

# Supporting Information

**Merging Catalyst-free Synthesis and Iodine Catalysis:  
One-Pot Synthesis of Dihydrofuropyrimidines and  
Spirodihydrofuropyrimidine Pyrazolones**

**Ya-Yun Zheng, Kai-Xiang Feng, Ai-Bao Xia,\* Jie Liu, Cheng-Ke  
Tang, Zhan-Yu Zhou, and Dan-Qian Xu\***

*Catalytic Hydrogenation Research Centre, State Key Laboratory*

*Breeding Base of Green Chemistry-Synthesis Technology,*

*Zhejiang University of Technology, Hangzhou, 310014, Zhejiang, China*

*Fax (+86) 0571 88320066;*

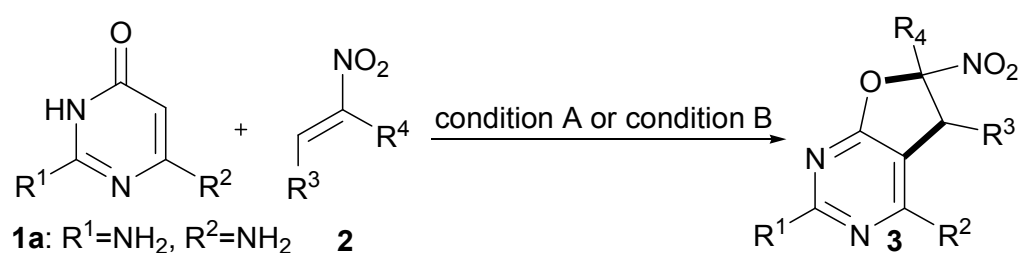
*E-mail: xiaobao@zjut.edu.cn; chrc@zjut.edu.cn*

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## 1. General information

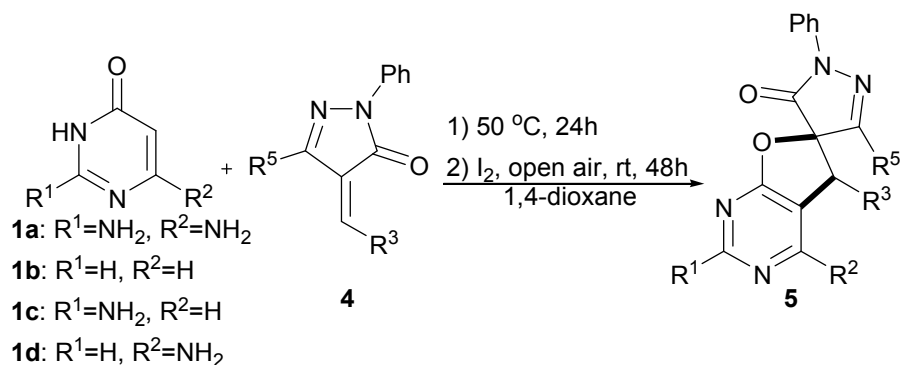
NMR data were obtained on Bruker AVANCE III 500MHz for  $^1\text{H}$  at 500 MHz and for  $^{13}\text{C}$  at 125 MHz with TMS as the internal standard. HRMS data were measured on an Agilent 6120 LC/TOF-MS with ESI source or Waters Premier GC/ TOF-MS with EI source. experiments were conducted using silica gel GF254 (200-300mesh) eluting with ethyl ether and petroleum ether. TLC experiments were carried out on glass-backed silica plates. Unless otherwise noted, chemicals were used without purification as commercially available.

## 2. General experimental procedure for synthesis of compounds **3** and **5**, and characterization of all products

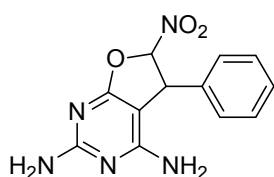


Condition A: the reactions were conducted in  $\text{CH}_3\text{CN}$  (1 mL) using **1** (0.1 mmol) and **2** (0.1 mmol) with stirring for 24 h at 50 °C. This was followed by the addition of KI (0.02 mmol) and TBHP (0.2 mmol), and the solution was then stirred for 24 h at room temperature. After completion, the reaction mixture was extracted with EtOAc (3\*10 mL), washed with water, dried and concentrated. The residue was purified by flash chromatography to give products **3a-3m** (eluent:petroleum ether-ethyl acetate).

Condition B: the reactions were conducted in MeOH (1 mL) using **1** (0.1 mmol) and **2** (0.1 mmol) with stirring for 24 h at room temperature. This was followed by the addition of  $\text{nBu}_4\text{NI}$  (0.02 mmol) and  $\text{H}_2\text{O}_2$  (0.2 mmol), and the solution was then stirred for 24 h at room temperature. After completion, the reaction mixture was extracted with EtOAc (3\*10 mL), washed with water, dried and concentrated. The residue was purified by flash chromatography to give products **3n-3v** (eluent:petroleum ether-ethyl acetate).

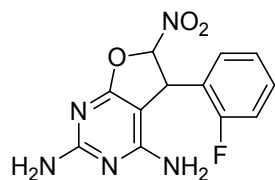


All the reactions were conducted in 1,4-dioxane (1 mL) using **1** (0.12 mmol) and **4** (0.1 mmol) with stirring for 24 h at 50 °C. This was followed by the addition of I<sub>2</sub> (0.01 mmol) under open air condition, and the solution was then stirred for 48 h at room temperature. After completion, the reaction mixture was extracted with EtOAc (3\*10 mL), washed with water, dried and concentrated. The residue was purified by flash chromatography to give products **5a-5v** (eluent:petroleum ether-ethyl acetate).



**6-nitro-5-phenyl-5,6-dihydrofuro[2,3-d]pyrimidine-2,4-**

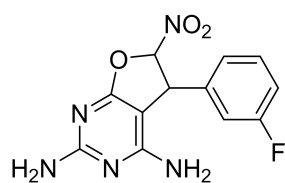
**diamine**, yield: 46.7 mg, 85.5%; white solid; mp 225-227°C; <sup>1</sup>H NMR (500 MHz, Acetone ): δ 7.45 – 7.40 (m, 2H), 7.38 – 7.34 (m, 1H), 7.26 (d, *J* = 7.1 Hz, 2H), 6.28 (d, *J* = 1.5 Hz, 1H), 5.96 (s, 2H), 5.91 (s, 2H), 4.90 (d, *J* = 1.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, Acetone): δ 175.6, 165.7, 162.1, 138.9, 130.0(×2), 129.0, 128.2(×2), 110.4, 85.3, 52.4. HRMS (ESI+) calcd for [C<sub>12</sub>H<sub>11</sub>N<sub>5</sub>O<sub>3</sub> + Na]<sup>+</sup> *m/z* 296.0754, found 296.0758.



**5-(2-fluorophenyl)-6-nitro-5,6-dihydrofuro[2,3-d]pyrimidine-**

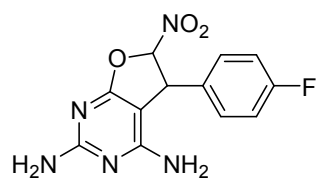
**2,4-diamine**, yield: 45.6 mg, 78.3%; white solid; mp 223-228°C; <sup>1</sup>H NMR (500 MHz, Acetone): δ 7.45 – 7.40 (m, 1H), 7.26 – 7.19 (m, 2H), 7.03 – 6.99 (m, 1H) , 6.36 (d, *J*

= 0.8 Hz, 1H), 5.94 (s, 2H), 5.91 (s, 2H), 5.14 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz, Acetone):  $\delta$  174.5, 165.0, 163.1(d,  $^1J_{\text{C-F}} = 243.8$  Hz), 161.2, 140.9(d,  $^3J_{\text{C-F}} = 7.0$  Hz), 131.1(d,  $^3J_{\text{C-F}} = 8.5$  Hz), 123.3(d,  $^4J_{\text{C-F}} = 2.9$  Hz), 114.9(d,  $^2J_{\text{C-F}} = 21.1$  Hz), 114.2(d,  $^2J_{\text{C-F}} = 22.3$  Hz), 109.1, 83.9, 51.1. HRMS (ESI+) calcd for  $[\text{C}_{12}\text{H}_{10}\text{FN}_5\text{O}_3 + \text{Na}]^+$   $m/z$  314.0660, found 314.0667.



**5-(3-fluorophenyl)-6-nitro-5,6-dihydrofuro[2,3-d]pyrimidine-**

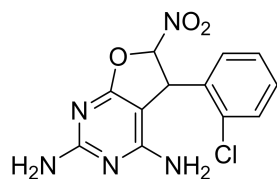
**2,4-diamine**, yield: 41.4 mg, 71.2%; white solid; mp 175-176°C;  $^1\text{H}$  NMR (500 MHz, Acetone), 7.50 – 7.46 (m, 1H) 7.16 – 7.11 (m, 2H), 7.04 – 7.02 (m, 1H), 6.34 (d,  $J = 1.5$  Hz, 1H), 5.87 (s, 4H), 4.95 (d,  $J = 1.2$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz, Acetone) 175.0, 164.9, 161.3, 160.9(d,  $^1J_{\text{C-F}} = 245.3$  Hz), 130.3(d,  $^3J_{\text{C-F}} = 8.2$  Hz), 128.6(d,  $^3J_{\text{C-F}} = 3.5$  Hz), 124.7(d,  $^4J_{\text{C-F}} = 3.2$  Hz), 124.5(d,  $^2J_{\text{C-F}} = 14.0$  Hz), 115.7(d,  $^2J_{\text{C-F}} = 21.1$  Hz), 108.5, 82.3, 45.3(d,  $^3J_{\text{C-F}} = 3.1$  Hz). HRMS (ESI+) calcd for  $[\text{C}_{12}\text{H}_{10}\text{FN}_5\text{O}_3 + \text{Na}]^+$   $m/z$  314.0660, found 314.0665.



**5-(4-fluorophenyl)-6-nitro-5,6-dihydrofuro[2,3-**

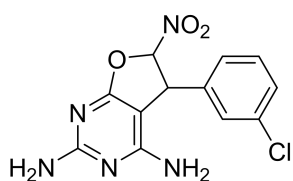
**d]pyrimidine-2,4-diamine** yield: 49.6 mg, 85.3%; white solid; mp 204-209°C;  $^1\text{H}$  NMR (500 MHz, Acetone):  $\delta$  7.32 – 7.28 (m, 2H), 7.21 – 7.17 (m, 2H), 6.28 (d,  $J = 1.5$  Hz, 1H), 5.87 (s, 2H), 5.84 (s, 2H), 4.93 (d,  $J = 1.1$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz, Acetone):  $\delta$  174.7, 164.9, 162.6(d,  $^1J_{\text{C-F}} = 231.1$  Hz), 134.1(d,  $^4J_{\text{C-F}} = 3.0$  Hz), 161.2, 129.4(d,  $^3J_{\text{C-F}} = 8.4$  Hz)( $\times 2$ ), 115.8(d,  $^2J_{\text{C-F}} = 21.7$  Hz)( $\times 2$ ), 109.4, 84.3, 50.8 HRMS

(ESI+) calcd for  $[C_{12}H_{10}FN_5O_3 + Na]^+$   $m/z$  314.0660, found 314.0663.



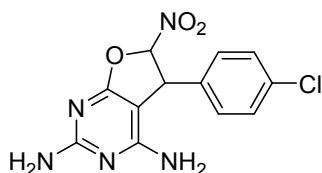
**5-(2-chlorophenyl)-6-nitro-5,6-dihydrofuro[2,3-d]pyrimidine-**

**2,4-diamine**, yield: 37.6 mg, 61.3%; white solid; mp 165-167°C;  $^1H$  NMR (500 MHz, Acetone):  $\delta$  7.56 (dd,  $J = 7.8, 1.4$  Hz, 1H), 7.42 – 7.31 (m, 2H), 6.94 (dd,  $J = 7.6, 1.6$  Hz, 1H), 6.30 (d,  $J = 1.2$  Hz, 1H), 6.00 (s, 2H), 5.94 (s, 2H), 5.24 (s, 1H);  $^{13}C$  NMR (125 MHz, Acetone):  $\delta$  175.3, 165.00, 161.3, 134.4, 133.9, 130.2, 129.9, 128.7, 127.7, 108.7, 82.7, 48.3. HRMS (ESI+) calcd for  $[C_{12}H_{10}ClN_5O_3 + Na]^+$   $m/z$  330.0364, found 330.0365.



**5-(3-chlorophenyl)-6-nitro-5,6-dihydrofuro[2,3-d]pyrimidin**

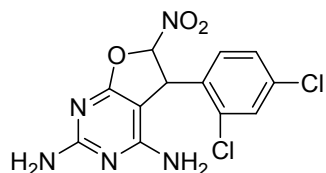
**e-2,4-diamine**, yield: 38.7 mg, 63.0%; white solid; mp 200-202°C;  $^1H$  NMR (500 MHz, Acetone):  $\delta$  7.47 – 7.39 (m, 2H), 7.29 (t,  $J = 1.9$  Hz, 1H), 7.22 (dd,  $J = 7.6, 1.1$  Hz, 1H), 6.35 (d,  $J = 1.5$  Hz, 1H), 5.91 (s, 2H), 5.89 (s, 2H), 4.94 (d,  $J = 1.3$  Hz, 1H);  $^{13}C$  NMR (125 MHz, Acetone):  $\delta$  174.8, 164.9, 161.2, 140.4, 134.3, 130.8, 128.2, 127.5, 125.9, 109.0, 83.8, 51.0. HRMS (ESI+) calcd for  $[C_{12}H_{10}ClN_5O_3 + Na]^+$   $m/z$  330.0364, found 330.0369.



**5-(4-chlorophenyl)-6-nitro-5,6-dihydrofuro[2,3-**

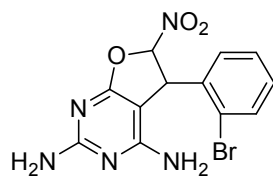
**d]pyrimidine-2,4-diamine**, yield: 54.3 mg, 88.4%; white solid; mp 187-190°C;  $^1H$  NMR (500 MHz, Acetone):  $\delta$  7.47 – 7.45 (m, 2H), 7.30 – 7.27 (m, 2H), 6.31 (d,  $J =$

1.5 Hz, 1H), 5.95 (s, 2H), 5.92 (s, 2H), 4.93 (d,  $J = 1.2$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz, Acetone): 174.7, 164.9, 161.2, 136.9, 133.5, 129.1( $\times 2$ ), 129.1( $\times 2$ ), 109.2, 84.0, 50.9. HRMS (ESI+) calcd for  $[\text{C}_{12}\text{H}_{10}\text{ClN}_5\text{O}_3 + \text{Na}]^+$   $m/z$  330.0364, found 330.0361.



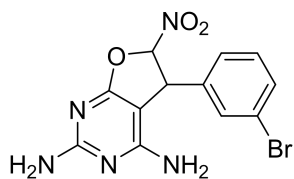
**5-(2,4-dichlorophenyl)-6-nitro-5,6-dihydrofuro[2,3-**

**d]pyrimidine-2,4-diamine**, yield: 51.3 mg, 75.2%; white solid; mp 217-219°C;  $^1\text{H}$  NMR (500 MHz, Acetone):  $\delta$  7.64 (d,  $J = 2.2$  Hz, 1H), 7.41 (dd,  $J = 8.4, 2.1$  Hz, 1H), 6.93 (d,  $J = 8.4$  Hz, 1H), 6.34 (d,  $J = 1.2$  Hz, 1H), 5.99 (s, 2H), 5.90 (s, 2H), 5.22 (d,  $J = 0.4$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz, Acetone):  $\delta$  175.3, 165.0, 161.2, 136.1, 133.6, 130.1, 128.9, 128.3, 124.1, 108.9, 63.2, 50.4. HRMS (ESI+) calcd for  $[\text{C}_{12}\text{H}_9\text{Cl}_2\text{N}_5\text{O}_3 + \text{Na}]^+$   $m/z$  363.9975, found 363.9976.

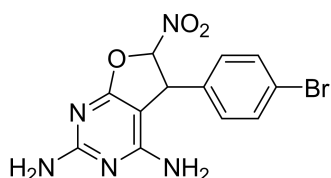


**5-(2-bromophenyl)-6-nitro-5,6-dihydrofuro[2,3-d]pyrimidine-**

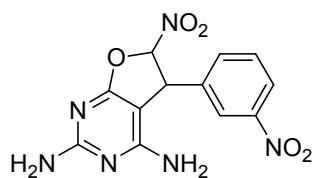
**2,4-diamine**, yield: 49.4 mg, 70.3%; white solid; mp 230-232°C;  $^1\text{H}$  NMR (500 MHz, Acetone):  $\delta$  7.74 (dd,  $J = 7.9, 1.2$  Hz, 1H), 7.42 – 7.30 (m, 2H), 6.97 – 6.84 (m, 1H), 6.28 (d,  $J = 1.2$  Hz, 1H), 5.94 (s, 2H), 5.90 (s, 2H), 5.23 (d,  $J = 0.8$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz, Acetone):  $\delta$  175.3, 165.0, 161.2, 136.1, 133.6, 130.1, 128.9, 128.3, 124.1, 109.0, 83.3, 50.4. HRMS (ESI+) calcd for  $[\text{C}_{12}\text{H}_{10}\text{BrN}_5\text{O}_3 + \text{Na}]^+$   $m/z$  373.9859, found 373.9854.



**5-(3-bromophenyl)-6-nitro-5,6-dihydrofuro[2,3-d]pyrimidine-2,4-diamine**, yield: 39.2 mg, 55.8%; white solid; mp 150-151°C; <sup>1</sup>H NMR (500 MHz, Acetone): δ 7.56-7.54 (m, 1H), 7.45 (t, *J* = 1.9 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.27-7.25 (m, 1H), 6.36 (d, *J* = 1.5 Hz, 1H), 5.95 (s, 2H), 5.94 (s, 2H), 4.94 (d, *J* = 1.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, Acetone): δ 174.8, 164.9, 161.1, 140.7, 131.2, 131.1, 130.4, 126.3, 122.5, 109.0, 83.7, 60.0. HRMS (ESI+) calcd for [C<sub>12</sub>H<sub>10</sub>BrN<sub>5</sub>O<sub>3</sub> + Na]<sup>+</sup> *m/z* 373.9859, found 373.9855.



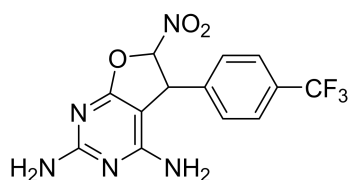
**5-(4-bromophenyl)-6-nitro-5,6-dihydrofuro[2,3-d]pyrimidine-2,4-diamine**, yield: 45.4 mg, 64.7%; white solid; mp 175-177°C; <sup>1</sup>H NMR (500 MHz, Acetone): δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.31 (d, *J* = 1.6 Hz, 1H), 5.97 (s, 2H), 5.94 (s, 2H), 4.92 (d, *J* = 1.6 Hz, 1H); <sup>13</sup>C NMR (125 MHz, Acetone): 174.8, 164.9, 161.2, 137.4, 132.1(×2), 129.5(×2), 121.6, 109.1, 83.9, 50.9. HRMS (ESI+) calcd for [C<sub>12</sub>H<sub>10</sub>BrN<sub>5</sub>O<sub>3</sub> + Na]<sup>+</sup> *m/z* 373.9859, found 373.9852.



**6-nitro-5-(3-nitrophenyl)-5,6-dihydrofuro[2,3-d]pyrimidine-2,4-diamine**, yield: yield: 34.5 mg, 54.3%; white solid; mp 195-198°C; <sup>1</sup>H NMR (500 MHz, Acetone): 8.25 – 8.23 (m, 1H), 8.15 – 8.14 (m, 1H), 7.70 – 7.77 (m, 2H), 6.42 (d, *J* = 1.5 Hz, 1H), 5.94 (s, 2H), 5.91 (s, 2H), 5.13 (d, *J* = 1.4 Hz, 1H); <sup>13</sup>C NMR (1

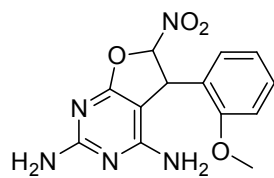


25 MHz, Acetone): 180.1, 170.2, 166.4, 153.9, 145.5, 139.0, 135.8, 128.3, 127.7, 114.0, 88.8, 56.1. HRMS (ESI+) calcd for  $[C_{12}H_{10}N_6O_5 + Na]^+$   $m/z$  341.0605, found 341.0602.



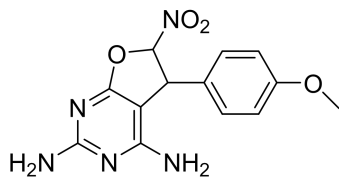
**6-nitro-5-(4-(trifluoromethyl)phenyl)-5,6-dihydrofuro**

**[2,3-d]pyrimidine-2,4-diamine**, yield: 55.8mg, 60%; white solid; mp 204-209°C;  $^1H$  NMR (500 MHz, Acetone):  $\delta$  7.78 (d,  $J = 8.2$  Hz, 2H), 7.50 (d,  $J = 8.2$  Hz, 2H), 6.36 (d,  $J = 1.4$  Hz, 1H), 5.89 (s, 4H), 5.04 (s, 1H);  $^{13}C$  NMR (125 MHz, Acetone):  $\delta$  174.8, 164.9, 161.2, 142.6, 129.7 (dd,  $^2J_{C-F} = 67.9$  Hz, 36.3 Hz), 128.3 ( $\times 2$ ), 126.0 (dd,  $^3J_{C-F} = 7.6$  Hz, 3.9 Hz) ( $\times 2$ ), 124.3 (dd,  $^1J_{C-F} = 532.5$  Hz, 269.7 Hz), 108.8, 83.6, 51.1. HRMS (ESI+) calcd for  $[C_{13}H_{10}F_3N_5O_3 + Na]^+$   $m/z$  364.0628, found 364.0624.

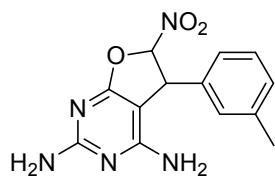


**5-(2-methoxyphenyl)-6-nitro-5,6-dihydrofuro[2,3-d]pyrimidi**

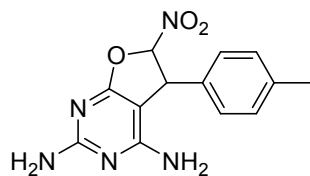
**ne-2,4-diamine**, yield: 35.6 mg, 58.8%; white solid; mp 150-152°C;  $^1H$  NMR (500 MHz, Acetone):  $\delta$  7.36 – 7.33 (m, 1H), 7.11 (d,  $J = 7.9$  Hz, 1H), 6.96 – 6.90 (m, 2H), 6.25 (d,  $J = 1.6$  Hz, 1H), 5.80 (s, 2H), 5.77 (s, 2H), 5.03 (d,  $J = 1.3$  Hz, 1H), 3.95 (s, 3H);  $^{13}C$  NMR (125 MHz, Acetone):  $\delta$  174.9, 164.7, 161.3, 157.2, 129.5, 127.4, 125.3, 120.7, 111.1, 109.5, 83.4, 55.1, 45.9. HRMS (ESI+) calcd for  $[C_{13}H_{13}N_5O_4 + Na]^+$   $m/z$  326.0860, found 326.0863.



**5-(4-methoxyphenyl)-6-nitro-5,6-dihydrofuro[2,3-d]pyrimidine-2,4-diamine**, yield: 45.8 mg, 75.5%; white solid; mp 198-200°C; <sup>1</sup>H NMR (500 MHz, Acetone): δ 7.17 (d, *J* = 8.6 Hz, 2H), 6.98 – 6.96 (m, 2H), 6.21 (d, *J* = 1.2 Hz, 1H), 5.76 (s, 2H), 5.72 (s, 2H), 4.83 (s, 1H), 3.81 (s, 3H); <sup>13</sup>C NMR (125 MHz, Acetone): δ 174.6, 164.8, 161.2, 159.7, 129.8, 128.4(×2), 114.4(×2), 109.8, 84.7, 54.7, 50.9. HRMS (ESI+) calcd for [C<sub>13</sub>H<sub>13</sub>N<sub>5</sub>O<sub>4</sub> + Na]<sup>+</sup> *m/z* 326.0860, found 326.0866.



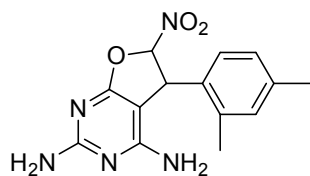
**6-nitro-5-(*m*-tolyl)-5,6-dihydrofuro[2,3-d]pyrimidine-2,4-diamine**, yield: 43.3 mg, 75.5% white solid; mp 231-232°C; <sup>1</sup>H NMR (500 MHz, Acetone): δ 7.31 – 7.28 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.26 (d, *J* = 1.5 Hz, 1H), 5.85 (s, 2H), 5.81 (s, 2H), 4.84 (d, *J* = 1.2 Hz, 1H), 2.34 (s, 3H); <sup>13</sup>C NMR (125 MHz, Acetone): δ 174.7, 164.7, 161.2, 138.7, 138.1, 129.0, 128.8, 127.8, 124.3, 109.6, 84.5, 51.5, 20.5. HRMS (ESI+) calcd for [C<sub>13</sub>H<sub>13</sub>N<sub>5</sub>O<sub>4</sub> + Na]<sup>+</sup> *m/z* 310.0911, found 310.0918.



**6-nitro-5-(*p*-tolyl)-5,6-dihydrofuro[2,3-d]pyrimidine-2,4-diamine**, yield: 46.8 mg, 81.5%; white solid; mp 201-202°C; <sup>1</sup>H NMR (500 MHz, Acetone): δ 7.22 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.22 (d, *J* = 1.5 Hz, 1H), 5.80 (s, 2H), 5.75 (s, 2H), 4.83 (d, *J* = 1.1 Hz, 1H), 2.33 (s, 3H); <sup>13</sup>C NMR (125 MHz,

Acetone):  $\delta$  179.9, 170.0, 166.4, 143.0, 140.3, 134.9( $\times 2$ ), 132.4( $\times 2$ ), 114.9, 89.8, 56.4,

25.3. HRMS (ESI+) calcd for  $[\text{C}_{13}\text{H}_{13}\text{N}_5\text{O}_4 + \text{Na}]^+$   $m/z$  310.0911, found 310.0915.



**5-(2,4-dimethylphenyl)-6-nitro-5,6-dihydrofuro[2,3-**

**d]pyrimidine-2,4-diamine**, yield: 45.9 mg, 76.3%; white solid; mp 203-205°C;  $^1\text{H}$

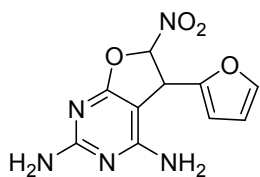
NMR (500 MHz, Acetone):  $\delta$  7.13 (s, 1H), 6.98 (d,  $J = 7.7$  Hz, 1H), 6.62 (d,  $J = 7.9$

Hz, 1H), 6.17 (d,  $J = 1.1$  Hz, 1H), 5.84 (s, 2H), 5.80 (s, 2H), 5.01 (s, 1H), 2.55 (s, 3H),

2.29 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz, Acetone):  $\delta$  175.2, 164.8, 161.2, 137.7, 136.8,

132.2, 131.9, 127.0, 126.3, 109.2, 83.9, 48.0, 20.0, 18.9. HRMS (ESI+) calcd for

$[\text{C}_{14}\text{H}_{15}\text{N}_5\text{O}_3 + \text{Na}]^+$   $m/z$  324.1067, found 324.1064.



**5-(furan-2-yl)-6-nitro-5,6-dihydrofuro[2,3-d]pyrimidine-2,4-**

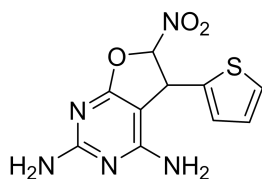
**diamine**, yield: 29.8 mg, 56.6%; white solid; mp 206-208°C;  $^1\text{H}$  NMR (500 MHz, Ac

etone):  $\delta$  7.58 (dd,  $J = 1.8, 0.7$  Hz, 1H), 6.45 (d,  $J = 1.4$  Hz, 1H), 6.41 (dd,  $J = 3.2, 1.9$

Hz, 1H), 6.26 (d,  $J = 3.3$  Hz, 1H), 5.99 (s, 2H), 5.89 (s, 2H), 5.00 (s, 1H);  $^{13}\text{C}$  NMR

(125 MHz, Acetone):  $\delta$  174.5, 164.8, 161.2, 150.2, 143.5, 110.6, 107.8, 106.6, 82.1, 4

5.5. HRMS (ESI+) calcd for  $[\text{C}_{10}\text{H}_9\text{N}_5\text{O}_4 + \text{Na}]^+$   $m/z$  286.0547, found 286.0549.



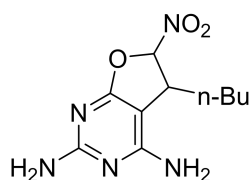
**6-nitro-5-(thiophen-2-yl)-5,6-dihydrofuro[2,3-d]pyrimidine-2,**

**4-diamine**, yield: 41.6 mg, 74.5%; white solid; mp 205-207°C;  $^1\text{H}$  NMR (500 MHz, A

cetone):  $\delta$  7.58 (dd,  $J = 1.8, 0.7$  Hz, 1H), 6.45 (d,  $J = 1.4$  Hz, 1H), 6.41 (dd,  $J = 3.2, 1.$

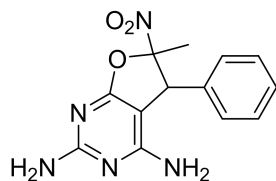
9 Hz, 1H), 6.26 (d,  $J = 3.3$  Hz, 1H), 5.99 (s, 2H), 5.89 (s, 2H), 5.00 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz, Acetone): 174.3, 164.9, 161.1, 141.7, 127.4, 125.9, 125.9, 109.2, 84.8, 46.

9. HRMS (ESI+) calcd for  $[\text{C}_{10}\text{H}_9\text{N}_5\text{O}_4 + \text{Na}]^+$   $m/z$  302.0318, found 302.0314.



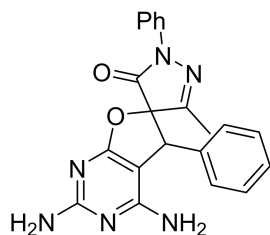
**5-butyl-6-nitro-5,6-dihydrofuro[2,3-d]pyrimidine-2,4-diamine**,

yield: 12.8 mg, 25.2%; white solid; mp 200-202°C;  $^1\text{H}$  NMR (500 MHz, Acetone):  $\delta$  6.90 (s, 1H), 6.53 (s, 3H), 4.61 (dd,  $J = 7.7, 4.2$  Hz, 1H), 1.95 – 1.88 (m, 1H), 1.72 – 1.58 (m, 1H), 1.72 – 1.58 (m, 5H) 0.92 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz, Acetone):  $\delta$  162.3, 159.3, 154.7, 88.4, 86.1, 31.6, 27.8, 27.5, 23.1, 14.1. HRMS (ESI+) calcd for  $[\text{C}_{10}\text{H}_{15}\text{N}_5\text{O}_3 + \text{Na}]^+$   $m/z$  276.1067, found 276.1065



**6-methyl-6-nitro-5-phenyl-5,6-dihydrofuro[2,3-d]pyrimidine**

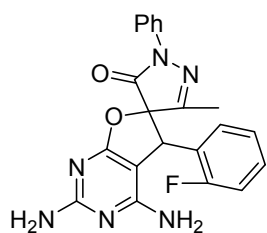
**-2,4-diamine**, yield: 31mg, 54%; white solid; mp 205-206°C;  $^1\text{H}$  NMR (500 MHz, Acetone):  $\delta$  7.45 – 7.17 (m, 5H), 5.88 (s, 2H), 5.78 (s, 2H), 4.94 (s, 1H), 1.50 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz, Acetone):  $\delta$  174.0, 164.7, 170.0, 135.7, 128.9( $\times 4$ ), 128.4, 118.3, 85.7, 53.6, 20.5. HRMS (ESI+) calcd for  $[\text{C}_{13}\text{H}_{13}\text{N}_5\text{O}_3 + \text{Na}]^+$   $m/z$  310.0917, found 310.0914.



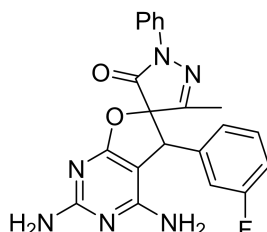
**2,4-diamino-3'-methyl-1',5-diphenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1H)-one**,

yield: 70.2 mg, 91%; white solid; mp 270-272°C;

<sup>1</sup>H NMR (500 MHz, DMSO):  $\delta$  7.81 (dd,  $J = 8.7, 1.2$  Hz, 2H), 7.50 (dd,  $J = 8.7, 7.4$  Hz, 2H), 7.40 – 7.35 (m, 3H), 7.30 – 7.04 (m, 3H), 6.32 (s, 2H), 6.15 (s, 2H), 4.94 (s, 1H), 1.22 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO):  $\delta$  174.5, 170.8, 164.1, 161.1, 158.9, 137.2, 135.5, 129.2( $\times 4$ ), 128.1, 125.5, 118.6( $\times 4$ ), 87.9, 82.4, 51.6, 13.8. HRMS (ESI+) calcd for [C<sub>21</sub>H<sub>18</sub>N<sub>6</sub>O<sub>2</sub> + Na]<sup>+</sup>  $m/z$  409.1383, found 409.1388.

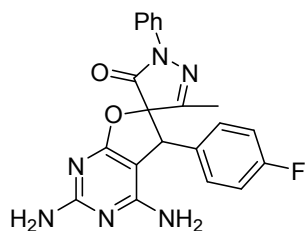


**2,4-diamino-5-(2-fluorophenyl)-3'-methyl-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, 76.8 mg, 95%; white solid; mp 241-242°C; <sup>1</sup>H NMR (500 MHz, DMSO):  $\delta$  7.79 (d,  $J = 7.3$  Hz, 2H), 7.55 – 7.47 (m, 2H), 7.44 – 7.37 (m, 1H), 7.32 – 7.19 (m, 3H), 7.08 – 7.01 (m, 1H), 6.34 (s, 2H), 6.27 (s, 2H), 5.15 (s, 1H), 1.32 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): 174.3, 170.4, 164.3, 161.1, 160.9(d, <sup>1</sup> $J_{C-F} = 243.5$  Hz), 158.2, 137.1, 130.1(d, <sup>3</sup> $J_{C-F} = 8.3$  Hz), 129.3(d, <sup>2</sup> $J_{C-F} = 3.6$  Hz), 129.2( $\times 2$ ), 125.5, 124.4(d, <sup>3</sup> $J_{C-F} = 2.8$ Hz), 122.6(d, <sup>4</sup> $J_{C-F} = 14.5$ Hz), 118.5( $\times 2$ ), 115.4(d, <sup>2</sup> $J_{C-F} = 20.9$ Hz), 87.0, 80.3, 45.5, 13.4. HRMS (ESI+) calcd for [C<sub>21</sub>H<sub>17</sub>FN<sub>6</sub>O<sub>2</sub> + Na]<sup>+</sup>  $m/z$  427.1289, found 427.1283.

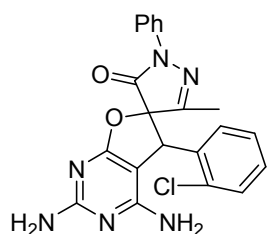


**4-diamino-5-(3-fluorophenyl)-3'-methyl-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 77.6 mg, 96%; white solid; mp 280-281°C; <sup>1</sup>H NMR (500 MHz, DMSO):  $\delta$  7.81 (d,  $J = 7.7$  Hz, 2H), 7.55 – 7.40 (m, 3H), 7.34 – 6.68 (m, 4H), 6.32 (s, 2H), 6.19 (s, 2H), 4.95 (s, 1H), 1.29 (s, 3H); <sup>13</sup>C N

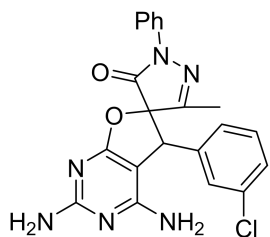
MR (125 MHz, DMSO): 174.5, 170.7, 164.1, 161.9(d,  $^1J_{C-F}$  = 243.0 Hz), 161.0, 158.7, 137.2, 131.6, 129.1( $\times 4$ ), 125.5, 118.6( $\times 4$ ), 87.8, 82.6, 50.8, 13.9. HRMS (ESI+) calcd for  $[C_{21}H_{17}FN_6O_2 + Na]^+$   $m/z$  427.1289, found 427.1285.



**2,4-diamino-5-(3-fluorophenyl)-3'-methyl-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 71.0 mg, 88%; white solid; mp 250-251°C;  $^1H$  NMR (500 MHz, DMSO):  $\delta$  7.81 – 7.79 (m, 2H), 7.49 (dd,  $J$  = 8.6, 7.3 Hz, 2H), 7.30 – 7.08 (m, 5H), 6.29 (s, 2H), 6.13 (s, 2H), 4.94 (s, 1H), 1.29 (s, 3H);  $^{13}C$  NMR (125 MHz, DMSO):  $\delta$  174.5, 170.7, 164.1, 161.9 (d,  $^1J_{C-F}$  = 243.0 Hz), 161.0, 158.7, 137.2, 131.6, 129.1 ( $\times 4$ ), 125.5, 118.6 ( $\times 4$ ), 87.8, 82.6, 50.8, 13.9. HRMS (ESI+) calcd for  $[C_{21}H_{17}FN_6O_2 + Na]^+$   $m/z$  427.1289, found 427.1283.



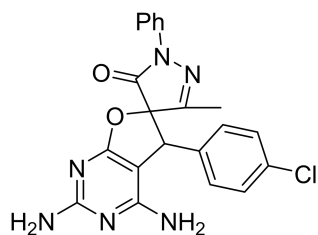
**2,4-diamino-5-(2-chlorophenyl)-3'-methyl-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 80.7 mg, 96%; white solid; mp 230-232°C;  $^1H$  NMR (500 MHz, DMSO):  $\delta$  7.77 (dd,  $J$  = 8.7, 1.2 Hz, 2H), 7.58 – 7.44 (m, 3H), 7.45 – 7.32 (m, 2H), 7.32 – 7.25 (m, 1H), 7.13 – 6.97 (m, 1H), 6.34 (s, 2H), 6.30 (s, 2H), 5.18 (s, 1H), 1.25 (s, 3H);  $^{13}C$  NMR (125 MHz, DMSO):  $\delta$  174.2, 170.3, 164.2, 160.9, 157.5, 137.0, 134.0, 133.1, 129.8, 129.7( $\times 2$ ), 129.2( $\times 2$ ), 127.3, 125.5, 118.5( $\times 2$ ), 86.6, 81.4, 48.7, 13.5. HRMS (ESI+) calcd for  $[C_{21}H_{17}ClN_6O_2 + Na]^+$   $m/z$  443.0994, found 443.0998.



**2,4-diamino-5-(3-chlorophenyl)-3'-methyl-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 62.2 mg, 74%; white solid;

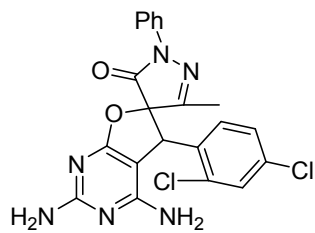
mp 220-222°C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 7.82 – 7.80 (m, 2H), 7.50 (dd, J = 8.7, 7.4 Hz, 2H), 7.43 (dd, J = 4.9, 2.3 Hz, 2H), 7.30-6.94 (m, 3H), 6.36 (s, 2H), 6.23 (s, 2H), 4.93 (s, 1H), 1.28 (s, 3H).; <sup>13</sup>C NMR (125 MHz, DMSO): δ 174.5, 170.6, 164.2, 161.0, 158.5, 137.2, 134.9, 129.1(×4), 125.6, 121.2, 118.6(×4), 87.7, 82.1, 51.0, 14.0.

HRMS (ESI+) calcd for [C<sub>21</sub>H<sub>17</sub>ClN<sub>6</sub>O<sub>2</sub> + Na]<sup>+</sup> *m/z* 443.0994, found 443.0996.



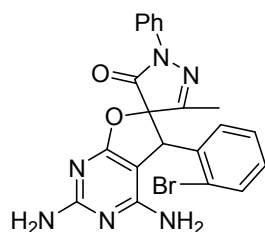
**2,4-diamino-5-(4-chlorophenyl)-3'-methyl-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 68.0 mg, 81%; white solid;

mp 229-231°C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 7.87 – 7.79 (m, 2H), 7.51 – 7.44 (m, 4H), 7.30 – 7.27 (m, 3H), 6.35 (s, 2H), 6.19 (s, 2H), 4.93 (s, 1H), 1.30 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 174.5, 170.7, 164.2, 161.0, 158.6, 137.2, 134.5, 132.7, 129.1(×4), 125.6, 118.6(×4), 87.7, 82.2, 50.9, 14.0. HRMS (ESI+) calcd for [C<sub>21</sub>H<sub>17</sub>ClN<sub>6</sub>O<sub>2</sub> + Na]<sup>+</sup> *m/z* 443.0994, found 443.0992.



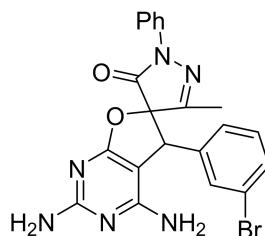
**2,4-diamino-5-(2,4-dichlorophenyl)-3'-methyl-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 82.6 mg, 91%; white solid;

e solid; mp 234-235°C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 7.81 – 7.75 (m, 2H), 7.71 (d, *J* = 2.2 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.32 – 7.25 (m, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.34 (s, 2H), 6.31 (s, 2H), 5.13 (s, 1H), 1.35 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 174.2, 170.1, 164.3, 160.8, 157.4, 137.0, 134.9, 133.4, 132.3, 131.2, 129.2(×2), 129.0, 127.4, 125.6, 118.5(×2), 86.4, 81.0, 48.6, 13.7. HRMS (ESI+) calcd for [C<sub>21</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>2</sub> + Na]<sup>+</sup> *m/z* 477.0603, found 477.0604.



**2,4-diamino-5-(2-bromophenyl)-3'-methyl-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 69.6 mg, 92.8%; white solid;

mp 164-165°C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 7.79 – 7.77 (m, 2H), 7.69 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.51-7.41(m, 3H), 7.33 – 7.26 (m, 2H), 7.03 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.30 (s, 2H), 6.27 (s,2H), 5.14 (s, 1H), 1.23 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 174.1, 170.1, 164.2, 160.8, 157.3, 137.0, 134.8, 133.1, 130.1, 130.0, 129.2(×2), 127.8, 125.5, 124.9, 118.5(×2), 86.4, 81.9, 50.7, 13.5. HRMS (ESI+) calcd for [C<sub>21</sub>H<sub>17</sub>BrN<sub>6</sub>O<sub>2</sub> + Na]<sup>+</sup> *m/z* 487.0489, found 487.0485.

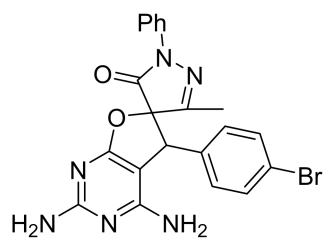


**2,4-diamino-5-(3-bromophenyl)-3'-methyl-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 72.4 mg, 78%; white solid; m

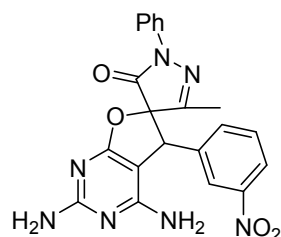
p 156-157°C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 7.81 – 7.79 (m, 2H), 7.58 – 7.48 (m, 3



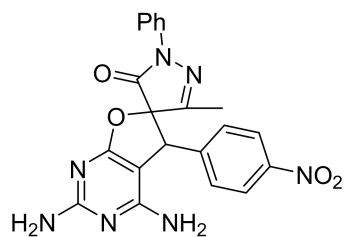
H), 7.37 – 7.01 (m, 4H), 6.37 (s, 2H), 6.25 (s, 2H), 4.93 (s, 1H), 1.28 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): 174.6, 170.5, 164.1, 160.9, 158.3, 137.2, 131.1, 129.2(×4), 125.6, 122.0, 118.7(×4), 105.1, 87.7, 50.8, 13.9. HRMS (ESI+) calcd for [C<sub>21</sub>H<sub>17</sub>BrN<sub>6</sub>O<sub>2</sub> + Na]<sup>+</sup> *m/z* 487.0489, found 487.0482.



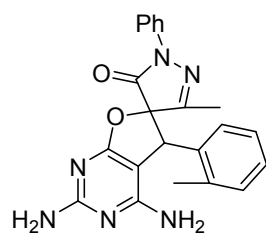
**2,4-diamino-5-(4-bromophenyl)-3'-methyl-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 88.2 mg, 95%; white solid; mp 282-284°C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 7.80 (dd, *J* = 8.7, 1.3 Hz, 2H), 7.59 – 7.58 (m, 2H), 7.50 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.30 – 7.27 (m, 3H), 6.33 (s, 2H), 6.18 (s, 2H), 4.91 (s, 1H), 1.30 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 174.5, 170.6, 164.2, 161.0, 158.5, 137.2, 134.9, 129.1(×4), 125.6, 121.2, 118.6(×4), 87.7, 82.1, 51.0, 14.0. HRMS (ESI+) calcd for [C<sub>21</sub>H<sub>17</sub>BrN<sub>6</sub>O<sub>2</sub> + Na]<sup>+</sup> *m/z* 487.0489, found 487.0487.



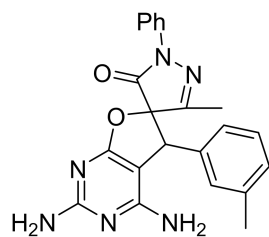
**2,4-diamino-3'-methyl-5-(3-nitrophenyl)-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 66.4 mg, 77%; white solid; mp 284-286°C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 8.24 – 7.27 (m, 9H), 6.39 (s, 2H), 6.27 (s, 2H), 5.09 (s, 1H), 1.27 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 174.6, 170.3, 164.3, 161.0, 147.9, 138.1, 137.2, 129.1(×4), 125.6, 123.2, 118.7(×4), 87.5(×2), 50.6, 14.0. HRMS (ESI+) calcd for [C<sub>21</sub>H<sub>17</sub>N<sub>7</sub>O<sub>4</sub> + Na]<sup>+</sup> *m/z* 454.1234, found 454.1237.



**2,4-diamino-3'-methyl-5-(4-nitrophenyl)-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 63.8 mg, 74%; white solid; mp 183-185°C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 8.26 – 8.24 (m, 2H), 7.83 – 7.81 (m, 2H), 7.52 – 7.27 (m, 5H), 6.36 (s, 1H), 6.24 (s, 2H), 5.07 (s, 2H), 1.30 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 174.6, 170.4, 164.3, 161.0, 158.0, 147.3, 143.3, 137.1, 129.1(×4), 125.6, 118.7(×4), 87.6, 81.9, 51.1, 14.0. HRMS (ESI+) calcd for [C<sub>21</sub>H<sub>17</sub>N<sub>7</sub>O<sub>4</sub> + Na]<sup>+</sup> *m/z* 454.1234, found 454.1238.



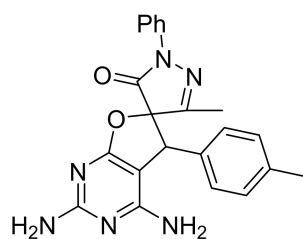
**2,4-diamino-3'-methyl-1'-phenyl-5-(o-tolyl)-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, 40.0 mg, 50%; white solid; mp 236-237°C; <sup>1</sup>H NMR (500 MHz, DMSO): 7.79 – 7.77 (m, 2H), 7.50 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.31 – 7.19 (m, 4H), 6.87 (d, *J* = 7.3 Hz, 1H), 6.31 (s, 2H), 6.16 (s, 2H), 5.09 (s, 1H), 2.13 (s, 3H), 1.19 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 174.3, 170.7, 164.0, 160.7, 159.2, 137.0, 136.7, 133.7, 130.9, 129.3(×2), 127.9, 127.8, 126.0, 125.7, 118.4(×2), 87.1, 82.9, 48.1, 18.7, 13.7. HRMS (ESI+) calcd for [C<sub>22</sub>H<sub>20</sub>N<sub>6</sub>O<sub>2</sub> + Na]<sup>+</sup> *m/z* 423.1540, found 423.1542.



**2,4-diamino-3'-methyl-1'-phenyl-5-(m-tolyl)-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 75.2 mg, 94%; white solid; mp 240-2

42°C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 7.81 – 7.79 (m, 2H), 7.50 (dd, *J* = 8.6, 7.4 Hz, 2 H), 7.30 – 7.25 (m, 2H), 7.17 – 6.83 (m, 3H), 6.30 (s, 2H), 6.11 (s, 2H), 4.89 (s, 1H), 2.27 (s, 3H), 1.25 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 174.5, 170.8, 164.1, 161.1, 158.9, 137.2, 135.4, 129.1(×4), 128.8, 125.5, 118.6(×4), 87.9, 82.5, 51.6, 21.0, 13.8.

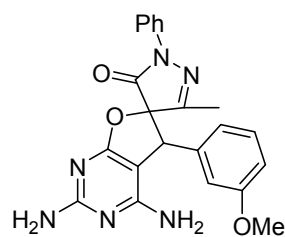
HRMS (ESI+) calcd for [C<sub>22</sub>H<sub>20</sub>N<sub>6</sub>O<sub>2</sub> + Na]<sup>+</sup> *m/z* 423.1540, found 423.1546.



**2,4-diamino-3'-methyl-1'-phenyl-5-(p-tolyl)-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 40 mg, 50%; white solid; mp 245-2

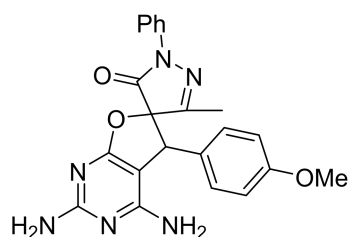
46°C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 7.81 – 7.79 (m, 2H), 7.50 (dd, *J* = 8.6, 7.4 Hz, 2 H), 7.30 – 7.26 (m, 1H), 7.19 – 6.92 (m, 4H), 6.32 (s, 2H), 6.10 (s, 2H), 4.90 (s, 1H), 2.30 (s, 3H), 1.26 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 174.5, 170.9, 164.1, 161.1, 159.1, 137.4, 137.2, 132.3, 129.2(×4), 125.5, 118.5(×4), 88.0, 82.6, 51.4, 20.7, 13.9.

HRMS (ESI+) calcd for [C<sub>22</sub>H<sub>20</sub>N<sub>6</sub>O<sub>2</sub> + Na]<sup>+</sup> *m/z* 423.1540, found 423.1543.

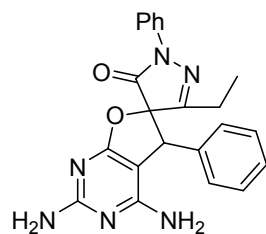


**2,4-diamino-5-(3-methoxyphenyl)-3'-methyl-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 70.7 mg, 85%; white soli

d; mp 191-192°C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 7.81 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.50 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.32 – 7.26 (m, 2H), 6.94 – 6.61 (m, 3H), 6.31 (s, 2H), 6.14 (s, 2H), 4.90 (s, 1H), 3.69 (s, 3H), 1.30 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 174.5, 170.7, 164.1, 161.1, 159.5, 158.9, 137.2, 136.9, 129.1(×4), 125.5, 118.5(×4), 87.9, 82.5, 55.1, 51.6, 13.8. HRMS (ESI+) calcd for [C<sub>22</sub>H<sub>20</sub>N<sub>6</sub>O<sub>3</sub> + Na]<sup>+</sup> *m/z* 439.1489, found 439.1485.

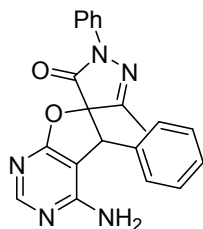


**2,4-diamino-5-(4-methoxyphenyl)-3'-methyl-1'-phenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 59.9 mg, 72%; white solid; mp 253-254°C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 7.81 – 7.79 (m, 2H), 7.49 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 6.94 (d, *J* = 6.4 Hz, 4H), 6.31 (s, 2H), 6.10 (s, 2H), 4.89 (s, 1H), 3.75 (s, 3H), 1.29 (s, 3H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 174.4, 170.9, 164.0, 161.0, 159.1, 137.2, 129.2(×4), 127.1, 125.5, 118.5(×4), 88.0, 82.9, 62.8, 55.2, 51.0, 13.9. HRMS (ESI+) calcd for [C<sub>22</sub>H<sub>20</sub>N<sub>6</sub>O<sub>3</sub> + Na]<sup>+</sup> *m/z* 439.1489, found 439.1486.



**2,4-diamino-3'-ethyl-1',5-diphenyl-5H-spiro[furo[2,3-d]pyrimidine-6,4'-pyrazol]-5'(1'H)-one**, yield: 59.2 mg, 74%; white solid; mp 155-156°C; <sup>1</sup>H NMR (500 MHz, Chloroform) δ 8.39 (s, 1H), 7.89-7.87 (m, 2H), 7.46 – 7.39 (m, 5H), 7.28 – 7.10 (m, 4H), 5.12 (s, 1H), 4.95 (s, 2H), 1.53 (s, 3H); <sup>13</sup>C NMR (125 MHz, D

MSO):  $\delta$  174.6, 171.1, 164.1, 162.8, 161.1, 137.3, 135.4, 129.2( $\times 4$ ), 128.1, 125.5, 118.6( $\times 4$ ), 88.3, 82.2, 51.9, 21.4, 9.0. HRMS (ESI+) calcd for  $[\text{C}_{22}\text{H}_{20}\text{N}_6\text{O}_2 + \text{Na}]^+$   $m/z$  423.1540, found 423.1548.

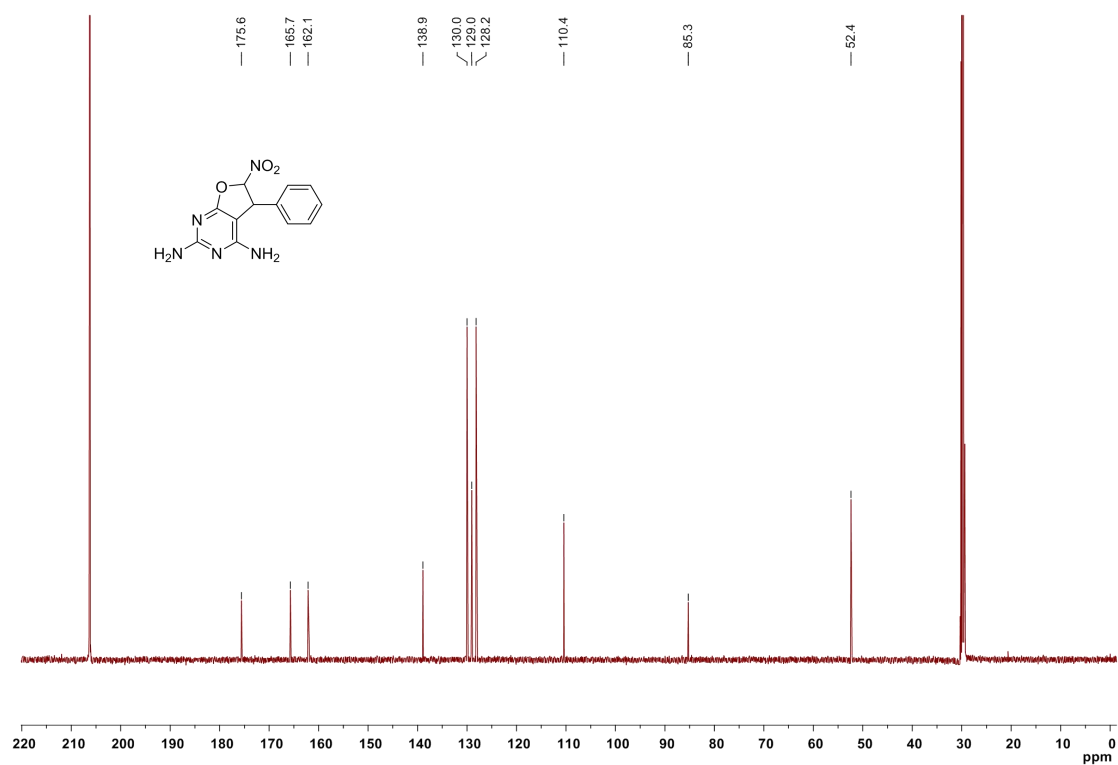
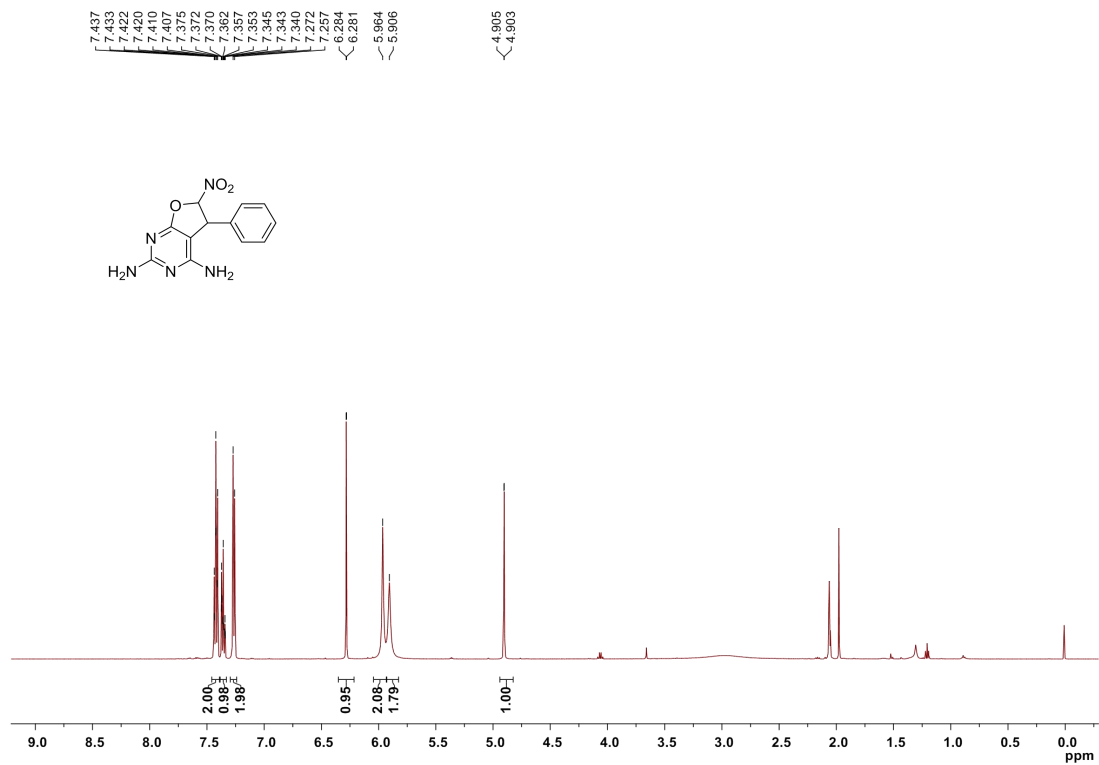


***4-amino-3'-methyl-1',5-diphenyl-5H-spiro[furo[2,3-d]pyrimidine-6,***

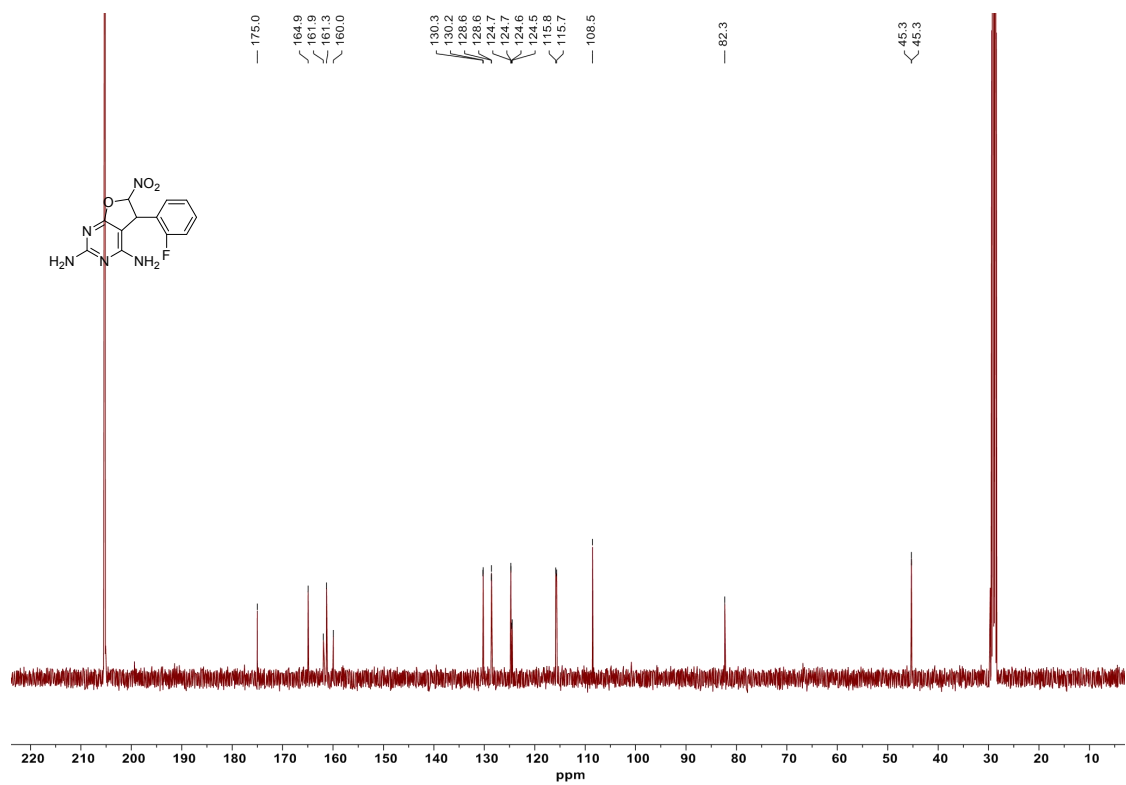
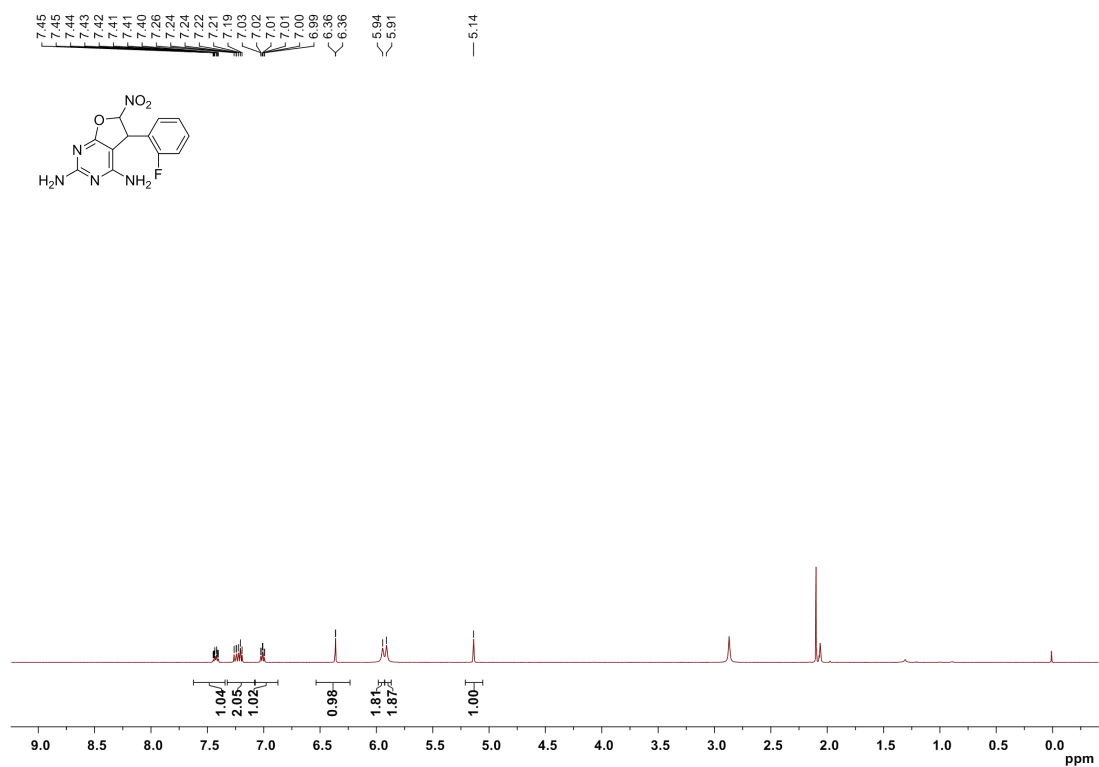
***4'-pyrazol]-5'(1H)-one***, yield: 22 mg, 30%; yellow oil;  $^1\text{H}$  NMR (500 MHz, Chloroform):  $\delta$  8.39 (s, 1H), 7.89 – 7.87 (m, 2H), 7.46 – 7.39 (m, 5H), 7.28 – 7.10 (m, 3H), 5.12 (s, 1H), 4.95 (s, 2H), 1.53 (s, 3H).;  $^{13}\text{C}$  NMR (125 MHz, Chloroform):  $\delta$  174.0, 170.3, 160.0, 159.5, 157.7, 137.4, 131.8, 129.4( $\times 4$ ), 129.0, 125.8, 118.9( $\times 4$ ), 67.1, 52.7, 41.0, 14.2. HRMS (ESI+) calcd for  $[\text{C}_{21}\text{H}_{17}\text{N}_5\text{O}_2 + \text{Na}]^+$   $m/z$  394.1274, found 394.1278.

### 3. NMR spectra

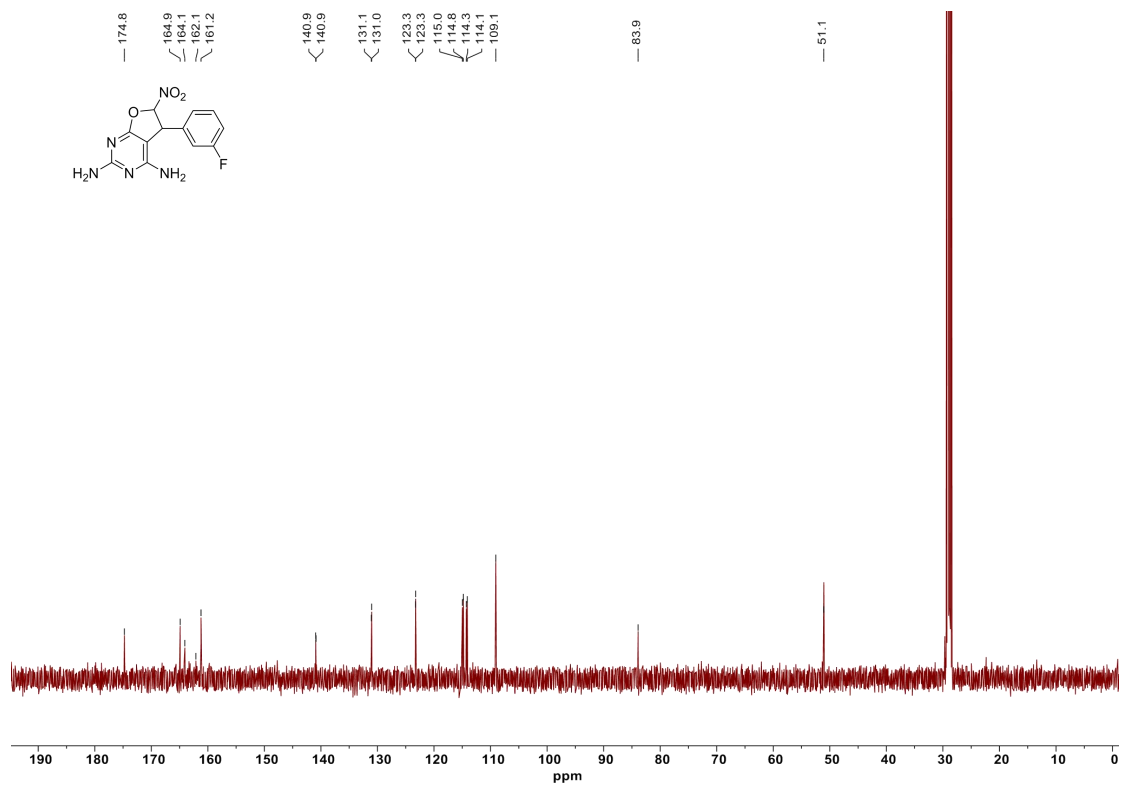
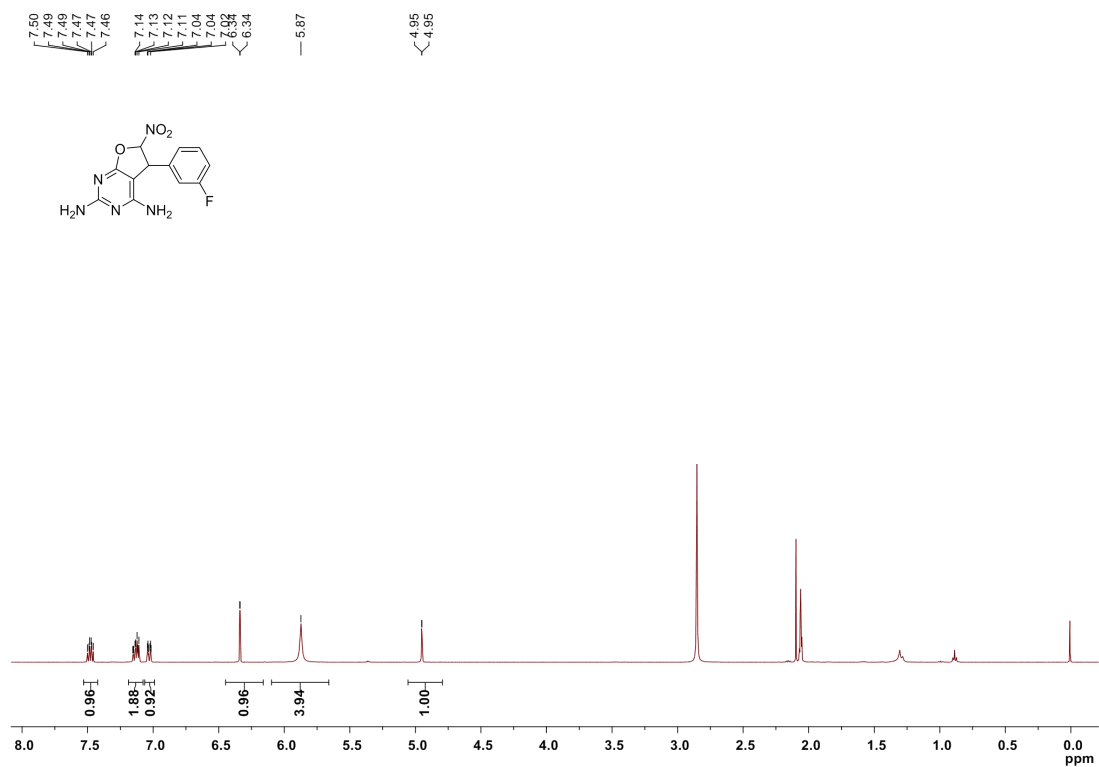
#### Compound 3a



# Compound 3b

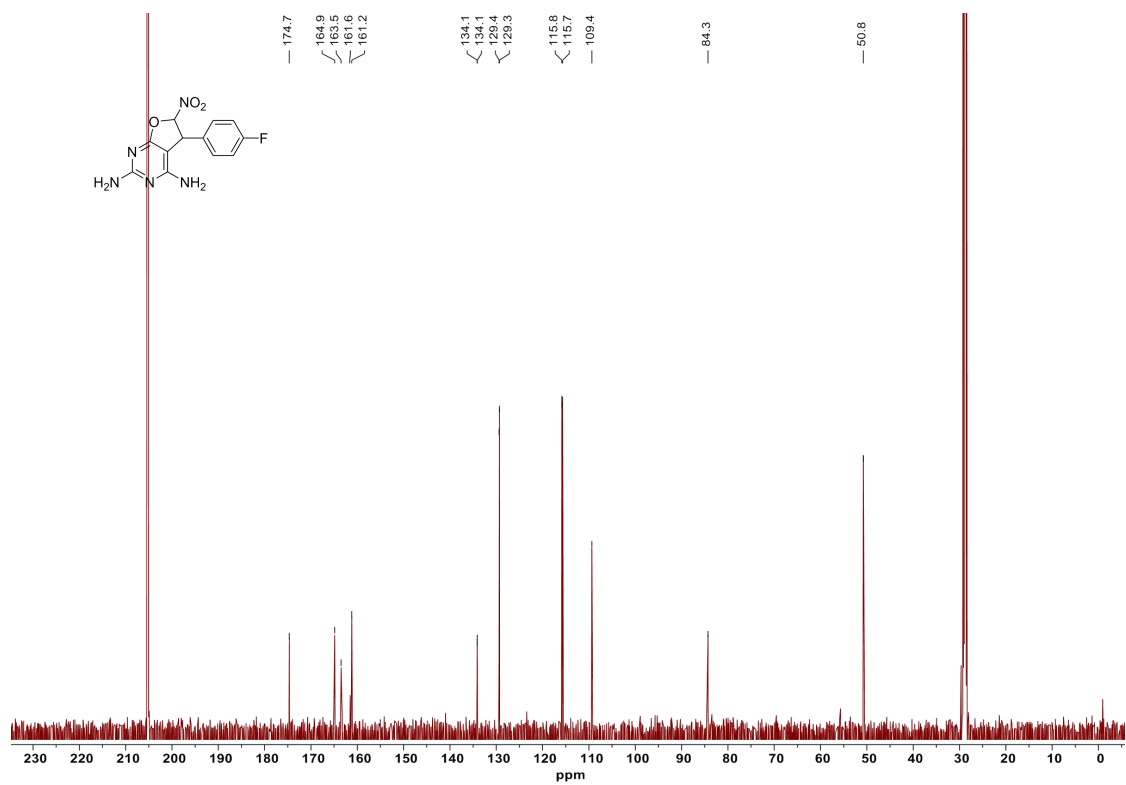
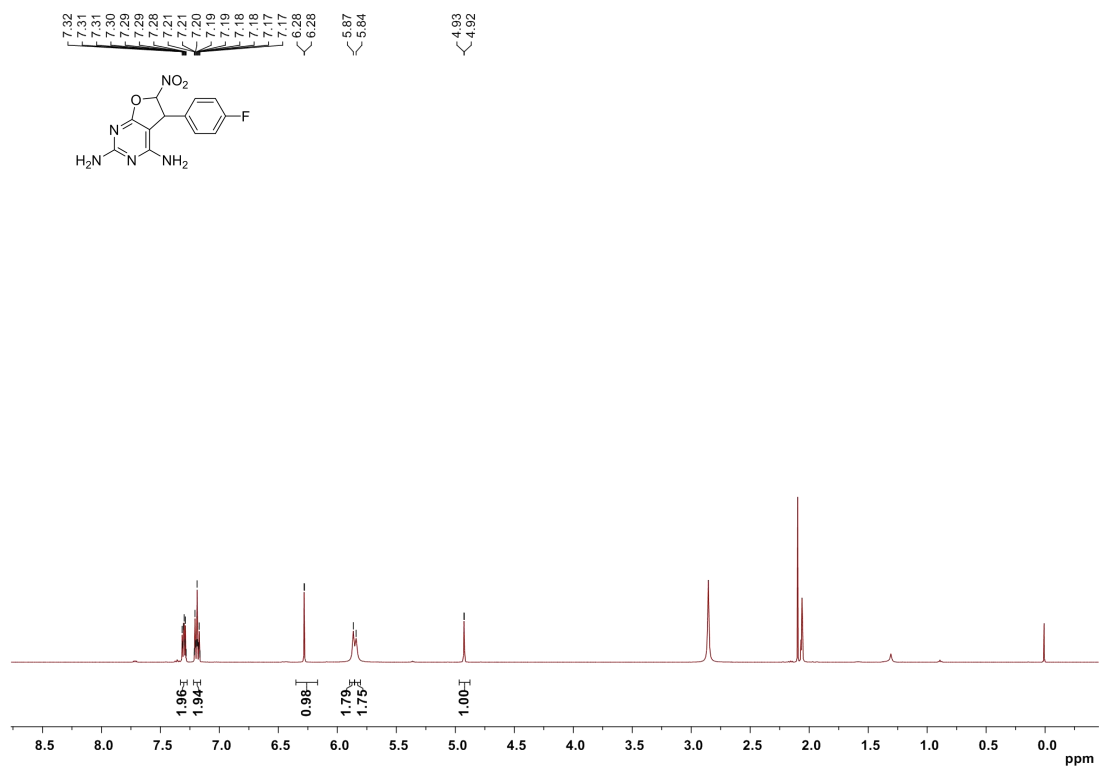


# Compound 3c

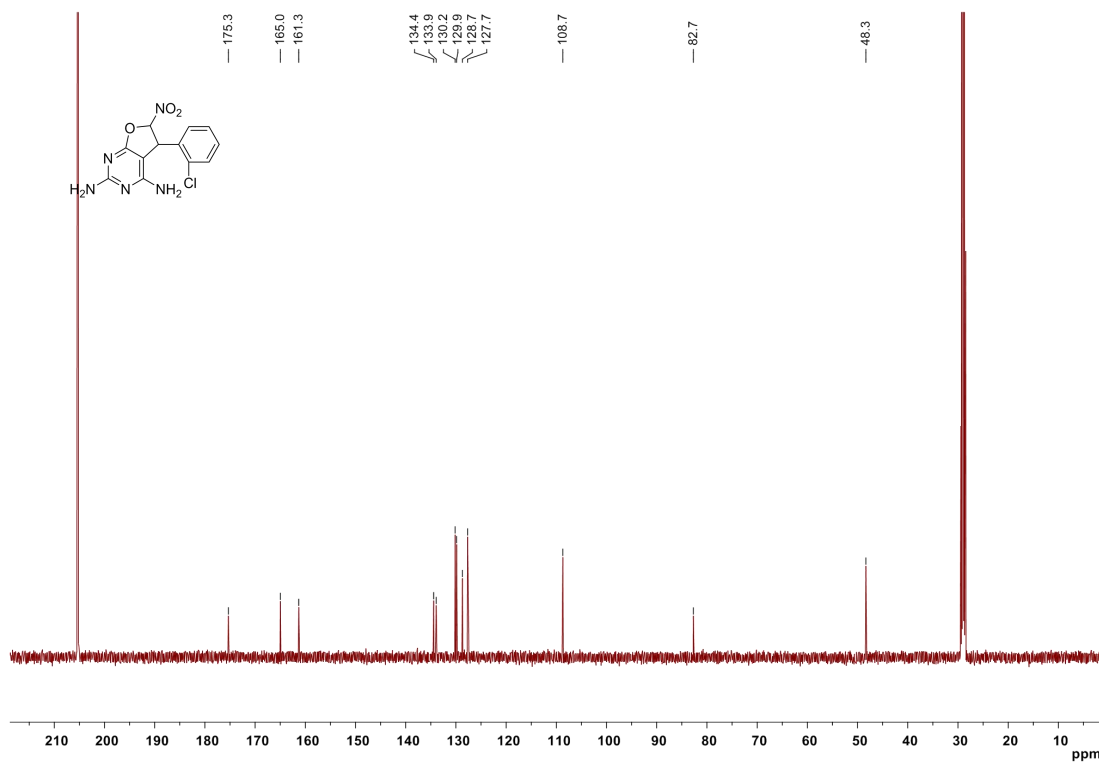
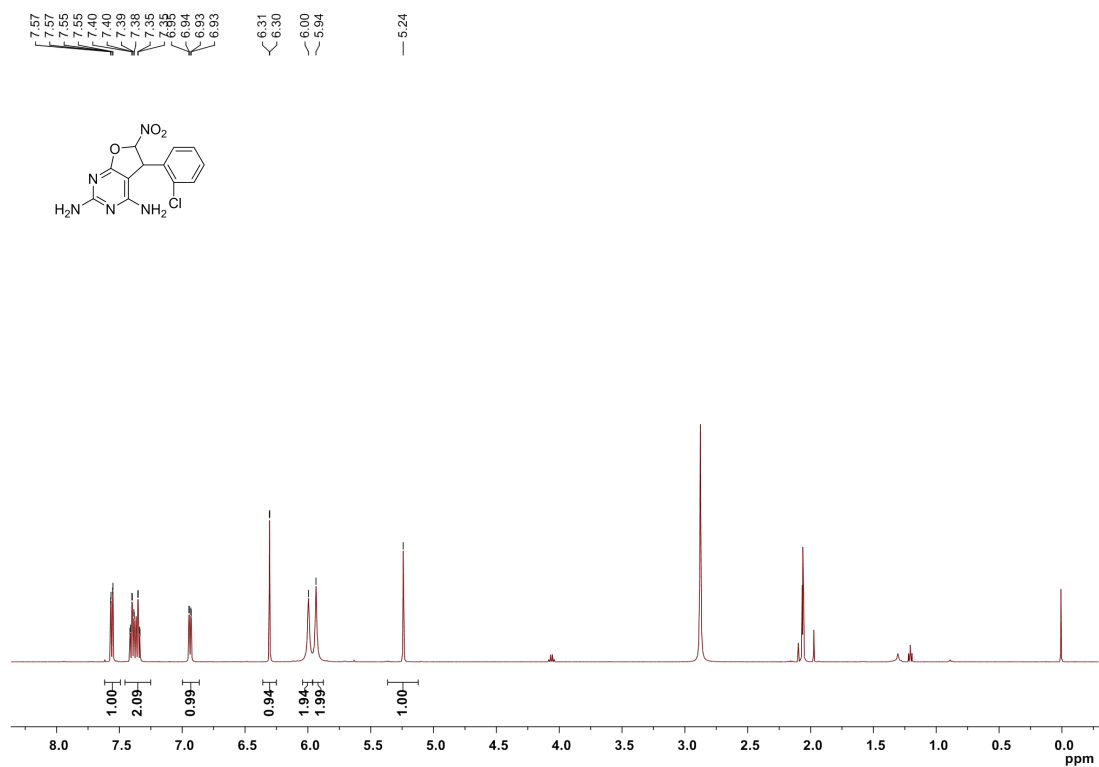




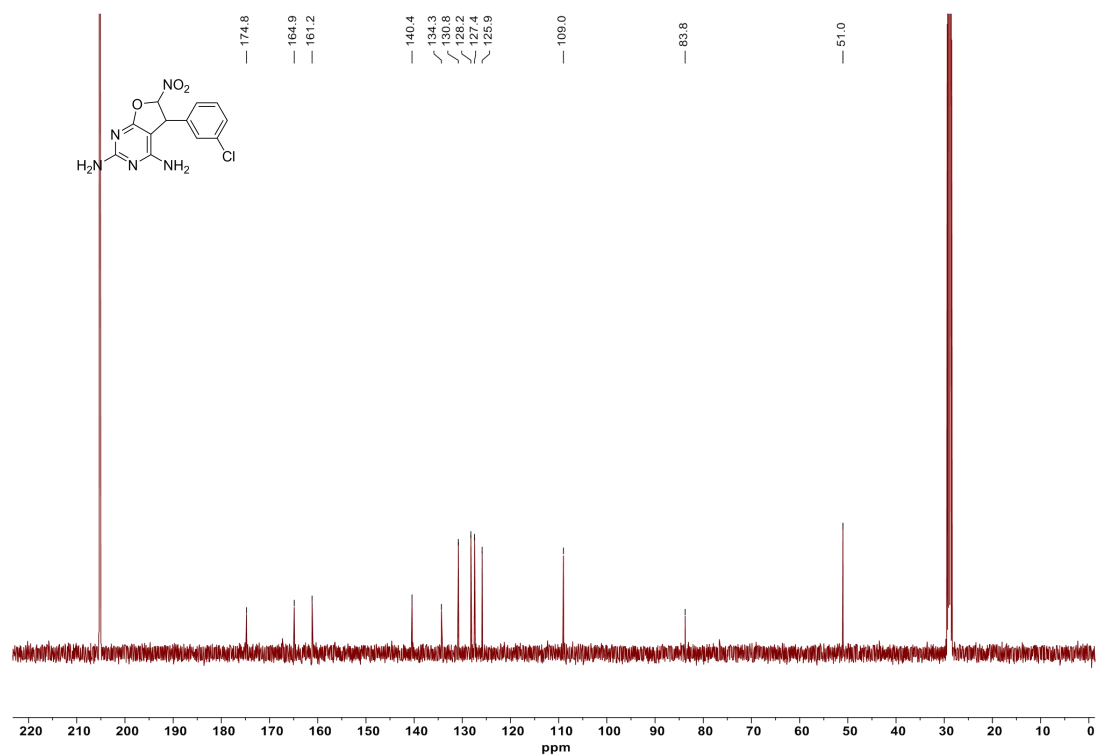
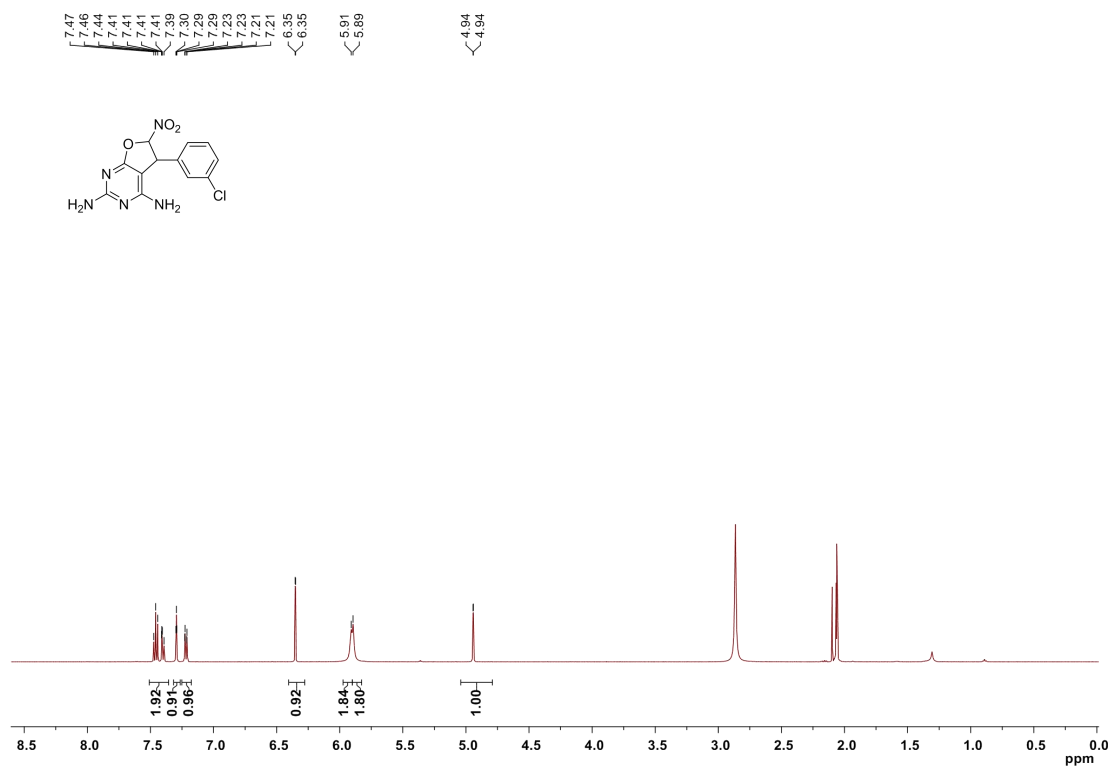
# Compound 3d



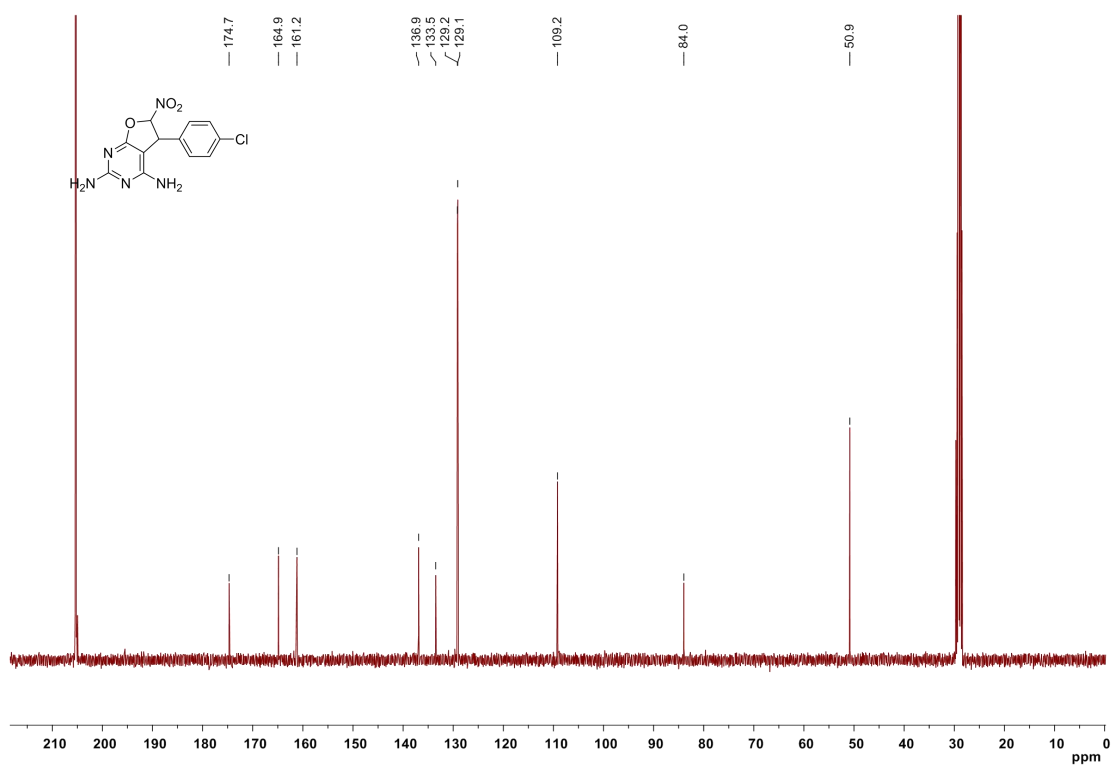
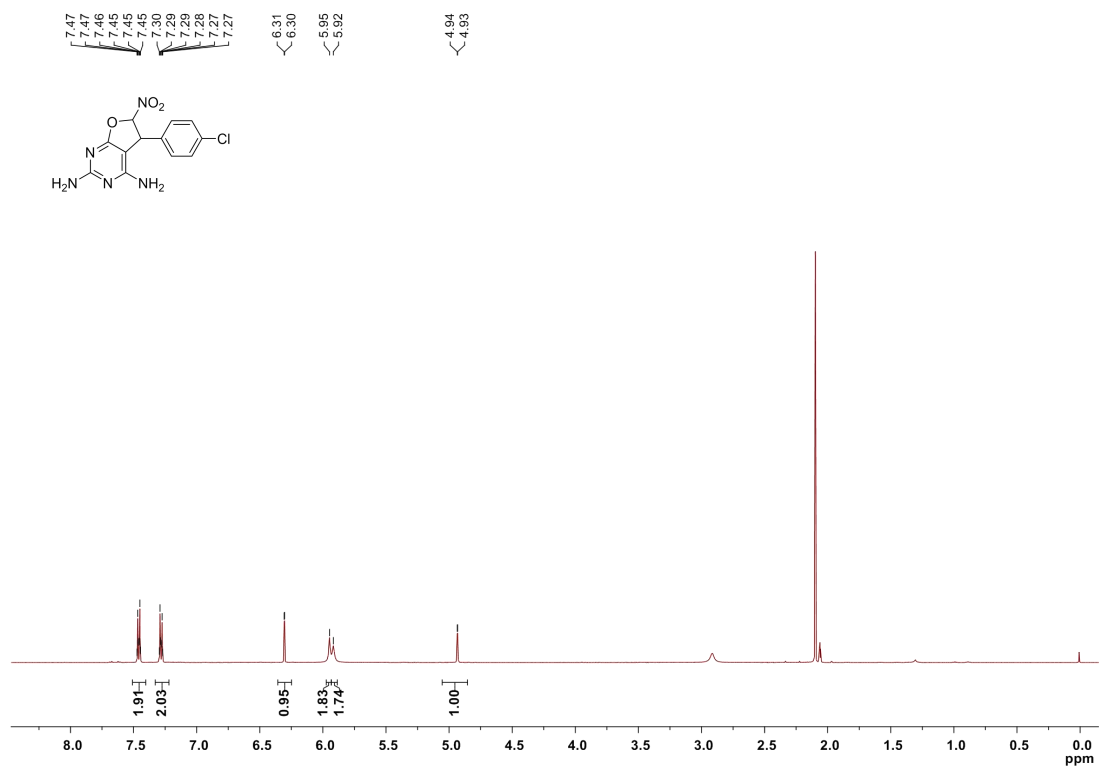
# Compound 3e



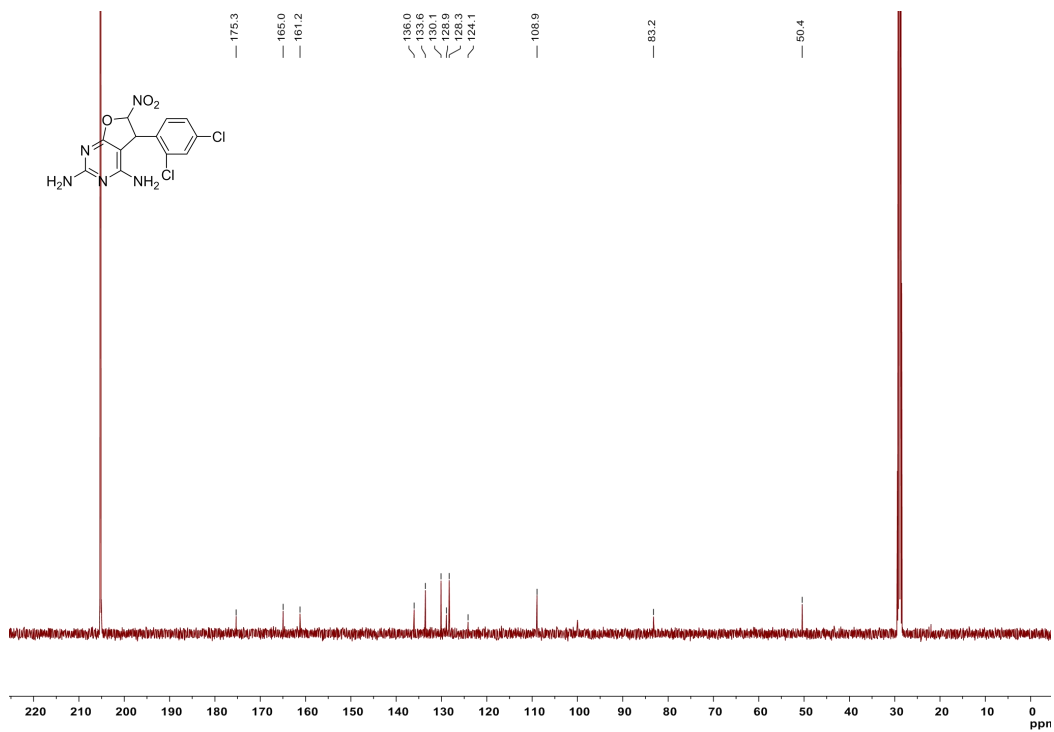
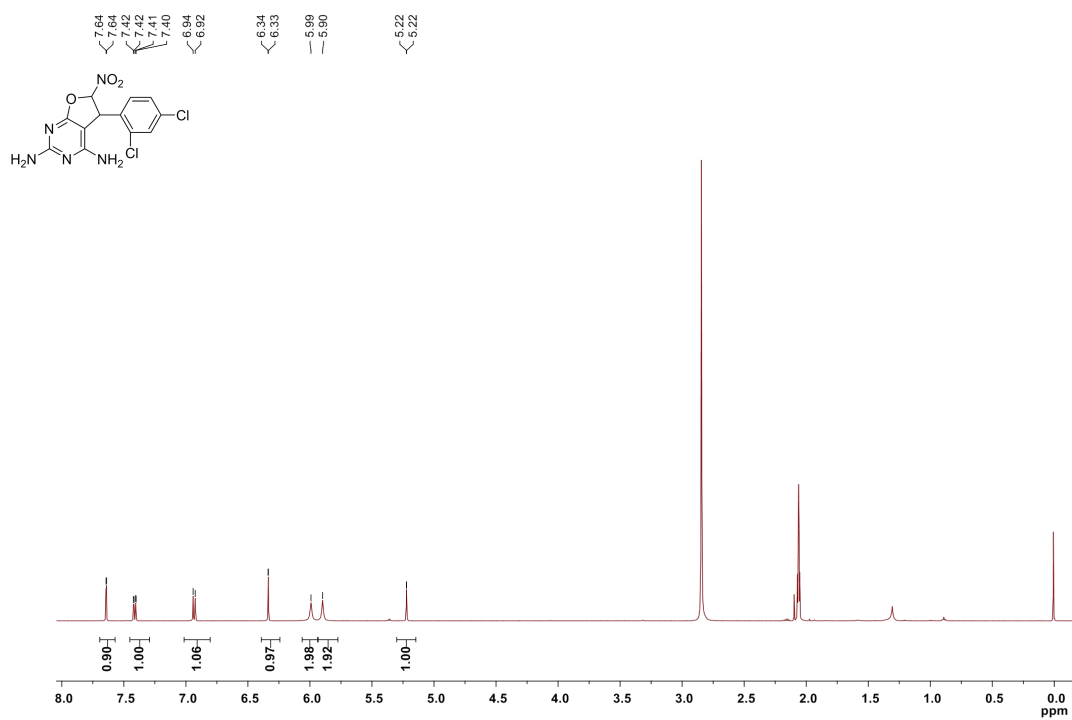
# Compound 3f



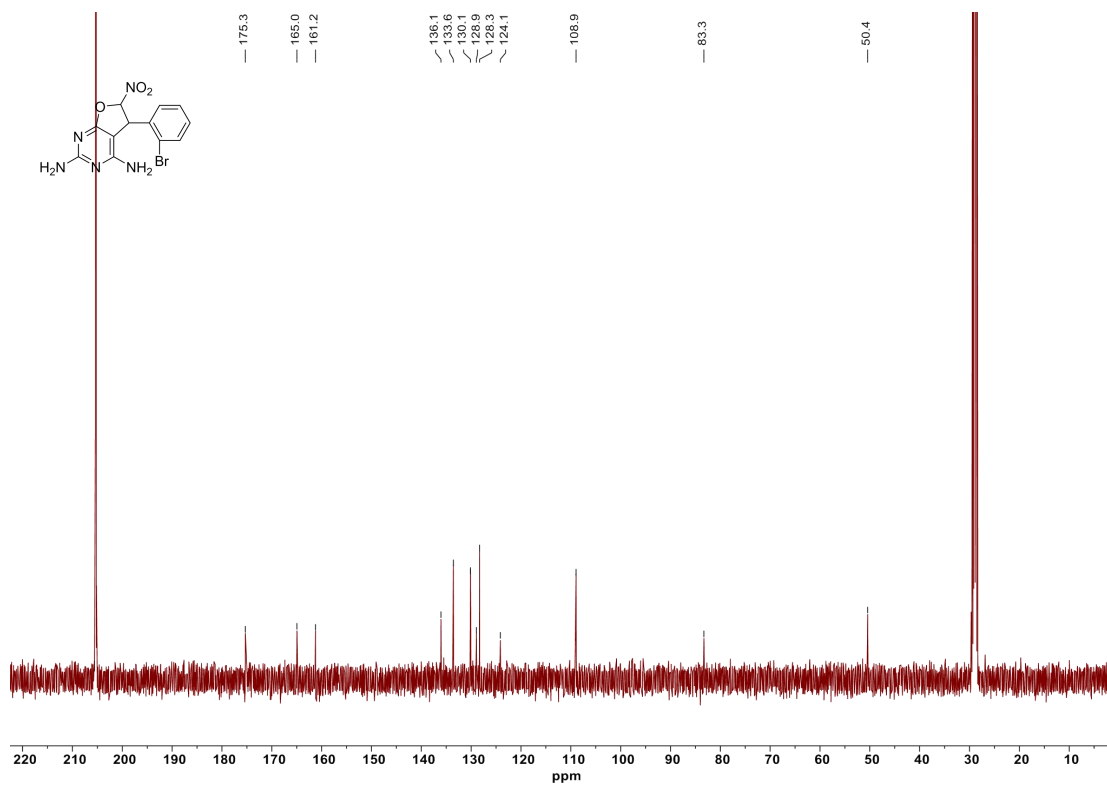
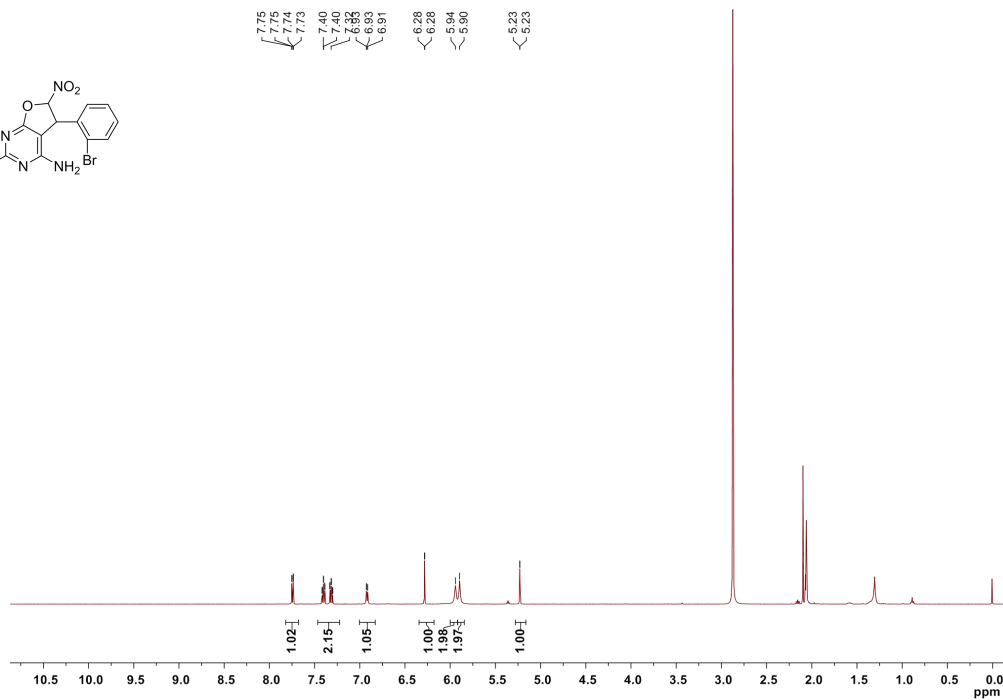
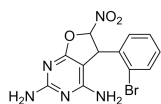
# Compound 3g



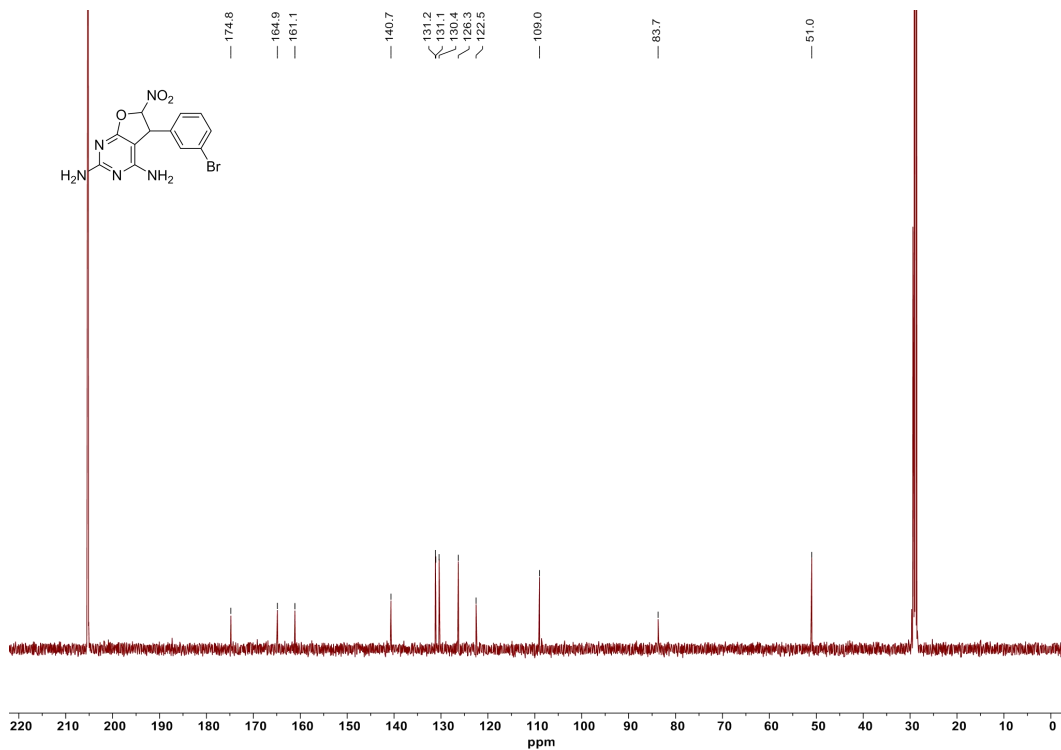
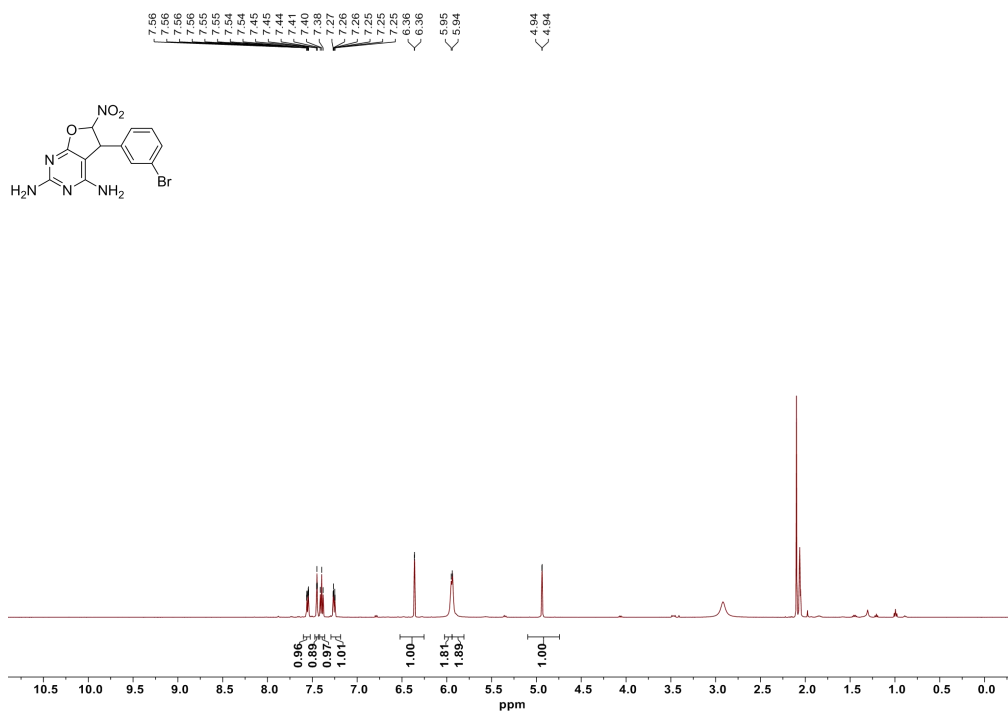
# Compound 3h



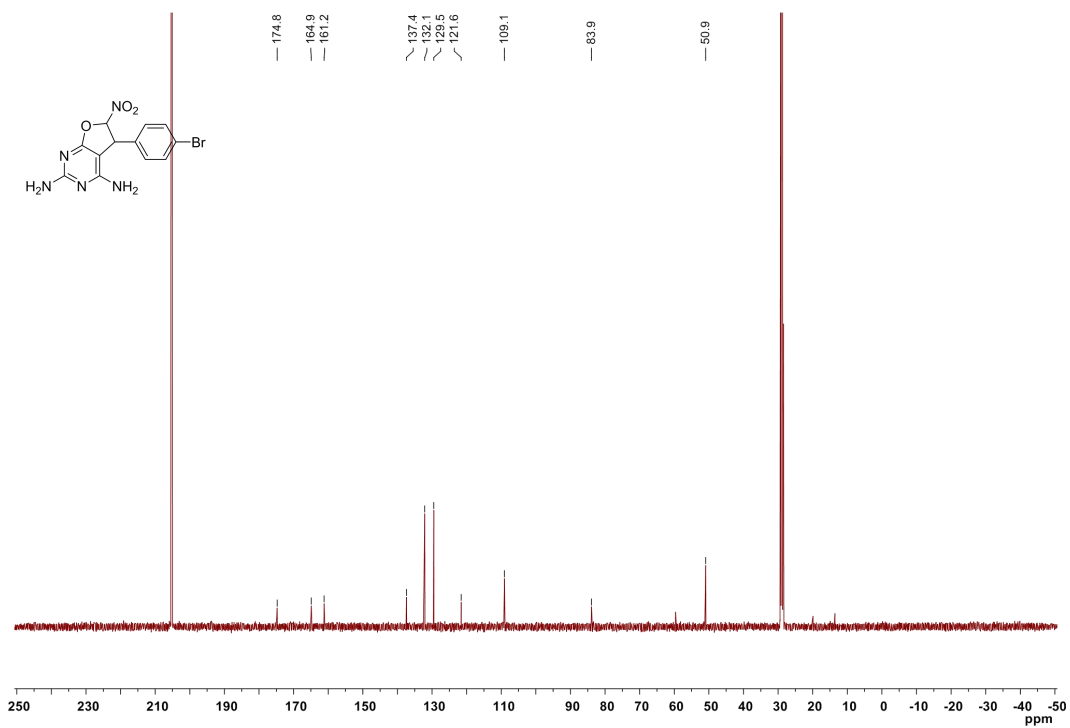
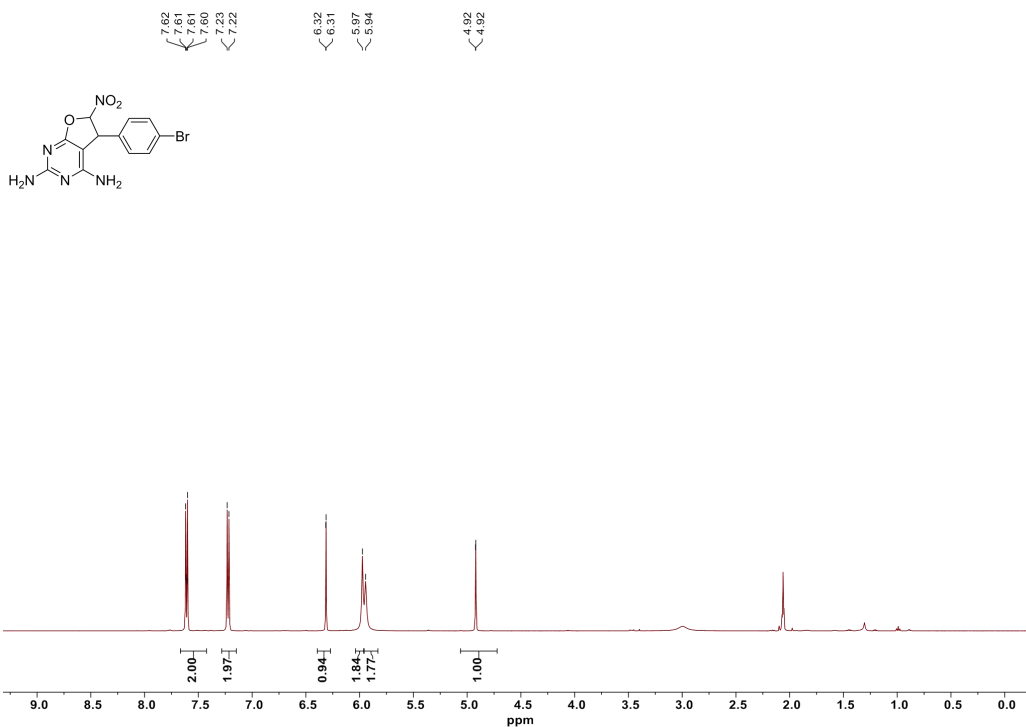
# Compound 3i



# Compound 3j

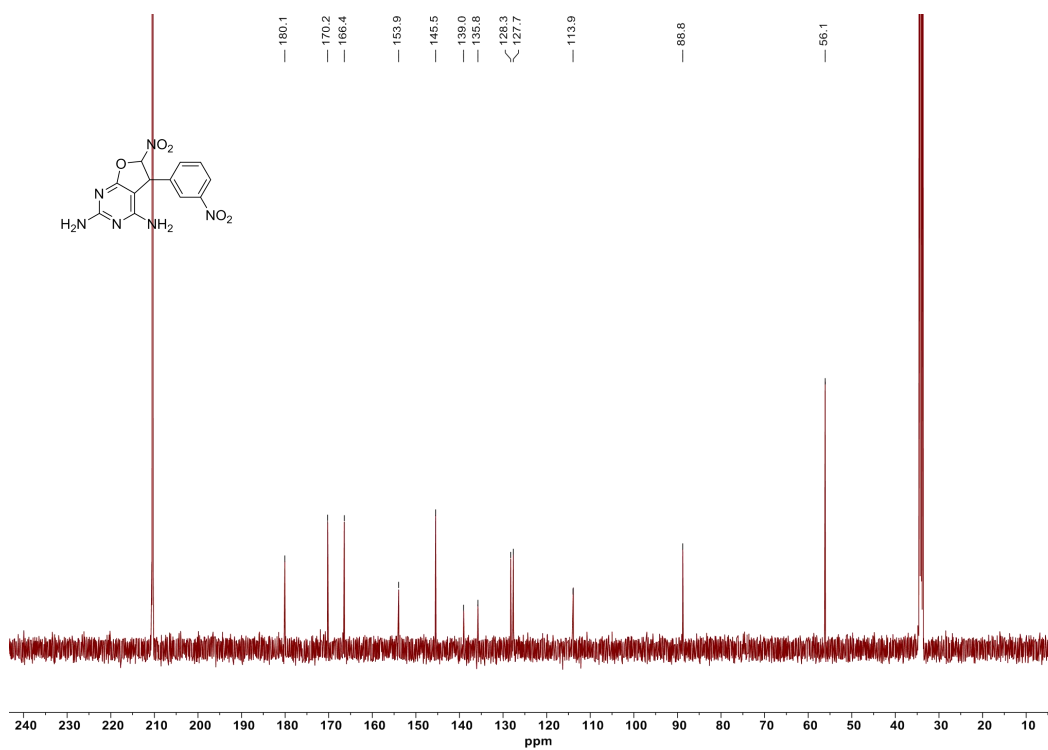
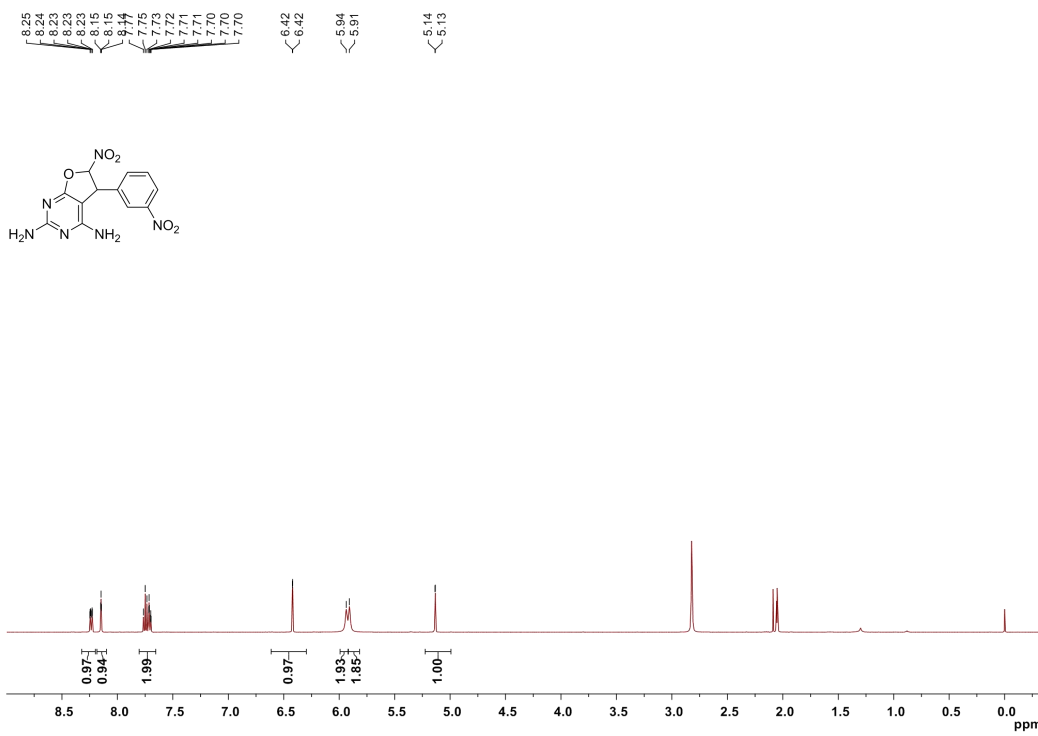


# Compound 3k

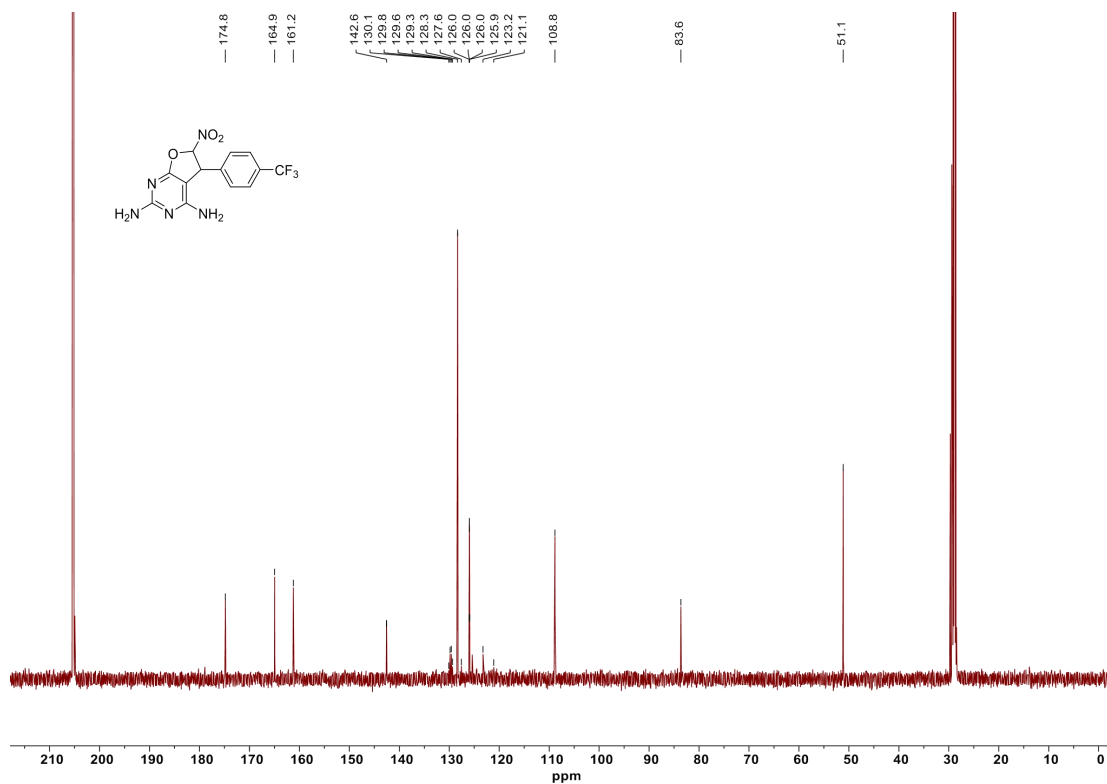
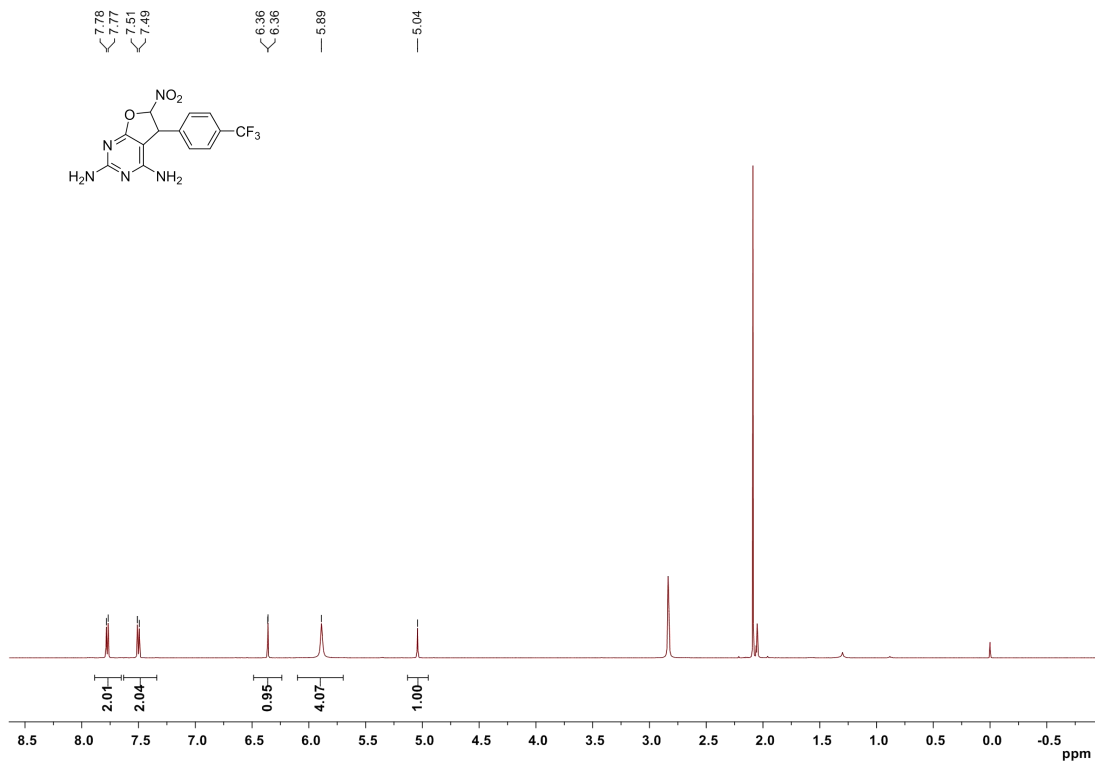




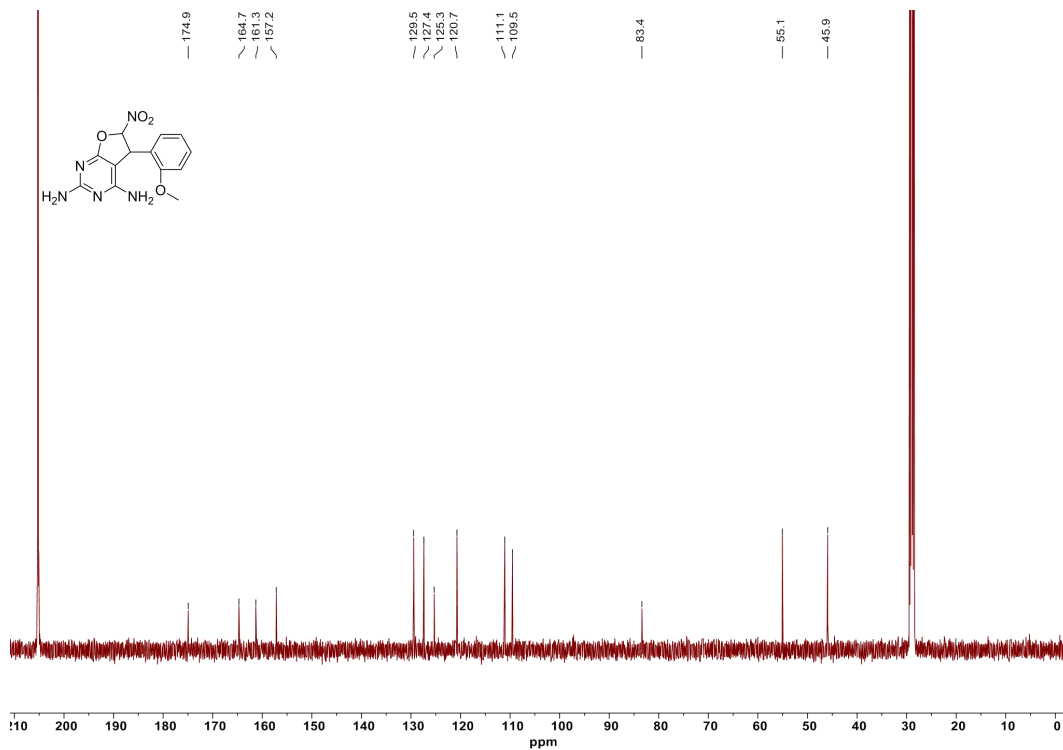
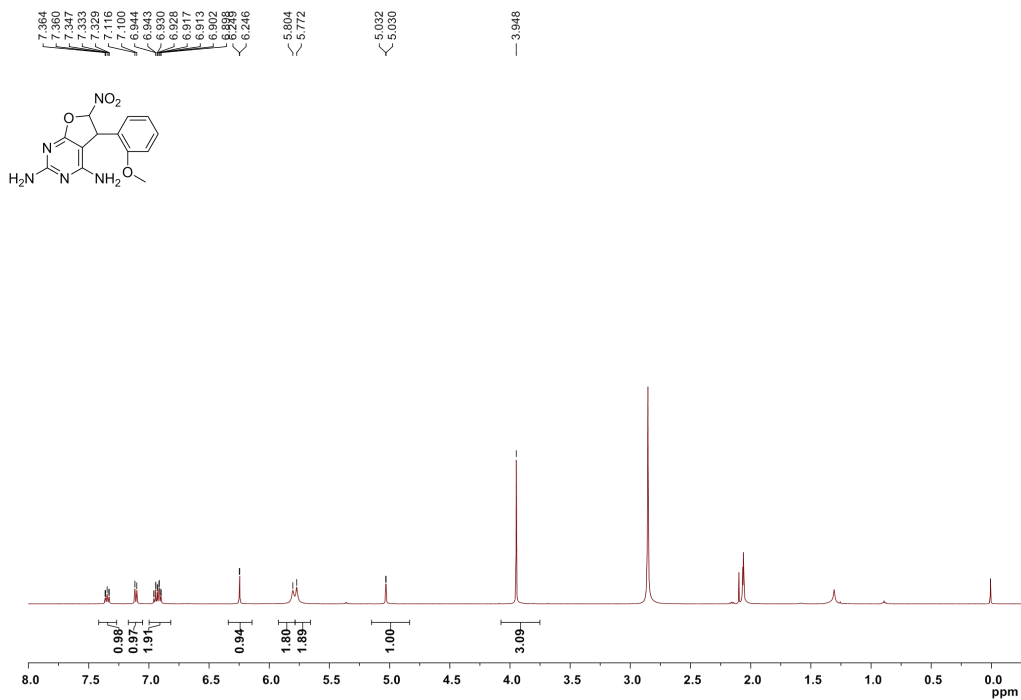
# Compound 31



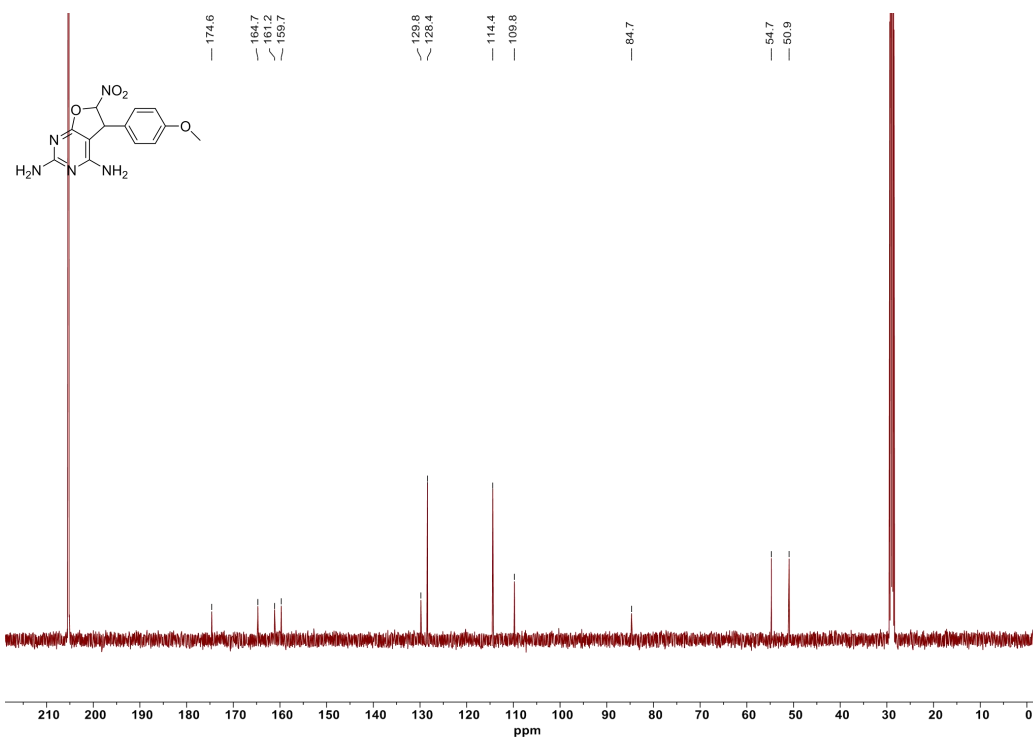
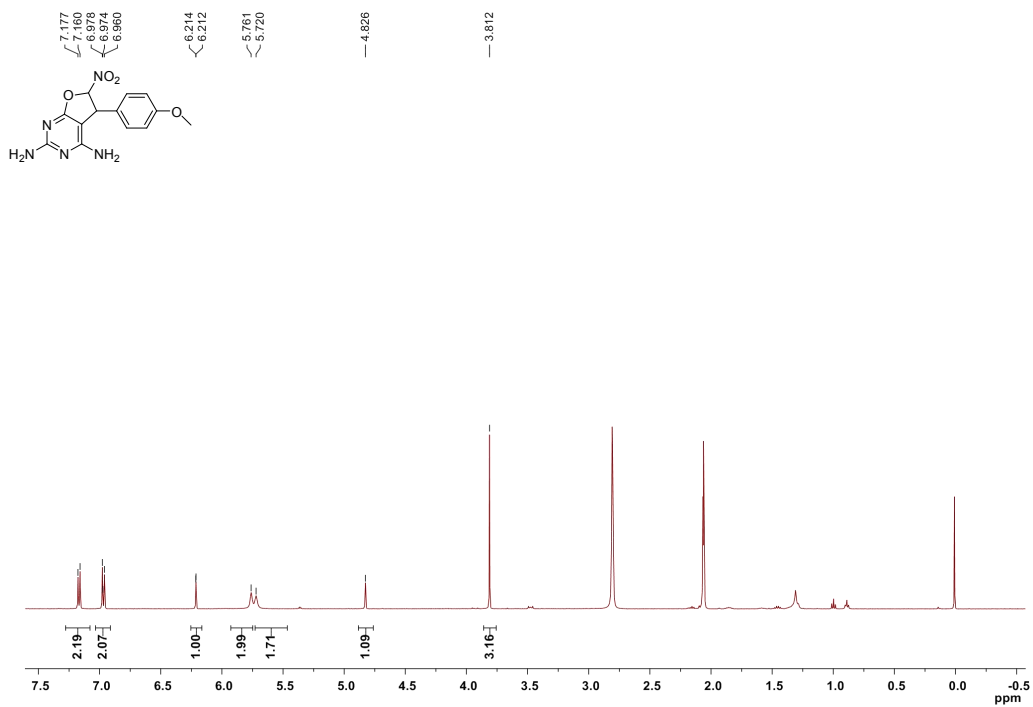
# Compound 3m



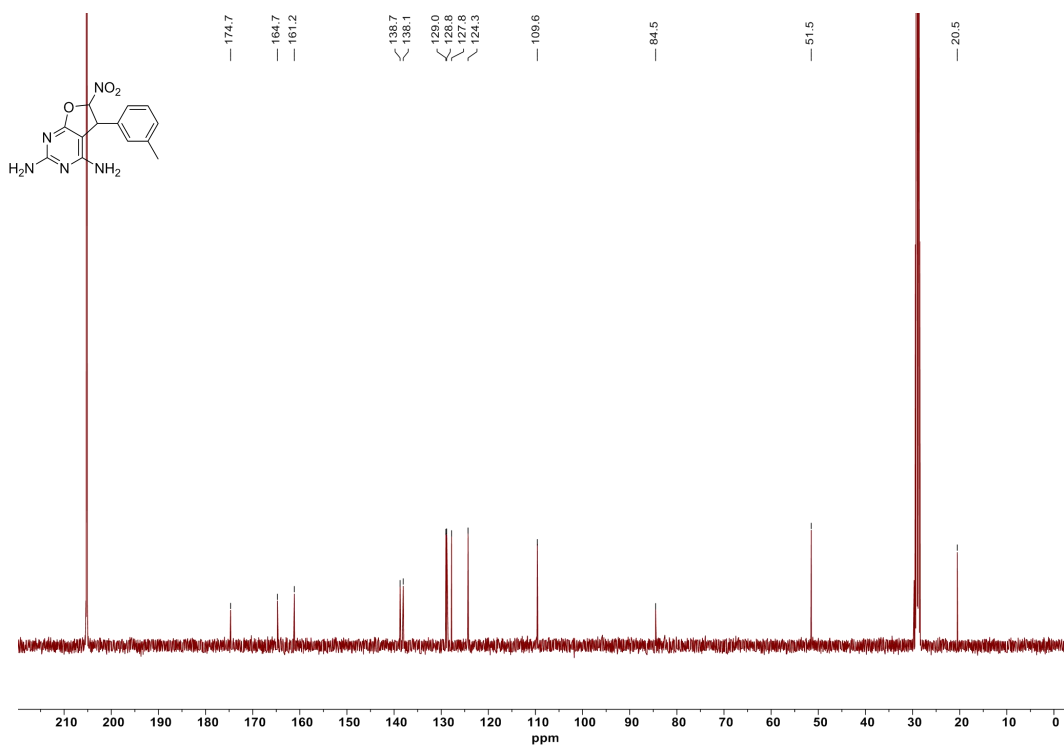
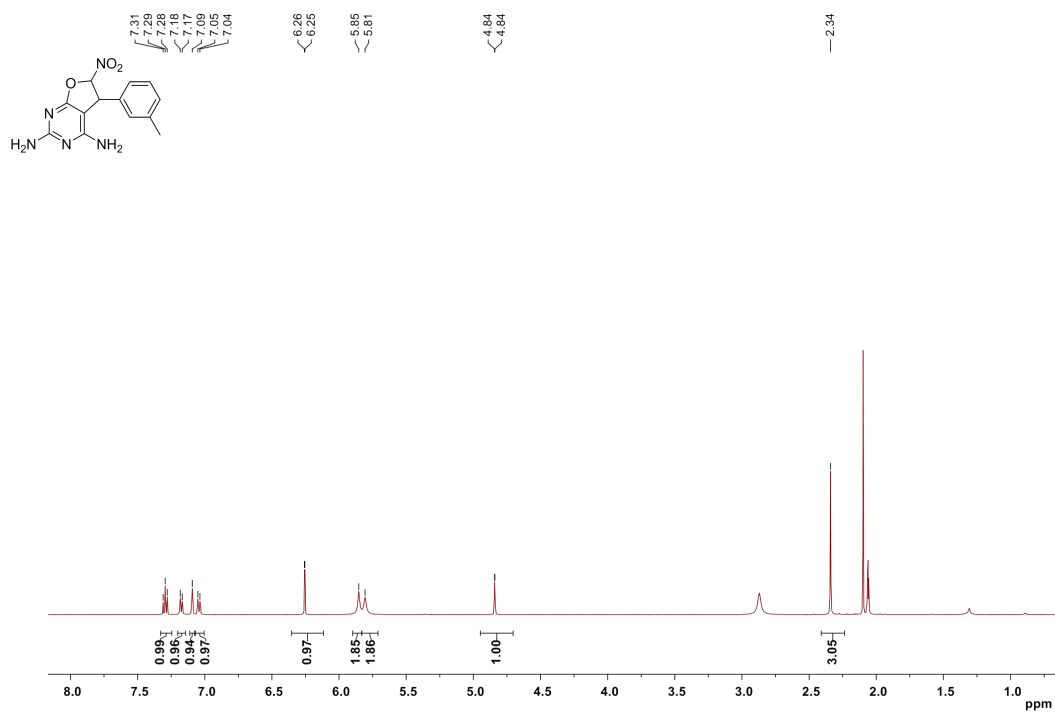
# Compound 3n



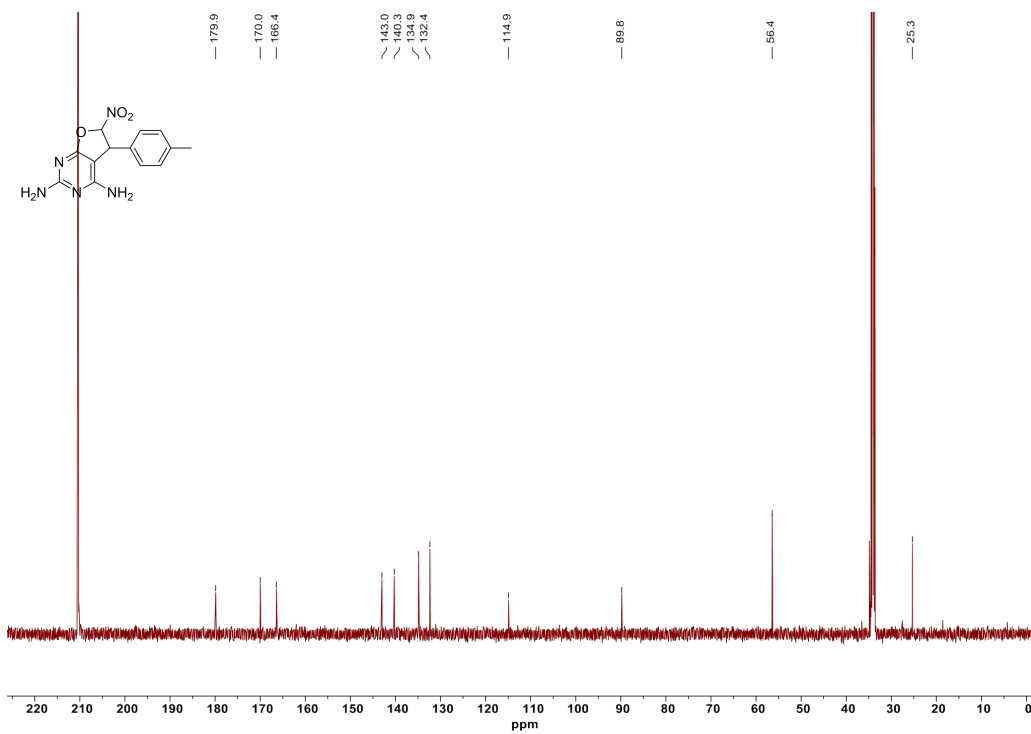
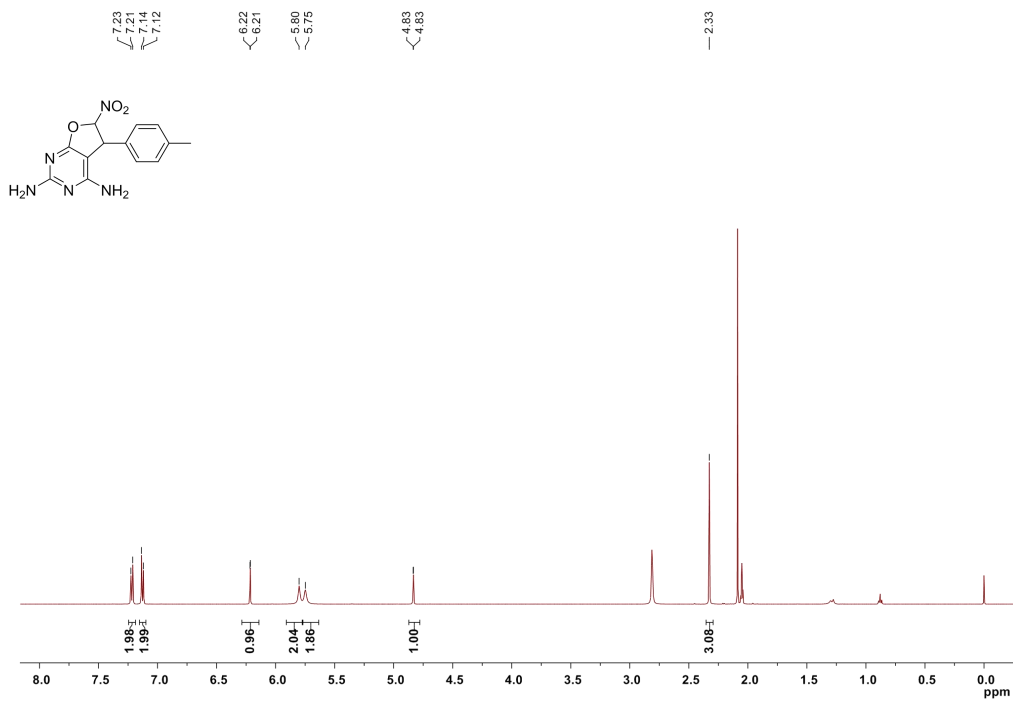
# Compound 3o



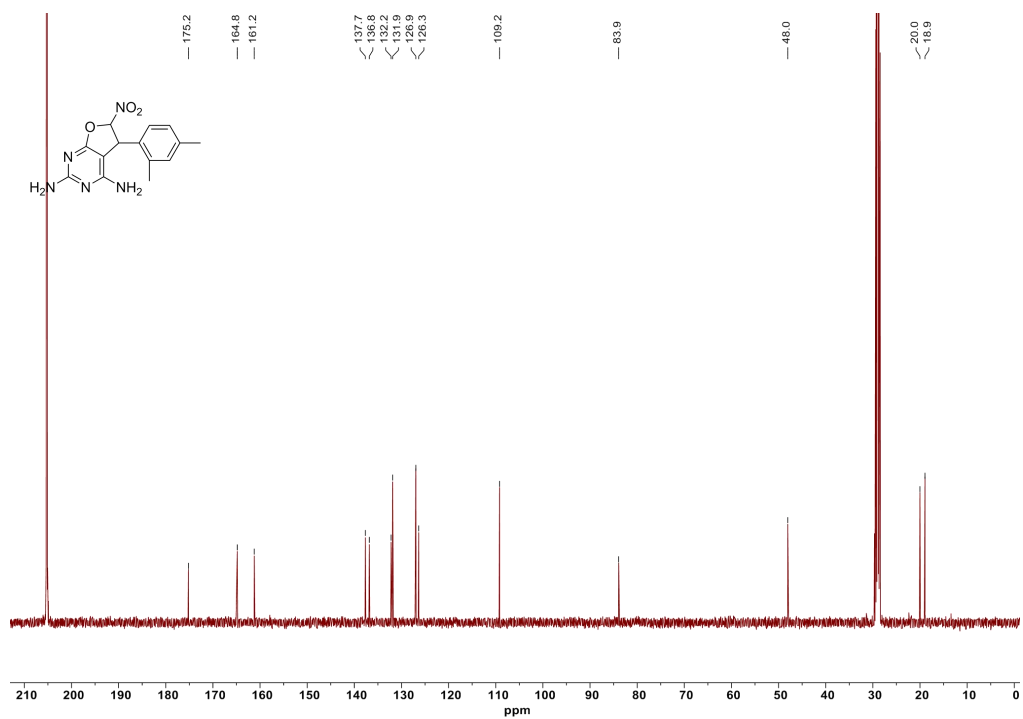
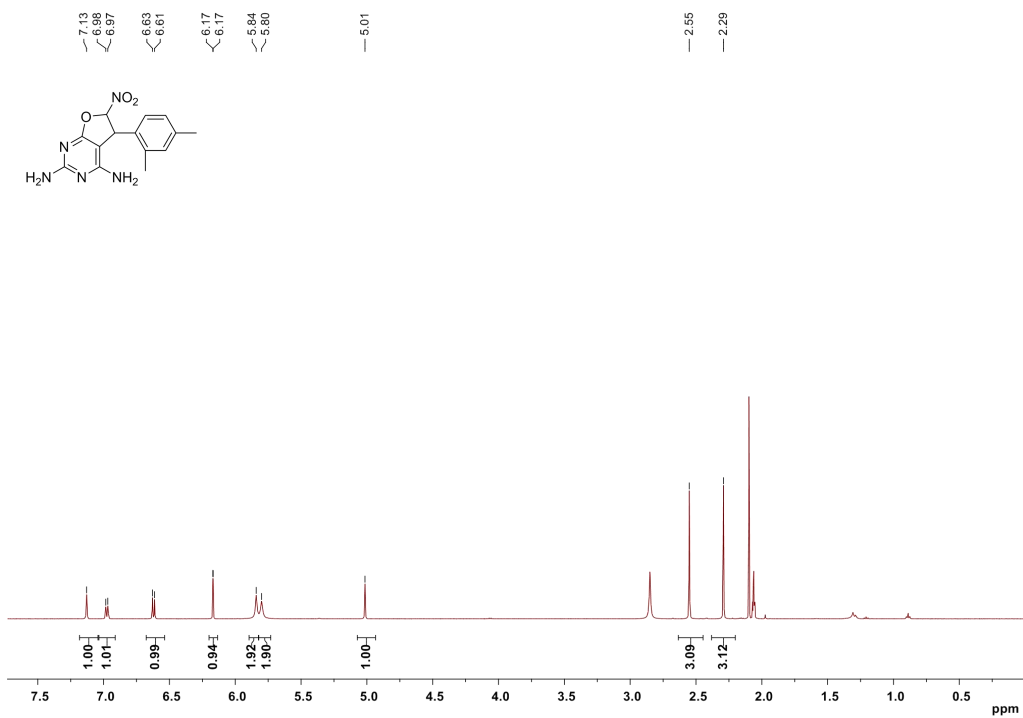
# Compound 3p



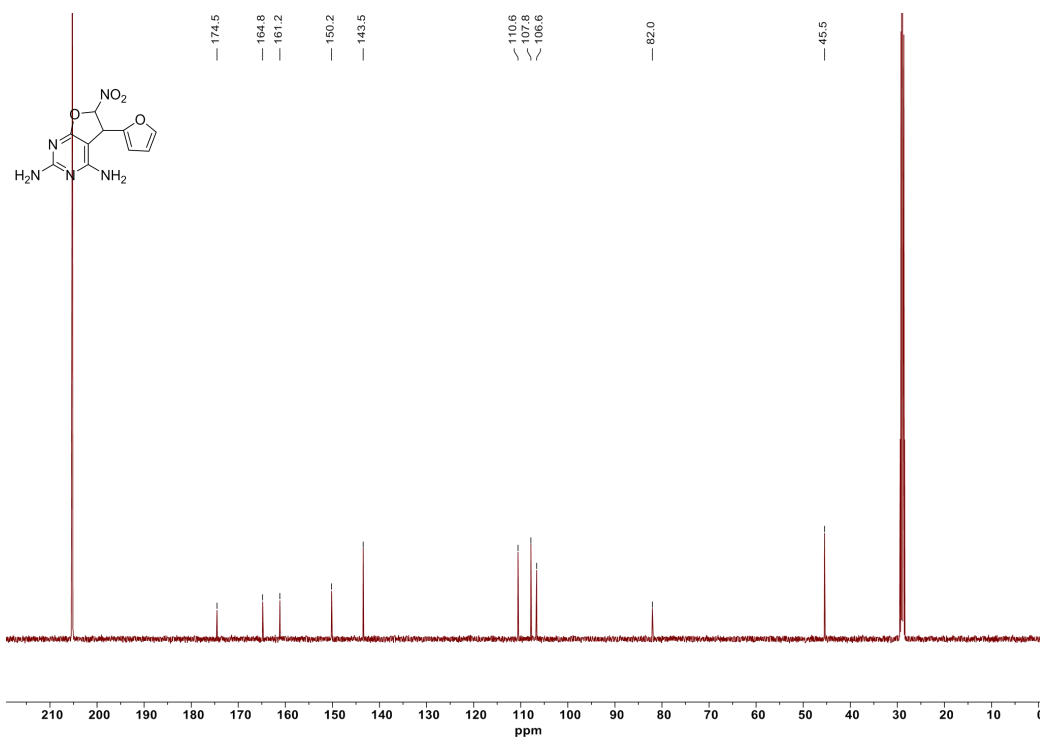
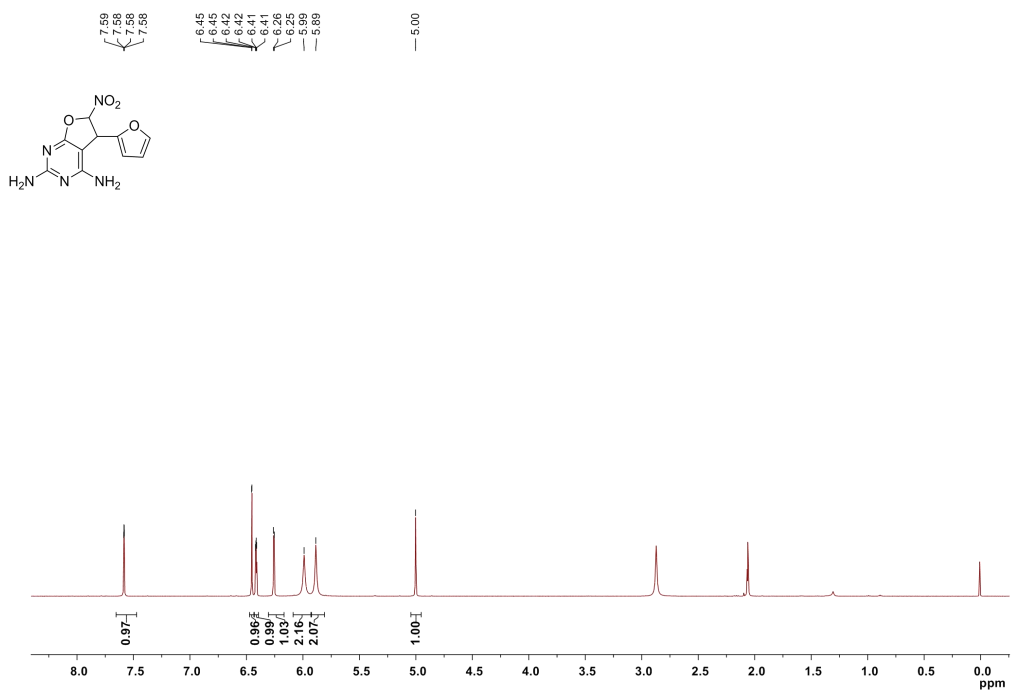
# Compound 3q



# Compound 3r

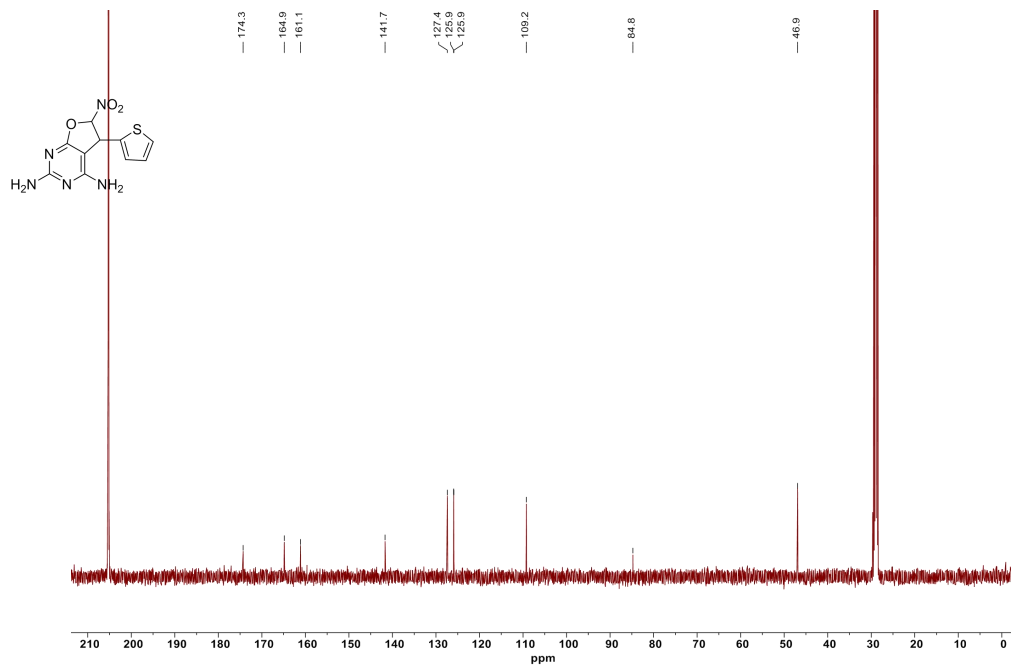
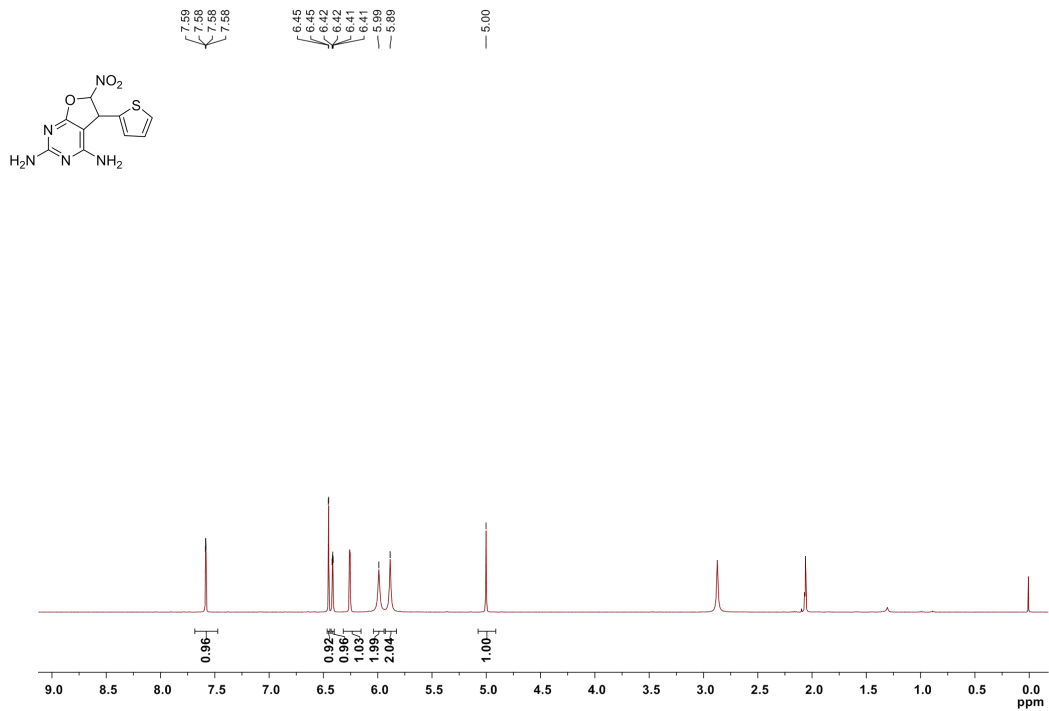


# Compound 3s

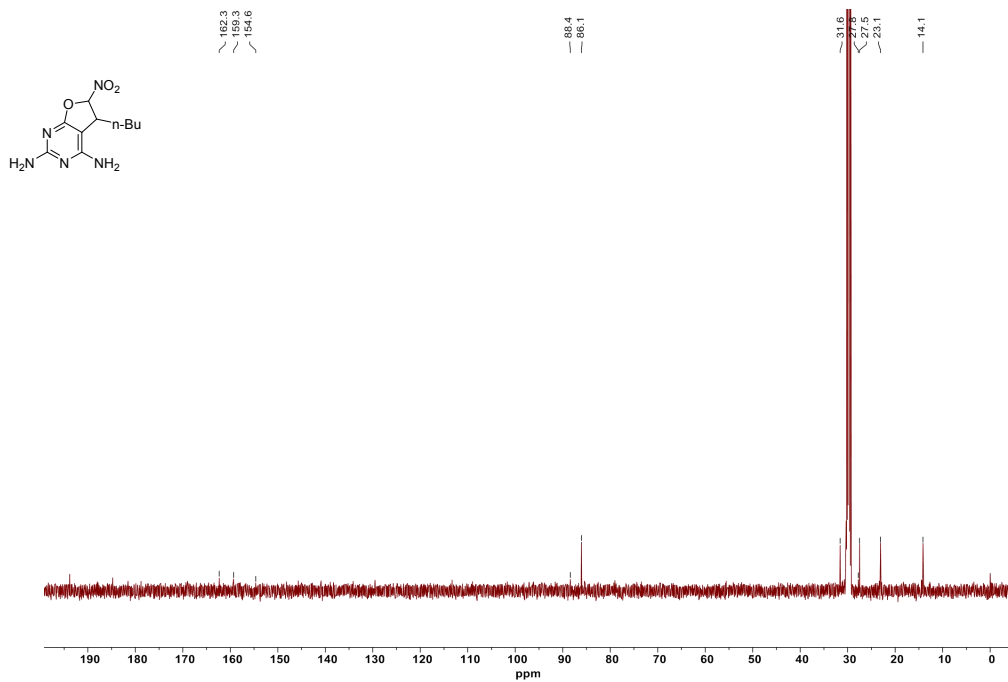
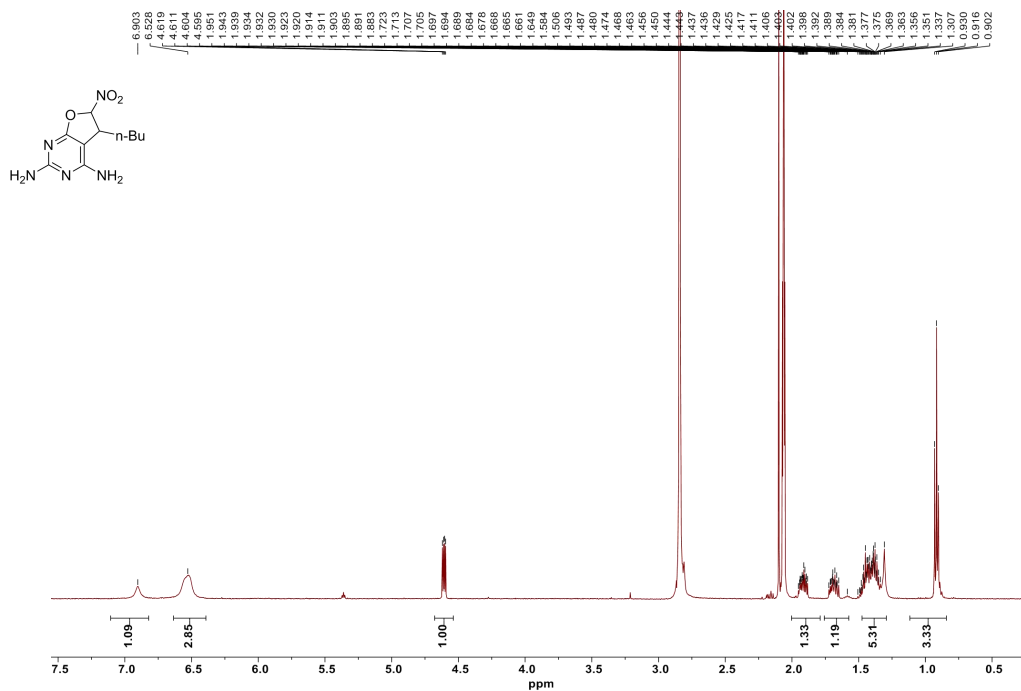




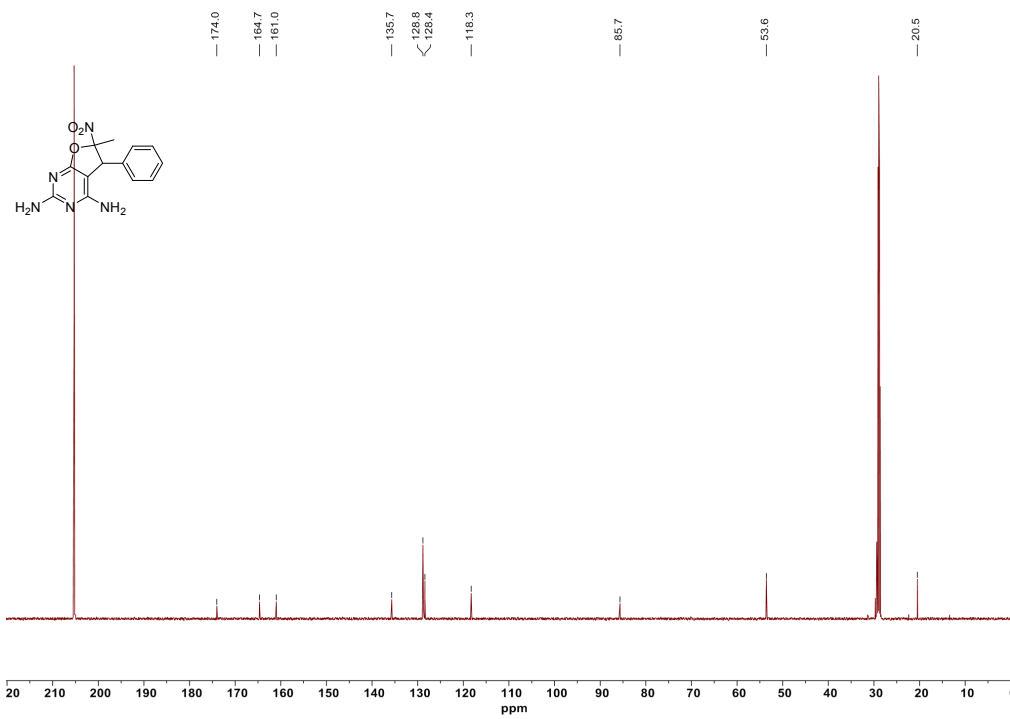
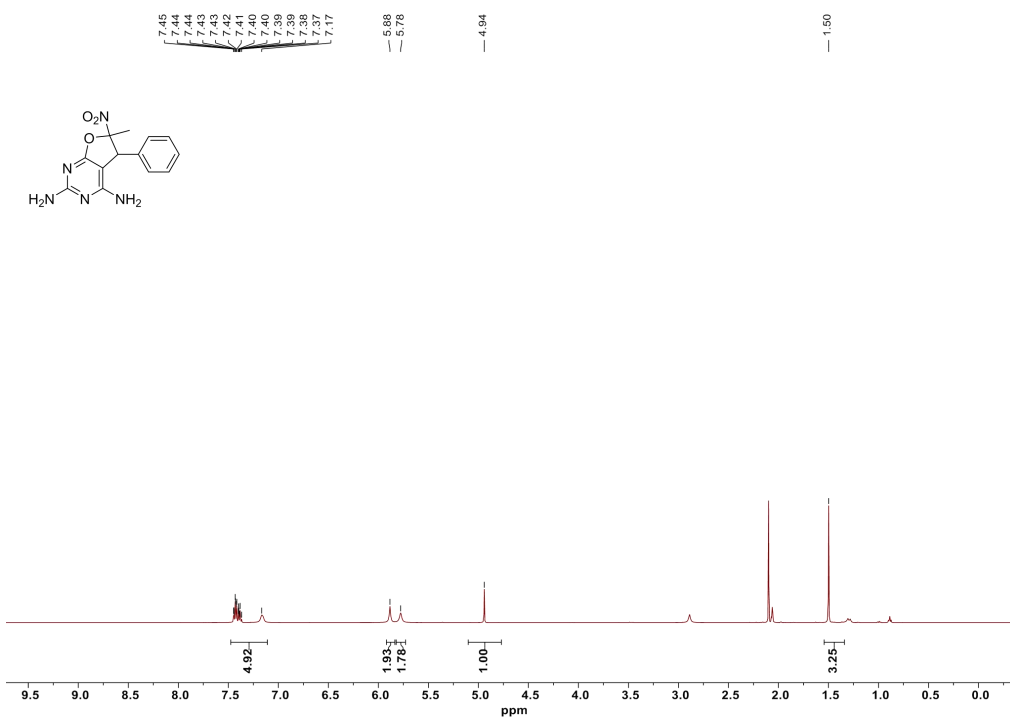
# Compound 3t



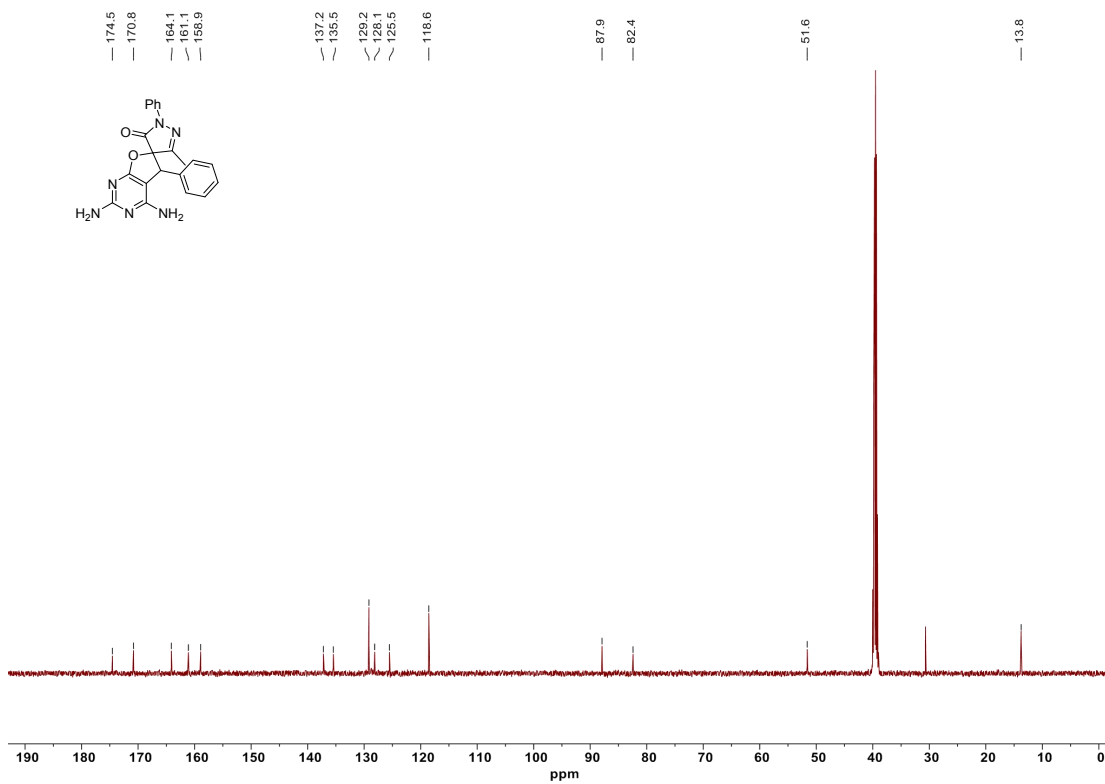
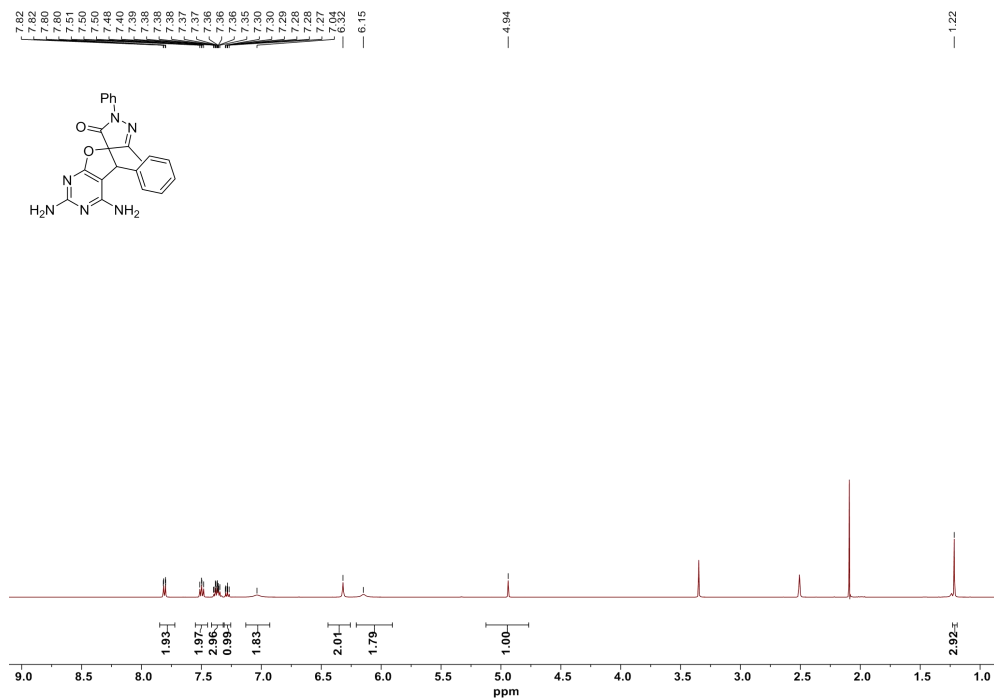
# Compound 3u



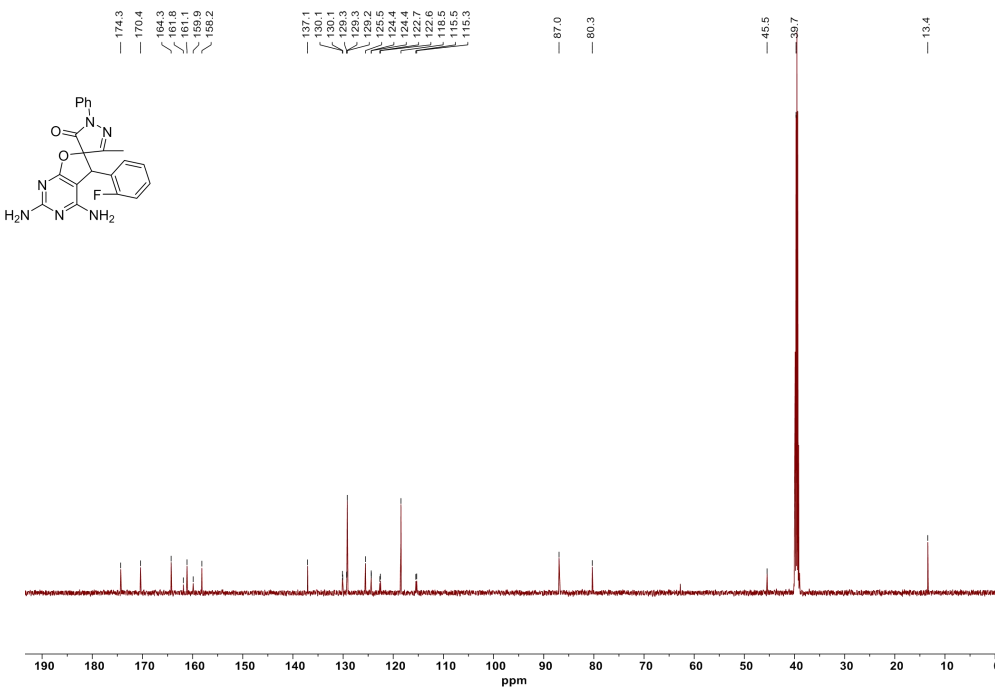
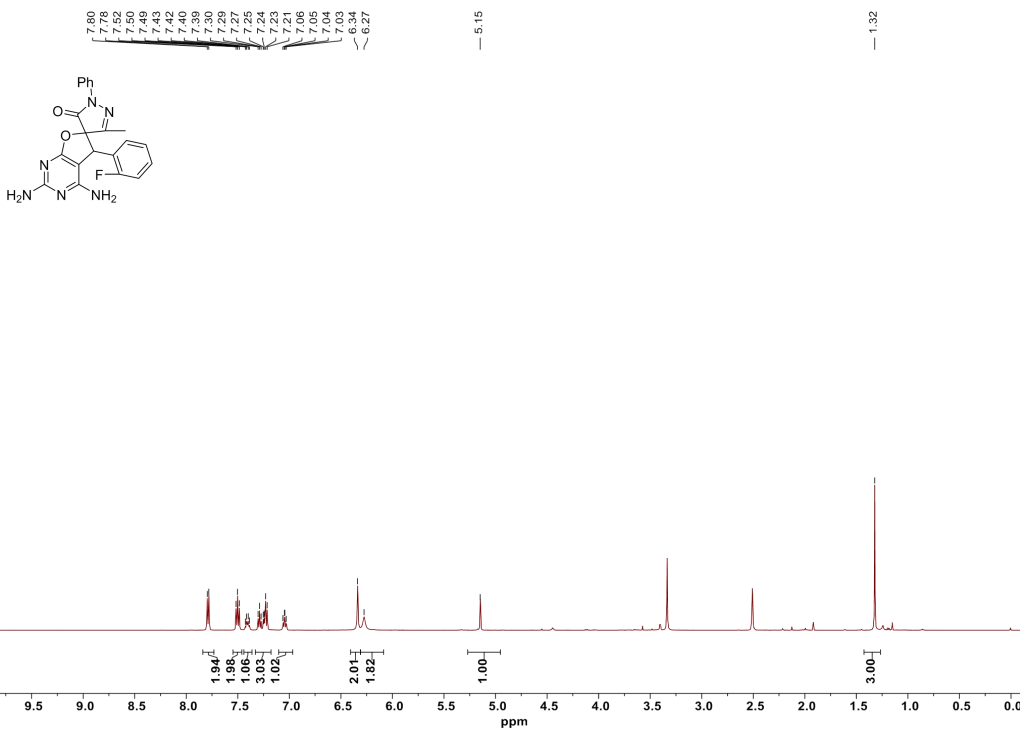
# Compound 3v



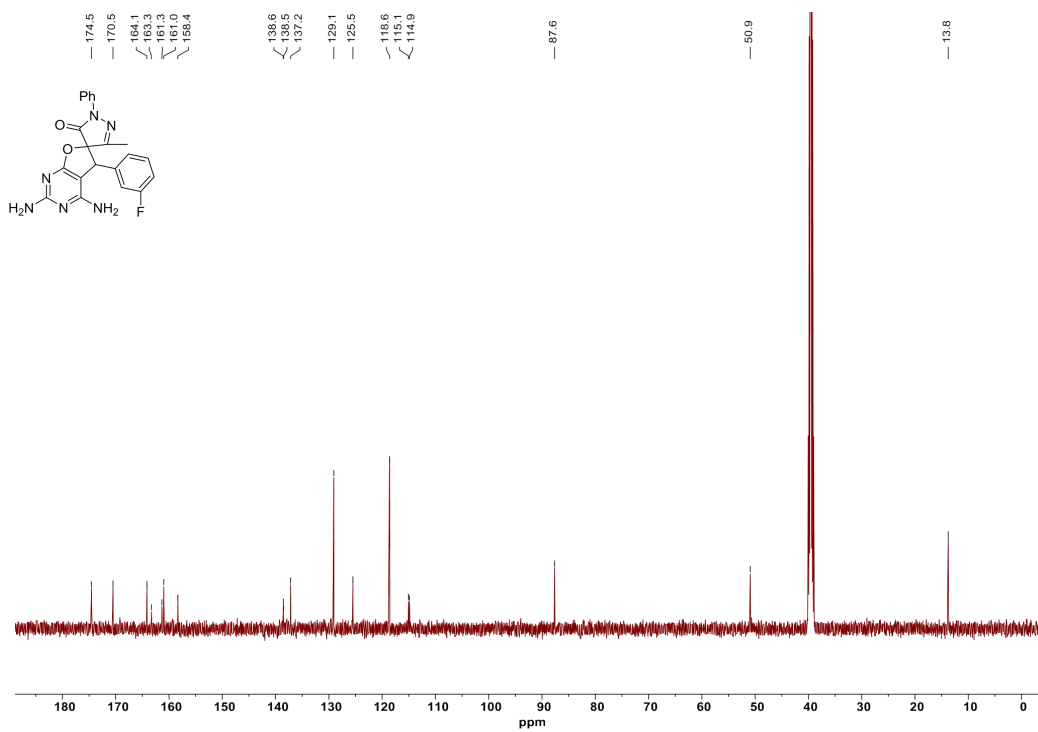
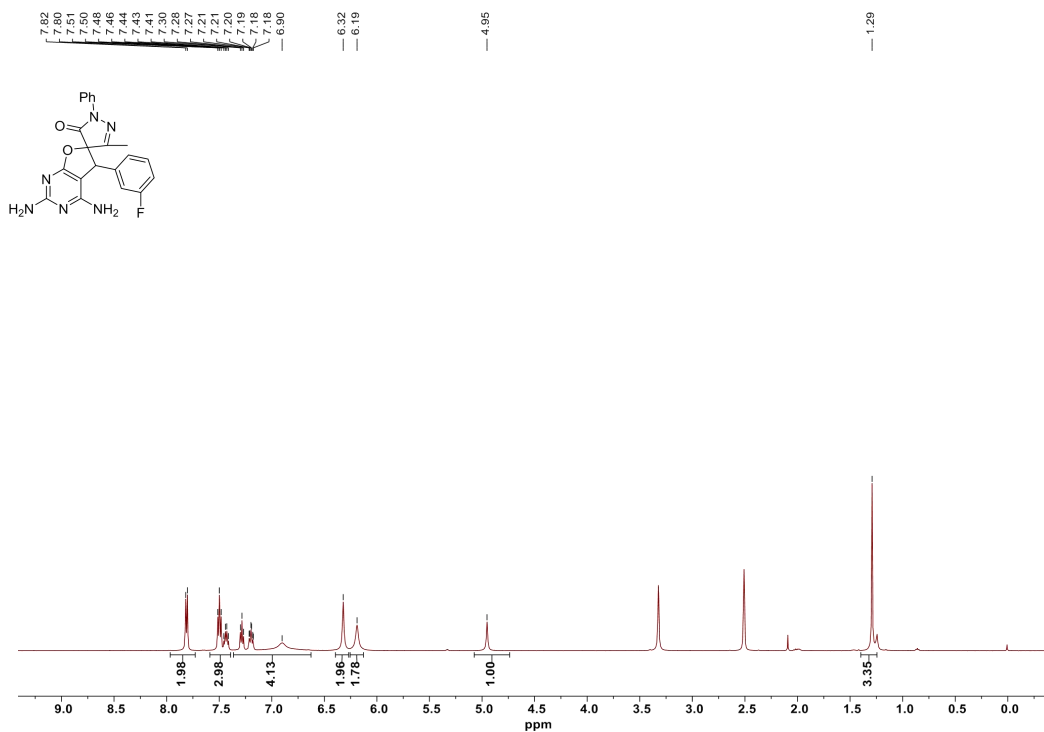
# Compound 5a



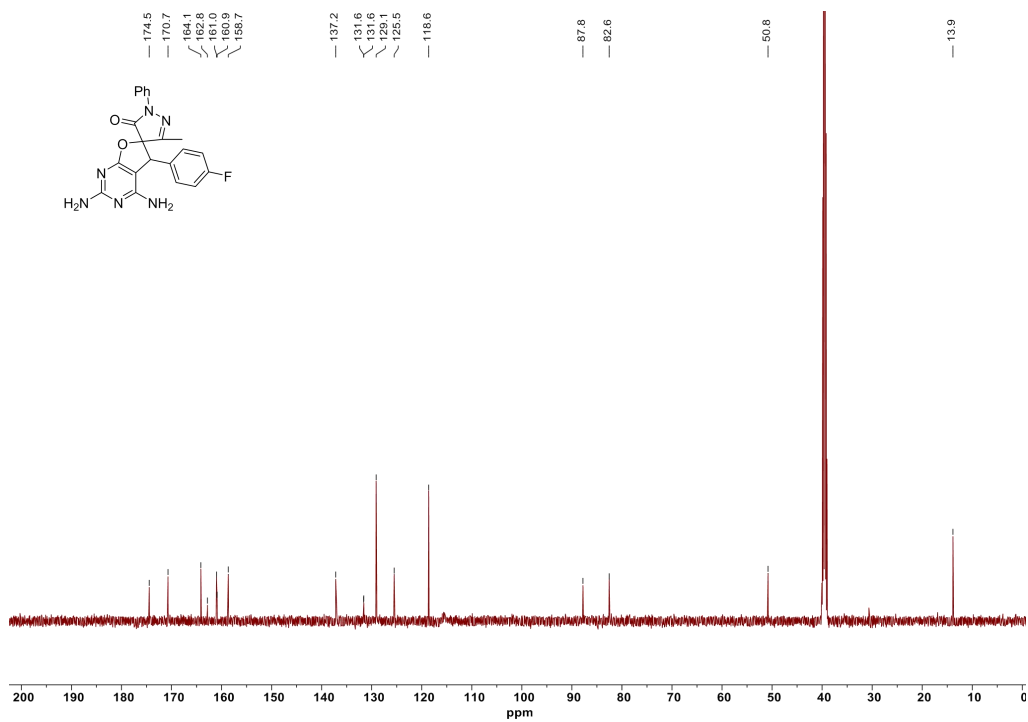
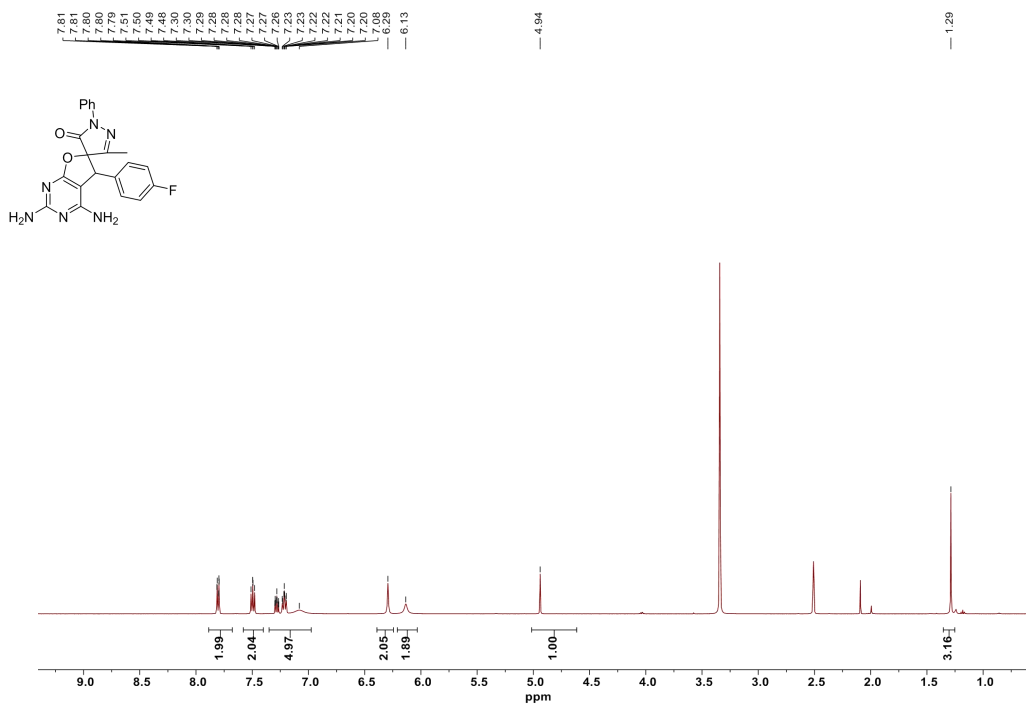
# Compound 5b



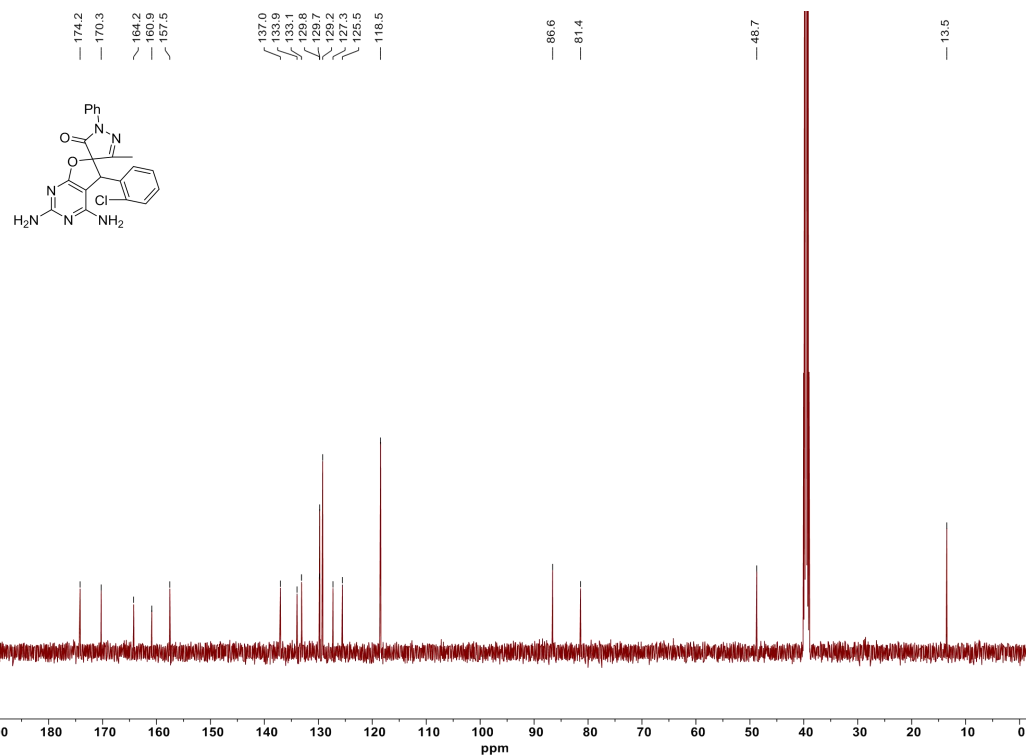
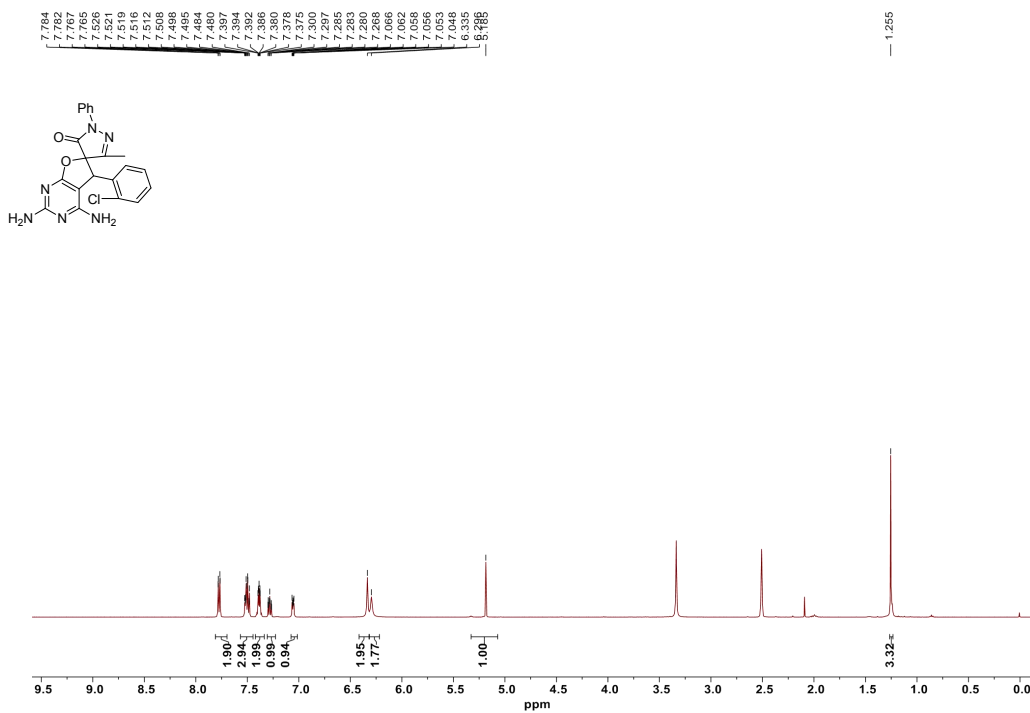
# Compound 5c



# Compound 5d

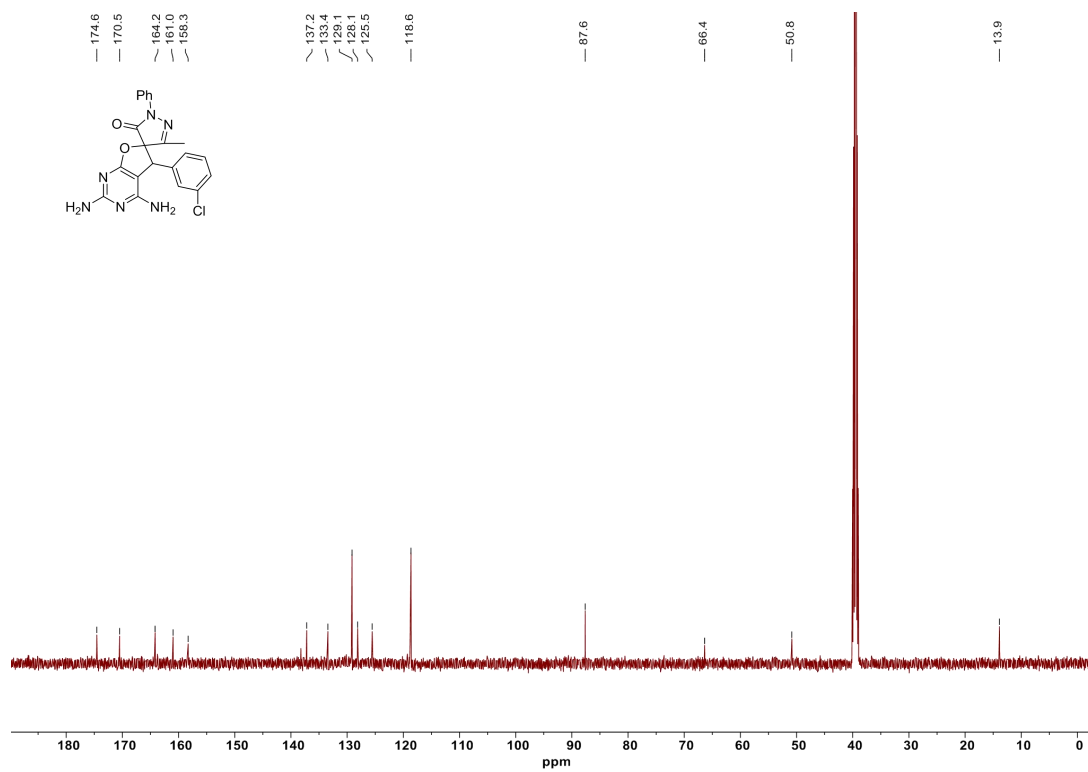
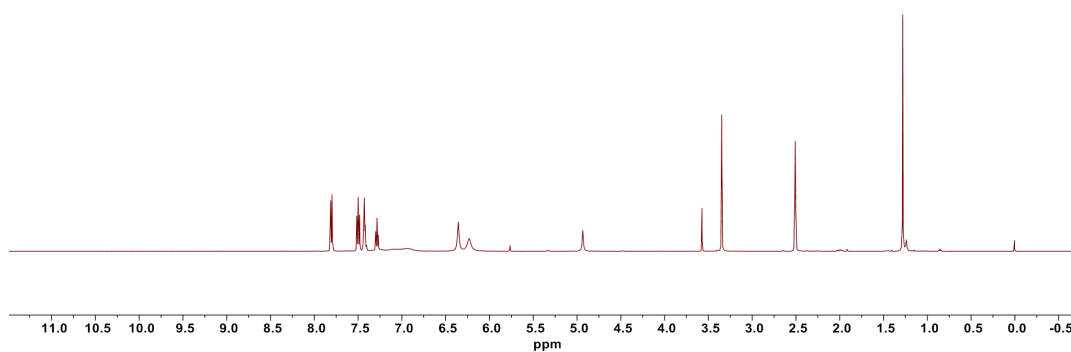
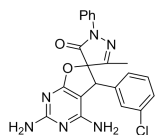


# Compound 5e

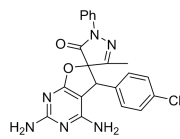
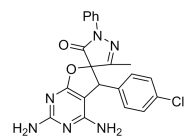
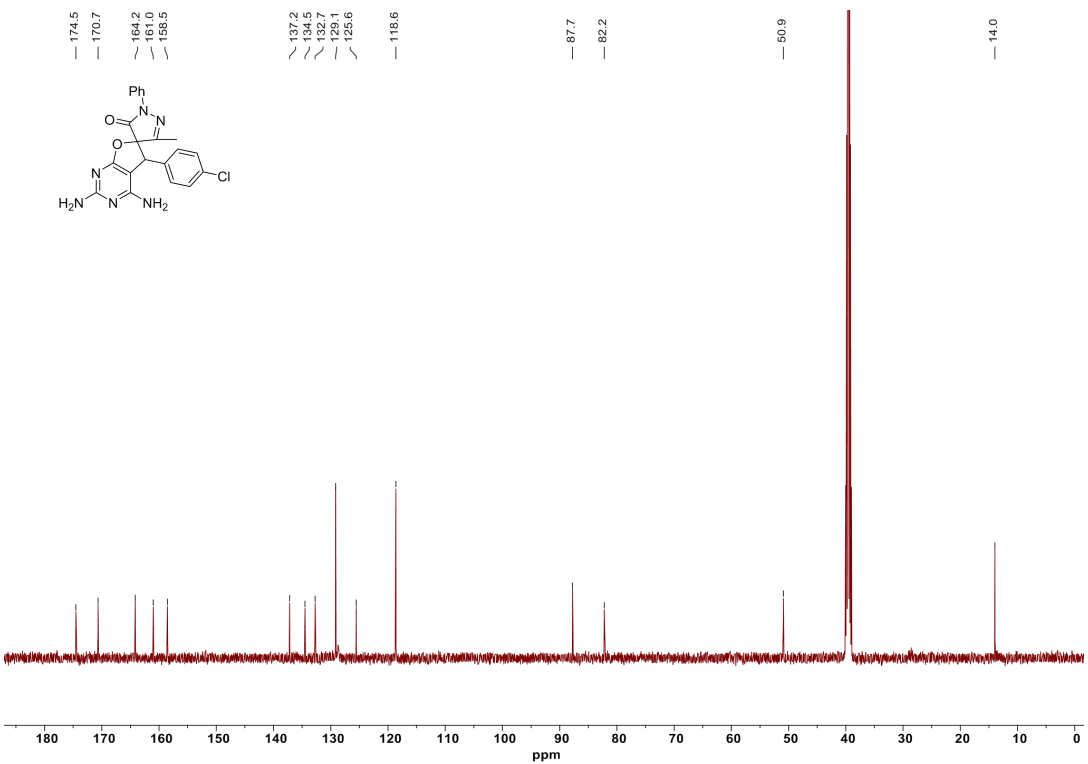
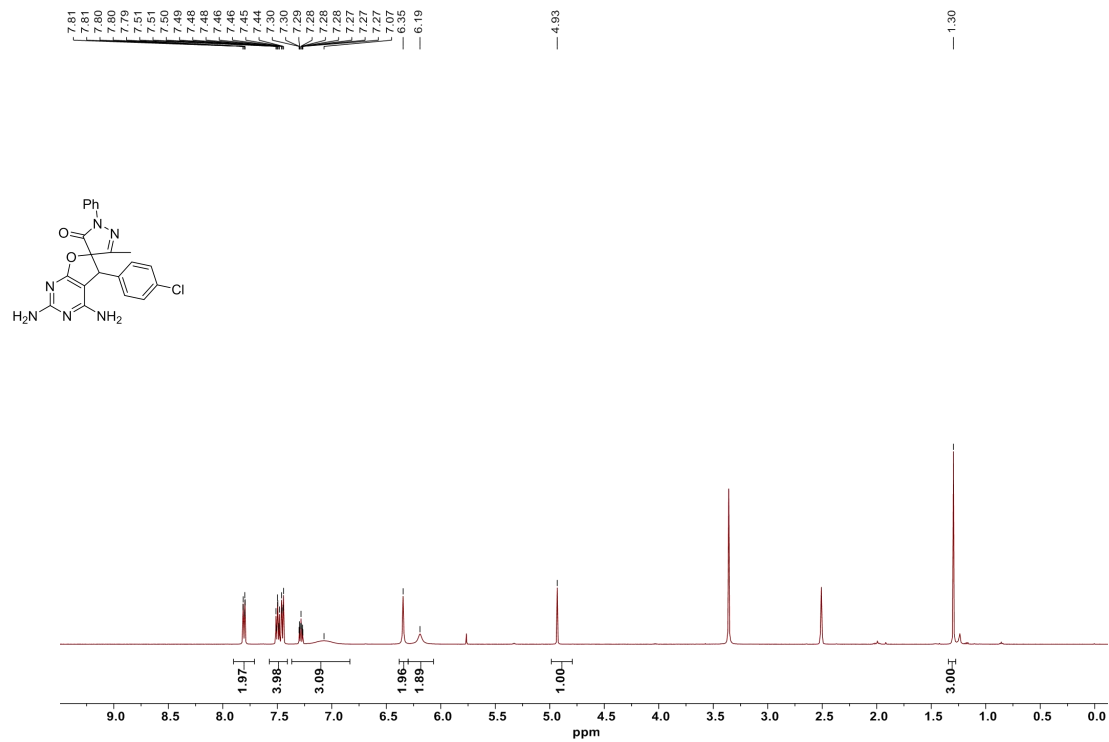




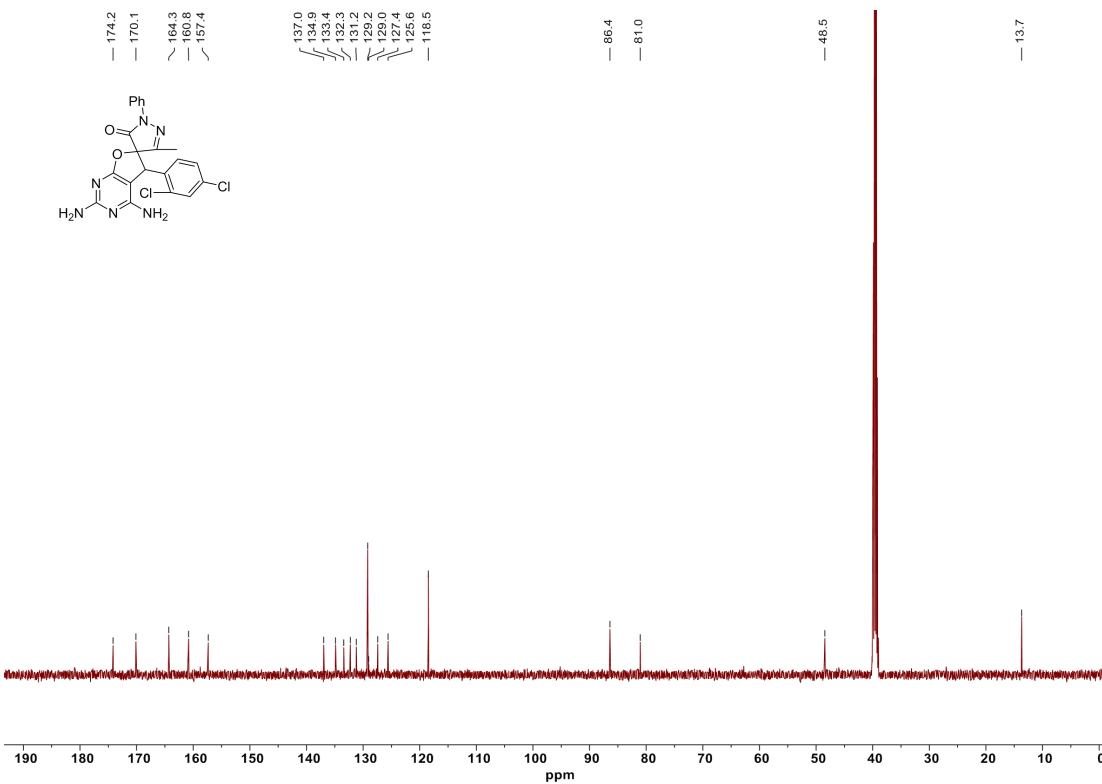
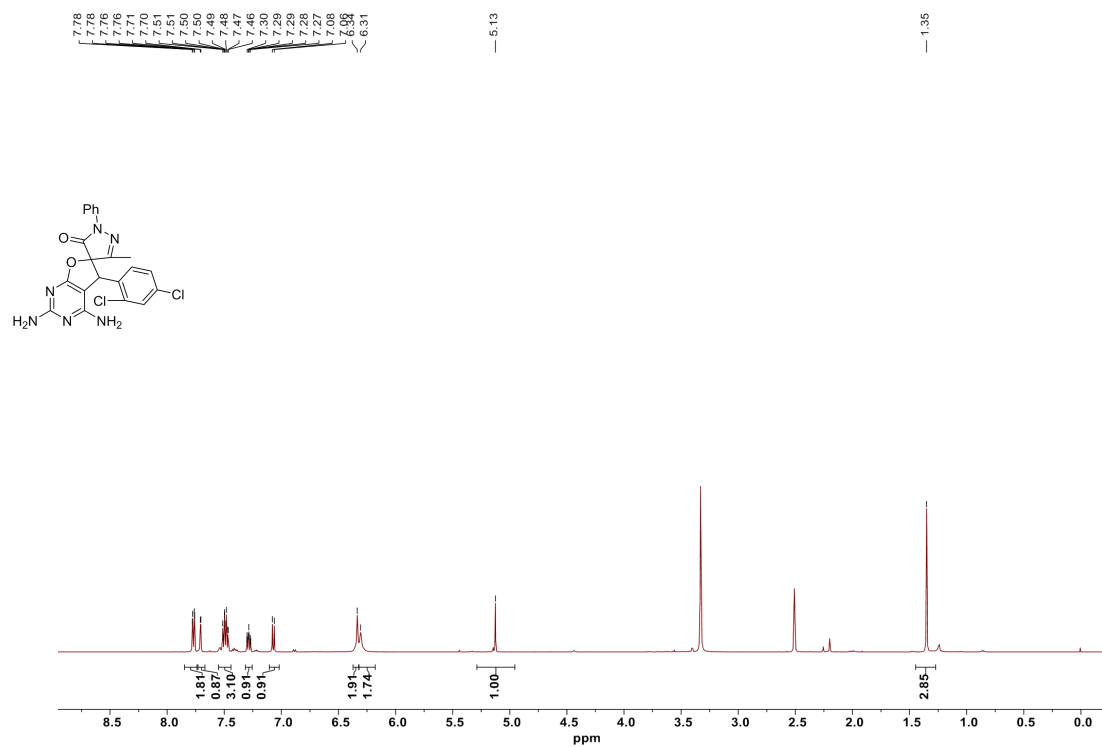
# Compound 5f



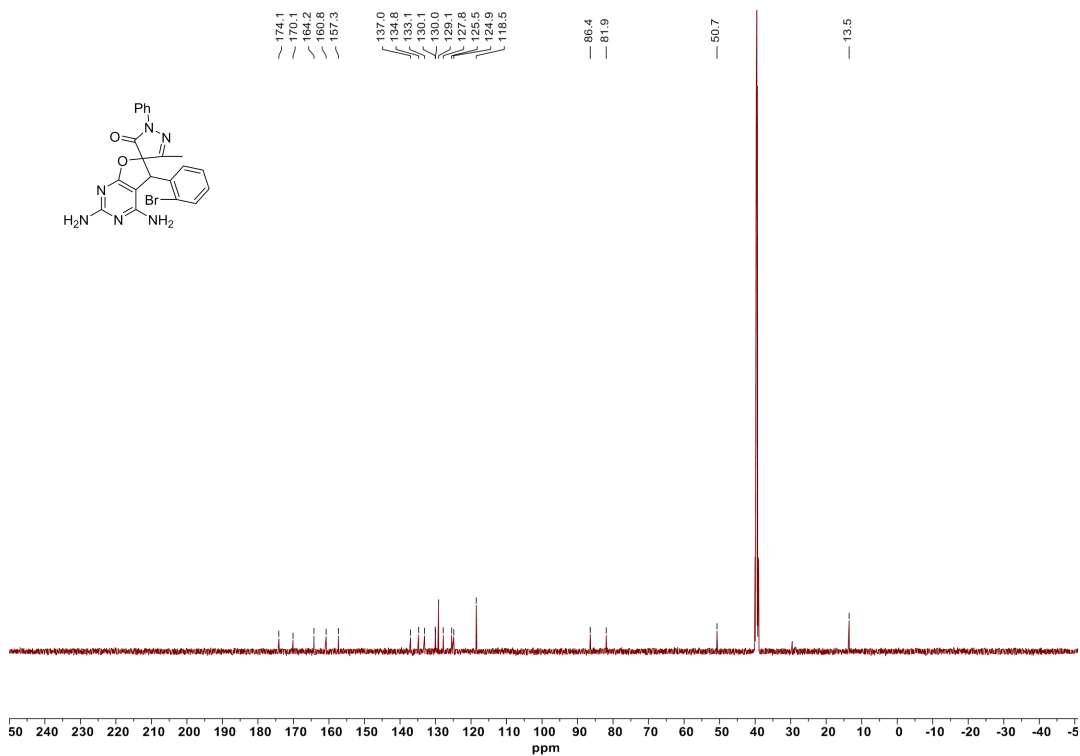
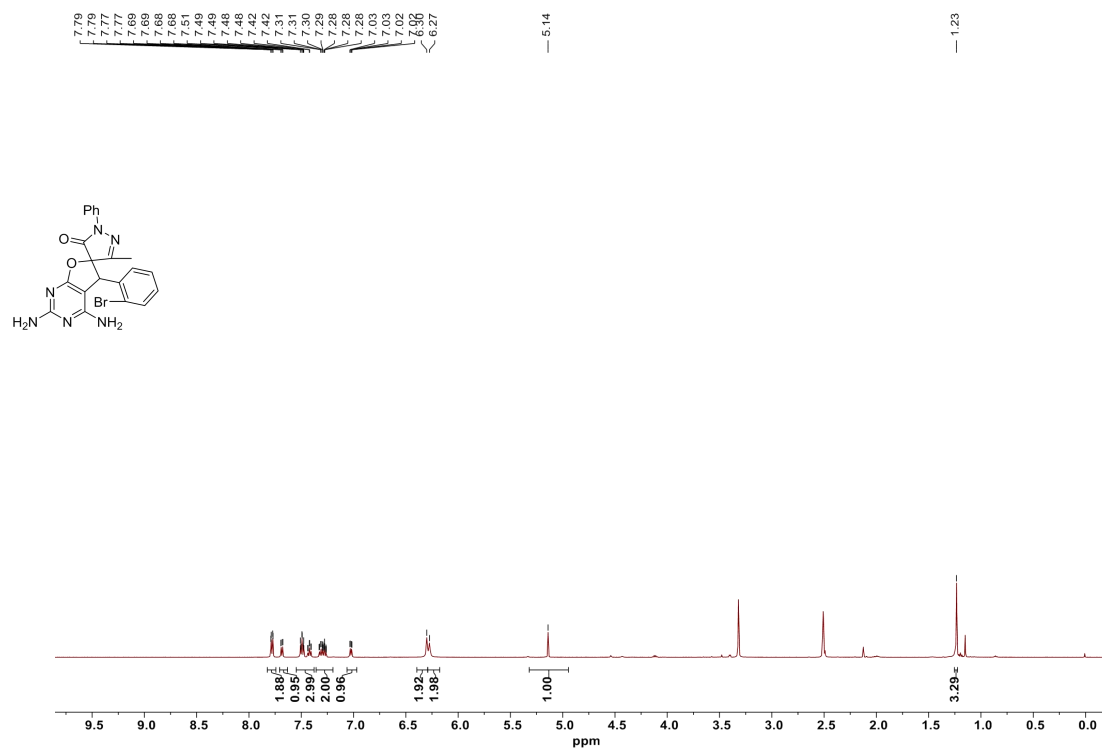
# Compound 5g



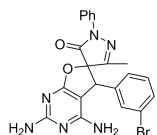
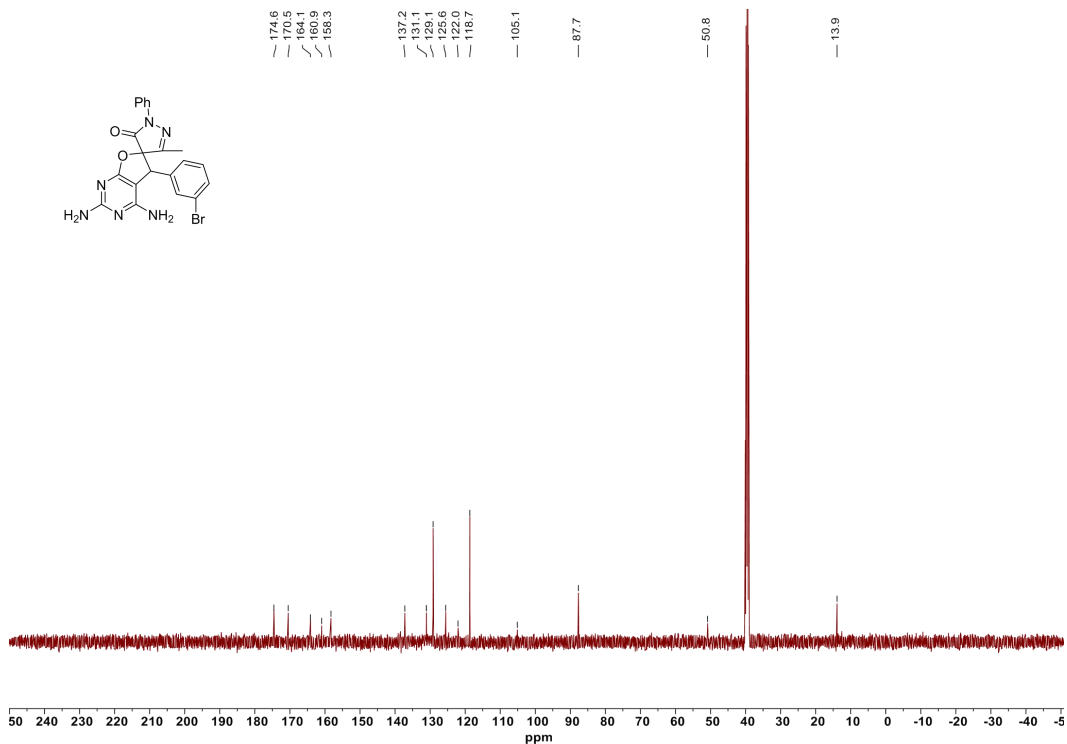
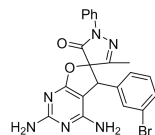
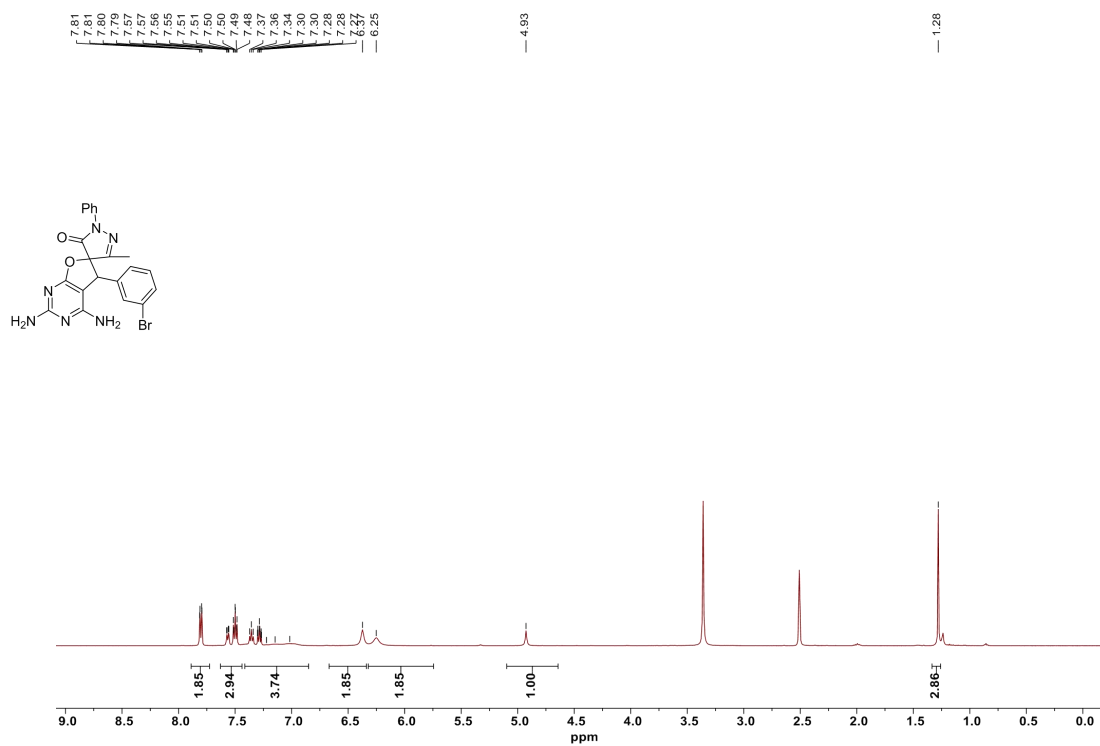
# Compound 5h



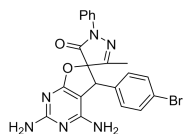
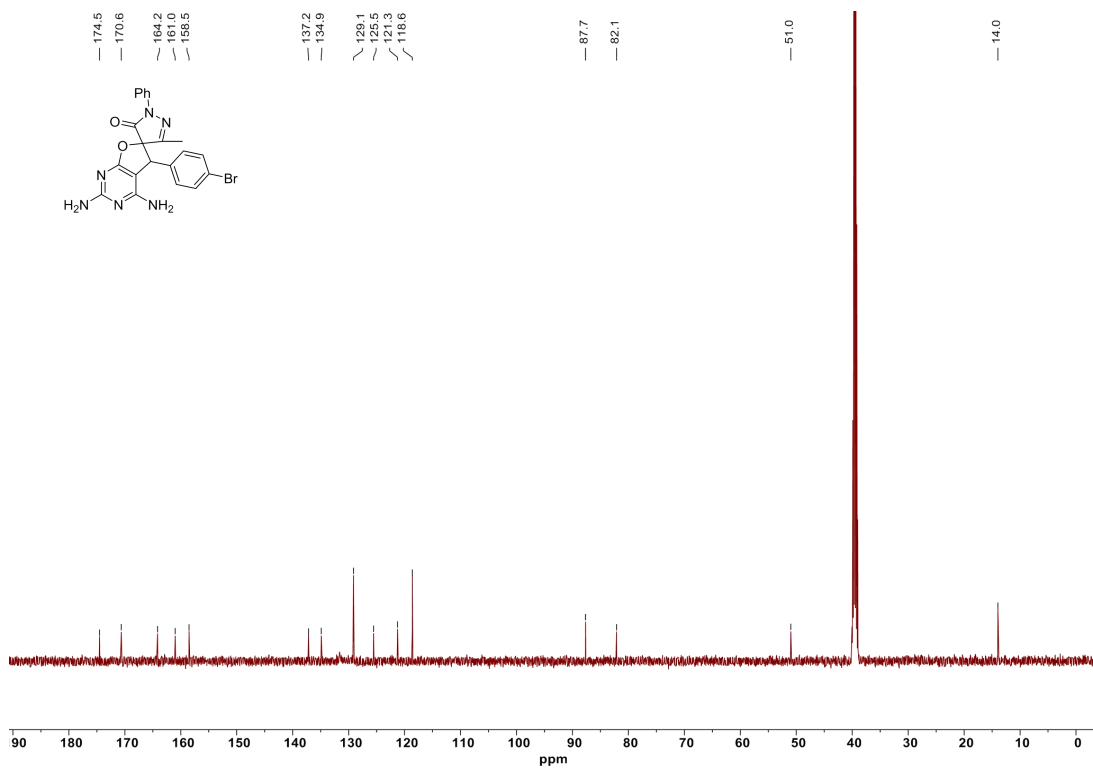
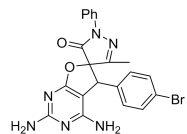
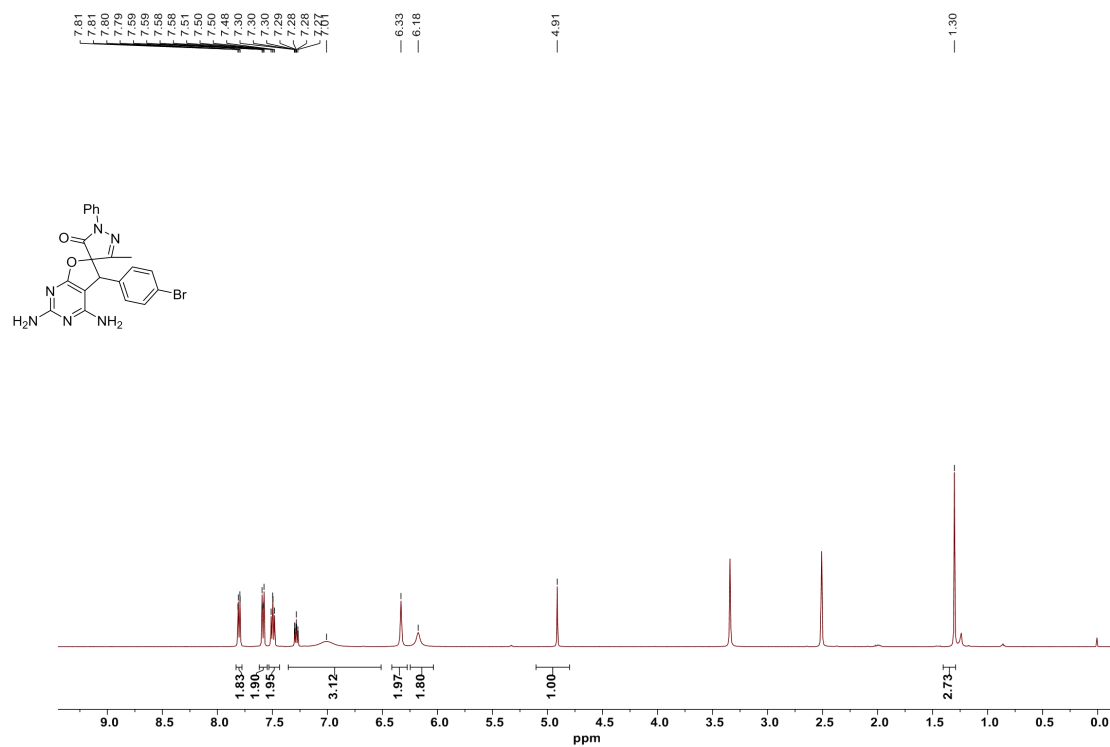
# Compound 5i



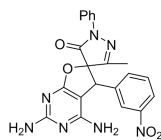
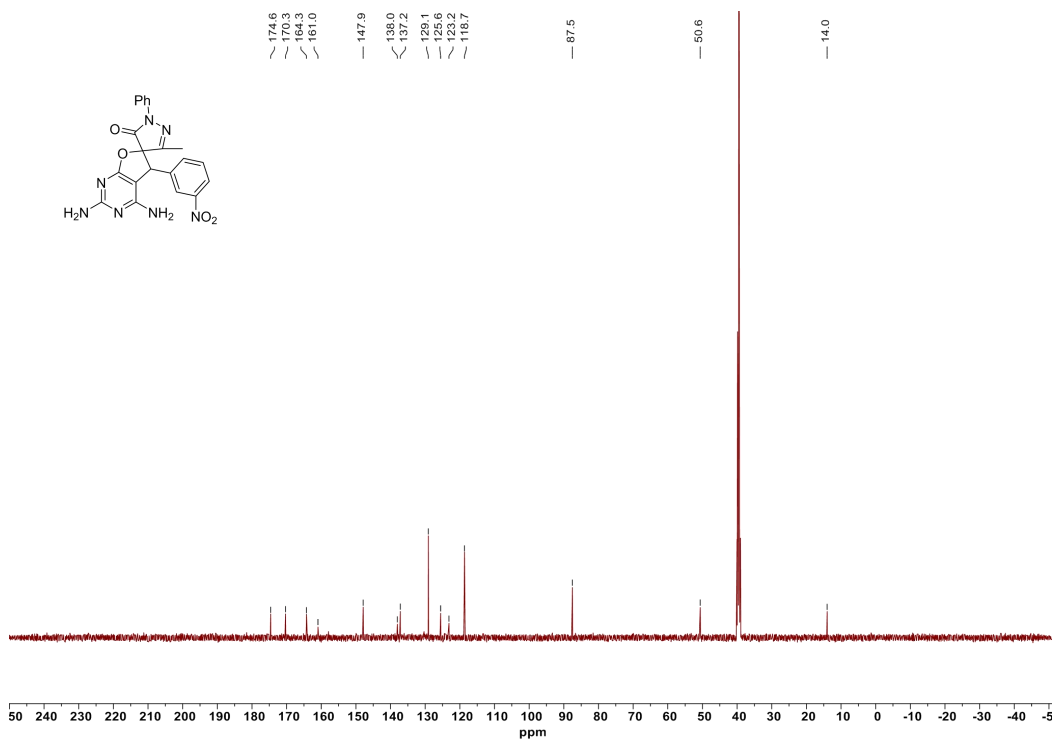
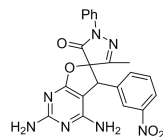
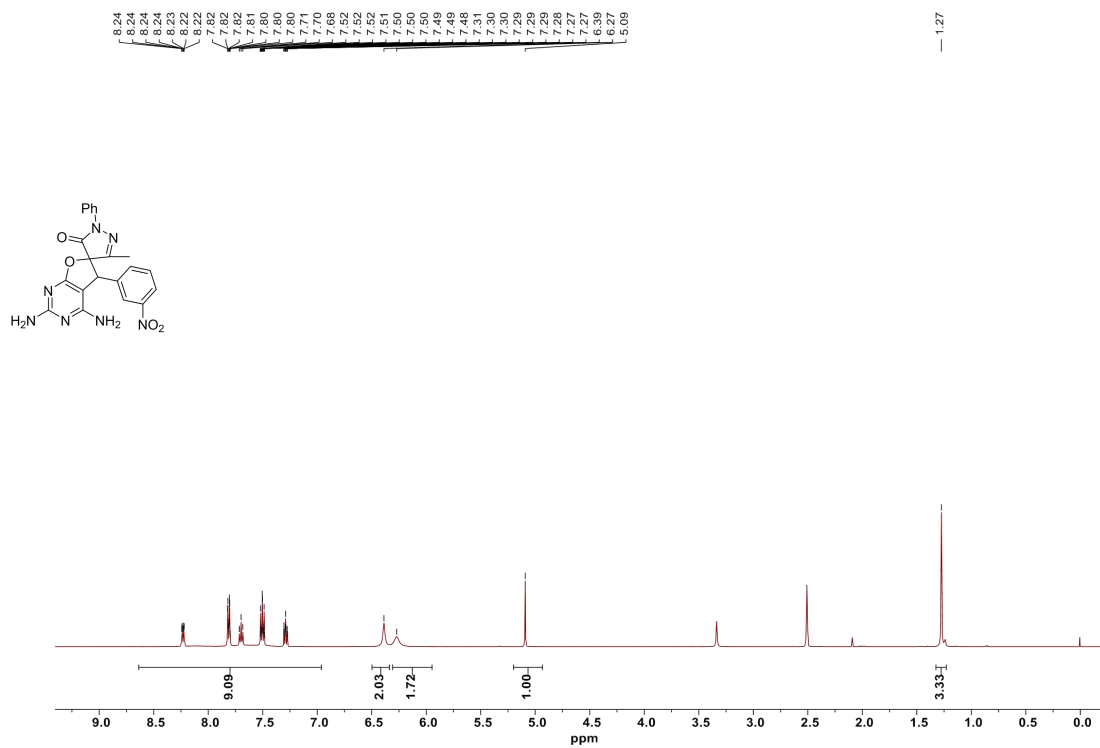
# Compound 5j



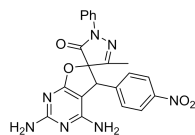
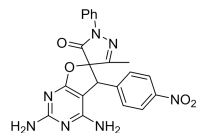
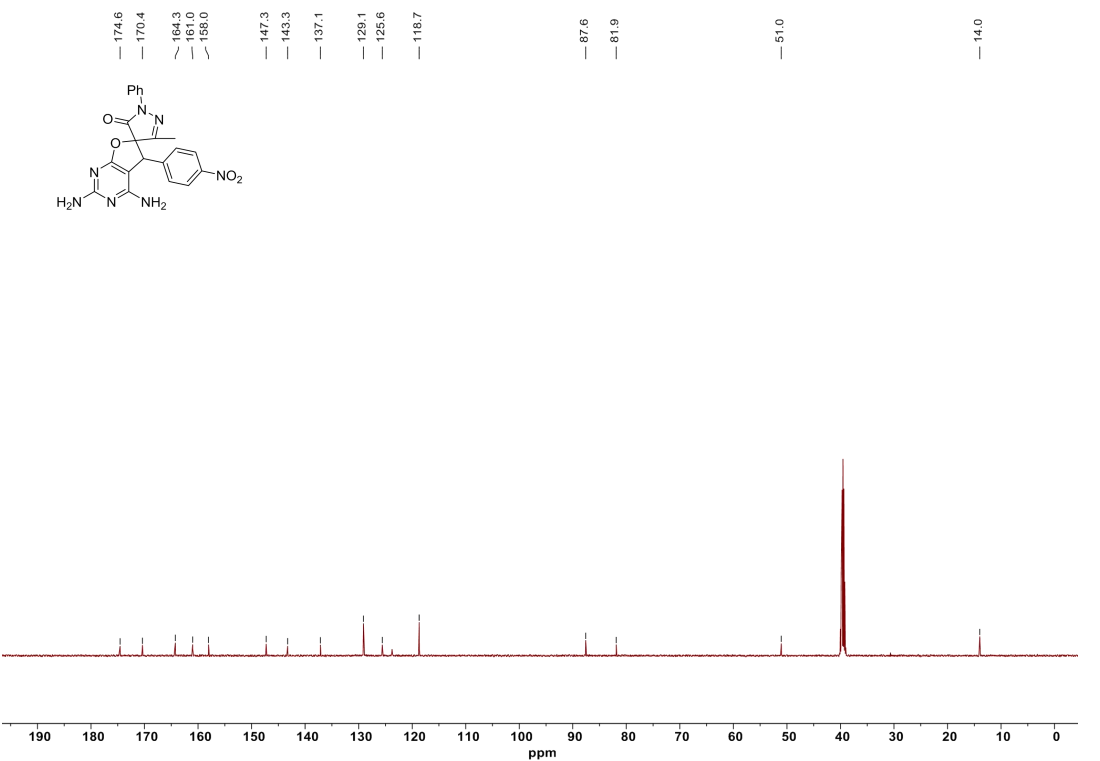
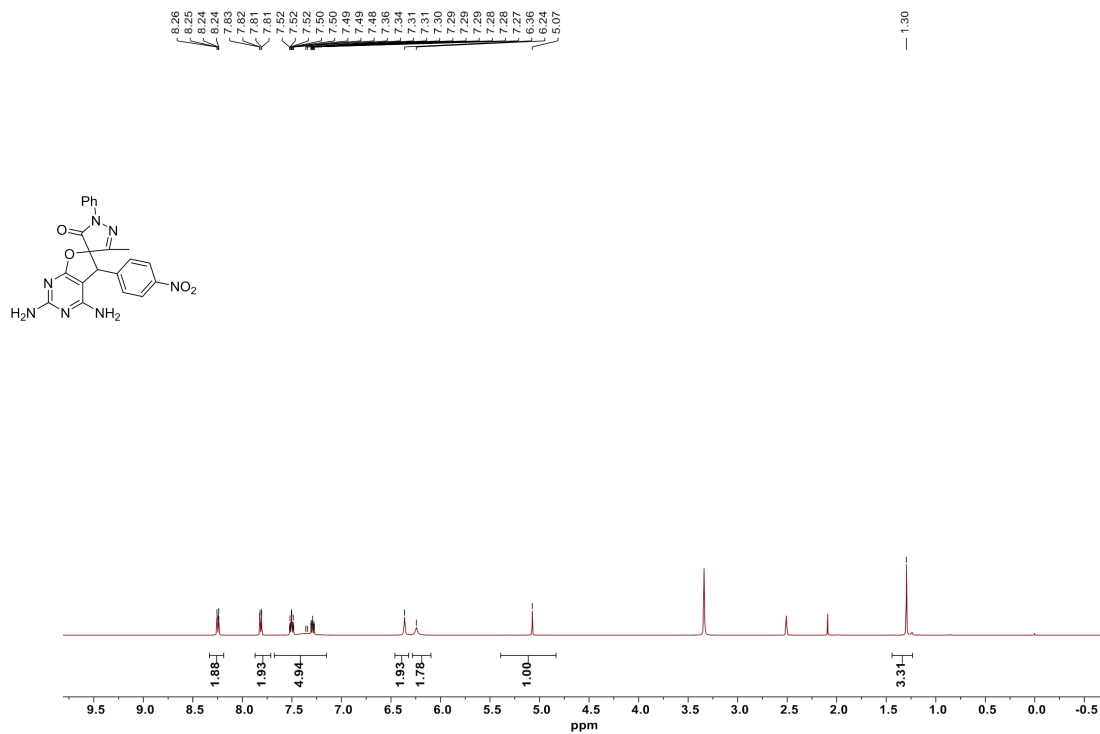
# Compound 5k



# Compound 51

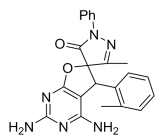
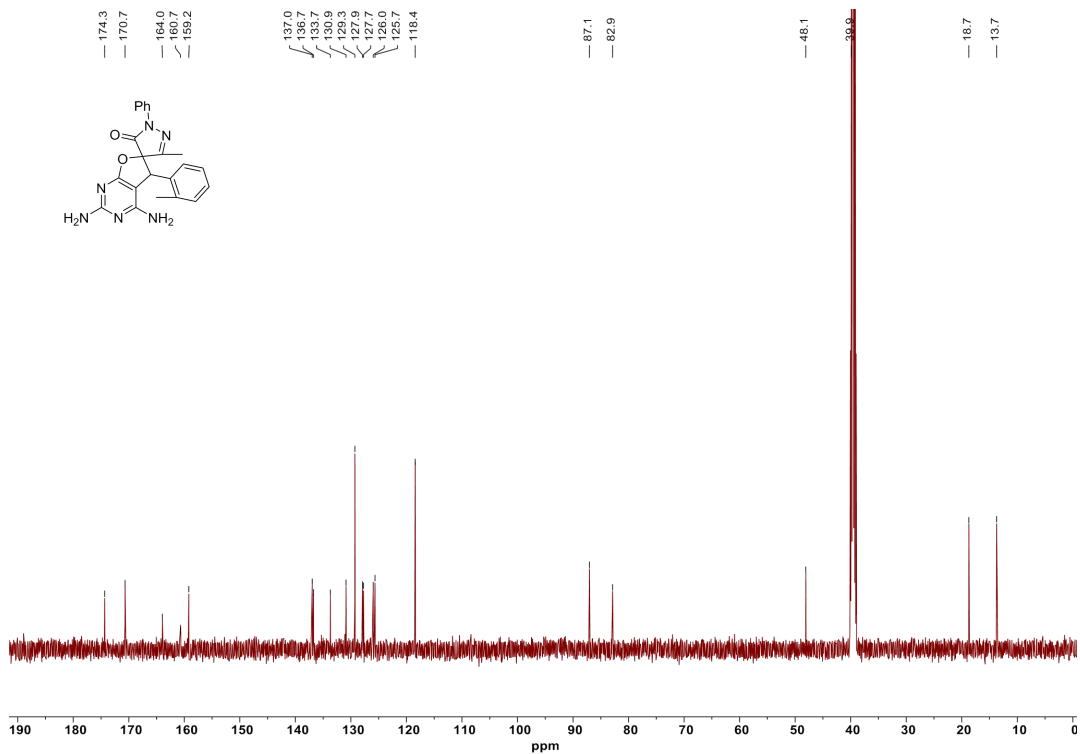
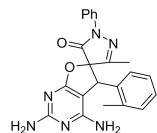
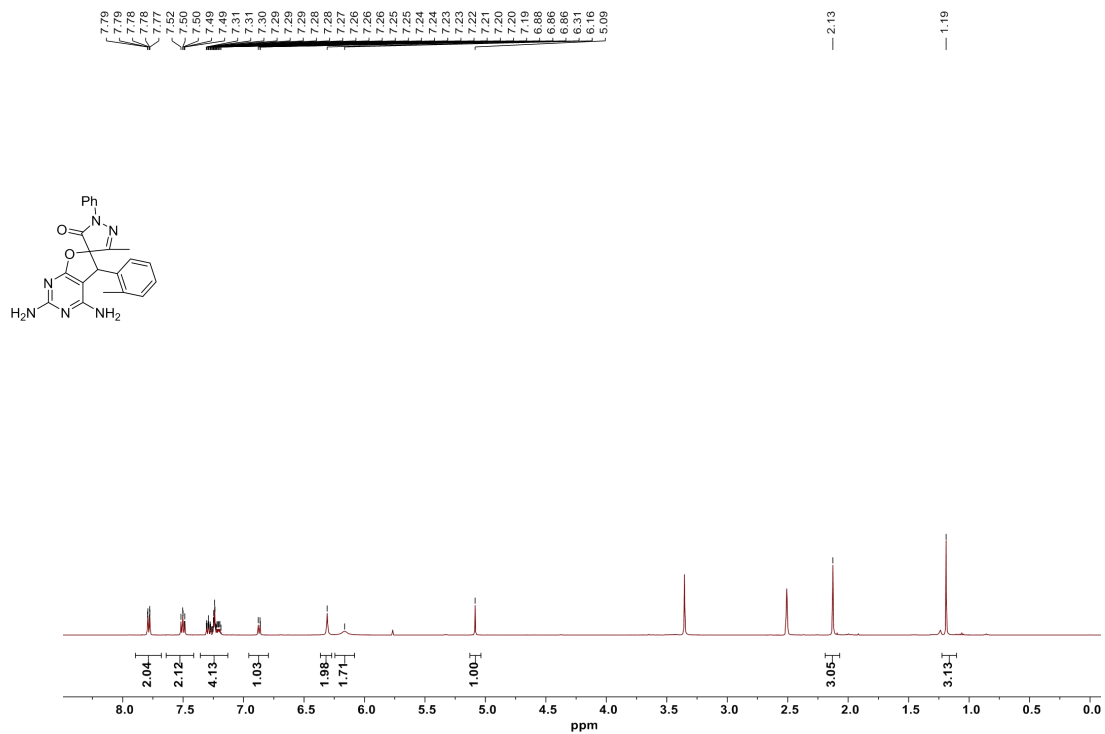


# Compound 5m

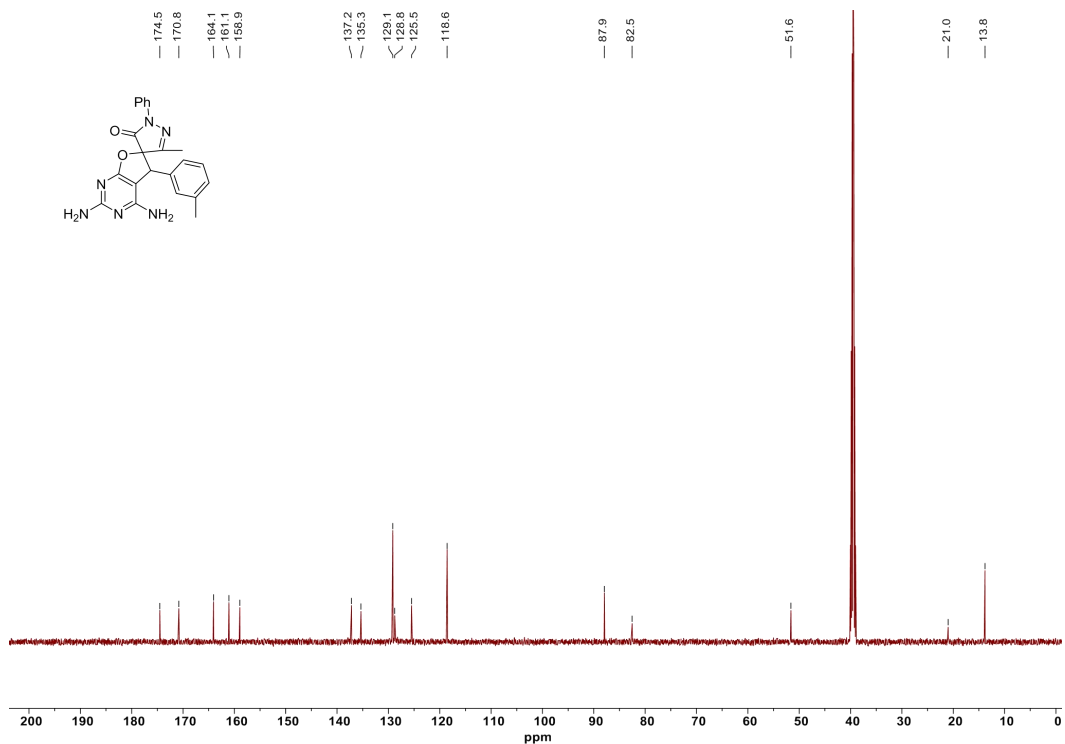
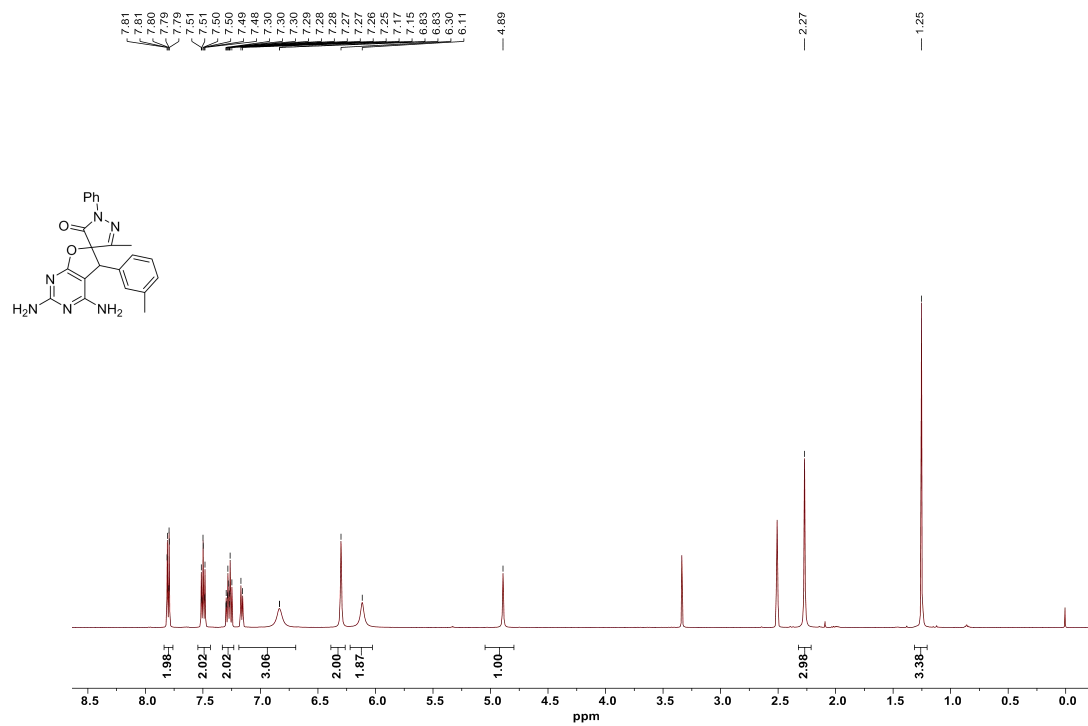




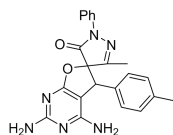
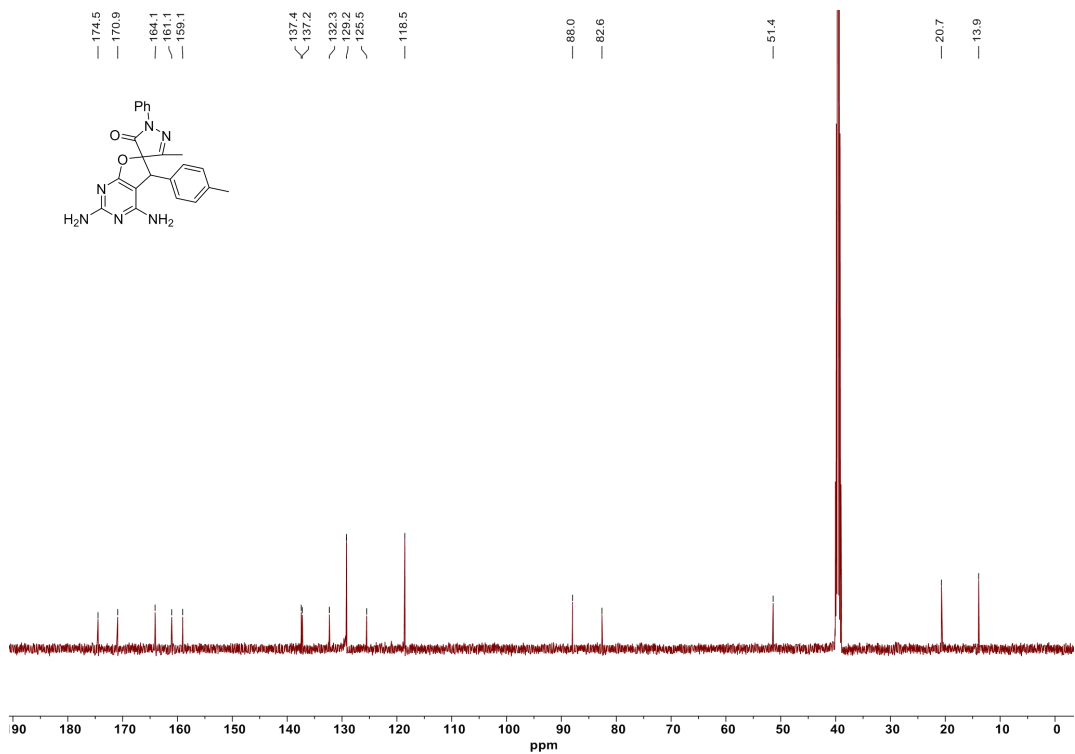
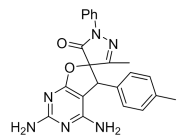
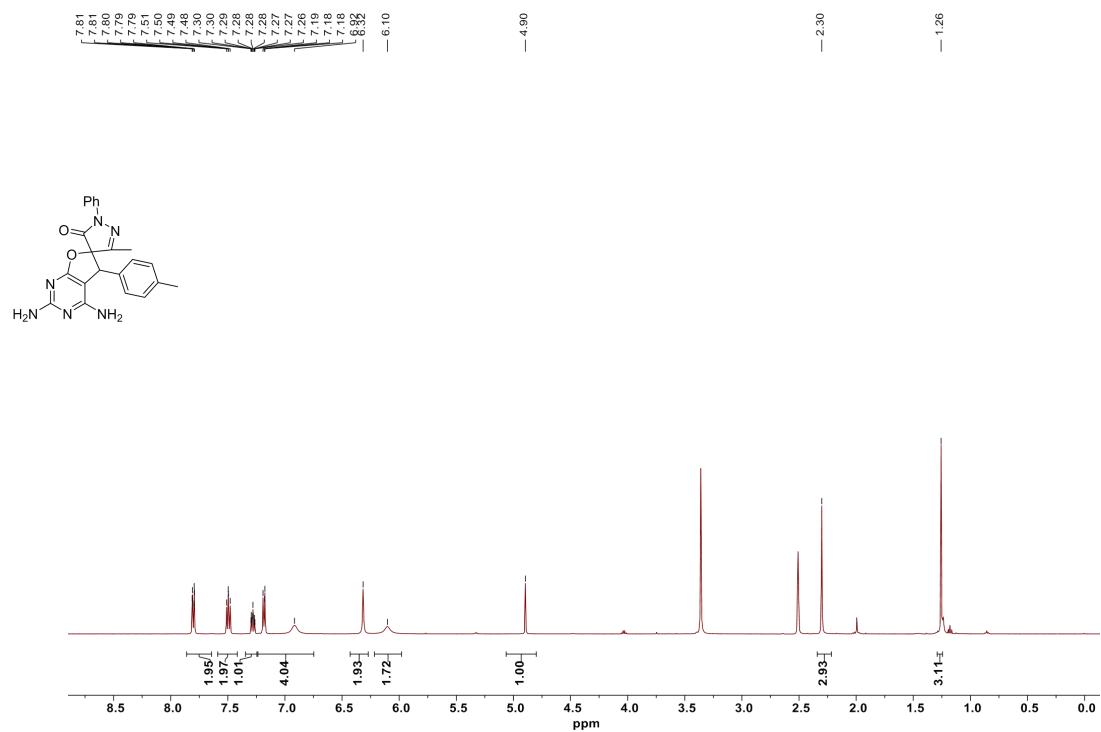
# Compound 5n



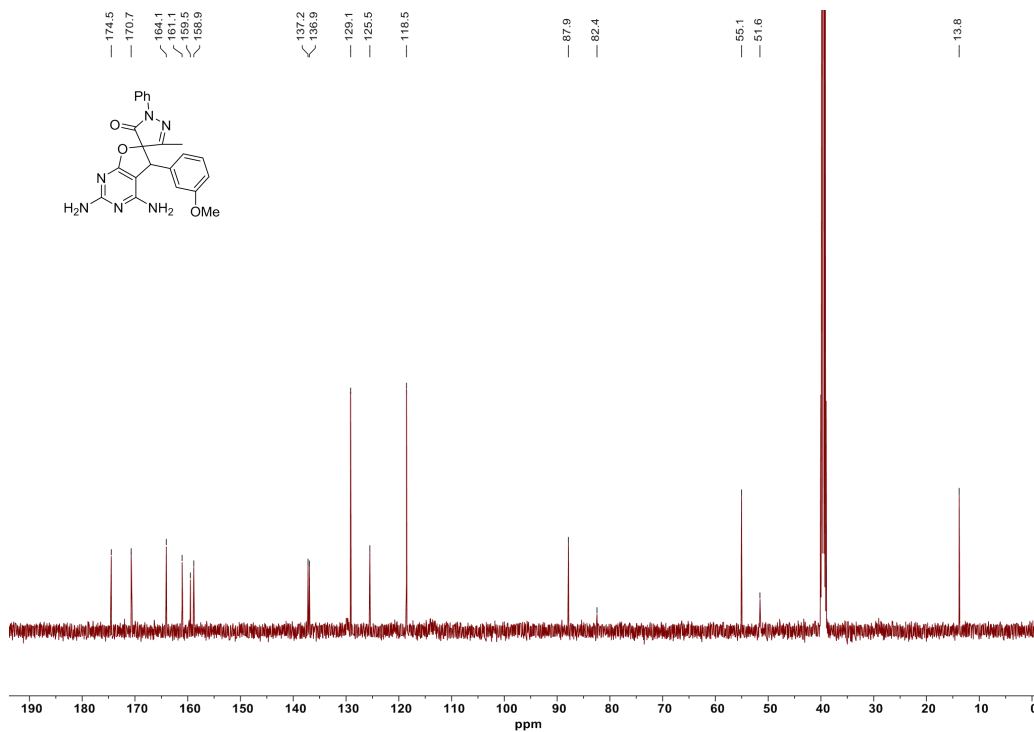
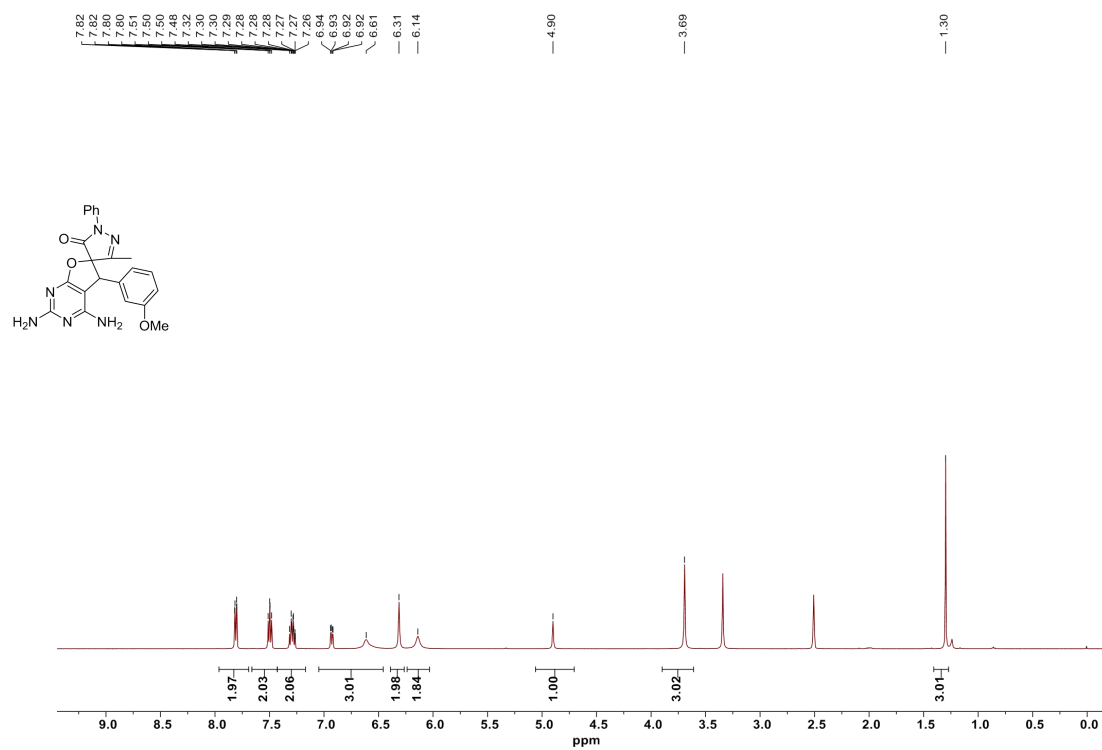
# Compound 5o



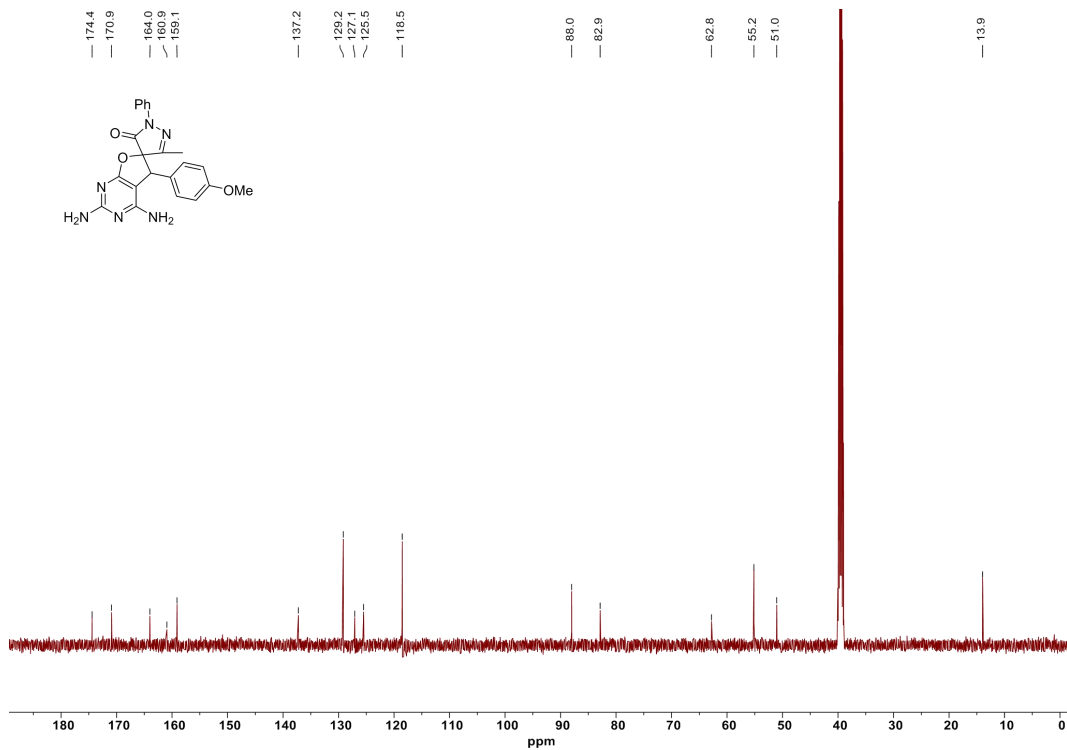
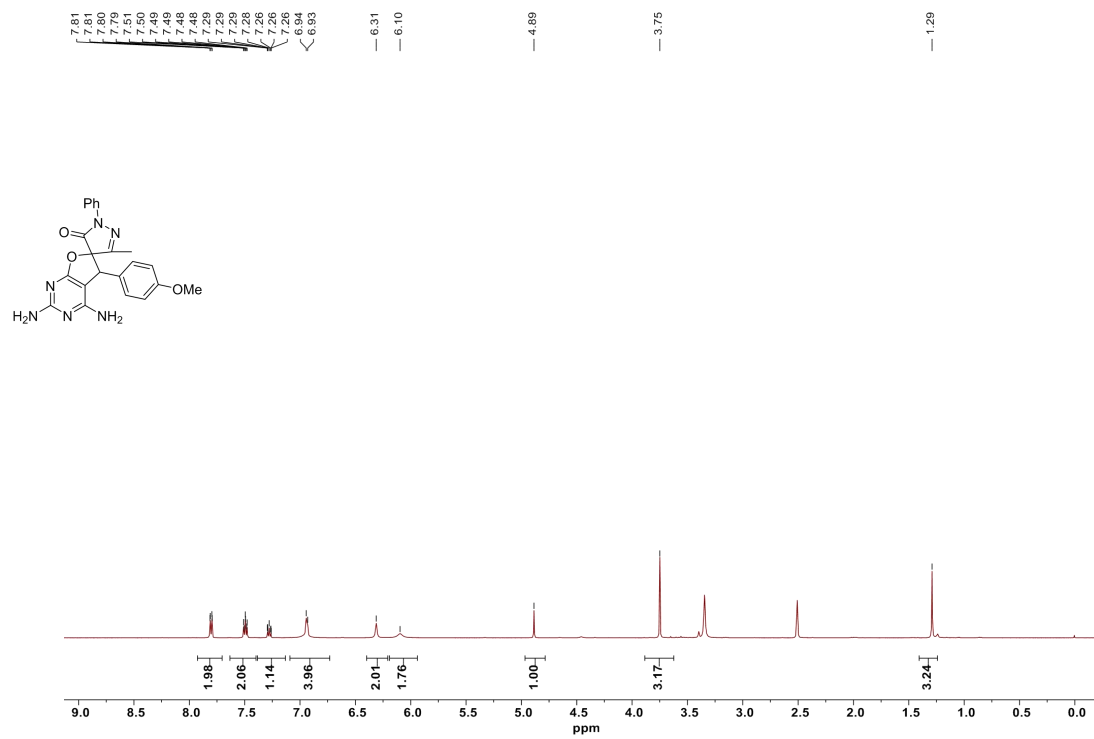
# Compound 5p



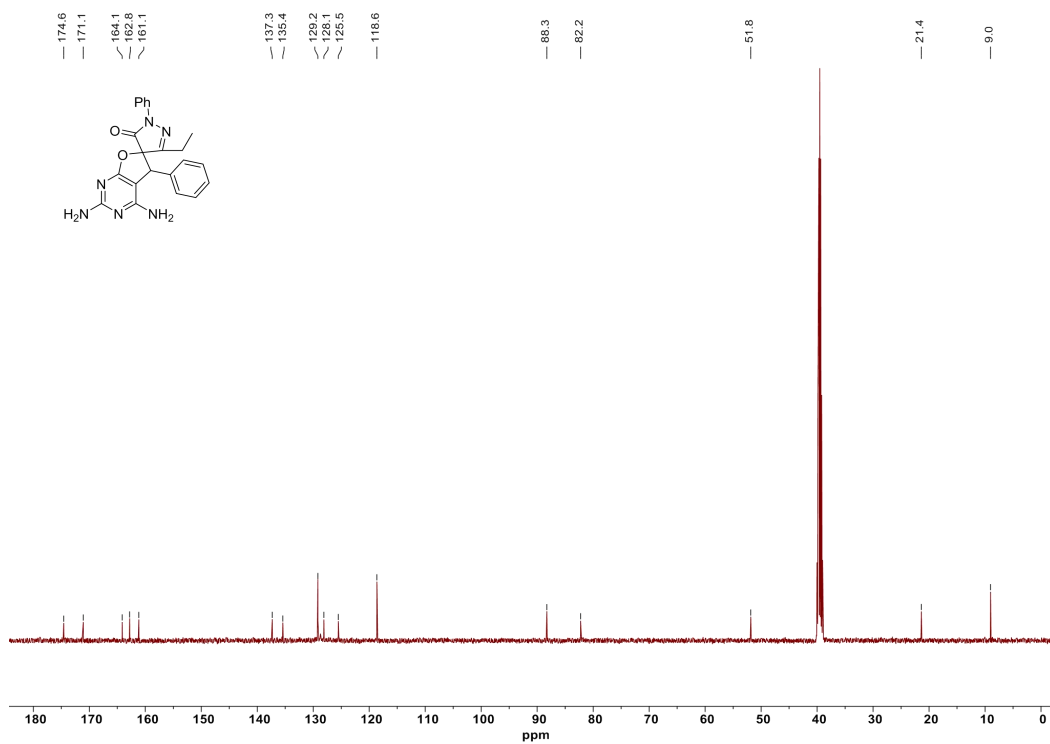
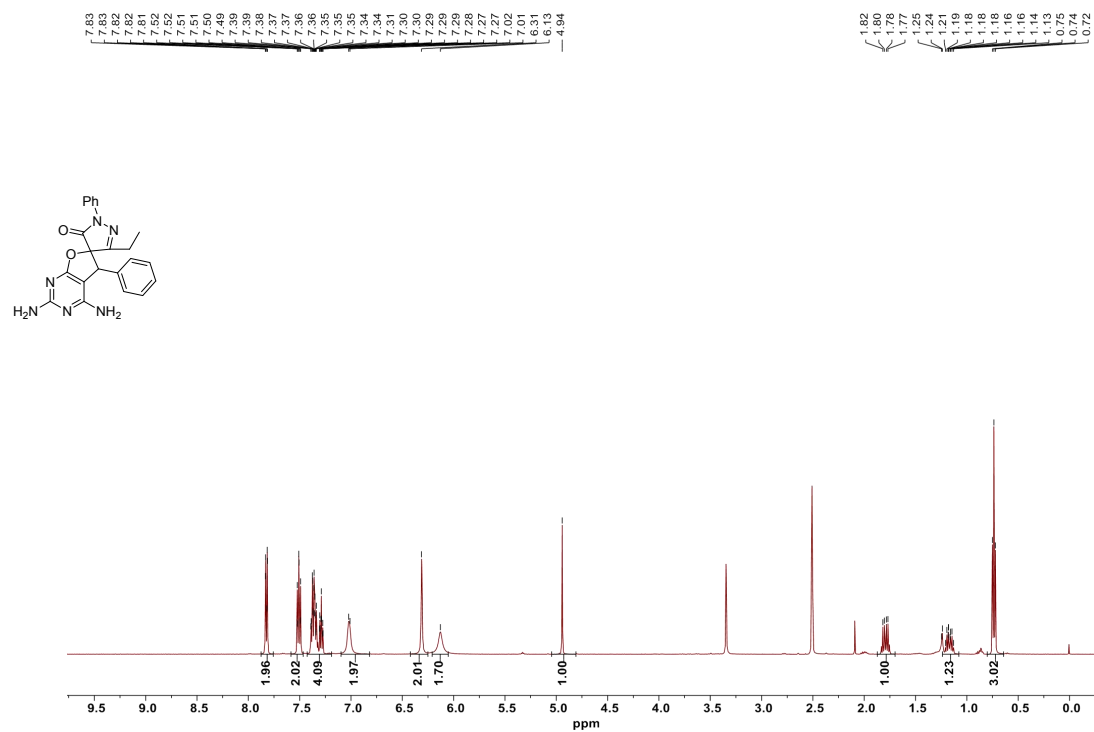
# Compound 5q



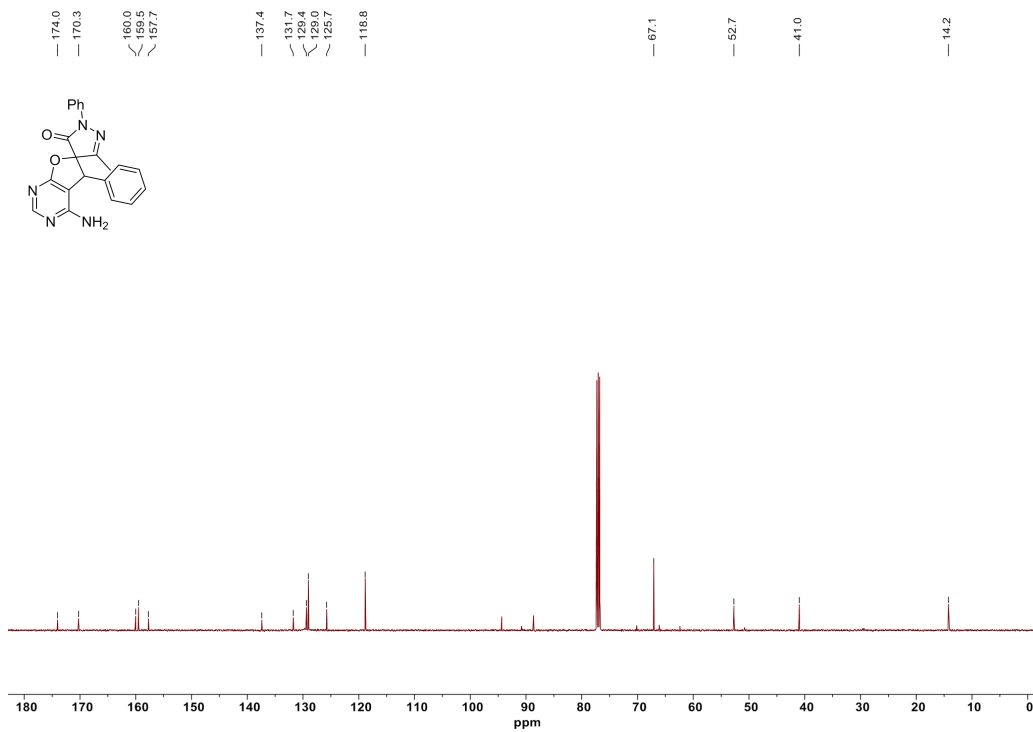
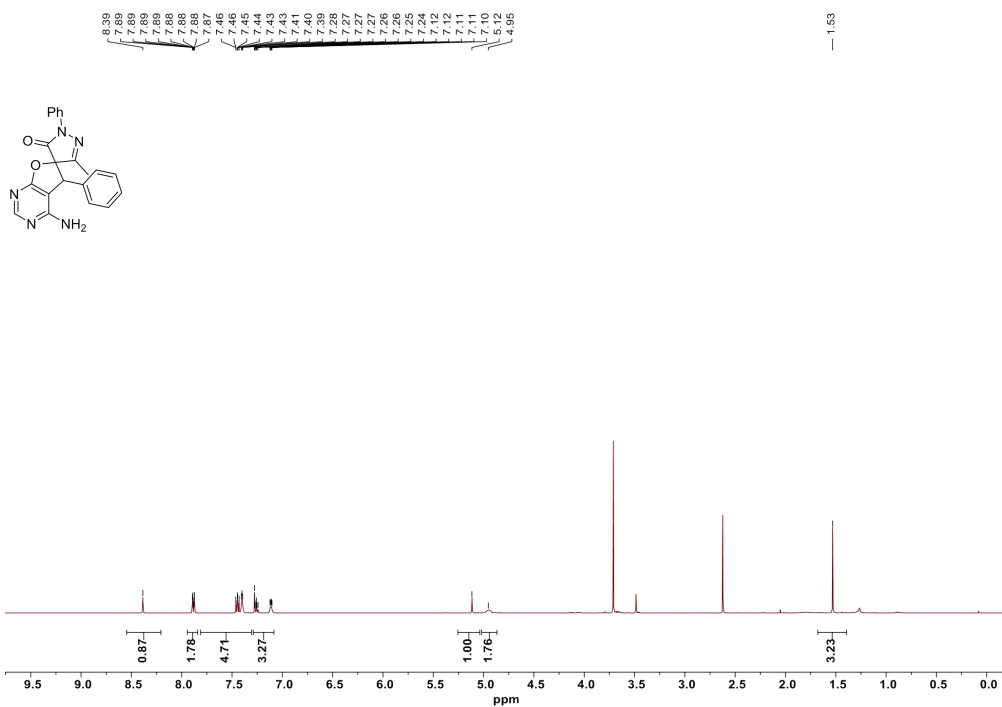
# Compound 5r



# Compound 5s

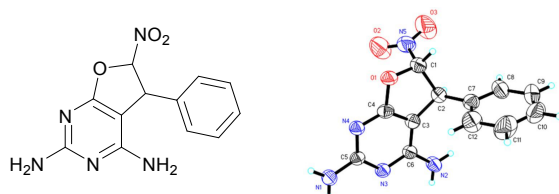


# Compound 5v



## 4. X-ray crystal structure of compounds 3a and 5a

### 4.1 X-ray crystal structure of the compound 3a



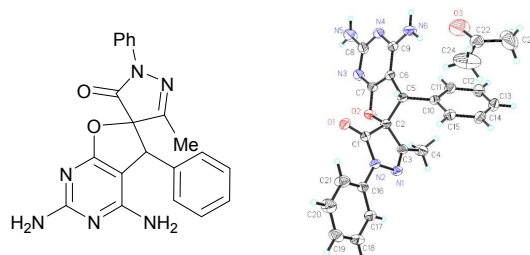
**Figure S1** X-ray crystal structure of the compound **3a**

**Table S1.** Crystal data and structure refinement parameters of the compound **3a**

Parameter	Value
CCDC deposition number	1893720
Empirical formula	C <sub>12</sub> H <sub>11</sub> N <sub>5</sub> O <sub>3</sub>
Formula weight	273.09
Temperature	296K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	P 1 21/c
Hall group	-P 2ybc
Cell dimensions	$a = 23.832(4)$ Å $\alpha = 90^\circ$ $b = 7.7110(10)$ Å $\beta = 107.350(12)^\circ$ $c = 19.479(3)$ Å $\gamma = 90^\circ$
Volume	3416.8(9) Å <sup>3</sup>
Z	8
Density (calculated)	1.288 Mg/m <sup>3</sup>
Absorption coefficient	0.513 mm <sup>-1</sup>
$F_{000}$	1392
Crystal size	0.10 × 0.08 × 0.06 mm <sup>3</sup>
Theta range for data collection	6.763° to 106.778°
Index ranges	-29 ≤ $h$ ≤ 29 -9 ≤ $k$ ≤ 8 -23 ≤ $l$ ≤ 23
Extinction method	SHELXL



## 4.2 X-ray crystal structure of the compound 5a



**Figure S2** X-ray crystal structure of the compound **5a**

**Table S2.** Crystal data and structure refinement parameters of the compound **5a**

Parameter	Value
CCDC deposition number	1893721
Empirical formula	C <sub>24</sub> H <sub>24</sub> N <sub>6</sub> O <sub>3</sub>
Formula weight	444.49
Temperature	296(2)K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Hall group	-P 2ybc
Cell dimensions	$a = 18.8434(7)$ Å $\alpha = 90^\circ$ $b = 9.6451(3)$ Å $\beta = 100.3240(10)^\circ$ $c = 12.5493(5)$ Å $\gamma = 90^\circ$
Volume	2243.87(14) Å <sup>3</sup>
Z	4
Density (calculated)	1.316 Mg/m <sup>3</sup>
Absorption coefficient	0.09 mm <sup>-1</sup>
$F_{000}$	936
Crystal size	0.17 × 0.15 × 0.13 mm <sup>3</sup>
Correction_type	multi-scan
Theta range for data collection	0.6672° to 0.7456°
Index ranges	$-23 \leq h \leq 22$ $-11 \leq k \leq 11$ $-12 \leq l \leq 15$
restraints /parameters	0/310
Goodness of fit on $F^2$	1.048
Extinction coef	0.033(6)