

## Supporting Information

### Four-component strategy for selective synthesis of azepino[5,4,3-*cd*]indoles and pyrazolo[3,4-*b*]pyridines

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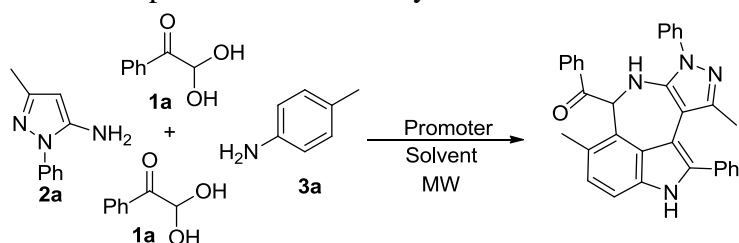
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#### Experimental

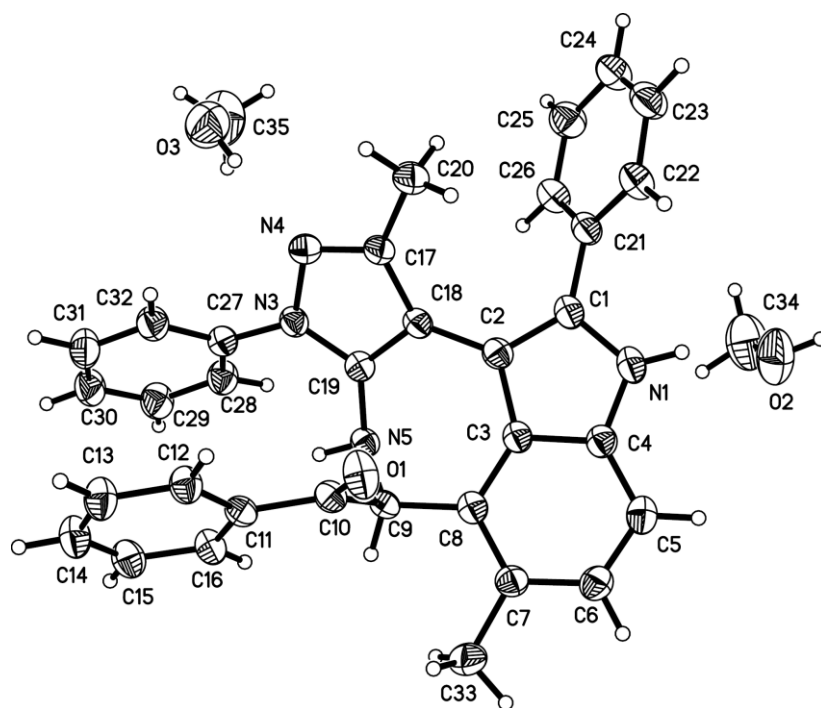
## General information

Microwave irradiation was carried out with Initiator 2.5 Microwave Synthesizers from Biotage, Uppsala, Sweden. Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $^{13}\text{C}$  NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in  $\text{CDCl}_3$  with chemical shift ( $\delta$ ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-Q II HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

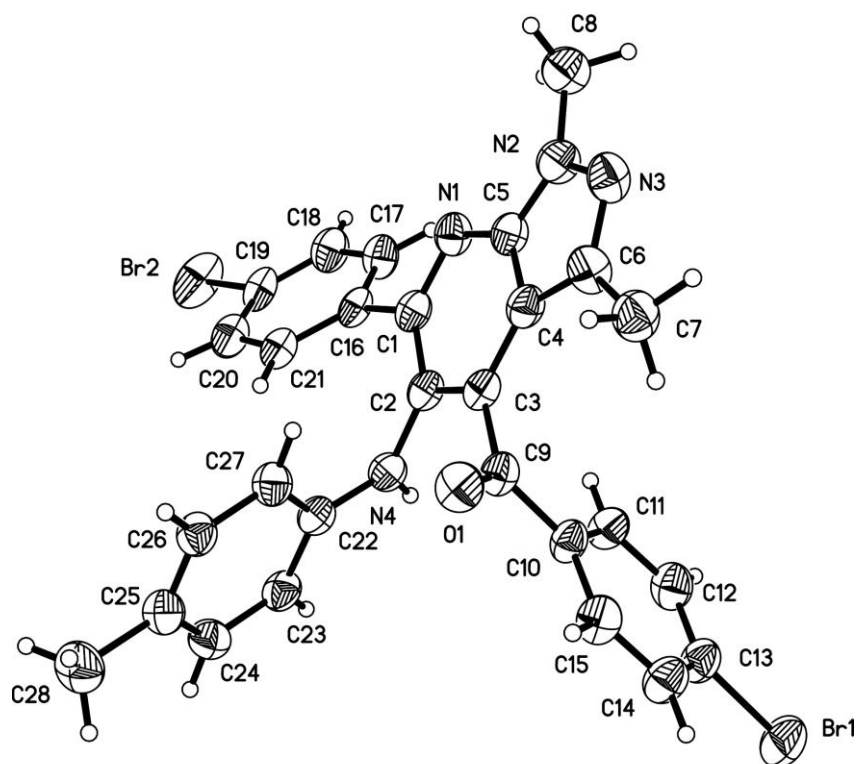
**Table 1.** Optimization for the Synthesis of **4a** under MW



Entry	Promoter (equiv.)	Solvent	T ( $^{\circ}\text{C}$ )	Time/ min	Yield / % <sup>a</sup>
1	<i>p</i> -TsOH (1.0)	DMF	100	15	38
2	$\text{H}_2\text{SO}_4$ (1.0)	DMF	100	15	Trace
3	$\text{CF}_3\text{COOH}$ (1.0)	DMF	100	15	Trace
4	$\text{FeCl}_3$ (1.0)	DMF	100	15	Trace
5	$\text{ZnCl}_2$ (1.0)	DMF	100	15	Trace
6	<i>p</i> -TsOH (1.0)	toluene	100	15	Trace
7	<i>p</i> -TsOH (1.0)	EtOH	100	15	24
8	<i>p</i> -TsOH (1.0)	1,4-dioxane	100	15	21
9	<i>p</i> -TsOH (1.0)	$\text{CH}_3\text{CN}$	100	15	20
10	<i>p</i> -TsOH (1.5)	DMF	100	15	30
11	<i>p</i> -TsOH (0.3)	DMF	100	15	22
12	<i>p</i> -TsOH (1.0)	DMF	115	15	46
13	<i>p</i> -TsOH (1.0)	DMF	120	15	45



**Fig. 1, X-ray Structure of 4a**



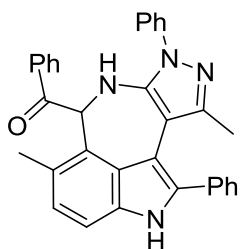
**Fig. 2, X-ray Structure of 5g**

## General procedure for the synthesis of 4

Example for the synthesis of **4a** (3,8-Dimethyl-1,4-diphenyl-1,5,9,10-tetrahydro pyrazolo[4',3':6,7]azepino[5,4,3-*cd*]indol-9-yl)(phenyl)methanone

**Microwave Heating:** 2,2-dihydroxy-1-phenylethanone (**1a**, 2.0 mmol, 0.30 g) was introduced in a 10-mL Initiator reaction vial, 3-methyl-1-phenyl-1*H*-pyrazol-5-amine (**2a**, 1.0 mmol, 0.17 g), *p*-toluidine (**3a**, 1.0 mmol, 0.11 g), *p*-TsOH (1.0 mmol, 0.19g) and 1.5ml DMF were then successively added. Subsequently, the reaction vial was capped and then pre-stirred for 20 seconds. The mixture was irradiated (Time: 15 min, Temperature: 115 °C; Absorption Level: High; Fixed Hold Time) until TLC (petroleum ether: acetone 3:1) revealed that conversion of the starting material **2a** was complete. The reaction mixture was cooled to room temperature and was then neutralized by 10% NaOH solution. Next, the system was diluted with cold water (20 mL). The solid product was collected by Büchner filtration and was purified by flash column chromatography (silica gel, mixtures of petroleum ether (b.p. 60-90 °C) / acetone,) to afford the desired pure azepino[5,4,3-*cd*]indoles **4a** as a pale yellow solid.

### (3,8-Dimethyl-1,4-diphenyl-1,5,9,10-tetrahydropyrazolo[4',3':6,7]azepino[5,4,3-*cd*]indol-9-yl)(phenyl)methanone (**4a**)



Pale yellow solid, m.p. 288-290 °C;

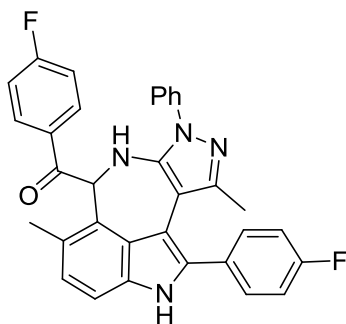
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) (δ, ppm): 11.31 (s, 1H, NH), 7.77 (d, *J* = 7.6 Hz, 2H, ArH), 7.57 (d, *J* = 7.6 Hz, 2H, ArH), 7.49 (t, *J* = 7.6 Hz, 2H, ArH), 7.41-7.31 (m, 2H, ArH), 7.27 (d, *J* = 8.0 Hz, 1H, ArH), 7.16-7.12 (m, 5H, ArH), 7.06 (d, *J* = 7.6 Hz, 2H, ArH), 6.94 (d, *J* = 8.0 Hz, 1H, ArH), 6.29 (d, *J* = 5.2 Hz, 1H, CH), 6.23-6.17 (m, 1H, CH), 2.17 (s, 3H, CH<sub>3</sub>), 1.36 (s, 2H, CH<sub>3</sub>).

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) (δ, ppm): 196.8, 143.2, 141.1, 137.8, 135.3, 134.8, 134.7, 132.5, 132.2, 130.3, 128.5, 128.2, 127.9, 127.9, 127.5, 126.0, 125.6, 124.1, 124.0, 123.0, 120.1, 110.0, 109.1, 104.3, 59.1, 18.7, 14.3.

IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3383, 1677, 1596, 1504, 1447, 1213, 1101, 965, 812, 754.

HRMS (ESI):  $m/z$  calcd for:  $\text{C}_{33}\text{H}_{25}\text{N}_4\text{O}$ , 493.2029  $[\text{M}-\text{H}]^-$ , found: 493.2028.

**(4-Fluorophenyl)(4-(4-fluorophenyl)-3,8-dimethyl-1-phenyl-1,5,9,10-tetrahydropyrazolo[4',3':6,7]azepino[5,4,3-cd]indol-9-yl)methanone (4b)**



White solid, m.p. 287-288 °C;

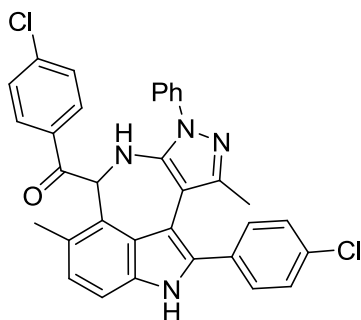
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ) ( $\delta$ , ppm): 11.29 (s, 1H, NH), 7.92-7.73 (m, 2H, ArH), 7.69-7.55 (m, 2H, ArH), 7.29-7.26 (m, 3H, ArH), 7.18-7.17 (m, 3H, ArH), 7.06 (d,  $J = 7.6$  Hz, 2H, ArH), 6.94 (d,  $J = 8.0$  Hz, 1H, ArH), 6.80 (t,  $J = 8.4$  Hz, 2H, ArH), 6.23 (s, 2H, ArH and CH), 2.19 (s, 3H,  $\text{CH}_3$ ), 1.42 (s, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ) ( $\delta$ , ppm): 195.5, 164.6 ( $^1J_{\text{CF}} = 250.2$  Hz), 161.5 ( $^1J_{\text{CF}} = 244.0$  Hz), 143.2, 141.2, 137.9, 135.4, 131.1 ( $^4J_{\text{CF}} = 2.8$  Hz), 131.1 ( $^4J_{\text{CF}} = 3.4$  Hz), 131.0 ( $^3J_{\text{CF}} = 9.3$  Hz), 130.5 ( $^3J_{\text{CF}} = 7.6$  Hz), 129.1, 128.1, 125.9, 125.5, 124.4, 124.1, 123.0, 115.5 ( $^2J_{\text{CF}} = 21.2$  Hz), 114.7 ( $^2J_{\text{CF}} = 21.8$  Hz), 110.1, 109.3, 104.3, 59.6, 18.7, 14.4.

IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3378, 1669, 1598, 1507, 1348, 1256, 1154, 840, 754, 689, 646.

HRMS (ESI):  $m/z$  calcd for:  $\text{C}_{33}\text{H}_{23}\text{F}_2\text{N}_4\text{O}$ , 529.1840  $[\text{M}-\text{H}]^-$ , found: 529.1860.

**(4-Chlorophenyl)(4-(4-chlorophenyl)-3,8-dimethyl-1-phenyl-1,5,9,10-tetrahydropyrazolo[4',3':6,7]azepino[5,4,3-cd]indol-9-yl)methanone (4c)**



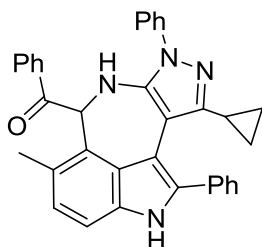
Pale yellow solid, m.p. >300 °C;

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) (δ, ppm): 11.37 (s, 1H, NH), 8.29 (d, *J* = 8.4 Hz, 1H), 7.84-7.76 (m, 1H, ArH), 7.70 (d, *J* = 8.4 Hz, 2H, ArH), 7.59-7.47 (m, 5H, ArH), 7.40 (d, *J* = 8.4 Hz, 1H, ArH), 7.27 (d, *J* = 8.0 Hz, 1H, ArH), 7.19 (d, *J* = 5.2 Hz, 2H, ArH), 7.11-7.03 (m, 3H, ArH), 6.97 (d, *J* = 8.0 Hz, 1H, ArH), 6.64 (d, *J* = 8.0 Hz, 1H, ArH), 6.19 (d, *J* = 8.0 Hz, 1H, CH), 2.18 (s, 3H, CH<sub>3</sub>), 1.42 (s, 3H, CH<sub>3</sub>).

IR (KBr, ν, cm<sup>-1</sup>): 3393, 3079, 1650, 1598, 1574, 1507, 1263, 1168, 1028, 755, 690.

HRMS (ESI): *m/z* calcd for: C<sub>33</sub>H<sub>23</sub>Cl<sub>2</sub>N<sub>4</sub>O, 561.1249 [M-H]<sup>-</sup>, found: 561.1230.

**(3-Cyclopropyl-8-methyl-1,4-diphenyl-1,5,9,10-tetrahydropyrazolo[4',3':6,7]azepino[5,4,3-*cd*]indol-9-yl)(phenyl)methanone (4d)**



Yellow solid, m.p. 291-292 °C;

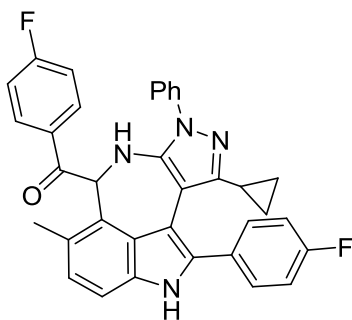
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) (δ, ppm): 11.28 (s, 1H, NH), 7.76 (d, *J* = 8.0 Hz, 2H, ArH), 7.60 (d, *J* = 7.6 Hz, 2H, ArH), 7.46 (t, *J* = 7.6 Hz, 2H, ArH), 7.34 (t, *J* = 6.4 Hz, 2H, ArH), 7.28 (d, *J* = 8.4 Hz, 1H, ArH), 7.18-7.08 (m, 5H, ArH), 7.03 (d, *J* = 7.6 Hz, 2H, ArH), 6.94 (d, *J* = 8.4 Hz, 1H, ArH), 6.27 (d, *J* = 5.2 Hz, 1H, NH), 6.22 (d, *J* = 5.2 Hz, 1H, CH), 2.18 (s, 3H, CH<sub>3</sub>), 0.96-0.84 (m, 1H, CH), 0.66-0.61 (m, 1H, CH<sub>2</sub>), 0.41 (t, *J* = 6.4 Hz, 2H, CH<sub>2</sub>), -0.12 (t, *J* = 7.2 Hz, 1H, CH<sub>2</sub>).

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) (δ, ppm): 197.0, 148.3, 140.8, 137.9, 135.4, 134.8, 134.6, 132.5, 132.2, 130.4, 128.5, 128.3, 128.1, 127.9, 127.1, 126.1, 125.6, 124.1, 124.0, 122.9, 110.0, 109.2, 104.0, 59.2, 18.7, 10.1, 10.0, 8.4.

IR (KBr, ν, cm<sup>-1</sup>): 3393, 3151, 3073, 3007, 1597, 1519, 1504, 1102, 763, 689.

HRMS (ESI): *m/z* calcd for: C<sub>35</sub>H<sub>27</sub>N<sub>4</sub>O, 519.2185 [M-H]<sup>-</sup>, found: 519.2199.

**(3-Cyclopropyl-4-(4-fluorophenyl)-8-methyl-1-phenyl-1,5,9,10-tetrahydropyrazolo[4',3':6,7]azepino[5,4,3-*cd*]indol-9-yl)(4-fluorophenyl)methanone (4e)**



Pale yellow solid, m.p. 296-298 °C;

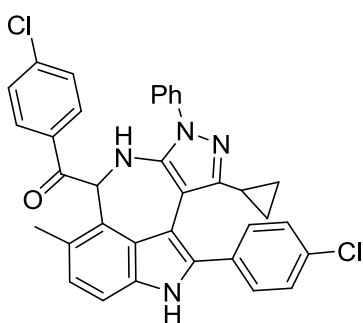
$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 11.33 (s, 1H, NH), 7.81-7.77 (m, 2H, ArH), 7.62-7.59 (m, 2H, ArH), 7.36-7.25 (m, 3H, ArH), 7.17 (d,  $J = 6.4$  Hz, 3H, ArH), 7.04 (d,  $J = 7.6$  Hz, 2H, ArH), 6.95 (d,  $J = 8.0$  Hz, 1H, ArH), 6.85 (t,  $J = 8.4$  Hz, 2H, ArH), 6.29-6.17 (m, 2H, ArH and CH), 2.18 (s, 3H, CH<sub>3</sub>), 0.98-0.86 (m, 1H, CH), 0.70-0.65 (m, 1H, CH<sub>2</sub>), 0.47-0.42 (m, 2H, CH<sub>2</sub>), -0.04--0.1 (m, 1H, CH<sub>2</sub>).

$^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 196.3, 165.0 ( $^1J_{\text{CF}} = 249.6$  Hz), 161.9 ( $^1J_{\text{CF}} = 242.8$  Hz), 148.7, 141.4, 138.5, 135.9, 131.8 ( $^4J_{\text{CF}} = 2.5$  Hz), 131.5 ( $^4J_{\text{CF}} = 3.1$  Hz), 131.4 ( $^3J_{\text{CF}} = 9.5$  Hz), 130.8 ( $^3J_{\text{CF}} = 9.1$  Hz), 128.7, 126.6, 126.0, 124.9, 124.6, 123.4, 116.0 ( $^2J_{\text{CF}} = 21.3$  Hz), 115.3 ( $^2J_{\text{CF}} = 21.7$  Hz), 110.6, 110.0, 104.5, 60.2, 19.1, 10.7, 10.5, 8.8.

IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3391, 3126, 3078, 1597, 1573, 1506, 1407, 1230, 837, 752.

HRMS (ESI):  $m/z$  calcd for: C<sub>35</sub>H<sub>25</sub>F<sub>2</sub>N<sub>4</sub>O, 555.1997 [M-H]<sup>-</sup>, found: 555.2008.

**(4-Chlorophenyl)(4-(4-chlorophenyl)-3-cyclopropyl-8-methyl-1-phenyl-1,5,9,10-tetrahydropyrrolo[4',3':6,7]azepino[5,4,3-cd]indol-9-yl)methanone (4f)**



Green solid, m.p. 297-299 °C;

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 11.35 (s, 1H, NH), 7.69 (d,  $J = 8.0$  Hz, 2H, ArH), 7.58 (d,  $J = 8.0$  Hz, 2H, ArH), 7.53 (d,  $J = 8.4$  Hz, 2H, ArH), 7.28 (d,  $J = 8.0$  Hz, 1H, ArH), 7.18-7.17 (m, 3H, ArH), 7.08 (d,  $J = 8.0$  Hz, 2H, ArH), 7.04-7.00 (m, 2H, ArH), 6.97 (d,  $J = 8.4$  Hz, 1H, ArH), 6.24 (s, 2H, CH and NH), 2.18 (s, 3H, CH<sub>3</sub>), 0.99-0.79 (m, 1H, CH), 0.69 (d,  $J = 4.8$  Hz, 1H, CH<sub>2</sub>),

0.49-0.43 (m, 2H, CH<sub>2</sub>), -0.07 (d, *J* = 6.4 Hz, 1H, CH<sub>2</sub>).

IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3439, 3110, 3076, 3013, 1596, 1579, 1520, 1246, 1092, 961, 831.

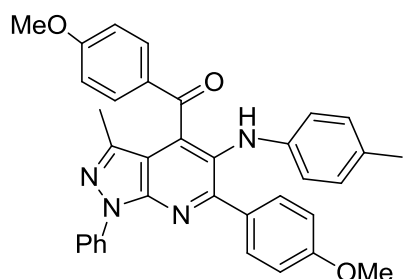
HRMS (ESI): *m/z* calcd for: C<sub>35</sub>H<sub>25</sub>Cl<sub>2</sub>N<sub>4</sub>O, 587.1406 [M-H]<sup>-</sup>, found: 587.1219.

## General procedure for the synthesis of 5

Example for the synthesis of **5i** (4-Bromophenyl)(6-(4-bromophenyl)-1,3-dimethyl-5-(*p*-tolylamino)-1*H*-pyrazolo[3,4-*b*]pyridin-4-yl)methanone

**Microwave Heating:** 1-(4-bromophenyl)-2,2-dihydroxyethanone (**1d**, 2.0 mmol, 0.46 g) was introduced in a 10-mL Initiator<sup>TM</sup> reaction vial, 1,3-dimethyl-1*H*-pyrazol-5-amine (**2c**, 1.0 mmol, 0.11 g), *p*-toluidine (**3a**, 1.0 mmol, 0.11 g), *p*-TsOH (1.0 mmol, 0.19g) and 1.5ml DMF were then successively added. Subsequently, the reaction vial was capped and then pre-stirred for 20 seconds. The mixture was irradiated (Time: 20 min, Temperature: 115 °C; Absorption Level: High; Fixed Hold Time) until TLC (petroleum ether : ethyl acetate 3:1) revealed that conversion of the starting material **1a** and **3a** were complete. The system was diluted with cold water (20 mL). The solid product was collected by Büchner filtration and was purified by flash column chromatography (silica gel, mixtures of petroleum ether (b.p. 60-90 °C) / ethyl acetate) to afford the desired pure pyrazolo[3,4-*b*]pyridines **5i**.

## (4-Methoxyphenyl)(6-(4-methoxyphenyl)-3-methyl-1-phenyl-5-(*p*-tolylamino)-1*H*-pyrazolo[3,4-*b*]pyridin-4-yl)methanone (**5a**)



Yellow solid, m.p. 272-273 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) ( $\delta$ , ppm): 8.36 (d, *J* = 8.0 Hz, 2H, ArH), 7.80 (d, *J* = 8.4 Hz, 2H, ArH), 7.68 (d, *J* = 8.4 Hz, 2H, ArH), 7.51 (t, *J* = 7.6 Hz, 2H, ArH), 7.28 (d, *J* = 7.2 Hz, 2H, ArH), 6.88 (d, *J* = 8.4 Hz, 2H, ArH), 6.84-6.79 (m, 4H, ArH), 6.37 (d, *J* = 8.0 Hz, 2H, ArH), 3.84 (s, 3H, OCH<sub>3</sub>), 3.81 (s, 3H, OCH<sub>3</sub>), 2.25 (s, 3H, CH<sub>3</sub>), 2.16 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ( $\delta$ , ppm): 192.9, 164.3, 160.3, 156.2, 148.7, 143.4, 141.7, 139.6, 139.2, 131.9, 130.8, 130.7, 129.6, 129.4, 129.4, 129.0, 128.9, 127.0, 125.4, 120.5, 115.5, 113.9,

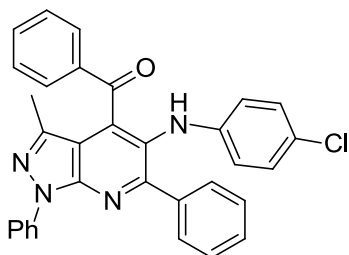


113.7, 55.5, 55.3, 20.5, 13.9.

IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3389, 1611, 1587, 1537, 1506, 1453, 1258, 1182, 1019, 880, 749.

HRMS (ESI):  $m/z$  calcd for:  $\text{C}_{35}\text{H}_{29}\text{N}_4\text{O}_3$ , 553.2340  $[\text{M}-\text{H}]^-$ , found: 553.2308.

**(5-((4-chlorophenyl)amino)-3-methyl-1,6-diphenyl-1*H*-pyrazolo[3,4-*b*]pyridin-4-yl)(phenyl)methanone (5b)**



Yellow solid, m.p. 289-291 °C;

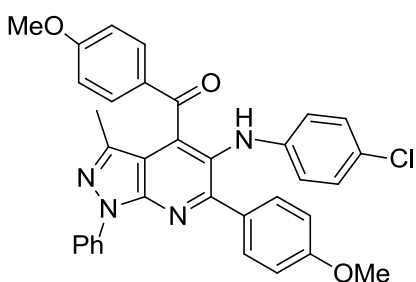
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) ( $\delta$ , ppm): 8.36 (d,  $J = 8.0$  Hz, 2H, ArH), 7.73-7.69 (m, 4H, ArH), 7.58 (t,  $J = 7.6$  Hz, 1H, ArH), 7.51 (t,  $J = 7.6$  Hz, 2H, ArH), 7.42-7.35 (m, 4H, ArH), 7.30 (d,  $J = 7.2$  Hz, 2H, ArH), 6.94 (d,  $J = 8.4$  Hz, 2H, ArH), 6.34 (d,  $J = 8.7$  Hz, 2H, ArH), 5.29 (s, 1H, NH), 2.27 (s, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) ( $\delta$ , ppm): 194.4, 157.0, 148.9, 144.4, 141.7, 139.8, 139.4, 138.02, 136.4, 134.3, 129.3, 129.1 (129.1, 129.1), 128.8, 128.4, 128.3, 126.1, 125.7, 124.4, 120.7, 116.1, 13.9.

IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3386, 1658, 1597, 1505, 1436, 1362, 1225, 1154, 840, 754.

HRMS (ESI):  $m/z$  calcd for:  $\text{C}_{32}\text{H}_{22}\text{ClN}_4\text{O}$ , 513.1482  $[\text{M}-\text{H}]^-$ , found: 513.1519.

**(5-((4-Chlorophenyl)amino)-6-(4-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-4-yl)(4-methoxyphenyl)methanone (5c)**



Yellow solid, m.p. 269-270 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) ( $\delta$ , ppm): 8.36 (d,  $J = 8.0$  Hz, 2H, ArH), 7.77 (d,  $J = 8.4$  Hz, 2H, ArH),

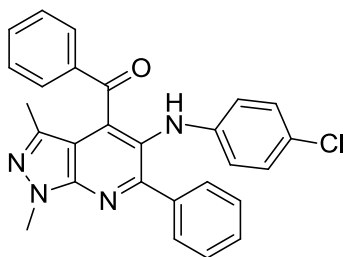
7.69 (d,  $J = 8.4$  Hz, 2H, ArH), 7.51 (t,  $J = 7.6$  Hz, 2H, ArH), 7.29 (d,  $J = 7.2$  Hz, 1H, ArH), 6.93 (d,  $J = 8.4$  Hz, 2H, ArH), 6.89-6.83 (m, 4H, ArH), 6.35 (d,  $J = 8.8$  Hz, 2H, ArH), 5.35 (s, 1H, NH) 3.84 (s, 3H, OCH<sub>3</sub>), 3.81 (s, 3H, OCH<sub>3</sub>), 2.24 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ( $\delta$ , ppm): 192.8, 164.6, 160.4, 156.6, 144.4, 141.8, 140.3, 139.4, 131.9, 130.6, 130.6, 129.4, 129.1, 128.8, 125.7, 125.6, 124.1, 120.6, 115.9, 114.1, 113.8, 55.6, 55.3, 13.8.

IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3373, 1650, 1598, 1573, 1507, 1421, 1168, 1028, 756, 690.

HRMS (ESI):  $m/z$  calcd for: C<sub>34</sub>H<sub>26</sub>ClN<sub>4</sub>O<sub>3</sub>, 573.1694 [M-H]<sup>-</sup>, found: 573.1714.

**(5-((4-Chlorophenyl)amino)-1,3-dimethyl-6-phenyl-1H-pyrazolo[3,4-*b*]pyridin-4-yl)(phenyl)methanone (5d)**



Yellow solid, m.p. 274-275 °C;

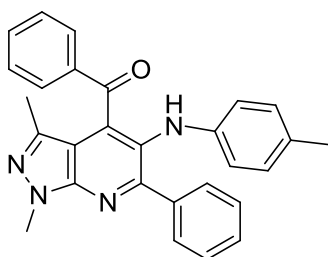
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) ( $\delta$ , ppm): 7.68-7.66 (m, 4H, ArH), 7.56 (t,  $J = 7.2$  Hz, 1H, ArH), 7.40-7.38 (m, 5H, ArH), 6.92 (d,  $J = 8.0$  Hz, 2H, ArH), 6.30 (d,  $J = 8.4$  Hz, 2H, ArH), 5.22 (s, 1H, CH), 4.17 (s, 3H, CH<sub>3</sub>), 2.19 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ( $\delta$ , ppm): 194.7, 157.3, 149.4, 144.7, 139.9, 139.7, 138.0, 136.4, 134.2, 129.3, 129.1, 128.9, 128.8, 128.4, 125.2, 124.1, 115.9, 111.4, 33.8, 13.7.

IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3378, 1604, 1593, 1543, 1325, 1172, 1011, 844, 771, 687, 563.

HRMS (ESI):  $m/z$  calcd for: C<sub>27</sub>H<sub>20</sub>ClN<sub>4</sub>O, 451.1326 [M-H]<sup>-</sup>, found: 451.1335.

**(1,3-Dimethyl-6-phenyl-5-(*p*-tolylamino)-1H-pyrazolo[3,4-*b*]pyridin-4-yl)(phenyl)methanone (5e)**



Yellow solid, m.p. 248-249 °C;

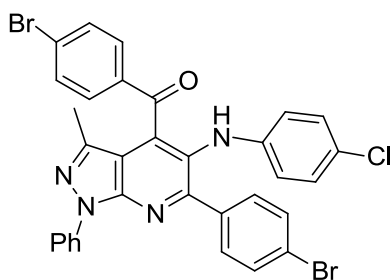
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (δ, ppm): 7.72-7.68 (m, 2H, ArH), 7.64 (d, *J* = 7.6 Hz, 2H, ArH), 7.54 (t, *J* = 7.2 Hz, 1H, ArH), 7.37-7.33 (m, 5H, ArH), 7.26 (s, 1H, ArH), 6.79 (d, *J* = 8.0 Hz, 2H, ArH), 6.30 (d, *J* = 8.0 Hz, 2H, ArH), 4.17 (s, 3H, CH<sub>3</sub>), 2.19 (s, 3H, CH<sub>3</sub>), 2.15 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (δ, ppm): 194.9, 156.9, 149.3, 143.7, 139.6, 138.7, 138.2, 136.6, 133.9, 129.4, 129.3, 129.1, 129.0, 128.9, 128.6, 128.4, 126.5, 115.5, 111.6, 33.8, 20.5, 13.8.

IR (KBr, ν, cm<sup>-1</sup>): 3381, 1655, 1575, 1519, 1364, 1263, 1209, 960, 871, 701, 670.

HRMS (ESI): *m/z* calcd for: C<sub>28</sub>H<sub>23</sub>N<sub>4</sub>O, 431.1872 [M-H]<sup>-</sup>, found: 431.1874.

**(4-Bromophenyl)(6-(4-bromophenyl)-5-((4-chlorophenyl)amino)-1,3-dimethyl-1*H*-pyrazolo[3,4-*b*]pyridin-4-yl)methanone (5f)**



Yellow solid, m.p. 299-300 °C;

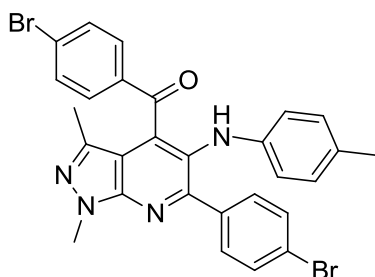
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (δ, ppm): 7.57 (d, *J* = 8.0 Hz, 2H, ArH), 7.54-7.45 (m, 5H, ArH), 7.26 (s, 1H, ArH), 6.95 (d, *J* = 8.4 Hz, 2H, ArH), 6.29 (d, *J* = 8.4 Hz, 2H, ArH), 5.20 (s, 1H, NH), 4.15 (s, 3H, CH<sub>3</sub>), 2.18 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (δ, ppm) 190.3, 155.3, 148.2, 144.8, 141.2, 140.5, 133.2, 132.7, 132.2(132.2), 131.9, 131.7, 131.6(131.6), 130.8, 130.6, 124.0, 122.0, 116.2, 33.9, 15.6.

IR (KBr, ν, cm<sup>-1</sup>): 3386, 1669, 1581, 1543, 1268, 1201, 1087, 987, 815, 798, 698.

HRMS (ESI): *m/z* calcd for: C<sub>27</sub>H<sub>18</sub>Br<sub>2</sub>ClN<sub>4</sub>O, 608.9516 [M-H]<sup>-</sup>, found: 608.9546.

**(4-Bromophenyl)(6-(4-bromophenyl)-1,3-dimethyl-5-(*p*-tolylamino)-1*H*-pyrazolo[3,4-*b*]pyridin-4-yl)methanone (5g)**



Yellow solid, m.p. >300 °C;

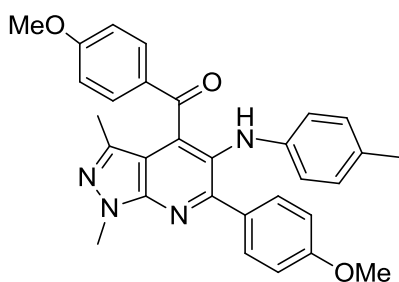
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (δ, ppm): 7.61 (d, *J* = 8.0 Hz, 2H, ArH), 7.49 (s, 5H, ArH), 7.47 (s, 1H, ArH), 6.79 (d, *J* = 8.0 Hz, 2H, ArH), 6.27 (d, *J* = 8.0 Hz, 2H, ArH), 5.14 (s, 1H, NH), 4.15 (s, 3H, CH<sub>3</sub>), 2.18 (s, 3H, CH<sub>3</sub>), 2.16 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (δ, ppm): 193.8, 159.5, 155.1, 149.2, 144.6, 143.2, 141.0, 139.4, 137.1, 132.0, 131.5, 130.7, 129.6, 129.4, 126.3, 123.6, 117.8, 115.4, 33.8, 20.5, 13.8.

IR (KBr, ν, cm<sup>-1</sup>): 3374, 1666, 1583, 1513, 1347, 1258, 1205, 1070, 1009, 812, 798.

HRMS (ESI): *m/z* calcd for: C<sub>28</sub>H<sub>21</sub>Br<sub>2</sub>N<sub>4</sub>O, 589.0062 [M-H]<sup>-</sup>, found: 589.0044.

**(4-Methoxyphenyl)(6-(4-methoxyphenyl)-1,3-dimethyl-5-(*p*-tolylamino)-1*H*-pyrazolo[3,4-*b*]pyridin-4-yl)methanone (5h)**



Yellow solid, m.p. 234-235 °C;

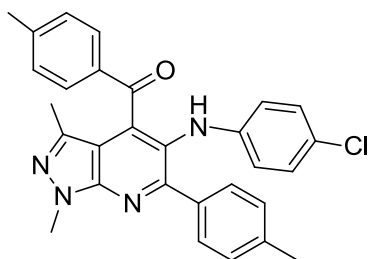
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (δ, ppm): 7.73 (d, *J* = 8.0 Hz, 2H, NH), 7.65 (d, *J* = 8.0 Hz, 2H, ArH), 6.87 (d, *J* = 7.6 Hz, 2H, ArH), 6.82-6.77 (m, 4H, ArH), 6.32 (d, *J* = 8.0 Hz, 2H, ArH), 5.16 (s, 1H, CH) 4.14 (s, 3H, CH<sub>3</sub>), 3.83 (s, 3H), 3.80 (s, 3H, OCH<sub>3</sub>), 2.16 (s, 3H, OCH<sub>3</sub>), 2.14 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (δ, ppm): 193.2, 164.2, 160.2, 156.6, 149.2, 143.8, 139.6, 139.3, 131.9, 130.9, 130.6, 129.7, 129.3, 128.6, 126.2, 115.3, 113.9, 113.8, 111.3, 55.5, 55.3, 33.8, 20.5, 13.7.

IR (KBr, ν, cm<sup>-1</sup>): 3373, 1657, 1602, 1515, 1264, 1166, 1029, 963, 814, 777, 615.

HRMS (ESI): *m/z* calcd for: C<sub>30</sub>H<sub>27</sub>N<sub>4</sub>O<sub>3</sub>, 491.2083 [M-H]<sup>-</sup>, found: 491.2076.

**(5-((4-Chlorophenyl)amino)-1,3-dimethyl-6-(*m*-tolyl)-1*H*-pyrazolo[3,4-*b*]pyridin-4-yl)(*p*-tolyl)methanone (5i)**



Yellow solid, m.p. 241-243 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (δ, ppm): 7.60 (d, *J* = 7.6 Hz, 2H, ArH), 7.55 (d, *J* = 8.0 Hz, 2H, ArH), 7.15 (t, *J* = 7.2 Hz, 4H, ArH), 6.79 (d, *J* = 8.0 Hz, 2H, ArH), 6.31 (d, *J* = 8.0 Hz, 2H, ArH), 5.12 (s, 1H, CH), 4.14 (s, 3H, CH<sub>3</sub>), 2.37 (s, 3H, CH<sub>3</sub>), 2.34 (s, 3H, CH<sub>3</sub>), 2.15 (s, 3H, CH<sub>3</sub>).

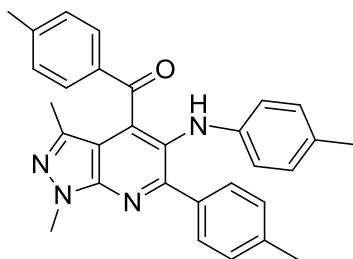
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (δ, ppm): 194.9, 156.9, 149.2, 143.7, 139.6, 138.7, 138.2, 136.6, 133.9, 129.4, 129.3, 129.1, 129.0, 128.9, 128.6, 128.4, 126.5, 115.5, 111.6, 33.8, 20.5, 13.8.

IR (KBr, ν, cm<sup>-1</sup>): 3389, 1661, 1576, 1498, 1254, 1386, 1109, 987, 762, 683.

HRMS (ESI): *m/z* calcd for: C<sub>29</sub>H<sub>24</sub>ClN<sub>4</sub>O, 479.1639 [M-H]<sup>-</sup>, found: 479.1641.

**(1,3-Dimethyl-6-(*m*-tolyl)-5-(*p*-tolylamino)-1*H*-pyrazolo[3,4-*b*]pyridin-4-yl)(*p*-tolyl)methanone**

**(5j)**



Yellow solid, m.p. 248-249 °C;

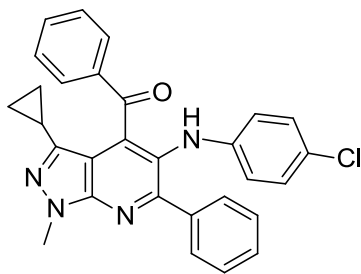
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (δ, ppm): 7.61 (d, *J* = 7.6 Hz, 2H, NH), 7.54 (d, *J* = 7.6 Hz, 2H, ArH), 7.15 (t, *J* = 8.0 Hz, 4H, ArH), 6.79 (d, *J* = 8.0 Hz, 2H, ArH), 6.32 (d, *J* = 8.0 Hz, 2H, ArH), 4.16 (s, 3H, CH<sub>3</sub>), 2.37 (s, 3H, CH<sub>3</sub>), 2.34 (s, 3H, CH<sub>3</sub>), 2.18 (s, 3H, CH<sub>3</sub>), 2.15 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (δ, ppm): 194.4, 157.1, 149.3, 145.0, 143.9, 139.6, 139.2, 138.9, 135.4, 134.1, 129.5, 129.4, 129.3, 129.1, 129.0, 128.7, 126.3, 115.4, 111.4, 33.8, 21.8, 21.3, 20.5, 13.8.

IR (KBr, ν, cm<sup>-1</sup>): 3371, 1664, 1589, 1514, 1348, 1229, 1001, 876, 698, 651.

HRMS (ESI): *m/z* calcd for: C<sub>30</sub>H<sub>27</sub>N<sub>4</sub>O, 459.2185 [M-H]<sup>-</sup>, found: 459.2177.

**(5-((4-Chlorophenyl)amino)-3-cyclopropyl-1-methyl-6-phenyl-1H-pyrazolo[3,4-b]pyridin-4-yl)(phenyl)methanone (5k)**



Yellow solid, m.p. 274-275 °C;

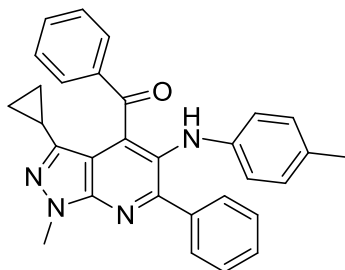
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (δ, ppm): 7.71 (d, *J* = 8.0 Hz, 2H, ArH), 7.68-7.64 (m, 2H, ArH), 7.55 (t, *J* = 7.2 Hz, 1H, ArH), 7.41-7.31 (m, 5H, ArH), 6.91 (d, *J* = 8.4 Hz, 2H, ArH), 6.31 (d, *J* = 8.4 Hz, 2H, ArH), 4.13 (s, 3H, CH<sub>3</sub>), 1.58-1.55 (m, 1H, CH), 0.78 (s, 2H, CH<sub>2</sub>), 0.60 (d, *J* = 5.6 Hz, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) (δ, ppm): 194.9, 157.3, 149.4, 144.8, 140.2, 138.2, 136.5, 134.1, 129.4, 129.0, 128.9, 128.7, 128.6, 128.3, 125.2, 124.0, 115.9, 112.0, 33.8, 21.1, 8.6, 7.1.

IR (KBr, ν, cm<sup>-1</sup>): 3383, 1663, 1596, 1576, 1497, 1321, 1208, 1089, 817, 726, 699.

HRMS (ESI): *m/z* calcd for: C<sub>29</sub>H<sub>22</sub>ClN<sub>4</sub>O, 477.1482 [M-H]<sup>-</sup>, found:477.1488.

**(3-Cyclopropyl-1-methyl-6-phenyl-5-(*p*-tolylamino)-1H-pyrazolo[3,4-b]pyridin-4-yl)(phenyl)methanone (5l)**



Yellow solid, m.p. 260-261 °C;

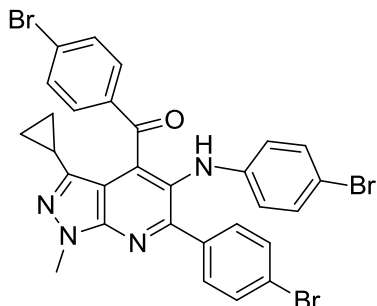
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (δ, ppm): 7.69 (d, *J* = 6.8 Hz, 4H, ArH), 7.53 (t, *J* = 7.6 Hz, 1H, ArH), 7.37-7.33 (m, 5H, ArH), 6.77 (d, *J* = 8.0 Hz, 2H, ArH), 6.32 (d, *J* = 8.4 Hz, 2H, ArH), 4.12 (s, 3H, CH<sub>3</sub>), 2.14 (s, 1H), 1.67-1.51 (m, 1H, CH), 0.76 (s, 2H, CH<sub>2</sub>), 0.60 (s, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (δ, ppm): 195.1, 157.1, 143.7, 139.1, 138.3, 136.7, 133.8, 129.4, 129.31, 129.1, 128.9, 128.8, 128.5, 128.3, 126.5, 115.5, 113.2, 46.7, 33.8, 20.5, 8.7, 7.1.

IR (KBr, ν, cm<sup>-1</sup>): 3386, 1659, 1613, 1597, 1589, 1517, 1322, 1209, 812, 669, 568.

HRMS (ESI):  $m/z$  calcd for:  $C_{30}H_{25}N_4O$ , 457.2029  $[M-H]^-$ , found: 457.2029.

**(4-Bromophenyl)(6-(4-bromophenyl)-5-((4-bromophenyl)amino)-3-cyclopropyl-1-methyl-1H-pyrazolo[3,4-*b*]pyridin-4-yl)methanone (5m)**



Yellow solid, m.p. 257-258 °C;

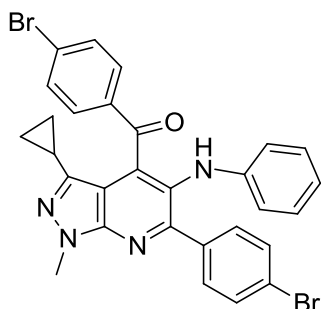
$^1H$  NMR (400 MHz,  $DMSO-d_6$ ) ( $\delta$ , ppm): 7.85 (s, 1H, NH), 7.71 (s, 1H, ArH), 7.69-7.66 (m, 5H, ArH), 7.54 (d,  $J = 8.0$  Hz, 2H, ArH), 6.95 (d,  $J = 8.4$  Hz, 2H, ArH), 6.19 (d,  $J = 8.4$  Hz, 2H, ArH), 4.03 (s, 3H,  $CH_3$ ), 1.70-1.27 (m, 1H, CH), 0.67 (s, 2H,  $CH_2$ ), 0.59 (s, 2H,  $CH_2$ ).

$^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ) ( $\delta$ , ppm): 193.9, 157.1, 149.4, 146.7, 143.9, 142.1, 137.9, 135.2, 132.5, 131.5, 131.3, 129.0, 125.1, 122.8, 115.5, 111.7, 108.5, 34.1, 8.6, 7.5.

IR (KBr,  $\nu$ ,  $cm^{-1}$ ): 3375, 1665, 1583, 1493, 1361, 1206, 1071, 1010, 812, 762, 716.

HRMS (ESI):  $m/z$  calcd for:  $C_{29}H_{20}Br_3N_4O$ , 678.9167  $[M-H]^-$ , found: 678.9163.

**(4-Bromophenyl)(6-(4-bromophenyl)-3-cyclopropyl-1-methyl-5-(*p*-tolylamino)-1H-pyrazolo[3,4-*b*]pyridin-4-yl)methanone (5n)**



Yellow solid, m.p. >300 °C;

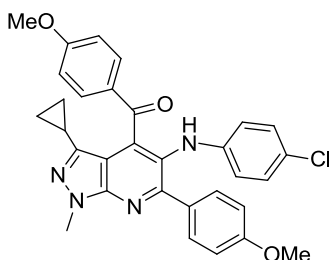
$^1H$  NMR (400 MHz,  $CDCl_3$ ) ( $\delta$ , ppm): 7.62 (d,  $J = 8.0$  Hz, 2H), 7.54 (d,  $J = 8.0$  Hz, 2H), 7.47 (t,  $J = 7.6$  Hz, 4H), 6.78 (d,  $J = 8.0$  Hz, 2H), 6.29 (d,  $J = 8.0$  Hz, 2H), 4.12 (s, 3H,  $CH_3$ ), 2.15 (s, 3H,  $CH_3$ ), 1.64-1.30 (m, 1H, CH), 0.77 (s, 2H,  $CH_2$ ), 0.62 (s, 2H,  $CH_2$ ).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) ( $\delta$ , ppm): 194.0, 155.8, 149.1, 144.5, 143.3, 138.7, 137.2, 135.3, 131.9, 131.4, 130.7, 130.7, 129.5, 129.2, 129.2, 126.3, 123.4, 115.3, 112.0, 33.8, 20.4, 8.7, 7.1.

IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3312, 1705, 1553, 1478, 1411, 1195, 1041, 812, 745, 723.

HRMS (ESI):  $m/z$  calcd for:  $\text{C}_{30}\text{H}_{23}\text{Br}_2\text{N}_4\text{O}$ , 615.0215  $[\text{M}-\text{H}]^-$ , found: 615.0241.

**(5-((4-Chlorophenyl)amino)-3-cyclopropyl-6-(4-methoxyphenyl)-1-methyl-1H-pyrazolo[3,4-b]pyridin-4-yl)(4-methoxyphenyl)methanone (5o)**



Yellow solid, m.p. 252-254 °C;

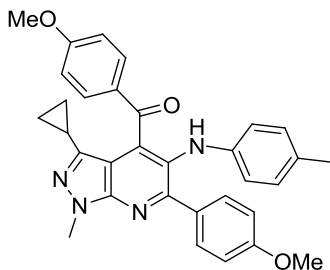
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) ( $\delta$ , ppm): 7.69 (d,  $J = 8.4$  Hz, 4H, ArH), 7.10-6.75 (m, 6H, ArH), 6.32 (d,  $J = 8.4$  Hz, 2H, ArH), 5.33 (s, 1H, NH), 4.10 (s, 3H,  $\text{CH}_3$ ), 3.84 (s, 3H,  $\text{OCH}_3$ ), 3.80 (s, 3H,  $\text{OCH}_3$ ), 1.75-1.31 (m, 5H, CH and  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) ( $\delta$ , ppm): 193.4, 164.3, 160.2, 156.8, 149.4, 144.8, 140.5, 131.9, 130.7, 130.5, 129.5, 128.7, 124.8, 123.7, 115.7, 113.9, 113.7, 111.6, 109.5, 55.6, 55.3, 33.8, 8.6.

IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3357, 1652, 1601, 1574, 1505, 1253, 1167, 1034, 837, 820, 772.

HRMS (ESI):  $m/z$  calcd for:  $\text{C}_{31}\text{H}_{26}\text{ClN}_4\text{O}_3$ , 537.1694  $[\text{M}-\text{H}]^-$ , found: 537.1728.

**(3-Cyclopropyl-6-(4-methoxyphenyl)-1-methyl-5-(p-tolylamino)-1H-pyrazolo[3,4-b]pyridin-4-yl)(4-methoxyphenyl)methanone (5p)**



Yellow solid, m.p. 235-237 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) ( $\delta$ , ppm): 7.73 (d,  $J = 8.4$  Hz, 2H, ArH), 7.68 (d,  $J = 8.4$  Hz, 2H, ArH), 6.86 (d,  $J = 8.4$  Hz, 2H, ArH), 6.81 (d,  $J = 8.4$  Hz, 2H, ArH), 6.77 (d,  $J = 8.0$  Hz, 2H, ArH), 6.33 (d,  $J = 8.0$  Hz, 2H, ArH and CH), 4.12 (s, 3H,  $\text{CH}_3$ ), 3.83 (s, 3H,  $\text{OCH}_3$ ), 3.79 (s, 3H,  $\text{OCH}_3$ ), 2.13 (s,



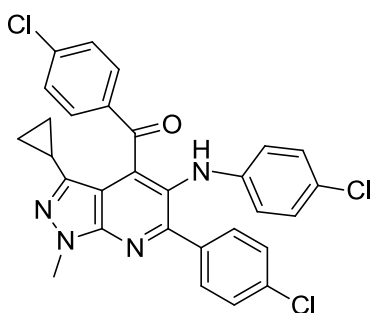
3H, CH<sub>3</sub>), 1.76-1.28 (m, 1H, CH), 0.60 (s, 4H, CH<sub>2</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (δ, ppm): 193.2, 164.2, 160.2, 156.6, 149.2, 143.8, 139.6, 139.3, 131.9, 130.9, 130.6, 129.7, 129.3, 128.8, 128.6, 126.2, 115.3, 113.9, 113.8, 111.3, 55.5, 55.3, 34.4, 33.8, 20.5, 13.7.

IR (KBr, ν, cm<sup>-1</sup>): 3366, 1651, 1600, 1575, 1516, 1258, 1164, 1034, 806, 776, 639.

HRMS (ESI): m/z calcd for: C<sub>32</sub>H<sub>29</sub>N<sub>4</sub>O<sub>3</sub>, 517.2240 [M-H]<sup>-</sup>, found: 517.2219.

**(4-Chlorophenyl)(6-(4-chlorophenyl)-5-((4-chlorophenyl)amino)-3-cyclopropyl-1-methyl-1H-pyrazolo[3,4-b]pyridin-4-yl)methanone (5q)**



Yellow solid, m.p. 284-285 °C;

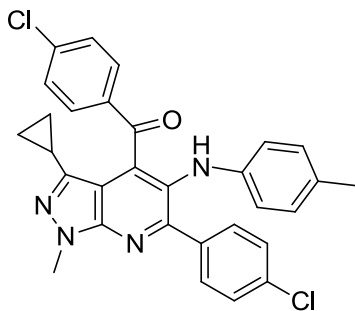
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (δ, ppm): 7.65 (s, 4H, ArH), 7.43-7.30 (m, 4H, ArH), 6.93 (d, *J* = 7.6 Hz, 2H, ArH), 6.31 (d, *J* = 7.6 Hz, 2H, ArH), 5.30 (s, 1H, NH), 4.13 (s, 3H, CH<sub>3</sub>), 1.23 (s, 1H, CH), 0.88-0.79 (m, 2H, CH<sub>2</sub>), 0.62 (s, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (δ, ppm): 193.6, 156.0, 144.4, 140.8, 139.7, 136.6, 136.5, 135.3, 134.8, 130.7, 130.4, 129.1, 128.9, 128.6, 128.3, 124.4, 115.8, 112.0, 33.8, 30.9, 29.7, 8.7, 7.14.

IR (KBr, ν, cm<sup>-1</sup>): 3375, 1664, 1587, 1497, 1361, 1371, 2091, 1091, 1014, 816, 764.

HRMS (ESI): m/z calcd for: C<sub>29</sub>H<sub>20</sub>Cl<sub>3</sub>N<sub>4</sub>O, 545.0703 [M-H]<sup>-</sup>, found: 545.0721.

**(4-Chlorophenyl)(6-(4-chlorophenyl)-3-cyclopropyl-1-methyl-5-(*p*-tolylamino)-1H-pyrazolo[3,4-b]pyridin-4-yl)methanone (5r)**



Yellow solid, m.p. 270-271 °C;

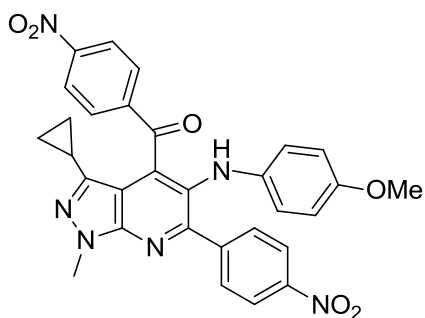
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (δ, ppm): 7.69 (d, *J* = 8.4 Hz, 2H, ArH), 7.62 (d, *J* = 8.4 Hz, 2H, ArH), 7.33-7.30 (m, 4H, ArH), 7.26 (s, 1H, ArH), 6.78 (d, *J* = 8.0 Hz, 2H, ArH), 6.29 (d, *J* = 8.0 Hz, 2H, ArH), 4.12 (s, 3H, CH<sub>3</sub>), 2.15 (s, 3H, CH<sub>3</sub>), 1.59-1.46 (m, 1H, CH), 0.78 (s, 2H, CH<sub>2</sub>), 0.62 (s, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (δ, ppm): 193.8, 155.8, 149.1, 144.5, 143.3, 140.44, 138.7, 136.7, 135.1, 134.9, 130.9, 130.4, 129.5, 129.1, 128.9, 128.5, 126.3, 115.3, 112.0, 33.8, 20.4, 8.7, 7.1.

IR (KBr, ν, cm<sup>-1</sup>): 3380, 1666, 1587, 1514, 1306, 1091, 1014, 957, 811.

HRMS (ESI): *m/z* calcd for: C<sub>30</sub>H<sub>23</sub>Cl<sub>2</sub>N<sub>4</sub>O, 525.1249 [M-H]<sup>-</sup>, found: 525.1247.

**(3-Cyclopropyl-5-((4-methoxyphenyl)amino)-1-methyl-6-(4-nitrophenyl)-1*H*-pyrazolo[3,4-*b*]pyridin-4-yl)(4-nitrophenyl)methanone (5s)**



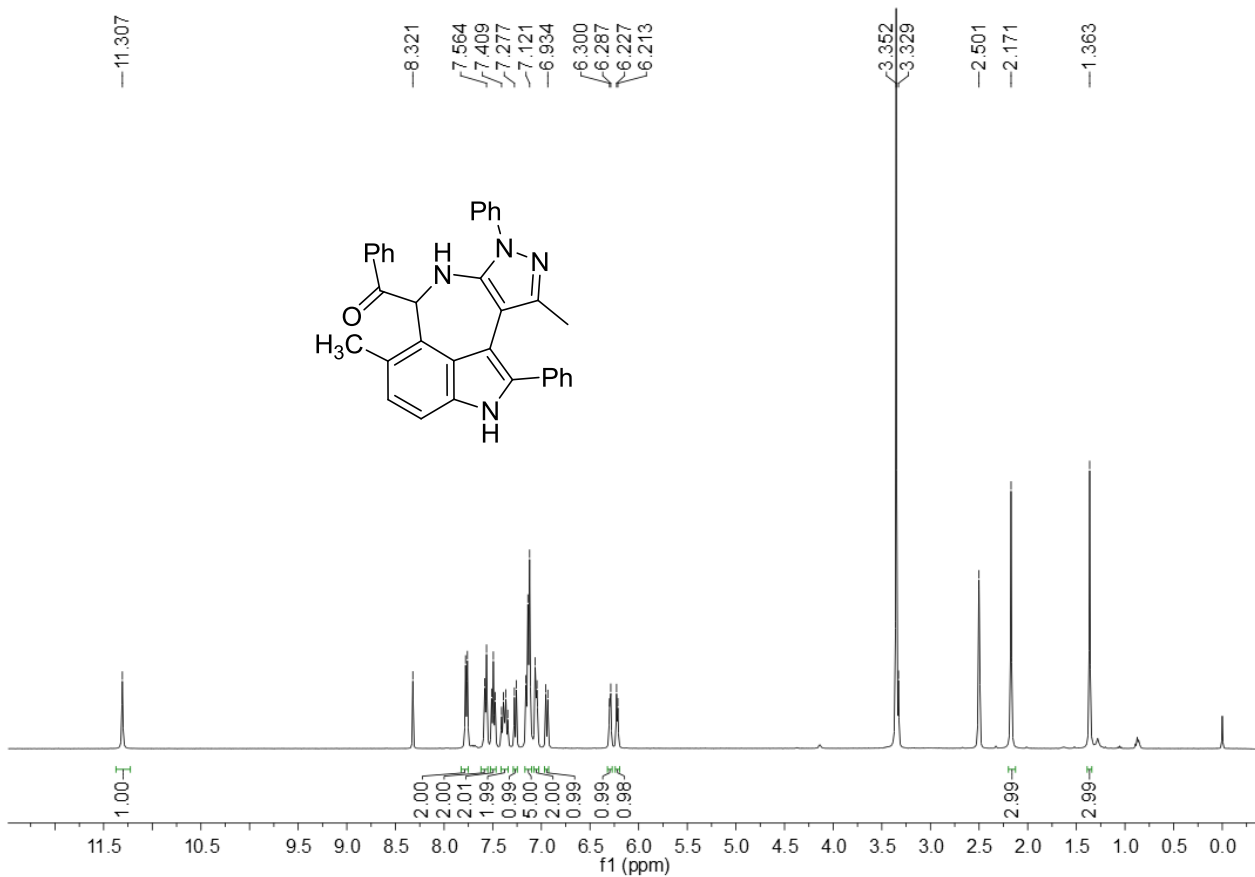
Yellow solid, m.p. 249-250 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (δ, ppm): 8.21 (d, *J* = 2.0 Hz, 2H, ArH), 8.19 (d, *J* = 2.0 Hz, 2H, ArH), 7.93 (d, *J* = 8.0 Hz, 2H, ArH), 7.85 (d, *J* = 8.4 Hz, 2H, ArH), 6.53 (d, *J* = 8.4 Hz, 2H, ArH), 6.34 (d, *J* = 8.4 Hz, 2H, ArH), 5.33 (s, 1H, NH), 4.14 (s, 3H, CH<sub>3</sub>), 3.65 (s, 3H, OCH<sub>3</sub>), 1.54-1.45 (m, 1H, CH), 0.78 (d, *J* = 4.0 Hz, 2H, CH<sub>2</sub>), 0.60 (d, *J* = 8.0 Hz, 2H, CH<sub>2</sub>).

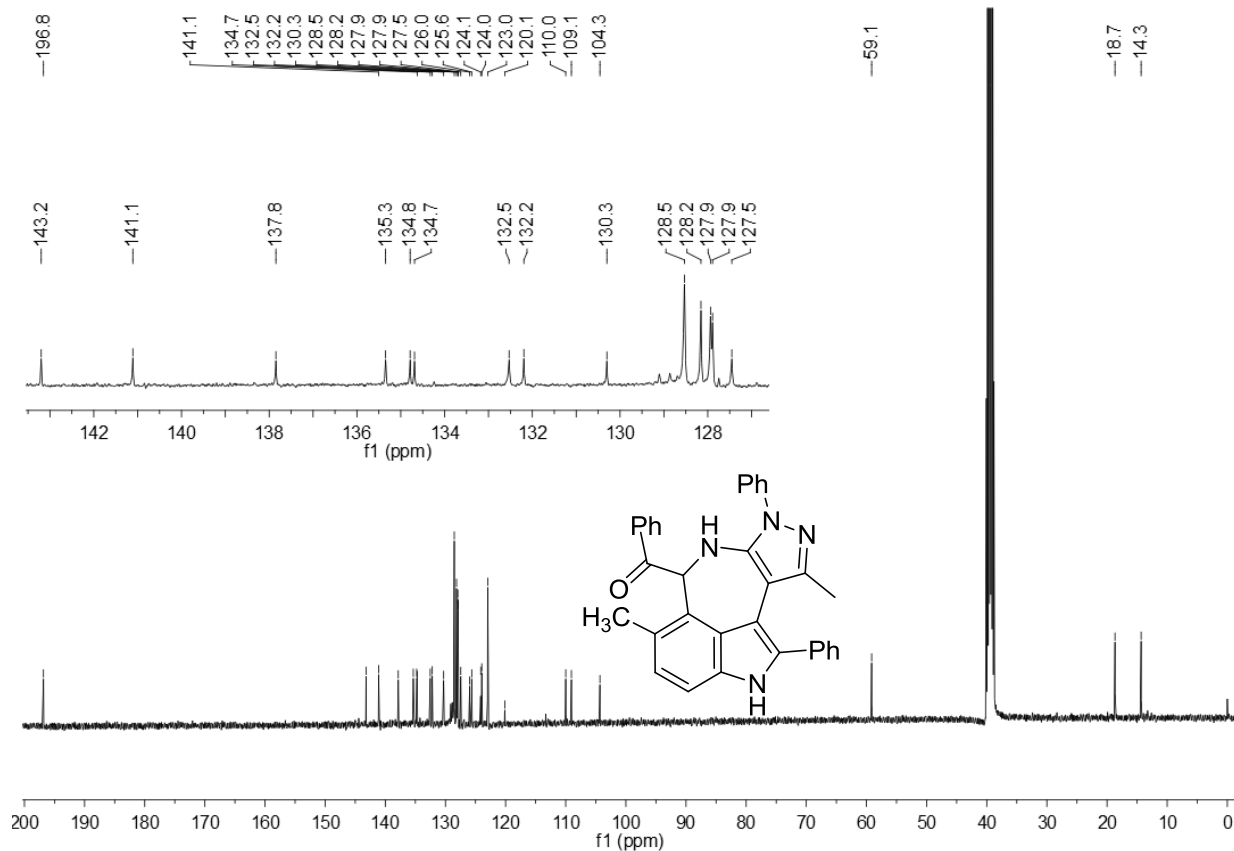
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (δ, ppm): 193.4, 154.1, 153.9, 150.6, 148.9, 147.9, 144.5, 144.24, 140.9, 138.6, 136.6, 130.2, 130.0, 128.3, 127.6, 123.8, 123.5, 117.4, 114.5, 112.3, 55.4, 33.9, 30.9, 29.7, 8.9, 7.2.

IR (KBr, ν, cm<sup>-1</sup>): 3392, 1668, 1600, 1574, 1521, 1344, 1240, 1037, 859, 709.

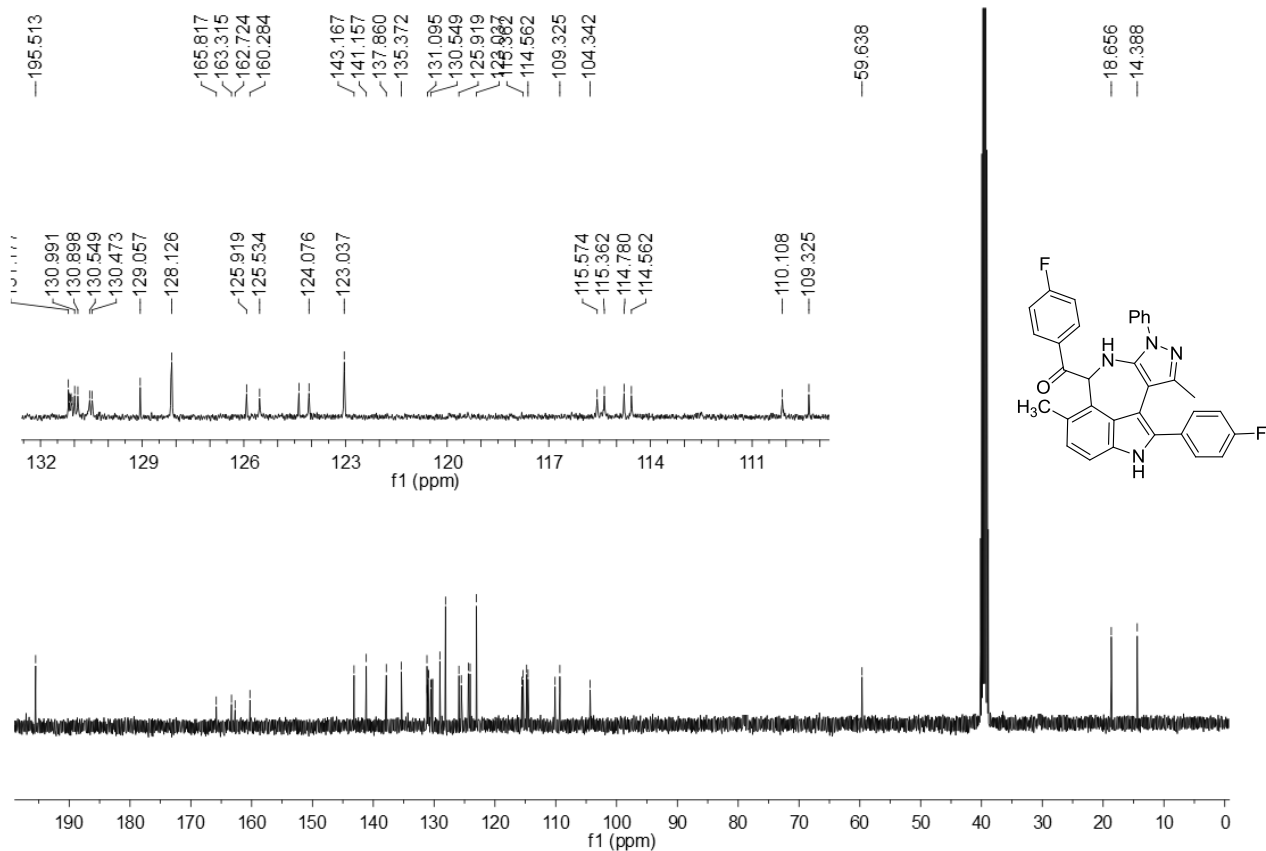
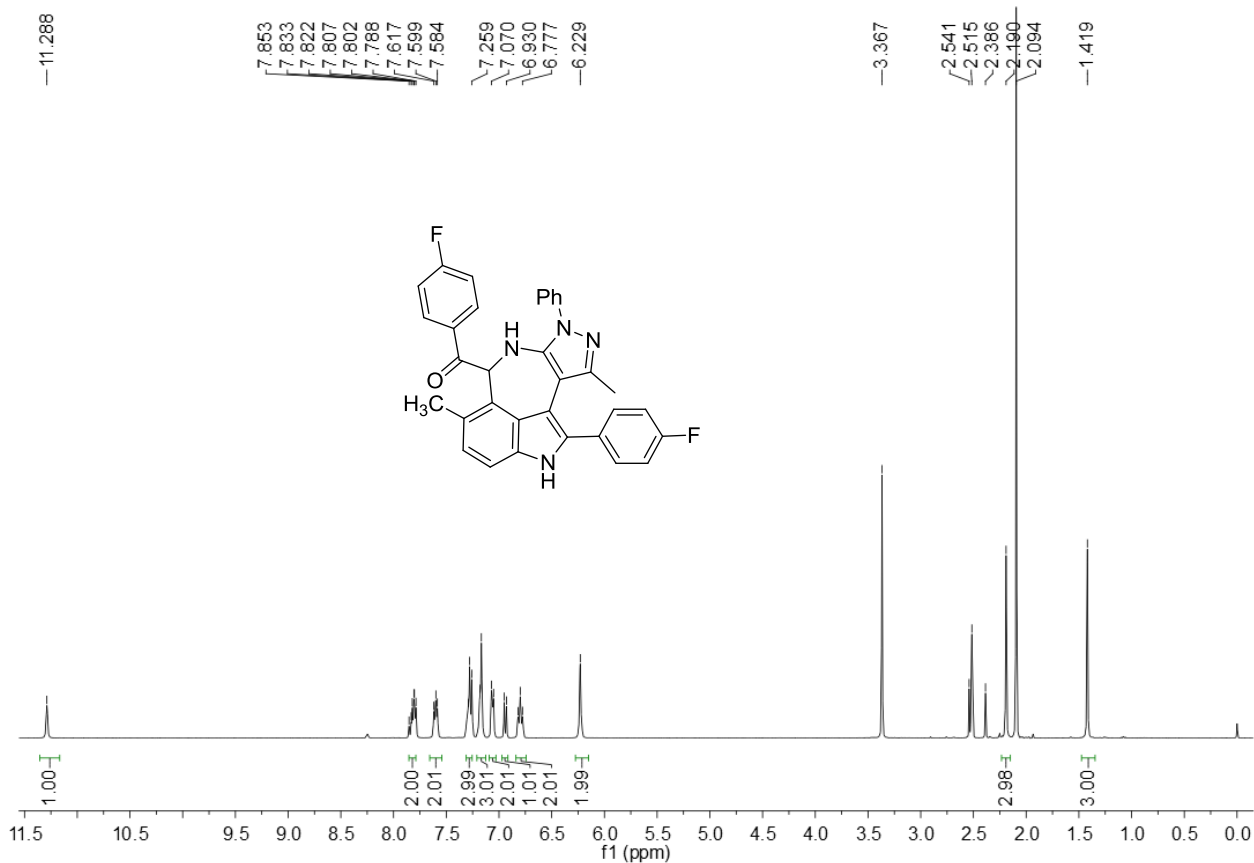
HRMS (ESI): *m/z* calcd for: C<sub>30</sub>H<sub>23</sub>N<sub>6</sub>O<sub>6</sub>, 563.1679 [M-H]<sup>-</sup>, found: 563.1701.



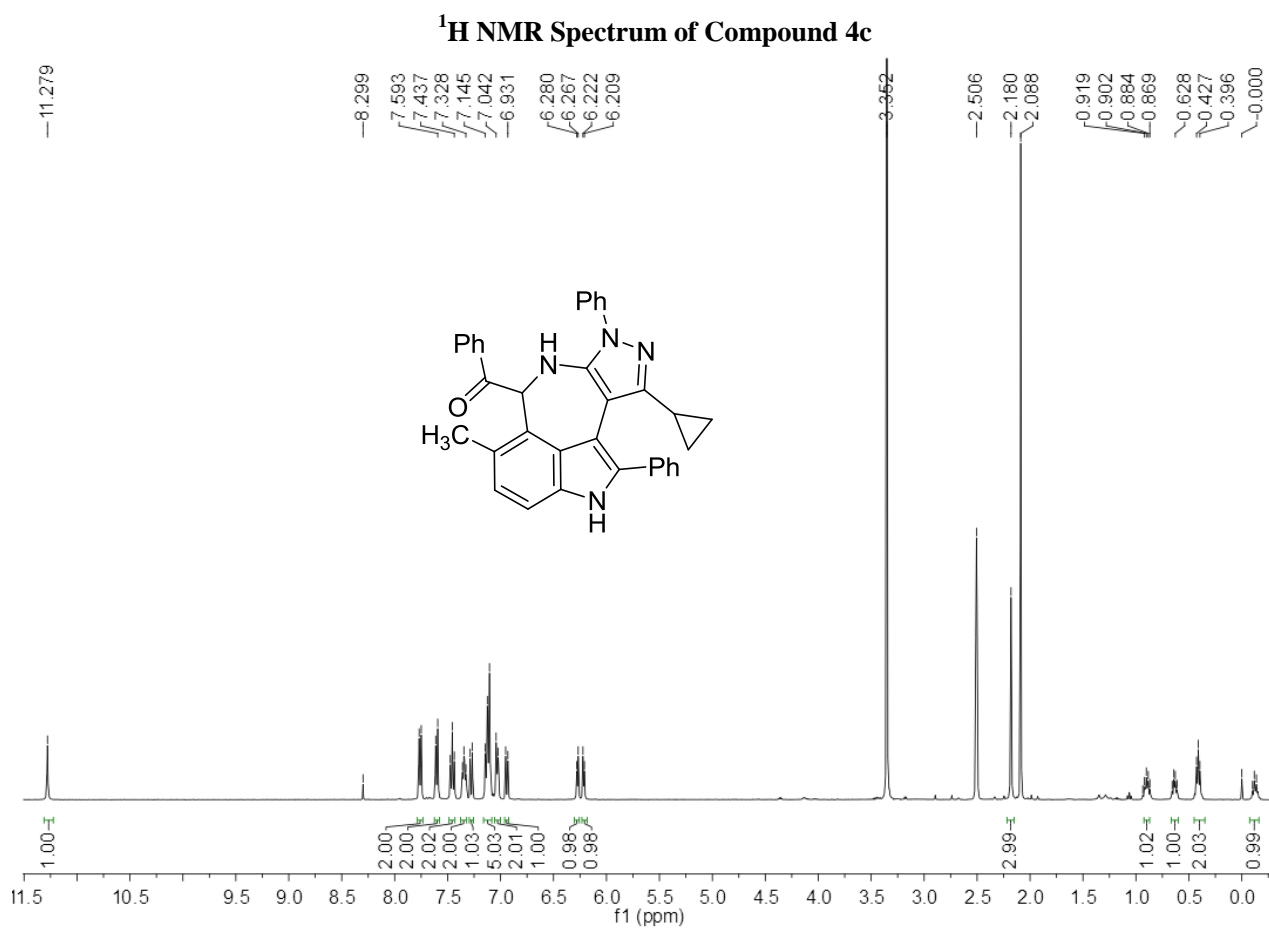
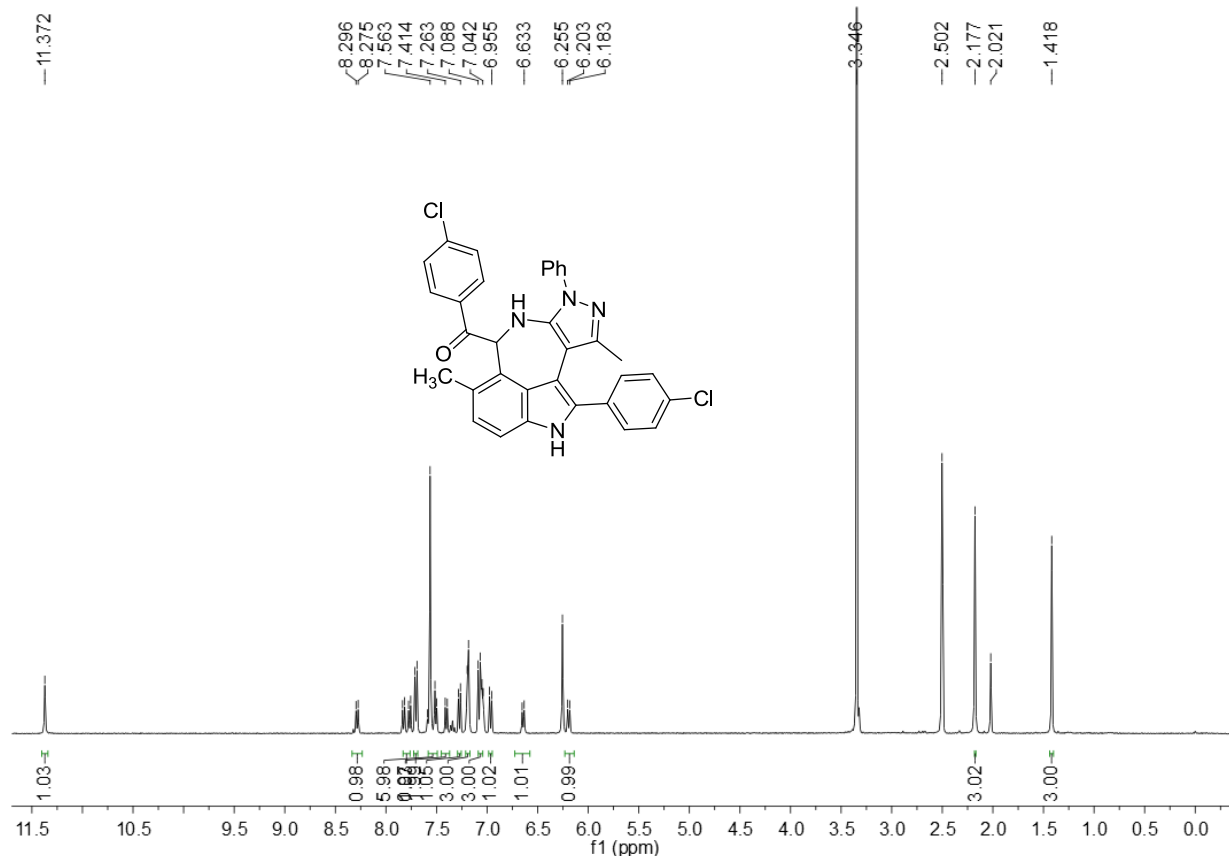
**<sup>1</sup>H NMR Spectrum of Compound 4a**



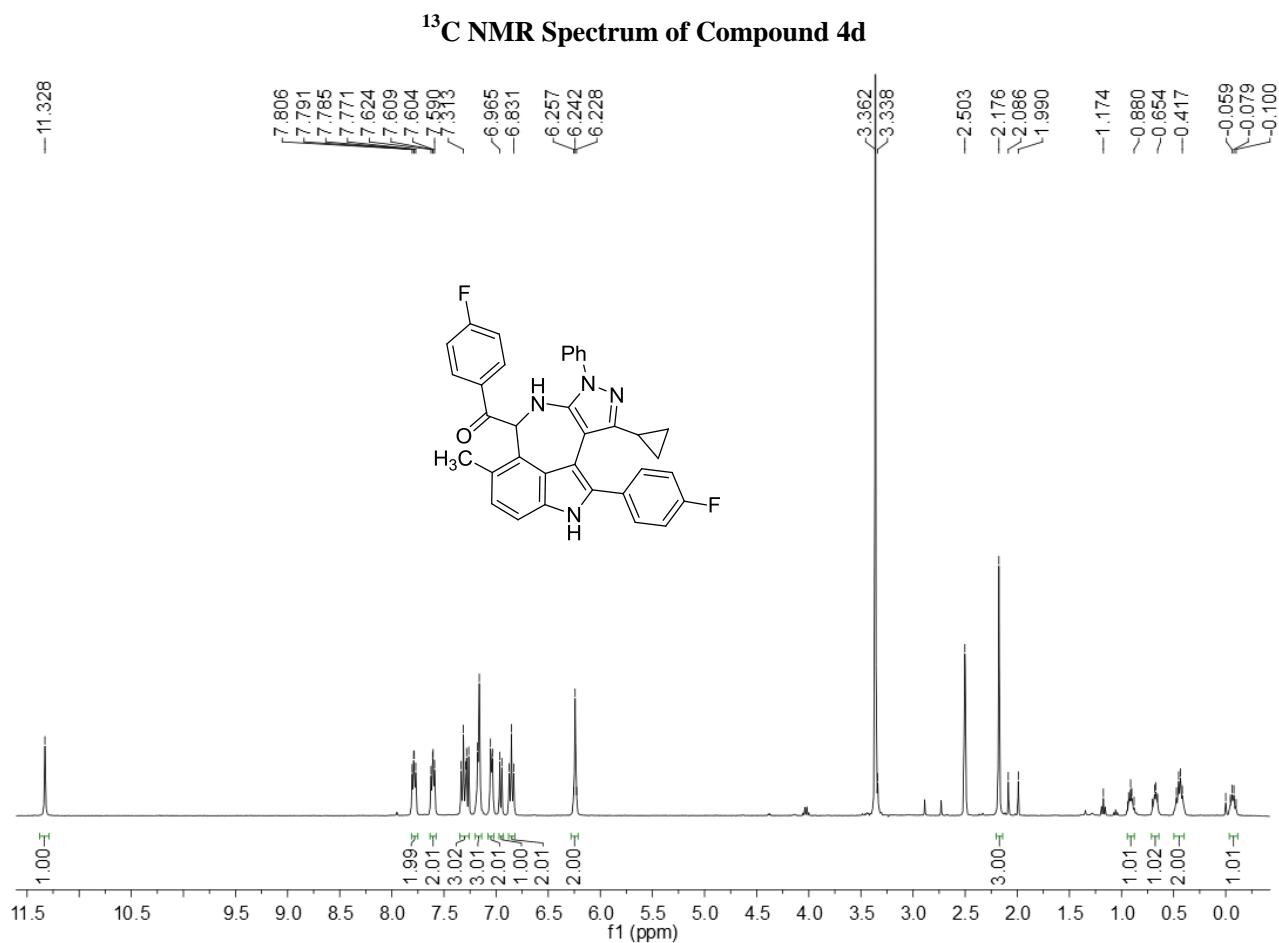
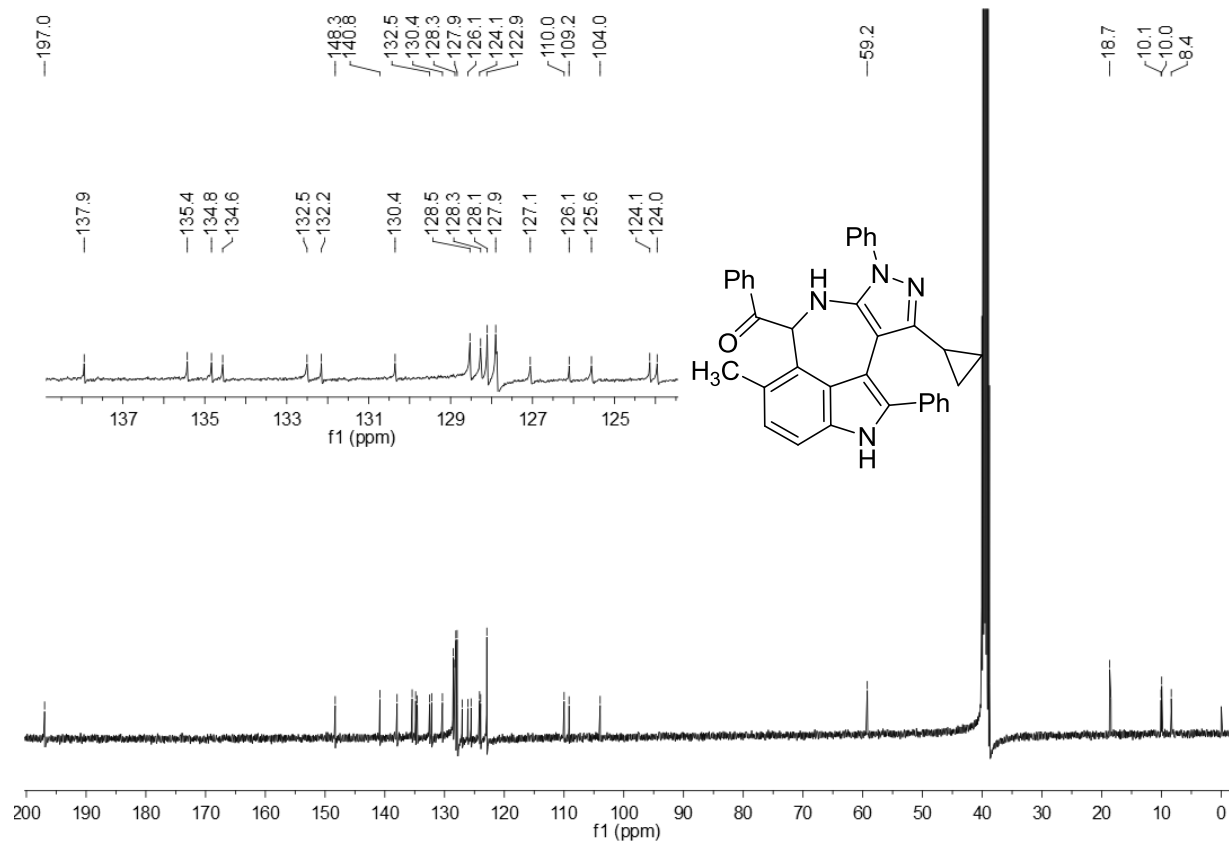
**<sup>13</sup>C NMR Spectrum of Compound 4a**

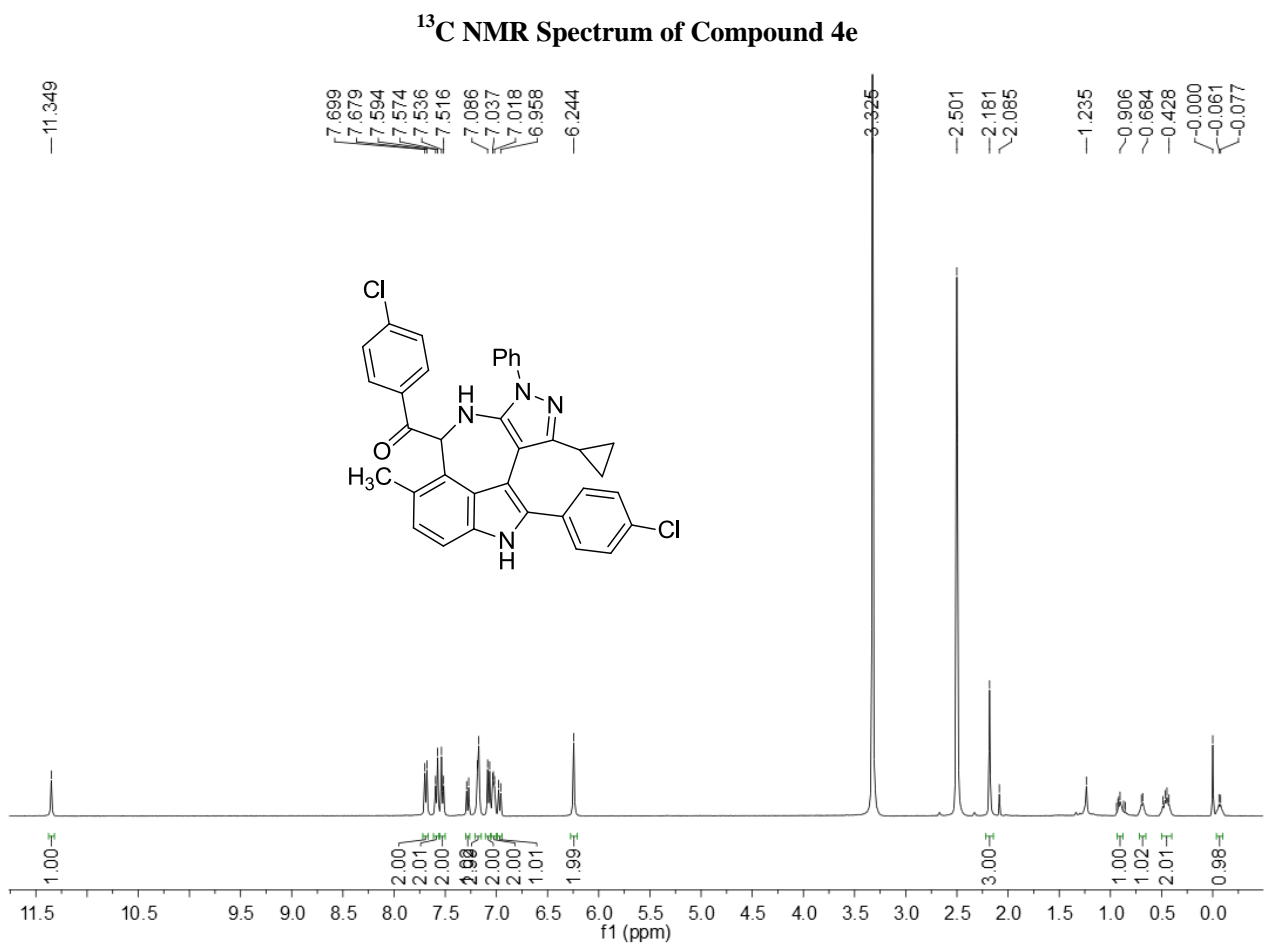
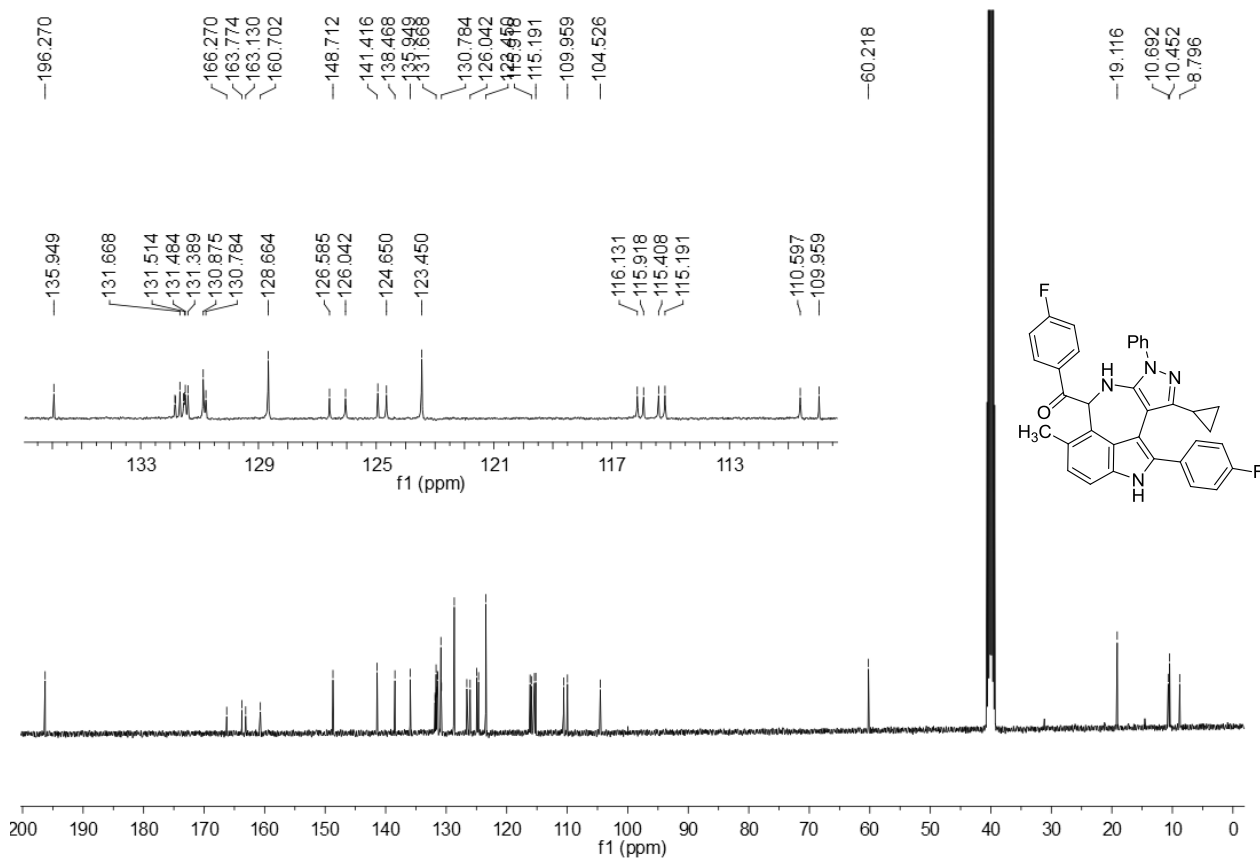


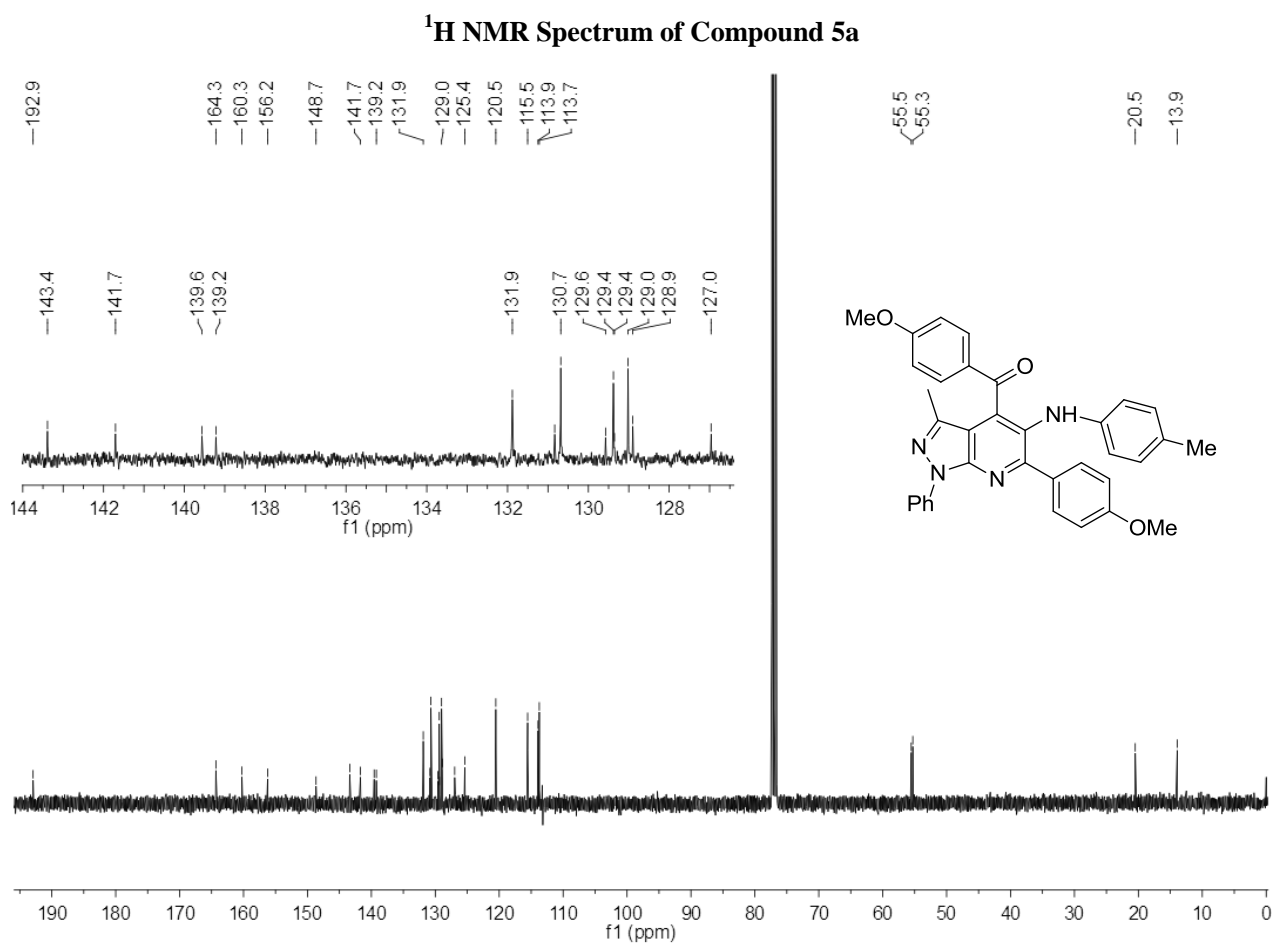
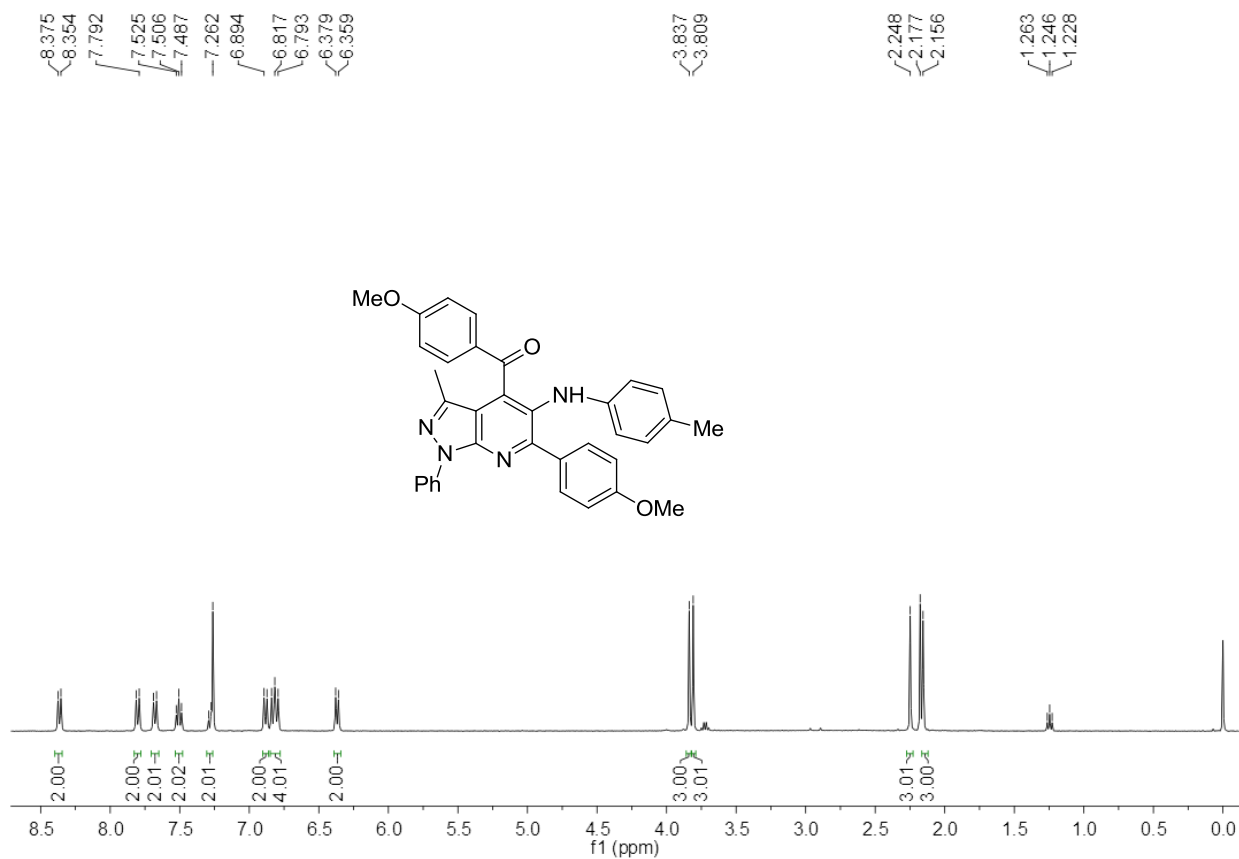
**<sup>13</sup>C NMR Spectrum of Compound 4b**



<sup>1</sup>H NMR Spectrum of Compound 4d

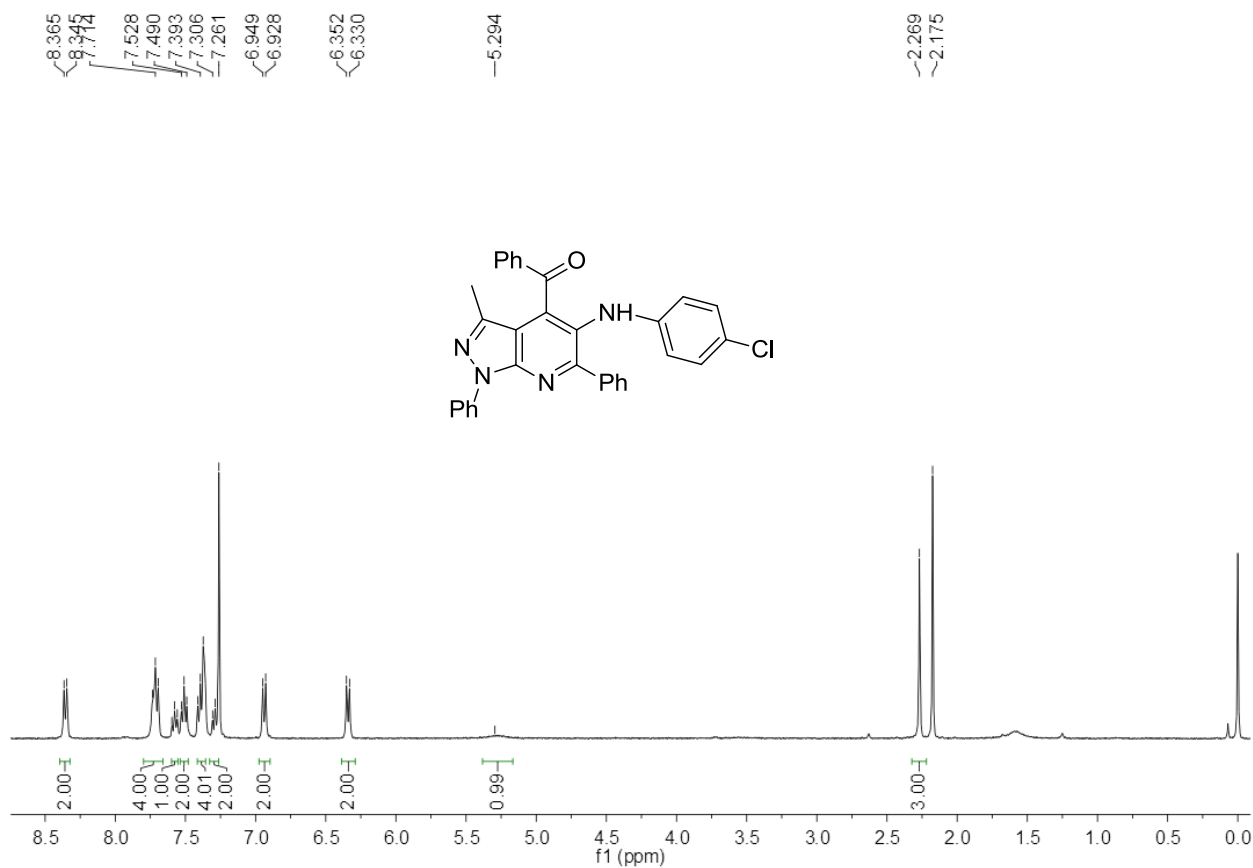




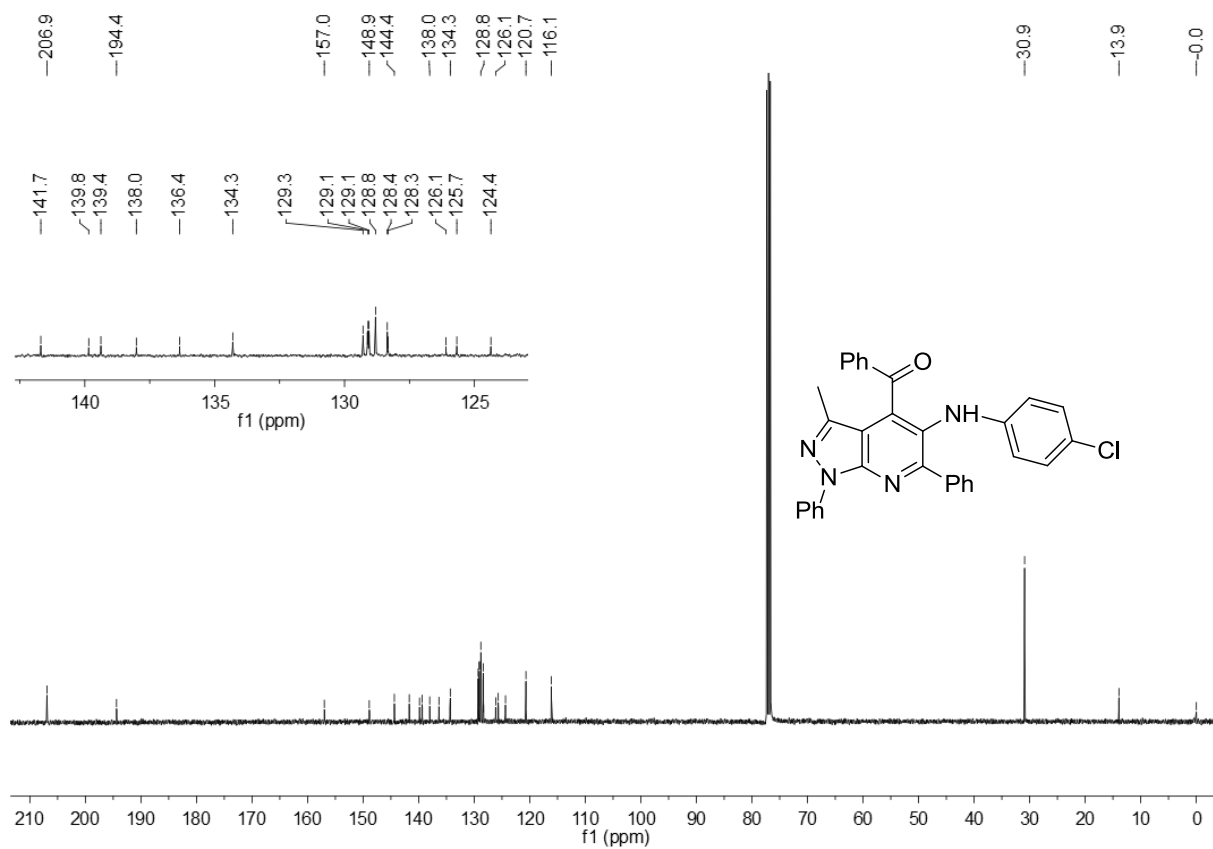


<sup>13</sup>C NMR Spectrum of Compound 5a

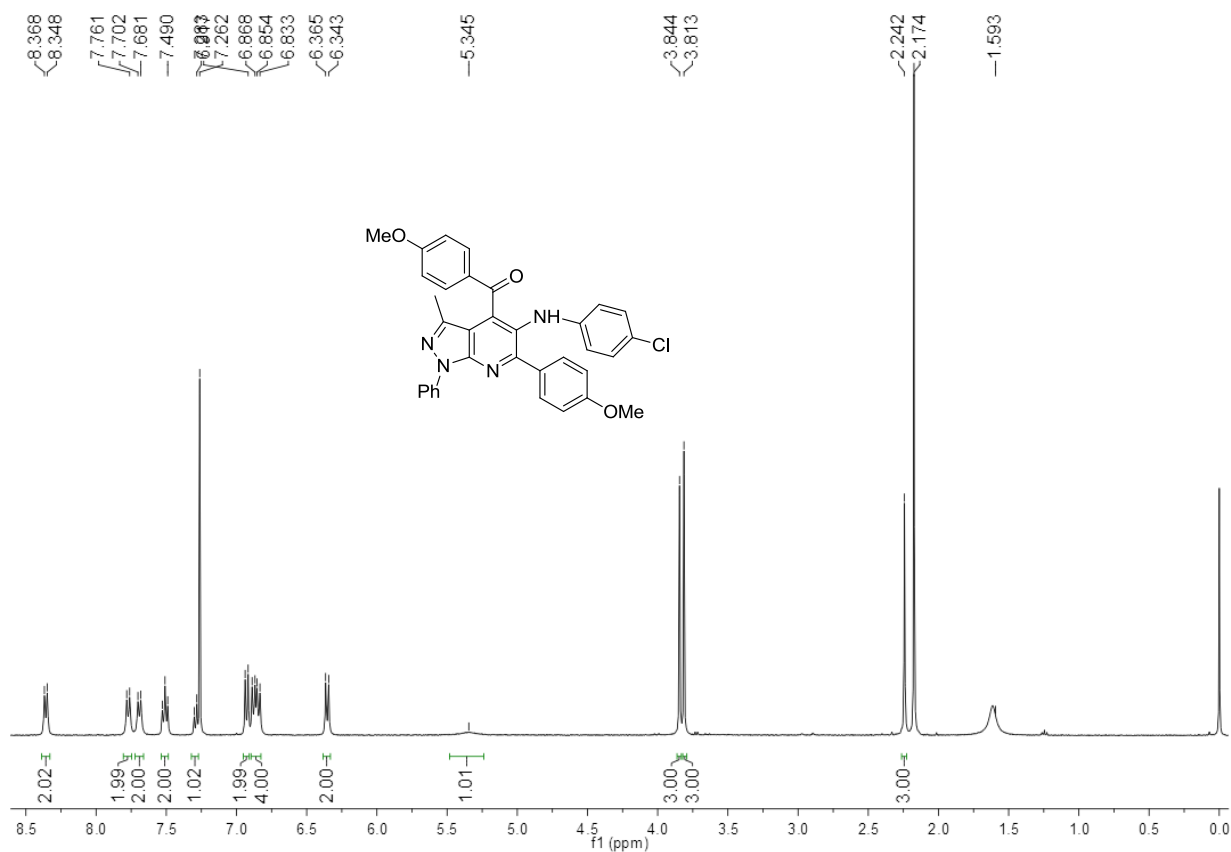




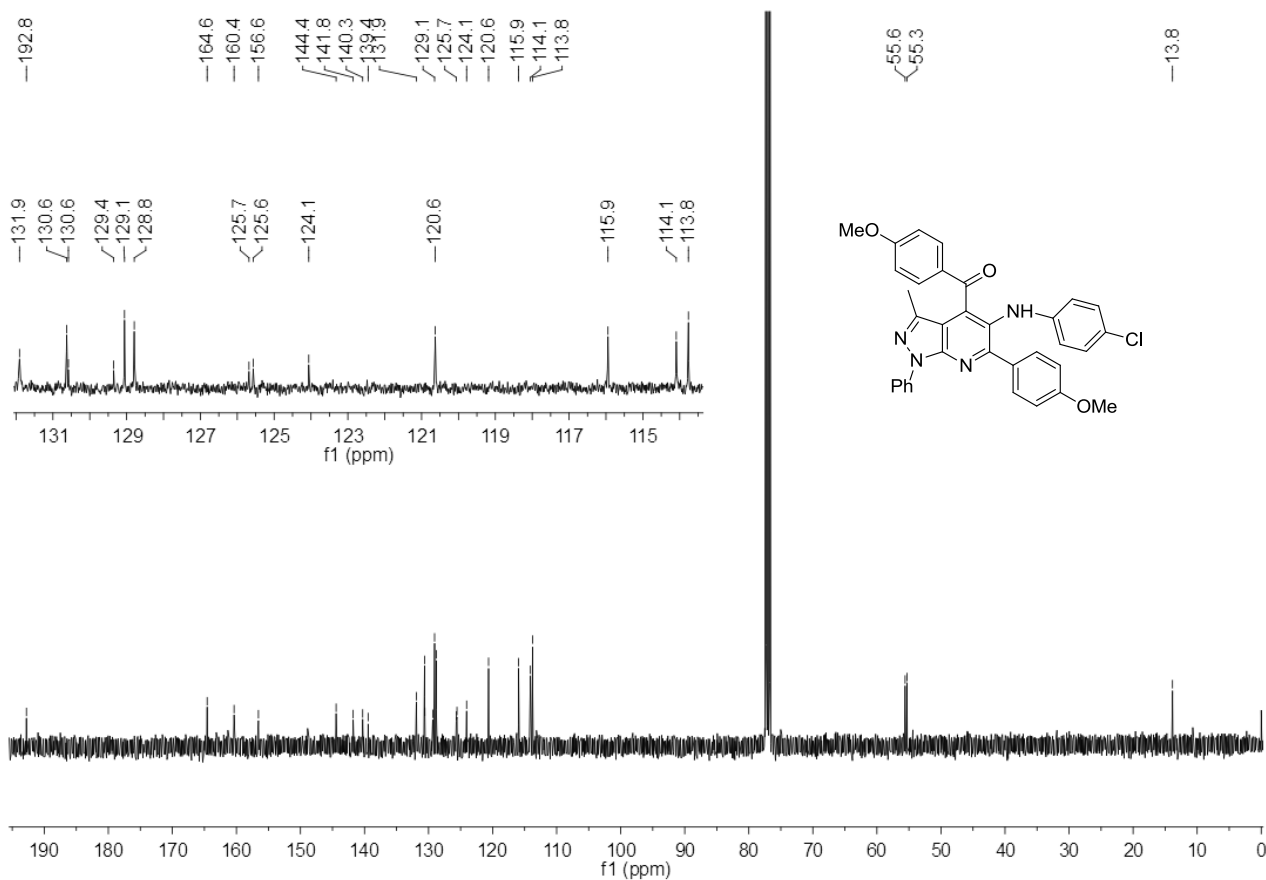
**<sup>1</sup>H NMR Spectrum of Compound 5b**



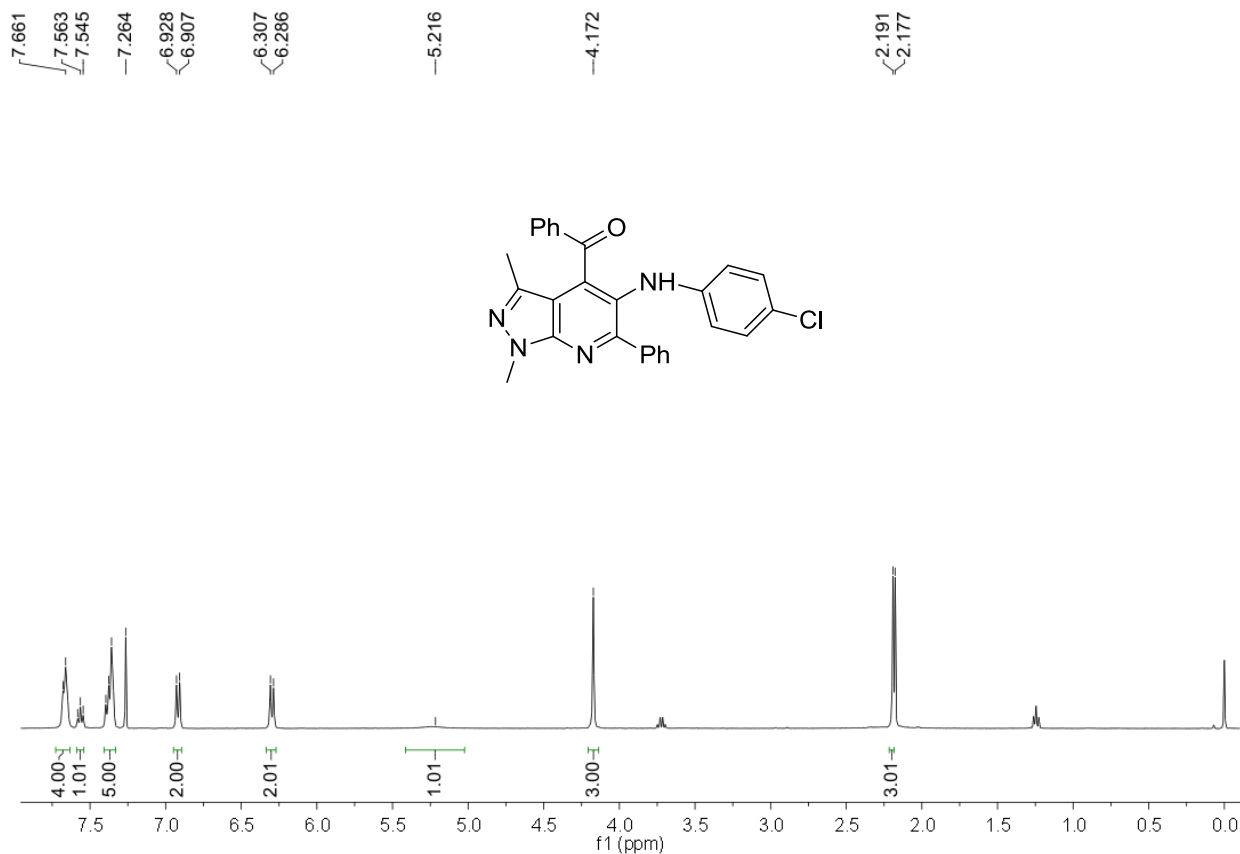
**<sup>13</sup>C NMR Spectrum of Compound 5b**



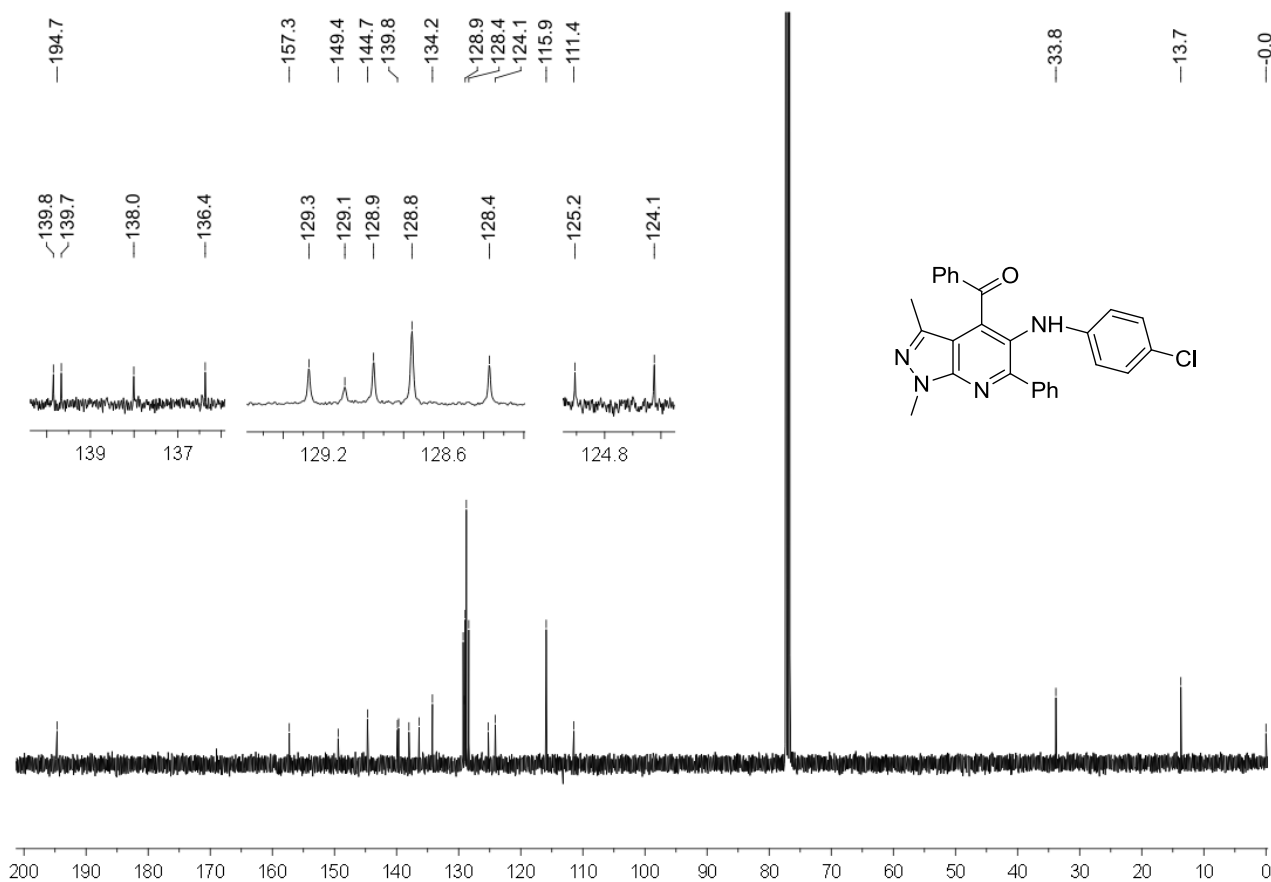
**<sup>1</sup>H NMR Spectrum of Compound 5c**



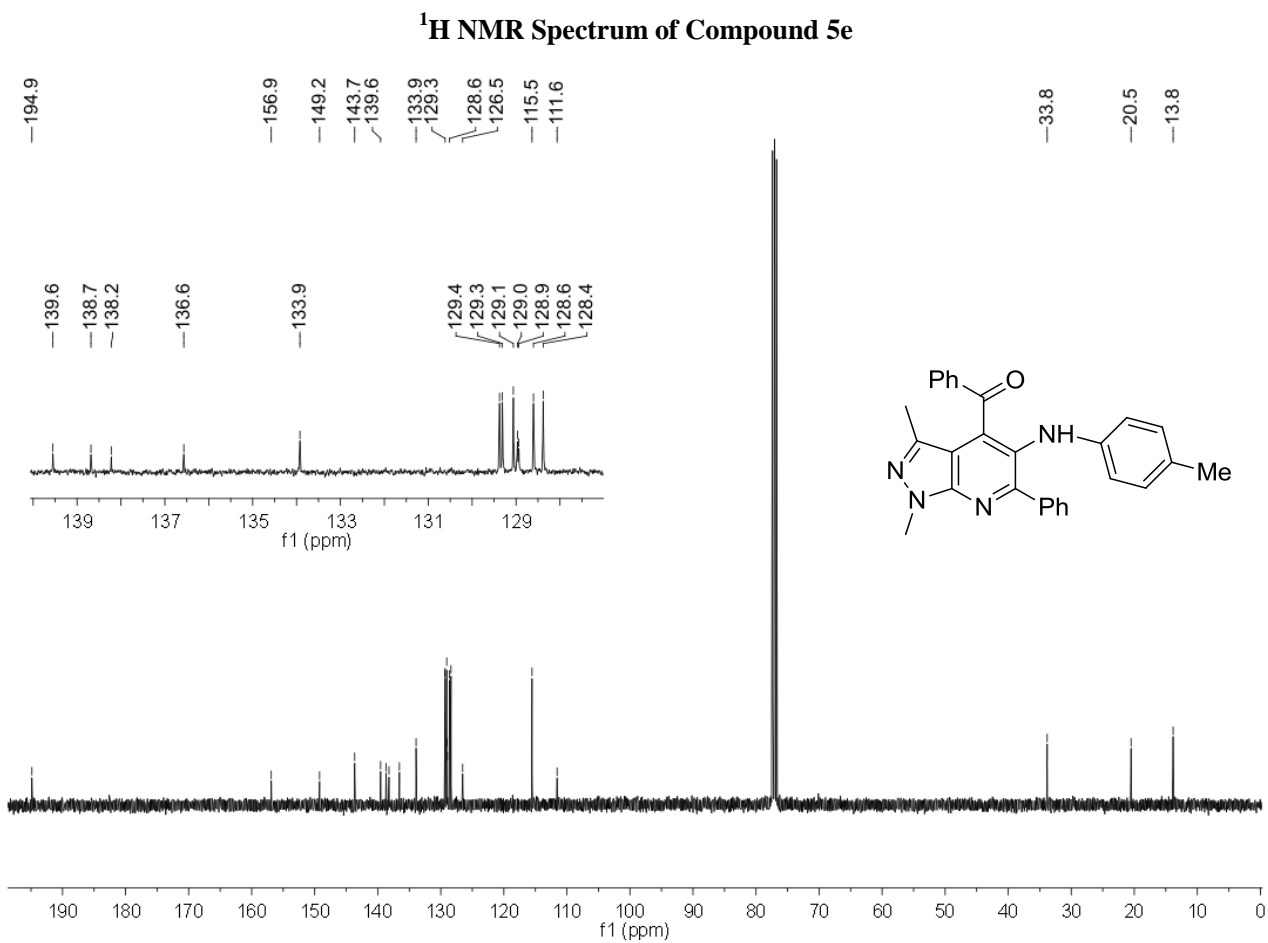
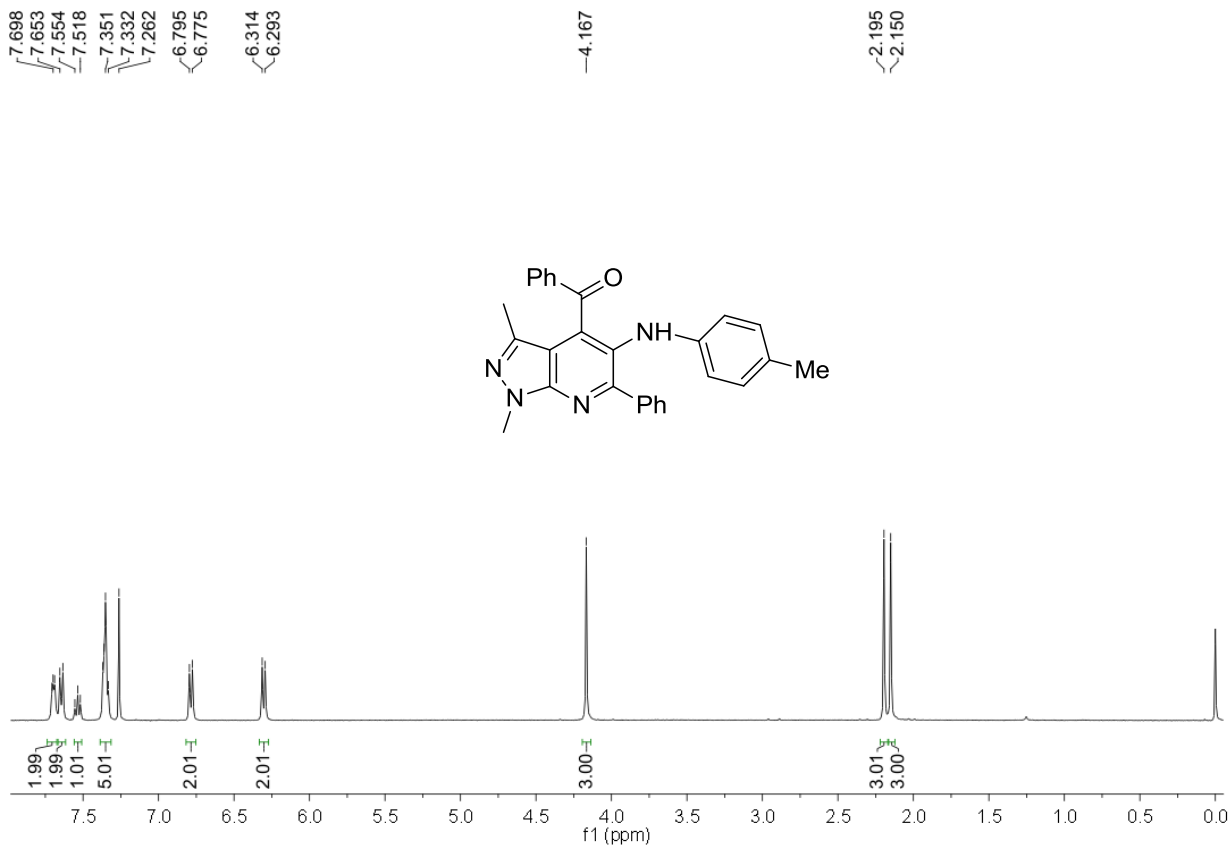
**<sup>13</sup>C NMR Spectrum of Compound 5c**

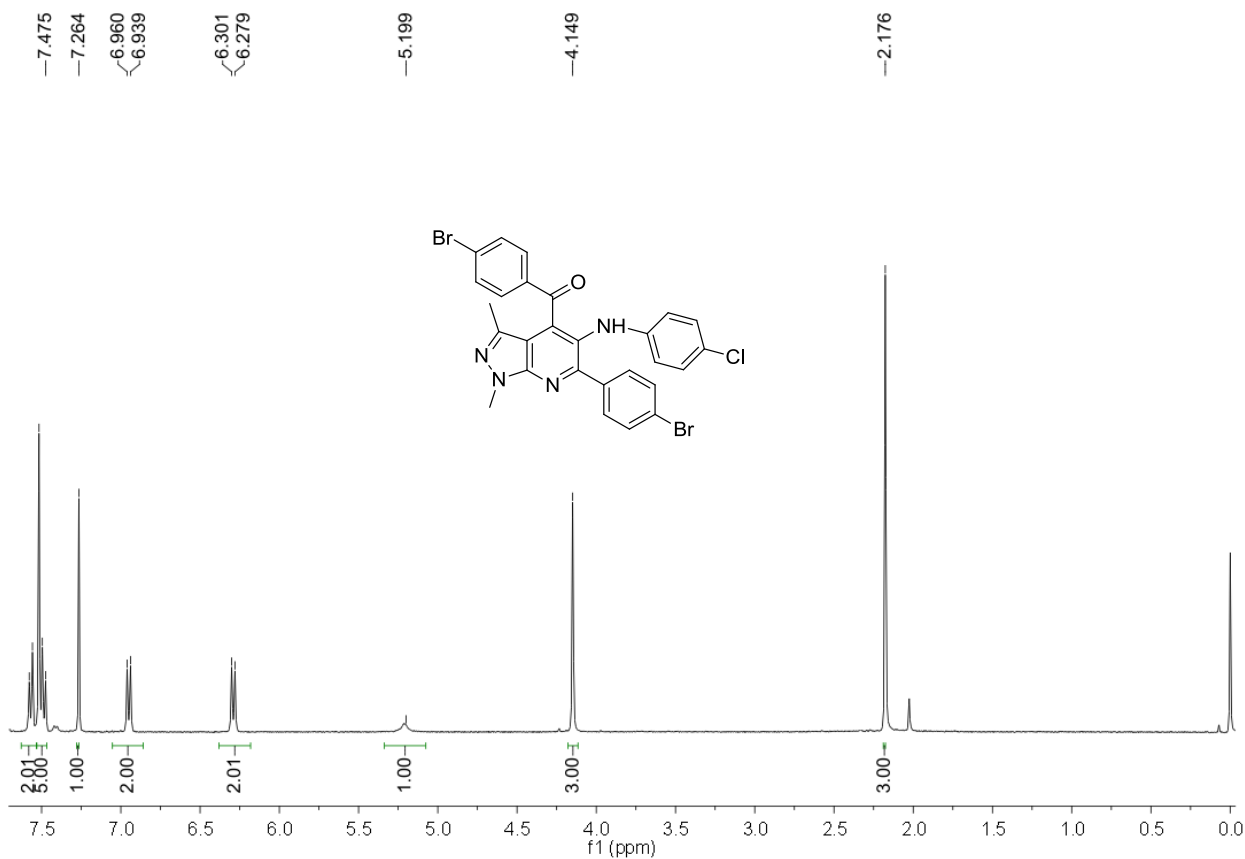


<sup>1</sup>H NMR Spectrum of Compound 5d

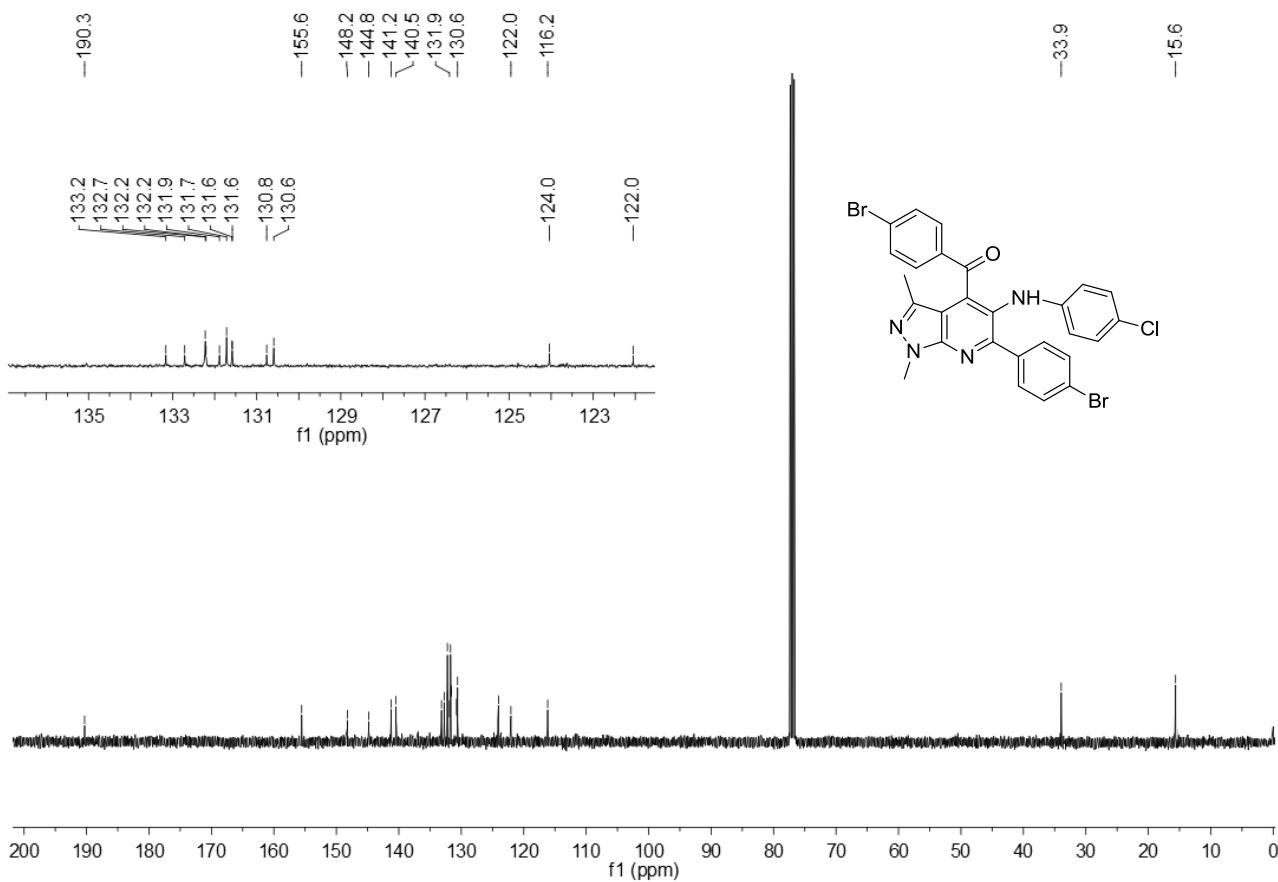


<sup>13</sup>C NMR Spectrum of Compound 5d

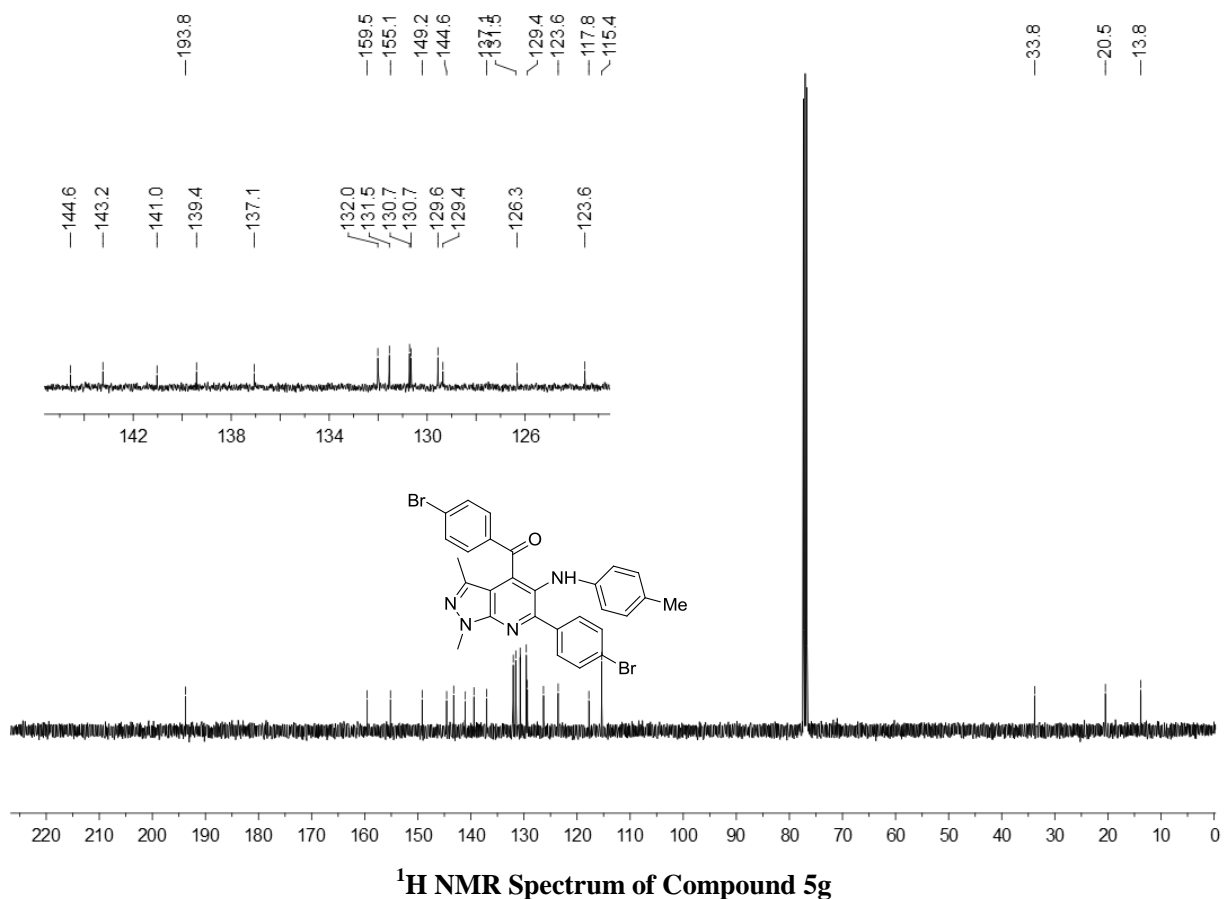
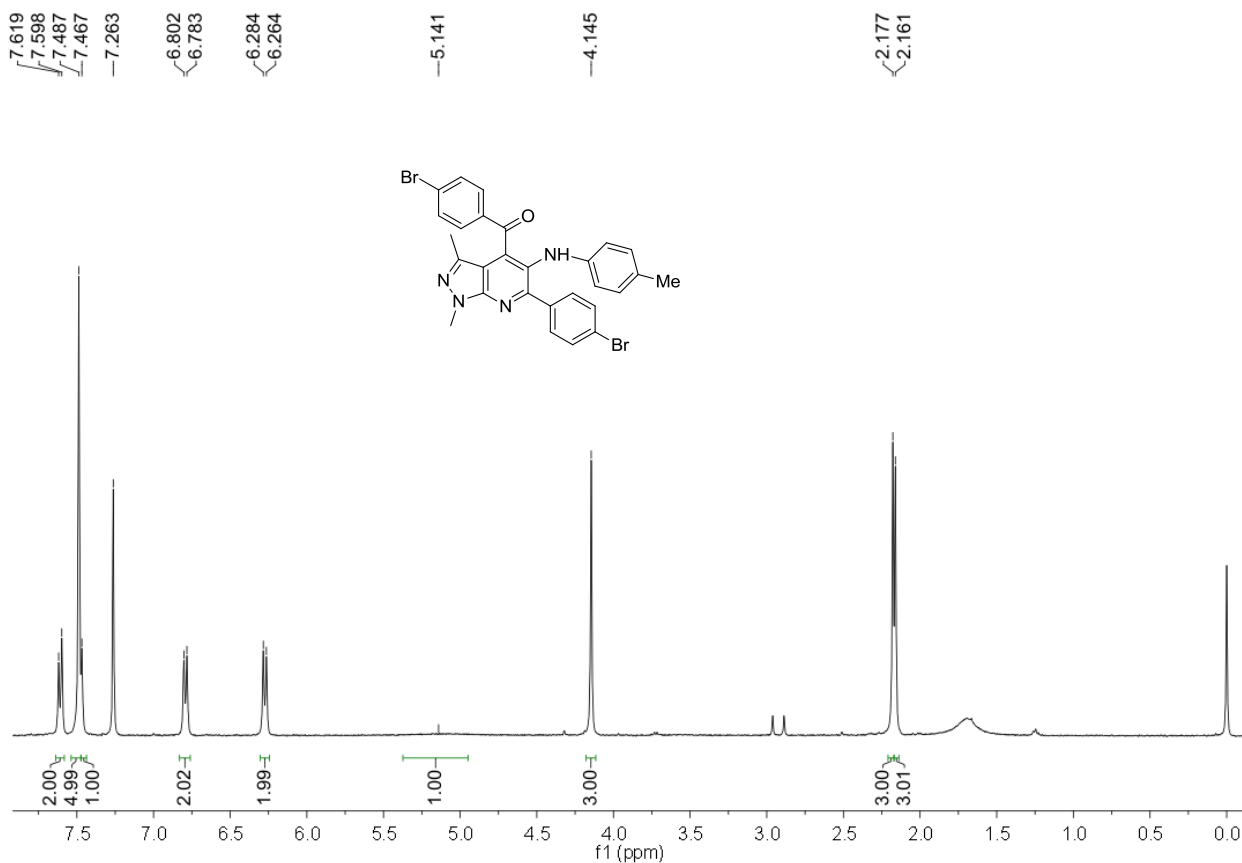


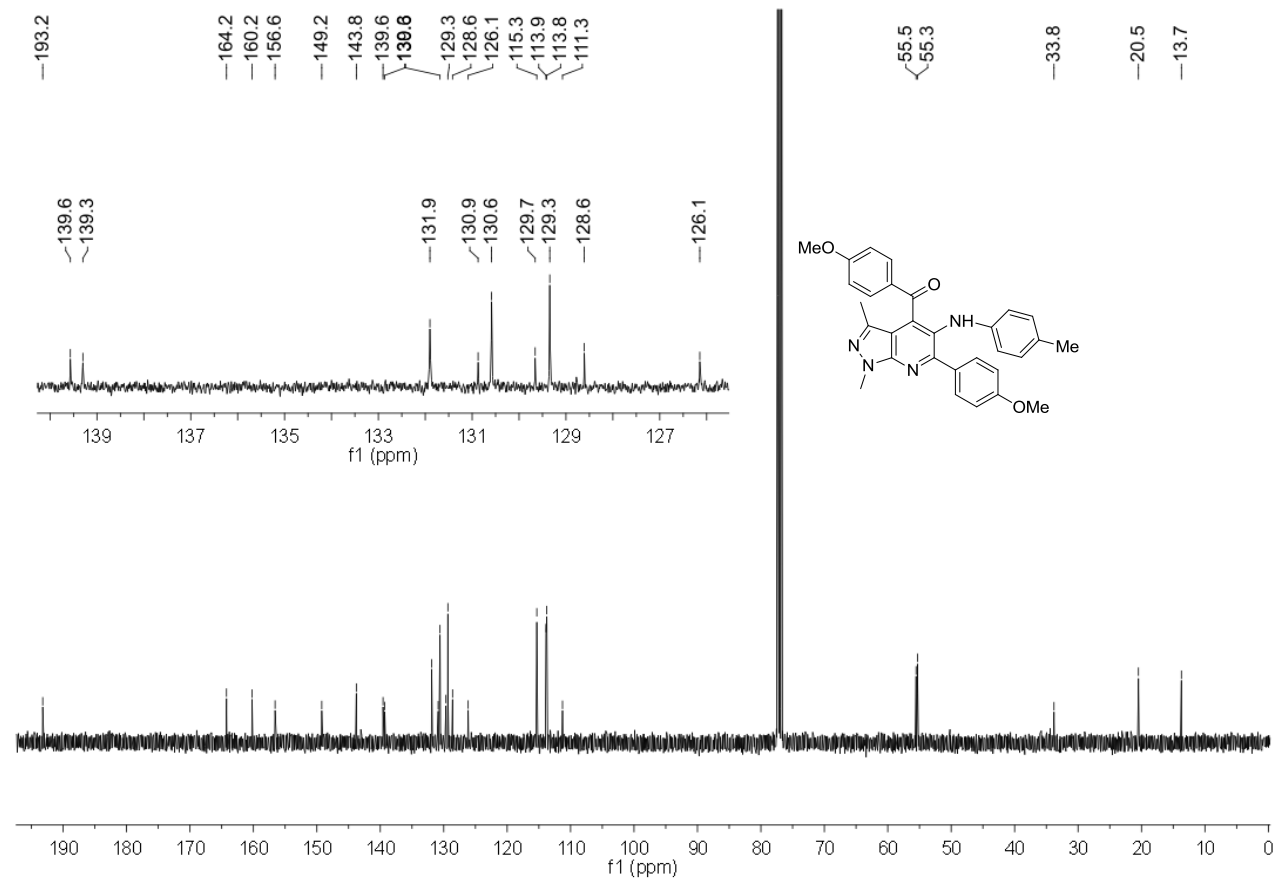
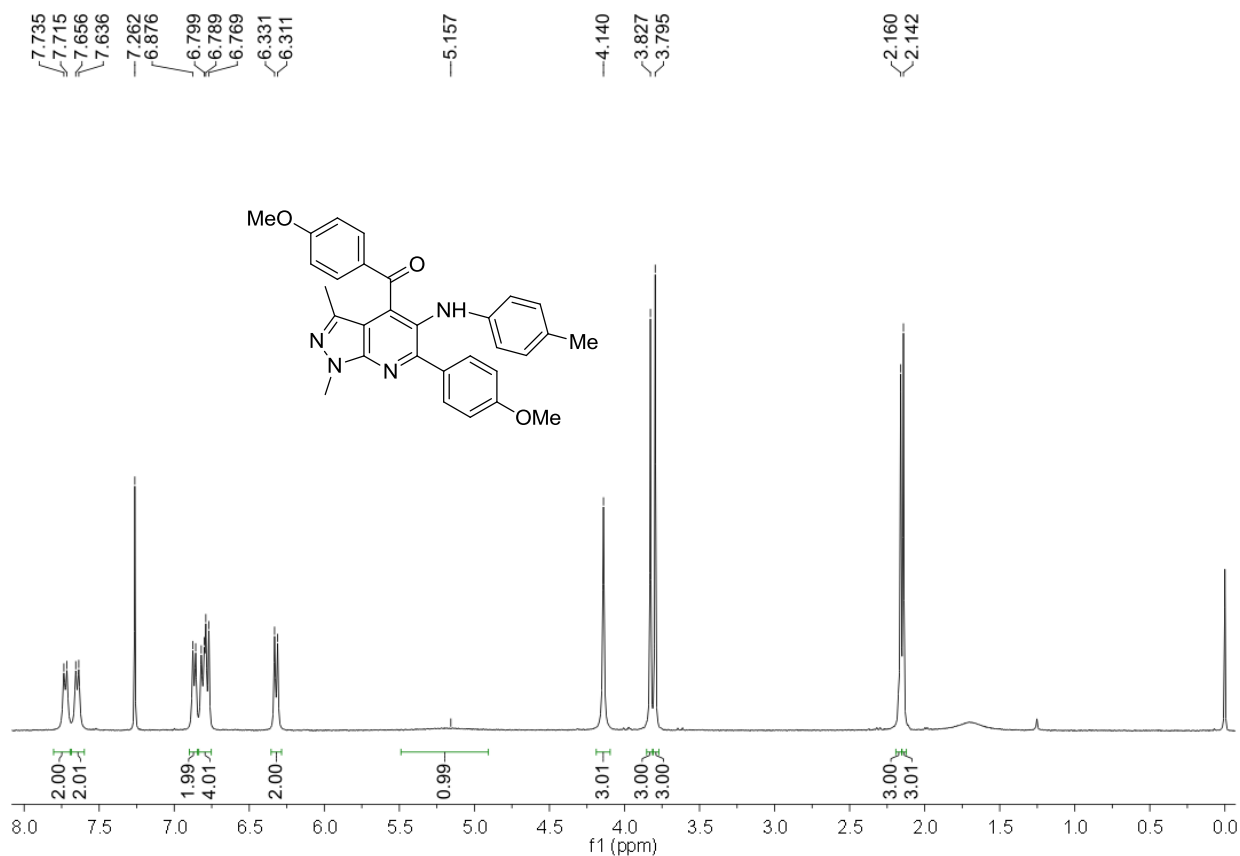


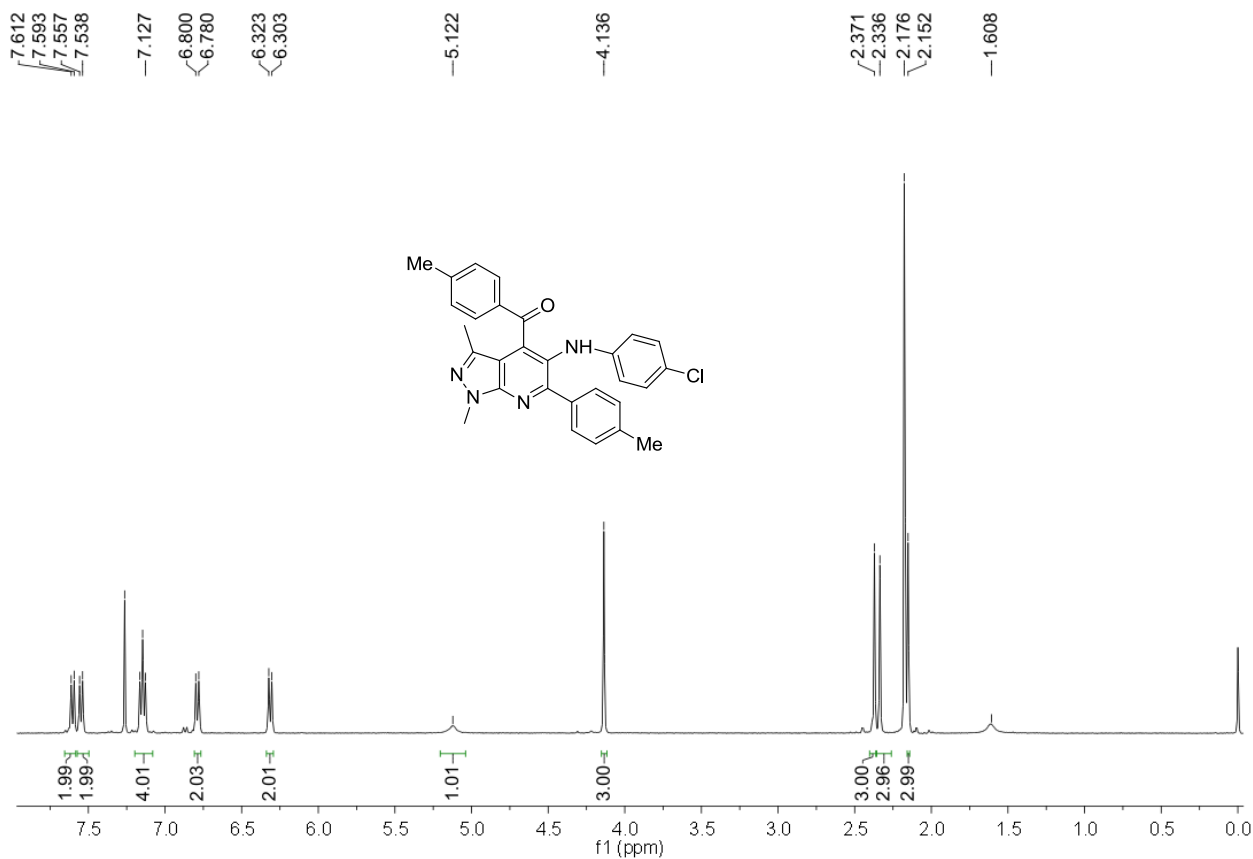
<sup>1</sup>H NMR Spectrum of Compound 5f



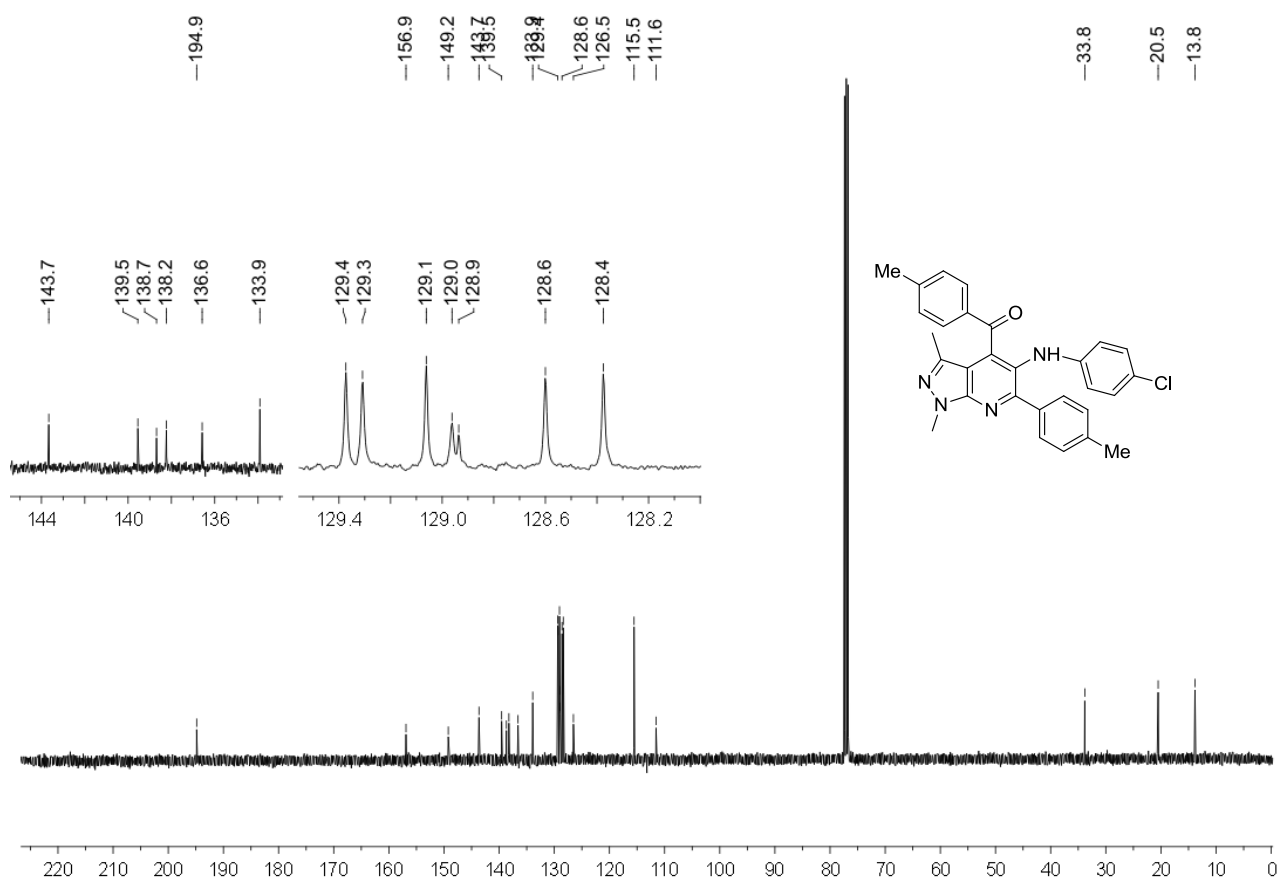
<sup>13</sup>C NMR Spectrum of Compound 5f





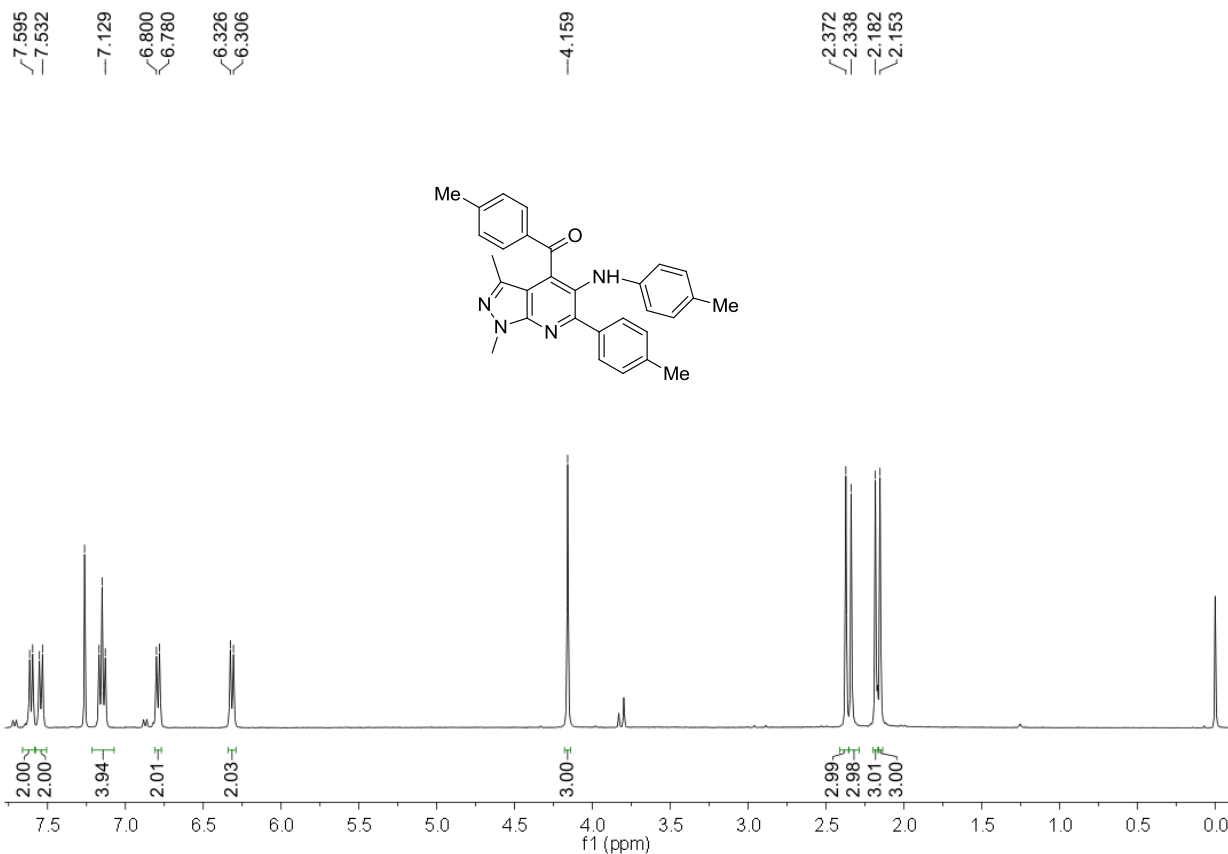


<sup>1</sup>H NMR Spectrum of Compound 5i

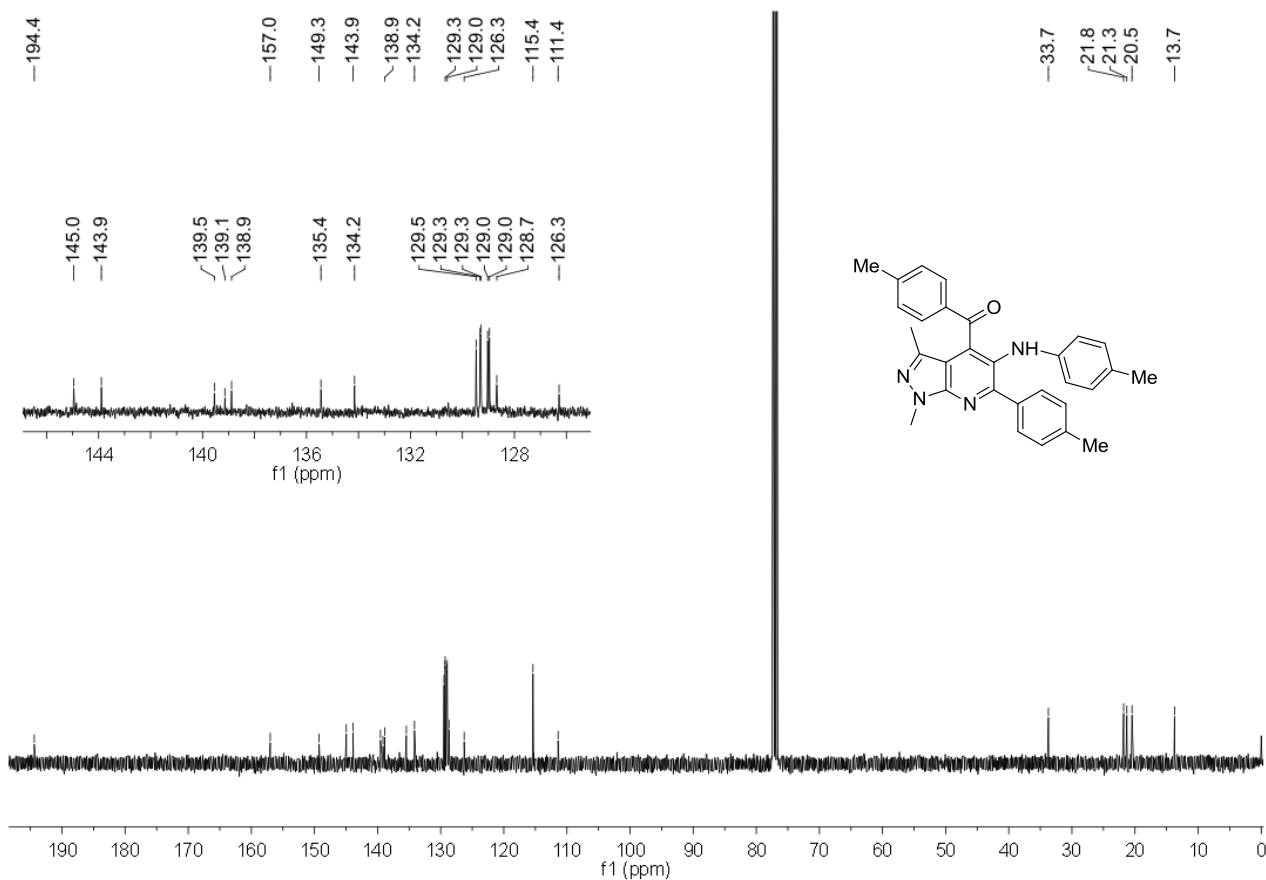


<sup>13</sup>C NMR Spectrum of Compound 5i

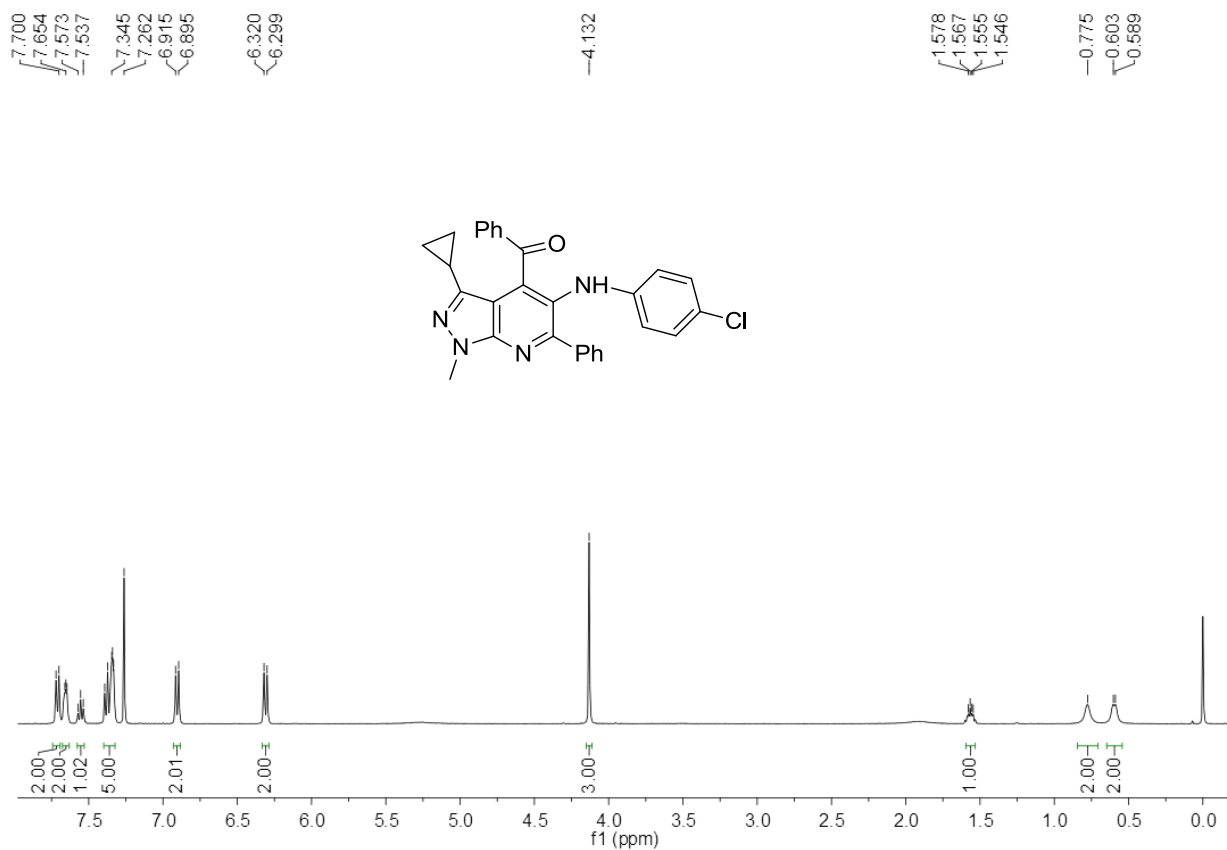




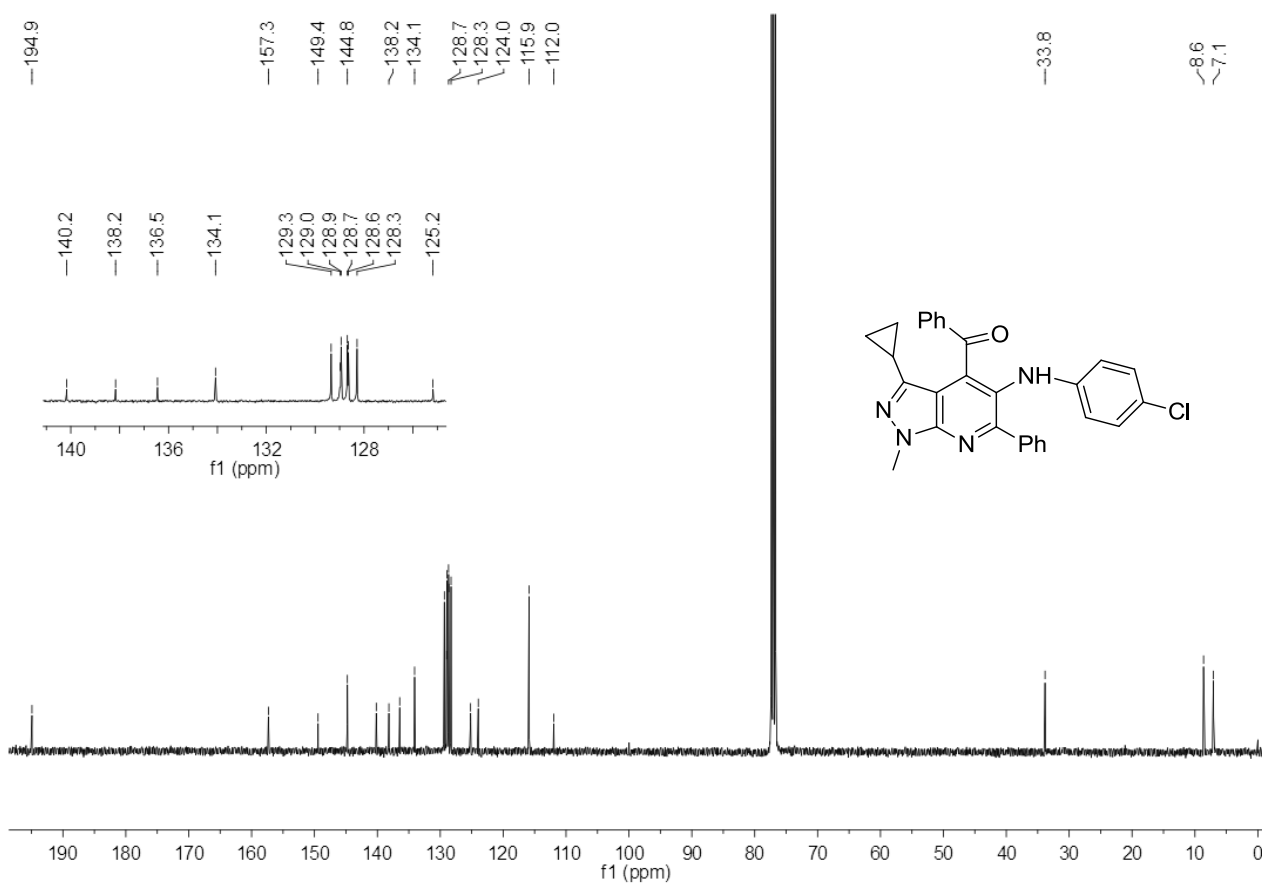
<sup>1</sup>H NMR Spectrum of Compound 5j



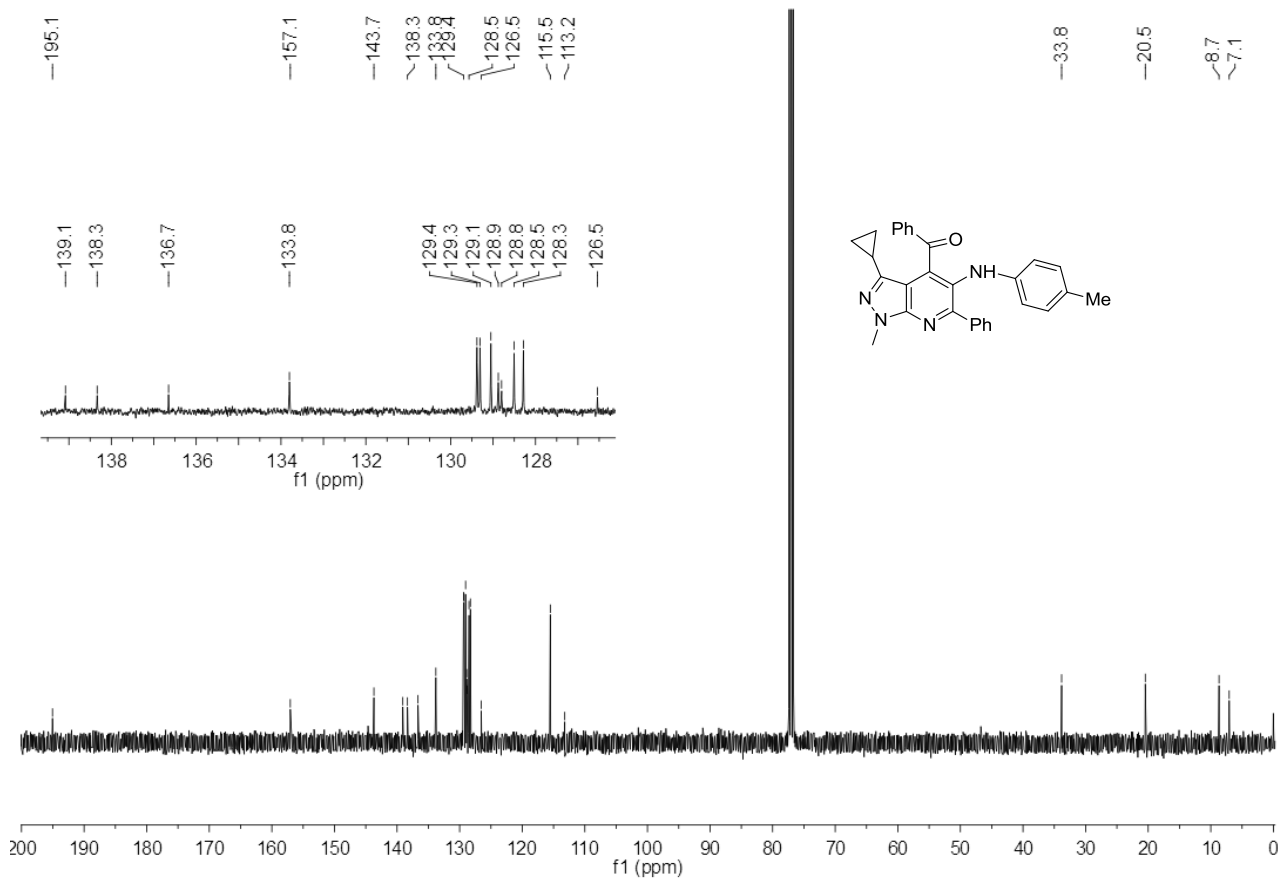
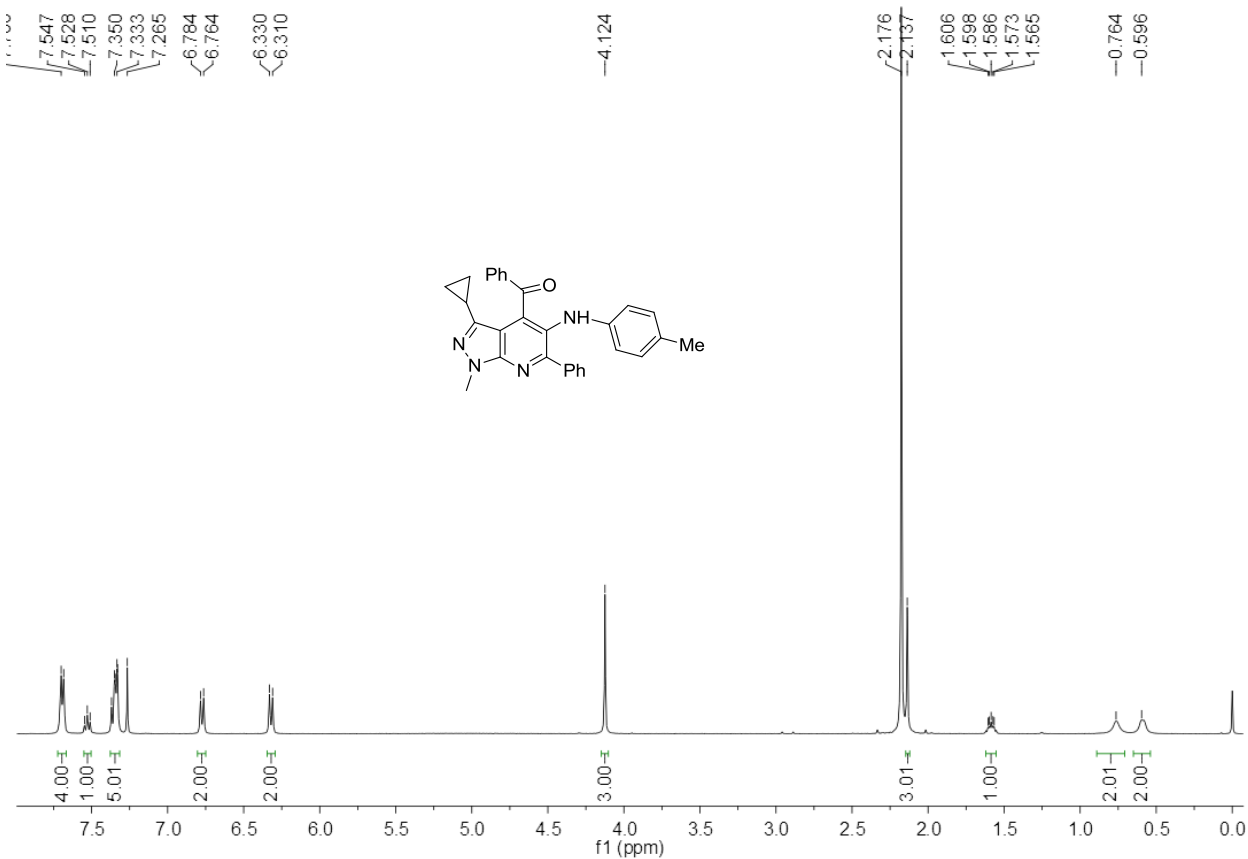
<sup>13</sup>C NMR Spectrum of Compound 5j

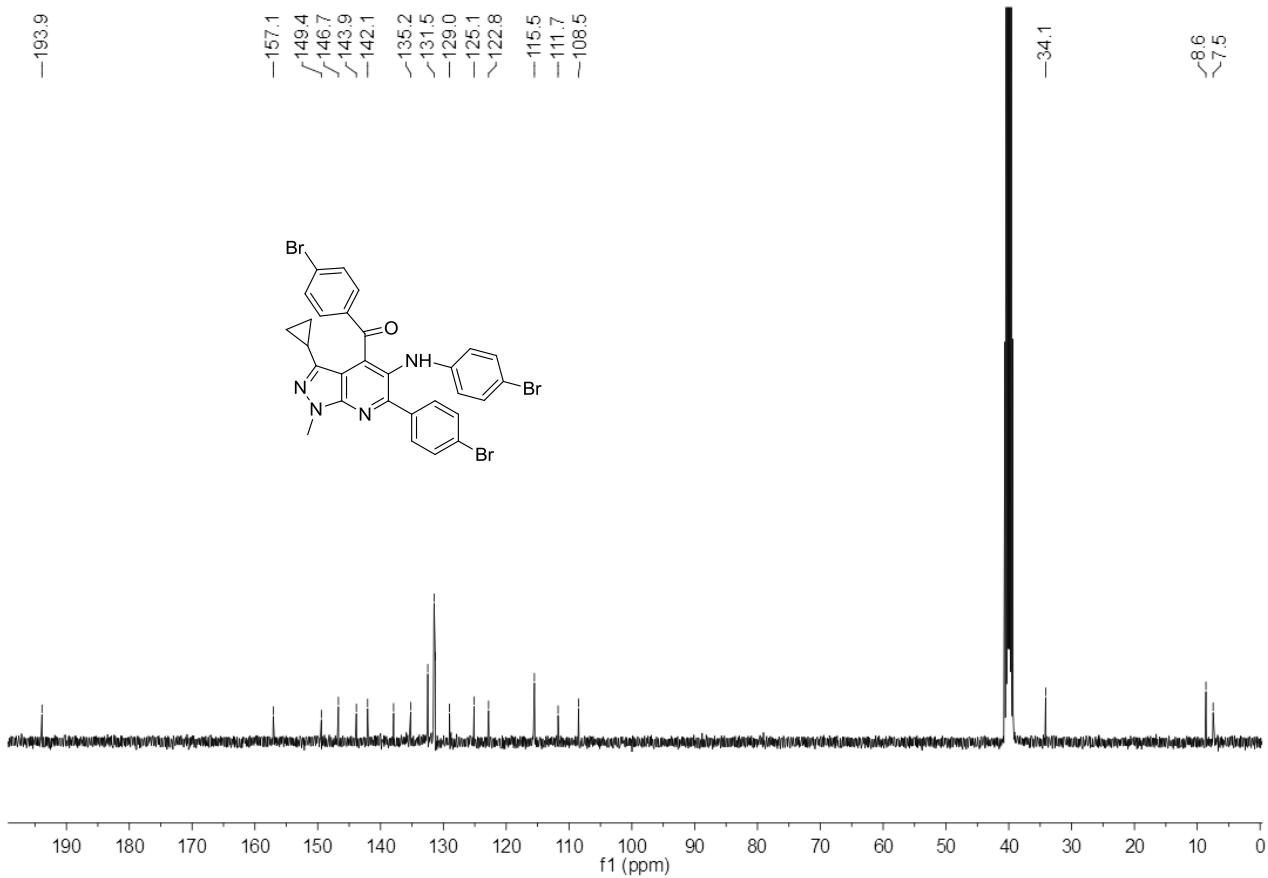
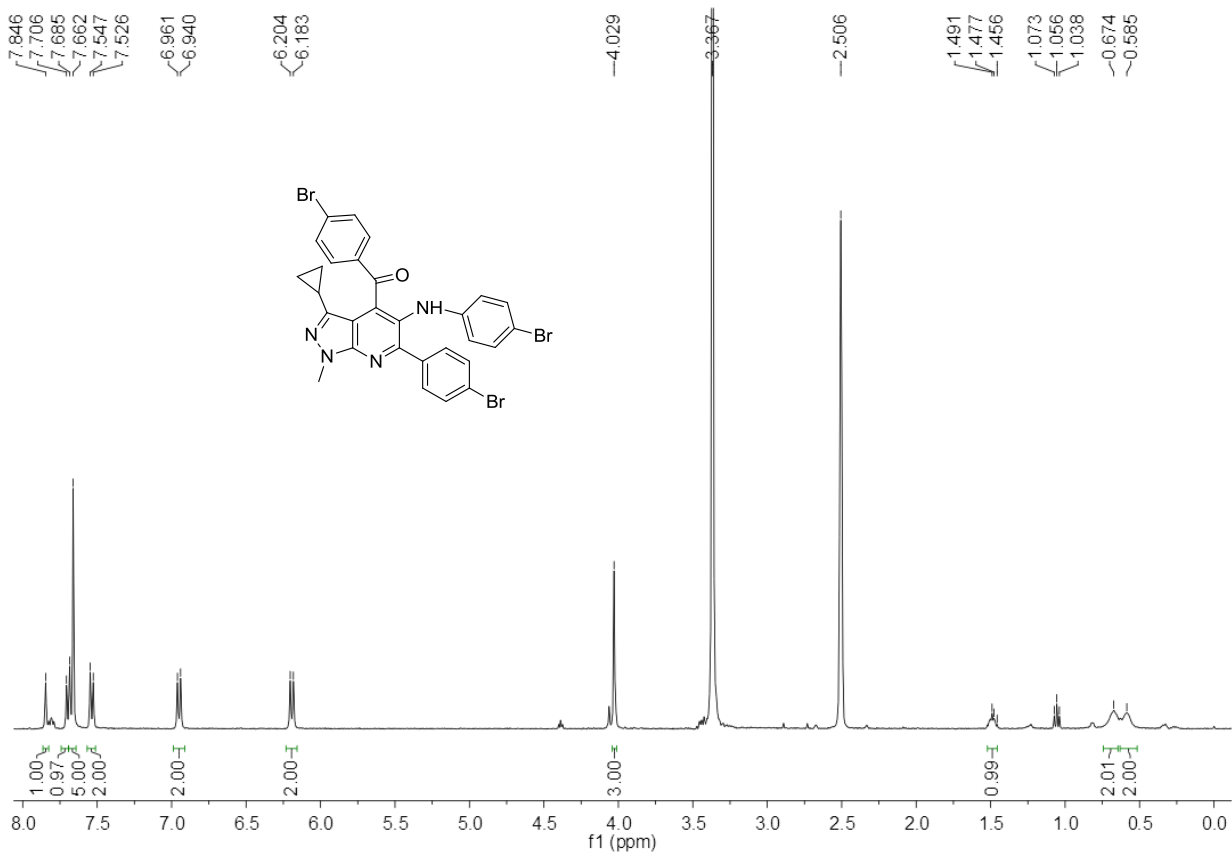


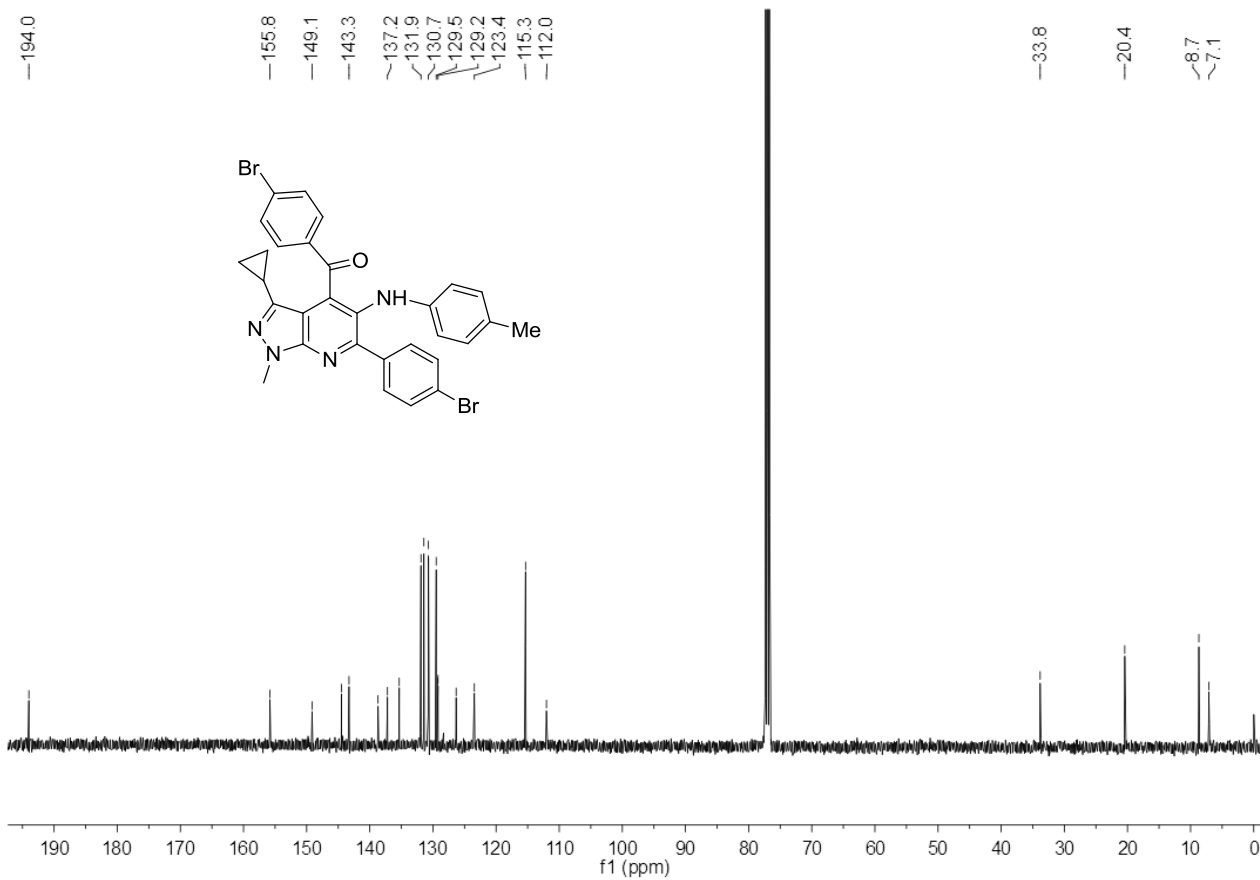
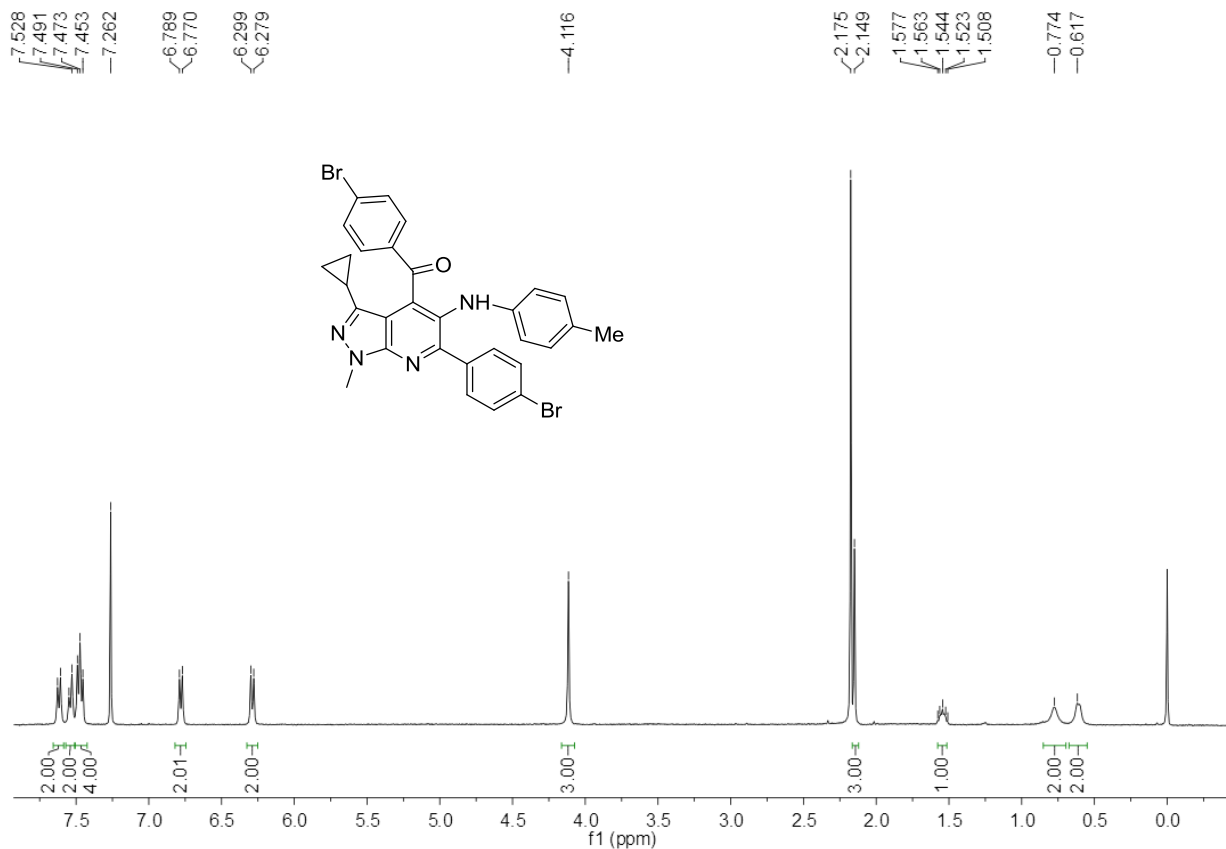
<sup>1</sup>H NMR Spectrum of Compound 5k

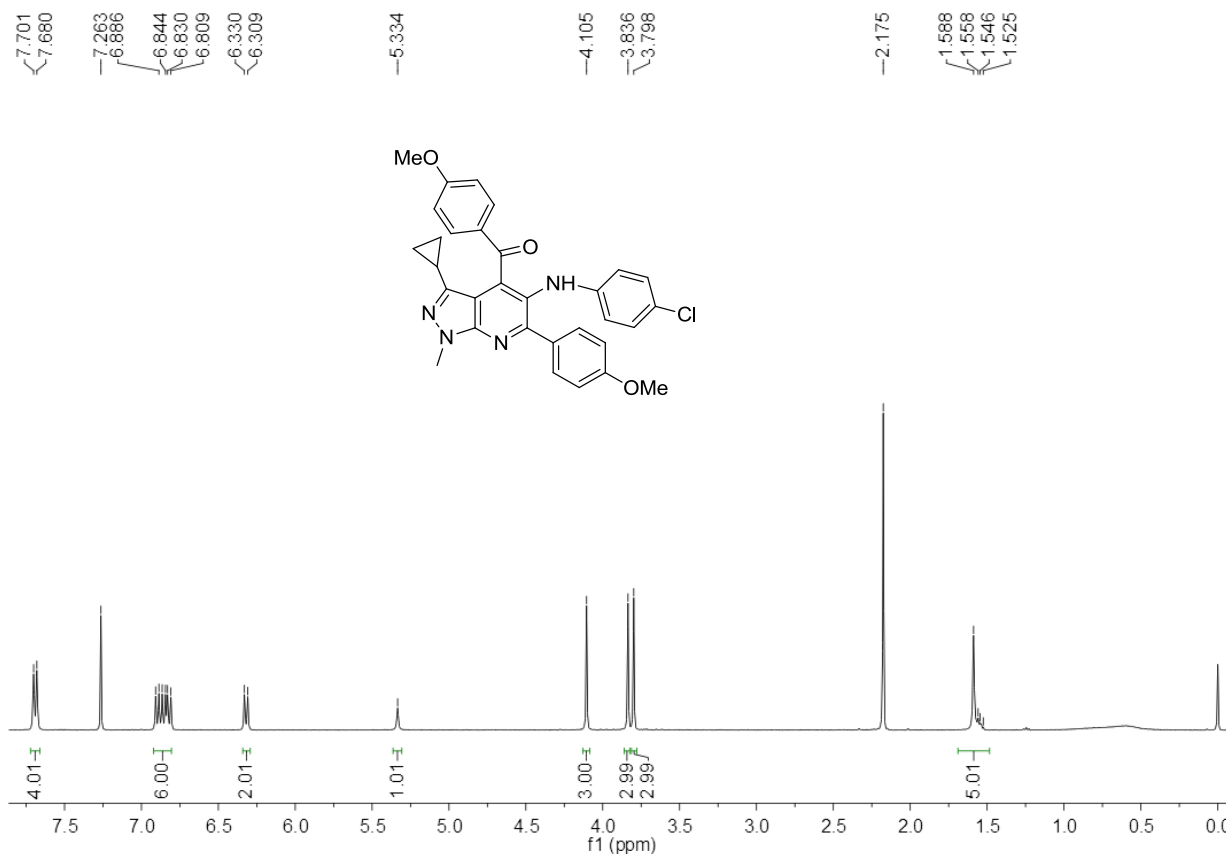


<sup>13</sup>C NMR Spectrum of Compound 5k

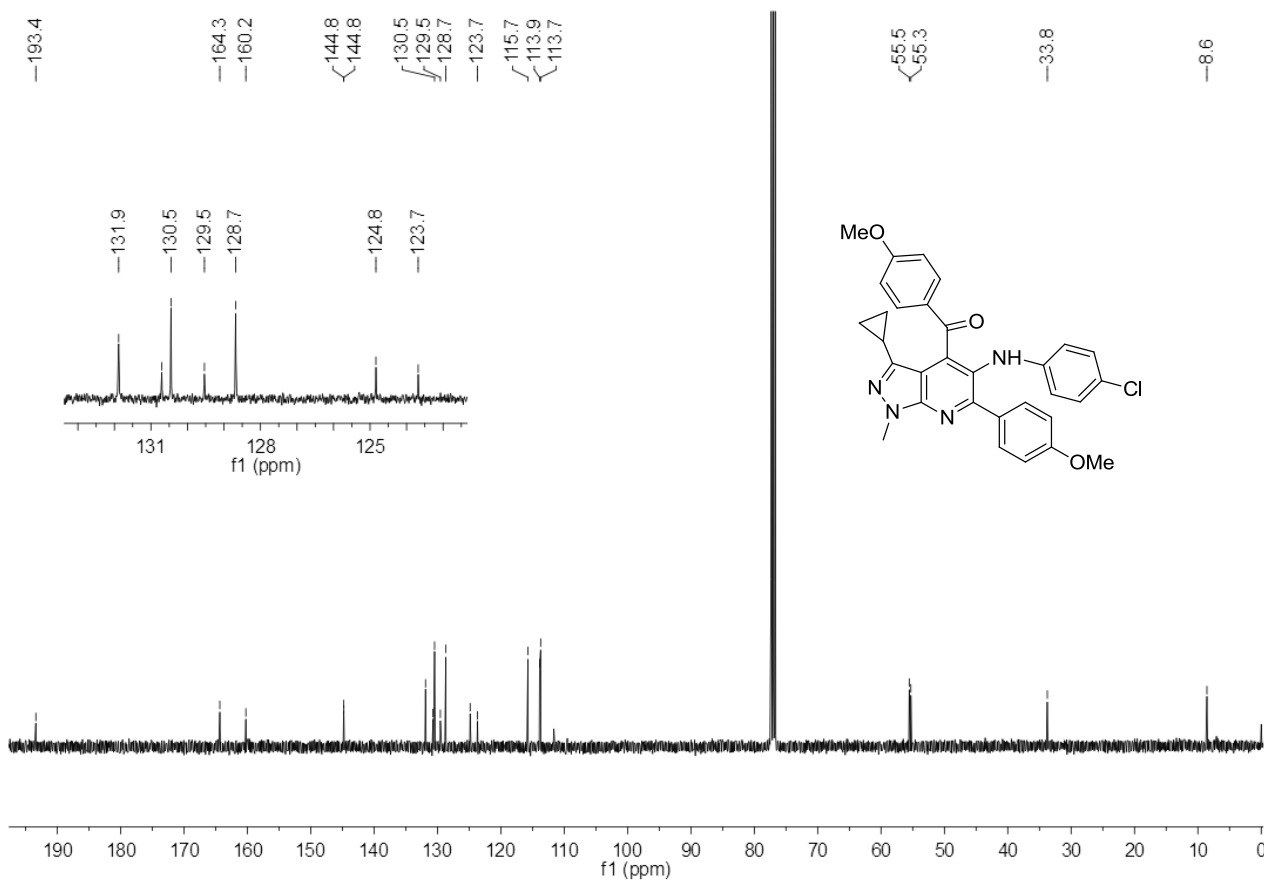








**<sup>1</sup>H NMR Spectrum of Compound 5o**



**<sup>13</sup>C NMR Spectrum of Compound 5o**

