

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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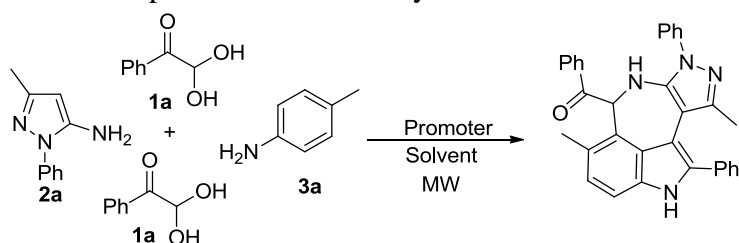
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Experimental

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 cm^{-1} . ^1H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl_3 with chemical shift (δ) 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 / % ^a
1	<i>p</i> -TsOH (1.0)	DMF	100	15	38
2	H_2SO_4 (1.0)	DMF	100	15	Trace
3	CF_3COOH (1.0)	DMF	100	15	Trace
4	FeCl_3 (1.0)	DMF	100	15	Trace
5	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)	CH_3CN	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

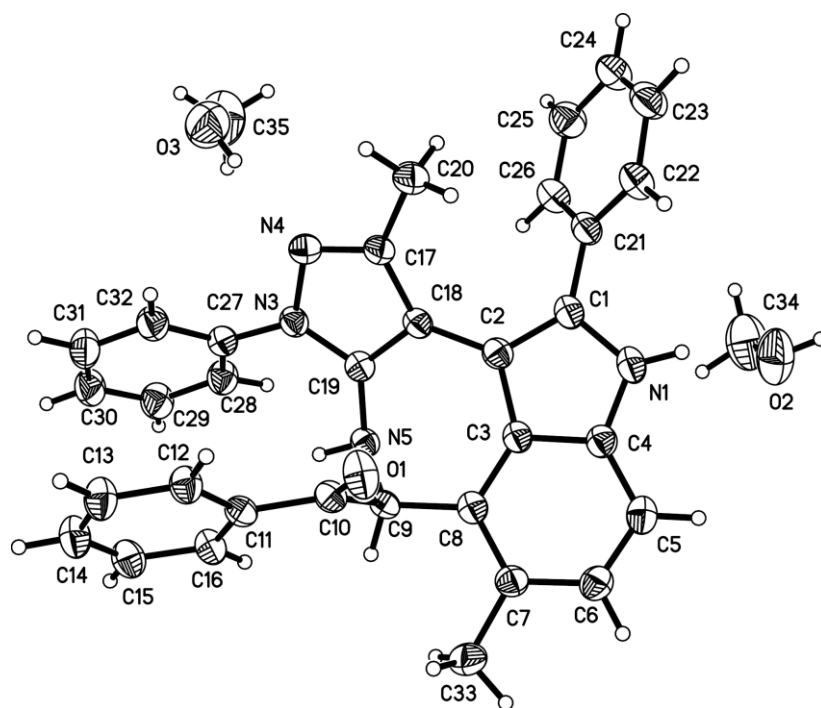


Fig. 1, X-ray Structure of 4a

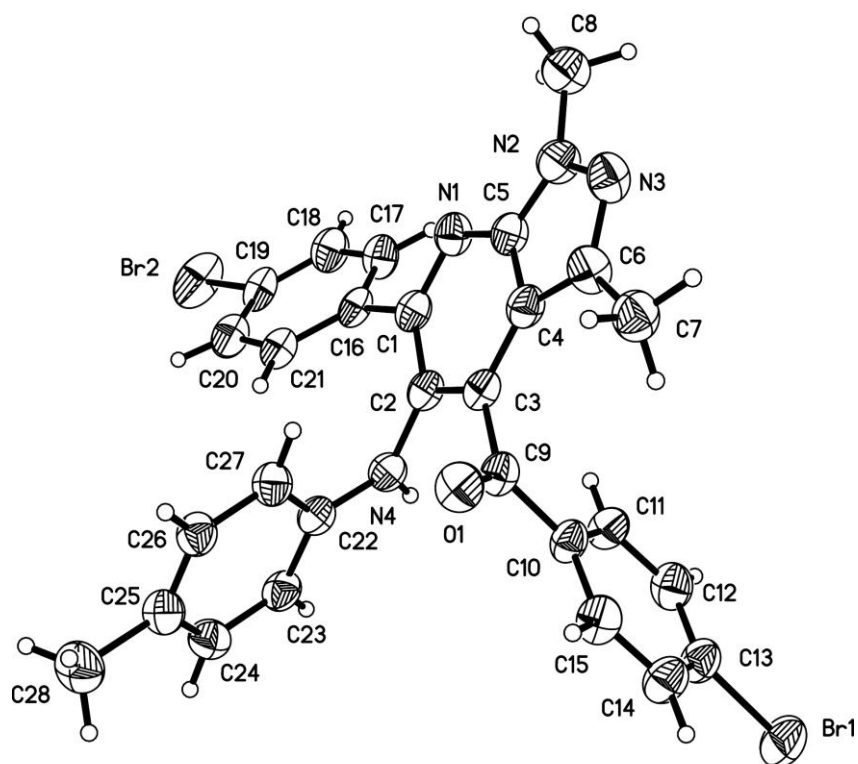


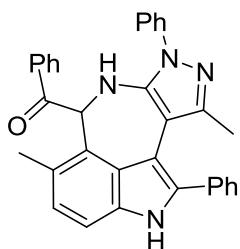
Fig. 2, X-ray Structure of 5g

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;

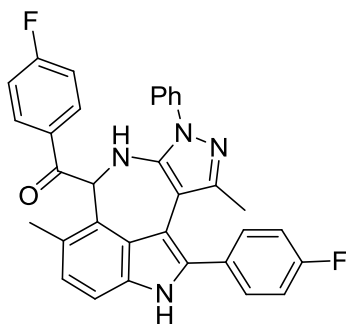
¹H NMR (400 MHz, DMSO-*d*₆) (δ, ppm): 11.31 (s, 1H, NH), 7.77 (d, *J* = 7.6 Hz, 2H, ArH), 7.57 (d, *J* = 7.6 Hz, 2H, ArH), 7.49 (t, *J* = 7.6 Hz, 2H, ArH), 7.41-7.31 (m, 2H, ArH), 7.27 (d, *J* = 8.0 Hz, 1H, ArH), 7.16-7.12 (m, 5H, ArH), 7.06 (d, *J* = 7.6 Hz, 2H, ArH), 6.94 (d, *J* = 8.0 Hz, 1H, ArH), 6.29 (d, *J* = 5.2 Hz, 1H, CH), 6.23-6.17 (m, 1H, CH), 2.17 (s, 3H, CH₃), 1.36 (s, 2H, CH₃).

¹³C NMR (100 MHz, DMSO-*d*₆) (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, ν , 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;

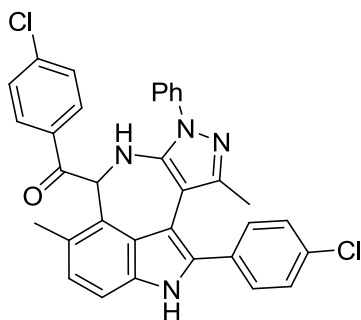
^1H NMR (400 MHz, $\text{DMSO}-d_6$) (δ , ppm): 11.29 (s, 1H, NH), 7.92-7.73 (m, 2H, ArH), 7.69-7.55 (m, 2H, ArH), 7.29-7.26 (m, 3H, ArH), 7.18-7.17 (m, 3H, ArH), 7.06 (d, $J = 7.6$ Hz, 2H, ArH), 6.94 (d, $J = 8.0$ Hz, 1H, ArH), 6.80 (t, $J = 8.4$ Hz, 2H, ArH), 6.23 (s, 2H, ArH and CH), 2.19 (s, 3H, CH_3), 1.42 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) (δ , 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, ν , 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)



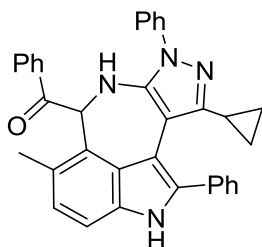
Pale yellow solid, m.p. >300 °C;

¹H NMR (400 MHz, DMSO-*d*₆) (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, CH₃), 1.42 (s, 3H, CH₃).

IR (KBr, ν, cm⁻¹): 3393, 3079, 1650, 1598, 1574, 1507, 1263, 1168, 1028, 755, 690.

HRMS (ESI): *m/z* calcd for: C₃₃H₂₃Cl₂N₄O, 561.1249 [M-H]⁻, 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;

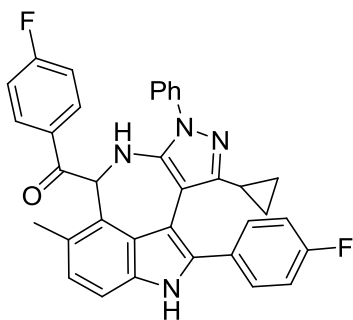
¹H NMR (400 MHz, DMSO-*d*₆) (δ, ppm): 11.28 (s, 1H, NH), 7.76 (d, *J* = 8.0 Hz, 2H, ArH), 7.60 (d, *J* = 7.6 Hz, 2H, ArH), 7.46 (t, *J* = 7.6 Hz, 2H, ArH), 7.34 (t, *J* = 6.4 Hz, 2H, ArH), 7.28 (d, *J* = 8.4 Hz, 1H, ArH), 7.18-7.08 (m, 5H, ArH), 7.03 (d, *J* = 7.6 Hz, 2H, ArH), 6.94 (d, *J* = 8.4 Hz, 1H, ArH), 6.27 (d, *J* = 5.2 Hz, 1H, NH), 6.22 (d, *J* = 5.2 Hz, 1H, CH), 2.18 (s, 3H, CH₃), 0.96-0.84 (m, 1H, CH), 0.66-0.61 (m, 1H, CH₂), 0.41 (t, *J* = 6.4 Hz, 2H, CH₂), -0.12 (t, *J* = 7.2 Hz, 1H, CH₂).

¹³C NMR (100 MHz, DMSO-*d*₆) (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⁻¹): 3393, 3151, 3073, 3007, 1597, 1519, 1504, 1102, 763, 689.

HRMS (ESI): *m/z* calcd for: C₃₅H₂₇N₄O, 519.2185 [M-H]⁻, 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;

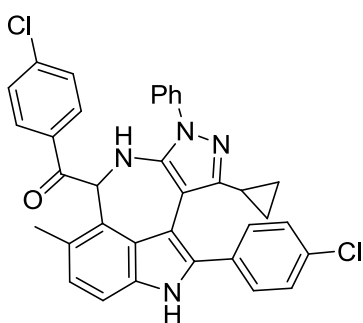
^1H NMR (400 MHz, DMSO- d_6) (δ , ppm): 11.33 (s, 1H, NH), 7.81-7.77 (m, 2H, ArH), 7.62-7.59 (m, 2H, ArH), 7.36-7.25 (m, 3H, ArH), 7.17 (d, $J = 6.4$ Hz, 3H, ArH), 7.04 (d, $J = 7.6$ Hz, 2H, ArH), 6.95 (d, $J = 8.0$ Hz, 1H, ArH), 6.85 (t, $J = 8.4$ Hz, 2H, ArH), 6.29-6.17 (m, 2H, ArH and CH), 2.18 (s, 3H, CH₃), 0.98-0.86 (m, 1H, CH), 0.70-0.65 (m, 1H, CH₂), 0.47-0.42 (m, 2H, CH₂), -0.04--0.1 (m, 1H, CH₂).

^{13}C NMR (100 MHz, DMSO- d_6) (δ , 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, ν , cm^{-1}): 3391, 3126, 3078, 1597, 1573, 1506, 1407, 1230, 837, 752.

HRMS (ESI): m/z calcd for: C₃₅H₂₅F₂N₄O, 555.1997 [M-H]⁻, 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;

^1H NMR (400 MHz, DMSO- d_6) (δ , 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, CH₃), 0.99-0.79 (m, 1H, CH), 0.69 (d, $J = 4.8$ Hz, 1H, CH₂),

0.49-0.43 (m, 2H, CH₂), -0.07 (d, *J* = 6.4 Hz, 1H, CH₂).

IR (KBr, ν , cm⁻¹): 3439, 3110, 3076, 3013, 1596, 1579, 1520, 1246, 1092, 961, 831.

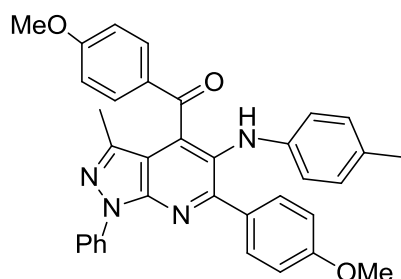
HRMS (ESI): *m/z* calcd for: C₃₅H₂₅Cl₂N₄O, 587.1406 [M-H]⁻, found: 587.1219.

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 InitiatorTM 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;

¹H NMR (400 MHz, CDCl₃) (δ , 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, OCH₃), 3.81 (s, 3H, OCH₃), 2.25 (s, 3H, CH₃), 2.16 (s, 3H, CH₃).

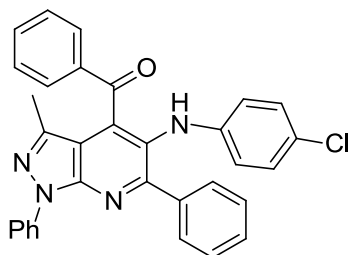
¹³C NMR (100 MHz, CDCl₃) (δ , ppm): 192.9, 164.3, 160.3, 156.2, 148.7, 143.4, 141.7, 139.6, 139.2, 131.9, 130.8, 130.7, 129.6, 129.4, 129.4, 129.0, 128.9, 127.0, 125.4, 120.5, 115.5, 113.9,

113.7, 55.5, 55.3, 20.5, 13.9.

IR (KBr, ν , 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;

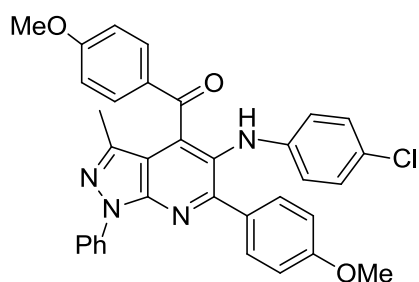
^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.36 (d, $J = 8.0$ Hz, 2H, ArH), 7.73-7.69 (m, 4H, ArH), 7.58 (t, $J = 7.6$ Hz, 1H, ArH), 7.51 (t, $J = 7.6$ Hz, 2H, ArH), 7.42-7.35 (m, 4H, ArH), 7.30 (d, $J = 7.2$ Hz, 2H, ArH), 6.94 (d, $J = 8.4$ Hz, 2H, ArH), 6.34 (d, $J = 8.7$ Hz, 2H, ArH), 5.29 (s, 1H, NH), 2.27 (s, 3H, CH_3).

^{13}C NMR (100 MHz, CDCl_3) (δ , 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, ν , 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;

^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.36 (d, $J = 8.0$ Hz, 2H, ArH), 7.77 (d, $J = 8.4$ Hz, 2H, ArH),

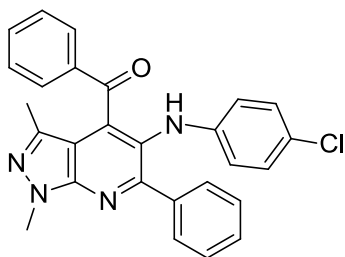
7.69 (d, $J = 8.4$ Hz, 2H, ArH), 7.51 (t, $J = 7.6$ Hz, 2H, ArH), 7.29 (d, $J = 7.2$ Hz, 1H, ArH), 6.93 (d, $J = 8.4$ Hz, 2H, ArH), 6.89-6.83 (m, 4H, ArH), 6.35 (d, $J = 8.8$ Hz, 2H, ArH), 5.35 (s, 1H, NH) 3.84 (s, 3H, OCH₃), 3.81 (s, 3H, OCH₃), 2.24 (s, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃) (δ , 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, ν , cm⁻¹): 3373, 1650, 1598, 1573, 1507, 1421, 1168, 1028, 756, 690.

HRMS (ESI): m/z calcd for: C₃₄H₂₆ClN₄O₃, 573.1694 [M-H]⁻, 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;

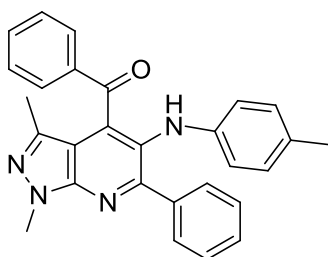
¹H NMR (400 MHz, CDCl₃) (δ , ppm): 7.68-7.66 (m, 4H, ArH), 7.56 (t, $J = 7.2$ Hz, 1H, ArH), 7.40-7.38 (m, 5H, ArH), 6.92 (d, $J = 8.0$ Hz, 2H, ArH), 6.30 (d, $J = 8.4$ Hz, 2H, ArH), 5.22 (s, 1H, CH), 4.17 (s, 3H, CH₃), 2.19 (s, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃) (δ , 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, ν , cm⁻¹): 3378, 1604, 1593, 1543, 1325, 1172, 1011, 844, 771, 687, 563.

HRMS (ESI): m/z calcd for: C₂₇H₂₀ClN₄O, 451.1326 [M-H]⁻, 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;

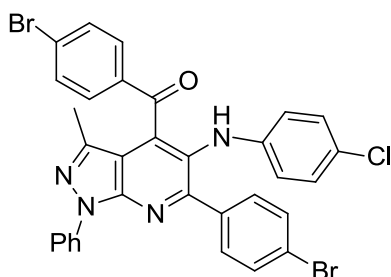
¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.72-7.68 (m, 2H, ArH), 7.64 (d, *J* = 7.6 Hz, 2H, ArH), 7.54 (t, *J* = 7.2 Hz, 1H, ArH), 7.37-7.33 (m, 5H, ArH), 7.26 (s, 1H, ArH), 6.79 (d, *J* = 8.0 Hz, 2H, ArH), 6.30 (d, *J* = 8.0 Hz, 2H, ArH), 4.17 (s, 3H, CH₃), 2.19 (s, 3H, CH₃), 2.15 (s, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃) (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⁻¹): 3381, 1655, 1575, 1519, 1364, 1263, 1209, 960, 871, 701, 670.

HRMS (ESI): *m/z* calcd for: C₂₈H₂₃N₄O, 431.1872 [M-H]⁻, 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;

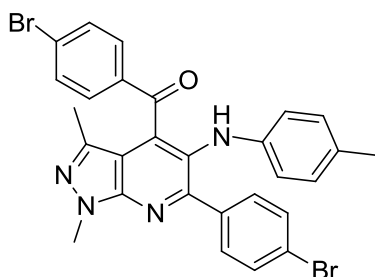
¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.57 (d, *J* = 8.0 Hz, 2H, ArH), 7.54-7.45 (m, 5H, ArH), 7.26 (s, 1H, ArH), 6.95 (d, *J* = 8.4 Hz, 2H, ArH), 6.29 (d, *J* = 8.4 Hz, 2H, ArH), 5.20 (s, 1H, NH), 4.15 (s, 3H, CH₃), 2.18 (s, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃) (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⁻¹): 3386, 1669, 1581, 1543, 1268, 1201, 1087, 987, 815, 798, 698.

HRMS (ESI): *m/z* calcd for: C₂₇H₁₈Br₂ClN₄O, 608.9516 [M-H]⁻, 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;

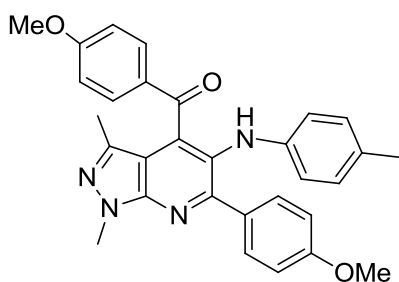
¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.61 (d, *J* = 8.0 Hz, 2H, ArH), 7.49 (s, 5H, ArH), 7.47 (s, 1H, ArH), 6.79 (d, *J* = 8.0 Hz, 2H, ArH), 6.27 (d, *J* = 8.0 Hz, 2H, ArH), 5.14 (s, 1H, NH), 4.15 (s, 3H, CH₃), 2.18 (s, 3H, CH₃), 2.16 (s, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃) (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⁻¹): 3374, 1666, 1583, 1513, 1347, 1258, 1205, 1070, 1009, 812, 798.

HRMS (ESI): *m/z* calcd for: C₂₈H₂₁Br₂N₄O, 589.0062 [M-H]⁻, 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;

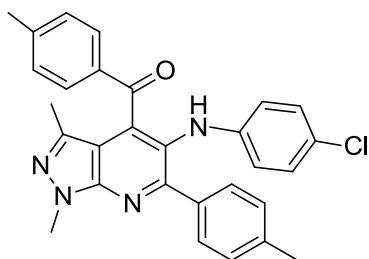
¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.73 (d, *J* = 8.0 Hz, 2H, NH), 7.65 (d, *J* = 8.0 Hz, 2H, ArH), 6.87 (d, *J* = 7.6 Hz, 2H, ArH), 6.82-6.77 (m, 4H, ArH), 6.32 (d, *J* = 8.0 Hz, 2H, ArH), 5.16 (s, 1H, CH) 4.14 (s, 3H, CH₃), 3.83 (s, 3H), 3.80 (s, 3H, OCH₃), 2.16 (s, 3H, OCH₃), 2.14 (s, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃) (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⁻¹): 3373, 1657, 1602, 1515, 1264, 1166, 1029, 963, 814, 777, 615.

HRMS (ESI): *m/z* calcd for: C₃₀H₂₇N₄O₃, 491.2083 [M-H]⁻, 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;

^1H NMR (400 MHz, CDCl_3) (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_3), 2.37 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.15 (s, 3H, CH_3).

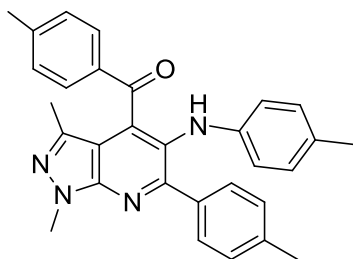
^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 194.9, 156.9, 149.2, 143.7, 139.6, 138.7, 138.2, 136.6, 133.9, 129.4, 129.3, 129.1, 129.0, 128.9, 128.6, 128.4, 126.5, 115.5, 111.6, 33.8, 20.5, 13.8.

IR (KBr, ν , cm^{-1}): 3389, 1661, 1576, 1498, 1254, 1386, 1109, 987, 762, 683.

HRMS (ESI): m/z calcd for: $\text{C}_{29}\text{H}_{24}\text{ClN}_4\text{O}$, 479.1639 $[\text{M}-\text{H}]^-$, found: 479.1641.

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

(5j)



Yellow solid, m.p. 248-249 °C;

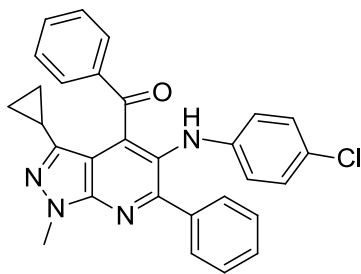
^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.61 (d, $J = 7.6$ Hz, 2H, NH), 7.54 (d, $J = 7.6$ Hz, 2H, ArH), 7.15 (t, $J = 8.0$ Hz, 4H, ArH), 6.79 (d, $J = 8.0$ Hz, 2H, ArH), 6.32 (d, $J = 8.0$ Hz, 2H, ArH), 4.16 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.15 (s, 3H, CH_3).

^{13}C NMR (100 MHz, CDCl_3) (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^{-1}): 3371, 1664, 1589, 1514, 1348, 1229, 1001, 876, 698, 651.

HRMS (ESI): m/z calcd for: $\text{C}_{30}\text{H}_{27}\text{N}_4\text{O}$, 459.2185 $[\text{M}-\text{H}]^-$, 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;

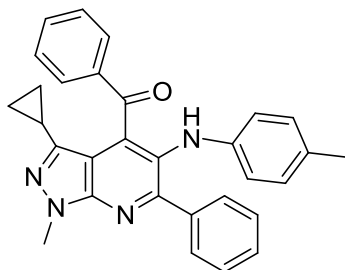
¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.71 (d, *J* = 8.0 Hz, 2H, ArH), 7.68-7.64 (m, 2H, ArH), 7.55 (t, *J* = 7.2 Hz, 1H, ArH), 7.41-7.31 (m, 5H, ArH), 6.91 (d, *J* = 8.4 Hz, 2H, ArH), 6.31 (d, *J* = 8.4 Hz, 2H, ArH), 4.13 (s, 3H, CH₃), 1.58-1.55 (m, 1H, CH), 0.78 (s, 2H, CH₂), 0.60 (d, *J* = 5.6 Hz, 2H, CH₂).

¹³C NMR (101 MHz, CDCl₃) (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⁻¹): 3383, 1663, 1596, 1576, 1497, 1321, 1208, 1089, 817, 726, 699.

HRMS (ESI): *m/z* calcd for: C₂₉H₂₂ClN₄O, 477.1482 [M-H]⁻, 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;

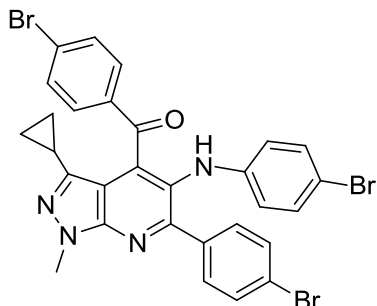
¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.69 (d, *J* = 6.8 Hz, 4H, ArH), 7.53 (t, *J* = 7.6 Hz, 1H, ArH), 7.37-7.33 (m, 5H, ArH), 6.77 (d, *J* = 8.0 Hz, 2H, ArH), 6.32 (d, *J* = 8.4 Hz, 2H, ArH), 4.12 (s, 3H, CH₃), 2.14 (s, 1H), 1.67-1.51 (m, 1H, CH), 0.76 (s, 2H, CH₂), 0.60 (s, 2H, CH₂).

¹³C NMR (100 MHz, CDCl₃) (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⁻¹): 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;

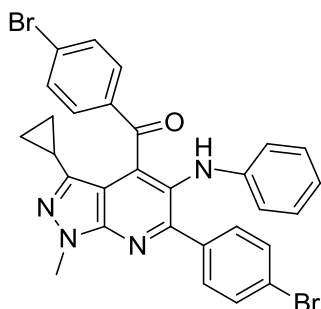
1H NMR (400 MHz, $DMSO-d_6$) (δ , ppm): 7.85 (s, 1H, NH), 7.71 (s, 1H, ArH), 7.69-7.66 (m, 5H, ArH), 7.54 (d, $J = 8.0$ Hz, 2H, ArH), 6.95 (d, $J = 8.4$ Hz, 2H, ArH), 6.19 (d, $J = 8.4$ Hz, 2H, ArH), 4.03 (s, 3H, CH_3), 1.70-1.27 (m, 1H, CH), 0.67 (s, 2H, CH_2), 0.59 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $DMSO-d_6$) (δ , 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, ν , 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;

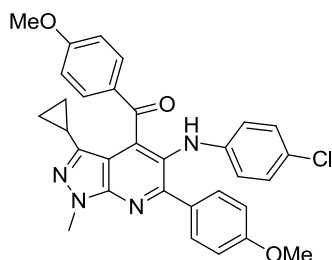
1H NMR (400 MHz, $CDCl_3$) (δ , ppm): 7.62 (d, $J = 8.0$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.47 (t, $J = 7.6$ Hz, 4H), 6.78 (d, $J = 8.0$ Hz, 2H), 6.29 (d, $J = 8.0$ Hz, 2H), 4.12 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 1.64-1.30 (m, 1H, CH), 0.77 (s, 2H, CH_2), 0.62 (s, 2H, CH_2).

^{13}C NMR (100 MHz, CDCl_3) (δ , 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, ν , 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;

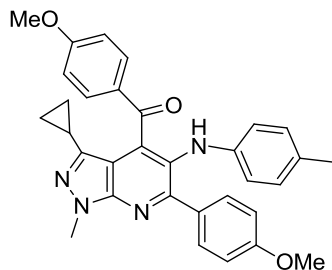
^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.69 (d, $J = 8.4$ Hz, 4H, ArH), 7.10-6.75 (m, 6H, ArH), 6.32 (d, $J = 8.4$ Hz, 2H, ArH), 5.33 (s, 1H, NH), 4.10 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 1.75-1.31 (m, 5H, CH and CH_2).

^{13}C NMR (100 MHz, CDCl_3) (δ , 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, ν , 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;

^1H NMR (400 MHz, CDCl_3) (δ , 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, CH_3), 3.83 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 2.13 (s,

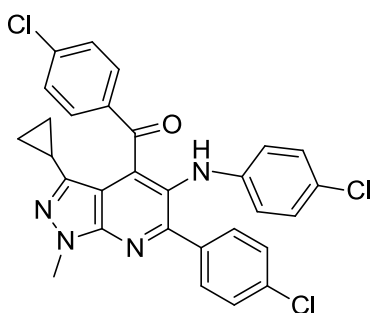
3H, CH₃), 1.76-1.28 (m, 1H, CH), 0.60 (s, 4H, CH₂).

¹³C NMR (100 MHz, CDCl₃) (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⁻¹): 3366, 1651, 1600, 1575, 1516, 1258, 1164, 1034, 806, 776, 639.

HRMS (ESI): m/z calcd for: C₃₂H₂₉N₄O₃, 517.2240 [M-H]⁻, 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;

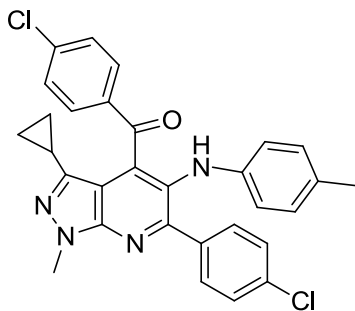
¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.65 (s, 4H, ArH), 7.43-7.30 (m, 4H, ArH), 6.93 (d, *J* = 7.6 Hz, 2H, ArH), 6.31 (d, *J* = 7.6 Hz, 2H, ArH), 5.30 (s, 1H, NH), 4.13 (s, 3H, CH₃), 1.23 (s, 1H, CH), 0.88-0.79 (m, 2H, CH₂), 0.62 (s, 2H, CH₂).

¹³C NMR (100 MHz, CDCl₃) (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⁻¹): 3375, 1664, 1587, 1497, 1361, 1371, 2091, 1091, 1014, 816, 764.

HRMS (ESI): m/z calcd for: C₂₉H₂₀Cl₃N₄O, 545.0703 [M-H]⁻, 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;

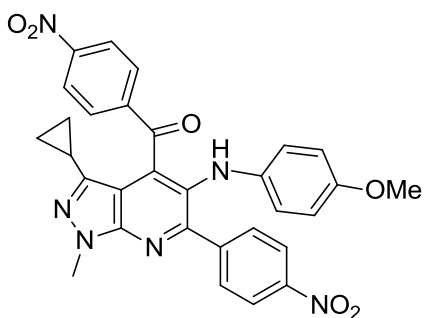
¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.69 (d, *J* = 8.4 Hz, 2H, ArH), 7.62 (d, *J* = 8.4 Hz, 2H, ArH), 7.33-7.30 (m, 4H, ArH), 7.26 (s, 1H, ArH), 6.78 (d, *J* = 8.0 Hz, 2H, ArH), 6.29 (d, *J* = 8.0 Hz, 2H, ArH), 4.12 (s, 3H, CH₃), 2.15 (s, 3H, CH₃), 1.59-1.46 (m, 1H, CH), 0.78 (s, 2H, CH₂), 0.62 (s, 2H, CH₂).

¹³C NMR (100 MHz, CDCl₃) (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⁻¹): 3380, 1666, 1587, 1514, 1306, 1091, 1014, 957, 811.

HRMS (ESI): *m/z* calcd for: C₃₀H₂₃Cl₂N₄O, 525.1249 [M-H]⁻, 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)



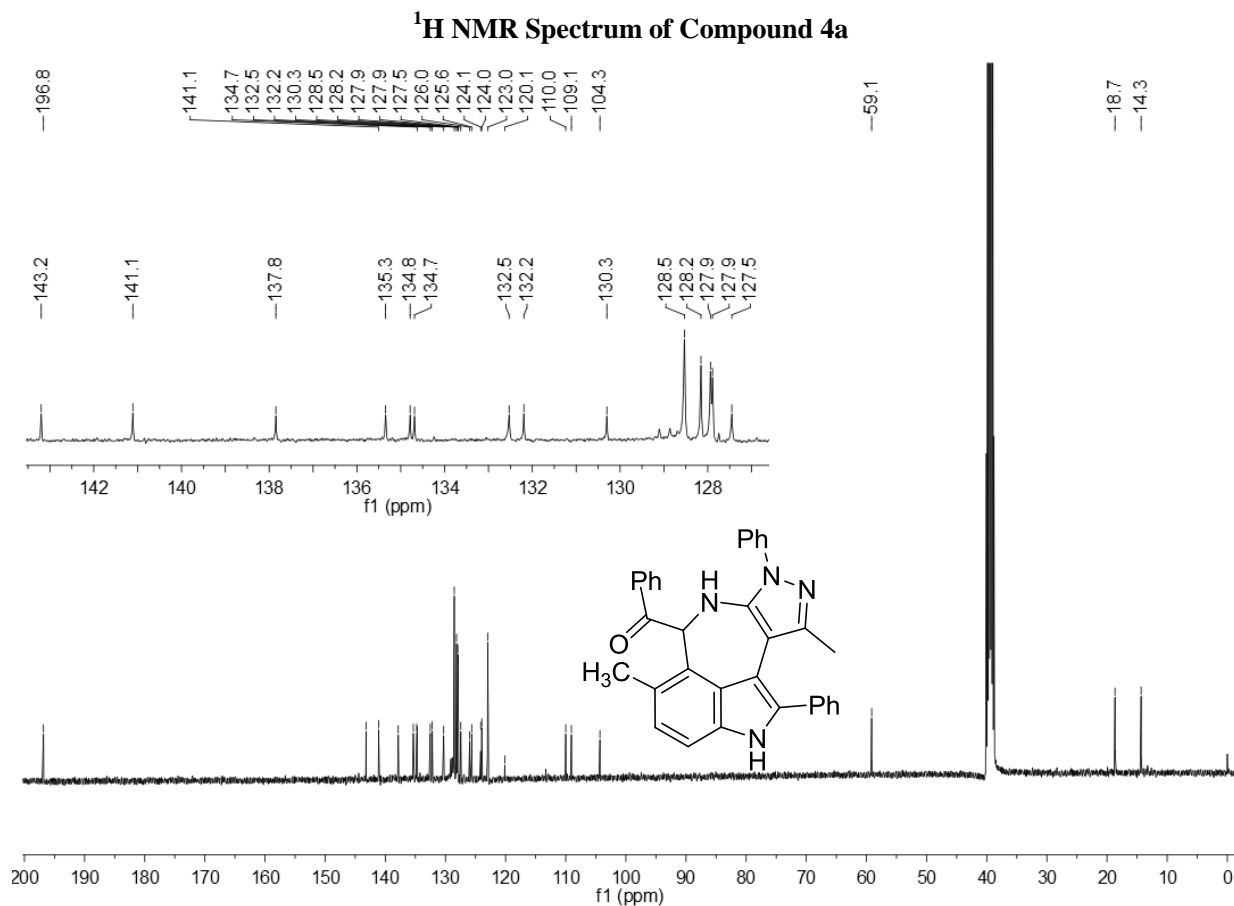
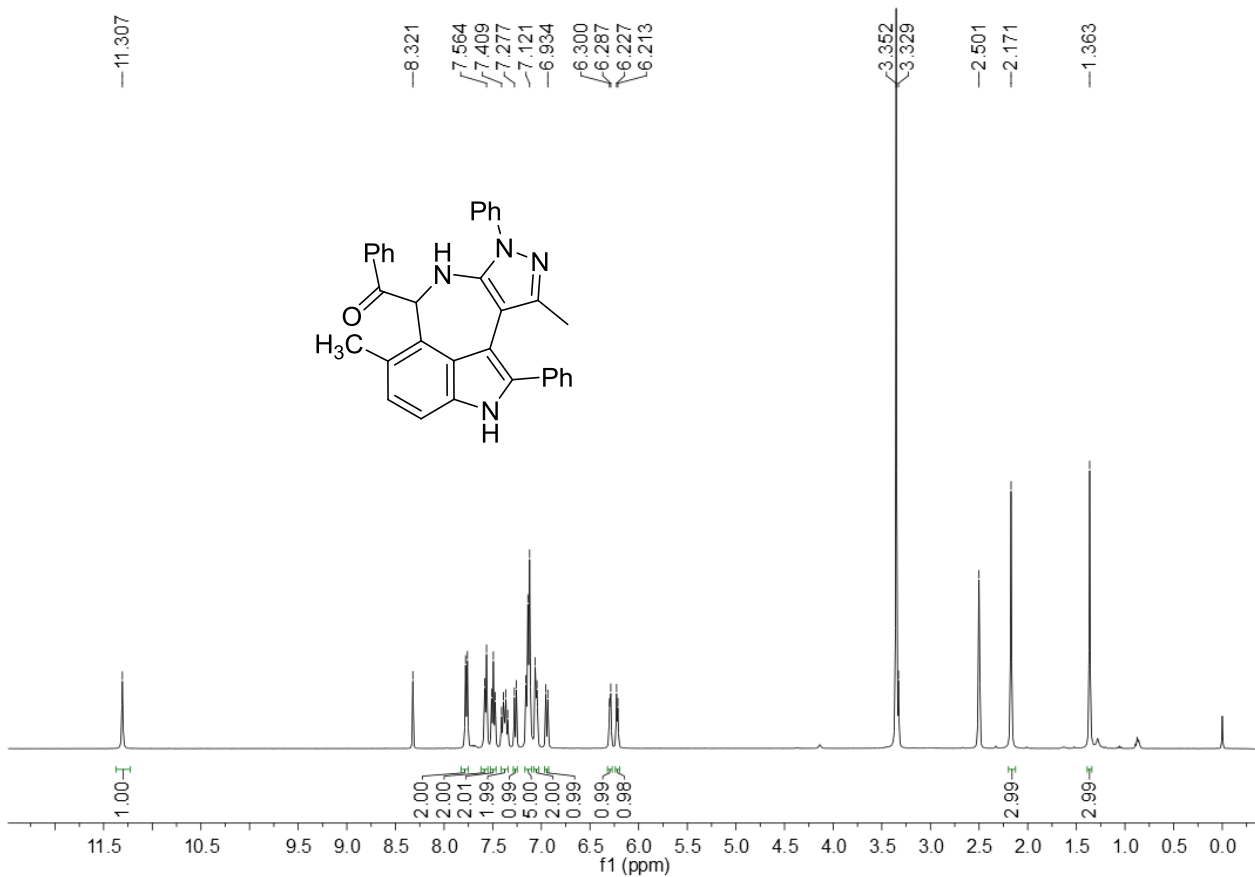
Yellow solid, m.p. 249-250 °C;

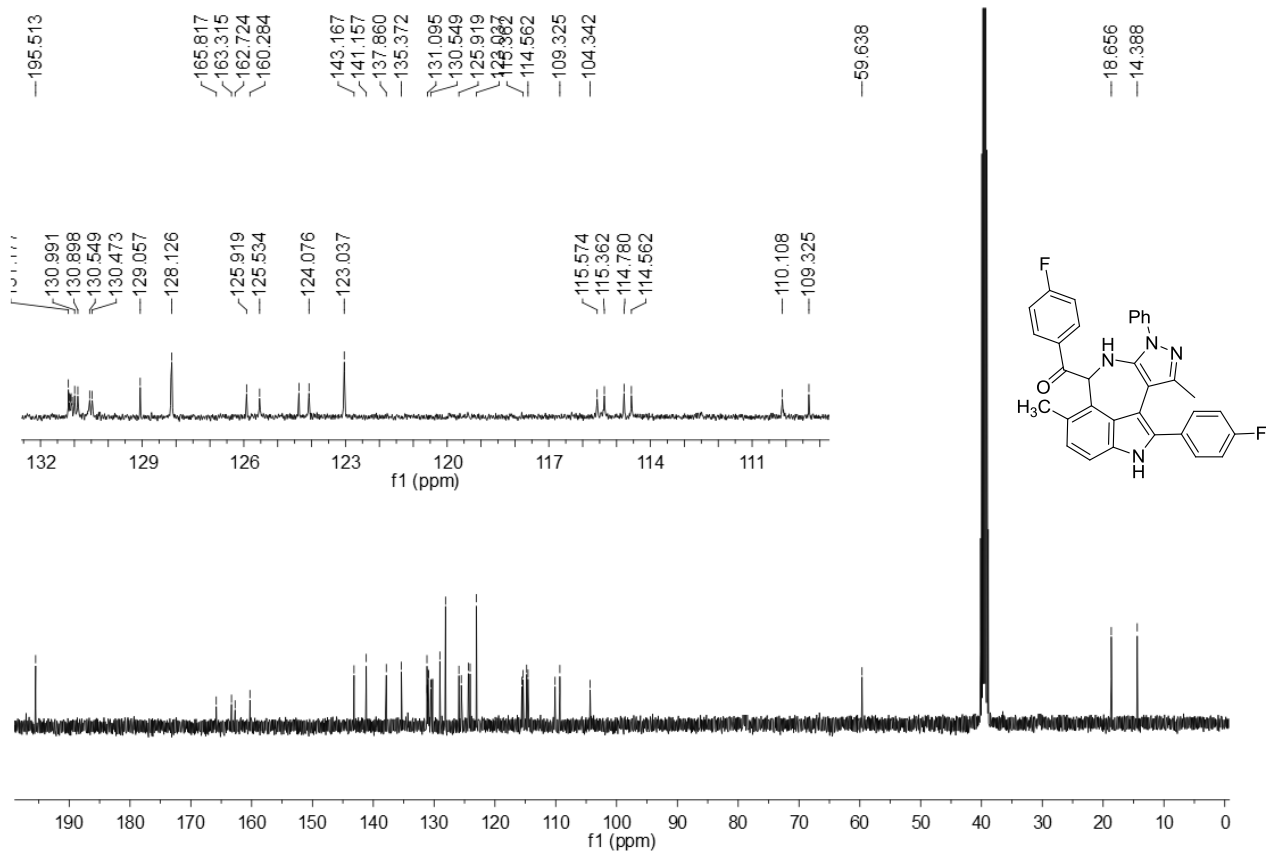
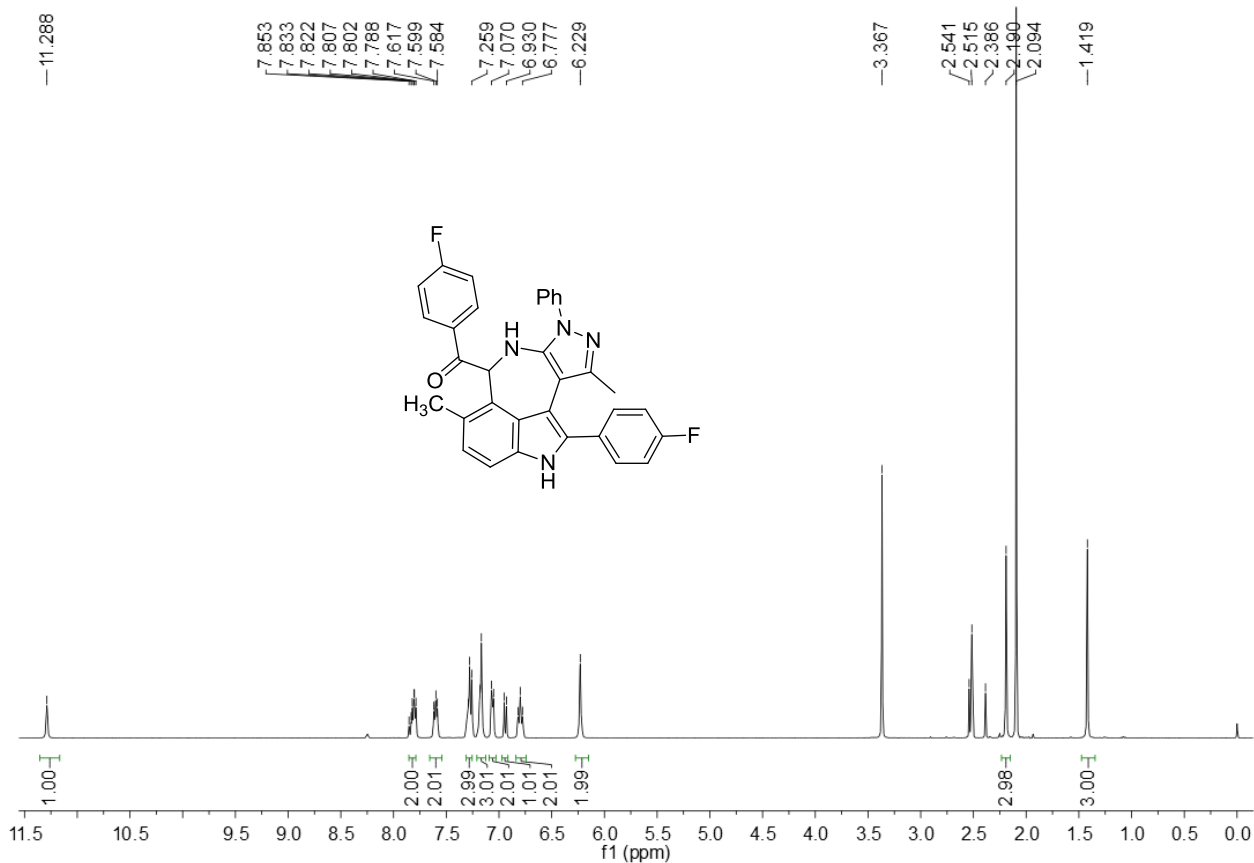
¹H NMR (400 MHz, CDCl₃) (δ, ppm): 8.21 (d, *J* = 2.0 Hz, 2H, ArH), 8.19 (d, *J* = 2.0 Hz, 2H, ArH), 7.93 (d, *J* = 8.0 Hz, 2H, ArH), 7.85 (d, *J* = 8.4 Hz, 2H, ArH), 6.53 (d, *J* = 8.4 Hz, 2H, ArH), 6.34 (d, *J* = 8.4 Hz, 2H, ArH), 5.33 (s, 1H, NH), 4.14 (s, 3H, CH₃), 3.65 (s, 3H, OCH₃), 1.54-1.45 (m, 1H, CH), 0.78 (d, *J* = 4.0 Hz, 2H, CH₂), 0.60 (d, *J* = 8.0 Hz, 2H, CH₂).

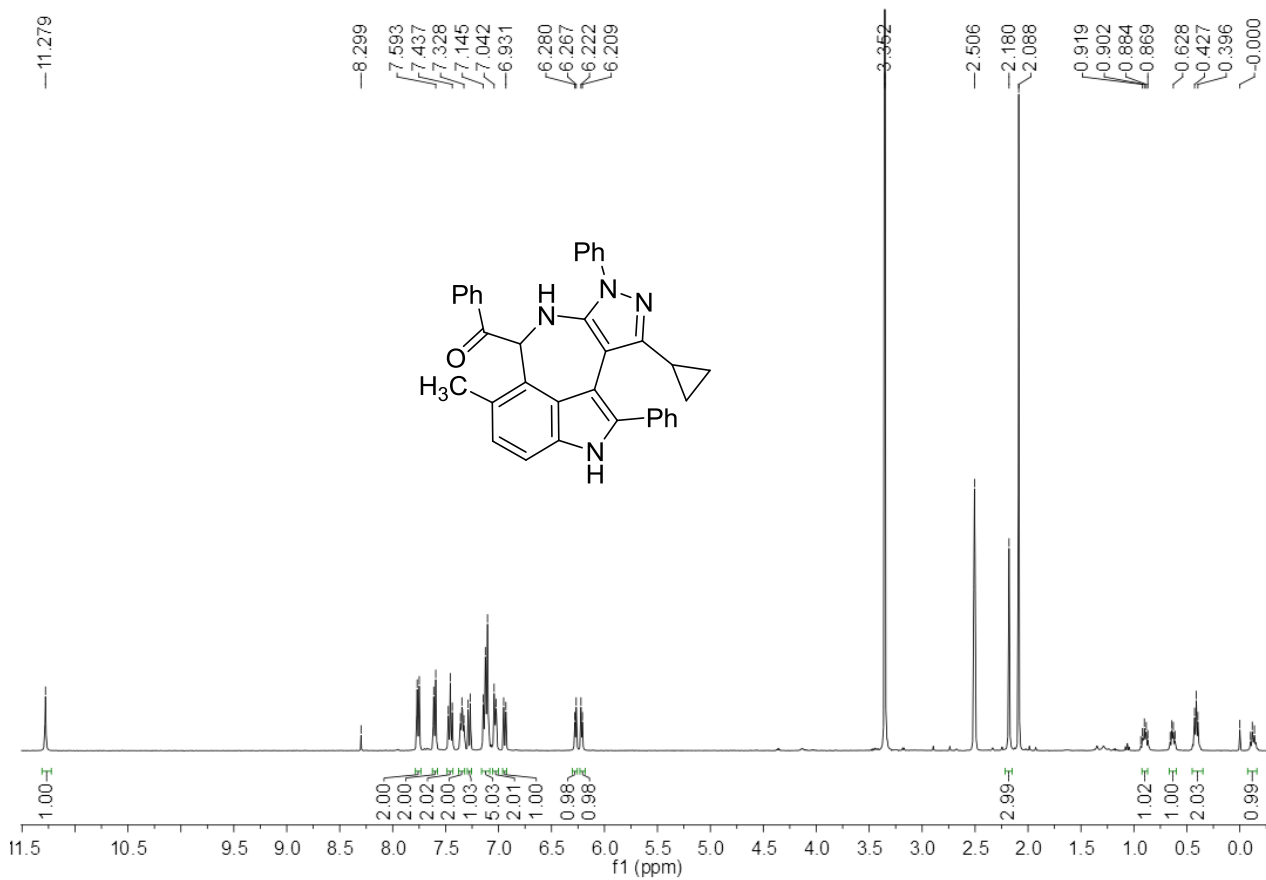
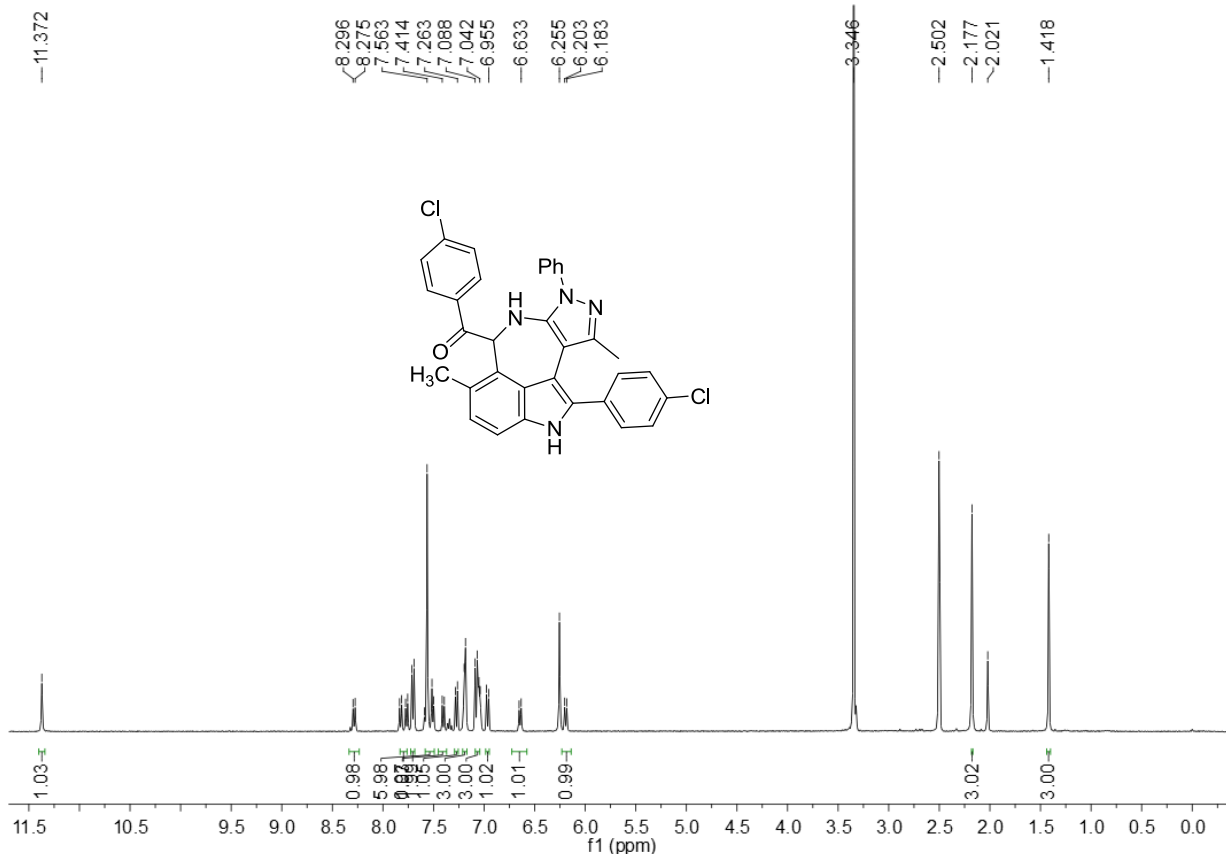
¹³C NMR (100 MHz, CDCl₃) (δ, ppm): 193.4, 154.1, 153.9, 150.6, 148.9, 147.9, 144.5, 144.24, 140.9, 138.6, 136.6, 130.2, 130.0, 128.3, 127.6, 123.8, 123.5, 117.4, 114.5, 112.3, 55.4, 33.9, 30.9, 29.7, 8.9, 7.2.

IR (KBr, ν, cm⁻¹): 3392, 1668, 1600, 1574, 1521, 1344, 1240, 1037, 859, 709.

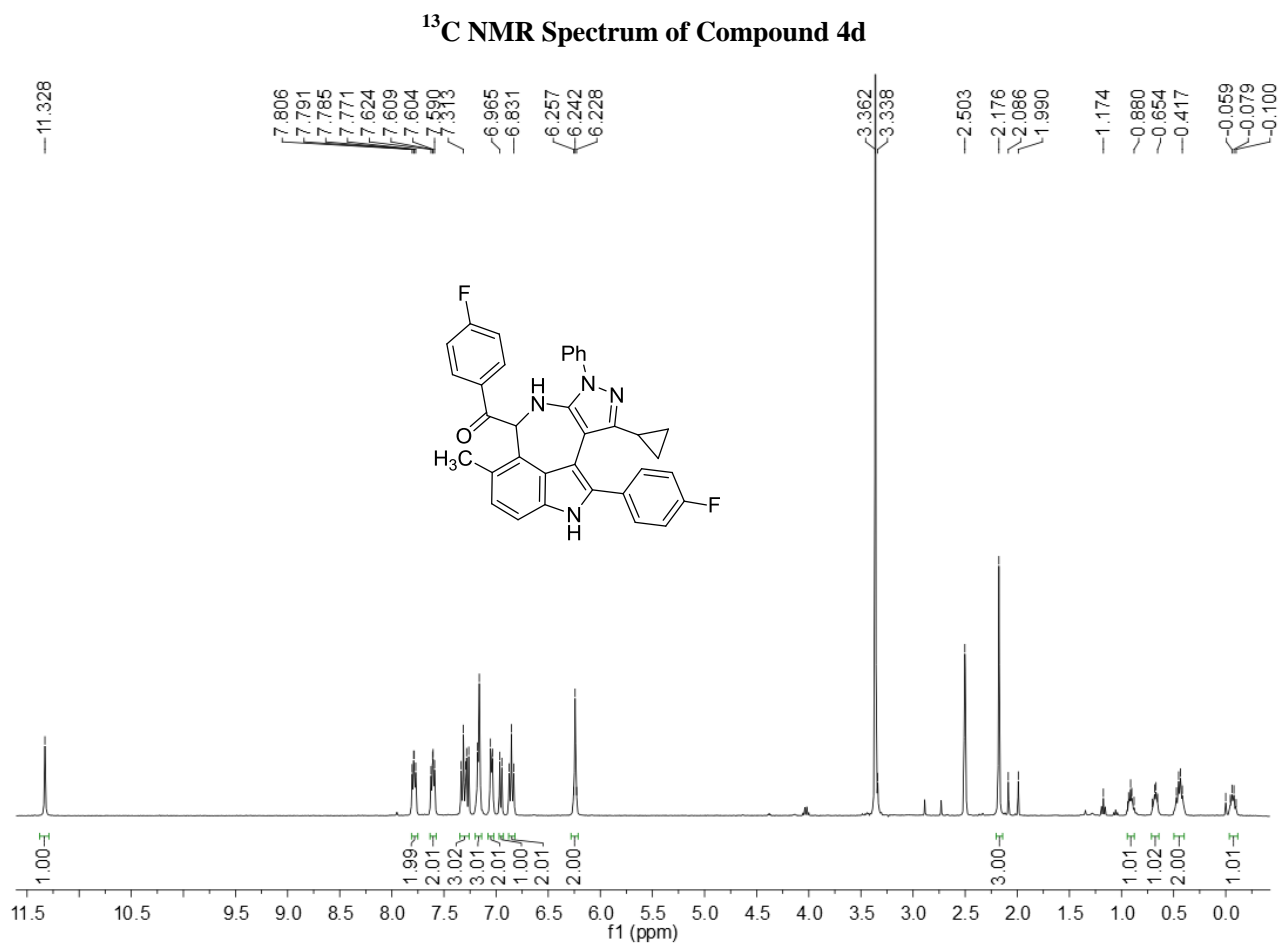
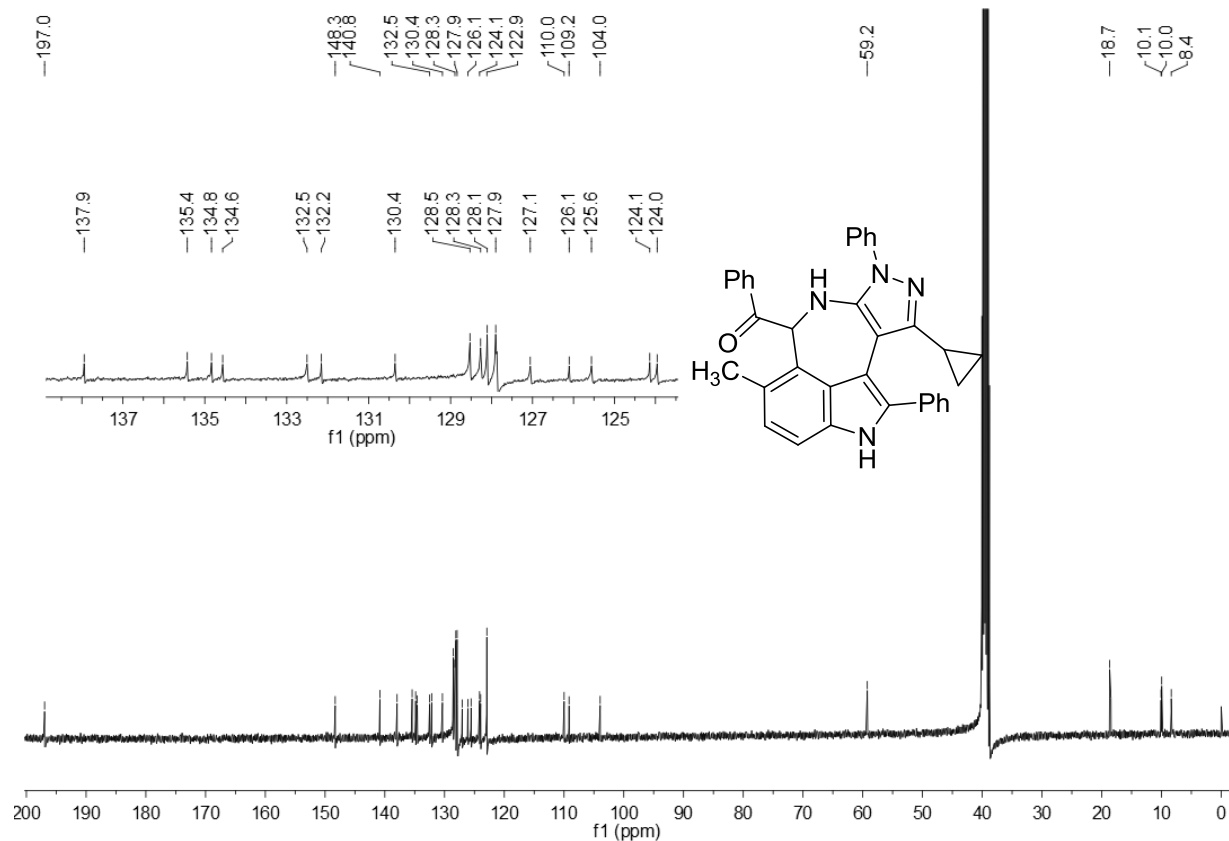
HRMS (ESI): *m/z* calcd for: C₃₀H₂₃N₆O₆, 563.1679 [M-H]⁻, found: 563.1701.

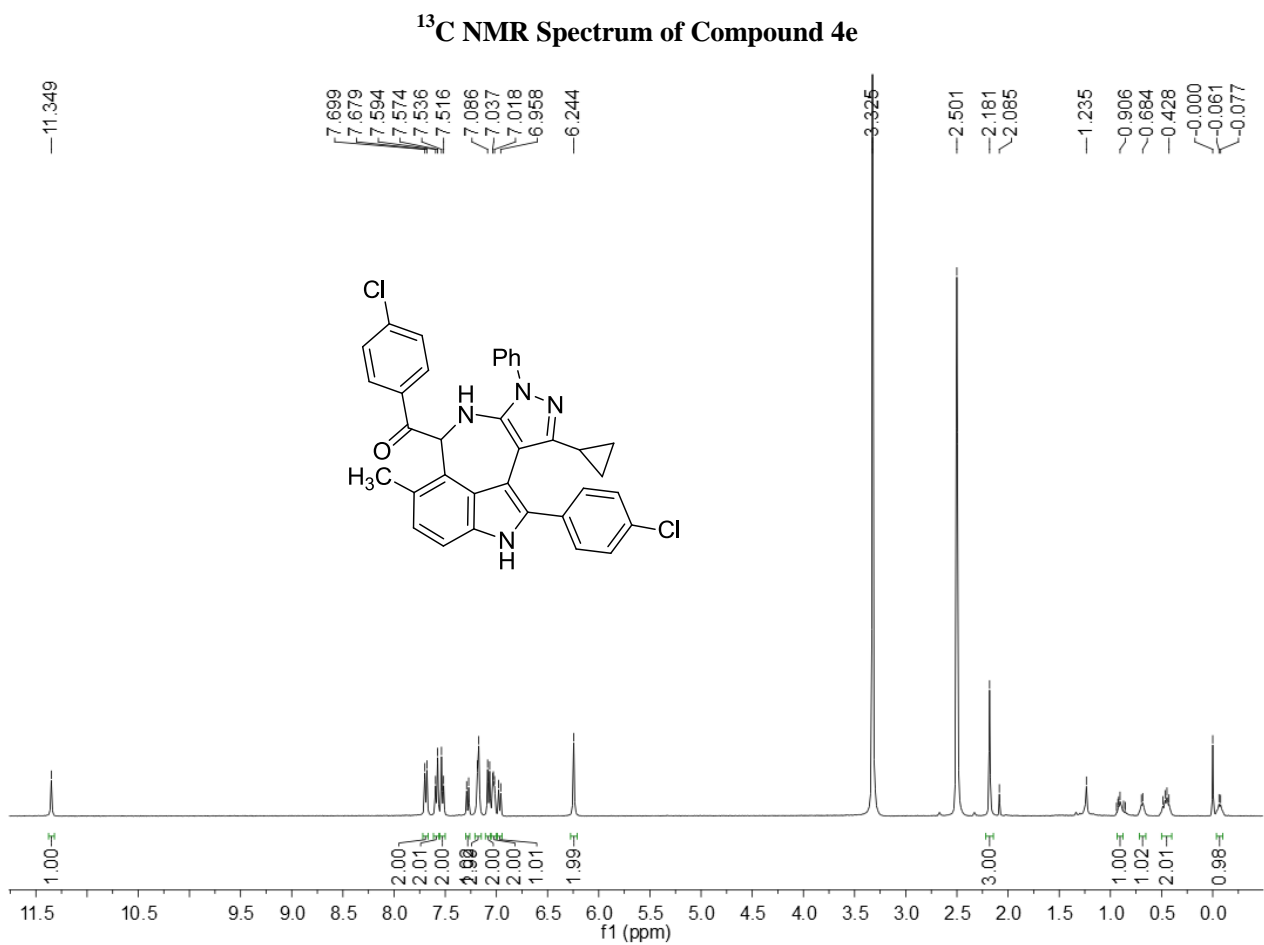
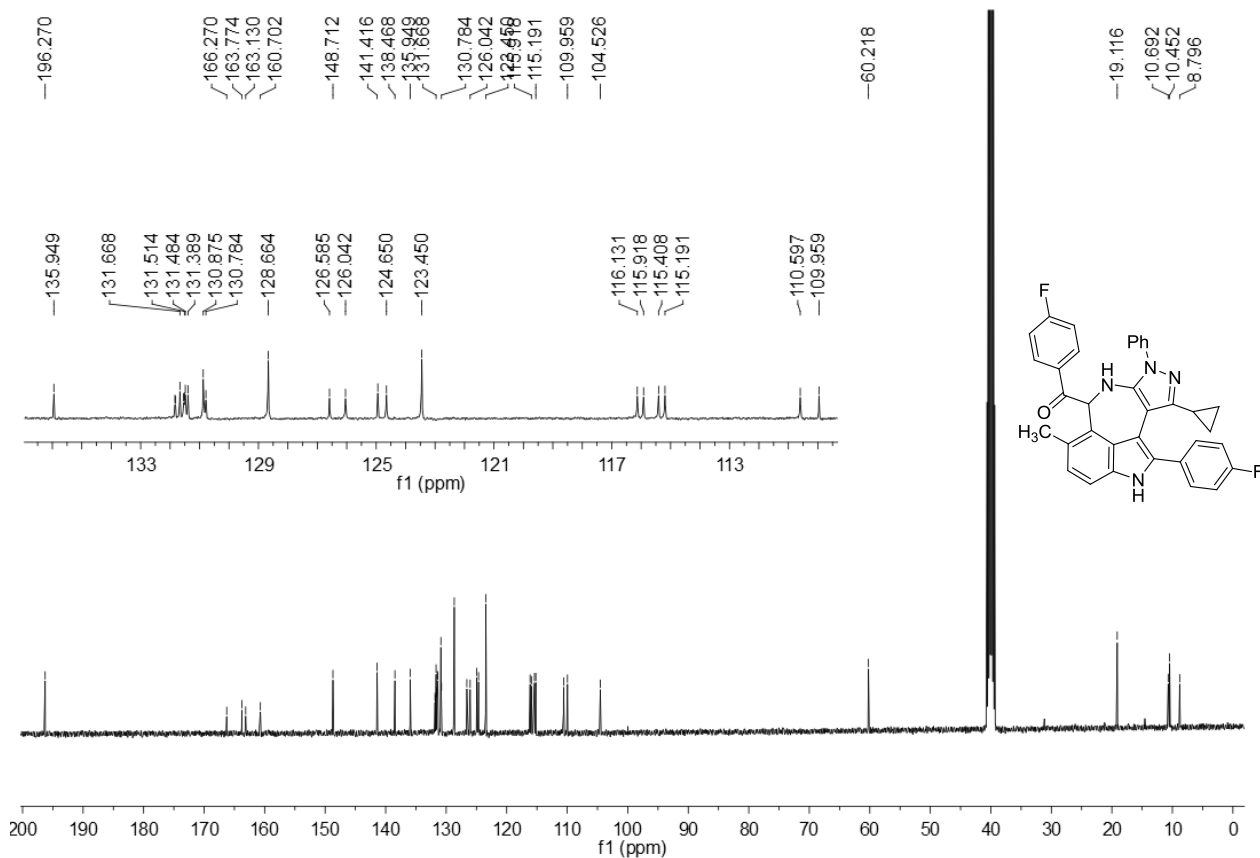


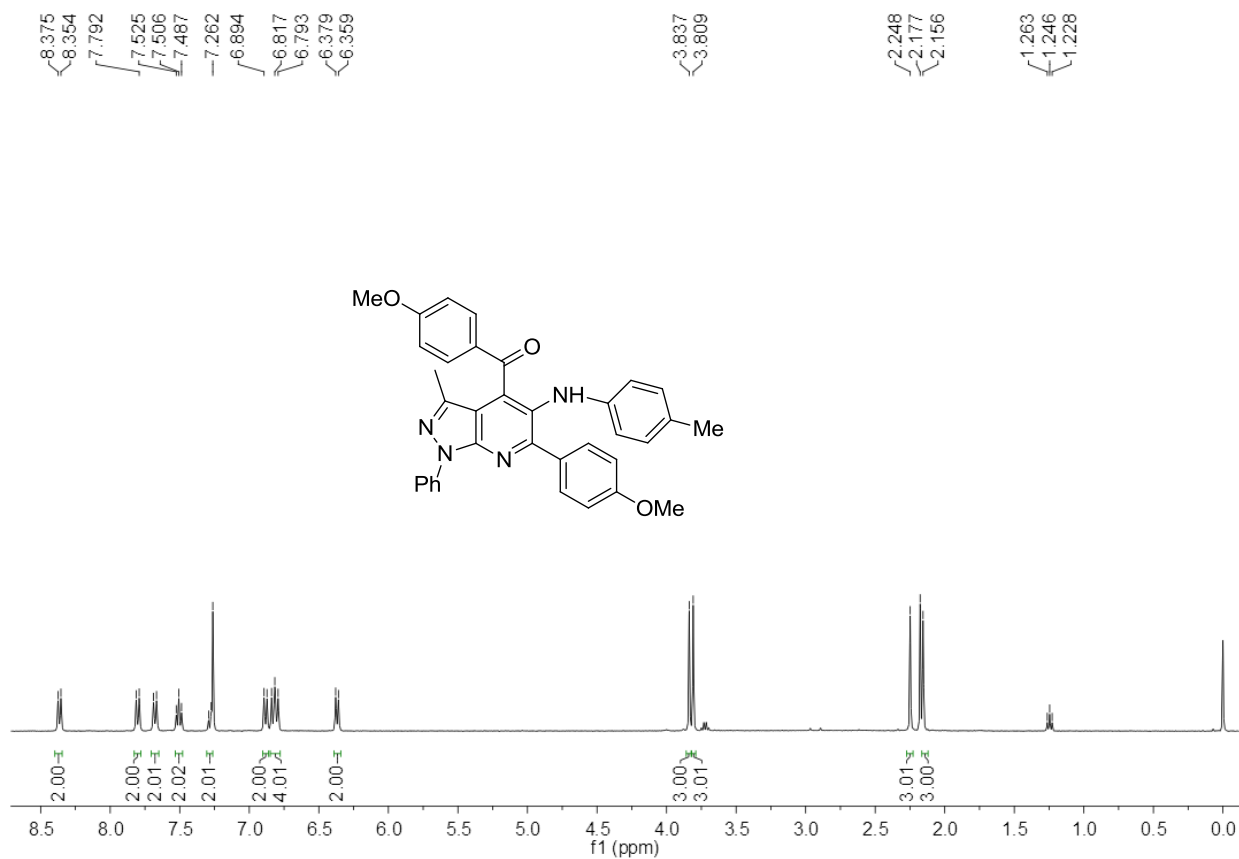




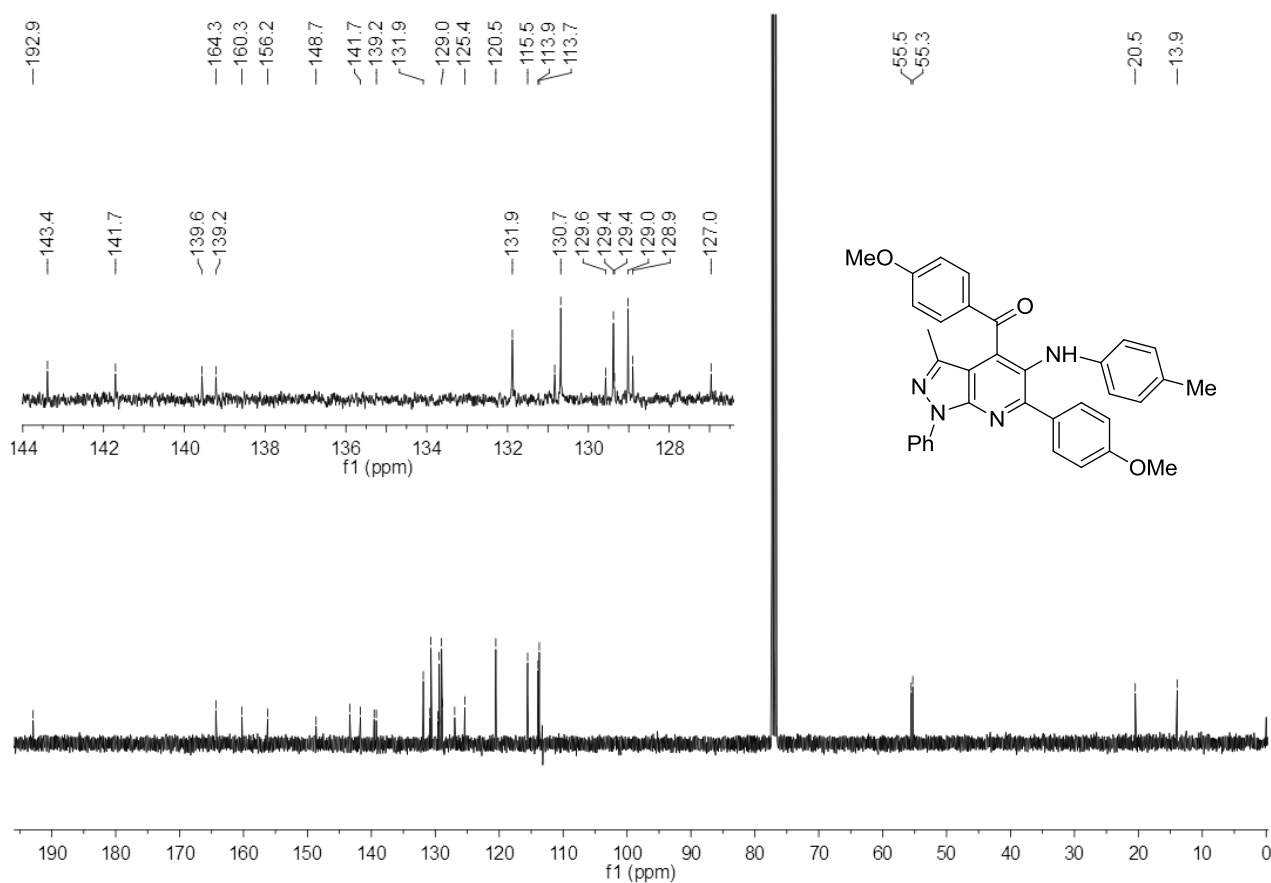
¹H NMR Spectrum of Compound 4d



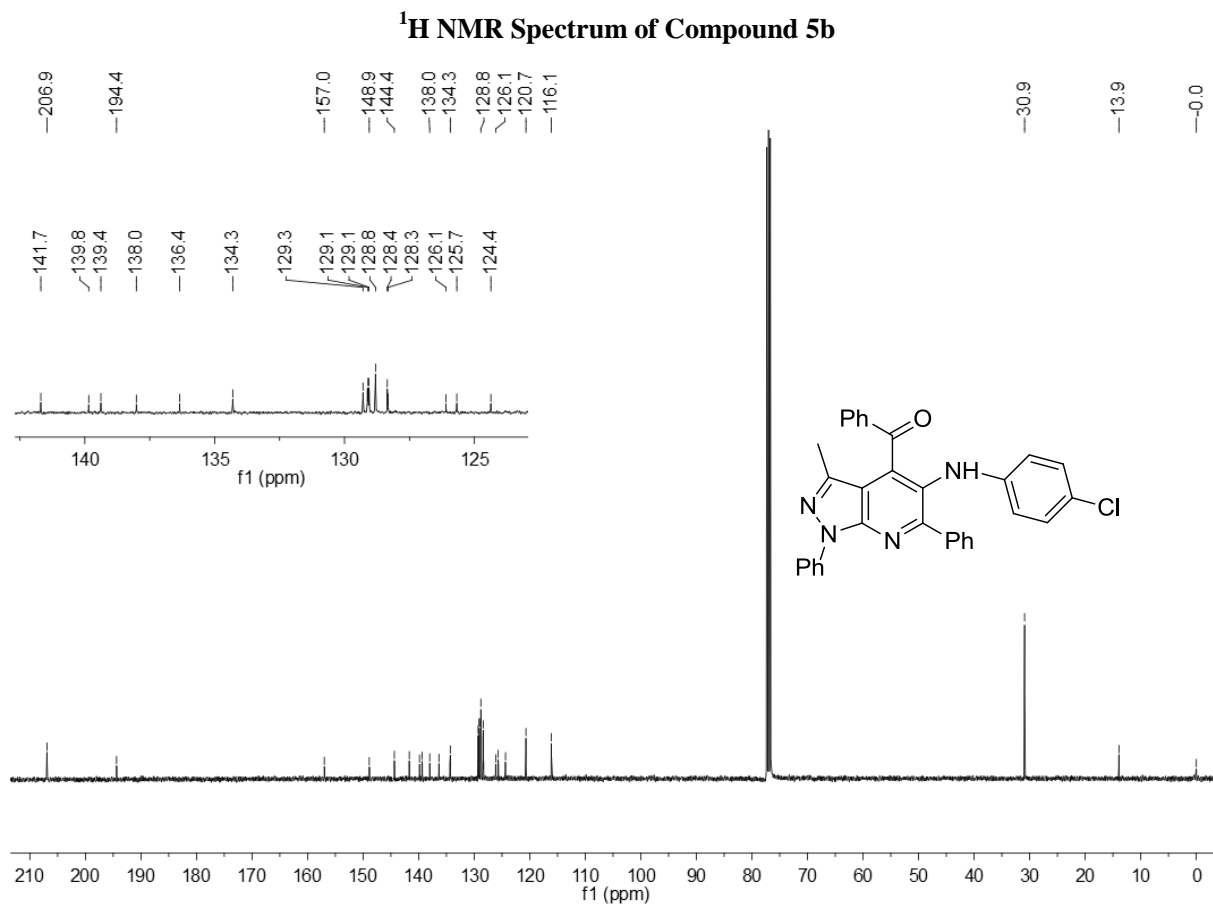
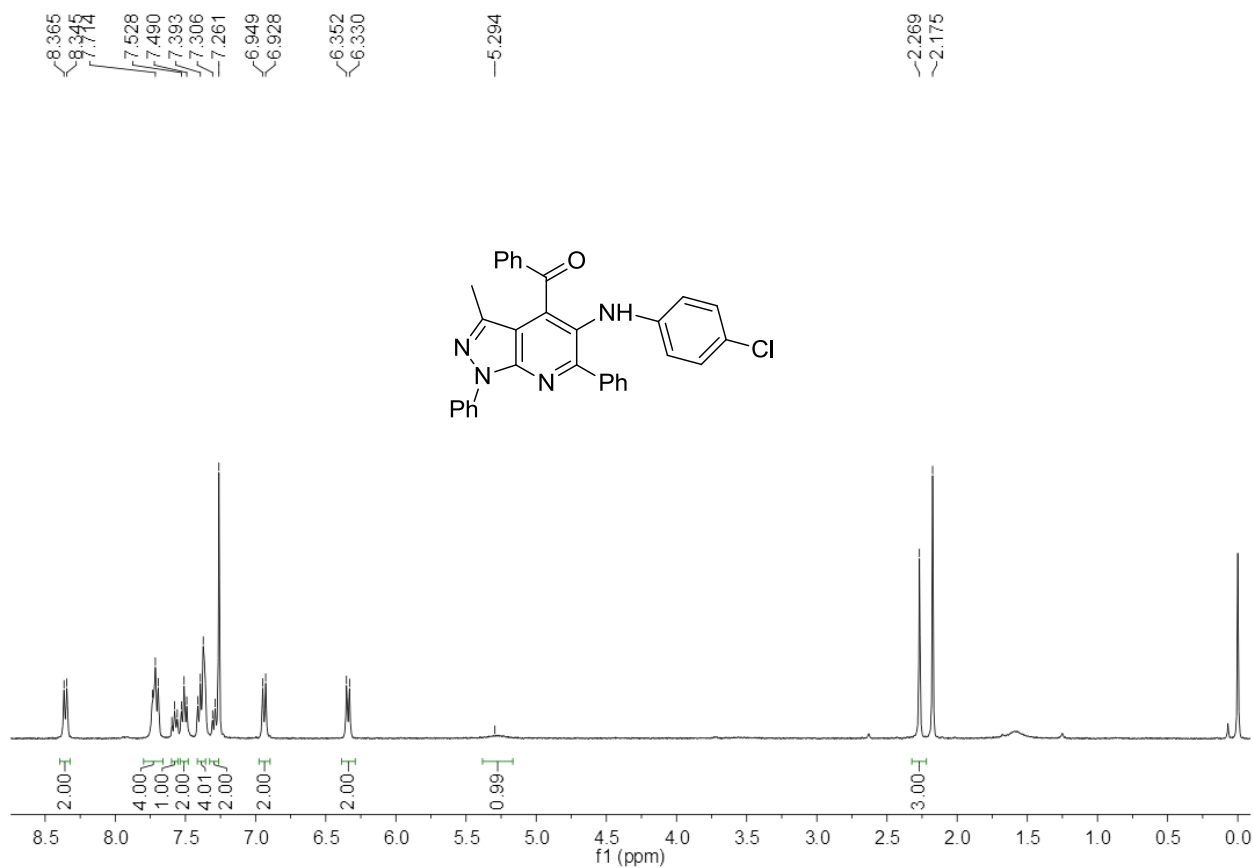


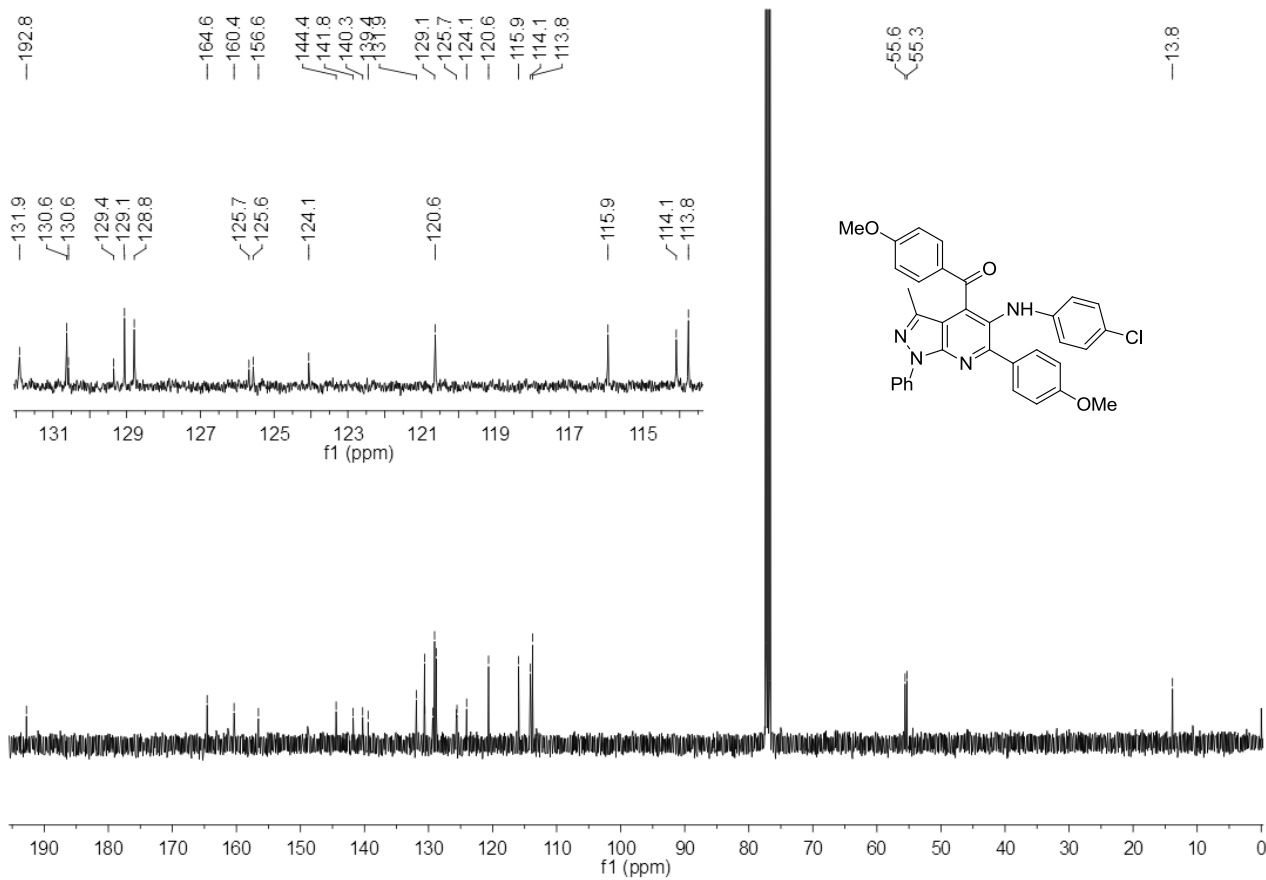
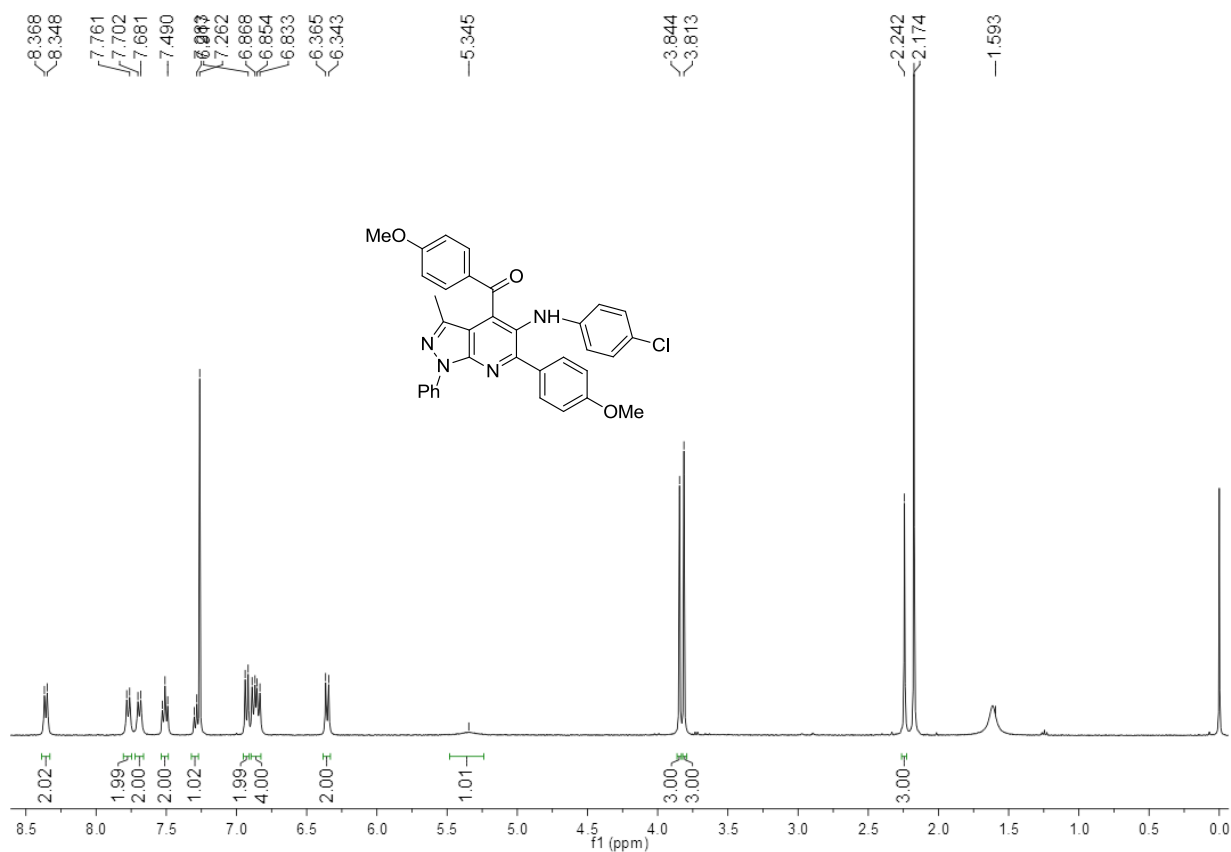


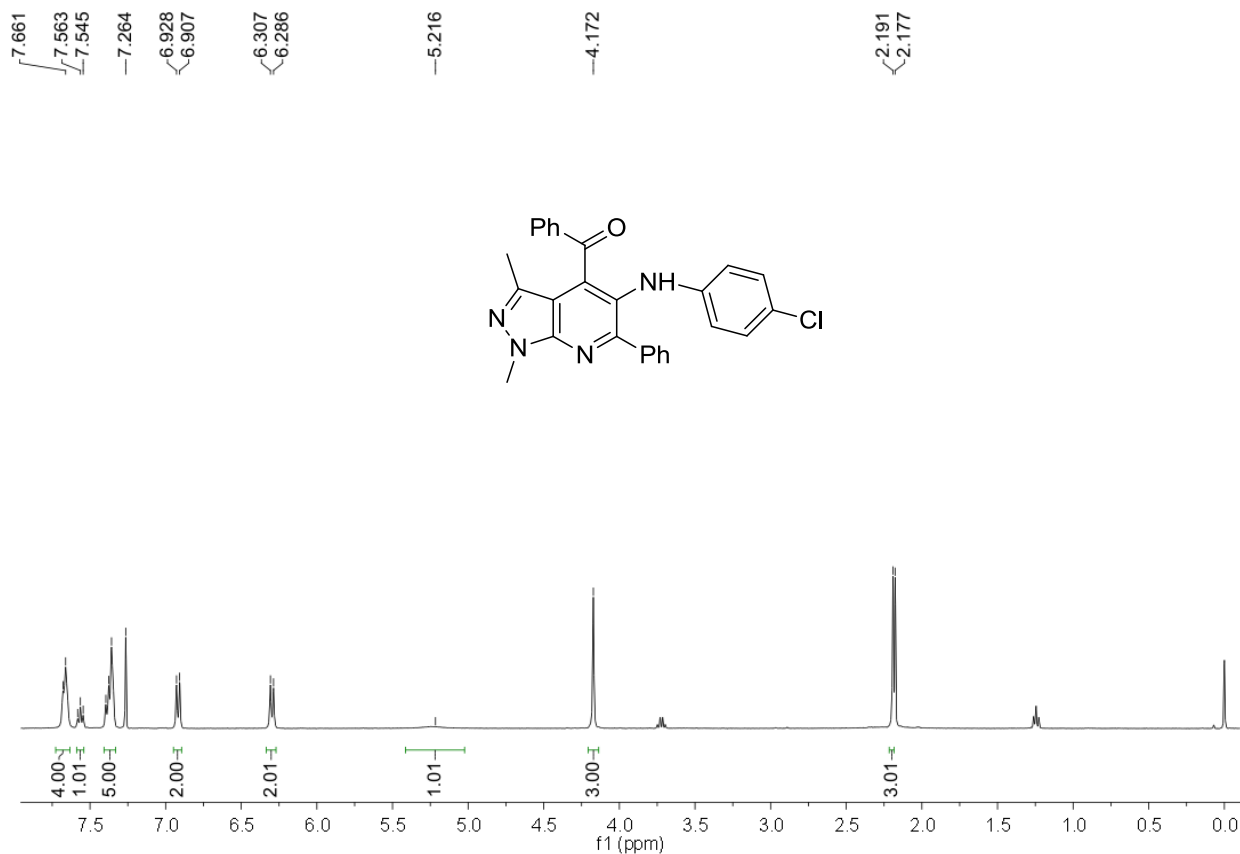
¹H NMR Spectrum of Compound 5a



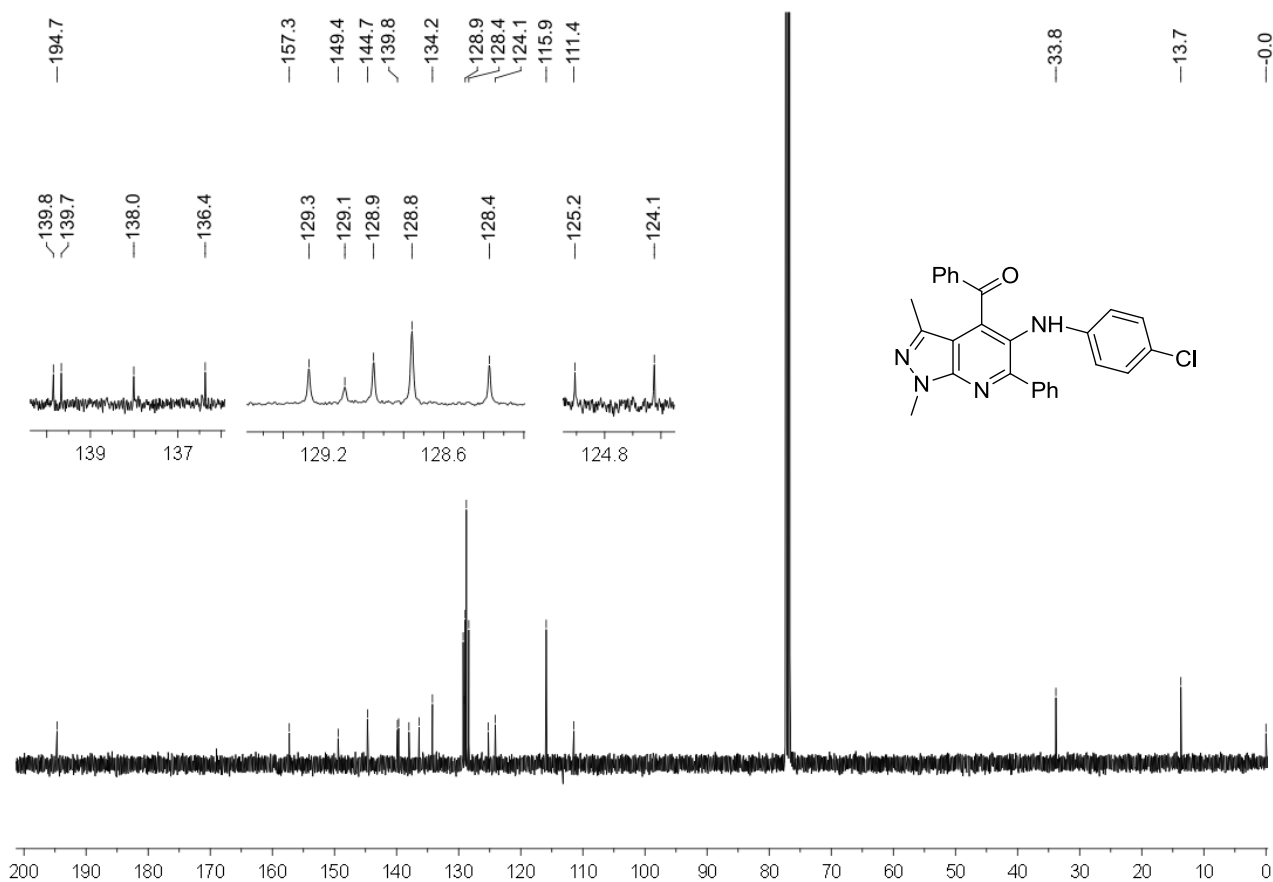
¹³C NMR Spectrum of Compound 5a



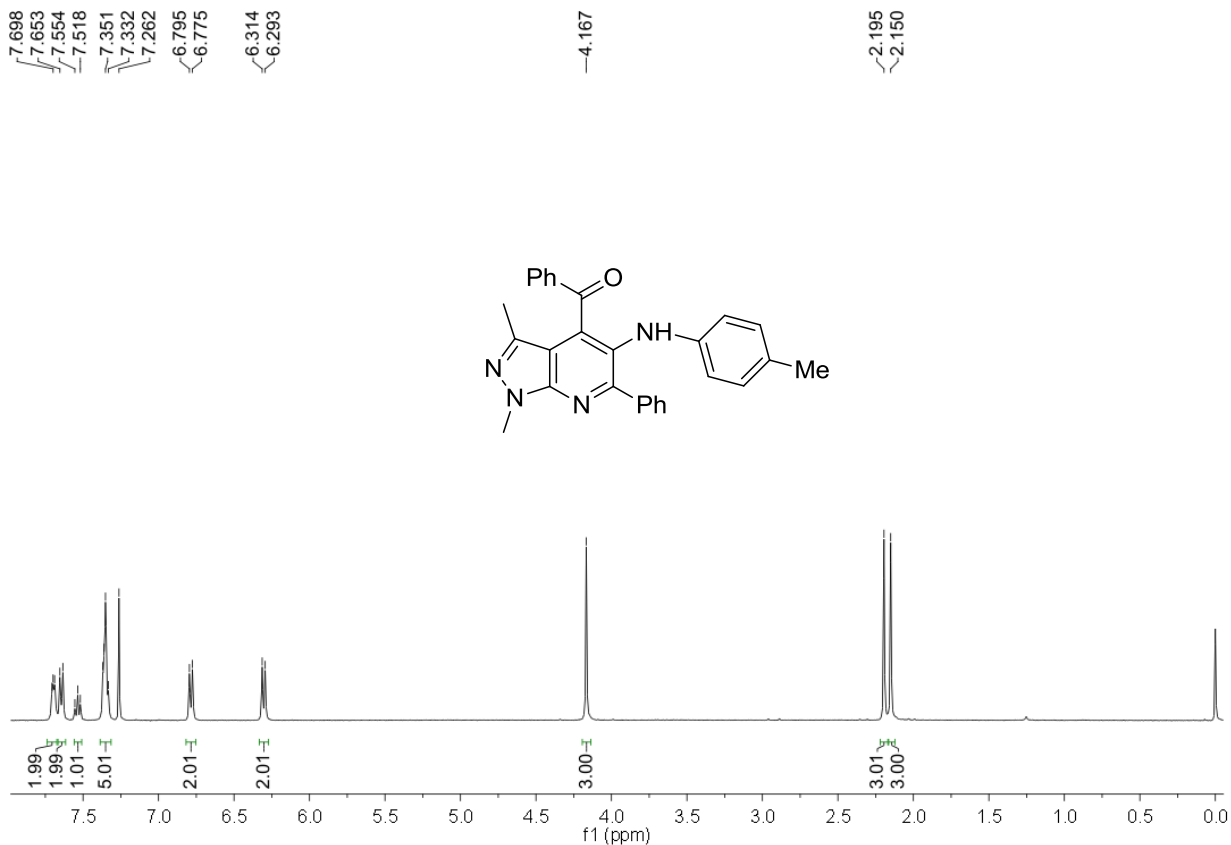




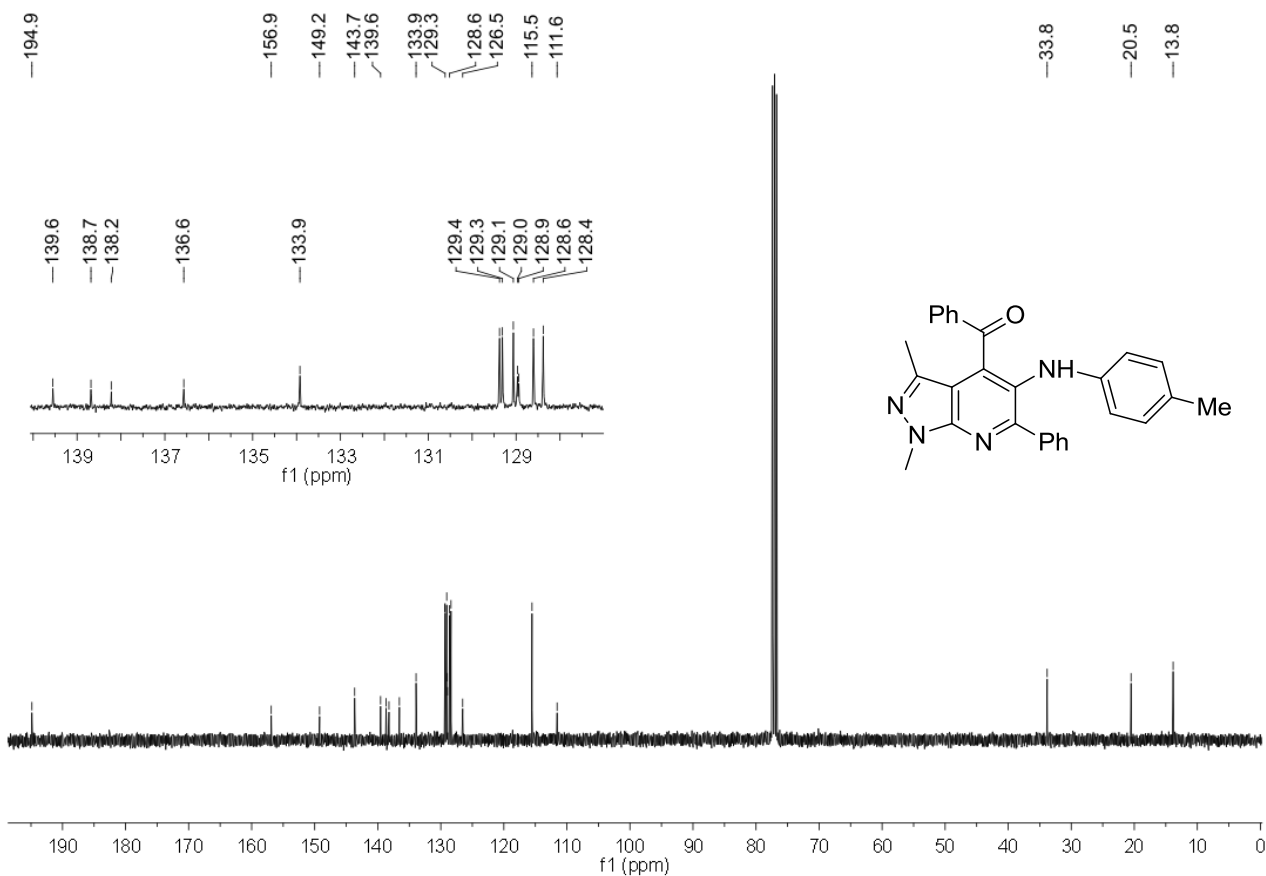
¹H NMR Spectrum of Compound 5d



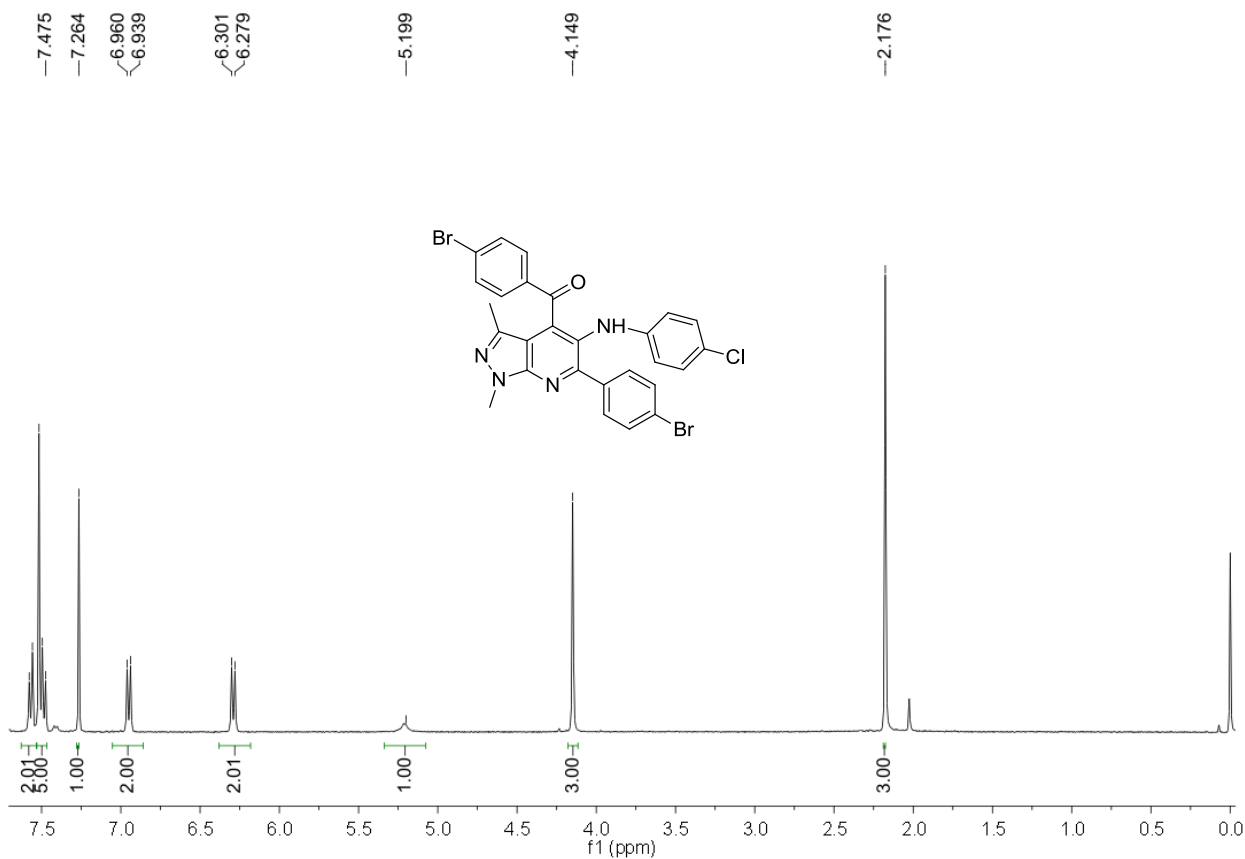
¹³C NMR Spectrum of Compound 5d



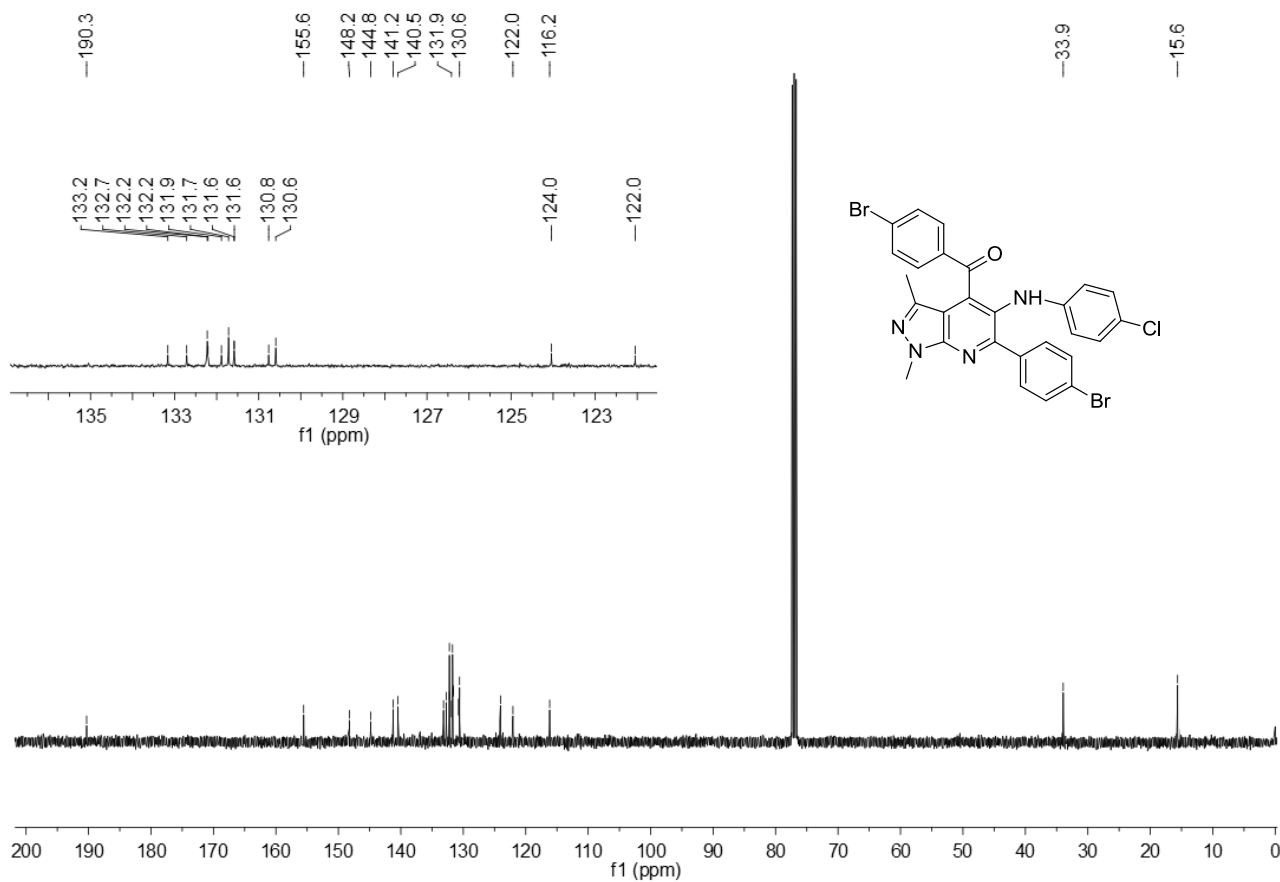
¹H NMR Spectrum of Compound 5e



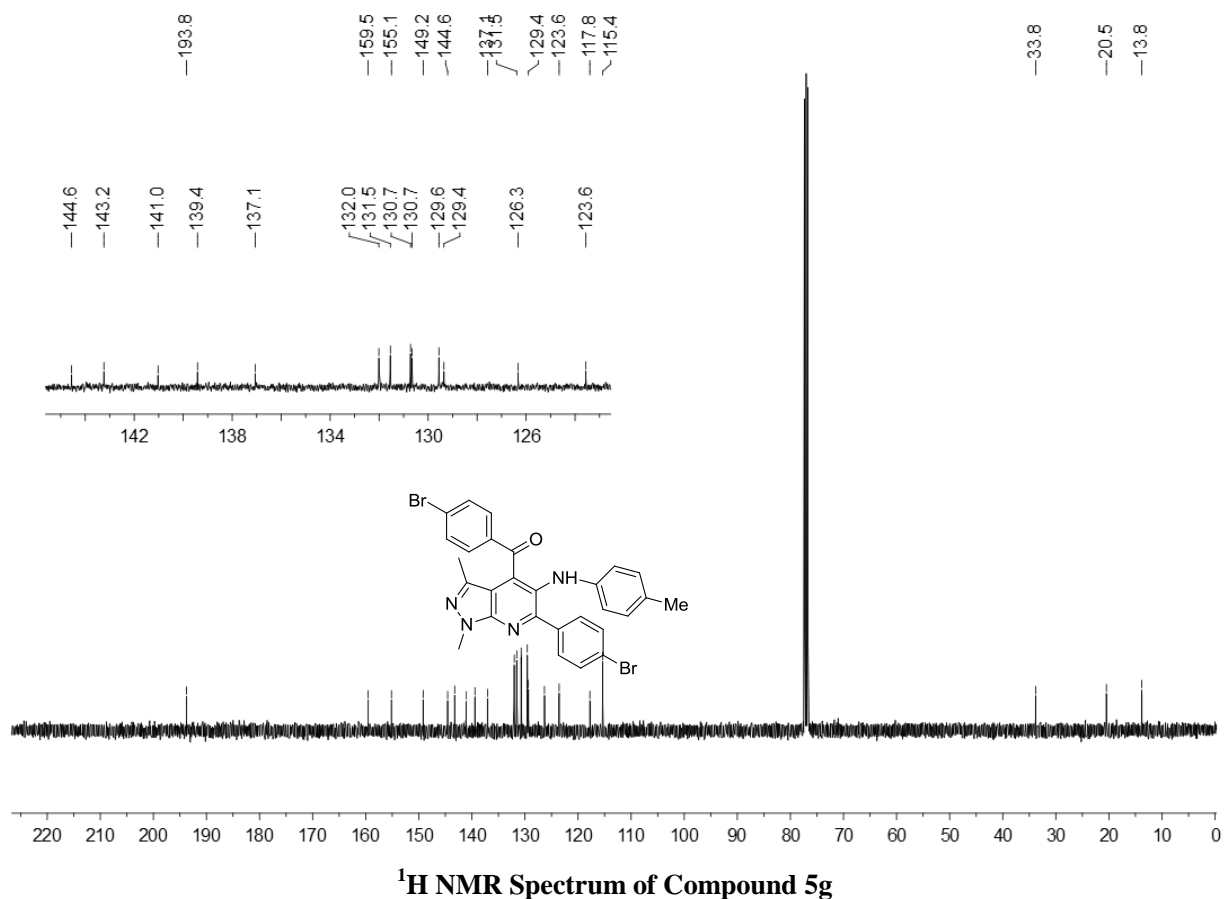
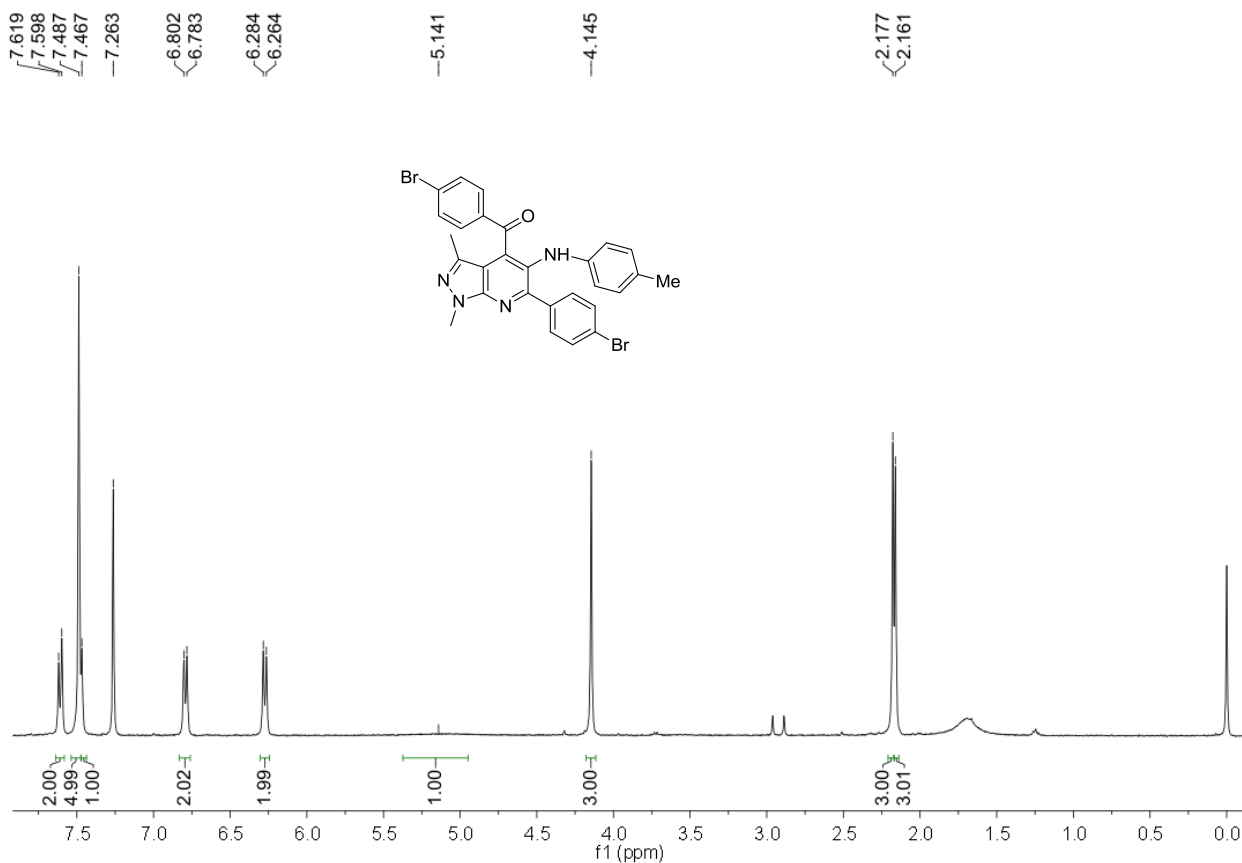
¹³C NMR Spectrum of Compound 5e

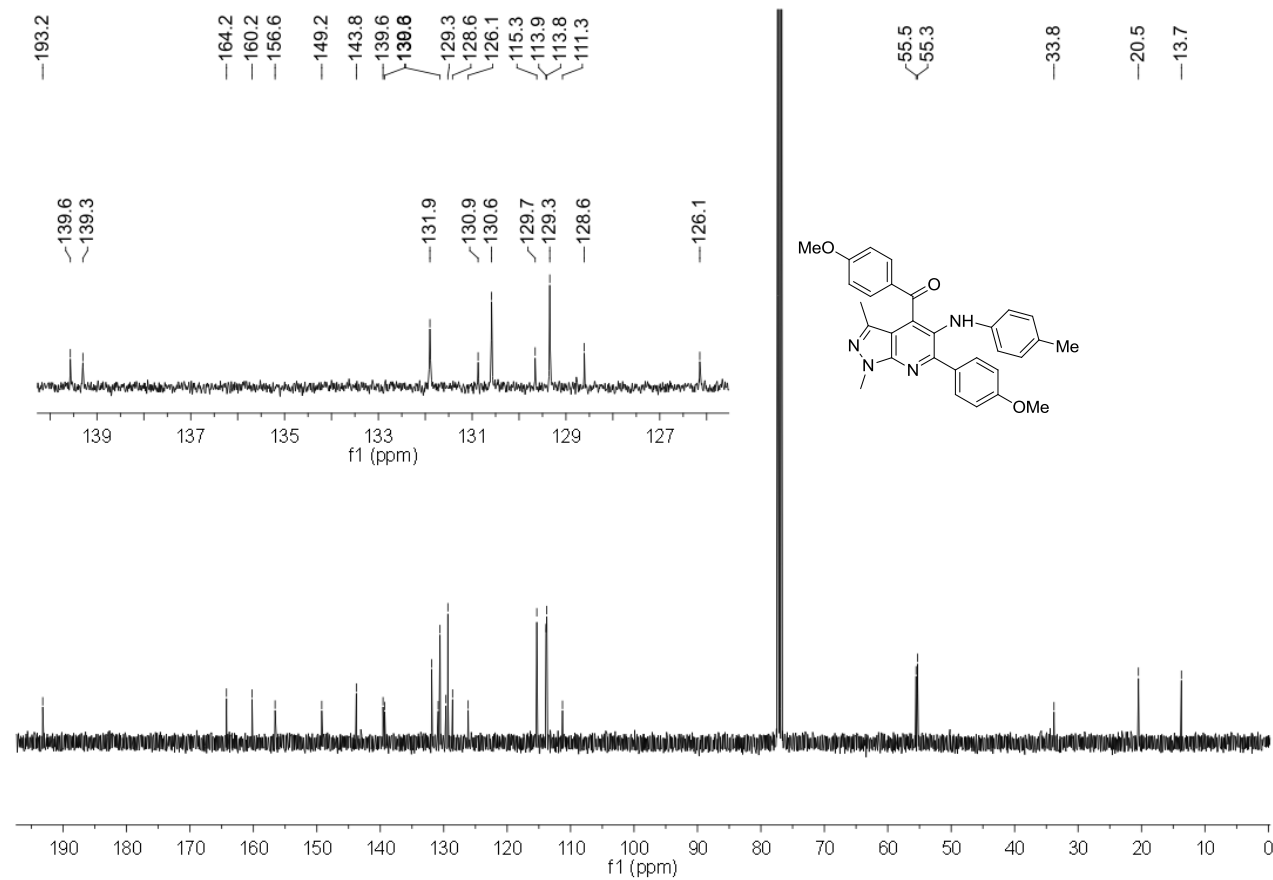
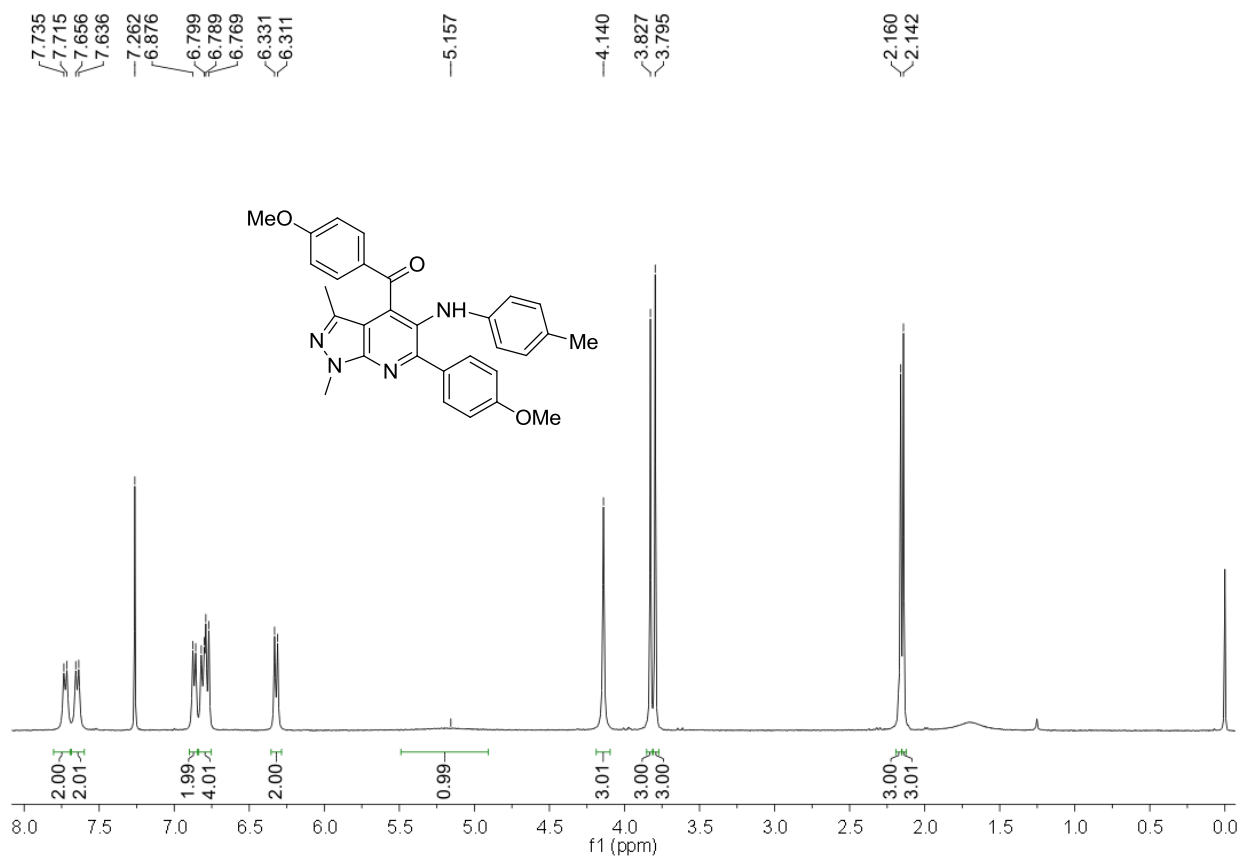


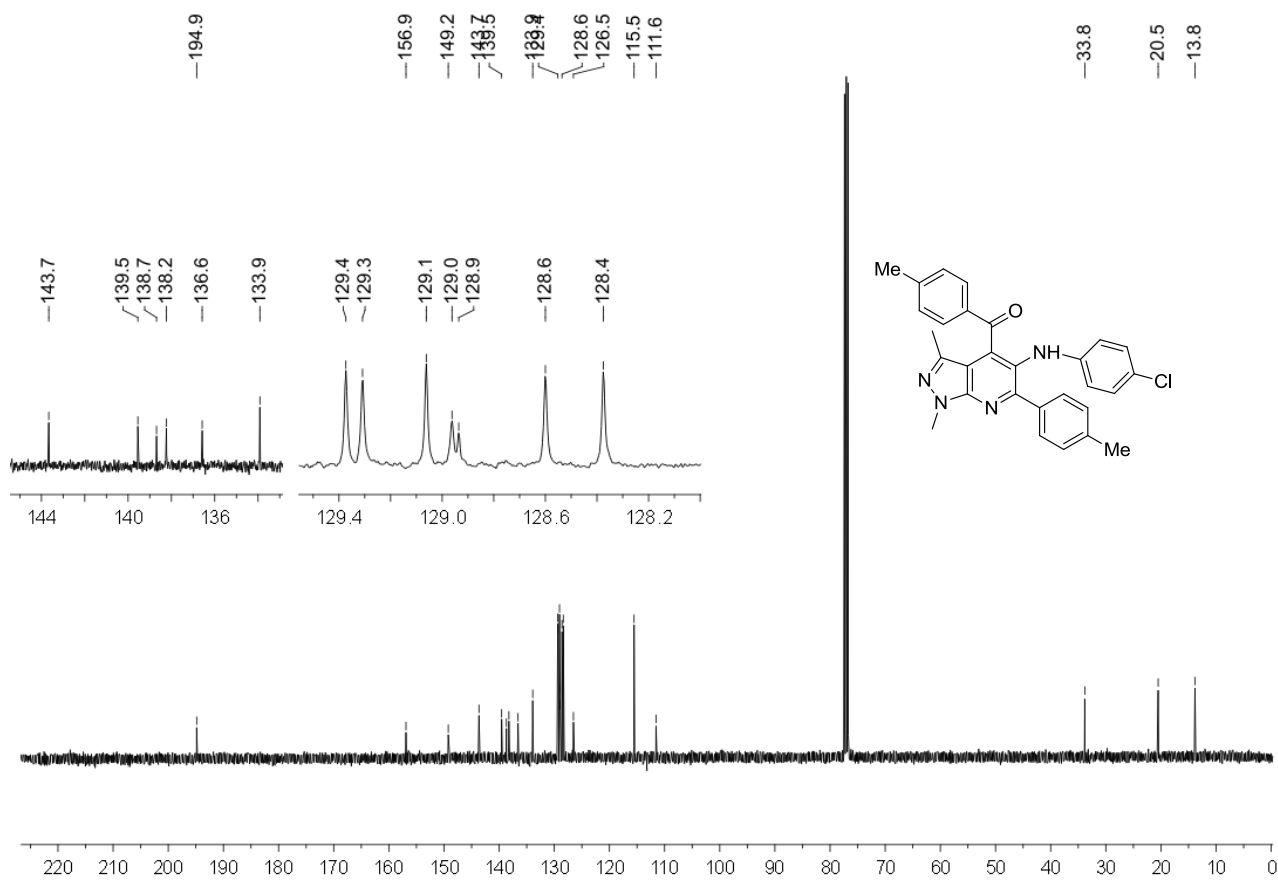
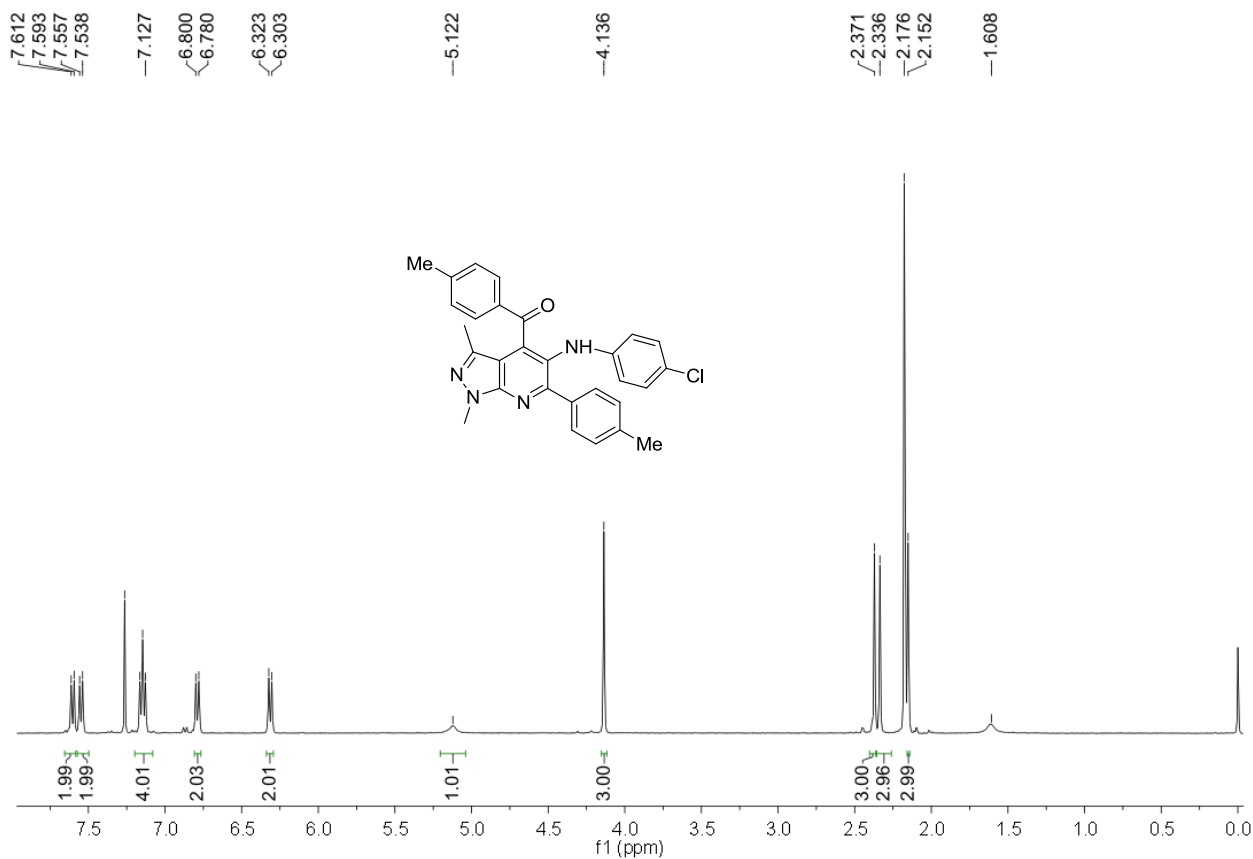
¹H NMR Spectrum of Compound 5f

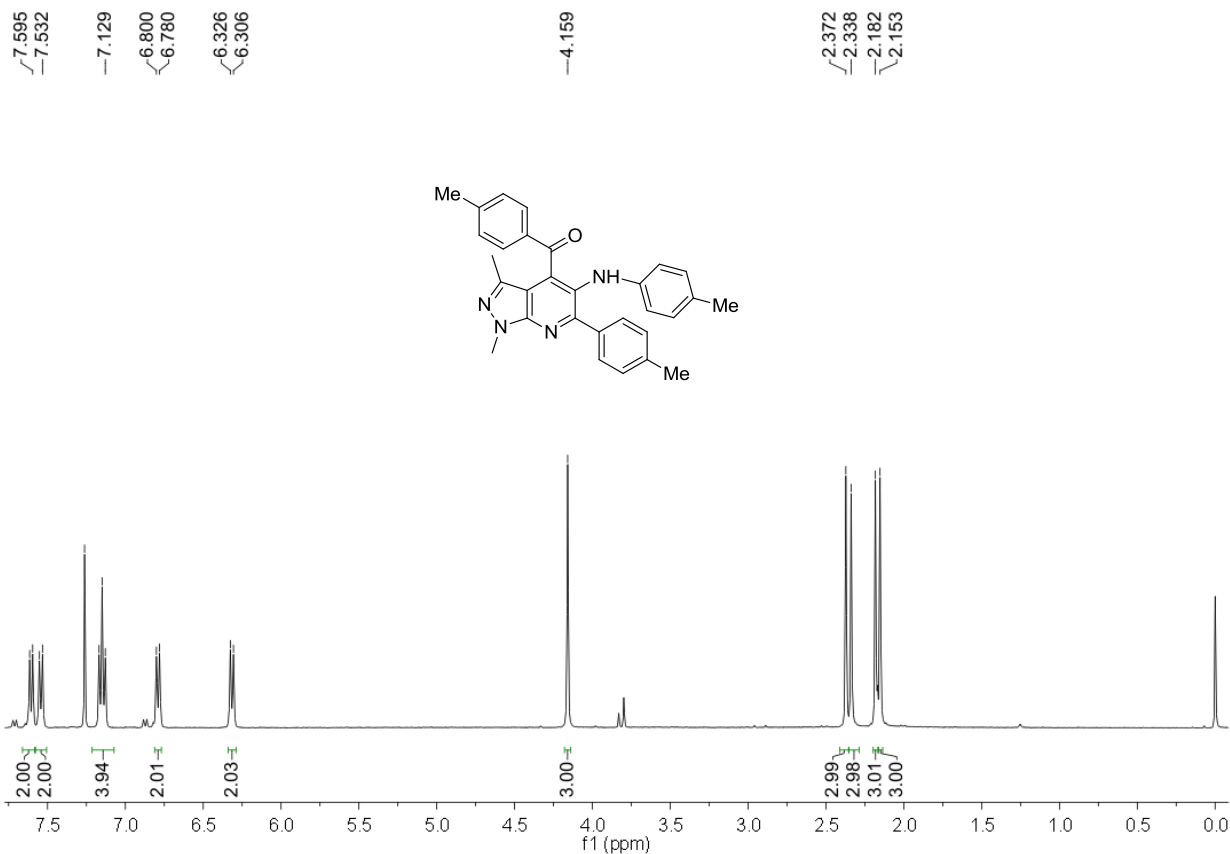


¹³C NMR Spectrum of Compound 5f

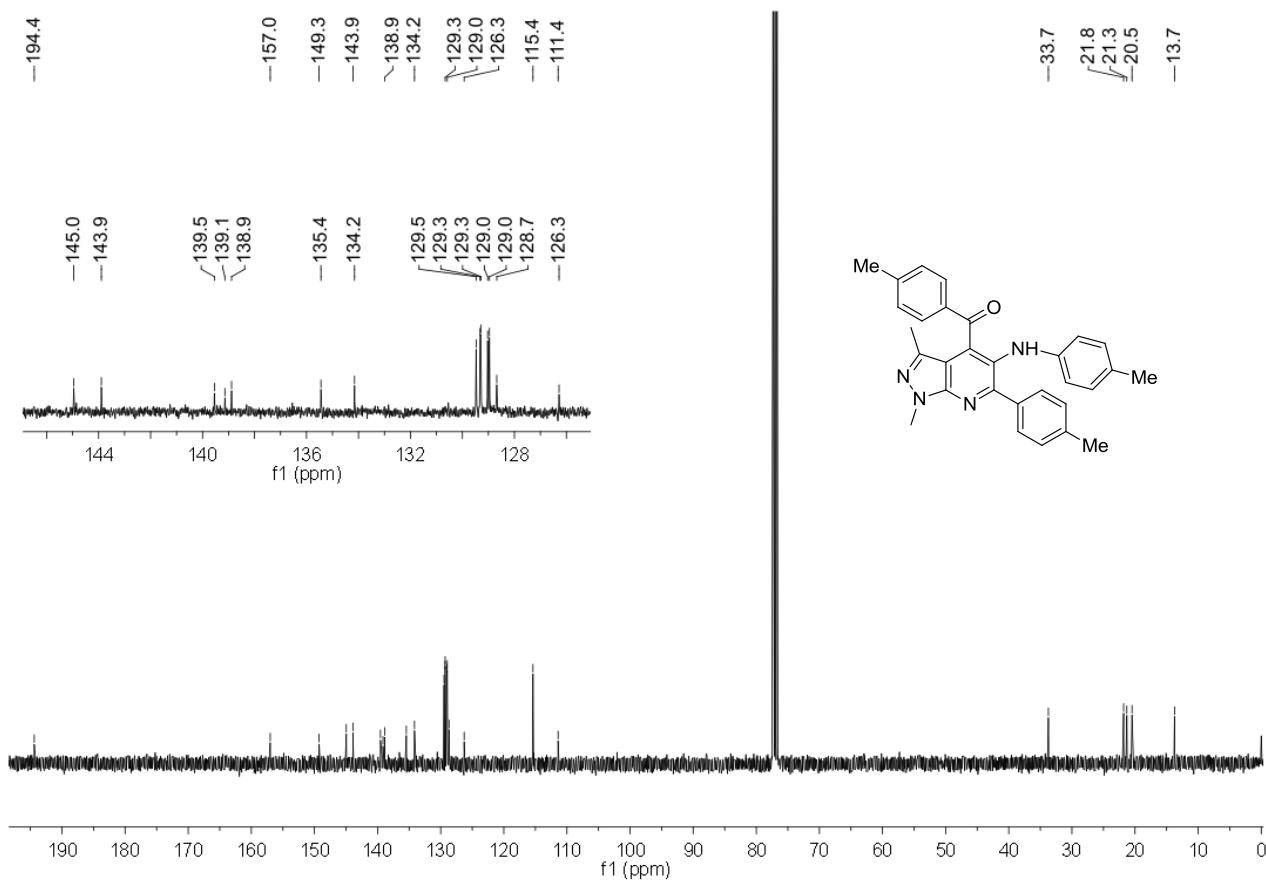








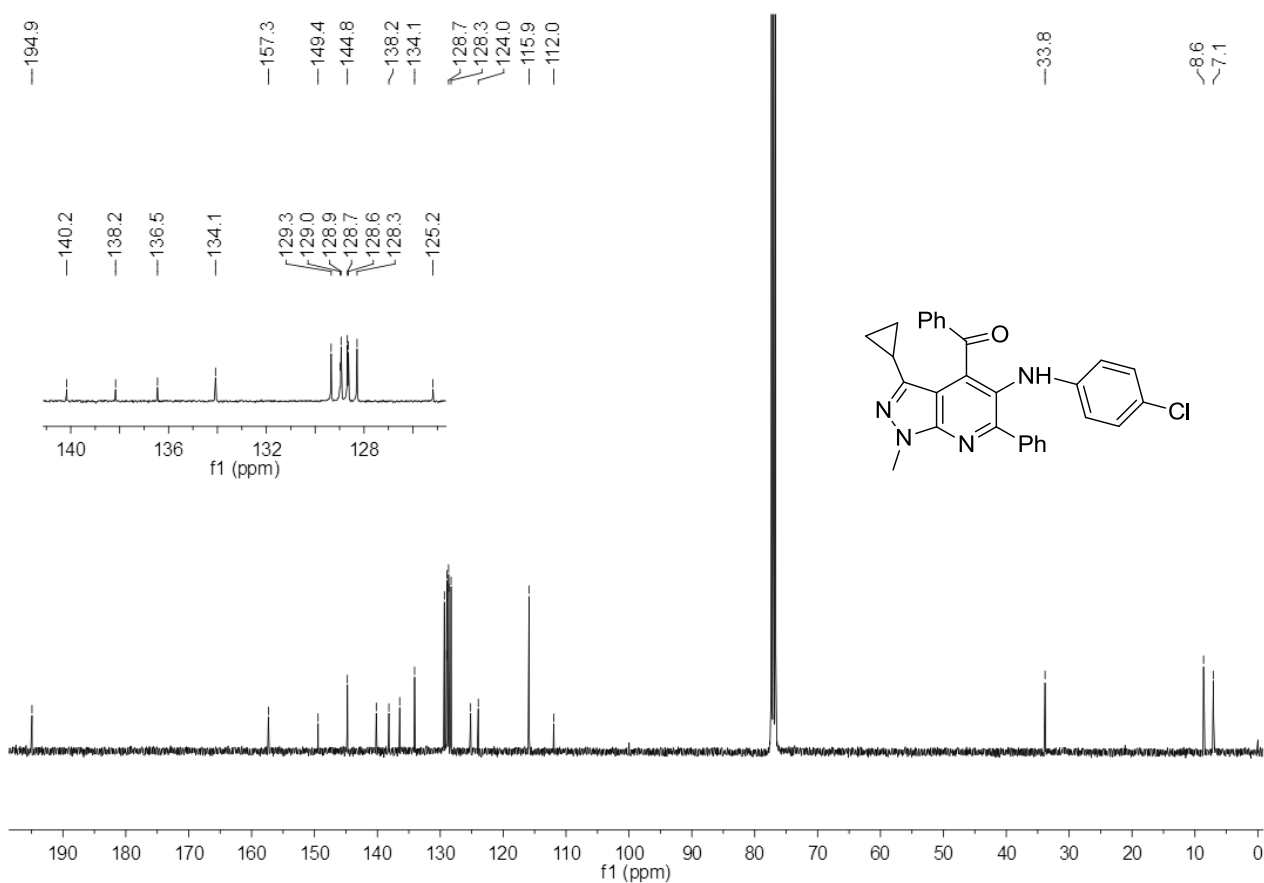
¹H NMR Spectrum of Compound 5j



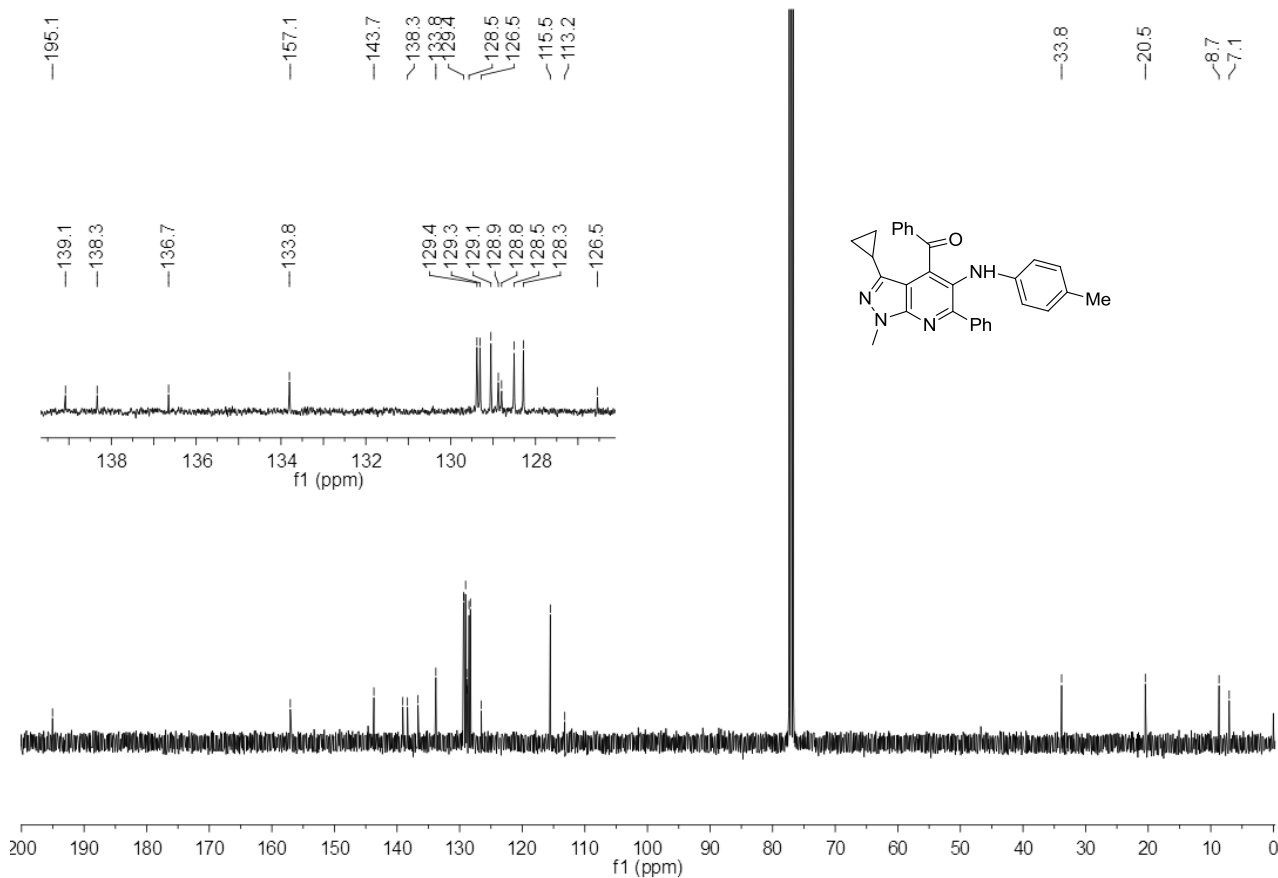
¹³C NMR Spectrum of Compound 5j

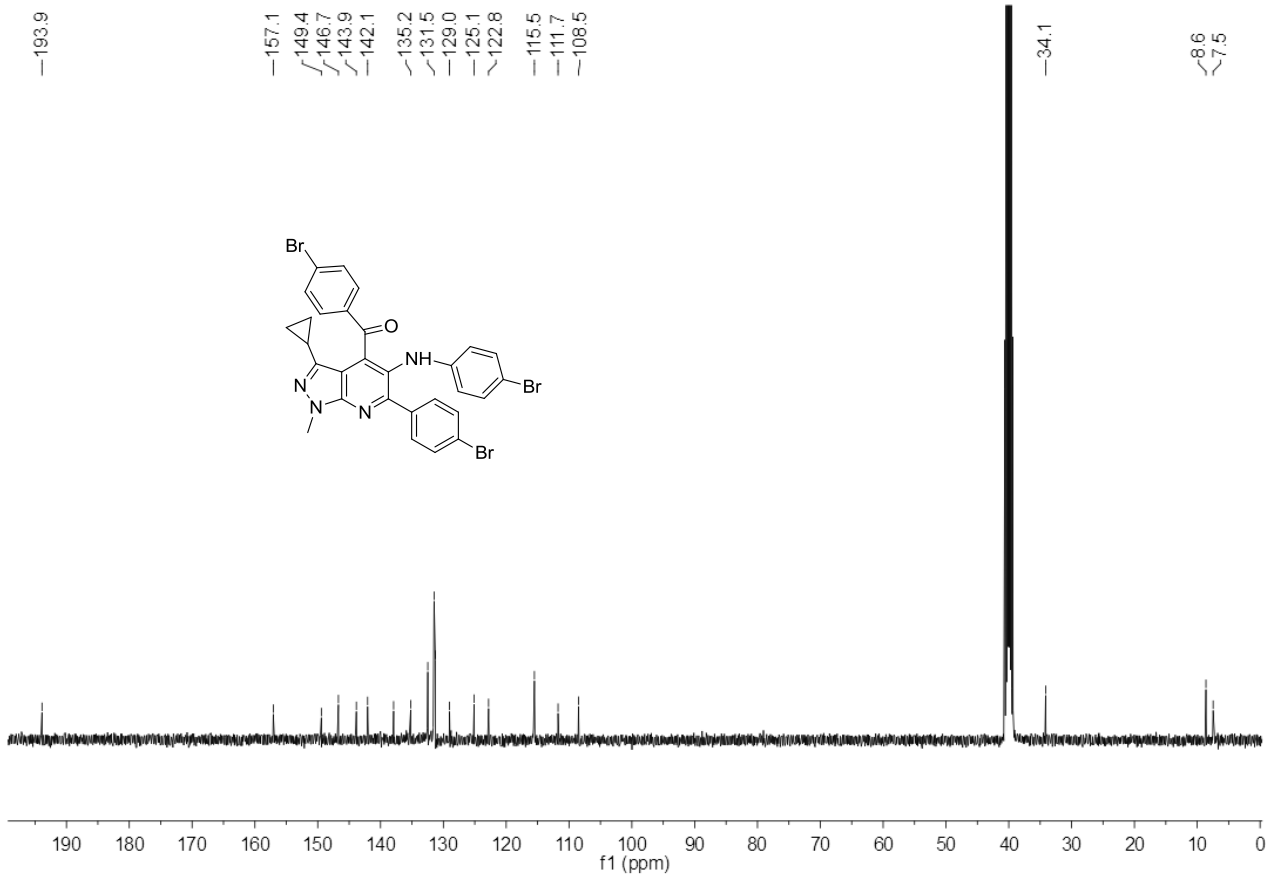
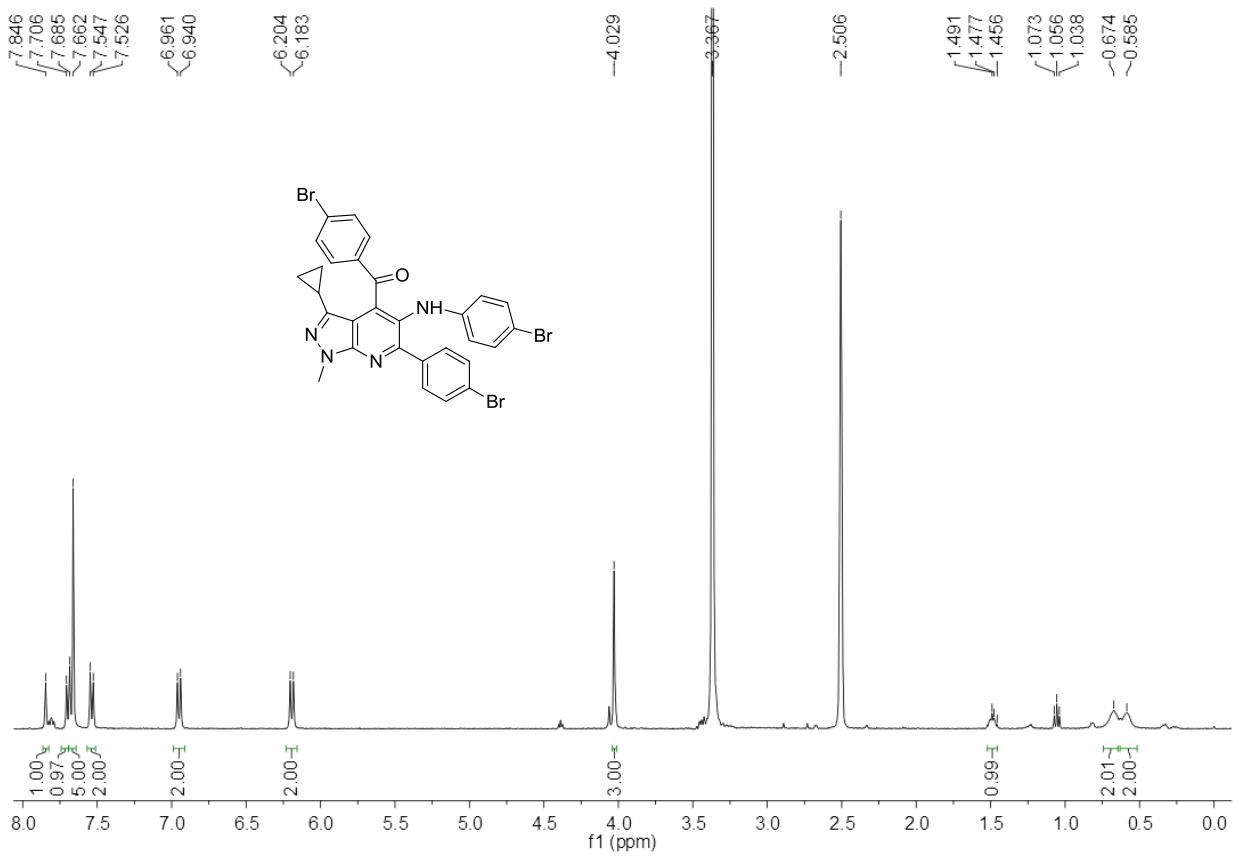


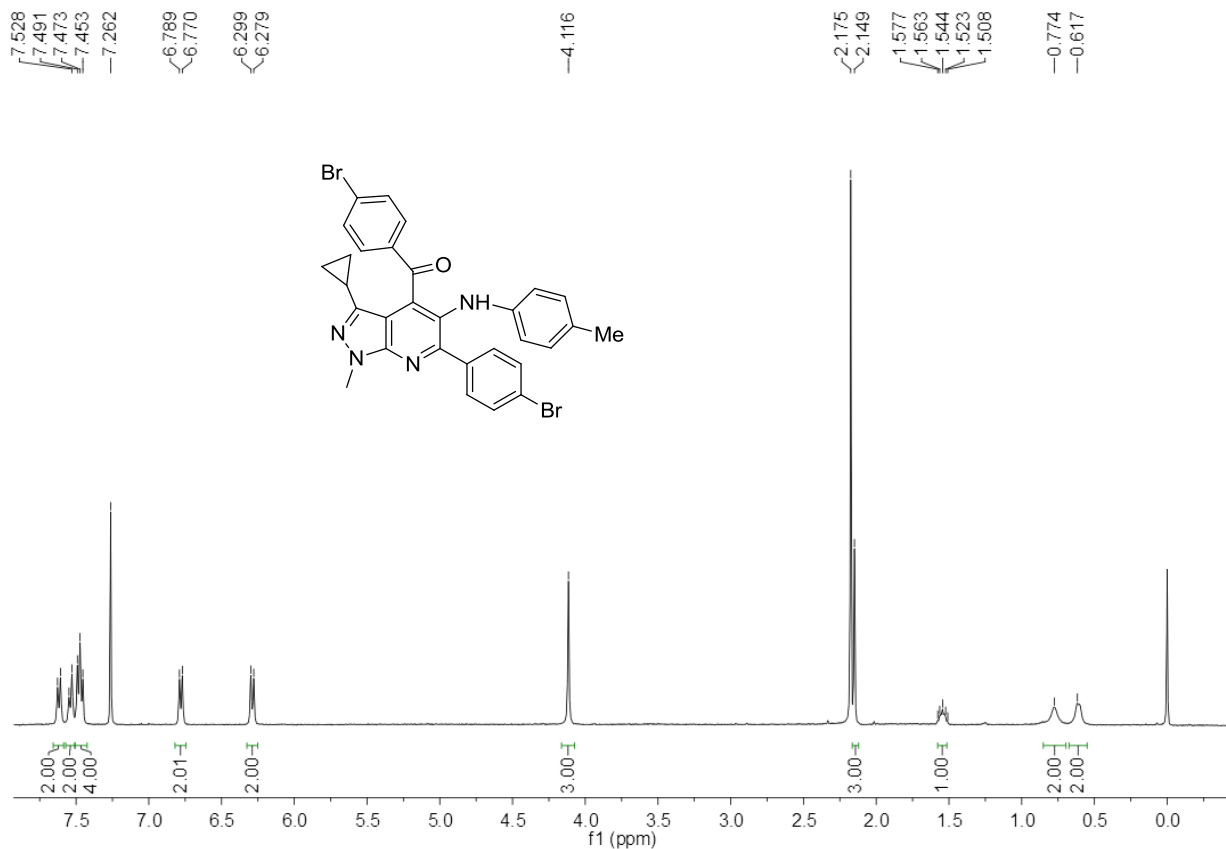
¹H NMR Spectrum of Compound 5k



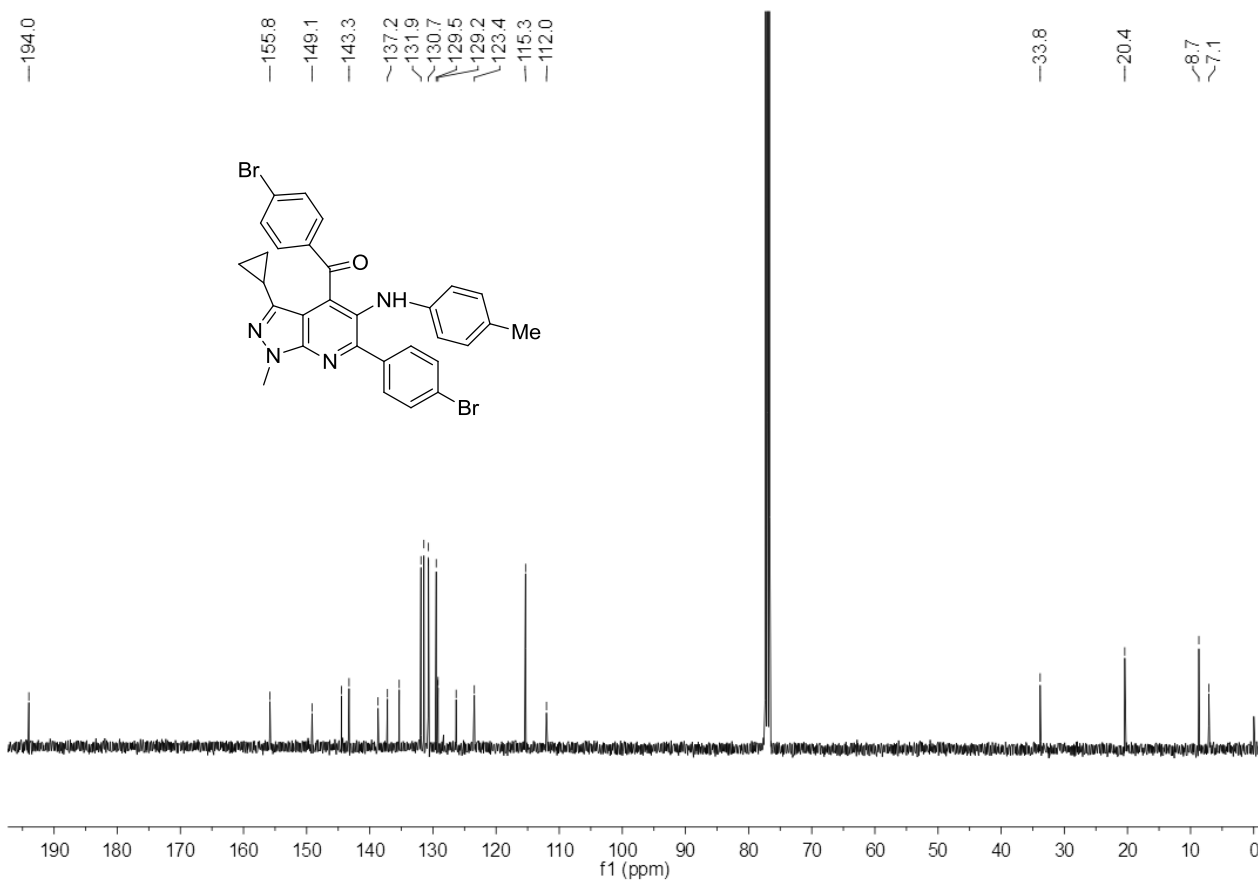
¹³C NMR Spectrum of Compound 5k



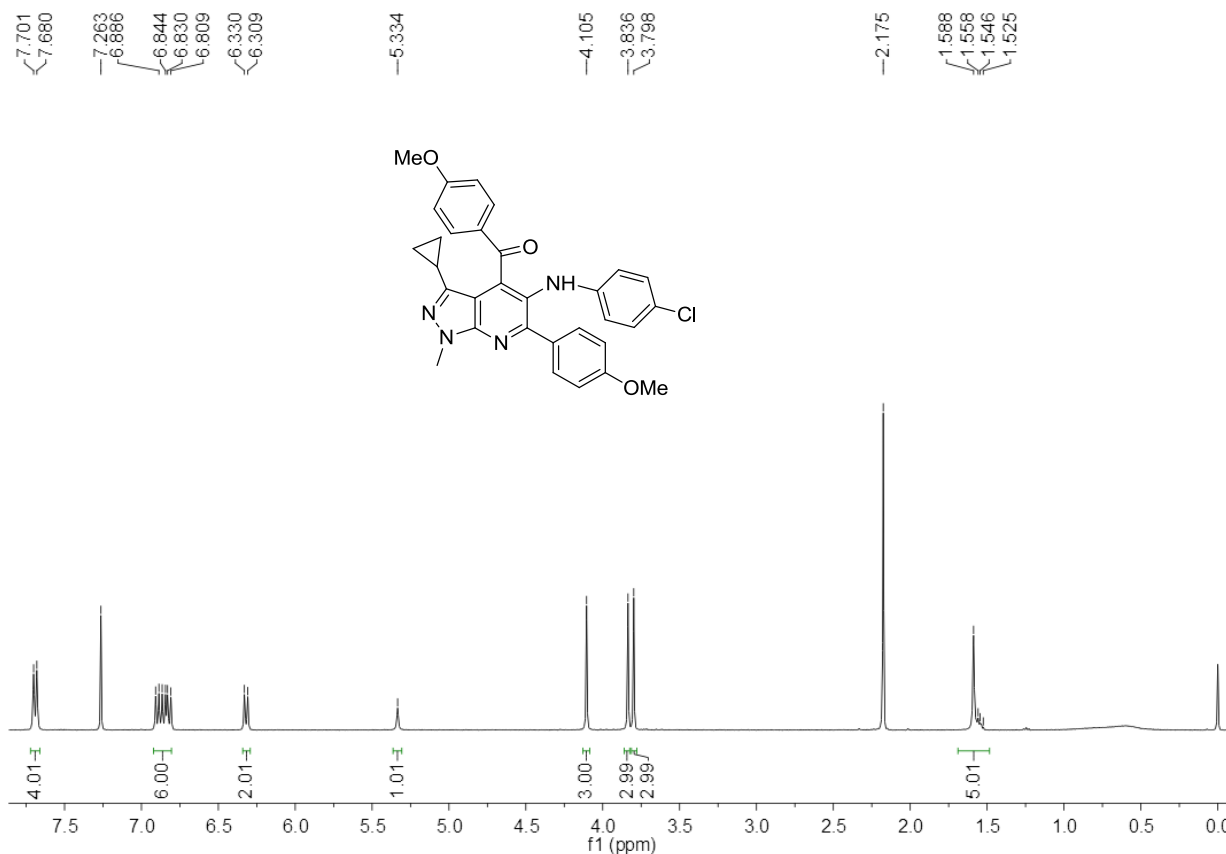




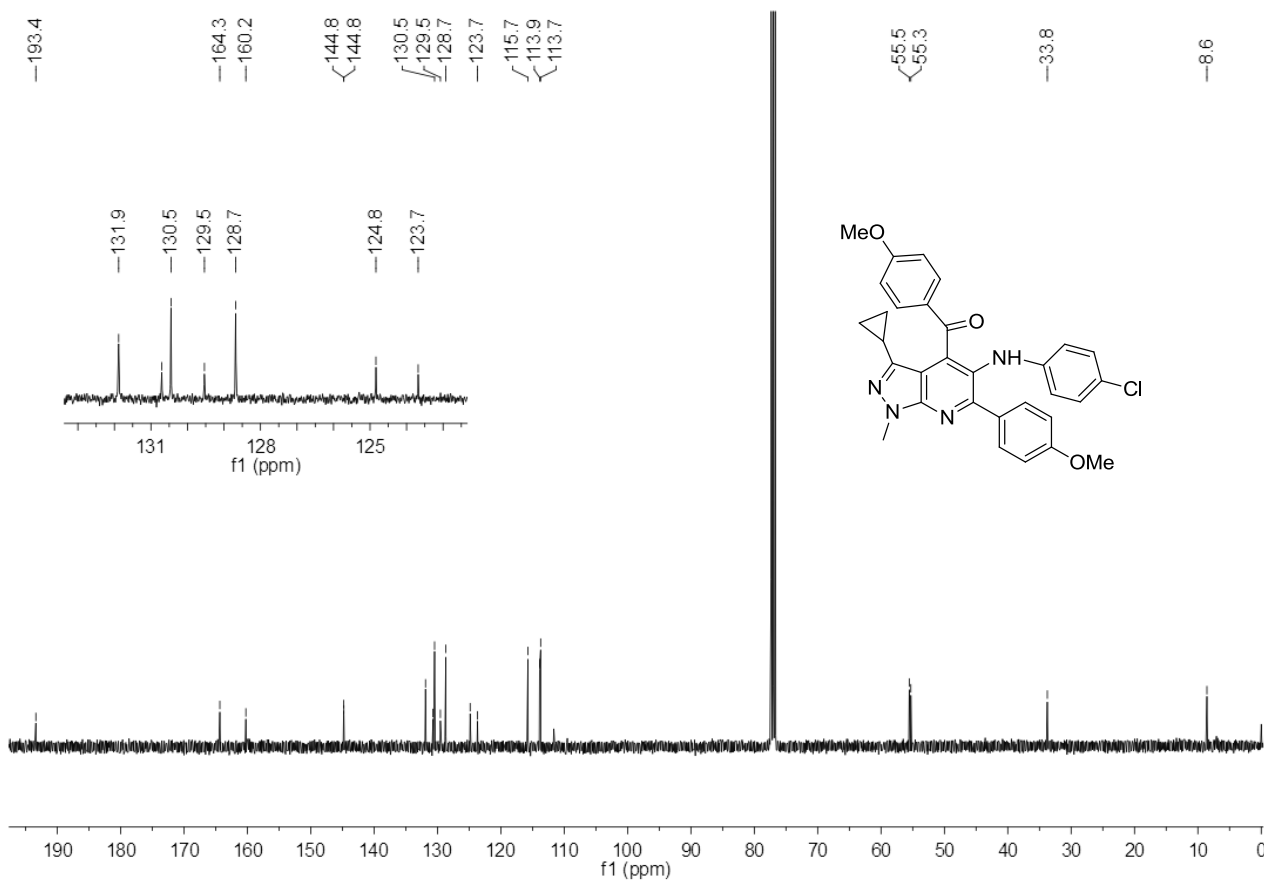
¹H NMR Spectrum of Compound 5n



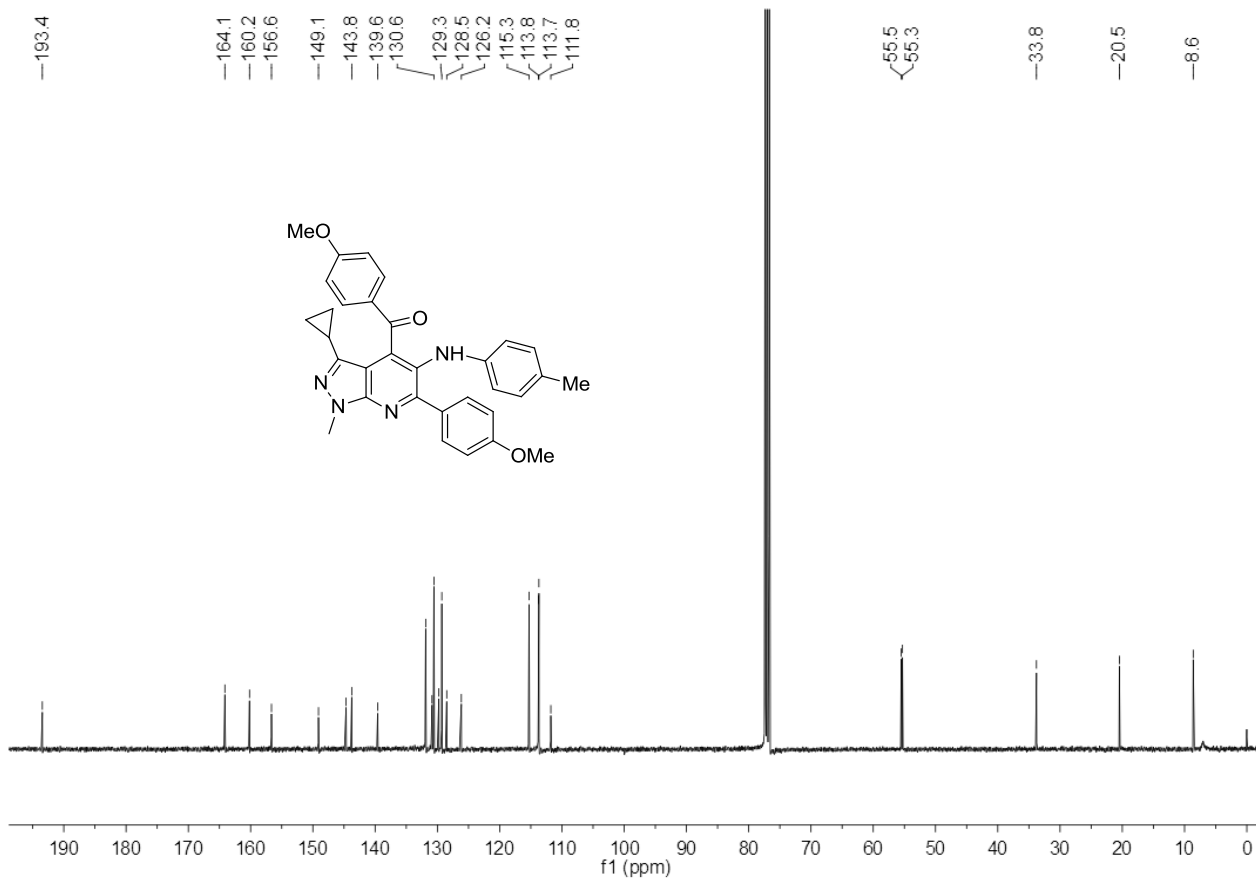
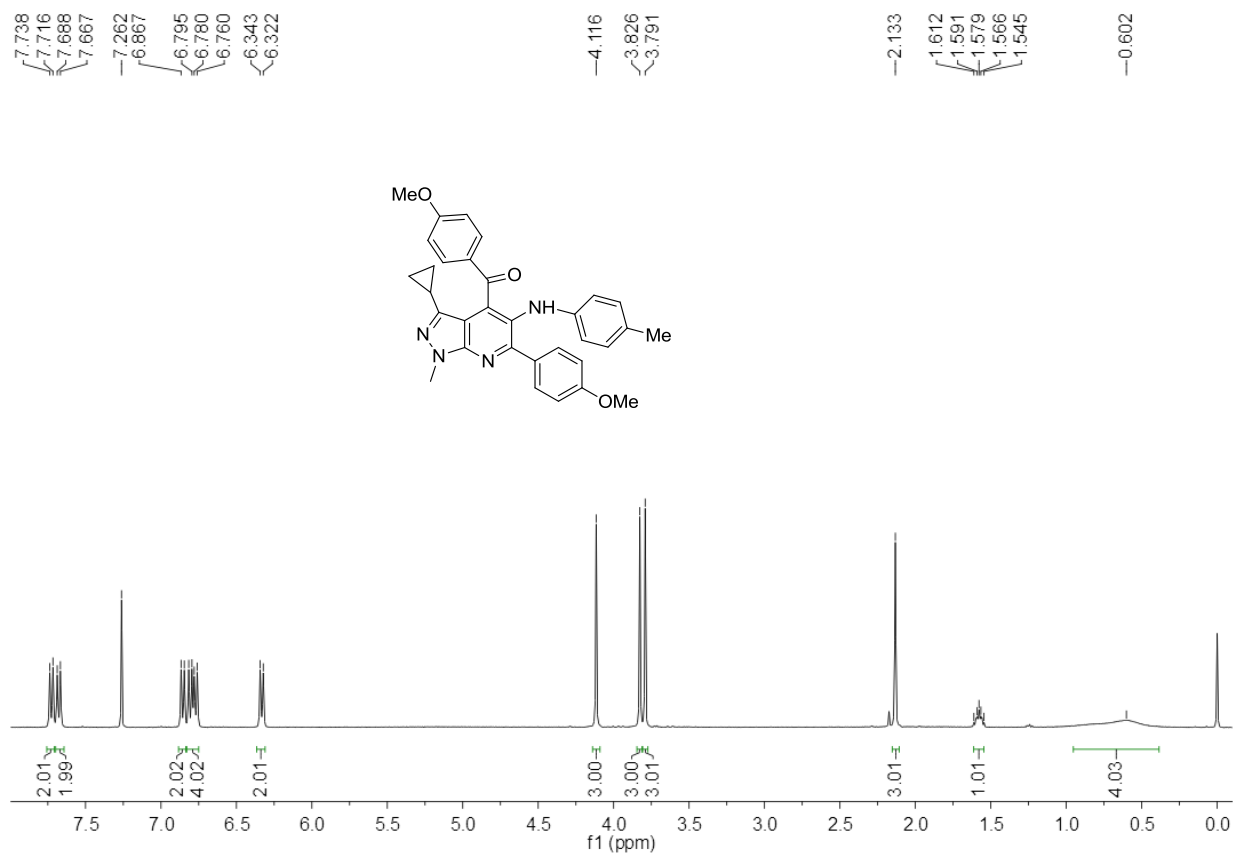
¹³C NMR Spectrum of Compound 5n

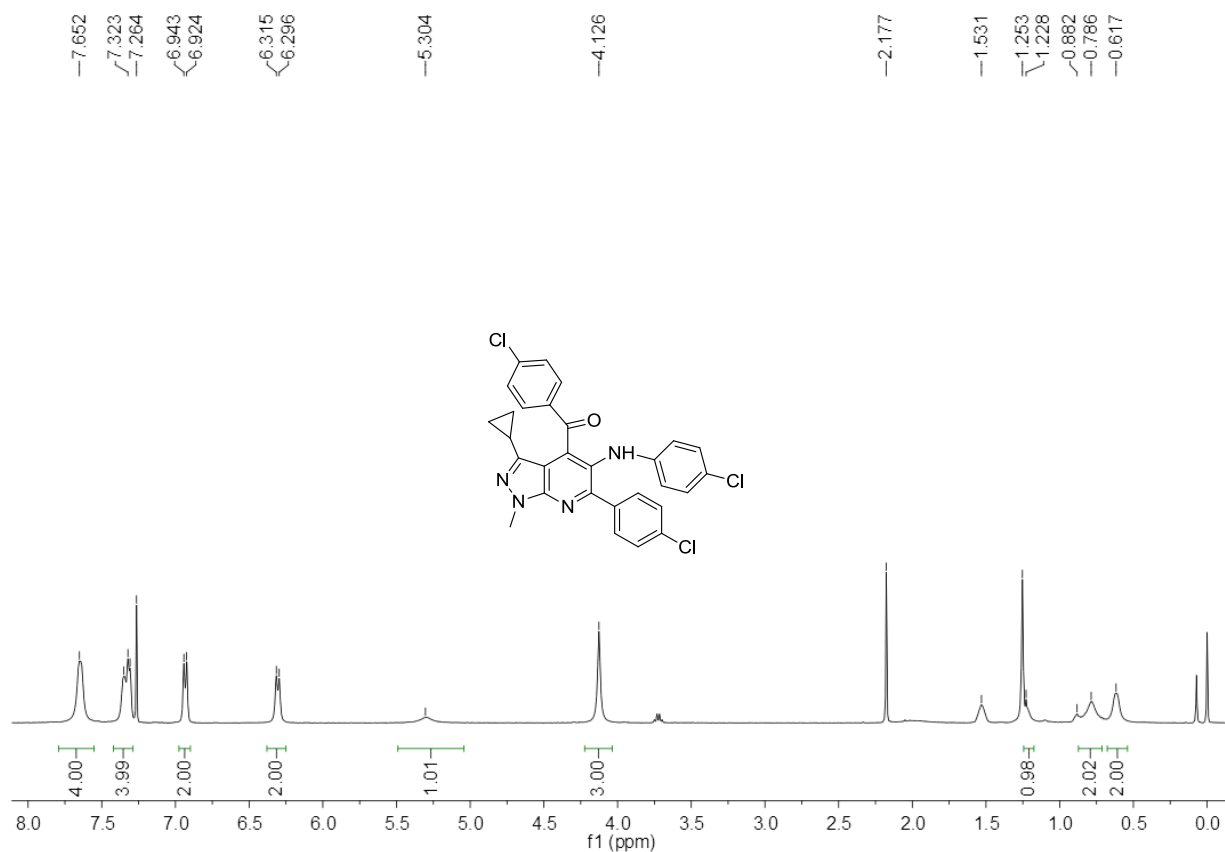


¹H NMR Spectrum of Compound 5o

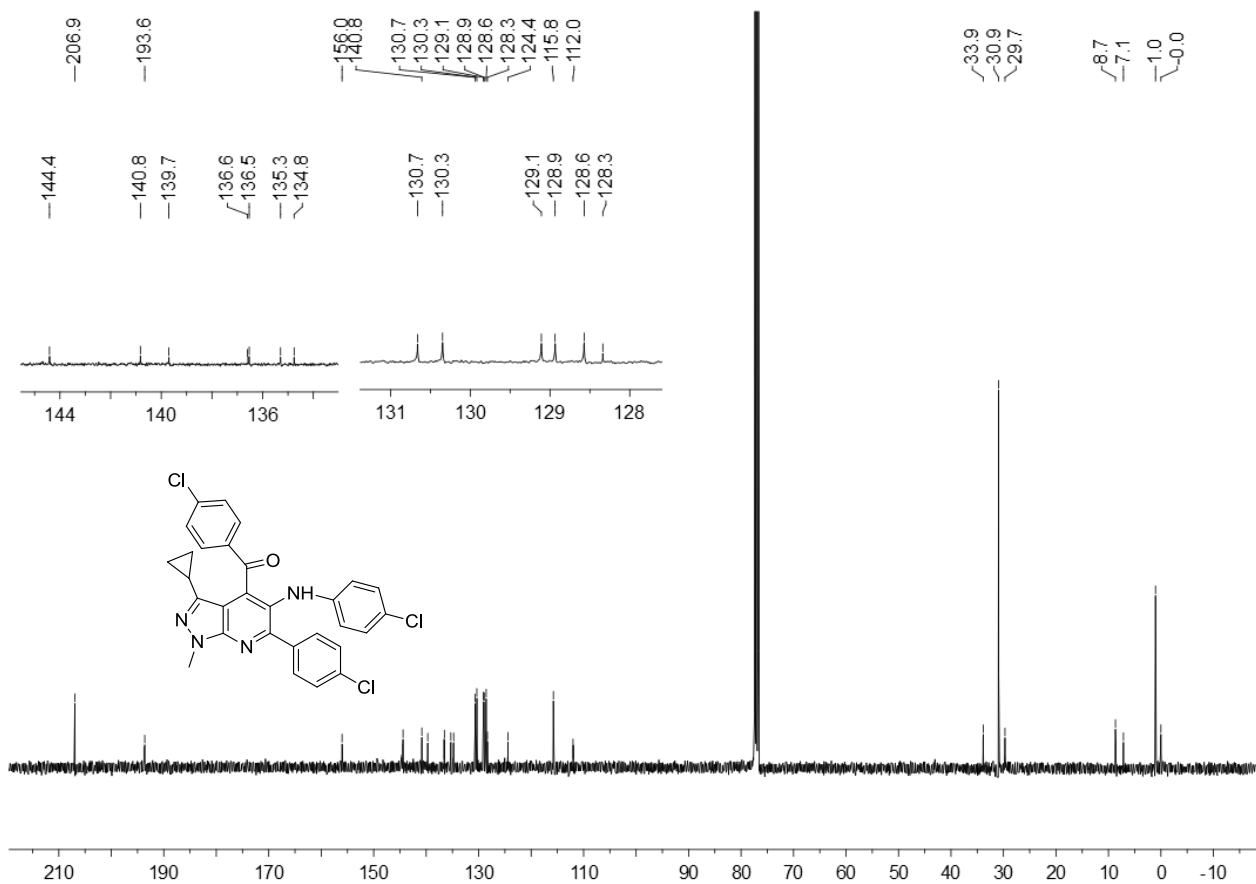


¹³C NMR Spectrum of Compound 5o

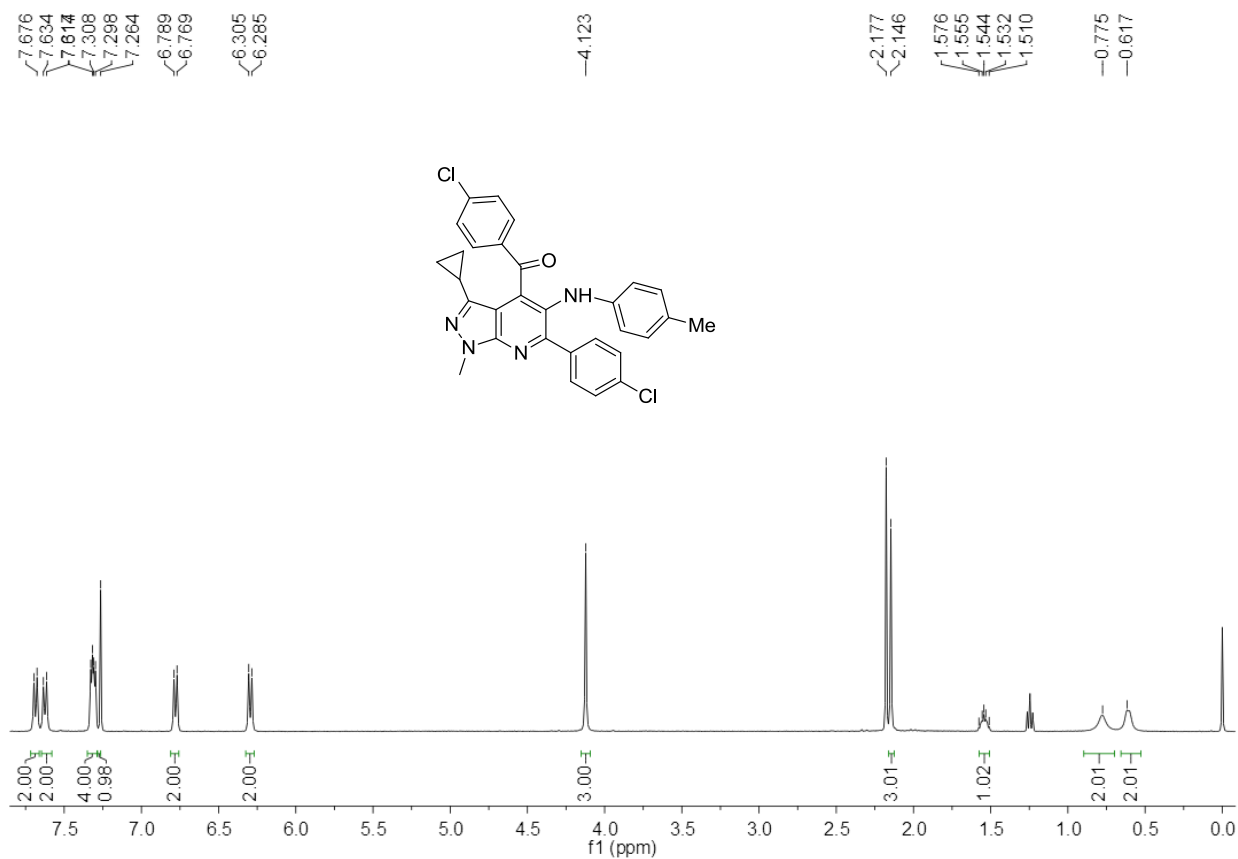




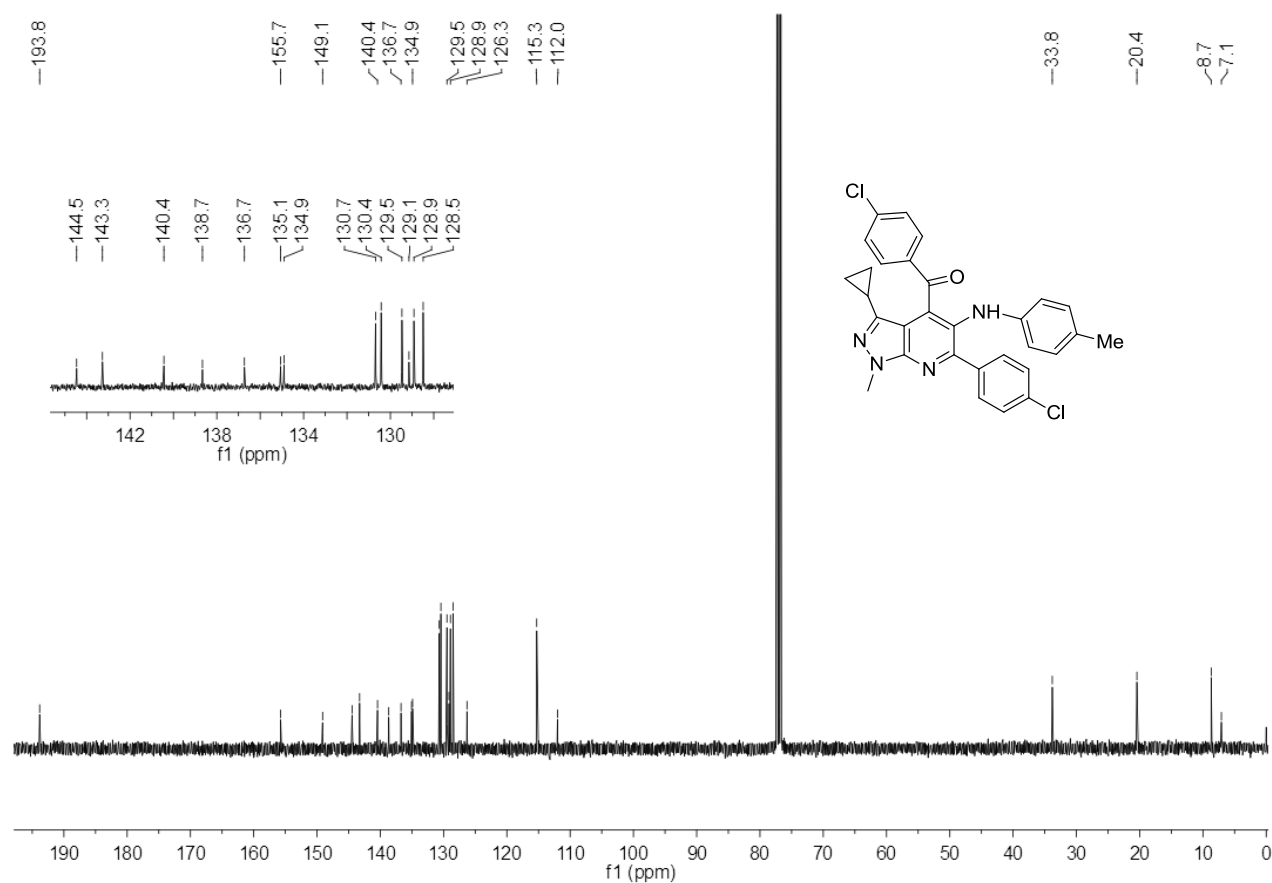
¹H NMR Spectrum of Compound 5q



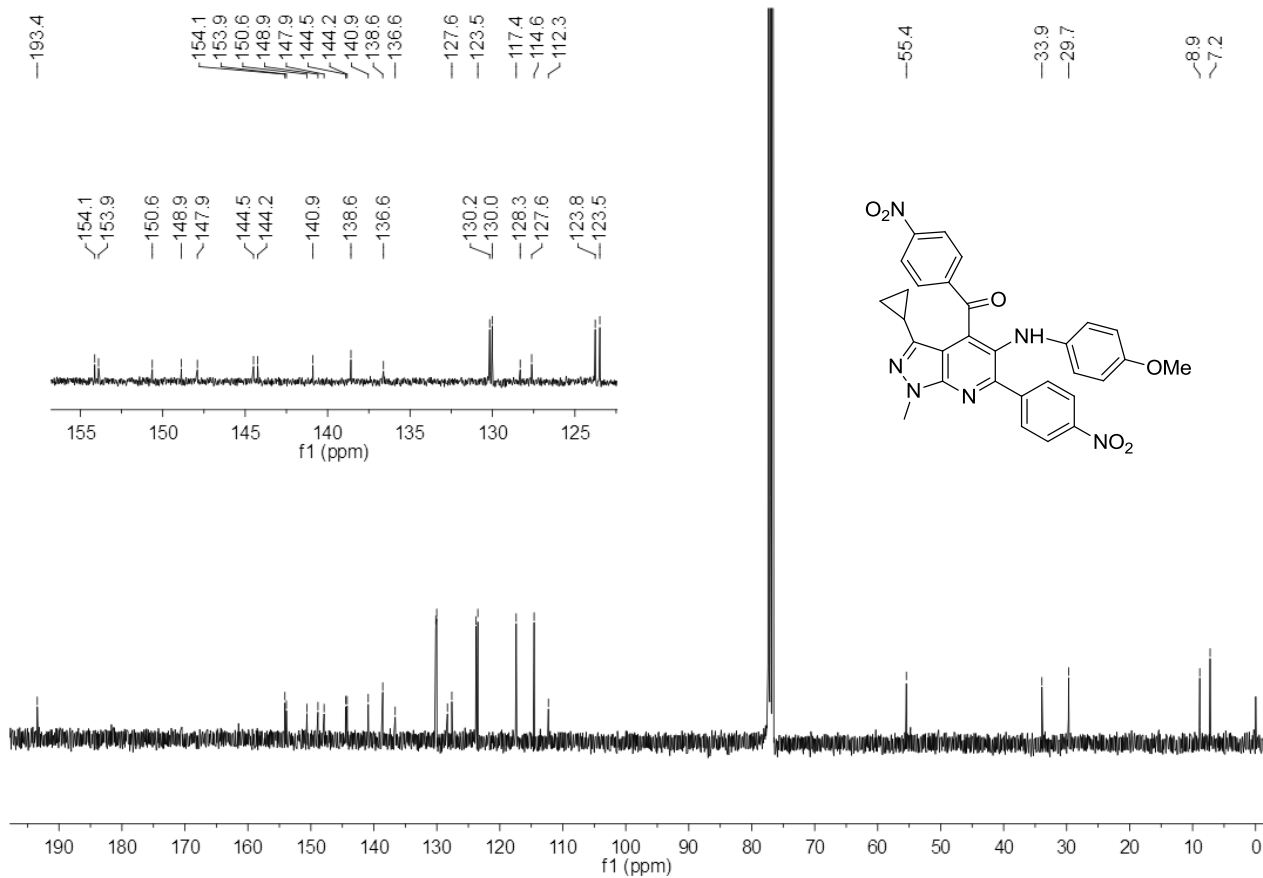
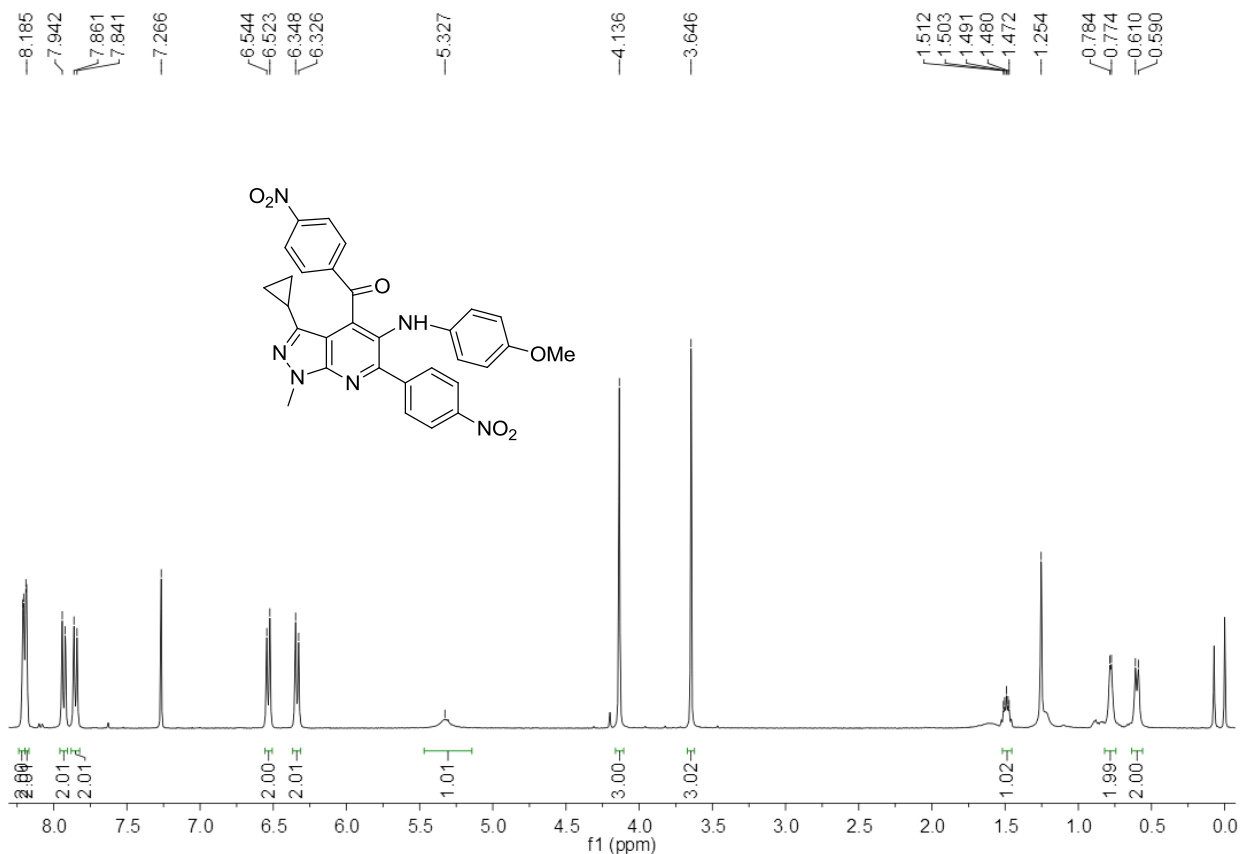
¹³C NMR Spectrum of Compound 5q



¹H NMR Spectrum of Compound 5r



¹³C NMR Spectrum of Compound 5r



¹³C NMR Spectrum of Compound 5s