

**Electrochemical Direct α -Amidation and α -Pyrazolation of
N-Alkoxy- and *N*-aryloxycarbonyl Pyrrolidines**

Supporting Information

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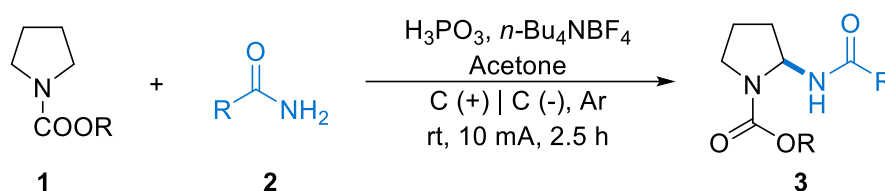
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1) General Information

Chemicals utilized in this work were directly purchased from commercial suppliers, and unless noted, without further purification before the usage. Silica gel plates (GF254, coating thickness 0.2-0.25 mm) were employed for thin-layer chromatography (TLC), and 200-300 mesh silica gel or neutral alumina was used for flash column chromatography. ^1H , ^{13}C , and ^{19}F NMR data was obtained on Bruker Ultrashield 400 and Bruker Ascend 400 NMR spectrometers. Chemical shifts were reported in ppm with tetramethylsilane as an internal standard, and coupling constants (J) in Hz. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T).

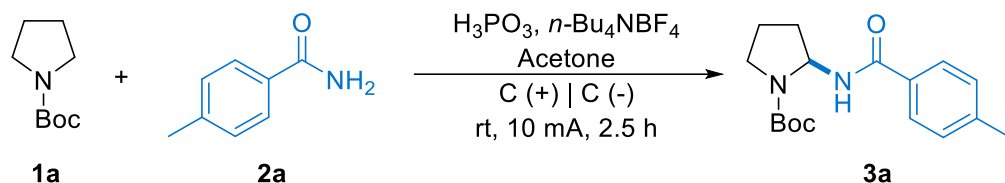
2) General Procedures for the electrolysis



1 (0.5 mmol, 1 eq.), **2** (1 mmol, 2 eq.), *n*-Bu₄NBF₄ (0.5 mmol, 1 eq.), H₃PO₃ (0.5 mmol, 1 eq.) and acetone (5 mL) were subsequently added into a 25 mL undivided cell. Graphite plate electrodes (1 cm×1 cm×2 mm, 1 cm distance) were inserted into the cell, and the electrolysis was carried out at room temperature using a constant current of 10 mA for 2.5 hours under argon atmosphere.

The solvent in the system was removed under reduced pressure, and the crude product was purified by flash column chromatography with ethyl acetate/petroleum ether as the eluent.

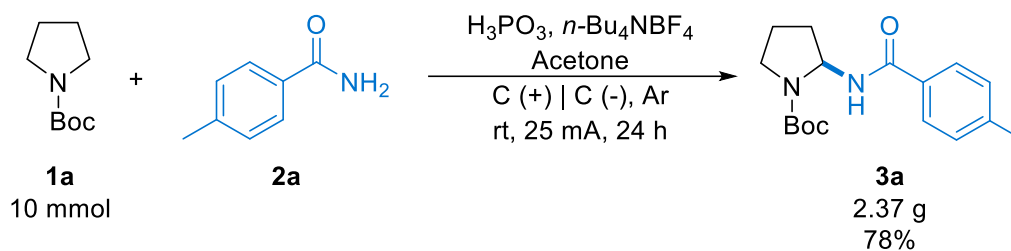
3) Optimization of reaction conditions



Entry	Variation from the standard condition	Yield (%)
1	None	91 (90 ^b)
2	No H ₃ PO ₃	67
3	CH ₃ COOH instead of H ₃ PO ₃	82
4	CF ₃ COOH instead of H ₃ PO ₃	84
5	H ₃ PO ₄ instead of H ₃ PO ₃	81
6	H ₃ PO ₃ (0.25 mmol, 0.5 eq)	79
7	Pt plate as the anode	13
8	Ni plate as the cathode	44
9	Pt plate as the cathode	53
10	Pt plate as both the anode and cathode	11
11	<i>n</i> -Bu ₄ NClO ₄ as the electrolyte	87
12	<i>n</i> -Bu ₄ NPF ₆ as the electrolyte	90
13	<i>n</i> -Bu ₄ NOTs as the electrolyte	43
14	<i>n</i> -Bu ₄ PBF ₄ as the electrolyte	86
15	Me ₄ NBF ₄ as the electrolyte	85
16	LiClO ₄ as the electrolyte	trace
17	MeCN as the solvent	90
18	MeNO ₂ as the solvent	61
19	DCM as the solvent	7
20	DCE as the solvent	trace
21	In open air	40
22	No electric current and electrolyte	0

^aStandard condition: undivided cell, graphite plate as both the anode and the cathode, **1a** (0.5 mmol, 1 eq), **2a** (1 mmol, 2 eq), H₃PO₃ (0.5 mmol, 1 eq), *n*-Bu₄NBF₄ (0.5 mmol, 1 eq), 5 mL of acetone, 10 mA, under an Ar atmosphere stirring for 2.5 h. Yields were determined by ¹H NMR using dibromomethane as the internal standard. ^bIsolated Yield.

4) Gram-scale synthesis

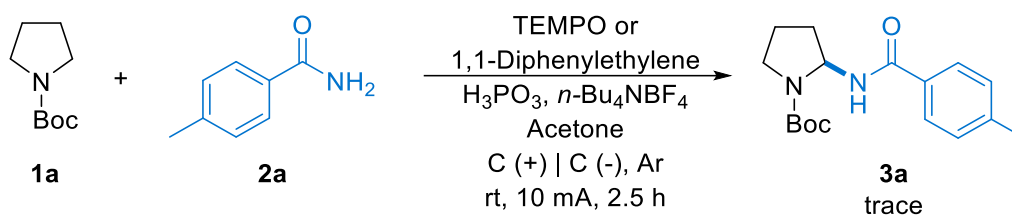


1a (10 mmol, 1 eq), **2a** (20 mmol, 2 eq), *n*-Bu₄NBF₄ (10 mmol, 1 eq.), H₃PO₃ (10 mmol, 1 eq.) and acetone (50 mL) were subsequently added into a 100 mL undivided cell. Graphite plate electrodes (3 cm×3 cm×2 mm, 3 cm distance) were inserted into the cell, and the electrolysis was carried out at room temperature with constant current of 25 mA for 24 hours under argon atmosphere.

The solvent in the system was removed under reduced pressure, and the crude product was purified by flash column chromatography with ethyl acetate/petroleum ether as the eluent.

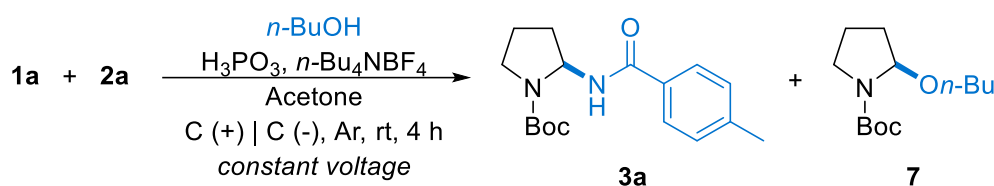
5) Control experiments and mechanistic studies

A) Radical-trapping experiment



1 (0.5 mmol, 1 eq.), 2 (1 mmol, 2 eq.), TEMPO or 1,1-diphenylethylene (1 mmol, 2 eq.), *n*-Bu₄NBF₄ (0.5 mmol, 1 eq.), H₃PO₃ (0.5 mmol, 1 eq.) and acetone (5 mL) were subsequently added into a 25 mL undivided cell. Graphite plate electrodes (1 cm×1 cm×2 mm, 1 cm distance) were inserted into the cell, and the electrolysis was carried out at room temperature with constant current of 10 mA for 2.5 hours under argon atmosphere.

B) Competition experiment



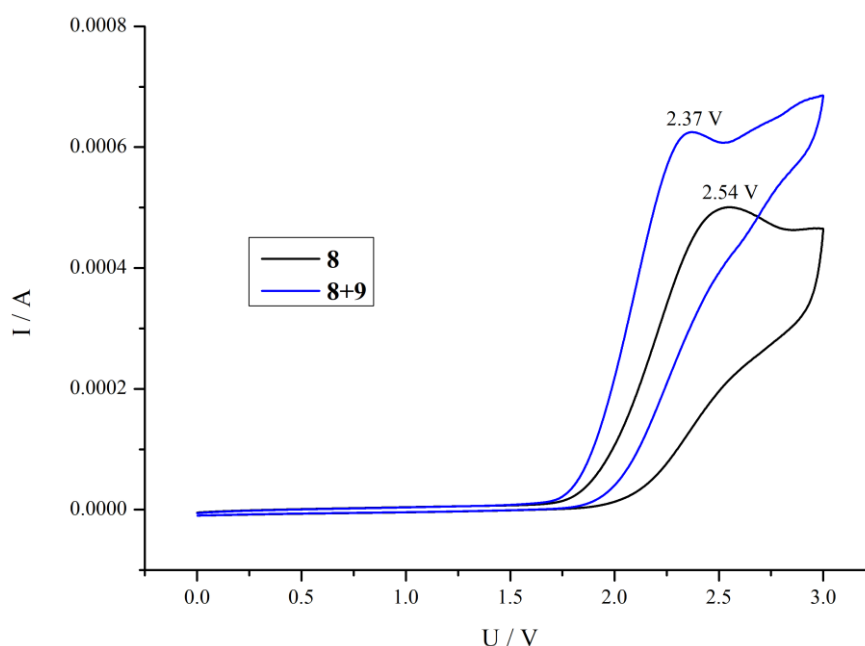
1 (0.5 mmol, 1 eq.), 2 (1 mmol, 2 eq.), *n*-butanol (1 mmol, 2 eq.), *n*-Bu₄NBF₄ (0.5 mmol, 1 eq.), H₃PO₃ (0.5 mmol, 1 eq.) and acetone (5 mL) were subsequently added into a 25 mL undivided cell. Graphite plate electrodes (1 cm×1 cm×2 mm, 1 cm distance) were inserted into the cell, and the electrolysis was carried out at room temperature with constant voltage for 4 hours under argon atmosphere. As shown in the chart below, the yield of 3a increased along with the voltage. However, the side product 7 also started to generate when the voltage reached 3.5 V. These results shown that the product 3a needs lower voltage to generate comparing with 7.

Entry	U / V	Yield of 3a (%)	Yield of 7 (%)
1	2.0	9	trace
2	2.5	17	trace
3	3.0	39	trace
4	3.5	52	4
5	4.0	72	12
6	I = 10 mA	60	12

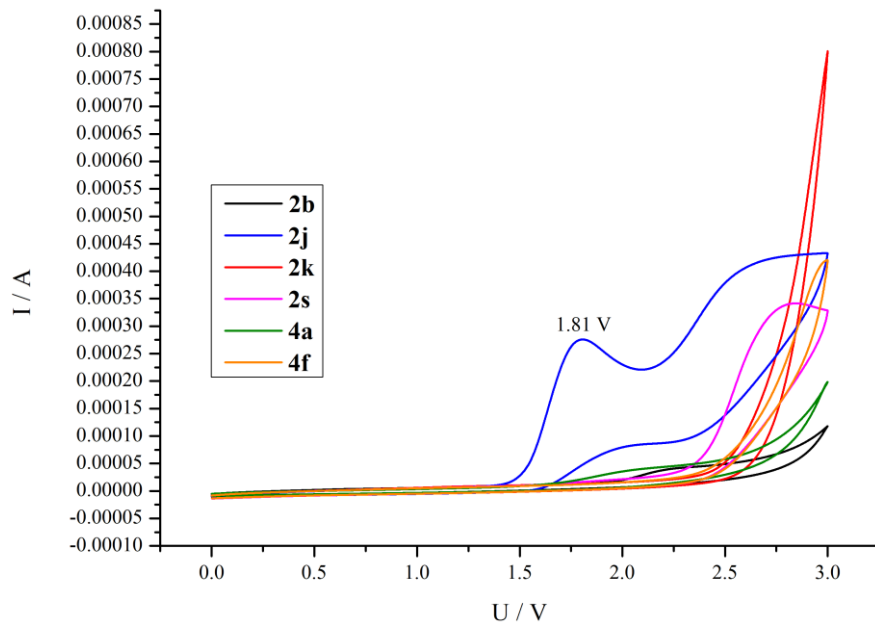
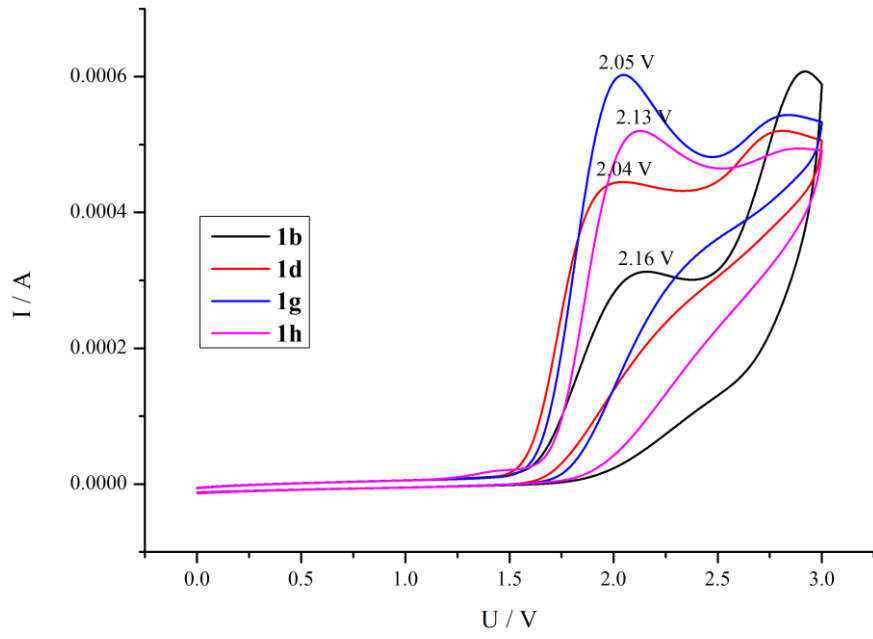
C) Cyclic Voltammetry (CV) Experiment

Cyclic voltammetry was performed in a three-electrode cell connected to a Schlenk line under air at room temperature. The working electrode was a glassy carbon electrode, the counter electrode was a platinum wire. The reference was an Ag/AgNO₃ electrode submerged in saturated aqueous AgNO₃ solution, and separated from reaction by a salt bridge. 10 mL of CH₃CN containing 0.1 M *n*-Bu₄NPF₆ were poured into the electrochemical cell in all experiments, and the concentration of all tested compounds was 2 mmol/L. The scan rate is 0.1 V/s, ranging from 0 V to 3 V.

Cyclic voltammetry experiment revealed that the oxidation peak potential of 1-methylsulfonylpyrrolidine (**8**) was 2.54 V. When methyl sulfonamide (**9**) was added, the oxidation peak potential was reduced to 2.37 V. The graph of the cyclic voltammetry experiment is demonstrated as below.

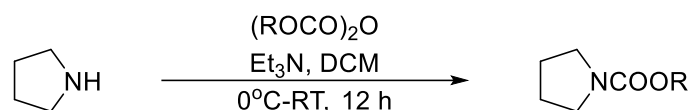


CV curves of selected pyrrolidines, amides and pyrazoles was additionally estimated, and illustrated as below. While most of the amides and pyrazoles have no or weak oxidation peaks, **2j** (4-MeOPhCONH₂) have a significant oxidation peak at 1.81 V.



6) Synthesis of the substrates

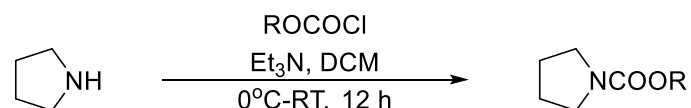
Procedure for the preparation of N-alkoxy/aryloxy carbonyl pyrrolidines (**1c**, **1d**)



Pyrrolidine (1 eq, 20 mmol), Et₃N (1.2 eq) and DCM (40 mL) were added to a dry 100 mL flask and stirred at 0°C. (ROCO)₂O (1.2 eq) was added dropwise, and then the mixture was stirred for 12 h at room temperature.

The mixture was washed with brine, the organic phase dried with anhydrous Na₂SO₄ and concentrated in *vacuo*. The crude product was purified with column chromatography.

Procedure for the preparation of N-alkoxy/aryloxy carbonyl pyrrolidines (**1e-1h**)

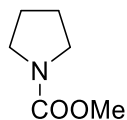


Pyrrolidine (1 eq, 20 mmol), Et₃N (1.2 eq) and DCM (40 mL) were added to a dry 100 mL flask and stirred at 0°C. ROCOCl (1.2 eq) was added dropwise, and then the mixture was stirred for 12 h at room temperature.

The mixture was washed with brine, the organic phase dried with anhydrous Na₂SO₄ and concentrated in *vacuo*. The crude product was purified with column chromatography.

7) Characterization data for the substrates and products

Methyl pyrrolidine-1-carboxylate (**1c**)^[1]

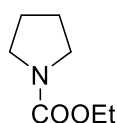


Colorless Oil. Yield 90 %.

¹H NMR (400 MHz, CDCl₃) δ 3.70 (s, 3H), 3.36 (s, 4H), 1.86 (t, *J* = 6.5 Hz, 4H).

The spectral data obtained were identical with those reported in literature.

Ethyl pyrrolidine-1-carboxylate (**1d**)^[1]

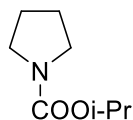


Colorless Oil. Yield 98 %.

¹H NMR (400 MHz, CDCl₃) δ 4.13 (q, *J* = 7.2 Hz, 2H), 3.36 (s, 4H), 1.86 (t, *J* = 6.5 Hz, 4H), 1.26 (t, *J* = 7.2 Hz, 3H).

The spectral data obtained were identical with those reported in literature.

Isopropyl pyrrolidine-1-carboxylate (**1e**)^[1]

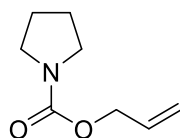


Colorless Oil. Yield 99 %.

¹H NMR (400 MHz, CDCl₃) δ 4.92 (hept, *J* = 6.1 Hz, 1H), 3.35 (s, 4H), 1.85 (t, *J* = 6.7 Hz, 4H), 1.24 (d, *J* = 6.3 Hz, 6H).

The spectral data obtained were identical with those reported in literature.

Allyl pyrrolidine-1-carboxylate (**1f**)^[2]

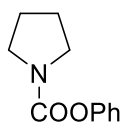


Colorless Oil. Yield 97 %.

¹H NMR (400 MHz, CDCl₃) δ 5.95 (ddd, *J* = 22.6, 10.8, 5.5 Hz, 1H), 5.31 (d, *J* = 17.3 Hz, 1H), 5.20 (d, *J* = 10.5 Hz, 1H), 4.59 (d, *J* = 5.3 Hz, 2H), 3.39 (s, 4H), 1.87 (s, 4H).

The spectral data obtained were identical with those reported in literature.

Phenyl pyrrolidine-1-carboxylate (**1h**)^[3]

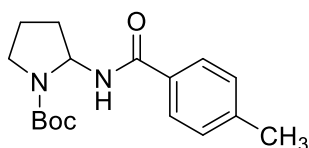


Colorless Oil. Yield 98 %.

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.30 (m, 2H), 7.22 – 7.09 (m, 3H), 3.52 (dt, *J* = 33.1, 6.3 Hz, 4H), 1.94 (td, *J* = 12.7, 6.7 Hz, 4H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**3a**)



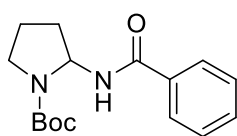
White Solid. mp 123–128 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 6.52 (d, *J* = 6.5 Hz, 1H), 5.85 (br s, 1H), 3.57 – 3.48 (m, 1H), 3.37 – 3.27 (m, 1H), 2.38 (s, 3H), 2.24 – 1.83 (m, 4H), 1.40 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 166.4, 154.2, 141.8, 131.7, 129.1, 126.9, 80.1, 64.6, 46.1, 33.9, 28.4, 22.5, 21.4.

HRMS (ESI) *m/z* calcd for C₁₇H₂₄N₂NaO₃⁺ (M+Na⁺): 327.1679, found: 327.1677.

tert-Butyl 2-benzamidopyrrolidine-1-carboxylate (**3b**)^[4]

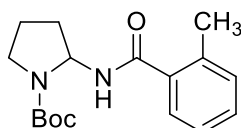


White Solid. mp 163 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.52 – 7.32 (m, 3H), 6.73 (s, 1H), 5.87 (br s, 1H), 3.57 – 3.45 (m, 1H), 3.31 (dd, *J* = 17.2, 9.3 Hz, 1H), 2.23 – 1.82 (m, 4H), 1.40 (s, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(2-methylbenzamido)pyrrolidine-1-carboxylate (**3c**)



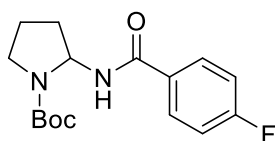
Colorless Oil.

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.22 (m, 2H), 7.19 – 7.14 (m, 2H), 6.27 (s, 1H), 5.81 – 5.69 (m, 1H), 3.51 – 3.36 (m, 1H), 3.33 – 3.20 (m, 1H), 2.43 (s, 3H), 2.19 – 1.81 (m, 4H), 1.46 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 168.7, 154.0, 136.3, 135.9, 130.9, 129.8, 126.7, 125.6, 80.2, 64.3, 46.0, 34.0, 28.4, 22.3, 19.6.

HRMS (ESI) *m/z* calcd for C₁₇H₂₄N₂NaO₃⁺ (M+Na⁺): 327.1679, found: 327.1675.

tert-Butyl 2-(4-fluorobenzamido)pyrrolidine-1-carboxylate (**3d**)



Colorless oil.

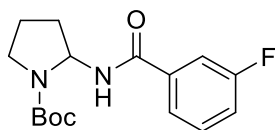
¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.69 (m, 2H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.67 (s, 1H), 5.85 (br s, 1H), 3.56 – 3.47 (m, 1H), 3.32 (dt, *J* = 10.3, 8.1 Hz, 1H), 2.18 – 1.90 (m, 4H), 1.40 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 165.9, 165.4, 163.4, 154.2, 130.6 (d, *J* = 3.2 Hz), 129.3 (d, *J* = 9.1 Hz), 115.5 (d, *J* = 21.8 Hz), 80.2, 64.6, 46.1, 33.9, 28.4, 22.5.

¹⁹F NMR (376 MHz, CDCl₃) δ -108.2.

HRMS (ESI) *m/z* calcd for C₁₆H₂₁FN₂NaO₃⁺ (M+Na⁺): 331.1428, found: 331.1433.

tert-Butyl 2-(3-fluorobenzamido)pyrrolidine-1-carboxylate (**3e**)



Colorless oil.

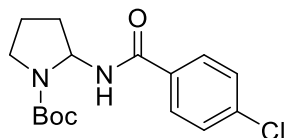
¹H NMR (400 MHz, CDCl₃) δ 7.49 (dd, *J* = 17.9, 8.5 Hz, 2H), 7.38 (d, *J* = 6.1 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 6.0 Hz, 1H), 5.85 (br s, 1H), 3.57 – 3.45 (m, 1H), 3.33 (dd, *J* = 18.1, 8.4 Hz, 1H), 2.27 – 1.84 (m, 5H), 1.41 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 165.2, 162.7 (d, *J* = 247.6 Hz), 154.2, 136.8 (d, *J* = 6.7 Hz), 130.2 (d, *J* = 7.6 Hz), 122.5, 118.4 (d, *J* = 21.3 Hz), 118.25 – 118.04 (m), 114.3 (d, *J* = 22.8 Hz), 80.3, 64.7, 46.1, 33.9, 28.4, 22.5.

¹⁹F NMR (376 MHz, CDCl₃) δ -111.82.

HRMS (ESI) m/z calcd for C₁₆H₂₁FN₂NaO₃⁺ (M+Na⁺): 331.1428, found: 331.1422.

tert-Butyl 2-(4-chlorobenzamido)pyrrolidine-1-carboxylate (**3f**)^[4]

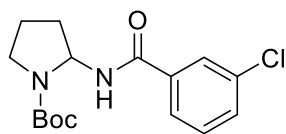


White Solid. mp 149 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 2H), 6.70 (s, 1H), 5.85 (br s, 1H), 3.56 – 3.46 (m, 1H), 3.32 (dt, *J* = 10.4, 8.1 Hz, 1H), 2.25 – 1.85 (m, 4H), 1.40 (s, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(3-chlorobenzamido)pyrrolidine-1-carboxylate (**3g**)



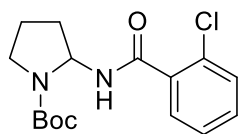
Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.72 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.72 (s, 1H), 5.86 (br s, 1H), 3.51 (dd, *J* = 13.8, 6.8 Hz, 1H), 3.39 – 3.23 (m, 1H), 2.26 – 1.86 (m, 4H), 1.41 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 165.1, 154.1, 136.3, 134.6, 131.4, 129.9, 127.3, 125.2, 80.3, 64.7, 46.1, 33.9, 28.4, 22.5.

HRMS (ESI) m/z calcd for C₁₆H₂₁ClN₂NaO₃⁺ (M+Na⁺): 347.1133, found: 347.1131.

tert-Butyl 2-(2-chlorobenzamido)pyrrolidine-1-carboxylate (**3h**)



Colorless oil.

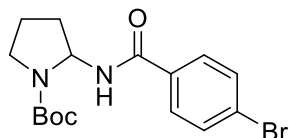
¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 6.8 Hz, 1H), 7.46 – 7.21 (m, 3H), 6.58 (s, 1H), 5.86 (br s, 1H), 3.55 – 3.44 (m, 1H), 3.36 – 3.24 (m, 1H), 2.19 – 1.89 (m, 4H), 1.46 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 165.1, 154.0, 134.9, 131.3, 130.6, 130.2, 130.1, 127.1,

80.4, 64.6, 46.0, 33.8, 28.4, 22.4.

HRMS (ESI) m/z calcd for $C_{16}H_{21}ClN_2NaO_3^+$ ($M+Na^+$): 347.1133, found: 347.1135.

tert-Butyl 2-(4-bromobenzamido)pyrrolidine-1-carboxylate (**3i**)



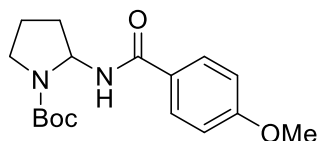
Colorless oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, $J = 8.2$ Hz, 2H), 7.54 (d, $J = 7.5$ Hz, 2H), 6.56 (d, $J = 6.4$ Hz, 1H), 5.84 (br s, 1H), 3.56 – 3.46 (m, 1H), 3.33 (dt, $J = 10.3, 8.1$ Hz, 1H), 2.20 – 1.87 (m, 4H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 133.3, 131.7, 128.6, 126.2, 80.3, 64.7, 46.1, 33.9, 28.4, 22.5.

HRMS (ESI) m/z calcd for $C_{16}H_{21}BrN_2NaO_3^+$ ($M+Na^+$): 391.0628, found: 391.0624.

tert-Butyl 2-(4-methoxybenzamido)pyrrolidine-1-carboxylate (**3j**)^[4]

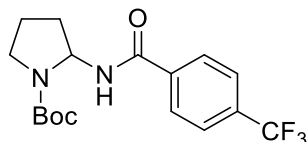


White Solid. mp 128 °C.

1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, $J = 8.6$ Hz, 2H), 6.89 (d, $J = 8.2$ Hz, 2H), 6.55 (d, $J = 6.5$ Hz, 1H), 5.84 (br s, 1H), 3.83 (s, 3H), 3.57 – 3.47 (m, 1H), 3.37 – 3.26 (m, 1H), 2.16 – 1.89 (m, 4H), 1.40 (s, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(4-(trifluoromethyl)benzamido)pyrrolidine-1-carboxylate (**3k**)^[4]

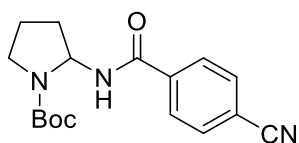


Colorless oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, $J = 6.3$ Hz, 2H), 7.67 (d, $J = 3.6$ Hz, 2H), 6.69 (d, $J = 6.1$ Hz, 1H), 5.88 (br s, 1H), 3.60 – 3.48 (m, 1H), 3.34 (dd, $J = 18.2, 8.2$ Hz, 1H), 2.25 – 1.88 (m, 4H), 1.39 (d, $J = 13.9$ Hz, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(4-cyanobenzamido)pyrrolidine-1-carboxylate (**3l**)^[4]

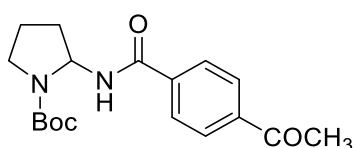


Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.89 (s, 2H), 7.71 (s, 2H), 7.12 – 6.87 (m, 1H), 5.89 (s, 1H), 3.57 – 3.48 (m, 1H), 3.39 – 3.29 (m, 1H), 2.27 – 1.87 (m, 4H), 1.41 (s, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(4-acetylbenzamido)pyrrolidine-1-carboxylate (**3m**)



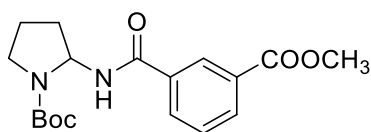
Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 6.2 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 6.59 (s, 1H), 5.80 (d, *J* = 61.7 Hz, 1H), 3.54 (dd, *J* = 10.3, 5.3 Hz, 1H), 3.35 (dd, *J* = 17.8, 8.5 Hz, 1H), 2.63 (s, 3H), 2.19 – 1.95 (m, 4H), 1.40 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 197.5, 165.5, 154.1, 139.2, 138.4, 128.5, 127.3, 80.3, 46.2, 33.9, 28.4, 26.8, 22.6.

HRMS (ESI) *m/z* calcd for C₁₈H₂₄N₂NaO₄⁺ (*M*+Na⁺): 355.1628, found: 355.1630.

tert-Butyl 2-(3-(methoxycarbonyl)benzamido)pyrrolidine-1-carboxylate (**3n**)



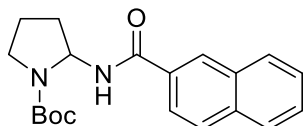
Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.36 (s, 1H), 8.17 – 7.95 (m, 2H), 7.49 (s, 1H), 7.17 (s, 1H), 5.86 (d, *J* = 31.2 Hz, 1H), 3.88 (s, 3H), 3.56 (d, *J* = 8.3 Hz, 1H), 3.34 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.18 – 1.93 (m, 4H), 1.40 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 166.4, 165.4, 154.1, 134.9, 132.2, 132.0, 130.2, 128.7, 127.6, 80.1, 64.6, 52.3, 46.1, 33.9, 28.3, 22.4.

HRMS (ESI) *m/z* calcd for C₁₈H₂₄N₂NaO₅⁺ (*M*+Na⁺): 371.1577, found: 371.1577.

tert-Butyl 2-(2-naphthamido)pyrrolidine-1-carboxylate (**3o**)^[4]

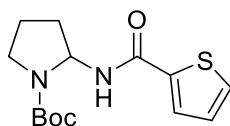


Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.25 (s, 1H), 7.89 – 7.80 (m, 4H), 7.56 – 7.51 (m, 2H), 6.67 (d, *J* = 4.7 Hz, 1H), 5.92 (br s, 1H), 3.57 (dd, *J* = 13.3, 6.8 Hz, 1H), 3.34 (dd, *J* = 17.7, 8.8 Hz, 1H), 2.29 – 1.84 (m, 4H), 1.41 (s, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(thiophene-2-carboxamido)pyrrolidine-1-carboxylate (**3p**)



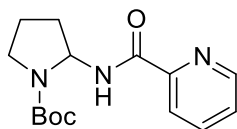
White solid. mp 187–189 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.42 (m, 2H), 7.07 (s, 1H), 6.38 – 6.26 (m, 1H), 5.81 – 5.68 (m, 1H), 3.60 – 3.48 (m, 1H), 3.34 (dd, *J* = 18.2, 8.2 Hz, 1H), 2.17 (s, 1H), 2.05 – 1.93 (m, 3H), 1.41 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 154.2, 138.9, 130.0, 128.2, 127.6, 80.4, 64.6, 46.1, 33.9, 28.4, 22.5.

HRMS (ESI) *m/z* calcd for C₁₄H₂₀N₂NaO₃S⁺ (*M*+Na⁺): 319.1087, found: 319.1088.

tert-Butyl 2-(picolinamido)pyrrolidine-1-carboxylate (**3q**)



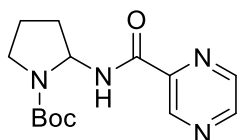
Colorless Oil.

¹H NMR (400 MHz, CDCl₃) δ 8.54 (s, 1H), 8.19 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 6.4 Hz, 1H), 7.44 (s, 1H), 5.87 (t, *J* = 6.5 Hz, 1H), 3.59 (s, 1H), 3.36 (d, *J* = 6.2 Hz, 1H), 2.22 – 1.90 (m, 4H), 1.50 – 1.29 (m, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 163.1, 154.1, 149.7, 148.0, 137.3, 126.2, 122.2, 80.0, 64.0, 46.0, 33.9, 28.3, 22.5.

HRMS (ESI) *m/z* calcd for C₁₅H₂₁N₃NaO₃⁺ (*M*+Na⁺): 314.1475, found: 314.1478.

tert-Butyl 2-(pyrazine-2-carboxamido)pyrrolidine-1-carboxylate (**3r**)



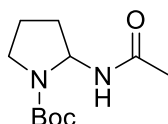
Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 9.41 (d, *J* = 1.3 Hz, 1H), 8.77 (s, 1H), 8.54 (s, 1H), 7.91 (d, *J* = 5.5 Hz, 1H), 5.88 (dd, *J* = 10.5, 5.1 Hz, 1H), 3.59 (s, 1H), 3.38 (d, *J* = 6.7 Hz, 1H), 2.29 – 1.92 (m, 4H), 1.45 – 1.37 (m, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 161.7, 154.0, 147.4, 144.4, 144.3, 142.5, 80.3, 64.1, 46.0, 33.8, 28.4, 22.5.

HRMS (ESI) *m/z* calcd for C₁₄H₂₀N₄NaO₃⁺ (*M*+Na⁺): 315.1428, found: 315.1429.

tert-Butyl 2-acetamidopyrrolidine-1-carboxylate (**3s**)^[4]

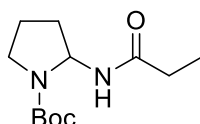


White Solid. mp 113 °C.

¹H NMR (400 MHz, CDCl₃) δ 6.36 (br s, 1H), 5.67 (br s, 1H), 3.49 – 3.41 (m, 1H), 3.33 – 3.22 (m, 1H), 2.11 – 1.83 (m, 7H), 1.45 (s, 9H).

The spectral data obtained were identical with those reported in literature.

tert-butyl 2-propionamidopyrrolidine-1-carboxylate (**3t**)



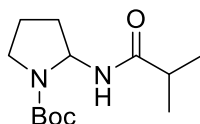
White Solid. mp 152–153 °C.

¹H NMR (400 MHz, CDCl₃) δ 5.91 – 5.34 (m, 2H), 3.50 – 3.45 (m, 1H), 3.31 – 3.25 (m, 1H), 2.18 (q, *J* = 7.5 Hz, 2H), 2.12 – 1.80 (m, 4H), 1.45 (s, 9H), 1.15 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 154.1, 80.1, 64.1, 46.0, 33.9, 29.8, 28.4, 22.4, 9.8.

HRMS (ESI) *m/z* calcd for C₁₂H₂₂N₂NaO₃⁺ (*M*+Na⁺): 265.1523, found: 265.1524.

tert-Butyl 2-isobutyramidopyrrolidine-1-carboxylate (**3u**)



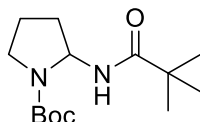
White Solid. mp 174–176 °C.

¹H NMR (400 MHz, CDCl₃) δ 5.95 (s, 1H), 5.65 (br s, 1H), 3.47 (dt, *J* = 10.6, 5.4 Hz, 1H), 3.33 – 3.22 (m, 1H), 2.36 – 2.29 (m, 1H), 2.13 – 1.82 (m, 4H), 1.44 (s, 9H), 1.14 (t, *J* = 6.7 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 175.6, 154.1, 80.0, 61.1, 46.0, 35.5, 34.0, 28.4, 22.3, 19.4.

HRMS (ESI) *m/z* calcd for C₁₃H₂₄N₂NaO₃⁺ (*M*+Na⁺): 279.1679, found: 279.1683.

tert-Butyl 2-pivalamidopyrrolidine-1-carboxylate (**3v**)^[4]

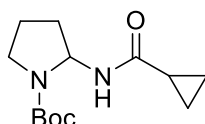


White Solid. mp 169–170 °C.

¹H NMR (400 MHz, CDCl₃) δ 5.79 (s, 1H), 5.57 (s, 1H), 3.55 – 3.44 (m, 1H), 3.34 – 3.23 (m, 1H), 2.15 – 1.81 (m, 4H), 1.45 (s, 9H), 1.19 (s, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(cyclopropanecarboxamido)pyrrolidine-1-carboxylate (**3w**)



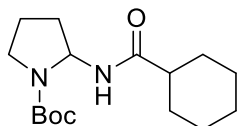
White Solid. mp 185–186 °C.

¹H NMR (400 MHz, CDCl₃) δ 6.13 (d, *J* = 6.1 Hz, 1H), 5.69 (br s, 1H), 3.55 – 3.41 (m, 1H), 3.28 (dd, *J* = 16.9, 8.3 Hz, 1H), 2.05 – 1.89 (m, 4H), 1.45 (s, 9H), 1.38 – 1.29 (m, 1H), 0.95 (s, 2H), 0.72 (d, *J* = 5.4 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 172.2, 154.2, 80.1, 63.9, 45.9, 33.9, 22.4, 14.6, 7.1, 7.0.

HRMS (ESI) *m/z* calcd for C₁₃H₂₂N₂NaO₃⁺ (*M*+Na⁺): 277.1523, found: 277.1525.

tert-butyl 2-(cyclohexanecarboxamido)pyrrolidine-1-carboxylate (**3x**)^[5]

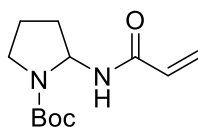


White Solid. mp 147–150 °C.

¹H NMR (400 MHz, CDCl₃) δ 5.86 (d, *J* = 6.0 Hz, 1H), 5.65 – 5.48 (m, 1H), 3.51 – 3.42 (m, 1H), 3.27 (dd, *J* = 18.2, 8.2 Hz, 1H), 2.04 (ddd, *J* = 11.8, 7.7, 3.4 Hz, 2H), 1.87 – 1.78 (m, 7H), 1.67 (s, 1H), 1.44 – 1.42 (m, 11H), 1.23 (dd, *J* = 18.8, 9.5 Hz, 3H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-acrylamidopyrrolidine-1-carboxylate (**3y**)^[5]

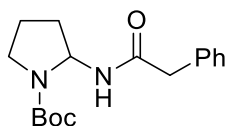


White Solid. mp 145–147 °C.

¹H NMR (400 MHz, CDCl₃) δ 6.33 – 6.02 (m, 3H), 5.81 – 5.48 (m, 2H), 3.48 (dt, *J* = 10.6, 5.4 Hz, 1H), 3.30 (dd, *J* = 17.9, 8.3 Hz, 1H), 2.16 – 1.85 (m, 4H), 1.43 (s, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(2-phenylacetamido)pyrrolidine-1-carboxylate (**3z**)



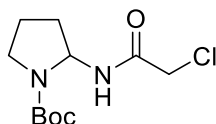
Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.24 (m, 5H), 5.81 (d, *J* = 6.0 Hz, 1H), 5.58 (s, 1H), 3.58 – 3.47 (m, 2H), 3.41 – 3.32 (m, 1H), 3.22 (dd, *J* = 17.1, 9.7 Hz, 1H), 2.11 – 1.68 (m, 4H), 1.37 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 169.7, 154.0, 134.9, 129.3, 129.0, 127.3, 80.1, 64.4, 46.0, 43.9, 33.7, 28.3, 22.3.

HRMS (ESI) *m/z* calcd for C₁₇H₂₄N₂NaO₃⁺ (*M*+Na⁺): 326.1679, found: 326.1676.

tert-Butyl 2-(2-chloroacetamido)pyrrolidine-1-carboxylate (**3aa**)



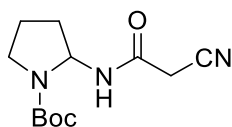
Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 6.69 (d, *J* = 4.9 Hz, 1H), 5.64 (td, *J* = 6.7, 1.7 Hz, 1H), 4.02 (s, 2H), 3.52 (d, *J* = 5.7 Hz, 1H), 3.32 (d, *J* = 7.1 Hz, 1H), 2.20 – 1.85 (m, 4H), 1.45 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 164.8, 153.9, 80.5, 64.6, 46.1, 42.5, 33.6, 28.4, 22.4.

HRMS (ESI) *m/z* calcd for C₁₁H₁₉ClN₂NaO₃⁺ (*M*+Na⁺): 285.0976, found: 285.0979.

tert-Butyl 2-(2-cyanoacetamido)pyrrolidine-1-carboxylate (**3ab**)



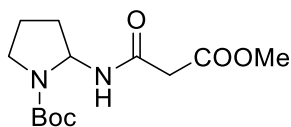
Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.01 – 6.85 (m, 1H), 5.66 – 5.58 (m, 1H), 3.51 – 3.35 (m, 3H), 3.29 (d, *J* = 6.7 Hz, 1H), 2.09 – 1.92 (m, 4H), 1.46 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 160.0, 154.0, 114.8, 80.6, 64.5, 46.0, 33.5, 28.4, 25.9, 22.3.

HRMS (ESI) *m/z* calcd for C₁₂H₁₉N₃NaO₃⁺ (*M*+Na⁺): 276.1319, found: 276.1322.

tert-Butyl 2-(3-methoxy-3-oxopropanamido)pyrrolidine-1-carboxylate (**3ac**)



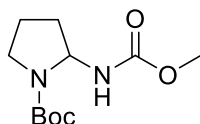
Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, *J* = 5.6 Hz, 1H), 5.66 (s, 1H), 3.75 (s, 3H), 3.55 – 3.44 (m, 1H), 3.30 (s, 3H), 2.05 – 1.91 (m, 4H), 1.44 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 169.7, 163.5, 154.0, 80.1, 64.0, 52.4, 45.9, 41.1, 33.7, 28.4, 22.4.

HRMS (ESI) *m/z* calcd for C₁₃H₂₂N₂NaO₅⁺ (*M*+Na⁺): 309.1421, found: 309.1418.

tert-Butyl 2-((methoxycarbonyl)amino)pyrrolidine-1-carboxylate (**3ad**)^[6]

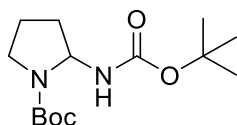


Colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.43 (s, 1H), 4.98 (br s, 1H), 3.66 (s, 3H), 3.50 – 3.41 (m, 1H), 3.27 (d, $J = 8.0$ Hz, 1H), 2.05 – 1.88 (m, 4H), 1.45 (s, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-((*tert*-butoxycarbonyl)amino)pyrrolidine-1-carboxylate (**3ae**)^[5]

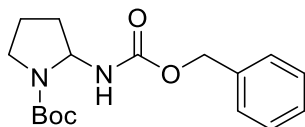


Colorless Solid. mp 127-129 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.40 (s, 1H), 4.94 (s, 1H), 3.49 – 3.38 (m, 1H), 3.30 – 3.18 (m, 1H), 2.11 – 1.80 (m, 4H), 1.46 (s, 9H), 1.44 (s, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(((benzyloxy)carbonyl)amino)pyrrolidine-1-carboxylate (**3af**)^[7]

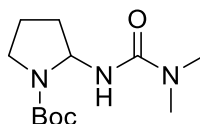


Colorless solid. mp 68-70 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.31 (dt, $J = 13.9, 6.7$ Hz, 5H), 5.46 (s, 1H), 5.26 – 5.03 (m, 3H), 3.49 – 3.38 (m, 1H), 3.25 (dd, $J = 17.4, 8.3$ Hz, 1H), 2.05 – 1.81 (m, 4H), 1.41 (s, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(3,3-dimethylureido)pyrrolidine-1-carboxylate (**3ag**)



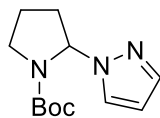
White Solid. mp 167–168 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.48 (s, 1H), 4.77 – 4.51 (m, 1H), 3.48 (s, 1H), 3.29 (dd, $J = 17.1, 8.5$ Hz, 1H), 2.89 (s, 6H), 2.21 – 1.75 (m, 4H), 1.45 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 157.5, 154.3, 79.9, 66.2, 46.1, 36.1, 34.3, 28.4, 22.3.

HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{23}\text{N}_3\text{NaO}_3^+$ ($\text{M}+\text{Na}^+$): 280.1632, found: 280.1633.

tert-Butyl 2-(1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5a**)



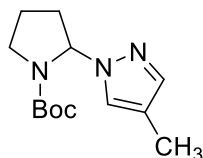
Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.70 – 7.39 (m, 2H), 6.21 (s, 1H), 6.10 – 5.90 (m, 1H), 3.67 (dt, $J = 16.6, 7.7$ Hz, 1H), 3.48 (dt, $J = 19.8, 8.7$ Hz, 1H), 2.60 – 2.15 (m, 3H), 2.01 (d, $J = 15.1$ Hz, 1H), 1.44 – 1.35 (m, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 154.4, 153.6, 139.5, 129.4, 127.9, 104.8, 104.6, 80.5, 80.3, 73.1, 72.6, 46.9, 46.4, 33.6, 32.1, 28.3, 28.2, 23.5, 22.3.

HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{19}\text{N}_3\text{NaO}_2^+$ ($\text{M}+\text{Na}^+$): 260.1369, found: 260.1374.

tert-Butyl 2-(4-methyl-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5b**)



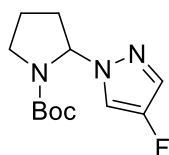
Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.17 (m, 2H), 6.02 – 5.80 (m, 1H), 3.73 – 3.56 (m, 1H), 3.46 (dt, $J = 18.1, 8.4$ Hz, 1H), 2.46 – 2.10 (m, 3H), 2.05 (s, 3H), 1.97 (s, 1H), 1.45 – 1.36 (m, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 154.4, 153.7, 140.0, 139.9, 128.1, 126.7, 80.4, 80.2, 73.0, 72.4, 46.8, 46.4, 33.5, 32.0, 28.3, 28.2, 23.5, 22.3, 8.8.

HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{21}\text{N}_3\text{NaO}_2^+$ ($\text{M}+\text{Na}^+$): 274.1526, found: 274.1529.

tert-Butyl 2-(4-fluoro-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5c**)



Colorless Oil.

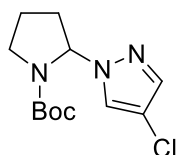
¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.31(m, 2H), 5.98 – 5.74 (m, 1H), 3.74 – 3.54 (m, 1H), 3.47 (dt, *J* = 18.6, 8.8 Hz, 1H), 2.51 – 2.08 (m, 3H), 1.99 (s, 1H), 1.46 – 1.38 (m, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 154.4, 153.5, 150.5, 148.0, 126.4, 126.3, 115.5, 115.2, 113.9, 113.7, 80.8, 80.5, 74.0, 73.4, 46.8, 46.5, 33.4, 31.6, 28.2, 23.4, 22.2.

¹⁹F NMR (376 MHz, CDCl₃) δ -177.9.

HRMS (ESI) *m/z* calcd for C₁₂H₁₈FN₃NaO₂⁺ (M+Na⁺): 278.1275, found: 278.1276.

tert-Butyl 2-(4-chloro-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5d**)^[8]

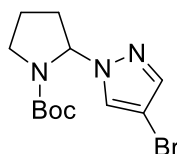


Colorless Oil.

¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.43 (m, *J* = 71.0 Hz, 2H), 6.01 – 5.81 (m, 1H), 3.64 (dt, *J* = 17.1, 8.3 Hz, 1H), 3.55 – 3.36 (m, 1H), 2.42 – 1.99 (m, 3H), 1.98 (s, 1H), 1.46 – 1.37 (m, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(4-bromo-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5e**)^[8]

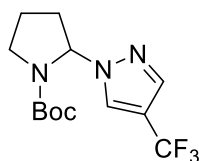


Colorless Oil.

¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.50 (m, 2H), 6.09 – 5.82 (m, 1H), 3.65 (dt, *J* = 17.1, 8.2 Hz, 1H), 3.55 – 3.36 (m, 1H), 2.44 – 2.11 (m, 3H), 1.99 (s, 1H), 1.45 – 1.36 (m, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(4-(trifluoromethyl)-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5f**)



Colorless Oil.

¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.70 (m, 2H), 6.13 – 5.80 (m, 1H), 3.68 (dt, *J* =

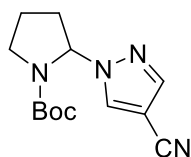
37.3, 7.5 Hz, 1H), 3.49 (td, $J = 17.5, 8.7$ Hz, 1H), 2.44 – 2.25 (m, 3H), 2.01 (s, 1H), 1.45 – 1.36 (m, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 154.3, 153.2, 137.1, 128.6, 127.5, 122.7 (q, $J = 266.0$ Hz), 112.7 (q, $J = 33.1$ Hz), 81.0, 80.8, 73.8, 73.4, 46.9, 46.5, 33.5, 31.9, 28.2, 28.1, 23.3, 22.2.

^{19}F NMR (376 MHz, CDCl_3) δ -56.3, -56.4.

HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{F}_3\text{N}_3\text{NaO}_2^+$ ($\text{M}+\text{Na}^+$): 328.1243, found: 328.1243.

tert-Butyl 2-(4-cyano-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5g**)



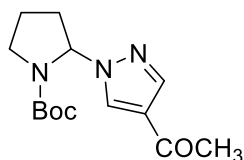
Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.07 – 7.79 (m, 2H), 6.04 – 5.95 (m, 1H), 3.71 – 3.60 (m, 1H), 3.55 – 3.41 (m, 1H), 2.44 – 2.17 (m, 3H), 2.04 (s, 1H), 1.46 – 1.37 (m, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 154.3, 153.1, 142.4, 142.3, 134.6, 133.2, 113.6, 113.5, 91.6, 91.4, 81.2, 81.0, 74.2, 73.8, 47.0, 46.6, 33.5, 31.8, 28.2, 23.3, 22.1.

HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{N}_4\text{NaO}_2^+$ ($\text{M}+\text{Na}^+$): 285.1322, found: 285.1325.

tert-Butyl 2-(4-acetyl-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5h**)



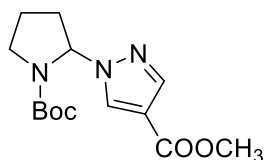
Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.16 – 7.84 (m, 2H), 6.12 – 5.86 (m, 1H), 3.79 – 3.60 (m, 1H), 3.58 – 3.40 (m, 1H), 2.43 (d, $J = 2.5$ Hz, 3H), 2.40 – 2.13 (m, 3H), 2.09 – 1.94 (m, 1H), 1.46 – 1.36 (m, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 192.2, 192.0, 154.2, 153.2, 140.6, 131.6, 130.6, 123.4, 123.3, 80.9, 80.7, 73.8, 73.5, 46.9, 46.5, 33.4, 32.1, 28.2, 27.8, 23.2, 22.1.

HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{21}\text{N}_3\text{NaO}_3^+$ ($\text{M}+\text{Na}^+$): 302.1475, found: 302.1477.

Methyl 1-(1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)-1H-pyrazole-4-carboxylate (**5i**)



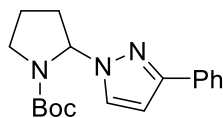
Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.12 – 7.88 (m, 2H), 6.08 – 5.88 (m, 1H), 3.82 (d, *J* = 6.8 Hz, 3H), 3.68 (dt, *J* = 16.0, 7.7 Hz, 1H), 3.48 (dq, *J* = 27.6, 9.2 Hz, 1H), 2.45 – 2.11 (m, 3H), 2.02 (dd, *J* = 10.3, 5.5 Hz, 1H), 1.46 – 1.36 (m, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 163.5, 163.4, 154.2, 153.3, 141.3, 132.4, 131.4, 113.9, 81.0, 80.7, 73.8, 73.5, 51.3, 47.0, 46.5, 33.5, 32.1, 28.3, 28.2, 23.2, 22.1.

HRMS (ESI) *m/z* calcd for C₁₄H₂₁N₃NaO₄⁺ (*M*+Na⁺): 318.1424, found: 318.1425.

tert-Butyl 2-(3-phenyl-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5j**)



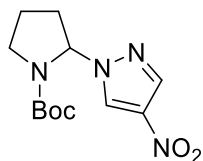
Colorless Oil.

¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.75 (m, 2H), 7.67 – 7.22 (m, 4H), 6.50 (s, 1H), 6.05 – 5.95 (m, 1H), 3.68 (dt, *J* = 16.5, 7.7 Hz, 1H), 3.57 – 3.36 (m, 1H), 2.61 – 2.10 (m, 3H), 1.98 (s, 1H), 1.45 – 1.36 (m, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 154.5, 153.7, 151.5, 133.8, 130.7, 129.1, 128.6, 127.5, 125.6, 101.9, 80.6, 80.3, 73.5, 72.9, 46.9, 46.5, 33.8, 32.2, 28.3, 23.6, 22.4.

HRMS (ESI) *m/z* calcd for C₁₈H₂₃N₃NaO₂⁺ (*M*+Na⁺): 336.1682, found: 336.1685.

tert-Butyl 2-(4-nitro-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5k**)^[5]

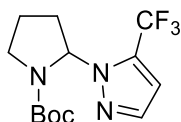


Colorless Oil.

¹H NMR (400 MHz, CDCl₃) δ 8.42 – 8.00 (m, 2H), 6.03 – 5.94 (m, 1H), 3.69 (dd, *J* = 19.4, 7.7 Hz, 1H), 3.60 – 3.41 (m, 1H), 2.53 – 2.13 (m, 3H), 2.06 (s, 1H), 1.47 – 1.39 (m, 9H).

The spectral data obtained were identical with those reported in literature.

tert-Butyl 2-(5-(trifluoromethyl)-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5l**)



Colorless Oil.

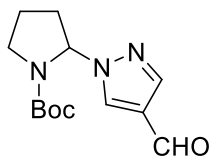
¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.50 (m, 1H), 6.49 – 6.46 (m, 1H), 6.06 – 5.99 (m, 1H), 3.78 – 3.57 (m, 1H), 3.57 – 3.37 (m, 1H), 2.55 – 2.10 (m, 3H), 2.00 (dd, *J* = 7.0, 2.6 Hz, 1H), 1.46 – 1.35 (m, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 154.4, 153.3, 142.5, 142.2, 130.5, 128.8, 122.7, 120.0, 103.55 (q, *J* = 2.0 Hz), 80.9, 80.7, 74.2, 73.6, 46.9, 46.5, 33.7, 32.0, 28.2, 28.1, 23.3, 22.1.

¹⁹F NMR (376 MHz, CDCl₃) δ -61.9, -62.0.

HRMS (ESI) *m/z* calcd for C₁₃H₁₈F₃N₃NaO₂⁺ (M+Na⁺): 328.1243, found: 328.1247.

tert-Butyl 2-(4-formyl-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5m**)



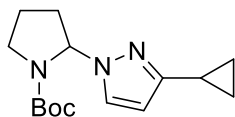
Colorless Oil.

¹H NMR (400 MHz, CDCl₃) δ 9.86 (s, 1H), 8.22 – 7.90 (m, 2H), 6.05 – 5.97 (m, 1H), 3.76 – 3.65 (m, 1H), 3.59 – 3.38 (m, 1H), 2.48 – 2.12 (m, 3H), 2.03 (s, 1H), 1.46 – 1.36 (m, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 184.2, 184.1, 154.3, 153.2, 141.0, 140.5, 133.2, 131.4, 123.5, 81.1, 80.9, 74.0, 73.7, 47.0, 46.6, 33.5, 32.0, 28.2, 23.3, 22.1.

HRMS (ESI) *m/z* calcd for C₁₃H₁₉N₃NaO₃⁺ (M+Na⁺): 288.1319, found: 288.1321.

tert-Butyl 2-(3-cyclopropyl-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5n**)



Colorless Oil.

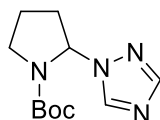
¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.20 (m, 1H), 5.93 – 5.80 (m, 2H), 3.73 – 3.54 (m, 1H), 3.54 – 3.32 (m, 1H), 2.49 – 1.87 (m, 5H), 1.44 – 1.35 (m, 9H), 0.88 (d, *J* = 6.8 Hz, 2H), 0.68 (d, *J* = 2.9 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 155.3, 153.7, 129.7, 128.2, 100.6, 80.4, 80.1, 73.0, 73.5, 46.8, 46.4, 33.5, 32.0, 28.3, 23.5, 22.3, 9.3, 8.0.

HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{23}\text{N}_3\text{NaO}_2^+$ ($\text{M}+\text{Na}^+$): 300.1682, found: 300.1682.

(5o)

tert-Butyl 2-(1H-1,2,4-triazol-1-yl)pyrrolidine-1-carboxylate (5o)^[5]

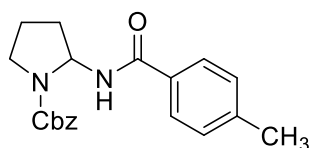


Colorless Oil.

^1H NMR (400 MHz, CDCl_3) δ 8.31 – 8.14 (m, 1H), 7.93 (d, J = 7.1 Hz, 1H), 6.12 – 6.02 (m, 1H), 3.70 – 3.62 (m, 1H), 3.57 – 3.38 (m, 1H), 2.43 – 2.31 (m, 3H), 2.04 (s, 1H), 1.41 (d, J = 23.7 Hz, 9H).

The spectral data obtained were identical with those reported in literature.

Benzyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (6b)^[9]

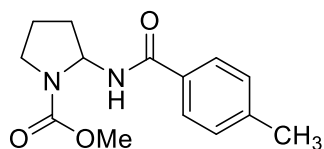


Colorless Oil.

^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, J = 7.6 Hz, 2H), 7.37 – 7.10 (m, 7H), 6.88 – 6.80 (m, 1H), 5.93 – 5.74 (m, 1H), 5.18 – 5.00 (m, 2H), 3.52 (s, 1H), 3.34 (s, 1H), 2.34 (s, 3H), 2.10 – 1.84 (m, 4H).

The spectral data obtained were identical with those reported in literature.

Methyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (6c)



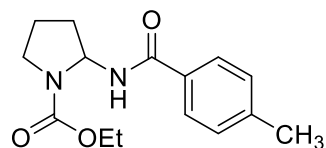
White Solid. mp 174–177 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.68 (s, 2H), 7.20 (s, 2H), 6.62 (s, 1H), 5.86 – 5.73 (m, 1H), 3.67 (s, 3H), 3.57 (s, 1H), 3.38 (s, 1H), 2.38 (s, 3H), 2.20 – 1.88 (m, 4H).

^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 155.5, 142.0, 131.4, 129.1, 127.1, 64.9, 52.7, 46.7, 34.0, 22.4, 21.4.

HRMS (ESI) m/z calcd for $C_{14}H_{18}N_2NaO_3^+$ ($M+Na^+$): 285.1210, found: 285.1211.

Ethyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**6d**)



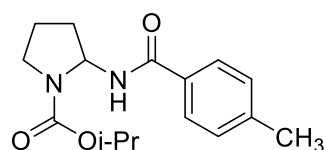
Colorless Oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.19 (d, $J = 6.6$ Hz, 2H), 6.86 – 6.67 (m, 1H), 5.90 – 5.72 (m, 1H), 4.10 (d, $J = 6.0$ Hz, 2H), 3.55 (s, 1H), 3.36 (dd, $J = 17.2, 8.6$ Hz, 1H), 2.37 (s, 3H), 2.14 – 1.92 (m, 4H), 1.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 155.0, 141.9, 131.5, 129.1, 127.1, 64.6, 61.4, 46.5, 33.9, 22.4, 21.4, 14.6.

HRMS (ESI) m/z calcd for $C_{15}H_{20}N_2NaO_3^+$ ($M+Na^+$): 299.1366, found: 299.1368.

Isopropyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**6e**)



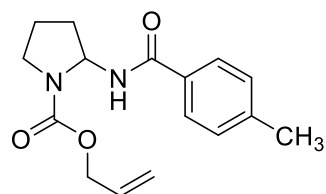
Colorless Oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, $J = 7.0$ Hz, 2H), 7.19 (d, $J = 7.5$ Hz, 2H), 6.74 – 6.64 (m, 1H), 5.90 – 5.71 (m, 1H), 4.89 (dt, $J = 12.0, 5.9$ Hz, 1H), 3.55 (dd, $J = 11.9, 5.4$ Hz, 1H), 3.35 (dd, $J = 17.6, 9.0$ Hz, 1H), 2.37 (s, 3H), 2.15 – 1.92 (m, 4H), 1.25 – 1.06 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 154.6, 141.8, 131.6, 129.1, 127.0, 68.7, 64.4, 46.4, 33.8, 22.2, 22.0, 21.4.

HRMS (ESI) m/z calcd for $C_{16}H_{22}N_2NaO_3^+$ ($M+Na^+$): 313.1523, found: 279.1683.

Allyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**6f**)



Colorless Oil.

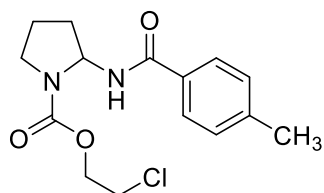
1H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.16 (d, $J = 7.3$ Hz, 2H), 7.12 – 6.79 (m,

1H), 6.02 – 5.67 (m, 2H), 5.33 – 5.04 (m, 2H), 4.62 – 4.48 (m, 2H), 3.54 (s, 1H), 3.36 (s, 1H), 2.36 (s, 3H), 2.20 – 1.91 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 166.6, 154.6, 141.8, 132.4, 131.4, 129.0, 127.1, 117.4, 65.9, 64.7, 46.6, 33.9, 22.3, 21.4.

HRMS (ESI) m/z calcd for C₁₆H₂₀N₂NaO₃⁺ (M+Na⁺): 311.1366, found: 311.1368.

2-Chloroethyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**6g**)



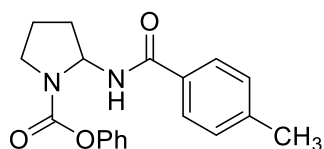
White Solid. mp 137–141 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 6.43 (d, *J* = 4.8 Hz, 1H), 5.90 – 5.75 (m, 1H), 4.38 – 4.25 (m, 2H), 3.76 – 3.51 (m, 3H), 3.42 (dd, *J* = 18.2, 8.4 Hz, 1H), 2.39 (s, 3H), 2.20 – 2.13 (m, 2H), 1.98 (d, *J* = 4.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 166.5, 154.2, 142.1, 131.3, 129.2, 127.0, 64.9, 46.7, 42.0, 33.9, 22.5, 21.5.

HRMS (ESI) m/z calcd for C₁₅H₁₉ClN₂NaO₃⁺ (M+Na⁺): 333.0976, found: 333.0977.

Phenyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**6h**)



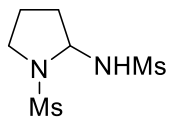
Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.63 (m, 2H), 7.38 – 7.19 (m, 3H), 7.19 – 7.01 (m, 5H), 6.12 – 5.76 (m, 1H), 3.83 – 3.28 (m, 2H), 2.32 (s, 3H), 2.19 – 1.73 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 166.6, 152.9, 151.1, 142.0, 131.3, 129.2, 127.2, 125.3, 121.6, 121.4, 66.3, 64.8, 47.1, 46.8, 33.9, 32.5, 23.3, 22.3, 21.5.

HRMS (ESI) m/z calcd for C₁₉H₂₀N₂NaO₃⁺ (M+Na⁺): 347.1366, found: 347.1366.

N-(1-(Methylsulfonyl)pyrrolidin-2-yl)methanesulfonamide (**11**)



Colorless Oil.

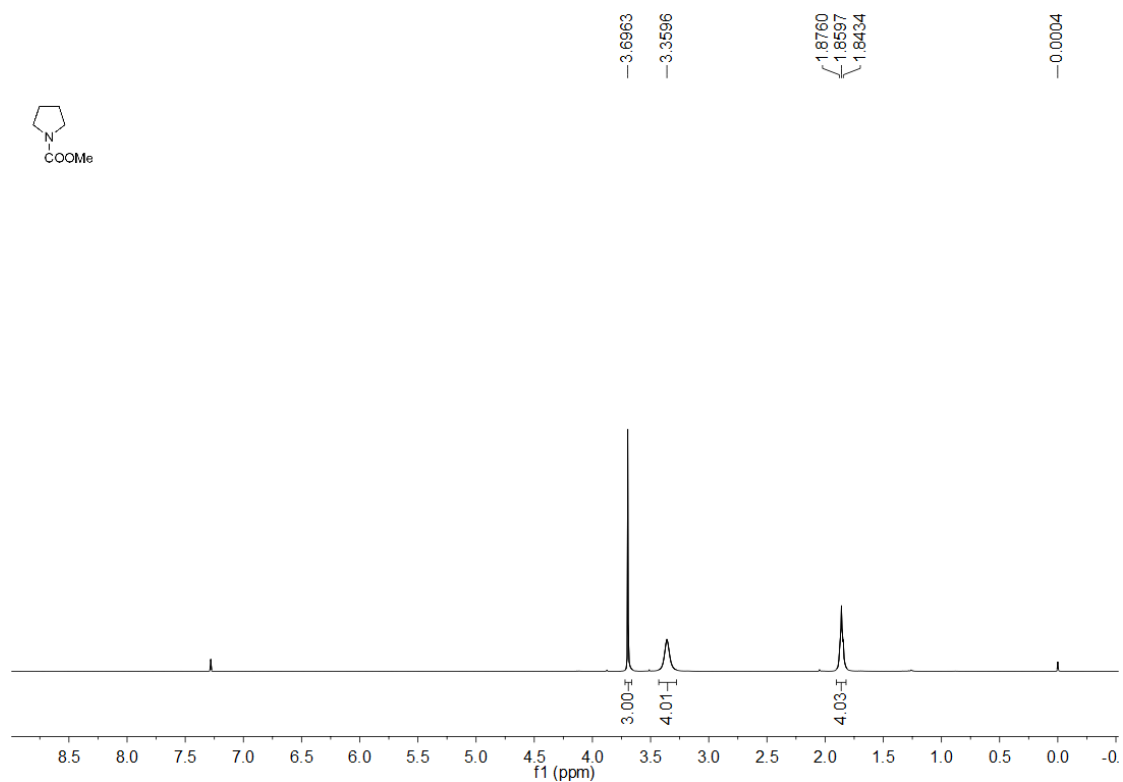
¹H NMR (400 MHz, CDCl₃) δ 5.80 (d, *J* = 8.1 Hz, 1H), 5.30 (t, *J* = 6.6 Hz, 1H), 3.56 – 3.47 (m, 1H), 3.30 (dd, *J* = 15.9, 8.1 Hz, 1H), 3.13 (s, 3H), 2.96 (s, 3H), 2.17 – 2.00 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 69.7, 47.7, 43.3, 41.8, 37.4, 35.2, 23.1.

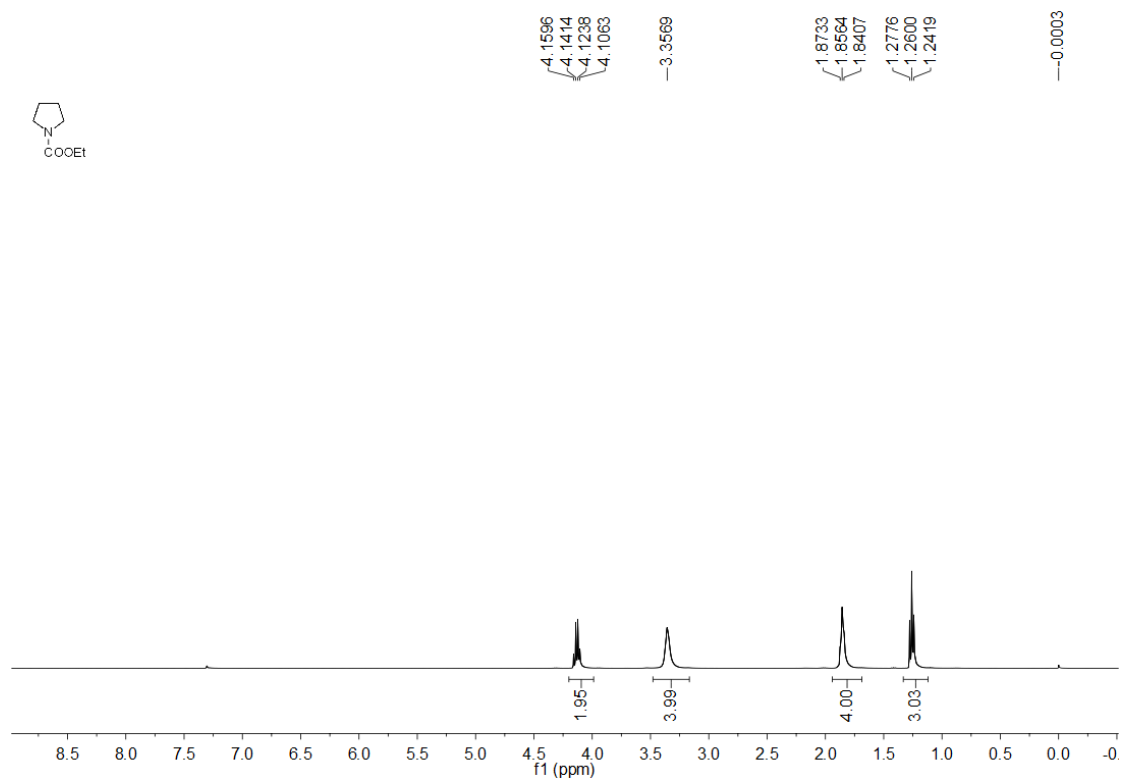
HRMS (ESI) *m/z* calcd for C₆H₁₃N₂O₄S₂⁻ (M-H⁻): 241.0322, found: 241.0323.

8) NMR spectra for the substrates and products

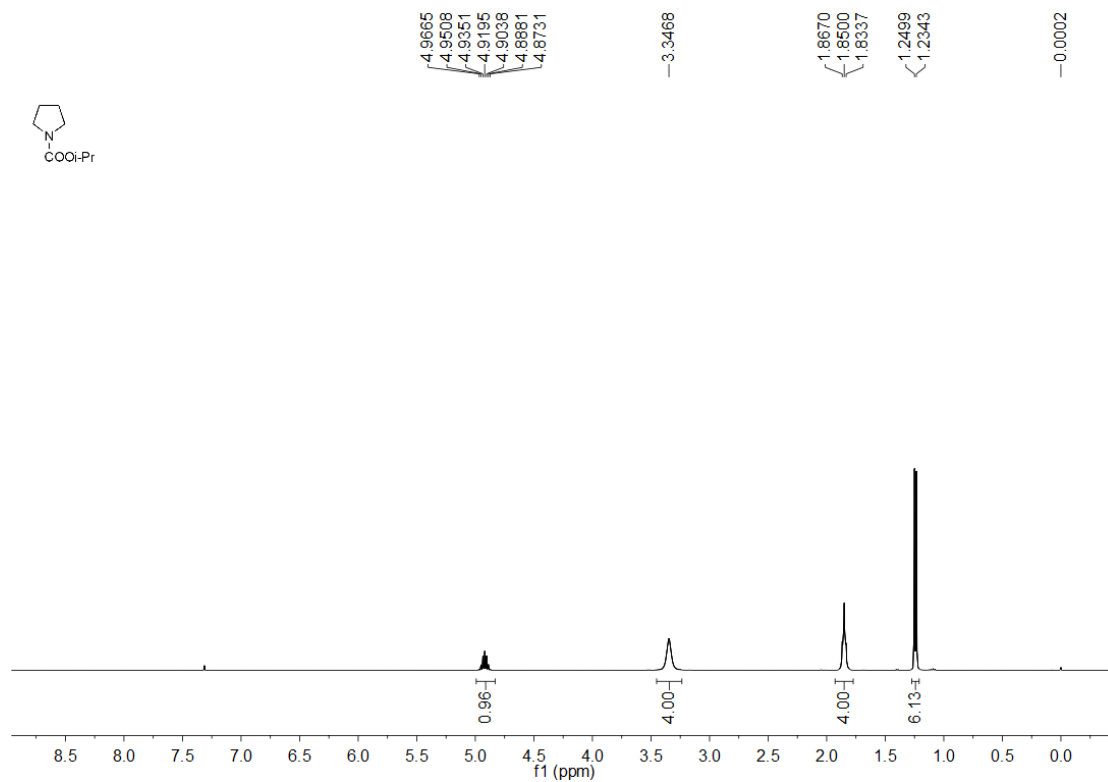
Methyl pyrrolidine-1-carboxylate (**1c**)



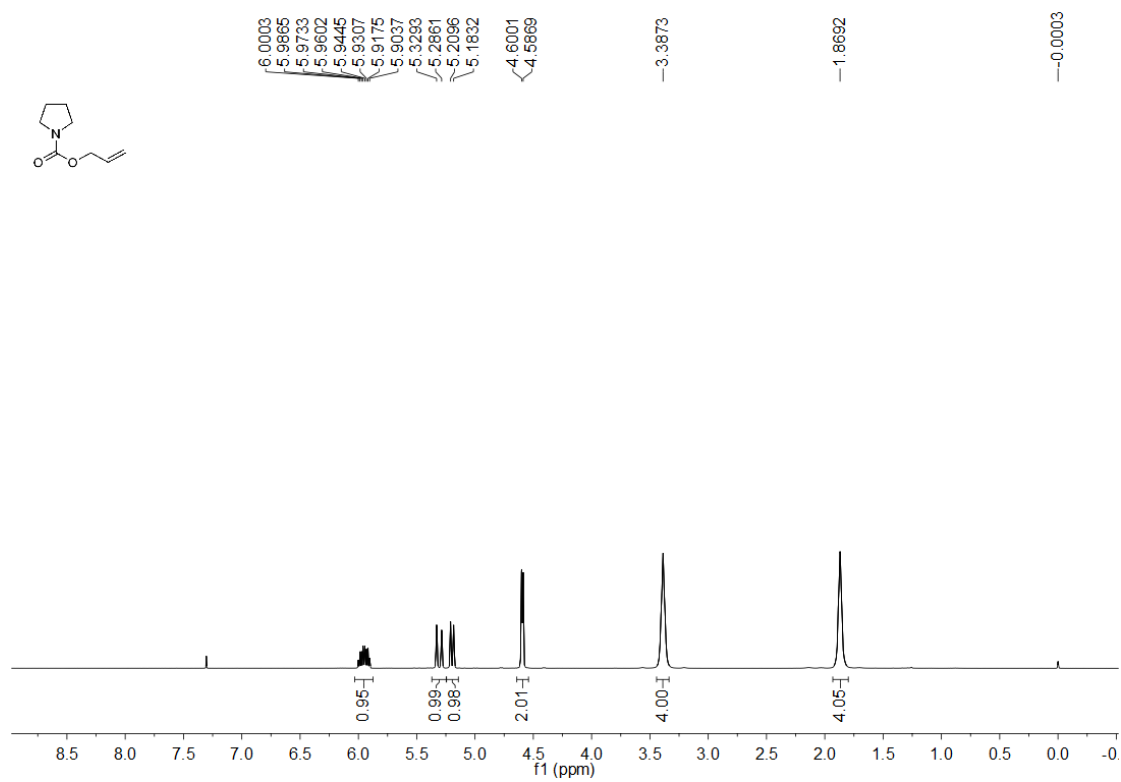
Ethyl pyrrolidine-1-carboxylate (**1d**)



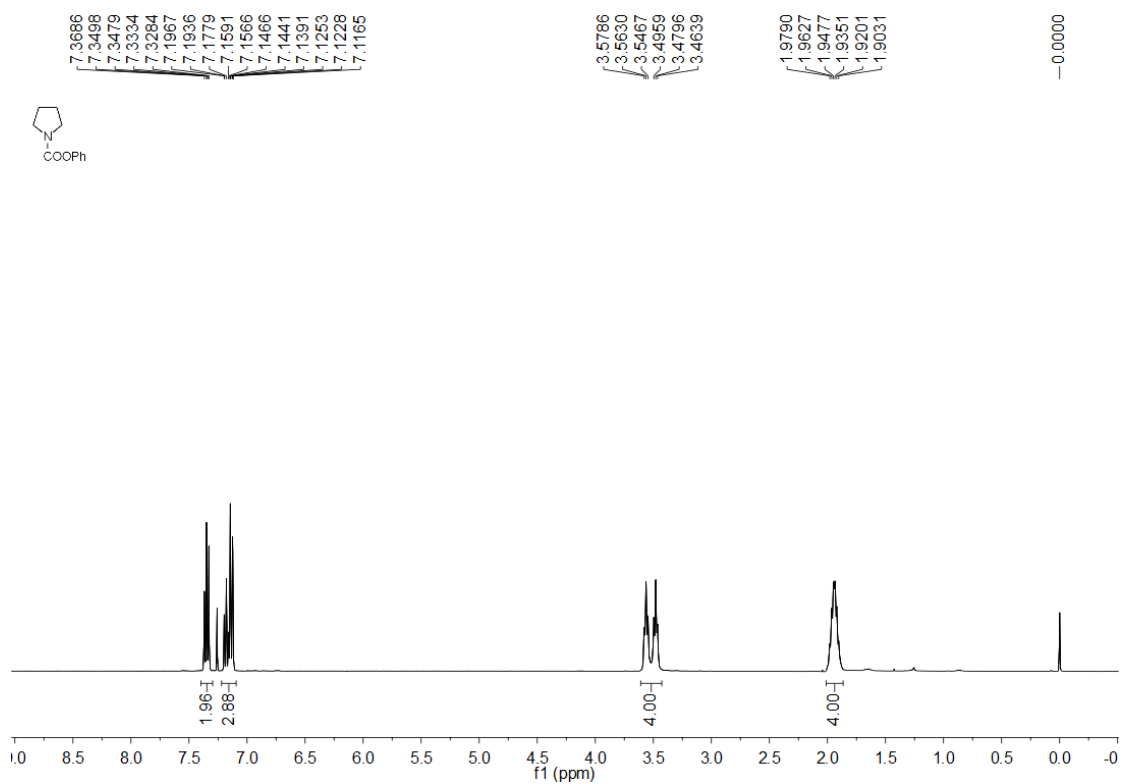
Isopropyl pyrrolidine-1-carboxylate (**1e**)



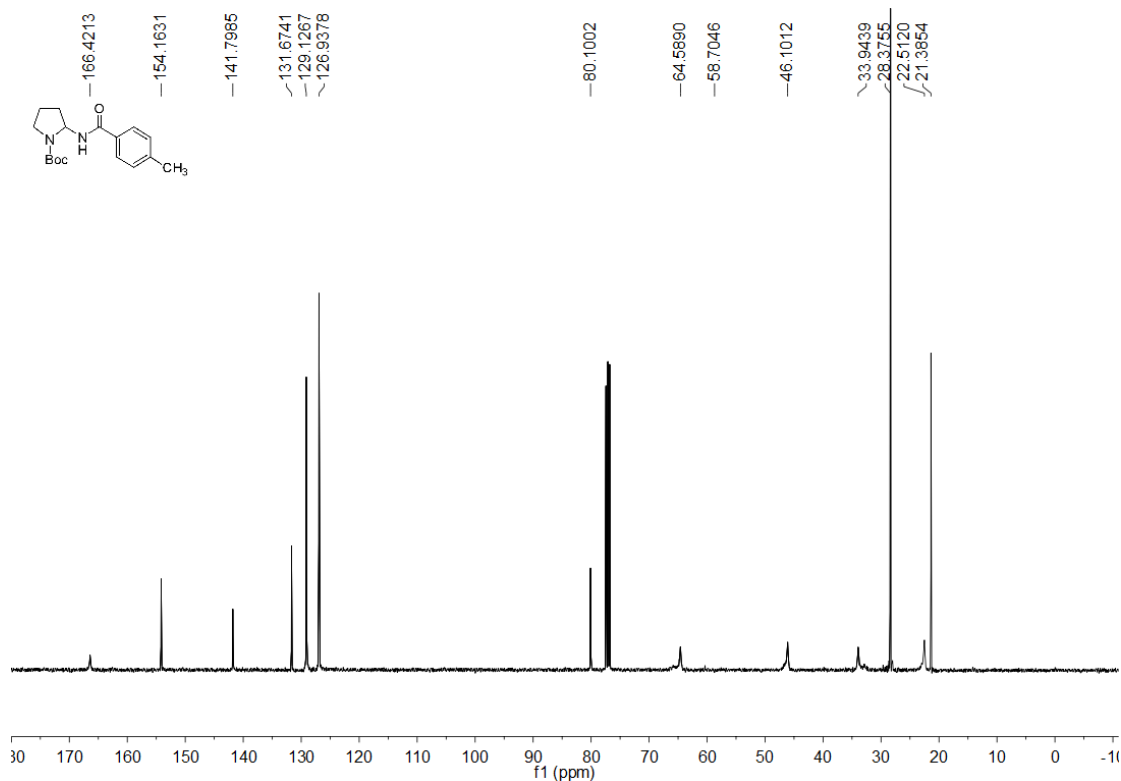
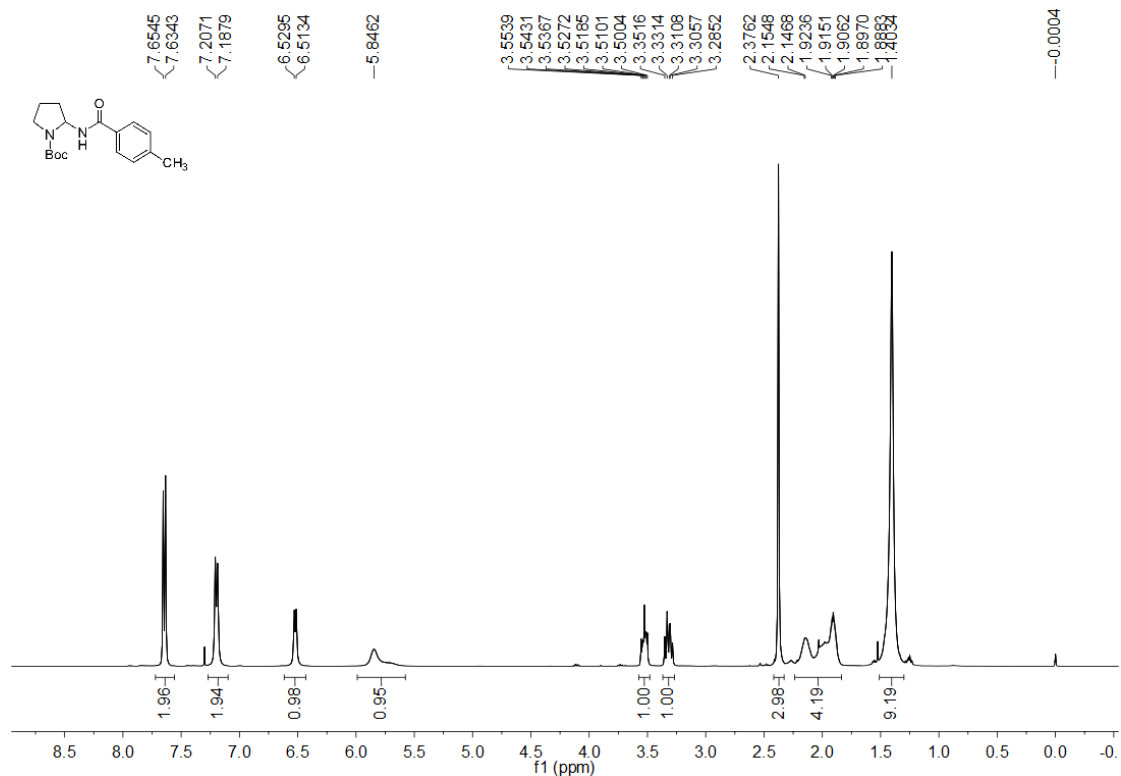
Allyl pyrrolidine-1-carboxylate (**1f**)



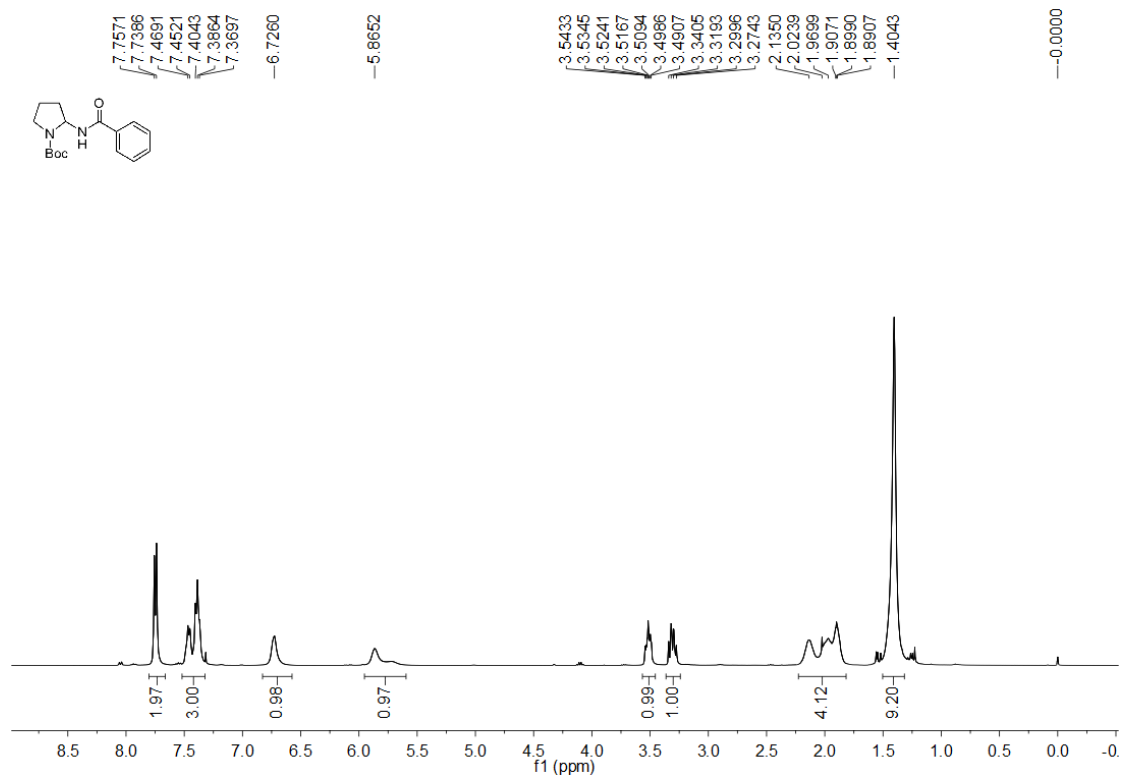
Phenyl pyrrolidine-1-carboxylate (**1h**)



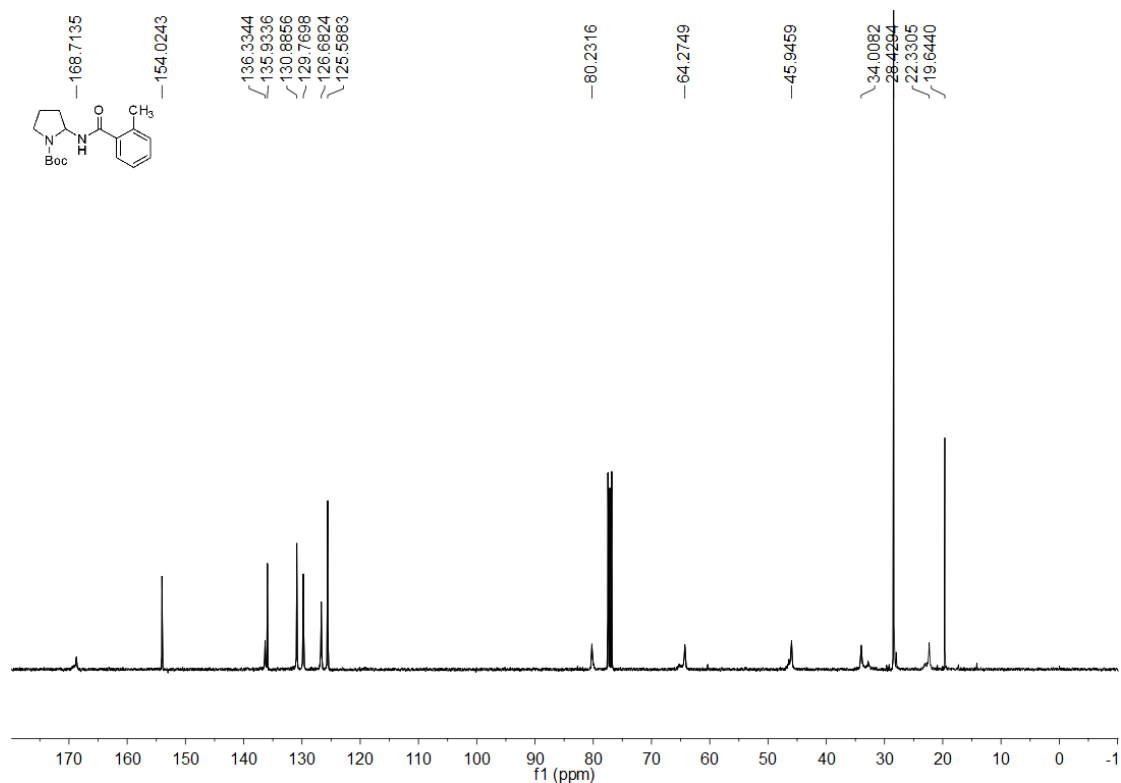
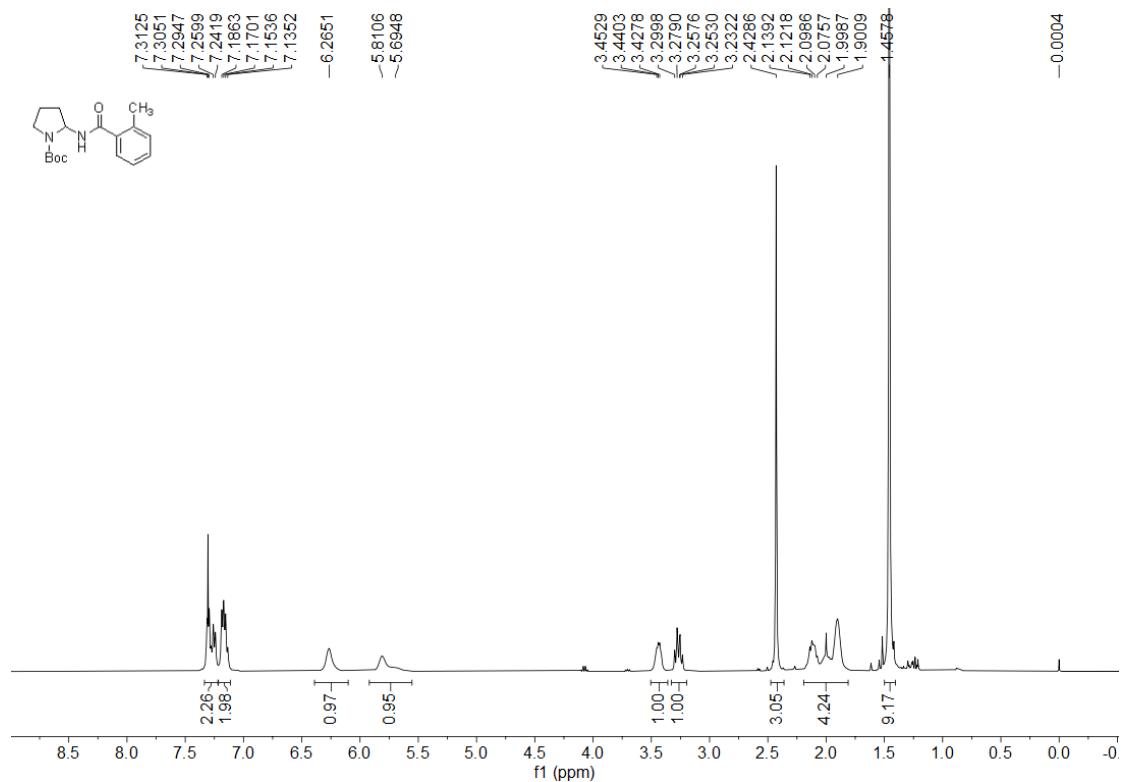
tert-Butyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**3a**)



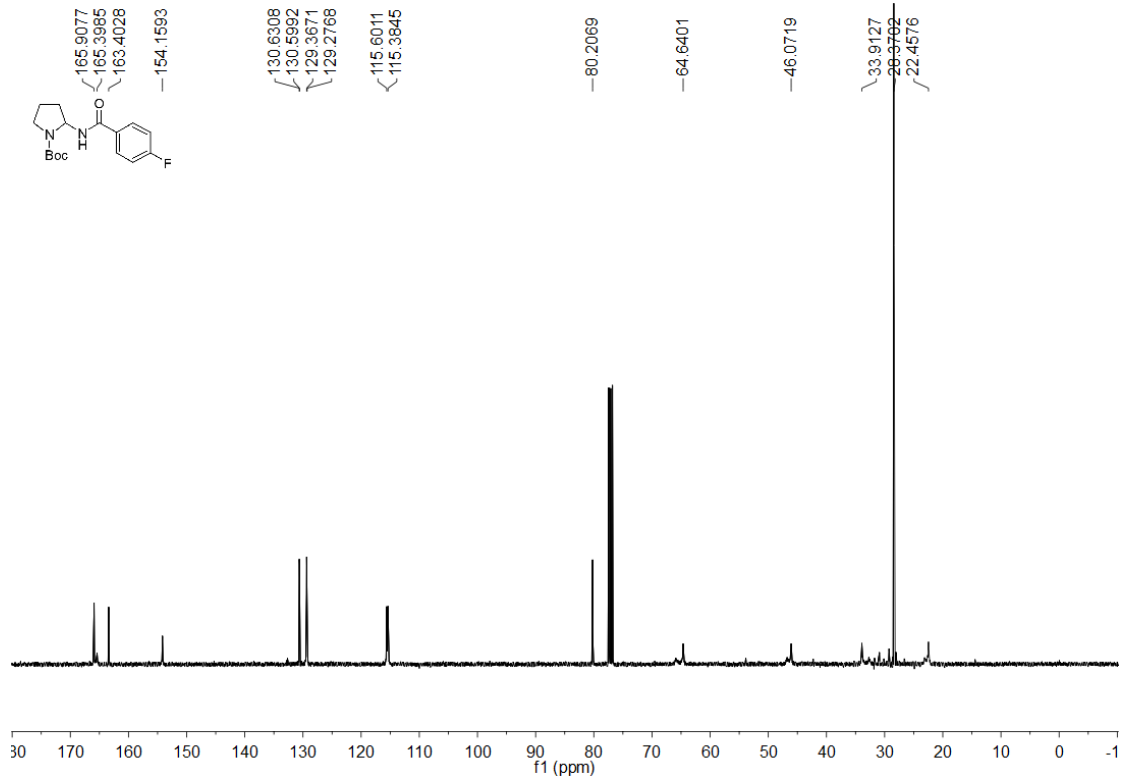
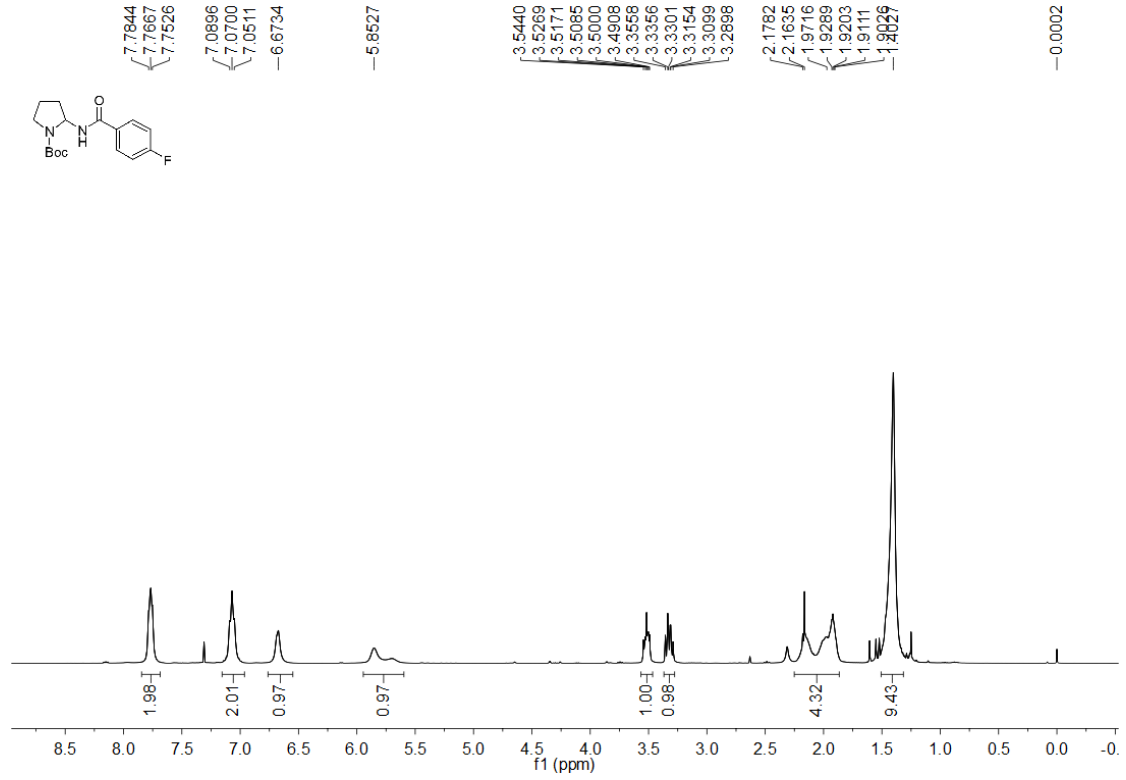
tert-Butyl 2-benzamidopyrrolidine-1-carboxylate (**3b**)

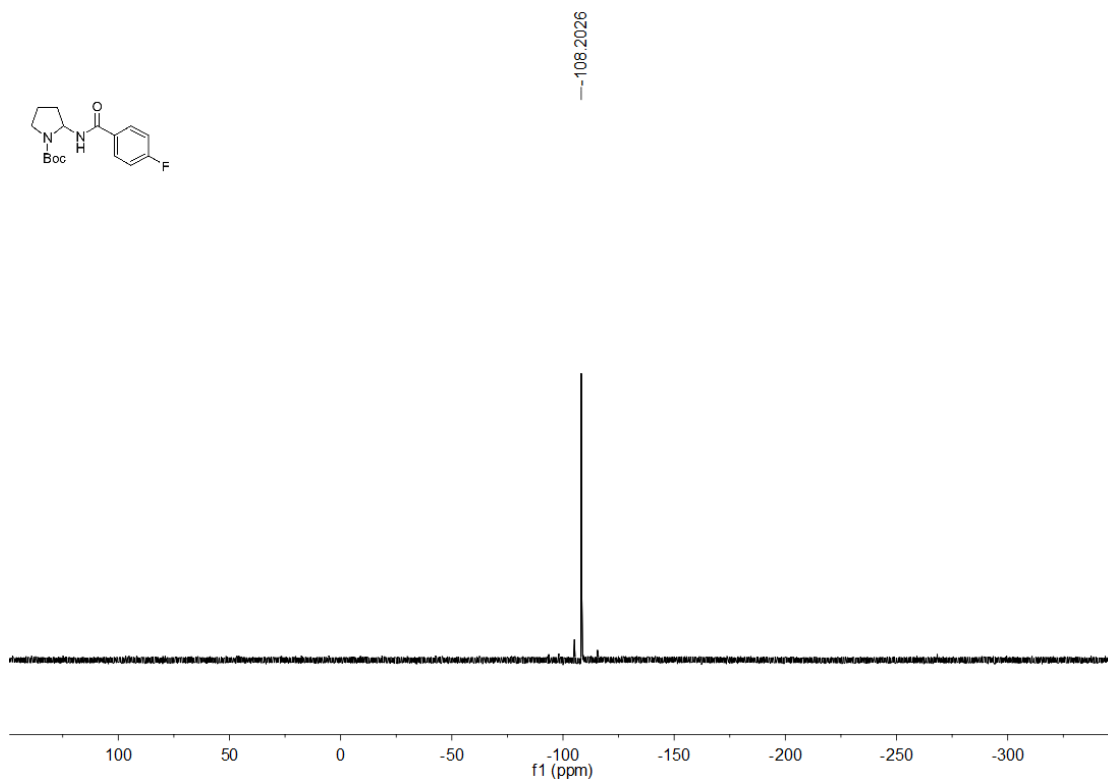
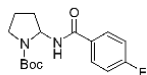


tert-Butyl 2-(2-methylbenzamido)pyrrolidine-1-carboxylate (**3c**)

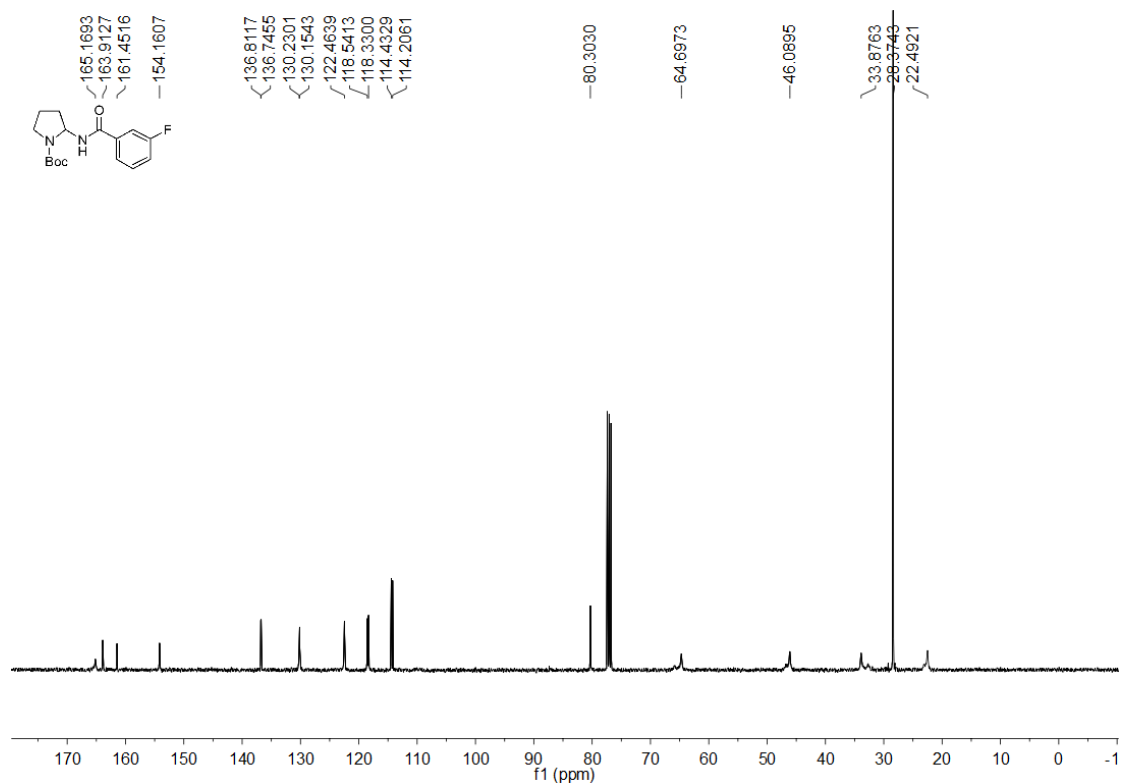
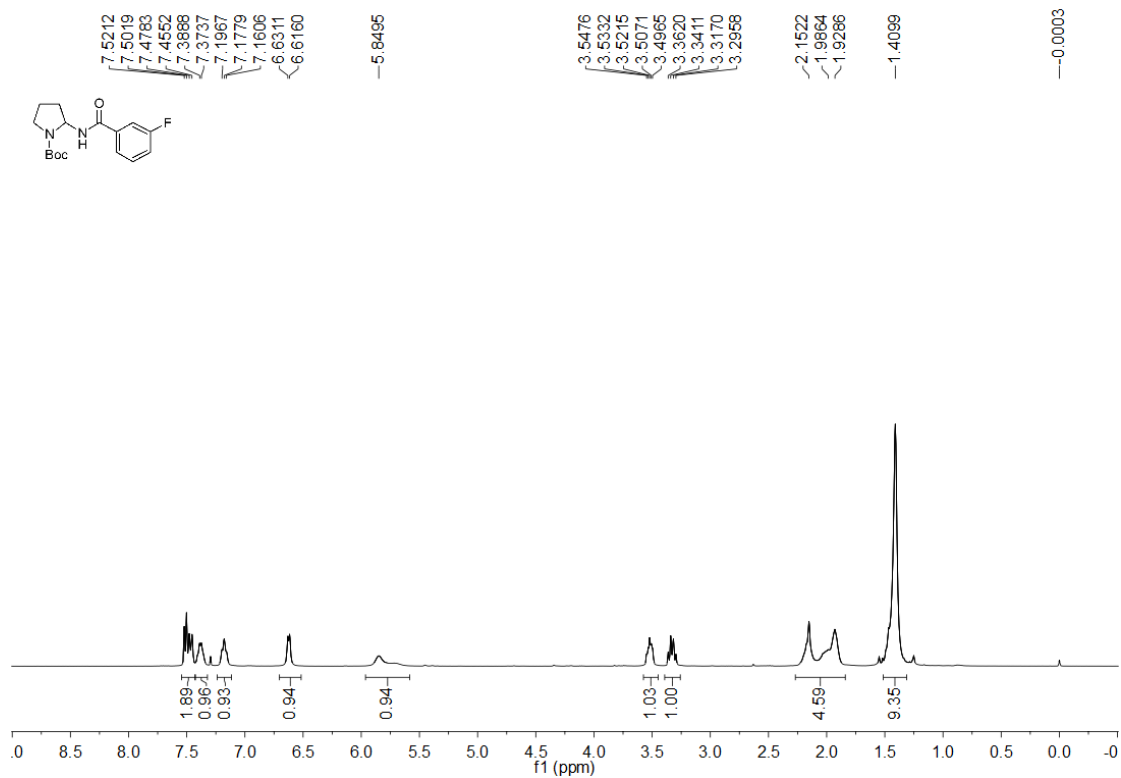


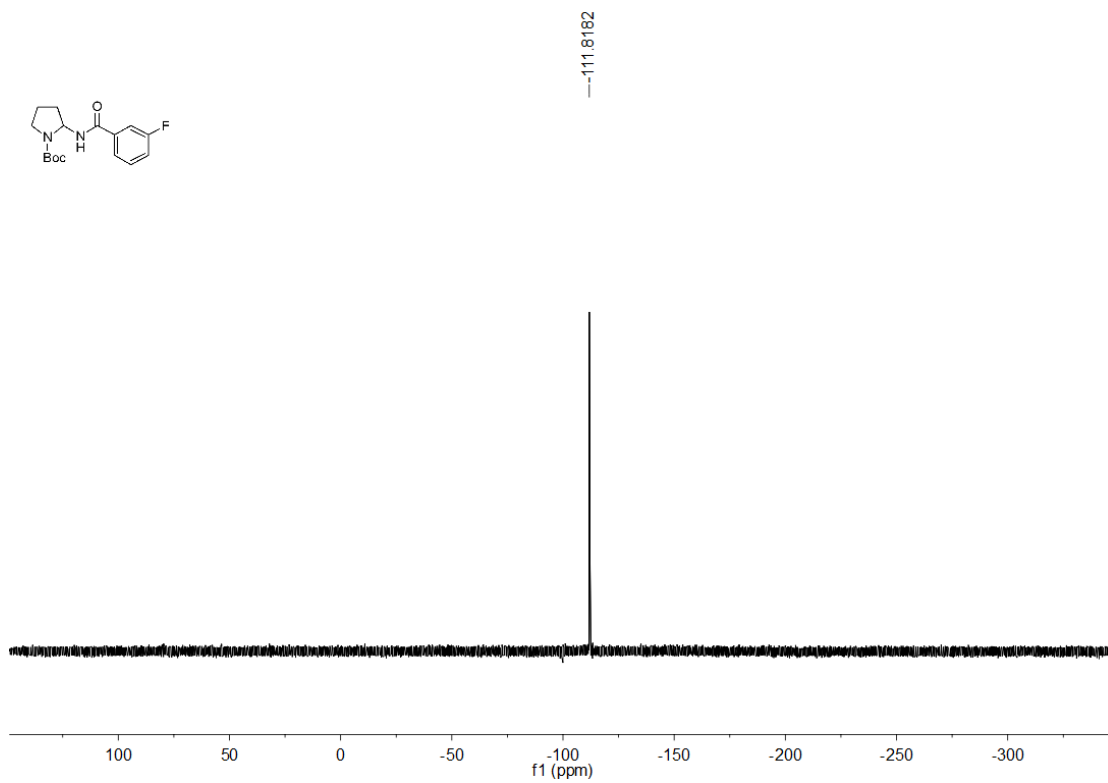
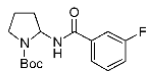
tert-Butyl 2-(4-fluorobenzamido)pyrrolidine-1-carboxylate (**3d**)



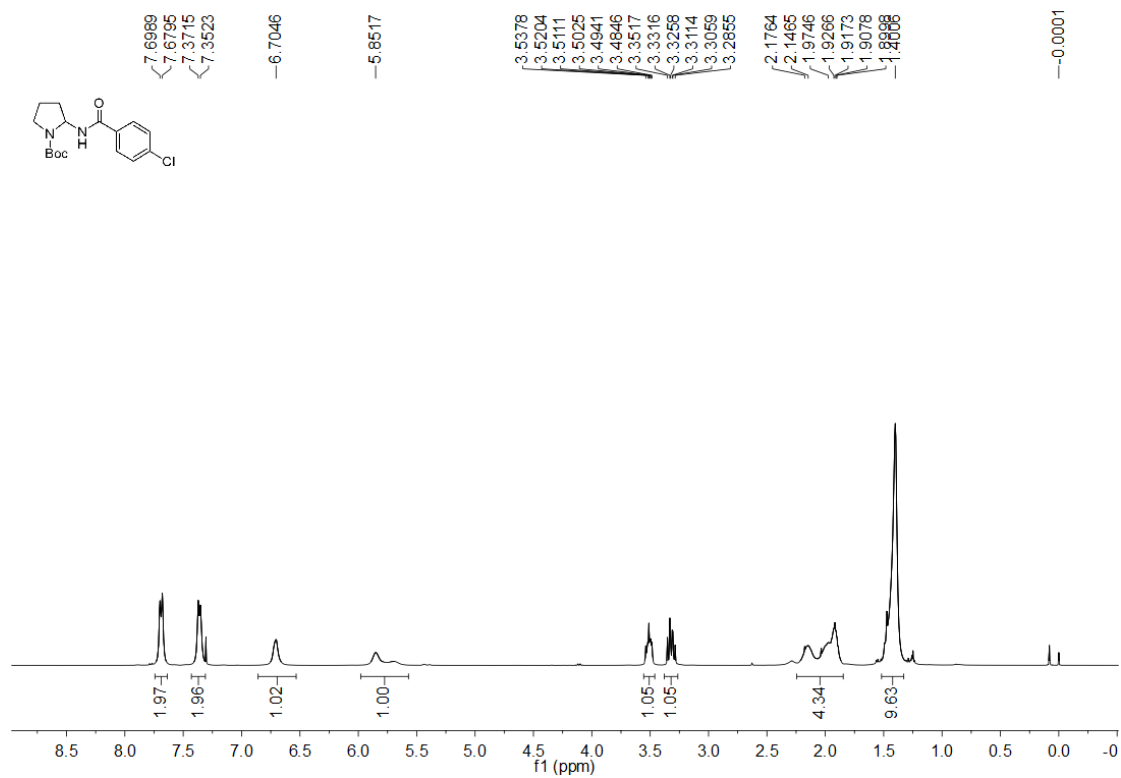


tert-Butyl 2-(3-fluorobenzamido)pyrrolidine-1-carboxylate (**3e**)

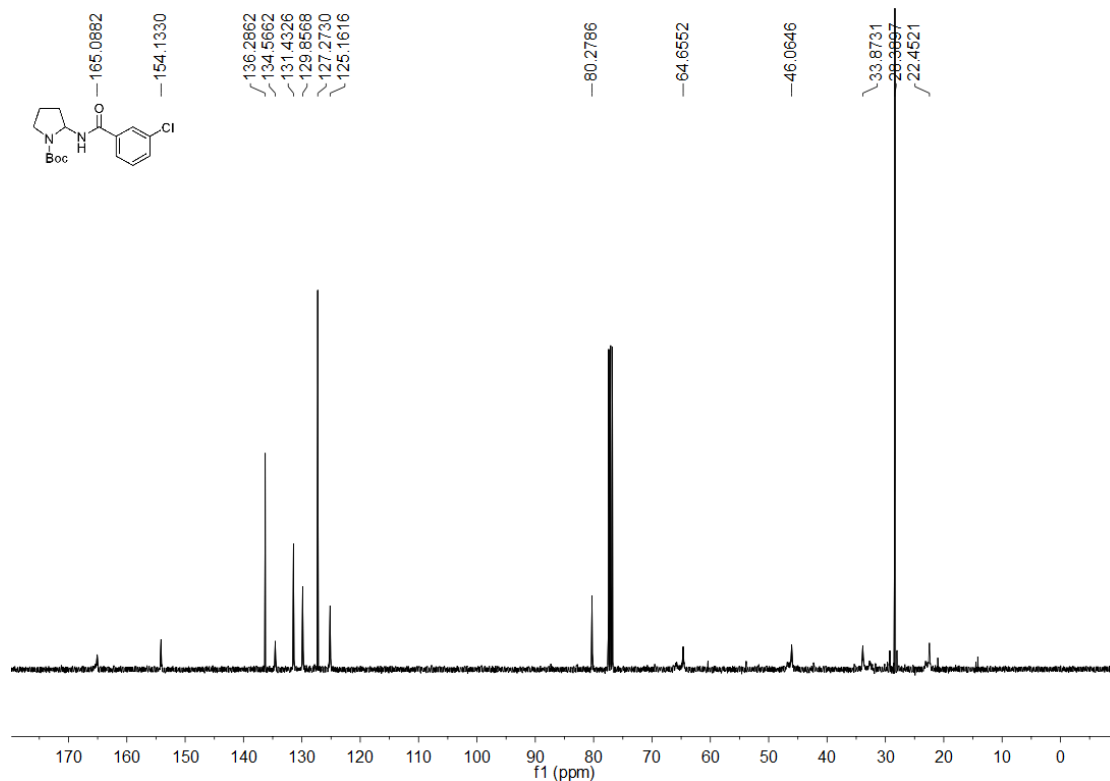
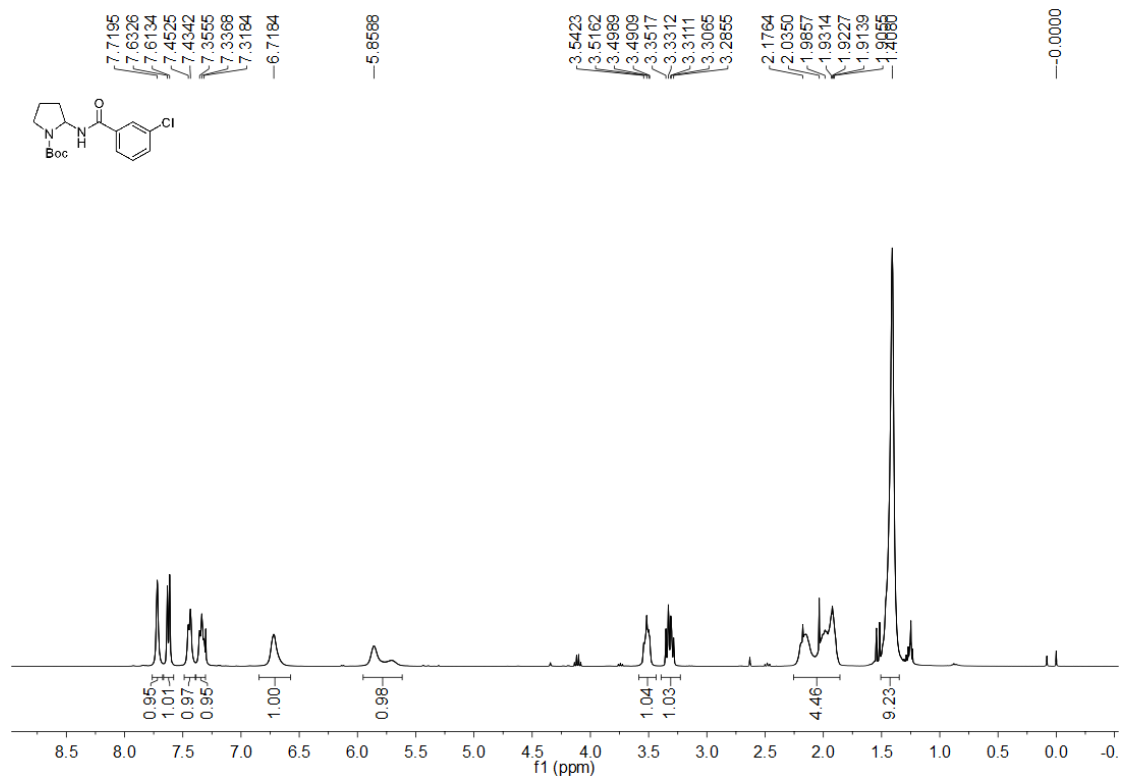




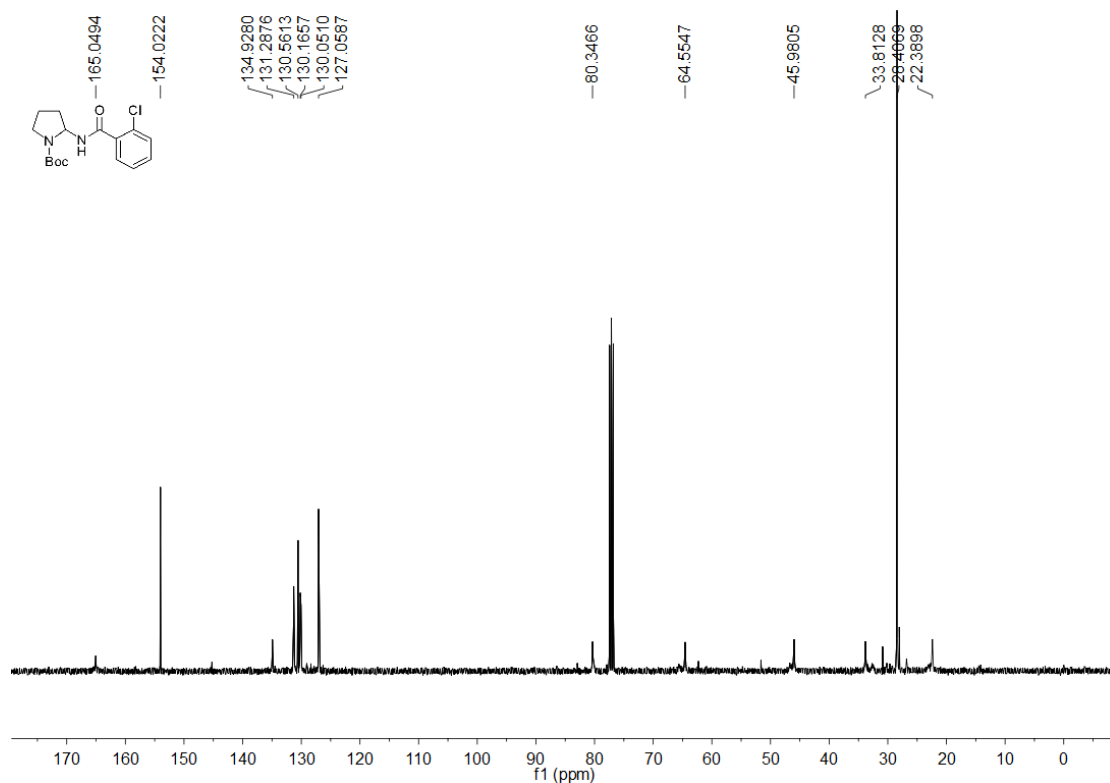
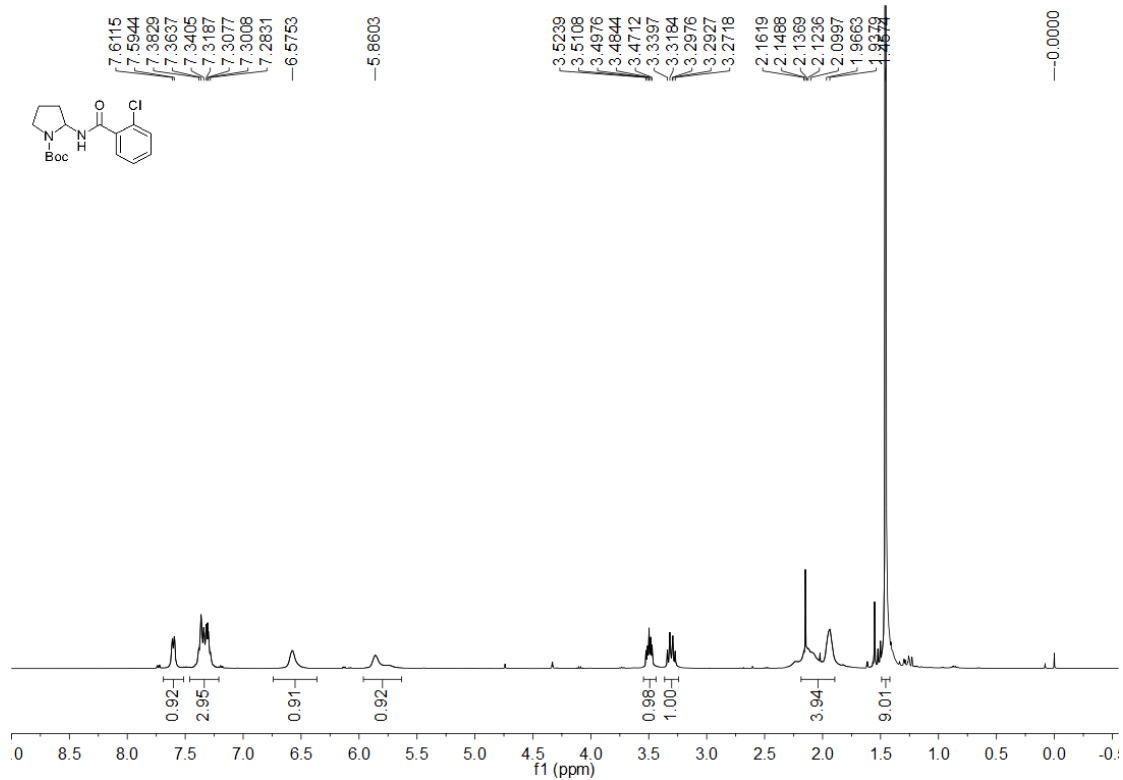
tert-Butyl 2-(4-chlorobenzamido)pyrrolidine-1-carboxylate (**3f**)



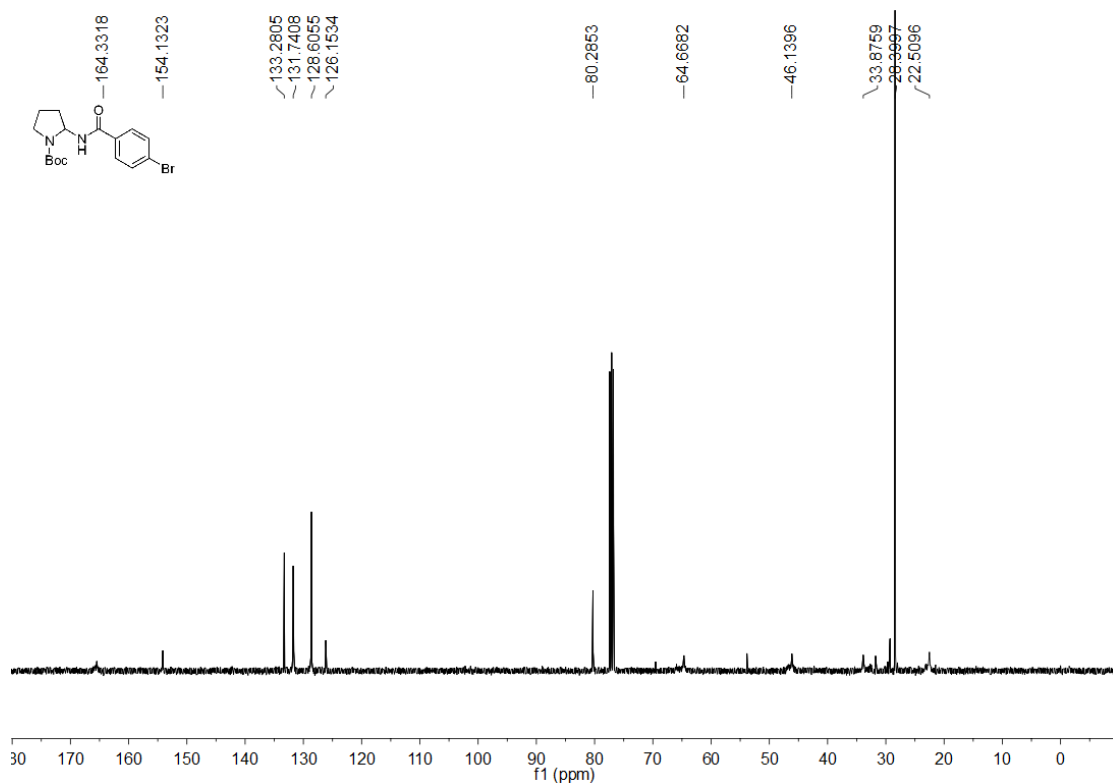
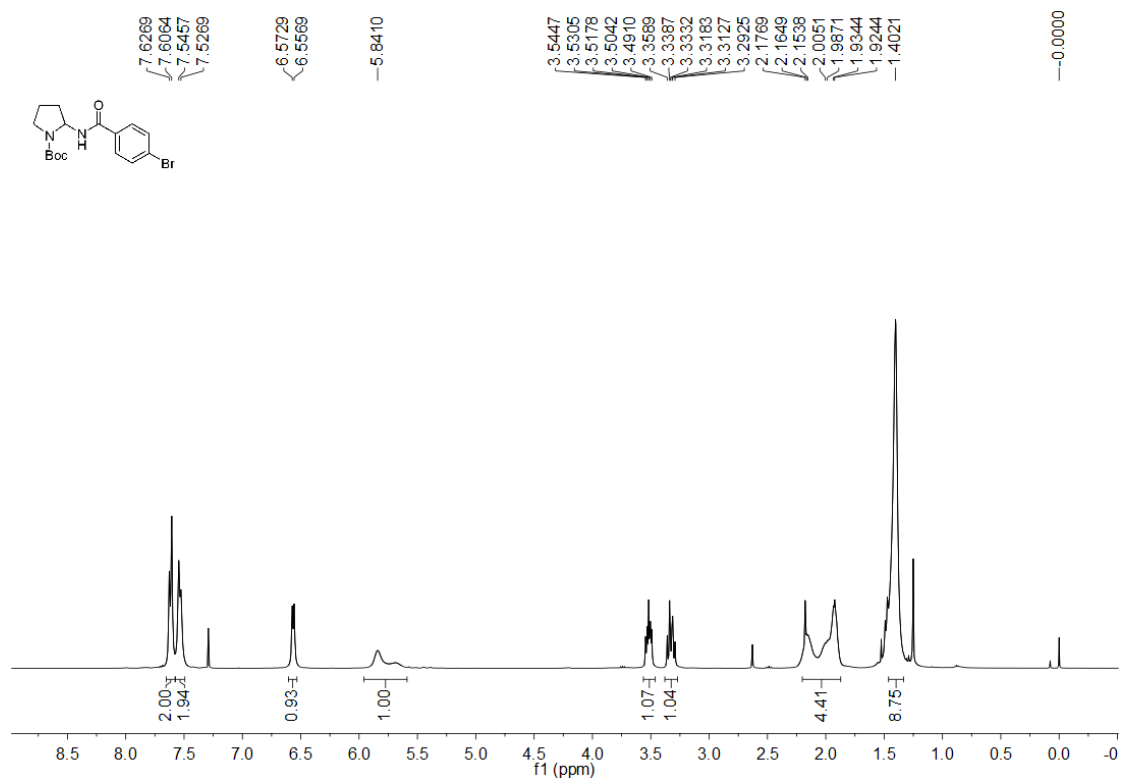
tert-Butyl 2-(3-chlorobenzamido)pyrrolidine-1-carboxylate (**3g**)



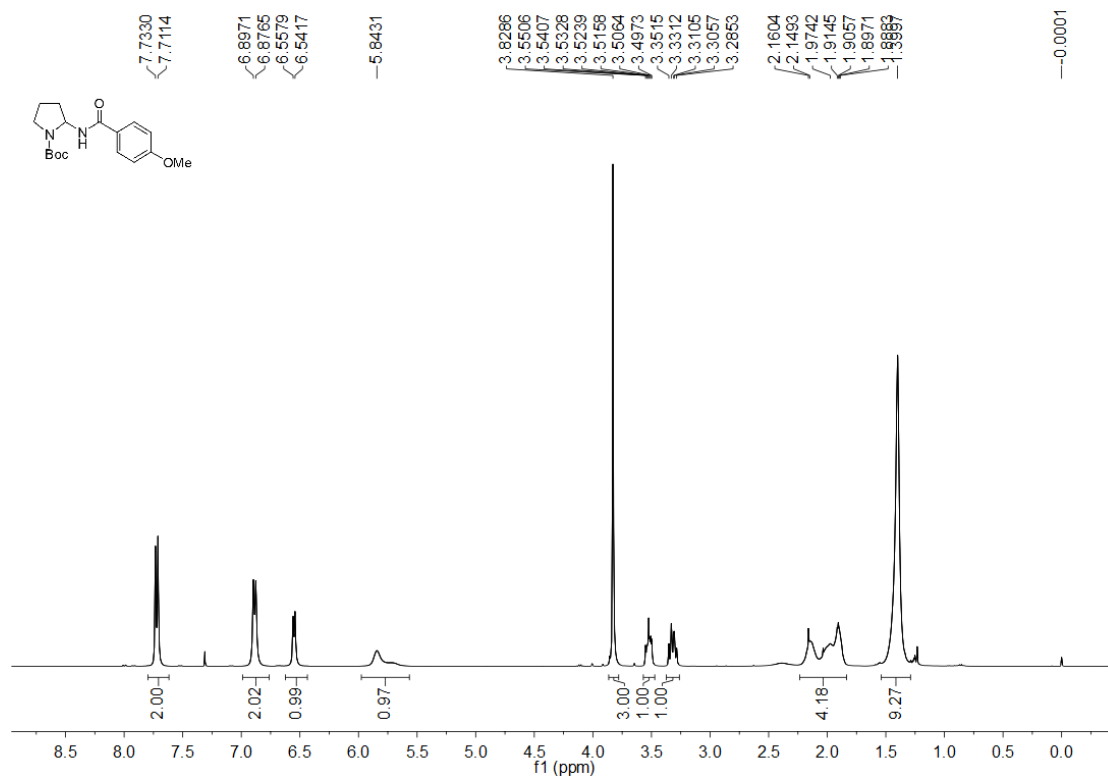
tert-Butyl 2-(2-chlorobenzamido)pyrrolidine-1-carboxylate (**3h**)



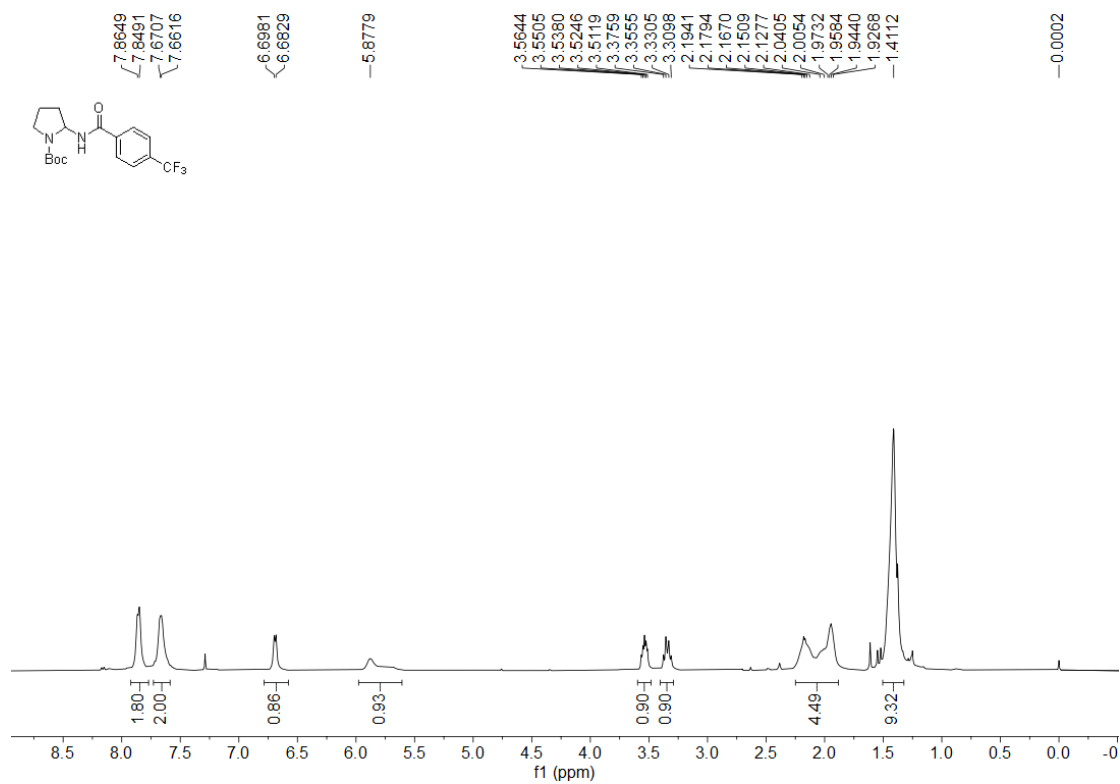
tert-Butyl 2-(4-bromobenzamido)pyrrolidine-1-carboxylate (**3i**)



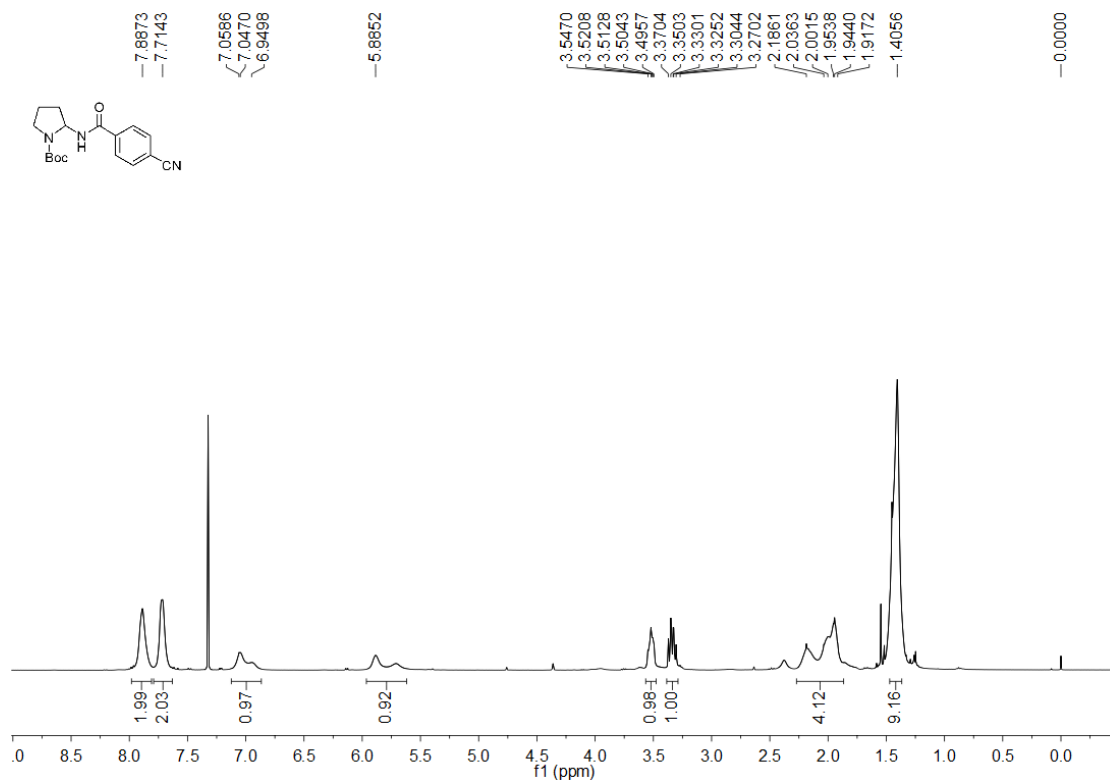
tert-Butyl 2-(4-methoxybenzamido)pyrrolidine-1-carboxylate (**3j**)



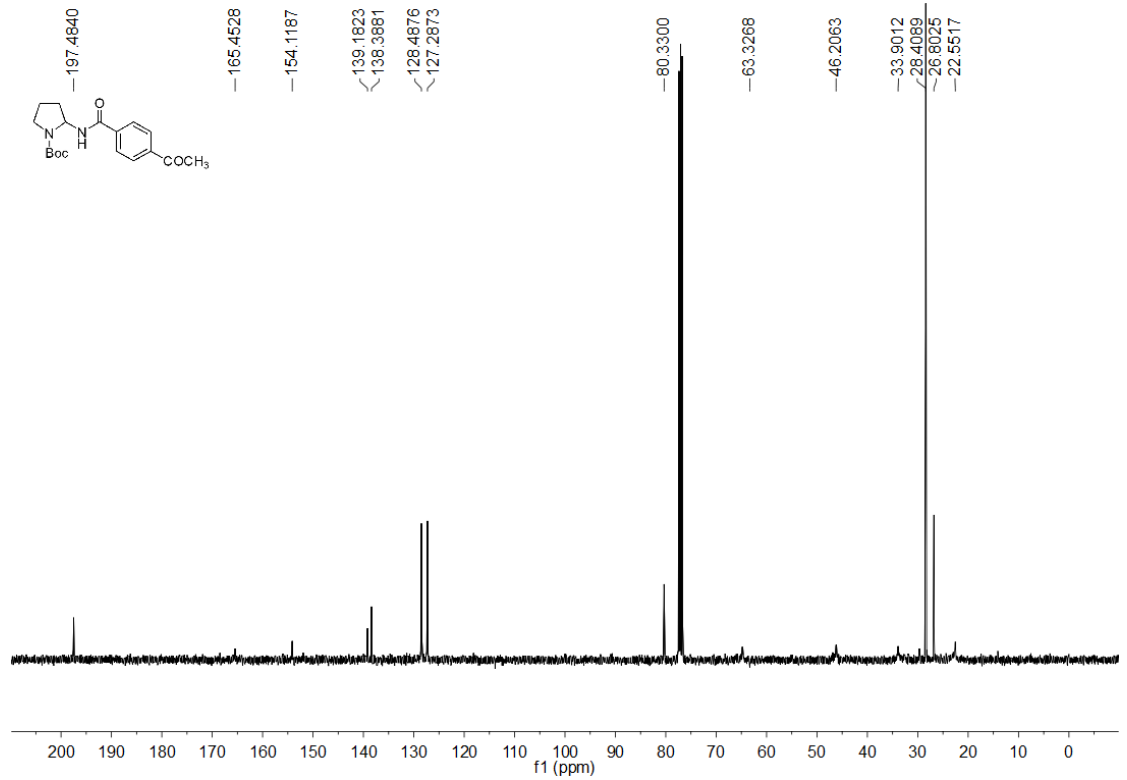
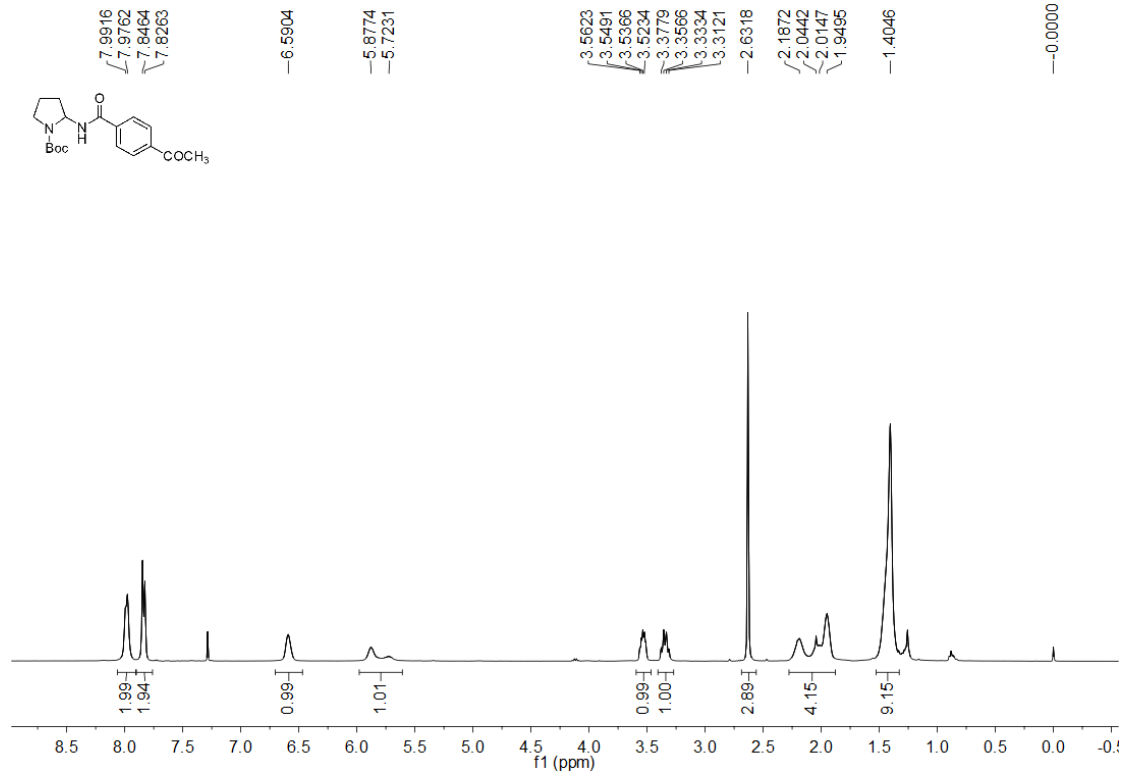
tert-Butyl 2-(4-(trifluoromethyl)benzamido)pyrrolidine-1-carboxylate (**3k**)



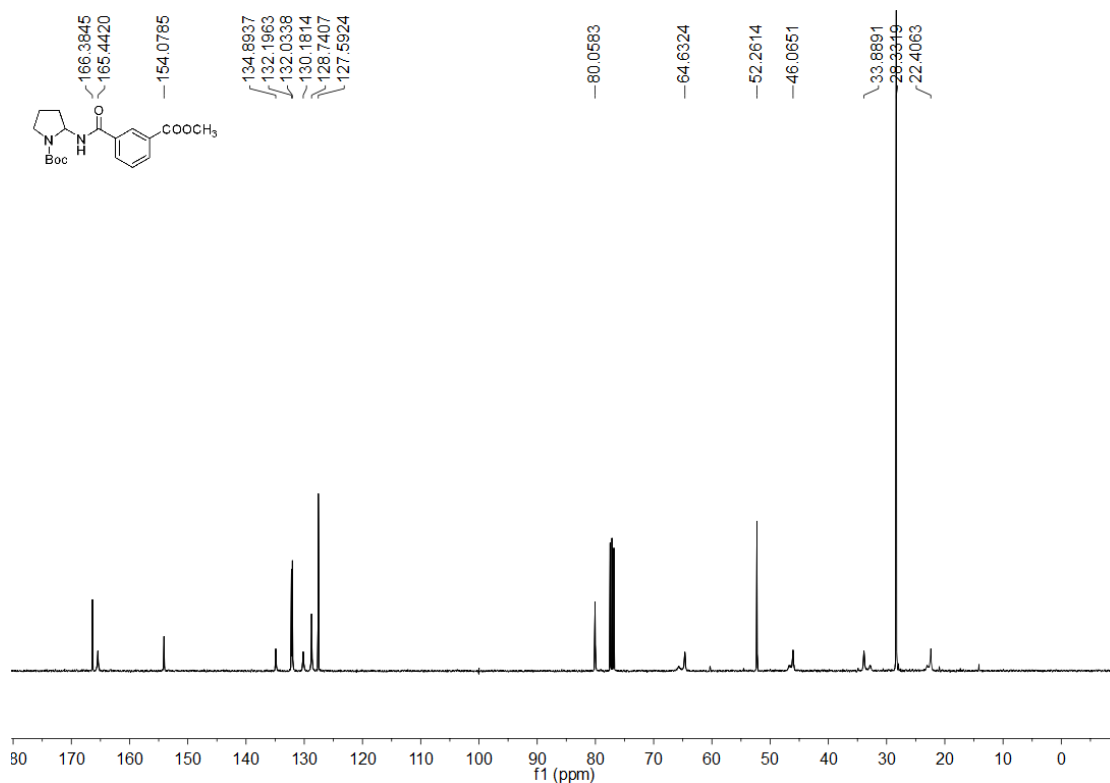
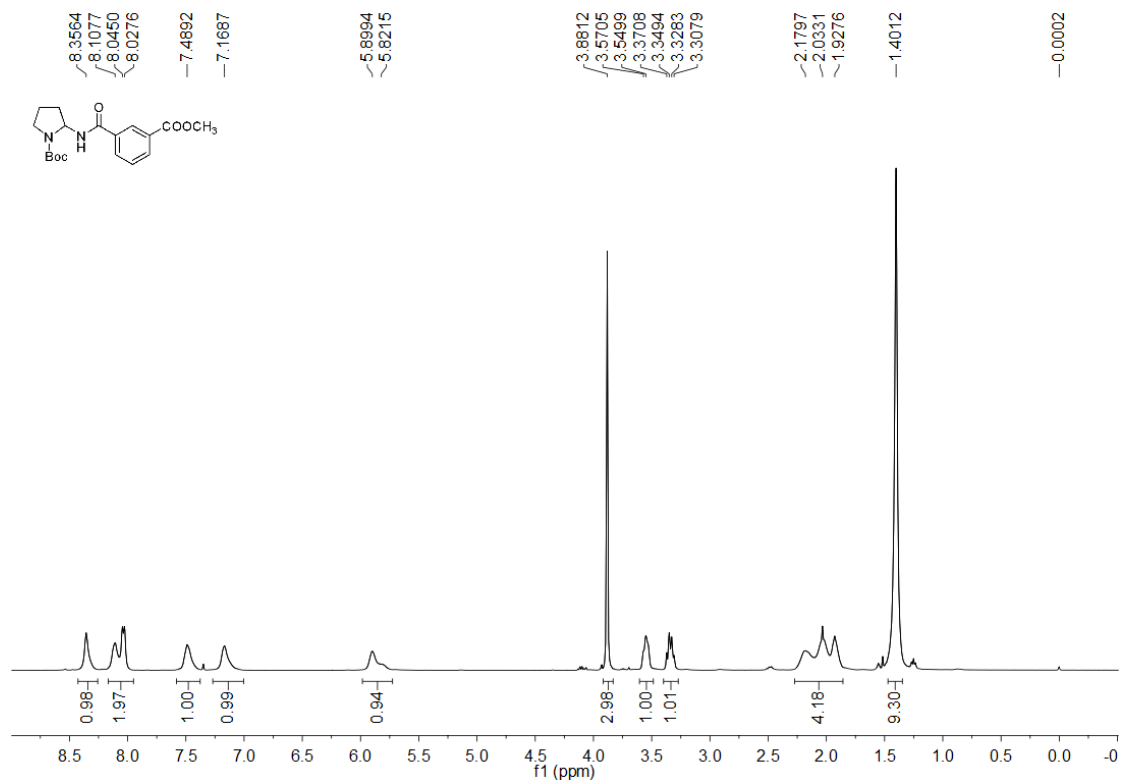
tert-Butyl 2-(4-cyanobenzamido)pyrrolidine-1-carboxylate (**31**)



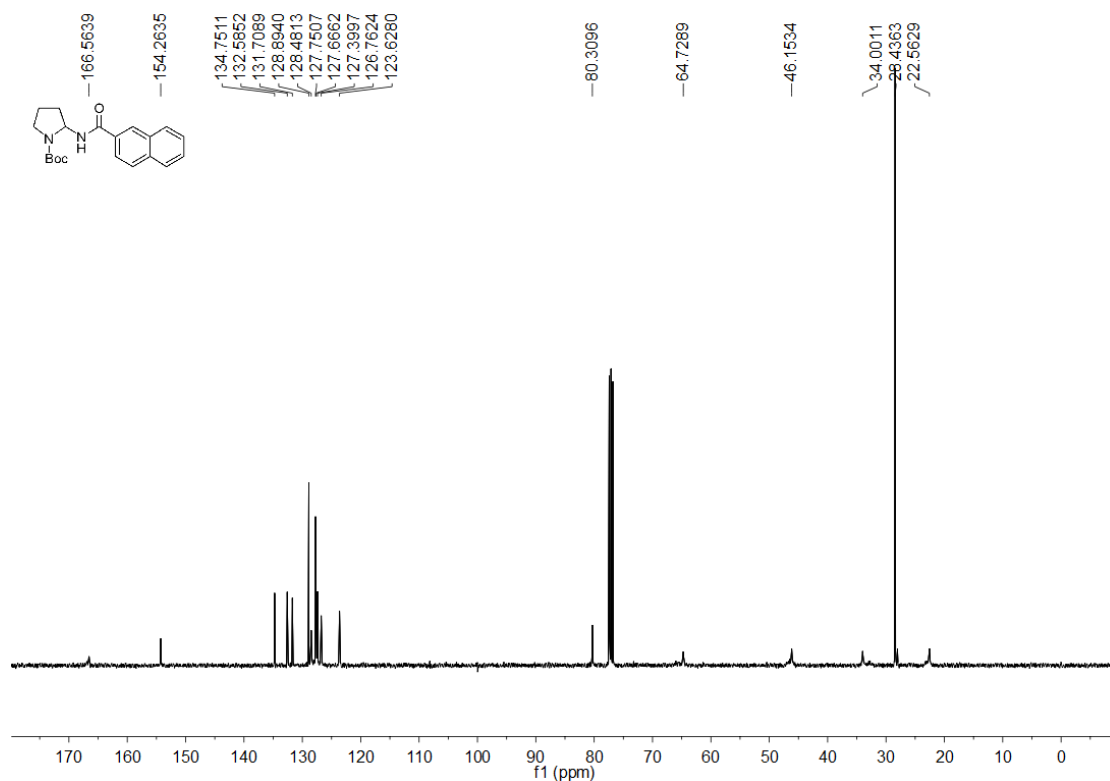
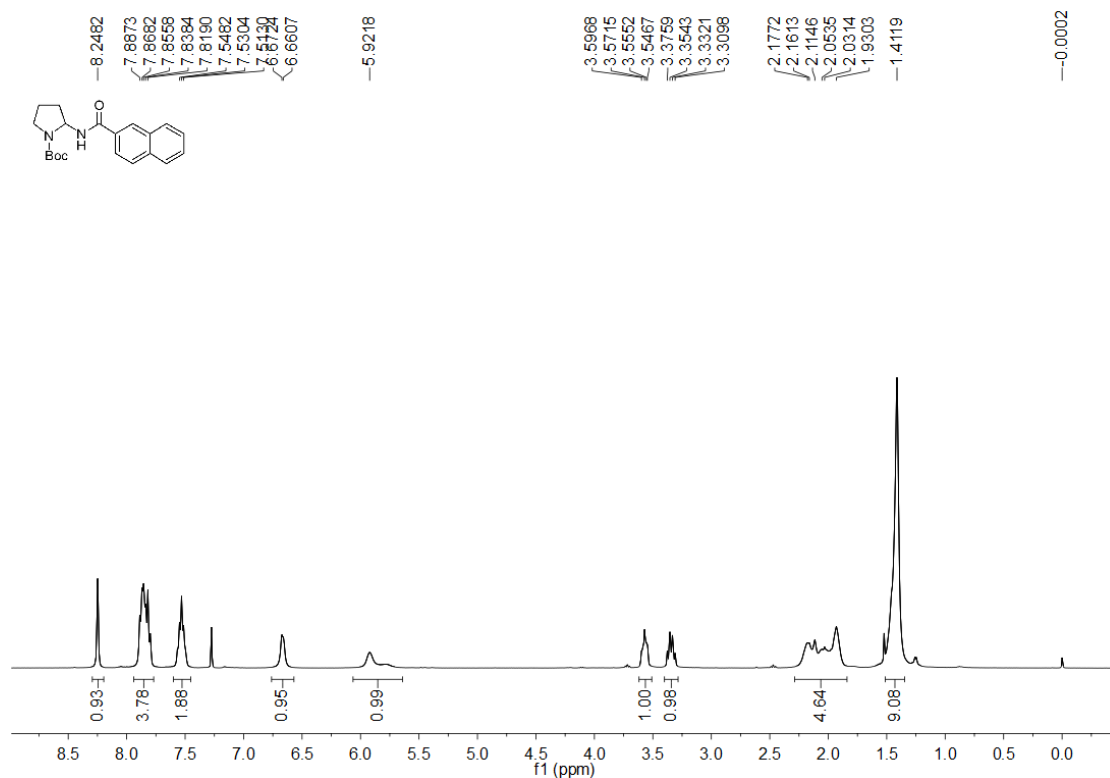
tert-Butyl 2-(4-acetylbenzamido)pyrrolidine-1-carboxylate (**3m**)



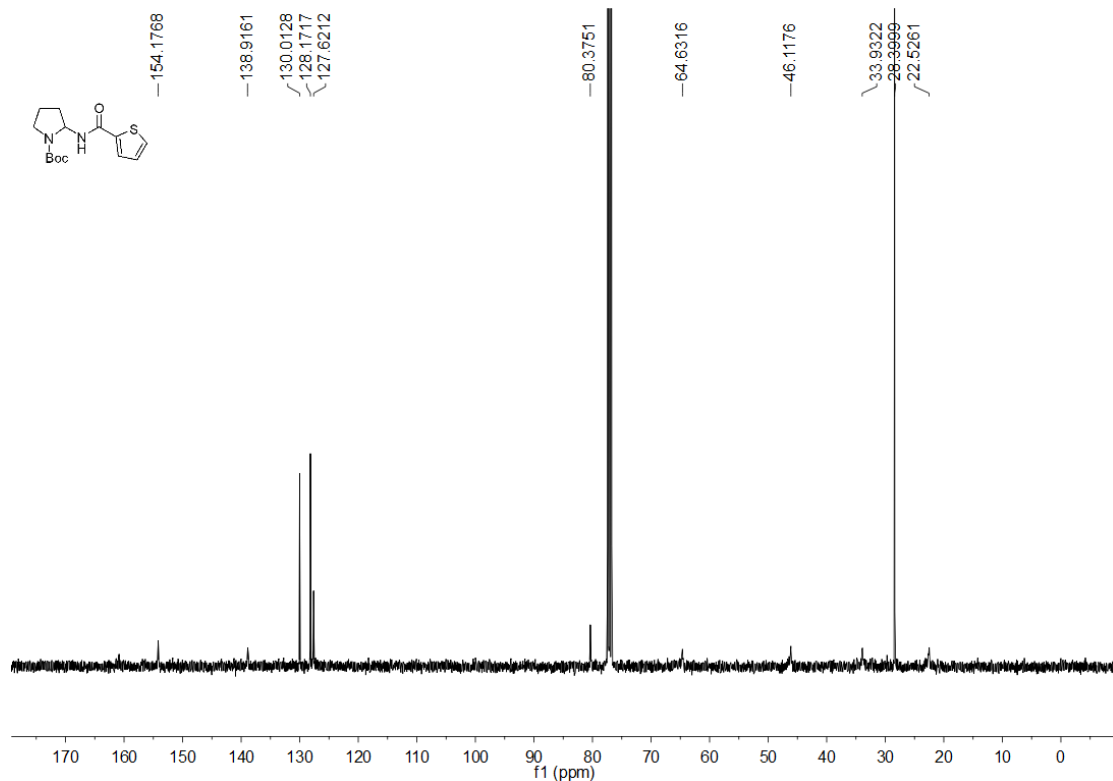
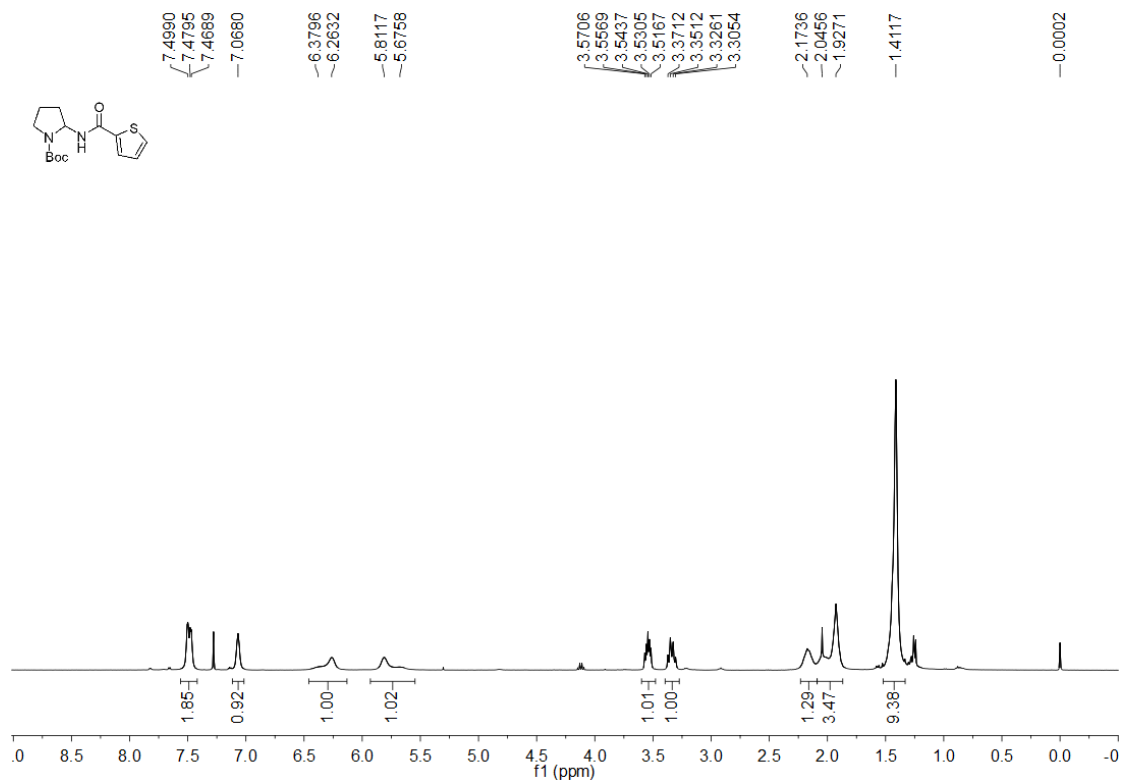
tert-Butyl 2-(3-(methoxycarbonyl)benzamido)pyrrolidine-1-carboxylate (**3n**)



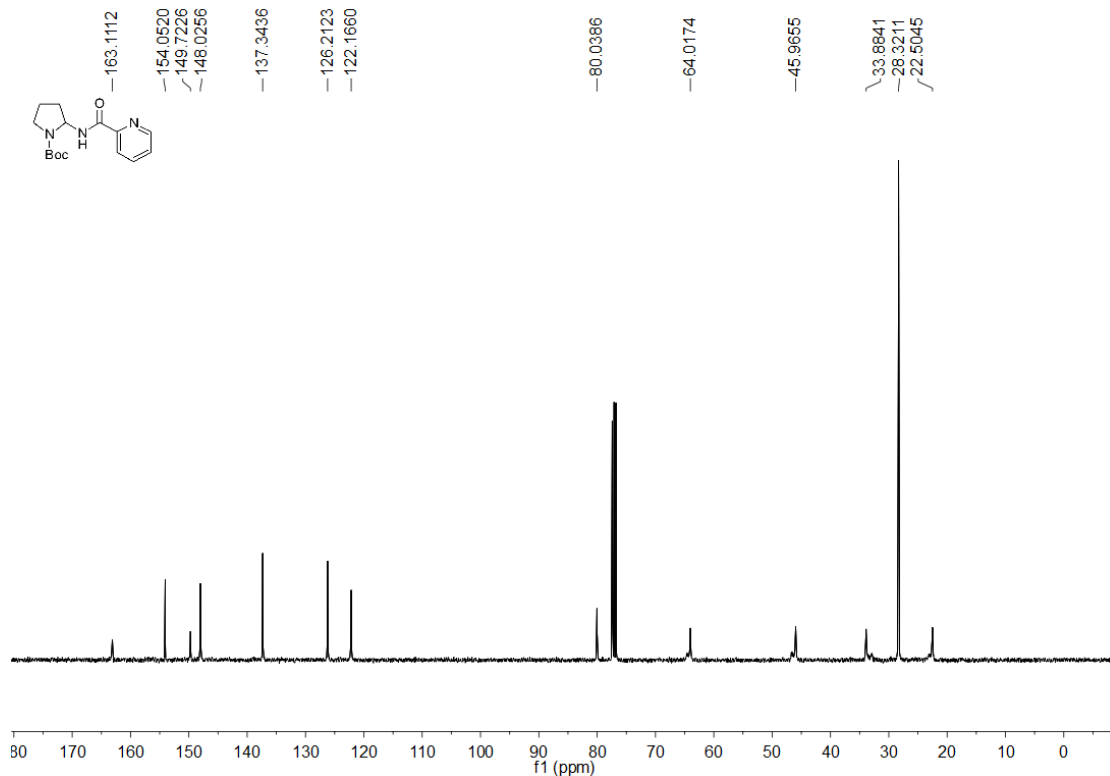
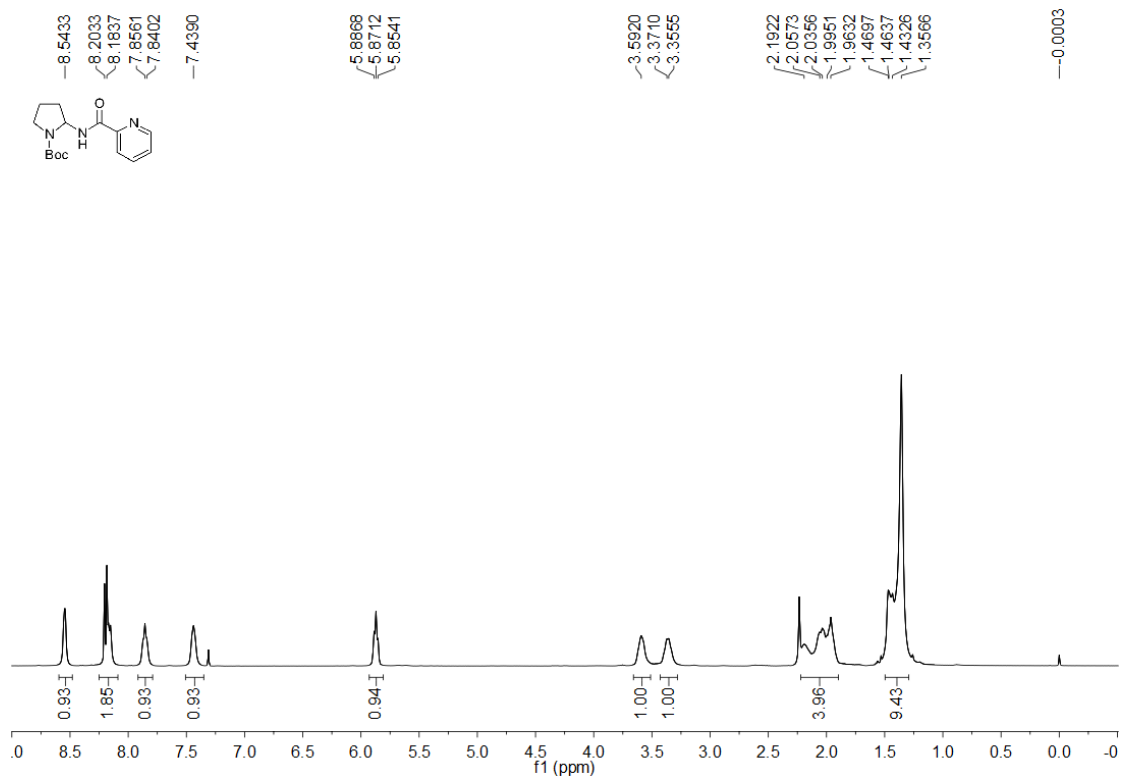
tert-Butyl 2-(2-naphthamido)pyrrolidine-1-carboxylate (**30**)



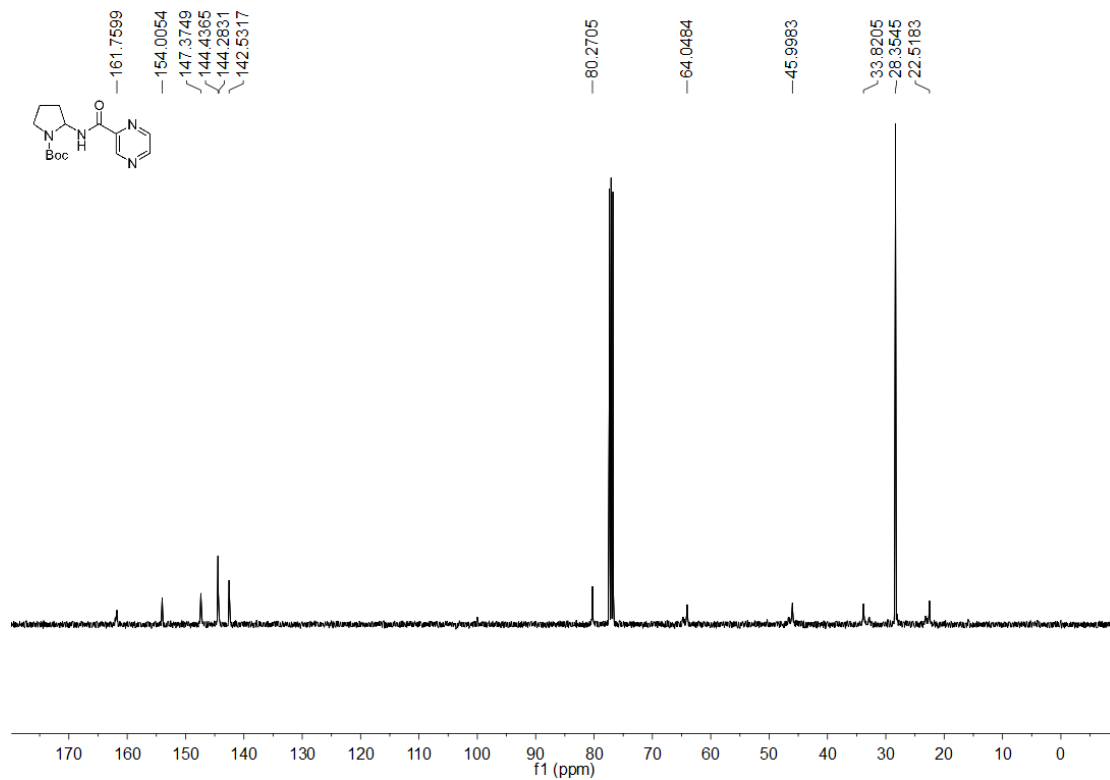
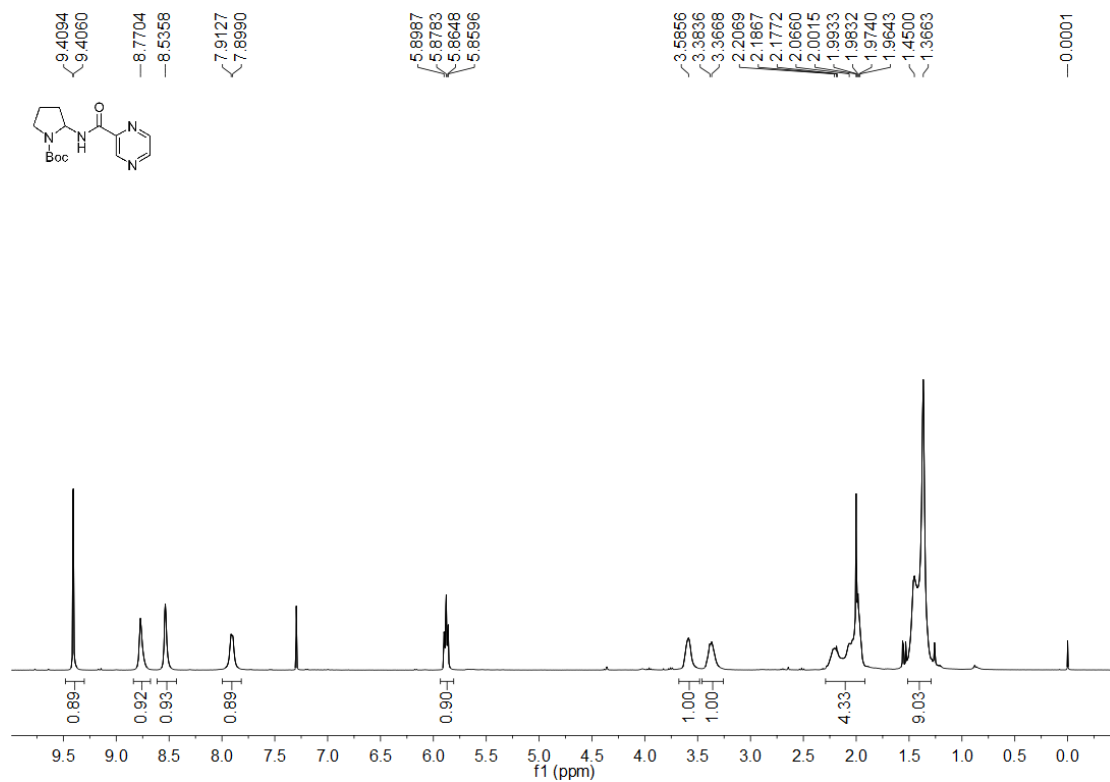
tert-Butyl 2-(thiophene-2-carboxamido)pyrrolidine-1-carboxylate (**3p**)



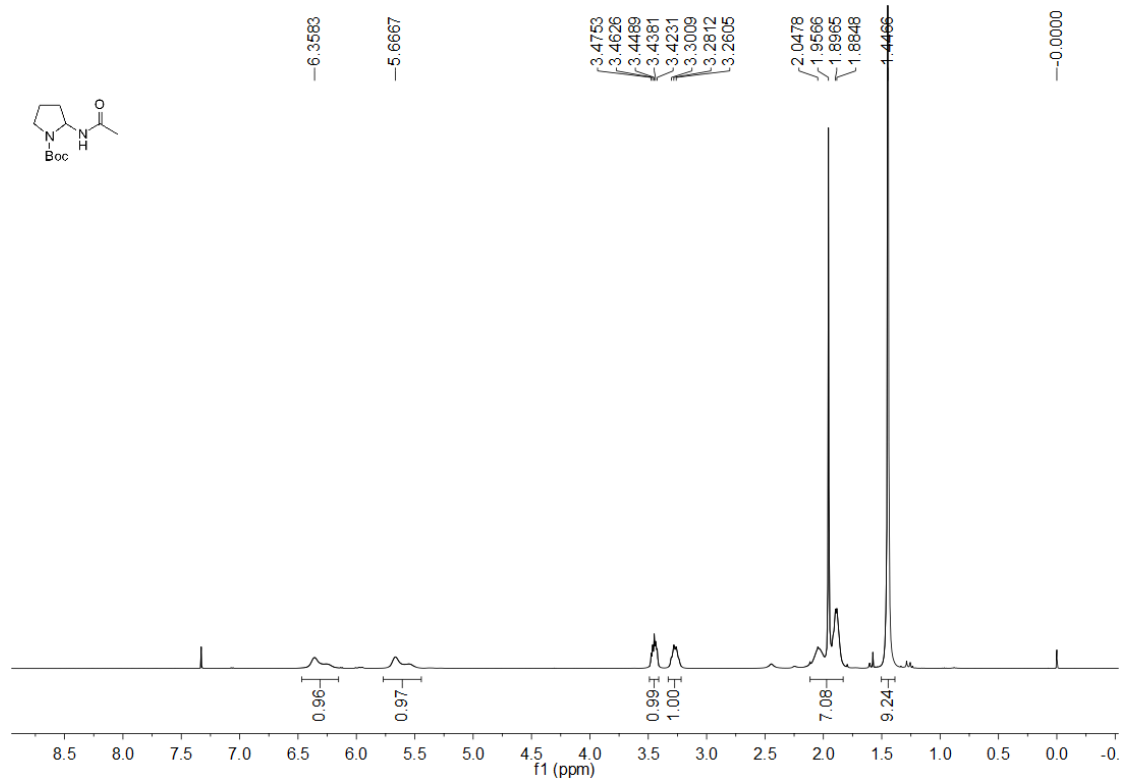
tert-Butyl 2-(picolinamido)pyrrolidine-1-carboxylate (**3q**)



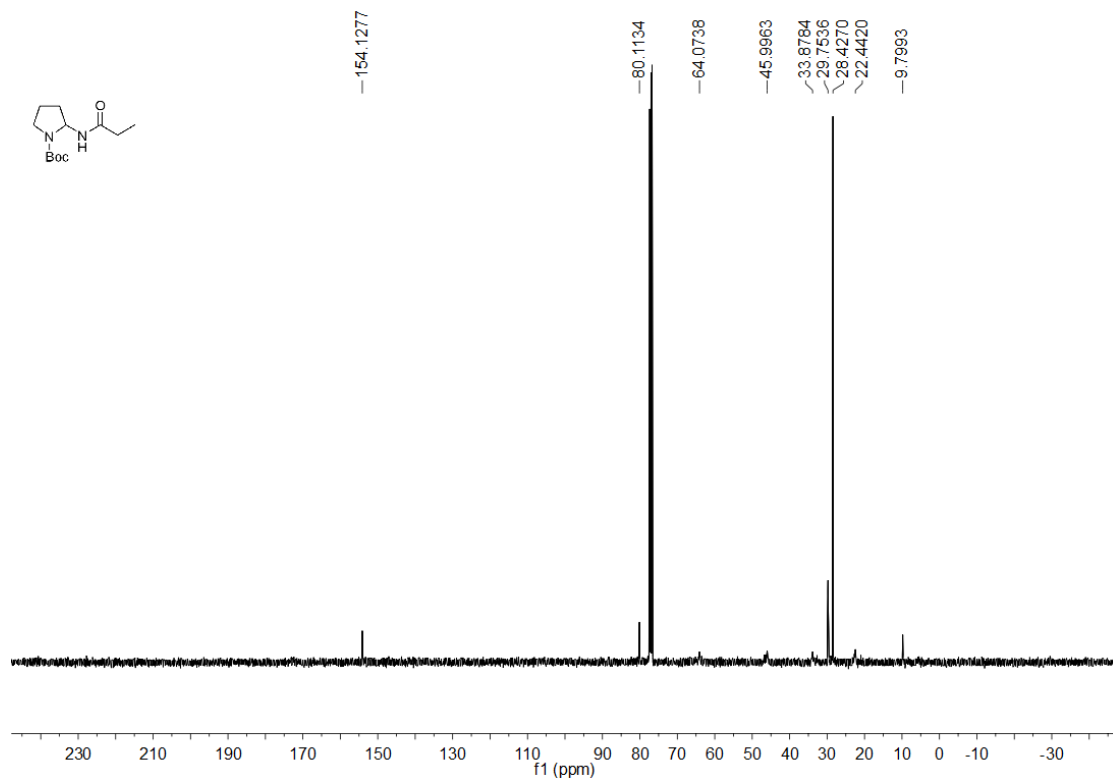
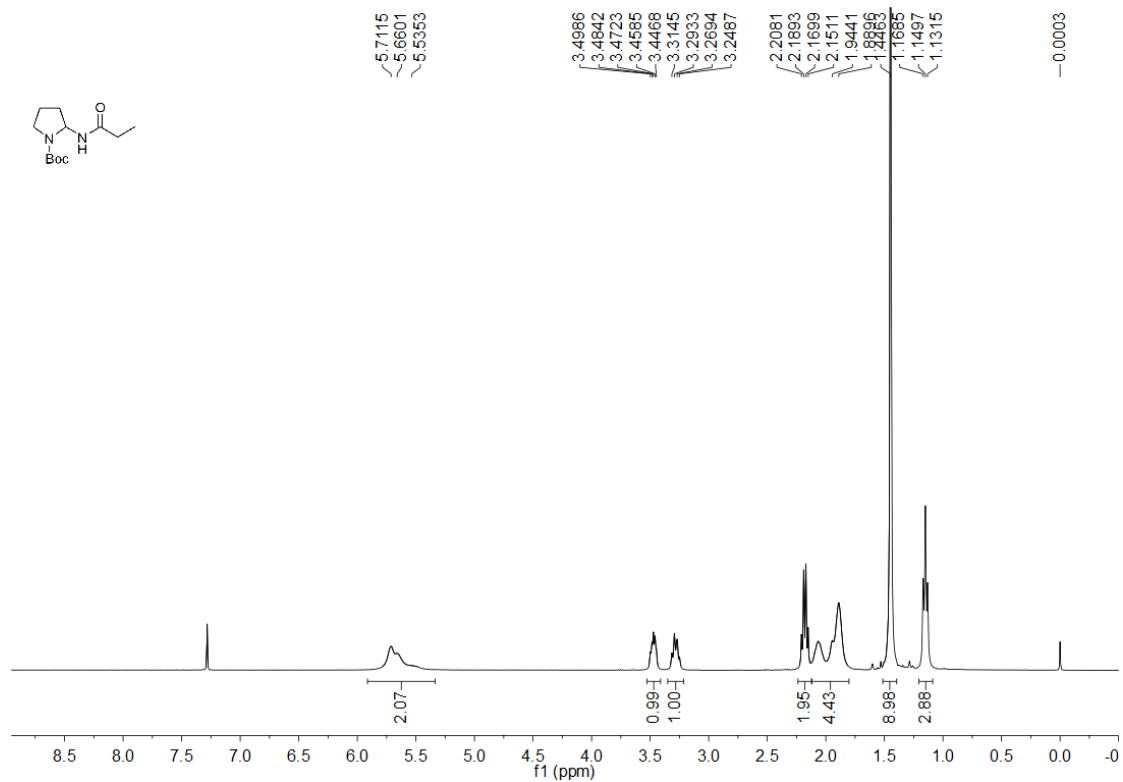
tert-Butyl 2-(pyrazine-2-carboxamido)pyrrolidine-1-carboxylate (**3r**)



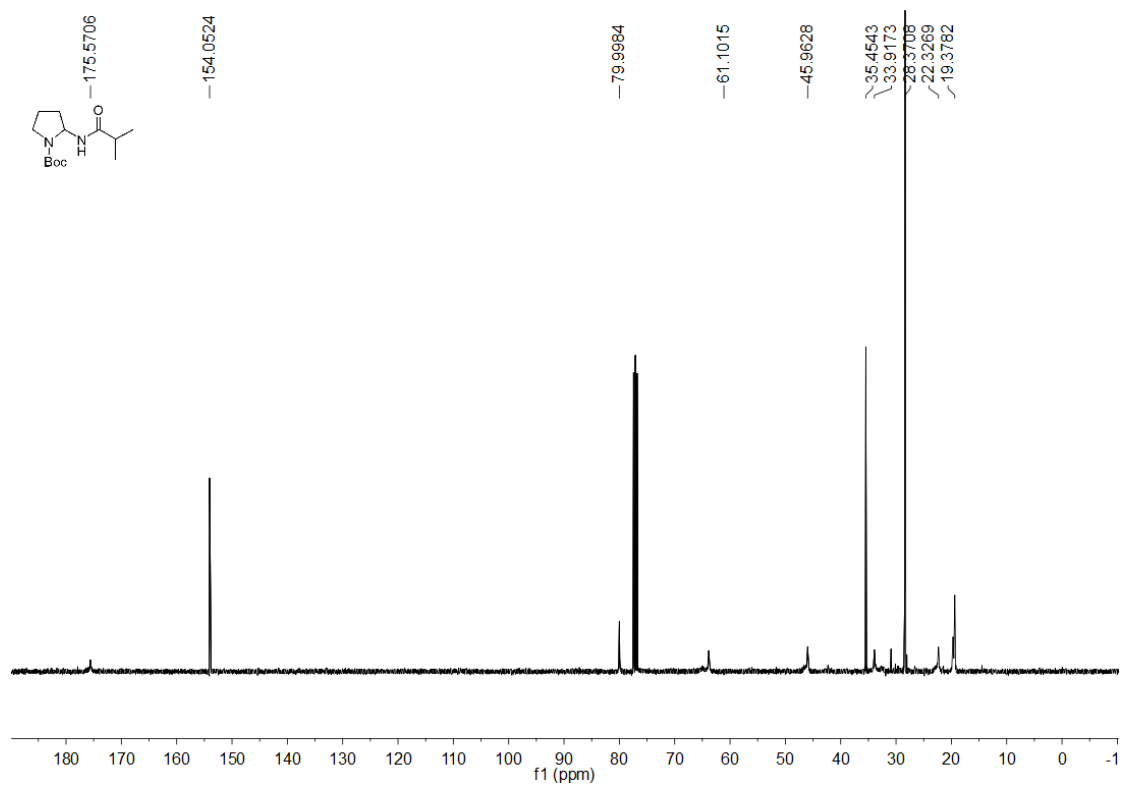
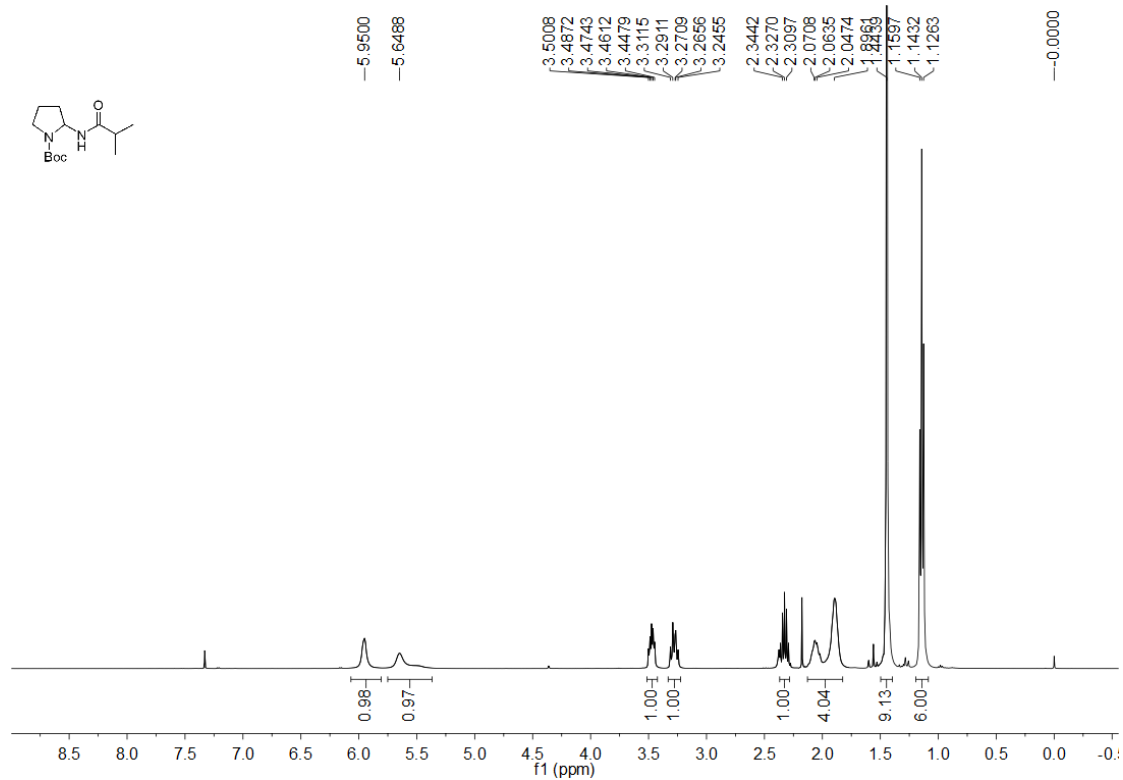
tert-Butyl 2-acetamidopyrrolidine-1-carboxylate (**3s**)



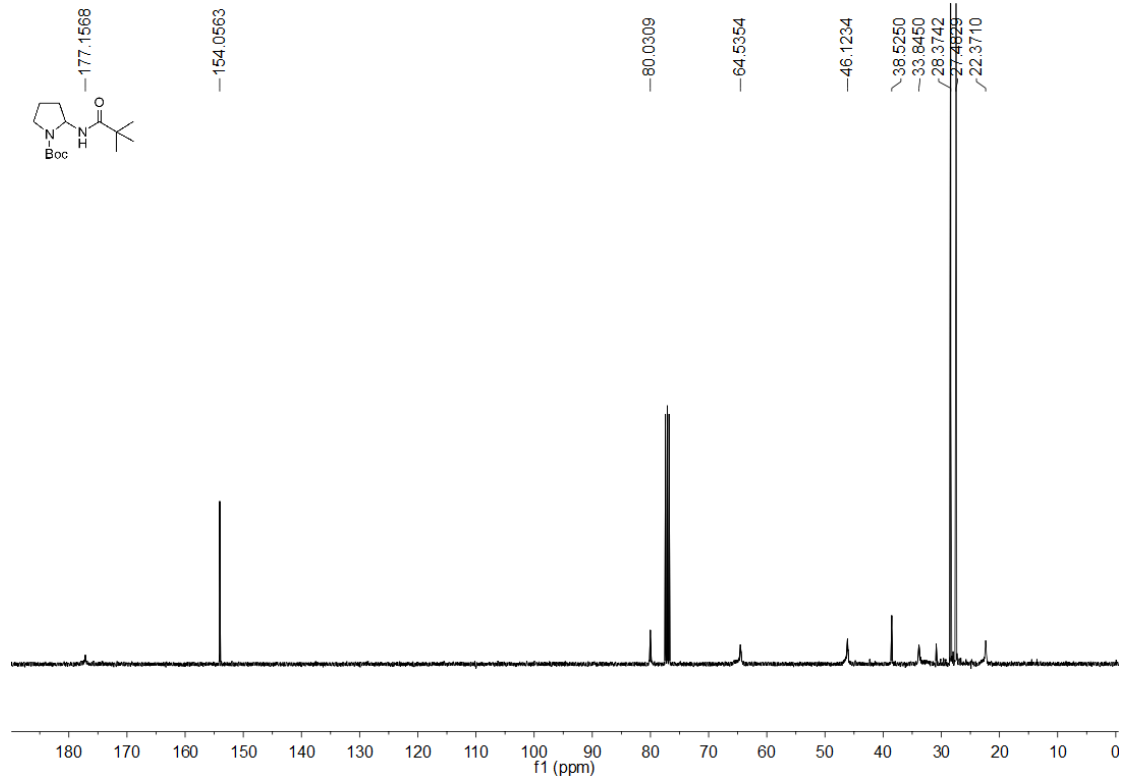
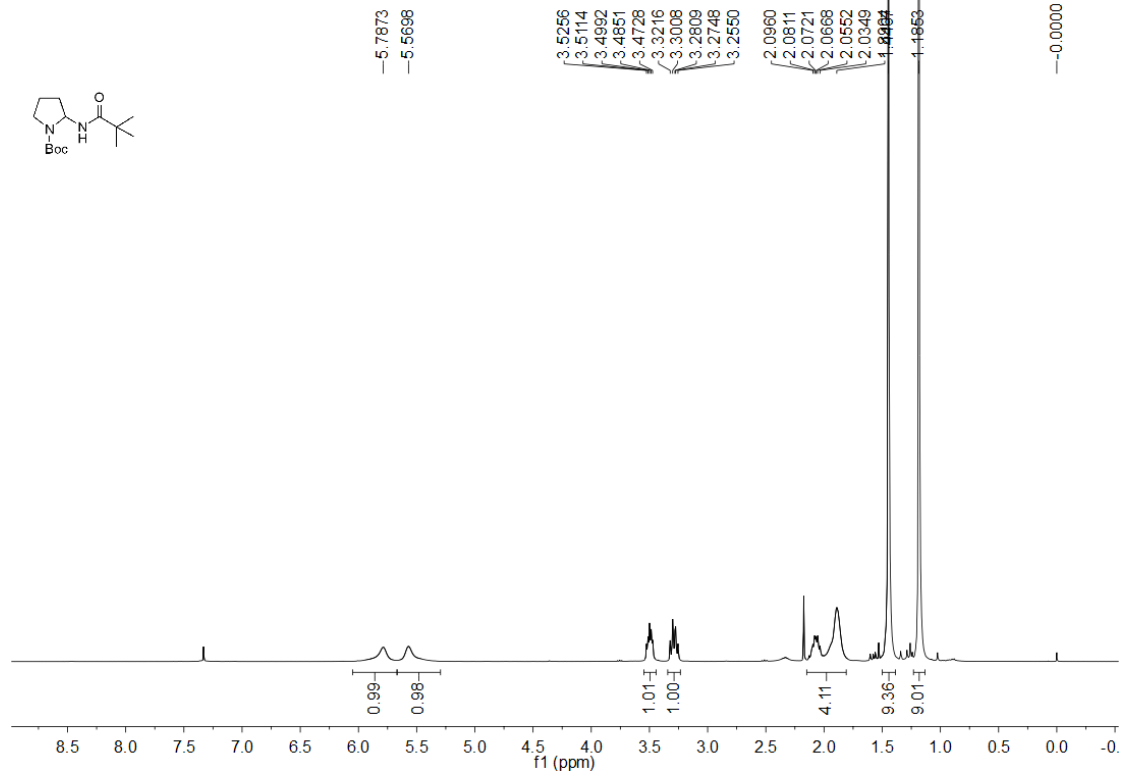
tert-butyl 2-propionamidopyrrolidine-1-carboxylate (**3t**)



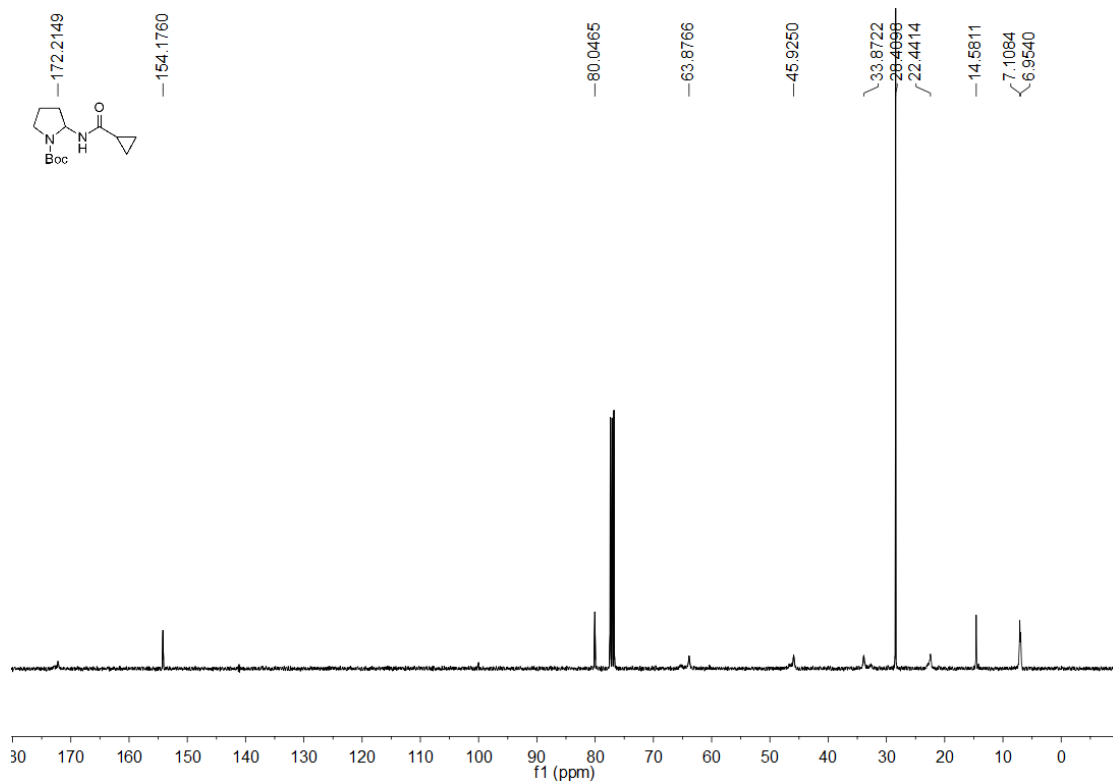
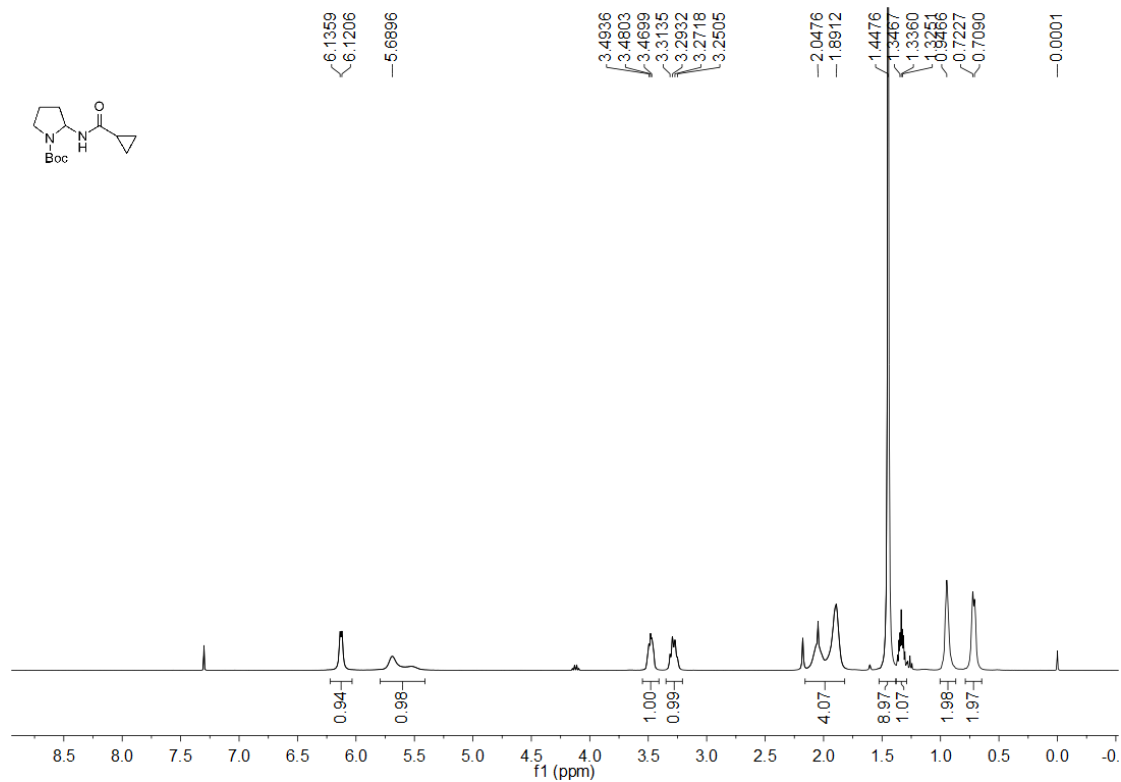
tert-Butyl 2-isobutyramidopyrrolidine-1-carboxylate (**3u**)



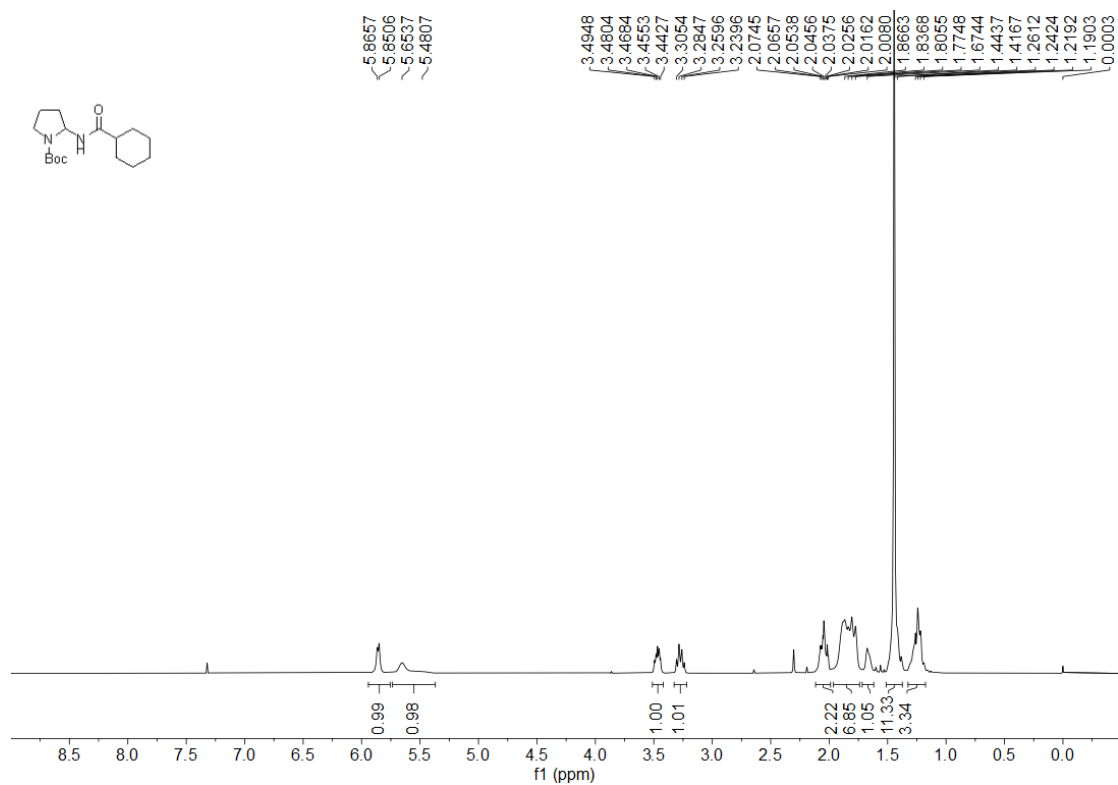
tert-Butyl 2-pivalamidopyrrolidine-1-carboxylate (**3v**)



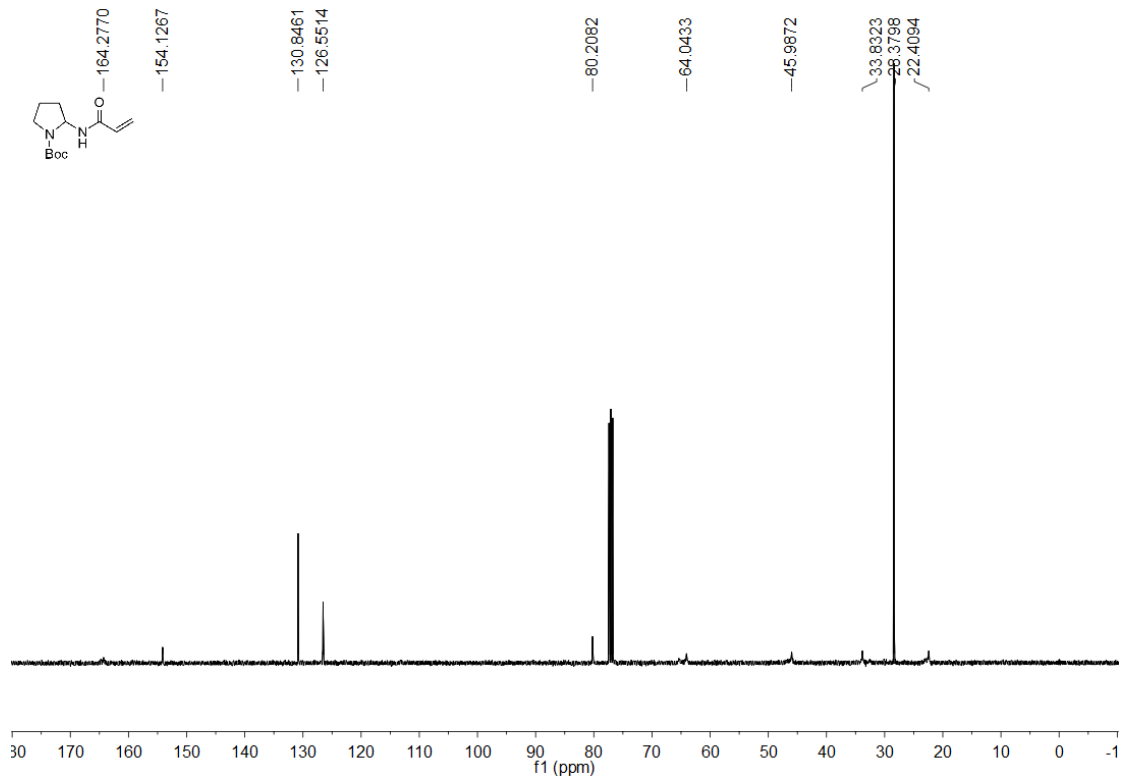
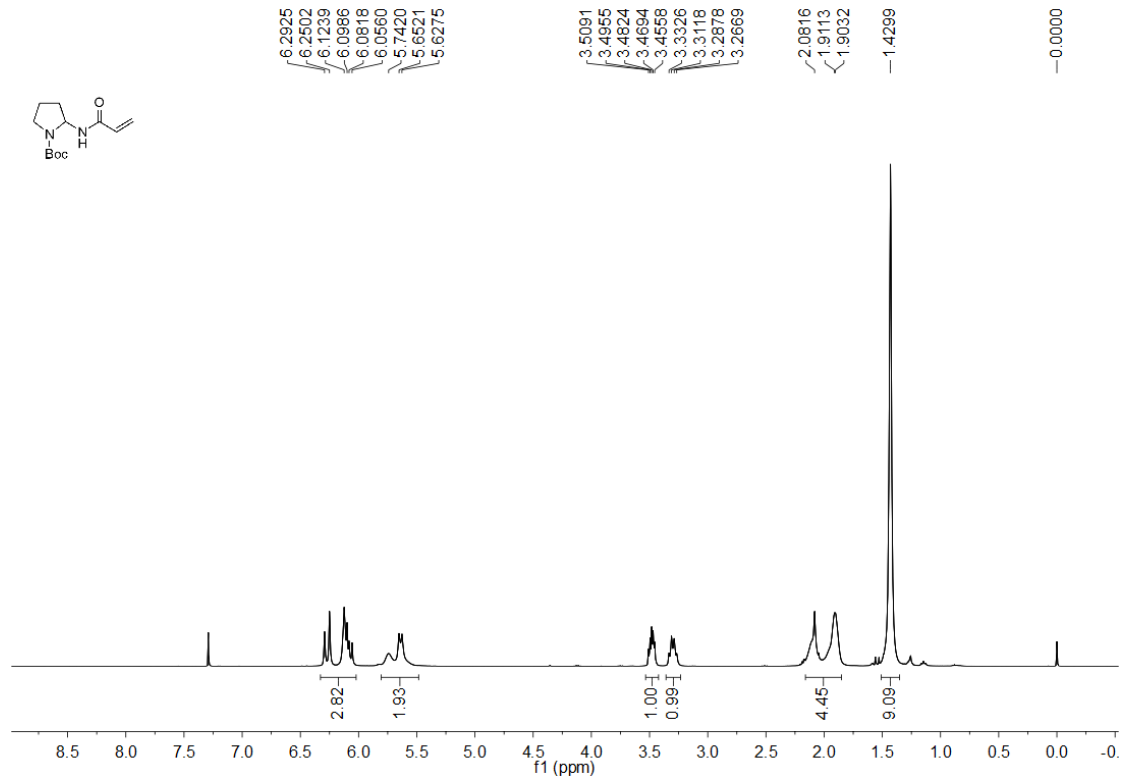
tert-Butyl 2-(cyclopropanecarboxamido)pyrrolidine-1-carboxylate (**3w**)



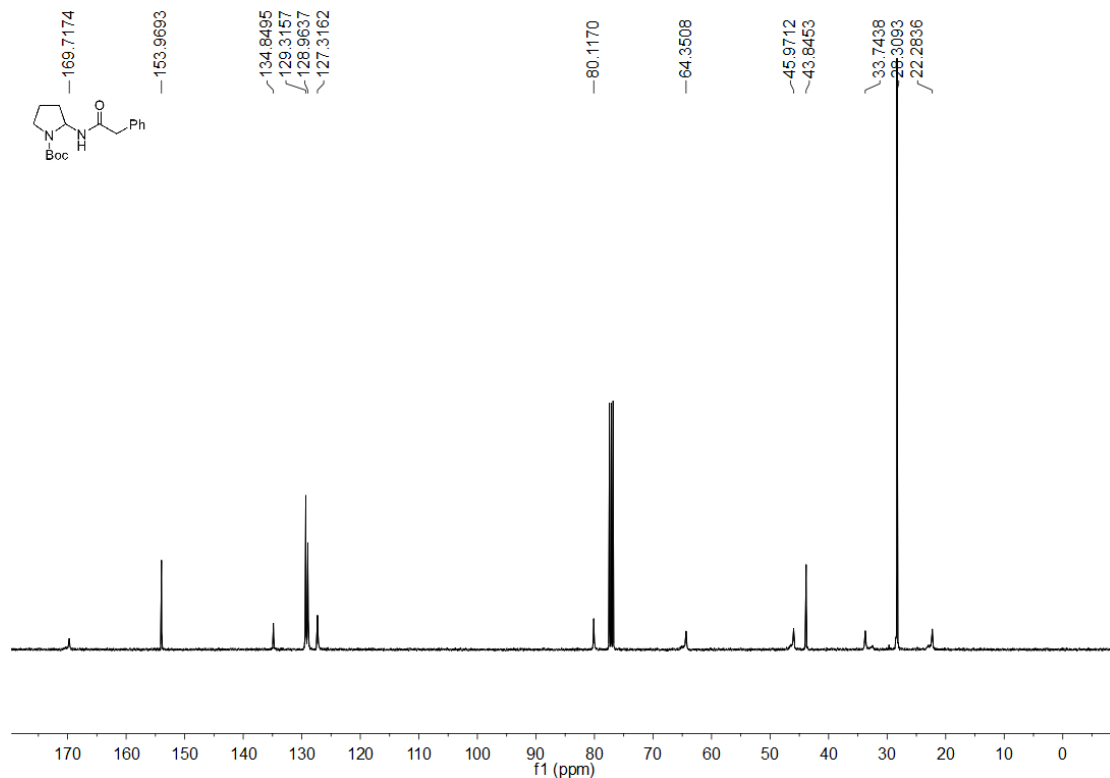
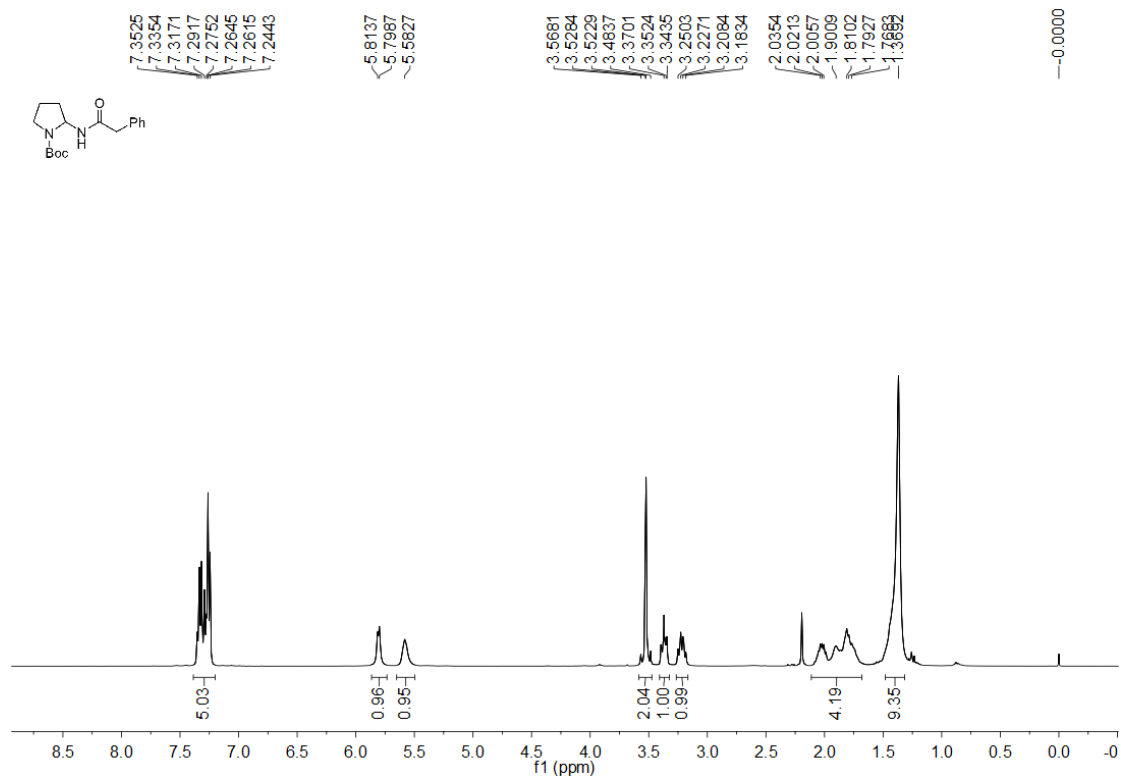
tert-butyl 2-(cyclohexanecarboxamido)pyrrolidine-1-carboxylate (**3x**)



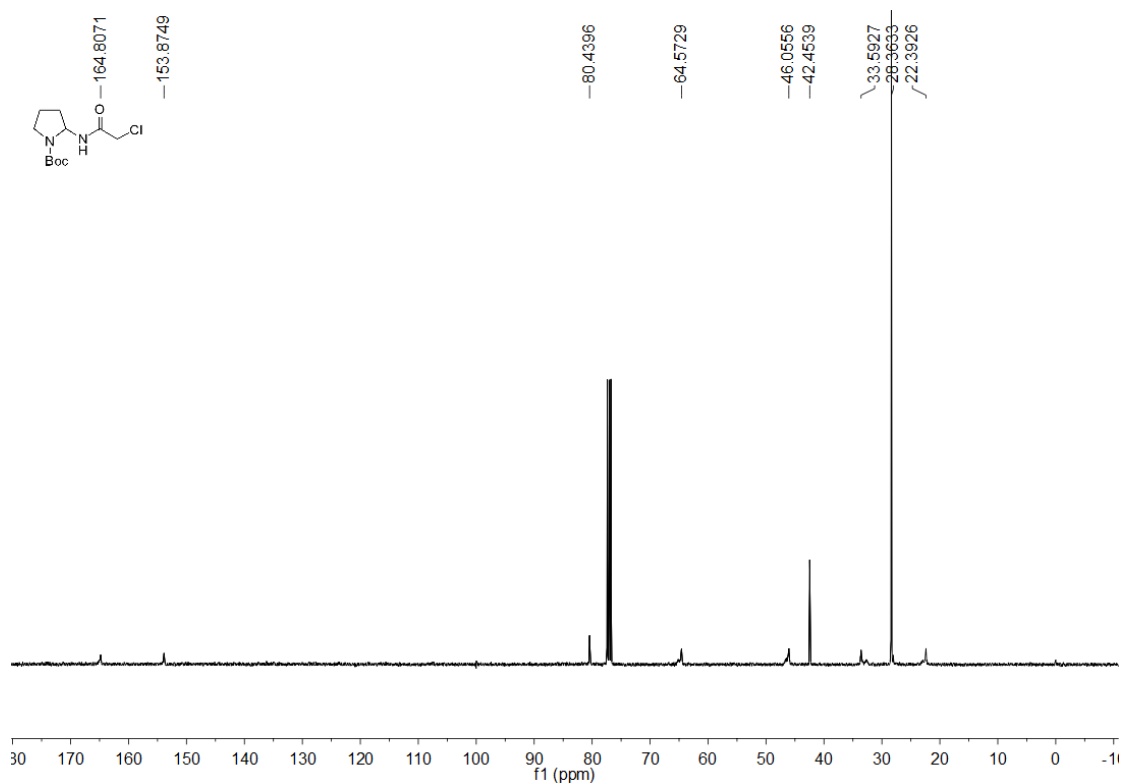
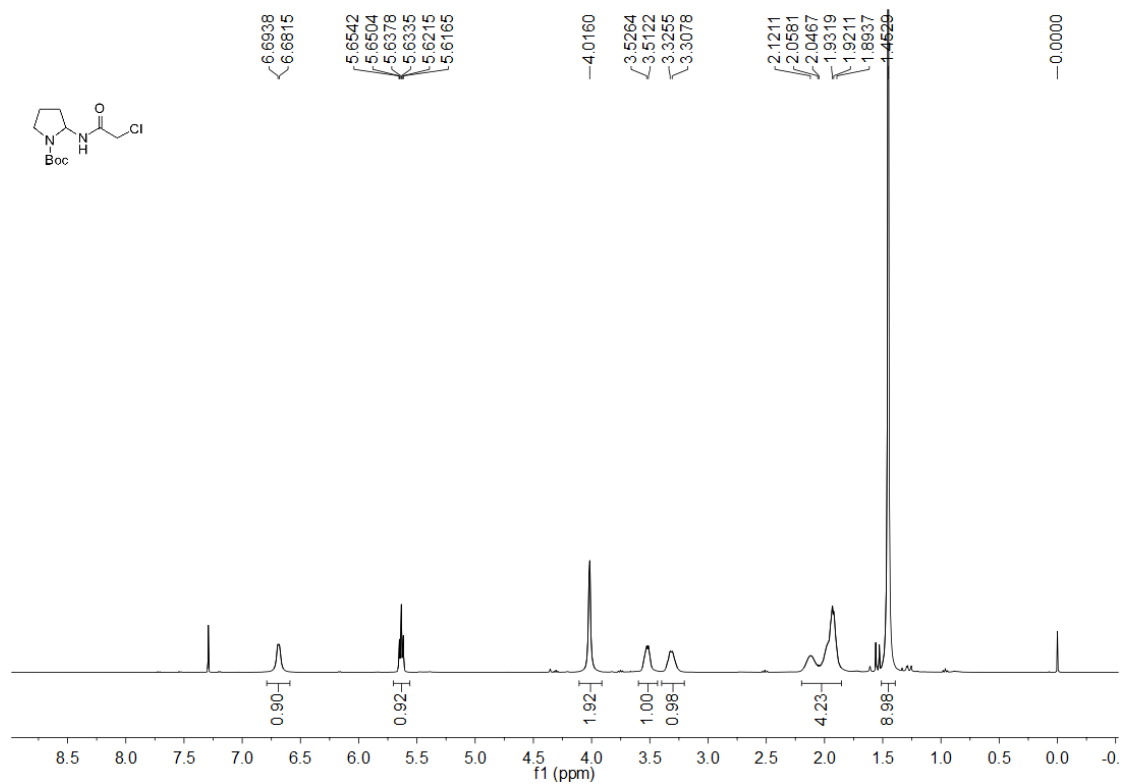
tert-Butyl 2-acrylamidopyrrolidine-1-carboxylate (**3y**)



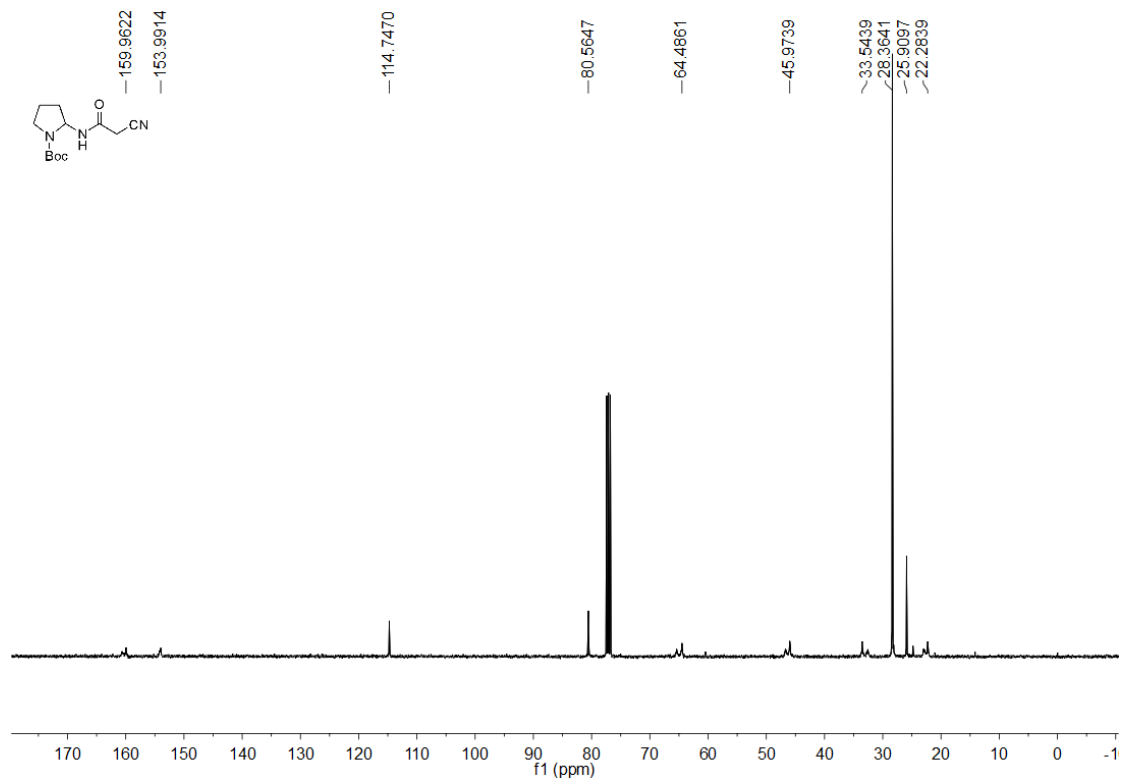
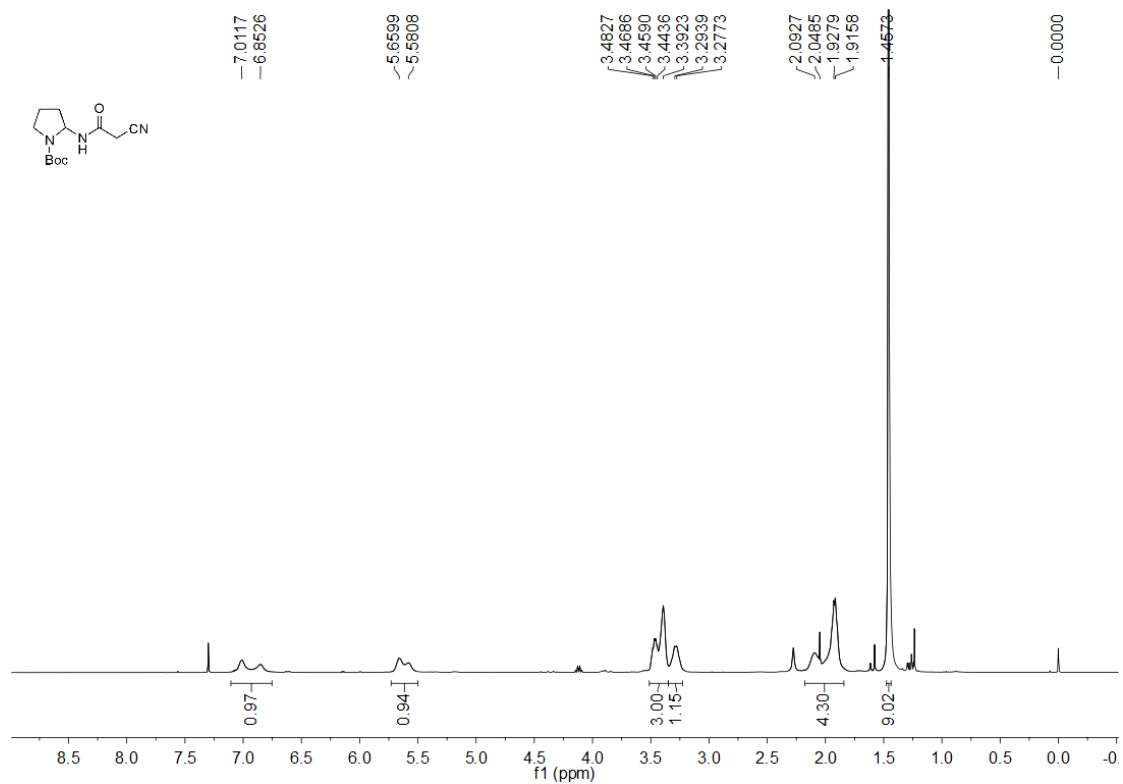
tert-Butyl 2-(2-phenylacetamido)pyrrolidine-1-carboxylate (**3z**)



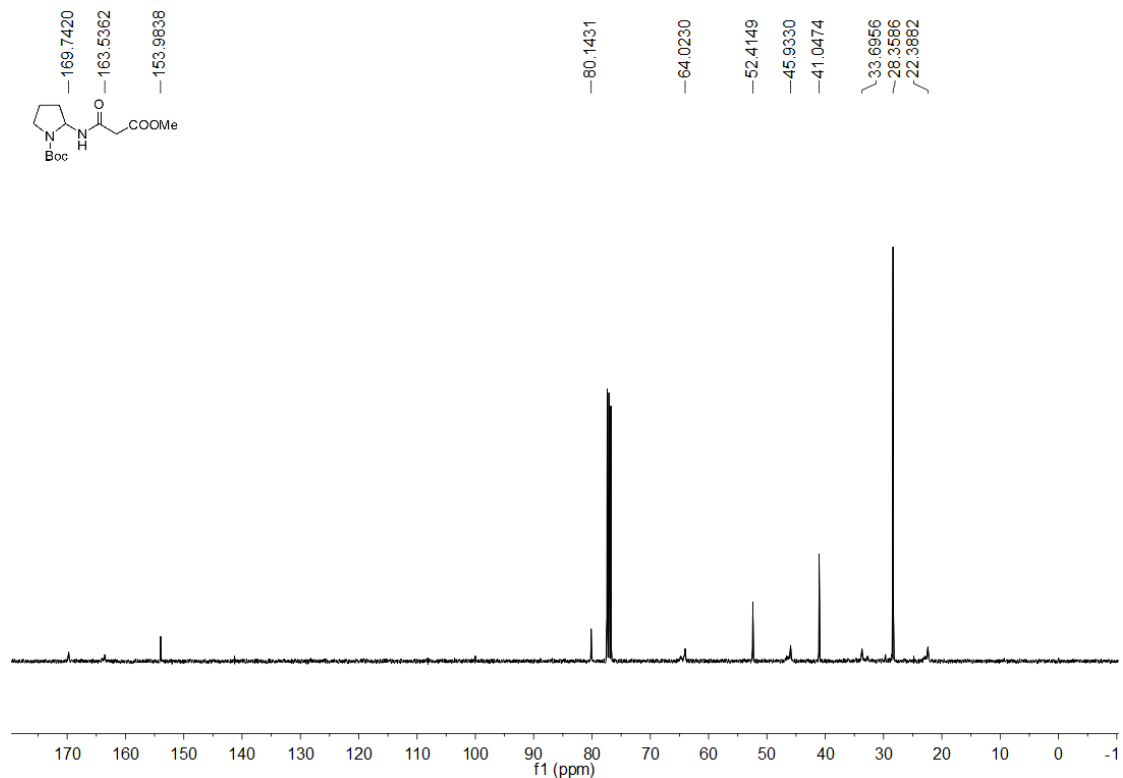
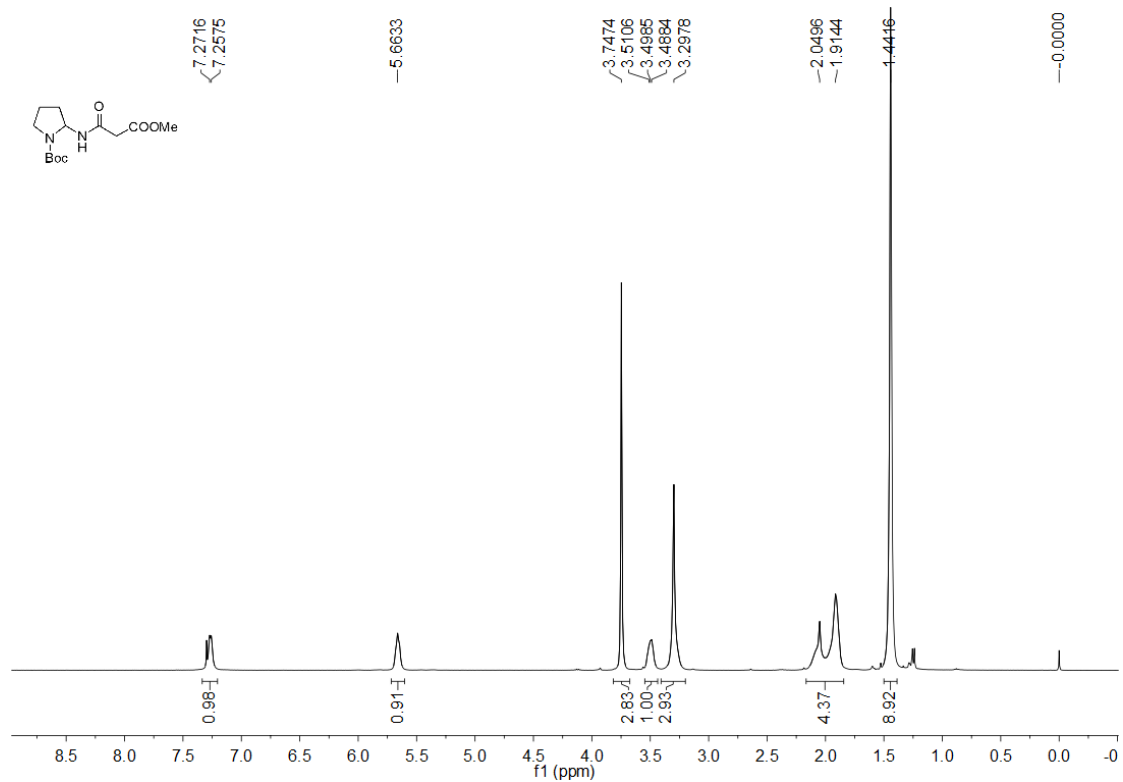
tert-Butyl 2-(2-chloroacetamido)pyrrolidine-1-carboxylate (**3aa**)



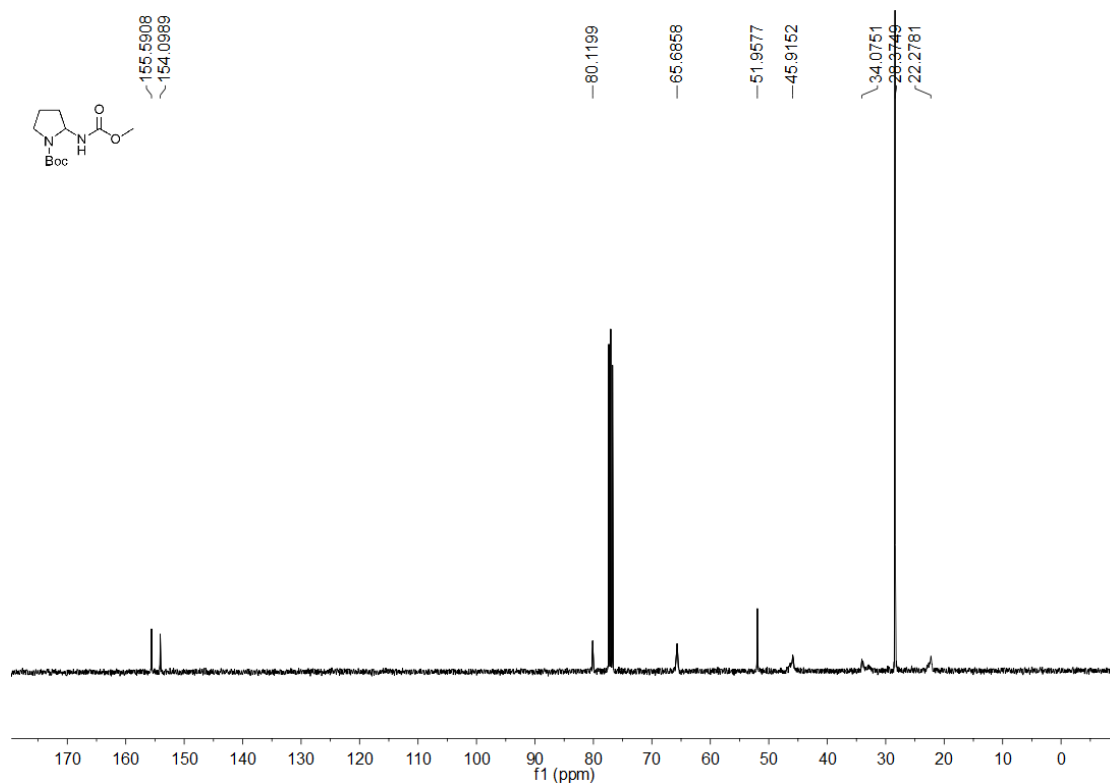
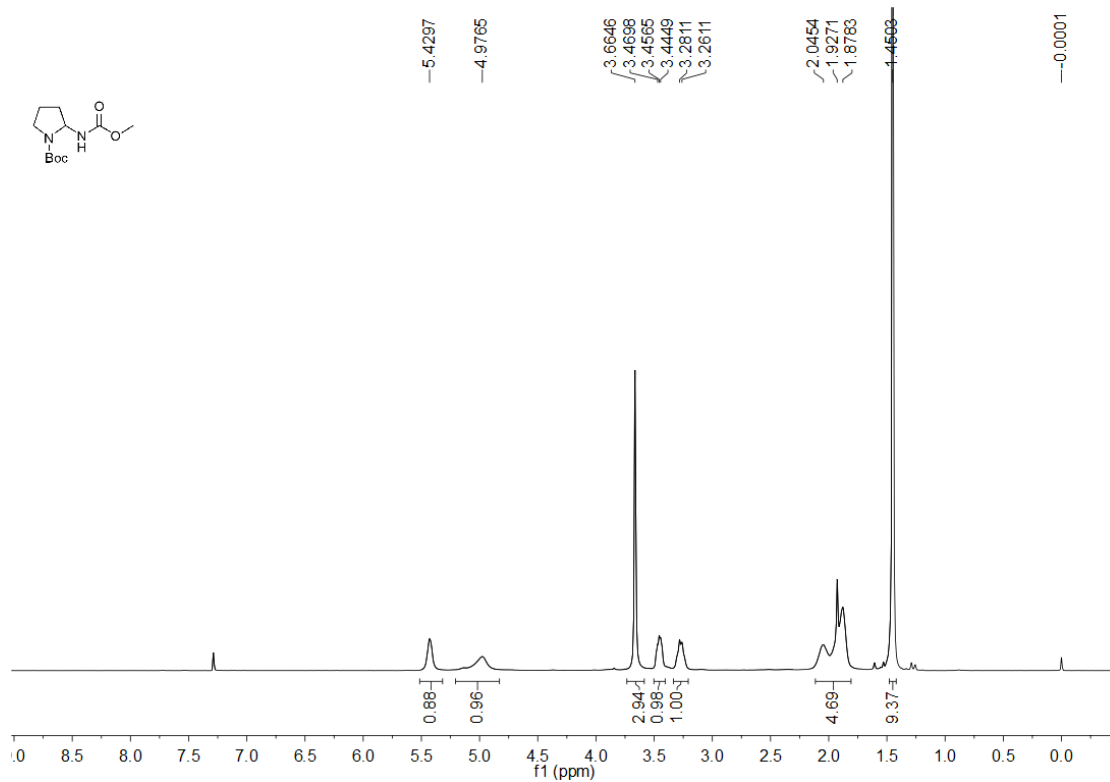
tert-Butyl 2-(2-cyanoacetamido)pyrrolidine-1-carboxylate (**3ab**)



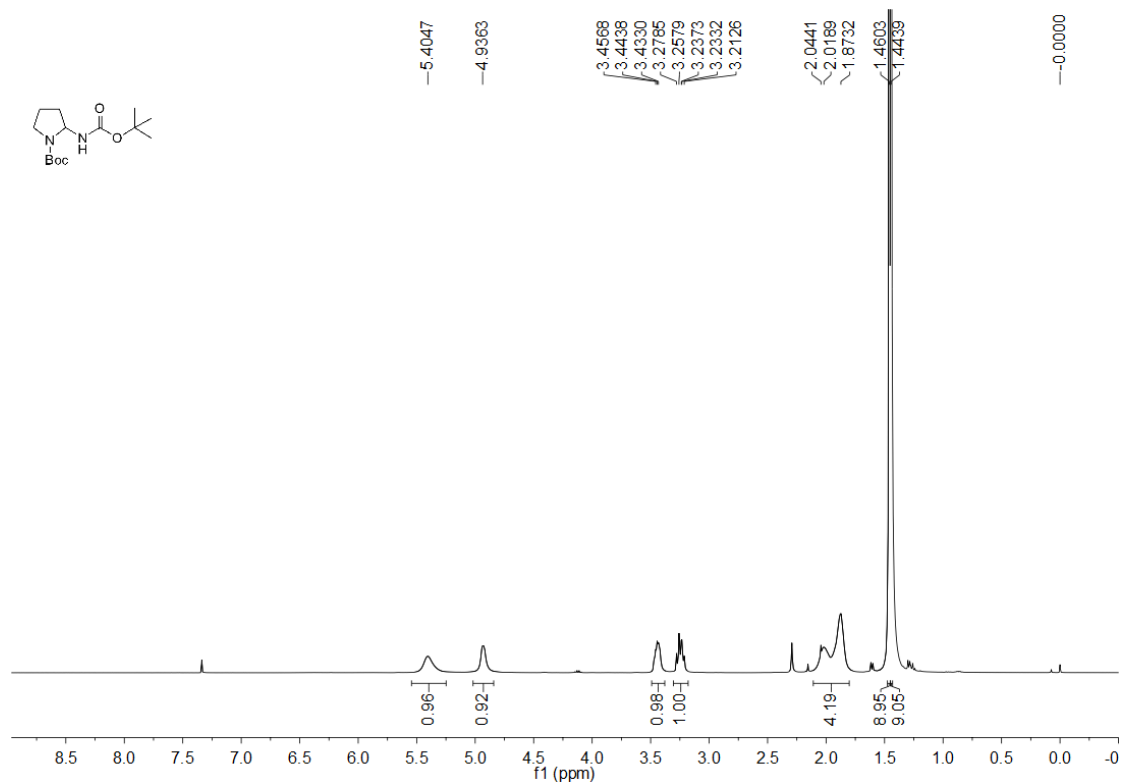
tert-Butyl 2-(3-methoxy-3-oxopropanamido)pyrrolidine-1-carboxylate (**3ac**)



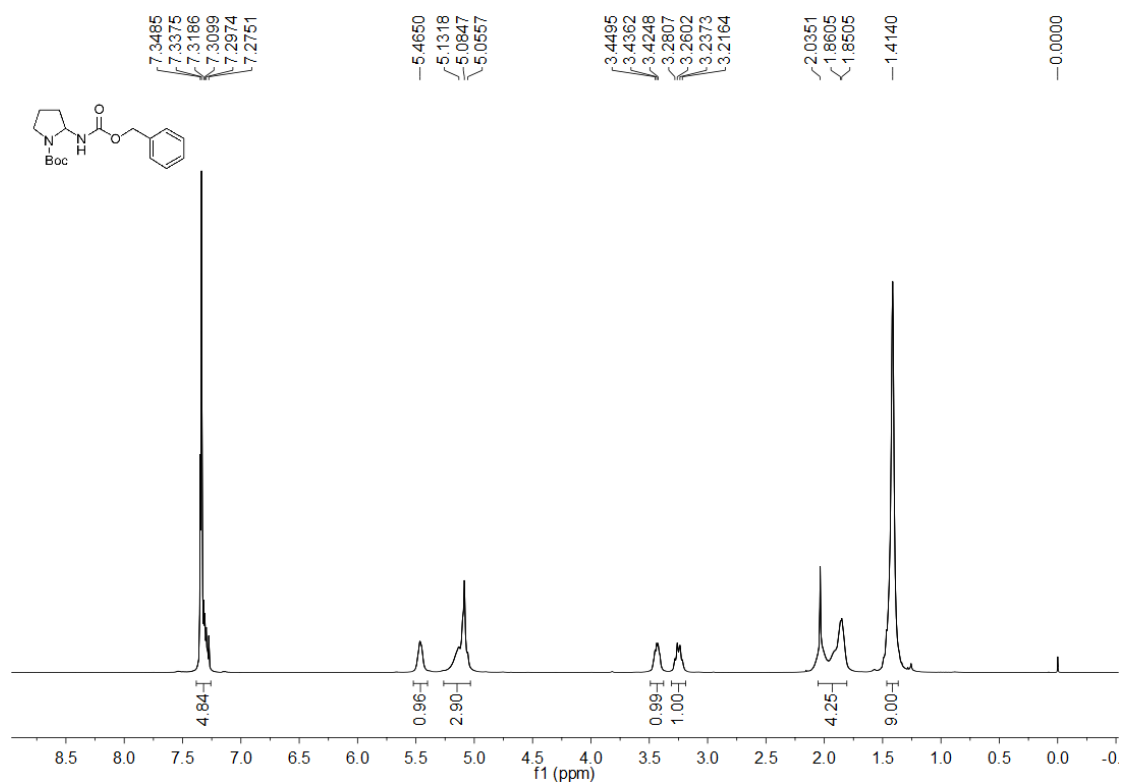
tert-Butyl 2-((methoxycarbonyl)amino)pyrrolidine-1-carboxylate (**3ad**)



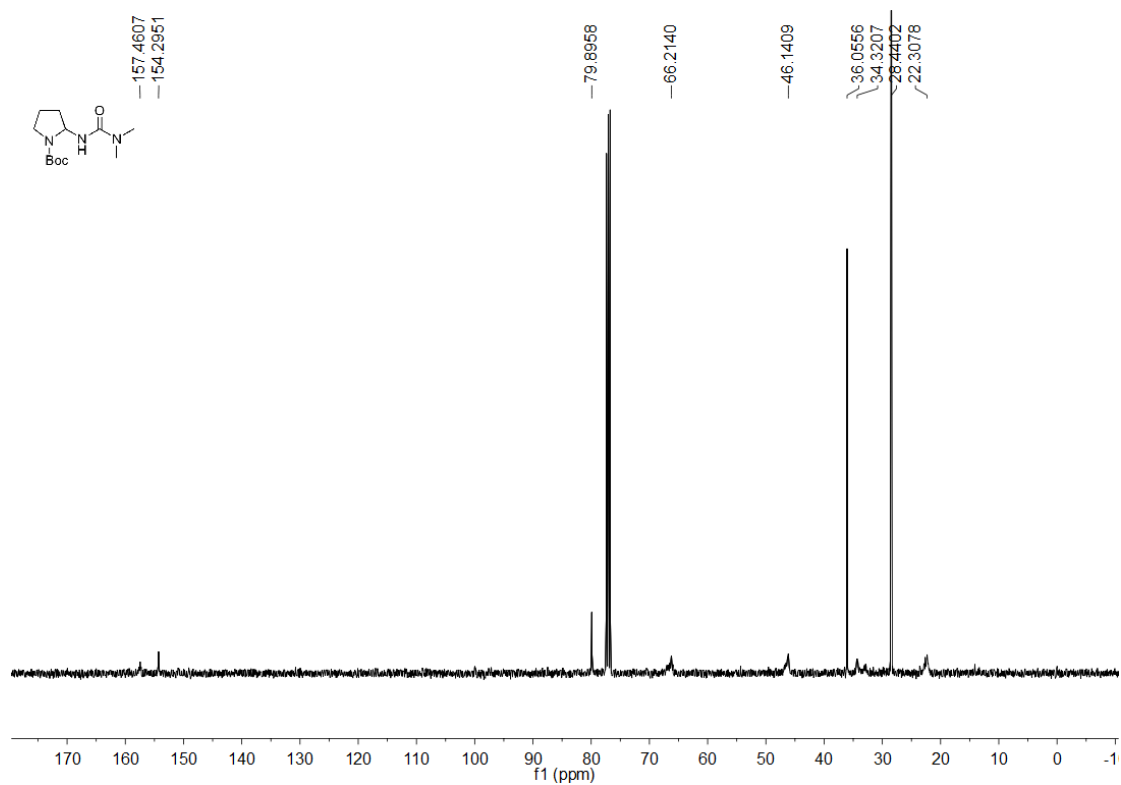
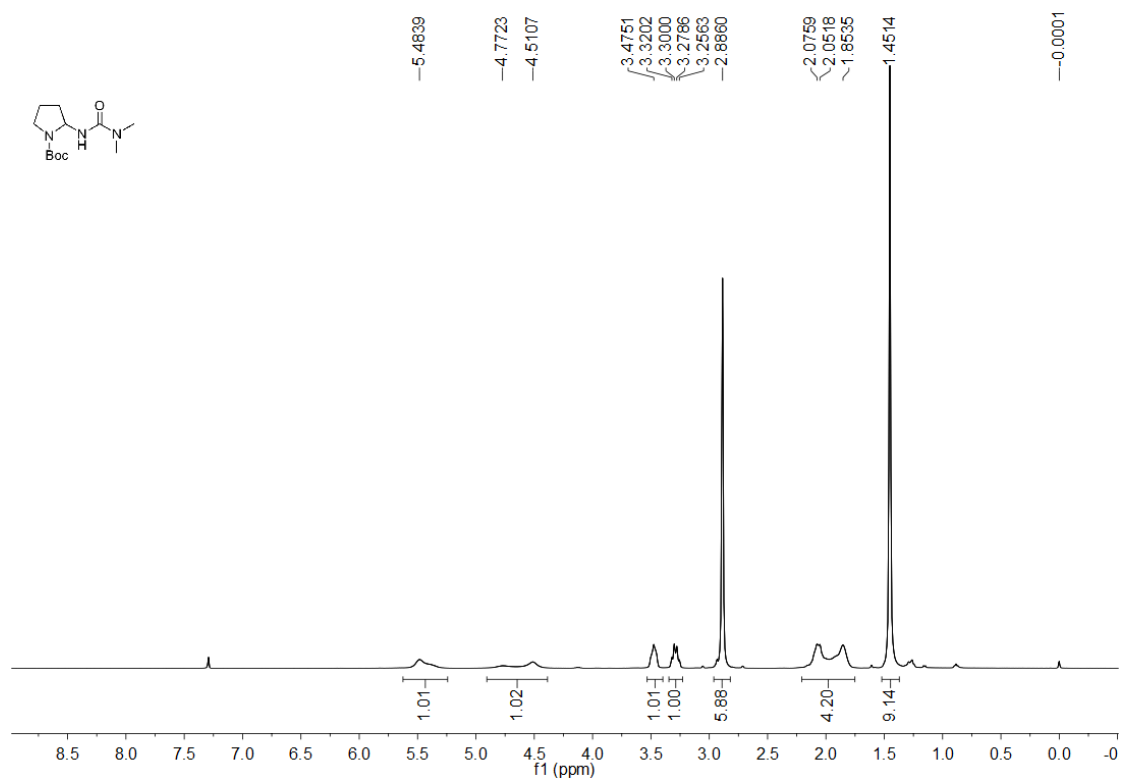
tert-Butyl 2-((*tert*-butoxycarbonyl)amino)pyrrolidine-1-carboxylate (**3ae**)



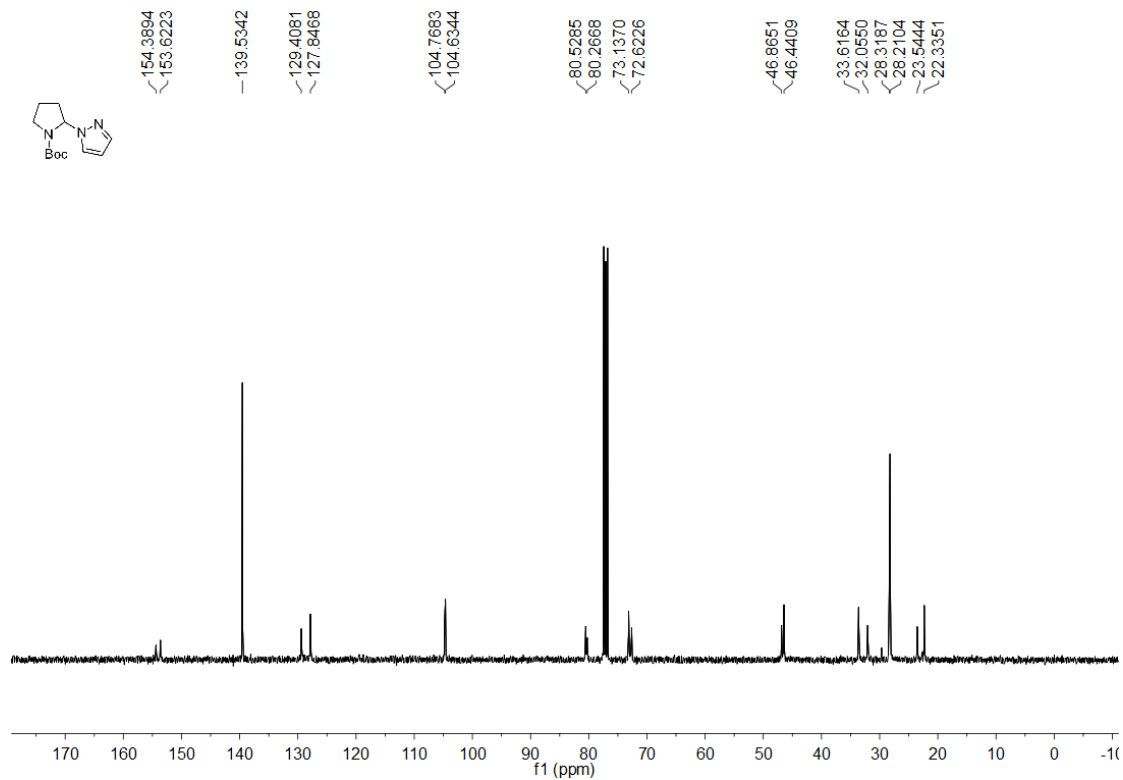
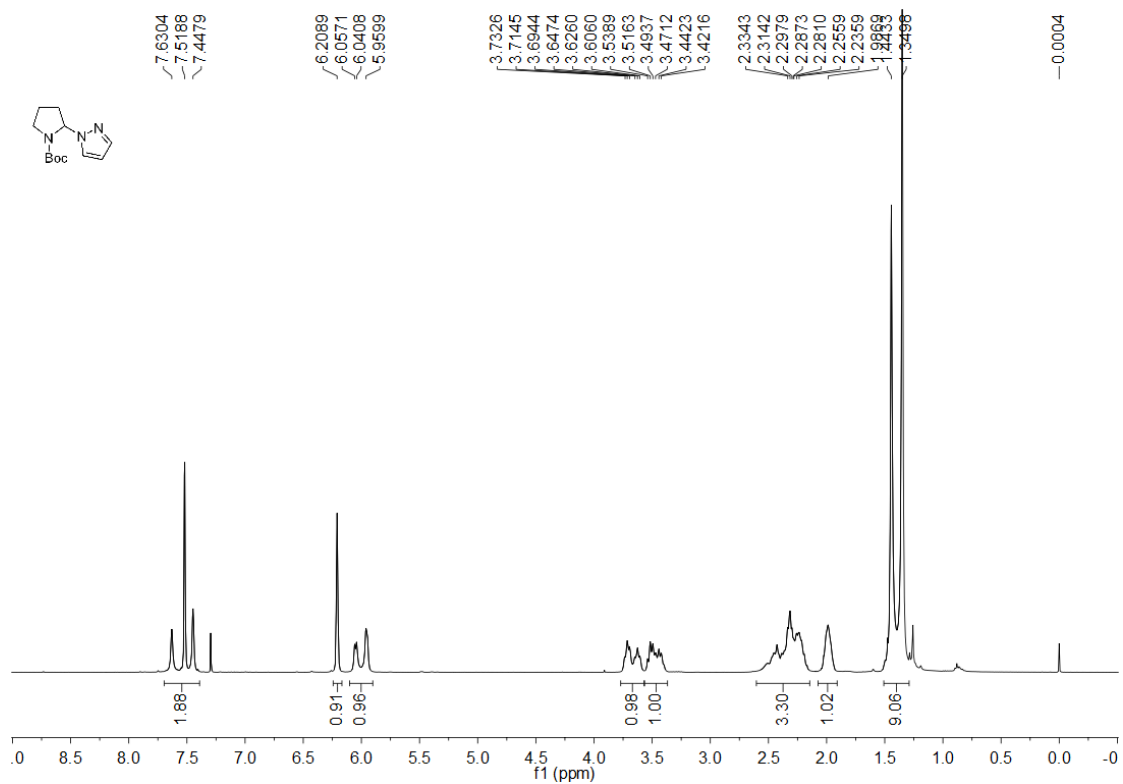
tert-Butyl 2-(((benzyloxy)carbonyl)amino)pyrrolidine-1-carboxylate (**3af**)



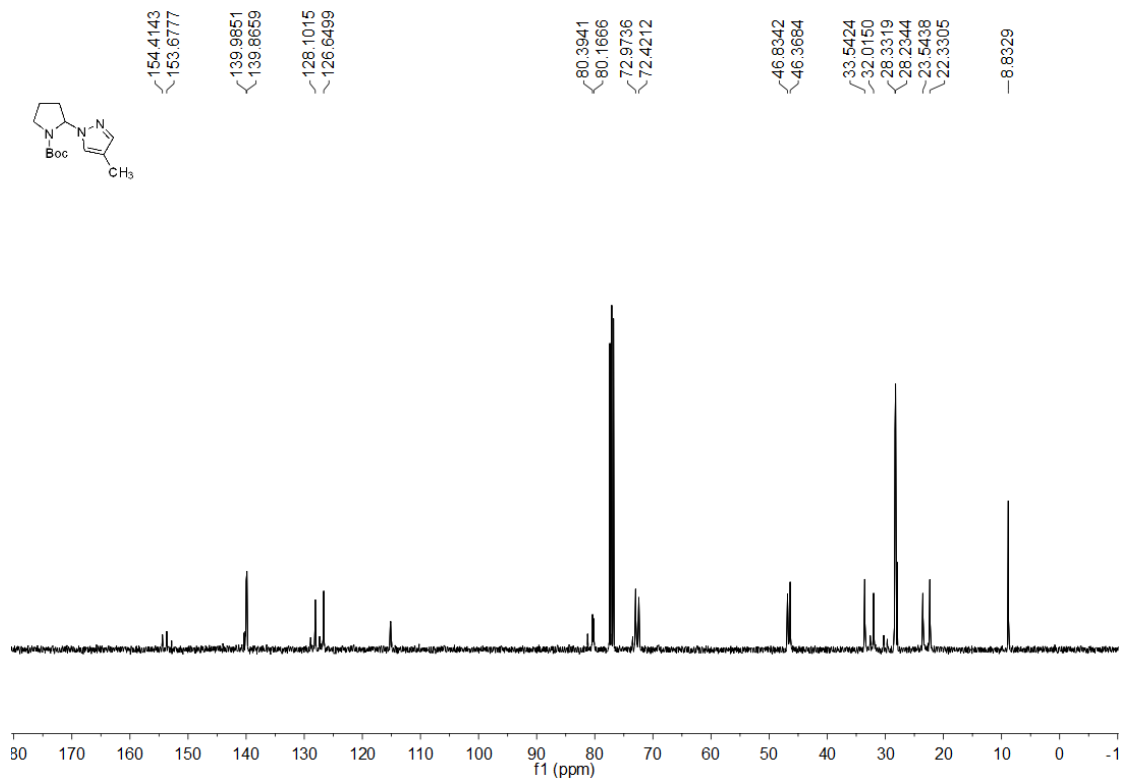
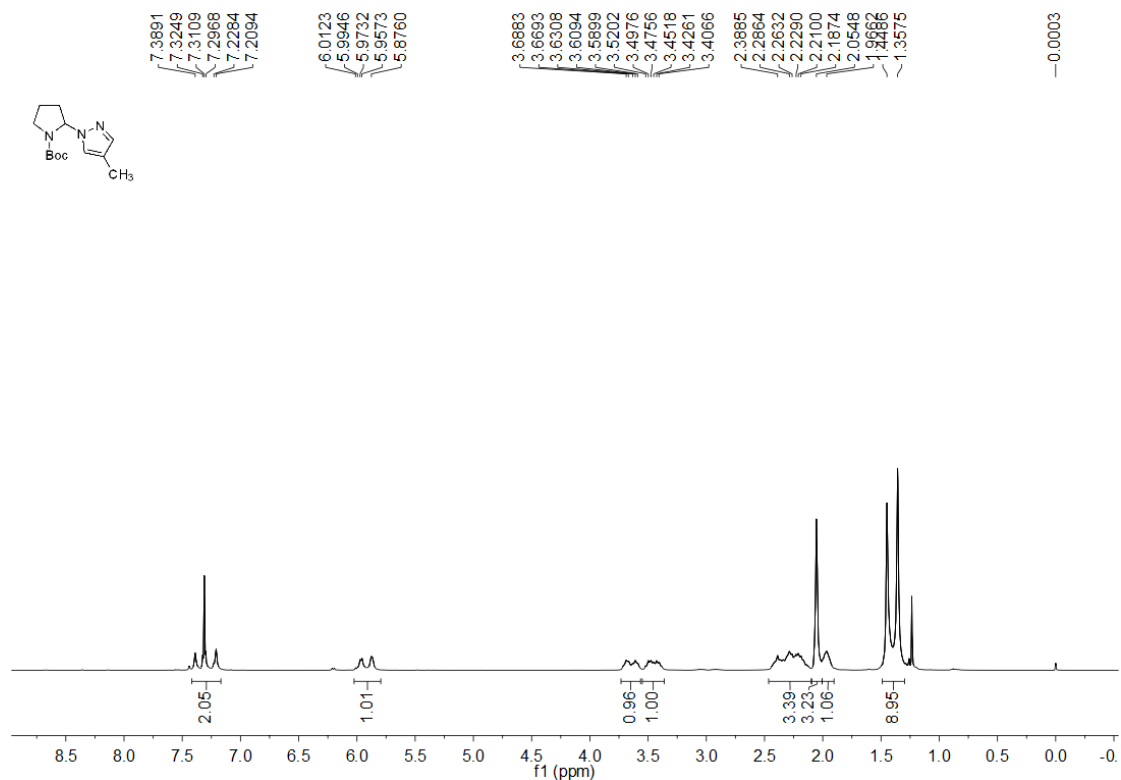
tert-Butyl 2-(3,3-dimethylureido)pyrrolidine-1-carboxylate (**3ag**)



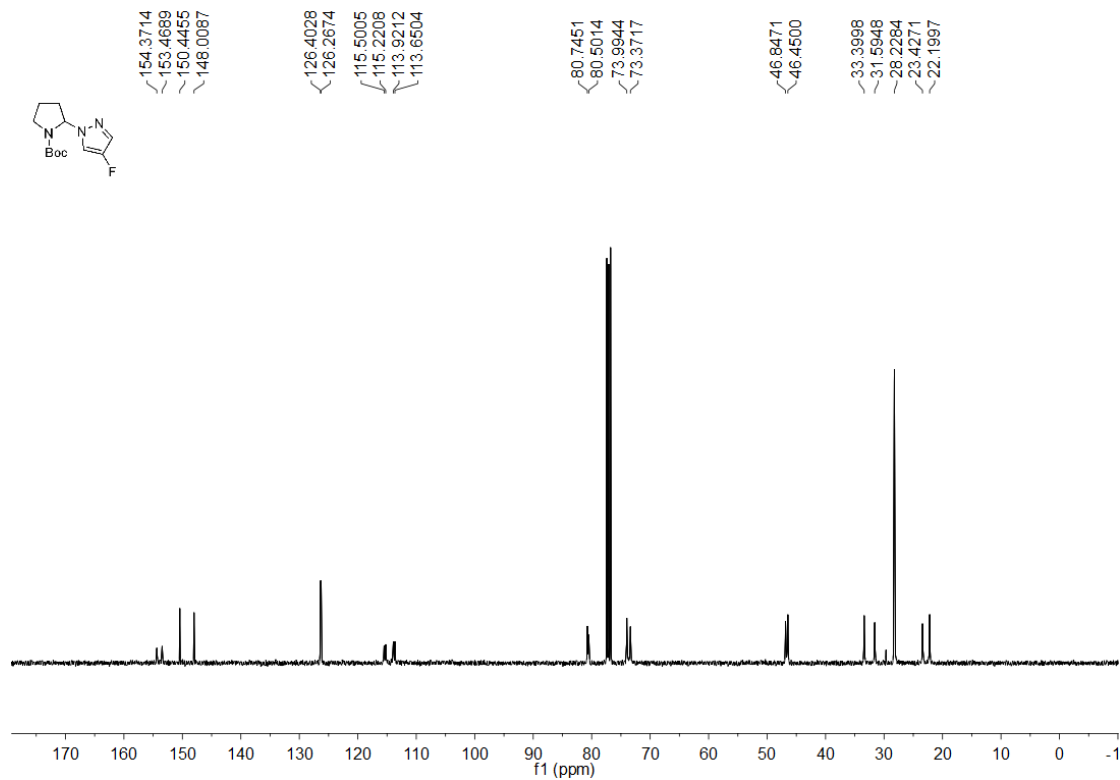
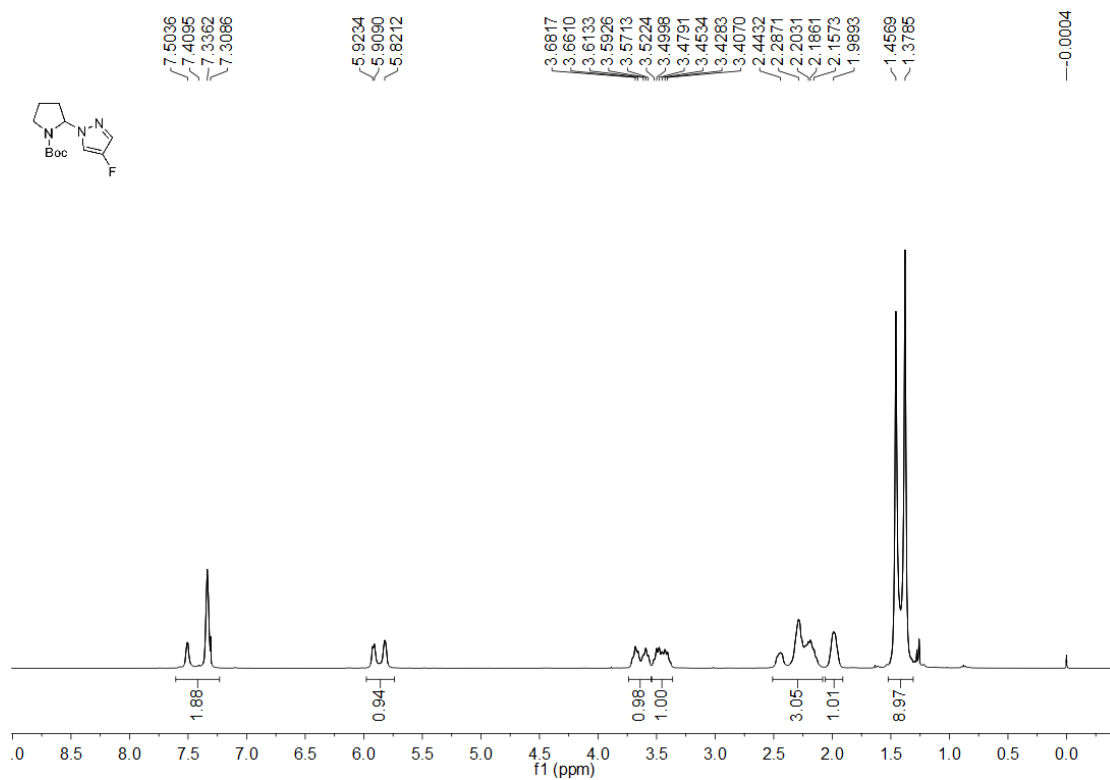
tert-Butyl 2-(1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5a**)

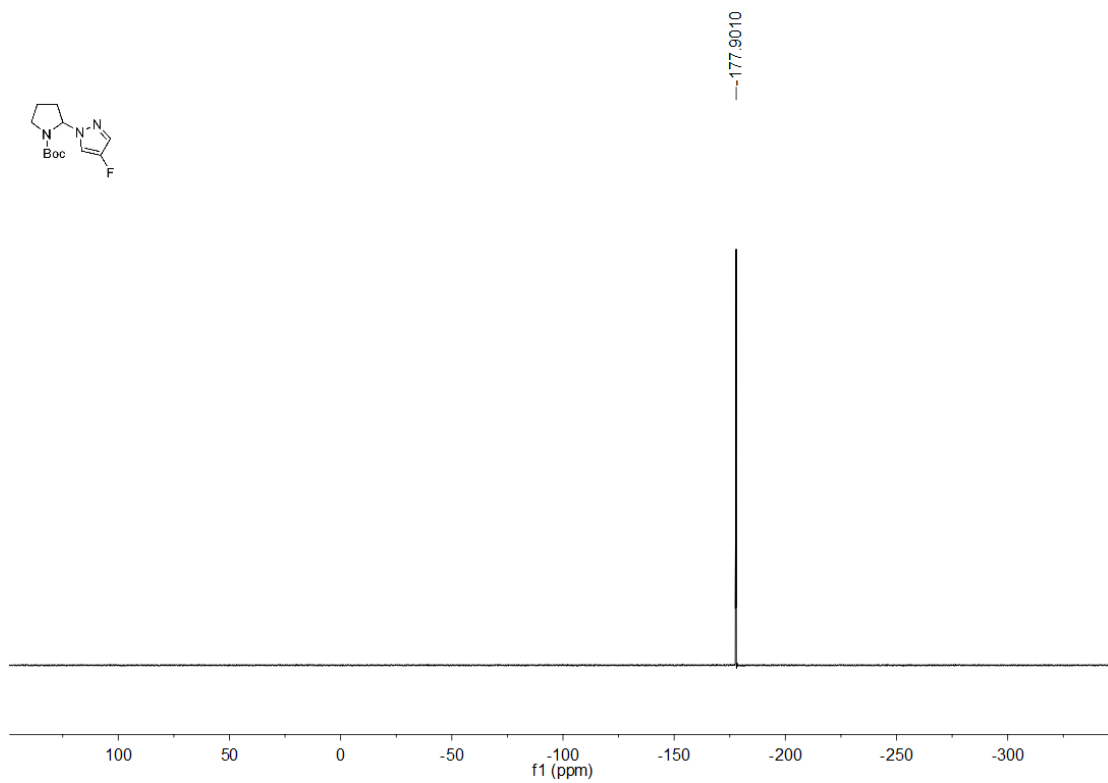


tert-Butyl 2-(4-methyl-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5b**)

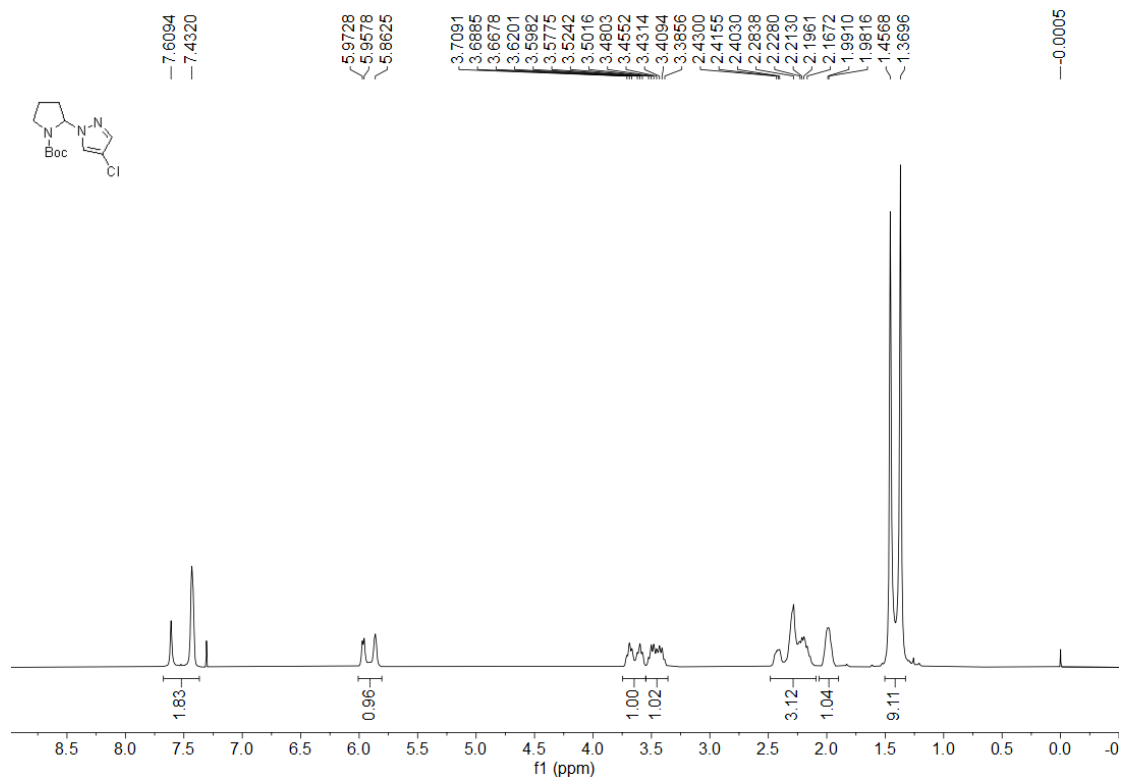


tert-Butyl 2-(4-fluoro-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5c**)

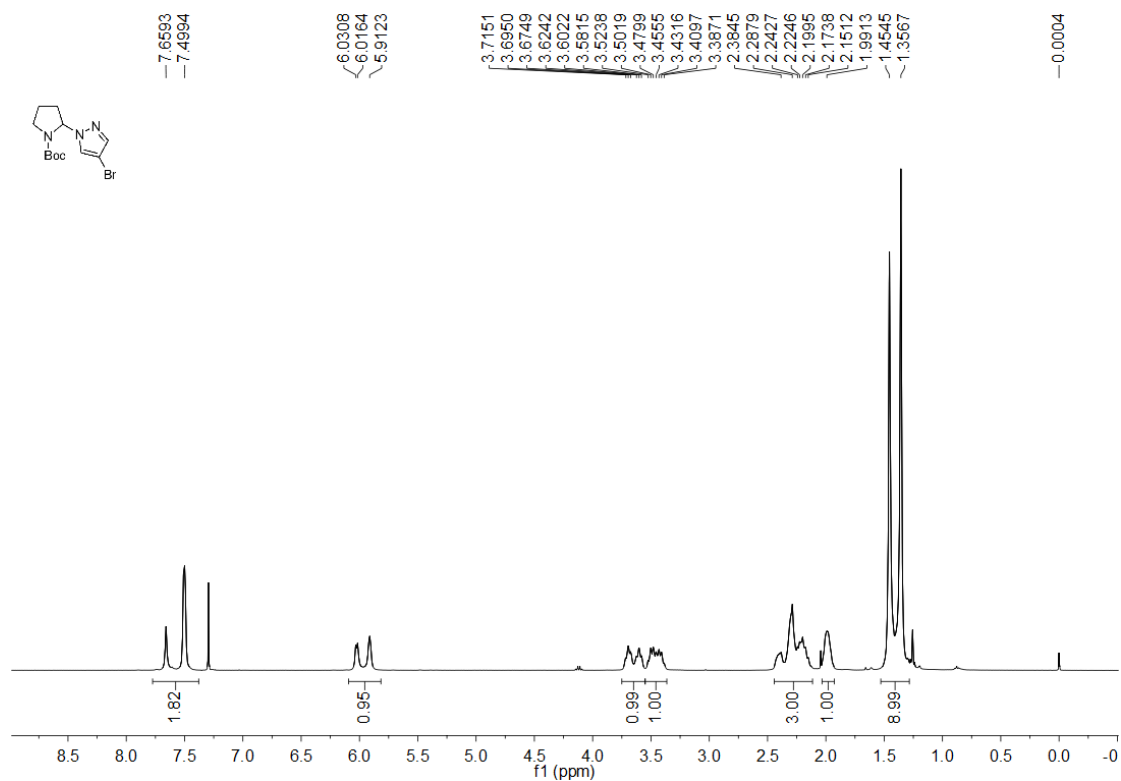




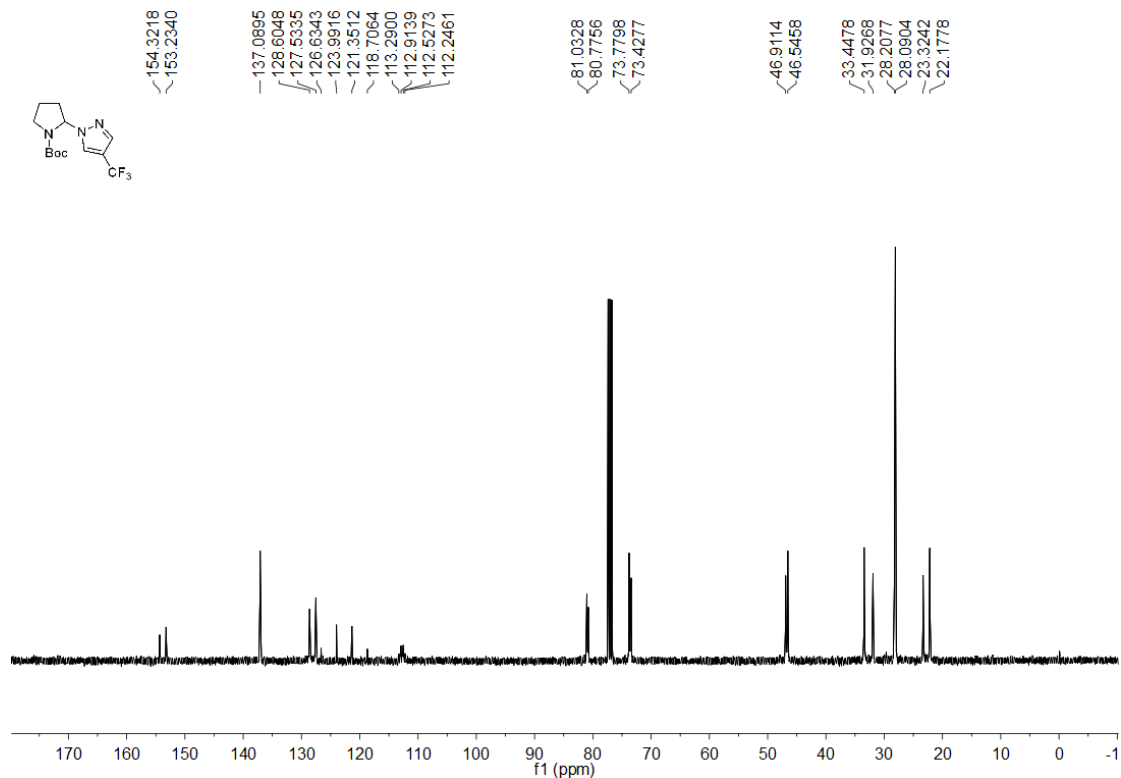
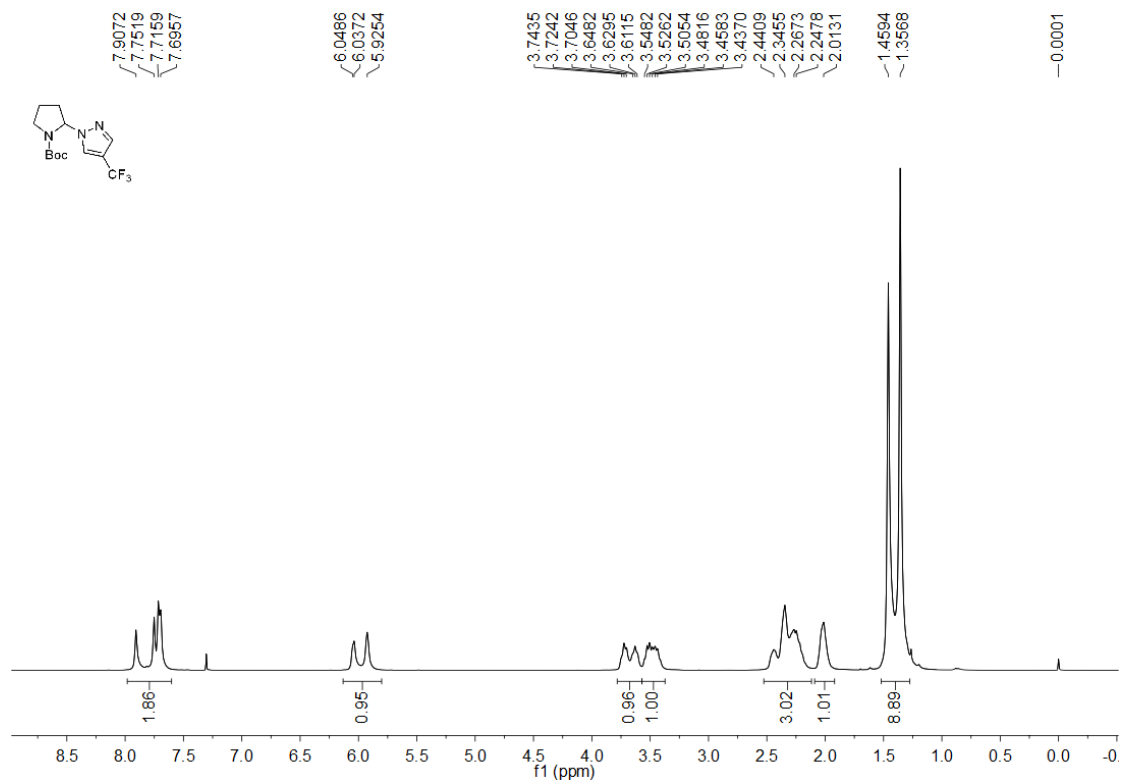
tert-Butyl 2-(4-chloro-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5d**)

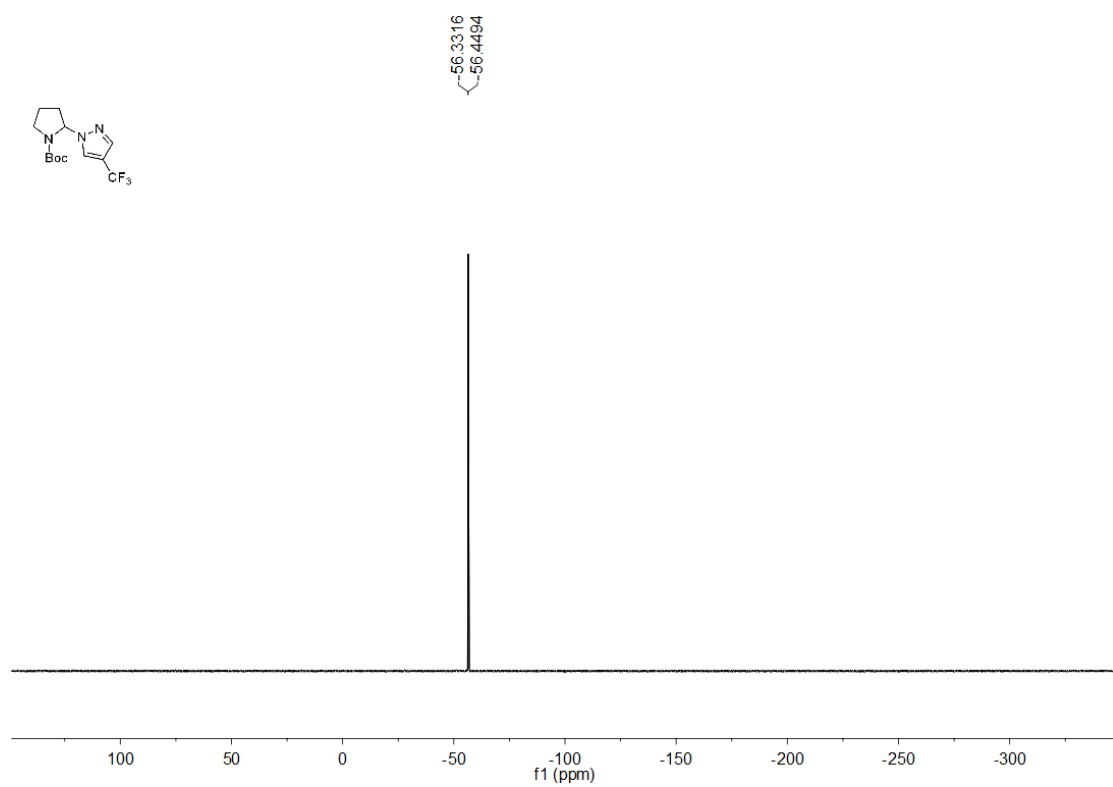


tert-Butyl 2-(4-bromo-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5e**)

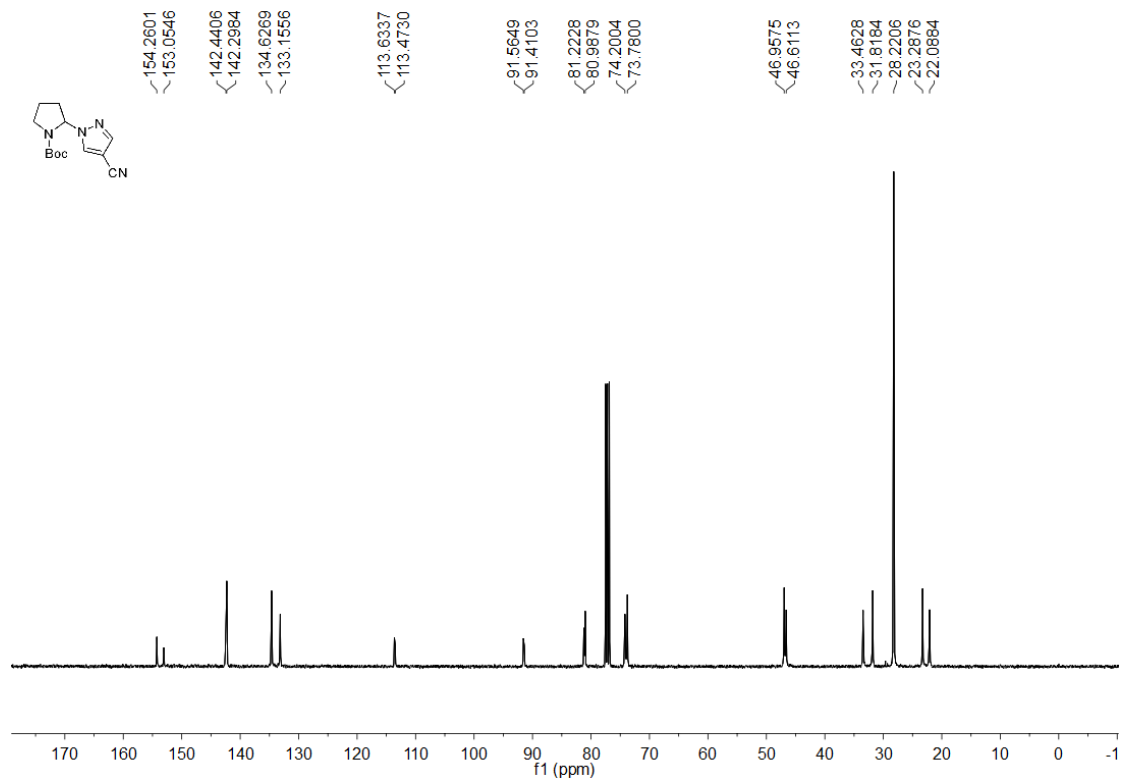
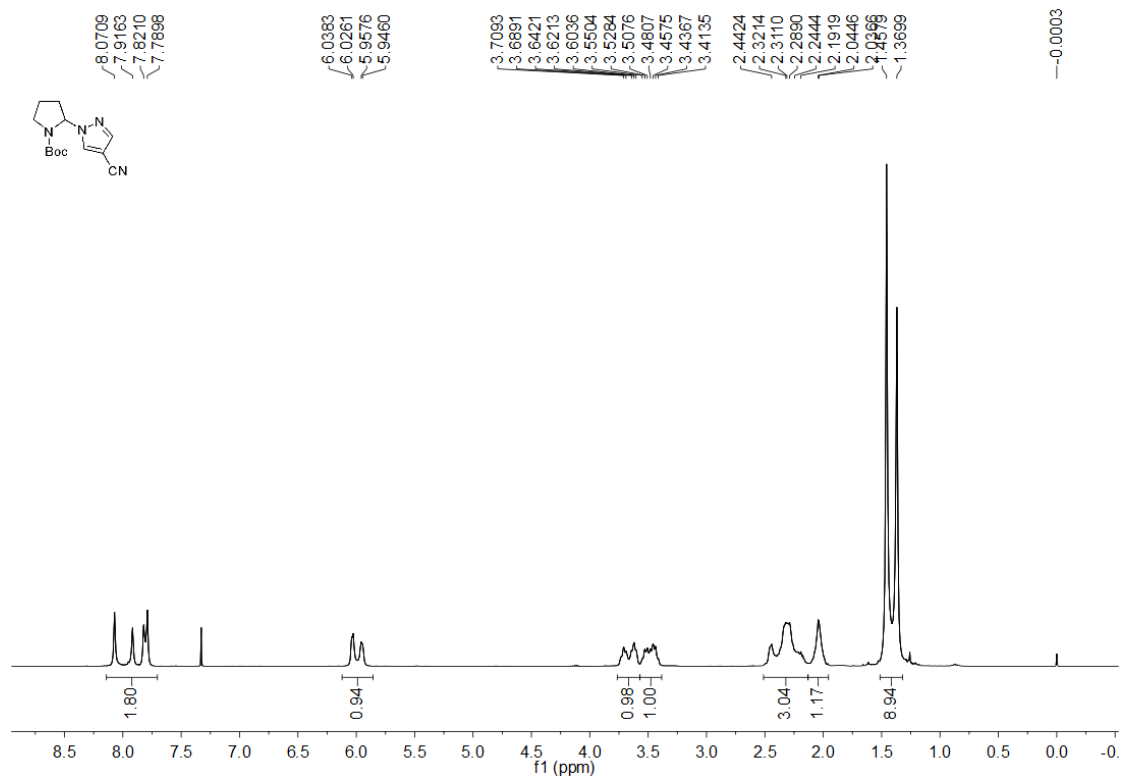


tert-Butyl 2-(4-(trifluoromethyl)-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5f**)

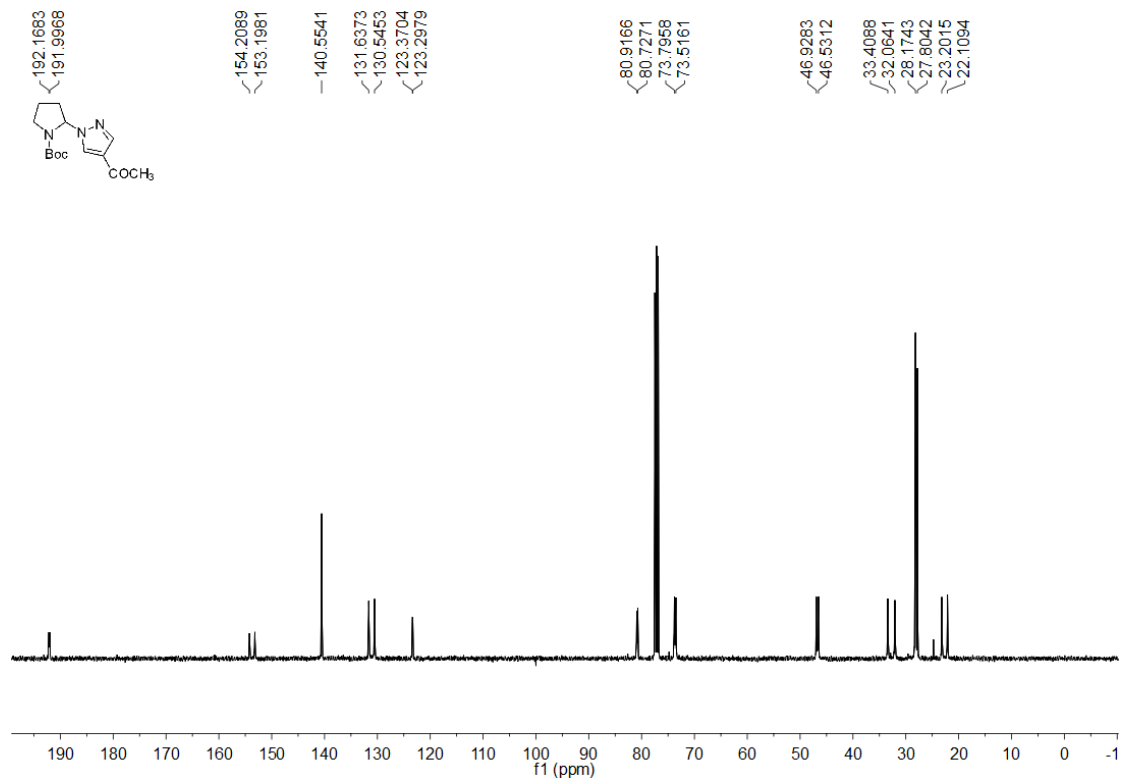
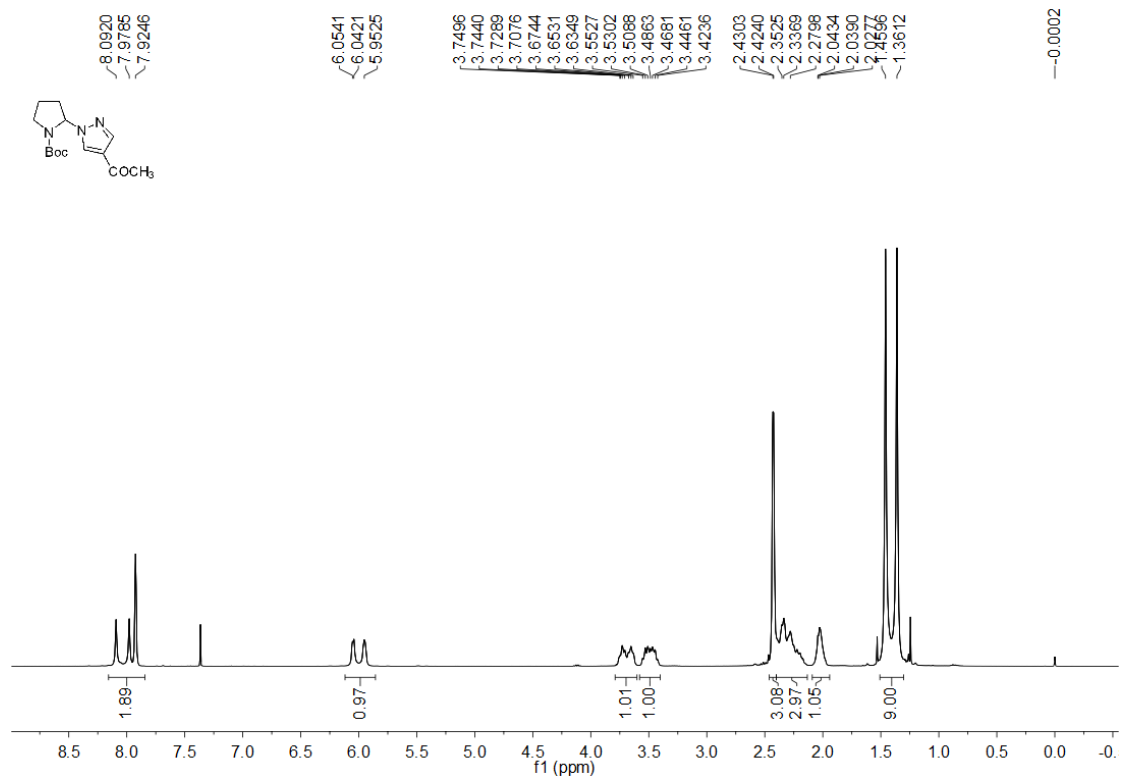




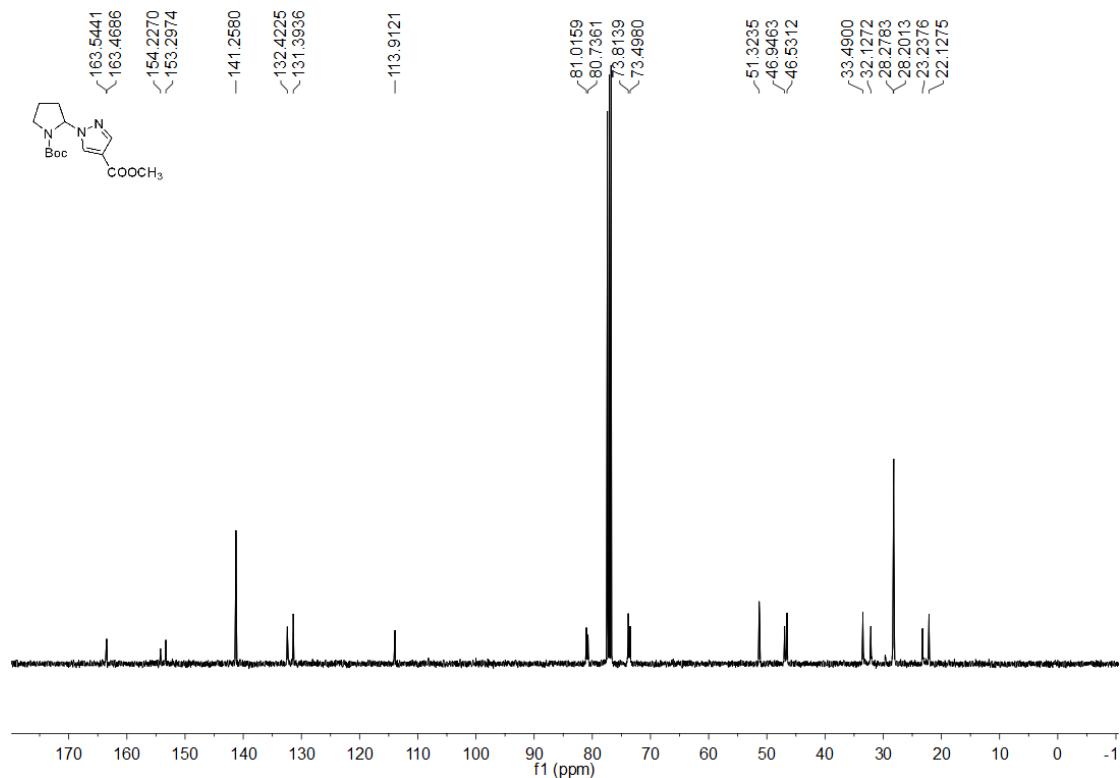
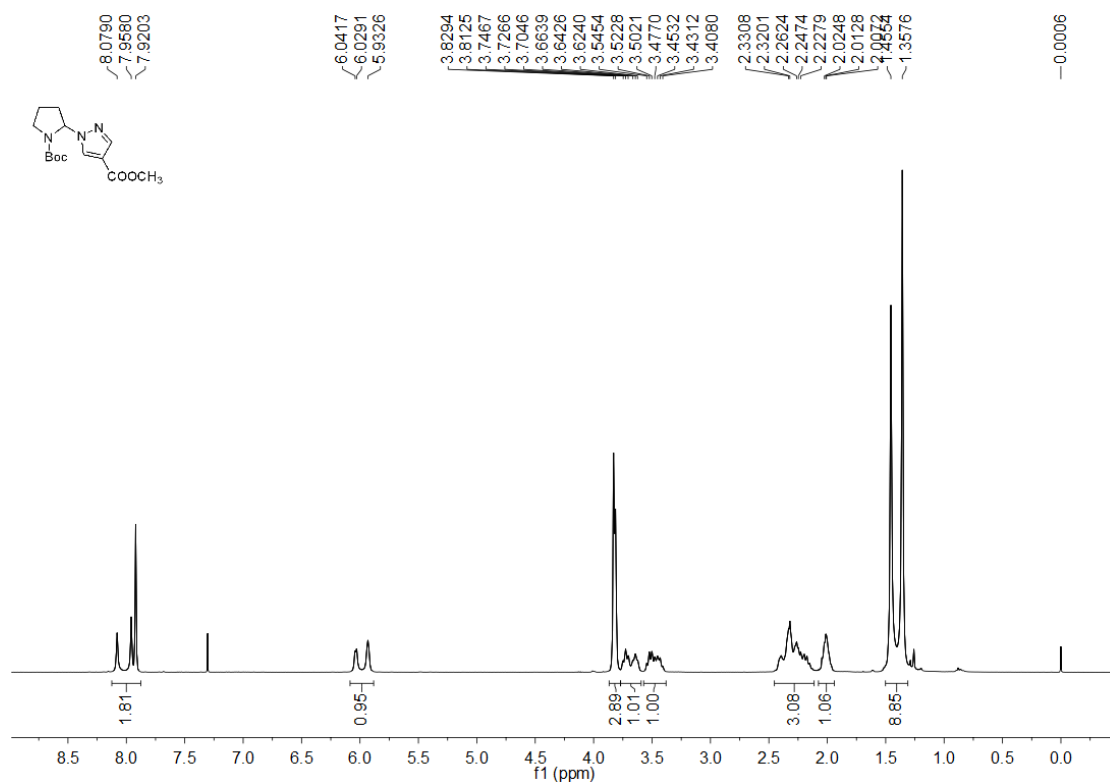
tert-Butyl 2-(4-cyano-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5g**)



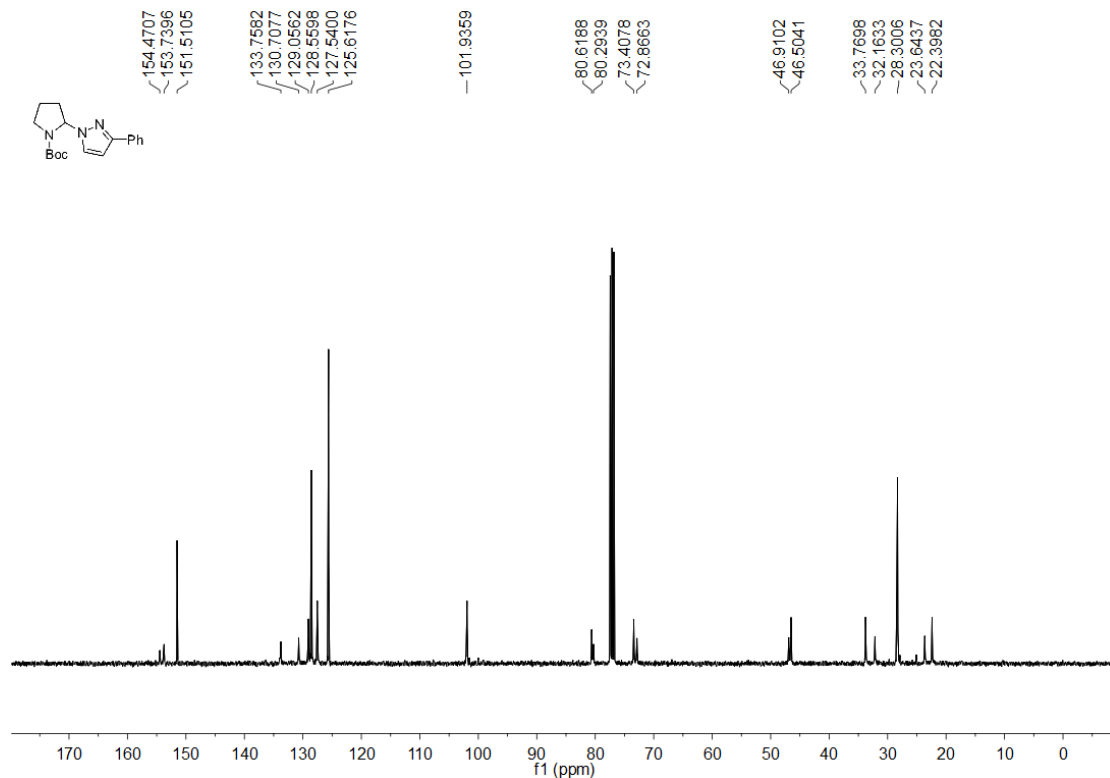
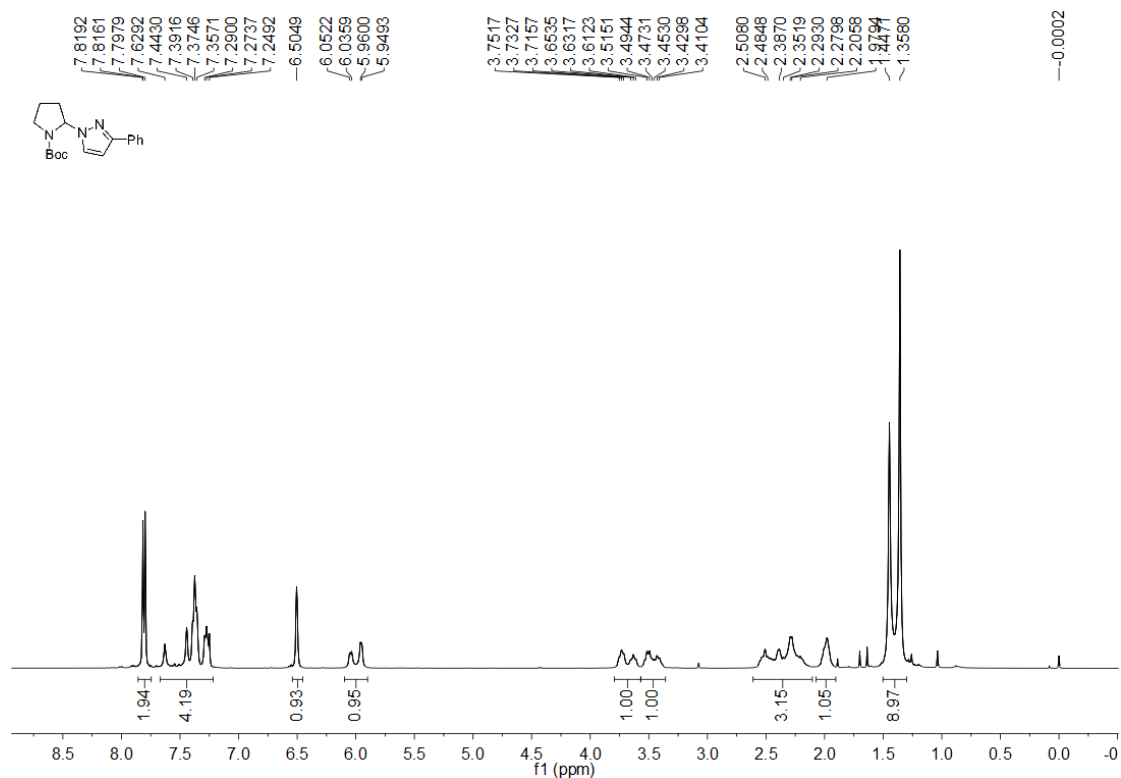
tert-Butyl 2-(4-acetyl-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5h**)



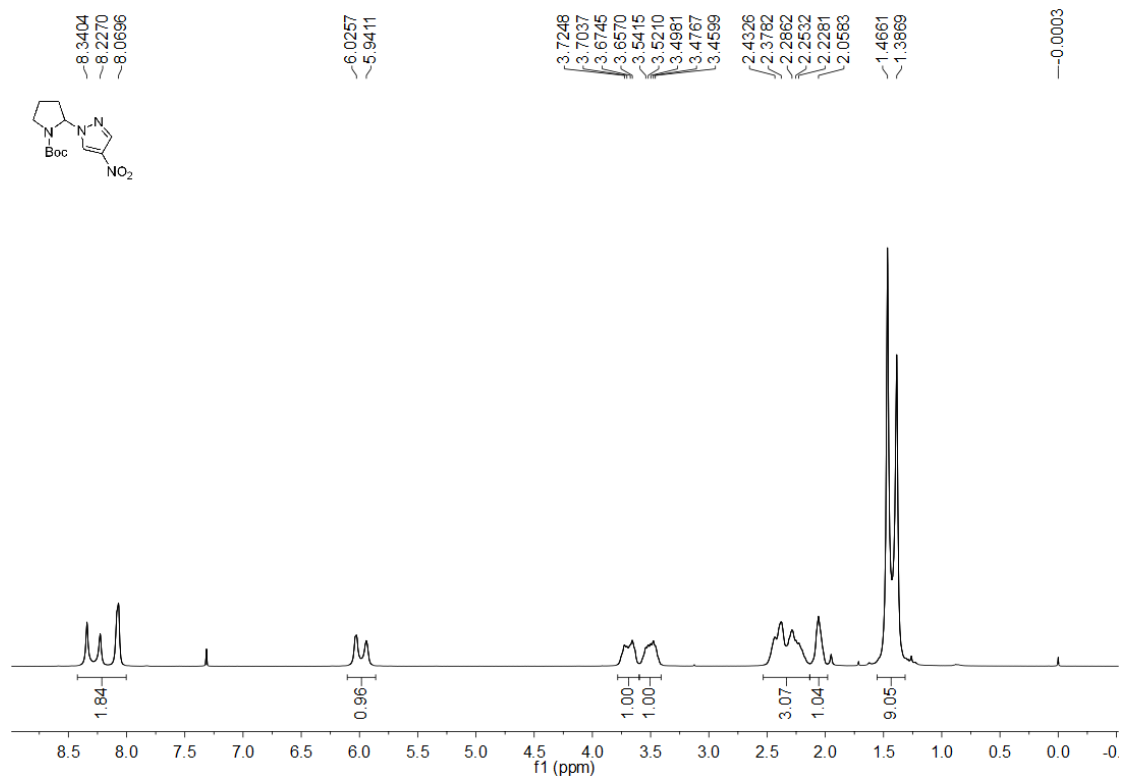
Methyl 1-(1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)-1H-pyrazole-4-carboxylate (**5i**)



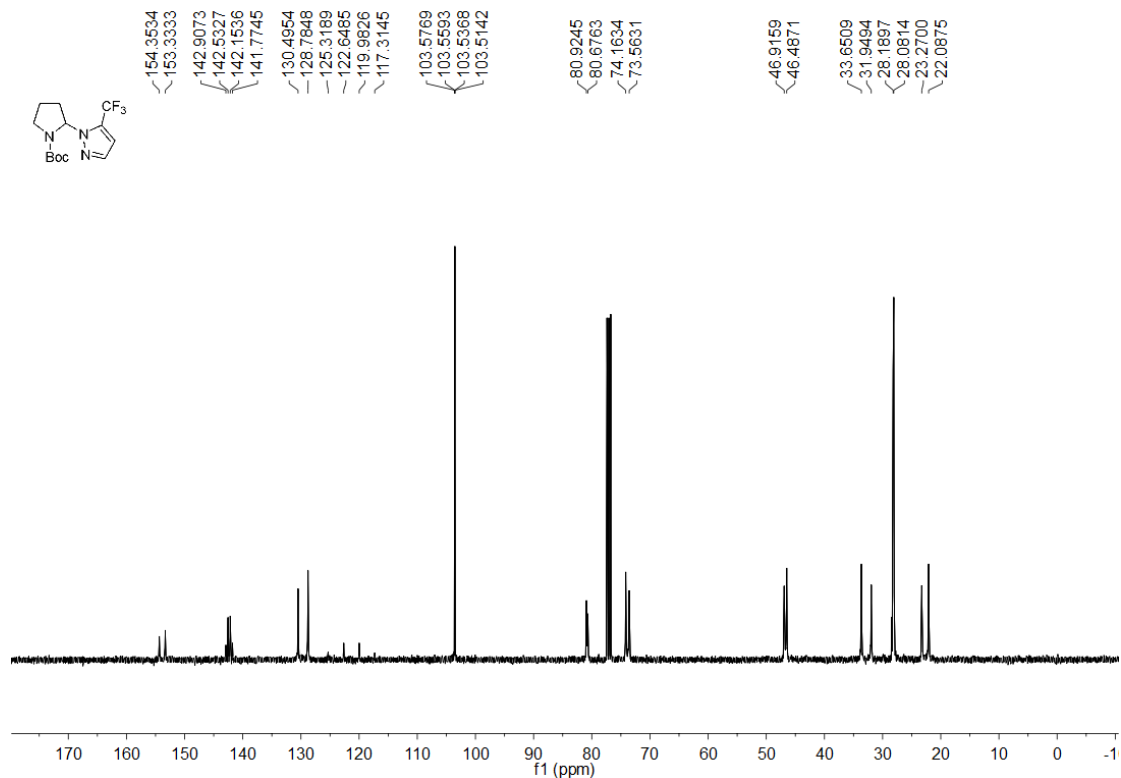
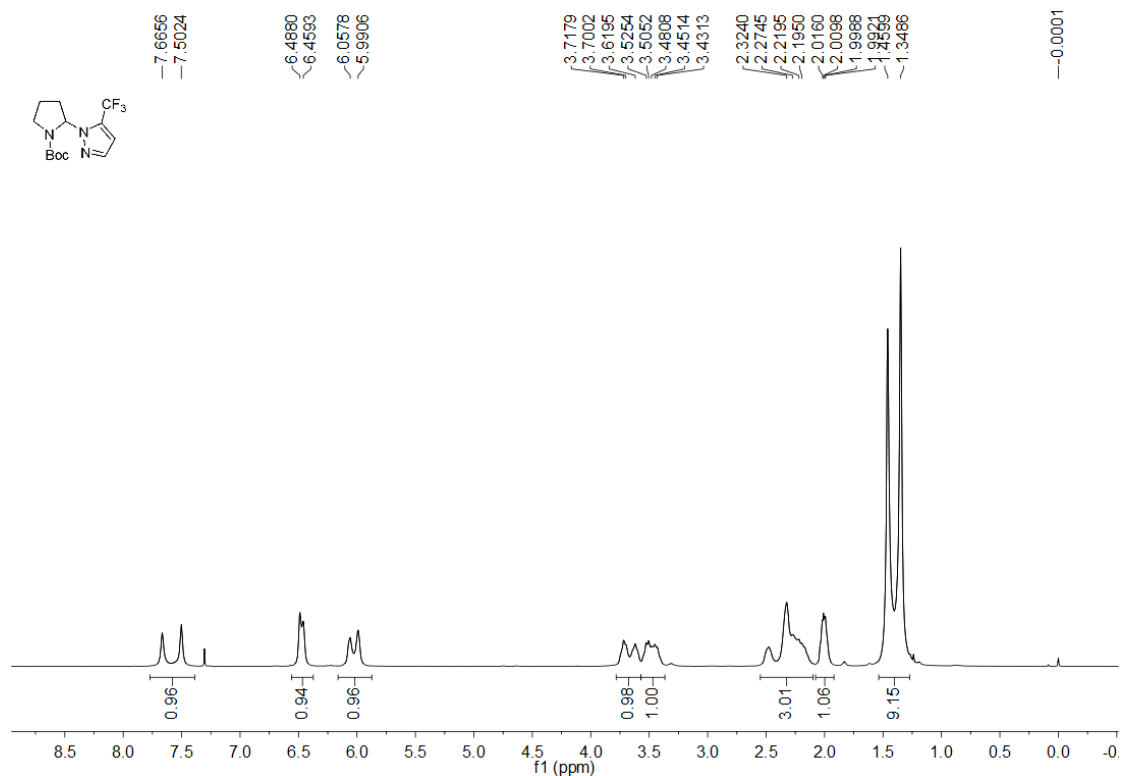
tert-Butyl 2-(3-phenyl-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5j**)

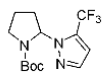


tert-Butyl 2-(4-nitro-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5k**)

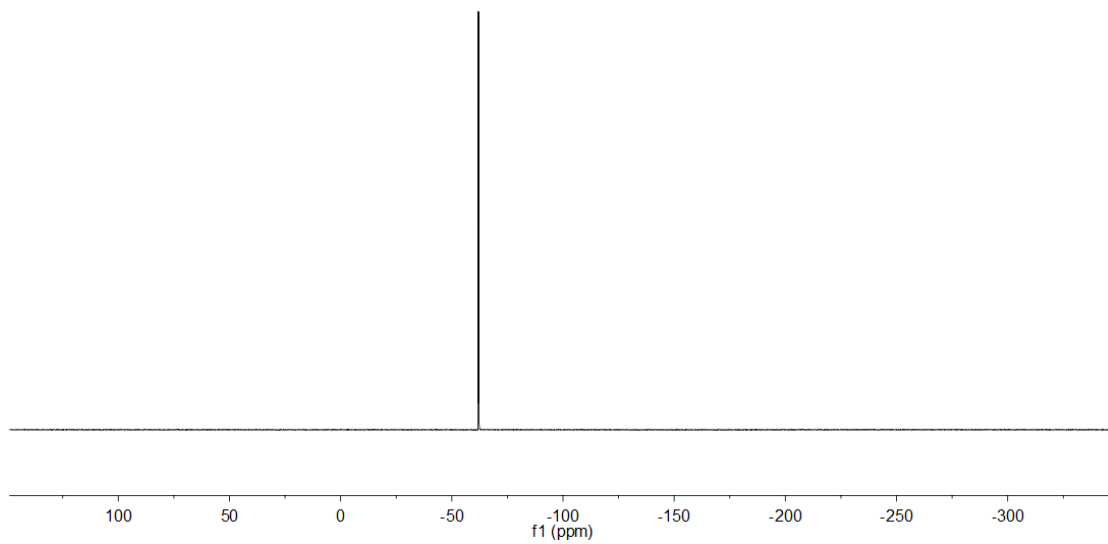


tert-Butyl 2-(5-(trifluoromethyl)-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5l**)

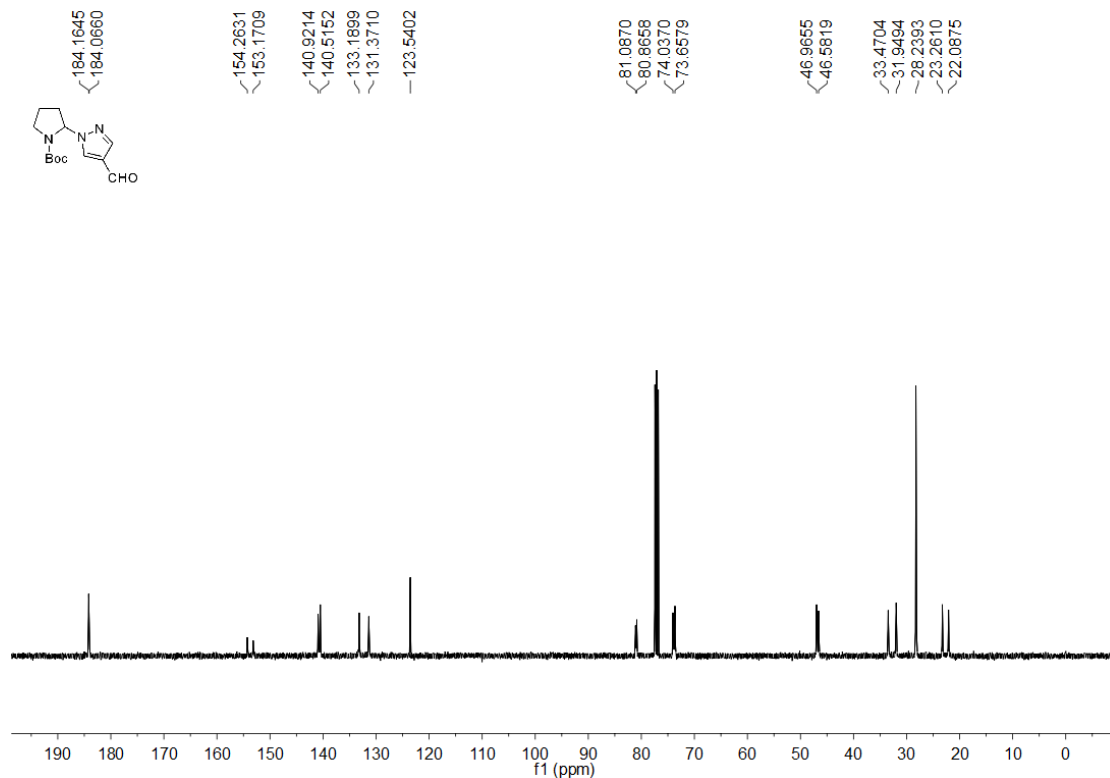
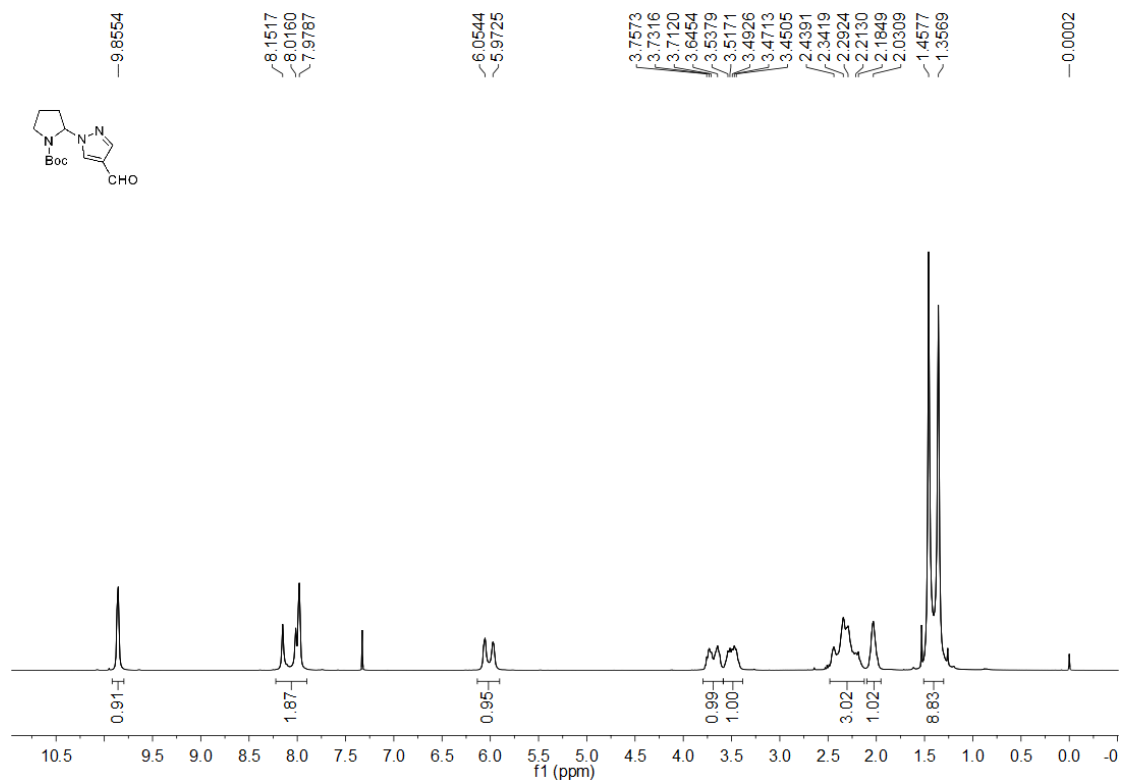




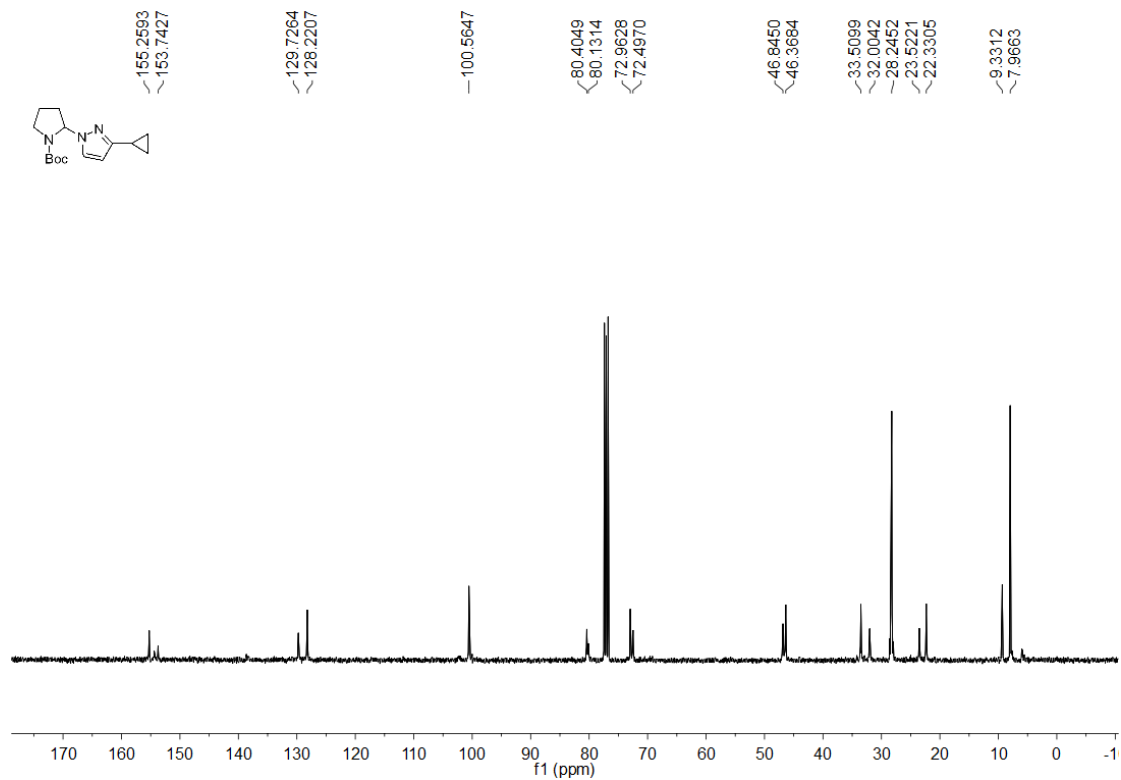
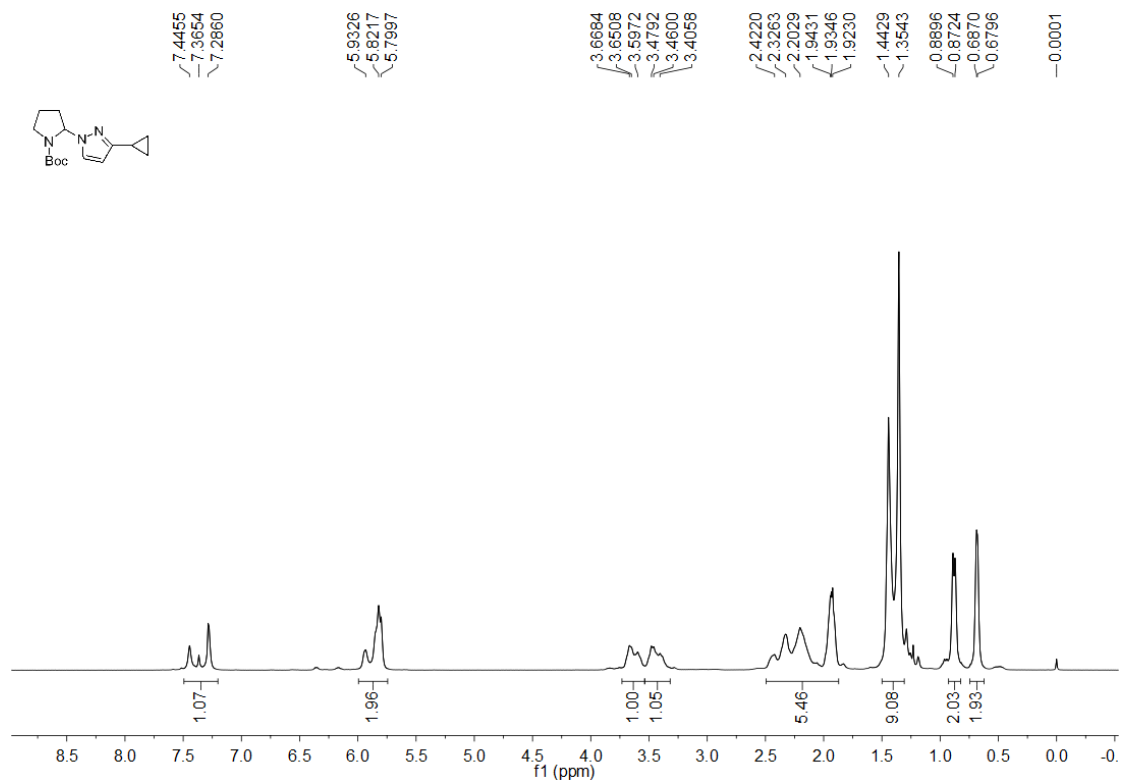
61.8879
61.9815



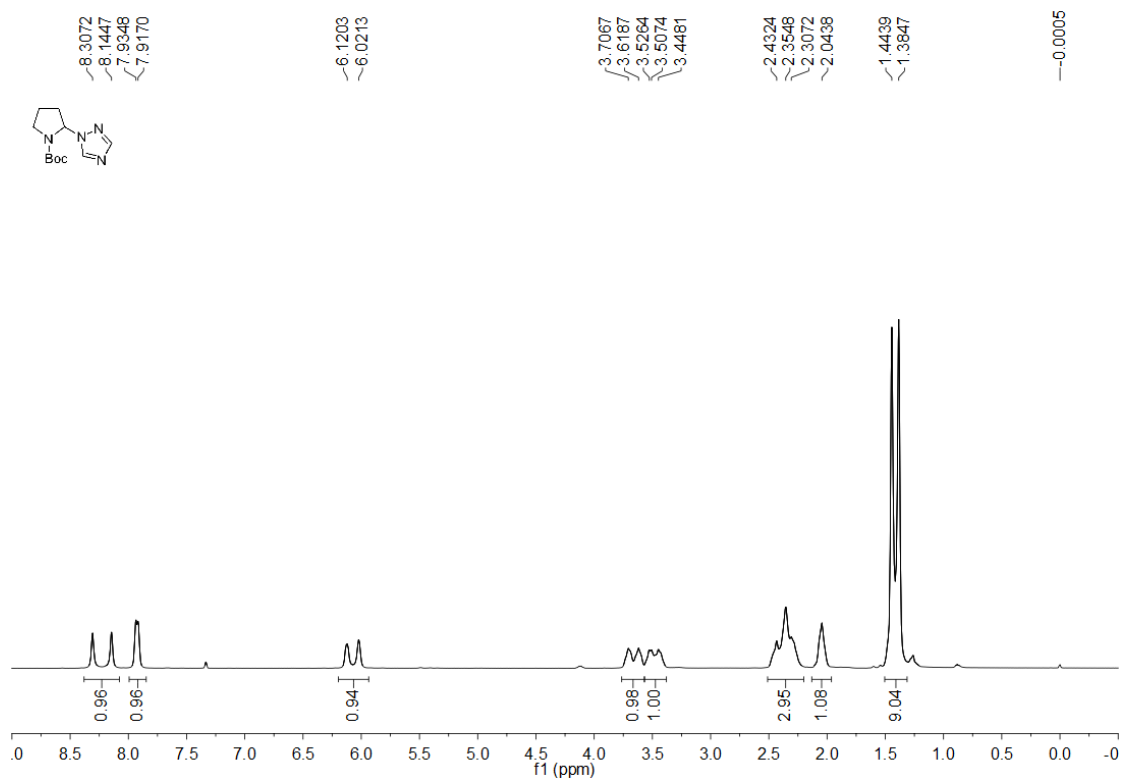
tert-Butyl 2-(4-formyl-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5m**)



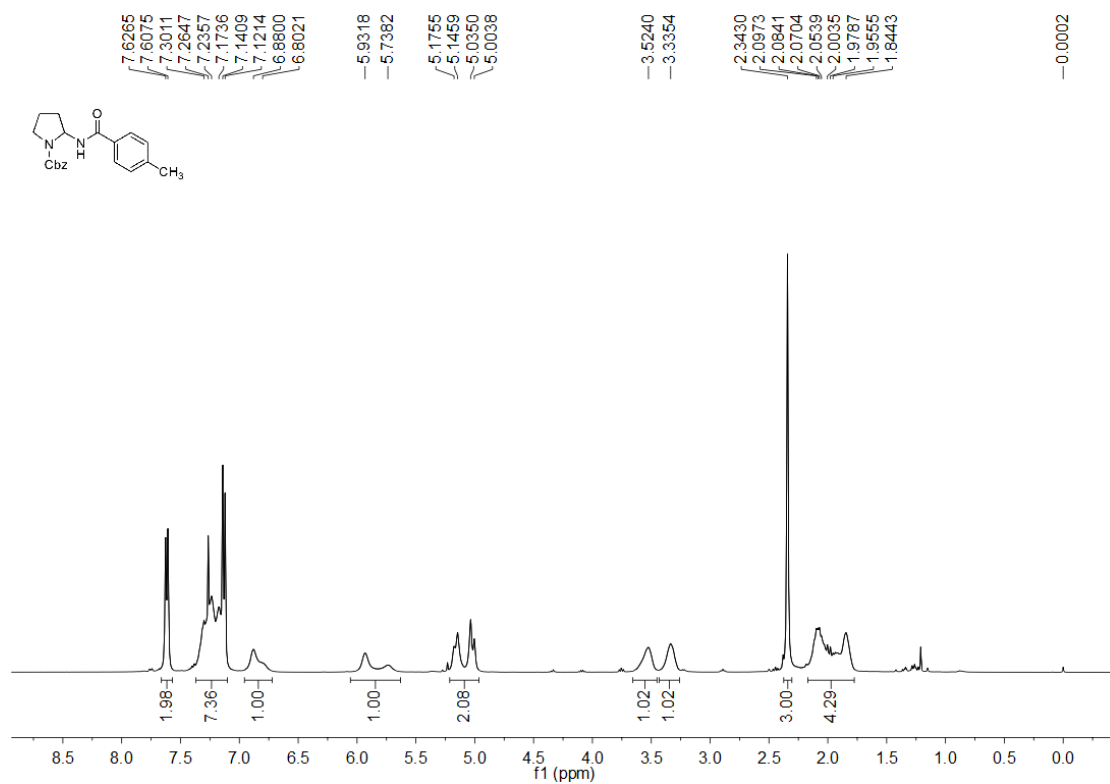
tert-Butyl 2-(3-cyclopropyl-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (**5n**)



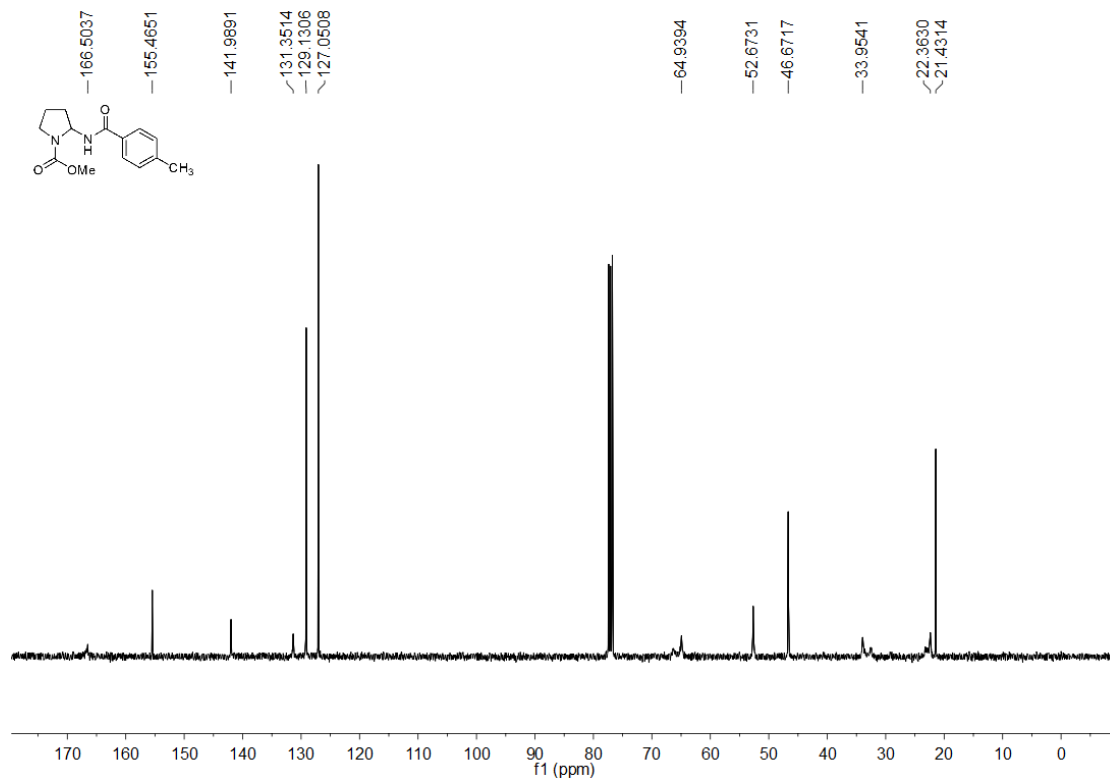
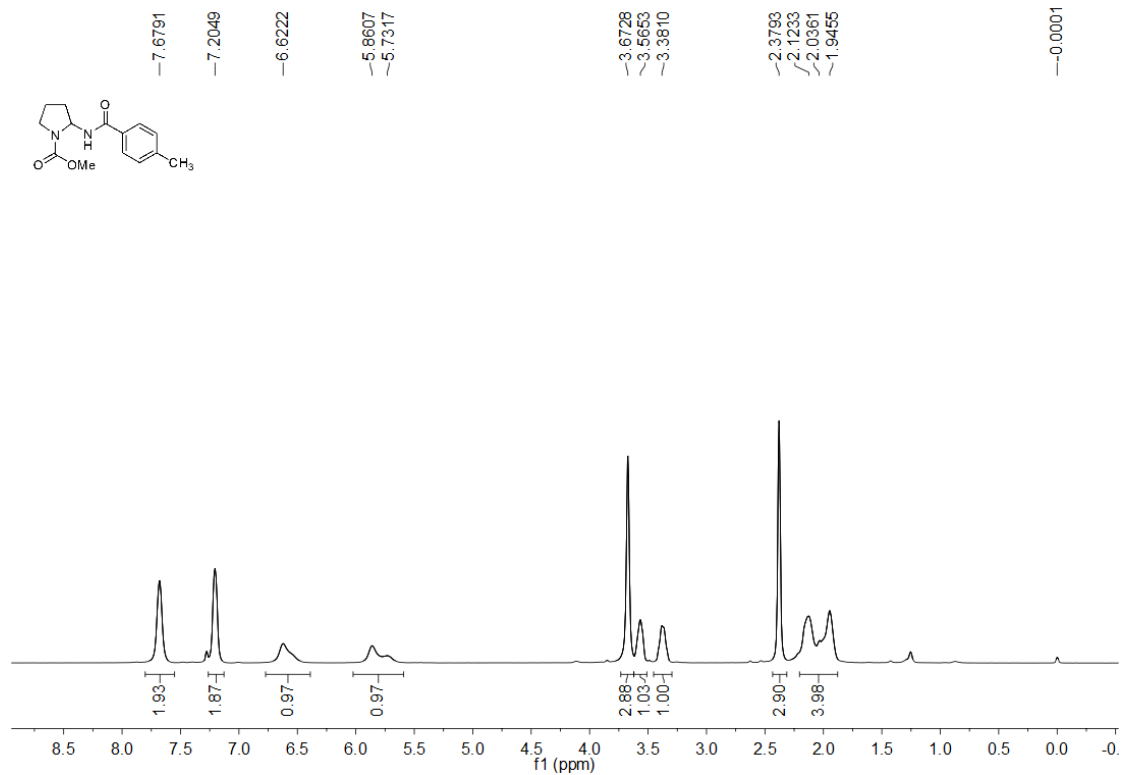
tert-Butyl 2-(1H-1,2,4-triazol-1-yl)pyrrolidine-1-carboxylate (**5o**)



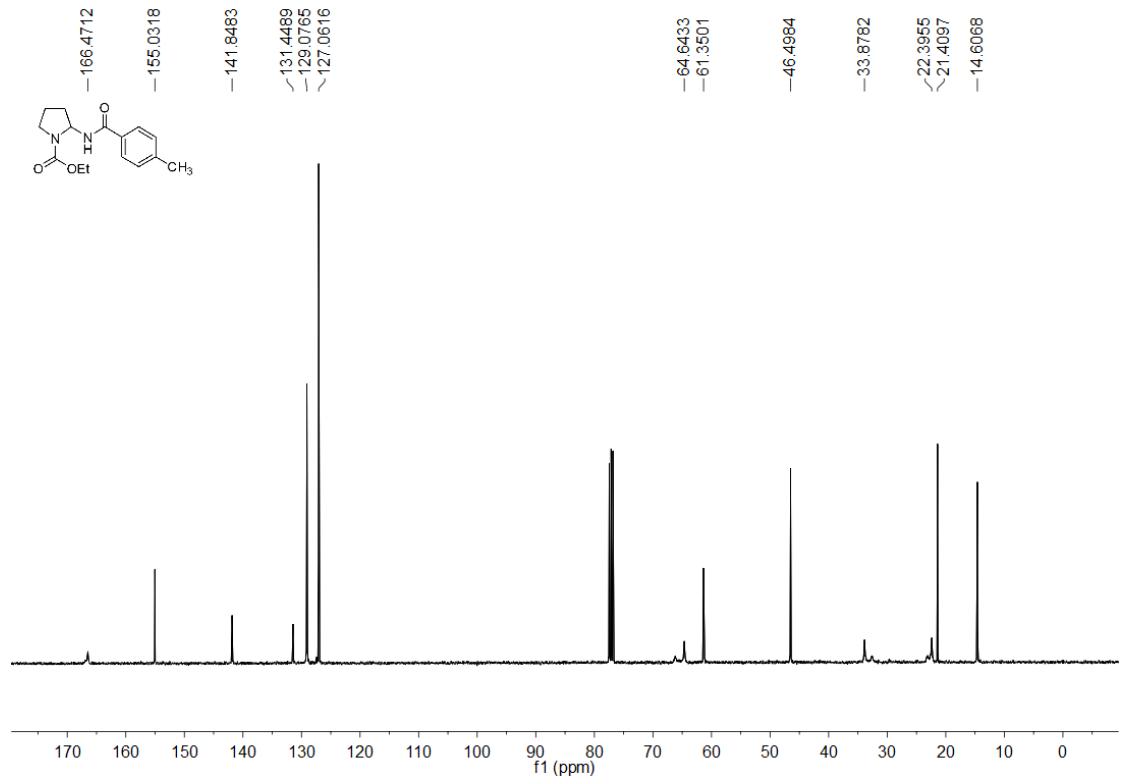
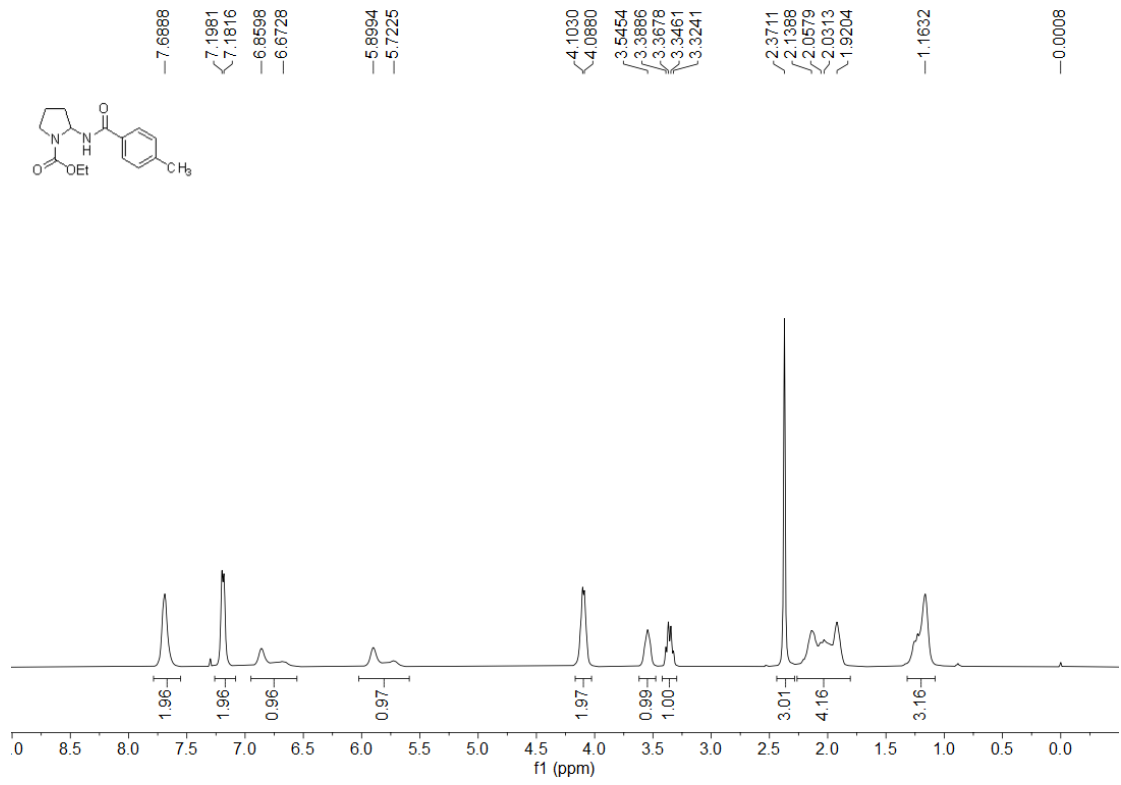
Benzyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**6b**)



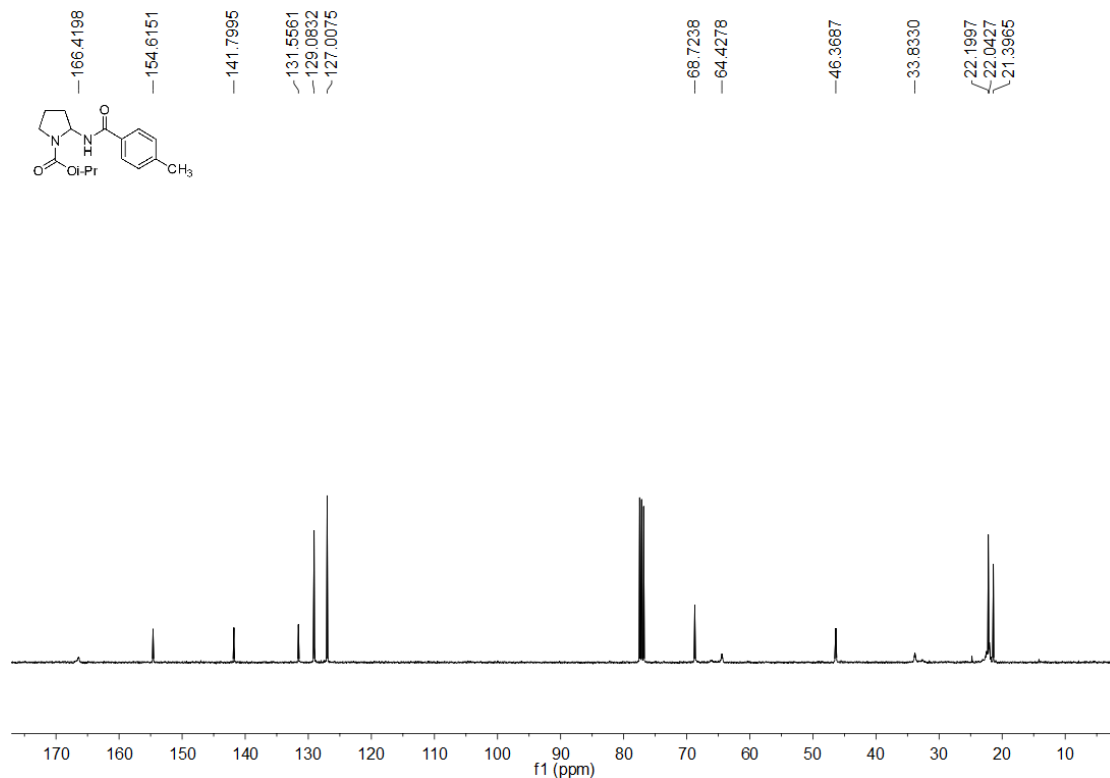
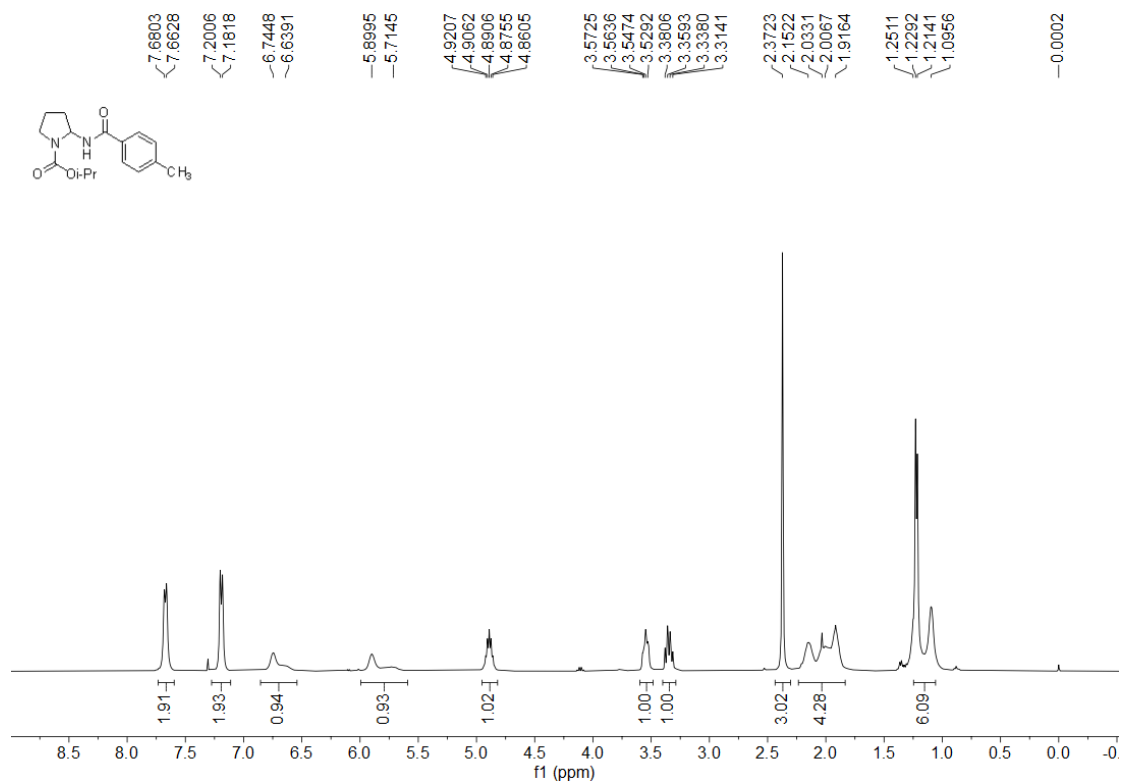
Methyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**6c**)



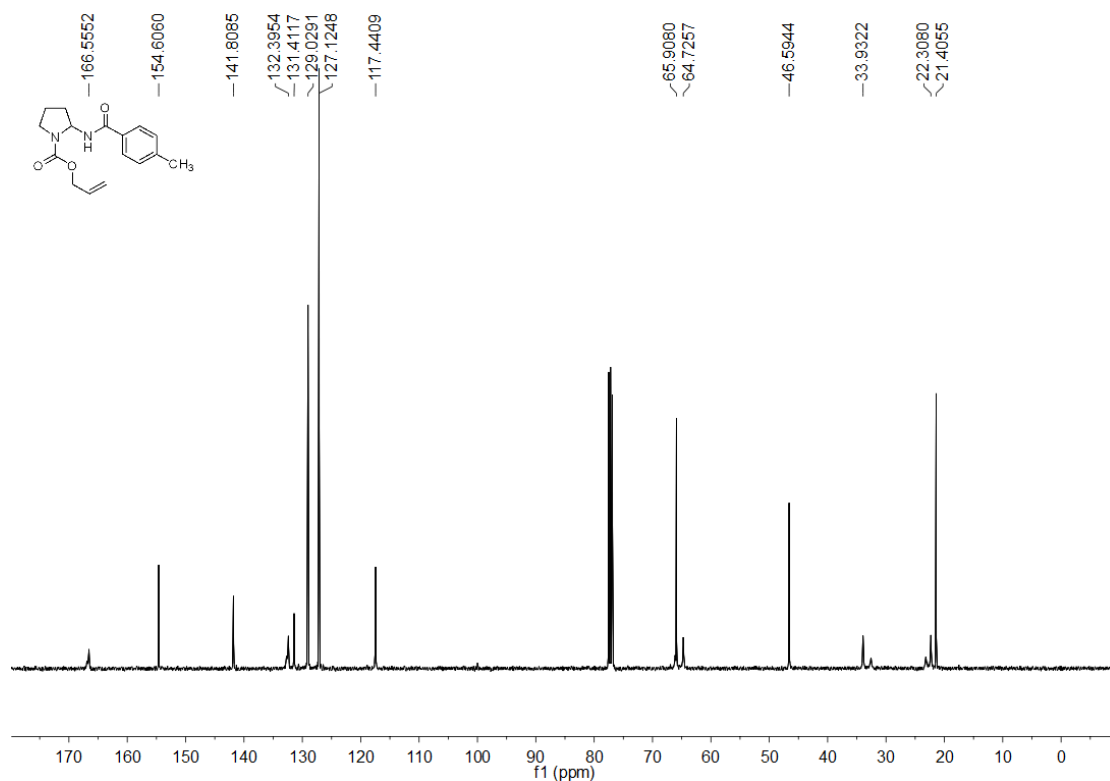
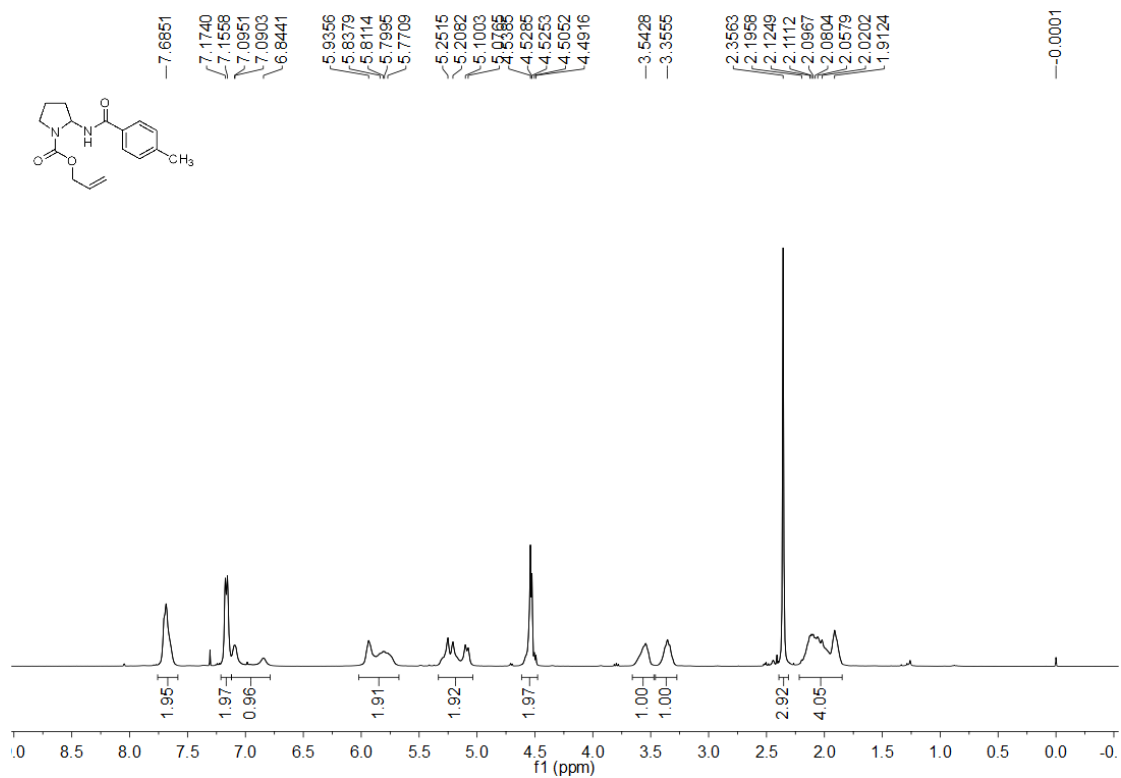
Ethyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**6d**)



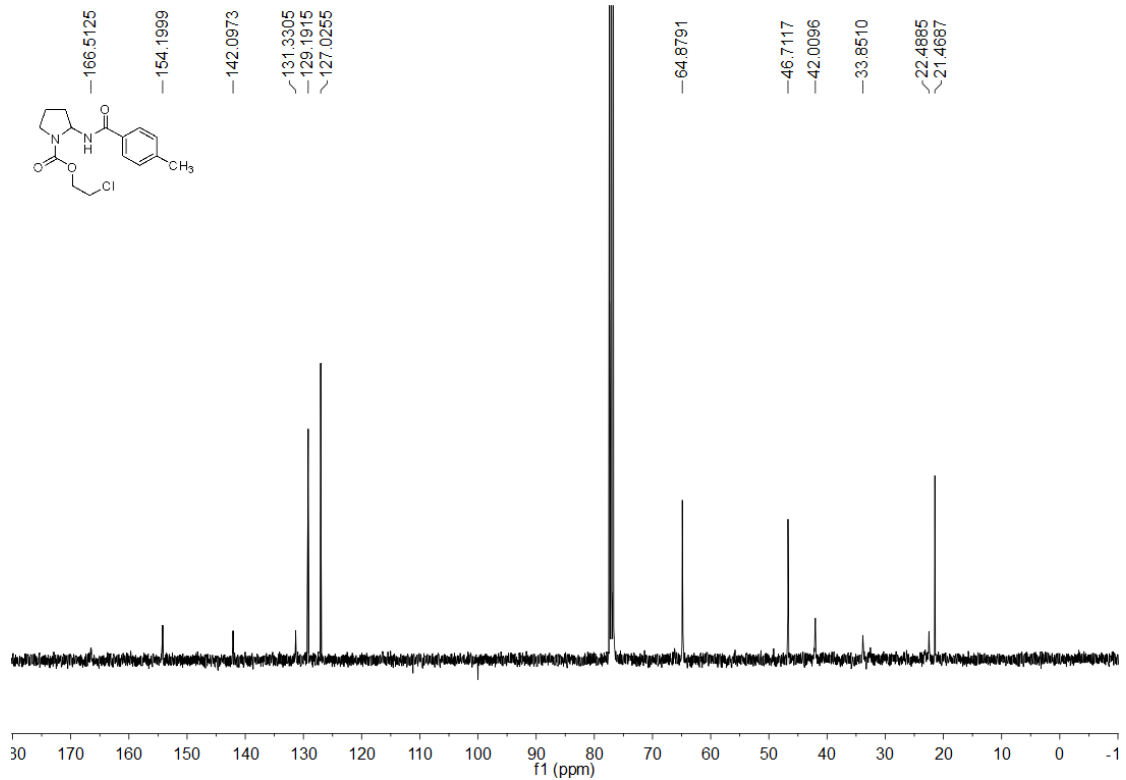
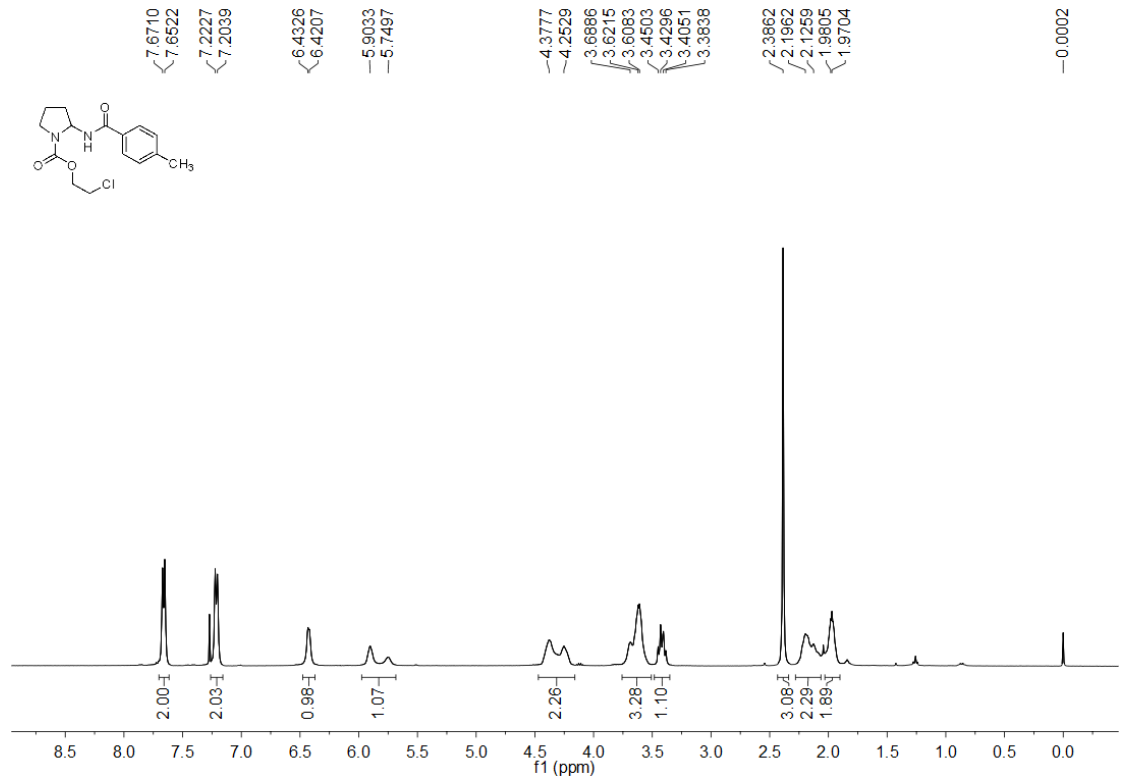
Isopropyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**6e**)



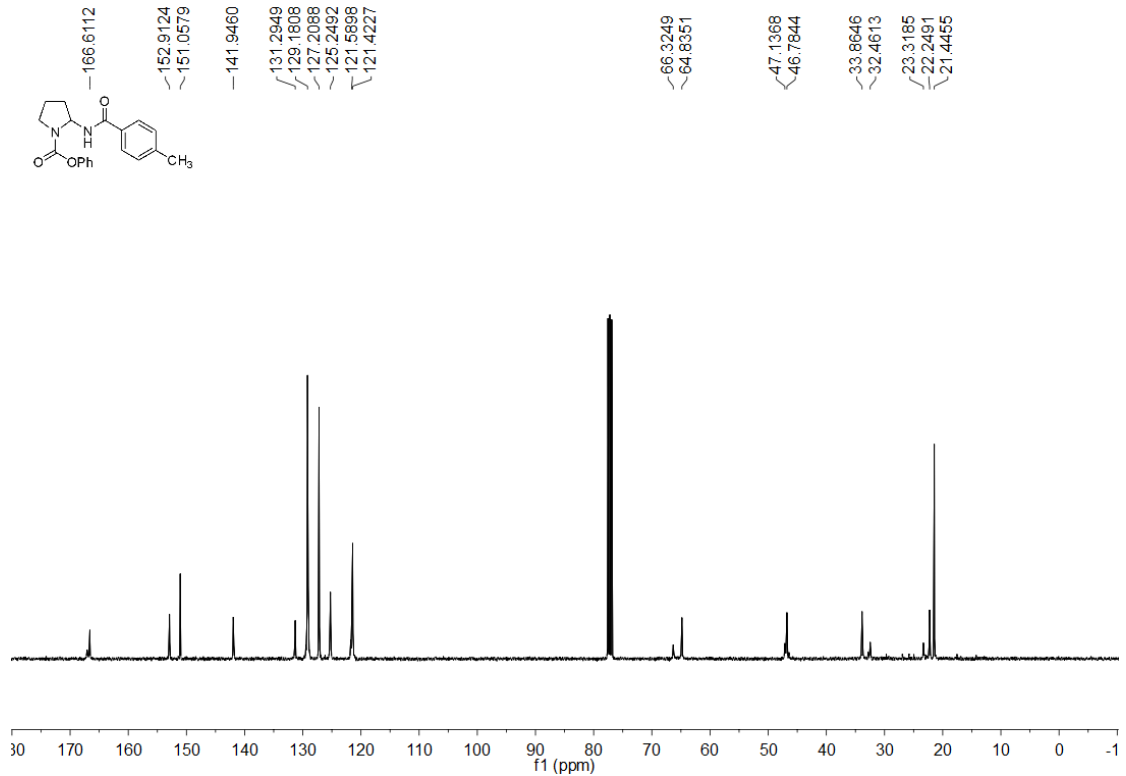
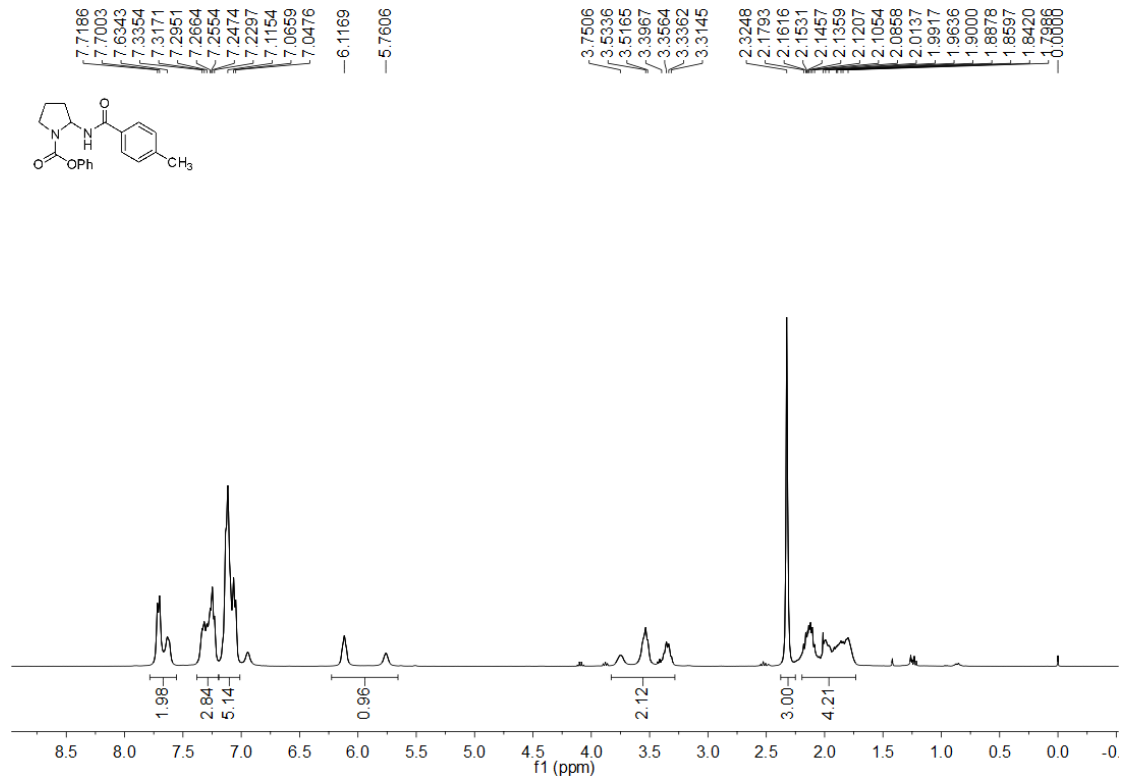
Allyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**6f**)



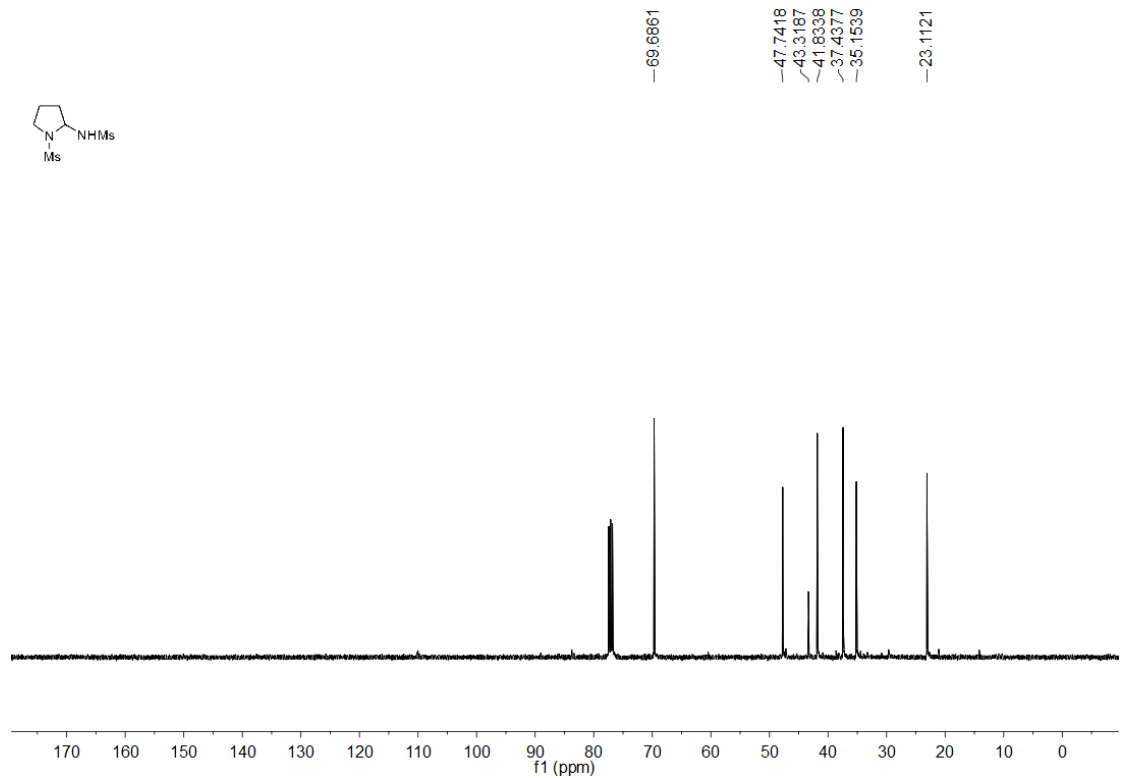
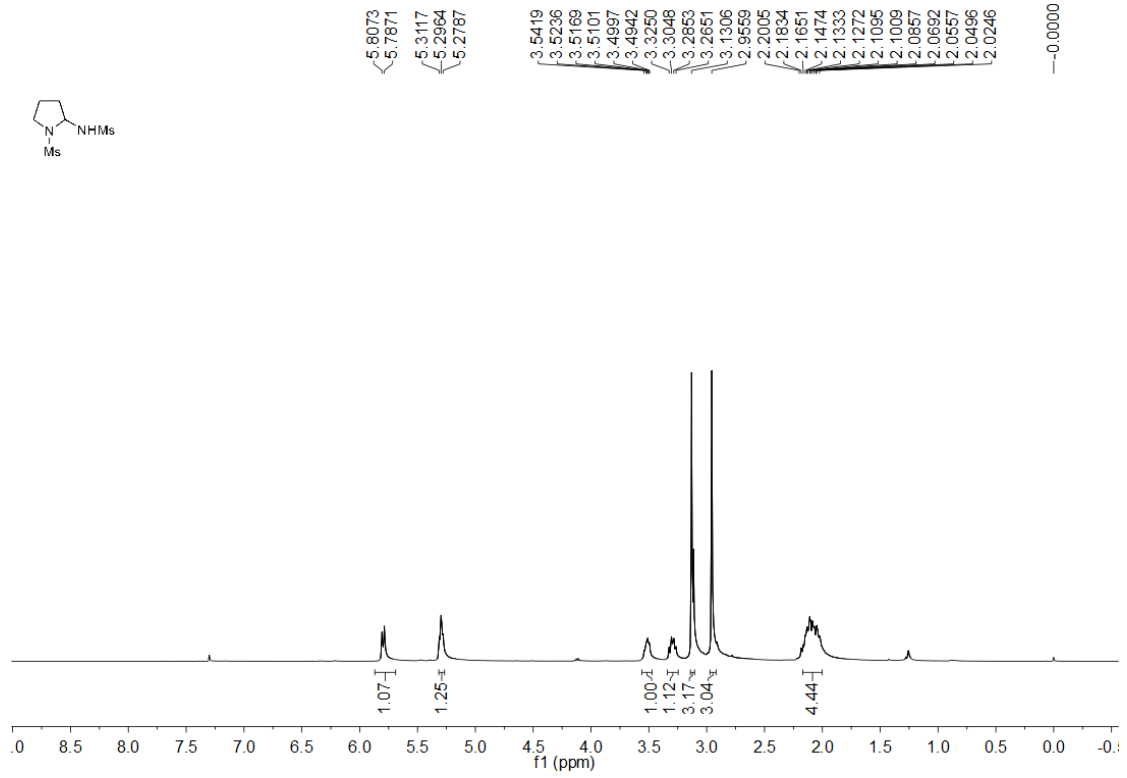
2-Chloroethyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**6g**)



Phenyl 2-(4-methylbenzamido)pyrrolidine-1-carboxylate (**6h**)



N-(1-(Methylsulfonyl)pyrrolidin-2-yl)methanesulfonamide (**11**)



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