

## Supporting Information

### **Mn(OAc)<sub>3</sub> promoted cross-coupling reaction of disulfides with dialkyl phosphites**

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## 1. General information

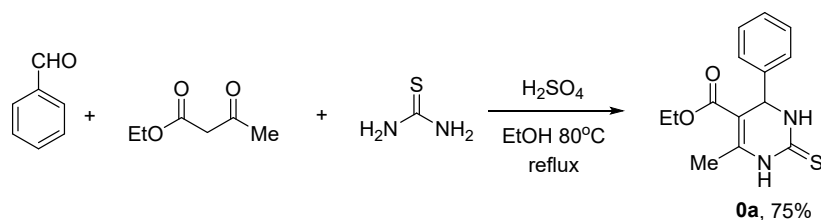
The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE III-600 MHz spectrometer with  $\text{CDCl}_3$  as the solvent. The chemical shifts in  $^1\text{H}$  NMR spectra were determined with  $\text{Si}(\text{CH}_3)_4$  as the internal standard ( $\delta = 0.00$  ppm); the chemical shifts in  $^{13}\text{C}$  NMR spectra were determined based on the chemical shift of  $\text{CDCl}_3$  ( $\delta = 77.00$  ppm). The coupling constants ( $J$  value) are reported in Hz (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, br = broad signal). The high resolution mass spectra (HRMS) were measured on a Thermo Scientific ORBITRAP ELITE by ESI. Flash column chromatography (FCC) was conducted on silica gel (200 – 300 mesh).

$\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ , DTBP, TBHP were purchased from Energy Chemical and used without further treatment. Unless otherwise noted, all other materials were obtained from commercial suppliers, and were used without further purification.

## 2. Experimental procedures

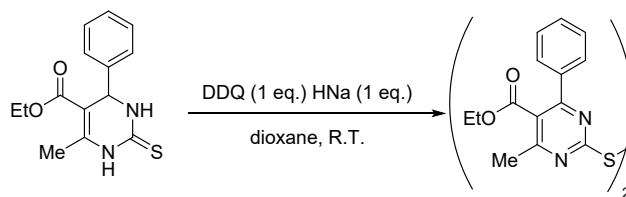
### Synthesis of starting material 1a:

#### Step 1



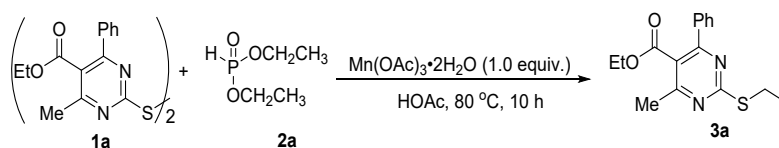
To the mixture of Benzaldehyde (6.3672 g, 60 mmol), Ethyl acetoacetate (7.8084 g, 60 mmol), thiocarbamide (5.480g, 72 mmol) in  $\text{CH}_3\text{CH}_2\text{OH}$  (15.0 mL) was added 20 drops 98%  $\text{H}_2\text{SO}_4$  in 100mL round-bottom flask. The reaction mixture was heated to 80 °C and stirred for 8 h. Extracting by Buchner funnel and dried white solid.

#### Step 2



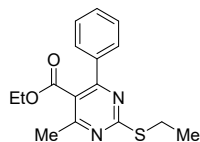
To the mixture of ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **0a** (1.470 g, 5 mmol), 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.135g, 5 mmol) HNa (0.120 g, 5 mmol), in dioxane (15.0 mL) in 100mL round-bottom flask. The reaction mixture at room temperature and stirred for 8 h. Then, 2mL diluted hydrochloric acid were added to the mixture to quench the reaction and extracted with ethyl acetate (3×100 mL). The combined organic layers were washed with aqueous NaHCO<sub>3</sub> and brine, dried over MgSO<sub>4</sub>, filtered, and the volatiles were removed in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether 1:10) to give the **1a**.

### Synthesis of product 3a



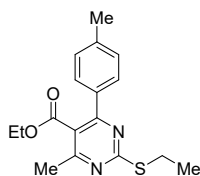
A 10 mL tube equipped with a magnetic stirring bar and a rubber stopper was charged with 1,2-Di(pyrimidin-2-yl) Disulfides **1a** (109.2 mg, 0.2 mmol), dialkyl phosphite ester **2a** (60.72 mg, 0.44 mmol), Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (26.8 mg, 0.2 mmol, 1 equiv.) and HOAc (2 mL). The mixture was stirred at 80 °C (oil bath) for 10 h and the reaction was monitored by TLC analysis. After the reaction mixture was cooled to room temperature, it was quenched with aqueous NH<sub>4</sub>Cl (2 mL), and the product was extracted with ethyl acetate (3×5 mL). The combined organic phases were washed with brine (3×5 mL), and dried over anhydrous NaSO<sub>4</sub>. The solvent was removed under reduced pressure with a rotary evaporator to give the crude product, which was purified by flash chromatography (PE and EA) to afford the corresponding products.

### 3. Characterization of products



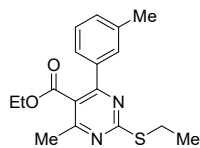
**Ethyl 2-(ethylthio)-4-methyl-6-phenylpyrimidine-5-carboxylate (3a).**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 55 mg, yield: 90%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.62 (m, 2H), 7.49 – 7.42 (m, 3H), 4.16 (t, *J* = 7.2 Hz, 1H), 3.22 (t, *J* = 7.2 Hz, 1H), 2.56 (s, 3H), 1.42 (d, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.24, 168.13, 165.50, 163.59, 137.79, 130.01, 128.40, 128.28, 120.93, 61.66, 25.35, 22.61, 14.50, 13.59; HRMS (ESI): *m/z* ([*M*+*H*]<sup>+</sup>) Calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>S 303.1162; Found 303.1165.



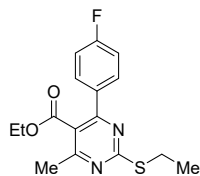
**Ethyl 2-(ethylthio)-4-methyl-6-(*p*-tolyl)pyrimidine-5-carboxylate (3b).**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 56 mg, yield: 89%; <sup>1</sup>H NMR (600 MHz, cdcl<sub>3</sub>) δ 7.57 – 7.52 (m, 2H), 7.24 – 7.22 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.20 (q, *J* = 7.2 Hz, 2H), 2.54 (s, 3H), 2.40 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.05, 168.33, 165.27, 163.35, 140.36, 134.85, 129.13, 128.27, 120.75, 61.64, 25.32, 22.57, 21.37, 14.52, 13.67; HRMS (ESI): *m/z* ([*M*+*H*]<sup>+</sup>) Calcd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S 317.1318; Found 317.1313.



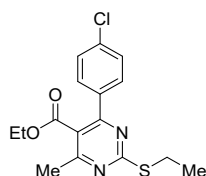
**Ethyl 2-(ethylthio)-4-methyl-6-(*m*-tolyl)pyrimidine-5-carboxylate (3c).**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 56 mg, yield: 88%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.40 (m, 2H), 7.33 – 7.31 (m, 1H), 7.30 – 7.26 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.22 (q, *J* = 7.2 Hz, 2H), 2.55 (s, 3H), 2.40 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.16, 168.18, 165.36, 163.75, 138.12, 137.69, 130.78, 128.90, 128.30, 125.40, 120.97, 61.62, 29.68, 22.61, 21.40, 14.50, 13.62; HRMS (ESI): *m/z* ([*M*+*H*]<sup>+</sup>) Calcd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S 317.1318; Found 317.1321.



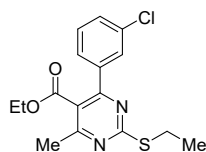
**Ethyl 2-(ethylthio)-4-(4-fluorophenyl)-6-methylpyrimidine-5-carboxylate (3d).**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 59 mg, yield: 92%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.63 (m, 2H), 7.14 – 7.11 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.21 (q, *J* = 7.2 Hz, 2H), 2.55 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.30, 168.06, 165.59, 164.78, 162.32, 133.83, 130.40, 130.38, 120.75, 115.61, 115.47, 61.76, 25.35, 22.63, 14.46, 13.70; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -109.69. HRMS (ESI): *m/z* ([M+H]<sup>+</sup>) Calcd for C<sub>16</sub>H<sub>18</sub>FN<sub>2</sub>O<sub>2</sub>S 321.1068; Found 321.1064.



**Ethyl 4-(4-chlorophenyl)-2-(ethylthio)-6-methylpyrimidine-5-carboxylate (3e).**

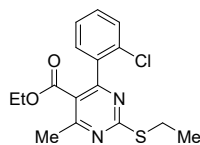
Colorless oil obtained by column chromatography (PE/EA = 30:1), 61 mg, yield: 90%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.54 (m, 2H), 7.24 – 7.20 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.21 (q, *J* = 7.2 Hz, 2H), 2.54 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.06, 168.35, 165.28, 163.37, 140.37, 134.86, 129.68, 129.14, 128.69, 128.28, 120.75, 61.65, 25.33, 21.38, 14.53, 13.68; HRMS (ESI): *m/z* ([M+H]<sup>+</sup>) Calcd for C<sub>16</sub>H<sub>18</sub>ClN<sub>2</sub>O<sub>2</sub>S 337.0772; Found 337.0775.



**Ethyl 4-(3-chlorophenyl)-2-(ethylthio)-6-methylpyrimidine-5-carboxylate (3f).**

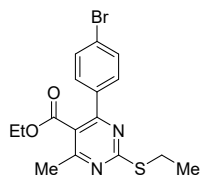
Colorless oil obtained by column chromatography (PE/EA = 30:1), 59 mg, yield: 87%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.54 (m, 1H), 7.50 – 7.43 (m, 1H), 7.38 – 7.35 (m, 1H), 7.24 – 7.23 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.21 (q, *J* = 7.2 Hz, 2H), 2.53 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.52, 167.69, 165.27, 163.35, 134.85, 130.01, 129.67, 129.12, 128.27, 126.44, 120.75, 61.64, 30.88, 21.36, 14.52, 14.41. HRMS (ESI): *m/z*

([M+H]<sup>+</sup>) Calcd for C<sub>16</sub>H<sub>18</sub>ClN<sub>2</sub>O<sub>2</sub>S 337.0772; Found 337.0775.



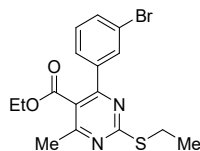
**Ethyl 4-(2-chlorophenyl)-2-(ethylthio)-6-methylpyrimidine-5-carboxylate (3g).**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 57 mg, yield: 85%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.42 (m, 1H), 7.38 – 7.34 (m, 1H), 7.33 – 7.30 (m, 2H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.19 (q, *J* = 7.2 Hz, 2H), 2.65 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.75, 166.73, 166.36, 163.75, 137.69, 132.12, 130.05, 129.90, 129.43, 126.56, 121.32, 61.33, 25.43, 23.50, 14.40, 13.39. HRMS (ESI): *m/z* ([M+H]<sup>+</sup>) Calcd for C<sub>16</sub>H<sub>18</sub>ClN<sub>2</sub>O<sub>2</sub>S 337.0772; Found 337.0776.



**Ethyl 4-(4-bromophenyl)-2-(ethylthio)-6-methylpyrimidine-5-carboxylate (3h).**

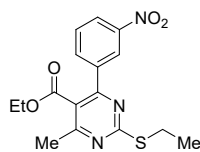
Colorless oil obtained by column chromatography (PE/EA = 30:1), 69 mg, yield: 91%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.56 (m, 2H), 7.52 – 7.50 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.20 (q, *J* = 7.2 Hz, 2H), 2.55 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.45, 167.90, 165.73, 162.36, 136.65, 131.66, 129.90, 124.72, 120.72, 61.63, 25.37, 22.66, 14.45, 13.70; HRMS (ESI): *m/z* ([M+H]<sup>+</sup>) Calcd for C<sub>16</sub>H<sub>18</sub>BrN<sub>2</sub>O<sub>2</sub>S 381.0267; Found 381.0264.



**Ethyl 4-(3-bromophenyl)-2-(ethylthio)-6-methylpyrimidine-5-carboxylate (3i).**

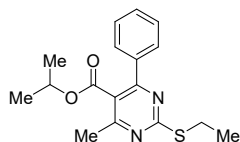
Colorless oil obtained by column chromatography (PE/EA = 30:1), 68 mg, yield: 89%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.78 – 7.77 (m, 1H), 7.60 – 7.58 (m, 1H), 7.55 – 7.54 (m, 1H), 7.32 – 7.29 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.21 (q, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.53, 167.69, 165.83, 161.99, 139.68, 132.94, 131.30, 129.92, 126.90, 122.48, 120.89, 61.86, 25.39, 22.70, 14.42, 13.70; HRMS (ESI): *m/z*

([M+H]<sup>+</sup>) Calcd for C<sub>16</sub>H<sub>18</sub>BrN<sub>2</sub>O<sub>2</sub>S 381.0267; Found 381.0265.



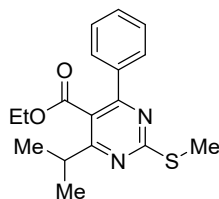
**Ethyl 2-(ethylthio)-4-methyl-6-(3-nitrophenyl)pyrimidine-5-carboxylate (3j).**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 65 mg, yield: 93%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.52 (s, 1H), 8.34 – 8.32 (m, 1H), 7.98 – 7.96 (m, 1H), 7.65 – 7.62 (m, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.22 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.96, 167.39, 166.22, 161.00, 139.31, 134.25, 129.51, 124.63, 123.47, 120.89, 62.07, 25.45, 22.85, 14.36, 13.73; HRMS (ESI): *m/z* ([M+H]<sup>+</sup>) Calcd for C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>O<sub>4</sub>S 348.1013; Found 348.1016.



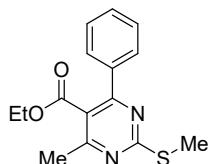
**Isopropyl 2-(ethylthio)-4-methyl-6-phenylpyrimidine-5-carboxylate (3k).**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 53 mg, yield: 83%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.60 (m, 2H), 7.48 – 7.39 (m, 3H), 5.09 – 5.01 (m, 1H), 3.21 (q, *J* = 7.2 Hz, 2H), 2.55 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.07 (s, 3H), 1.06 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.05, 167.57, 165.21, 163.44, 137.78, 129.94, 128.39, 128.36, 121.43, 69.53, 25.33, 22.52, 21.27, 14.52; HRMS (ESI): *m/z* ([M+H]<sup>+</sup>) Calcd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S 317.1318; Found 317.1315.



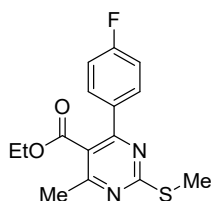
**Ethyl 4-isopropyl-2-(methylthio)-6-phenylpyrimidine-5-carboxylate (3l).**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 51 mg, yield: 80%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.63 – 7.62 (m, 2H), 7.46 – 7.40 (m, 3H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.23 – 3.16 (m, 1H), 2.61 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.98, 172.52, 168.22, 163.61, 137.84, 129.90, 128.40, 128.26, 120.38, 61.67, 33.17, 21.65, 14.19, 13.59; HRMS (ESI): *m/z* ([M+H]<sup>+</sup>) Calcd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S 317.1318;



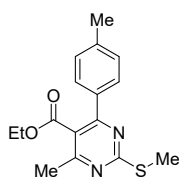
**Ethyl 4-methyl-2-(methylthio)-6-phenylpyrimidine-5-carboxylate (3m).**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 54 mg, yield: 94%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.67 – 7.60 (m, 2H), 7.49 – 7.40 (m, 3H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.61 (s, 3H), 2.56 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.47, 168.11, 165.44, 163.57, 137.76, 130.04, 128.41, 128.40, 128.30, 120.93, 61.66, 22.60, 14.16, 13.58; HRMS (ESI): *m/z* ([M+H]<sup>+</sup>) Calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>S 289.1005; Found 289.1007.



**Ethyl 4-(4-fluorophenyl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (3n).**

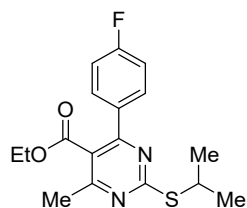
Colorless oil obtained by column chromatography (PE/EA = 30:1), 56 mg, yield: 91%; <sup>1</sup>H NMR (600 MHz, CDDl<sub>3</sub>) δ 7.66 – 7.61 (m, 2H), 7.14 – 7.09 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 2.55 (s, 3H), 1.08 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.54, 168.04, 165.53, 162.29, 133.82, 133.79, 130.46, 130.40, 120.75, 115.51, 115.47, 61.76, 22.61, 14.15, 13.69; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -109.58. HRMS (ESI): *m/z* ([M+H]<sup>+</sup>) Calcd for C<sub>15</sub>H<sub>16</sub>FN<sub>2</sub>O<sub>2</sub>S 307.0911; Found 307.0914.



**Ethyl 4-methyl-2-(methylthio)-6-(p-tolyl)pyrimidine-5-carboxylate (3o).**

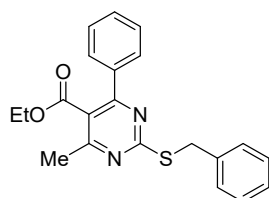
Colorless oil obtained by column chromatography (PE/EA = 30:1), 53 mg, yield: 88%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.53 (m, 2H), 7.25 – 7.22 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 2.54 (s, 3H), 2.40 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.30, 168.33, 165.22, 163.35, 140.41, 134.83, 129.14, 128.30, 120.75, 61.66, 22.56, 31.38, 14.14, 13.67; HRMS (ESI): *m/z* ([M+H]<sup>+</sup>) Calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>S 303.1162; Found 303.1159.





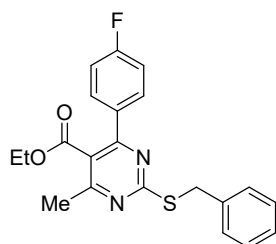
**Ethyl 4-(4-fluorophenyl)-2-(isopropylthio)-6-methylpyrimidine-5-carboxylate (3p).**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 55 mg, yield: 82%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.62 (m, 2H), 7.13 – 7.11 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 1H), 4.03 – 3.99 (m, 1H), 2.54 (s, 3H), 1.45 (s, 3H), 1.44 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.49, 168.17, 165.55, 164.77, 162.28, 133.86, 130.41, 130.36, 115.60, 115.46, 109.99, 61.74, 35.98, 22.83, 22.63, 13.70; HRMS (ESI): *m/z* ([*M*+*H*]<sup>+</sup>) Calcd for C<sub>17</sub>H<sub>20</sub>FN<sub>2</sub>O<sub>2</sub>S 335.1224; Found 335.1226.



**Ethyl 2-(benzylthio)-4-methyl-6-phenylpyrimidine-5-carboxylate (3q).**

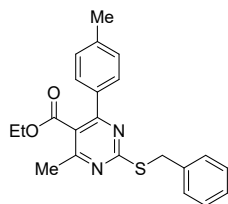
Colorless oil obtained by column chromatography (PE/EA = 30:1), 68 mg, yield: 93%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.59 (m, 2H), 7.48 – 7.42 (m, 4H), 7.37 – 7.36 (m, 1H), 7.31 – 7.23 (m, 3H), 4.46 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 171.60, 167.99, 165.59, 163.73, 137.66, 130.05, 129.07, 128.40, 128.38, 128.31, 127.75, 127.59, 127.12, 121.24, 61.69, 35.33, 22.59, 13.58; HRMS (ESI): *m/z* ([*M*+*H*]<sup>+</sup>) Calcd for C<sub>21</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S 365.1318; Found 365.1315.



**Ethyl 2-(benzylthio)-4-(4-fluorophenyl)-6-methylpyrimidine-5-carboxylate (3r).**

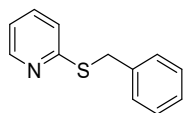
Colorless oil obtained by column chromatography (PE/EA = 30:1), 70 mg, yield: 92%; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.57 (m, 2H), 7.43 – 7.41 (m, 2H), 7.31 – 7.28 (m, 2H), 7.25 – 7.23 (m, 1H), 7.13 – 7.09 (m, 2H), 4.45 (s, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.55 (s, 3H), 1.08 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 171.66, 167.93, 165.67, 164.80, 163.14, 162.45, 137.56,

133.70, 130.48, 130.42, 129.02, 128.40, 127.16, 121.06, 115.60, 115.46, 61.79, 35.35, 22.60, 13.69;  
HRMS (ESI):  $m/z$  ( $[M+H]^+$ ) Calcd for  $C_{21}H_{19}FN_2O_2S$  383.1224; Found 383.1227.



**Ethyl 2-(benzylthio)-4-methyl-6-(p-tolyl)pyrimidine-5-carboxylate (3s).**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 67 mg, yield: 89%;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.52 – 7.51 (m, 2H), 7.44 – 7.43 (m, 2H), 7.31 – 7.28 (m, 2H), 7.25 – 7.22 (m, 3H), 4.46 (s, 2H), 4.19 (q,  $J = 7.2$  Hz, 2H), 2.54 (s, 3H), 2.40 (s, 3H), 1.09 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  171.45, 168.23, 165.38, 163.52, 140.42, 137.73, 134.74, 129.13, 129.06, 128.38, 128.33, 127.10, 121.08, 61.69, 35.32, 22.56, 21.39, 13.68; HRMS (ESI):  $m/z$  ( $[M+H]^+$ ) Calcd for  $C_{22}H_{23}N_3O_2S$  379.1475; Found 379.1477.



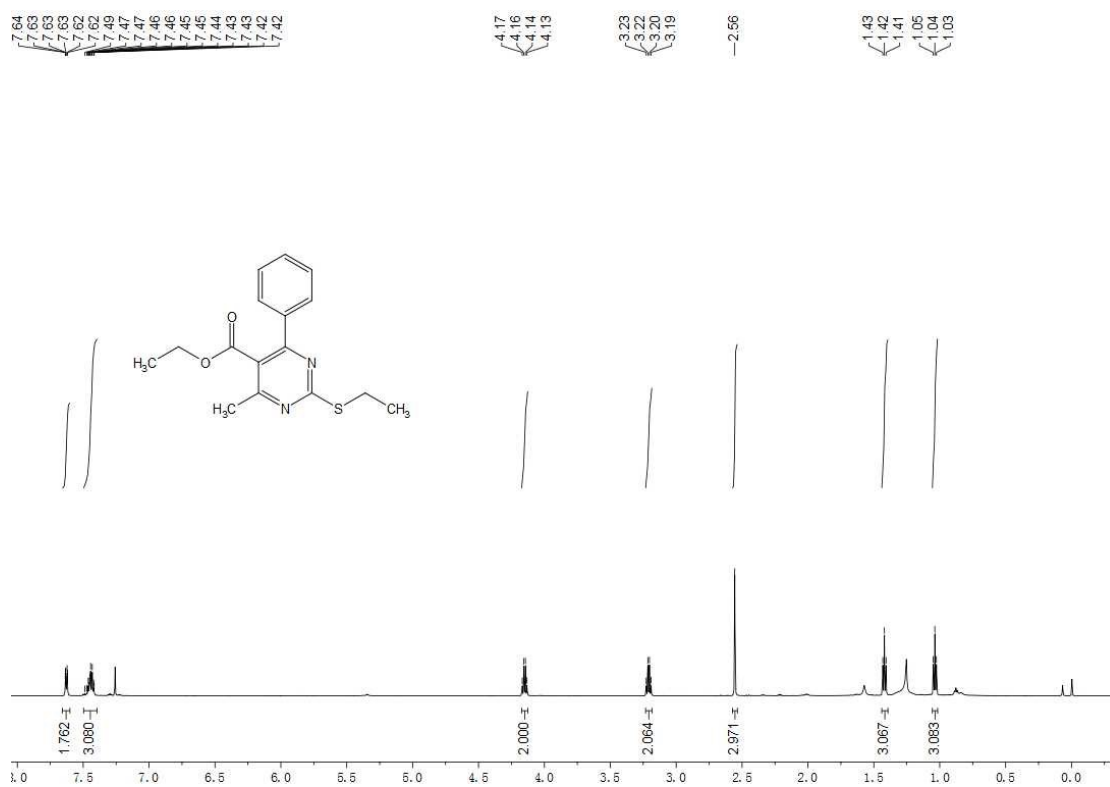
**2-(benzylthio)pyridine (3t).**

Colorless oil obtained by column chromatography (PE/EA = 30:1), 35 mg, yield: 87%;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  8.46 – 8.45 (m, 1H), 7.48 – 7.45 (m, 1H), 7.41 – 7.40 (m, 2H), 7.30 – 7.28 (m, 2H), 7.24 – 7.23 (m, 1H), 7.16 (d,  $J = 7.8$  Hz, 1H), 7.00 – 6.98 (m, 1H), 4.44 (s, 2H);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  158.79, 149.37, 137.94, 135.93, 128.93, 128.45, 127.06, 122.07, 119.56, 34.42; HRMS (ESI):  $m/z$  ( $[M+H]^+$ ) Calcd for  $C_{12}H_{12}NS$  202.0685; Found 202.0683.

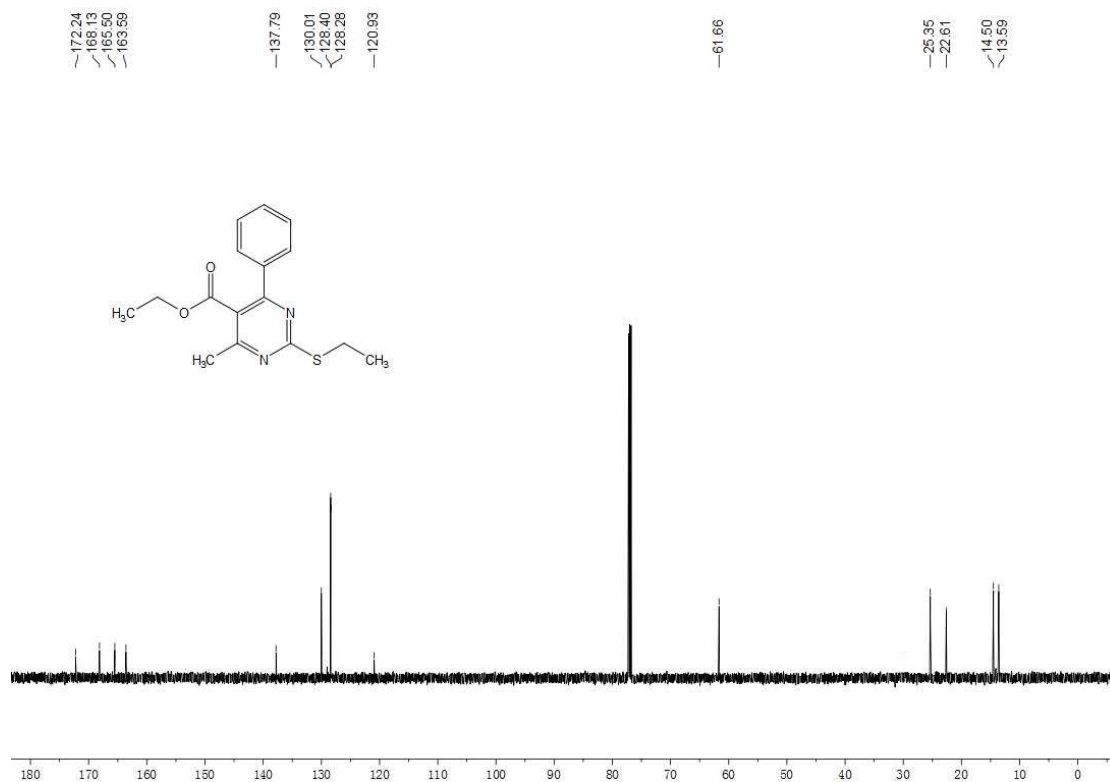
## 4. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

### 3a

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)



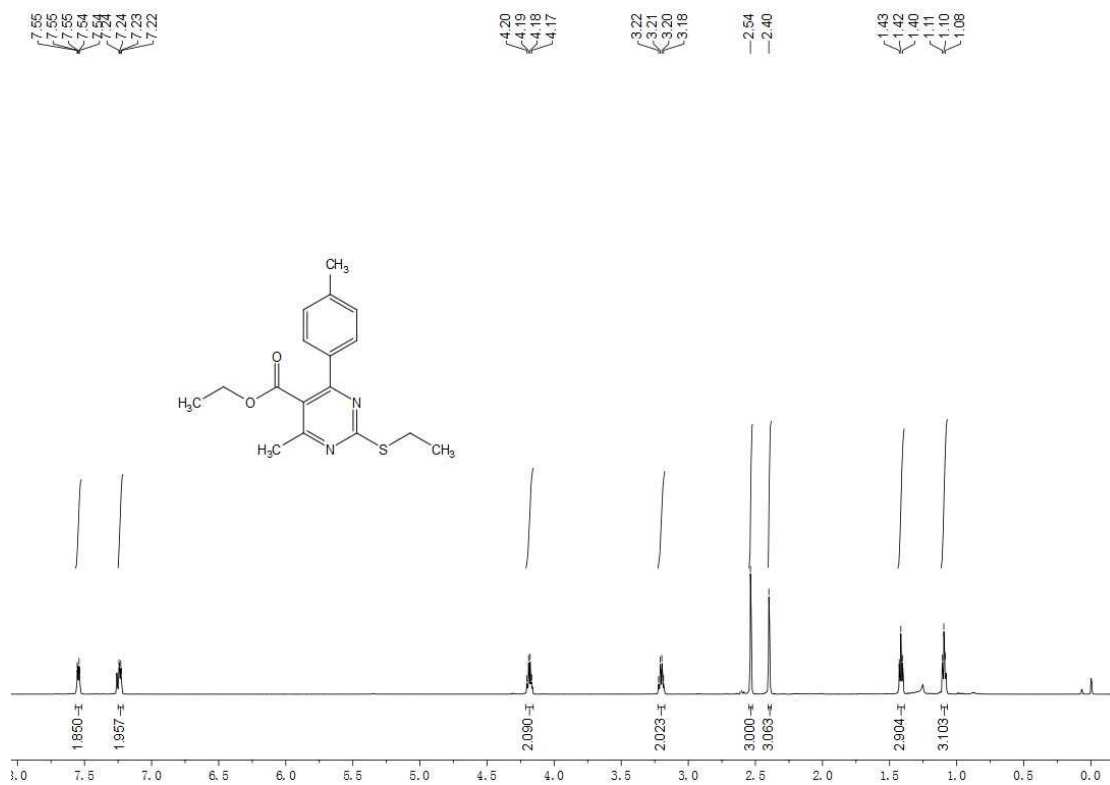
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)



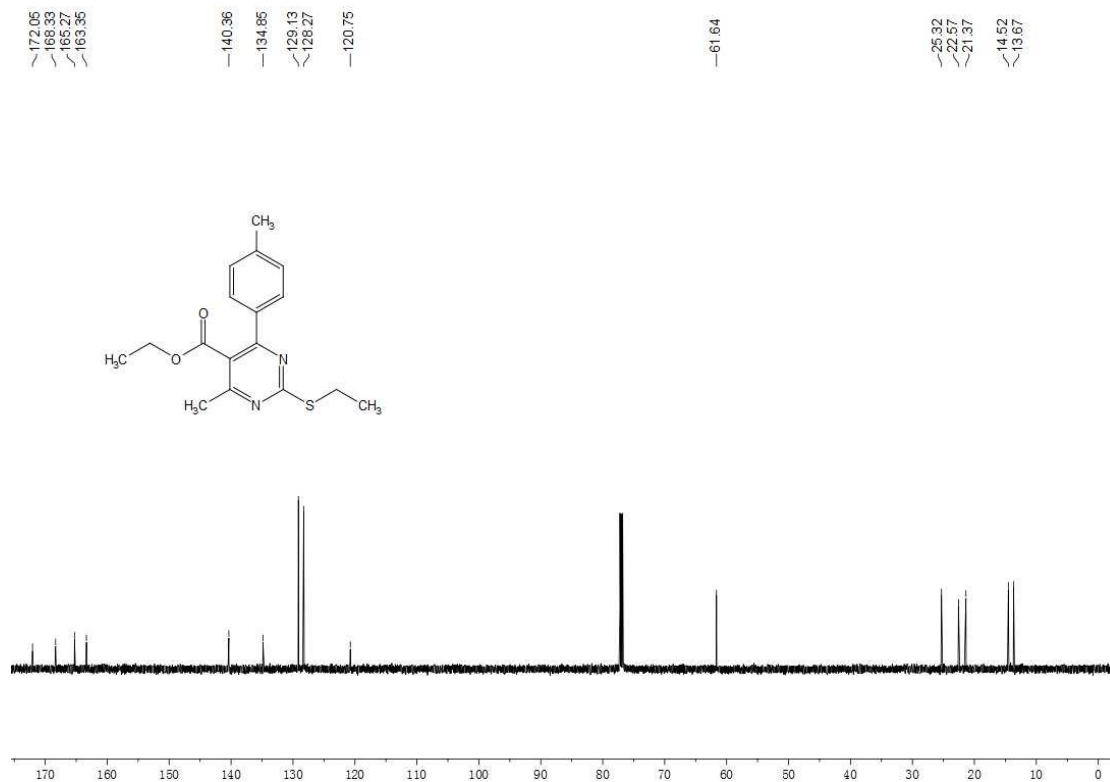


3b

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)

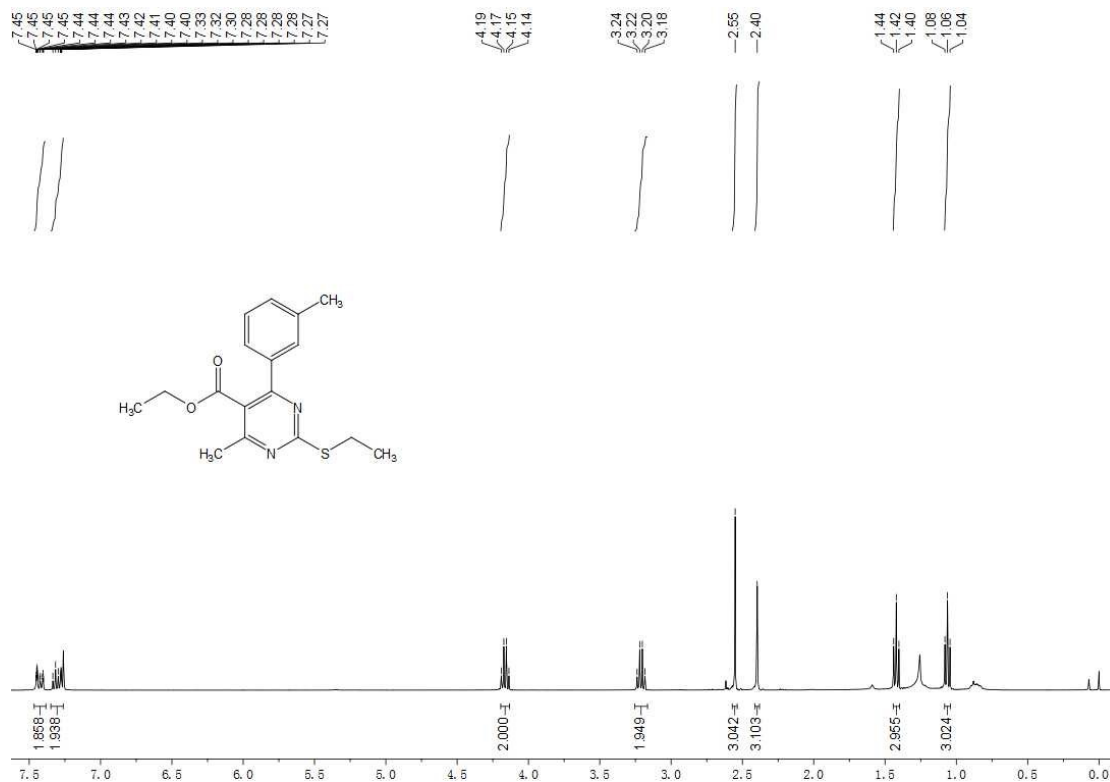


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)

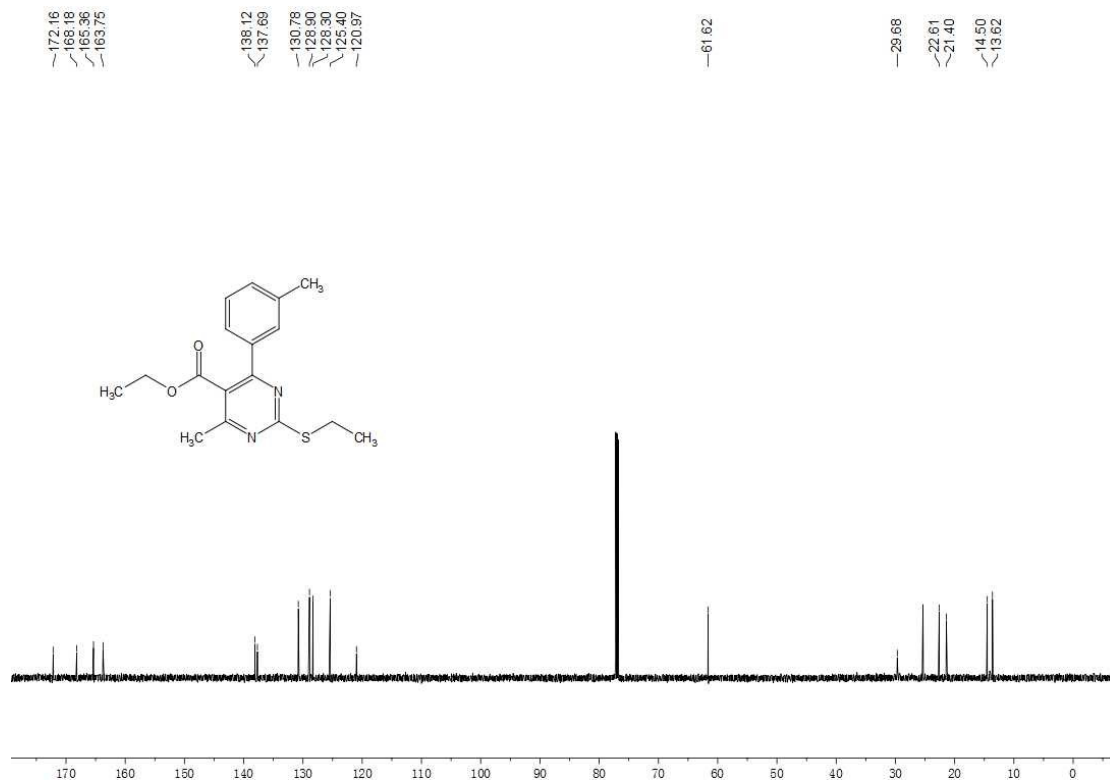


3c

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)

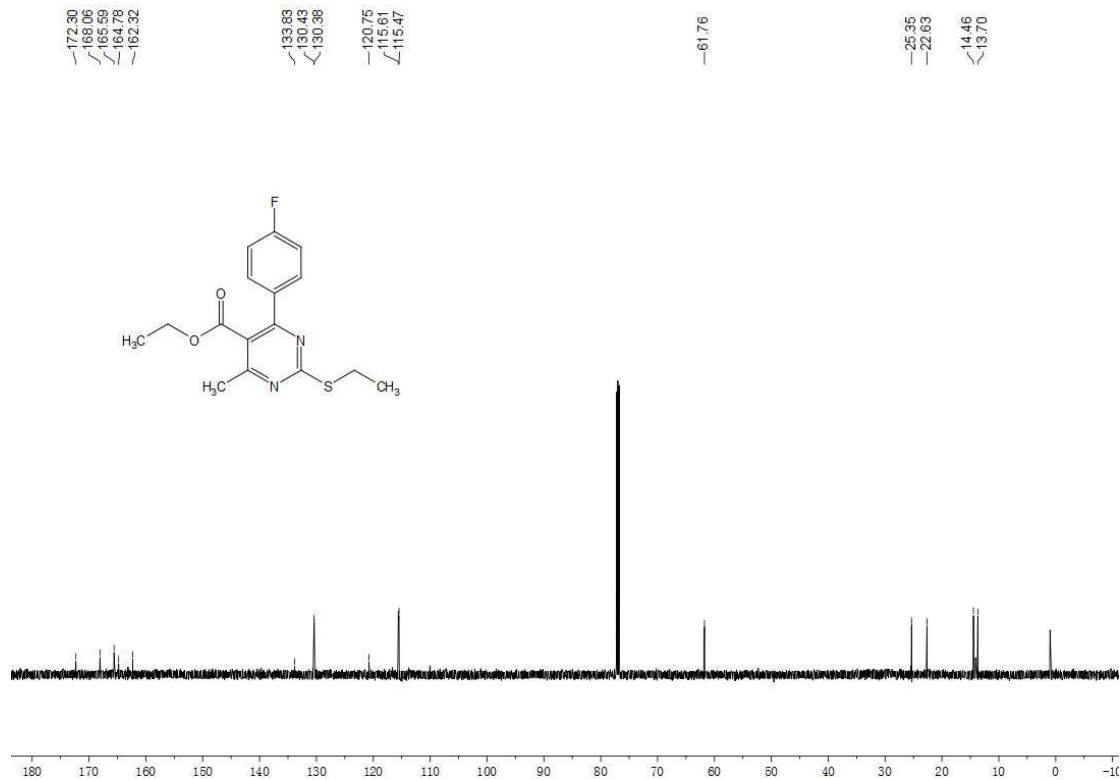


3d

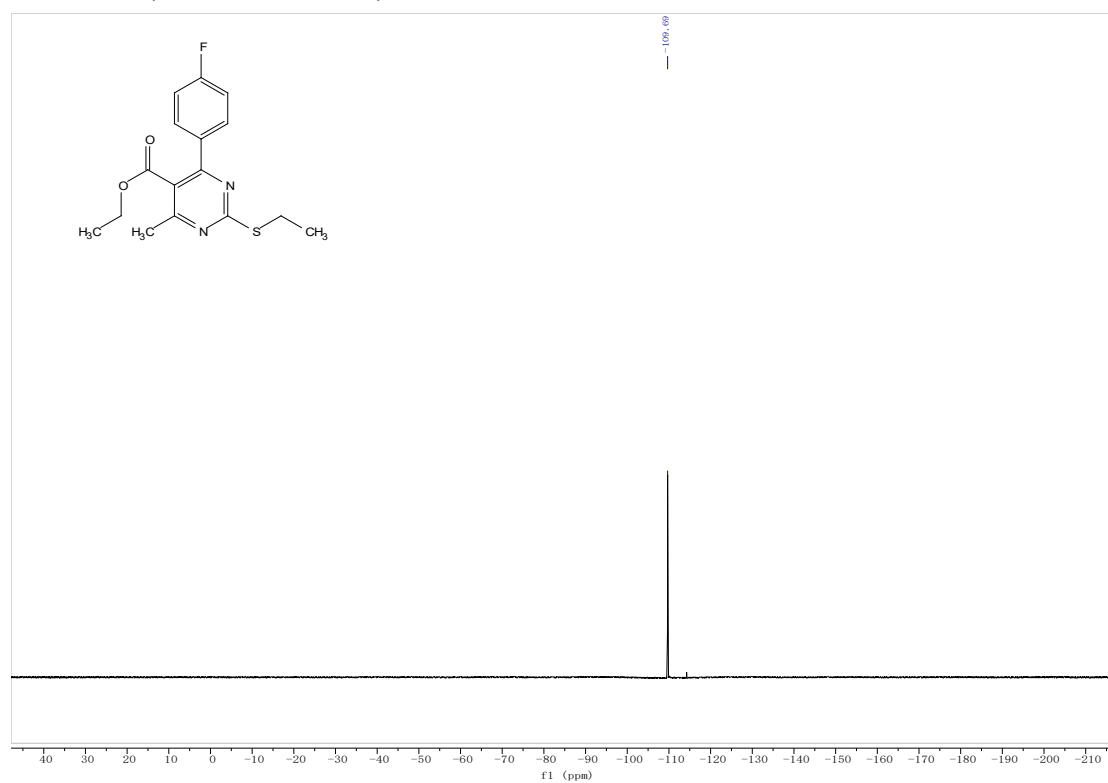
$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz)



$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 150 MHz)



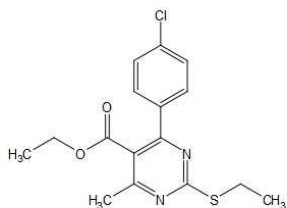
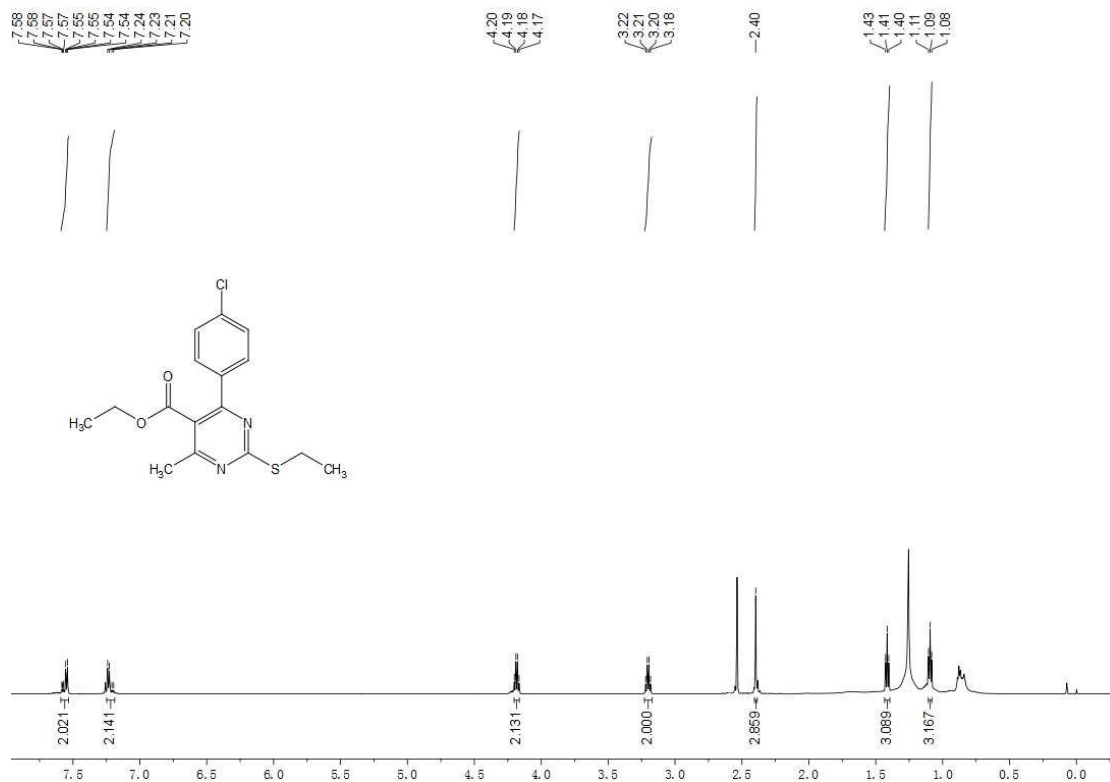
**<sup>19</sup>F NMR (CDCl<sub>3</sub> 376 MHz)**



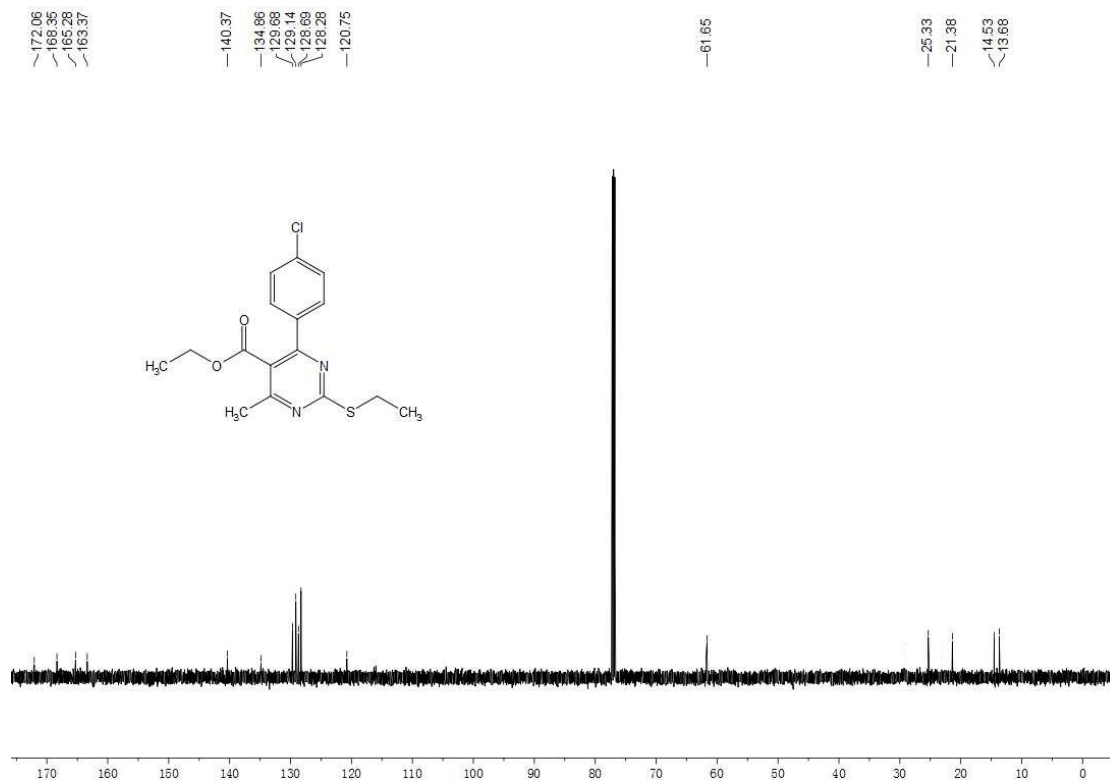


3e

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz)

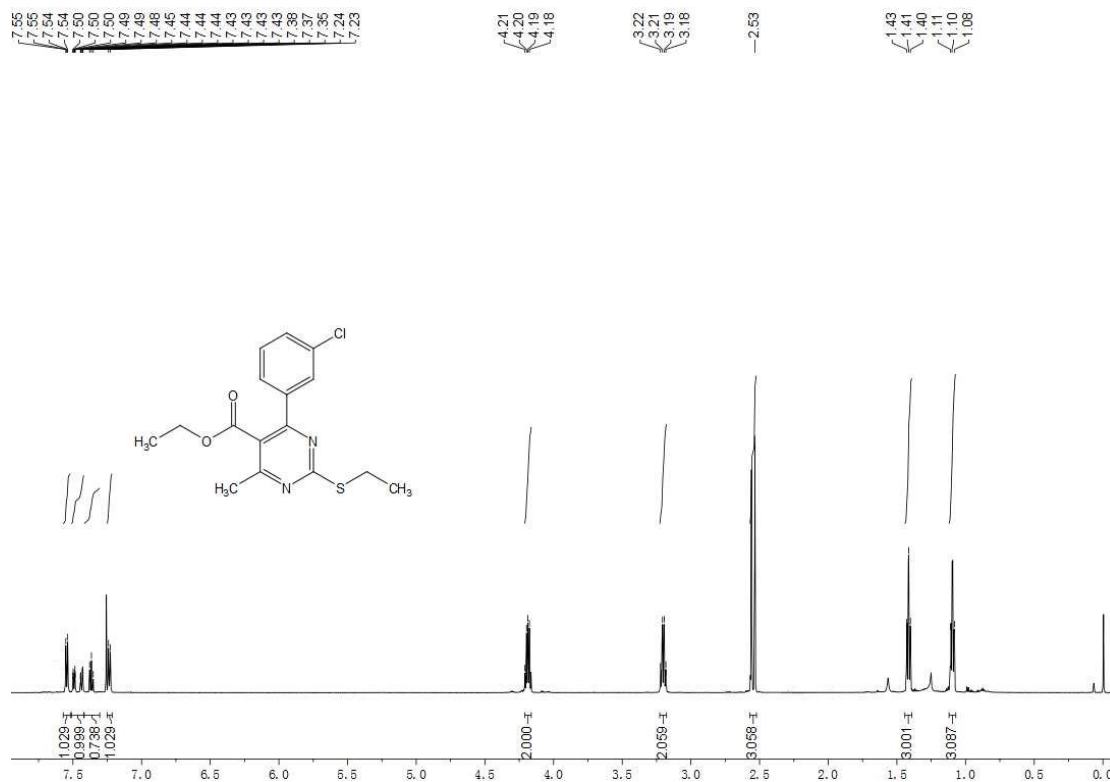


$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 150 MHz)

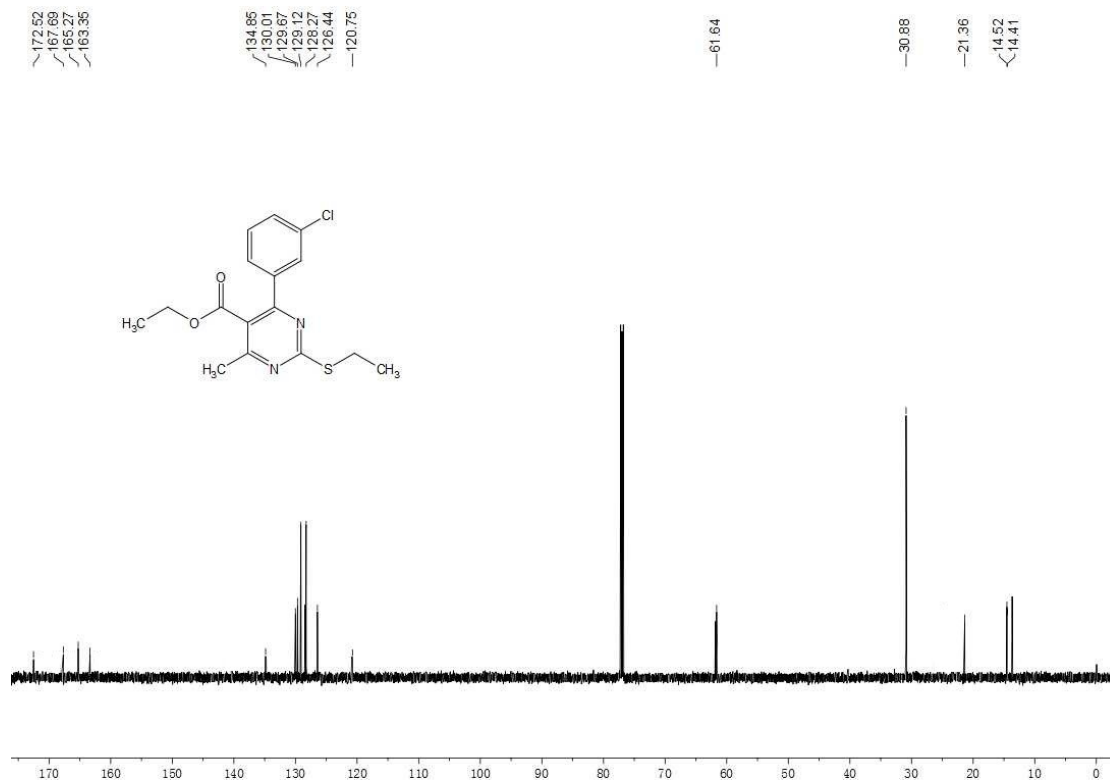


3f

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)

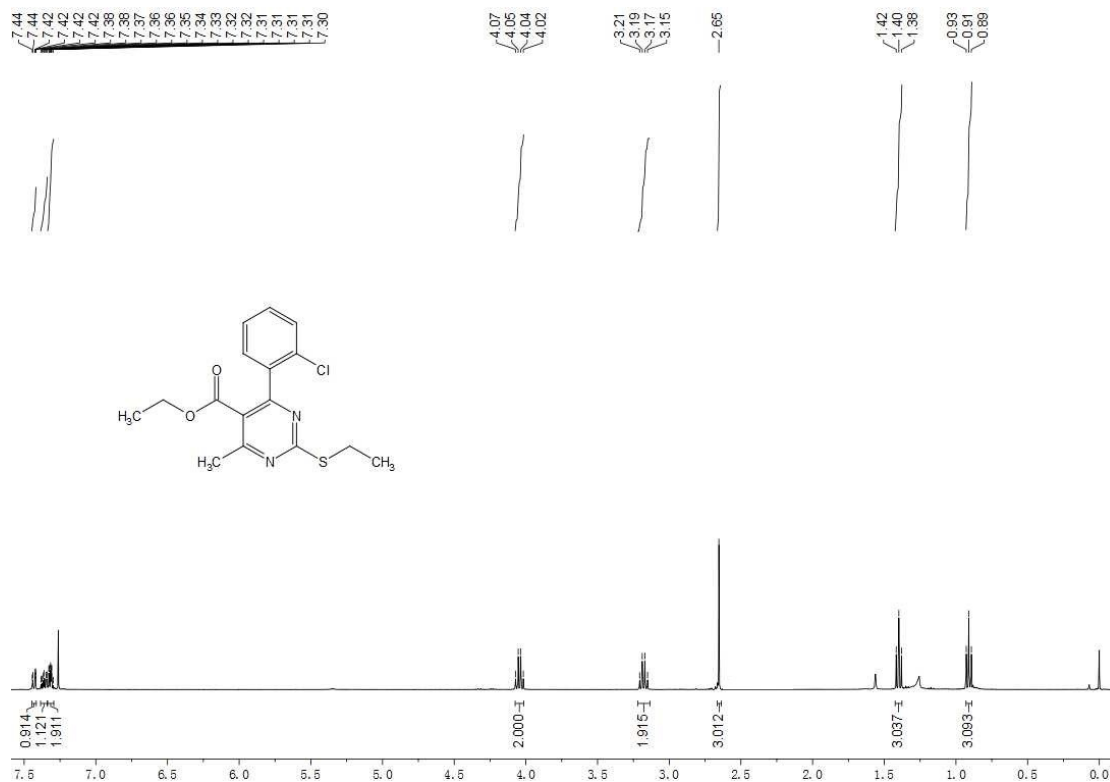


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)

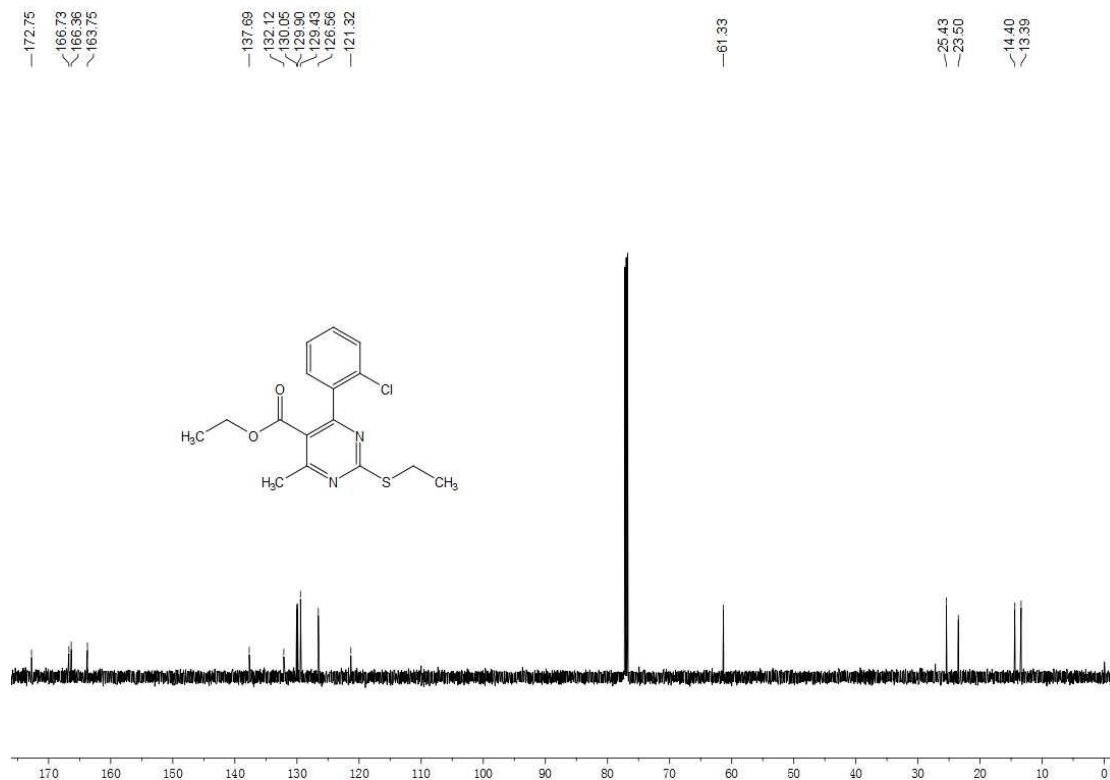


3g

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)

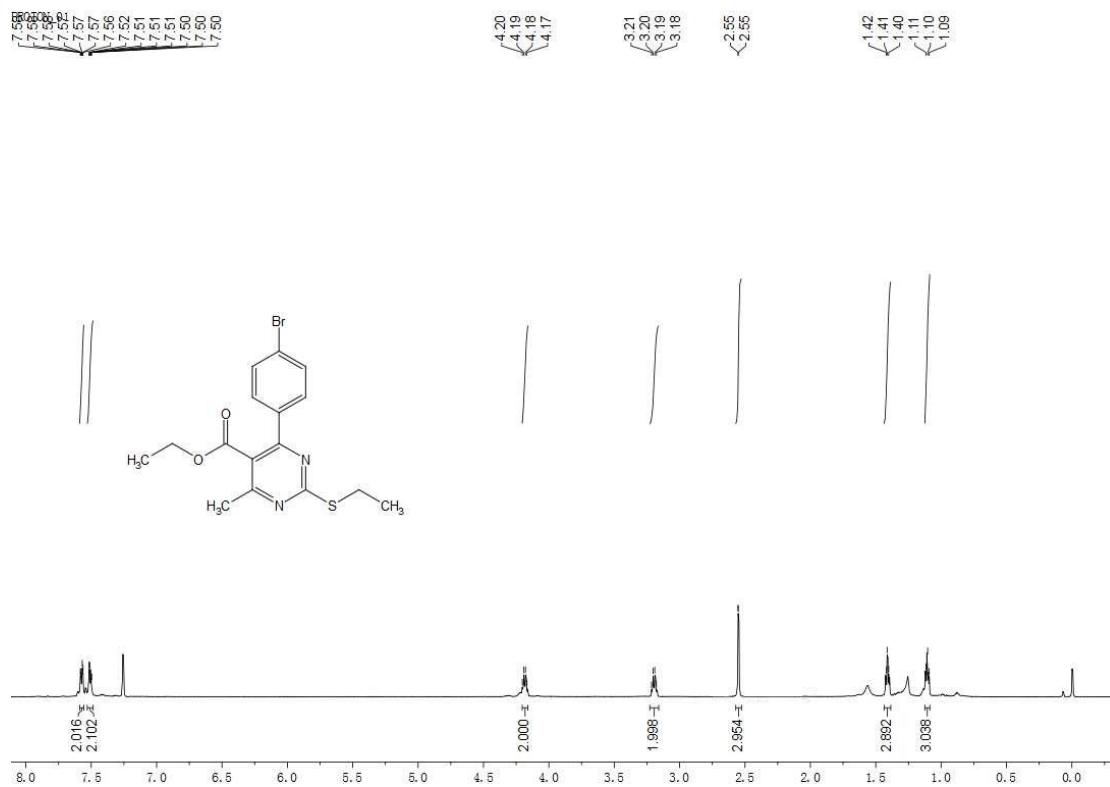


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)

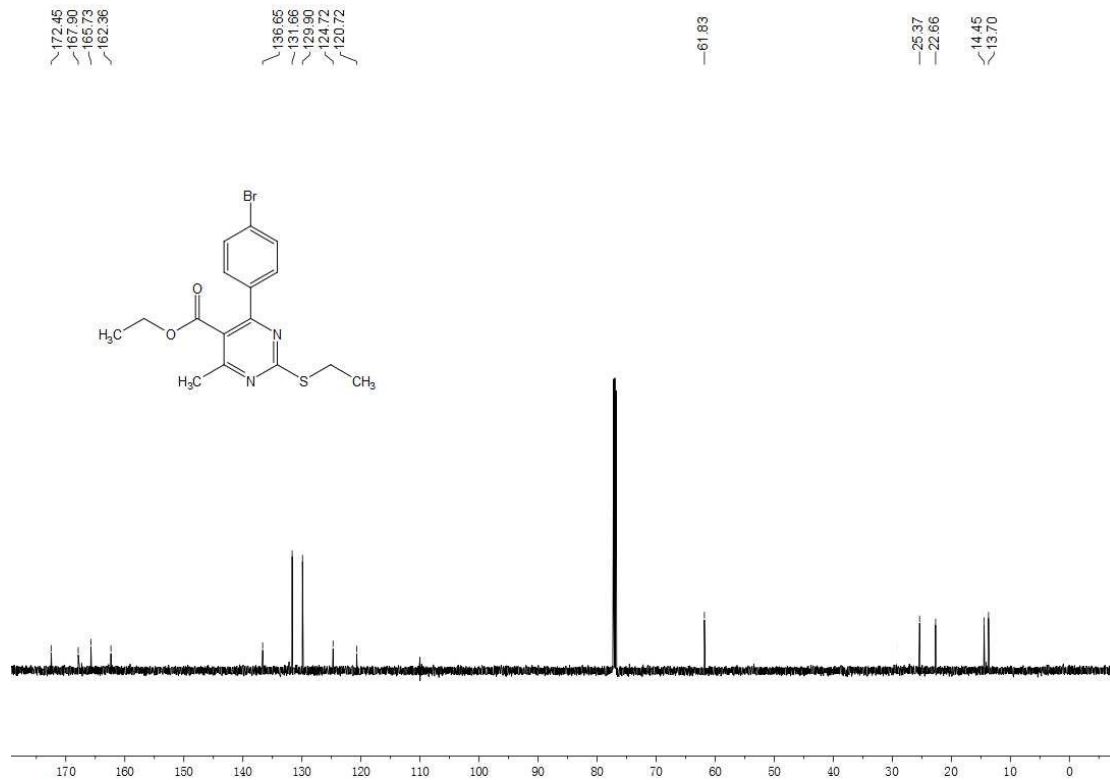


3h

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz)

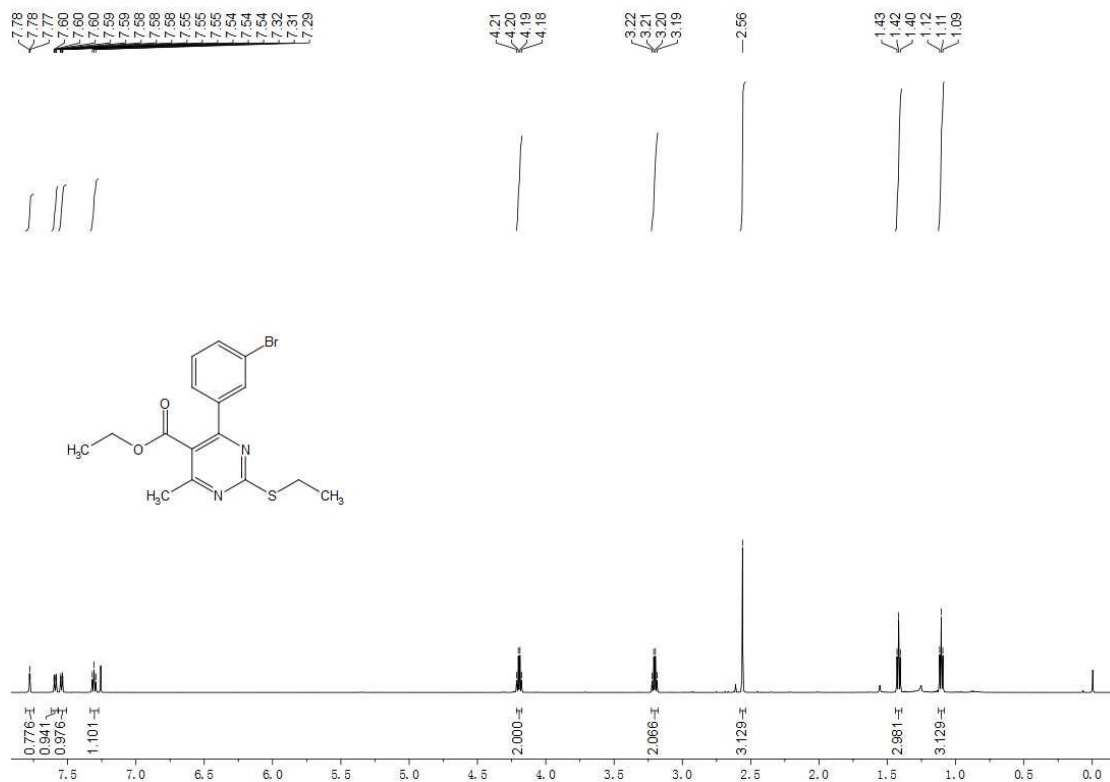


$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 150 MHz)

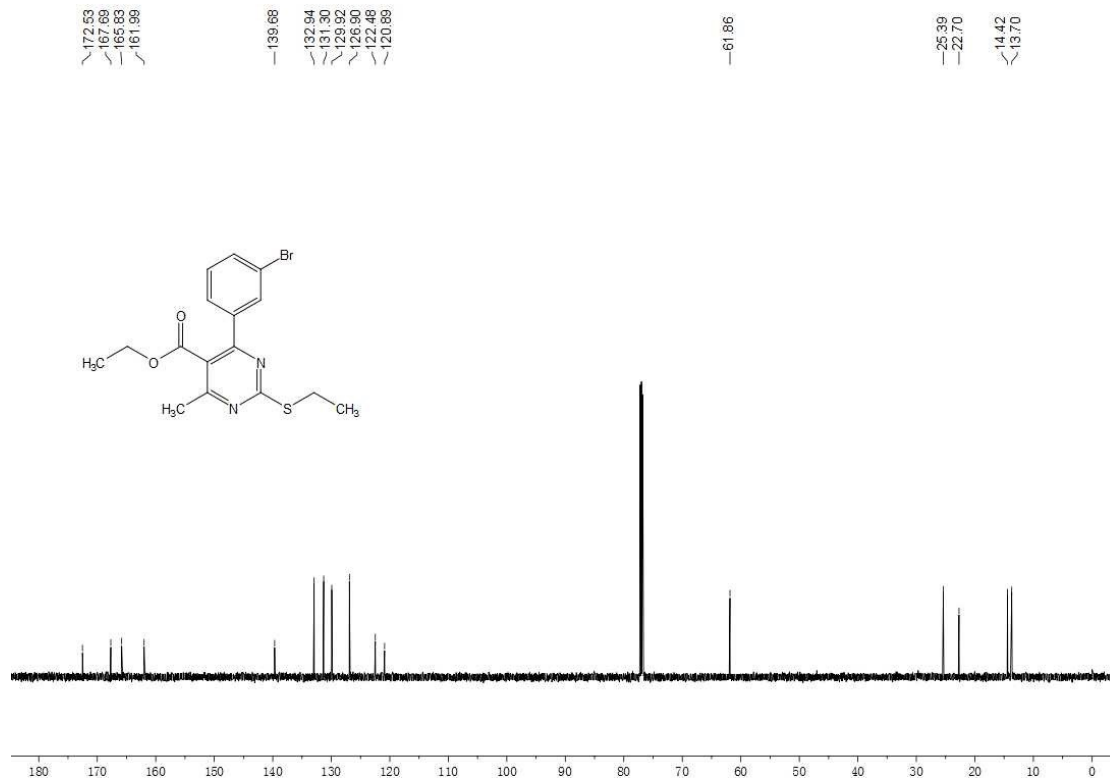


3i

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)**

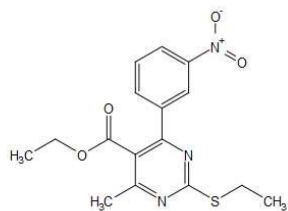
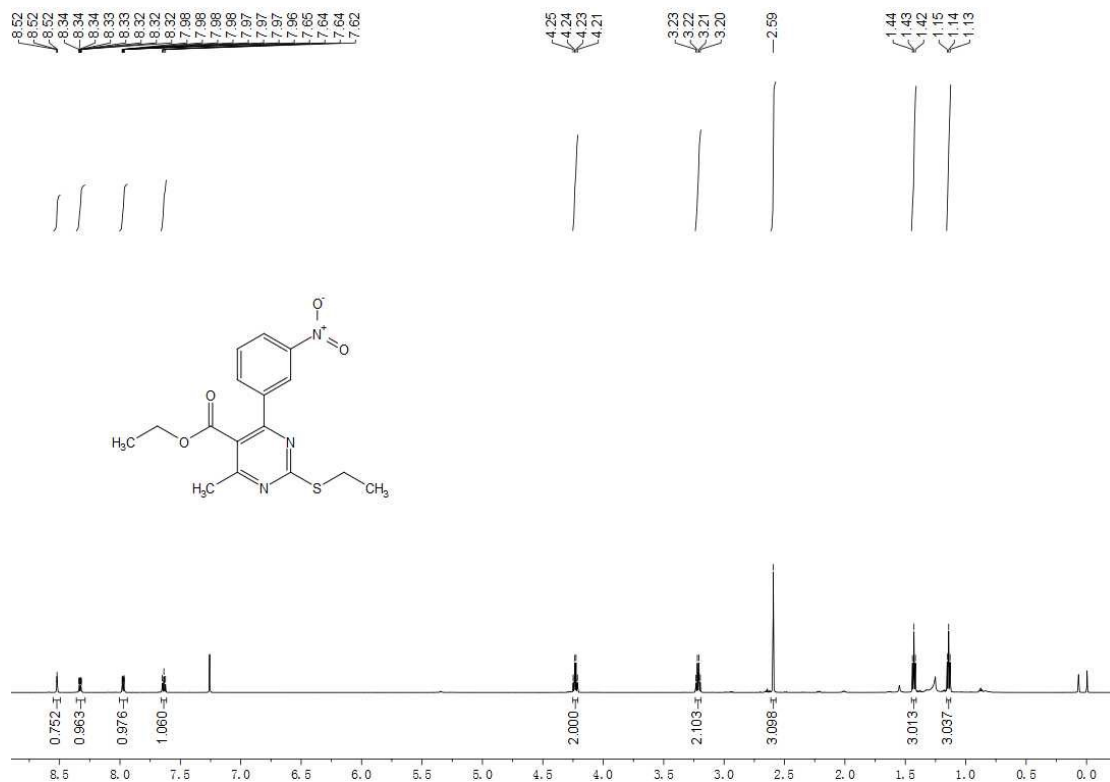


**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)**

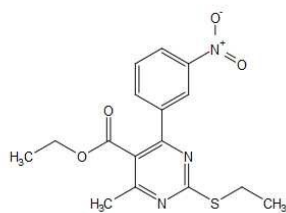
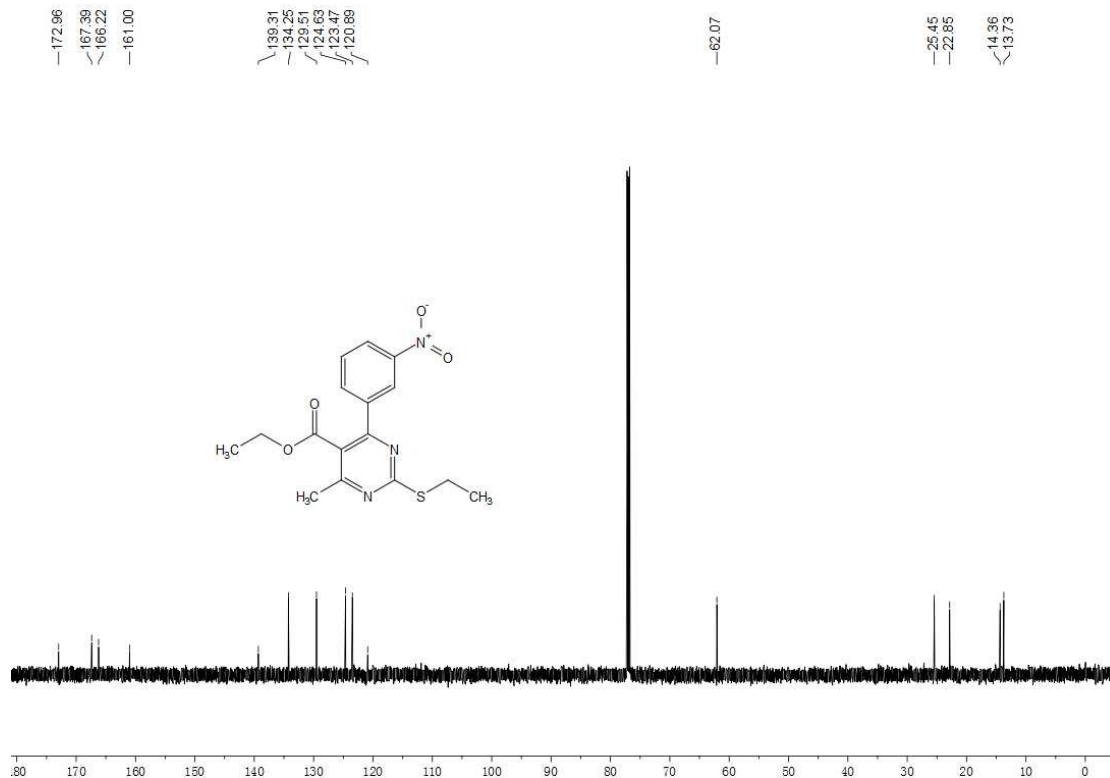


3j

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)

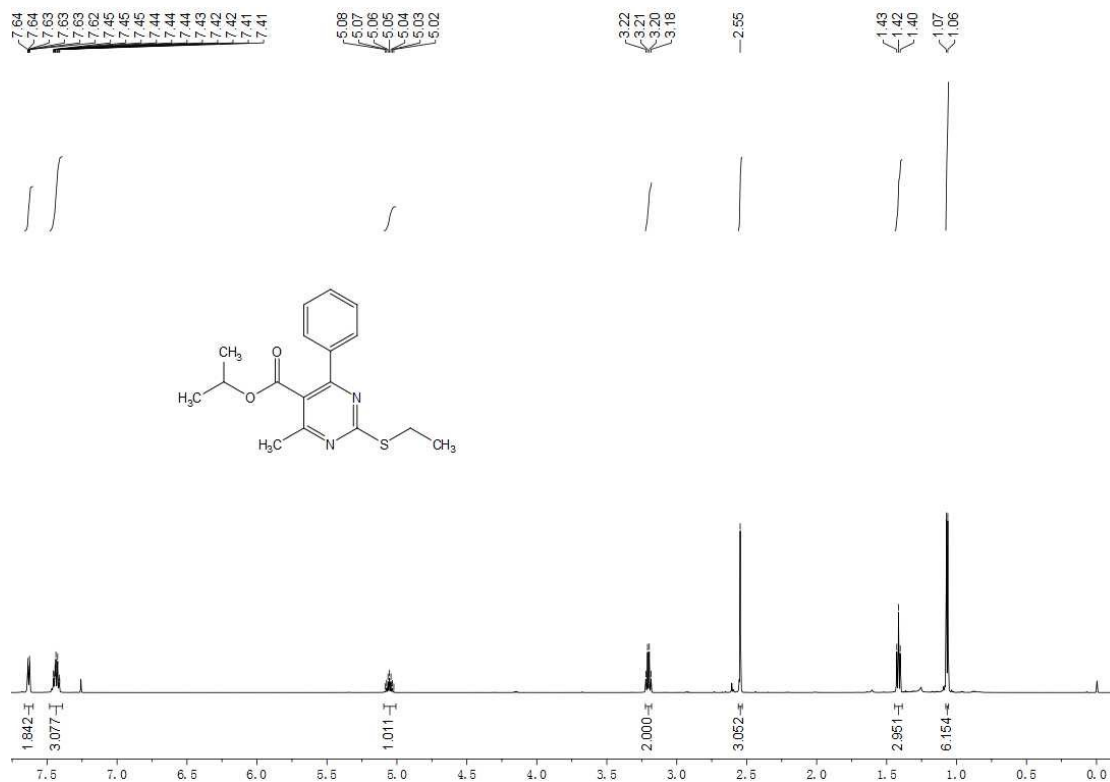


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)

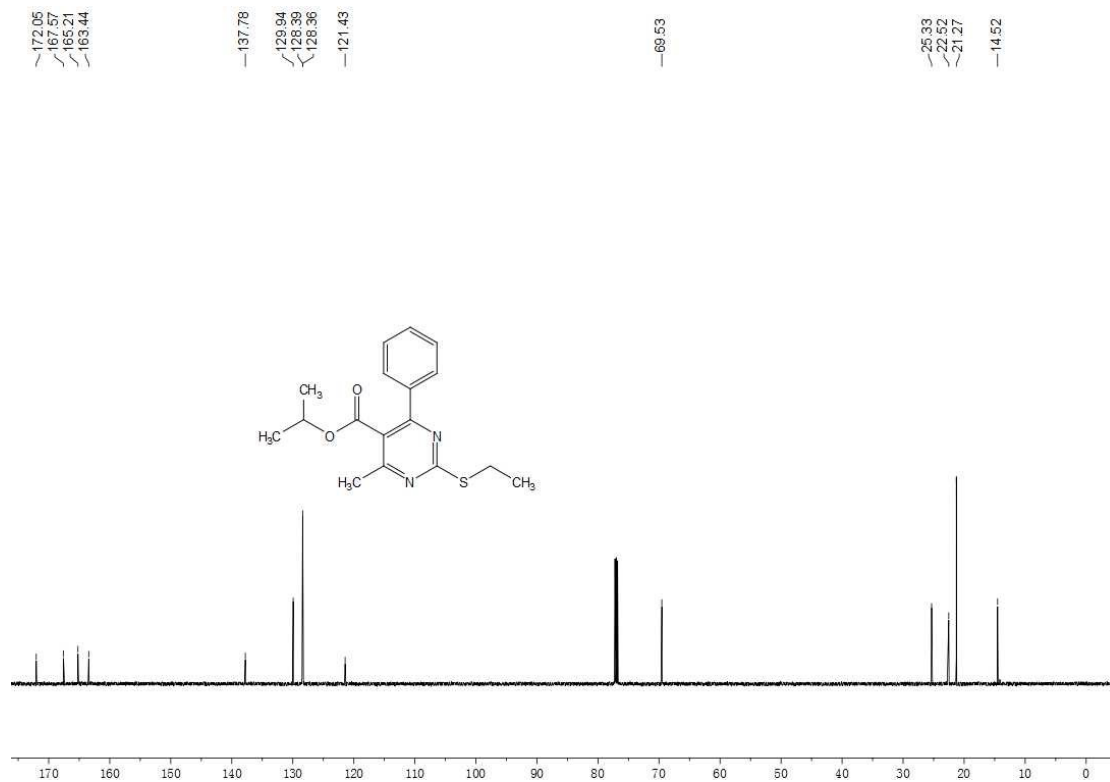


3k

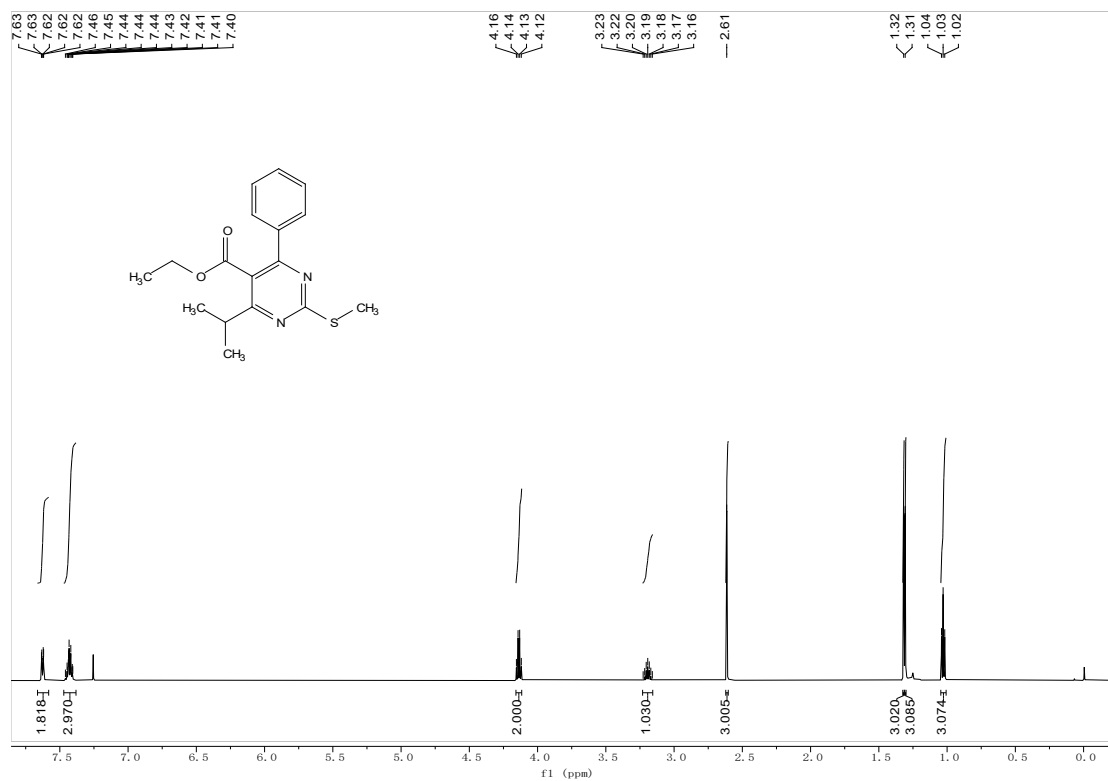
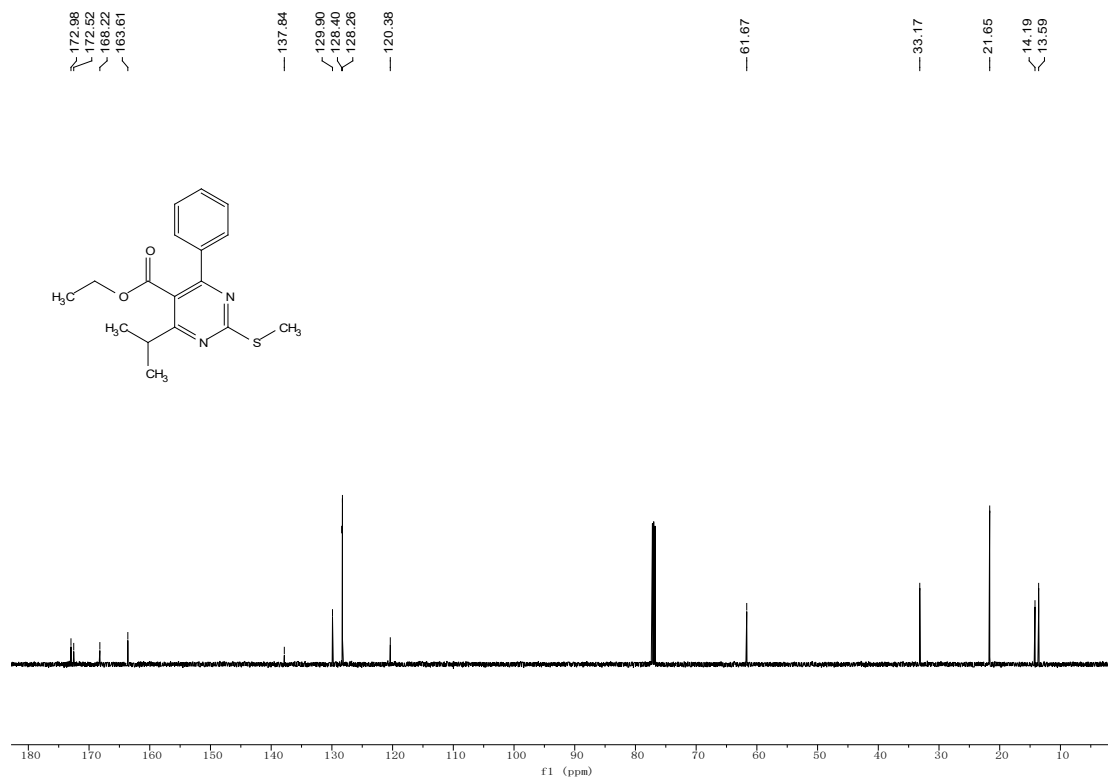
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)



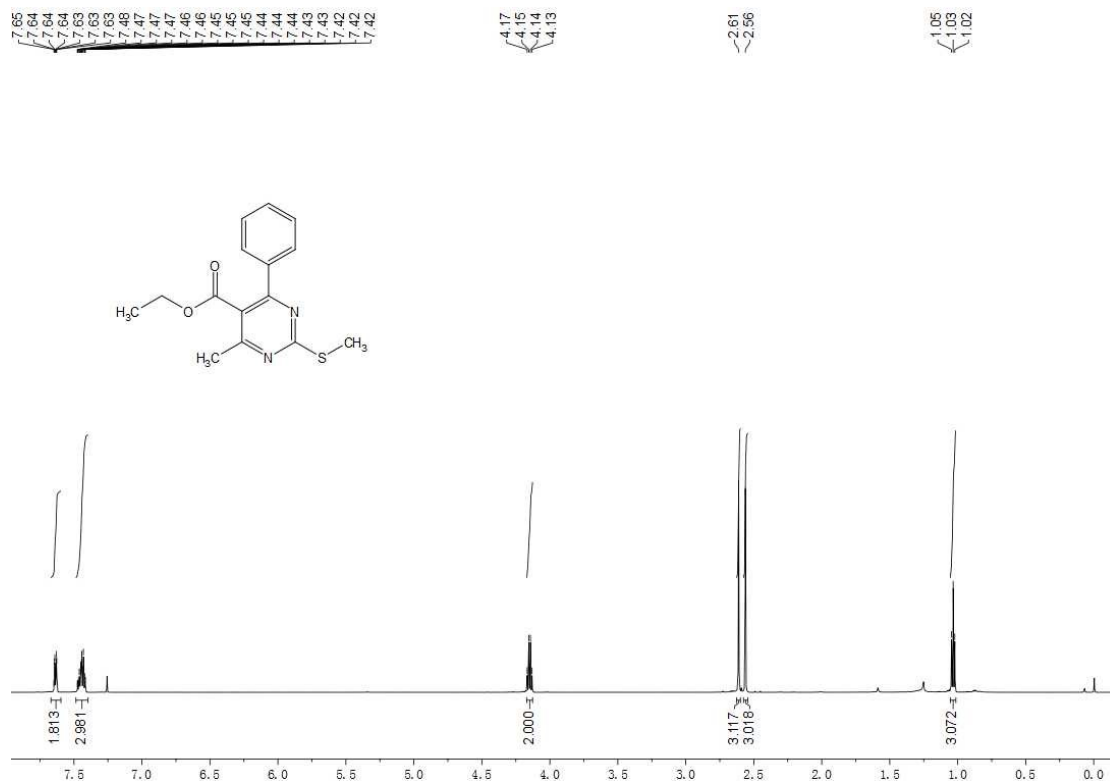
31

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)****<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)**

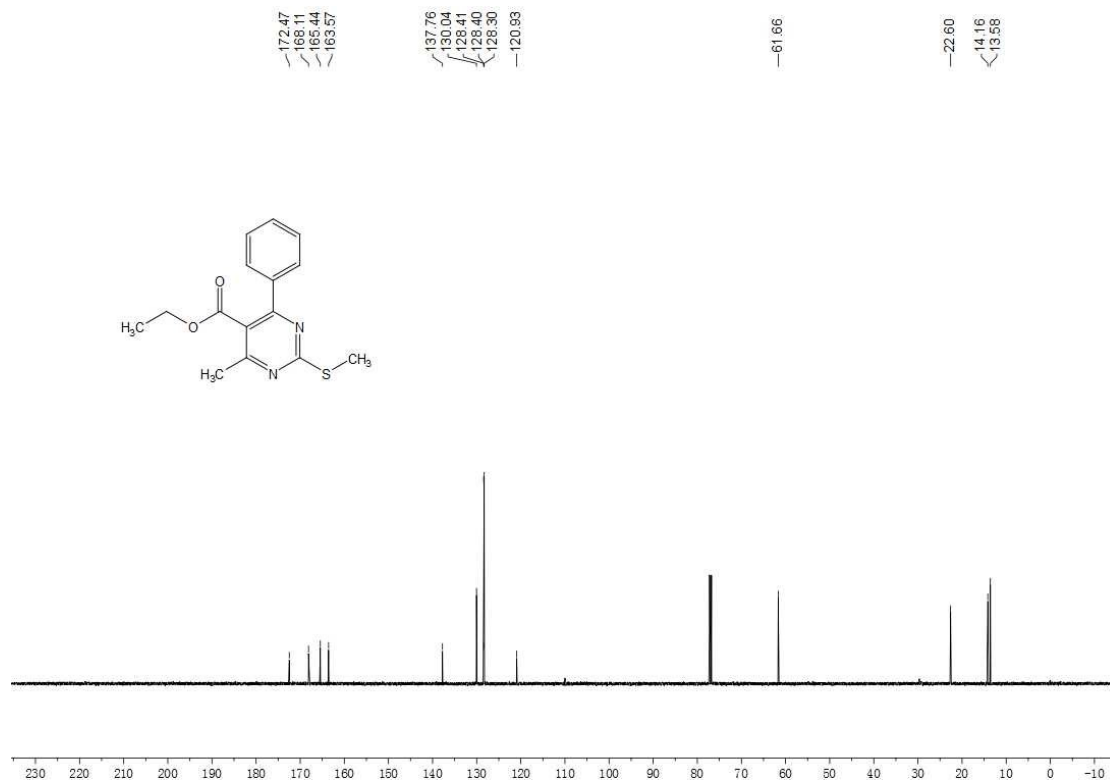


3m

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)



3n

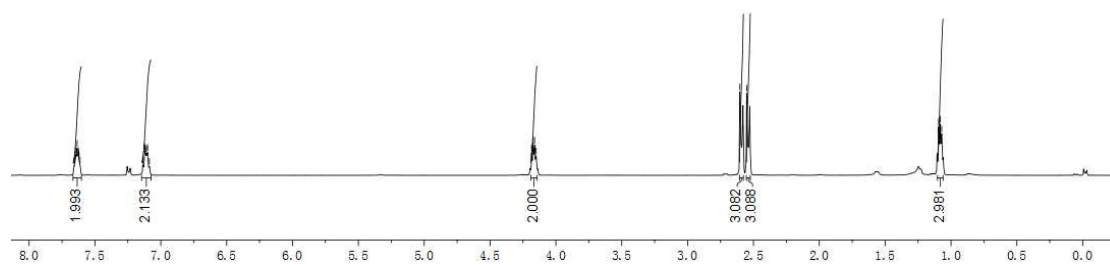
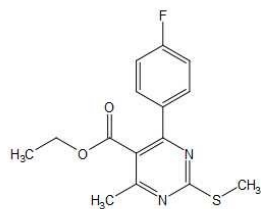
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)

7.66  
7.66  
7.65  
7.64  
7.64  
7.63  
7.62  
7.61  
7.14  
7.13  
7.12  
7.12  
7.11  
7.10  
7.09

4.18  
4.17  
4.16  
4.15

2.60  
2.55

1.09  
1.08  
1.07



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)

172.54  
168.04  
165.53  
162.29

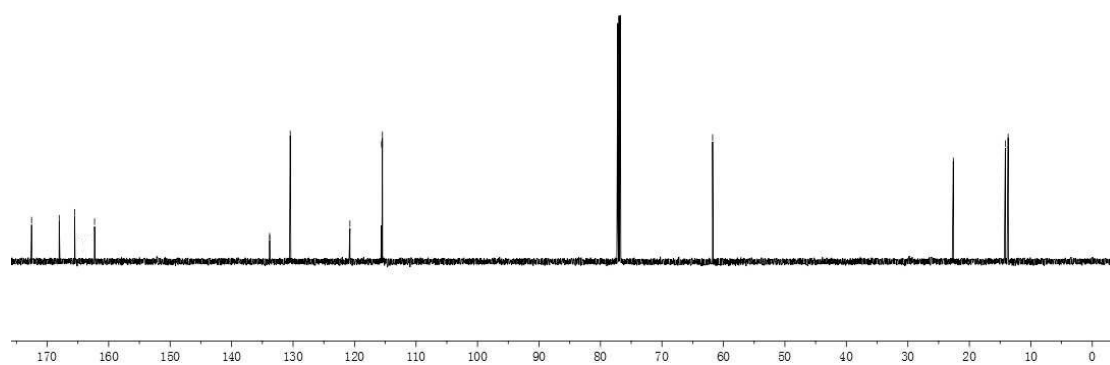
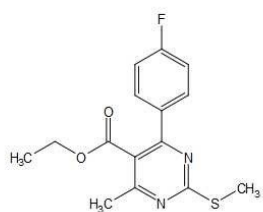
133.82  
133.79  
130.46  
130.40

120.75  
115.61  
113.47

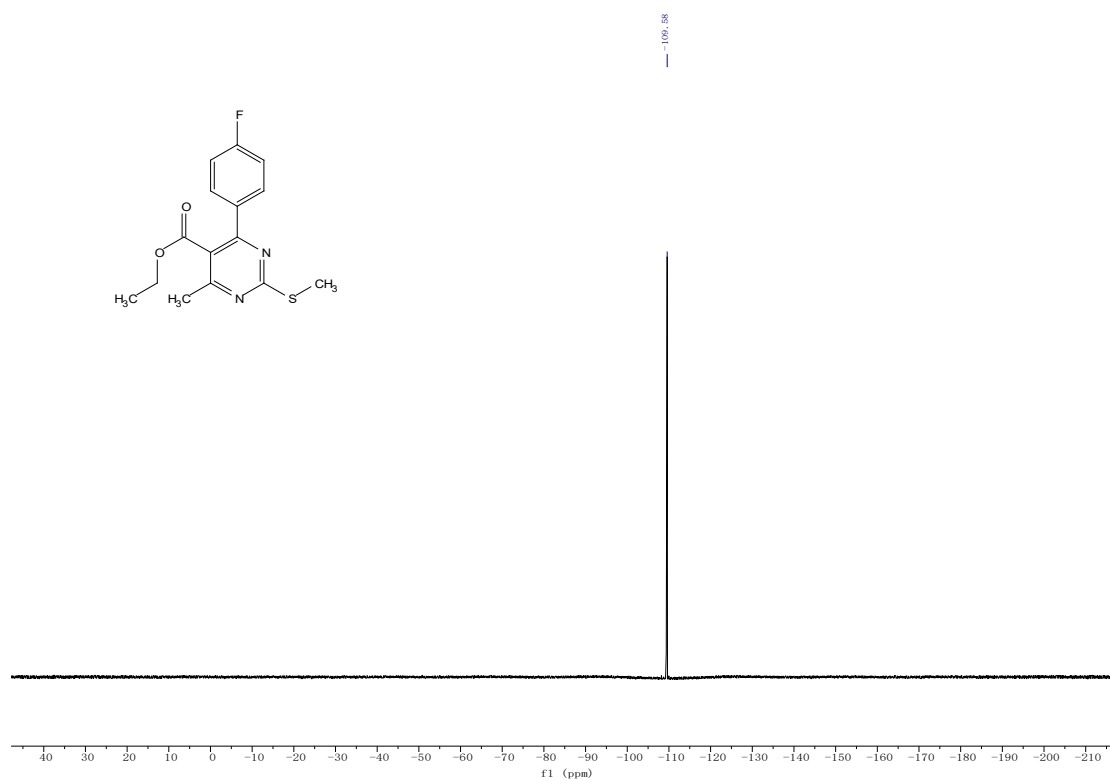
61.76

22.61

14.15  
13.69

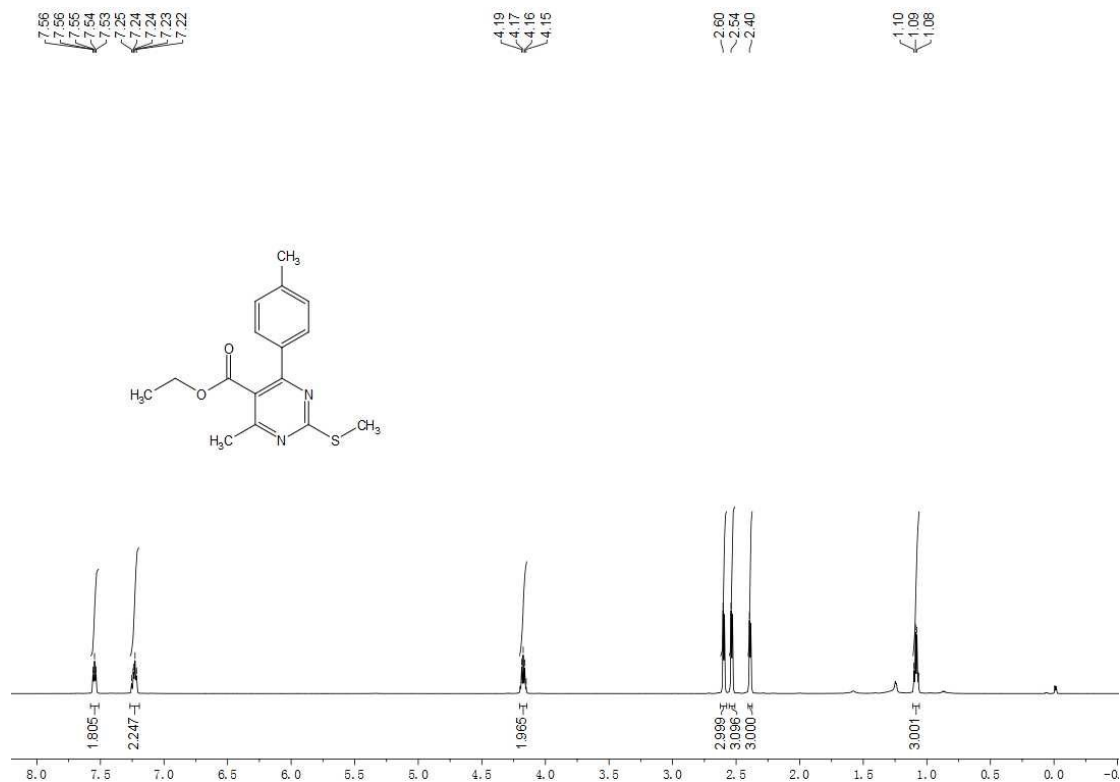


**$^{19}\text{F}$  NMR ( $\text{CDCl}_3$  376 MHz)**

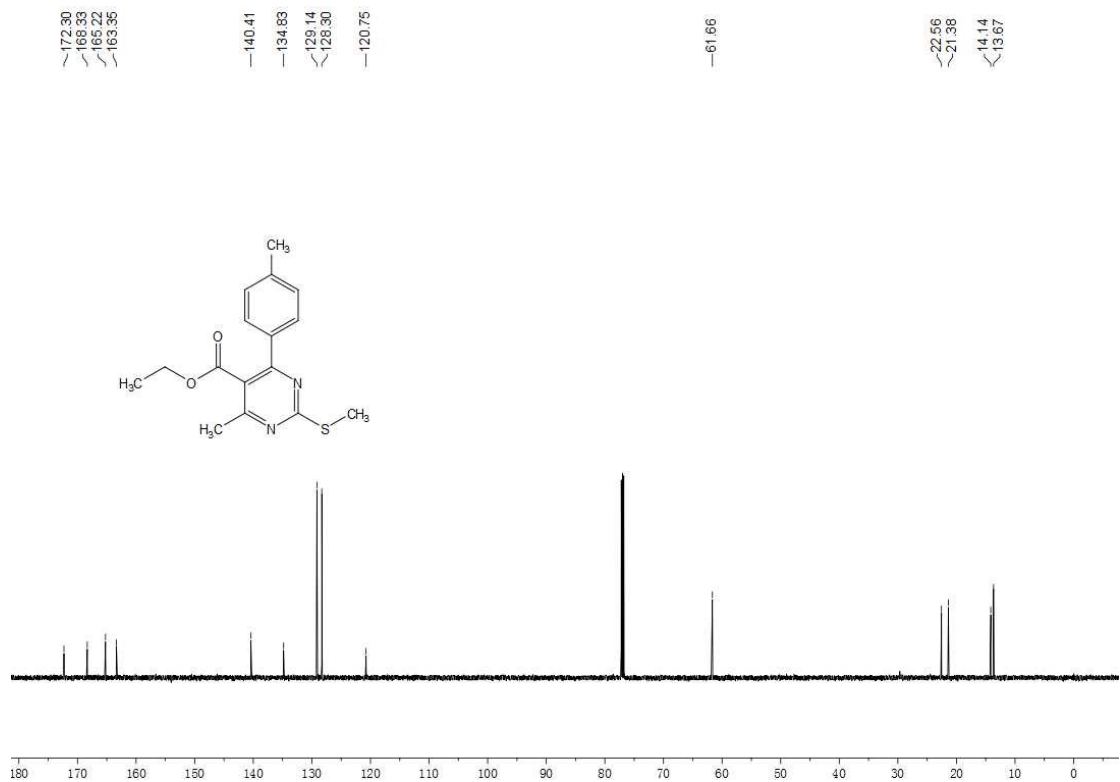


30

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)

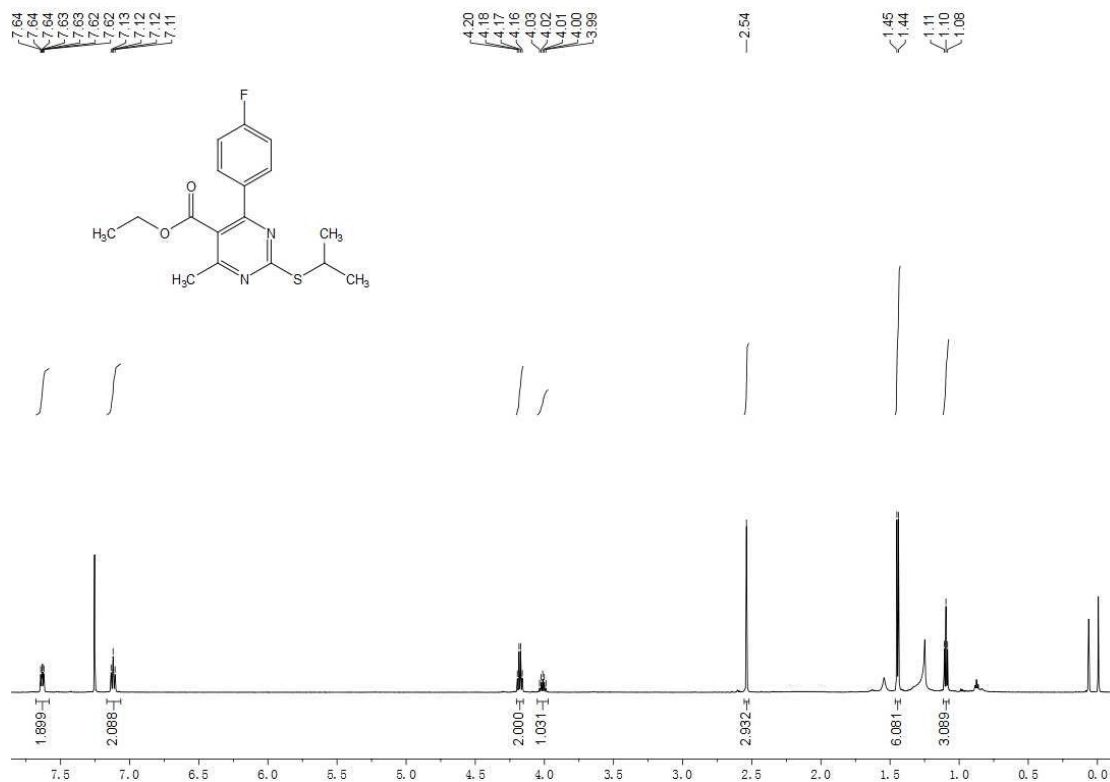


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)

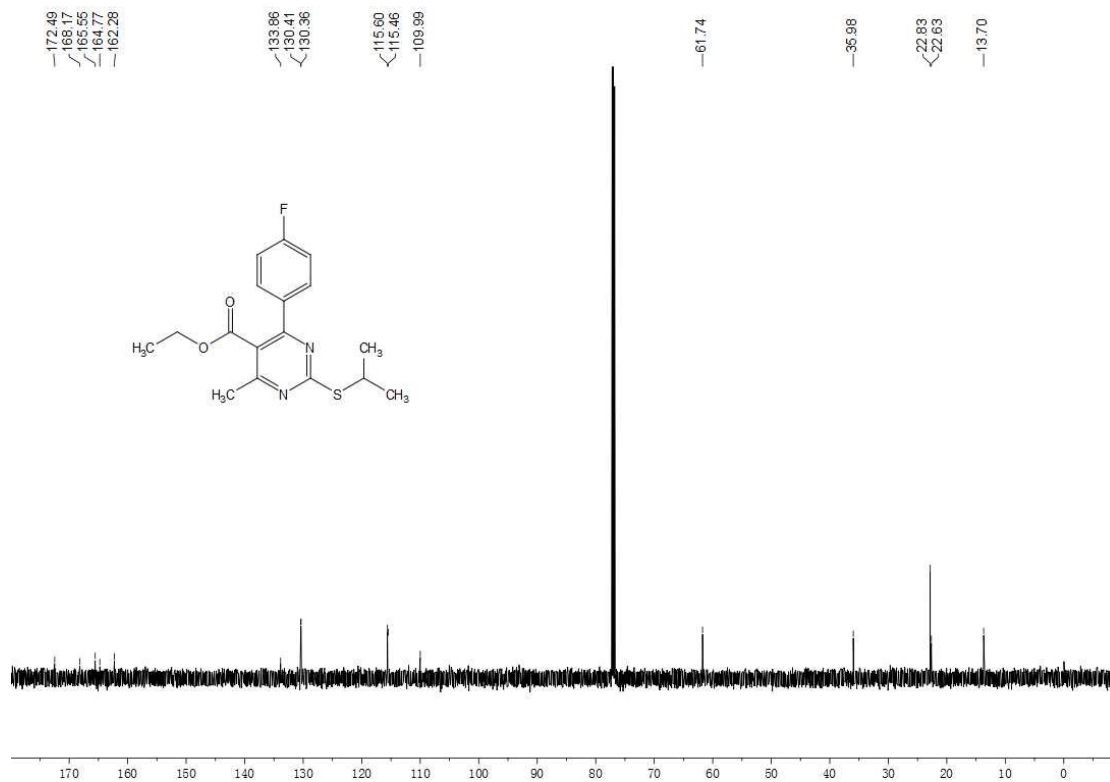


3p

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)

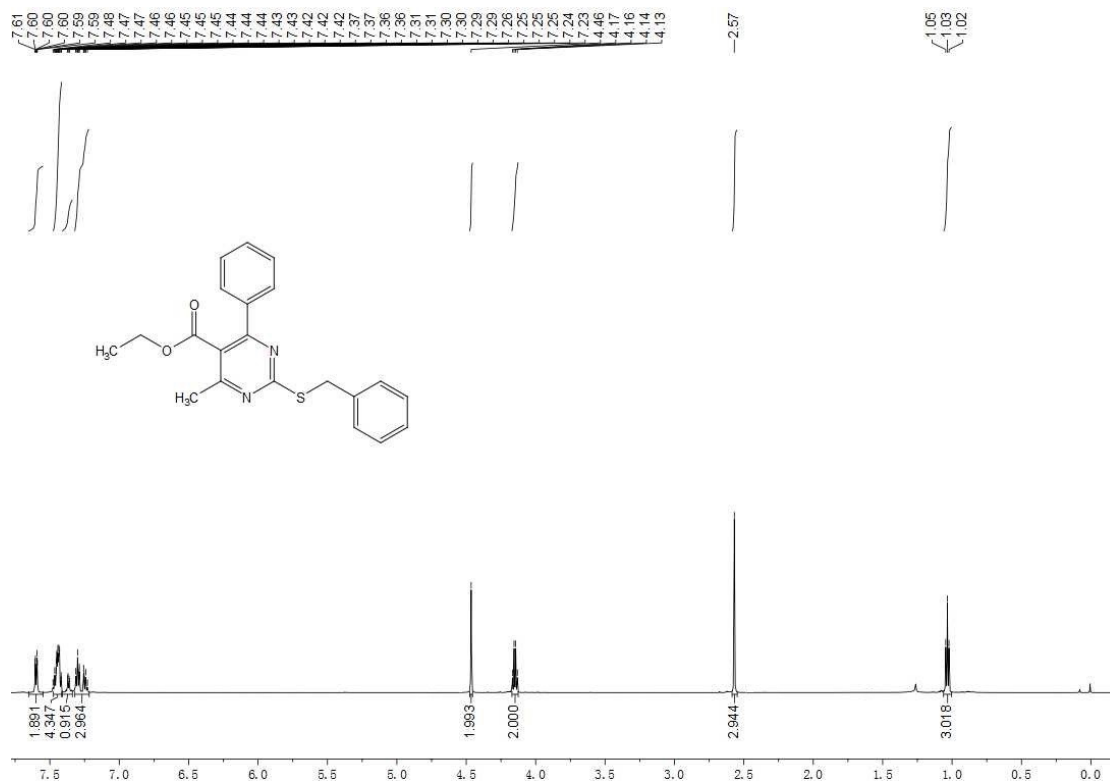


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)

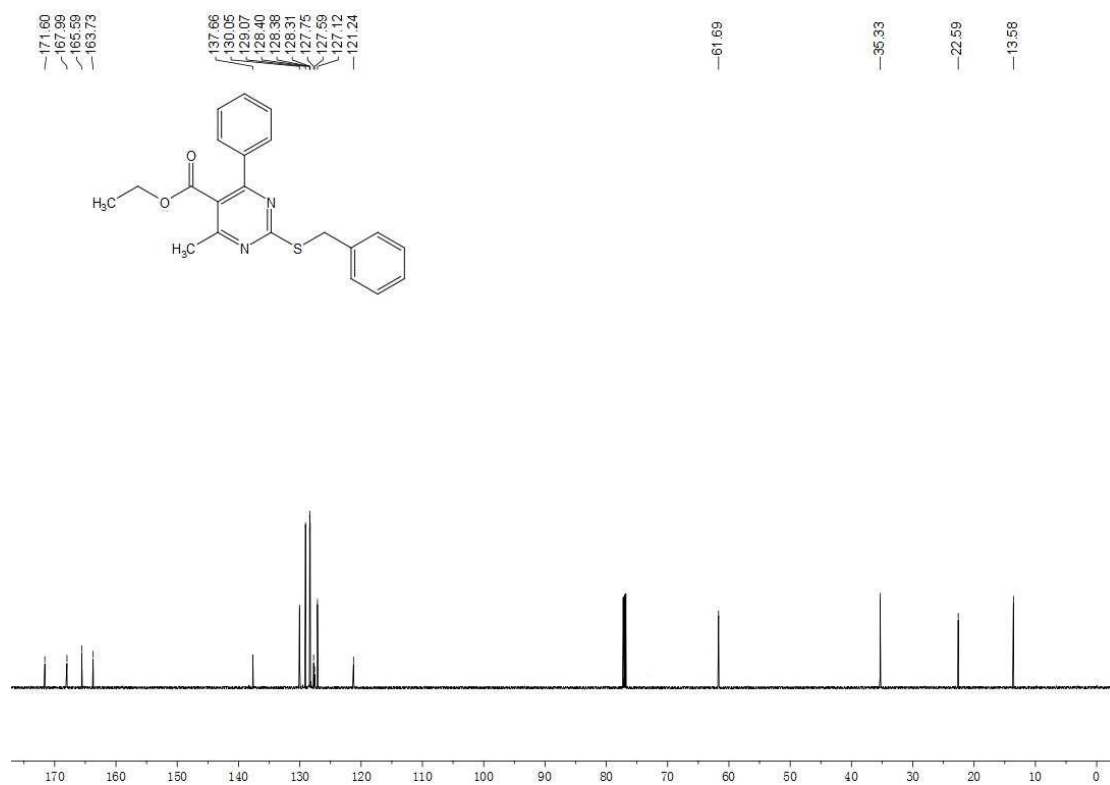


3q

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)

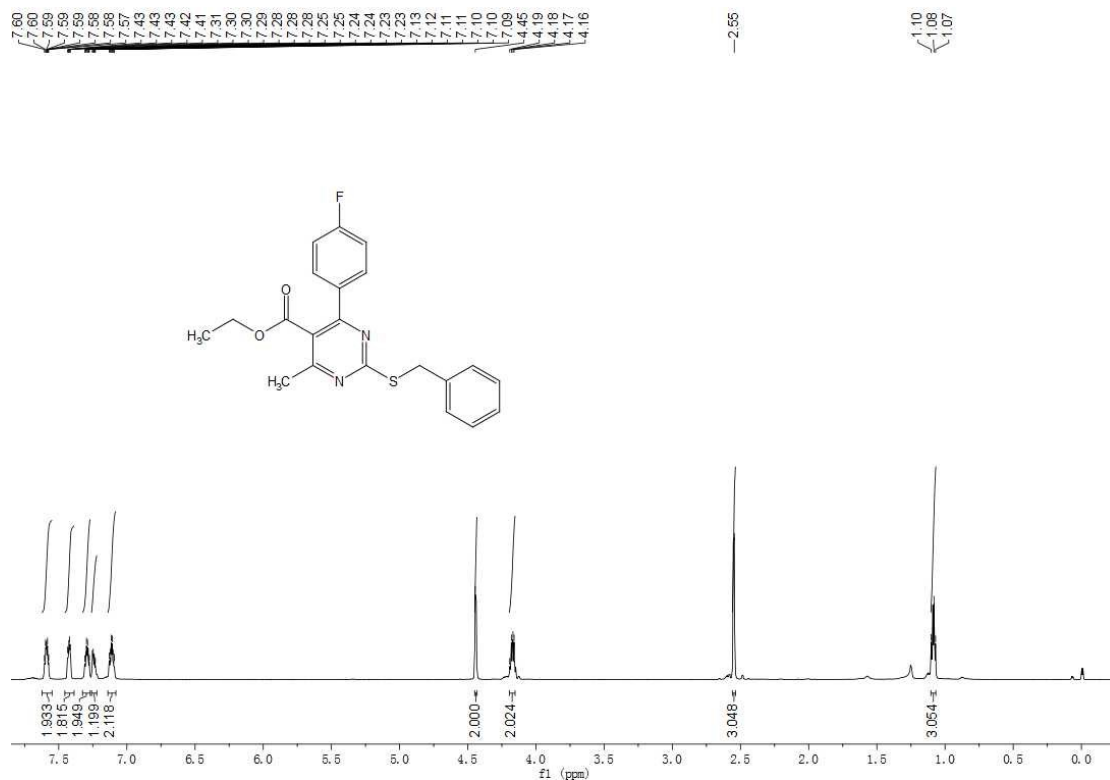


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)

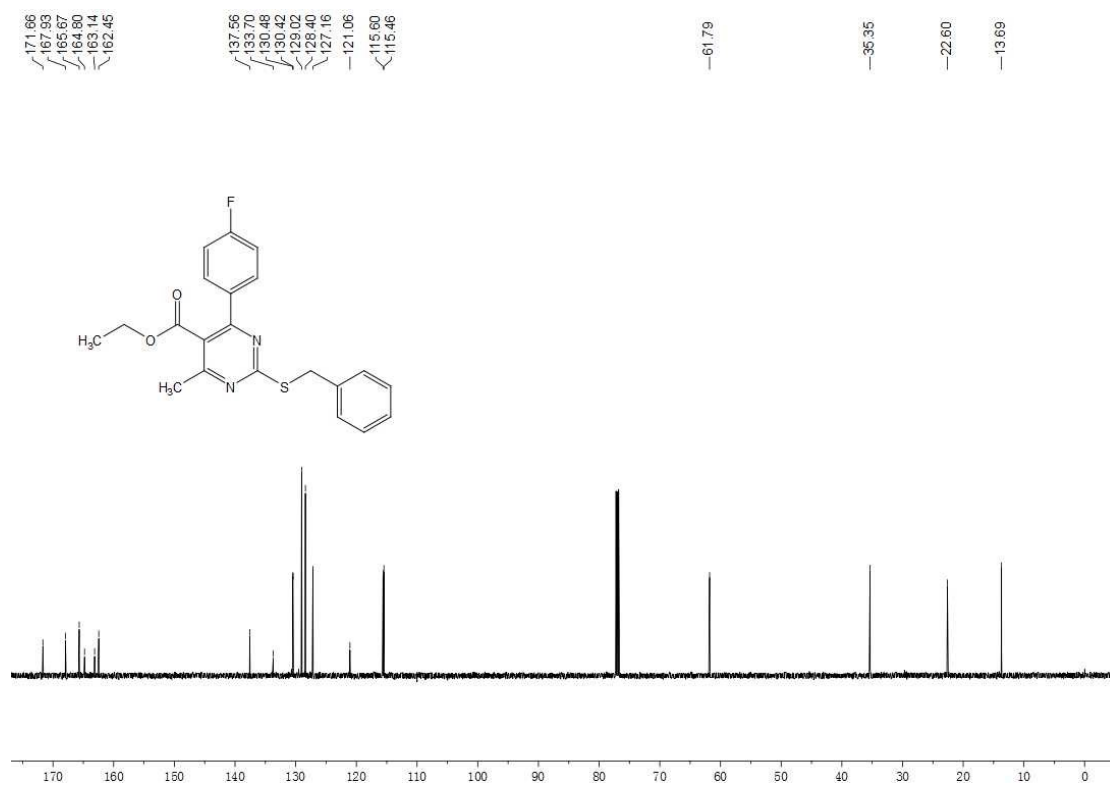


3r

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)

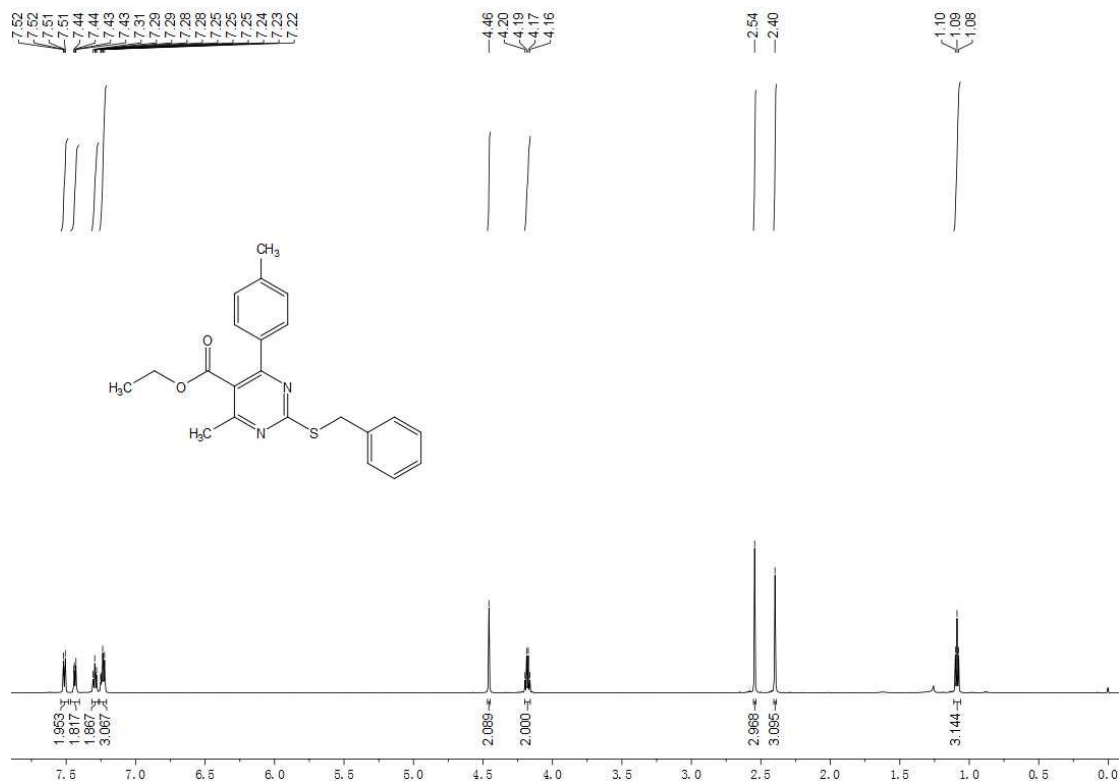


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)

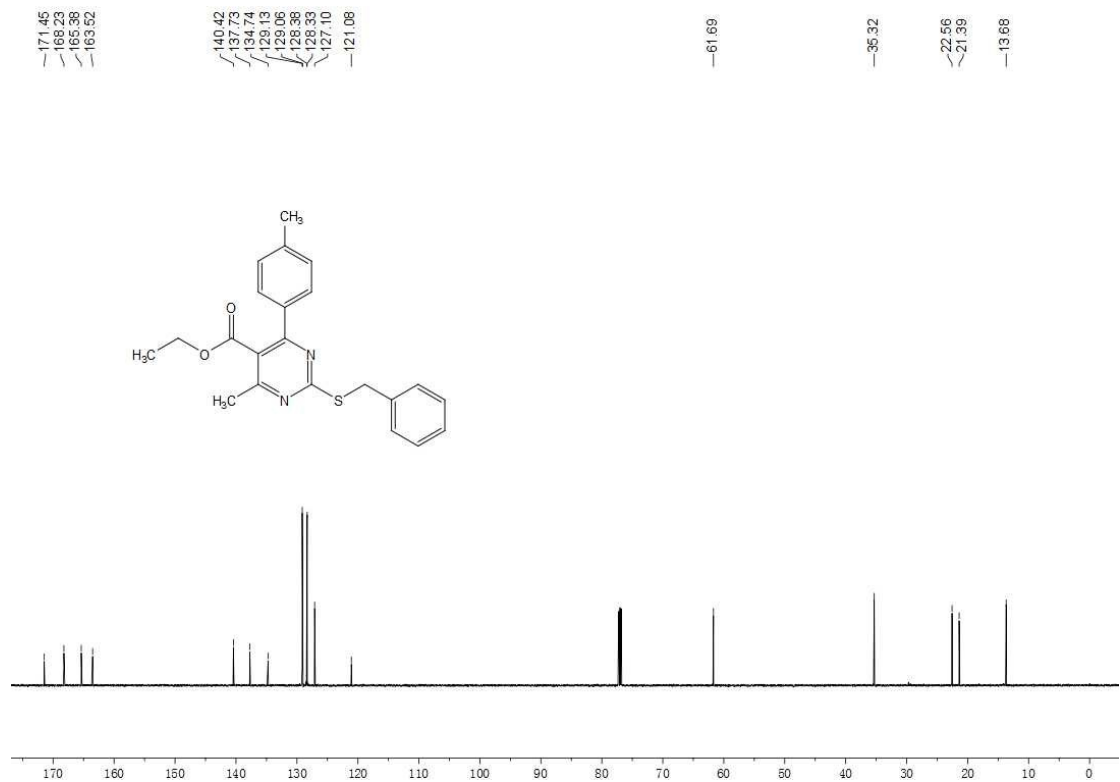


3s

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)



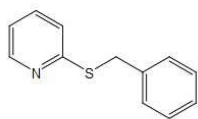
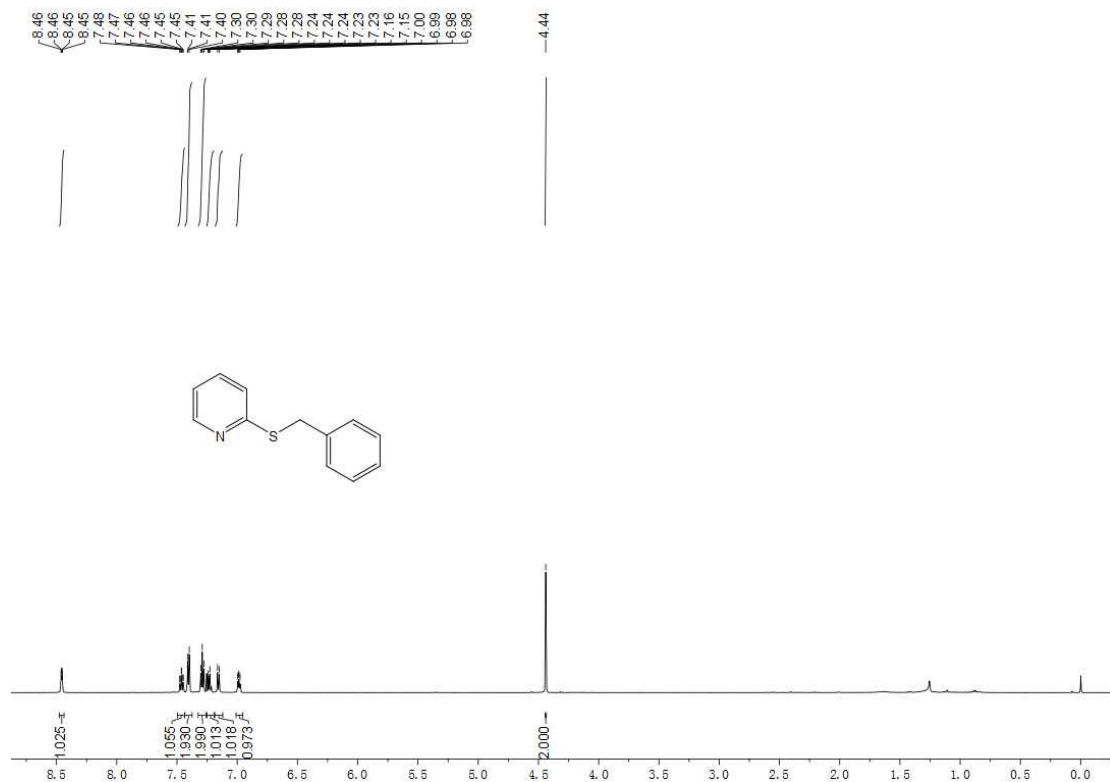
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)





3t

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)

