

# Supporting Information

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## **A: General Information and Starting Materials.**

**General Information.** Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra and carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were recorded on a Bruker ACF300 spectrometer (400 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ( $\text{CDCl}_3$ :  $\delta$  7.26,  $\text{DMSO-}d_6$ :  $\delta$  2.50). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ( $\text{CDCl}_3$ :  $\delta$  77.16,  $\text{DMSO-}d_6$ :  $\delta$  39.52). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

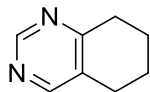
**Starting Materials.** All solvents and inorganic reagents were from commercial sources and used without purification unless otherwise noted.

## **B: General Procedure for Diels-Alder Reaction of Ketones with 1,3,5-triazine.**

To a solution of DMSO (0.25 mL) were added unsaturated ketones **1a** (0.10 mmol), 1,3,5-triazines **2** (0.20 mmol), catalyst **I** (0.01 mmol) and  $\text{Et}_3\text{N}$  (0.01 mmol). The reaction mixture was stirred at 90 °C for 48h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **3**.

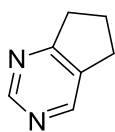
## C: Characterization Data.

### 5,6,7,8-tetrahydroquinazoline (3a)



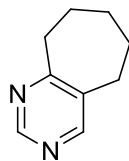
Yellow oli, 91% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 8.91 (s, 1H), 8.39 (s, 1H), 2.89-2.86 (t,  $J = 6.0$  Hz, 2H), 2.77-2.74 (t,  $J = 6.0$  Hz, 2H), 1.93-1.83 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 165.98, 156.81, 156.07, 130.36, 31.79, 25.59, 22.15, 21.99. HRMS (EI): exact mass calculated for M ( $\text{C}_8\text{H}_{10}\text{N}_2$ ) requires  $m/z$  134.0844, found  $m/z$  134.0847.

### 6,7-dihydro-5H-cyclopenta[d]pyrimidine (3b)



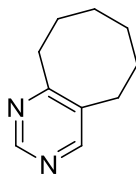
Claret oli, 85% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 8.97 (s, 1H), 8.52 (s, 1H), 3.04-2.04 (m, 4H), 2.20-2.12 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 174.72, 156.85, 151.93, 134.95, 34.03, 28.36, 22.43. HRMS (EI): exact mass calculated for M ( $\text{C}_7\text{H}_8\text{N}_2$ ) requires  $m/z$  120.0687, found  $m/z$  120.0684.

### 6,7,8,9-tetrahydro-5H-cyclohepta[d]pyrimidine (3c)



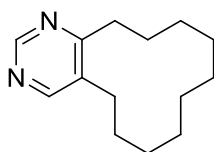
Yellow oli, 93% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 8.90 (s, 1H), 8.38 (s, 1H), 3.01-2.98 (t,  $J = 6.0$  Hz, 2H), 2.78-2.75 (t,  $J = 6.0$  Hz, 2H), 1.94-1.88 (t,  $J = 12.0$  Hz, 2H), 1.74-1.67 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 171.30, 156.30, 155.45, 135.50, 38.99, 32.28, 31.88, 27.43, 25.73. HRMS (EI): exact mass calculated for M ( $\text{C}_9\text{H}_{12}\text{N}_2$ ) requires  $m/z$  148.1000, found  $m/z$  148.1004.

### 5,6,7,8,9,10-hexahydrocycloocta[d]pyrimidine (3d)



Yellow oil, 95% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 8.98 (s, 1H), 8.40 (s, 1H), 2.94-2.91 (t,  $J = 6.0$  Hz, 2H), 2.78-2.75 (t,  $J = 6.0$  Hz, 2H), 1.85-1.82 (t,  $J = 6.0$  Hz, 2H), 1.74-1.71 (m, 2H), 1.42-1.38 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 169.37, 156.85, 156.19, 133.99, 33.92, 31.80, 29.92, 28.94, 25.74, 25.58. HRMS (EI): exact mass calculated for M ( $\text{C}_{10}\text{H}_{14}\text{N}_2$ ) requires  $m/z$  162.1557, found  $m/z$  162.1555.

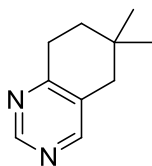
### 5,6,7,8,9,10,11,12,13,14-decahydrobenzo[12]annulene (3e)



Yellow oil, 80% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 8.96 (s, 1H), 8.47 (s, 1H), 2.81-2.78 (t,  $J = 6.0$  Hz, 2H), 2.69-2.66 (t,  $J = 6.0$  Hz, 2H), 1.93-1.86 (m, 2H), 1.79-1.70 (m, 2H), 1.49-1.35 (m, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 168.90, 157.70, 156.21, 133.74, 31.06, 29.14, 27.17, 26.37, 26.24, 25.99, 25.49, 25.04, 24.96, 22.99, 22.90.

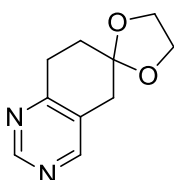
HRMS (EI): exact mass calculated for M (C<sub>14</sub>H<sub>22</sub>N<sub>2</sub>) requires m/z 218.1783, found m/z 218.1780.

### 6,6-dimethyl-5,6,7,8-tetrahydroquinazoline (3f)



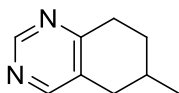
Yellow oli, 90% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 8.94 (s, 1H), 8.37 (s, 1H), 2.93-2.89 (t, *J*=8.0Hz, 2H), 2.53 (s, 2H), 1.71-1.67 (t, *J*=8.0Hz, 2H), 1.03 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 165.18, 157.26, 156.13, 129.43, 39.40, 34.76, 29.14, 28.99, 27.73. HRMS (EI): exact mass calculated for M (C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>) requires m/z 162.1157, found m/z 162.1160.

### 7',8'-dihydro-5'H-spiro[[1,3]dioxolane-2,6'-quinazoline] (3g)



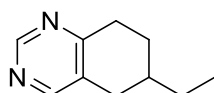
Yellow oli, 92% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 7.58-7.56 (m, 2H), 7.51-7.48 (m, 1H), 7.46-7.43 (m, 2H), 7.35-7.32 (m, 2H), 7.26-7.23 (m, 1H), 7.15-7.14 (m, 1H), 3.94 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 164.61, 157.08, 156.40, 127.90, 106.73, 64.72, 35.54, 30.87, 30.56. HRMS (EI): exact mass calculated for M (C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>) requires m/z 192.0899, found m/z 192.0900.

### 6-methyl-5,6,7,8-tetrahydroquinazoline (3h)



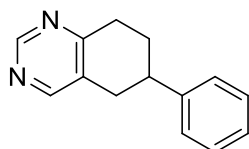
Yellow oli, 85% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 8.92 (s, 1H), 8.38 (s, 1H), 2.95-2.79 (m, 3H), 2.41-2.34 (m, 1H), 2.03-1.98 (m, 1H), 1.93-1.88 (m, 1H), 1.57-1.48 (m, 1H), 1.12-1.10 (d, *J* = 8.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 165.67, 156.71, 156.05, 129.90, 33.86, 31.43, 30.20, 28.27, 21.36. HRMS (EI): exact mass calculated for M (C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>) requires m/z 148.1000, found m/z 148.10010.

### 6-ethyl-5,6,7,8-tetrahydroquinazoline (3i)



Yellow oil, 93% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 8.92 (s, 1H), 8.39 (s, 1H), 3.94-2.64 (m, 3H), 2.41-2.34 (m, 1H), 2.08-2.05 (m, 1H), 1.67 (s, 1H), 1.46-1.43 (t, *J*=6.0 Hz, 3H), 1.02-0.99 (t, *J*=6.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 165.87, 156.80, 156.03, 129.89, 34.90, 31.70, 31.45, 28.55, 27.86, 11.38. HRMS (EI): exact mass calculated for M (C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>) requires m/z 162.1157, found m/z 162.1150.

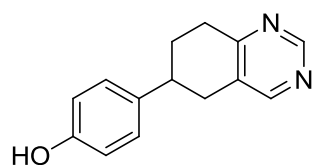
### 6-phenyl-5,6,7,8-tetrahydroquinazoline (3j)



Yellow solid, 90% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 8.97 (s, 1H), 7.37-7.26 (m, 5H), 3.06-3.02 (m, 4H), 2.93-2.86 (m, 1H), 2.27-2.23 (m, 1H), 2.07-2.02 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,

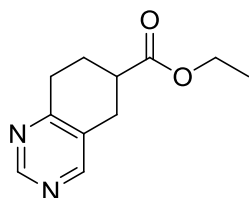
400 MHz):  $\delta$  (ppm) 165.35, 156.85, 156.38, 144.83, 129.88, 128.74, 126.75, 126.72, 39.56, 33.59, 32.13, 29.33. HRMS (EI): exact mass calculated for M ( $C_{14}H_{14}N_2$ ) requires  $m/z$  210.1157, found  $m/z$  210.1160.

#### 4-(5,6,7,8-tetrahydroquinazolin-6-yl)phenol (3k)



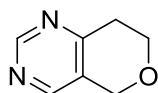
Claret solid, 87% yield.  $^1H$  NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  (ppm) 9.23 (s, 1H), 8.89 (s, 1H), 8.49 (s, 1H), 7.12-7.10 (d,  $J=8.0$  Hz, 2H), 6.64-6.62 (d,  $J=8.0$  Hz, 2H), 3.38 (s, 3H), 2.95-2.88 (m, 4H).  $^{13}C$  NMR ((DMSO- $d_6$ , 400 MHz):  $\delta$  (ppm) 165.30, 157.17, 156.26, 156.21, 135.98, 130.47, 128.03, 115.63, 40.58, 40.37, 40.16, 39.96, 39.75, 39.54, 39.33, 38.29, 33.50, 32.10, 29.65. HRMS (EI): exact mass calculated for M ( $C_{14}H_{14}N_2O$ ) requires  $m/z$  226.1106, found  $m/z$  226.1110.

#### Ethyl 5,6,7,8-tetrahydroquinazoline-6-carboxylate (3l)



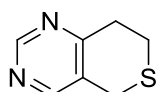
Yellow oil, 93% yield.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  (ppm) 8.96(s, 1H), 8.46 (s, 1H), 4.22-4.17 (m, 2H), 3.03-2.94 (m, 4H), 2.82-2.76 (m, 1H), 2.32-2.30 (t,  $J=4.0$  Hz, 1H), 2.07-1.97 (m, 1H), 1.31-1.27 (t,  $J=8.0$  Hz, 3H).  $^{13}C$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  (ppm) 174.08, 164.65, 156.92, 156.39, 128.44, 60.88, 38.62, 30.64, 27.76, 24.76, 14.19. HRMS (EI): exact mass calculated for M ( $C_{11}H_{14}N_2O_2$ ) requires  $m/z$  206.1055, found  $m/z$  206.1058.

#### 7,8-dihydro-5H-pyrano[4,3-d]pyrimidine (3m)



Yellow oli, 91% yield.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  (ppm) 9.02 (s, 1H), 8.39 (s, 1H), 4.78 (s, 2H), 4.10-4.07 (t,  $J = 6.0$  Hz, 2H), 3.01-2.98 (t,  $J = 6.0$  Hz, 2H).  $^{13}C$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  (ppm) 162.49, 157.10, 152.87, 141.0, 136.6, 130.4, 130.2, 130.0, 128.5, 126.7, 125.6, 124.4, 119.7, 128.62, 64.93, 64.79, 31.10. HRMS (EI): exact mass calculated for M ( $C_7H_8N_2O$ ) requires  $m/z$  136.0637, found  $m/z$  136.0630.

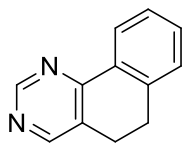
#### 7,8-dihydro-5H-thiopyrano[4,3-d]pyrimidine (3n)



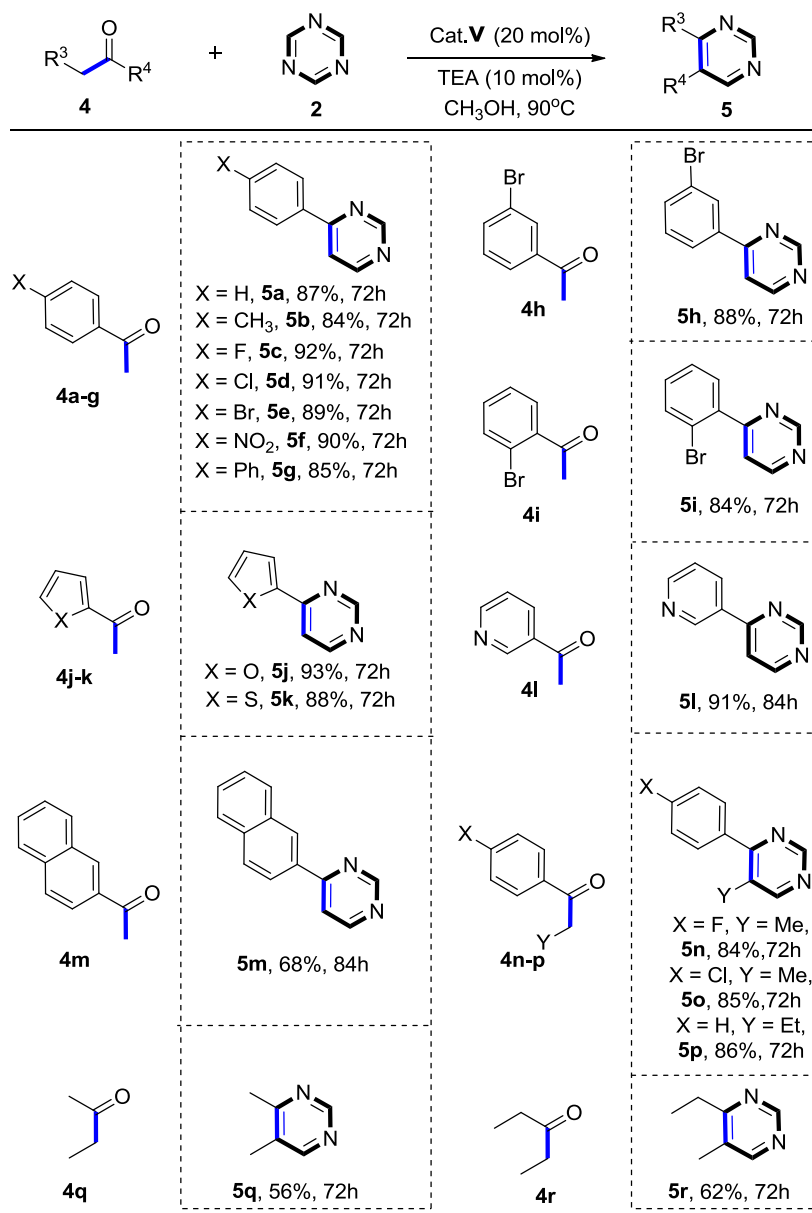
Yellow oil, 89% yield.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  (ppm) 8.98 (s, 1H), 8.44 (s, 1H), 3.78 (s, 2H), 3.21-3.18 (t,  $J = 6.0$  Hz, 2H), 3.03-2.99 (m, 2H).  $^{13}C$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  (ppm) 164.80, 156.80, 155.66, 128.15, 33.15, 27.12, 25.79. HRMS (EI): exact mass calculated for M ( $C_7H_8N_2S$ ) requires  $m/z$  152.0408, found  $m/z$  152.0410.

#### 5,6-dihydrobenzo[h]quinazoline (3o)

Yellow oli, 83% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 9.02 (s, 1H), 8.99 (s, 1H), 7.76-7.74 (t,  $J=4.0$  Hz, 1H), 7.36-7.28 (m, 3H), 3.07-3.02 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 165.78, 157.09, 150.72, 136.62, 129.75, 129.34, 128.68, 127.73, 127.52, 123.38, 30.76, 27.66. HRMS (EI): exact mass calculated for M ( $\text{C}_{12}\text{H}_{10}\text{N}_2$ ) requires  $m/z$  182.0844, found  $m/z$  182.0850.

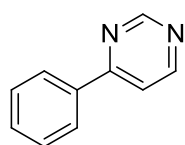


## D: Cycloadditions of Electron-deficient Acetylbenzenes with 1,3,5-Triazine.



To a solution of CH<sub>3</sub>OH (0.5 mL) were added electron-deficient acetyl benzenes **4a** (0.10 mmol), 1,3,5-triazine **2a** (0.20 mmol) and catalyst V (0.02 mmol). The reaction mixture was stirred at 90 °C for the time given and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product.

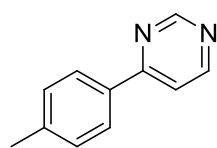
### 4-phenylpyrimidine (**5a**)



Colourless solid, 87% yield, 72h. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 9.28 (s, 1H), 8.77-8.76 (d, *J* = 4.0 Hz, 1H), 8.11-8.08 (m, 2H), 7.73-7.71 (m, 2H), 7.53-7.51 (t, *J* = 4.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 163.94, 159.13, 157.49, 136.52, 131.12, 129.07, 127.16, 117.05. HRMS (EI): exact mass calculated for M (C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)

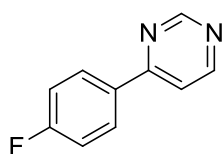
requires m/z 156.0687, found m/z 156.0688.

#### 4-(p-tolyl)pyrimidine (5b)



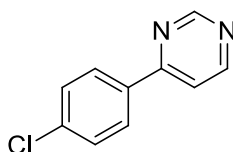
Yellow solid, 84% yield, 72h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 9.25 (s, 1H), 8.74-8.72 (d,  $J = 8.0$  Hz, 1H), 8.01-7.98 (d,  $J = 12.0$  Hz, 2H), 7.70-7.68 (m, 1H), 7.33-7.31 (d,  $J = 8.0$  Hz, 2H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 163.88, 159.08, 157.34, 141.60, 133.71, 129.81, 127.06, 116.70, 21.48. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_{11}\text{H}_{10}\text{N}_2)$  requires m/z 170.0844, found m/z 170.0840.

#### 4-(4-fluorophenyl)pyrimidine (5c)



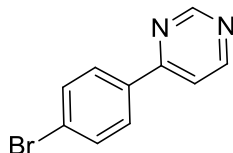
Colourless solid, 92% yield, 72h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 9.26 (s, 1H), 8.77-8.76 (d,  $J = 4.0$  Hz, 1H), 8.13-8.09 (m, 2H), 7.69-7.67 (m, 1H), 7.22-7.18 (t,  $J = 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 166.02, 163.51, 162.79, 159.12, 157.55, 136.66, 136.63 (d,  $J = 12.0$  Hz), 129.28, 128.20 (d,  $J = 32.0$  Hz), 116.65, 116.25, 116.04. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_{10}\text{H}_7\text{FN}_2)$  requires m/z 174.0593, found m/z 174.0592.

#### 4-(4-chlorophenyl)pyrimidine (5d)



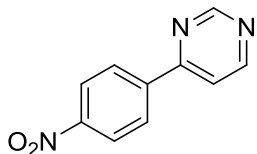
Yellow solid, 91% yield, 72h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 9.27 (d, 1H), 8.79-8.78 (d,  $J = 4.0$  Hz, 1H), 8.07-8.04 (m, 2H), 7.71-7.69 (m, 1H), 7.51-7.48 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 162.72, 159.16, 157.66, 137.46, 134.91, 129.33, 128.43, 116.77. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_{10}\text{H}_7\text{ClN}_2)$  requires m/z 190.0298, found m/z 190.0296.

#### 4-(4-bromophenyl)pyrimidine (5e)



Yellow solid, 89% yield, 72h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 9.27 (s, 1H), 8.79-8.77 (d,  $J = 8.0$  Hz, 1H), 7.98-7.96 (d,  $J = 8.0$  Hz, 2H), 7.70-7.68 (d,  $J = 8.0$  Hz, 1H), 7.66-7.64 (d,  $J = 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 162.75, 159.18, 157.70, 135.36, 132.29, 128.64, 125.90, 116.72. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_{10}\text{H}_7\text{BrN}_2)$  requires m/z 233.9793, found m/z 233.9791.

#### 4-(4-nitrophenyl)pyrimidine (5f)

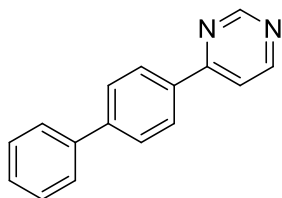


Yellow solid, 90% yield, 72h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 9.36 (d, 1H), 8.90-8.89 (d,  $J = 4.0$  Hz, 1H), 8.39-8.37 (m, 2H), 8.30-3.28 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm)



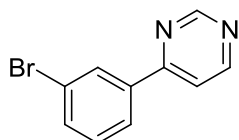
161.46, 159.39, 158.23, 149.42, 142.32, 128.16, 124.22, 117.64. HRMS (EI): exact mass calculated for M (C<sub>10</sub>H<sub>7</sub>N<sub>3</sub>O<sub>2</sub>) requires m/z 201.0538, found m/z 201.0535.

#### 4-([1,1'-biphenyl]-4-yl)pyrimidine (5g)



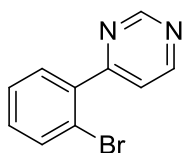
Colourless solid, 85% yield, 72h. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 9.21 (s, 1H), 8.70-8.69 (d, *J* = 4.0 Hz, 1H), 8.11-8.09 (d, *J* = 8.0 Hz, 2H), 7.68-7.66 (t, *J* = 4.0 Hz, 2H), 7.59-7.57 (d, *J* = 8.0 Hz, 2H), 7.42-7.38 (t, *J* = 8.0 Hz, 2H), 7.33-7.30 (t, *J* = 6.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 163.51, 159.16, 157.47, 143.94, 140.09, 135.29, 128.96, 128.00, 127.73, 127.61, 127.18, 116.89. HRMS (EI): exact mass calculated for M (C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>) requires m/z 232.1000, found m/z 232.1010.

#### 4-(3-bromophenyl)pyrimidine (5h)



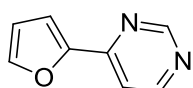
Colourless solid, 88% yield, 72h. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 9.30-9.29 (d, *J* = 4.0 Hz, 1H), 8.82-8.81 (d, *J* = 4.0 Hz, 1H), 8.28-8.27 (t, *J* = 2 Hz, 1H), 8.03-8.00 (m, 1H), 7.72-7.70 (m, 2H), 7.67-7.64 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 162.45, 159.17, 157.76, 138.52, 134.02, 130.57, 130.29, 125.67, 123.37, 117.09. HRMS (EI): exact mass calculated for M (C<sub>10</sub>H<sub>7</sub>BrN<sub>2</sub>) requires m/z 233.9793, found m/z 233.9796.

#### 4-(2-bromophenyl)pyrimidine (5i)



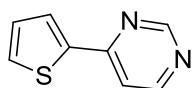
Colourless solid, 84% yield, 72h. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 9.25 (d, 1H), 9.73-8.72 (d, *J* = 4.0 Hz, 1H), 7.63-7.61 (t, *J* = 4.0 Hz, 2H), 7.52-7.50 (dd, *J* = 8.0 Hz, 1H), 7.38-7.34 (m, 1H), 7.26-7.22 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 165.28, 158.97, 156.61, 138.59, 133.72, 131.37, 131.01, 127.87, 121.98, 121.32. HRMS (ESI): exact mass calculated for [M] (C<sub>10</sub>H<sub>7</sub>BrN<sub>2</sub>) requires m/z 233.0793, found m/z 233.9795.

#### 4-(furan-2-yl)pyrimidine (5j)



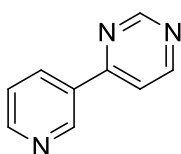
Yellow solid, 93% yield, 72h. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 9.16 (d, 1H), 8.73-8.72 (d, *J* = 4 Hz, 1H), 7.62-7.61 (t, *J* = 2.0 Hz, 2H), 7.31-7.27 (d, *J* = 8.0 Hz, 1H), 6.61-6.60 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 158.94, 157.42, 156.17, 151.44, 145.34, 114.81, 112.65, 112.64. HRMS (EI): exact mass calculated for M (C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>O) requires m/z 146.0480, found m/z 146.0482.

#### 4-(thiophen-2-yl)pyrimidine (5k)



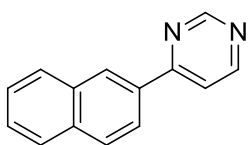
Yellow solid, 91% yield, 72h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 9.14 (d, 1H), 8.69-8.68 (d,  $J = 4.0$  Hz, 1H), 7.79-7.78 (m, 1H), 7.59-7.55 (m, 2H), 7.19-7.16 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 159.06, 158.82, 157.18, 141.95, 130.50, 128.56, 127.72, 115.21. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_8\text{H}_6\text{N}_2\text{S})$  requires  $m/z$  162.0252, found  $m/z$  162.0250.

#### 4-(pyridin-3-yl)pyrimidine (5l)



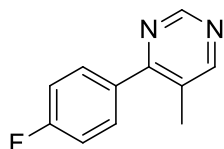
Yellow solid, 91% yield, 84h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 8.93-8.91 (d,  $J = 8.0$  Hz, 2H), 8.86-8.85 (d,  $J = 4.0$  Hz, 1H), 8.78-8.77 (d,  $J = 4.0$  Hz, 1H), 8.46-8.44 (d,  $J = 8.0$  Hz, 1H), 7.80-7.78 (m, 1H), 7.51-7.48 (M, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 161.60, 159.37, 157.87, 151.86, 148.48, 134.63, 132.22, 123.85, 117.07. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_9\text{H}_7\text{N}_3)$  requires  $m/z$  157.0640, found  $m/z$  157.0637.

#### 4-(naphthalen-2-yl)pyrimidine (5m)



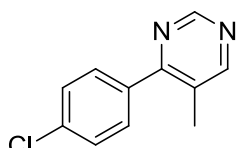
Yellow solid, 68% yield, 72h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 9.33 (s, 1H), 8.82-8.80 (d,  $J = 8.0$  Hz, 1H), 8.63 (s, 1H), 8.19-8.16 (m, 1H), 7.99-7.97 (d,  $J = 8.0$  Hz, 2H), 7.91-7.86 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 163.76, 159.16, 157.50, 134.67, 133.70, 133.24, 129.07, 128.88, 127.79, 127.60, 127.56 (d,  $J = 16.0$  Hz), 126.75, 123.75, 117.20. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_{14}\text{H}_{10}\text{N}_2)$  requires  $m/z$  206.0844, found  $m/z$  206.0840.

#### 4-(4-fluorophenyl)-5-methylpyrimidine (5n)



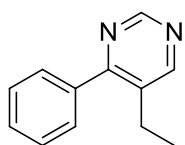
Colourless solid, 84% yield, 72h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 9.13 (s, 1H), 8.65 (s, 1H), 7.66-7.63 (m, 2H), 7.22-7.17 (t,  $J = 10.0$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 163.74, 158.98, 156.69, 136.24, 135.73, 130.30, 129.8, 128.75, 128.11, 17.17. HRMS (EI): exact mass calculated for  $[\text{M}](\text{C}_{11}\text{H}_9\text{FN}_2)$  requires  $m/z$  188.0750, found  $m/z$  188.0741.

#### 4-(4-chlorophenyl)-5-methylpyrimidine (5o)



Yellow oil, 88% yield, 72h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 9.13 (s, 1H), 8.65 (s, 1H), 7.60-7.58 (d,  $J = 8.0$  Hz, 2H), 7.49-7.47 (d,  $J = 8.0$  Hz, 2H), 2.40 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 163.83, 158.90, 156.60, 136.17, 135.77, 130.31, 128.76, 128.17, 17.18. HRMS (EI): exact mass calculated for  $\text{M}(\text{C}_{11}\text{H}_9\text{ClN}_2)$  requires  $m/z$  204.0454, found  $m/z$  204.0450.

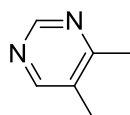
#### 5-ethyl-4-phenylpyrimidine (5p)



Colourless solid, 86% yield, 72h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 9.13 (s, 1H), 7.57-7.48 (m, 5H), 2.79-2.73 (m, 2H), 1.21-1.18 (t,  $J = 6.0$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 165.20, 157.70, 156.30, 137.92, 134.14, 129.27, 128.57, 128.50, 23.19, 14.84.

HRMS (EI): exact mass calculated for M ( $\text{C}_{12}\text{H}_{12}\text{N}_2$ ) requires  $m/z$  184.1000, found  $m/z$  184.1006.

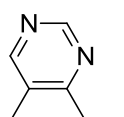
#### 4,5-dimethylpyrimidine (5q)



Yellow oil, 56% yield, 72h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 8.86 (s, 1H), 8.34 (s, 1H), 2.42 (s, 3H), 2.20 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 165.65, 156.39, 156.35(d,  $J = 16.0$  Hz), 129.32, 22.03, 15.82. HRMS (EI): exact mass calculated for M ( $\text{C}_6\text{H}_8\text{N}_2$ ) requires  $m/z$

108.0687, found  $m/z$  108.0682.

#### 4-ethyl-5-methylpyrimidine (5r)

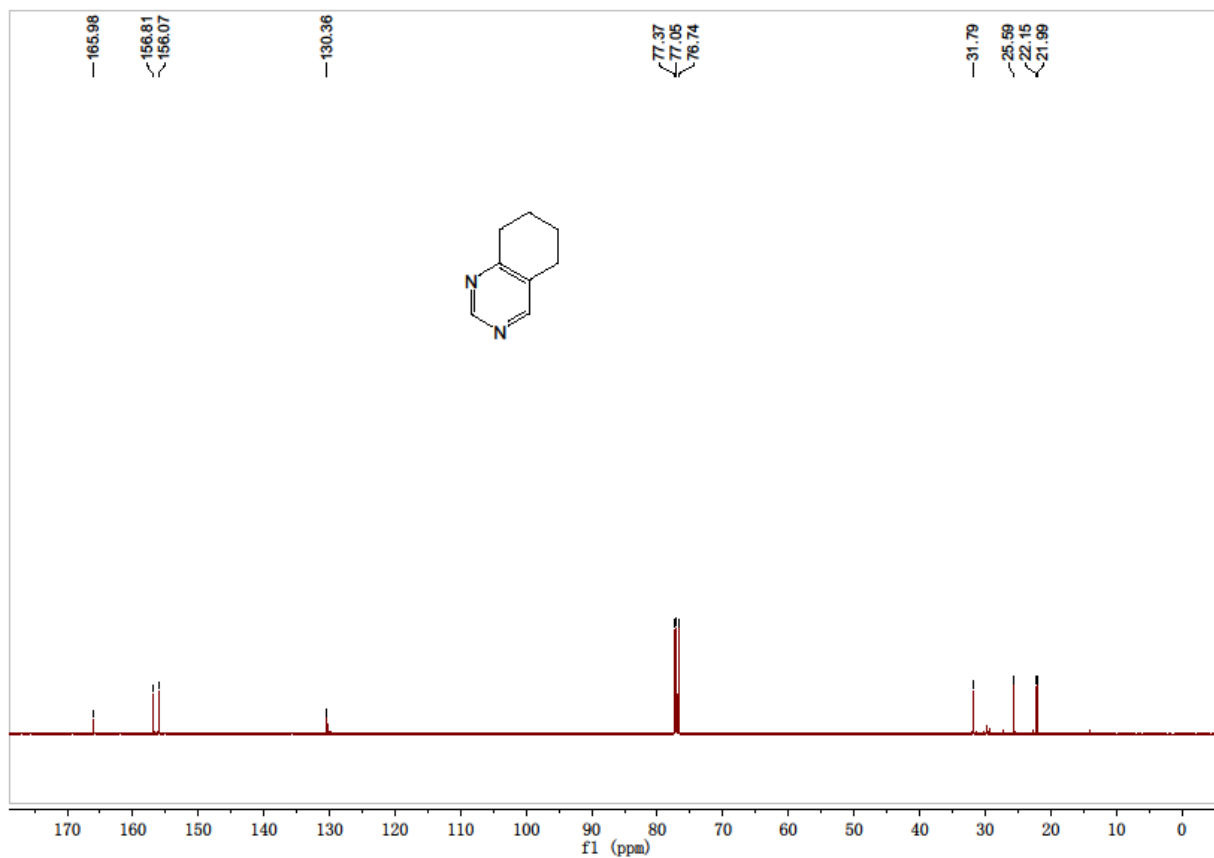
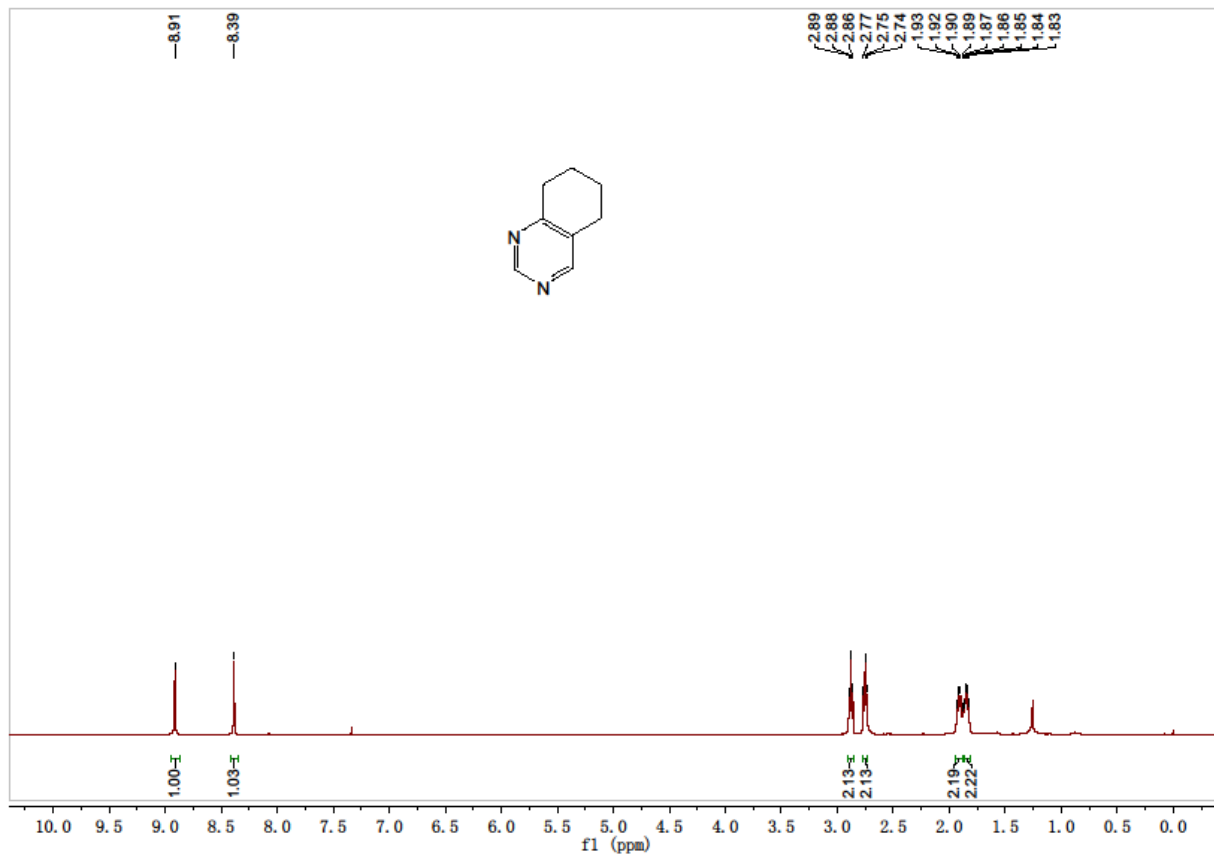


Colourless oil, 62% yield, 72h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 8.90 (s, 1H), 8.33 (m, 1H), 2.74-2.68 (m, 2H), 2.21 (s, 3H), 1.25-1.21 (t,  $J = 8.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 169.73, 156.70, 156.57(d,  $J = 52.0$  Hz), 128.60, 27.97, 15.36, 11.66. HRMS (EI): exact

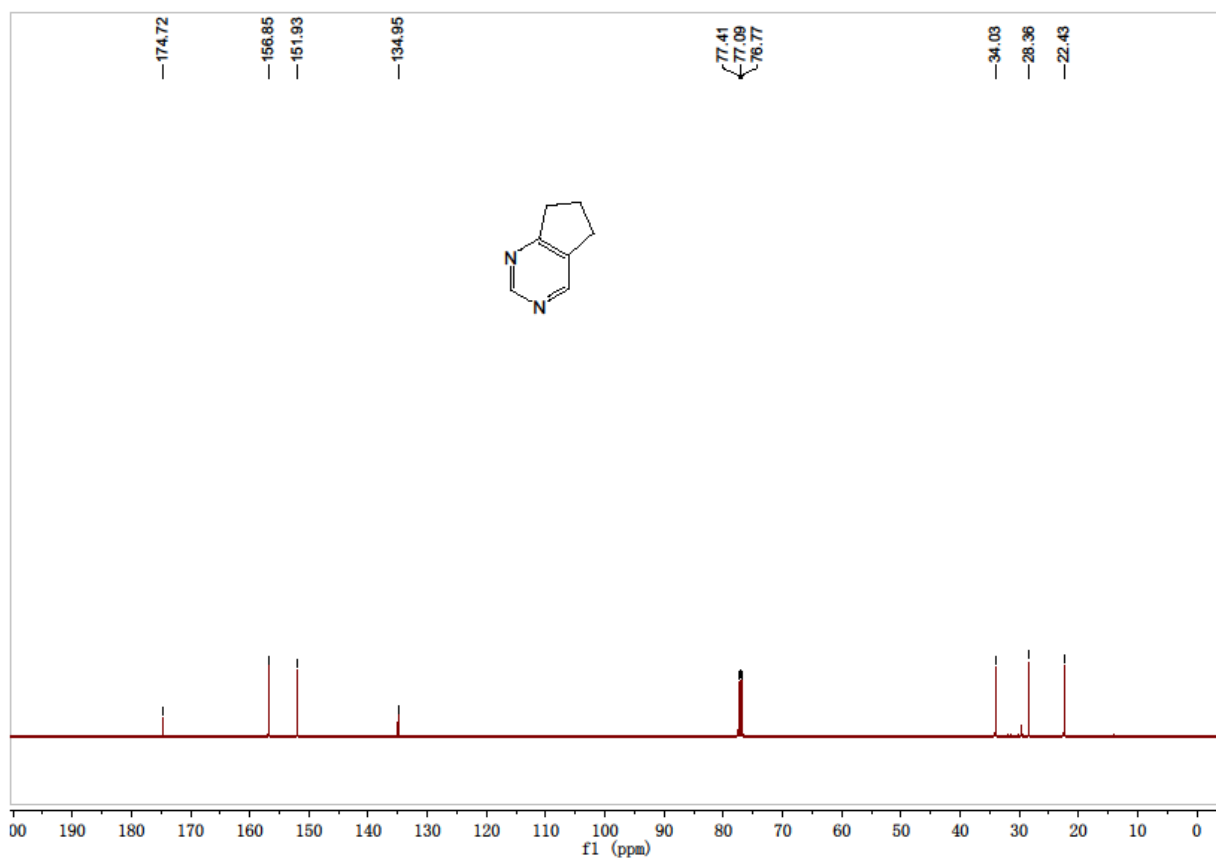
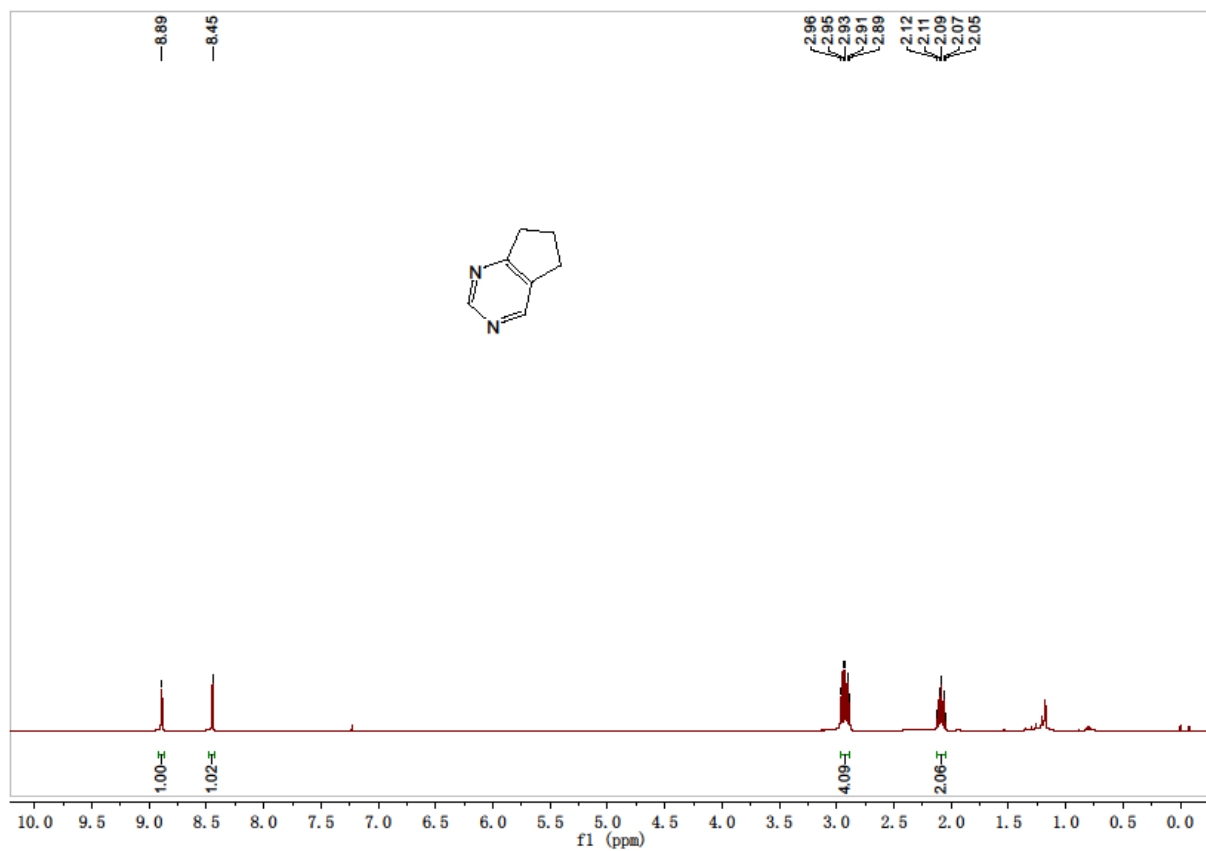
mass calculated for M ( $\text{C}_7\text{H}_{10}\text{N}_2$ ) requires  $m/z$  122.0844, found  $m/z$  122.0840.

# F: NMR Spectra.

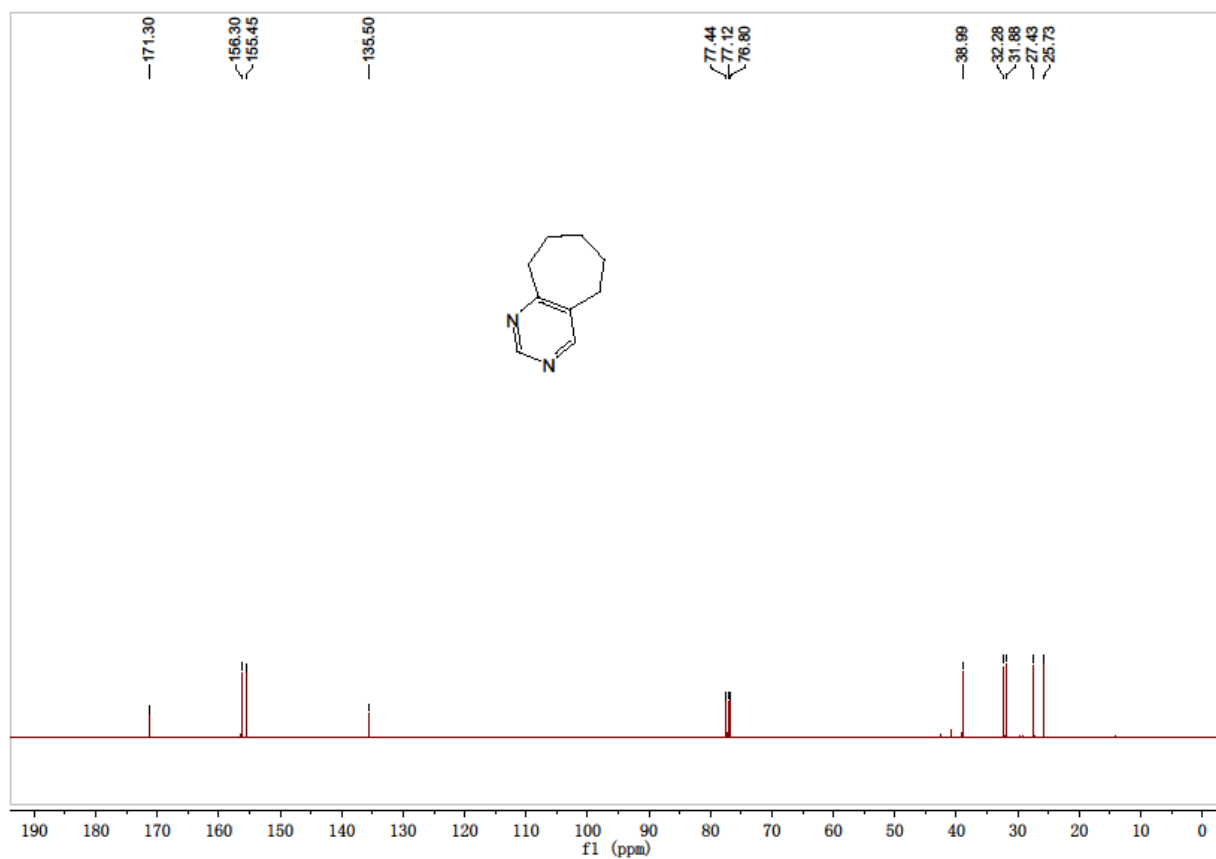
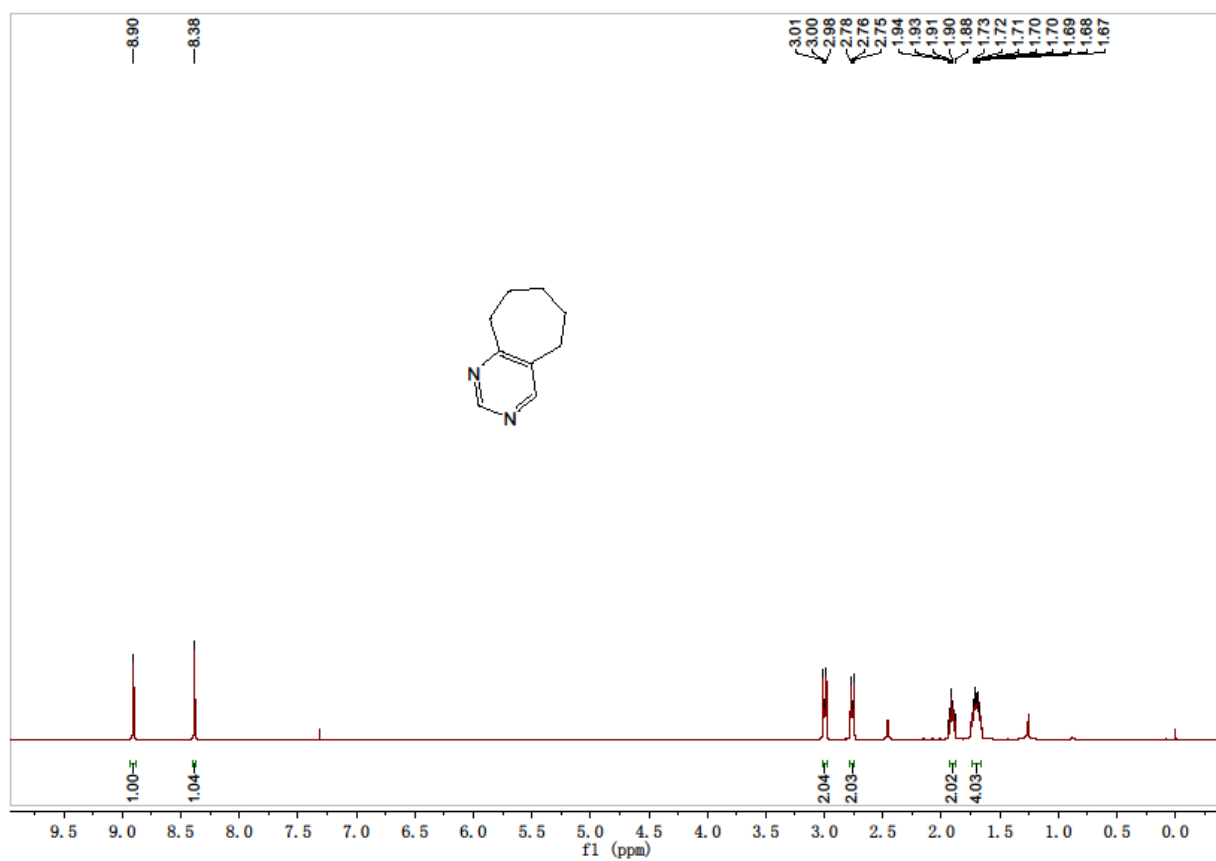
## 5,6,7,8-tetrahydroquinazoline (3a)



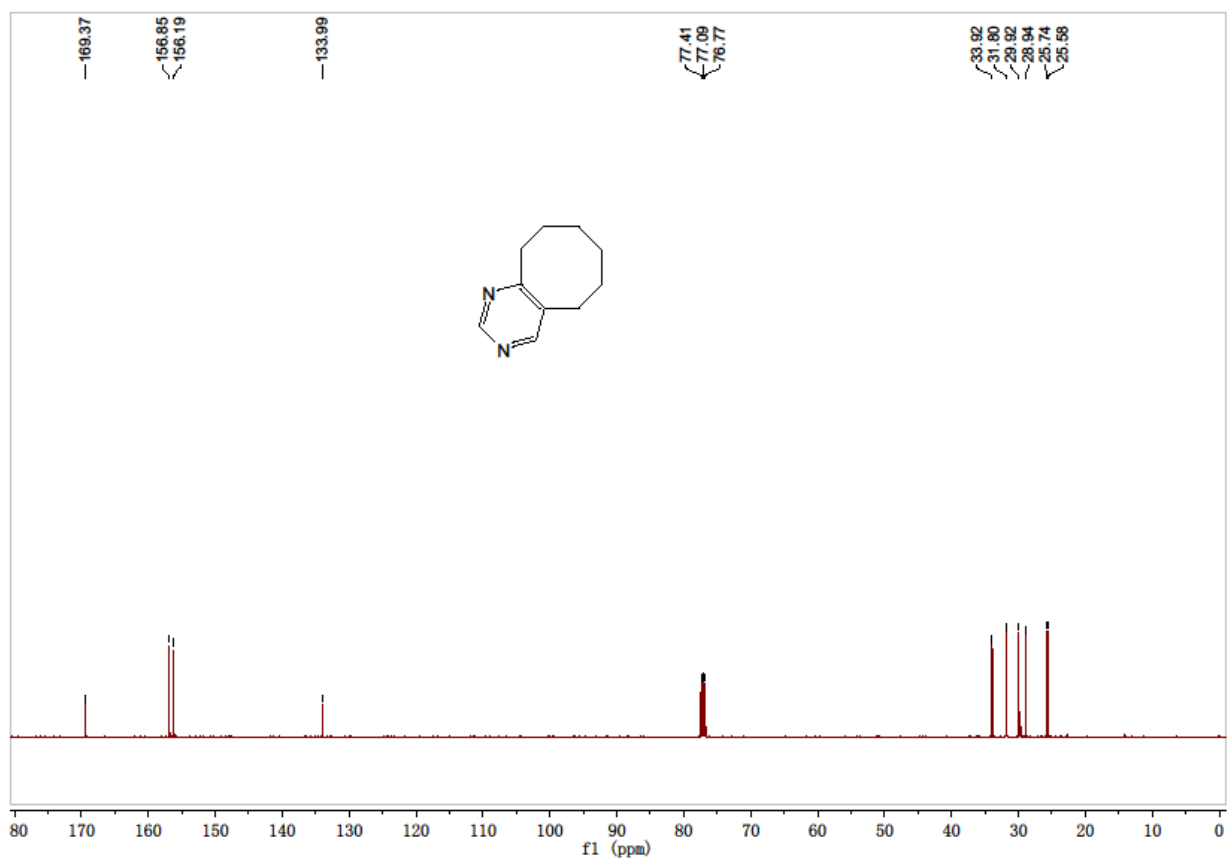
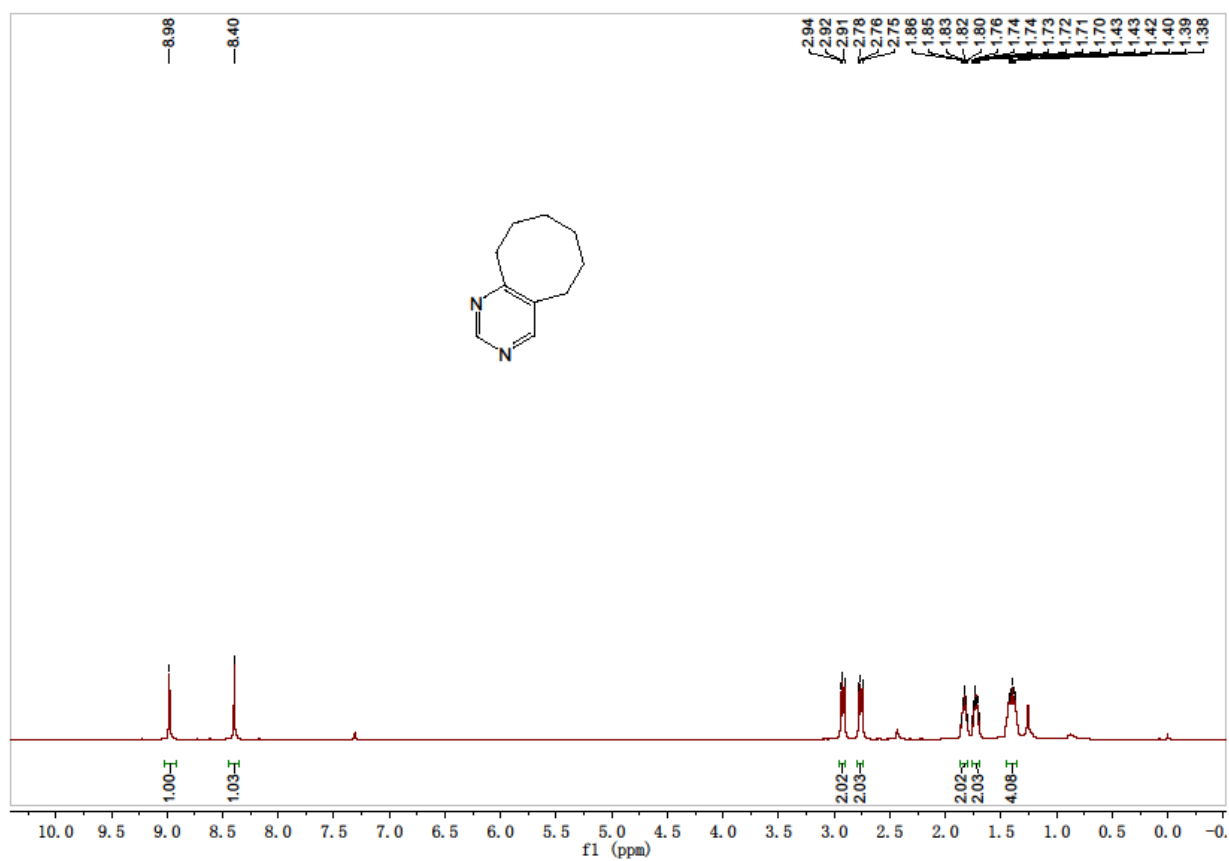
### 6,7-dihydro-5H-cyclopenta[d]pyrimidine (3b)



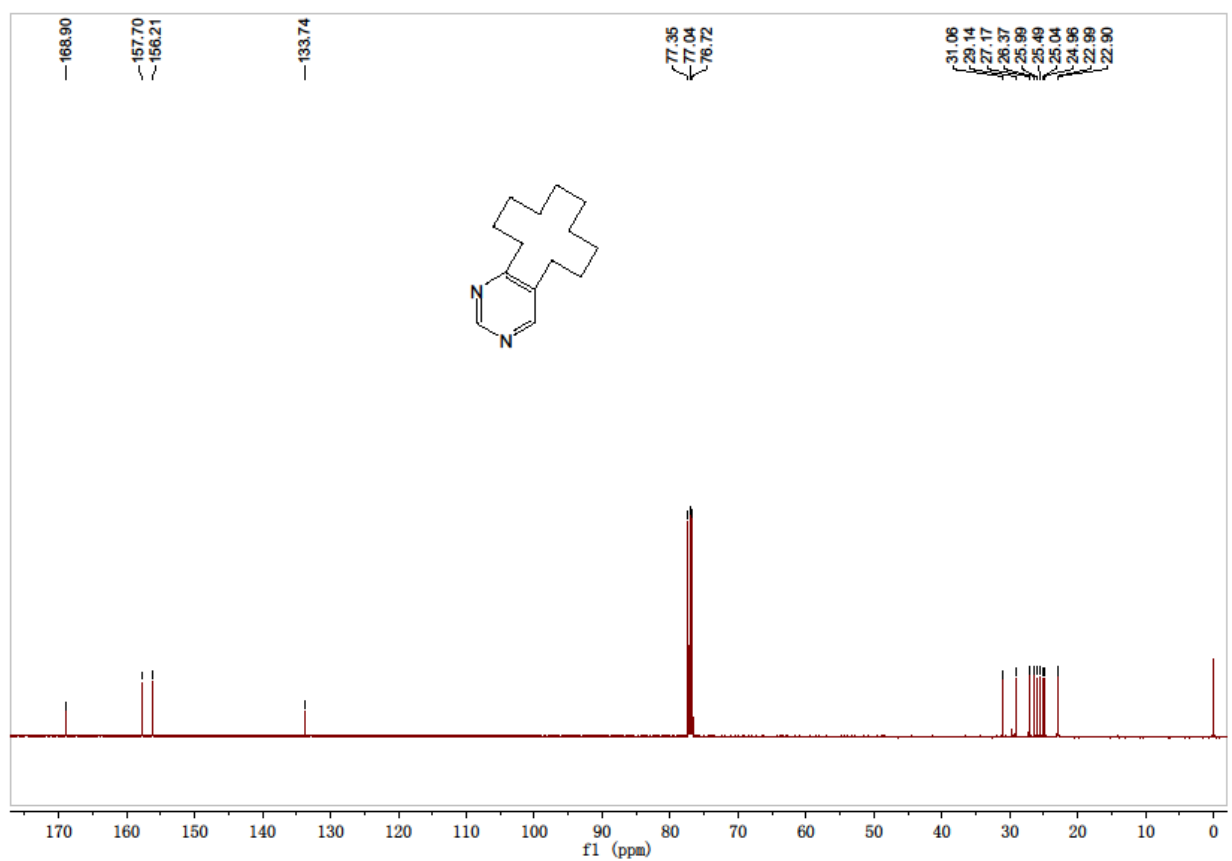
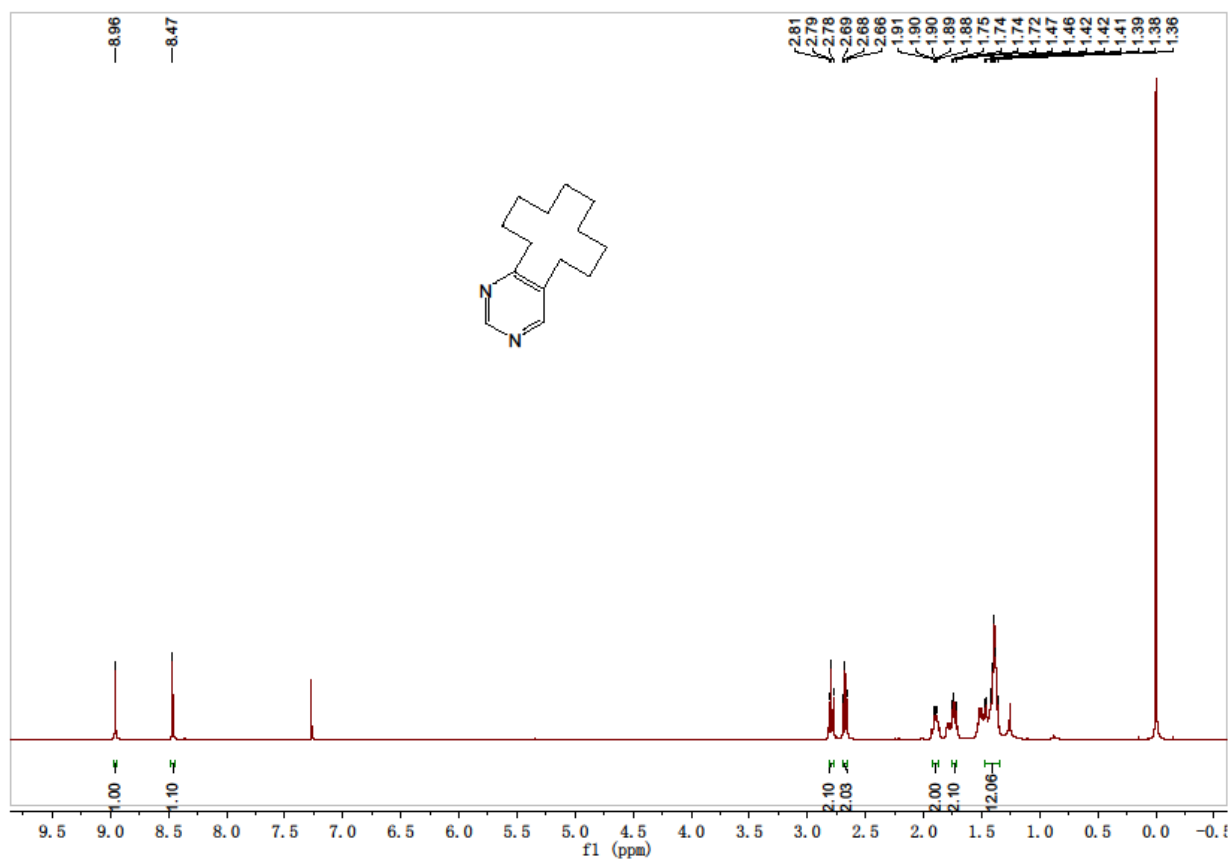
6,7,8,9-tetrahydro-5H-cyclohepta[d]pyrimidine (3c)



### 5,6,7,8,9,10-hexahydrocycloocta[d]pyrimidine (3d)

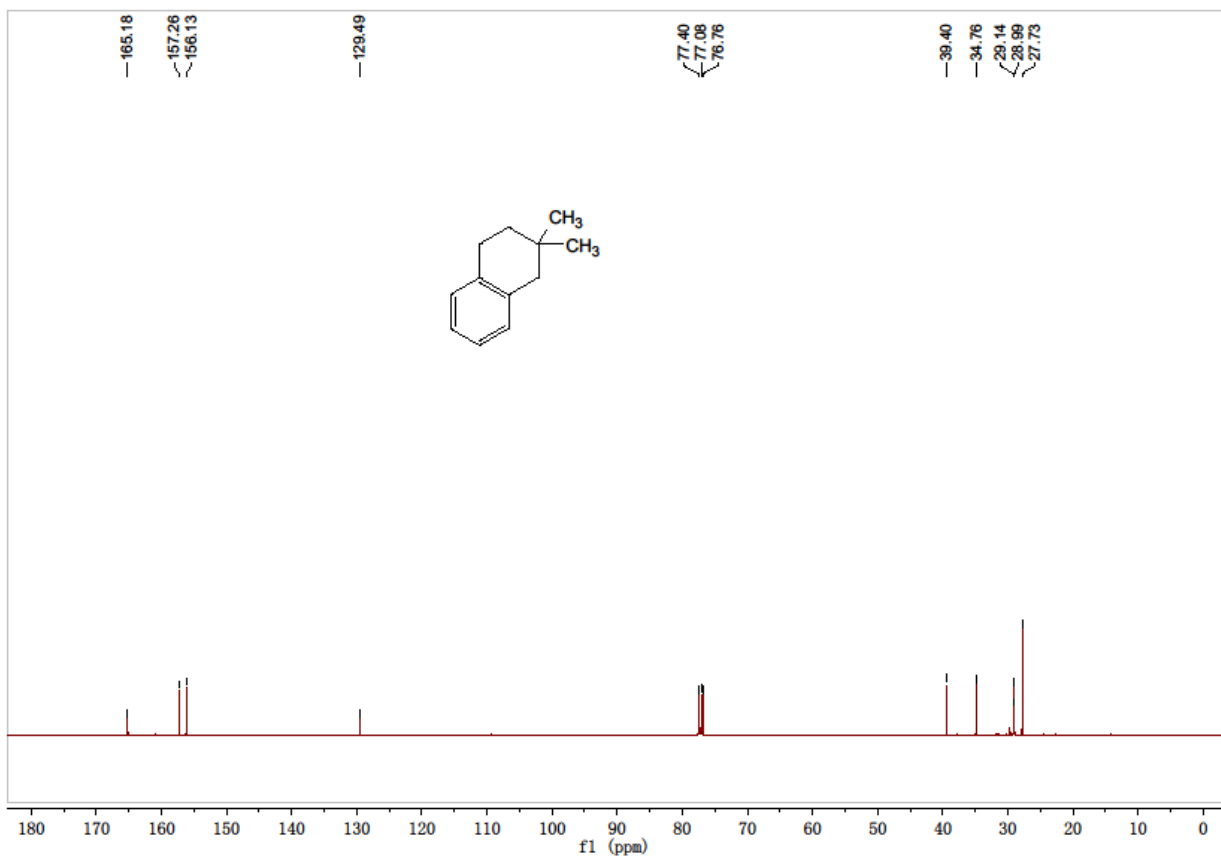
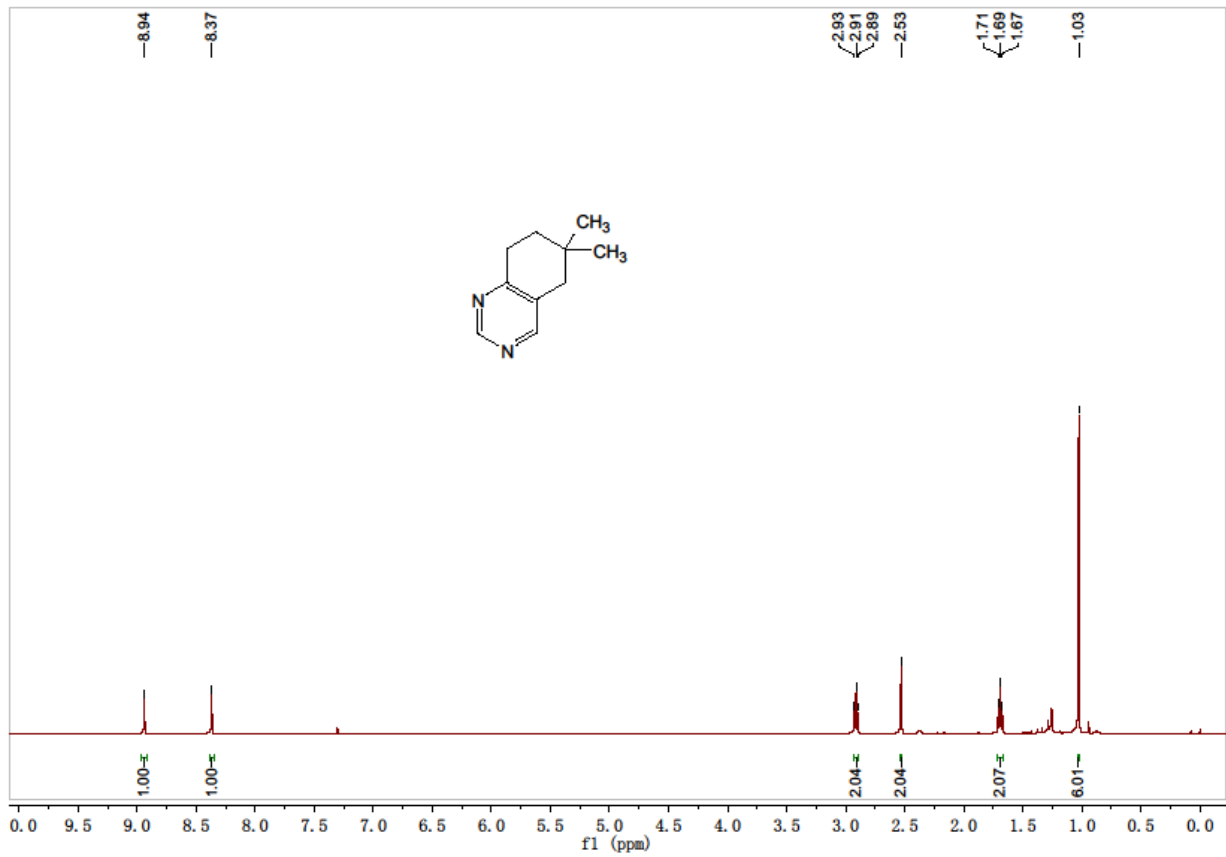


### 5,6,7,8,9,10,11,12,13,14-decahydrobenzo[12]annulene (3e)

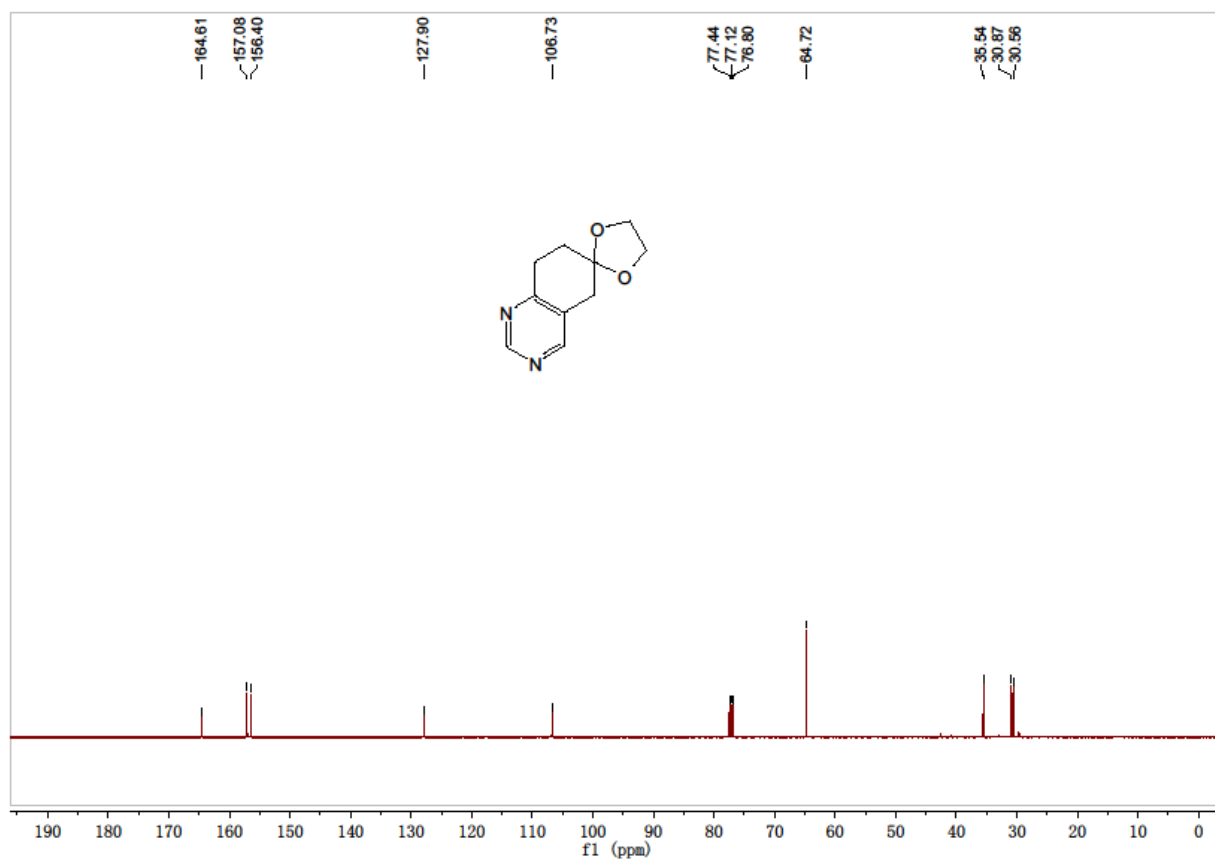
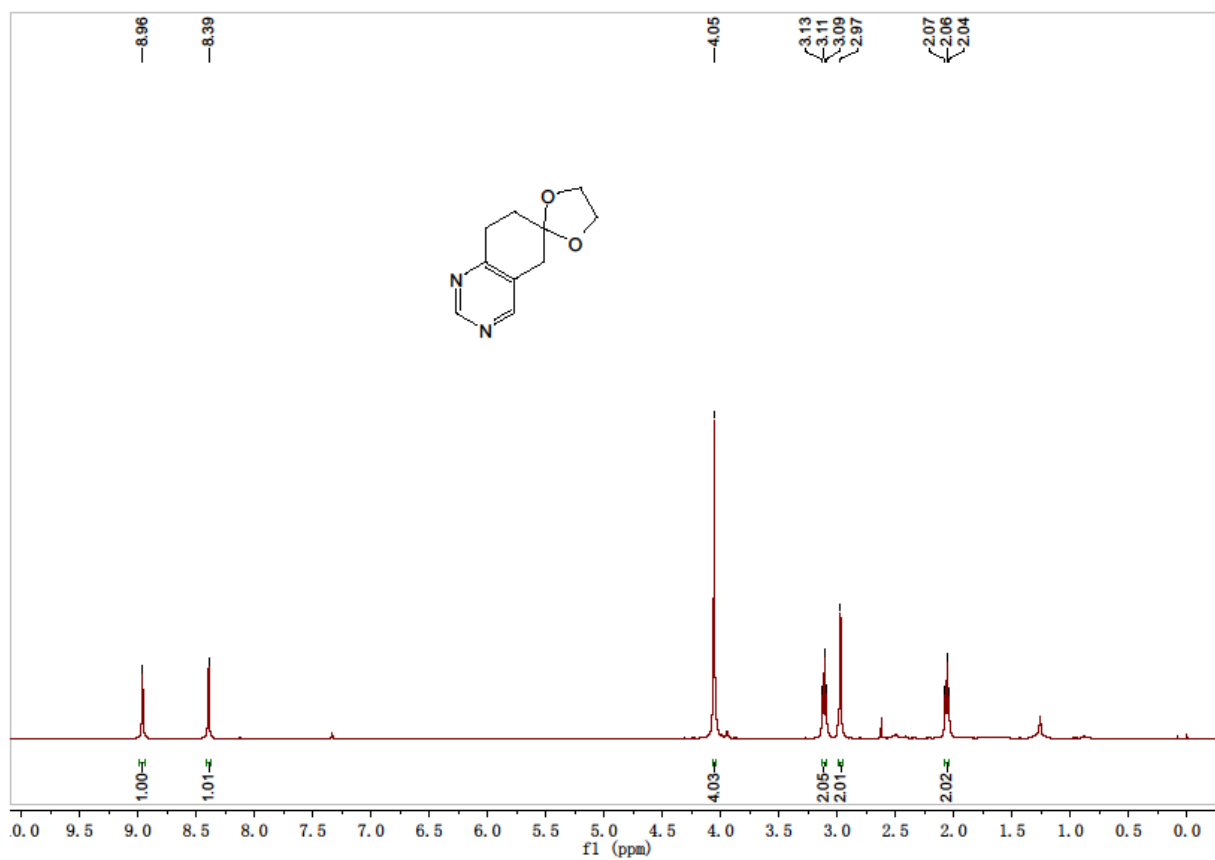




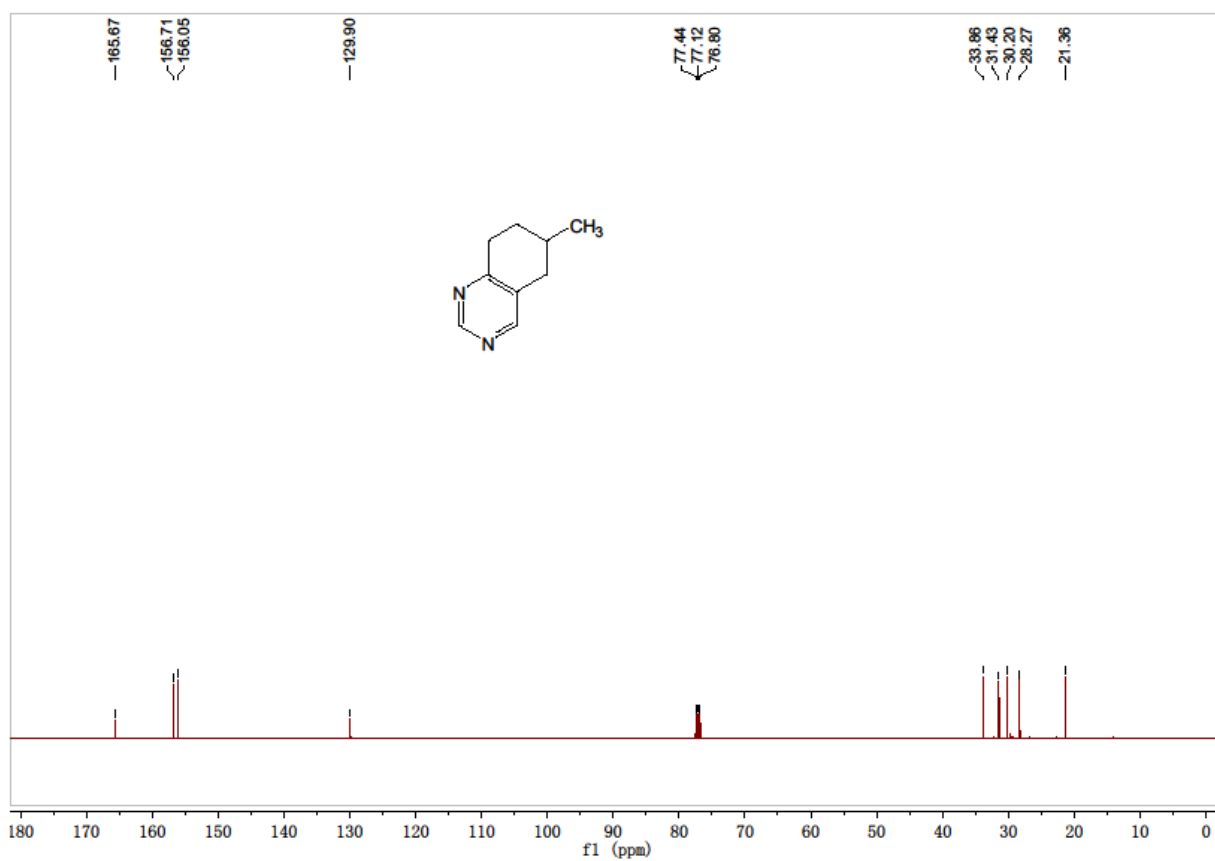
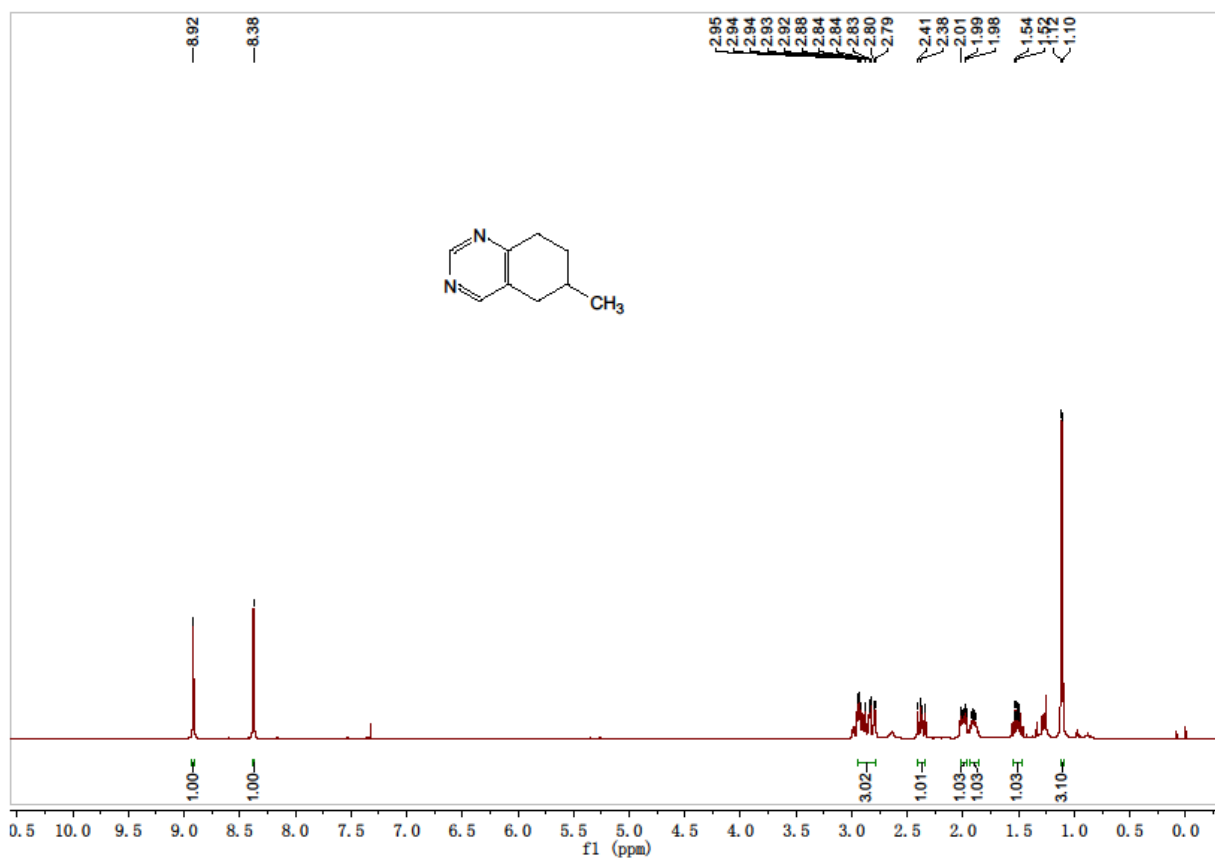
### 6,6-dimethyl-5,6,7,8-tetrahydroquinazoline (3f)



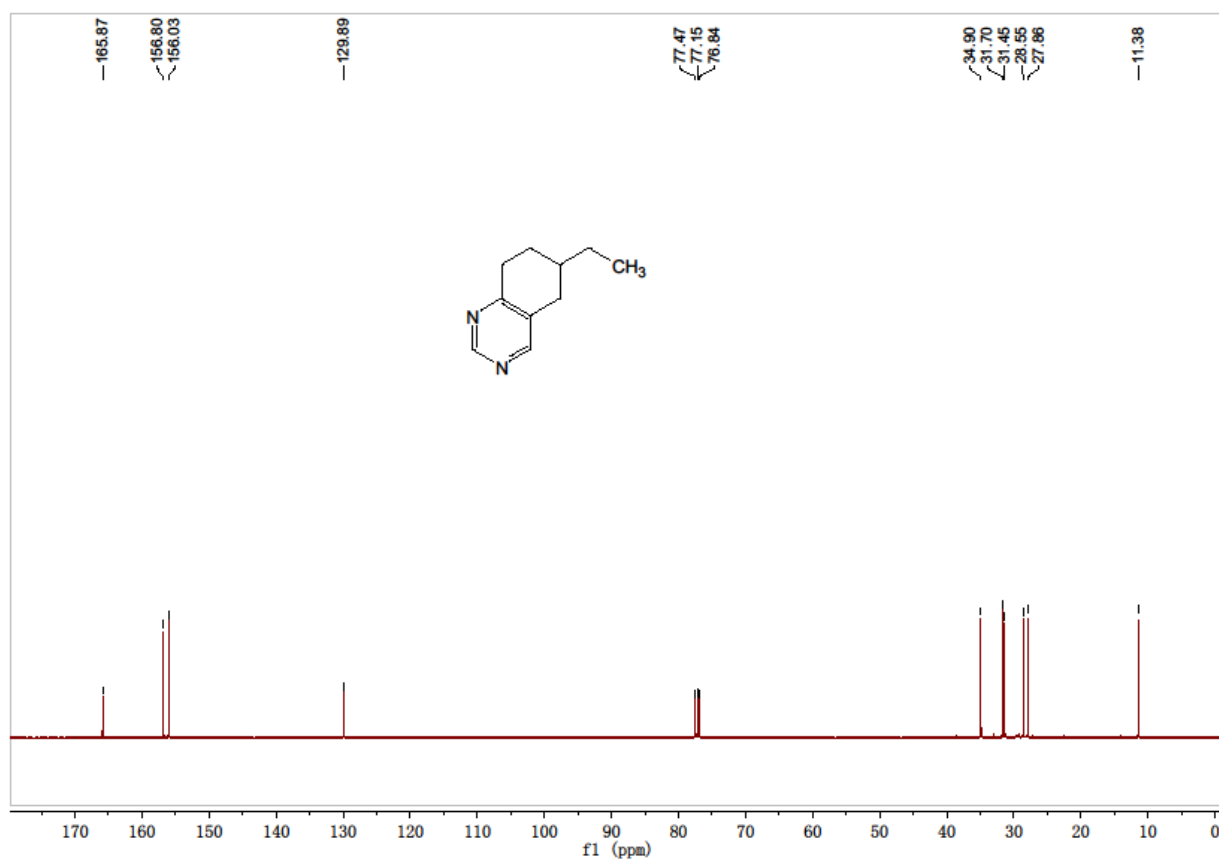
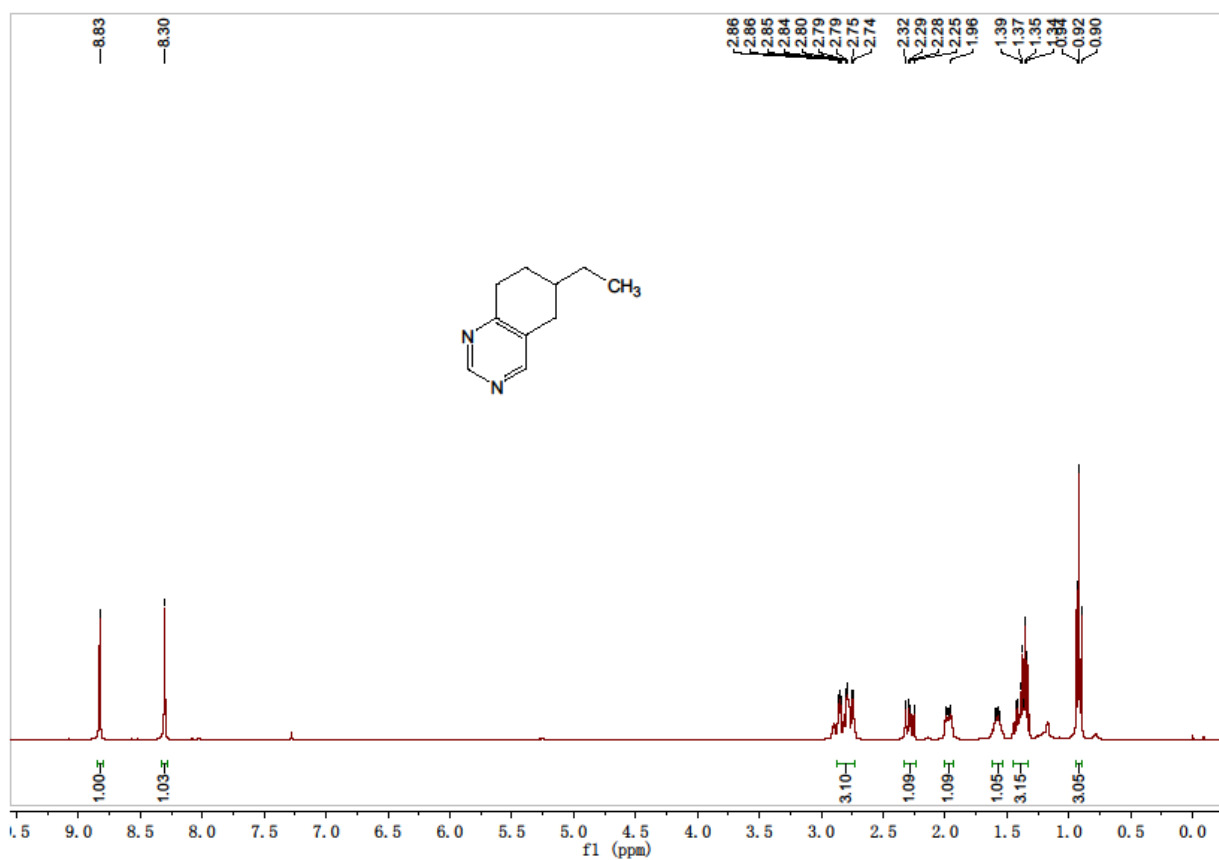
7',8'-dihydro-5'H-spiro[[1,3]dioxolane-2,6'-quinazoline] (3g)



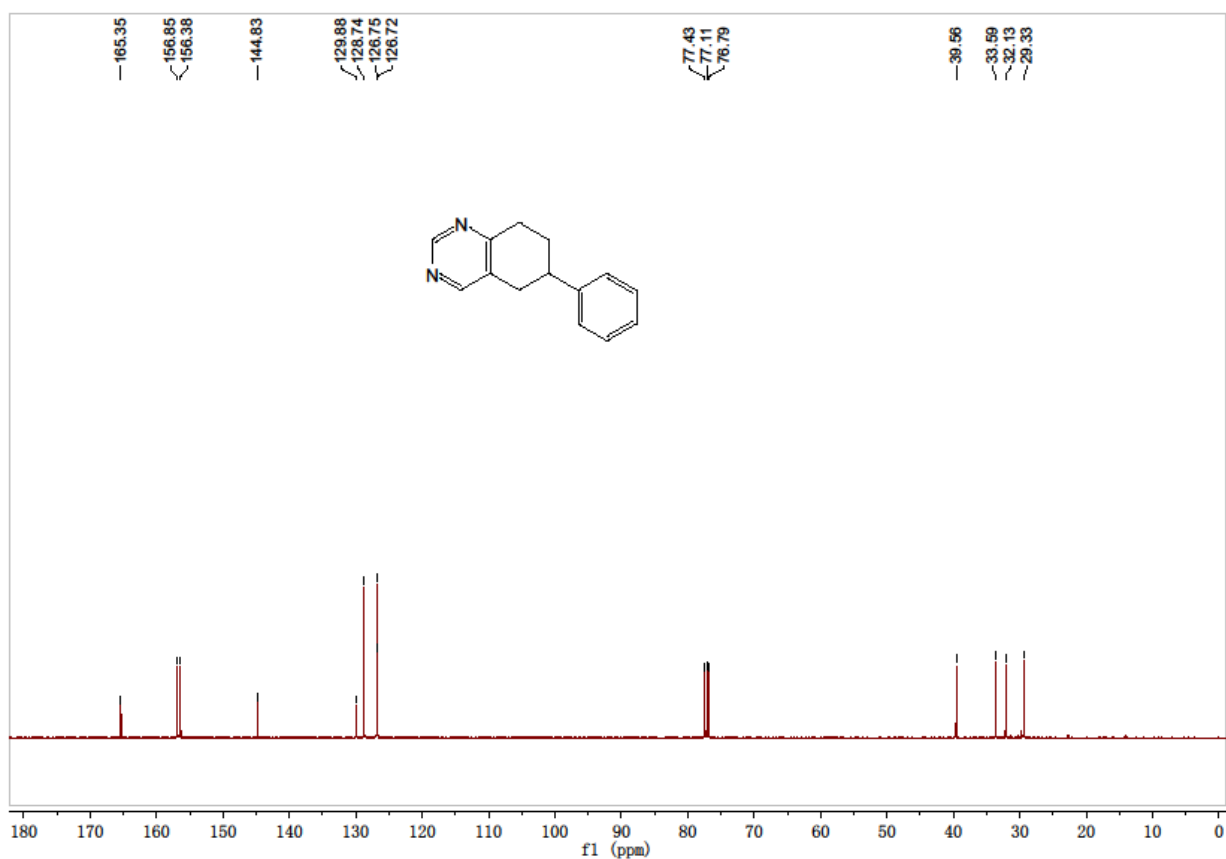
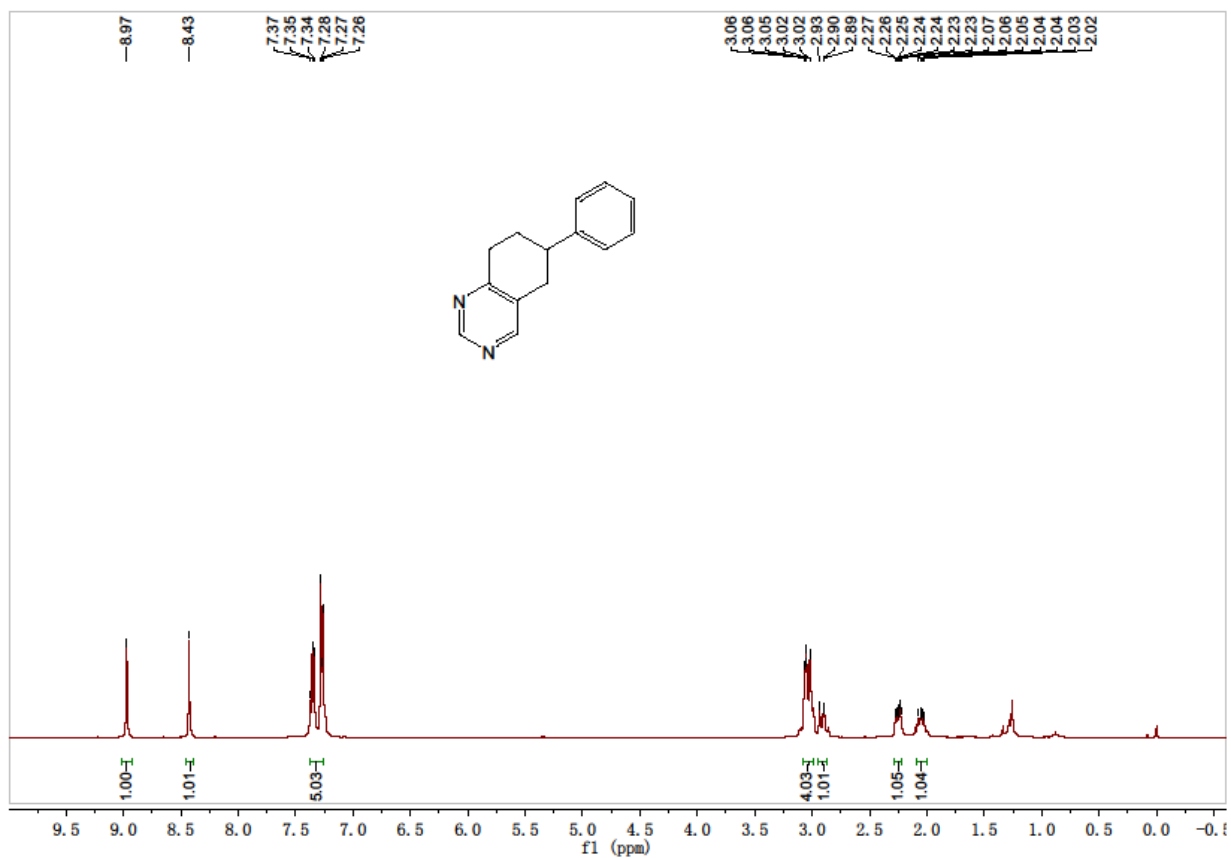
### 6-methyl-5,6,7,8-tetrahydroquinazoline (3h)



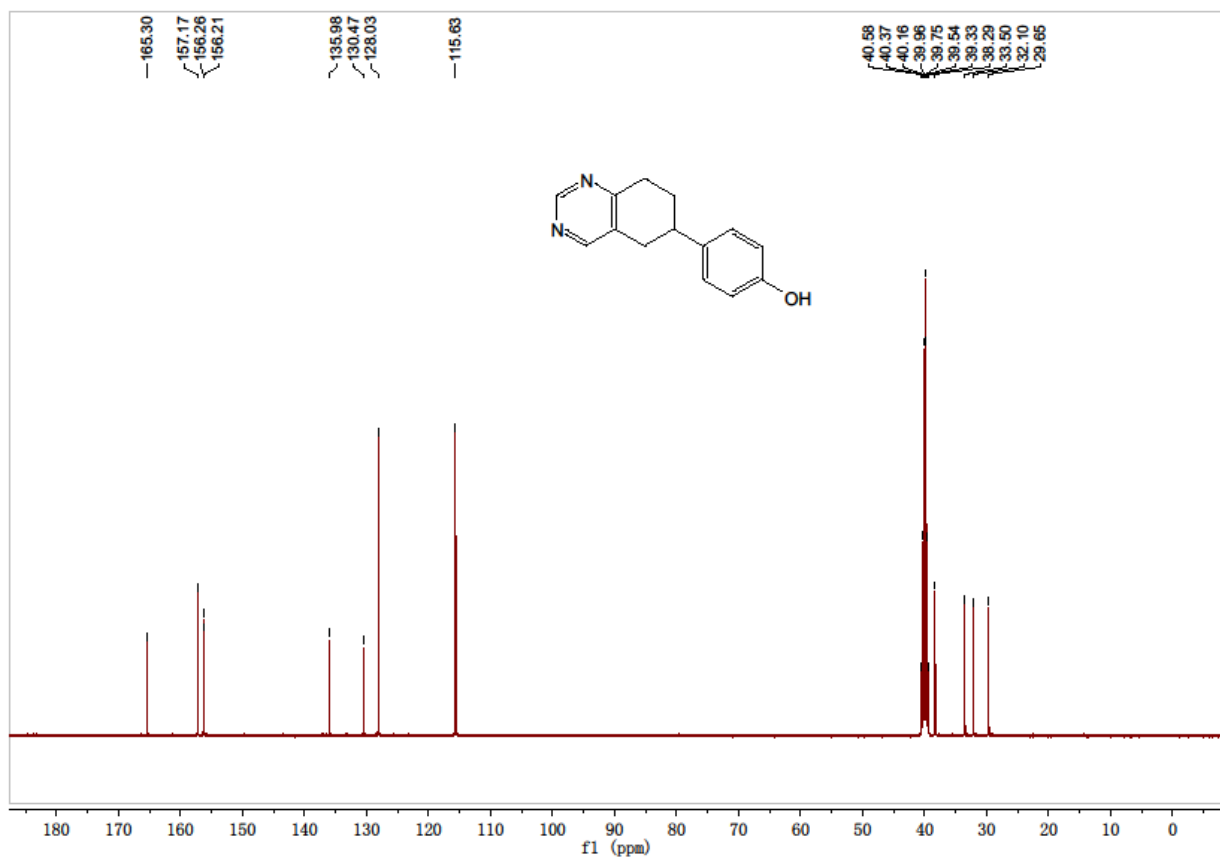
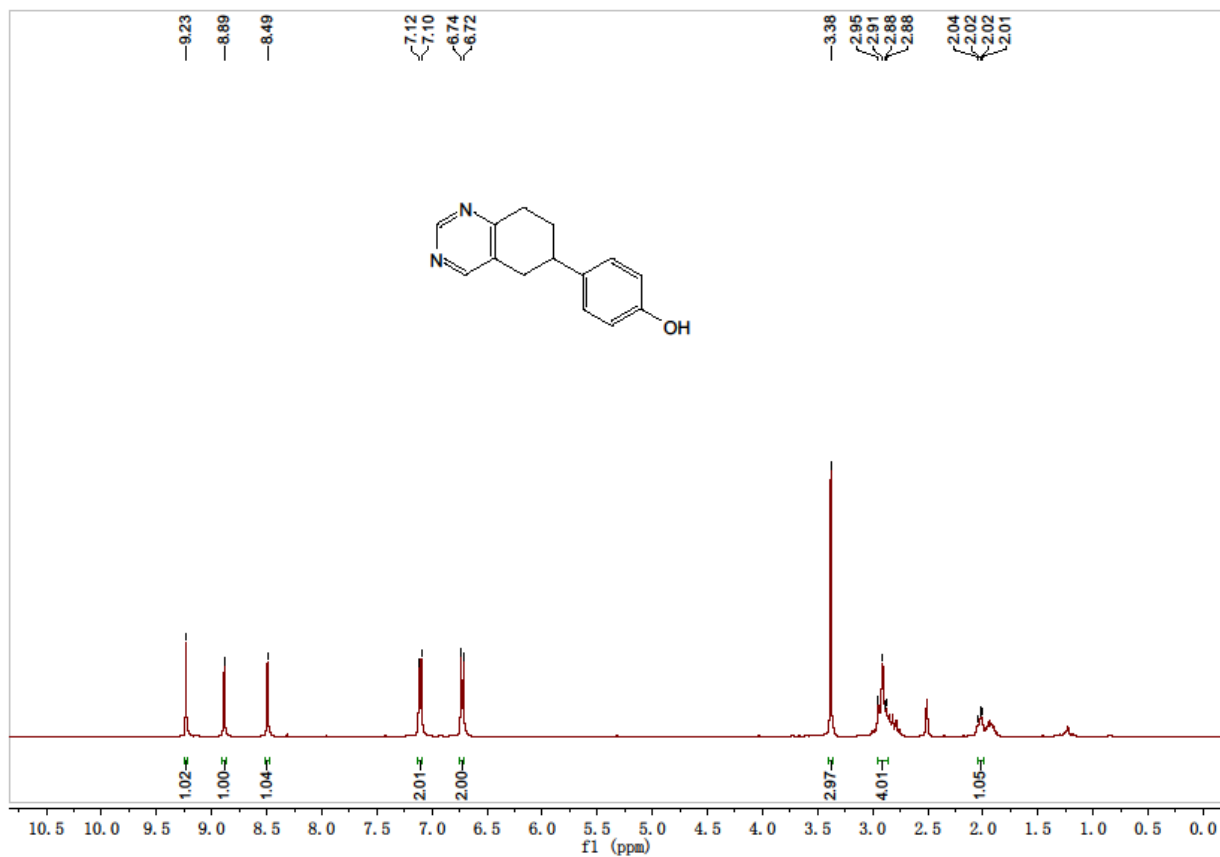
### 6-ethyl-5,6,7,8-tetrahydroquinazoline (3i)



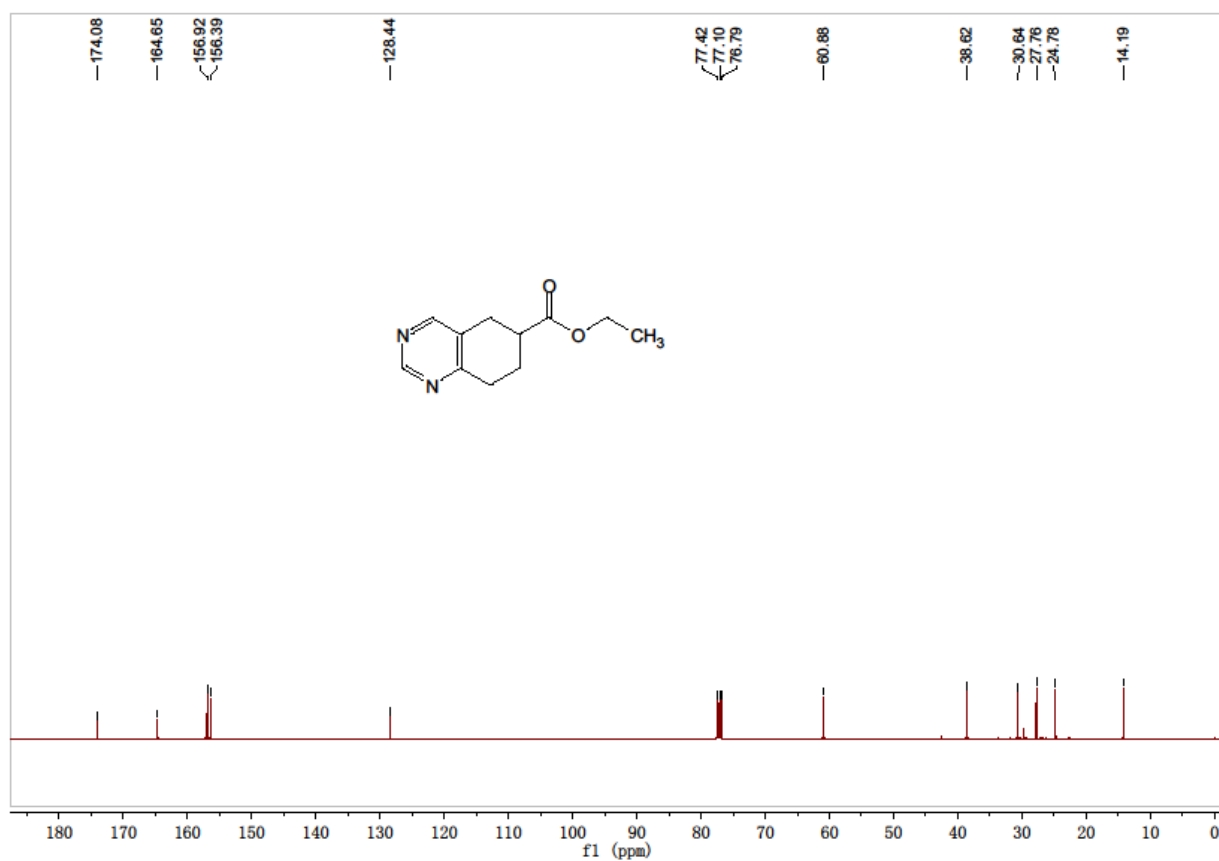
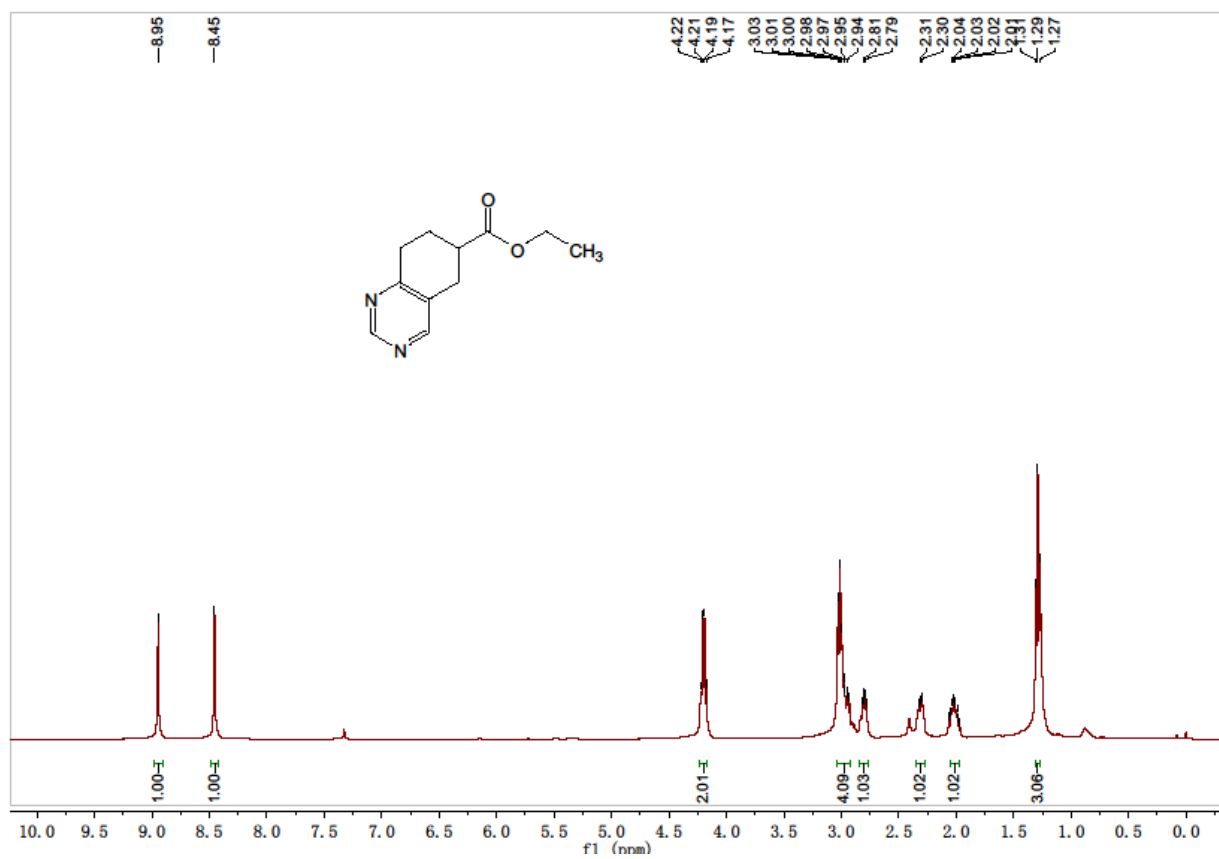
### 6-phenyl-5,6,7,8-tetrahydroquinazoline (3j)



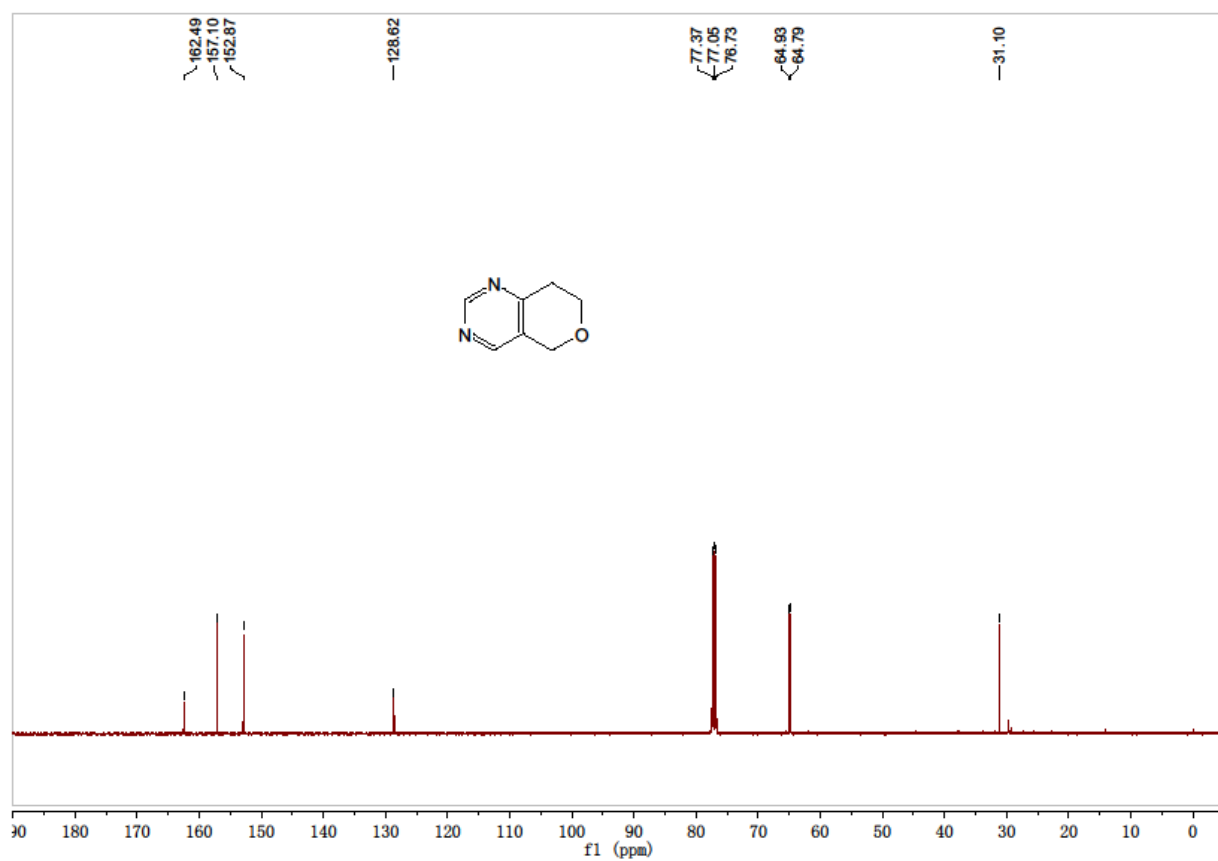
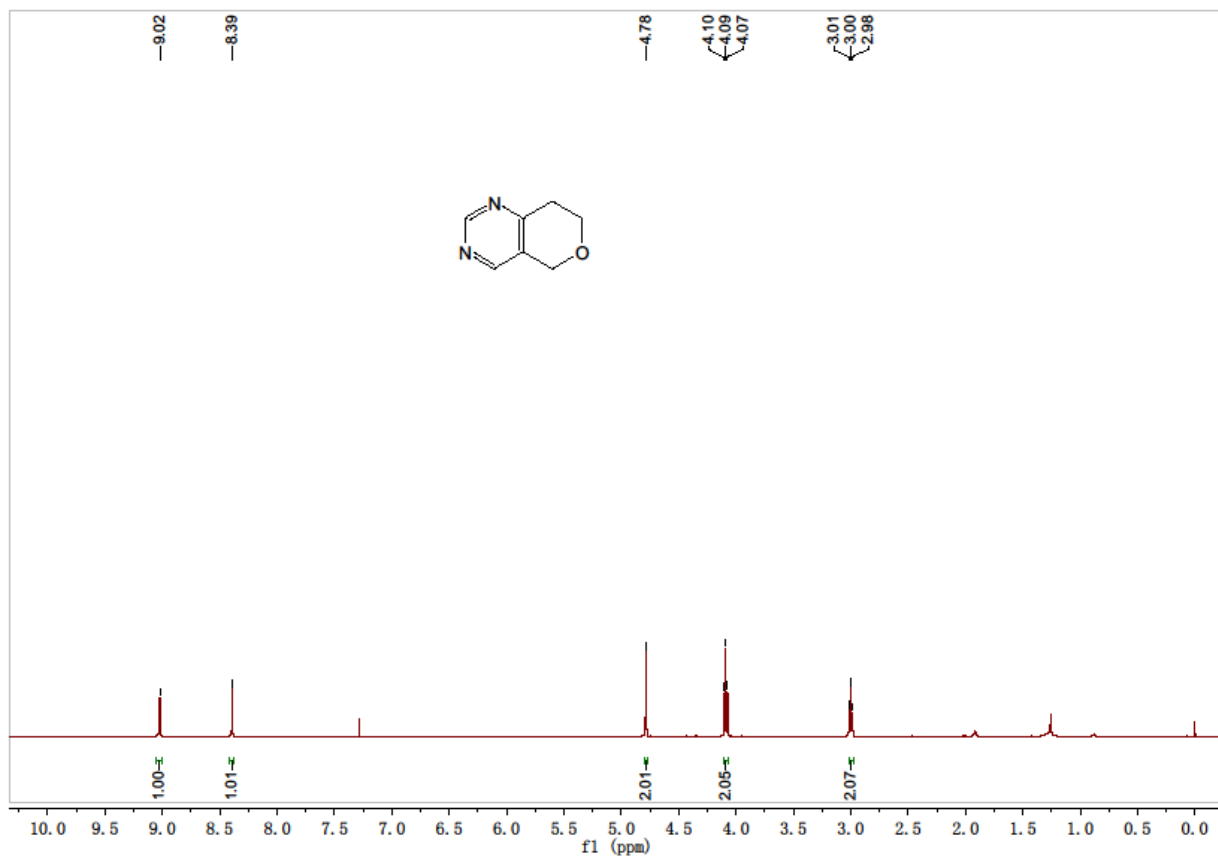
### 4-(5,6,7,8-tetrahydroquinazolin-6-yl)phenol (3k)



### Ethyl 5,6,7,8-tetrahydroquinazoline-6-carboxylate (3l)

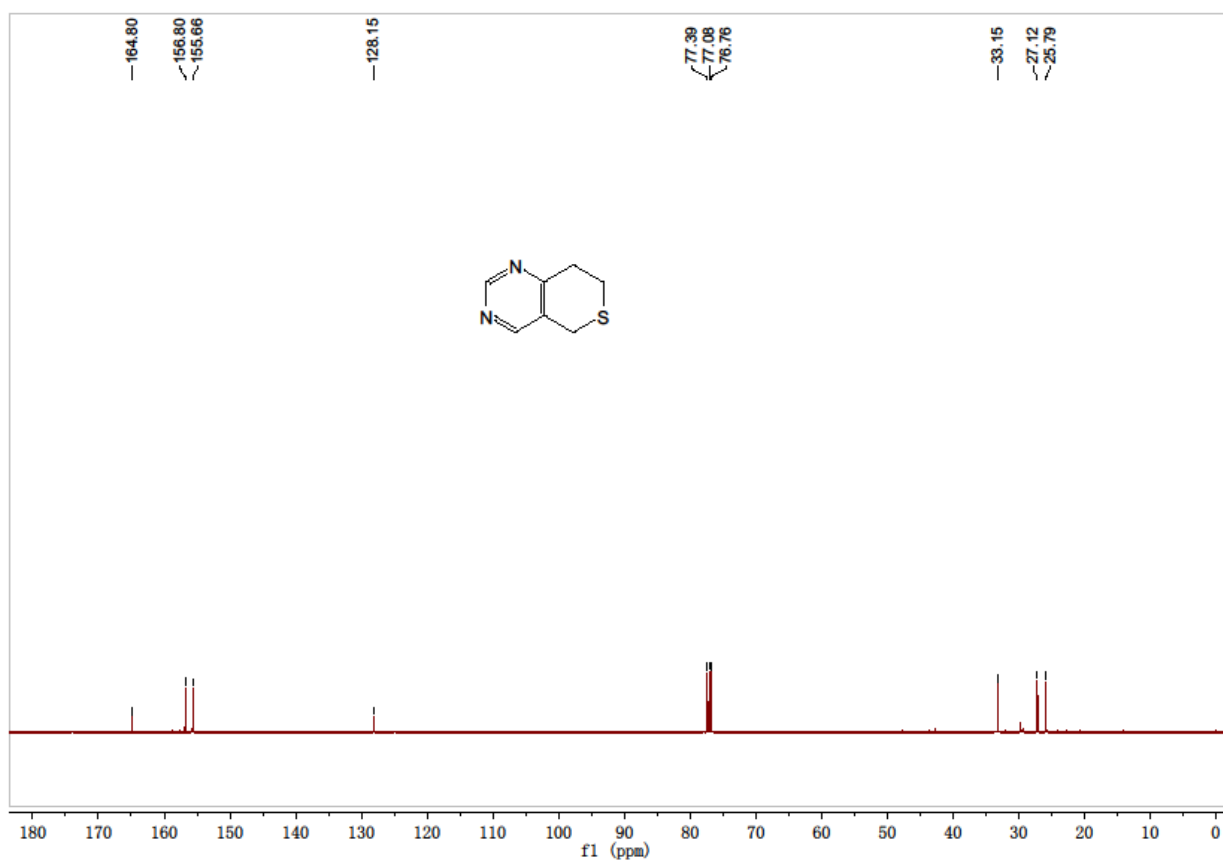
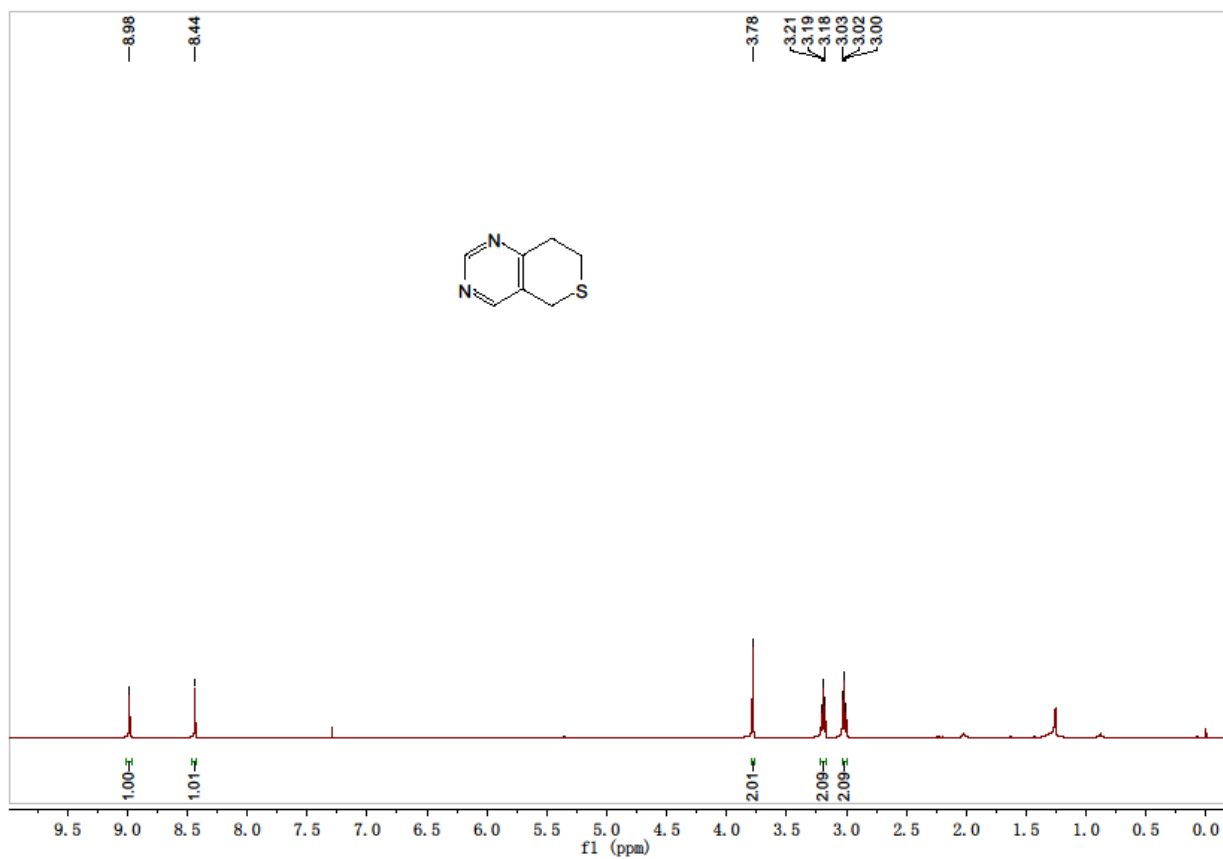


### 7,8-dihydro-5H-pyrano[4,3-d]pyrimidine (3m)

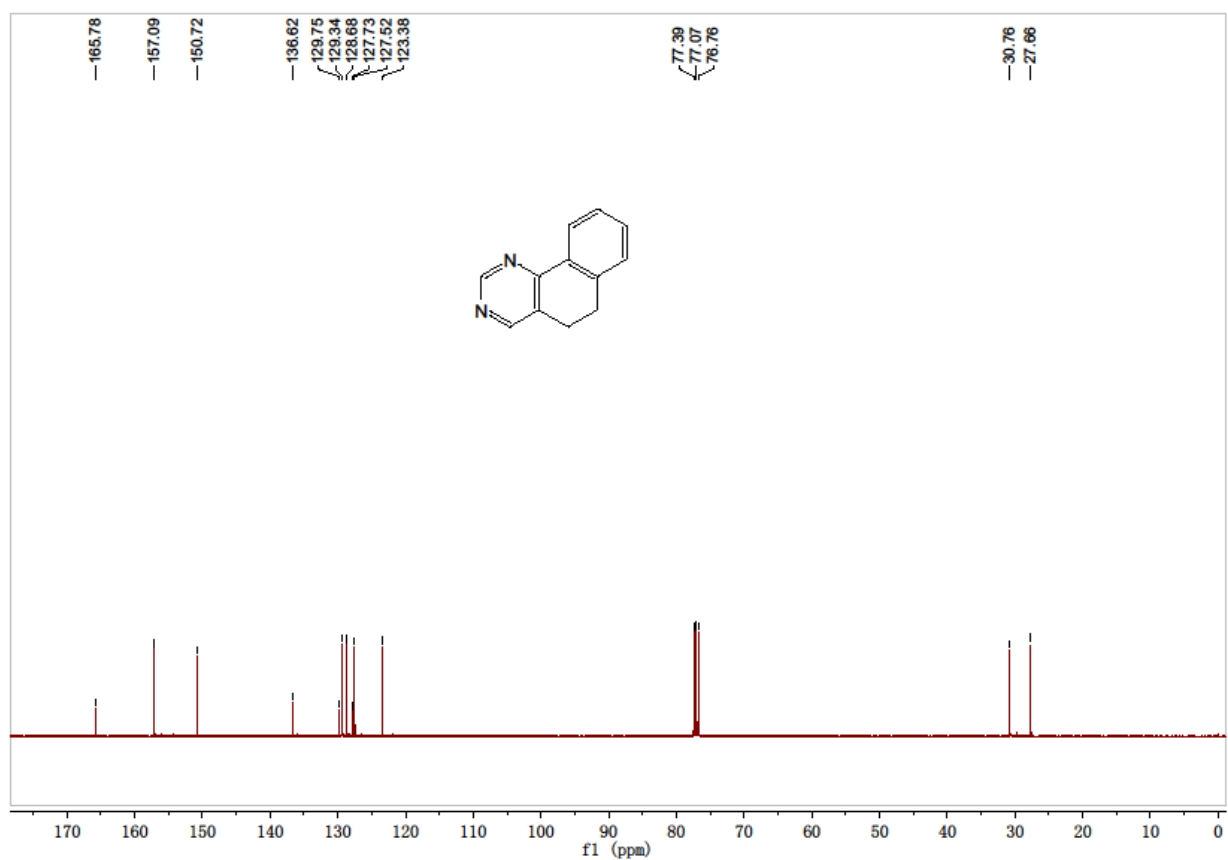
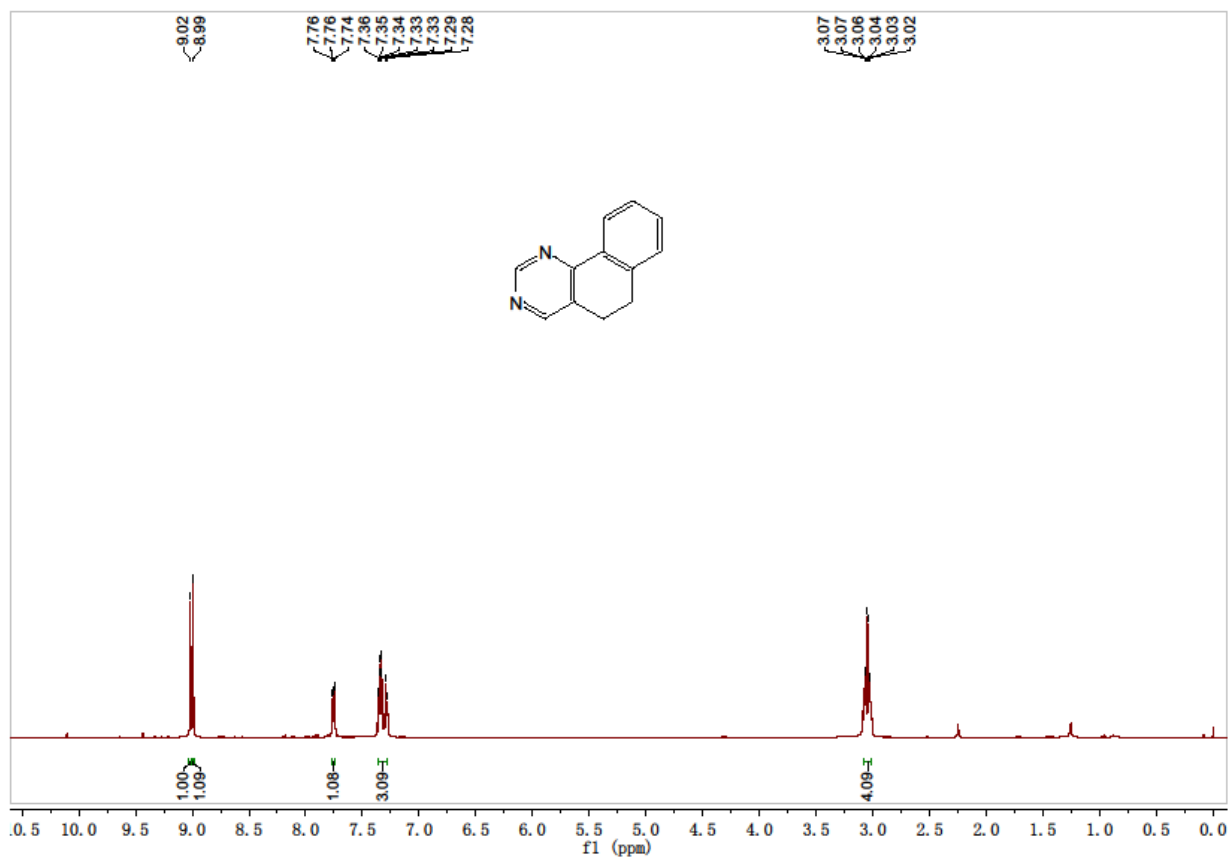




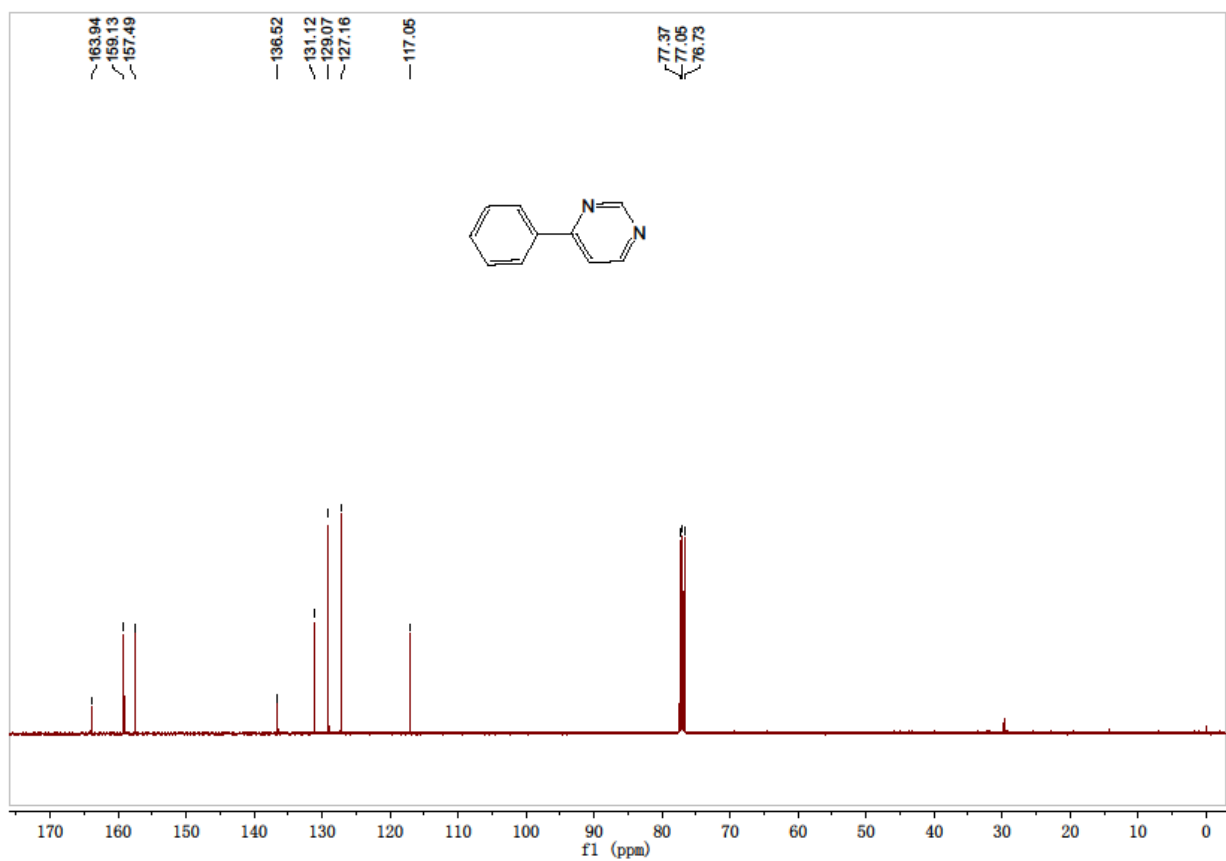
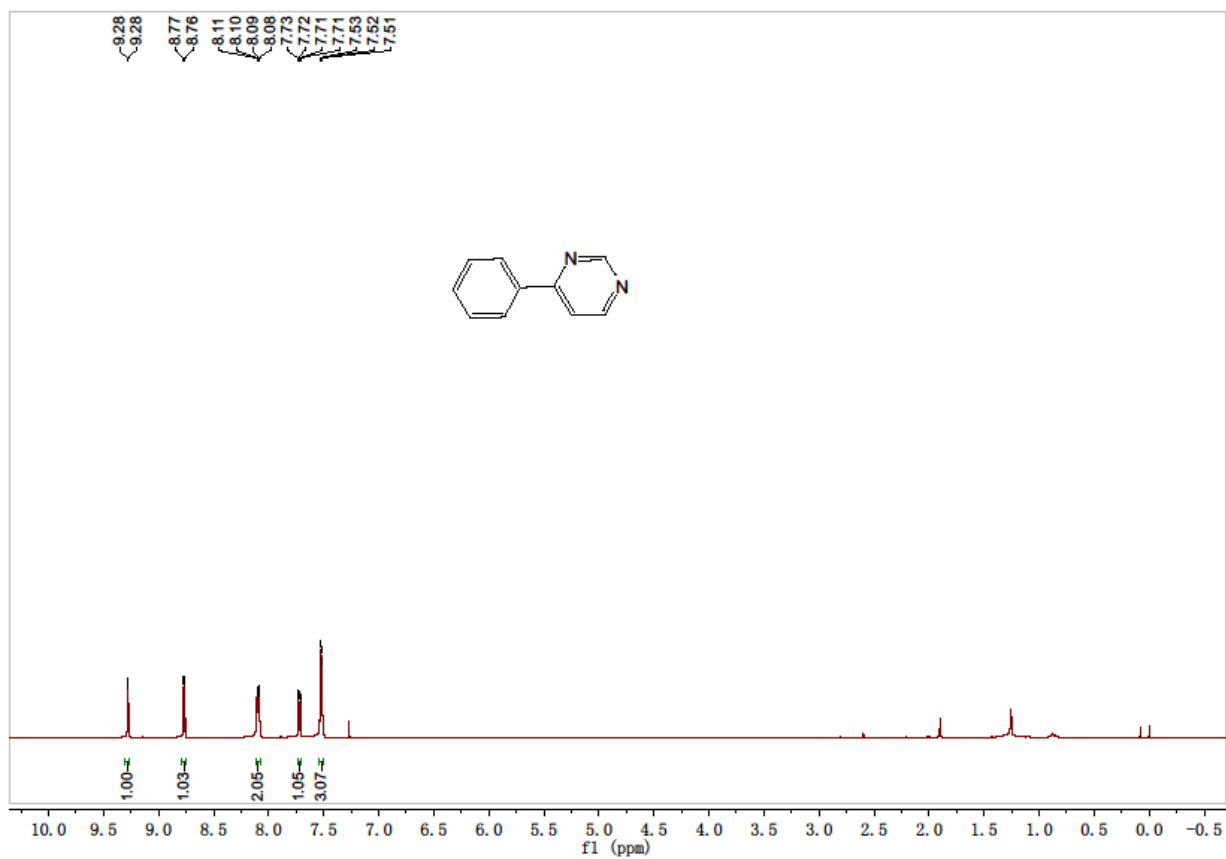
### 7,8-dihydro-5H-thiopyrano[4,3-d]pyrimidine (3n)



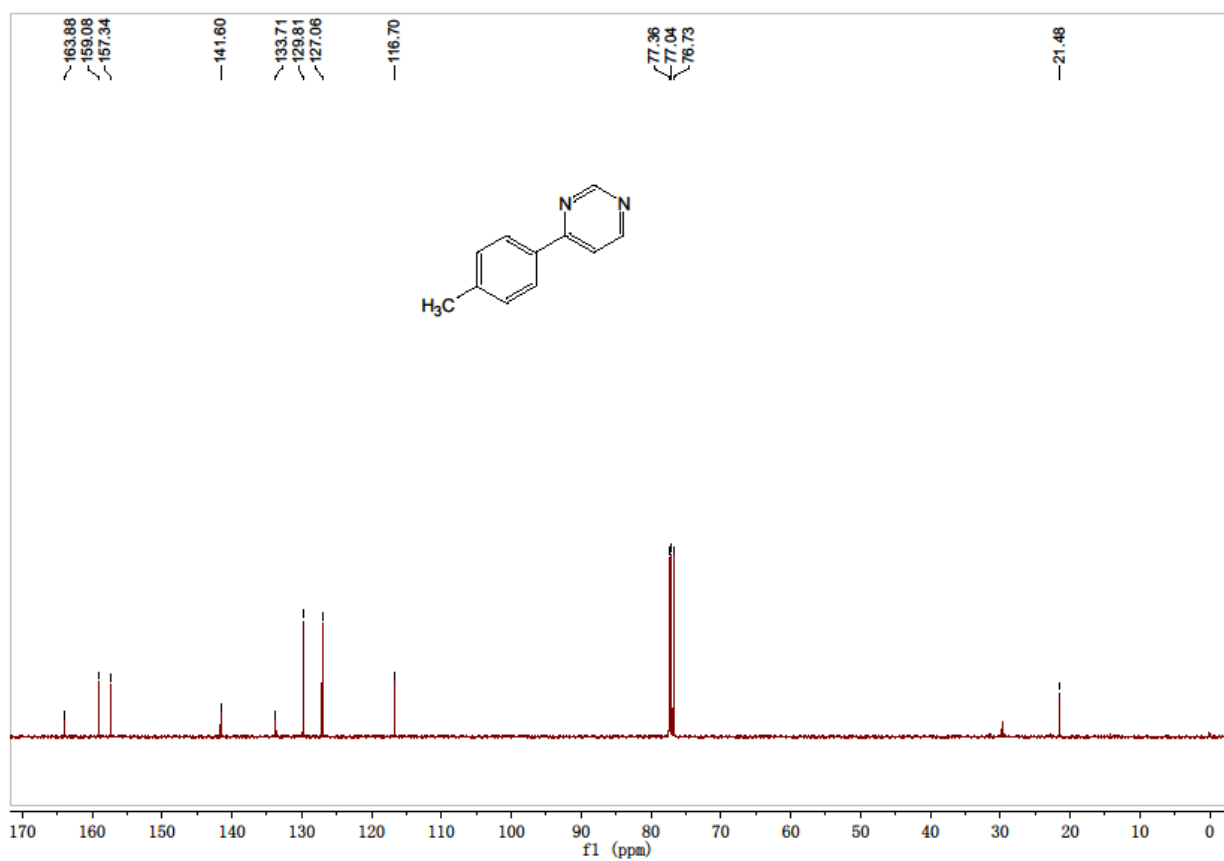
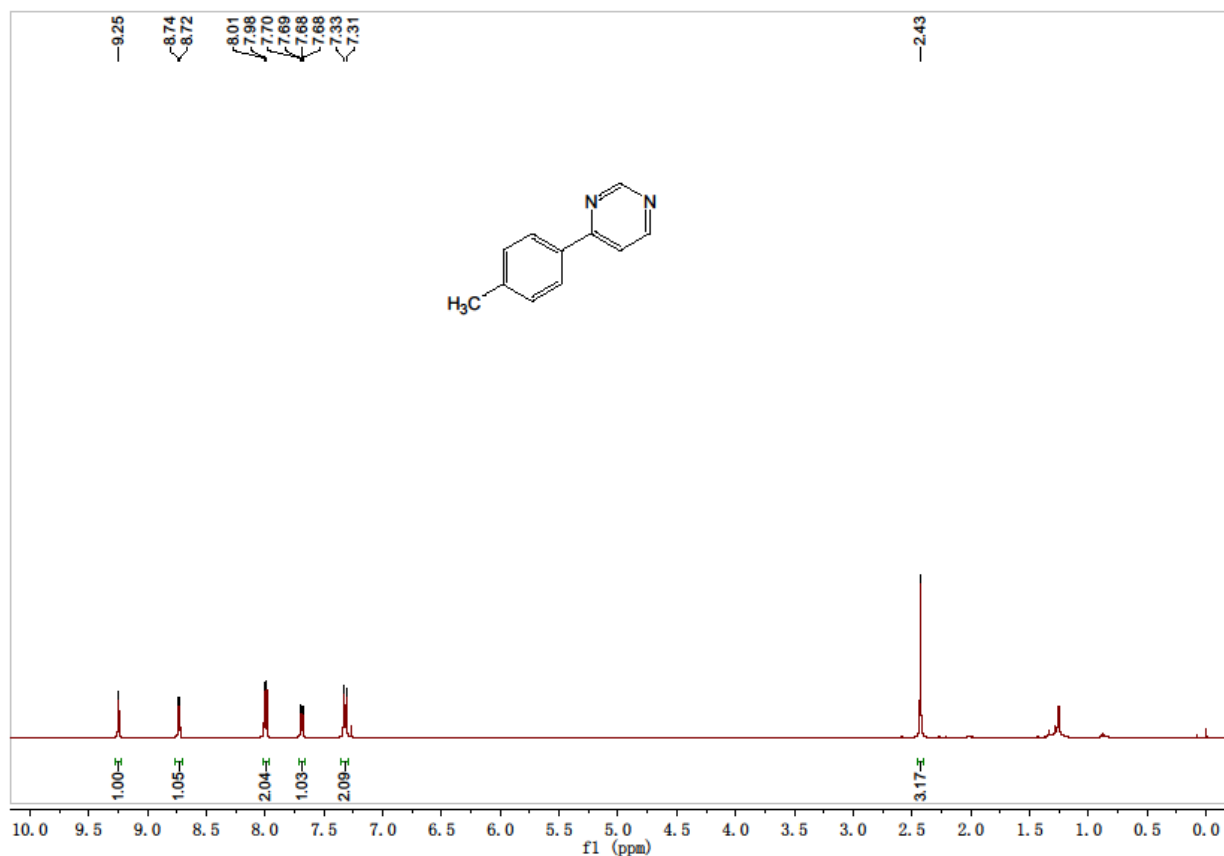
### 5,6-dihydrobenzo[h]quinazoline (3o)



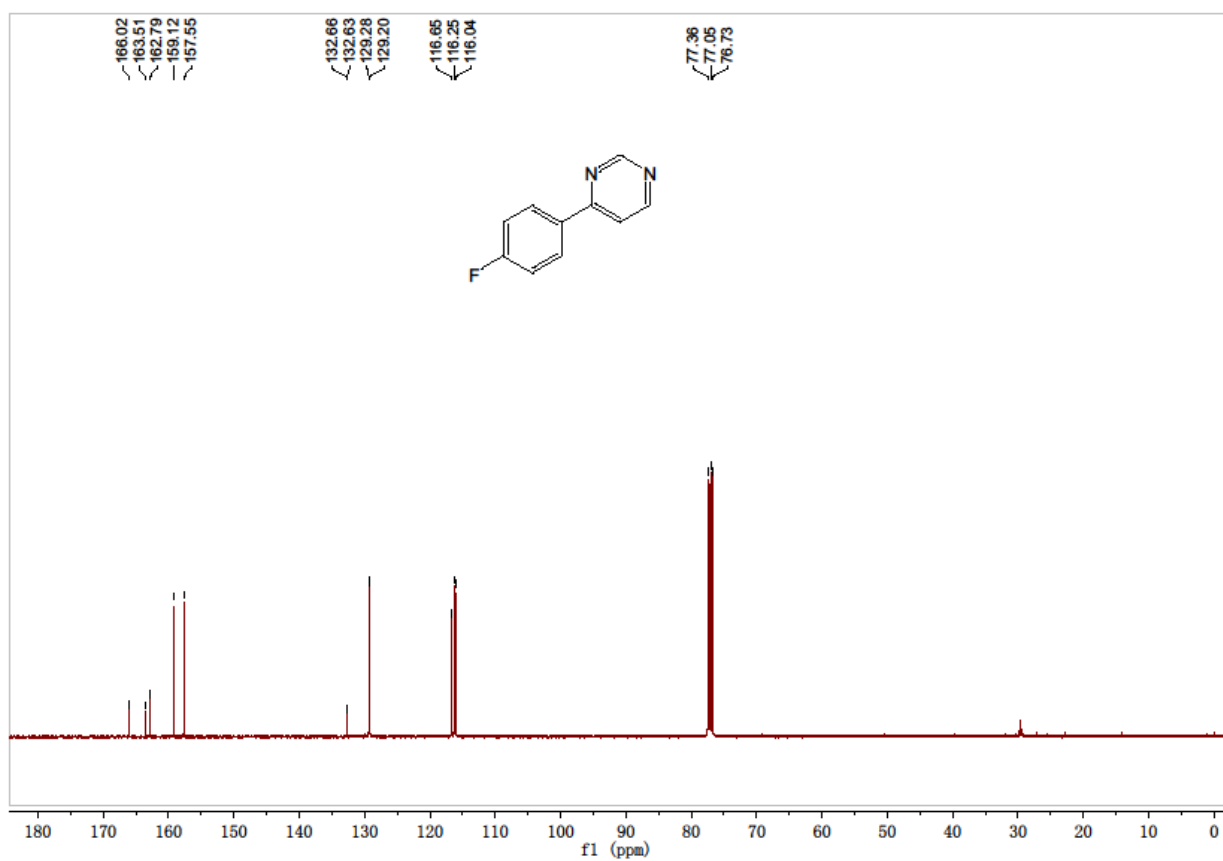
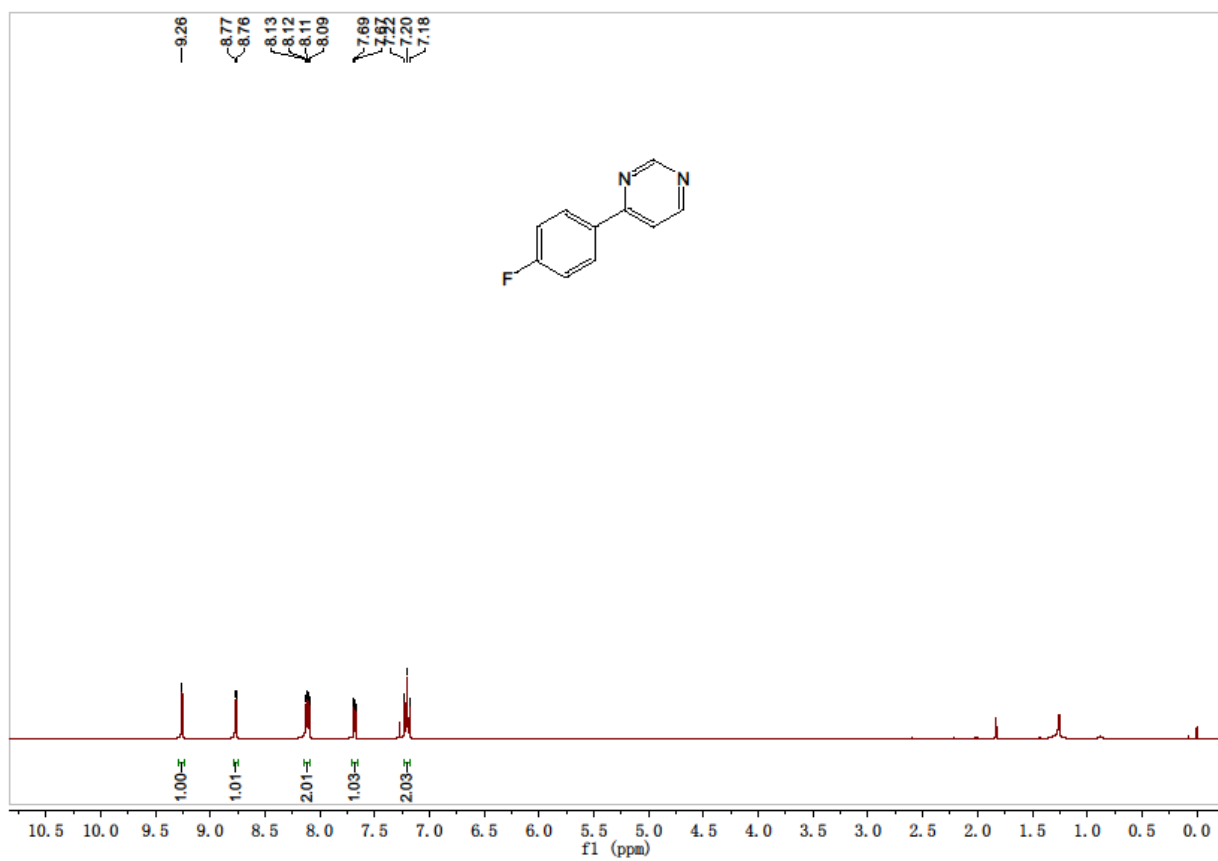
### 4-phenylimidazole (5a)



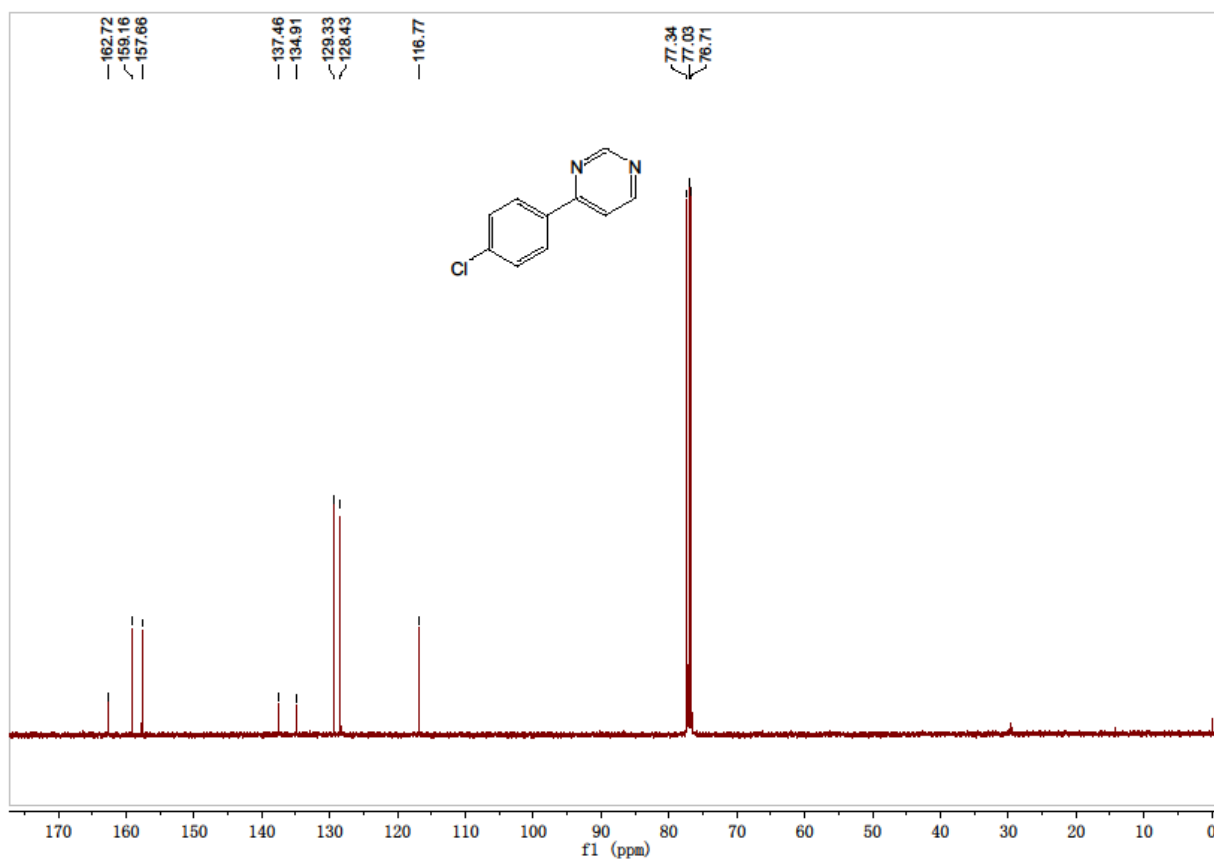
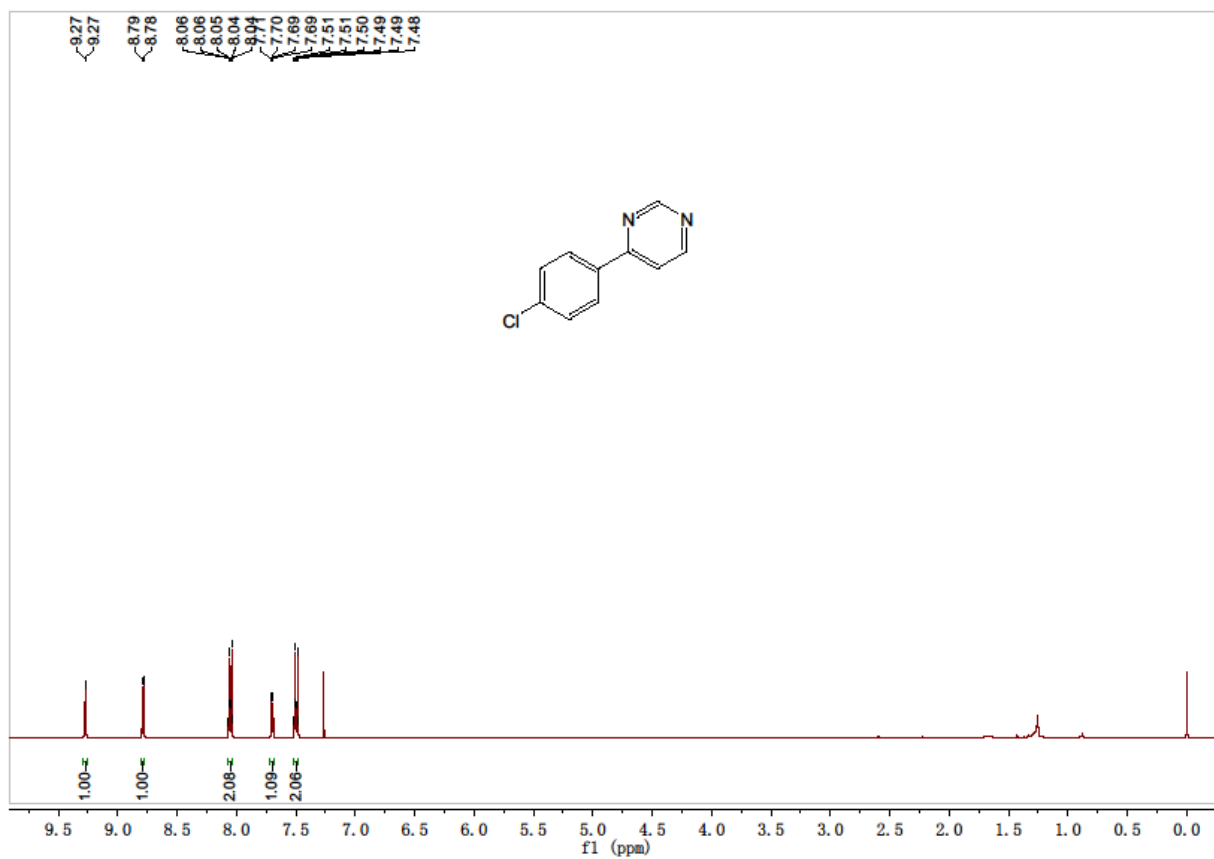
### 4-(p-tolyl)pyrimidine (5b)



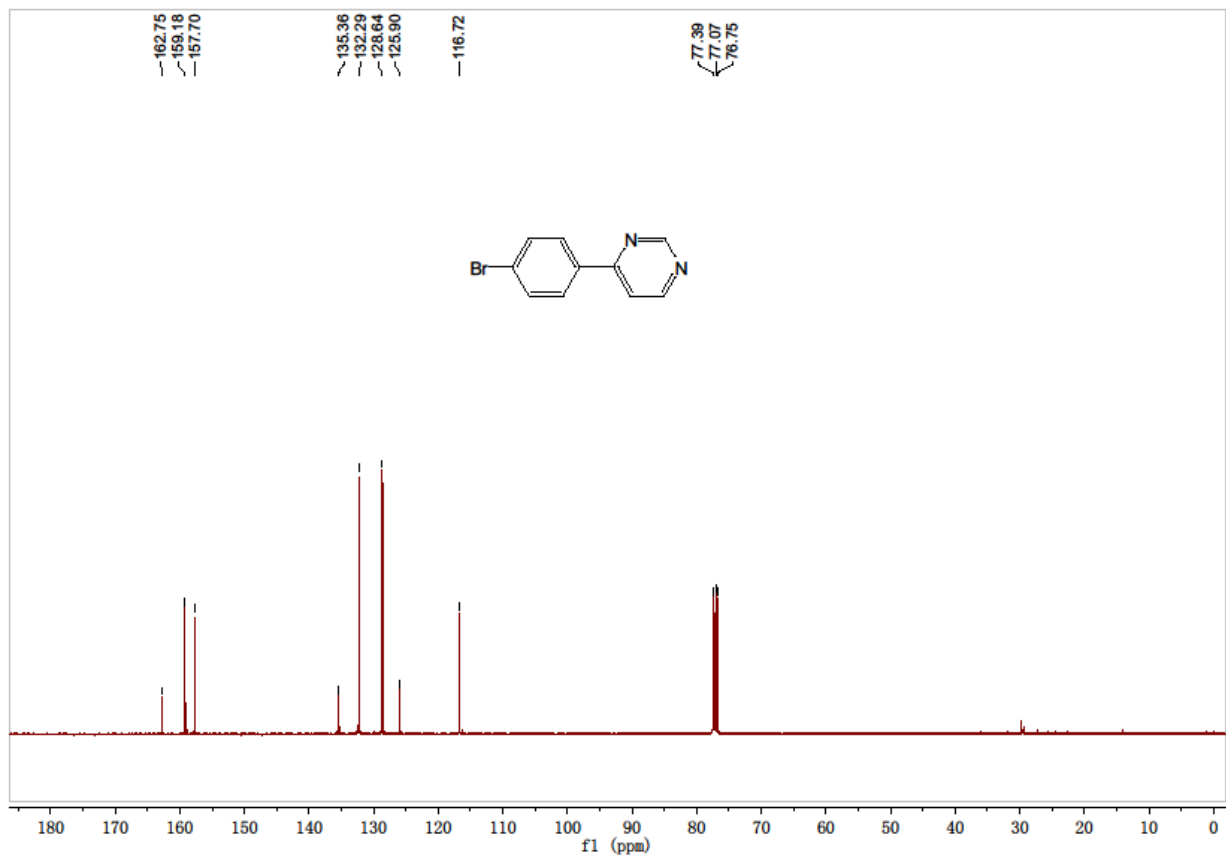
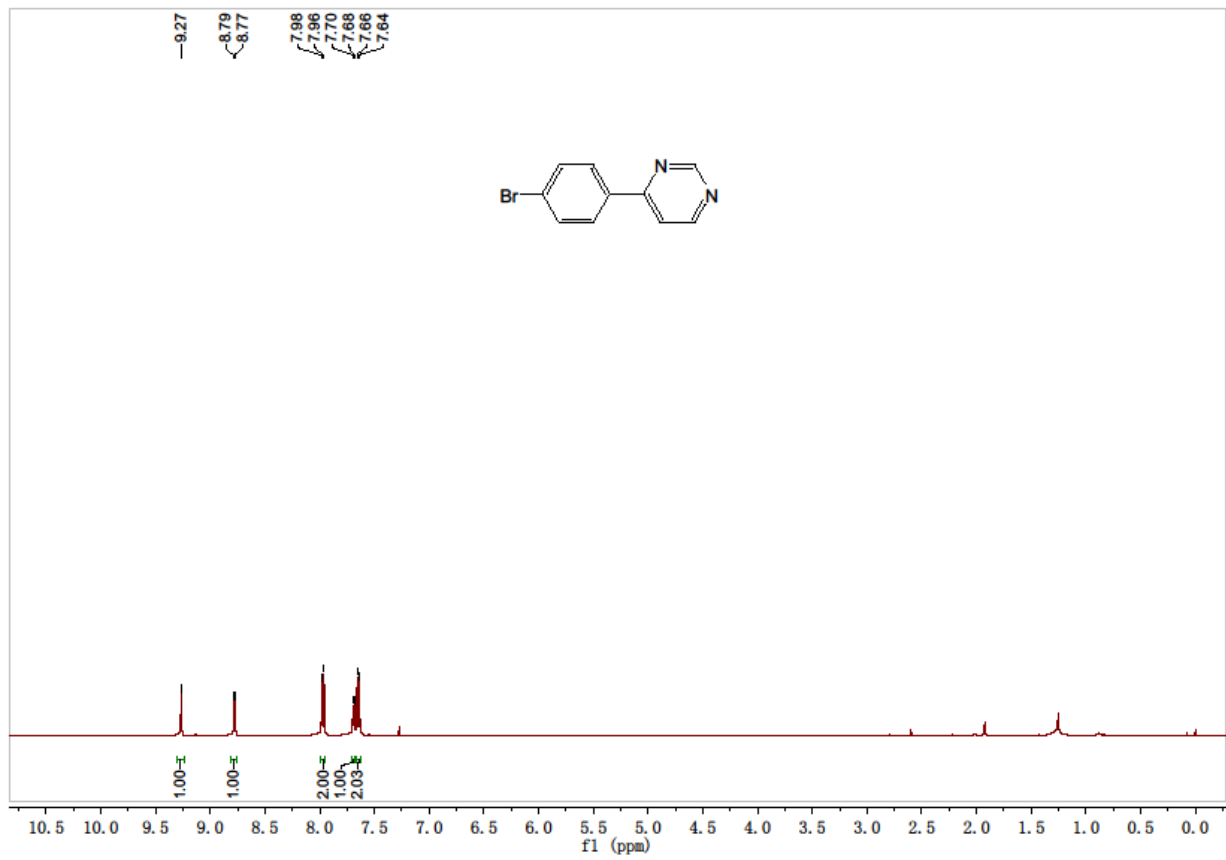
### 4-(4-fluorophenyl)pyrimidine (5c)



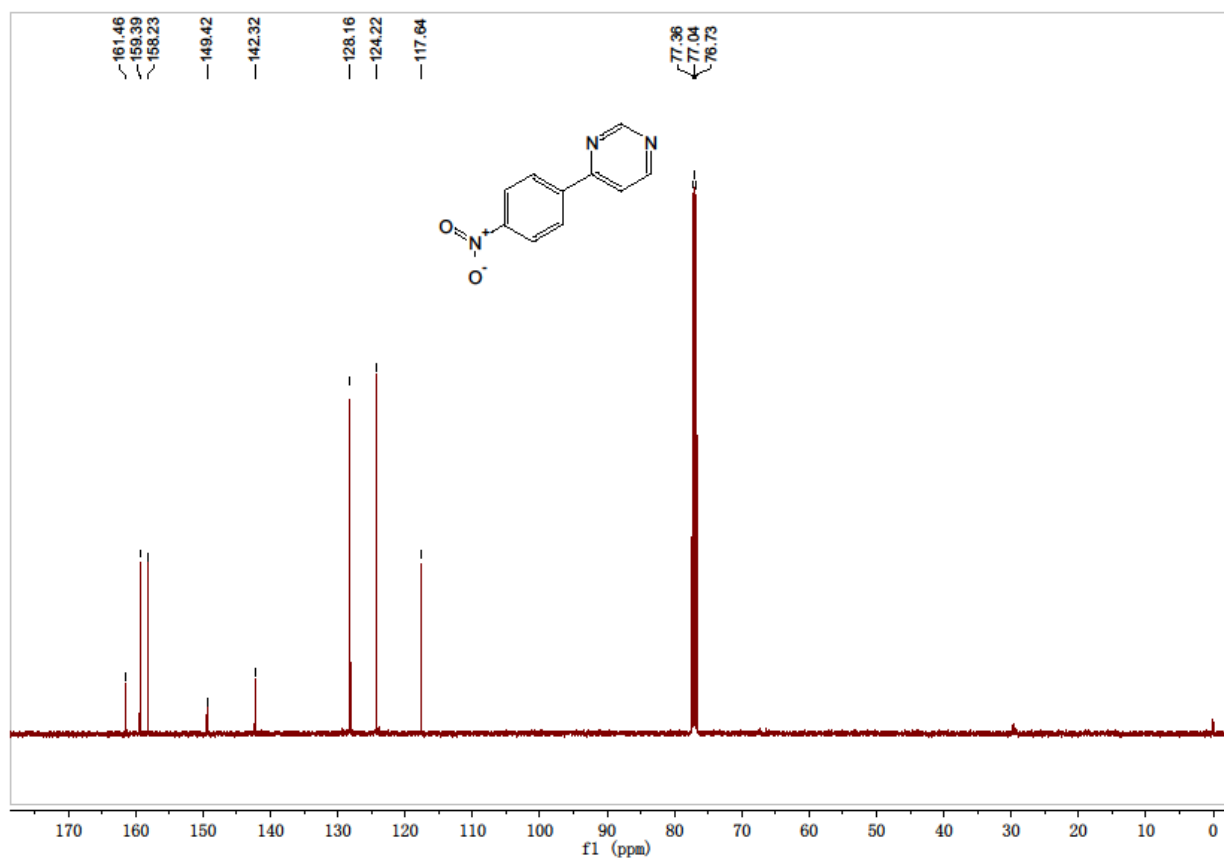
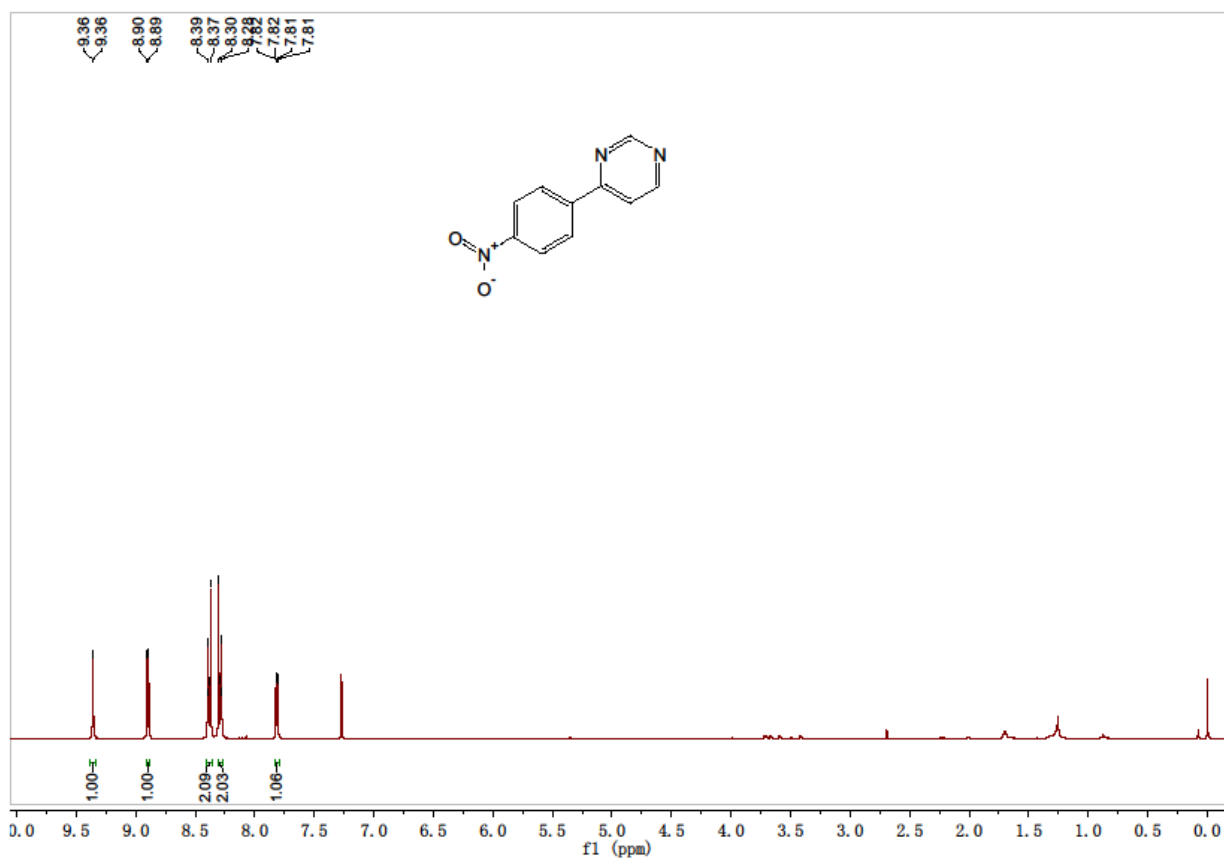
### 4-(4-chlorophenyl)pyrimidine (5d)



### 4-(4-bromophenyl)pyrimidine (5e)



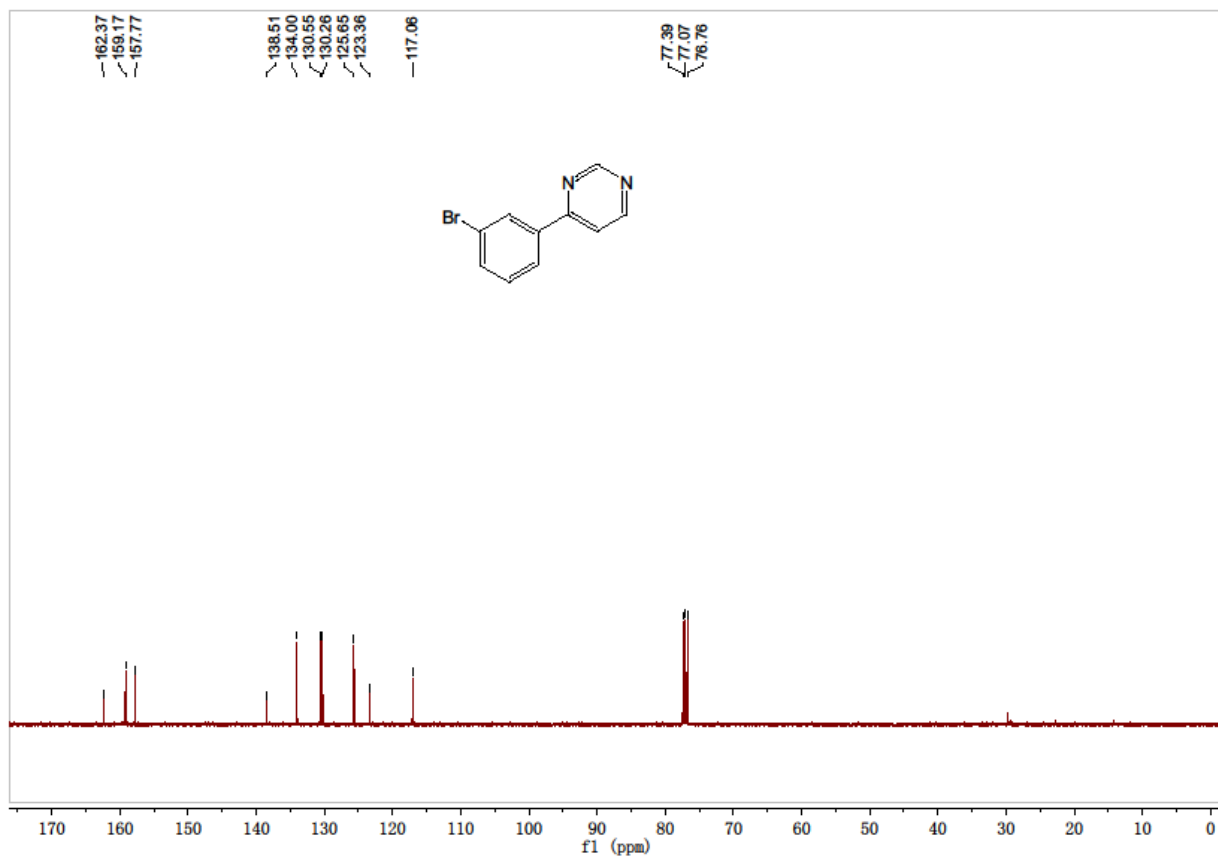
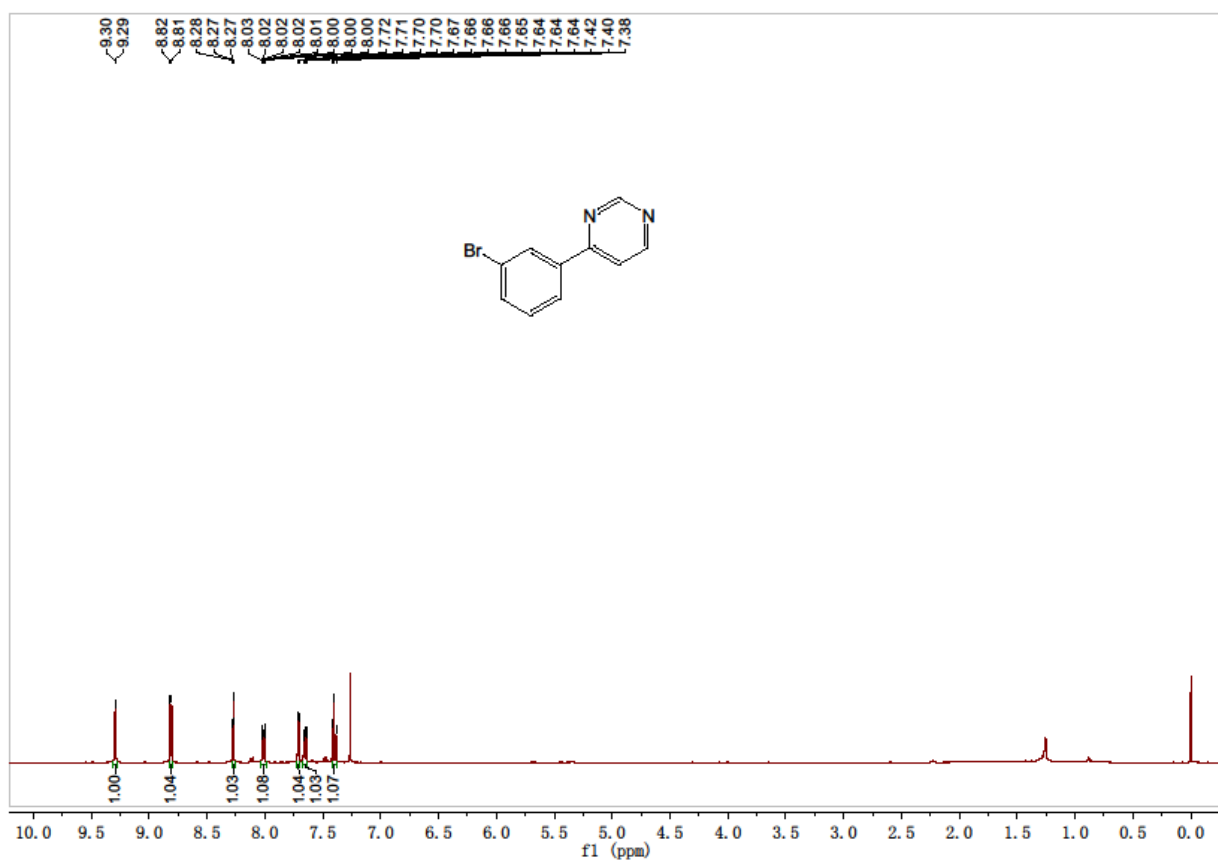
### 4-(4-nitrophenyl)pyrimidine (5f)



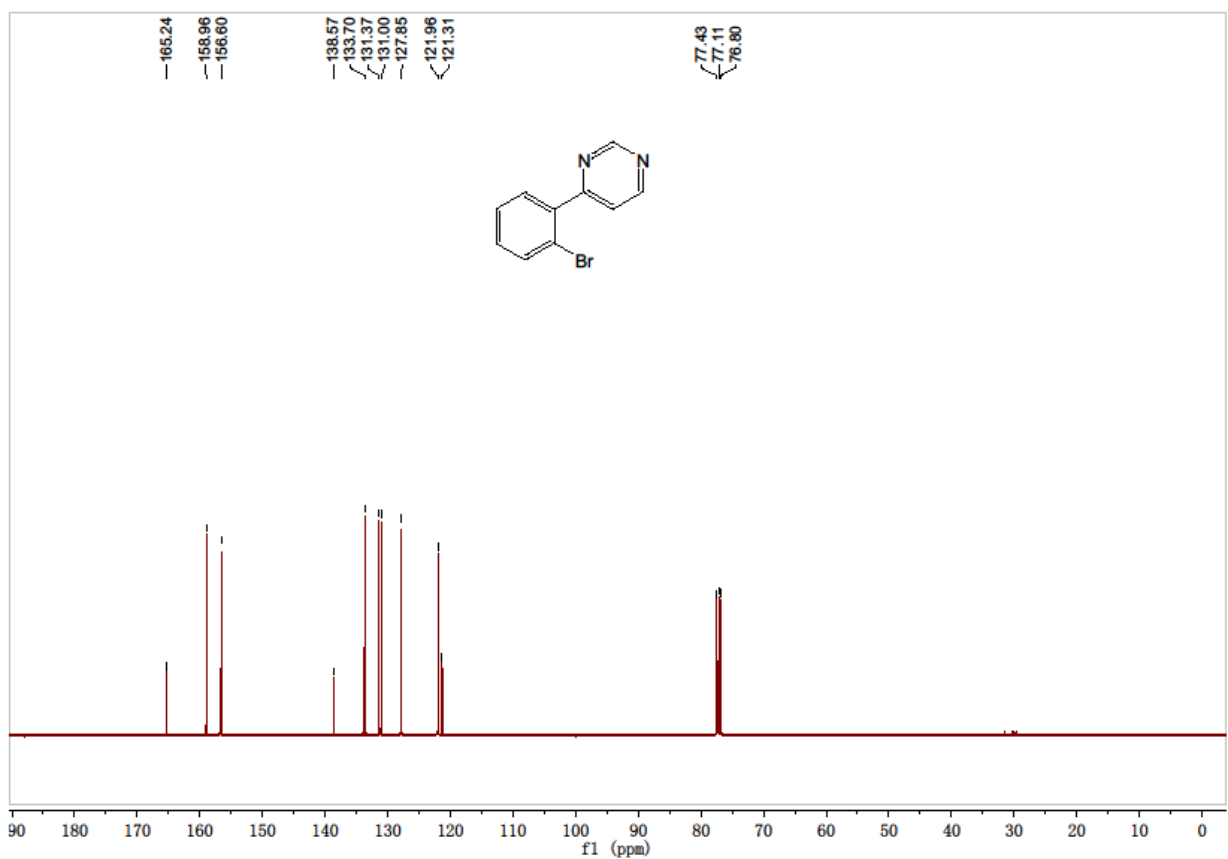
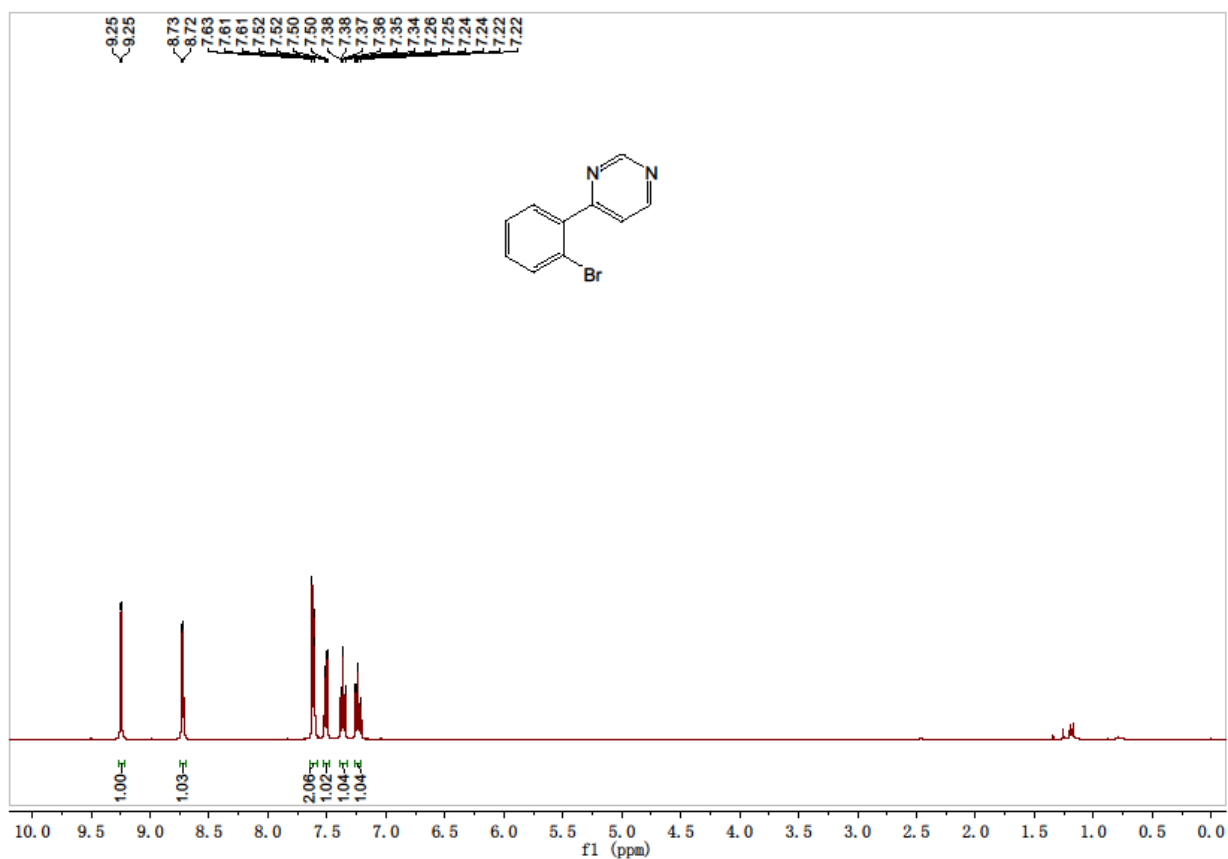




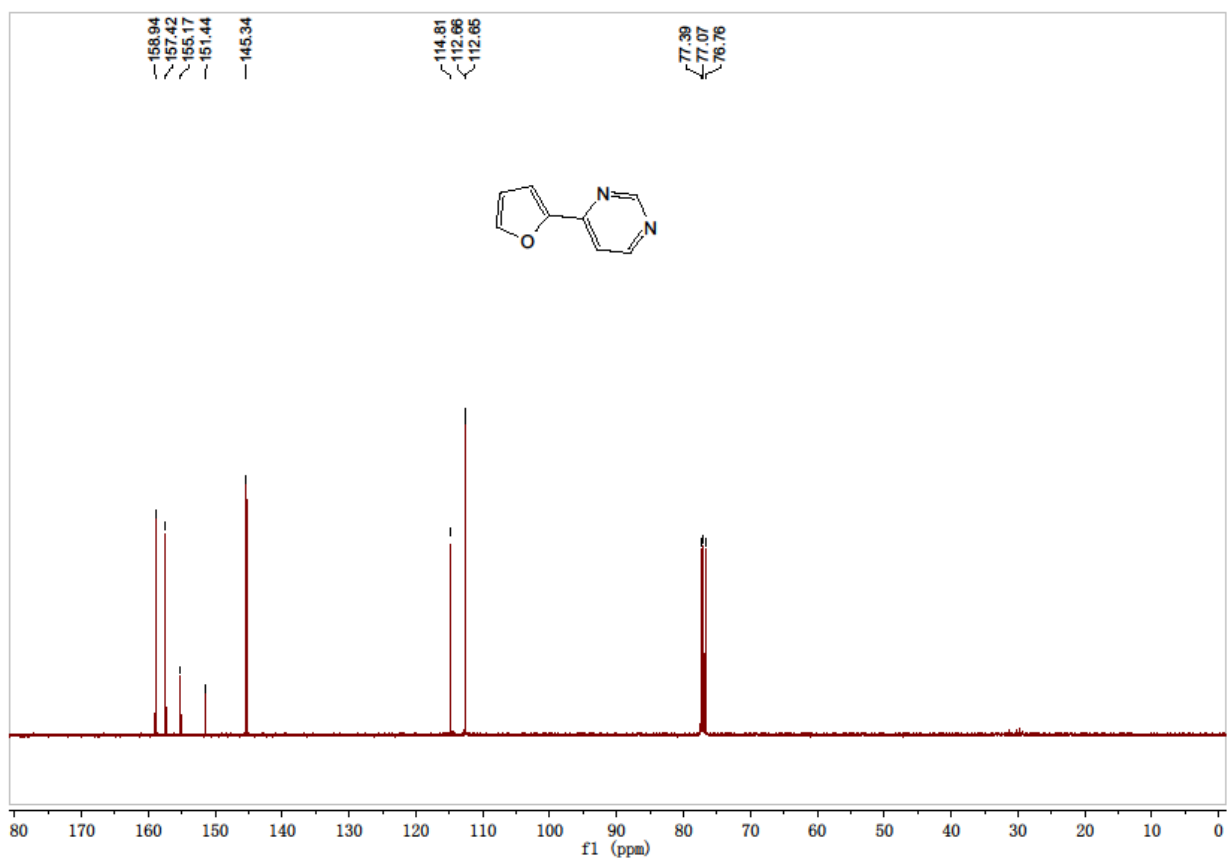
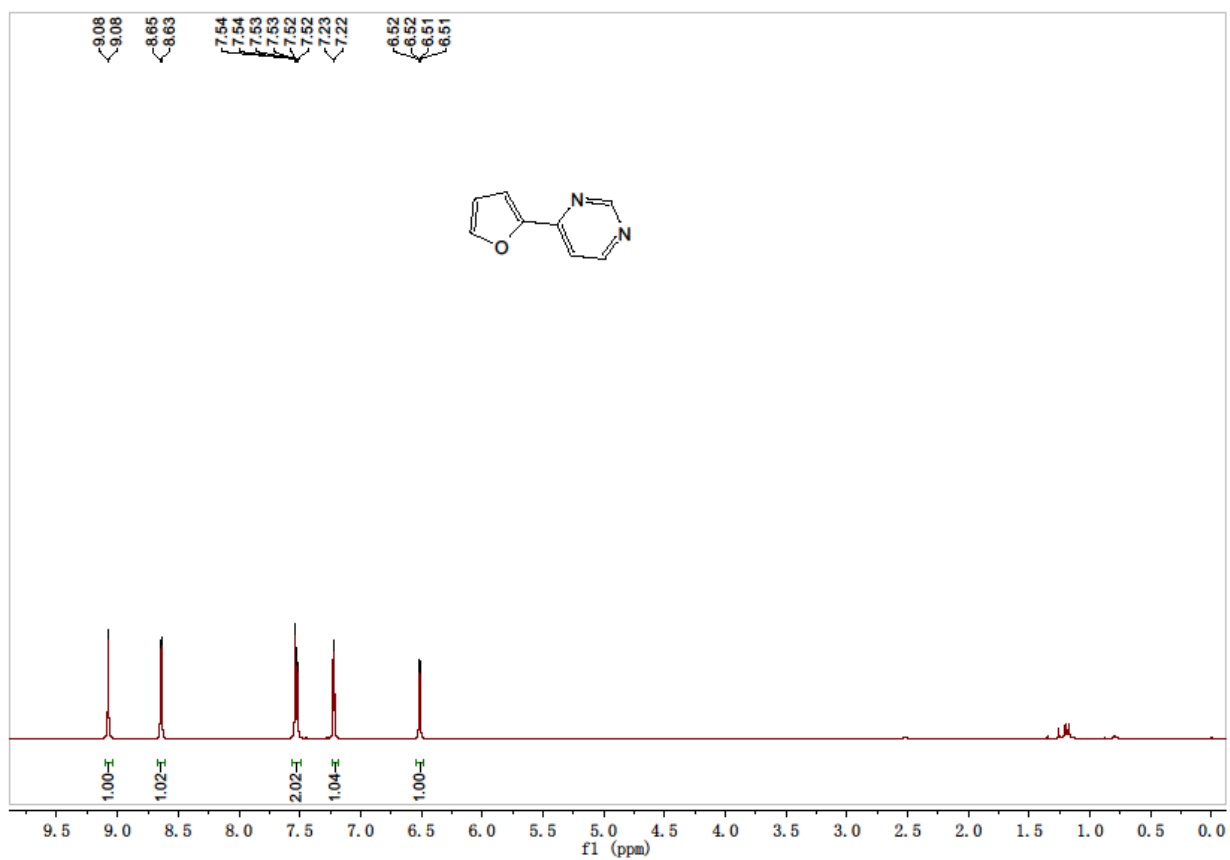
### 4-(3-bromophenyl)pyrimidine (5h)



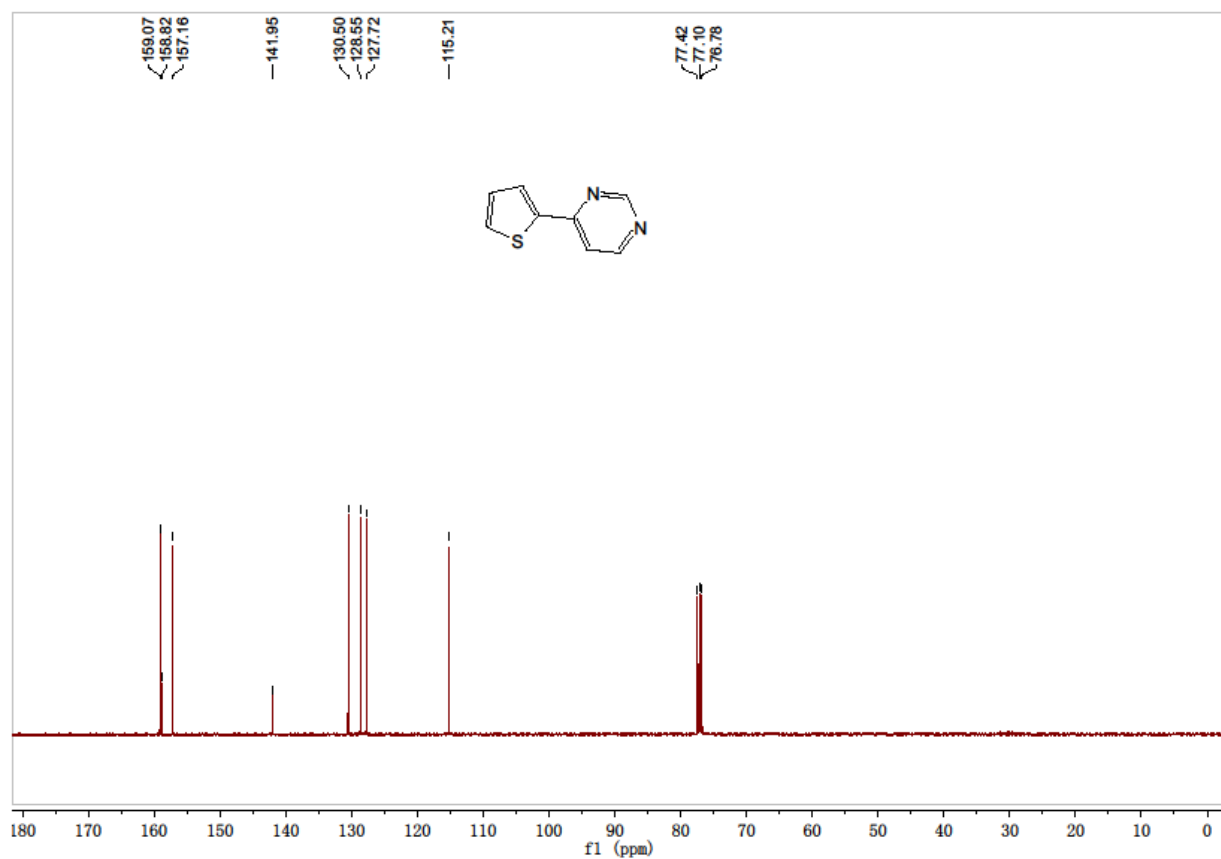
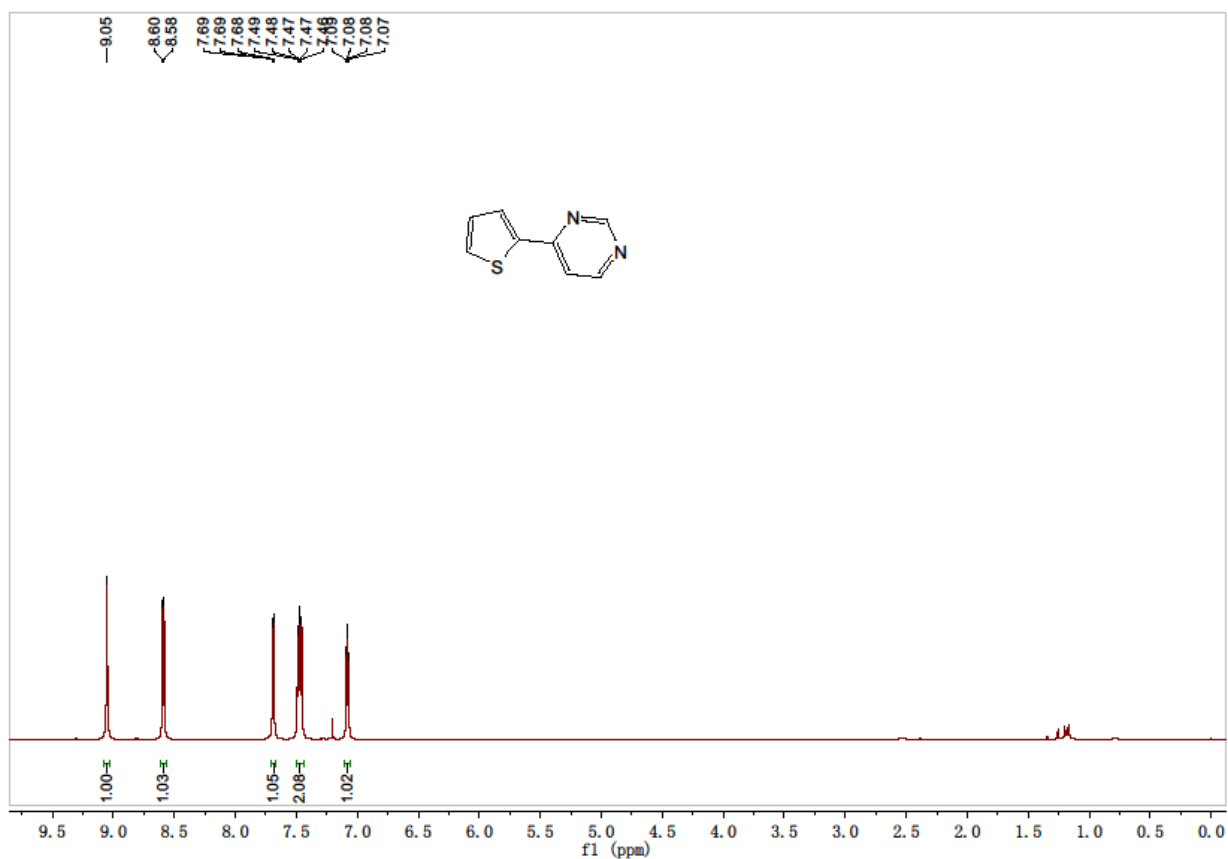
### 4-(2-bromophenyl)pyrimidine (5i)



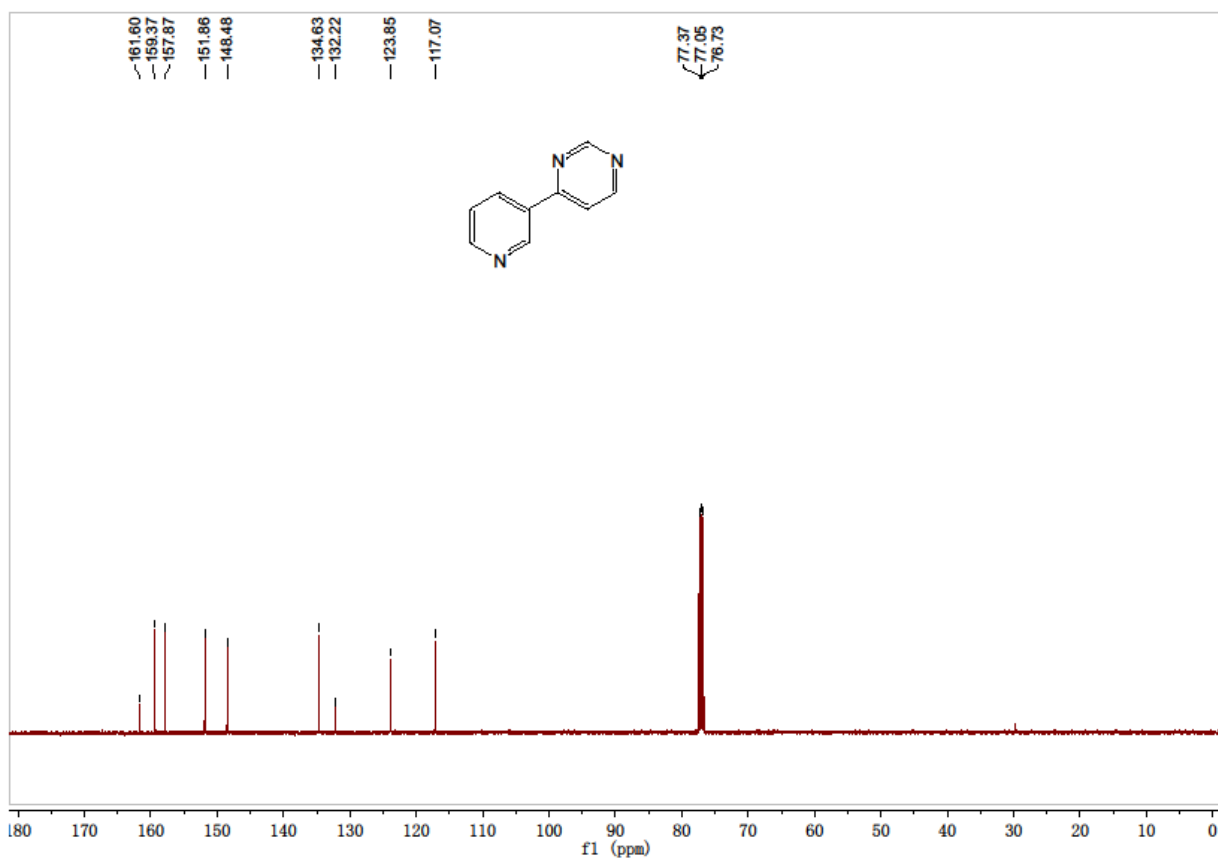
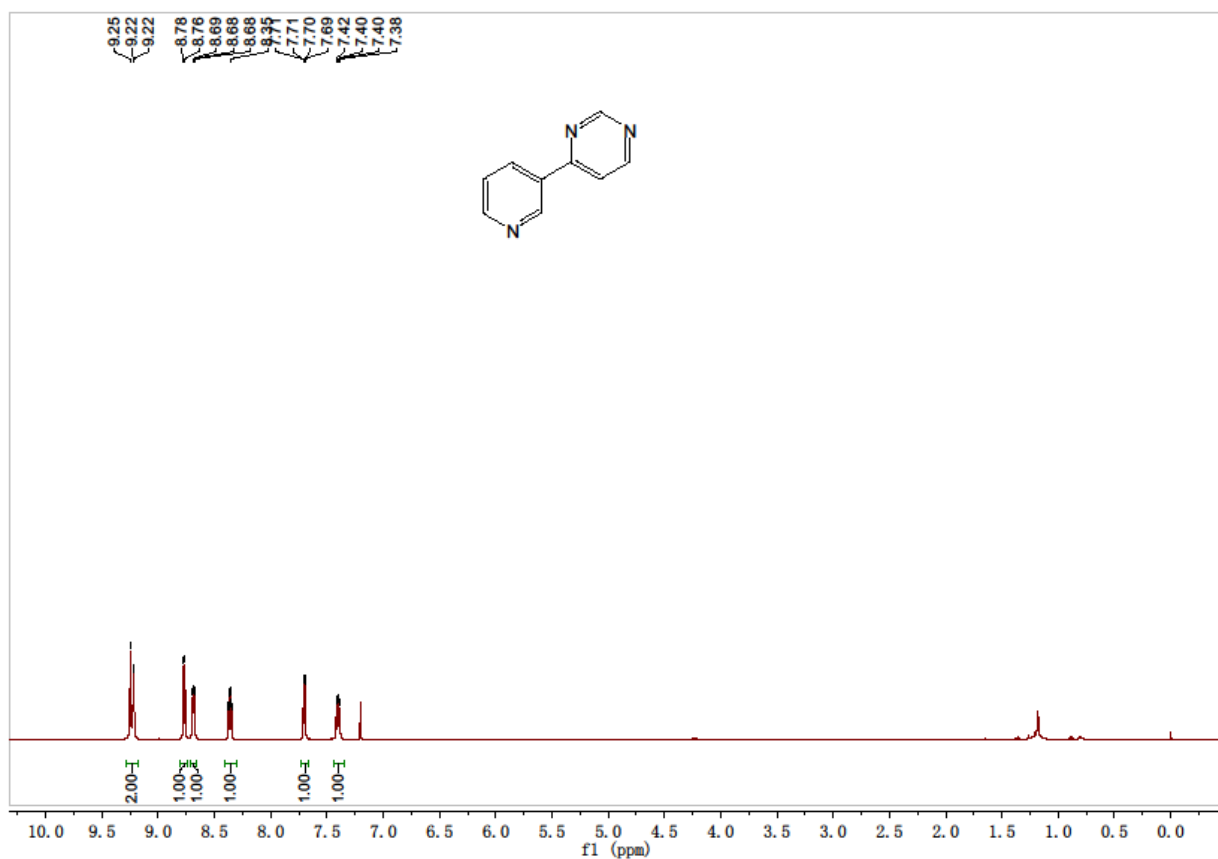
### 4-(furan-2-yl)pyrimidine (5j)



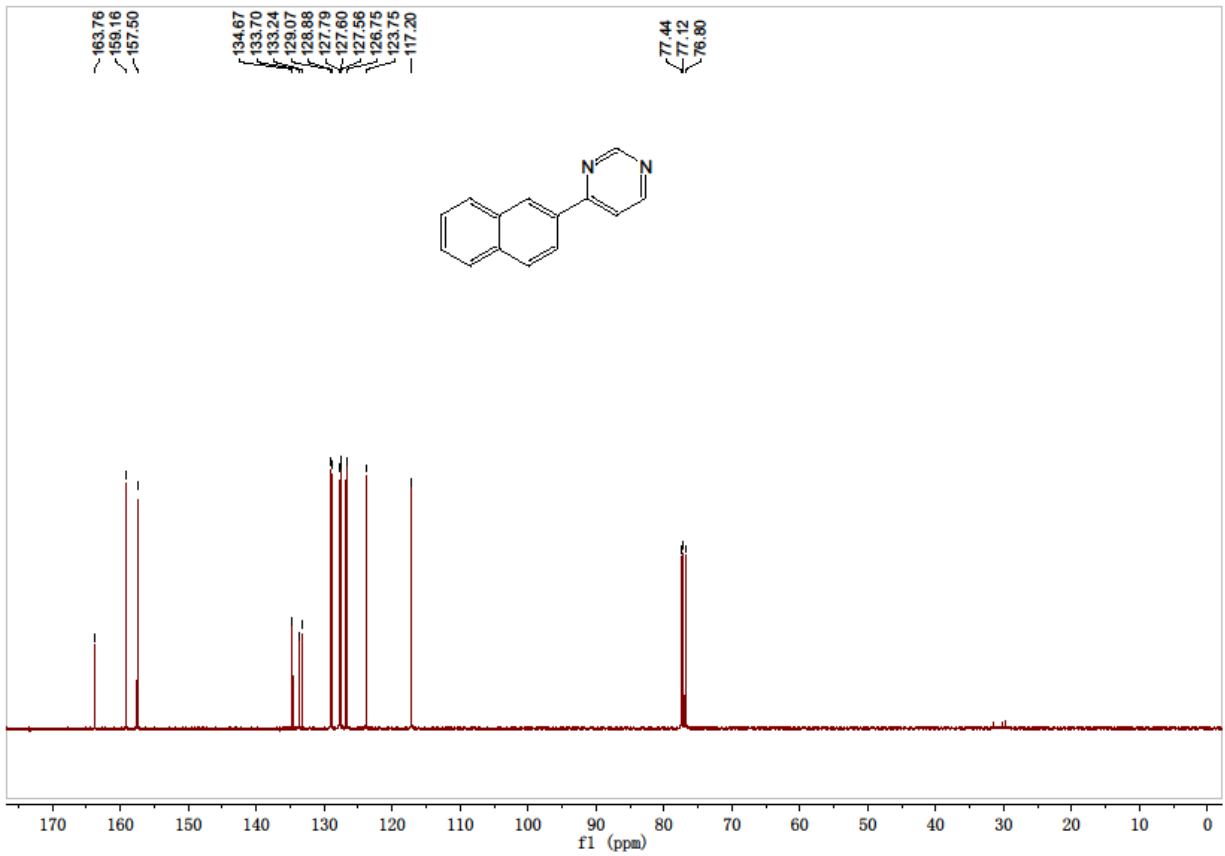
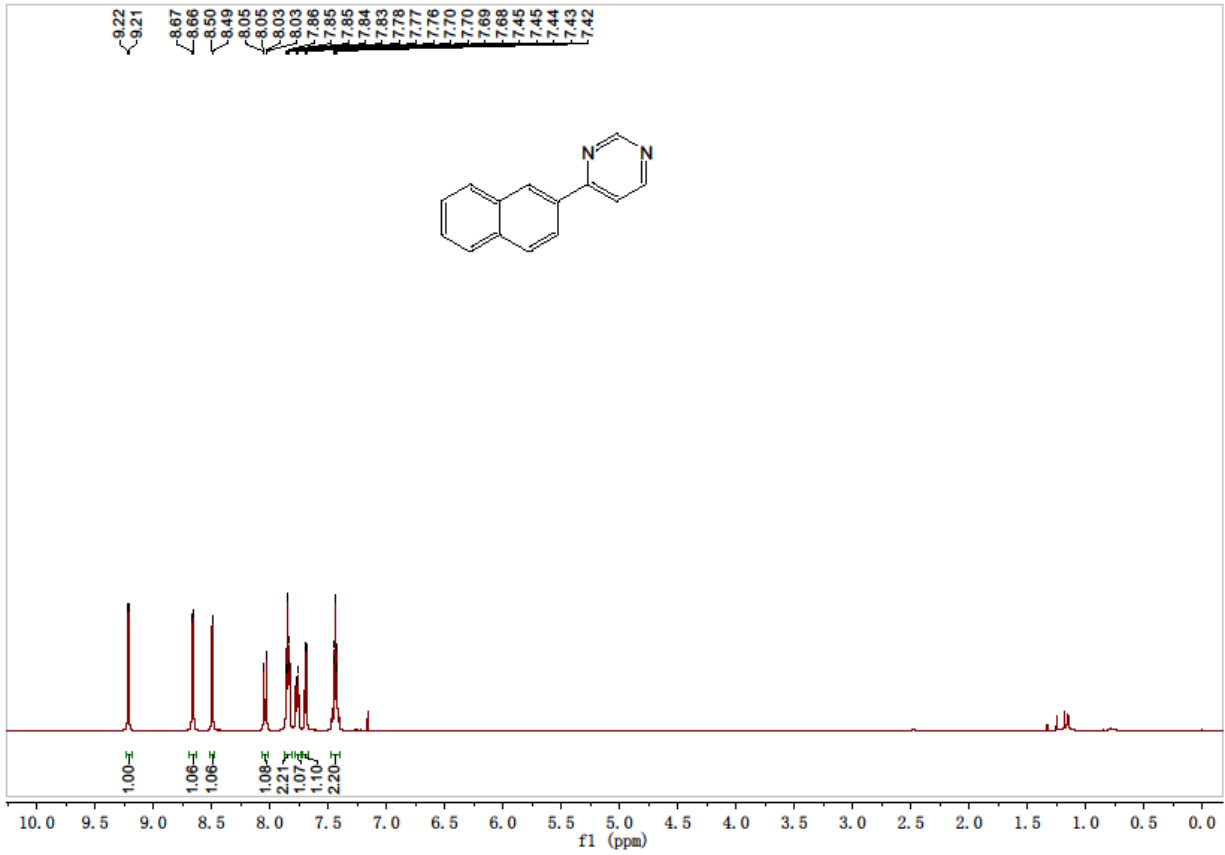
### 4-(thiophen-2-yl)pyrimidine (5k)



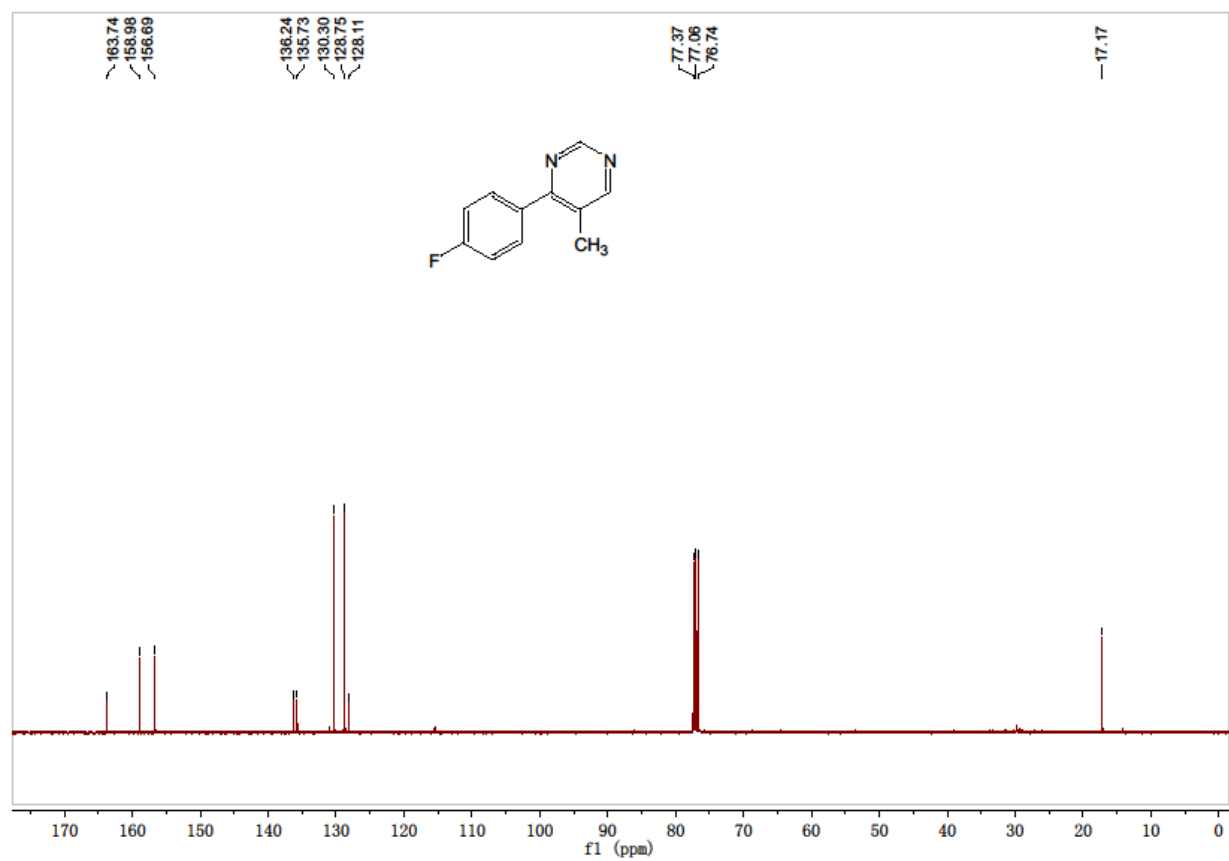
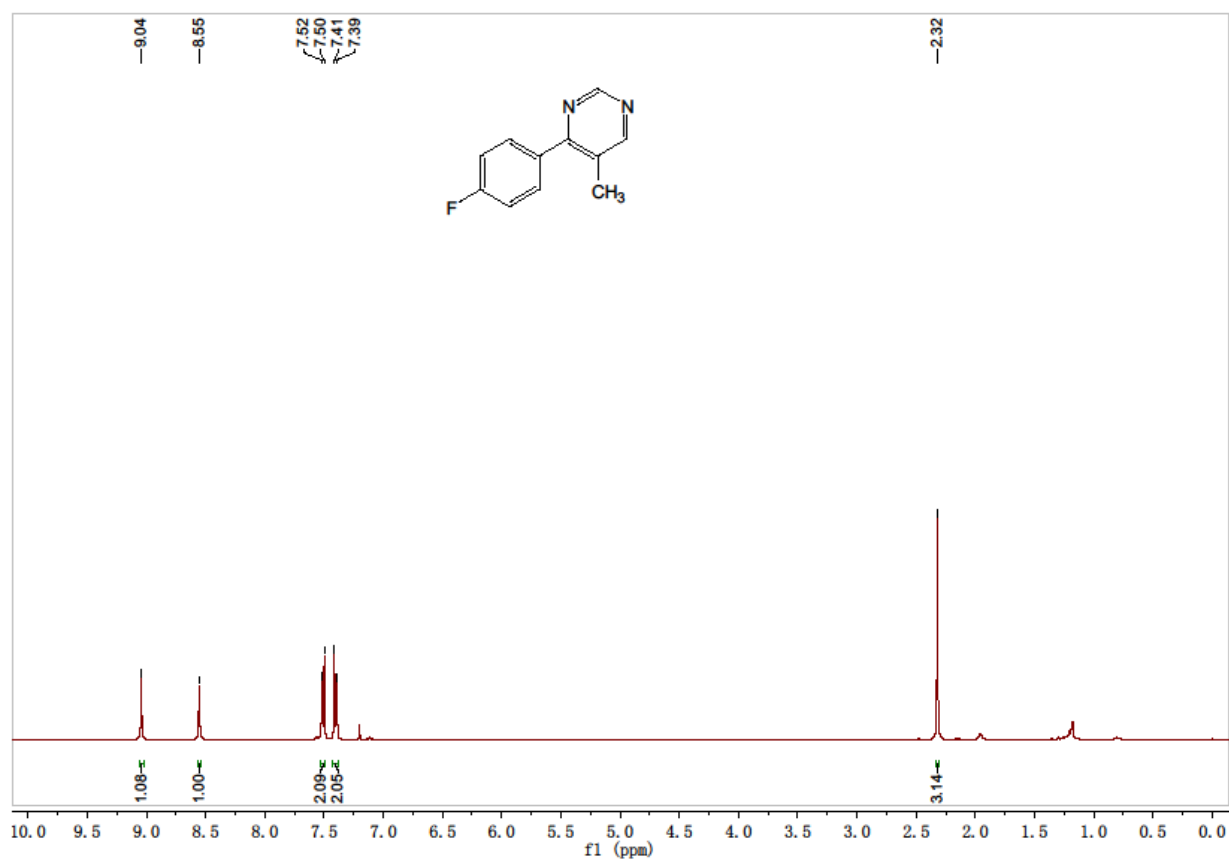
### 4-(pyridin-3-yl)pyrimidine (5l)



4-(naphthalen-2-yl)pyrimidine (5m)

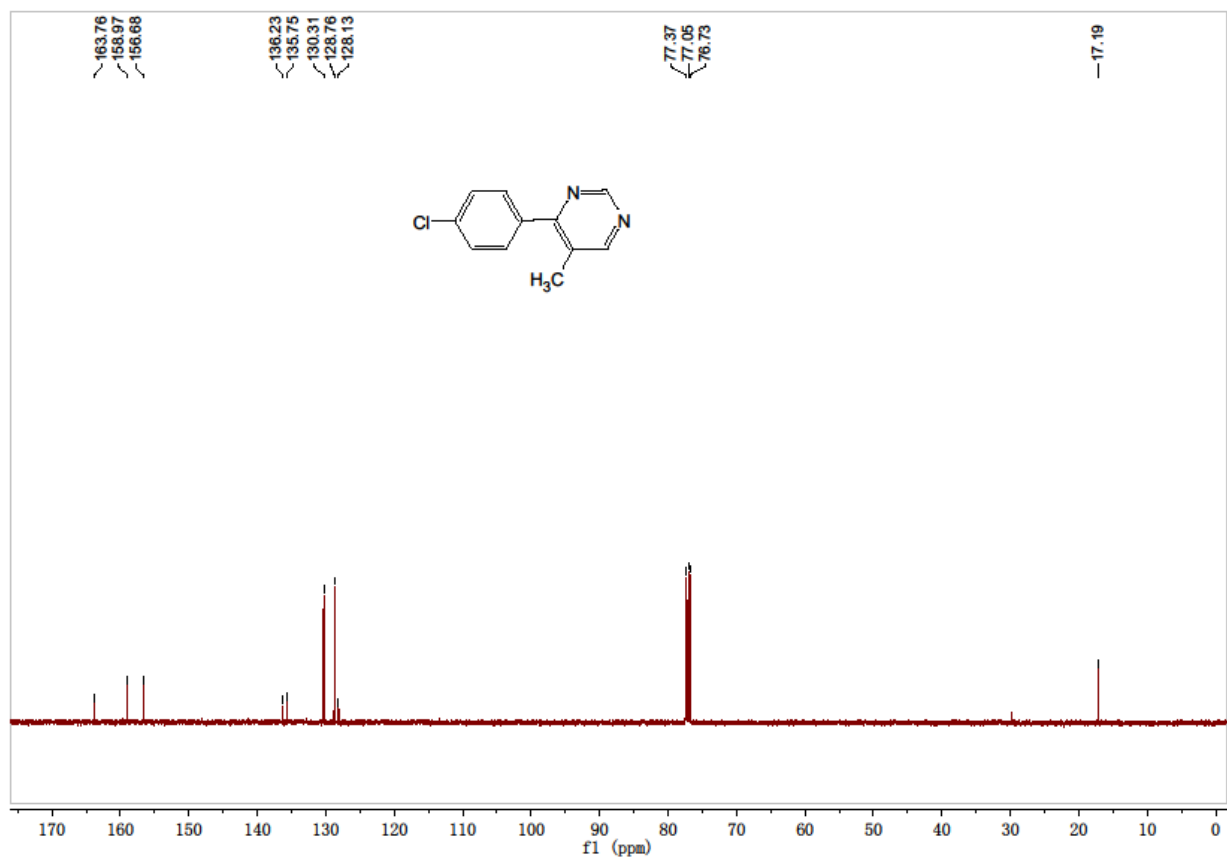
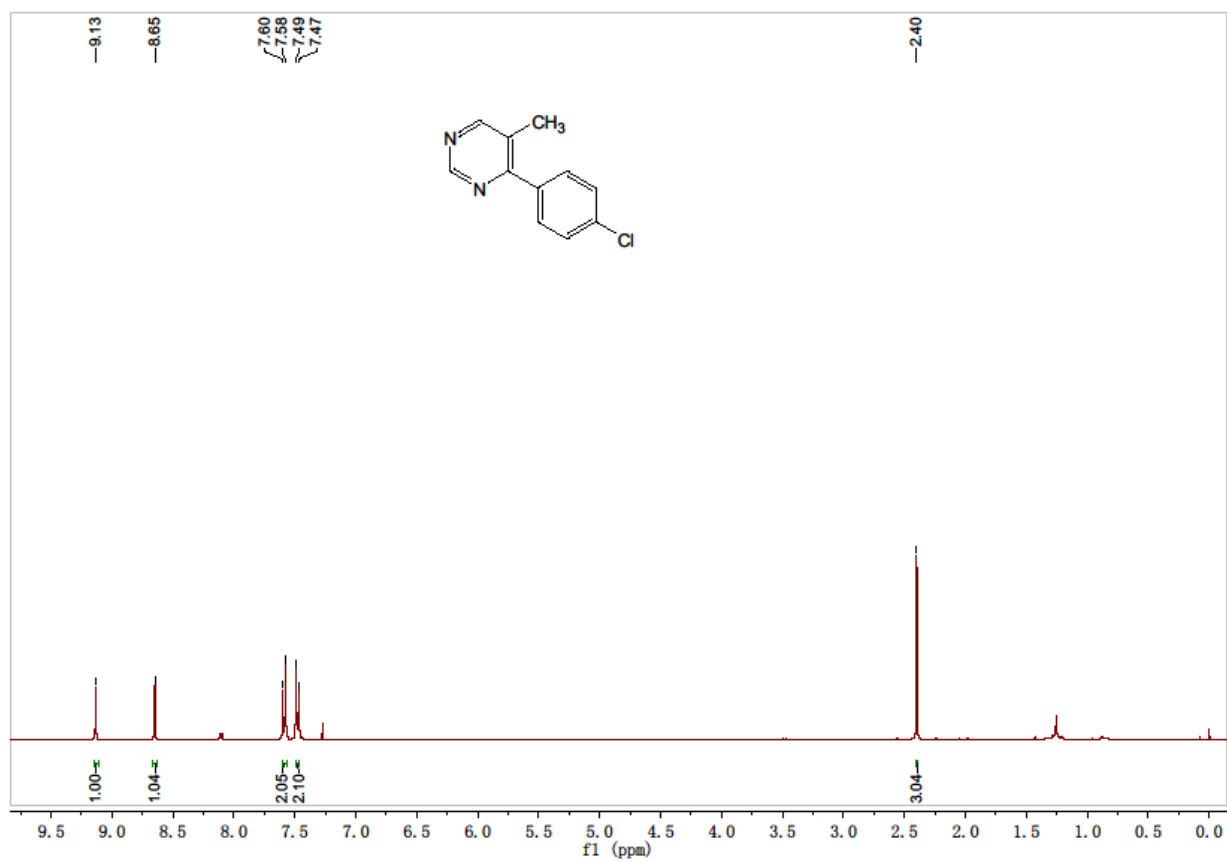


### 4-(4-fluorophenyl)-5-methylpyrimidine (5n)

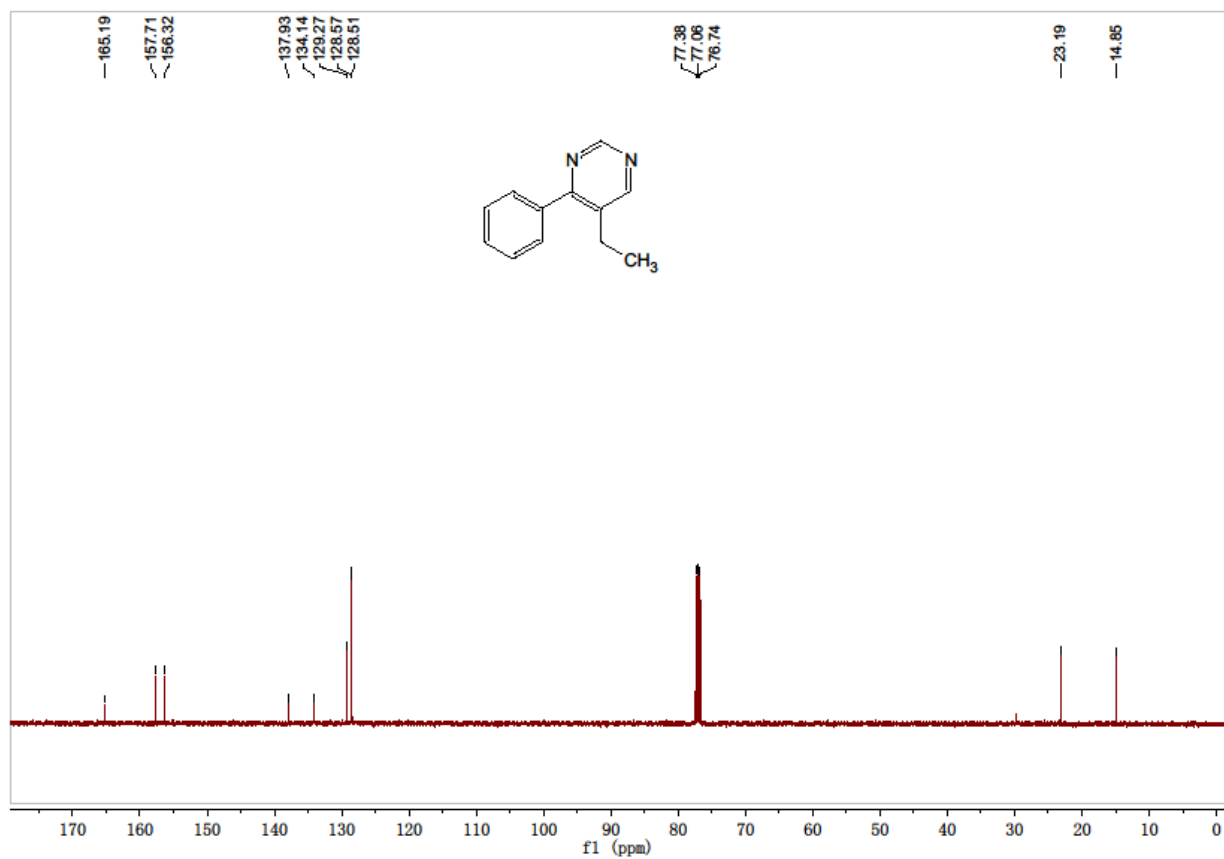
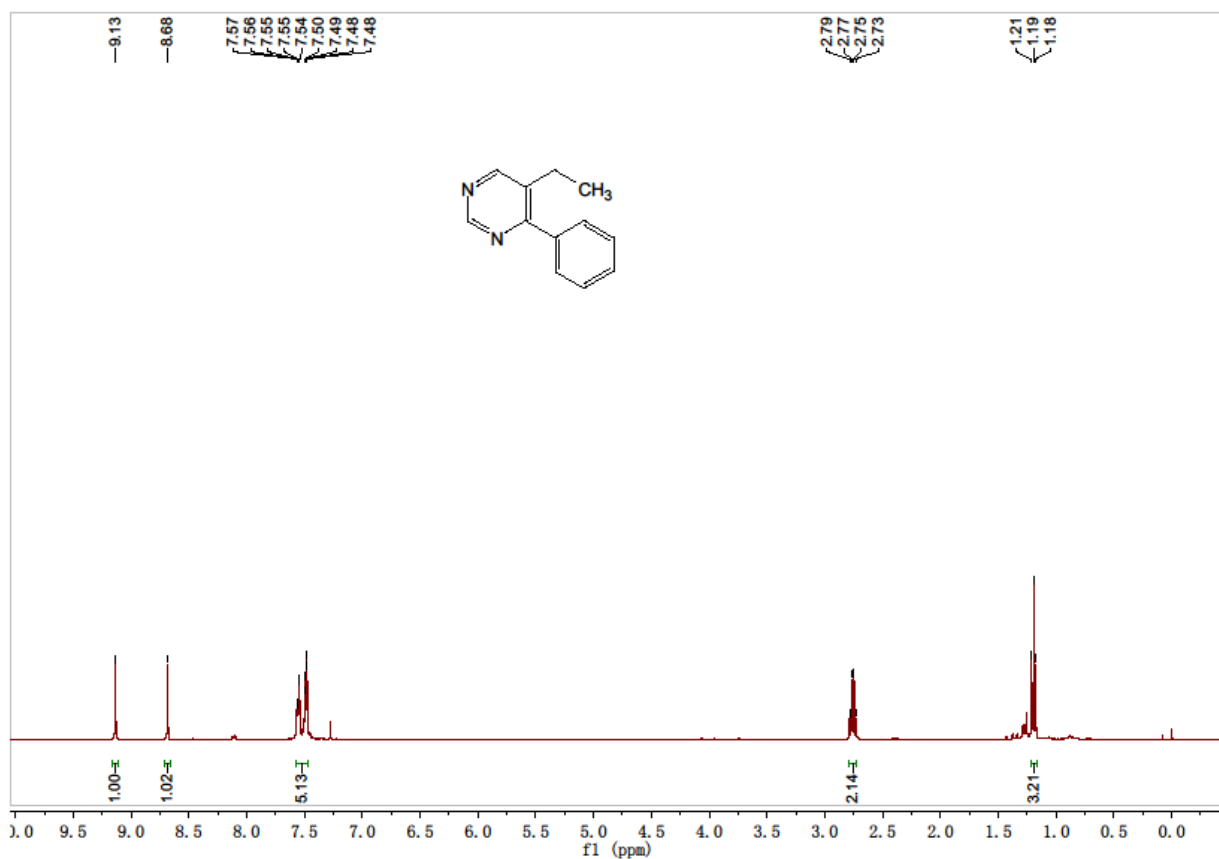




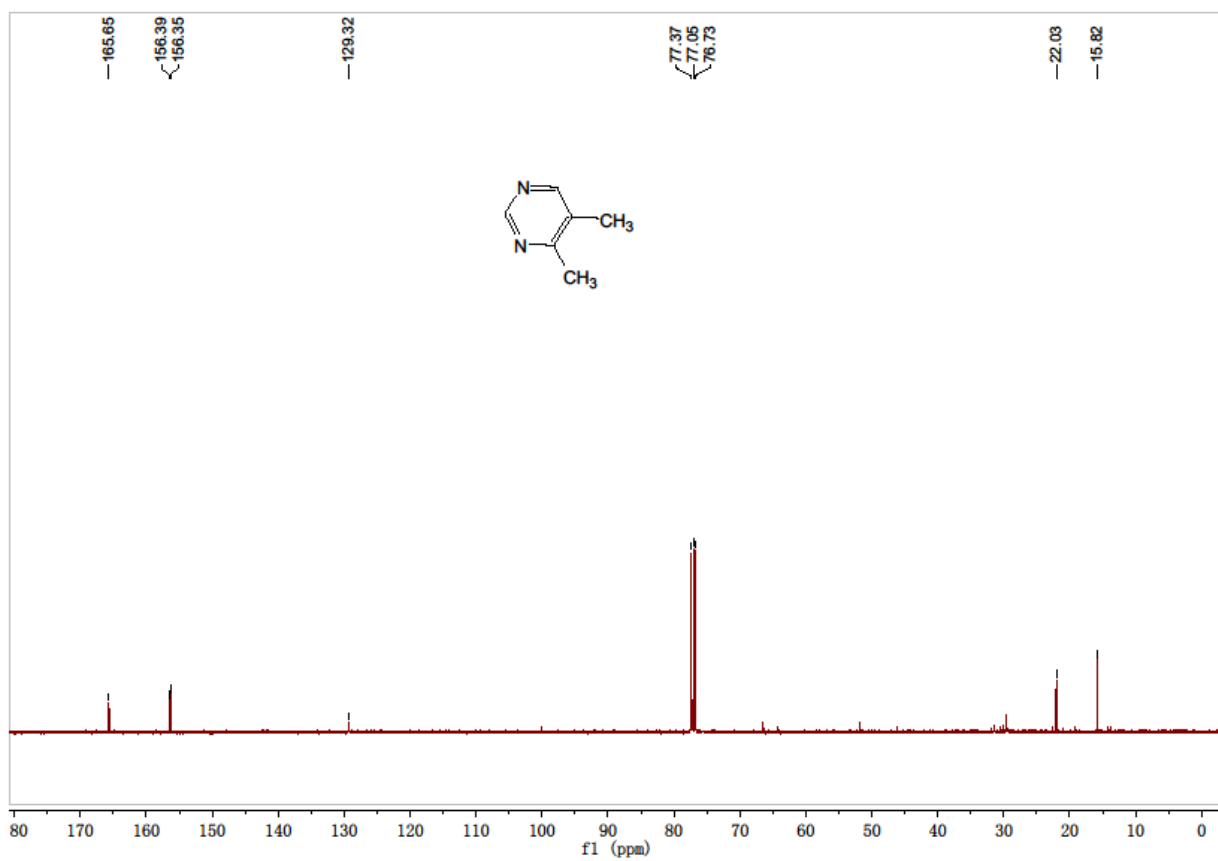
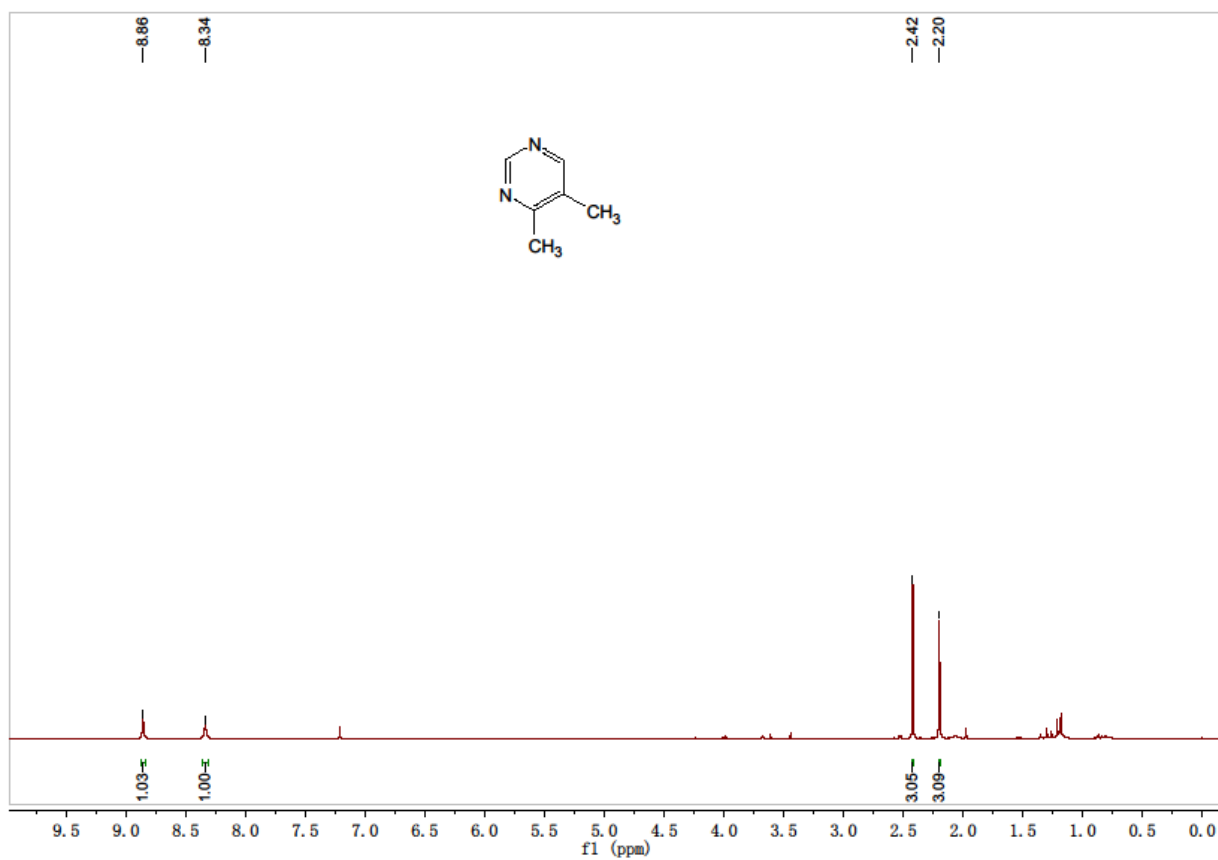
### 4-(4-chlorophenyl)-5-methylpyrimidine (5o)



### 5-ethyl-4-phenylpyrimidine (5p)



### 4,5-dimethylpyrimidine (5q)



### 4-ethyl-5-methylpyrimidine (5r)

