Supporting Information

Insights into Cascade and Sequential one pot pathways of reductive amination for aldehydes paired with bio-derived levulinic acid to *N*-substituted pyrrolidones using molecular hydrogen

Tejas A. Gokhale, Amol B. Raut, Sheetal K. Chawla and Bhalchandra M. Bhanage*

Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai- 400019 INDIA.

Email ID: bm.bhanage@gmail.com, bm.bhanage@ictmumbai.edu.in

INDEX

Analytical methods

The properties and run conditions of the GC–MS (Shimadzu QP 2010) instrument (Rtx-5MS, 30 m × 25 mm) were: the column oven temperature was set to 80 °C to hold for 4 minutes. Then the temperature was raised to 260 °C with a ramp rate of 15 °C/min. This temperature was held out for 20 min. The solvent cut time and MS start time was set at 4 minutes. The yield of product was calculated by using a Perkin Elmer Clarus 400 Gas Chromatography with FID with capillary column of 30 m. The quantitative determinations for parameter optimization reactions were carried out using dioxane (HPLC grade) as the internal standard for GC calculations.

Material Characterization

The catalytic nanocomposites were characterized using the following techniques such as: Powder X-ray Diffraction (PXRD) analysis utilized Shimadzu XR-6100 instrument with Cu (Kα= 1.54 Å) scan rate of 2 deg/min with 0.15 mm receiving slit, X-ray Photoelectron Spectroscopy (XPS) analysis was recorded on AXIS Supra by (Kratos Analytical, UK) with pressure below $2X10^{-9}$ Pa with Al Kα source, with take-off angle of 90° for analysis. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) were carried out on TESCAN MIRA 3 model with secondary electron detector in the range of 10 to 20 kV. High Resolution Transmission Electron Microscopy (HR-TEM) imaging was carried out on FEI Tecnai G2 F30 with accelerating potential of 300 kV. Ammonia Temperature Programmed Desorption (NH_3-TPD) were carried out on Micrometrics Autochem II Chemisorption analyzer with 30.20 cm^3 STP/min of measured flow rate, ATR-IR spectra was recorded on PerkinElmer 2000 FTIR spectrophotometer with ATR attachment in the wavenumber range of 4000−400 cm^{-1}. Brunauer-Emmett-Teller (BET surface analysis) was analyzed on Micrometrics ASAP 2020 Surface Area and Porosity Analyzer with N_2 gas using bath temperature at -195.48 °C. NMR spectra were recorded with an Agilent Technologies (^{1}H NMR at 400 MHz, ^{13}C NMR at 101 MHz) spectrometer.

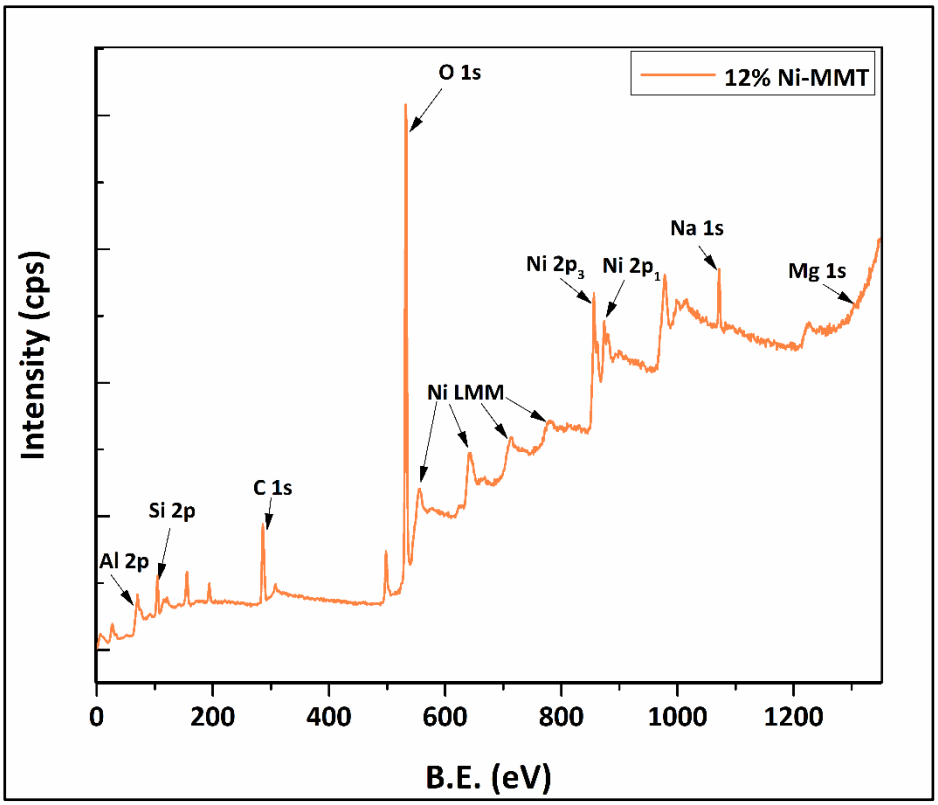


Figure S1 XPS survey for 12% Ni-MMT

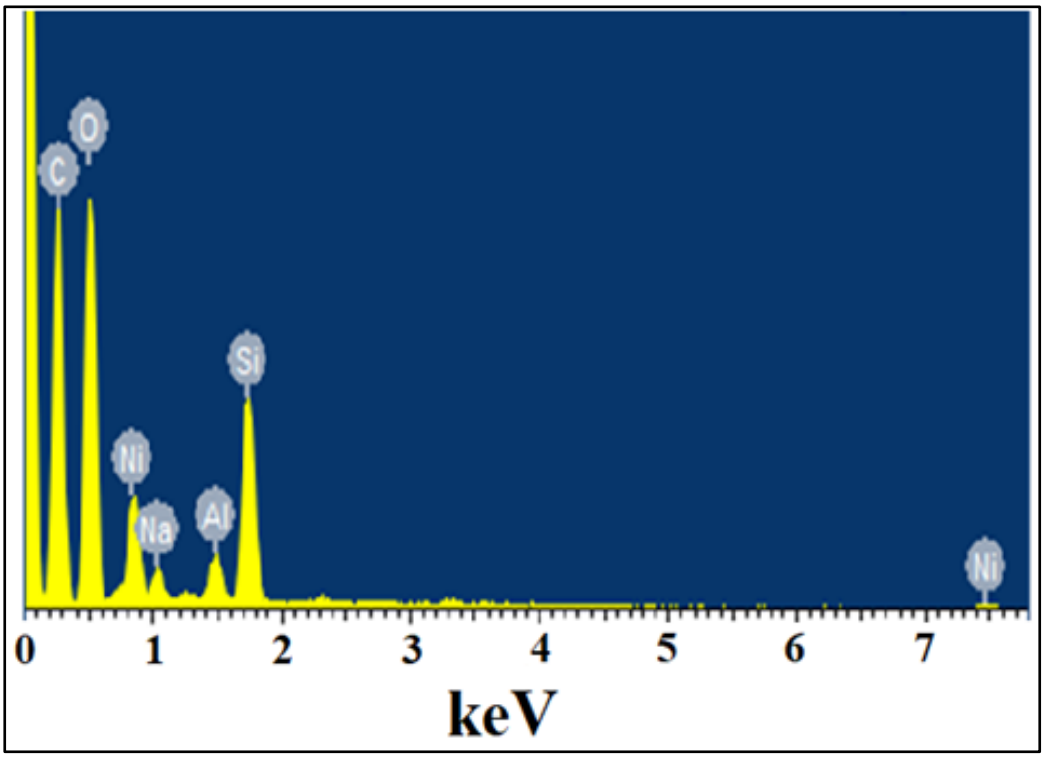


Figure S2 EDX spectra for 12% Ni-MMT

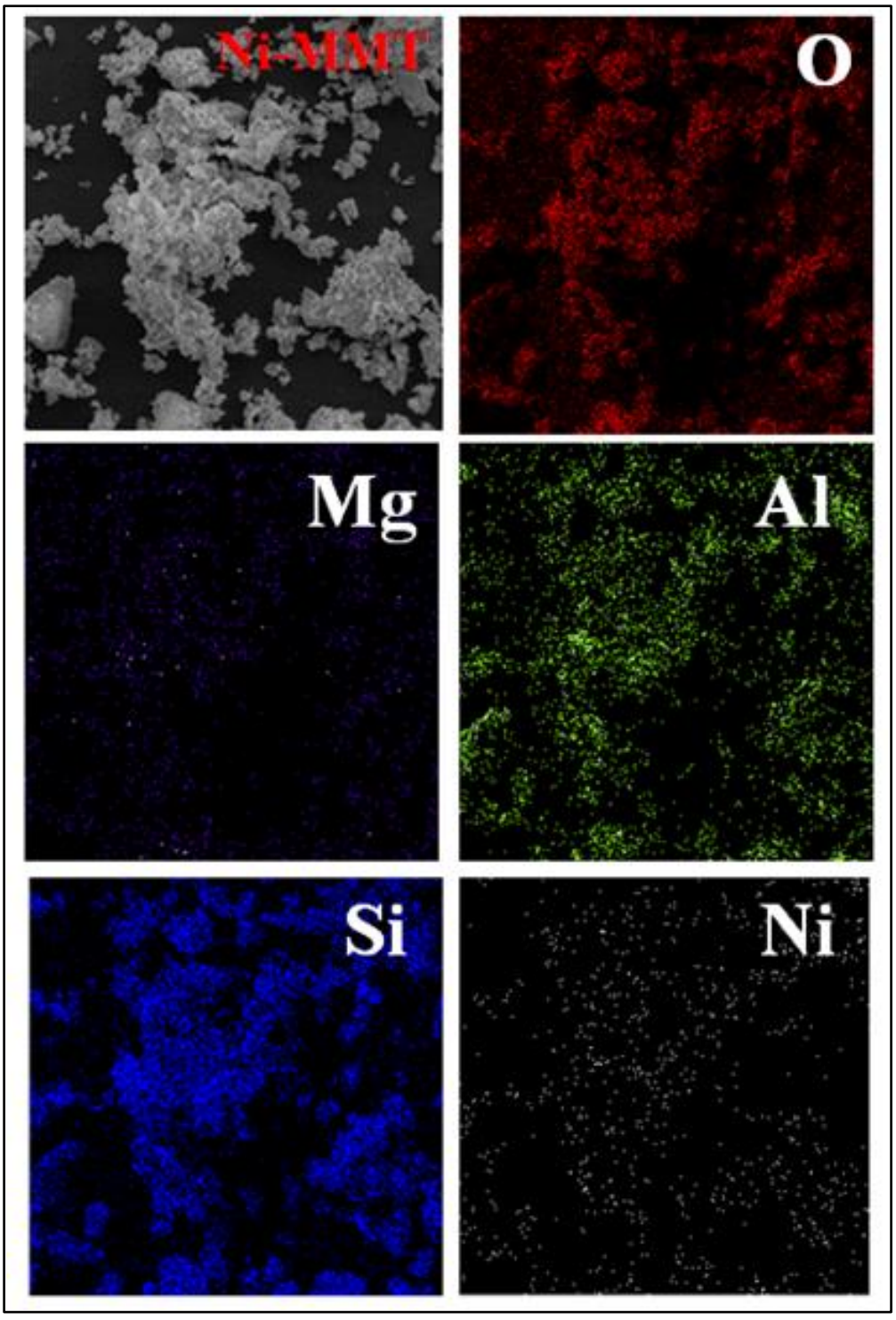


Figure S3 Elemental mappings of 12% Ni-MMT for O, Mg, Al, Si and Ni

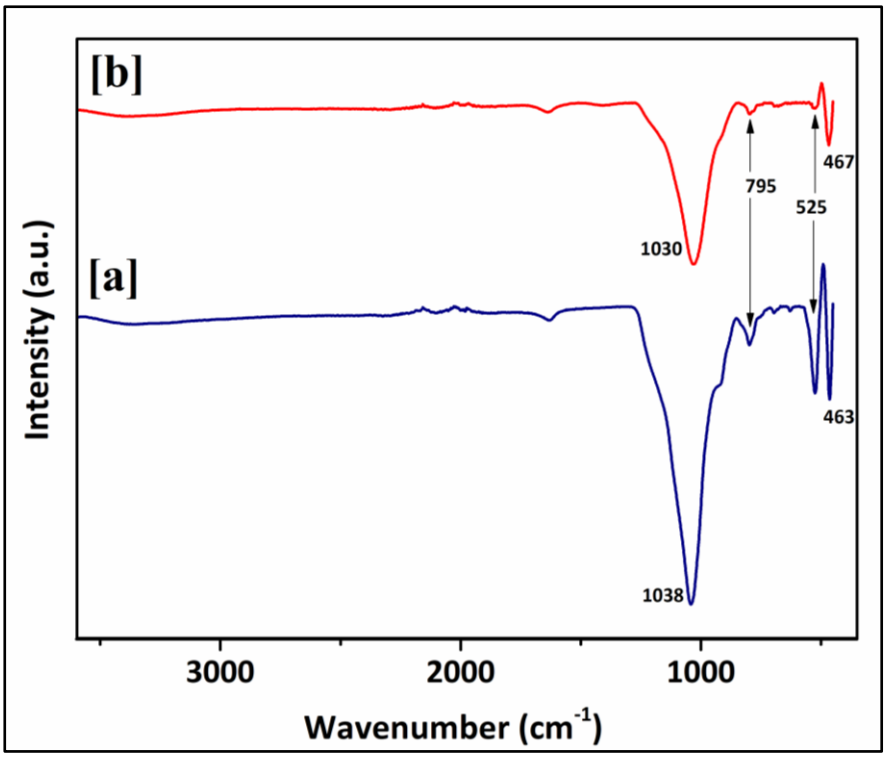


Figure S4 ATR-IR spectra for [a] MMT support & [b] 12% Ni-MMT nanocomposite[1]

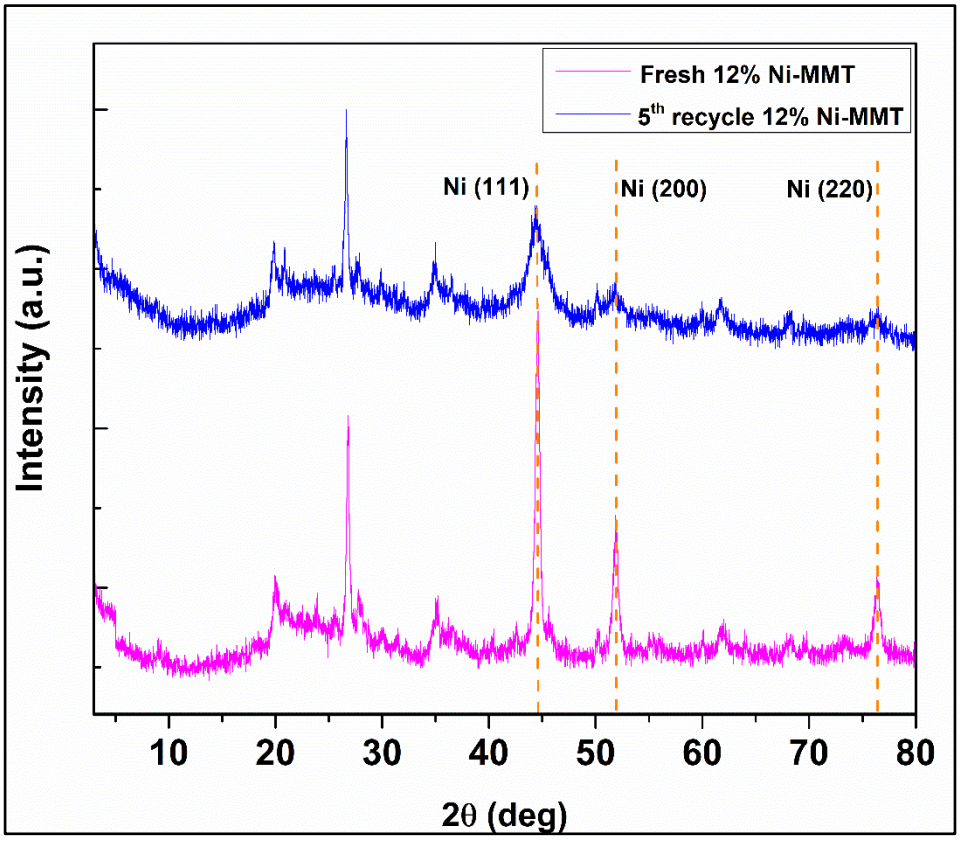


Figure S5 PXRD spectra for fresh and 5th recycle 12% Ni-MMT nanocomposite

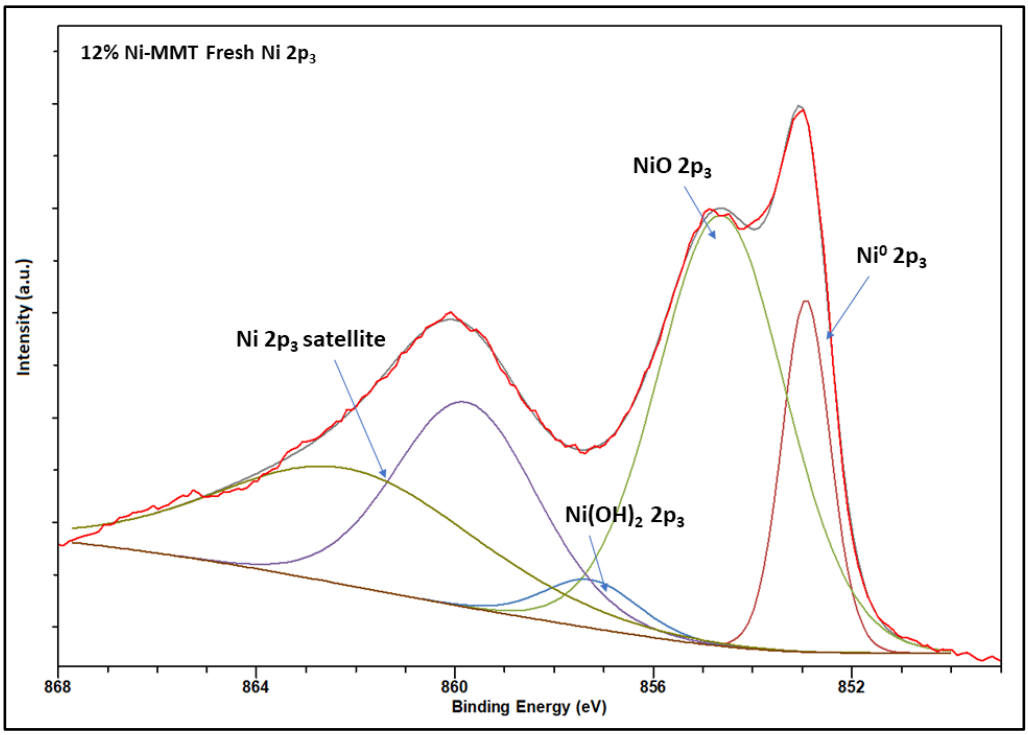


Figure S6 Deconvoluted XPS Ni 2p region for Fresh 12% Ni-MMT

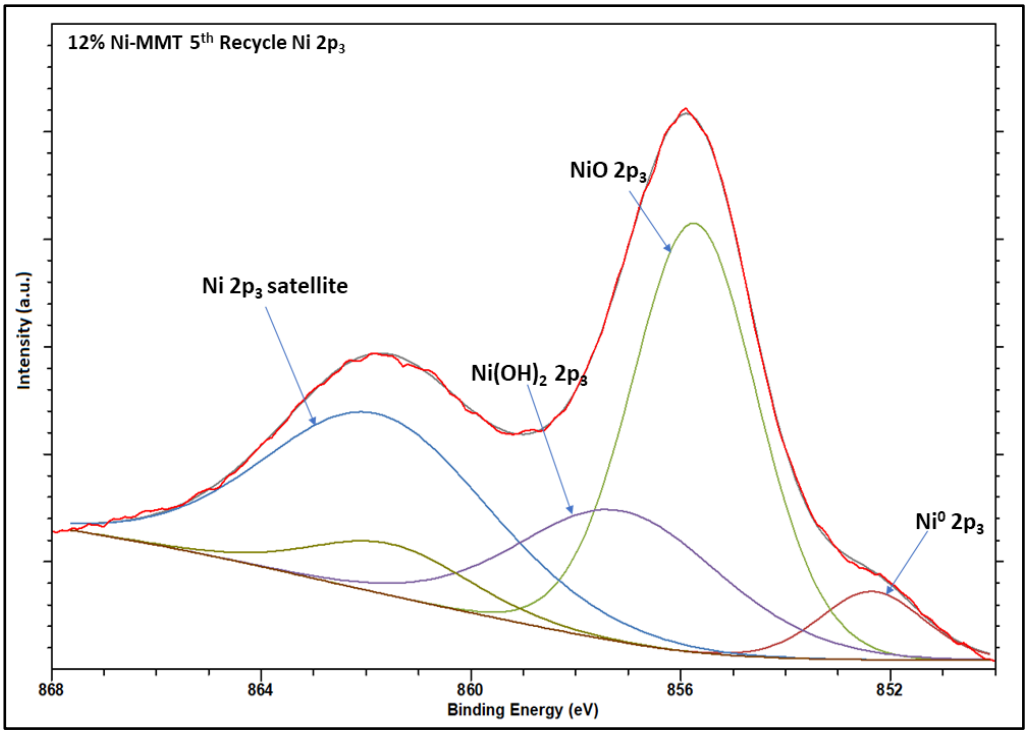
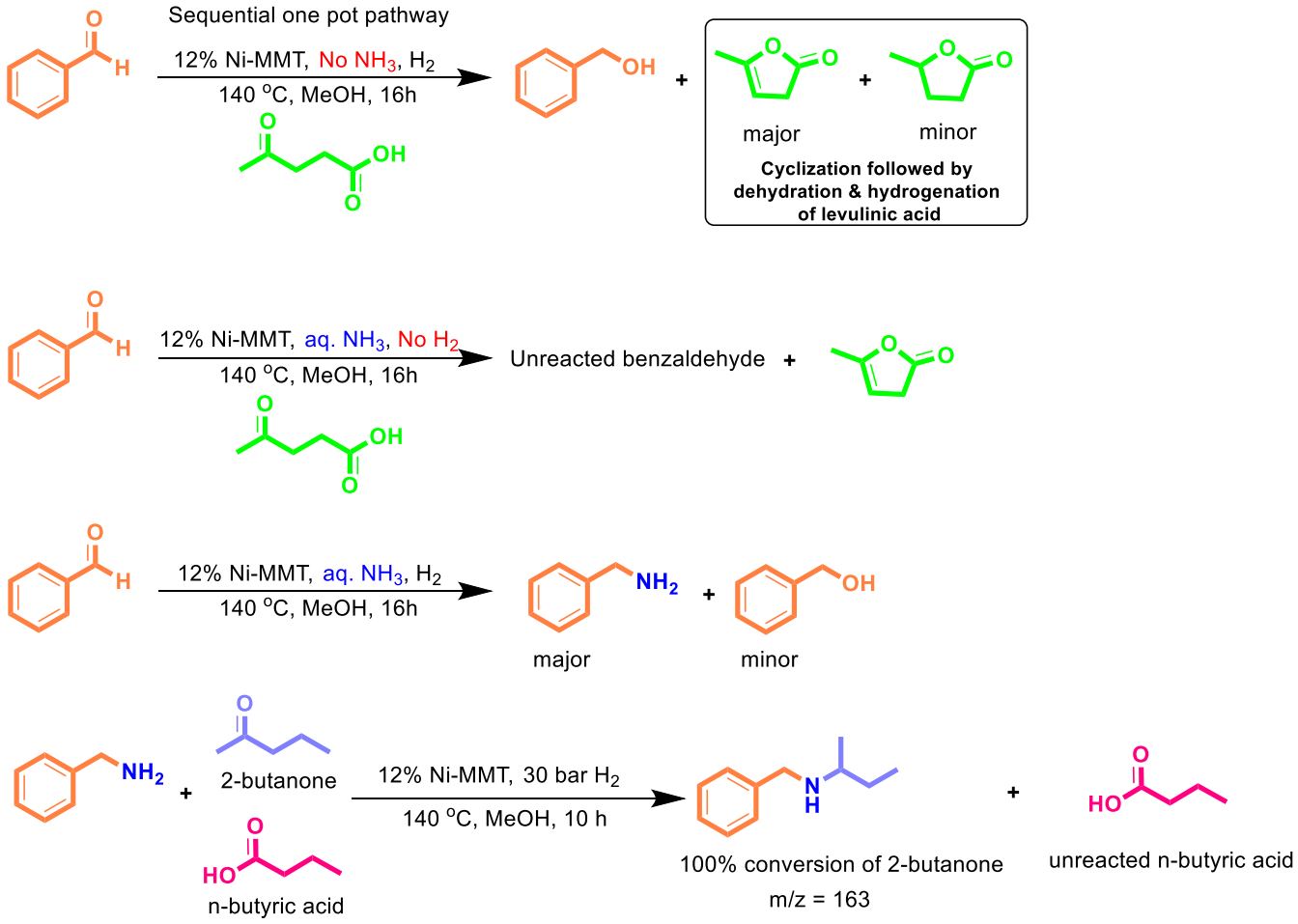


Figure S7 Deconvoluted XPS Ni 2p region for 5th recycle 12% Ni-MMT

Table S1 XPS Ni $2p_3$ peak composition for Fresh and Recycle 12% Ni-MMT

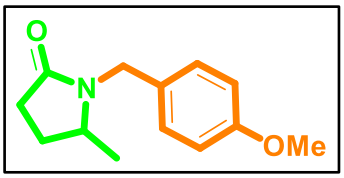
Sample	Species		
	Ni^0	NiO	$Ni(OH)_2$
12% Ni-MMT Fresh	14.1%	38.7%	3.3%
12% Ni-MMT 5th Recycle	3.1%	24.2%	41.7%

Control Experiments for dual reductive amination process[2]



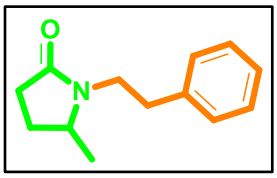
^{1}H and ^{13}C NMR of products

a) 1-(4-methoxybenzyl)-5-methylpyrrolidin-2-one (3b) [3]



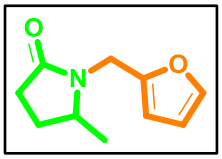
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, 2H), 6.80 (d, 2H), 4.86 (d, J = 14.8 Hz, 1H), 3.88 (d, J = 14.8 Hz, 1H), 3.75 (s, 3H), 3.47 (m, 1H), 2.39 (m, 2H), 2.09 (m, 1H), 1.54 (m, 1H), 1.12 (d, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.77 (s), 158.89 (s), 129.22 (s), 129.13 (s), 128.89 (s), 113.94 (s), 113.88 (s), 55.19 (s), 52.62 (s), 43.22 (s), 30.27 (s), 26.58 (s), 19.55 (s).

b) 5-methyl-1-phenethylpyrrolidin-2-one (3f) [3]



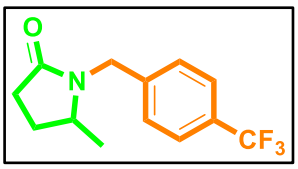
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (m, 2H), 7.17 (m, 3H), 3.83 – 3.73 (m, 1H), 3.49 (m, 1H), 3.11 (m, 1H), 2.84 (m, 1H), 2.74 (m, 1H), 2.31 (m, 2H), 2.08 (m, 1H), 1.50 (m, 1H), 1.12 (d, J = 6.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.87 (s), 138.89 (s), 128.67 (s), 128.59 (s), 128.44 (s), 128.38 (s), 126.36 (s), 53.76 (s), 41.71 (s), 33.84 (s), 30.16 (s), 26.75 (s), 19.65 (s).

c) 1-(furan-2-ylmethyl)-5-methylpyrrolidin-2-one (3h) [3]



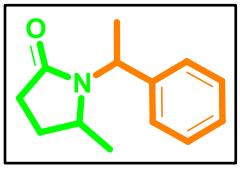
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 1.0 Hz, 1H), 6.31 – 6.25 (m, 1H), 6.20 (d, J = 3.0 Hz, 1H), 4.84 (d, J= 15.6 Hz, 1H), 4.05 (d, J= 15.6 Hz, 1H), 3.57 (m, 1H), 2.37 (m, 2H), 2.14 (m, 1H), 1.55 (m, 1H), 1.19 (d, J = 6.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.89 (s), 142.15 (s), 142.11 (s), 110.30 (s), 108.10 (s), 53.31 (s), 36.78 (s), 30.15 (s), 26.60 (s), 19.51 (s).

d) 5-methyl-1-(4-(trifluoromethyl)benzyl)pyrrolidin-2-one (3i) [3]



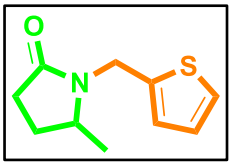
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2H), 7.32 (d, 2H), 4.87 (d, J = 15.3 Hz, 1H), 4.09 (d, J = 15.3 Hz, 1H), 3.50 (m, 1H), 2.41 (m, 2H), 2.16 (m, 1H), 1.59 (m, 1H), 1.12 (d, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.13 (s), 141.11 (s), 129.66 (s), 128.10 (s,), 128.10 (s), 125.52 (s,), 125.52 (s), 124.06 (s), 53.13 (s), 43.61 (s), 30.05 (s), 26.69 (s), 19.62 (s).

e) 5-methyl-1-(1-phenylethyl)pyrrolidin-2-one (3k)[3]



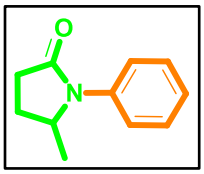
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.15 (m, 5H), 5.42 – 5.32 (m, 1H), 3.78 (m, 0.4 H), 3.34 (m, 0.6H), 2.47 (m, 1H), 2.31 (m, 1H), 2.02 (m, 1.3H), 1.58 (m, 2H), 1.50 (s, 1.7H), 1.11 (d, 1.6H), 0.72 (d, J = 6.3 Hz, 1.6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.02 (s), 139.64 (s), 128.41 (s), 128.18 (s), 127.34 (s), 126.97 (s), 52.80 (s), 50.20 (s), 30.17 (s), 27.36 (s), 22.10 (s), 18.22 (s).

f) 5-methyl-1-(thiophen-2-ylmethyl)pyrrolidin-2-one (3l) [3]



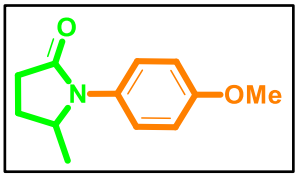
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, J = 4.8, 1.1 Hz, 1H), 6.93 – 6.87 (m, 2H), 5.01 (d, J = 15.4 Hz, 1H), 4.16 (d, J = 15.4 Hz, 1H), 3.58 (m, 1H), 2.36 (m, 2H), 2.11 (m, 1H), 1.54 (m, 1H), 1.18 (d, J = 6.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.84 (s), 139.22 (s), 126.71 (s), 126.36 (s), 125.18 (s), 52.70 (s), 38.46 (s), 30.20 (s), 26.60 (s), 19.54 (s).

g) 5-methyl-1-phenylpyrrolidin-2-one (4a)[4]



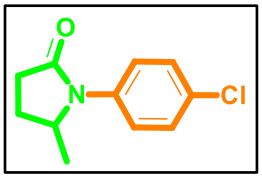
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, 3H), 7.19 (s, 1H), 4.27 (m, 1H), 2.57 (m, 2H), 2.36 (m, 1H), 1.73 (m, 1H), 1.18 (d, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.17 (s), 137.55 (s), 128.93 (s), 125.72 (s), 124.04 (s), 55.61 (s), 31.28 (s), 26.72 (s), 20.12 (s).

h) 1-(4-methoxyphenyl)-5-methylpyrrolidin-2-one (4b)[4]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, 2H), 6.89 (d, 2H), 4.14 (m, 1H), 3.77 (s, 3H), 2.52 (m, 2H), 2.33 (m, 1H), 1.70 (m, 1H), 1.13 (d, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.28 (s), 157.66 (s), 130.35 (s), 126.05 (s), 125.77 (s), 114.50 (s), 114.30 (s), 56.10 (s), 55.40 (s), 31.08 (s), 26.80 (s), 20.22 (s).

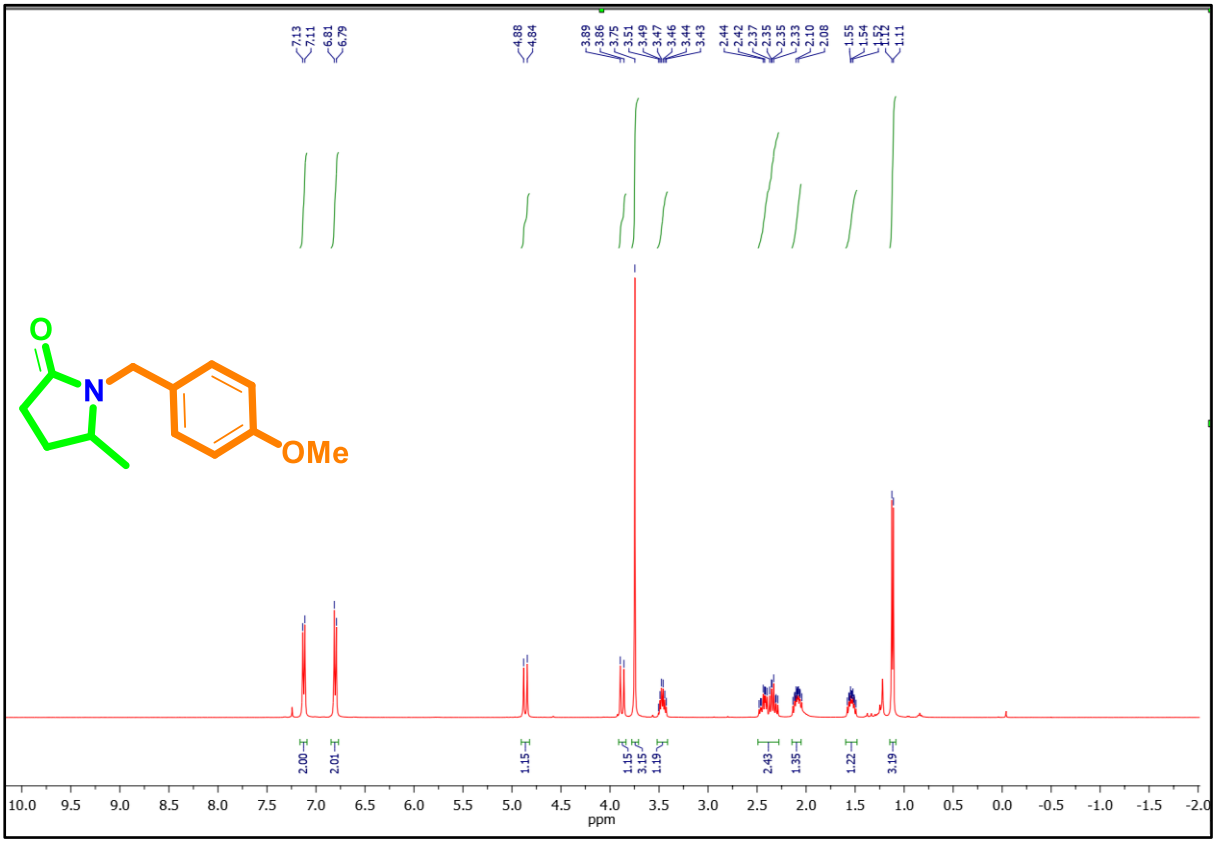
i) 1-(4-chlorophenyl)-5-methylpyrrolidin-2-one (4e)[4]



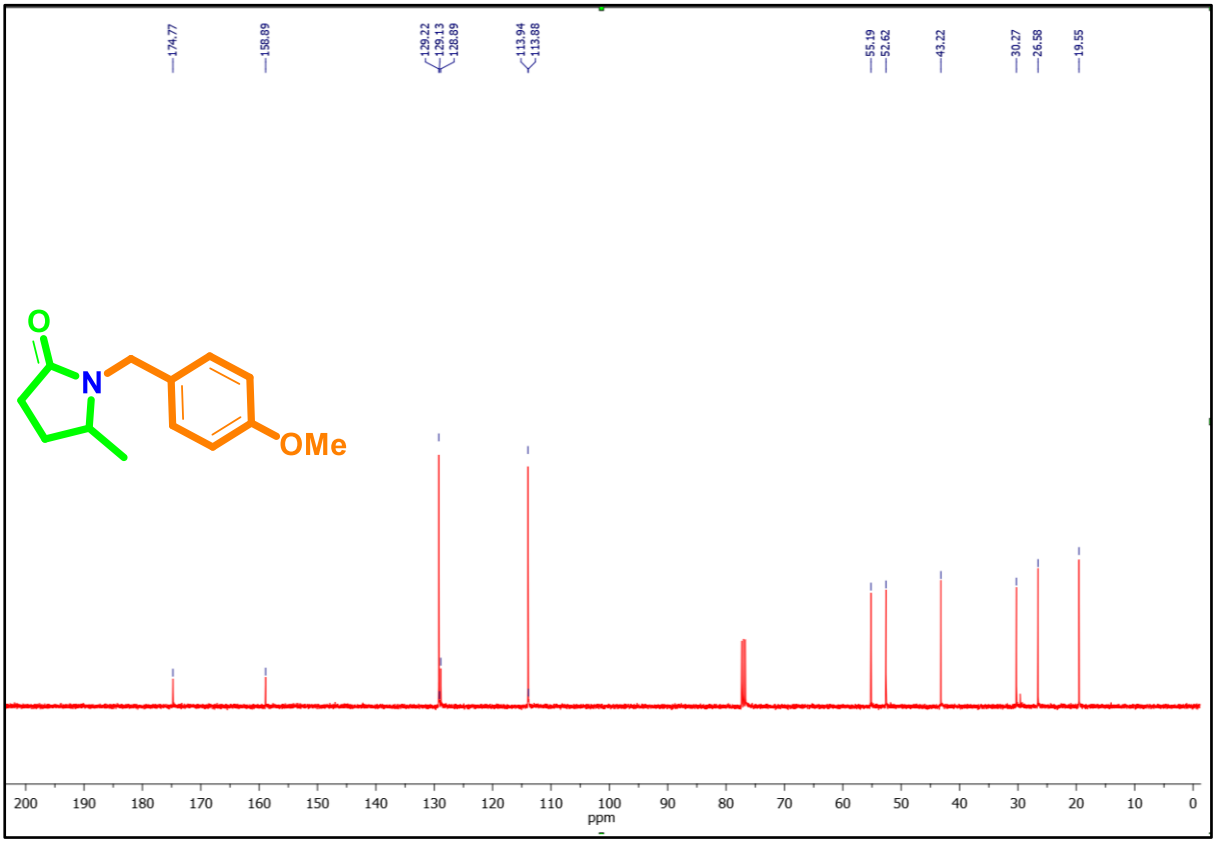
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 4H), 4.24 (dd, J = 12.5, 6.2 Hz, 1H), 2.66 – 2.45 (m, 2H), 2.39 – 2.29 (m, 1H), 1.72 (m, 1H), 1.17 (d, J = 6.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.19 (s), 136.13 (s), 130.87 (s), 129.03 (s), 129.03 (s), 124.88 (s),124.88 (s), 55.42 (s), 31.19 (s), 26.57 (s), 19.95 (s).

1-(4-methoxybenzyl)-5-methylpyrrolidin-2-one (3b)

^{1}H NMR

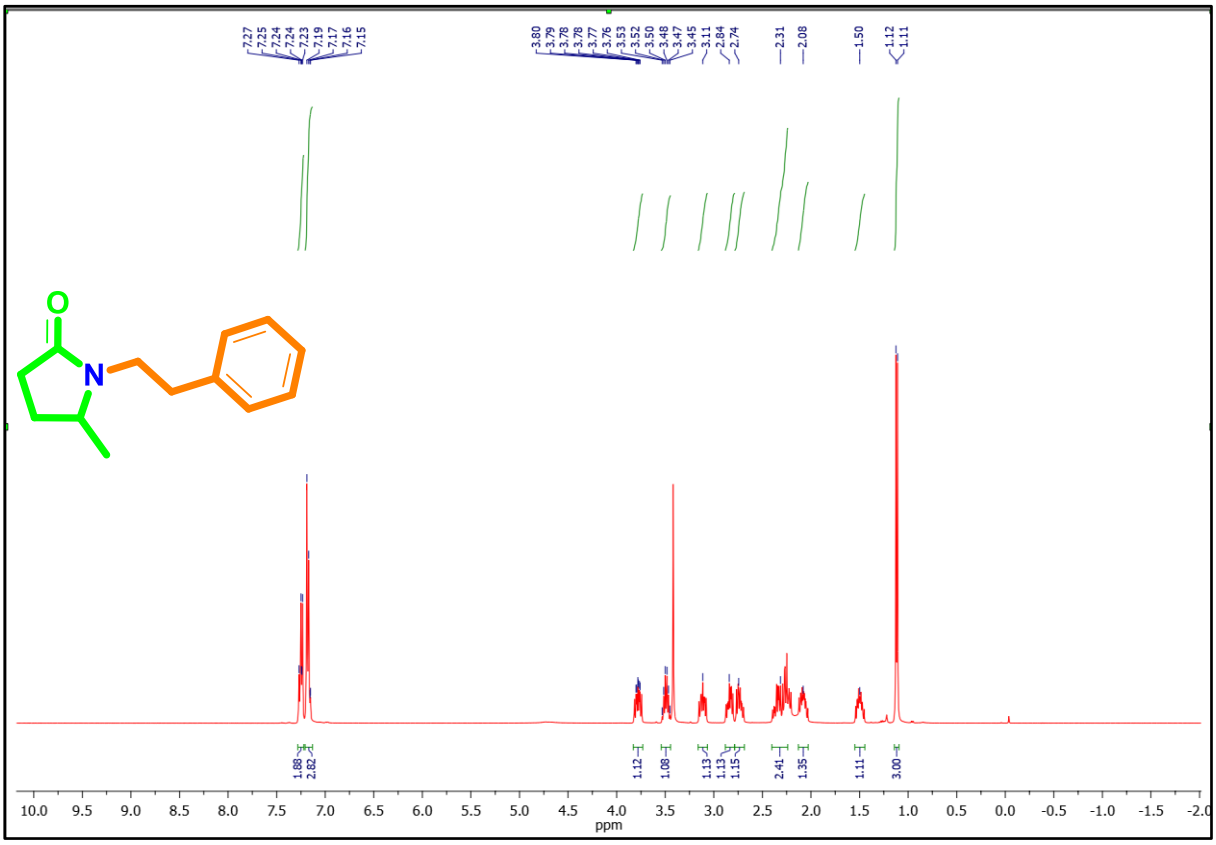


^{13}C NMR

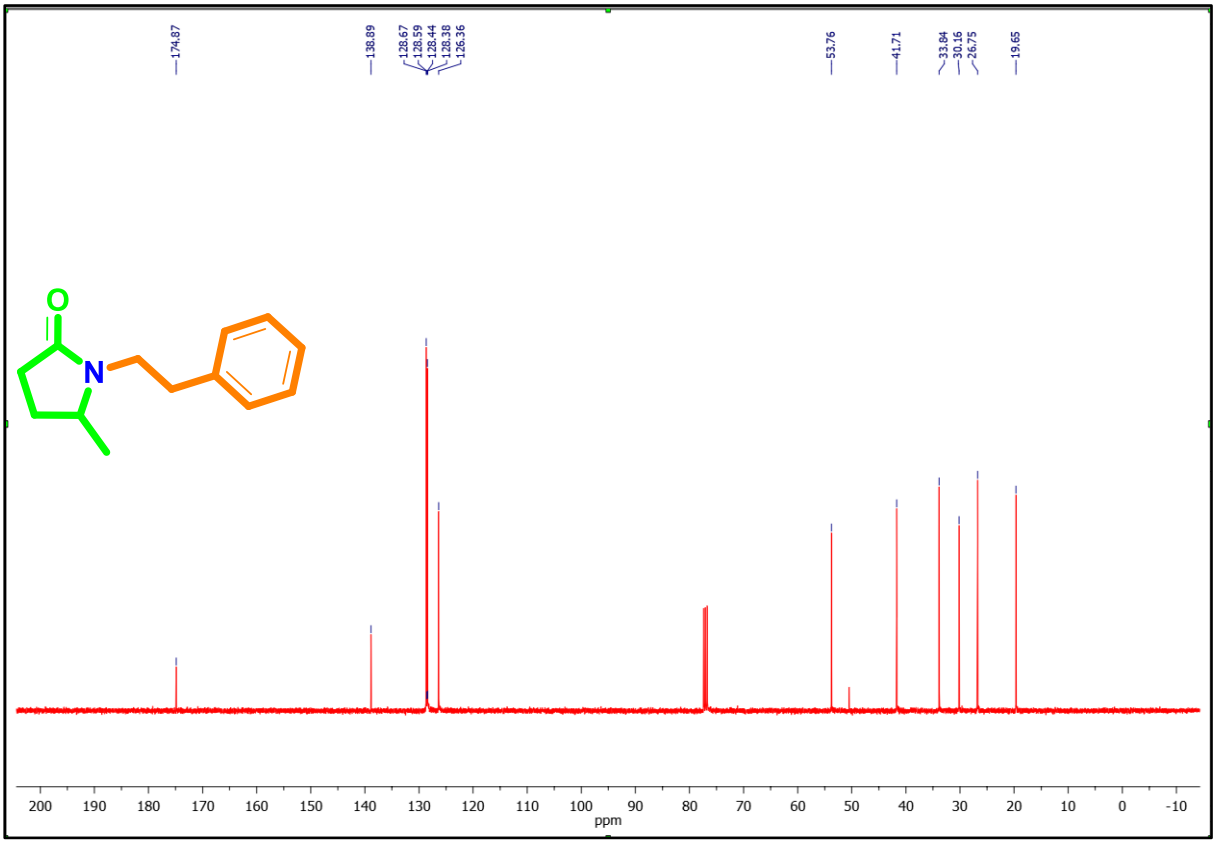


5-methyl-1-phenethylpyrrolidin-2-one (3f)

^{1}H NMR

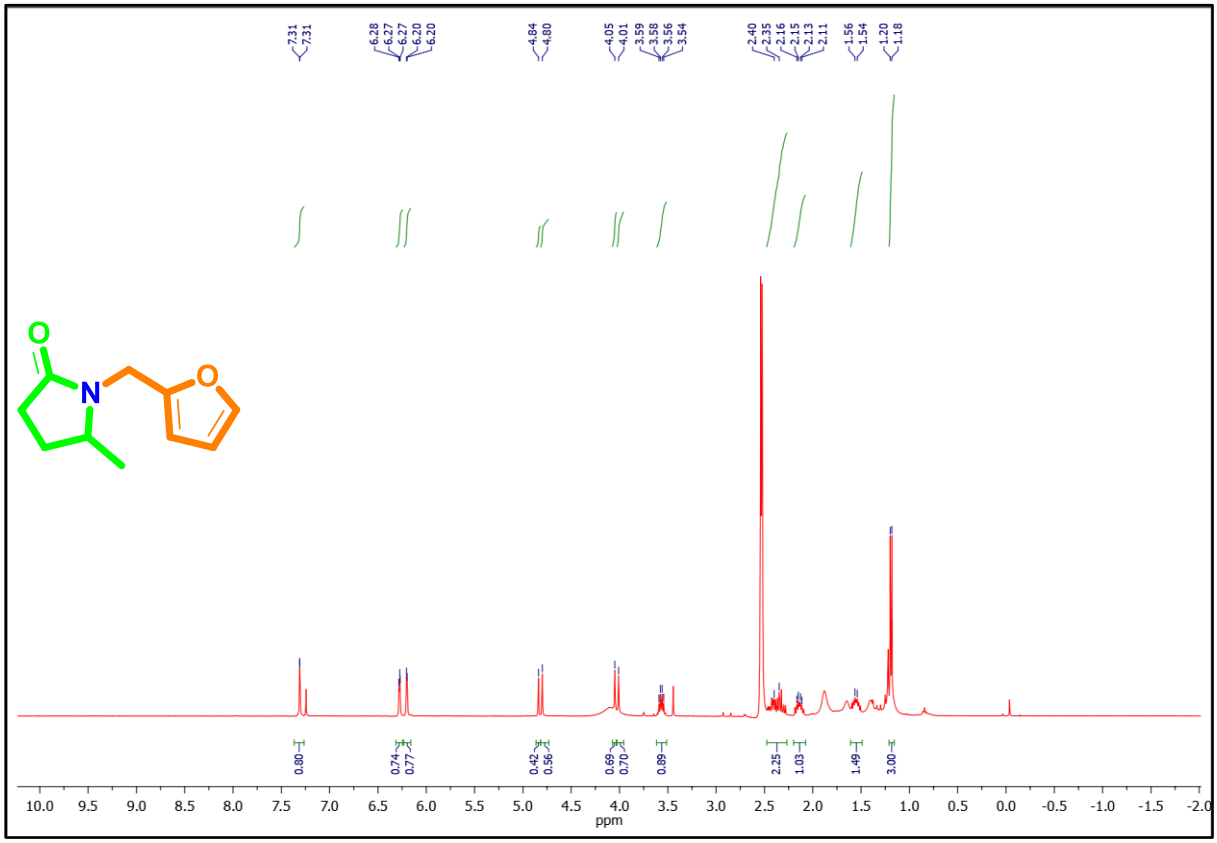


^{13}C NMR

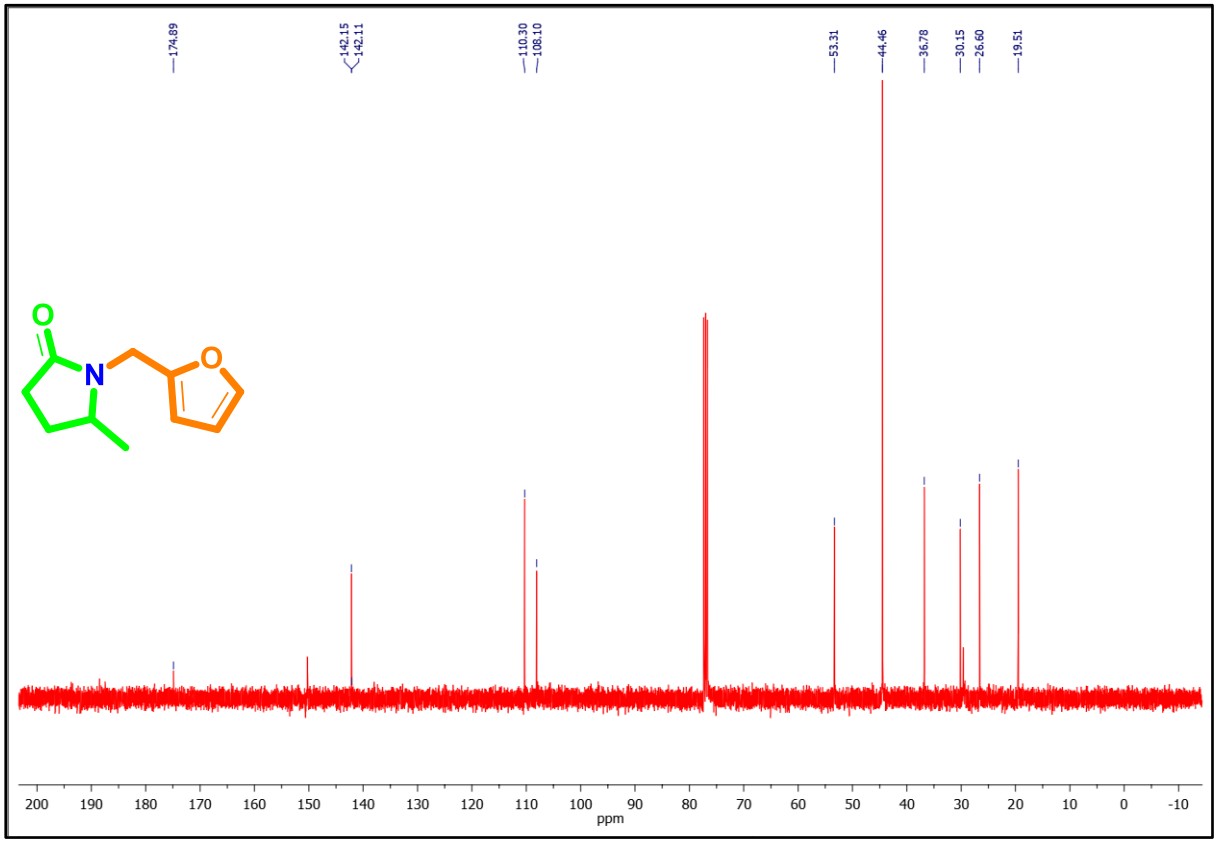


1-(furan-2-ylmethyl)-5-methylpyrrolidin-2-one (3h)

^{1}H NMR

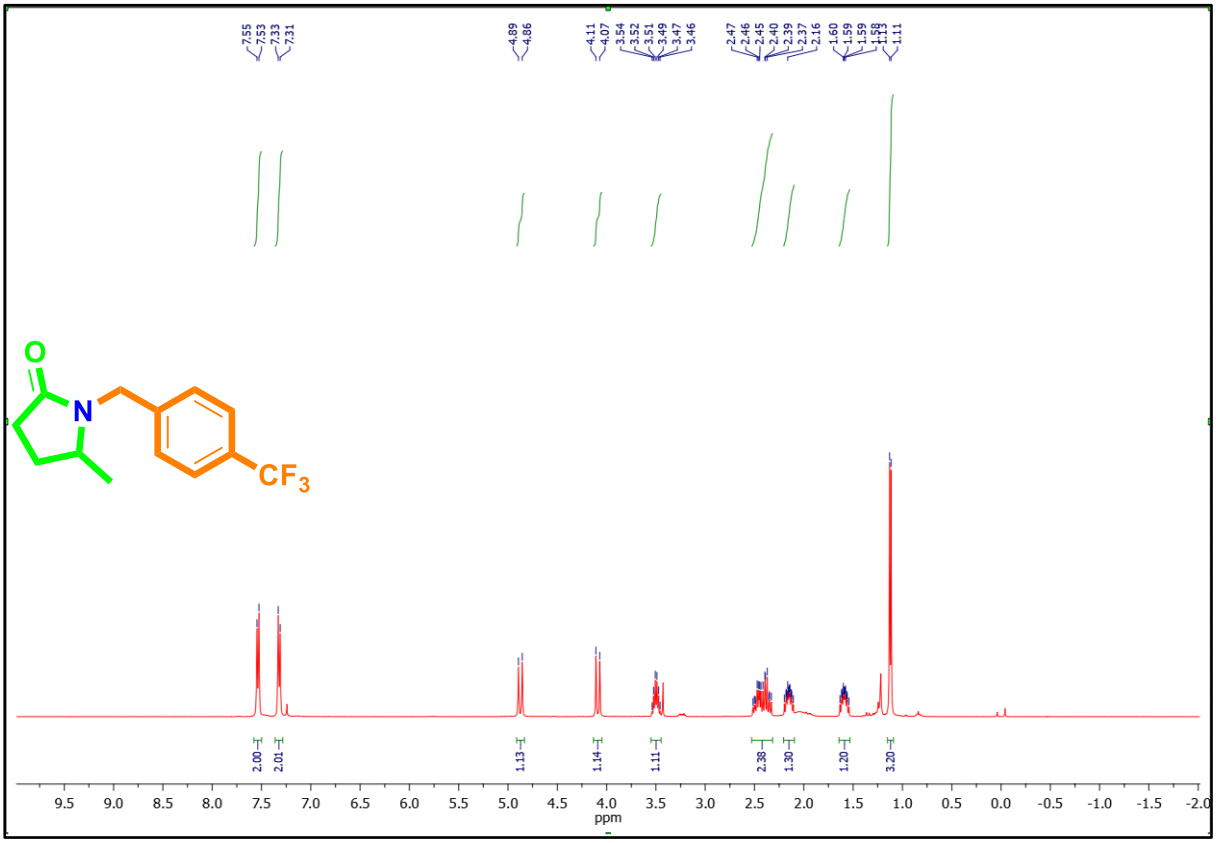


^{13}C NMR

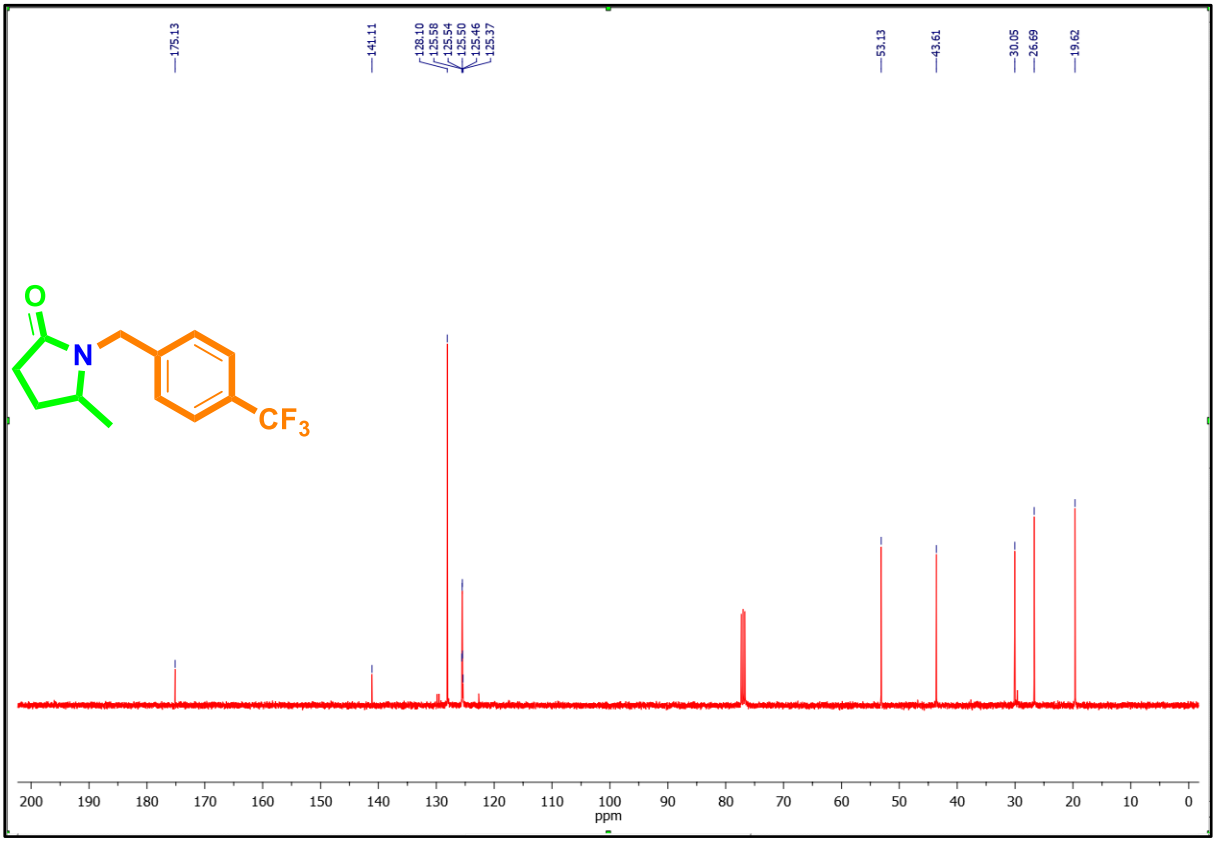


5-methyl-1-(4-(trifluoromethyl)benzyl)pyrrolidin-2-one (3i)

^{1}H NMR

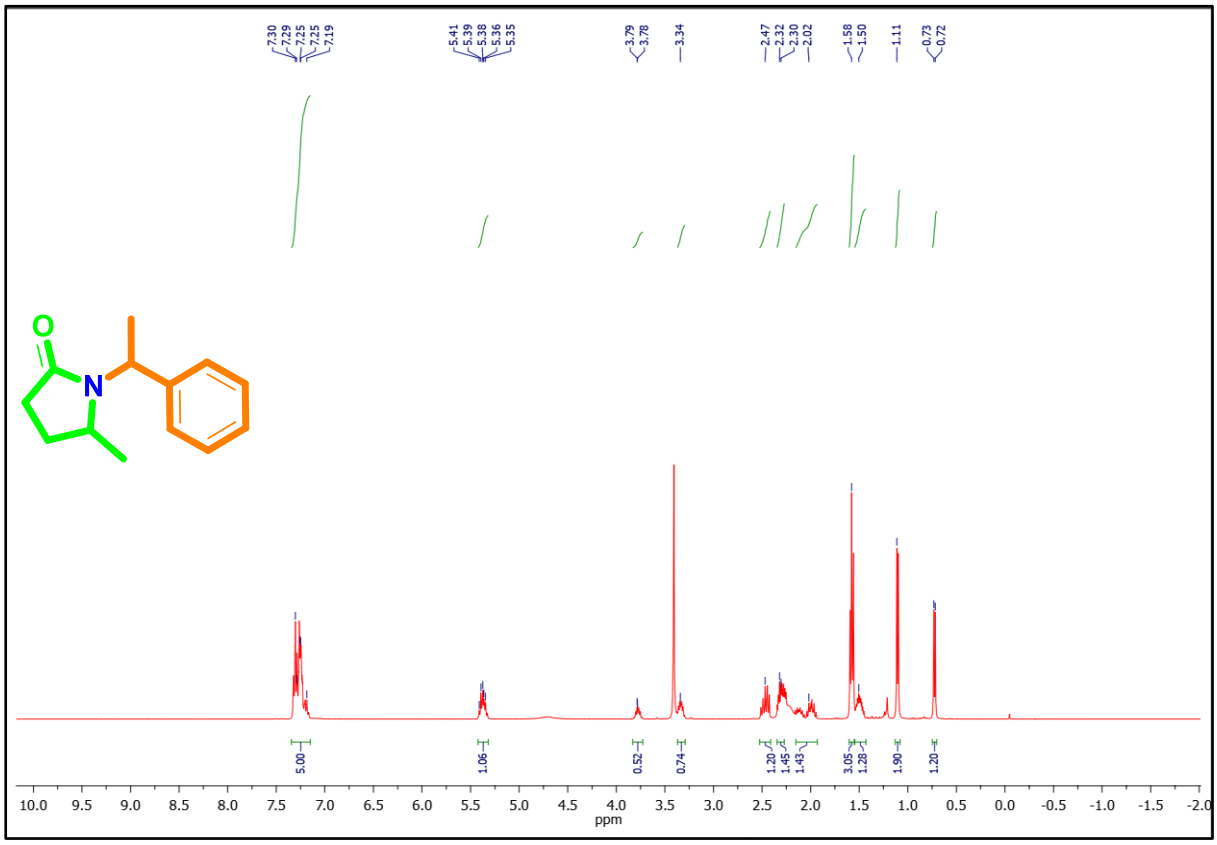


^{13}C NMR

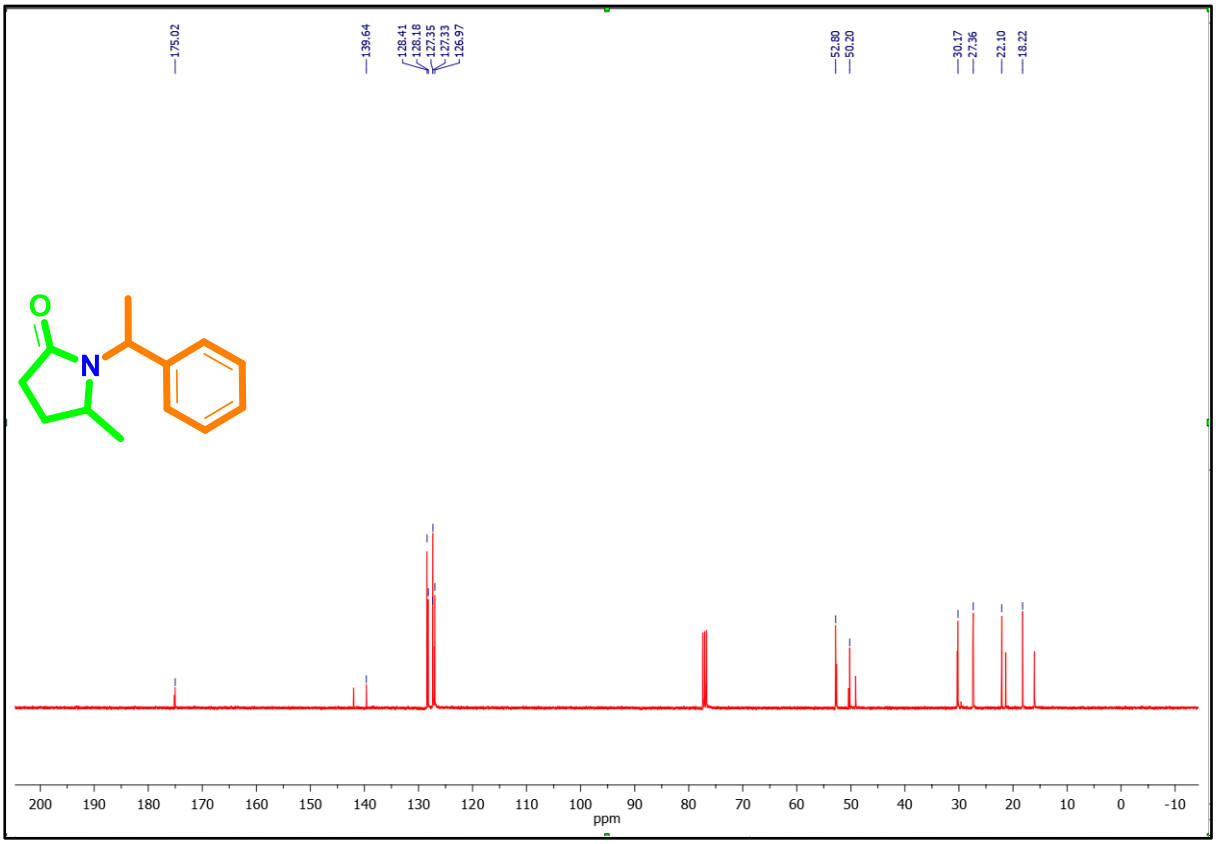


5-methyl-1-(1-phenylethyl)pyrrolidin-2-one (3k)

^{1}H NMR

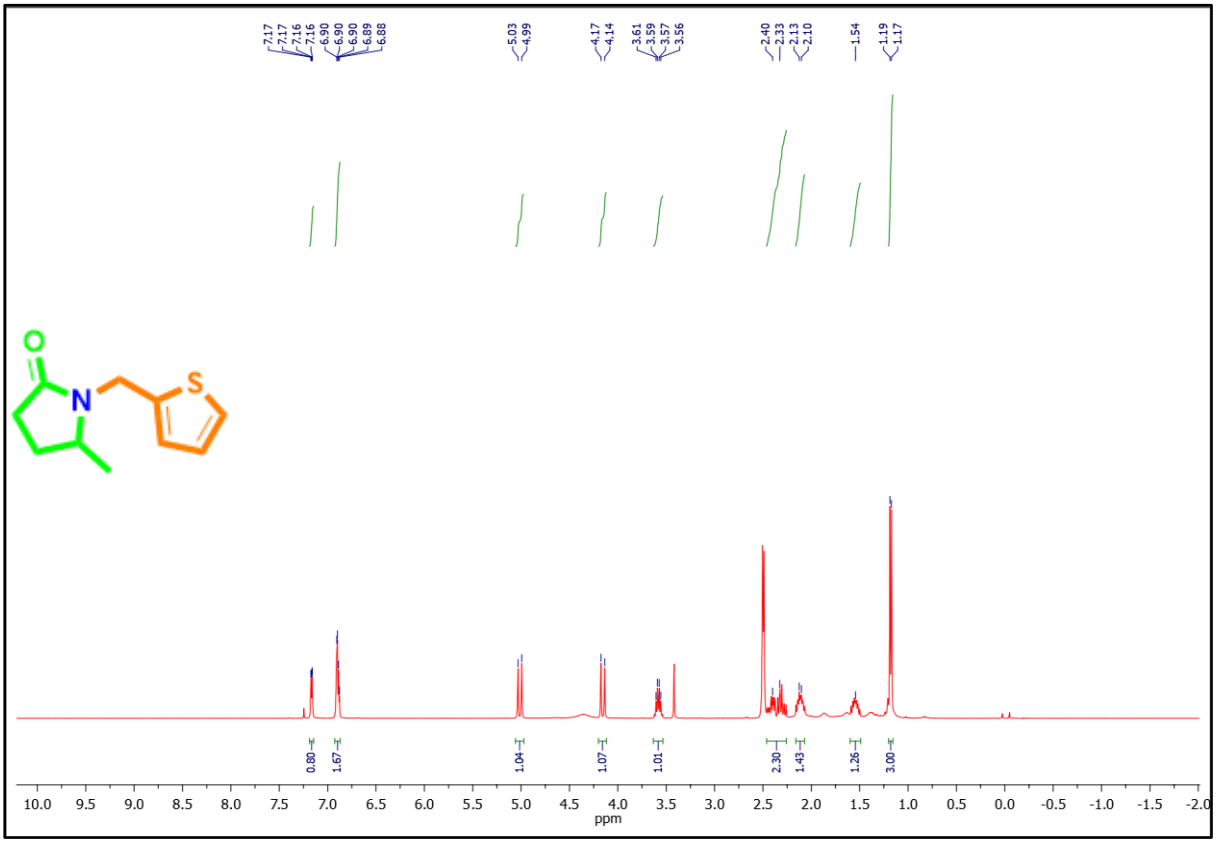


^{13}C NMR

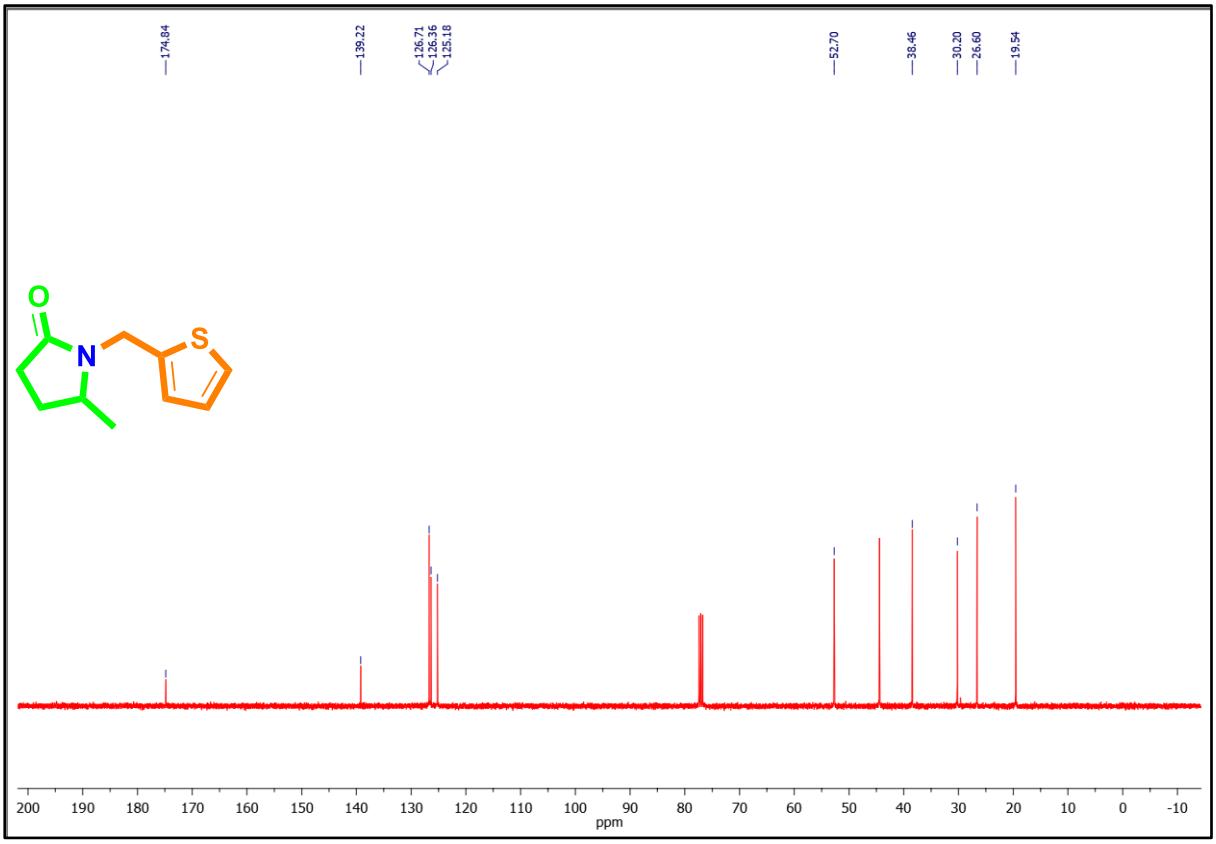


5-methyl-1-(thiophen-2-ylmethyl)pyrrolidin-2-one (3l)

^{1}H NMR

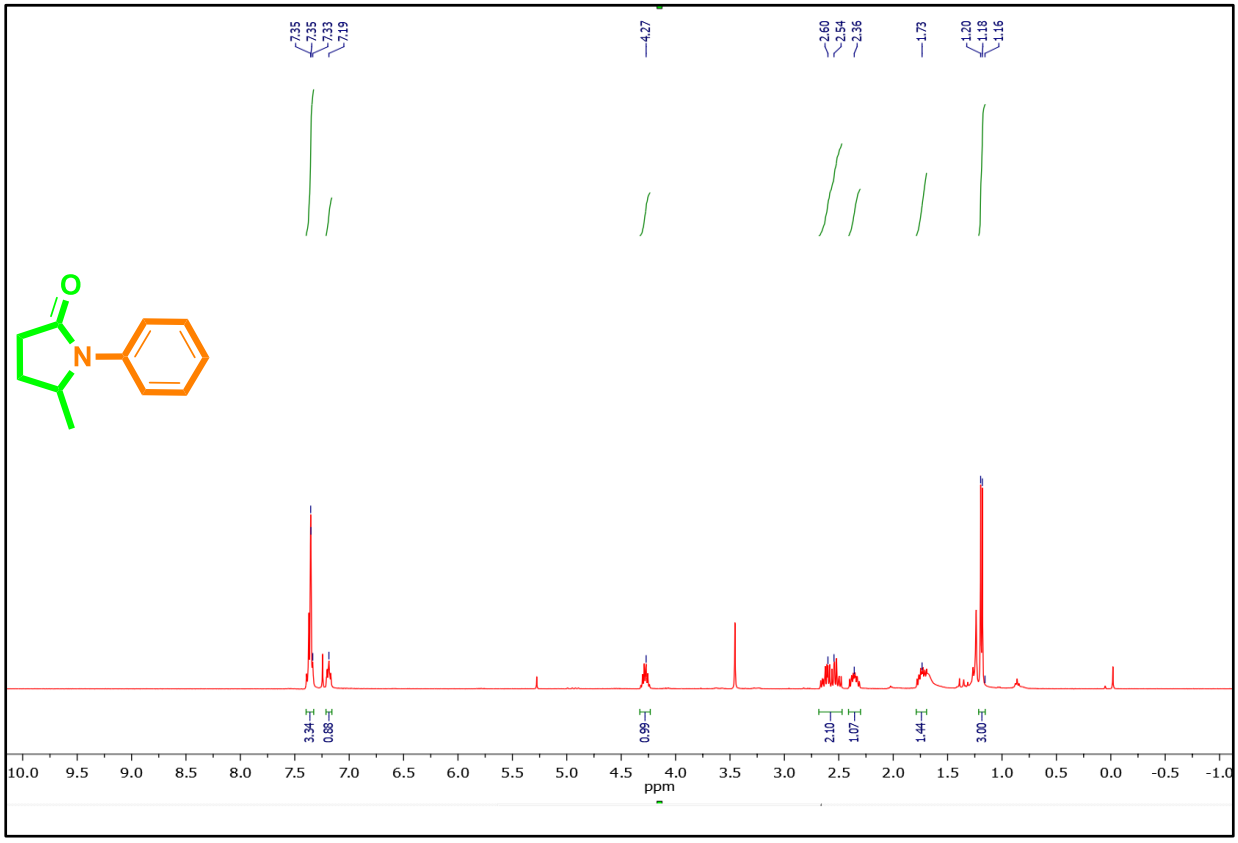


^{13}C NMR

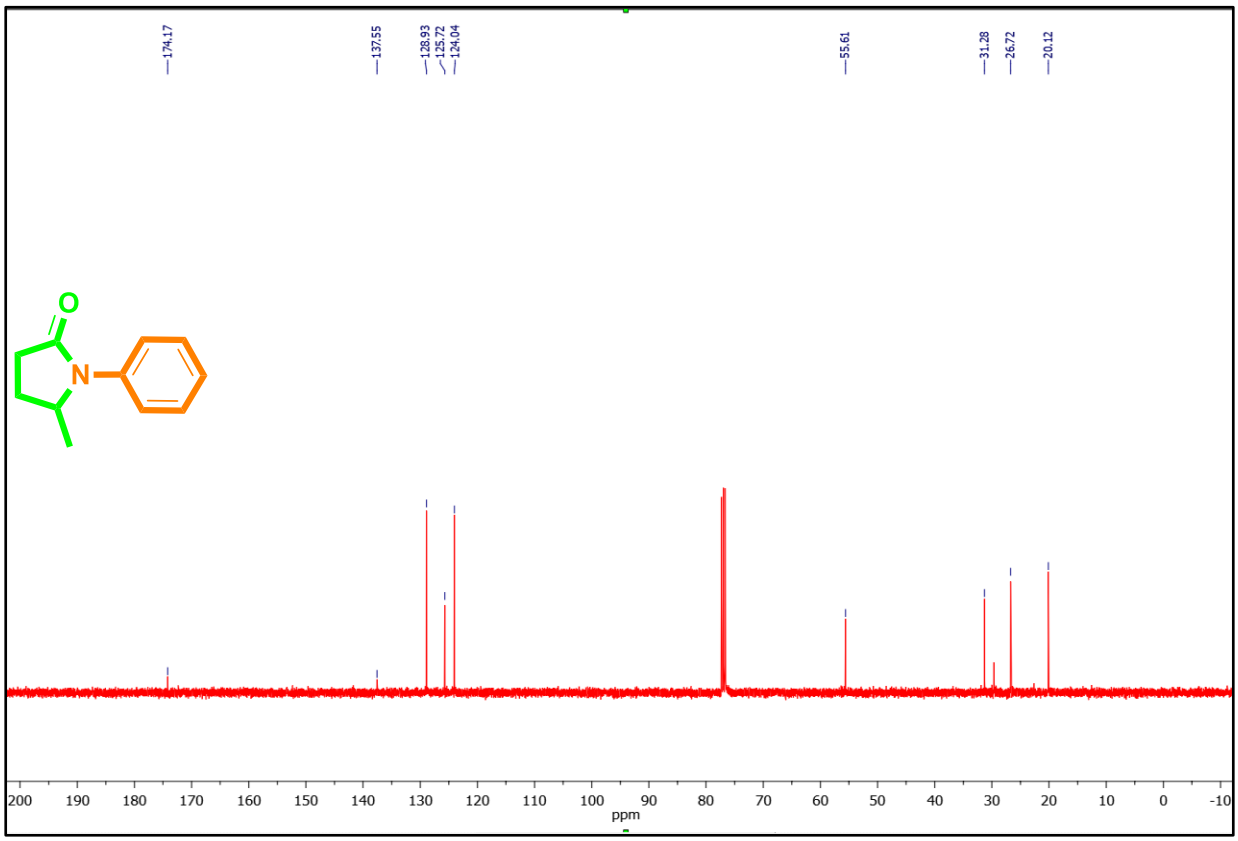


5-methyl-1-phenylpyrrolidin-2-one (4a)

^{1}H NMR

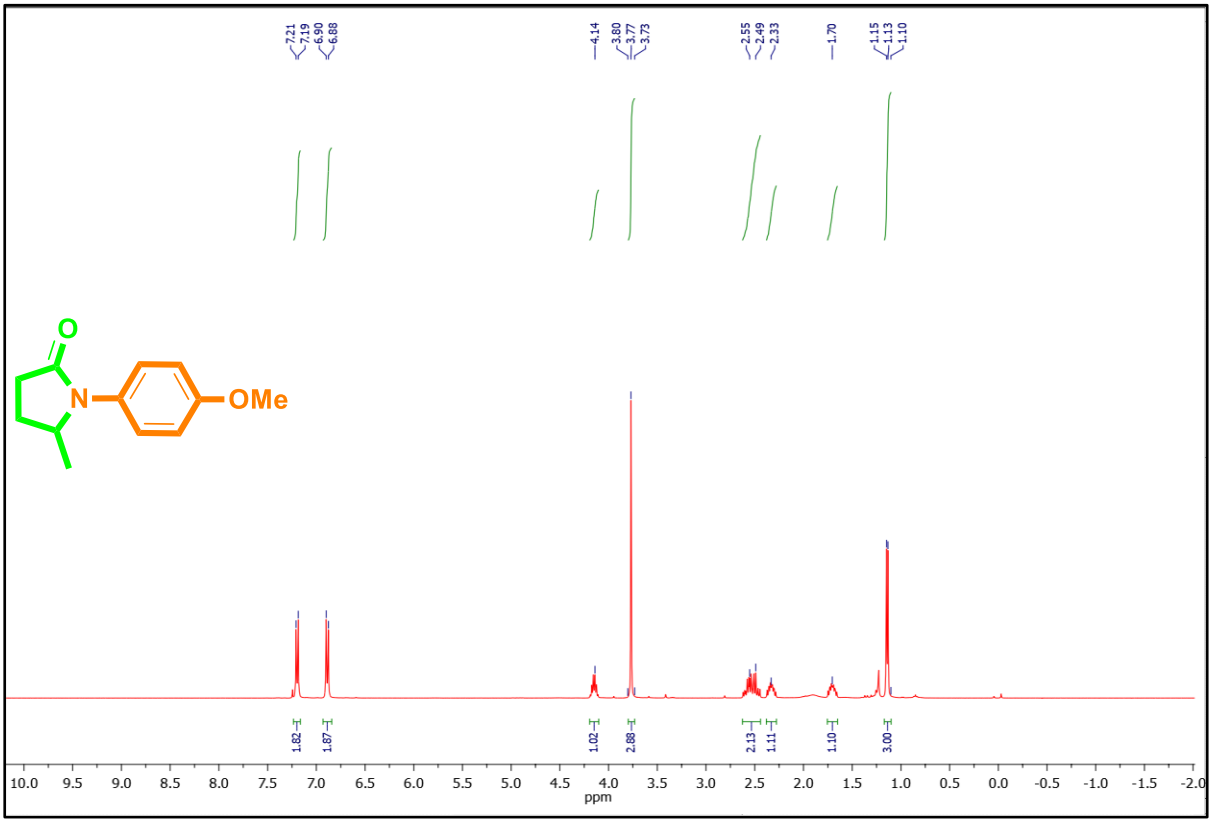


^{13}C NMR

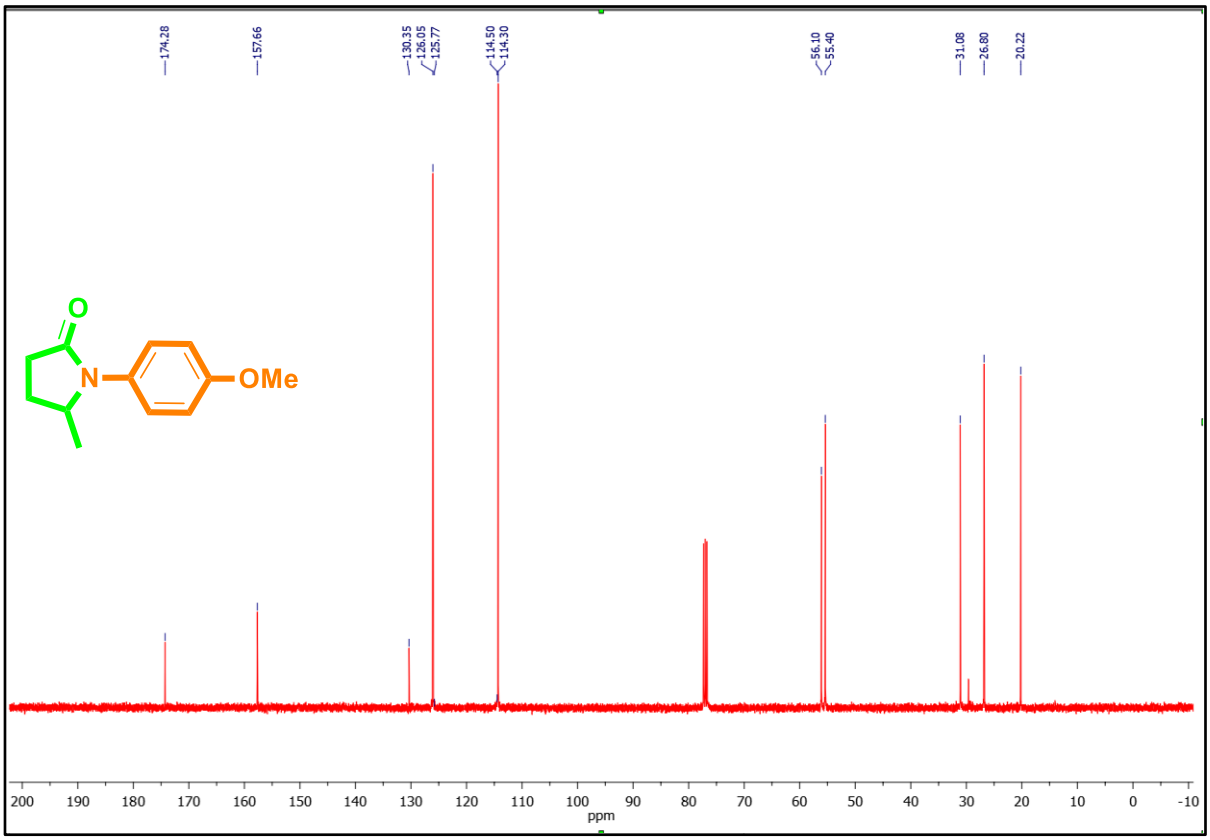


1-(4-methoxyphenyl)-5-methylpyrrolidin-2-one (4b)

^{1}H NMR

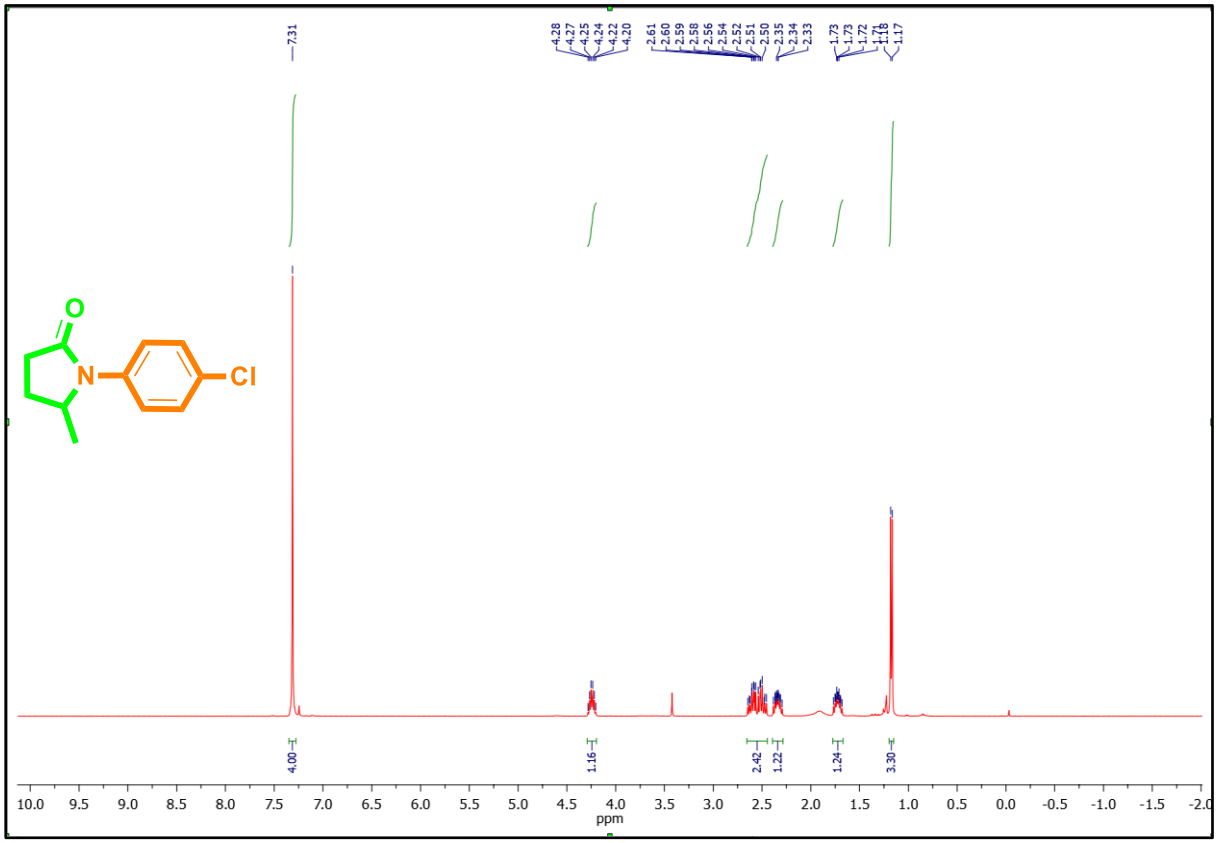


^{13}C NMR

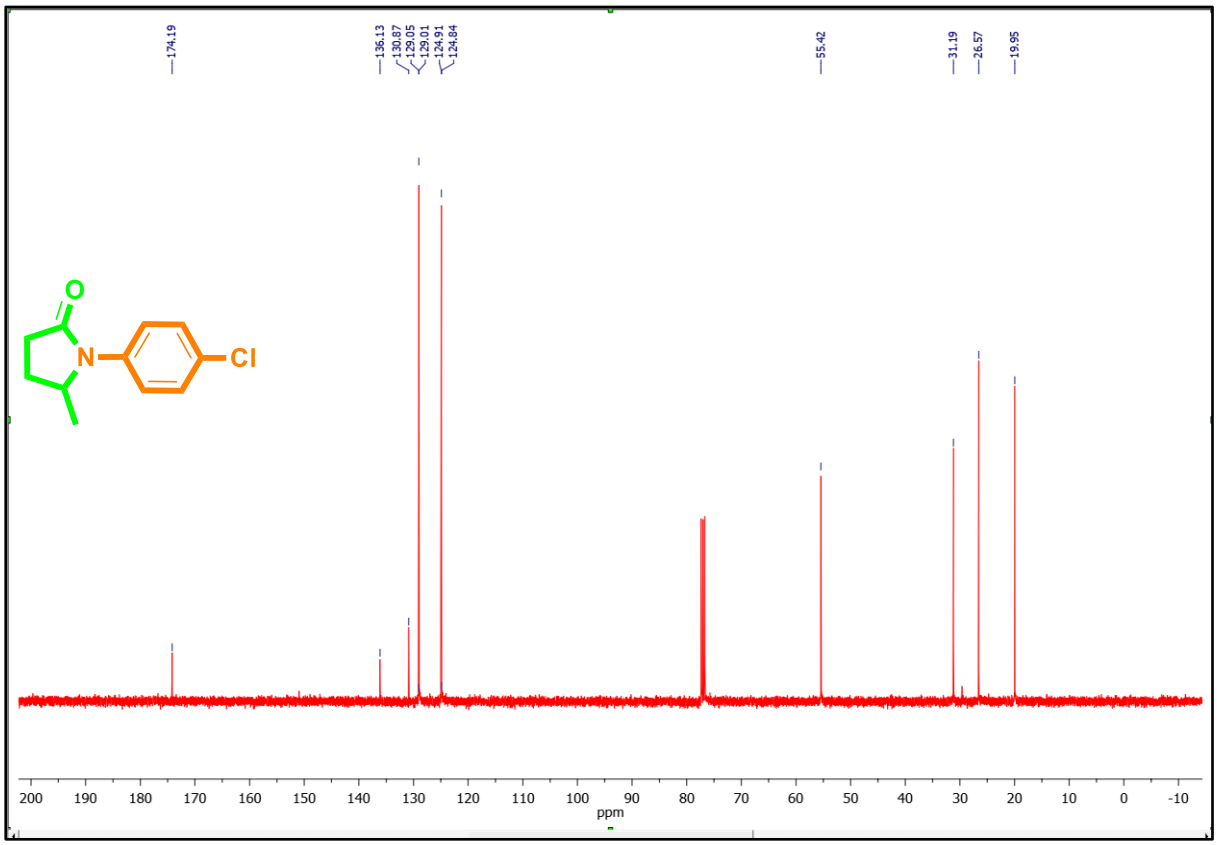


1-(4-chlorophenyl)-5-methylpyrrolidin-2-one (4e)

^{1}H NMR

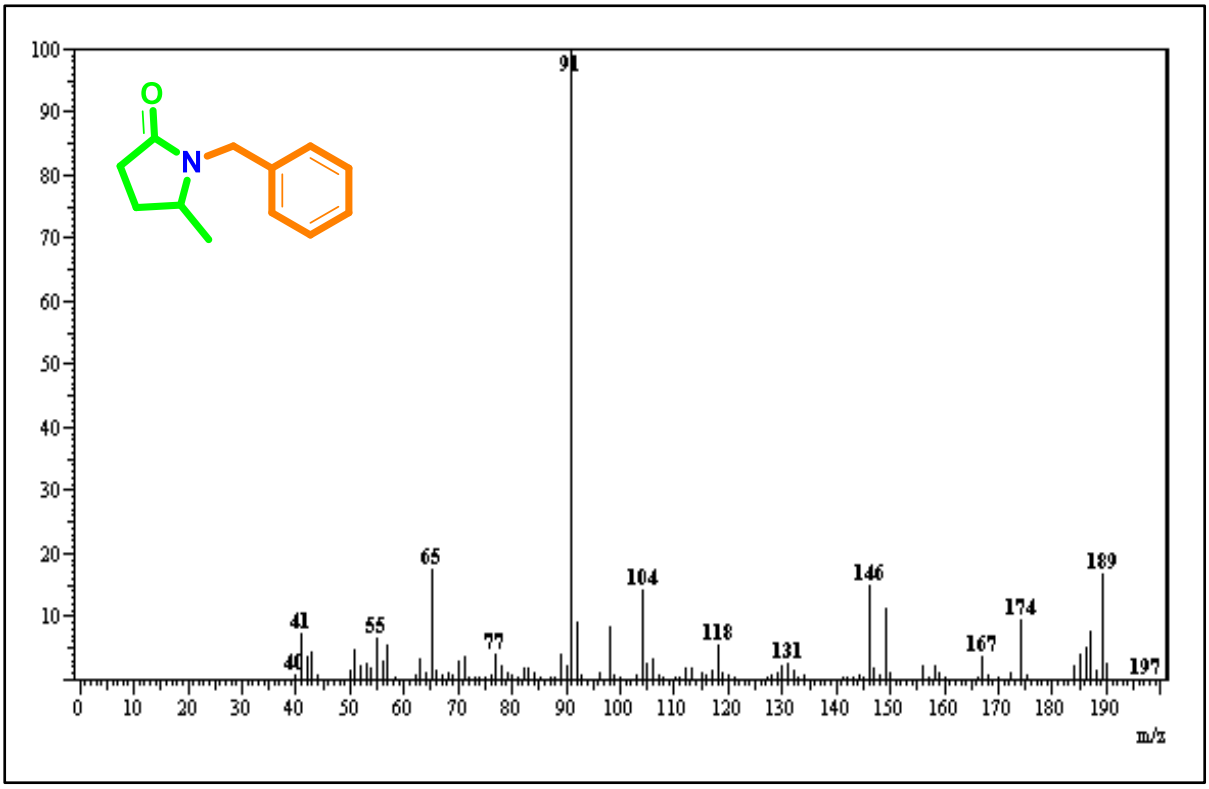


^{13}C NMR

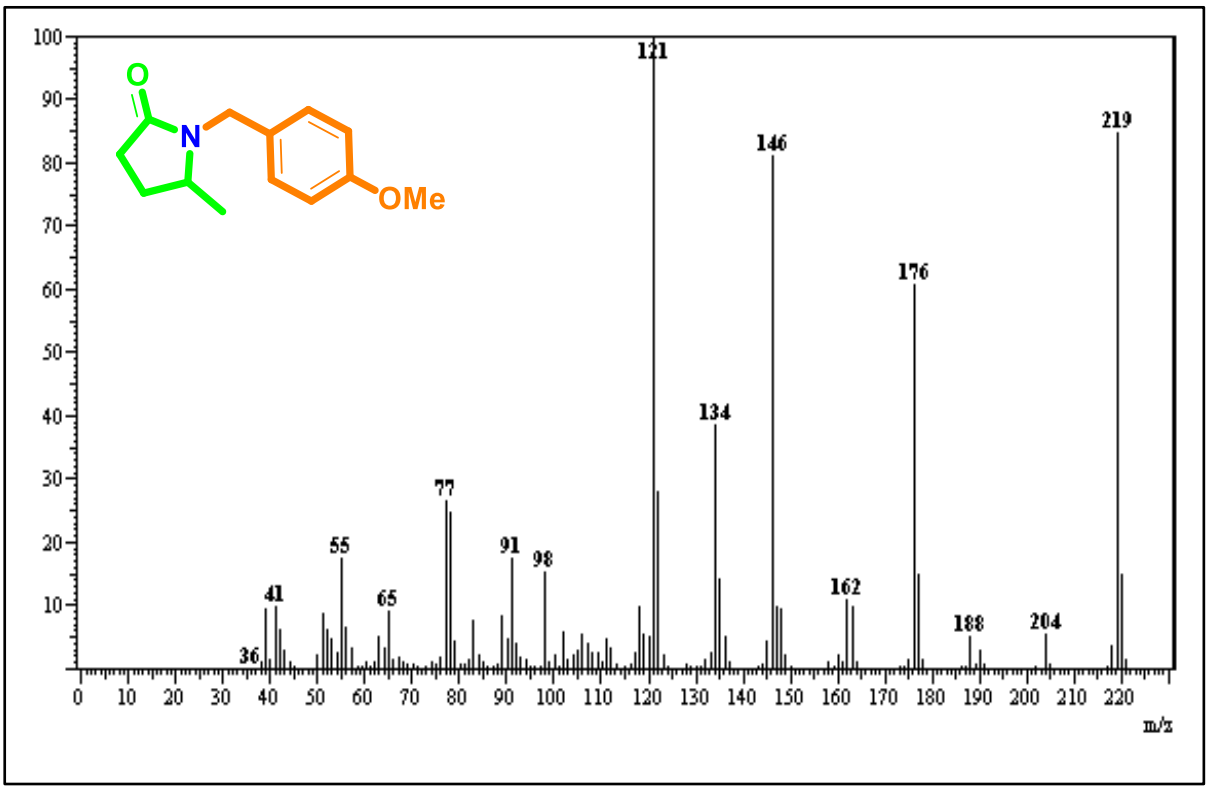


GC-MS spectra of all products

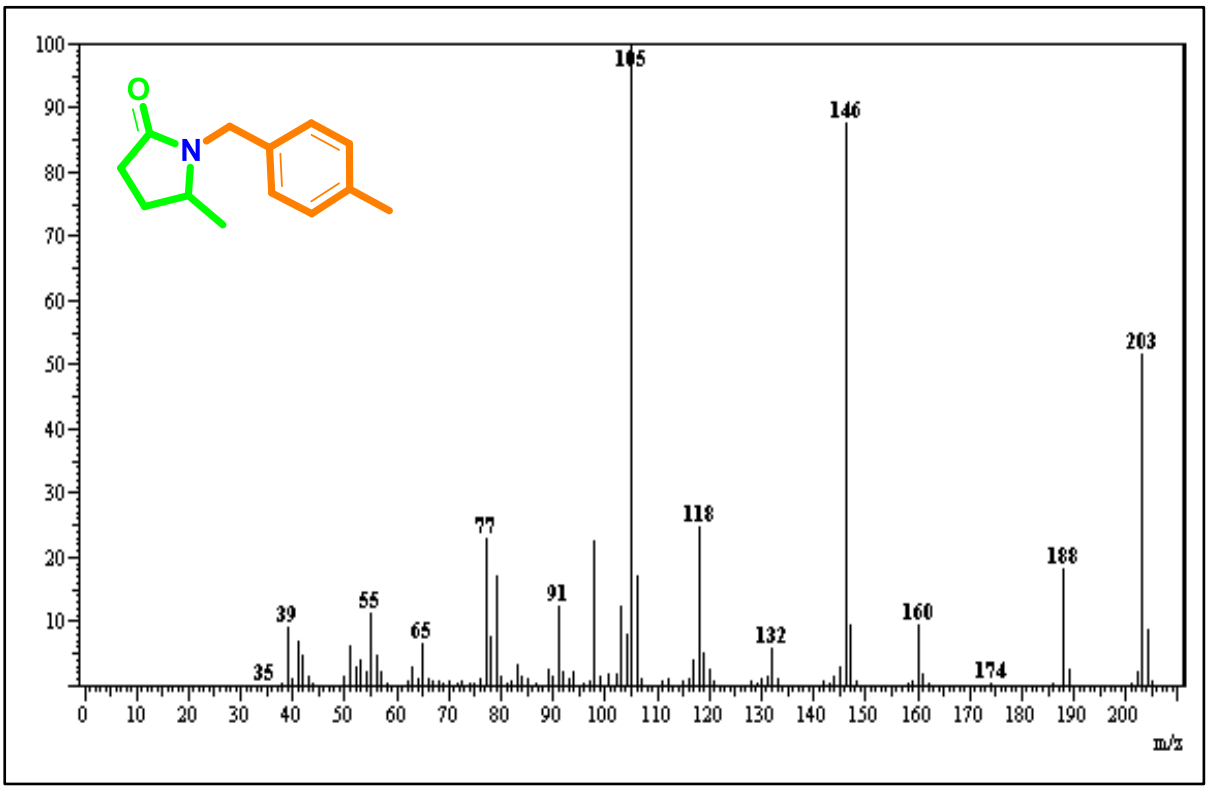
1-benzyl-5-methylpyrrolidin-2-one (3a):



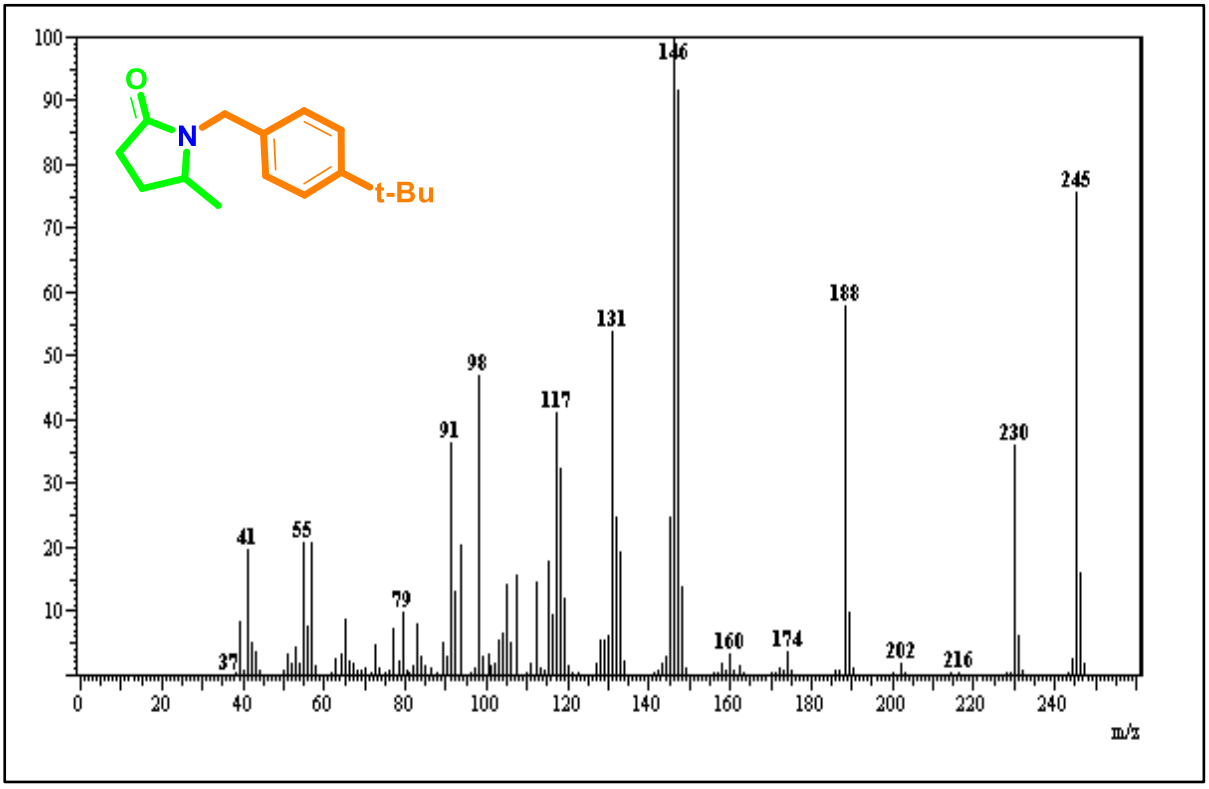
1-(4-methoxybenzyl)-5-methylpyrrolidin-2-one (3b):



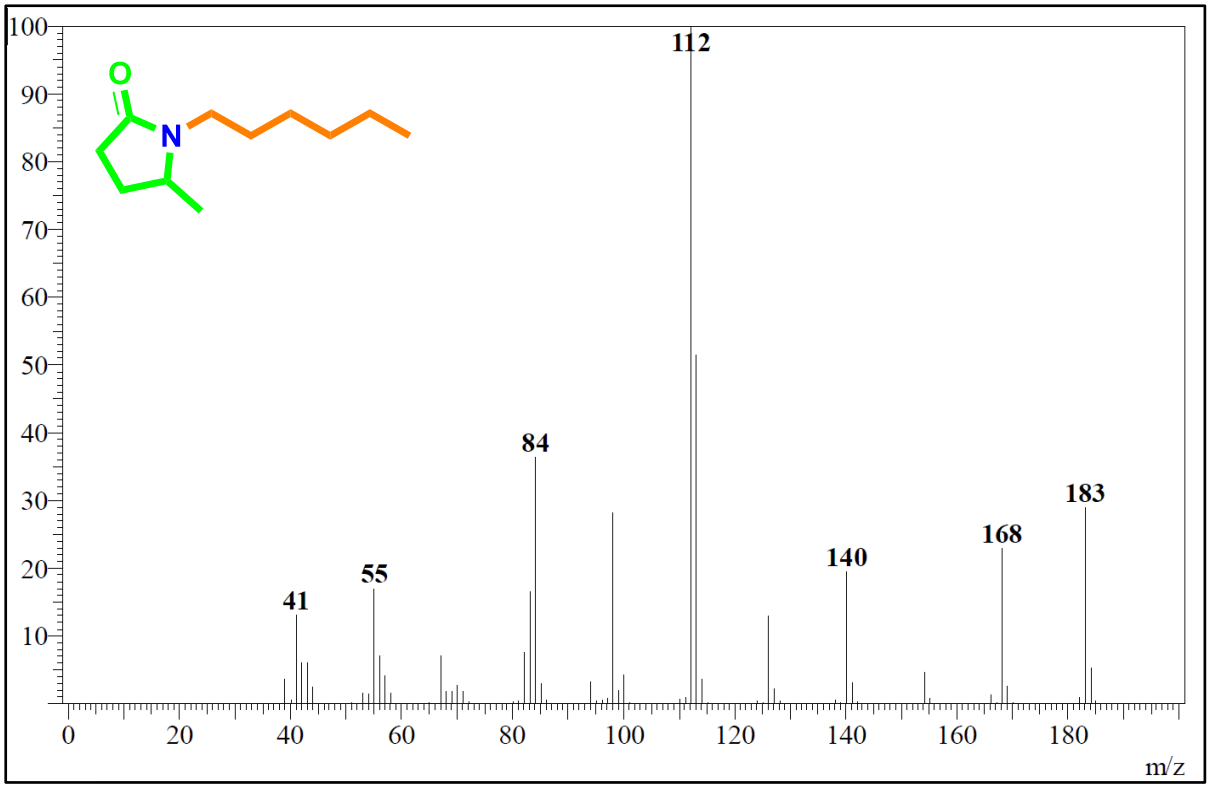
5-methyl-1-(4-methylbenzyl)pyrrolidin-2-one (3c):



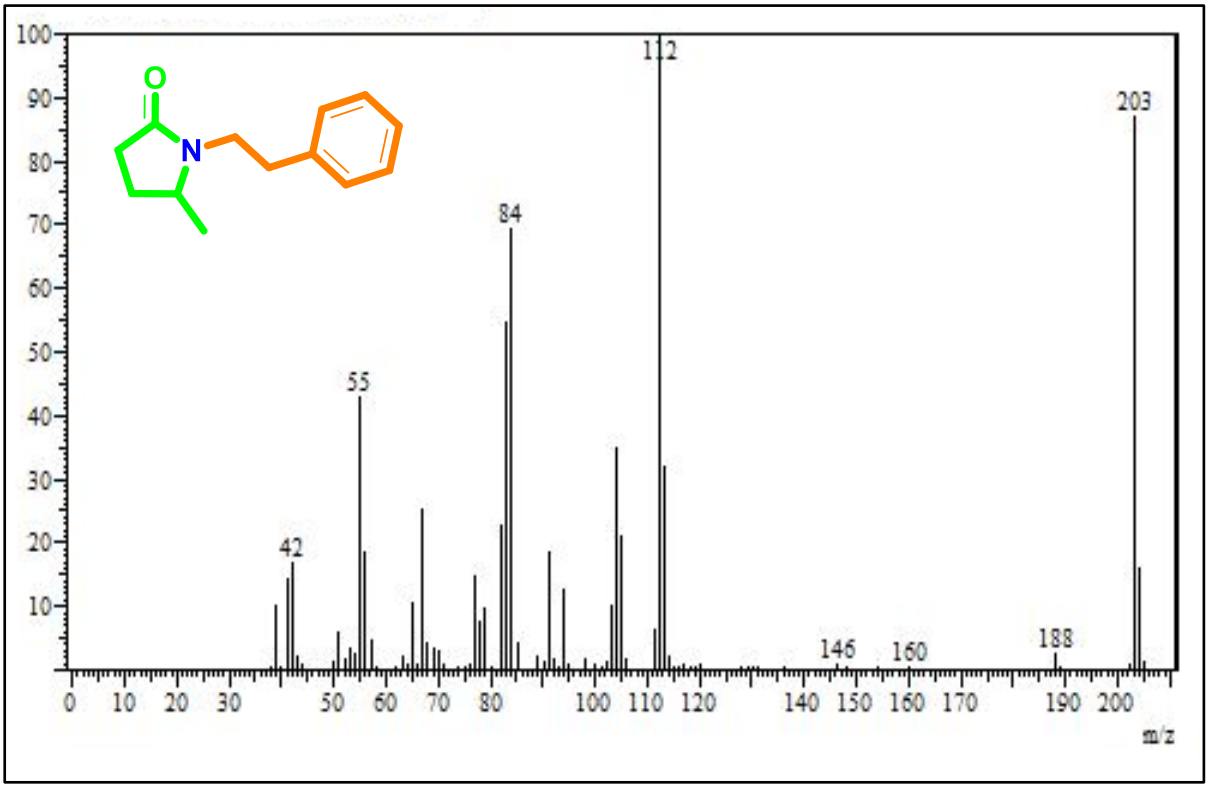
1-(4-(tert-butyl)benzyl)-5-methylpyrrolidin-2-one (3d):



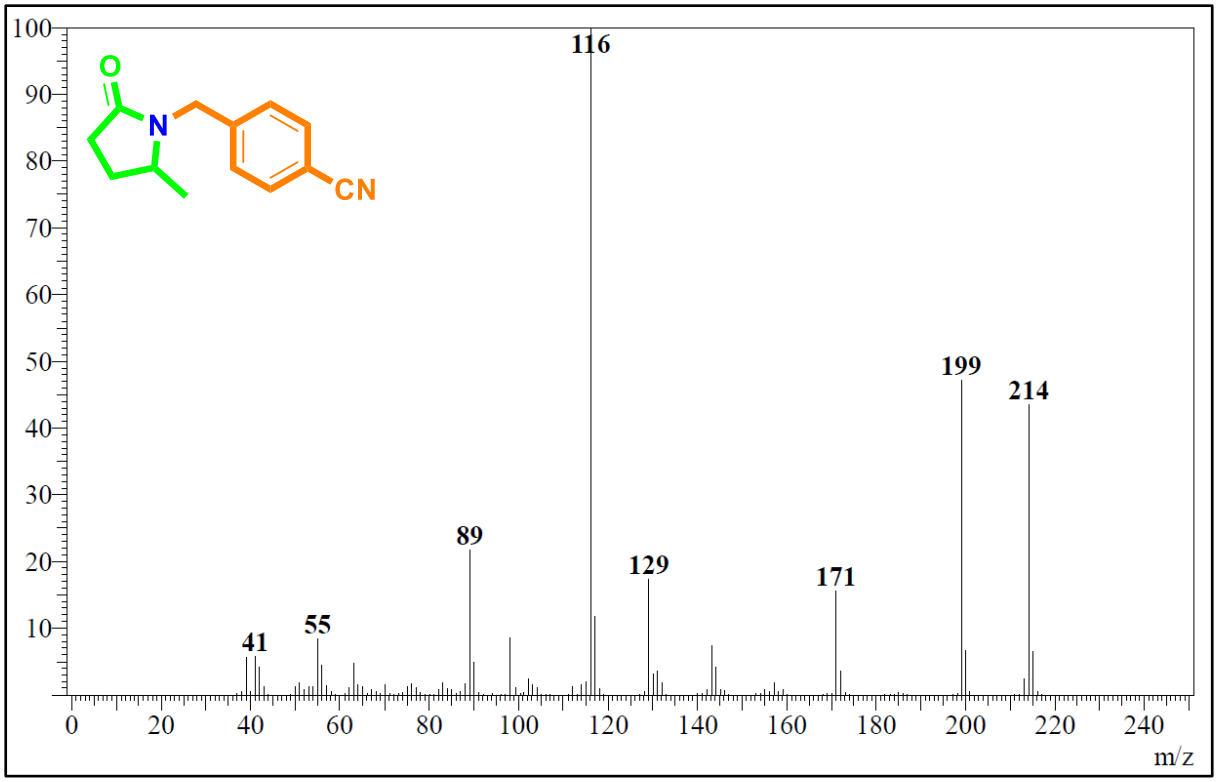
1-hexyl-5-methylpyrrolidin-2-one (3e):



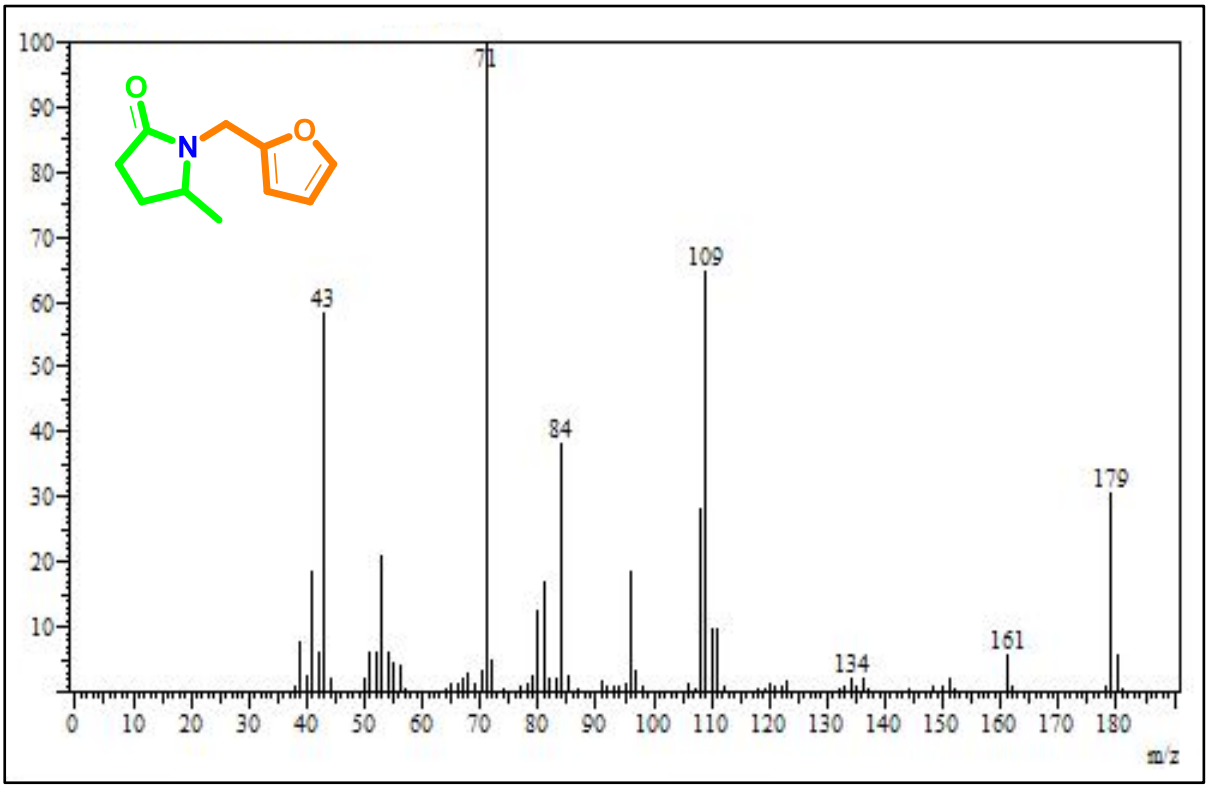
5-methyl-1-phenethylpyrrolidin-2-one (3f):



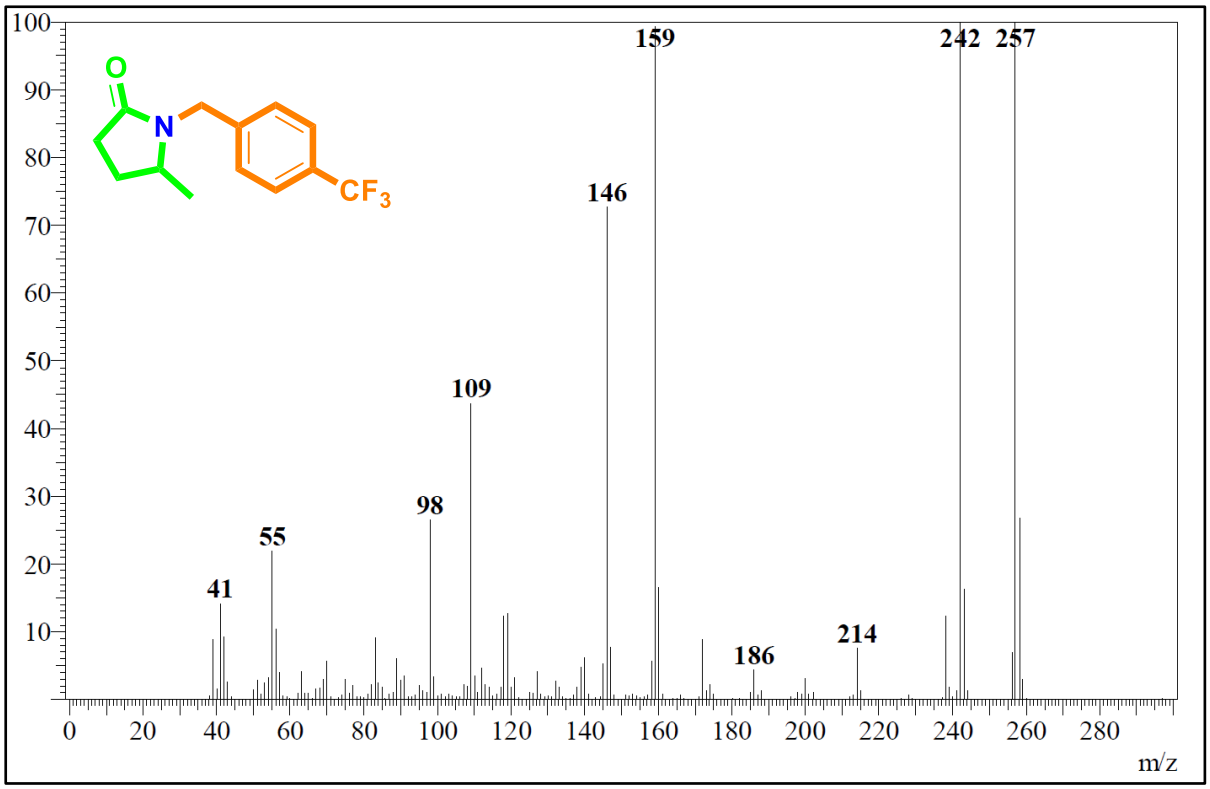
4-((2-methyl-5-oxopyrrolidin-1-yl)methyl)benzonitrile (3g):



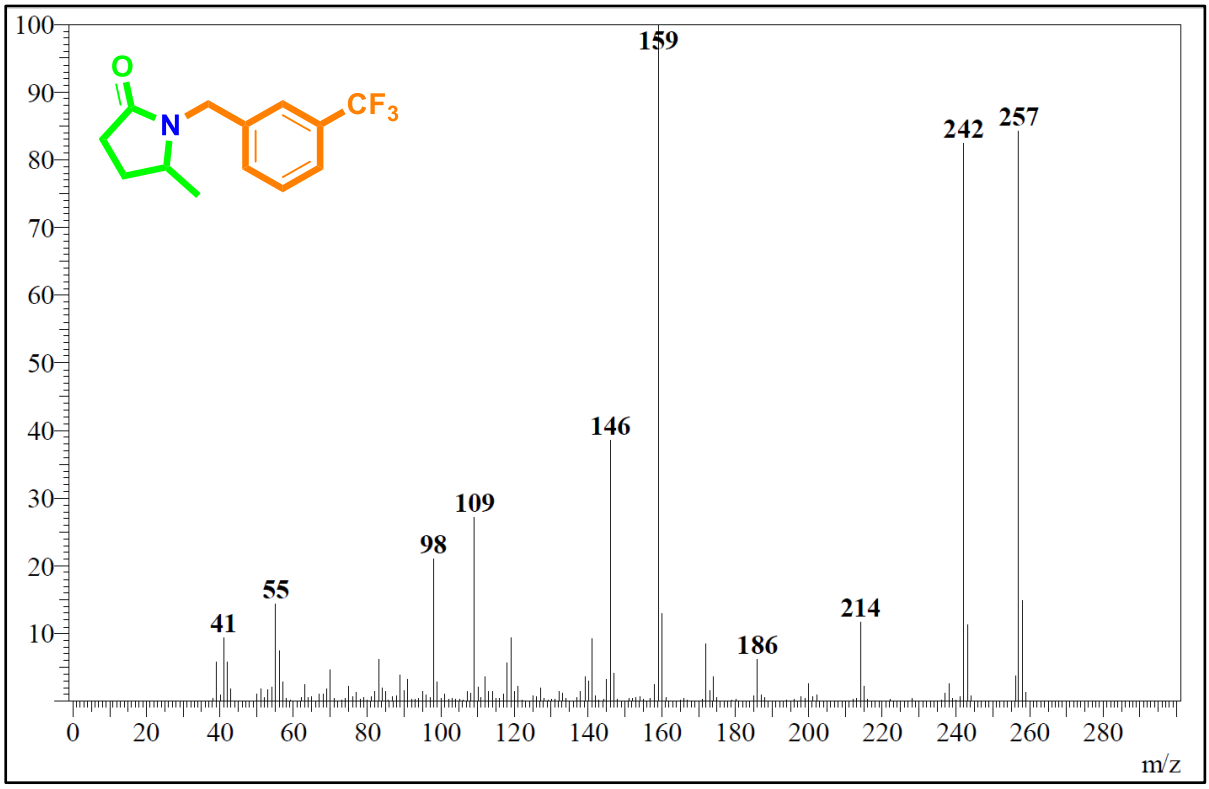
1-(furan-2-ylmethyl)-5-methylpyrrolidin-2-one (3h):



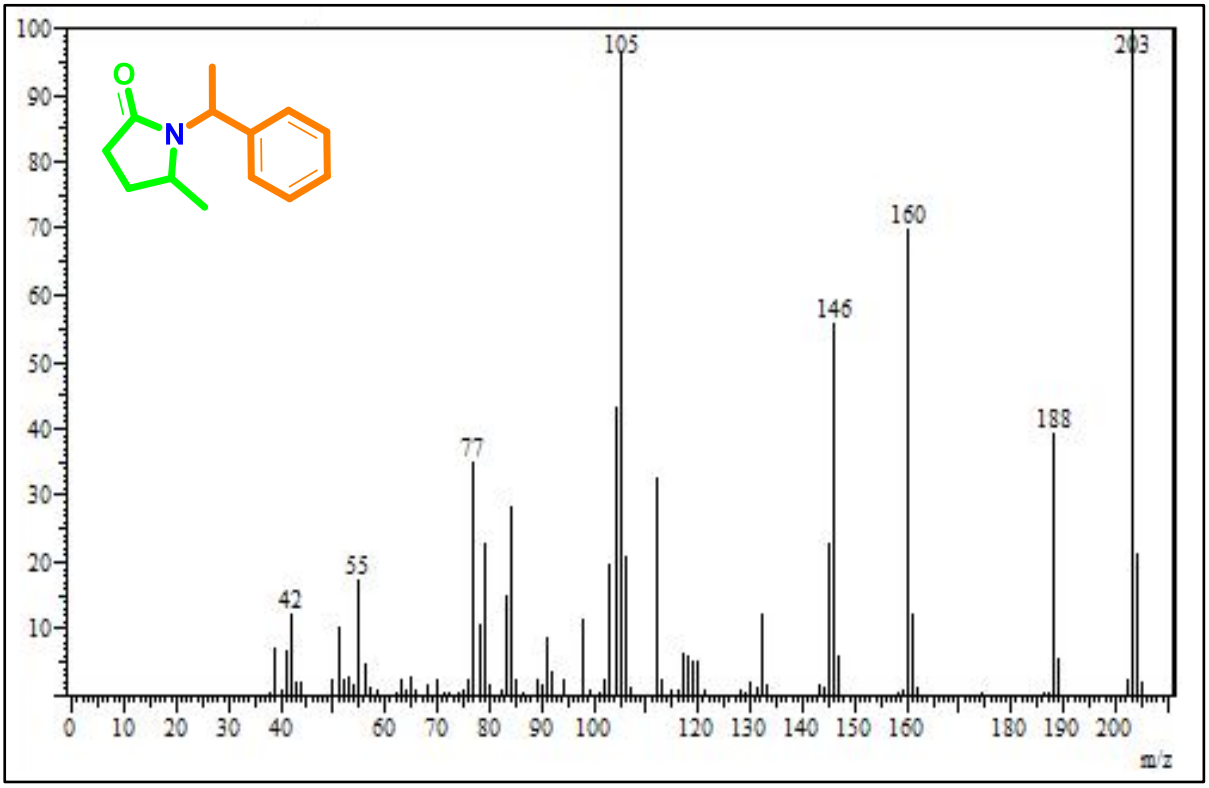
5-methyl-1-(4-(trifluoromethyl)benzyl)pyrrolidin-2-one (3i):



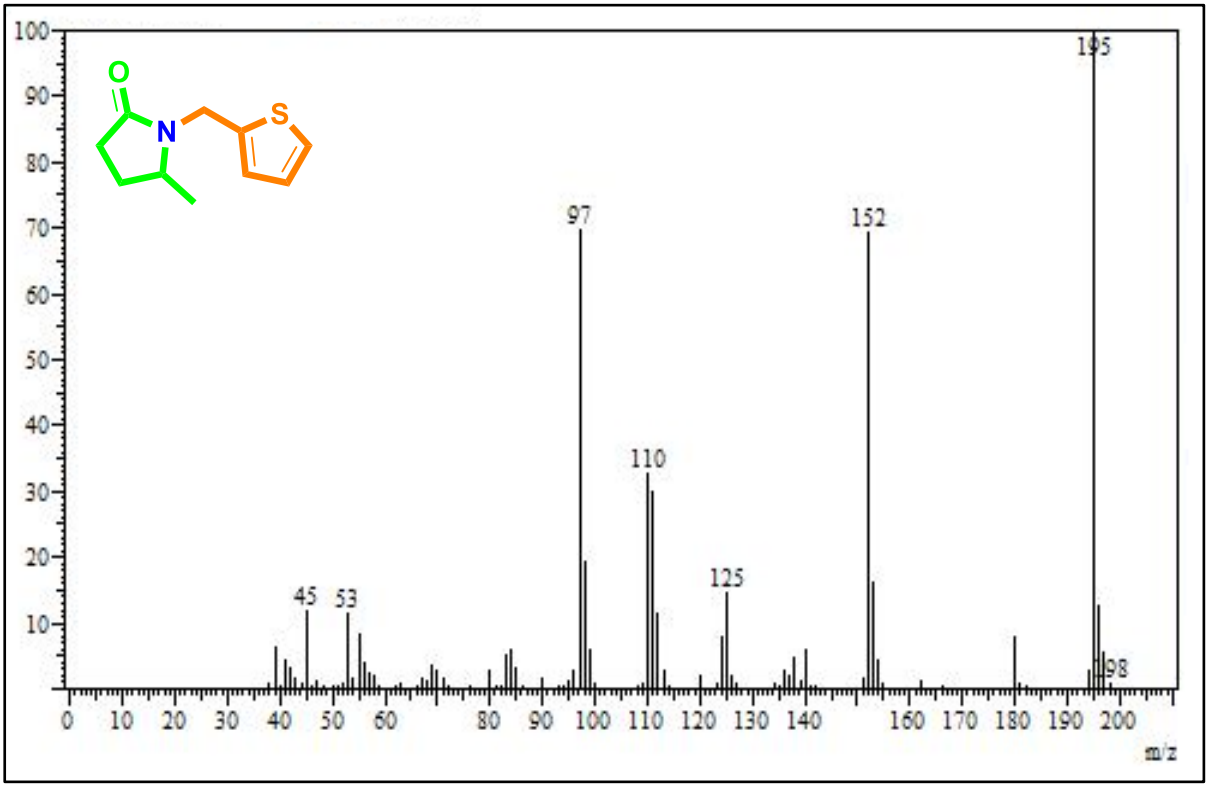
5-methyl-1-(3-(trifluoromethyl)benzyl)pyrrolidin-2-one (3j):



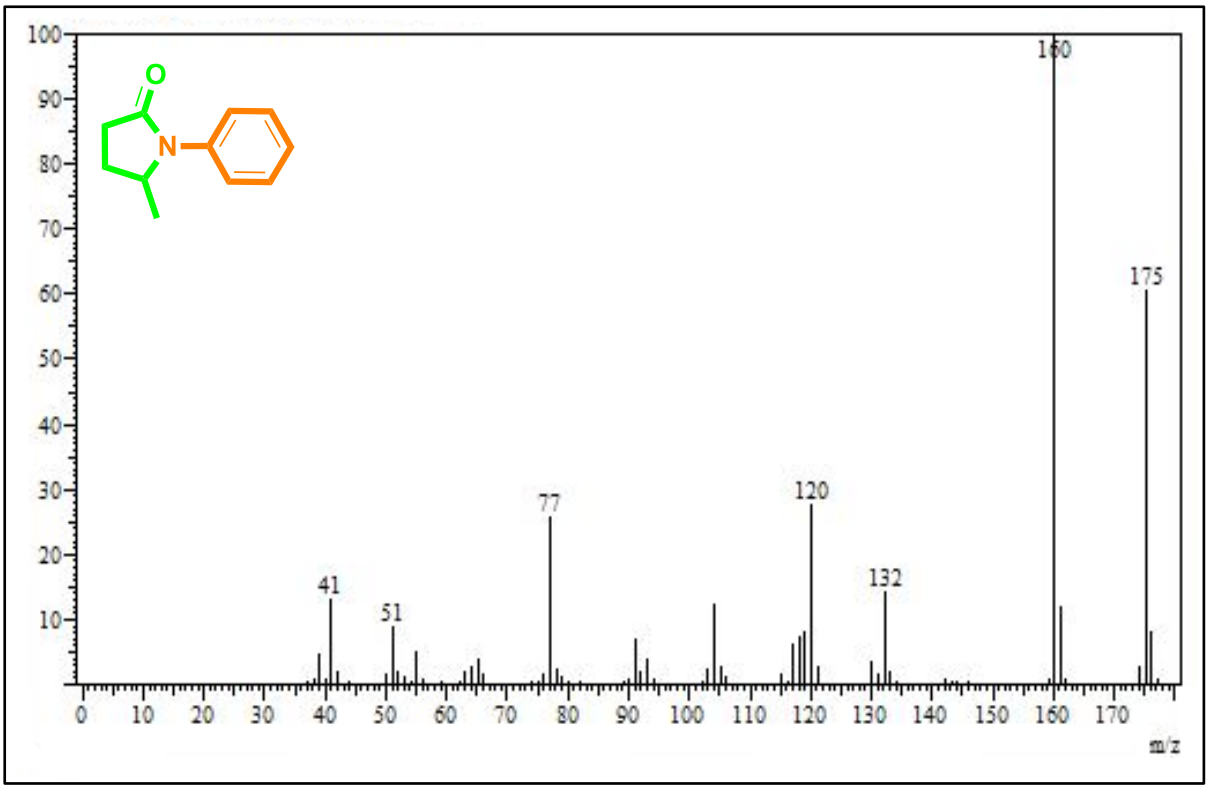
5-methyl-1-(1-phenylethyl)pyrrolidin-2-one (3k):



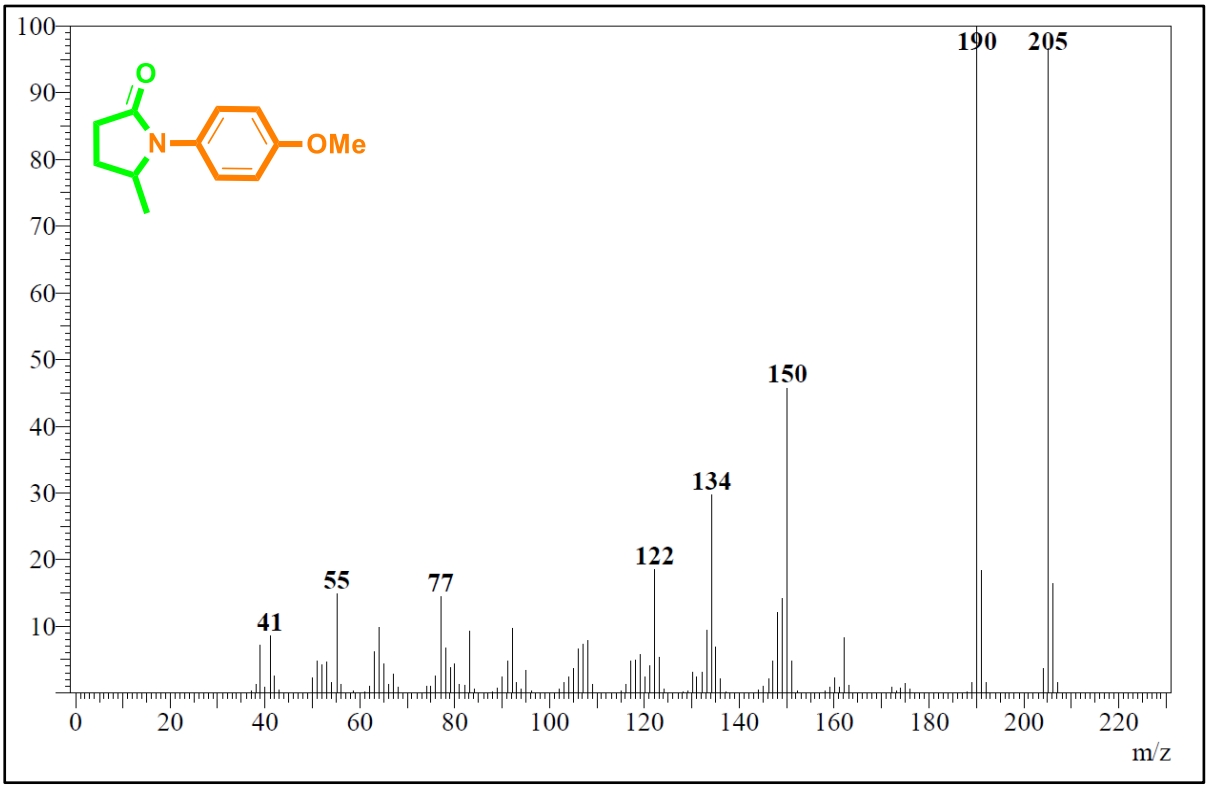
5-methyl-1-(thiophen-2-ylmethyl)pyrrolidin-2-one (3l):



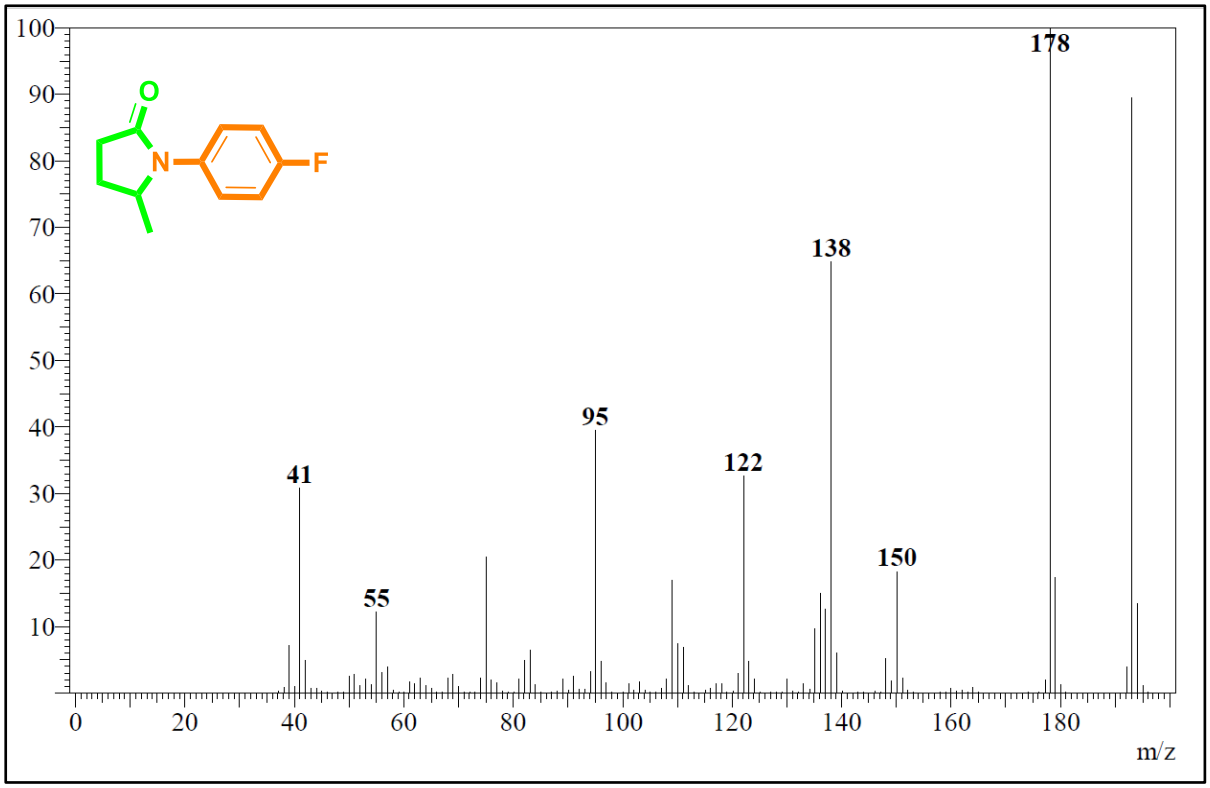
5-Methyl-1-phenyl-pyrrolidin-2-one (4a):



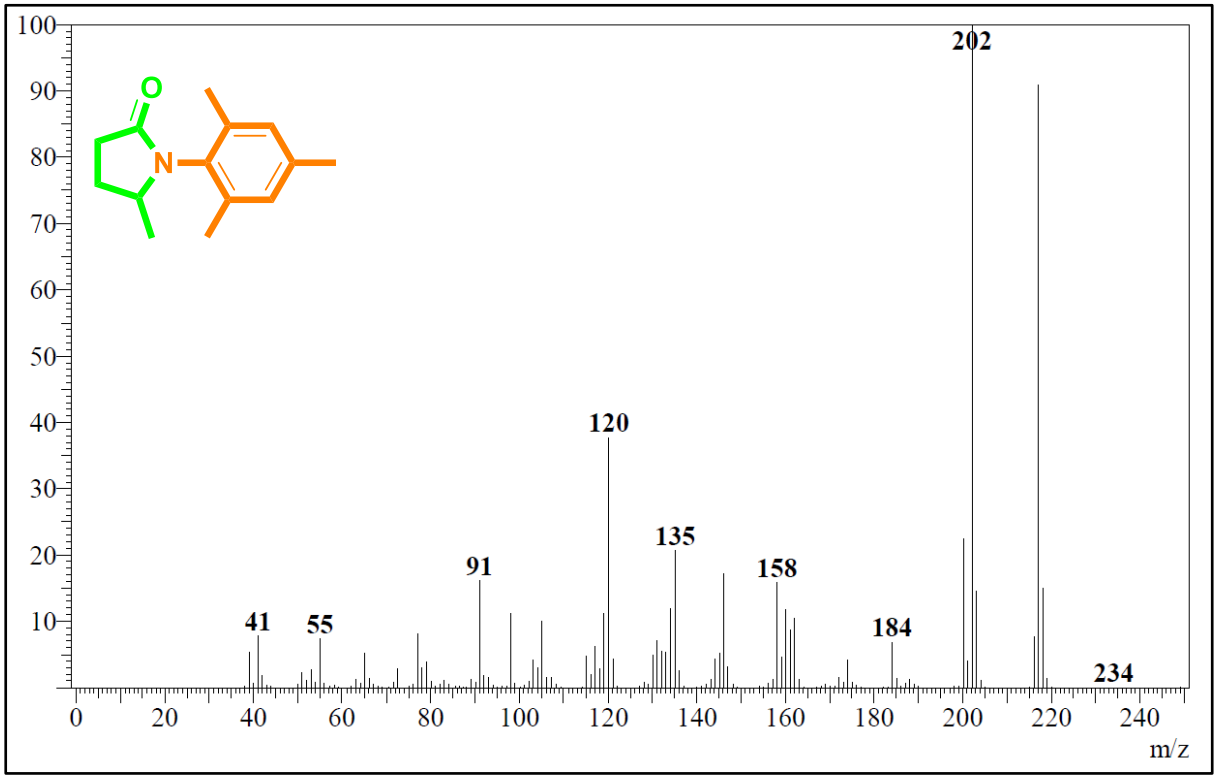
1-(4-methoxyphenyl)-5-methylpyrrolidin-2-one (4b):



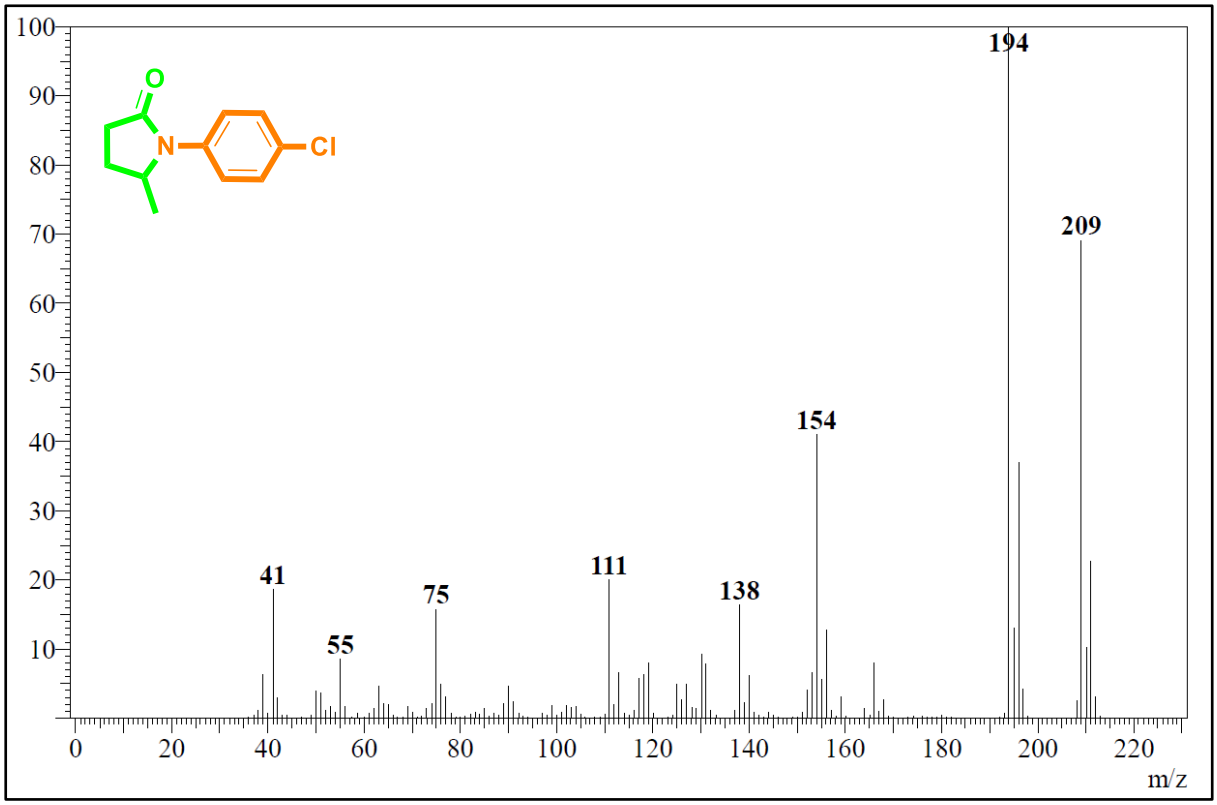
1-(4-fluorophenyl)-5-methylpyrrolidin-2-one (4c):



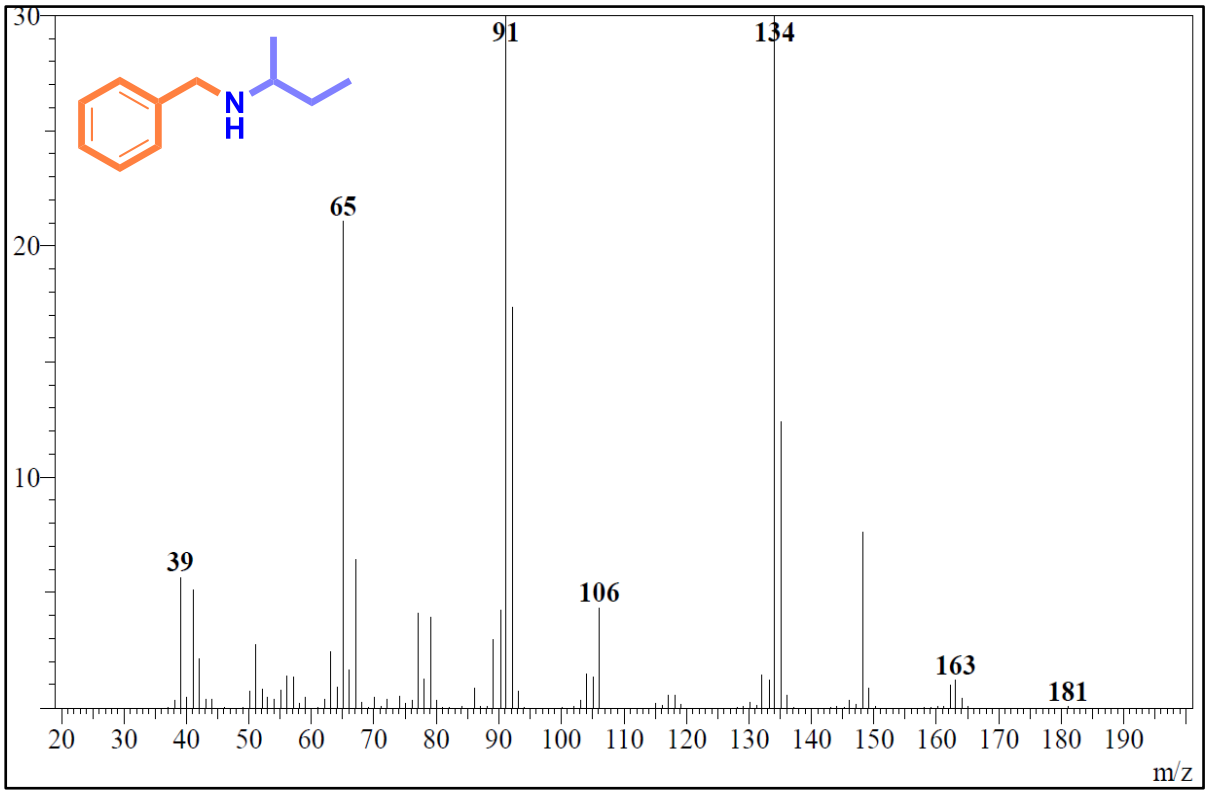
1-mesityl-5-methylpyrrolidin-2-one (4d):



1-(4-chlorophenyl)-5-methylpyrrolidin-2-one (4e):



N-benzylbutan-2-amine



References

[1] A. M. Hengne, B. S. Kadu, N. S. Biradar, R. C. Chikate, C. V. Rode, *RSC Adv.* 2016, **6**, 59753–59761.

[2] Z. Xue, Q. Liu, J. Wang, T. Mu, *Green Chem.* 2018, **20**, 4391–4408.

[3] Z. Sun, J. Chen, T. Tu, *Green Chem.* 2017, **19**, 789–794.

[4] C. Wu, X. Luo, H. Zhang, X. Liu, G. Ji, Z. Liu and Z. Liu, *Green Chem.*, 2017, **19**, 3525-3529.