

# Visible – light promoted sulfonamidation of enol acetates to $\alpha$ -amino ketones based on redox – neutral photocatalysis

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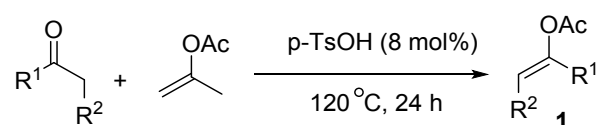
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## 1. General information:

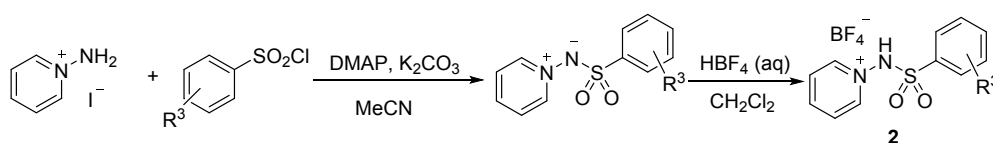
Column chromatography silica gel (200–300 mesh) and TLC plate were purchased from Qingdao Meijin Chemical Inc(Qingdao; China); HRMS data were obtained in the ESI mode on an Agilent 6530 Q-TOF/MS system.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker 400 MHz spectrometer and chemical shifts were given in  $\delta$  with TMS as an internal reference.

## 2. General procedure for synthesis of enol acetates **1** [1]:



A 100 mL flask equipped with a magnetic stir bar, a reflux condenser and a drying tube was charged with ketone (50.0 mmol, 1.00 equiv), isopropenyl acetate (250 mmol, 5.00 equiv) and  $p\text{-TsOH}\cdot\text{H}_2\text{O}$  (4.00 mmol, 0.08 equiv). The reaction mixture was heated to  $120^\circ\text{C}$ . After 24 h the reaction mixture was allowed to cool to room temperature and the remaining isopropenyl acetate was subsequently evaporated under reduced pressure. The residue was redissolved in  $\text{Et}_2\text{O}$  (100 mL) and the resulting solution was washed with  $\text{H}_2\text{O}$  (3 $\times$ 50 mL) and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated *in vacuo* to give a dark red oil. The pure product was obtained by distillation under reduced pressure or by purification on  $\text{SiO}_2$  column chromatography (DCM/hexanes, 1:1). All enol acetates **1a–1s** were synthesized and purified according to the above procedure and are in agreement with literature reference.<sup>[2–7]</sup>

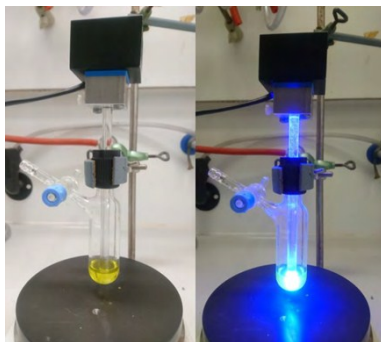
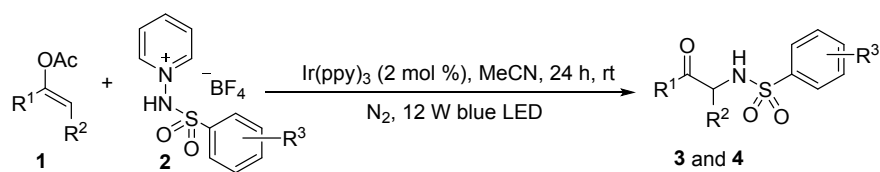
## 3. General procedure for the synthesis of *N*-arylsulfonyl-1-aminopyridine salts **2**<sup>[8]</sup>



To a mixture of 1-aminopyridinium iodide (1 equiv) and  $\text{CH}_3\text{CN}$  (0.13 M) were added  $\text{DMAP}$  (10 mol %),  $\text{K}_2\text{CO}_3$  (3.6 equiv) and sulfonyl chloride (1 equiv) at  $0^\circ\text{C}$

under N<sub>2</sub>. Then, the cooling bath was removed and the reaction mixture was stirred at R.T. for 6 h. The suspension was filtered and concentrated in vacuo. The residue was suspended in CH<sub>2</sub>Cl<sub>2</sub> and filtered to remove inorganic impurities. After the solvent was removed under reduced pressure, the crude product was purified by silica gel flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 10/1) and washed with a small amount of CH<sub>2</sub>Cl<sub>2</sub> to afford aminopyridinium ylide. The ylide product (1 equiv) was diluted with CH<sub>2</sub>Cl<sub>2</sub> (0.3 M) and tetrafluoroboric acid solution (40 wt.% in H<sub>2</sub>O) (1.3 equiv) was added to the solution at R.T.. The mixture was stirred for 30 min, then the product was precipitated. The mixture was filtered, washed with diethyl ether and pentane and dried in vacuo. The pure product was obtained as a white solid.

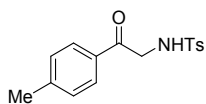
#### 4. General procedure for the synthesis of $\alpha$ -sulfonylamino ketones **3** and **4**



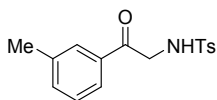
A Schlenk tube equipped with a magnetic stir bar was charged with 0.2 mmol enolacetate **1**, 2.0 equivalent of *N*-arylsulfonyl-1-aminopyridine salts **2**, 1 mol% of photocatalysis Ir(ppy)<sub>3</sub> and 2 mL DMSO under N<sub>2</sub> atmosphere. The flask was sealed by a plastic screw-cap with a Teflon sealed inlet for a glass rod. A high power LED ( $\lambda = 455$  nm) was attached to the top of the glass rod, which then could act as an optical fiber. After irradiation at room temperature for 24 h, the LED was removed, the solvent was poured to 20 mL water and extracted with 20 mL EtOAc for three times. The combined organic layer was then washed with 20 mL water for three times and

evaporated giving crude product, which was purified on silica gel chromatography and eluted with PE/EtOAc to give target compounds **3** or **4**.

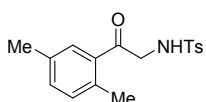
## 5. Spectra data of $\alpha$ -sulfonylamino ketones



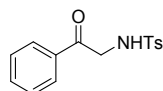
Obtained as white solid, mp: 123–125 °C;  $^1\text{H NMR}$  (400Hz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J = 8.0\text{Hz}$ , 2H), 7.66(d,  $J = 8.0\text{ Hz}$ , 4H), 7.29 (d,  $J = 8.4\text{Hz}$ , 2H), 7.26 (d,  $J = 8.4\text{Hz}$ , 2H), 5.73 (s, 1H), 4.44 (d,  $J = 4.4\text{Hz}$ , 2H), 2.42(s, 3H), 2.40 (s, 3H);  $^{13}\text{C NMR}$  (100Hz,  $\text{CDCl}_3$ ):  $\delta$  192.1, 145.5, 143.7, 136.3, 131.4, 129.8 ( $\times 2$ ), 129.6 ( $\times 2$ ), 128.0 ( $\times 2$ ), 127.2 ( $\times 2$ ), 48.5, 21.7, 21.5; HRMS (ESI $^+$ ): calcd 304.1002 for  $\text{C}_{16}\text{H}_{18}\text{NO}_3\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 304.1005.



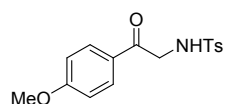
Obtained as white solid, mp: 103–106 °C;  $^1\text{H NMR}$  (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (d,  $J = 8.0\text{ Hz}$ , 2H), 7.67 – 7.34 m, 4H), 7.30 (d,  $J = 8.0\text{Hz}$ , 2H), 5.72 (s, 1H), 4.46 (d,  $J = 4.0\text{Hz}$ , 2H), 2.41 (s, 6H);  $^{13}\text{C NMR}$  (100Hz,  $\text{CDCl}_3$ ):  $\delta$  192.7, 143.7, 138.9, 136.2, 135.2, 133.8, 129.8( $\times 2$ ), 128.8, 128.4, 127.2( $\times 2$ ), 125.1, 48.7, 21.5, 21.3; HRMS (ESI $^+$ ): calcd 304.1002 for  $\text{C}_{16}\text{H}_{18}\text{NO}_3\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 304.1002.



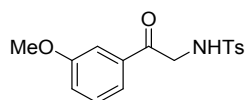
Obtained as white solid, mp: 118–121 °C;  $^1\text{H NMR}$  (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (d,  $J = 8.4\text{Hz}$ , 2H), 7.36 (s, 1H), 7.30 (d,  $J = 8.0\text{Hz}$ , 2H), 7.24 (d,  $J = 7.8\text{ Hz}$ , 1H), 7.14 (d,  $J = 8.0\text{ Hz}$ ), 5.71 (t,  $J = 4.4\text{Hz}$ , 1H), 4.38 (d,  $J = 4.0\text{ Hz}$ , 2H), 2.41 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H);  $^{13}\text{C NMR}$  (100Hz,  $\text{CDCl}_3$ ):  $\delta$  195.2, 143.7, 136.6, 136.3, 135.7, 133.7, 133.4, 132.4, 129.8 ( $\times 2$ ), 129.1, 127.2 ( $\times 2$ ), 50.1, 21.5, 21.1, 20.8; HRMS (ESI $^+$ ): calcd 318.1164 for  $\text{C}_{17}\text{H}_{20}\text{NO}_3\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 318.1155.



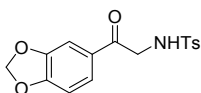
Obtained as white solid, mp: 115–117 °C;  $^1\text{H NMR}$  (400Hz,  $\text{CDCl}_3$ ):  $\delta$  7.88–7.84 (m, 2H), 7.80 (d,  $J = 8.4\text{Hz}$ , 2H), 7.61–7.59 (m, 1H), 7.49–7.45 (m, 2H), 7.29 (d,  $J = 8.0\text{ Hz}$ , 2H), 5.75 (t,  $J = 4.4\text{Hz}$ , 1H), 4.48 (d,  $J = 4.4\text{ Hz}$ , 2H), 2.40 (s, 3H);  $^{13}\text{C NMR}$  (100Hz,  $\text{CDCl}_3$ ):  $\delta$  192.6, 143.7, 136.3, 134.4, 133.9, 129.8 ( $\times 2$ ), 129.0 ( $\times 2$ ), 127.9 ( $\times 2$ ), 127.2 ( $\times 2$ ), 48.7, 21.5; HRMS (ESI $^+$ ): calcd 290.0851 for  $\text{C}_{15}\text{H}_{16}\text{NO}_3\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 290.0852.



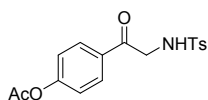
Obtained as white solid, mp: 98–100 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.84 (d,  $J = 9.2$  Hz, 2H), 7.79 (d,  $J = 8.0$  Hz, 2H), 7.30 (d,  $J = 8.4$ Hz, 2H), 6.94 (d,  $J = 9.2$  Hz, 2H), 5.72 (t,  $J = 4.4$  Hz, 1H), 4.41 (d,  $J = 4.4$ Hz, 2H), 3.88 (s, 3H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  190.8, 164.5, 143.7, 136.1, 130.2 ( $\times 2$ ), 129.8 ( $\times 2$ ), 127.2 ( $\times 2$ ), 126.8, 114.2 ( $\times 2$ ), 55.6, 48.2, 21.5; HRMS (ESI $^+$ ): calcd 320.0957 for  $\text{C}_{16}\text{H}_{18}\text{NO}_4\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 320.0959.



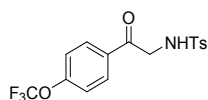
Obtained as white solid, mp: 79–81 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (d,  $J = 8.0$  Hz, 2H), 7.44–7.36 (m, 3H), 7.30 (d,  $J = 8.0$  Hz, 2H), 7.17–7.14 (m, 1H), 5.70 (t,  $J = 4.4$ Hz, 1H), 4.46 (d,  $J = 4.4$ Hz, 2H), 3.85 (s, 3H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  192.5, 160.0, 143.8, 136.1, 135.1, 130.0, 129.8 ( $\times 2$ ), 127.2 ( $\times 2$ ), 120.8, 120.3, 112.2, 55.5, 48.8, 21.5; HRMS (ESI $^+$ ): calcd 320.0957 for  $\text{C}_{16}\text{H}_{18}\text{NO}_4\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 320.0974.



Obtained as the white solid, mp: 148–150 °C;  $^1\text{H}$  NMR (400Hz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J = 6.8$ Hz, 2H), 7.45 (dd,  $J = 2.0, 8.0$  Hz), 7.33 (d,  $J = 2.0$  Hz, 1H), 7.31 (d,  $J = 8.0$  Hz, 2H), 6.86 (d,  $J = 8.0$  Hz, 1H), 6.08 (s, 2H), 5.67 (t,  $J = 4.0$  Hz, 1H), 4.39 (d,  $J = 4.4$  Hz, 2H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  190.5, 152.9, 148.5, 143.7, 136.3, 129.8 ( $\times 2$ ), 128.6, 27.2 ( $\times 2$ ), 124.3, 108.2, 107.6, 102.1, 48.3, 21.5; HRMS (ESI $^+$ ): calcd 334.0749 for  $\text{C}_{16}\text{H}_{16}\text{NO}_5\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 334.0780.

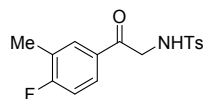


Obtained as white solid, mp: 123–125 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90 (d,  $J = 8.8$ Hz, 2H), 7.79 (d,  $J = 8.4$ Hz, 2H), 7.30 (d,  $J = 8.0$ Hz, 2H), 7.22 (d,  $J = 8.8$  Hz, 2H), 5.68 (t,  $J = 4.4$  Hz, 1H), 4.45 (d,  $J = 4.4$  Hz, 2H), 2.41 (s, 3H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  191.4, 168.7, 155.3, 143.9, 136.0, 131.3, 129.9 ( $\times 2$ ), 129.6 ( $\times 2$ ), 127.2 ( $\times 2$ ), 122.3 ( $\times 2$ ), 48.6, 21.5, 21.1; HRMS (ESI $^+$ ): calcd 348.0900 for  $\text{C}_{17}\text{H}_{18}\text{NO}_5\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 348.0909.

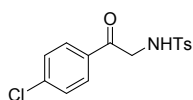


Obtained as white solid, mp: 160–163 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93 (d,  $J = 8.8$ Hz, 2H), 7.80, (d,  $J = 8.4$ Hz, 2H), 7.31 (d,  $J = 8.4$  Hz, 4H), 5.64 (t,  $J = 4.4$  Hz, 1H), 7.47 (d,  $J = 4.8$ Hz, 2H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  191.2, 153.5,

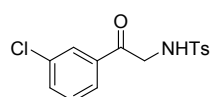
143.9, 136.1, 132.0, 130.0 (×2), 129.9 (×2), 127.2 (×4), 120.6, 48.7, 21.5; HRMS (ESI<sup>+</sup>): calcd for 374.0674 for C<sub>16</sub>H<sub>15</sub>F<sub>3</sub>NO<sub>4</sub>S<sup>+</sup>[M+H]<sup>+</sup>; Found, 374.0667.



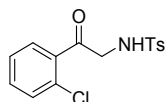
Obtained as white solid, mp: 112–114 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.76 – 7.69 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 8.8 Hz, 1H), 5.72 (t, *J* = 4.4 Hz, 1H), 4.44 (d, *J* = 4.6 Hz, 2H), 2.41 (s, 3H), 2.32 (d, *J* = 1.6 Hz, 3H); <sup>13</sup>C NMR (100Hz, CDCl<sub>3</sub>): 191.3, 165.0 (d, <sup>1</sup>*J*<sub>F-C</sub> = 254 Hz), 143.8, 136.1, 131.8 (d, <sup>3</sup>*J*<sub>F-C</sub> = 6.8 Hz), 129.8 (d, <sup>4</sup>*J*<sub>F-C</sub> = 3.4 Hz), 129.8(×2), 127.9 (<sup>3</sup>*J*<sub>F-C</sub> = 9.5 Hz), 127.2 (×2), 126.1 (d, <sup>2</sup>*J*<sub>F-C</sub> = 17.6Hz), 115.7 (d, <sup>2</sup>*J*<sub>F-C</sub> = 23.2 Hz), 48.5, 21.5, 14.5 (d, <sup>3</sup>*J*<sub>F-C</sub> = 3.5 Hz); HRMS (ESI<sup>+</sup>): calcd 322.0913 for C<sub>16</sub>H<sub>17</sub>FNO<sub>3</sub>S<sup>+</sup>[M+H]<sup>+</sup>; Found, 322.0913.



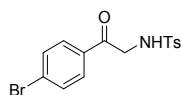
Obtained as white solid, mp: 164–166 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 7.83–7.79 (m, 4H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.63 (s, 1H), 4.45 (d, *J* = 4.4Hz, 2H), 2.42 (s, 3H); <sup>13</sup>C NMR (100Hz, CDCl<sub>3</sub>): δ 191.5, 143.9, 141.1, 136.1, 132.1, 129.9 (×2), 129.4 (×2), 129.2 (×2), 127.2 (×2), 48.6, 21.5; HRMS (ESI<sup>+</sup>): calcd 324.0416 for C<sub>15</sub>H<sub>15</sub>ClNO<sub>3</sub>S<sup>+</sup>[M+H]<sup>+</sup>; Found, 324.0454.



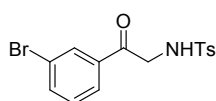
Obtained as white solid, mp: 140–142 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 7.83 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.70 (s, 1H), 4.46 (d, *J* = 4.4 Hz, 2H), 2.41 (s, 3H); <sup>13</sup>C NMR (100Hz, CDCl<sub>3</sub>): δ 191.7, 143.9, 136.0, 135.4, 135.3, 134.3, 130.3, 129.9 (×2), 128.0, 127.2 (×2), 125.9, 48.8, 21.5; HRMS (ESI<sup>+</sup>): calcd 324.0416 for C<sub>15</sub>H<sub>15</sub>ClNO<sub>3</sub>S<sup>+</sup>[M+H]<sup>+</sup>; Found, 324.0443.



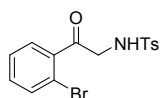
Obtained as white solid, mp: 72–74 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 7.78 (d, *J* = 8.4Hz, 2H), 7.50–7.43 (m, 3H), 7.36–7.30 (m, 3H), 5.64 (t, *J* = 4.8Hz, 1H), 4.45 (d, *J* = 4.8Hz, 2H), 2.42 (s, 3H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ 195.2, 143.8, 136.3, 135.2, 133.2, 131.9, 131.0, 129.9, 129.8 (×2), 127.3 (×2), 127.1, 51.9, 21.5; HRMS (ESI<sup>+</sup>): calcd 324.0456 for C<sub>15</sub>H<sub>15</sub>ClNO<sub>3</sub>S<sup>+</sup>[M+H]<sup>+</sup>; Found 324.0443.



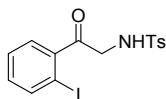
Obtained as white solid, mp: 163–165 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J = 8.4\text{Hz}$ , 2H), 7.73 (d,  $J = 8.8\text{ Hz}$ , 2H), 7.62 (d,  $J = 8.8\text{ Hz}$ , 2H), 7.30 (d,  $J = 8.0\text{ Hz}$ , 2H), 5.68 (t,  $J = 4.4\text{ Hz}$ , 1H), 4.44 (d,  $J = 4.4\text{ Hz}$ , 2H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  191.8, 143.9, 136.1, 132.5, 132.4 ( $\times 2$ ), 129.9 ( $\times 2$ ), 129.8, 129.3 ( $\times 2$ ), 127.2 ( $\times 2$ ), 48.7, 21.5; HRMS (ESI $^+$ ): calcd 367.9951 for  $\text{C}_{15}\text{H}_{15}\text{BrNO}_3\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 367.9962. calcd 367.9930 for  $\text{C}_{15}\text{H}_{15}\text{BrNO}_3\text{S}^+[\text{M}+\text{H}+2]^+$ ; Found, 367.9947.



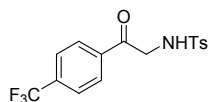
Obtained as white solid, mp: 141–143 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98 (s, 1H), 7.84–7.73 (m, 4H), 7.37 (t,  $J = 7.6\text{ Hz}$ , 1H), (7.31 (d,  $J = 8.0\text{ Hz}$ , 2H), 5.66 (s, 1H), 4.45 (d,  $J = 4.8\text{ Hz}$ , 2H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ ):  $\delta$  191.6, 143.9, 137.2, 136.1, 135.5, 130.9, 130.6, 129.9 ( $\times 2$ ), 127.2 ( $\times 2$ ), 126.4, 123.3, 48.8, 21.5; HRMS (ESI $^+$ ): calcd 367.9955 for  $\text{C}_{15}\text{H}_{15}\text{BrNO}_3\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 367.9974. calcd 369.9930 for  $\text{C}_{15}\text{H}_{15}\text{BrNO}_3\text{S}^+[\text{M}+\text{H}+2]^+$ ; Found, 369.9974.



Obtained as white solid, mp: 96–98 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J = 8.4\text{ Hz}$ , 2H), 7.63–7.58 (m, 1H), 7.39–7.31 (m, 5H), 5.63 (t,  $J = 4.8\text{Hz}$ , 1H), 4.42 (d,  $J = 4.8\text{ Hz}$ , 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  196.3, 143.9, 137.4, 136.2, 134.2, 133.0, 129.8 ( $\times 2$ ), 129.3, 127.6, 127.3 ( $\times 2$ ), 126.5, 51.4, 21.5; HRMS (ESI $^+$ ): calcd 367.9951 for  $\text{C}_{15}\text{H}_{15}\text{BrNO}_3\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 367.9955. calcd 369.9930 for  $\text{C}_{15}\text{H}_{15}\text{BrNO}_3\text{S}^+[\text{M}+\text{H}+2]^+$ ; Found, 369.9974.

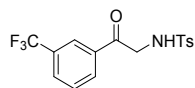


Obtained as white solid, mp: 84–86 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (d,  $J = 8.0\text{ Hz}$ , 1H), 7.8 (d,  $J = 8.0\text{ Hz}$ , 2H), 7.43 (t,  $J = 7.6\text{ Hz}$ , 1H), 7.33 (t,  $J = 8.0\text{ Hz}$ , 3H), 7.19 (dd,  $J = 1.6, 7.6\text{ Hz}$ , 1H), 5.56 (s, 1H), 4.37 (d,  $J = 4.8\text{ Hz}$ , 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  196.5, 143.9, 141.4, 140.0, 136.2, 133.0, 129.9( $\times 2$ ), 128.4, 128.3, 127.3 ( $\times 2$ ), 91.5, 50.6, 21.6; HRMS (ESI $^+$ ): calcd 416.9817 for  $\text{C}_{15}\text{H}_{15}\text{INO}_3\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 416.9854.

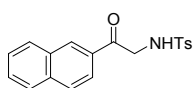


Obtained as white solid, mp: 146 – 149 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98 (d,  $J = 8.0\text{ Hz}$ , 2H), 7.80 (d,  $J = 8.0\text{ Hz}$ , 2H), 7.75 (d,  $J = 8.4\text{ Hz}$ , 2H),

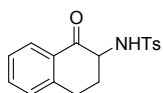
7.32 (d,  $J = 8.4$  Hz, 2H), 5.64 (t,  $J = 4.4$  Hz, 1H), 4.51 (d,  $J = 4.4$  Hz, 2H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ): 191.9, 144.0, 136.4, 136.1, 135.9 (q,  $^2J_{\text{F-C}} = 32.7\text{Hz}$ ), 130.0 ( $\times 2$ ), 128.3 ( $\times 2$ ), 127.2 ( $\times 2$ ), 126.1 (q,  $^3J_{\text{F-C}} = 3.7$  Hz), 124.6 (q,  $^1J_{\text{F-C}} = 271.1$  Hz), 49.0, 21.5; HRMS (ESI<sup>+</sup>): calcd 358.0719 for  $\text{C}_{16}\text{H}_{15}\text{F}_3\text{NO}_3\text{S}^+ [\text{M}+\text{H}]^+$ ; Found, 358.0708.



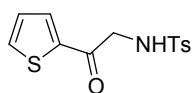
Obtained as white solid, mp: 125–127 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  8.11 (s, 1H), 8.06 (d,  $J = 8.0$  Hz, 1H), 7.87 (d,  $J = 8.0$  Hz, 1H), 7.80 (d,  $J = 8.4$  Hz, 2H), 7.64 (t,  $J = 8.0$  Hz, 1H), 7.31 (d,  $J = 8.0$  Hz, 2H), 5.75 (t,  $J = 4.4$  Hz, 1H), 4.52 (d,  $J = 4.4$  Hz, 2H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  191.7, 143.9, 136.1, 134.4, 131.6 (q,  $^2J_{\text{F-C}} = 33.0$  Hz), 131.0, 130.7 (q,  $^3J_{\text{F-C}} = 3.6$  Hz), 129.9 ( $\times 2$ ), 129.8, 127.2 ( $\times 2$ ), 124.7 (q,  $^3J_{\text{F-C}} = 3.7$  Hz), 123.4 (q,  $^1J_{\text{F-C}} = 271.0$  Hz), 48.9, 21.5; HRMS (ESI<sup>+</sup>): calcd 358.0719 for  $\text{C}_{16}\text{H}_{15}\text{FNO}_3\text{S}^+ [\text{M}+\text{H}]^+$ ; Found, 358.0722.



Obtained as white solid, mp: 99–101 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  8.53 (d,  $J = 8.0$  Hz, 1H), 8.06 (d,  $J = 8.4$  Hz, 1H), 7.88 (d,  $J = 8.4$  Hz, 1H), 7.84 (s, 1H), 7.83 (d,  $J = 8.4$  Hz, 2H), 7.61–7.55 (m, 2H), 7.50 (t,  $J = 7.6$  Hz, 1H), 7.30 (d,  $J = 8.4$  Hz, 2H), 5.80 (t,  $J = 4.4$  Hz, 1H), 4.54 (d,  $J = 4.4$  Hz, 2H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  195.6, 143.8, 136.2, 134.5, 134.0, 131.5, 130.1, 129.9 ( $\times 2$ ), 128.6 ( $\times 2$ ), 128.4, 127.3 ( $\times 2$ ), 126.9, 125.4, 124.3, 50.4, 21.5; HRMS (ESI<sup>+</sup>): calcd 340.1007 for  $\text{C}_{19}\text{H}_{18}\text{NO}_3\text{S}^+ [\text{M}+\text{H}]^+$ ; Found, 340.1071.



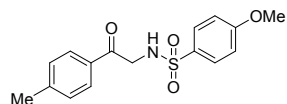
Obtained as white solid, mp: 97–99 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (d,  $J = 8.0$  Hz, 1H), 7.81 (d,  $J = 8.4$  Hz, 2H), 7.51 (dt,  $J = 1.0, 7.2$  Hz, 1H), 7.32–7.24 (m, 4H), 6.09 (d,  $J = 2.4$  Hz, 1H), 3.90–3.85 (m, 1H), 3.13–2.98 (m, 2H), 2.77–2.73 (m, 1H), 2.41 (s, 3H), 2.16–2.05 (m, 1H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  193.8, 143.8, 143.7, 136.2, 134.5, 130.6, 129.8 ( $\times 2$ ), 129.0, 127.9, 127.2 ( $\times 2$ ), 126.9, 59.1, 31.9, 28.1, 21.5; HRMS (ESI<sup>+</sup>): calcd 316.1007 for  $\text{C}_{17}\text{H}_{18}\text{NO}_3\text{S}^+ [\text{M}+\text{H}]^+$ ; Found, 316.1005.



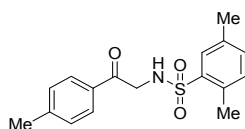
Obtained as white solid, mp: 102–104 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J = 8.4$  Hz, 2H), 7.74 – 7.71 (m, 2H), 7.30 (d,  $J = 8.0$  Hz, 1H), 7.16 (dd,  $J = 4.0, 4.8$  Hz, 1H), 5.72 (t,  $J = 4.4$  Hz, 1H), 4.41 (d,  $J = 4.4$  Hz, 2H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,



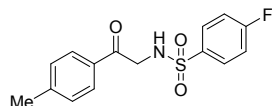
CDCl<sub>3</sub>):  $\delta$  185.5, 143.8, 140.2, 136.2, 135.0, 132.5, 129.8 ( $\times 2$ ), 128.4, 127.2 ( $\times 2$ ), 48.7, 21.5; HRMS (ESI<sup>+</sup>): calcd 296.0410 for C<sub>17</sub>H<sub>18</sub>NO<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup>; Found, 296.0407.



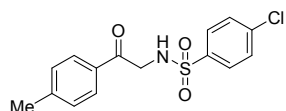
Obtained as yellow brown solid, mp: 121–124 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  7.85 (d, *J* = 8.8Hz, 2H), 7.76 (d, *J* = 8.4Hz, 2H), 7.28 (d, *J* = 7.6Hz, 2H), 6.97 (d, *J* = 8.8Hz, 2H), 5.67 (s, 1H), 4.44 (d, *J* = 4.4Hz, 2H), 3.86 (s, 3H), 2.43 (s, 3H); <sup>13</sup>C NMR (100Hz, CDCl<sub>3</sub>):  $\delta$  192.2, 163.1, 145.6, 131.3, 130.7, 129.7 ( $\times 2$ ), 129.3 ( $\times 2$ ), 128.0 ( $\times 2$ ), 114.4 ( $\times 2$ ), 55.6, 48.5, 21.8; HRMS (ESI<sup>+</sup>): calcd 320.0957 for C<sub>16</sub>H<sub>18</sub>NO<sub>4</sub>S<sup>+</sup> [M+H]<sup>+</sup>; Found, 320.0966.



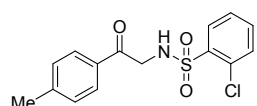
Obtained as light yellow solid, mp: 81–83 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  7.88 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.12 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 5.76 (t, *J* = 4.0 Hz, 1H), 4.40 (d, *J* = 4.0 Hz, 2H), 2.68 (s, 3H), 2.42 (s, 3H), 2.35 (s, 3H); <sup>13</sup>C NMR (100Hz, CDCl<sub>3</sub>):  $\delta$  192.2, 145.6, 143.7, 137.2, 134.0, 133.5, 131.3, 129.7, 129.6 ( $\times 2$ ), 128.0 ( $\times 2$ ), 126.7, 48.4, 21.7, 21.2, 20.1; HRMS (ESI<sup>+</sup>): calcd 318.1164 for C<sub>17</sub>H<sub>20</sub>NO<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup>; Found, 318.1182.



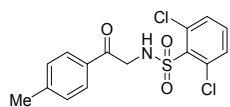
Obtained as white solid, mp: 149–152 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): 7.95–7.92 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.21–7.16 (m, 2H), 5.76 (s, 1H), 4.47 (d, *J* = 4.8 Hz, 2H), 2.43 (s, 3H); <sup>13</sup>C NMR (100Hz, CDCl<sub>3</sub>):  $\delta$  191.9, 165.2 (d, <sup>1</sup>*J*<sub>F-C</sub> = 253.0 Hz), 145.7, 135.4, 131.2, 129.9 (d, <sup>2</sup>*J*<sub>F-C</sub> = 19.3 Hz,  $\times 2$ ), 129.7 ( $\times 2$ ), 128.0 ( $\times 2$ ), 116.4 (d, <sup>2</sup>*J*<sub>F-C</sub> = 22.5 Hz,  $\times 2$ ), 48.5, 21.8; HRMS (ESI<sup>+</sup>): calcd 308.0757 for C<sub>15</sub>H<sub>15</sub>FNO<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup>; Found, 308.0732.



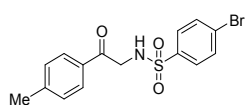
Obtained as white solid, mp: 167–168 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  7.85 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.79 (s, 1H), 4.47 (d, *J* = 4.4Hz, 2H), 2.43 (s, 3H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>):  $\delta$  191.8, 145.8, 139.4, 137.8, 131.2, 129.7 ( $\times 2$ ), 129.5 ( $\times 2$ ), 128.6 ( $\times 2$ ), 128.0 ( $\times 2$ ), 48.5, 21.8; HRMS (ESI<sup>+</sup>): calcd 324.0461 for C<sub>15</sub>H<sub>15</sub>ClNO<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup>; Found, 324.0418.



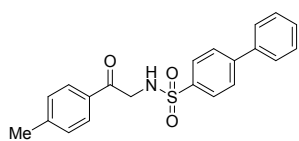
Obtained as white solid, mp: 109–111 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J = 8\text{Hz}$ , 2H), 7.48–7.36 (m, 2H), 7.30–7.28 (m, 4H), 6.58 (t,  $J = 4\text{Hz}$ , 1H), 4.59 (d,  $J = 4\text{Hz}$ , 2H), 2.43 (t,  $J = 4\text{Hz}$ , 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ): 191.6, 145.7, 135.1, 132.6, 131.8, 131.5 ( $\times 2$ ), 131.1, 129.7 ( $\times 2$ ), 129.3, 128.1 ( $\times 2$ ). 48.9, 21.8; HRMS (ESI $^+$ ): calcd 324.0461 for  $\text{C}_{15}\text{H}_{15}\text{ClNO}_3\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 324.0434.



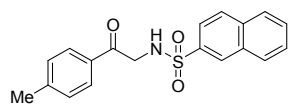
Obtained as white solid, mp: 104–106 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79–7.76 (m, 3H), 7.65 (d,  $J = 8.8\text{ Hz}$ , 2H), 7.29 (d,  $J = 8.8\text{ Hz}$ , 2H), 5.75 (s, 1H), 4.76 (d,  $J = 4.4\text{ Hz}$ , 2H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ): 191.8, 145.8, 138.3, 132.5 ( $\times 2$ ), 131.2, 129.7 ( $\times 2$ ), 128.7 ( $\times 2$ ), 127.8 ( $\times 2$ ), 127.9, 48.4, 21.8; HRMS (ESI $^+$ ): calcd 358.0071 for  $\text{C}_{15}\text{H}_{14}\text{Cl}_2\text{NO}_3\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 358.0033.



Obtained as white solid: mp: 164–166 °C;  $^1\text{H}$  NMR (400Hz,  $\text{CDCl}_3$ ):  $\delta$  7.77–7.78 (d,  $J = 8.4\text{ Hz}$ , 2H), 7.76 (d,  $J = 8.0\text{ Hz}$ , 2H), 7.64 (d,  $J = 8.8\text{ Hz}$ , 2H), 7.28 (d,  $J = 8.0\text{ Hz}$ , 2H), 5.81 (s, 1H), 4.47 (d,  $J = 4.4\text{ Hz}$ , 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  191.9, 145.7, 138.5, 132.5 ( $\times 2$ ), 131.3, 129.7 ( $\times 2$ ), 128.7 ( $\times 2$ ), 128.0 ( $\times 2$ ), 127.8, 48.5, 21.8; HRMS (ESI $^+$ ): calcd 367.9951 for  $\text{C}_{15}\text{H}_{15}\text{BrNO}_3\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 367.9901. calcd 369.9930 for  $\text{C}_{15}\text{H}_{15}\text{BrNO}_3\text{S}^+[\text{M}+\text{H}+2]^+$ ; Found, 369.9907.



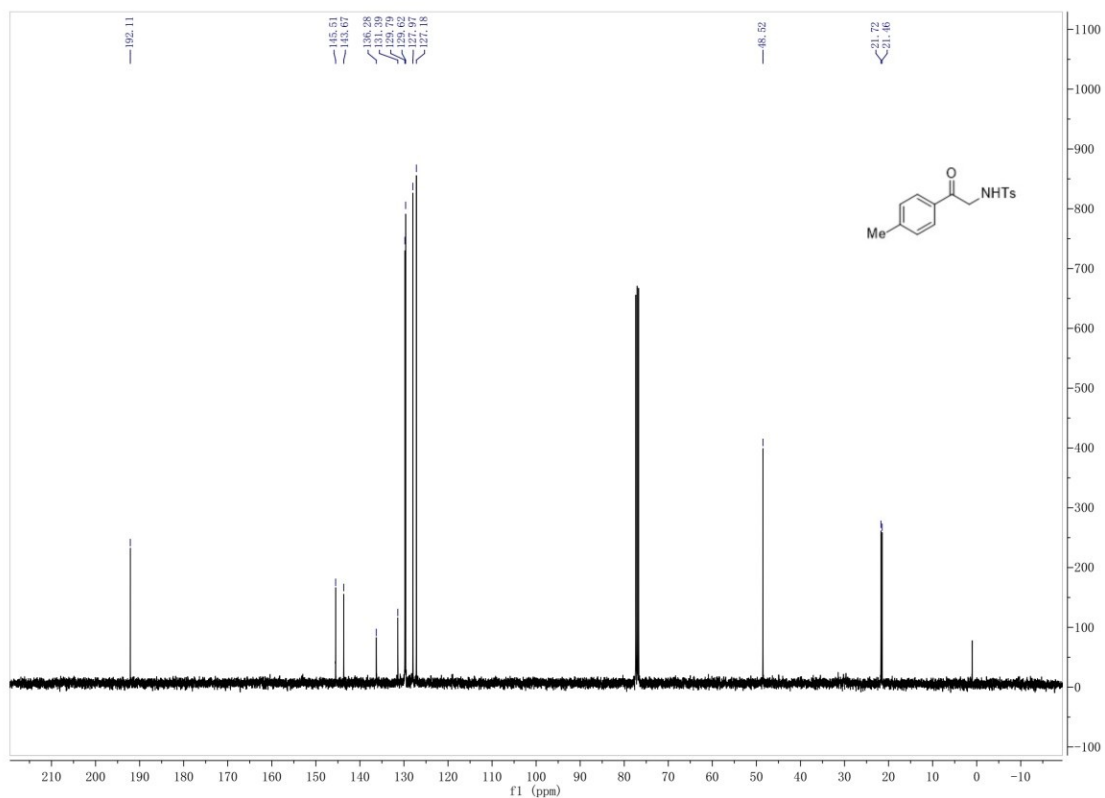
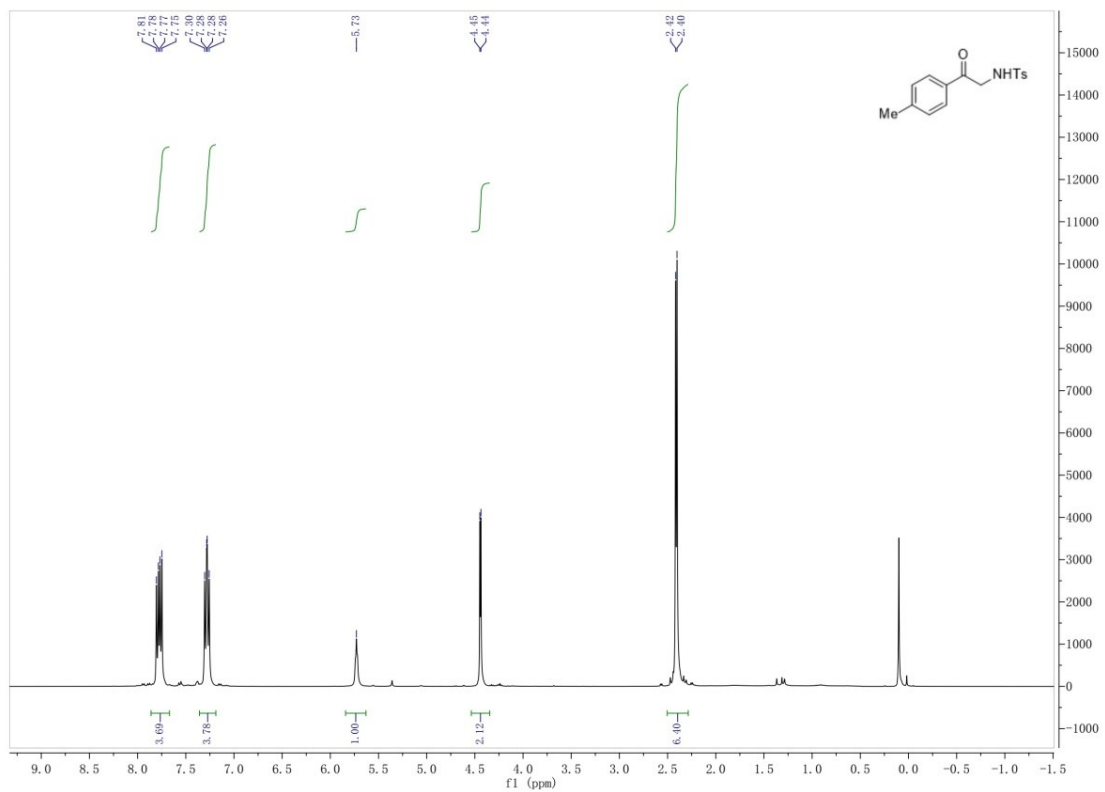
Obtained as white solid, mp: 159–161 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.99–7.96 (m, 2H), 7.78 (d,  $J = 8.4\text{ Hz}$ , 2H), 7.73–7.70 (m, 2H), 7.61–7.58 (m, 2H), 7.51–7.43 (m, 3H), 7.28 (d,  $J = 8.0\text{ Hz}$ , 2H), 5.77 (t,  $J = 4.0\text{ Hz}$ , 1H), 4.52 (d,  $J = 4.0\text{ Hz}$ , 2H), 2.46–2.38 (s, 3H);  $^{13}\text{C}$  NMR (100Hz,  $\text{CDCl}_3$ ):  $\delta$  192.0, 145.9, 145.6, 139.3, 137.8, 131.4, 129.7 ( $\times 2$ ), 129.0 ( $\times 2$ ), 128.5, 128.0 ( $\times 2$ ), 127.8 ( $\times 2$ ), 127.7 ( $\times 2$ ), 127.3 ( $\times 2$ ). 48.5, 21.7; HRMS (ESI $^+$ ): calcd 366.1164 for  $\text{C}_{21}\text{H}_{20}\text{NO}_3\text{S}^+[\text{M}+\text{H}]^+$ ; Found, 366.1160.

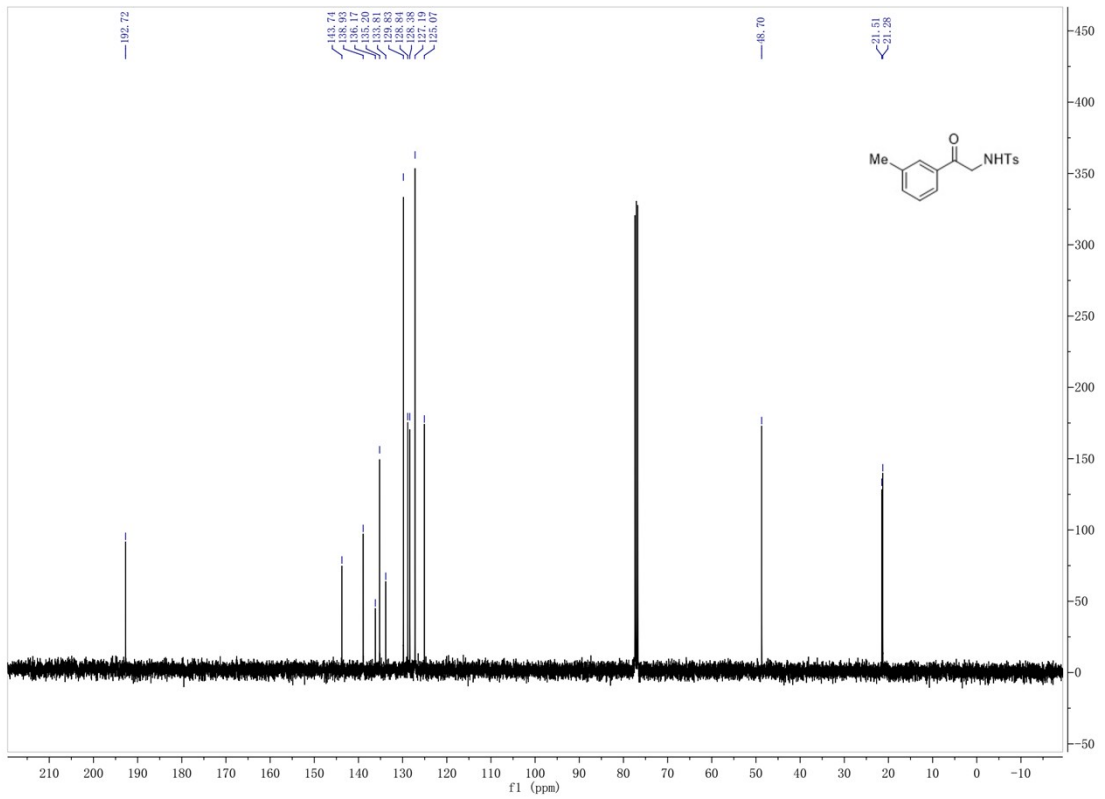
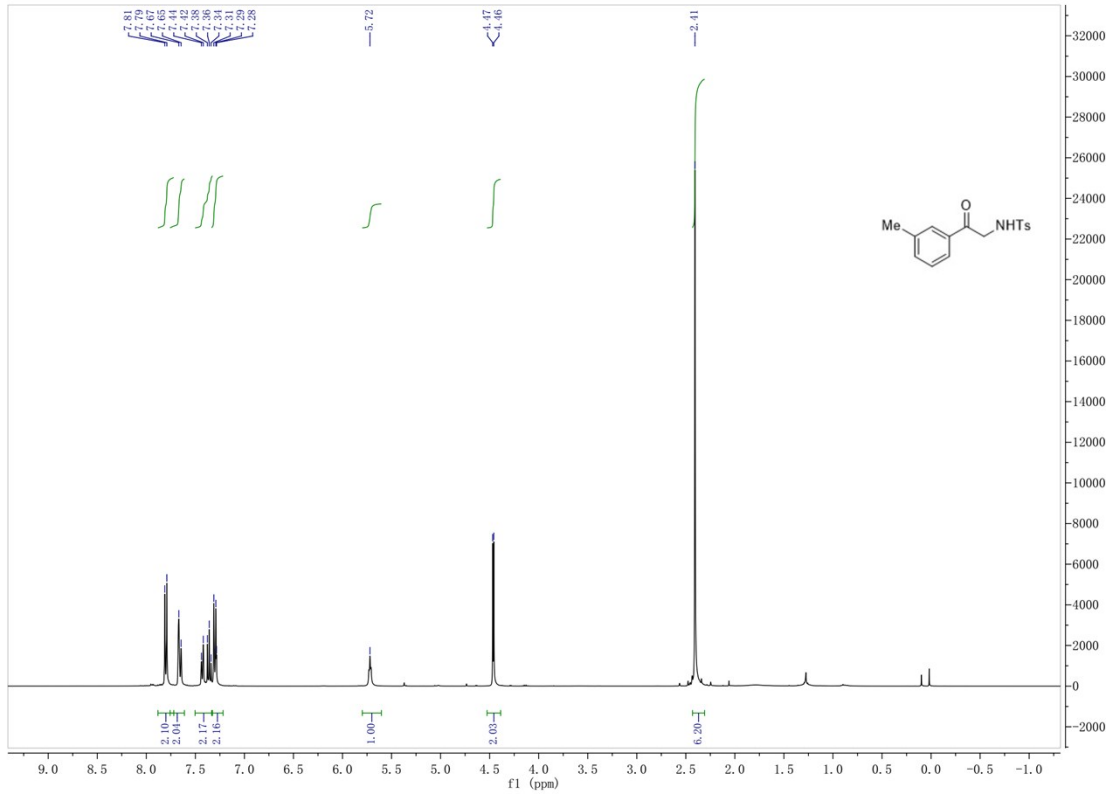


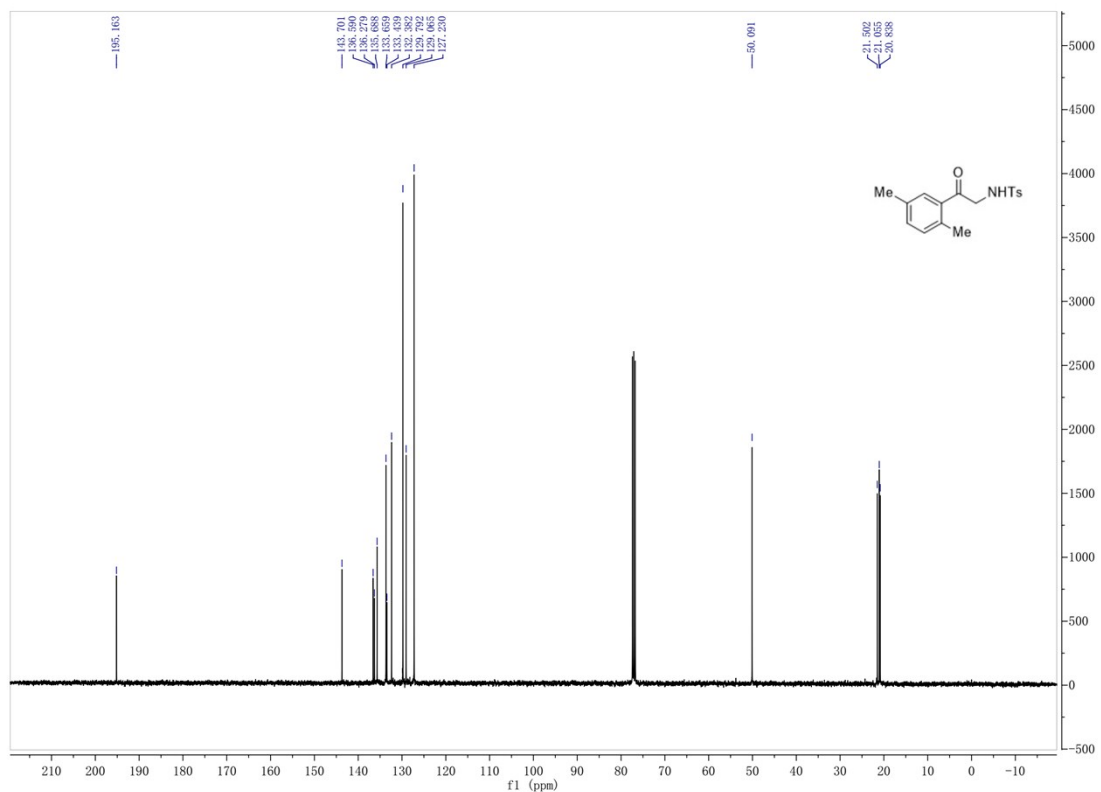
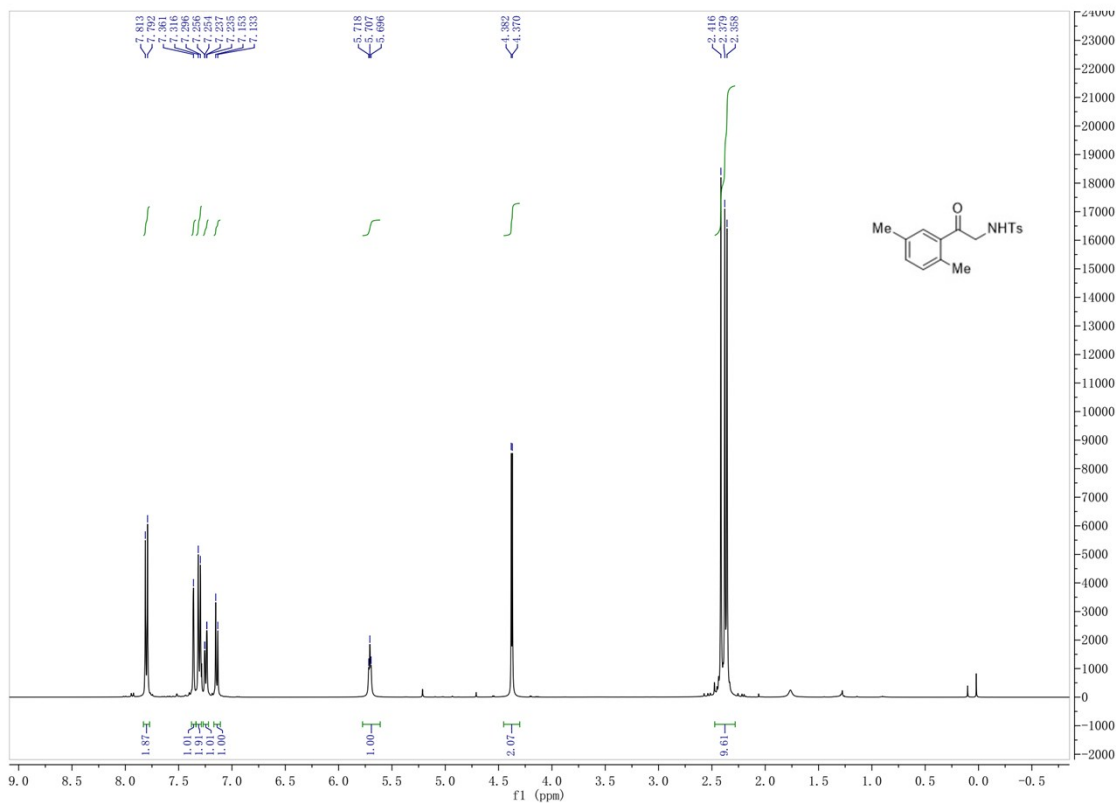
Obtained as white solid, mp: 137–139 °C;  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  8.49 (s, 1H), 7.98–7.88 (m, 4H), 7.73 (d,  $J = 8.0\text{ Hz}$ , 2H), 7.65 – 7.60

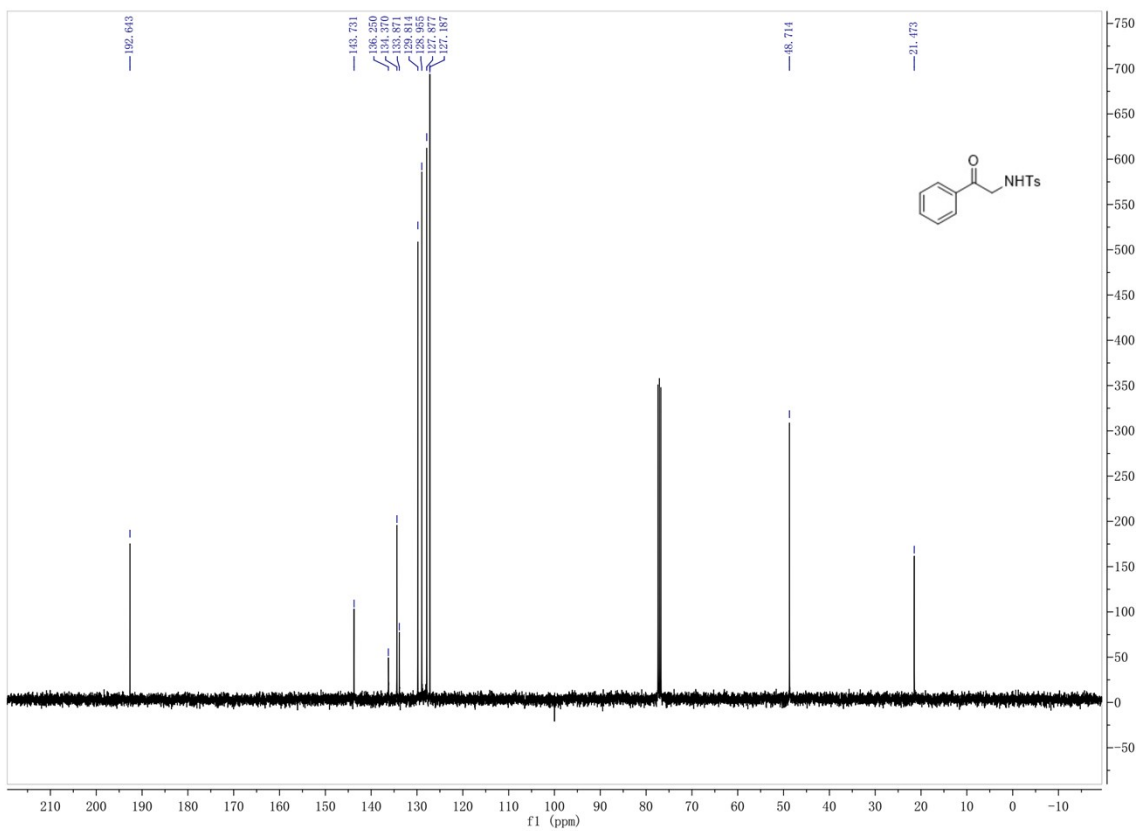
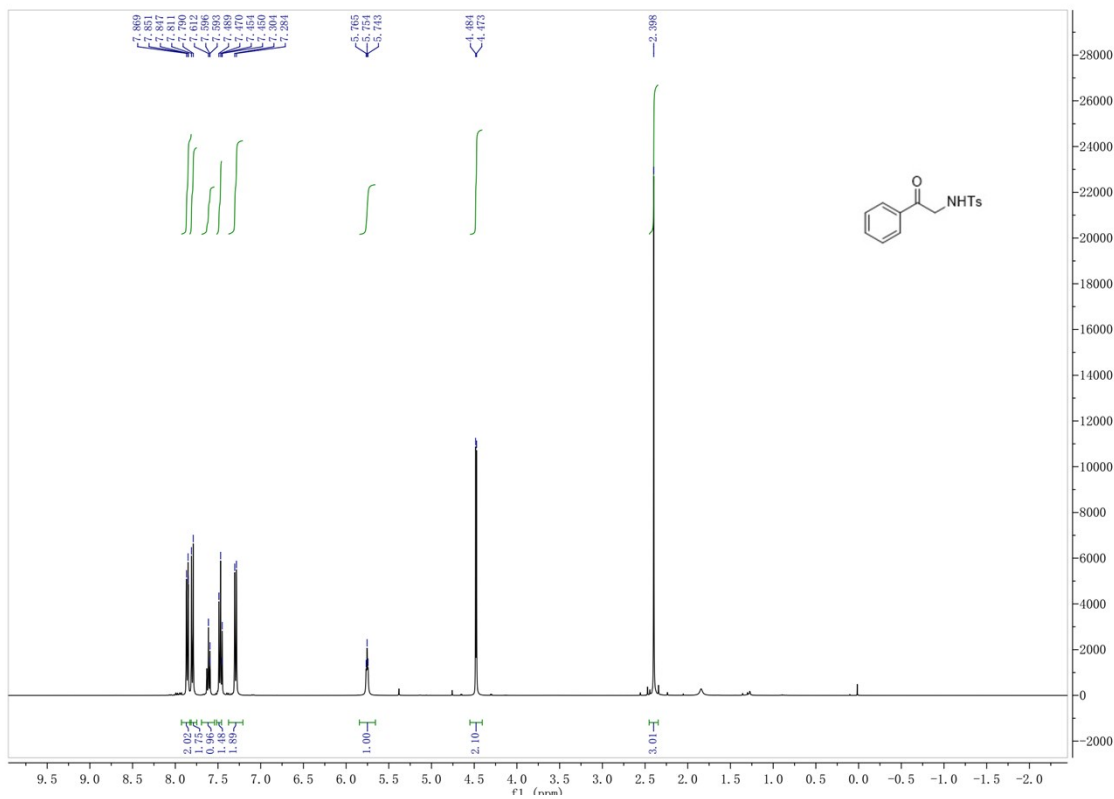
(m, 2H), 7.24 (d,  $J = 8.0$  Hz, 2H), 5.84 (s, 1H), 4.49 (d,  $J = 4.0$  Hz, 2H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.0, 145.6, 136.0, 134.9, 132.1, 131.3, 129.7, 129.6 ( $\times 2$ ), 129.2, 128.9, 128.6, 128.0 ( $\times 2$ ), 127.9, 127.6, 122.3, 48.5, 21.6; HRMS (ESI $^+$ ): calcd 340.1007 for  $\text{C}_{19}\text{H}_{18}\text{NO}_3\text{S}^+$   $[\text{M}+\text{H}]^+$ ; Found, 340.1000.

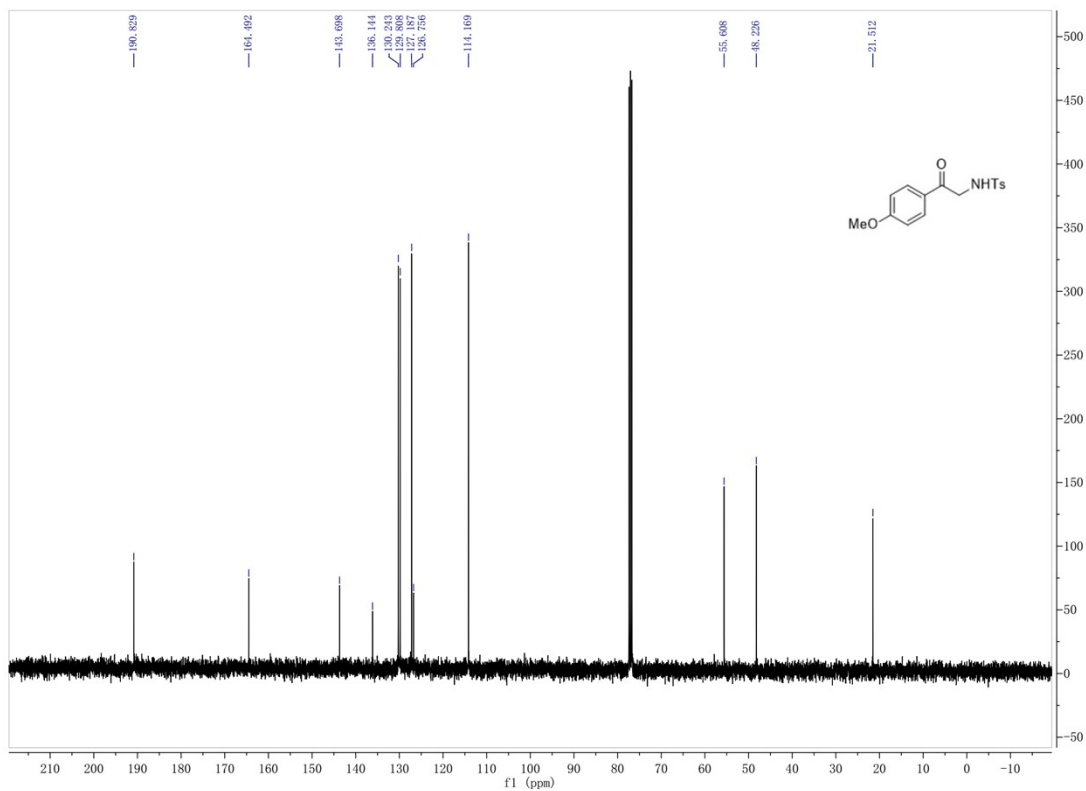
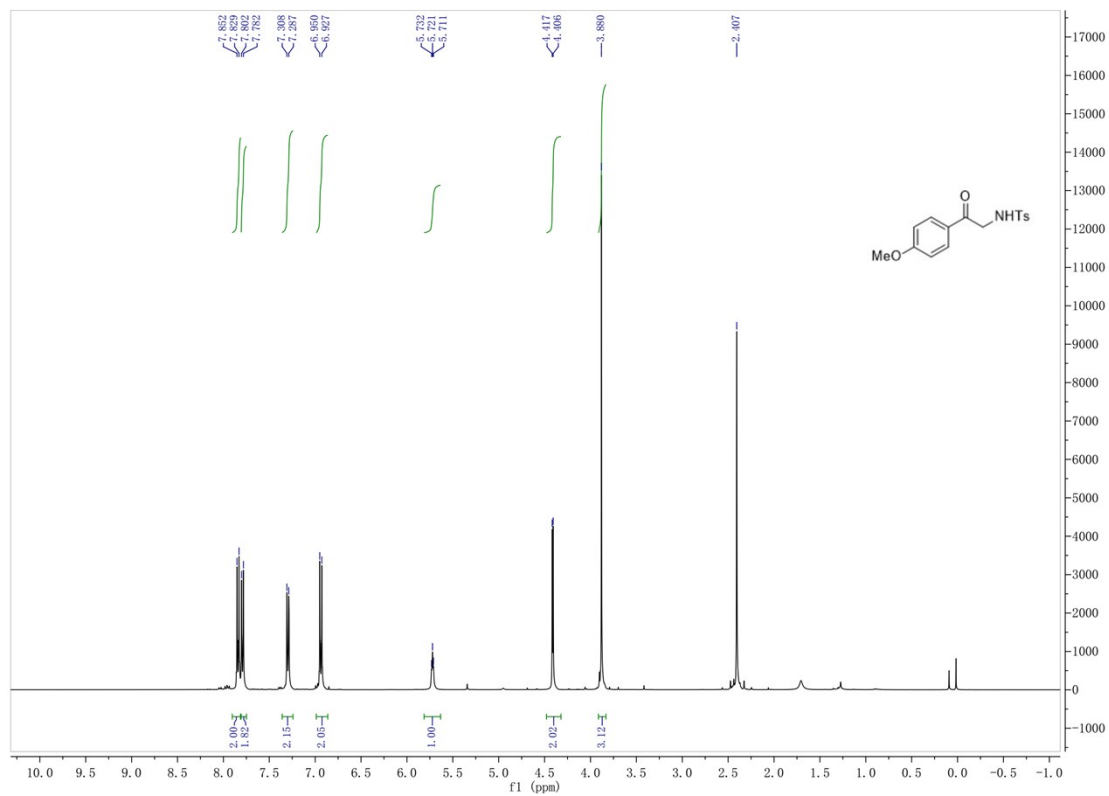
## 6. NMR spectra of $\alpha$ -sulfonylamino ketones



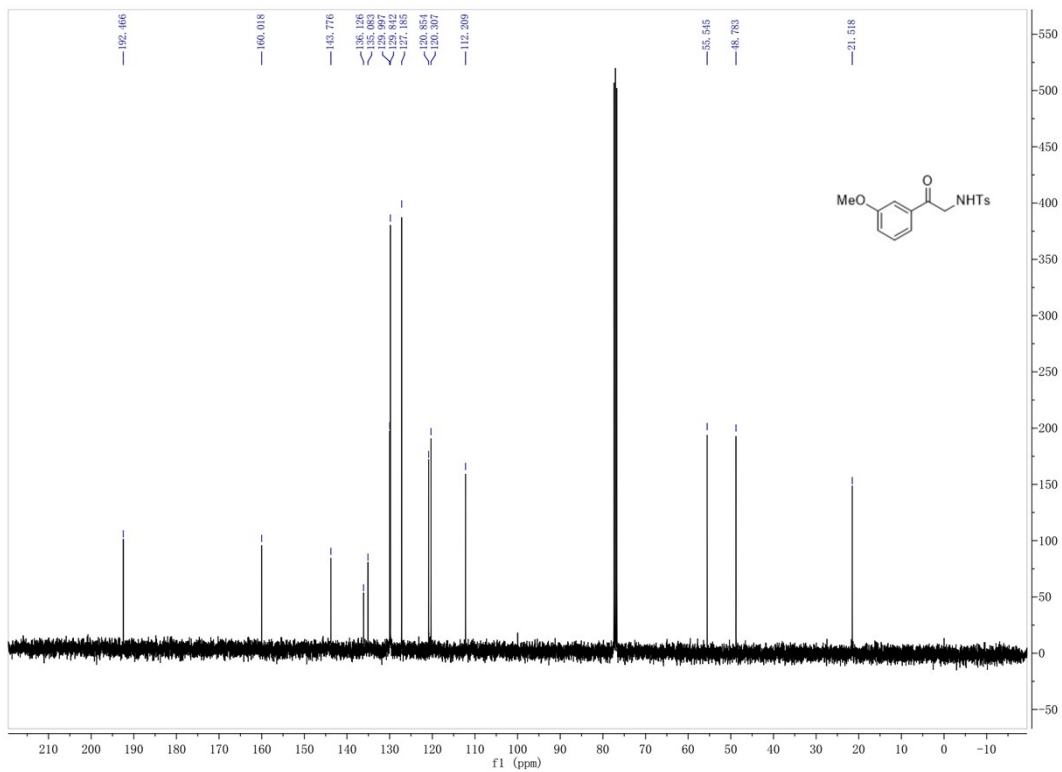
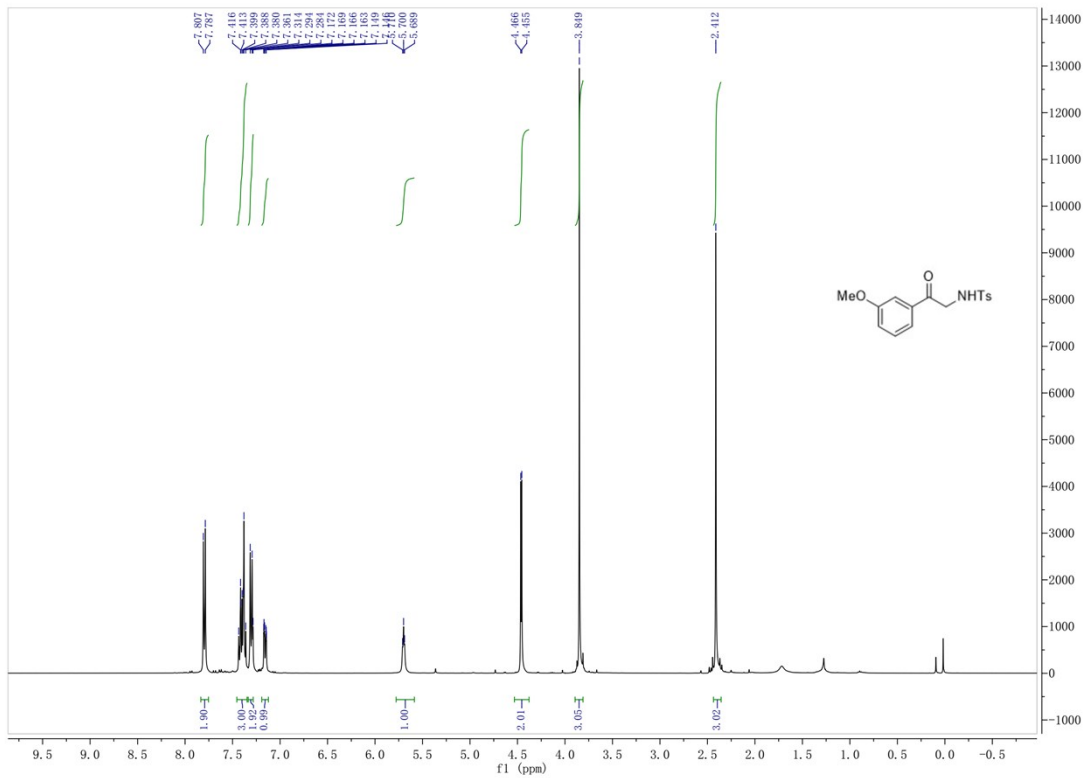


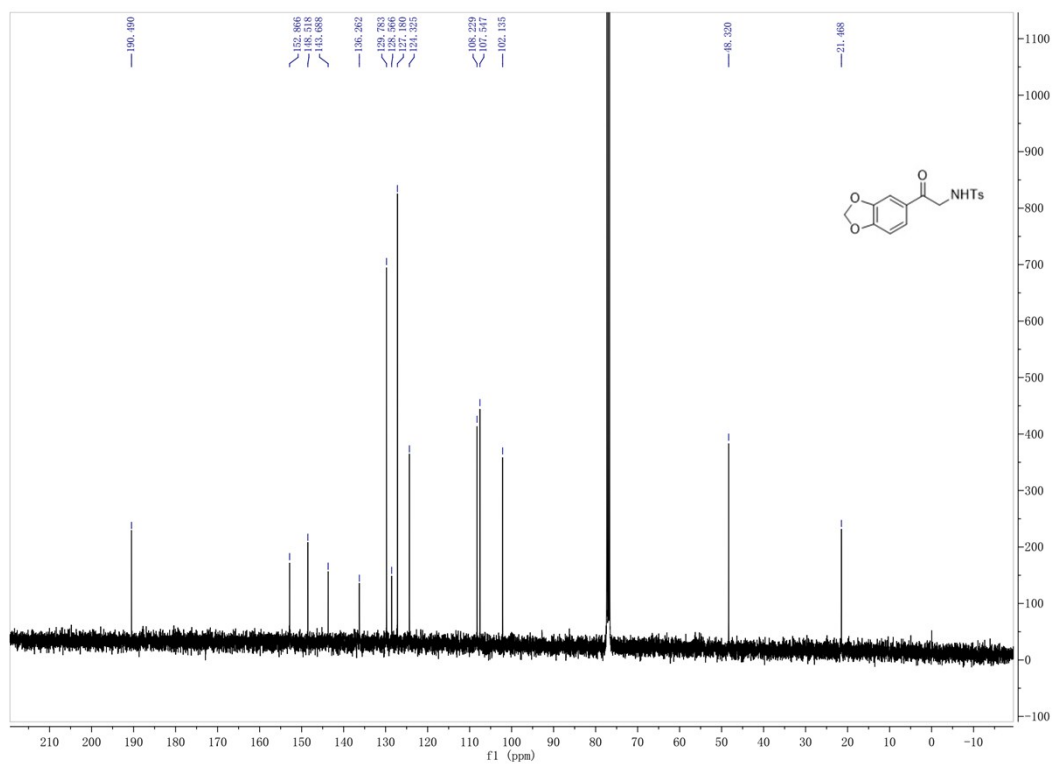
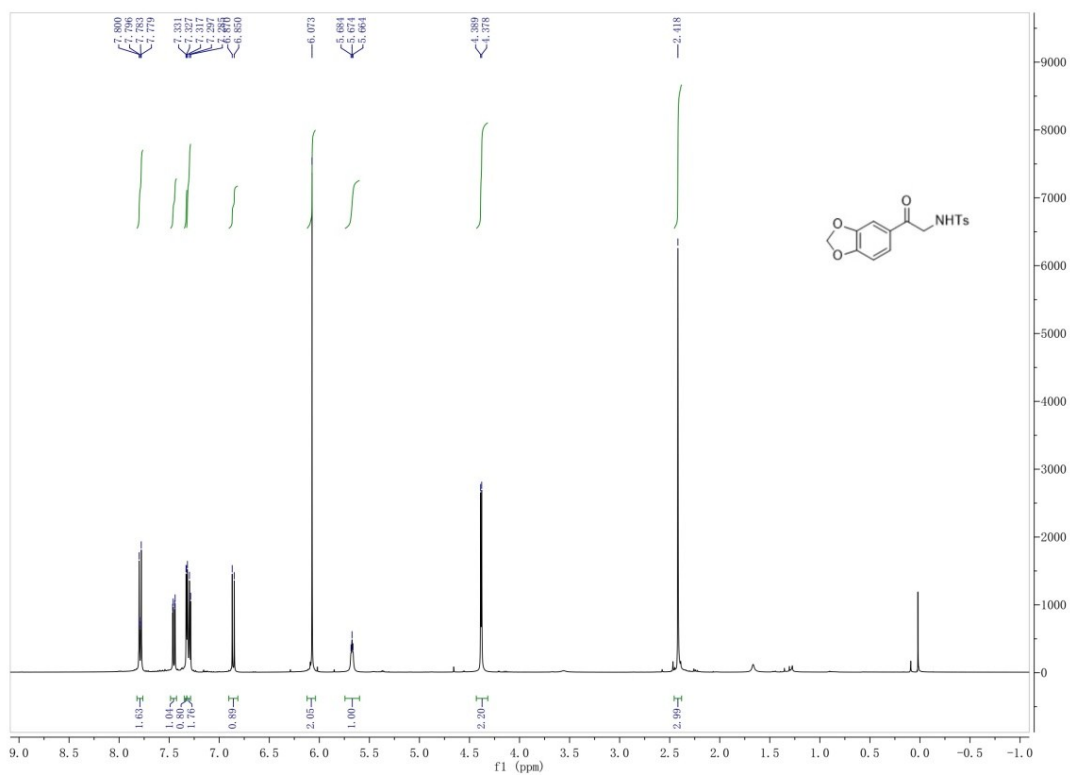


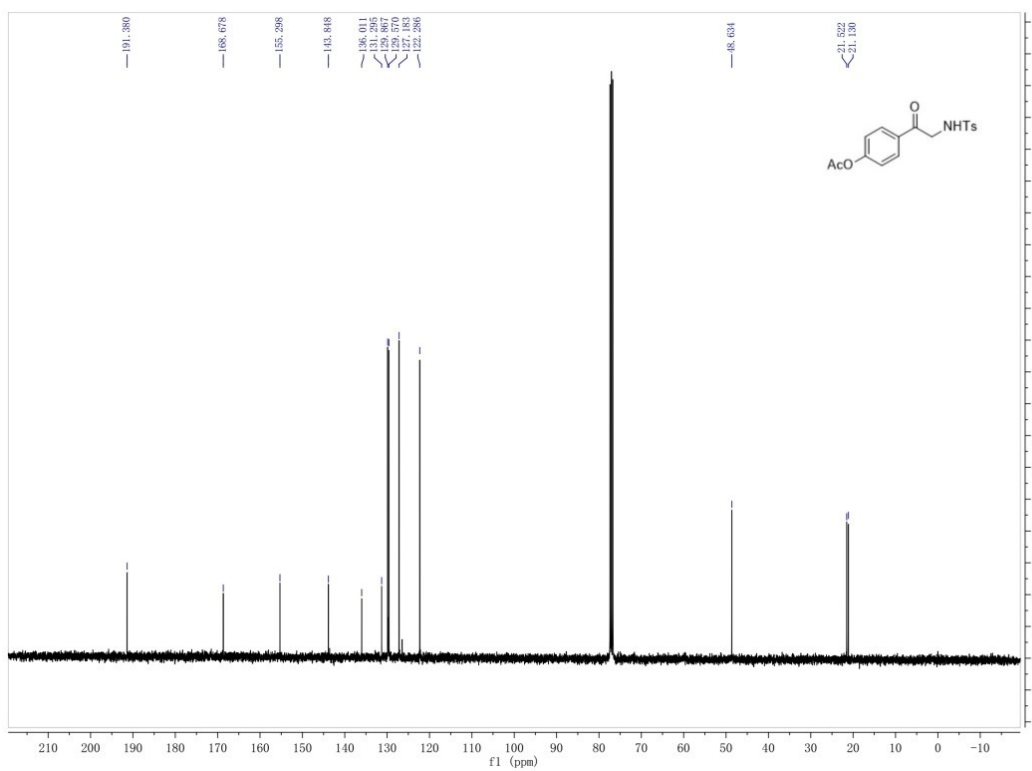
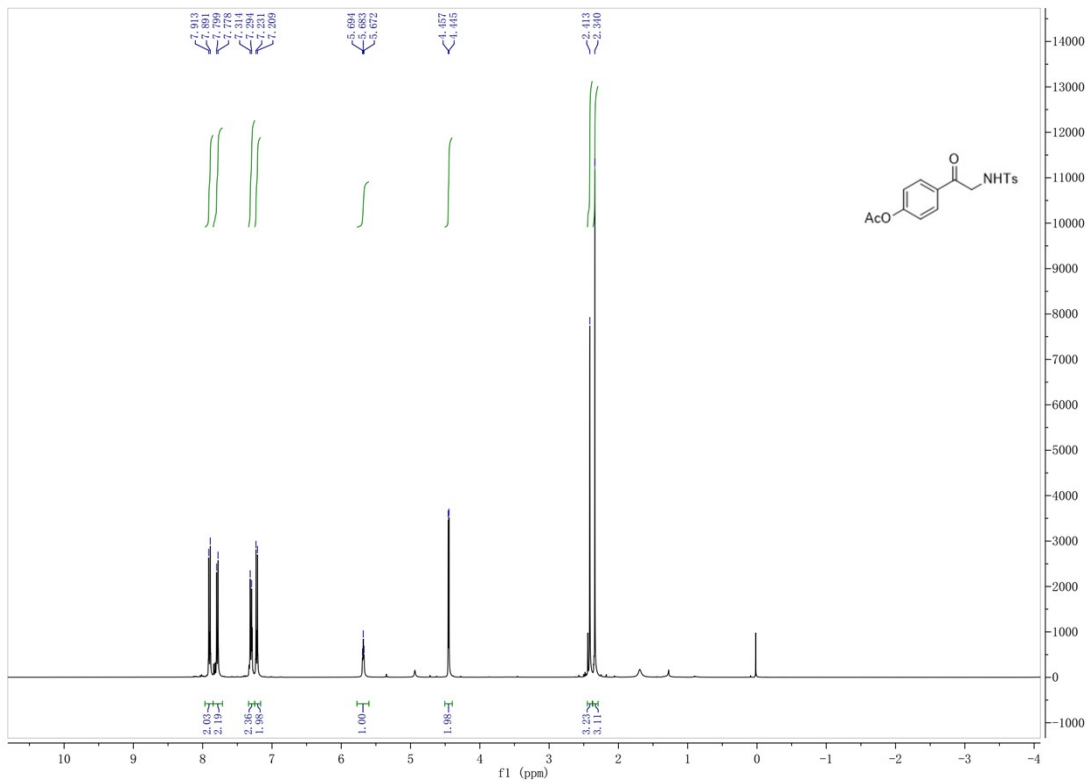


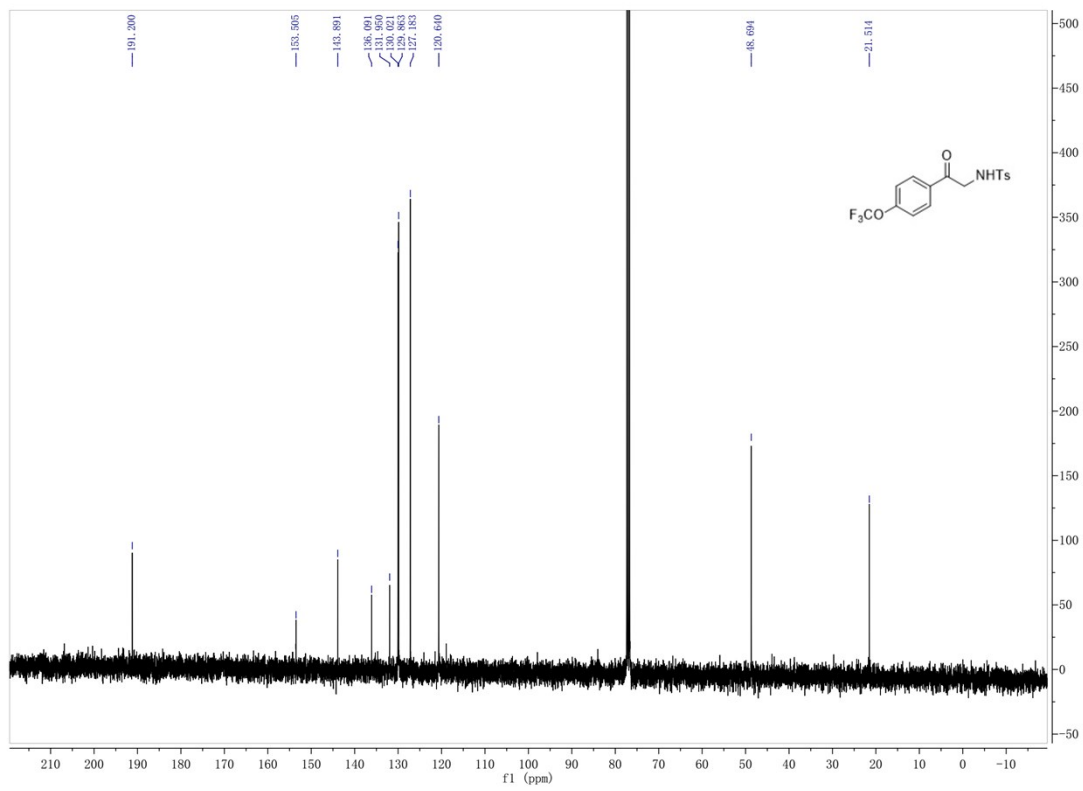
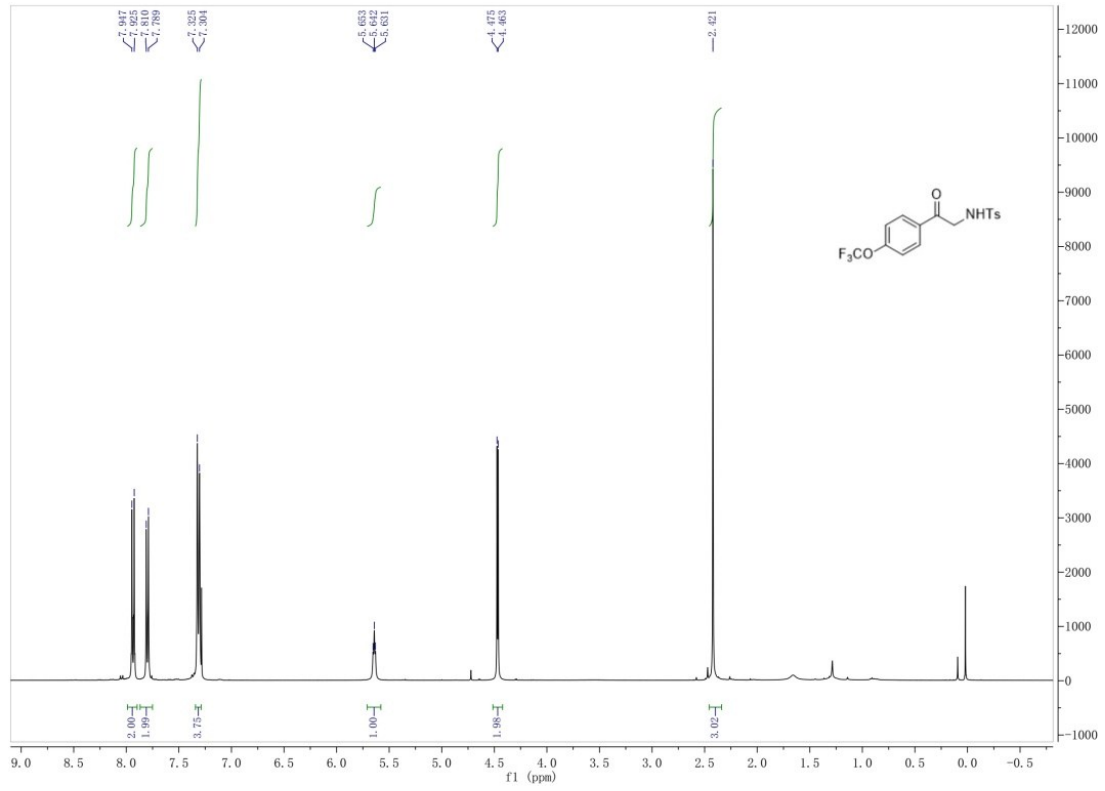


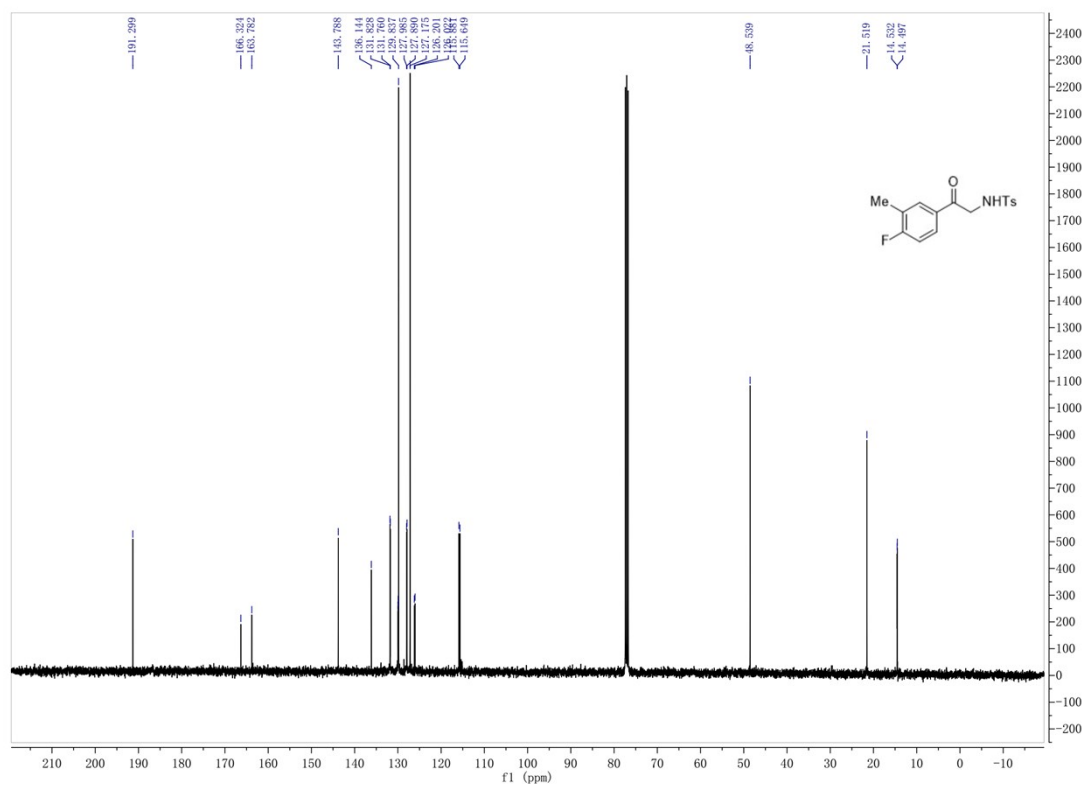
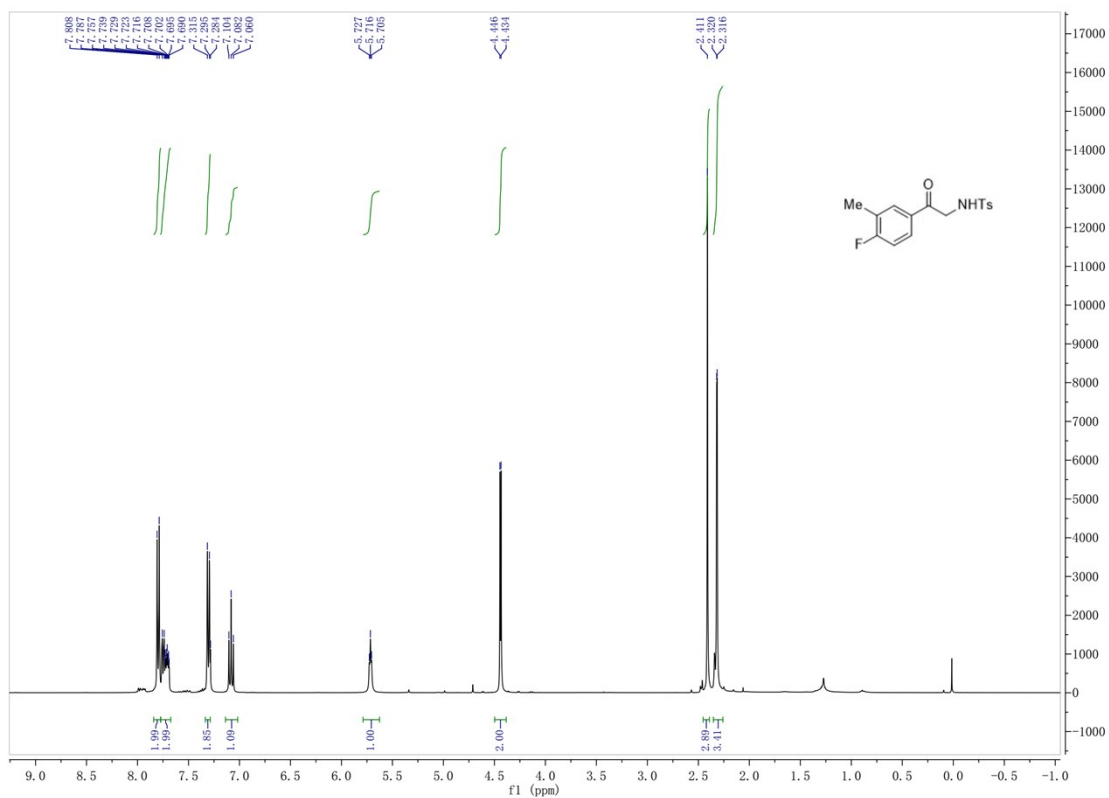


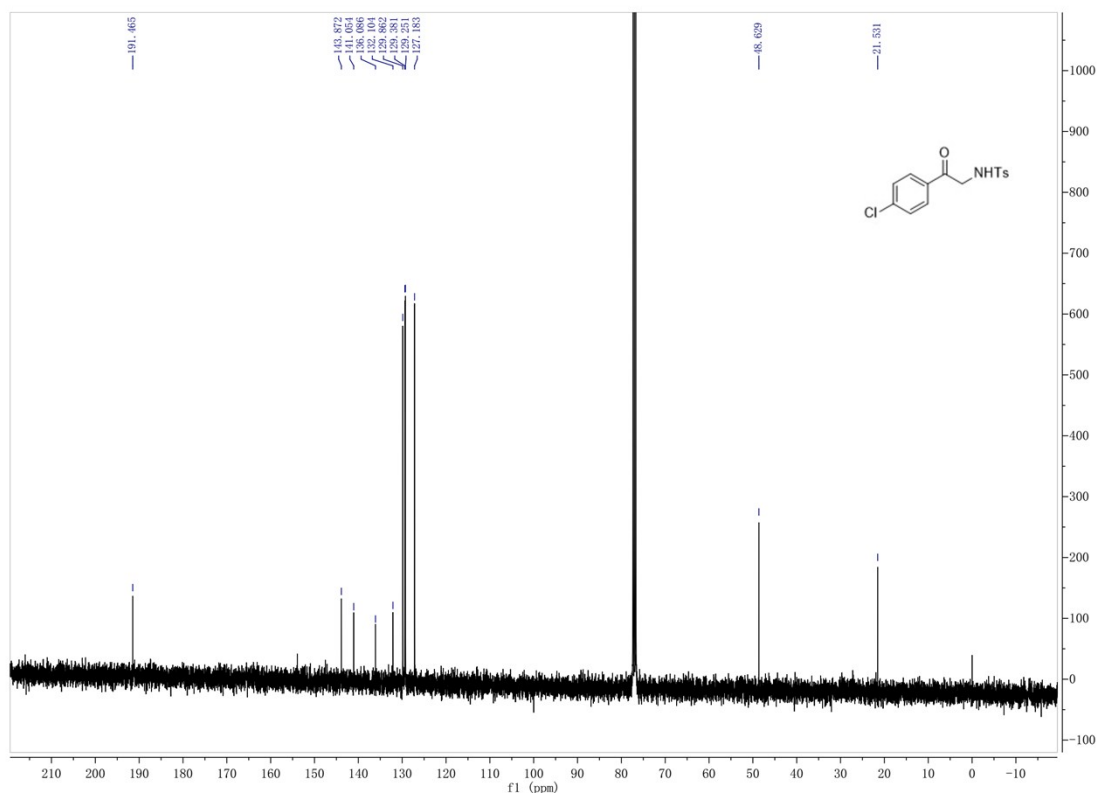
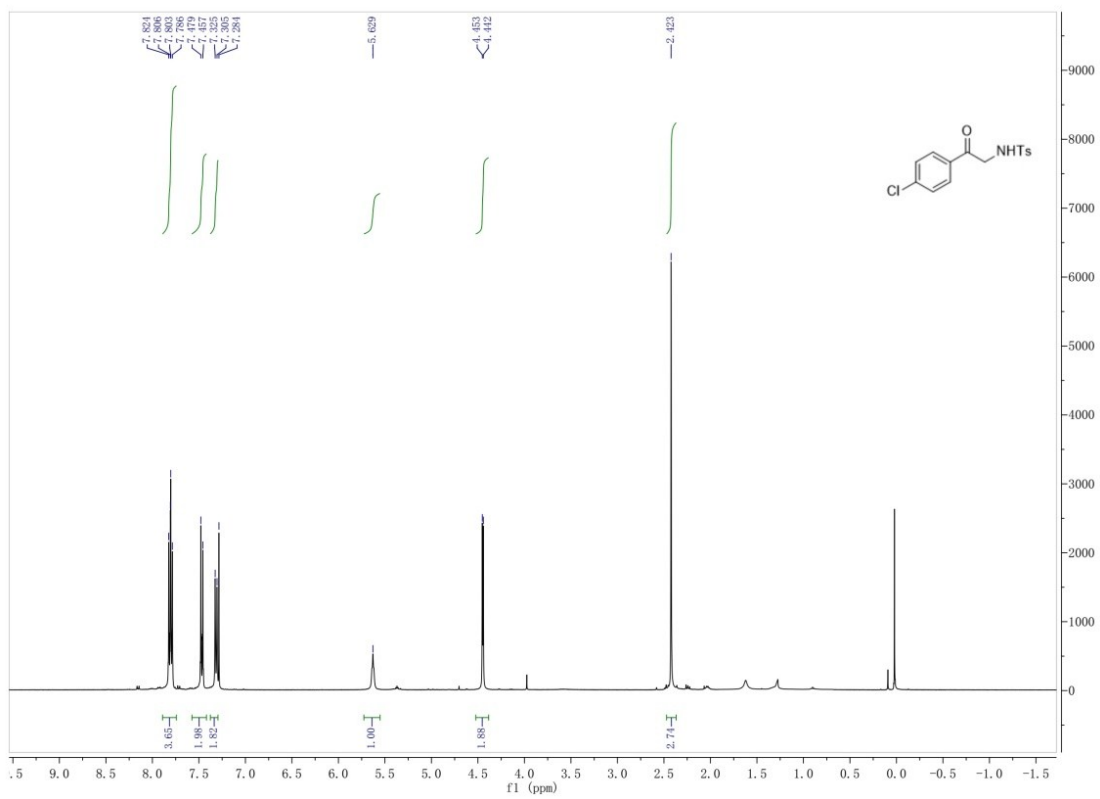


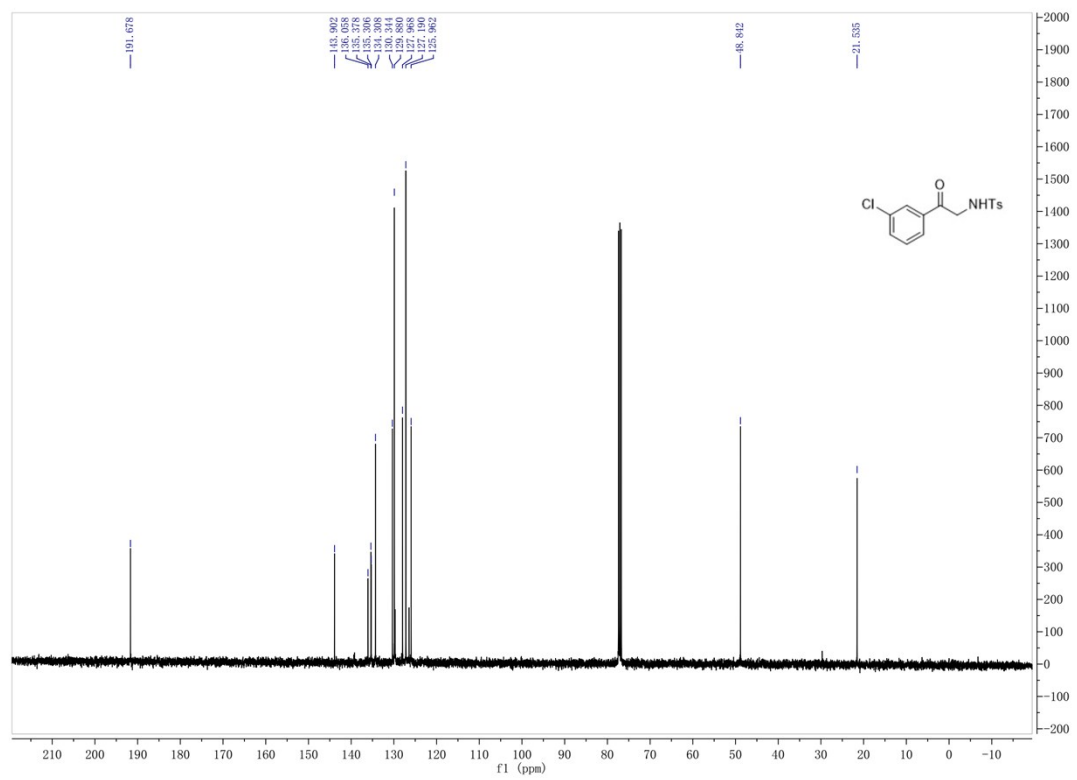
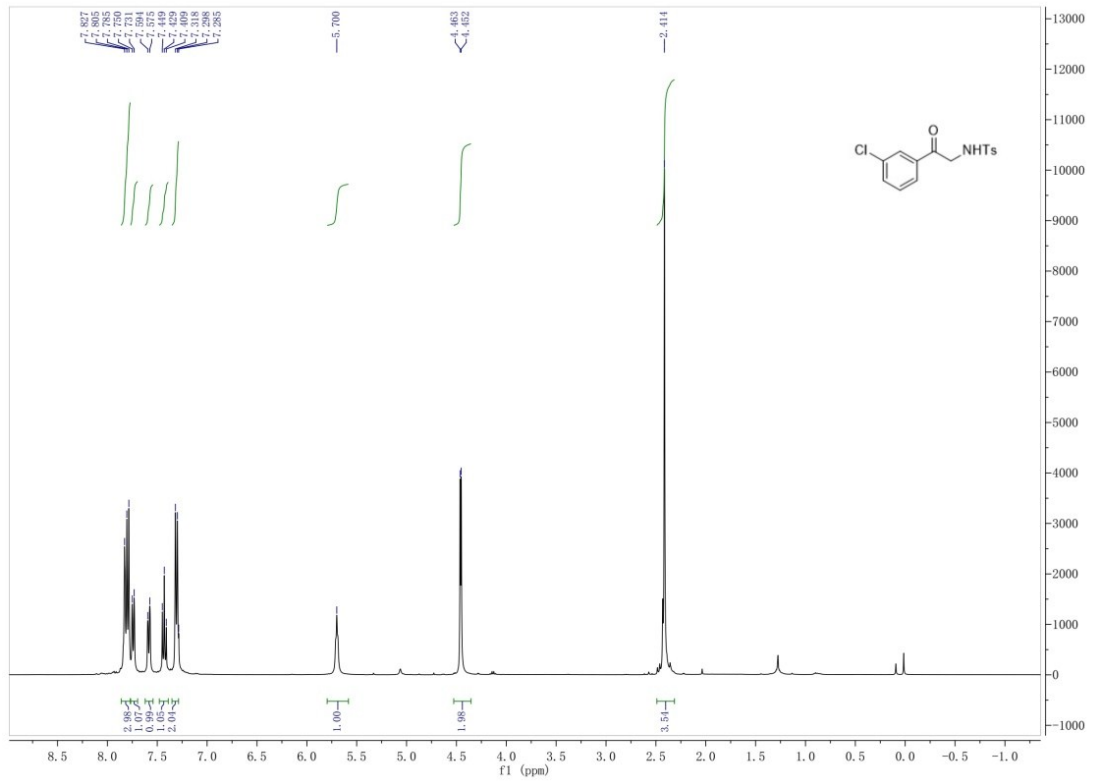


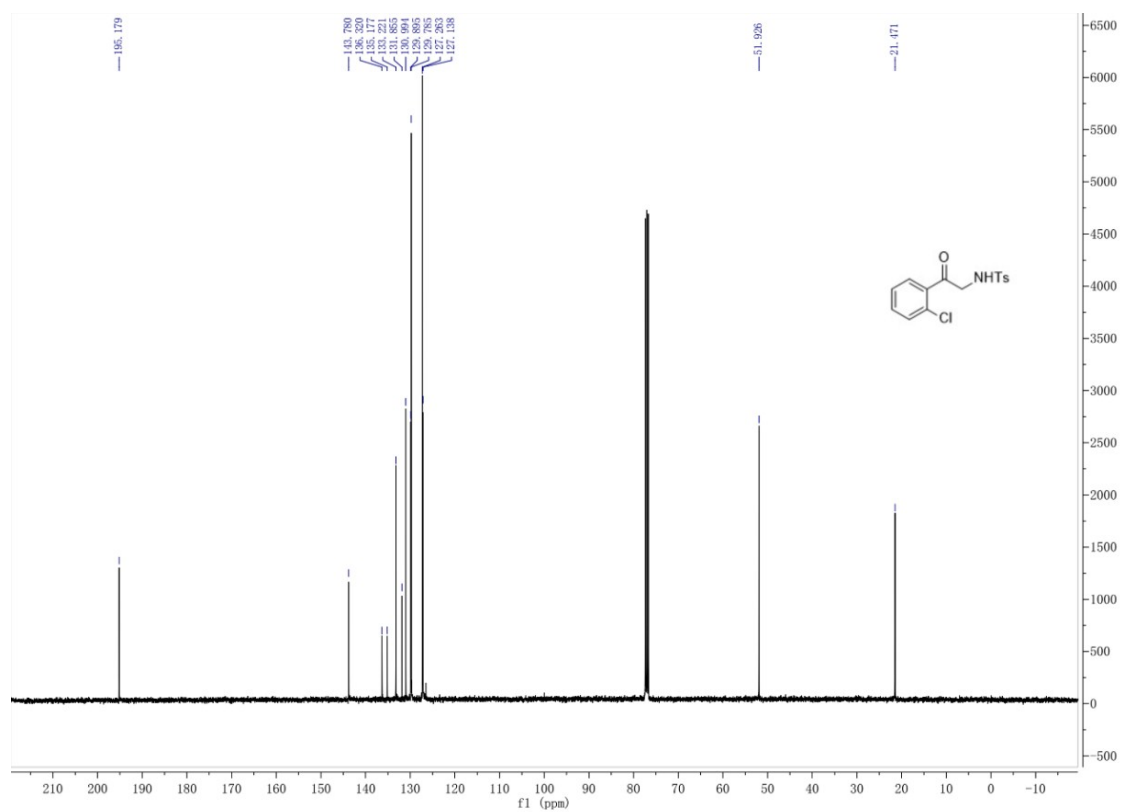
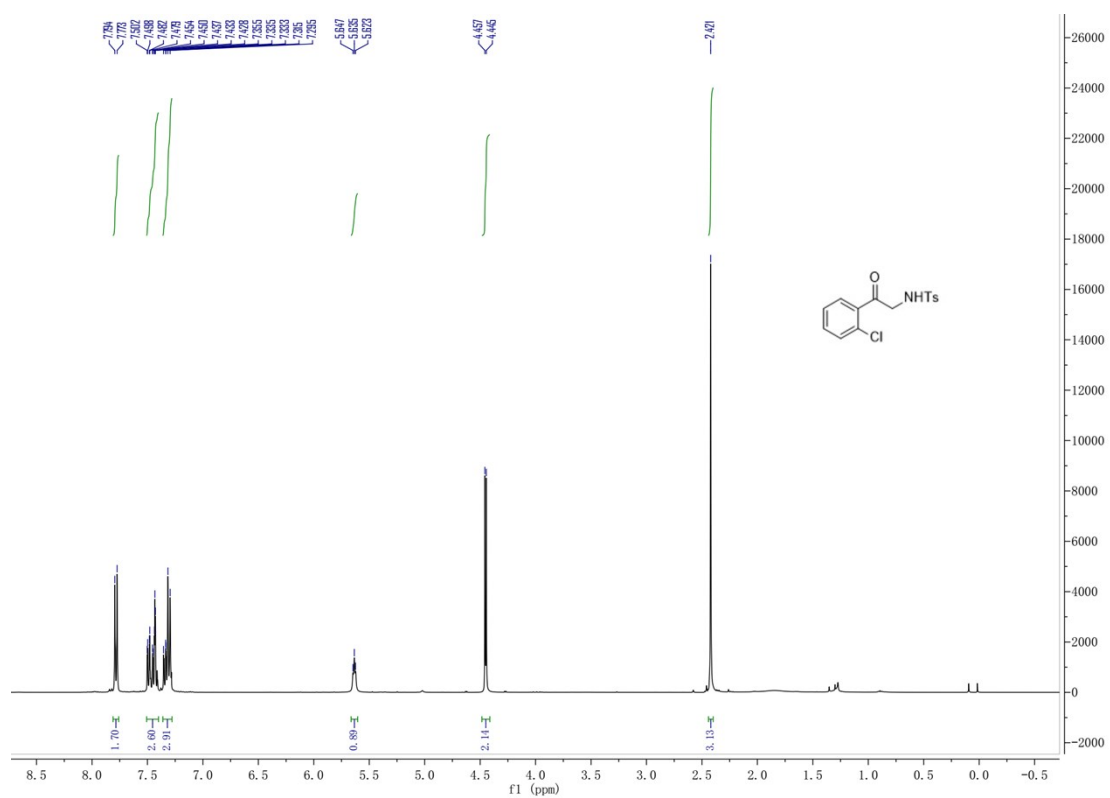




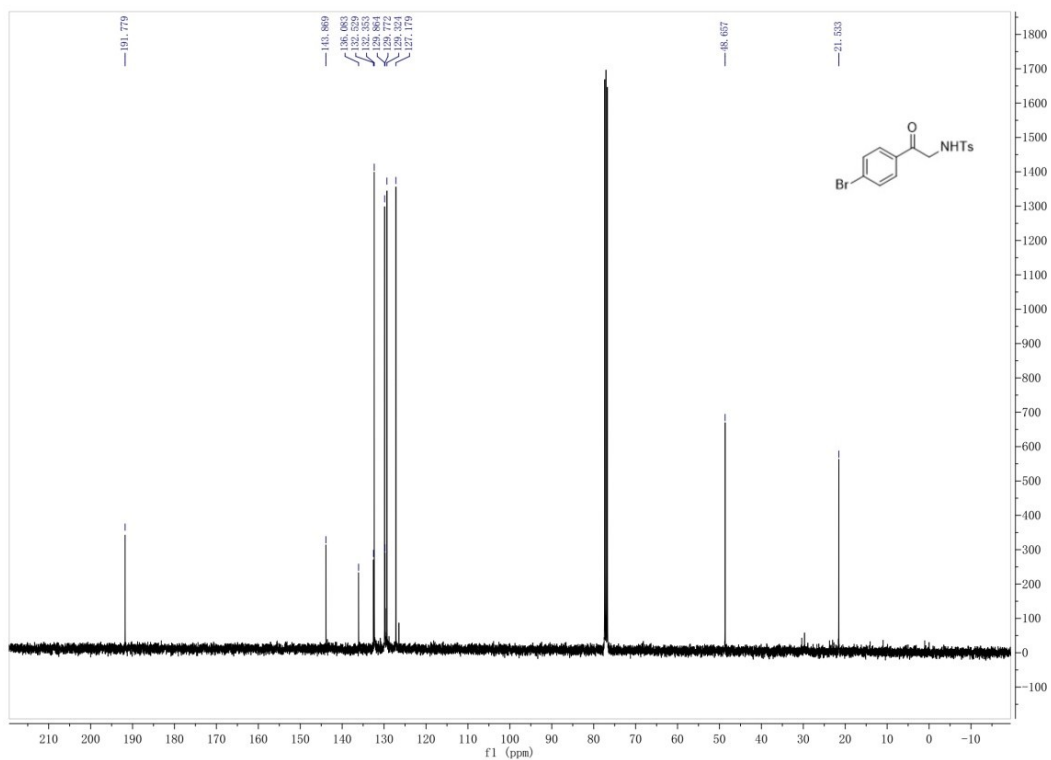
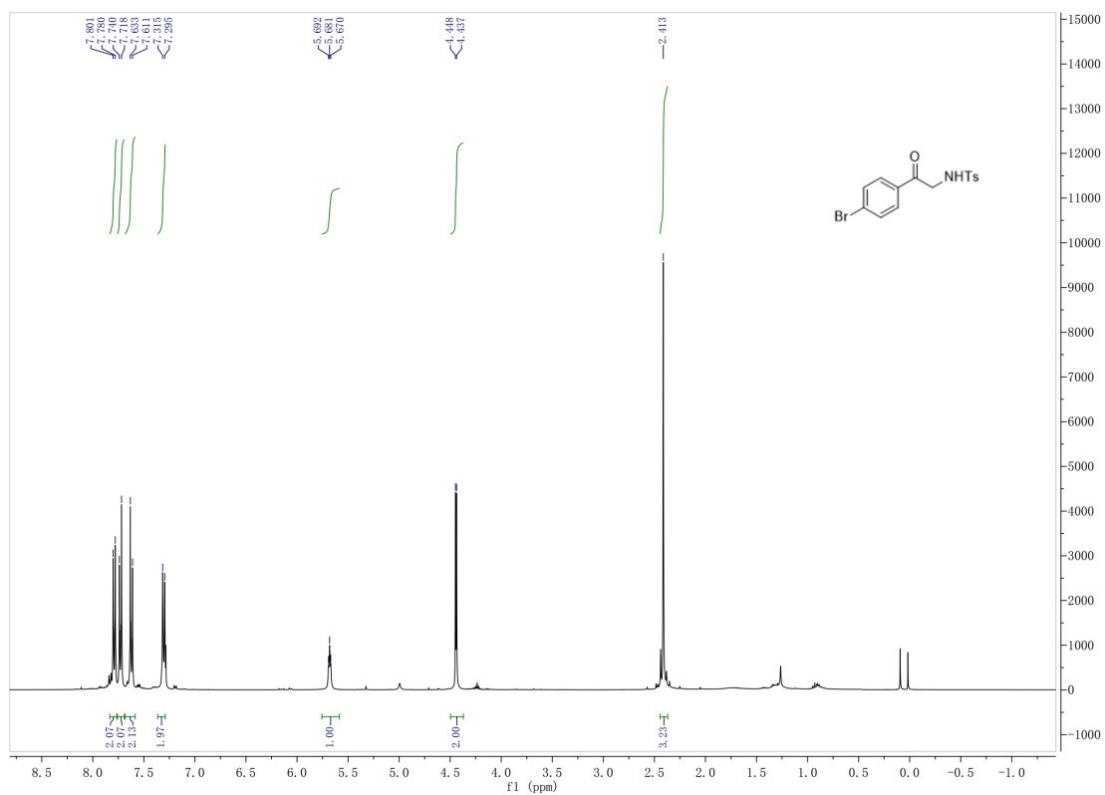


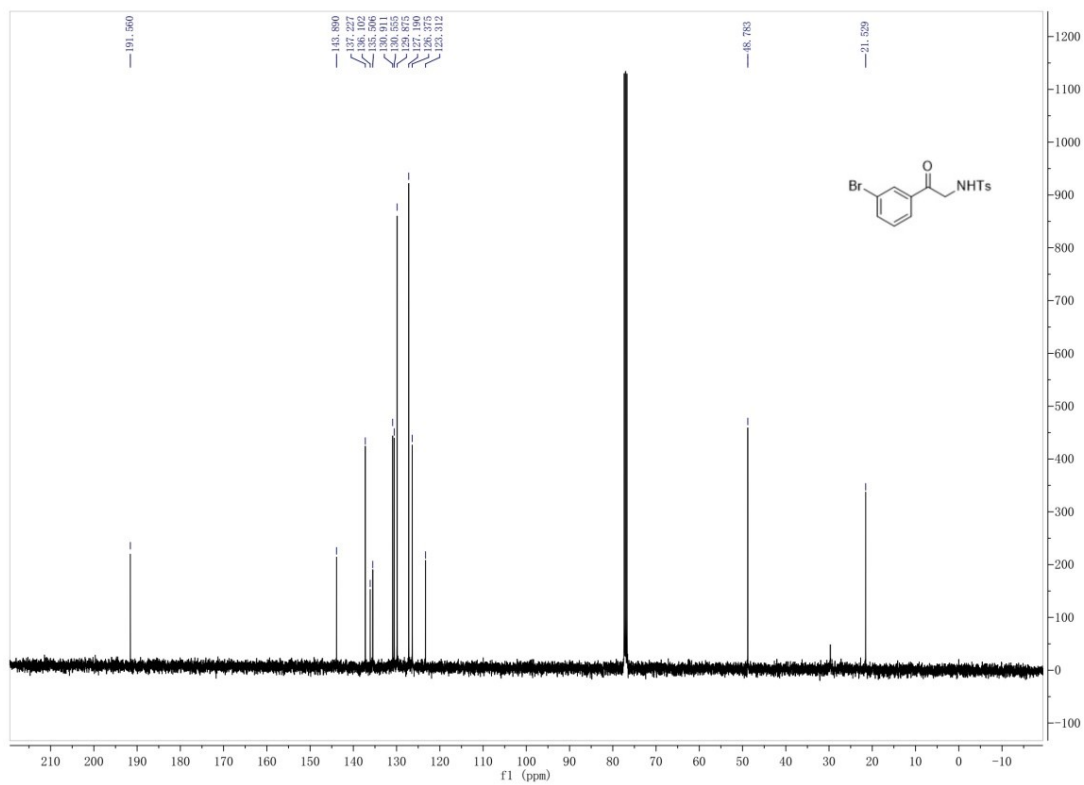
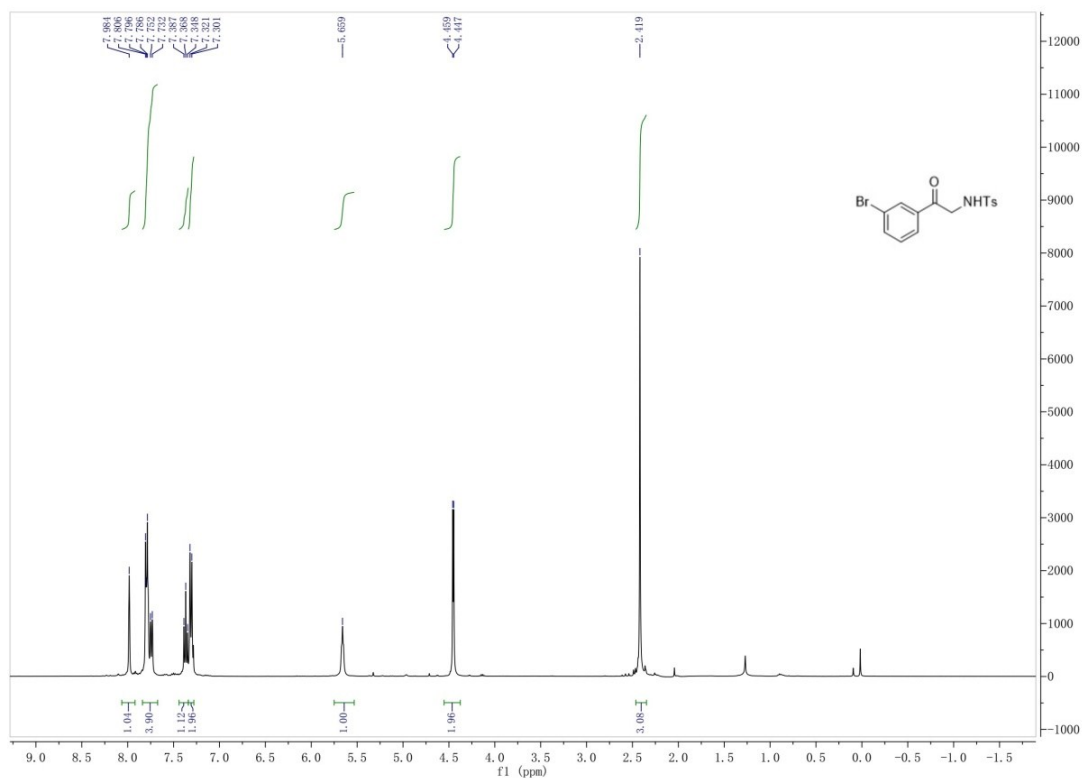


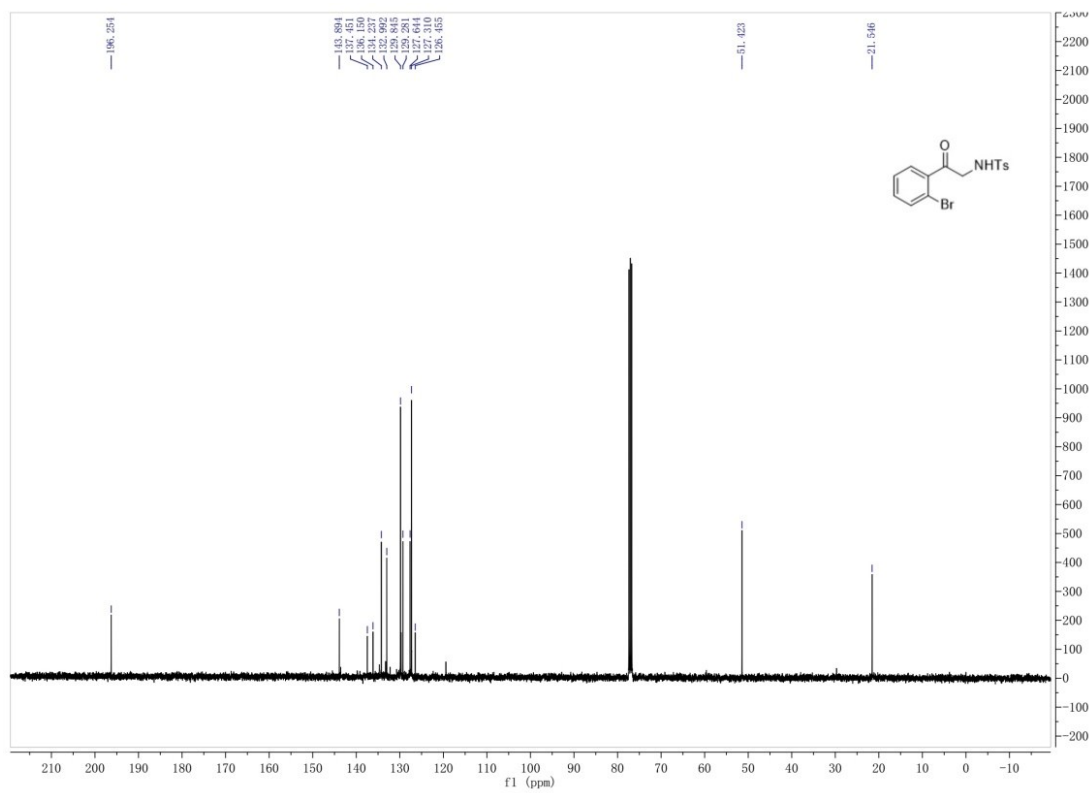
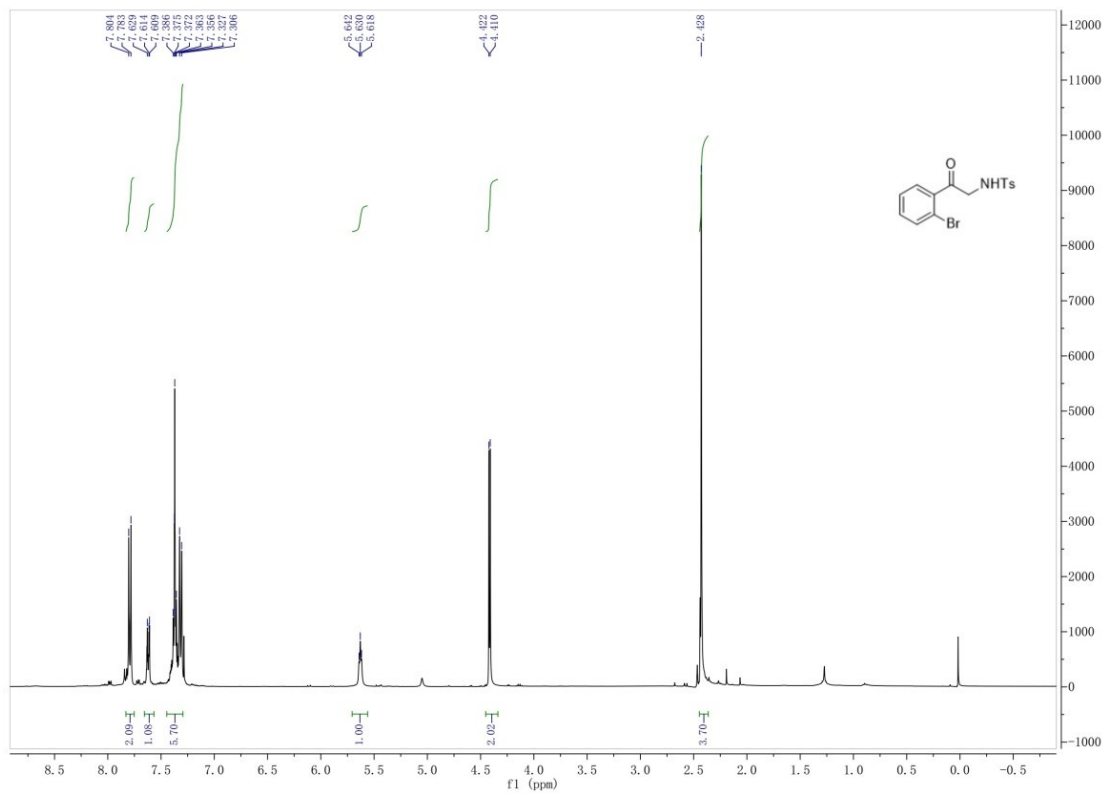


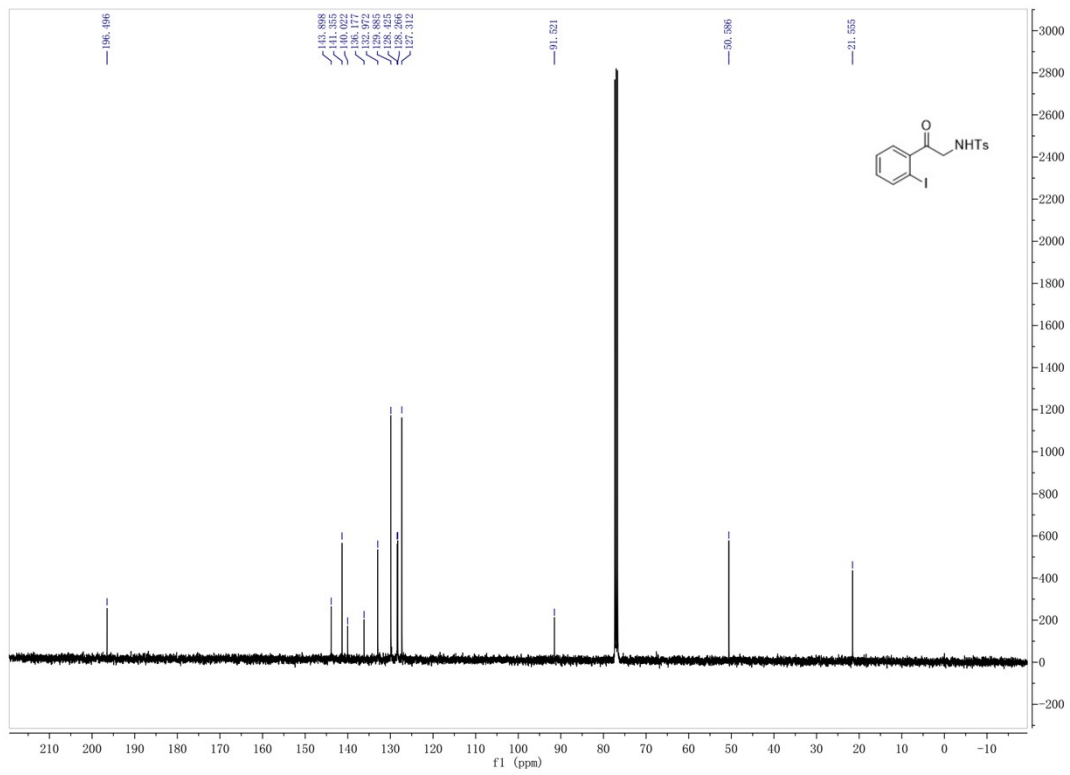
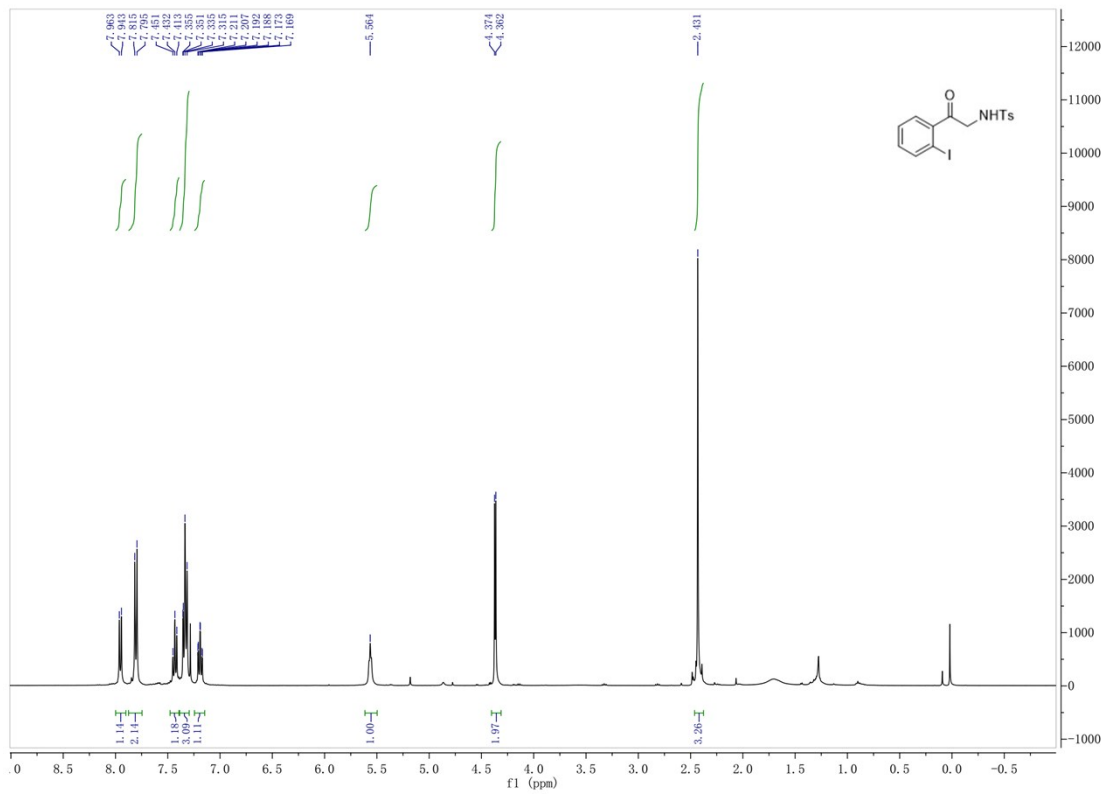




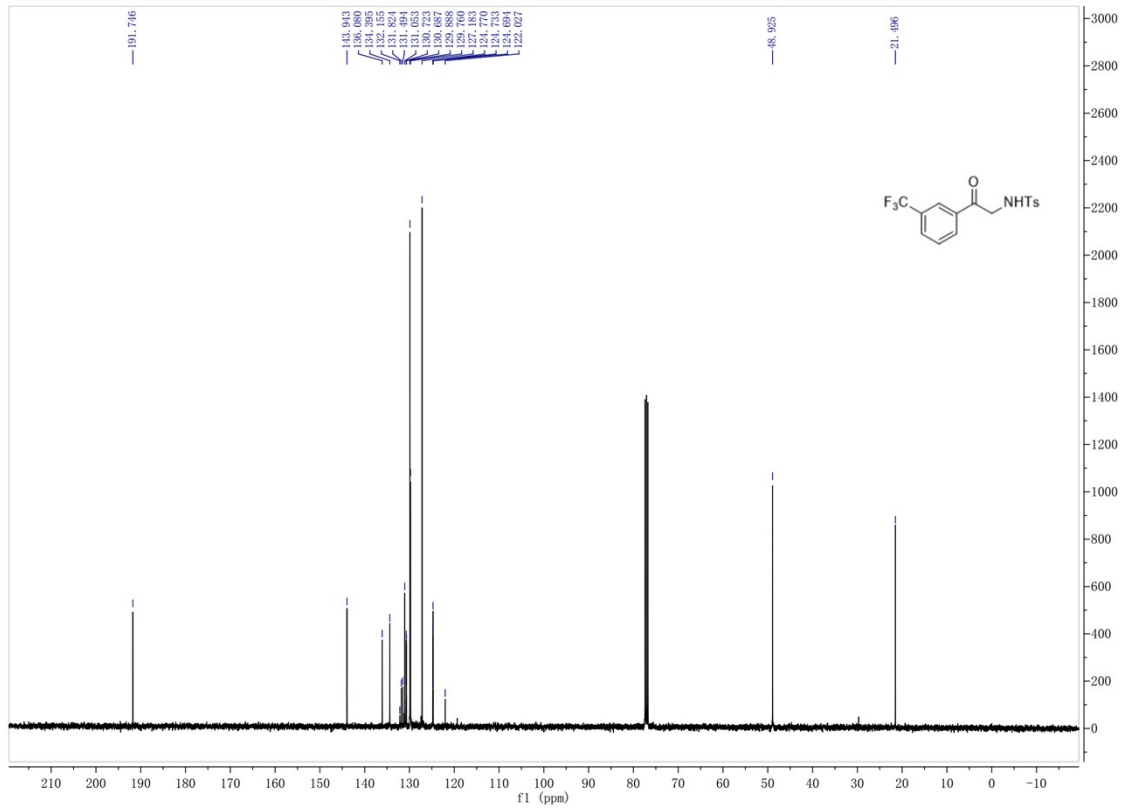
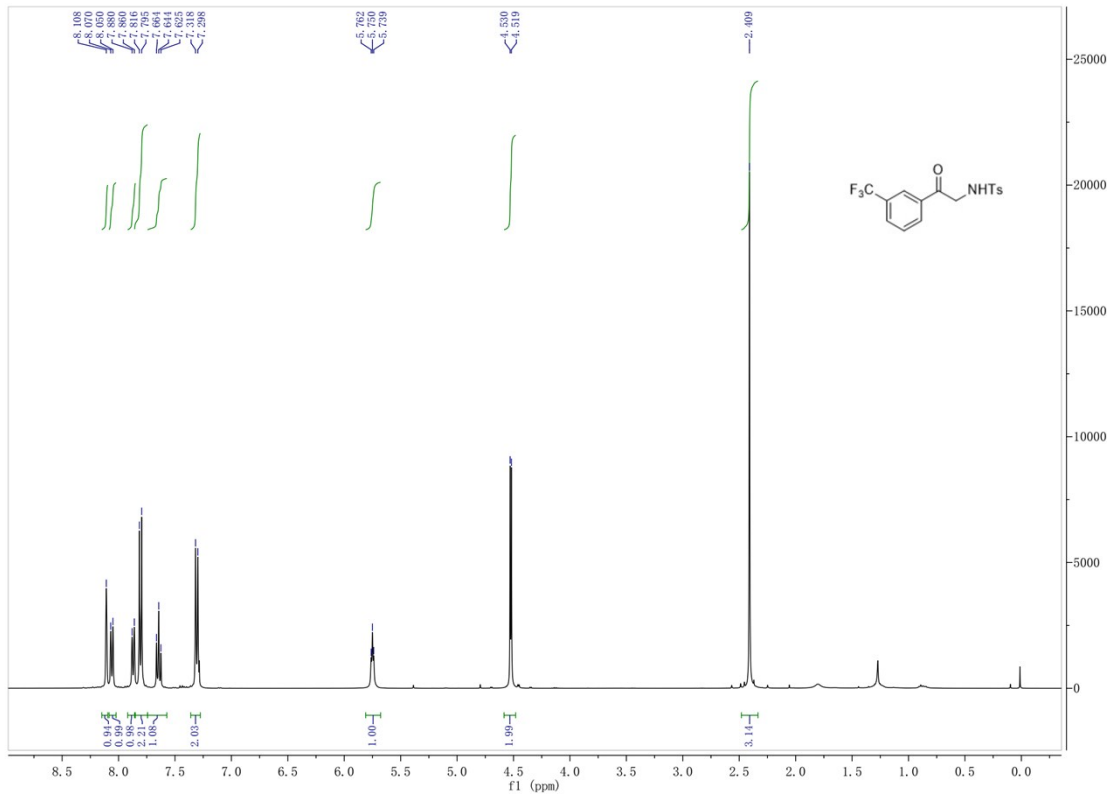


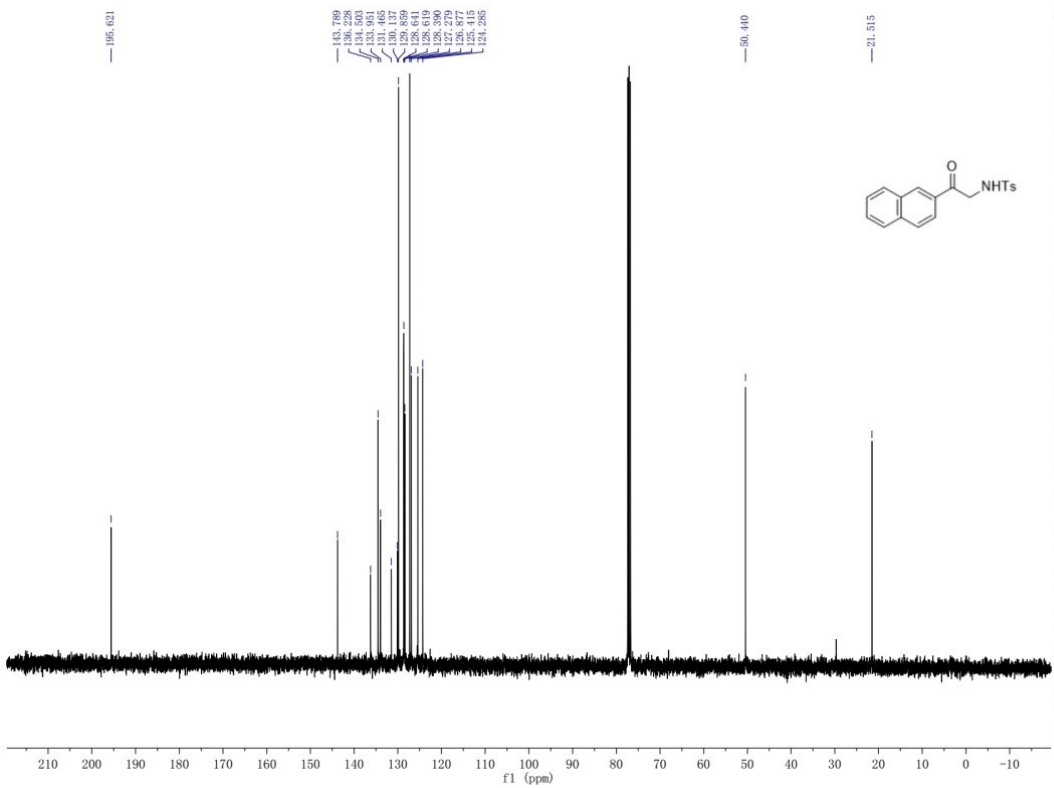
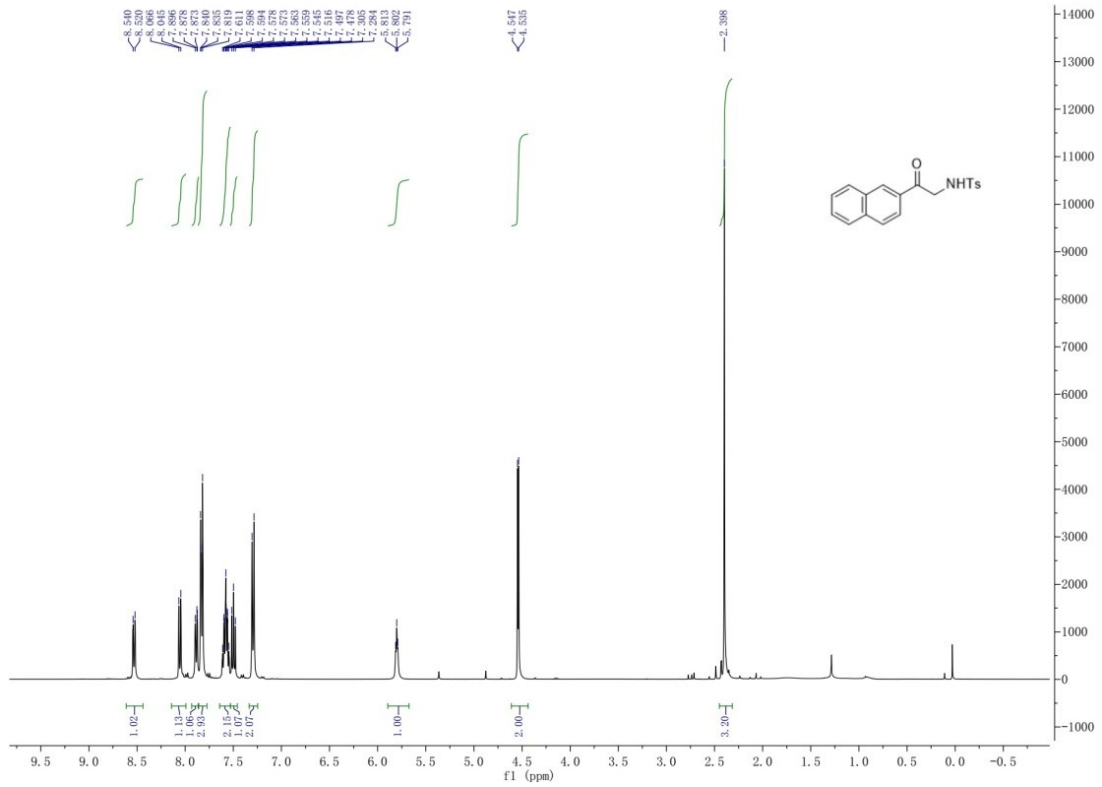


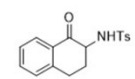
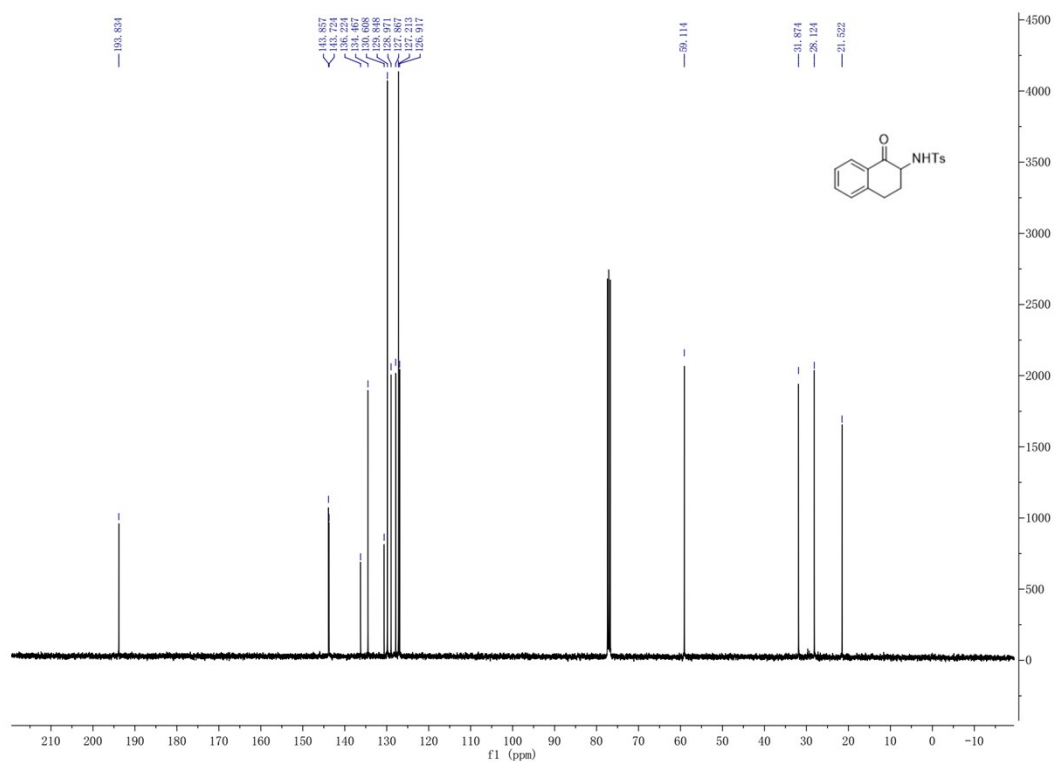
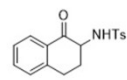
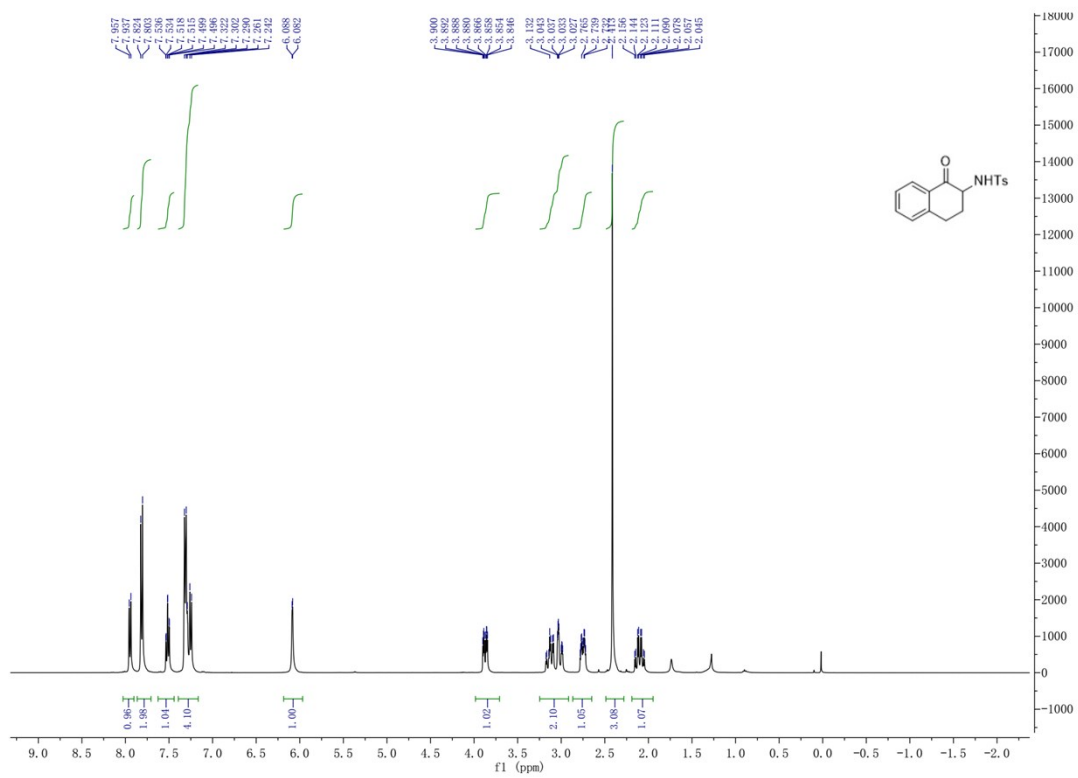




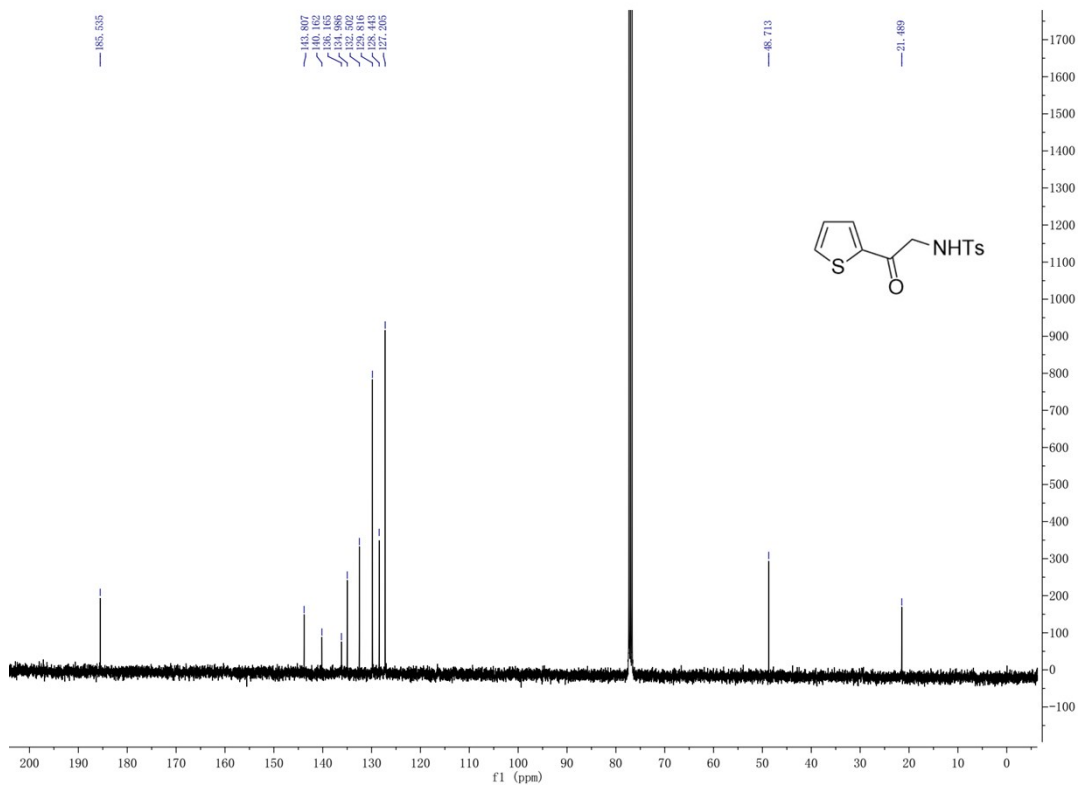
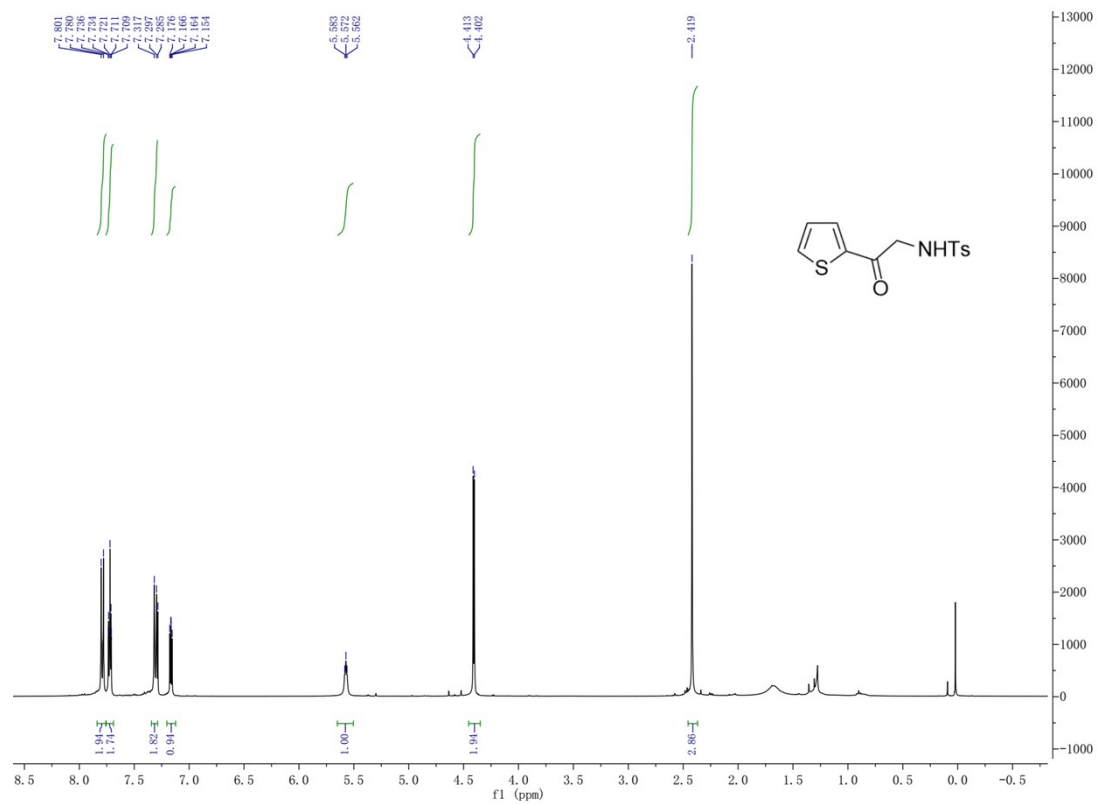


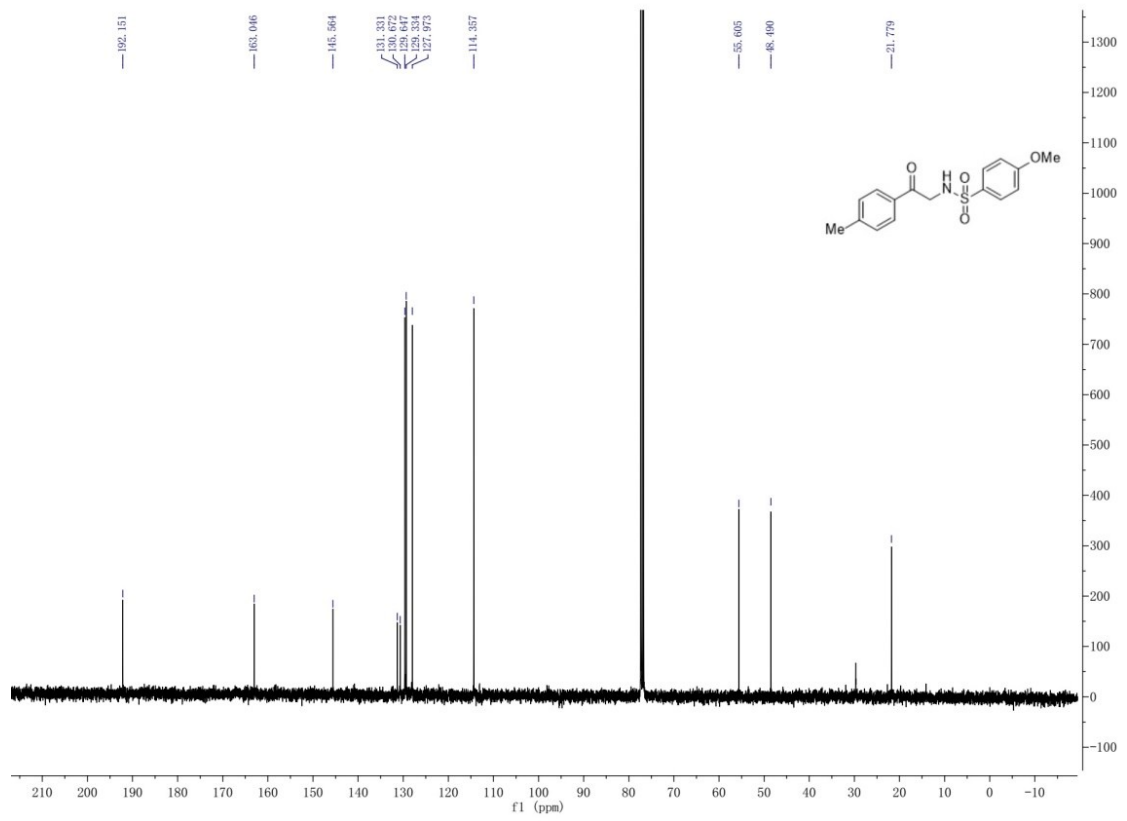
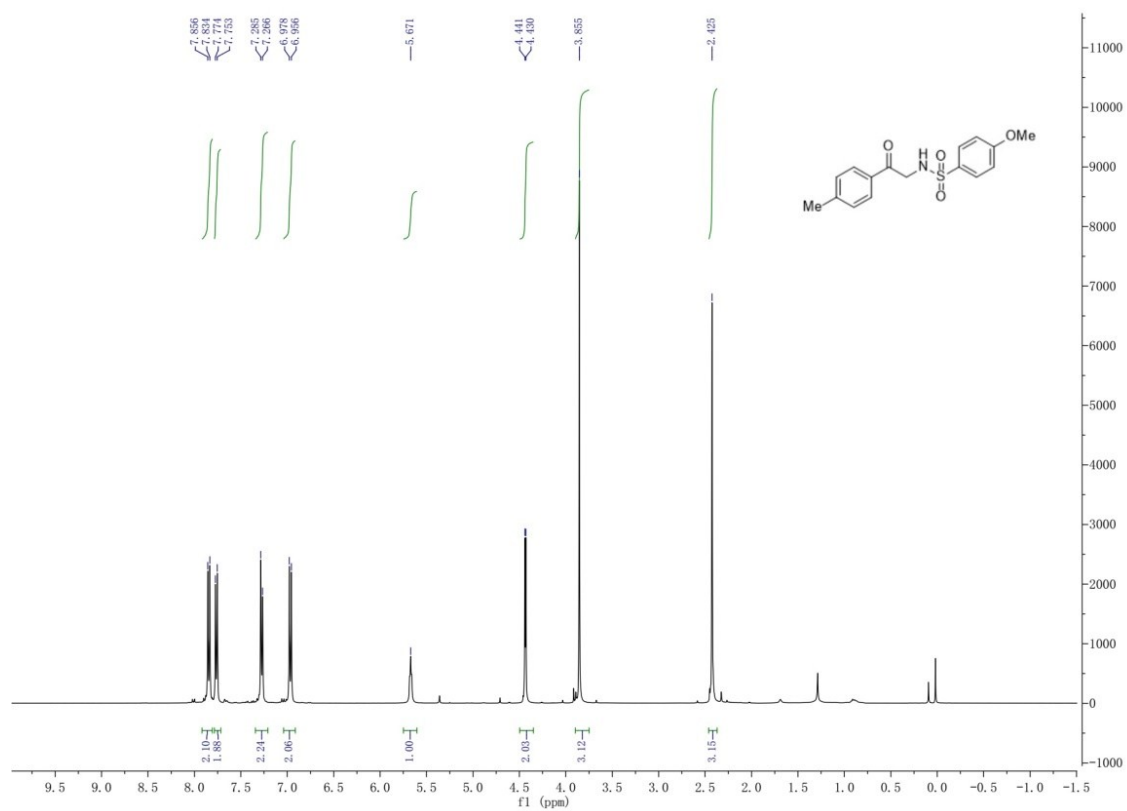


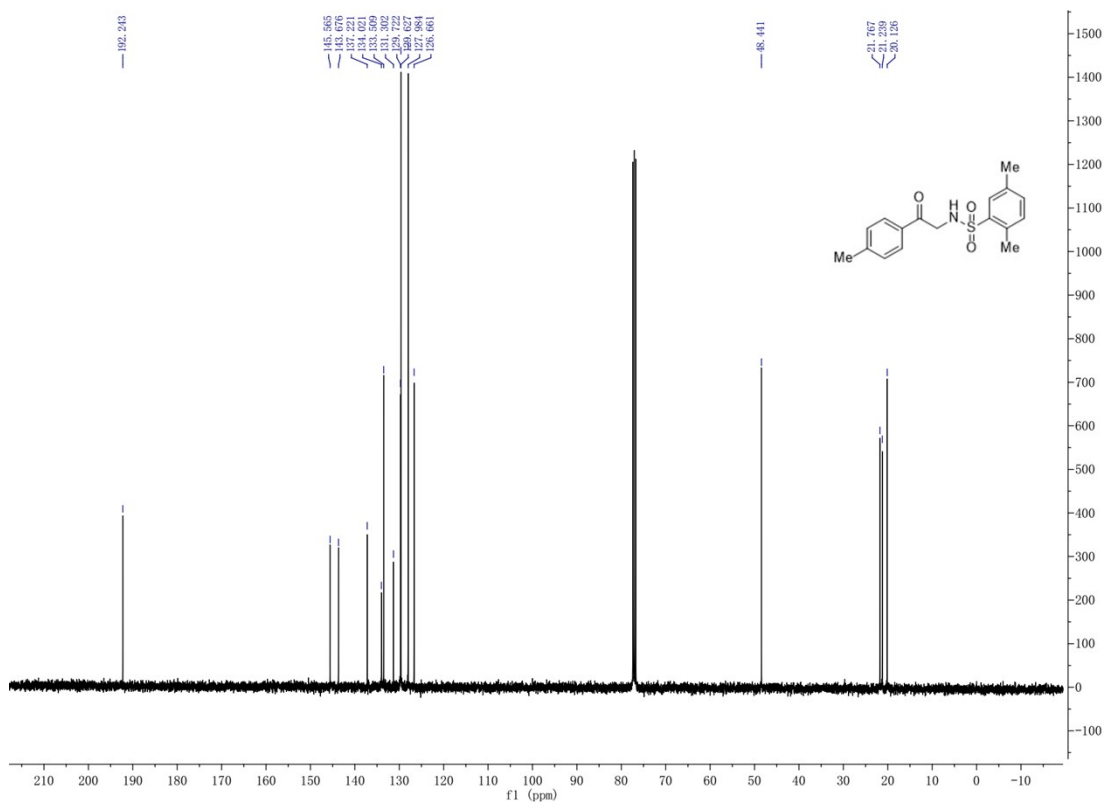
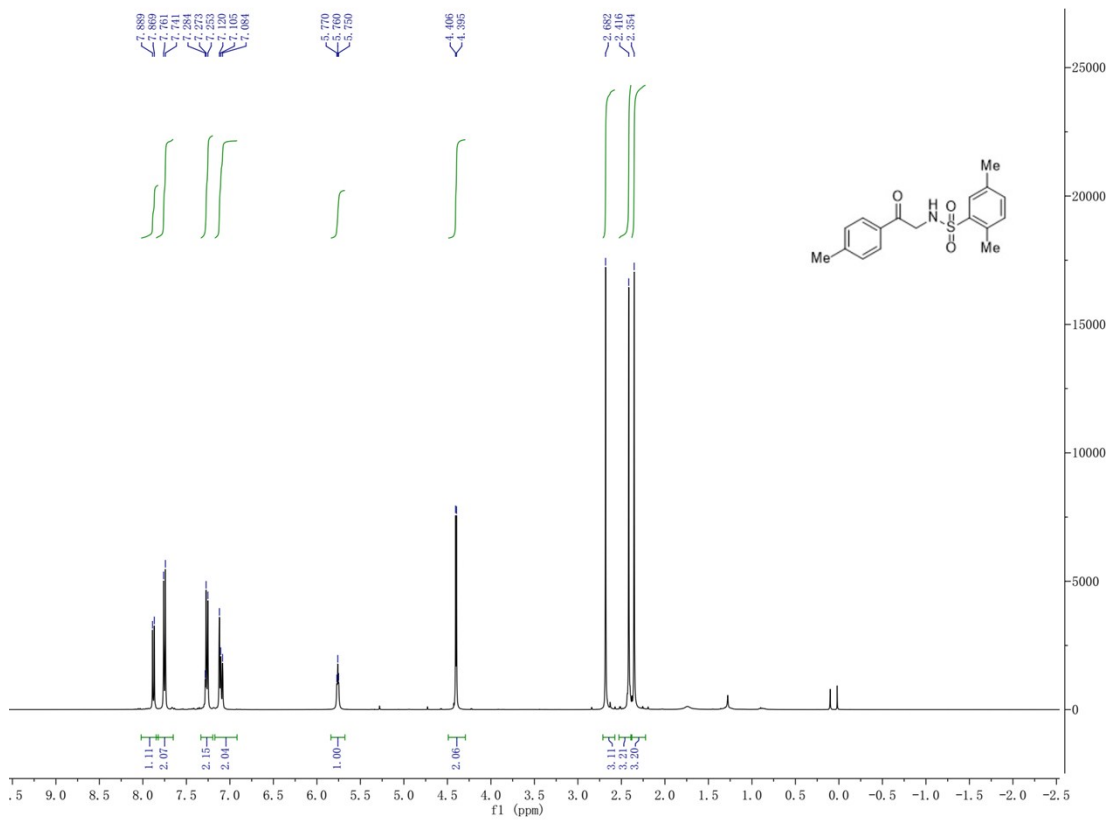


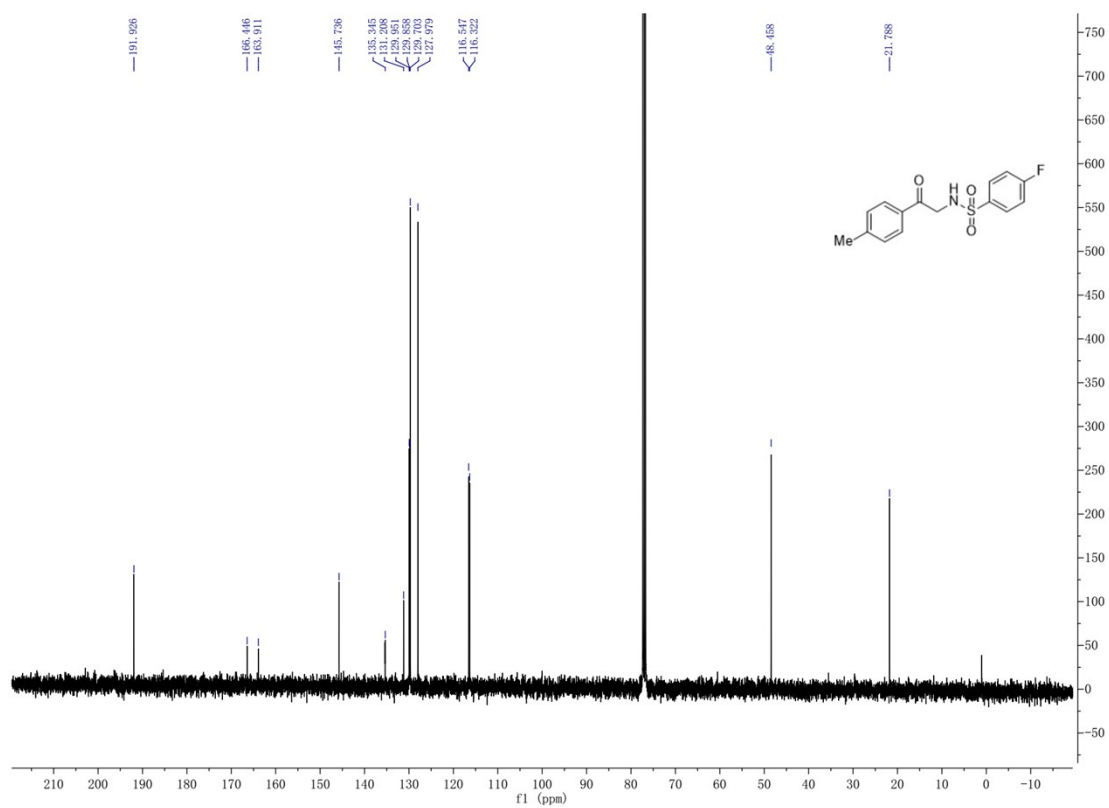
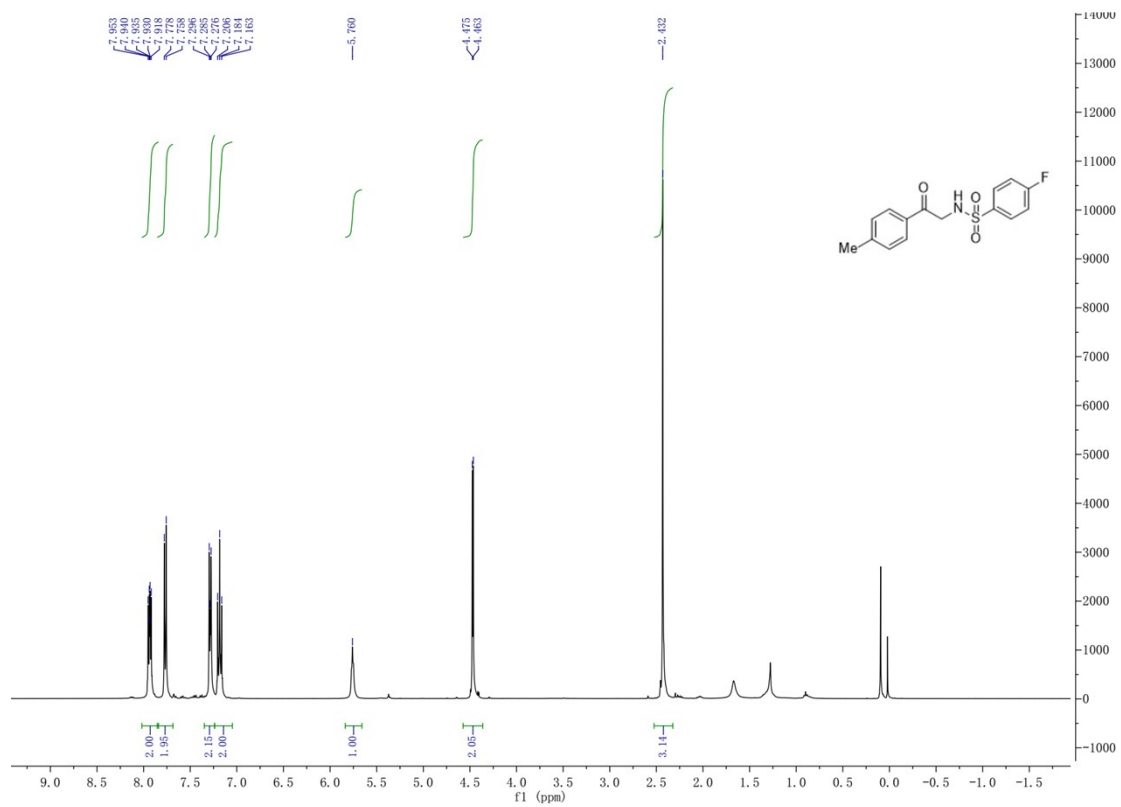


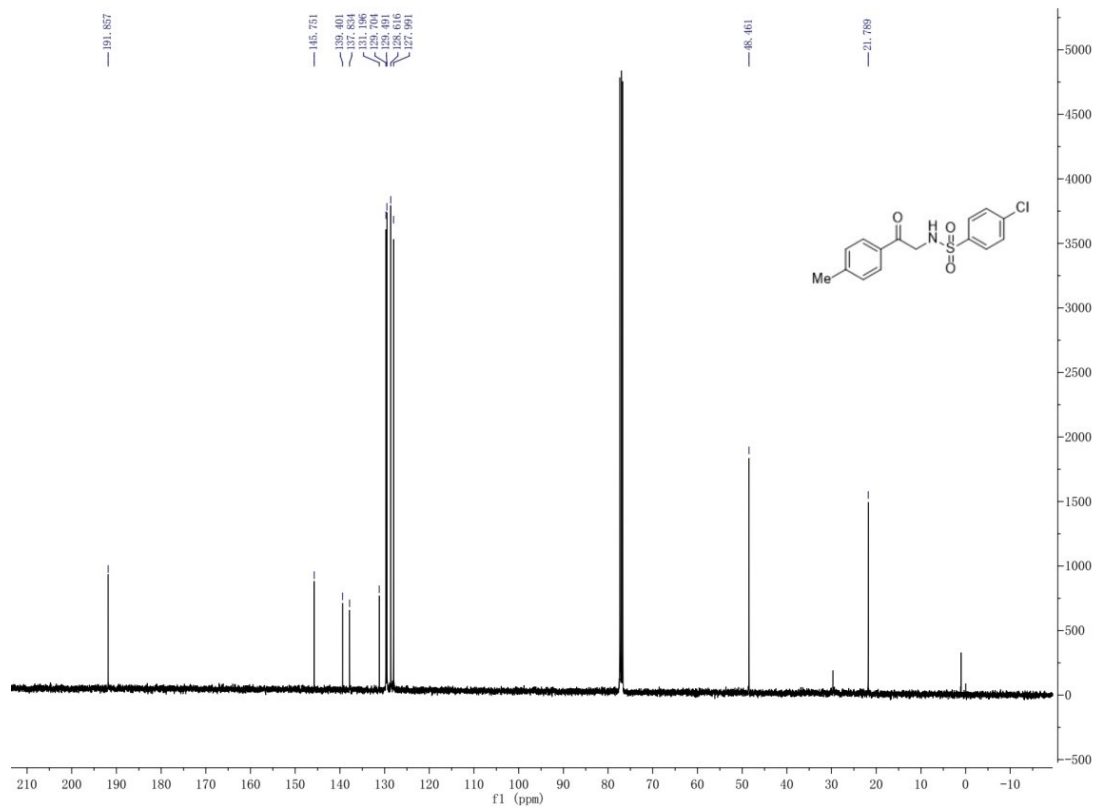
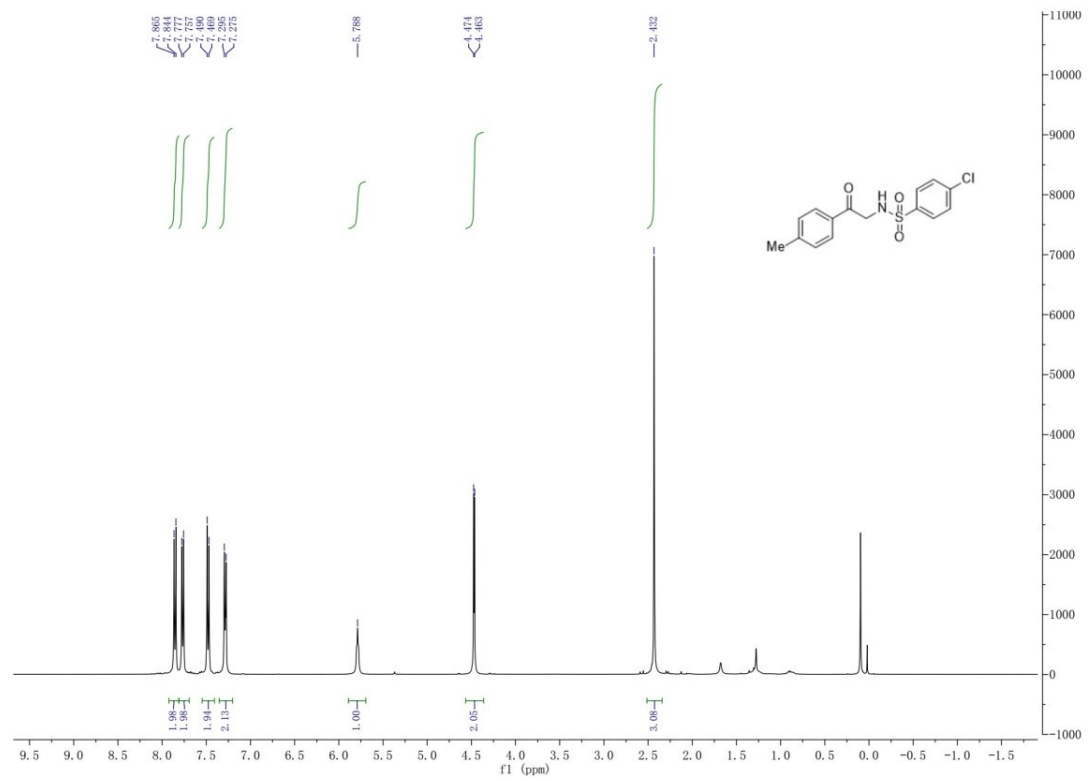


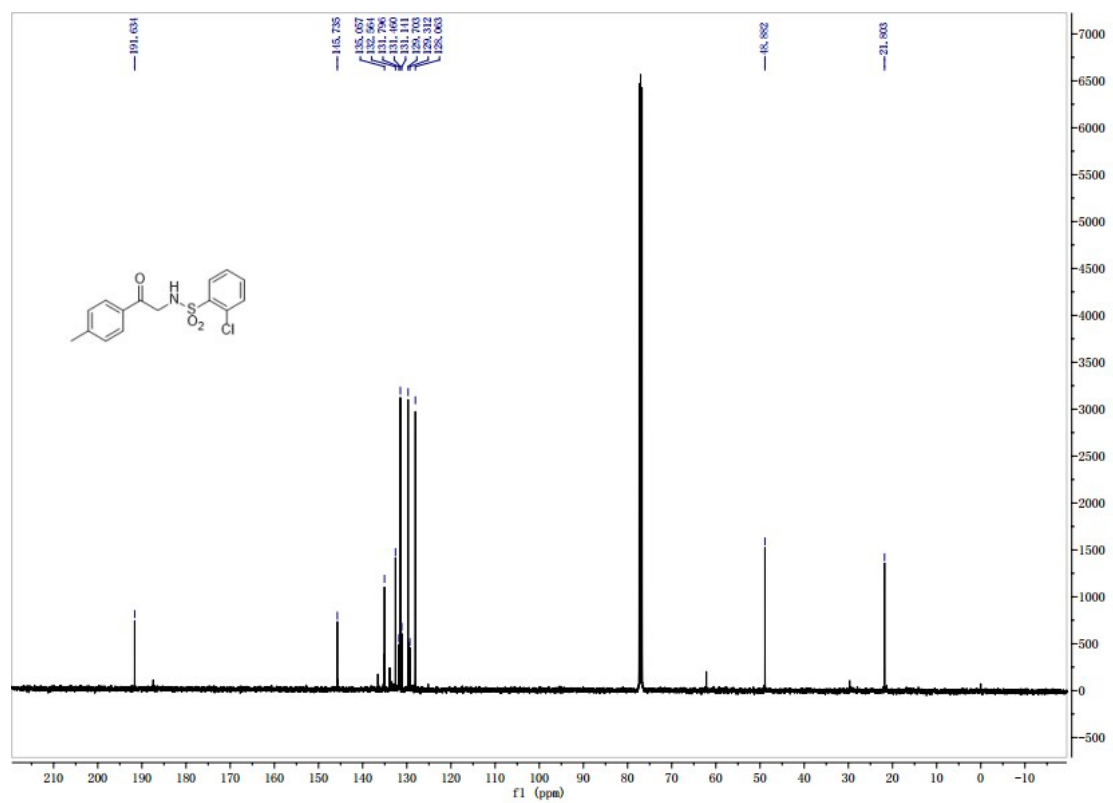
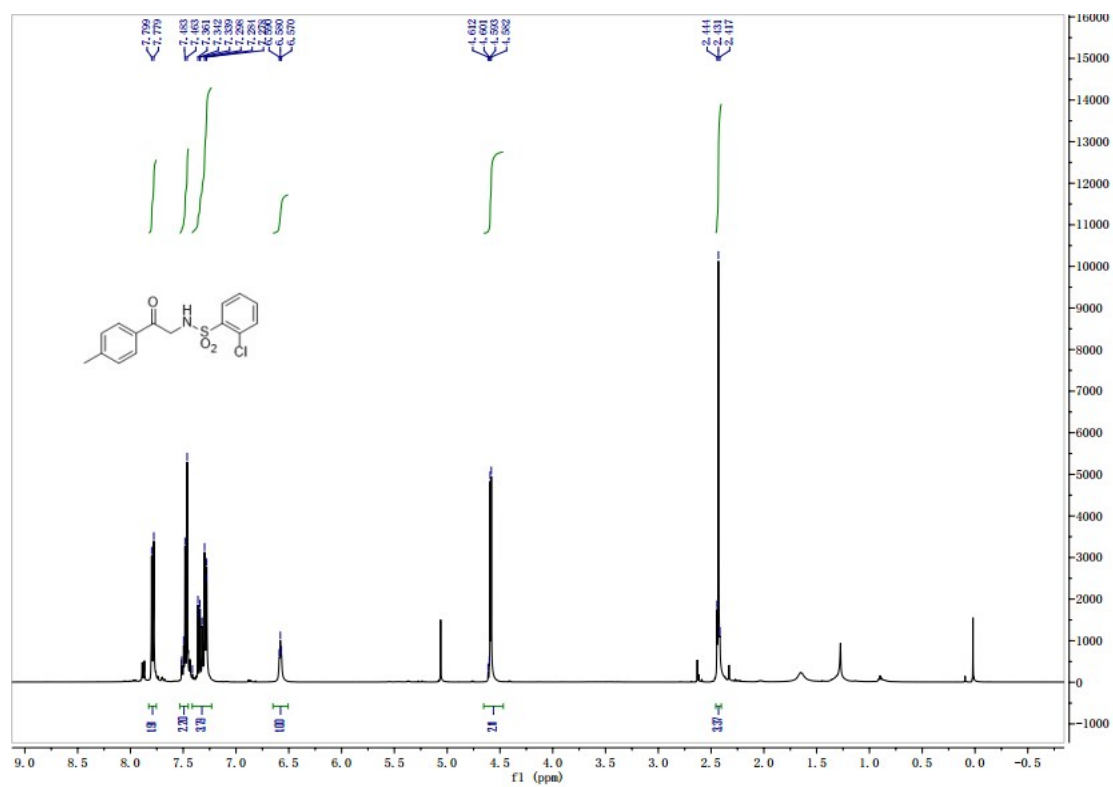


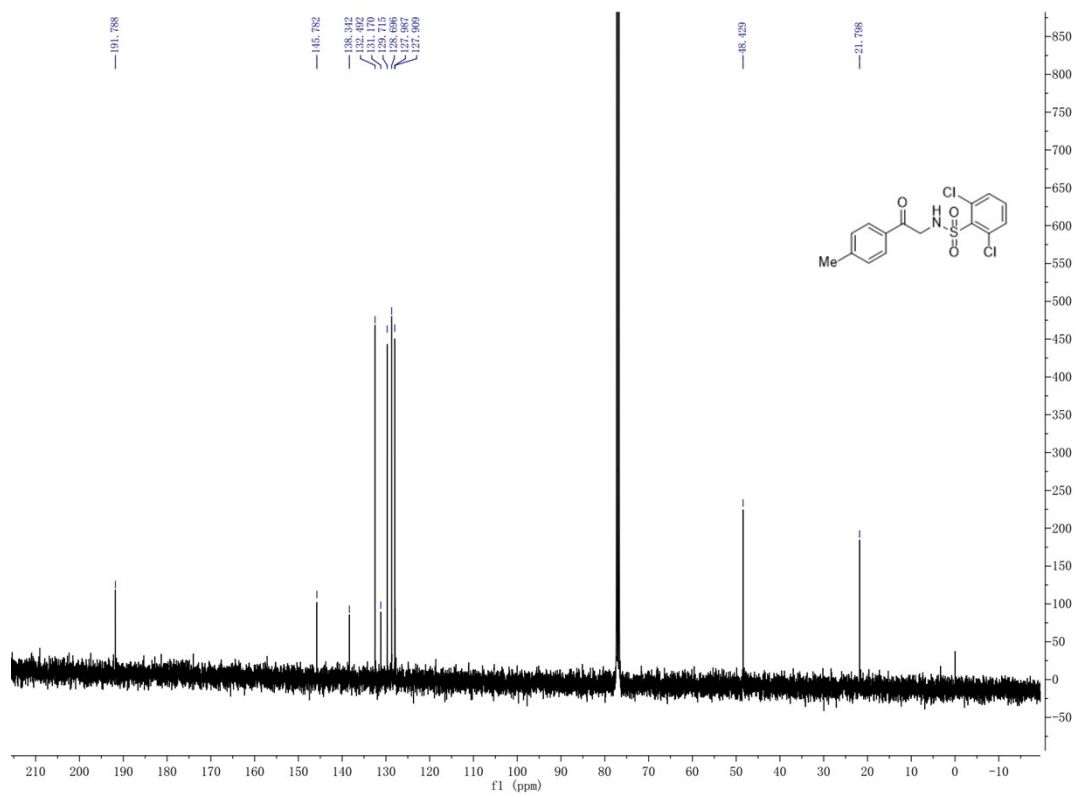
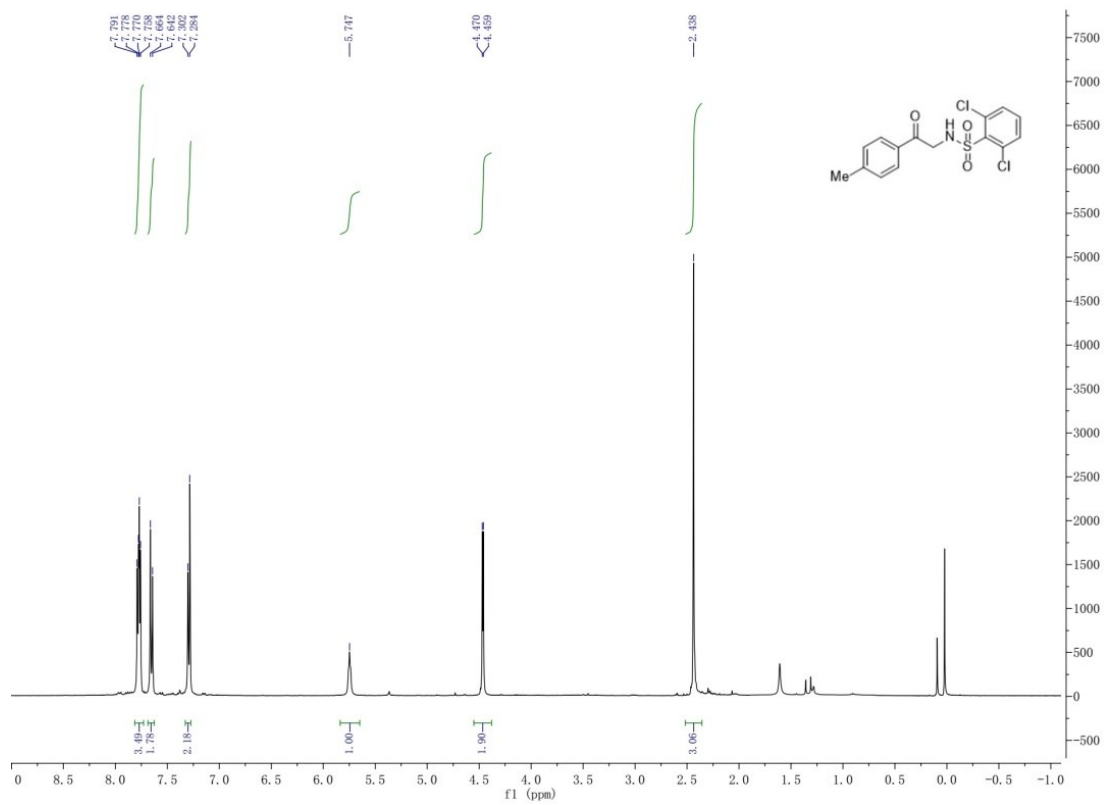


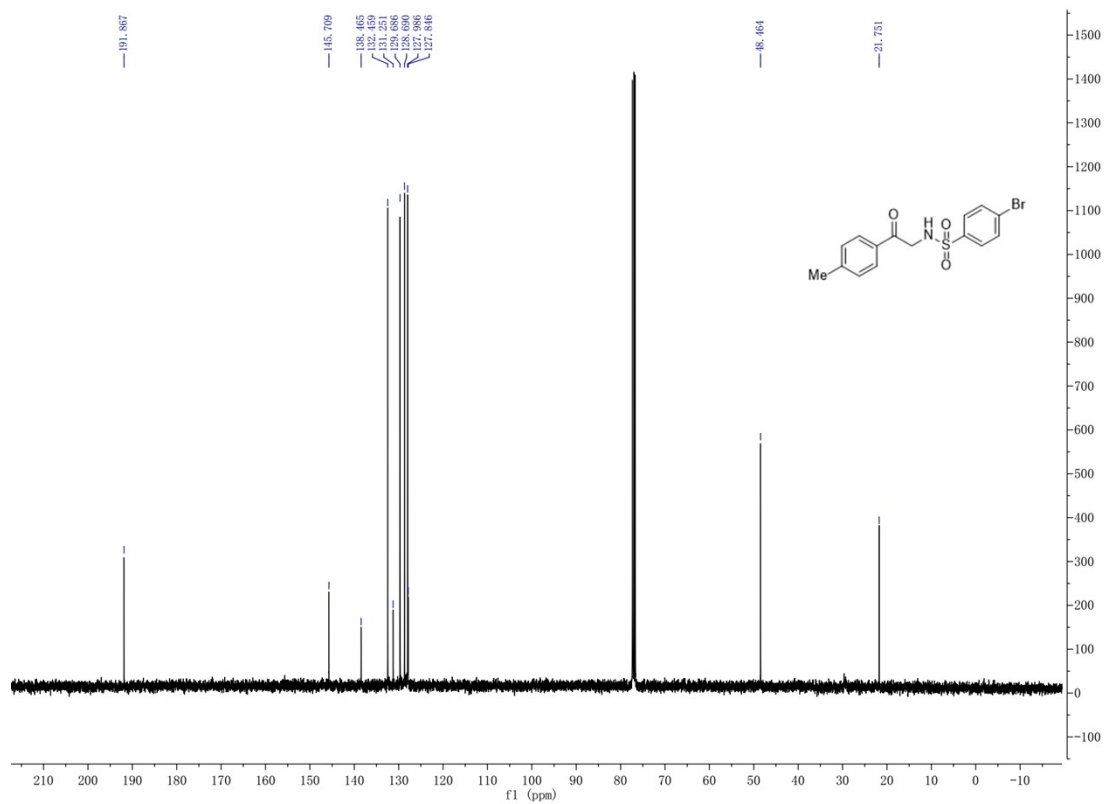
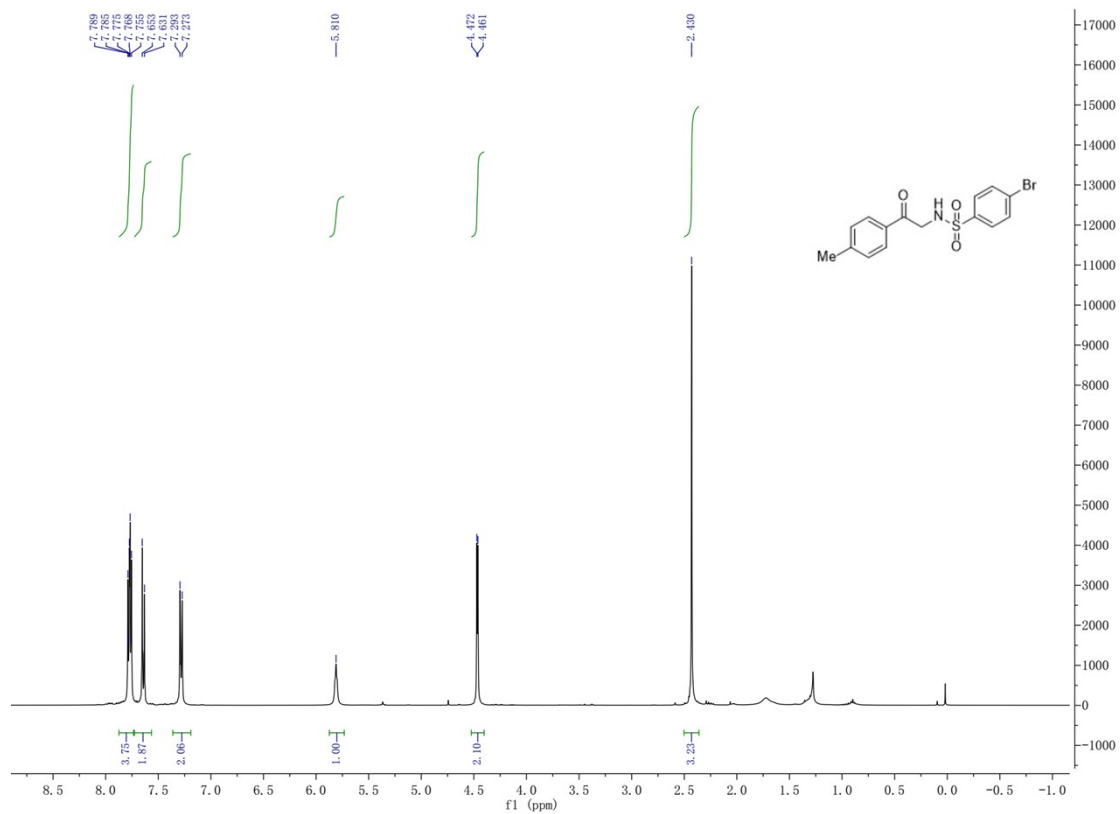




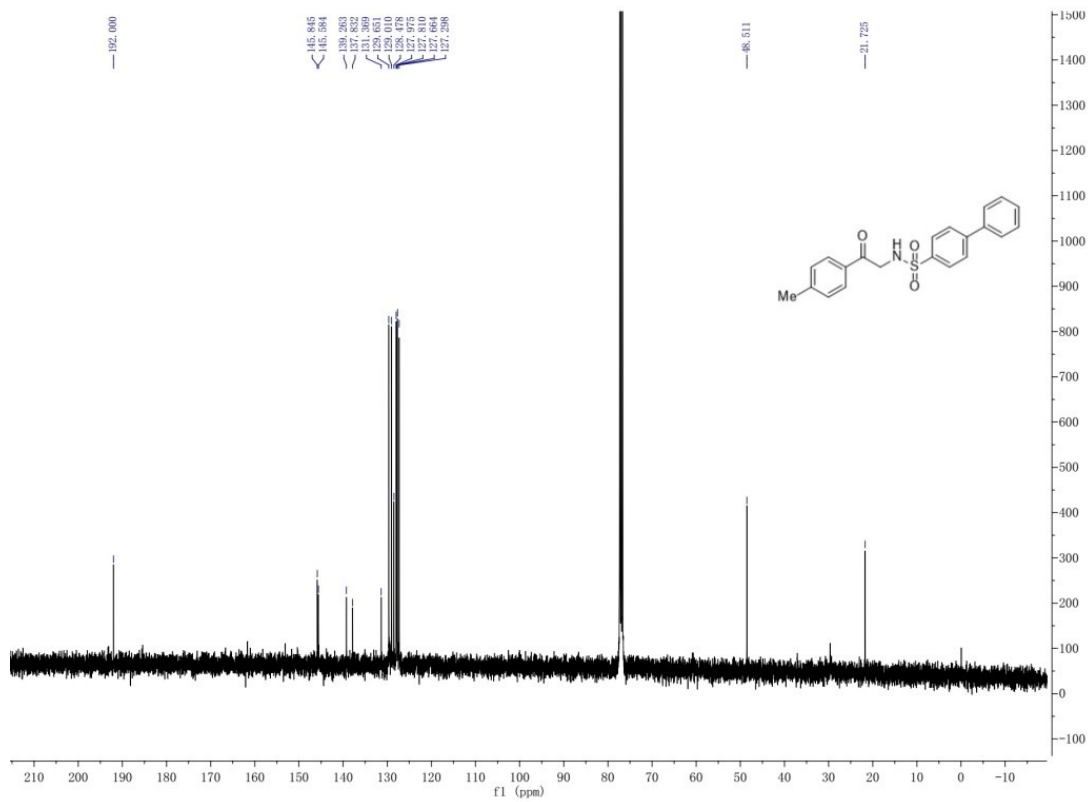
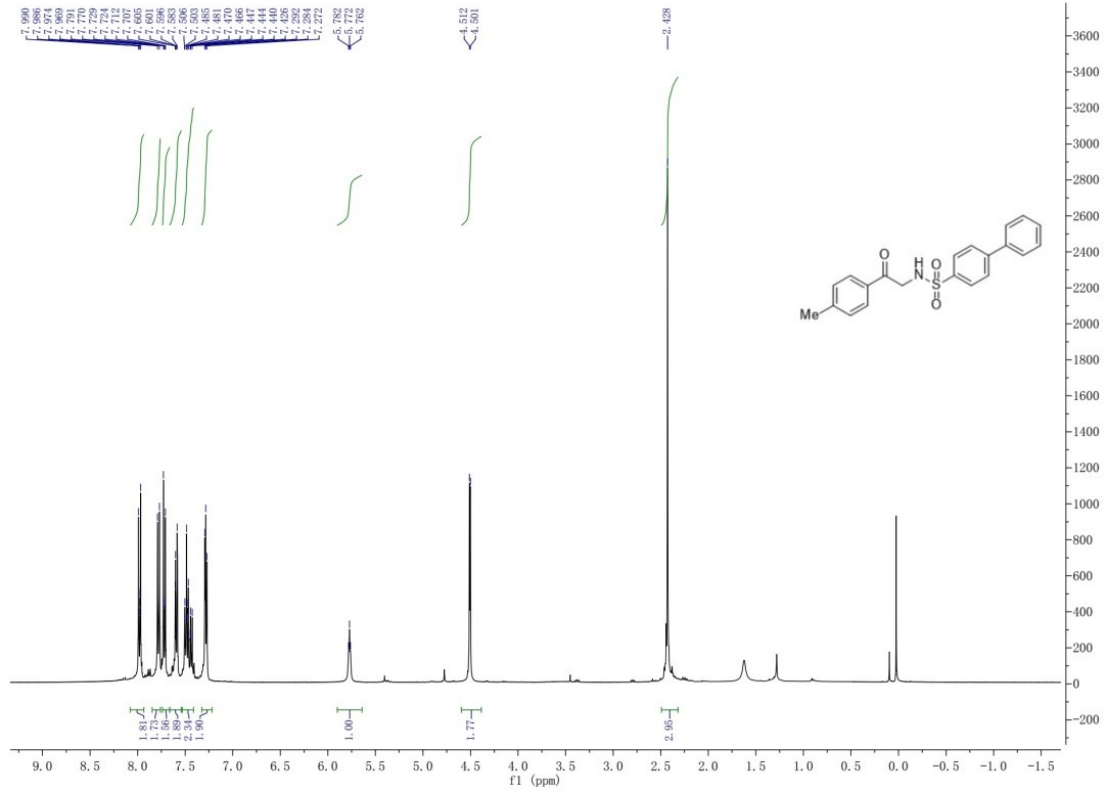


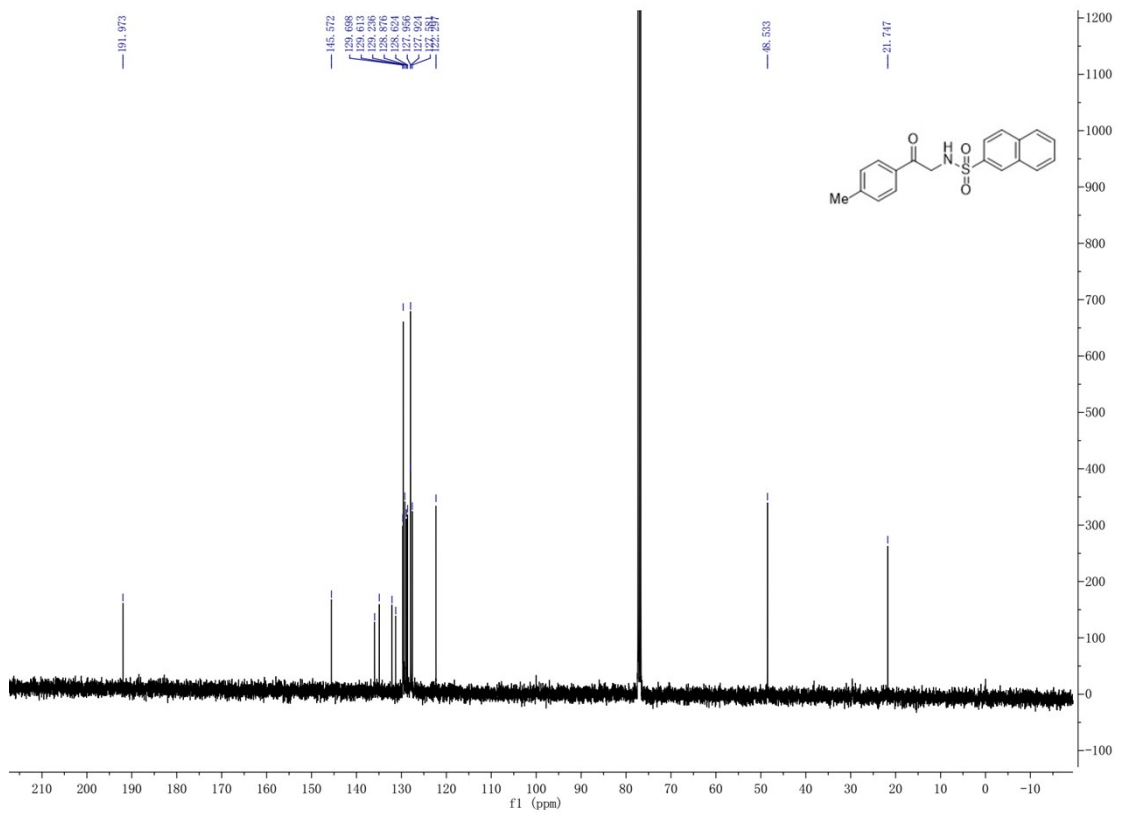
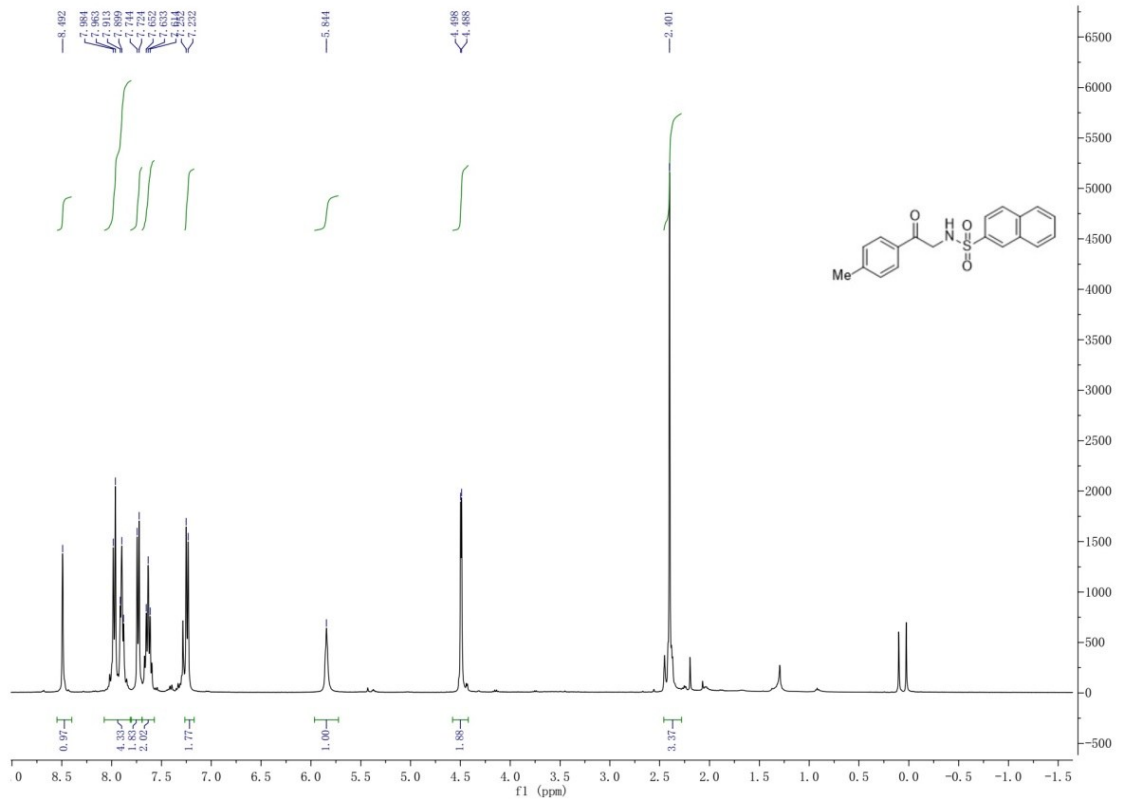












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