Synthesis of naphthyridin-2(1*H*)-one derivatives *via* a ring expansion of 3-substituted-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one derivatives

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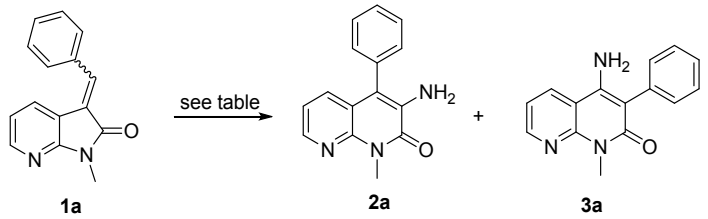
I. General information

Reagents and solvents were purchased from commercial sources (Aldrich, Acros, and VWR international). Reagents were used without further purification unless otherwise noted. Microwave assisted reactions were performed in a closed vessel with a Biotage Initiator + Alstra™ instrument. Reactions were monitored using Merck Kieselgel 60 F254 aluminium plates. TLC was visualized by UV fluorescence (254 nm). NMR spectra were recorded on Bruker AVANCE AV 300 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks chloroform (δ = 7.16 ppm) or d6-DMSO (δ = 2.50 ppm) for ^{1}H NMR, chloroform (δ = 77.16 ppm) or d6-DMSO (δ = 39.52 ppm) for ^{13}C NMR as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, bs = broad singlet. Coupling constants (J) are reported in hertz (Hz). High-resolution mass spectra (HRMS) were performed on a Thermo Q Exactive LC-MS HR/AM Orbitrap.

3-Benzylidene-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one derivatives (**1a**, **1e**, **1g**, **1t**) and 3-benzylidene-1-methylindolin-2-one (**1u**) were prepared according to literature procedures.[1]

II. Optimization study

Table S1. Optimization of the reaction conditions. [a]



1a **2a** **3a**

Entry	[N_3] (equiv)	DBU (equiv)	AcOH (equiv)	Solvent	temp (°C)	time	Yield (%)[b]	**2a/3a**
1	Me_3SiN_3 (10)	0.3	10	toluene	RT	2 weeks	21	0/100
2	Me_3SiN_3 (10)	0	10	toluene	RT	2 weeks	trace	
3	NaN_3 (10)	0.3	10	toluene	RT	1 week	51	22/78
4	DPPA (10)	0.3	10	toluene	RT	1 week	-	
5	Me_3SiN_3 (10)	1	10	toluene	RT	1 week	84	21/79
6	NaN_3 (10)	1	10	toluene	RT	1 week	90	30/70
7	NaN_3 (10)	0.3	10	DMF	RT	36 h	-[c]	
8	Me_3SiN_3 (10)	0.3	10	toluene	120	48 h	54	26/74
9	NaN_3 (10)	0.3	10	toluene	120	48 h	-[c]	
10	Me_3SiN_3 (10)	1	10	toluene	120	48 h	55	25/75
11	Me_3SiN_3 (10)	0.3	10	toluene	130, MW	2 h	80	25/75
12	Me_3SiN_3 (10)	0.3	10	toluene	130, MW	1 h	55	27/73
13	Me_3SiN_3 (10)	0.3	10	toluene	110, MW	2 h	56	30/70
14	Me_3SiN_3 (10)	0.5	10	toluene	110, MW	2 h	86	18/82
15	Me_3SiN_3 (10)	0.5	10	toluene	110, MW	1 h	75	20/80
16	**Me_3SiN_3 (10)**	**1**	**10**	**toluene**	**110, MW**	**1 h**	**94**	**20/80**
17	Me_3SiN_3 (10)	1	10	toluene	110, MW	30 min	82	19/81
18	Me_3SiN_3 (10)	1	10	toluene	110, MW	40 min	89	28/72
19	Me_3SiN_3 (10)	1	10	methanol	110, MW	40 min	78	23/77
20	Me_3SiN_3 (10)	1	10	DMF	110, MW	40 min	76	50/50
21	Me_3SiN_3 (10)	1	10	H_2O	110, MW	40 min	66	23/77
22	Me_3SiN_3 (10)	1	10	H_2O	110, MW	1 h	54	26/74
23	**NaN_3 (10)**	**1**	**10**	**H_2O**	**110, MW**	**1 h**	**91**	**40/60**
24	NaN_3 (10)	1	5	H_2O	110, MW	1 h	74	65/35
25	NaN_3 (10)	1	0	H_2O	110, MW	1 h	-	
26	NaN_3 (10)	K_2CO_3	10	H_2O	110, MW	1 h	35	30/70
27	NaN_3 (10)	DIPEA	10	H_2O	110, MW	1 h	72	33/67
28	NaN_3 (10)	1	10	toluene	110, MW	1 h	83	16/84
29	NaN_3 (10)	1	10	toluene/H_2O 1/1	110, MW	1 h	-	

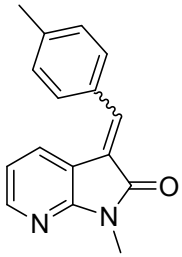
[a] Conditions: **1a** (0.25 mmol), N_3 source (2.5 mmol), AcOH (2.5 mmol), DBU in solvent (2 mL) at the indicated temperature. [b] Isolated yield.
[c] Degradation. DBU - 1,8-diazabicyclo[5.4.0]undec-7-ene, DIPEA – diisopropylethylamine, MW - microwaves

III. General procedures for the condensation of aldehyde on 7-azaoxindole.

Procedure A: A solution of the 1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1 mmol), the appropriate aldehyde (1.5 mmol) and piperidine (0.4 mmol) in toluene (2.5 mL) under an Ar atmosphere was stirred at ambient temperature for 16 h. The reaction mixture was treated with H_2O and the aqueous layer was extracted with EtOAc. The organic layers were dried over $MgSO_4$, filtrered, concentrated in vacuo and purified by flash chromatography to afford the desired 3-benzylidene-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one derivative **1**.

Procedure B: A solution of the 1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1 mmol), the appropriate aldehyde (1.2 mmol) and piperidine (0.1 mmol) in ethanol (5 mL) was stirred under reflux for 1 h. The reaction mixture was concentrated in vacuo and purified by flash chromatography to afford the desired 3-benzylidene-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one derivative **1**.

1-Methyl-3-(4-methylbenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1b)

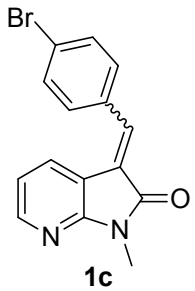


1b

Following the typical procedure B, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 4-methylbenzaldehyde (140 µL, 1.2 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adduct **1b** as a yellow solid (93% yield) with a ratio *E/Z* = 96/4.

M.p. = 173-175 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 8.17 (dd, *J* = 5.2, 1.5 Hz, 1H), 7.95 (s, 1H), 7.90 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.84 (dd, *J* = 7.5, 5.2 Hz, 1H), 3.39 (s, 3H), 2.44 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 168.4, 157.0, 147.7, 140.8, 139.4, 131.7, 129.7, 129.7, 129.3, 124.8, 117.5, 116.2, 25.5, 21.7. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{16}H_{15}N_2O$ 251.11789, found 257.11781.

3-(4-Bromobenzylidene)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1c)



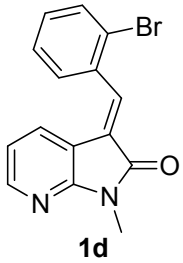
1c

Following the typical procedure B, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 4-bromobenzaldehyde (222 mg, 1.2 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adduct **1c** as a yellow solid (90% yield) with a ratio *E/Z* = 90/10.

M.p. = 155-157 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 8.19 - 8.14 (dd, *J* = 5.2, 1.5 Hz, 1H), 7.85 (s, 1H), 7.76 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.66-7.58 (m, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 6.82 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.36 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 168.0, 157.3, 148.3, 137.5, 133.7, 132.3, 131.0, 129.5, 126.1, 124.5, 117.7, 115.8, 25.5. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated

for $C_{15}H_{12}{}^{79}BrN_2O$ 315.01275, found 315.01266 and calculated for $C_{15}H_{12}{}^{81}BrN_2O$ 317.01071, found 317.01055.

3-(2-Bromobenzylidene)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1d)

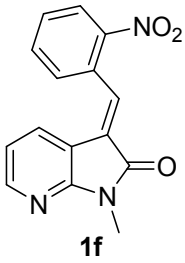


1d

Following the typical procedure A, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 2-bromobenzaldehyde (233 µL, 2 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adduct **1d** as a yellow solid (95% yield) with a ratio *E/Z* = 82/18.

M.p. = 156-158 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 8.16 (dd, *J* = 5.2, 1.5 Hz, 1H), 7.95 (s, 1H), 7.71 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.51-7.28 (m, 3H), 6.77 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.38 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 167.6, 157.2, 148.2, 137.6, 135.1, 133.5, 131.3, 130.2, 129.8, 127.5, 127.0, 126.9, 124.4, 117.7, 115.8, 25.5. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{12}{}^{79}BrN_2O$ 315.01275, found 315.01276 and calculated for $C_{15}H_{12}{}^{81}BrN_2O$ 317.01071, found 317.01063.

1-Methyl-3-(2-nitrobenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1f)

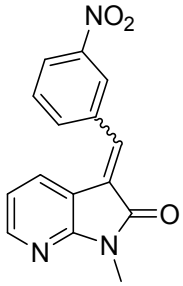


1f

Following the typical procedure B, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 2-nitrobenzaldehyde (181 mg, 1.2 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adduct **1f** as an orange solid (98% yield).

M.p. = 203-205 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 8.36-8.28 (m, 1H), 8.19 (s, 1H), 8.14 (dd, *J* = 5.3, 1.5 Hz, 1H), 7.75 (dd, *J* = 7.0, 1.6 Hz, 1H), 7.67 (t, *J* = 7.0 Hz, 2H), 7.07 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.71 (dd, *J* = 7.5, 5.3 Hz, 1H), 3.37 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 167.2, 157.3, 148.4, 147.4, 135.2, 134.1, 131.0, 130.9, 130.7, 129.5, 126.8, 125.7, 117.6, 115.5, 25.5. **HRMS (ESI)** $[M+H]^+$ *m/z* calculated for $C_{15}H_{12}N_3O_3$ 282.08732, found 282.08729.

1-Methyl-3-(3-nitrobenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1g)



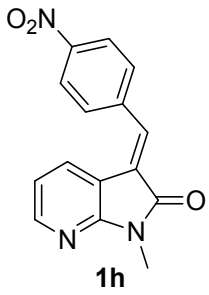
1g

Following the typical procedure B, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 3-nitrobenzaldehyde (181 mg, 1.2 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adduct **1g** as a yellow solid (85% yield) with a ratio *E/Z* = 78/22.

M.p. = 198-200 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 8.49 (s, 1H), 8.30 (dd, *J* = 7.7, 1.2 Hz, 1H), 8.20 (dd, *J* = 5.3, 1.2 Hz, 1H), 7.90 (d, *J* = 5.9 Hz, 2H), 7.85-7.57 (m, 2H), 6.84 (dd, *J* = 7.7, 5.3 Hz, 1H), 3.37 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 167.6, 157.6, 149.0, 148.6, 136.3,

135.2, 135.2, 130.2, 129.6, 128.0, 124.5, 123.9, 117.9, 115.2, 25.6. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{12}N_3O_3$ 282.08732, found 282.08731.

1-Methyl-3-(4-nitrobenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1h)

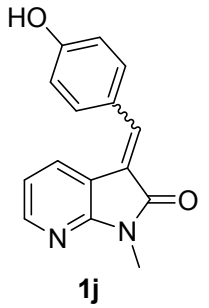


1h

Following the typical procedure B, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 3-nitrobenzaldehyde (181 mg, 1.2 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adduct **1h** as an orange solid (98% yield).

M.p. = 192-194 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 8.41-8.29 (m, 2H), 8.21 (dd, *J* = 5.3, 1.4 Hz, 1H), 7.93 (s, 1H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.65 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.84 (dd, *J* = 7.6, 5.3 Hz, 1H), 3.38 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 167.5, 157.7, 149.1, 141.2, 135.3, 132.6, 130.2, 129.8, 124.3, 123.6, 118.0, 115.2, 25.7. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{12}N_3O_3$ 282.08732, found 282.08730.

3-(4-Hydroxybenzylidene)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1j)

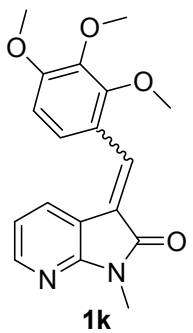


1j

Following the typical procedure B, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 4-hydroxybenzaldehyde (146 mg, 1.2 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adduct **1j** as a yellow solid (85% yield) with a ratio *E/Z* = 80/20.

M.p. = 216-218 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 10.31 (bs, 1H), 8.15 (dd, *J* = 5.2, 1.3 Hz, 1H), 8.00 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.76 (s, 1H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.01-6.90 (m, 3H), 3.22 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 167.6, 160.0, 156.1, 147.1, 139.1, 132.4, 128.8, 124.5, 121.5, 117.7, 115.9, 115.5, 25.1. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{13}N_2O_2$ 253.09715, found 253.09699.

1-Methyl-3-(2,3,4-trimethoxybenzylidene)-1*H*-pyrrolo[2,3-b]pyridin-2(3*H*)-one (1k)



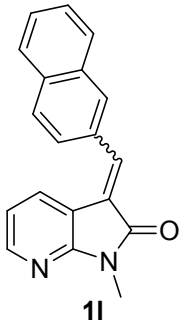
1k

Following the typical procedure B, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 2,3,4-trimethoxybenzaldehyde (235 mg, 1.2 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adduct **1k** as a yellow solid (98% yield) with a ratio *E/Z* = 91/9.

M.p. = 107-109 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 8.14 (dd, *J* = 5.2, 1.5 Hz, 1H), 8.03 (s, 1H), 7.81 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 6.81 (dd, *J* = 7.5, 5.2 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.91 (s, 3H), 3.37 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 168.4, 156.9, 156.1, 153.6, 147.6, 142.5, 135.3, 129.2, 125.0, 124.4, 121.4,

117.4, 116.4, 107.0, 61.8, 61.2, 56.3, 25.4. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{18}H_{19}N_2O_4$ 327.13393, found 327.13349.

1-Methyl-3-(naphthalen-2-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1l)

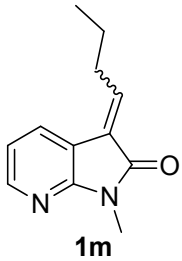


1l

Following the typical procedure B, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 2-naphtaldehyde (187 mg, 1.2 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adduct **1l** as a yellow solid (85% yield) with a ratio *E/Z* = 83/17.

M.p. = 153-155 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.31 (s, 1H), 8.20 (dd, *J* = 5.2, 1.4 Hz, 1H), 8.16-7.95 (m, 4H), 7.88 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.81 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.68-7.55 (m, 2H), 6.97 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.26 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 167.2, 156.6, 148.0, 138.3, 133.5, 132.6, 131.5, 129.9, 129.2, 128.6, 128.4, 127.8, 127.7, 126.9, 126.4, 125.1, 117.9, 115.1, 25.1. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{19}H_{15}N_2O$ 287.11789, found 287.11791.

3-Butylidene-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1m)

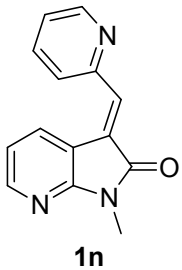


1m

Following the typical procedure A, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and butyraldehyde (135 µL, 1.5 mmol) afforded, after purification by silica gel chromatography (petroleum ether/EtOAc), the adduct **1m** as a pale yellow solid (65% yield) with a ratio *E/Z* = 83/17.

M.p. = 52-54 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 8.16 (dd, *J* = 5.3, 1.3 Hz, 1H), 7.72 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.99-6.87 (m, 1H), 3.33 (s, 3H), 2.63 (q, *J* = 7.5 Hz, 2H), 1.78-1.52 (m, 2H), 1.12-0.97 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 167.7, 156.7, 147.2, 144.2, 130.0, 126.4, 117.7, 117.1, 31.6, 25.3, 22.0, 14.1. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{12}H_{15}N_2O$ 203.11789, found 203.11774.

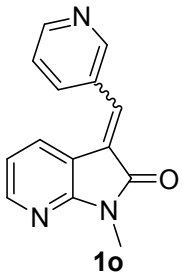
1-Methyl-3-(pyridin-2-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1n)



1n

Following the typical procedure B, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 2-pyridinecarboxaldehyde (114 µL, 1.2 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adduct **1n** as an orange solid (86% yield).

M.p. = 182-184 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 9.28 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.85 (dd, *J* = 4.7, 1.0 Hz, 1H), 8.19 (dd, *J* = 5.2, 1.6 Hz, 1H), 7.87 - 7.72 (m, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.33 (ddd, *J* = 7.6, 4.7, 1.0 Hz, 1H), 6.99 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.37 (s, 3H). **^{13}C NMR**



1o

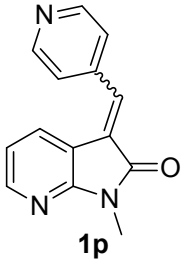
(75 MHz, $CDCl_3$) δ 169.0, 157.8, 153.5, 149.8, 148.2, 137.0, 136.2, 135.6, 128.6, 127. 5, 124.2, 118.2, 116.7, 25.6. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{14}H_{12}N_3O$ 238.09749, found 238.09736.

1-Methyl-3-(pyridin-3-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1o)

Following the typical procedure A, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 3-pyridinecarboxaldehyde (140 µL, 1.5 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adduct **1o** as a yellow solid (70% yield) with a ratio *E/Z* = 64/36.

M.p. = 115-117 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.88 (s, 1H), 8.67 (d, *J* = 4.2 Hz, 1H), 8.17 (dd, *J* = 5.3, 1.4 Hz, 1H), 7.87 (s, 1H), 7.70 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.50-7.38 (m, 2H), 6.82 (dd, *J* = 7.6, 5.3 Hz, 1H), 3.36 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 167.6, 157.4, 150.7, 150.0, 148.8, 136.5, 134.5, 130.7, 129.4, 127.6, 123.7, 117.8, 115.5, 25.5. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{14}H_{12}N_3O$ 238.09749, found 238.09734.

1-Methyl-3-(pyridin-4-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1p)

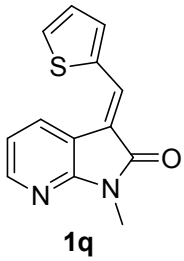


1p

Following the typical procedure B, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 4-pyridinecarboxaldehyde (114 µL, 1.2 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adduct **1p** as a yellow solid (81% yield) with a ratio *E/Z* = 91/9.

M.p. = 149-151 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 8.75 (d, *J* = 5.7 Hz, 2H), 8.19 (dd, *J* = 5.3, 1.5 Hz, 1H), 7.81 (s, 1H), 7.63 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.43 (d, *J* = 5.7 Hz, 2H), 6.82 (dd, *J* = 7.5, 5.3 Hz, 1H), 3.35 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 167.5, 157.6, 150.6, 149.0, 142.6, 134.7, 130.0, 128.7, 123.1, 117.8, 115.2, 25.5. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{14}H_{12}N_3O$ 238.09749, found 238.09735.

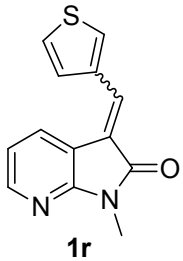
1-Methyl-3-(thiophen-2-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1q)



1q

Following the typical procedure A, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 2-thiophenecarboxaldehyde (190 µL, 2 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adduct **1q** as a yellow solid (73% yield).

M.p. = 201-203 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 8.44 (dd, *J* = 7.6, 1.4 Hz, 1H), 8.19 (dd, *J* = 5.3, 1.4 Hz, 1H), 8.07 (s, 1H), 7.66 (d, *J* = 5.0 Hz, 1H), 7.60 (d, *J* = 3.7 Hz, 1H), 7.22 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.99 (dd, *J* = 7.6, 5.3 Hz, 1H), 3.40 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 168.9, 156.8,



1r

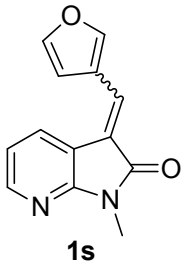
147.2, 137.6, 135.8, 131.5, 130.3, 130.2, 128.6, 121.5, 117.6, 116.0, 25.7. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{13}H_{11}N_2OS$ 243.05866, found 243.05866.

1-Methyl-3-(thiophen-3-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1r)

Following the typical procedure A, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 3-thiophenecarboxaldehyde (175 µL, 2 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adduct **1r** as a yellow solid (76% yield) with a ratio *E/Z* = 53/47.

M.p. = 92-94 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 8.87 (d, *J* = 2.5 Hz, 1H), 8.21-8.13 (m, 2H), 7.99-7.89 (m, 2H), 7.87 (s, 1H), 7.75-7.66 (m, 2H), 7.53 (s, 1H), 7.46 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.41-7.39 (m, 1H), 7.36 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.97 (dd, *J* = 7.5, 5.3 Hz, 1H), 6.88 (dd, *J* = 7.5, 5.3 Hz, 1H), 3.40 (s, 3H), 3.37 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 168.6, 166.1, 156.9, 154.8, 147.6, 146.5, 136.0, 135.8, 134.4, 132.5, 131.5, 131.1, 129.5, 128.4, 127.0, 125.7, 125.6, 124.3, 121.6, 119.4, 117.7, 117.6, 116.2, 25.5, 25.4. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{13}H_{11}N_2OS$ 243.05866, found 243.05862.

1-Methyl-3-(furan-3-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1s)



1s

Following the typical procedure B, the reaction of 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (148 mg, 1 mmol) and 3-furaldehyde (110 µL, 1.2 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adduct **1s** as a yellow solid (86% yield) with a ratio *E/Z* = 50/50.

M.p. = 106-108 °C. **^{1}H NMR (300 MHz, $CDCl_3$) δ** 8.64 (d, *J* = 0.6 Hz, 1H), 8.18-816 (m, 2H), 7.97 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.87 (d, *J* = 0.6 Hz, 1H), 7.75 (s, 1H), 7.66 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.57 (t, *J* = 1.5 Hz, 1H), 7.50 (t, *J* = 1.5 Hz, 1H), 7.35 (s, 1H), 7.28 (d, *J* = 1.8 Hz, 1H), 6.94 (ddd, *J* = 12.5, 7.4, 5.3 Hz, 2H), 6.78 (d, *J* = 1.8 Hz, 1H), 3.38 (s, 3H), 3.36 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 168.5, 166.3, 156.9, 155.1, 149.4, 147.7, 147.1, 146.3, 144.5, 143.7, 129.5, 128.6, 127.6, 125.5, 124.4, 122.2, 121.5, 121.1, 118.9, 117.7, 117.6, 116.2, 112.9, 110.7, 25.5, 25.1. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{13}H_{11}N_2O_2$ 227.08150, found 227.08123.

IV. General procedures for the synthesis of naphthyridin-2(1*H*)-one derivatives

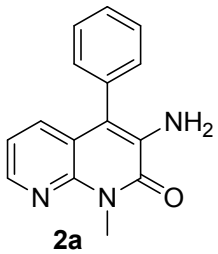
Procedure C: A mixture of 3-benzylidene-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one derivative **1** (0.25 mmol), sodium azide (2.5 mmol), DBU (0.25 mmol), acetic acid (2.5 mmol) and H_2O (2 mL) placed in a sealed vessel was heated at 110 °C under microwave irradiation for 1 h. The reaction mixture was concentrated in vacuo and purified by flash chromatography to afford the desired adducts **2** and **3**.

Procedure D: A mixture of 3-benzylidene-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one derivative **1** (0.25 mmol), azidotrimethylsilane (2.5 mmol), DBU (0.25 mmol), acetic acid (2.5 mmol) and toluene (2 mL) placed in a sealed vessel was heated at 110 °C under microwave irradiation for 1 h. The reaction mixture was concentrated in vacuo and purified by flash chromatography to afford the desired adducts **2** and **3**.

Procedure E: A mixture of 3-benzylidene-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one derivative **1** (0.25 mmol), sodium azide (2.5 mmol), DBU (0.25 mmol), acetic acid (2.5 mmol) and MeOH (2 mL) placed in a sealed vessel was heated at 110 °C under microwave irradiation for 1 h. The reaction mixture was concentrated in vacuo and purified by flash chromatography to afford the desired adducts **2** and **3**.

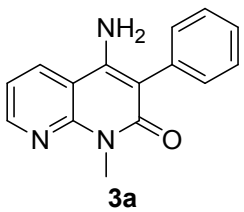
3-Amino-1-methyl-4-phenyl-1,8-naphthyridin-2(1*H*)-one (2a) and **4-amino-1-methyl-3-phenyl-1,8-naphthyridin-2(1*H*)-one (3a)**

Following the typical procedure C, the reaction of 3-benzylidene-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1a** (59 mg, 0.25 mmol) and sodium azide (162 mg, 2.5 mmol) afforded, after purification by alumina gel chromatography (dichloromethane/EtOAc), the adducts **2a** as a pale yellow solid (29% yield) and **3a** as a white solid (53% yield).



2a

M.p. = 193-195 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.34 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.59 (m, 2H), 7.54-7.44 (m, 1H), 7.36-7.30 (m, 2H), 7.27 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.14 (dd, *J* = 7.9, 4.6 Hz, 1H), 5.11 (bs, 2H), 3.82 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.3, 143.8, 143.7, 134.1, 133.9, 130.9, 129.9, 129.5, 128.2, 118.6, 118.1, 115.1, 28.7. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{14}N_3O$ 252.11314, found 252.11302.



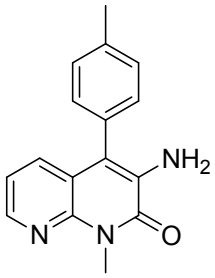
3a

M.p. = 229-231 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.62 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.53 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.40-7.21 (m, 4H), 6.06 (bs, 2H), 3.61 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 161.9, 149.8, 149.0, 146.5,

135.0, 132.4, 131.0, 128.5, 126.9, 116.9, 110.2, 106.2, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{14}N_3O$ 252.11314, found 252.11299.

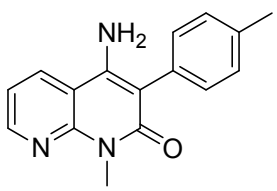
3-Amino-1-methyl-4-(*p*-tolyl)-1,8-naphthyridin-2(1*H*)-one (2b) and 4-amino-1-methyl-3-(*p*-tolyl)-1,8-naphthyridin-2(1*H*)-one (3b)

Following the typical procedure D, the reaction of 1-methyl-3-(4-methylbenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1b** (62 mg, 0.25 mmol) and azidotrimethylsilane (332 µL, 2.5 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adducts **2b** as a white solid (17% yield) and **3b** as a pale yellow solid (58% yield).



2b

M.p. = 200-201 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.33 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.29 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.13 (dd, *J* = 7.9, 4.5 Hz, 1H), 5.08 (bs, 2H), 3.82 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.3, 143.7, 137.4, 134.1, 130.9, 130.8, 130.1, 129.7, 118.5, 118.2, 115.1, 28.6, 20.9. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{16}H_{16}N_3O$ 266.12879, found 266.12842.

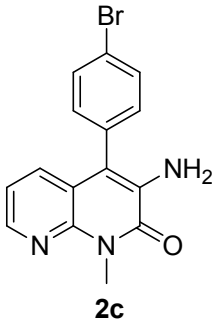


3b

M.p. = 163-165 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.60 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.51 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.26 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.03 (bs, 2H), 3.60 (s, 3H), 2.36 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 161.9, 149.7, 149.0, 146.5, 136.0, 132.4, 131.9, 130.8, 129.1, 116.9, 110.2, 106.1, 27.8, 20.9. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{16}H_{16}N_3O$ 266.12879, found 266.12855.

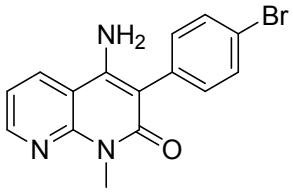
3-Amino-4-(4-bromophenyl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (2c) and **4-amino-3-(4-bromophenyl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (3c)**

Following the typical procedure C, the reaction of 3-(4-bromobenzylidene)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1c** (79 mg, 0.25 mmol) and sodium azide (162 mg, 2.5 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adduct **2c** as a white solid (33% yield) and **3c** as a pale brown solid (53% yield).



2c

M.p. = 203-204 °C: **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.34 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.84-7.67 (m, 2H), 7.30-7.25 (m, 3H), 7.13 (dd, *J* = 7.9, 4.6 Hz, 1H), 5.29 (bs, 2H), 3.82 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.2, 143.7, 143.6, 134.4, 133.2, 132.5, 132.3, 130.7, 121.5, 118.7, 117.9, 113.5, 28.7. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{13}{}^{79}BrN_3O$ 330.02365, found 330.02351 and calculated for $C_{15}H_{13}{}^{81}BrN_3O$ 332.02160, found 332.02132.

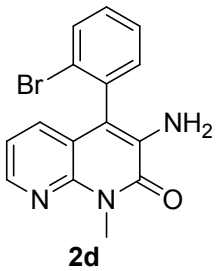


3c

M.p. = 231-232 °C: **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.62 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.53 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66-7.58 (m, 2H), 7.31-7.20 (m, 3H), 6.24 (bs, 2H), 3.60 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 161.7, 149.9, 149.1, 146.8, 134.4, 133.4, 132.5, 131.4, 120.1, 117.0, 110.2, 104.7, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{13}{}^{79}BrN_3O$ 330.02365, found 330.02359 and calculated for $C_{15}H_{13}{}^{81}BrN_3O$ 332.02160, found 332.02148.

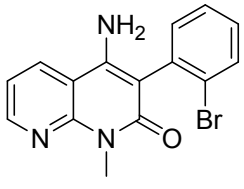
3-Amino-4-(2-bromophenyl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (2d) and **4-amino-3-(2-bromophenyl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (3d)**

Following the typical procedure C, the reaction of 3-(2-bromobenzylidene)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1d** (79 mg, 0.25 mmol) and sodium azide (162 mg, 2.5 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adduct **2d** as a yellow solid (34% yield) and **3d** as a white solid (46% yield).



2d

M.p. = 87-89 °C: **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.33 (dd, *J* = 4.6, 1.6 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.57 (td, *J* = 7.5, 1.0 Hz, 1H), 7.44 (td, *J* = 7.8, 1.7 Hz, 1H), 7.34 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.14 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.00 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.21 (bs, 2H), 3.83 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.3, 143.6, 143.5, 134.6, 134.5, 133.3, 132.3, 130.5, 130.4, 128.9, 124.2, 118.7, 117.5, 113.9, 28.7. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{13}{}^{79}BrN_3O$ 330.02365, found 330.02356 and calculated for $C_{15}H_{13}{}^{81}BrN_3O$ 332.02160, found 330.02145.



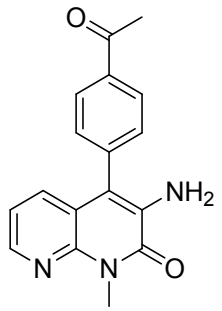
3d

M.p. = 147-149 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.63 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.54 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.73 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.45 (td, *J* = 7.4, 1.2 Hz, 1H), 7.34-7.24 (m, 3H), 6.10 (bs, 2H), 3.60 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 161.1, 149.9, 149.3, 146.9, 136.0, 133.3, 132.6, 132.5, 129.4, 128.1, 125.8, 116.9, 110.1, 106.0, 27.7. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for

$C_{15}H_{13}{}^{79}BrN_3O$ 330.02365, found 330.02370 and calculated for $C_{15}H_{13}{}^{81}BrN_3O$ 332.02160, found 330.02159.

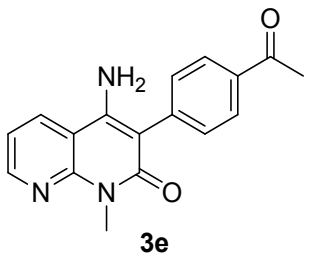
4-(4-Acetylphenyl)-3-amino-1-methyl-1,8-naphthyridin-2(1*H*)-one (2e) and **3-(4-acetylphenyl)-4-amino-1-methyl-1,8-naphthyridin-2(1*H*)-one (3e)**

Following the typical procedure C, the reaction of 3-(4-acetylbenzylidene)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1e** (70 mg, 0.25 mmol) and sodium azide (162 mg, 2.5 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adducts **2e** as a white solid (25% yield) and **3e** as a white solid (57% yield).



2e

M.p. = 220-221 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.35 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.26-8.06 (m, 2H), 7.59-7.40 (m, 2H), 7.26 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.14 (dd, *J* = 7.9, 4.6 Hz, 1H), 5.31 (bs, 2H), 3.83 (s, 3H), 2.66 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 197.7, 143.8, 143.6, 139.1, 136.3, 134.2, 130.6, 130.5, 129.3, 118.7, 117.7, 113.7, 28.7, 26.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{17}H_{16}N_3O_2$ 294.12370, found 294.12334.

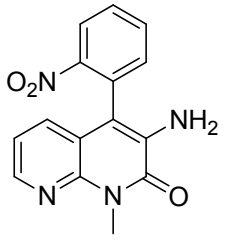


3e

M.p. = 275-276 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.63 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.56 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 8.0, 4.6 Hz, 1H), 6.28 (bs, 2H), 3.61 (s, 3H), 2.62 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 197.7, 161.6, 150.0, 149.1, 146.9, 140.5, 135.3, 132.5, 131.4, 128.3, 117.0, 110.1, 105.0, 27.8, 26.7. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{17}H_{16}N_3O_2$ 294.12370, found 294.12349.

3-Amino-1-methyl-4-(2-nitrophenyl)-1,8-naphthyridin-2(1*H*)-one (2f) and **4-amino-1-methyl-3-(2-nitrophenyl)-1,8-naphthyridin-2(1*H*)-one (3f)**

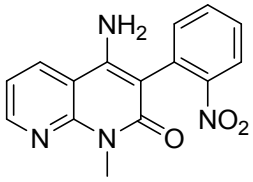
Following the typical procedure C, the reaction of 1-methyl-3-(2-nitrobenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1f** (70 mg, 0.25 mmol) and sodium azide (162 mg, 2.5 mmol) afforded, after purification by silica gel chromatography (dichloromethane/EtOAc), the adducts **2f** as a red solid (50% yield) and **3f** as a yellow solid (42% yield).



2f

M.p. = 206-208 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.33 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.27 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.91 (td, *J* = 7.6, 1.1 Hz, 1H), 7.78 (td, *J* = 8.1, 1.4 Hz, 1H), 7.48 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.11 (dd, *J* = 7.9, 4.6 Hz, 1H), 7.03 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.47 (bs, 2H), 3.83 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.1,

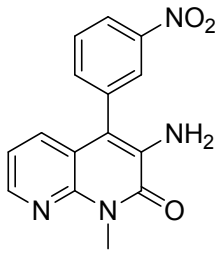
149.0, 143.6, 143.4, 135.0, 134.6, 133.1, 130.1, 130.1, 128.6, 125.3, 118.7, 117.8, 111.3, 28.7. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{13}N_4O_3$ 297.09822, found 297.09818.



3f

M.p. = 127-129 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.64 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.57 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.08 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.77 (td, *J* = 7.5, 1.1 Hz, 1H), 7.61 (td, *J* = 7.5, 1.1 Hz, 1H), 7.49 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.32 (dd, *J* = 8.0, 4.6 Hz, 1H), 6.47 (bs, 2H), 3.56 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 161.0, 150.1, 150.1, 149.0, 146.8, 133.8, 133.5, 132.5, 130.0, 128.6, 124.4, 117.2, 110.3, 102.8, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{13}N_4O_3$ 297.09822, found 297.09818.

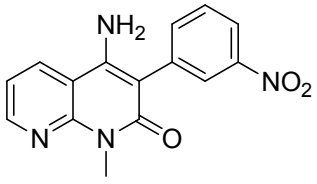
3-Amino-1-methyl-4-(3-nitrophenyl)-1,8-naphthyridin-2(1*H*)-one (2g) and **4-amino-1-methyl-3-(3-nitrophenyl)-1,8-naphthyridin-2(1*H*)-one (3g)**



2g

Following the typical procedure D, the reaction of 1-methyl-3-(3-nitrobenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1g** (70 mg, 0.25 mmol) and azidotrimethylsilane (332 µL, 2.5 mmol) afforded, after purification by alumina gel chromatography (dichloromethane/EtOAc), the adducts **2g** as an orange solid (19% yield) and **3g** as a yellow solid (54% yield).

M.p. = 216-218 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.39-8.29 (m, 2H), 8.15 (s, 1H), 7.92-7.74 (m, 2H), 7.27 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.14 (dd, *J* = 7.9, 4.6 Hz, 1H), 5.54 (bs, 2H), 3.83 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.2, 148.8, 143.7, 143.5, 137.2, 135.7, 135.0, 131.0, 130.4, 125.3, 123.0, 118.7, 117.8, 112.1, 28.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{13}N_4O_3$ 297.09822, found 297.09805.



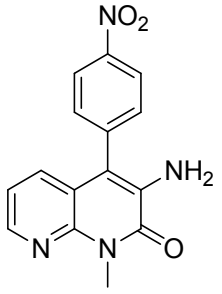
3g

M.p. = 283-285 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.64 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.57 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.23-8.16 (m, 1H), 8.15-8.08 (m, 1H), 7.82-7.67 (m, 2H), 7.30 (dd, *J* = 8.0, 4.6 Hz, 1H), 6.47 (bs, 2H), 3.62 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 161.7, 150.2, 149.2, 148.1, 147.4, 138.5, 137.0, 132.6, 129.8, 126.1, 121.8, 117.1, 110.2, 103.6, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{13}N_4O_3$ 297.09822, found 297.09817.

3-Amino-1-methyl-4-(4-nitrophenyl)-1,8-naphthyridin-2(1*H*)-one (2h) and **4-amino-1-methyl-3-(4-nitrophenyl)-1,8-naphthyridin-2(1*H*)-one (3h)**

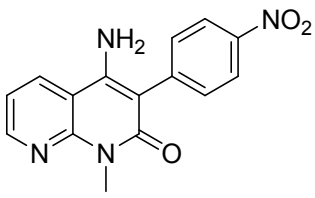
Following the typical procedure D, the reaction of 1-methyl-3-(4-nitrobenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1h** (70 mg, 0.25 mmol) and azidotrimethylsilane (332 µL, 2.5 mmol) afforded, after

purification by silica gel chromatography (dichloromethane/methanol), the adducts **2h** as an orange solid (78% yield) and **3h** as a yellow solid (18% yield).



2h

M.p. = 257-259 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.41 (d, *J* = 8.7 Hz, 2H), 8.34 (dd, *J* = 4.6, 1.6 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.26 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.14 (dd, *J* = 7.9, 4.6 Hz, 1H), 5.47 (bs, 2H), 3.82 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.3, 147.3, 144.0, 143.6, 141.7, 134.7, 132.0, 130.6, 124.8, 118.9, 117.6, 112.7, 28.9. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{13}N_4O_3$ 297.09822, found 297.09816.

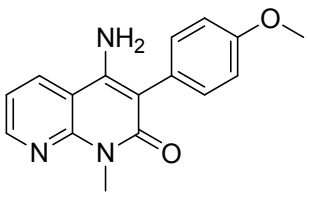


3h

M.p. = 301-303 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.64 (d, *J* = 4.6 Hz, 1H), 8.57 (d, *J* = 7.9 Hz, 1H), 8.29 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.30 (dd, *J* = 7.9, 4.6 Hz, 1H), 6.47 (s, 2H), 3.61 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 161.4, 150.3, 149.2, 147.3, 146.1, 143.1, 132.7, 123.5, 117.1, 110.1, 103.8, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{13}N_4O_3$ 297.09822, found 297.09811.

4-Amino-3-(4-methoxyphenyl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (3i)

Following the typical procedure D, the reaction of 3-(4-methoxybenzylidene)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1i** (66 mg, 0.25 mmol) and azidotrimethylsilane (332 µL, 2.5 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adduct **3i** as an off-white solid (37% yield).

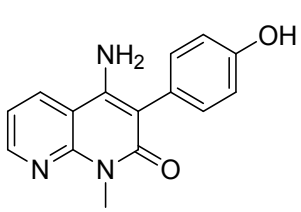


3i

M.p. = 241-243 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.60 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.50 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.26 (dd, *J* = 7.9, 4.6 Hz, 1H), 7.23-7.17 (m, 2H), 7.04-6.97 (m, 2H), 6.02 (bs, 2H), 3.80 (s, 3H), 3.61 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 162.0, 158.1, 149.6, 149.0, 146.6, 132.3, 132.0, 126.9, 116.9, 114.0, 110.2, 105.9, 55.0, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{16}H_{16}N_3O_2$ 282.12370, found 282.12347.

4-Amino-3-(4-hydroxyphenyl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (3j)

Following the typical procedure D, the reaction of 3-(4-hydroxybenzylidene)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1j** (63 mg, 0.25 mmol) and azidotrimethylsilane (332 µL, 2.5 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adduct **3j** as a white solid (30% yield).

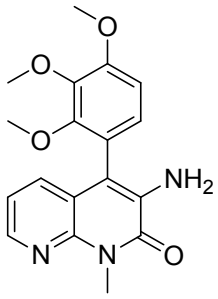


3j

M.p. = 293-295 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 9.43 (s, 1H), 8.59 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.48 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.25 (dd, *J* = 8.0, 4.6 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.96 (bs, 2H), 3.60 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 162.1, 156.3, 149.5, 148.9, 146.4, 132.3, 131.9, 125.1, 116.9, 115.4, 110.2, 106.4, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{15}H_{14}N_3O_2$ 268.10805, found 268.10782.

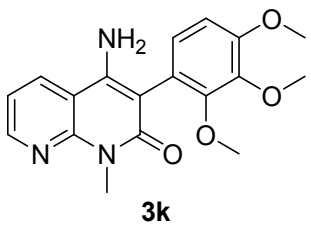
3-Amino-1-methyl-4-(2,3,4-trimethoxyphenyl)-1,8-naphthyridin-2(1*H*)-one (2k) and **4-amino-1-methyl-3-(2,3,4-trimethoxyphenyl)-1,8-naphthyridin-2(1*H*)-one (3k)**

Following the typical procedure D, the reaction of 1-methyl-3-(2,3,4-trimethoxybenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1k** (81 mg, 0.25 mmol) and azidotrimethylsilane (332 µL, 2.5 mmol) afforded, after purification by alumina gel chromatography (dichloromethane/EtOAc), the adducts **2k** as a white solid (9% yield) and **3k** as a white solid (35% yield).



2k

M.p. = 180-182 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.32 (dd, *J* = 4.5, 1.8 Hz, 1H), 7.21-7.11 (m, 2H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 5.13 (bs, 2H), 3.87 (s, 3H), 3.83 (s, 6H), 3.55 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.3, 153.7, 151.7, 143.6, 143.5, 142.4, 134.9, 131.1, 125.5, 119.6, 118.5, 118.4, 112.3, 108.8, 60.7, 60.5, 55.9, 28.6. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{18}H_{20}N_3O_4$ 342.14483, found 342.14467.



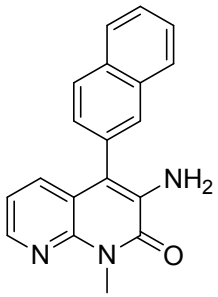
3k

M.p. = 250-252 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.60 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.48 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.26 (dd, *J* = 8.0, 4.7 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 5.94 (bs, 2H), 3.83 (s, 3H), 3.78 (s, 3H), 3.63 (s, 3H), 3.60 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 161.9, 153.0, 152.4, 149.6, 149.2, 147.1, 142.2, 132.2, 126.5, 121.2, 116.8, 110.2, 108.1, 103.3, 60.4, 60.2, 55.8, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{18}H_{20}N_3O_4$ 342.14483, found 342.14452.

3-Amino-1-methyl-4-(naphthalen-2-yl)-1,8-naphthyridin-2(1*H*)-one (2l) and **4-amino-1-methyl-3-(naphthalen-2-yl)-1,8-naphthyridin-2(1*H*)-one (3l)**

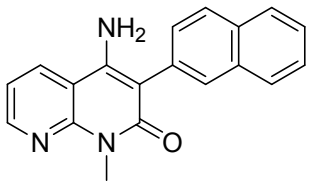
Following the typical procedure D, the reaction of 1-methyl-3-(naphthalen-2-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1l** (36 mg, 0.125 mmol) and azidotrimethylsilane (166 µL, 1.25 mmol)

afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adducts **2l** as an off-white solid (24% yield) and **3l** as a white solid (51% yield).



2l

M.p. = 191-193 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.35 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.08-7.96 (m, 2H), 7.92 (s, 1H), 7.68-7.52 (m, 2H), 7.43 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.32 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.12 (dd, *J* = 7.9, 4.6 Hz, 1H), 5.27 (bs, 2H), 3.85 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.3, 143.7, 134.5, 133.5, 132.6, 131.5, 131.0, 129.1, 129.1, 128.1, 127.7, 126.5, 126.4, 118.6, 118.2, 114.8, 28.7. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{19}H_{16}N_3O$ 302.12879, found 302.12832.

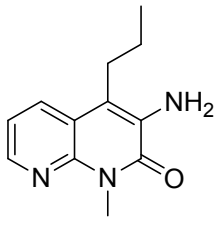


3l

M.p. = 247-248 °C **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.64 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.57 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.00-7.88 (m, 3H), 7.84 (s, 1H), 7.58-7.48 (m, 2H), 7.41 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.29 (dd, *J* = 8.0, 4.7 Hz, 1H), 6.24 (bs, 2H), 3.64 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 162.0, 149.8, 149.1, 146.9, 133.4, 132.8, 132.5, 132.2, 129.7, 129.5, 127.9, 127.7, 127.4, 125.8, 125.7, 117.0, 110.3, 105.9, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{19}H_{15}N_3O$ 302.12879, found 302.12855.

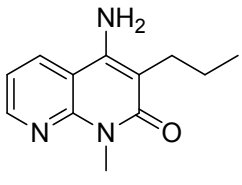
3-Amino-1-methyl-4-propyl-1,8-naphthyridin-2(1*H*)-one (2m) and **4-amino-1-methyl-3-propyl-1,8-naphthyridin-2(1*H*)-one (3m)**

Following the typical procedure C, the reaction of 3-butylidene-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1m** (25 mg, 0.125 mmol) and sodium azide (81 mg, 1.25 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adducts **2m** as a white solid (33% yield) and **3m** as a white solid (52% yield).



2m

M.p. = 138-140 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.32 (dd, *J* = 4.6, 1.6 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.24 (dd, *J* = 8.0, 4.6 Hz, 1H), 5.57 (bs, 2H), 3.75 (s, 3H), 2.74-2.68 (m, 2H), 1.53-1.43 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.3, 143.8, 143.3, 134.3, 129.9, 118.5, 117.6, 114.0, 28.5, 26.7, 20.6, 13.9. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{12}H_{16}N_3O$ 218.12879, found 218.12848.



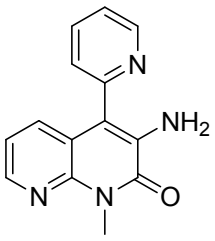
3m

M.p. = 206-208 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.53 (dd, *J* = 4.6, 1.2 Hz, 1H), 8.41 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.22 (dd, *J* = 7.9, 4.6 Hz, 1H), 6.32 (bs, 2H), 3.59 (s, 3H), 2.5 (m, 2H), 1.48-1.35 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (75**

MHz, d6-DMSO) δ 162.7, 148.8, 148.5, 145.9, 131.5, 116.7, 110.3, 105.0, 27.7, 26.4, 20.5, 14.1. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{12}H_{16}N_3O$ 218.12879, found 218.12846.

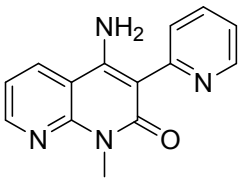
3-Amino-1-methyl-4-(pyridin-2-yl)-1,8-naphthyridin-2(1*H*)-one (2n) and **4-amino-1-methyl-3-(pyridin-2-yl)-1,8-naphthyridin-2(1*H*)-one (3n)**

Following the typical procedure C, the reaction of 1-methyl-3-(pyridin-2-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1n** (59 mg, 0.25 mmol) and sodium azide (162 mg, 2.5 mmol) afforded, after purification by silica gel chromatography (dichloromethane/methanol), the adducts **2n** as a pale brown solid (40% yield) and **3n** as a yellow solid (51% yield).



2n

M.p. = 133-135 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.79 (d, *J* = 4.1 Hz, 1H), 8.36 (dd, *J* = 4.6, 1.6 Hz, 1H), 7.98 (td, *J* = 7.7, 1.8 Hz, 1H), 7.59-7.51 (m, 2H), 7.51-7.42 (m, 1H), 7.17 (dd, *J* = 8.0, 4.6 Hz, 1H), 5.78 (bs, 2H), 3.83 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.6, 153.7, 150.1, 143.7, 143.6, 137.4, 134.9, 130.9, 125.7, 122.8, 118.6, 117.0, 112.7, 28.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{14}H_{13}N_4O$ 253.10839, found 253.10826.

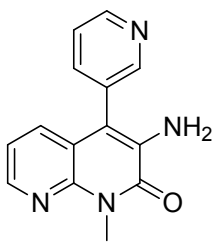


3n

M.p. = 195-197 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.70-8.57 (m, 3H), 8.38 (bs, 2H), 8.24 (d, *J* = 8.3 Hz, 1H), 7.81 (td, *J* = 7.9, 1.9 Hz, 1H), 7.36-7.21 (m, 2H), 3.66 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 162.0, 156.3, 150.6, 149.5, 148.9, 146.8, 135.8, 132.7, 126.0, 120.7, 117.1, 110.3, 100.9, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{14}H_{13}N_4O$ 253.10839, found 253.10820.

3-Amino-1-methyl-4-(pyridin-3-yl)-1,8-naphthyridin-2(1*H*)-one (2o) and **4-amino-1-methyl-3-(pyridin-3-yl)-1,8-naphthyridin-2(1*H*)-one (3o)**

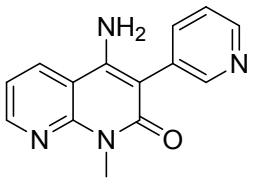
Following the typical procedure C, the reaction of 1-methyl-3-(pyridin-3-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1o** (59 mg, 0.25 mmol) and sodium azide (162 mg, 2.5 mmol) afforded, after purification by silica gel chromatography (dichloromethane/methanol), the adducts **2o** as a yellow solid (36% yield) and **3o** as an off-white (48% yield).



2o

M.p. = 210-212 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.70 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.52 (d, *J* = 1.6 Hz, 1H), 8.35 (dd, *J* = 4.5, 1.8 Hz, 1H), 7.82-7.75 (m, 1H), 7.61 (ddd, *J* = 7.8, 4.8, 0.8 Hz, 1H), 7.23-7.12 (m, 2H), 5.44 (bs, 2H), 3.83 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.2, 150.5, 149.1, 143.7, 143.6, 138.2, 135.2, 130.4, 130.1,

124.5, 118.7, 118.1, 111.1, 28.7. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{14}H_{13}N_4O$ 253.10839, found 253.10811.

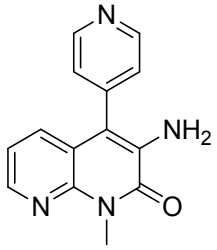


3o

M.p. = 275-277 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.63 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.56 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.52 (dd, *J* = 4.8, 1.9 Hz, 1H), 8.46 (d, *J* = 1.5 Hz, 1H), 7.69 (dt, *J* = 7.8, 1.9 Hz, 1H), 7.46 (ddd, *J* = 7.8, 4.8, 0.7 Hz, 1H), 7.28 (dd, *J* = 8.0, 4.6 Hz, 1H), 6.36 (s, 2H), 3.61 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 161.9, 151.7, 150.1, 149.2, 147.7, 147.5, 138.8, 132.5, 131.1, 123.6, 117.0, 110.1, 102.5, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{14}H_{13}N_4O$ 253.10839, found 253.10814.

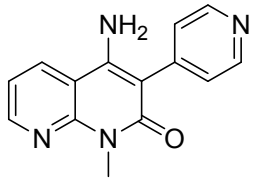
3-Amino-1-methyl-4-(pyridin-4-yl)-1,8-naphthyridin-2(1*H*)-one (2p) and **4-amino-1-methyl-3-(pyridin-4-yl)-1,8-naphthyridin-2(1*H*)-one (3p)**

Following the typical procedure C, the reaction of 1-methyl-3-(pyridin-4-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1p** (59 mg, 0.25 mmol) and sodium azide (162 mg, 2.5 mmol) afforded, after purification by alumina gel chromatography (dichloromethane/methanol), the adducts **2p** as a white solid (70% yield) and **3p** as a white solid (16% yield).



2p

M.p. = 278-279 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.76 (dd, *J* = 4.4, 1.6 Hz, 2H), 8.35 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.37 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.27 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.15 (dd, *J* = 7.9, 4.6 Hz, 1H), 5.46 (bs, 2H), 3.82 (s, 3H). **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{14}H_{13}N_4O$ 253.10839, found 253.10820.

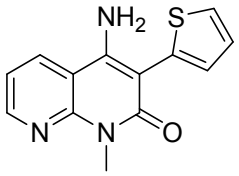


3p

M.p. = 289-291 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.64-8.57 (m, 4H), 7.39 (d, *J* = 5.1 Hz, 2H), 7.29 (dd, *J* = 8.0, 4.7 Hz, 1H), 6.49 (bs, 2H), 3.56 (s, 3H). **^{13}C NMR (75 MHz, D6-DMSO) δ** 161.2, 150.3, 149.2, 149.1, 147.2, 144.1, 132.7, 126.5, 117.1, 110.1, 103.1, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{14}H_{13}N_4O$ 253.10839, found 253.10807.

4-Amino-1-methyl-3-(thiophen-2-yl)-1,8-naphthyridin-2(1*H*)-one (3q)

Following the typical procedure D, the reaction of 1-methyl-3-(thiophen-2-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1q** (60 mg, 0.25 mmol) and azidotrimethylsilane (332 µL, 2.5 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adduct **3q** as a grey solid (36% yield).

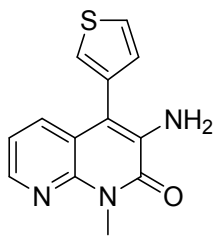


3q

M.p. = 237-239 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.62 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.56 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.28 (dd, *J* = 8.0, 4.6 Hz, 1H), 7.18-7.12 (m, 2H), 6.57 (bs, 2H), 3.62 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 161.4, 150.2, 148.8, 147.6, 135.8, 132.7, 127.4, 126.4, 126.3, 117.2, 109.8, 98.8, 27.9. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{13}H_{12}N_3OS$ 258.06956, found 258.06946.

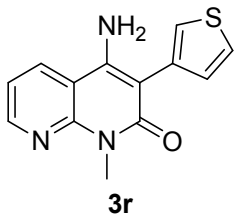
3-Amino-1-methyl-4-(thiophen-3-yl)-1,8-naphthyridin-2(1*H*)-one (2r) and **4-amino-1-methyl-3-(thiophen-3-yl)-1,8-naphthyridin-2(1*H*)-one (3r)**

Following the typical procedure D, the reaction of 1-methyl-3-(thiophen-3-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1r** (60 mg, 0.25 mmol) and azidotrimethylsilane (332 µL, 2.5 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adducts **2r** as an off-white solid (16% yield) and **3r** as an off-white solid (55% yield).



2r

M.p. = 175-176 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.35 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.83 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.66 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.44 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.20-7.14 (m, 2H), 5.24 (bs, 2H), 3.81 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.1, 143.8, 143.6, 134.8, 133.4, 131.0, 128.7, 127.6, 125.8, 118.6, 118.0, 110.3, 28.7. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{13}H_{12}N_3O$ 258.06956, found 258.06931.

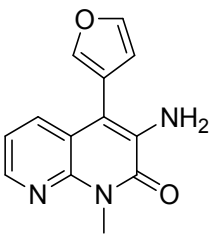


3r

M.p. = 234-236 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.61 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.53 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.60 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.50 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.27 (dd, *J* = 8.0, 4.6 Hz, 1H), 7.16 (dd, *J* = 4.9, 1.2 Hz, 1H), 6.26 (bs, 2H), 3.61 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 161.6, 149.8, 148.9, 146.9, 134.4, 132.4, 130.0, 125.0, 124.8, 117.0, 110.0, 101.2, 27.8. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{13}H_{12}N_3O$ 258.06956, found 258.06943.

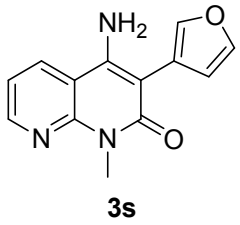
3-Amino-4-(furan-3-yl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (2s) and **4-amino-3-(furan-3-yl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (3s)**

Following the typical procedure D, the reaction of 1-methyl-3-(furan-3-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1s** (56 mg, 0.25 mmol) and azidotrimethylsilane (332 µL, 2.5 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adducts **2s** as a white solid (11% yield) and **3s** as an off-white solid (57% yield).



2s

M.p. = 132-134 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.35 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.95-7.92 (m, 2H), 7.63 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.20 (dd, *J* = 7.9, 4.6 Hz, 1H), 6.63 (dd, *J* = 1.7, 0.8 Hz, 1H), 5.39 (bs, 2H), 3.80 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.0, 144.3, 143.7, 143.7, 142.3, 135.1, 131.0, 118.6, 117.8, 116.9, 111.7, 106.0, 28.6. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{13}H_{12}N_3O_2$ 242.09240, found 242.09210.

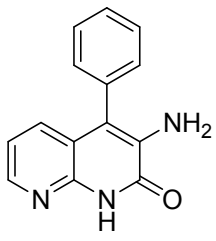


3s

M.p. = 224-227 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.60 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.53 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.84 (d, *J* = 0.6 Hz, 1H), 7.75 (t, *J* = 1.5 Hz, 1H), 7.27 (dd, *J* = 8.0, 4.6 Hz, 1H), 6.73-6.64 (m, 1H), 6.37 (bs, 2H), 3.62 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 162.0, 150.2, 149.2, 147.3, 142.8, 142.5, 132.8, 118.3, 117.4, 112.8, 110.4, 97.7, 28.3. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{13}H_{12}N_3O_2$ 242.09240, found 242.09206.

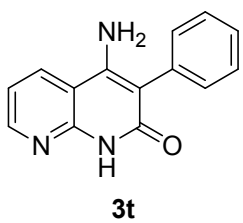
3-Amino-4-phenyl-1,8-naphthyridin-2(1*H*)-one (2t) and **4-amino-3-phenyl-1,8-naphthyridin-2(1*H*)-one (3t)**

Following the typical procedure C, the reaction of 3-benzylidene-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one **1t** (56 mg, 0.25 mmol) and sodium azide (162 mg, 2.5 mmol) afforded, after purification by alumina gel chromatography (dichloromethane/methanol), the adducts **2t** as a white solid (23% yield) and **3t** as an off-white solid (23% yield).



2t

M.p. = 219-221 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 12.37 (bs, 1H), 8.20 (dd, *J* = 4.6, 1.6 Hz, 1H), 7.61-7.56 (m, 2H), 7.52-7.44 (m, 1H), 7.37-7.30 (m, 2H), 7.21 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.06 (dd, *J* = 8.0, 4.6 Hz, 1H), 5.04 (bs, 2H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 158.6, 144.2, 143.8, 134.7, 134.0, 130.4, 129.8, 129.5, 128.1, 118.4, 117.2, 116.1. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{14}H_{12}N_3O$ 238.09749, found 238.09724.

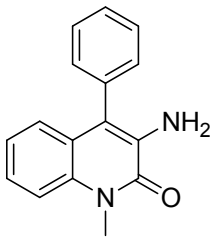


3t

M.p. = 387-389 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 11.33 (bs, 1H), 8.47 (d, *J* = 5.7 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.40-7.26 (m, 3H), 7.26-7.11 (m, 1H), 6.09 (bs, 2H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 162.4, 150.3, 149.2, 147.7, 134.6, 132.1, 131.0, 128.5, 126.8, 117.0, 109.2, 106.3(s). **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{14}H_{12}N_3O$ 238.09749, found 238.09713.

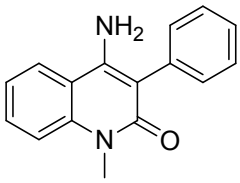
3-Amino-1-methyl-4-phenylquinolin-2(1*H*)-one (2u) and **4-amino-1-methyl-3-phenylquinolin-2(1*H*)-one (3u)**

Following the typical procedure E, the reaction of 3-benzylidene-1-methylindolin-2-one **1u** (59 mg, 0.25 mmol) and sodium azide (162 mg, 2.5 mmol) afforded, after purification by silica gel chromatography (cyclohexane/EtOAc), the adducts **2u** as a white solid (26% yield) and **3u** as a white solid (57% yield).



2u

M.p. = 133-135 °C. **^{1}H NMR (300 MHz, CDCl3) δ** 7.58-7.53 (m, 2H), 7.51-7.41 (m, 1H), 7.40-7.30 (m, 4H), 7.13-7.06 (m, 2H), 3.87 (s, 3H), 3.65 (bs, 2H). **^{13}C NMR (75 MHz, CDCl3) δ** 158.3, 135.0, 134.2, 133.2, 130.0, 129.6, 128.3, 125.8, 124.8, 122.8, 122.6, 120.6, 114.0, 30.3. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{16}H_{15}N_2O$ 251.11789, found 251.11754.



3u

M.p. = 210-211 °C. **^{1}H NMR (300 MHz, d6-DMSO) δ** 8.09 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.67-7.55 (m, 1H), 7.47-7.42 (m, 3H), 7.35-7.20 (m, 4H), 5.84 (bs, 2H), 3.55 (s, 3H). **^{13}C NMR (75 MHz, d6-DMSO) δ** 161.0, 147.4, 139.2, 135.6, 131.0, 130.6, 128.5, 126.8, 123.6, 120.8, 114.6, 114.5, 106.0, 28.9. **HRMS (ESI)** *m/z* $[M+H]^+$ calculated for $C_{16}H_{15}N_2O$ 251.11789, found 251.11783.

V. Single-Crystal X-ray Structure Analysis of 2a and 3a

Methods for X-ray crystallography

All the data were collected with a R-Axis Rapid Rigaku MSC diffractometer[2] using the Cu kα rotating anode and an image plate as detector. The structures were solved by direct methods and refined using Shelx suite of programs[3] in the integrated WinGX system[4]. The positions of the H atoms were deduced from coordinates of the non-H atoms and confirmed by Fourier synthesis, except for H atoms linked to heteroatoms and whose coordinates have been refined. The non-H atoms were refined with anisotropic temperature parameters. H atoms were included for structure factor calculations but not refined. The program Mercury 3.9[5] was used for analysis and drawing figures.

Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre (CCDC 1528553 and CCDC 1528554 for **2a**-**3a** respectively). Copies of these data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

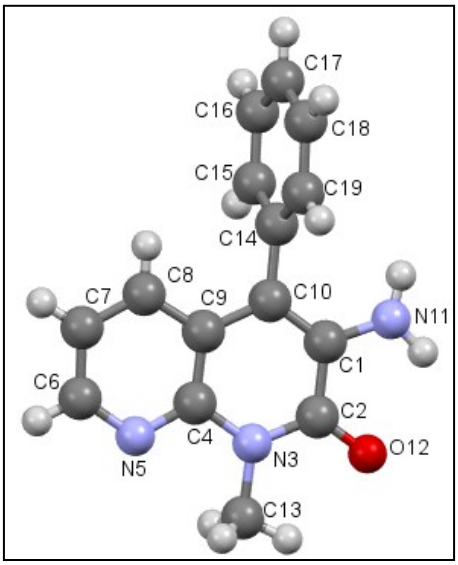


Figure S1. Crystal structure of compound **2a**.

Table S2. Crystal data and structure refinement for **2a**.

Identification code	ccx073t1	
Empirical formula	C15 H13 N3 O	
Formula weight	251.28	
Temperature	153(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 12.9903(2) Å	α= 90°.
	b = 7.8379(1) Å	β= 114.935(8)°.
	c = 13.2745(9) Å	γ = 90°.
Volume	1225.58(9) $Å^3$	
Z	4	
Density (calculated)	1.362 Mg/m^3	
Absorption coefficient	0.712 mm^{-1}	
F(000)	528	
Crystal size	0.20 x 0.20 x 0.12 mm^3	
θ range for data collection	6.70 to 68.24°.	
Index ranges	-15<=h<=15, -9<=k<=8, -15<=l<=15	
Reflections collected	9942	
Independent reflections	2216 [R_{int} = 0.0271]	
Completeness to θ = 68.24°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9195 and 0.8708	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2216 / 0 / 182	
Goodness-of-fit on F^2	1.011	
Final R indices [I>2σ(I)]	R_1 = 0.0344, wR^2 = 0.1015	
R indices (all data)	R_1 = 0.0402, wR^2 = 0.1084	
Extinction coefficient	0.0079(8)	
Largest diff. peak and hole	0.211 and -0.155 $e.Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2a**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	3428(1)	4151(2)	7033(1)	24(1)
C(2)	3028(1)	2723(2)	6244(1)	24(1)
N(3)	1885(1)	2372(1)	5778(1)	25(1)
C(4)	1111(1)	3254(2)	6062(1)	24(1)
N(5)	33(1)	2745(1)	5567(1)	29(1)
C(6)	-718(1)	3577(2)	5829(1)	31(1)
C(7)	-430(1)	4908(2)	6585(1)	31(1)
C(8)	688(1)	5423(2)	7089(1)	28(1)
C(9)	1505(1)	4603(2)	6834(1)	23(1)
C(10)	2686(1)	5072(2)	7306(1)	23(1)
N(11)	4564(1)	4441(2)	7436(1)	31(1)
O(12)	3702(1)	1892(1)	6000(1)	30(1)
C(13)	1463(1)	1008(2)	4941(1)	36(1)
C(14)	3069(1)	6576(2)	8064(1)	23(1)
C(15)	2826(1)	8216(2)	7627(1)	28(1)
C(16)	3134(1)	9628(2)	8326(1)	31(1)
C(17)	3678(1)	9409(2)	9464(1)	31(1)
C(18)	3933(1)	7786(2)	9905(1)	32(1)
C(19)	3635(1)	6368(2)	9211(1)	27(1)

Table S4. Bond lengths [Å] and angles [°] for **2a**.

C(1)-N(11)	1.3609(15)	C(7)-C(8)	1.3787(17)
C(1)-C(10)	1.3696(16)	C(8)-C(9)	1.3992(17)
C(1)-C(2)	1.4695(17)	C(9)-C(10)	1.4379(16)
C(2)-O(12)	1.2386(14)	C(10)-C(14)	1.4926(16)
C(2)-N(3)	1.3747(15)	C(14)-C(15)	1.3914(17)
N(3)-C(4)	1.3964(15)	C(14)-C(19)	1.3931(17)
N(3)-C(13)	1.4706(16)	C(15)-C(16)	1.3896(18)
C(4)-N(5)	1.3337(15)	C(16)-C(17)	1.3827(19)
C(4)-C(9)	1.4097(17)	C(17)-C(18)	1.3805(19)
N(5)-C(6)	1.3354(16)	C(18)-C(19)	1.3904(18)
C(6)-C(7)	1.3856(18)		

N(11)-C(1)-C(10)	125.19(11)	C(7)-C(8)-C(9)	120.01(12)
N(11)-C(1)-C(2)	113.94(11)	C(8)-C(9)-C(4)	116.12(11)
C(10)-C(1)-C(2)	120.88(10)	C(8)-C(9)-C(10)	123.74(11)
O(12)-C(2)-N(3)	121.63(11)	C(4)-C(9)-C(10)	120.13(11)
O(12)-C(2)-C(1)	120.75(11)	C(1)-C(10)-C(9)	119.34(11)
N(3)-C(2)-C(1)	117.61(10)	C(1)-C(10)-C(14)	121.52(10)
C(2)-N(3)-C(4)	122.88(10)	C(9)-C(10)-C(14)	119.12(10)
C(2)-N(3)-C(13)	118.30(10)	C(15)-C(14)-C(19)	119.10(11)
C(4)-N(3)-C(13)	118.82(10)	C(15)-C(14)-C(10)	119.72(11)
N(5)-C(4)-N(3)	116.44(11)	C(19)-C(14)-C(10)	121.15(11)
N(5)-C(4)-C(9)	124.51(11)	C(14)-C(15)-C(16)	120.42(12)
N(3)-C(4)-C(9)	119.05(10)	C(17)-C(16)-C(15)	120.08(12)
C(4)-N(5)-C(6)	117.19(11)	C(18)-C(17)-C(16)	119.90(12)
N(5)-C(6)-C(7)	123.53(11)	C(17)-C(18)-C(19)	120.37(12)
C(8)-C(7)-C(6)	118.64(12)	C(14)-C(19)-C(18)	120.11(12)

Symmetry transformations used to generate equivalent atoms.

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	21(1)	25(1)	24(1)	4(1)	9(1)	1(1)
C(2)	24(1)	23(1)	24(1)	4(1)	11(1)	2(1)
N(3)	24(1)	23(1)	28(1)	-2(1)	11(1)	-1(1)
C(4)	22(1)	23(1)	25(1)	3(1)	10(1)	-1(1)
N(5)	24(1)	28(1)	32(1)	2(1)	10(1)	-3(1)
C(6)	21(1)	34(1)	35(1)	6(1)	11(1)	-2(1)
C(7)	26(1)	34(1)	38(1)	4(1)	18(1)	2(1)
C(8)	27(1)	29(1)	29(1)	0(1)	14(1)	-1(1)
C(9)	23(1)	24(1)	23(1)	4(1)	11(1)	0(1)
C(10)	23(1)	24(1)	23(1)	2(1)	9(1)	-1(1)
N(11)	22(1)	34(1)	38(1)	-8(1)	12(1)	-2(1)
O(12)	28(1)	29(1)	34(1)	-2(1)	14(1)	5(1)
C(13)	33(1)	31(1)	41(1)	-13(1)	12(1)	-3(1)
C(14)	18(1)	28(1)	26(1)	-1(1)	12(1)	-2(1)
C(15)	30(1)	30(1)	26(1)	2(1)	13(1)	0(1)
C(16)	32(1)	25(1)	42(1)	0(1)	22(1)	-1(1)
C(17)	24(1)	36(1)	38(1)	-12(1)	17(1)	-7(1)
C(18)	25(1)	42(1)	27(1)	-5(1)	10(1)	-4(1)
C(19)	22(1)	31(1)	28(1)	2(1)	10(1)	-1(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2a**.

	x	y	z	U(eq)
H(6)	-1492	3238	5478	37
H(7)	-991	5455	6753	37
H(8)	904	6335	7608	33
H(13A)	2102	485	4848	54
H(13B)	930	1491	4231	54
H(13C)	1075	141	5186	54
H(15)	2449	8373	6845	34
H(16)	2970	10744	8021	37
H(17)	3875	10373	9942	37
H(18)	4315	7638	10686	38
H(19)	3817	5255	9520	33
H(11A)	4881(13)	5260(20)	7910(13)	37(4)
H(11B)	4957(14)	3790(20)	7127(13)	48(5)

Table S7. Torsion angles [°] for **2a**.

N(11)-C(1)-C(2)-O(12)	0.41(17)	N(3)-C(4)-C(9)-C(10)	0.97(17)
C(10)-C(1)-C(2)-O(12)	-179.97(11)	N(11)-C(1)-C(10)-C(9)	-178.73(11)
N(11)-C(1)-C(2)-N(3)	-178.49(11)	C(2)-C(1)-C(10)-C(9)	1.69(17)
C(10)-C(1)-C(2)-N(3)	1.14(17)	N(11)-C(1)-C(10)-C(14)	2.48(19)
O(12)-C(2)-N(3)-C(4)	178.07(11)	C(2)-C(1)-C(10)-C(14)	-177.10(10)
C(1)-C(2)-N(3)-C(4)	-3.04(17)	C(8)-C(9)-C(10)-C(1)	177.69(11)
O(12)-C(2)-N(3)-C(13)	-2.18(18)	C(4)-C(9)-C(10)-C(1)	-2.76(17)
C(1)-C(2)-N(3)-C(13)	176.71(10)	C(8)-C(9)-C(10)-C(14)	-3.49(18)
C(2)-N(3)-C(4)-N(5) -	178.11(10)	C(4)-C(9)-C(10)-C(14)	176.06(10)
C(13)-N(3)-C(4)-N(5)	2.14(16)	C(1)-C(10)-C(14)-C(15)	103.96(14)
C(2)-N(3)-C(4)-C(9)	2.02(17)	C(9)-C(10)-C(14)-C(15)	-74.83(15)
C(13)-N(3)-C(4)-C(9)	-177.73(11)	C(1)-C(10)-C(14)-C(19)	-78.15(15)
N(3)-C(4)-N(5)-C(6)	-179.95(10)	C(9)-C(10)-C(14)-C(19)	103.06(13)
C(9)-C(4)-N(5)-C(6)	-0.08(18)	C(19)-C(14)-C(15)-C(16)	-0.72(18)
C(4)-N(5)-C(6)-C(7)	-0.70(18)	C(10)-C(14)-C(15)-C(16)	177.21(11)
N(5)-C(6)-C(7)-C(8)	0.8(2)	C(14)-C(15)-C(16)-C(17)	-0.41(18)
C(6)-C(7)-C(8)-C(9)	-0.14(19)	C(15)-C(16)-C(17)-C(18)	1.16(18)
C(7)-C(8)-C(9)-C(4)	-0.55(18)	C(16)-C(17)-C(18)-C(19)	-0.77(18)
C(7)-C(8)-C(9)-C(10)	179.02(11)	C(15)-C(14)-C(19)-C(18)	1.11(18)
N(5)-C(4)-C(9)-C(8)	0.69(18)	C(10)-C(14)-C(19)-C(18)	-176.79(10)
N(3)-C(4)-C(9)-C(8)	-179.45(10)	C(17)-C(18)-C(19)-C(14)	-0.37(18)
N(5)-C(4)-C(9)-C(10)	-178.90(11)		

Symmetry transformations used to generate equivalent atoms.

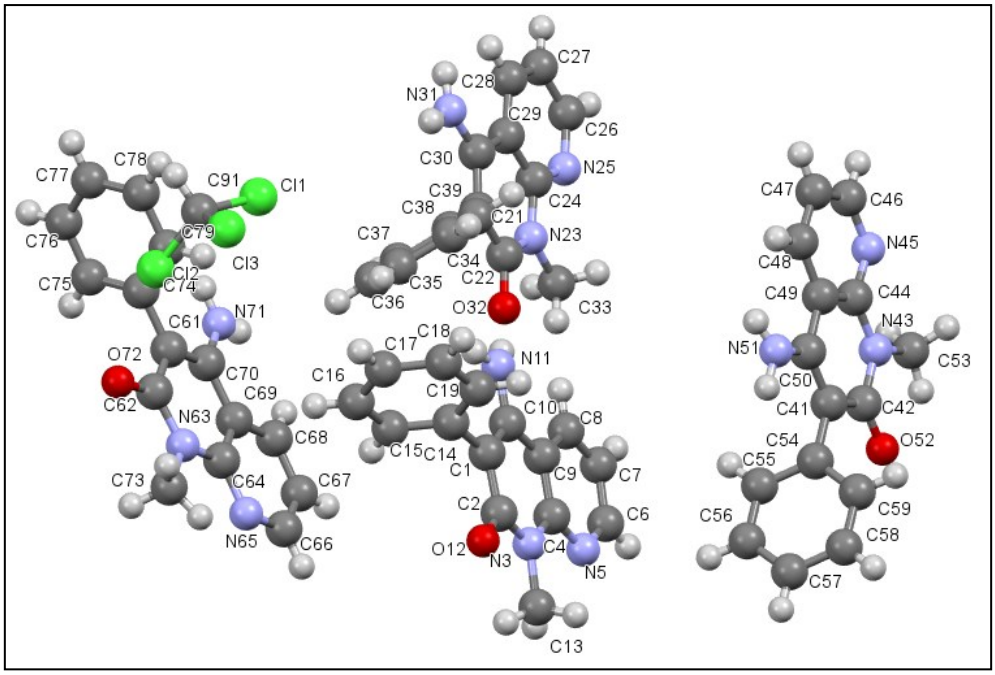


Figure S2. Crystal structure of compound **3a**.

Table S8. Crystal data and structure refinement for **3a**.

Identification code	ccx481t2	
Empirical formula	C61.50 H53.50 Cl4.50 N12 O4	
Formula weight	1184.19	
Temperature	153(2) K	
Wavelength	1.54187 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.82470(10) Å	α= 74.323(5)°.
	b = 14.6849(2) Å	β= 82.323(6)°.
	c = 19.4686(13) Å	γ = 77.013(5)°.
Volume	2894.6(2) $Å^3$	
Z	2	
Density (calculated)	1.359 Mg/m^3	
Absorption coefficient	2.552 mm^{-1}	
F(000)	1230	
Crystal size	0.15 x 0.15 x 0.05 mm^3	
θ range for data collection	2.36 to 68.25°.	
Index ranges	-13<=h<=13, -17<=k<=17, -23<=l<=23	
Reflections collected	44251	
Independent reflections	10437 [R_{int} = 0.0324]	
Completeness to θ = 68.25°	98.4 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8830 and 0.7008
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10437 / 0 / 750
Goodness-of-fit on F^2	1.026
Final R indices [I>2σ(I)]	R_1 = 0.0546, wR^2 = 0.1556
R indices (all data)	R_1 = 0.0609, wR^2 = 0.1704
Extinction coefficient	0.00164(18)
Largest diff. peak and hole	1.146 and -0.854 e.$Å^{-3}$

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3a**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	5771(2)	3851(2)	1911(1)	30(1)
C(2)	6496(2)	2997(2)	1733(1)	36(1)
N(3)	6475(2)	2115(1)	2229(1)	37(1)
C(4)	5698(2)	2043(2)	2859(1)	29(1)
N(5)	5708(2)	1148(1)	3274(1)	35(1)
C(6)	4953(2)	1065(2)	3883(1)	35(1)
C(7)	4186(2)	1831(2)	4101(1)	34(1)
C(8)	4182(2)	2750(2)	3670(1)	32(1)
C(9)	4949(2)	2875(2)	3030(1)	28(1)
C(10)	5003(2)	3815(2)	2541(1)	28(1)
N(11)	4278(2)	4611(1)	2707(1)	36(1)
O(12)	7169(2)	2997(1)	1158(1)	49(1)
C(13)	7311(3)	1254(2)	2070(2)	62(1)
C(14)	5883(2)	4790(2)	1388(1)	31(1)
C(15)	6923(2)	5208(2)	1373(1)	37(1)
C(16)	7061(3)	6064(2)	872(1)	40(1)
C(17)	6157(3)	6508(2)	377(1)	41(1)
C(18)	5114(3)	6103(2)	393(1)	41(1)
C(19)	4973(2)	5250(2)	900(1)	37(1)
C(21)	2232(2)	6358(2)	3998(1)	30(1)
C(22)	2481(2)	5360(2)	4389(1)	32(1)
N(23)	1805(2)	5098(1)	5039(1)	31(1)
C(24)	884(2)	5752(2)	5310(1)	30(1)
N(25)	235(2)	5395(1)	5923(1)	35(1)
C(26)	-646(2)	6019(2)	6206(1)	37(1)
C(27)	-908(2)	7004(2)	5901(1)	37(1)
C(28)	-249(2)	7367(2)	5266(1)	33(1)
C(29)	654(2)	6743(2)	4949(1)	30(1)
C(30)	1372(2)	7046(2)	4269(1)	31(1)

N(31)	1177(2)	7989(1)	3918(1)	39(1)
O(32)	3292(2)	4730(1)	4165(1)	40(1)
C(33)	2087(3)	4088(2)	5450(1)	41(1)
C(34)	2968(2)	6622(2)	3295(1)	33(1)
C(35)	4251(3)	6628(2)	3258(2)	43(1)
C(36)	4937(3)	6861(2)	2602(2)	54(1)
C(37)	4338(3)	7104(2)	1975(2)	53(1)
C(38)	3070(3)	7101(2)	2002(1)	51(1)
C(39)	2375(3)	6864(2)	2660(1)	41(1)
C(41)	-329(2)	1092(2)	3434(1)	32(1)
C(42)	-873(2)	528(2)	4080(1)	32(1)
N(43)	-1872(2)	1000(1)	4463(1)	32(1)
C(44)	-2326(2)	1984(2)	4255(1)	28(1)
N(45)	-3279(2)	2351(1)	4686(1)	32(1)
C(46)	-3728(2)	3298(2)	4496(1)	34(1)
C(47)	-3276(2)	3920(2)	3891(1)	33(1)
C(48)	-2305(2)	3539(2)	3454(1)	31(1)
C(49)	-1804(2)	2547(2)	3626(1)	28(1)
C(50)	-770(2)	2075(2)	3205(1)	30(1)
N(51)	-276(2)	2605(2)	2592(1)	40(1)
O(52)	-486(2)	-352(1)	4308(1)	42(1)
C(53)	-2422(3)	422(2)	5121(1)	43(1)
C(54)	760(2)	581(2)	3040(1)	33(1)
C(55)	2002(2)	670(2)	3083(1)	36(1)
C(56)	3029(2)	164(2)	2743(1)	42(1)
C(57)	2837(3)	-433(2)	2343(1)	44(1)
C(58)	1619(3)	-512(2)	2280(1)	44(1)
C(59)	580(3)	-11(2)	2627(1)	40(1)
C(61)	9061(2)	4898(2)	8794(1)	30(1)
C(62)	9928(2)	4690(2)	8206(1)	32(1)
N(63)	10298(2)	3736(1)	8162(1)	37(1)
C(64)	9908(2)	2989(2)	8687(1)	37(1)
N(65)	10330(2)	2100(2)	8586(1)	49(1)
C(66)	9961(3)	1370(2)	9078(2)	58(1)
C(67)	9178(3)	1474(2)	9684(2)	56(1)

C(68)	8741(3)	2386(2)	9788(1)	44(1)
C(69)	9100(2)	3180(2)	9283(1)	34(1)
C(70)	8668(2)	4171(2)	9334(1)	30(1)
N(71)	7881(2)	4365(2)	9899(1)	35(1)
O(72)	10364(2)	5320(1)	7735(1)	39(1)
C(73)	11148(3)	3542(2)	7542(2)	52(1)
C(74)	8609(2)	5932(2)	8793(1)	31(1)
C(75)	9209(3)	6382(2)	9156(1)	41(1)
C(76)	8775(3)	7358(2)	9136(1)	47(1)
C(77)	7758(3)	7885(2)	8754(1)	44(1)
C(78)	7150(2)	7444(2)	8393(1)	43(1)
C(79)	7570(2)	6471(2)	8414(1)	37(1)
C(91)	6602(3)	8899(2)	3318(2)	51(1)
Cl(1)	5455(1)	8358(1)	3935(1)	56(1)
Cl(2)	8149(1)	8362(1)	3561(1)	77(1)
Cl(3)	6461(1)	8818(1)	2447(1)	59(1)

Table S10. Bond lengths [Å] and angles [°] for **3a**.

C(1)-C(10)	1.382(3)	C(41)-C(54)	1.488(3)
C(1)-C(2)	1.424(3)	C(42)-O(52)	1.241(3)
C(1)-C(14)	1.495(3)	C(42)-N(43)	1.389(3)
C(2)-O(12)	1.251(3)	N(43)-C(44)	1.384(3)
C(2)-N(3)	1.394(3)	N(43)-C(53)	1.467(3)
N(3)-C(4)	1.384(3)	C(44)-N(45)	1.350(3)
N(3)-C(13)	1.462(3)	C(44)-C(49)	1.407(3)
C(4)-N(5)	1.342(3)	N(45)-C(46)	1.332(3)
C(4)-C(9)	1.402(3)	C(46)-C(47)	1.388(3)
N(5)-C(6)	1.340(3)	C(47)-C(48)	1.376(3)
C(6)-C(7)	1.372(3)	C(48)-C(49)	1.400(3)
C(7)-C(8)	1.382(3)	C(49)-C(50)	1.455(3)
C(8)-C(9)	1.394(3)	C(50)-N(51)	1.353(3)
C(9)-C(10)	1.458(3)	C(54)-C(59)	1.390(3)
C(10)-N(11)	1.346(3)	C(54)-C(55)	1.395(3)
C(14)-C(19)	1.390(3)	C(55)-C(56)	1.387(3)
C(14)-C(15)	1.392(3)	C(56)-C(57)	1.384(4)
C(15)-C(16)	1.391(3)	C(57)-C(58)	1.374(4)
C(16)-C(17)	1.391(4)	C(58)-C(59)	1.399(4)
C(17)-C(18)	1.383(4)	C(61)-C(70)	1.380(3)
C(18)-C(19)	1.394(3)	C(61)-C(62)	1.435(3)
C(21)-C(30)	1.380(3)	C(61)-C(74)	1.488(3)
C(21)-C(22)	1.440(3)	C(62)-O(72)	1.241(3)
C(21)-C(34)	1.489(3)	C(62)-N(63)	1.390(3)
C(22)-O(32)	1.253(3)	N(63)-C(64)	1.384(3)
C(22)-N(23)	1.378(3)	N(63)-C(73)	1.469(3)
N(23)-C(24)	1.377(3)	C(64)-N(65)	1.341(3)
N(23)-C(33)	1.469(3)	C(64)-C(69)	1.409(3)
C(24)-N(25)	1.341(3)	N(65)-C(66)	1.327(4)
C(24)-C(29)	1.416(3)	C(66)-C(67)	1.380(4)
N(25)-C(26)	1.338(3)	C(67)-C(68)	1.377(4)
C(26)-C(27)	1.387(3)	C(68)-C(69)	1.398(3)
C(27)-C(28)	1.379(3)	C(69)-C(70)	1.452(3)
C(28)-C(29)	1.386(3)	C(70)-N(71)	1.351(3)
C(29)-C(30)	1.454(3)	C(74)-C(75)	1.387(3)
C(30)-N(31)	1.350(3)	C(74)-C(79)	1.394(3)
C(34)-C(35)	1.383(4)	C(75)-C(76)	1.395(4)
C(34)-C(39)	1.392(3)	C(76)-C(77)	1.375(4)

C(35)-C(36)	1.386(4)	C(77)-C(78)	1.381(4)
C(36)-C(37)	1.381(5)	C(78)-C(79)	1.390(3)
C(37)-C(38)	1.368(5)	C(91)-Cl(2)	1.752(3)
C(38)-C(39)	1.395(4)	C(91)-Cl(3)	1.760(3)
C(41)-C(50)	1.382(3)	C(91)-Cl(1)	1.774(3)
C(41)-C(42)	1.440(3)		

C(10)-C(1)-C(2)	121.57(19)	C(42)-C(41)-C(54)	117.32(18)
C(10)-C(1)-C(14)	121.39(19)	O(52)-C(42)-N(43)	119.1(2)
C(2)-C(1)-C(14)	117.04(19)	O(52)-C(42)-C(41)	122.9(2)
O(12)-C(2)-N(3)	118.1(2)	N(43)-C(42)-C(41)	117.98(19)
O(12)-C(2)-C(1)	123.5(2)	C(44)-N(43)-C(42)	122.36(18)
N(3)-C(2)-C(1)	118.4(2)	C(44)-N(43)-C(53)	119.84(19)
C(4)-N(3)-C(2)	121.85(19)	C(42)-N(43)-C(53)	117.77(18)
C(4)-N(3)-C(13)	120.12(19)	N(45)-C(44)-N(43)	116.08(19)
C(2)-N(3)-C(13)	118.0(2)	N(45)-C(44)-C(49)	123.52(19)
N(5)-C(4)-N(3)	116.27(19)	N(43)-C(44)-C(49)	120.4(2)
N(5)-C(4)-C(9)	123.6(2)	C(46)-N(45)-C(44)	116.99(19)
N(3)-C(4)-C(9)	120.14(19)	N(45)-C(46)-C(47)	124.2(2)
C(6)-N(5)-C(4)	117.04(19)	C(48)-C(47)-C(46)	118.4(2)
N(5)-C(6)-C(7)	124.0(2)	C(47)-C(48)-C(49)	119.8(2)
C(6)-C(7)-C(8)	118.6(2)	C(48)-C(49)-C(44)	117.1(2)
C(7)-C(8)-C(9)	119.7(2)	C(48)-C(49)-C(50)	124.1(2)
C(8)-C(9)-C(4)	117.15(19)	C(44)-C(49)-C(50)	118.75(19)
C(8)-C(9)-C(10)	123.5(2)	N(51)-C(50)-C(41)	121.4(2)
C(4)-C(9)-C(10)	119.3(2)	N(51)-C(50)-C(49)	119.28(19)
N(11)-C(10)-C(1)	122.4(2)	C(41)-C(50)-C(49)	119.27(19)
N(11)-C(10)-C(9)	119.1(2)	C(59)-C(54)-C(55)	117.8(2)
C(1)-C(10)-C(9)	118.51(19)	C(59)-C(54)-C(41)	121.4(2)
C(19)-C(14)-C(15)	118.8(2)	C(55)-C(54)-C(41)	120.7(2)
C(19)-C(14)-C(1)	121.0(2)	C(56)-C(55)-C(54)	121.2(2)
C(15)-C(14)-C(1)	120.1(2)	C(57)-C(56)-C(55)	120.2(2)
C(14)-C(15)-C(16)	120.7(2)	C(58)-C(57)-C(56)	119.3(2)
C(15)-C(16)-C(17)	120.0(2)	C(57)-C(58)-C(59)	120.6(2)
C(18)-C(17)-C(16)	119.7(2)	C(54)-C(59)-C(58)	120.7(2)
C(17)-C(18)-C(19)	120.2(2)	C(70)-C(61)-C(62)	121.5(2)
C(14)-C(19)-C(18)	120.6(2)	C(70)-C(61)-C(74)	121.7(2)
C(30)-C(21)-C(22)	121.5(2)	C(62)-C(61)-C(74)	116.81(18)
C(30)-C(21)-C(34)	121.21(19)	O(72)-C(62)-N(63)	118.5(2)
C(22)-C(21)-C(34)	117.27(19)	O(72)-C(62)-C(61)	123.2(2)

O(32)-C(22)-N(23)	119.22(19)	N(63)-C(62)-C(61)	118.32(19)
O(32)-C(22)-C(21)	122.5(2)	C(64)-N(63)-C(62)	121.8(2)
N(23)-C(22)-C(21)	118.24(19)	C(64)-N(63)-C(73)	120.7(2)
C(24)-N(23)-C(22)	122.14(18)	C(62)-N(63)-C(73)	117.5(2)
C(24)-N(23)-C(33)	119.51(19)	N(65)-C(64)-N(63)	116.3(2)
C(22)-N(23)-C(33)	118.35(19)	N(65)-C(64)-C(69)	123.4(2)
N(25)-C(24)-N(23)	116.37(19)	N(63)-C(64)-C(69)	120.4(2)
N(25)-C(24)-C(29)	122.9(2)	C(66)-N(65)-C(64)	117.5(2)
N(23)-C(24)-C(29)	120.7(2)	N(65)-C(66)-C(67)	124.0(3)
C(26)-N(25)-C(24)	117.5(2)	C(68)-C(67)-C(66)	118.5(2)
N(25)-C(26)-C(27)	123.5(2)	C(67)-C(68)-C(69)	119.7(2)
C(28)-C(27)-C(26)	118.8(2)	C(68)-C(69)-C(64)	116.9(2)
C(27)-C(28)-C(29)	119.5(2)	C(68)-C(69)-C(70)	123.9(2)
C(28)-C(29)-C(24)	117.7(2)	C(64)-C(69)-C(70)	119.2(2)
C(28)-C(29)-C(30)	123.8(2)	N(71)-C(70)-C(61)	121.5(2)
C(24)-C(29)-C(30)	118.5(2)	N(71)-C(70)-C(69)	119.8(2)
N(31)-C(30)-C(21)	121.6(2)	C(61)-C(70)-C(69)	118.7(2)
N(31)-C(30)-C(29)	119.5(2)	C(75)-C(74)-C(79)	118.8(2)
C(21)-C(30)-C(29)	118.83(19)	C(75)-C(74)-C(61)	121.5(2)
C(35)-C(34)-C(39)	118.7(2)	C(79)-C(74)-C(61)	119.7(2)
C(35)-C(34)-C(21)	120.9(2)	C(74)-C(75)-C(76)	120.2(2)
C(39)-C(34)-C(21)	120.4(2)	C(77)-C(76)-C(75)	120.6(2)
C(34)-C(35)-C(36)	120.7(3)	C(76)-C(77)-C(78)	119.8(2)
C(37)-C(36)-C(35)	120.2(3)	C(77)-C(78)-C(79)	120.0(2)
C(38)-C(37)-C(36)	119.8(3)	C(78)-C(79)-C(74)	120.6(2)
C(37)-C(38)-C(39)	120.3(3)	Cl(2)-C(91)-Cl(3)	109.47(17)
C(34)-C(39)-C(38)	120.3(3)	Cl(2)-C(91)-Cl(1)	111.30(15)
C(50)-C(41)-C(42)	121.2(2)	Cl(3)-C(91)-Cl(1)	110.82(16)
C(50)-C(41)-C(54)	121.4(2)		

Symmetry transformations used to generate equivalent atoms.

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	35(1)	25(1)	27(1)	-5(1)	-2(1)	-5(1)
C(2)	47(1)	29(1)	29(1)	-3(1)	1(1)	-8(1)
N(3)	45(1)	24(1)	35(1)	-5(1)	7(1)	-2(1)
C(4)	31(1)	25(1)	28(1)	-6(1)	2(1)	-5(1)
N(5)	42(1)	24(1)	36(1)	-4(1)	2(1)	-5(1)
C(6)	43(1)	25(1)	34(1)	-1(1)	0(1)	-10(1)
C(7)	40(1)	29(1)	31(1)	-5(1)	4(1)	-10(1)
C(8)	35(1)	28(1)	33(1)	-8(1)	2(1)	-7(1)
C(9)	32(1)	23(1)	29(1)	-5(1)	-4(1)	-6(1)
C(10)	30(1)	24(1)	29(1)	-5(1)	-4(1)	-5(1)
N(11)	51(1)	21(1)	31(1)	-3(1)	2(1)	-4(1)
O(12)	68(1)	34(1)	34(1)	-3(1)	17(1)	-3(1)
C(13)	82(2)	31(1)	55(2)	-8(1)	24(2)	7(1)
C(14)	39(1)	25(1)	27(1)	-5(1)	0(1)	-4(1)
C(15)	45(1)	33(1)	33(1)	-3(1)	-6(1)	-10(1)
C(16)	48(1)	35(1)	38(1)	-7(1)	3(1)	-16(1)
C(17)	58(2)	26(1)	31(1)	-1(1)	4(1)	-8(1)
C(18)	49(2)	32(1)	35(1)	1(1)	-6(1)	-4(1)
C(19)	40(1)	33(1)	35(1)	-4(1)	-5(1)	-8(1)
C(21)	33(1)	25(1)	31(1)	-9(1)	-2(1)	-2(1)
C(22)	37(1)	27(1)	33(1)	-9(1)	-6(1)	-3(1)
N(23)	36(1)	23(1)	31(1)	-6(1)	-1(1)	-3(1)
C(24)	30(1)	30(1)	30(1)	-9(1)	-5(1)	-5(1)
N(25)	37(1)	34(1)	33(1)	-5(1)	-3(1)	-7(1)
C(26)	35(1)	41(1)	33(1)	-9(1)	1(1)	-8(1)
C(27)	32(1)	39(1)	41(1)	-14(1)	-2(1)	-3(1)
C(28)	30(1)	30(1)	38(1)	-10(1)	-3(1)	-2(1)
C(29)	28(1)	28(1)	33(1)	-8(1)	-4(1)	-4(1)
C(30)	32(1)	26(1)	32(1)	-7(1)	-4(1)	-4(1)
N(31)	45(1)	24(1)	38(1)	-5(1)	6(1)	1(1)
O(32)	49(1)	25(1)	40(1)	-10(1)	2(1)	2(1)
C(33)	55(2)	24(1)	39(1)	-3(1)	-5(1)	-2(1)
C(34)	40(1)	20(1)	37(1)	-10(1)	0(1)	-2(1)
C(35)	43(1)	38(1)	51(2)	-17(1)	1(1)	-11(1)
C(36)	50(2)	45(2)	72(2)	-24(1)	18(1)	-20(1)

C(37)	76(2)	31(1)	49(2)	-12(1)	23(1)	-14(1)
C(38)	74(2)	37(1)	35(1)	-7(1)	2(1)	-6(1)
C(39)	47(1)	39(1)	35(1)	-8(1)	0(1)	-4(1)
C(41)	36(1)	26(1)	32(1)	-5(1)	1(1)	-5(1)
C(42)	33(1)	25(1)	34(1)	-7(1)	4(1)	-3(1)
N(43)	35(1)	24(1)	32(1)	-1(1)	2(1)	-6(1)
C(44)	28(1)	26(1)	30(1)	-6(1)	-2(1)	-5(1)
N(45)	30(1)	30(1)	35(1)	-7(1)	1(1)	-5(1)
C(46)	30(1)	32(1)	39(1)	-11(1)	-2(1)	-2(1)
C(47)	32(1)	24(1)	40(1)	-9(1)	-5(1)	0(1)
C(48)	32(1)	27(1)	31(1)	-3(1)	-3(1)	-7(1)
C(49)	29(1)	25(1)	30(1)	-5(1)	-2(1)	-7(1)
C(50)	34(1)	26(1)	29(1)	-6(1)	1(1)	-7(1)
N(51)	50(1)	25(1)	36(1)	-1(1)	9(1)	-3(1)
O(52)	53(1)	23(1)	43(1)	-2(1)	7(1)	-3(1)
C(53)	46(1)	33(1)	40(1)	4(1)	7(1)	-8(1)
C(54)	42(1)	23(1)	29(1)	-2(1)	2(1)	-2(1)
C(55)	41(1)	30(1)	32(1)	-7(1)	2(1)	-1(1)
C(56)	40(1)	37(1)	40(1)	-3(1)	0(1)	0(1)
C(57)	49(2)	34(1)	37(1)	-6(1)	6(1)	6(1)
C(58)	59(2)	33(1)	38(1)	-12(1)	0(1)	-1(1)
C(59)	44(1)	32(1)	40(1)	-9(1)	1(1)	-4(1)
C(61)	29(1)	29(1)	28(1)	-3(1)	-1(1)	-5(1)
C(62)	32(1)	30(1)	30(1)	-3(1)	-2(1)	-3(1)
N(63)	37(1)	33(1)	32(1)	-6(1)	8(1)	-1(1)
C(64)	38(1)	31(1)	35(1)	-3(1)	0(1)	0(1)
N(65)	63(2)	31(1)	45(1)	-7(1)	4(1)	2(1)
C(66)	81(2)	28(1)	53(2)	-8(1)	9(2)	5(1)
C(67)	82(2)	29(1)	47(2)	3(1)	4(1)	-8(1)
C(68)	60(2)	33(1)	34(1)	0(1)	0(1)	-8(1)
C(69)	39(1)	29(1)	29(1)	-3(1)	-2(1)	-2(1)
C(70)	29(1)	30(1)	27(1)	-4(1)	-2(1)	-2(1)
N(71)	42(1)	28(1)	29(1)	-3(1)	6(1)	-4(1)
O(72)	44(1)	36(1)	33(1)	-1(1)	6(1)	-11(1)
C(73)	55(2)	42(1)	48(2)	-11(1)	17(1)	0(1)
C(74)	34(1)	29(1)	25(1)	-2(1)	1(1)	-7(1)
C(75)	48(1)	38(1)	36(1)	-5(1)	-11(1)	-9(1)
C(76)	69(2)	38(1)	39(1)	-10(1)	-5(1)	-19(1)
C(77)	60(2)	27(1)	39(1)	-4(1)	7(1)	-7(1)
C(78)	42(1)	33(1)	44(1)	0(1)	-4(1)	-2(1)

C(79)	37(1)	33(1)	38(1)	-4(1)	-5(1)	-6(1)
C(91)	63(2)	28(1)	61(2)	-8(1)	-7(1)	-9(1)
Cl(1)	64(1)	39(1)	60(1)	-4(1)	1(1)	-10(1)
Cl(2)	63(1)	76(1)	94(1)	-8(1)	-27(1)	-20(1)
Cl(3)	65(1)	52(1)	58(1)	-15(1)	-2(1)	-9(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **3a**.

	x	y	z	U(eq)
H(6)	4948	436	4182	42
H(7)	3668	1733	4538	41
H(8)	3659	3293	3809	38
H(13A)	7631	816	2514	93
H(13B)	8028	1441	1738	93
H(13C)	6833	927	1851	93
H(15)	7545	4906	1708	45
H(16)	7772	6345	868	48
H(17)	6257	7086	29	49
H(18)	4492	6406	58	49
H(19)	4248	4981	912	44
H(11A)	4440(30)	5130(20)	2409(16)	44
H(11B)	4010(30)	4600(20)	3112(17)	44
H(26)	-1118	5773	6638	44
H(27)	-1531	7422	6126	45
H(28)	-413	8040	5048	39
H(33A)	2657	3699	5155	62
H(33B)	1294	3845	5590	62
H(33C)	2498	4044	5880	62
H(35)	4667	6471	3687	52
H(36)	5821	6852	2584	65
H(37)	4806	7274	1527	64
H(38)	2660	7260	1571	61
H(39)	1493	6867	2675	50
H(31A)	1630(30)	8160(20)	3543(18)	50
H(31B)	700(30)	8450(20)	4109(16)	50
H(46)	-4401	3565	4793	41
H(47)	-3627	4591	3780	39
H(48)	-1975	3949	3037	37
H(53A)	-1974	-252	5199	65
H(53B)	-3325	462	5076	65
H(53C)	-2335	671	5527	65
H(55)	2146	1086	3349	43
H(56)	3868	227	2786	50
H(57)	3541	-785	2114	52
H(58)	1481	-910	1997	53

H(59)	-256	-76	2581	48
H(51A)	-400(30)	3210(20)	2502(16)	48
H(51B)	420(30)	2280(20)	2341(16)	48
H(66)	10253	738	9009	70
H(67)	8946	927	10023	68
H(68)	8198	2477	10199	53
H(73A)	12020	3562	7614	78
H(73B)	10872	4032	7109	78
H(73C)	11121	2902	7488	78
H(75)	9917	6025	9419	49
H(76)	9186	7660	9390	57
H(77)	7475	8551	8737	53
H(78)	6443	7805	8132	51
H(79)	7146	6171	8166	44
H(71A)	7680(30)	3940(20)	10274(16)	44
H(71B)	7590(30)	4960(20)	9938(15)	44
H(91)	6447	9597	3316	62

Table S13. Torsion angles [°] for **3a**.

C(10)-C(1)-C(2)-O(12)	177.6(2)	C(54)-C(41)-C(42)-O(52)	-1.2(3)
C(14)-C(1)-C(2)-O(12)	-2.7(4)	C(50)-C(41)-C(42)-N(43)	1.0(3)
C(10)-C(1)-C(2)-N(3)	-3.6(3)	C(54)-C(41)-C(42)-N(43)	178.6(2)
C(14)-C(1)-C(2)-N(3)	176.0(2)	O(52)-C(42)-N(43)-C(44)	177.9(2)
O(12)-C(2)-N(3)-C(4)	-176.0(2)	C(41)-C(42)-N(43)-C(44)	-1.9(3)
C(1)-C(2)-N(3)-C(4)	5.2(3)	O(52)-C(42)-N(43)-C(53)	-0.2(3)
O(12)-C(2)-N(3)-C(13)	4.2(4)	C(41)-C(42)-N(43)-C(53)	-180.0(2)
C(1)-C(2)-N(3)-C(13)	-174.6(3)	C(42)-N(43)-C(44)-N(45)	-178.4(2)
C(2)-N(3)-C(4)-N(5)	176.3(2)	C(53)-N(43)-C(44)-N(45)	-0.4(3)
C(13)-N(3)-C(4)-N(5)	-4.0(4)	C(42)-N(43)-C(44)-C(49)	1.8(3)
C(2)-N(3)-C(4)-C(9)	-3.3(3)	C(53)-N(43)-C(44)-C(49)	179.9(2)
C(13)-N(3)-C(4)-C(9)	176.5(3)	N(43)-C(44)-N(45)-C(46)	179.83(19)
N(3)-C(4)-N(5)-C(6)	-179.5(2)	C(49)-C(44)-N(45)-C(46)	-0.4(3)
C(9)-C(4)-N(5)-C(6)	0.1(3)	C(44)-N(45)-C(46)-C(47)	-0.2(3)
C(4)-N(5)-C(6)-C(7)	-0.2(4)	N(45)-C(46)-C(47)-C(48)	0.3(3)
N(5)-C(6)-C(7)-C(8)	0.1(4)	C(46)-C(47)-C(48)-C(49)	0.2(3)
C(6)-C(7)-C(8)-C(9)	0.0(3)	C(47)-C(48)-C(49)-C(44)	-0.8(3)
C(7)-C(8)-C(9)-C(4)	-0.1(3)	C(47)-C(48)-C(49)-C(50)	-179.3(2)
C(7)-C(8)-C(9)-C(10)	179.8(2)	N(45)-C(44)-C(49)-C(48)	0.9(3)
N(5)-C(4)-C(9)-C(8)	0.1(3)	N(43)-C(44)-C(49)-C(48)	-179.37(19)
N(3)-C(4)-C(9)-C(8)	179.6(2)	N(45)-C(44)-C(49)-C(50)	179.5(2)
N(5)-C(4)-C(9)-C(10)	-179.8(2)	N(43)-C(44)-C(49)-C(50)	-0.8(3)
N(3)-C(4)-C(9)-C(10)	-0.3(3)	C(42)-C(41)-C(50)-N(51)	-178.9(2)
C(2)-C(1)-C(10)-N(11)	-177.7(2)	C(54)-C(41)-C(50)-N(51)	3.6(4)
C(14)-C(1)-C(10)-N(11)	2.7(3)	C(42)-C(41)-C(50)-C(49)	-0.1(3)
C(2)-C(1)-C(10)-C(9)	0.2(3)	C(54)-C(41)-C(50)-C(49)	-177.5(2)
C(14)-C(1)-C(10)-C(9)	-179.41(19)	C(48)-C(49)-C(50)-N(51)	-2.7(3)
C(8)-C(9)-C(10)-N(11)	-0.2(3)	C(44)-C(49)-C(50)-N(51)	178.8(2)
C(4)-C(9)-C(10)-N(11)	179.7(2)	C(48)-C(49)-C(50)-C(41)	178.4(2)
C(8)-C(9)-C(10)-C(1)	-178.1(2)	C(44)-C(49)-C(50)-C(41)	-0.1(3)
C(4)-C(9)-C(10)-C(1)	1.8(3)	C(50)-C(41)-C(54)-C(59)	-106.5(3)
C(10)-C(1)-C(14)-C(19)	-81.8(3)	C(42)-C(41)-C(54)-C(59)	76.0(3)
C(2)-C(1)-C(14)-C(19)	98.6(3)	C(50)-C(41)-C(54)-C(55)	74.5(3)
C(10)-C(1)-C(14)-C(15)	99.6(3)	C(42)-C(41)-C(54)-C(55)	-103.0(3)
C(2)-C(1)-C(14)-C(15)	-80.0(3)	C(59)-C(54)-C(55)-C(56)	-1.9(3)
C(19)-C(14)-C(15)-C(16)	-0.9(4)	C(41)-C(54)-C(55)-C(56)	177.1(2)
C(1)-C(14)-C(15)-C(16)	177.7(2)	C(54)-C(55)-C(56)-C(57)	1.1(4)
C(14)-C(15)-C(16)-C(17)	-0.3(4)	C(55)-C(56)-C(57)-C(58)	0.6(4)

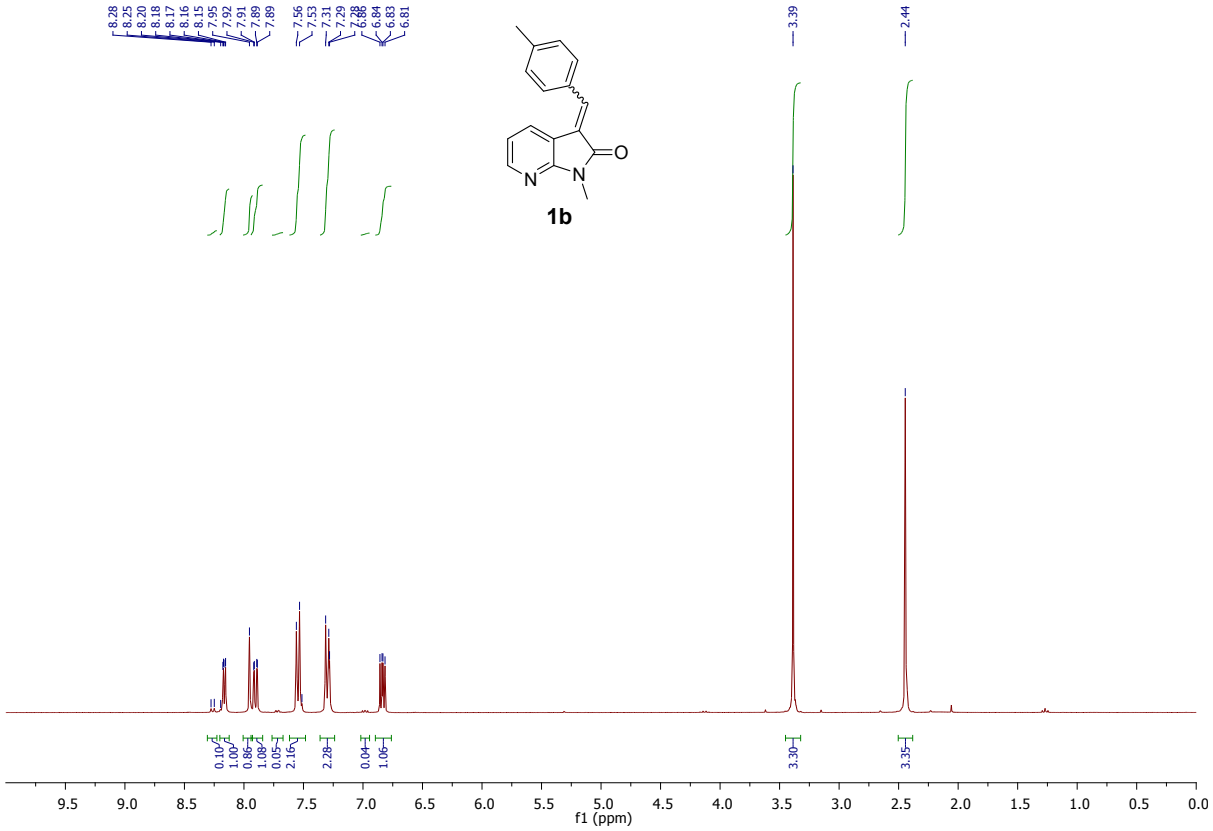
C(15)-C(16)-C(17)-C(18)	1.0(4)	C(56)-C(57)-C(58)-C(59)	-1.3(4)
C(16)-C(17)-C(18)-C(19)	-0.4(4)	C(55)-C(54)-C(59)-C(58)	1.2(3)
C(15)-C(14)-C(19)-C(18)	1.5(4)	C(41)-C(54)-C(59)-C(58)	-177.8(2)
C(1)-C(14)-C(19)-C(18)	-177.1(2)	C(57)-C(58)-C(59)-C(54)	0.4(4)
C(17)-C(18)-C(19)-C(14)	-0.9(4)	C(70)-C(61)-C(62)-O(72)	-175.3(2)
C(30)-C(21)-C(22)-O(32)	-177.2(2)	C(74)-C(61)-C(62)-O(72)	4.7(3)
C(34)-C(21)-C(22)-O(32)	1.2(3)	C(70)-C(61)-C(62)-N(63)	4.6(3)
C(30)-C(21)-C(22)-N(23)	1.9(3)	C(74)-C(61)-C(62)-N(63)	-175.44(19)
C(34)-C(21)-C(22)-N(23)	-179.63(19)	O(72)-C(62)-N(63)-C(64)	176.4(2)
O(32)-C(22)-N(23)-C(24)	-178.9(2)	C(61)-C(62)-N(63)-C(64)	-3.5(3)
C(21)-C(22)-N(23)-C(24)	2.0(3)	O(72)-C(62)-N(63)-C(73)	-2.3(3)
O(32)-C(22)-N(23)-C(33)	1.2(3)	C(61)-C(62)-N(63)-C(73)	177.8(2)
C(21)-C(22)-N(23)-C(33)	-178.0(2)	C(62)-N(63)-C(64)-N(65)	-179.9(2)
C(22)-N(23)-C(24)-N(25)	175.56(19)	C(73)-N(63)-C(64)-N(65)	-1.3(4)
C(33)-N(23)-C(24)-N(25)	-4.5(3)	C(62)-N(63)-C(64)-C(69)	0.9(4)
C(22)-N(23)-C(24)-C(29)	-4.3(3)	C(73)-N(63)-C(64)-C(69)	179.5(2)
C(33)-N(23)-C(24)-C(29)	175.6(2)	N(63)-C(64)-N(65)-C(66)	-179.4(3)
N(23)-C(24)-N(25)-C(26)	178.62(19)	C(69)-C(64)-N(65)-C(66)	-0.2(4)
C(29)-C(24)-N(25)-C(26)	-1.5(3)	C(64)-N(65)-C(66)-C(67)	-0.2(5)
C(24)-N(25)-C(26)-C(27)	-0.6(3)	N(65)-C(66)-C(67)-C(68)	0.5(5)
N(25)-C(26)-C(27)-C(28)	1.4(4)	C(66)-C(67)-C(68)-C(69)	-0.3(5)
C(26)-C(27)-C(28)-C(29)	0.0(3)	C(67)-C(68)-C(69)-C(64)	-0.1(4)
C(27)-C(28)-C(29)-C(24)	-1.9(3)	C(67)-C(68)-C(69)-C(70)	178.5(3)
C(27)-C(28)-C(29)-C(30)	178.0(2)	N(65)-C(64)-C(69)-C(68)	0.4(4)
N(25)-C(24)-C(29)-C(28)	2.8(3)	N(63)-C(64)-C(69)-C(68)	179.5(2)
N(23)-C(24)-C(29)-C(28)	-177.4(2)	N(65)-C(64)-C(69)-C(70)	-178.3(2)
N(25)-C(24)-C(29)-C(30)	-177.1(2)	N(63)-C(64)-C(69)-C(70)	0.9(4)
N(23)-C(24)-C(29)-C(30)	2.7(3)	C(62)-C(61)-C(70)-N(71)	178.1(2)
C(22)-C(21)-C(30)-N(31)	177.1(2)	C(74)-C(61)-C(70)-N(71)	-1.9(3)
C(34)-C(21)-C(30)-N(31)	-1.3(3)	C(62)-C(61)-C(70)-C(69)	-2.9(3)
C(22)-C(21)-C(30)-C(29)	-3.3(3)	C(74)-C(61)-C(70)-C(69)	177.1(2)
C(34)-C(21)-C(30)-C(29)	178.3(2)	C(68)-C(69)-C(70)-N(71)	0.7(4)
C(28)-C(29)-C(30)-N(31)	0.7(3)	C(64)-C(69)-C(70)-N(71)	179.2(2)
C(24)-C(29)-C(30)-N(31)	-179.4(2)	C(68)-C(69)-C(70)-C(61)	-178.4(2)
C(28)-C(29)-C(30)-C(21)	-178.9(2)	C(64)-C(69)-C(70)-C(61)	0.2(3)
C(24)-C(29)-C(30)-C(21)	1.1(3)	C(70)-C(61)-C(74)-C(75)	85.8(3)
C(30)-C(21)-C(34)-C(35)	107.1(3)	C(62)-C(61)-C(74)-C(75)	-94.2(3)
C(22)-C(21)-C(34)-C(35)	-71.3(3)	C(70)-C(61)-C(74)-C(79)	-95.1(3)
C(30)-C(21)-C(34)-C(39)	-73.2(3)	C(62)-C(61)-C(74)-C(79)	84.9(3)
C(22)-C(21)-C(34)-C(39)	108.3(2)	C(79)-C(74)-C(75)-C(76)	-0.2(4)

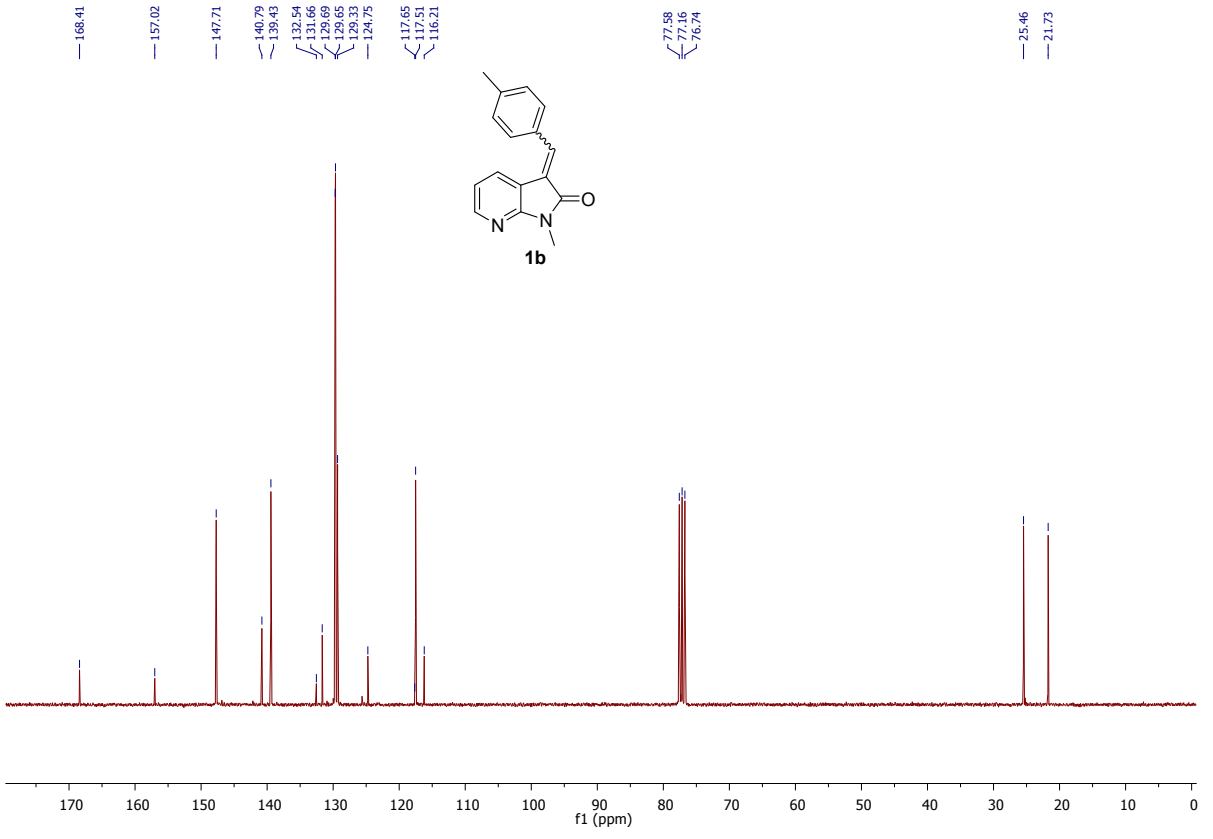
C(39)-C(34)-C(35)-C(36)	-0.6(4)	C(61)-C(74)-C(75)-C(76)	179.0(2)
C(21)-C(34)-C(35)-C(36)	179.0(2)	C(74)-C(75)-C(76)-C(77)	-0.5(4)
C(34)-C(35)-C(36)-C(37)	1.0(4)	C(75)-C(76)-C(77)-C(78)	0.9(4)
C(35)-C(36)-C(37)-C(38)	-1.1(4)	C(76)-C(77)-C(78)-C(79)	-0.5(4)
C(36)-C(37)-C(38)-C(39)	0.8(4)	C(77)-C(78)-C(79)-C(74)	-0.2(4)
C(35)-C(34)-C(39)-C(38)	0.4(4)	C(75)-C(74)-C(79)-C(78)	0.6(4)
C(21)-C(34)-C(39)-C(38)	-179.3(2)	C(61)-C(74)-C(79)-C(78)	-178.6(2)
C(37)-C(38)-C(39)-C(34)	-0.5(4)		

Symmetry transformations used to generate equivalent atoms:

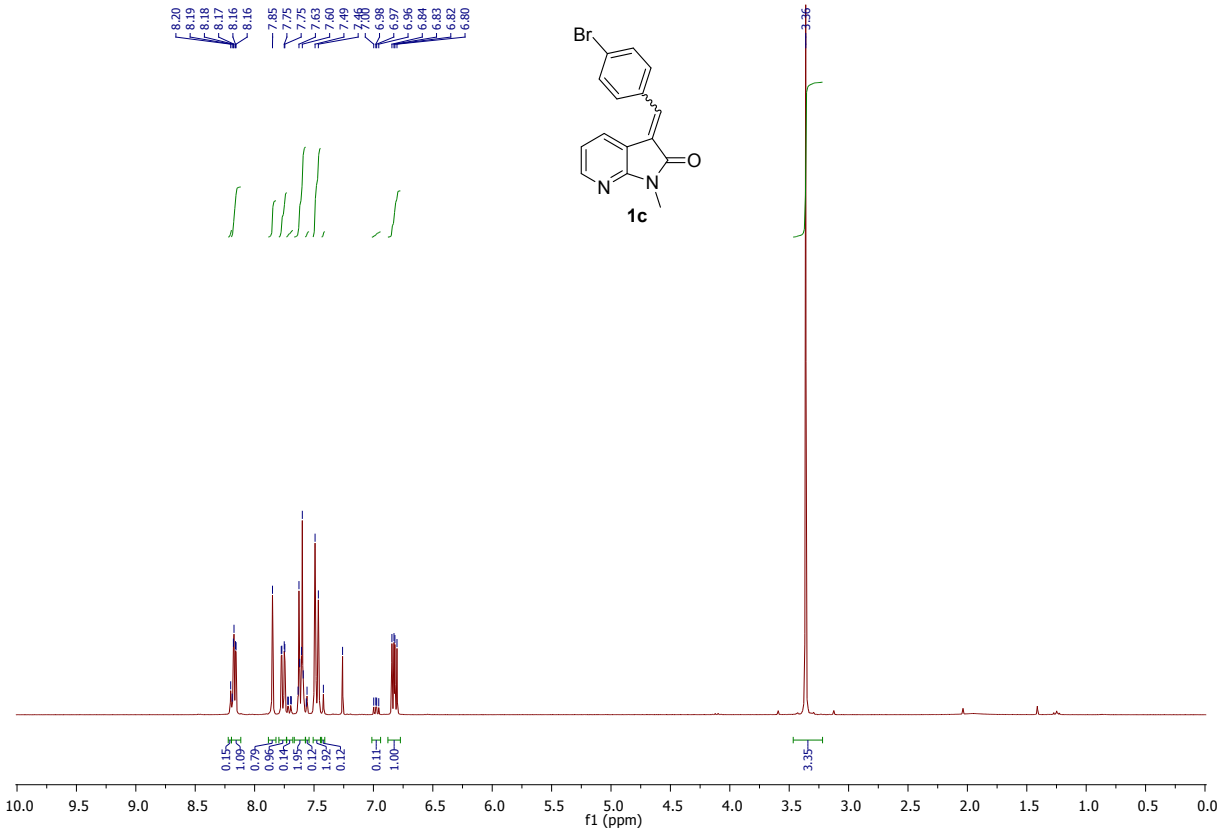
VI. Copies of ^{1}H and ^{13}C NMR Spectra

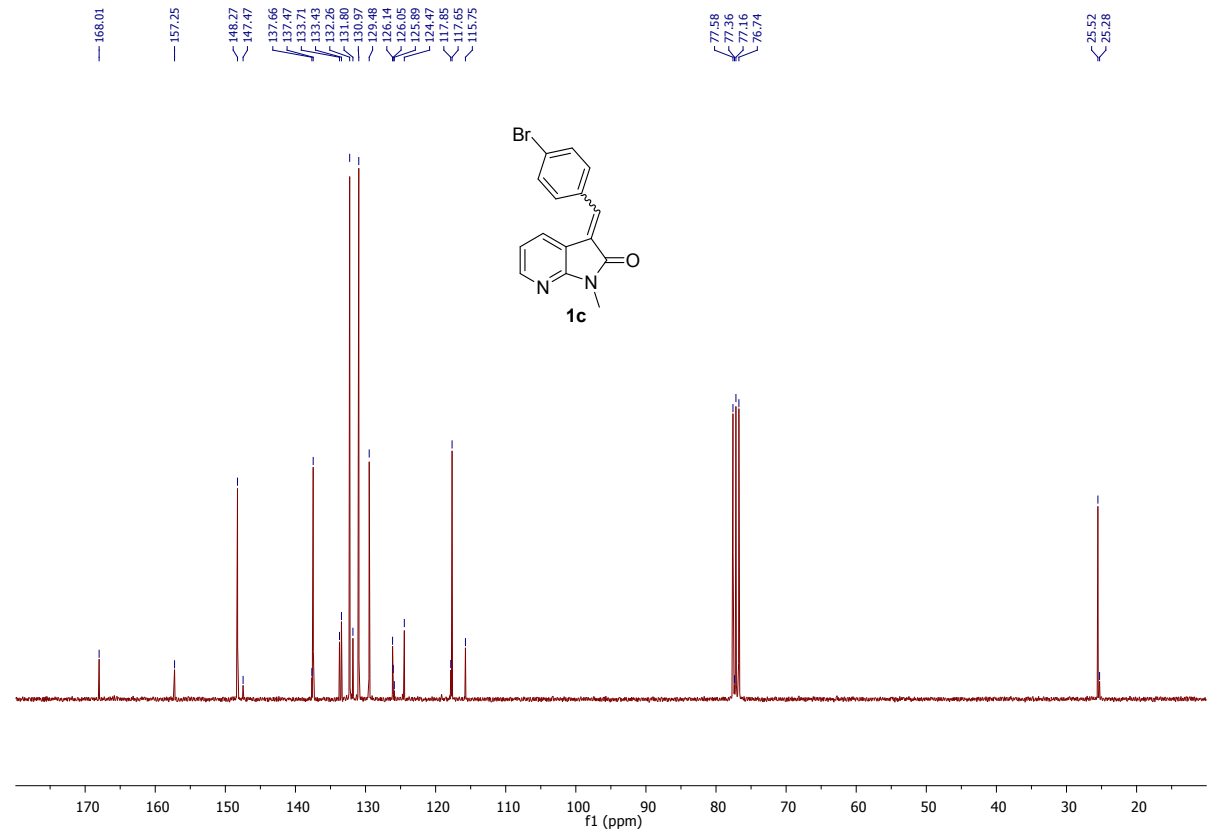
1-Methyl-3-(4-methylbenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1b)



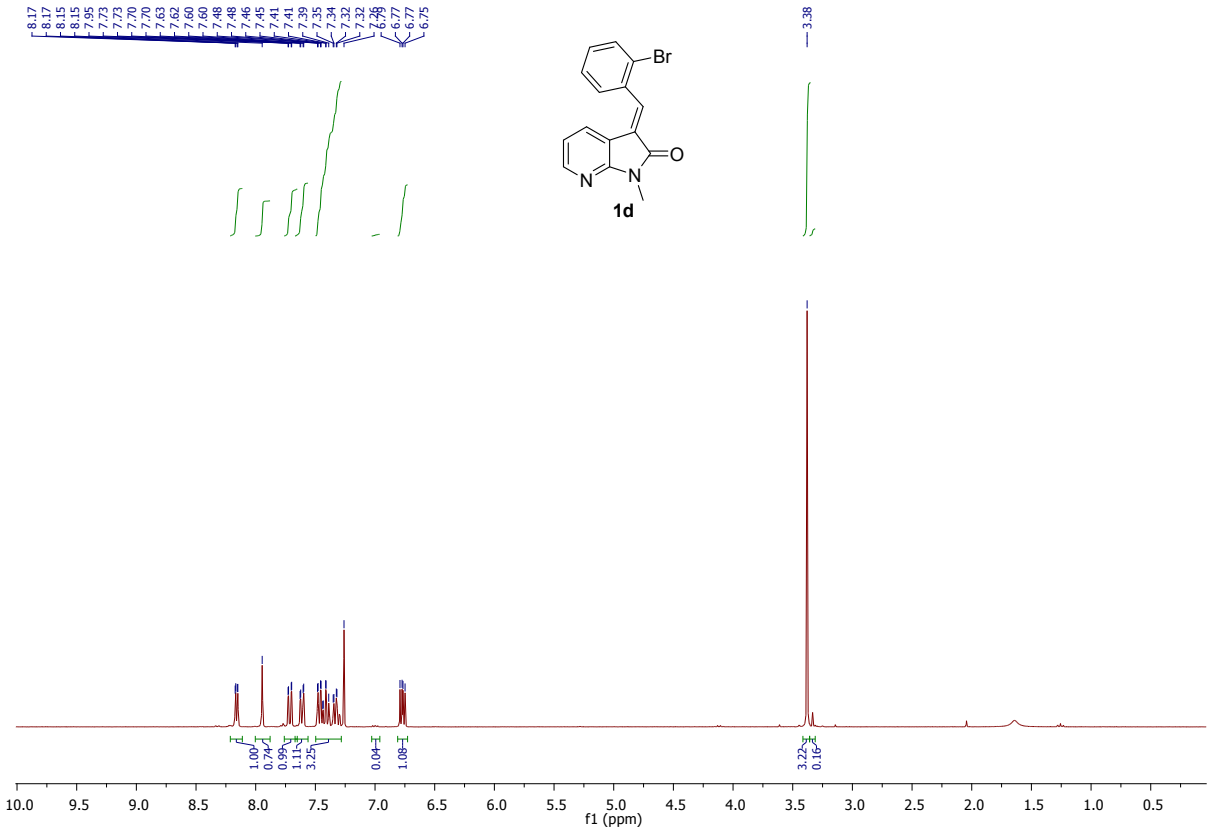


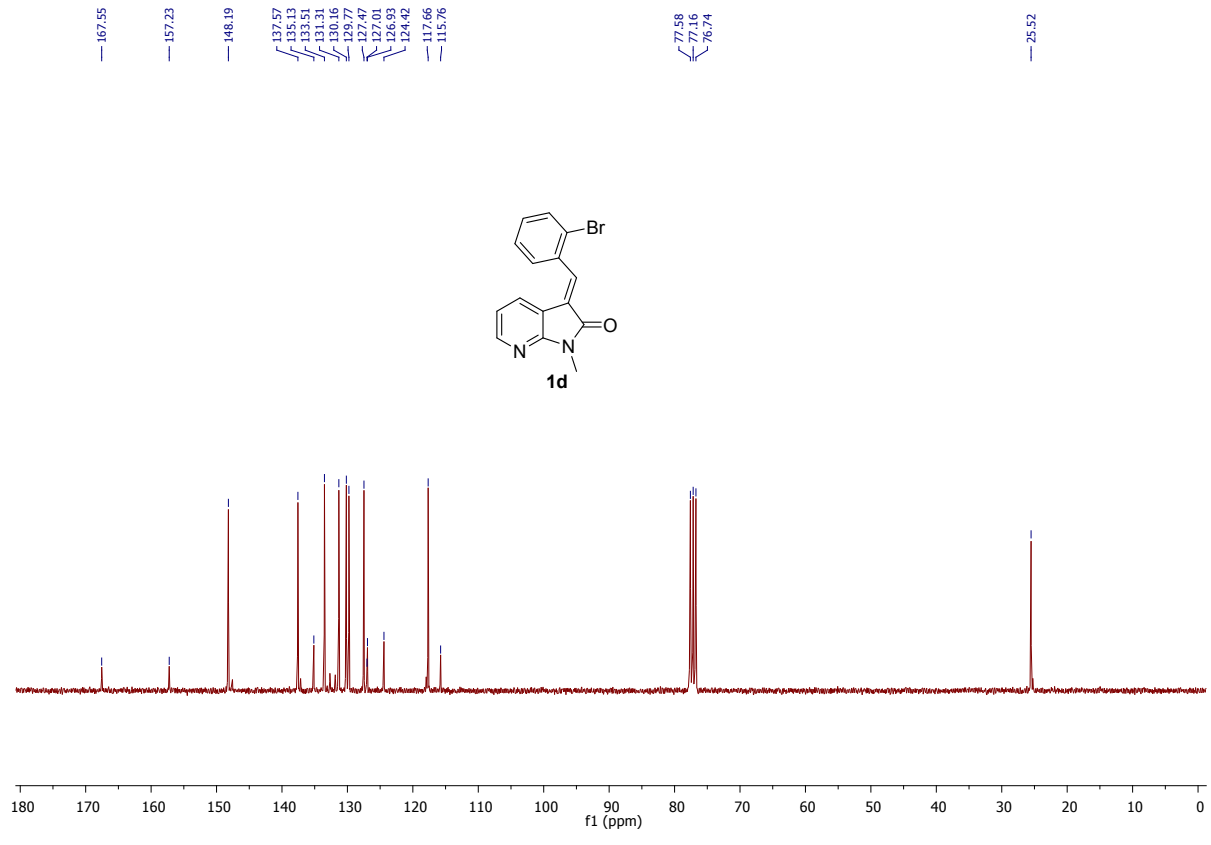
3-(4-Bromobenzylidene)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1c)



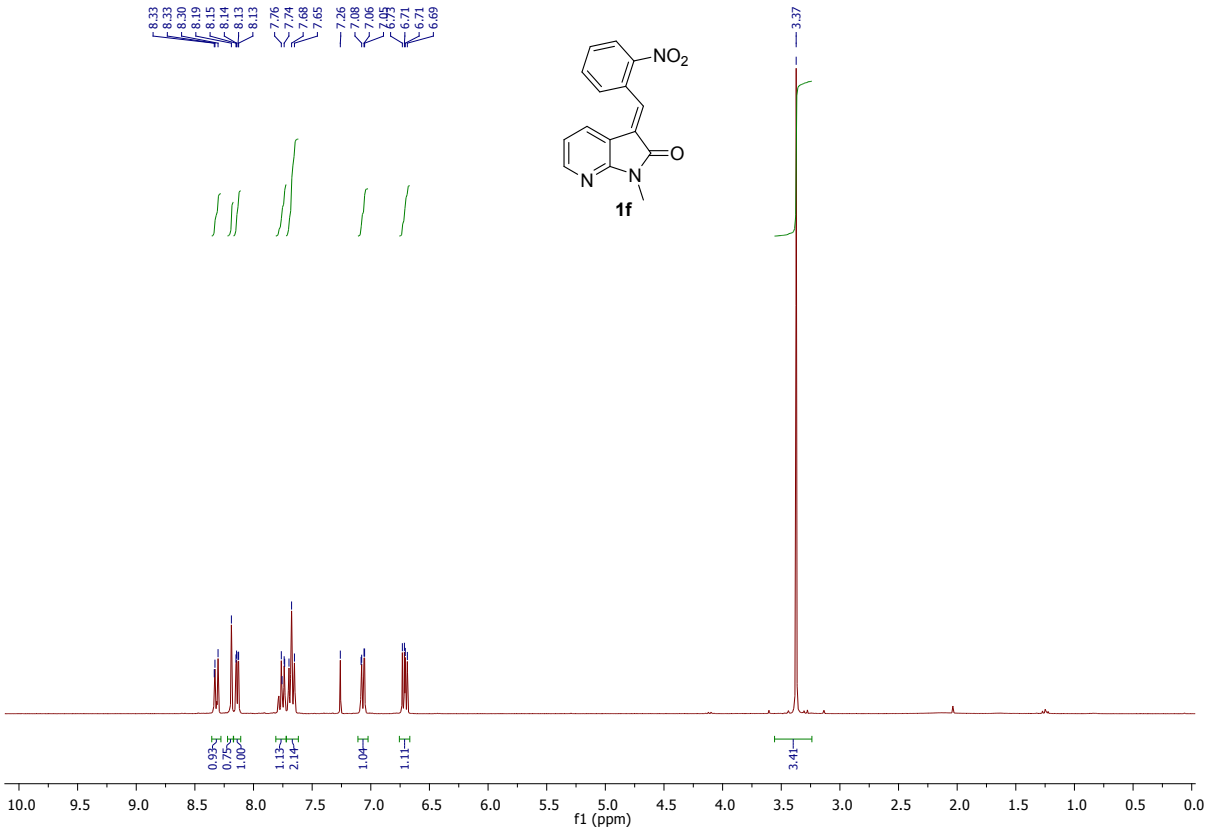


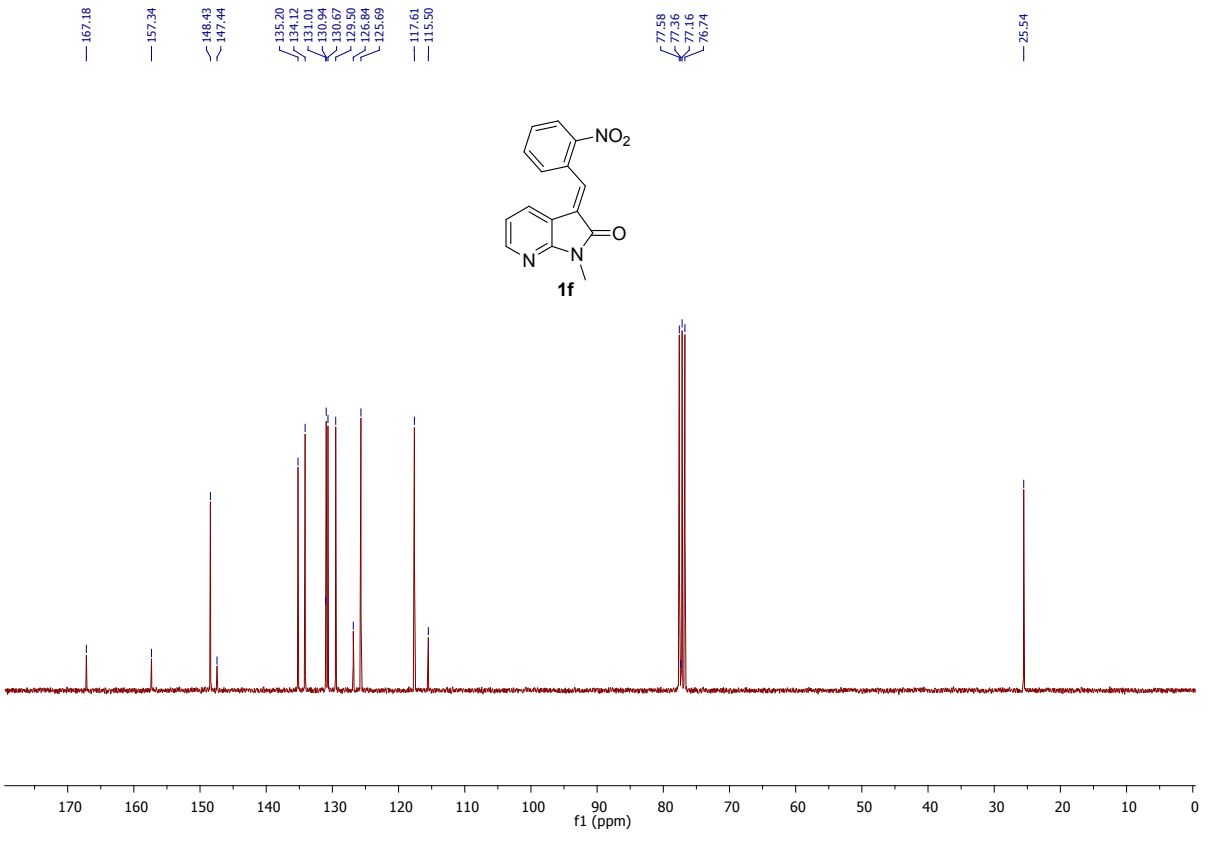
3-(2-Bromobenzylidene)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1d)



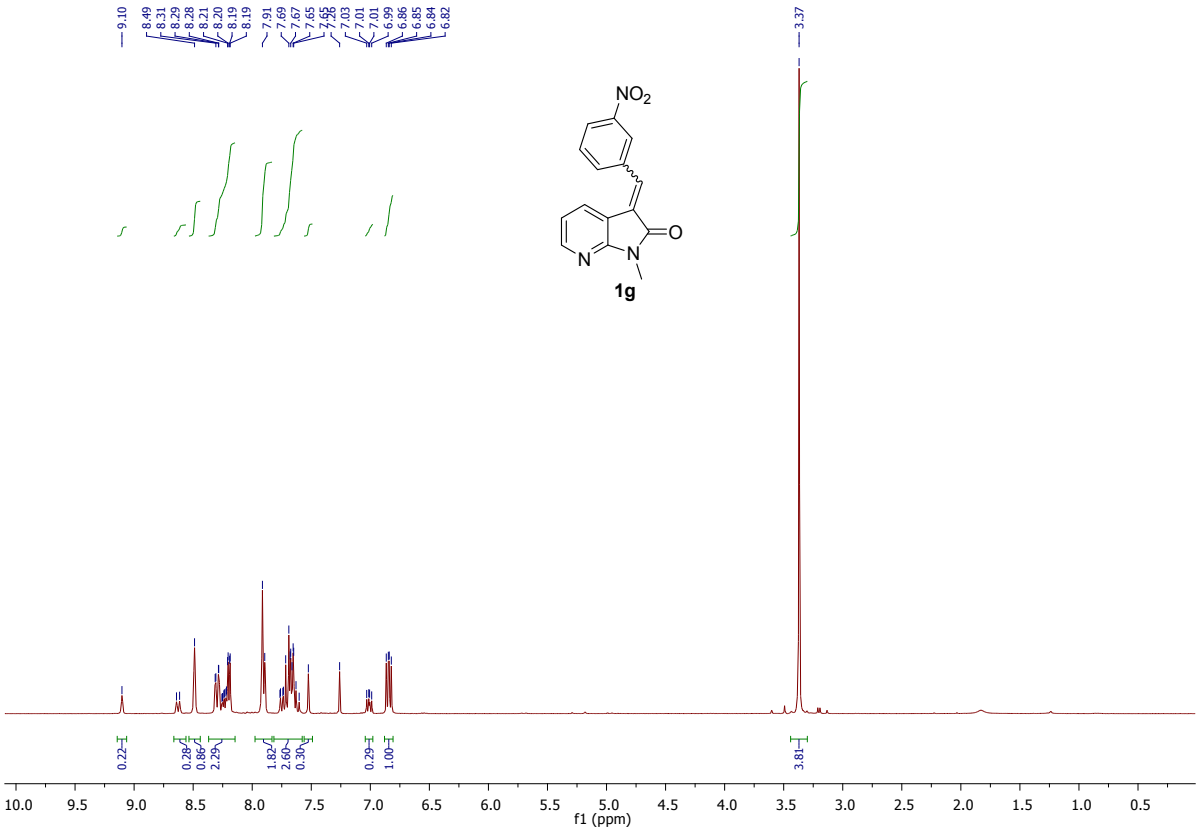


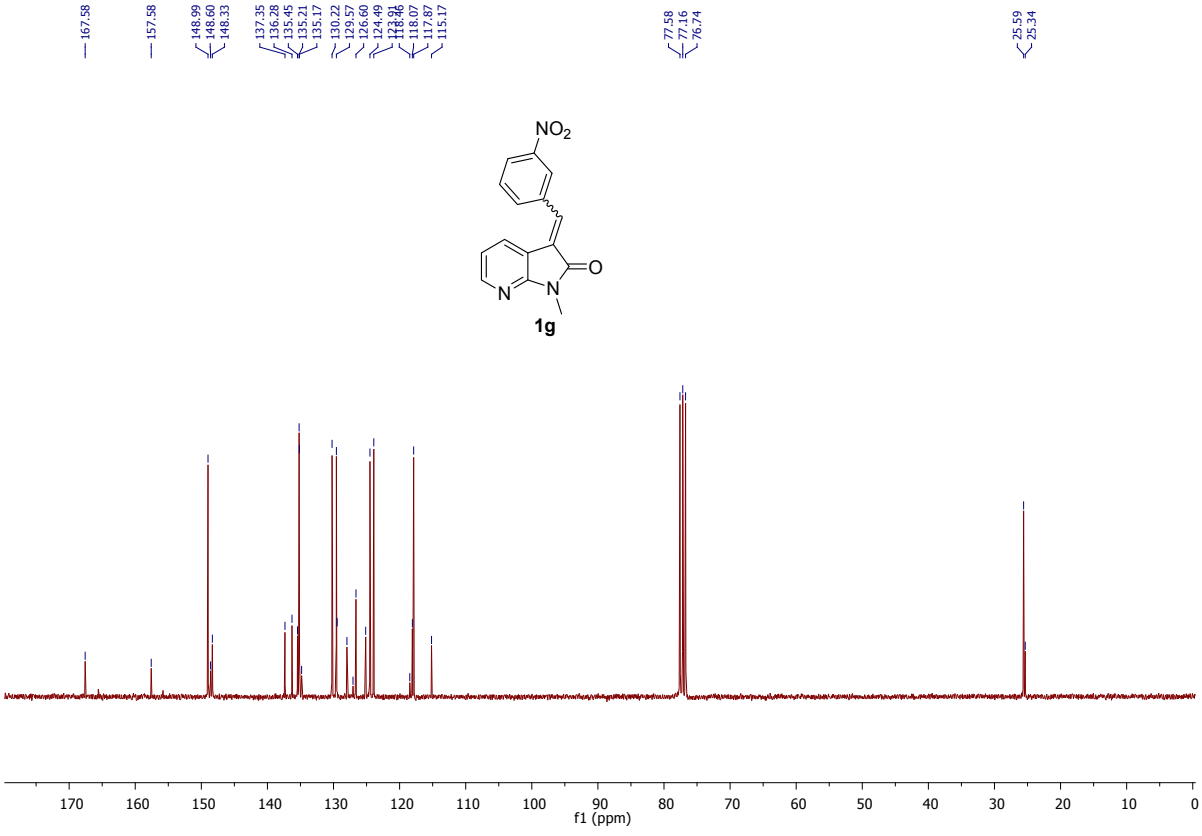
1-Methyl-3-(2-nitrobenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1f)



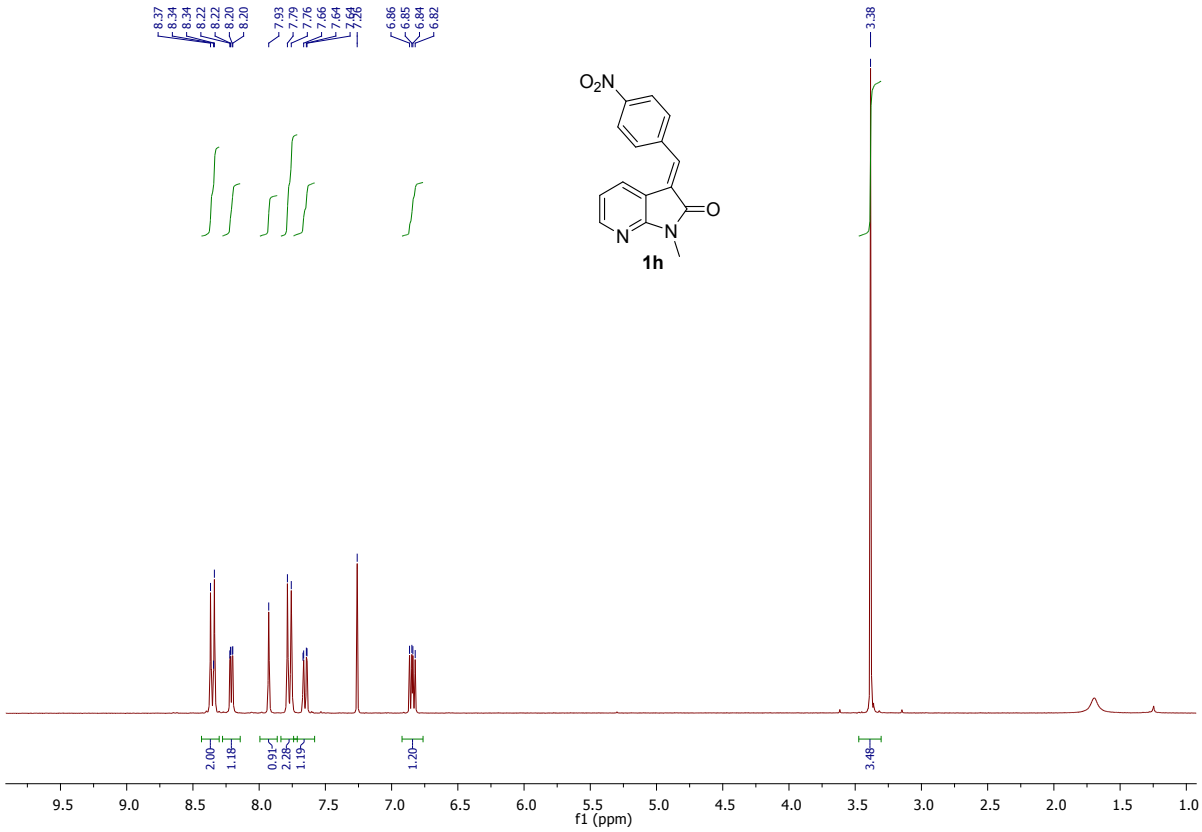


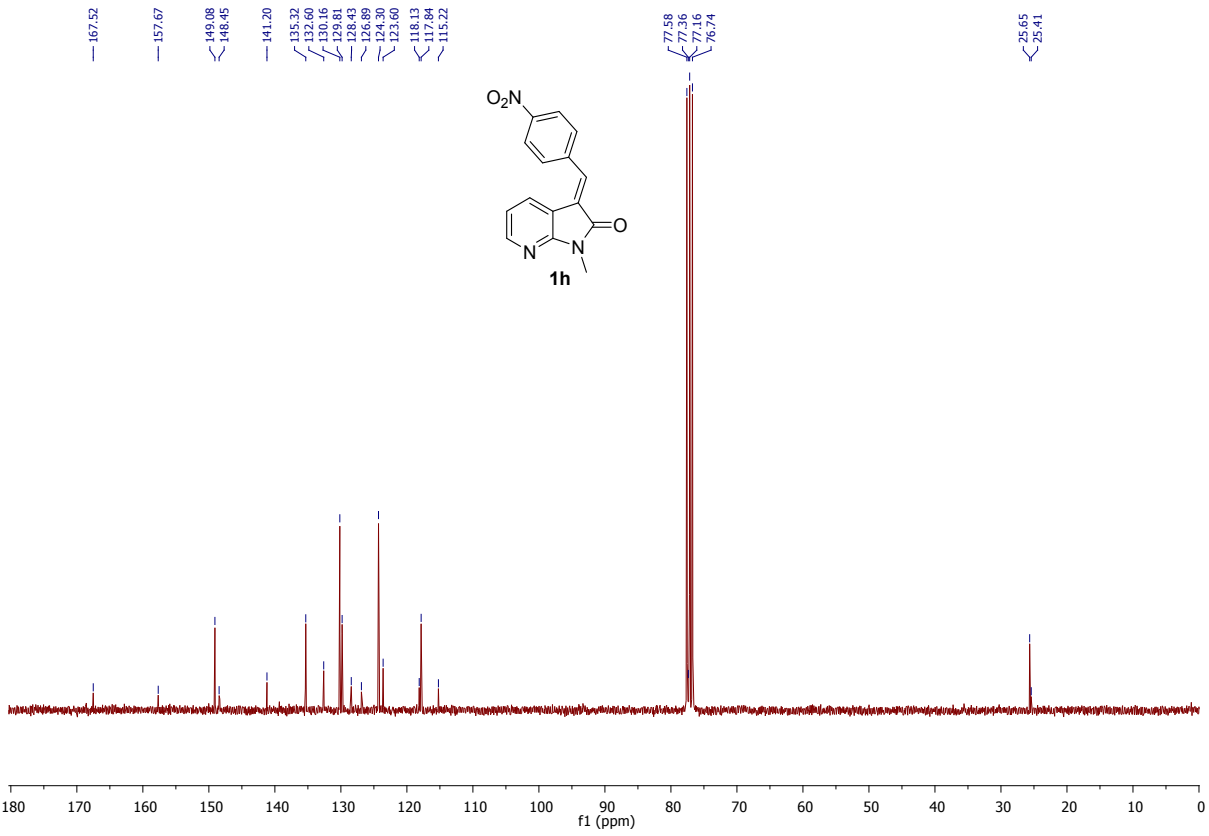
1-Methyl-3-(3-nitrobenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1g)



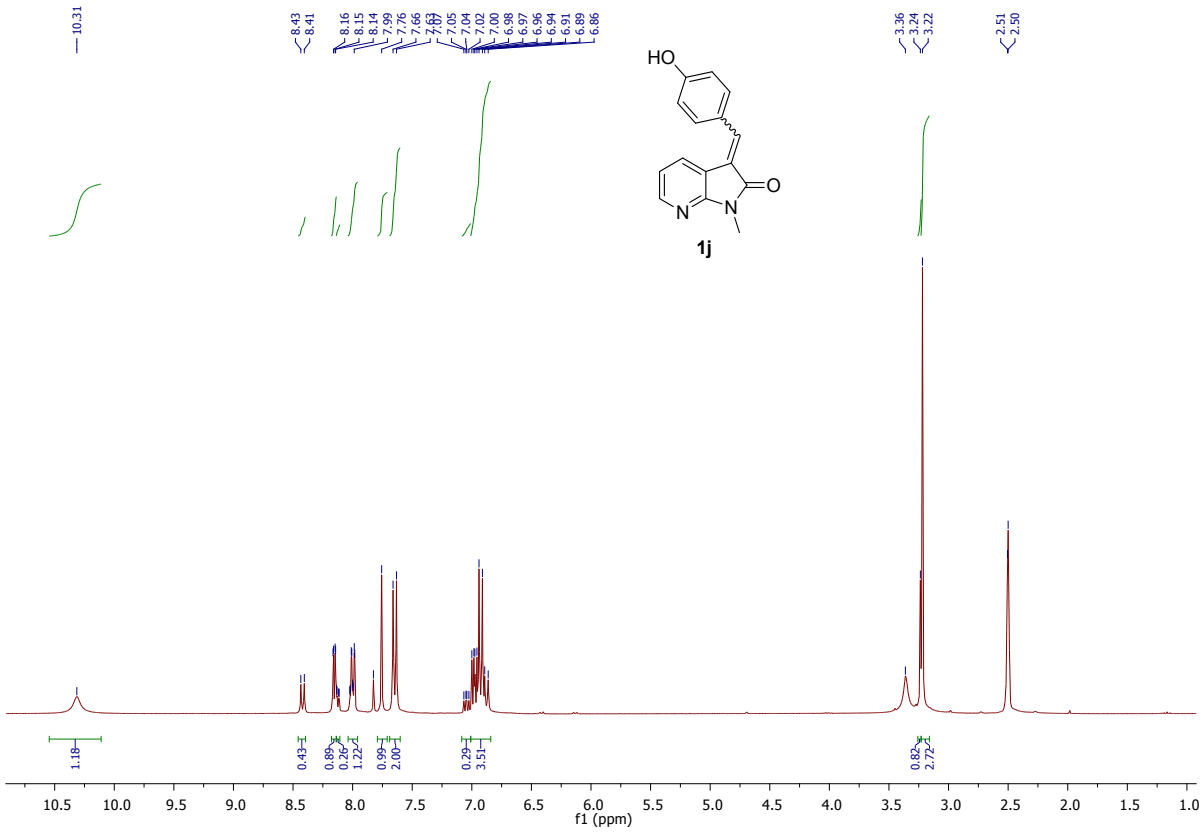


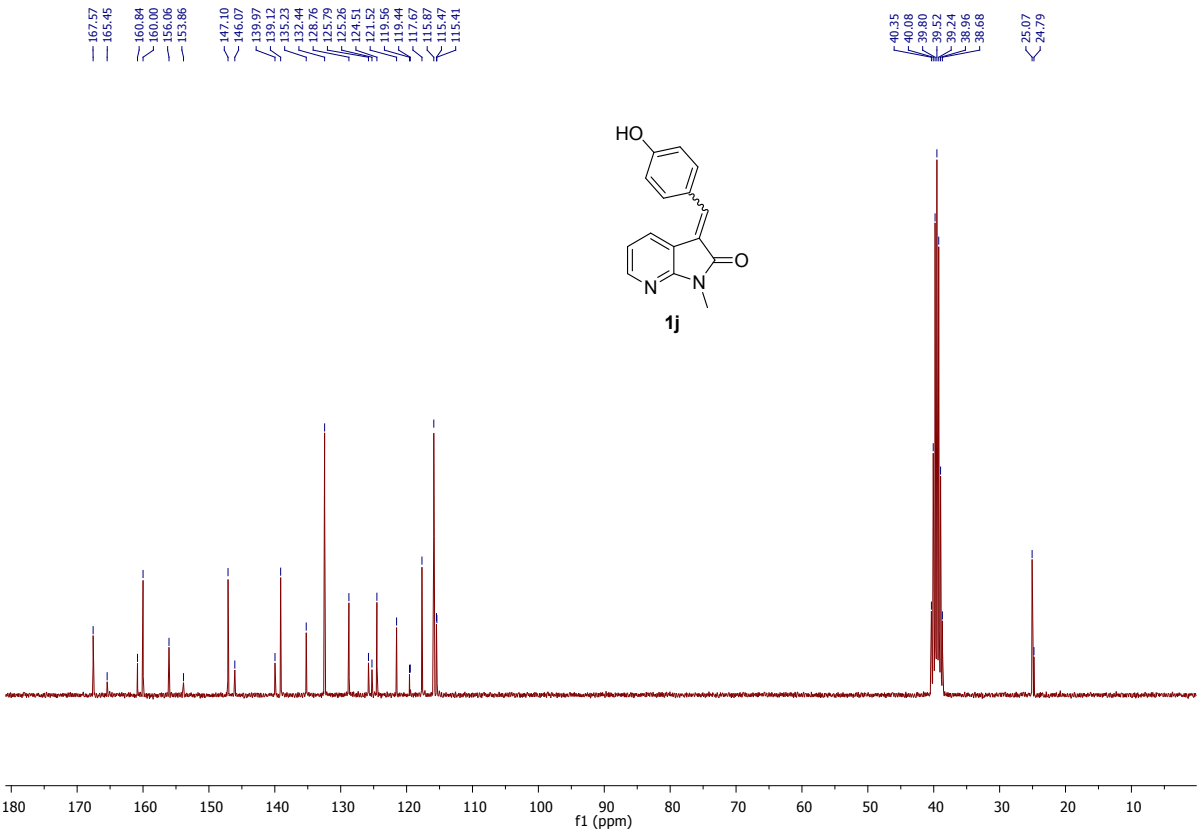
1-Methyl-3-(4-nitrobenzylidene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1h)



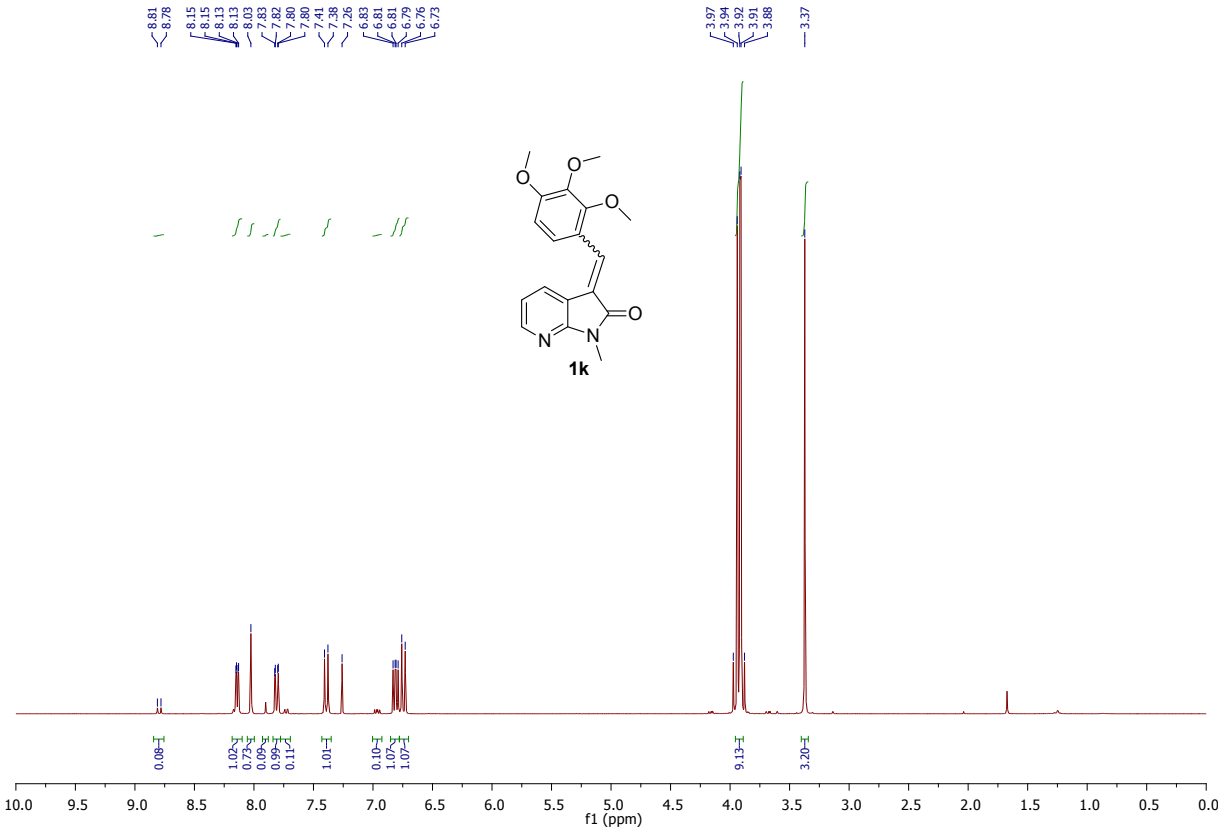


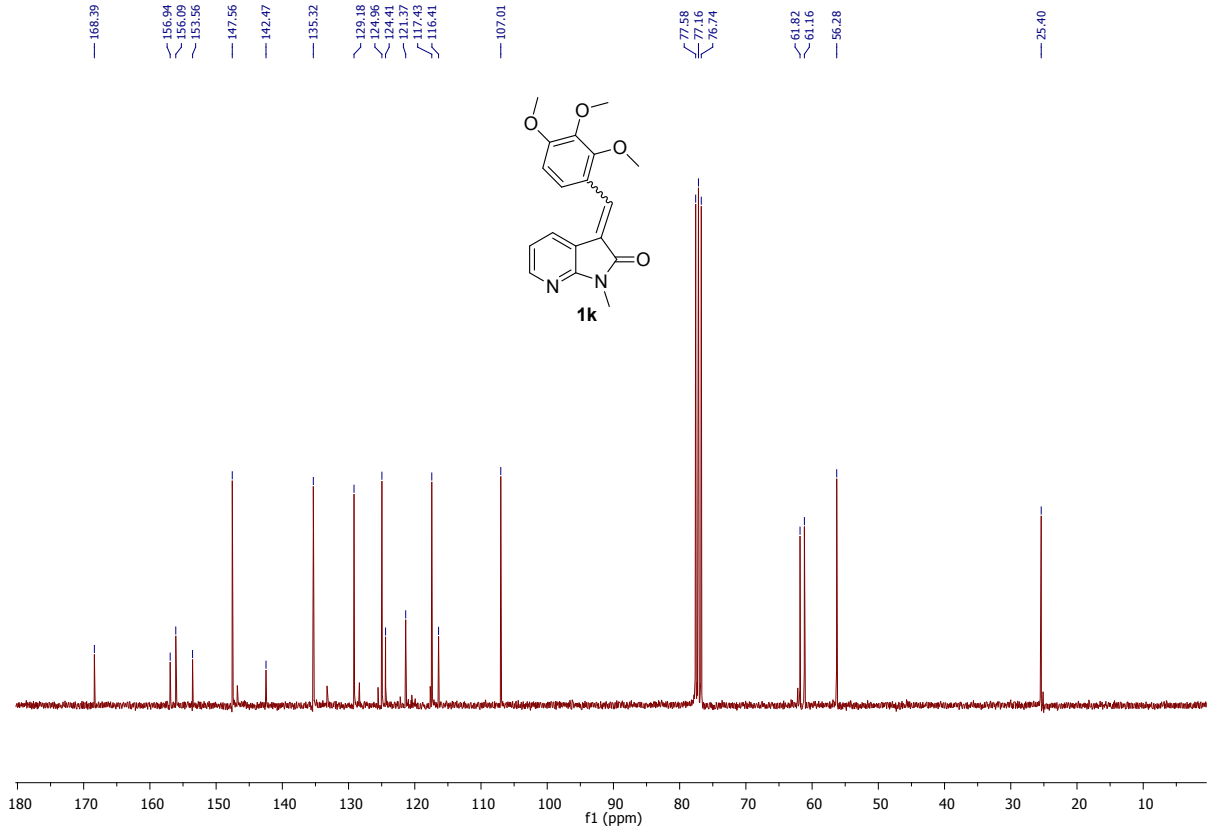
3-(4-Hydroxybenzylidene)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1j)



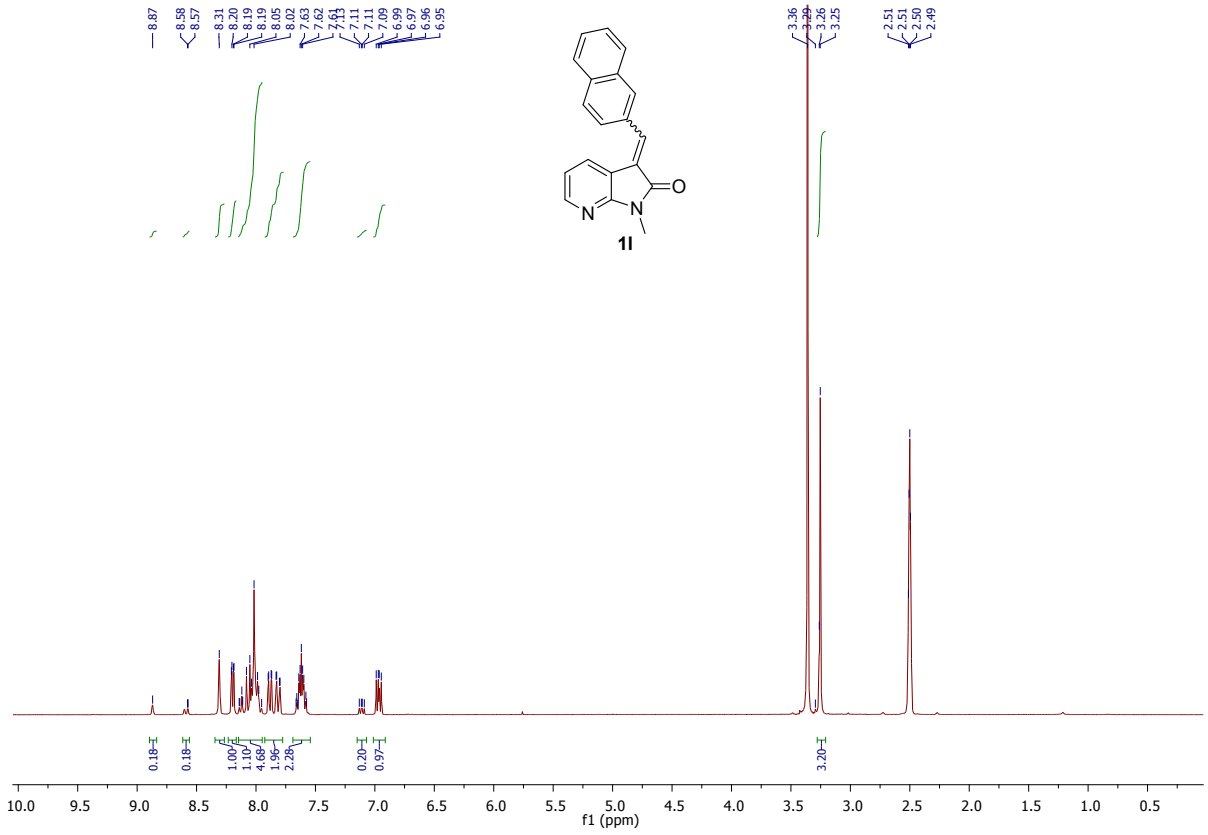


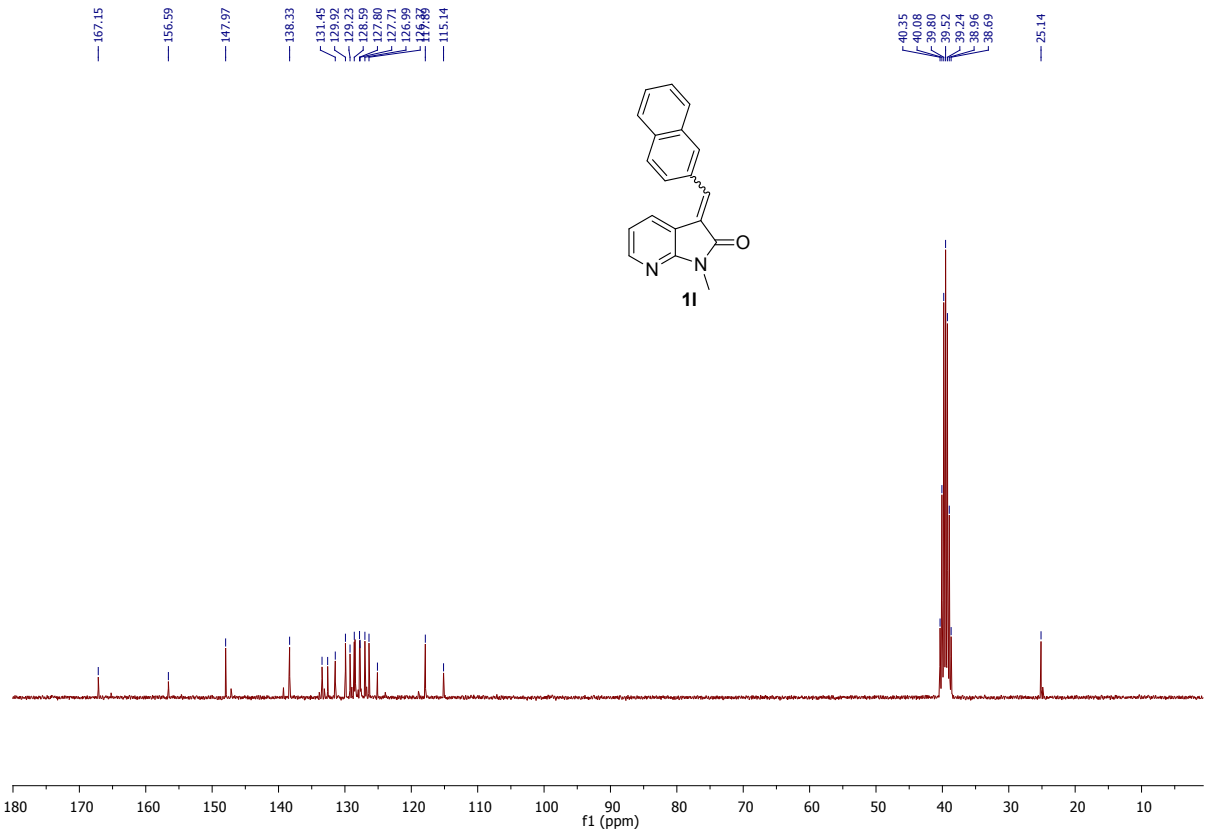
1-Methyl-3-(2,3,4-trimethoxybenzylidene)-1*H*-pyrrolo[2,3-b]pyridin-2(3*H*)-one (1k)



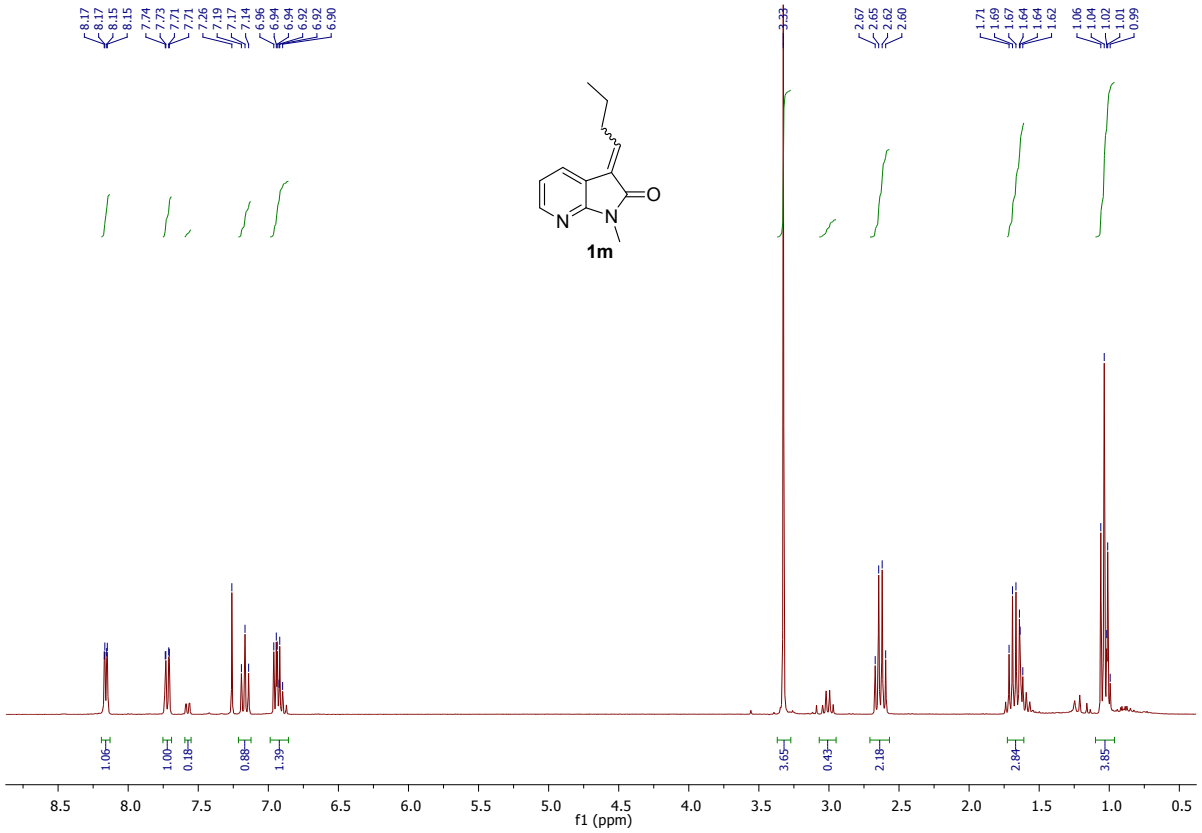


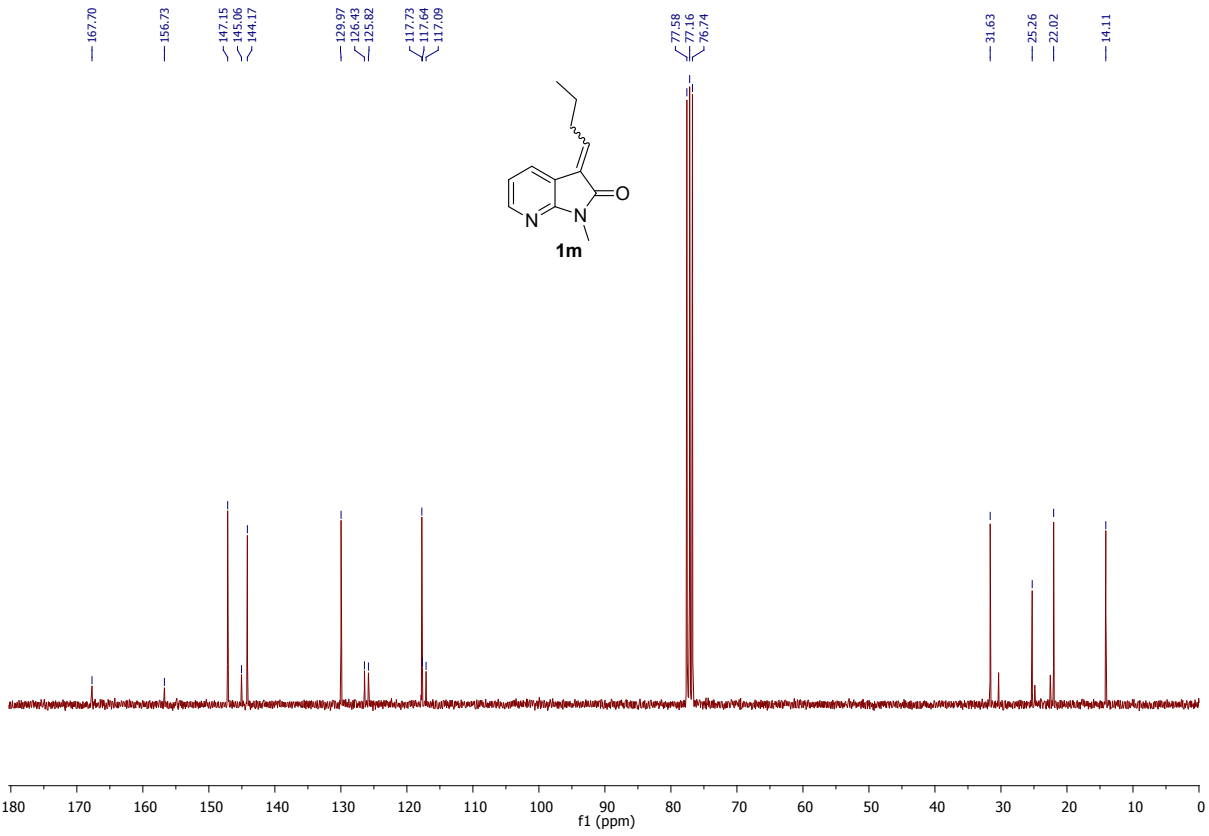
1-Methyl-3-(naphthalen-2-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1l)



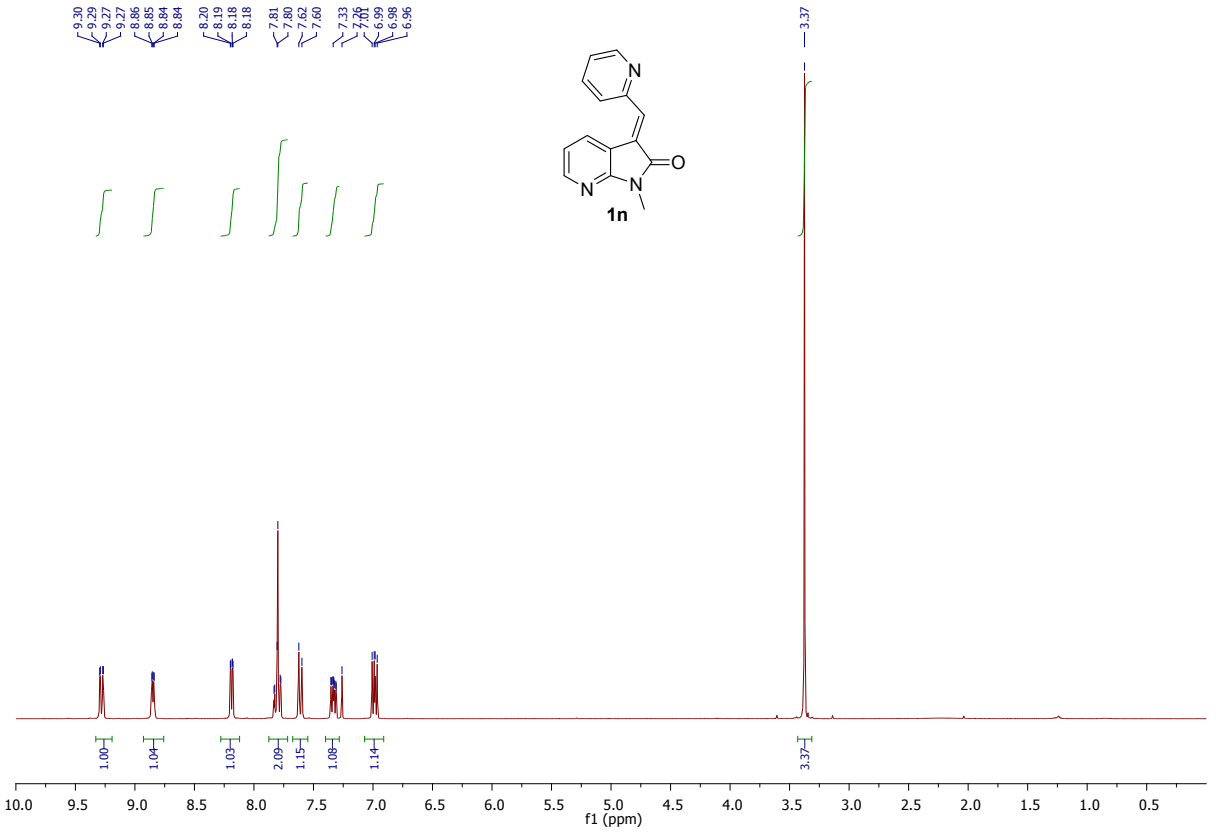


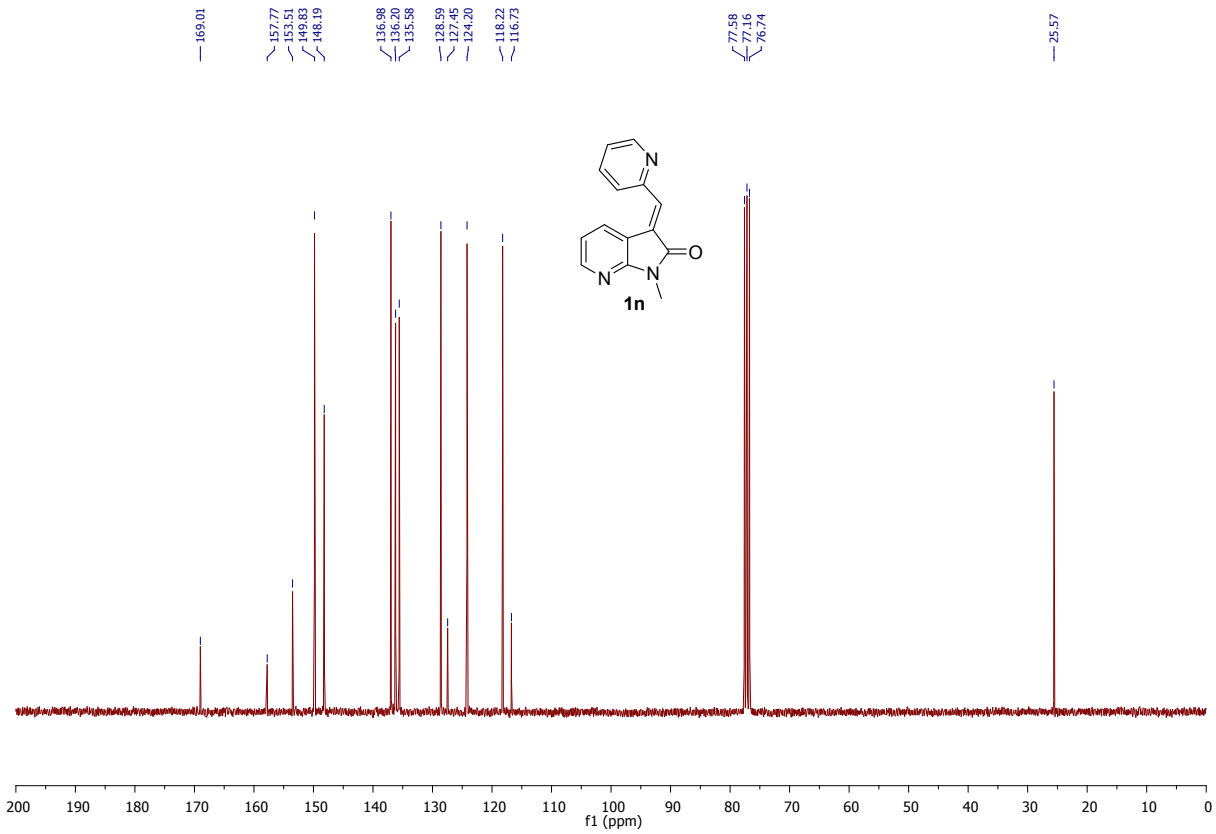
3-Butylidene-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1m)



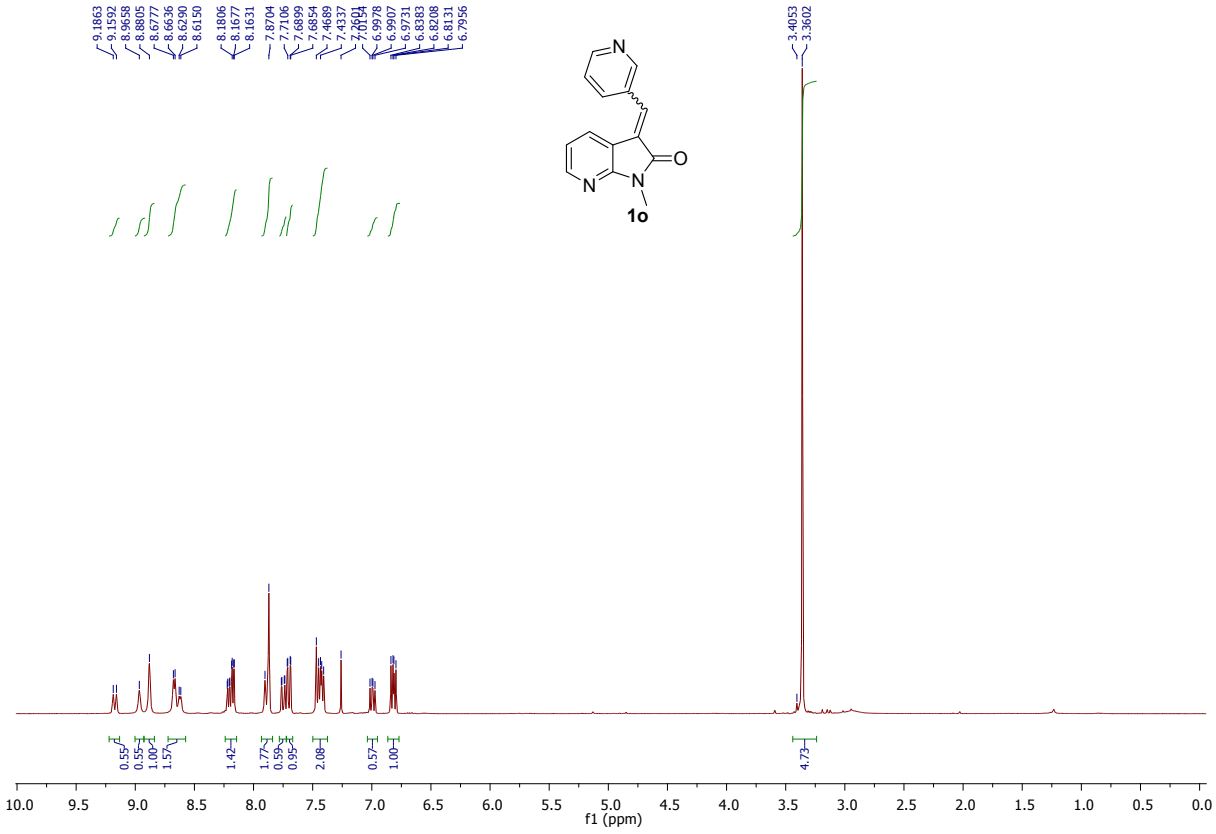


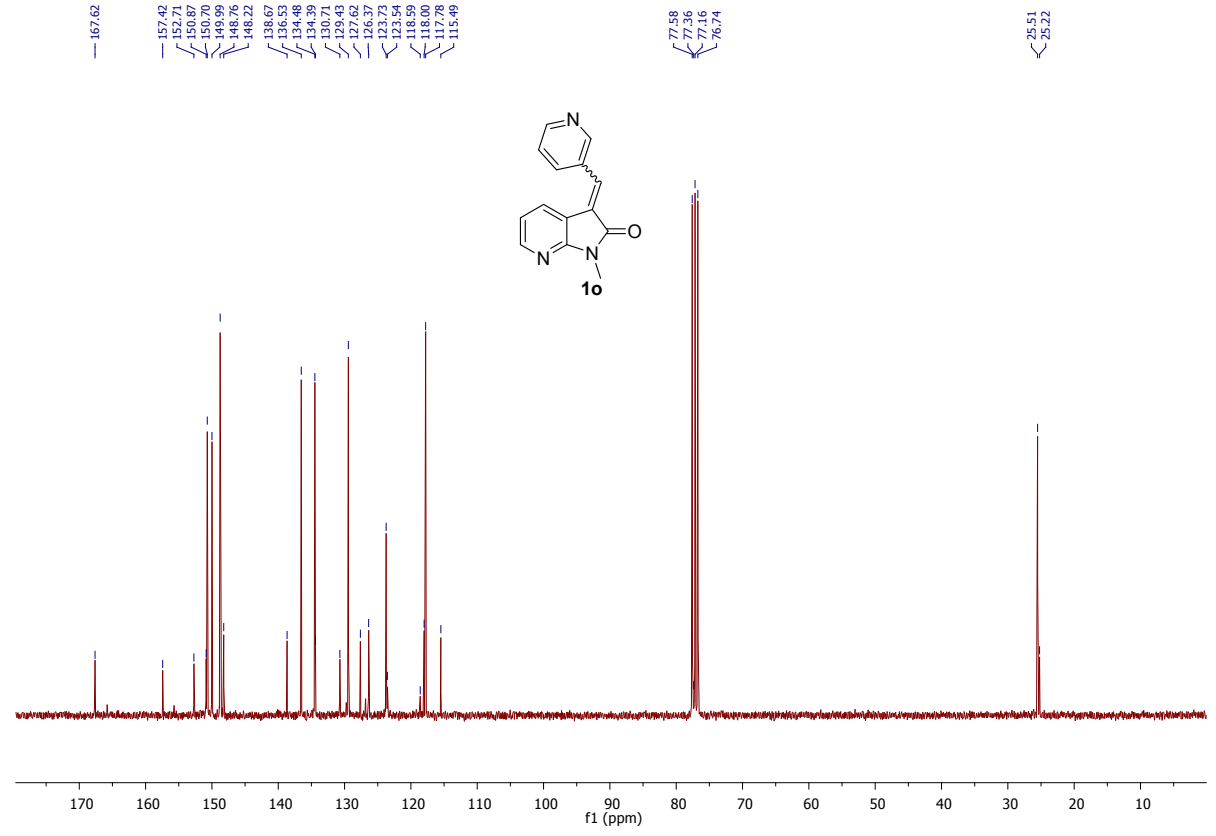
1-Methyl-3-(pyridin-2-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1n)



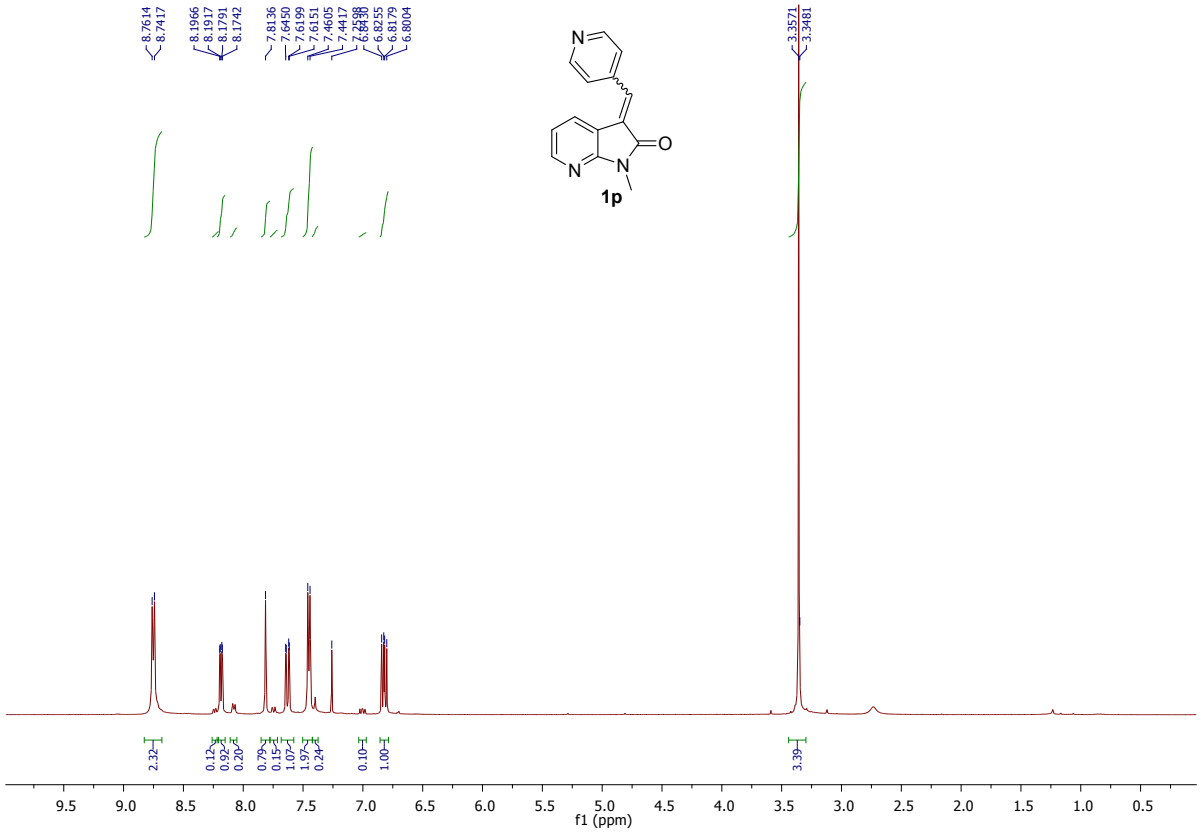


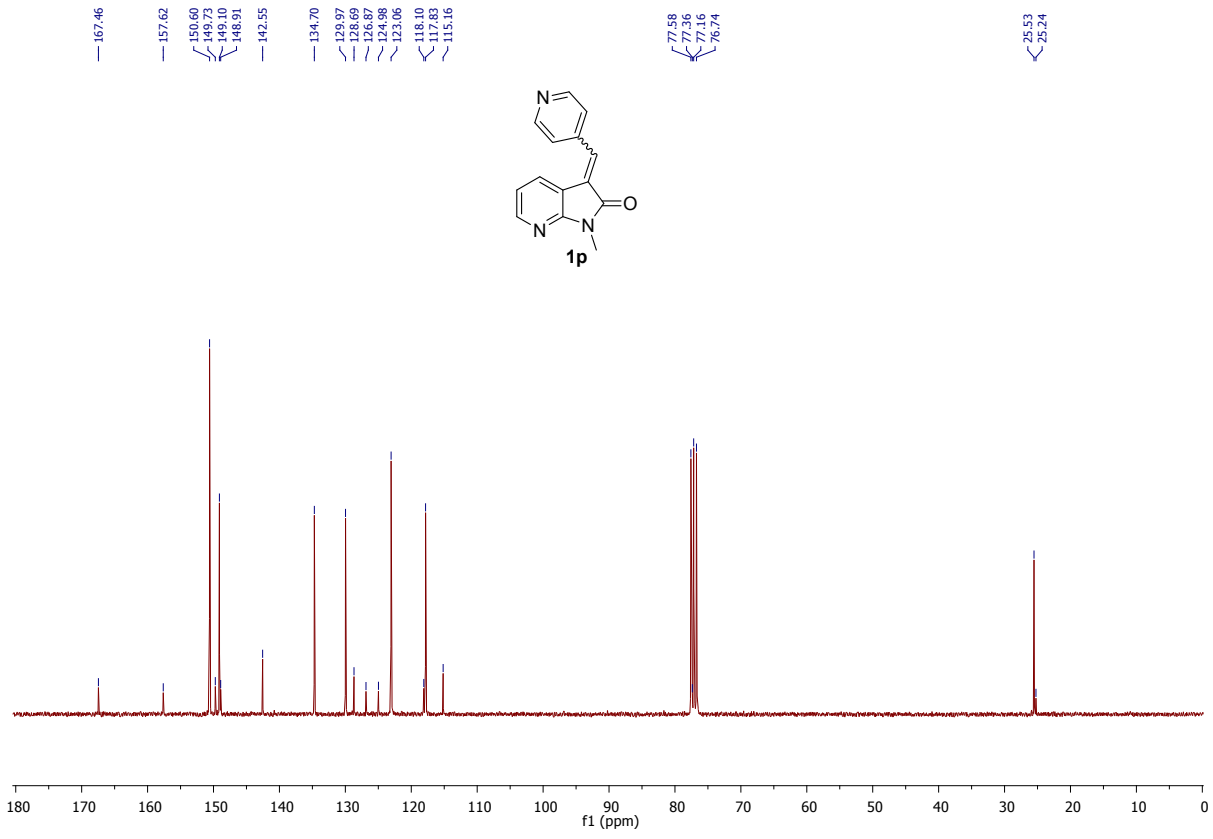
1-Methyl-3-(pyridin-3-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1o)



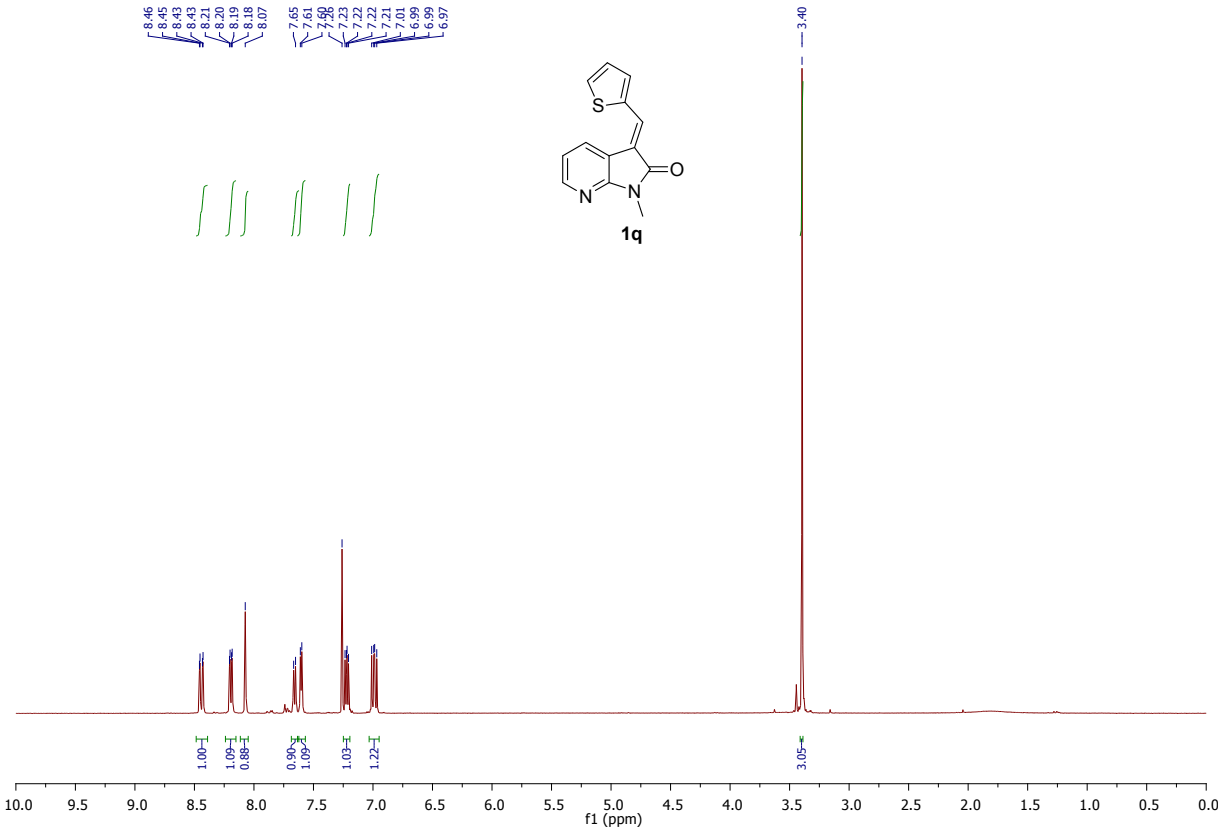


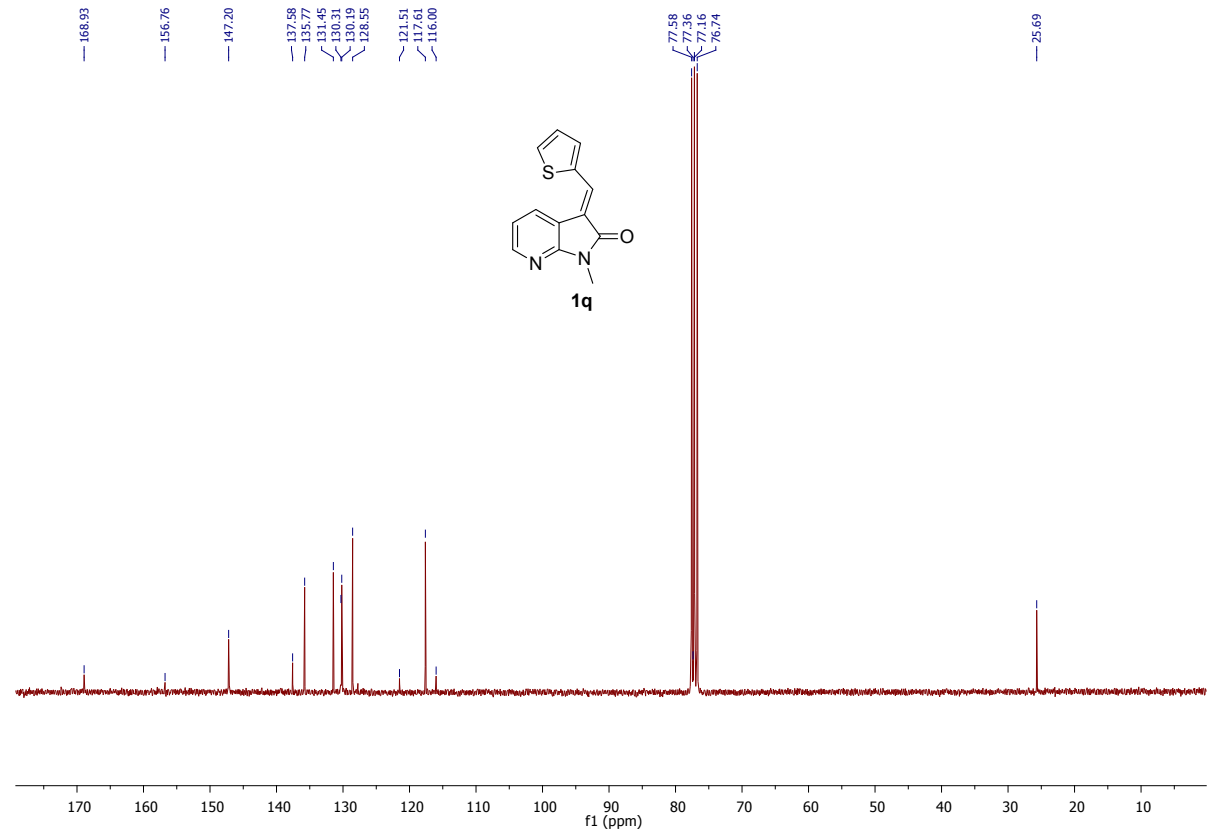
1-Methyl-3-(pyridin-4-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1p)



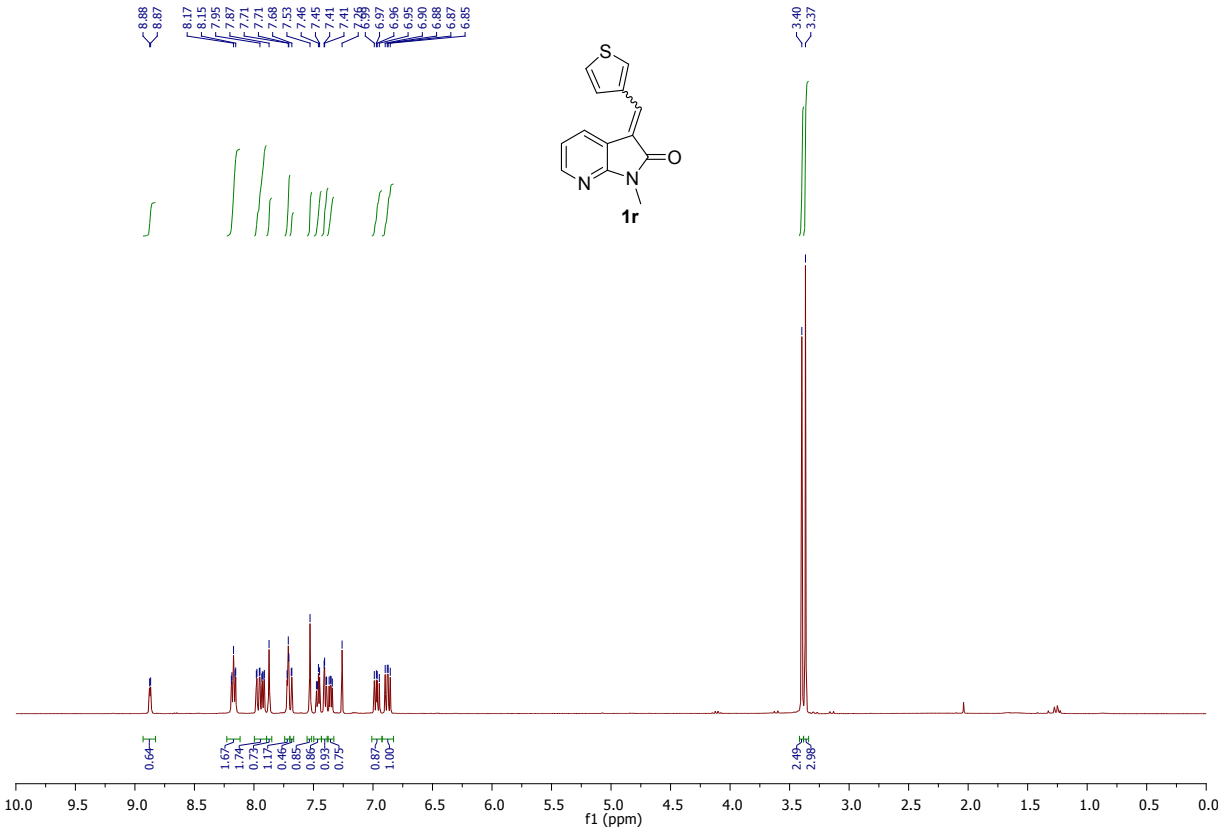


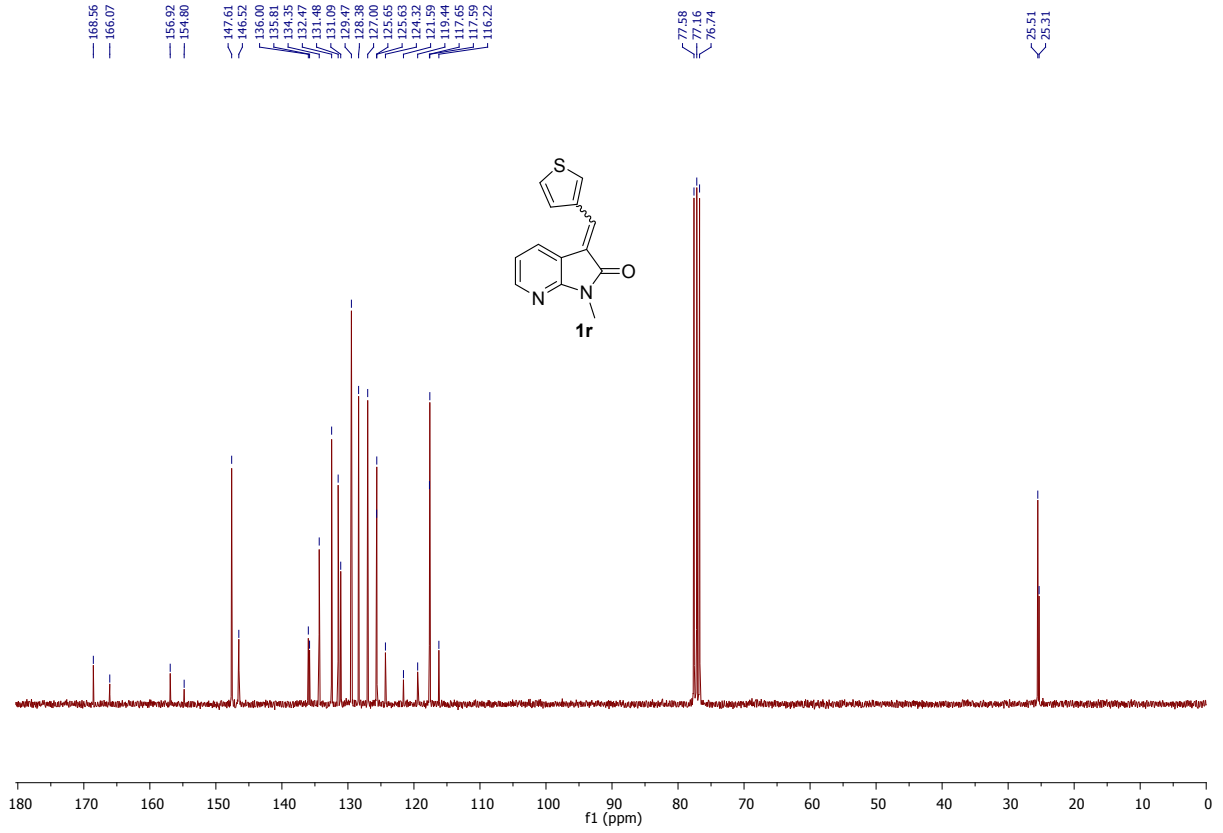
1-Methyl-3-(thiophen-2-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1q)



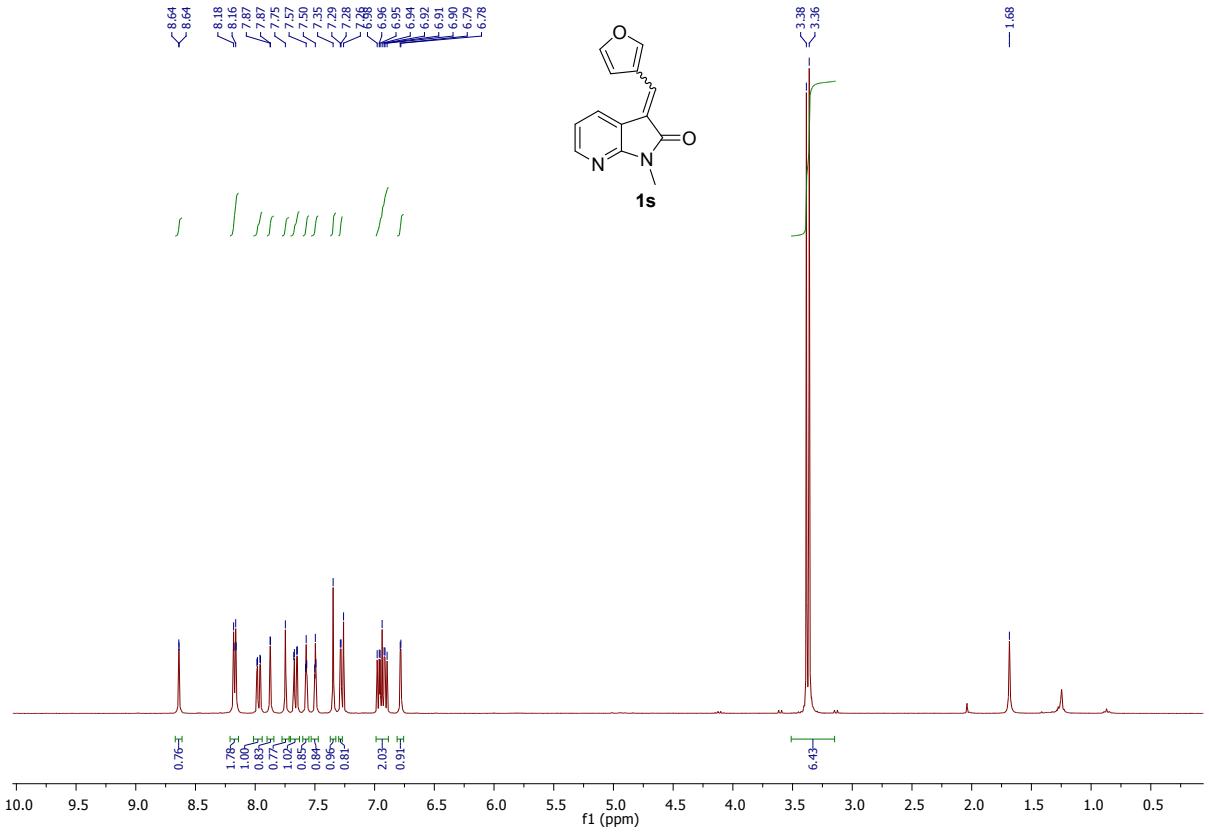


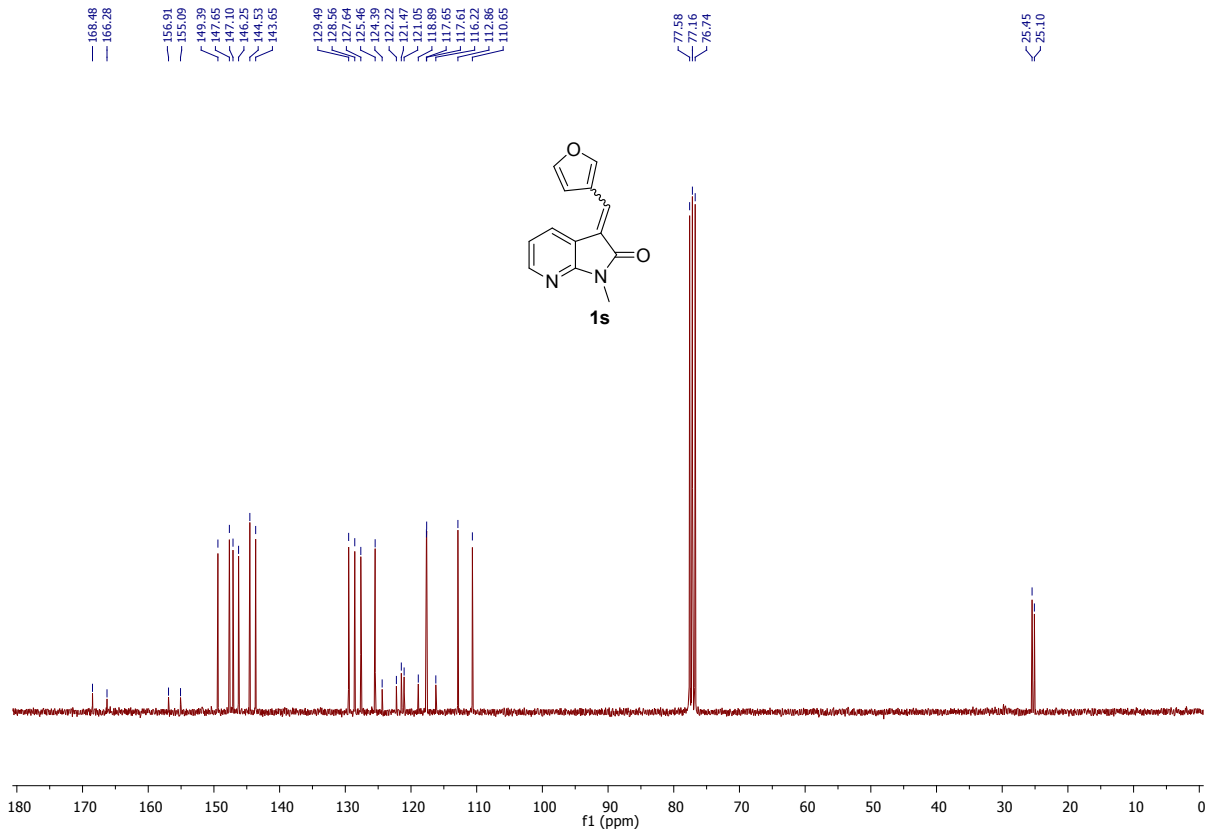
1-Methyl-3-(thiophen-3-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1r)



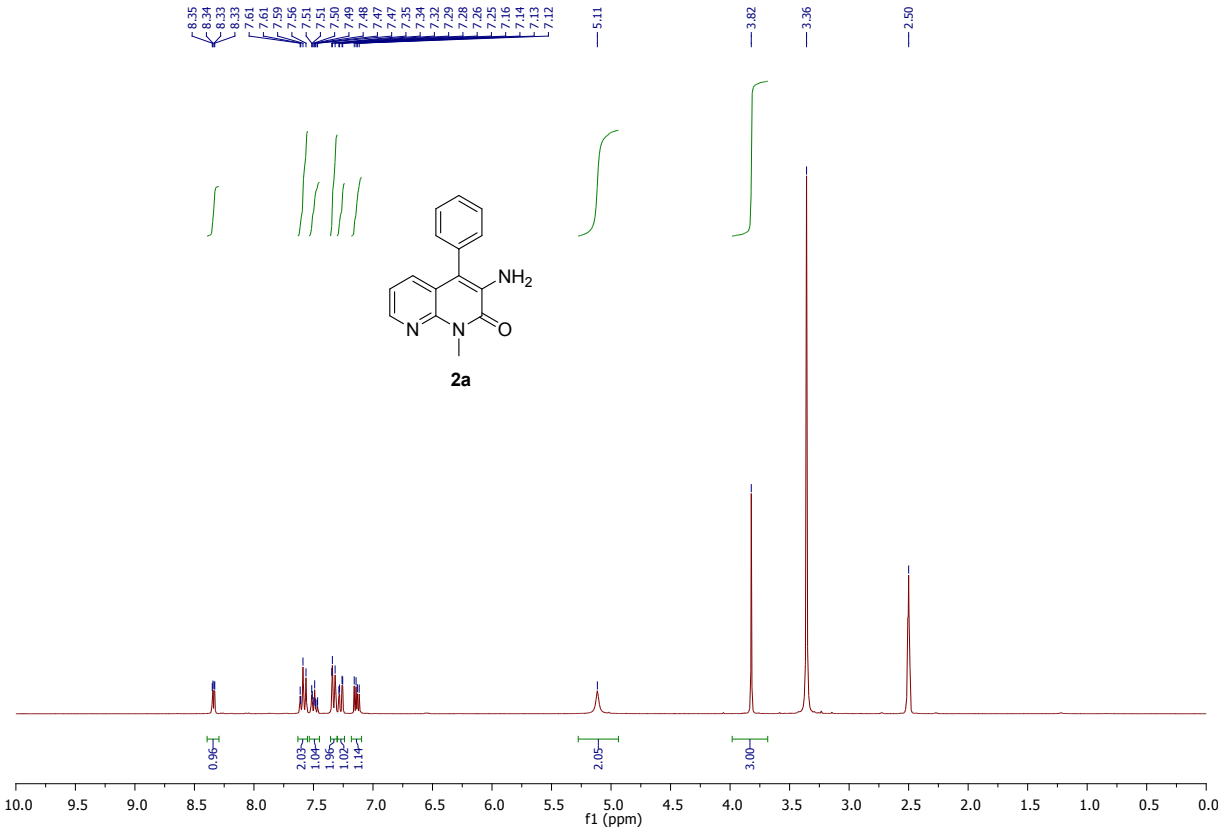


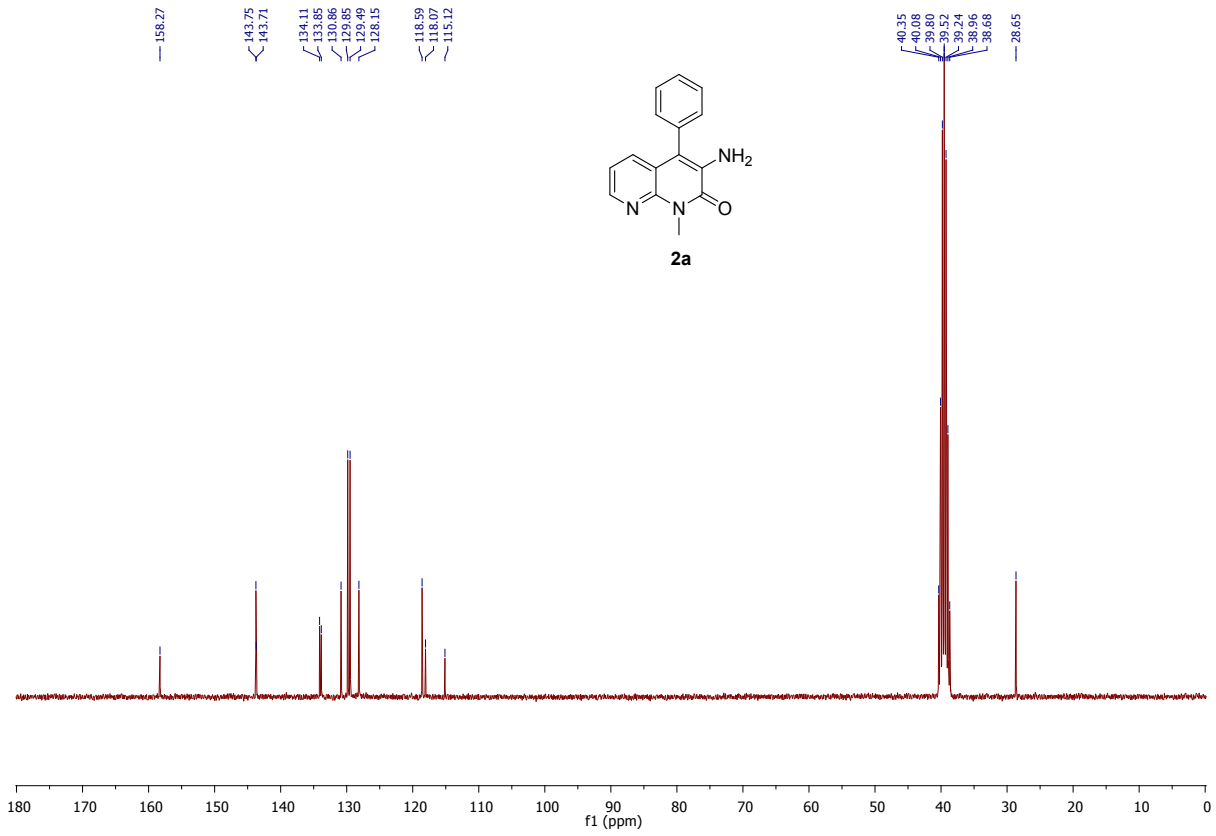
1-Methyl-3-(furan-3-ylmethylene)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (1s)



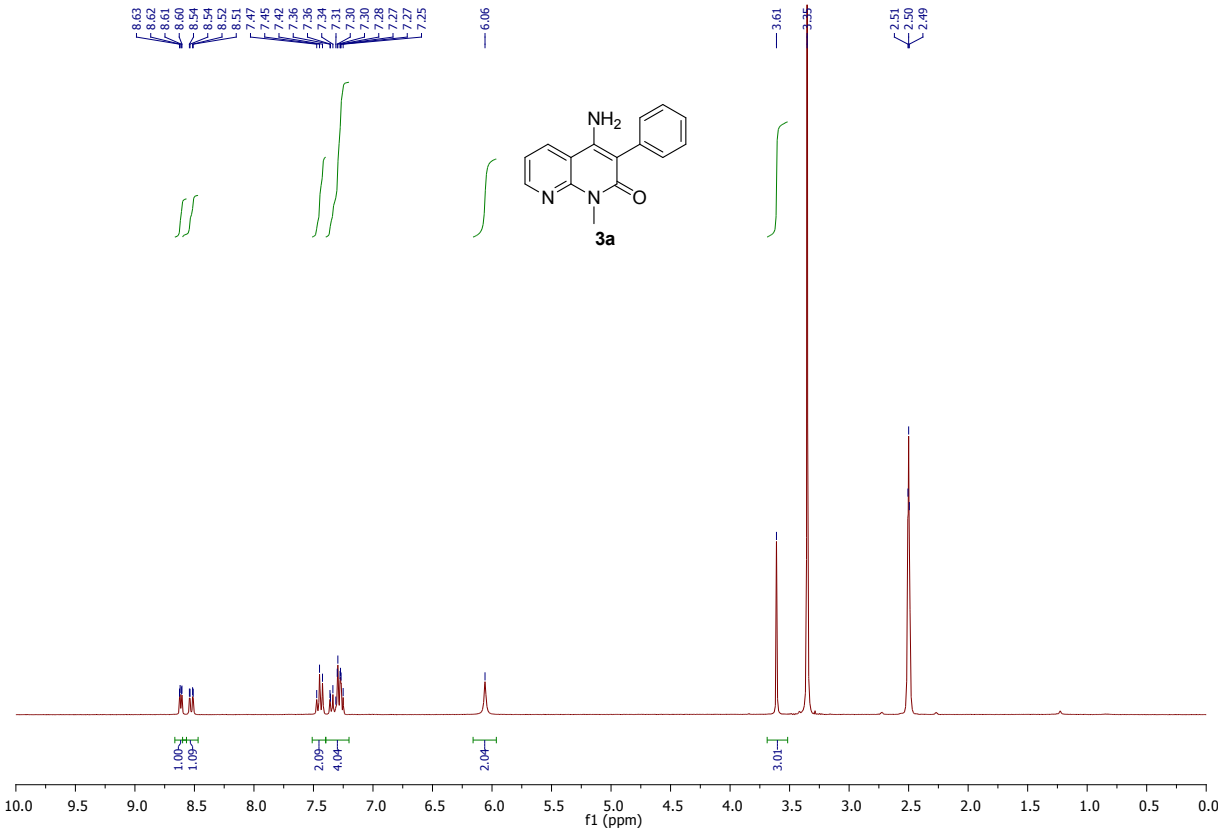


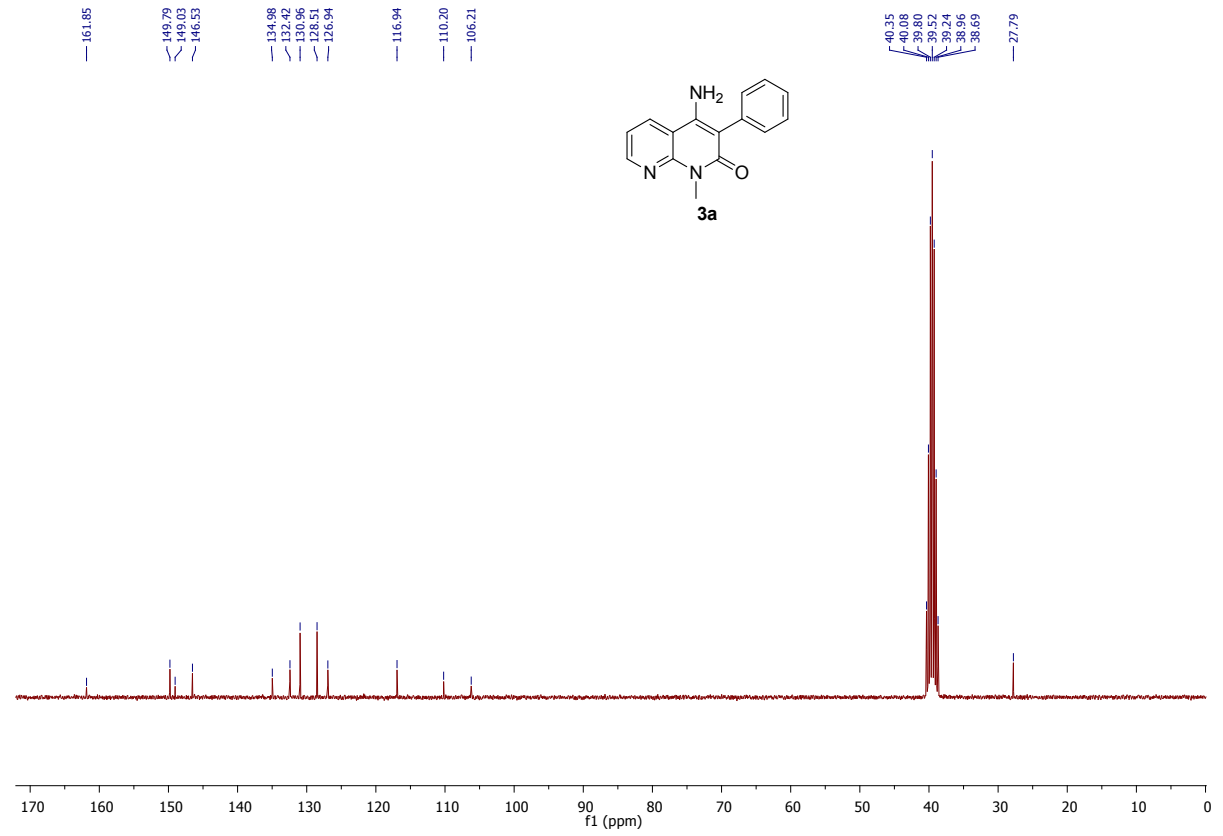
3-Amino-1-methyl-4-phenyl-1,8-naphthyridin-2(1*H*)-one (2a)



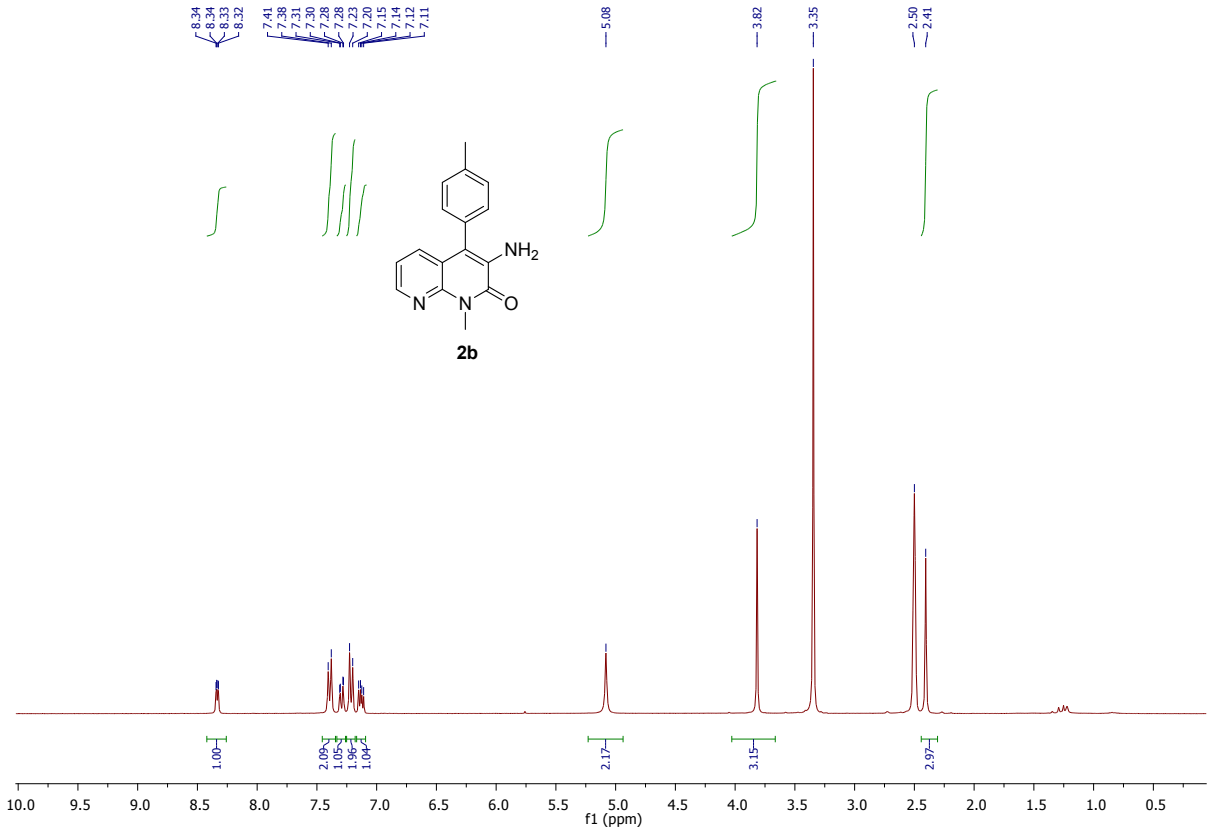


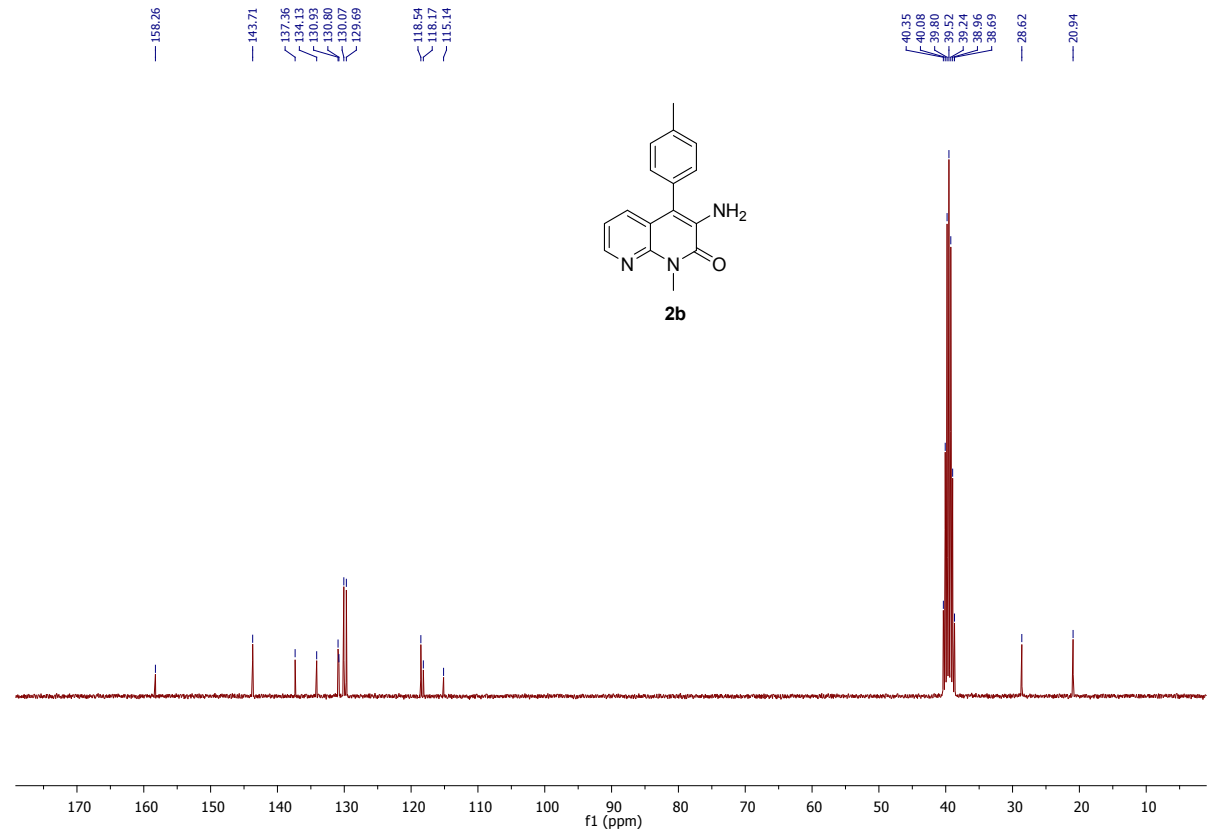
4-Amino-1-methyl-3-phenyl-1,8-naphthyridin-2(1*H*)-one (3a)



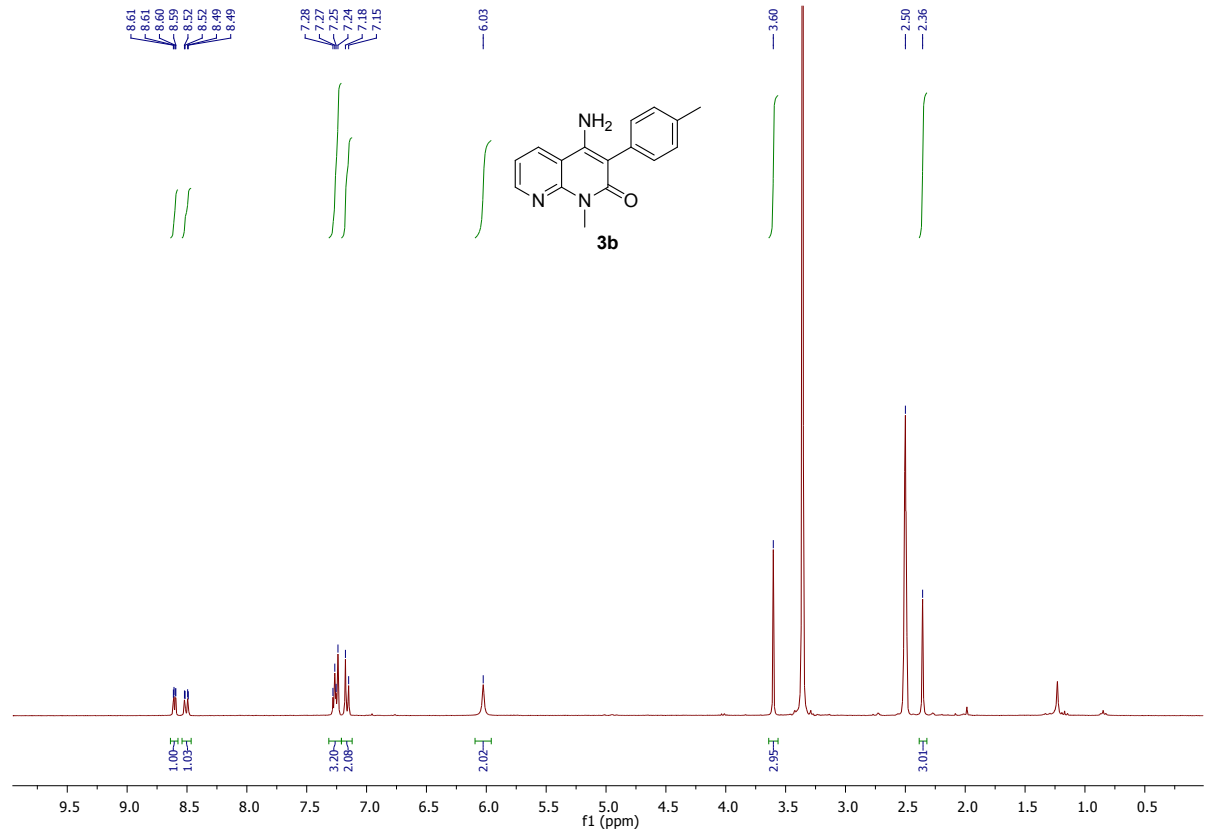


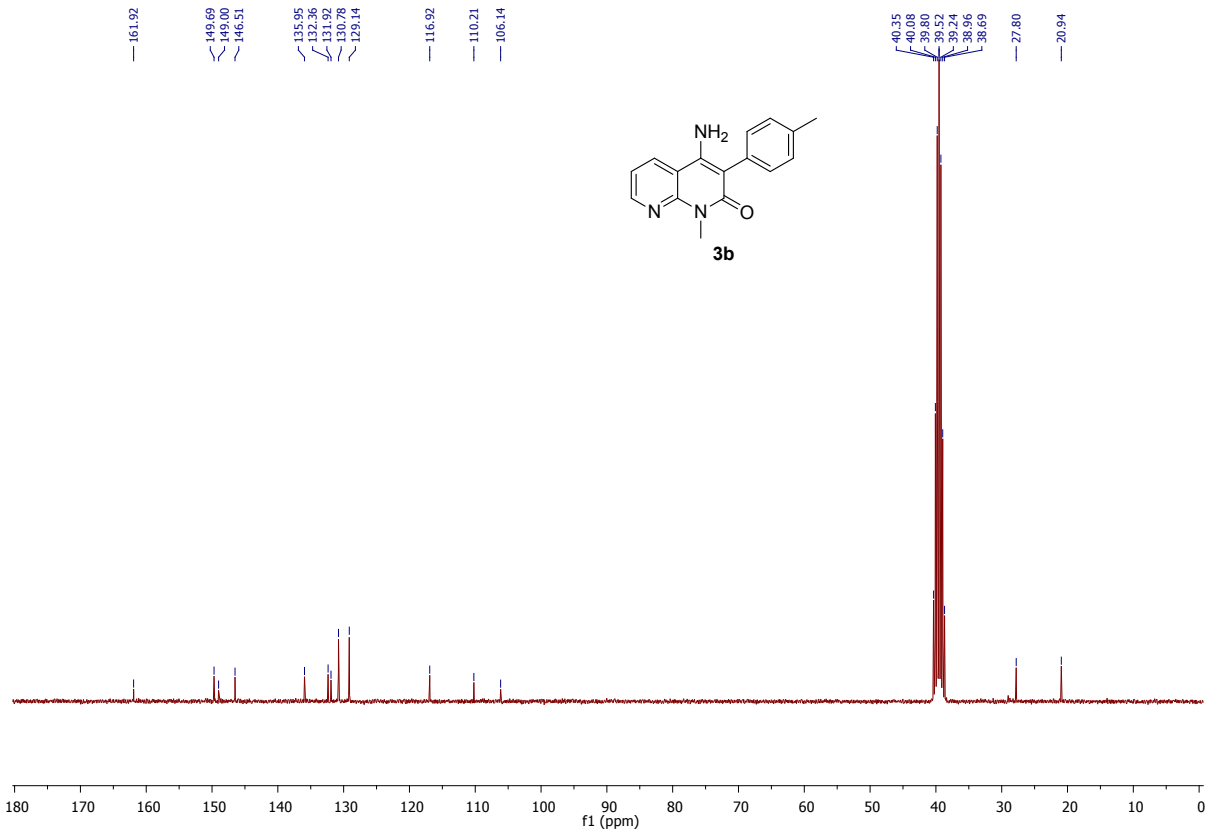
3-Amino-1-methyl-4-(*p*-tolyl)-1,8-naphthyridin-2(1*H*)-one (2b)



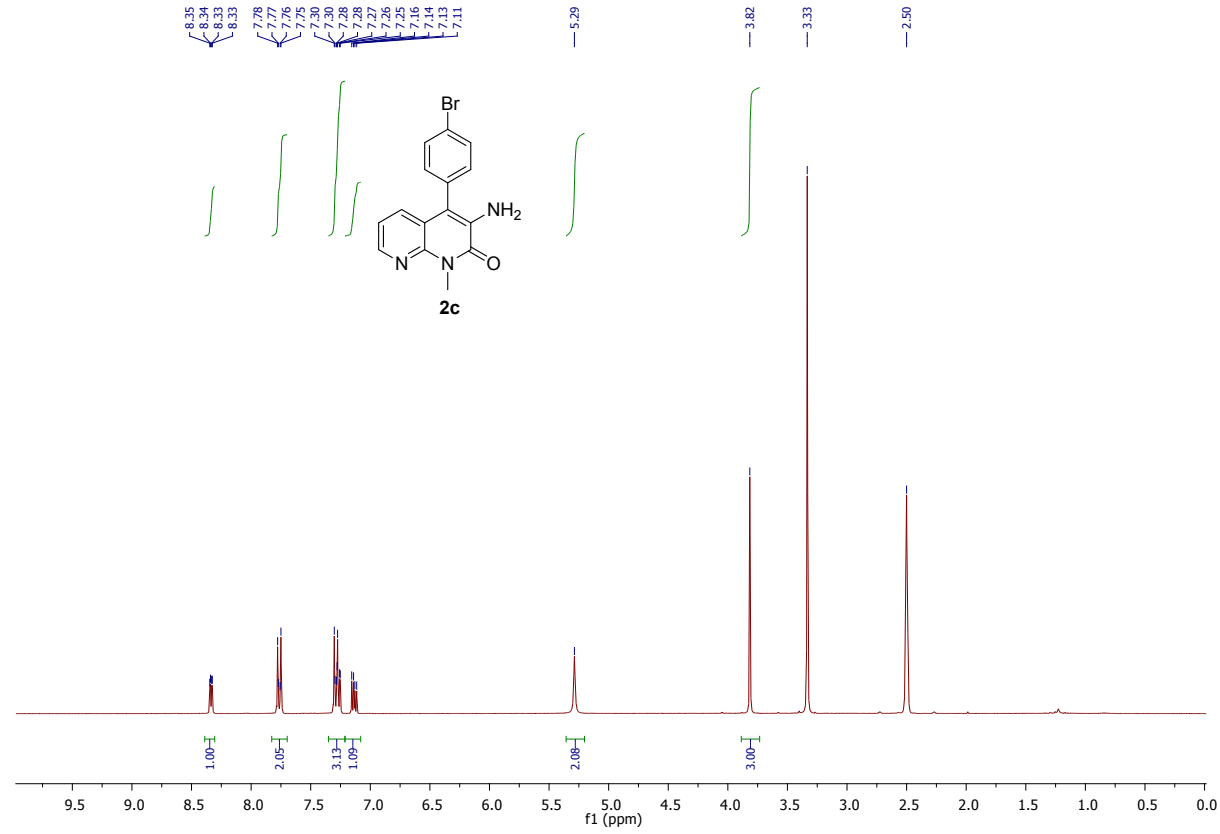


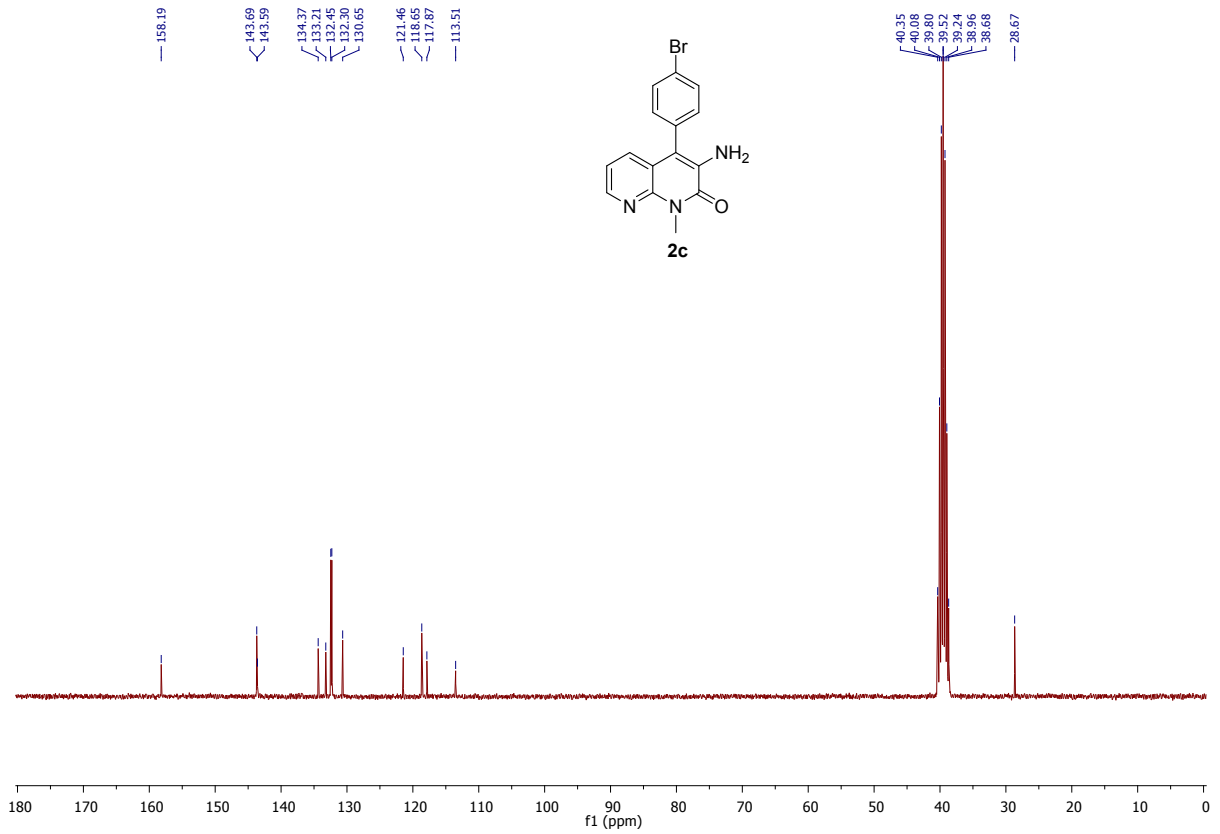
4-Amino-1-methyl-3-(*p*-tolyl)-1,8-naphthyridin-2(1*H*)-one (3b)



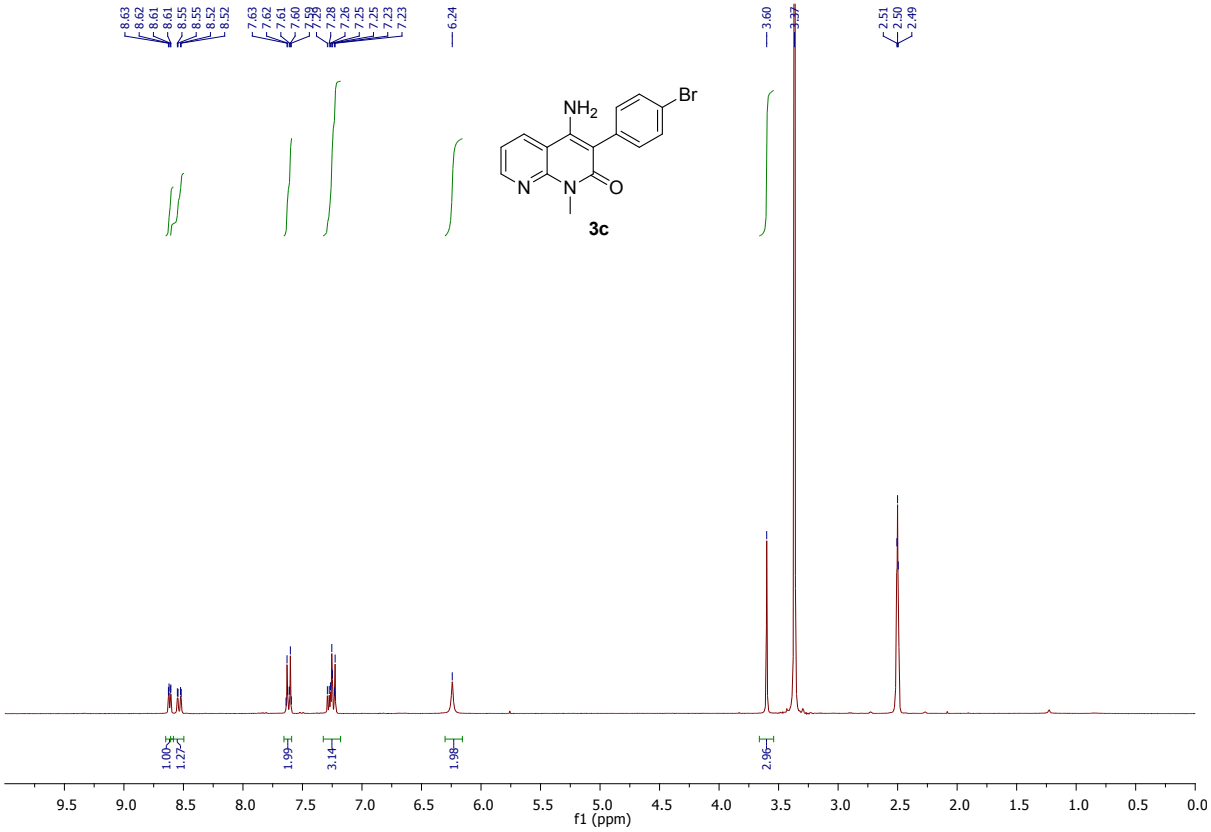


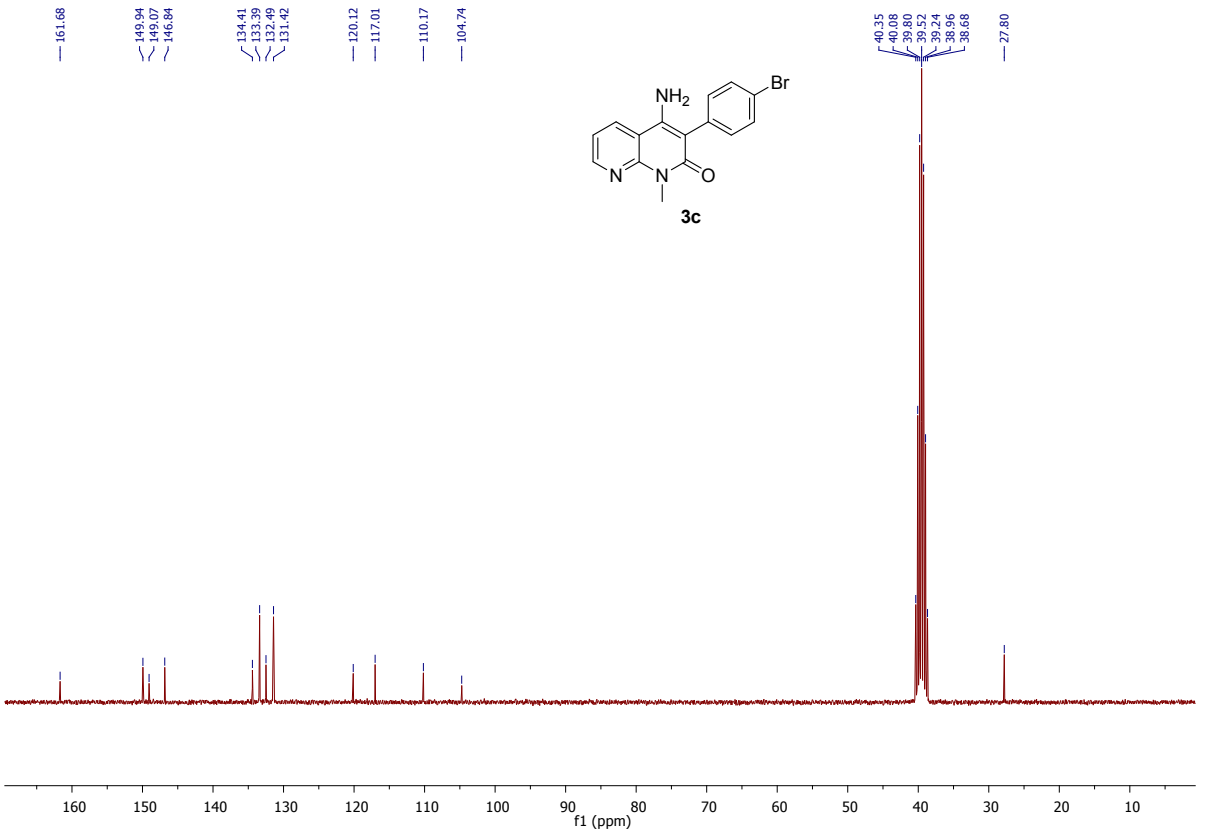
3-Amino-4-(4-bromophenyl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (2c)



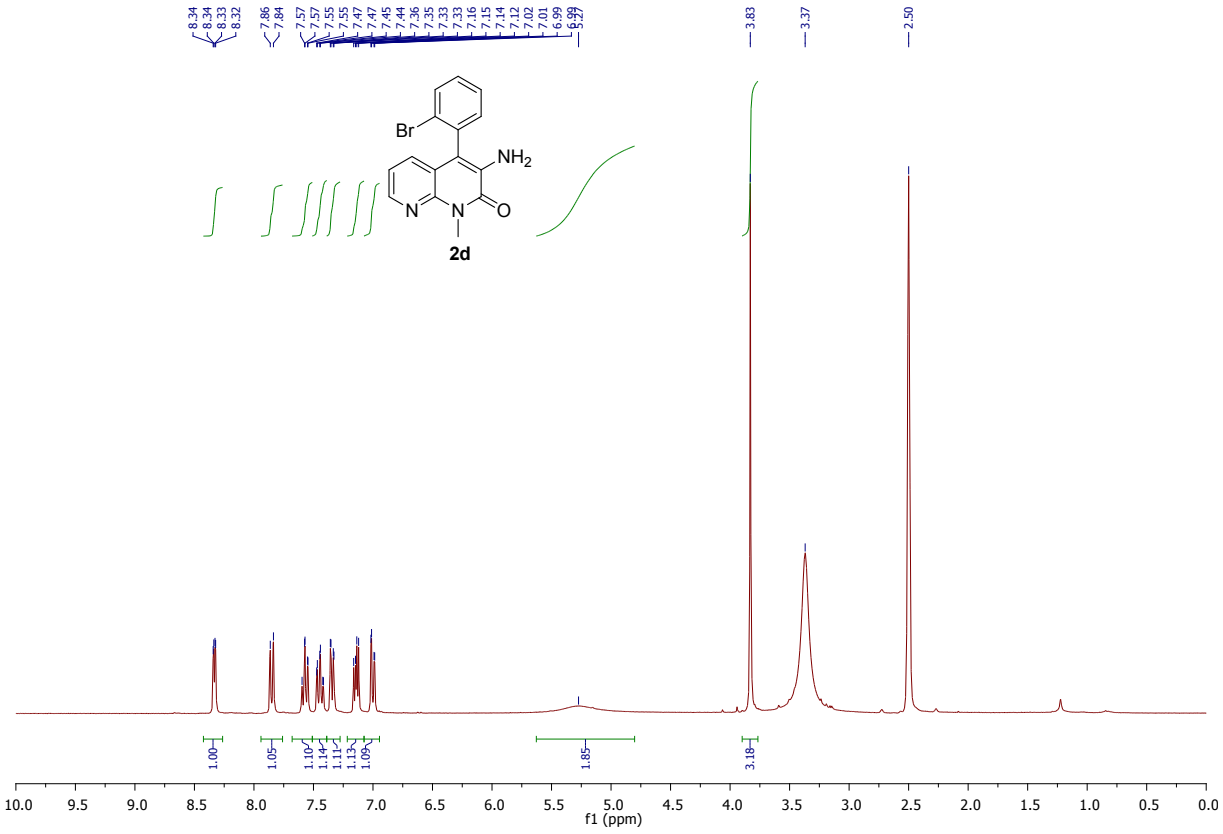


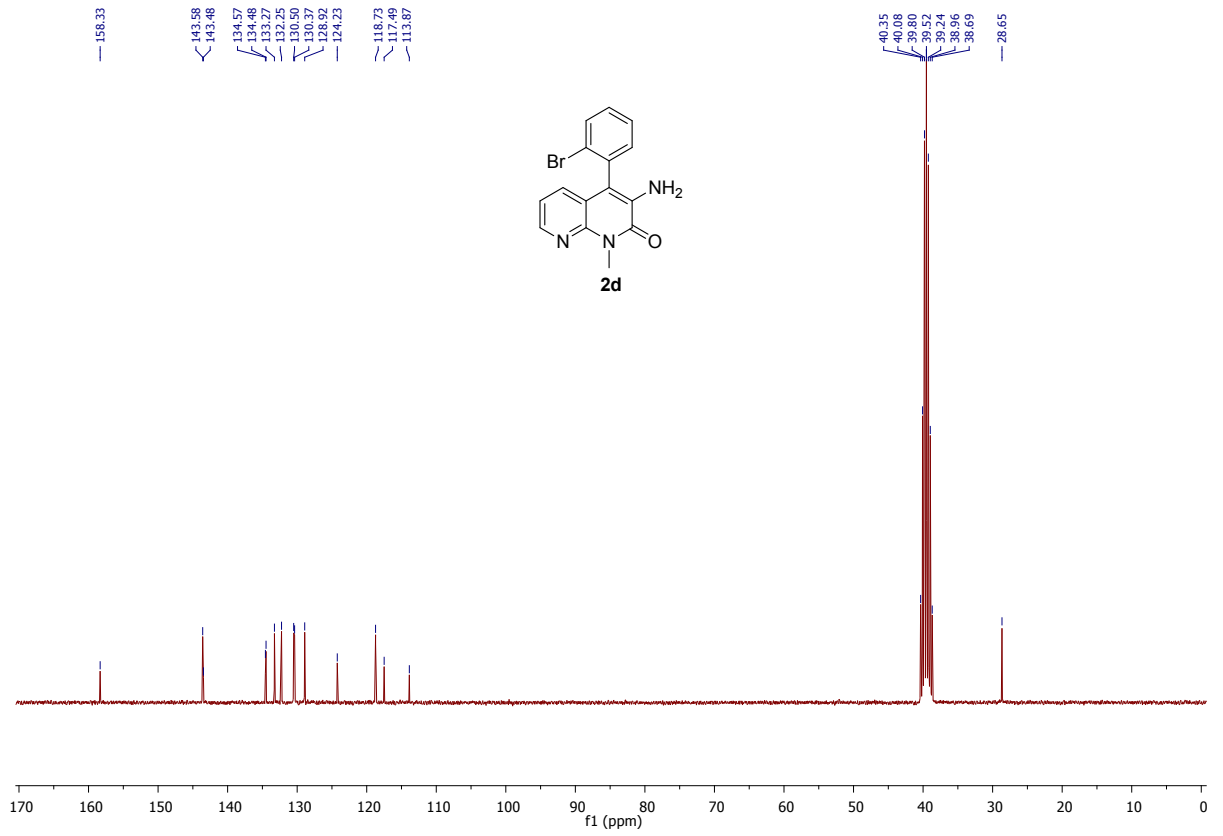
4-Amino-3-(4-bromophenyl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (3c)



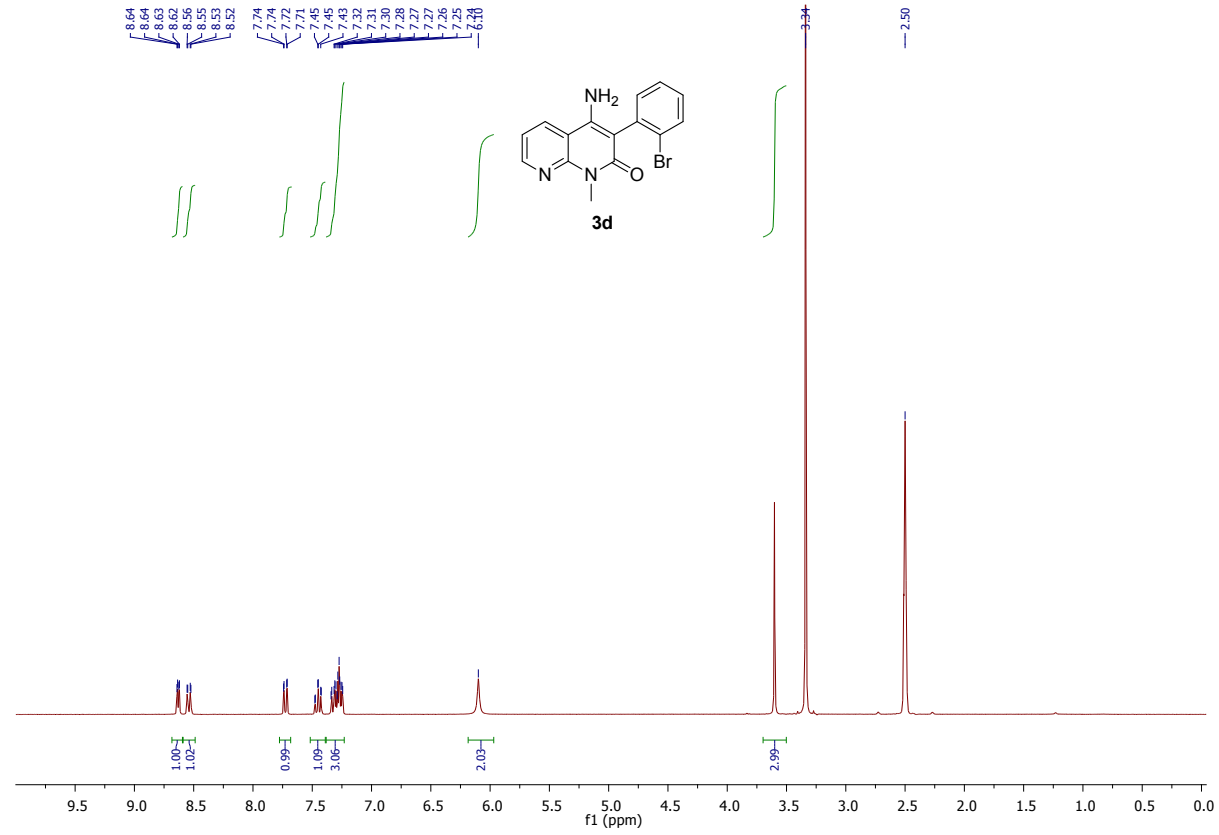


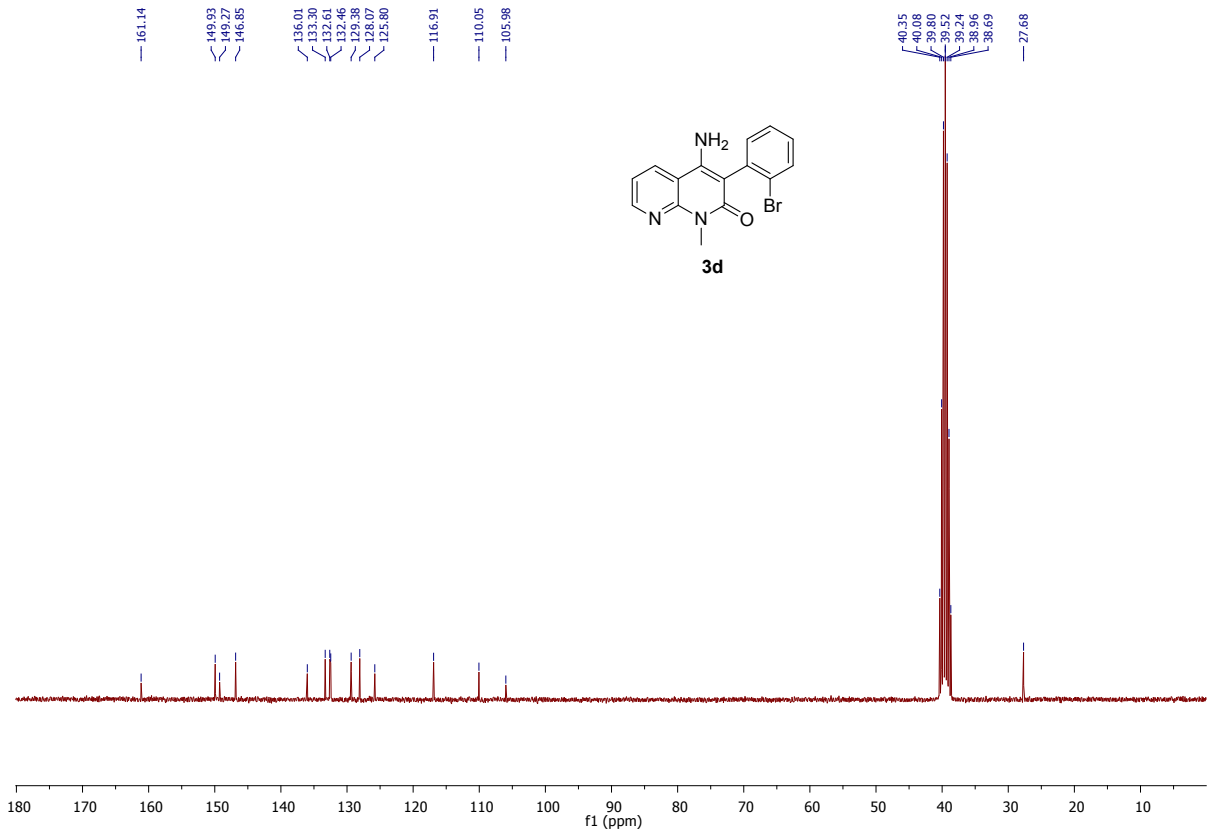
3-Amino-4-(2-bromophenyl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (2d)



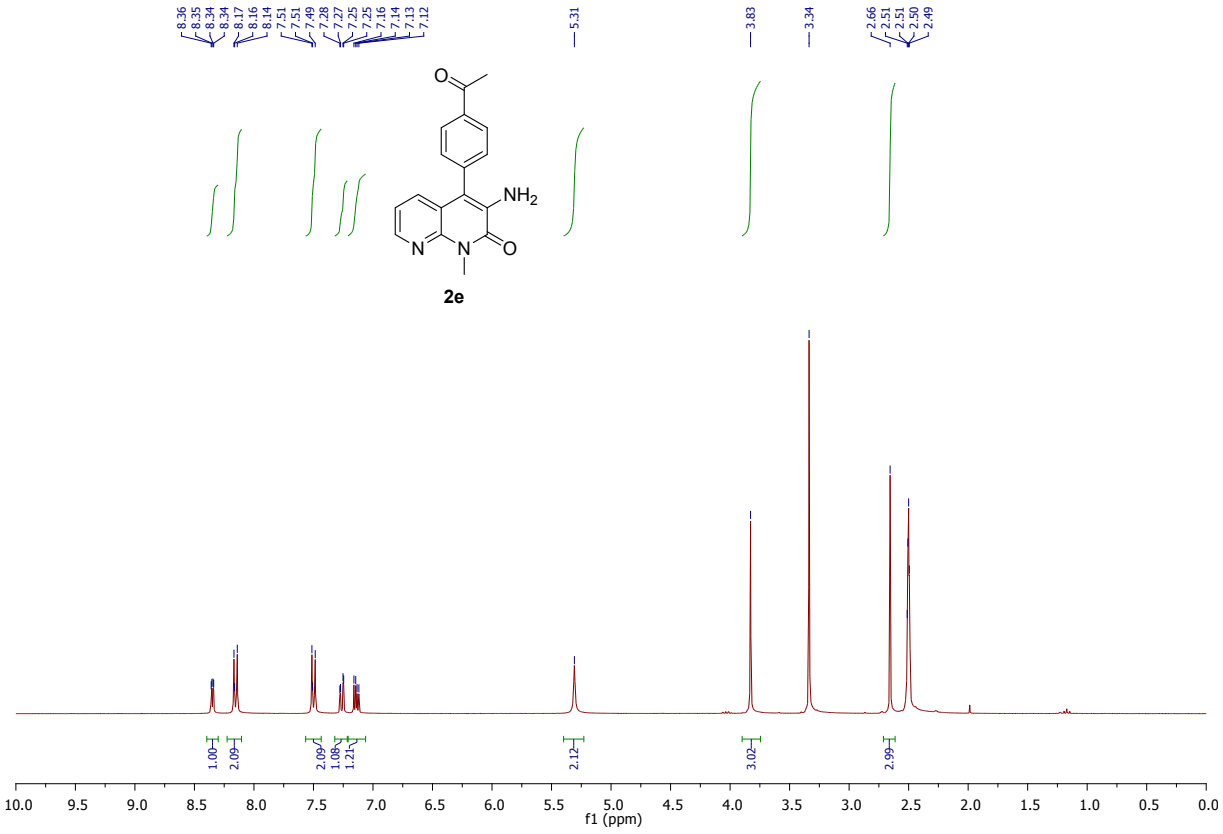


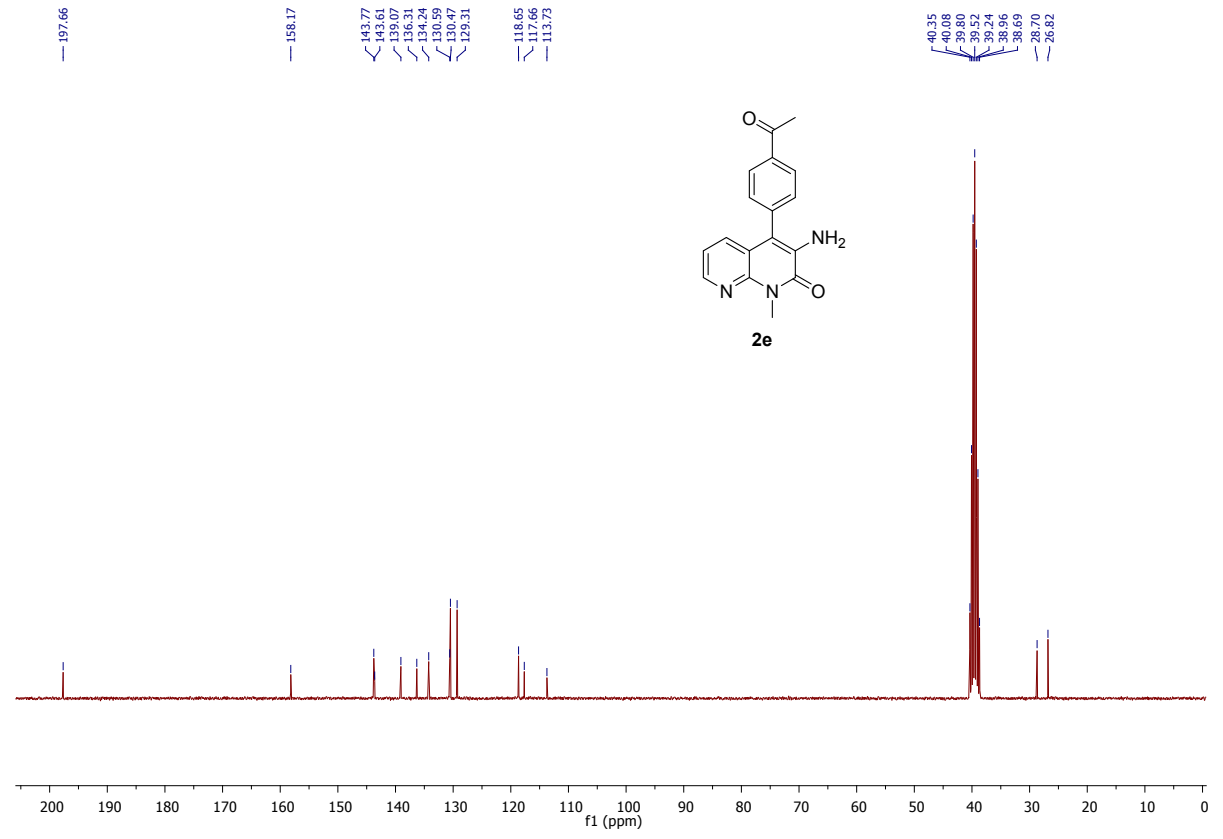
4-Amino-3-(2-bromophenyl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (3d)



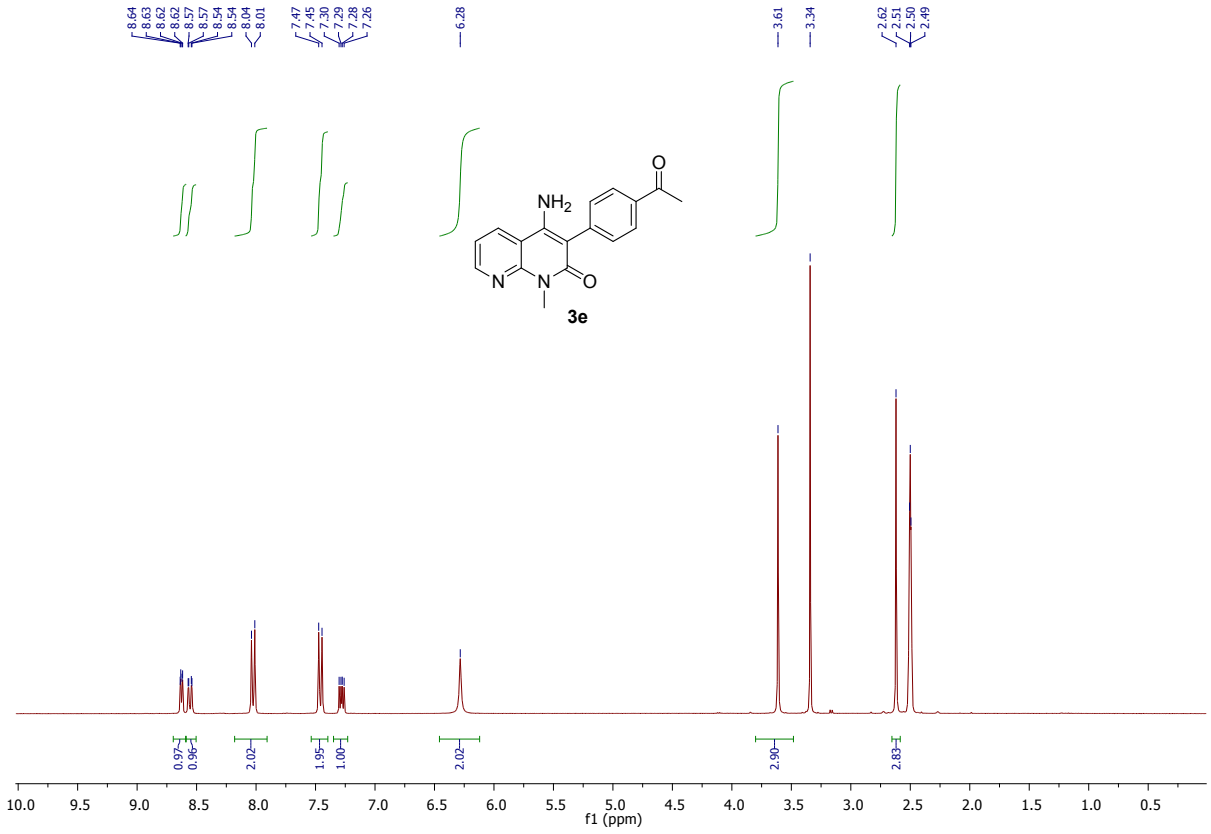


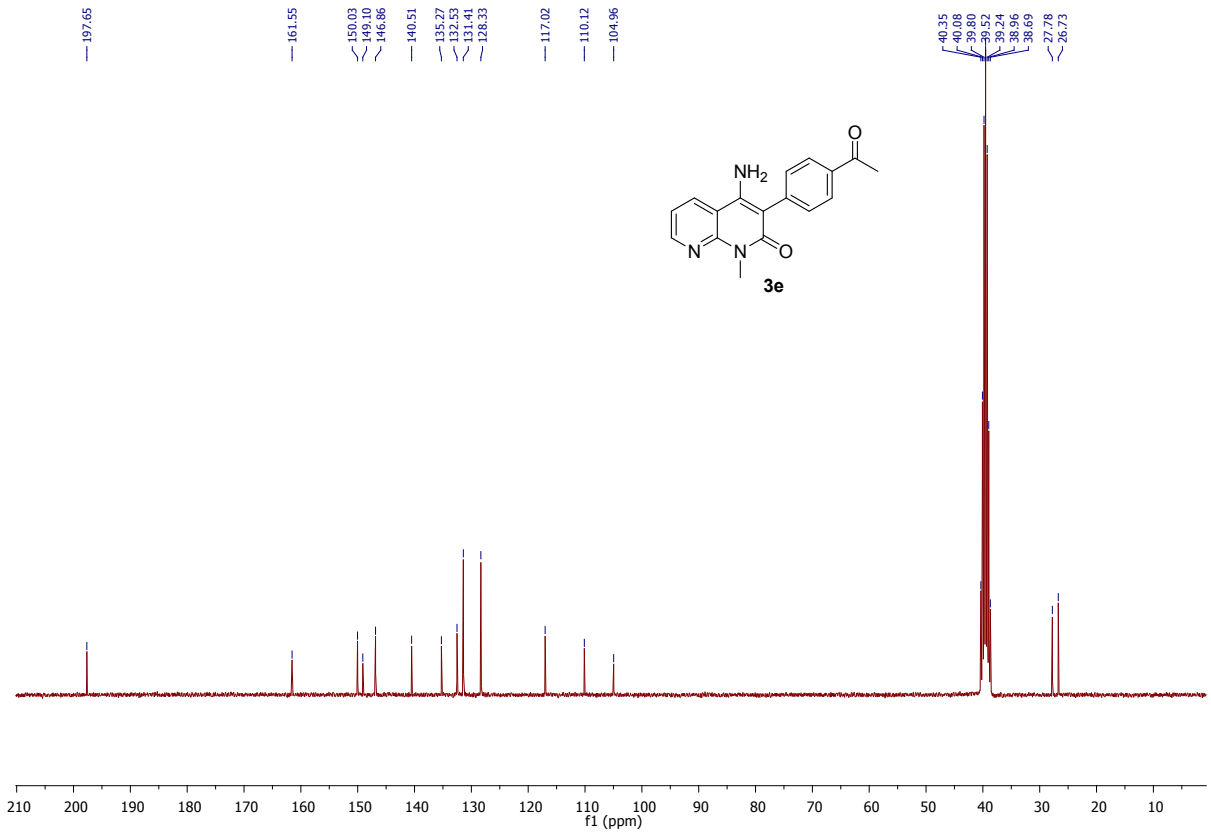
4-(4-Acetylphenyl)-3-amino-1-methyl-1,8-naphthyridin-2(1*H*)-one (2e)



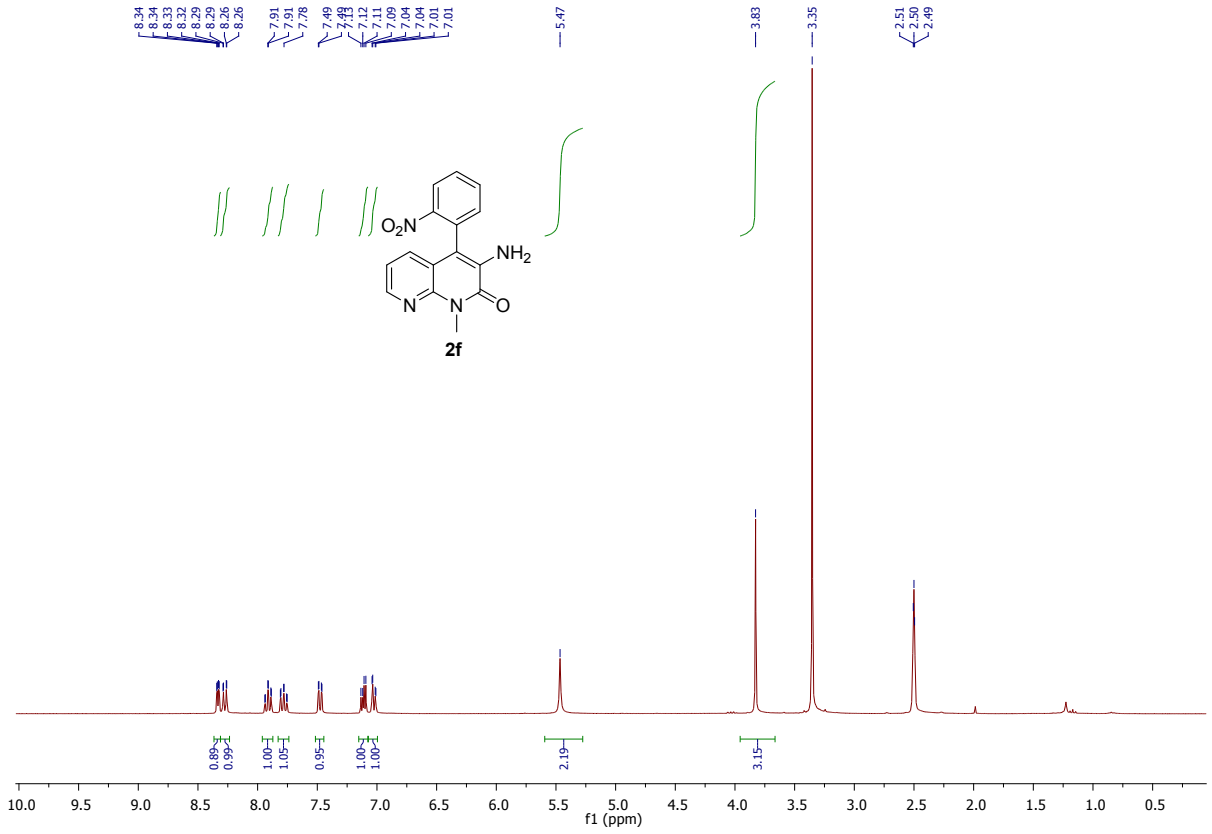


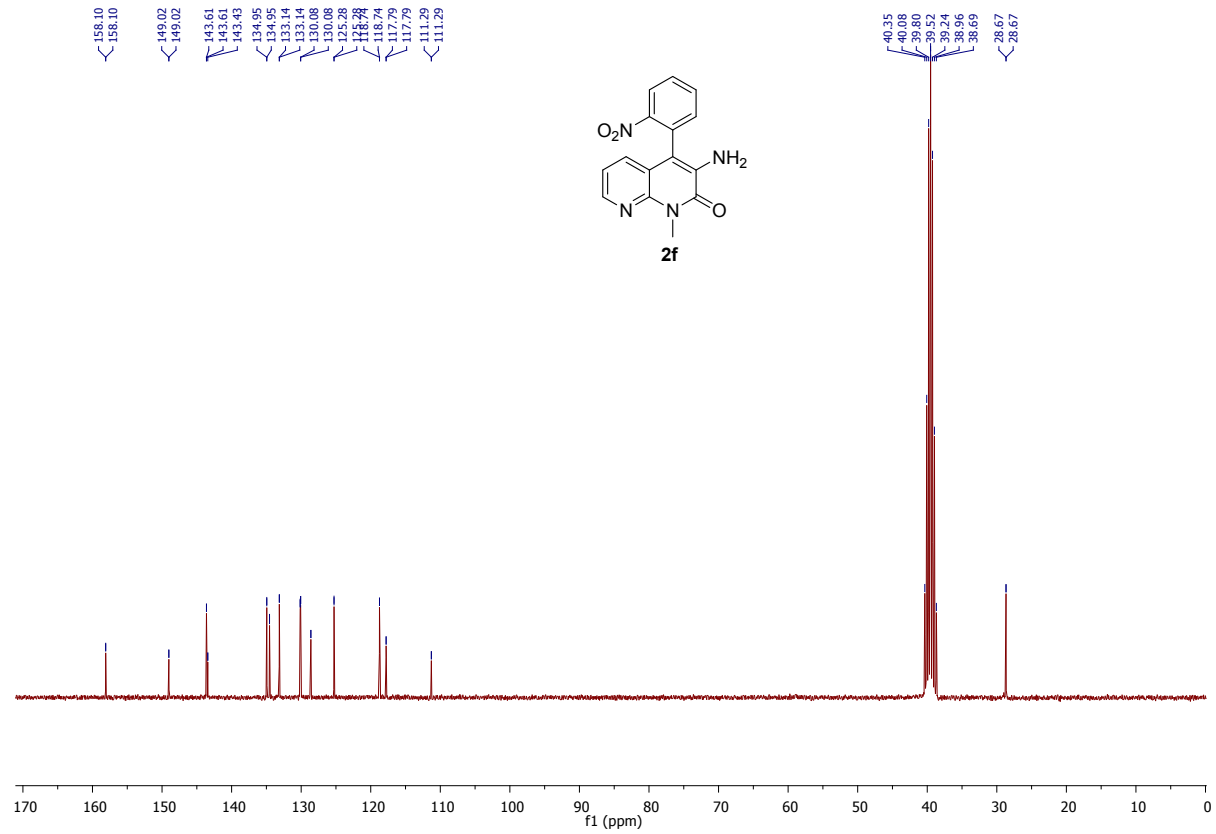
3-(4-Acetylphenyl)-4-amino-1-methyl-1,8-naphthyridin-2(1*H*)-one (3e)



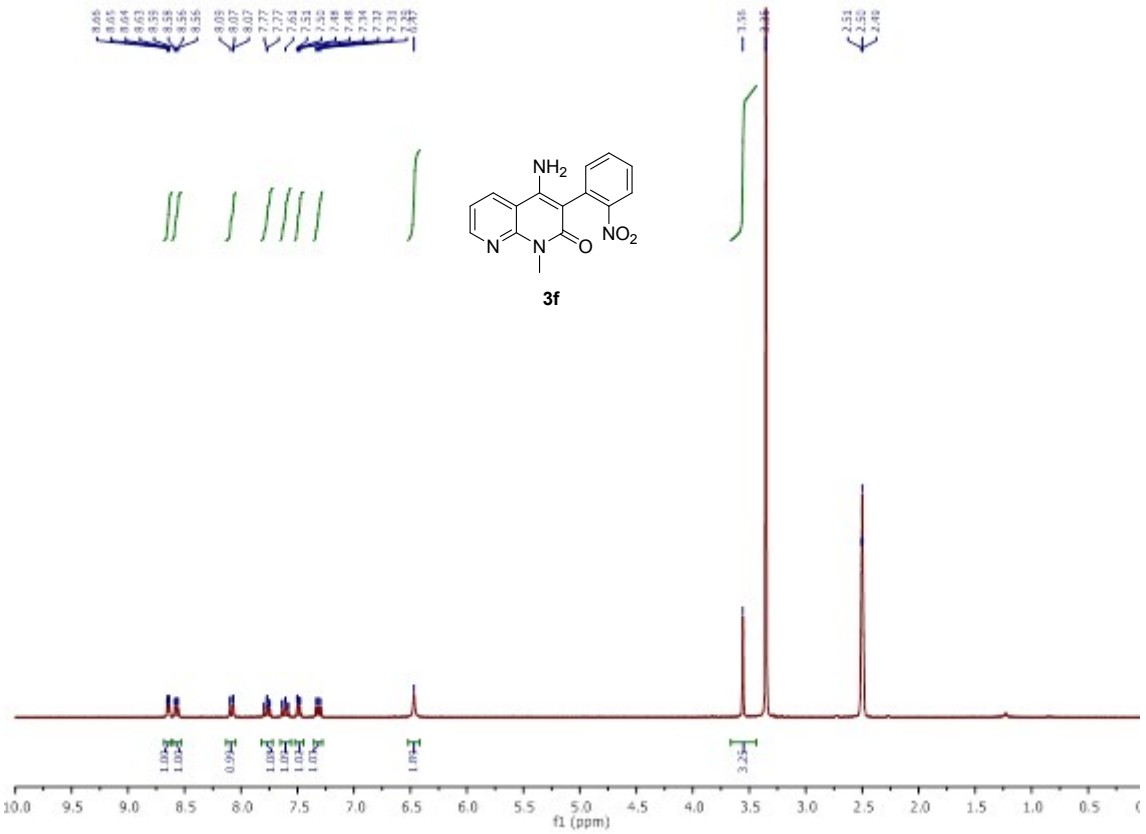


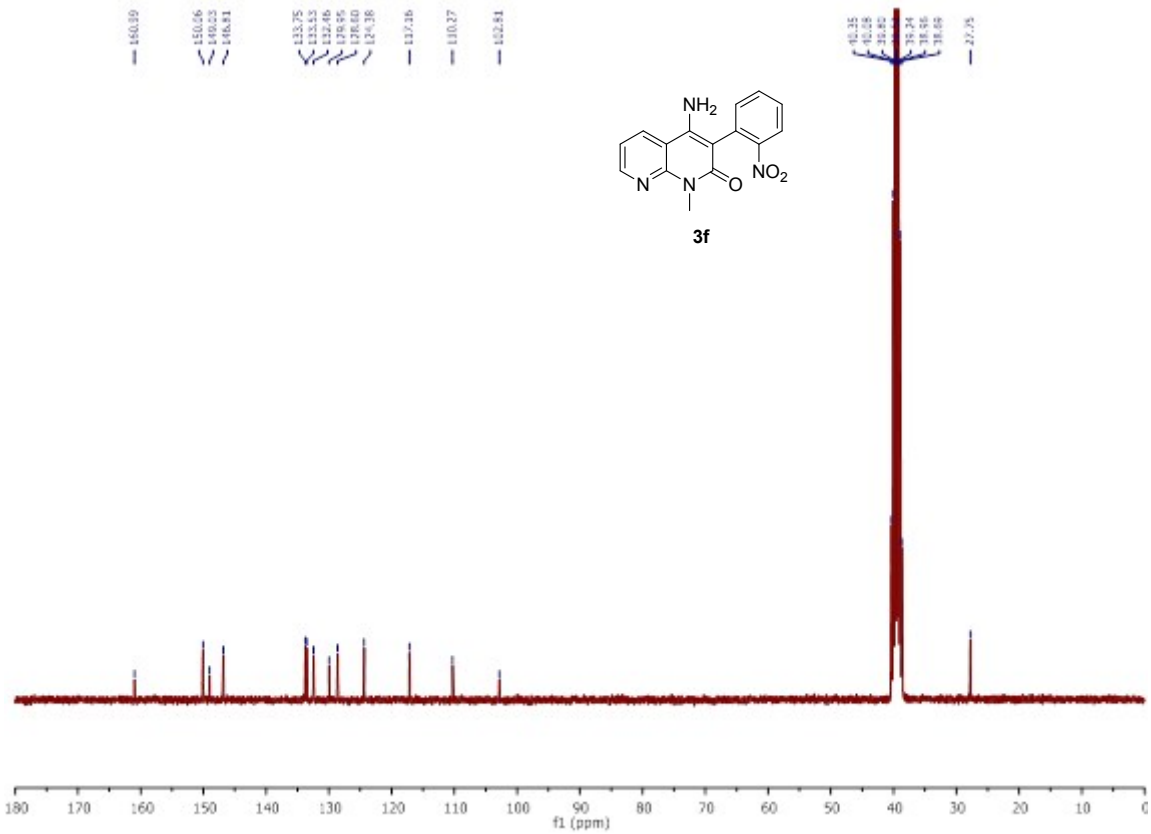
3-Amino-1-methyl-4-(2-nitrophenyl)-1,8-naphthyridin-2(1*H*)-one (2f)



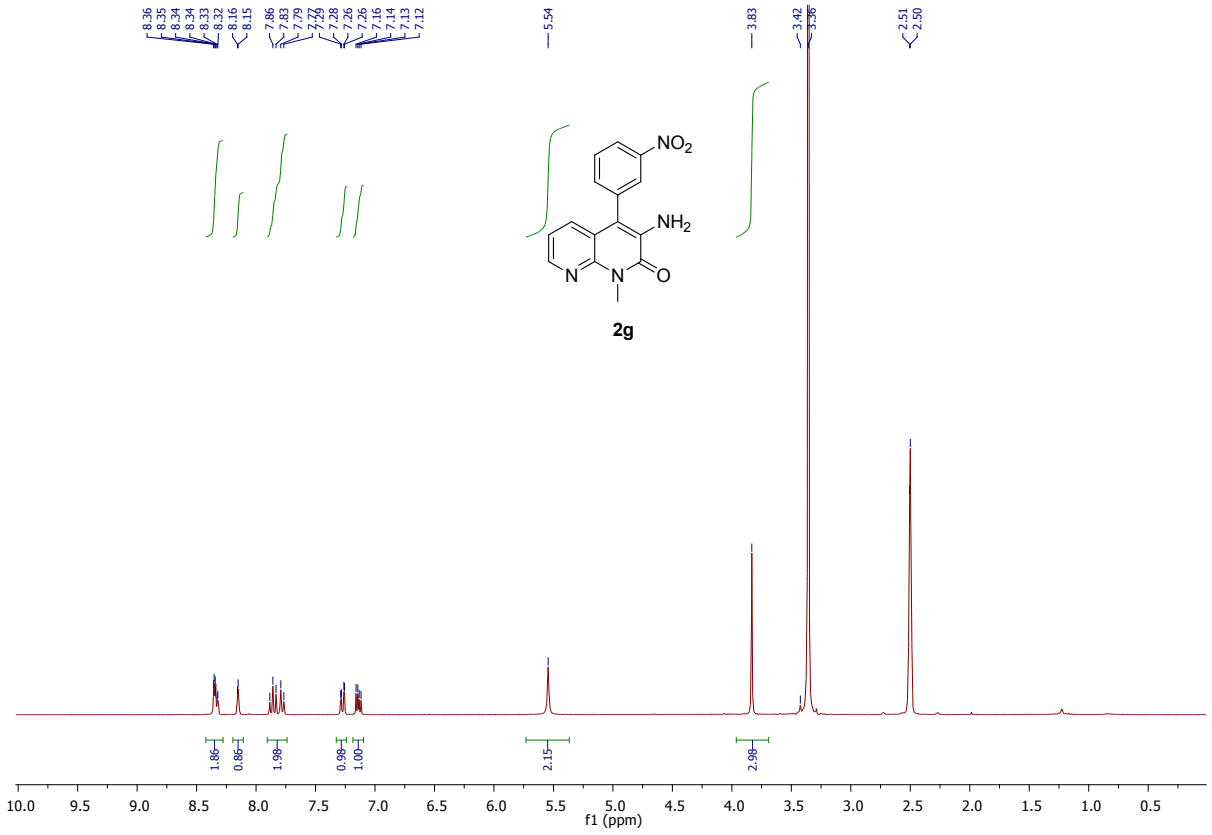


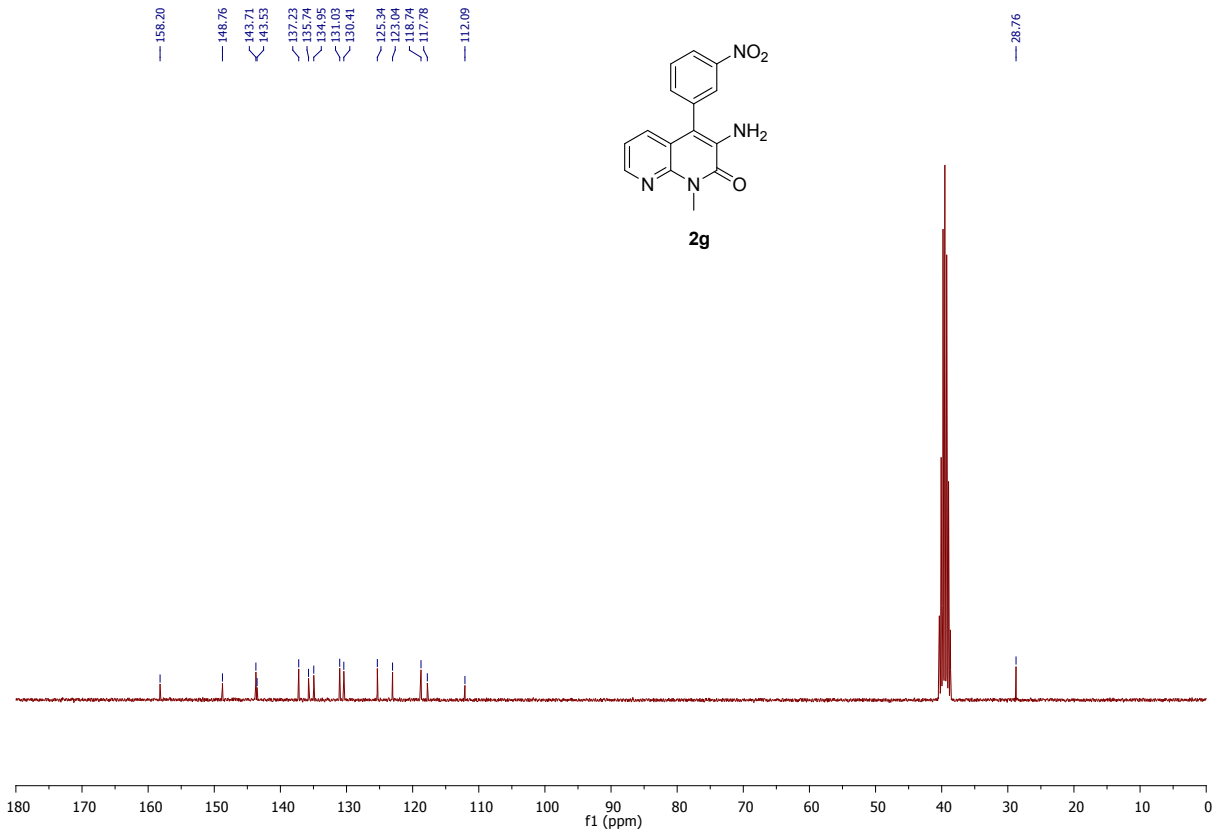
4-Amino-1-methyl-3-(2-nitrophenyl)-1,8-naphthyridin-2(1*H*)-one (3f)



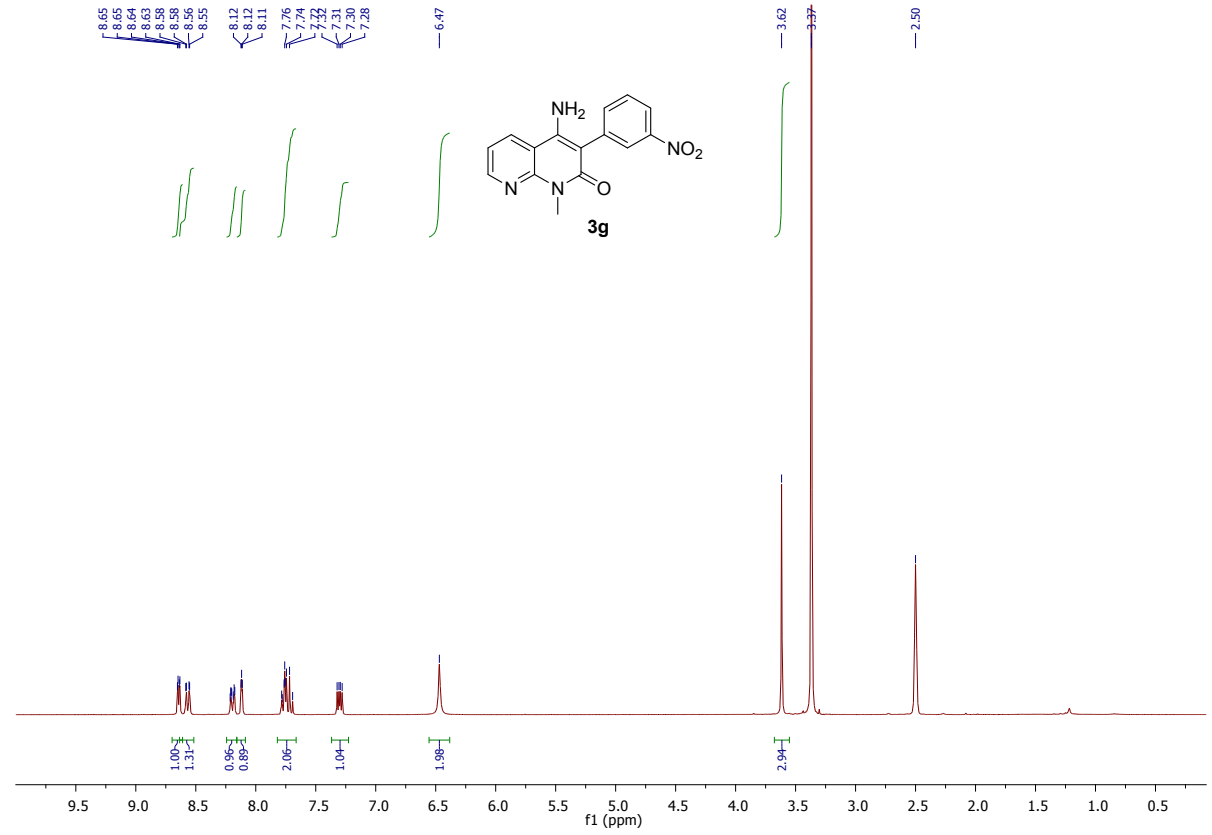


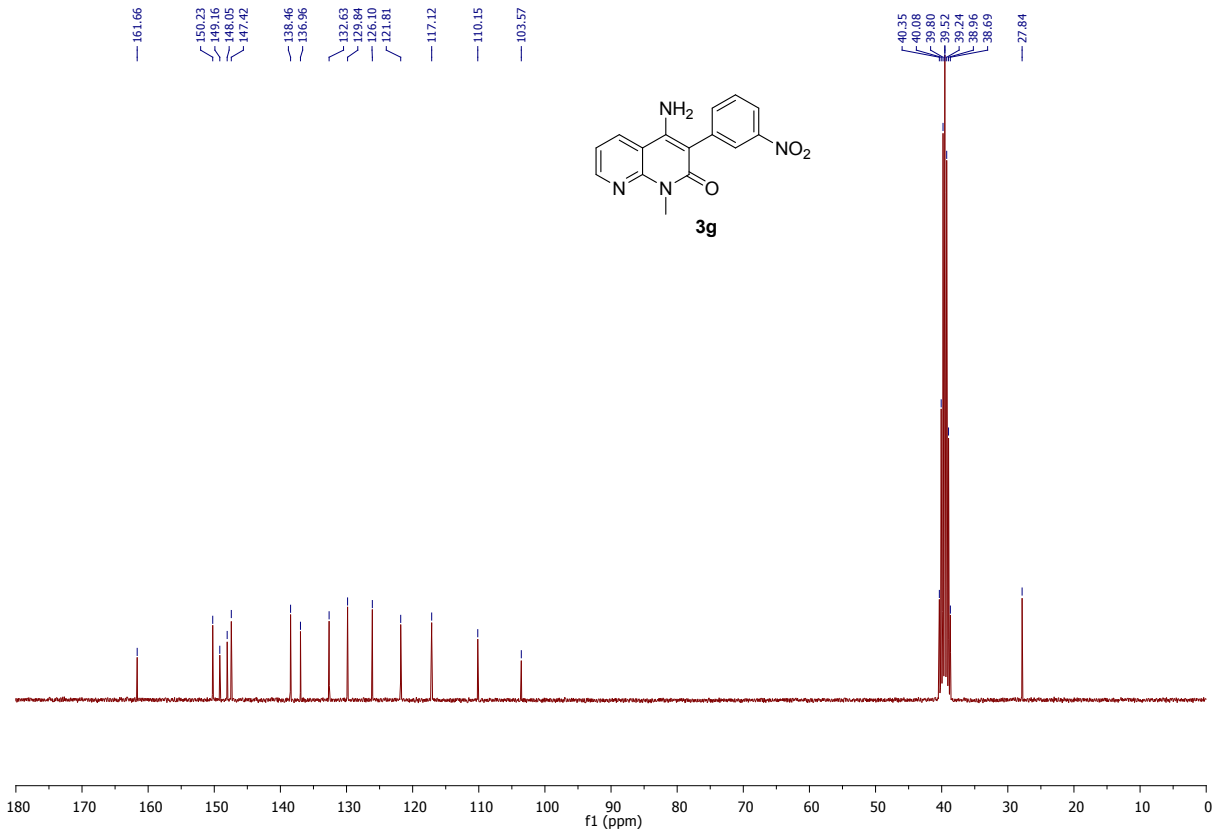
3-Amino-1-methyl-4-(3-nitrophenyl)-1,8-naphthyridin-2(1*H*)-one (2g)



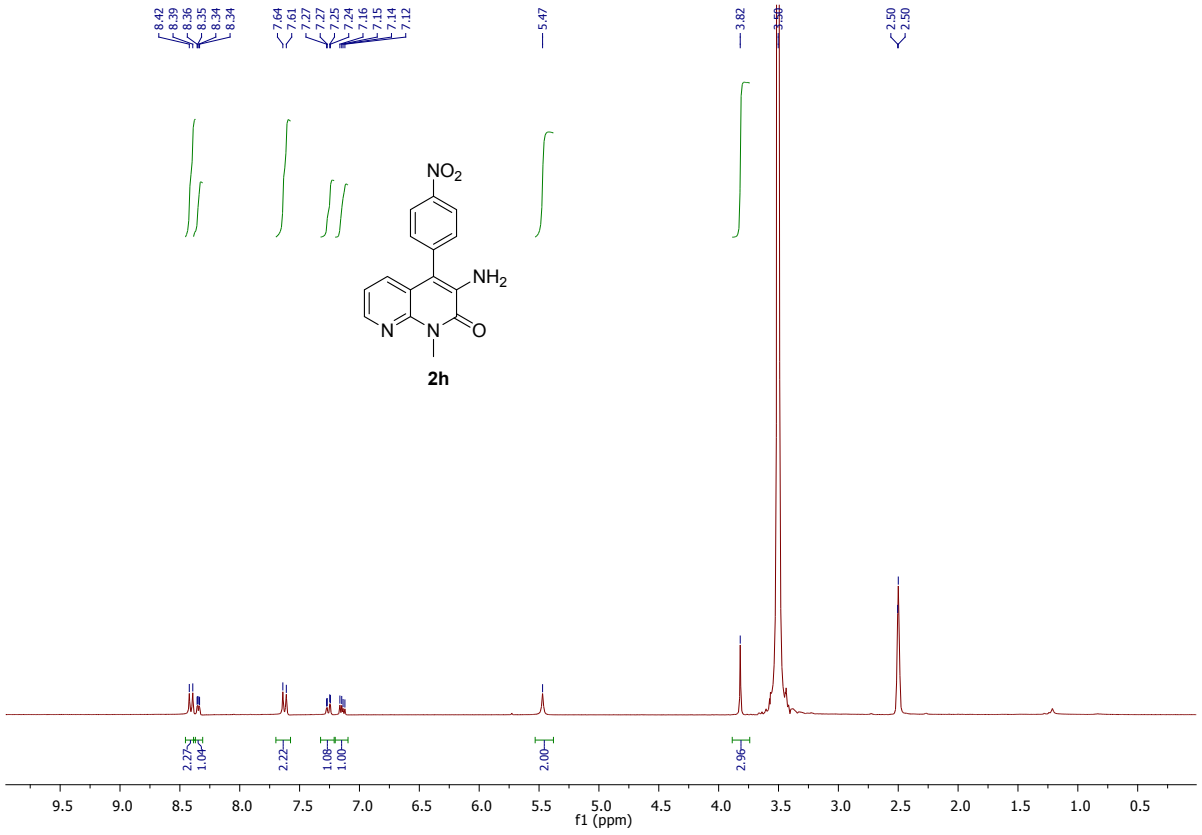


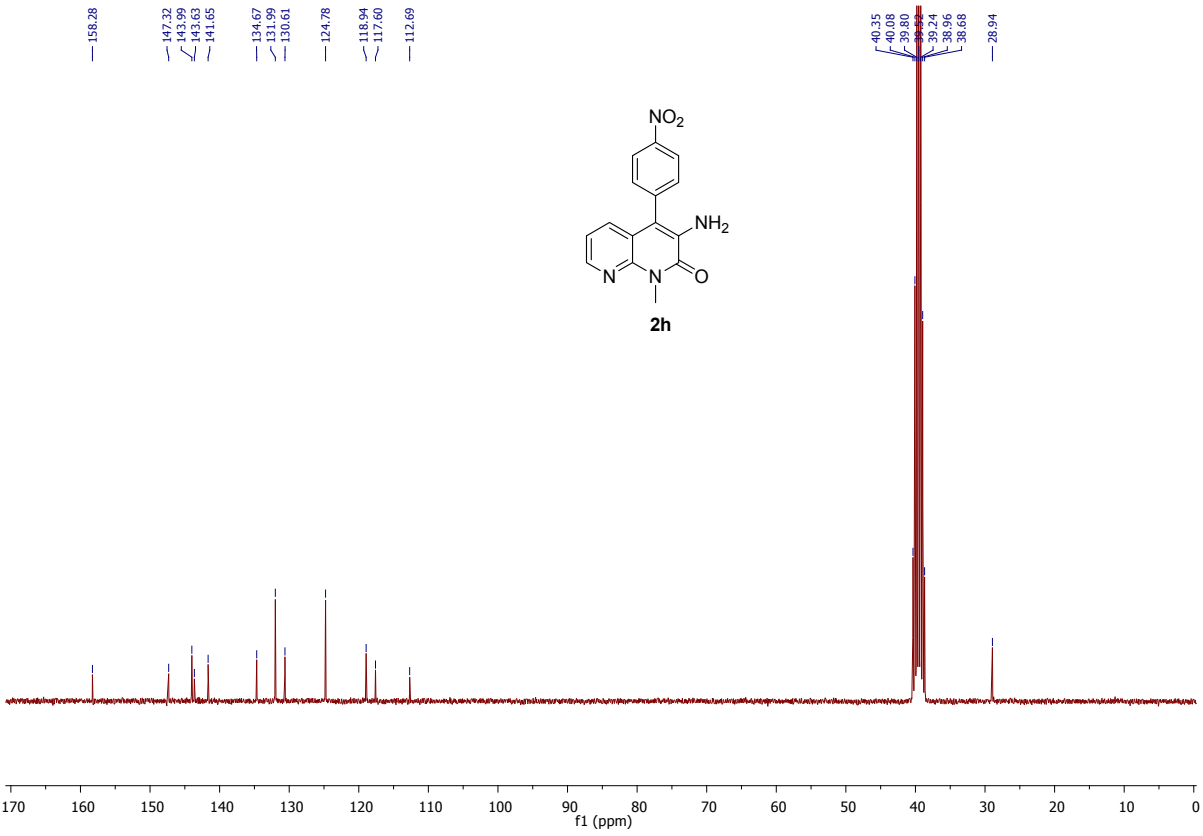
4-Amino-1-methyl-3-(3-nitrophenyl)-1,8-naphthyridin-2(1*H*)-one (3g)



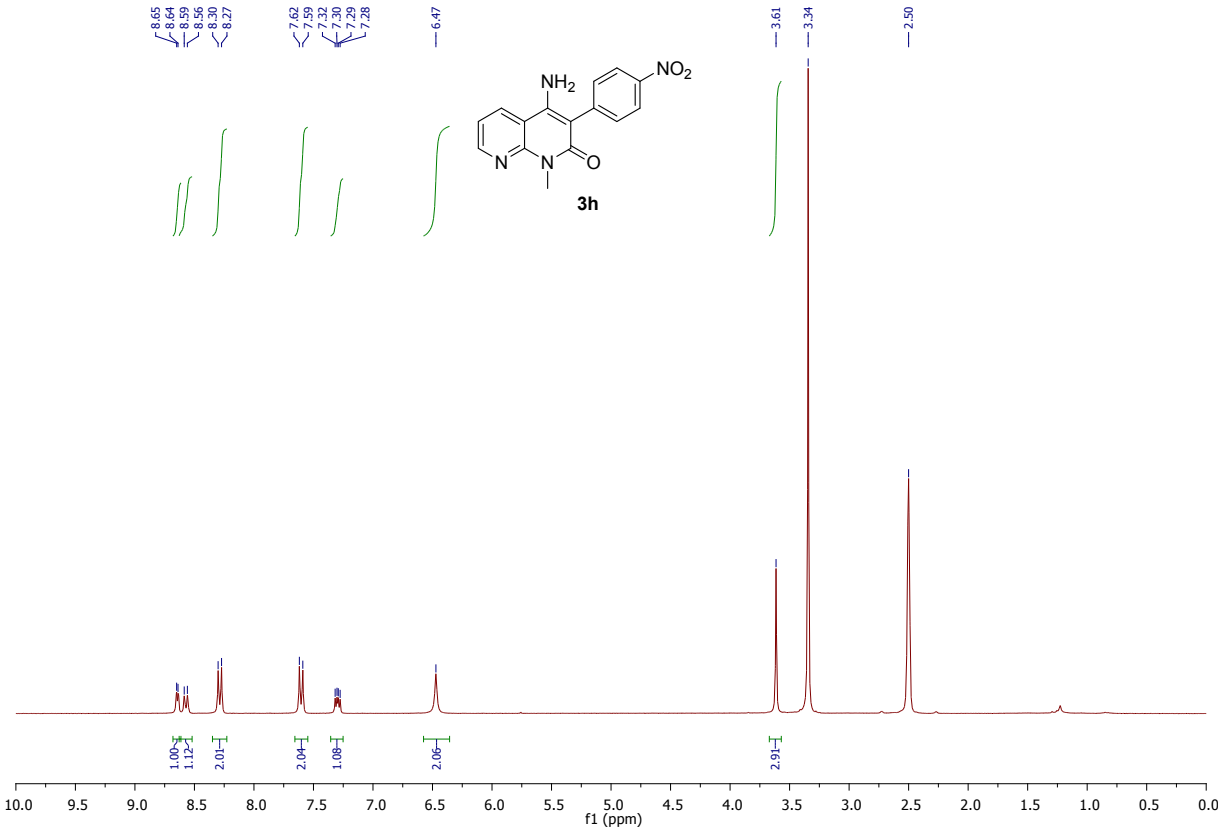


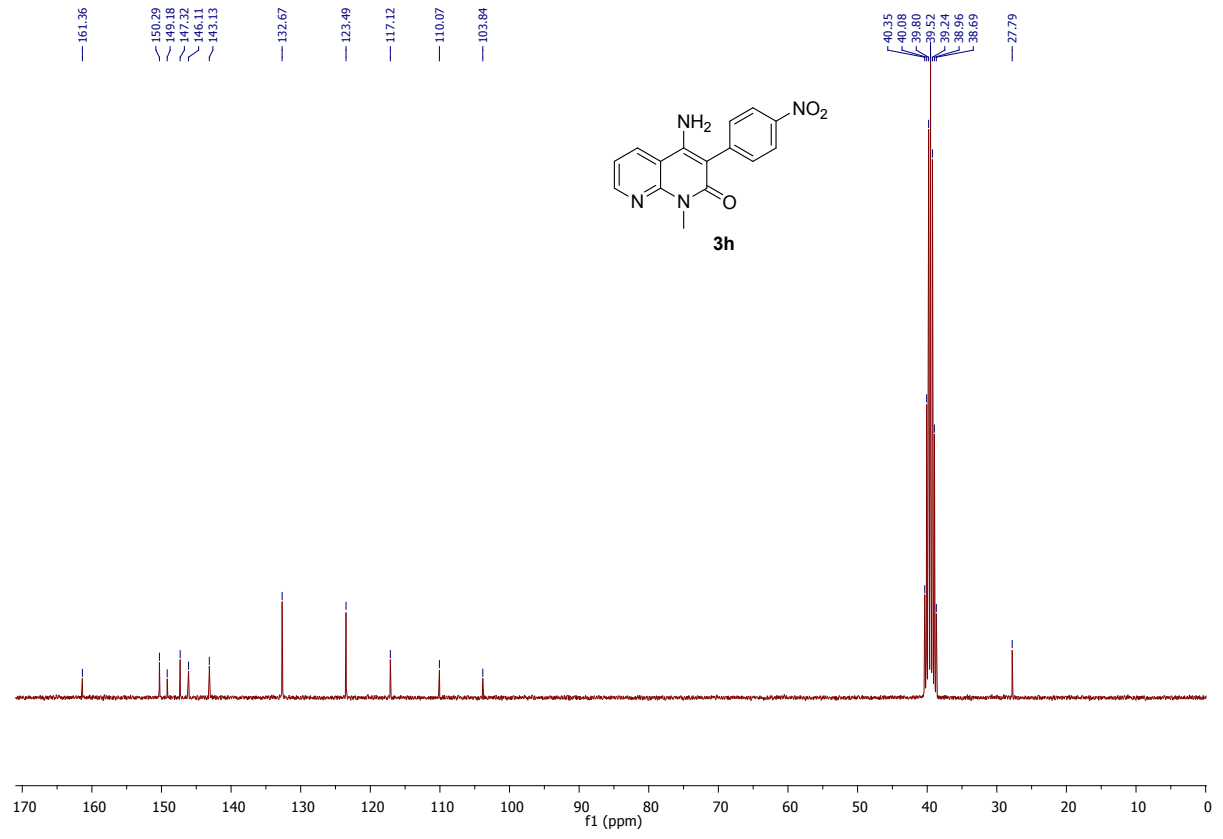
3-Amino-1-methyl-4-(4-nitrophenyl)-1,8-naphthyridin-2(1*H*)-one (2h)



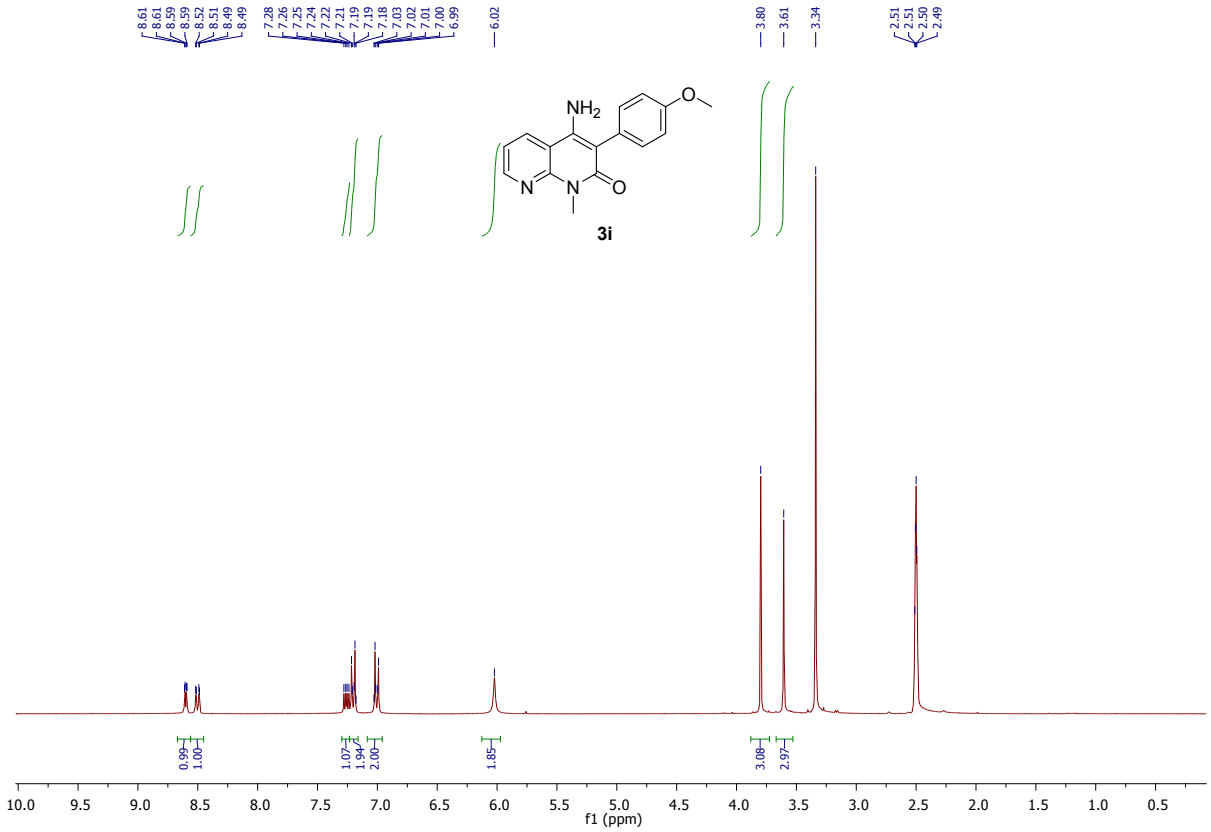


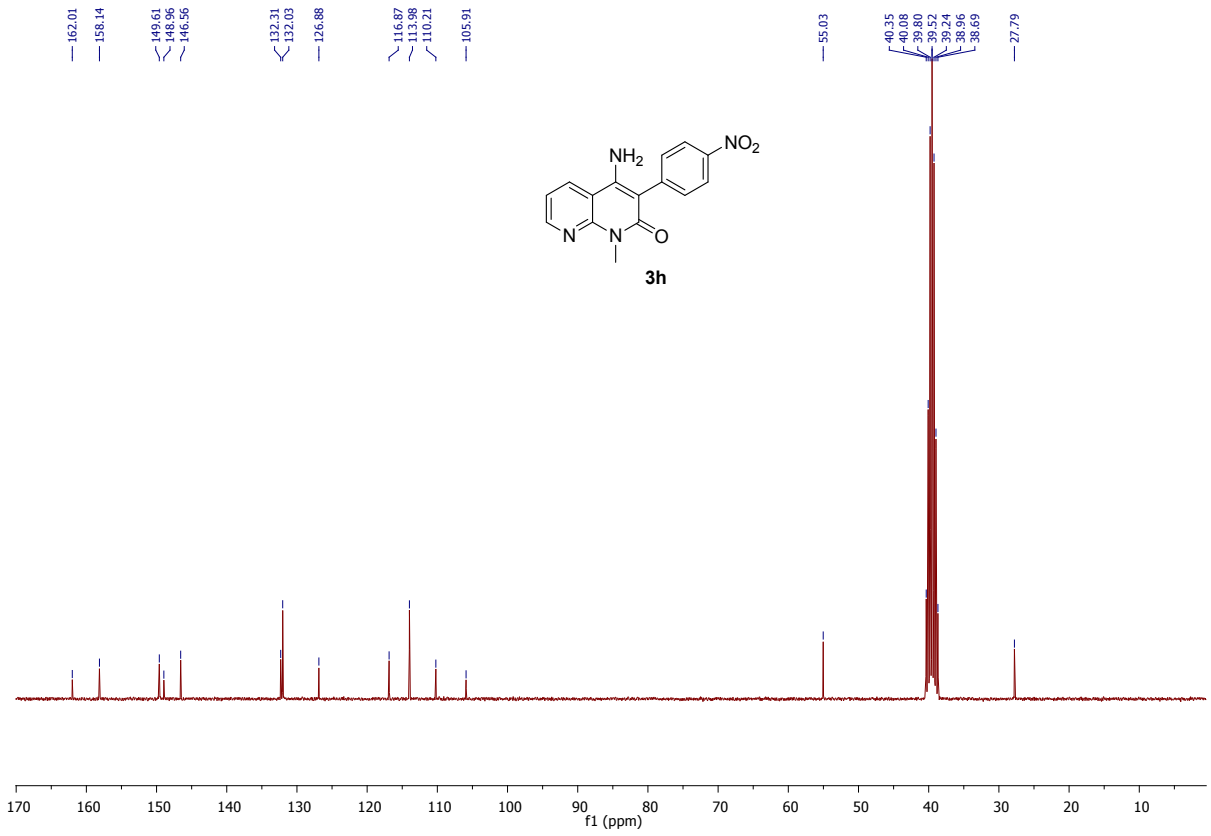
4-Amino-1-methyl-3-(4-nitrophenyl)-1,8-naphthyridin-2(1*H*)-one (3h)



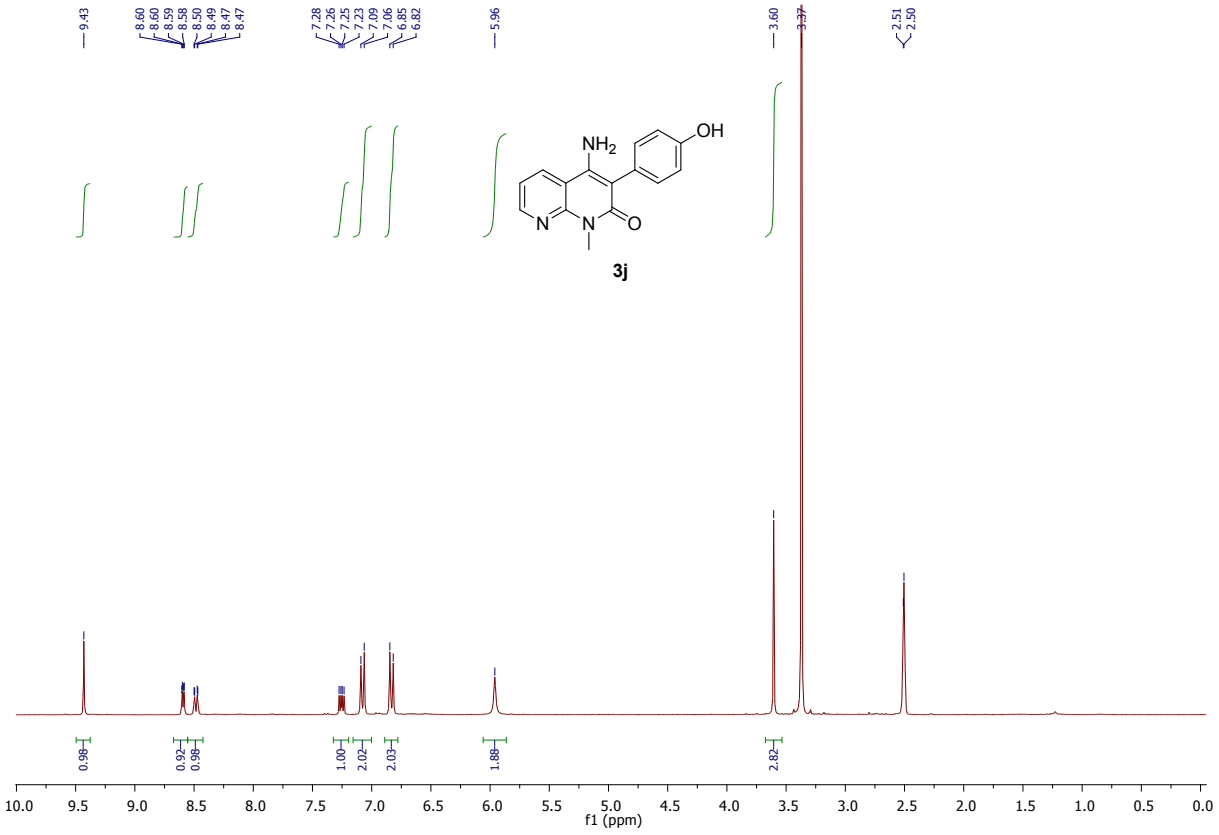


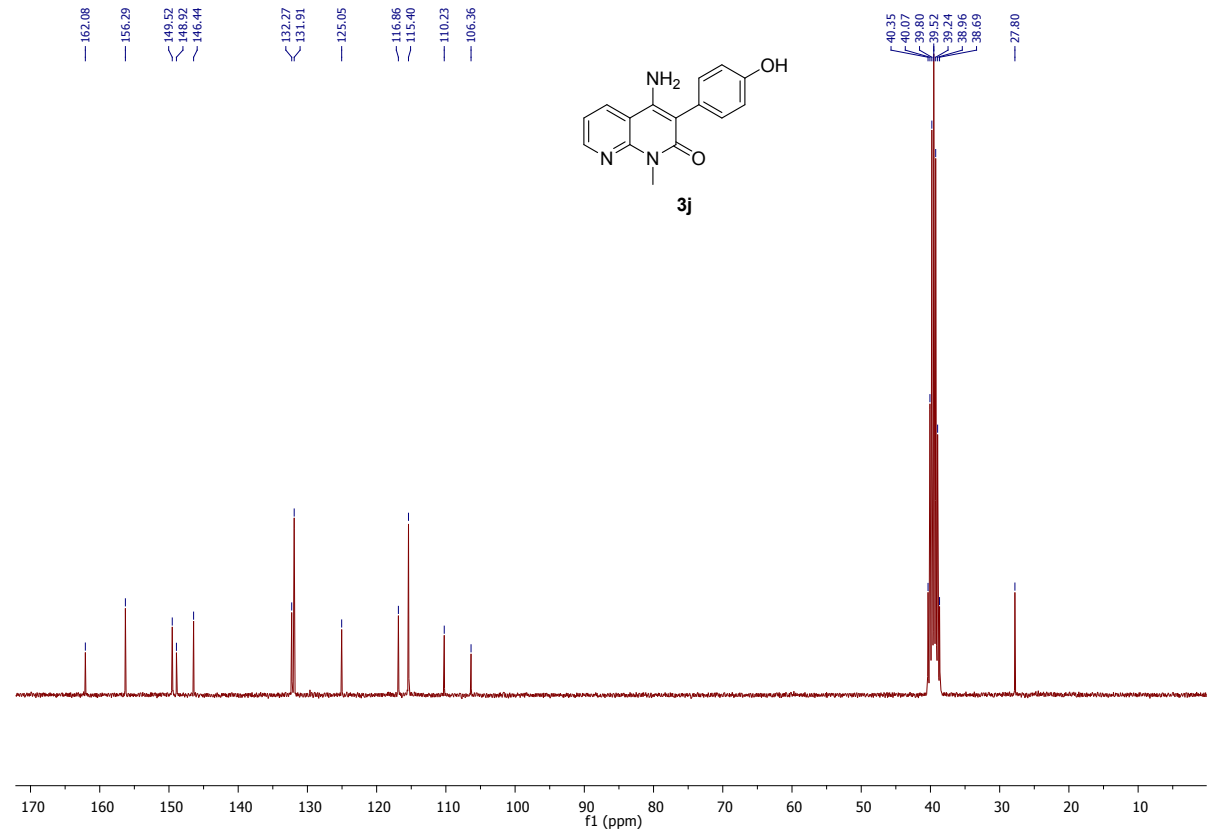
4-Amino-3-(4-methoxyphenyl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (3i)



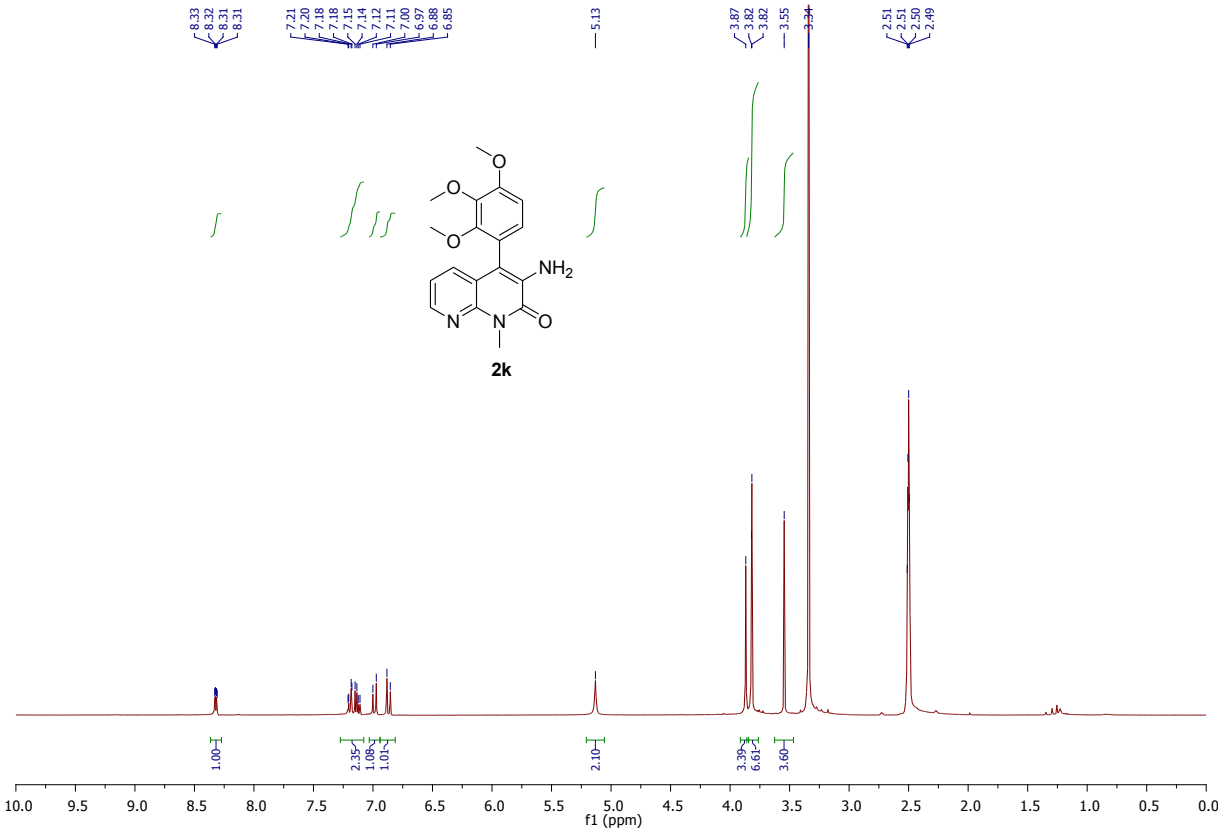


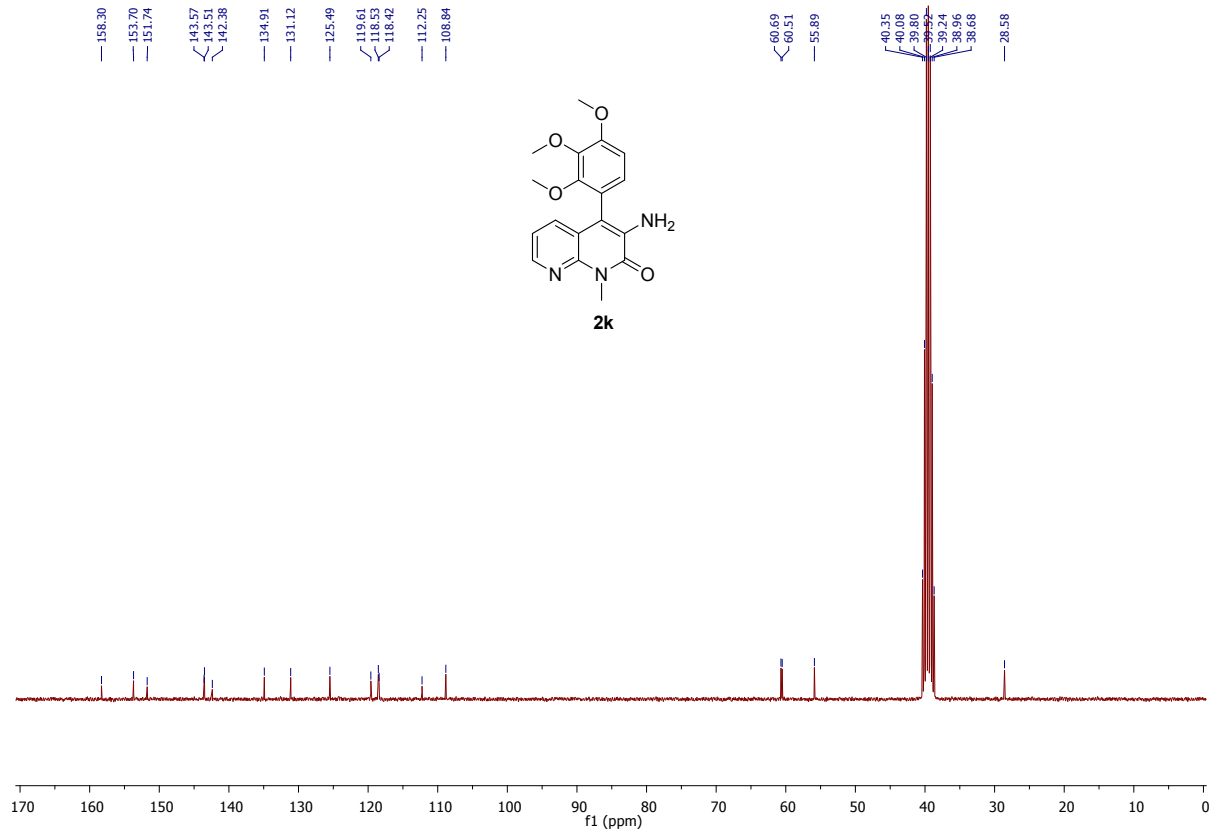
4-Amino-3-(4-hydroxyphenyl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (3j)



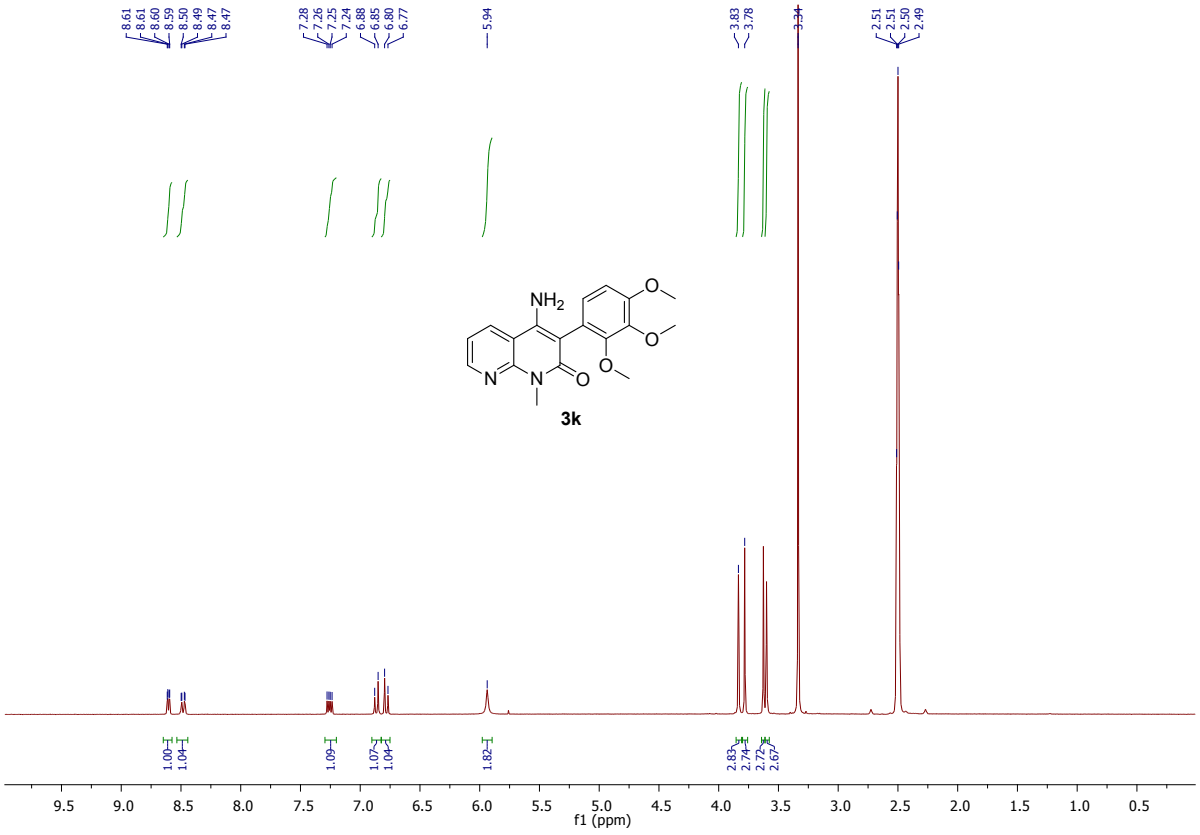


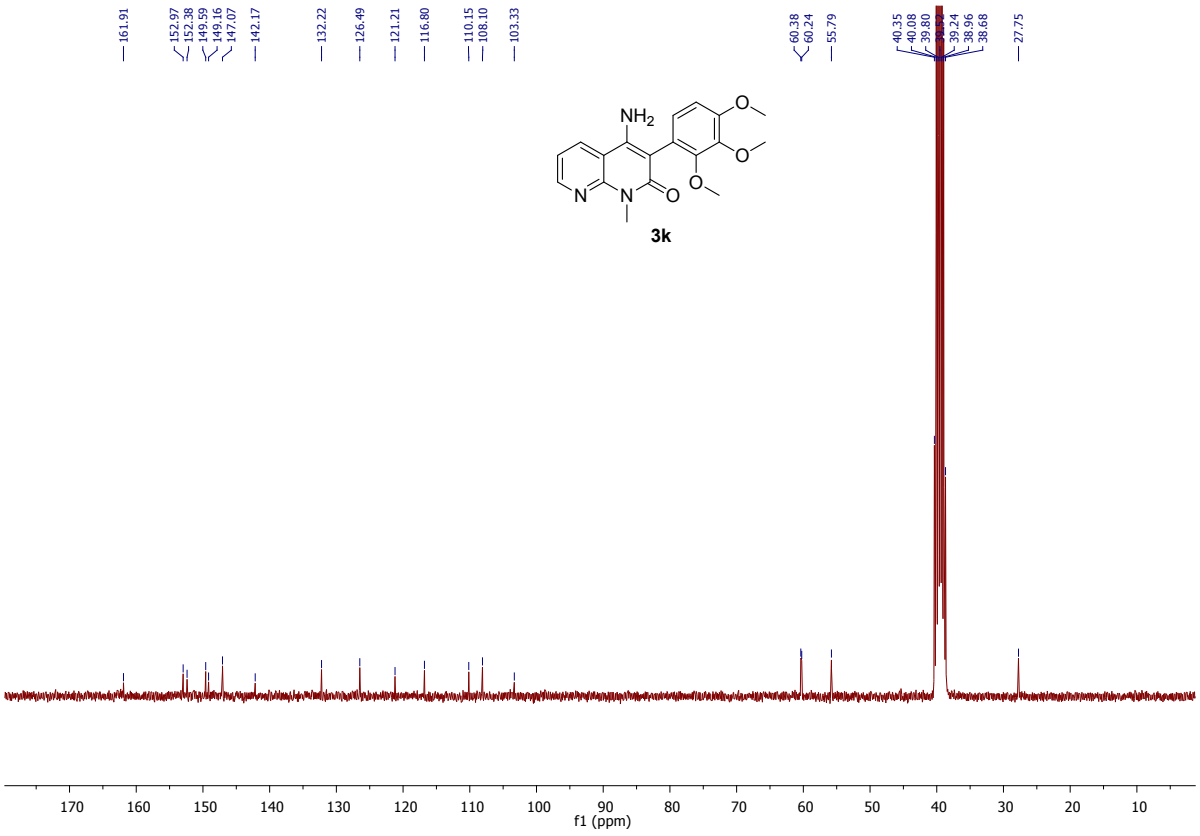
3-Amino-1-methyl-4-(2,3,4-trimethoxyphenyl)-1,8-naphthyridin-2(1*H*)-one (2k)



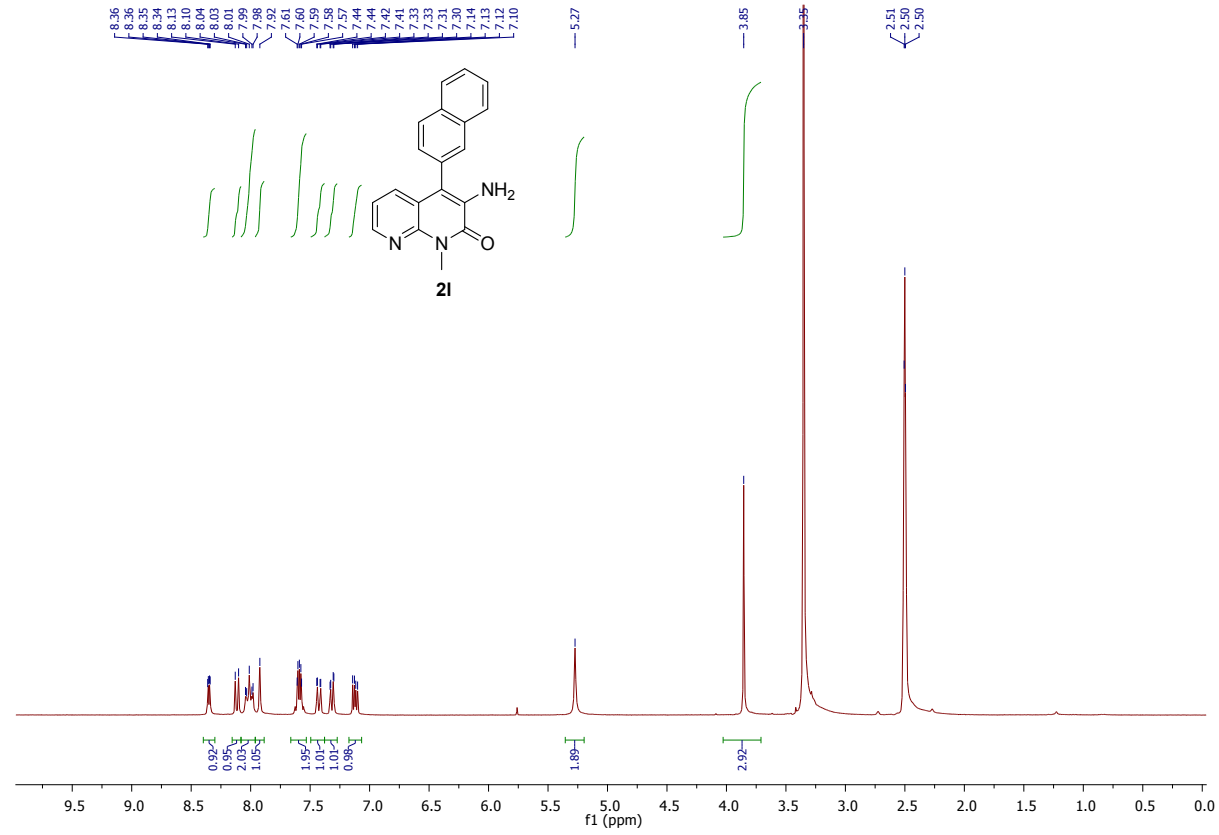


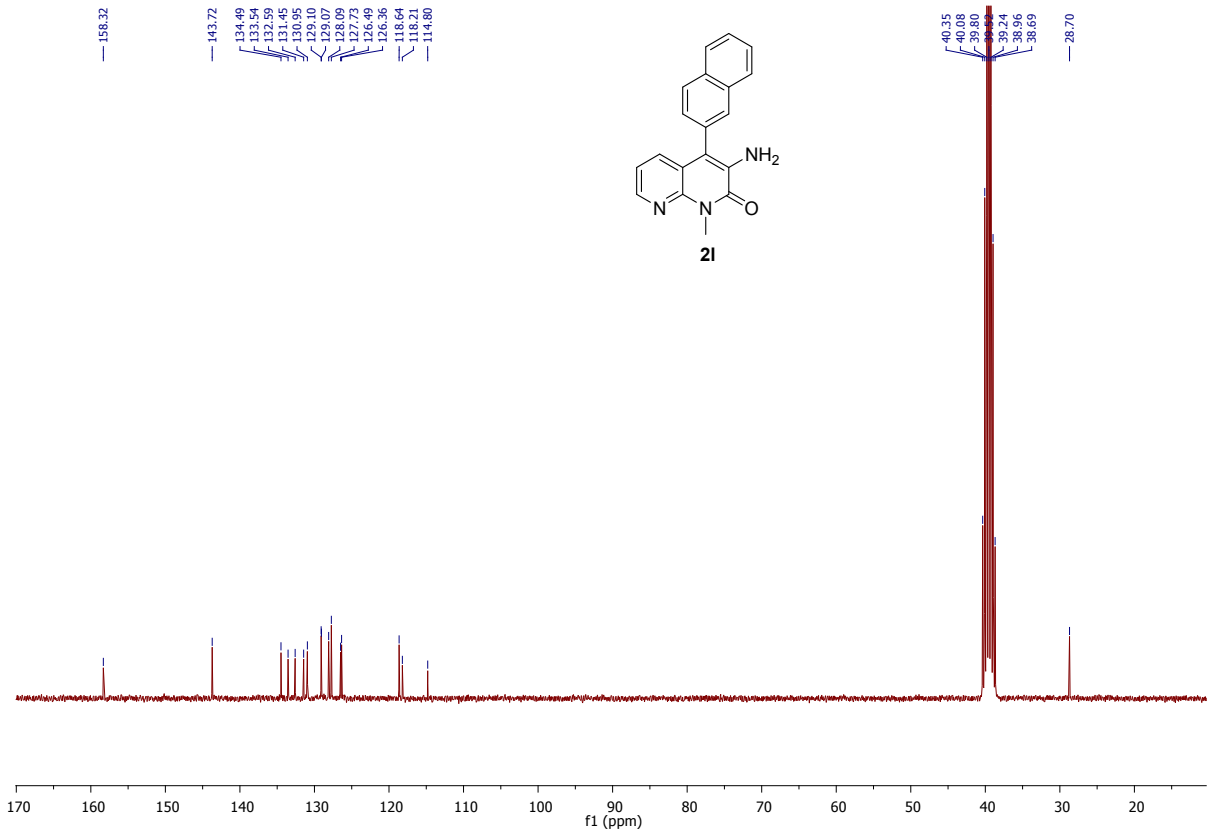
4-Amino-1-methyl-3-(2,3,4-trimethoxyphenyl)-1,8-naphthyridin-2(1*H*)-one (3k)



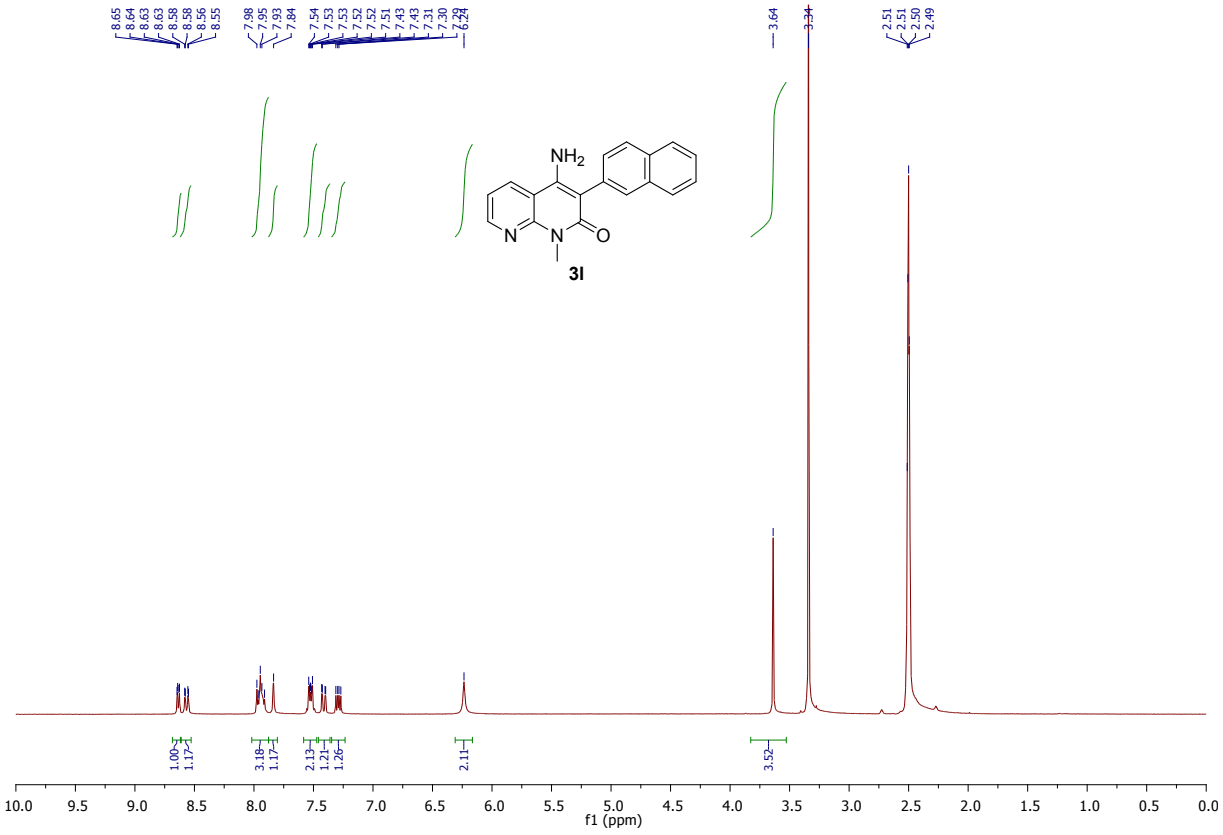


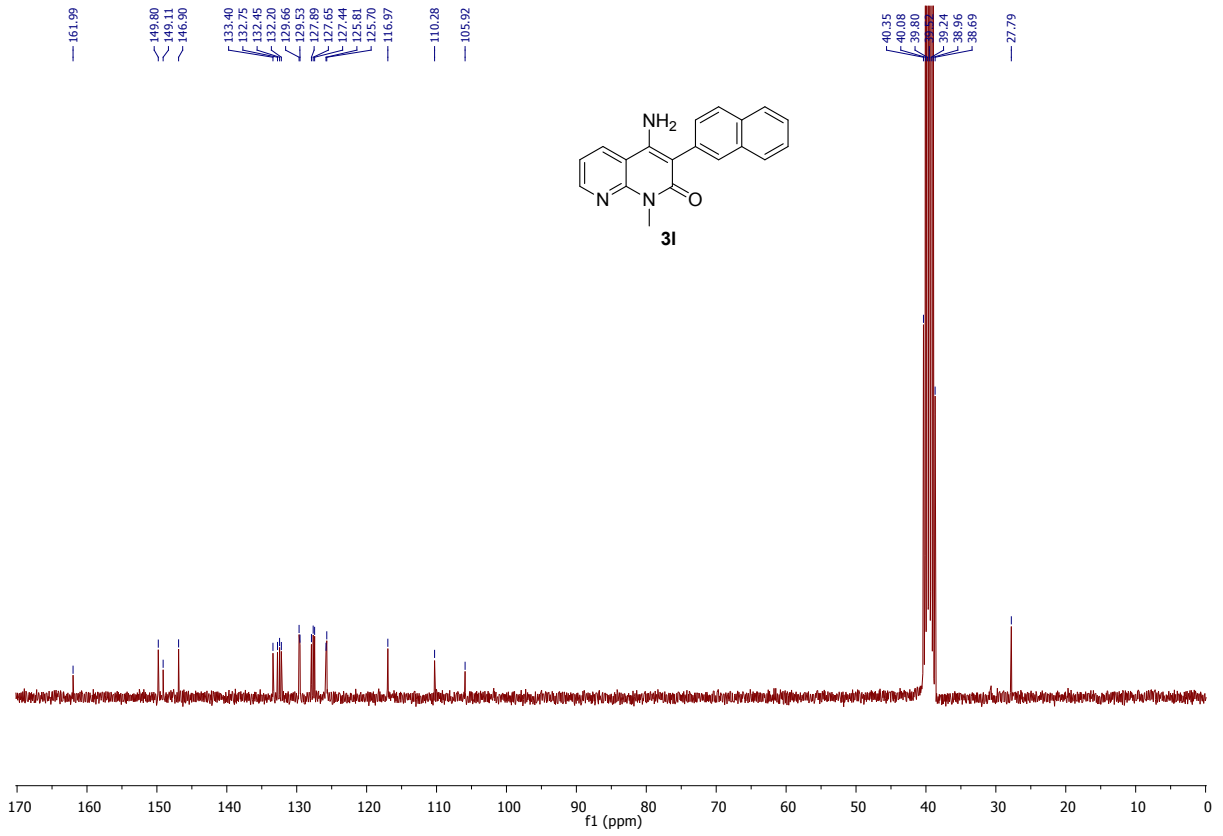
3-Amino-1-methyl-4-(naphthalen-2-yl)-1,8-naphthyridin-2(1*H*)-one (2l)





4-Amino-1-methyl-3-(naphthalen-2-yl)-1,8-naphthyridin-2(1*H*)-one (3l)





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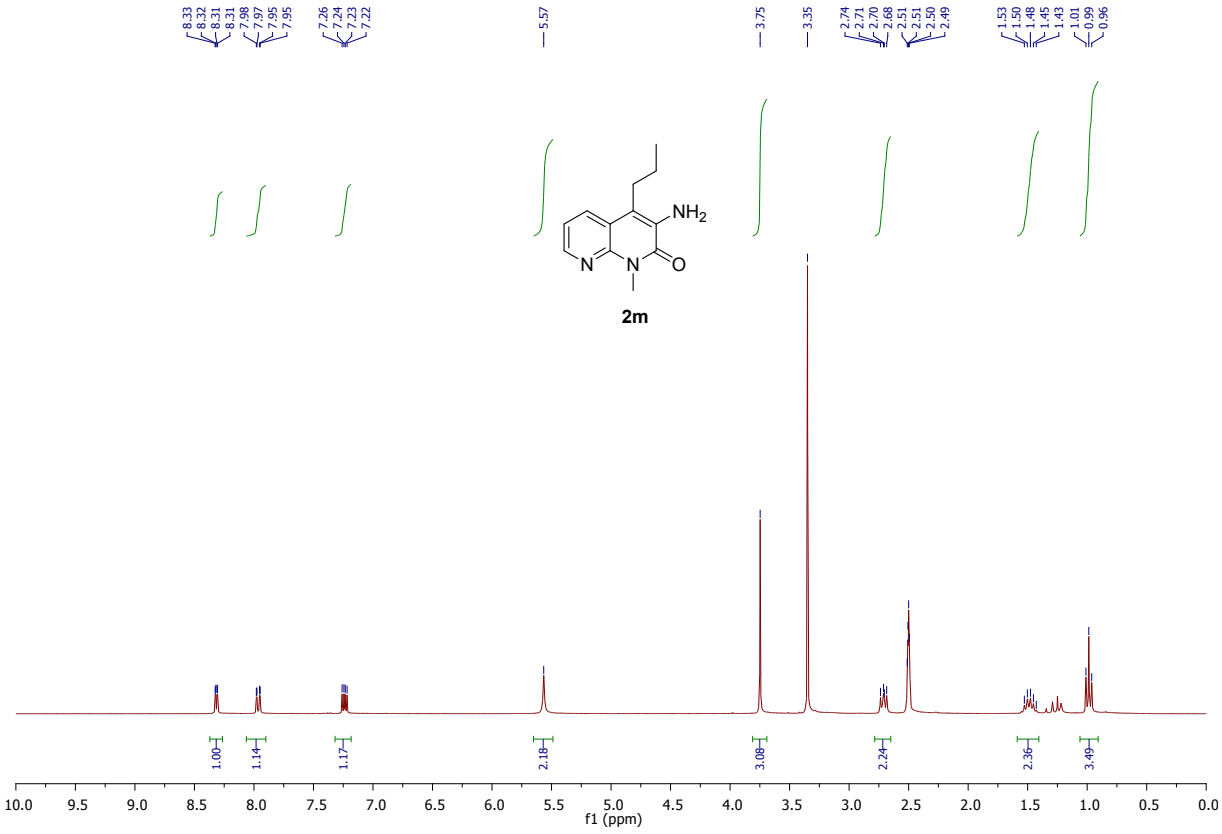

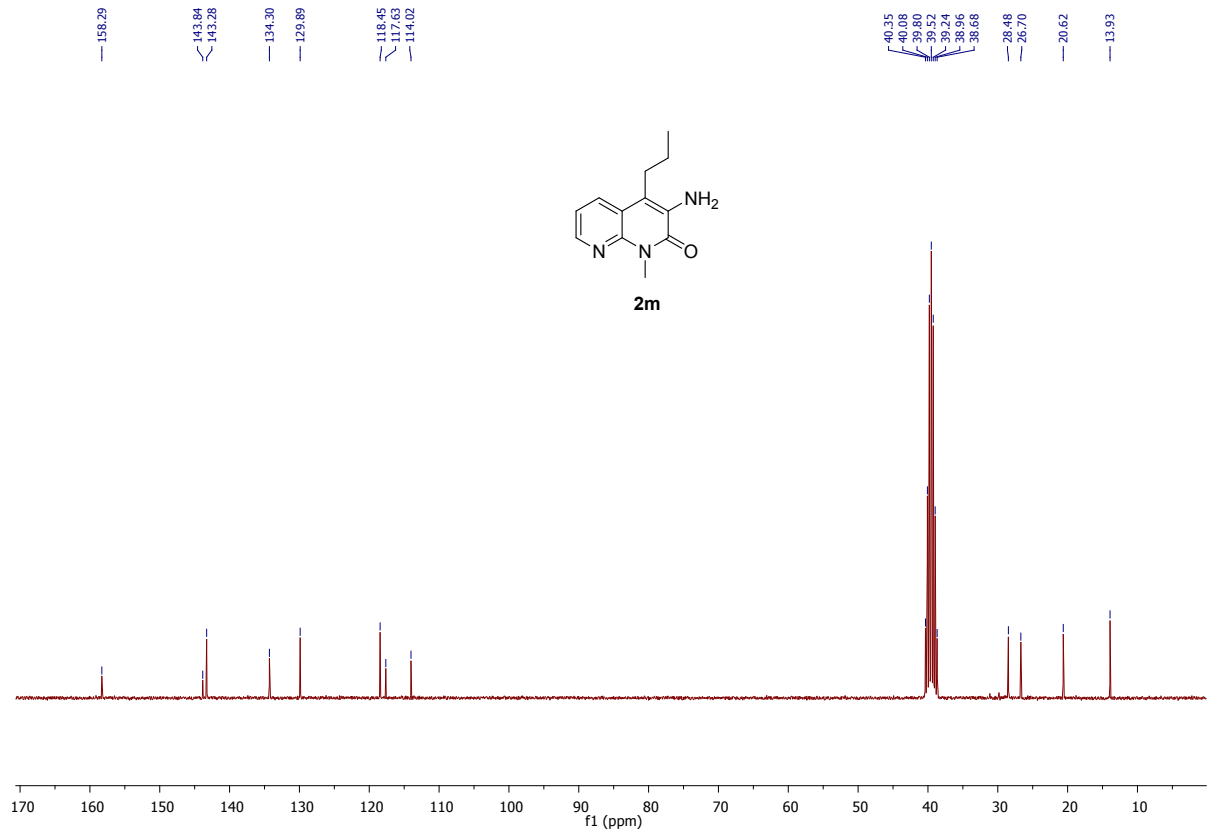

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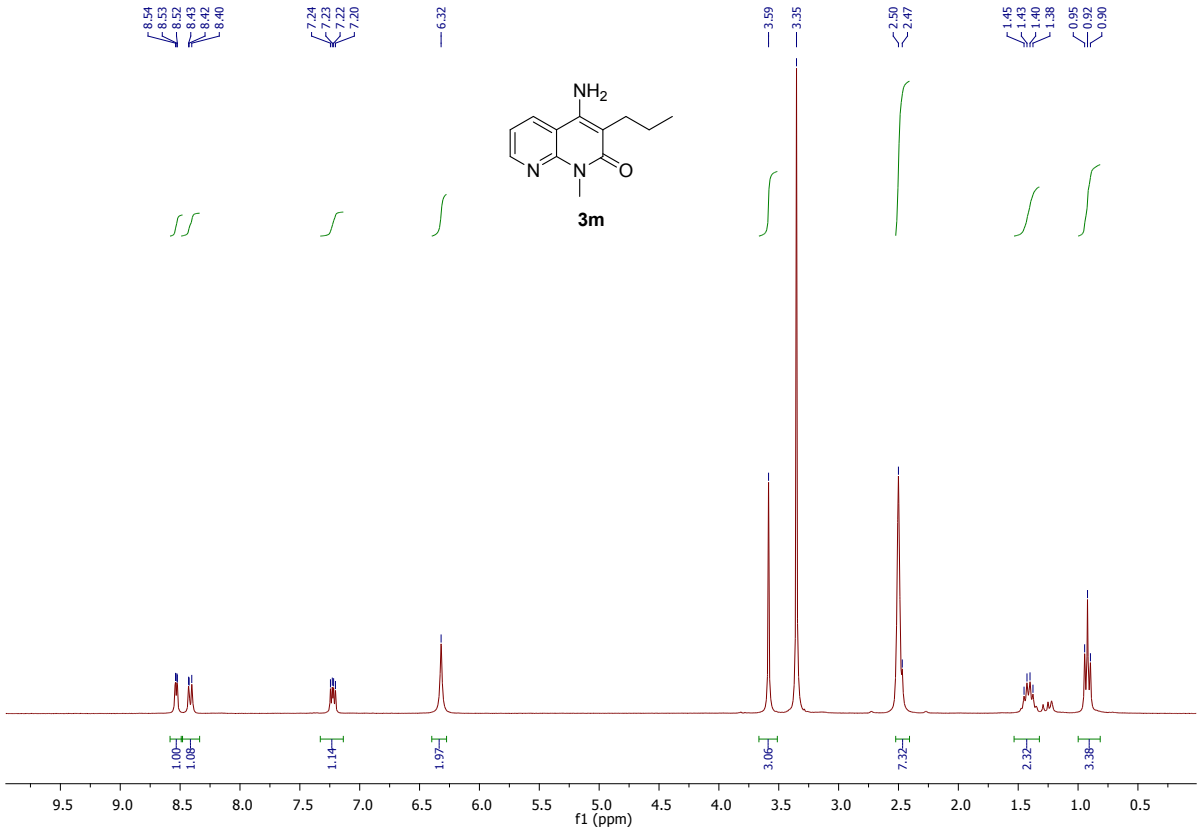

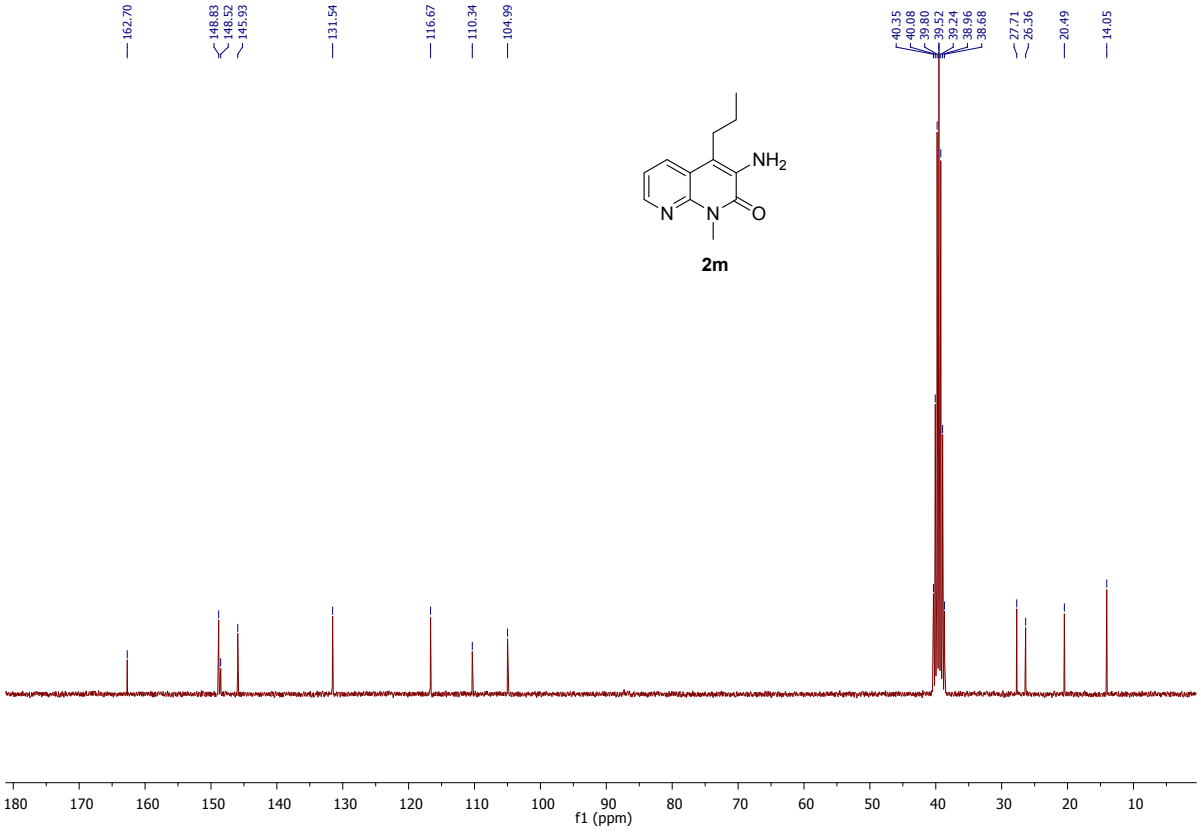

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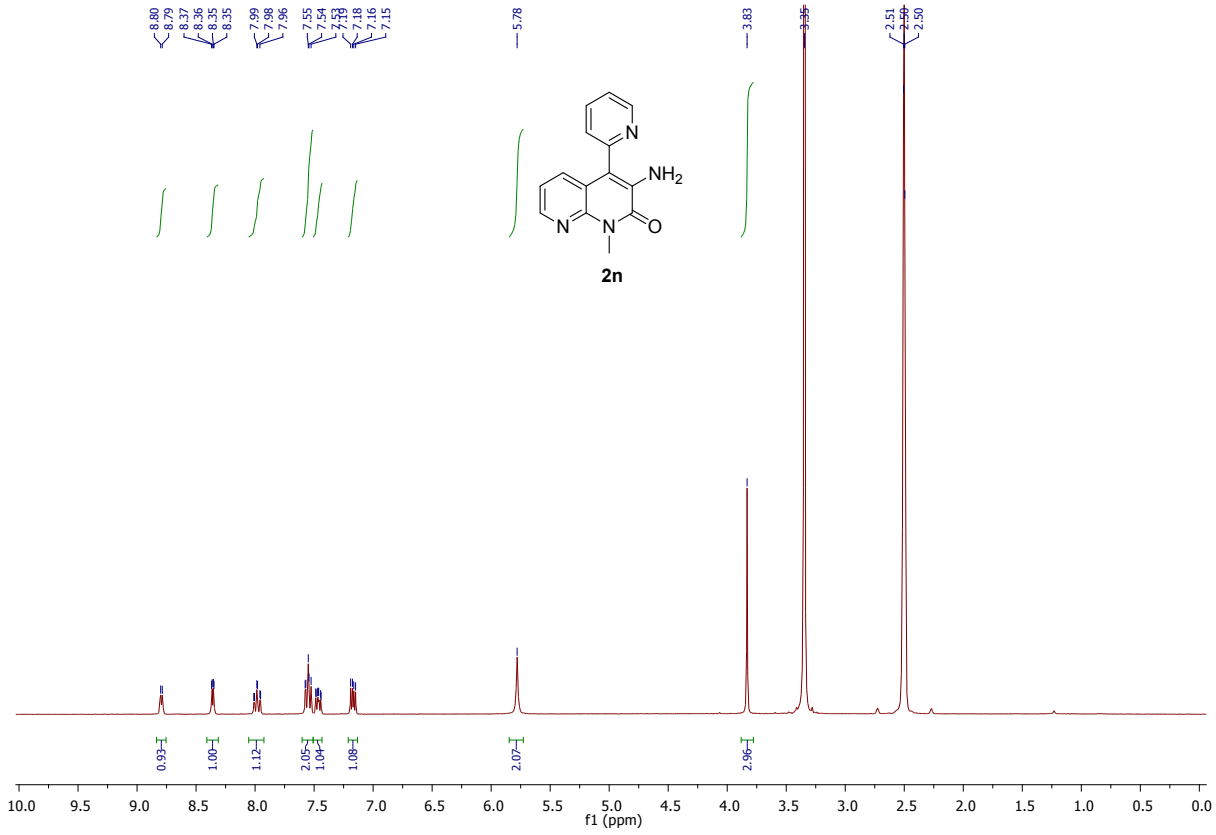

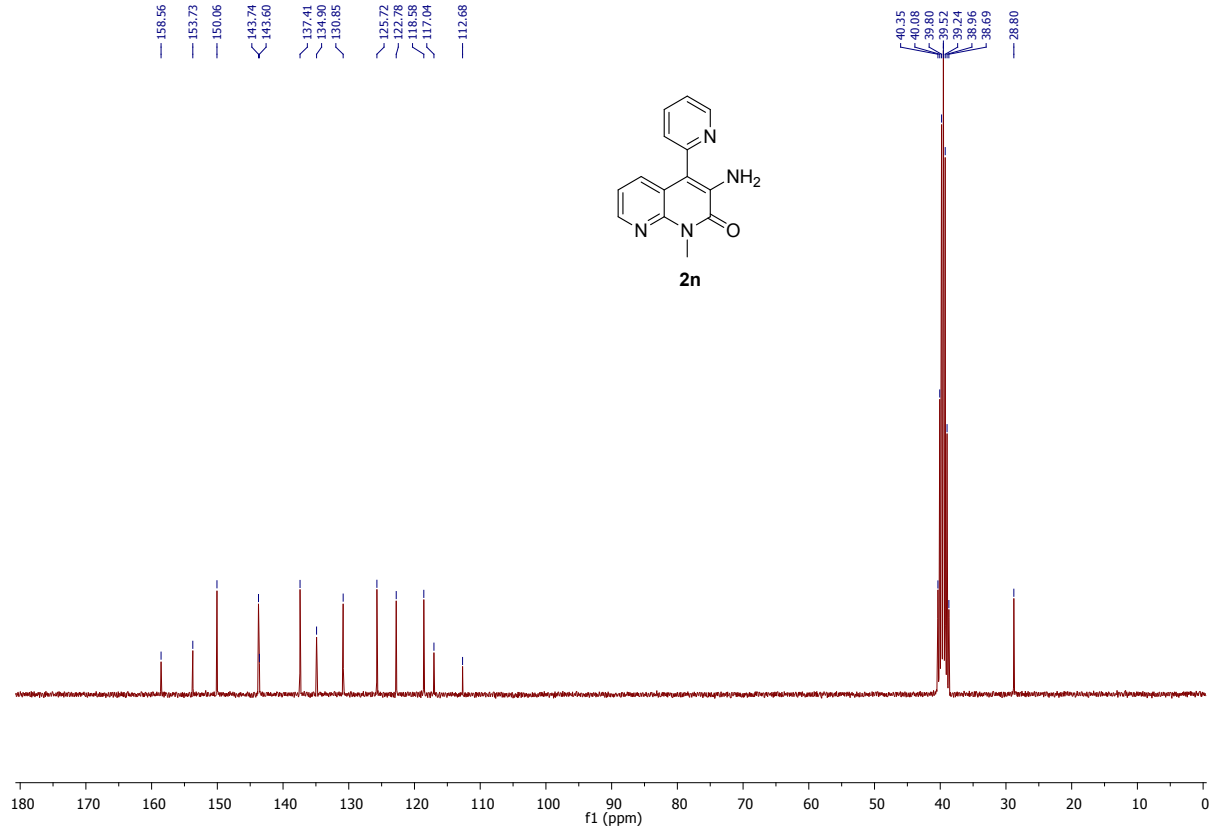

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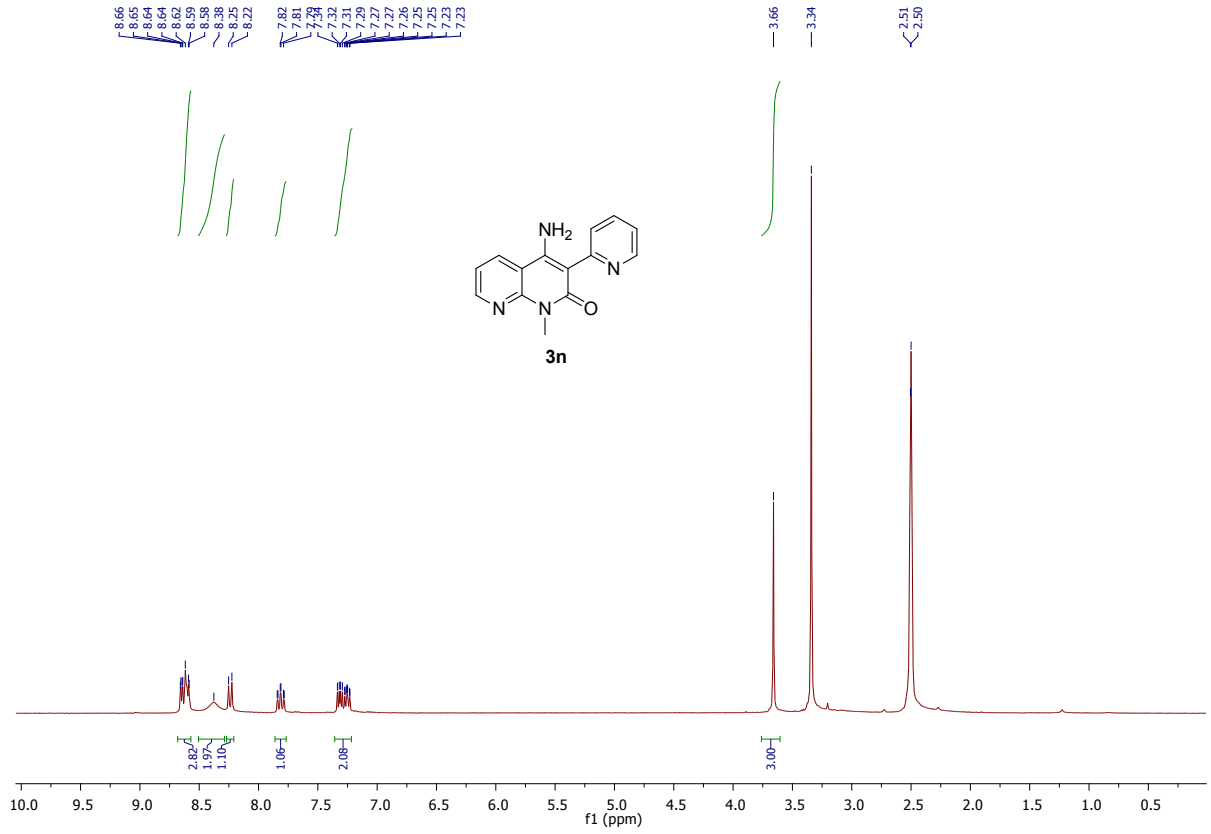

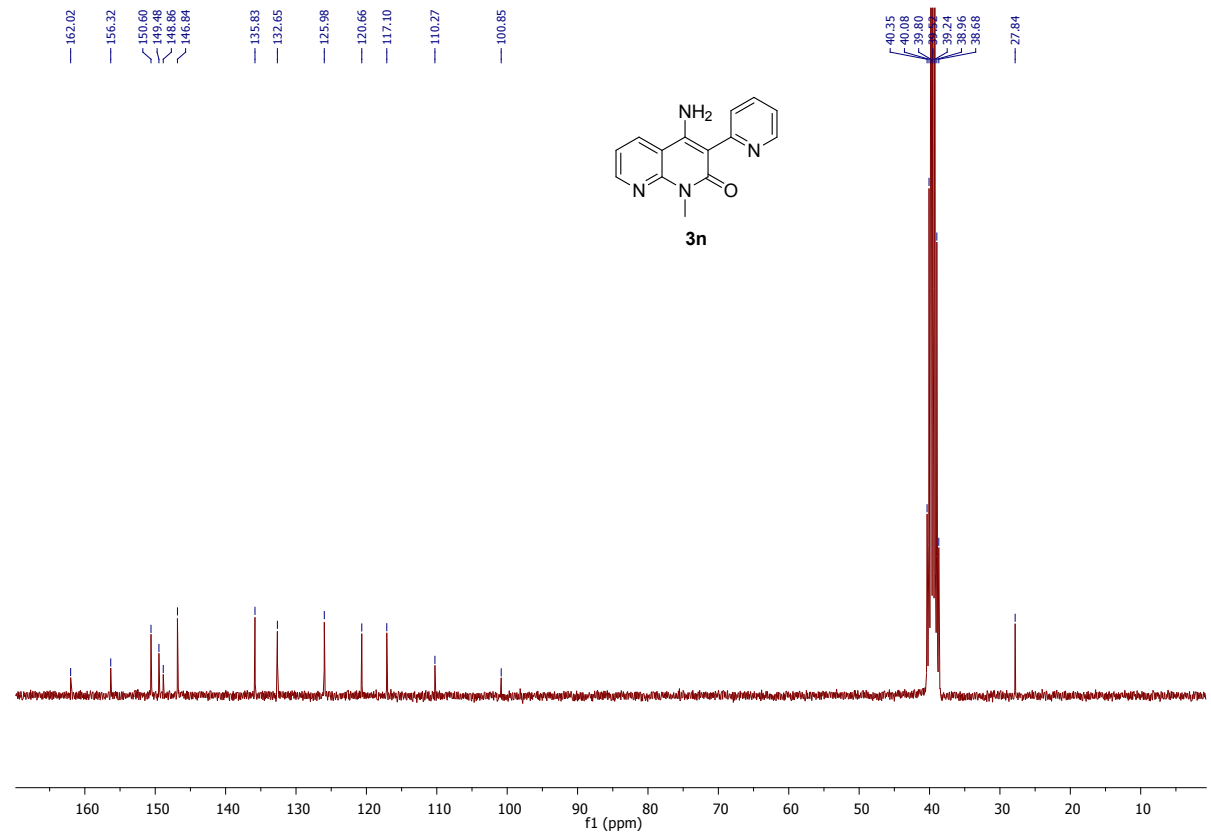

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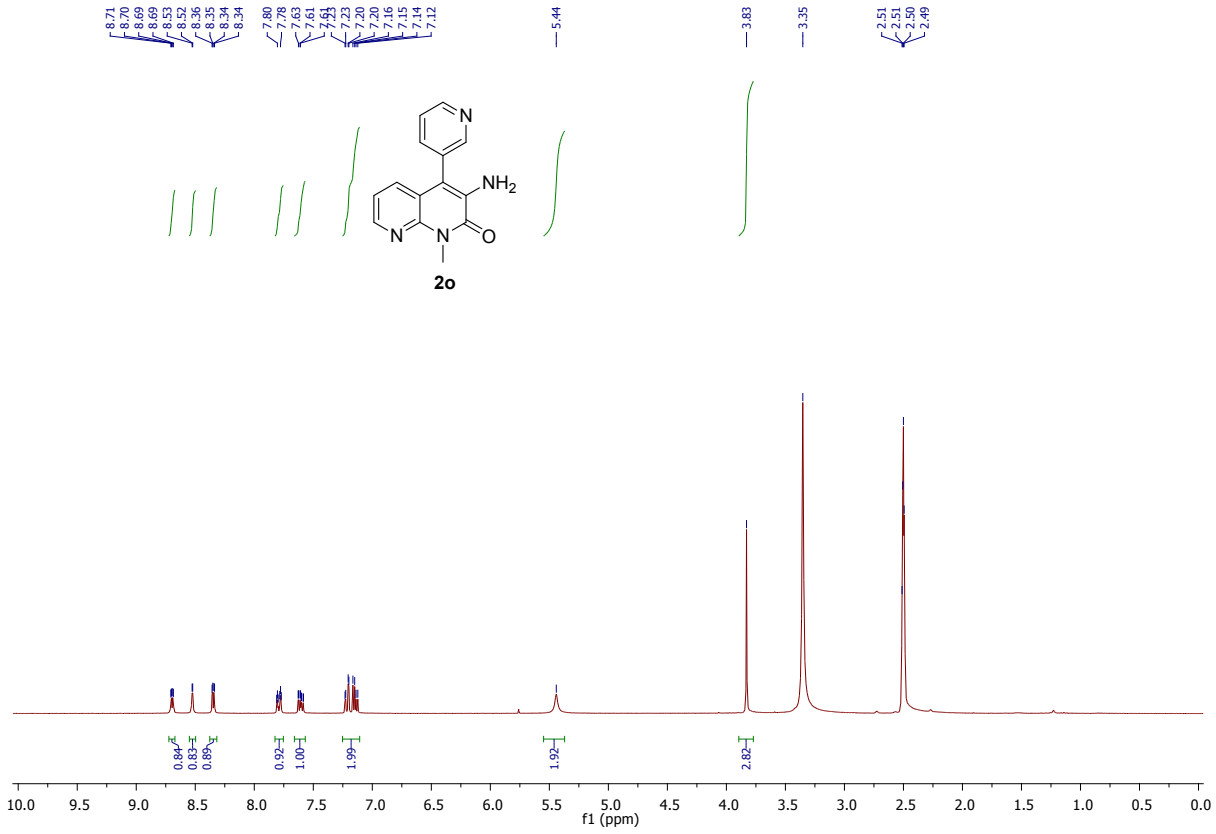

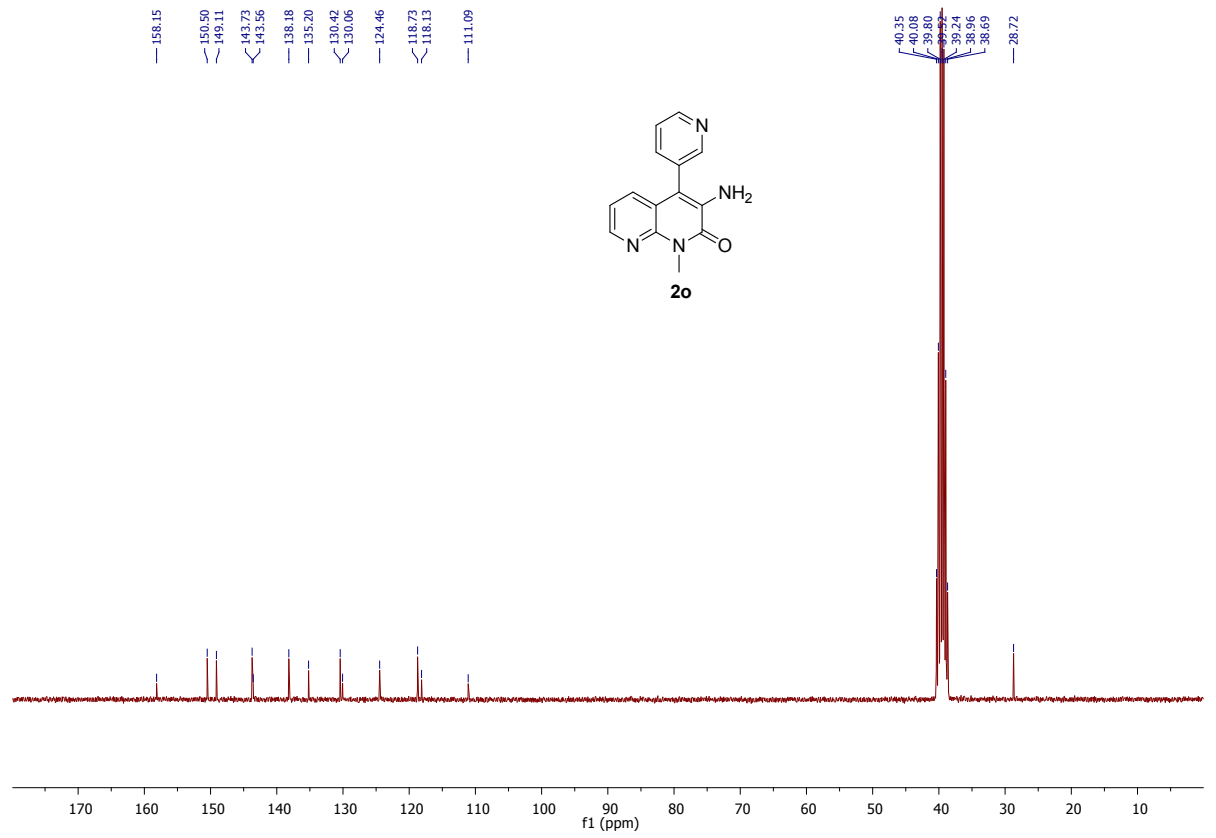

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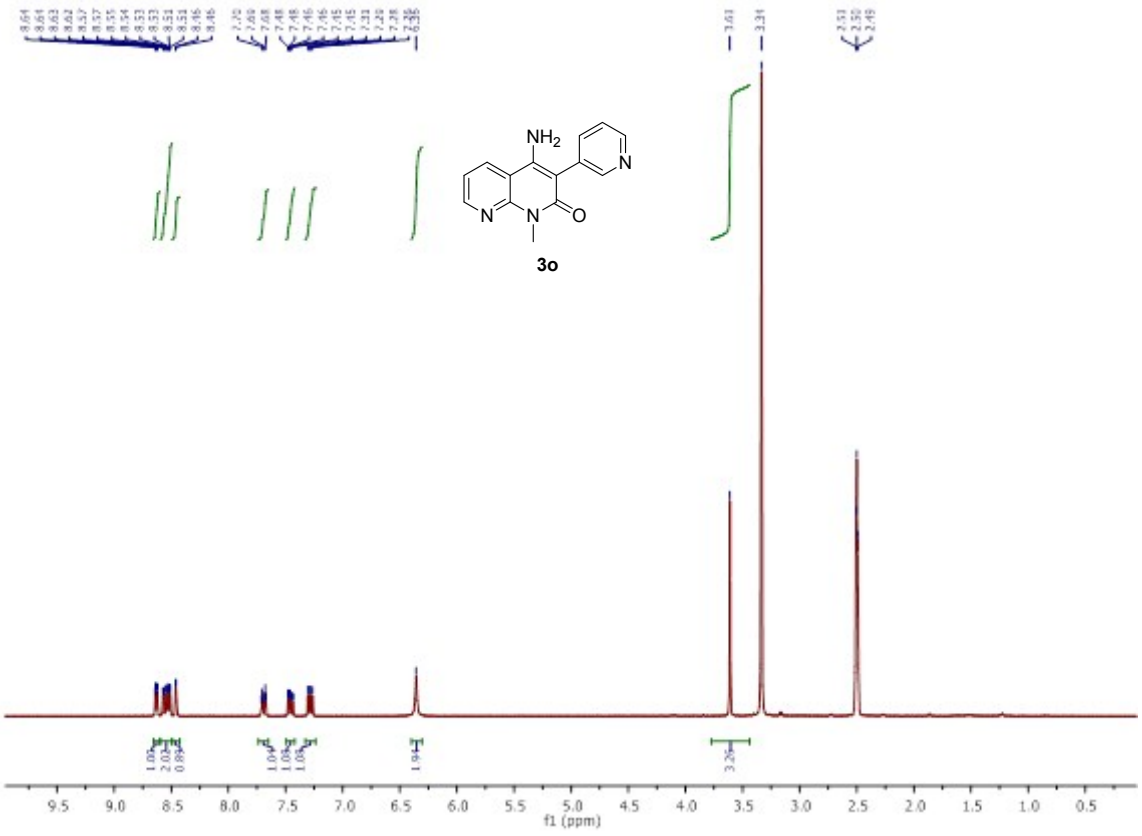
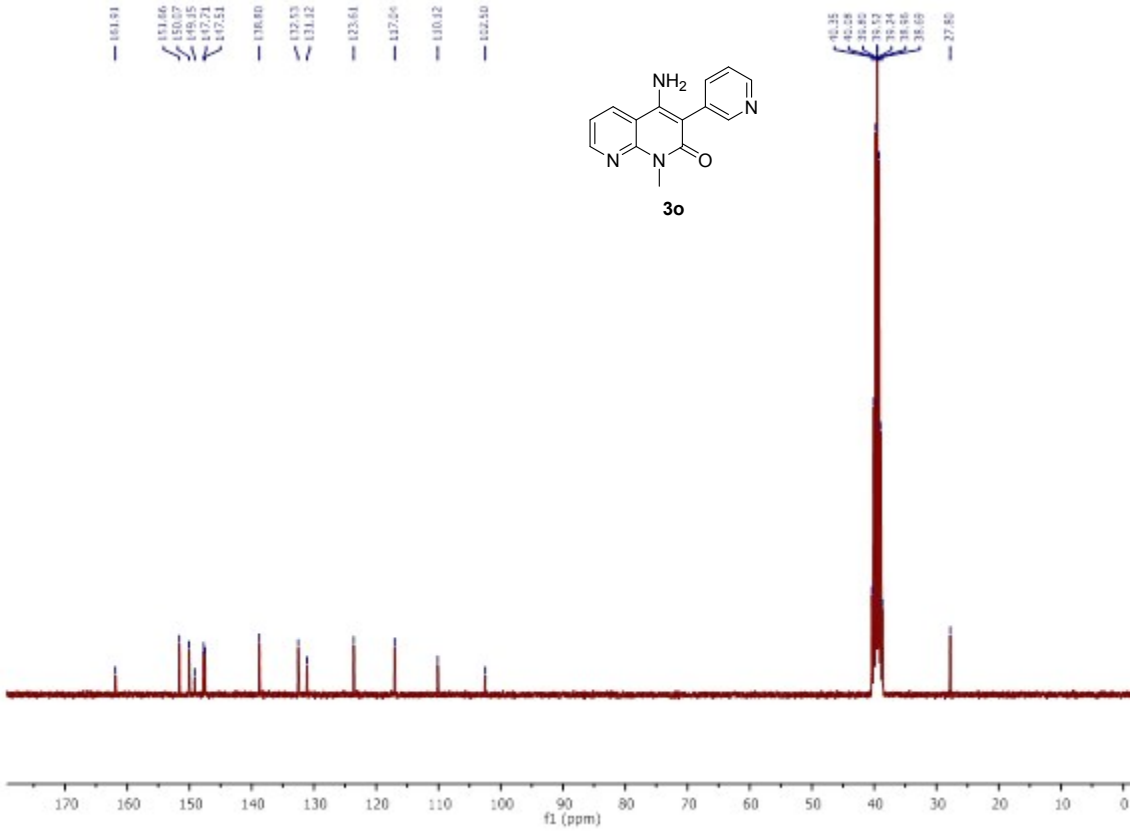
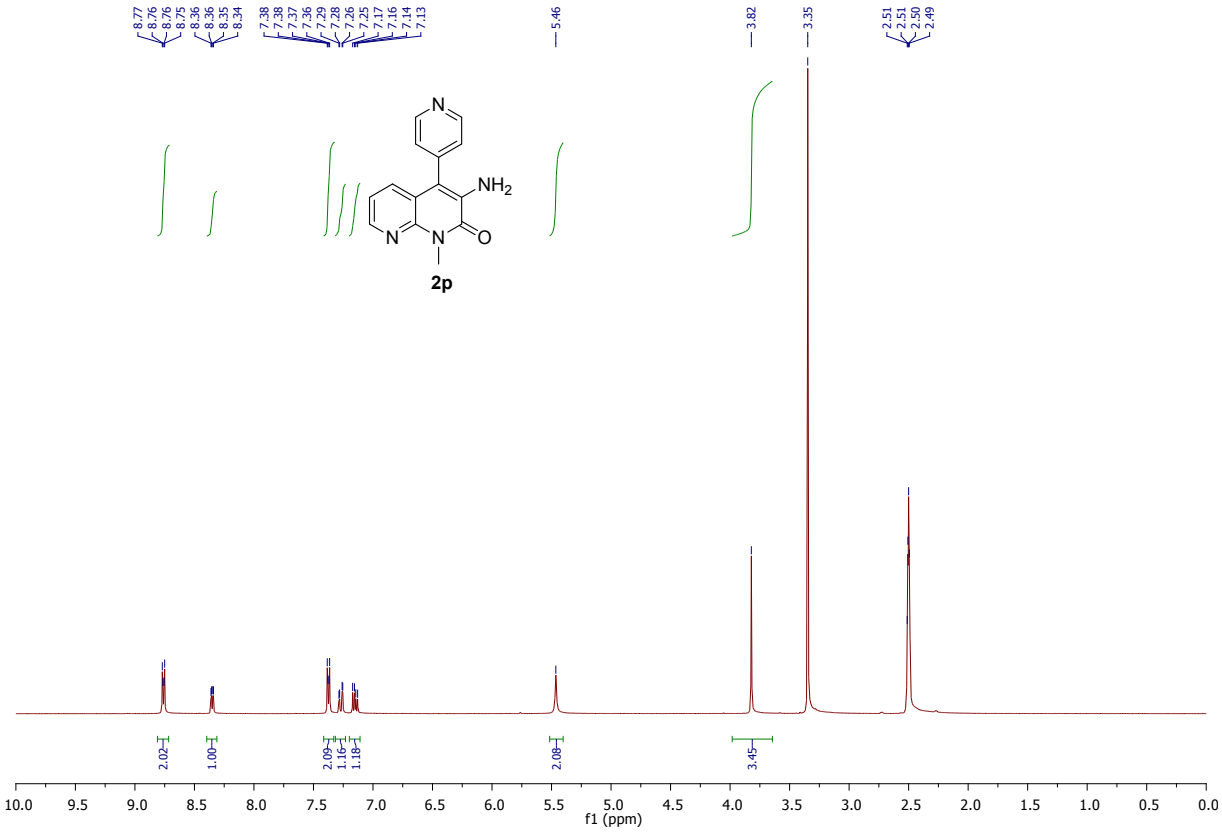
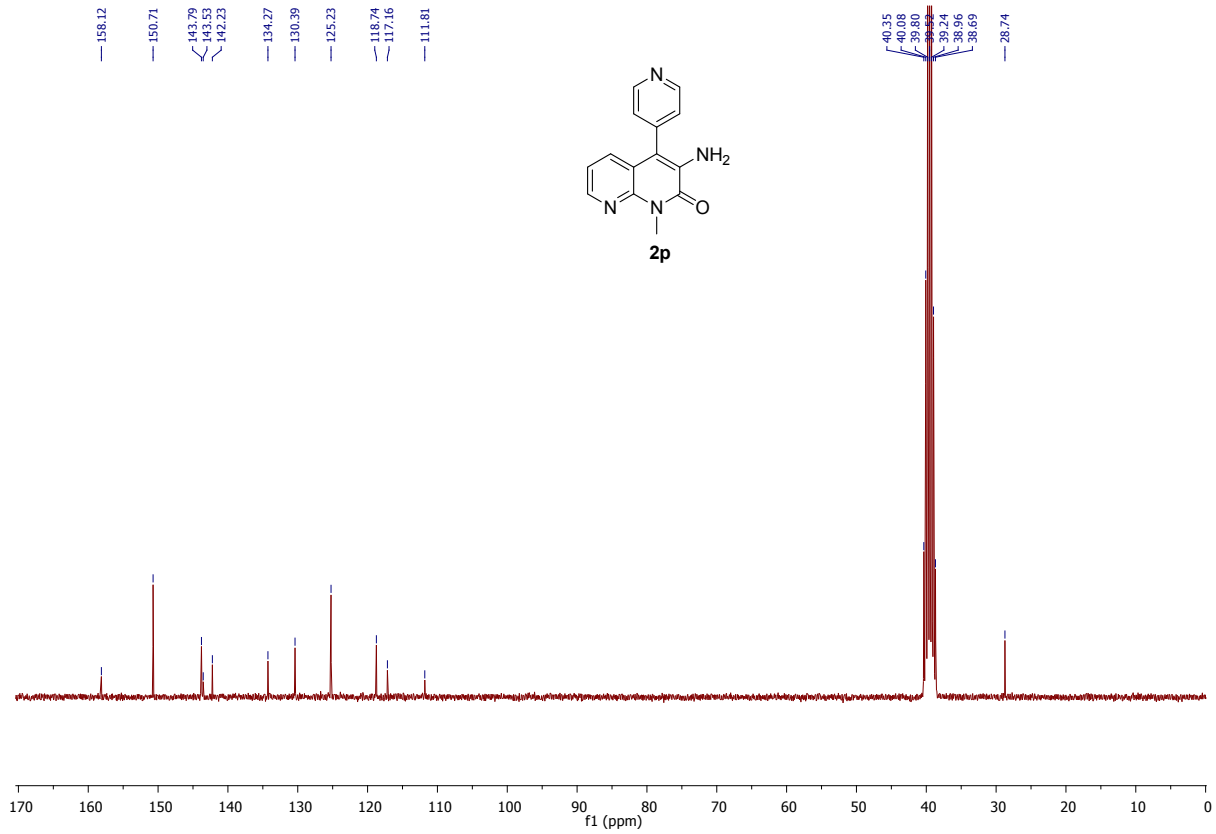




3-Amino-1-methyl-4-(pyridin-4-yl)-1,8-naphthyridin-2(1*H*)-one (2p)





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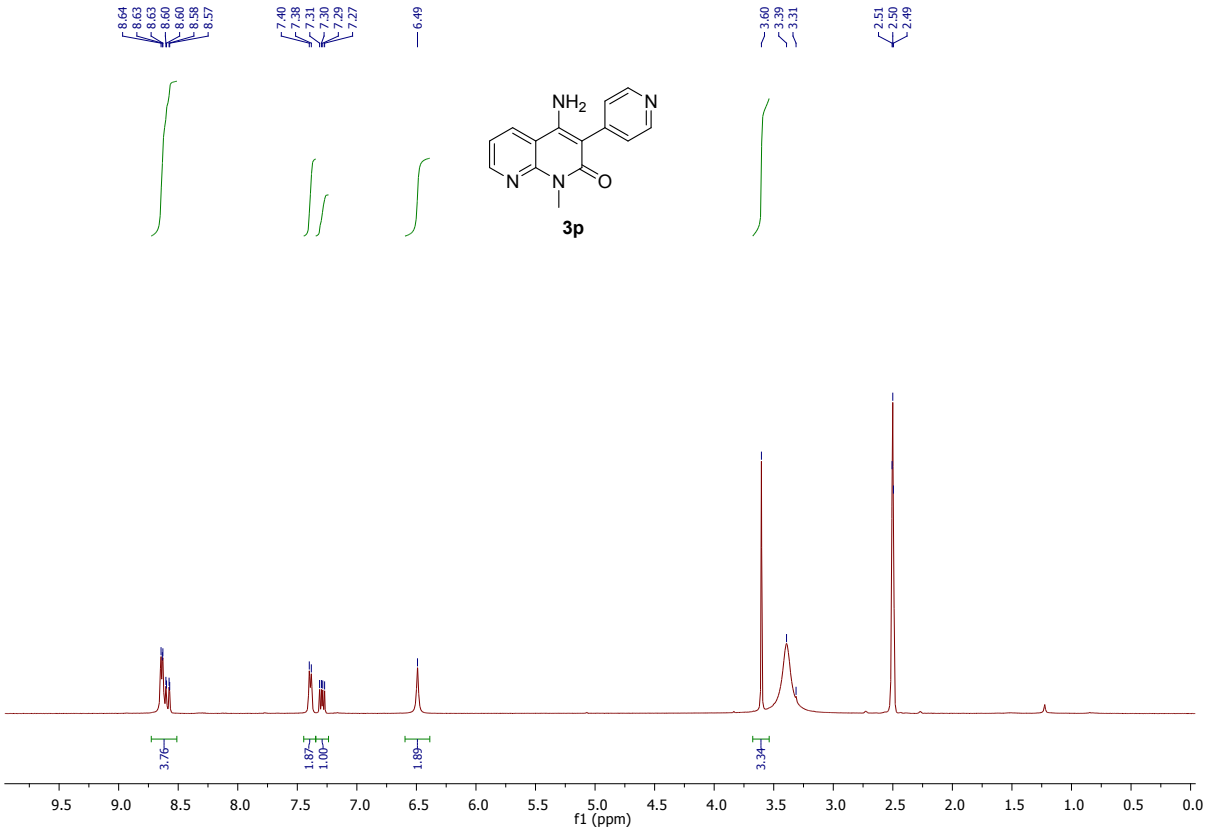

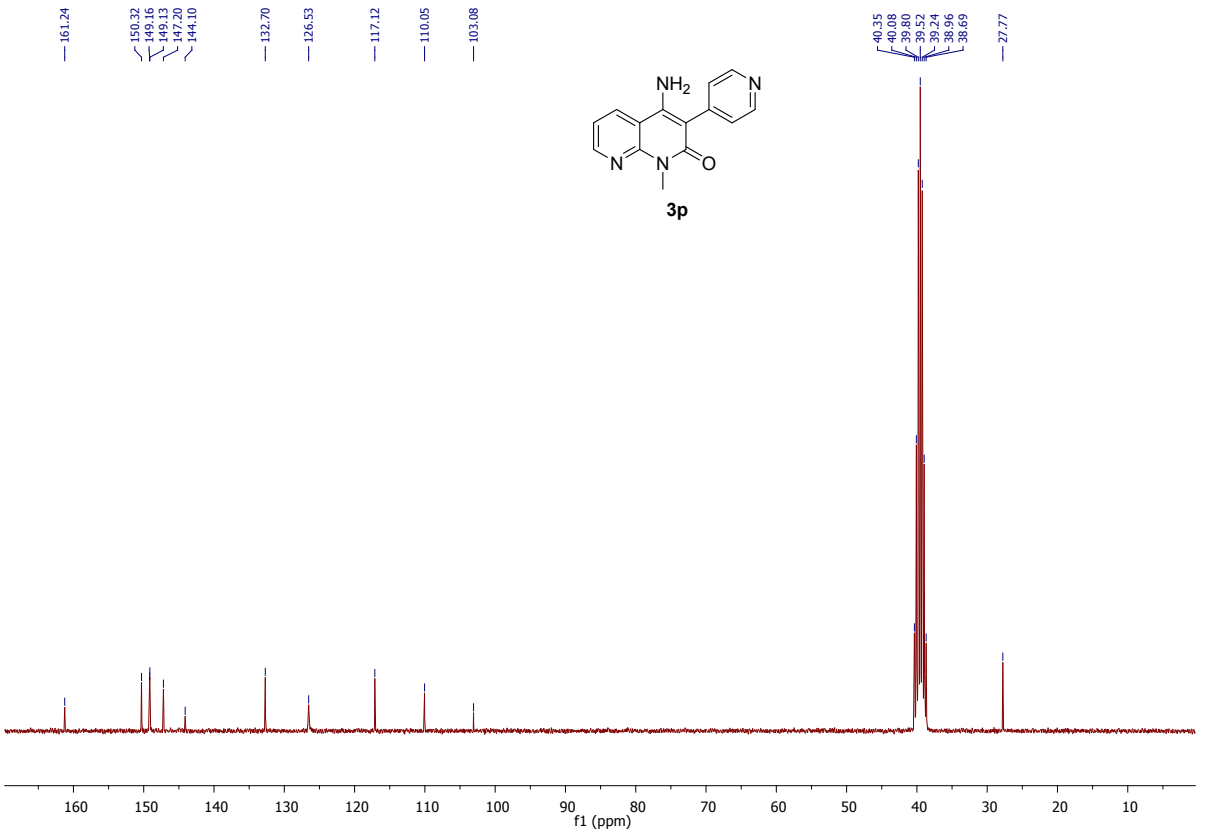

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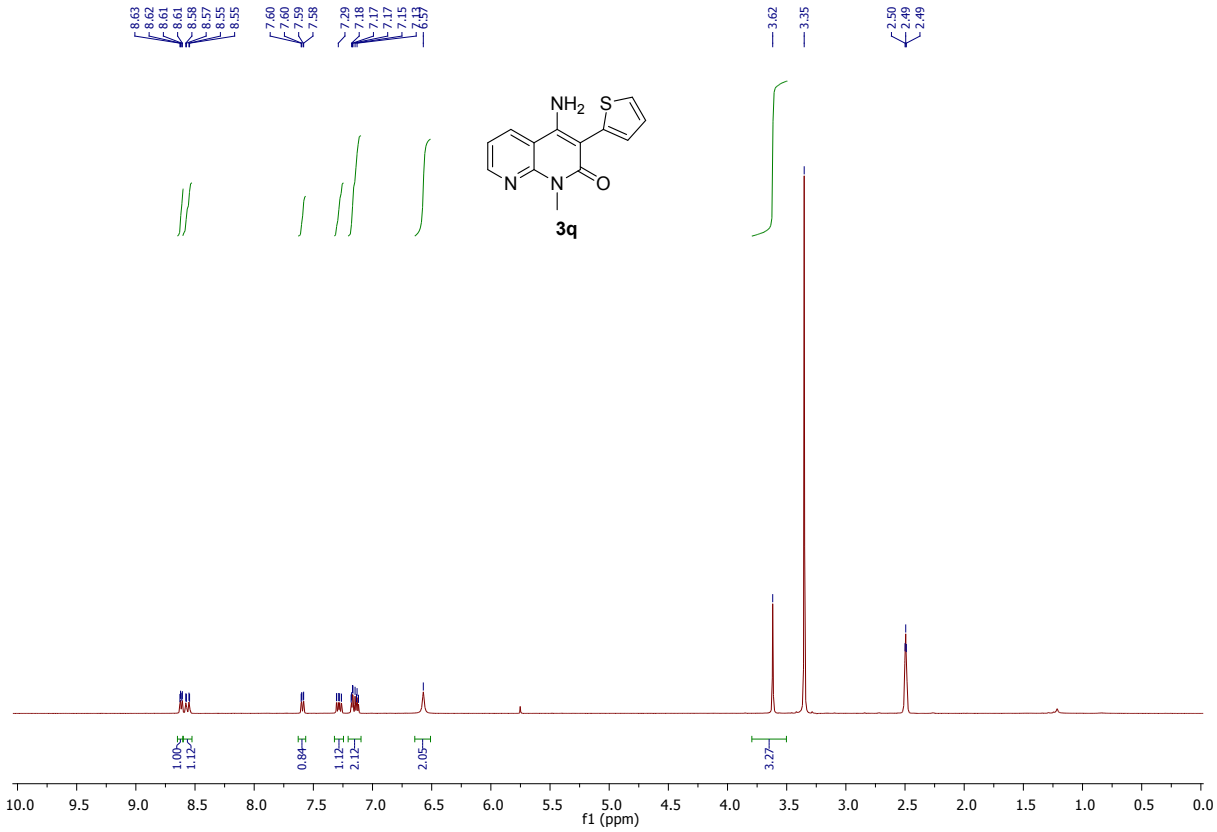

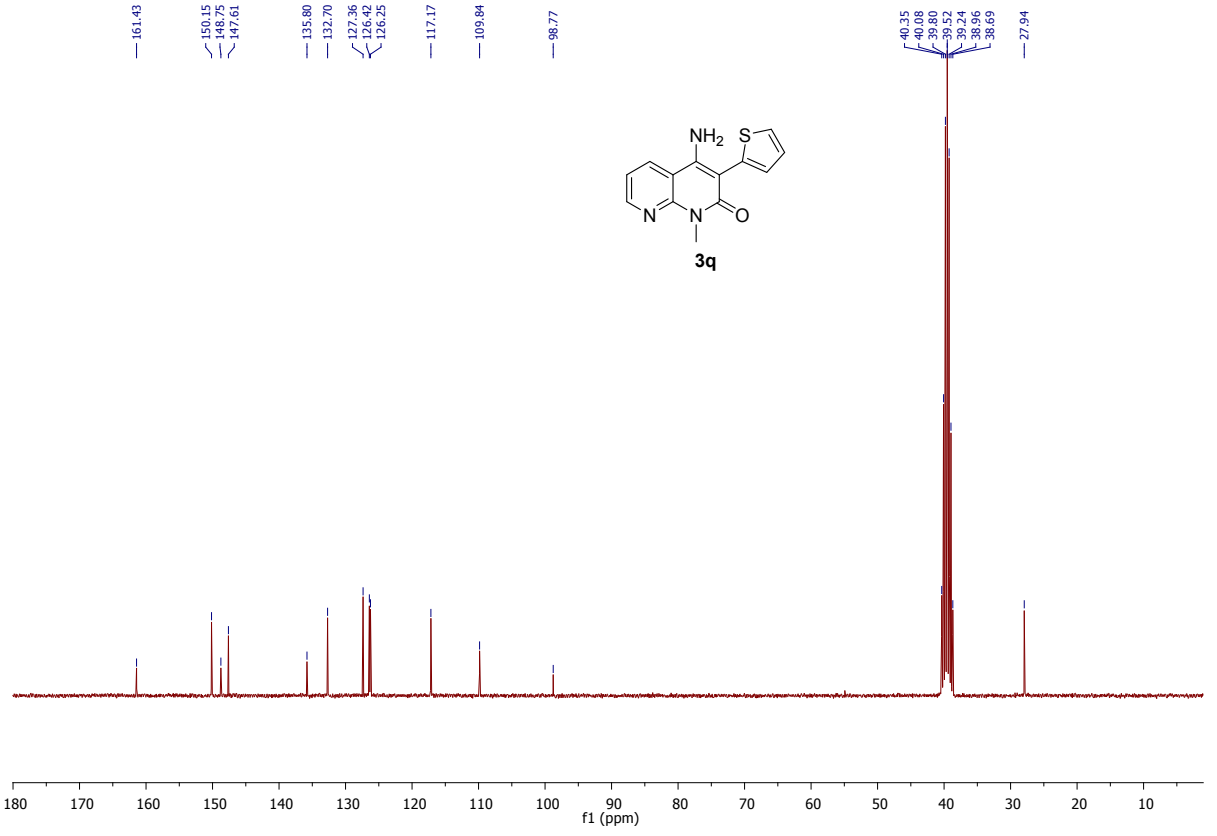

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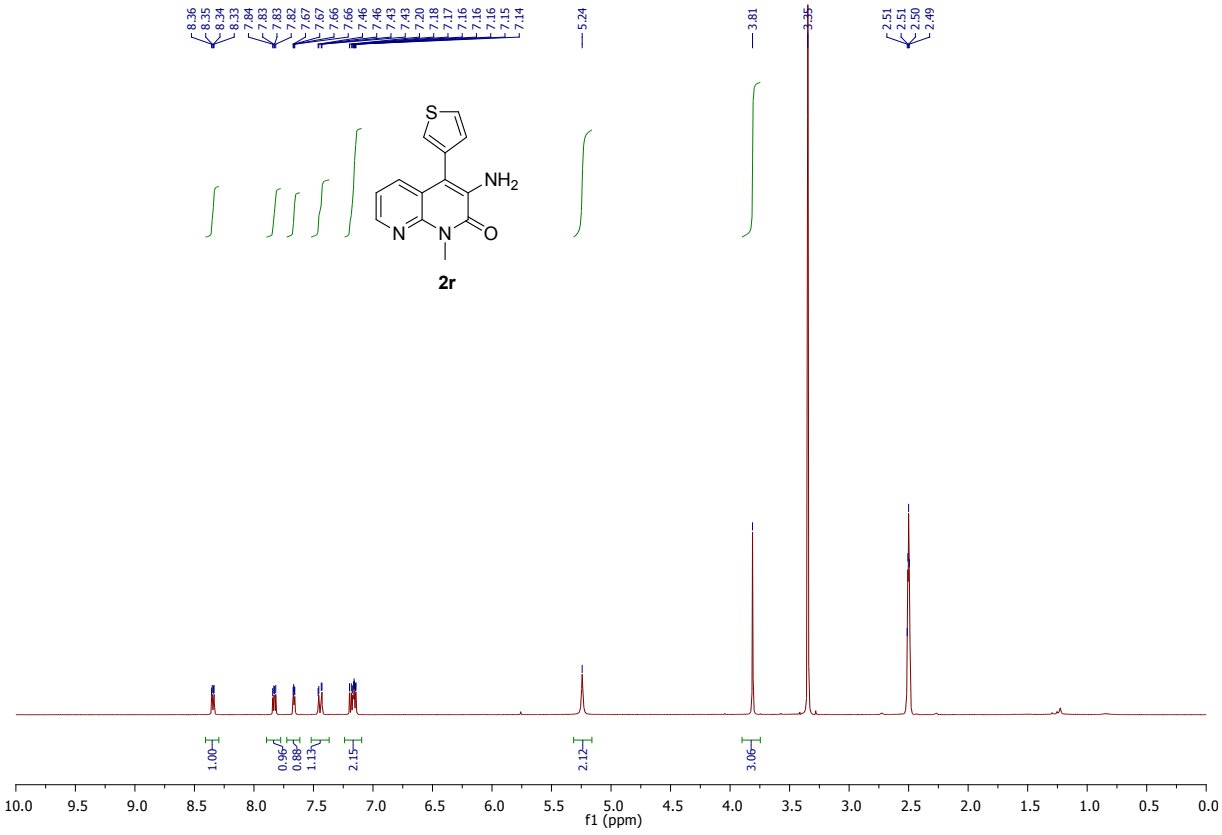
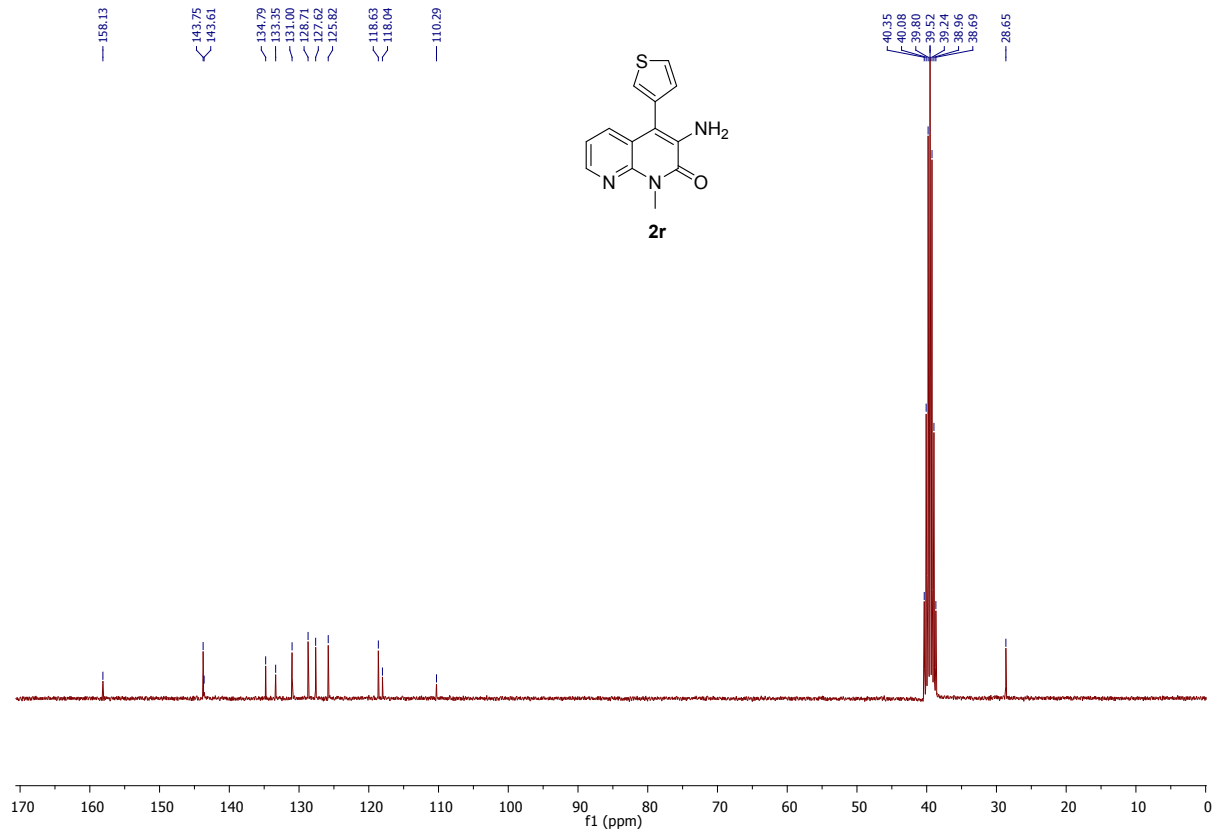
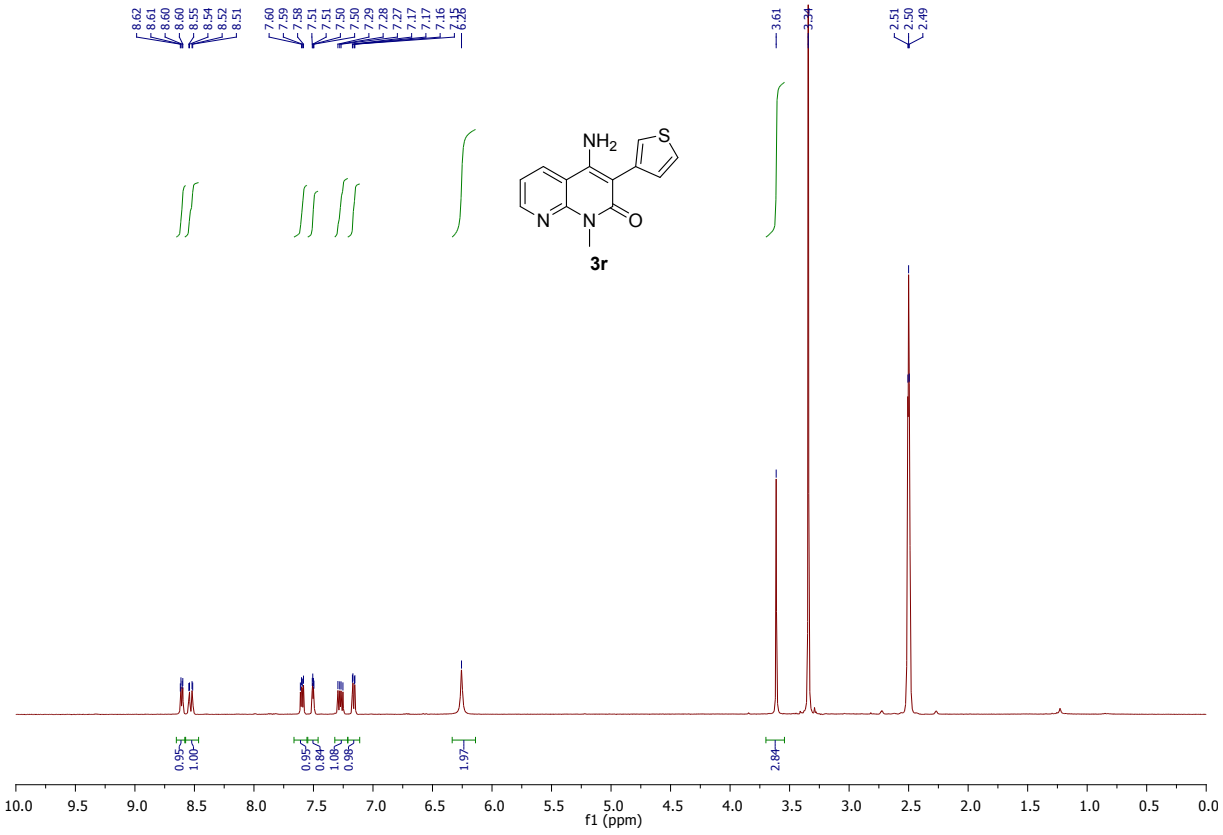
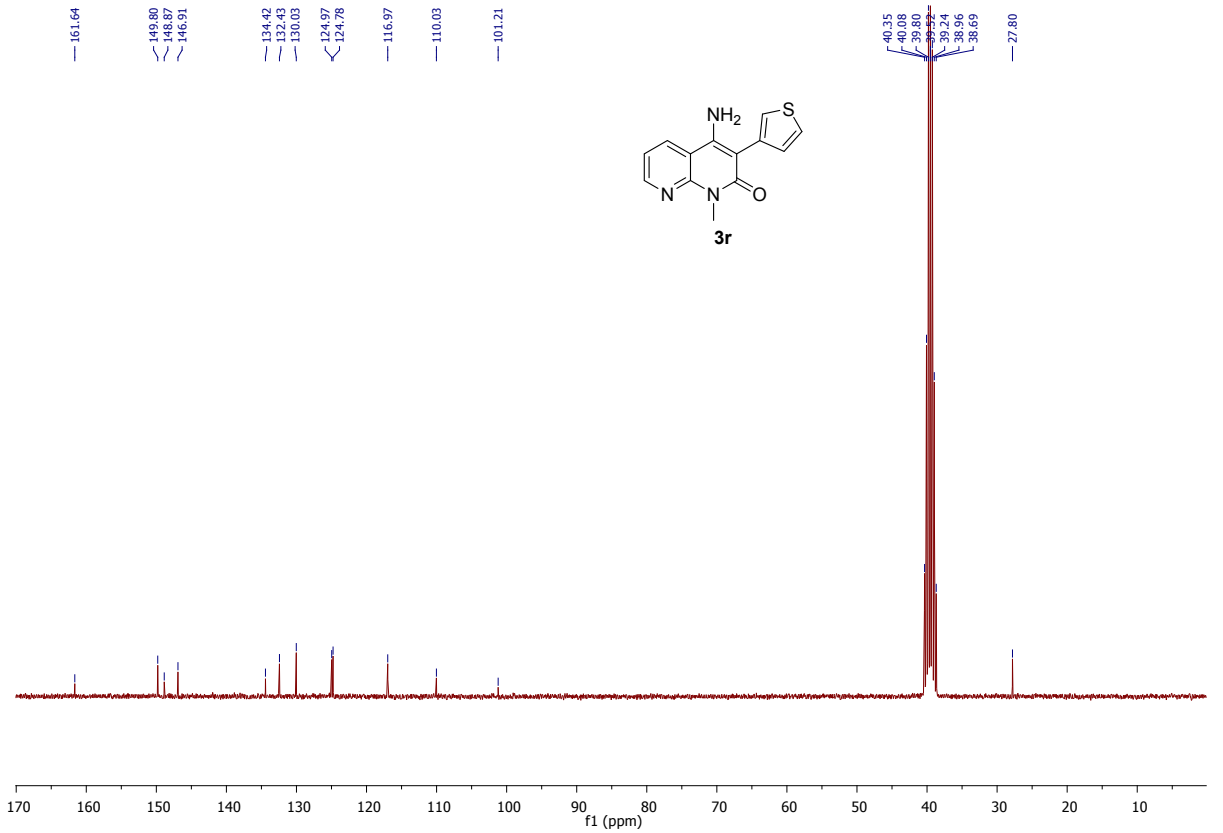


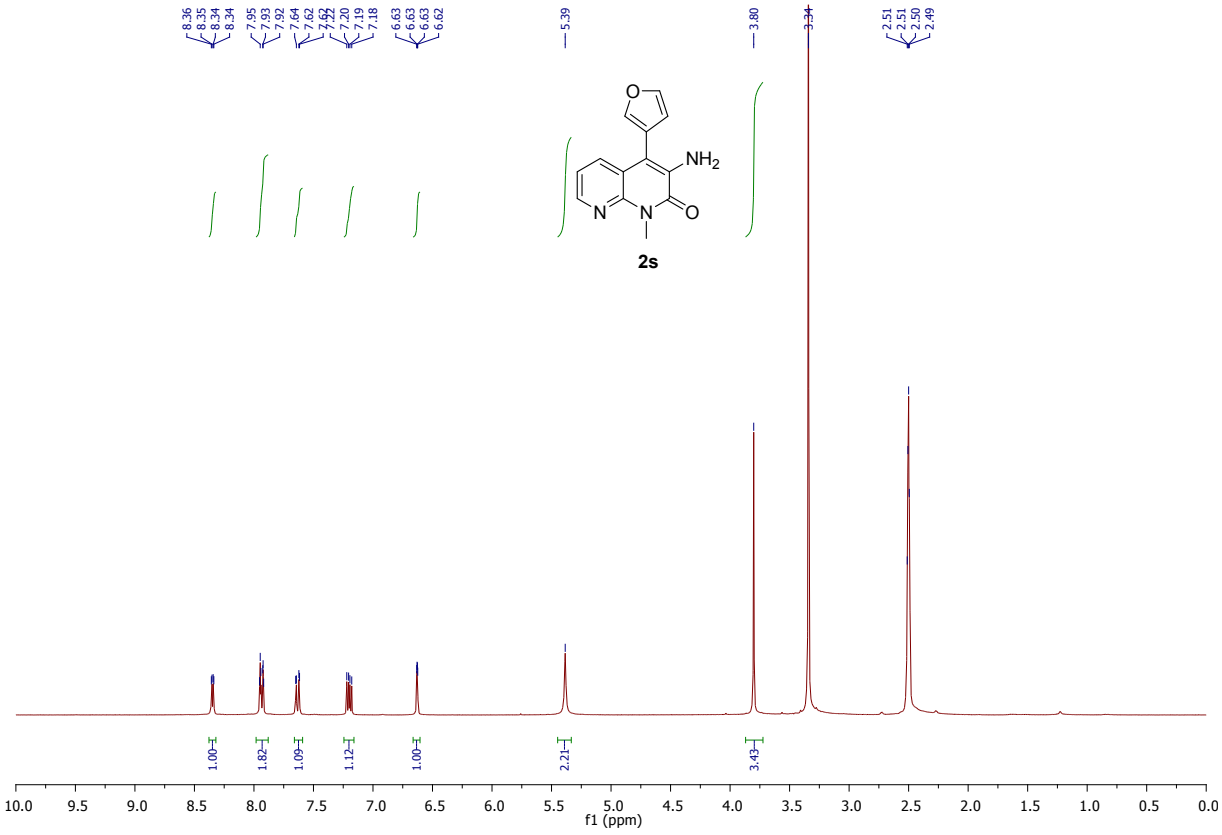


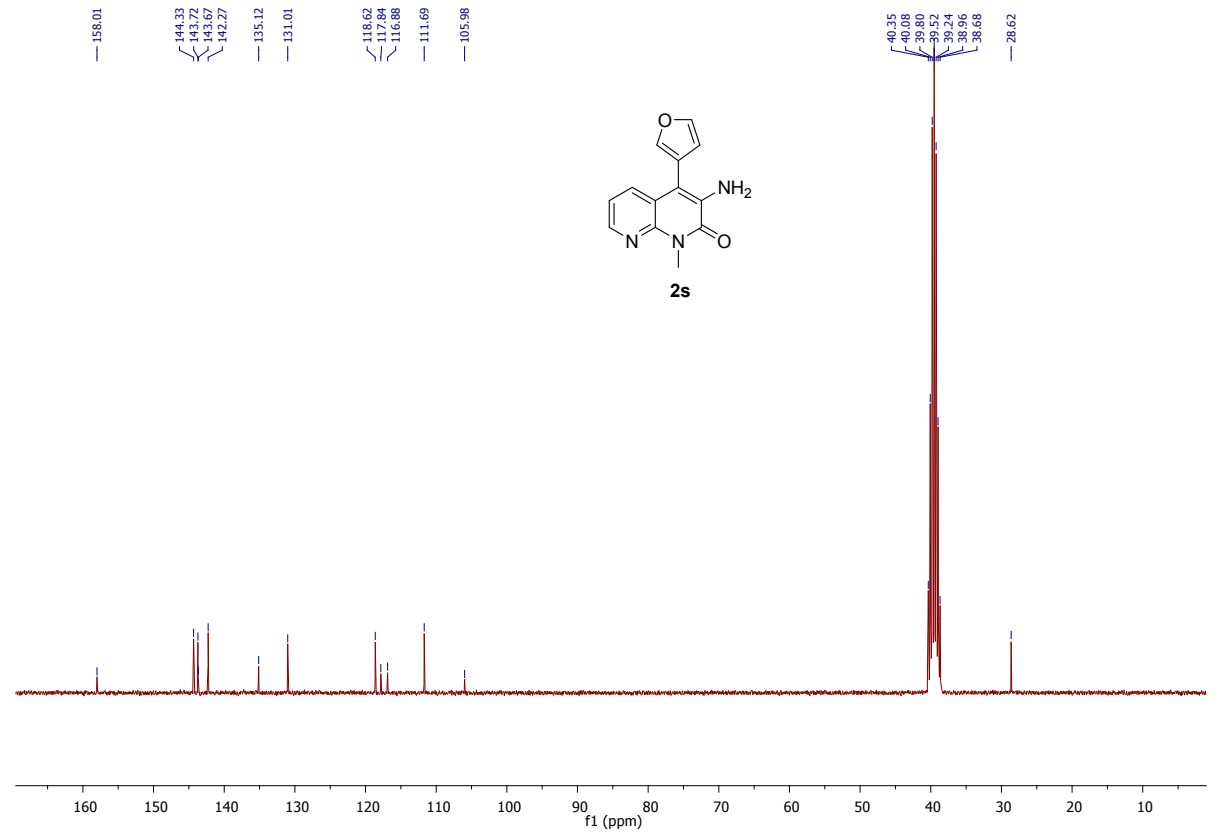
4-Amino-1-methyl-3-(thiophen-3-yl)-1,8-naphthyridin-2(1*H*)-one (3r)





3-Amino-4-(furan-3-yl)-1-methyl-1,8-naphthyridin-2(1*H*)-one (2s)





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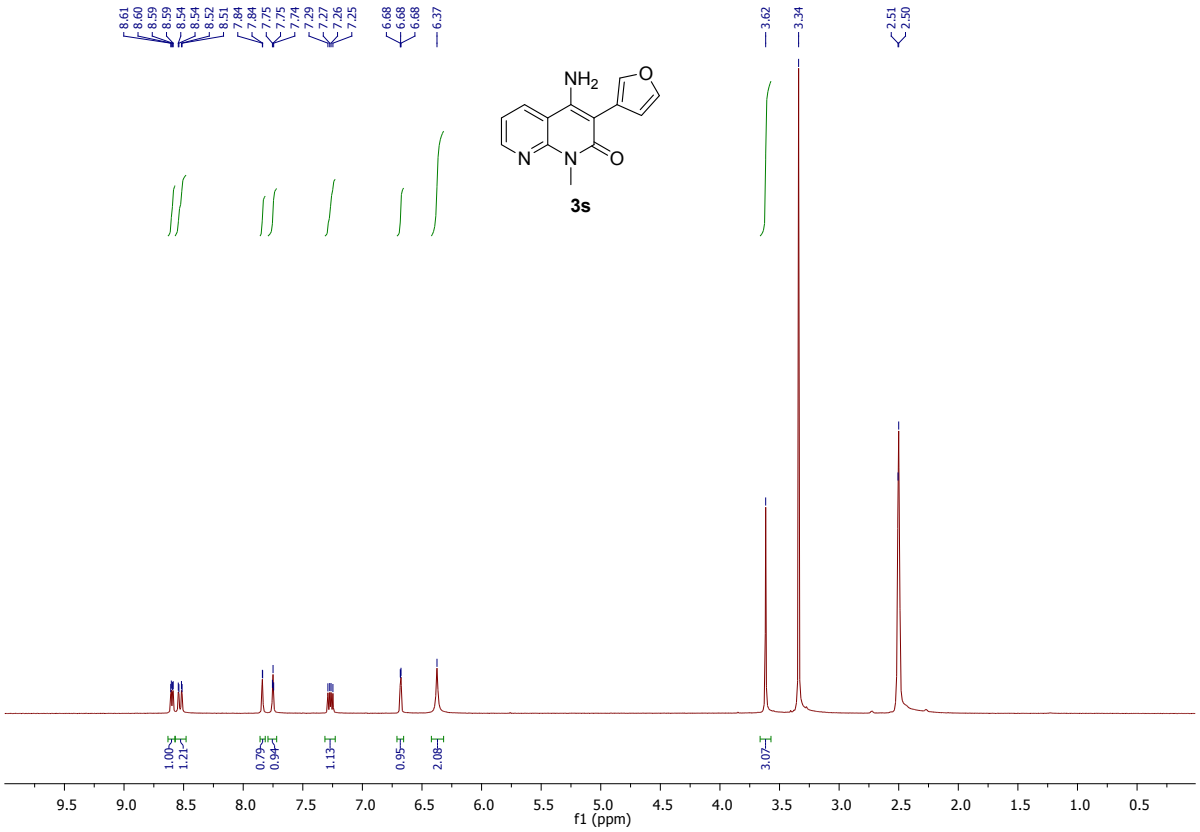

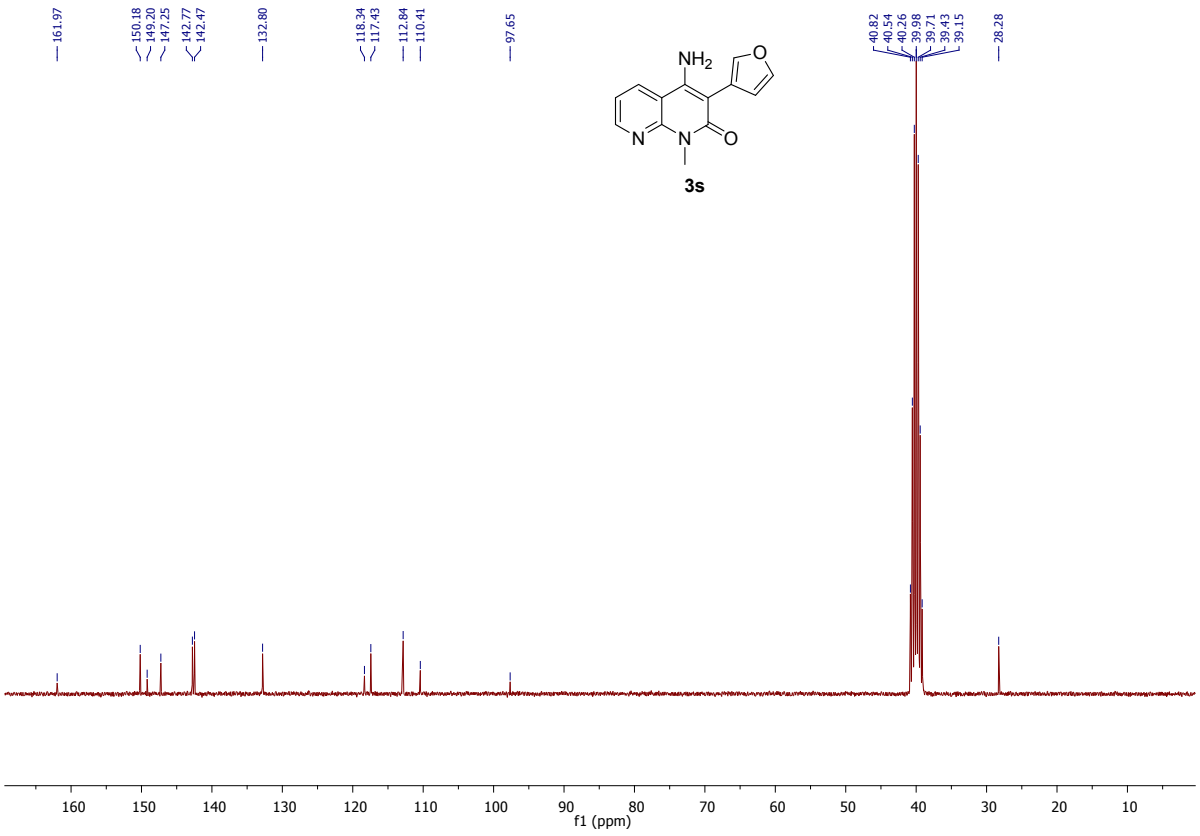

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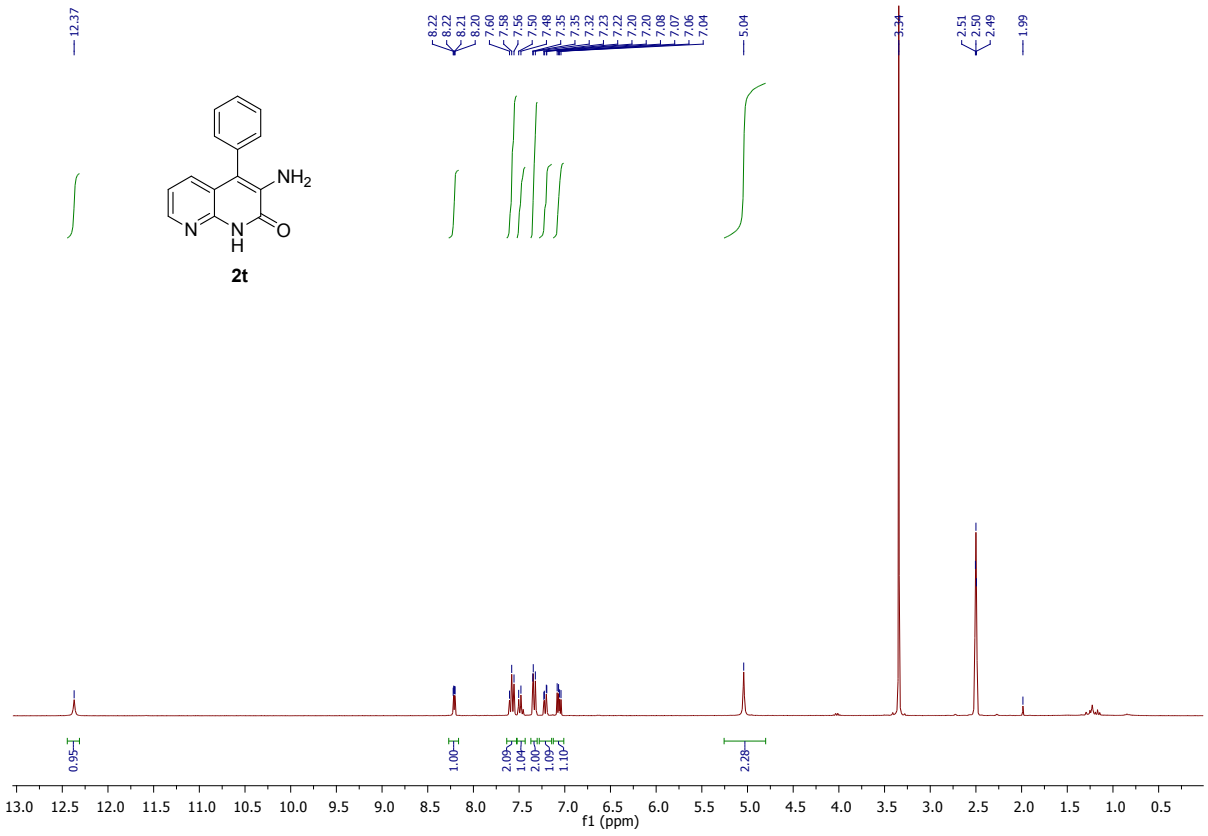

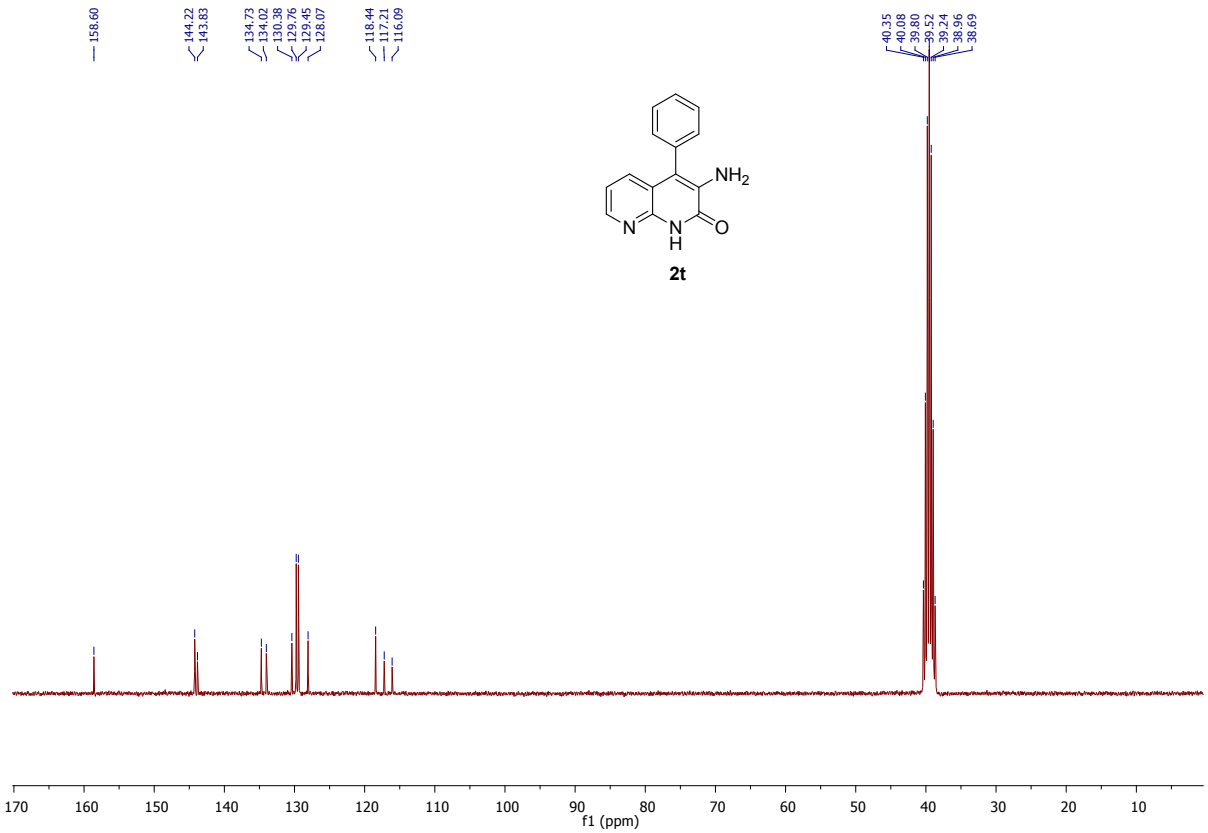

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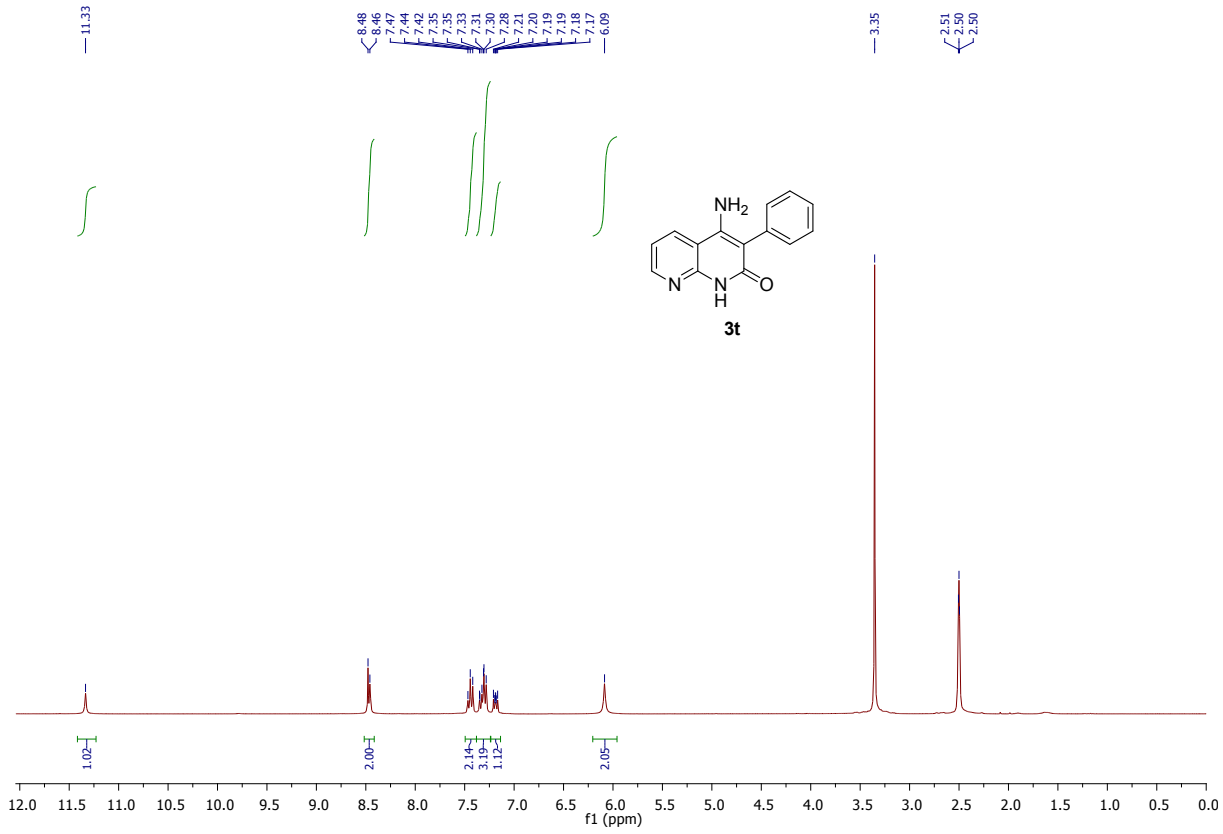
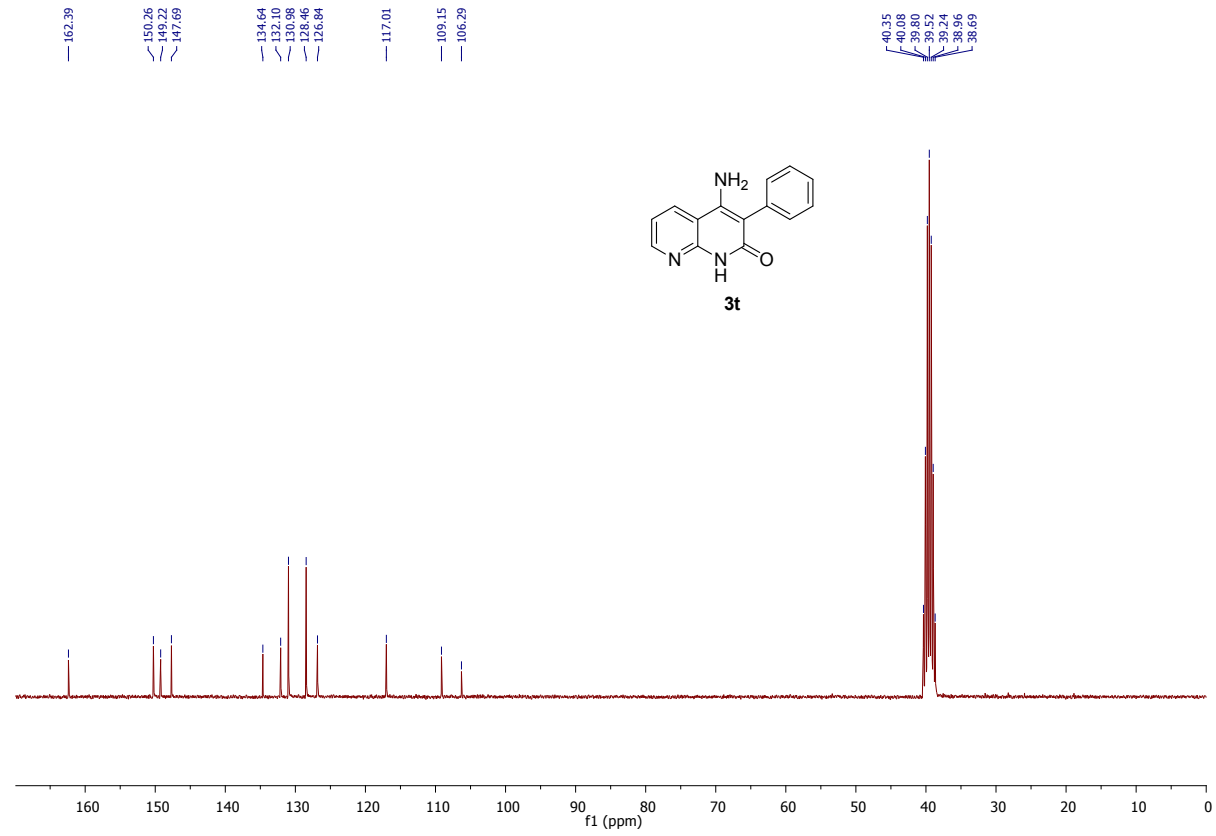
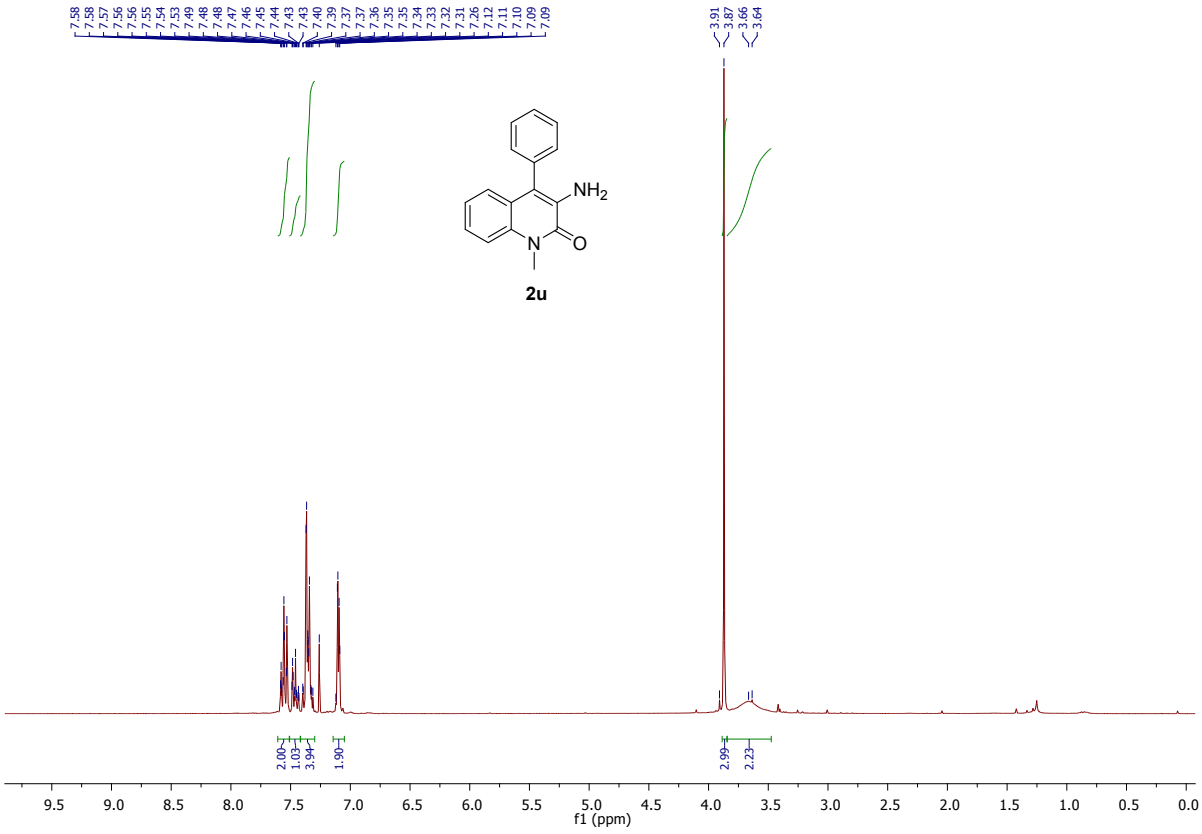
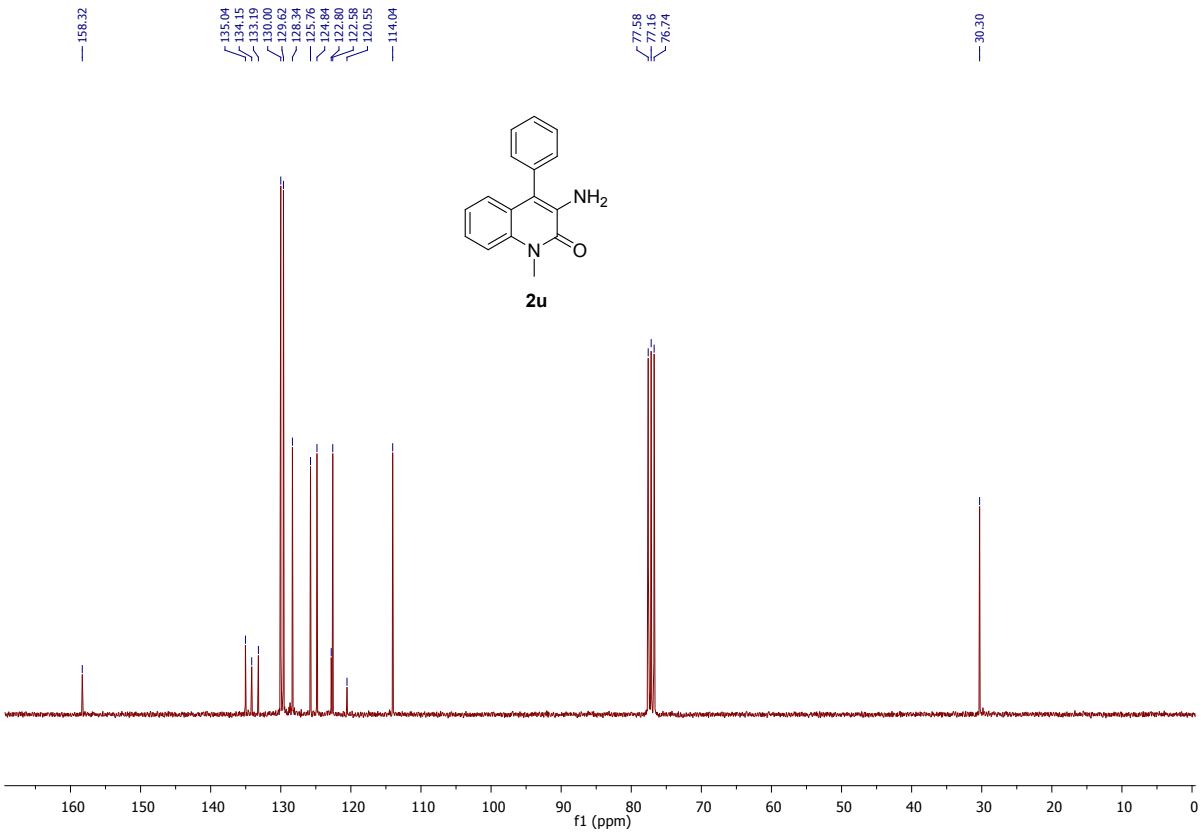


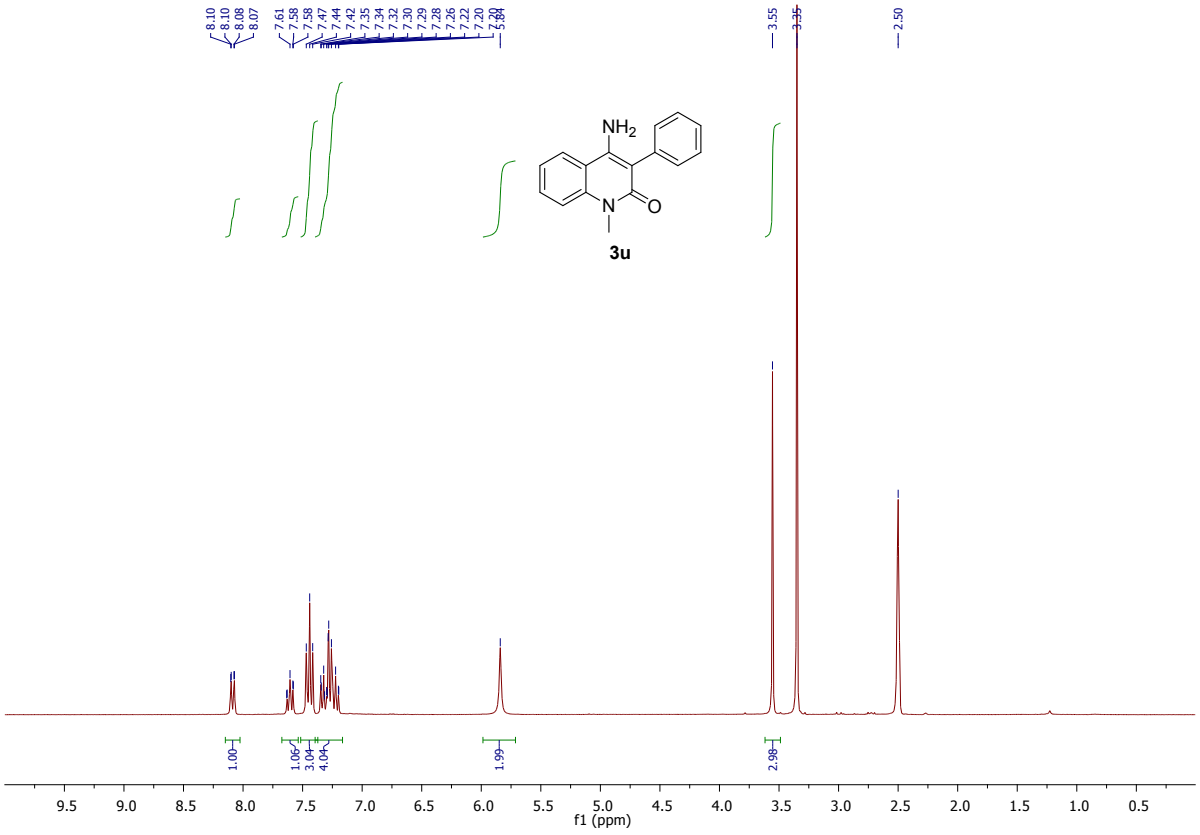


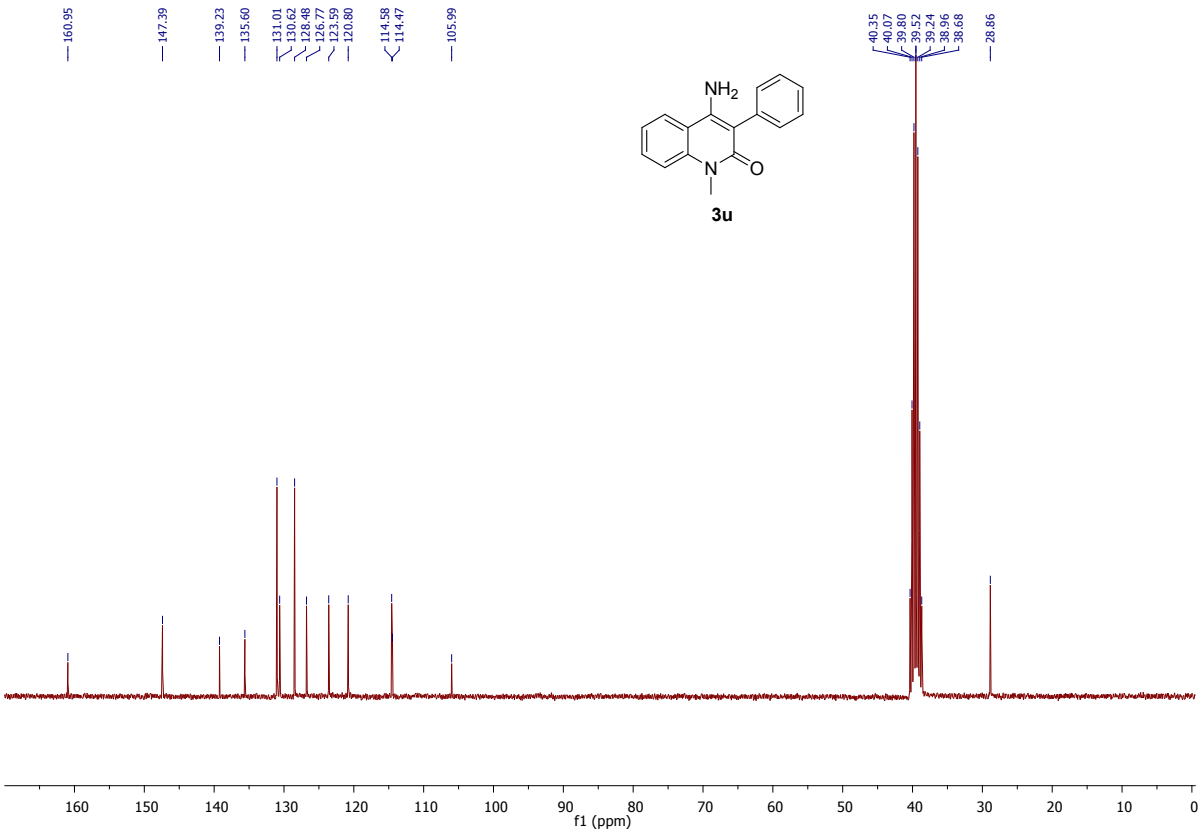
3-Amino-1-methyl-4-phenylquinolin-2(1*H*)-one (2u)





4-Amino-1-methyl-3-phenylquinolin-2(1*H*)-one (3u)





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