

Supporting Information

**Palladium-Catalyzed Highly Selective and Direct Ortho C–H  
Arylation of Pyrrolo[2,3-*d*]pyrimidine Derivatives**

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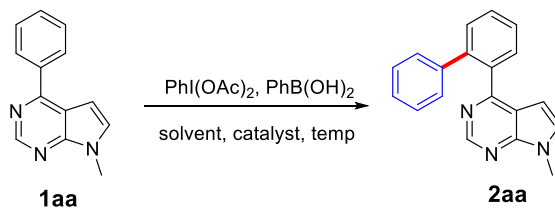
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## 1. General Information

Chemicals were purchased from commercial suppliers and used as delivered. Deuterated solvents were purchased and used without further purification. NMR spectra were obtained on a Bruker ADNANCE III 500 MHz with TMS as the internal standard and CDCl<sub>3</sub> as the solvent. Chemical shifts are given in parts per million (ppm) and coupling constants in Hz. In the <sup>1</sup>H and <sup>13</sup>C spectra, chemical shifts are reported relative to deuterated solvents (CDCl<sub>3</sub>: 7.26/77.2 ppm). The following abbreviations were used for <sup>1</sup>H NMR to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), m (multiplet), br s (broad singlet). Melting points were measured on a BUCHI B-540 and uncorrected. FT-IR were recorded on a Bruker Tensor 27 spectrometer. Analytical thin-layer chromatography was carried out using commercial aluminum sheets precoated (0.2 mm layer thickness) with silica gel GF254, and visualization was effected with short wavelength UV light (254 nm). HRMS (ESI) were determined on a Therm LCQ TM Deca XP plus spectrometer. Product purification by flash chromatography was performed using 200-400 mesh silica gel.

## 2. Condition Optimization

Table S1. Condition optimization<sup>a</sup>

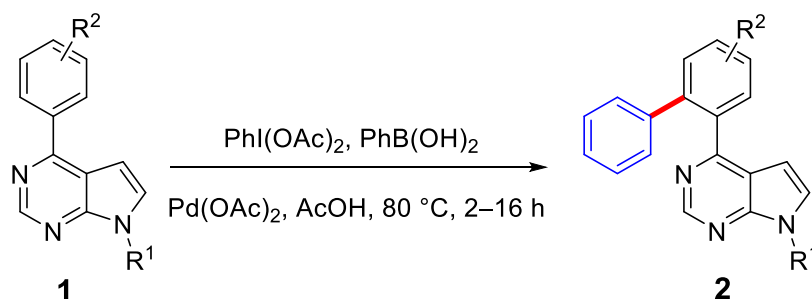


Entry	Catalyst (mol%)	Temp. (°C)	PhI(OAc) <sub>2</sub> , PhB(OH) <sub>2</sub> (equiv.)	Solvent	Time (h)	Yield (%) <sup>b</sup>
1	Pd(OAc) <sub>2</sub> (5)	40	2.0	AcOH	30	46
2	Pd(OAc) <sub>2</sub> (5)	20	2.0	AcOH	30	NR
3	Pd(OAc) <sub>2</sub> (5)	60	2.0	AcOH	20	70
4	Pd(OAc) <sub>2</sub> (5)	70	2.0	AcOH	2	80
5	Pd(OAc) <sub>2</sub> (5)	80	2.0	AcOH	2	88
6	Pd(OAc) <sub>2</sub> (5)	100	2.0	AcOH	0.3	50
7	-	80	2.0	AcOH	7	NR
8	Pd(PPh <sub>3</sub> ) <sub>4</sub> (5)	80	2.0	AcOH	7	35
9	PdCl <sub>2</sub> (5)	80	2.0	AcOH	7	Trace
10	Rh(OAc) <sub>2</sub> (5)	80	2.0	AcOH	7	NR
11	Co(OAc) <sub>2</sub> (100)	80	2.0	AcOH	20	11
12	Cu(OAc) <sub>2</sub> (100)	80	2.0	AcOH	7	NR
13	Pd(OAc) <sub>2</sub> (5)	80	1.0	AcOH	3	39
14	Pd(OAc) <sub>2</sub> (5)	80	1.5	AcOH	3	70
15	Pd(OAc) <sub>2</sub> (5)	80	2.5	AcOH	3	84
16	Pd(OAc) <sub>2</sub> (5)	80	3.0	AcOH	3	86
17	Pd(OAc) <sub>2</sub> (5)	80	2.0	MeCN	5	34
18	Pd(OAc) <sub>2</sub> (5)	80	2.0	DCE	5	30
19	Pd(OAc) <sub>2</sub> (5)	80	2.0	iPrOH	5	NR
20	Pd(OAc) <sub>2</sub> (5)	80	2.0	1,4-dioxane	5	26
21	Pd(OAc) <sub>2</sub> (5)	80	2.0	toluene	5	28

<sup>a</sup>0.4 mmol scale. <sup>b</sup>Isolated yields.

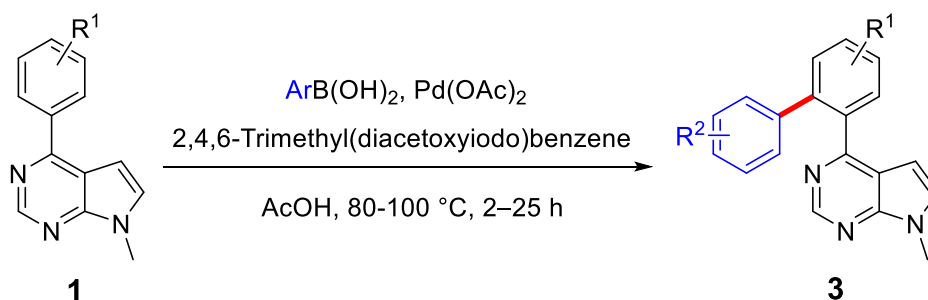
### 3. General Procedures for Pd-Catalyzed Arylation

(1) General Procedure A for Mono-Arylation Using Symmetrical Arylating Agents



The reaction of 7-methyl-4-([1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine **2aa** was exemplified here. Diacetoxyiodobenzene (258 mg, 0.8 mmol), phenylboronic acid (98 mg, 0.8 mmol) and AcOH (2.5 mL) were added in a pressure vessel. The reaction mixture was stirred at 80 °C for 1 h. This was followed by the addition of 7-methyl-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine **1a** (84 mg, 0.4 mmol) and Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) to the above reaction mixture. It was stirred at 80 °C for 2 h. After completion of the reaction, it was then cooled to room temperature, extracted with DCM (3×50 mL) and washed with water (30 mL), saturated sodium bicarbonate (30 mL) and brine (50 mL) before the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 4:1) on silica gel to provide the desired product 7-methyl-4-([1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine **2aa** (100.3 mg, 88% yield).

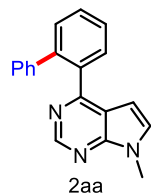
(2) General Procedure B for Mono-Arylation Using Unsymmetrical Arylating Agents



The reaction of 7-methyl-4-(4'-methyl-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine **3aa** was exemplified here. 2,4,6-Trimethyl(diacetoxyiodo)benzene (291 mg, 0.8 mmol), 4-tolylboronic acid (109 mg, 0.8 mmol) and AcOH (2.5 mL) were added in a pressure vessel. The reaction mixture was stirred at 100 °C for 1 h. This was followed by the addition of 7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine **1a** (84 mg, 0.4 mmol) and Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) to the above reaction mixture. It was stirred at 100 °C for 12 h. After completion of the reaction, it was then cooled to room temperature, extracted with DCM (3×50 mL) and washed with water (30 mL), saturated sodium bicarbonate (30 mL) and brine (50 mL) before the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 4:1) on silica gel to provide the desired product 7-methyl-4-(4'-methyl-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine **3aa** (91 mg, 76% yield).

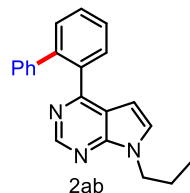
#### 4. Characterization of Compounds **2**, **3**, **4a-4c**

##### 7-methyl-4-([1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (**2aa**)



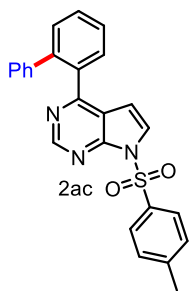
Yellow solid (100.4 mg, 88% yield). Mp: 96–98 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.86 (s, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.51 (m, 2H), 7.46 (m, 1H), 7.14 (m, 2H), 7.11–7.07 (m, 3H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.03 (d, *J* = 3.6 Hz, 1H), 3.75 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.4, 151.2, 150.6, 141.0, 140.9, 136.8, 130.6, 130.5, 129.2, 129.2, 129.0, 127.9, 127.3, 126.5, 117.4, 100.0, 30.9. HRMS *m/z* (ESI): calcd for C<sub>19</sub>H<sub>16</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 286.1339, found: 286.1351.

##### 7-propyl-4-([1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (**2ab**)



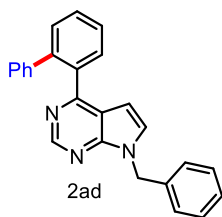
Yellow viscous oil (109.9 mg, 88% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.85 (s, 1H), 7.67 (d, *J* = 7.1 Hz, 1H), 7.53–7.49 (m, 2H), 7.47–7.44 (m, 1H), 7.14 (m, 2H), 7.10–7.06 (m, 3H), 6.92 (d, *J* = 3.6 Hz, 1H), 6.01 (d, *J* = 3.6 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 1.84–1.76 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.3, 151.0, 150.4, 141.0, 140.9, 136.9, 130.5, 130.3, 129.1, 128.9, 128.1, 127.7, 127.2, 126.4, 117.4, 99.9, 45.9, 23.3, 11.0. HRMS *m/z* (ESI): calcd for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>Na [M+Na]<sup>+</sup>: 336.1471, found: 336.1478.

##### 7-tosyl-4-([1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (**2ac**)



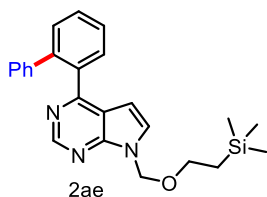
Yellow solid (146.4 mg, 86% yield). Mp: 185–187 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.01 (s, 1H), 8.00 (d,  $J = 7.9$  Hz, 2H), 7.60 (d,  $J = 7.5$  Hz, 1H), 7.56–7.52 (m, 2H), 7.47 (d,  $J = 7.5$  Hz, 1H), 7.43 (d,  $J = 3.9$  Hz, 1H), 7.29 (d,  $J = 8.1$  Hz, 2H), 7.10–7.03 (m, 5H), 6.07 (d,  $J = 3.9$  Hz, 1H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.7, 153.0, 150.8, 145.5, 140.9, 140.1, 135.6, 134.6, 130.5, 130.4, 129.7, 129.6, 128.9, 128.0, 127.9, 127.4, 126.7, 126.0, 119.3, 104.2, 21.4. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{25}\text{H}_{19}\text{N}_3\text{O}_2\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 448.1090, found: 448.1097.

#### 7-benzyl-4-((1,1'-biphenyl)-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2ad)



Yellow solid (124.6 mg, 86% yield). Mp: 157–159 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.95 (s, 1H), 7.75 (m, 1H), 7.60–7.54 (m, 2H), 7.54–7.50 (m, 1H), 7.33–7.25 (m, 3H), 7.22–7.17 (m, 2H), 7.17–7.11 (m, 3H), 7.11–7.06 (m, 2H), 6.92 (d,  $J = 3.6$  Hz, 1H), 6.08 (d,  $J = 3.6$  Hz, 1H), 5.40 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 151.5, 150.7, 141.1, 141.0, 136.9, 136.8, 130.6, 130.4, 129.2, 129.1, 128.6, 128.1, 127.9, 127.7, 127.3, 127.2, 126.5, 117.4, 100.7, 47.6. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{25}\text{H}_{20}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 362.1652, found: 362.1657.

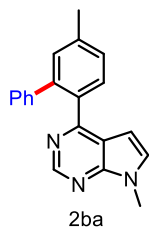
#### 7-SEM-4-((1,1'-biphenyl)-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2ae)



Yellow viscous oil (120.3 mg, 75% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 (s, 1H), 7.69 (dt,  $J = 7.6, 1.0$  Hz, 1H), 7.54 (dd,  $J = 5.0, 1.1$  Hz, 2H), 7.49 (m, 1H), 7.16–7.13

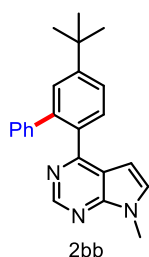
(m, 2H), 7.12–7.06 (m, 4H), 6.07 (d,  $J = 3.6$  Hz, 1H), 5.57 (s, 2H), 3.45 (t,  $J = 8.1$  Hz, 2H), 0.88 (t,  $J = 8.2$  Hz, 2H),  $-0.07$  (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 151.7, 151.3, 141.1, 140.9, 136.8, 130.6, 130.5, 129.3, 129.1, 127.9, 127.9, 127.4, 126.6, 117.5, 101.4, 72.6, 66.2, 17.6,  $-1.5$ . HRMS  $m/z$  (ESI): calcd for  $\text{C}_{24}\text{H}_{28}\text{N}_3\text{OSi}$  [ $\text{M}+\text{H}$ ] $^+$ : 402.1996, found: 402.2002.

#### 7-methyl-4-(5-methyl-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2ba)



Yellow viscous oil (90.5 mg, 76% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 (s, 1H), 7.57 (d,  $J = 7.8$  Hz, 1H), 7.36 (s, 1H), 7.30 (d,  $J = 7.8$  Hz, 1H), 7.18–7.13 (m, 2H), 7.13–7.08 (m, 3H), 6.90 (d,  $J = 3.5$  Hz, 1H), 6.04 (d,  $J = 3.5$  Hz, 1H), 3.78 (s, 3H), 2.47 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6, 151.3, 150.6, 141.1, 140.9, 139.2, 134.1, 131.3, 130.7, 129.1, 129.1, 128.1, 127.9, 126.5, 117.4, 100.2, 31.0, 21.3. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{20}\text{H}_{18}\text{N}_3$  [ $\text{M}+\text{H}$ ] $^+$ : 300.1495, found: 300.1506.

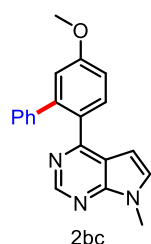
#### 7-methyl-4-(5-(tert-butyl)-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2bb)



Yellow solid (118.3 mg, 87% yield). Mp: 162–164 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 (s, 1H), 7.62 (d,  $J = 8.0$  Hz, 1H), 7.55–7.50 (m, 2H), 7.19–7.16 (m, 2H), 7.15–7.10 (m, 3H), 6.92 (d,  $J = 3.6$  Hz, 1H), 6.08 (d,  $J = 3.6$  Hz, 1H), 3.79 (s, 3H), 1.41 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 152.4, 151.4, 150.8, 141.7, 140.7, 134.2, 130.6, 129.2, 129.0, 128.0, 127.8, 126.5, 124.5, 117.5, 100.3, 34.8, 31.3, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{23}\text{H}_{24}\text{N}_3$  [ $\text{M}+\text{H}$ ] $^+$ : 342.1965, found: 342.1977.

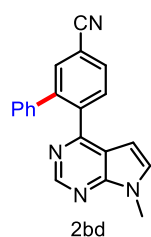
#### 7-methyl-4-(5-methoxy-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2bc)





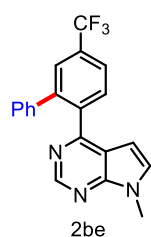
White solid (103.0 mg, 82% yield). Mp: 126–128 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (s, 1H), 7.63 (d,  $J$  = 8.5 Hz, 1H), 7.18–7.14 (m, 2H), 7.14–7.09 (m, 3H), 7.06 (d,  $J$  = 2.6 Hz, 1H), 7.02 (dd,  $J$  = 8.5, 2.6 Hz, 1H), 6.90 (d,  $J$  = 3.5 Hz, 1H), 6.02 (d,  $J$  = 3.5 Hz, 1H), 3.89 (s, 3H), 3.77 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.3, 159.3, 151.3, 150.7, 142.7, 141.1, 132.3, 129.7, 129.1, 129.0, 128.0, 126.8, 117.5, 115.9, 113.0, 100.2, 55.4, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$ : 316.1444, found: 316.1447.

**7-methyl-4-(5-carbonitrile-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2bd)**



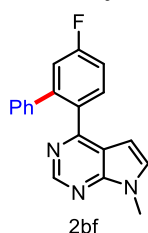
White solid (80.9 mg, 65% yield). Mp: 166–168 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 (s, 1H), 7.82 (s, 1H), 7.76 (d,  $J$  = 1.1 Hz, 2H), 7.16–7.09 (m, 5H), 6.98 (d,  $J$  = 3.6 Hz, 1H), 5.97 (d,  $J$  = 3.6 Hz, 1H), 3.80 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.2, 151.3, 150.8, 142.2, 141.2, 138.7, 134.1, 131.6, 130.6, 130.1, 128.8, 128.3, 127.6, 118.4, 117.1, 113.1, 99.5, 31.1. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{20}\text{H}_{14}\text{N}_4\text{Na}$   $[\text{M}+\text{Na}]^+$ : 333.1111, found: 333.1111.

**7-methyl-4-(5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidin e (2be)**



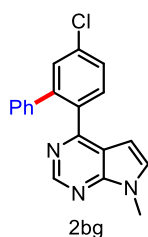
White solid (101.8 mg, 72% yield). Mp: 128–130 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.88 (s, 1H), 7.78 (t,  $J$  = 8.1 Hz, 2H), 7.73 (dd,  $J$  = 8.1, 1.1 Hz, 1H), 7.19–7.10 (m, 5H), 6.95 (d,  $J$  = 3.6 Hz, 1H), 6.01 (d,  $J$  = 3.6 Hz, 1H), 3.78 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.0, 151.3, 150.9, 141.8, 140.3, 139.6, 131.3 ( $J_{\text{C-F}}$  = 32.5 Hz), 131.3, 129.8, 129.0, 128.2, 127.4 ( $J_{\text{C-F}}$  = 3.8 Hz), 127.3, 124.0 ( $J_{\text{C-F}}$  = 3.7 Hz), 124.0 ( $J_{\text{C-F}}$  = 237.1 Hz), 117.3, 99.7, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{20}\text{H}_{14}\text{F}_3\text{N}_3\text{Na}$  [ $\text{M}+\text{Na}$ ] $^+$ : 376.1032, found: 376.1034.

#### 7-methyl-4-(5-fluoro-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2bf)



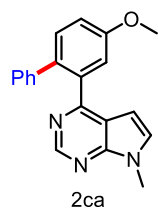
Yellow solid (93.1 mg, 77% yield). Mp: 108–110 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 (s, 1H), 7.64 (dd,  $J$  = 8.5, 5.8 Hz, 1H), 7.23 (dd,  $J$  = 9.7, 2.6 Hz, 1H), 7.16 (m, 1H), 7.14–7.08 (m, 5H), 6.92 (d,  $J$  = 3.5 Hz, 1H), 5.99 (d,  $J$  = 3.5 Hz, 1H), 3.77 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.0 ( $J_{\text{C-F}}$  = 249.3 Hz), 158.5, 151.3, 150.7, 143.3 ( $J_{\text{C-F}}$  = 8.0 Hz), 139.9, 133.0 ( $J_{\text{C-F}}$  = 3.0 Hz), 132.7 ( $J_{\text{C-F}}$  = 8.7 Hz), 129.4, 128.9, 128.1, 127.1, 117.4, 117.2 ( $J_{\text{C-F}}$  = 21.9 Hz), 114.3 ( $J_{\text{C-F}}$  = 21.3 Hz), 99.9, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{19}\text{H}_{14}\text{FN}_3\text{Na}$  [ $\text{M}+\text{Na}$ ] $^+$ : 326.1064, found: 326.1068.

#### 7-methyl-4-(5-chloro-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2bg)



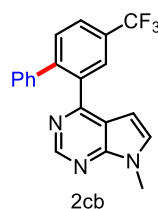
Yellow solid (87.1 mg, 68% yield). Mp: 84–86 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.85 (s, 1H), 7.60 (d,  $J$  = 8.2 Hz, 1H), 7.53 (d,  $J$  = 2.1 Hz, 1H), 7.45 (dd,  $J$  = 8.2, 2.2 Hz, 1H), 7.12 (s, 5H), 6.93 (d,  $J$  = 3.6 Hz, 1H), 5.99 (d,  $J$  = 3.6 Hz, 1H), 3.78 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.3, 151.4, 150.8, 142.8, 139.7, 135.4, 135.2, 132.2, 130.5, 129.6, 129.0, 128.2, 127.5, 127.2, 117.4, 99.9, 31.1. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{19}\text{H}_{15}\text{ClN}_3$  [ $\text{M}+\text{H}$ ] $^+$ : 320.0949, found: 320.0964.

7-methyl-4-(4-methoxy-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (2ca)



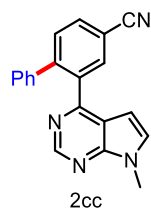
Yellow solid (115.8 mg, 92% yield). Mp: 130–132 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.88 (s, 1H), 7.44 (d,  $J = 8.5$  Hz, 1H), 7.19 (d,  $J = 2.7$  Hz, 1H), 7.13–7.03 (m, 6H), 6.89 (d,  $J = 3.5$  Hz, 1H), 6.01 (d,  $J = 3.5$  Hz, 1H), 3.85 (s, 3H), 3.75 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 158.7, 151.2, 150.6, 140.7, 137.8, 133.6, 131.7, 129.3, 129.0, 127.9, 126.1, 117.3, 115.5, 115.3, 100.1, 55.4, 30.9. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$ : 316.1444, found: 316.1458.

7-methyl-4-(4-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (2cb)



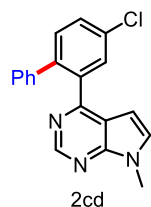
White solid (104.1 mg, 74% yield). Mp: 141–143 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.88 (s, 1H), 7.94 (d,  $J = 1.7$  Hz, 1H), 7.78 (dd,  $J = 8.1, 1.4$  Hz, 1H), 7.64 (d,  $J = 8.1$  Hz, 1H), 7.17–7.11 (m, 5H), 6.94 (d,  $J = 3.5$  Hz, 1H), 5.98 (d,  $J = 3.5$  Hz, 1H), 3.78 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.8, 151.3, 150.8, 144.5, 139.6, 137.5, 131.0, 129.8, 129.6 ( $J_{\text{C-F}} = 32.7$  Hz), 128.9, 128.2, 127.8 ( $J_{\text{C-F}} = 3.9$  Hz), 127.4, 125.9 ( $J_{\text{C-F}} = 3.8$  Hz), 124.0 ( $J_{\text{C-F}} = 273.0$  Hz), 117.3, 99.6, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{20}\text{H}_{14}\text{F}_3\text{N}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 376.1032, found: 376.1036.

7-methyl-4-(4-carbonitrile-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (2cc)



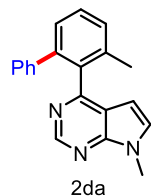
Yellow solid (85.6 mg, 69% yield). Mp: 159–161 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 (s, 1H), 7.96 (d,  $J = 1.7$  Hz, 1H), 7.81 (dd,  $J = 8.0, 1.8$  Hz, 1H), 7.64 (d,  $J = 8.0$  Hz, 1H), 7.18–7.11 (m, 5H), 6.98 (d,  $J = 3.6$  Hz, 1H), 5.98 (d,  $J = 3.6$  Hz, 1H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.9, 151.3, 150.9, 145.6, 139.2, 137.4, 134.5, 132.4, 131.4, 130.1, 128.8, 128.3, 127.8, 118.3, 117.2, 111.4, 99.5, 31.1. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{20}\text{H}_{15}\text{N}_4$   $[\text{M}+\text{H}]^+$ : 311.1291, found: 311.1304.

#### 7-methyl-4-(4-chloro-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2cd)



Yellow solid (90.8 mg, 71% yield). Mp: 136–138 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 (s, 1H), 7.65 (d,  $J = 2.2$  Hz, 1H), 7.51–7.43 (m, 2H), 7.15–7.06 (m, 5H), 6.92 (d,  $J = 3.6$  Hz, 1H), 5.99 (d,  $J = 3.6$  Hz, 1H), 3.77 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.9, 151.2, 150.7, 139.8, 139.5, 138.3, 133.3, 131.8, 130.5, 129.6, 129.3, 128.9, 128.1, 126.9, 117.2, 99.8, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{19}\text{H}_{15}\text{ClN}_3$   $[\text{M}+\text{H}]^+$ : 320.0949, found: 320.0952.

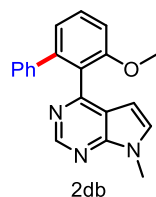
#### 7-methyl-4-(3-methyl-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2da)



Yellow viscous oil (95.3 mg, 80% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 (s, 1H), 7.41 (t,  $J = 7.6$  Hz, 1H), 7.31 (m, 2H), 7.14–7.07 (m, 2H), 7.04–6.99 (m, 3H), 6.94 (d,  $J = 3.6$  Hz, 1H), 6.03 (d,  $J = 3.6$  Hz, 1H), 3.78 (s, 3H), 2.11 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 151.0, 150.7, 141.3, 136.6, 136.0, 129.4, 129.3, 129.0, 128.5, 127.6, 127.5, 126.3, 118.4, 99.8, 31.0, 20.1. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{20}\text{H}_{17}\text{N}_3\text{Na}$

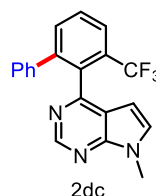
[M+Na]<sup>+</sup>: 322.1315, found: 322.1317.

**7-methyl-4-(3-methoxy-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2db)**



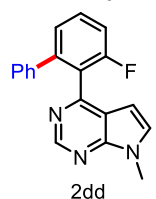
White solid (112.0 mg, 89% yield). Mp: 169–170 °C <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.84 (s, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.12–7.06 (m, 3H), 7.06–6.99 (m, 4H), 6.93 (d, *J* = 3.5 Hz, 1H), 6.09 (d, *J* = 3.5 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.3, 157.1, 150.8, 150.5, 142.9, 140.7, 129.7, 129.1, 128.9, 127.5, 126.4, 125.6, 122.5, 119.1, 110.0, 99.9, 55.8, 30.9. HRMS *m/z* (ESI): calcd for C<sub>20</sub>H<sub>17</sub>N<sub>3</sub>ONa [M+Na]<sup>+</sup>: 338.1264, found: 338.1266.

**7-methyl-4-(3-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2dc)**



Yellow viscous oil (81.8 mg, 58% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.85 (s, 1H), 7.86–7.80 (m, 1H), 7.67–7.60 (m, 2H), 7.10–7.04 (m, 2H), 7.04–6.99 (m, 3H), 6.96 (d, *J* = 3.5 Hz, 1H), 6.01 (d, *J* = 3.5 Hz, 1H), 3.77 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 156.6, 150.5, 150.4, 143.4, 139.6, 134.9, 133.7, 129.7, 129.4 (*J*<sub>C-F</sub> = 30.7 Hz), 129.0, 128.8, 127.6, 127.0, 125.4 (*J*<sub>C-F</sub> = 5.2 Hz), 123.8 (*J*<sub>C-F</sub> = 275.0 Hz), 118.8, 99.6, 31.0. HRMS *m/z* (ESI): calcd for C<sub>20</sub>H<sub>15</sub>F<sub>3</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 354.1213, found: 354.1229.

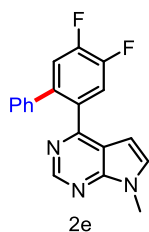
**7-methyl-4-(3-fluoro-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2dd)**



Yellow viscous oil (88.1 mg, 73% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.83 (s, 1H),

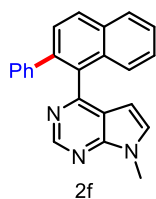
7.46 (m, 1H), 7.29 (dd,  $J = 7.7, 1.0$  Hz, 1H), 7.18 (m, 1H), 7.11–7.05 (m, 5H), 6.99 (d,  $J = 3.5$  Hz, 1H), 6.15 (d,  $J = 3.5$  Hz, 1H), 3.76 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.2 ( $J_{\text{C-F}} = 248.9$  Hz), 154.0, 150.8, 150.6, 143.5 ( $J_{\text{C-F}} = 2.6$  Hz), 139.6 ( $J_{\text{C-F}} = 2.4$  Hz), 130.2 ( $J_{\text{C-F}} = 9.0$  Hz), 129.7, 128.8, 127.8, 126.9, 125.9 ( $J_{\text{C-F}} = 3.0$  Hz), 124.5 ( $J_{\text{C-F}} = 15.6$  Hz), 118.9, 114.5 ( $J_{\text{C-F}} = 22.3$  Hz), 99.5, 30.8. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{19}\text{H}_{14}\text{FN}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 326.1064, found: 326.1068.

#### 7-methyl-4-(4,5-difluoro-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2e)



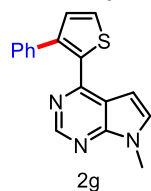
Yellow viscous oil (70.3 mg, 55% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79 (s, 1H), 7.40 (m, 1H), 7.29 (m, 1H), 7.17–7.12 (m, 5H), 6.97 (d,  $J = 3.6$  Hz, 1H), 6.06 (d,  $J = 3.6$  Hz, 1H), 3.79 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.4 ( $J_{\text{C-F}} = 2.5$  Hz), 151.3 (dd,  $J_{\text{C-F}} = 251.7, 14.1$  Hz), 151.1, 150.8, 148.0 (dd,  $J_{\text{C-F}} = 248.4, 13.0$  Hz), 134.6 ( $J_{\text{C-F}} = 4.1$  Hz), 132.7 ( $J_{\text{C-F}} = 2.4$  Hz), 131.1 ( $J_{\text{C-F}} = 12.6$  Hz), 130.2 ( $J_{\text{C-F}} = 1.7$  Hz), 129.7, 127.9, 127.7, 126.2 (dd,  $J_{\text{C-F}} = 7.1, 4.2$  Hz), 117.5, 116.1 ( $J_{\text{C-F}} = 17.4$  Hz), 99.7, 31.1. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{19}\text{H}_{13}\text{F}_2\text{N}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 344.0970, found: 344.0977.

#### 7-methyl-4-(2-phenylnaphthalen-1-yl)-7H-pyrrolo[2,3-d]pyrimidine (2f)



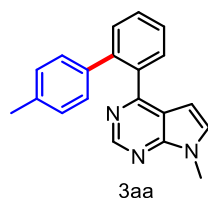
White solid (108.3 mg, 81% yield). Mp: 49–51 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.00 (s, 1H), 8.02 (d,  $J = 8.5$  Hz, 1H), 7.93 (d,  $J = 8.1$  Hz, 1H), 7.64 (d,  $J = 8.5$  Hz, 1H), 7.49–7.44 (m, 2H), 7.39–7.35 (m, 1H), 7.24–7.20 (m, 2H), 7.12–7.06 (m, 3H), 6.92 (d,  $J = 3.5$  Hz, 1H), 5.93 (d,  $J = 3.5$  Hz, 1H), 3.80 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7, 151.0, 150.8, 141.3, 138.8, 132.8, 132.7, 131.8, 129.5, 129.3, 129.1, 128.0, 127.9, 127.7, 126.7, 126.5, 126.0, 125.9, 119.4, 99.9, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 336.1495, found: 336.1500.

7-methyl-4-(3-phenylthiophen-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (2g)



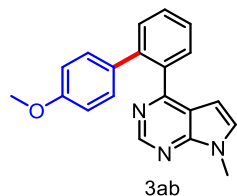
White solid (85.2 mg, 73% yield). Mp: 134–136 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 (s, 1H), 7.55 (d,  $J = 5.1$  Hz, 1H), 7.31–7.30 (m, 1H), 7.29 (d,  $J = 2.2$  Hz, 1H), 7.25–7.21 (m, 4H), 6.81 (d,  $J = 3.6$  Hz, 1H), 5.58 (d,  $J = 3.6$  Hz, 1H), 3.76 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  152.2, 151.5, 151.2, 141.7, 136.7, 136.6, 130.8, 129.1, 128.9, 128.5, 128.4, 127.3, 115.4, 100.9, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{17}\text{H}_{13}\text{N}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 314.0722, found: 314.0730.

7-methyl-4-(4'-methyl-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (3aa)



White solid (98.0 mg, 82% yield). Mp: 151–153 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 (s, 1H), 7.63 (d,  $J = 7.4$  Hz, 1H), 7.51 (d,  $J = 4.0$  Hz, 2H), 7.44 (m, 1H), 7.04 (d,  $J = 8.1$  Hz, 2H), 6.95–6.88 (m, 3H), 6.05 (d,  $J = 3.5$  Hz, 1H), 3.78 (s, 3H), 2.21 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 151.3, 150.7, 141.1, 138.1, 136.8, 136.2, 130.7, 130.6, 129.3, 129.3, 129.0, 128.8, 127.1, 117.5, 100.2, 31.0, 21.1. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{20}\text{H}_{17}\text{N}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 322.1315, found: 322.1320.

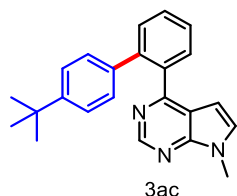
7-methyl-4-(4'-methoxy-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (3ab)



Yellow solid (110.8 mg, 88% yield). Mp: 122–124 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 (s, 1H), 7.62 (dt,  $J = 7.6, 1.0$  Hz, 1H), 7.53–7.48 (m, 2H), 7.46–7.41 (m, 1H), 7.11–7.03 (m, 2H), 6.92 (d,  $J = 3.6$  Hz, 1H), 6.68–6.61 (m, 2H), 6.03 (d,  $J = 3.6$  Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 158.4, 151.4, 150.7, 140.6, 136.8, 133.5, 130.7, 130.4, 130.1, 129.3, 129.2, 126.9, 117.4, 113.5, 100.2,

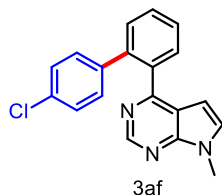
55.1, 31.0. HRMS  $m/z$  (ESI): calcd for  $C_{20}H_{18}N_3O$   $[M+H]^+$ : 316.1444, found: 316.1459.

7-methyl-4-(4'-(tert-butyl)-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (3ac)



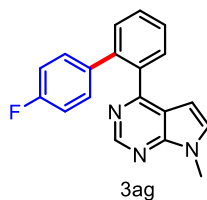
White solid (125.3 mg, 92% yield). Mp: 129–131 °C  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.88 (s, 1H), 7.66 (dd,  $J = 7.5, 1.4$  Hz, 1H), 7.56–7.47 (m, 2H), 7.44 (td,  $J = 7.4, 1.6$  Hz, 1H), 7.15–7.10 (m, 2H), 7.10–7.05 (m, 2H), 6.87 (d,  $J = 3.6$  Hz, 1H), 6.05 (d,  $J = 3.6$  Hz, 1H), 3.75 (s, 3H), 1.21 (s, 9H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  159.6, 151.1, 150.6, 149.3, 140.9, 137.8, 136.7, 130.6, 130.4, 129.1, 129.0, 128.6, 126.9, 124.7, 117.4, 100.1, 34.1, 31.1, 30.8. HRMS  $m/z$  (ESI): calcd for  $C_{23}H_{24}N_3$   $[M+H]^+$ : 342.1965, found: 342.1981.

7-methyl-4-(4'-chloro-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (3af)



Black solid (80.8 mg, 65% yield). Mp: 175–177 °C  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.84 (s, 1H), 7.68–7.62 (m, 1H), 7.56–7.45 (m, 3H), 7.09–7.04 (m, 4H), 6.97 (d,  $J = 3.5$  Hz, 1H), 6.05 (d,  $J = 3.5$  Hz, 1H), 3.80 (s, 3H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  159.1, 151.3, 150.8, 139.8, 139.5, 136.8, 132.7, 130.7, 130.3, 130.3, 129.5, 129.3, 128.1, 127.6, 117.4, 99.9, 31.0. HRMS  $m/z$  (ESI): calcd for  $C_{19}H_{15}ClN_3$   $[M+H]^+$ : 320.0949, found: 320.0964.

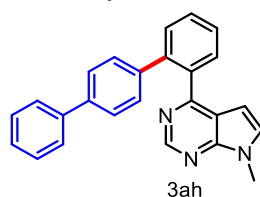
7-methyl-4-(4'-fluoro-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (3ag)





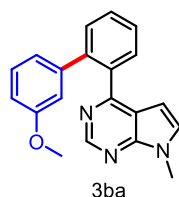
White solid (102.6 mg, 85% yield). Mp: 177–179 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.85 (s, 1H), 7.67–7.61 (m, 1H), 7.55–7.43 (m, 3H), 7.13–7.05 (m, 2H), 6.94 (d,  $J$  = 3.5 Hz, 1H), 6.83–6.75 (m, 2H), 6.02 (d,  $J$  = 3.5 Hz, 1H), 3.78 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.7 ( $J_{\text{C-F}}$  = 246.6 Hz), 159.2, 151.3, 150.8, 140.0, 137.0 ( $J_{\text{C-F}}$  = 3.4 Hz), 136.9, 130.6, 130.6, 130.5, 130.4, 129.3 ( $J_{\text{C-F}}$  = 18.3 Hz), 127.4, 117.4, 114.8 ( $J_{\text{C-F}}$  = 21.5 Hz), 99.9, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{19}\text{H}_{14}\text{FN}_3\text{Na}$  [ $\text{M}+\text{Na}$ ] $^+$ : 326.1064, found: 326.1065.

### 7-methyl-4-([1,1':4',1''-terphenyl]-2-yl)-7H-pyrrolo[2,3-*d*]pyrimidine (3ah)



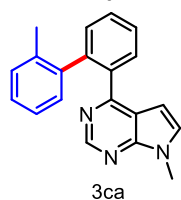
Yellow solid (117.3 mg, 81% yield). Mp: 60–62 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.92 (s, 1H), 7.70 (dd,  $J$  = 7.5, 1.4 Hz, 1H), 7.62–7.54 (m, 2H), 7.54–7.48 (m, 3H), 7.41–7.35 (m, 4H), 7.29 (t,  $J$  = 7.3 Hz, 1H), 7.26–7.22 (m, 2H), 6.92 (d,  $J$  = 3.6 Hz, 1H), 6.11 (d,  $J$  = 3.5 Hz, 1H), 3.77 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 151.2, 150.7, 140.6, 140.3, 140.0, 139.1, 136.8, 130.7, 130.5, 129.4, 129.4, 129.3, 128.6, 127.4, 127.1, 126.7, 126.5, 117.4, 100.1, 30.9. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{25}\text{H}_{20}\text{N}_3$  [ $\text{M}+\text{H}$ ] $^+$ : 362.1652, found: 362.1642.

### 7-methyl-4-(3'-methoxy-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-*d*]pyrimidine (3ba)



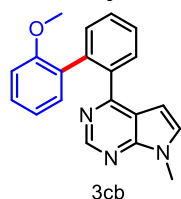
Yellow viscous oil (75.8 mg, 60% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 (s, 1H), 7.65–7.62 (m, 1H), 7.56–7.50 (m, 2H), 7.50–7.45 (m, 1H), 7.02 (t,  $J$  = 7.9 Hz, 1H), 6.92 (d,  $J$  = 3.6 Hz, 1H), 6.78–6.74 (m, 1H), 6.70–6.68 (m, 1H), 6.66–6.62 (m, 1H), 6.05 (d,  $J$  = 3.6 Hz, 1H), 3.78 (s, 3H), 3.53 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 159.0, 151.2, 150.6, 142.3, 140.9, 136.9, 130.6, 130.3, 129.3, 129.2, 128.9, 127.4, 121.6, 117.5, 114.4, 112.8, 100.0, 54.9, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}$  [ $\text{M}+\text{H}$ ] $^+$ : 316.1444, found: 316.1453.

7-methyl-4-(2'-methyl-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (3ca)



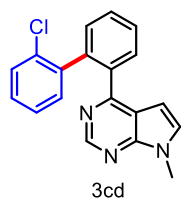
Yellow solid (66.0 mg, 55% yield). Mp: 115–117 °C <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.77 (s, 1H), 7.67 (dd, *J* = 6.9, 2.2 Hz, 1H), 7.54–7.47 (m, 2H), 7.41–7.38 (m, 1H), 7.09 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.07–7.01 (m, 1H), 7.01–6.94 (m, 3H), 6.18 (d, *J* = 3.6 Hz, 1H), 3.79 (s, 3H), 2.02 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.4, 151.1, 150.9, 140.9, 140.7, 137.8, 135.7, 131.0, 130.4, 130.2, 129.7, 129.1, 128.8, 127.2, 126.9, 125.1, 117.3, 100.0, 31.0, 20.3. HRMS *m/z* (ESI): calcd for C<sub>20</sub>H<sub>18</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 300.1495, found: 300.1509.

7-methyl-4-(2'-methoxy-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (3cb)



White solid (81.8 mg, 65% yield). Mp: 129–131 °C <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.80 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.55–7.50 (m, 2H), 7.50–7.45 (m, 1H), 7.19 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.12 (td, *J* = 7.9, 1.8 Hz, 1H), 6.93 (d, *J* = 3.5 Hz, 1H), 6.84 (td, *J* = 7.4, 1.1 Hz, 1H), 6.59 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.20 (d, *J* = 3.5 Hz, 1H), 3.78 (s, 3H), 3.23 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.9, 155.8, 151.0, 150.7, 137.8, 137.6, 131.4, 131.4, 130.1, 130.0, 128.9, 128.8, 128.5, 127.2, 120.5, 116.8, 110.3, 100.2, 54.5, 31.0. HRMS *m/z* (ESI): calcd for C<sub>20</sub>H<sub>17</sub>N<sub>3</sub>ONa [M+Na]<sup>+</sup>: 338.1264, found: 338.1265.

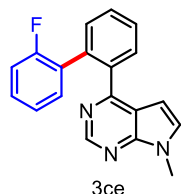
7-methyl-4-(2'-chloro-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (3cd)



Yellow solid (88.4 mg, 69% yield). Mp: 147–149 °C <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ

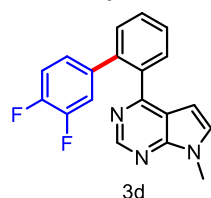
8.77 (s, 1H), 7.74–7.69 (m, 1H), 7.55–7.47 (m, 3H), 7.23 (dd,  $J = 7.9, 1.3$  Hz, 1H), 7.09–7.02 (m, 2H), 7.00–6.95 (m, 2H), 6.33 (d,  $J = 3.6$  Hz, 1H), 3.77 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 150.9, 150.8, 139.6, 138.3, 137.7, 132.7, 132.1, 131.3, 130.2, 129.3, 128.6, 128.1, 127.9, 126.1, 117.4, 99.8, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{19}\text{H}_{15}\text{ClN}_3$   $[\text{M}+\text{H}]^+$ : 320.0949, found: 320.0960.

### 7-methyl-4-(2'-fluoro-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (3ce)



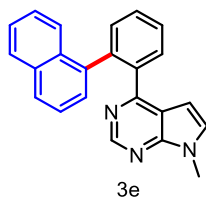
Yellow viscous oil (103.2 mg, 85% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (s, 1H), 7.74–7.70 (m, 1H), 7.55–7.50 (m, 3H), 7.12–7.06 (m, 2H), 6.97 (d,  $J = 3.5$  Hz, 1H), 6.90 (td,  $J = 7.5, 1.2$  Hz, 1H), 6.87–6.83 (m, 1H), 6.22 (d,  $J = 3.5$  Hz, 1H), 3.78 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3 ( $J_{\text{C-F}} = 247.1$  Hz), 158.9, 151.1, 150.8, 137.7, 134.9, 131.8 ( $J_{\text{C-F}} = 3.4$  Hz), 131.3 ( $J_{\text{C-F}} = 1.3$  Hz), 130.3, 129.3, 128.9, 128.8, 128.7, 127.9, 123.7 ( $J_{\text{C-F}} = 3.6$  Hz), 117.1, 115.3 ( $J_{\text{C-F}} = 22.5$  Hz), 99.7, 30.9. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{19}\text{H}_{15}\text{FN}_3$   $[\text{M}+\text{H}]^+$ : 304.1245, found: 304.1259.

### 7-methyl-4-(3',4'-difluoro-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (3d)



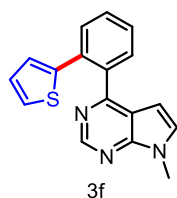
Yellow solid (68.3 mg, 53% yield). Mp: 133–135 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.85 (s, 1H), 7.65 (dd,  $J = 7.5, 1.5$  Hz, 1H), 7.56–7.44 (m, 3H), 7.03–6.95 (m, 2H), 6.92–6.85 (m, 1H), 6.84–6.79 (m, 1H), 6.08 (d,  $J = 3.5$  Hz, 1H), 3.82 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 151.3, 150.9, 149.8 (dd,  $J_{\text{C-F}} = 248.4, 12.8$  Hz), 149.3 (dd,  $J_{\text{C-F}} = 248.6, 12.7$  Hz), 139.0, 138.1 (dd,  $J_{\text{C-F}} = 6.1, 3.9$  Hz), 136.9, 130.8, 130.3, 129.7, 129.4, 127.9, 125.2 (dd,  $J_{\text{C-F}} = 6.1, 3.6$  Hz), 117.9 ( $J_{\text{C-F}} = 17.5$  Hz), 117.4, 116.7 ( $J_{\text{C-F}} = 17.2$  Hz), 99.8, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{19}\text{H}_{13}\text{F}_2\text{N}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 344.0970, found: 344.0976.

### 7-methyl-4-(2-(naphthalen-1-yl)phenyl)-7H-pyrrolo[2,3-d]pyrimidine (3e)



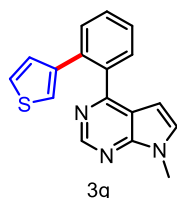
Black viscous oil (75.1 mg, 56% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.70 (s, 1H), 7.86 (d,  $J = 8.3$  Hz, 1H), 7.80–7.75 (m, 1H), 7.72 (d,  $J = 8.0$  Hz, 1H), 7.63 (dd,  $J = 6.2, 3.4$  Hz, 1H), 7.60–7.57 (m, 3H), 7.36–7.29 (m, 2H), 7.25–7.20 (m, 2H), 6.77 (d,  $J = 3.5$  Hz, 1H), 6.01 (d,  $J = 3.5$  Hz, 1H), 3.66 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 150.9, 150.5, 139.4, 138.6, 138.4, 133.4, 132.0, 131.7, 130.5, 129.1, 128.8, 128.0, 128.0, 127.6, 127.3, 126.0, 125.7, 125.4, 124.9, 117.4, 100.0, 30.9. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 336.1495, found: 336.1510.

#### 7-methyl-4-(2-(thiophen-2-yl)phenyl)-7H-pyrrolo[2,3-d]pyrimidine (3f)



Black viscous oil (73.2 mg, 63% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.94 (s, 1H), 7.65–7.58 (m, 2H), 7.53–7.43 (m, 2H), 7.09 (dd,  $J = 5.1, 1.2$  Hz, 1H), 7.00 (d,  $J = 3.5$  Hz, 1H), 6.73 (dd,  $J = 5.1, 3.6$  Hz, 1H), 6.64 (dd,  $J = 3.6, 1.2$  Hz, 1H), 6.13 (d,  $J = 3.5$  Hz, 1H), 3.83 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 151.1, 150.7, 142.3, 136.3, 133.5, 130.7, 130.6, 129.8, 129.4, 127.7, 127.1, 126.9, 125.6, 117.8, 100.0, 31.1. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{17}\text{H}_{13}\text{N}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 314.0722, found: 314.0726.

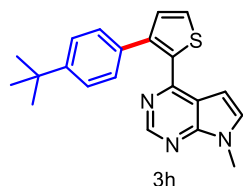
#### 7-methyl-4-(2-(thiophen-3-yl)phenyl)-7H-pyrrolo[2,3-d]pyrimidine (3g)



Yellow solid (93.2 mg, 80% yield). Mp: 126–128 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (s, 1H), 7.61 (dd,  $J = 7.6, 1.5$  Hz, 1H), 7.56 (dd,  $J = 7.6, 1.5$  Hz, 1H), 7.48 (td,  $J = 7.5, 1.6$  Hz, 1H), 7.43 (td,  $J = 7.4, 1.4$  Hz, 1H), 7.03–6.96 (m, 2H), 6.94 (d,  $J = 3.5$  Hz, 1H), 6.70 (dd,  $J = 4.5, 1.8$  Hz, 1H), 6.05 (d,  $J = 3.5$  Hz, 1H), 3.79 (s, 3H).  $^{13}\text{C}$

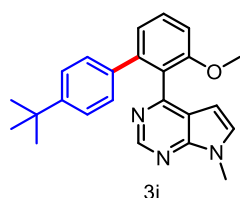
NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.3, 151.3, 150.7, 141.3, 136.7, 135.5, 130.5, 129.9, 129.3, 129.2, 128.3, 127.2, 124.8, 122.7, 117.4, 99.8, 30.9. HRMS *m/z* (ESI): calcd for C<sub>17</sub>H<sub>13</sub>N<sub>3</sub>SNa [M+Na]<sup>+</sup>: 314.0722, found: 314.0722.

7-methyl-4-(3-(4-(tert-butyl)phenyl)thiophen-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (3h)



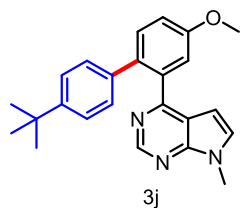
Yellow solid (95.6 mg, 69% yield). Mp: 147–149 °C <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.90 (s, 1H), 7.55 (d, *J* = 5.1 Hz, 1H), 7.28–7.23 (m, 5H), 6.78 (d, *J* = 3.6 Hz, 1H), 5.55 (d, *J* = 3.6 Hz, 1H), 3.79 (s, 3H), 1.29 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  152.5, 151.6, 151.3, 150.4, 141.9, 136.6, 133.8, 130.9, 128.8, 128.7, 128.3, 125.5, 115.5, 101.2, 34.5, 31.3, 31.1. HRMS *m/z* (ESI): calcd for C<sub>21</sub>H<sub>21</sub>N<sub>3</sub>SNa [M+Na]<sup>+</sup>: 370.1348, found: 370.1349.

7-methyl-4-(4'-(tert-butyl)-3-methoxy-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (3i)



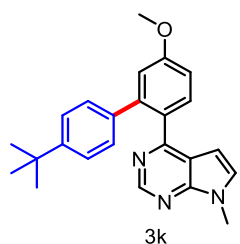
Yellow viscous oil (126.5 mg, 85% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.82 (s, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.09 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.07–7.02 (m, 2H), 7.02–6.97 (m, 3H), 6.94 (d, *J* = 3.5 Hz, 1H), 6.12 (d, *J* = 3.5 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 1.18 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  157.3, 157.3, 150.8, 150.5, 149.2, 142.8, 137.6, 129.7, 129.0, 128.5, 125.6, 124.4, 122.7, 119.3, 109.8, 100.0, 55.8, 34.2, 31.1, 30.8. HRMS *m/z* (ESI): calcd for C<sub>24</sub>H<sub>26</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 372.2070, found: 372.2074.

7-methyl-4-(4'-(tert-butyl)-4-methoxy-[1,1'-biphenyl]-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (3j)



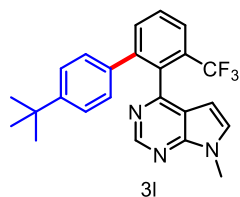
Yellow viscous oil (137.8 mg, 93% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 (s, 1H), 7.43 (d,  $J = 8.5$  Hz, 1H), 7.18 (d,  $J = 2.7$  Hz, 1H), 7.08 (d,  $J = 8.4$  Hz, 2H), 7.04 (dd,  $J = 8.5, 2.7$  Hz, 1H), 7.01 (d,  $J = 8.4$  Hz, 2H), 6.85 (d,  $J = 3.6$  Hz, 1H), 6.00 (d,  $J = 3.6$  Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 1.18 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 158.5, 151.1, 150.6, 148.8, 137.7, 137.5, 133.5, 131.6, 129.0, 128.5, 124.6, 117.3, 115.4, 115.3, 100.1, 55.2, 34.0, 31.0, 30.7. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{24}\text{H}_{26}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$ : 372.2070, found: 372.2075.

**7-methyl-4-(4'-(tert-butyl)-5-methoxy-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (3k)**



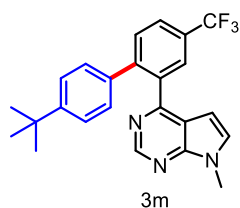
Yellow solid (127.8 mg, 86% yield). Mp: 148–150 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (s, 1H), 7.62 (d,  $J = 8.5$  Hz, 1H), 7.18–7.11 (m, 2H), 7.11–7.04 (m, 3H), 7.00 (dd,  $J = 8.5, 2.6$  Hz, 1H), 6.88 (d,  $J = 3.5$  Hz, 1H), 6.02 (d,  $J = 3.5$  Hz, 1H), 3.90 (s, 3H), 3.79 (s, 3H), 1.22 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.2, 159.5, 151.3, 150.7, 149.7, 142.7, 138.0, 132.3, 129.7, 128.7, 128.7, 124.9, 117.5, 115.8, 112.8, 100.4, 55.4, 34.3, 31.2, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{24}\text{H}_{26}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$ : 372.2070, found: 372.2074.

**7-methyl-4-(4'-(tert-butyl)-3-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (3l)**



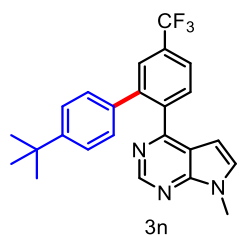
Yellow solid (98.3 mg, 60% yield). Mp: 58–60 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.85 (s, 1H), 7.81 (dd,  $J$  = 6.9, 2.3 Hz, 1H), 7.67–7.59 (m, 2H), 7.05–7.00 (m, 2H), 6.99–6.94 (m, 3H), 6.02 (d,  $J$  = 3.5 Hz, 1H), 3.78 (s, 3H), 1.16 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.8, 150.5, 150.4, 149.9, 143.4, 136.6, 133.8, 129.6, 129.2 ( $J_{\text{C-F}}$  = 7.5 Hz), 128.8, 128.7, 125.2 ( $J_{\text{C-F}}$  = 5.3 Hz), 124.5, 123.9 ( $J_{\text{C-F}}$  = 274.7 Hz), 119.0, 116.0, 99.8, 34.3, 31.1, 30.9. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{24}\text{H}_{23}\text{F}_3\text{N}_3$   $[\text{M}+\text{H}]^+$ : 410.1839, found: 410.1857.

**7-methyl-4-(4'-(tert-butyl)-4-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (3m)**



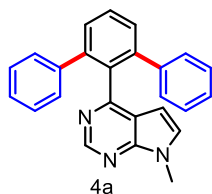
Yellow solid (113.2 mg, 69% yield). Mp: 58–60 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.88 (s, 1H), 7.94 (d,  $J$  = 1.9 Hz, 1H), 7.76 (dd,  $J$  = 8.1, 1.9 Hz, 1H), 7.65 (d,  $J$  = 8.1 Hz, 1H), 7.19–7.13 (m, 2H), 7.10–7.04 (m, 2H), 6.93 (d,  $J$  = 3.6 Hz, 1H), 5.98 (d,  $J$  = 3.6 Hz, 1H), 3.80 (s, 3H), 1.21 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.0, 151.3, 150.9, 150.5, 144.5, 137.5, 136.6, 131.0, 129.6, 129.3 ( $J_{\text{C-F}}$  = 32.8 Hz), 128.7, 127.8 ( $J_{\text{C-F}}$  = 3.9 Hz), 125.8 ( $J_{\text{C-F}}$  = 3.8 Hz), 125.1, 124.1 ( $J_{\text{C-F}}$  = 272.5 Hz), 117.4, 99.8, 34.3, 31.1, 30.9. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{24}\text{H}_{22}\text{F}_3\text{N}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 432.1658, found: 432.1658.

**7-methyl-4-(4'-(tert-butyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine (3n)**



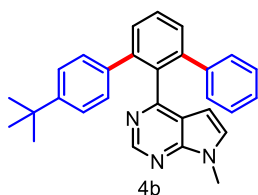
Yellow solid (102.8 mg, 63% yield). Mp: 125–127 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.88 (s, 1H), 7.80 (s, 1H), 7.77 (d,  $J = 8.0$  Hz, 1H), 7.71 (dd,  $J = 8.2, 1.8$  Hz, 1H), 7.19–7.13 (m, 2H), 7.10–7.05 (m, 2H), 6.97 (d,  $J = 3.6$  Hz, 1H), 6.03 (d,  $J = 3.6$  Hz, 1H), 3.83 (s, 3H), 1.22 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 151.4, 150.9, 150.4, 141.9, 140.2, 136.7, 131.3 ( $J_{\text{C-F}} = 32.6$  Hz), 131.3, 129.6, 128.7, 127.5 ( $J_{\text{C-F}} = 3.9$  Hz), 125.2, 124.1 ( $J_{\text{C-F}} = 273.1$  Hz), 123.8 ( $J_{\text{C-F}} = 3.9$  Hz), 117.5, 100.0, 34.4, 31.2, 31.1. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{24}\text{H}_{23}\text{F}_3\text{N}_3$   $[\text{M}+\text{H}]^+$ : 410.1839, found: 410.1844.

#### 7-methyl-4-([1,1':3',1''-terphenyl]-2'-yl)-7H-pyrrolo[2,3-*d*]pyrimidine (4a)



White solid (76.8 mg, 53% yield). Mp: 151–153 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.61 (s, 1H), 7.57 (dd,  $J = 8.3, 7.0$  Hz, 1H), 7.48 (d,  $J = 7.4$  Hz, 2H), 7.11–7.06 (m, 4H), 7.06–7.02 (m, 6H), 6.84 (d,  $J = 3.5$  Hz, 1H), 6.00 (d,  $J = 3.5$  Hz, 1H), 3.68 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.0, 150.4, 150.2, 142.0, 141.1, 135.2, 129.4, 129.3, 128.9, 128.7, 127.5, 126.4, 119.3, 99.7, 30.8. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{25}\text{H}_{20}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 362.1652, found: 362.1660.

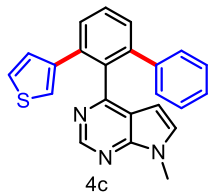
#### 7-methyl-4-(4-(tert-butyl)-[1,1':3',1''-terphenyl]-2'-yl)-7H-pyrrolo[2,3-*d*]pyrimidine (4b)



Yellow solid (98.5 mg, 59% yield). Mp: 159–161 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.62 (s, 1H), 7.55 (t,  $J = 7.6$  Hz, 1H), 7.49 (dd,  $J = 7.7, 1.4$  Hz, 1H), 7.46 (dd,  $J = 7.6, 1.4$  Hz, 1H), 7.11–7.06 (m, 3H), 7.06–7.05 (m, 1H), 7.05–7.01 (m, 3H), 7.01–6.97 (m, 2H), 6.82 (d,  $J = 3.5$  Hz, 1H), 5.99 (d,  $J = 3.5$  Hz, 1H), 3.68 (s, 3H), 1.20 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 150.3, 150.2, 149.2, 142.0, 142.0, 141.2, 138.1, 135.0, 129.5, 129.2, 129.2, 129.0, 128.7, 128.6, 127.5, 126.4, 124.4, 119.3, 100.0, 34.2, 31.2, 30.8. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{29}\text{H}_{27}\text{N}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 440.2097, found: 440.2098.

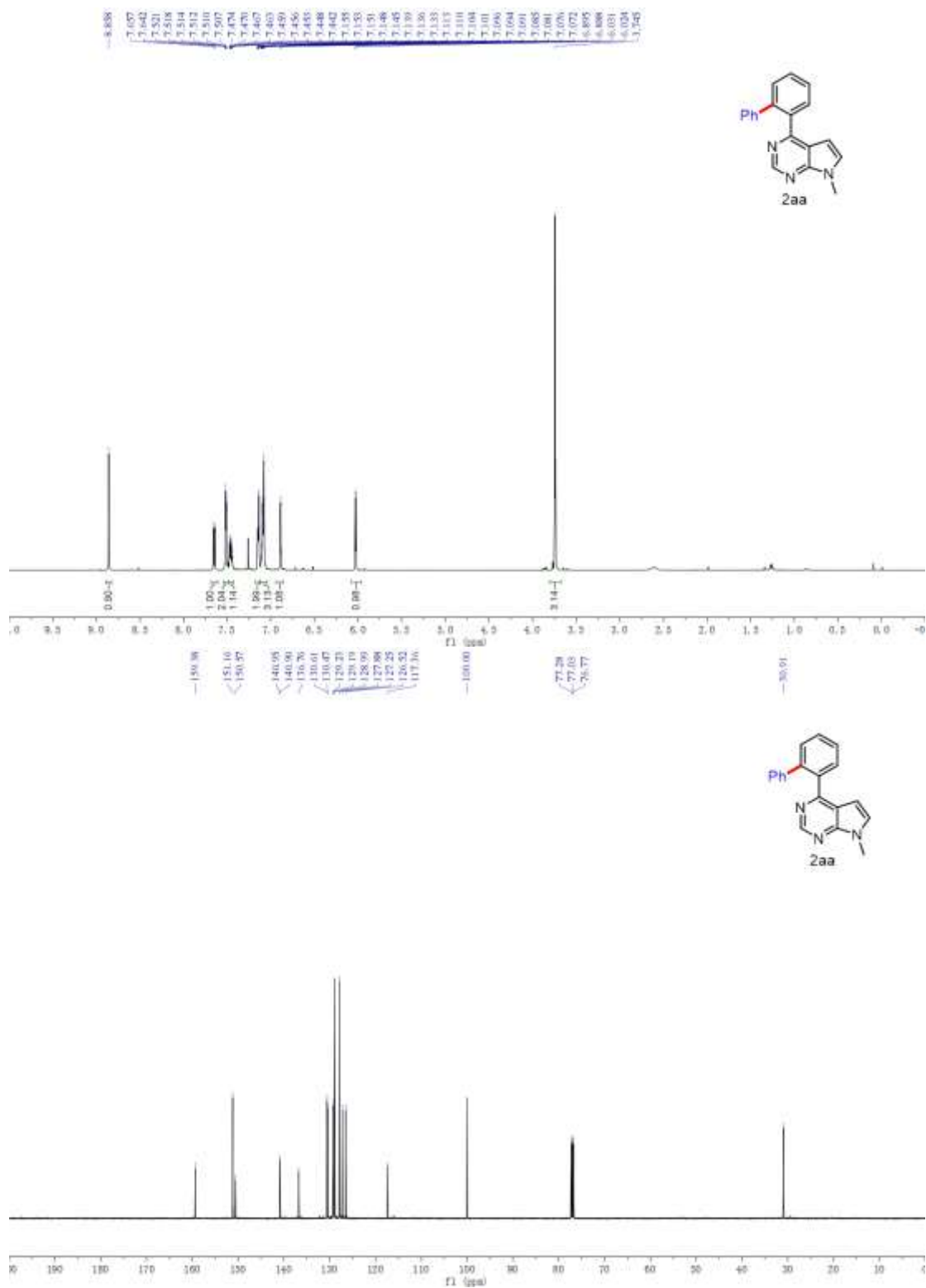


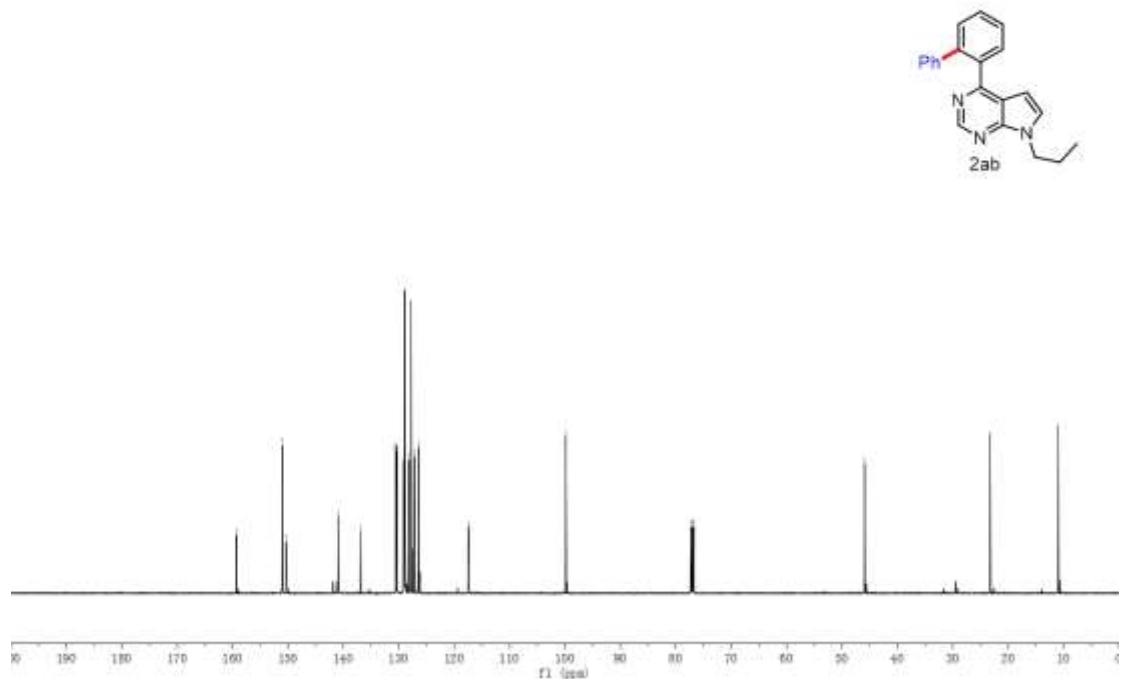
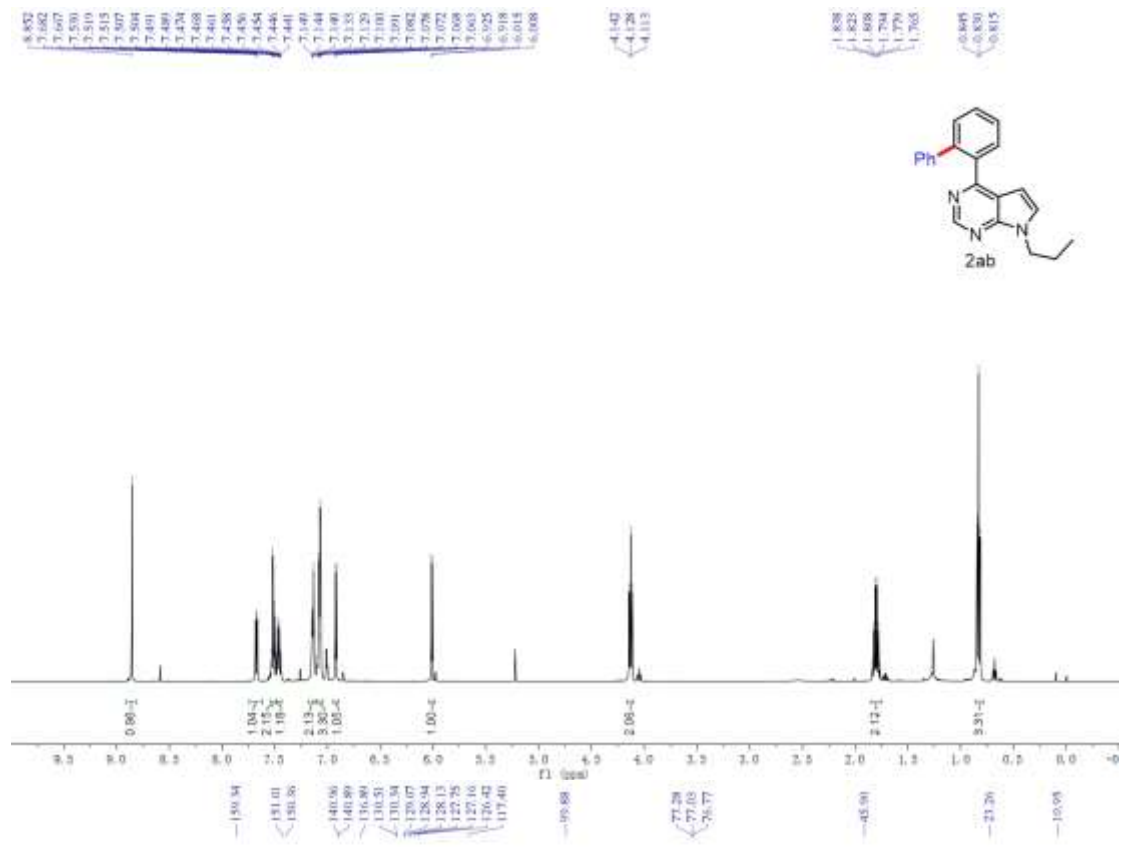
7-methyl-4-(3-(thiophen-3-yl)-[1,1'-biphenyl]-2-yl)-7H-pyrrolo[2,3-d]pyrimidine  
(4c)

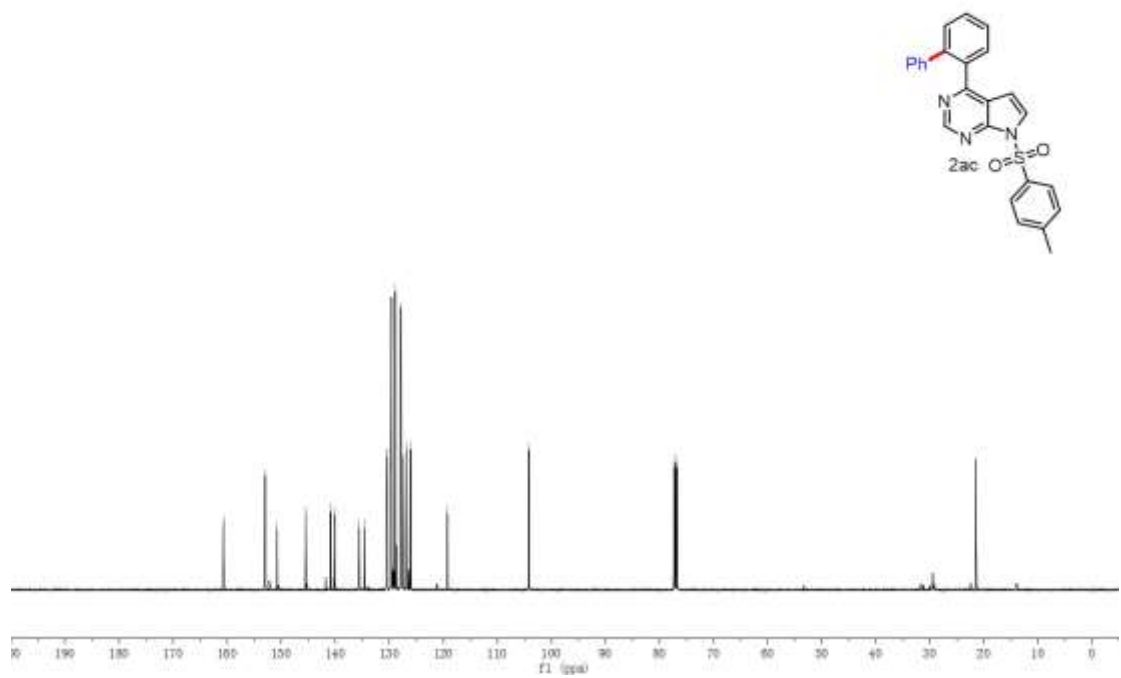
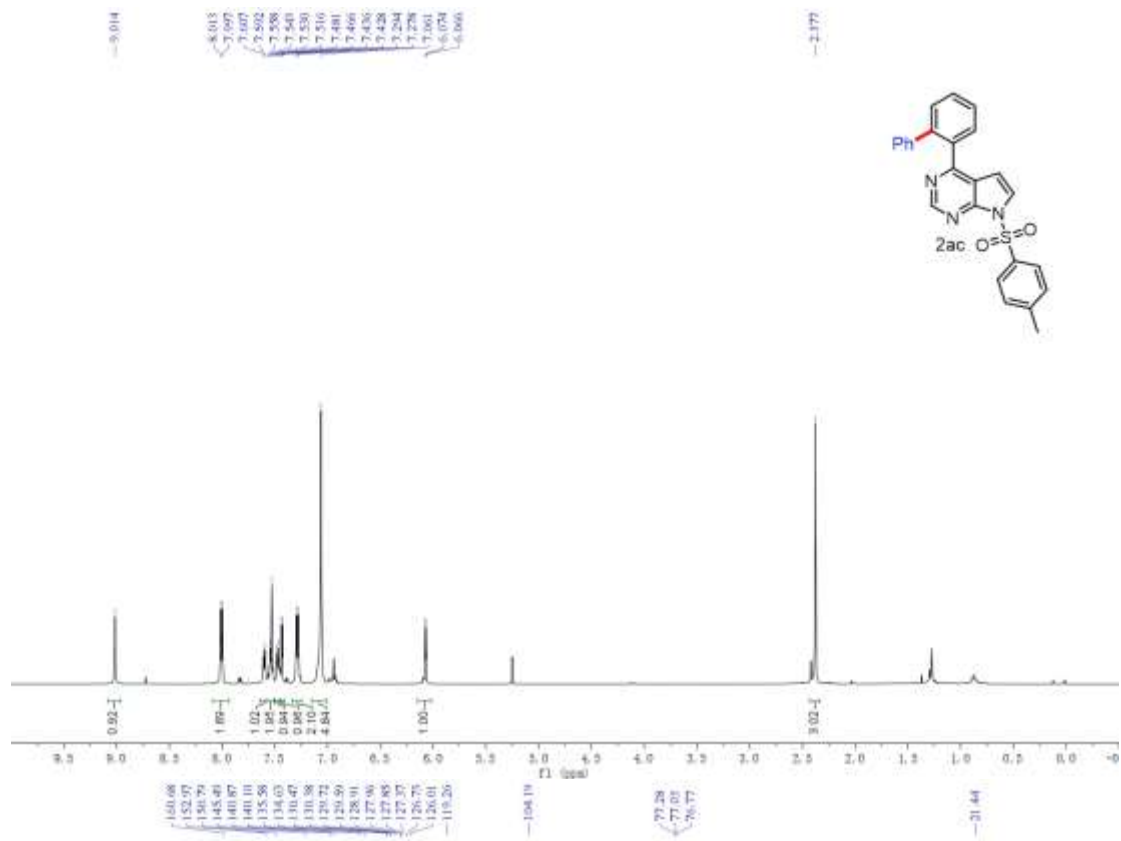


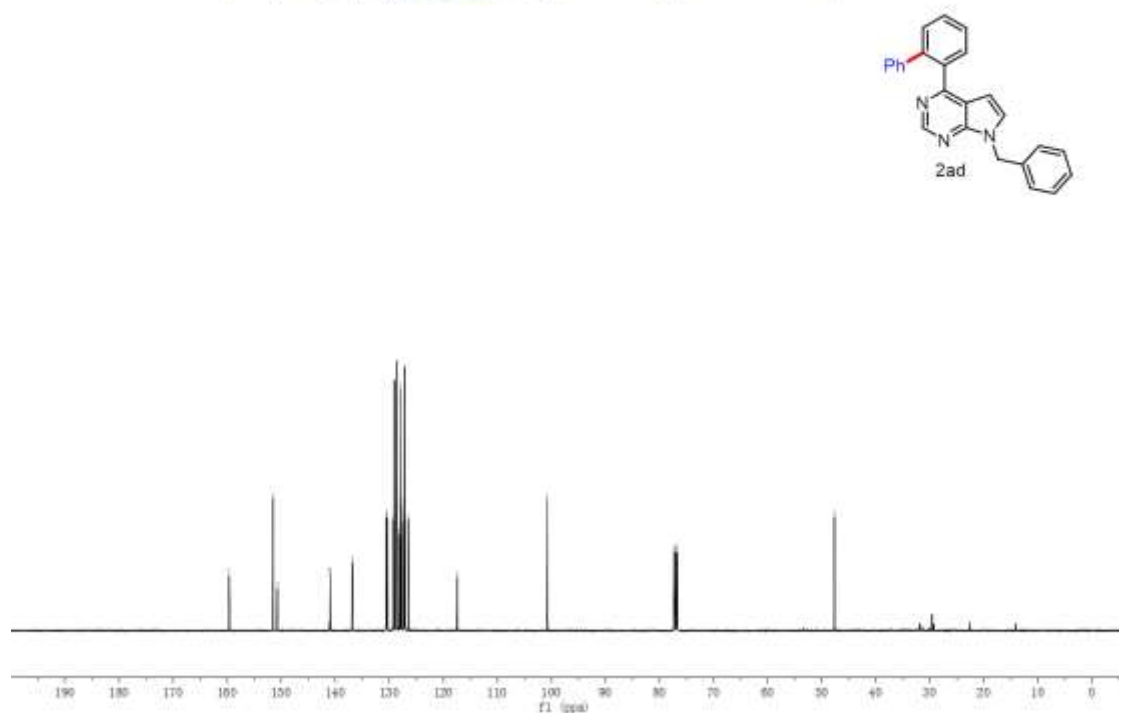
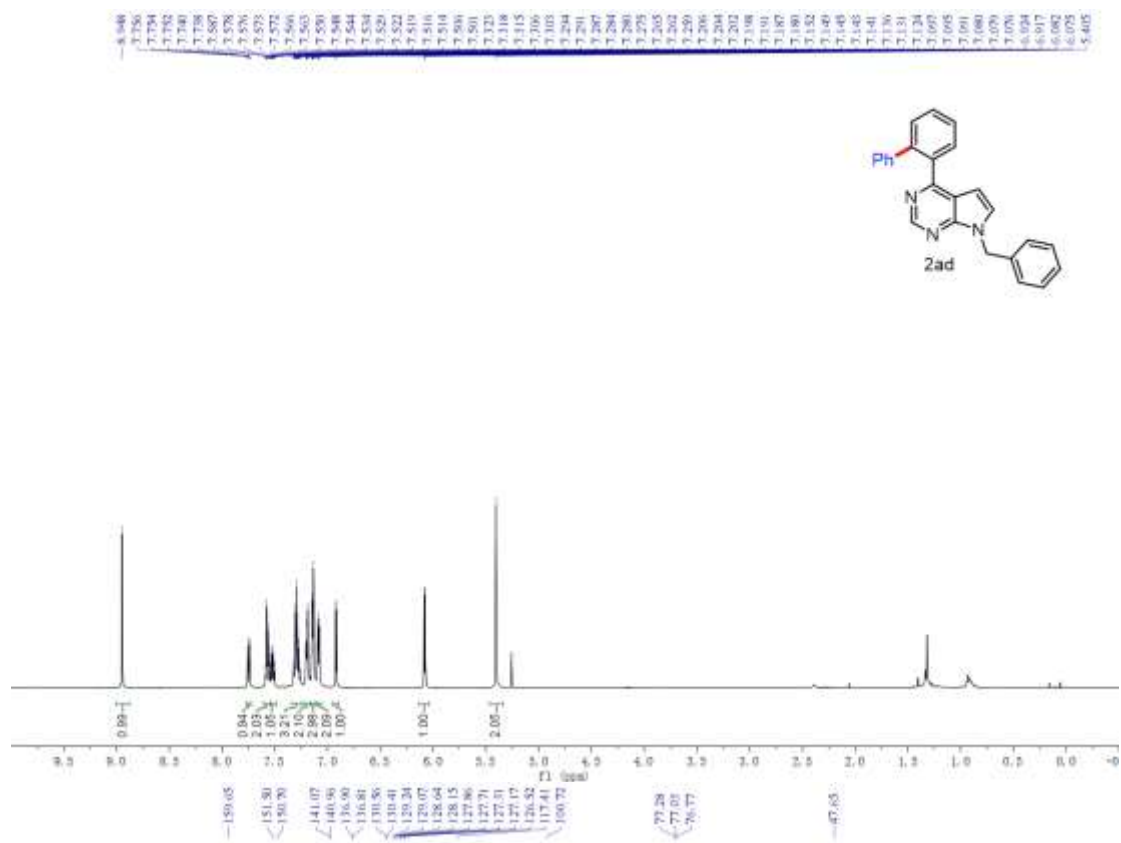
Yellow solid (98.5 mg, 59% yield). Mp: 156–158 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.61 (s, 1H), 7.60 (dd,  $J = 7.4, 1.6$  Hz, 1H), 7.51 (dd,  $J = 7.6, 1.5$  Hz, 1H), 7.50–7.42 (m, 2H), 7.14 (d,  $J = 5.2$  Hz, 1H), 7.06–6.99 (m, 3H), 6.97 (d,  $J = 5.1$  Hz, 1H), 6.88 (d,  $J = 3.6$  Hz, 1H), 6.85–6.79 (m, 2H), 6.01 (d,  $J = 3.6$  Hz, 1H), 3.79 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 150.9, 150.9, 139.6, 137.7, 136.8, 135.8, 134.0, 131.3, 131.2, 130.8, 129.2, 128.9, 128.3, 128.1, 127.5, 127.1, 123.8, 117.1, 99.8, 31.0. HRMS  $m/z$  (ESI): calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 368.1216, found: 368.1220.

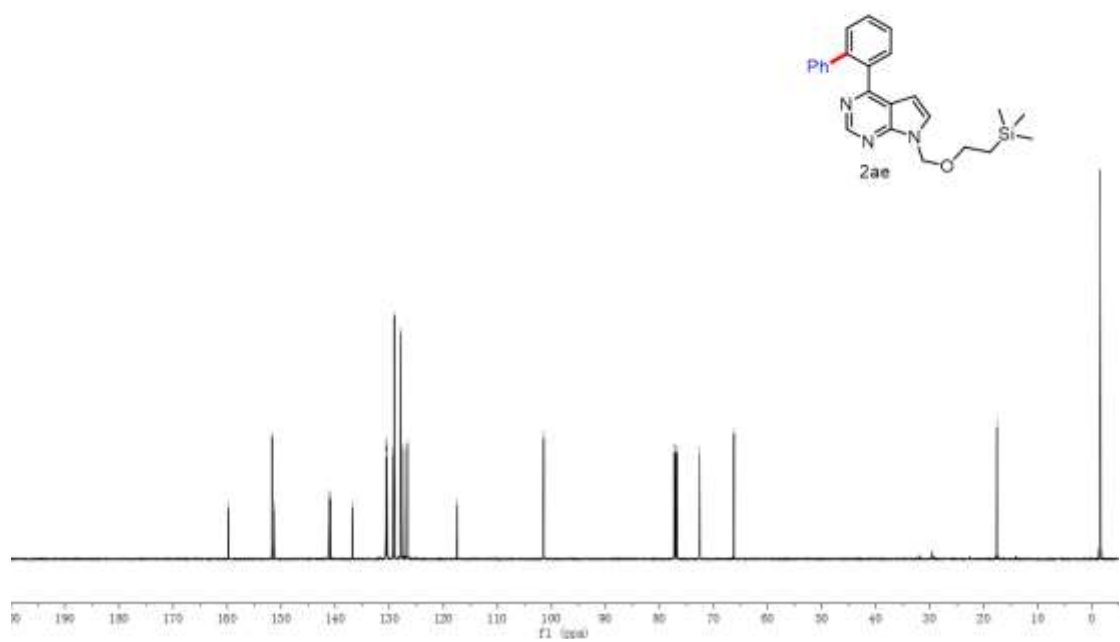
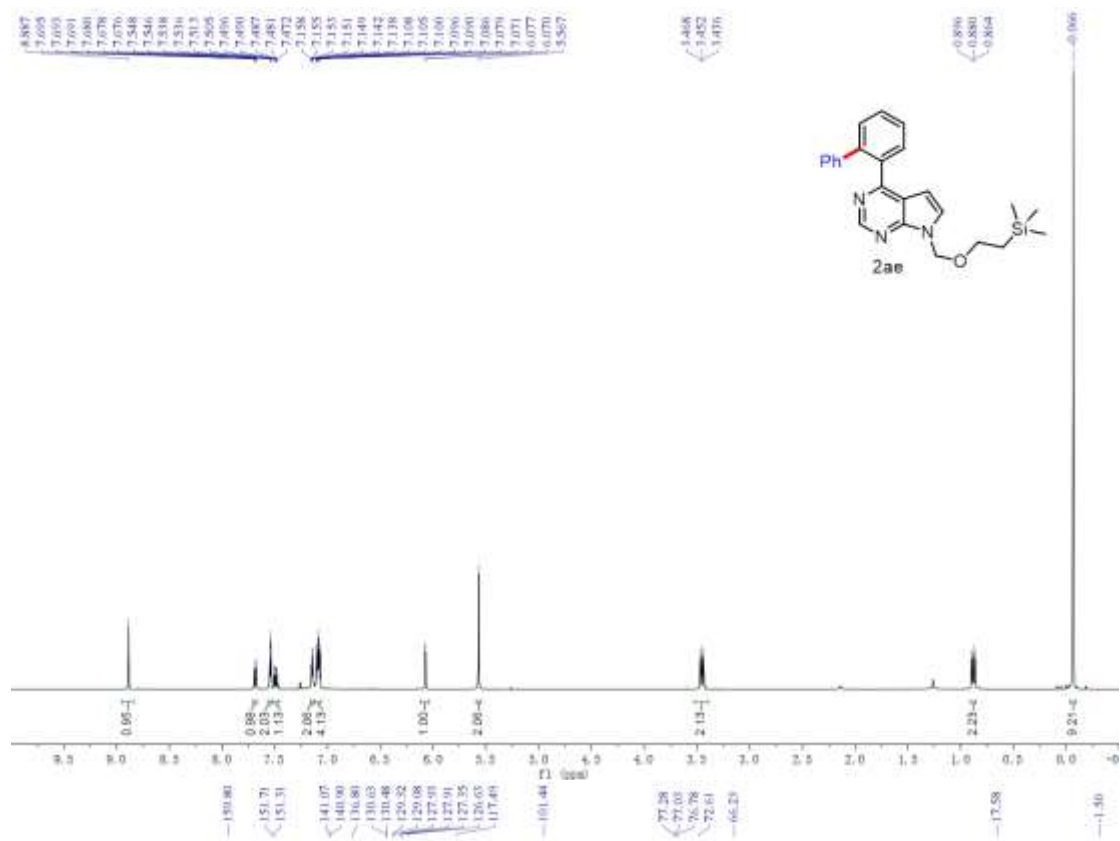
## 5. NMR Spectra of Compounds

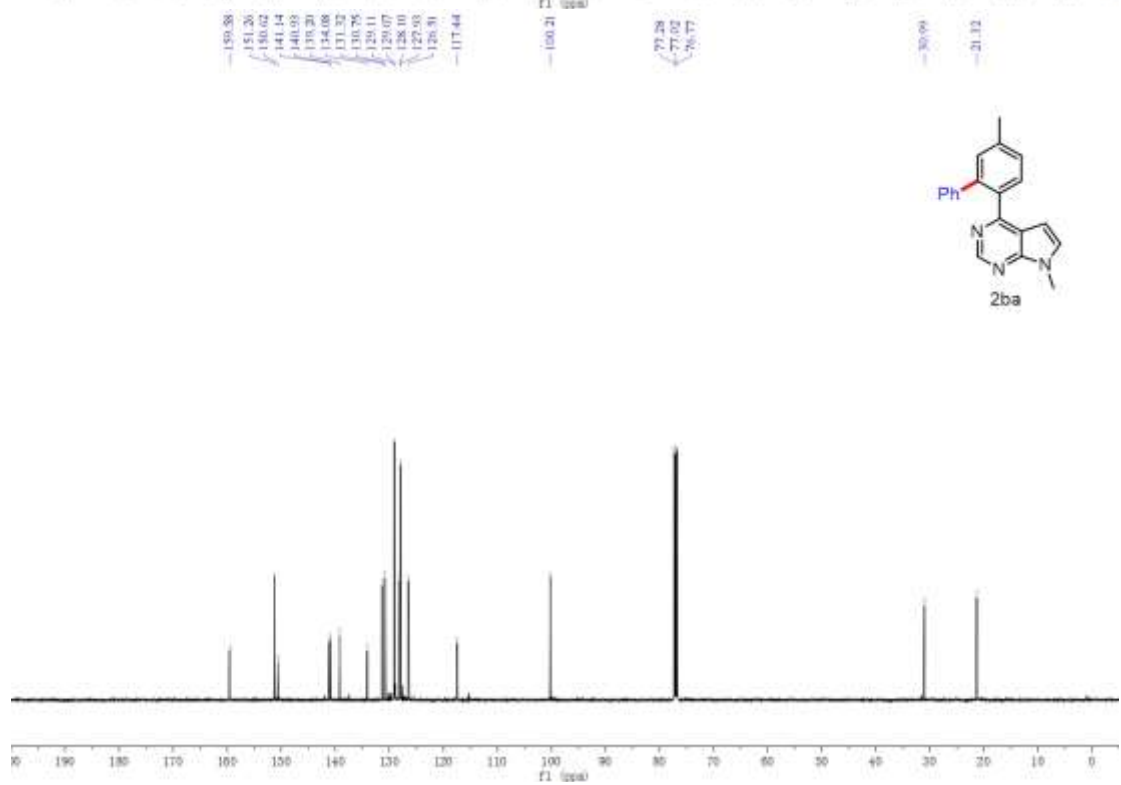
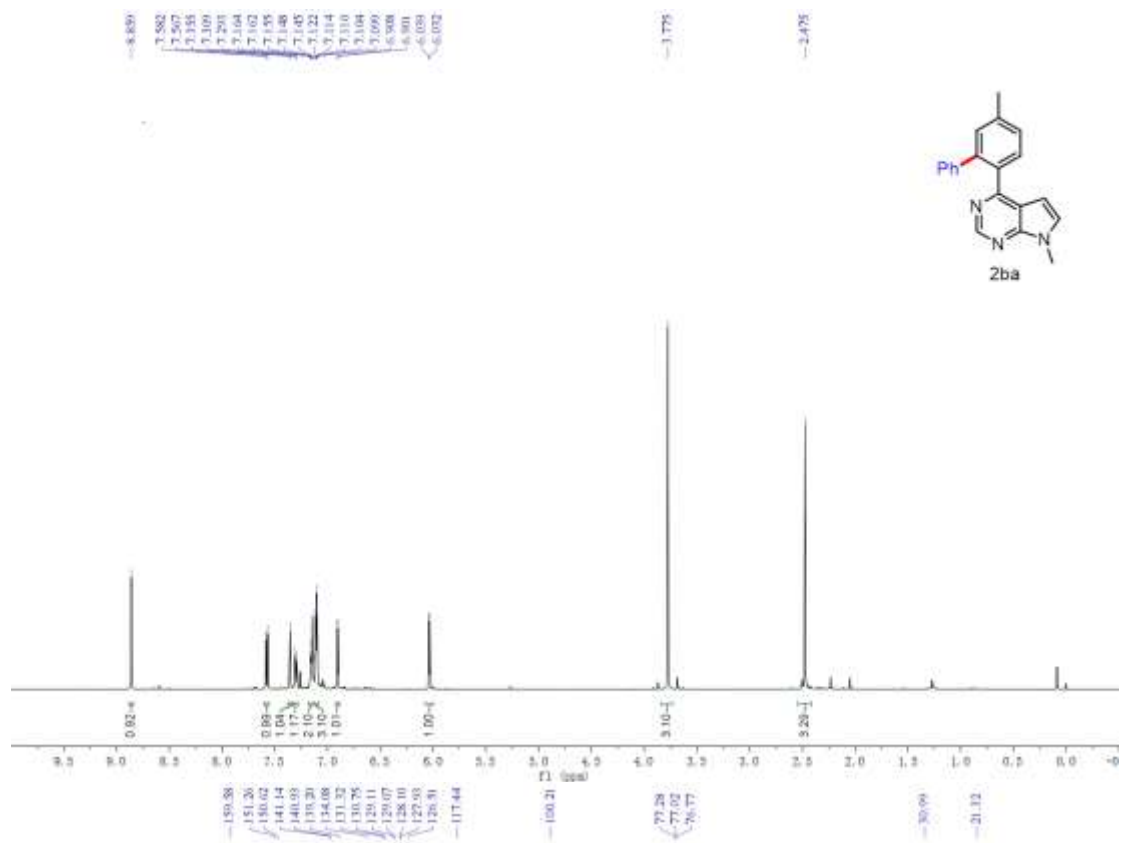


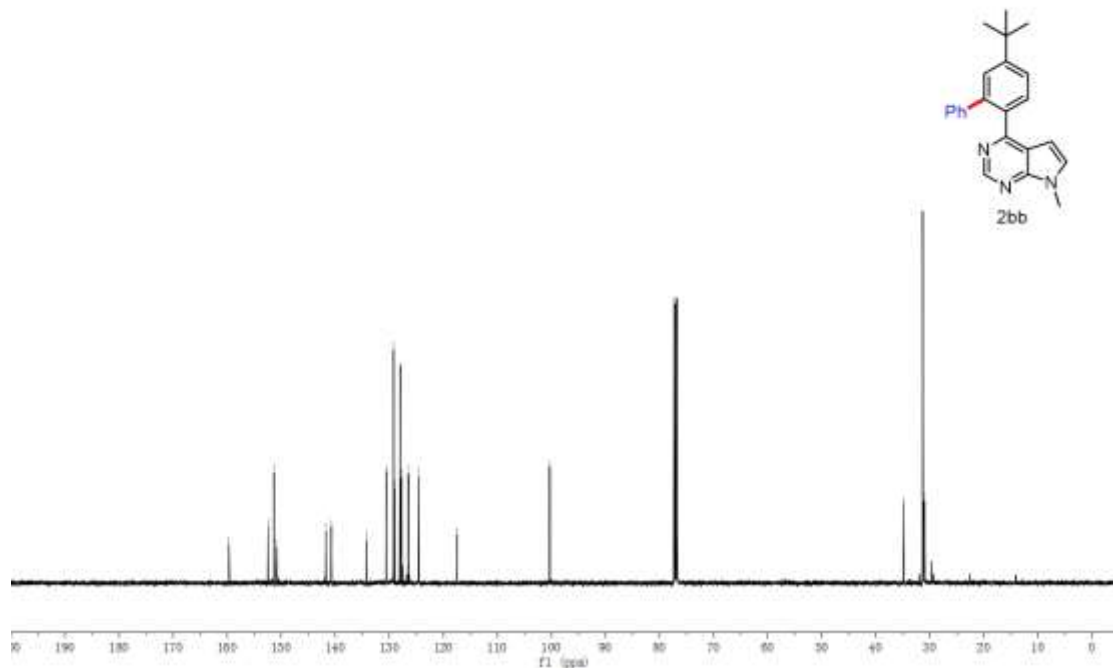
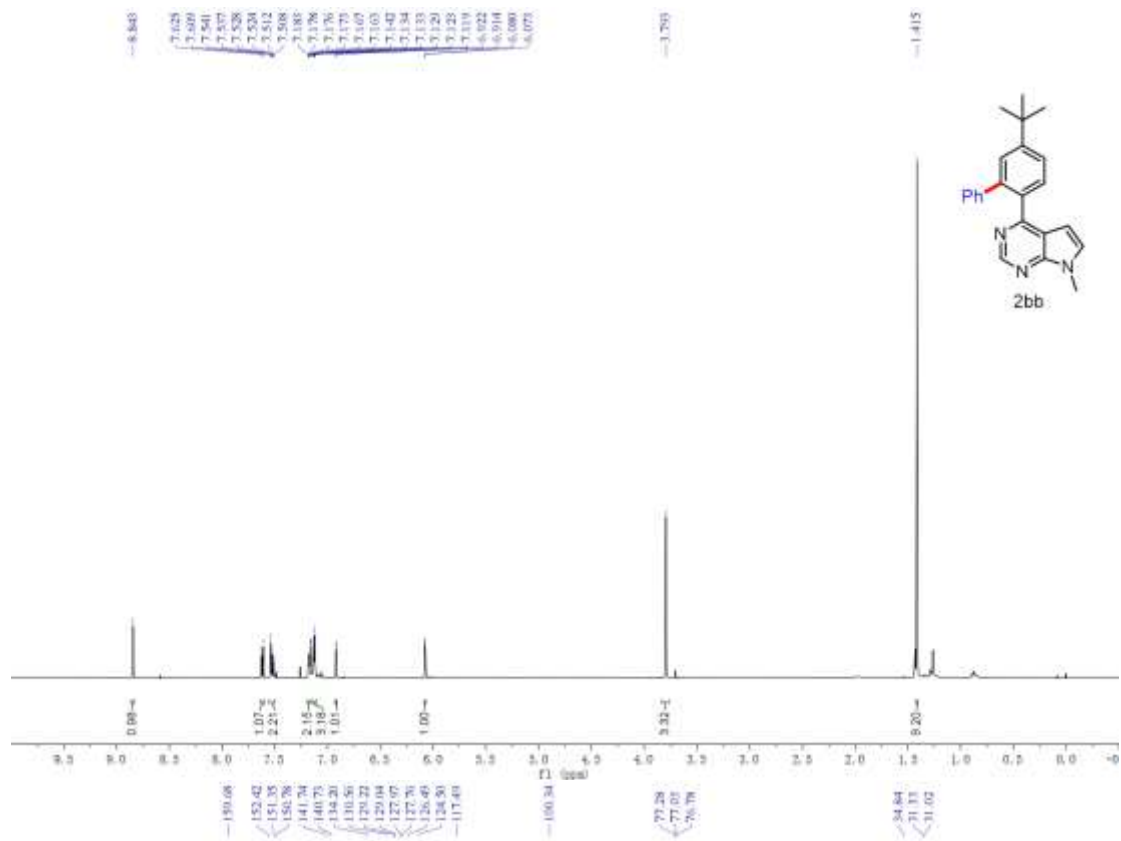




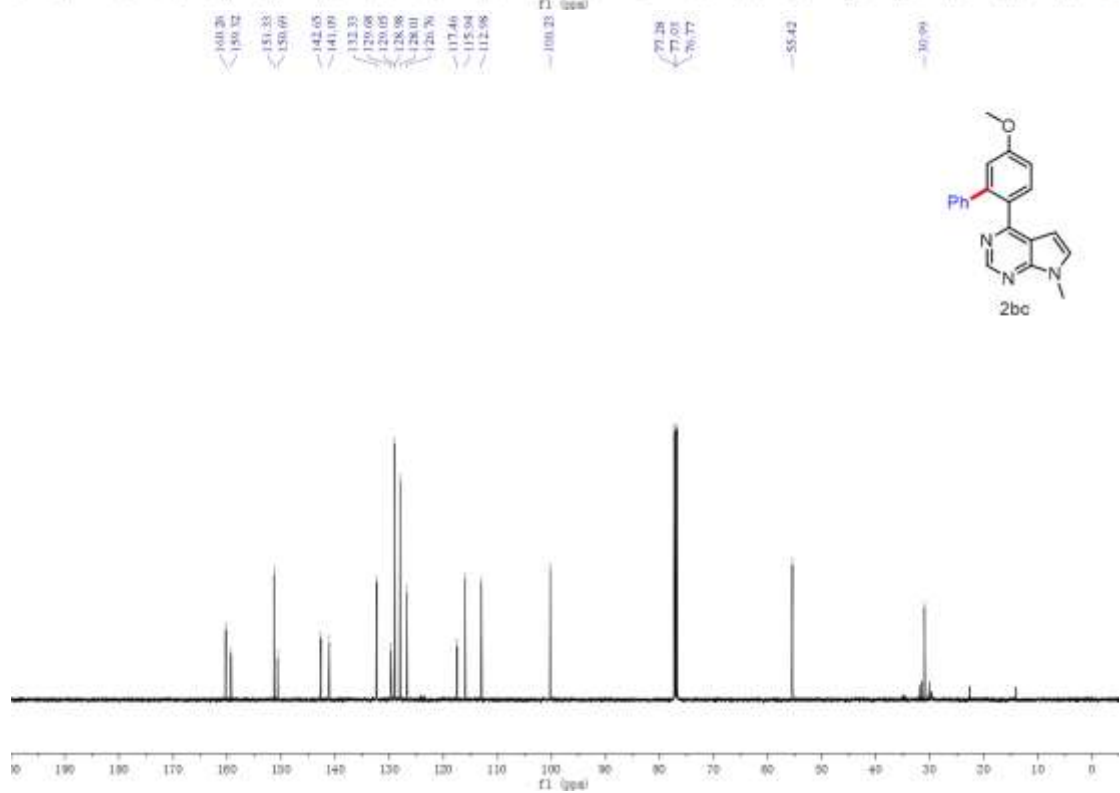
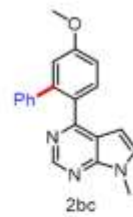
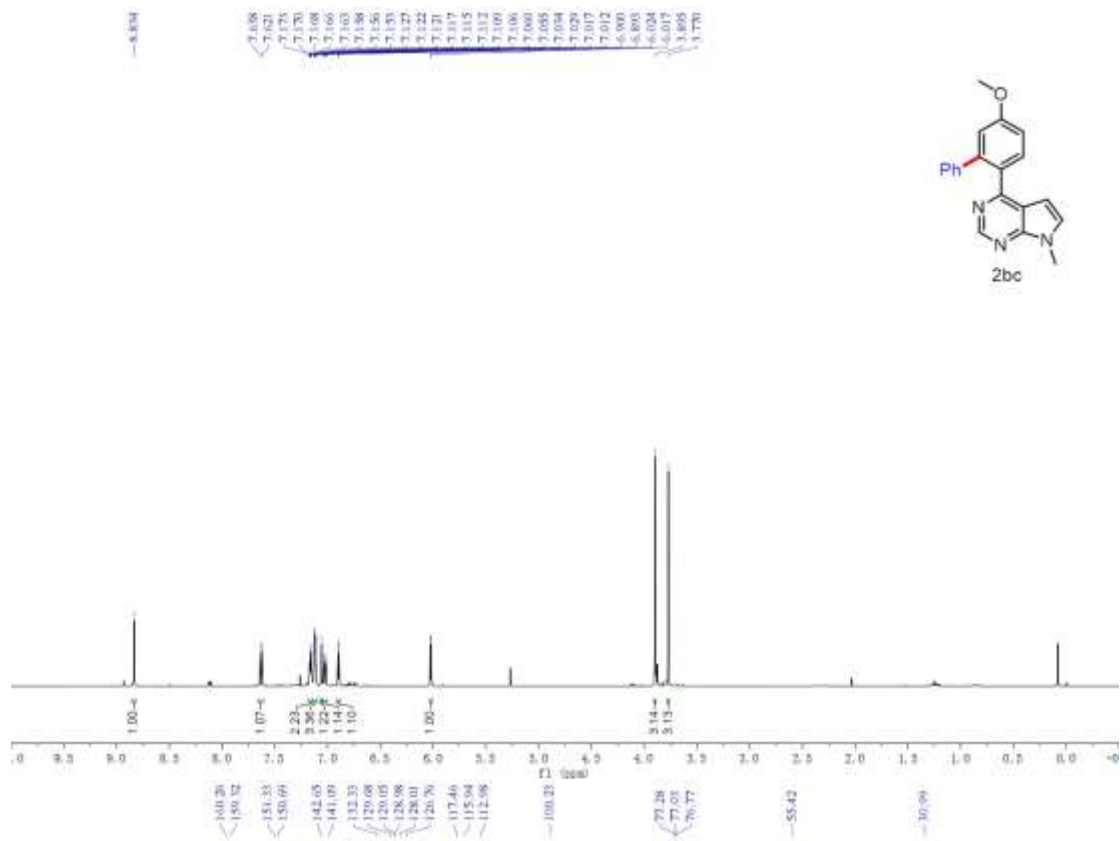


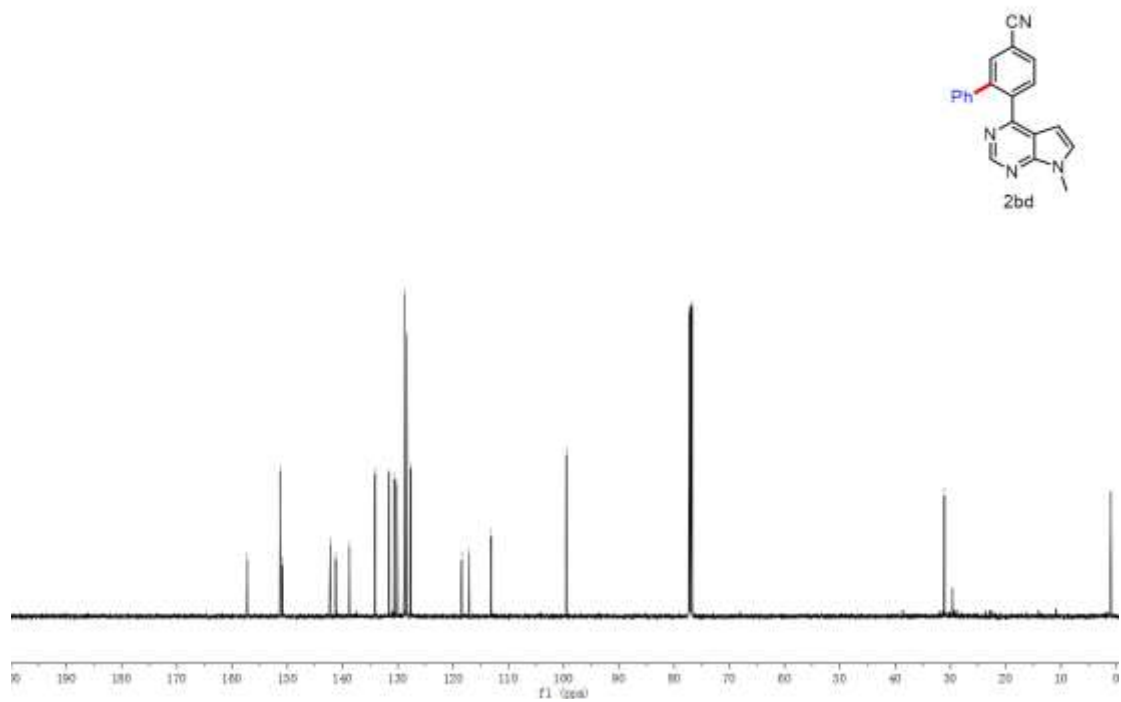
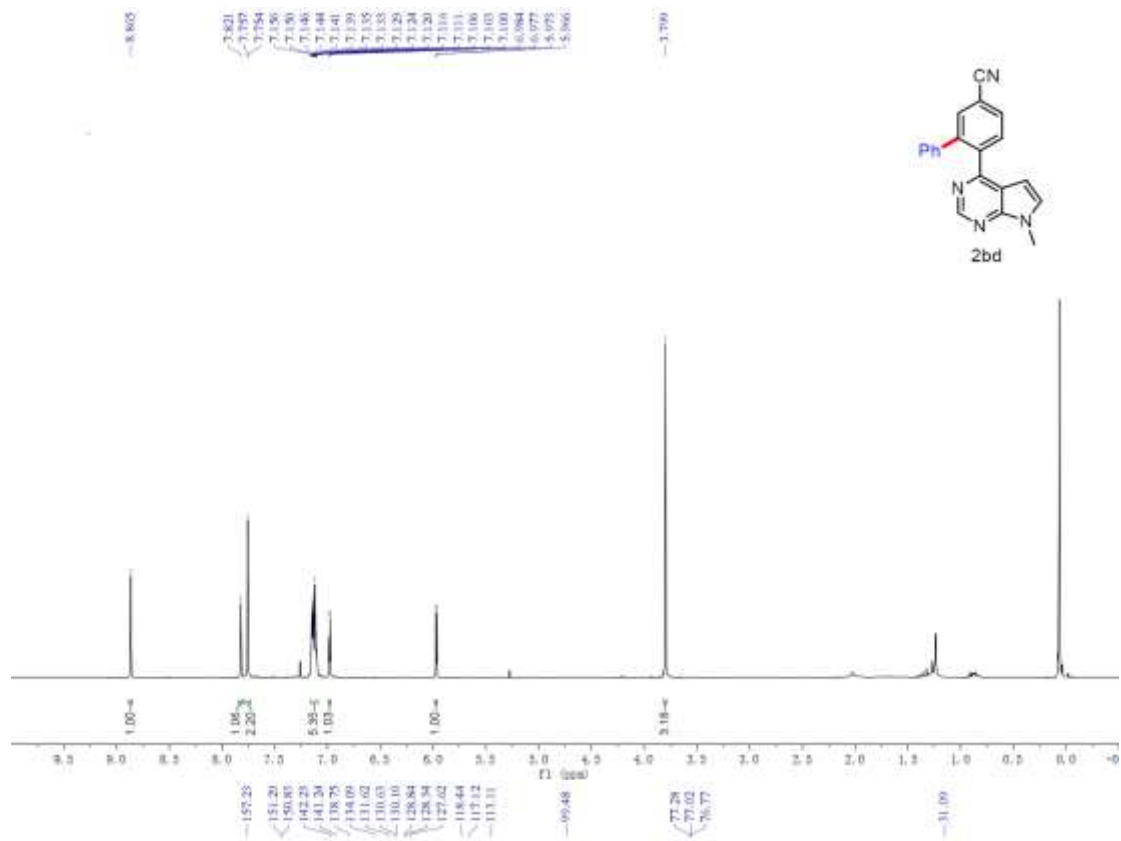


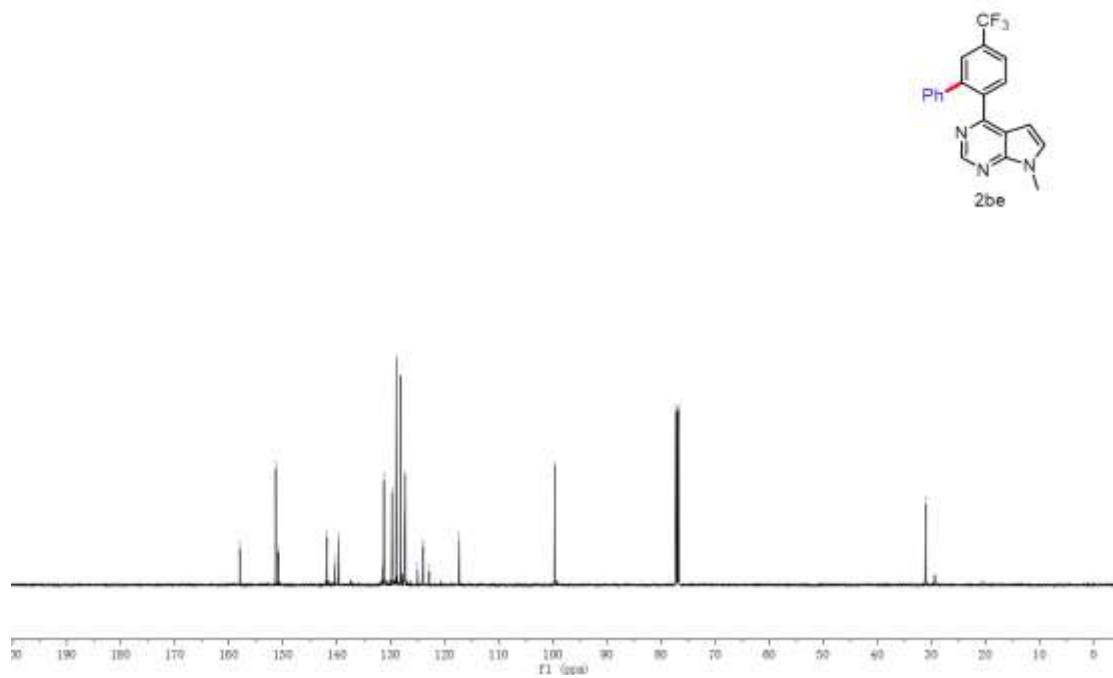
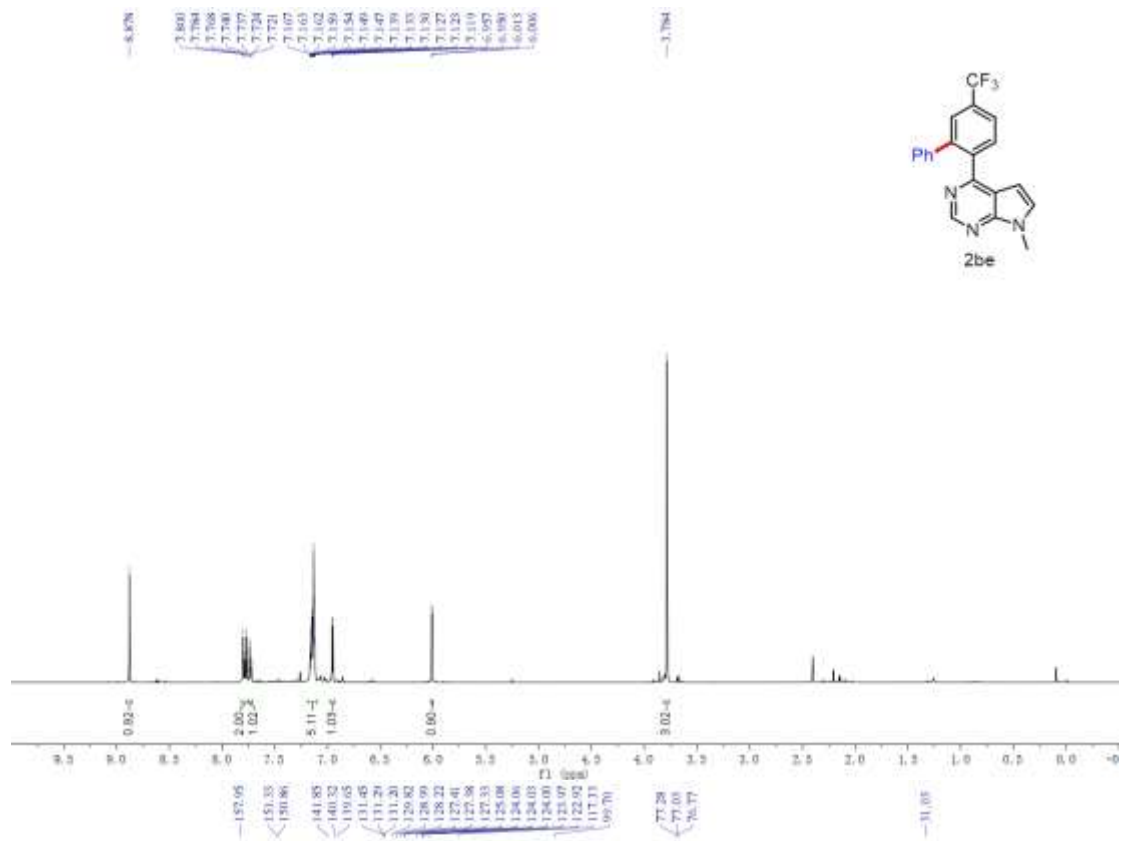


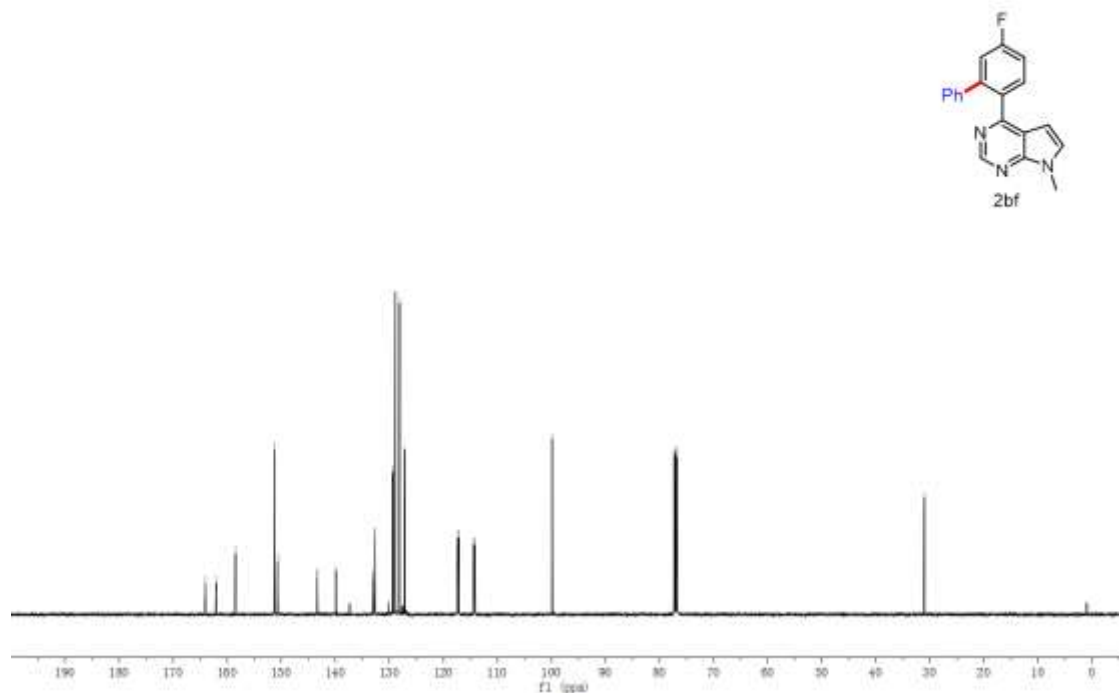
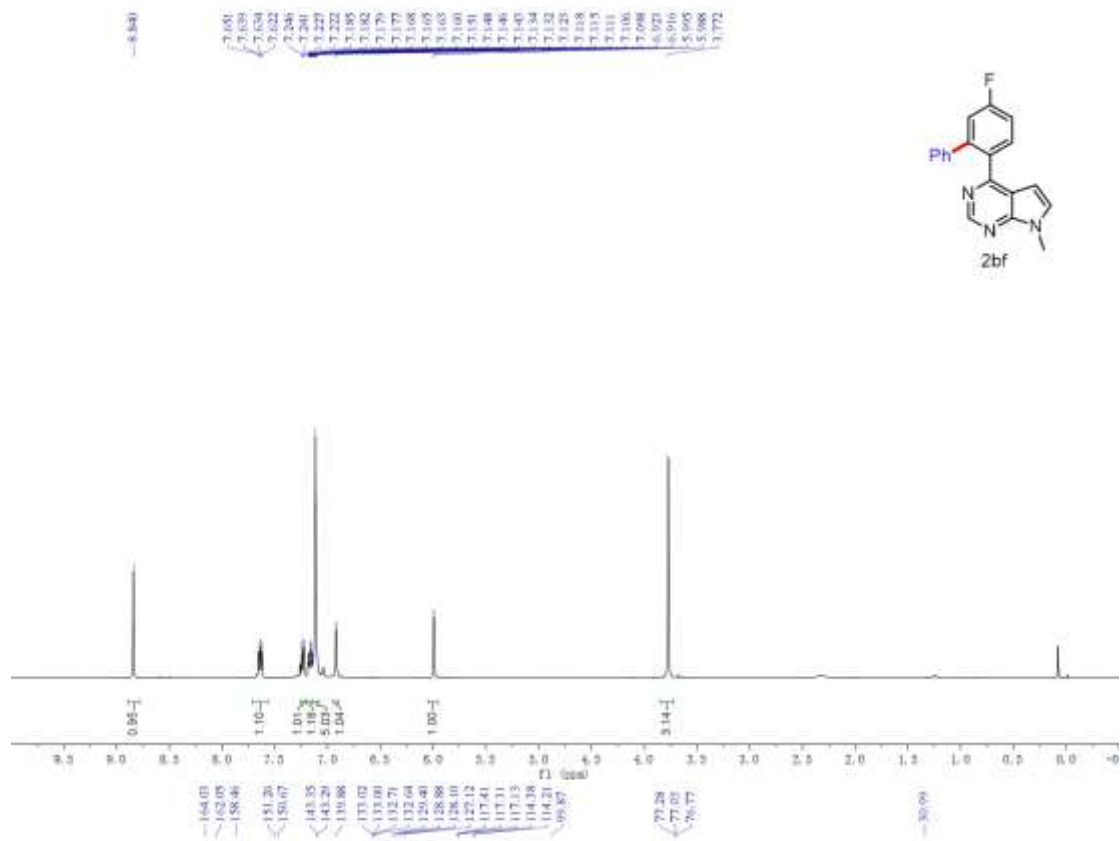


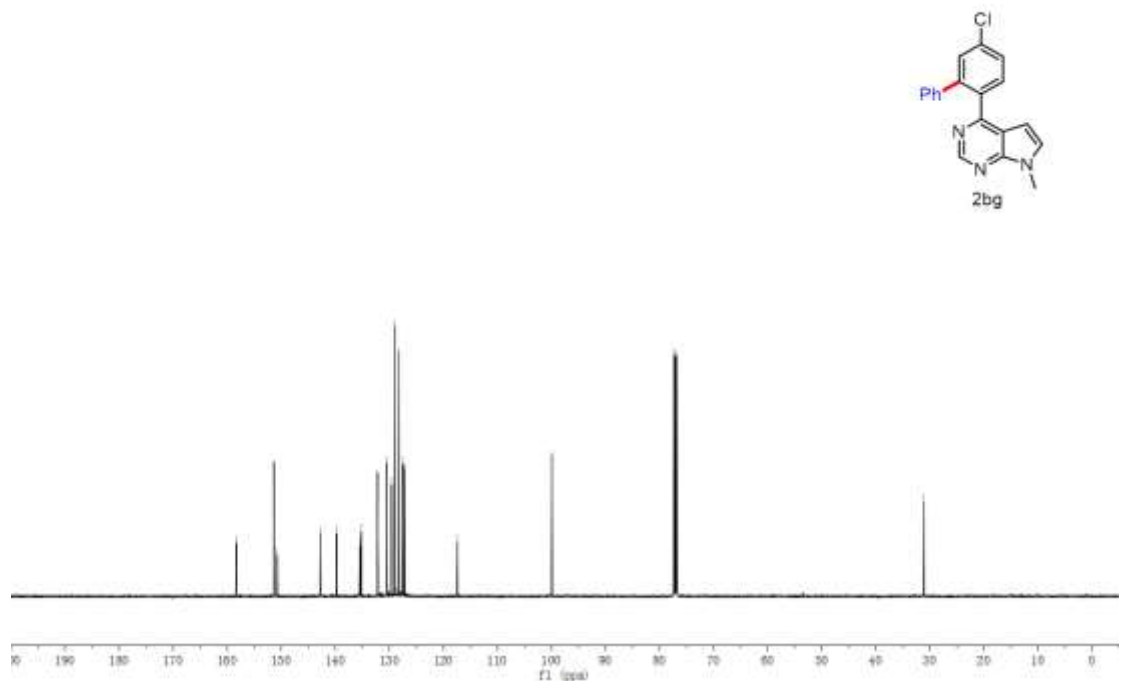
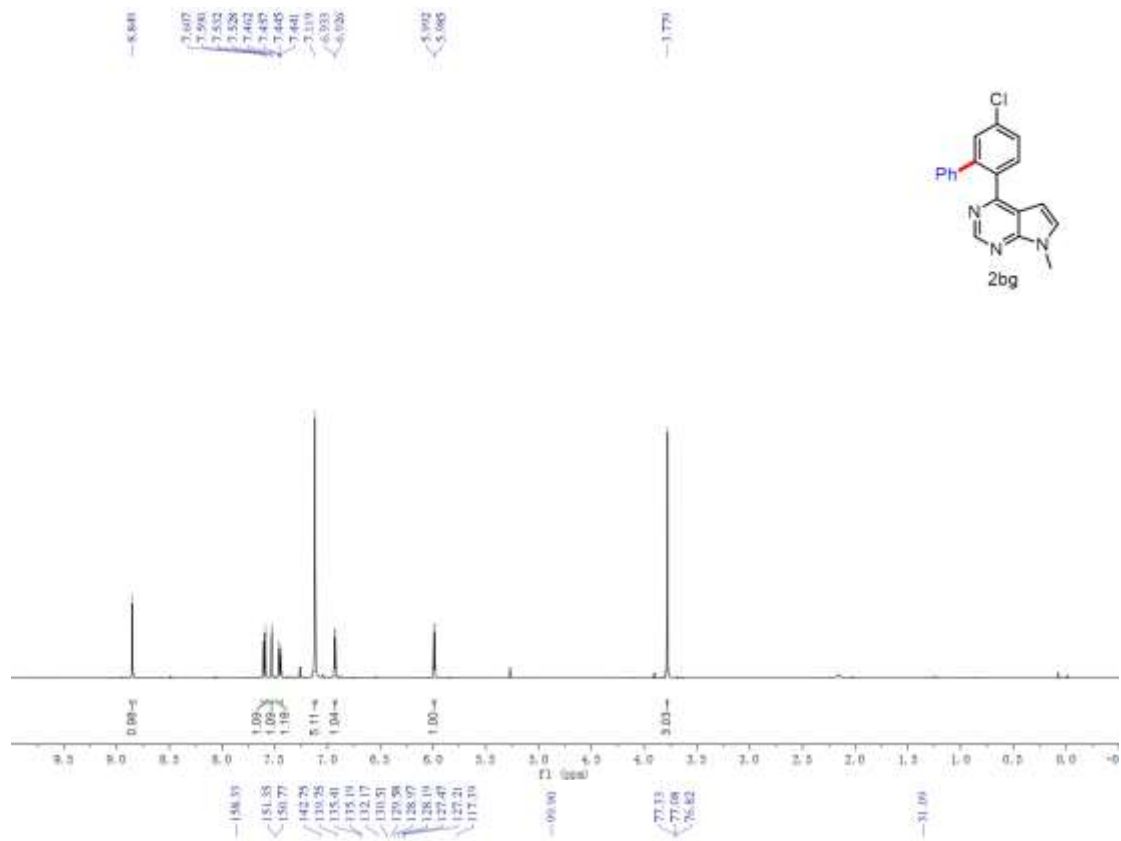


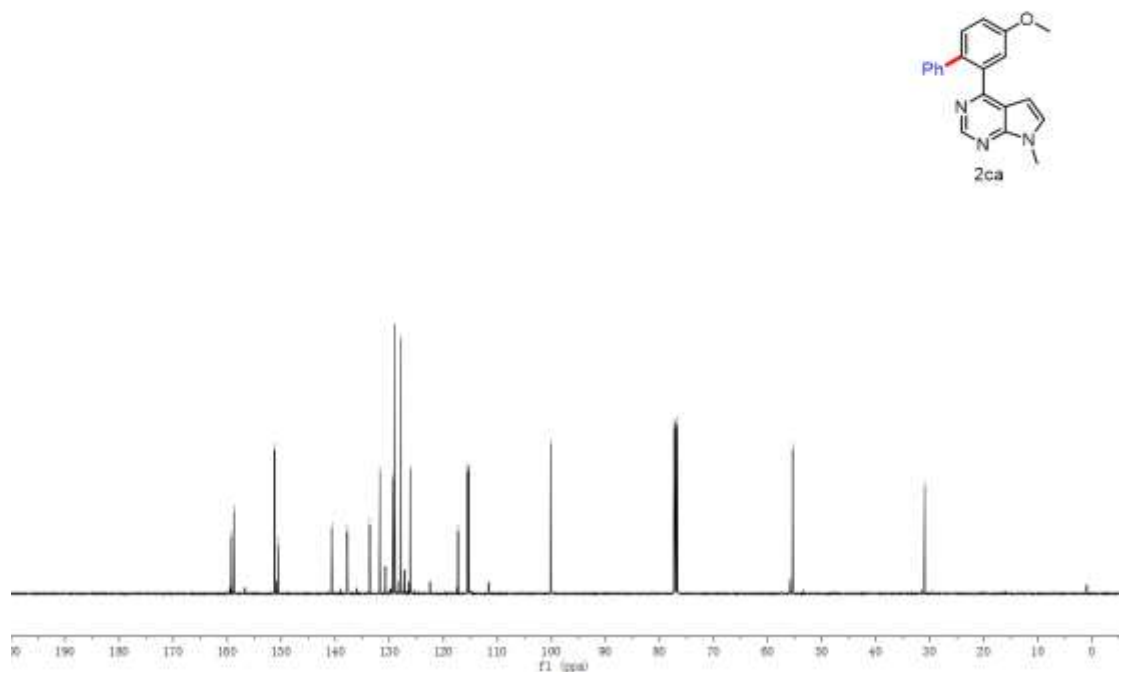
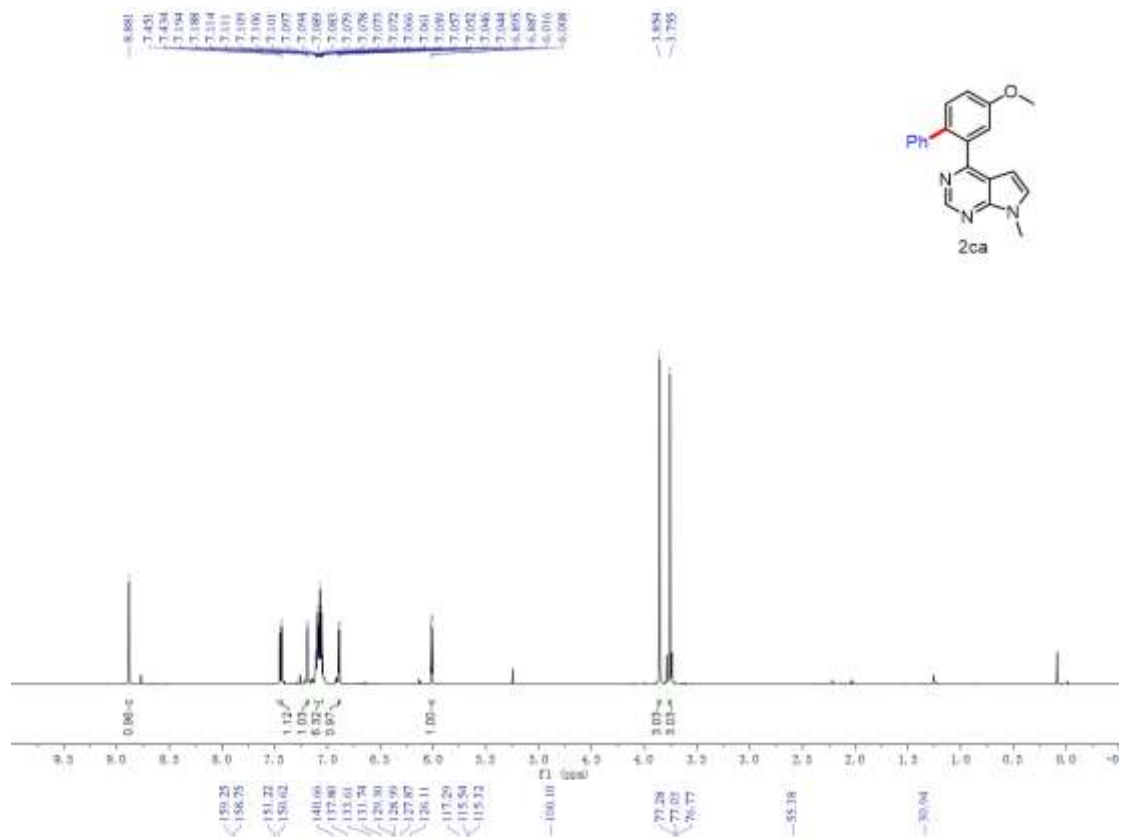


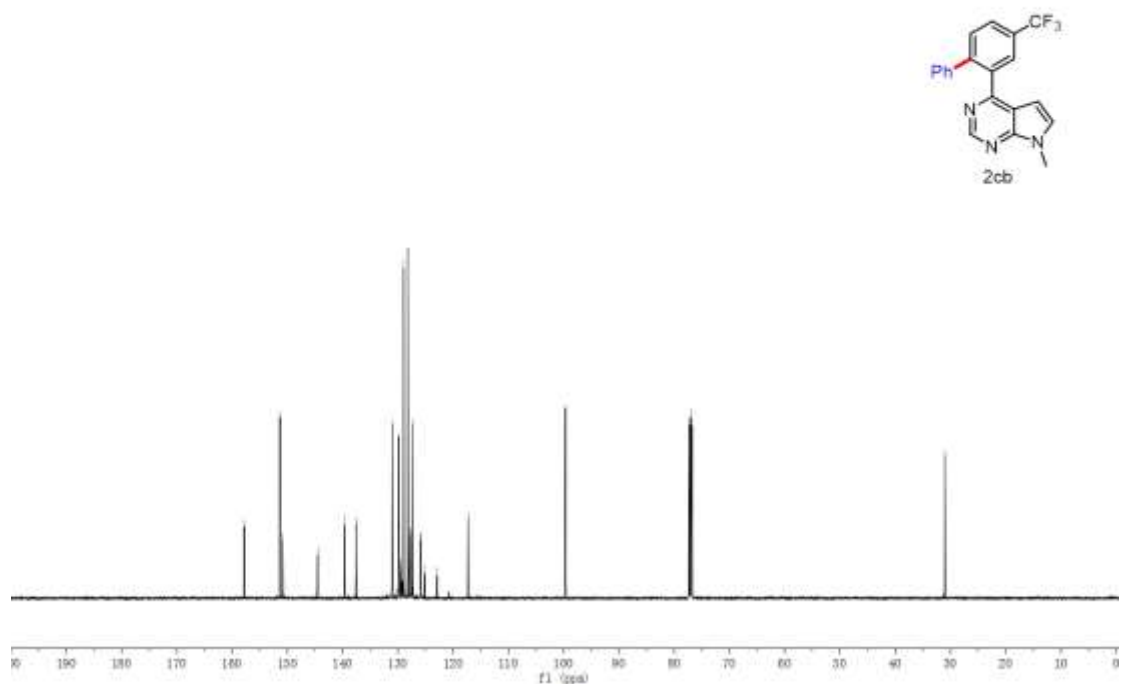
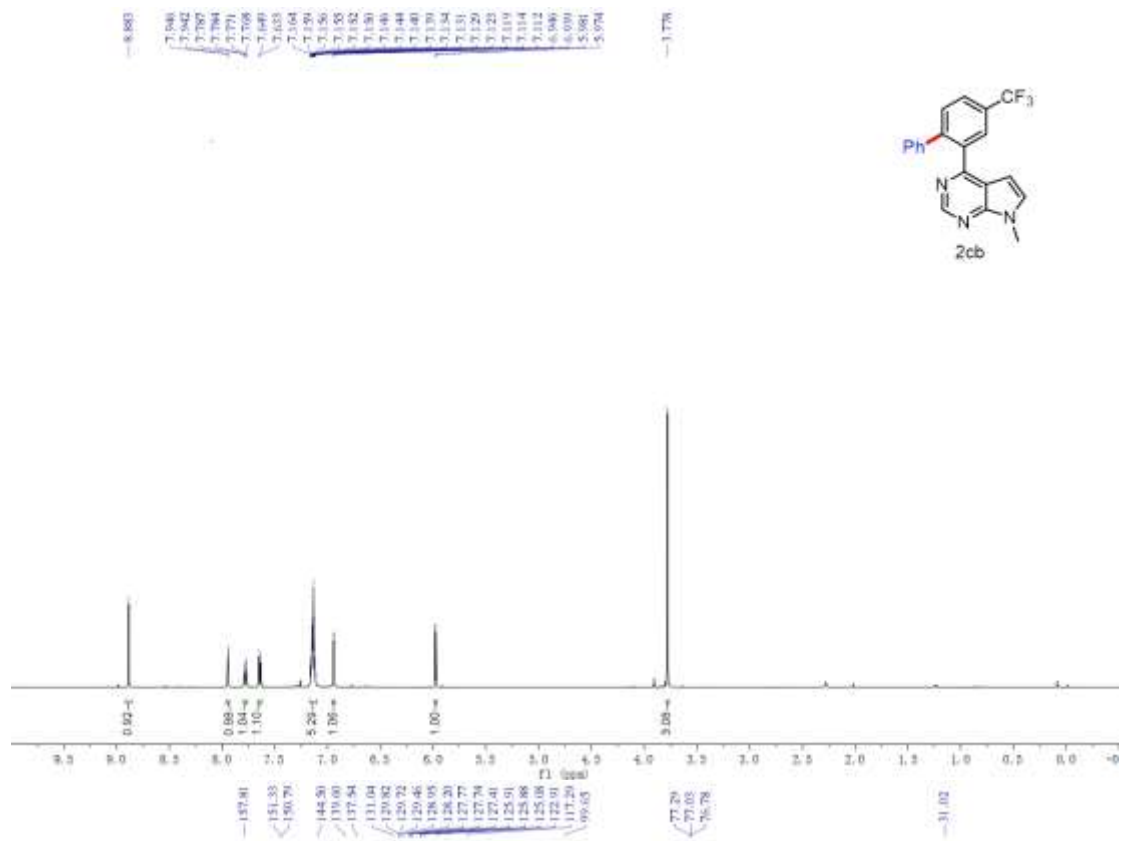


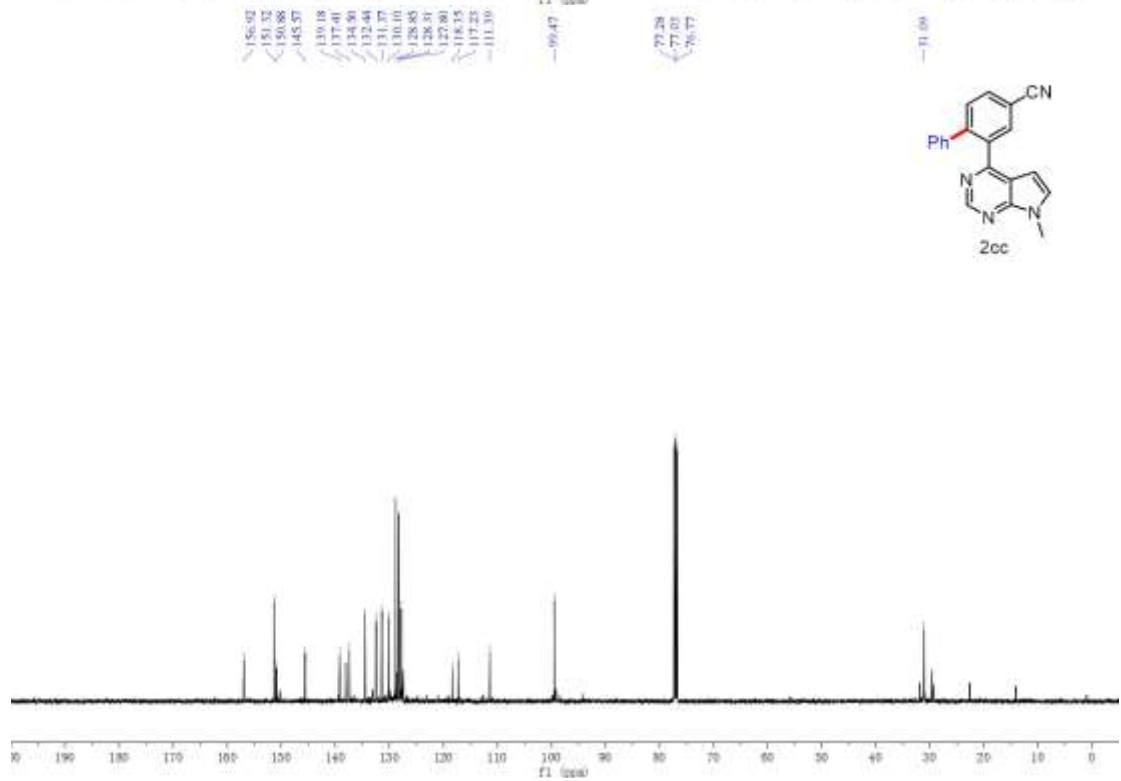
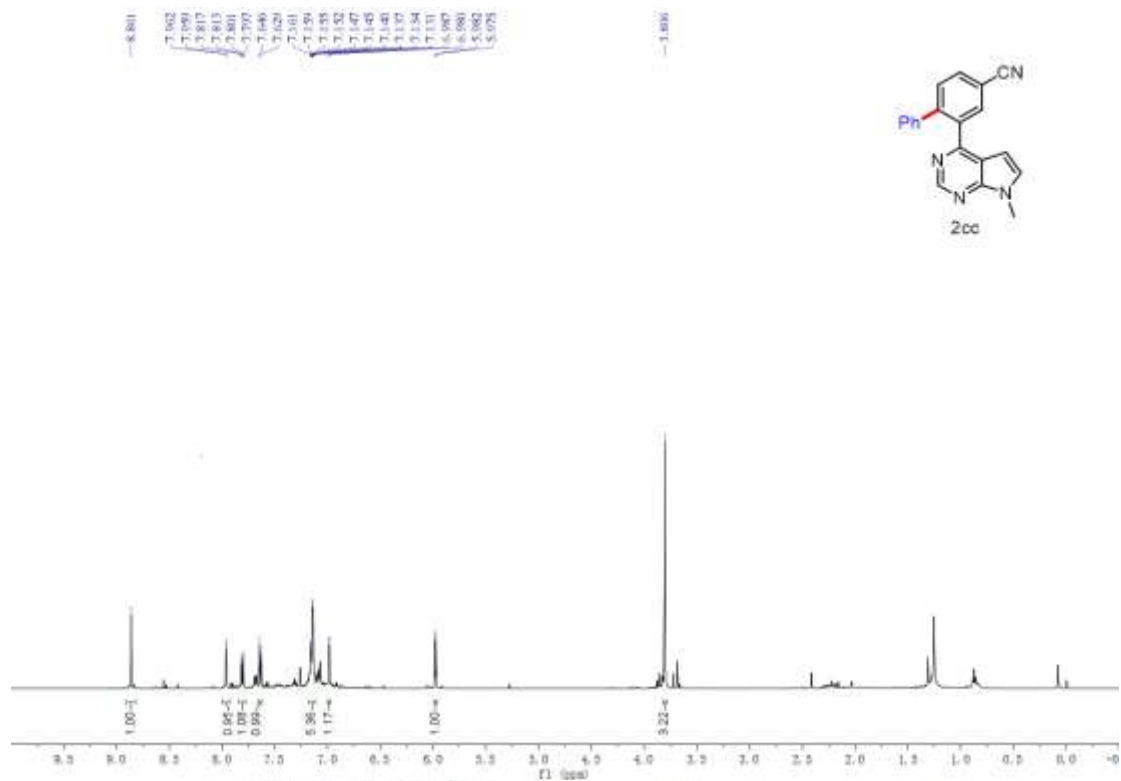




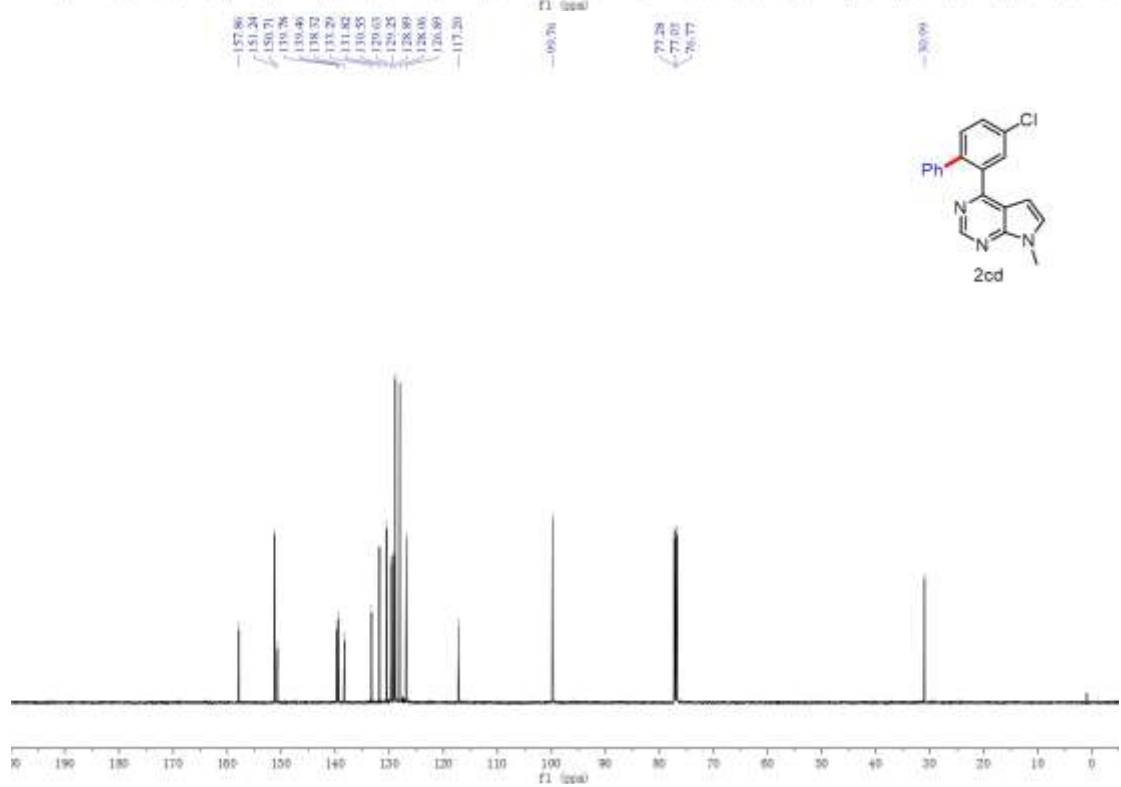
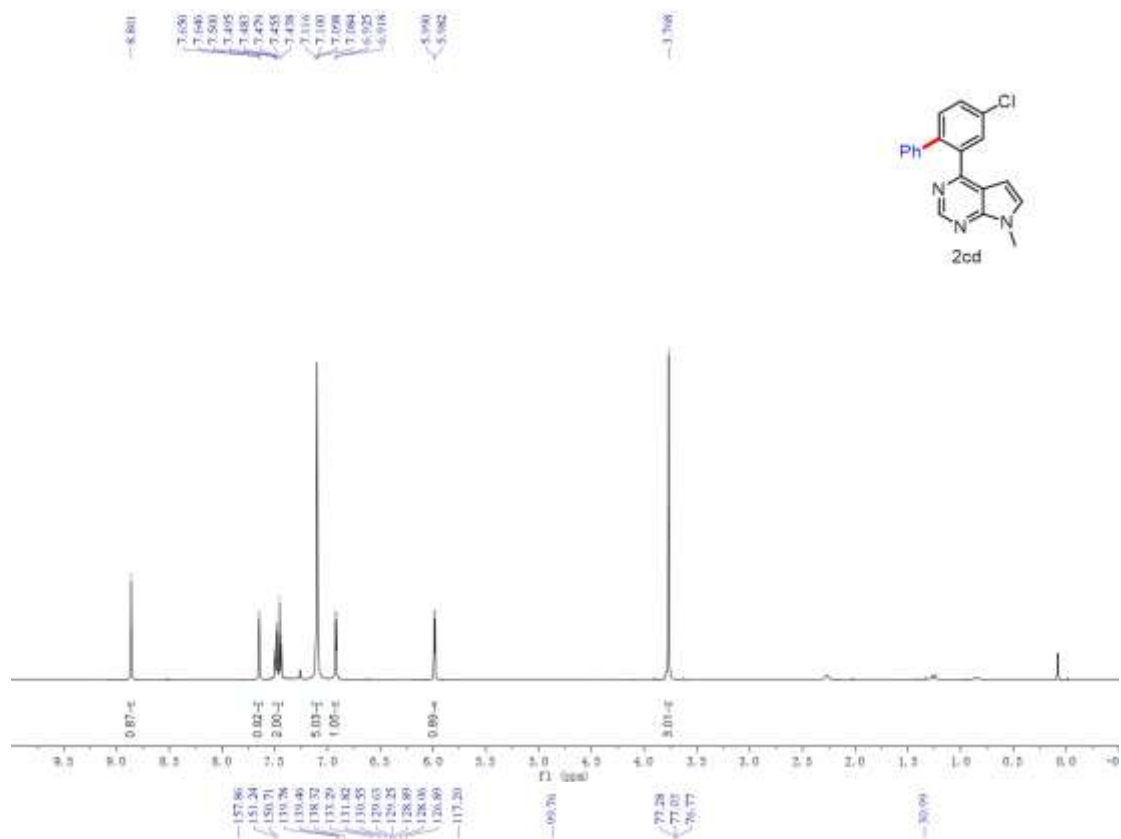


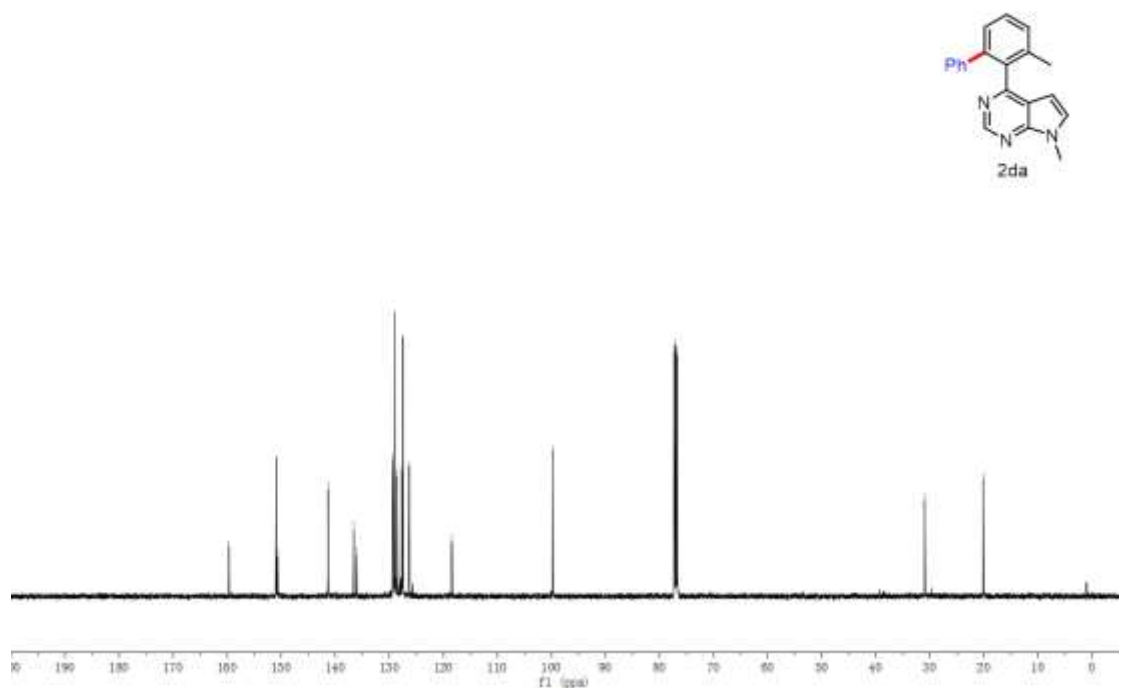
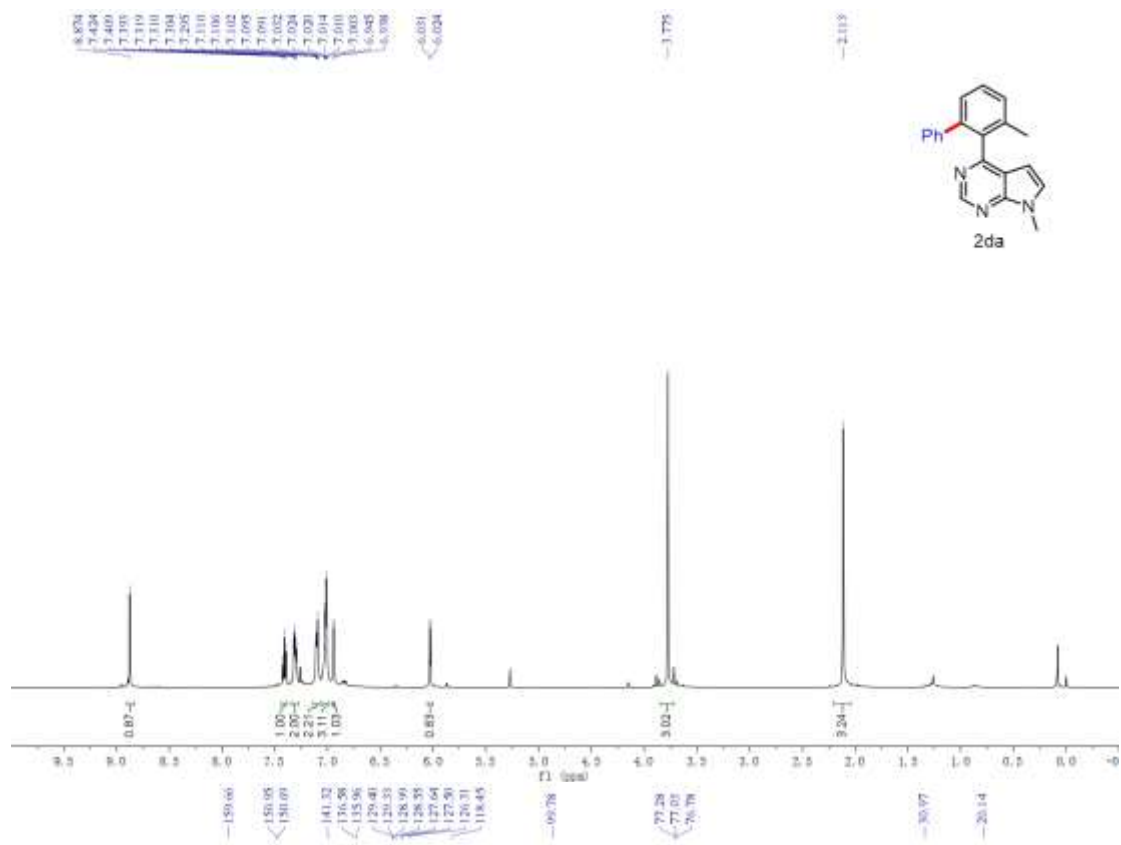


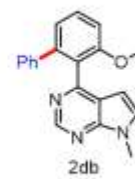
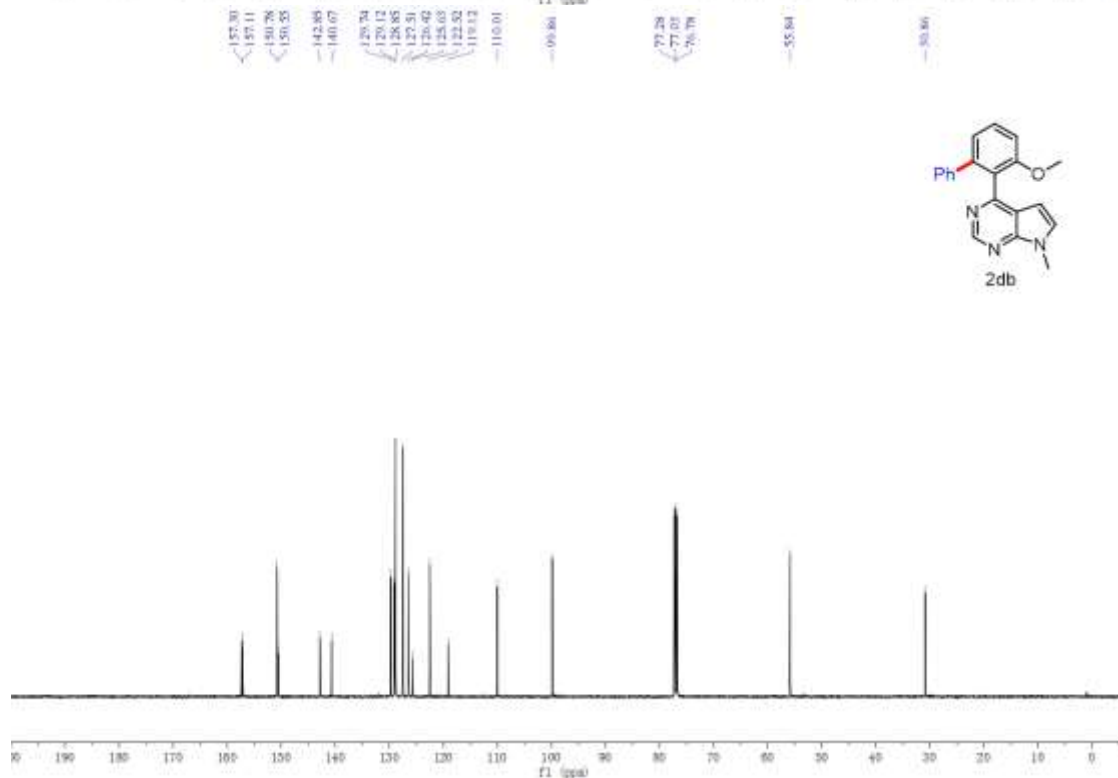
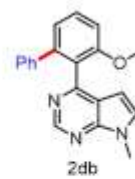
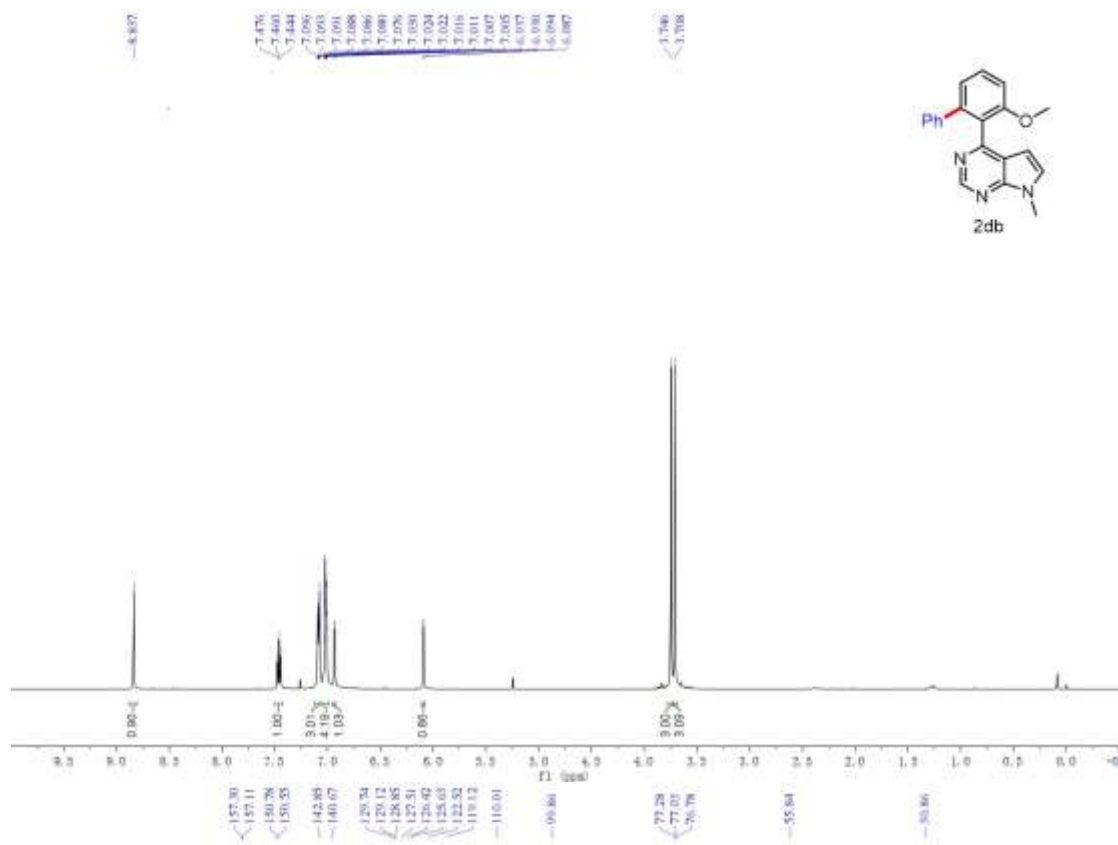


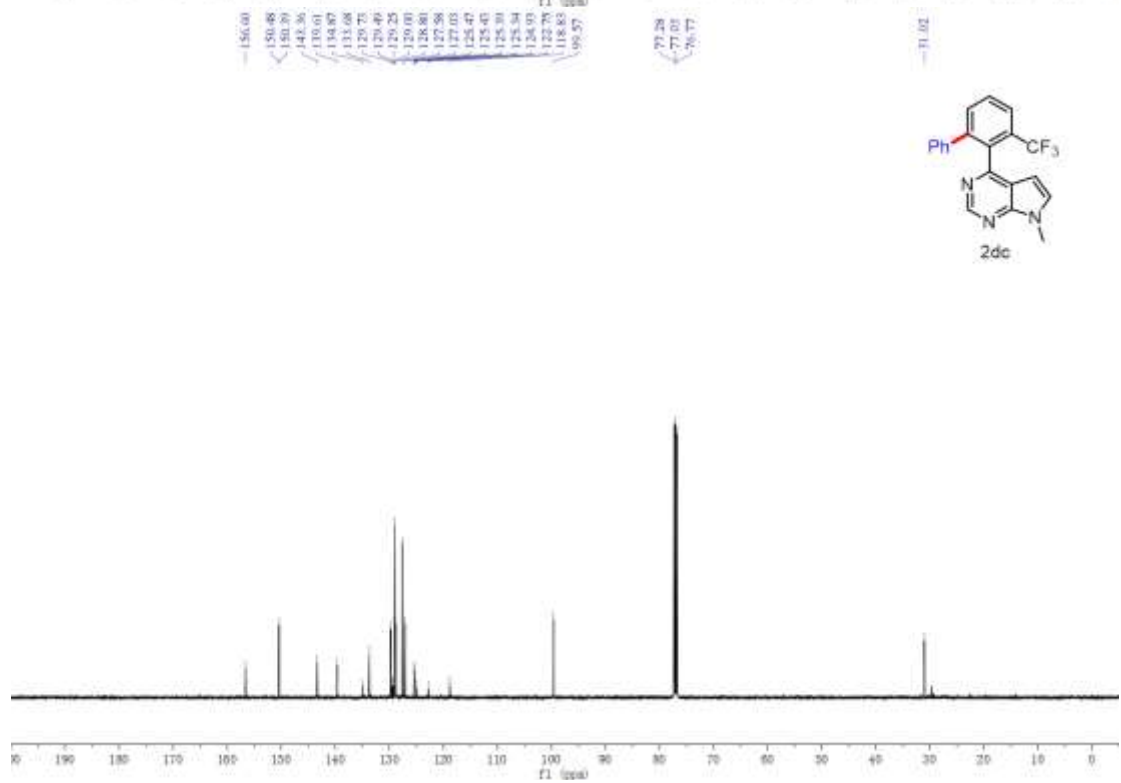
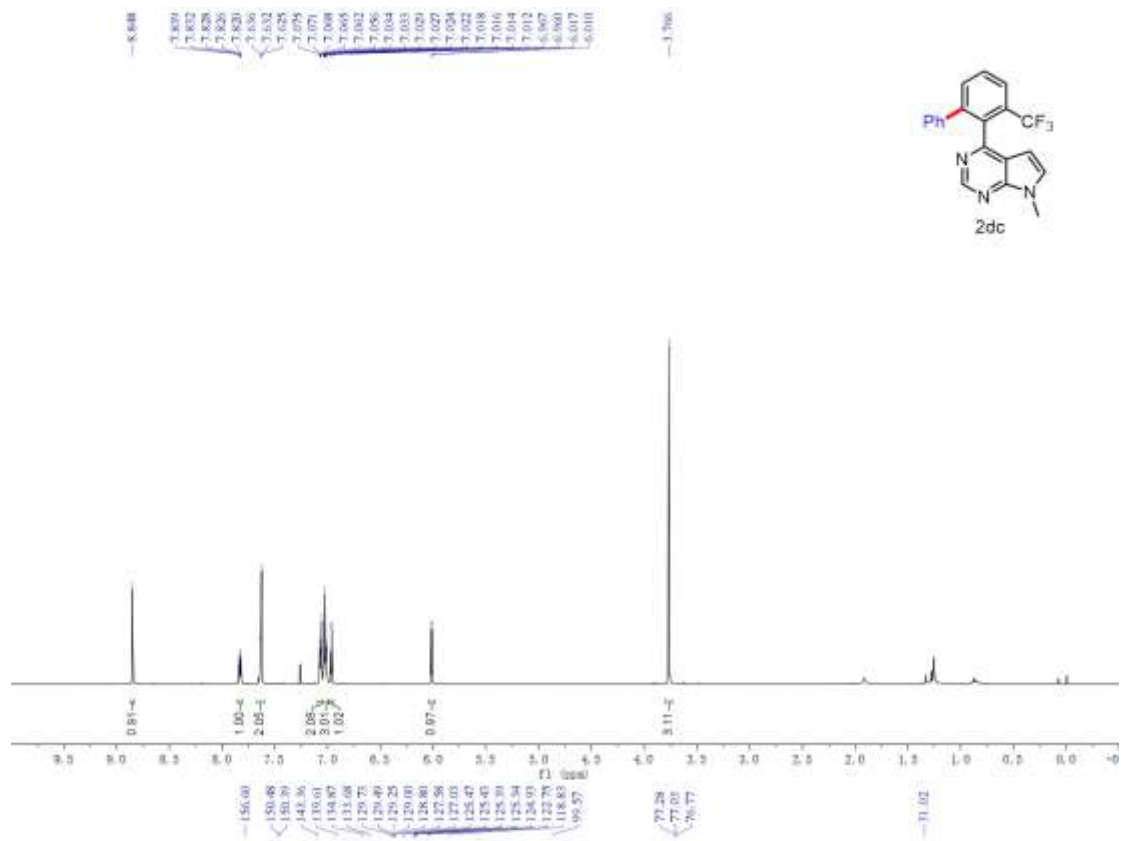


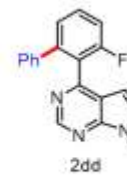
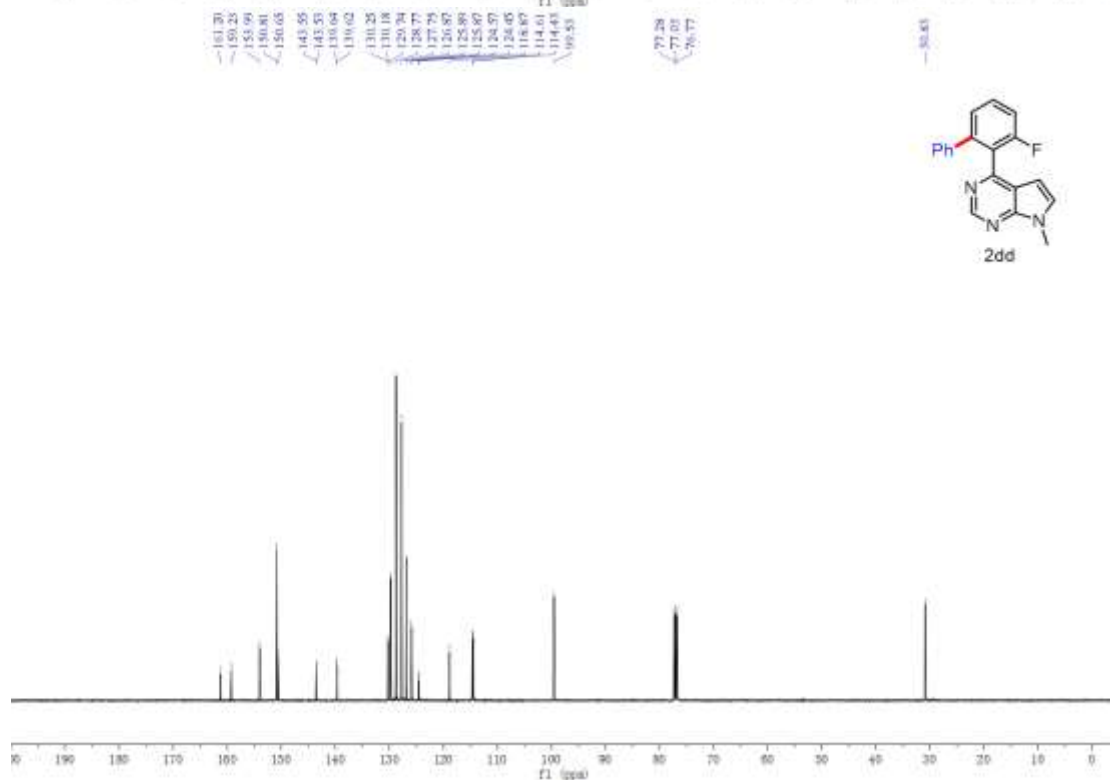
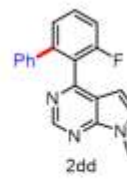
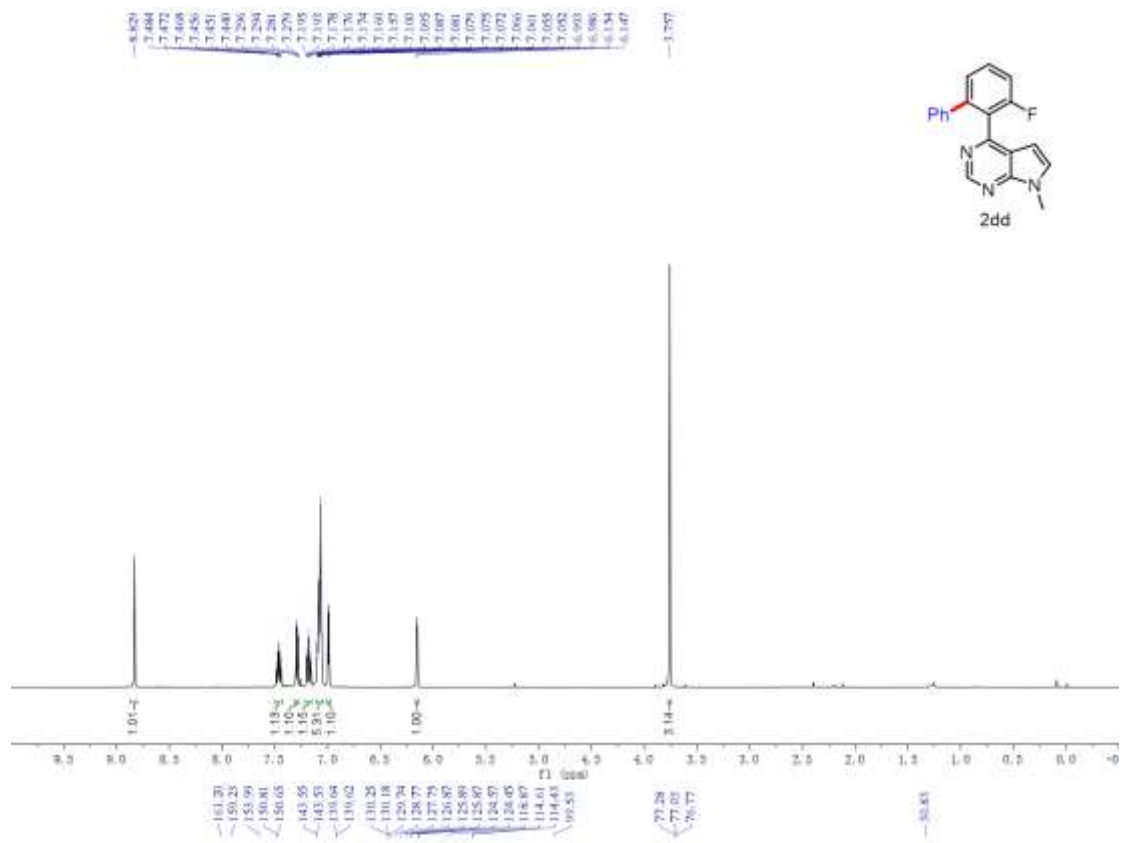


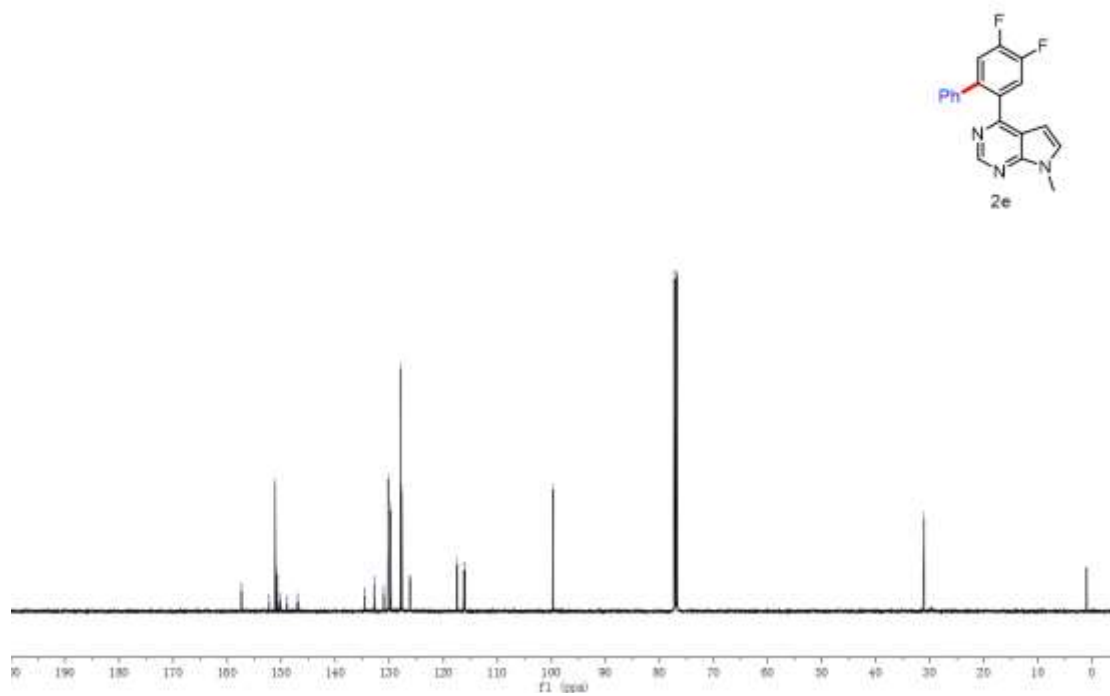
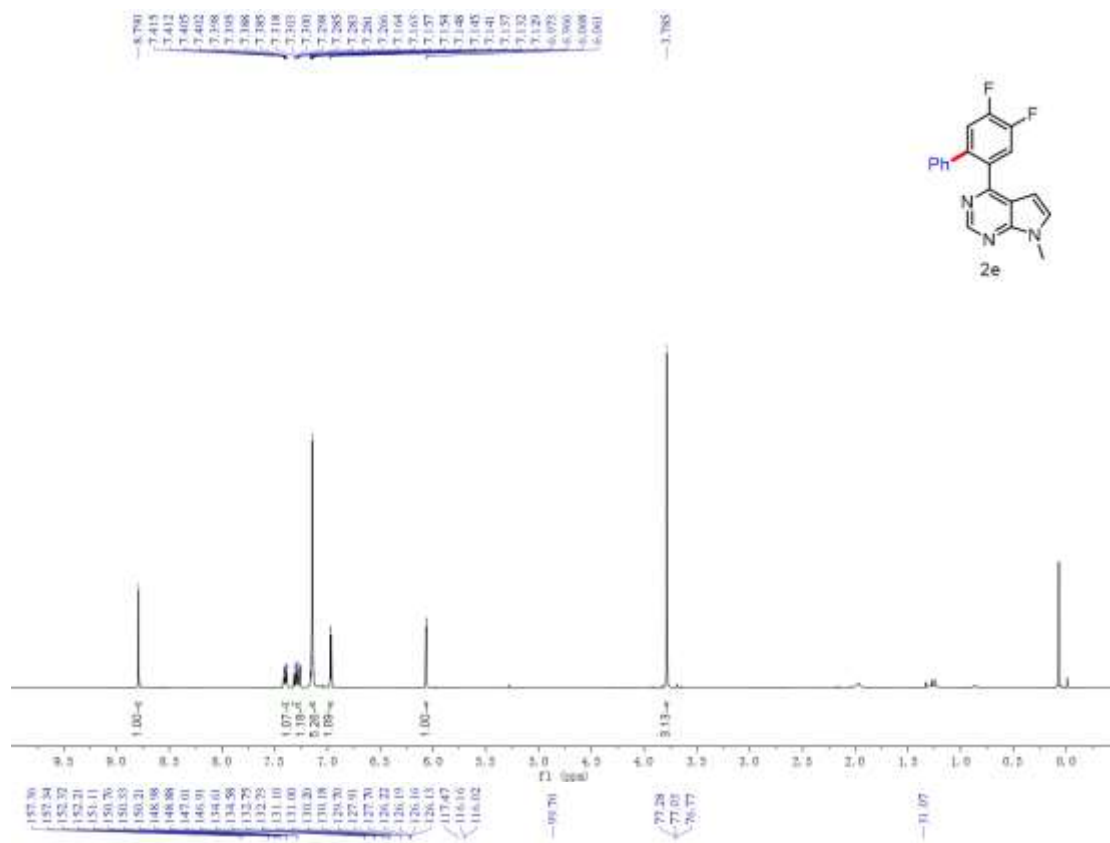


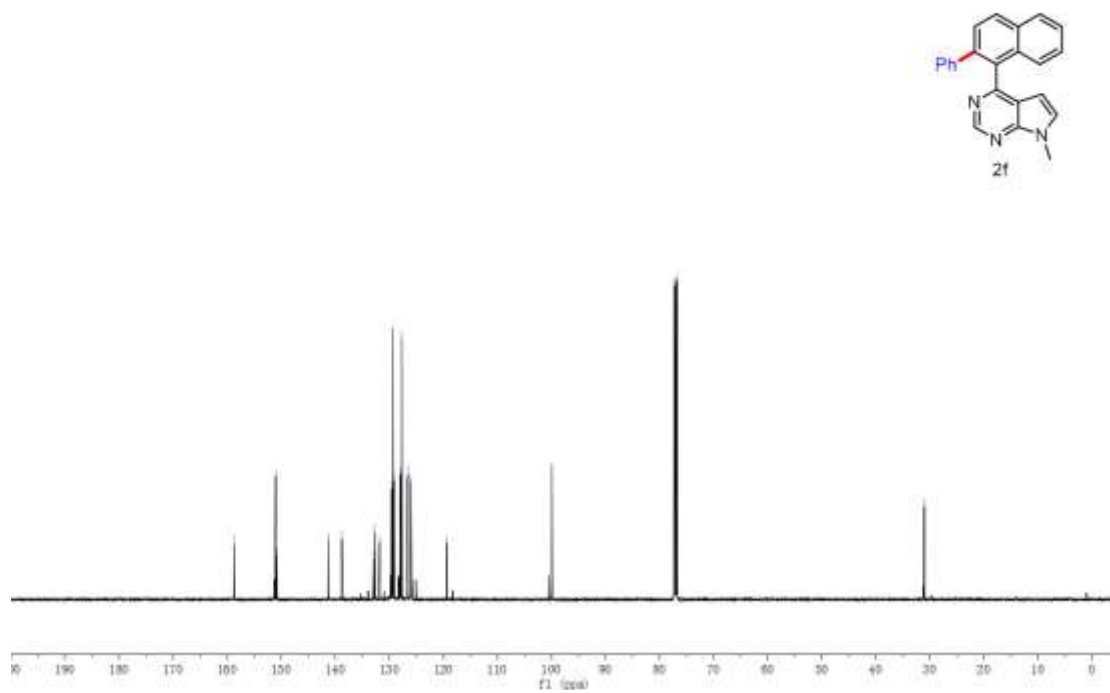
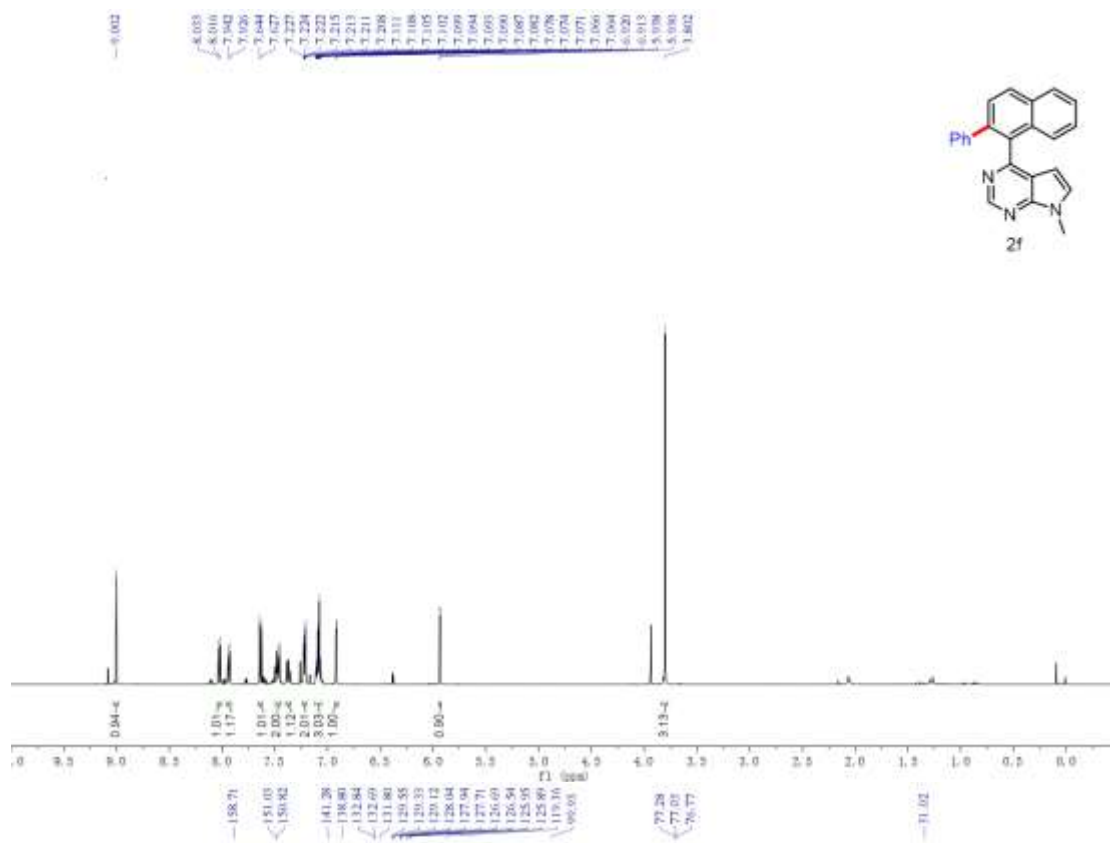


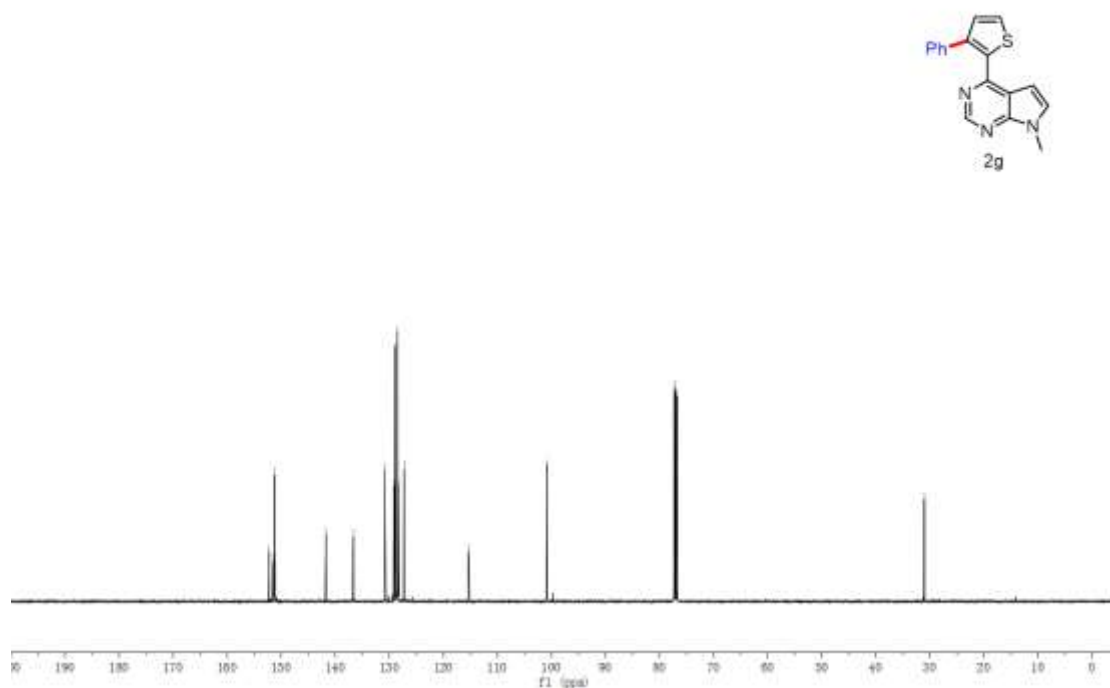
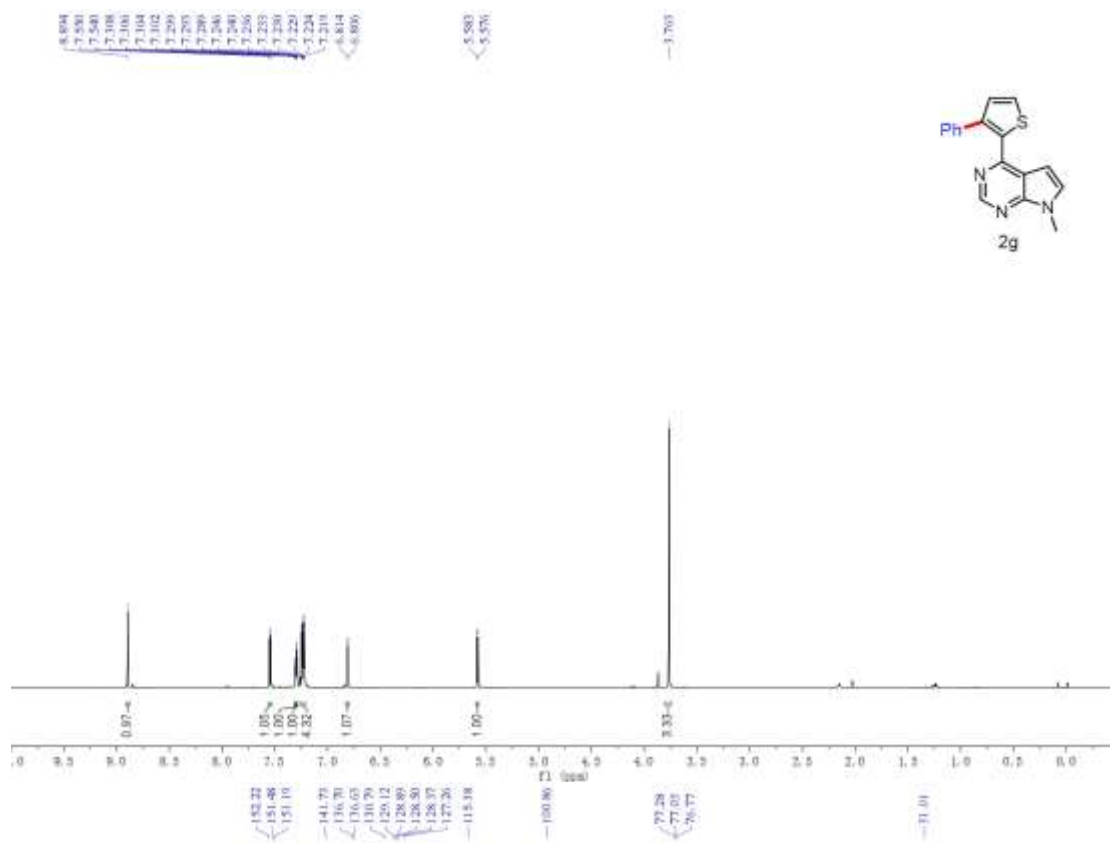




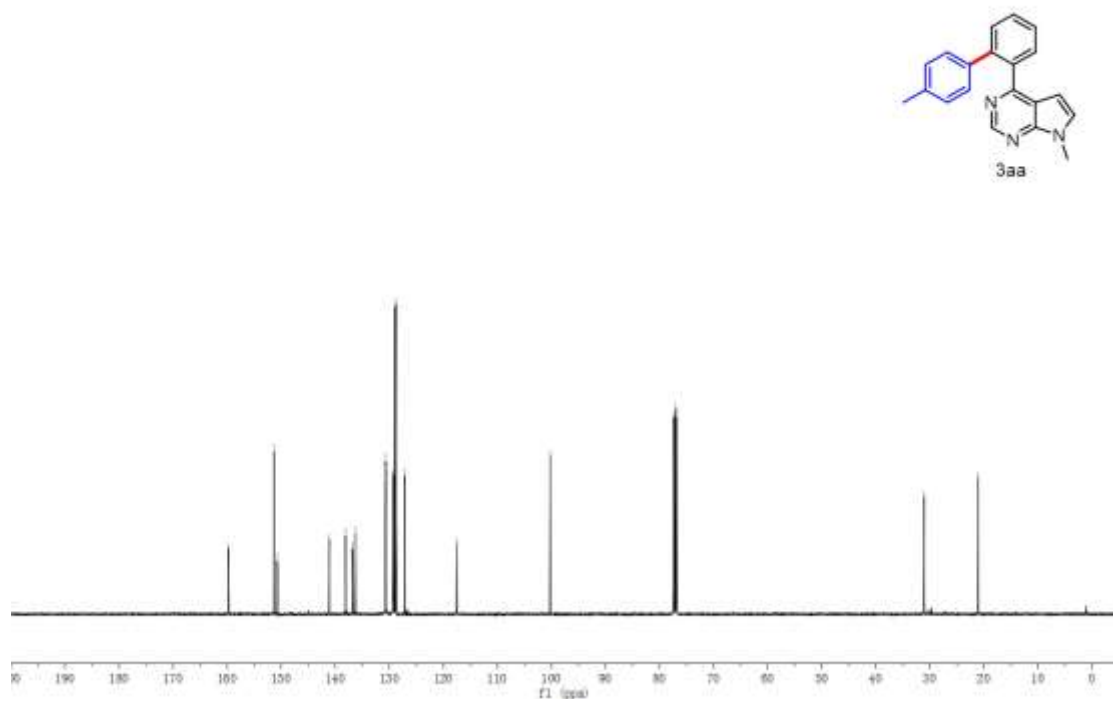
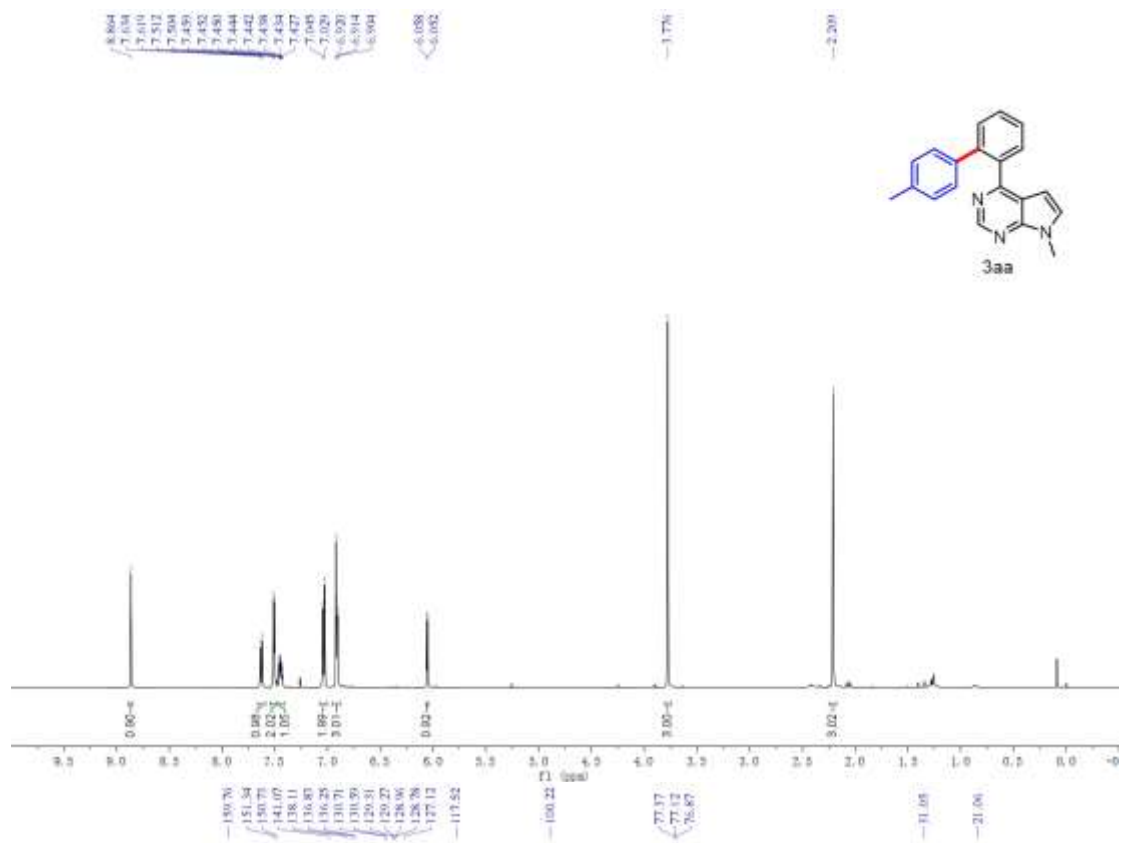




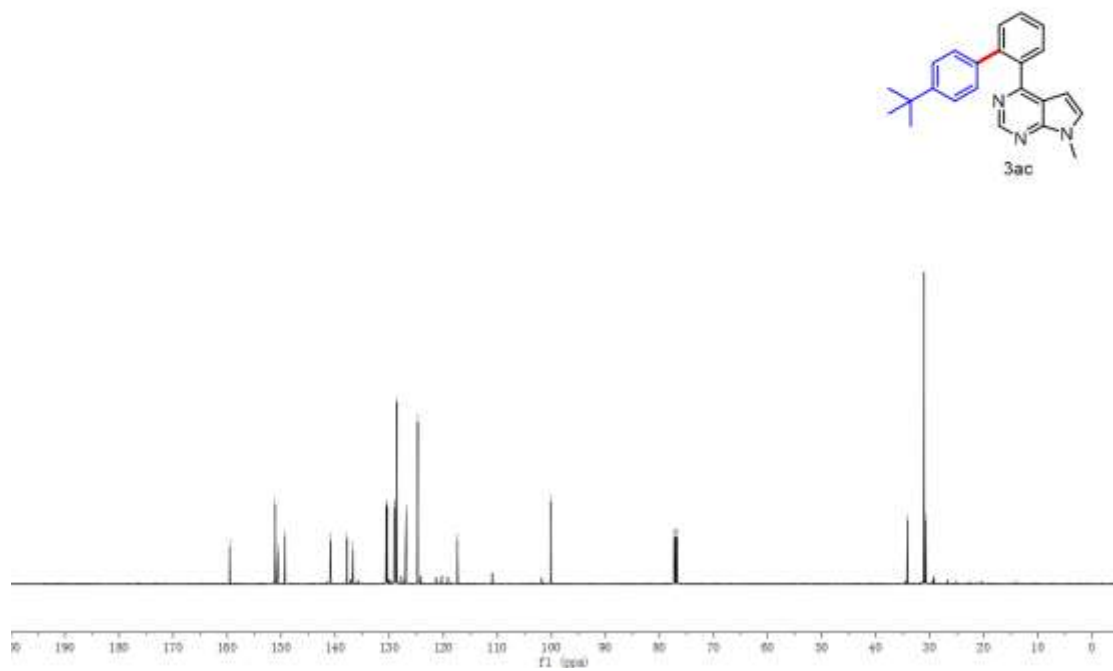
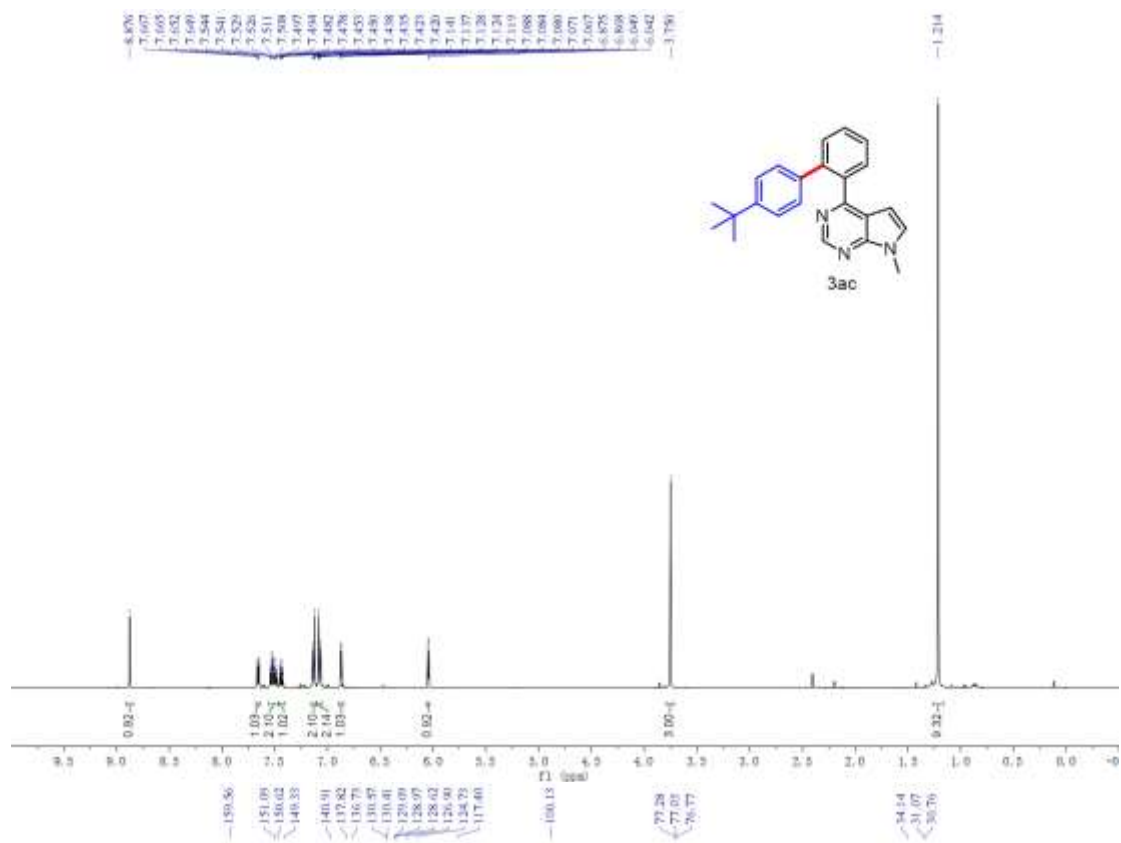


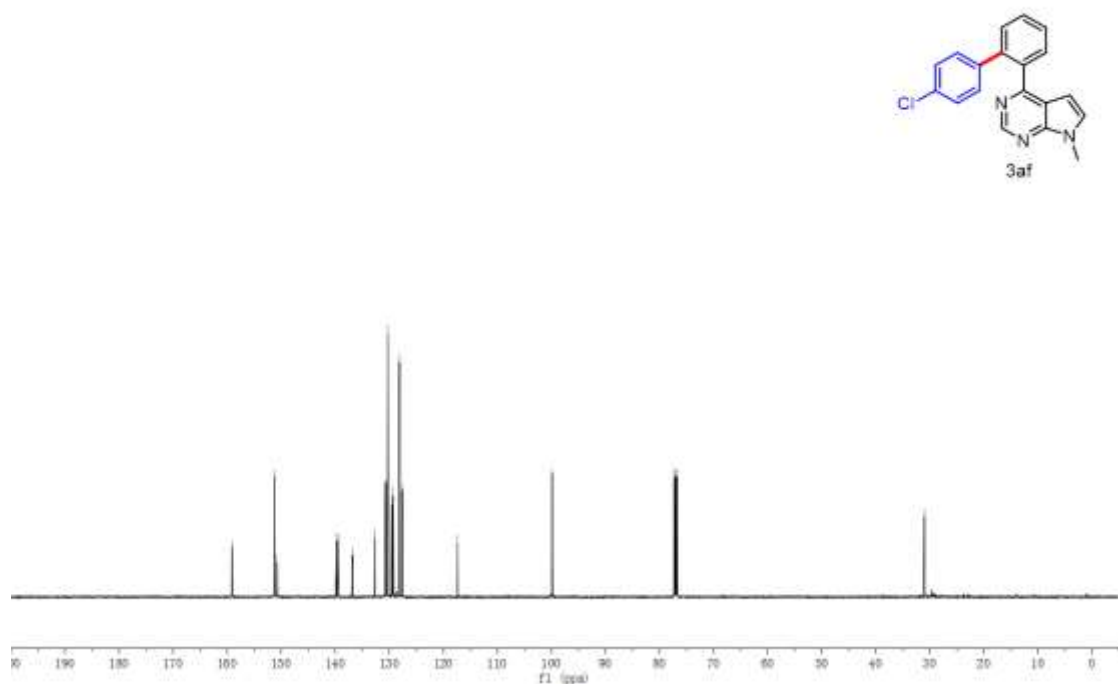
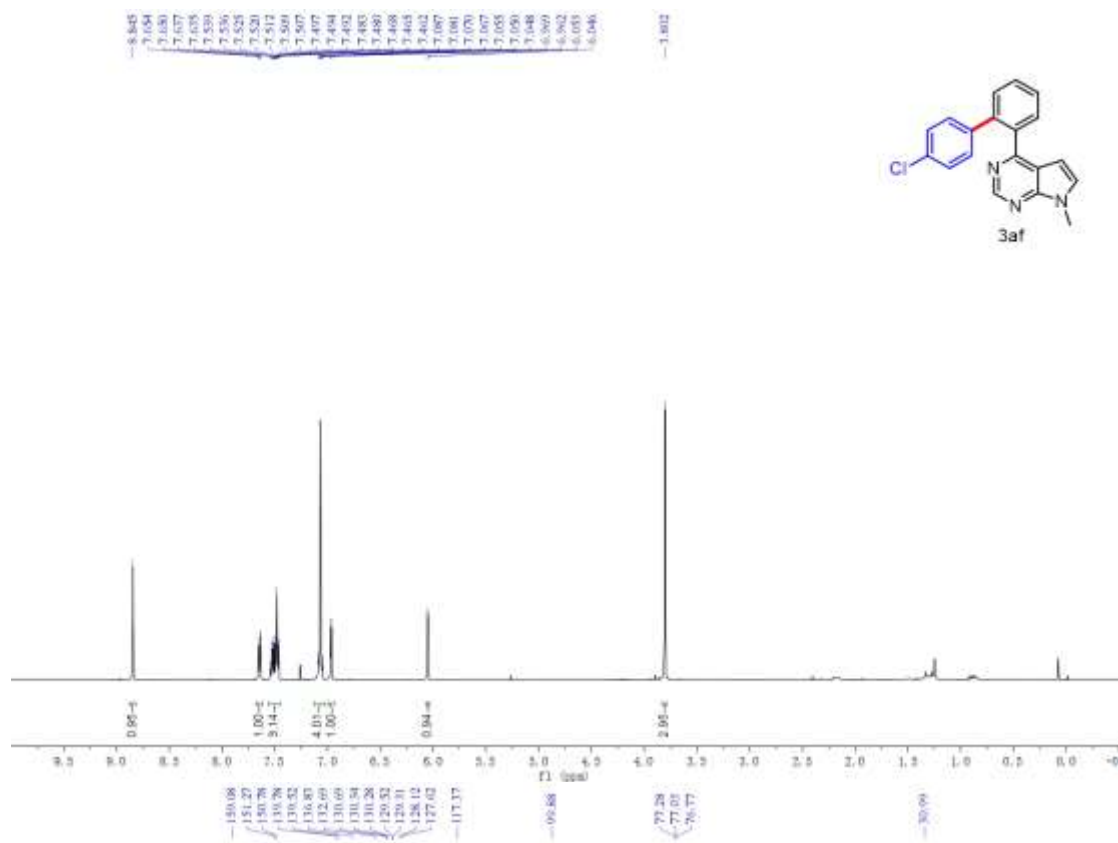


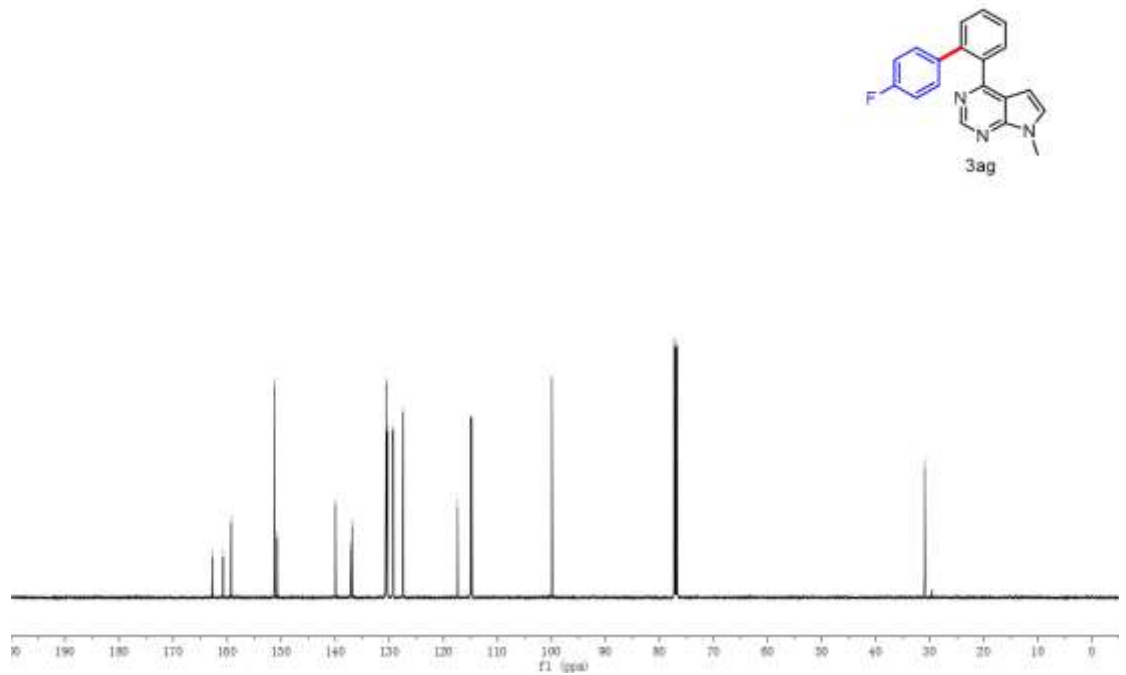
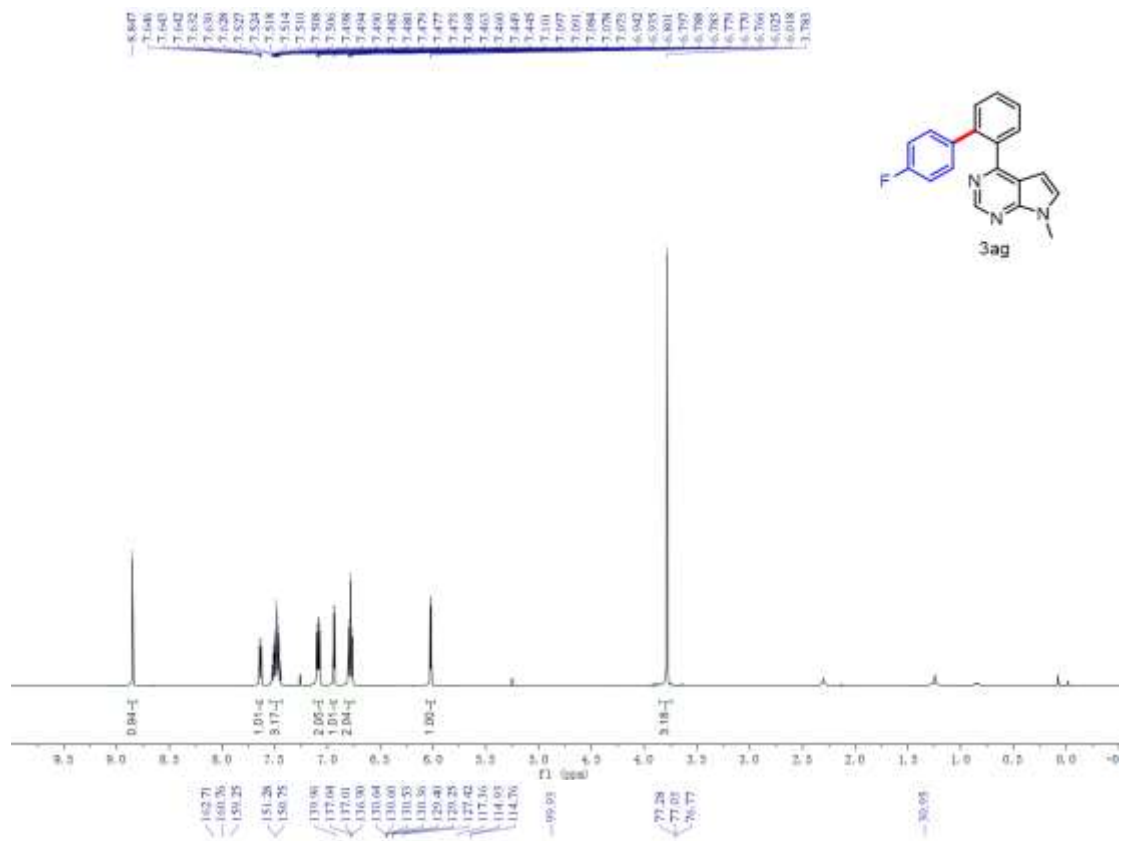


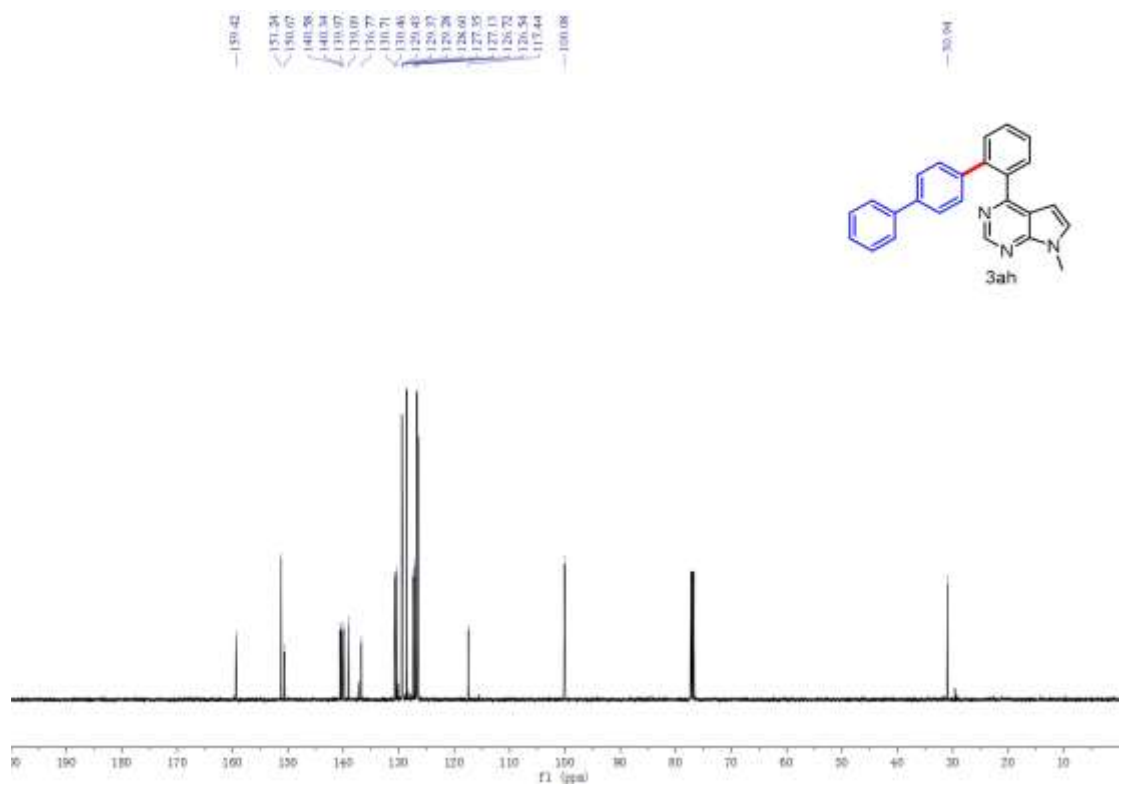
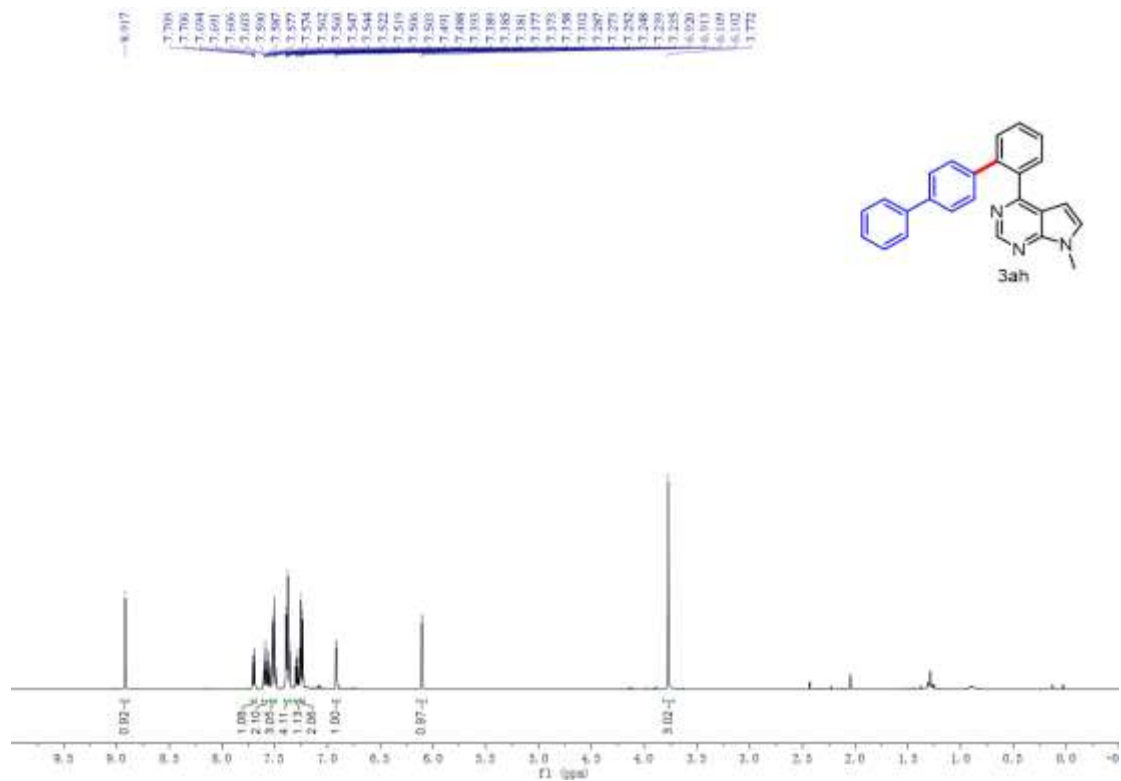




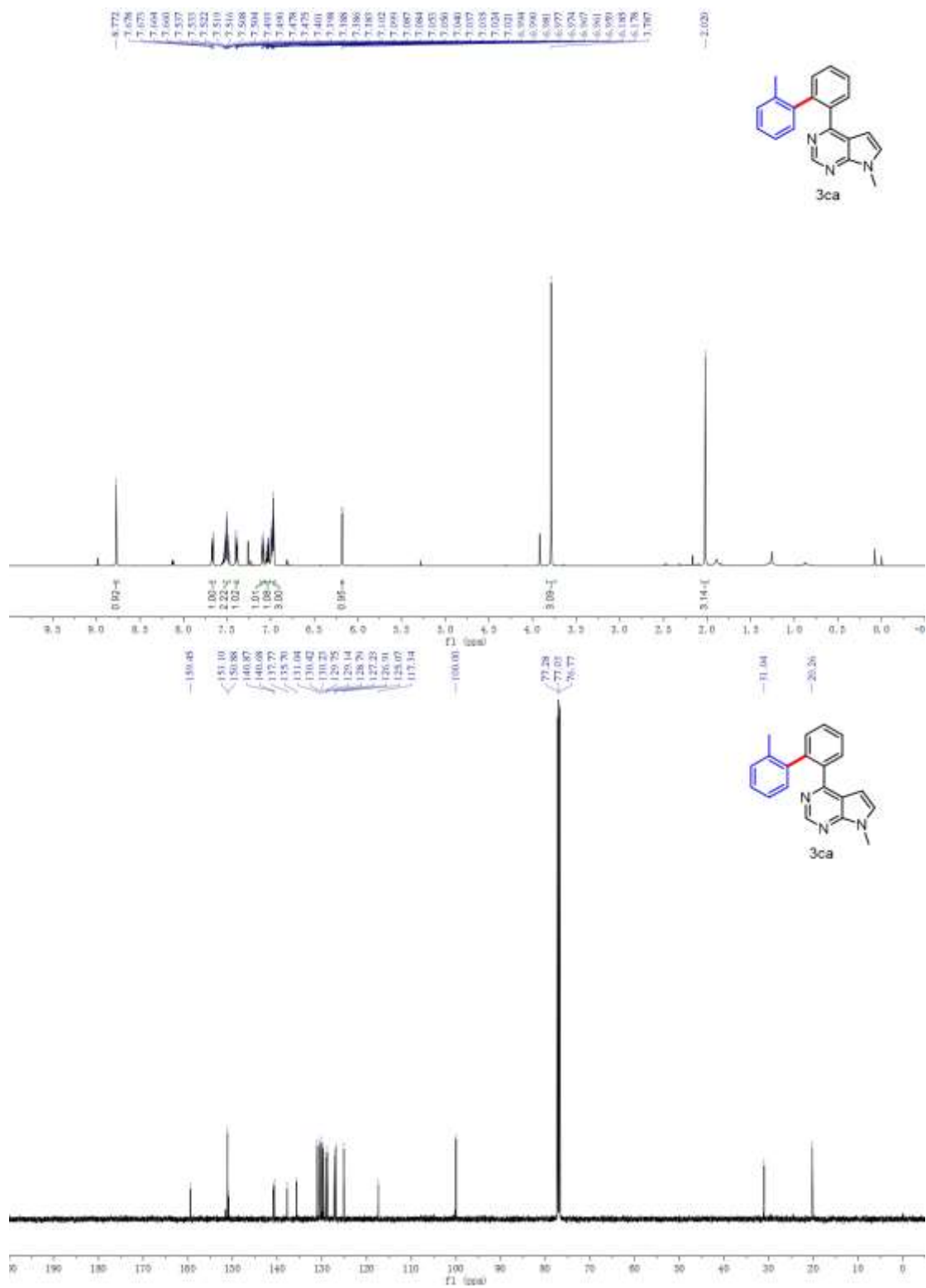




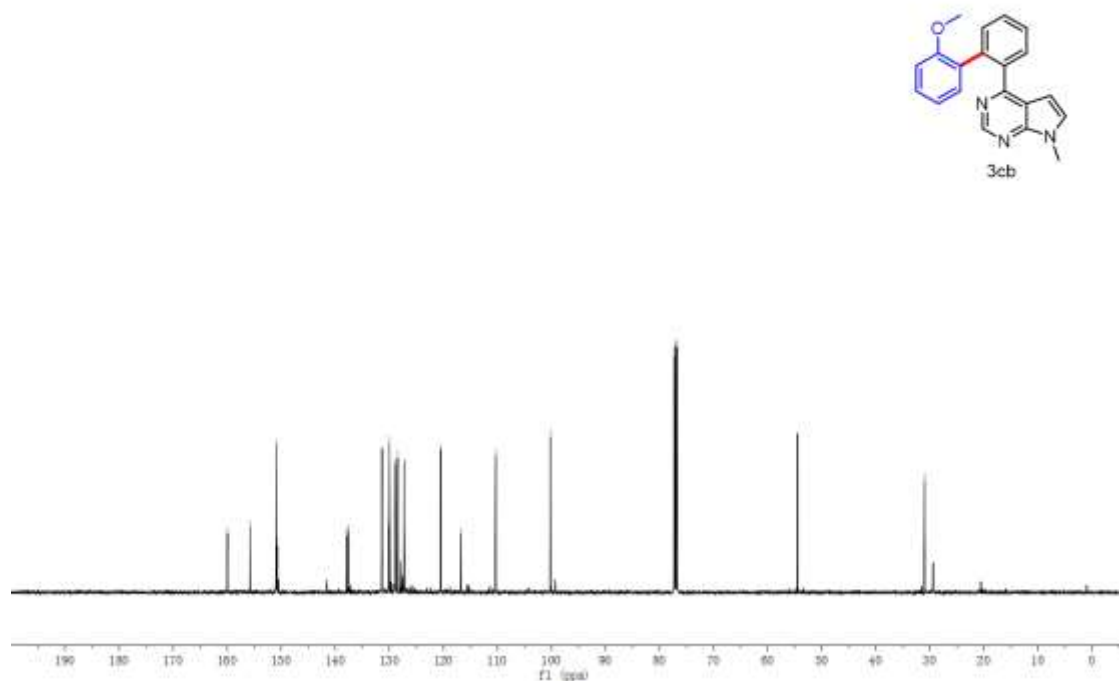
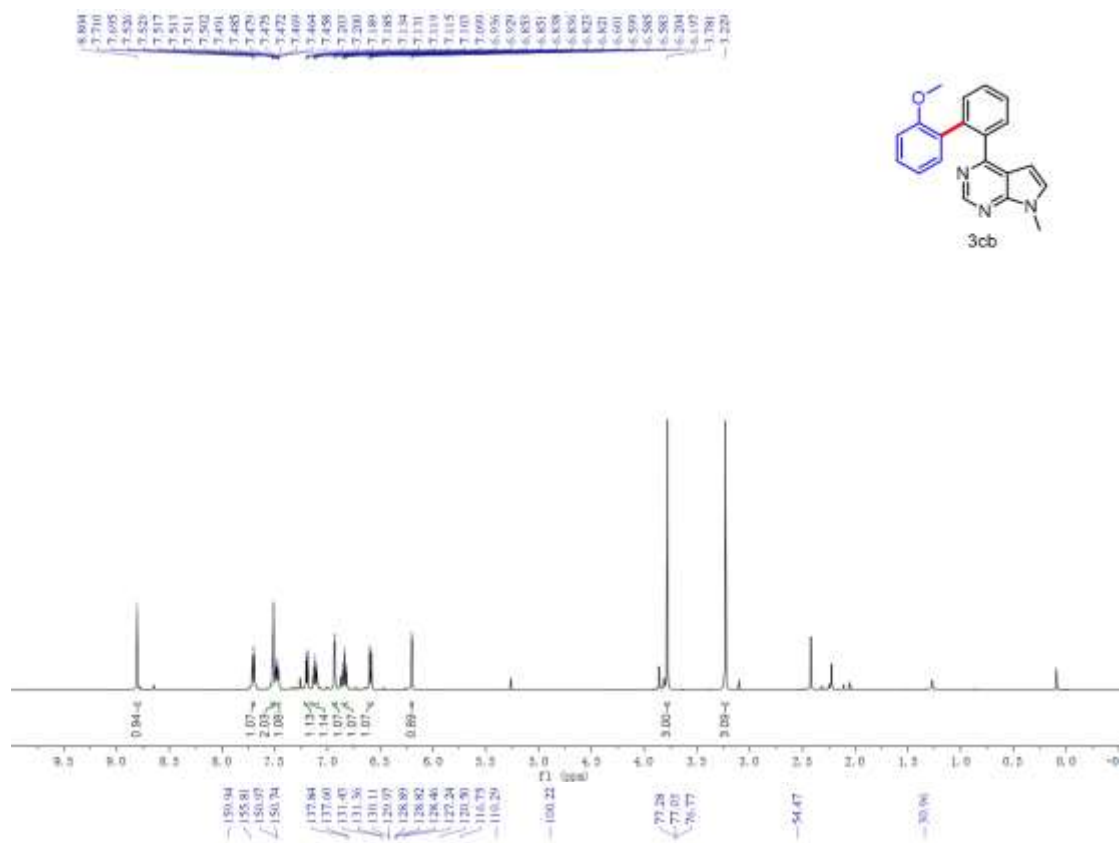


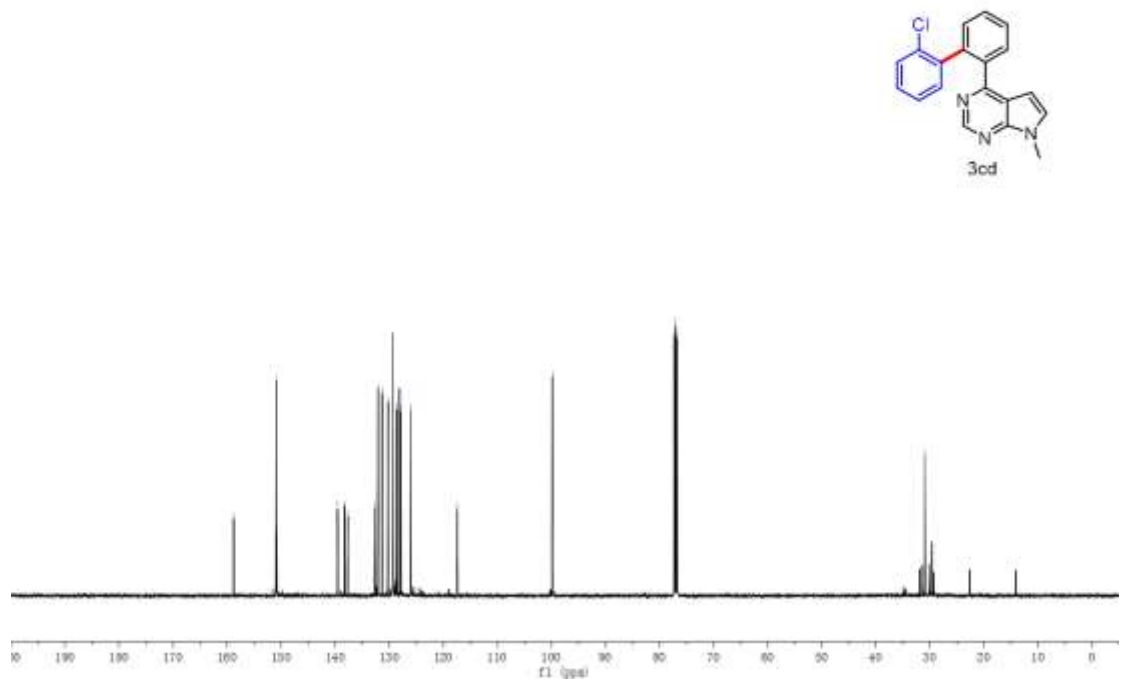
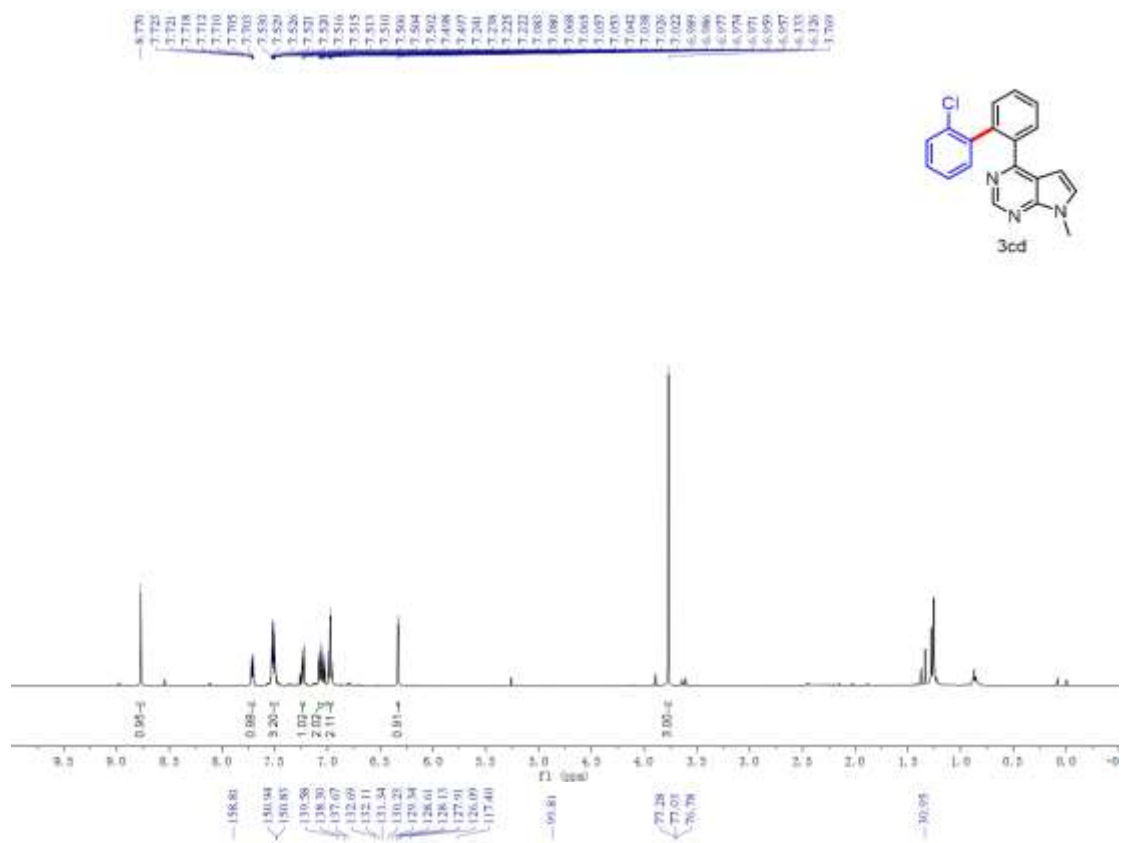


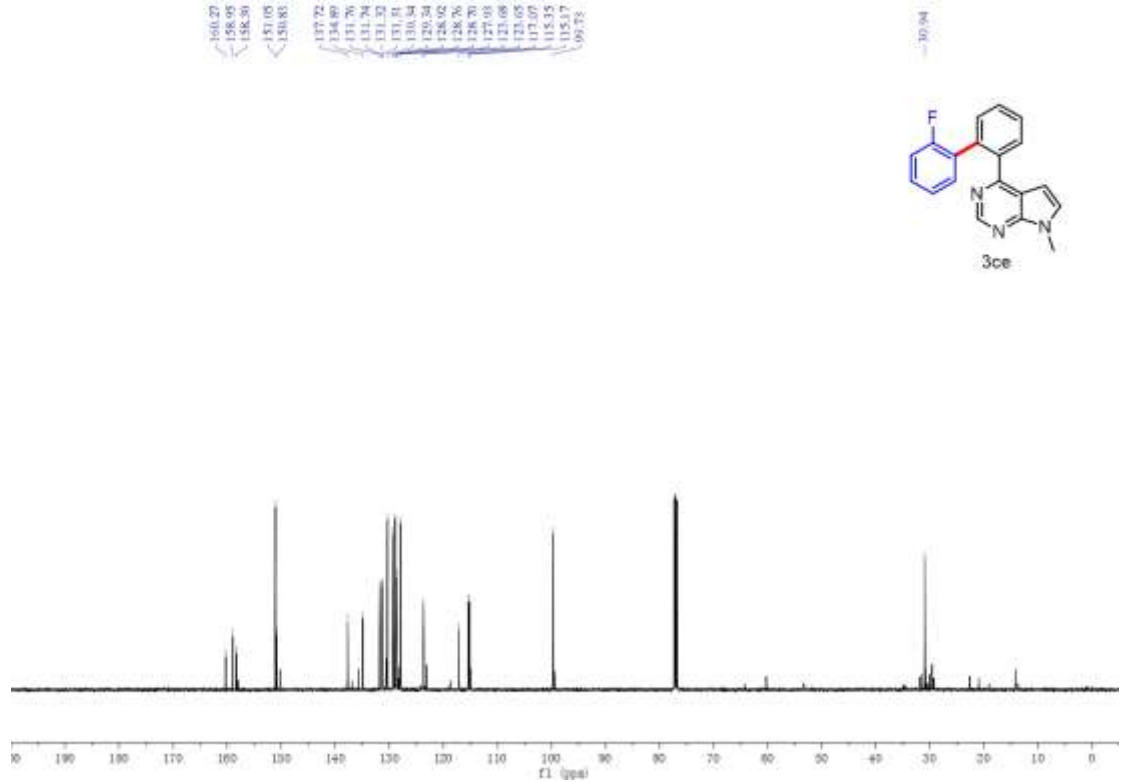
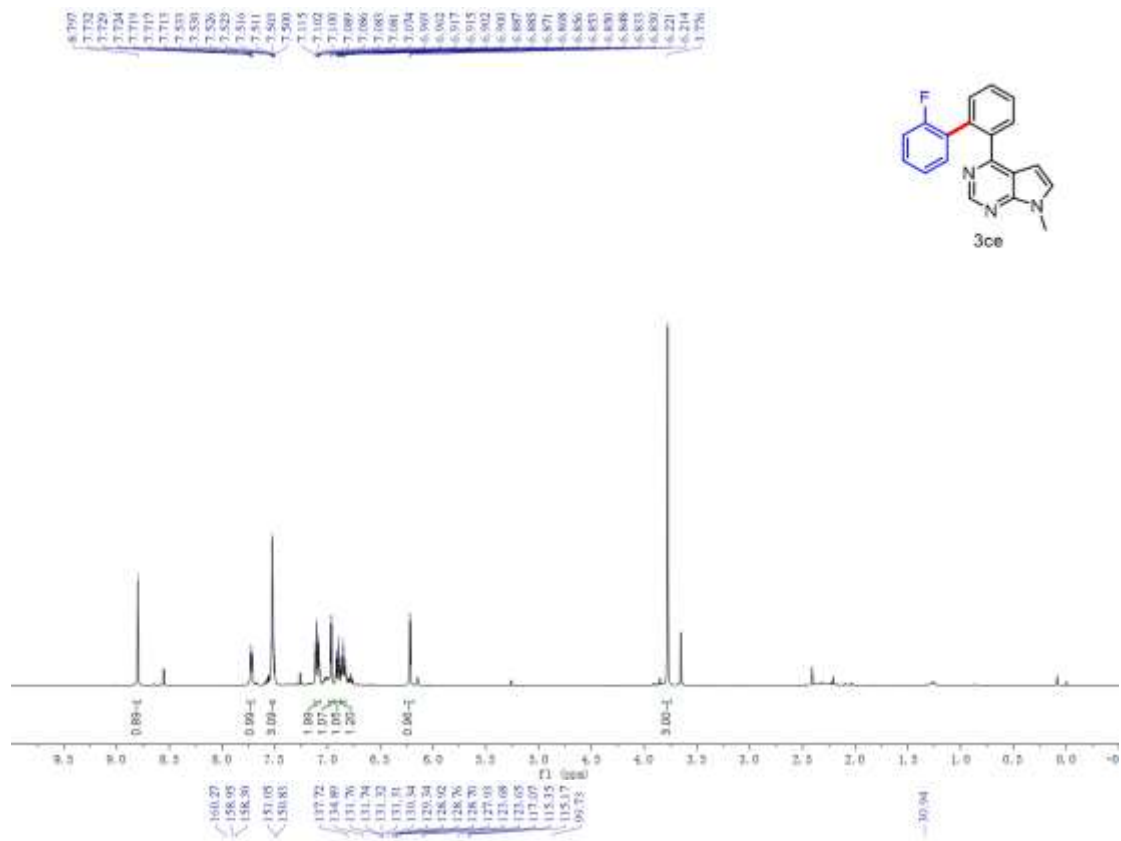


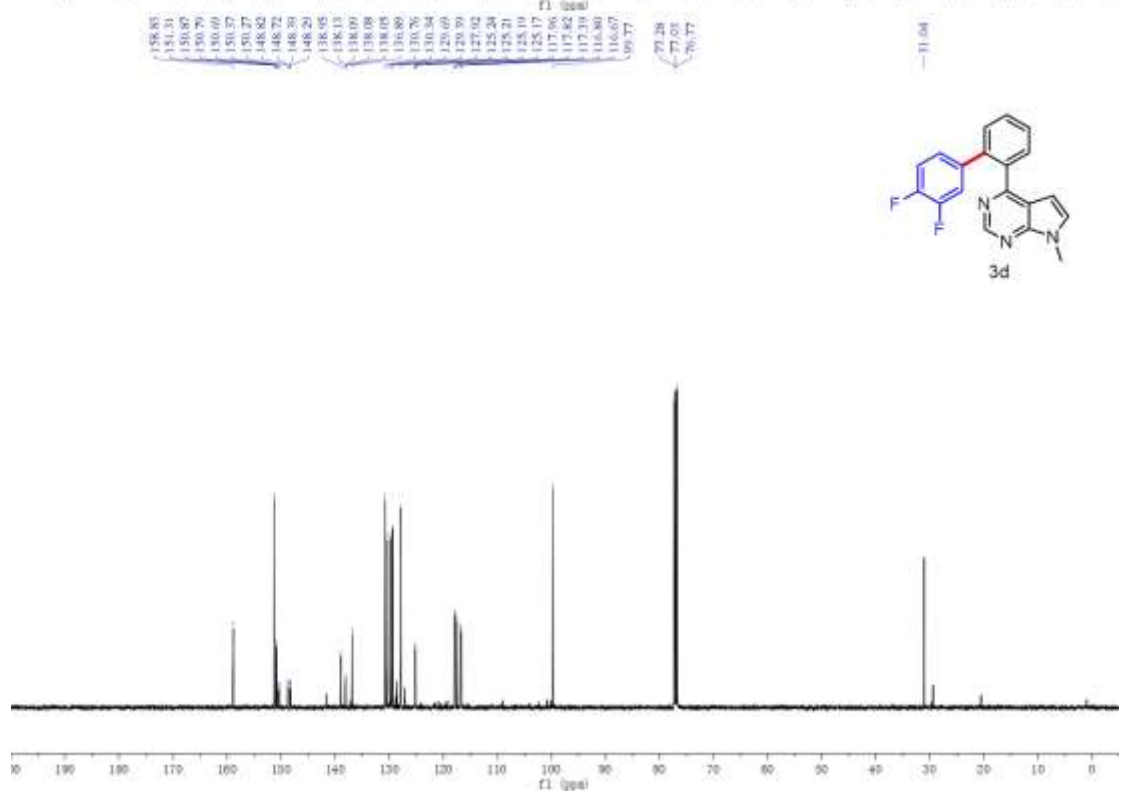
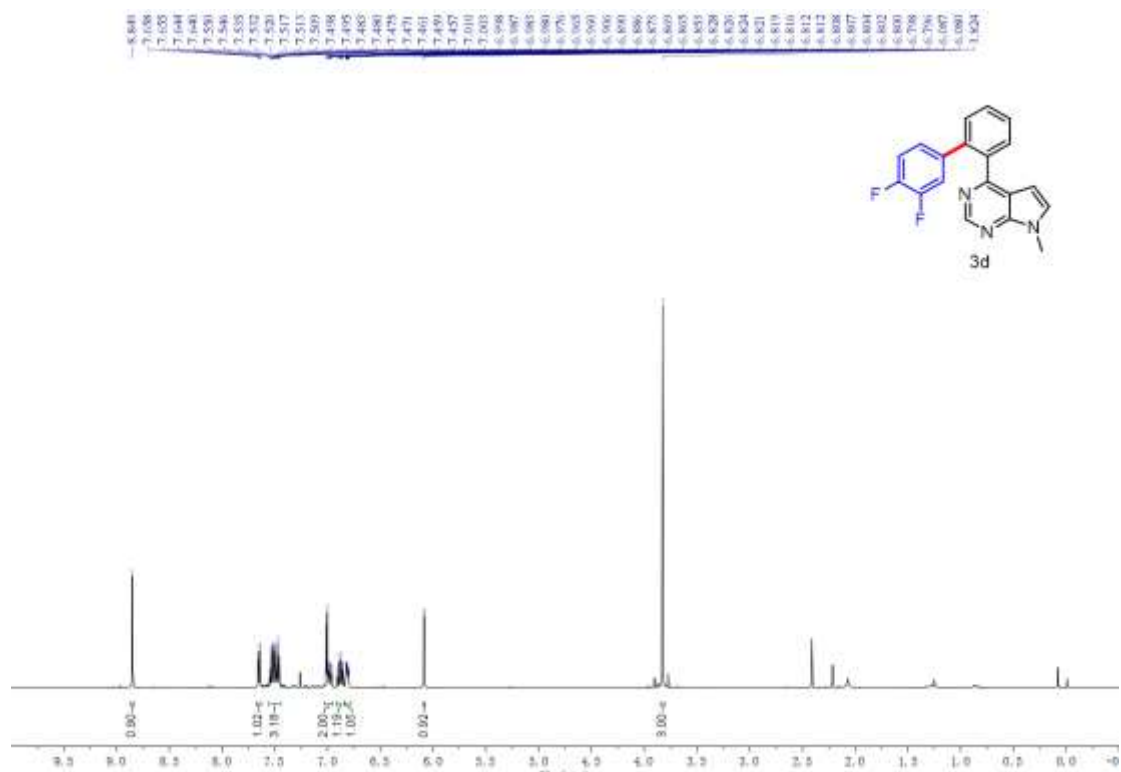


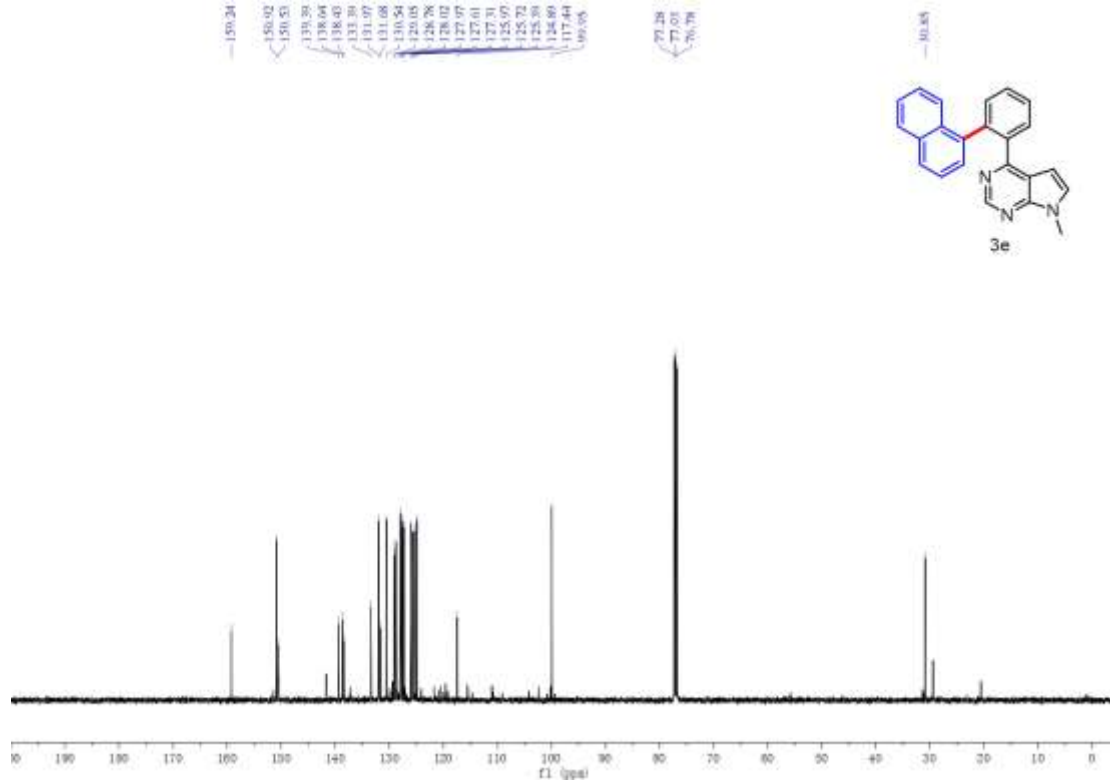
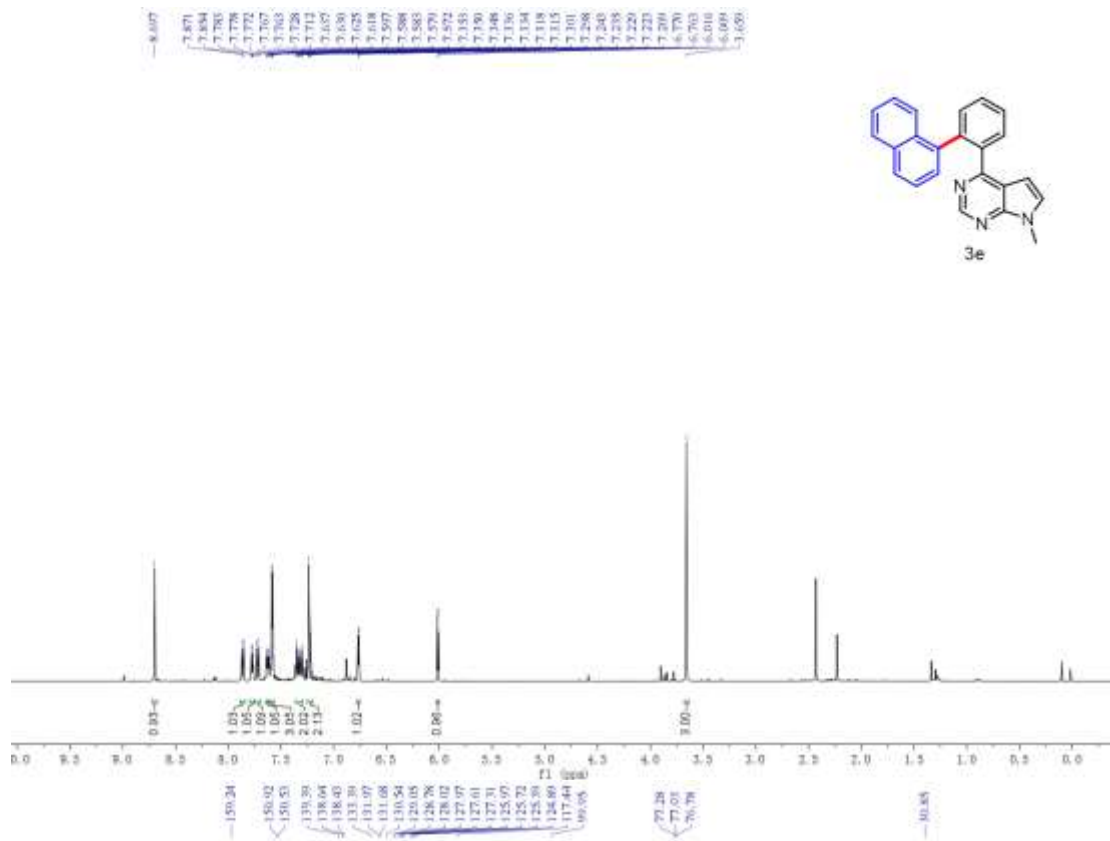




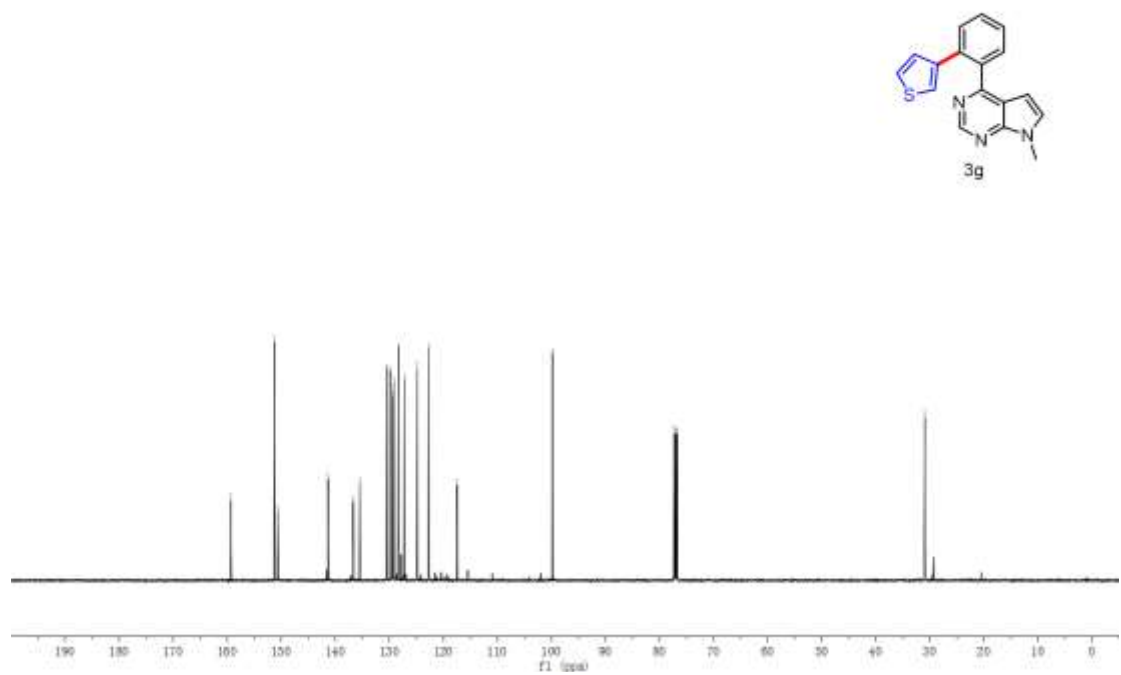
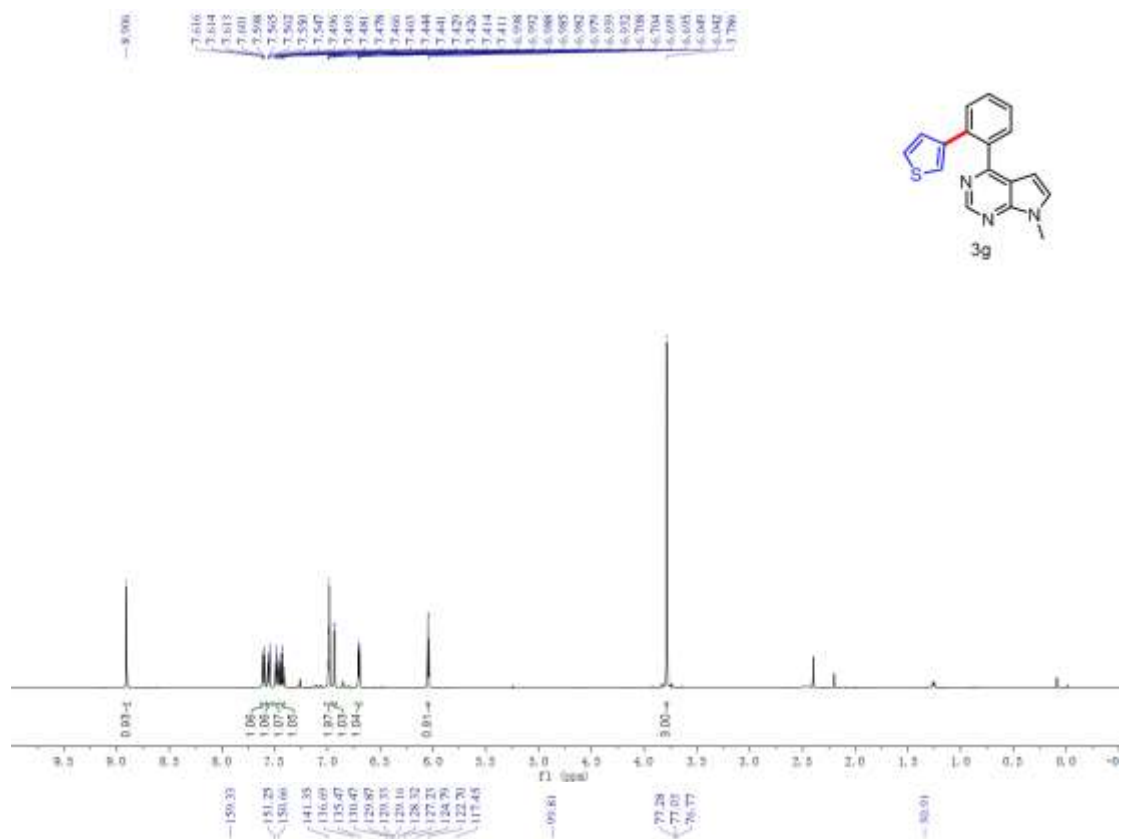






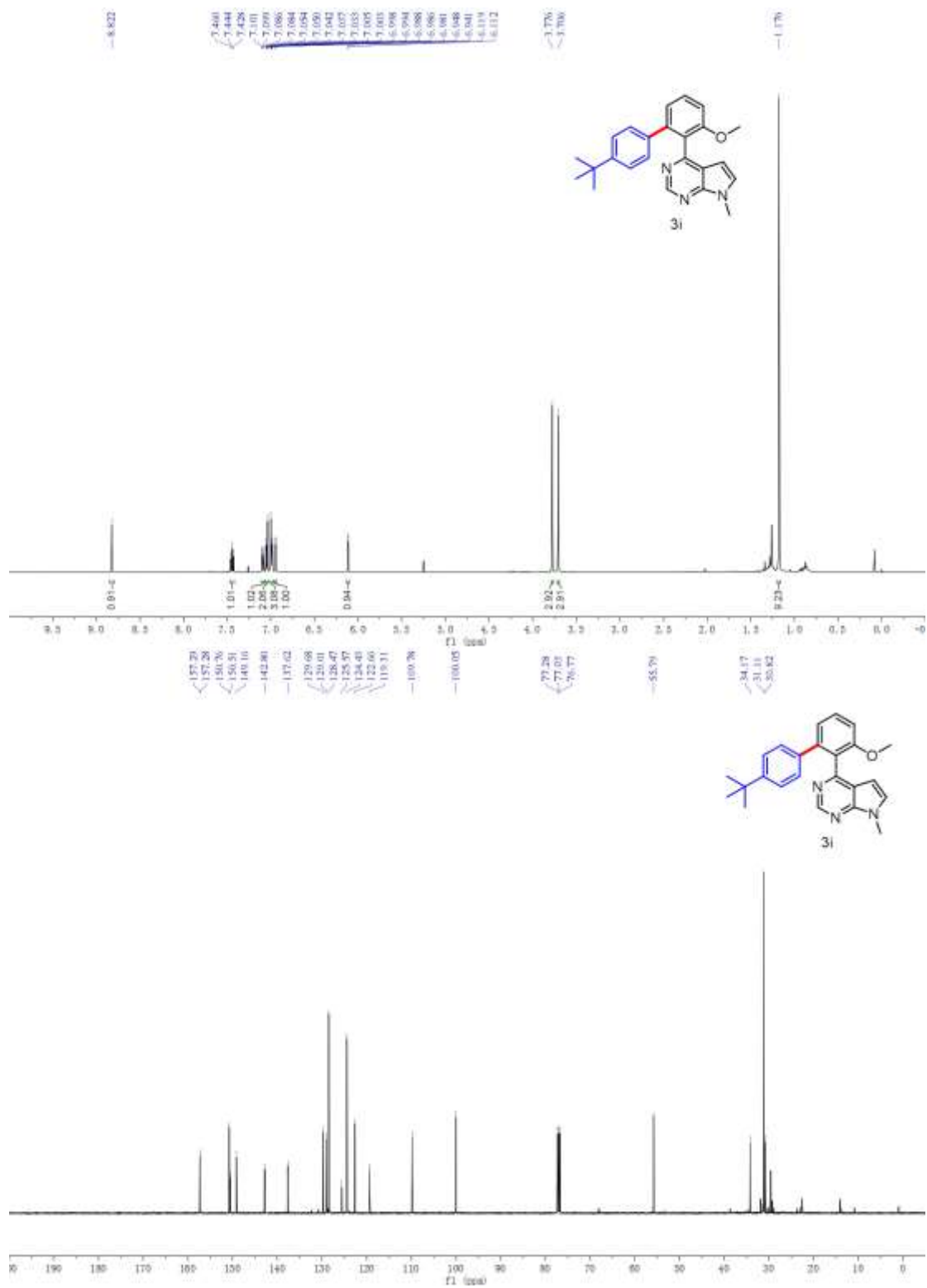


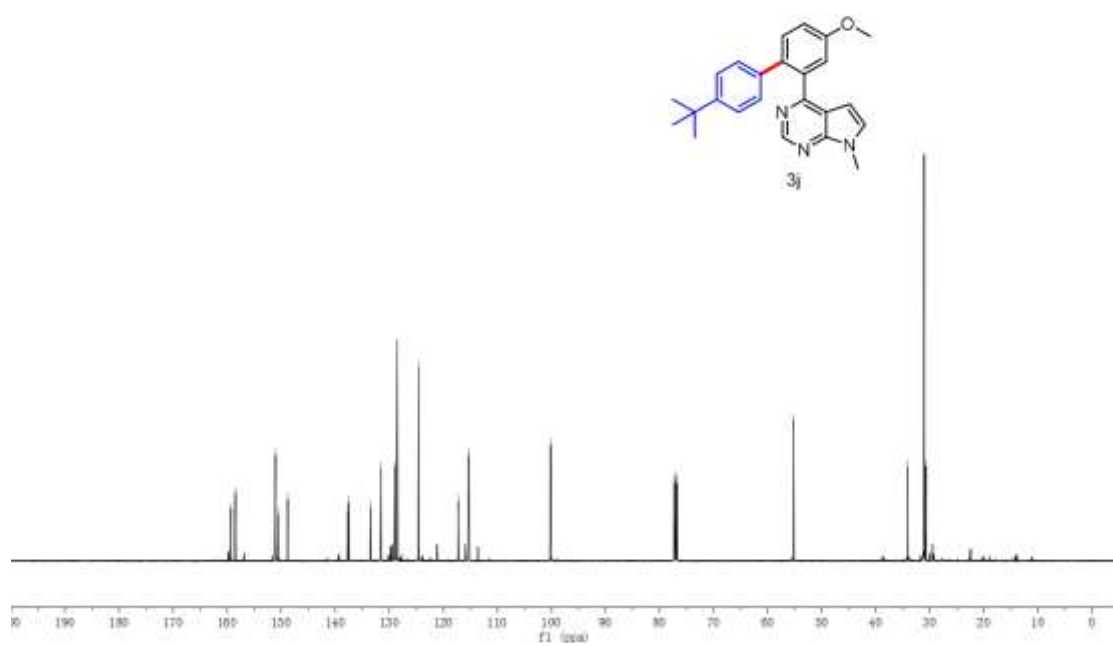
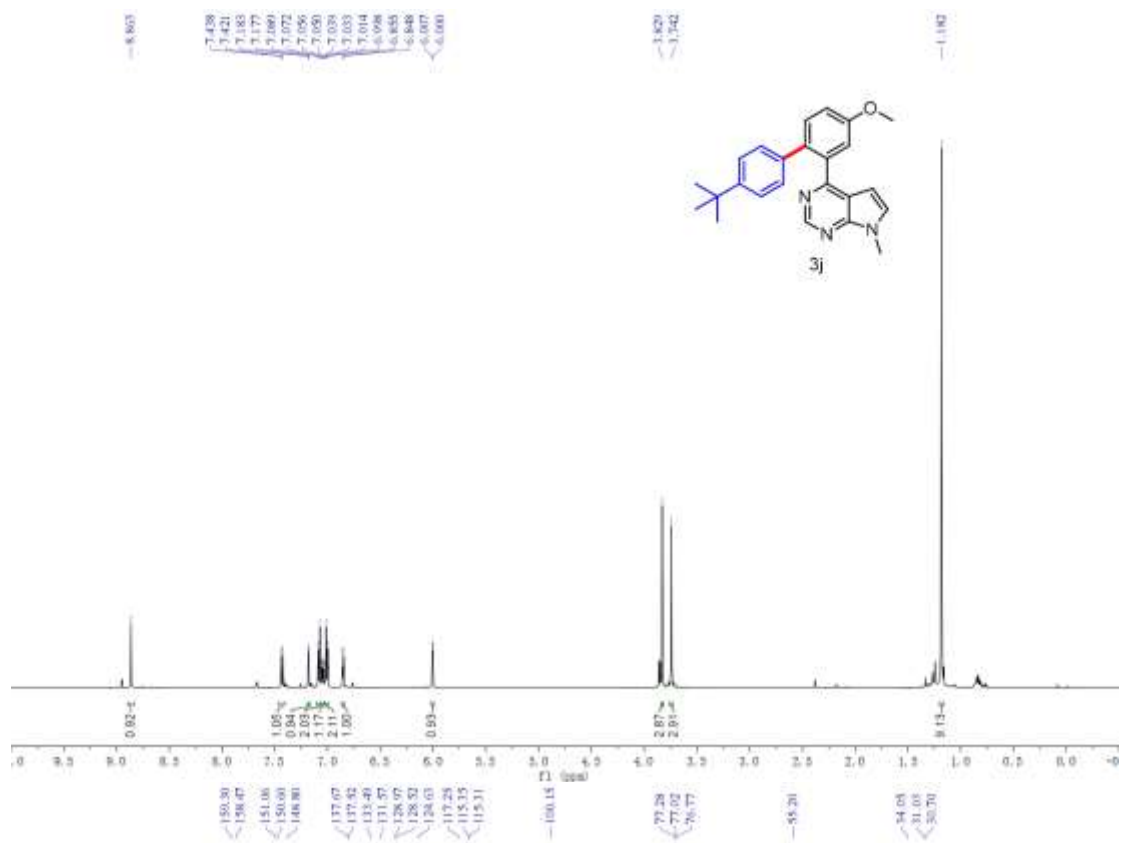


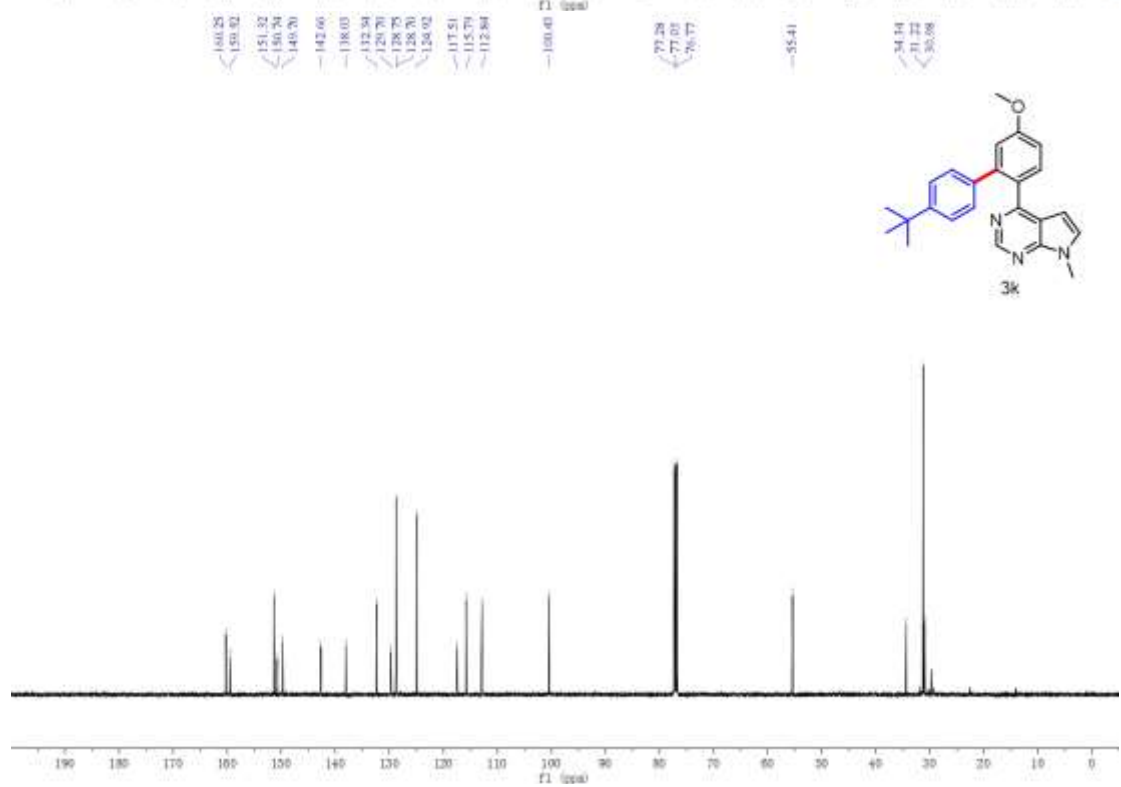
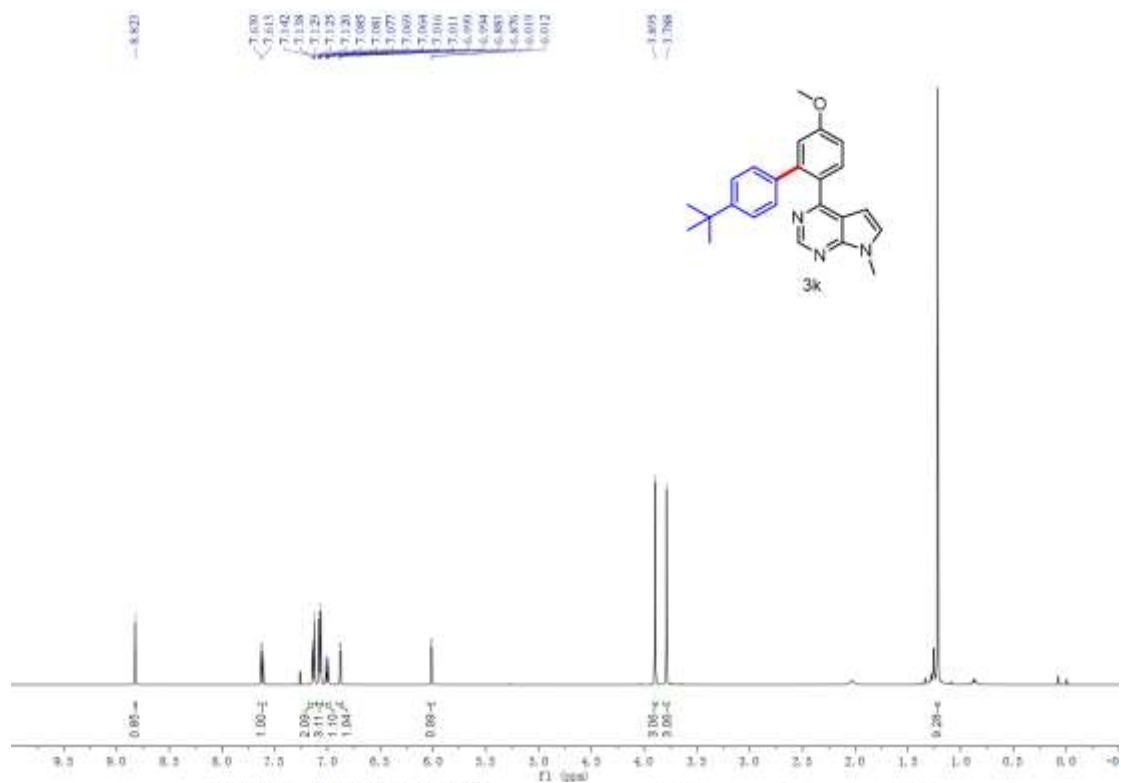


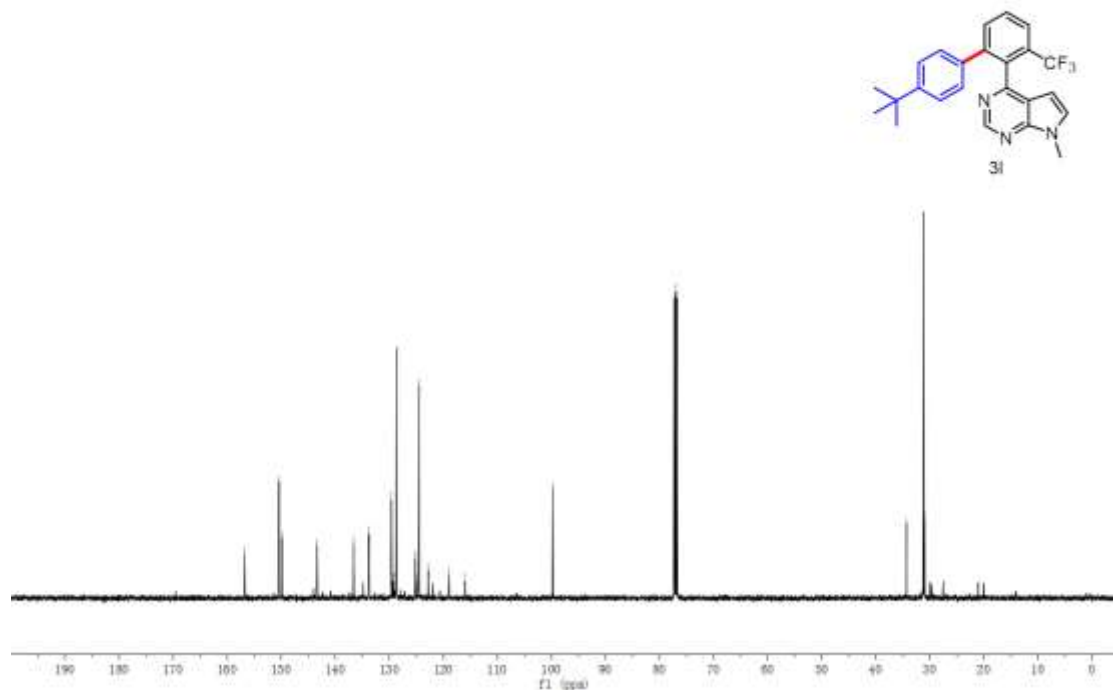
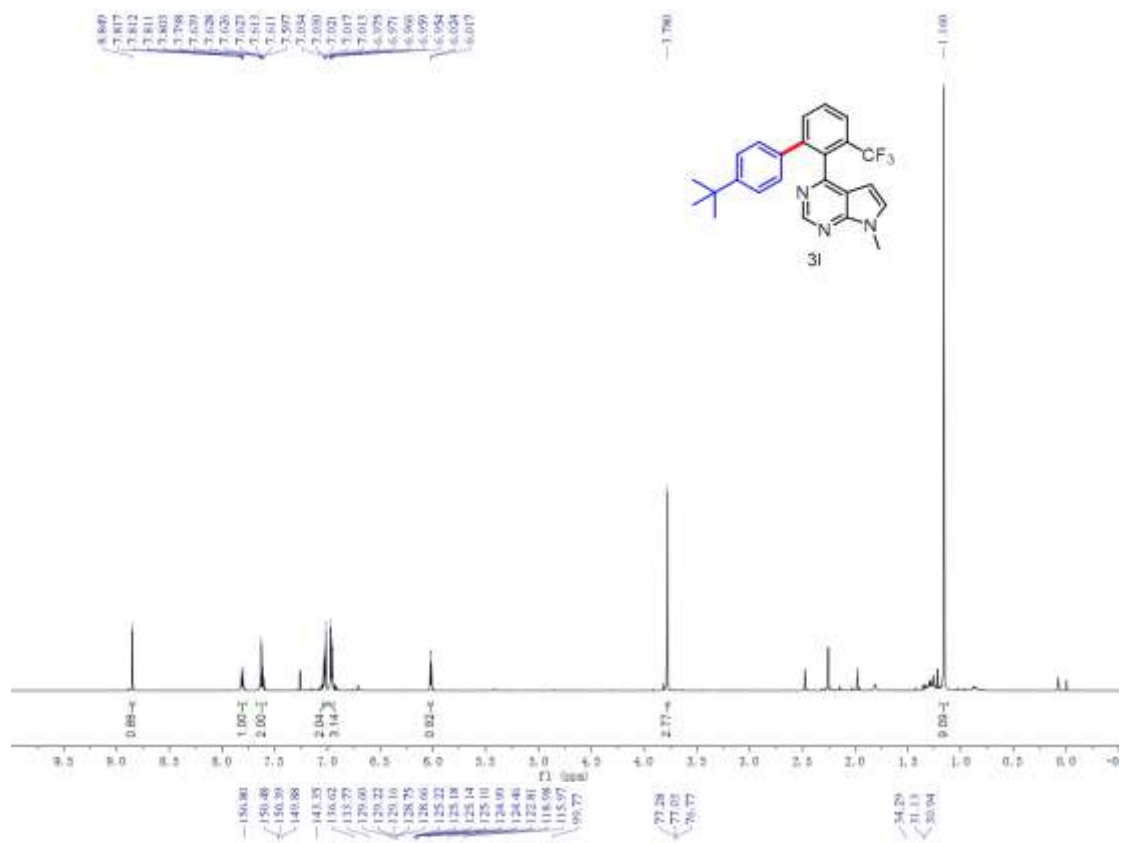


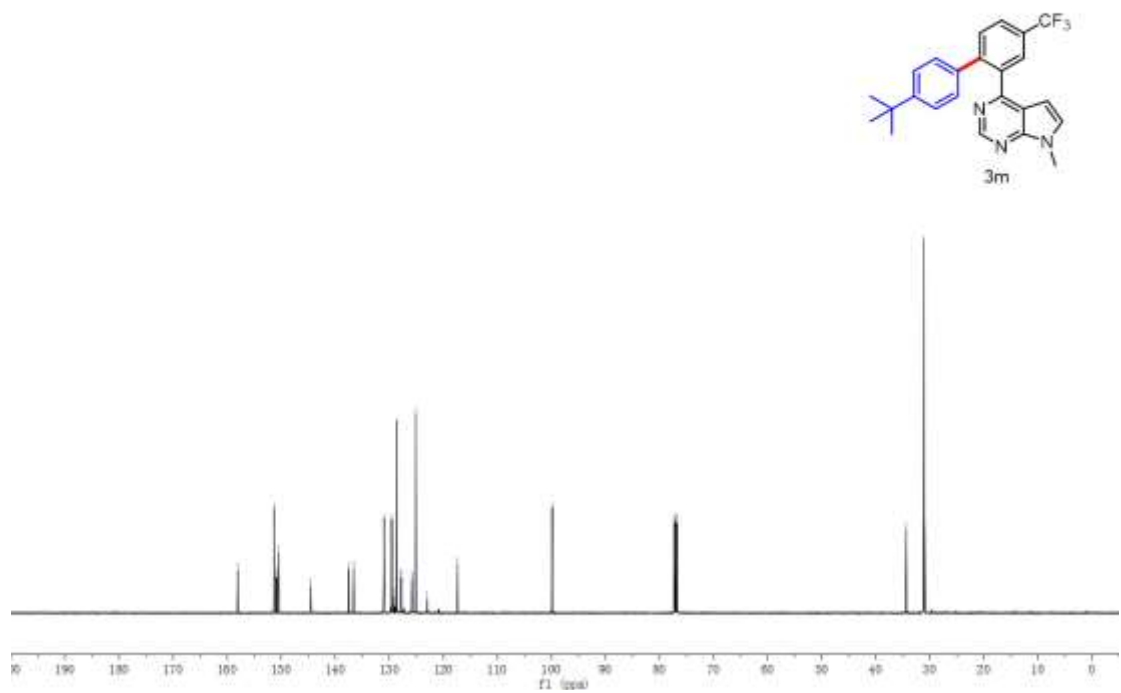
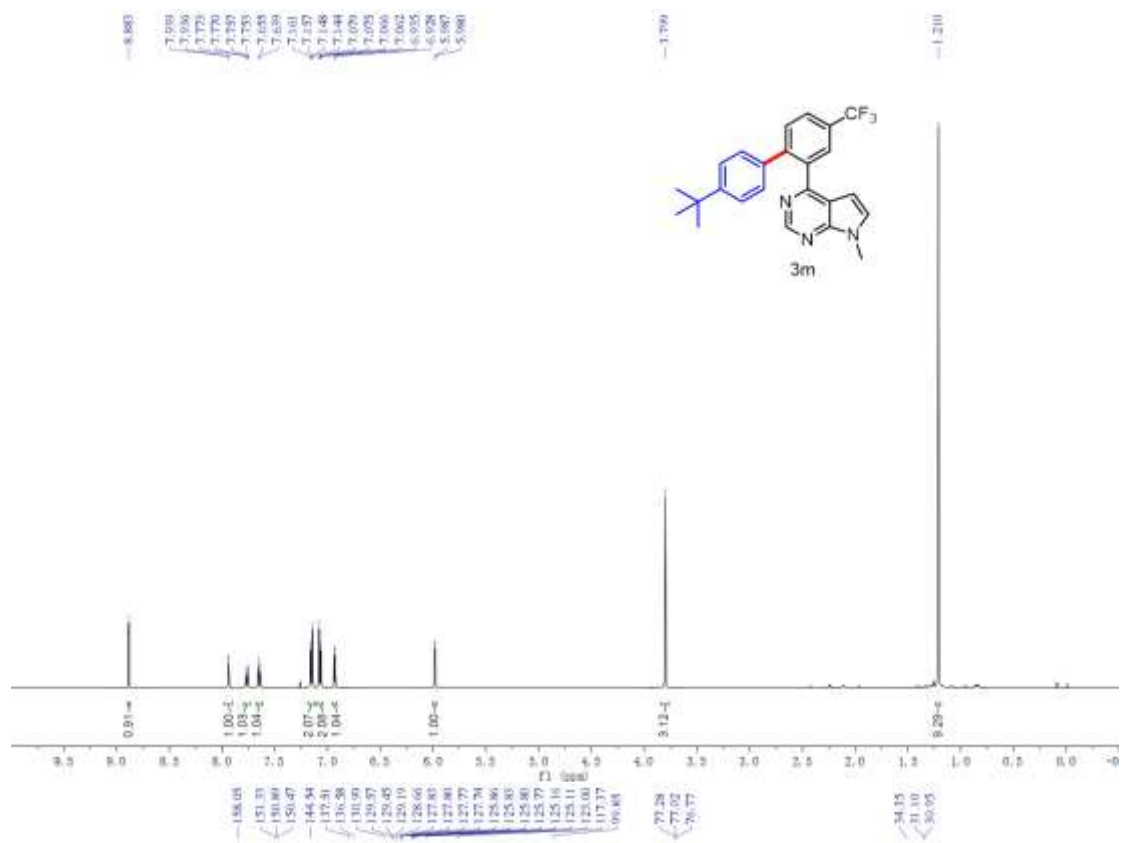


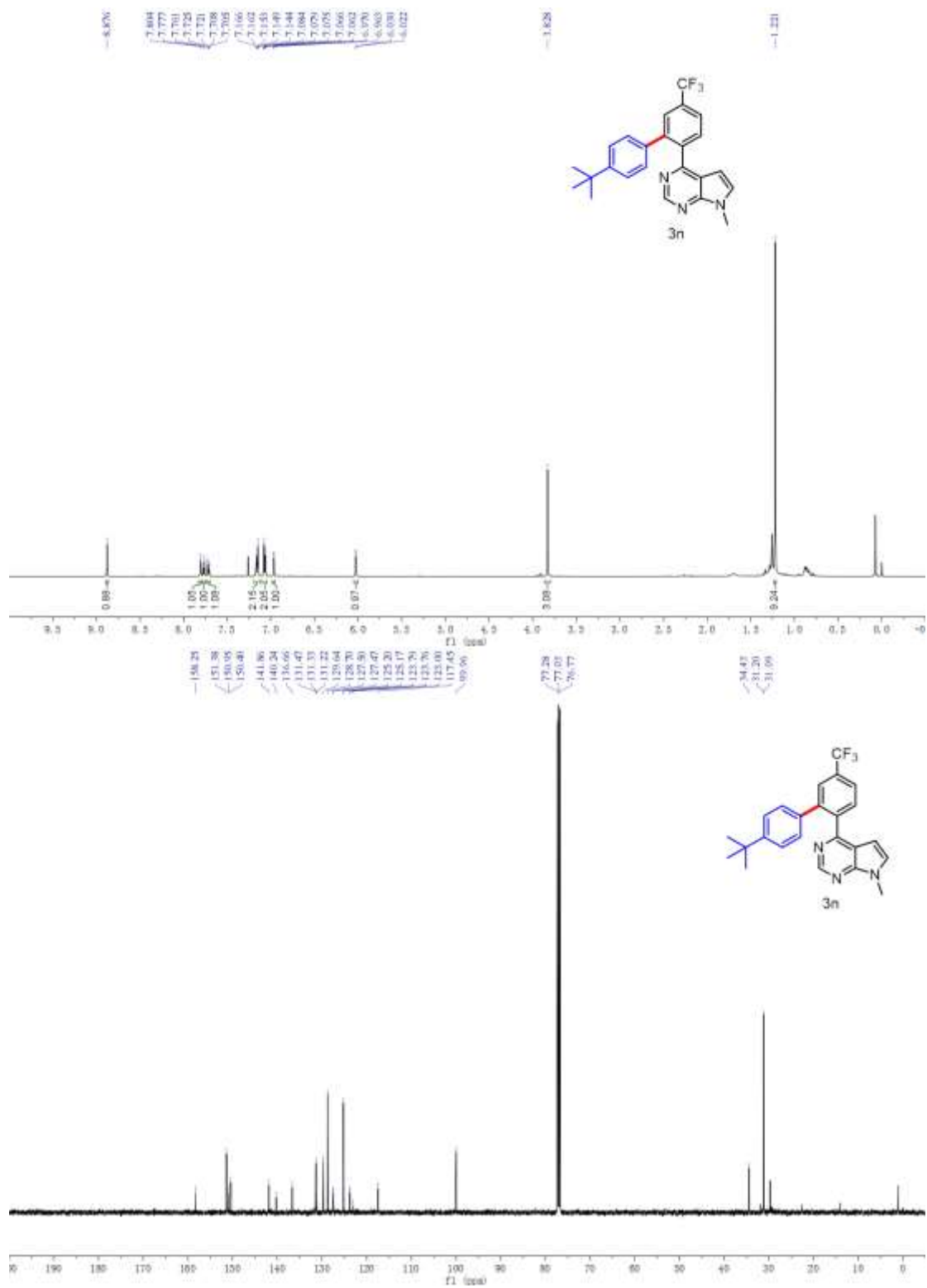


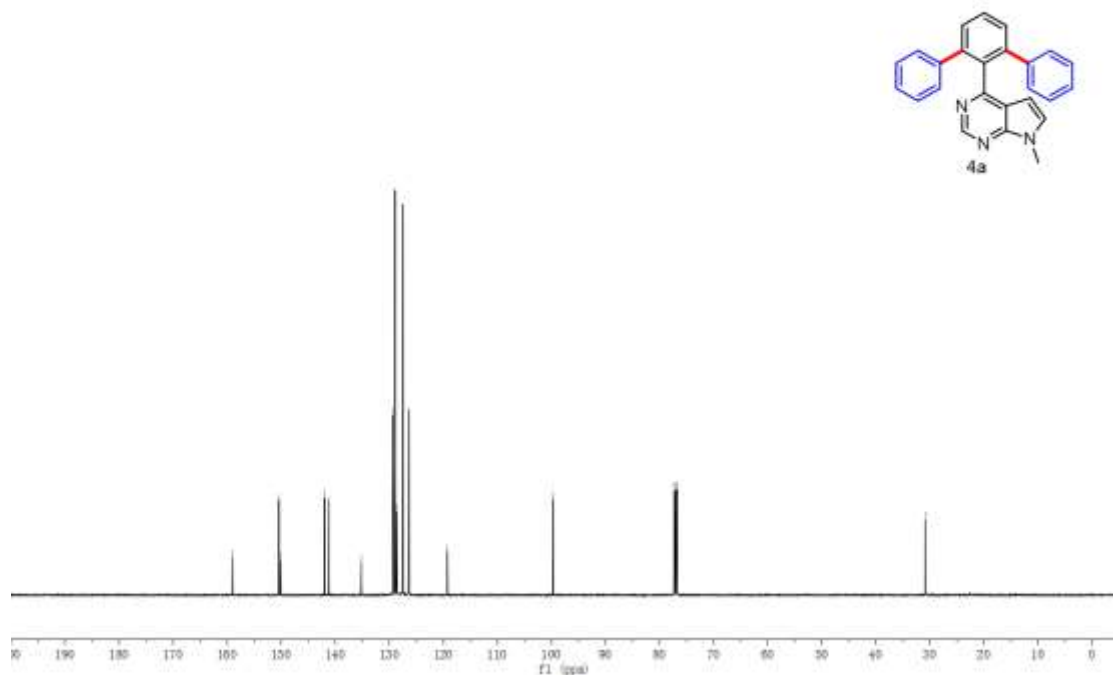
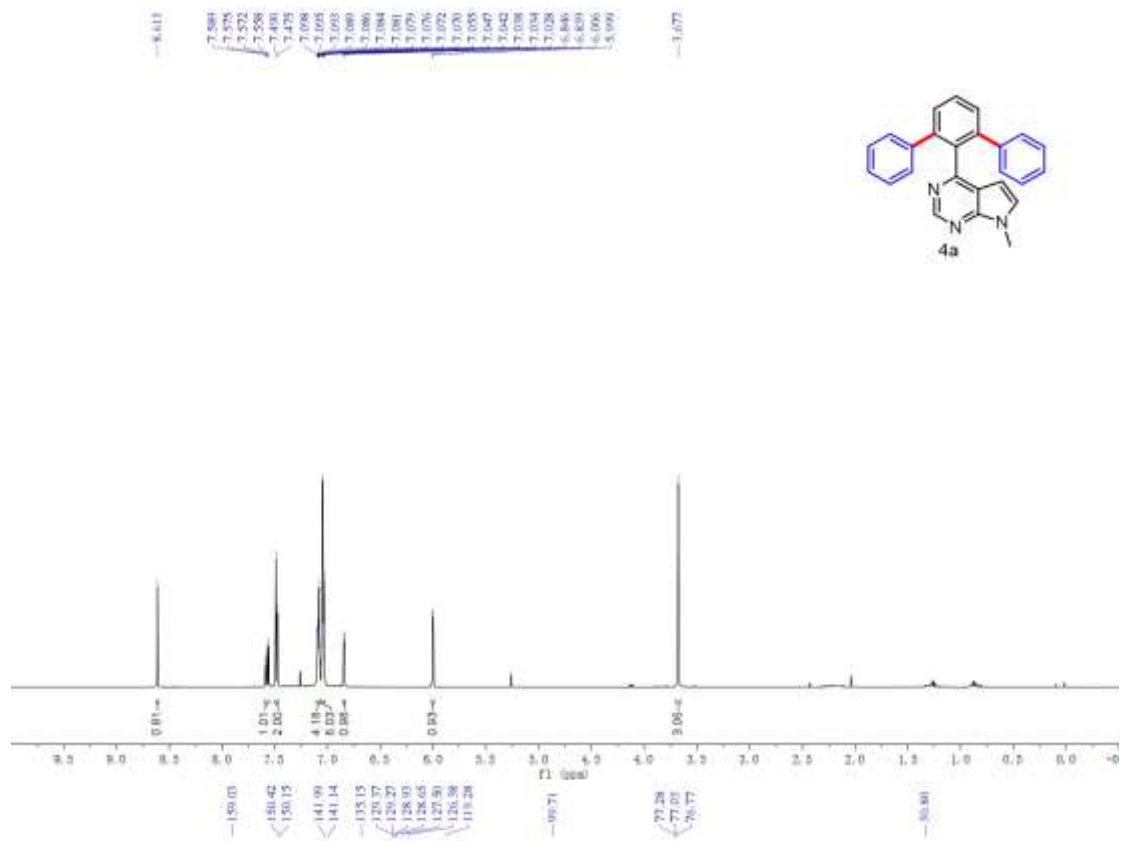






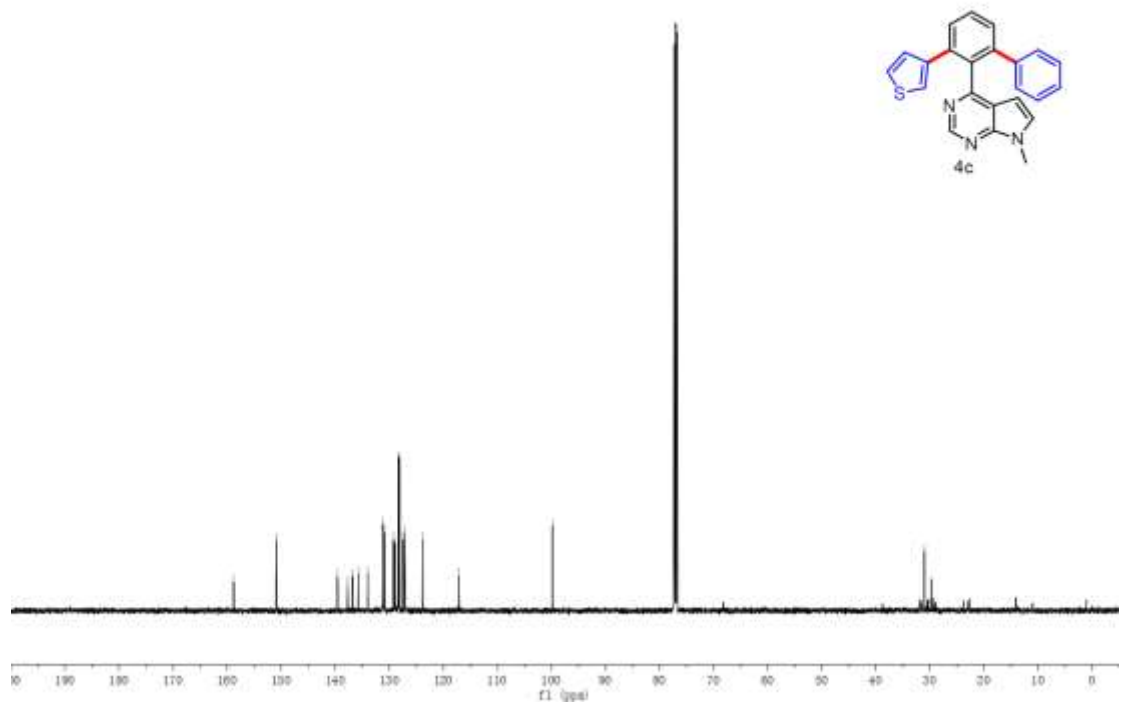
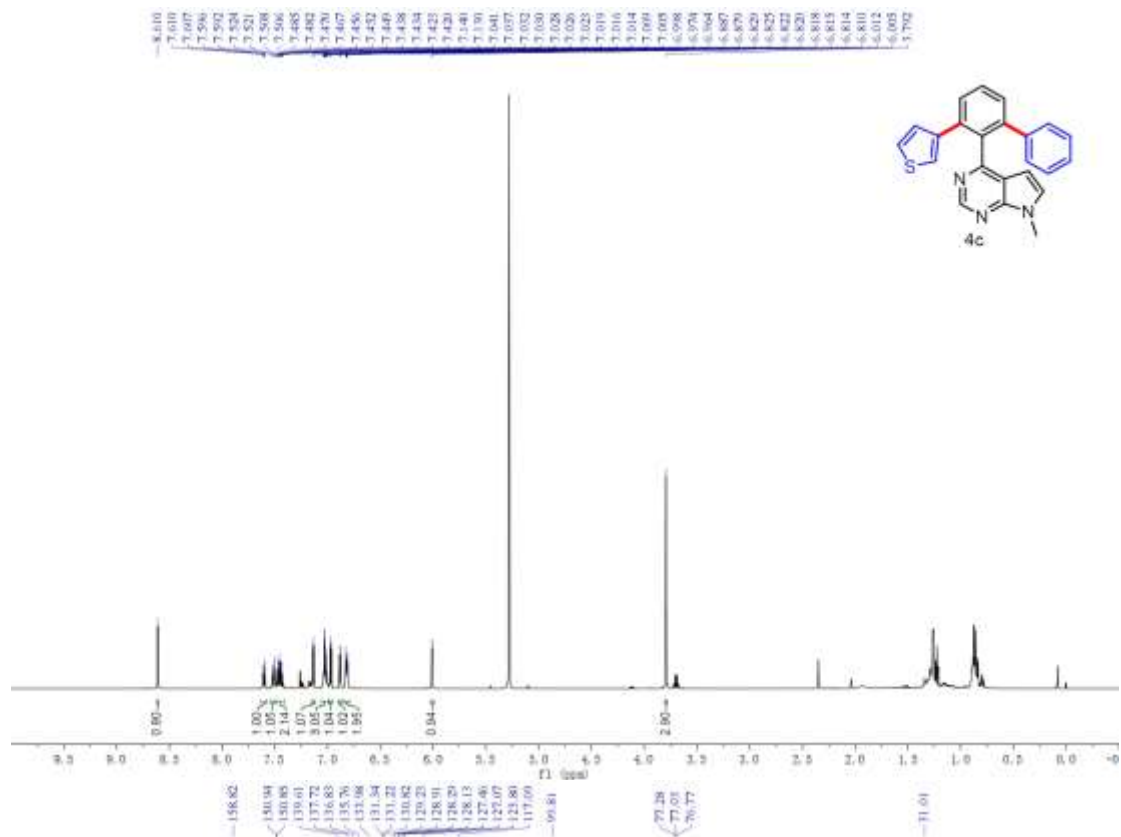












## 6. Single Crystal X-ray Diffraction Data for Compounds 3ac

Figure S1. X-ray crystal structure of 3ac.

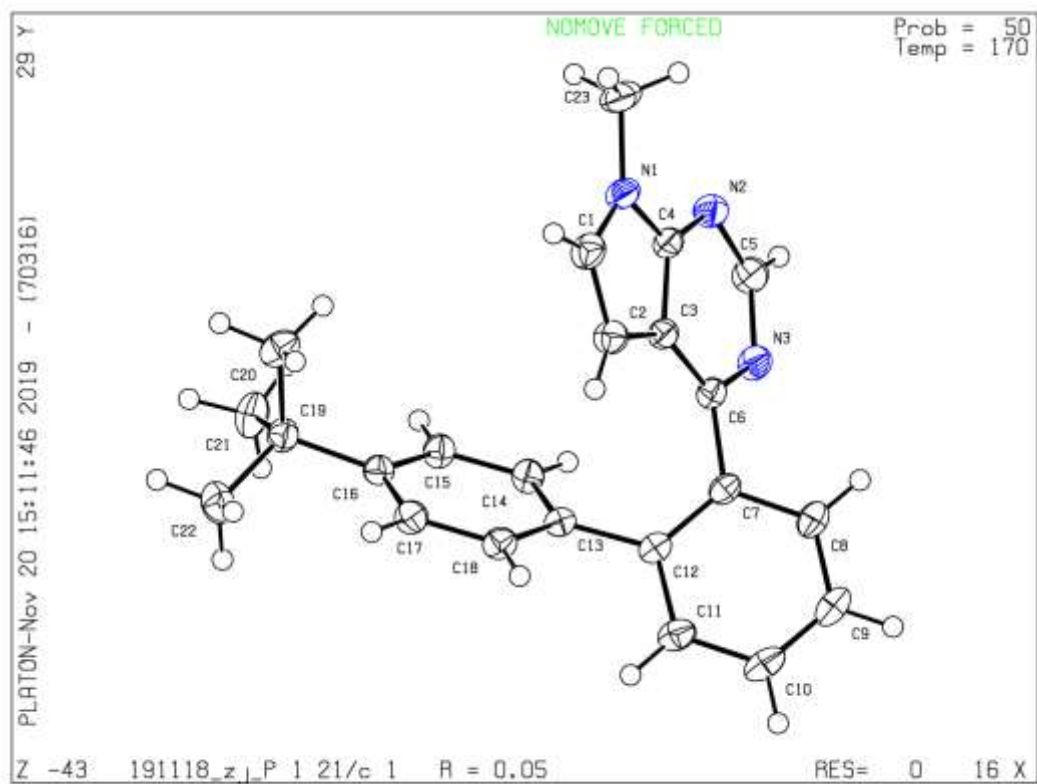
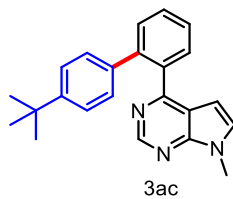


Table S2. Crystal data and structure refinement for 3ac.

**Datablock: 191118\_zj\_22b\_0ma**

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Bond precision:	C-C = 0.0014 Å	Wavelength=0.71073	
Cell:	a=16.0465(3)	b=9.2007(2)	c=12.4727(2)
	alpha=90	beta=92.170(1)	gamma=90
Temperature:	170 K		
	Calculated	Reported	
Volume	1840.14(6)	1840.14(6)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C23 H23 N3	C23 H23 N3	
Sum formula	C23 H23 N3	C23 H23 N3	
Mr	341.44	341.44	
Dx, g cm <sup>-3</sup>	1.232	1.232	
Z	4	4	
Mu (mm <sup>-1</sup> )	0.073	0.073	
F000	728.0	728.0	
F000'	728.23		
h, k, lmax	25, 14, 19	23, 12, 17	
Nref	7340	5919	
Tmin, Tmax	0.969, 0.978	0.698, 0.747	
Tmin'	0.966		
Correction method= # Reported T Limits: Tmin=0.698 Tmax=0.747			
AbsCorr = MULTI-SCAN			
Data completeness=	0.806	Theta(max)= 33.694	
R(reflections)=	0.0454( 5001)	wR2(reflections)= 0.1278( 5919)	
S =	1.051	Npar= 239	

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