Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Manuscript Title:

Improving yield of graphene oxide catalysed n-heterocyclization of amines through fed batch mode

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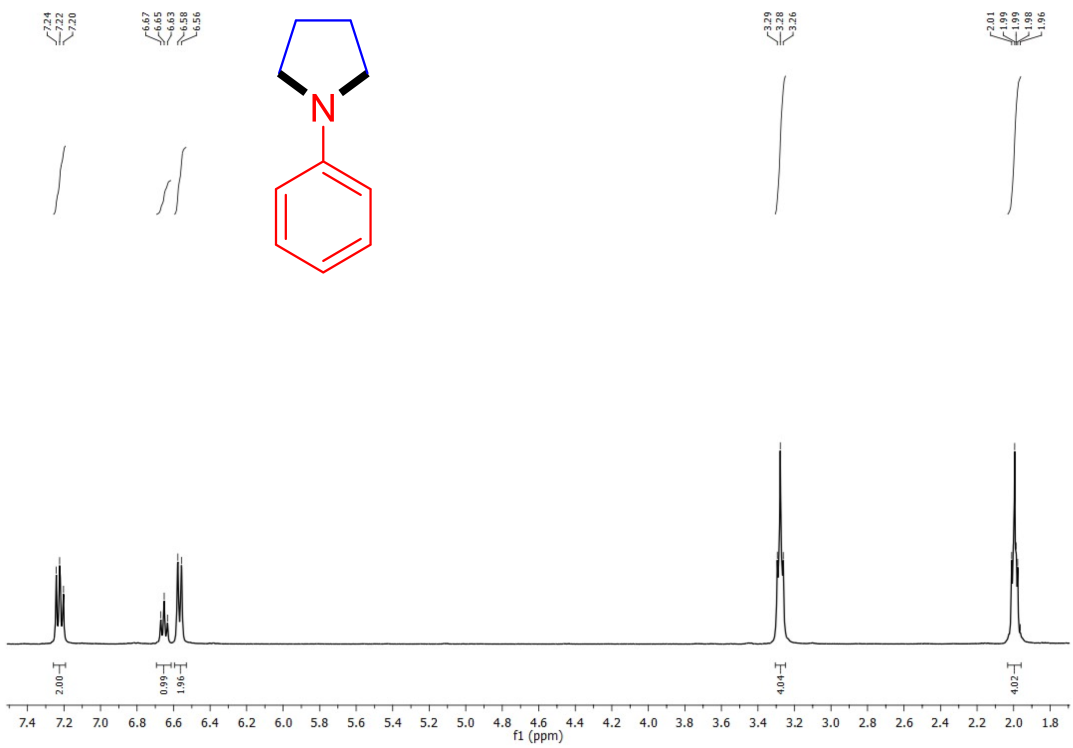
JPM and OSG have contributed equally

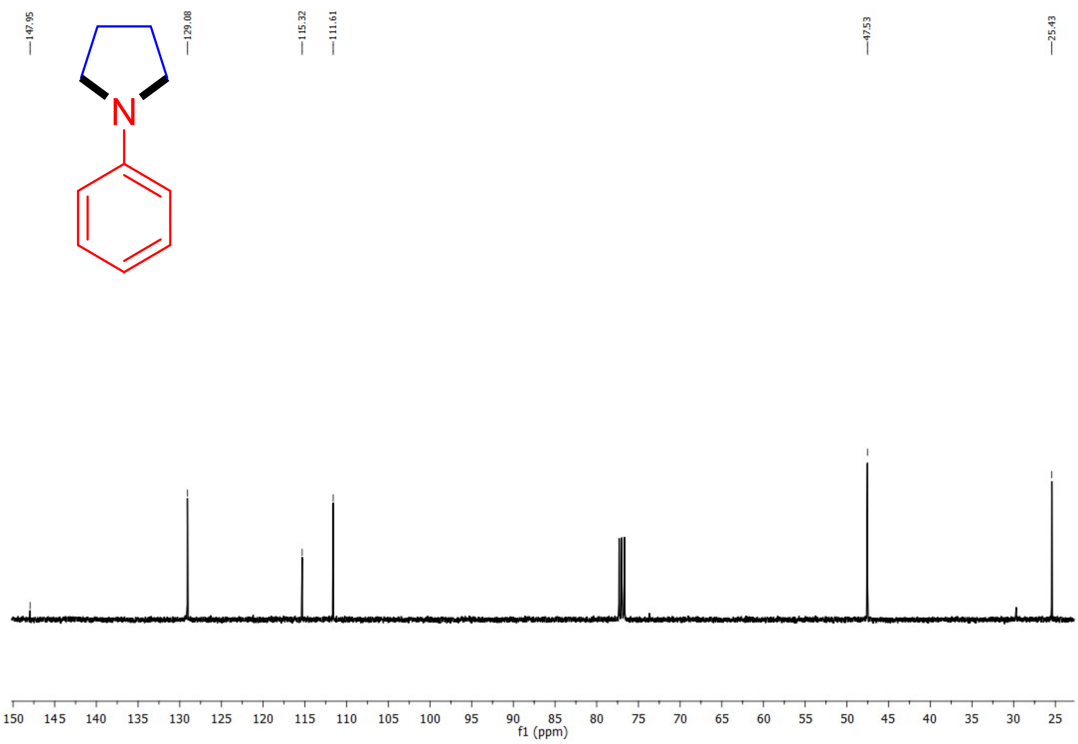
Relative abundance of oxygen functionalities in graphene oxide obtained through the deconvolution of XPS spectra

Compound	Peak	% Area
GO	C1s (Survey)	69.5
	C-C	48.15
	C-OH	34.56
	C=O	17.29
	O1s (Survey)	27.80
	O/C ratio	0.43

^{1}H and ^{13}C NMR spectra of the derivatives synthesized

a) 1-phenylpyrrolidine (3a)
^{1}H NMR (400 MHz, cdcl$_3$) δ 7.19 (dd, *J* = 32.0, 23.4 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 3.28 (t, *J* = 6.5 Hz, 4H), 2.10 – 1.80 (m, 4H).
^{13}C NMR (101 MHz, cdcl$_3$) δ 147.95, 129.08, 115.32, 111.61, 47.53, 25.43.
^{1}H NMR Spectrum



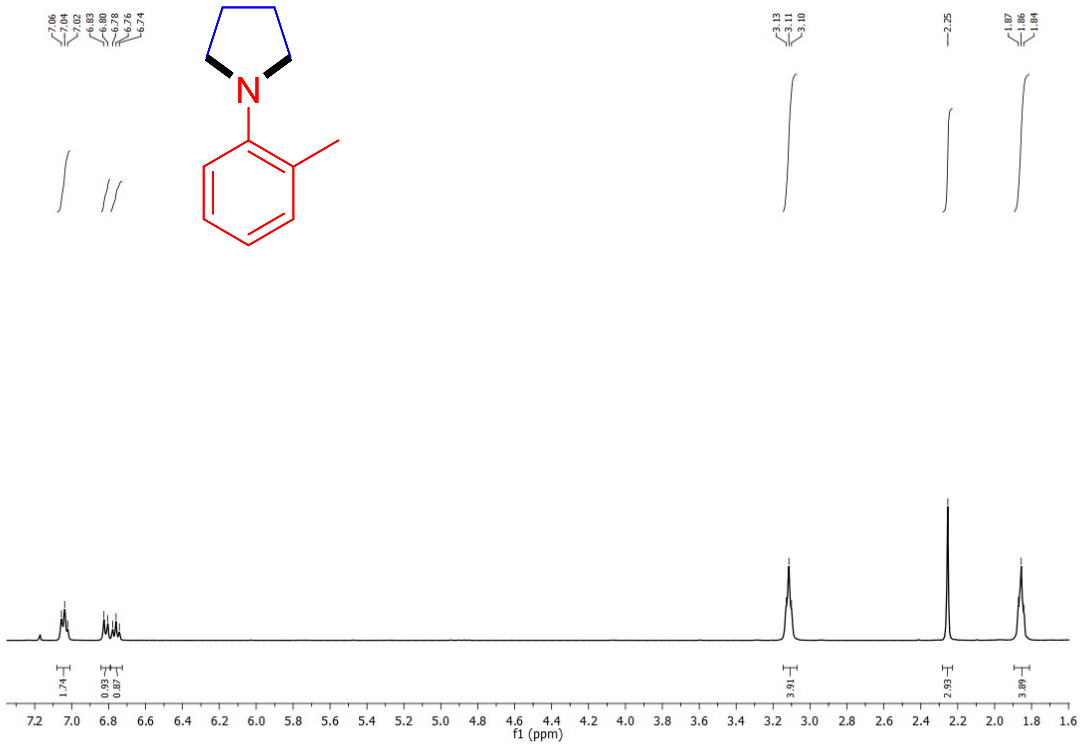

147.95
129.08
115.32
111.61
47.53
25.43
N
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

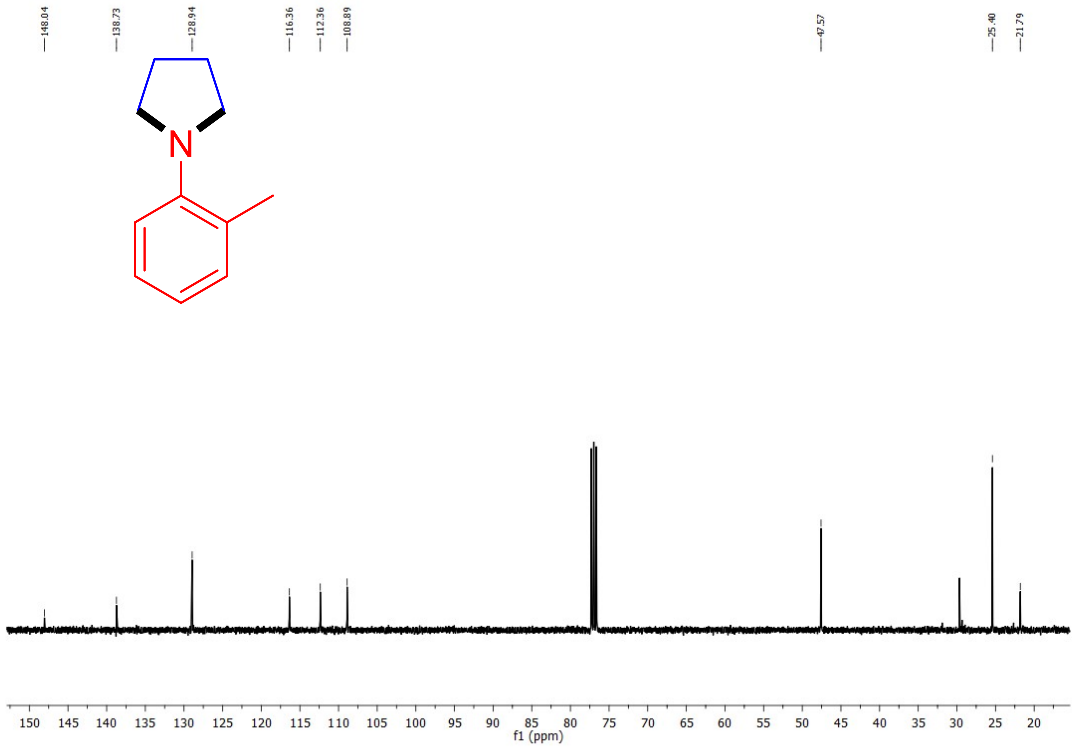
b) 1-(o-tolyl)pyrrolidine (3b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (t, J = 6.8 Hz, 2H), 6.81 (d, J = 8.4 Hz, 1H), 6.76 (t, J = 7.3 Hz, 1H), 3.11 (t, J = 5.8 Hz, 4H), 2.25 (s, 3H), 1.86 (t, J = 5.9 Hz, 4H).

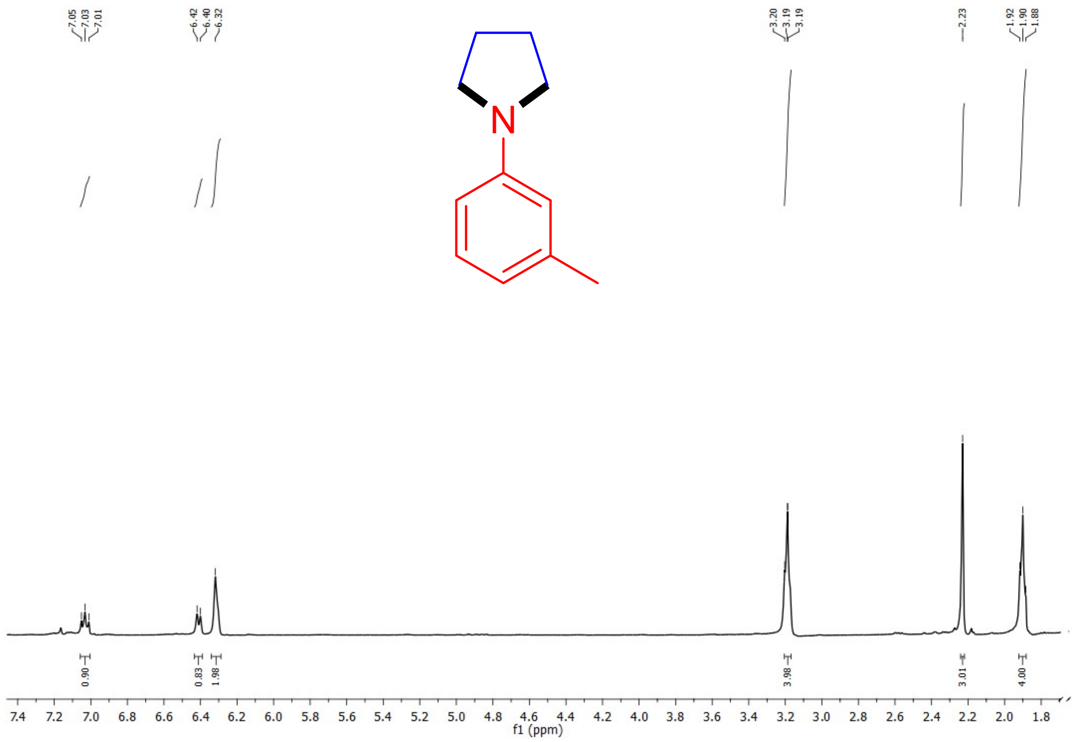
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.04, 138.73, 128.94, 116.36, 112.36, 108.89, 47.57, 25.40, 21.79.

^{1}H NMR Spectrum



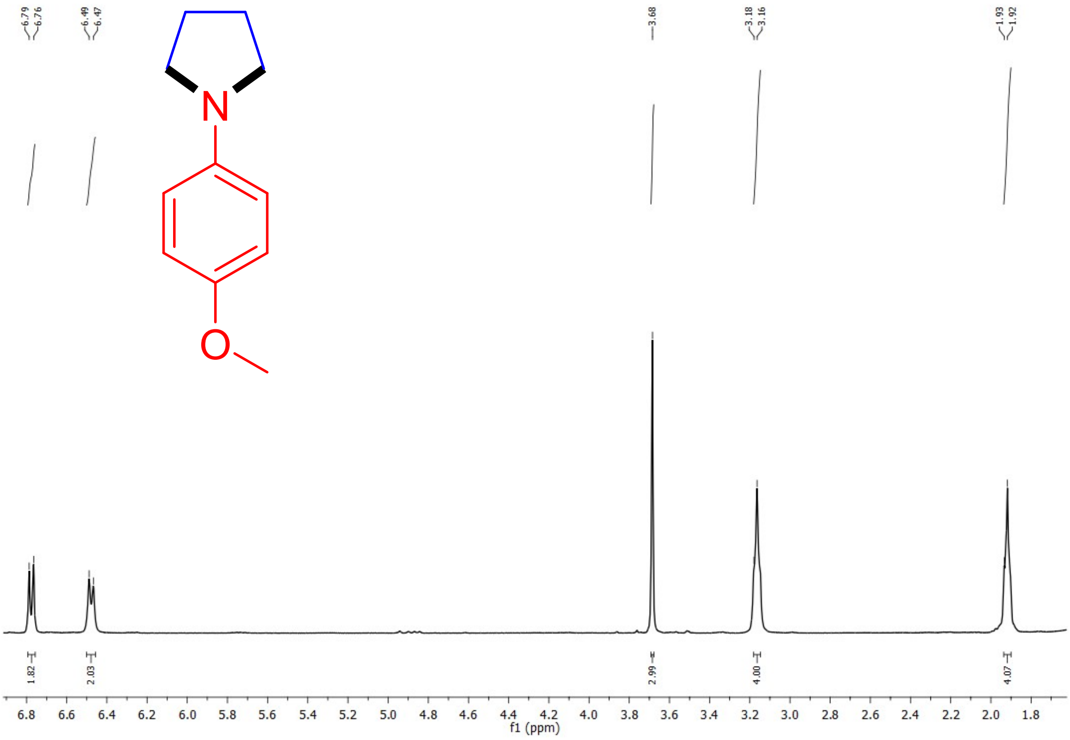


c) 1-(m-tolyl)pyrrolidine (3c)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (t, *J* = 8.1 Hz, 1H), 6.41 (d, *J* = 7.2 Hz, 1H), 6.32 (d, 2H), 3.21 – 3.17 (m, 4H), 2.23 (s, 3H), 1.90 (t, *J* = 6.4 Hz, 4H).

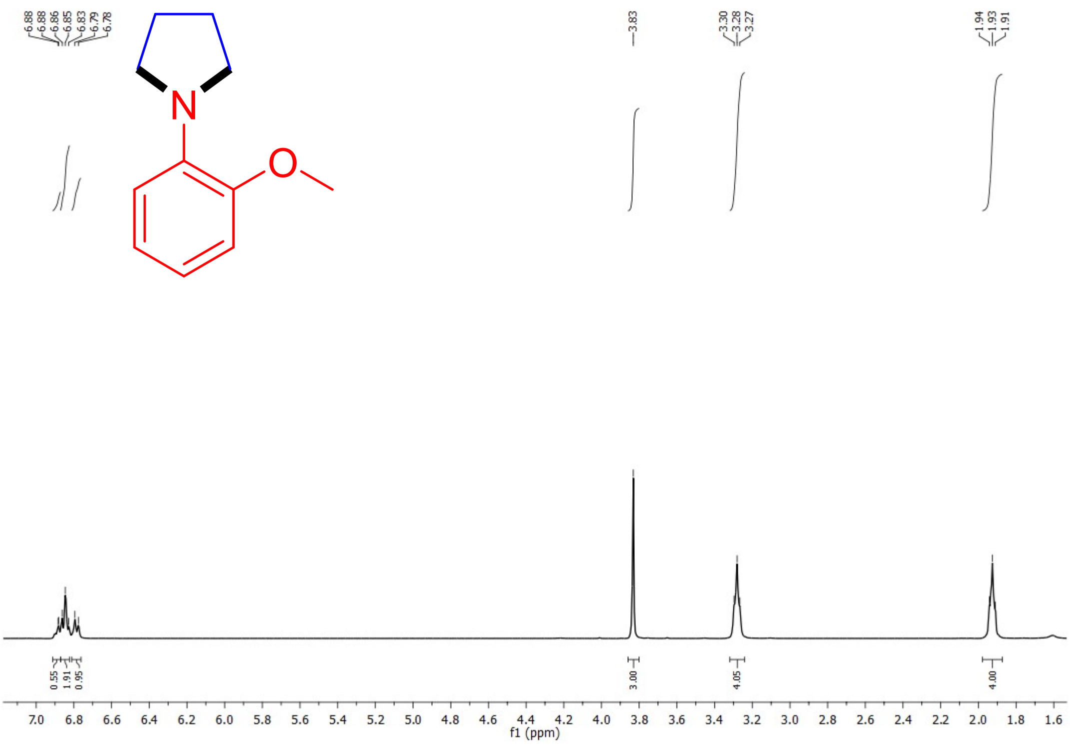


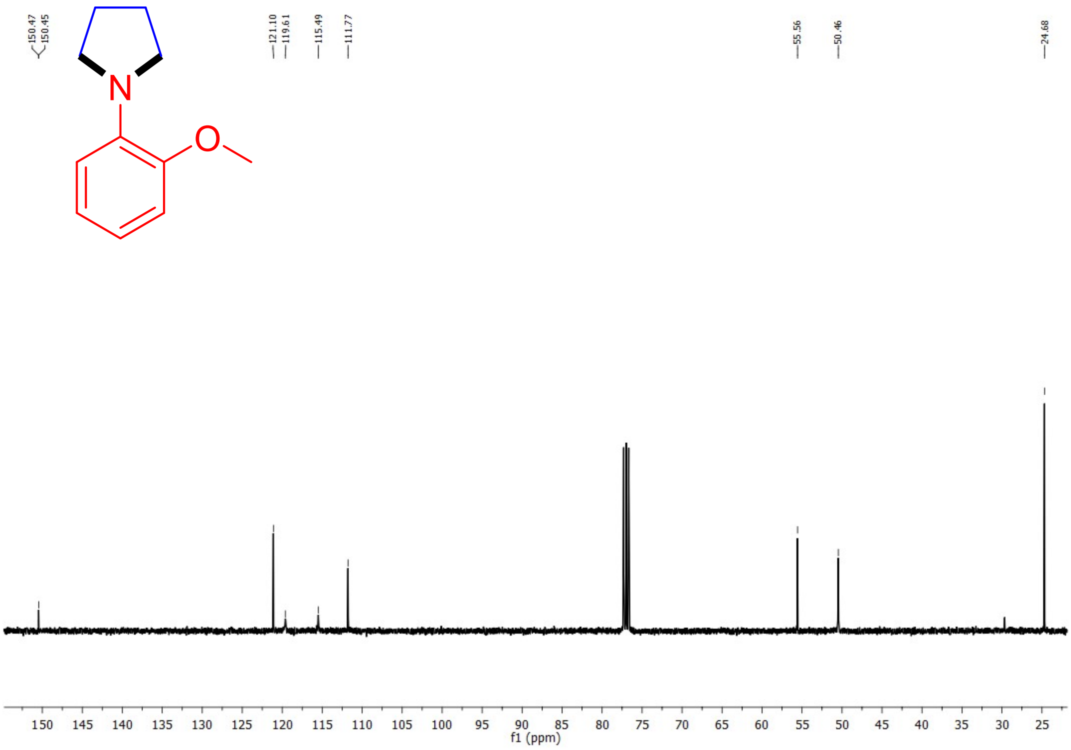
d) 1-(4-methoxyphenyl)pyrrolidine (3d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (d, J = 8.9 Hz, 2H), 6.48 (d, J = 8.5 Hz, 2H), 3.68 (s, 3H), 3.17 (d, J = 6.0 Hz, 4H), 1.93 (d, J = 6.3 Hz, 4H).



e) 1-(2-methoxyphenyl)pyrrolidine (3e)
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, J = 1.1 Hz, 1H), 6.84 (t, J = 6.9 Hz, 2H), 6.79 (d, J = 7.5 Hz, 2H), 3.83 (s, 3H), 3.28 (t, J = 6.0 Hz, 4H), 1.93 (t, J = 6.1 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.47, 150.45, 121.10, 119.61, 115.49, 111.77, 55.56, 50.46, 24.68.
^{1}H NMR spectrum

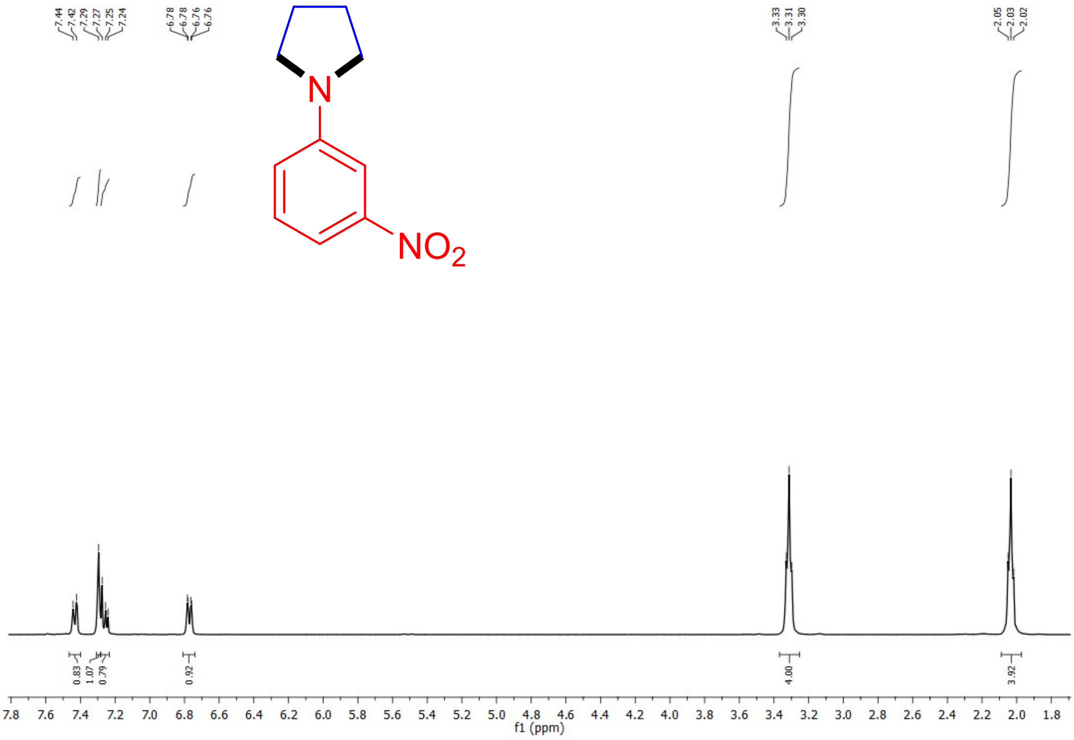


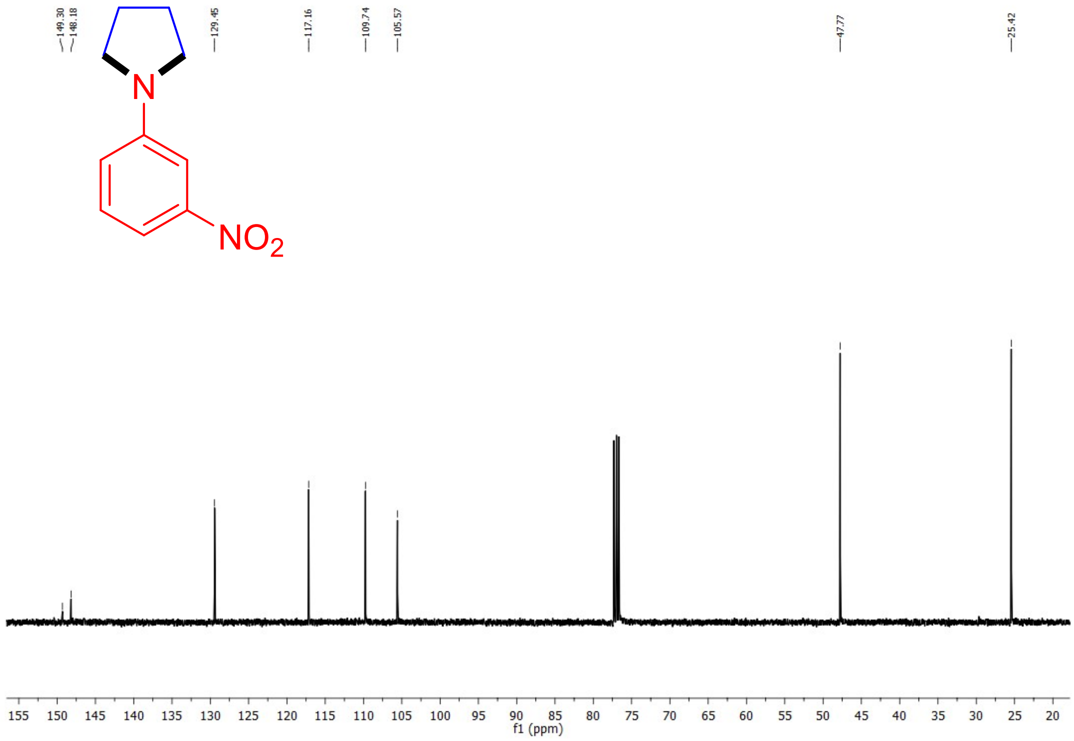


f) 1-(3-nitrophenyl)pyrrolidine (3f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.29 (s, 1H), 7.28 – 7.23 (m, 1H), 6.77 (dd, *J* = 8.1, 1.6 Hz, 1H), 3.31 (t, *J* = 6.4 Hz, 4H), 2.03 (t, *J* = 6.5 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.30, 148.18, 129.45, 117.16, 109.74, 105.57, 47.77, 25.42.

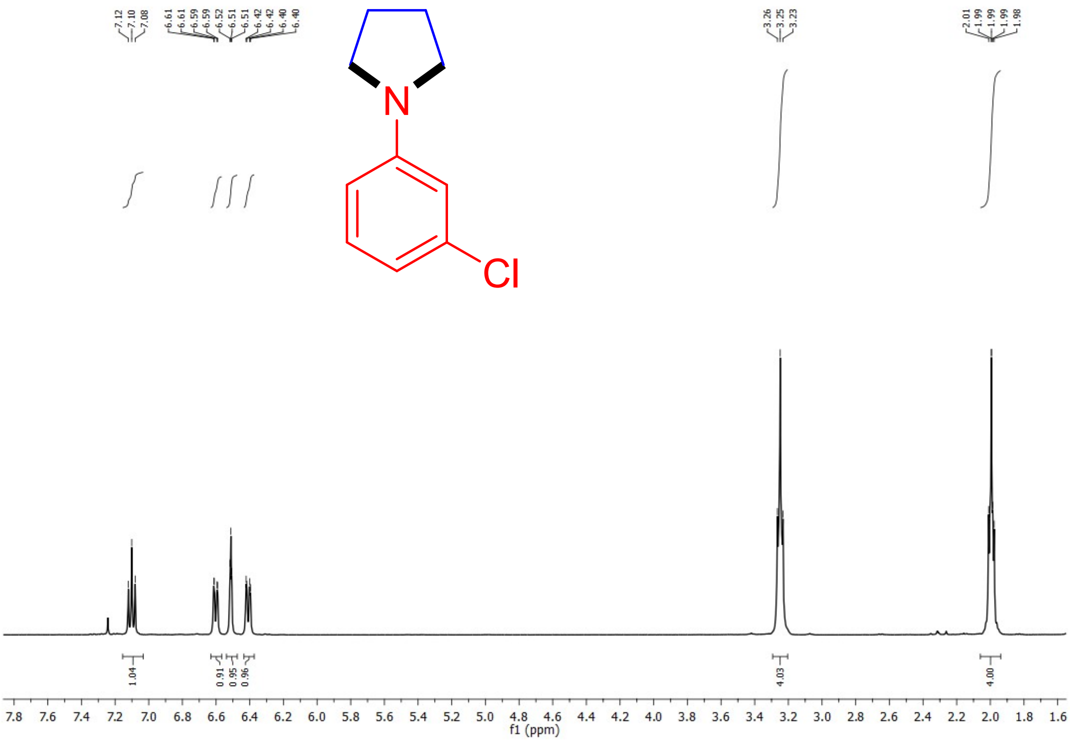


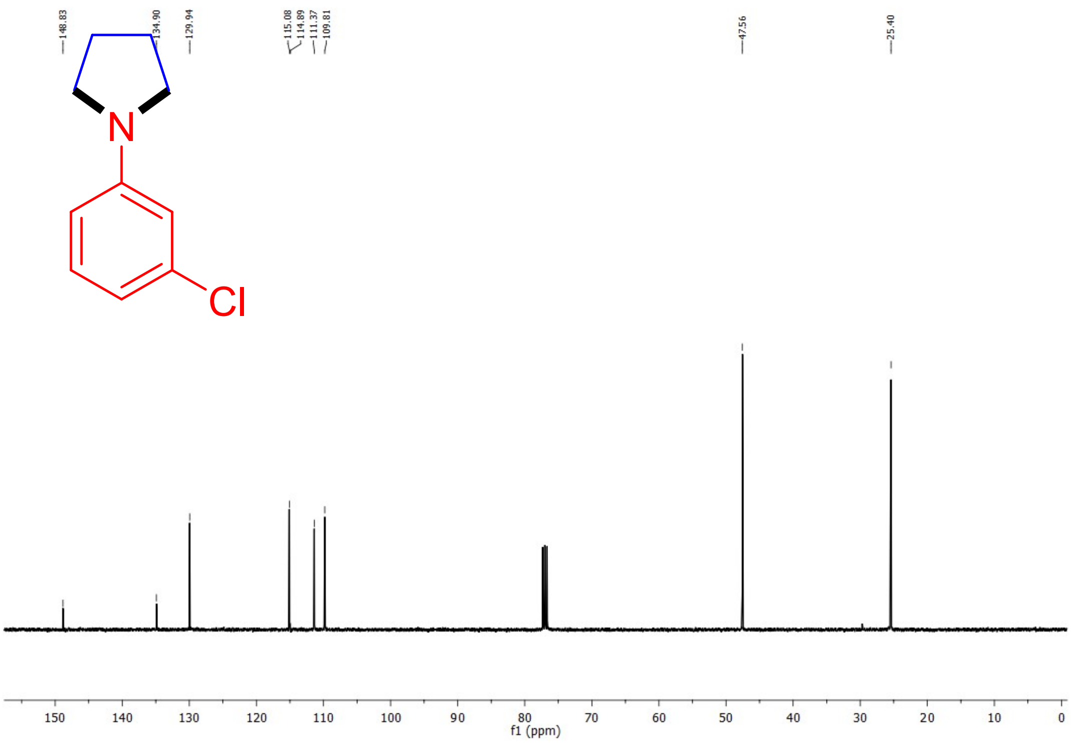


g) 1-(3-chlorophenyl)pyrrolidine (3g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, J = 8.1 Hz, 1H), 6.60 (dd, J = 7.8, 1.1 Hz, 1H), 6.51 (t, J = 2.0 Hz, 1H), 6.41 (dd, J = 8.3, 1.9 Hz, 1H), 3.25 (t, J = 6.6 Hz, 4H), 2.06-1.94 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.83, 134.90, 129.94, 115.08, 114.89, 111.37, 109.81, 47.56, 25.40.

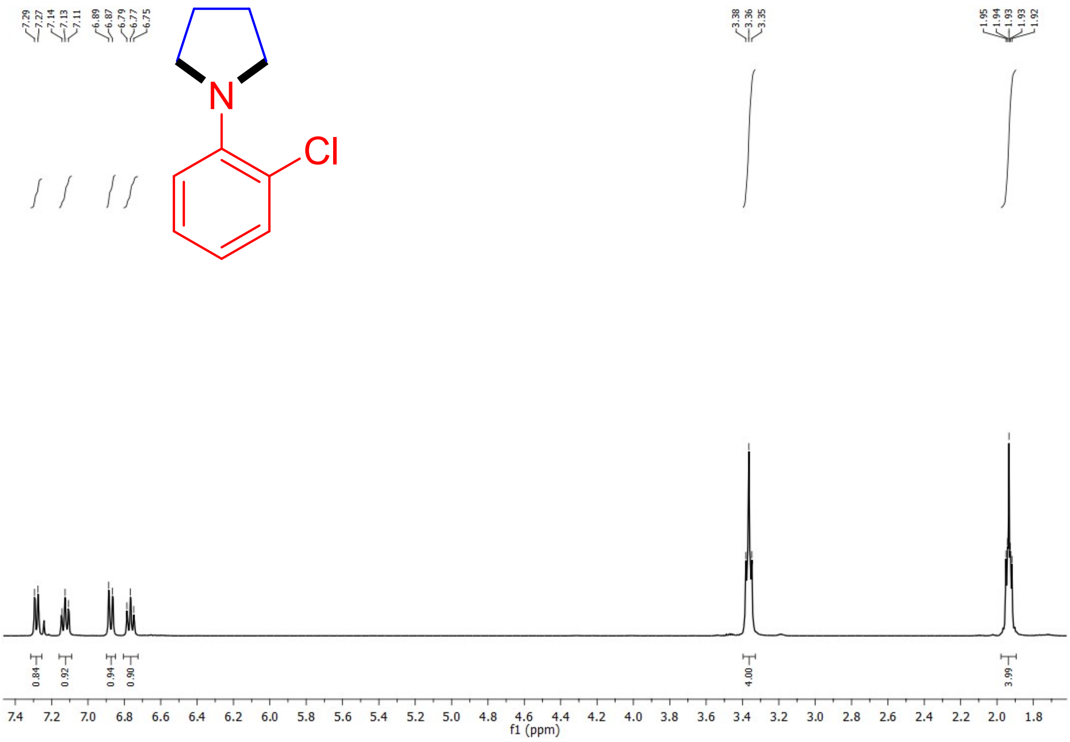


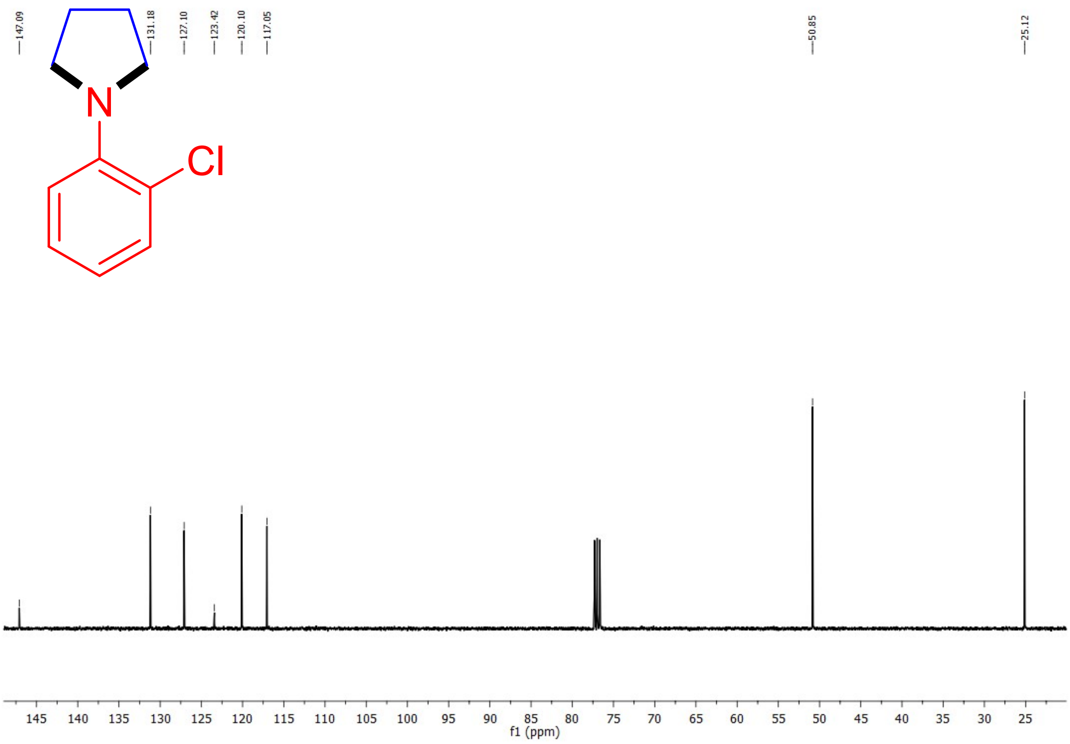


h) 1-(2-chlorophenyl)pyrrolidine (3h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 7.9 Hz, 1H), 7.13 (t, J = 7.0 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 6.77 (t, J = 7.6 Hz, 1H), 3.36 (t, J = 6.6 Hz, 4H), 1.98 – 1.89 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.09, 131.18, 127.10, 123.42, 120.10, 117.05, 50.85, 25.12.





i) 1-(4-chlorophenyl)pyrrolidine (3i)

[1]H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.8 Hz, 2H), 6.45 (d, J = 8.8 Hz, 2H), 3.23 (t, J = 6.4 Hz, 4H), 2.01-1.96 (m, 4H).

[13]C NMR (101 MHz, $CDCl_3$) δ 146.49, 128.79, 120.05, 112.58, 47.69, 25.44.

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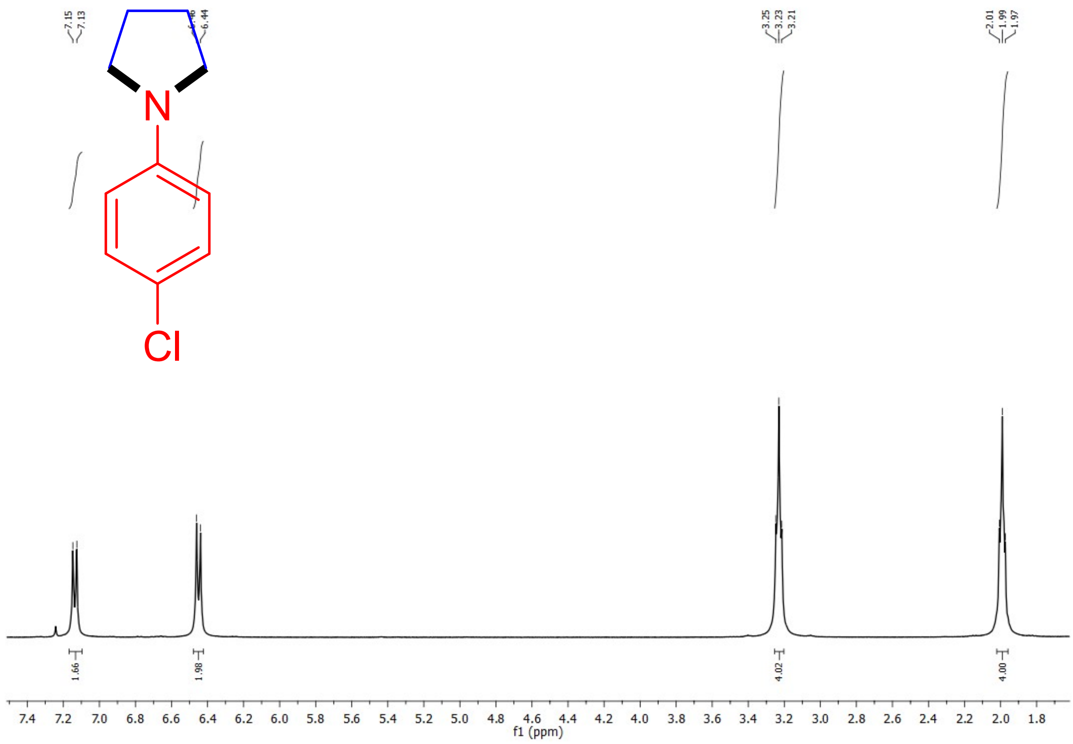
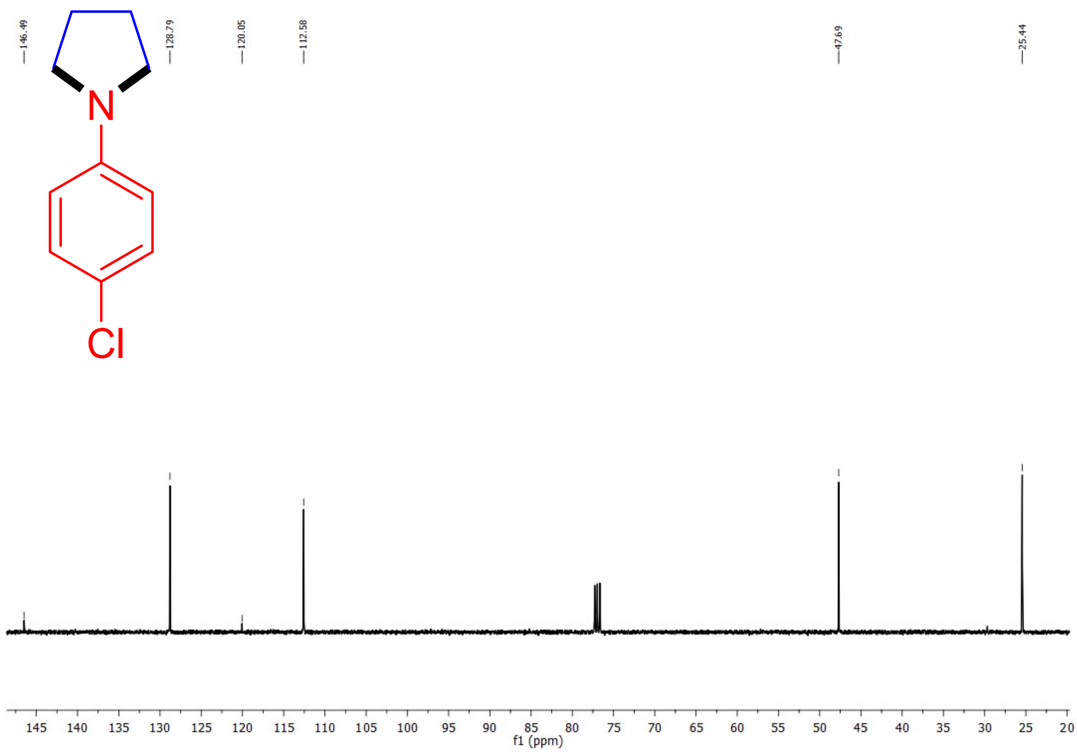
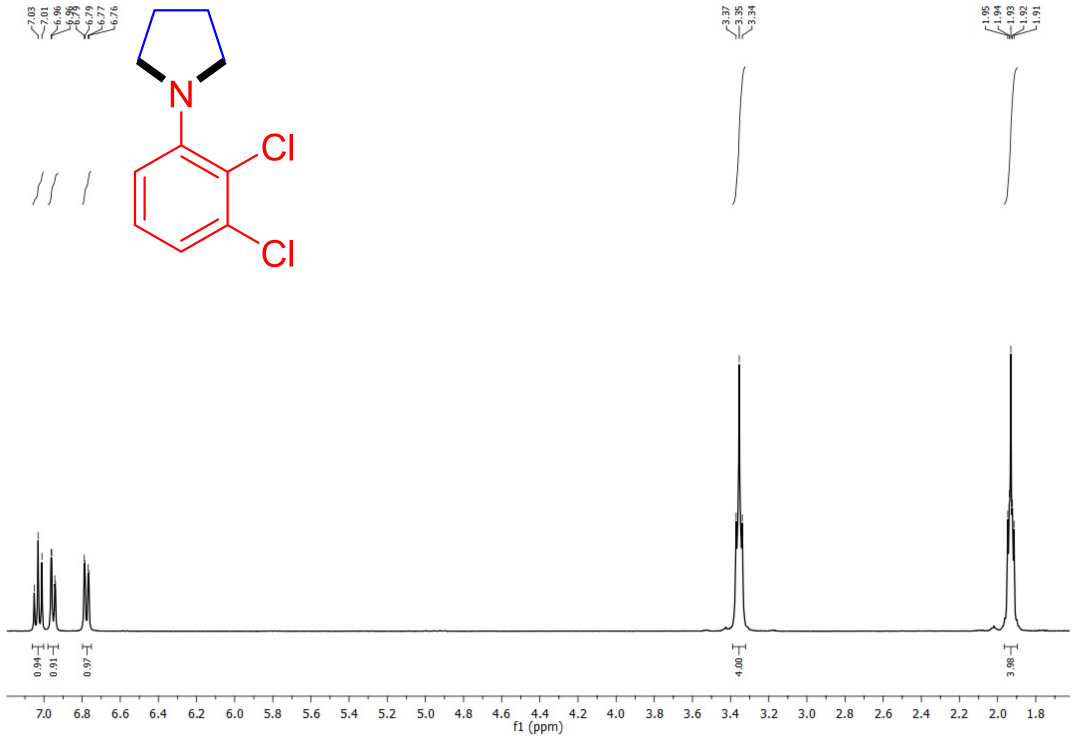


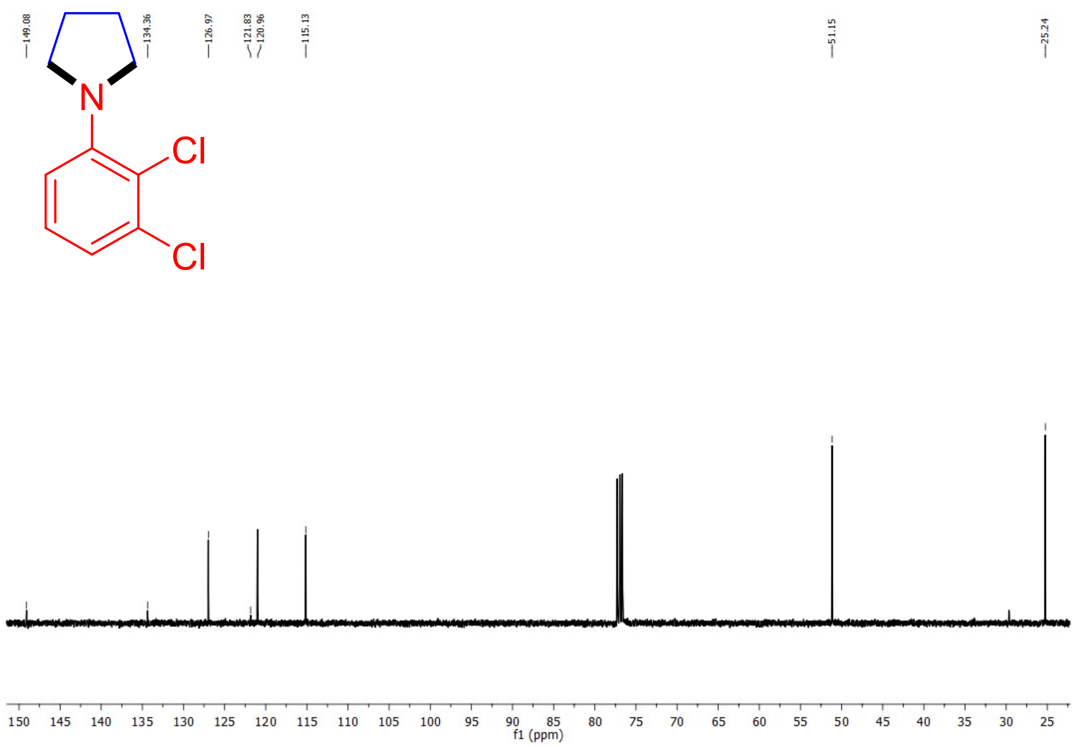


j) 1-(2,3-dichlorophenyl)pyrrolidine (3j)

^{1}H NMR (400 MHz, cdcl$_3$) δ 7.03 (t, J = 8.1 Hz, 1H), 6.95 (dd, J = 7.9, 1.5 Hz, 1H), 6.78 (dd, J = 8.2, 1.4 Hz, 1H), 3.35 (t, J = 6.6 Hz, 4H), 1.97 – 1.89 (m, 4H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 149.08, 134.36, 126.97, 121.83, 120.96, 115.13, 51.15, 25.24.

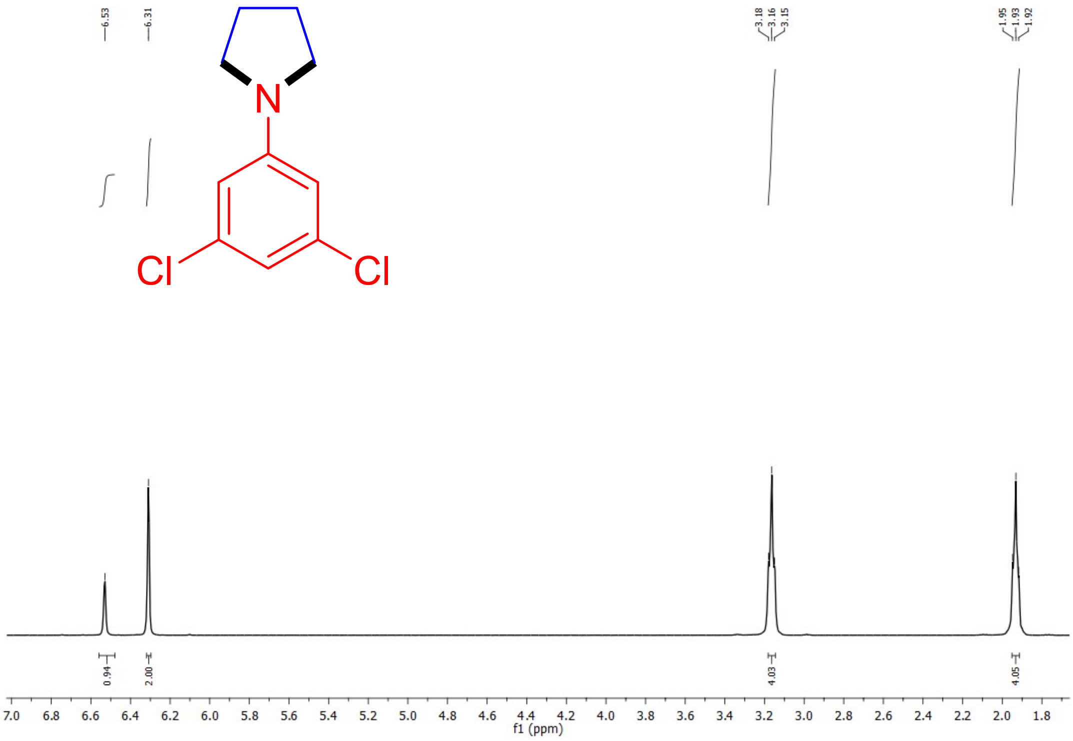


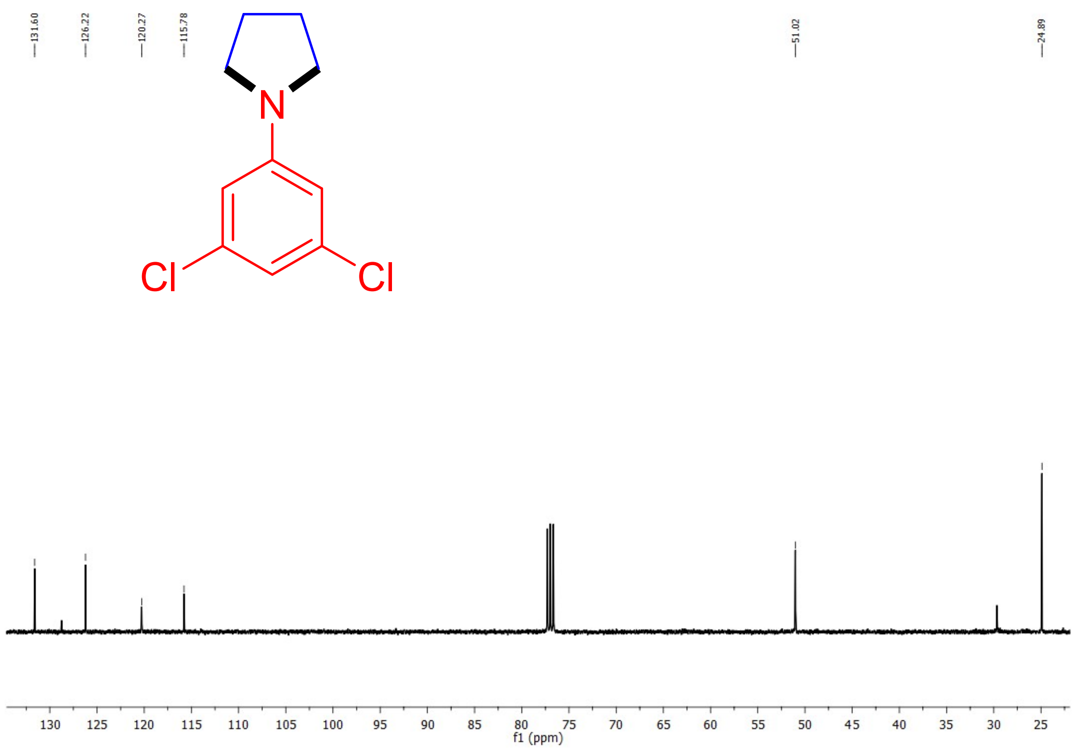


k) 1-(3,5-dichlorophenyl)pyrrolidine (3k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (s, 1H), 6.31 (s, 2H), 3.16 (t, *J* = 6.0 Hz, 4H), 1.93 (t, *J* = 6.1 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.60, 126.22, 120.27, 115.78, 51.02, 24.89



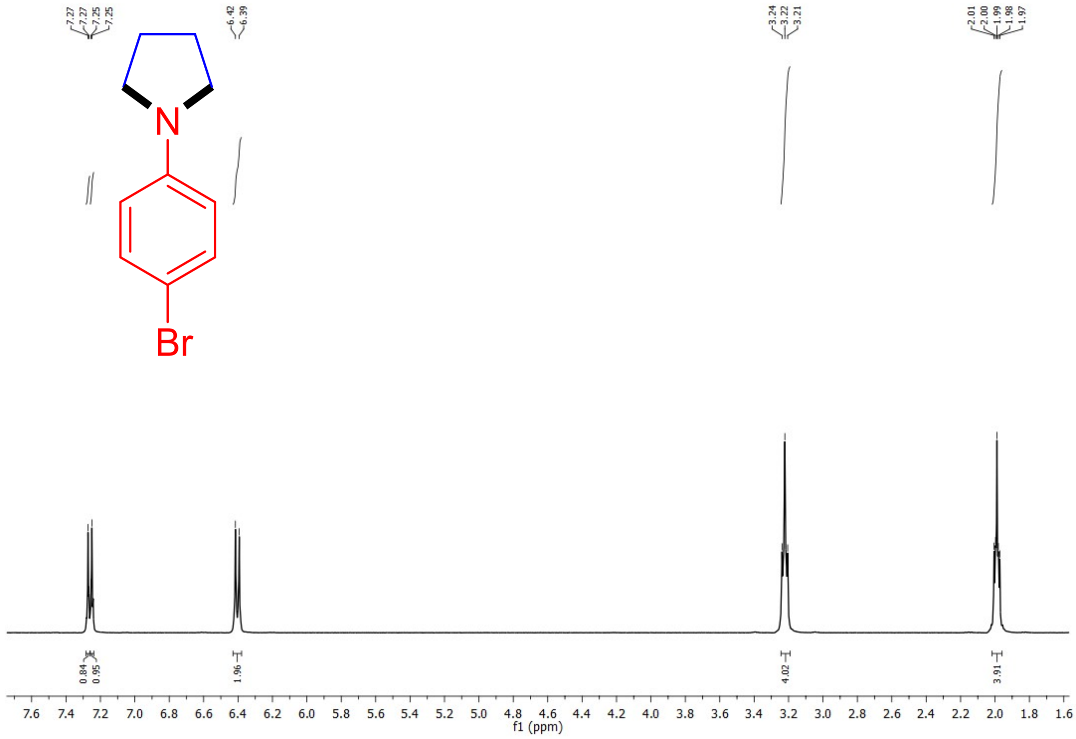


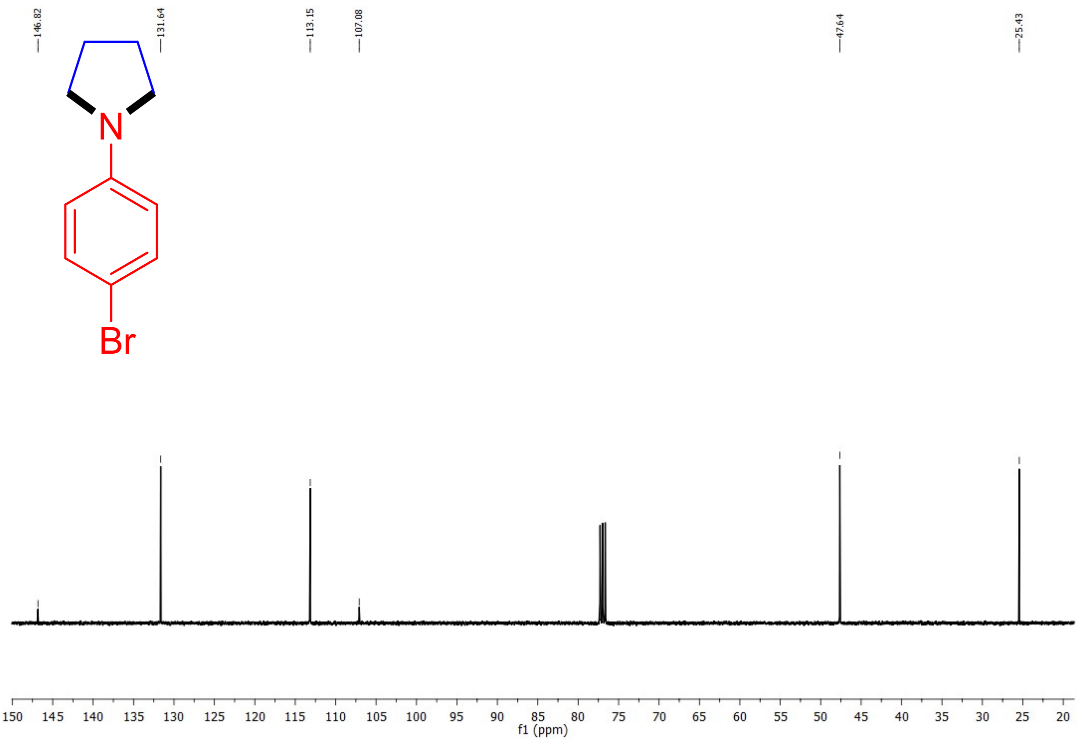
l) 1-(4-bromophenyl)pyrrolidine (3l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 2.1 Hz, 1H), 7.25 (d, J = 2.1 Hz, 1H), 6.40 (d, J = 8.9 Hz, 2H), 3.22 (t, J = 6.6 Hz, 4H), 2.02 – 1.96 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.82, 131.64, 113.15, 107.08, 47.64, 25.43.

HRMS (ESI) m/z: (M)+ calcd for C10H13BrN, 226.0011; found, 226.0046

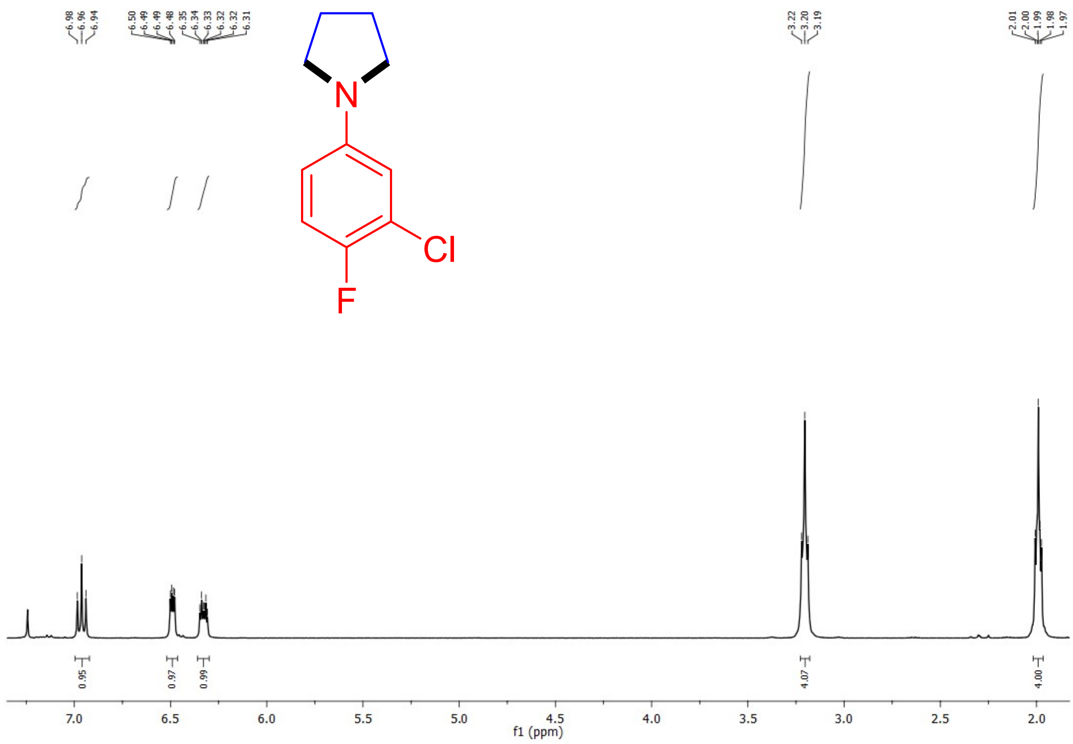


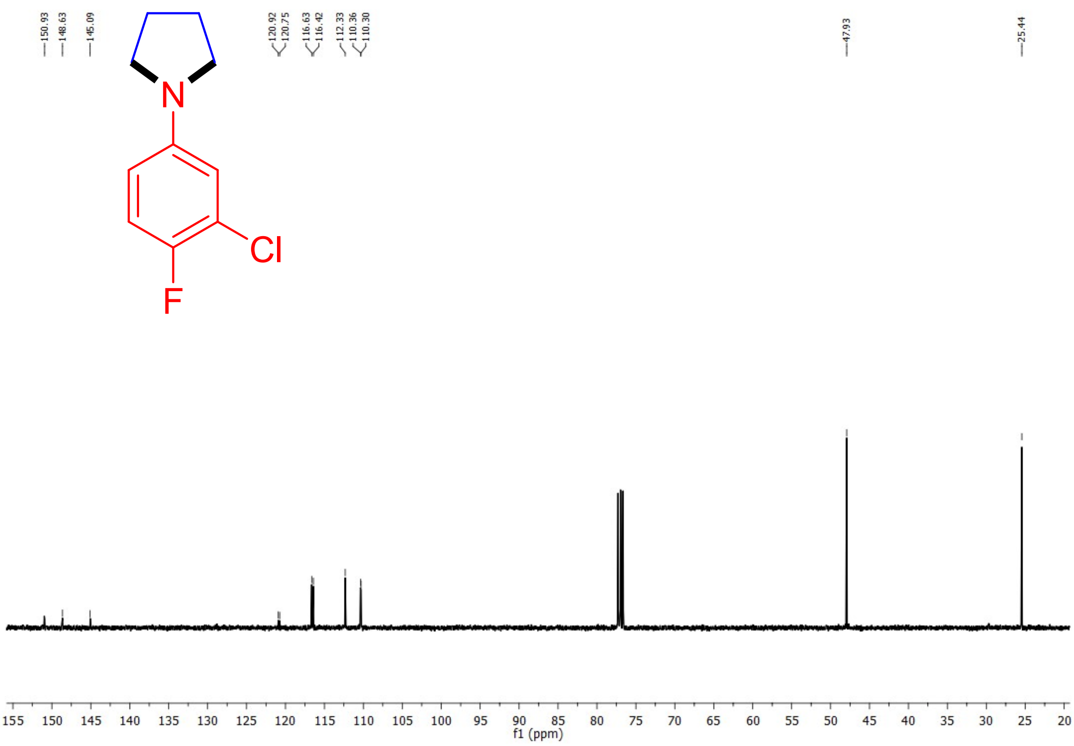


m) 1-(3-chloro-4-fluorophenyl)pyrrolidine (3m)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (t, J = 9.0 Hz, 1H), 6.49 (dd, J = 6.0, 2.9 Hz, 1H), 6.33 (dt, J = 8.9, 3.3 Hz, 1H), 3.20 (t, J = 6.5 Hz, 4H), 2.02 – 1.97 (m, 4H).

^{13}C NMR (101 MHz, $cdcl_3$) δ 150.93, 148.63 (J = 235.8 Hz F coupling), 145.09, 120.92, 120.75, 116.63, 116.42, 112.33, 110.36, 110.30, 47.93, 25.44.

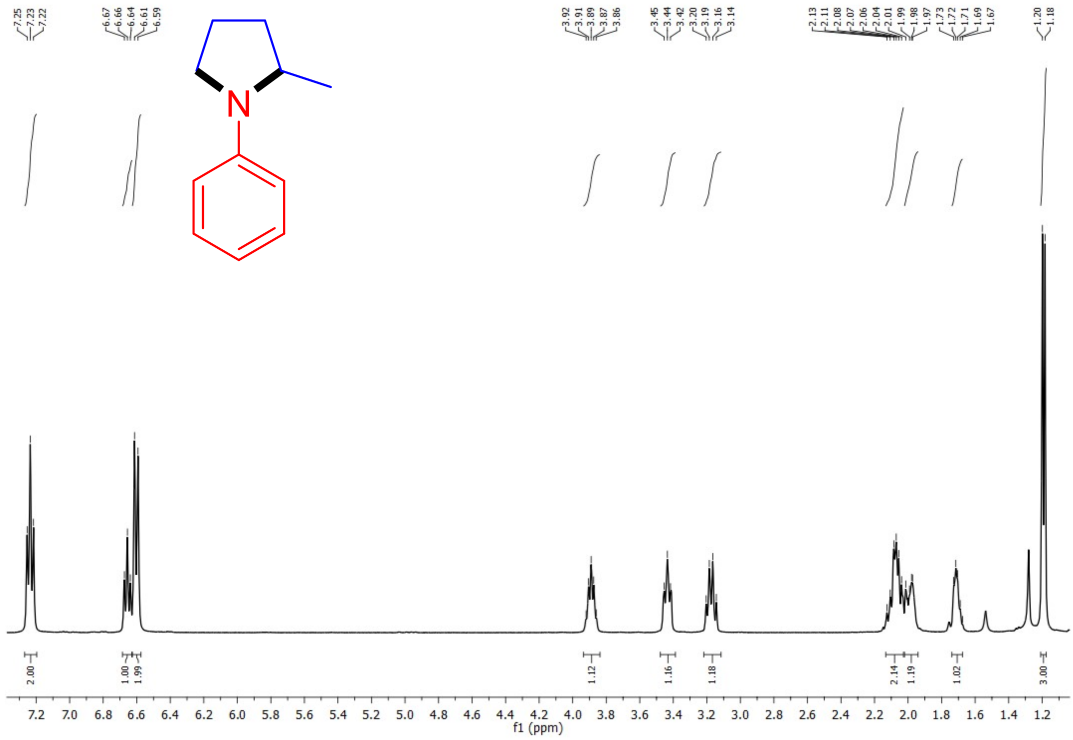


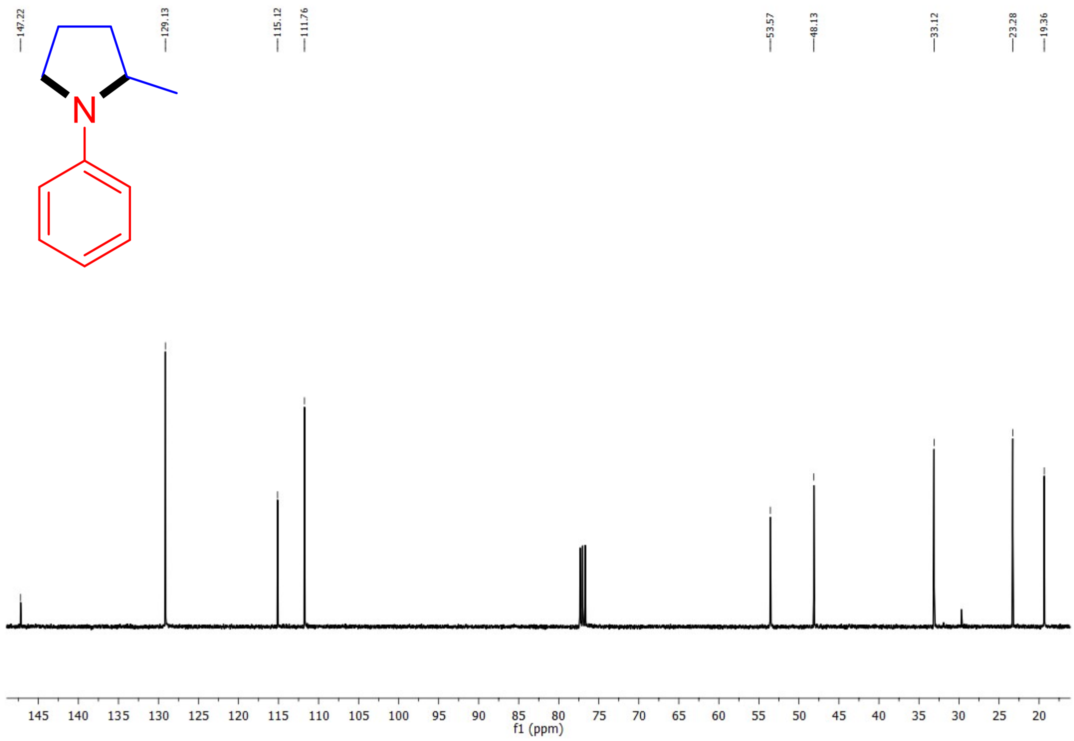


n) 3-methyl-1-phenylpyrrolidine (3n)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 7.6 Hz, 2H), 6.66 (t, J = 7.1 Hz, 1H), 6.60 (d, J = 8.3 Hz, 2H), 3.96 – 3.77 (m, 1H), 3.44 (t, J = 7.5 Hz, 1H), 3.17 (dd, J = 16.3, 8.0 Hz, 1H), 2.08 (dt, J = 12.8, 7.4 Hz, 2H), 1.99 (dd, J = 10.6, 5.8 Hz, 1H), 1.74 – 1.66 (m, 1H), 1.19 (d, J = 6.2 Hz, 3H).[2]

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.22, 129.13, 115.12, 111.76, 53.57, 48.13, 33.12, 23.28, 19.36.

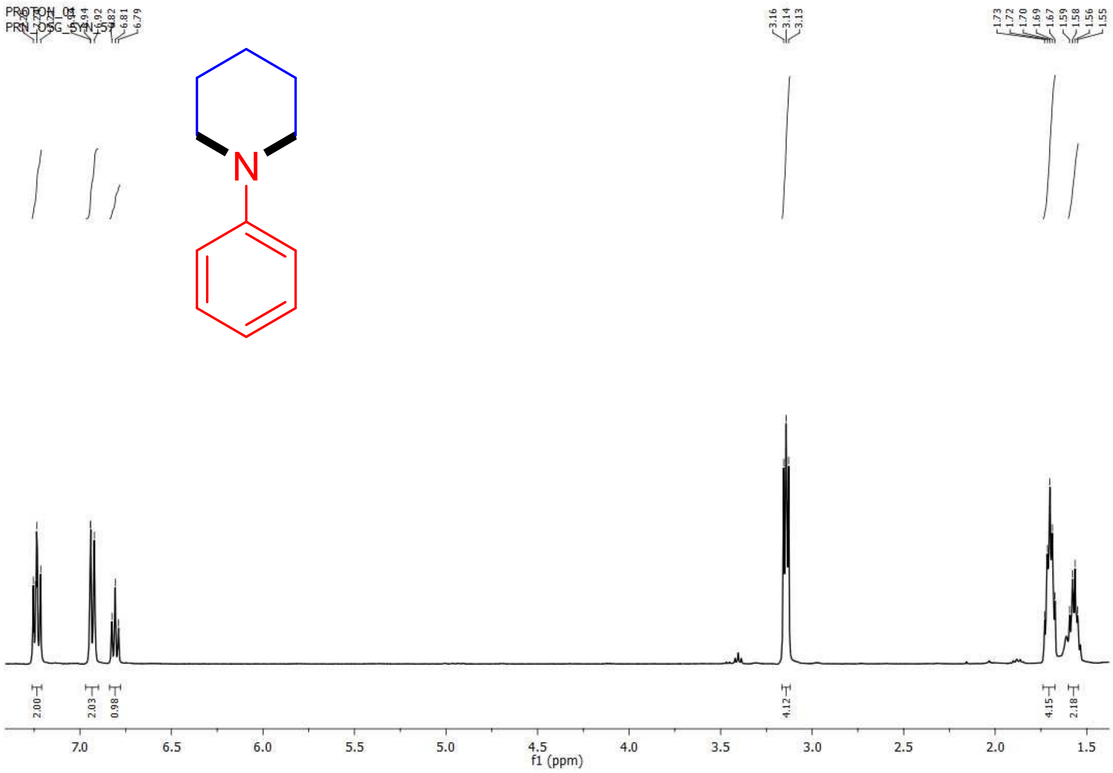


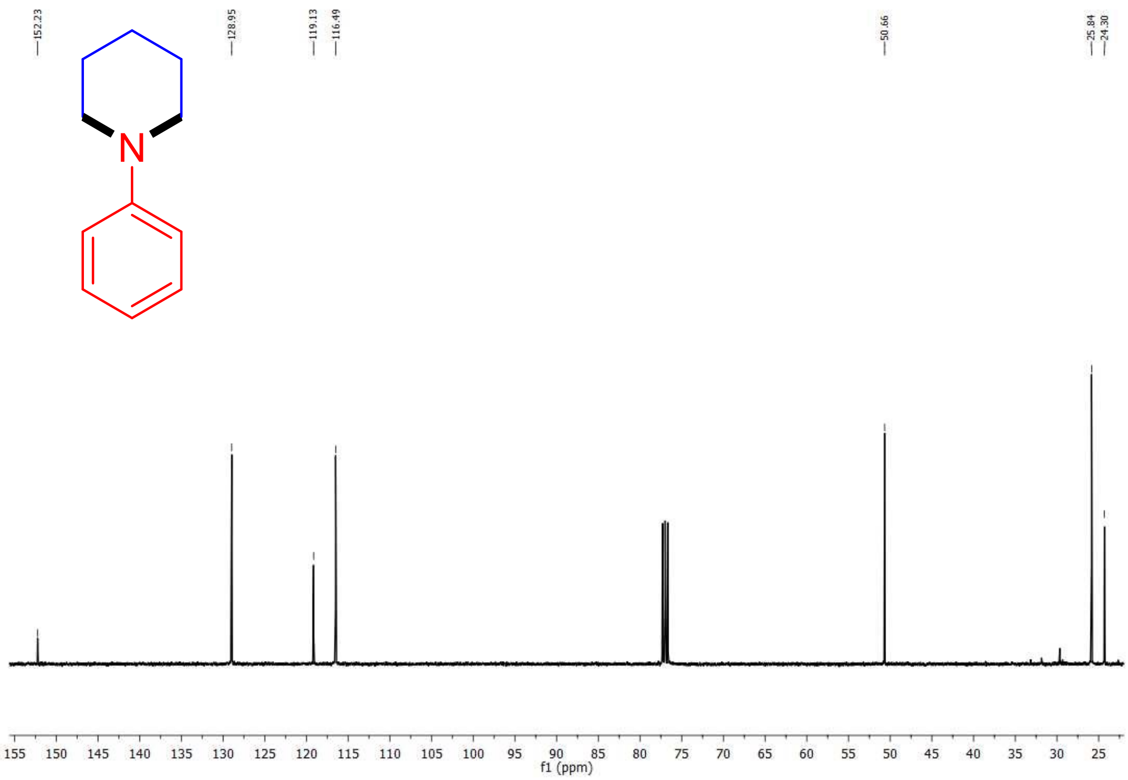


o) 1-phenylpiperidine (3o)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 8.0 Hz, 2H), 7.00 – 6.86 (m, 2H), 6.81 (t, J = 7.3 Hz, 1H), 3.19 – 3.09 (m, 4H), 1.70 (dt, J = 11.3, 5.7 Hz, 4H), 1.57 (dd, J = 11.4, 5.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.23, 128.95, 119.13, 116.49, 50.66, 25.84, 24.30.

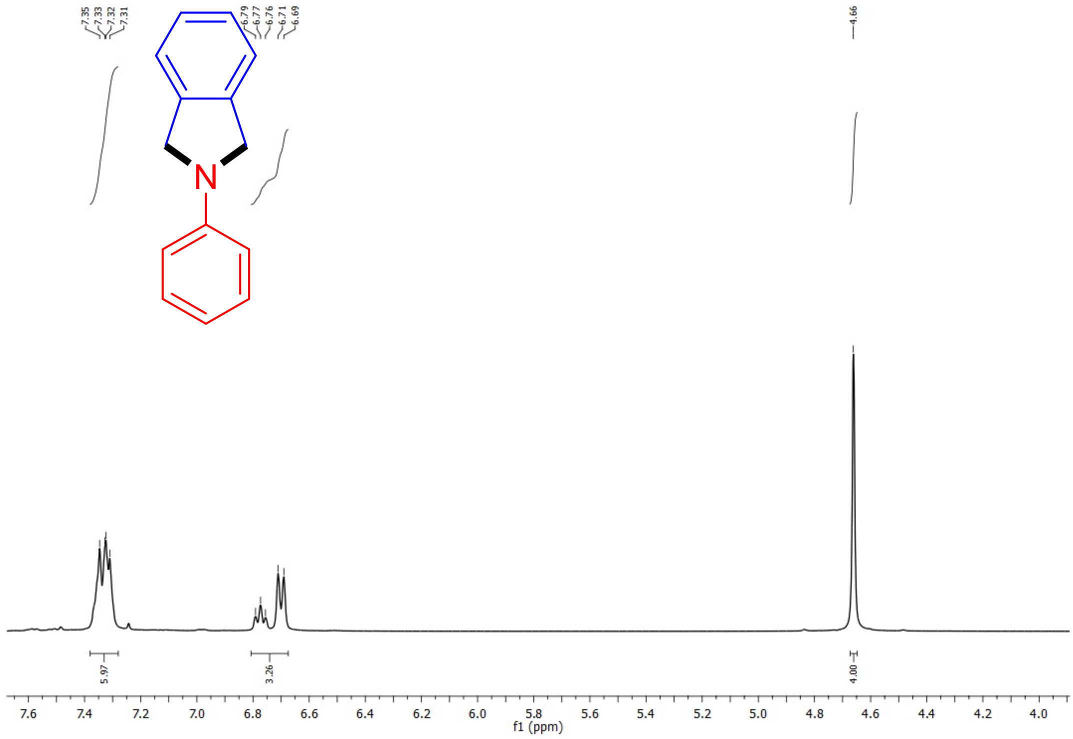


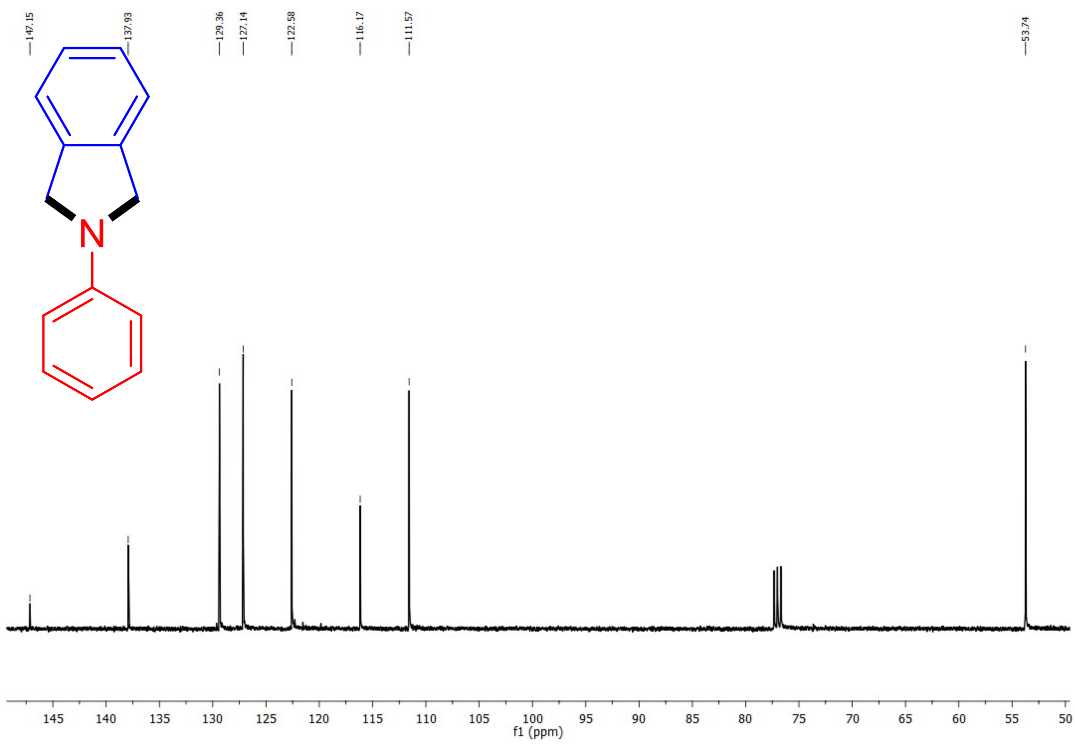


p) 2-phenylisoindoline (3p)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.9, 6.6 Hz, 6H), 6.85 – 6.62 (m, 3H), 4.66 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.15, 137.93, 129.36, 127.14, 122.58, 116.17, 111.57, 53.7





References:

(1) Korbad, B. L.; Lee, S.-H. Synthesis of N-Aryl Substituted, Five- and Six-Membered Azacycles Using Aluminum-Amide Complexes. *Chem. Commun.* **2014**, *50* (64), 8985–8988. https://doi.org/10.1039/C4CC04111A.

(2) Ju, Y.; Varma, R. S. Aqueous N-Heterocyclization of Primary Amines and Hydrazines with Dihalides: Microwave-Assisted Syntheses of N-Azacycloalkanes, Isoindole, Pyrazole, Pyrazolidine, and Phthalazine Derivatives. *J. Org. Chem.* **2006**, *71* (1), 135–141. https://doi.org/10.1021/jo051878h.