Electronic Supplementary Material (ESI) for Green Chemistry.

Reductive Amination/Cyclization of Levulinic Acid to Pyrrolidones versus Pyrrolidines by Switching the Catalyst from $AlCl_3$ to $RuCl_3$ under mild conditions

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1. General information

All reagents and solvents were purchased from commercial sources (J&K, Beijing InnoChem Science & Technology Co., Energy Chemical), and were used without further purification.

Liquid NMR spectra were recorded on Bruck 400 spectrometer using $CDCl_3$ as the solvent. The reaction mixture was analyzed by means of GC (Agilent 4890D) with a FID detector and a nonpolar capillary column (DB-5) (30m×0.25mm×0.25μm). The column oven was temperature-programmed with a 2 min hold at 323 K, followed by the temperature increase to 528K at a rate of

15 K/min and kept at 538 K for 10 min. High-purity nitrogen was used as a carrier gas.

2. Typical procedures for the reductive amination reaction of LA to pyrrolidones

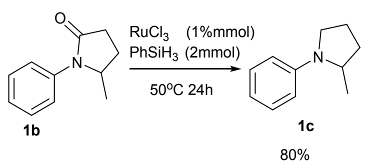
The reaction was conducted in a screw-capped vial (15 mL inner volume) equipped with a magnetic stirrer. Typically, $AlCl_3.6H_2O$ (0.05mmol), amine (1.0 mmol), LA (1.0 mmol), and $PhSiH_3$ (3.0 mmol) were successively added to the vial, and heated at 30°C for the desired time. After the reaction, the vial was cooled to room temperature. The yield of 5-methyl-1-phenylpyrrolidin-2-one was determined by GC with a FID detector, and the yields of other N-substituted pyrrolidinones were determined by ^1H NMR using mesitylene as an internal standard. The crude mixture was diluted by ether and isolated by column chromatography on silica gel (eluent: petroleum ether and EtOAc).

3. Typical procedures for the reductive amination reaction of LA to cyclic amines

The reaction was conducted in a screw-capped vial (15 mL inner volume) equipped with a magnetic stirrer. Typically, $RuCl_3.3H_2O$ (0.01mmol), amine (1.0 mmol), LA (1.0 mmol), and $PhSiH_3$ (4.0 mmol) were successively added into the vial, and heated at 45°C for 24h. Then the vial was cooled to room temperature. The yield of 2-methyl-1-phenylpyrrolidine was determined by GC with a FID detector, and the yields of other N-substituted pyrrolidines were determined by ^1H NMR using mesitylene as an internal standard. The crude mixture was diluted by ether and isolated by column chromatography on silica gel (eluent: petroleum ether and CH_2Cl_2).

4. Synthesis of 2-methyl-1-phenylpyrrolidine (1c) using 5-methyl-1-phenylpyrrolidin-2-one (1b) as the substrate.

To a screw-capped vial (15 mL inner volume), $RuCl_3.3H_2O$ (0.01mmol), 5-methyl-1-phenylpyrrolidin-2-one (1.0 mmol), and $PhSiH_3$ (2.0 mmol) were added successively, and heated at 50°C for 24h. Then the vial was cooled to room temperature. The product yield was determined by GC with a FID detector.



Scheme S1: Synthesis of 2-methyl-1-phenylpyrrolidine (1c) using 5-methyl-1-phenylpyrrolidin-2-one (1b) as the substrate.

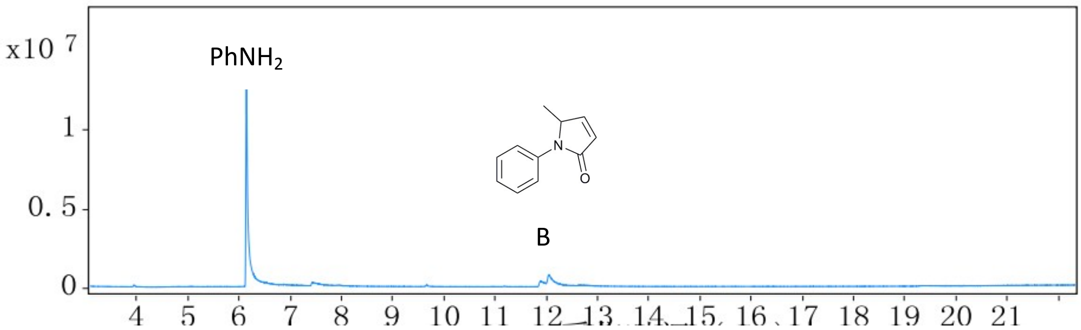
5. Screening of reductants using $RuCl_3.3H_2O$ as the catalyst

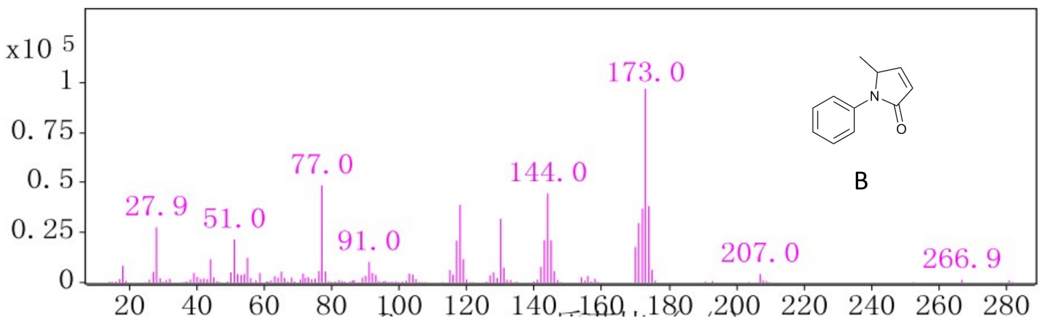
Table S1:Screening of reductants using $RuCl_3.3H_2O$ as the catalyst[a]

Entry	Reductant/n[b]	Yield[c]	
		1b	1c
1	$EtSiH_2$/6	28	0
2	$PhSiH_2$/6	0	0
3	EtO_3SiH/12	50	0
4	Ph_3SiH/12	0	0
5	$(CH_3O)_2CH_3SiH$/12	78	0
6	$(CH_3)_2PhSiH$/12	96	0

[a] Reaction conditions: aniline (1mmol), LA (1mmol), $RuCl_3.3H_2O$ (1 mol%). [b] n refers to mmol of hydrosilane. [c]Determined by GC analysis using dodecane as the internal standard.

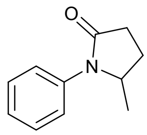
6. The GC-MS spectra of the mixture of LA, aniline and $AlCl_3$





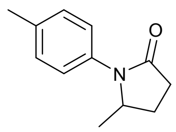
7. NMR data of the resultant pyrrolidones

5-Methyl-1-phenylpyrrolidin-2-one



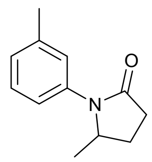
Isolated yield: 92% ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 4H), 7.20 (dd, J = 6.7, 4.7 Hz, 1H), 4.42 – 4.18 (m, 1H), 2.75 – 2.26 (m, 3H), 1.83 – 1.66 (m, 1H), 1.20 (d, J = 6.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl3) δ 174.18, 137.63, 128.97, 125.72, 124.04, 55.61, 31.35, 26.75, 20.16 ppm.HRMS (ESI) for $C_{11}H_{13}NO$ [M+Na]+ :calc.:198.0889. Found: 198.0889.

5-Methyl-1-(p-tolyl)pyrrolidin-2-one



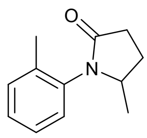
Isolated yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (m, J = 8.4 Hz, 4H), 4.23 (m, J = 13.0, 6.3 Hz, 1H), 2.56 (m, J = 16.8, 9.4, 6.9 Hz, 2H), 2.32 (s, 4H), 1.72 (m, J = 13.0, 9.4, 7.3 Hz, 1H), 1.17 (d, J = 6.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.14, 135.55, 134.89, 129.52, 124.17, 55.71, 31.19, 26.73, 20.89, 20.12 ppm. HRMS (ESI) for $C_{12}H_{15}NNaO$ [M+Na]+ :calc.: 212.1046. Found: 212.1047.

5-Methyl-1-(m-tolyl)pyrrolidin-2-one



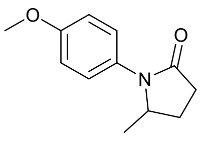
Isolated yield: 87%,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (m, J = 46.0, 26.8, 7.6 Hz, 4H), 4.26 (dd, J = 13.0, 6.4 Hz, 1H), 2.58 (m, J = 16.8, 9.4, 6.9 Hz, 2H), 2.36 (s, 4H), 1.80 – 1.68 (m, 1H), 1.19 (d, J = 6.2 Hz, 3H)ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.16, 138.78, 137.40, 128.70, 126.67, 125.03, 121.20, 55.74, 31.26, 26.72, 21.40, 20.15 ppm. HRMS (ESI) for $C_{12}H_{15}NNaO$ $[M+Na]^+$:calc.: 212.1046. Found: 212.1046.

5-Methyl-1-(o-tolyl)pyrrolidin-2-one



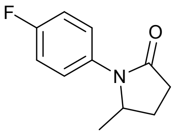
Isolated yield: 50%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dt, J = 22.4, 4.6 Hz, 3H), 7.12 – 7.00 (m, 1H), 4.06 (d, J = 5.7 Hz, 1H), 2.68 – 2.32 (m, 3H), 2.22 (s, 3H), 1.86 – 1.70 (m, 1H), 1.11 (d, J = 6.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.19, 136.43, 136.15, 131.14, 127.81, 126.67, 56.87, 30.88, 27.85, 20.29, 18.08 ppm. HRMS (ESI) for $C_{12}H_{15}NNaO[M+Na]^+$:calc.: 212.1046. Found: 212.1047.

1-(4-Methoxyphenyl)-5-methylpyrrolidin-2-one



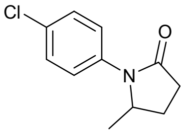
Isolated yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 4.17 (dd, *J* = 13.3, 6.2 Hz, 1H), 3.80 (s, 3H), 2.67 – 2.45 (m, 2H), 2.35 (dddd, *J* = 13.3, 9.3, 7.3, 6.1 Hz, 1H), 1.79 – 1.66 (m, 1H), 1.17 (d, *J* = 6.2 Hz, 3H) ppm；^{13}C NMR (101 MHz, $CDCl_3$) δ 174.28 , 157.69 , 130.40 , 126.07 , 114.34 , 56.11 , 55.42 , 31.10 , 26.83 , 20.24 ppm. HRMS (ESI) for $C_{12}H_{15}NNaO_2$ $[M+Na]^+$:calc.: 228.0995. Found: 228.0997.

1-(4-Fluorophenyl)-5-methylpyrrolidin-2-one



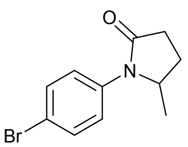
Isolated yield:88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.07 (t, *J* = 8.7 Hz, 2H), 4.22 (dd, *J* = 13.3, 6.2 Hz, 1H), 2.57 (ddd, *J* = 16.9, 9.4, 6.8 Hz, 2H), 2.44 – 2.26 (m, 1H), 1.78 – 1.71 (m, 1H), 1.18 (d, *J* = 6.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.24, 160.43 (d, *J* = 245.4 Hz), 133.54, 125.98 (d, *J* = 8.3 Hz), 115.78 (d, *J* = 22.5 Hz), 55.84, 31.10, 26.73, 20.10 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -136.11 ppm. HRMS (ESI) for $C_{11}H_{12}FNNaO$ $[M+Na]^+$:calc.: 216.0795. Found: 216.0796.

1-(4-Chlorophenyl)-5-methylpyrrolidin-2-one



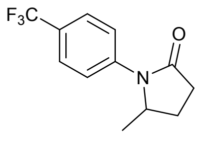
Isolated yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 4H), 4.27 (dd, *J* = 13.1, 6.2 Hz, 1H), 2.57 (ddd, *J* = 16.7, 9.5, 6.8 Hz, 2H), 2.45 – 2.24 (m, 1H), 1.75 (dddd, *J* = 12.8, 9.5, 7.1, 5.6 Hz, 1H), 1.20 (d, *J* = 6.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.17, 136.12, 130.86, 129.01, 124.89, 55.40, 31.18, 26.56, 19.95 ppm.HRMS (ESI) for $C_{11}H_{12}ClNNaO$ $[M+Na]^+$:calc.: 232.0500. Found: 232.0501.

1-(4-Bromophenyl)-5-methylpyrrolidin-2-one

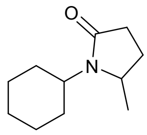


Isolated yield: 87%. ^{1}H NMR (400 MHz, CDCl3) δ 7.51 – 7.32 (m, 2H), 7.32 – 7.16 (m, 2H), 4.19 (dd, J = 12.2, 6.0 Hz, 1H), 2.67 – 2.16 (m, 3H), 1.79 – 1.52 (m, 1H), 1.11 (dd, J = 6.1, 1.2 Hz, 3H) ppm. 13C NMR (101 MHz, CDCl3) δ 173.98, 136.55, 131.79, 124.99 , 118.41 , 55.15, 31.08, 26.38, 19.78 ppm. HRMS (ESI) for $C_{11}H_{12}BrNNaO$ $[M+Na]^+$:calc.: 275.9994. Found: 275.9995.

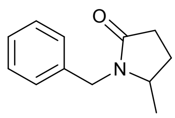
5-Methyl-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one

 Isolated yield: 40%. ^{1}H NMR (CDCl3, 400 MHz): δ 7.64 (d, J = 8.8Hz, 2H), 7.58 (d, J = 8.8Hz, 2H), 4.39 (m, 1H), 2.69 (m, 1H), 2.60-2.52 (m, 1H), 2.41 (m, 1H), 1.80 (m, 1H), 1.26 (d, J = 6.0Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.83, 126.72, 122.82, 112.41 – 112.21 (m), 54.98, 31.51, 30.42, 26.52, 20.66 ppm.^{19}F NMR (471 MHz, $CDCl_3$) δ -82.31.HRMS (ESI) for $C_{12}H_{12}F_3NNaO$ $[M+Na]^+$:calc.: 266.0763. Found: 266.0763.

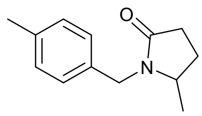
1-Cyclohexyl-5-methylpyrrolidin-2-one

 Isolated yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 – 3.62 (m, 2H), 2.53 – 2.34 (m, 1H), 2.33 – 2.02 (m, 2H), 1.90 – 1.01 (m, 14H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.41, 77.32, 77.00, 76.68, 52.80, 52.47, 31.78, 30.27, 30.03, 27.43, 25.88 (d, *J* = 5.7 Hz), 25.50, 22.31 ppm. HRMS (ESI) for $C_{11}H_{19}NNaO$ $[M+Na]^+$:calc.: 204.1359. Found: 204.1360.

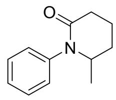
1-Benzyl-5-methylpyrrolidin-2-one

 Isolated yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.13 (m, 5H), 4.96 (d, *J* = 15.0 Hz, 1H), 3.99 (d, *J* = 15.0 Hz, 1H), 3.59 – 3.42 (m, 1H), 2.58 – 2.29 (m, 2H), 2.23 – 2.07 (m, 1H), 1.67 – 1.51 (m, 1H), 1.16 (d, *J* = 6.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.94 , 136.88, 128.60, 127.97, 127.39, 52.81, 43.90, 30.28, 26.67, 19.60 ppm. HRMS (ESI) for $C_{12}H_{15}NNaO$ $[M+Na]^+$: calc.:212.1046. Found: 212.1046.

5-Methyl-1-(4-methylbenzyl)pyrrolidin-2-one

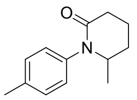
 Isolated yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 4H), 4.93 (d, *J* = 14.9 Hz, 1H), 3.92 (d, *J* = 14.9 Hz, 1H), 3.50 (dd, *J* = 13.5, 6.2 Hz, 1H), 2.43 (m, *J* = 25.5, 10.0, 7.0 Hz, 2H), 2.32 (s, 3H), 2.19 – 2.09 (m, 1H), 1.57 (m, *J* = 12.9, 9.6, 7.2, 5.9 Hz, 1H), 1.15 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.83, 137.01, 133.76, 129.24, 127.96, 52.68, 43.57, 30.28, 26.62, 21.04, 19.55 ppm. HRMS (ESI) for $C_{13}H_{17}NNaO$ $[M+Na]^+$: calc.:226.1202. Found: 226.1203.

6-Methyl-1-phenylpiperidin-2-one



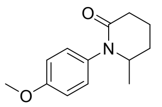
Isolated yield:87%. [1]H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.17 – 7.12 (m, 2H), 3.96 – 3.84 (m, 1H), 2.59 – 2.43 (m, 2H), 2.14 – 2.02 (m, 1H), 2.02 – 1.89 (m, 1H), 1.82 (m, *J* = 13.3, 9.7, 6.7, 3.0 Hz, 1H), 1.70 (m, *J* = 8.5, 6.1, 2.9 Hz, 1H), 1.05 (d, *J* = 6.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.35, 141.57, 129.14, 128.11, 127.10, 55.75, 32.76, 30.86, 20.89 , 18.33ppm. HRMS (ESI) for $C_{12}H_{16}NO$ $[M+H]^+$: calc.: 190.1226. Found: 190.1226.

6-Methyl-1-(p-tolyl)piperidin-2-one



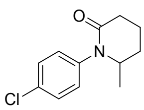
Isolated yield: 88%. [1]H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.94 – 3.77 (m, 1H), 2.52 (t, *J* = 6.6 Hz, 2H), 2.34 (s, 3H), 2.15 – 2.03 (m, 1H), 2.03 – 1.90 (m, 1H), 1.90 – 1.76 (m, 1H), 1.76 – 1.65 (m, 1H), 1.06 (d, *J* = 6.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.35, 138.95, 136.78, 129.81, 127.82, 55.73, 32.81, 30.86, 21.10, 20.89, 18.36 ppm. HRMS (ESI) for $C_{13}H_{18}NO$ $[M+H]^+$: calc.: 204.1383. Found: 204.1383.

1-(4-Methoxyphenyl)-6-methylpiperidin-2-one



Isolated yield: 87%. [1]H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.85 (dd, *J* = 12.1, 6.1 Hz, 1H), 3.80 (s, 3H), 2.52 (t, *J* = 6.6 Hz, 2H), 2.16 – 1.96 (m, 2H), 1.91 – 1.66 (m, 2H), 1.08 (d, *J* = 6.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.57, 158.26, 134.18, 128.94, 114.36, 55.84, 55.33, 32.67, 30.77, 20.78, 18.25 ppm. HRMS (ESI) for $C_{13}H_{18}NO_2$ $[M+H]^+$: calc.:220.1332. Found: 220.1332.

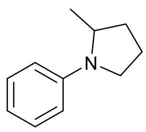
1-(4-Chlorophenyl)-6-methylpiperidin-2-one



Isolated yield:85%. [1]H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 3.96 – 3.82 (m, 1H), 2.53 (t, *J* = 6.6 Hz, 2H), 2.18 – 1.65 (m, 4H), 1.07 (d, *J* = 6.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.32, 139.99, 132.67, 129.33 (d, *J* = 12.5 Hz), 55.69, 32.69, 30.78, 20.84, 18.27 ppm. HRMS (ESI) for $C_{12}H_{15}ClNO$ $[M+H]^+$: calc.:224.0837. Found: 224.0836.

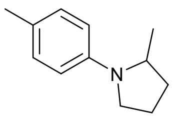
8. NMR data of the resultant pyrrolidines

2-Methyl-1-phenylpyrrolidine



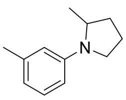
Isolated yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.8 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 2H), 3.86 (p, *J* = 6.1 Hz, 1H), 3.40 (dd, *J* = 11.6, 5.1 Hz, 1H), 3.14 (dd, *J* = 16.4, 8.0 Hz, 1H), 2.12 – 1.90 (m, 3H), 1.68 (dd, *J* = 10.1, 5.9 Hz, 1H), 1.16 (d, *J* = 6.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.31, 129.22, 115.22, 111.85, 53.64, 48.21, 33.20, 23.36, 19.43 ppm. HRMS (ESI) for $C_{11}H_{16}N$ $[M+H]^+$: calc.:224.0837. Found: 224.0836.

2-Methyl-1-(p-tolyl)pyrrolidine



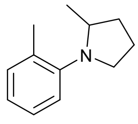
Isolated yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.4 Hz, 2H), 6.52 (d, *J* = 8.5 Hz, 2H), 3.90 – 3.78 (m, 1H), 3.41 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.13 (dd, *J* = 16.4, 8.0 Hz, 1H), 2.25 (s, 3H), 2.12 – 1.90 (m, 3H), 1.69 (dd, *J* = 4.7, 2.3 Hz, 1H), 1.17 (d, *J* = 6.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.27, 129.63, 124.15, 111.85, 53.68, 48.40, 33.13, 23.31, 20.19, 19.47 ppm. HRMS (ESI) for $C_{12}H_{18}N$ $[M+H]^+$: calc.: 176.1434. Found: 176.1434.

2-Methyl-1-(m-tolyl)pyrrolidine



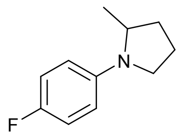
Isolated yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, *J* = 8.1 Hz, 1H), 6.47 (d, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 5.0 Hz, 2H), 3.86 (p, *J* = 6.1 Hz, 1H), 3.40 (dd, *J* = 11.7, 5.1 Hz, 1H), 3.14 (dd, *J* = 16.4, 8.1 Hz, 1H), 2.30 (s, 3H), 2.13 – 1.87 (m, 3H), 1.67 (dd, *J* = 9.4, 6.3 Hz, 1H), 1.16 (d, *J* = 6.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.29, 138.75, 128.99, 116.11, 112.44, 109.00, 53.51, 48.15, 33.07, 23.25, 21.87, 19.41 ppm. HRMS (ESI) for $C_{12}H_{18}N$ $[M+H]^+$: calc.: 176.1434. Found: 176.1434.

2-Methyl-1-(o-tolyl)pyrrolidine



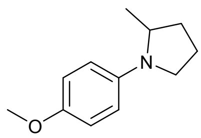
Isolated yield:60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 9.1 Hz, 2H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.87 (t, *J* = 7.3 Hz, 1H), 3.73 – 3.45 (m, 2H), 2.76 (m, *J* = 8.8, 4.5 Hz, 1H), 2.27 (s, 3H), 2.11 (dd, *J* = 7.9, 2.7 Hz, 1H), 1.83 (m, *J* = 16.8, 12.1, 8.1, 3.9 Hz, 2H), 1.56 (m, *J* = 17.9, 8.9 Hz, 1H), 0.99 (d, *J* = 6.0 Hz, 3H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 148.56, 132.02, 131.23, 126.12, 121.32, 118.36, 55.01, 53.10, 33.84, 23.62, 19.58, 19.12 ppm. HRMS (ESI) for $C_{12}H_{18}N$ $[M+H]^+$: calc.: 176.1434. Found: 176.1434.

1-(4-Fluorophenyl)-2-methylpyrrolidine



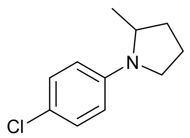
Isolated yield:79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (t, *J* = 8.7 Hz, 2H), 6.47 (dd, *J* = 9.0, 4.3 Hz, 2H), 3.78 (dd, *J* = 12.5, 6.2 Hz, 1H), 3.37 (dd, *J* = 11.1, 5.0 Hz, 1H), 3.10 (dd, *J* = 16.0, 8.4 Hz, 1H), 2.13 – 1.90 (m, 3H), 1.75 – 1.61 (m, 1H), 1.14 (d, *J* = 6.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.79, 153.48, 143.98, 115.55, 115.33, 112.17 (d, *J* = 7.1 Hz), 53.99, 48.68, 33.18, 23.36, 19.31ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -151.18 ppm.HRMS (ESI) for $C_{11}H_{15}FN$ $[M+H]^+$: calc.:180.1183.Found:180.1184

1-(4-Methoxyphenyl)-2-methylpyrrolidine



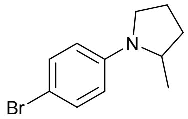
Isolated yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 3.82 – 3.69 (m, 4H), 3.47 – 3.31 (m, 1H), 3.10 (q, *J* = 8.3 Hz, 1H), 2.12 – 1.85 (m, 3H), 1.75 – 1.57 (m, 1H), 1.15 (d, *J* = 6.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.63, 142.42, 115.11, 112.76, 56.05, 54.09, 48.94, 33.26, 23.43, 19.65 ppm.HRMS (ESI) for $C_{12}H_{18}NO$ $[M+H]^+$: calc.:192.1383.Found:192.1383

N-(4-chlorophenyl)-2-methylpyrrolidine

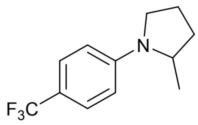


Isolated yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.15 (d, J = 7.5 Hz, 2H), 6.46 (d, J = 7.5 Hz, 2H), 3.85 (m, J = 6.2 Hz, 1H), 3.39 (t, J = 8.1 Hz, 1H), 3.16 (m, J = 16.2, 7.8 Hz, 1H), 2.16-2.00 (m, 2H), 1.93 (m, 1H), 1.79-1.63 (m, 1H), 1.17 (d, J = 6.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ145.83, 128.96, 119.89, 112.82, 53.80, 48.31, 33.09, 23.33, 19.15 ppm. HRMS (ESI) for $C_{11}H_{15}ClN$ $[M+H]^+$: calc.:196.0888.Found:196.0888

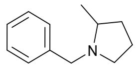
1-(4-Bromophenyl)-2-methylpyrrolidine

 Isolated yield:82%. ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.50 (d, 2H), 6.39 (d, 2H), 3.55 (m, J = 6.4, 3.2 Hz, 1H), 3.03 (m, J = 9.5, 7.6, 2.5 Hz, 1H), 2.88 – 2.74 (m, 1H), 1.87 – 1.52 (m, 3H), 1.46 – 1.24 (m, 1H), 1.00 (d, J = 6.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.23, 131.80, 113.41, 106.93, 53.79, 48.35, 33.21, 23.40, 19.17 ppm. HRMS (ESI) for $C_{11}H_{15}BrN[M+H]^+$: calc.:240.0382. Found: 240.0383

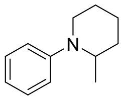
2-Methyl-1-(4-(trifluoromethyl)phenyl)pyrrolidine

 Isolated yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 8.7 Hz, 2H), 4.07 – 3.80 (m, 1H), 3.45 (dd, *J* = 9.5, 7.6 Hz, 1H), 3.21 (d, *J* = 8.8 Hz, 1H), 2.20 – 1.96 (m, 3H), 1.82 – 1.69 (m, 1H), 1.20 (d, *J* = 6.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.11, 126.73, 126.43, 124.05, 116.63, 116.30, 111.02, 53.68, 47.96, 32.98, 23.14, 18.84 ppm.^{19}F NMR (471 MHz, $CDCl_3$) δ -80.60 ppm. HRMS (ESI) for C12H15F3N $[M+H]^+$: calc.:230.1151 . Found: 230.1151.

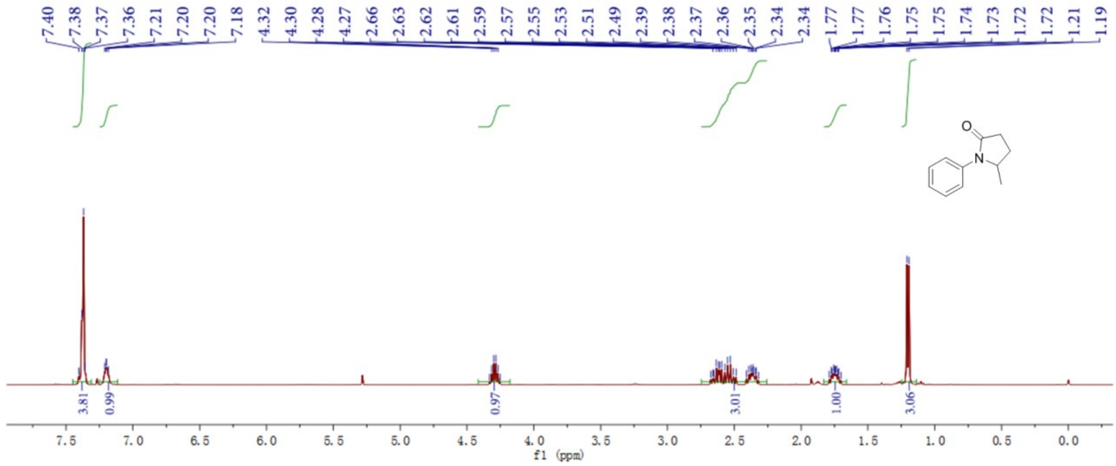
1-Benzyl-2-methylpyrrolidine

 Isolated yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.15 (m, 5H), 4.01 (d, *J* = 12.8 Hz, 1H), 3.14 (d, *J* = 12.8 Hz, 1H), 2.90 (t, *J* = 8.6 Hz, 1H), 2.46 – 2.30 (m, 1H), 2.10 (q, *J* = 8.9 Hz, 1H), 2.02 – 1.86 (m, 1H), 1.80 – 1.53 (m, 2H), 1.52 – 1.36 (m, 1H), 1.16 (d, *J* = 6.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.64, 128.03, 127.10, 125.70, 58.56, 57.34, 53.04, 31.76, 20.51, 18.17 ppm. HRMS (ESI) for $C_{12}H_{18}N$ $[M+H]^+$: calc.: 176.1434. Found: 176.1434.

2-Methyl-1-phenylpiperidine

 Isolated yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.4 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 3H), 6.81 (t, *J* = 7.2 Hz, 1H), 3.98 – 3.80 (m, 1H), 3.28 – 3.10 (m, 1H), 2.97 (dd, *J* = 15.3, 6.3 Hz, 1H), 1.99 – 1.47 (m, 6H), 0.99 (d, *J* = 6.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.48, 128.99, 119.25, 117.73, 51.49, 45.19, 31.87, 26.16, 19.88, 13.98 ppm. HRMS (ESI) for $C_{12}H_{18}N$ $[M+H]^+$: calc.: 176.1434. Found: 176.1434.

9. NMR spectra of the products



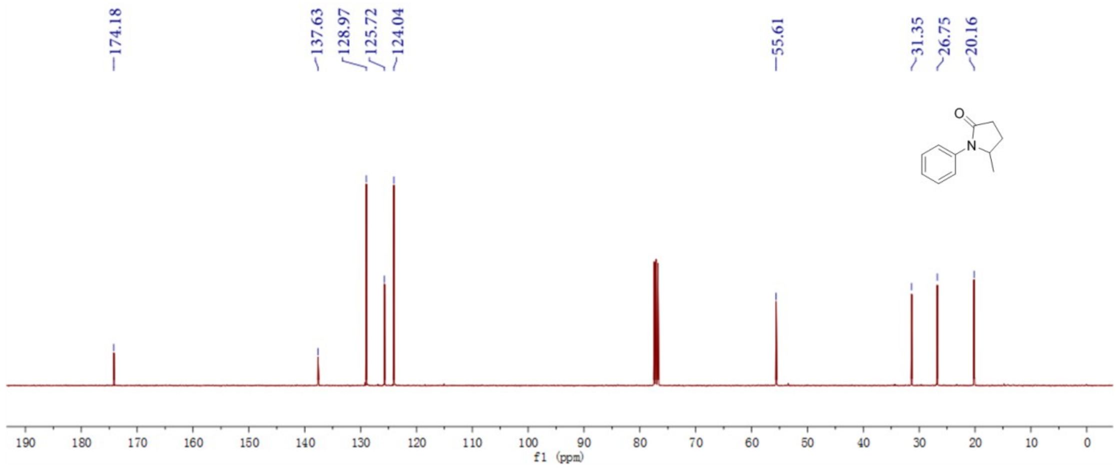


Figure S1 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-methyl-1-phenylpyrrolidin-2-one

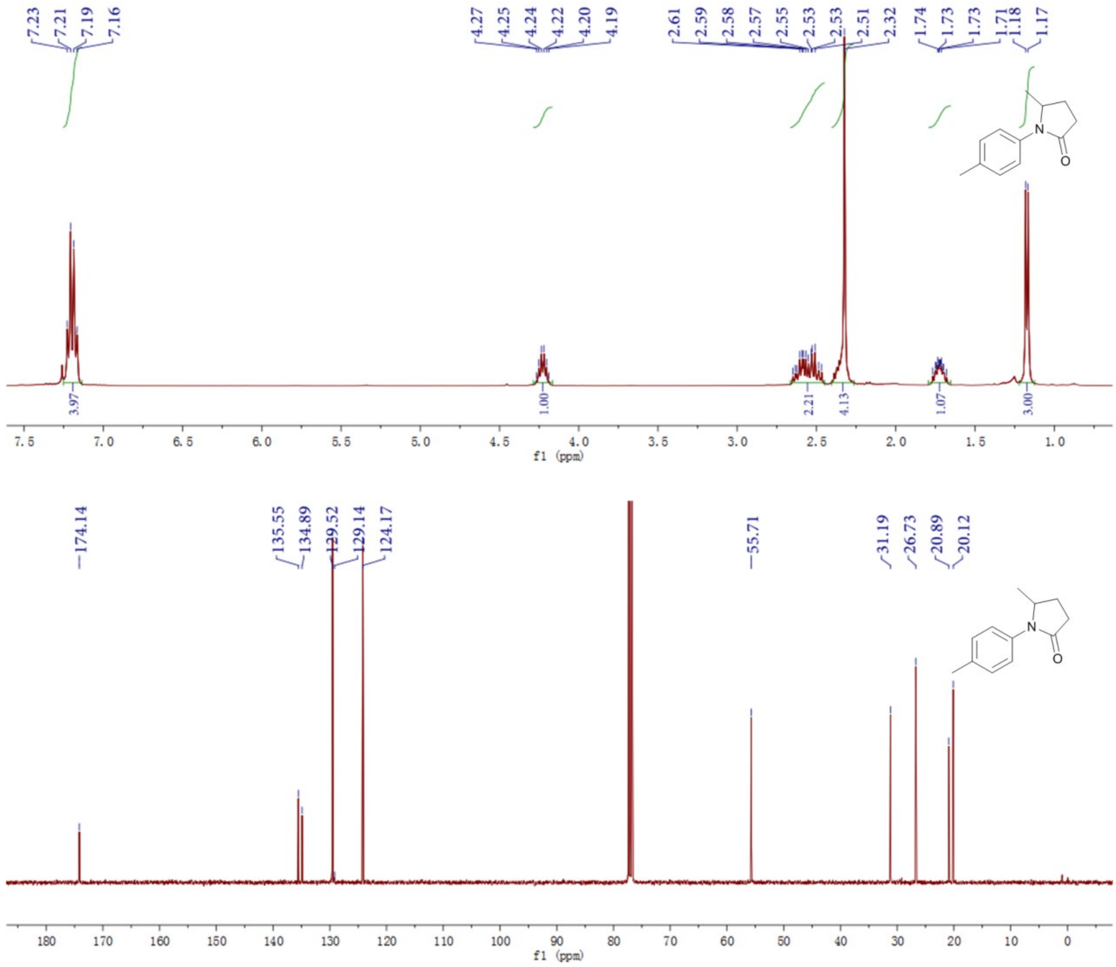


Figure S2 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-methyl-1-(p-tolyl)pyrrolidin-2-one

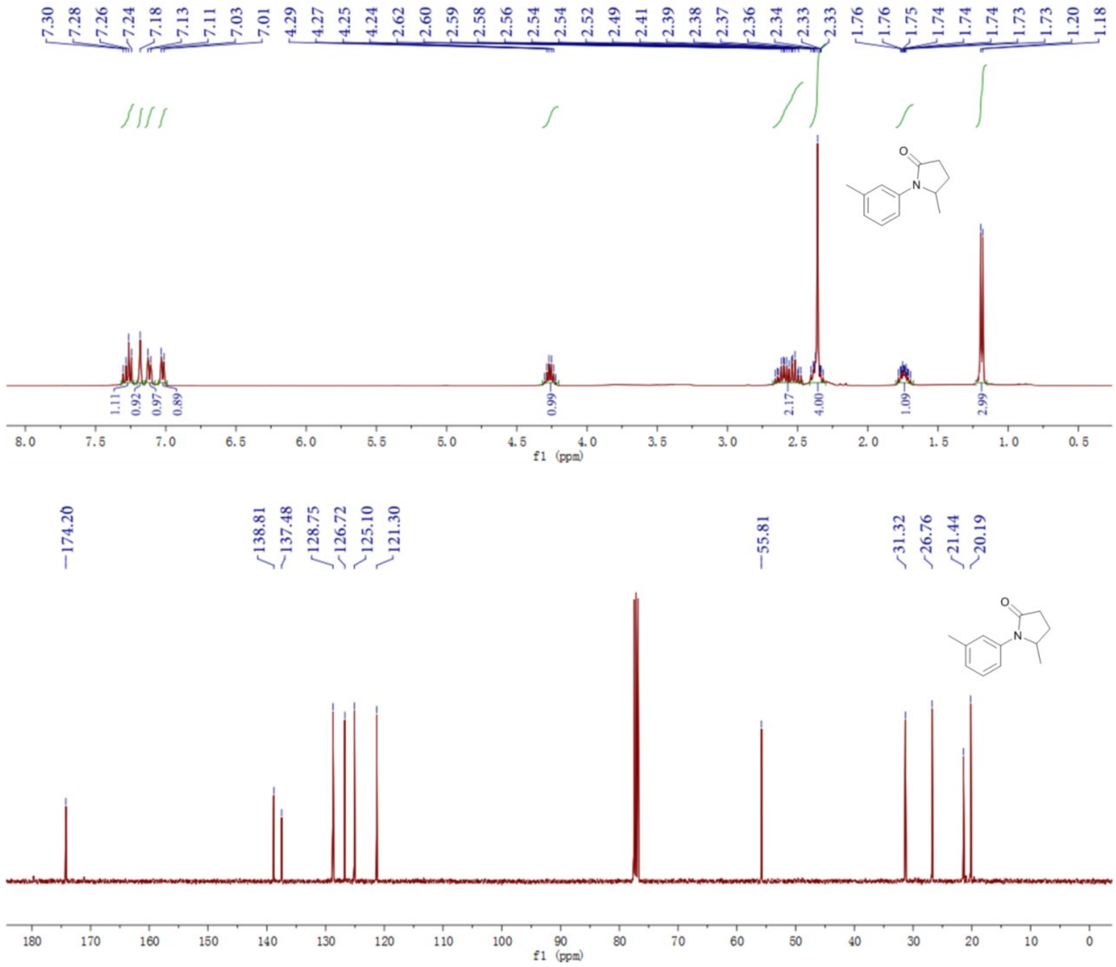
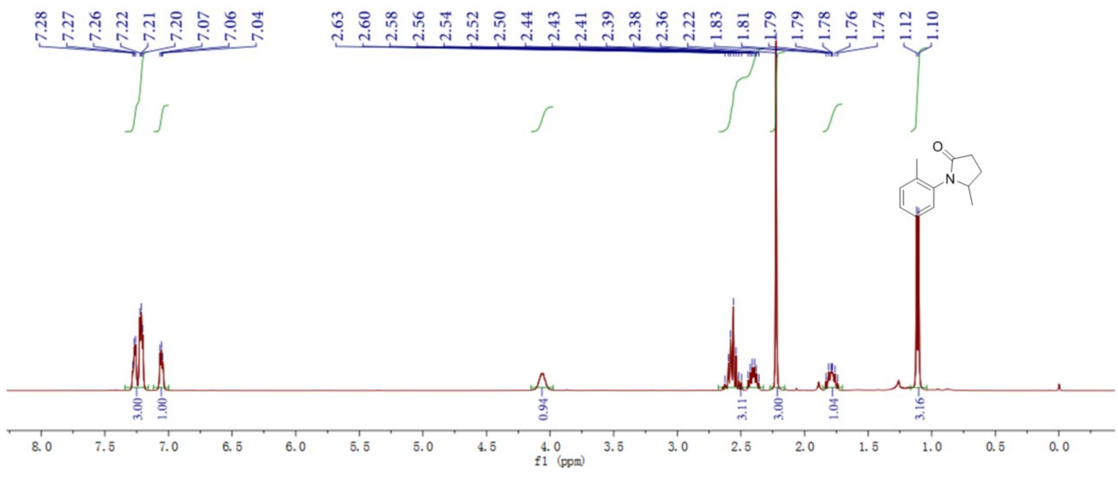


Figure S3 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-methyl-1-(m-tolyl)pyrrolidin-2-one



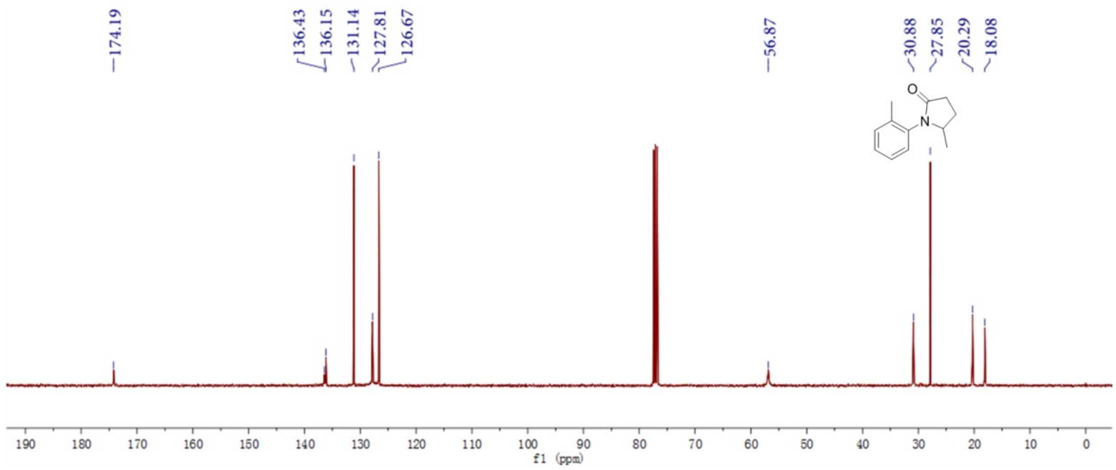
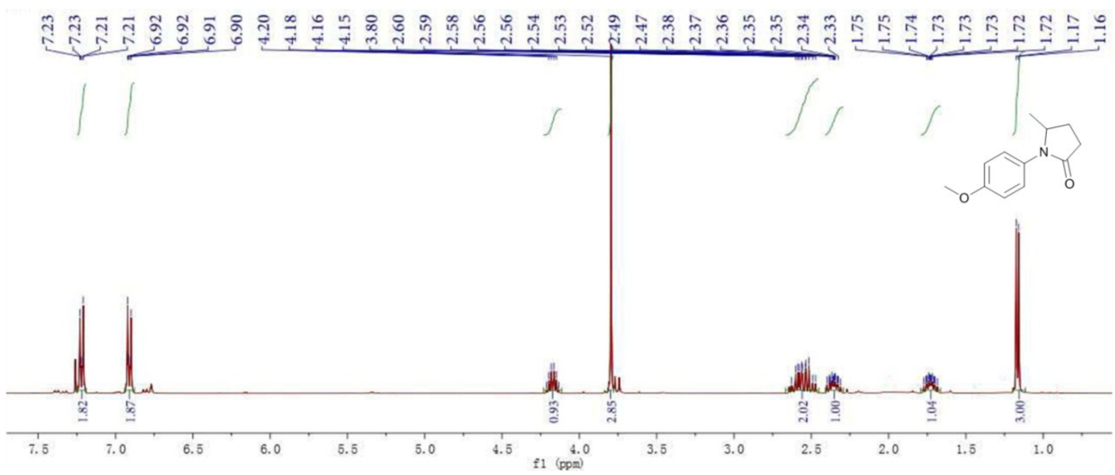


Figure S4 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-methyl-1-(o-tolyl)pyrrolidin-2-one



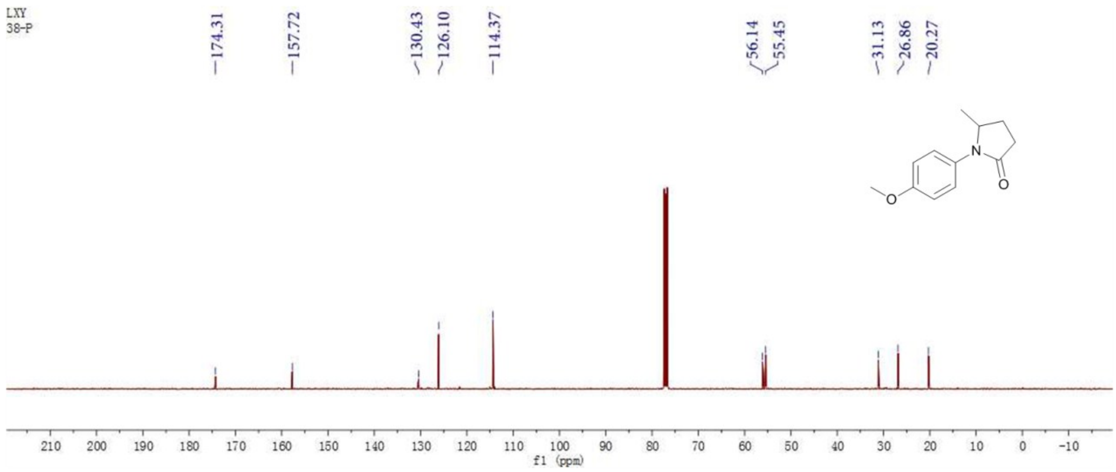


Figure S5 ^1H (top) and ^{13}C (bottom) NMR spectra of 1-(4-methoxyphenyl)-5-methylpyrrolidin-2-one

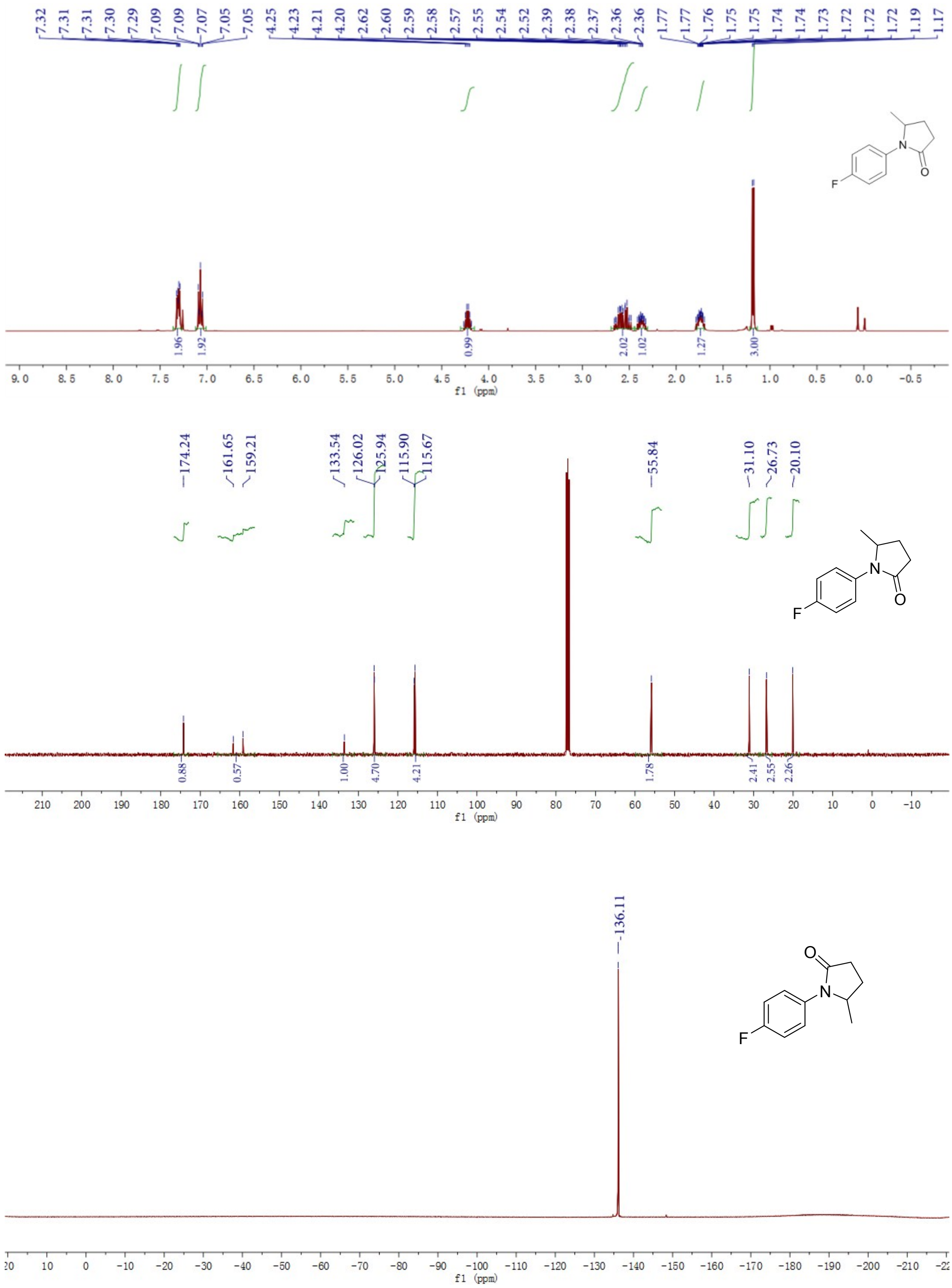
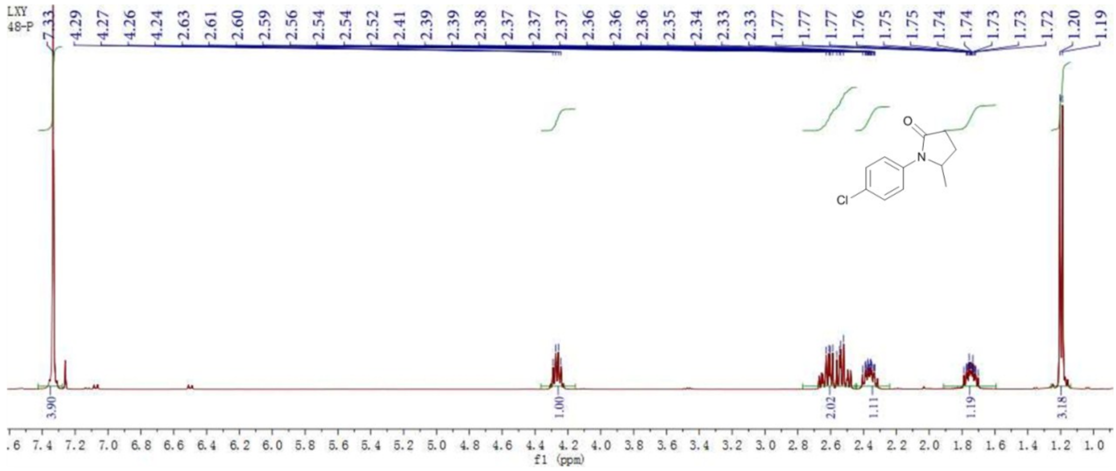


Figure S6 ^{1}H (top), ^{13}C (middle) and ^{19}F (bottom) NMR spectra of 1-(4-fluorophenyl)-5-methylpyrrolidin-2-one



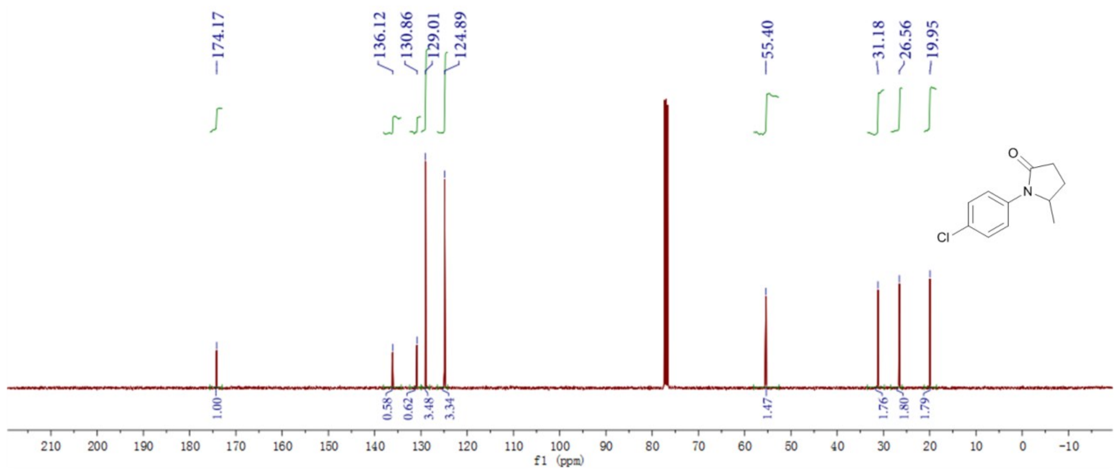
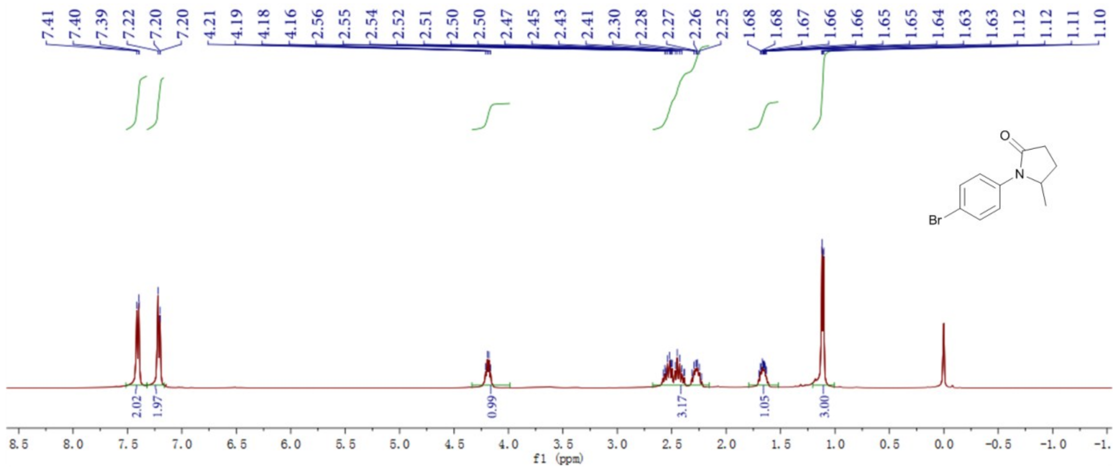


Figure S7 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-(4-chlorophenyl)-5-methylpyrrolidin-2-one



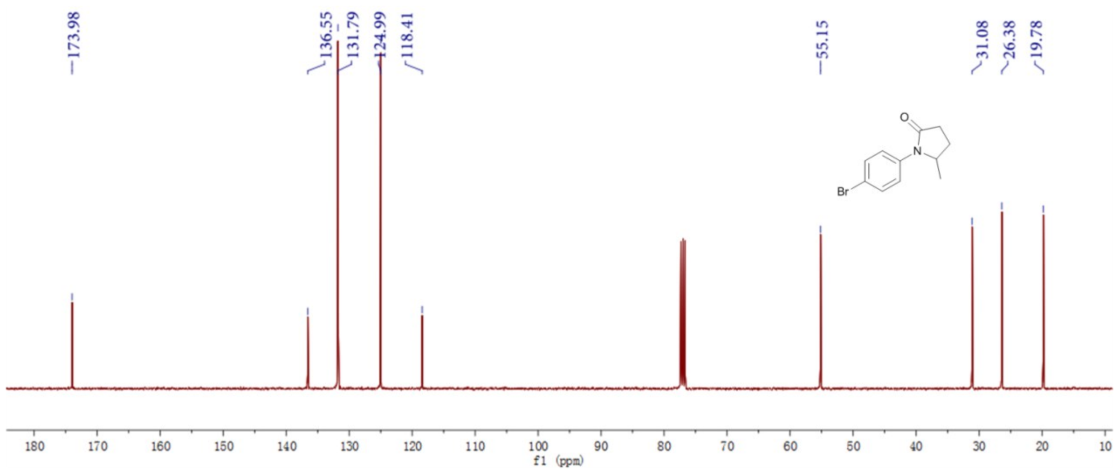
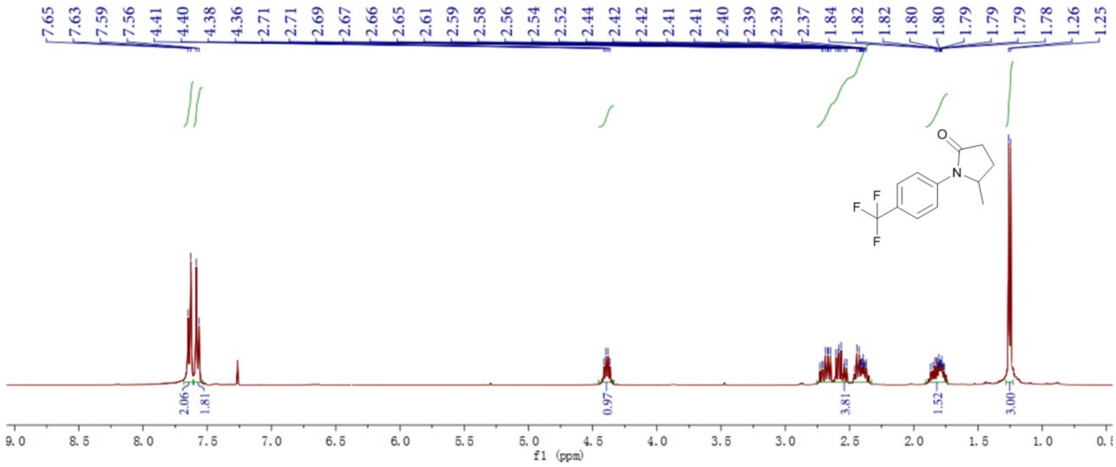
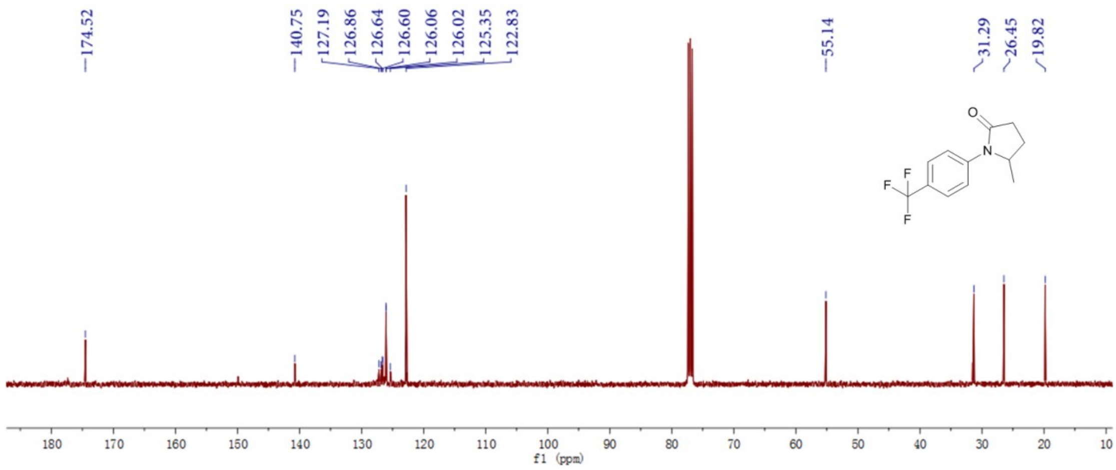


Figure S8 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-(4-bromophenyl)-5-methylpyrrolidin-2-one





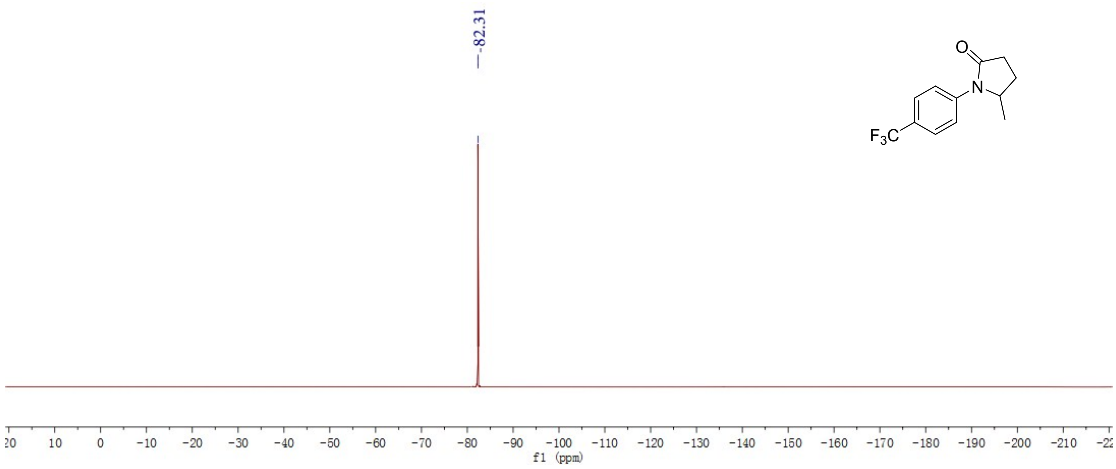
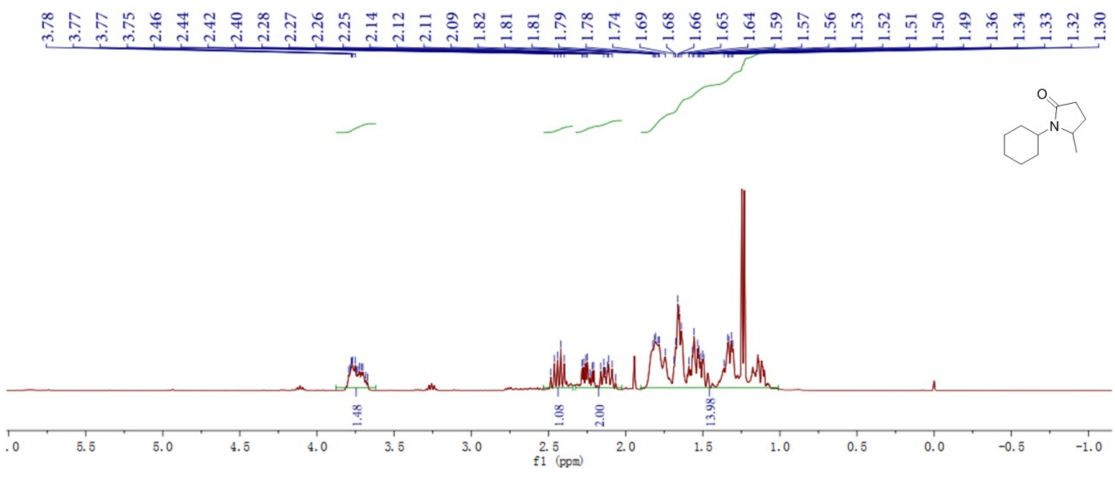


Figure S9 ^{1}H (top), ^{13}C (middle) and ^{19}F (bottom) NMR spectra of 5-methyl-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one



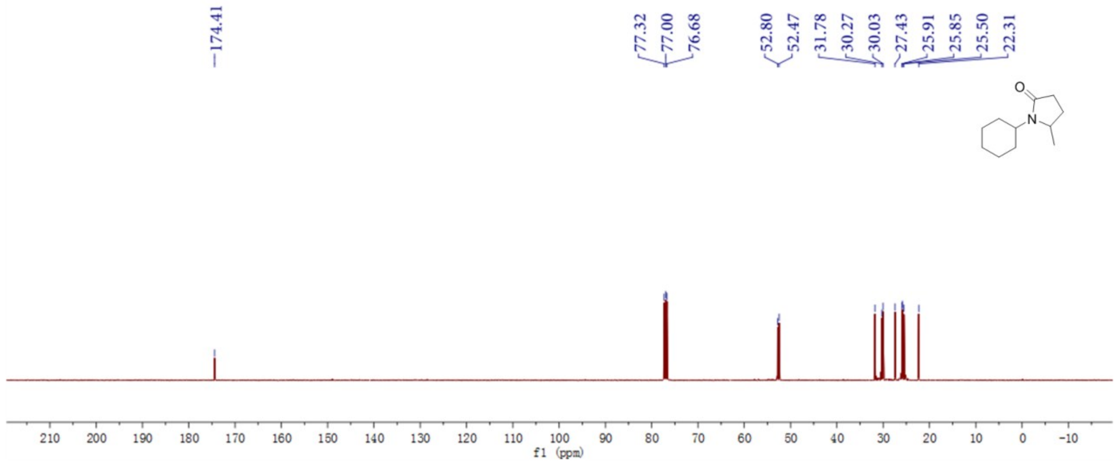
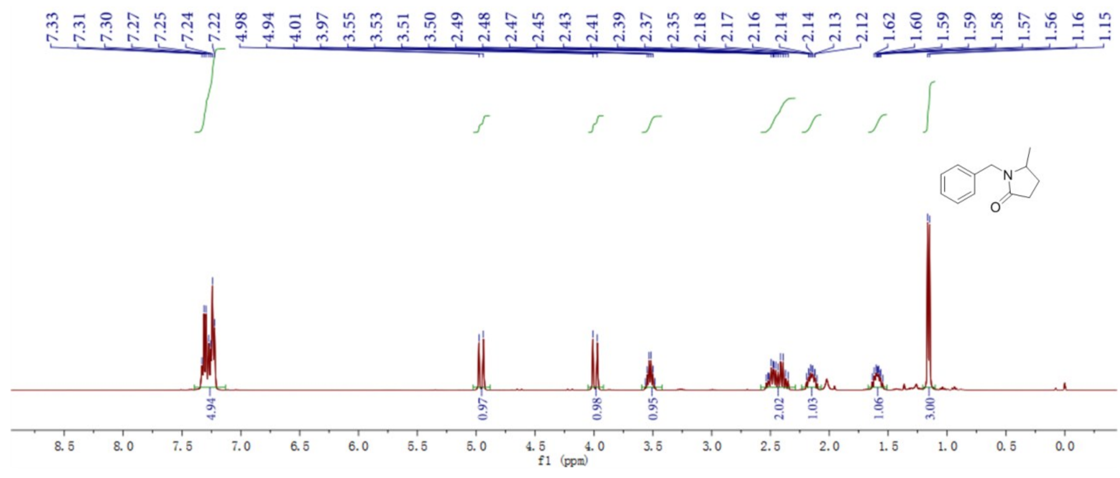


Figure S10 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-cyclohexyl-5-methylpyrrolidin-2-one



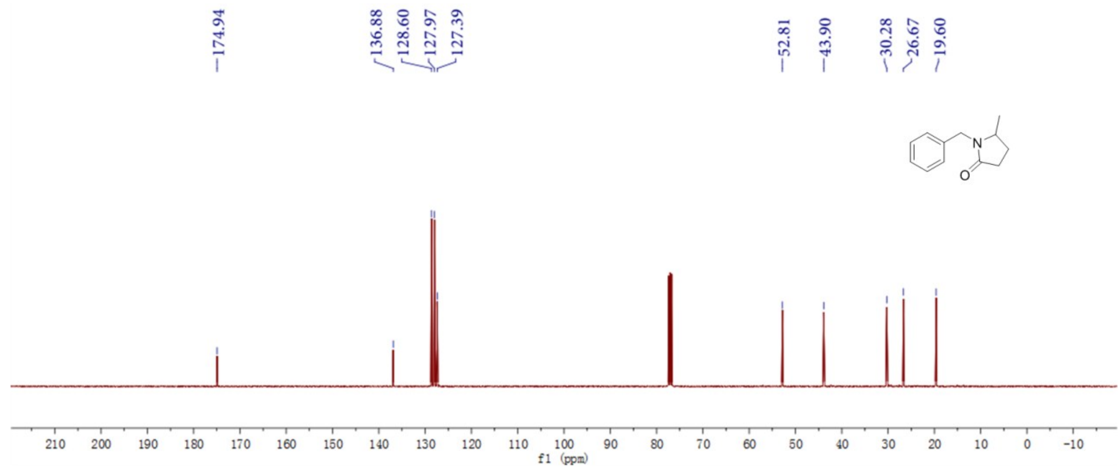
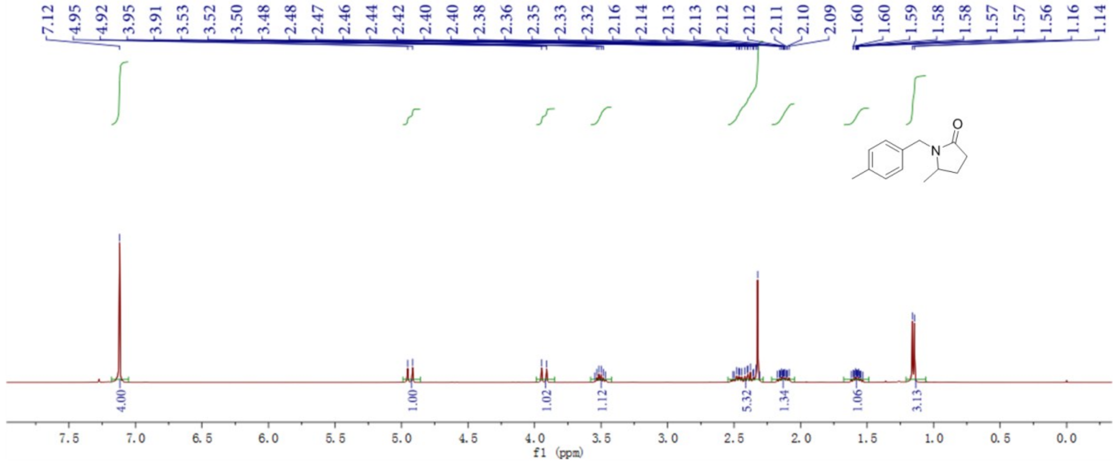


Figure S11 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-benzyl-5-methylpyrrolidin-2-one



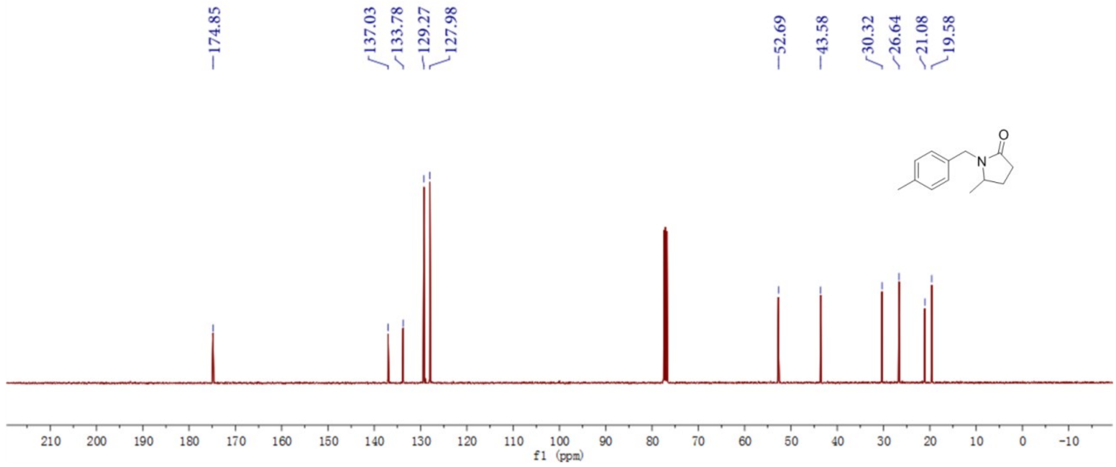
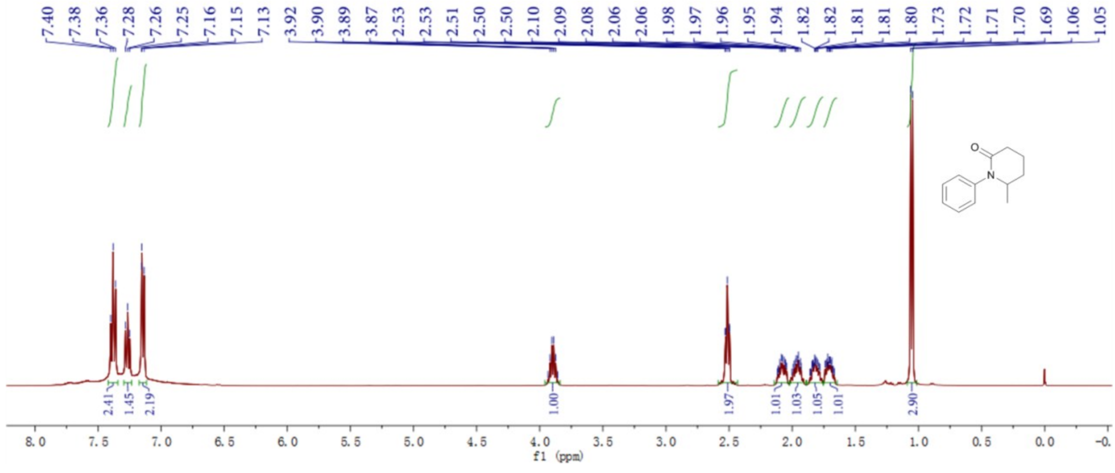


Figure S12 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-methyl-1-(4-methylbenzyl)pyrrolidin-2-one



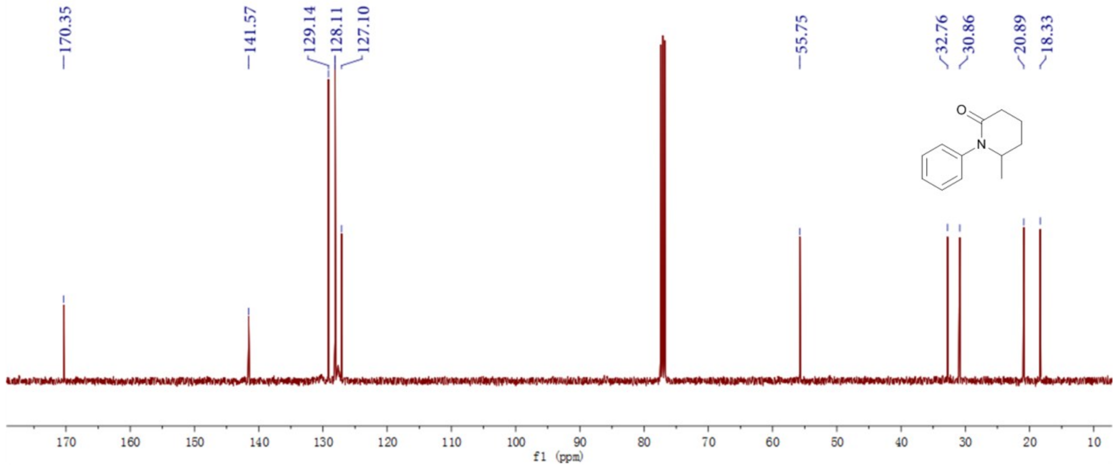


Figure S13 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 6-methyl-1-phenylpiperidin-2-one

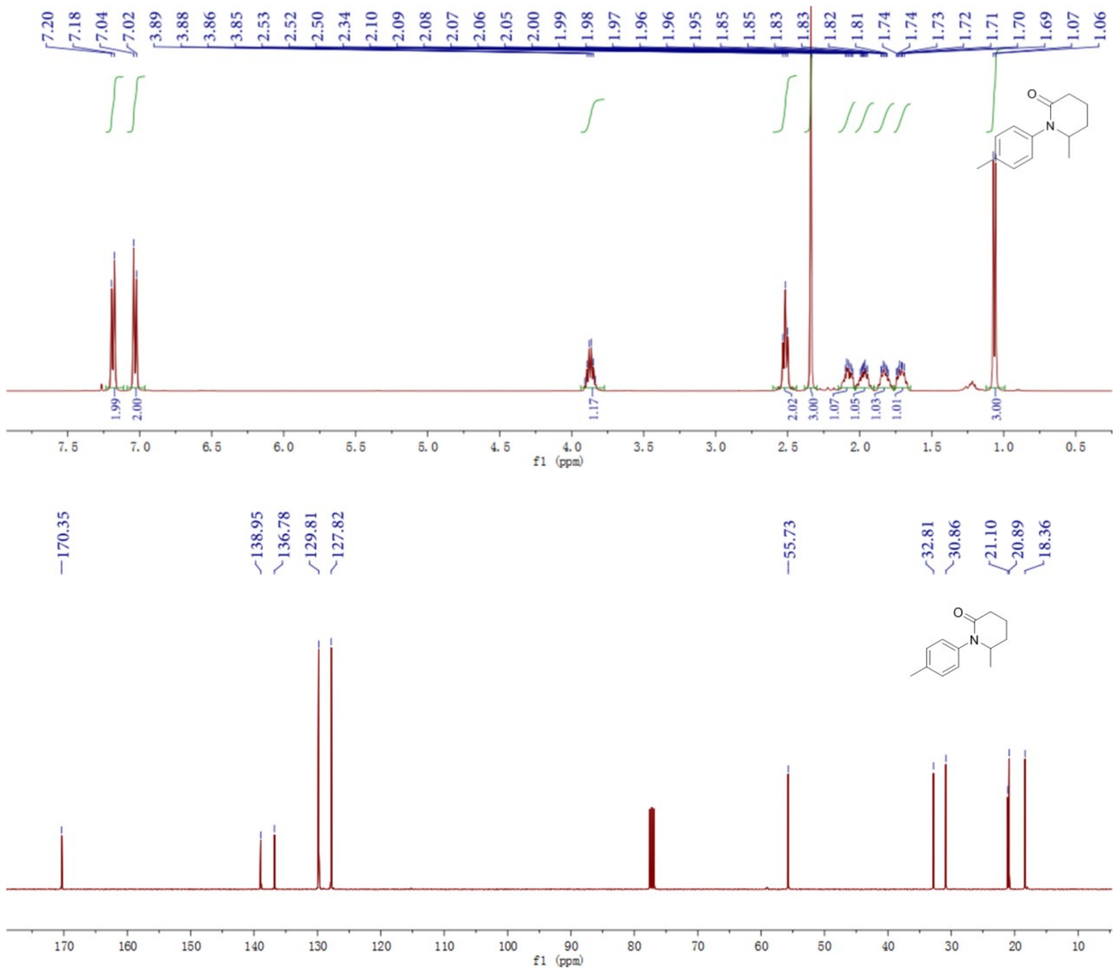
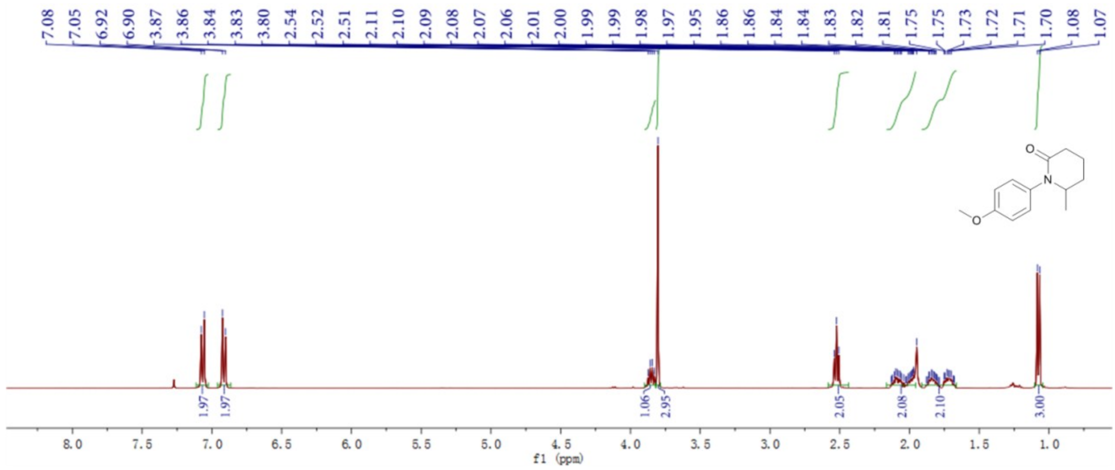


Figure S14 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 6-methyl-1-(p-tolyl)piperidin-2-one



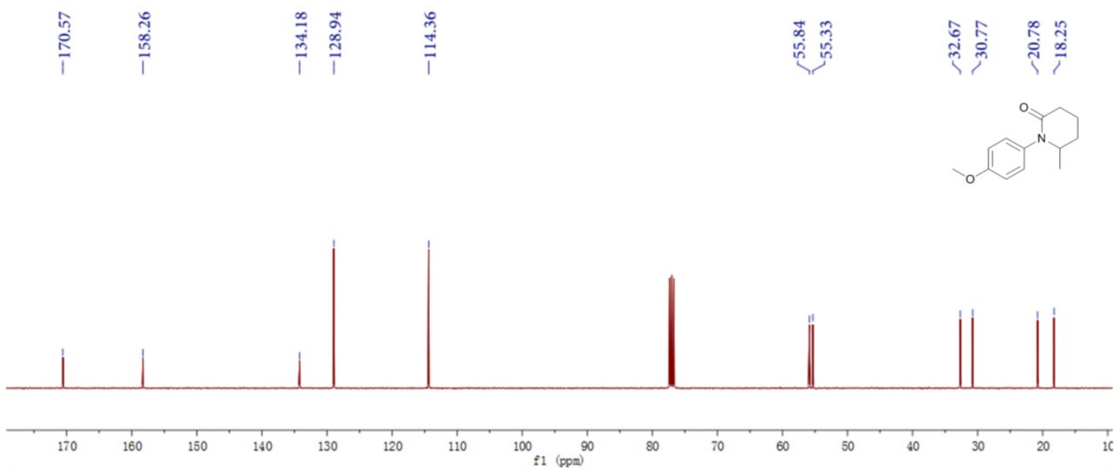


Figure S15 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-(4-methoxyphenyl)-6-methylpiperidin-2-one

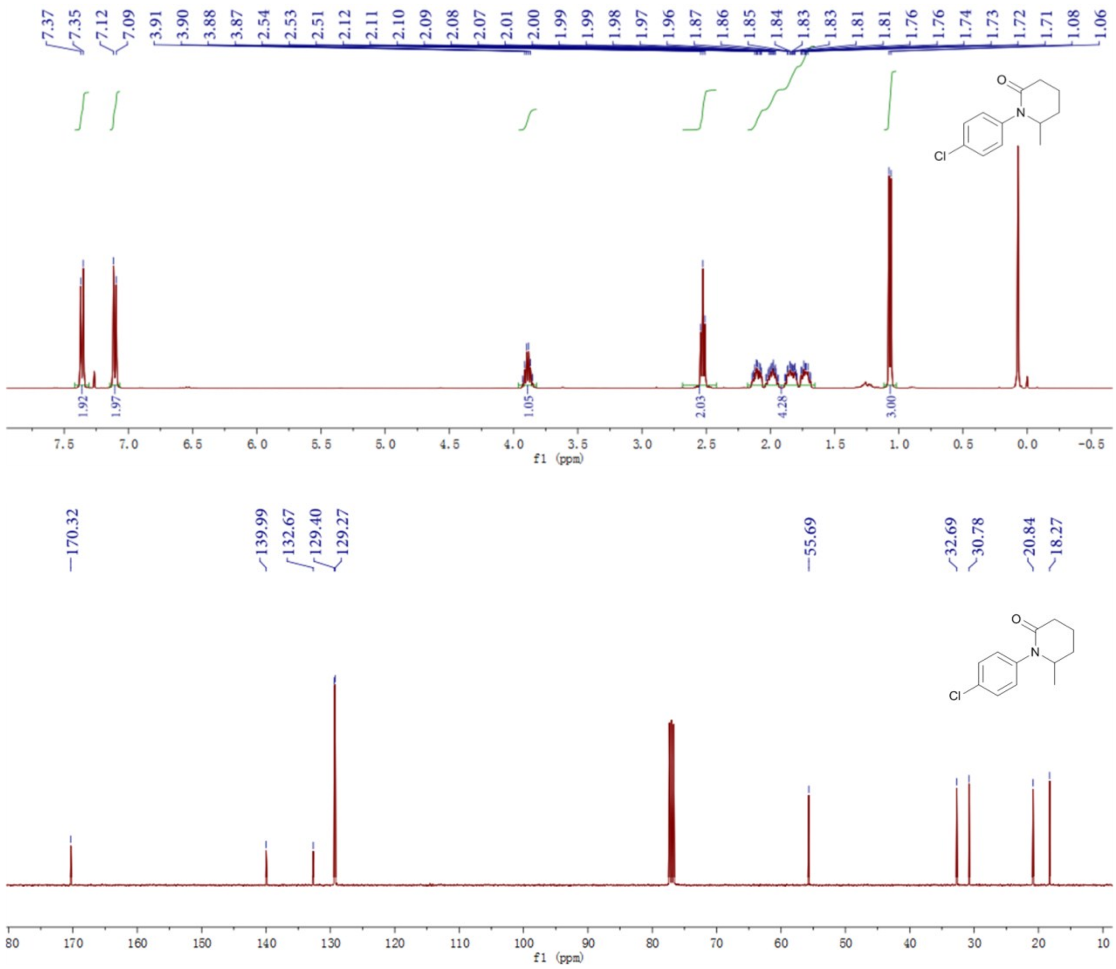


Figure S16 [1]H (top) and [13]C (bottom) NMR spectra of 1-(4-chlorophenyl)-6-methylpiperidin-2-one

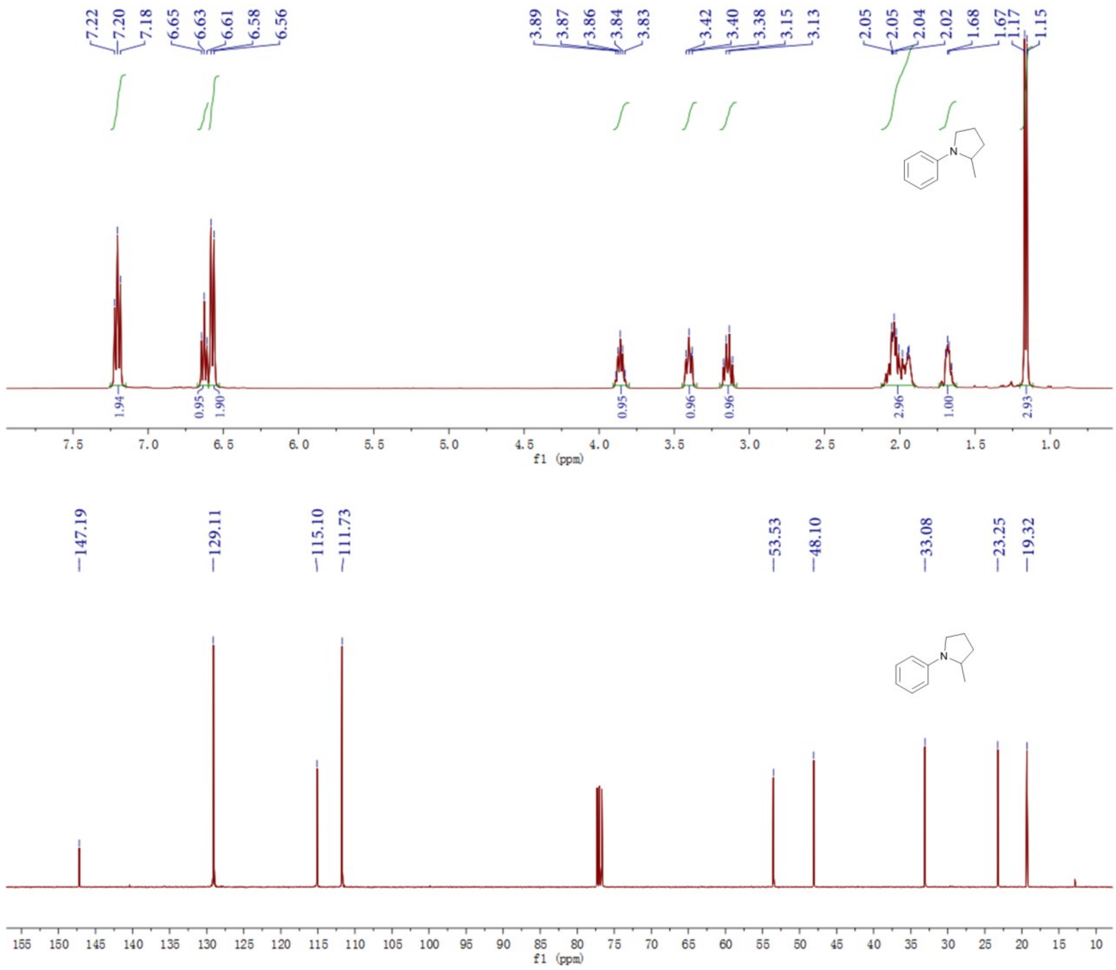
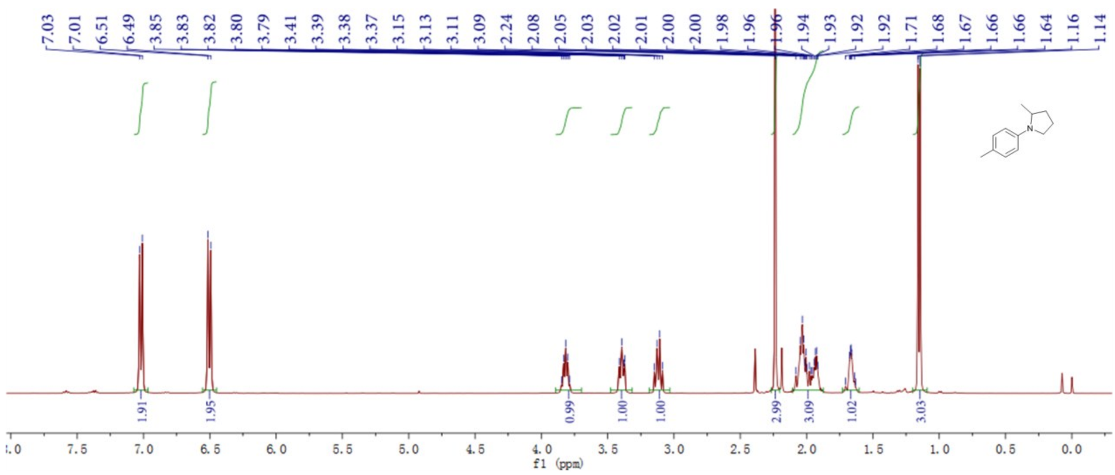


Figure S17 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-methyl-1-phenylpyrrolidine



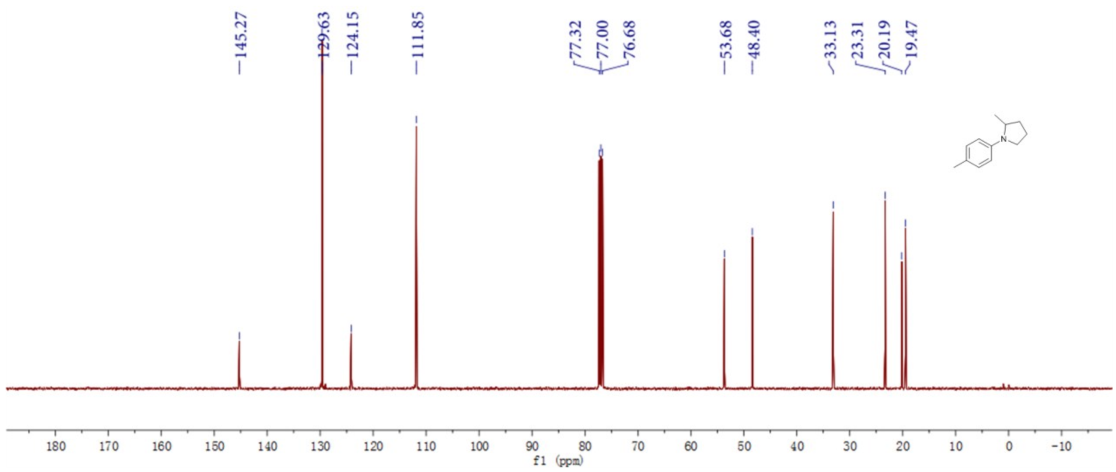


Figure S18 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-methyl-1-(p-tolyl)pyrrolidine

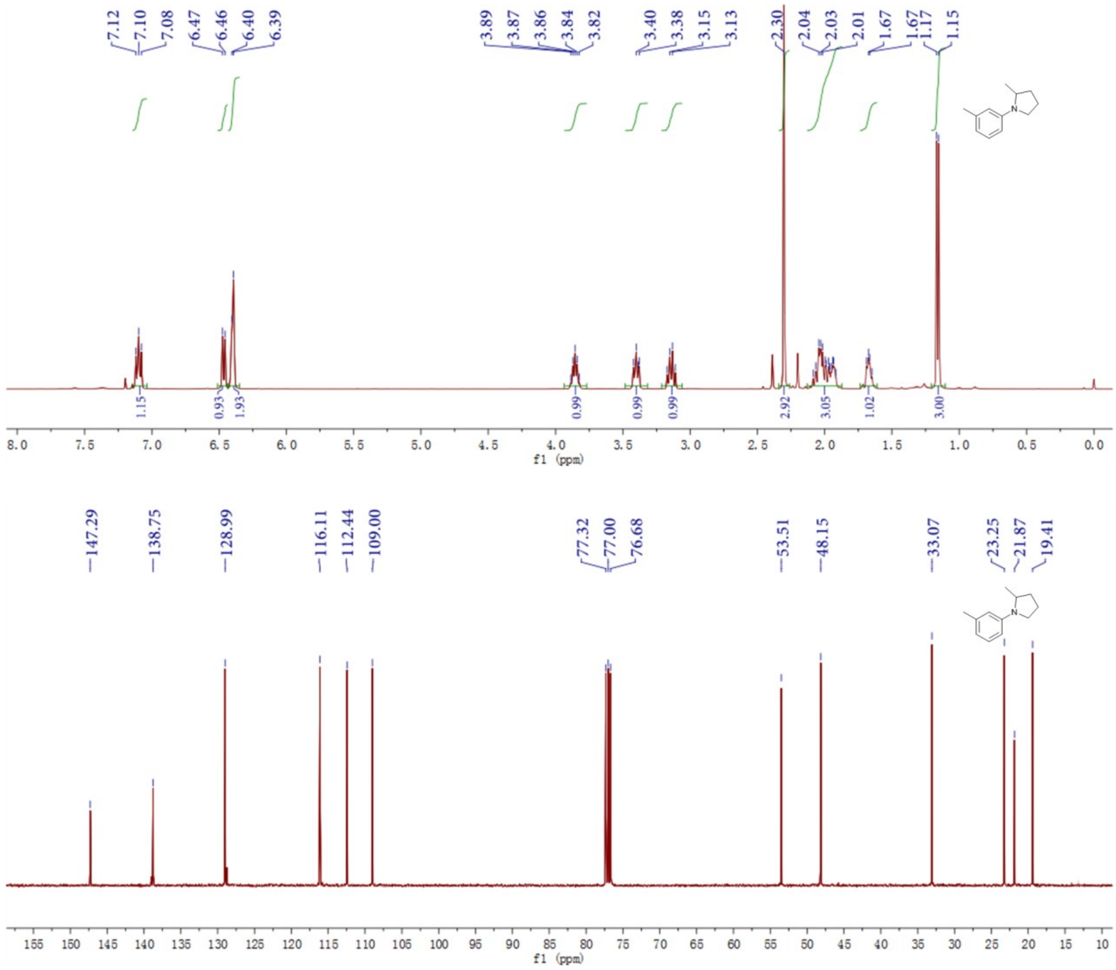
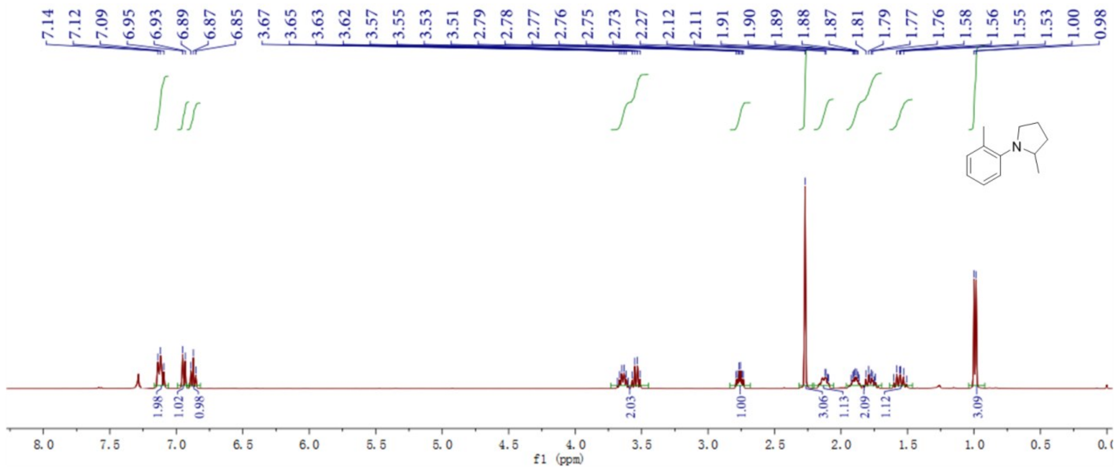


Figure S19 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-methyl-1-(m-tolyl)pyrrolidine



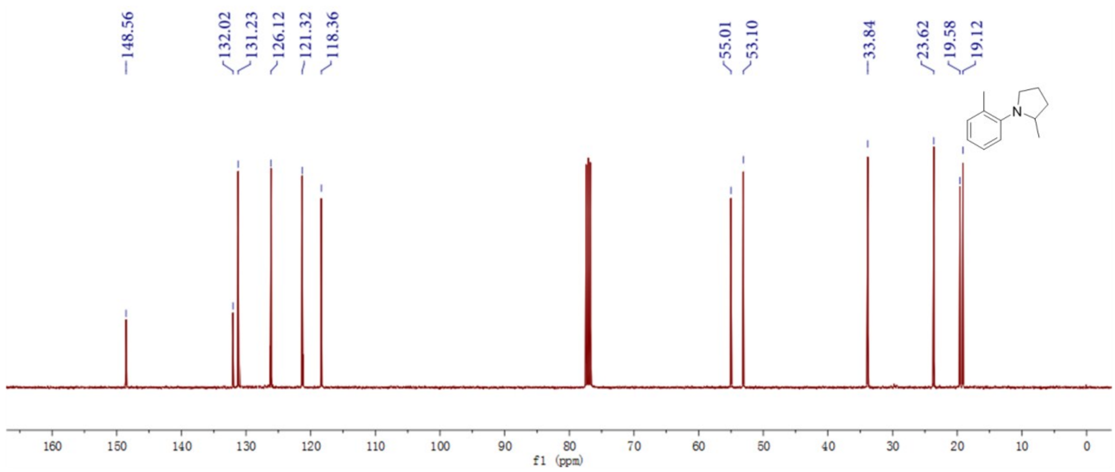
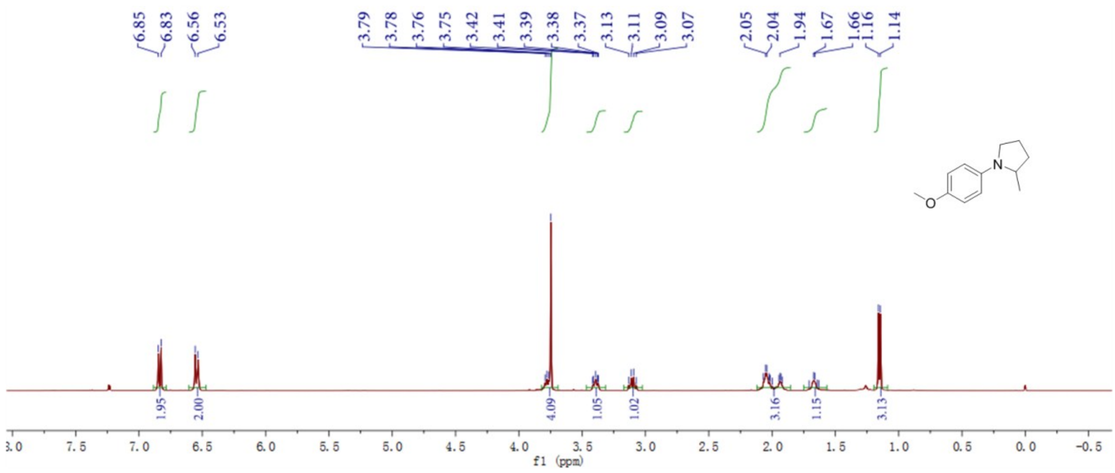


Figure S20 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-methyl-1-(o-tolyl)pyrrolidine



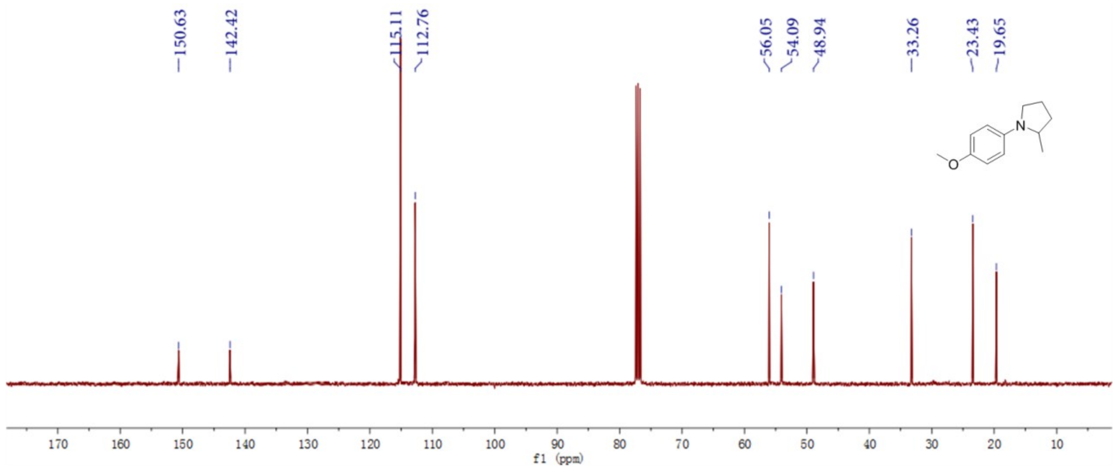


Figure S21 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-(4-methoxyphenyl)-2-methylpyrrolidine

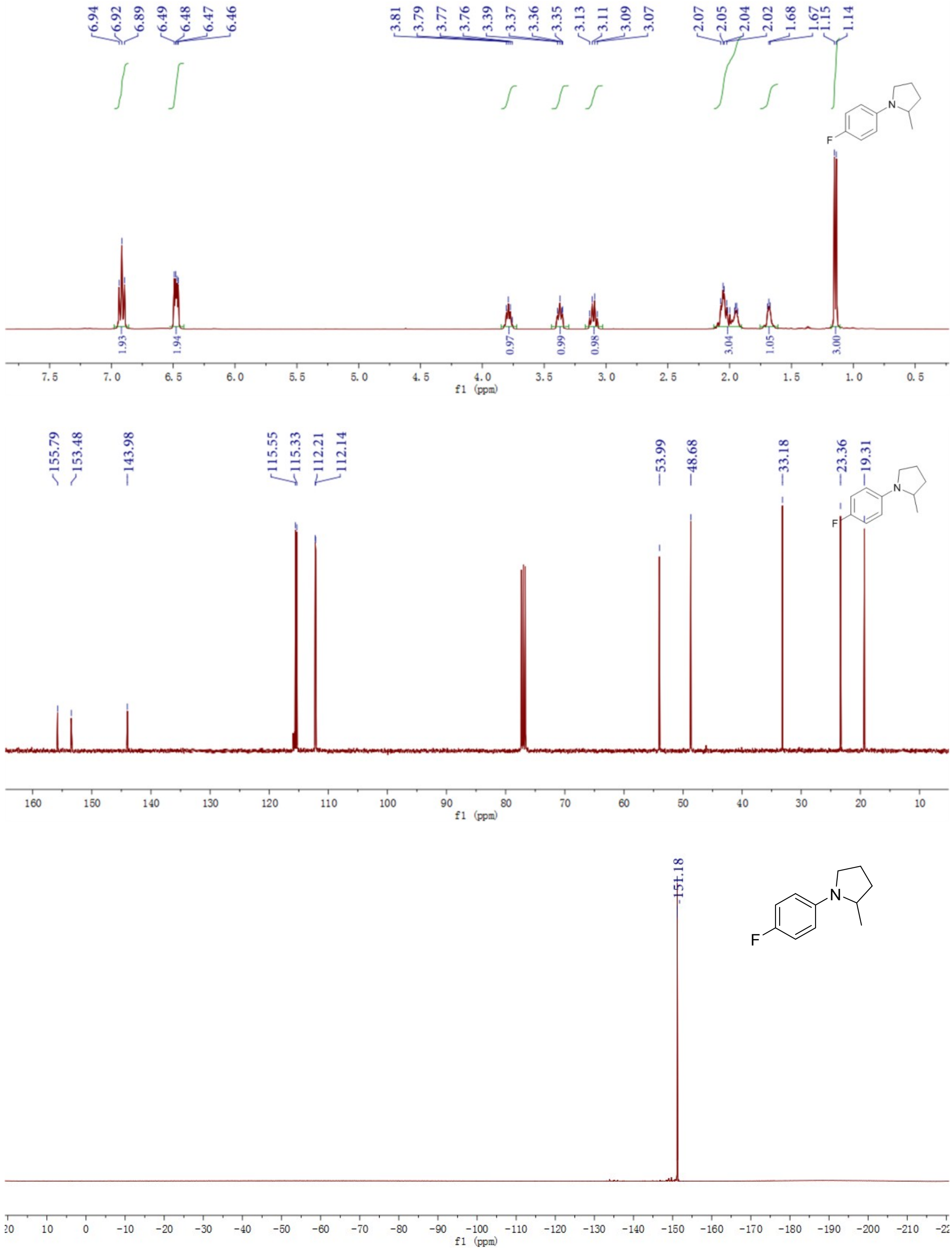
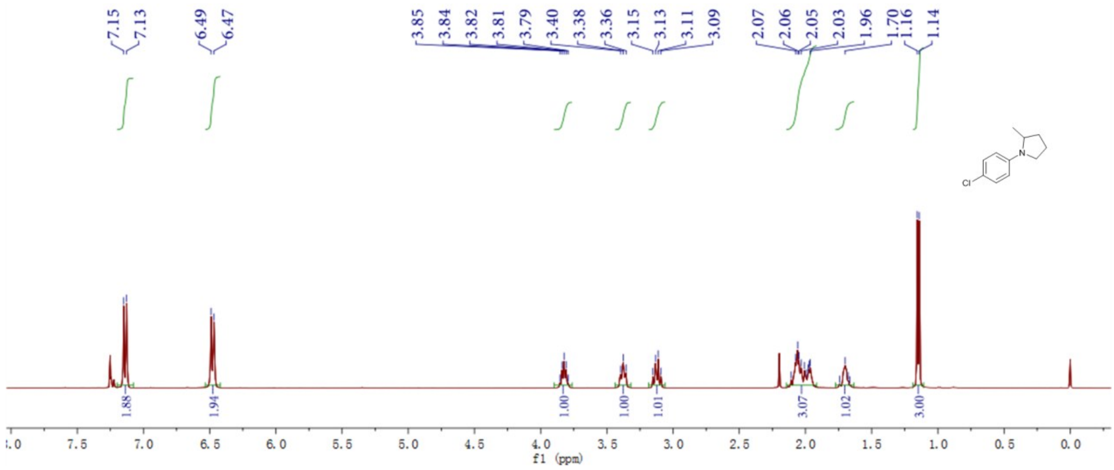


Figure S22 ^{1}H (top), ^{13}C (middle) and ^{19}F (bottom) NMR spectra of 1-(4-fluorophenyl)-2-methylpyrrolidine



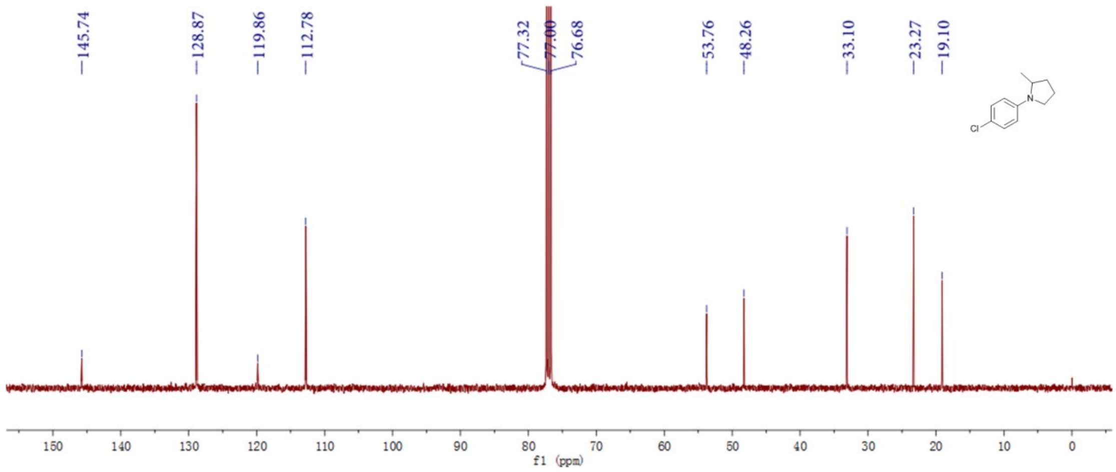
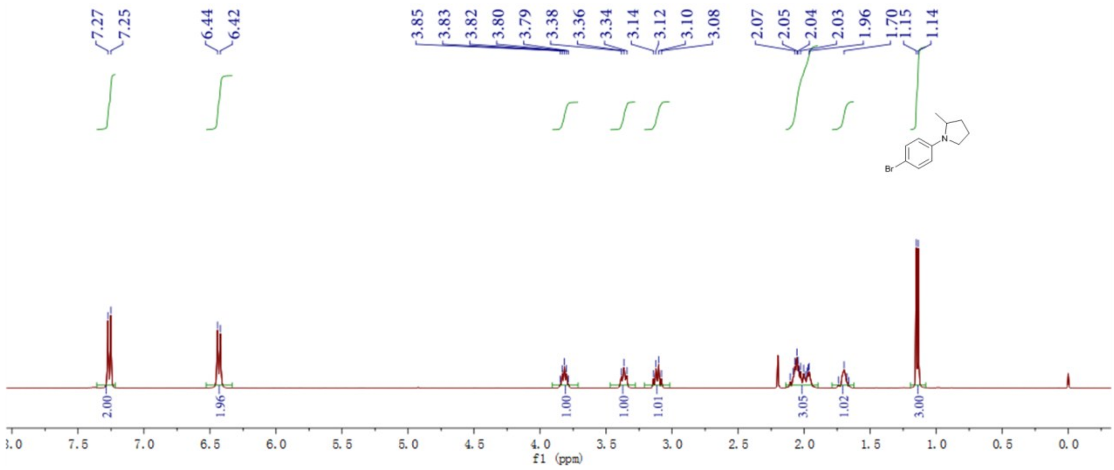


Figure S23 ^{1}H (top) and ^{13}C (bottom) NMR spectra of N-(4-chlorophenyl)-2-methylpyrrolidine



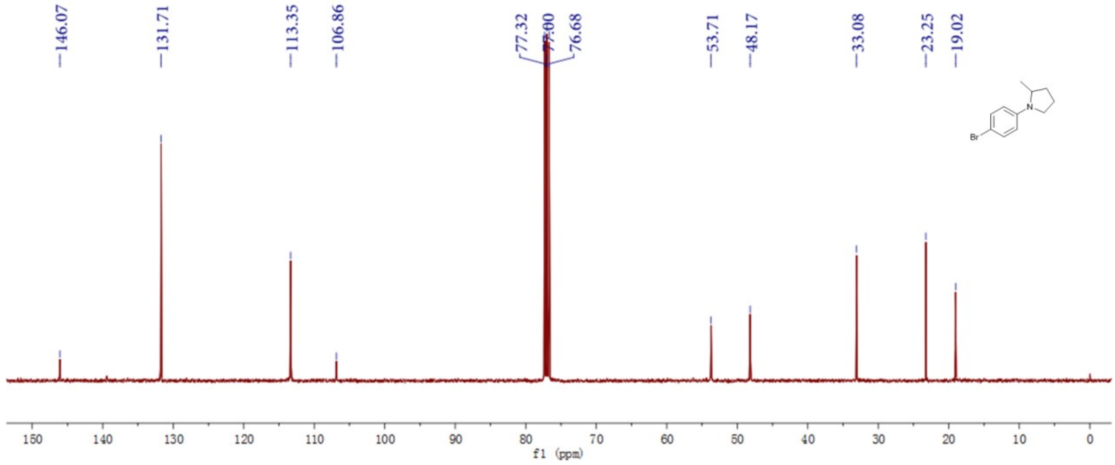
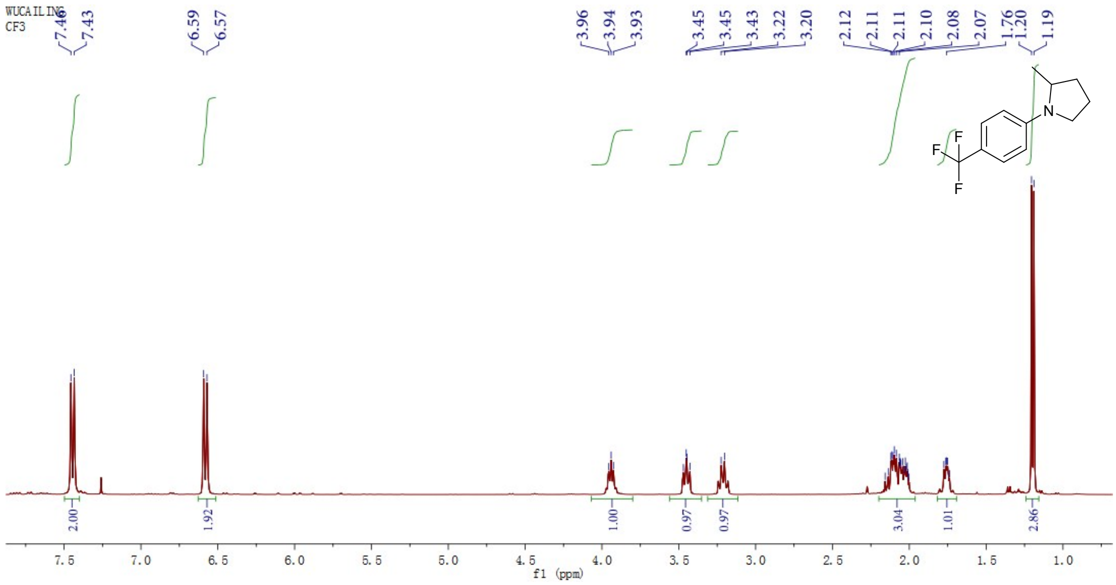
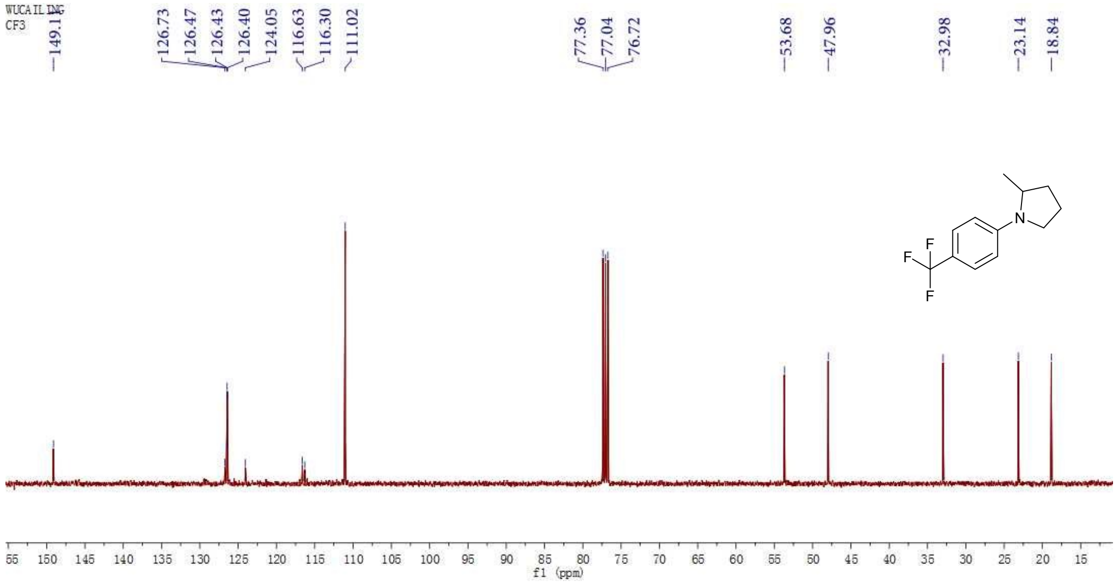


Figure S24 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-(4-bromophenyl)-2-methylpyrrolidine





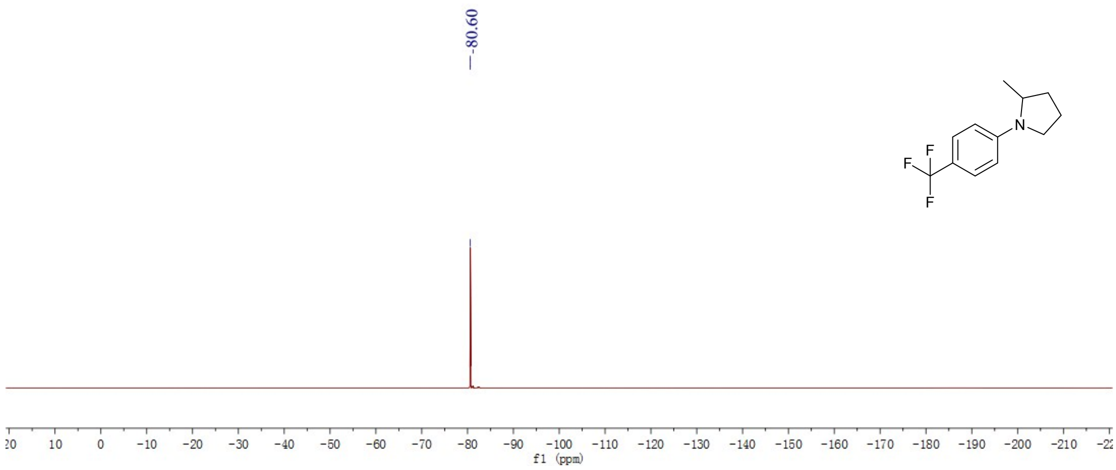
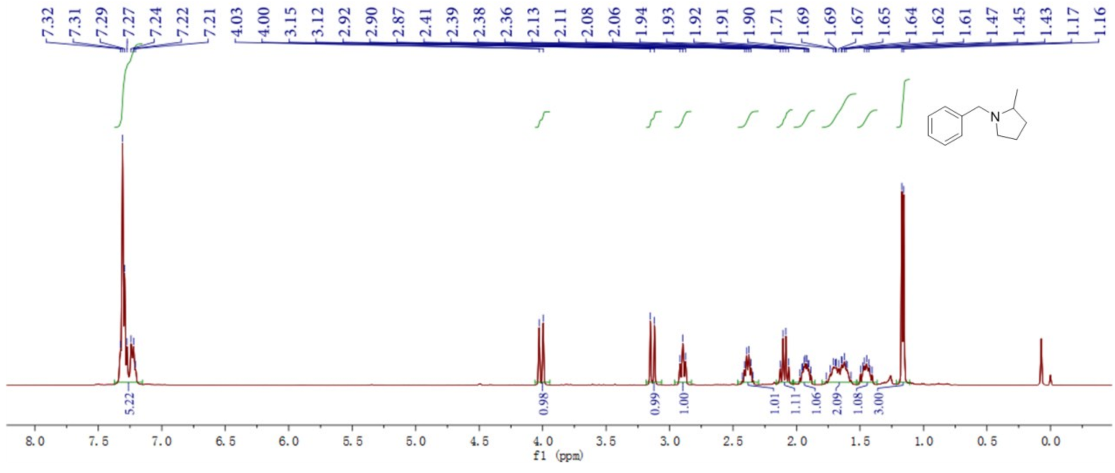


Figure S25 ^{1}H (top), ^{13}C(middle) and ^{19}F (bottom) NMR spectra of 2-methyl-1-(4-(trifluoromethyl)phenyl)pyrrolidine



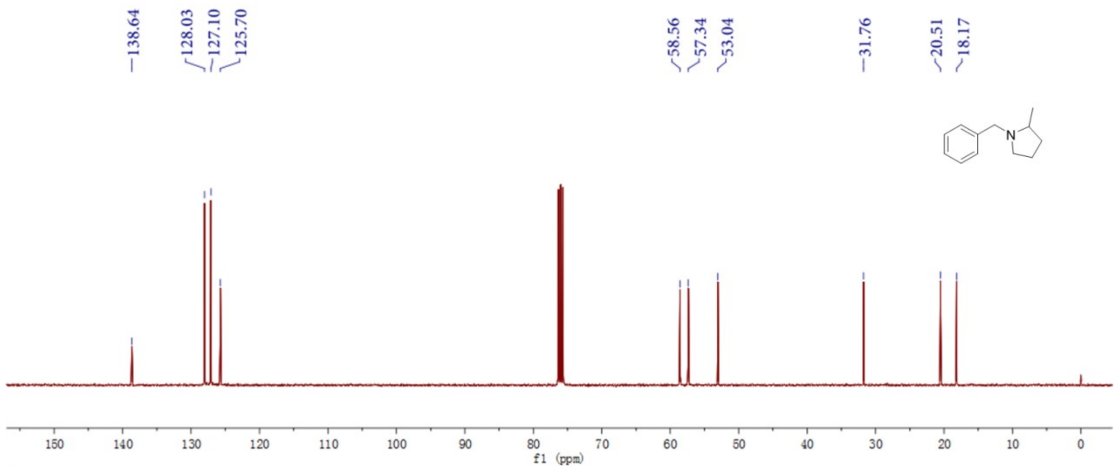


Figure S26 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-benzyl-2-methylpyrrolidine

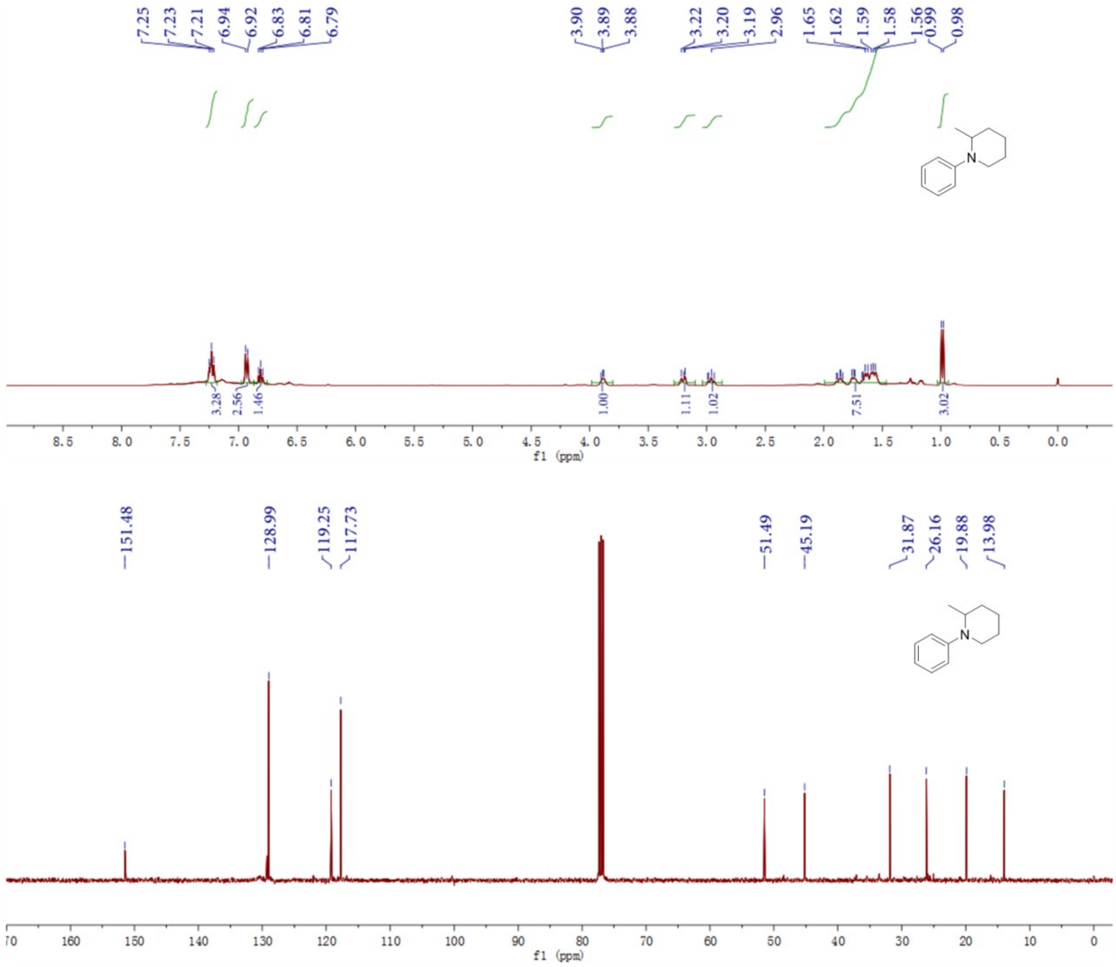


Figure S27 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-methyl-1-phenylpiperidine