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Supporting Information

Cobalt(II)/silver relay catalytic isocyanide insertion-cycloaddition cascades: A new access toward pyrrolo[2,3-*b*]indoles

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Experimental

General Information

^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ (or DMSO-d_6) 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 (APCI-TOF) was determined by using microTOF-QⅡ HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

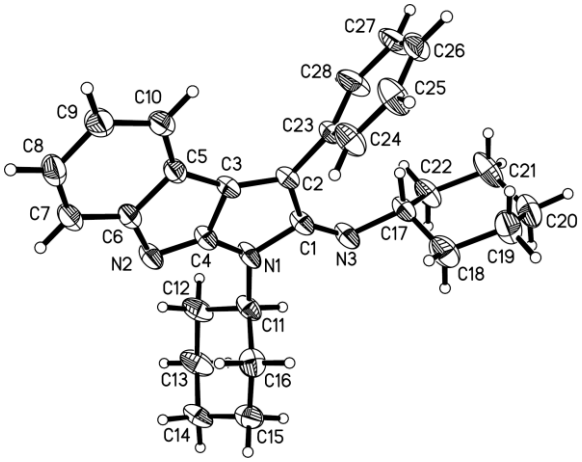
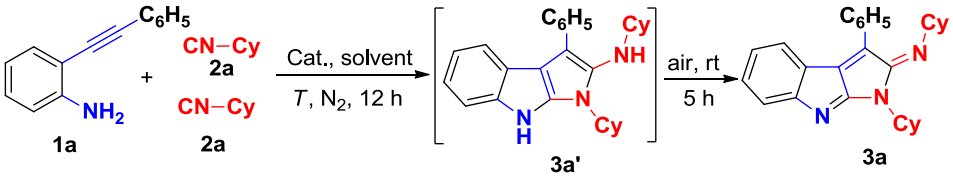


Fig 1, X-ray Structure of **3a**

Table 1. Optimization of the reaction conditions[a]



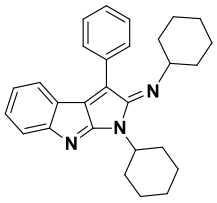
Entry	Cat. (mol %)	Solvent	*T* (°C)	Yield (%)
1	$CoCl_2$ (10)	1,4-dioxane	100	10%
2	$Cu(OAc)_2$ (10)	1,4-dioxane	100	NR
3	$Pd(OAc)_2$ (10)	1,4-dioxane	100	trace
4	$Rh_2(OAc)_4$ (10)	1,4-dioxane	100	trace
5	$Co(acac)_2$ (10)	1,4-dioxane	100	18%
6	$Co(acac)_2$ (10)/AgOTf (10)	1,4-dioxane	100	67
7	**$Co(acac)_2$ (10)/AgOTf (10)**	**1,4-dioxane**	**120**	**86**
8	$Co(acac)_2$ (20)/AgOTf (10)	1,4-dioxane	120	63
9	$Co(acac)_2$ (30)/AgOTf (10)	1,4-dioxane	120	55
10	$Co(acac)_2$ (5)/AgOTf (10)	1,4-dioxane	120	65
11	$Co(acac)_2$ (10)/AgOTf (5)	1,4-dioxane	120	49
12	$Co(acac)_2$ (10)/AgOTf (20)	1,4-dioxane	120	72
13	$Co(acac)_2$ (10)/AgOTf (10)	DMF	120	82
15	$Co(acac)_2$ (10)/AgOTf (10)	DMSO	120	62
16	$Co(acac)_2$ (10)/AgOTf (10)	Toluene	120	35
17	$Co(acac)_2$ (10)/AgOTf (10)	1,4-dioxane	120	65 [c]
18	$Co(acac)_2$ (10)/AgOTf (10)	1,4-dioxane	120	69 [d]
19	AgOTf (10)	1,4-dioxane	120	NR

[a]Reaction conditions: 2-(phenylethynyl)aniline (**1a**, 0.5 mmol) and isocyanocyclohexane (**2a**, 1.2 mmol), catalyst (10 mol %), dry solvent (4.0 mL), N_2, 12 h; after completion, all the reaction mixture were stirred at room temperature under air conditions for 5 h. [b] Isolated yield. [c] Isolated yield under air conditions. [d] Isolated yield under O_2 conditions. NR = No Reaction.

Experimental Section

Typical procedure for the synthesis of **3a**: Under a nitrogen atmosphere, 2-(phenylethynyl)aniline (**1a**, 96.5 mg, 0.5 mmol), $Co(acac)_2$ (12.8 mg, 0.05 mmol, 10 mol %) and AgOTf (12.8 mg, 0.05 mmol, 10 mol %) were introduced into a 25-mL Schlenk reaction flask, cyclohexyl isocyanide (**2a**, 130.8 mg, 1.2 mmol, 2.4 equiv) and dry 1,4-dioxane (4.0 mL) were then successively added into this reaction mixture. The reaction system was stirred at 120 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was continuously stirred at room temperature under air conditions for 5 h until the reaction solution turned red. Next, the solvent was removed under vacuum. The residue was separated by column chromatography on silica gel (eluent, petroleum ether/ethyl acetate) to afford the pure red solid **3a** in 86% yield.

(*E*)-*N*-(1-Cyclohexyl-3-phenylpyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3a)



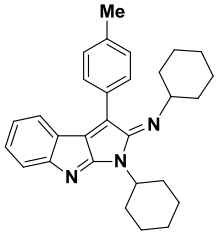
Red solid, m.p.: 132-133 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.65-7.43 (m, 5H, Ar-H), 7.17 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.07-6.85 (m, *2*H, Ar-H), 6.72 (t, *J* = 7.4 Hz, 1H, Ar-H), 4.14 (t, *J* = 12.0 Hz, 1H, CH), 3.64 (t, *J* = 9.6 Hz, 1H, CH), 2.18-2.10 (m, 2H, CH_2), 1.89–1.06 (m, 16H, CH_2), 0.85–0.58 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 164.4, 153.9, 142.9, 133.9, 132.1, 128.8, 128.6, 127.8, 126.5, 123.7, 123.6, 121.8, 118.5, 56.7, 52.2, 35.0, 30.2, 26.0, 25.4, 25.3, 24.0.

HRMS (APCI): m/z calcd for: $C_{28}H_{31}N_3$, 410.2596 $[M+H]^+$; found: 410.2555.

(*E*)-*N*-(1-Cyclohexyl-3-(*p*-tolyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3b)



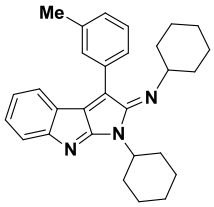
Red solid, m.p.: 127-128 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.49-7.31 (m, 4H, Ar-H), 7.16 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.10-6.86 (m, 2H, Ar-H), 6.72 (t, *J* = 7.4 Hz, 1H, Ar-H), 4.13 (t, *J* = 12.0 Hz, 1H, CH), 3.75 (t, *J* = 9.4 Hz, 1H, CH), 2.40 (s, 3H, CH_3), 2.13 (q, *J* = 12.0 Hz, 2H, CH_2), 1.86-1.14 (m, 16H, CH_2), 0.91-0.68 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.1, 163.2, 152.8, 141.7, 137.7, 130.9, 129.7, 128.2, 126.7, 125.8, 122.8, 122.5, 120.6, 117.4, 55.5, 51.1, 34.0, 29.1, 25.0, 24.5, 24.2, 22.9, 20.4.

HRMS (APCI): m/z calcd for: $C_{29}H_{33}N_3$, 424.2753 $[M+H]^+$; found: 424.2755.

(*E*)-*N*-(1-Cyclohexyl-3-(*m*-tolyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3c)



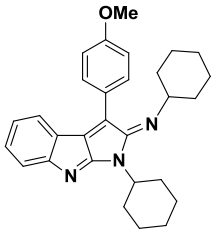
Red solid, m.p.: 113-114 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.28-7.23 (m, 3H, Ar-H), 7.19-7.11 (m, 2H, Ar-H), 6.98 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.68 (t, *J* = 7.0 Hz, 1H, Ar-H), 4.21 (t, *J* = 12.2 Hz, 1H, CH), 3.65 (t, *J* = 9.4 Hz, 1H, CH), 2.40 (s, 3H, CH_3), 2.23 (q, *J* = 11.2 Hz, 2H, CH_2), 1.94-1.22 (m, 16H, CH_2), 0.84 (q, *J* = 12.0 Hz, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 164.2, 153.9, 142.6, 138.3, 133.7, 132.1, 129.5, 128.5, 128.4, 126.8, 124.9, 123.7, 123.6, 121.8, 118.5, 56.8, 52.3, 35.0, 30.2, 26.0, 25.5, 25.3, 24.0, 21.4.

HRMS (APCI): m/z calcd for: $C_{29}H_{33}N_3$, 424.2753 $[M+H]^+$; found: 424.2754.

(*E*)-*N*-(1-Cyclohexyl-3-(4-methoxyphenyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3d)



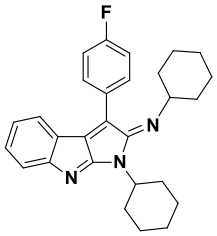
Red solid, m.p.: 154-155 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.50 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.16 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.12-7.03 (m, 3H, Ar-H), 6.95 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.73 (t, *J* = 7.4 Hz, 1H, Ar-H), 4.13 (t, *J* = 12.0 Hz, 1H, CH), 3.92-3.72 (m, 4H, CH and CH_3), 2.13 (q, *J* = 12.4 Hz, 2H, CH_2), 1.90-1.17 (m, 16H, CH_2), 0.96-0.72 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 164.2, 160.0, 153.8, 142.3, 131.9, 129.3, 126.7, 125.8, 123.8, 123.4, 121.7, 118.4, 114.0, 56.4, 55.4, 52.2, 35.1, 30.2, 26.0, 25.5, 25.3, 24.0.

HRMS (APCI): m/z calcd for: $C_{29}H_{33}N_3O$, 440.2702 $[M+H]^+$; found: 440.2703.

(*E*)-*N*-(1-Cyclohexyl-3-(4-fluorophenyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3e)



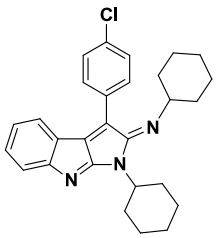
Red solid, m.p.: 130-131 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ =7.73-7.59 (m, 2H, Ar-H), 7.38 (t, *J* = 8.8 Hz, 2H, Ar-H), 7.18 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.09-6.85 (m, 2H, Ar-H), 6.73 (t, *J* = 7.4 Hz, 1H, Ar-H), 4.13 (t, *J* = 12.0 Hz, 1H, CH), 3.62 (s, 1H, CH), 2.22-2.04 (m, 2H, CH_2), 1.86-1.21 (m, 16H, CH_2), 0.77 (d, *J* = 11.8 Hz, 2H, CH_2).

^{13}C NMR (100 MHz, DMSO) δ =170.9, 164.4, 162.9 (*J* = 247.5 Hz), 153.6, 143.4, 132.4, 129.8, 129.7, 125.2, 123.6, 121.8, 118.6, 115.9 (*J* = 21.7 Hz), 56.7, 52.3, 35.0, 30.2, 26.0, 25.4, 25.2, 24.0.

HRMS (APCI): m/z calcd for: $C_{28}H_{30}FN_3$, 428.2502 $[M+H]^+$; found: 428.2503.

(E)-*N*-(3-(4-Chlorophenyl)-1-cyclohexylpyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3f)



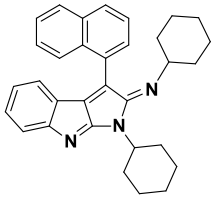
Red solid, m.p.: 154-155 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.47-7.37 (m, 4H, Ar-H), 7.18-7.11 (m, 2H, Ar-H), 6.91 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.73-6.61 (m, 1H, Ar-H), 4.28-4.13 (m, 1H, CH), 3.71-3.55 (m, 1H, CH), 2.30-2.15 (m, 2H, CH_2), 1.89-1.33 (m, 16H, CH_2), 0.96-0.81 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ =170.9, 164.4, 153.4, 143.5, 134.8, 132.5, 132.4, 129.3, 128.9, 124.9, 123.6, 123.4, 121.9, 118.6, 56.8, 52.3, 35.0, 30.1, 26.0, 25.4, 25.2, 24.0.

HRMS (APCI): m/z calcd for: $C_{28}H_{30}ClN_3$, 444.2207 $[M+H]^+$; found: 444.2209.

(E)-*N*-(1-Cyclohexyl-3-(naphthalen-1-yl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3g)



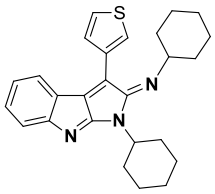
Red solid, m.p.: 177-178 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.17-8.02 (m, 2H, Ar-H), 7.77-7.03 (m, 7H, Ar-H), 6.69-6.41 (m, 2H, Ar-H), 4.19 (t, *J* = 12.2 Hz, 1H, CH), 3.12 (s, 1H, CH), 2.31-2.09 (m, 2H, CH_2), 1.93-1.06 (m, 16H, CH_2), 1.00-0.76 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.2, 164.4, 154.5, 144.0, 133.4, 132.1, 131.2, 131.1, 129.1, 128.5, 126.9, 126.6, 125.7, 125.3, 125.2, 124.7, 124.2, 123.7, 121.8, 118.5, 57.4, 52.3, 35.0, 34.6, 30.3, 30.2, 26.0, 26.0, 25.3, 25.2, 24.1, 23.7.

HRMS (APCI): m/z calcd for: $C_{32}H_{33}N_3$, 460.2753 $[M+H]^+$; found: 460.2757.

(*E*)-*N*-(1-Cyclohexyl-3-(thiophen-3-yl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3h)



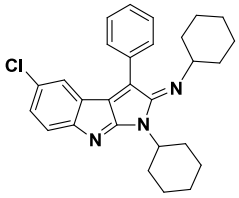
Red solid, m.p.: 119-120 °C.

H NMR (400 MHz, $CDCl_3$) δ = 7.48-7.39 (m, 2H, Ar-H), 7.20-7.12 (m, 3H, Ar-H), 7.03 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.78-6.63 (m, 1H, Ar-H), 4.29-4.12 (m, 1H, CH), 3.79-3.67 (m, 1H, CH), 2.28-2.17 (m, 2H, CH_2), 1.90-1.36 (m, 16H, CH_2), 1.03-0.86 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 164.2, 153.8, 143.5, 133.4, 132.2, 127.5, 126.5, 124.2, 123.6, 121.8, 121.5, 118.5, 56.8, 52.2, 35.2, 30.1, 26.0, 25.4, 25.2, 24.1.

HRMS (APCI): m/z calcd for: $C_{26}H_{29}N_3S$, 416.2160 $[M+H]^+$; found: 416.2160.

(E)-*N*-(5-chloro-1-cyclohexyl-3-phenylpyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3j)

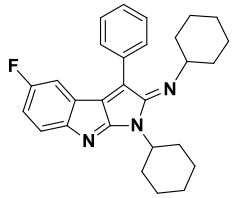


Red solid, m.p.: 143-144 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51-7.37 (m, 5H, Ar-H), 7.14-7.02 (m, 2H, Ar-H), 6.87 (s, 1H, Ar-H), 4.31-4.13 (m, 1H, CH), 3.69-3.55 (m, 1H, CH), 2.29-2.14 (m, 2H, CH_2), 1.92-1.32 (m, 16H, CH_2), 0.88-0.77 (m, 2H, CH_2).

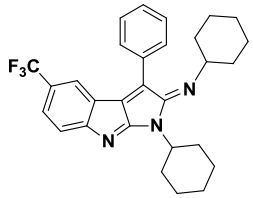
^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 162.6, 153.4, 142.0, 133.3, 131.5, 129.1, 128.8, 127.8, 127.6, 126.8, 125.0, 123.5, 119.1, 58.4, 52.3, 35.0, 30.2, 26.0, 25.4, 25.2, 24.0.
HRMS (APCI): m/z calcd for: $C_{28}H_{30}ClN_3$, 444.2207 $[M+H]^+$; found: 444.2203.

(*E*)-*N*-(1-Cyclohexyl-5-fluoro-3-phenylpyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3k)



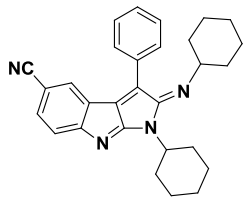
Red solid, m.p.: 95-96 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50-7.42 (m, 5H, Ar-H), 7.09-7.02 (m, 1H, Ar-H), 6.87-6.81 (m, 1H, Ar-H), 6.73-6.57 (m, 1H, Ar-H), 4.27-4.17 (m, 1H, CH), 3.70-3.57 (m, 1H, CH), 2.28-2.16 (m, 2H, CH_2), 1.90-1.36 (m, 16H, CH_2), 0.90-0.79 (m, 2H, CH_2).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 158.6 (*J* = 237.6 Hz), 157.4, 153.4, 142.4 (*J* = 3.4 Hz), 133.4, 129.1, 128.8, 127.8, 127.6, 124.5 (*J* = 9.4 Hz), 118.4 (*J* = 8.1 Hz), 117.7 (*J* = 23.1 Hz), 111.1 (*J* = 25.4 Hz), 58.3, 52.2, 35.0, 30.1, 26.0, 25.4, 25.2, 24.0.
HRMS (APCI): m/z calcd for: $C_{28}H_{30}FN_3$, 428.2502 $[M+H]^+$; found: 428.2498.

(*E*)-*N*-(1-Cyclohexyl-3-phenyl-5-(trifluoromethyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3l)



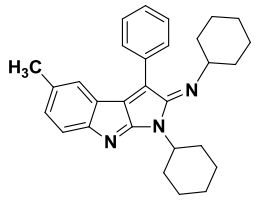
Red solid, m.p.: 186-187 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51-7.48 (m, 3H, Ar-H), 7.47-7.40 (m, 3H, Ar-H), 7.22 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.12 (s, 1H, Ar-H), 4.29-4.20 (m, 1H, CH), 3.71-3.62 (m, 1H, CH), 2.29-2.17 (m, 2H, CH_2), 1.90-1.34 (m, 16H, CH_2), 0.90-0.79 (m, 2H, CH_2).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.4, 167.1, 153.3, 141.6, 133.1, 129.4 (d, *J* = 3.8 Hz), 129.3, 128.9, 128.0, 127.6, 124.4 (d, *J* = 269.7), 124.0, 123.7 (q, *J* = 32.1), 120.1 (d, *J* = 3.4 Hz), 118.1, 57.0, 52.4, 35.0, 30.2, 26.0, 25.4, 25.2, 24.0.
HRMS (APCI): m/z calcd for: $C_{29}H_{30}F_3N_3$, 478.2470 $[M+H]^+$; found: 478.2474.

(*E*)-1-Cyclohexyl-2-(cyclohexylimino)-3-phenyl-1,2-dihydropyrrolo[2,3-*b*]indole-5-carbonitrile (3m)



Red solid, m.p.: 182-183 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54–7.49 (m, 3H, Ar-H), 7.48–7.37 (m, 3H, Ar-H), 7.25–7.08 (m, 2H, Ar-H), 4.34–4.16 (m, 1H, CH), 3.79–3.60 (m, 1H, CH), 2.30–2.13 (m, 2H, CH_2), 1.98–1.30 (m, 16H, CH_2), 0.93-0.77 (m, 2H, CH_2).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.8, 168.0, 153.1, 141.0, 136.5, 132.8, 129.5, 129.0, 128.5, 127.5, 126.4, 124.4, 119.5, 118.8, 104.2, 57.2, 52.5, 34.9, 30.2, 25.9, 25.3, 25.2, 23.9.
HRMS (APCI): m/z calcd for: $C_{29}H_{30}N_4$, 435.2549 $[M+H]^+$; found: 435.2551.

(*E*)-*N*-(1-Cyclohexyl-5-methyl-3-phenylpyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3n)



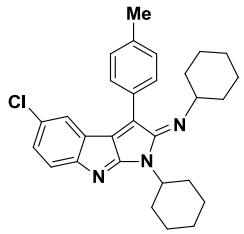
Red solid, m.p.: 121-122 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49–7.41 (m, 5H, Ar-H), 7.06-6.91 (m, 2H, Ar-H), 6.71 (s, 1H, Ar-H), 4.25-4.13 (m, 1H, CH), 3.66-3.56 (m, 1H, CH), 2.28-2.17 (m, 2H, CH_2), 2.12 (s, 3H, CH_3), 1.85 (d, *J* = 9.2 Hz, 4H, CH_2), 1.68-1.31 (m, 12H, CH_2), 0.87-0.76 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.7, 161.9, 153.9, 142.9, 134.0, 132.5, 131.2, 128.7, 128.6, 127.8, 126.3, 124.4, 123.7, 118.1, 58.4, 52.1, 35.0, 30.1, 26.0, 25.4, 25.2, 24.0, 20.8.

HRMS (APCI): m/z calcd for: $C_{29}H_{33}N_3$, 424.2753 $[M+H]^+$; found: 424.2752.

(*E*)-*N*-(5-Chloro-1-cyclohexyl-3-(*p*-tolyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3o)



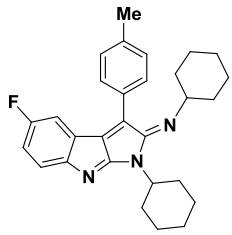
Red solid, m.p.: 173-174 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33-7.26 (m, 4H, Ar-H), 7.14-7.06 (m, 2H, Ar-H), 6.93 (s, 1H, Ar-H), 4.31-4.14 (m, 1H, CH), 3.86-3.64 (m, 1H, CH), 2.47 (s, 3H, CH_3), 2.29-2.14 (m, 2H, CH_2), 1.95-1.32 (m, 16H, CH_2), 1.01-0.78 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.2, 162.6, 153.4, 141.8, 139.2, 131.3, 130.2, 129.4, 128.2, 127.6, 126.7, 125.2, 123.4, 119.0, 56.7, 52.2, 35.0, 30.2, 26.0, 25.4, 25.2, 23.9, 21.5.

HRMS (APCI): m/z calcd for: $C_{29}H_{32}ClN_3$, 458.2363 $[M+H]^+$; found: 458.2360.

(*E*)-*N*-(1-Cyclohexyl-5-fluoro-3-(*p*-tolyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3p)



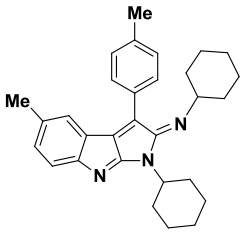
Red solid, m.p.: 150-151 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33-7.25 (m, 4H, Ar-H), 7.10-7.01 (m, 1H, Ar-H), 6.85-6.76 (m, 1H, Ar-H), 6.76-6.62 (m, 1H, Ar-H), 4.29-4.11 (m, 1H, CH), 3.81-3.68 (m, 1H, CH), 2.44 (s, 3H, CH_3), 2.29-2.14 (m, 2H, CH_2), 1.89-1.30 (m, 16H, CH_2), 0.97-0.79 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 160.0, 158.6 (*J* = 237.5 Hz), 153.4, 142.1 (*J* = 2.8 Hz), 139.1, 130.3, 129.4, 128.2, 127.6, 124.6 (*J* = 9.6Hz), 118.3 (*J* = 8.1 Hz), 117.5 (*J* = 23.1 Hz), 111.0 (*J* = 25.5 Hz), 56.6, 52.2, 35.0, 30.1, 26.0, 25.4, 25.2, 23.9, 21.5.

HRMS (APCI): m/z calcd for: $C_{29}H_{32}FN_3$, 442.2659 $[M+H]^+$; found: 442.2660.

(*E*)-*N*-(1-Cyclohexyl-5-methyl-3-(*p*-tolyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)cyclohexanamine (3q)



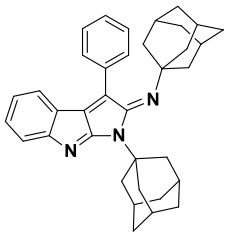
Red solid, m.p.: 157-158 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34-7.25 (m, 4H, Ar-H), 7.06-6.90 (m, 2H, Ar-H), 6.78 (s, 1H, Ar-H), 4.28-4.15 (m, 1H, CH), 3.77-3.67 (m, 1H, CH), 2.47 (s, 3H, CH_3), 2.35-2.21 (m, 2H, CH_2), 2.15 (s, 3H, CH_3), 1.92-1.33 (m, 16H, CH_2), 0.97-0.77 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.8, 161.9, 153.9, 142.7, 138.7, 132.3, 131.1, 130.8, 129.3, 127.7, 126.7, 124.3, 123.8, 118.0, 56.4, 52.1, 35.0, 30.1, 26.0, 25.5, 25.3, 24.0, 21.5, 20.8.

HRMS (APCI): m/z calcd for: $C_{30}H_{35}N_3$, 438.2909 $[M+H]^+$; found: 438.2912.

(*E*)-*N*-(1-(Adamantan-1-yl)-3-phenylpyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)adamantan-1-amine (3r)



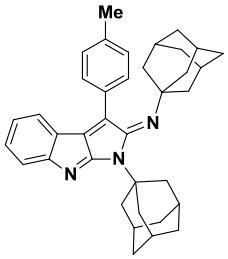
Red solid, m.p.: 229-230 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.62-7.48 (m, 3H, Ar-H), 7.43 (m, 2H, Ar-H), 7.15-7.09 (m, 1H, Ar-H), 6.98 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.64 (t, *J* = 7.0 Hz, 1H, Ar-H), 6.52 (d, *J* = 6.6 Hz, 1H, Ar-H), 2.62 (d, *J* = 2.0 Hz, 4H), 2.12 (s, 3H), 1.81 (s, 3H), 1.76-1.61 (m, 10H), 1.45 (d, *J* = 11.6 Hz, 3H), 1.33-1.22 (m, 5H), 0.92-0.76 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.6, 163.6, 150.8, 145.4, 134.7, 132.0, 129.3, 128.6, 128.3, 126.2, 123.3, 123.2, 121.5, 118.1, 60.4, 57.6, 44.5, 41.4, 36.6, 35.9, 30.1, 29.6.

HRMS (APCI): m/z calcd for: $C_{36}H_{39}N_3$, 514.3222 $[M+H]^+$; found: 514.3221.

(*E*)-*N*-(1-(Adamantan-1-yl)-3-(*p*-tolyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)adamantan-1-amine (3s)



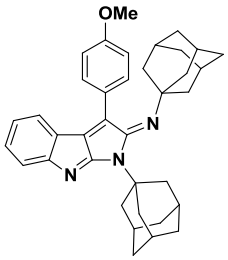
Red solid, m.p.: 257-258 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27-7.01 (m, 6H, Ar-H), 6.70-6.53 (m, 2H, Ar-H), 2.66 (d, *J* = 2.4 Hz, 6H), 2.43 (s, 3H, CH_3), 2.16 (s, 3H), 1.86 (s, 3H), 1.80-1.65 (m, 12H), 1.52-1.29 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.6, 163.4, 151.0, 145.3, 138.5, 131.9, 131.6, 129.2, 128.9, 126.6, 123.4, 123.1, 121.4, 118.1, 60.3, 57.6, 44.5, 41.4, 36.6, 36.0, 30.1, 29.6, 21.4.

HRMS (APCI): m/z calcd for: $C_{37}H_{41}N_3$, 528.3379 $[M+H]^+$; found: 528.3383.

(E)-*N*-(1-(adamantan-1-yl)-3-(4-methoxyphenyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)adamantan-1-amine (3t)



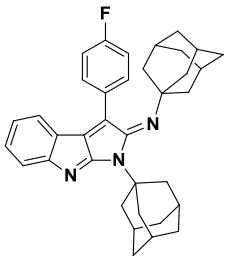
Red solid, m.p.: 237-238 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26-6.95 (m, 6H, Ar-H), 6.70-6.53 (m, 2H, Ar-H), 3.87 (s, 3H, CH_3), 2.66 (d, *J* = 2.2 Hz, 6H), 2.16 (s, 3H), 1.87 (s, 3H), 1.80-1.64 (m, 12H), 1.52-1.32 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.5, 163.4, 159.9, 151.0, 145.4, 131.9, 130.5, 126.7, 126.3, 123.4, 123.1, 121.4, 118.1, 113.7, 60.3, 57.6, 55.4, 44.5, 41.4, 36.6, 36.0, 30.1, 29.6.

HRMS (APCI): m/z calcd for: $C_{37}H_{41}N_3O$, 544.3328 $[M+H]^+$; found: 544.3329.

(*E*)-*N*-(1-(Adamantan-1-yl)-3-(4-fluorophenyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)adamantan-1-amine (3u)



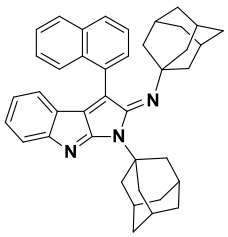
Red solid, m.p.: 28-219 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.28 (m, 2H, Ar-H), 7.24-6.97 (m, 4H, Ar-H), 6.68-6.54 (m, 2H, Ar-H), 2.65 (d, *J* = 2.0 Hz, 6H), 2.17 (d, *J* = 3.2 Hz, 3H), 1.88 (s, 3H), 1.80-1.64 (m, 12H), 1.54-1.31 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.8 (*J* = 245.2 Hz), 150.5, 146.0, 132.3 (*J* = 2.3 Hz), 131.2, 131.1 (*J* = 3.1 Hz), 130.7, 125.0, 123.1, 121.6, 118.2 (*J* = 1.8 Hz), 115.5 (*J* = 18.9 Hz), 60.5, 57.6, 44.6, 41.3, 36.5, 35.9, 30.1, 29.6.

HRMS (APCI): m/z calcd for: $C_{36}H_{38}FN_3$, 532.3128 $[M+H]^+$; found: 532.3127.

(*E*)-*N*-(1-(Adamantan-1-yl)-3-(naphthalen-1-yl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)adamantan-1-amine (3v)



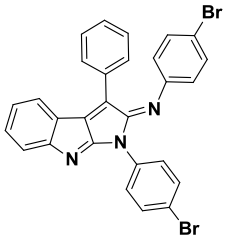
Red solid, m.p.: 247-248 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94-7.88 (m, 2H, Ar-H), 7.70 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.55-7.44 (m, 4H, Ar-H), 7.12-6.99 (m, 2H, Ar-H), 6.42 (t, *J* = 7.4 Hz, 1H, Ar-H), 6.11 (d, *J* = 7.2 Hz, 1H, Ar-H), 2.73 (d, *J* = 2.0 Hz, 6H), 2.19 (s, 3H), 1.82-1.42 (m, 15H), 1.37-1.08 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.5, 163.6, 150.8, 146.4, 133.3, 132.0, 131.9, 131.7, 129.0, 128.4, 127.3, 126.9, 126.4, 125.8, 124.7, 124.5, 123.7, 123.2, 121.5, 118.0, 60.5, 57.7, 44.1, 41.4, 36.6, 35.8, 30.1, 29.4.

HRMS (APCI): m/z calcd for: $C_{40}H_{41}N_3$, 564.3379 $[M+H]^+$; found: 564.3372.

(*E*)-4-Bromo-*N*-(1-(4-bromophenyl)-3-phenylpyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)aniline (3w)



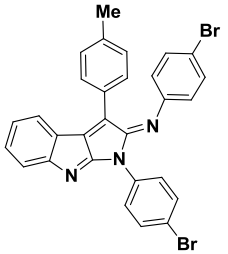
Red solid, m.p.: 181-182 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.50 (s, 8H, Ar-H), 7.30 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.23-7.05 (m, 4H, Ar-H), 7.00 (d, *J* = 7.0 Hz, 1H, Ar-H), 6.68 (d, *J* = 8.6 Hz, 2H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.5, 162.1, 153.5, 144.8, 143.3, 134.1, 132.6, 132.0, 131.0, 130.6, 130.0, 128.5, 127.8, 124.3, 124.1, 123.8, 122.6, 120.7, 120.0, 117.2.

HRMS (APCI): m/z calcd for: $C_{28}H_{17}Br_2N_3$, 553.9867 $[M+H]^+$; found: 553.9876.

(*E*)-4-Bromo-*N*-(1-(4-bromophenyl)-3-(*p*-tolyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)aniline (3x)



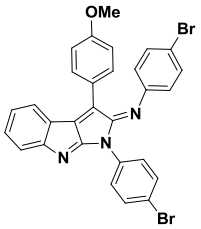
Red solid, m.p.: 197-198 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.67-6.95 (m, 14H, Ar-H), 6.67 (d, *J* = 8.8 Hz, 2H, Ar-H), 2.39 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.1, 161.9, 153.5, 144.9, 140.2, 134.2, 132.3, 132.0, 130.9, 130.5, 129.2, 128.4, 127.8, 127.7, 124.2, 123.7, 122.6, 120.7, 120.0, 117.2(19), 117.2(15), 21.5.

HRMS (APCI): m/z calcd for: $C_{29}H_{19}Br_2N_3$, 568.0024 $[M+H]^+$; found: 568.0037.

(*E*)-4-Bromo-*N*-(1-(4-bromophenyl)-3-(4-methoxyphenyl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)aniline (3y)



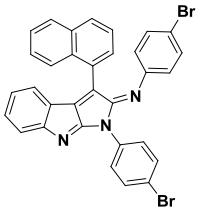
Red solid, m.p.: 176-177 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.07-7.05 (m, 13H, Ar-H), 7.00 (t, *J* = 7.6 Hz, 1H, Ar-H), 6.70-6.64 (m, 2H, Ar-H), 3.85 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.4, 161.7, 161.1, 153.7, 144.9, 134.3, 131.9, 131.0, 127.8, 124.4, 123.9, 123.7, 122.9, 122.5, 120.7, 120.0, 117.1, 114.1, 55.5.

HRMS (APCI): m/z calcd for: $C_{29}H_{19}Br_2N_3O$, 583.9973 $[M+H]^+$; found: 583.9989.

(*E*)-4-Bromo-*N*-(1-(4-bromophenyl)-3-(naphthalen-1-yl)pyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)aniline (3z)



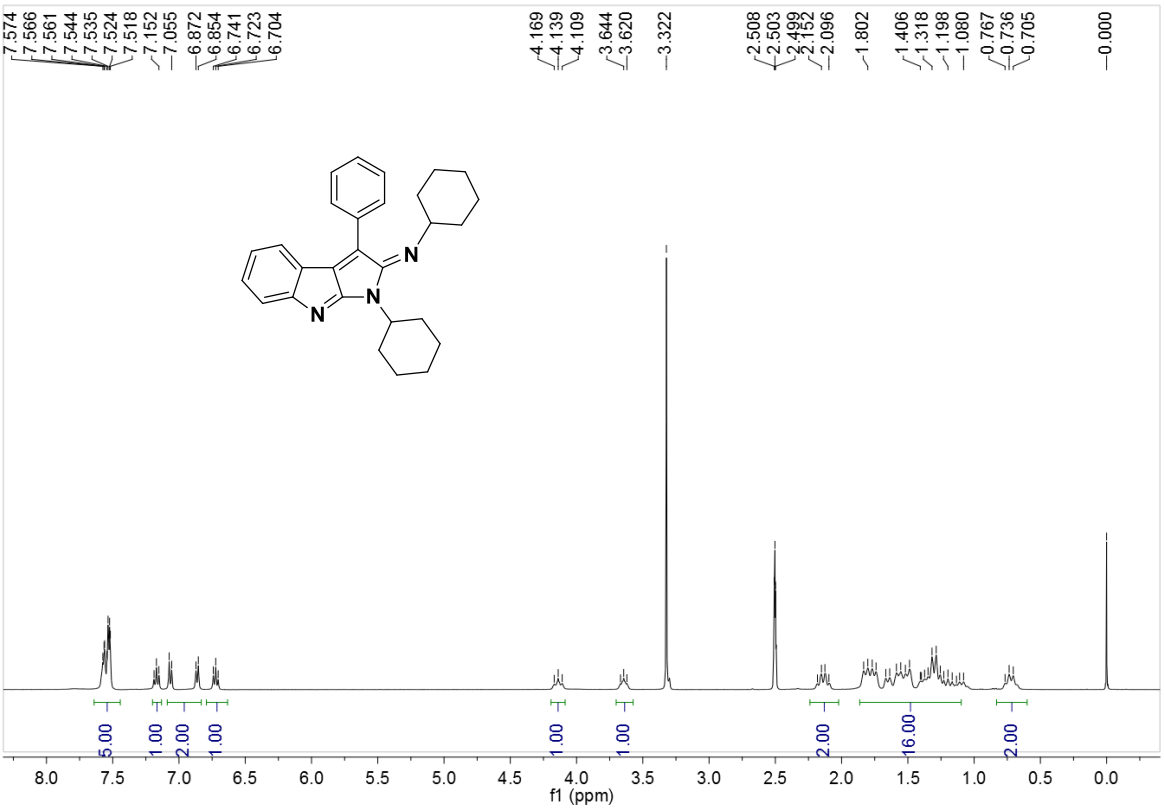
Red solid, m.p.: 188-189 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76-7.43 (m, 9H, Ar-H), 7.24-7.16 (m, 3H, Ar-H), 6.72 (s, 3H, Ar-H), 6.52 (s, 2H, Ar-H), 6.21 (s, 2H, Ar-H).

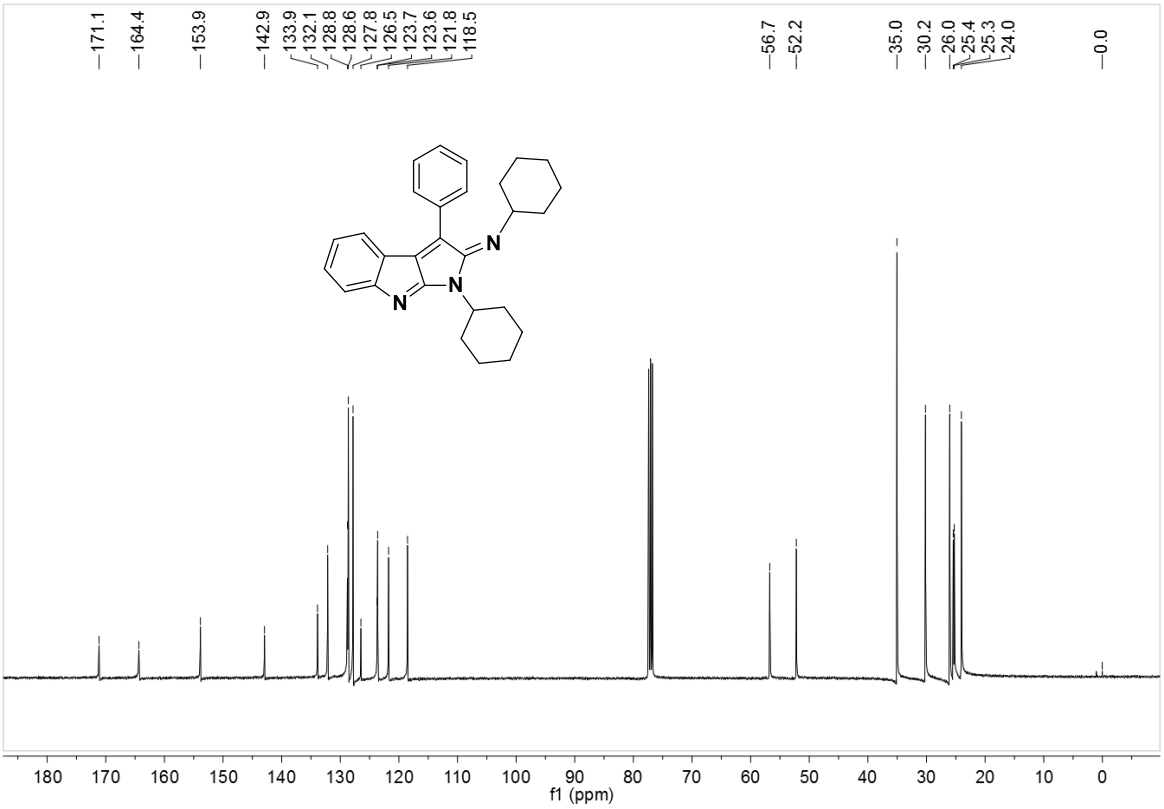
^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.6, 161.6, 155.8, 143.4, 142.0, 132.8, 132.2, 131.9, 131.1, 129.1, 128.7, 128.3, 127.7, 127.4, 126.3, 125.9, 125.4, 124.5, 123.8, 122.7, 120.9, 119.2, 118.8, 116.0.

HRMS (APCI): m/z calcd for: $C_{32}H_{19}Br_2N_3$, 604.0024 $[M+H]^+$; found: 604.0026.

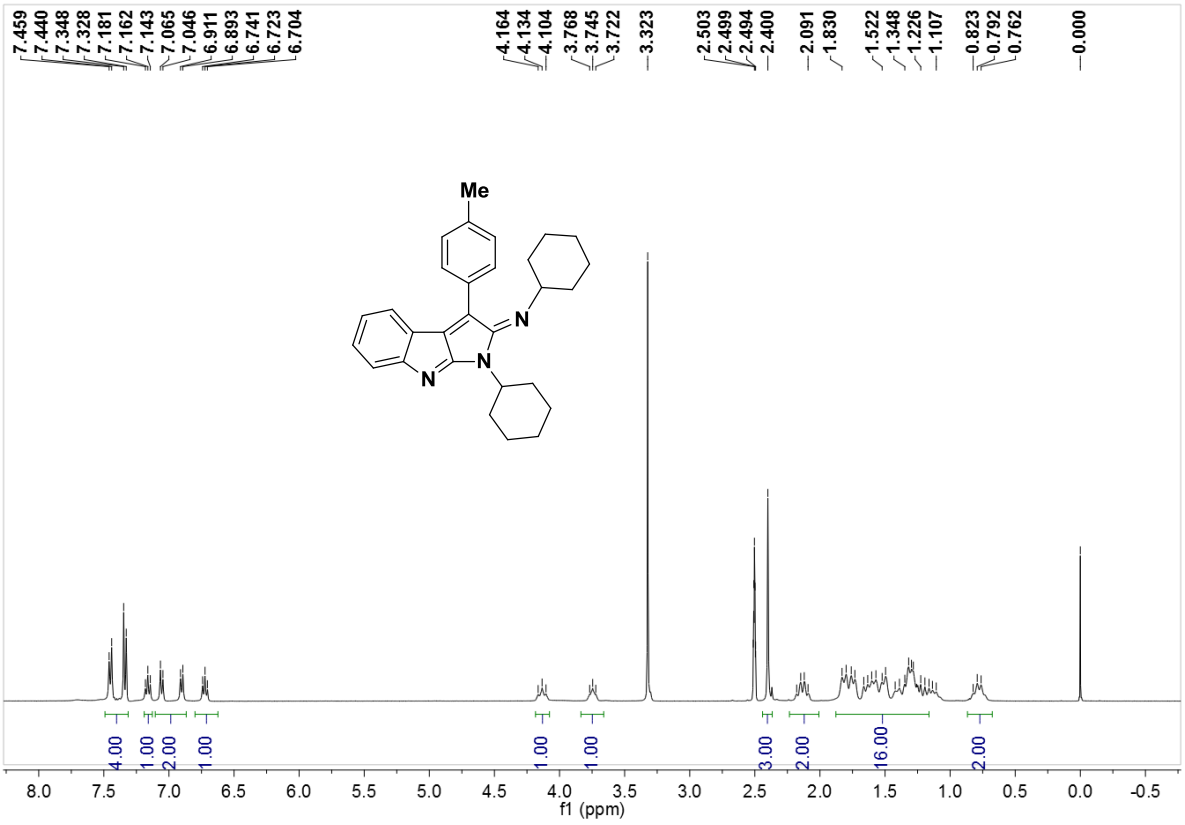
Copies of ^{1}H NMR and ^{13}C NMR of compounds 3



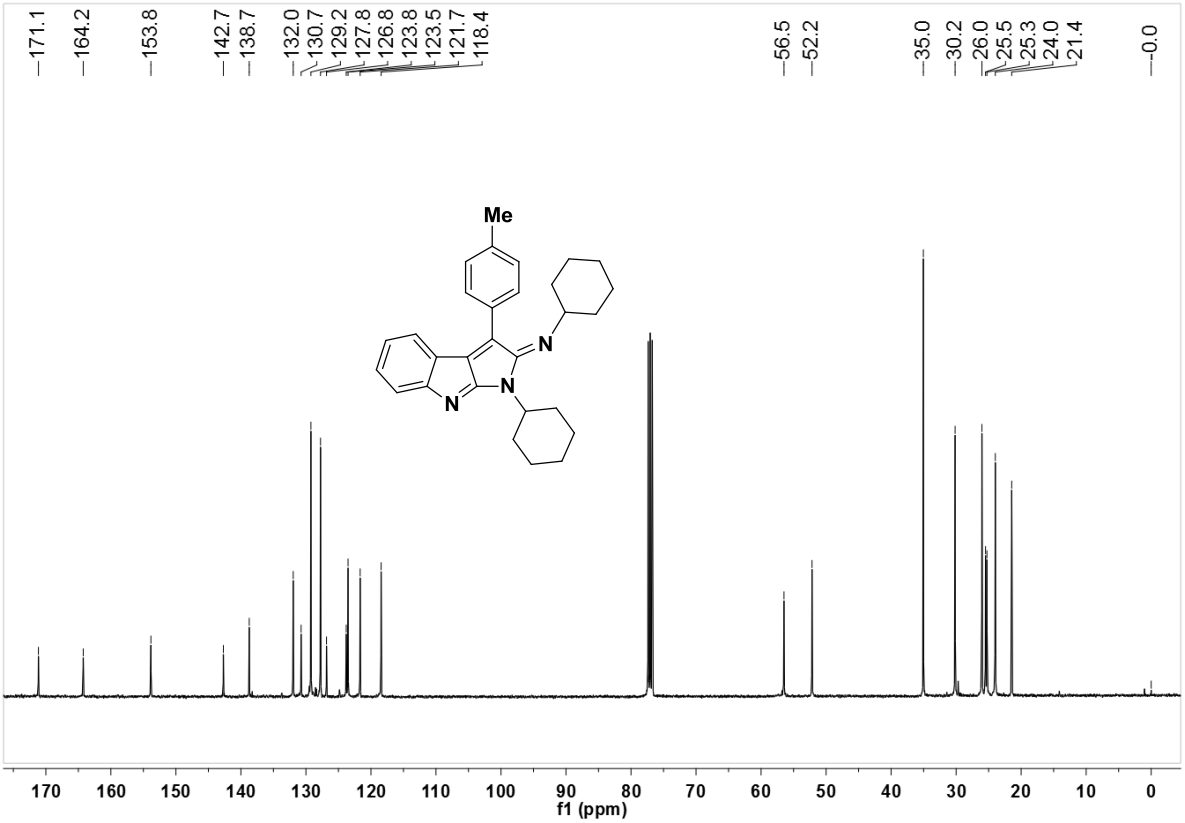
^{1}H NMR Spectrum of Compound 3a



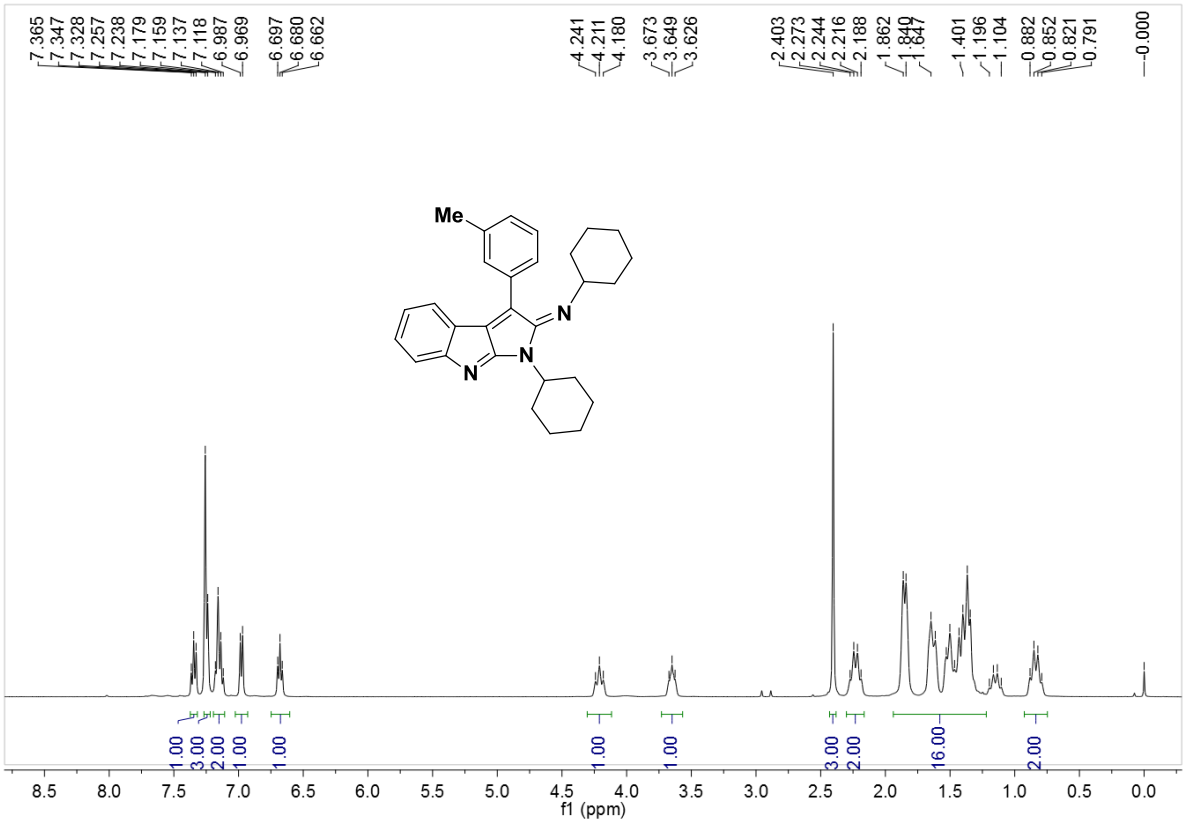
^{13}C NMR Spectrum of Compound 3a



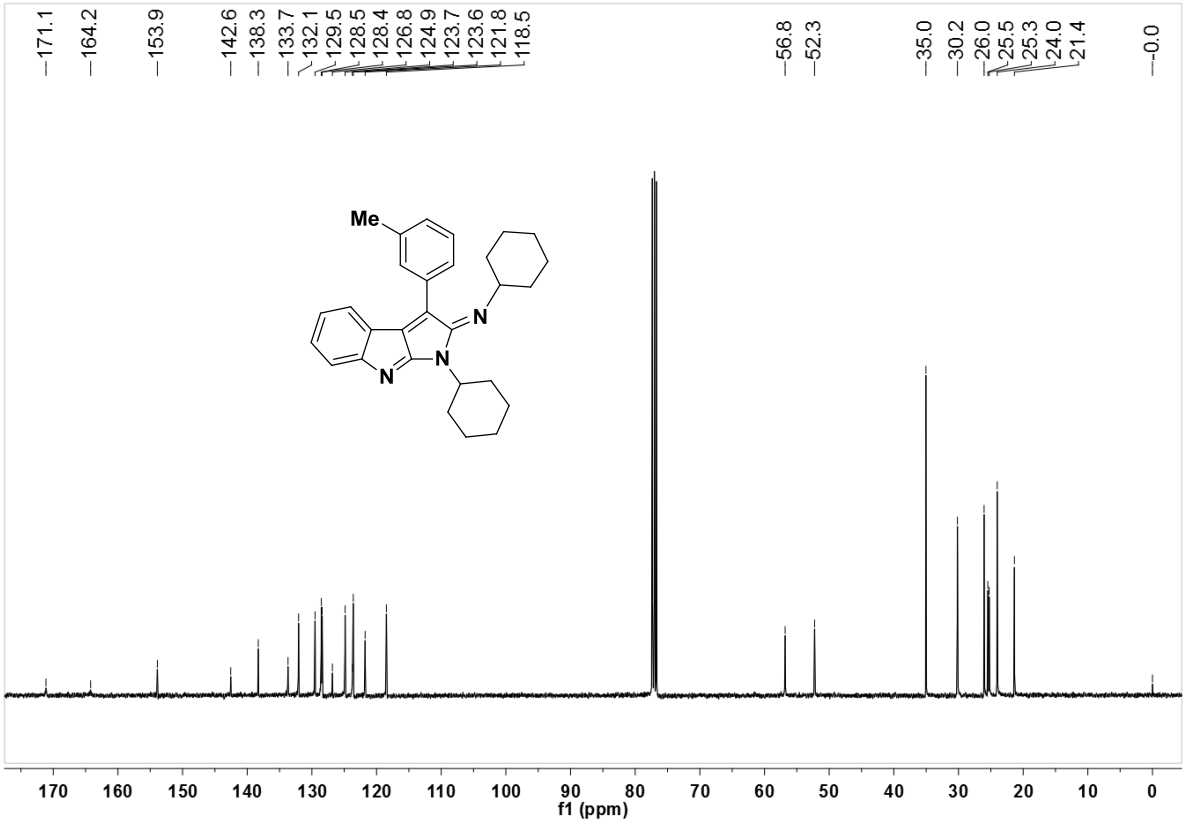
^{1}H NMR Spectrum of Compound 3b



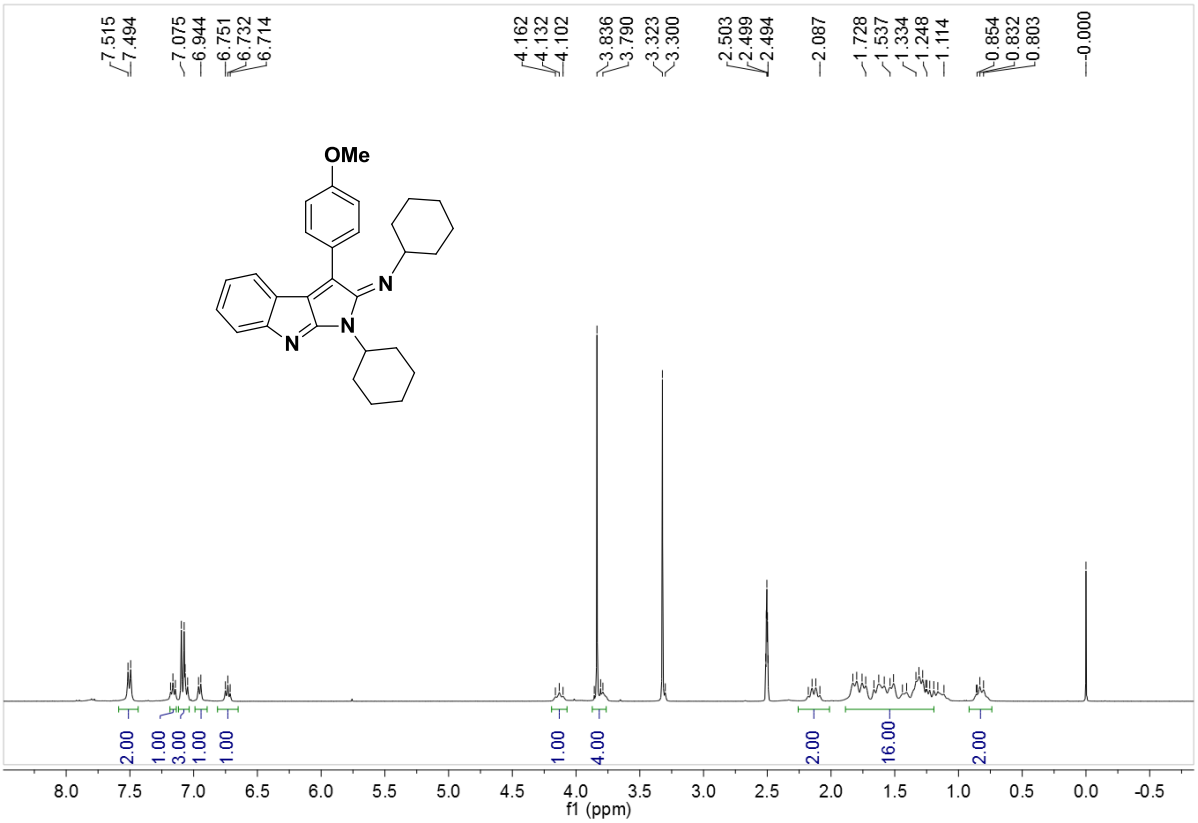
^{13}C NMR Spectrum of Compound 3b



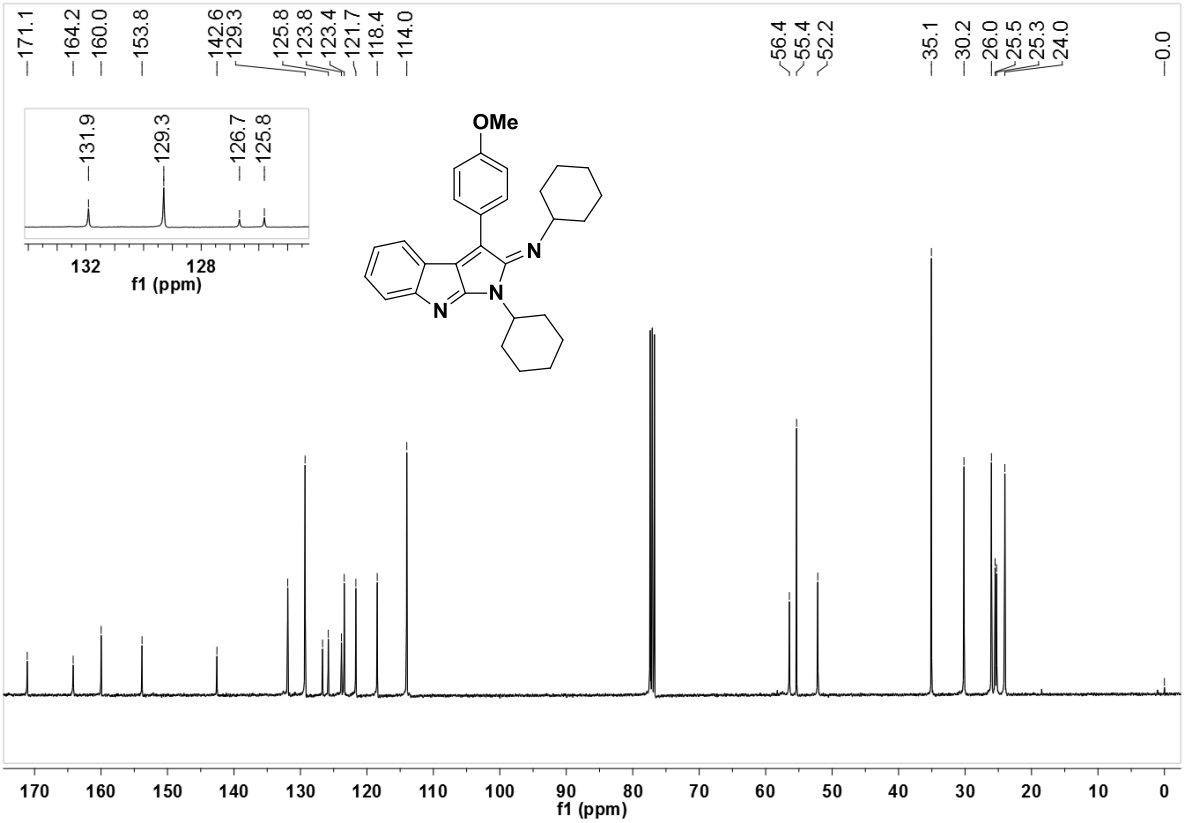
^{1}H NMR Spectrum of Compound 3c



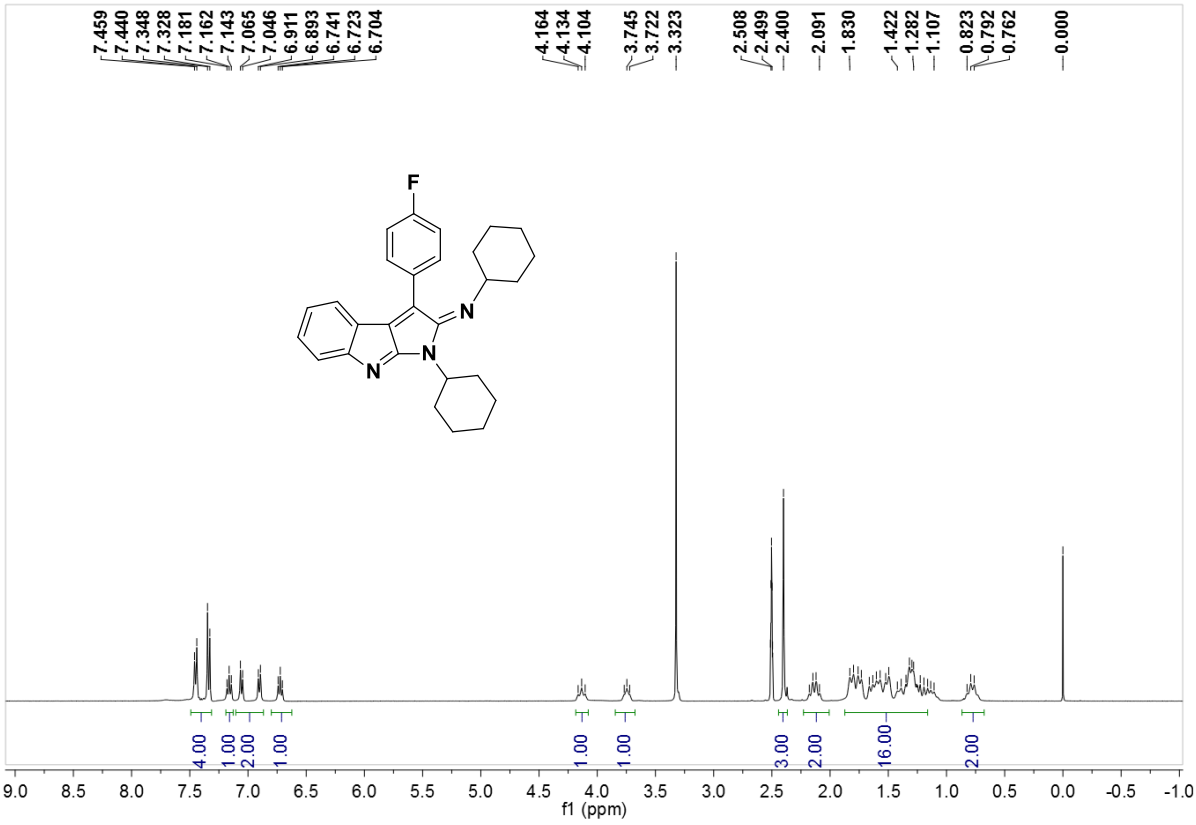
^{13}C NMR Spectrum of Compound 3c



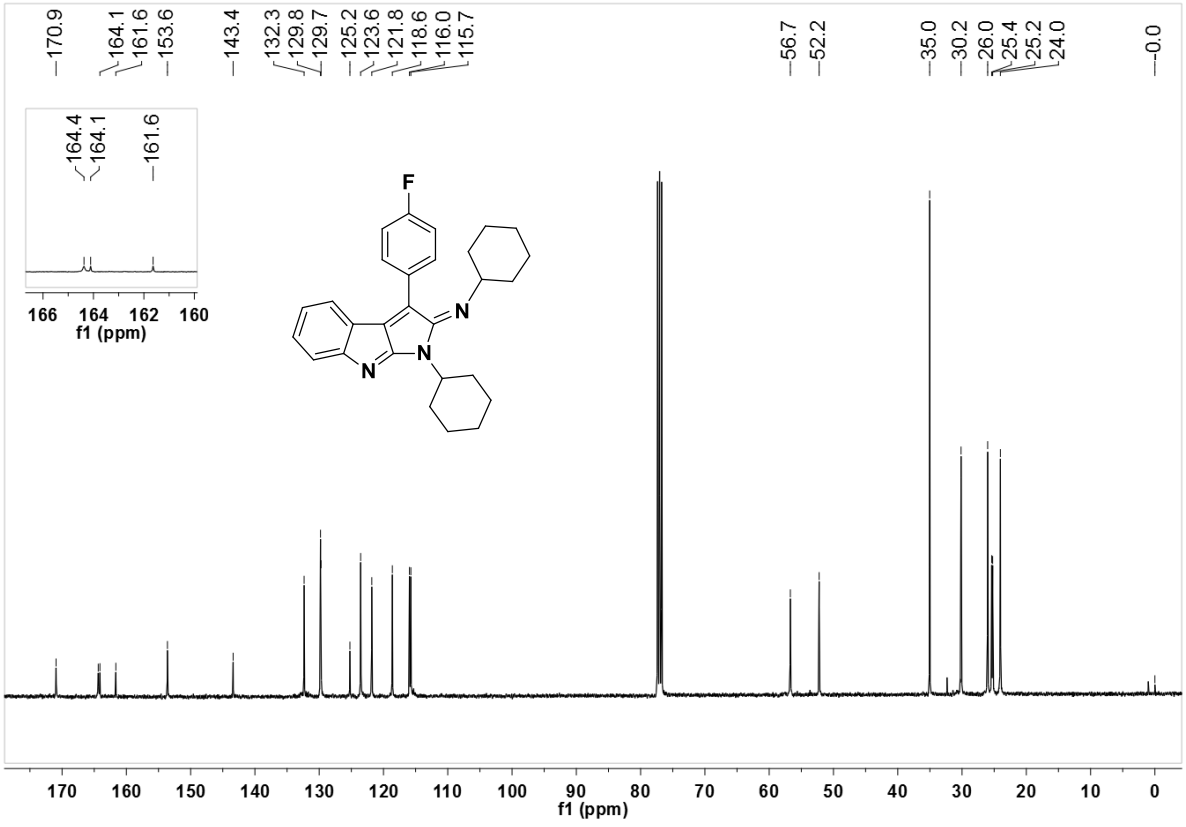
^{1}H NMR Spectrum of Compound 3d



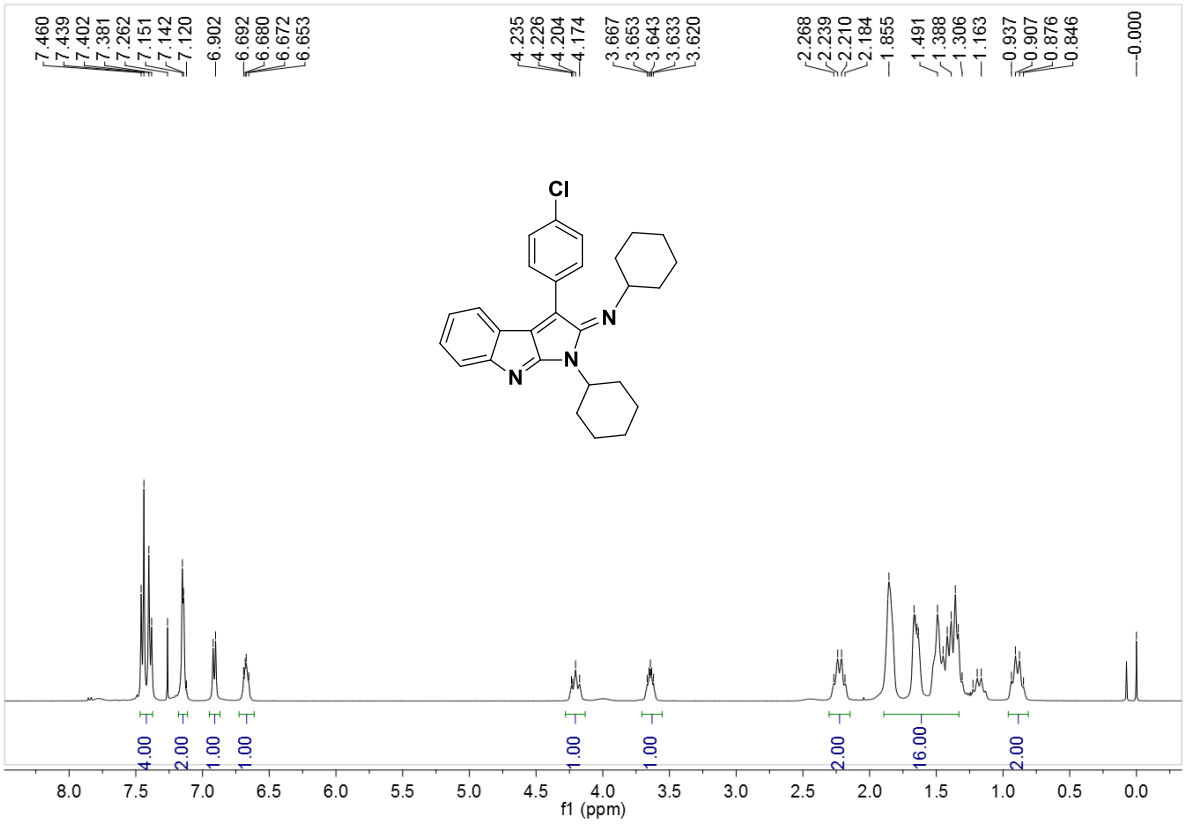
^{13}C NMR Spectrum of Compound 3d



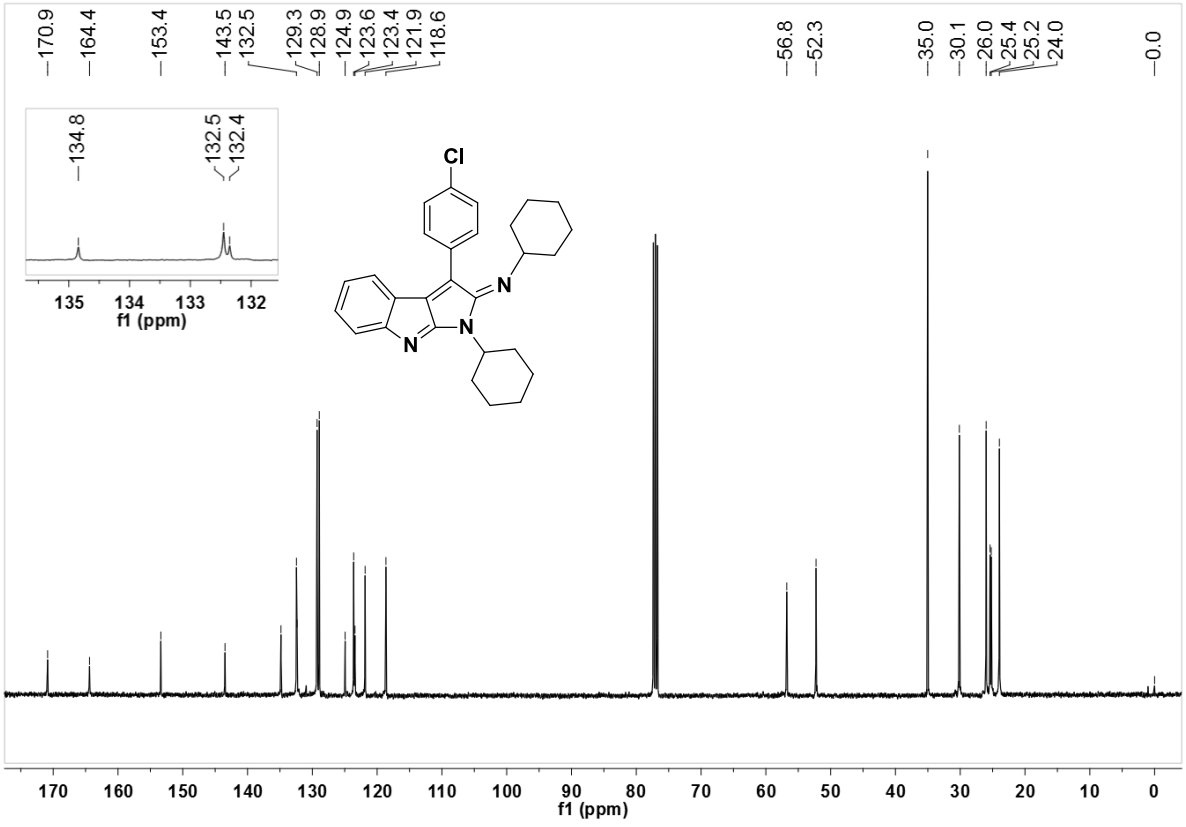
^{1}H NMR Spectrum of Compound 3e



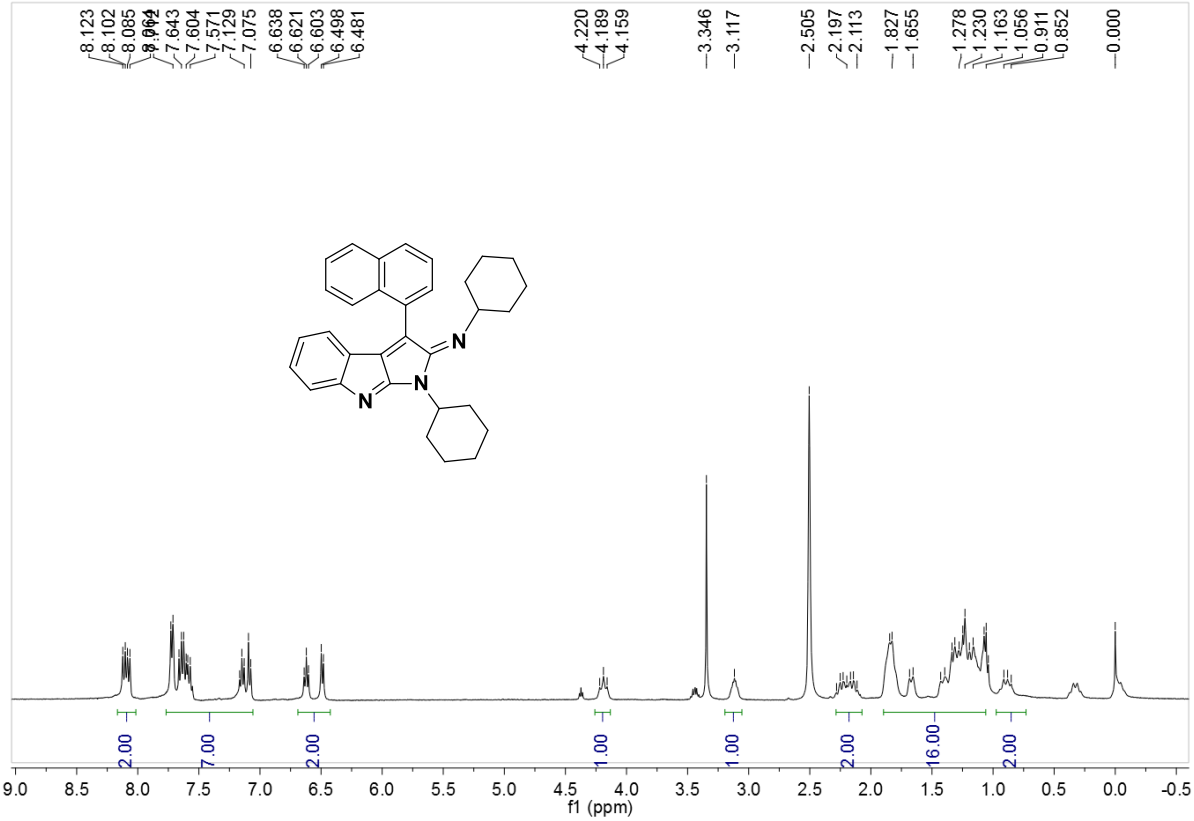
^{13}C NMR Spectrum of Compound 3e



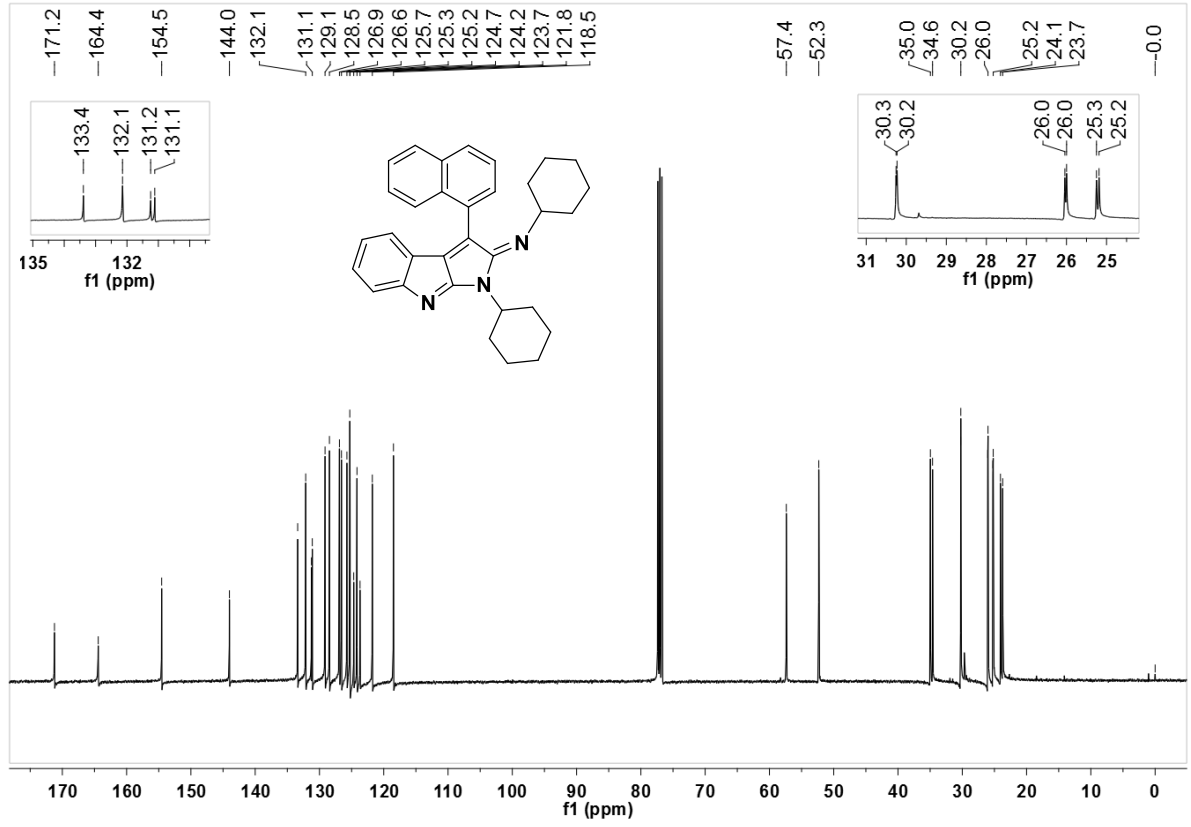
^{1}H NMR Spectrum of Compound 3f



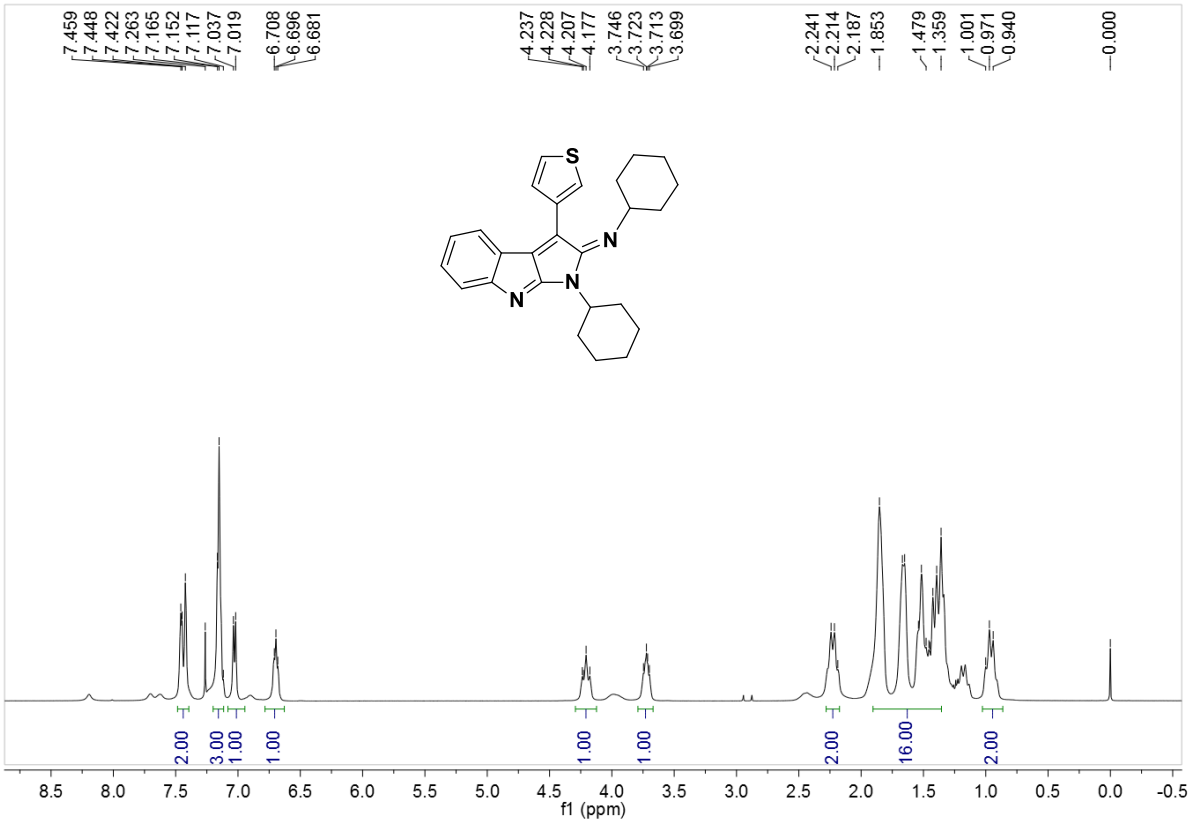
^{13}C NMR Spectrum of Compound 3f



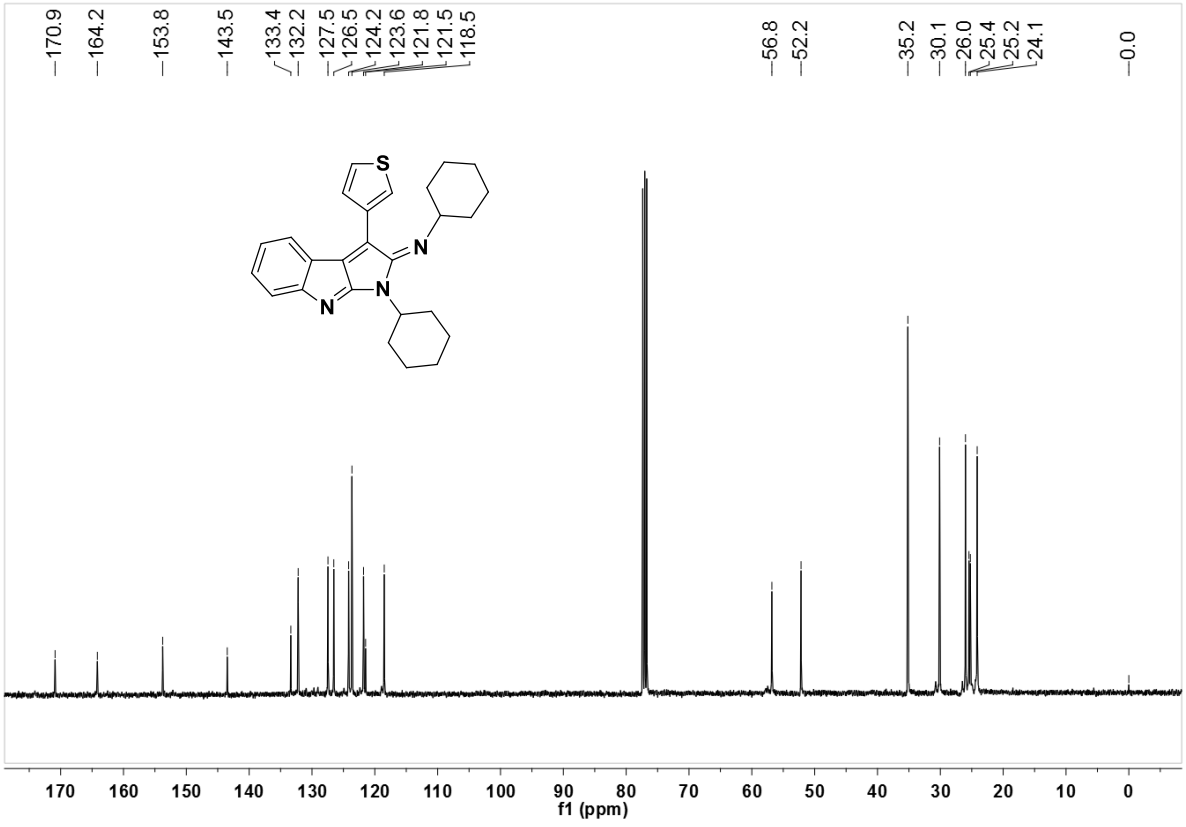
^{1}H NMR Spectrum of Compound 3g



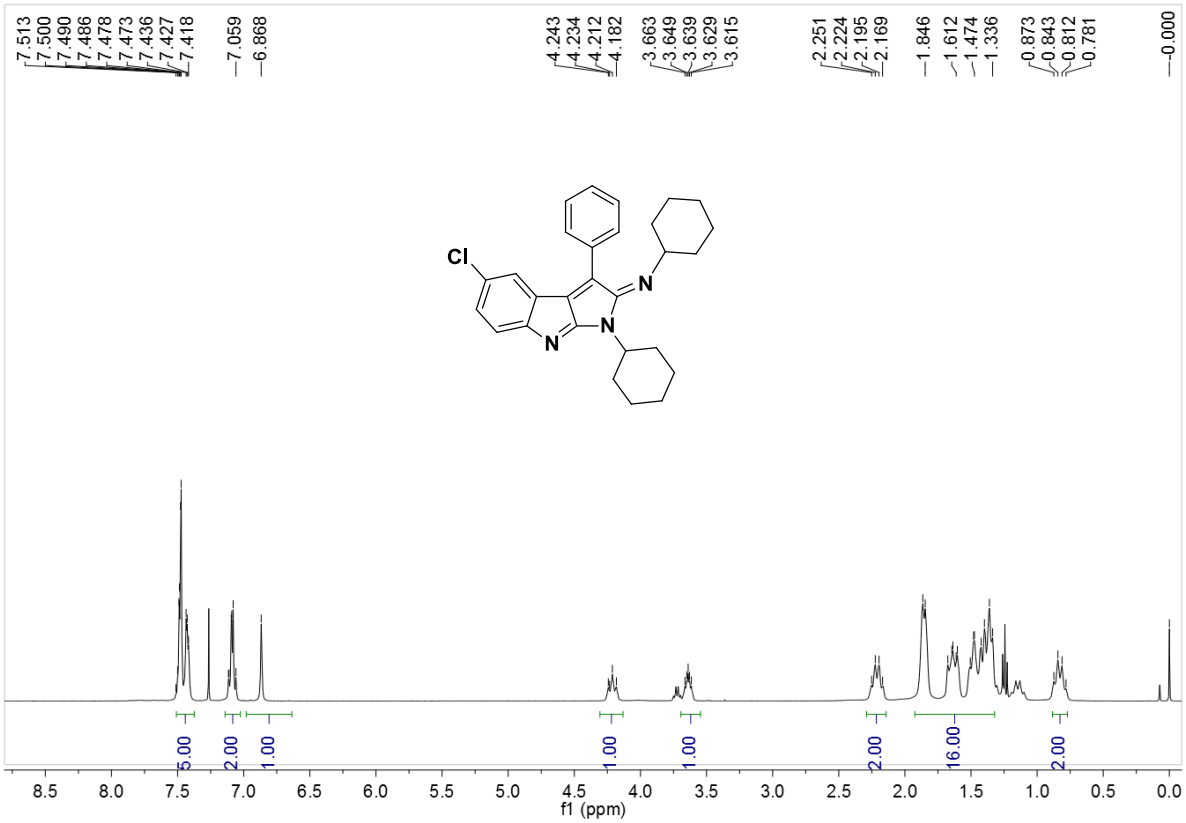
^{13}C NMR Spectrum of Compound 3g



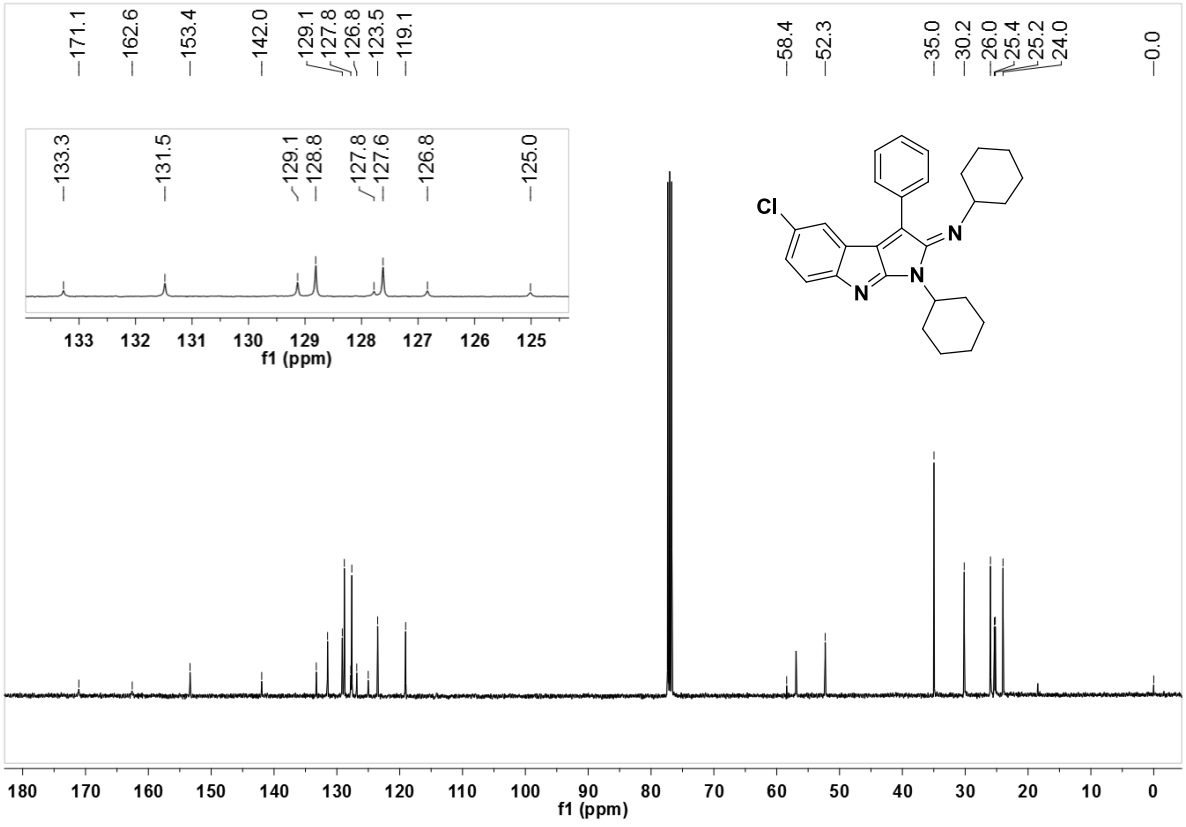
^{1}H NMR Spectrum of Compound 3h



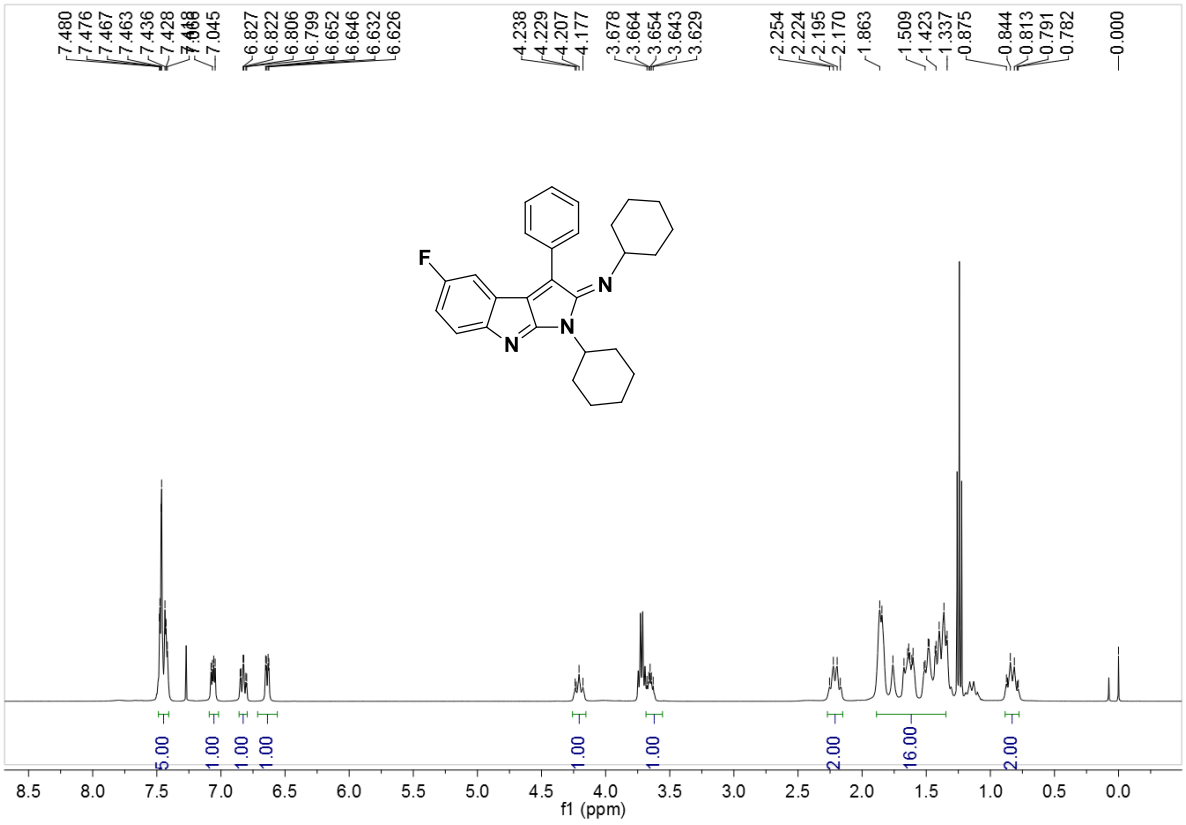
^{13}C NMR Spectrum of Compound 3h



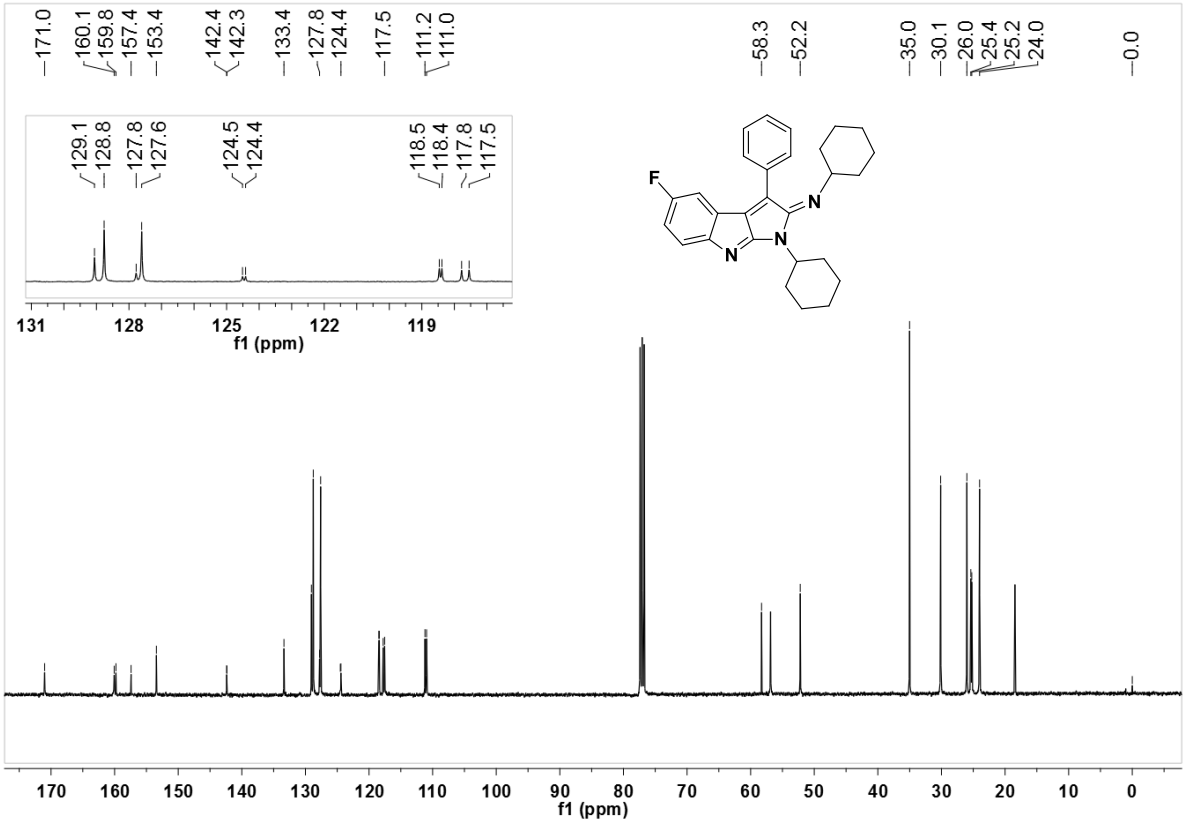
^{1}H NMR Spectrum of Compound 3j



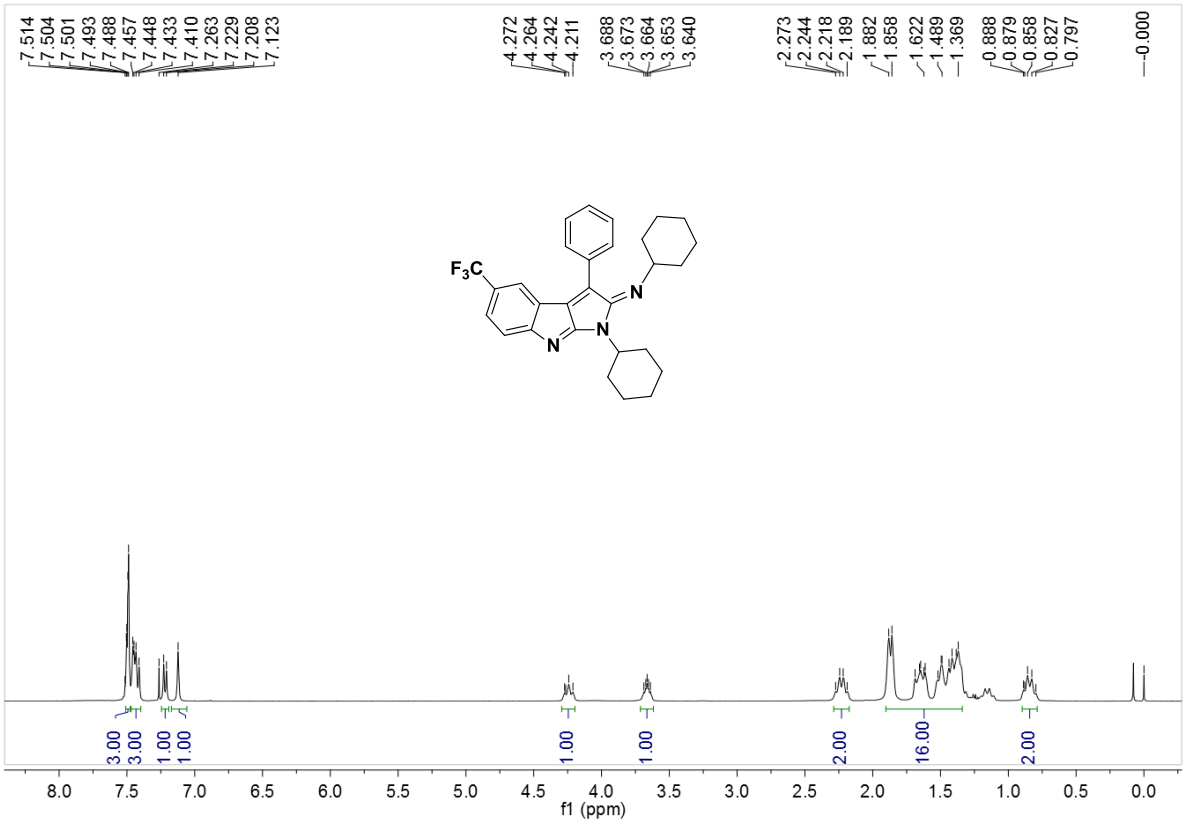
^{13}C NMR Spectrum of Compound 3j



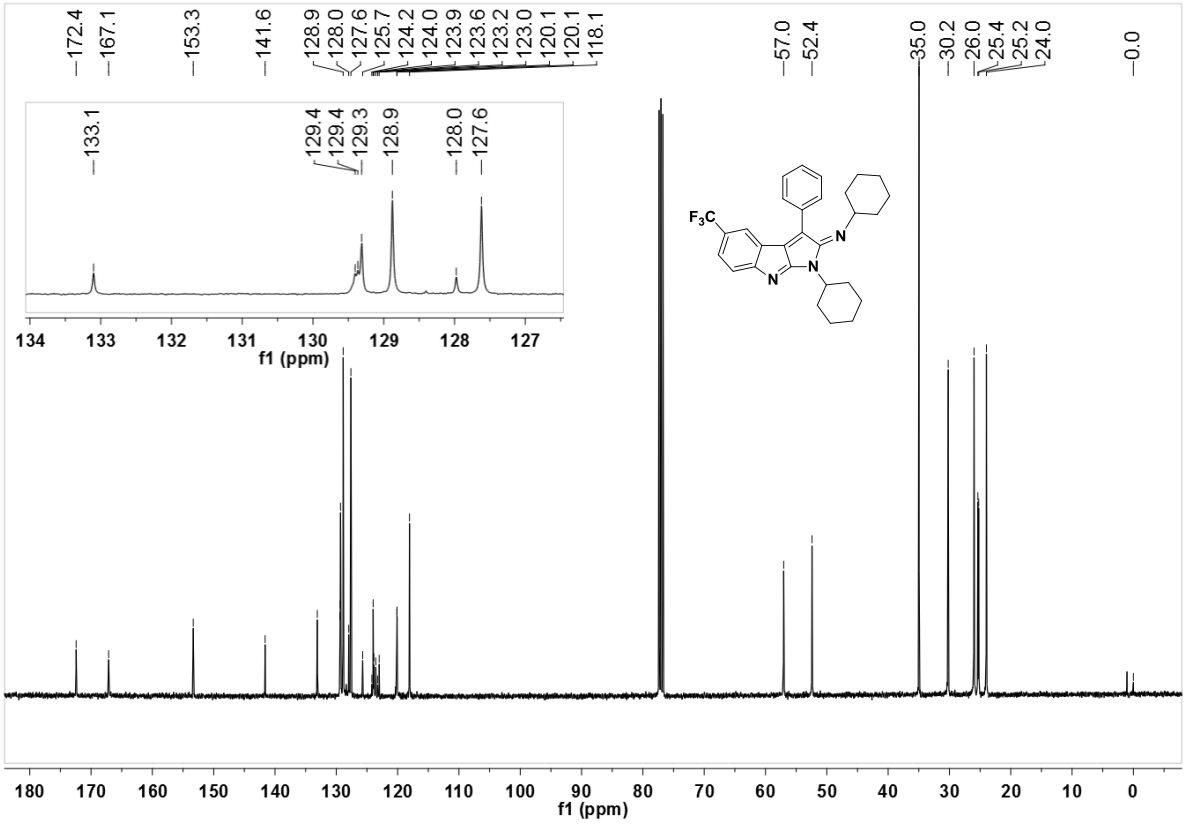
^{1}H NMR Spectrum of Compound 3k



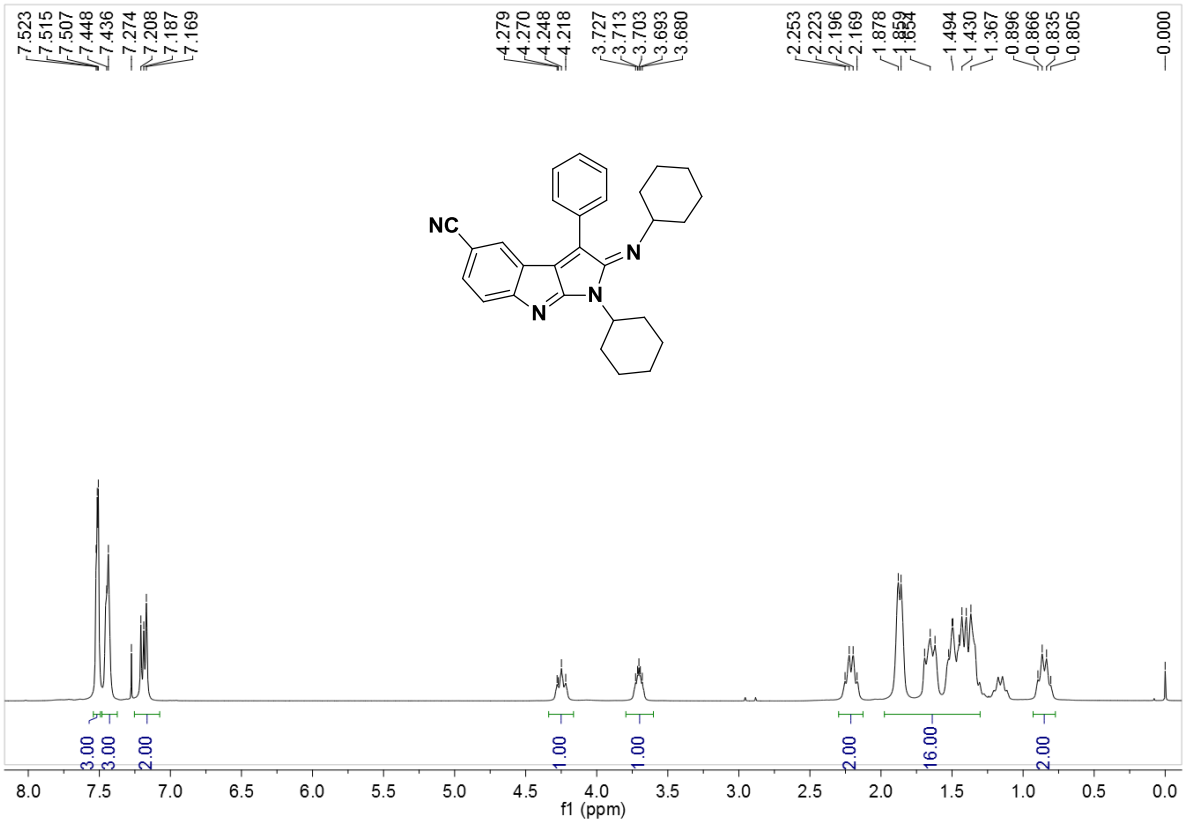
^{13}C NMR Spectrum of Compound 3k



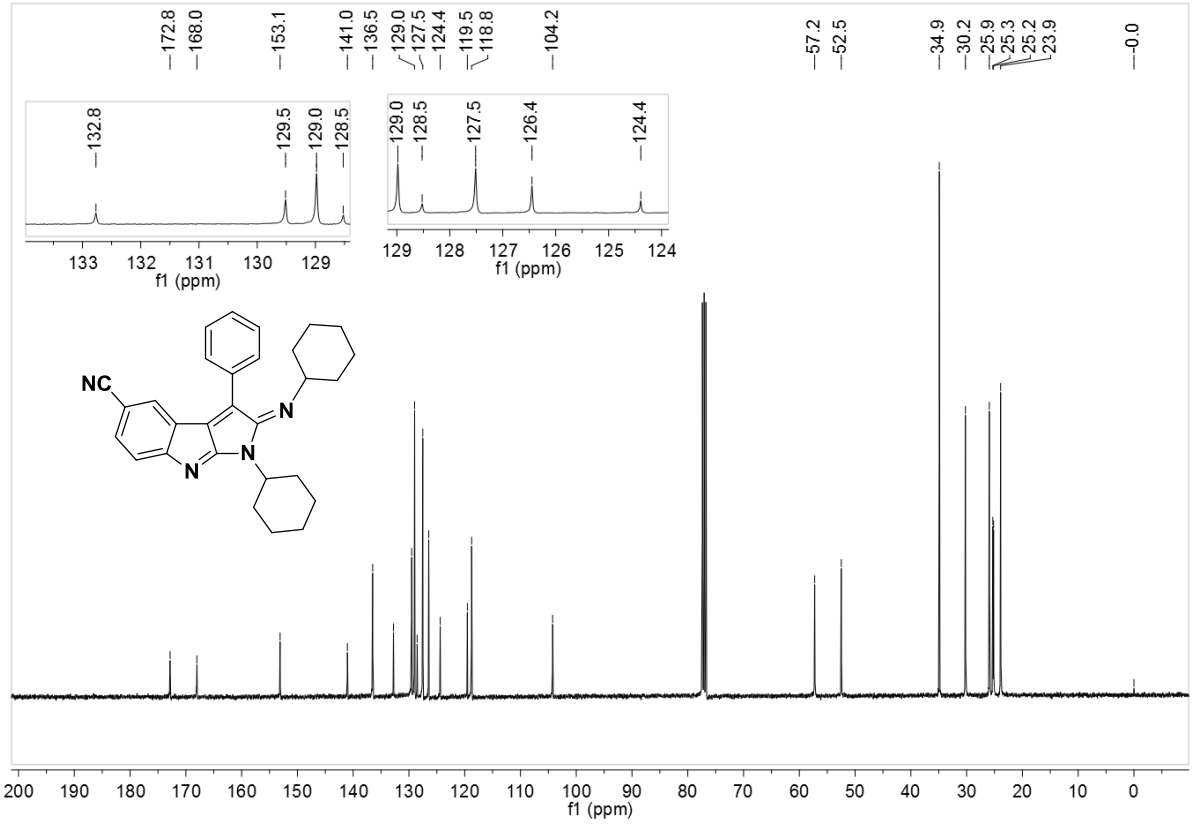
^{1}H NMR Spectrum of Compound 3l



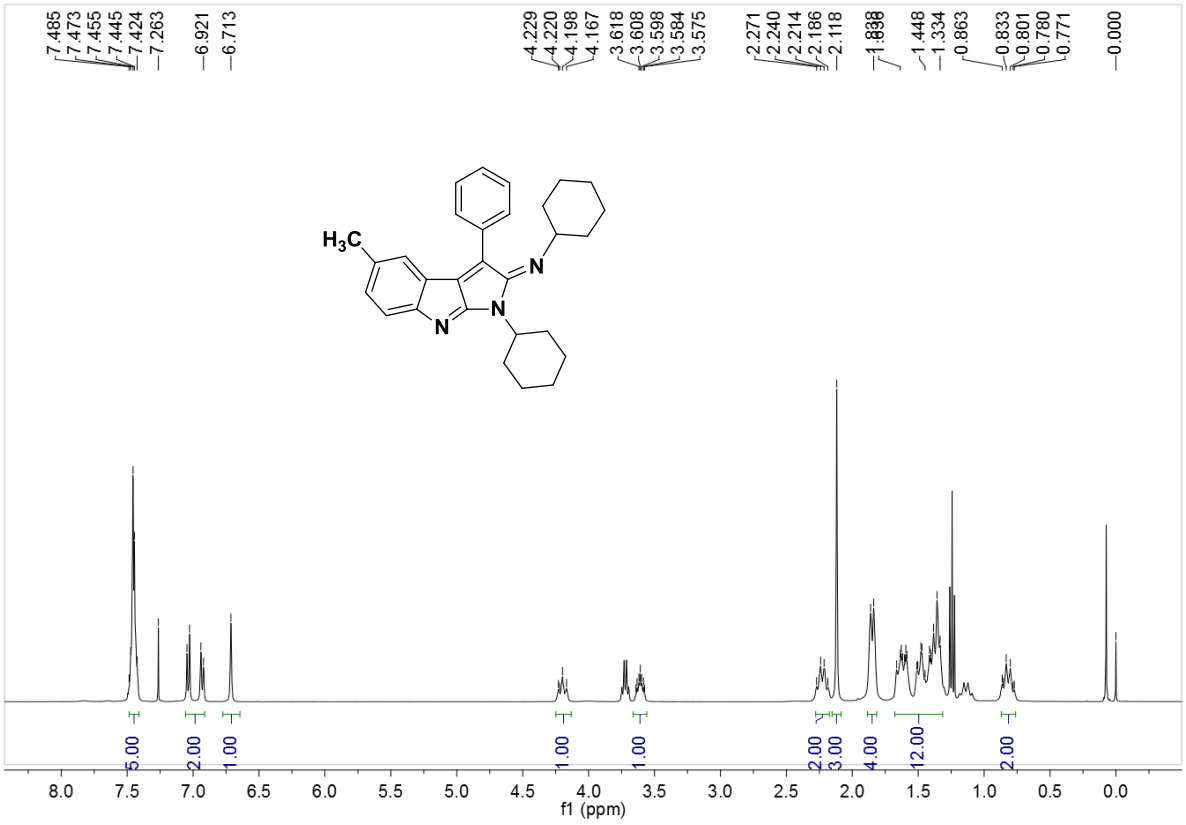
^{13}C NMR Spectrum of Compound 3l



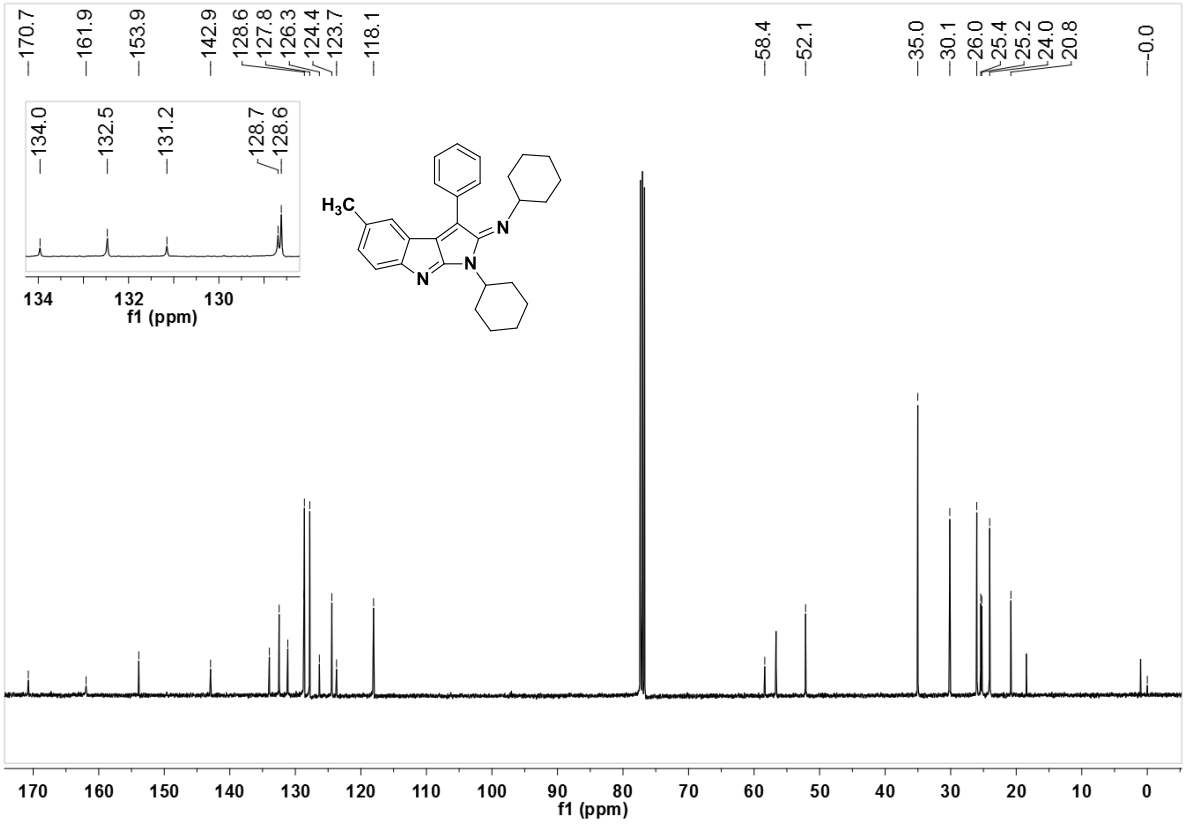
^{1}H NMR Spectrum of Compound 3m



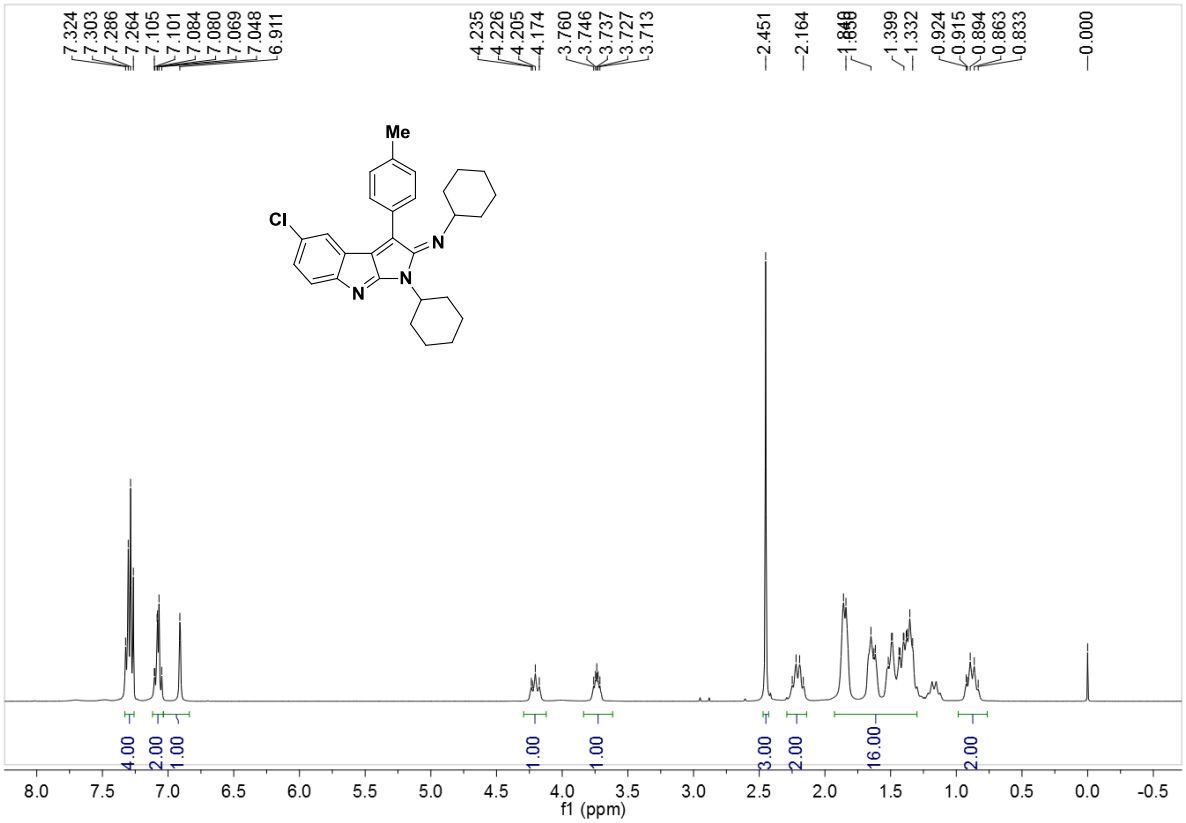
^{13}C NMR Spectrum of Compound 3m



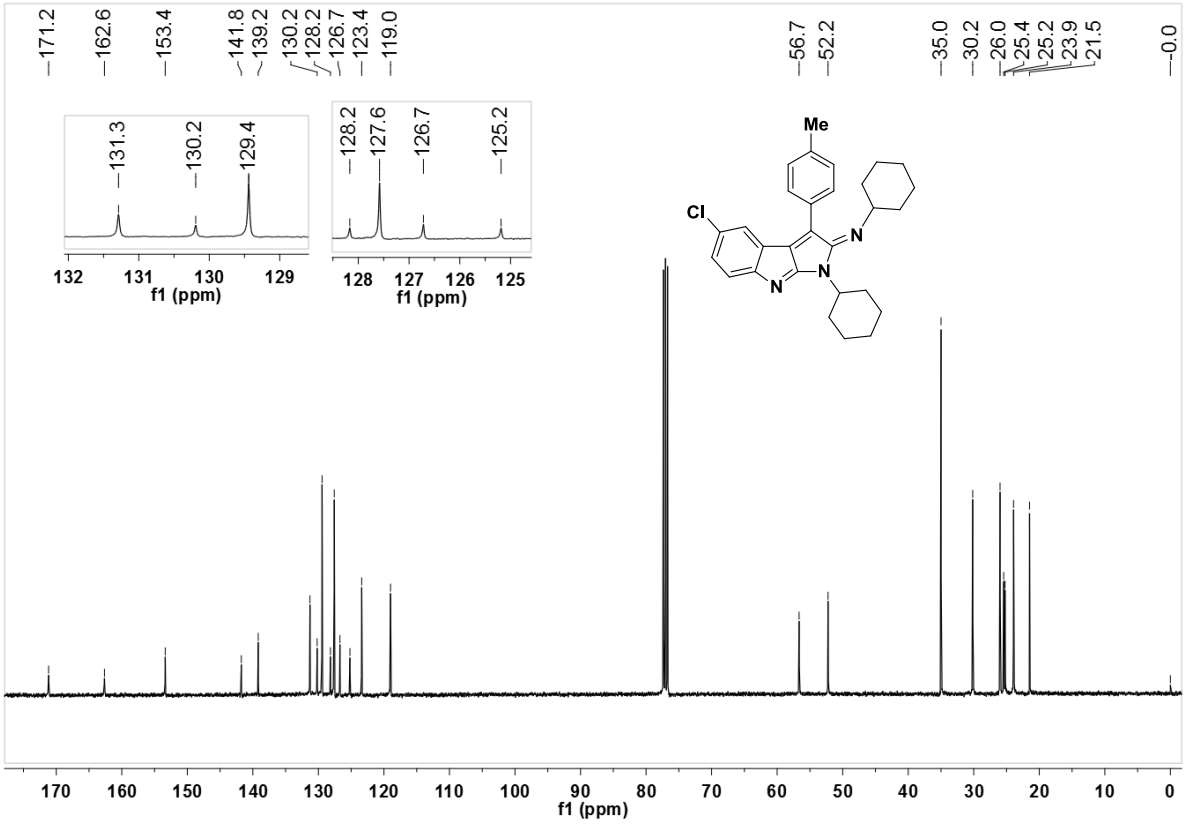
^{1}H NMR Spectrum of Compound 3n



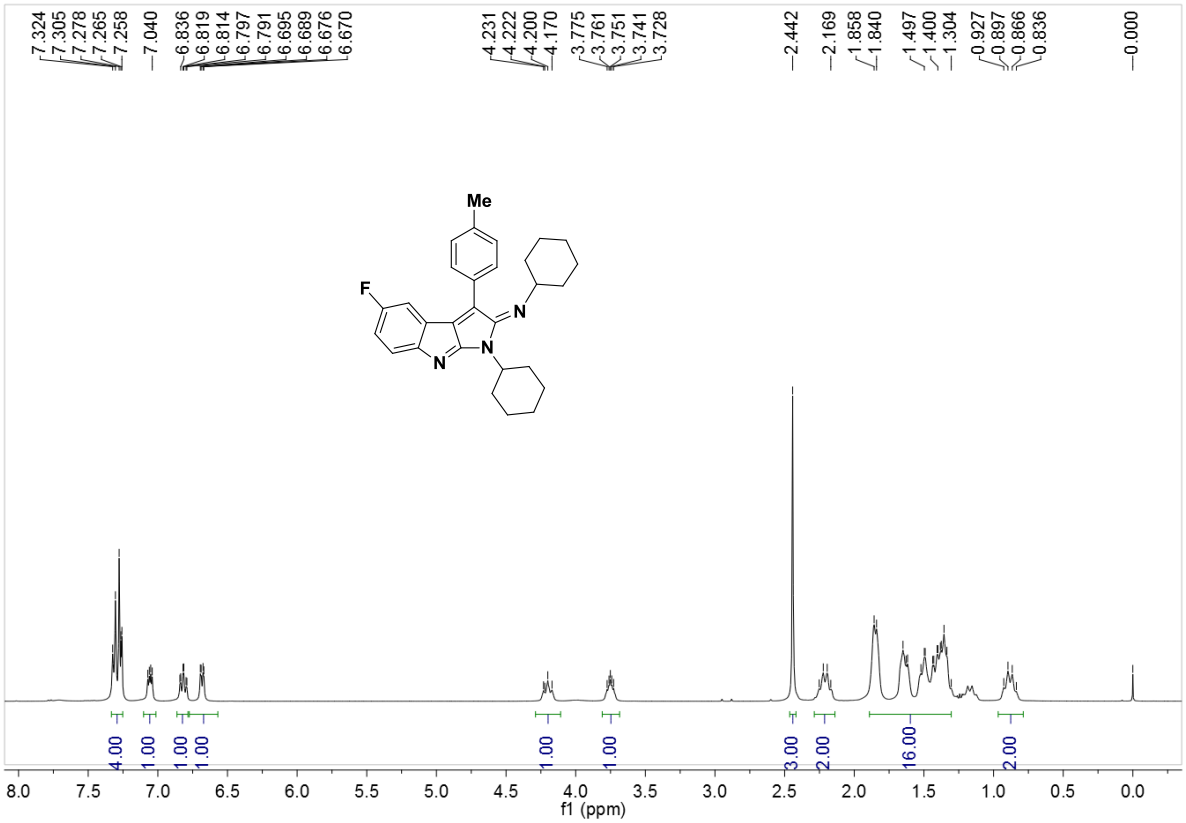
^{13}C NMR Spectrum of Compound 3n



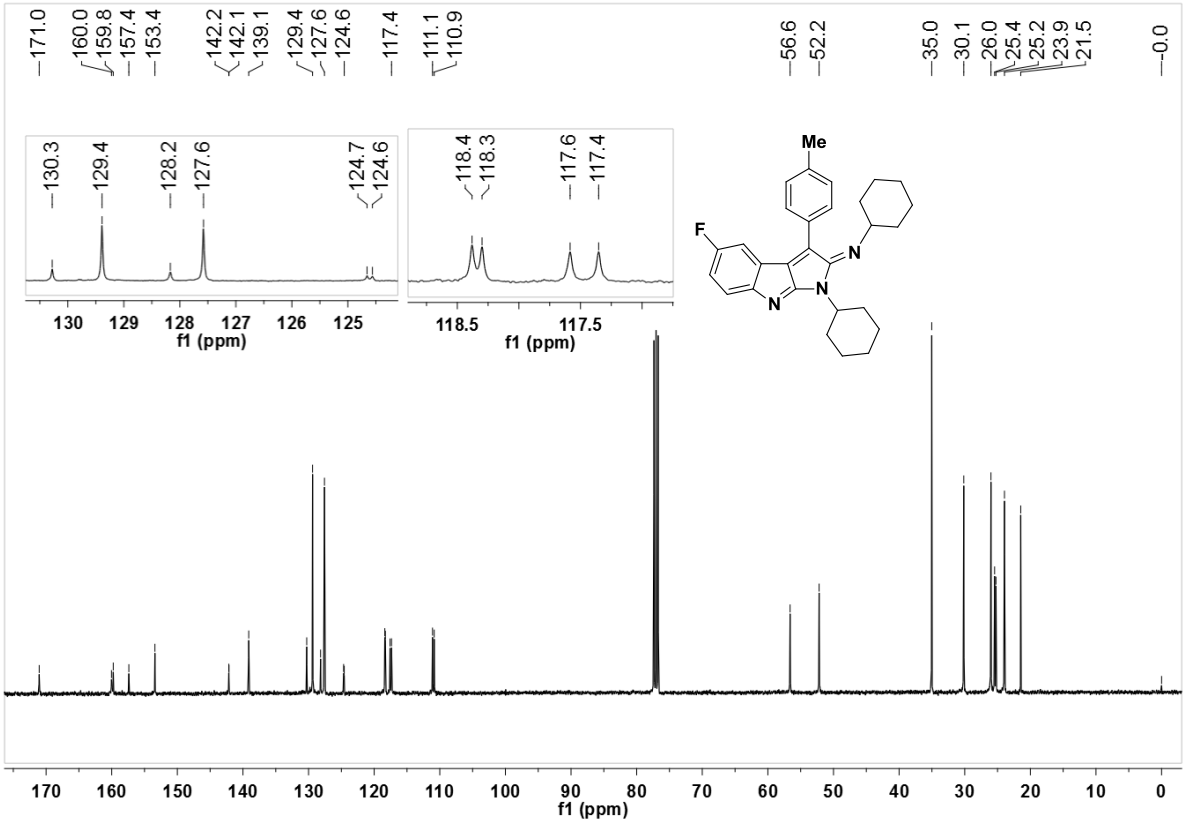
^{1}H NMR Spectrum of Compound 3o



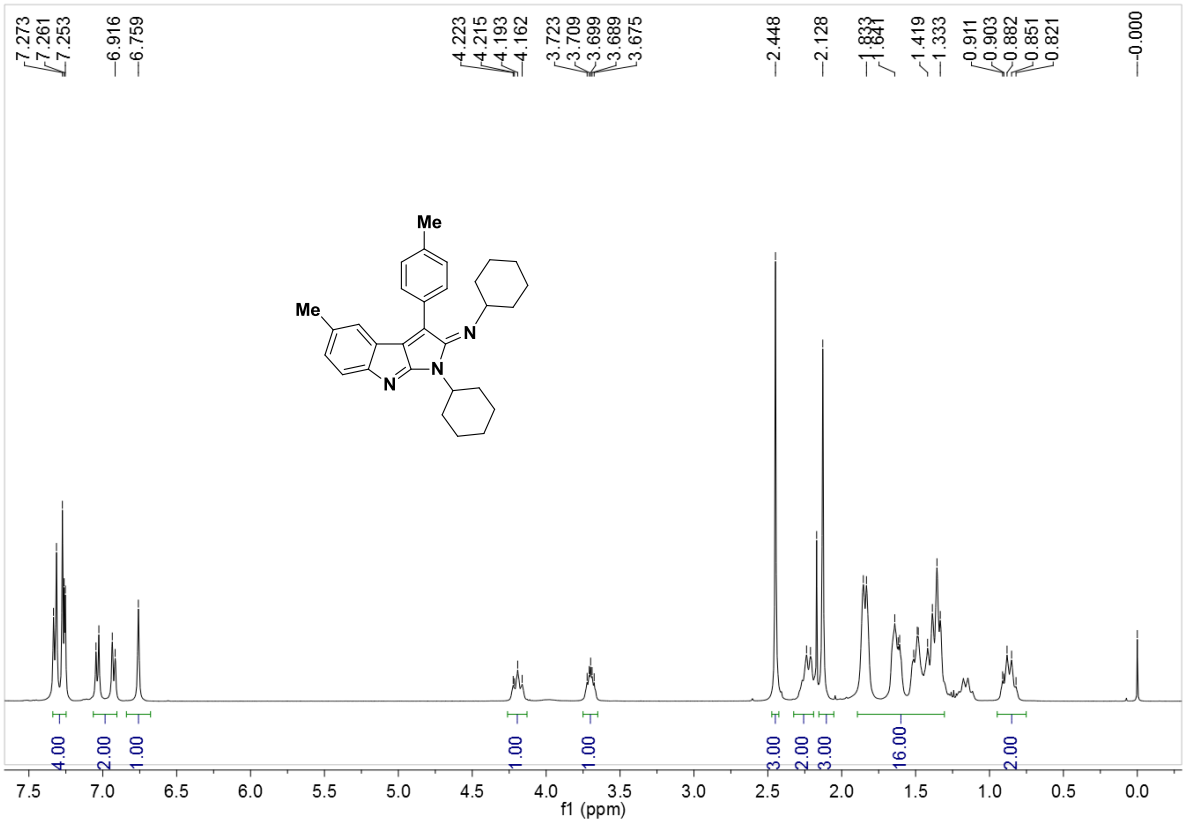
^{13}C NMR Spectrum of Compound 3o



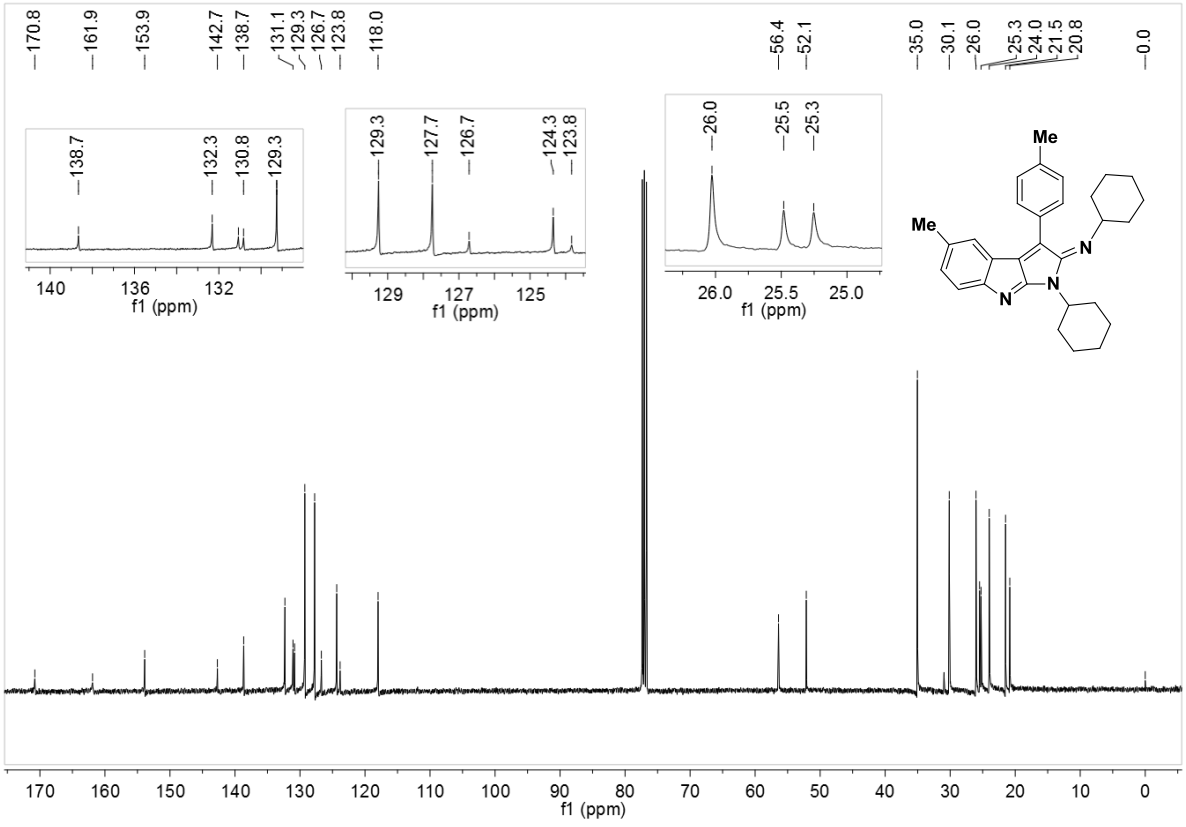
^{1}H NMR Spectrum of Compound 3p



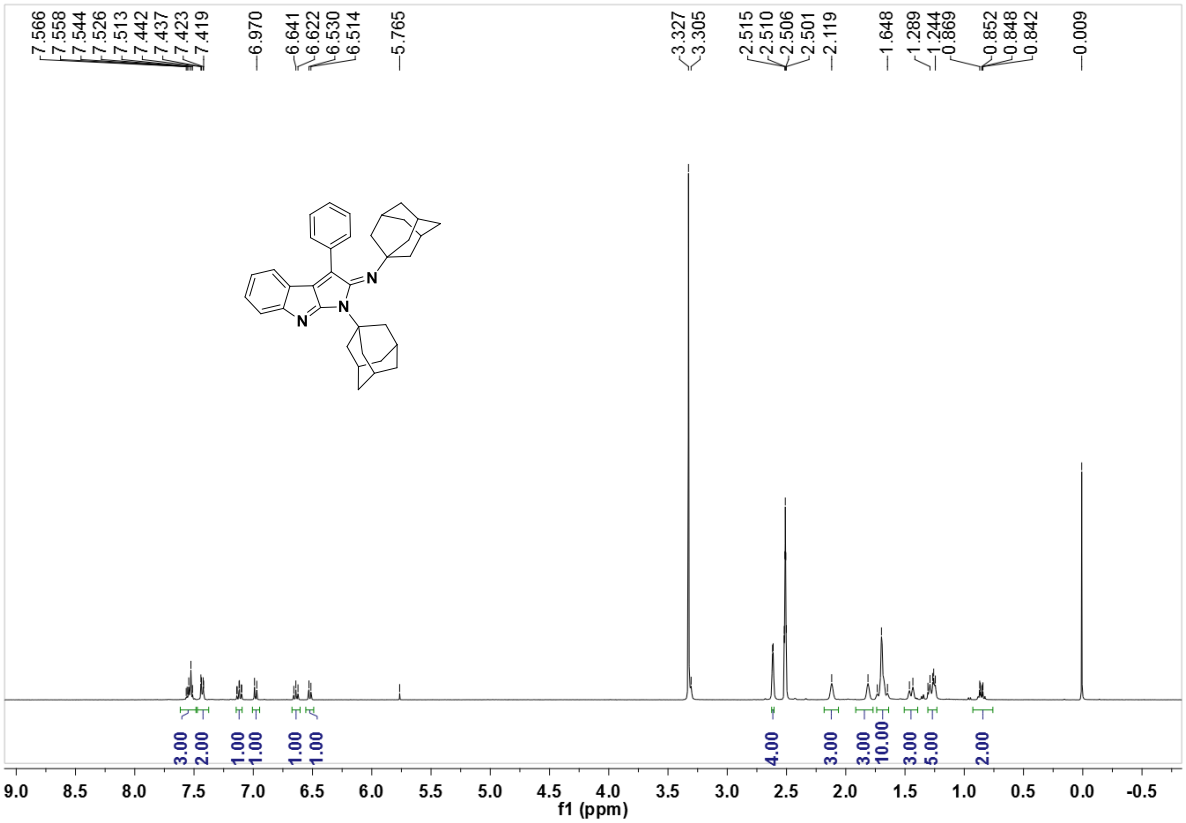
^{13}C NMR Spectrum of Compound 3p



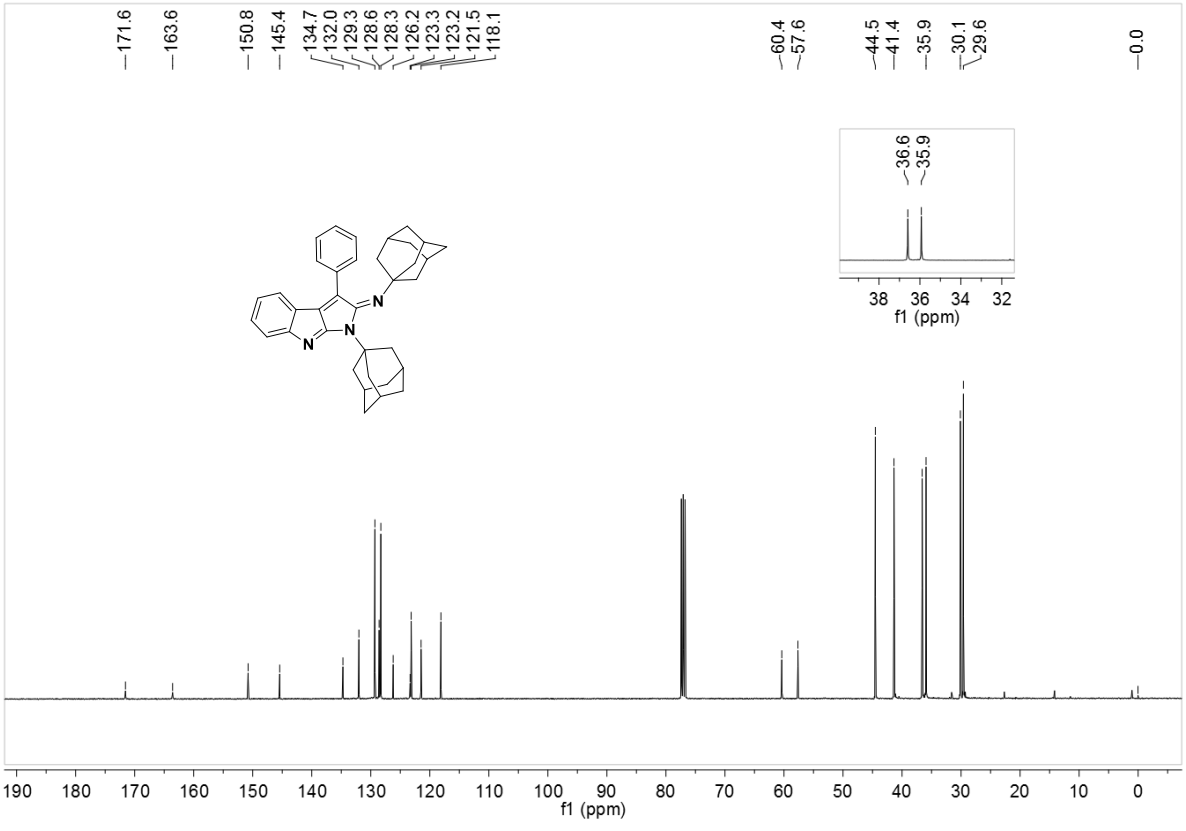
^{1}H NMR Spectrum of Compound 3q



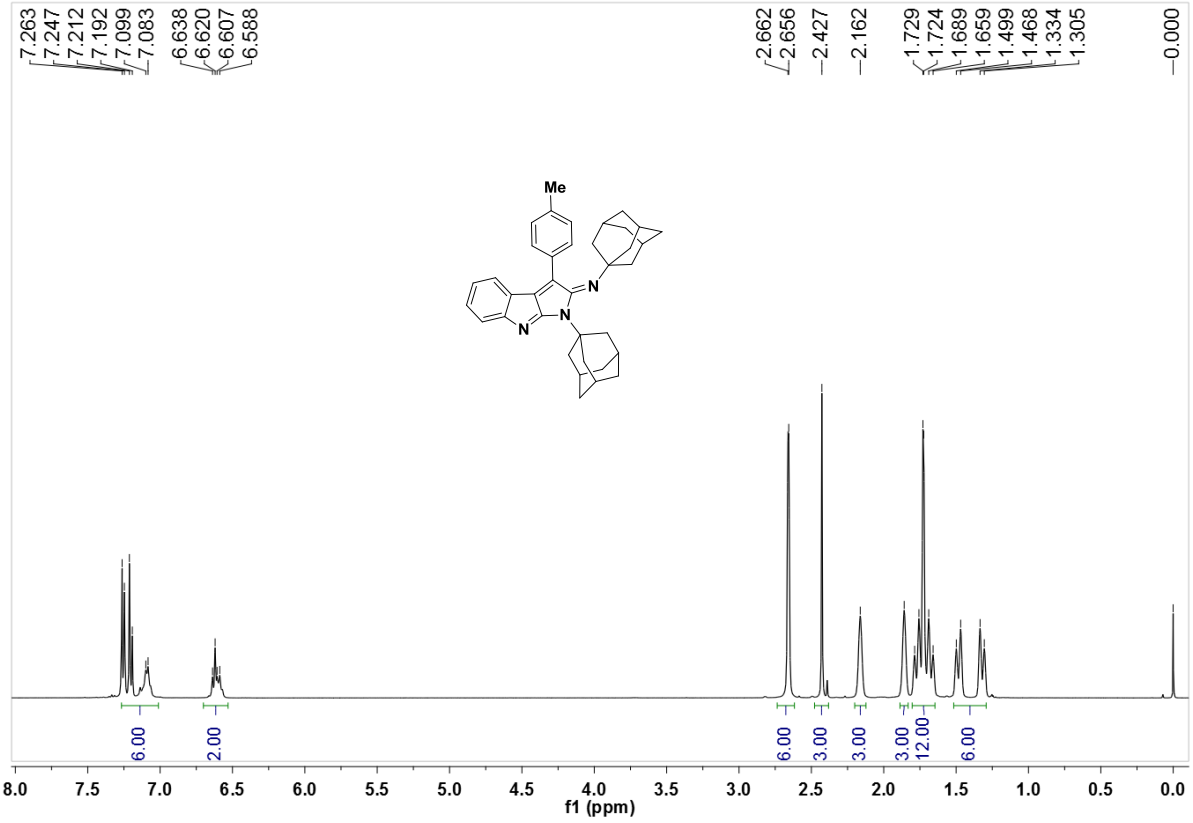
^{13}C NMR Spectrum of Compound 3q



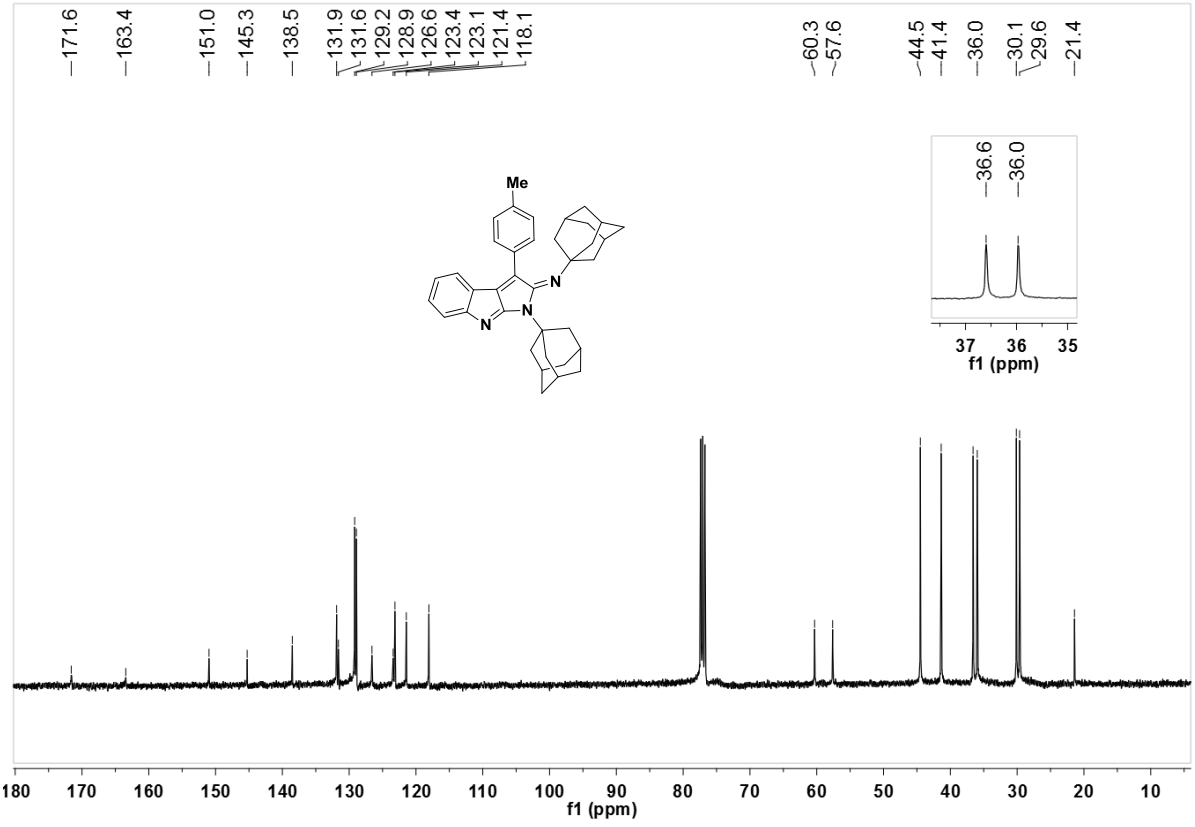
^{1}H NMR Spectrum of Compound 3r



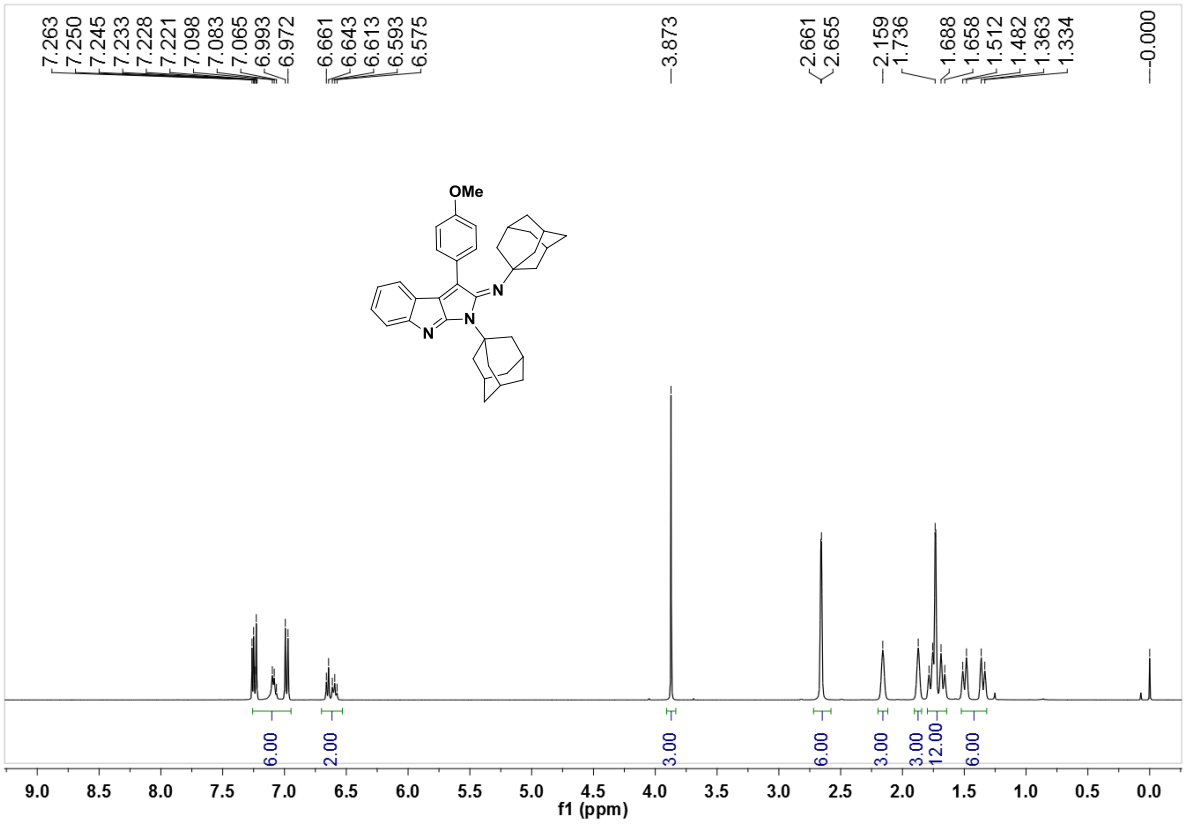
^{13}C NMR Spectrum of Compound 3r



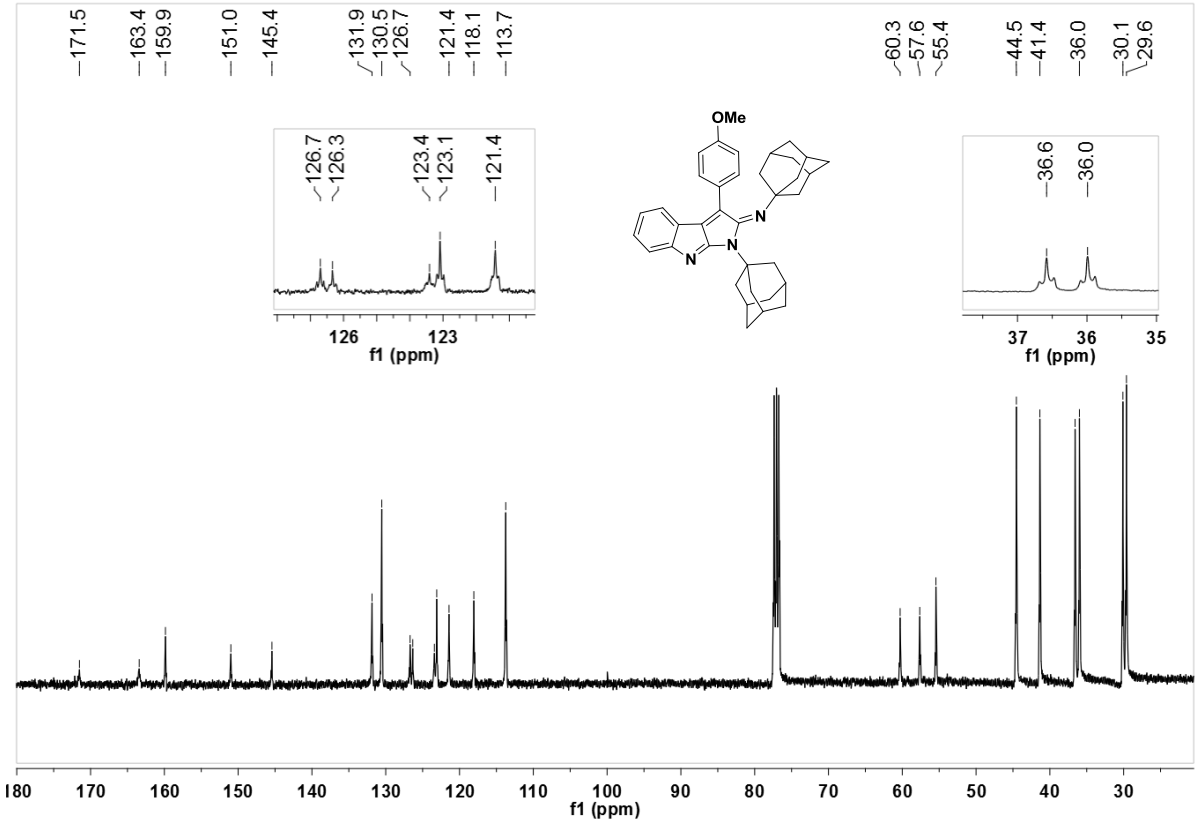
^{1}H NMR Spectrum of Compound 3s



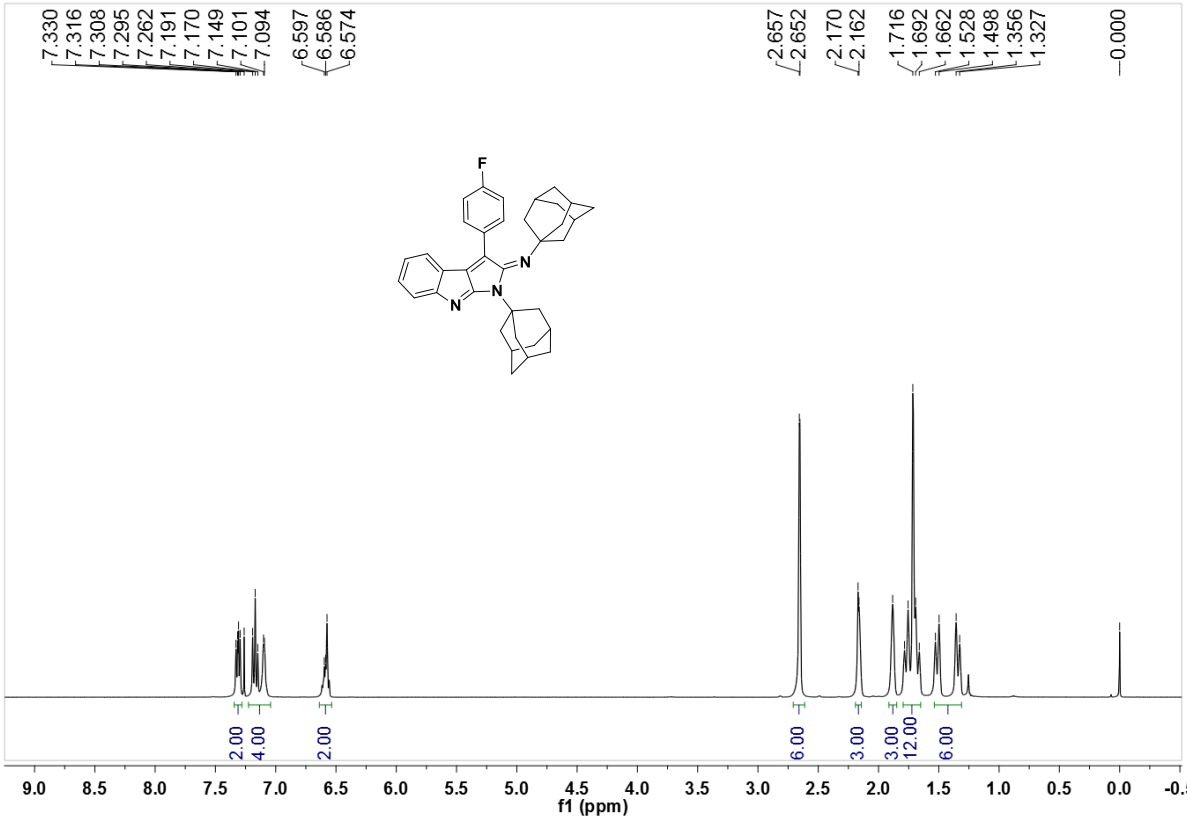
^{13}C NMR Spectrum of Compound 3s



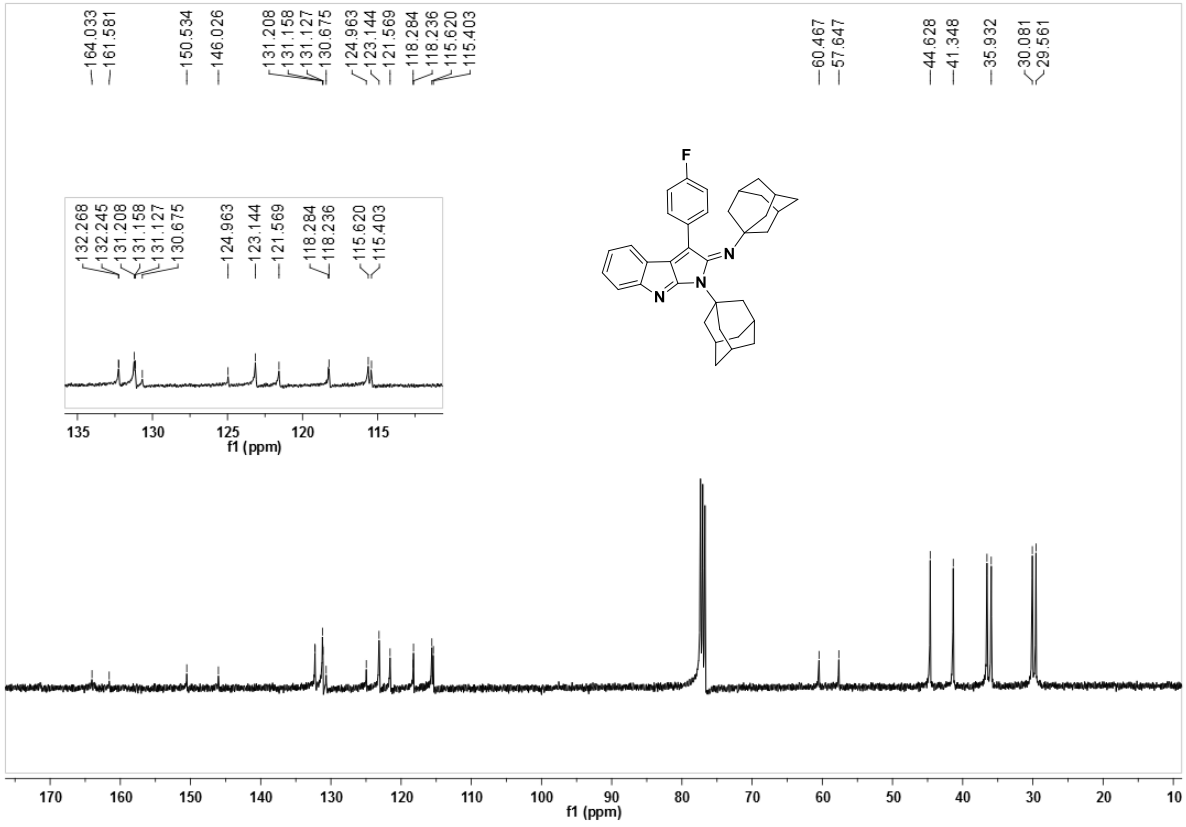
^{1}H NMR Spectrum of Compound 3t



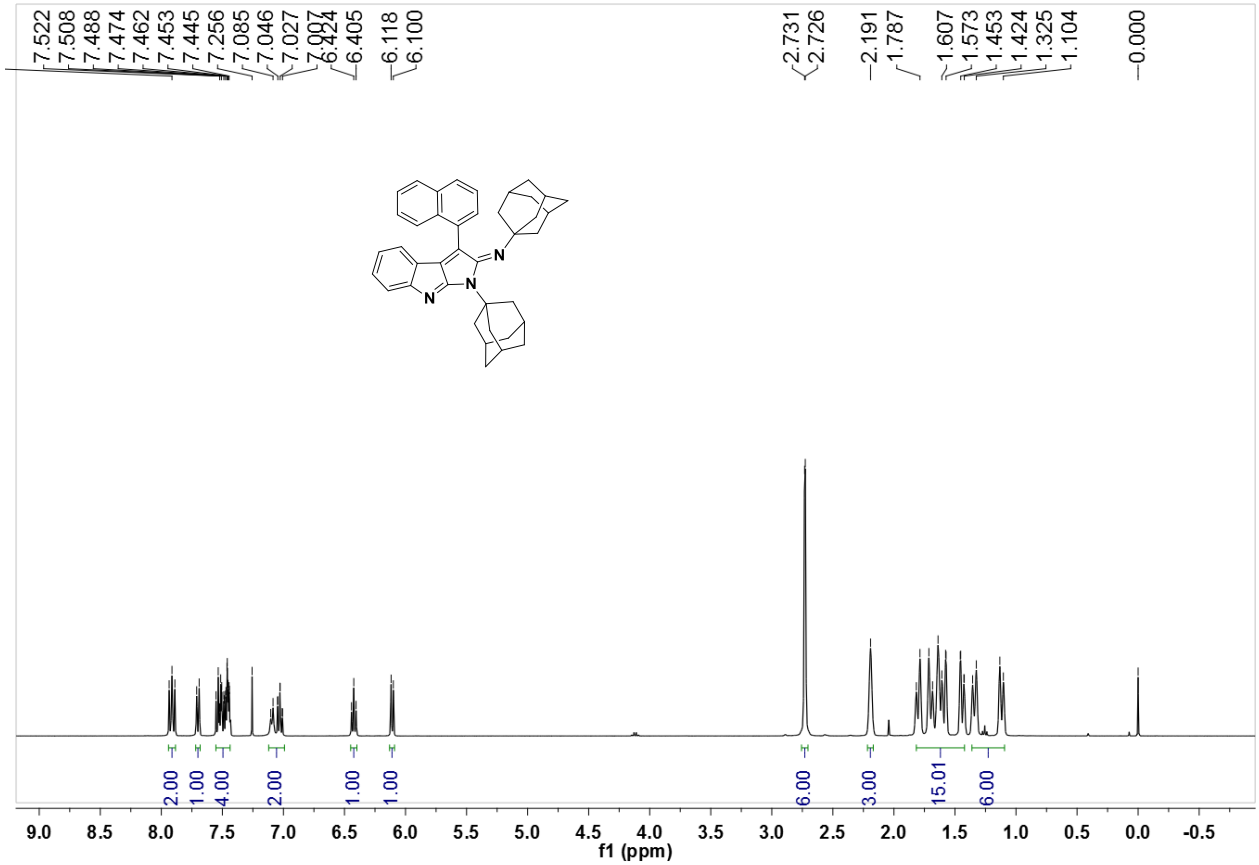
^{13}C NMR Spectrum of Compound 3t



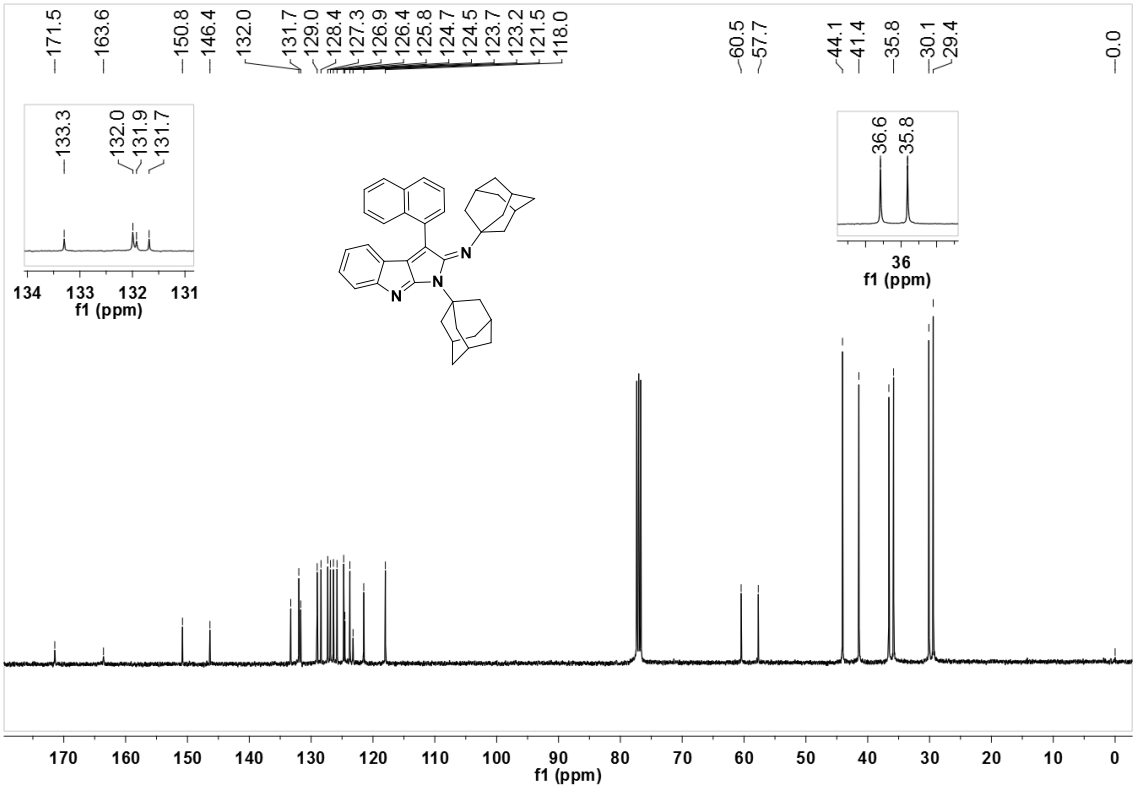
^{1}H NMR Spectrum of Compound 3u



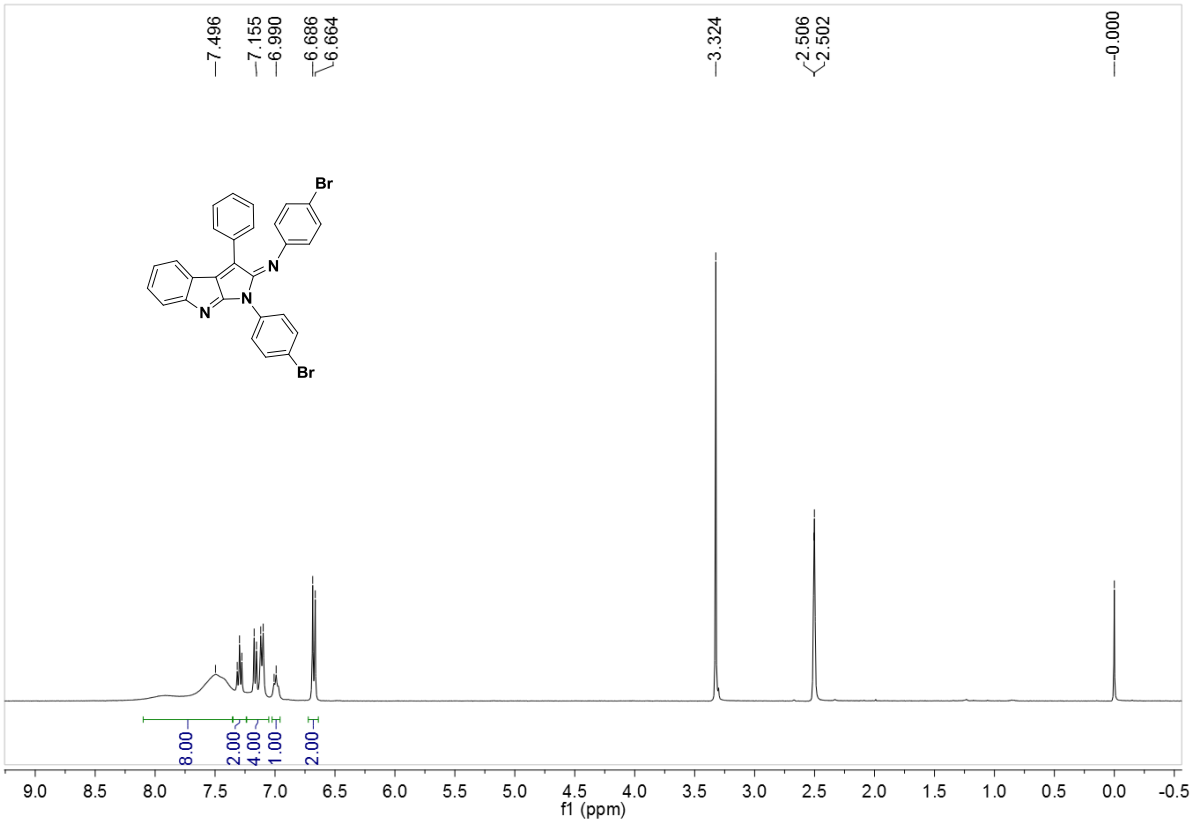
^{13}C NMR Spectrum of Compound 3u



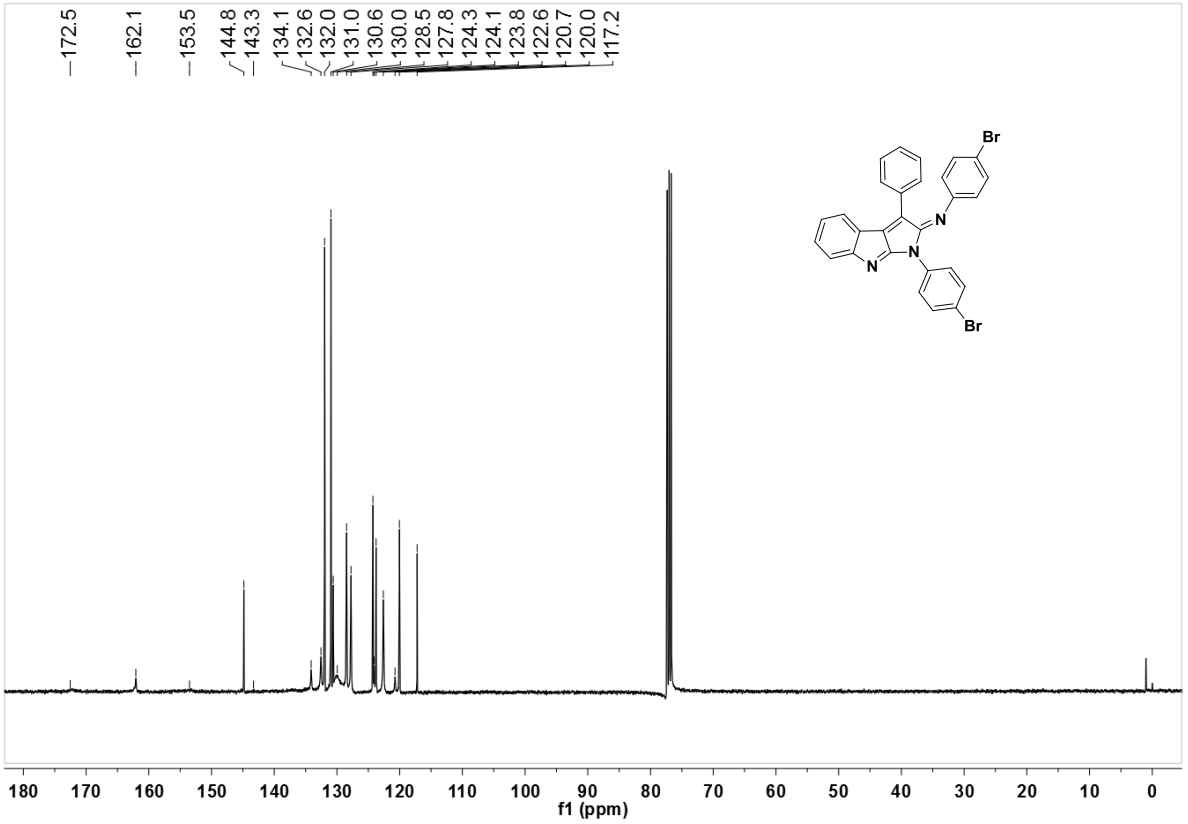
^{1}H NMR Spectrum of Compound 3v



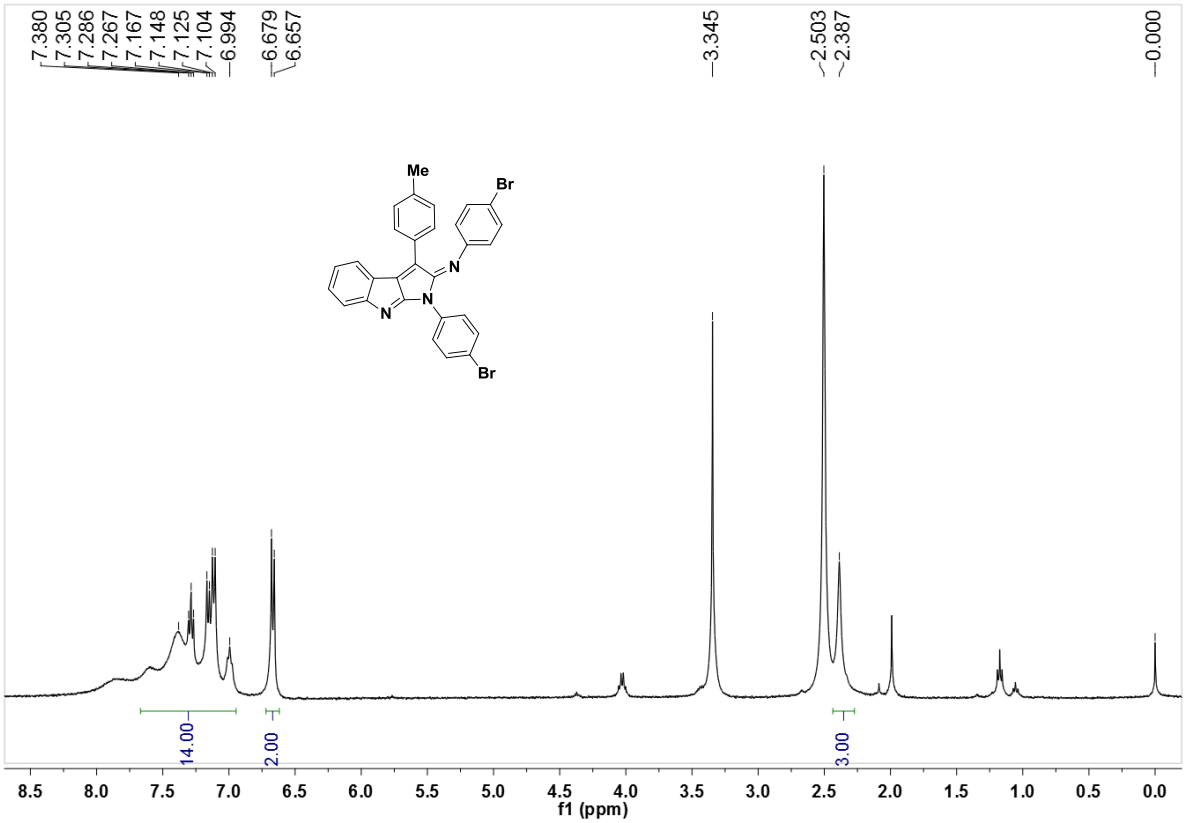
^{13}C NMR Spectrum of Compound 3v



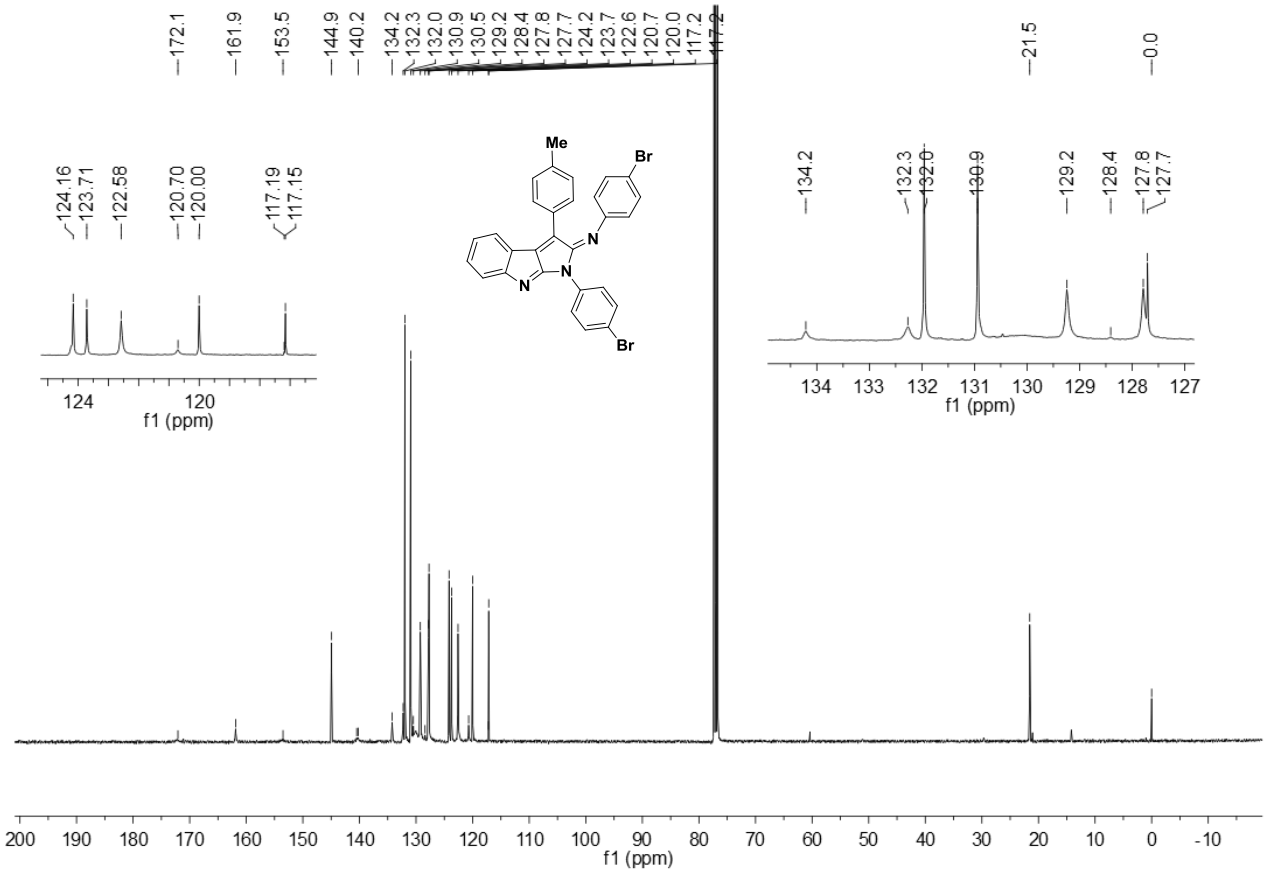
^{1}H NMR Spectrum of Compound 3w



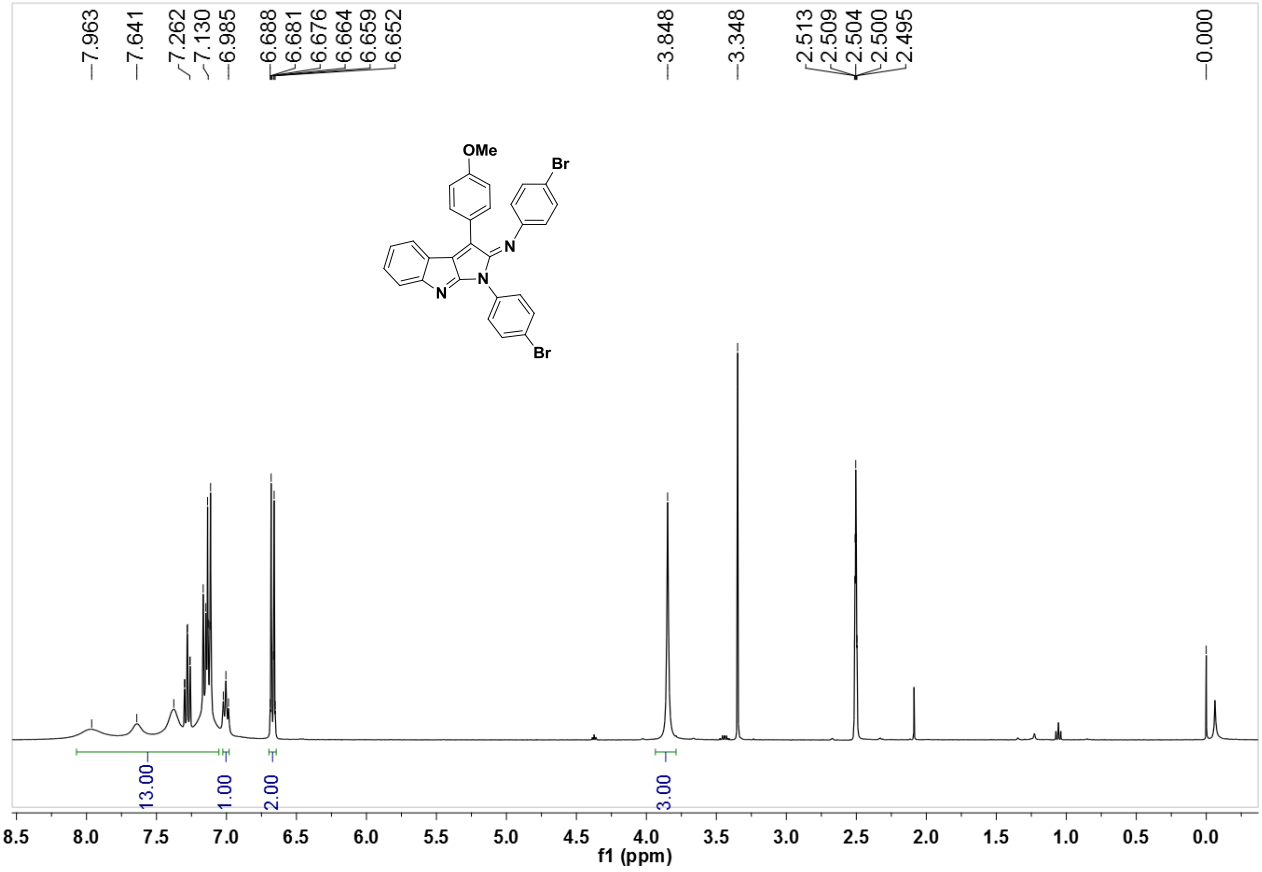
^{13}C NMR Spectrum of Compound 3w



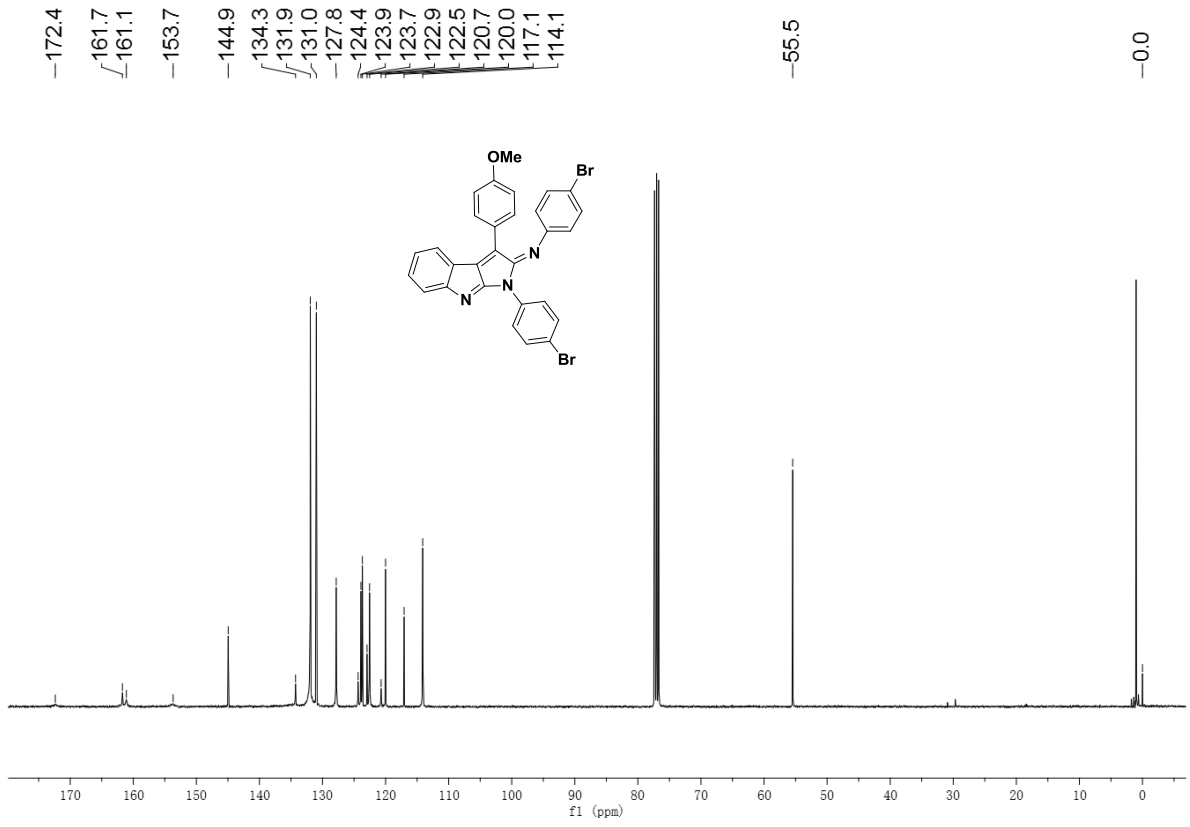
^{1}H NMR Spectrum of Compound 3x



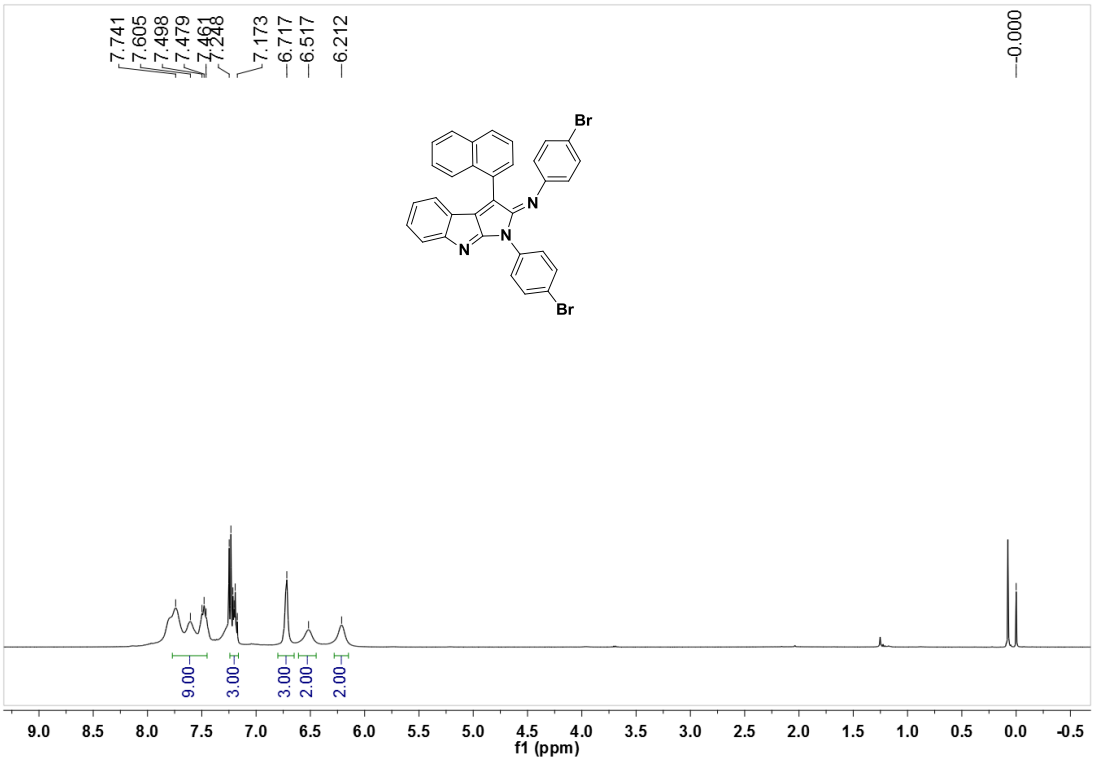
^{13}C NMR Spectrum of Compound 3x



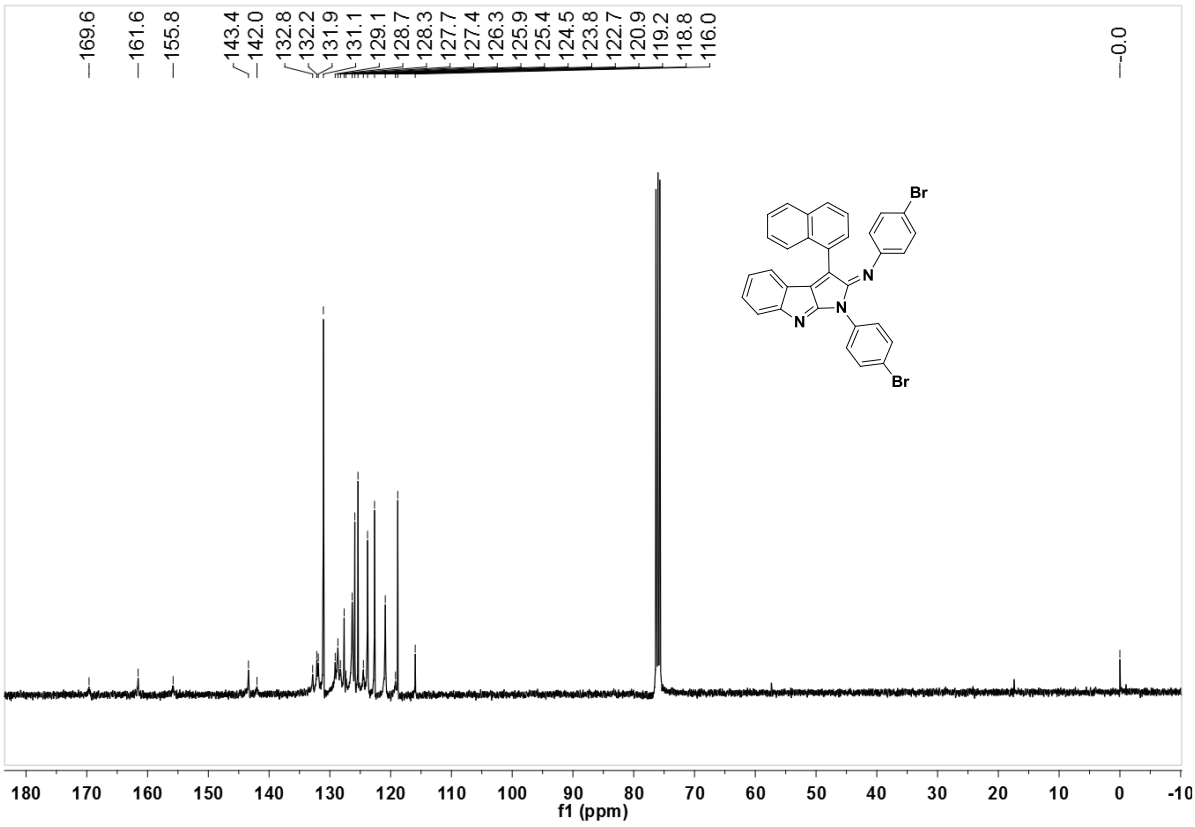
^{1}H NMR Spectrum of Compound 3y



^{13}C NMR Spectrum of Compound 3y



^{1}H NMR Spectrum of Compound 3z



^{13}C NMR Spectrum of Compound 3z

The reaction system was detected by GCMS

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'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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'-x, -y, -z'

'x, -y, z-1/2'

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_diffrn_measurement_device_type 'CCD area detector'

_diffrn_measurement_method 'phi and omega scans'

_diffrn_detector_area_resol_mean ?

_diffrn_standards_number ?

_diffrn_standards_interval_count ?

_diffrn_standards_interval_time ?

_diffrn_standards_decay_% ?

_diffrn_reflns_number 15177

_diffrn_reflns_av_R_equivalents 0.1087

_diffrn_reflns_av_sigmaI/netI 0.1003

_diffrn_reflns_limit_h_min -37

_diffrn_reflns_limit_h_max 34

_diffrn_reflns_limit_k_min -10

_diffrn_reflns_limit_k_max 10

_diffrn_reflns_limit_l_min -20

_diffrn_reflns_limit_l_max 23

_diffrn_reflns_theta_min 2.44

_diffrn_reflns_theta_max 25.02

_reflns_number_total 4054

_reflns_number_gt 2203

_reflns_threshold_expression >2sigma(I)

_computing_data_collection 'Bruker FRAMBO'

_computing_cell_refinement 'Bruker FRAMBO'

_computing_data_reduction 'Bruker SAINT'

_computing_structure_solution 'SHELXS-97 (Sheldrick, 1990)'

_computing_structure_refinement 'SHELXL-97 (Sheldrick, 1997)'

_computing_molecular_graphics 'Bruker SHELXTL'

_computing_publication_material 'Bruker SHELXTL'

_refine_special_details

;

Refinement of F^2^ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2^. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

;

_refine_ls_structure_factor_coef Fsqd

_refine_ls_matrix_type full

_refine_ls_weighting_scheme calc

_refine_ls_weighting_details

'calc w=1/[\s^2^(Fo^2^)+(0.0876P)^2^+0.4143P] where P=(Fo^2^+2Fc^2^)/3'

_atom_sites_solution_primary direct

_atom_sites_solution_secondary difmap

_atom_sites_solution_hydrogens geom

_refine_ls_hydrogen_treatment mixed

_refine_ls_extinction_method SHELXL

_refine_ls_extinction_coef 0.0023(5)

_refine_ls_extinction_expression

'Fc^*^=kFc[1+0.001xFc^2^\l^3^/sin(2\q)]^-1/4^'

_refine_ls_number_reflns 4054

_refine_ls_number_parameters 281

_refine_ls_number_restraints 0

_refine_ls_R_factor_all 0.1276

_refine_ls_R_factor_gt 0.0697

_refine_ls_wR_factor_ref 0.2090

_refine_ls_wR_factor_gt 0.1612

_refine_ls_goodness_of_fit_ref 1.000

_refine_ls_restrained_S_all 1.000

_refine_ls_shift/su_max 0.000

_refine_ls_shift/su_mean 0.000

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_adp_type

_atom_site_occupancy

_atom_site_symmetry_multiplicity

_atom_site_calc_flag

_atom_site_refinement_flags

_atom_site_disorder_assembly

_atom_site_disorder_group

N1 N 0.11588(10) 0.3468(2) 0.08028(16) 0.0545(7) Uani 1 1 d . . .

N2 N 0.07391(10) 0.4362(3) 0.14936(16) 0.0553(7) Uani 1 1 d . . .

N3 N 0.15229(11) 0.3627(3) 0.00317(16) 0.0590(8) Uani 1 1 d . . .

C1 C 0.12352(13) 0.4229(3) 0.02242(19) 0.0517(8) Uani 1 1 d . . .

C2 C 0.09385(11) 0.5683(3) 0.00056(18) 0.0438(7) Uani 1 1 d . . .

C3 C 0.07239(11) 0.5726(3) 0.04502(18) 0.0450(7) Uani 1 1 d . . .

C4 C 0.08784(12) 0.4393(3) 0.09736(19) 0.0482(8) Uani 1 1 d . . .

C5 C 0.04337(11) 0.6601(3) 0.06967(18) 0.0477(8) Uani 1 1 d . . .

C6 C 0.04665(12) 0.5755(3) 0.13392(19) 0.0498(8) Uani 1 1 d . . .

C7 C 0.02458(13) 0.6291(4) 0.1742(2) 0.0623(9) Uani 1 1 d . . .

H7 H 0.0272 0.5755 0.2174 0.075 Uiso 1 1 calc R . .

C8 C -0.00160(14) 0.7642(4) 0.1495(2) 0.0705(11) Uani 1 1 d . . .

H8 H -0.0168 0.8012 0.1764 0.085 Uiso 1 1 calc R . .

C9 C -0.00566(14) 0.8452(4) 0.0860(2) 0.0709(11) Uani 1 1 d . . .

H9 H -0.0237 0.9354 0.0702 0.085 Uiso 1 1 calc R . .

C10 C 0.01702(12) 0.7933(3) 0.0453(2) 0.0593(9) Uani 1 1 d . . .

H10 H 0.0144 0.8478 0.0023 0.071 Uiso 1 1 calc R . .

C11 C 0.14656(13) 0.2201(3) 0.1297(2) 0.0537(9) Uani 1 1 d . . .

H11 H 0.1613 0.1710 0.1016 0.064 Uiso 1 1 calc R . .

C12 C 0.11577(15) 0.1031(3) 0.1416(2) 0.0679(10) Uani 1 1 d . . .

H12A H 0.0911 0.0607 0.0900 0.081 Uiso 1 1 calc R . .

H12B H 0.0982 0.1516 0.1646 0.081 Uiso 1 1 calc R . .

C13 C 0.14846(17) -0.0241(4) 0.1969(2) 0.0815(12) Uani 1 1 d . . .

H13A H 0.1279 -0.0938 0.2060 0.098 Uiso 1 1 calc R . .

H13B H 0.1628 -0.0801 0.1708 0.098 Uiso 1 1 calc R . .

C14 C 0.18977(15) 0.0344(4) 0.2762(2) 0.0700(10) Uani 1 1 d . . .

H14A H 0.2111 -0.0494 0.3078 0.084 Uiso 1 1 calc R . .

H14B H 0.1756 0.0793 0.3055 0.084 Uiso 1 1 calc R . .

C15 C 0.22062(14) 0.1514(4) 0.2647(2) 0.0673(10) Uani 1 1 d . . .

H15A H 0.2385 0.1026 0.2424 0.081 Uiso 1 1 calc R . .

H15B H 0.2451 0.1935 0.3165 0.081 Uiso 1 1 calc R . .

C16 C 0.18905(13) 0.2782(3) 0.2098(2) 0.0634(10) Uani 1 1 d . . .

H16A H 0.2100 0.3454 0.2004 0.076 Uiso 1 1 calc R . .

H16B H 0.1752 0.3367 0.2360 0.076 Uiso 1 1 calc R . .

C17 C 0.16565(13) 0.4353(3) -0.05028(19) 0.0523(9) Uani 1 1 d . . .

H17 H 0.1423 0.5189 -0.0785 0.063 Uiso 1 1 calc R . .

C18 C 0.21746(16) 0.4988(4) -0.0013(2) 0.0792(11) Uani 1 1 d . . .

H18A H 0.2403 0.4184 0.0311 0.095 Uiso 1 1 calc R . .

H18B H 0.2181 0.5759 0.0348 0.095 Uiso 1 1 calc R . .

C19 C 0.23506(17) 0.5684(4) -0.0541(3) 0.0825(12) Uani 1 1 d . . .

H19A H 0.2146 0.6562 -0.0820 0.099 Uiso 1 1 calc R . .

H19B H 0.2694 0.6024 -0.0207 0.099 Uiso 1 1 calc R . .

C20 C 0.23173(17) 0.4558(4) -0.1140(3) 0.0816(13) Uani 1 1 d . . .

H20A H 0.2549 0.3732 -0.0862 0.098 Uiso 1 1 calc R . .

H20B H 0.2412 0.5042 -0.1489 0.098 Uiso 1 1 calc R . .

C21 C 0.1795(2) 0.3934(4) -0.1637(2) 0.0848(14) Uani 1 1 d . . .

H21A H 0.1787 0.3170 -0.2002 0.102 Uiso 1 1 calc R . .

H21B H 0.1569 0.4745 -0.1956 0.102 Uiso 1 1 calc R . .

C22 C 0.16195(16) 0.3232(3) -0.1112(2) 0.0664(10) Uani 1 1 d . . .

H22A H 0.1275 0.2900 -0.1447 0.080 Uiso 1 1 calc R . .

H22B H 0.1823 0.2348 -0.0838 0.080 Uiso 1 1 calc R . .

C23 C 0.09113(11) 0.6898(3) -0.05455(18) 0.0425(7) Uani 1 1 d . . .

C24 C 0.11390(15) 0.8260(3) -0.0235(2) 0.0678(10) Uani 1 1 d . . .

H24 H 0.1303 0.8414 0.0317 0.081 Uiso 1 1 calc R . .

C25 C 0.11319(17) 0.9403(4) -0.0717(3) 0.0781(12) Uani 1 1 d . . .

H25 H 0.1290 1.0320 -0.0490 0.094 Uiso 1 1 calc R . .

C26 C 0.08963(15) 0.9208(4) -0.1519(3) 0.0687(11) Uani 1 1 d . . .

H26 H 0.0891 0.9988 -0.1846 0.082 Uiso 1 1 calc R . .

C27 C 0.06667(15) 0.7867(5) -0.1849(2) 0.0849(12) Uani 1 1 d . . .

H27 H 0.0507 0.7721 -0.2401 0.102 Uiso 1 1 calc R . .

C28 C 0.06706(15) 0.6731(4) -0.1368(2) 0.0781(12) Uani 1 1 d . . .

H28 H 0.0507 0.5824 -0.1600 0.094 Uiso 1 1 calc R . .

loop_

_atom_site_aniso_label

_atom_site_aniso_U_11

_atom_site_aniso_U_22

_atom_site_aniso_U_33

_atom_site_aniso_U_23

_atom_site_aniso_U_13

_atom_site_aniso_U_12

N1 0.088(2) 0.0440(13) 0.0510(17) 0.0141(12) 0.0499(17) 0.0128(13)

N2 0.0788(19) 0.0518(14) 0.0488(17) 0.0118(12) 0.0425(17) 0.0082(13)

N3 0.091(2) 0.0496(15) 0.0522(18) 0.0137(13) 0.0480(18) 0.0149(15)

C1 0.076(2) 0.0438(16) 0.044(2) 0.0080(14) 0.037(2) 0.0060(16)

C2 0.0550(18) 0.0449(15) 0.0326(17) 0.0032(13) 0.0234(16) 0.0002(14)

C3 0.0583(18) 0.0449(15) 0.0320(16) 0.0060(13) 0.0237(16) 0.0035(14)

C4 0.064(2) 0.0445(16) 0.0427(19) 0.0066(14) 0.0327(18) 0.0025(15)

C5 0.0549(18) 0.0499(16) 0.0445(19) 0.0080(15) 0.0301(17) 0.0023(15)

C6 0.0573(19) 0.0555(17) 0.0425(19) 0.0083(15) 0.0300(17) 0.0020(16)

C7 0.077(2) 0.075(2) 0.046(2) 0.0128(17) 0.039(2) 0.0083(19)

C8 0.084(3) 0.085(2) 0.066(3) 0.012(2) 0.055(2) 0.019(2)

C9 0.084(3) 0.073(2) 0.069(3) 0.022(2) 0.049(2) 0.032(2)

C10 0.066(2) 0.067(2) 0.051(2) 0.0173(17) 0.035(2) 0.0173(17)

C11 0.087(2) 0.0369(15) 0.049(2) 0.0100(14) 0.044(2) 0.0121(16)

C12 0.095(3) 0.0480(17) 0.048(2) 0.0114(16) 0.028(2) -0.0039(18)

C13 0.121(3) 0.0501(19) 0.060(3) 0.0181(18) 0.038(3) 0.002(2)

C14 0.095(3) 0.068(2) 0.041(2) 0.0159(18) 0.031(2) 0.011(2)

C15 0.075(2) 0.071(2) 0.051(2) 0.0054(18) 0.029(2) 0.0193(19)

C16 0.076(2) 0.0474(17) 0.074(3) 0.0048(18) 0.044(2) 0.0021(17)

C17 0.080(2) 0.0449(16) 0.048(2) 0.0111(14) 0.044(2) 0.0151(16)

C18 0.111(3) 0.074(2) 0.058(3) -0.011(2) 0.048(3) -0.018(2)

C19 0.098(3) 0.087(2) 0.075(3) -0.004(2) 0.054(3) -0.023(2)

C20 0.115(4) 0.072(2) 0.097(3) 0.022(2) 0.083(3) 0.020(2)

C21 0.162(5) 0.060(2) 0.066(3) -0.0076(19) 0.082(3) -0.011(3)

C22 0.106(3) 0.0559(18) 0.049(2) -0.0045(16) 0.048(2) -0.0119(19)

C23 0.0565(18) 0.0410(15) 0.0370(18) 0.0073(13) 0.0291(16) 0.0081(14)

C24 0.108(3) 0.0515(18) 0.053(2) -0.0063(17) 0.049(2) -0.011(2)

C25 0.127(4) 0.0475(19) 0.078(3) 0.0039(19) 0.066(3) -0.013(2)

C26 0.083(3) 0.063(2) 0.076(3) 0.034(2) 0.052(3) 0.017(2)

C27 0.095(3) 0.102(3) 0.037(2) 0.023(2) 0.021(2) -0.017(3)

C28 0.093(3) 0.083(2) 0.035(2) 0.0090(19) 0.017(2) -0.026(2)

_geom_special_details

;

All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.

;

loop_

_geom_bond_atom_site_label_1

_geom_bond_atom_site_label_2

_geom_bond_distance

_geom_bond_site_symmetry_2

_geom_bond_publ_flag

N1 C4 1.358(3) . ?

N1 C1 1.433(3) . ?

N1 C11 1.460(4) . ?

N2 C4 1.294(4) . ?

N2 C6 1.434(4) . ?

N3 C1 1.257(4) . ?

N3 C17 1.455(4) . ?

C1 C2 1.507(4) . ?

C2 C3 1.343(4) . ?

C2 C23 1.486(4) . ?

C3 C5 1.449(4) . ?

C3 C4 1.462(4) . ?

C5 C10 1.368(4) . ?

C5 C6 1.413(4) . ?

C6 C7 1.370(4) . ?

C7 C8 1.381(4) . ?

C7 H7 0.9300 . ?

C8 C9 1.375(4) . ?

C8 H8 0.9300 . ?

C9 C10 1.388(4) . ?

C9 H9 0.9300 . ?

C10 H10 0.9300 . ?

C11 C12 1.508(4) . ?

C11 C16 1.520(5) . ?

C11 H11 0.9800 . ?

C12 C13 1.521(5) . ?

C12 H12A 0.9700 . ?

C12 H12B 0.9700 . ?

C13 C14 1.500(5) . ?

C13 H13A 0.9700 . ?

C13 H13B 0.9700 . ?

C14 C15 1.505(5) . ?

C14 H14A 0.9700 . ?

C14 H14B 0.9700 . ?

C15 C16 1.506(4) . ?

C15 H15A 0.9700 . ?

C15 H15B 0.9700 . ?

C16 H16A 0.9700 . ?

C16 H16B 0.9700 . ?

C17 C22 1.500(4) . ?

C17 C18 1.498(5) . ?

C17 H17 0.9800 . ?

C18 C19 1.524(5) . ?

C18 H18A 0.9700 . ?

C18 H18B 0.9700 . ?

C19 C20 1.492(5) . ?

C19 H19A 0.9700 . ?

C19 H19B 0.9700 . ?

C20 C21 1.505(6) . ?

C20 H20A 0.9700 . ?

C20 H20B 0.9700 . ?

C21 C22 1.521(4) . ?

C21 H21A 0.9700 . ?

C21 H21B 0.9700 . ?

C22 H22A 0.9700 . ?

C22 H22B 0.9700 . ?

C23 C24 1.364(4) . ?

C23 C28 1.379(4) . ?

C24 C25 1.368(4) . ?

C24 H24 0.9300 . ?

C25 C26 1.349(5) . ?

C25 H25 0.9300 . ?

C26 C27 1.358(5) . ?

C26 H26 0.9300 . ?

C27 C28 1.366(4) . ?

C27 H27 0.9300 . ?

C28 H28 0.9300 . ?

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_geom_angle_atom_site_label_2

_geom_angle_atom_site_label_3

_geom_angle

_geom_angle_site_symmetry_1

_geom_angle_site_symmetry_3

_geom_angle_publ_flag

C4 N1 C1 107.8(2) . . ?

C4 N1 C11 125.7(2) . . ?

C1 N1 C11 123.6(2) . . ?

C4 N2 C6 102.9(2) . . ?

C1 N3 C17 123.0(2) . . ?

N3 C1 N1 118.4(3) . . ?

N3 C1 C2 134.8(3) . . ?

N1 C1 C2 106.8(2) . . ?

C3 C2 C23 125.8(2) . . ?

C3 C2 C1 106.4(2) . . ?

C23 C2 C1 127.7(2) . . ?

C2 C3 C5 146.8(3) . . ?

C2 C3 C4 109.4(2) . . ?

C5 C3 C4 103.5(2) . . ?

N2 C4 N1 134.6(3) . . ?

N2 C4 C3 116.0(3) . . ?

N1 C4 C3 109.4(2) . . ?

C10 C5 C6 120.9(3) . . ?

C10 C5 C3 135.1(3) . . ?

C6 C5 C3 104.1(2) . . ?

C7 C6 C5 119.9(3) . . ?

C7 C6 N2 126.6(3) . . ?

C5 C6 N2 113.5(2) . . ?

C6 C7 C8 118.8(3) . . ?

C6 C7 H7 120.6 . . ?

C8 C7 H7 120.6 . . ?

C9 C8 C7 121.4(3) . . ?

C9 C8 H8 119.3 . . ?

C7 C8 H8 119.3 . . ?

C8 C9 C10 120.5(3) . . ?

C8 C9 H9 119.8 . . ?

C10 C9 H9 119.8 . . ?

C5 C10 C9 118.5(3) . . ?

C5 C10 H10 120.7 . . ?

C9 C10 H10 120.7 . . ?

N1 C11 C12 111.7(3) . . ?

N1 C11 C16 110.2(2) . . ?

C12 C11 C16 111.0(3) . . ?

N1 C11 H11 107.9 . . ?

C12 C11 H11 107.9 . . ?

C16 C11 H11 107.9 . . ?

C11 C12 C13 111.3(3) . . ?

C11 C12 H12A 109.4 . . ?

C13 C12 H12A 109.4 . . ?

C11 C12 H12B 109.4 . . ?

C13 C12 H12B 109.4 . . ?

H12A C12 H12B 108.0 . . ?

C14 C13 C12 112.3(3) . . ?

C14 C13 H13A 109.1 . . ?

C12 C13 H13A 109.1 . . ?

C14 C13 H13B 109.1 . . ?

C12 C13 H13B 109.1 . . ?

H13A C13 H13B 107.9 . . ?

C13 C14 C15 111.0(3) . . ?

C13 C14 H14A 109.4 . . ?

C15 C14 H14A 109.4 . . ?

C13 C14 H14B 109.4 . . ?

C15 C14 H14B 109.4 . . ?

H14A C14 H14B 108.0 . . ?

C14 C15 C16 112.2(3) . . ?

C14 C15 H15A 109.2 . . ?

C16 C15 H15A 109.2 . . ?

C14 C15 H15B 109.2 . . ?

C16 C15 H15B 109.2 . . ?

H15A C15 H15B 107.9 . . ?

C15 C16 C11 112.4(3) . . ?

C15 C16 H16A 109.1 . . ?

C11 C16 H16A 109.1 . . ?

C15 C16 H16B 109.1 . . ?

C11 C16 H16B 109.1 . . ?

H16A C16 H16B 107.8 . . ?

N3 C17 C22 110.1(2) . . ?

N3 C17 C18 109.0(3) . . ?

C22 C17 C18 111.2(3) . . ?

N3 C17 H17 108.8 . . ?

C22 C17 H17 108.8 . . ?

C18 C17 H17 108.8 . . ?

C17 C18 C19 111.8(3) . . ?

C17 C18 H18A 109.3 . . ?

C19 C18 H18A 109.3 . . ?

C17 C18 H18B 109.3 . . ?

C19 C18 H18B 109.3 . . ?

H18A C18 H18B 107.9 . . ?

C20 C19 C18 110.9(3) . . ?

C20 C19 H19A 109.5 . . ?

C18 C19 H19A 109.5 . . ?

C20 C19 H19B 109.5 . . ?

C18 C19 H19B 109.5 . . ?

H19A C19 H19B 108.0 . . ?

C19 C20 C21 111.0(3) . . ?

C19 C20 H20A 109.4 . . ?

C21 C20 H20A 109.4 . . ?

C19 C20 H20B 109.4 . . ?

C21 C20 H20B 109.4 . . ?

H20A C20 H20B 108.0 . . ?

C20 C21 C22 111.5(3) . . ?

C20 C21 H21A 109.3 . . ?

C22 C21 H21A 109.3 . . ?

C20 C21 H21B 109.3 . . ?

C22 C21 H21B 109.3 . . ?

H21A C21 H21B 108.0 . . ?

C17 C22 C21 111.0(2) . . ?

C17 C22 H22A 109.4 . . ?

C21 C22 H22A 109.4 . . ?

C17 C22 H22B 109.4 . . ?

C21 C22 H22B 109.4 . . ?

H22A C22 H22B 108.0 . . ?

C24 C23 C28 116.9(3) . . ?

C24 C23 C2 119.4(3) . . ?

C28 C23 C2 123.6(3) . . ?

C23 C24 C25 121.6(3) . . ?

C23 C24 H24 119.2 . . ?

C25 C24 H24 119.2 . . ?

C26 C25 C24 120.3(3) . . ?

C26 C25 H25 119.8 . . ?

C24 C25 H25 119.8 . . ?

C25 C26 C27 119.7(3) . . ?

C25 C26 H26 120.2 . . ?

C27 C26 H26 120.2 . . ?

C26 C27 C28 119.9(4) . . ?

C26 C27 H27 120.1 . . ?

C28 C27 H27 120.1 . . ?

C27 C28 C23 121.6(3) . . ?

C27 C28 H28 119.2 . . ?

C23 C28 H28 119.2 . . ?

loop_

_geom_torsion_atom_site_label_1

_geom_torsion_atom_site_label_2

_geom_torsion_atom_site_label_3

_geom_torsion_atom_site_label_4

_geom_torsion

_geom_torsion_site_symmetry_1

_geom_torsion_site_symmetry_2

_geom_torsion_site_symmetry_3

_geom_torsion_site_symmetry_4

_geom_torsion_publ_flag

C17 N3 C1 N1 -175.3(3) . . . . ?

C17 N3 C1 C2 2.2(6) . . . . ?

C4 N1 C1 N3 174.0(3) . . . . ?

C11 N1 C1 N3 12.4(5) . . . . ?

C4 N1 C1 C2 -4.2(3) . . . . ?

C11 N1 C1 C2 -165.8(3) . . . . ?

N3 C1 C2 C3 -176.4(4) . . . . ?

N1 C1 C2 C3 1.3(3) . . . . ?

N3 C1 C2 C23 -0.4(6) . . . . ?

N1 C1 C2 C23 177.3(3) . . . . ?

C23 C2 C3 C5 -2.9(7) . . . . ?

C1 C2 C3 C5 173.2(5) . . . . ?

C23 C2 C3 C4 -174.2(3) . . . . ?

C1 C2 C3 C4 1.9(3) . . . . ?

C6 N2 C4 N1 177.6(3) . . . . ?

C6 N2 C4 C3 0.0(4) . . . . ?

C1 N1 C4 N2 -172.2(4) . . . . ?

C11 N1 C4 N2 -11.1(6) . . . . ?

C1 N1 C4 C3 5.4(3) . . . . ?

C11 N1 C4 C3 166.5(3) . . . . ?

C2 C3 C4 N2 173.4(3) . . . . ?

C5 C3 C4 N2 -1.7(4) . . . . ?

C2 C3 C4 N1 -4.7(4) . . . . ?

C5 C3 C4 N1 -179.8(3) . . . . ?

C2 C3 C5 C10 10.6(8) . . . . ?

C4 C3 C5 C10 -177.9(4) . . . . ?

C2 C3 C5 C6 -169.0(5) . . . . ?

C4 C3 C5 C6 2.5(3) . . . . ?

C10 C5 C6 C7 -2.1(5) . . . . ?

C3 C5 C6 C7 177.6(3) . . . . ?

C10 C5 C6 N2 177.6(3) . . . . ?

C3 C5 C6 N2 -2.7(3) . . . . ?

C4 N2 C6 C7 -178.6(3) . . . . ?

C4 N2 C6 C5 1.7(4) . . . . ?

C5 C6 C7 C8 1.5(5) . . . . ?

N2 C6 C7 C8 -178.1(3) . . . . ?

C6 C7 C8 C9 -0.3(6) . . . . ?

C7 C8 C9 C10 -0.6(6) . . . . ?

C6 C5 C10 C9 1.2(5) . . . . ?

C3 C5 C10 C9 -178.3(3) . . . . ?

C8 C9 C10 C5 0.0(6) . . . . ?

C4 N1 C11 C12 58.9(4) . . . . ?

C1 N1 C11 C12 -142.8(3) . . . . ?

C4 N1 C11 C16 -64.9(4) . . . . ?

C1 N1 C11 C16 93.3(3) . . . . ?

N1 C11 C12 C13 -176.9(3) . . . . ?

C16 C11 C12 C13 -53.5(4) . . . . ?

C11 C12 C13 C14 55.3(4) . . . . ?

C12 C13 C14 C15 -54.9(4) . . . . ?

C13 C14 C15 C16 53.9(4) . . . . ?

C14 C15 C16 C11 -53.6(4) . . . . ?

N1 C11 C16 C15 177.5(3) . . . . ?

C12 C11 C16 C15 53.2(4) . . . . ?

C1 N3 C17 C22 -134.5(3) . . . . ?

C1 N3 C17 C18 103.2(4) . . . . ?

N3 C17 C18 C19 176.6(3) . . . . ?

C22 C17 C18 C19 55.0(4) . . . . ?

C17 C18 C19 C20 -55.5(4) . . . . ?

C18 C19 C20 C21 55.7(5) . . . . ?

C19 C20 C21 C22 -56.2(4) . . . . ?

N3 C17 C22 C21 -175.7(3) . . . . ?

C18 C17 C22 C21 -54.7(4) . . . . ?

C20 C21 C22 C17 55.5(4) . . . . ?

C3 C2 C23 C24 66.9(4) . . . . ?

C1 C2 C23 C24 -108.4(4) . . . . ?

C3 C2 C23 C28 -113.8(4) . . . . ?

C1 C2 C23 C28 70.9(5) . . . . ?

C28 C23 C24 C25 -0.4(5) . . . . ?

C2 C23 C24 C25 178.8(3) . . . . ?

C23 C24 C25 C26 0.0(6) . . . . ?

C24 C25 C26 C27 -0.2(6) . . . . ?

C25 C26 C27 C28 0.7(6) . . . . ?

C26 C27 C28 C23 -1.2(6) . . . . ?

C24 C23 C28 C27 1.0(6) . . . . ?

C2 C23 C28 C27 -178.2(3) . . . . ?

_diffrn_measured_fraction_theta_max 0.999

_diffrn_reflns_theta_full 25.02

_diffrn_measured_fraction_theta_full 0.999

_refine_diff_density_max 0.233

_refine_diff_density_min -0.188

_refine_diff_density_rms 0.045