<sub>2</sub>S (M+O+H)<sup>+</sup> 331.0554, found 331.0557.

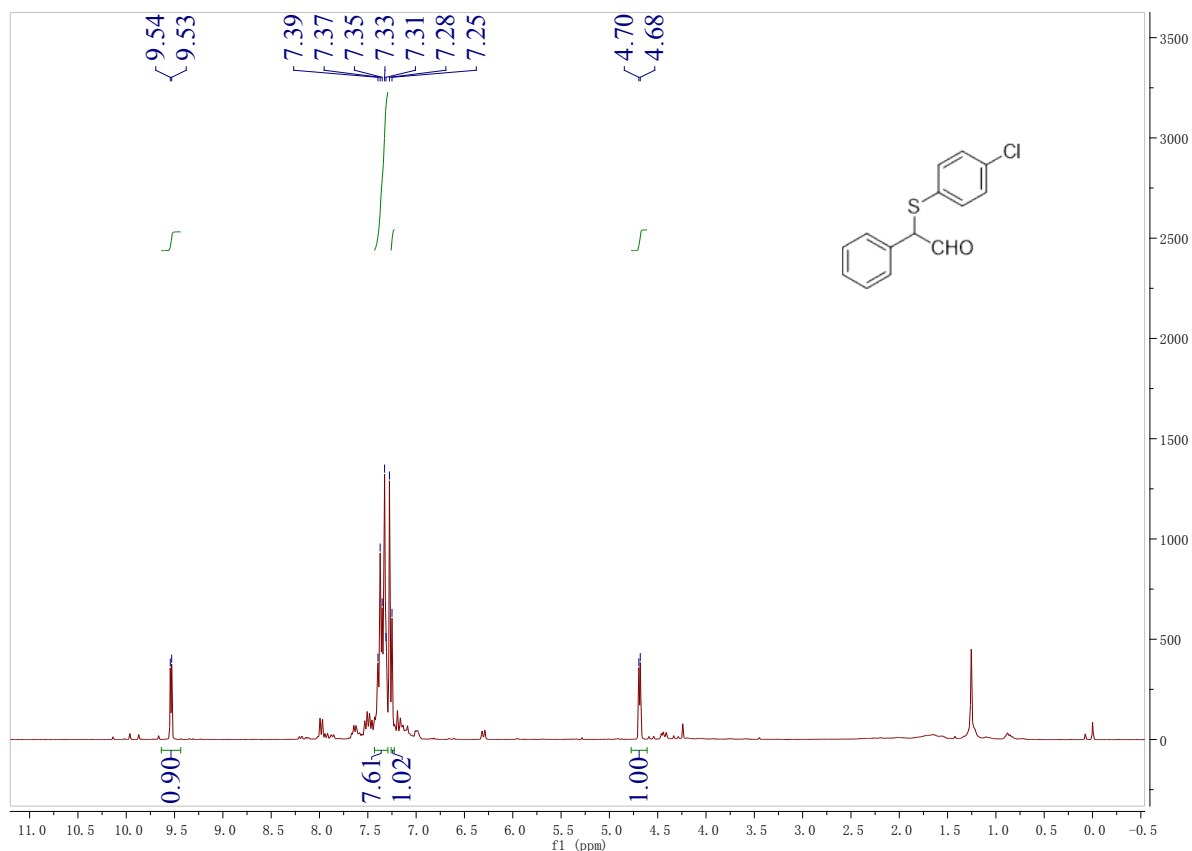
*1-((4-chlorophenyl)thio)-1-phenylpropan-2-one 3u* The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), 2-methyl-1,3-diphenylprop-2-en-1-one (44.4 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a yellow oil (33.0 mg, 60% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.39-7.13 (m, 9H), 4.94 (s, 1H), 2.17 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 202.7, 135.2, 134.2, 134.0, 132.0, 129.2, 129.0, 128.5, 128.4, 64.8, 27.4. <sup>13</sup>C

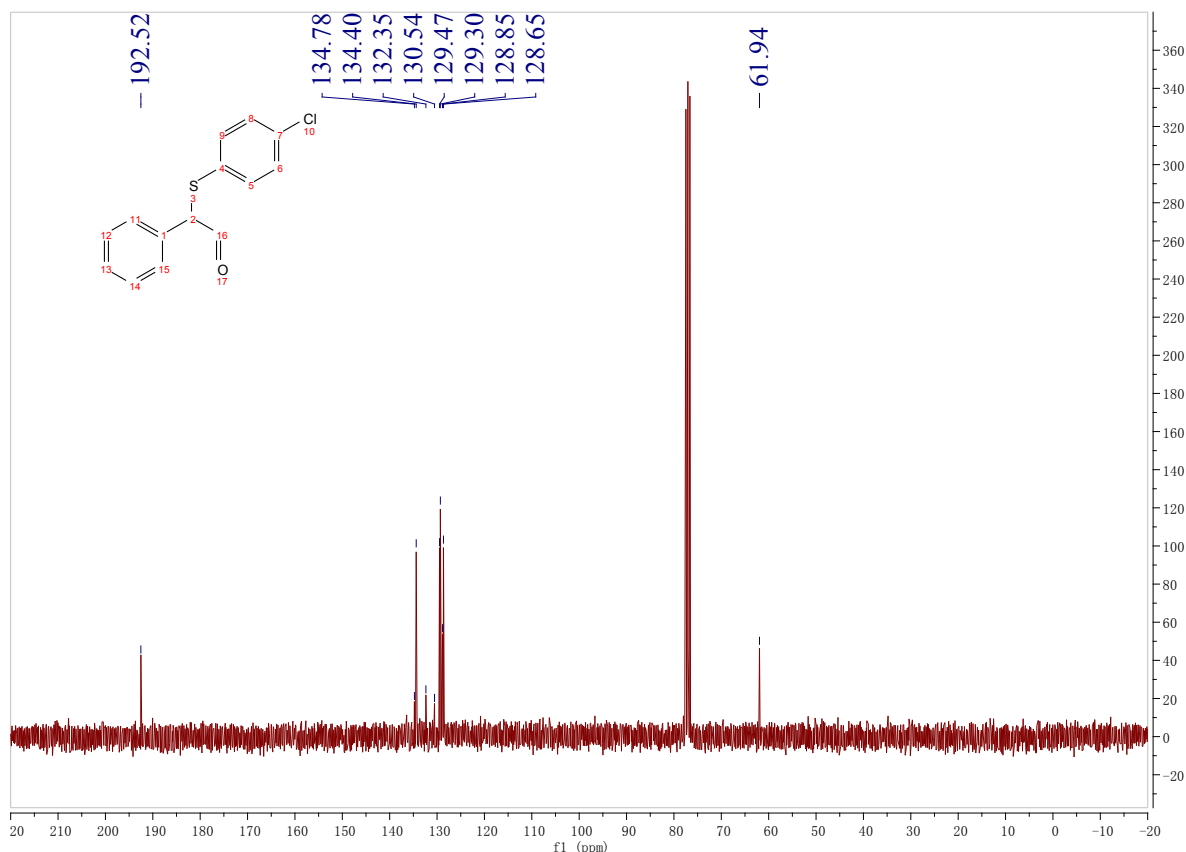
NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  202.6, 135.2, 134.1, 134.0, 132.0, 129.2, 129.0, 128.6, 128.5, 64.8, 27.4. GC-MS(EI):276m/z. The analytic data is in accordance with literature.<sup>2</sup>

*2-((4-chlorophenyl)thio)-2-cyclohexylethan-1-ol* **4t** The title compound was obtained according to the general procedure b using the following amounts and conditions: 4-chlorobenzenethiol (57.6 mg, 0.4 mmol), 3-cyclohexyl-1-phenylprop-2-en-1-one (42.8 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg), 4 mL dichloromethane, RT, 12 h. The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a yellow oil (32.0 mg, 60% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (d, *J* = 8.6 Hz, 2H), 7.26-7.22 (m, 2H), 3.86 -3.48 (m, 2H), 3.01 (dd, *J* = 11.8, 6.1 Hz, 1H), 2.15-1.88 (m, 2H), 1.71 (dd, *J* = 28.3, 8.7 Hz, 5H), 1.37-1.09 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  134.1, 133.3, 133.2, 129.1, 62.2, 60.3, 39.6, 30.7, 30.4, 26.3. HRMS (ESI) *m/z* M+O+H<sup>+</sup> calcd for C<sub>14</sub>H<sub>20</sub>ClO<sub>2</sub>S<sup>+</sup> 287.0867, found 287.0864.

### Explanation for the abnormal HRMS and the structure of the products:

- <sup>1</sup>H & <sup>13</sup>C NMR spectra of 2-((4-chlorophenyl)thio)-2-phenylacetaldehyde **3a** were shown below. Although impurities always existed due to the instability of such compound, the aldehyde structure can still be identified.

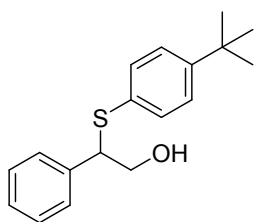




2. Some of the reduction products were known compounds. The NMR spectra were in accordance with the literature.

For example,  $^1\text{H}$  NMR data of **4d** is in accordance with the literature reports (Synthetic Communications, 2010, 40, 2113-2121). We also synthesized such reduction compound using the known method (Synthetic Communications, 2010, 40, 2113-2121). They have the exact same NMR spectra.

3. Additionally, taking product **4e** (the structure was listed below) as an example, we compared the HRMS data of two samples prepared by our method and the known method, respectively.

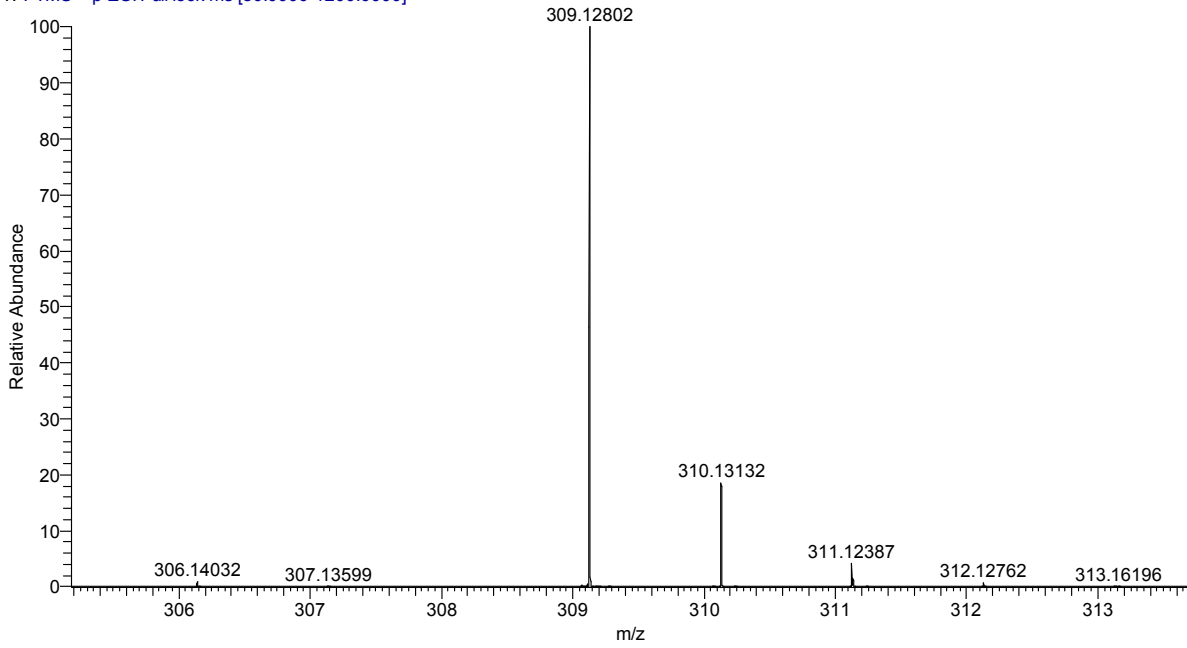


2-((4-(*tert*-butyl)phenyl)thio)-2-phenylethan-1-ol  
 Chemical Formula:  $\text{C}_{18}\text{H}_{22}\text{OS}$   
 Exact Mass: 286.1391  
 Molecular Weight: 286.4330  
 m/z: 286.1391 (100.0%), 287.1425 (19.5%), 288.1349 (4.5%), 288.1458 (1.8%)  
 Elemental Analysis: C, 75.48; H, 7.74; O, 5.59; S, 11.19

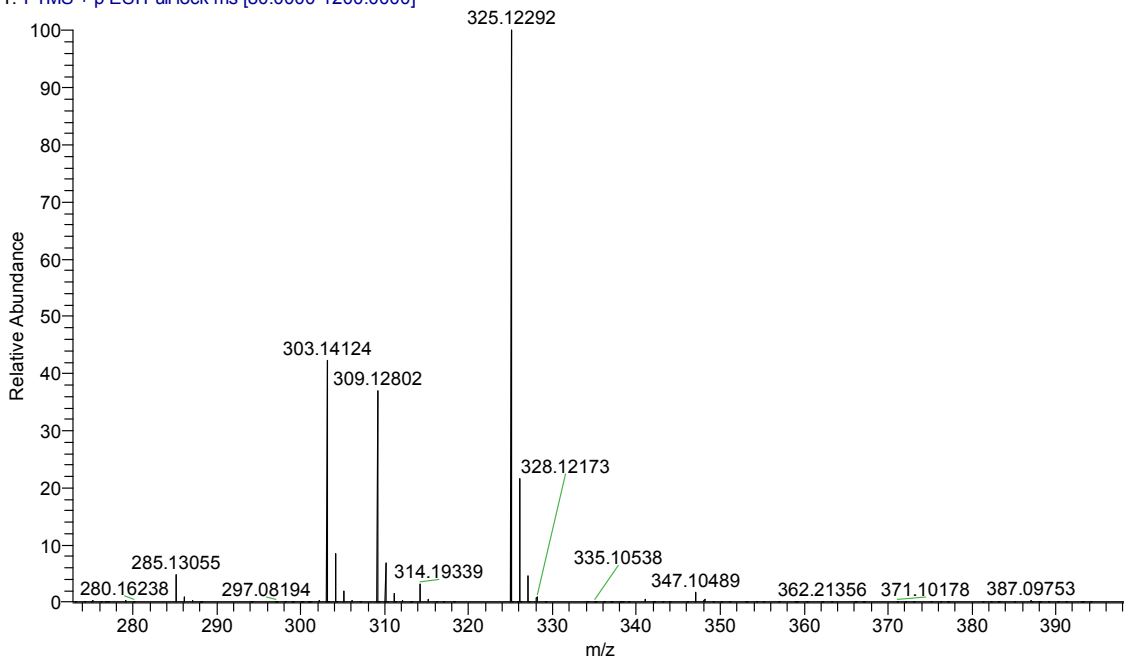
Calculated for  $[\text{M}+\text{Na}]^+$ : 309.1289;  $[\text{M}+\text{O}+\text{H}]^+$ : 303.1419,  $[\text{M}+\text{O}+\text{Na}]^+$ : 325.1238

# Compound 4e using this method

1-22 #8 RT: 0.07 AV: 1 NL: 3.47E7  
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]

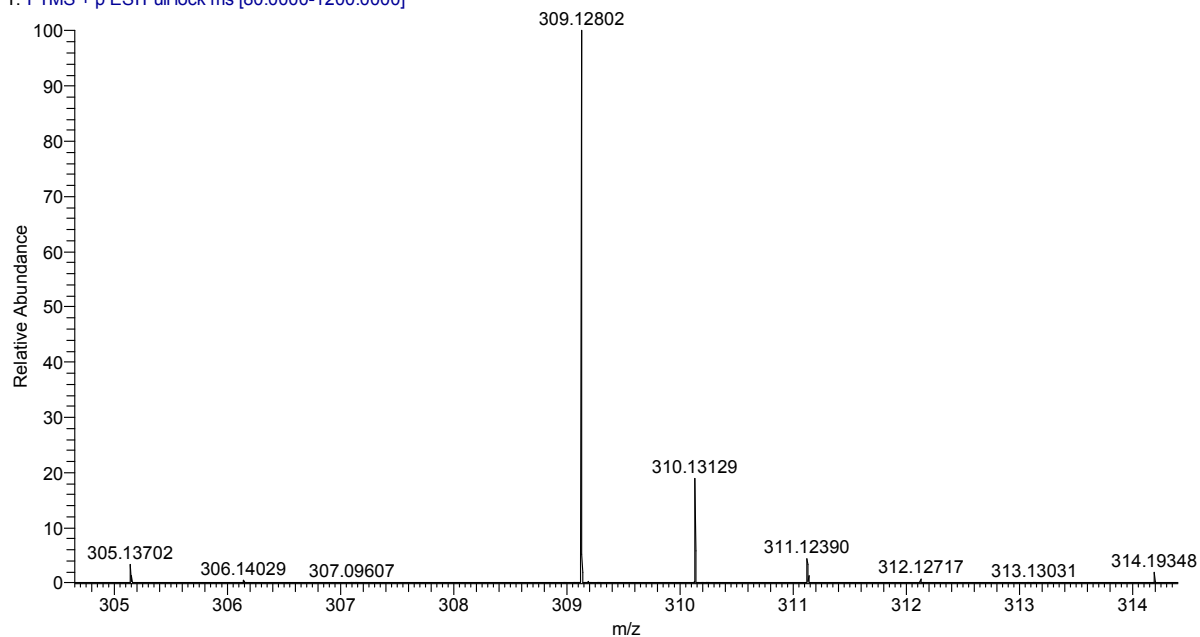


1-22 #8 RT: 0.07 AV: 1 NL: 9.39E7  
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]

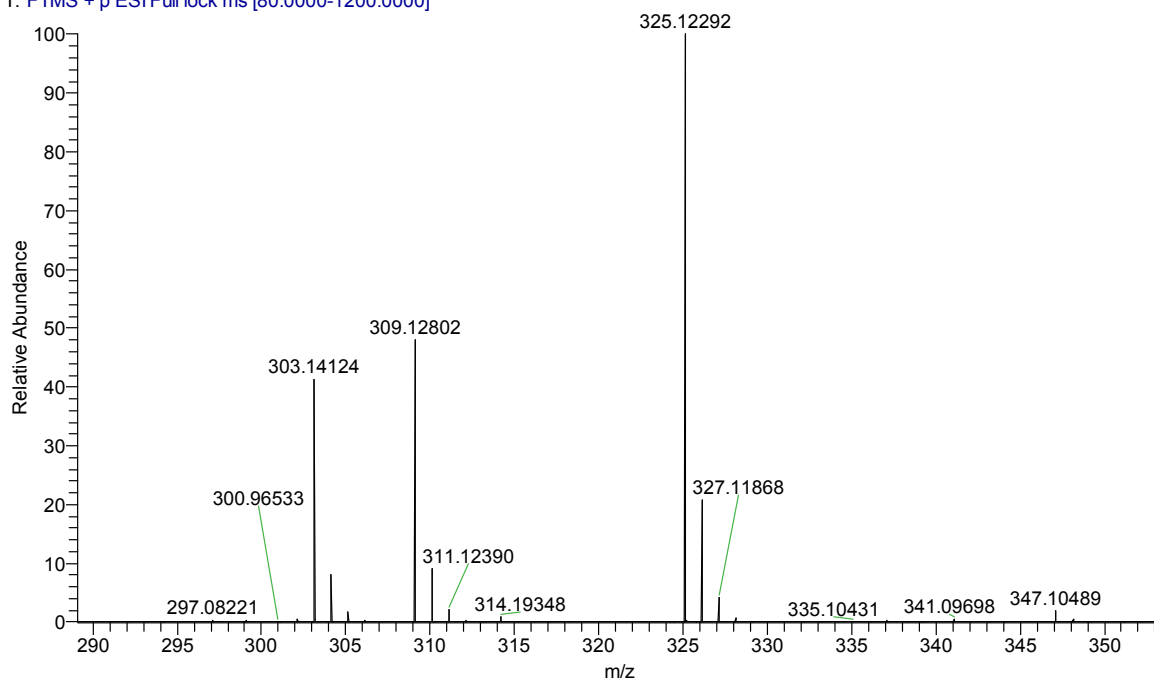


## Compound 4e using known method

1-24 #9 RT: 0.07 AV: 1 NL: 4.35E7  
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]



1-24 #9 RT: 0.07 AV: 1 NL: 9.03E7  
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]



For compound **4e**, the  $M+Na^+$ ,  $M+O+H^+$  and  $M+O+Na^+$  peaks can be found from above two samples. So, based on the above results, it is possible that the samples could be easily oxidized in situ during the HRMS test.

#### 4. BDE energy calculation

Entry	1	2
	 A	 B
BDE energy	271 kJ/mol	332 KJ/mol

For entry 1

$$E(A) = -1932.64156470 \text{ Haree}$$

$$E(B) = -344.920629011 \text{ Haree}$$

$$E(C) = -1587.61744319 \text{ Haree}$$

$$E = 0.103492499 \text{ Haree}$$

$$= 271.73925 \text{ KJ/mo}$$

For entry 2

$$E(A) = -1858.60270007 \text{ Haree}$$

$$E(B) = -344.920629011 \text{ Haree}$$

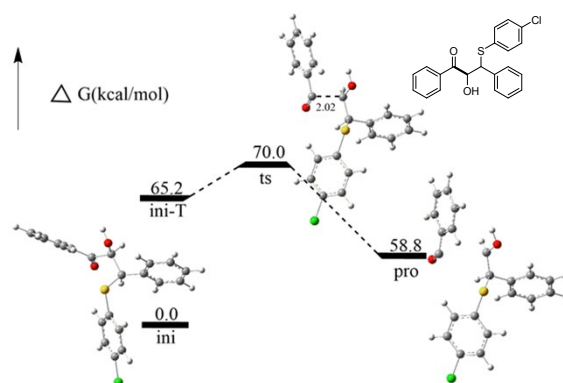
$$E(C) = -1513.55539829 \text{ Haree}$$

$$E = 0.126672769 \text{ Haree}$$

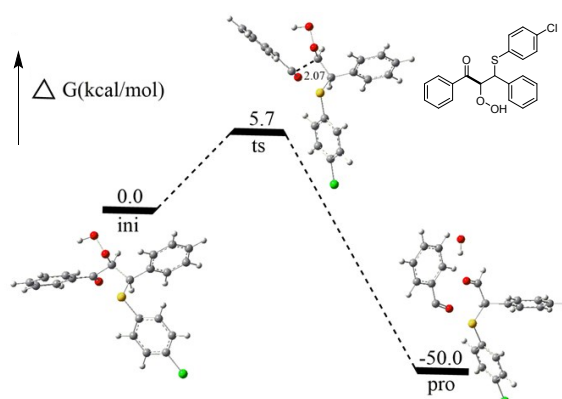
$$= 332.579355 \text{ KJ/mol}$$

#### 5. Chemical calculations for potential react intermediate

For A



For B





The geometries of all stationary points were optimized using the B3LYP density functional method with the 6-31G(d) basis set for all the atoms. Vibrational frequency analyses at the same level of theory were performed on all optimized structures to characterize stationary points as local minima or transition states. Transition state was verified to have one imaginary vibrational frequency and was connected to appropriate reactant and product by optimizations along the reaction coordinate. To consider solvation effects, single-point energy computations using the PCM model with acetonitrile as the solvent were performed based on the optimized gas-phase geometries of all species. The single-point energy calculations were carried out using the B3LYP functional in combination with the 6-311++G(d,p) basis set to provide better energy correction. The solution-phase Gibbs free energy was determined by adding the solvation single-point energy and the gas-phase thermal correction to the Gibbs free energy obtained from the vibrational frequencies. The Gaussian 09 suite of program was used throughout.

## Structures

ini

Standard orientation:

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Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	
-----						
1	6	0	-2.883461	-0.355987	-1.133389	
2	6	0	-1.714355	-0.979480	-0.677427	
3	6	0	-1.811197	-2.162272	0.067937	
4	6	0	-3.057427	-2.714373	0.362266	
5	6	0	-4.208660	-2.074227	-0.096877	
6	6	0	-4.135101	-0.898629	-0.843076	
7	1	0	-2.812631	0.556201	-1.716345	
8	1	0	-0.906978	-2.653342	0.414470	
9	1	0	-3.136049	-3.630574	0.937612	
10	1	0	-5.042079	-0.417861	-1.193846	
11	17	0	-5.782434	-2.765984	0.269704	

12	16	0	-0.103956	-0.307103	-1.091599
13	6	0	0.140209	0.855616	0.352973
14	1	0	-0.143775	0.288342	1.243995
15	6	0	-0.700625	2.112920	0.279206
16	6	0	-0.575069	3.037554	-0.769680
17	6	0	-1.632204	2.368265	1.294867
18	6	0	-1.359565	4.188791	-0.792479
19	1	0	0.138058	2.850473	-1.565642
20	6	0	-2.420994	3.520108	1.269572
21	1	0	-1.744736	1.657503	2.110399
22	6	0	-2.285434	4.434475	0.225678
23	1	0	-1.247961	4.897604	-1.608646
24	1	0	-3.140463	3.698423	2.064232
25	1	0	-2.896383	5.332946	0.202909
26	6	0	1.652446	1.140758	0.533982
27	1	0	1.762433	1.936218	1.280321
28	8	0	2.171164	1.594196	-0.691427
29	6	0	2.435530	-0.097254	1.085871
30	8	0	2.131274	-0.272647	2.342530
31	6	0	3.485102	-0.838133	0.453727
32	6	0	3.749370	-0.819809	-0.946634
33	6	0	4.313404	-1.662926	1.272724
34	6	0	4.806012	-1.557287	-1.471517
35	1	0	3.094000	-0.276567	-1.616402
36	6	0	5.354849	-2.393382	0.723831
37	1	0	4.127997	-1.695800	2.342136
38	6	0	5.621852	-2.343880	-0.651402
39	1	0	4.982738	-1.528728	-2.543916
40	1	0	5.973033	-3.006982	1.374567
41	1	0	6.441220	-2.916712	-1.075129
42	8	0	3.424460	2.268722	-0.441207

43            1            0            4.052986    1.556975    -0.690178

-----  
Zero-point correction=                    0.325133 (Hartree/Particle)  
Thermal correction to Energy=            0.348936  
Thermal correction to Enthalpy=         0.349880  
Thermal correction to Gibbs Free Energy= 0.265656  
Sum of electronic and zero-point Energies= -1893.987242  
Sum of electronic and thermal Energies= -1893.963439  
Sum of electronic and thermal Enthalpies= -1893.962495  
Sum of electronic and thermal Free Energies= -1894.046719  
E(b3lyp/6-311++g(d,p)/pcm)=-1894.65665137

Ts

Standard orientation:

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Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-3.193929	-0.389931	-1.450133
2	6	0	-1.984061	-0.715530	-0.825388
3	6	0	-1.967072	-1.697056	0.177107
4	6	0	-3.147543	-2.328804	0.563308
5	6	0	-4.342262	-1.995317	-0.076399
6	6	0	-4.376437	-1.034907	-1.085310
7	1	0	-3.212117	0.374374	-2.220646
8	1	0	-1.031498	-1.966530	0.658586
9	1	0	-3.139209	-3.084143	1.341960
10	1	0	-5.314746	-0.784366	-1.568703
11	17	0	-5.830449	-2.801593	0.400775
12	16	0	-0.472828	0.068695	-1.382685

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13	6	0	0.058804	0.944325	0.185183
14	1	0	-0.333567	0.348929	1.011139
15	6	0	-0.465862	2.364829	0.301098
16	6	0	-0.125558	3.363421	-0.623668
17	6	0	-1.310760	2.691129	1.370267
18	6	0	-0.624263	4.656199	-0.480164
19	1	0	0.527162	3.124915	-1.457695
20	6	0	-1.812841	3.985965	1.511360
21	1	0	-1.582172	1.925755	2.093481
22	6	0	-1.469665	4.972349	0.587182
23	1	0	-0.352477	5.419922	-1.203871
24	1	0	-2.471756	4.220462	2.343045
25	1	0	-1.857705	5.981528	0.695472
26	6	0	1.562480	0.876481	0.332234
27	1	0	1.990852	1.258738	1.255849
28	8	0	2.223954	1.267342	-0.784794
29	6	0	1.878988	-1.122000	0.787352
30	8	0	1.380043	-1.189635	1.910998
31	6	0	3.268295	-1.386477	0.390297
32	6	0	3.666091	-1.341001	-0.965099
33	6	0	4.195395	-1.830427	1.359414
34	6	0	4.968038	-1.684054	-1.325755
35	1	0	2.938980	-1.060916	-1.721465
36	6	0	5.485897	-2.190221	0.982164
37	1	0	3.882098	-1.884463	2.397266
38	6	0	5.884520	-2.108529	-0.355790
39	1	0	5.262704	-1.643656	-2.371196
40	1	0	6.190445	-2.528239	1.737948
41	1	0	6.894084	-2.386987	-0.643929
42	8	0	3.563879	1.691127	-0.439184
43	1	0	4.059250	0.879299	-0.689176

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Zero-point correction=                0.324097 (Hartree/Particle)
Thermal correction to Energy=         0.347755
Thermal correction to Enthalpy=       0.348699
Thermal correction to Gibbs Free Energy= 0.265330
Sum of electronic and zero-point Energies= -1893.976032
Sum of electronic and thermal Energies= -1893.952373
Sum of electronic and thermal Enthalpies= -1893.951429
Sum of electronic and thermal Free Energies= -1894.034798
E(b3lyp/6-311++g(d,p)/pcm)=-1894.64721289

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Pro

Standard orientation:

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-----
Center      Atomic      Atomic      Coordinates (Angstroms)
Number      Number      Type        X           Y           Z
-----
  1          6          0         -3.041733   -0.099372   -1.460772
  2          6          0         -1.882253   -0.686283   -0.939233
  3          6          0         -1.997619   -1.715145    0.006570
  4          6          0         -3.253837   -2.141580    0.435867
  5          6          0         -4.395958   -1.545864   -0.099654
  6          6          0         -4.303309   -0.529416   -1.048460
  7          1          0         -2.956906    0.698753   -2.191216
  8          1          0         -1.106493   -2.184131    0.412575
  9          1          0         -3.346214   -2.935325    1.169620
 10         1          0         -5.202319   -0.077041   -1.453337
 11         17         0         -5.982271   -2.089272    0.431071
 12         16         0         -0.274658   -0.166631   -1.548526
 13          6          0          0.319197    0.803299   -0.078560
 14          1          0          0.338522    0.129818    0.788757

```

15	6	0	-0.511116	2.027017	0.266540
16	6	0	-0.586463	3.110571	-0.621523
17	6	0	-1.194990	2.096795	1.485693
18	6	0	-1.331680	4.241066	-0.292432
19	1	0	-0.068153	3.058522	-1.575678
20	6	0	-1.945411	3.227760	1.812753
21	1	0	-1.147362	1.259512	2.177478
22	6	0	-2.013448	4.302554	0.926018
23	1	0	-1.380534	5.075188	-0.987108
24	1	0	-2.477660	3.265686	2.759260
25	1	0	-2.596301	5.183524	1.180528
26	6	0	1.752990	1.223737	-0.322843
27	1	0	2.247059	1.704328	0.542962
28	8	0	2.350996	1.082062	-1.372591
29	6	0	1.985596	-2.614341	0.787717
30	8	0	1.157342	-2.324081	1.604807
31	6	0	3.290765	-1.971285	0.540533
32	6	0	4.006669	-2.303280	-0.619269
33	6	0	3.806222	-1.026076	1.445567
34	6	0	5.220247	-1.675555	-0.887647
35	1	0	3.592565	-3.039021	-1.302164
36	6	0	5.023870	-0.406616	1.177173
37	1	0	3.244190	-0.792349	2.345216
38	6	0	5.727207	-0.727147	0.006146
39	1	0	5.770736	-1.919221	-1.791431
40	1	0	5.429544	0.325457	1.867285
41	1	0	6.670150	-0.232853	-0.202740
42	8	0	4.852795	1.930707	-0.295584
43	1	0	4.143550	1.608331	-0.905947

-----  
Zero-point correction=

0.321067 (Hartree/Particle)

Thermal correction to Energy= 0.347276  
 Thermal correction to Enthalpy= 0.348220  
 Thermal correction to Gibbs Free Energy= 0.256993  
 Sum of electronic and zero-point Energies= -1894.049721  
 Sum of electronic and thermal Energies= -1894.023512  
 Sum of electronic and thermal Enthalpies= -1894.022568  
 Sum of electronic and thermal Free Energies= -1894.113795  
 E(b3lyp/6-311++g(d,p)/pcm)=-1894.72763235

For OH

ini

Standard orientation:

-----						
Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	
-----						
1	6	0	-2.737791	-0.658545	-1.445339	
2	6	0	-1.554808	-0.869413	-0.727150	
3	6	0	-1.543093	-1.805791	0.317209	
4	6	0	-2.698798	-2.509541	0.649969	
5	6	0	-3.865660	-2.287826	-0.082773	
6	6	0	-3.896058	-1.371389	-1.131764	
7	1	0	-2.753403	0.069178	-2.250481	
8	1	0	-0.626402	-1.984690	0.872140	
9	1	0	-2.692777	-3.231950	1.459284	
10	1	0	-4.813293	-1.209124	-1.687880	
11	17	0	-5.323578	-3.183054	0.326311	
12	16	0	-0.061512	0.001644	-1.202059	
13	6	0	0.194841	1.077964	0.310220	
14	1	0	-0.156293	0.486239	1.157707	
15	6	0	-0.576054	2.379972	0.264985	

16	6	0	-0.357524	3.350071	-0.725504
17	6	0	-1.542324	2.629579	1.248545
18	6	0	-1.081612	4.540747	-0.719453
19	1	0	0.381647	3.165658	-1.497212
20	6	0	-2.270446	3.821147	1.252650
21	1	0	-1.728081	1.883745	2.018134
22	6	0	-2.040717	4.781520	0.268410
23	1	0	-0.899204	5.283583	-1.491853
24	1	0	-3.017264	3.994092	2.023123
25	1	0	-2.606185	5.709665	0.266749
26	6	0	1.709688	1.236728	0.534404
27	1	0	1.826846	1.923778	1.388870
28	8	0	2.296619	1.796194	-0.629013
29	1	0	3.233952	1.969162	-0.449177
30	6	0	2.318238	-0.100249	1.034793
31	8	0	1.829783	-0.571552	2.053113
32	6	0	3.511235	-0.741034	0.398370
33	6	0	3.814666	-0.661966	-0.972528
34	6	0	4.338814	-1.506401	1.240106
35	6	0	4.928904	-1.331432	-1.480042
36	1	0	3.165148	-0.108249	-1.638559
37	6	0	5.459169	-2.154766	0.731810
38	1	0	4.081521	-1.579105	2.291844
39	6	0	5.756755	-2.067908	-0.631710
40	1	0	5.146941	-1.279494	-2.543203
41	1	0	6.097671	-2.733467	1.393647
42	1	0	6.628423	-2.579336	-1.031542

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Zero-point correction= 0.325399 (Hartree/Particle)

Thermal correction to Energy= 0.347655

Thermal correction to Enthalpy= 0.348599



Thermal correction to Gibbs Free Energy= 0.269241  
 Sum of electronic and zero-point Energies= -1818.963974  
 Sum of electronic and thermal Energies= -1818.941718  
 Sum of electronic and thermal Enthalpies= -1818.940773  
 Sum of electronic and thermal Free Energies= -1819.020132  
 E(b3lyp/6-311++g(d,p)/pcm)=-1819.345596

Ini-T

Standard orientation:

-----						
Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	
-----						
1	6	0	-2.689532	-0.447608	-1.088623	
2	6	0	-1.459887	-0.972426	-0.669000	
3	6	0	-1.438637	-2.166319	0.064920	
4	6	0	-2.625415	-2.825788	0.383982	
5	6	0	-3.837908	-2.281597	-0.038641	
6	6	0	-3.882777	-1.097268	-0.773277	
7	1	0	-2.711731	0.472142	-1.663737	
8	1	0	-0.487602	-2.582400	0.383080	
9	1	0	-2.610737	-3.751060	0.950179	
10	1	0	-4.835957	-0.692063	-1.095886	
11	17	0	-5.339055	-3.106806	0.359199	
12	16	0	0.078813	-0.166655	-1.118376	
13	6	0	0.244854	1.024636	0.312249	
14	1	0	0.002103	0.452096	1.211907	
15	6	0	-0.686760	2.215922	0.220897	

16	6	0	-0.637041	3.120895	-0.851446
17	6	0	-1.618940	2.435350	1.243989
18	6	0	-1.494921	4.218239	-0.889289
19	1	0	0.075238	2.956974	-1.653054
20	6	0	-2.481806	3.532859	1.203939
21	1	0	-1.673073	1.738583	2.077424
22	6	0	-2.420628	4.428663	0.137281
23	1	0	-1.443482	4.911638	-1.724751
24	1	0	-3.201012	3.682843	2.004751
25	1	0	-3.090274	5.283851	0.102055
26	6	0	1.730080	1.435692	0.472972
27	1	0	1.738240	2.238529	1.225793
28	8	0	2.224784	1.910787	-0.755488
29	1	0	3.109264	2.284267	-0.608178
30	6	0	2.610715	0.296496	1.058400
31	8	0	2.334561	0.107096	2.326844
32	6	0	3.620155	-0.492998	0.421197
33	6	0	3.808238	-0.566100	-0.989456
34	6	0	4.479548	-1.280287	1.248833
35	6	0	4.822815	-1.350137	-1.518927
36	1	0	3.149299	-0.017881	-1.649126
37	6	0	5.477957	-2.064416	0.694027
38	1	0	4.357837	-1.232474	2.326732
39	6	0	5.666885	-2.106770	-0.693445
40	1	0	4.950864	-1.384228	-2.598084
41	1	0	6.124557	-2.643761	1.348569
42	1	0	6.452660	-2.720174	-1.124404

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Zero-point correction= 0.321542 (Hartree/Particle)

Thermal correction to Energy= 0.344316

Thermal correction to Enthalpy= 0.345260

Thermal correction to Gibbs Free Energy= 0.263275  
 Sum of electronic and zero-point Energies= -1818.859927  
 Sum of electronic and thermal Energies= -1818.837153  
 Sum of electronic and thermal Enthalpies= -1818.836209  
 Sum of electronic and thermal Free Energies= -1818.918193  
 E(b3lyp/6-311++g(d,p)/pcm)=-1819.241714

TS

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.211551	-0.239389	-1.386500
2	6	0	-1.983679	-0.667547	-0.868064
3	6	0	-1.959143	-1.697378	0.085051
4	6	0	-3.147135	-2.276424	0.526934
5	6	0	-4.360170	-1.839981	-0.007790
6	6	0	-4.404368	-0.829617	-0.965976
7	1	0	-3.235397	0.561782	-2.118476
8	1	0	-1.009993	-2.043847	0.484457
9	1	0	-3.132240	-3.069695	1.266912
10	1	0	-5.356604	-0.499765	-1.367710
11	17	0	-5.860051	-2.580054	0.538253
12	16	0	-0.463906	0.045806	-1.495059
13	6	0	0.194355	0.838870	0.066401
14	1	0	-0.153347	0.217994	0.893263
15	6	0	-0.292486	2.263100	0.278955
16	6	0	-0.001133	3.294374	-0.626920
17	6	0	-1.048338	2.560722	1.420536
18	6	0	-0.456054	4.589947	-0.391568

19	1	0	0.577465	3.076615	-1.519253
20	6	0	-1.507916	3.858311	1.653875
21	1	0	-1.284357	1.769784	2.128494
22	6	0	-1.211071	4.877258	0.749325
23	1	0	-0.223350	5.378583	-1.102327
24	1	0	-2.098441	4.069144	2.541493
25	1	0	-1.566663	5.888340	0.928538
26	6	0	1.699425	0.745806	0.085136
27	1	0	2.169302	1.075487	1.015093
28	8	0	2.290909	1.174588	-1.055298
29	1	0	3.259267	1.136525	-0.950843
30	6	0	2.111402	-1.210461	0.389820
31	8	0	1.468932	-1.460124	1.416225
32	6	0	3.579768	-1.263719	0.238454
33	6	0	4.190760	-1.093635	-1.021492
34	6	0	4.386047	-1.592677	1.349825
35	6	0	5.573402	-1.210509	-1.153655
36	1	0	3.567943	-0.914265	-1.893166
37	6	0	5.763741	-1.721409	1.202340
38	1	0	3.911370	-1.742892	2.314489
39	6	0	6.365956	-1.521392	-0.044499
40	1	0	6.031958	-1.080582	-2.130497
41	1	0	6.374763	-1.974135	2.065353
42	1	0	7.442091	-1.622272	-0.153722

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Zero-point correction=	0.321192 (Hartree/Particle)
Thermal correction to Energy=	0.343563
Thermal correction to Enthalpy=	0.344507
Thermal correction to Gibbs Free Energy=	0.263923
Sum of electronic and zero-point Energies=	-1818.850253
Sum of electronic and thermal Energies=	-1818.827881

Sum of electronic and thermal Enthalpies= -1818.826937  
 Sum of electronic and thermal Free Energies= -1818.907522  
 E(b3lyp/6-311++g(d,p)/pcm)=-1819.234066

PRO

Standard orientation:

-----						
Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	
-----						
1	6	0	-3.006097	-0.248455	-1.334735	
2	6	0	-1.784597	-0.720804	-0.837888	
3	6	0	-1.777394	-1.824455	0.029313	
4	6	0	-2.971521	-2.438420	0.403525	
5	6	0	-4.175862	-1.954032	-0.108571	
6	6	0	-4.205856	-0.866114	-0.978555	
7	1	0	-3.017157	0.607644	-2.001675	
8	1	0	-0.834269	-2.203137	0.413202	
9	1	0	-2.968534	-3.290479	1.075173	
10	1	0	-5.152222	-0.501979	-1.364301	
11	17	0	-5.685026	-2.733249	0.352774	
12	16	0	-0.248960	0.042473	-1.355764	
13	6	0	0.214381	0.967587	0.233670	
14	1	0	-0.077309	0.300497	1.050468	
15	6	0	-0.553880	2.272241	0.371710	
16	6	0	-0.254721	3.393830	-0.417387	
17	6	0	-1.587085	2.366656	1.312912	
18	6	0	-0.972108	4.577866	-0.261811	
19	1	0	0.542931	3.332857	-1.150905	
20	6	0	-2.308031	3.552901	1.466484	
21	1	0	-1.830929	1.504156	1.928870	

22	6	0	-2.001914	4.662906	0.680125
23	1	0	-0.727625	5.438975	-0.878661
24	1	0	-3.107372	3.606419	2.201110
25	1	0	-2.559987	5.587989	0.798038
26	6	0	1.693747	1.072980	0.292861
27	1	0	2.203430	1.105479	1.253174
28	8	0	2.326456	1.619056	-0.787246
29	1	0	3.284457	1.495375	-0.685656
30	6	0	2.339403	-1.907432	0.456741
31	8	0	1.801174	-2.172417	1.494717
32	6	0	3.740253	-1.475924	0.233434
33	6	0	4.136361	-1.073751	-1.051503
34	6	0	4.676279	-1.504094	1.282531
35	6	0	5.454856	-0.680607	-1.280220
36	1	0	3.400663	-1.069590	-1.850300
37	6	0	5.994394	-1.123579	1.044133
38	1	0	4.353220	-1.825217	2.268474
39	6	0	6.382990	-0.707866	-0.234041
40	1	0	5.763574	-0.366883	-2.273612
41	1	0	6.721058	-1.147370	1.851832
42	1	0	7.412242	-0.410766	-0.416301

-----  
Zero-point correction= 0.319019 (Hartree/Particle)

Thermal correction to Energy= 0.343610

Thermal correction to Enthalpy= 0.344555

Thermal correction to Gibbs Free Energy= 0.256028

Sum of electronic and zero-point Energies= -1818.858830

Sum of electronic and thermal Energies= -1818.834238

Sum of electronic and thermal Enthalpies= -1818.833294

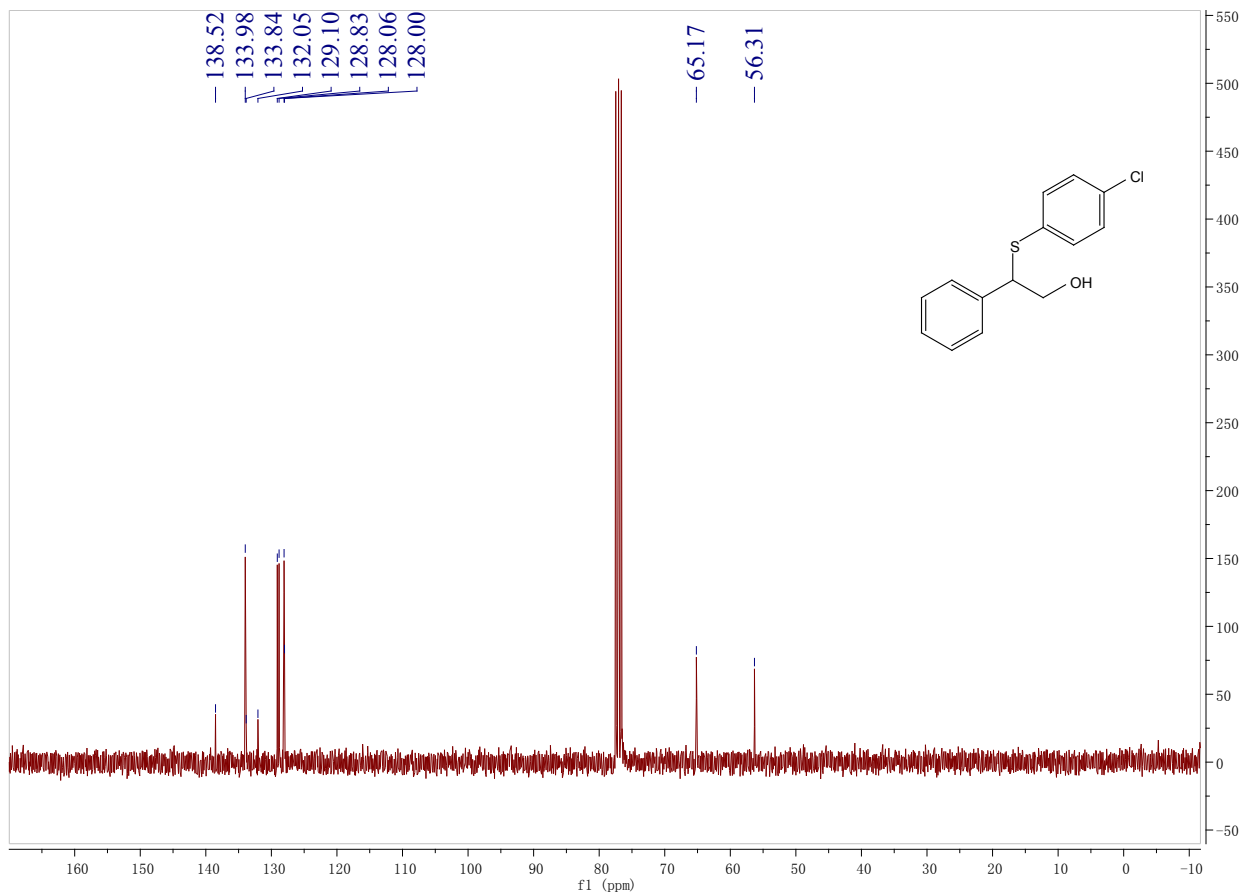
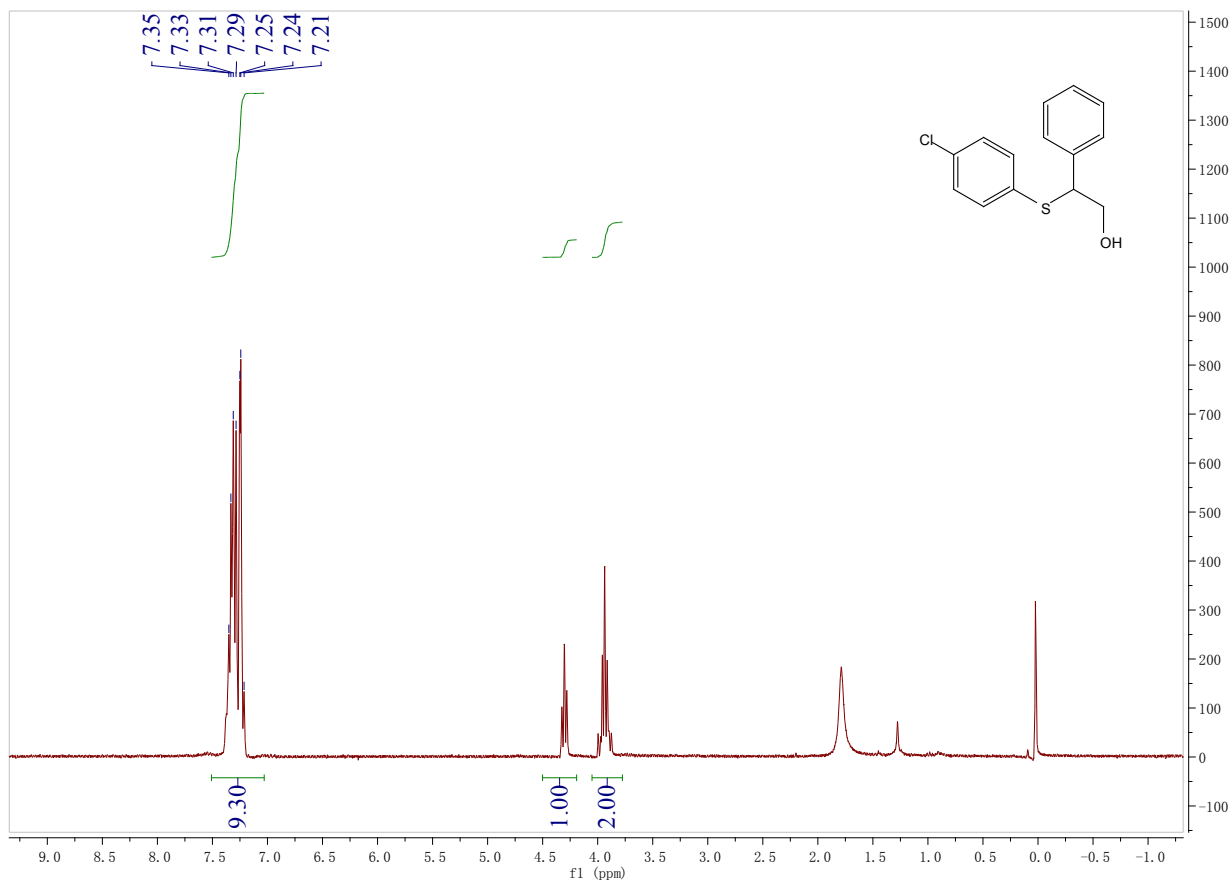
Sum of electronic and thermal Free Energies= -1818.921821

E(b3lyp/6-311++g(d,p)/pcm)=-1819.251800

## References

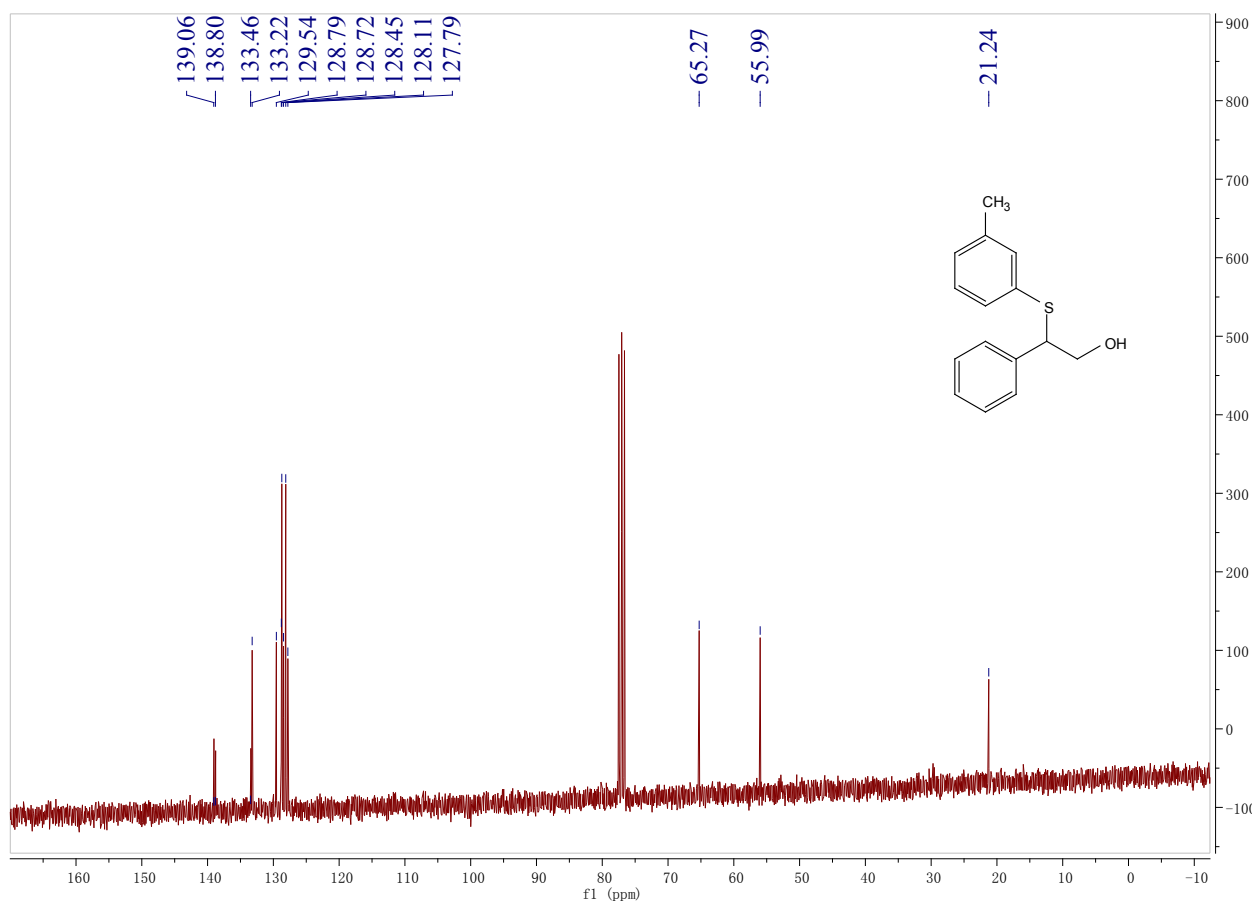
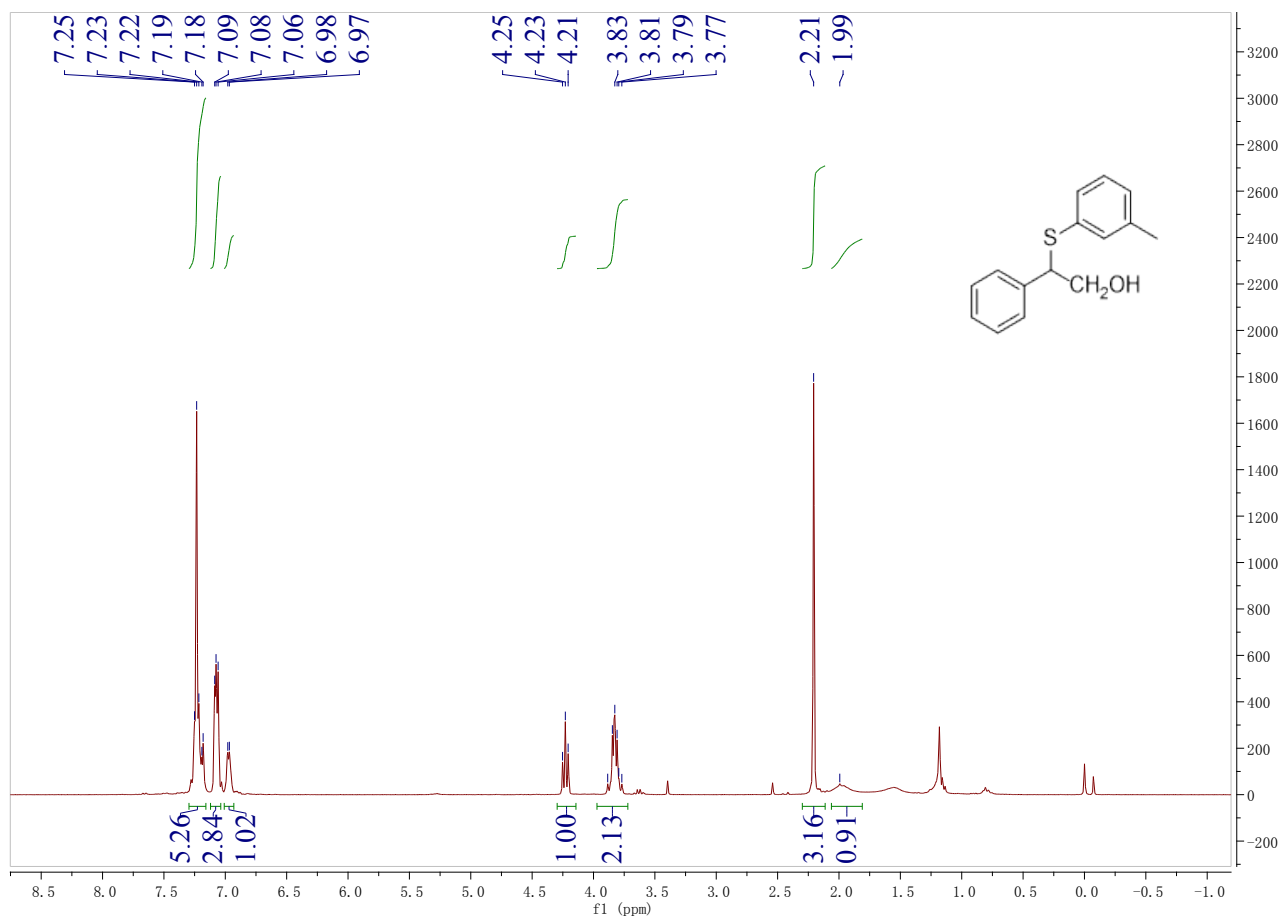
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2. H. Keipour, A. Jalba, N. Tanbouza, V. Carreras, T. Ollevier, *Org. Bio. Chem.*, 2019, **17**, 3098.

4a

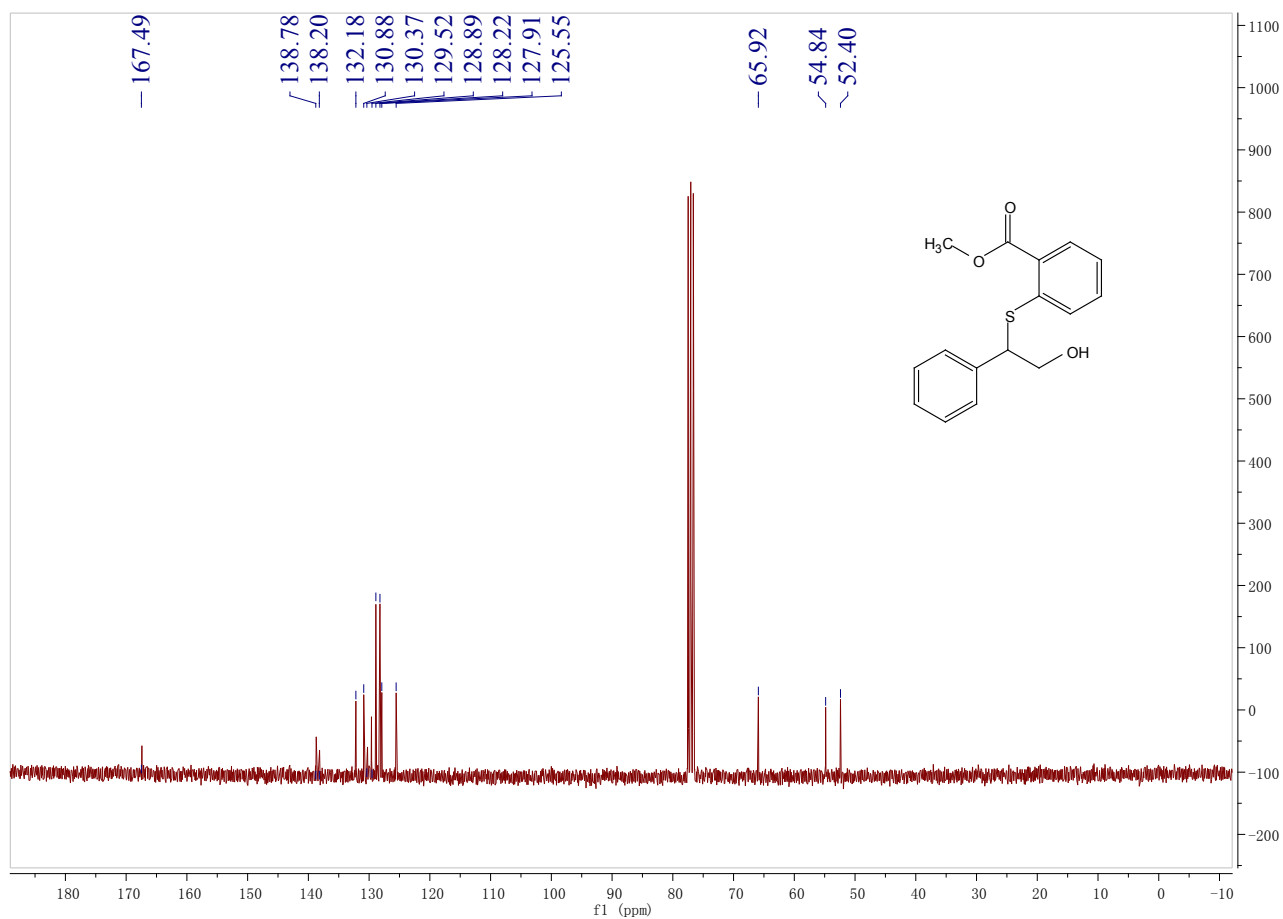
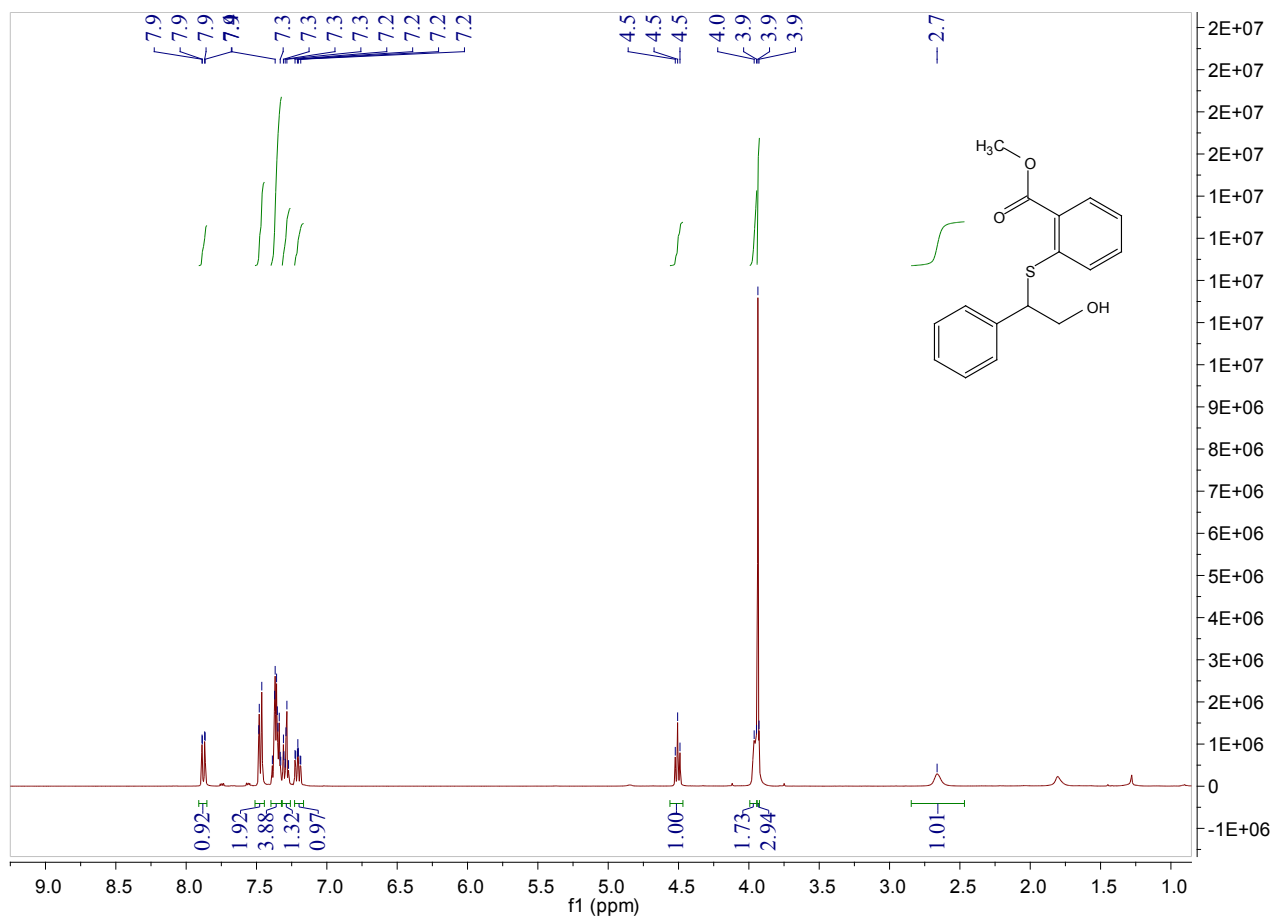




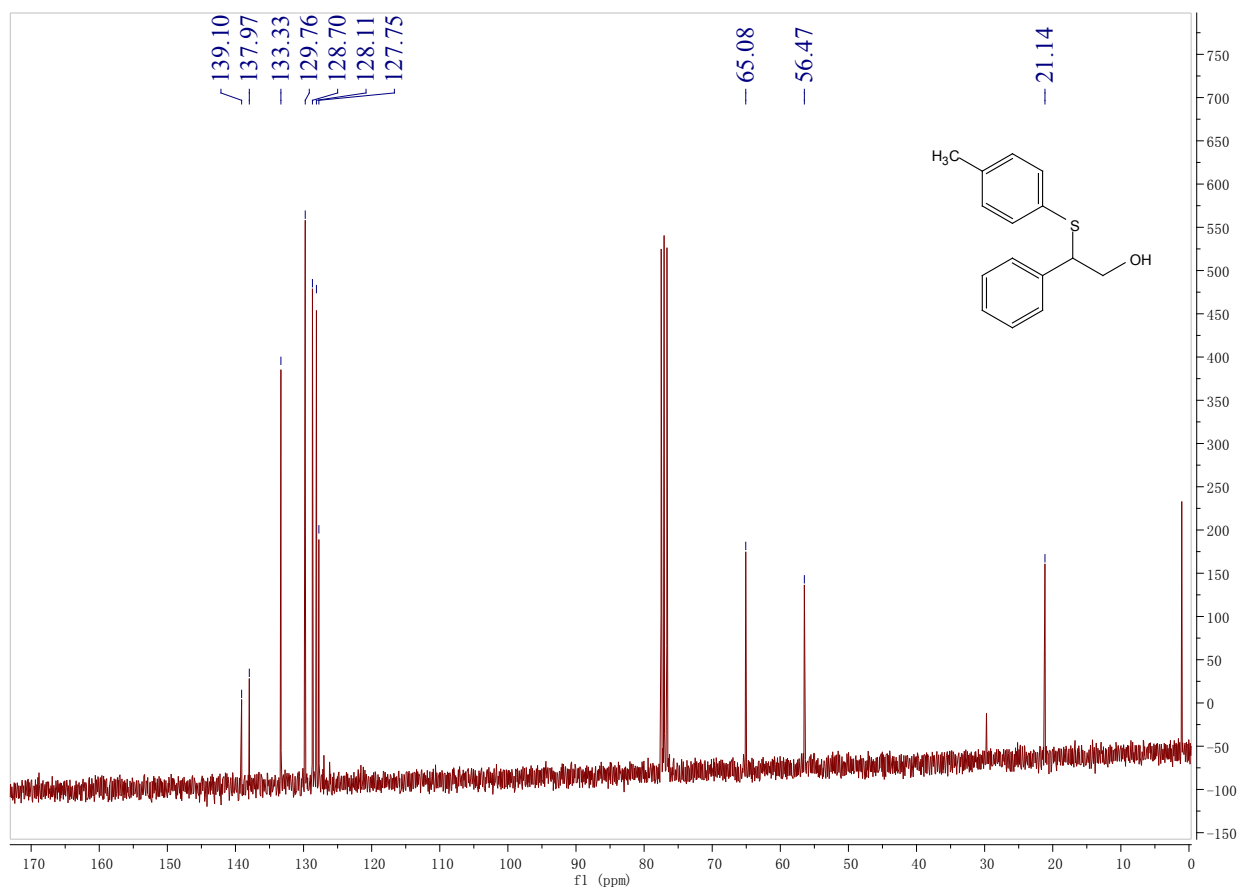
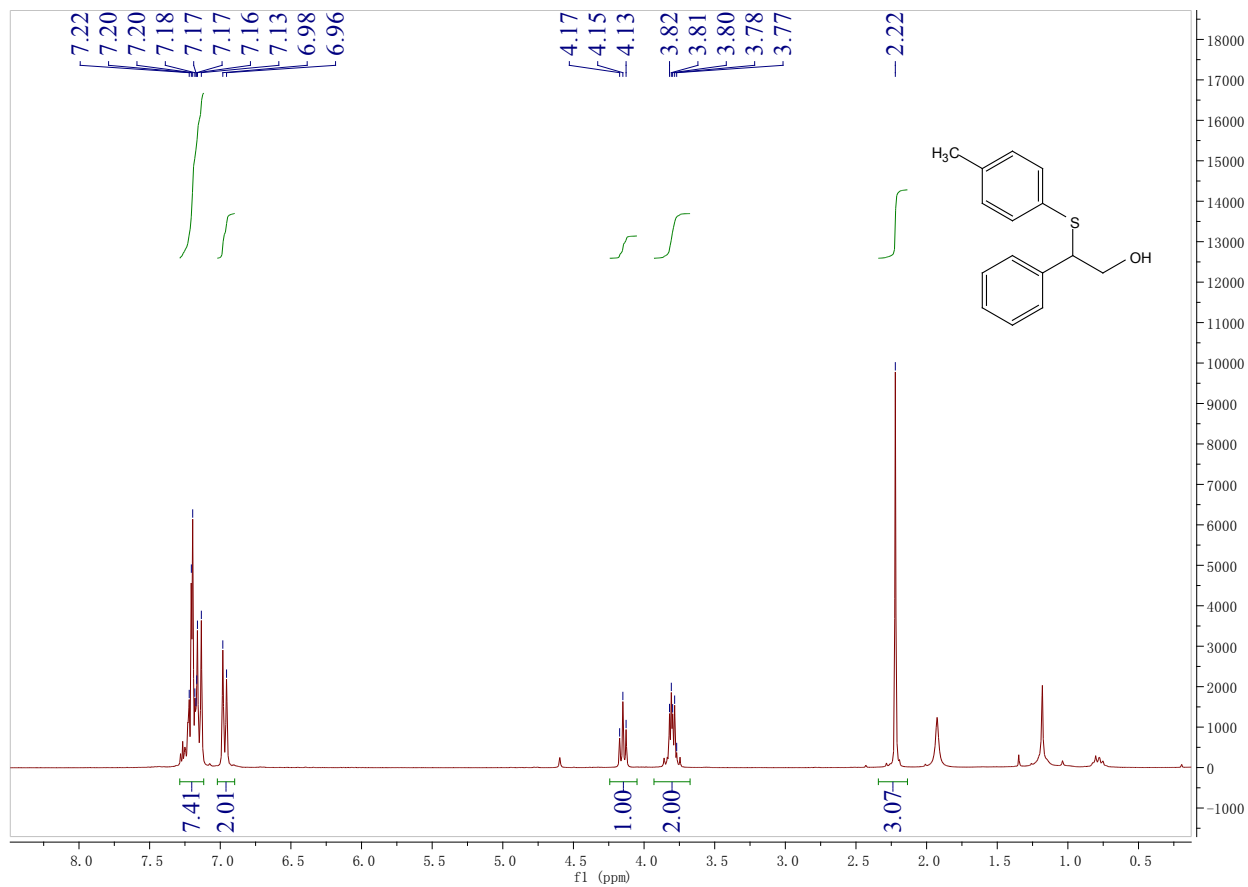
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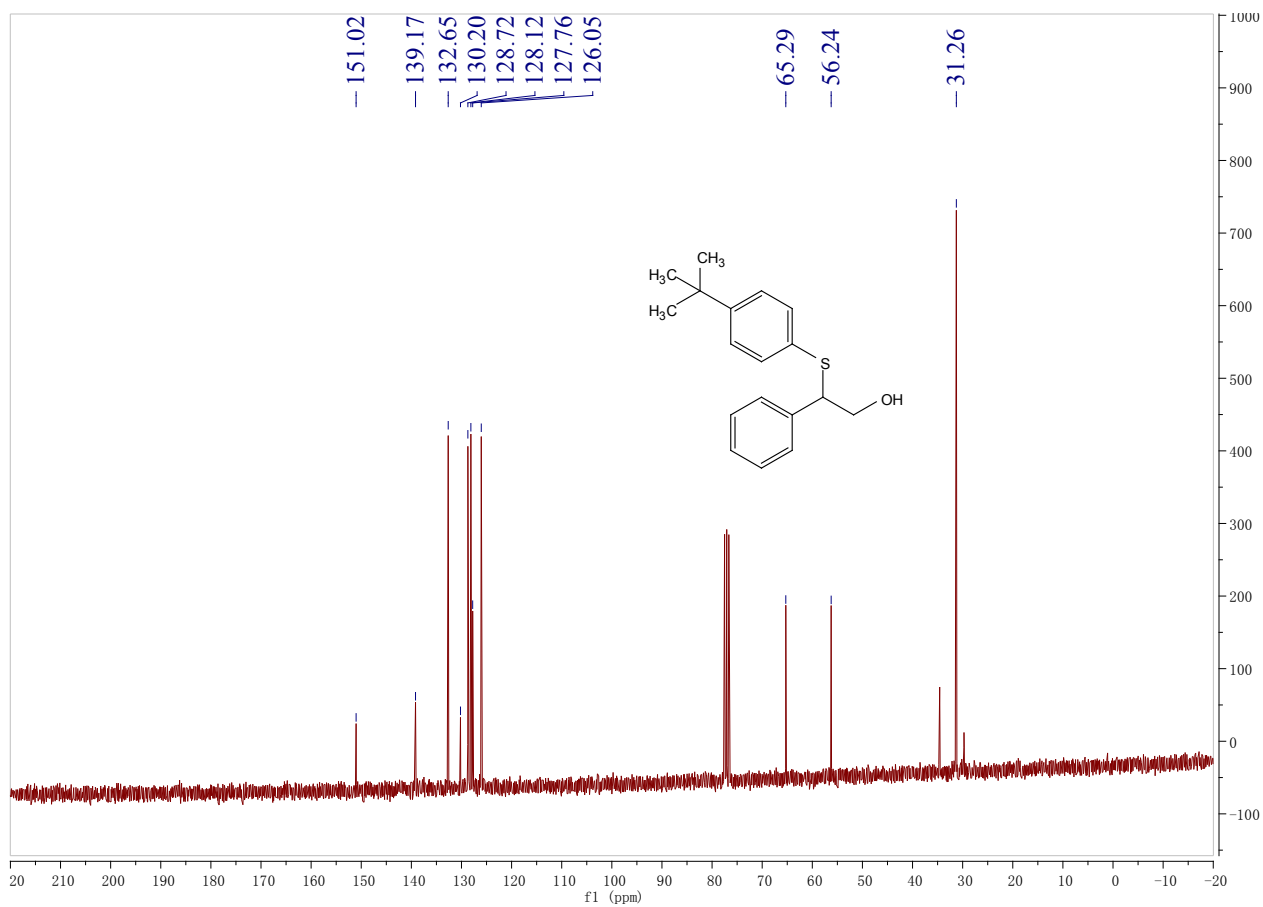
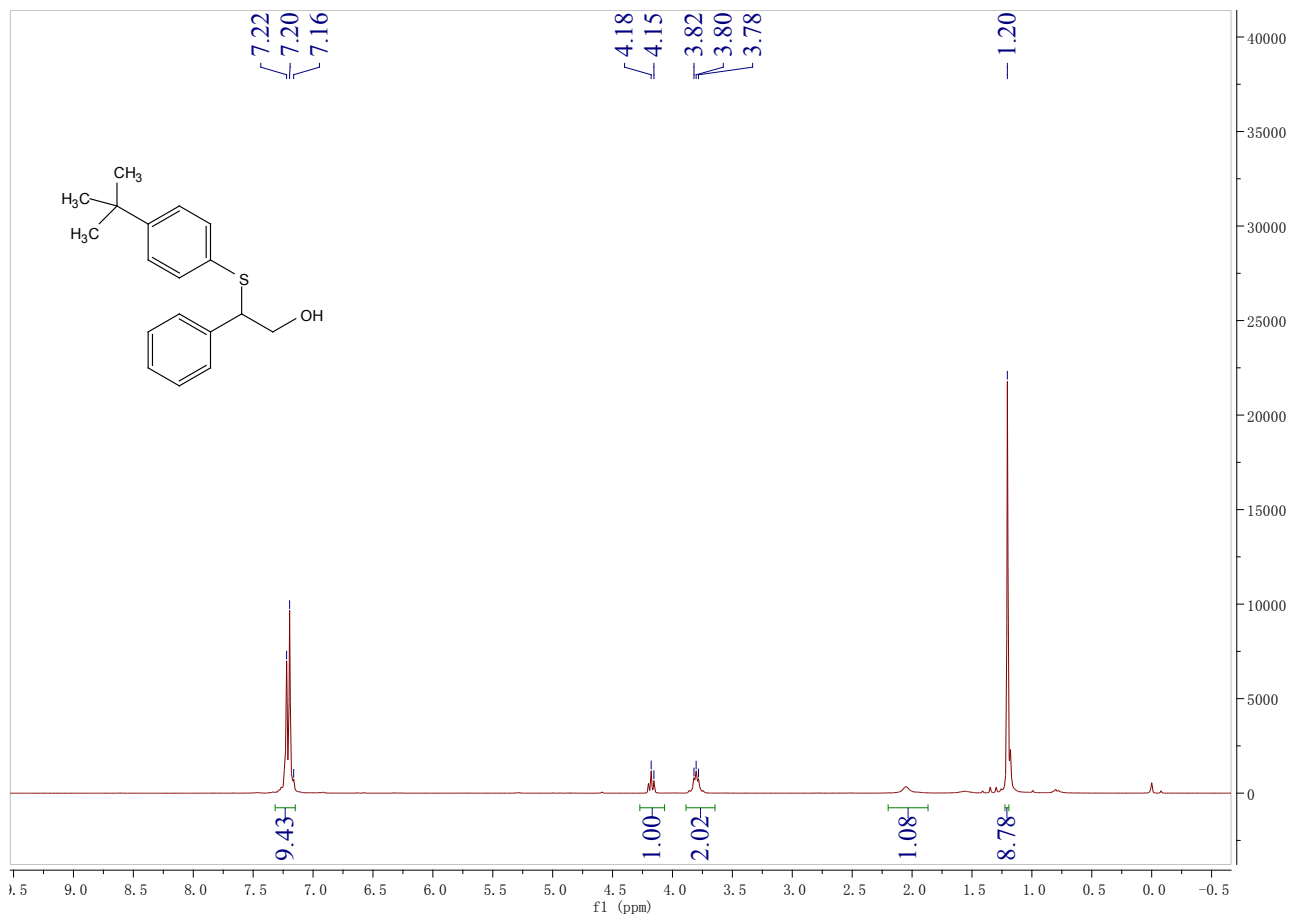
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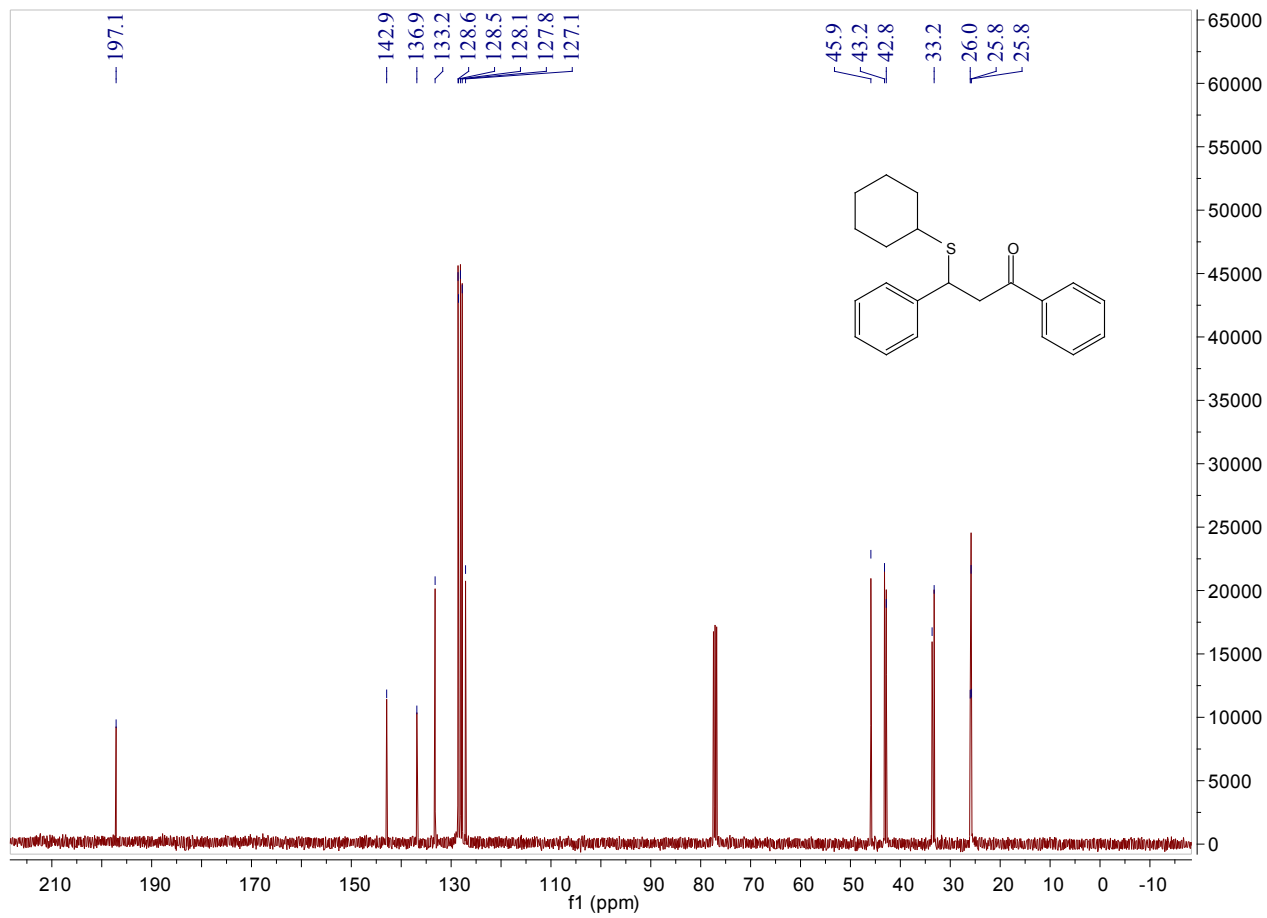
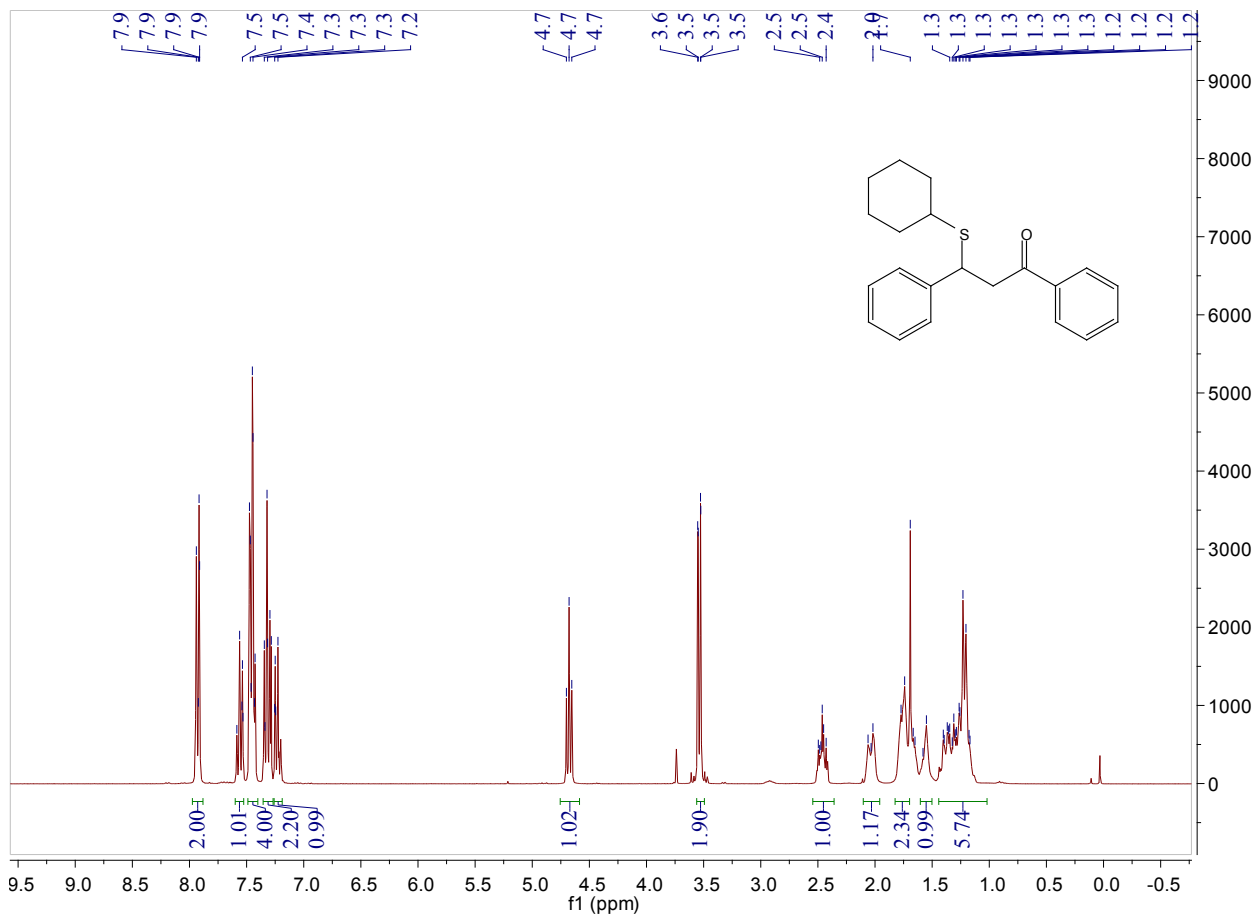
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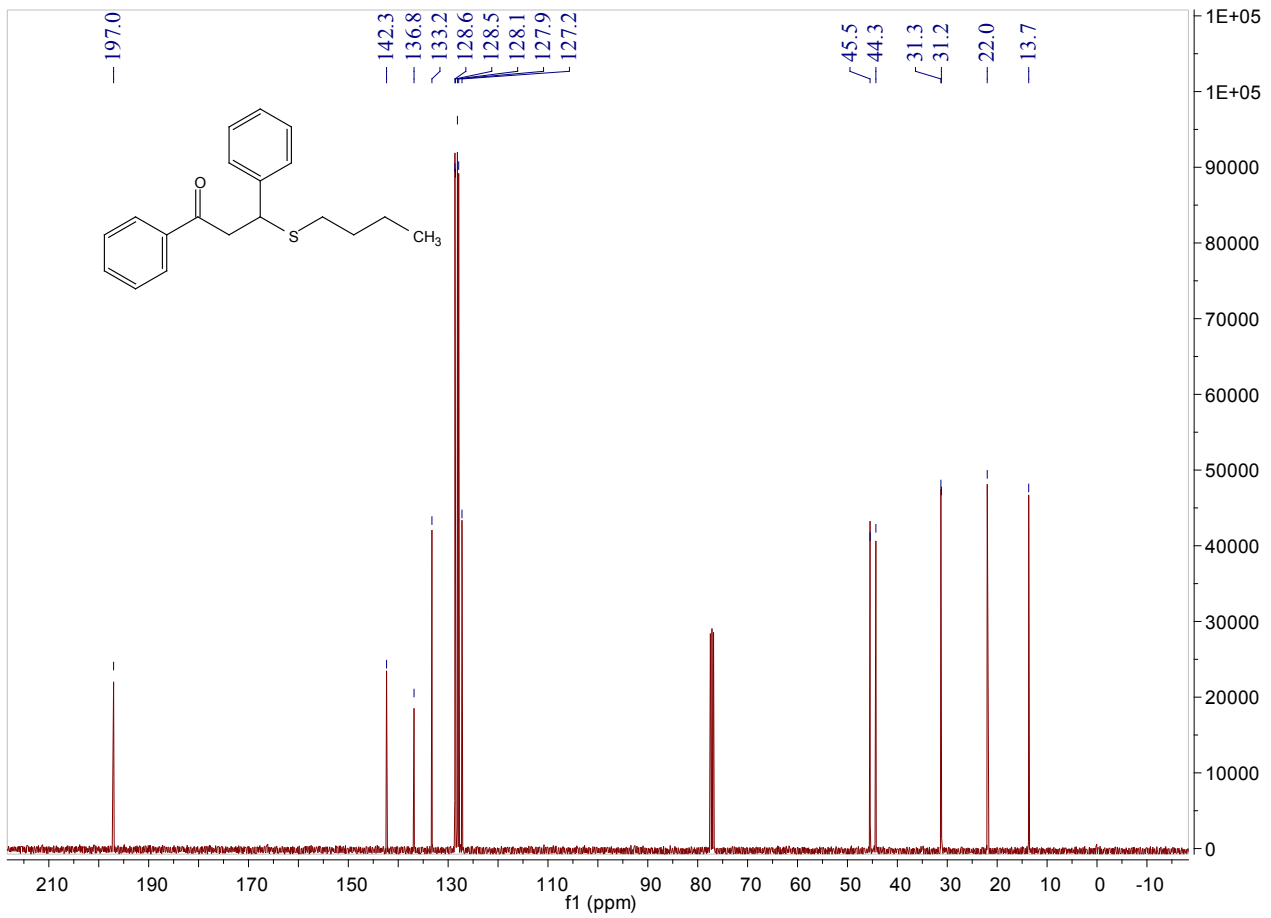
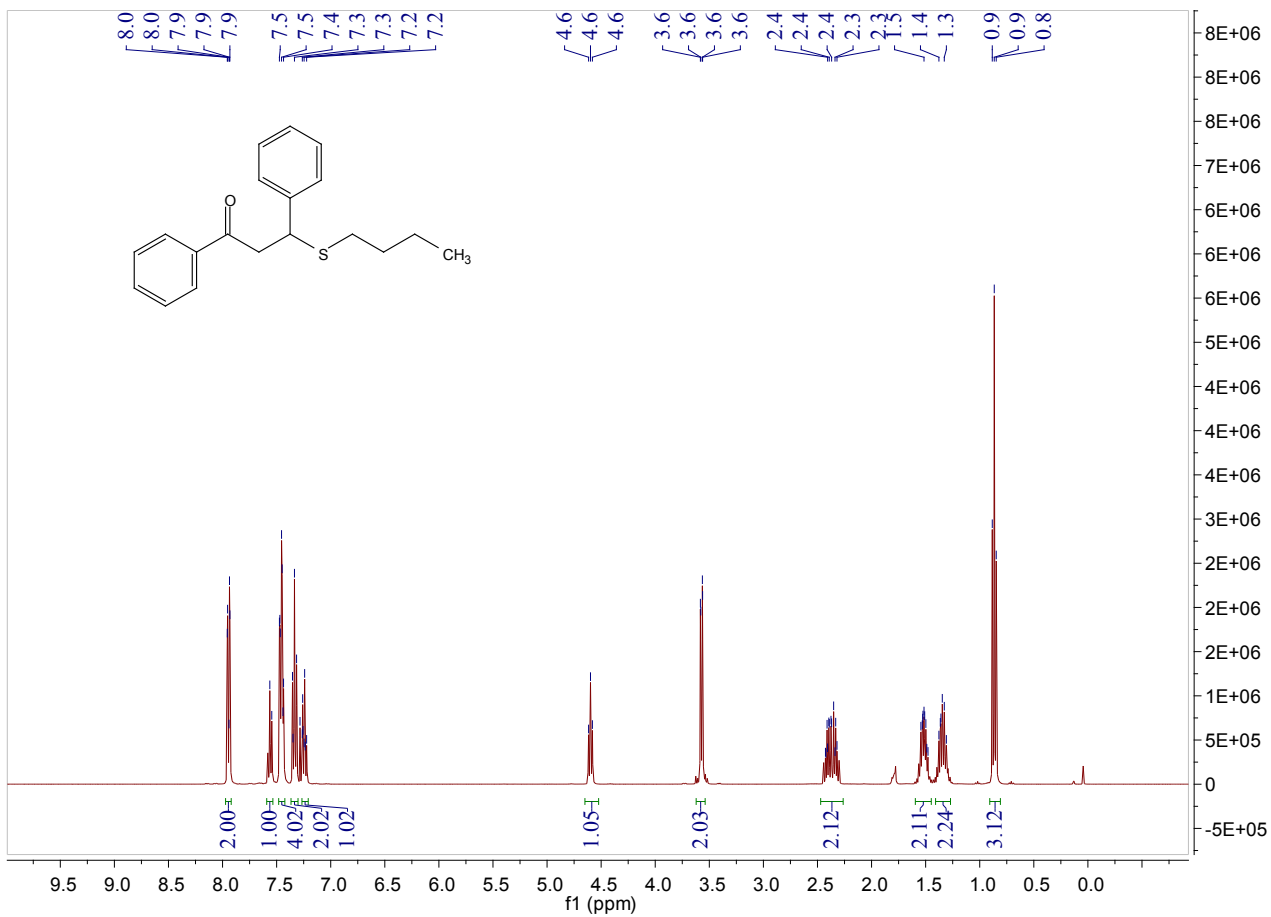
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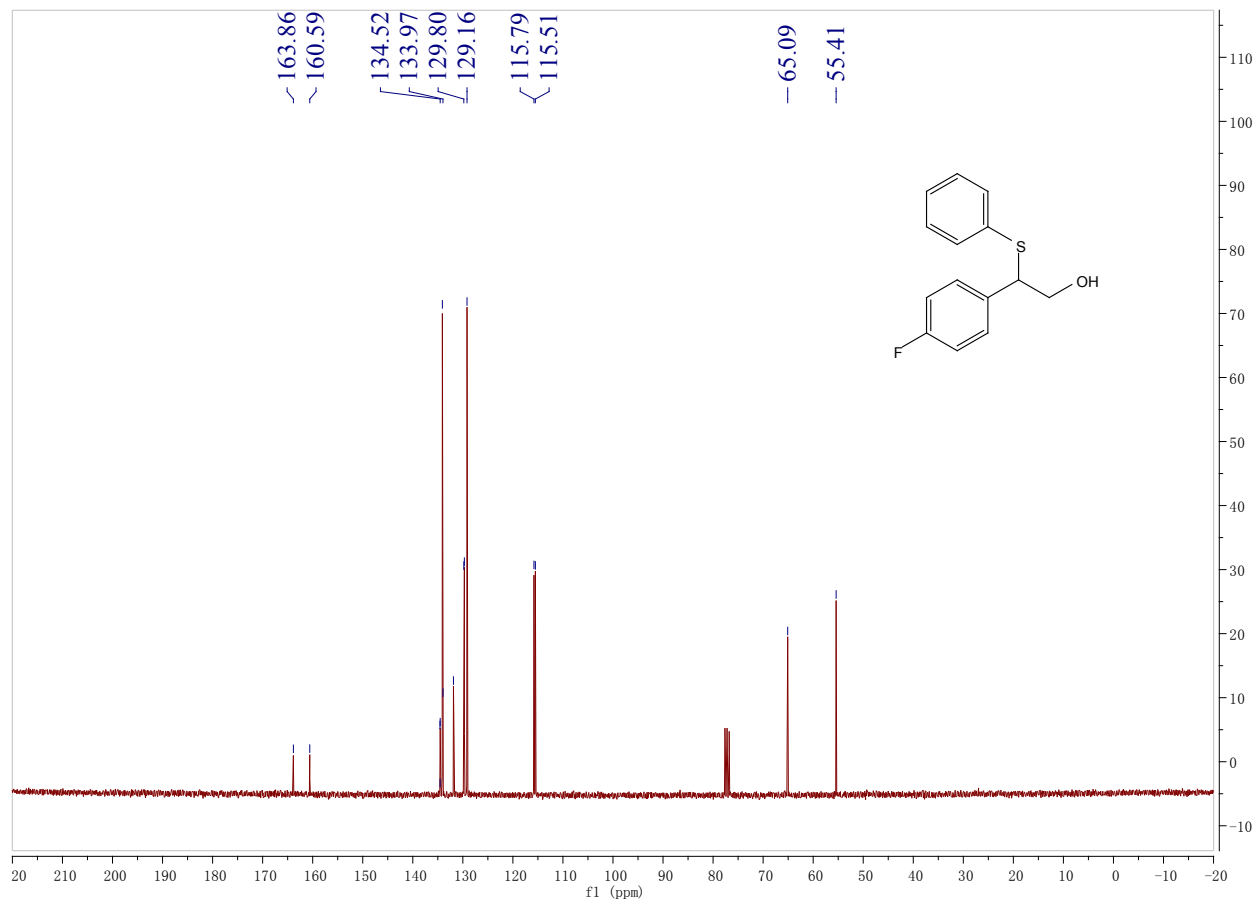
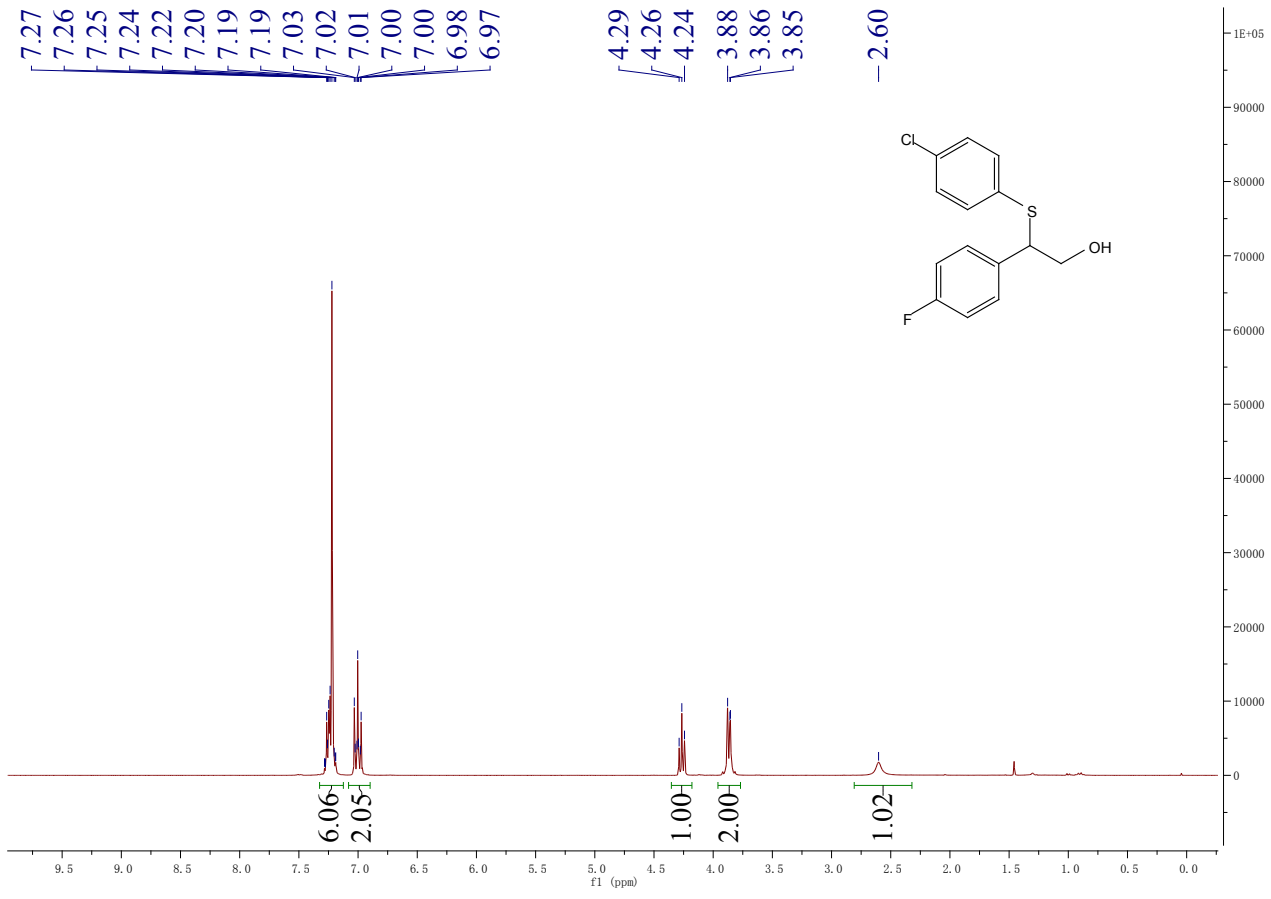
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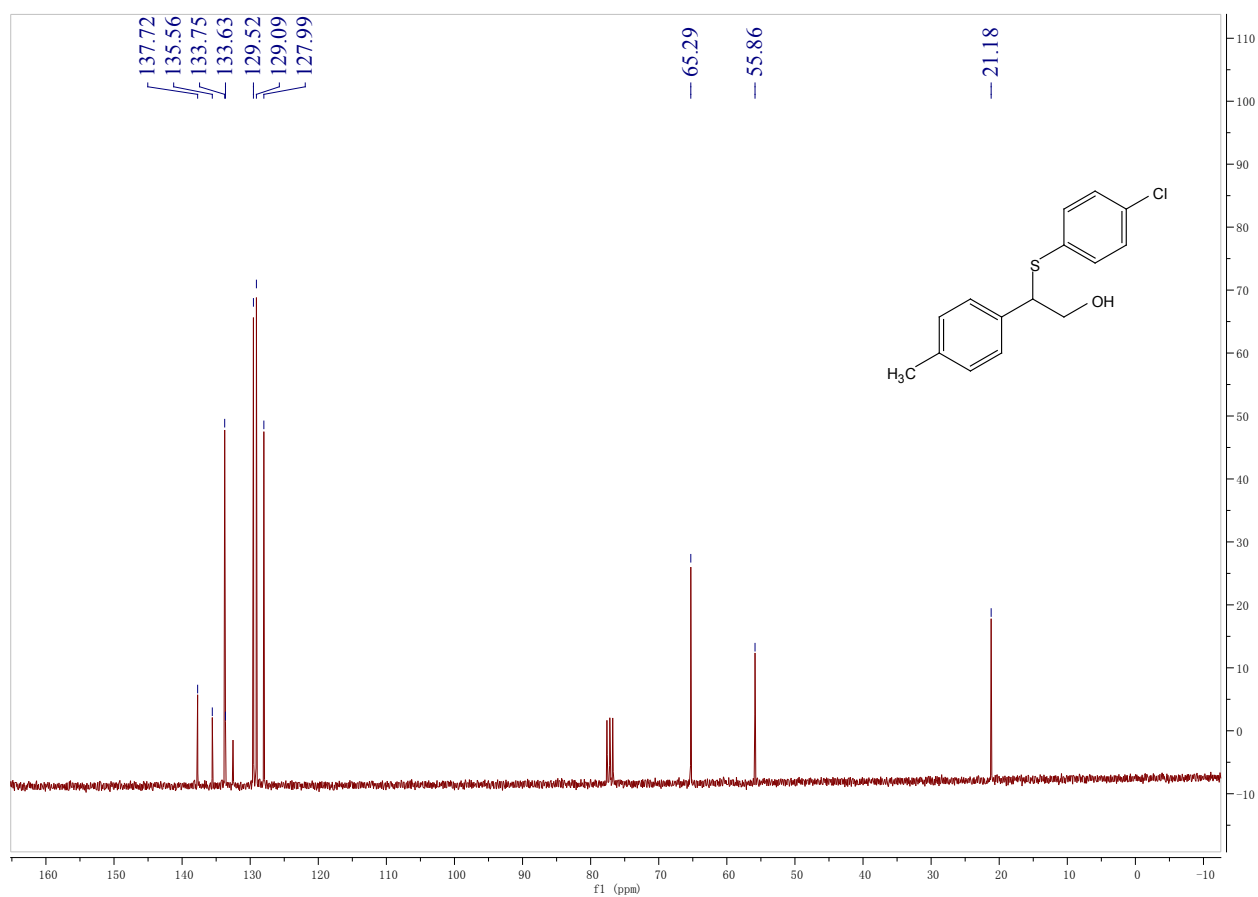
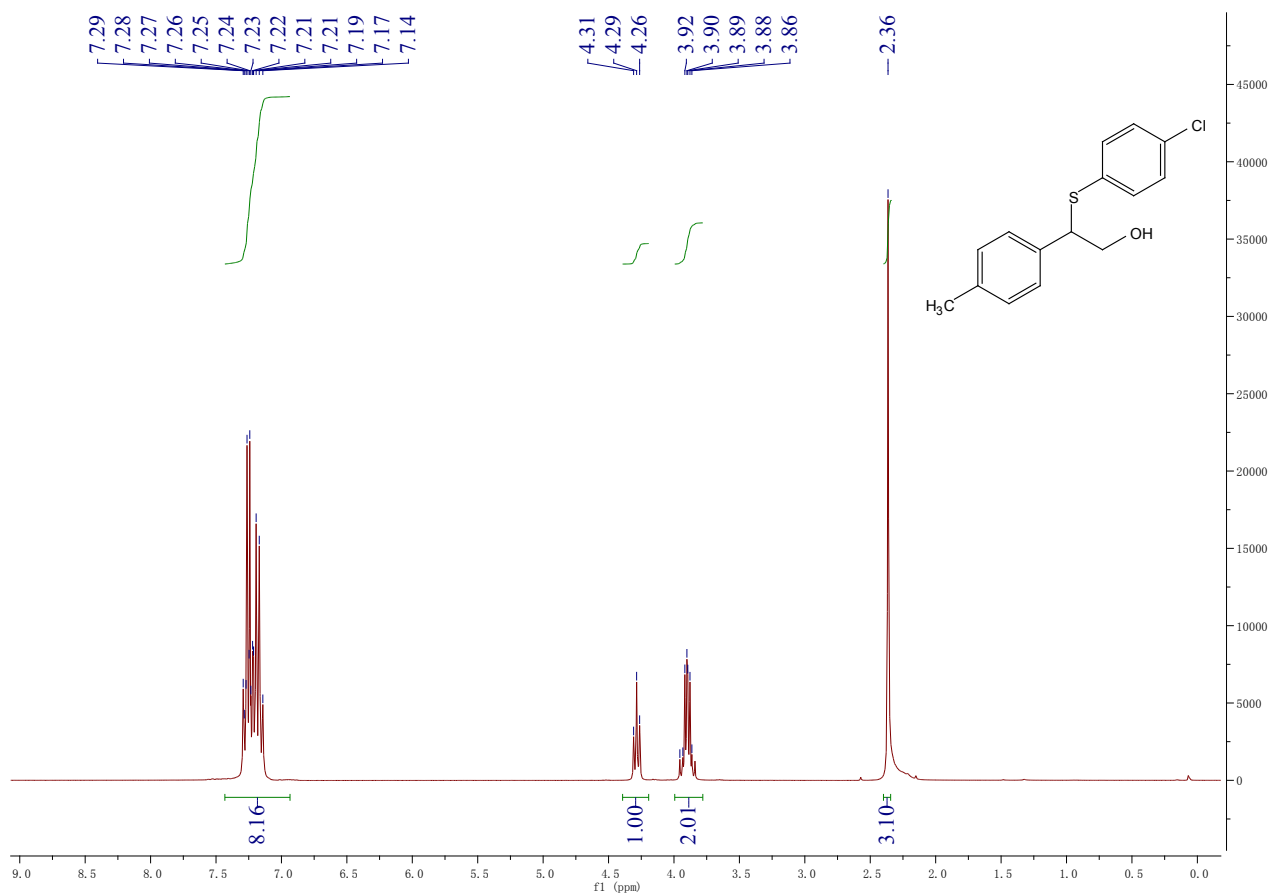
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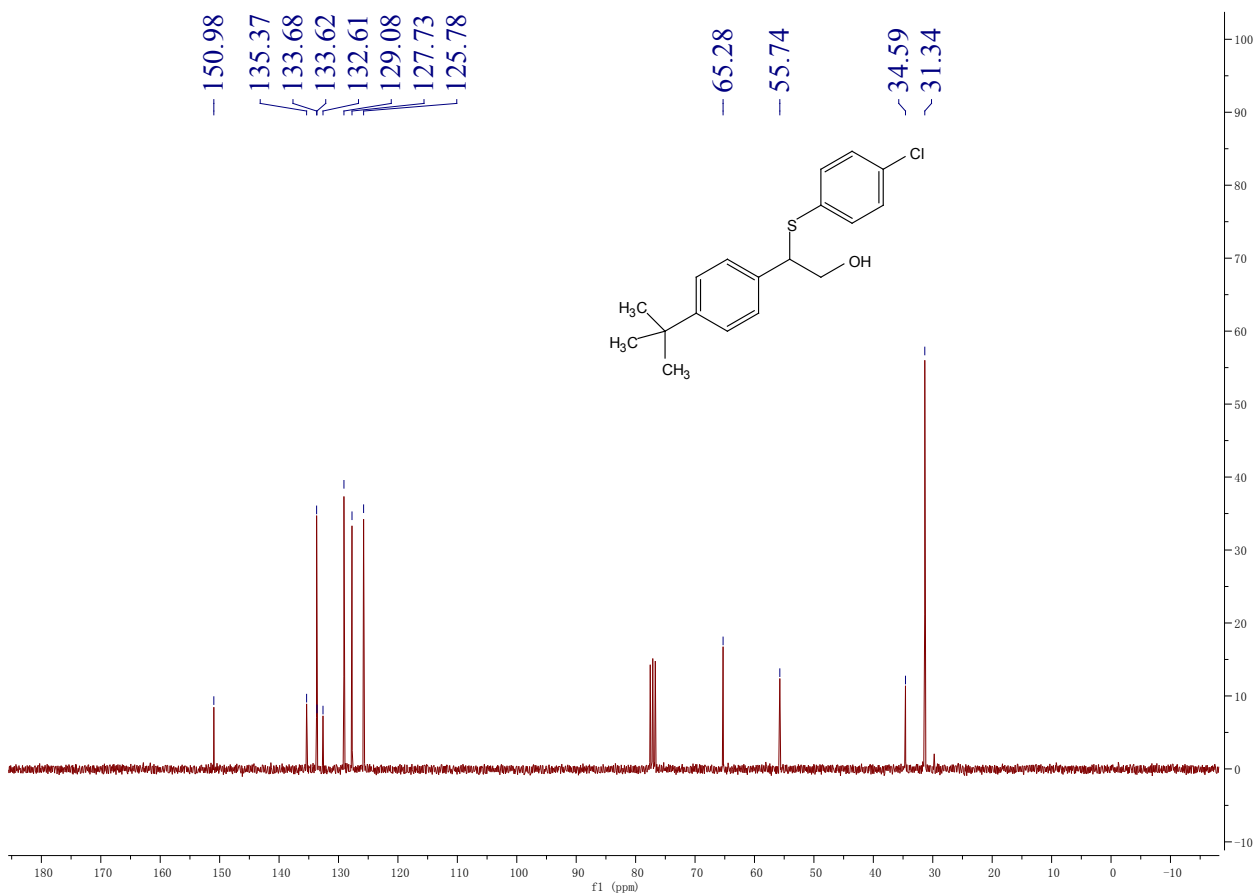
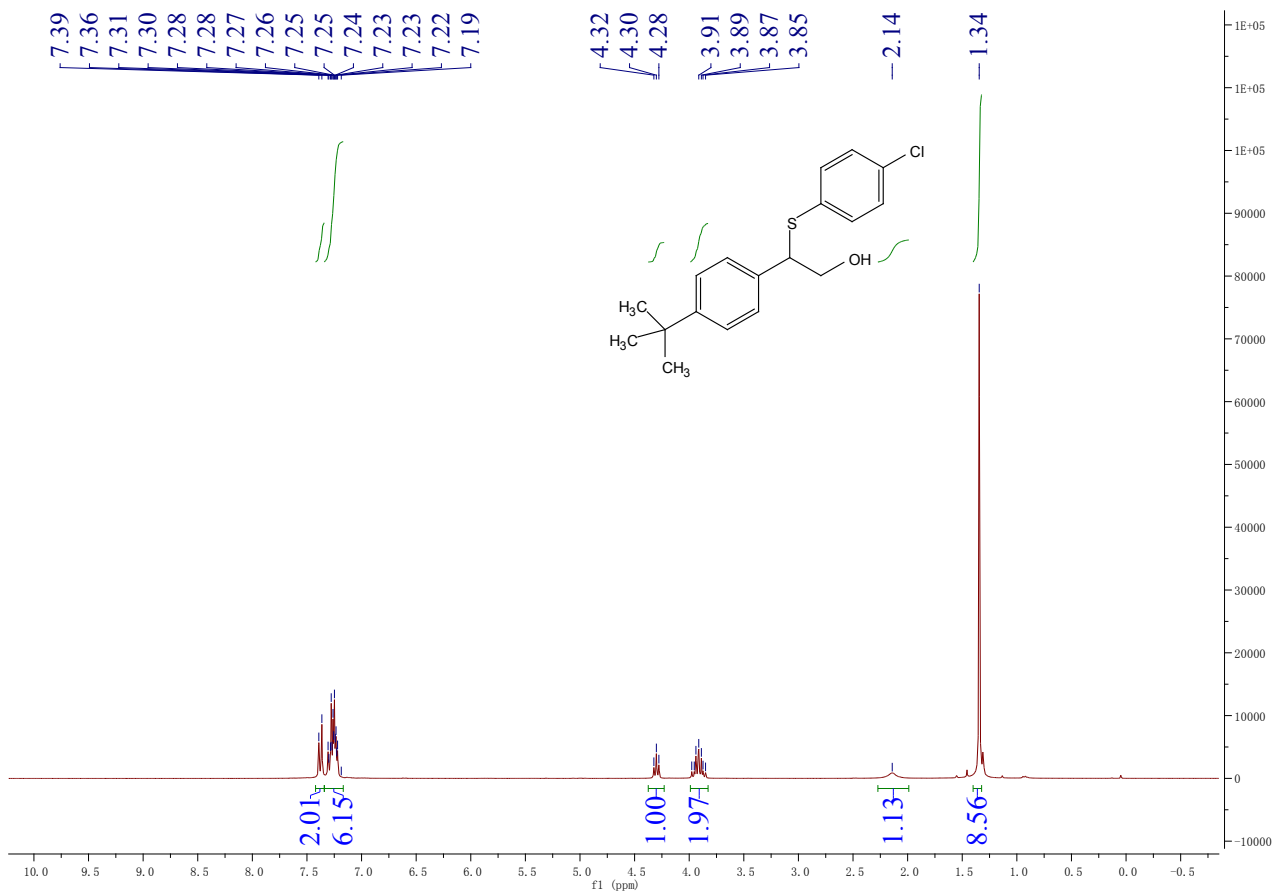


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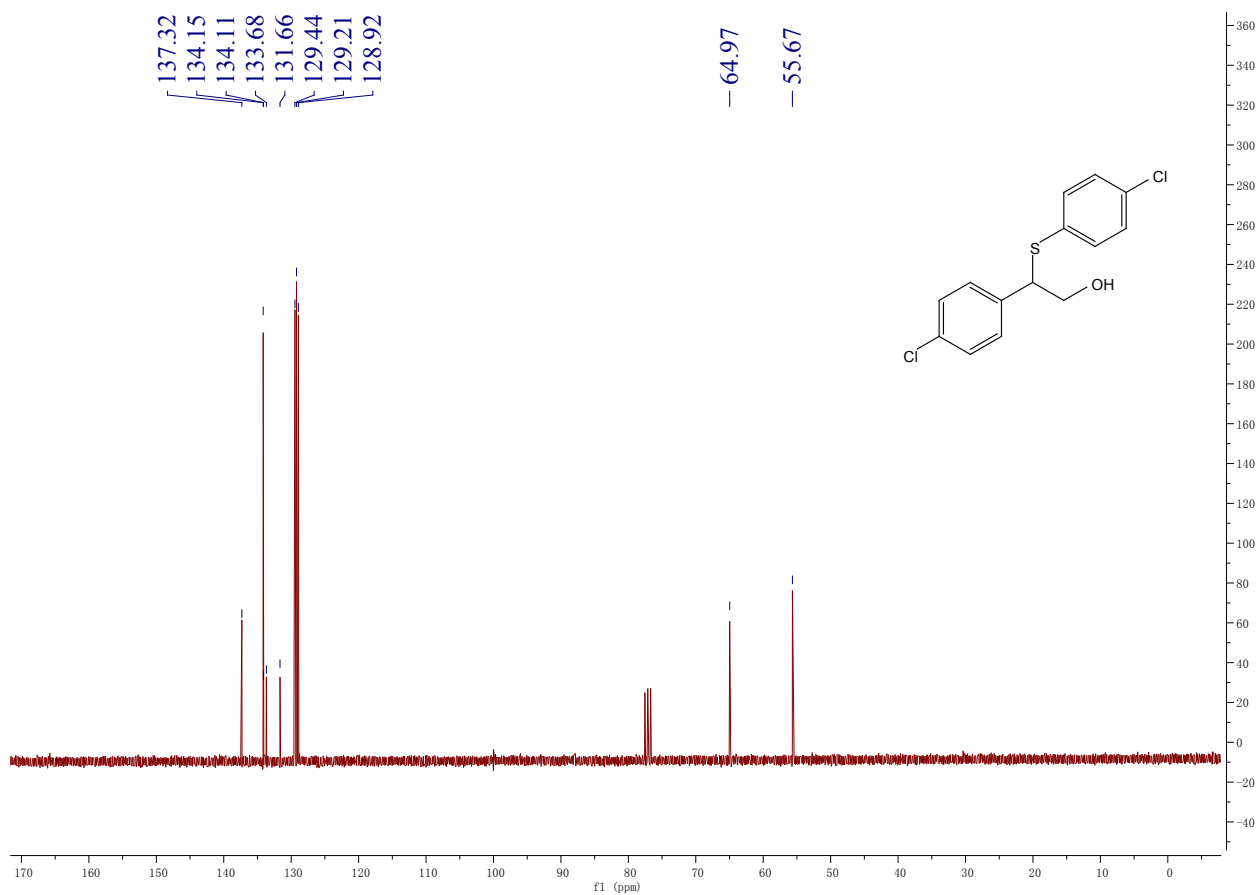
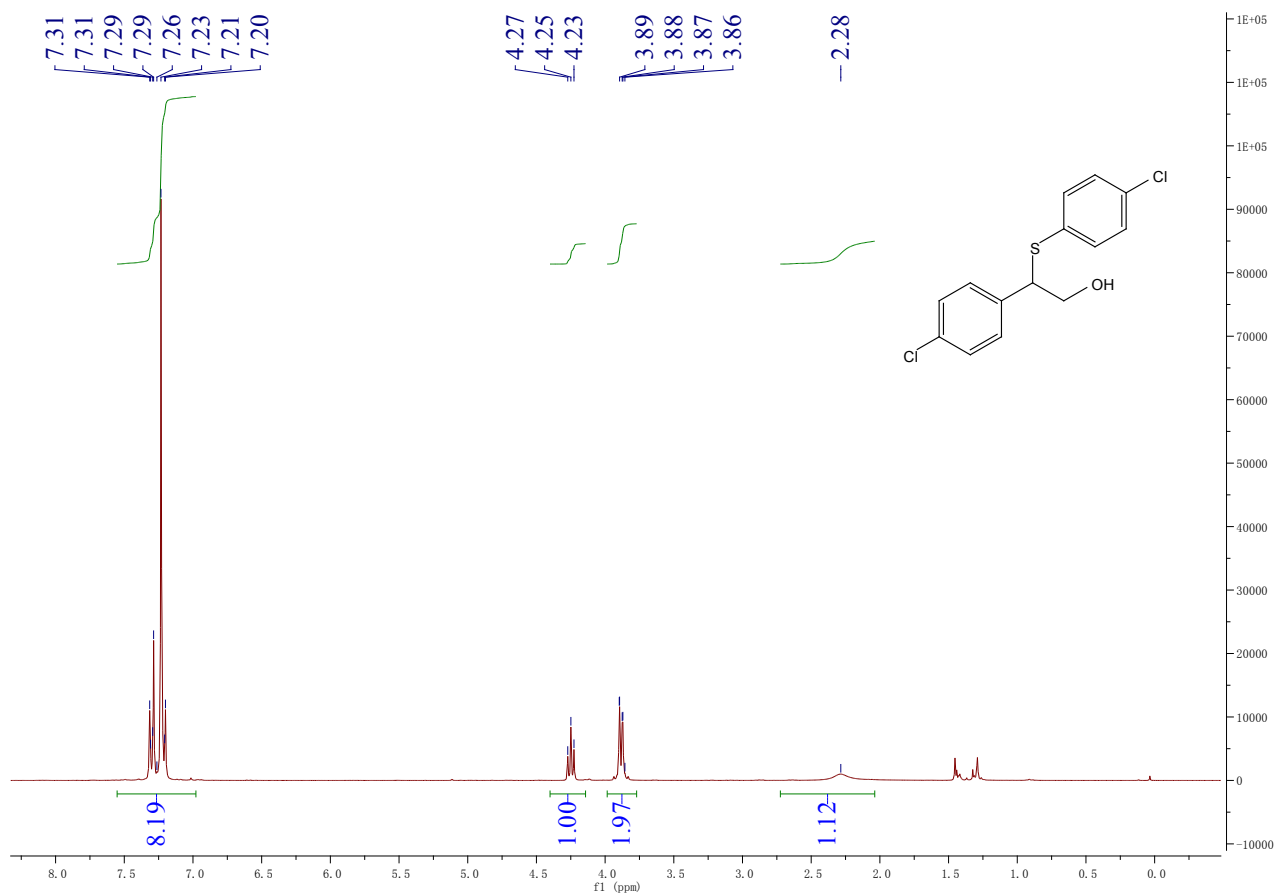




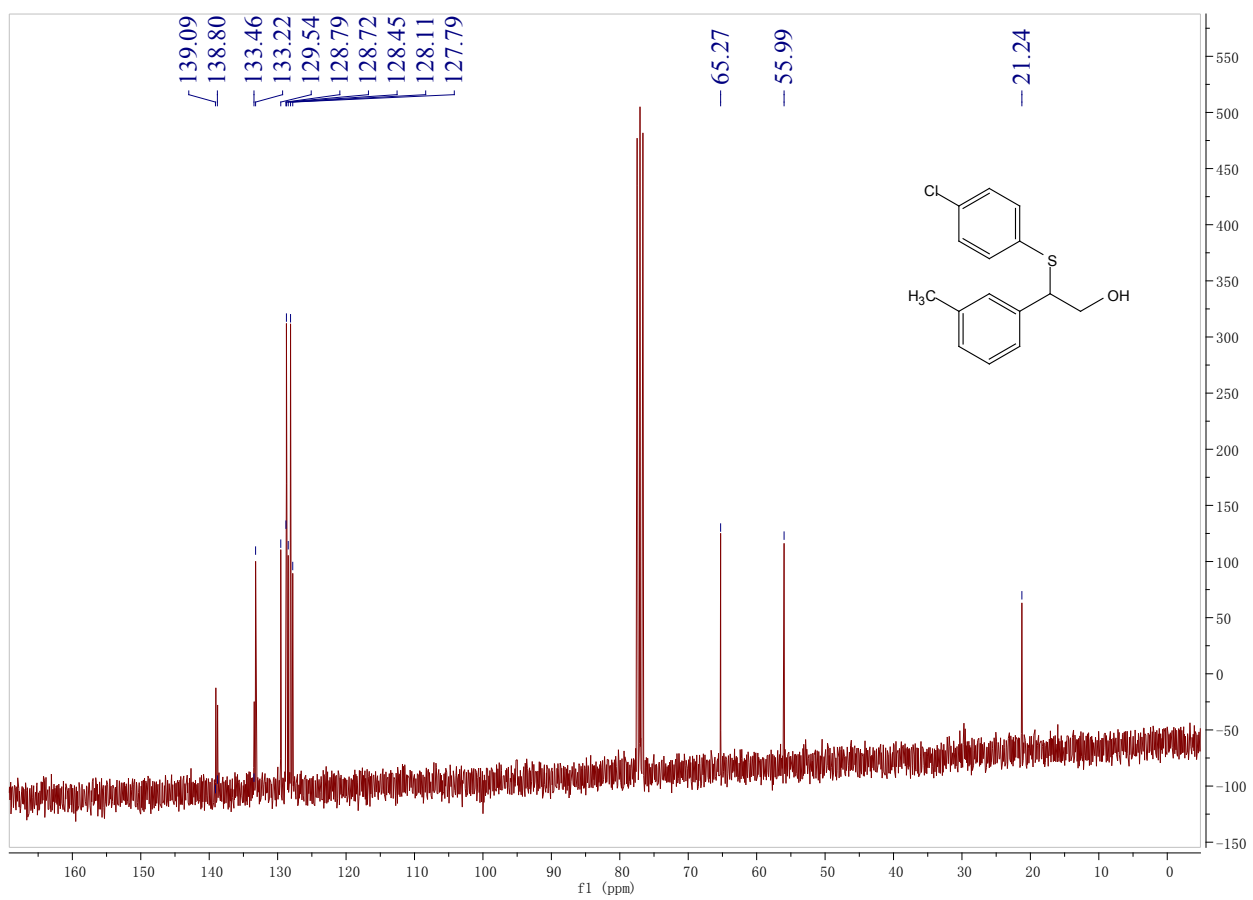
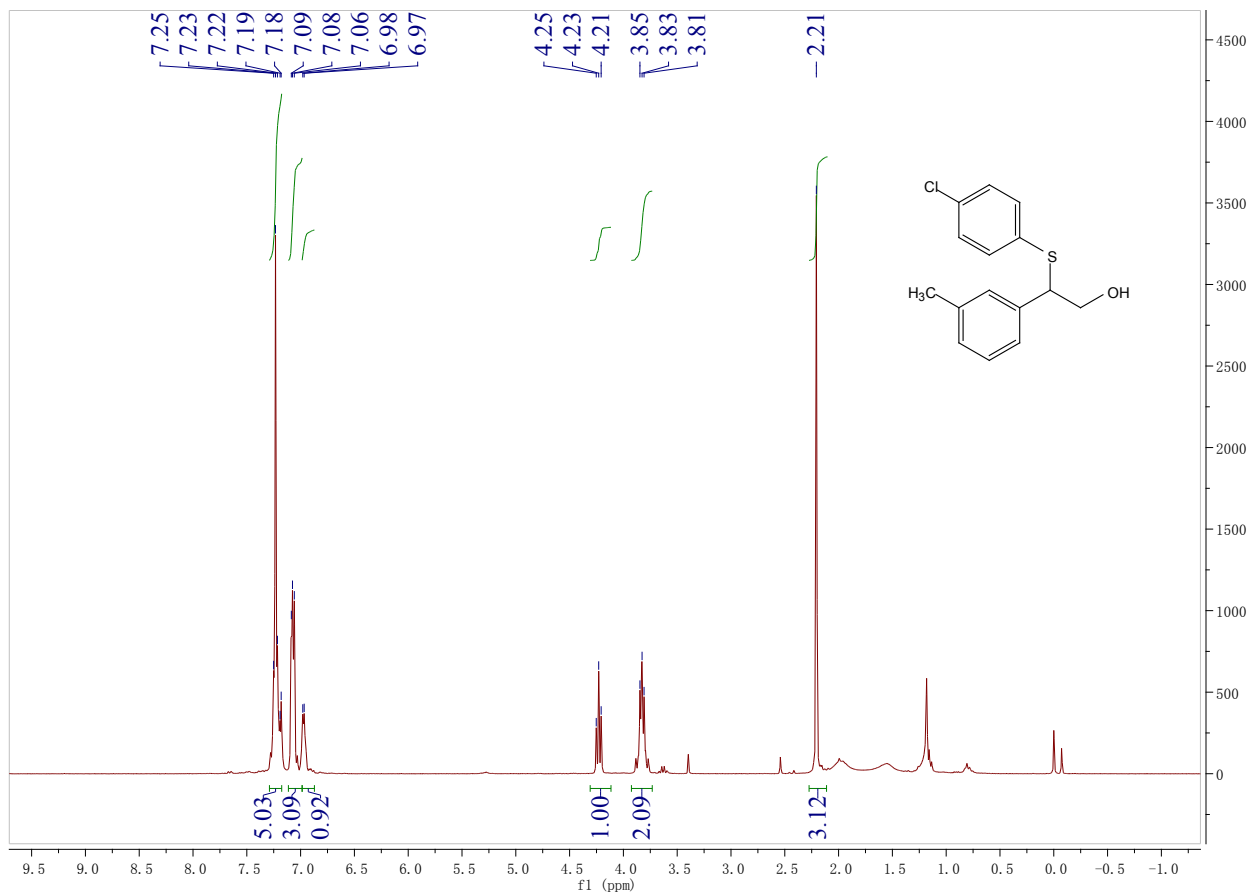
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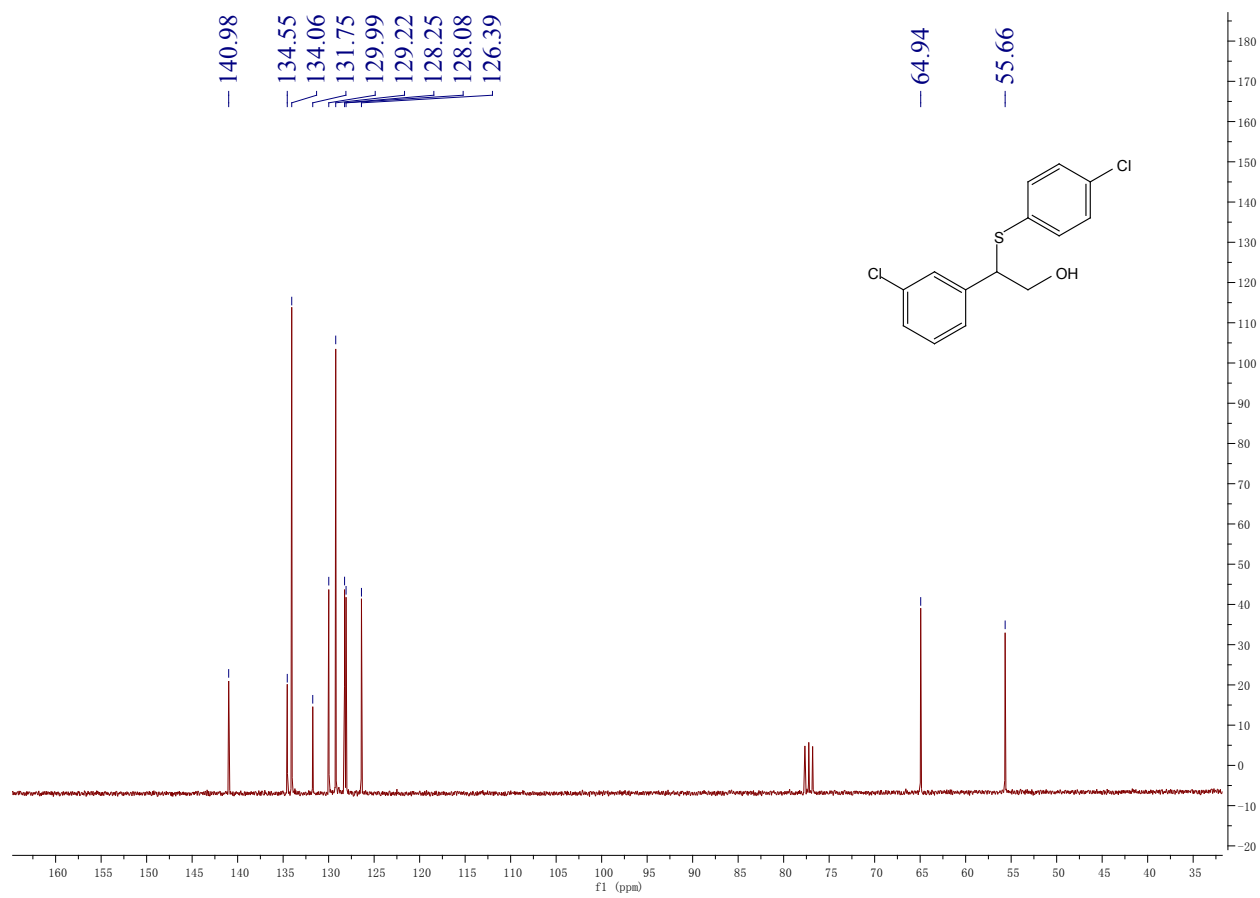
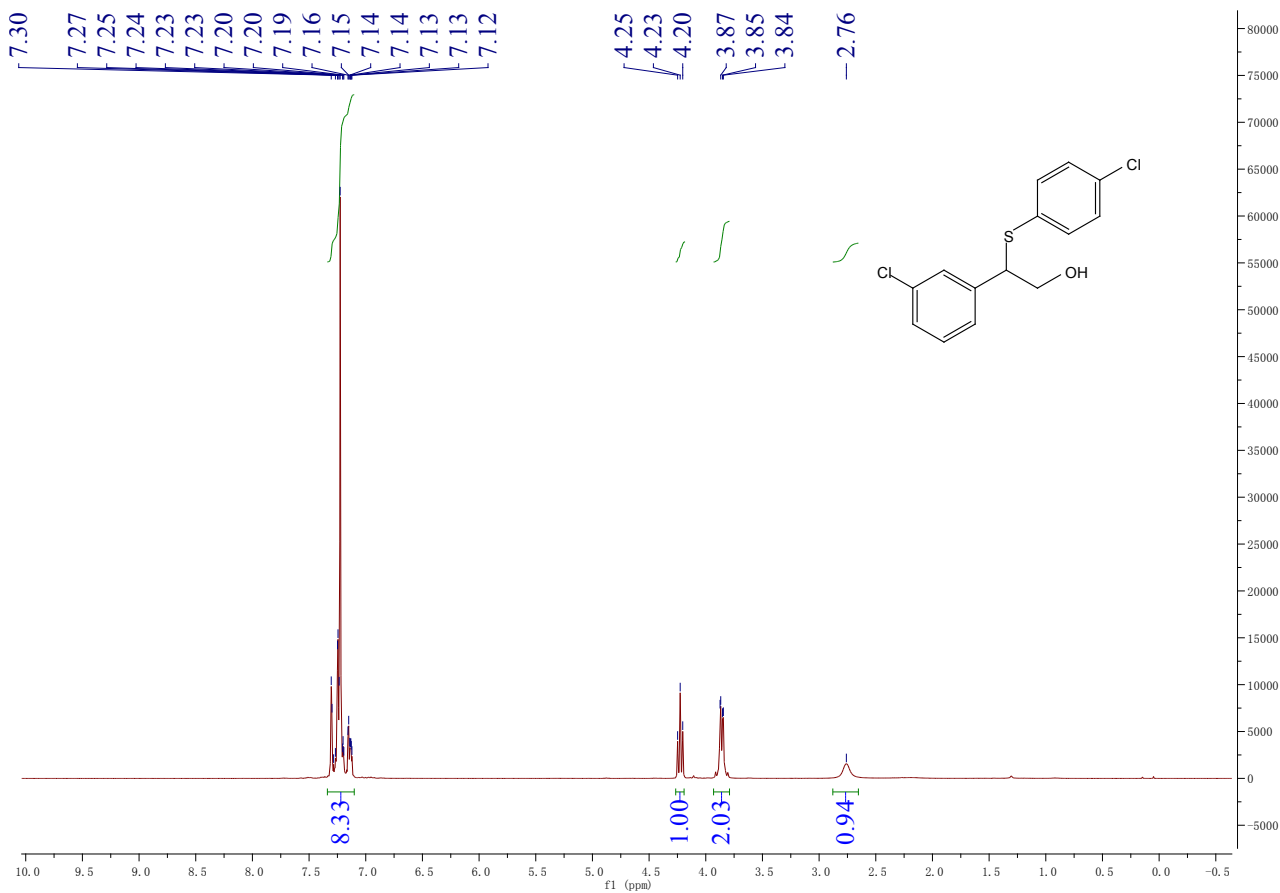
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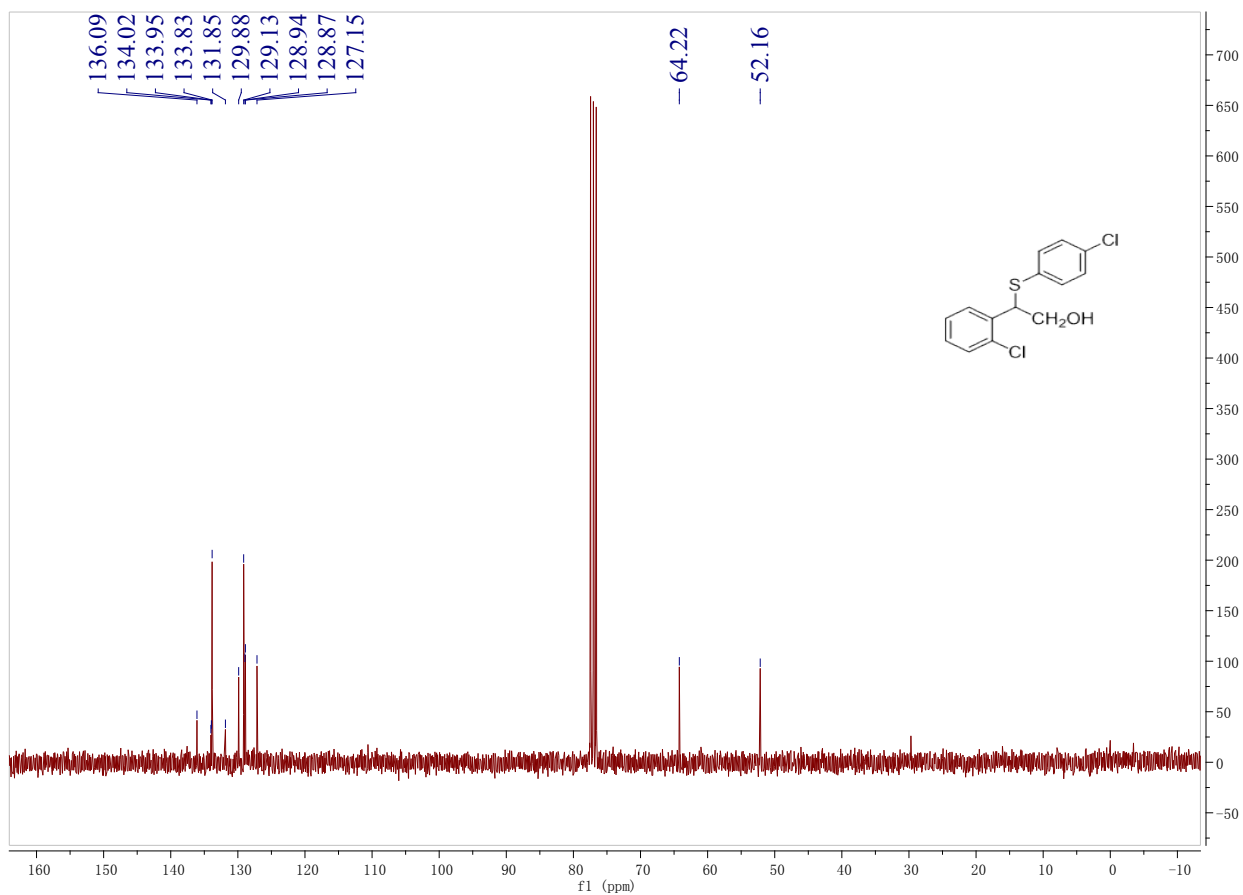
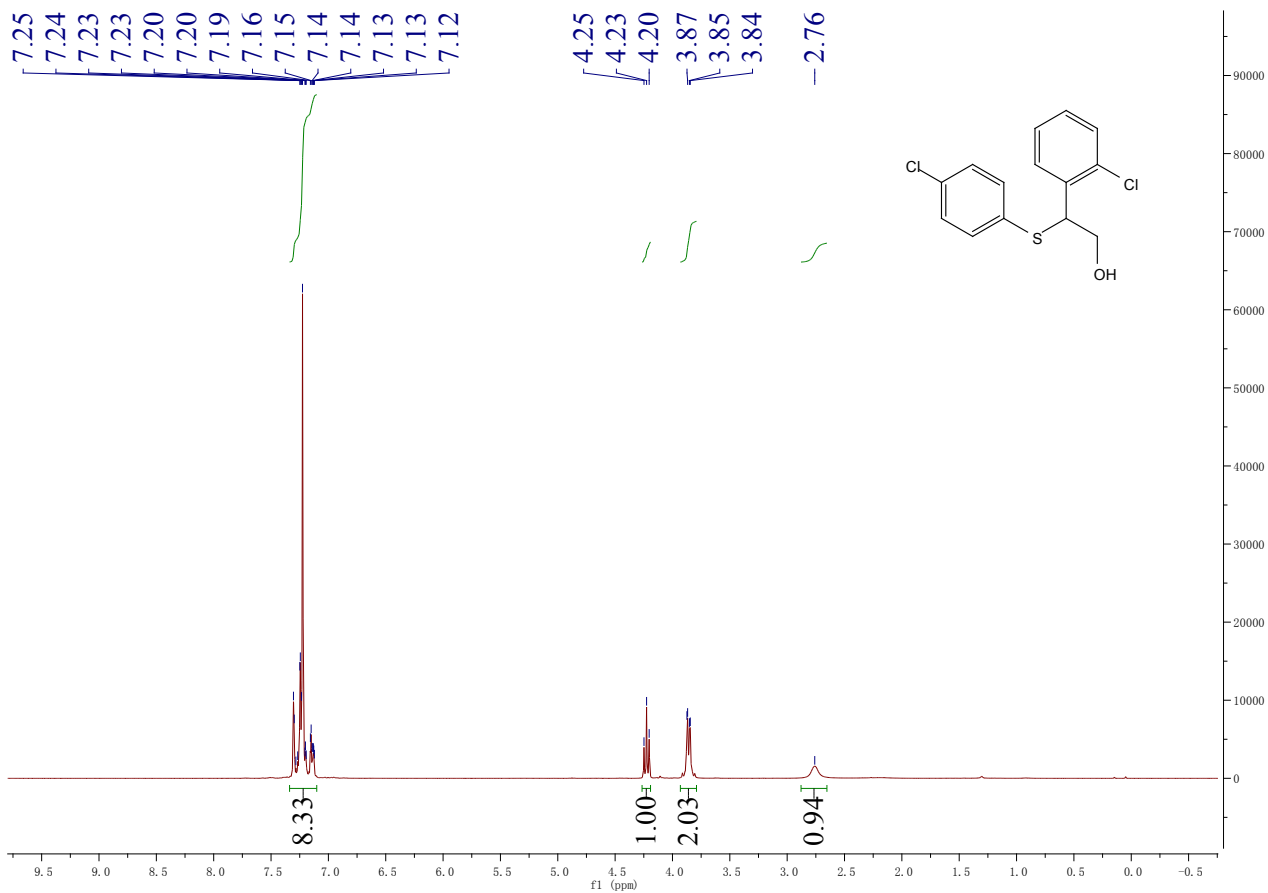
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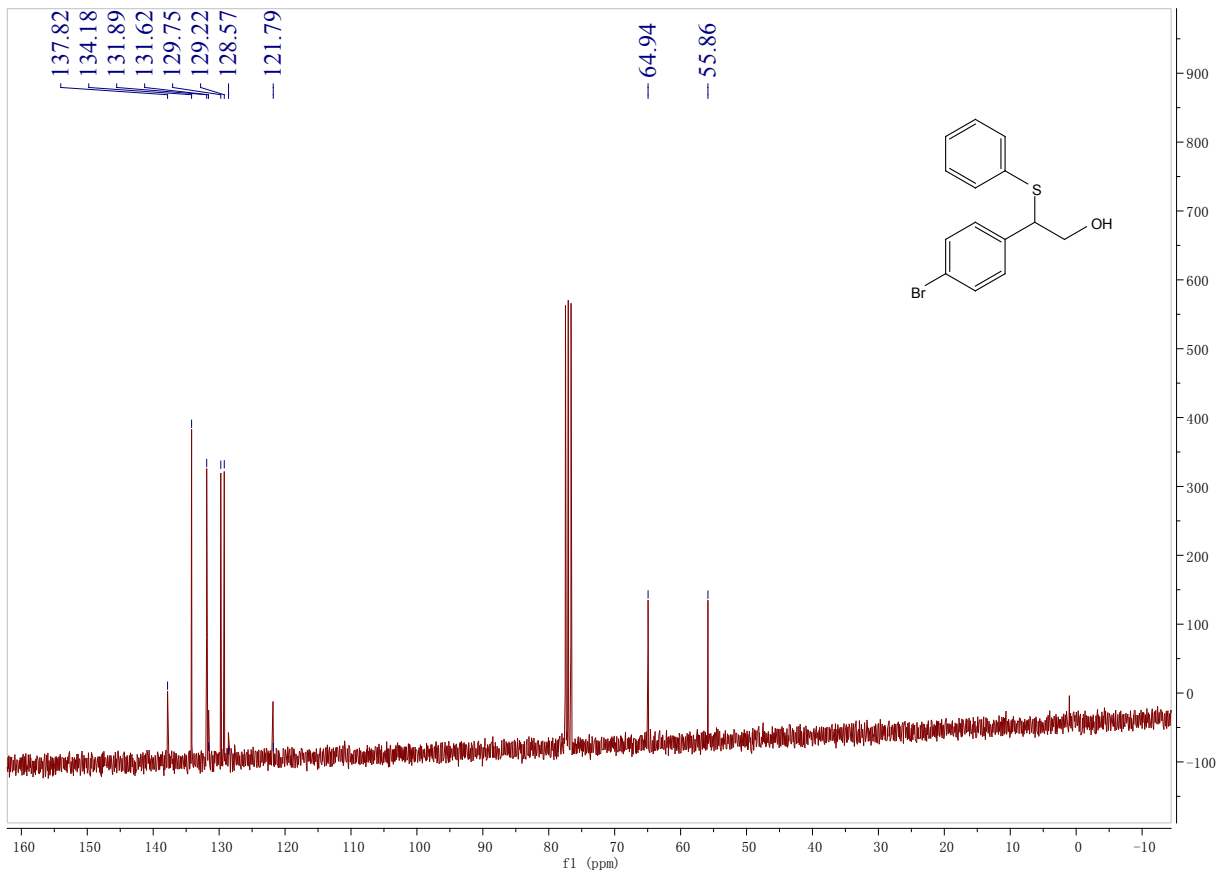
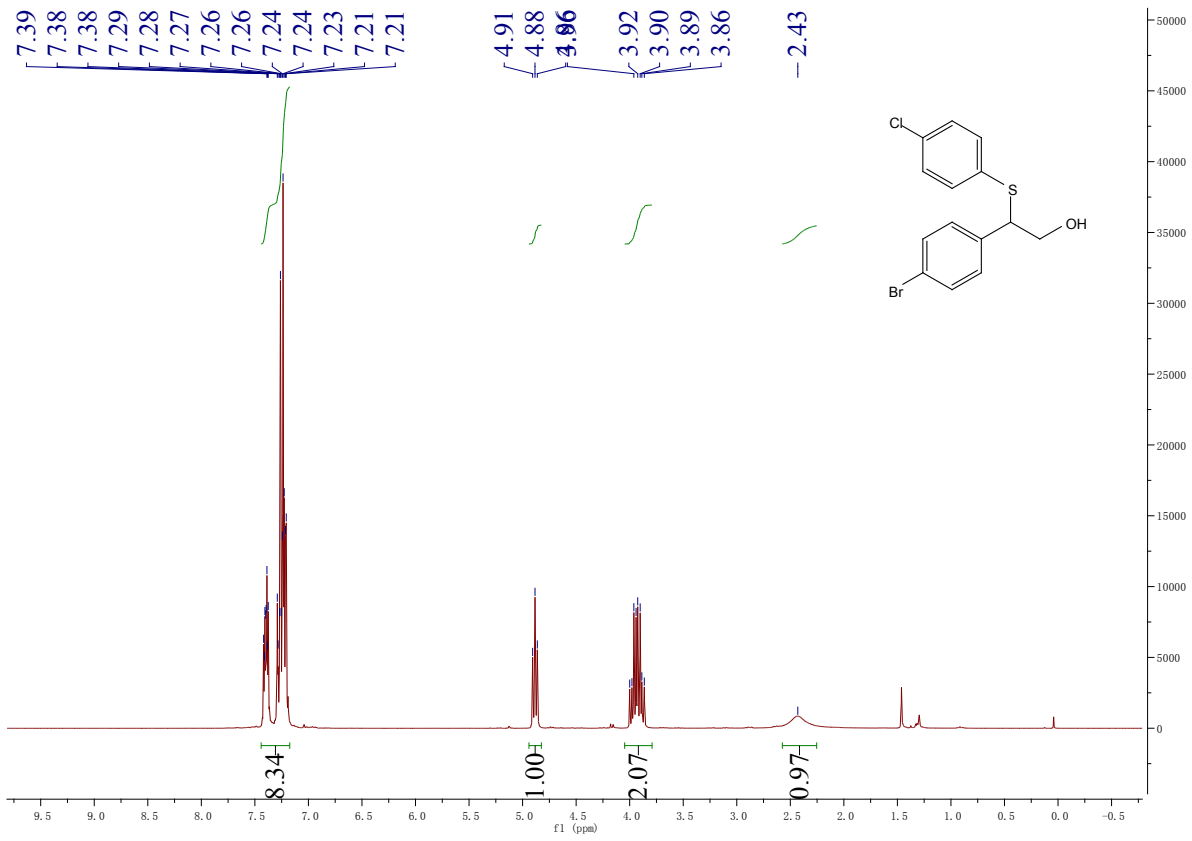
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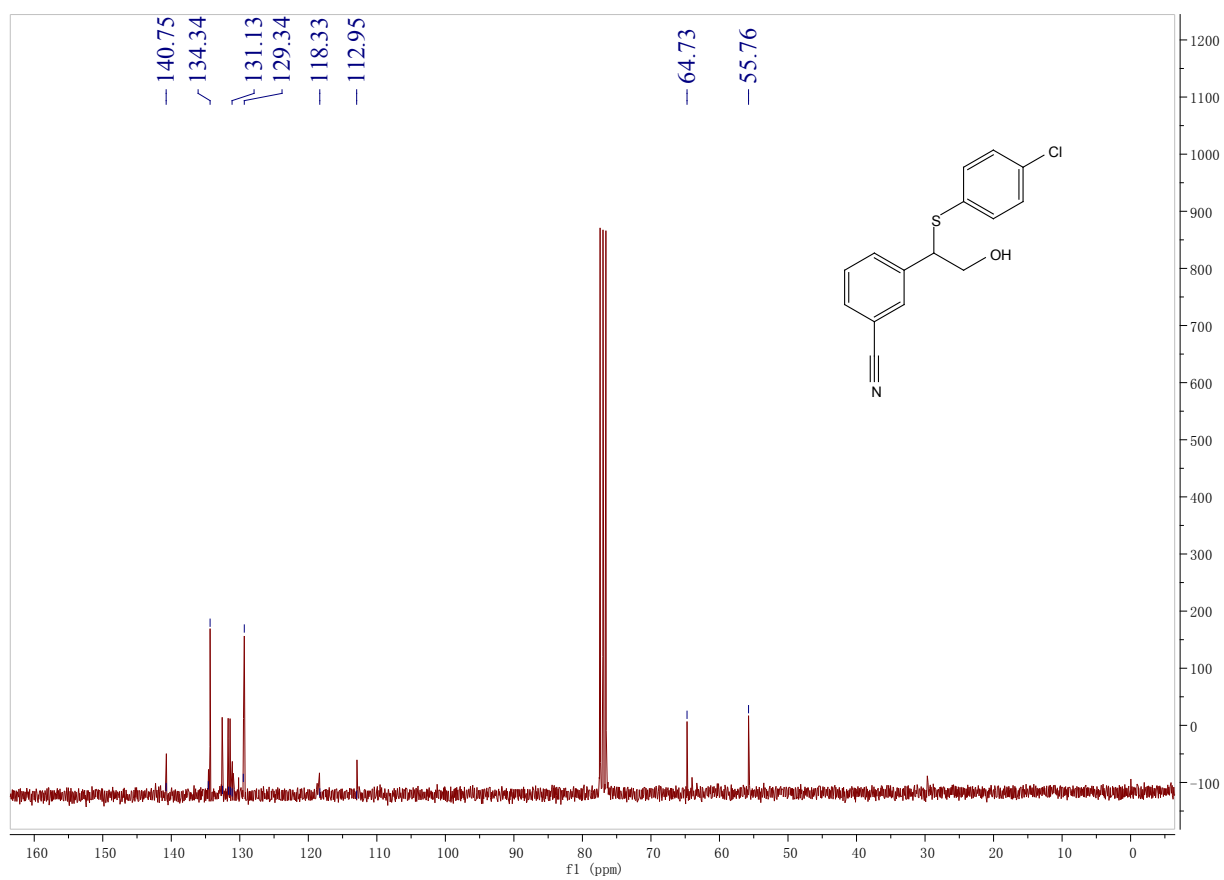
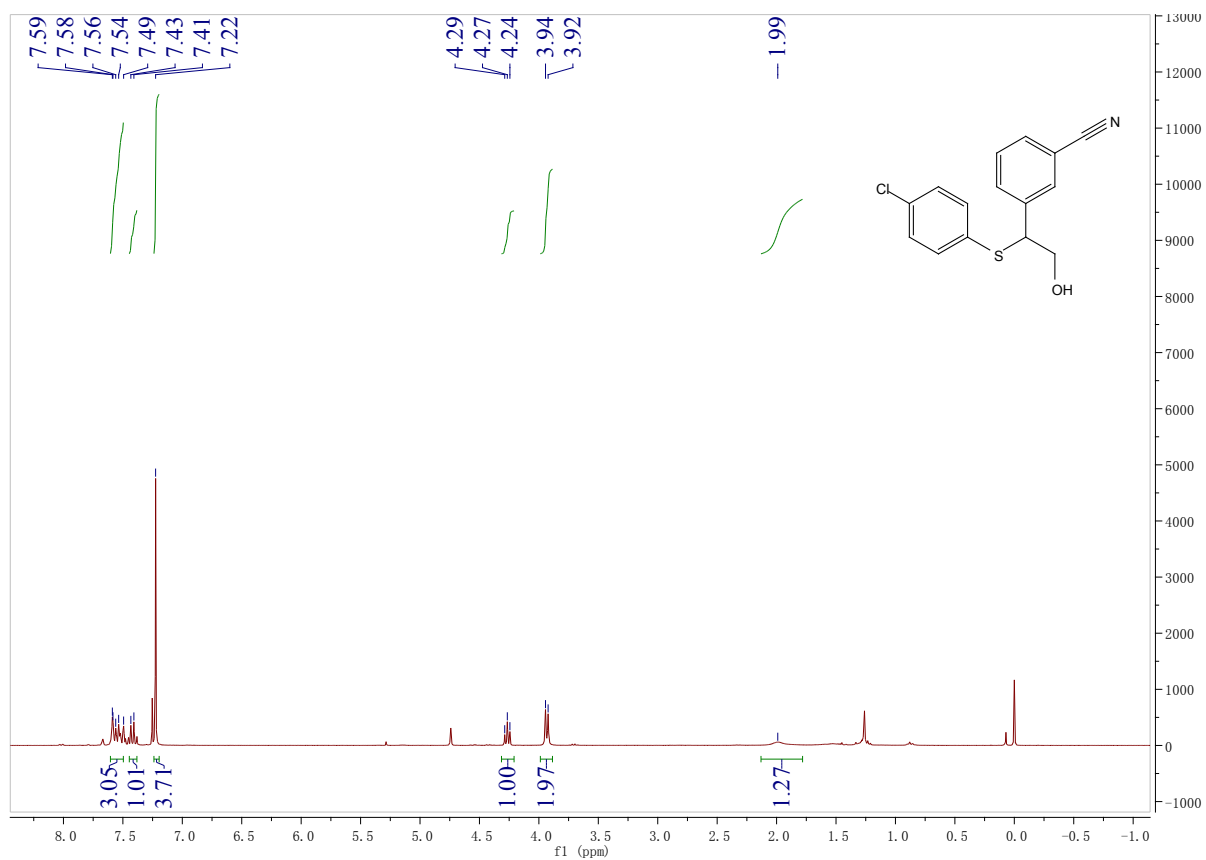
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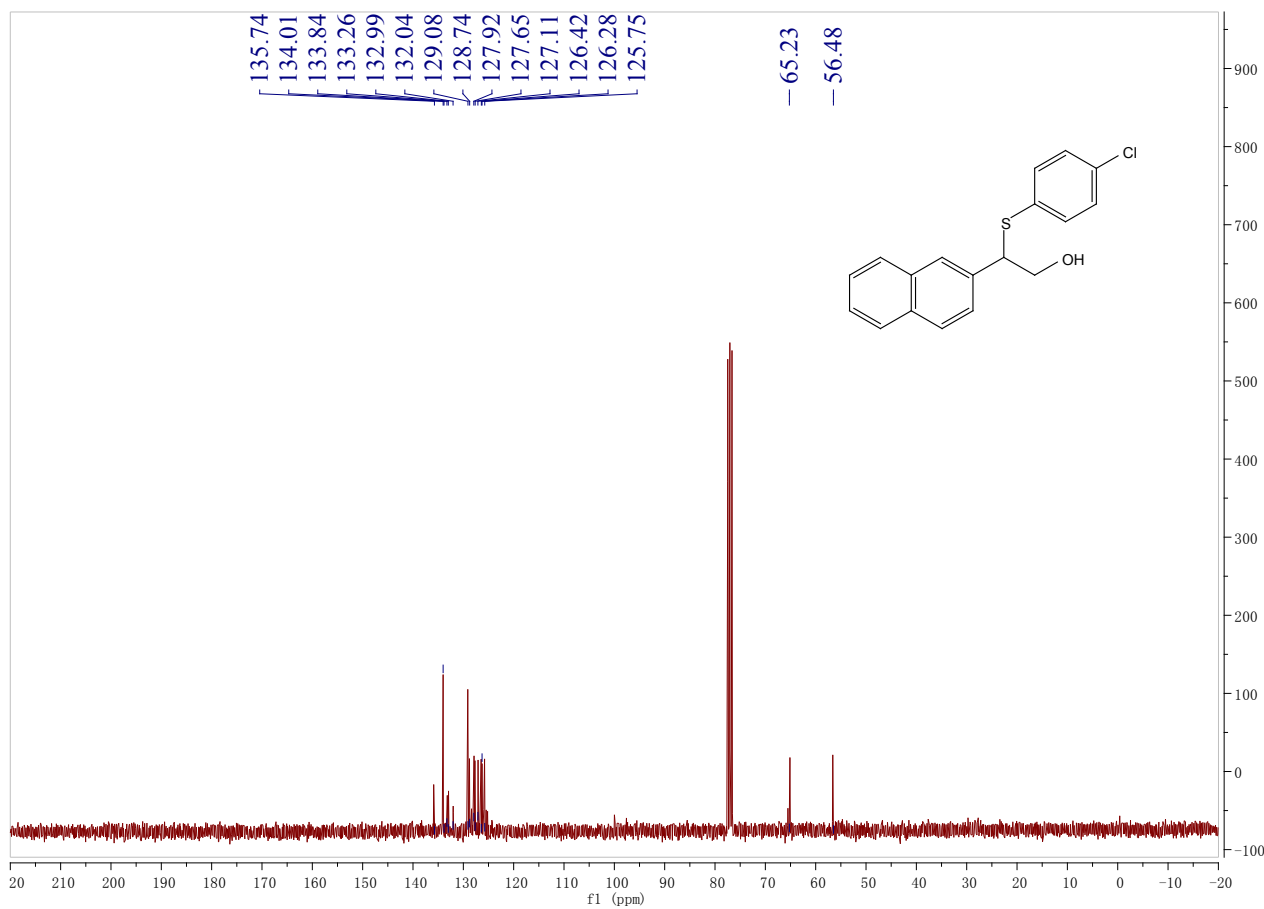
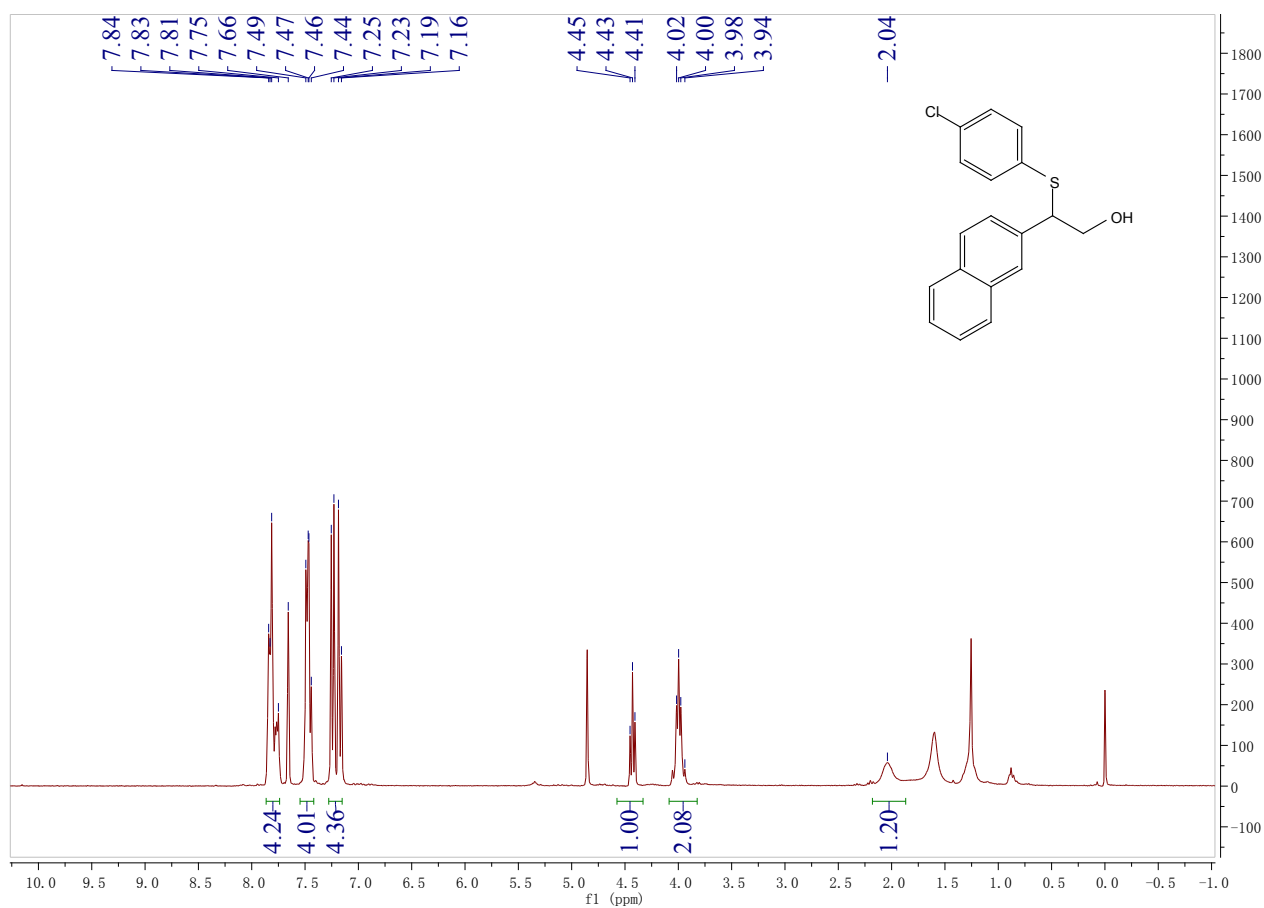
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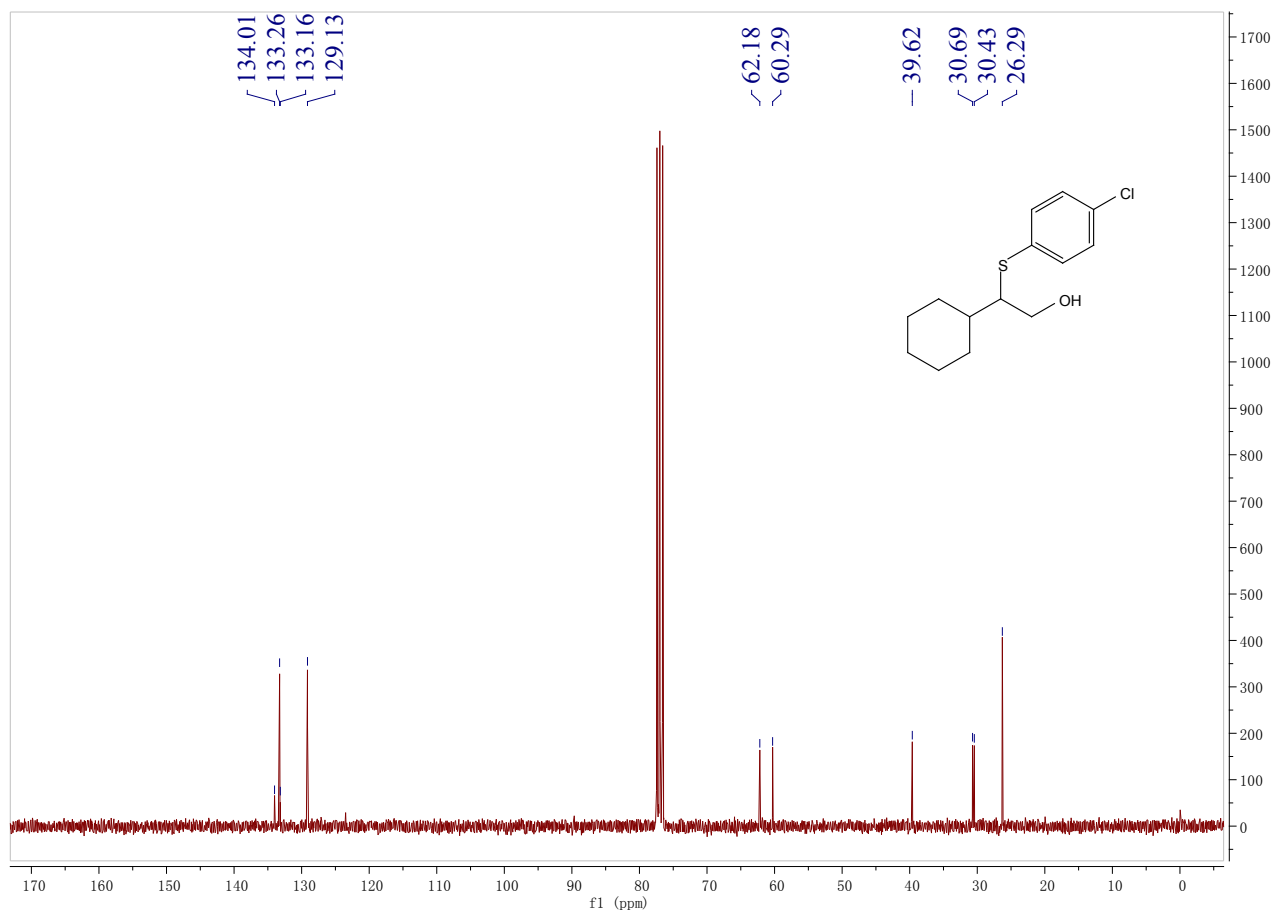
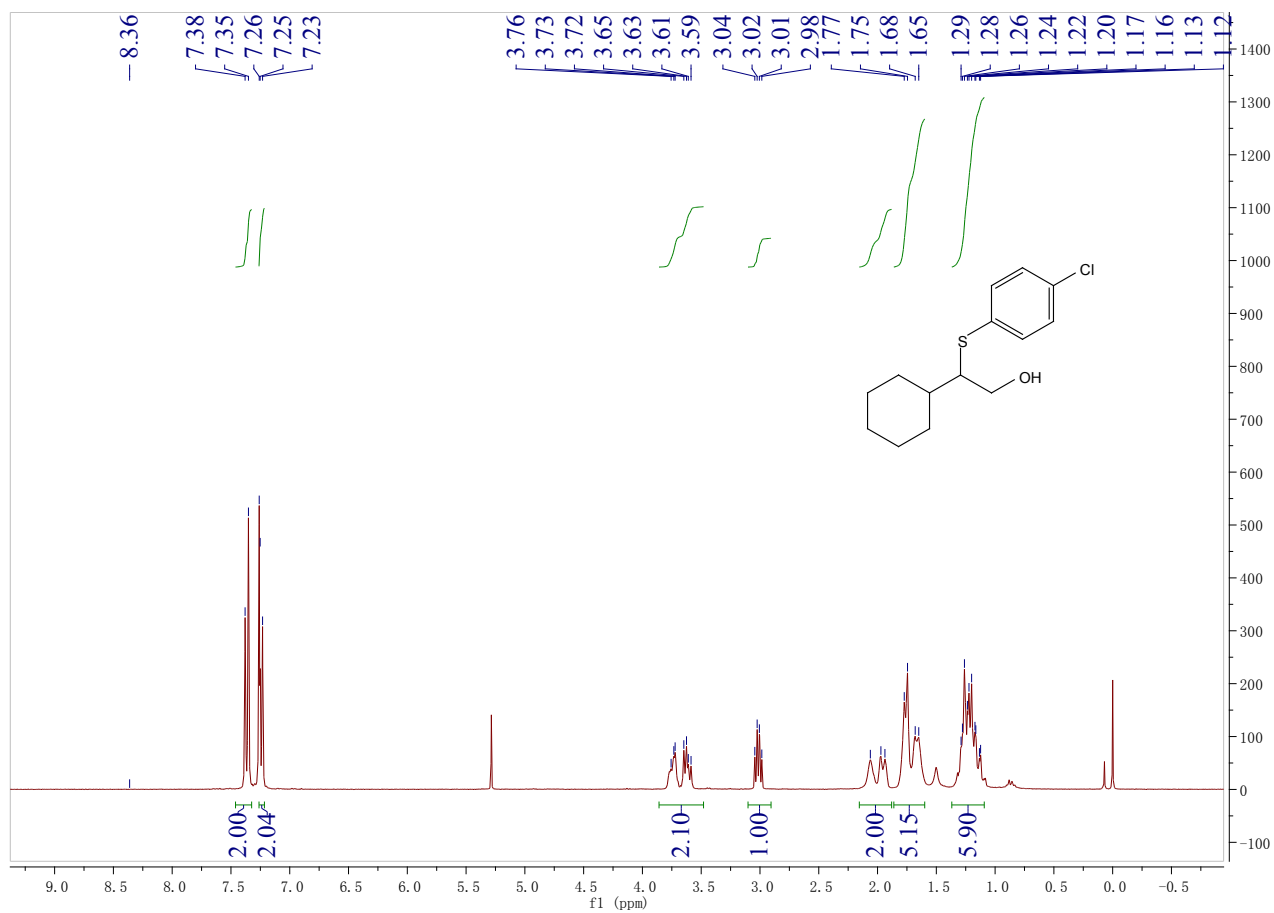


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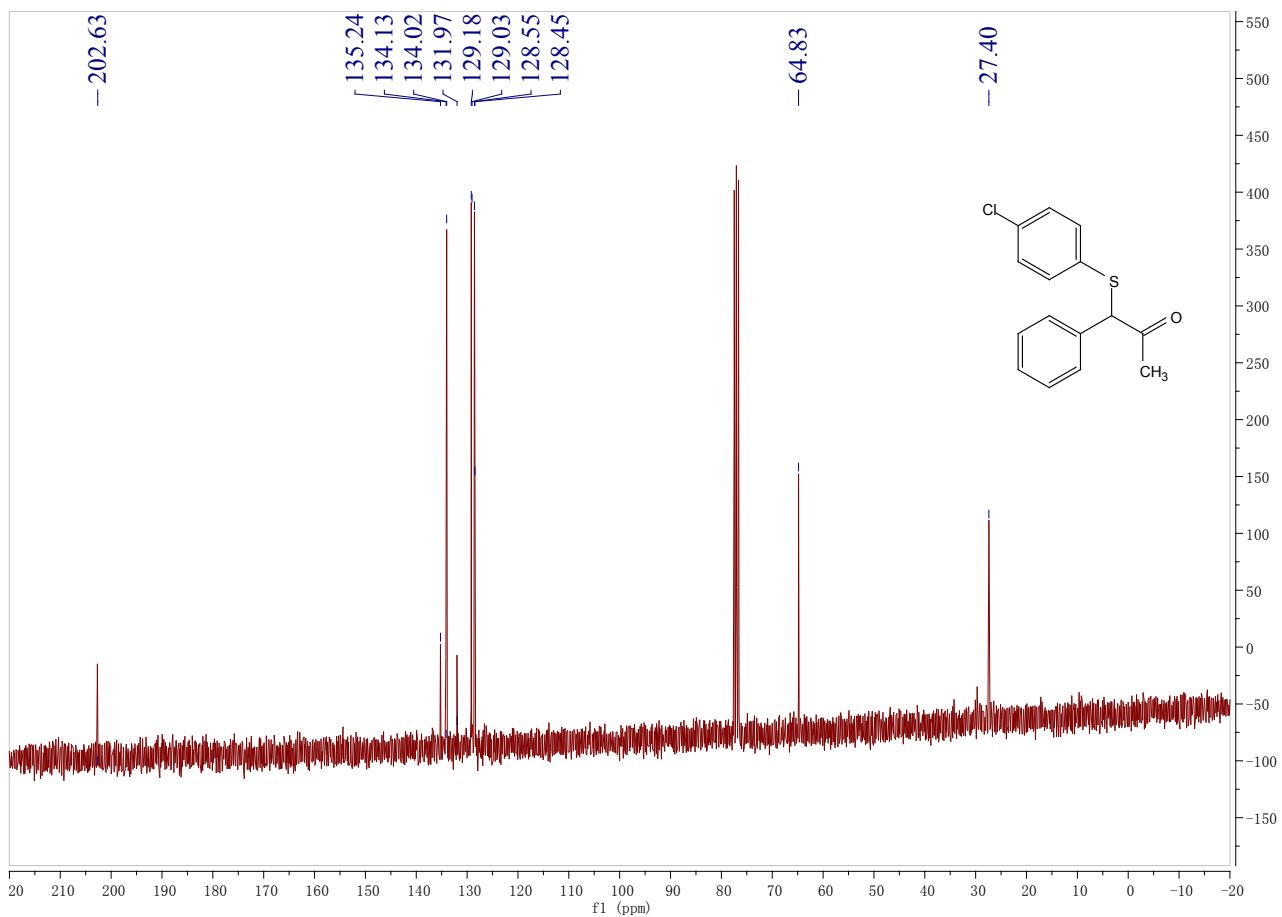
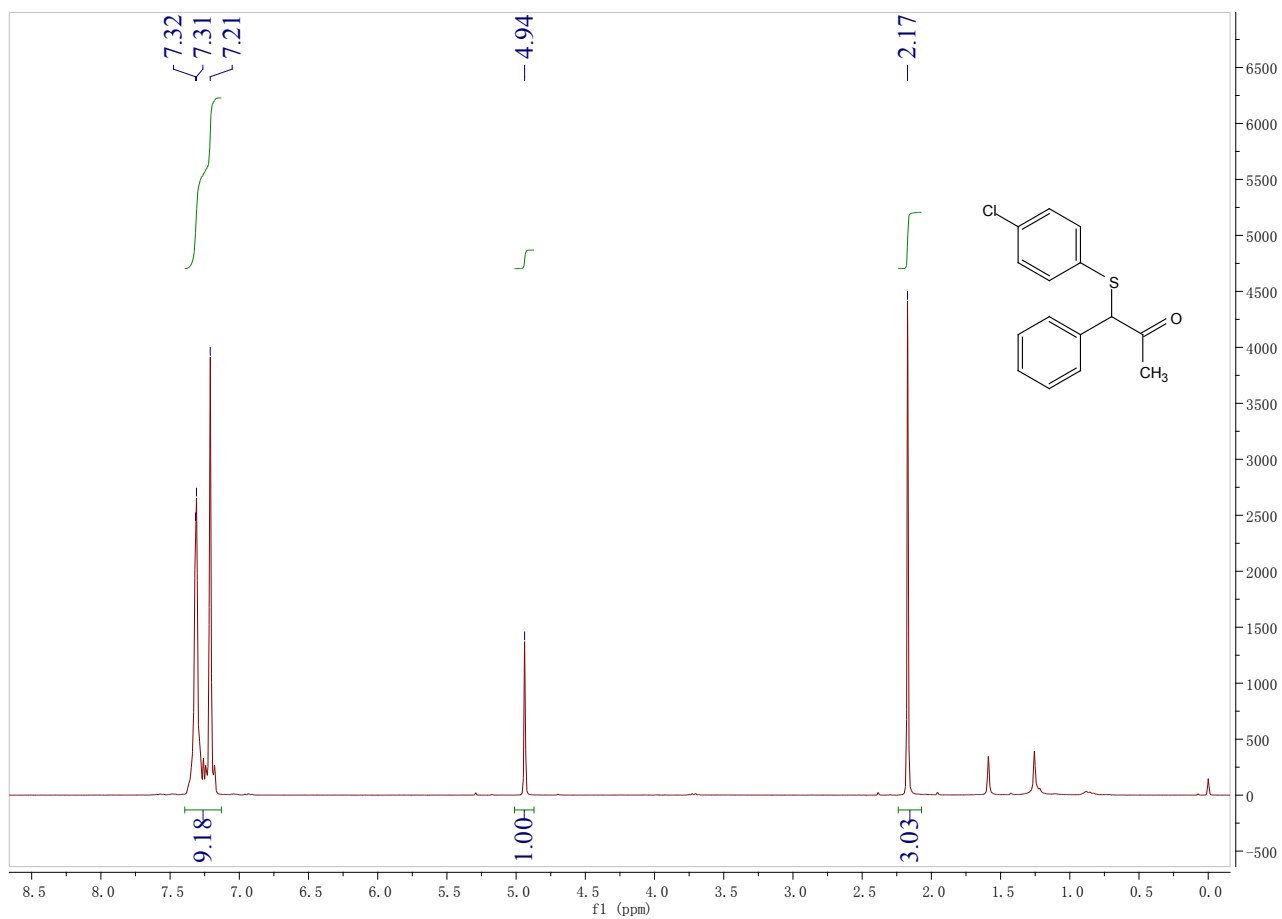


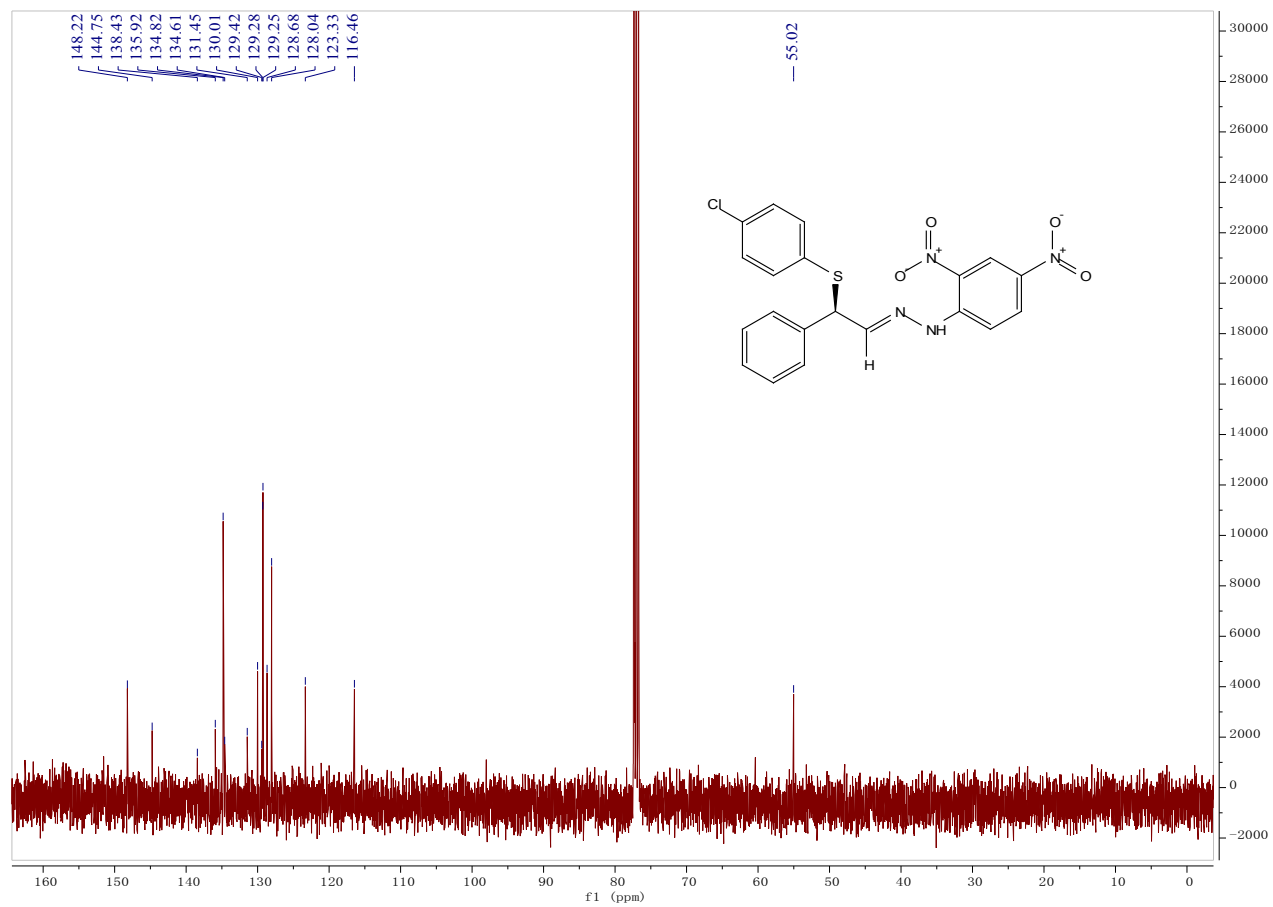
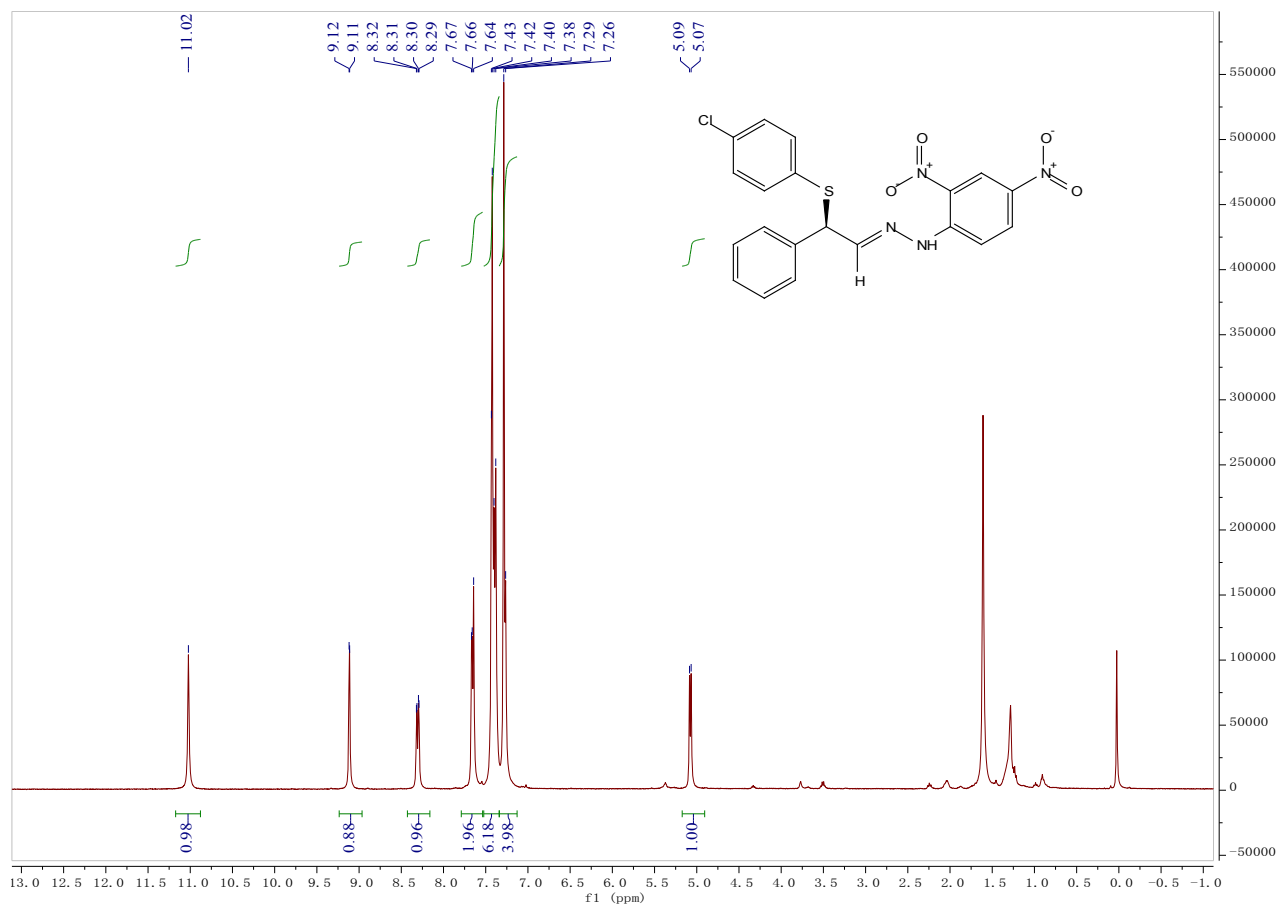


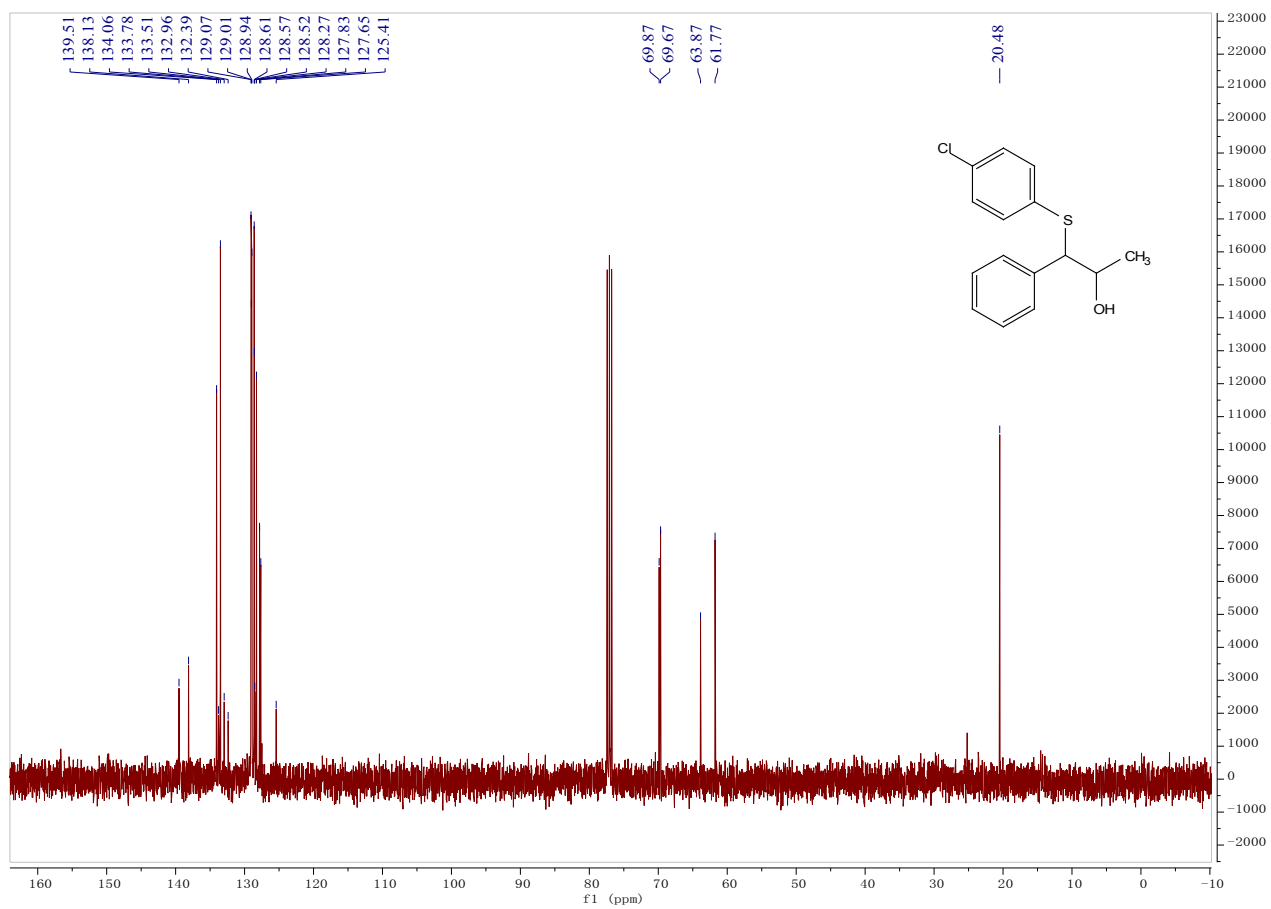
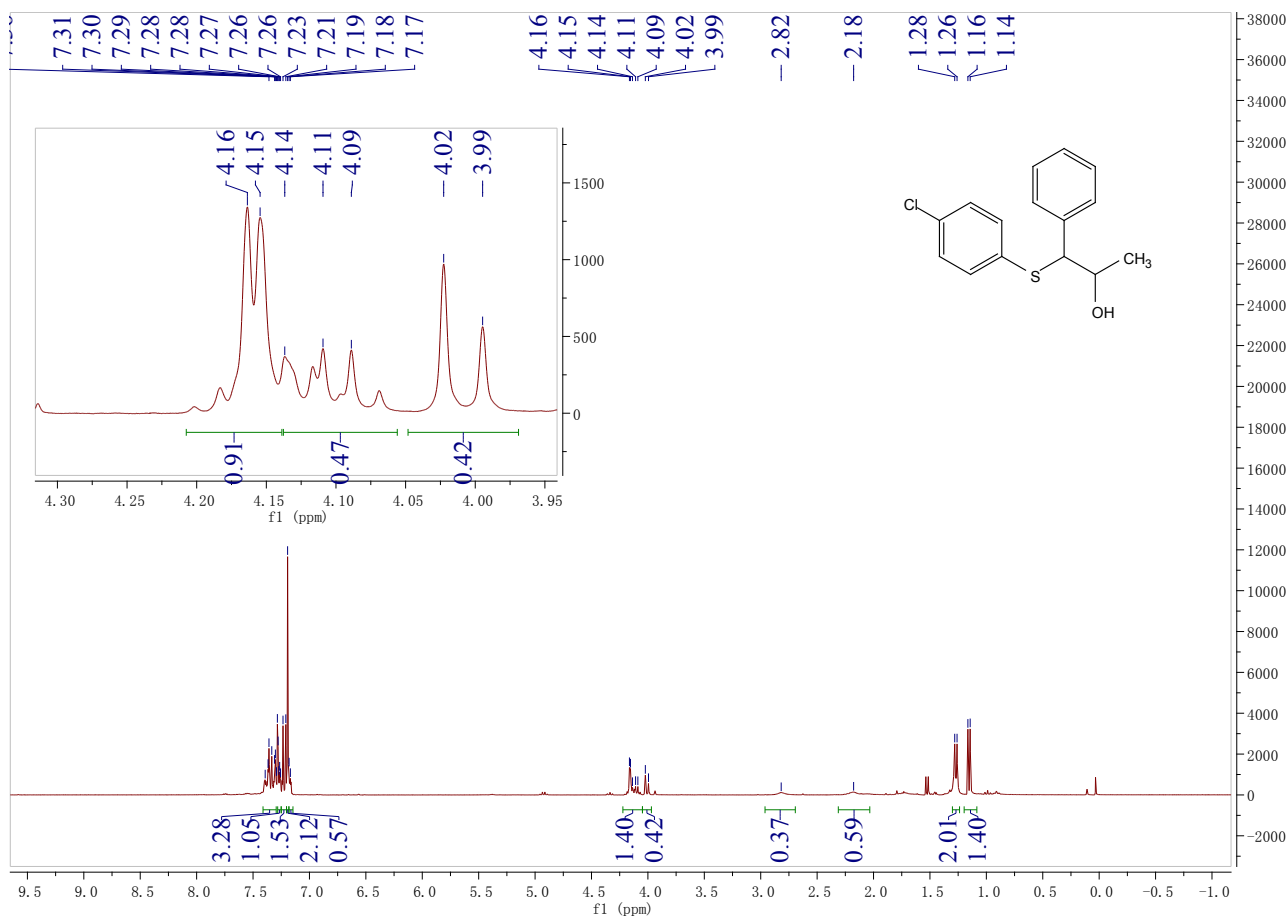
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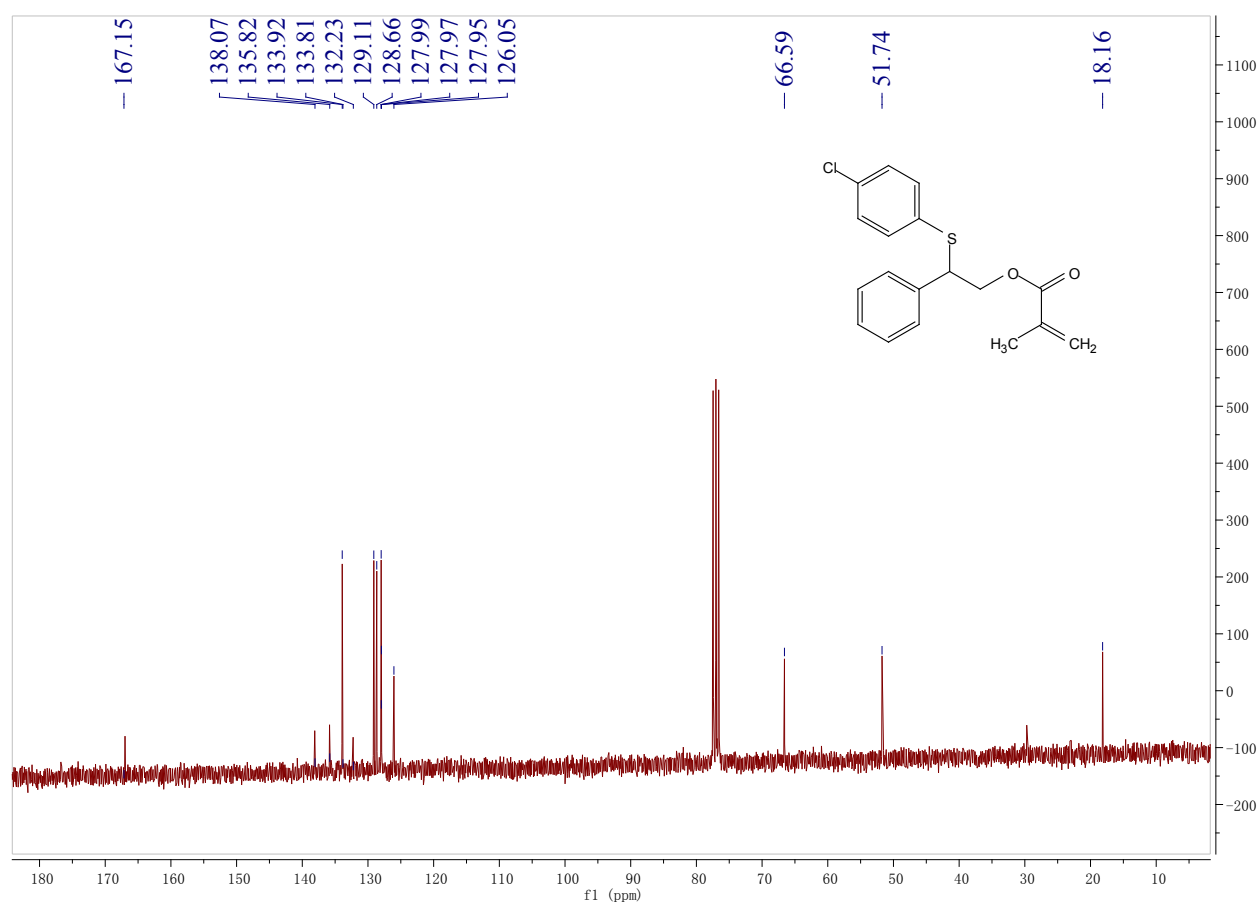
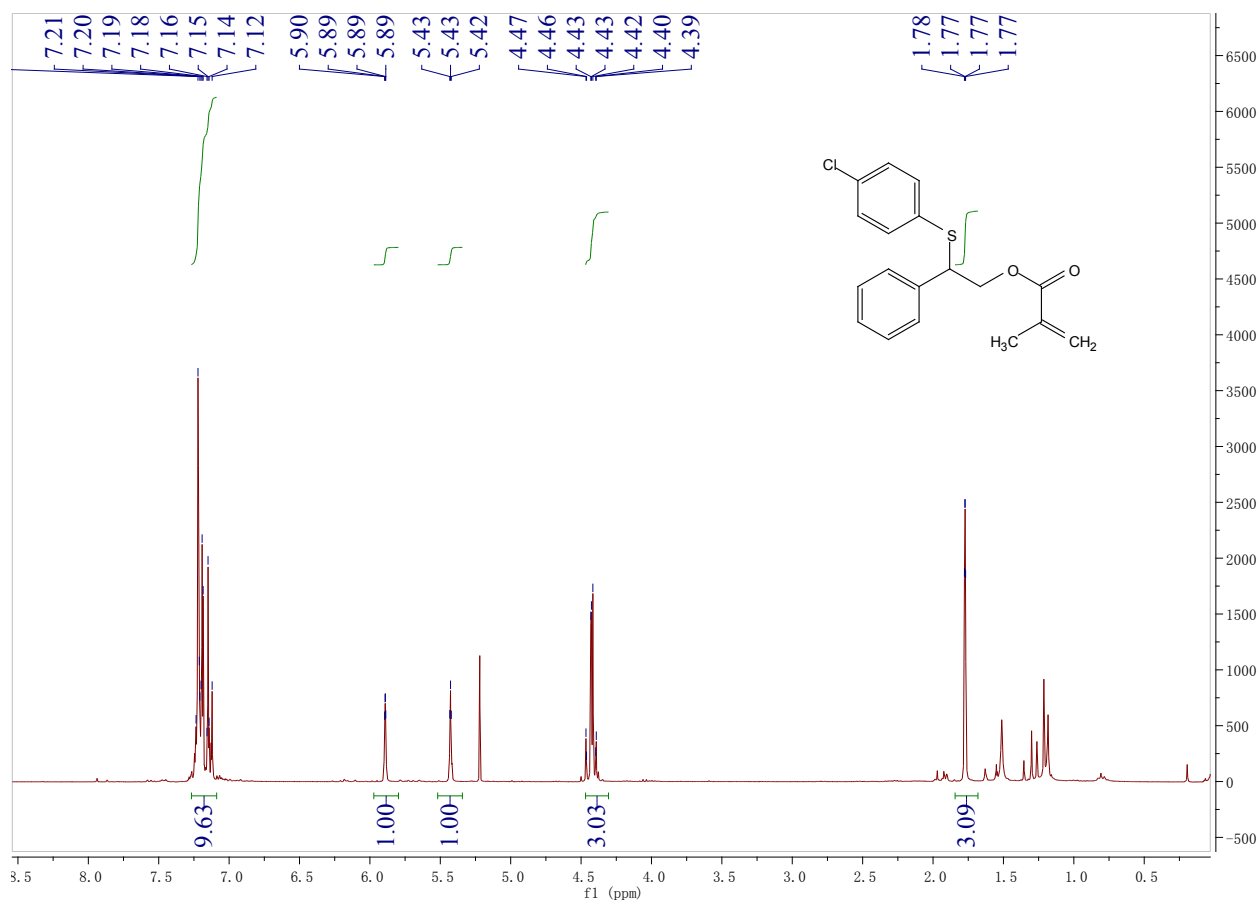


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