

# Supporting Information

## **$\alpha$ -Carbonyl Rh-Carbenoid Initiated Cascade Assembly of Diazobarbiturates with Alkylidene Pyrazolones for Synthesis of Spirofuopyrimidines**

Yue Zhang, Yu-Hang Mi, Kuo Wang and Hong-Wu Zhao

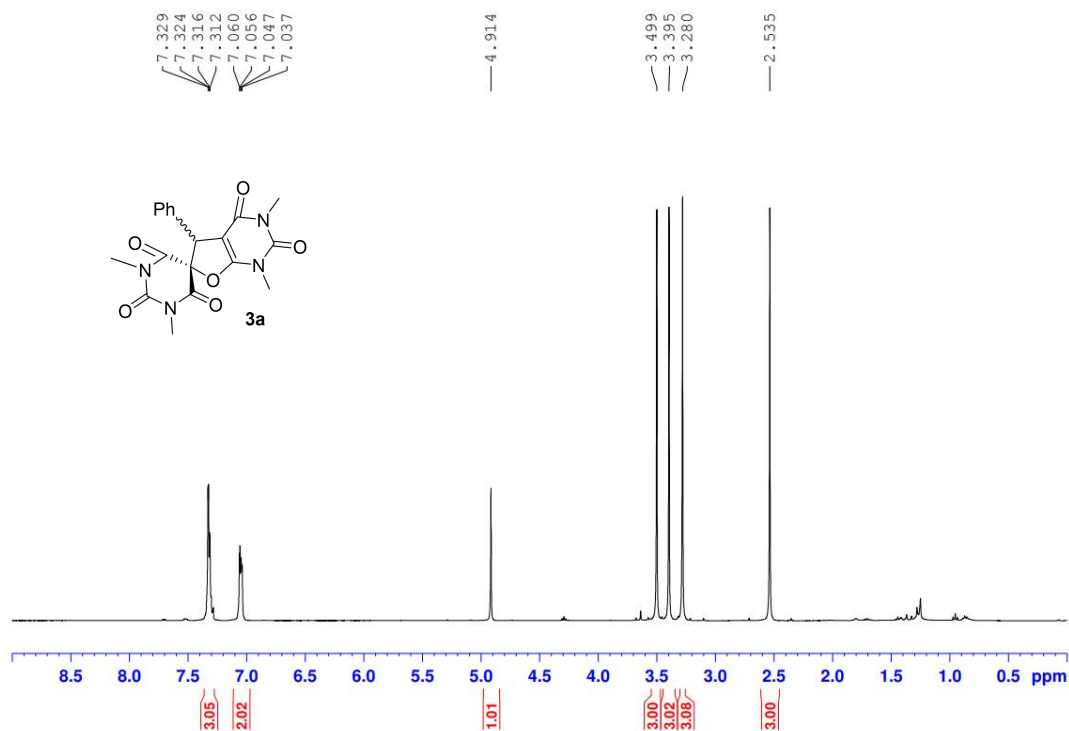
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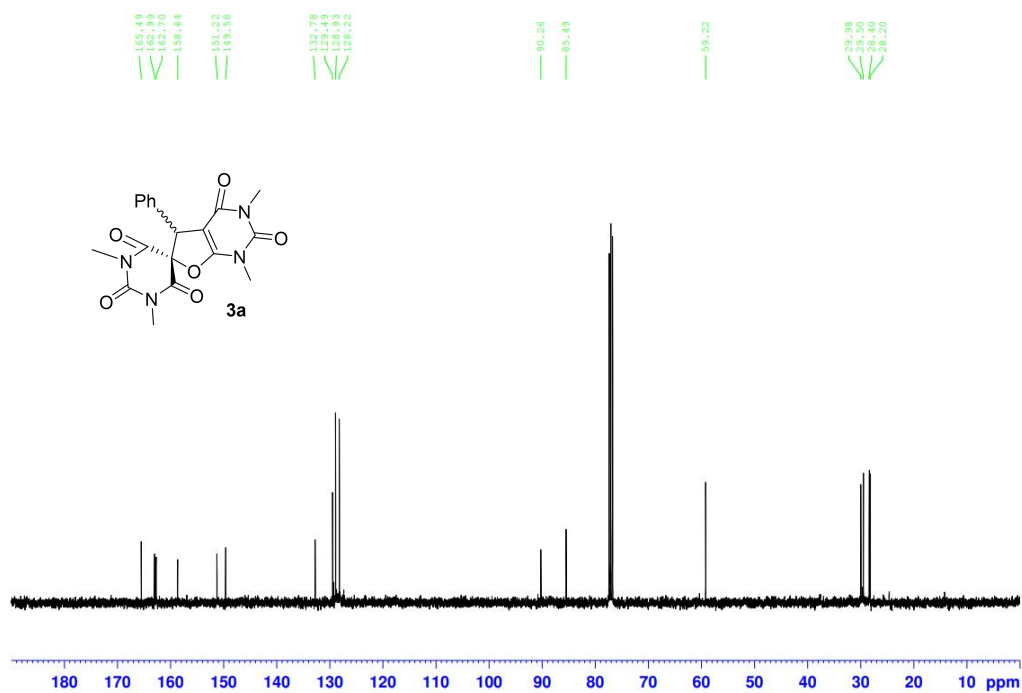
## 1. NMR Spectra of Products 3

1,1',3,3'-tetramethyl-5-phenyl-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone (3a):

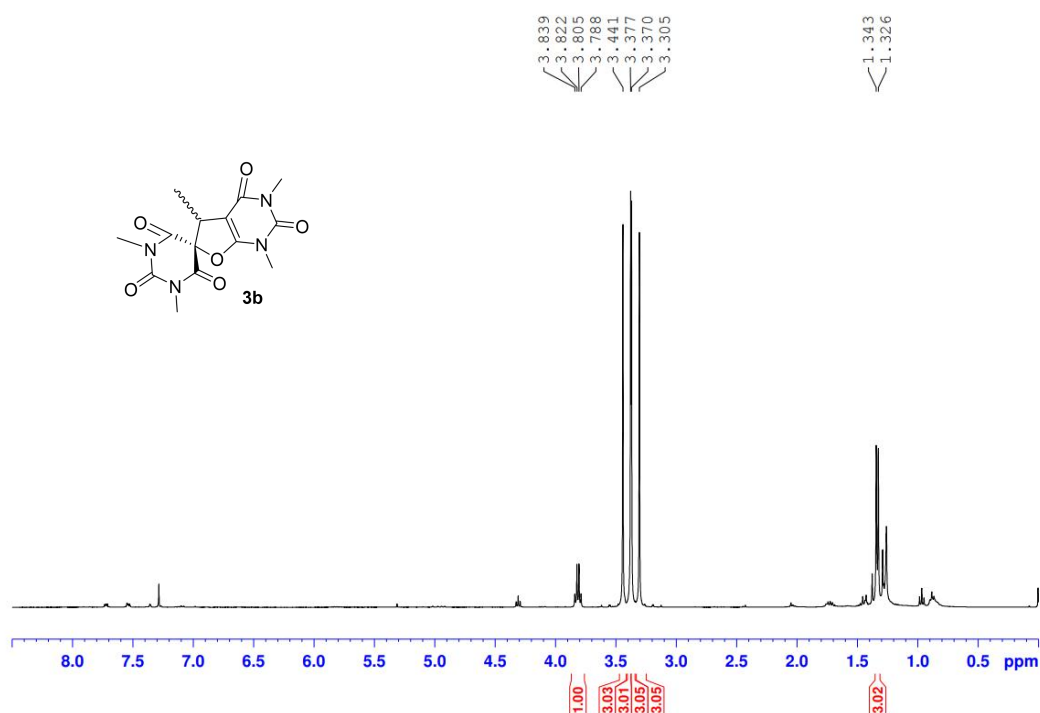
$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) of 3a



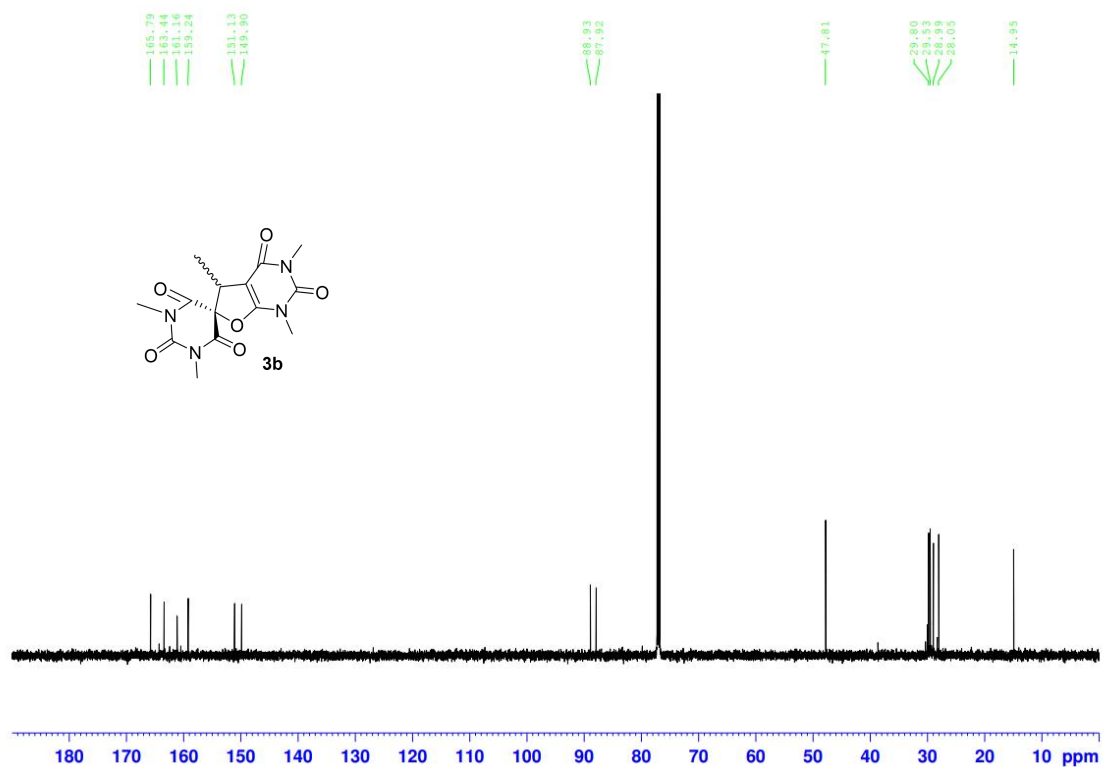
$^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ) of 3a



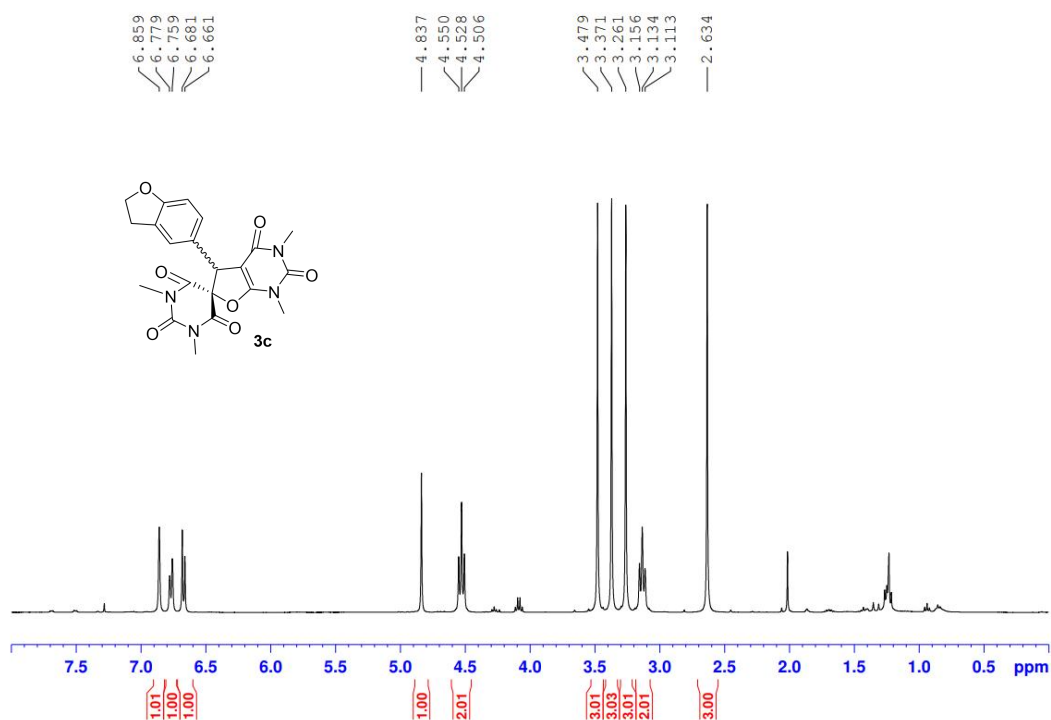
**1,1',3,3',5-pentamethyl-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3b):**  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3b



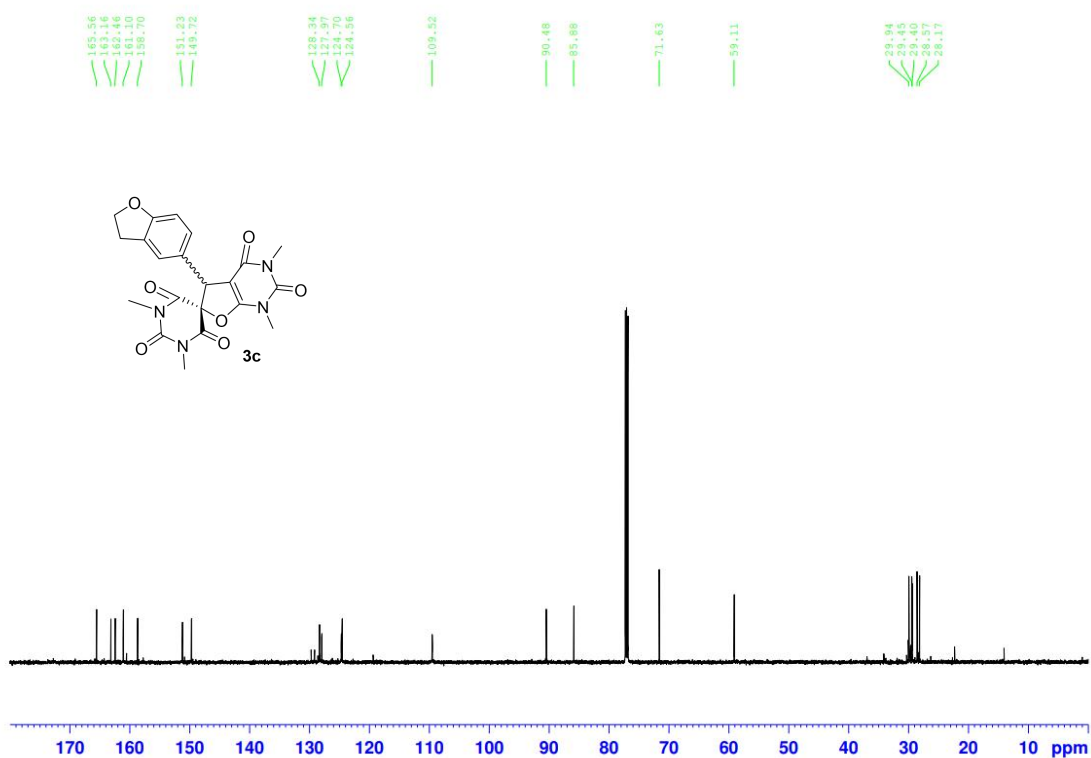
<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3b



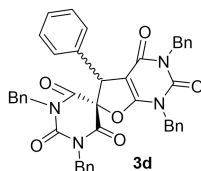
**5-(2,3-dihydrobenzofuran-5-yl)-1,1',3,3'-tetramethyl-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3c):  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3c**



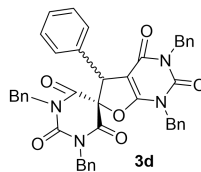
**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3c**



**<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3d**

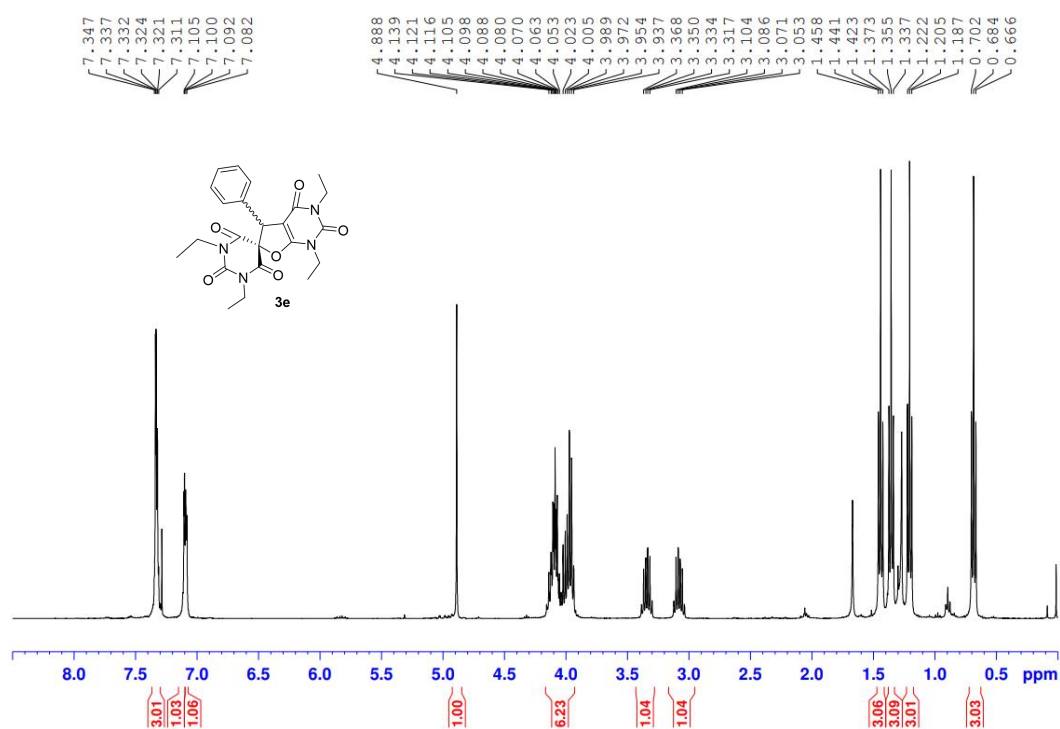


**$^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ) of 3d**

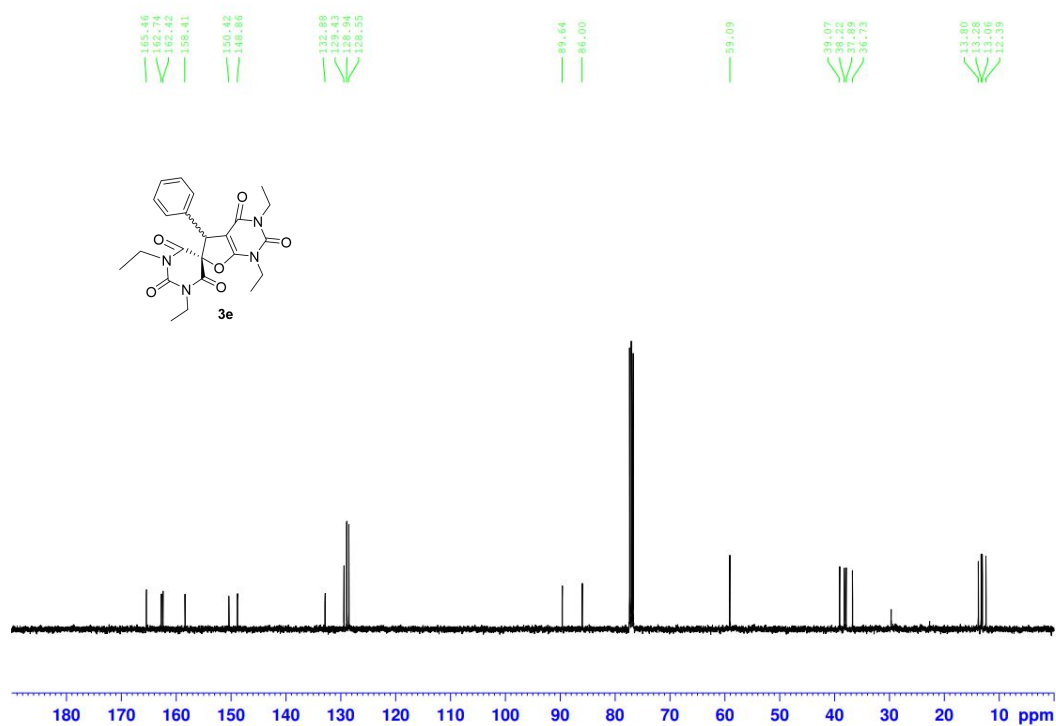


**1,1',3,3'-tetraethyl-5-phenyl-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6,6'(1'H,3H,3'H)-pentaone (3e):**

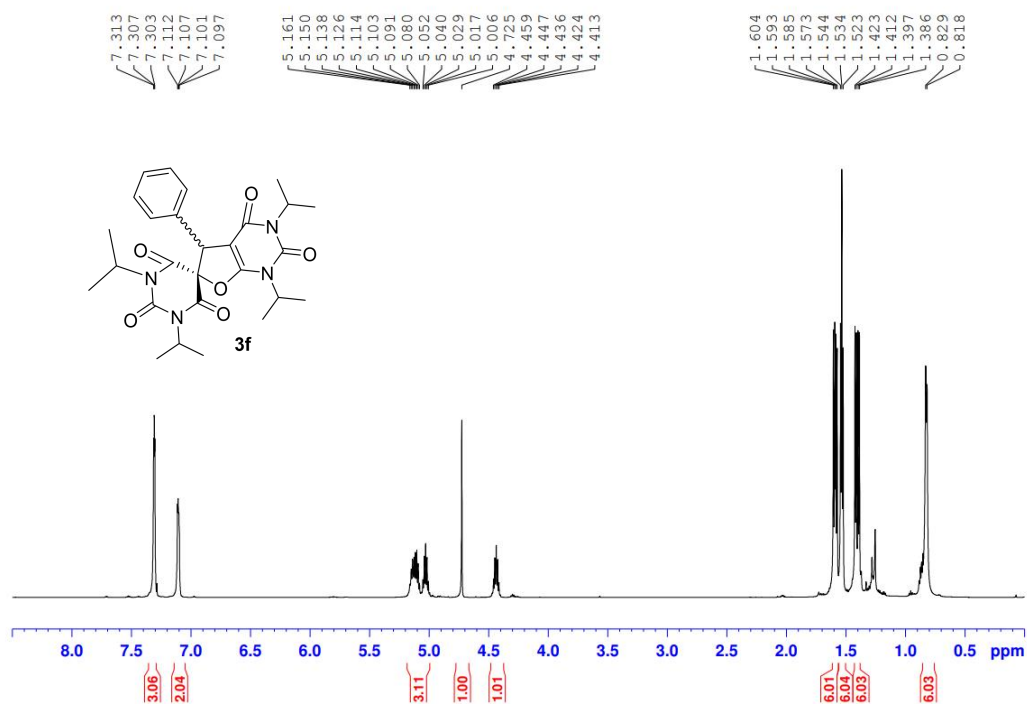
**<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3e**



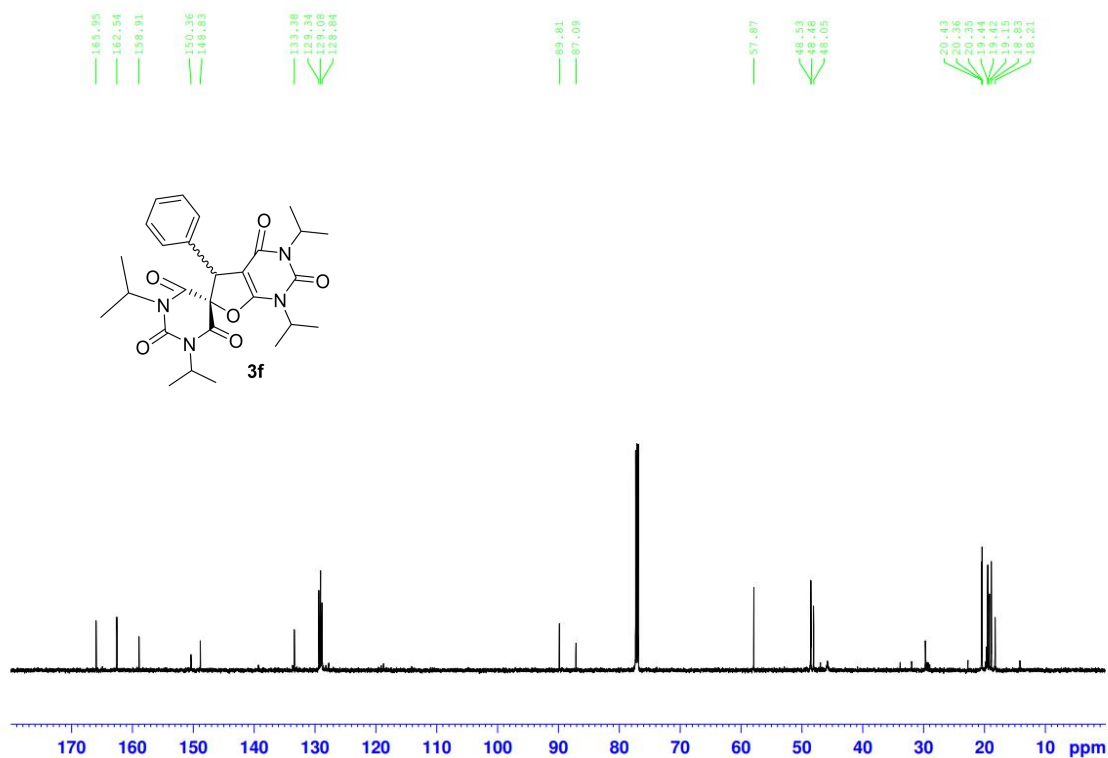
**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3e**



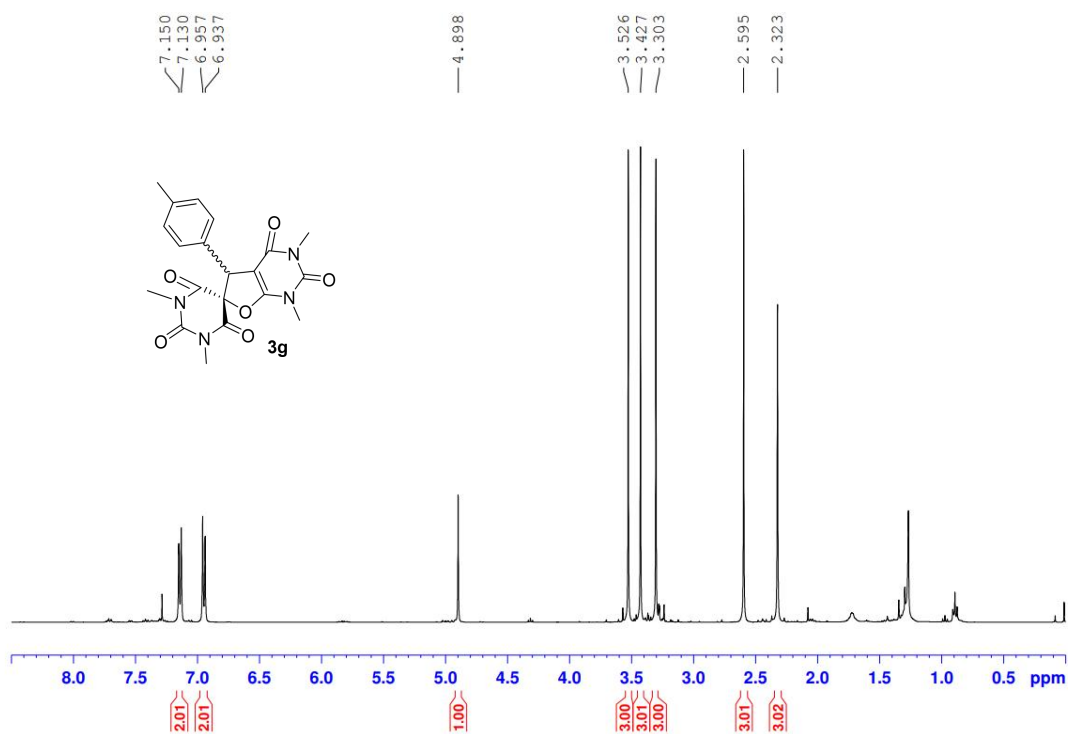
**1,1',3,3'-tetraisopropyl-5-phenyl-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3f):**  
**<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3f**



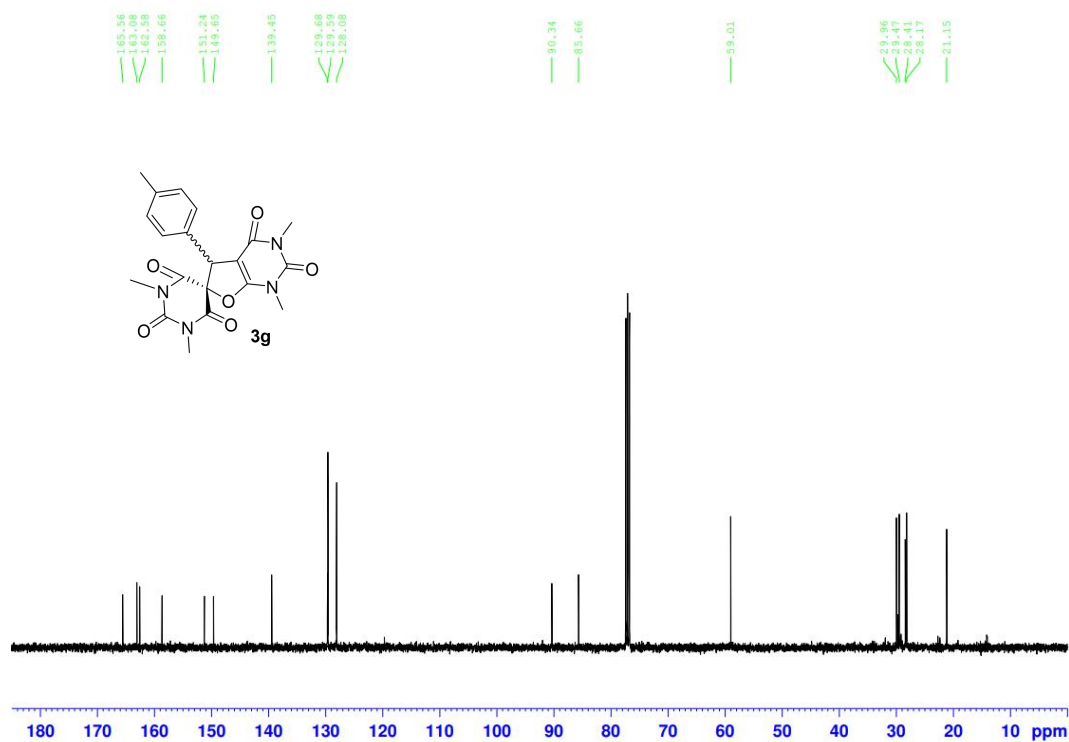
**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3f**



**1,1',3,3'-tetramethyl-5-(p-tolyl)-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3g):**  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3g

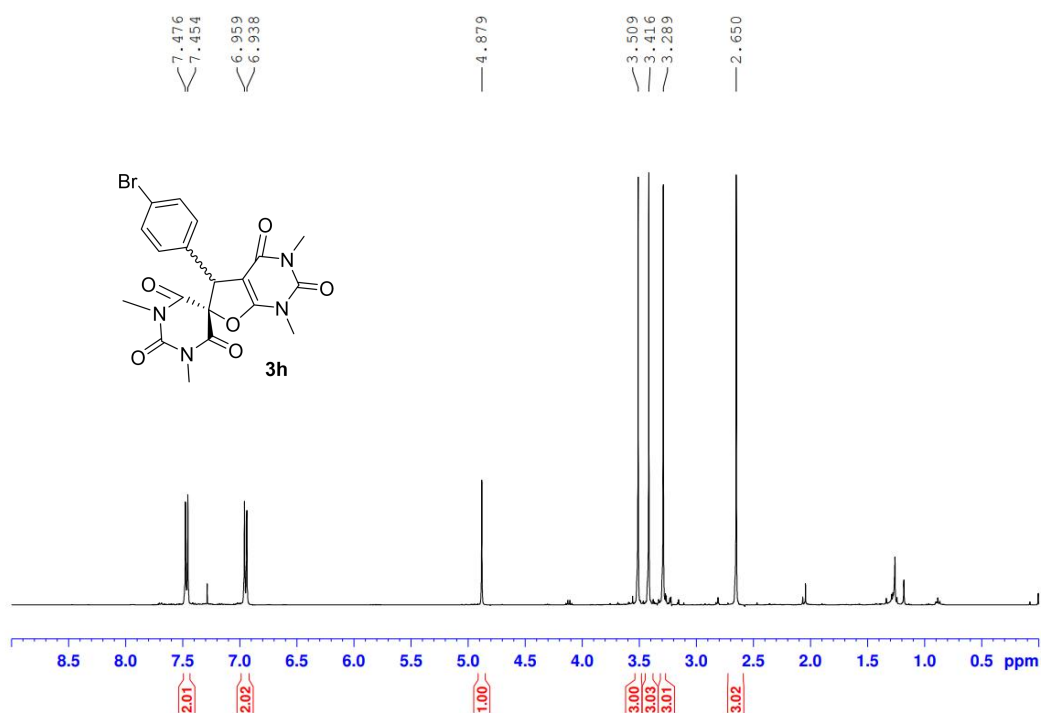


**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3g**

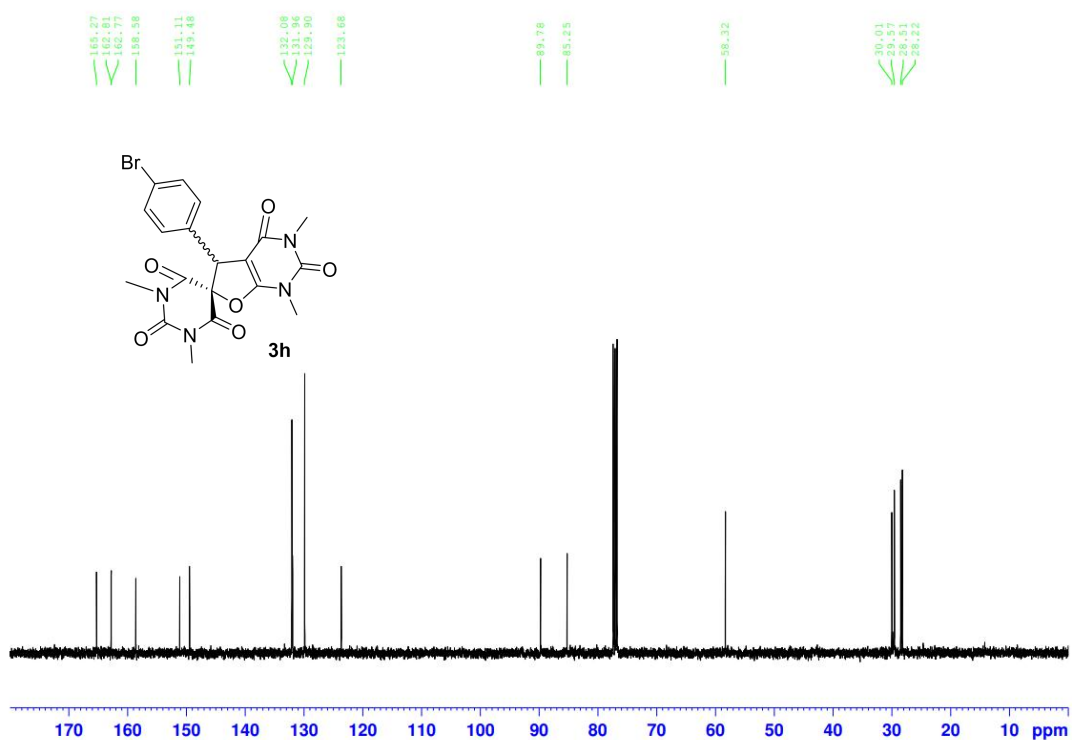




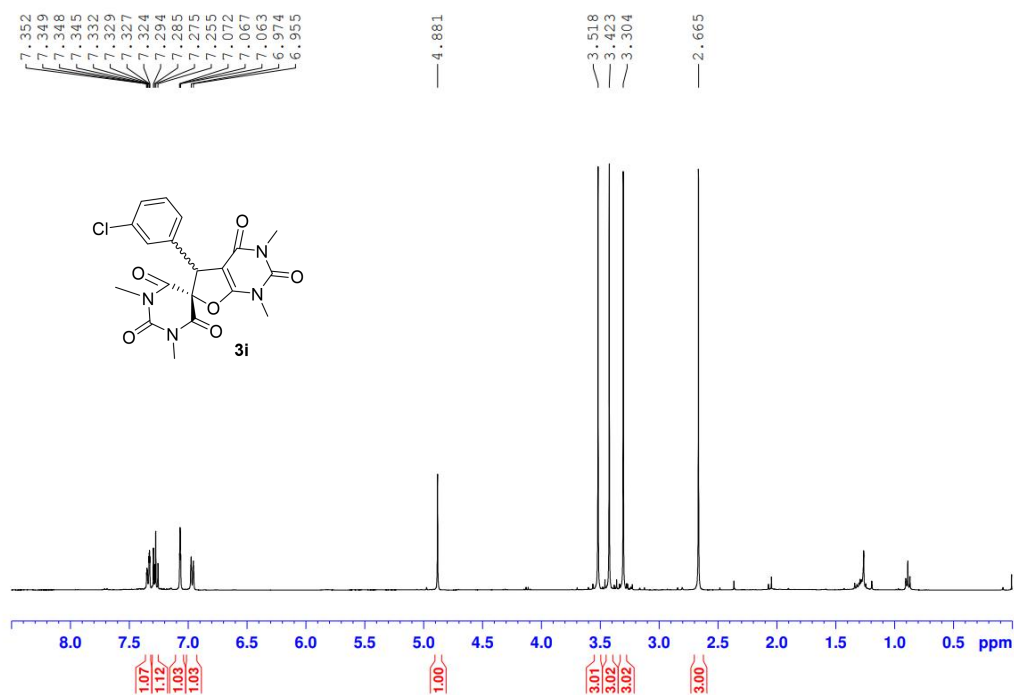
**5-(4-bromophenyl)-1,1',3,3'-tetramethyl-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3h):**  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3h



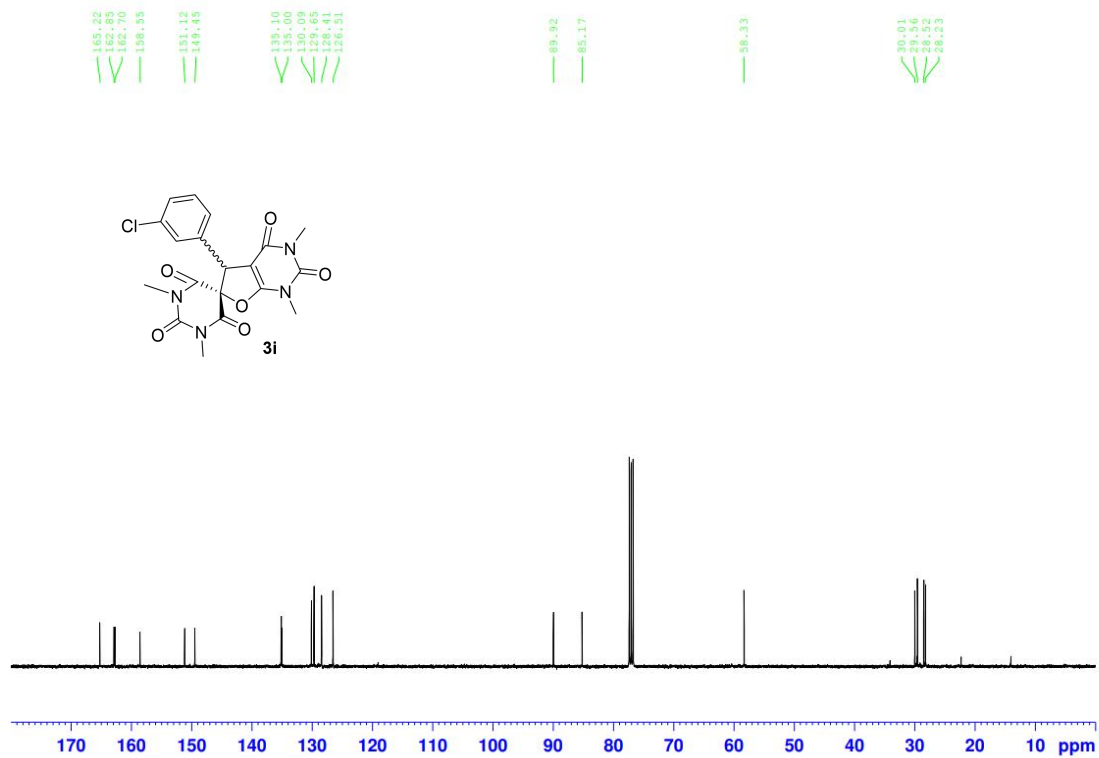
<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3h



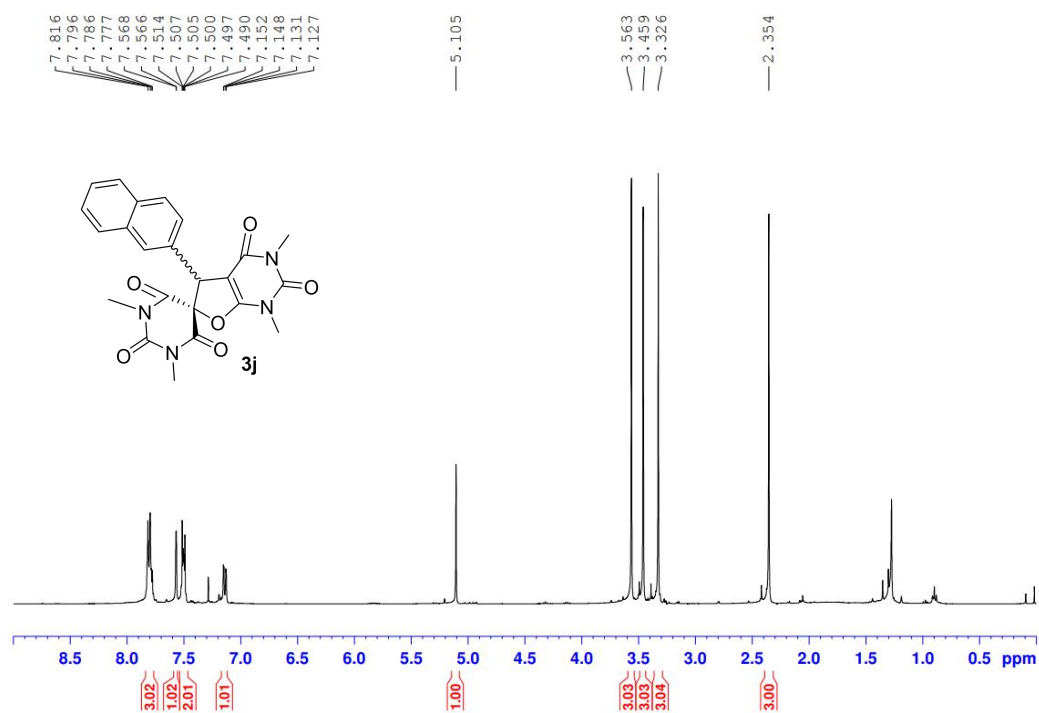
**5-(3-chlorophenyl)-1,1',3,3'-tetramethyl-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyr  
imidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone (3i):**  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3i



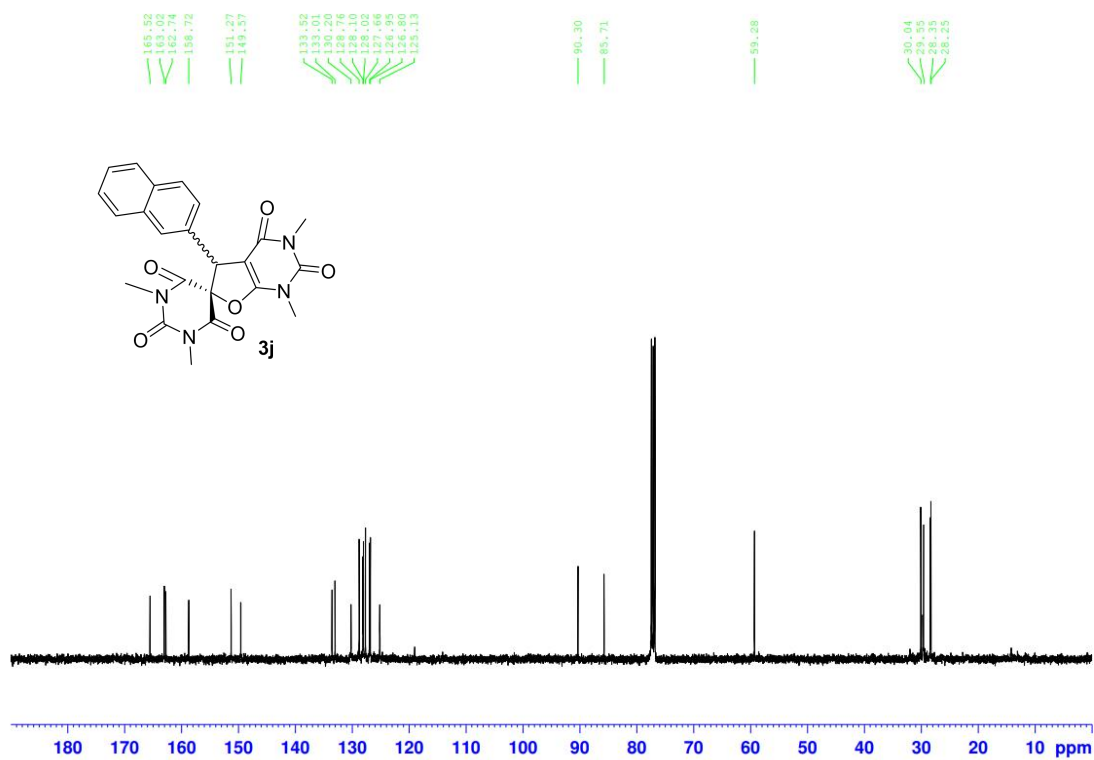
<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3i



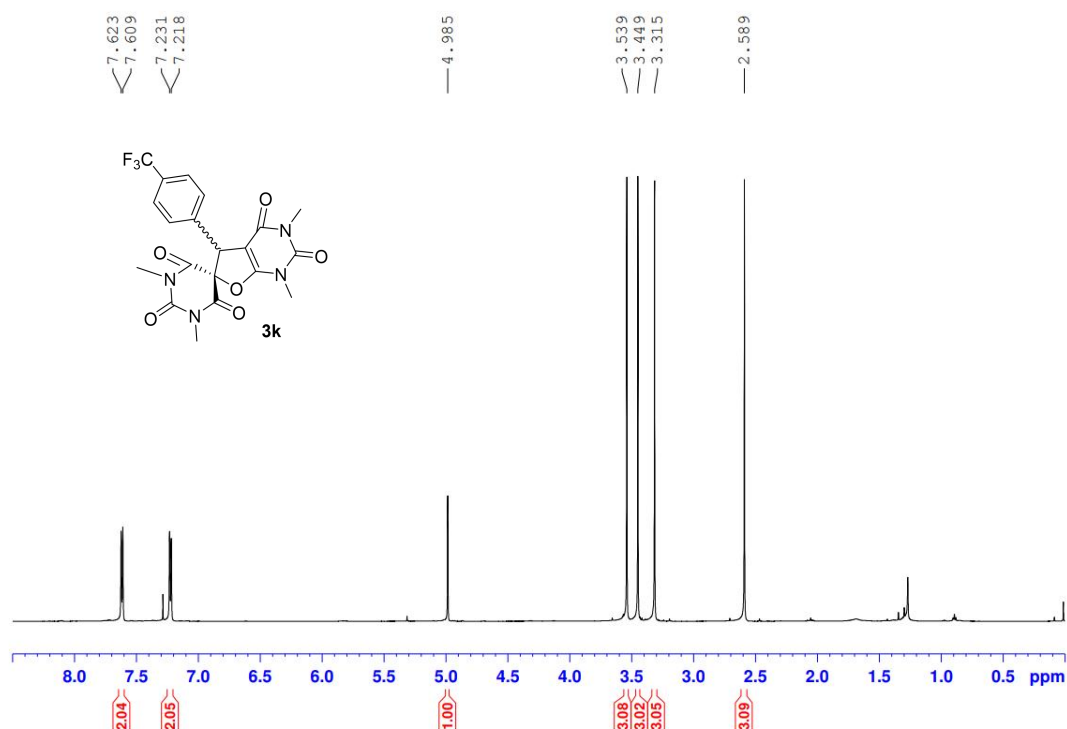
**1,1',3,3'-tetramethyl-5-(4-(naphthalen-2-yl)phenyl)-1,5-dihydro-2H,2'H-spiro[fur  
o[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3j):**  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3j



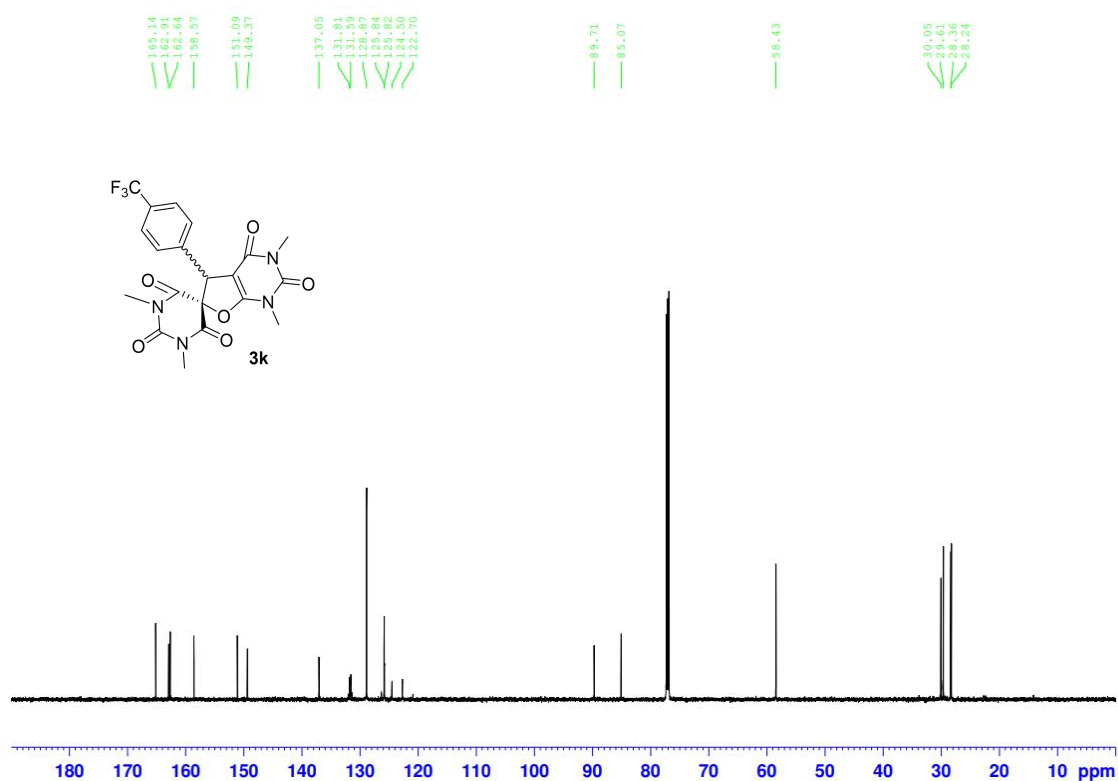
**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3j**



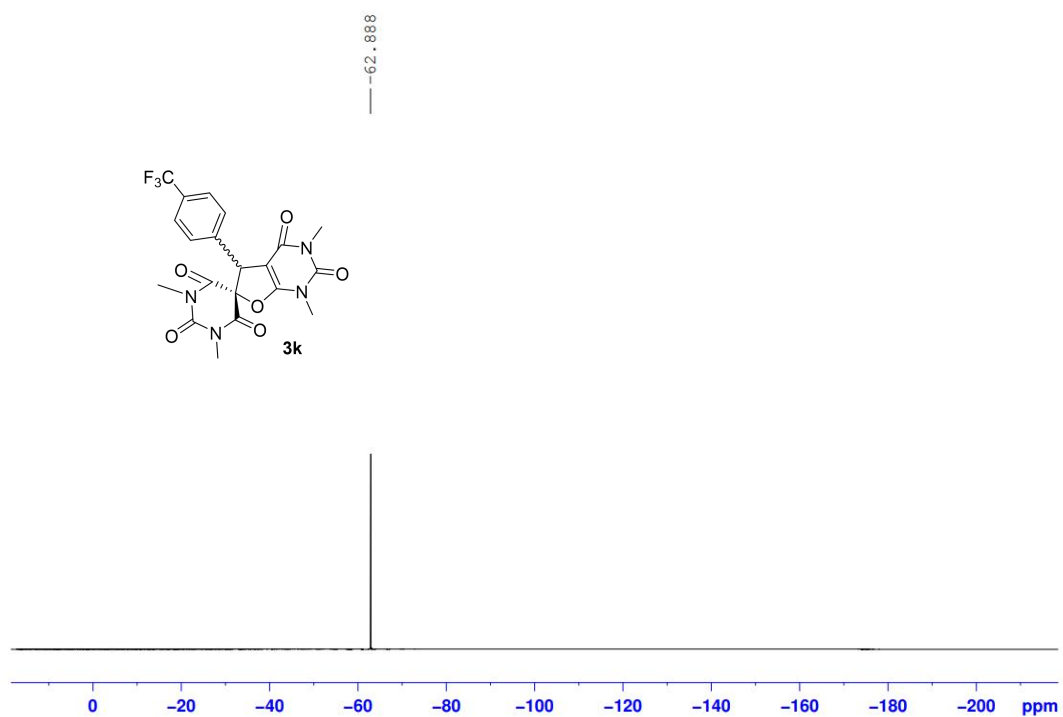
**1,1',3,3'-tetramethyl-5-(4-(trifluoromethyl)phenyl)-1,5-dihydro-2H,2'H-spiro[fur  
o[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3k):**  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3k



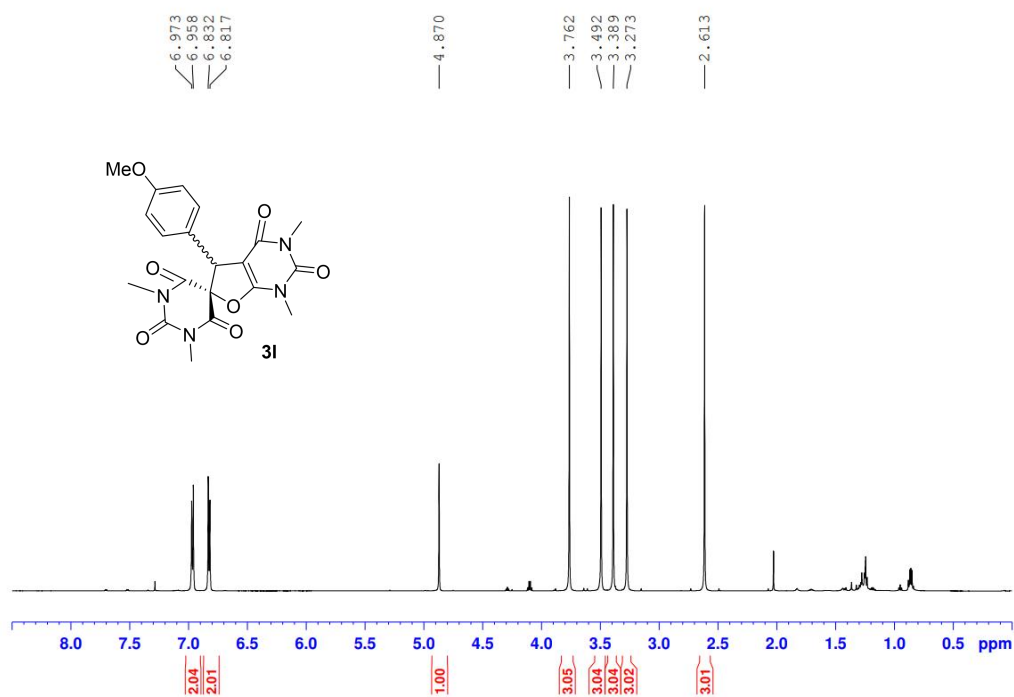
**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3k**



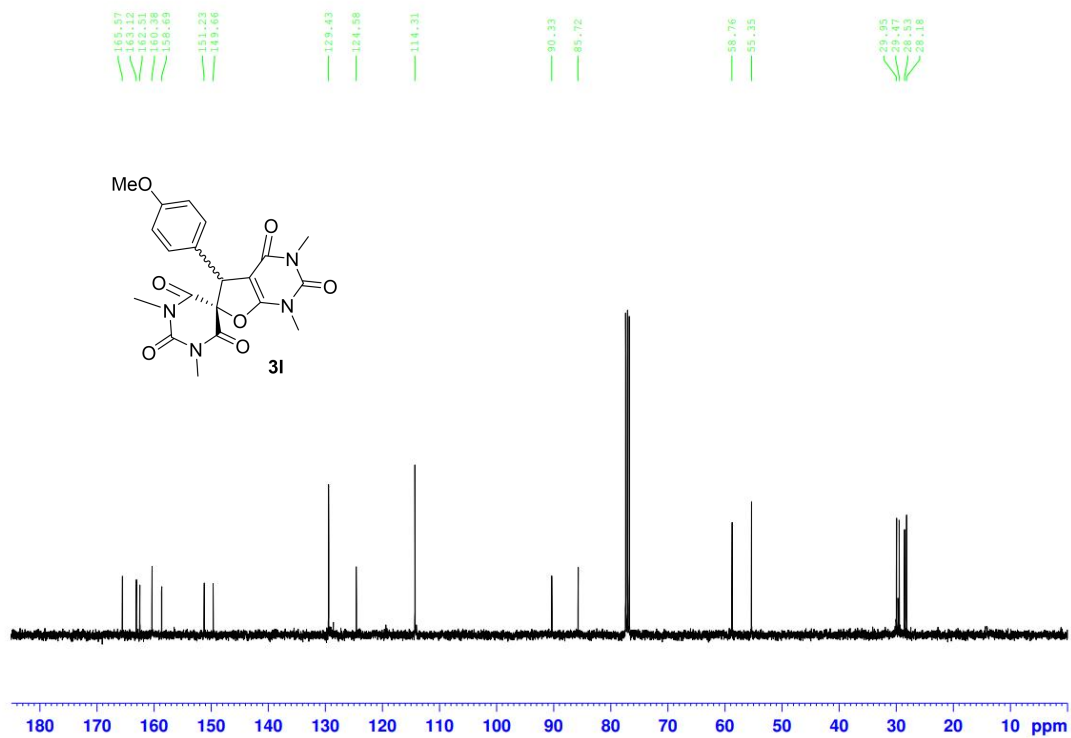
**$^{19}\text{F}$  NMR (376MHz,  $\text{CDCl}_3$ ) of 3k**



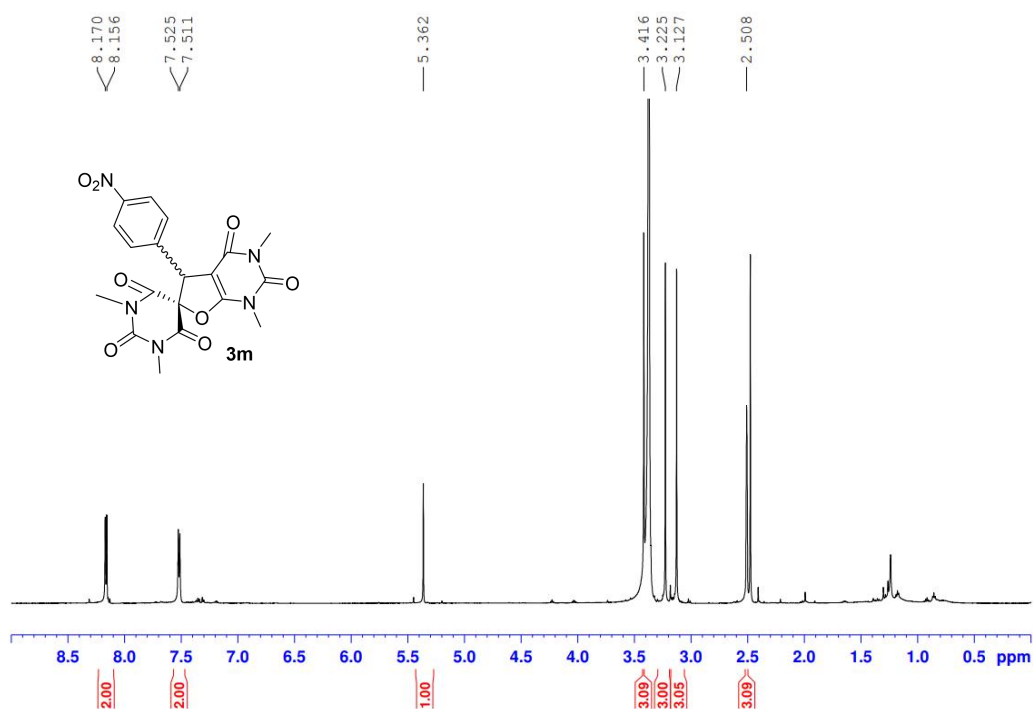
**5-(4-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3I):**  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3I



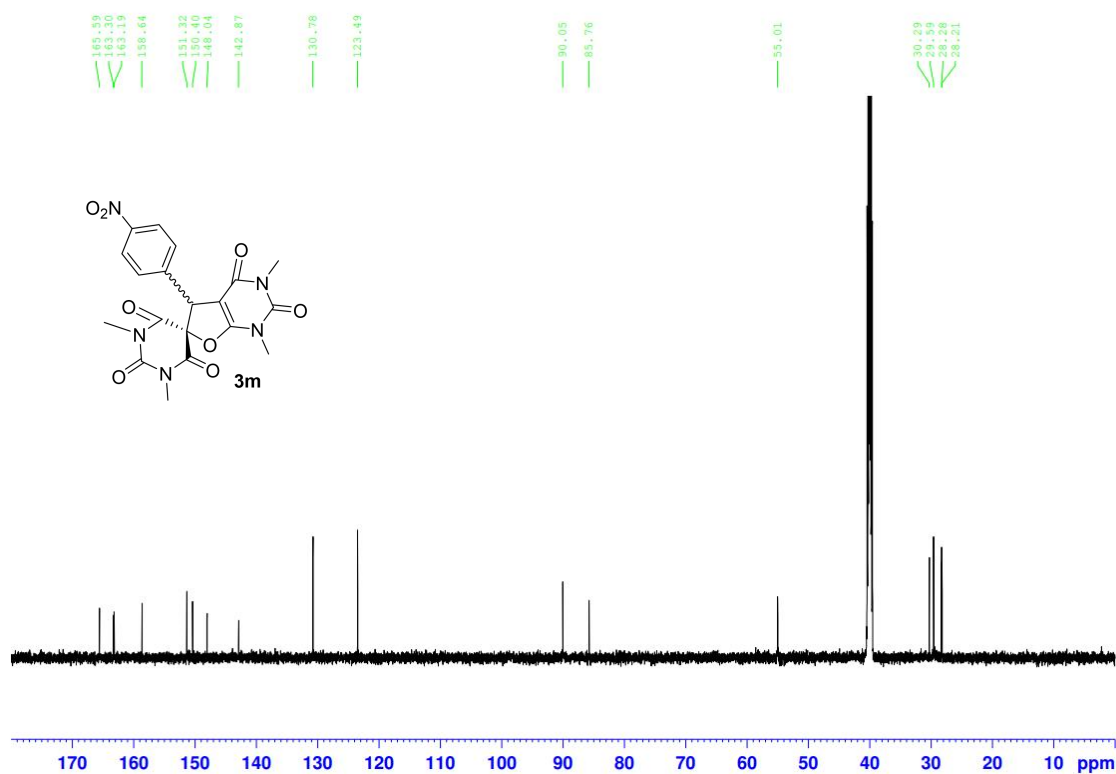
**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3I**



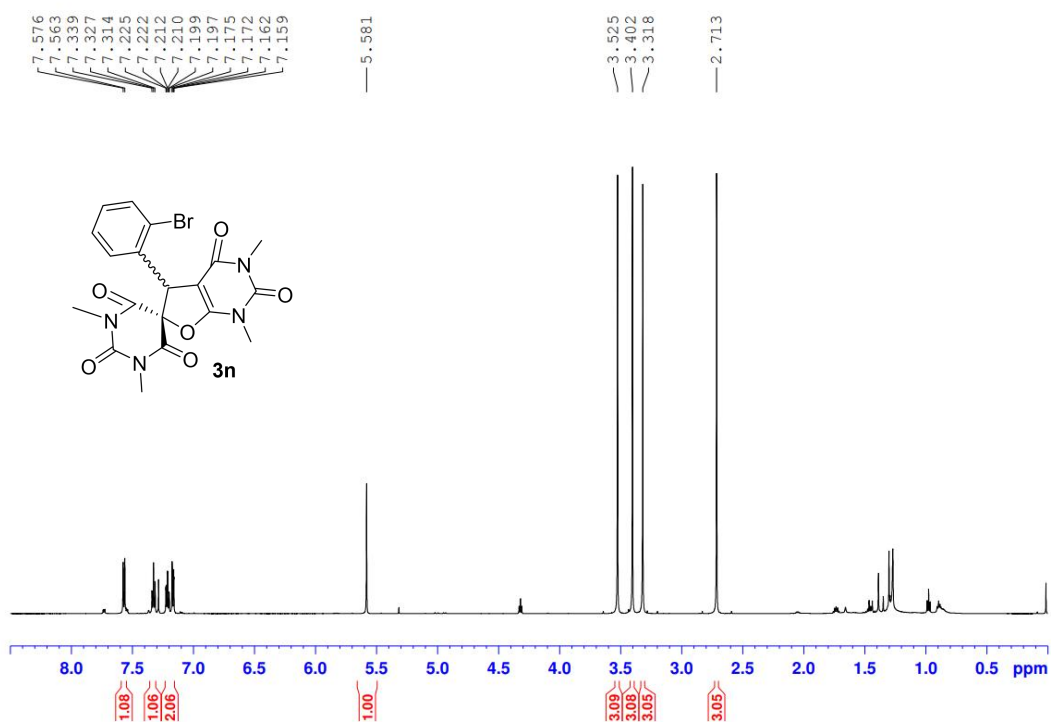
**1,1',3,3'-tetramethyl-5-(4-nitrophenyl)-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3m):**  
**<sup>1</sup>H NMR (400MHz,DMSO) of 3m**



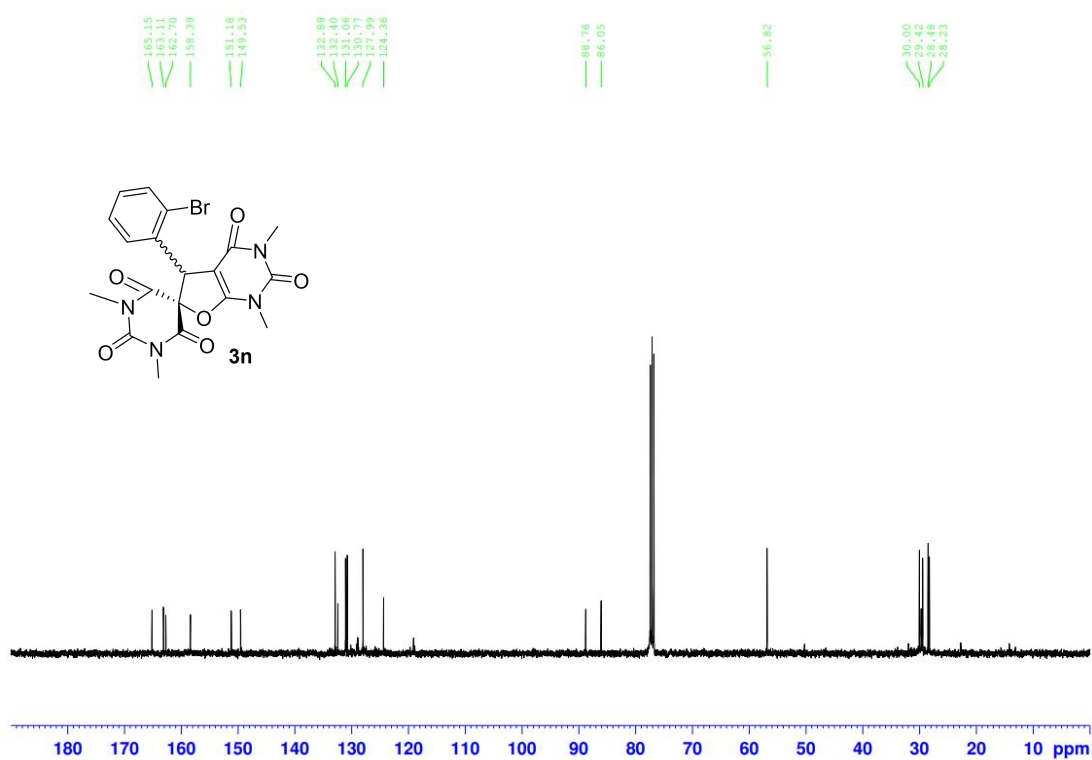
**<sup>13</sup>C NMR (100MHz,DMSO) of 3m**



**5-(2-bromophenyl)-1,1',3,3'-tetramethyl-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3n):**  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3n

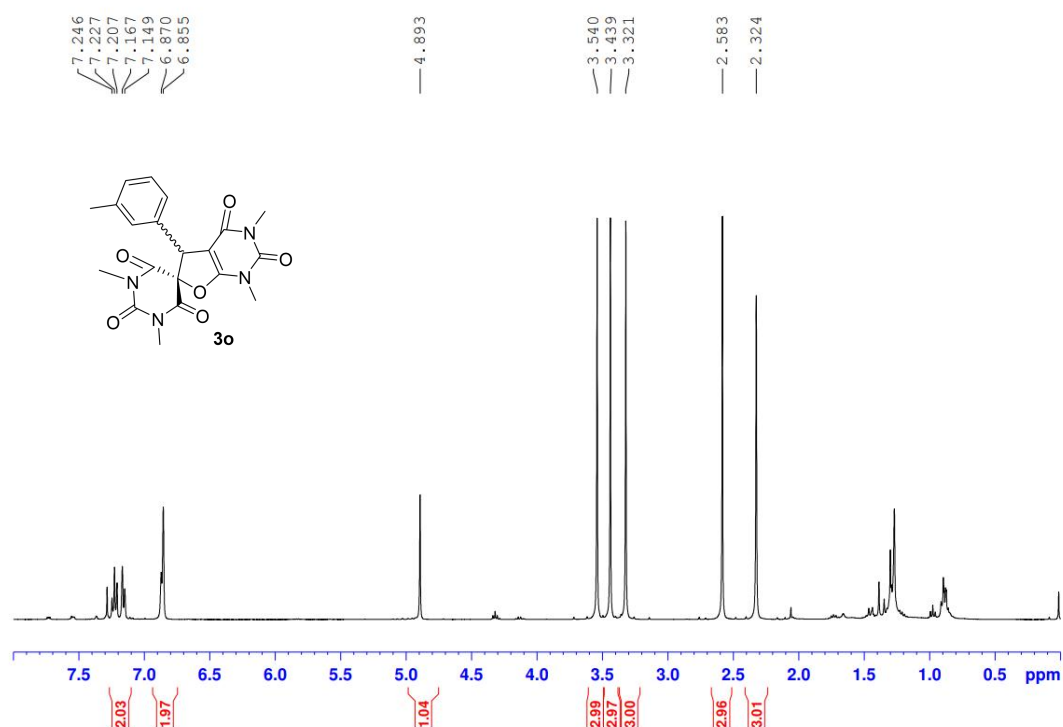


<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3n

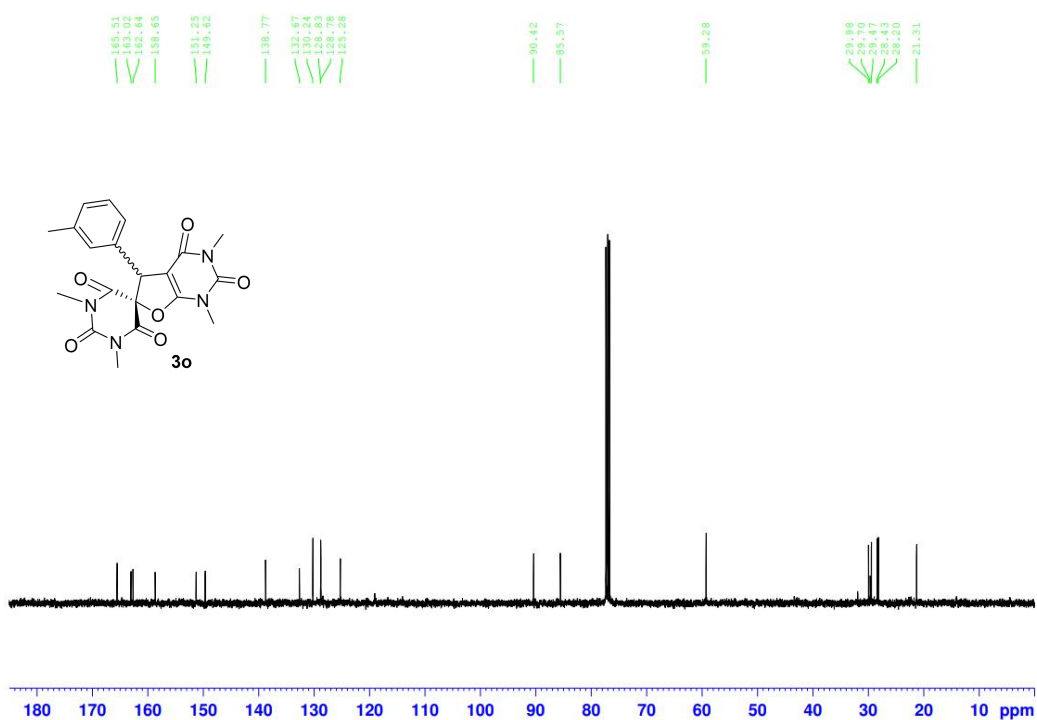




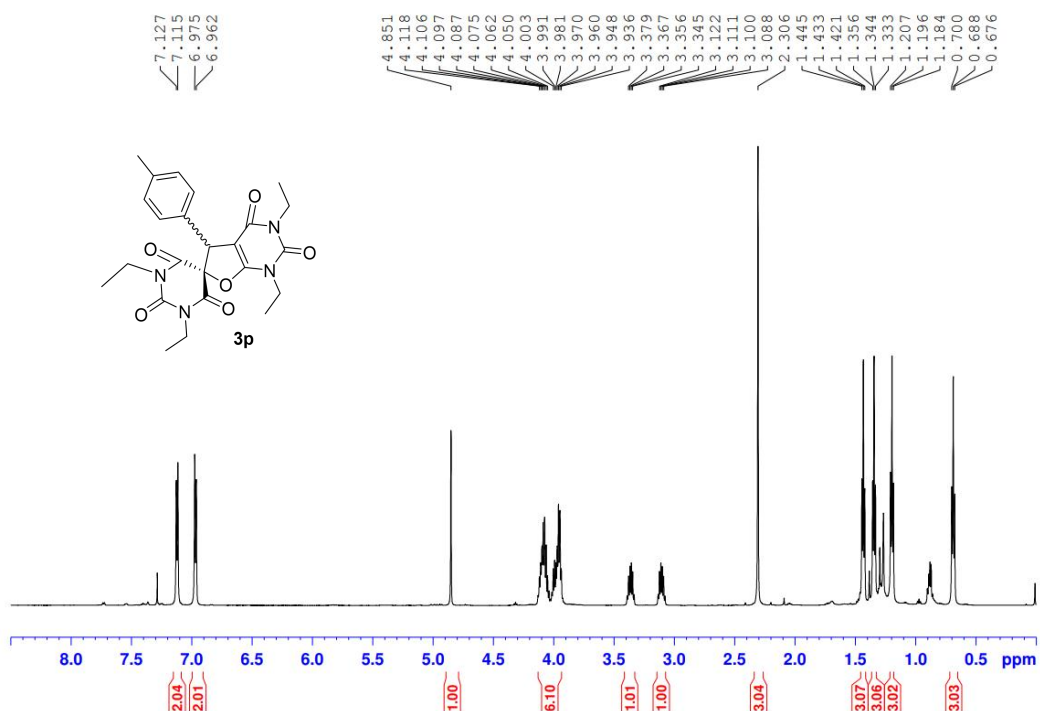
**1,1',3,3'-tetramethyl-5-(m-tolyl)-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone (3o):**  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3o



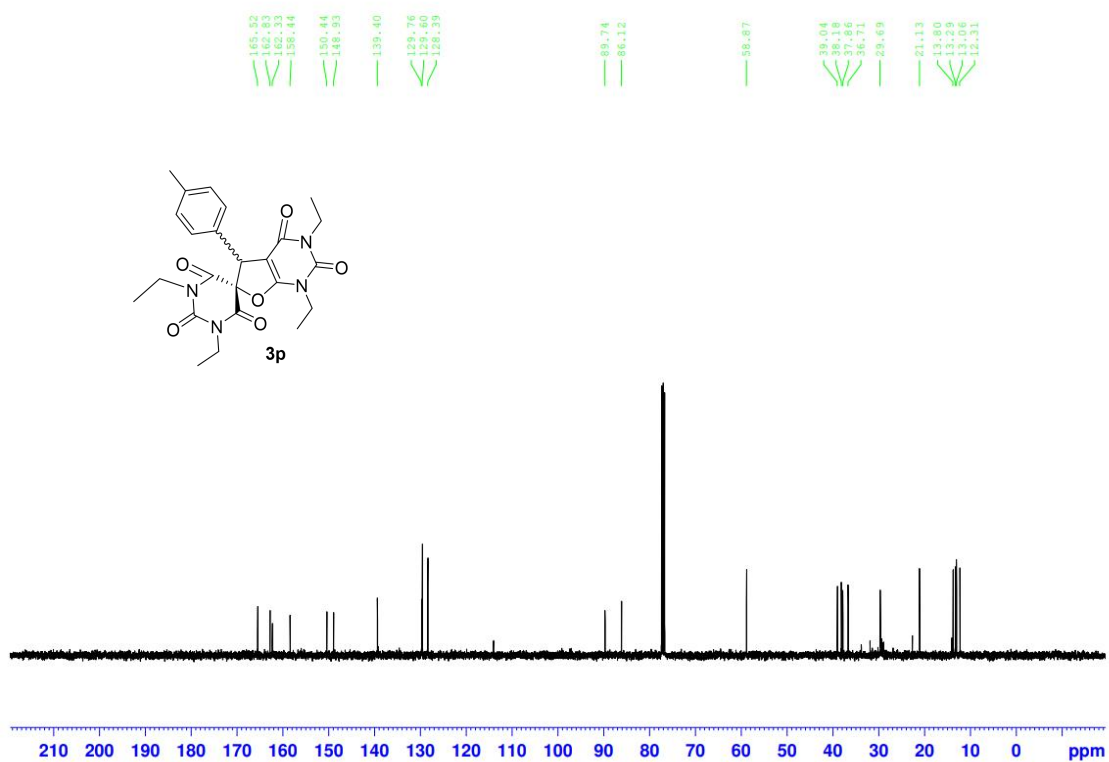
**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3o**



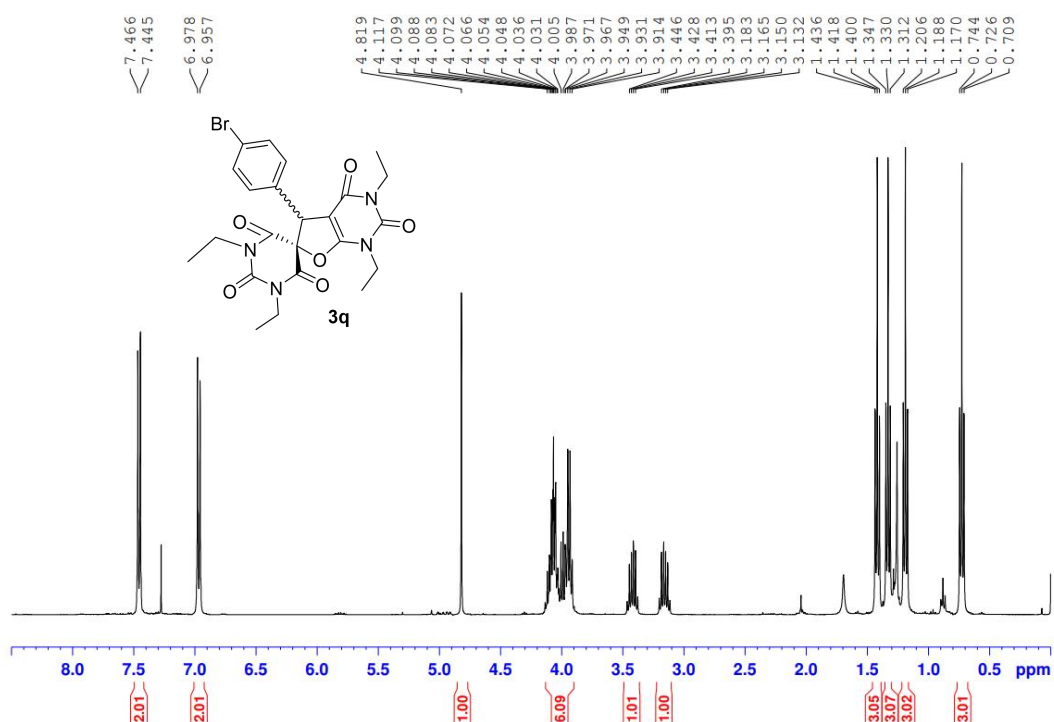
**1,1',3,3'-tetraethyl-5-(p-tolyl)-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone (3p):**  
**<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3p**



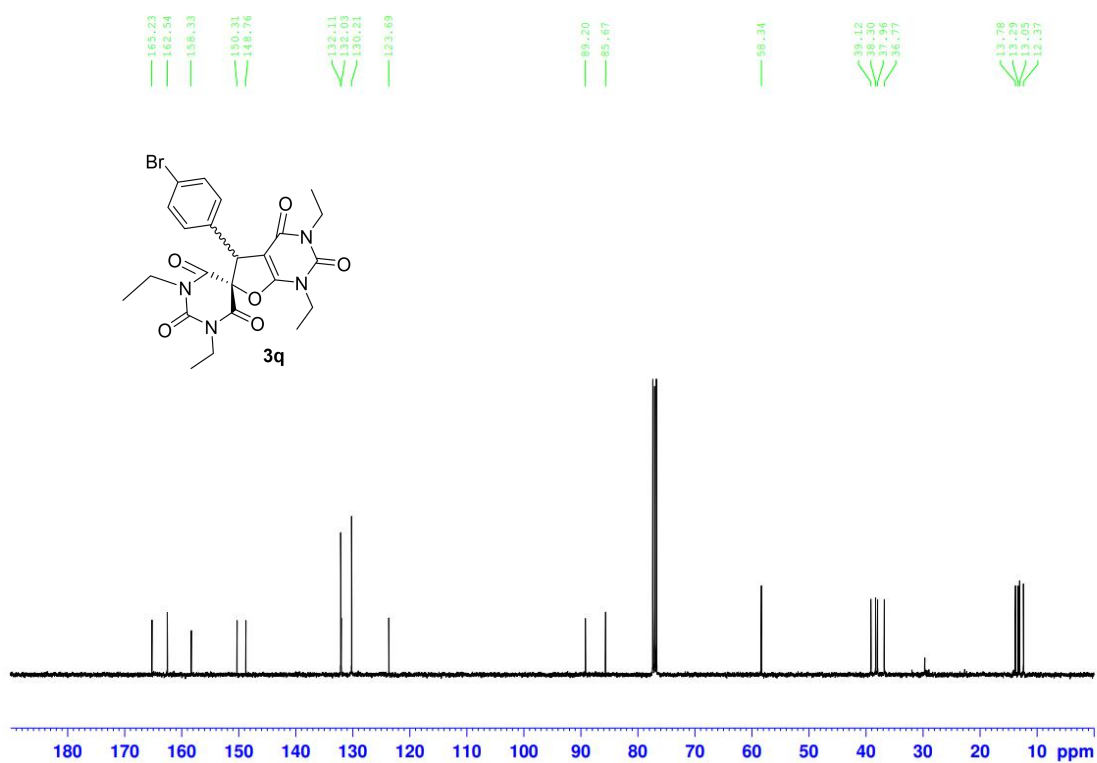
**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3p**



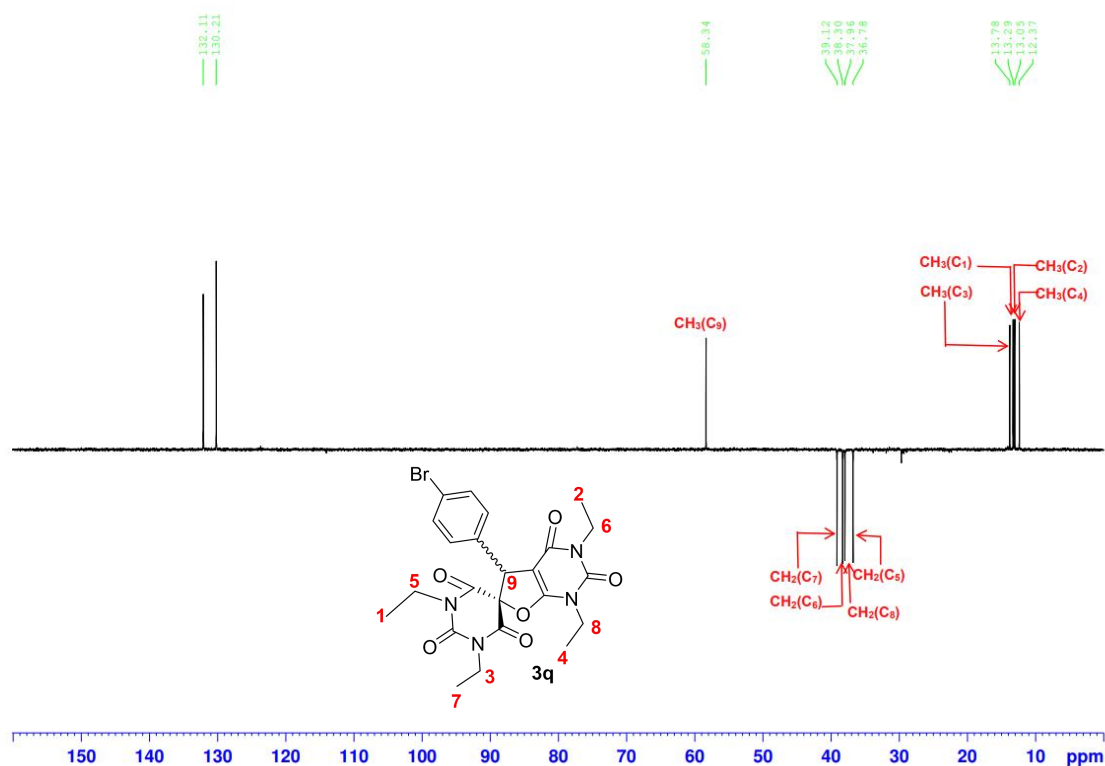
**5-(4-bromophenyl)-1,1',3,3'-tetraethyl-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3q):**  
**<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3q**



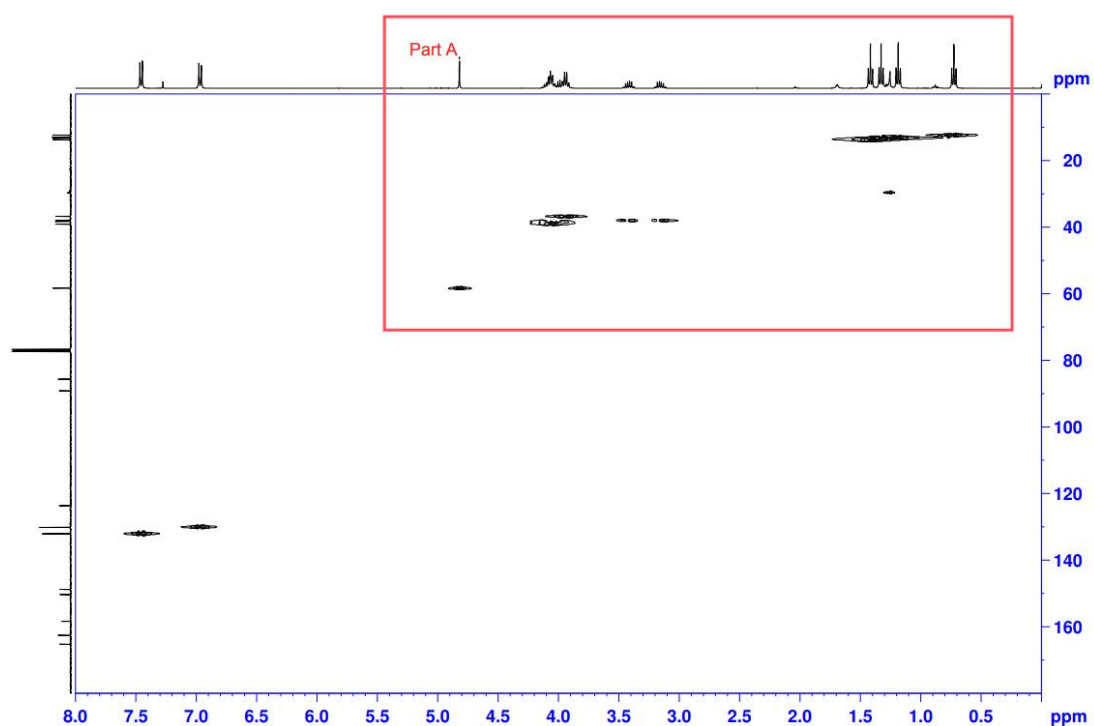
**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3q**



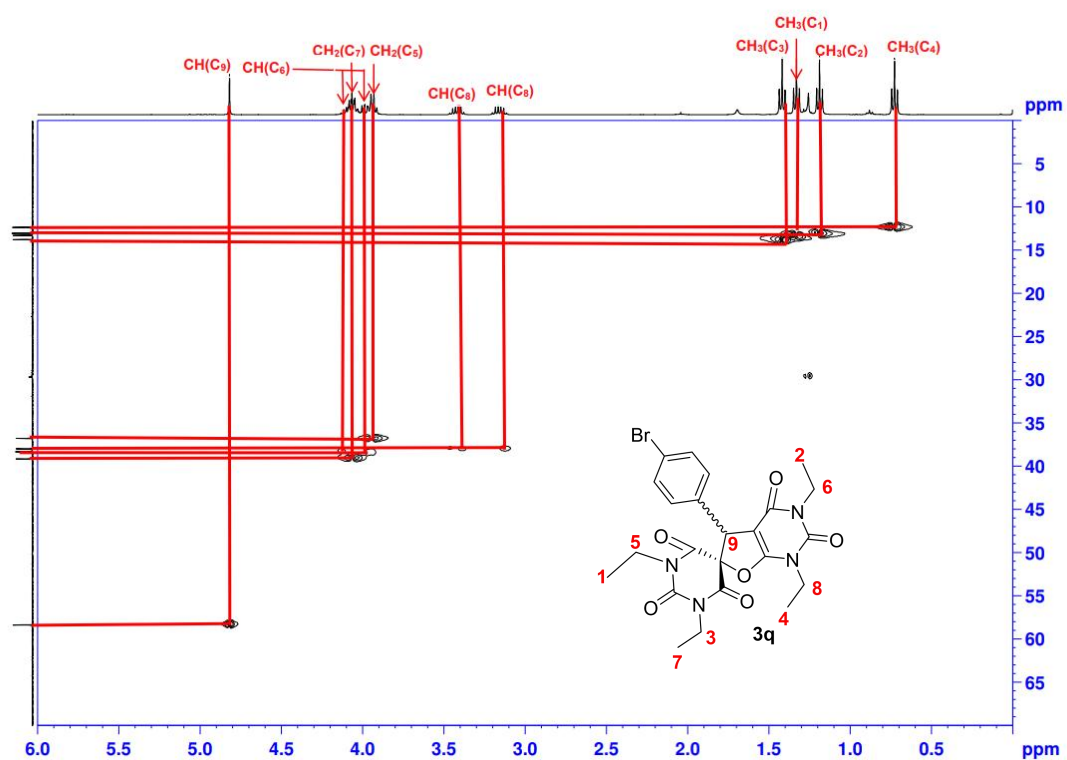
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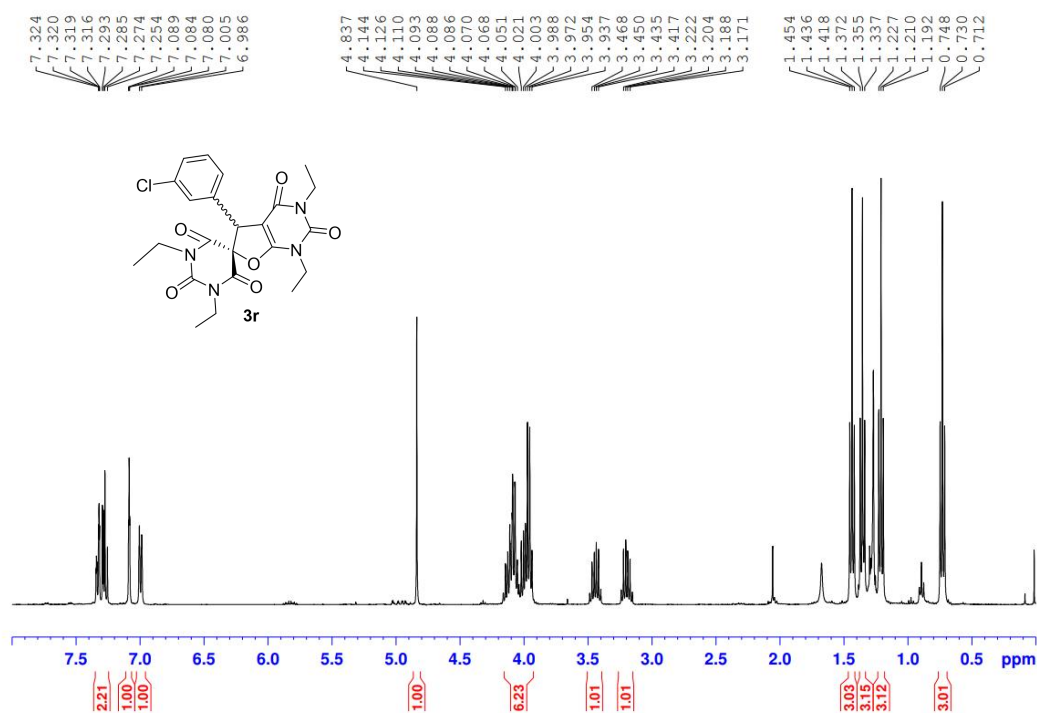
## HSQC of 3q



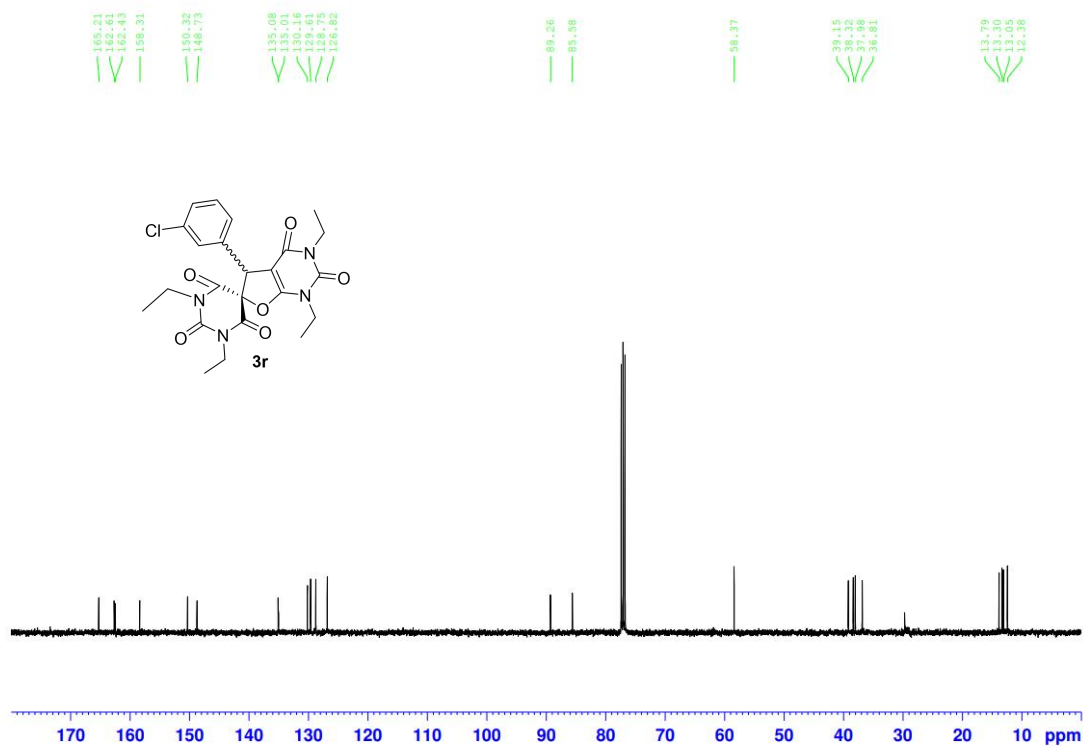
## HSQC of Part A



**5-(3-chlorophenyl)-1,1',3,3'-tetraethyl-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3r):**  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3r

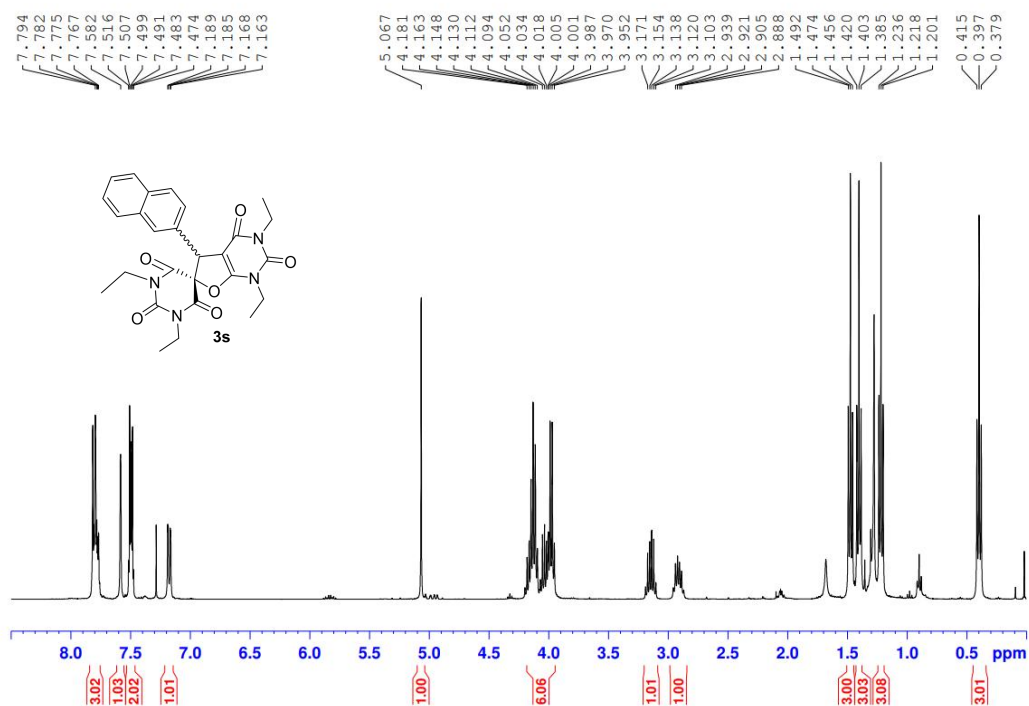


**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3r**

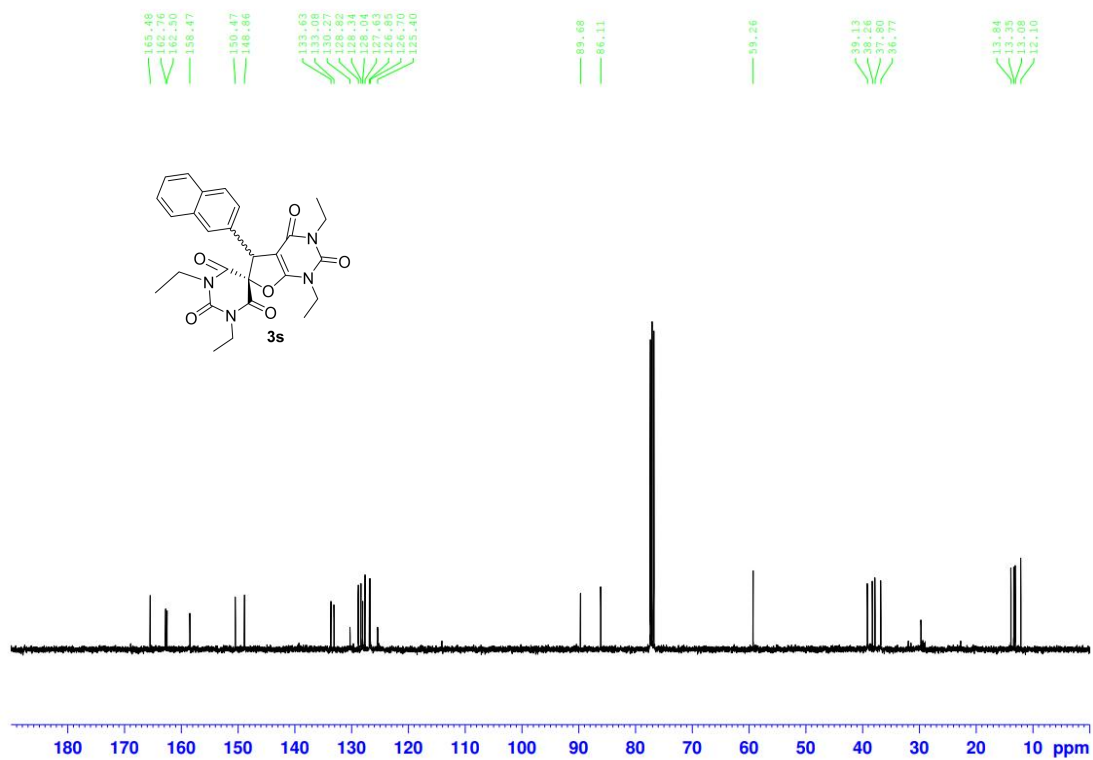


**1,1',3,3'-tetraethyl-5-(4-(naphthalen-2-yl)phenyl)-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone (3s):**

**<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3s**

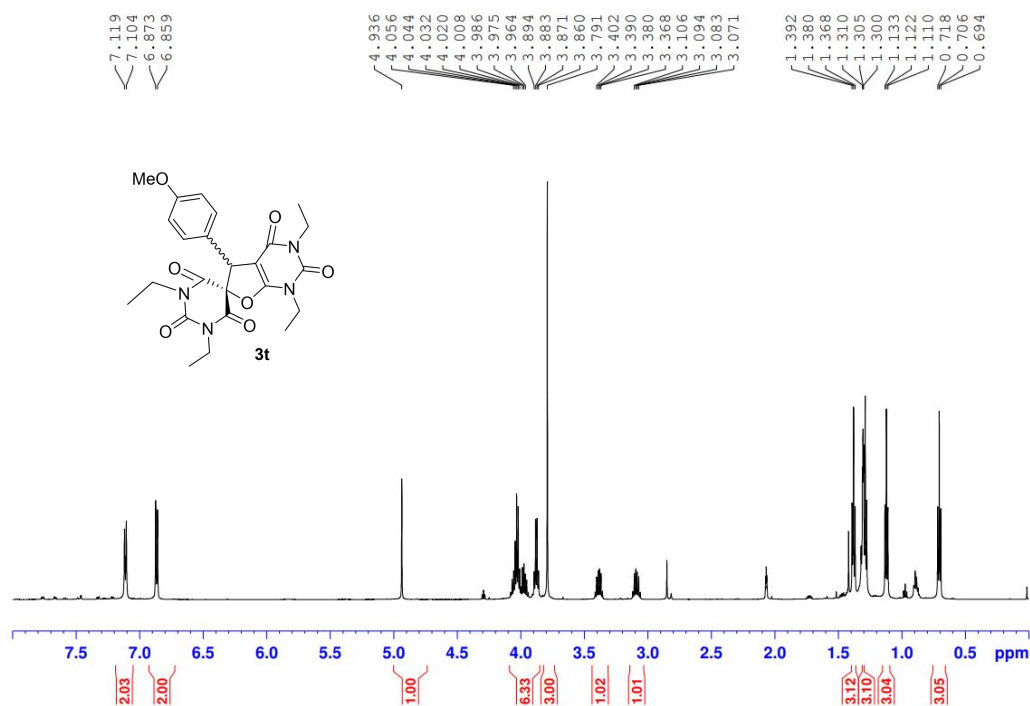


**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3s**

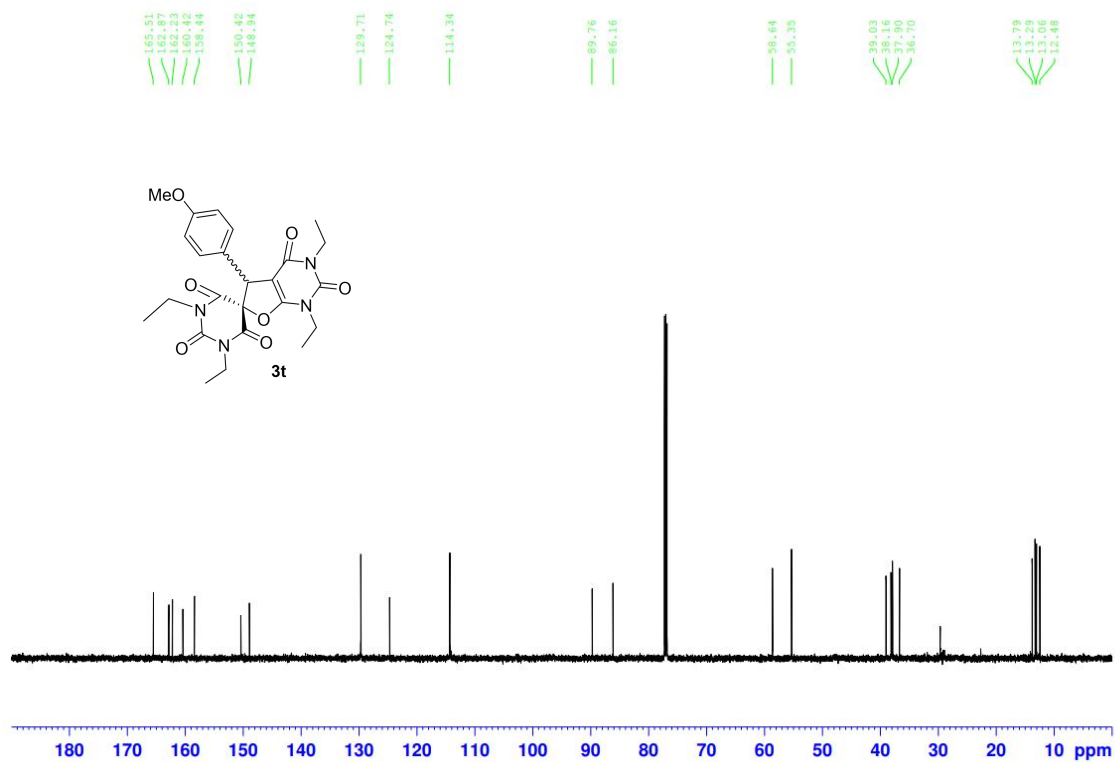


**1,1',3,3'-tetraethyl-5-(4-methoxyphenyl)-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3t):**

**<sup>1</sup>H NMR (400MHz,(CD<sub>3</sub>)<sub>2</sub>CO) of 3t**

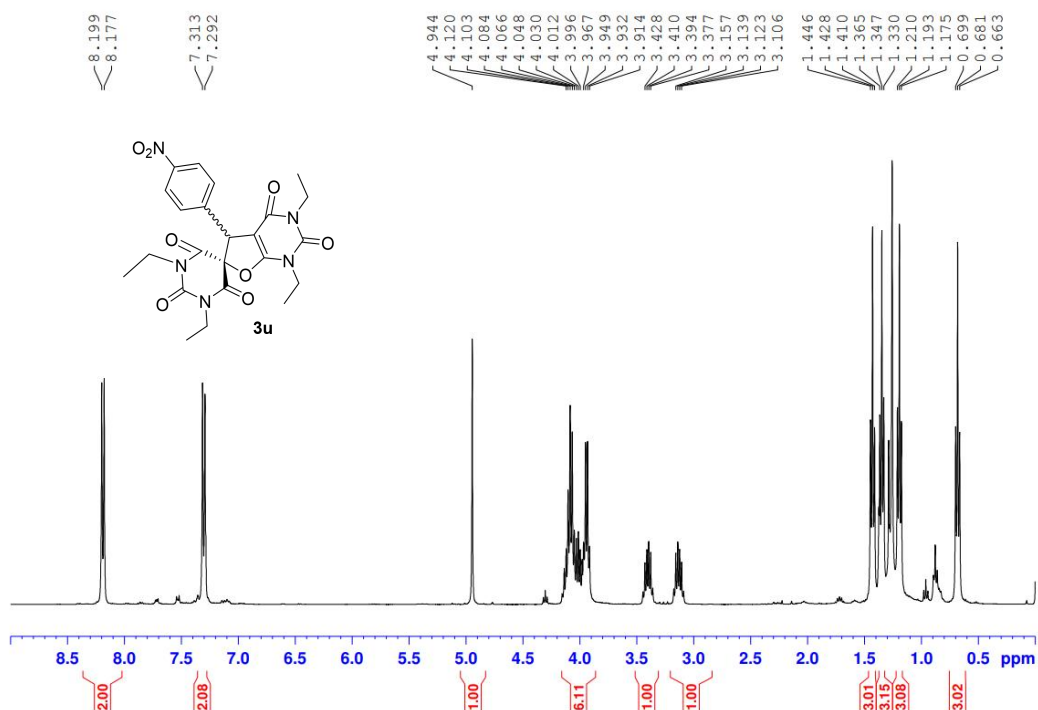


**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3t**

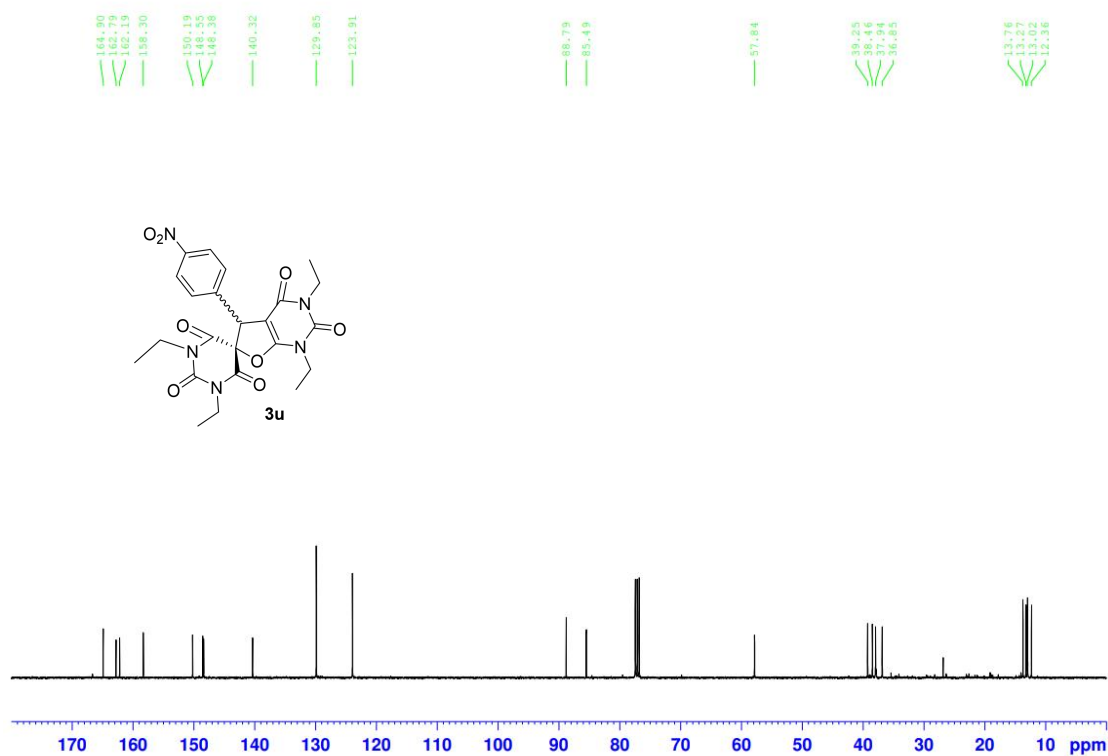




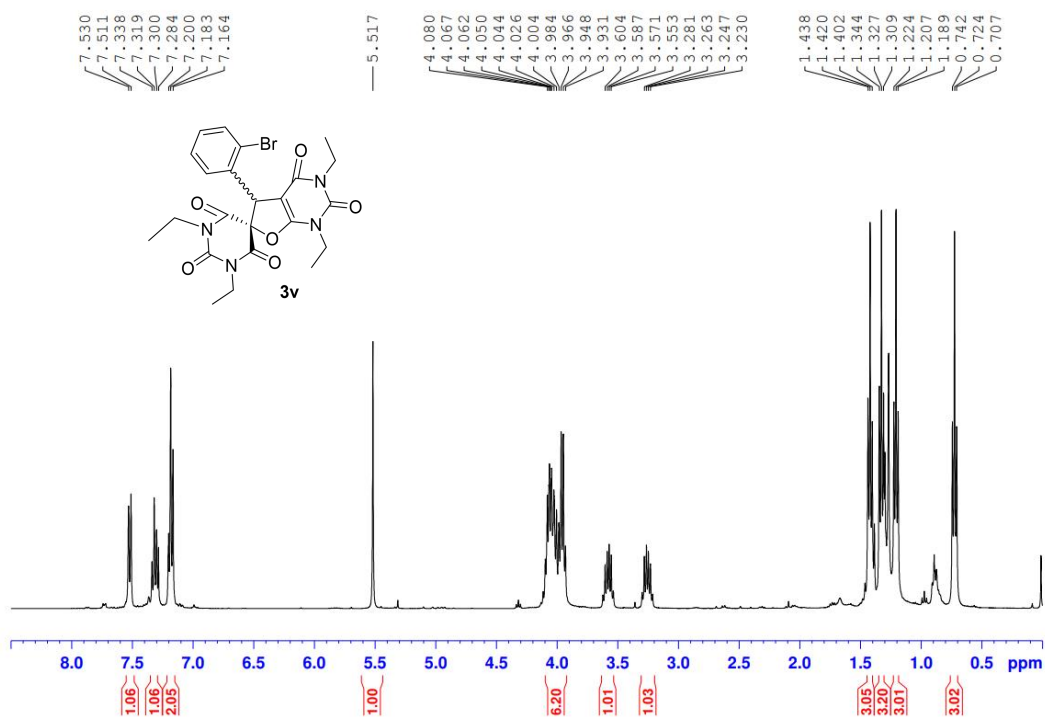
**1,1',3,3'-tetraethyl-5-(4-nitrophenyl)-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone(3u):**  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3u



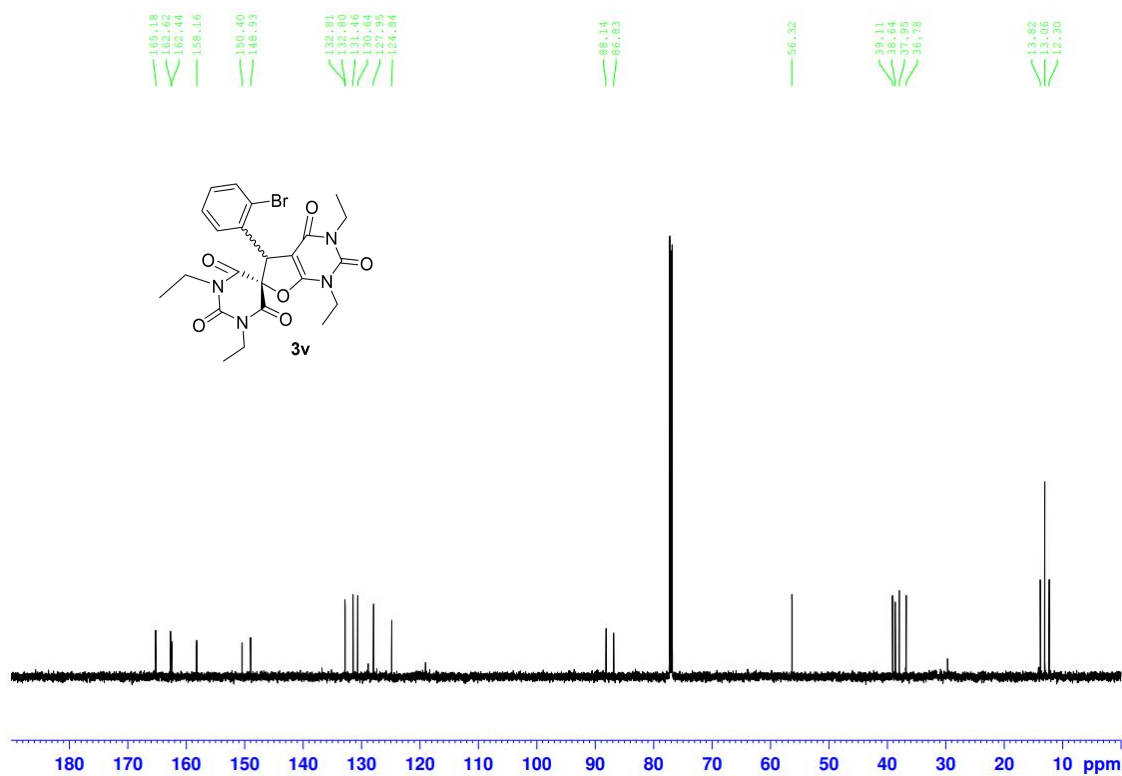
**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3u**



**5-(2-bromophenyl)-1,1',3,3'-tetraethyl-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone (3v):**  
<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3v

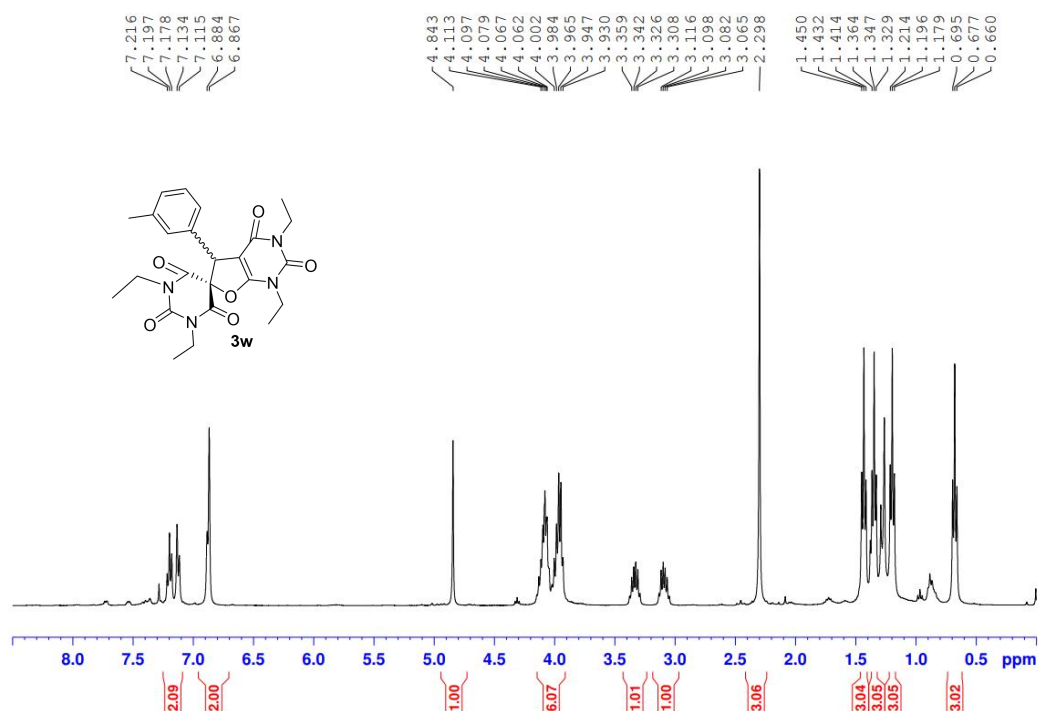


**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3v**

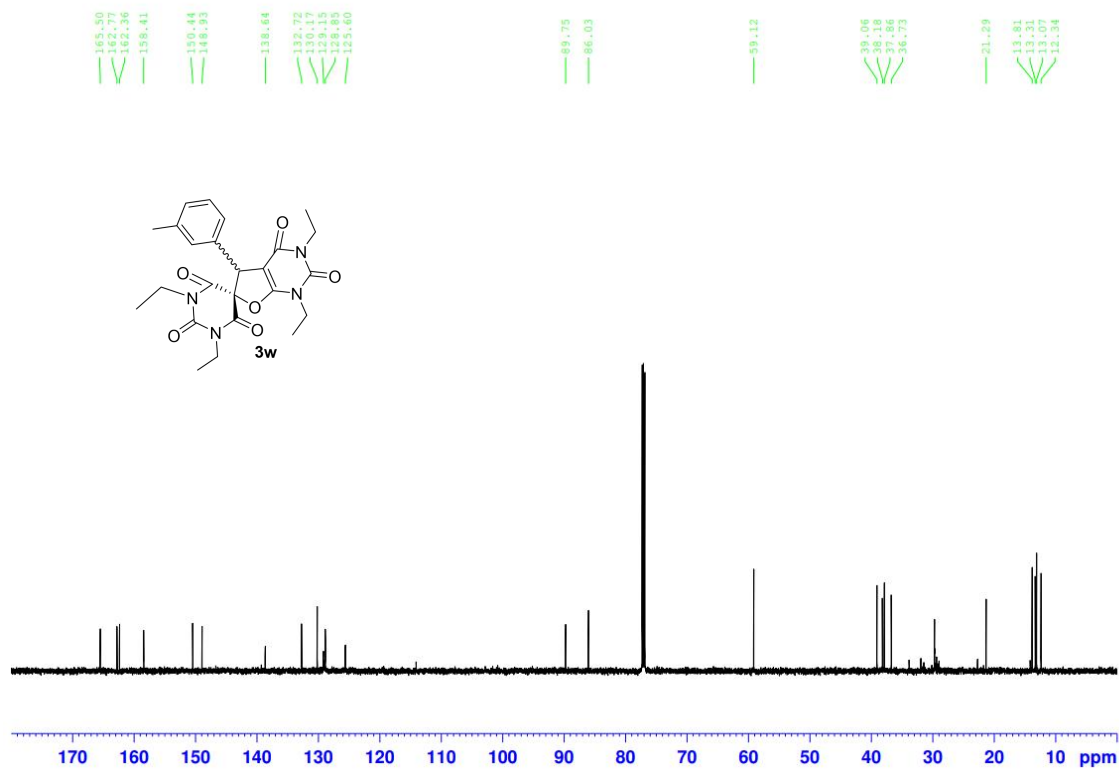


**1,1',3,3'-tetraethyl-5-(m-tolyl)-1,5-dihydro-2H,2'H-spiro[furo[2,3-d]pyrimidine-6,5'-pyrimidine]-2,2',4,4',6,6'(1'H,3H,3'H)-pentaone (3w):**

**<sup>1</sup>H NMR (400MHz,CDCl<sub>3</sub>) of 3w**

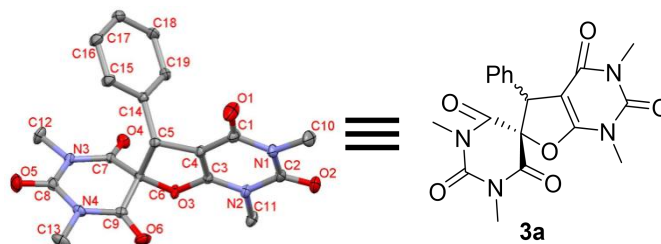


**<sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>) of 3w**



## 2. X-Ray Crystal Data of Product 3a

Single crystal of **3a** was obtained from the mixed solution of CH<sub>2</sub>Cl<sub>2</sub> and petroleum ether via slow evaporation in a sample bottle. A suitable crystal was selected and its X-ray intensity data were measured at Rigaku-mm007 diffractometer with Mo K $\alpha$  radiation. The crystal structure was solved by using the crysalispro and olex2 structure solution programs.



**Figure S1.** X-ray single crystal structure of **3a** (with thermal ellipsoids shown at the 50% probability level)

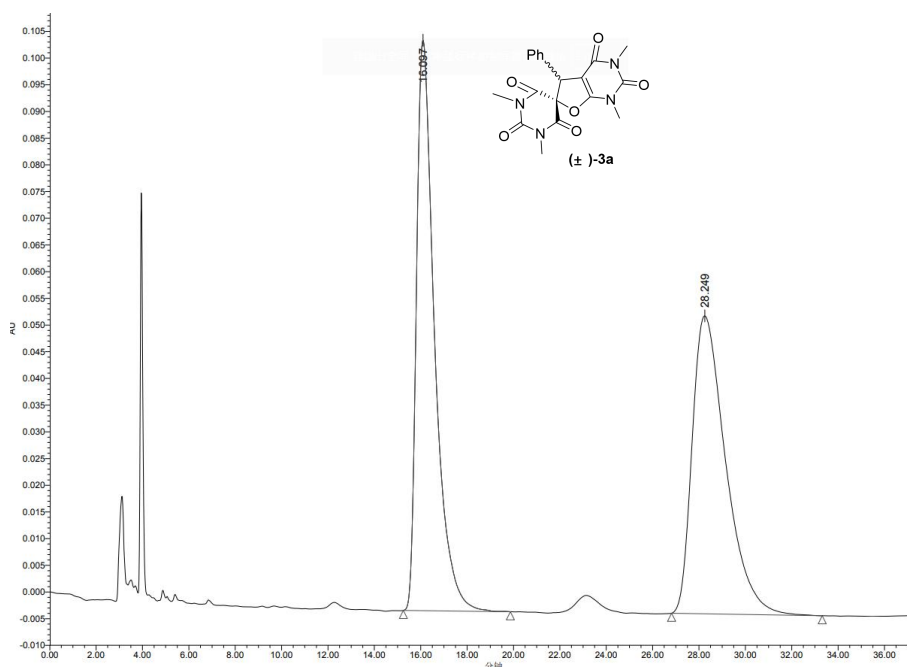
**Table S1.** Crystal data and structure refinement for **3a**.

Identification code	<b>3a</b>
Empirical formula	C <sub>19</sub> H <sub>18</sub> N <sub>4</sub> O <sub>6</sub>
Formula weight	398.37
Temperature/K	113.15
Crystal system	triclinic
Space group	P1
a/Å	5.58300(10)
b/Å	8.7281(2)
c/Å	9.9792(2)
$\alpha$ /°	112.035(2)
$\beta$ /°	93.0010 (10)
$\gamma$ /°	98.9300(10)
Volume/Å <sup>3</sup>	442.033(17)
Z	1
$\rho$ calcd/cm <sup>3</sup>	1.497
$\mu$ /mm <sup>-1</sup>	0.114
F(000)	208.0
Crystal size/mm <sup>3</sup>	0.29 × 0.25 × 0.2
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	5.128 to 69.374

Index ranges	$-8 \leq h \leq 6, -13 \leq k \leq 13, -15 \leq l \leq 15$
Reflections collected	11342
Independent reflections	5697 [ $R_{\text{int}} = 0.0257, R_{\text{sigma}} = 0.0335$ ]
Data/restraints/parameters	5697/3/266
Goodness-of-fit on $F^2$	1.037
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R1 = 0.0430, wR2 = 0.1105$
Final R indexes [all data]	$R1 = 0.0456, wR2 = 0.1134$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.38/-0.24
Flack parameter	0.7(3)

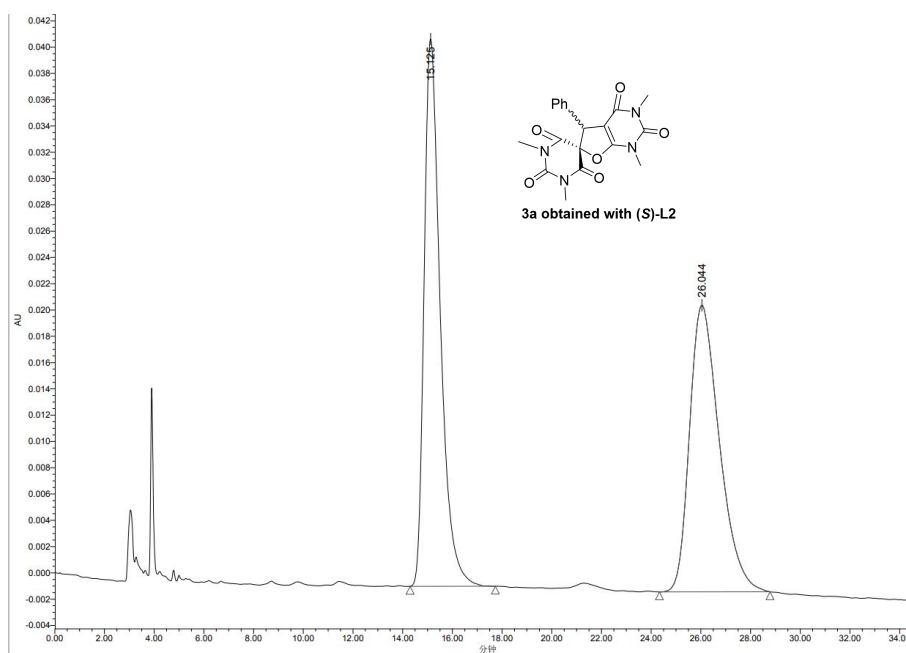
### 3. Copies of HPLC Spectra of Products 3a

HPLC separation: Chiralcel OD-H, solvent: hexane/ethanol=80/20, flow rate=1.0 mL/min,  $\lambda$ =254 nm.



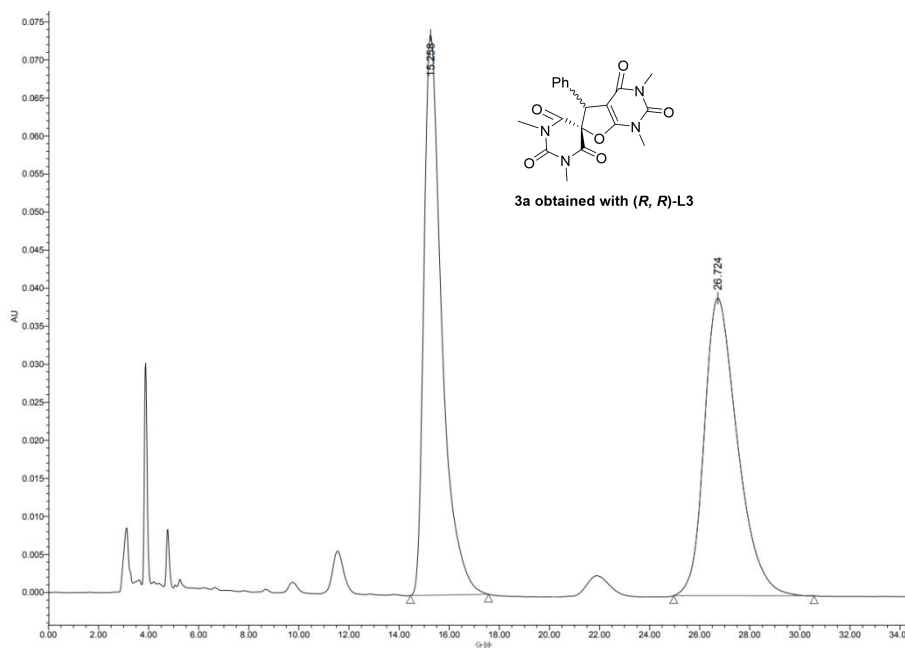
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	16.097	5783726	50.84	106869
2	28.249	5593542	49.16	55795



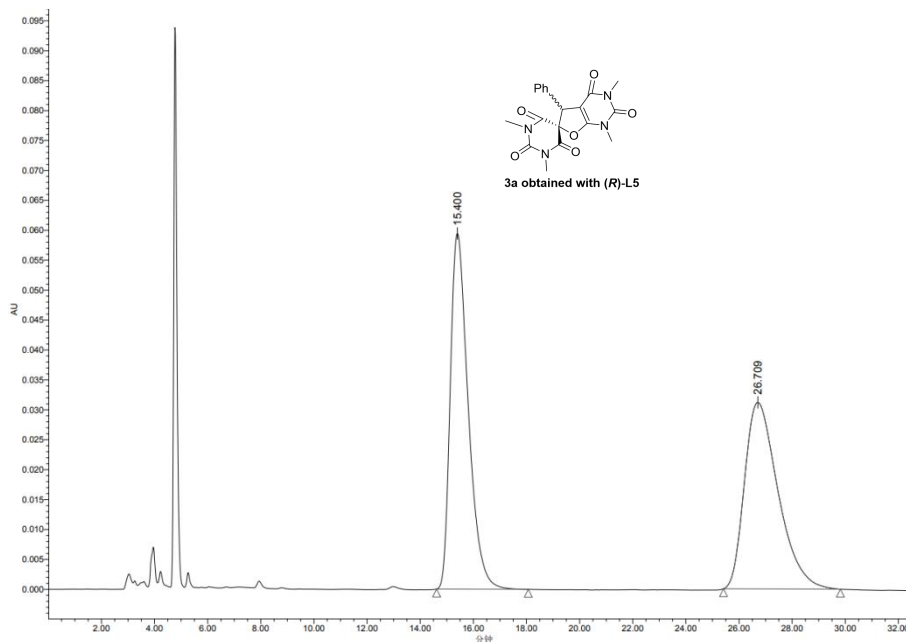
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	15.125	1880625	50.85	41659
2	26.044	1817752	49.15	21810



<Column Performance Report>

entry	R.T	Area	%Area	Height
1	15.258	3675491	50.55	73621
2	26.724	3595180	49.45	39107

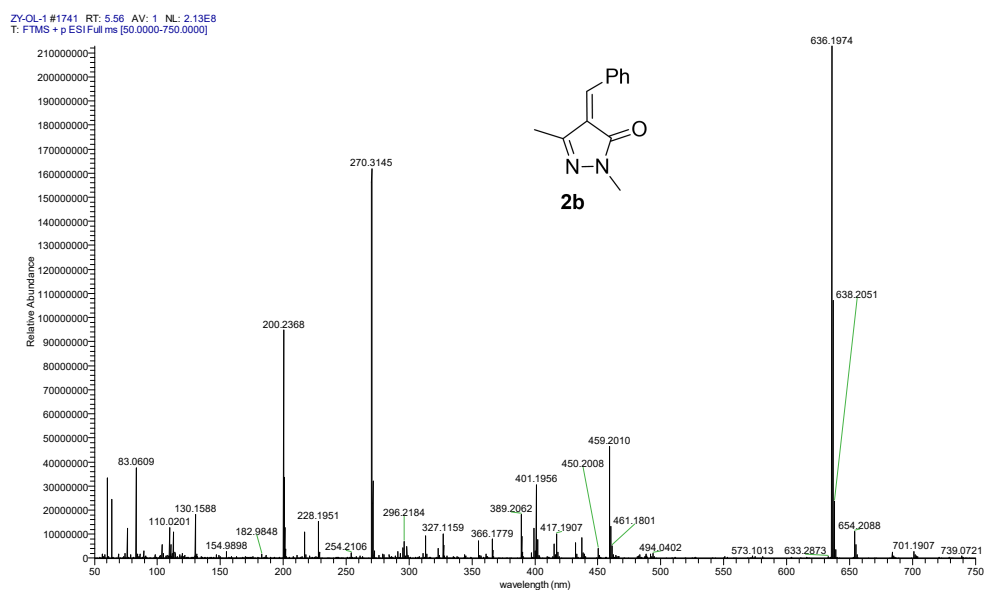
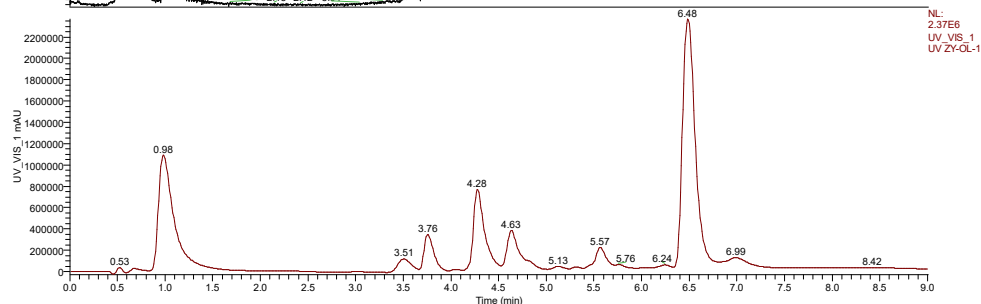
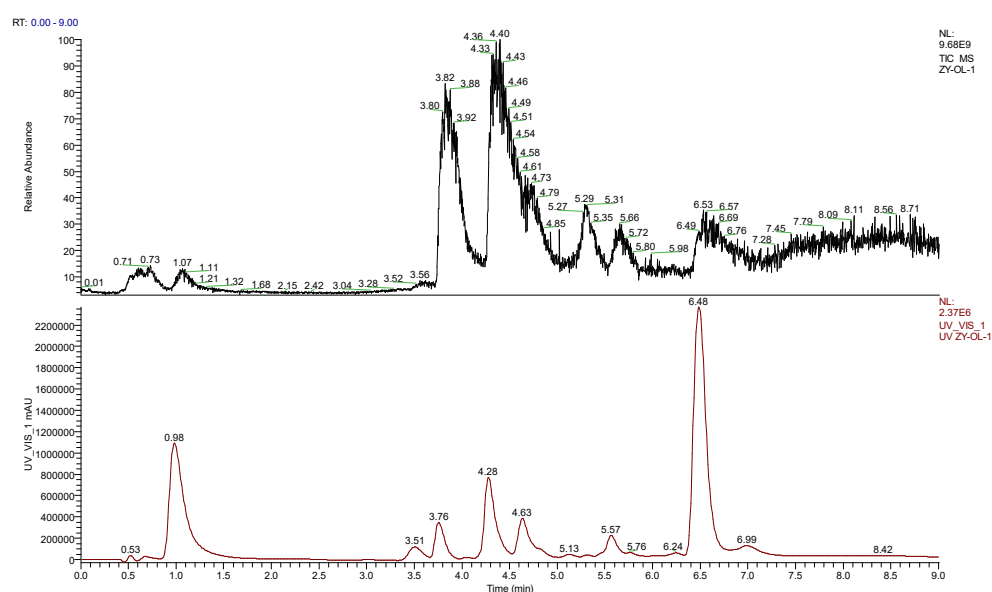


<Column Performance Report>

entry	R.T	Area	%Area	Height
1	15.400	2784942	50.43	59438
2	26.709	2737853	49.57	31167

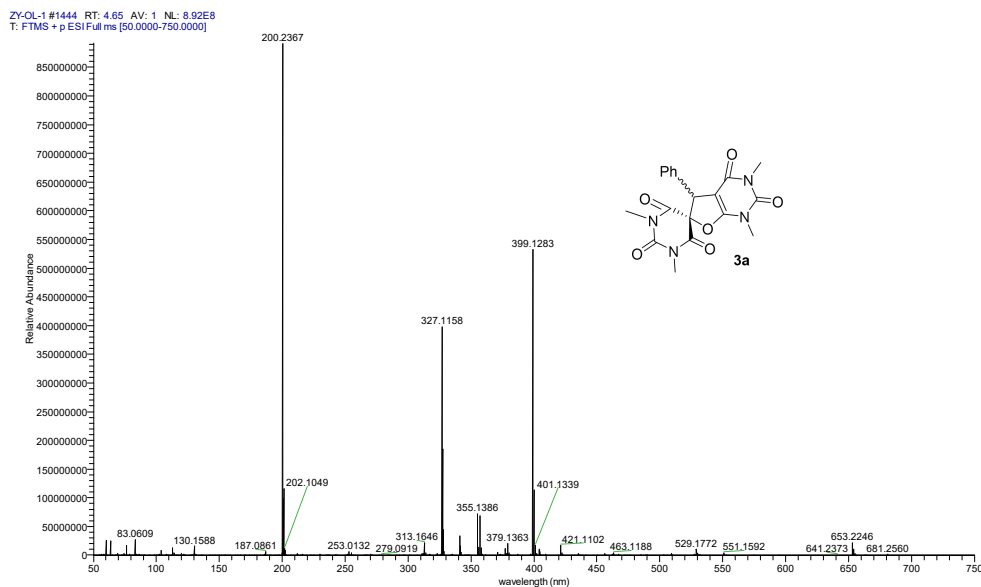
## 4. Reaction Mechanism Investigation by LC-HRMS Analysis

In order to clarify the reaction mechanism, we took out a sample from the reaction mixture of substrates **1a** and **2b**, and performed its LC-HRMS analysis as shown below. The LC-HRMS analysis indicated the existence of the key species **2b**, **3a**, and **5** in the reaction mixture. On the basis of the discovery **5**, we assumed the reaction mechanism for the cascade assembly of **1a** with **2b**.

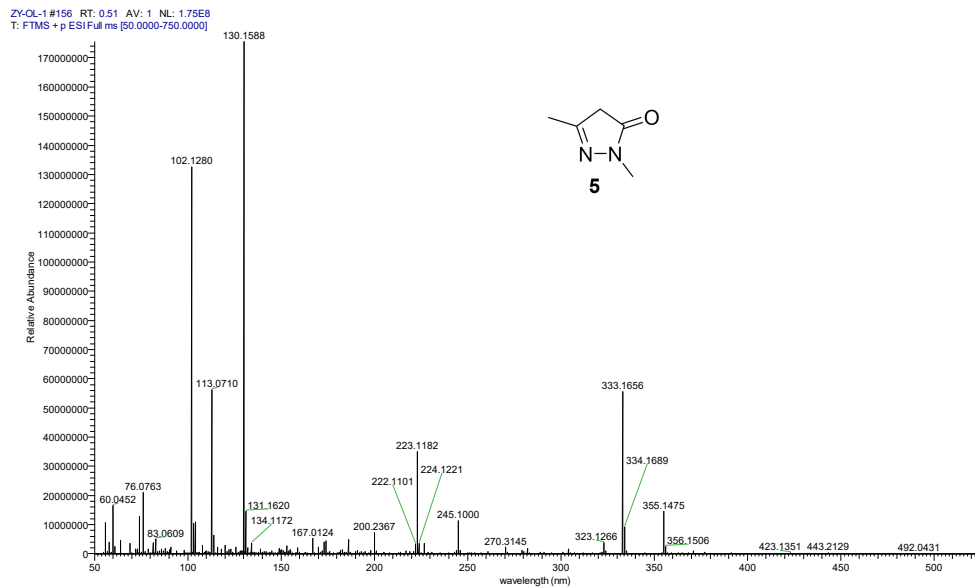




m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
201.10162	201.10224	-3.08	7.5	C <sub>12</sub> H <sub>13</sub> ON <sub>2</sub>



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
399.12830	399.12991	-1.61	12.5	C <sub>19</sub> H <sub>19</sub> O <sub>6</sub> N <sub>4</sub>



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
113.07100	113.07094	0.54	2.5	C <sub>5</sub> H <sub>9</sub> ON <sub>2</sub>