

## Supplementary Information

# Facile Tin(II)-catalyzed Synthesis of *N*-Heterocycles from Dicarboxylic Acids and Arylamines

Van Hieu Tran,<sup>a,b</sup> and Hee-Kwon Kim<sup>a,b,\*</sup>

<sup>a</sup>Department of Nuclear Medicine, Molecular Imaging & Therapeutic Medicine Research Center, Jeonbuk National University Medical School and Hospital, Jeonju, 54907, Republic of Korea

<sup>b</sup>Research Institute of Clinical Medicine of Jeonbuk National University-Biomedical Research Institute of Jeonbuk National University Hospital, Jeonju, 54907, Republic of Korea

\* Corresponding author: Hee-Kwon Kim

Tel: +82 63 250 2768; Fax: +82 63 255 1172.

*E-mail address:* hkkim717@jbnu.ac.kr (H-K Kim).

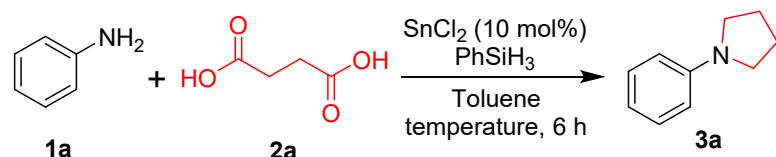
## **Table of Contents**

1. General Information .....	S2
2. Screening of reaction temperature for synthesis of azacycles .....	S3
3. Screening of amount of reagents for synthesis of azacycles .....	S4
4. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra .....	S5

## **1. General information**

All chemicals are available on the market and solvents may be used directly from the bottle. Thin-layer chromatography (TLC) analysis was used to monitor the reaction's development. TLC analysis was carried out on an aluminum plate coated with silica gel 60 F254, then TLC spots were observed by exposing the plate to UV light (254 nm). The flash chromatography was carried out using 230–400 mesh silica gel and analytical level solvent. A Stuart SMP10 Melting Point Apparatus was used to determine melting points. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a 400 MHz Bruker Avance spectrometer at 400 MHz and a 100 MHz, respectively. Chemical shifts (ppm) relative to the remaining protonated solvent resonance were recorded, whereas coupling constants (J) were expressed in Hz.

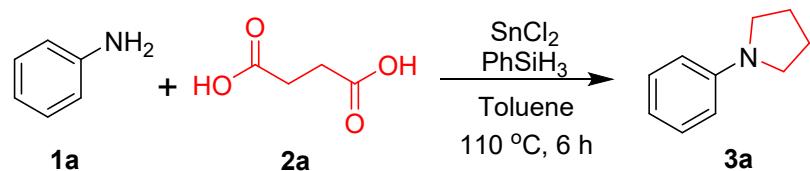
**2. Table S1. Screening of reaction temperature for synthesis of azacycles<sup>a</sup>**



Entry	Aniline (equiv.)	Succinic acid (equiv.)	PhSiH <sub>3</sub> (equiv.)	Temperature (°C)	Yield <sup>b</sup> (%)
1	1.0	1.1	4	60	NR <sup>c</sup>
2	1.0	1.1	4	80	NR <sup>c</sup>
3	1.0	1.1	4	90	NR <sup>c</sup>
4	1.0	1.1	4	100	NR <sup>c</sup>
5	1.0	1.1	4	110	85
6	1.0	1.1	4	120	85
7	1.0	1.1	4	130	86

<sup>a</sup> Reaction conditions: compound 1 (1.0 mmol), succinic acid (1.1 equiv.) PhSiH<sub>3</sub> (4.0 equiv.),- catalyst (10 mol %), toluene (3 mL), 6 h. <sup>b</sup> Isolated yield after purification by flash column chromatography. <sup>c</sup> No reaction.

**3. Table S2. Screening of amount of reagents for synthesis of azacycles<sup>a</sup>**

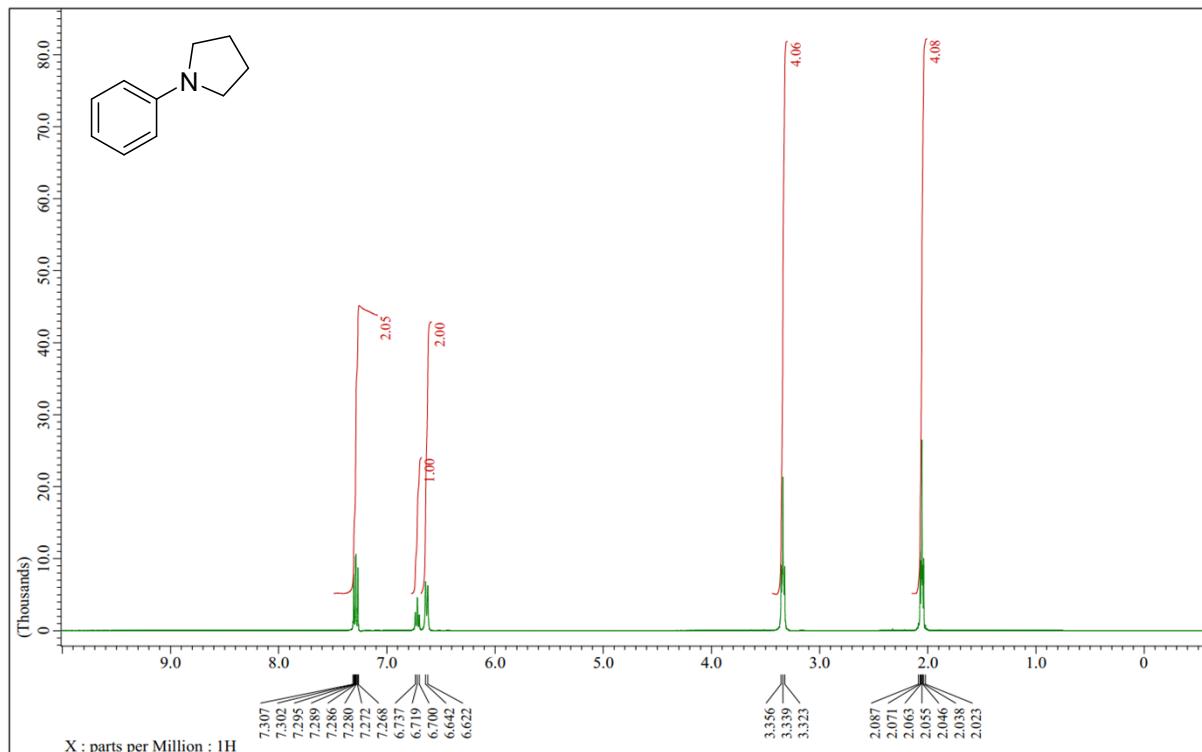


Entry	Aniline (equiv.)	Succinic acid (equiv.)	SnCl <sub>2</sub> (equiv.)	PhSiH <sub>3</sub> (equiv.)	Yield <sup>b</sup> (%)
1	1.0	1.1	0.2	4	86
2	1.0	1.1	0.15	4	85
3	1.0	1.1	0.1	4	85
4	1.0	1.1	0.05	4	22
5	1.0	1.1	0.02	4	13
6	1.0	1.1	0	4	NR <sup>c</sup>
7	1.0	1.1	0.1	6	85
8	1.0	1.1	0.1	5	85
9	1.0	1.1	0.1	3	58
10	1.0	1.1	0.1	2	16
11	1.0	1.1	0.1	1	NR <sup>c</sup>
12	1.0	1.1	0.1	0	NR <sup>c</sup>

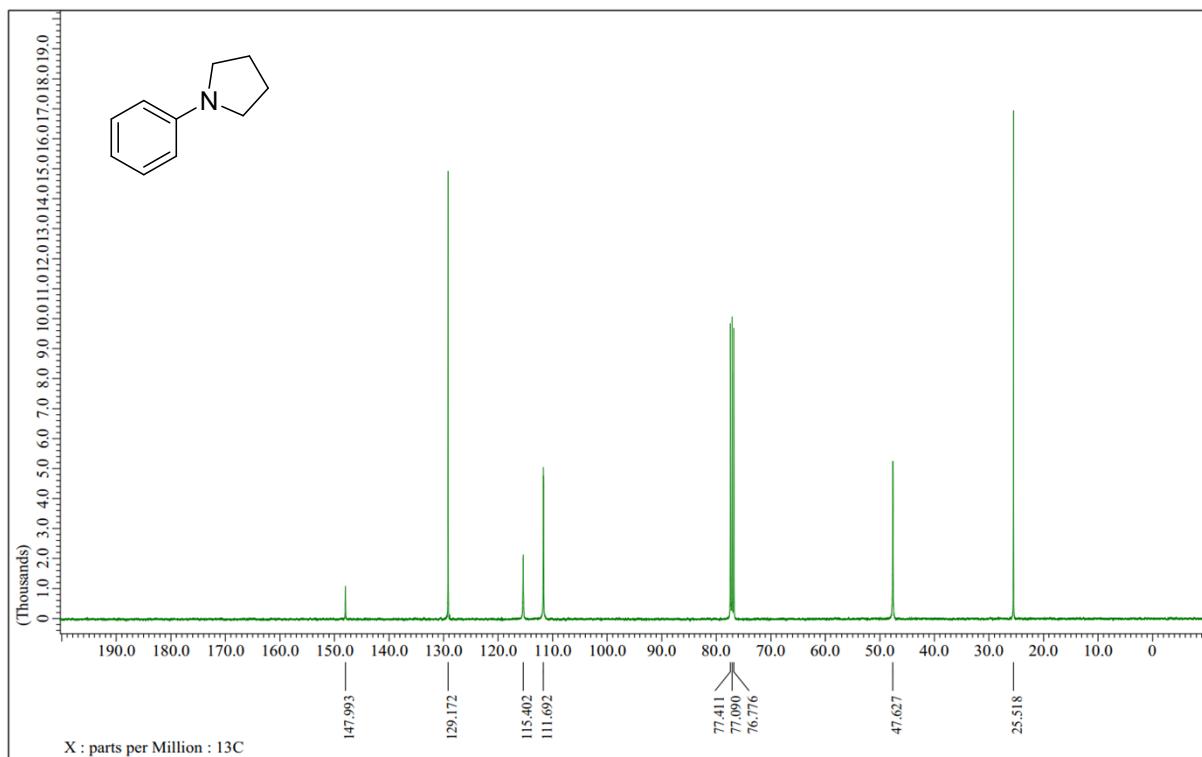
<sup>a</sup> Reaction conditions: compound **1a** (1.0 mmol), succinic acid **2a** (1.1 equiv.), PhSiH<sub>3</sub>, catalyst, toluene (3 mL), 6 h, 110 °C. <sup>b</sup> Isolated yield after purification by flash column chromatography. <sup>c</sup> No reaction.

#### 4. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compounds

##### 1-phenylpyrrolidine (3a)

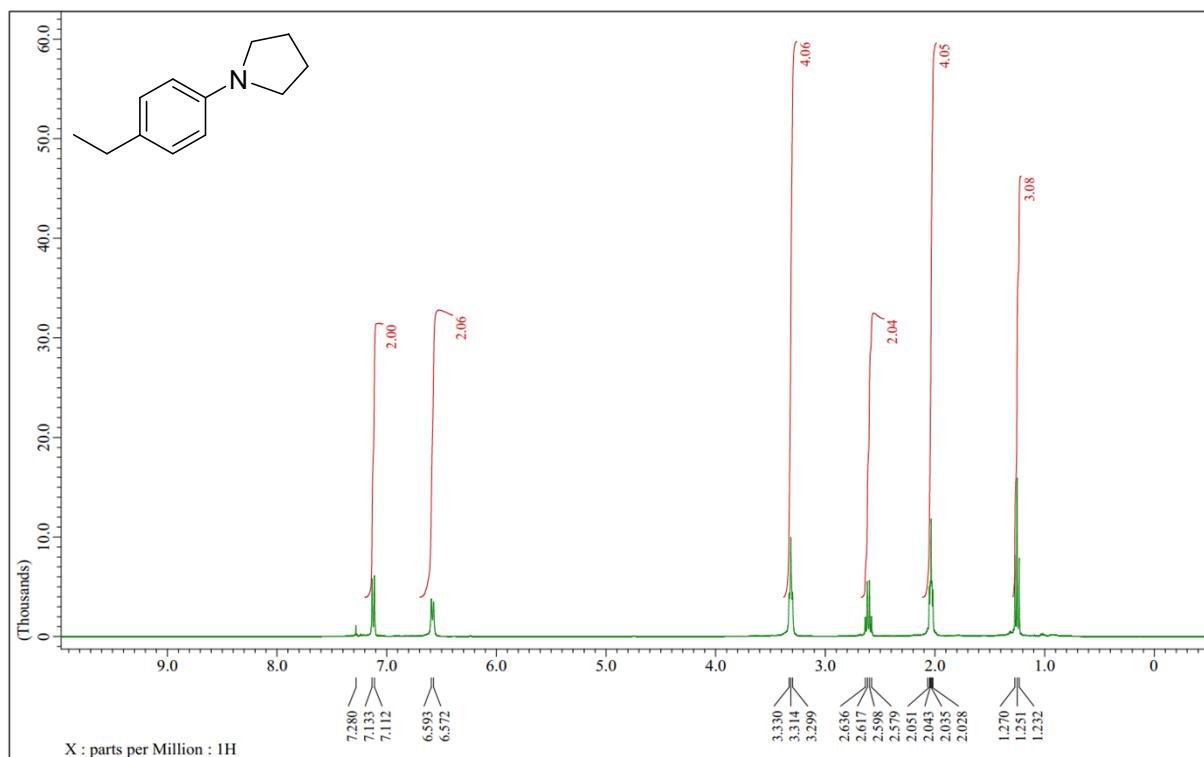


$^1\text{H}$  NMR spectrum of 1-phenylpyrrolidine (3a)

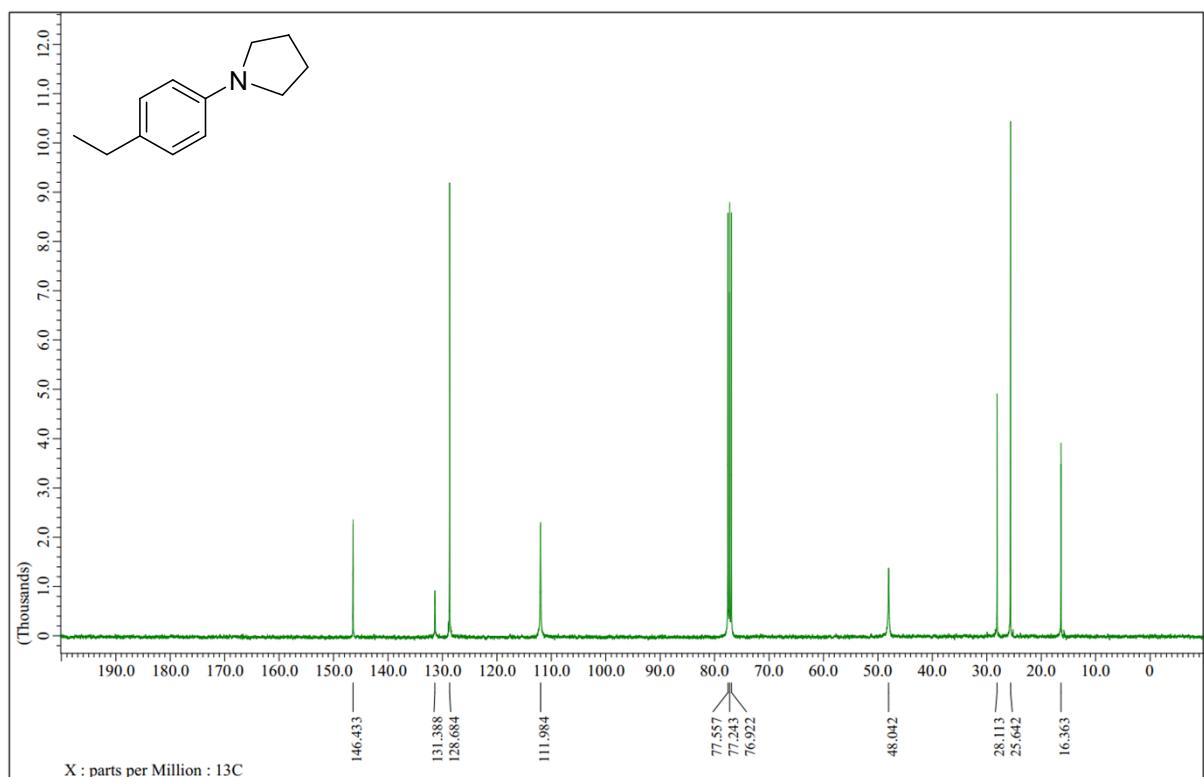


$^{13}\text{C}$  NMR spectrum of 1-phenylpyrrolidine (3a)

**1-(4-ethylphenyl)pyrrolidine (3b)**

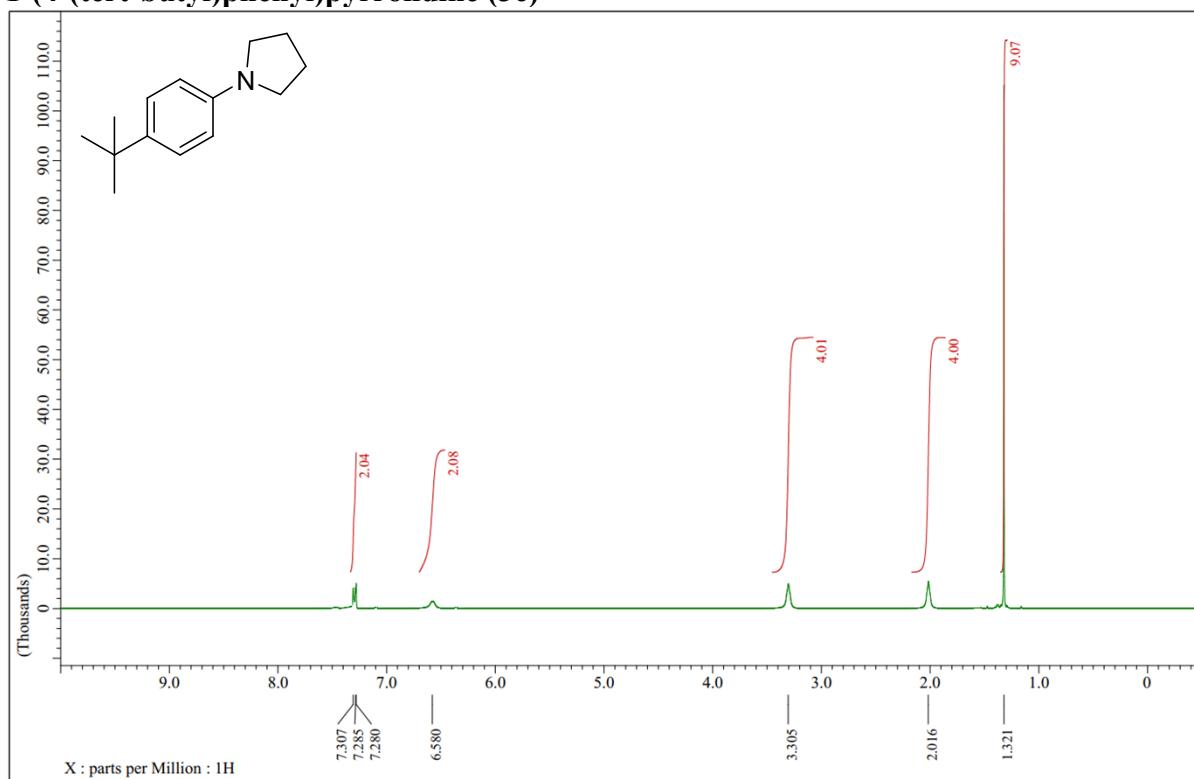


<sup>1</sup>H NMR spectrum of 1-(4-ethylphenyl)pyrrolidine (**3b**)

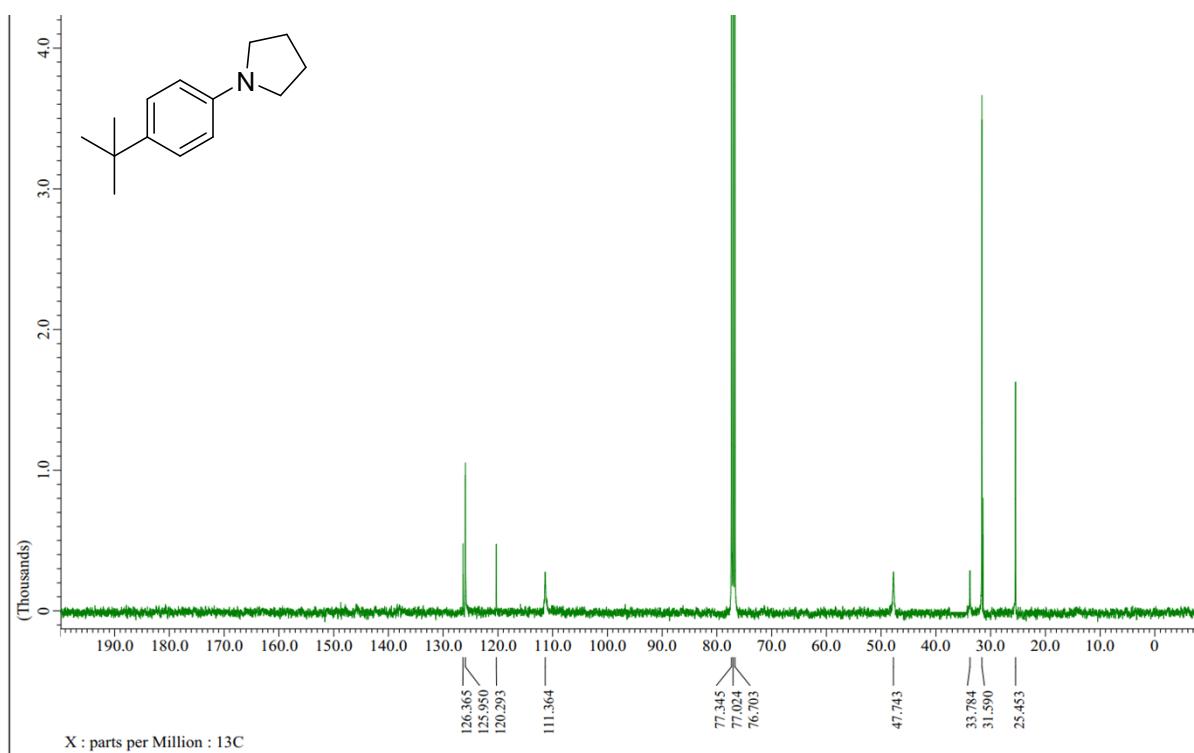


<sup>13</sup>C NMR spectrum of 1-(4-ethylphenyl)pyrrolidine (**3b**)

**1-(4-(tert-butyl)phenyl)pyrrolidine (3c)**

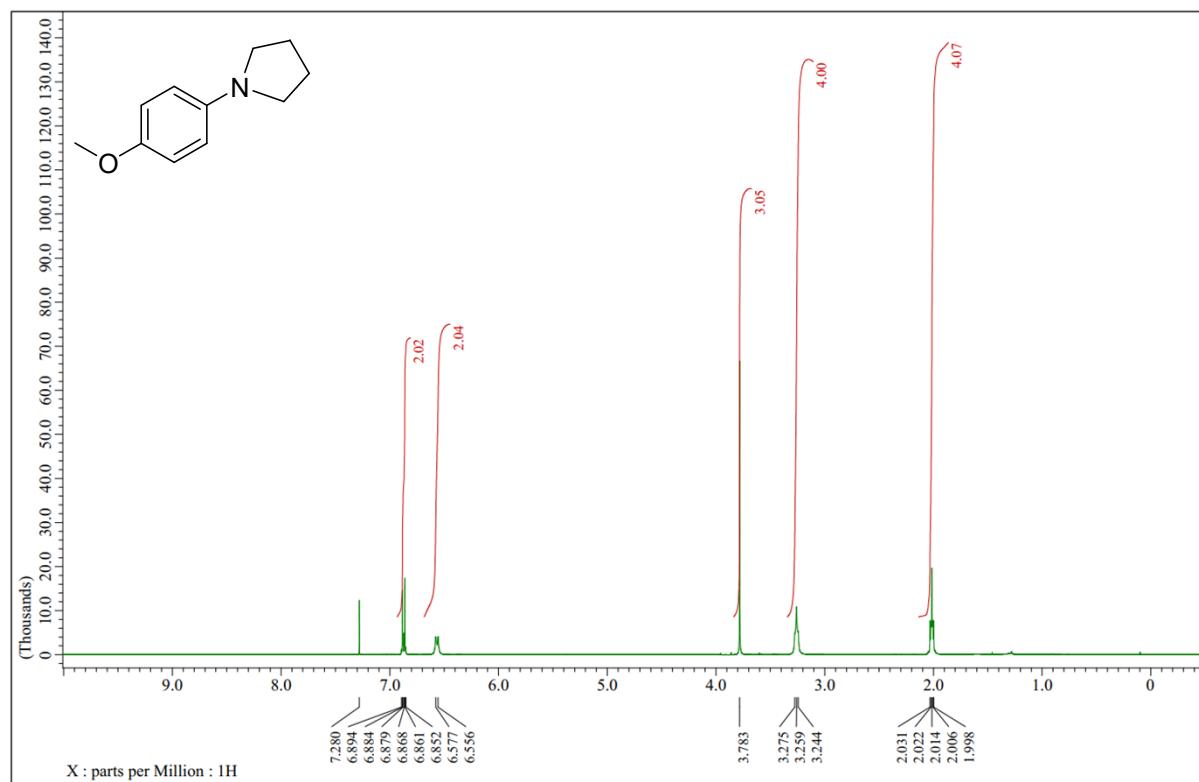


<sup>1</sup>H NMR spectrum of 1-(4-(tert-butyl)phenyl)pyrrolidine (3c)

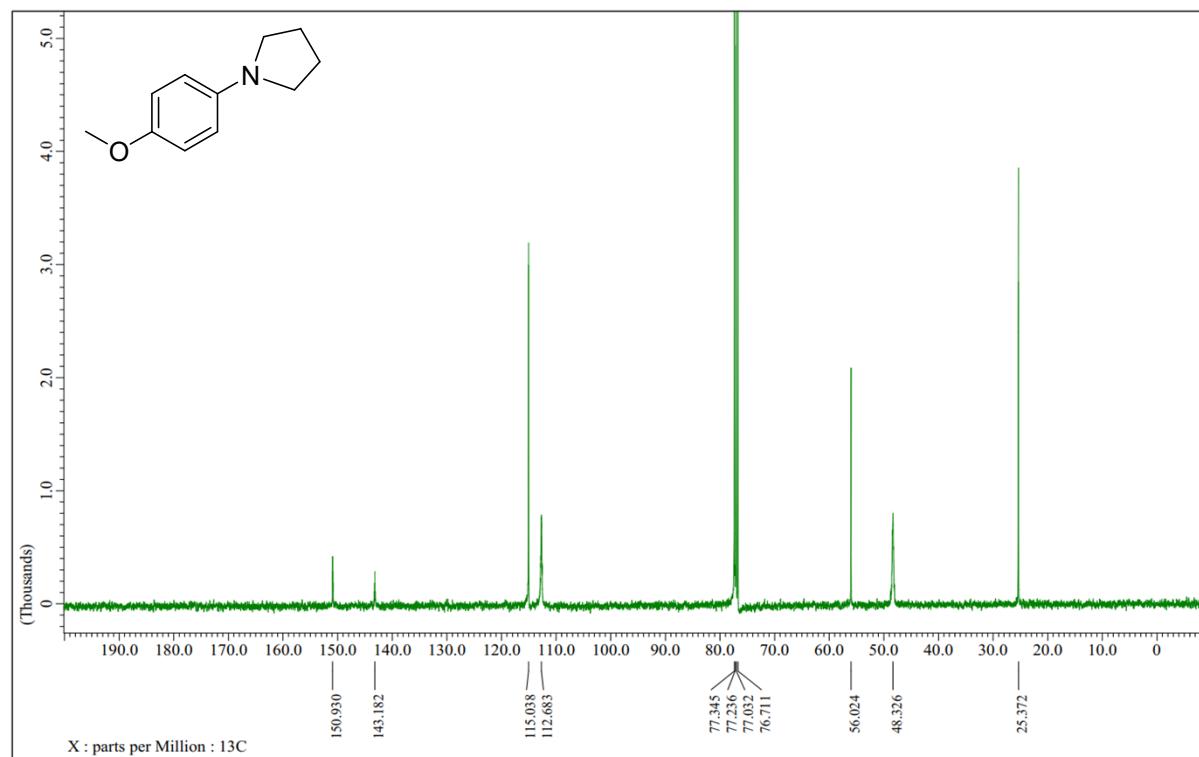


<sup>13</sup>C NMR spectrum of 1-(4-(tert-butyl)phenyl)pyrrolidine (3c)

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

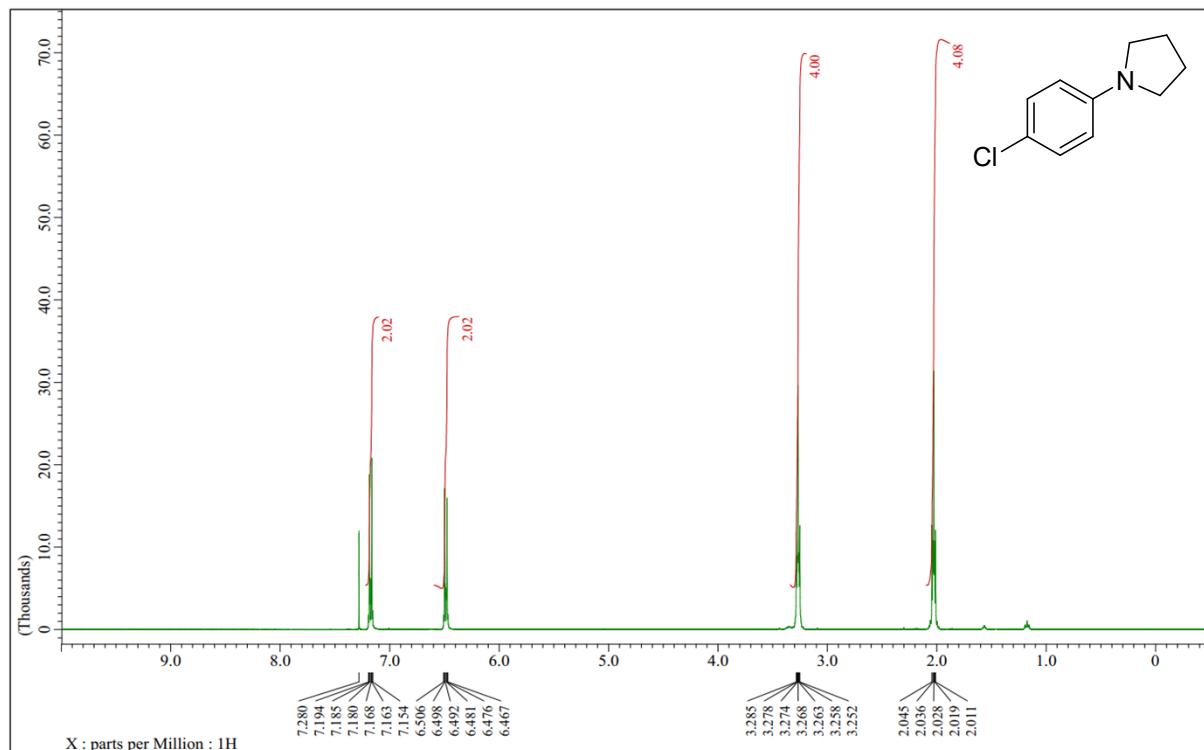


<sup>1</sup>H NMR spectrum of 1-(4-methoxyphenyl)pyrrolidine (3d)

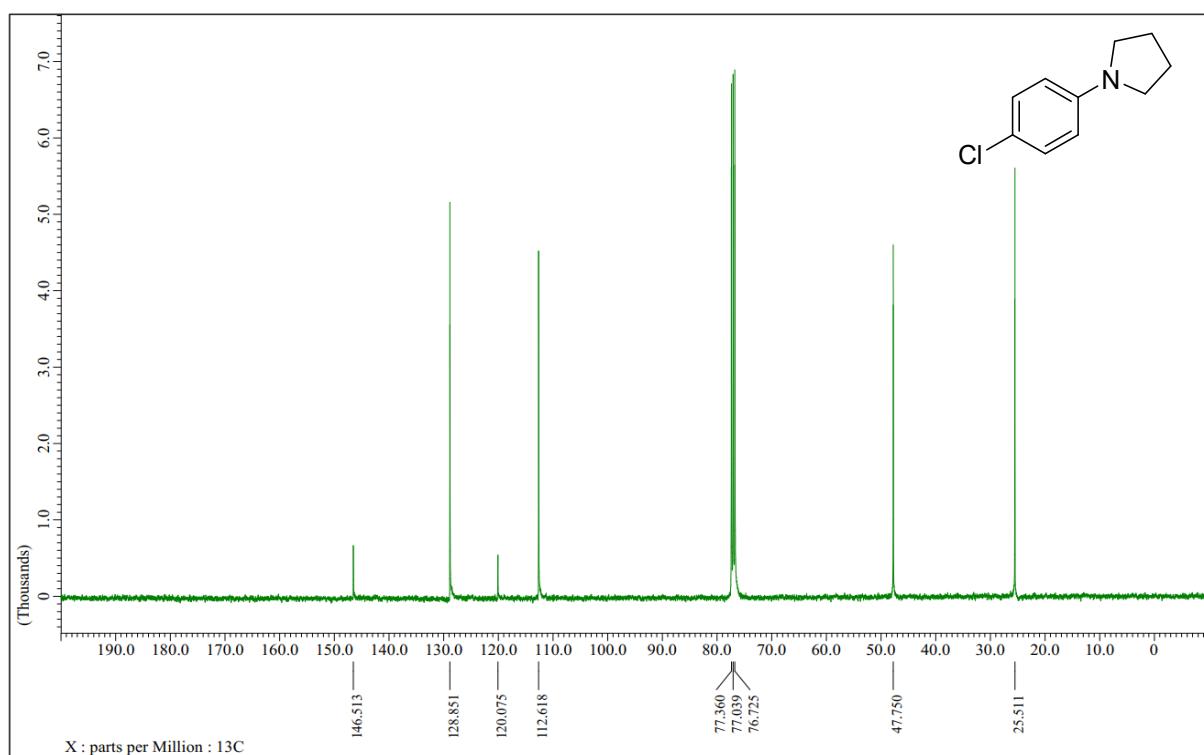


<sup>13</sup>C NMR spectrum of 1-(4-methoxyphenyl)pyrrolidine (3d)

### 1-(4-chlorophenyl)pyrrolidine (3e)

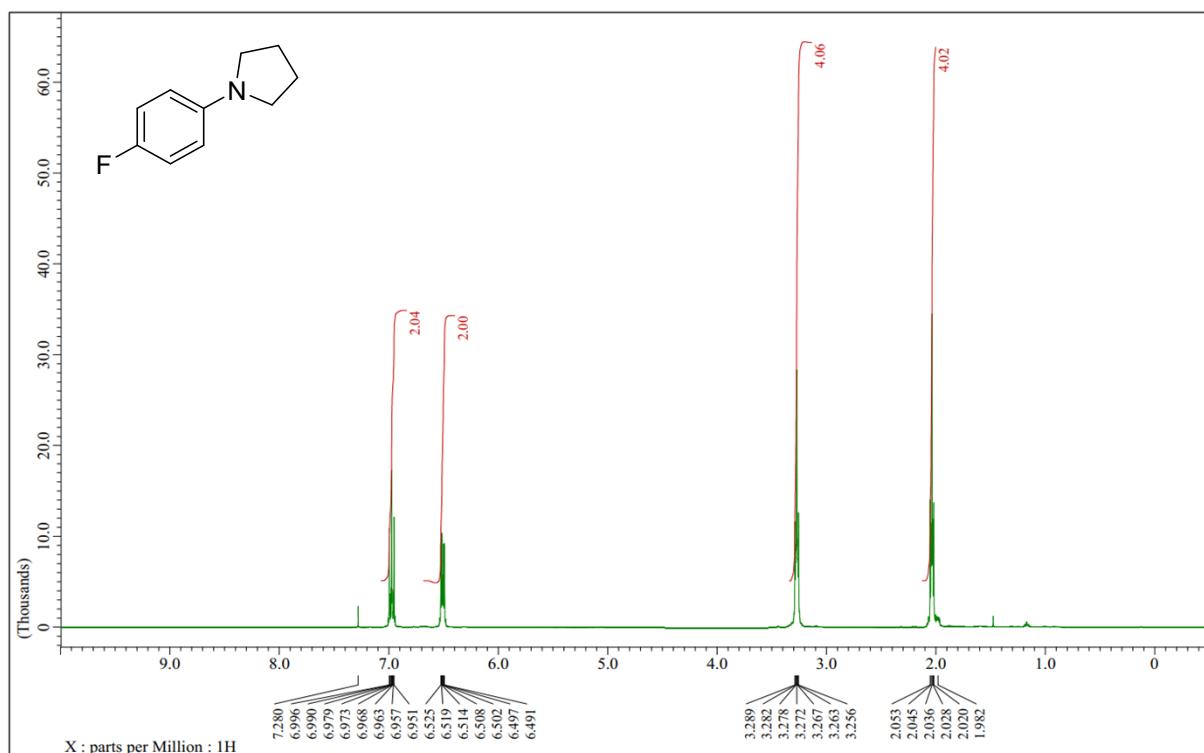


<sup>1</sup>H NMR spectrum of 1-(4-chlorophenyl)pyrrolidine (3e)

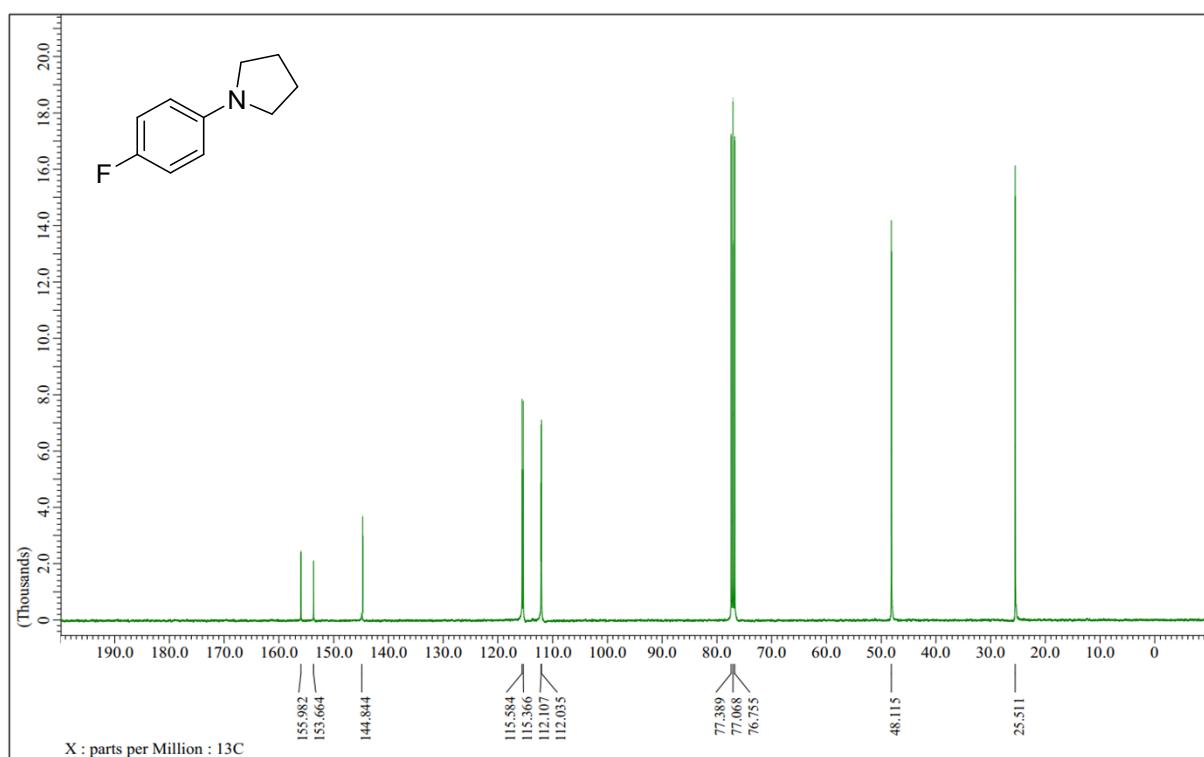


<sup>13</sup>C NMR spectrum of 1-(4-chlorophenyl)pyrrolidine (3e)

**1-(4-fluorophenyl)pyrrolidine (3f)**

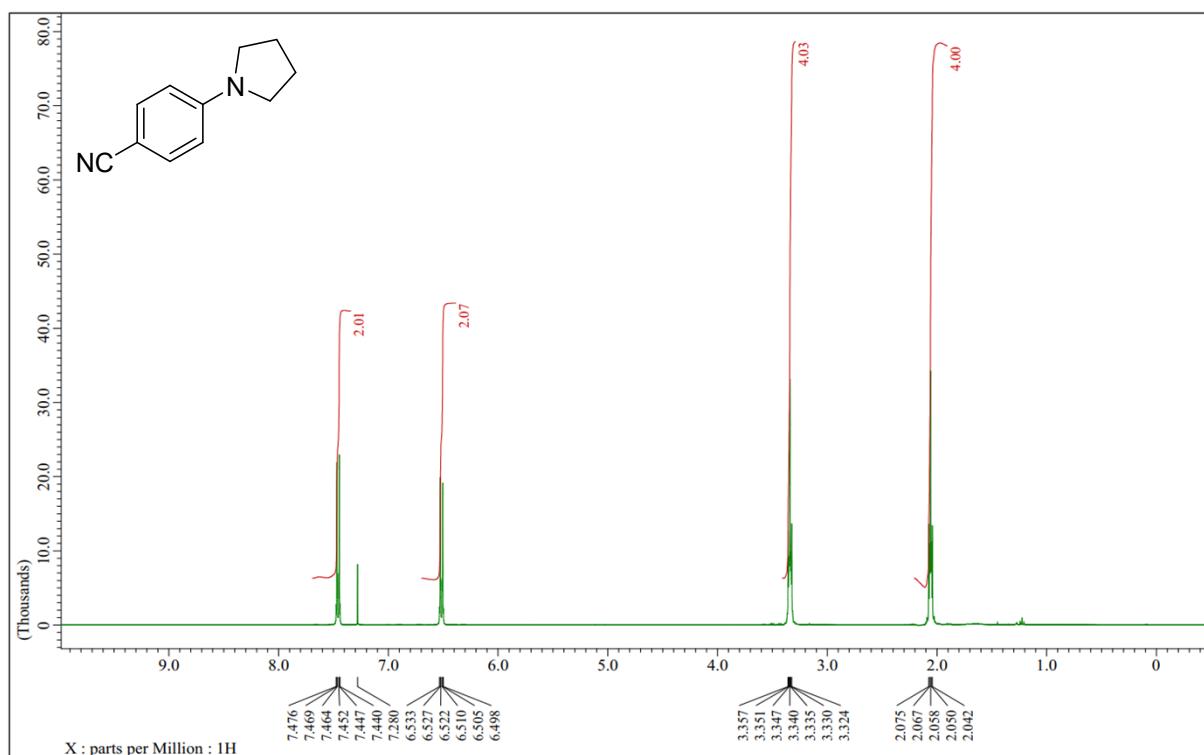


<sup>1</sup>H NMR spectrum of 1-(4-fluorophenyl)pyrrolidine (3f)

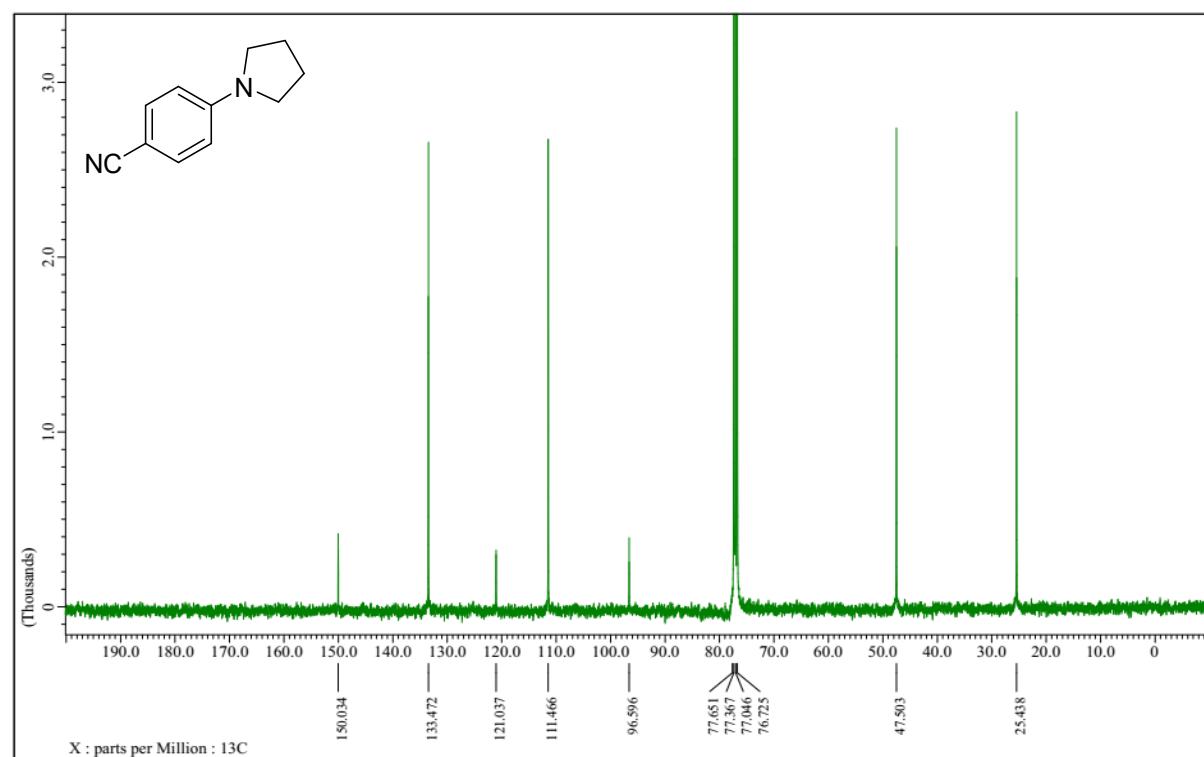


<sup>13</sup>C NMR spectrum of 1-(4-fluorophenyl)pyrrolidine (3f)

**4-(pyrrolidin-1-yl)benzonitrile (3g)**

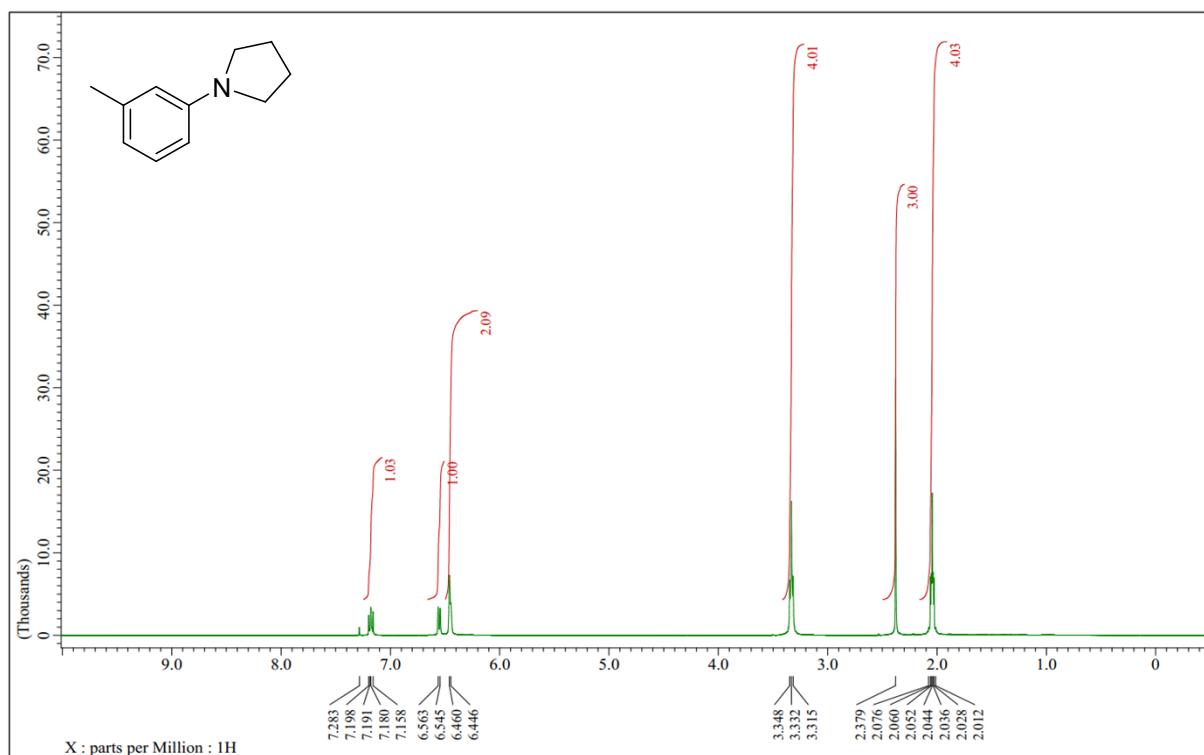


<sup>1</sup>H NMR spectrum of 4-(pyrrolidin-1-yl)benzonitrile (3g)

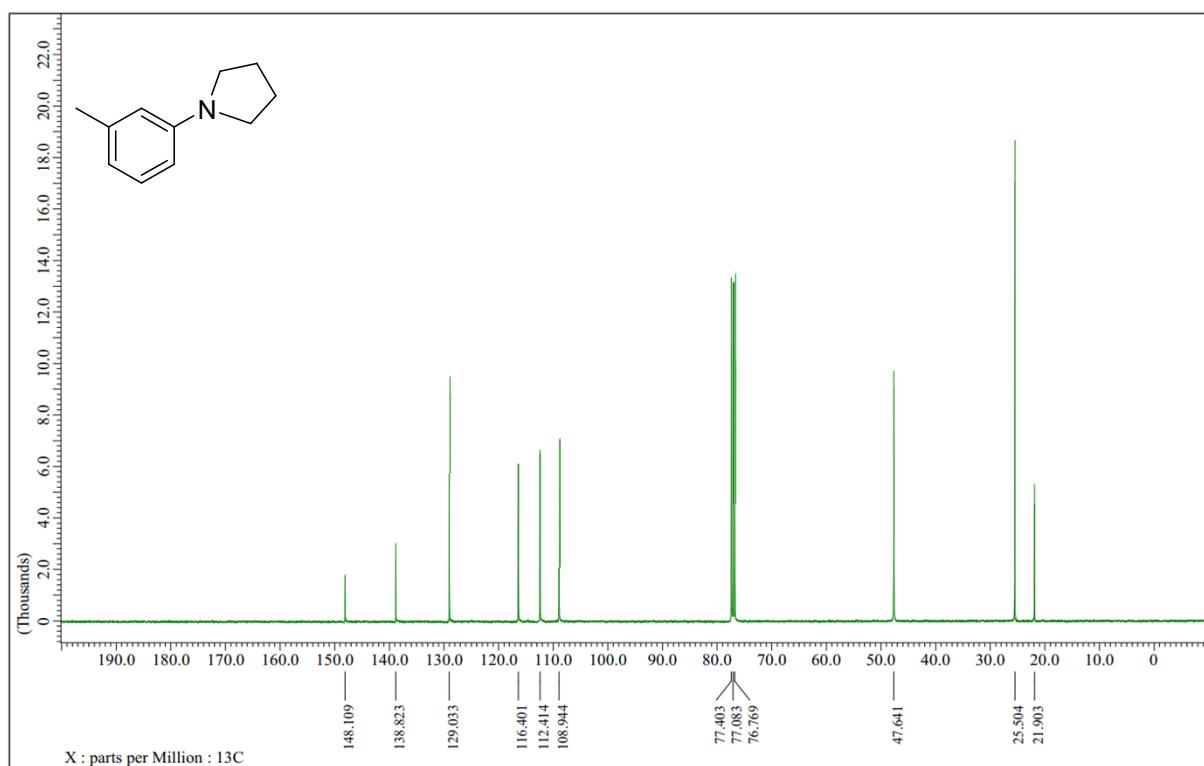


<sup>13</sup>C NMR spectrum of 4-(pyrrolidin-1-yl)benzonitrile (3g)

### **1-*m*-tolylpyrrolidine (3h)**

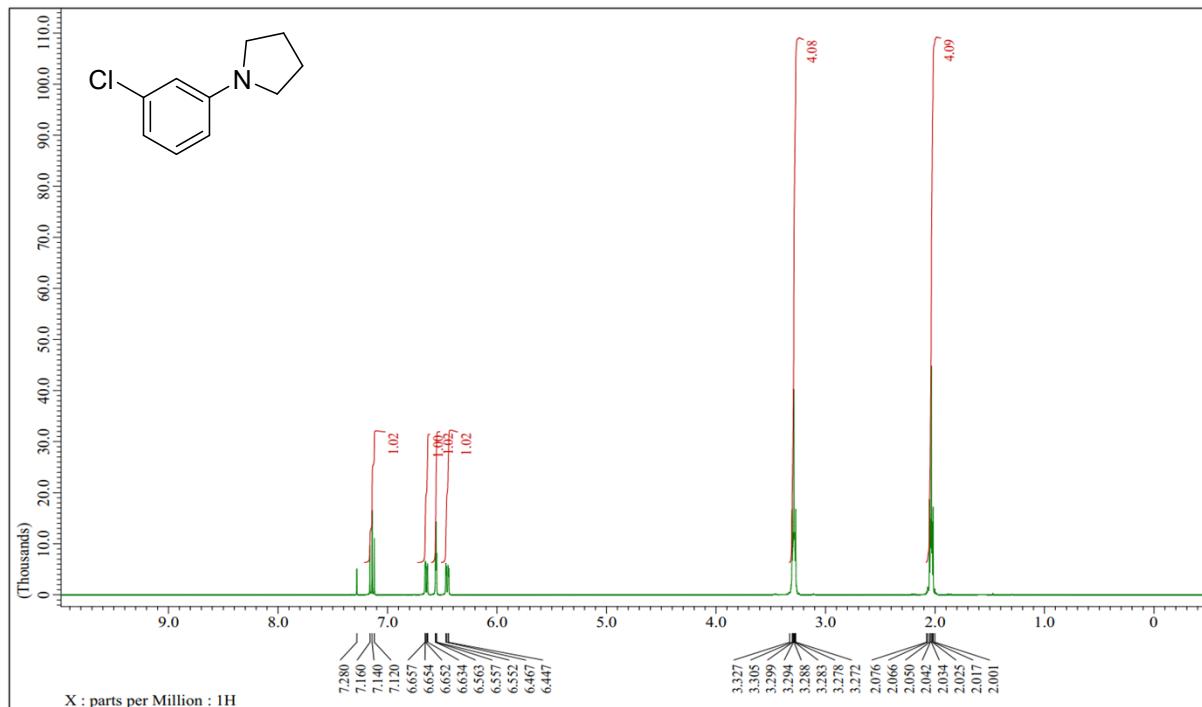


<sup>1</sup>H NMR spectrum of 1-*m*-tolylpyrrolidine (3h)

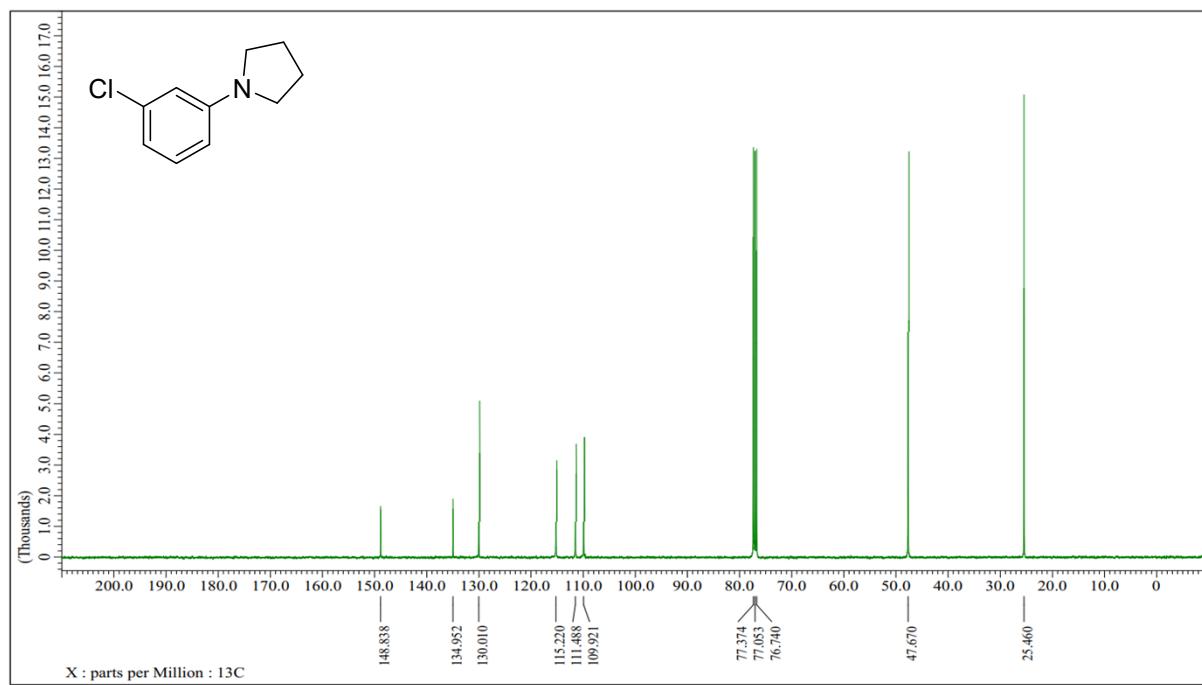


<sup>13</sup>C NMR spectrum of 1-*m*-tolylpyrrolidine (3h)

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

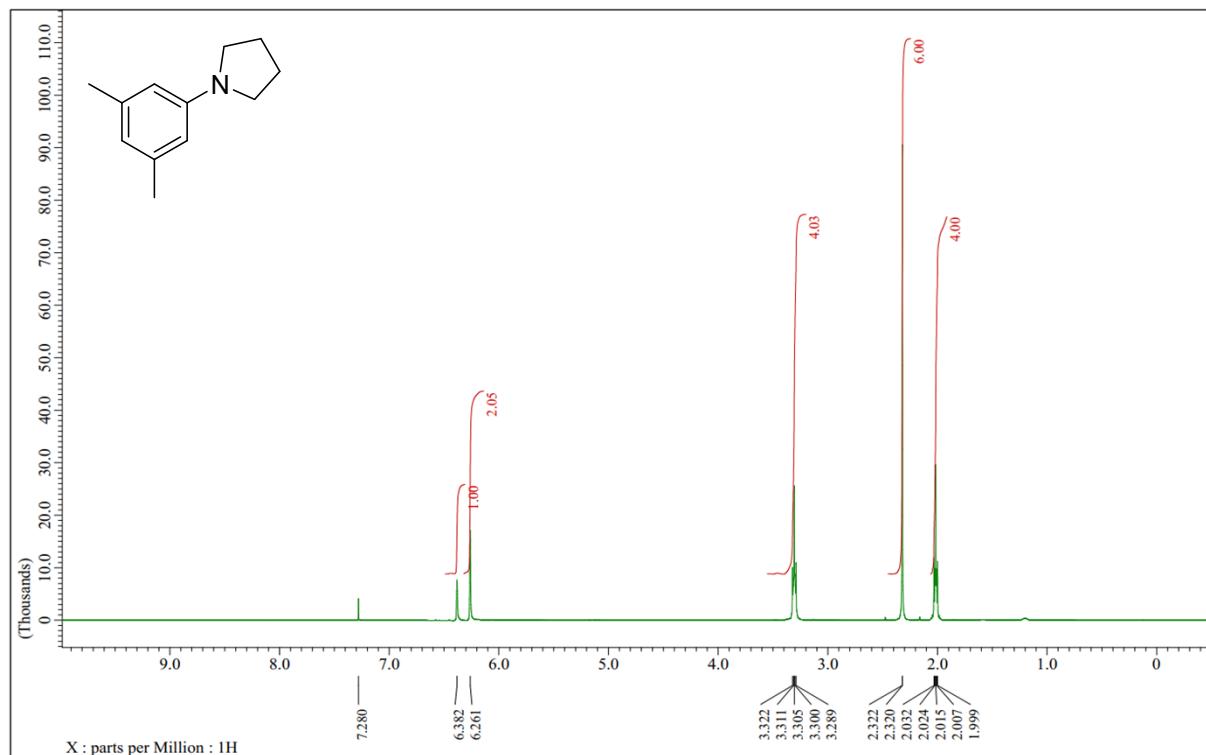


<sup>1</sup>H NMR spectrum of 1-(3-chlorophenyl)pyrrolidine (3i)

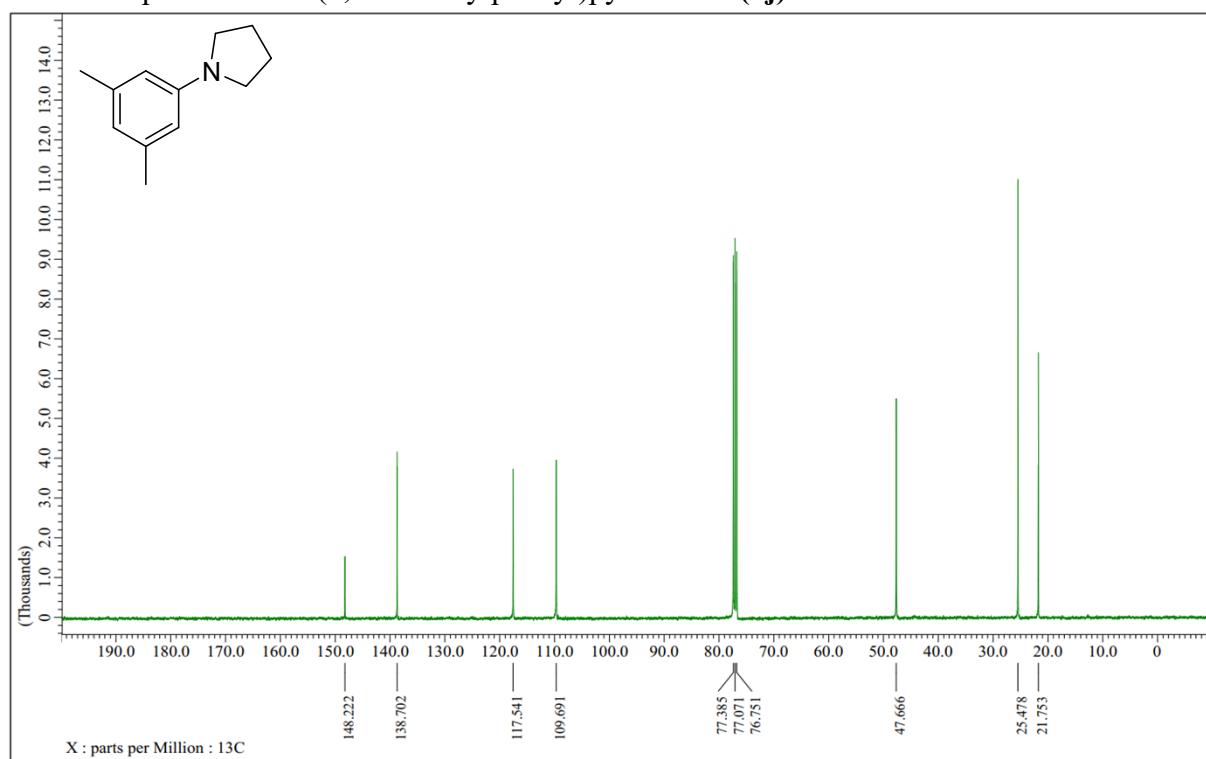


<sup>13</sup>C NMR spectrum of 1-(3-chlorophenyl)pyrrolidine (3i)

### 1-(3,5-dimethylphenyl)pyrrolidine (3j)

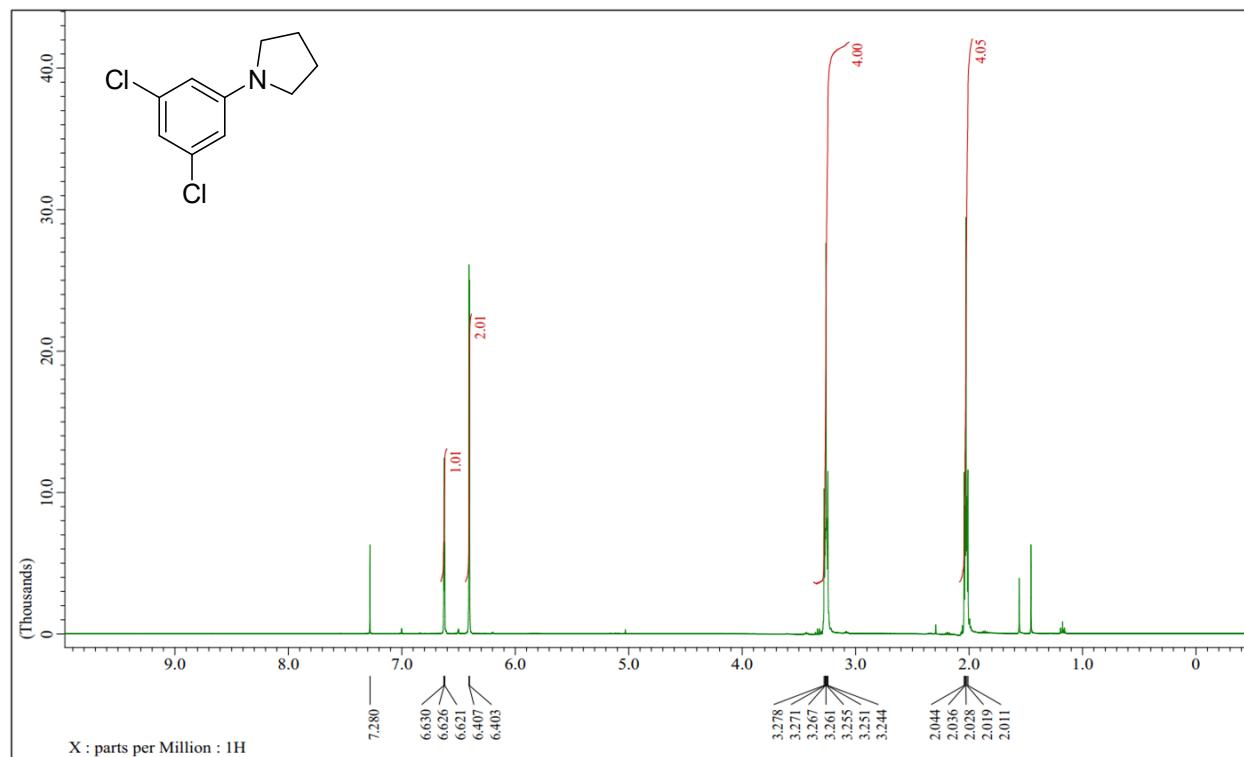


<sup>1</sup>H NMR spectrum of 1-(3,5-dimethylphenyl)pyrrolidine (3j)

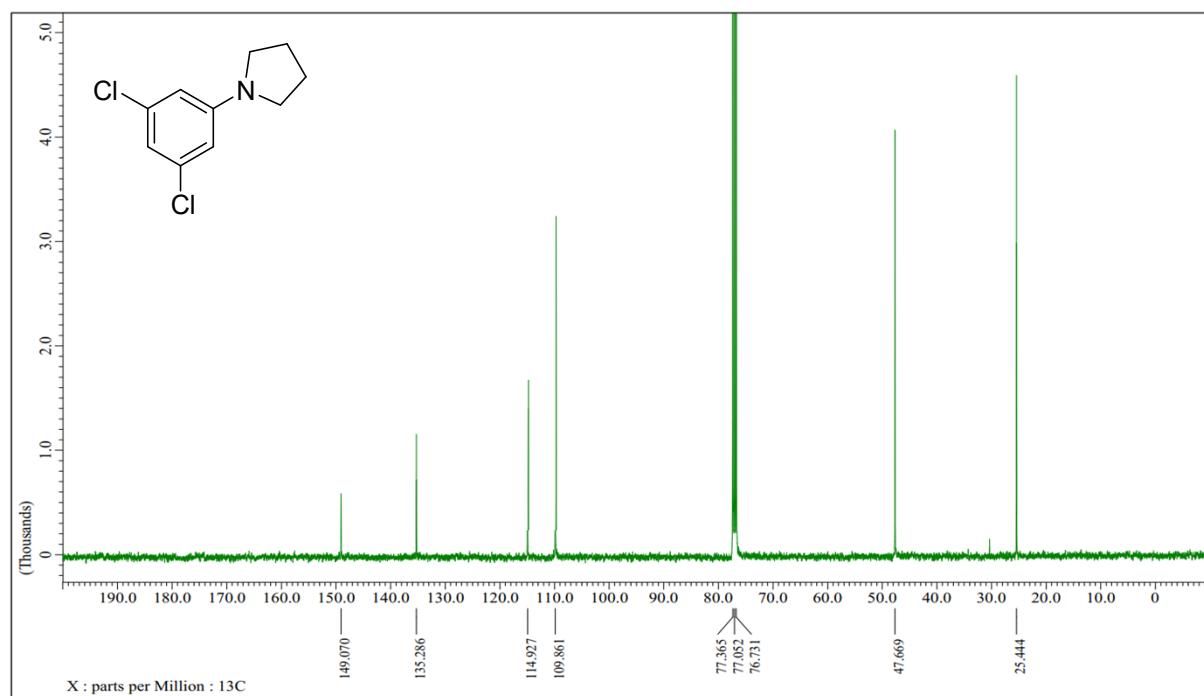


<sup>13</sup>C NMR spectrum of 1-(3,5-dimethylphenyl)pyrrolidine (3j)

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

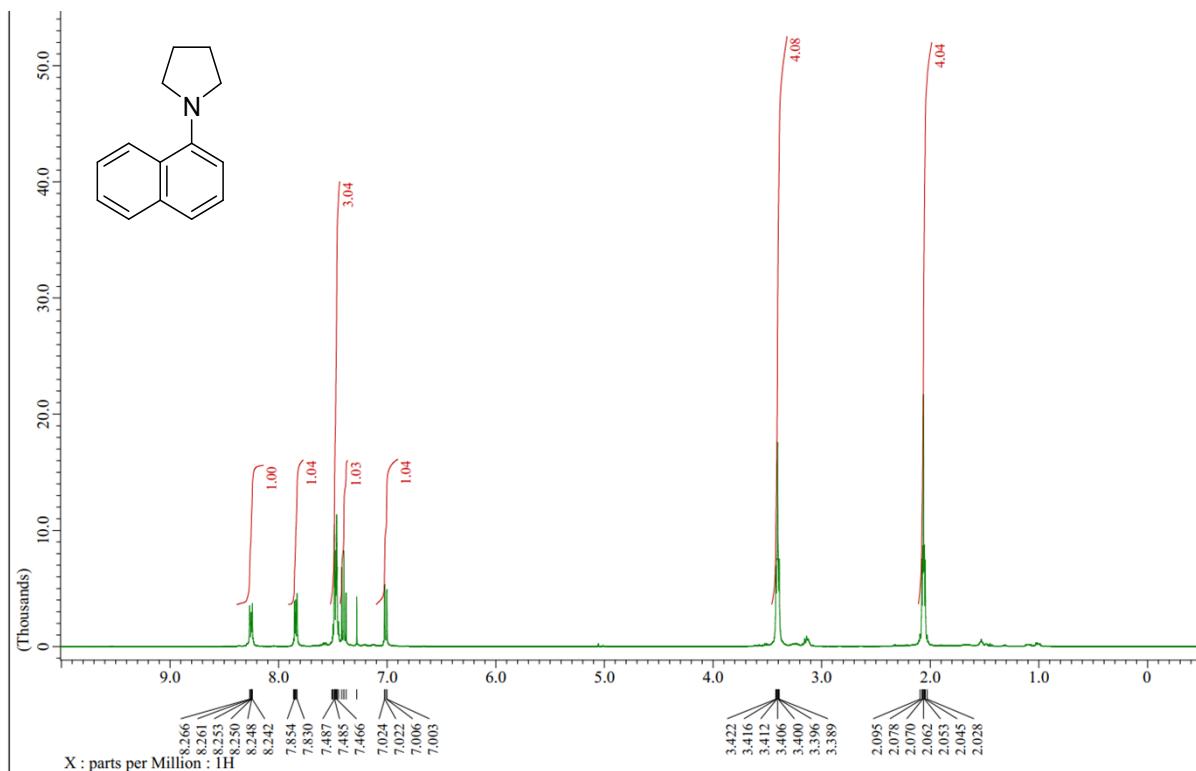


<sup>1</sup>H NMR spectrum of 1-(3,5-dichlorophenyl)pyrrolidine (3k)

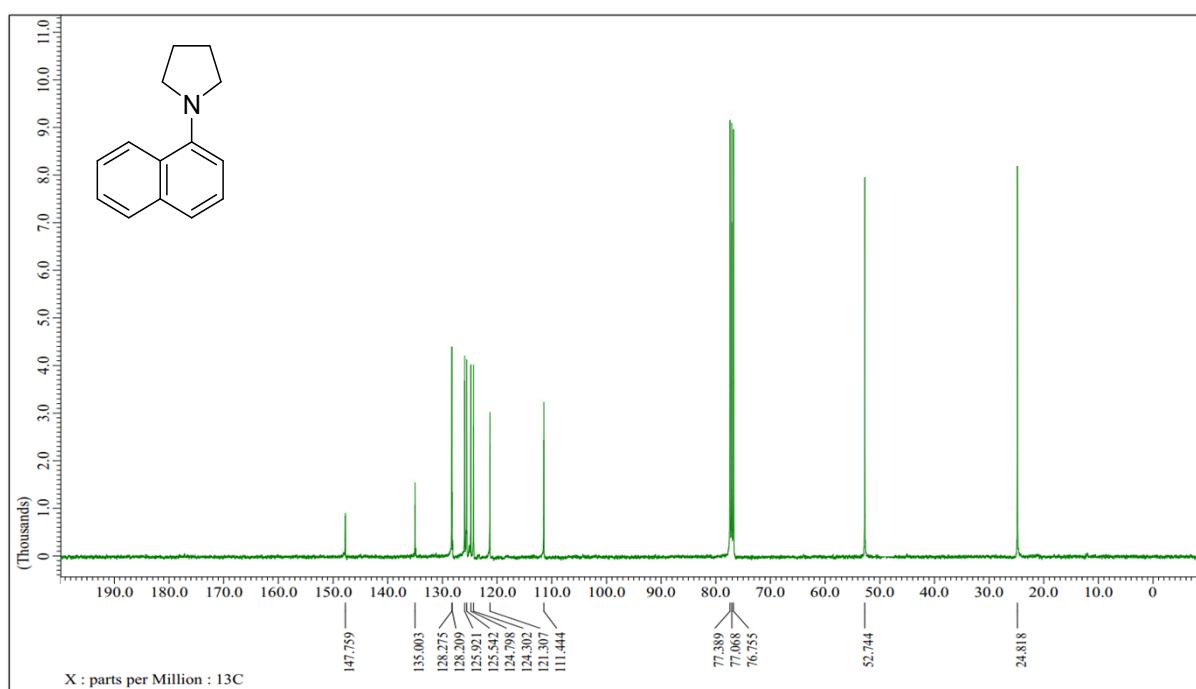


<sup>13</sup>C NMR spectrum of 1-(3,5-dichlorophenyl)pyrrolidine (3k)

**1-(naphthalen-1-yl) pyrrolidine (**3l**)**

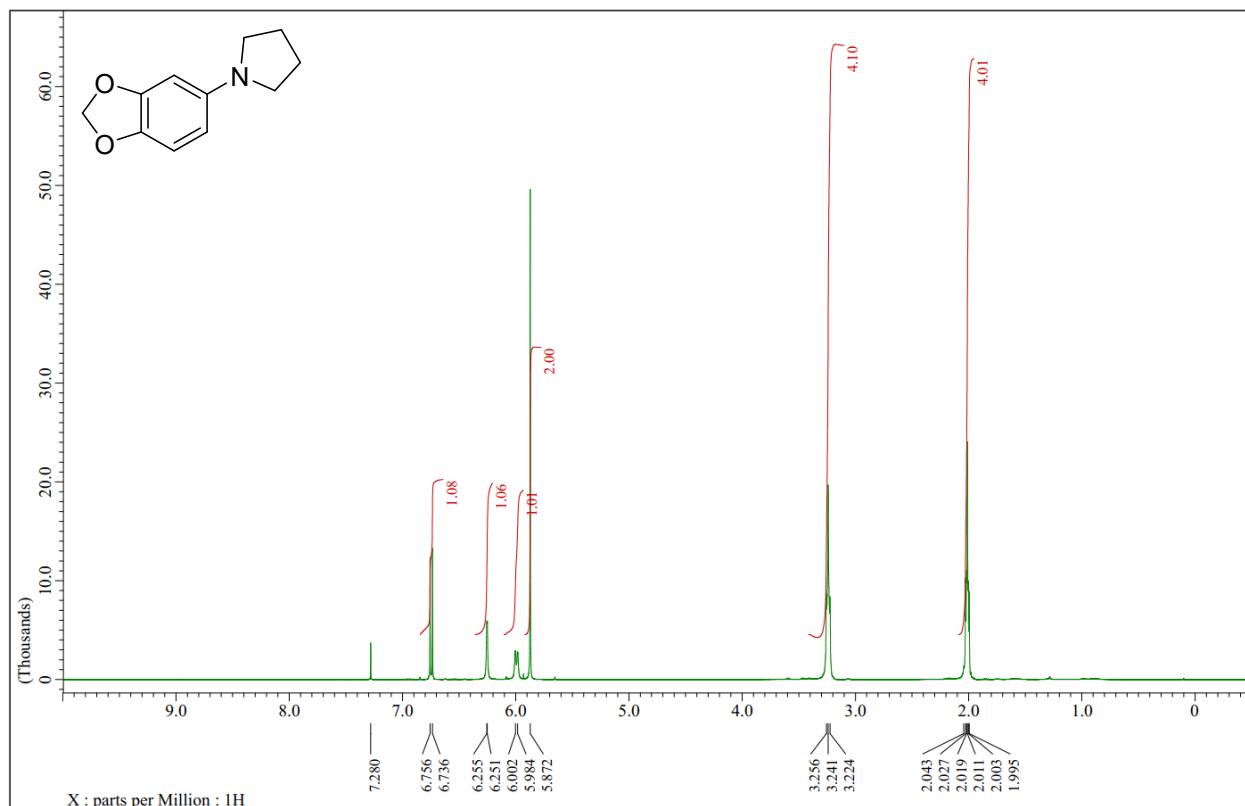


<sup>1</sup>H NMR spectrum of 1-(naphthalen-1-yl) pyrrolidine (**3l**)

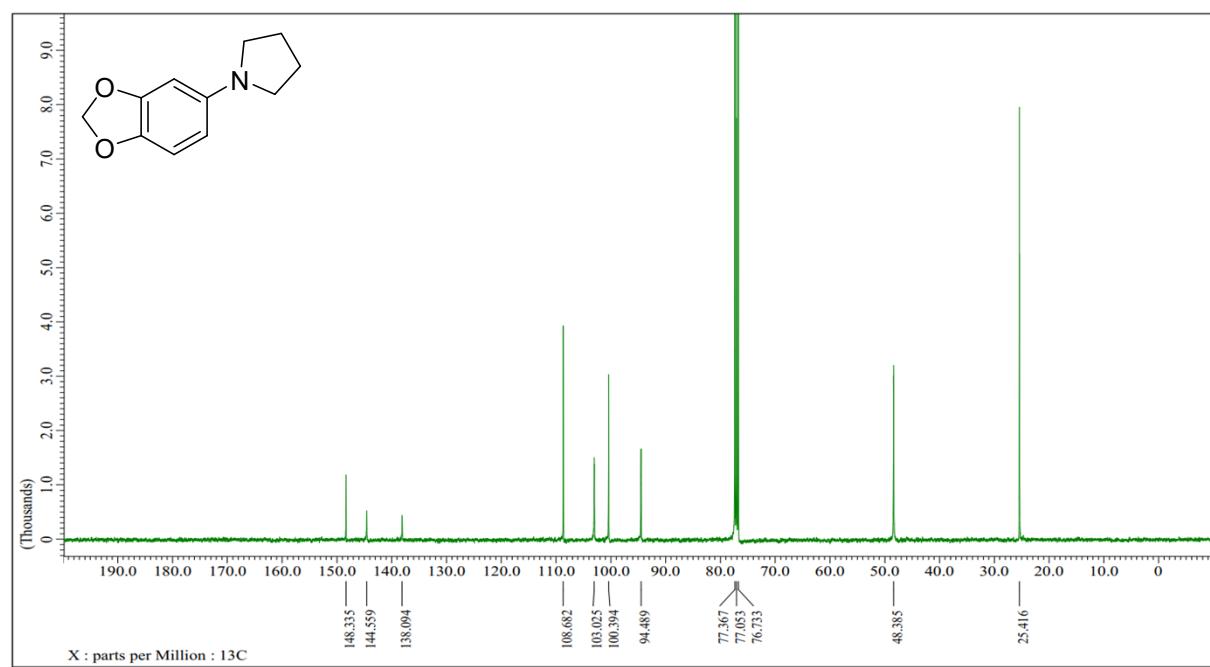


<sup>13</sup>C NMR spectrum of 1-(naphthalen-1-yl)pyrrolidine (**3l**)

**1-(benzo[d][1,3]dioxol-5-yl)pyrrolidine (3m)**

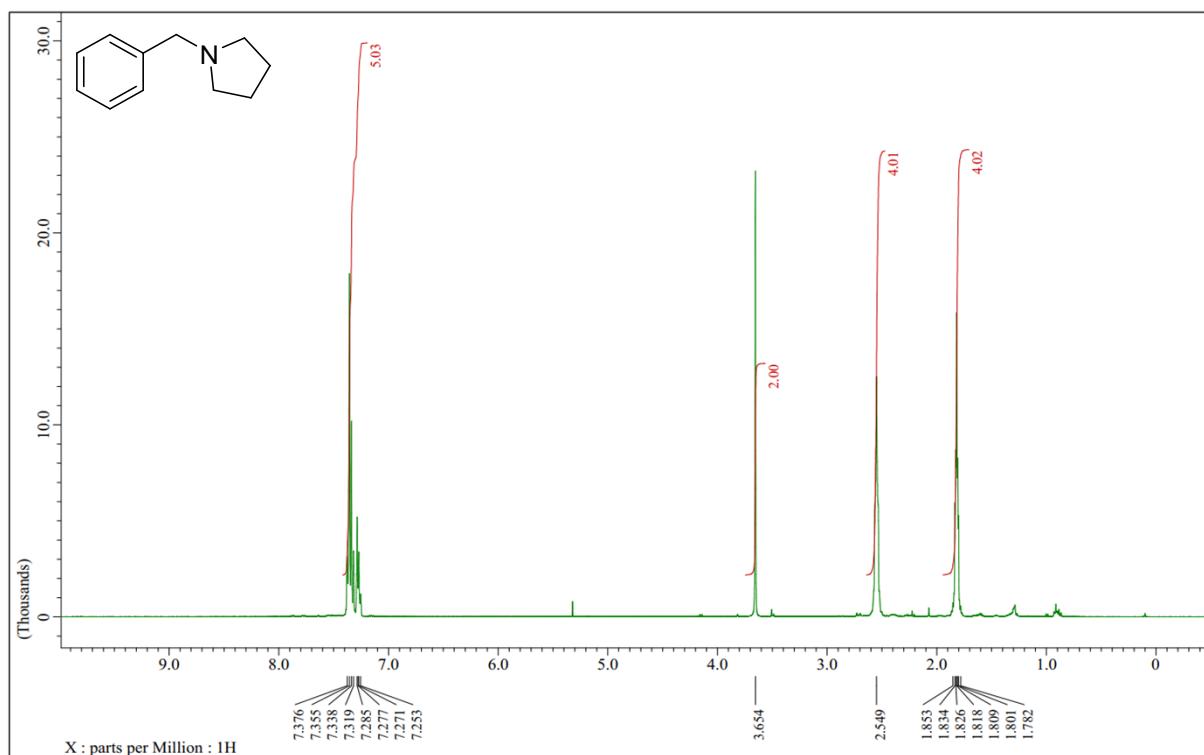


<sup>1</sup>H NMR spectrum of 1-(benzo[d][1,3]dioxol-5-yl)pyrrolidine (3m)

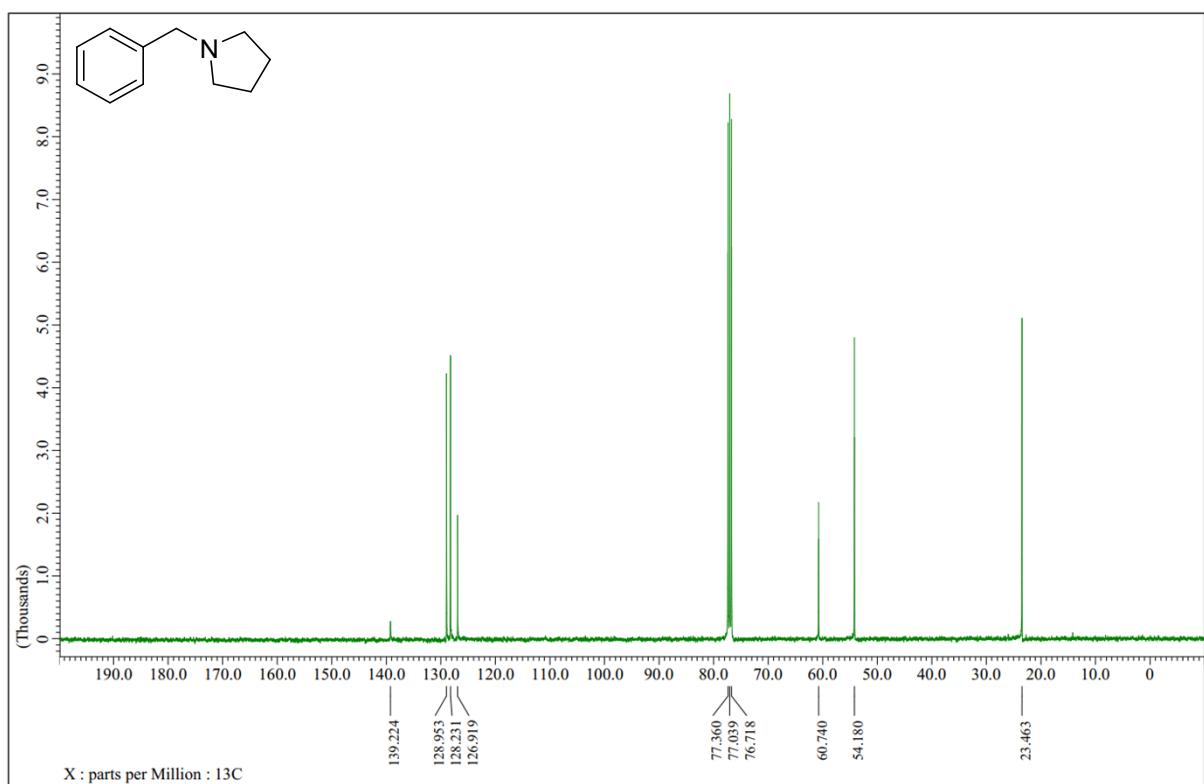


<sup>13</sup>C NMR spectrum of 1-(benzo[d][1,3]dioxol-5-yl)pyrrolidine (3m)

### 1-benzylpyrrolidine (3n)

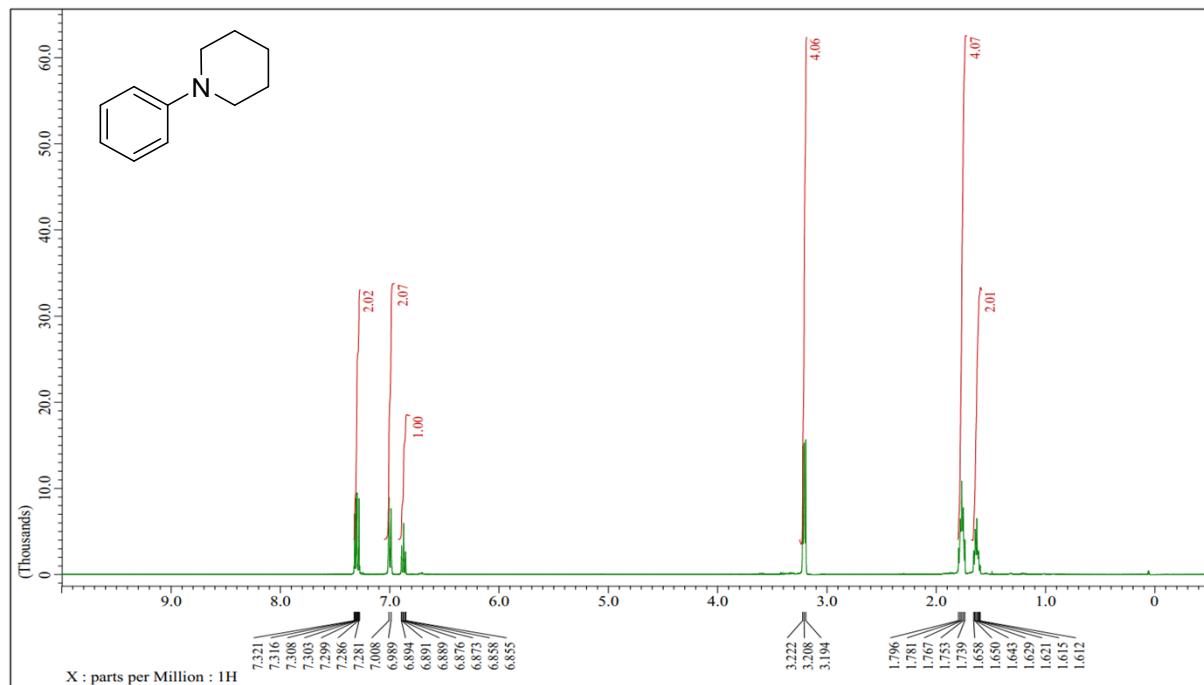


<sup>1</sup>H NMR spectrum of 1-benzylpyrrolidine (3n)

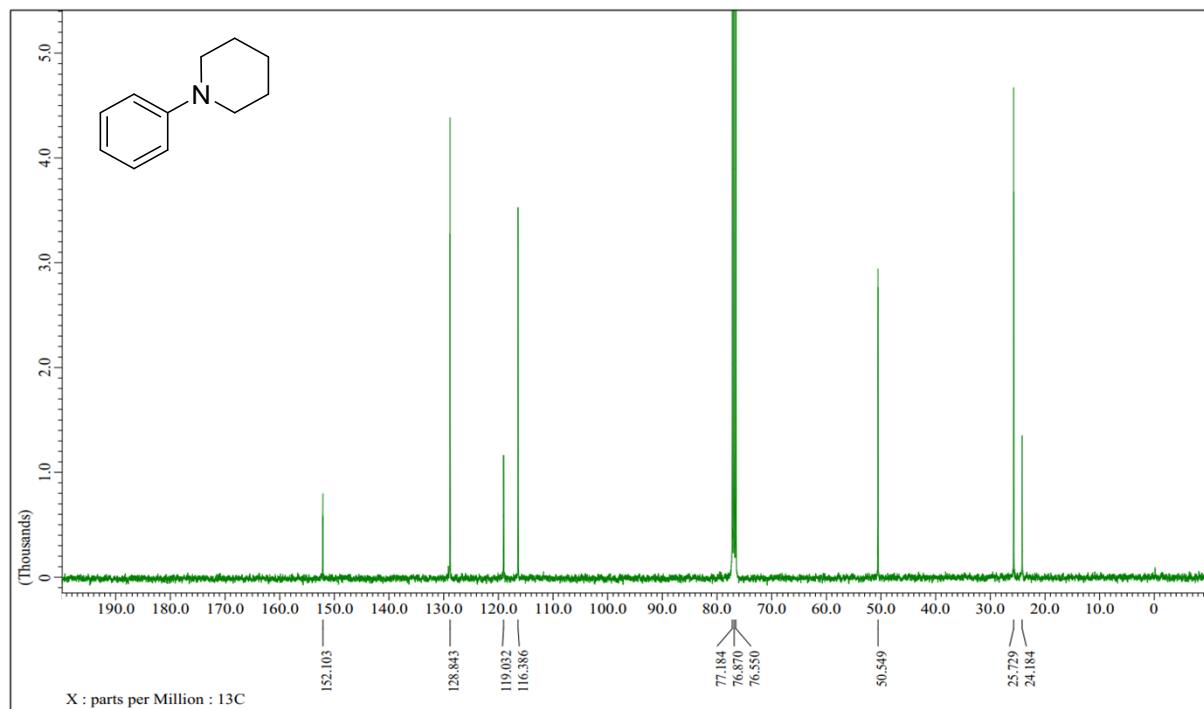


<sup>13</sup>C NMR spectrum of 1-benzylpyrrolidine (3n)

### 1-phenylpiperidine (5a)

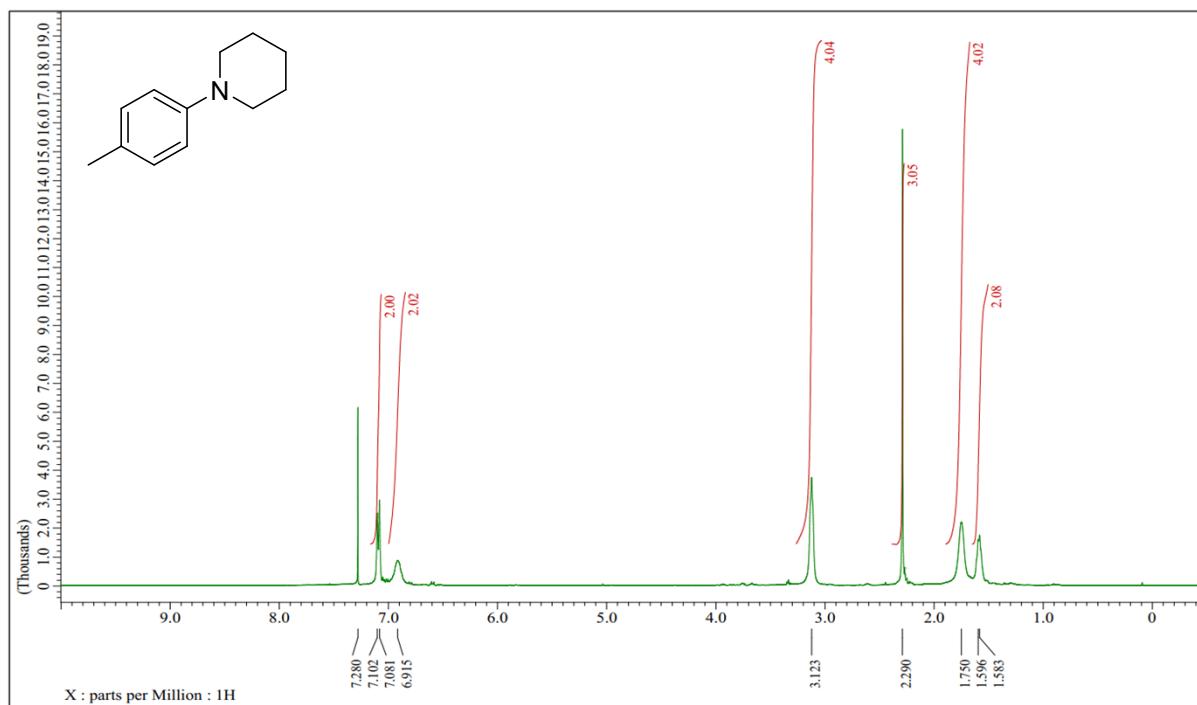


<sup>1</sup>H NMR spectrum of 1-phenylpiperidine (5a)

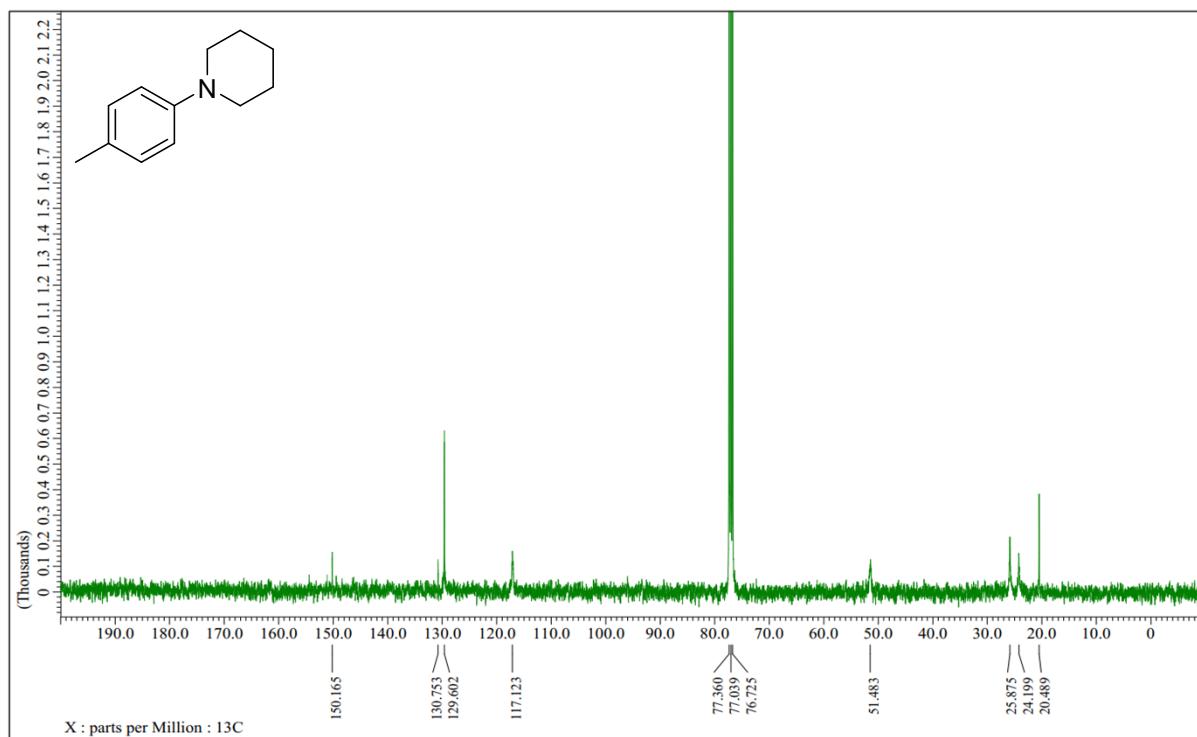


<sup>13</sup>C NMR spectrum of 1-phenylpiperidine (5a)

**1-(*p*-tolyl)piperidine (**5b**)**

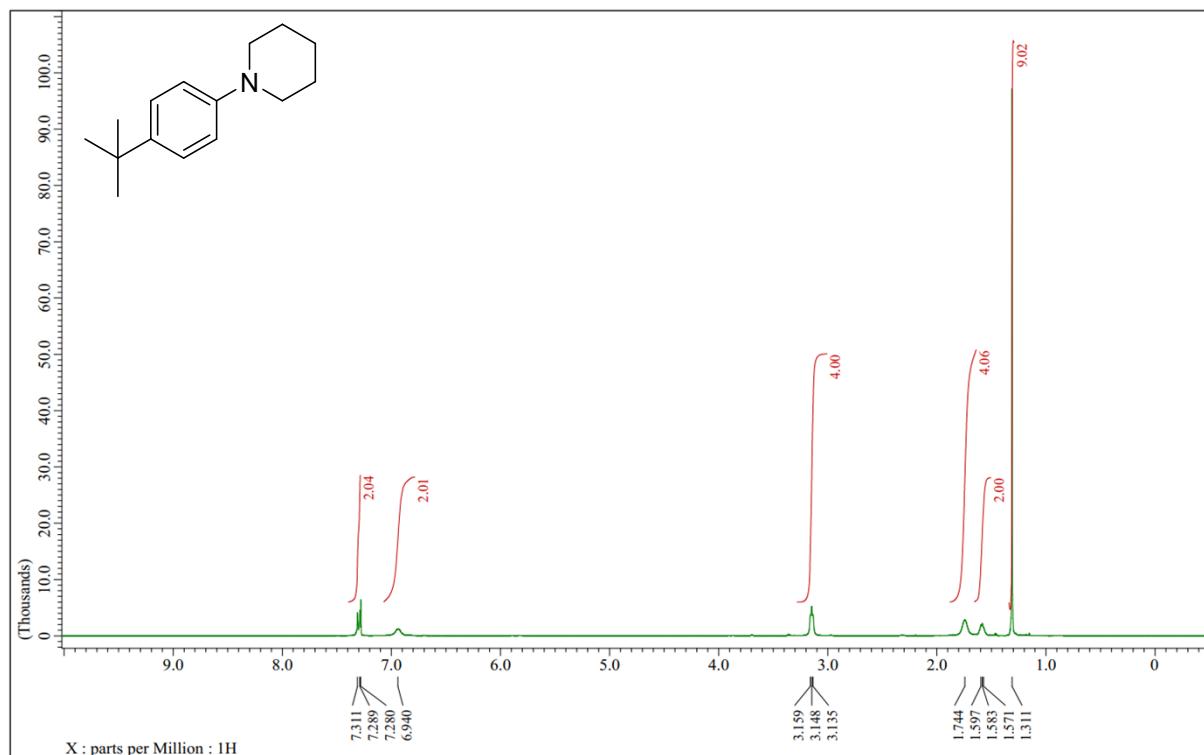


<sup>1</sup>H NMR spectrum of 1-(*p*-tolyl)piperidine (**5b**)

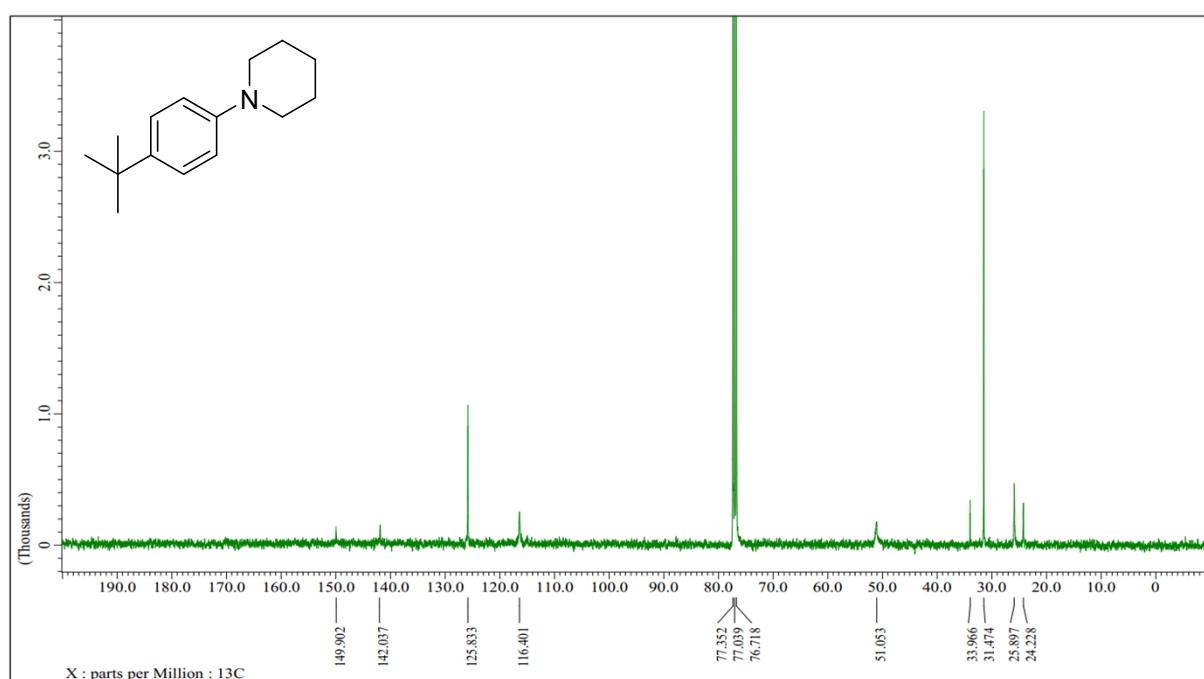


<sup>13</sup>C NMR spectrum of 1-(*p*-tolyl)piperidine (**5b**)

**1-(4-(*tert*-butyl)phenyl)piperidine (**5c**)**

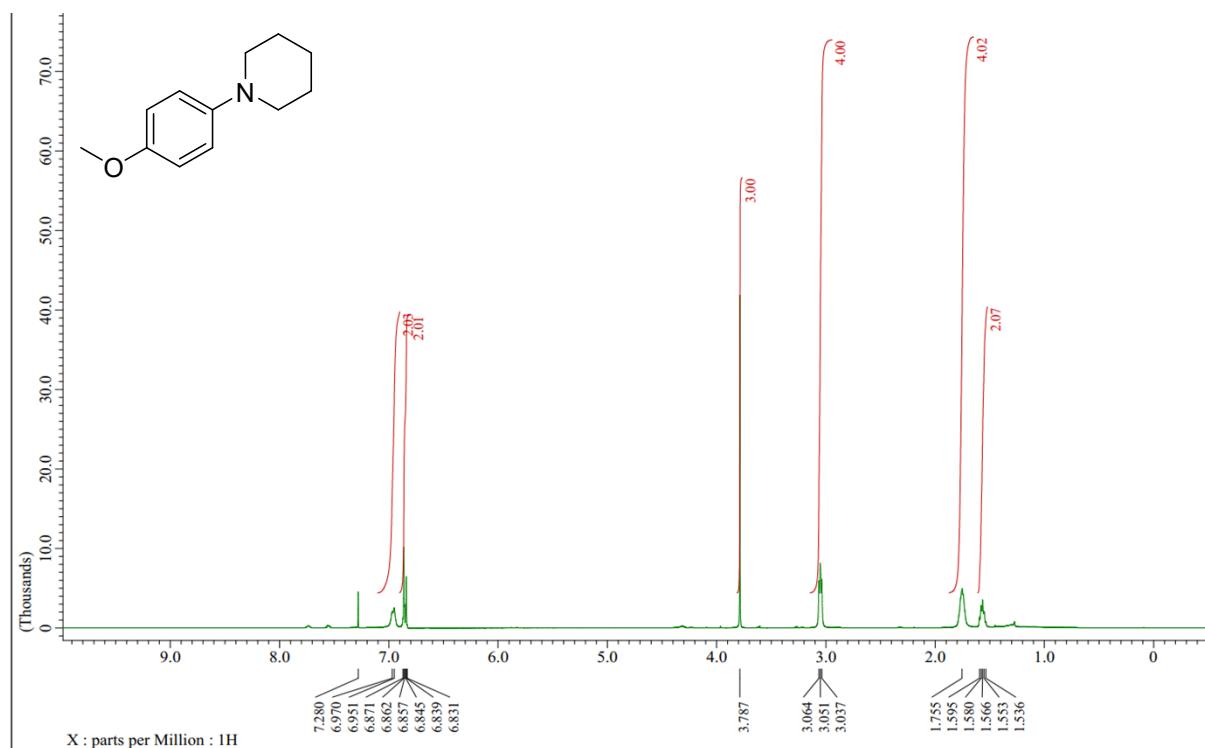


<sup>1</sup>H NMR spectrum of 1-(4-(*tert*-butyl)phenyl)piperidine (**5c**)

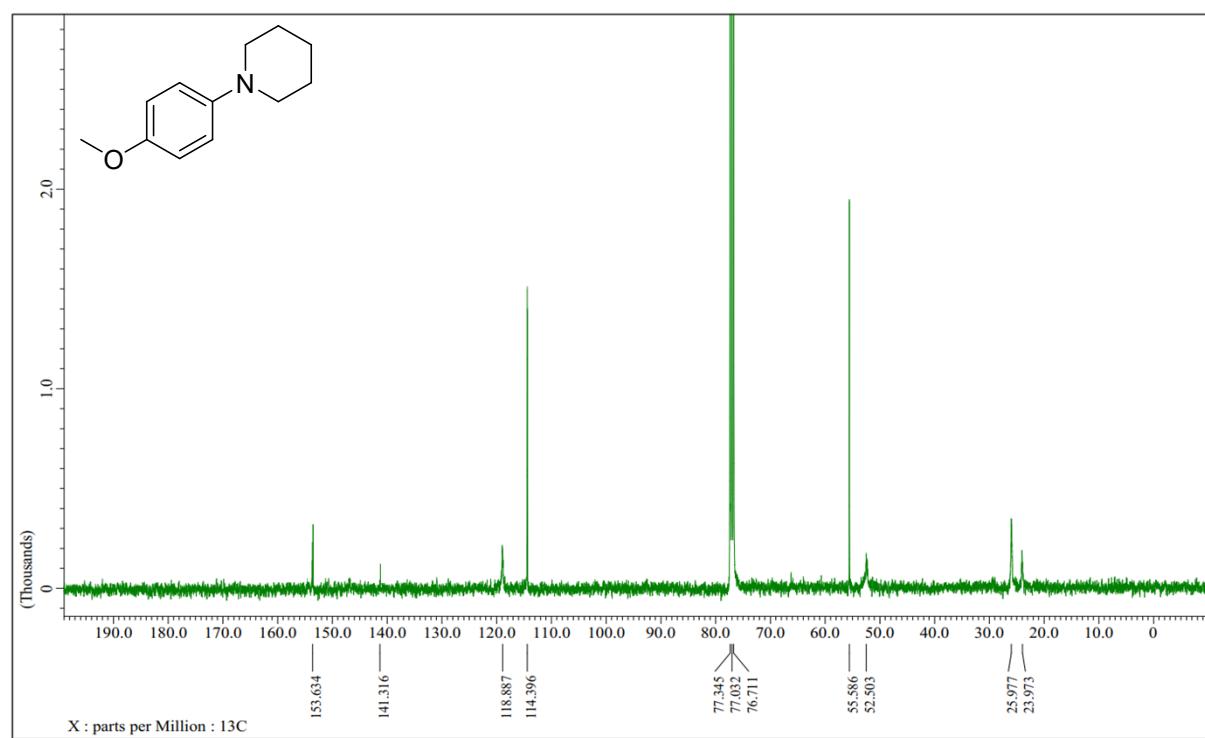


<sup>13</sup>C NMR spectrum of 1-(4-(*tert*-butyl)phenyl)piperidine (**5c**)

**1-(4-methoxyphenyl)piperidine (5d)**

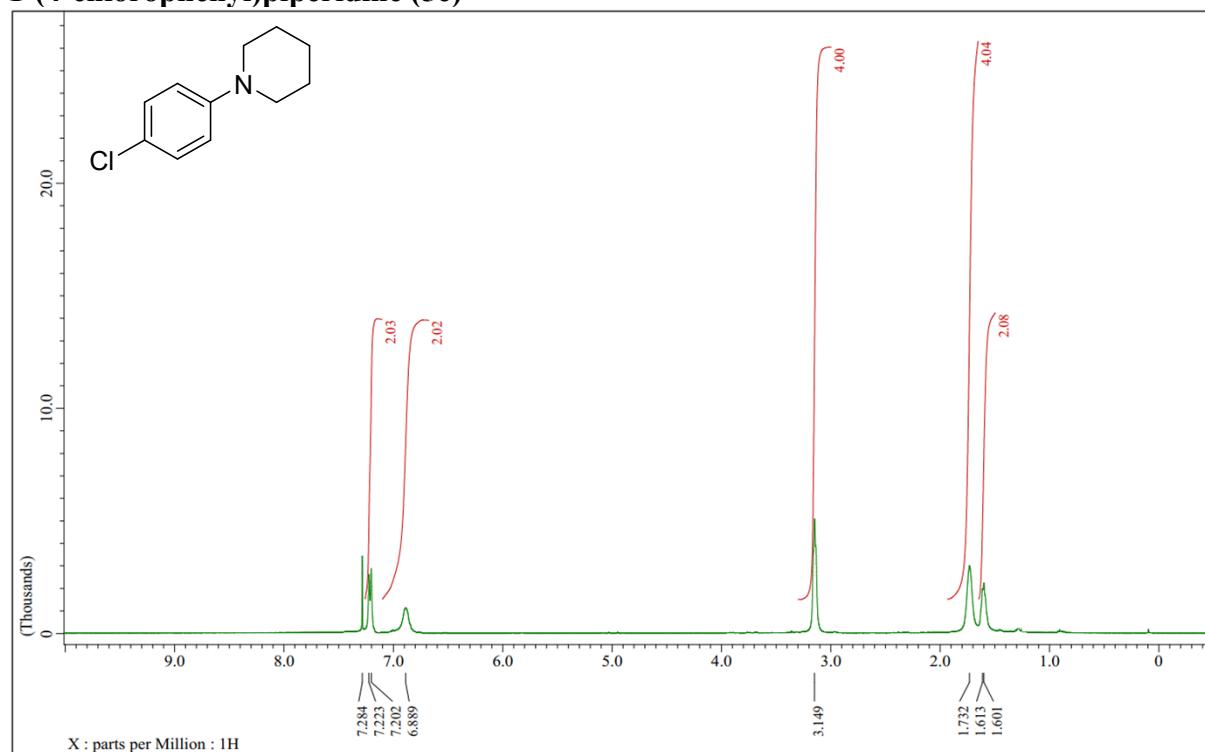


<sup>1</sup>H NMR spectrum of 1-(4-methoxyphenyl)piperidine (5d)

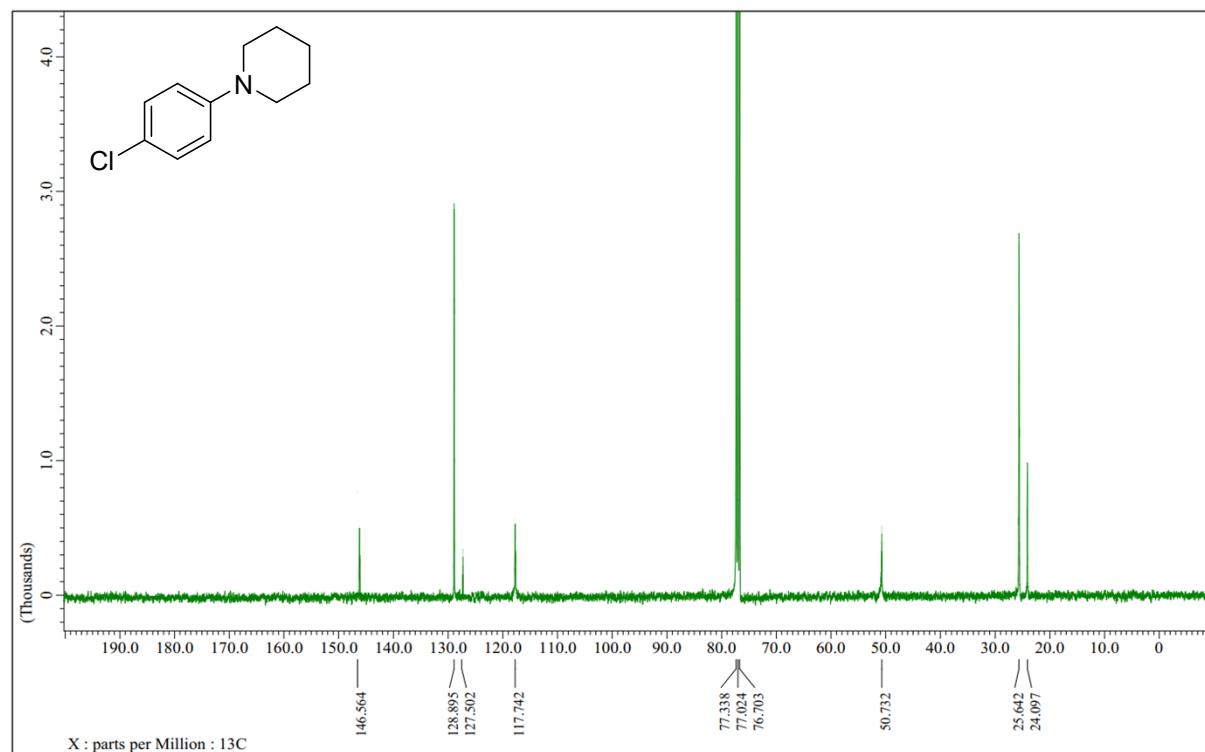


<sup>13</sup>C NMR spectrum of 1-(4-methoxyphenyl)piperidine (5d)

**1-(4-chlorophenyl)piperidine (5e)**

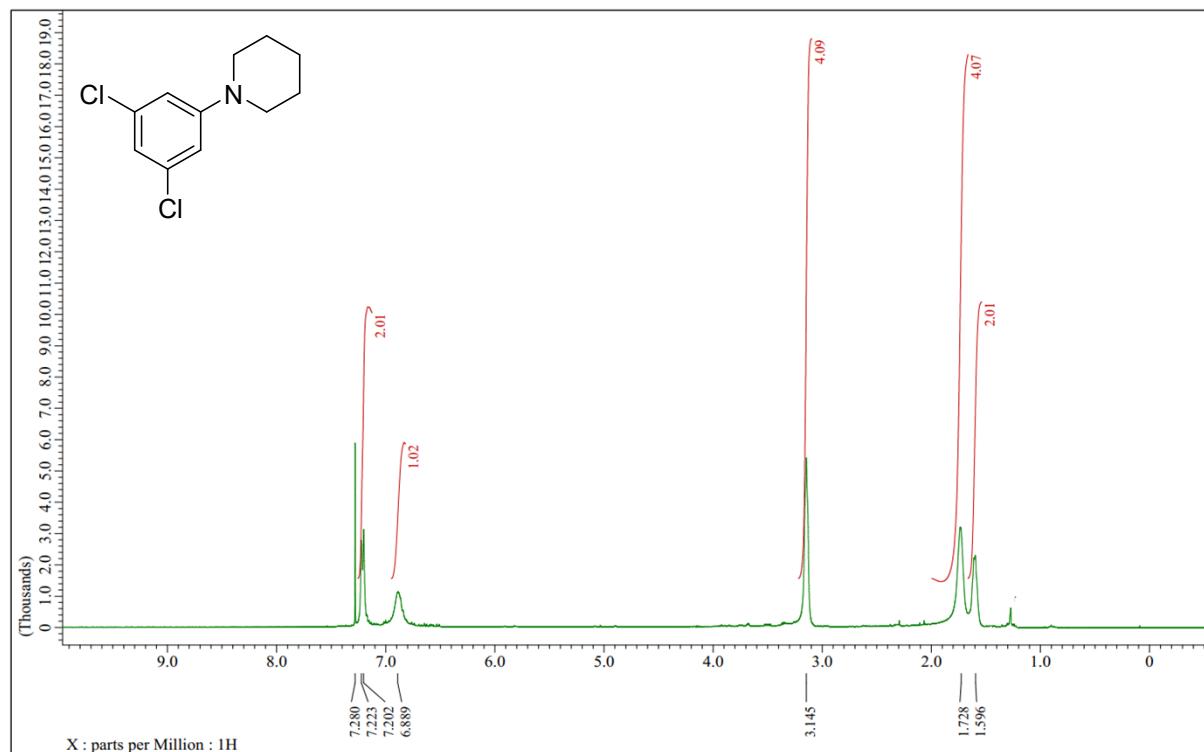


<sup>1</sup>H NMR spectrum of 1-(4-chlorophenyl)piperidine (5e)

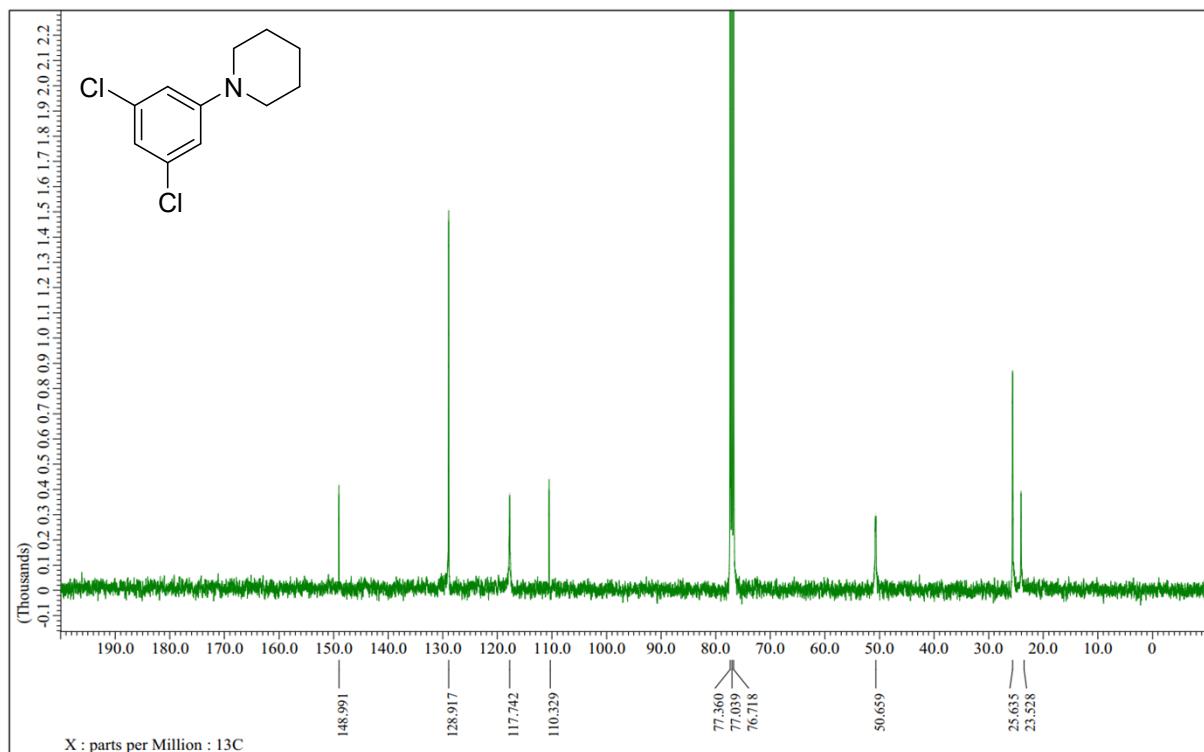


<sup>13</sup>C NMR spectrum of 1-(4-chlorophenyl)piperidine (5e)

**1-(3,5-dichlorophenyl)piperidine (5f)**

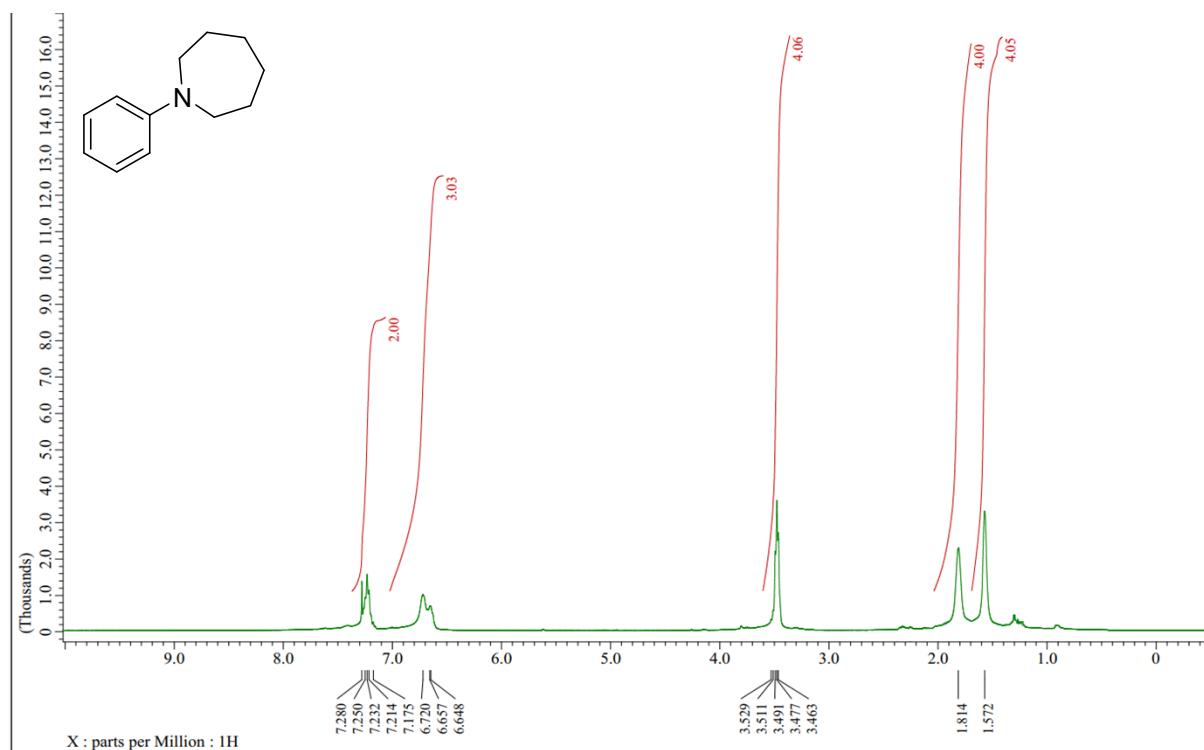


<sup>1</sup>H NMR spectrum of 1-(3,5-dichlorophenyl)piperidine (5f)

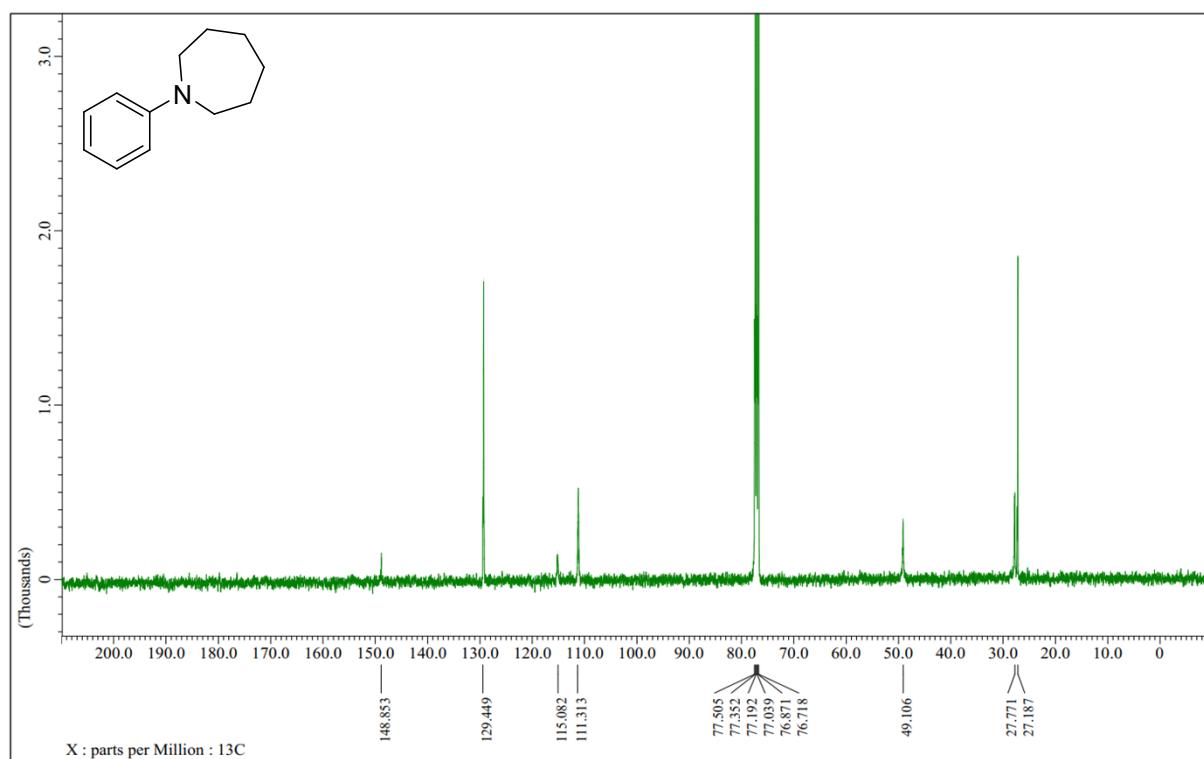


<sup>13</sup>C NMR spectrum of 1-(3,5-dichlorophenyl)piperidine (5f)

**1-phenylazepane (5g)**

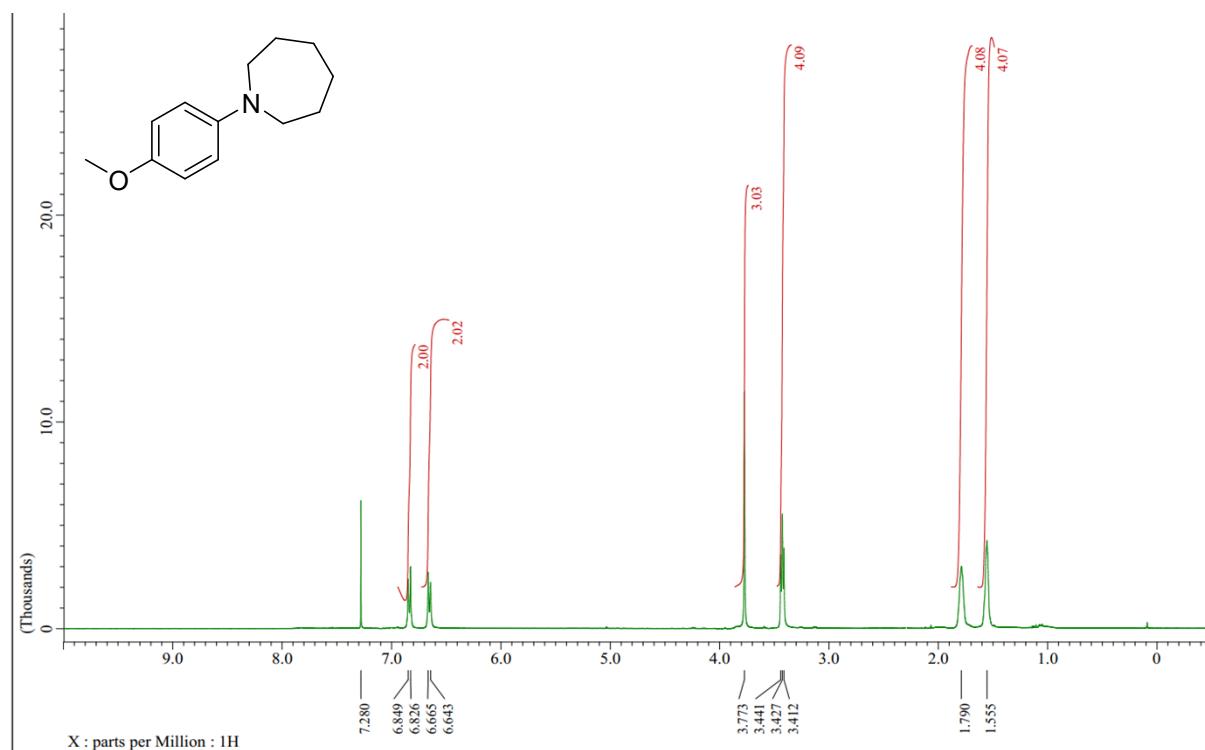


<sup>1</sup>H NMR spectrum of 1-phenylazepane (**5g**)

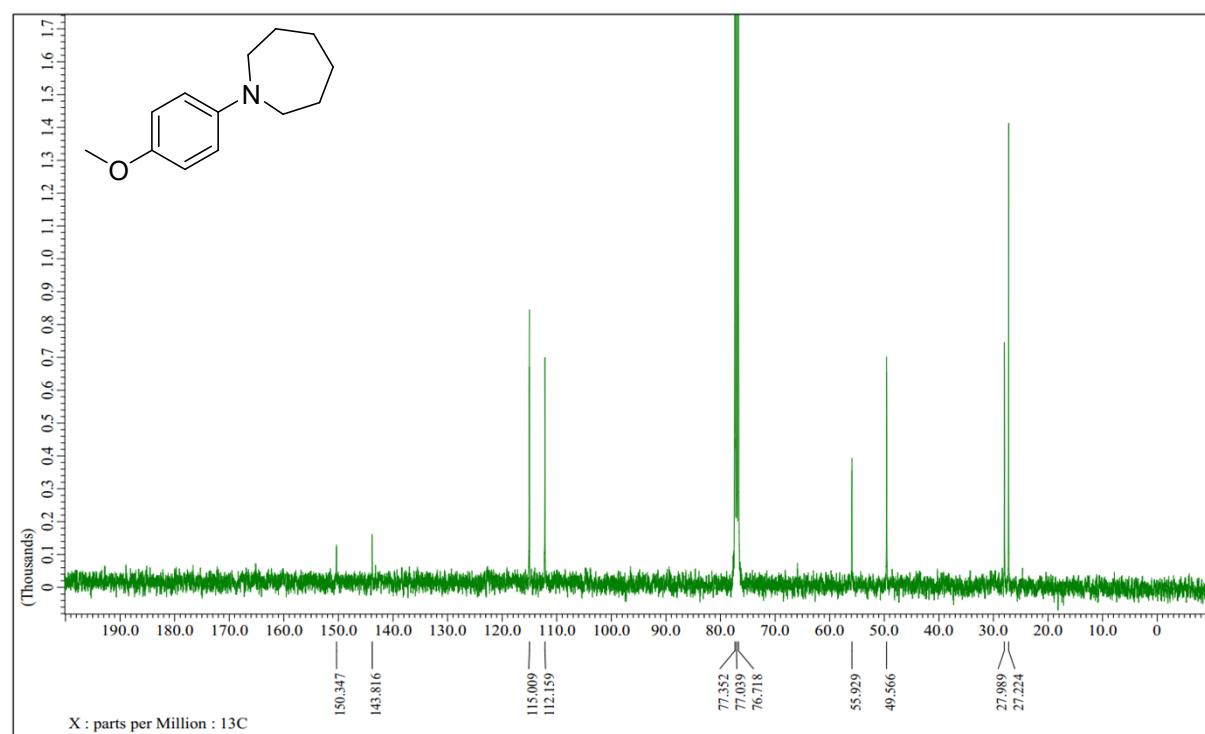


<sup>13</sup>C NMR spectrum of 1-phenylazepane (**5g**)

**1-(4-methoxyphenyl)azepane (5h)**

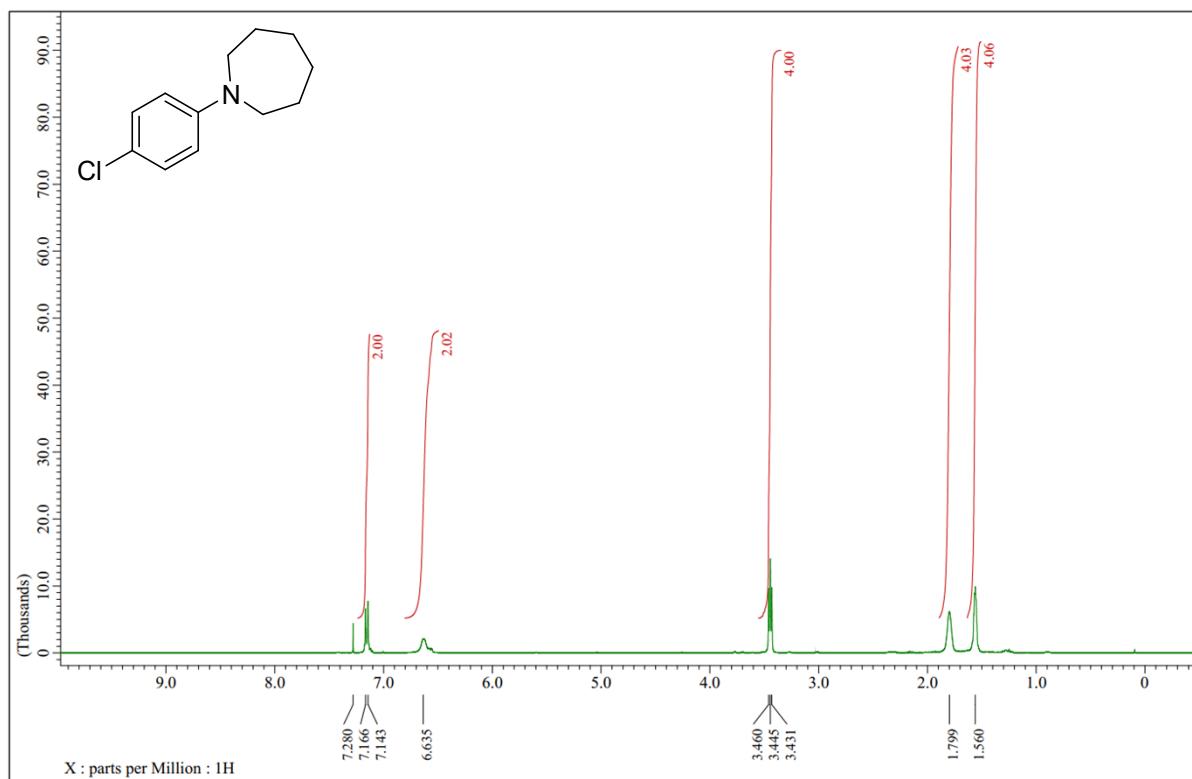


<sup>1</sup>H NMR spectrum of 1-(4-methoxyphenyl)azepane (**5h**)

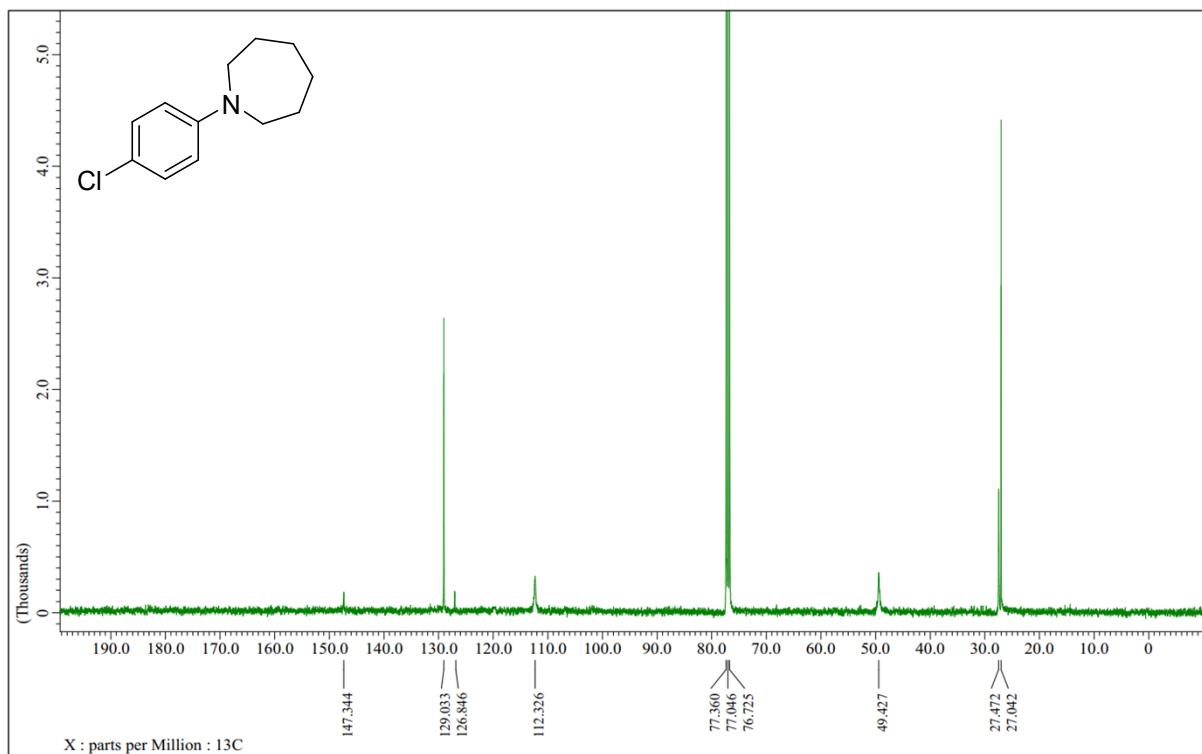


<sup>13</sup>C NMR spectrum of 1-(4-methoxyphenyl)azepane (**5h**)

**1-(4-chlorophenyl)azepane (**5i**)**

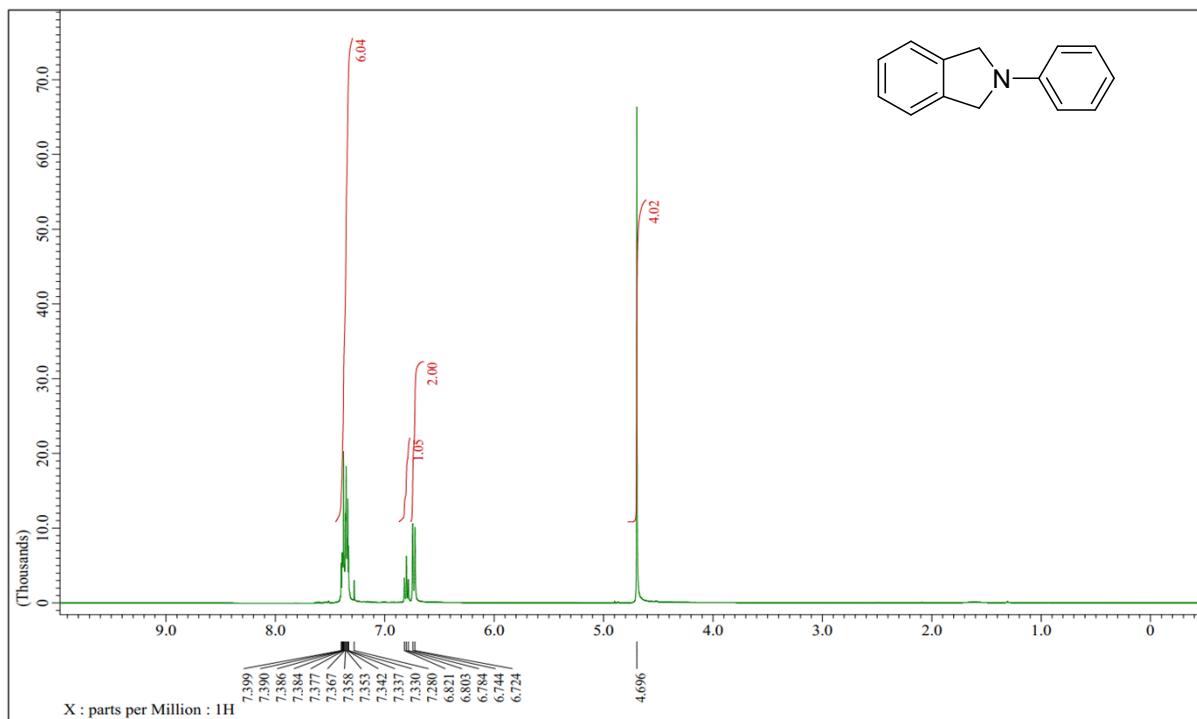


<sup>1</sup>H NMR spectrum of 1-(4-chlorophenyl)azepane (**5i**)

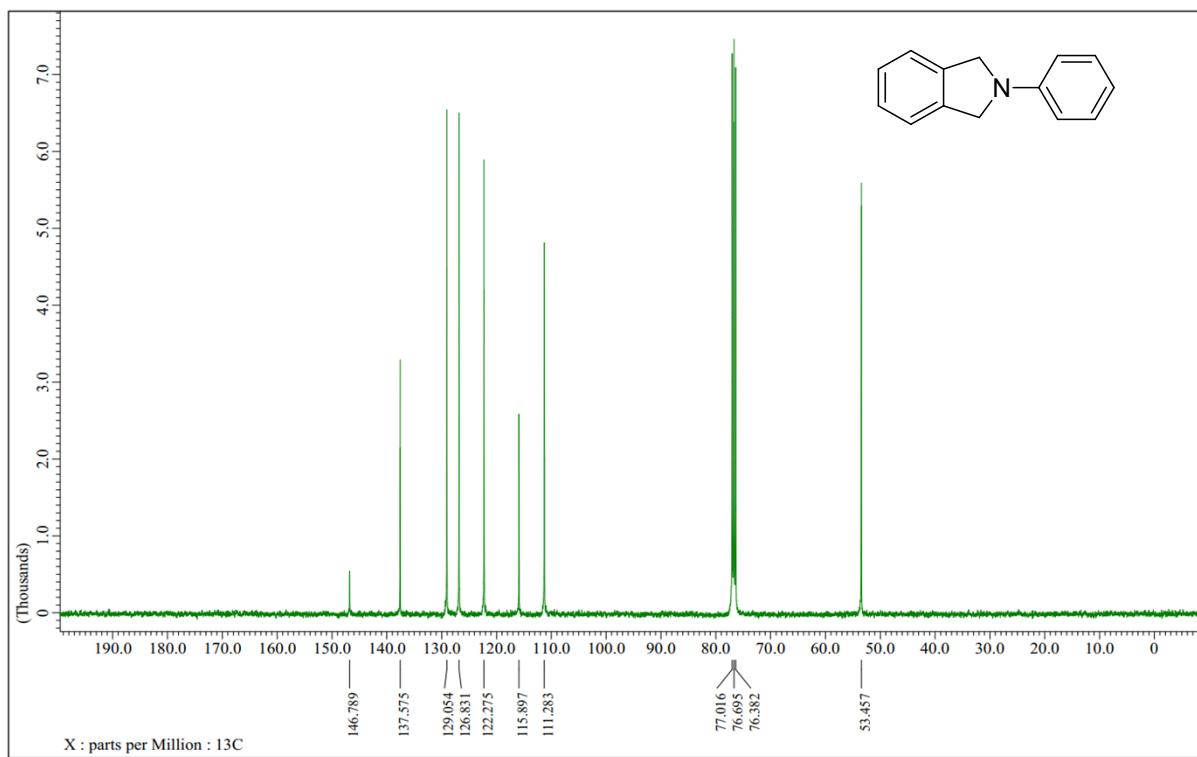


<sup>13</sup>C NMR spectrum of 1-(4-chlorophenyl)azepane (**5i**)

## 2-phenylisoindoline (5j)

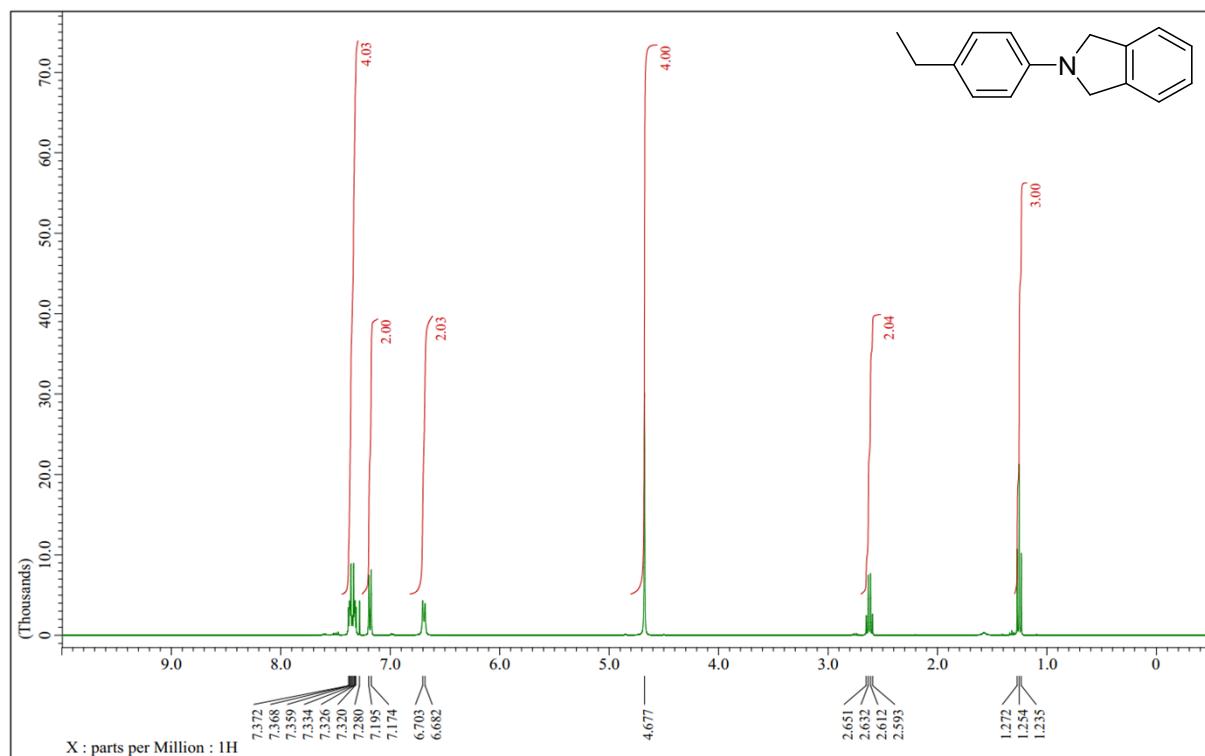


<sup>1</sup>H NMR spectrum of 2-phenylisoindoline (5j)

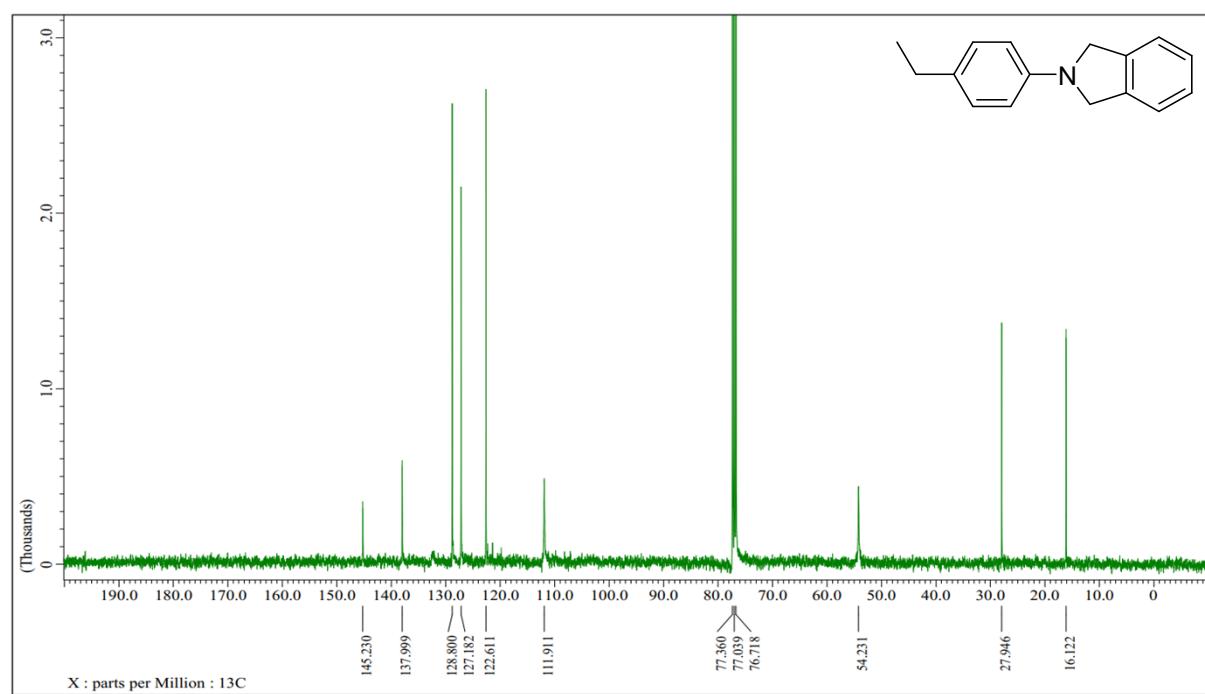


<sup>13</sup>C NMR spectrum of 2-phenylisoindoline (5j)

**2-(4-ethylphenyl)isoindoline (**5k**)**

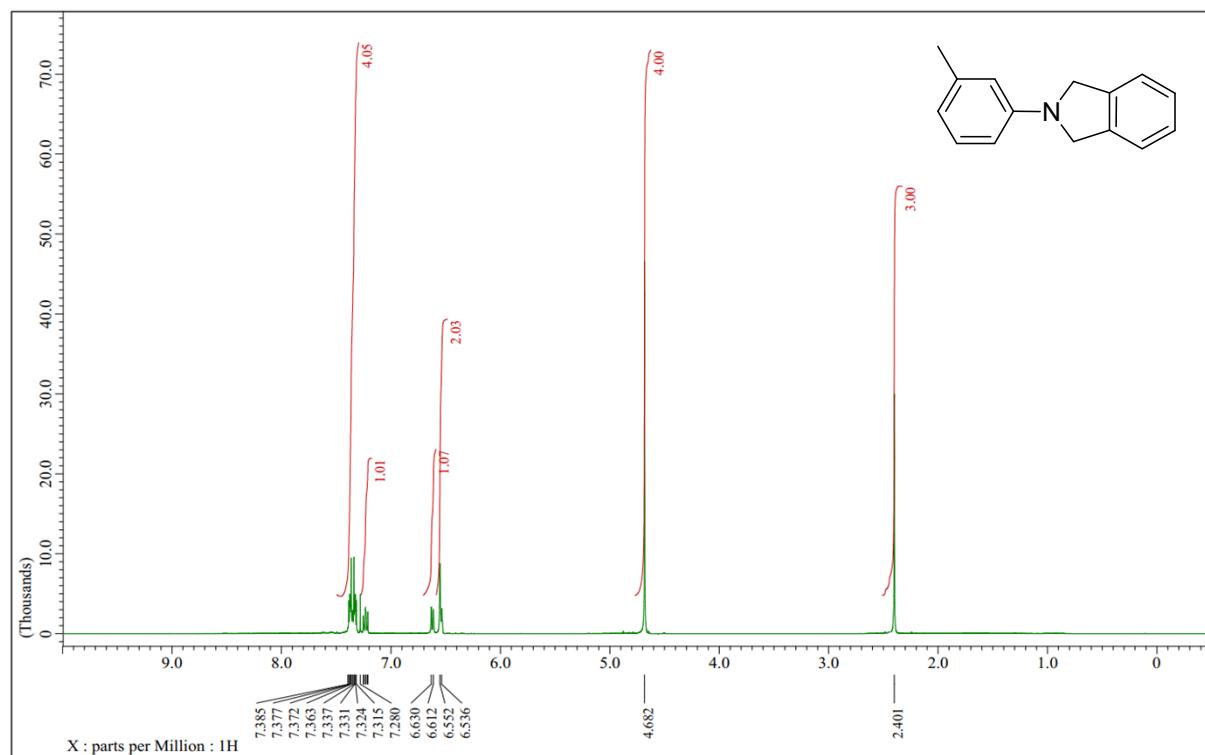


<sup>1</sup>H NMR spectrum of 2-(4-ethylphenyl)isoindoline (**5k**)

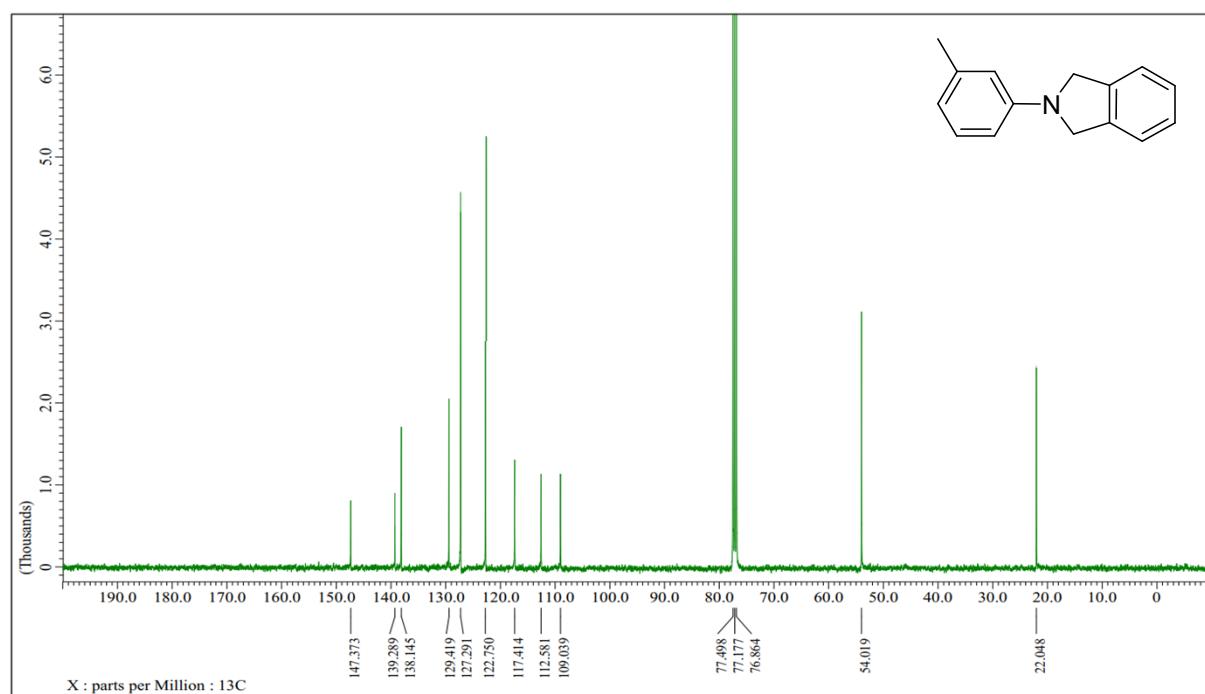


<sup>13</sup>C NMR spectrum of 2-(4-ethylphenyl)isoindoline (**5k**)

**2-m-tolylisoindoline (5l)**

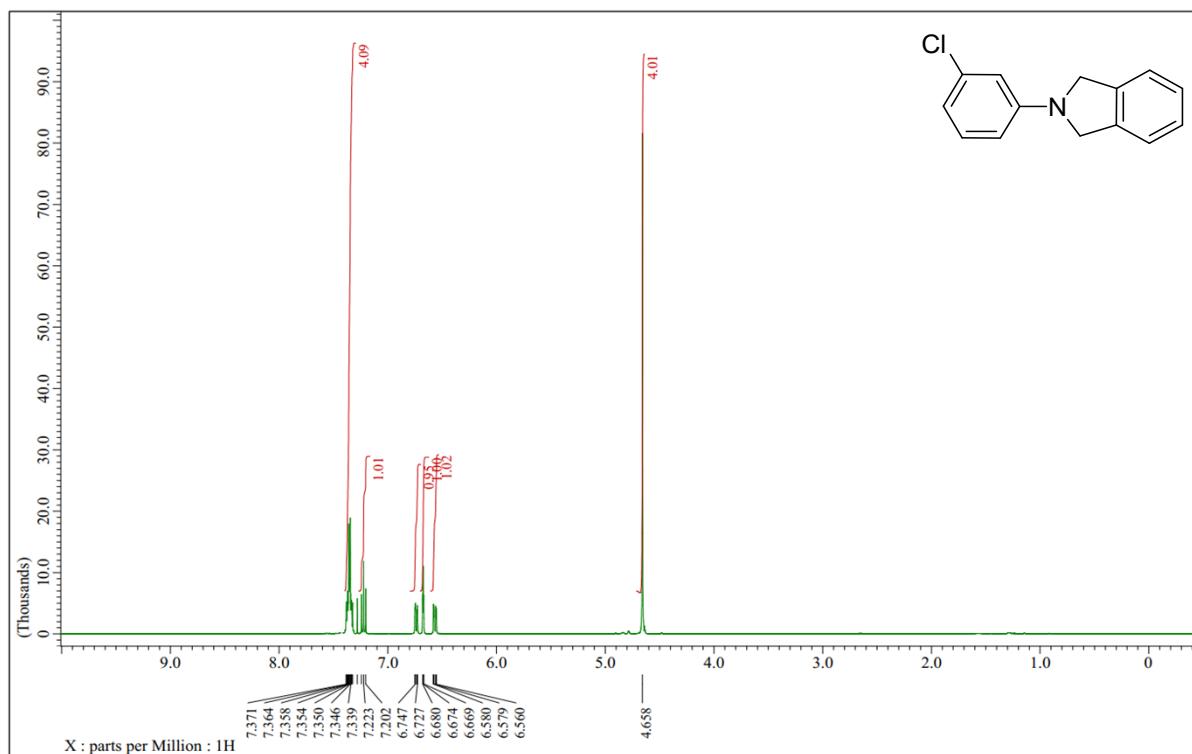


<sup>1</sup>H NMR spectrum of 2-m-tolylisoindoline (5l)

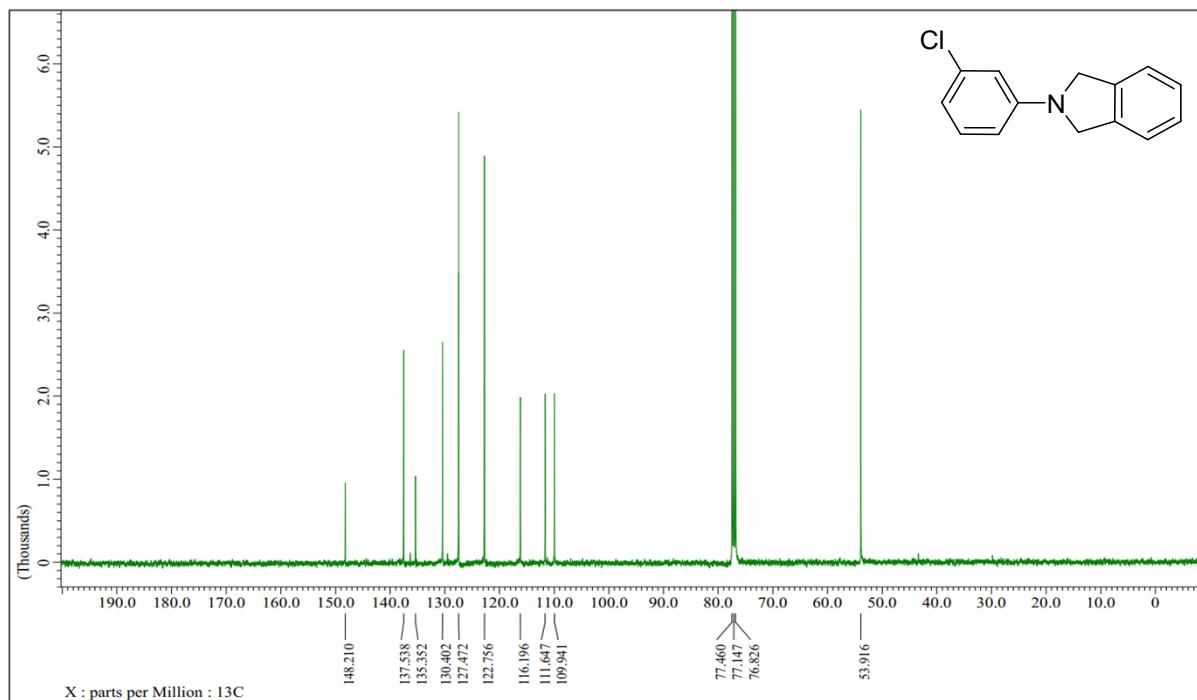


<sup>13</sup>C NMR spectrum of 2-m-tolylisoindoline (5l)

**2-(3-chlorophenyl)isoindoline (5m)**

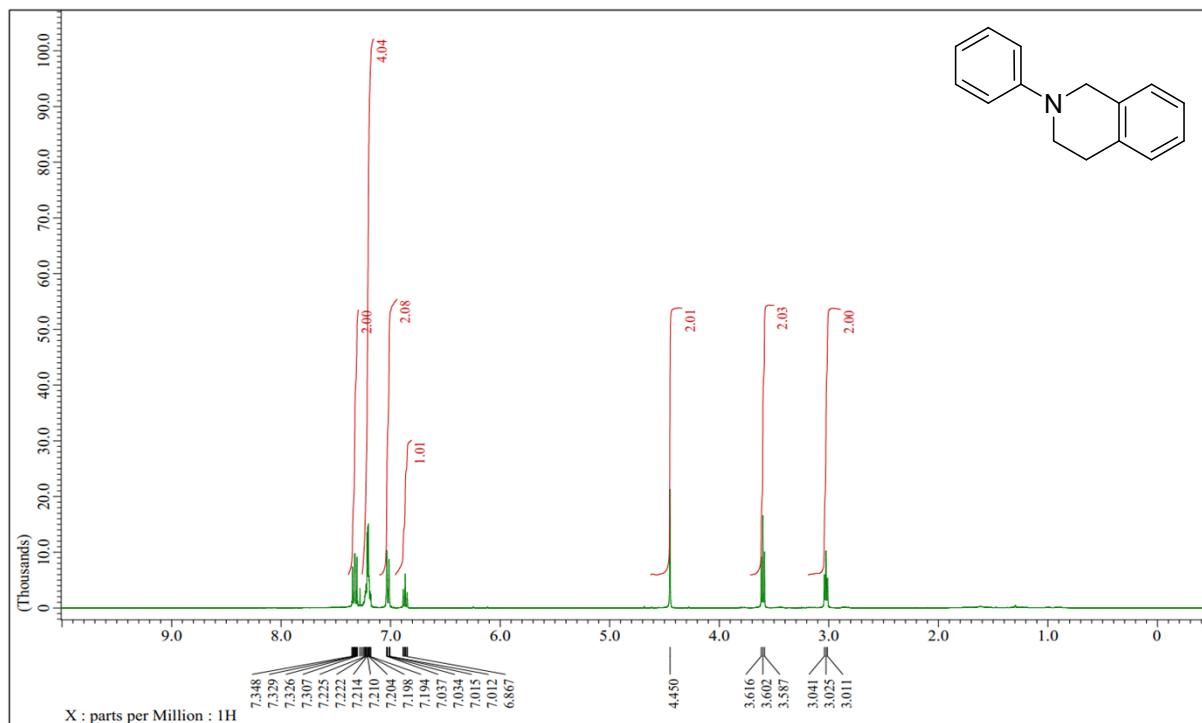


<sup>1</sup>H NMR spectrum of 2-(3-chlorophenyl)isoindoline (5m)

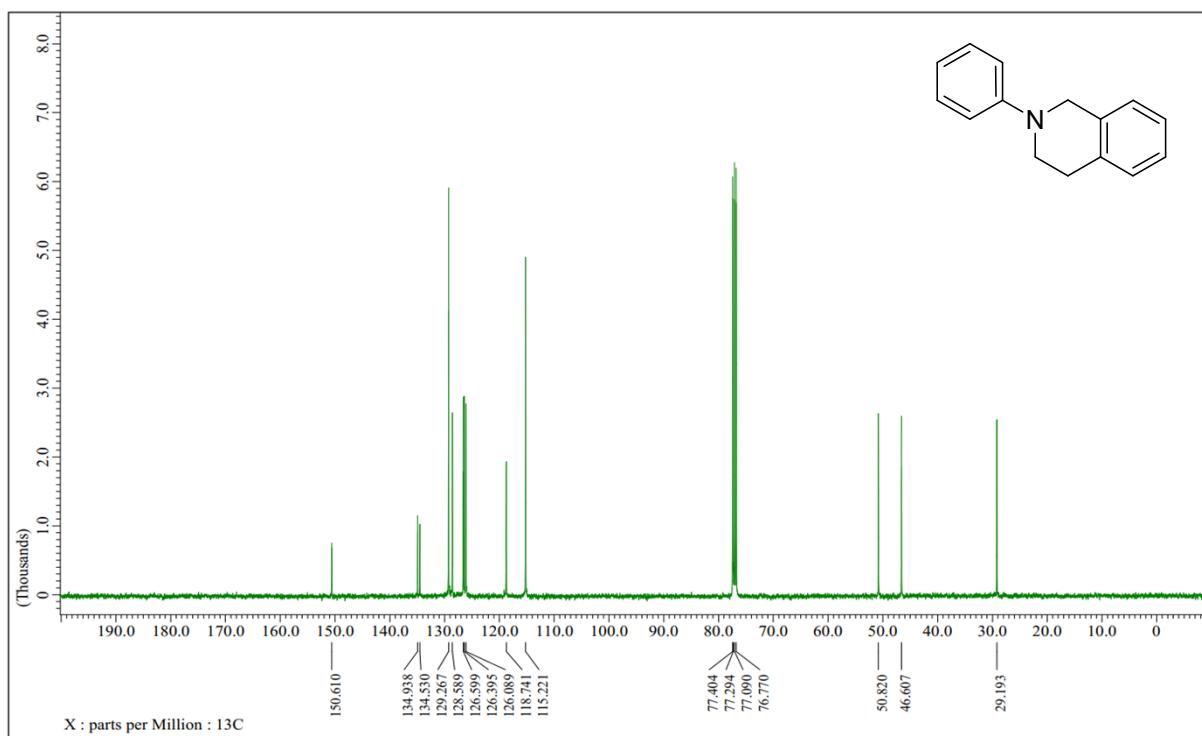


<sup>13</sup>C NMR spectrum of 2-(3-chlorophenyl)isoindoline (5m)

**2-phenyl-1,2,3,4-tetrahydroisoquinoline (5n)**

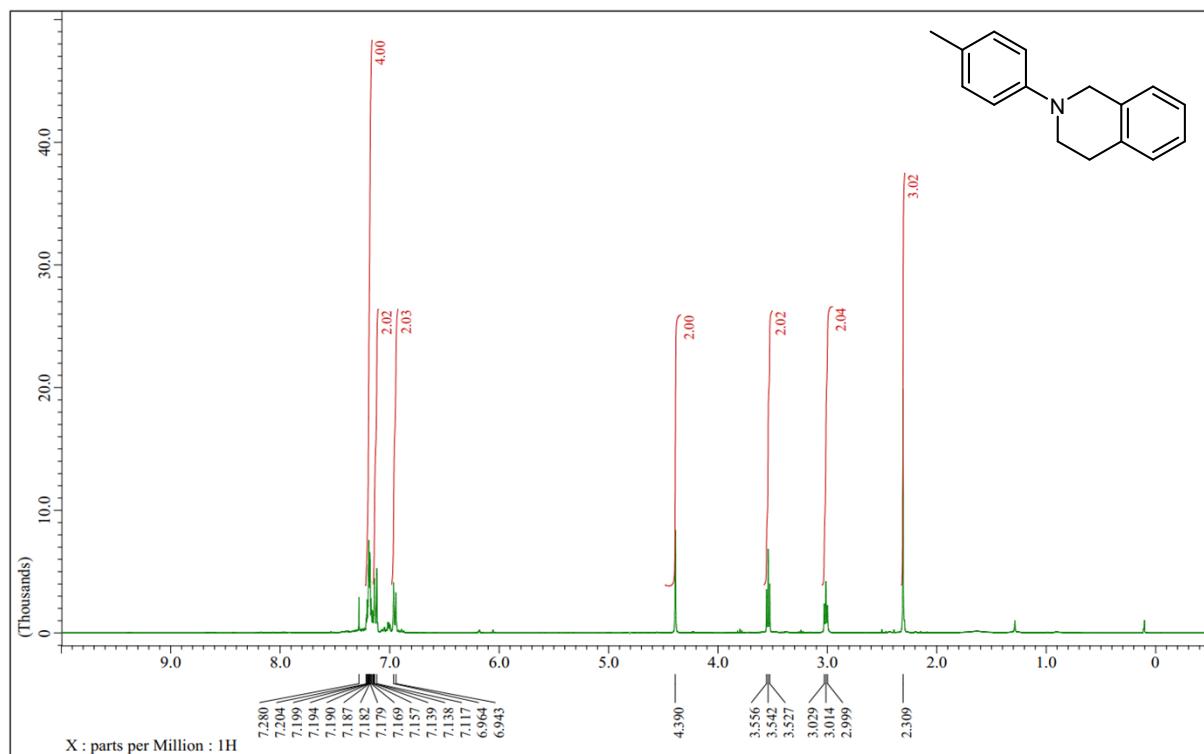


<sup>1</sup>H NMR spectrum of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (**5n**)

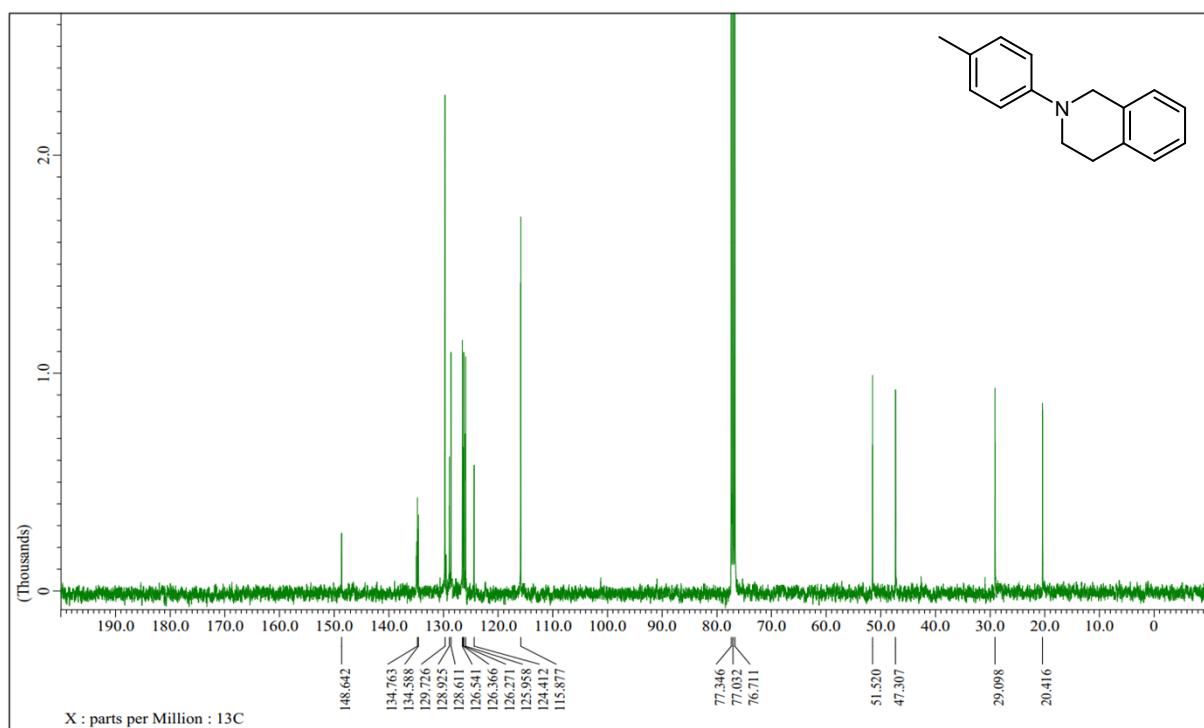


<sup>13</sup>C NMR spectrum of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (**5n**)

**2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (**5o**)**

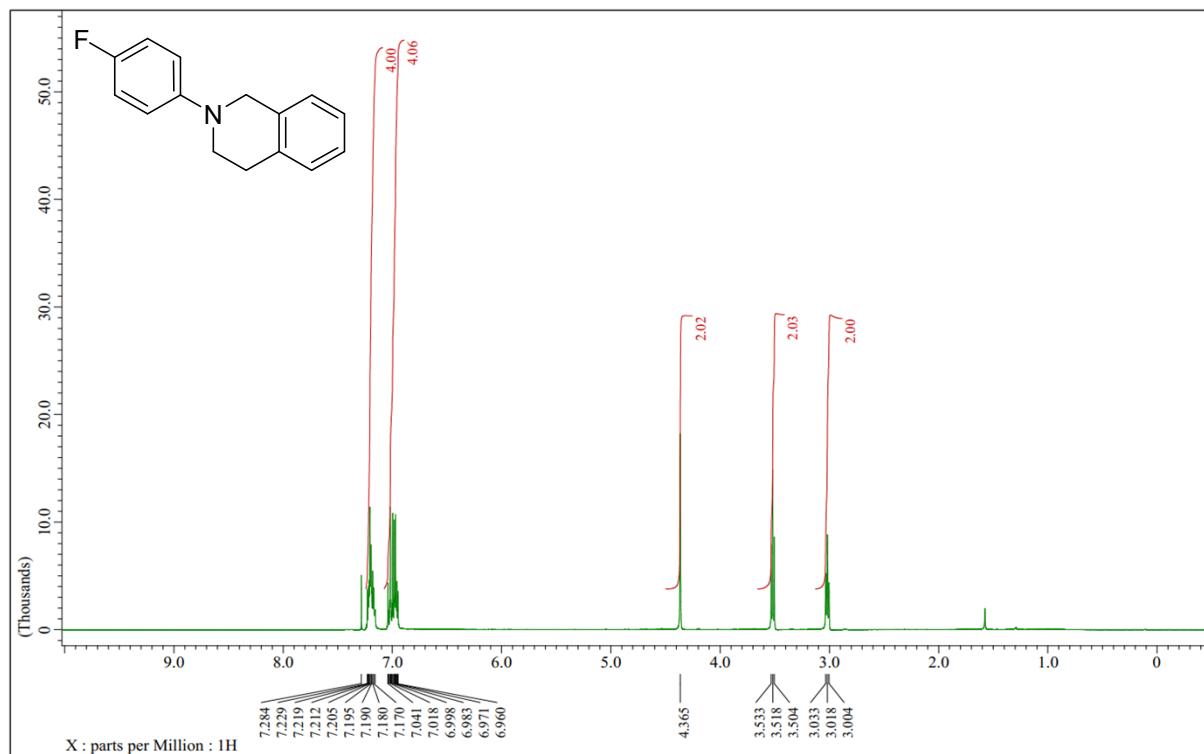


<sup>1</sup>H NMR spectrum of 2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (**5o**)

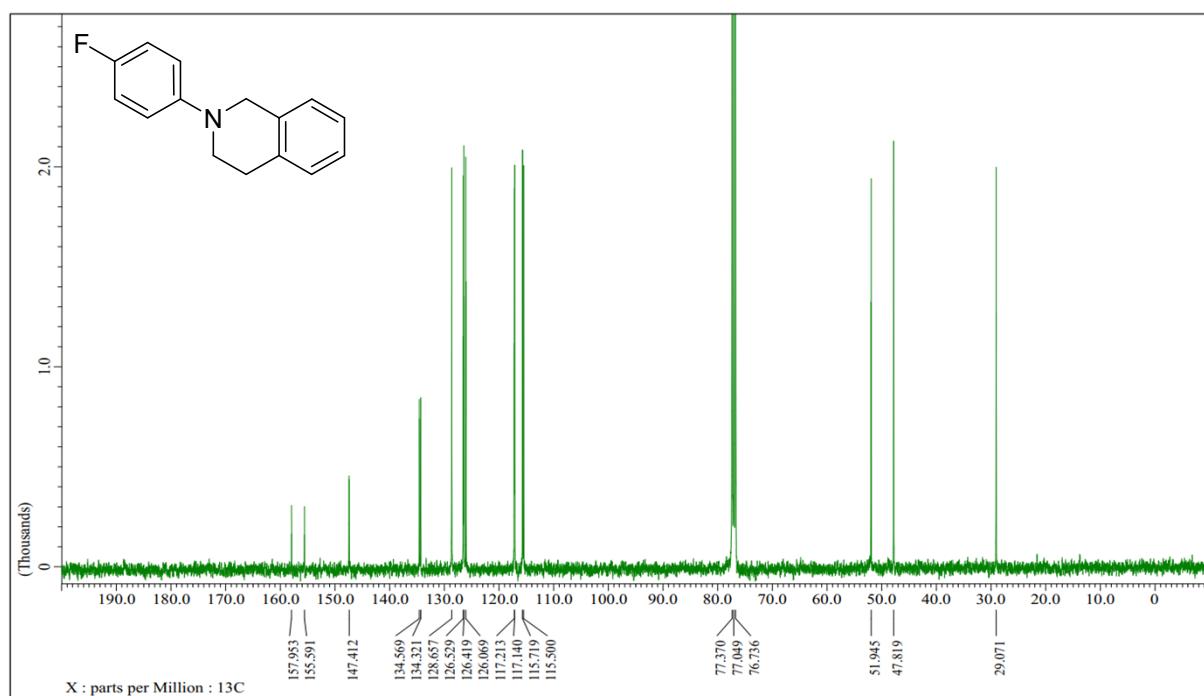


<sup>13</sup>C NMR spectrum of 2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (**5o**)

**2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (5p)**

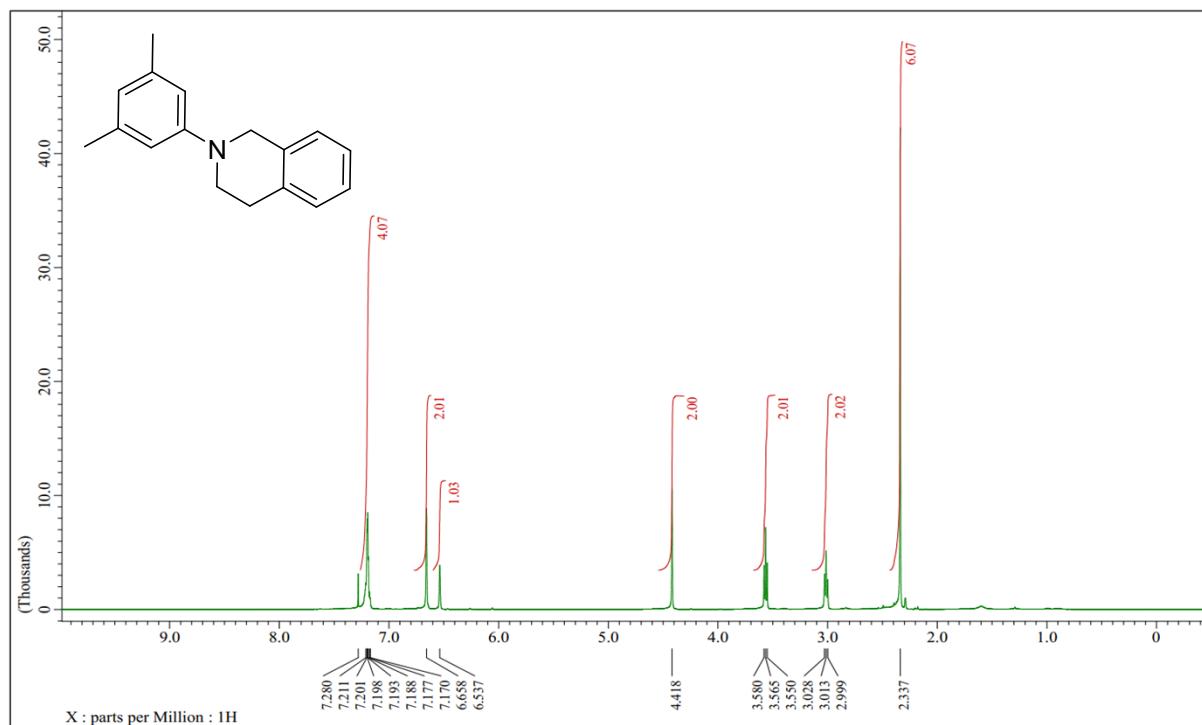


<sup>1</sup>H NMR spectrum of 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (5p)

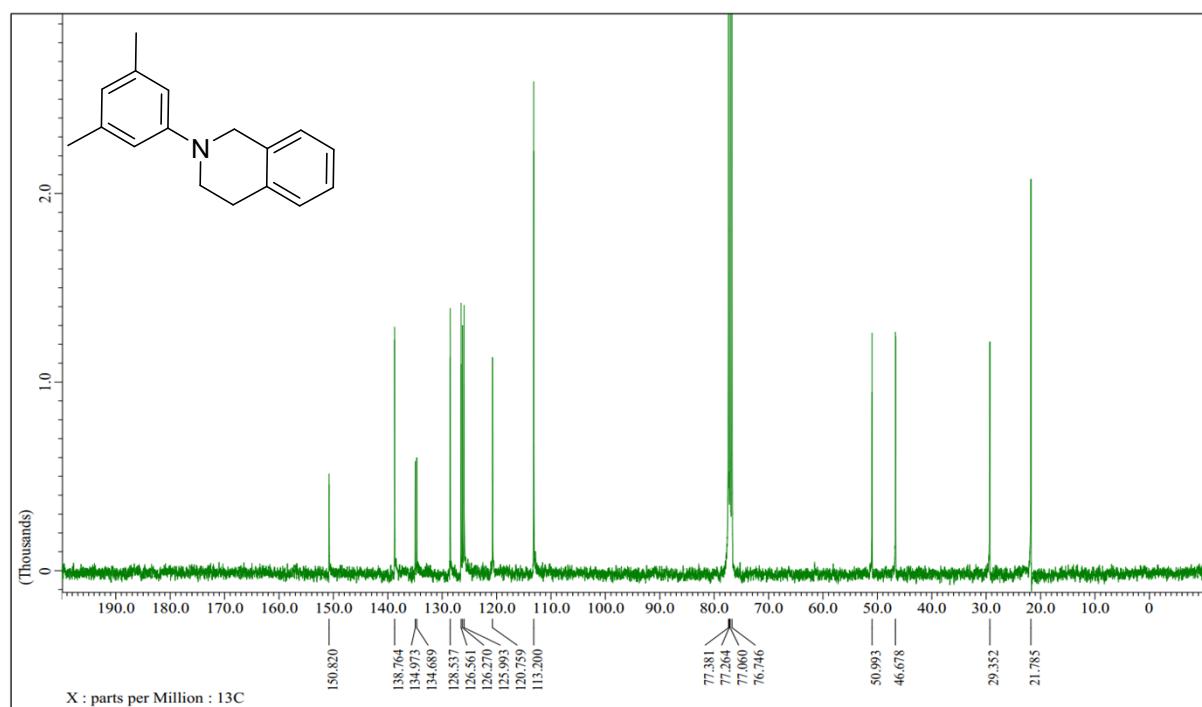


<sup>13</sup>C NMR spectrum of 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (5p)

**2-(3,5-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (**5q**)**

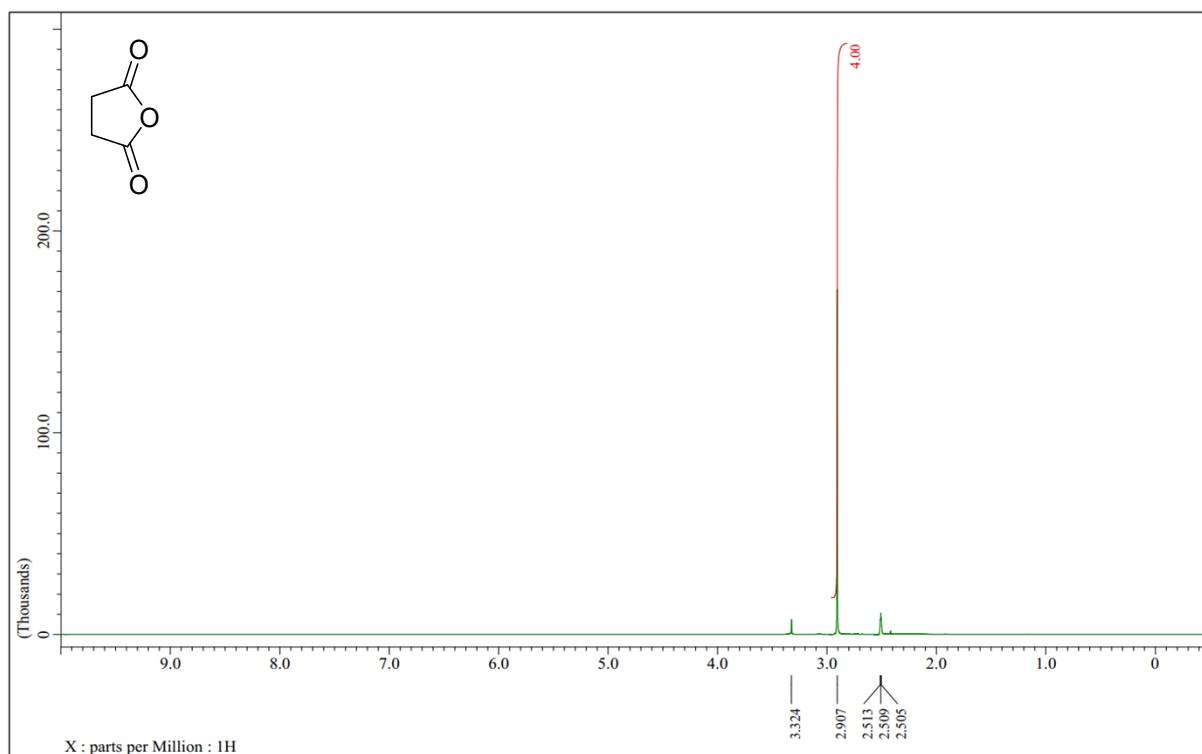


<sup>1</sup>H NMR spectrum of 2-(3,5-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (**5q**)

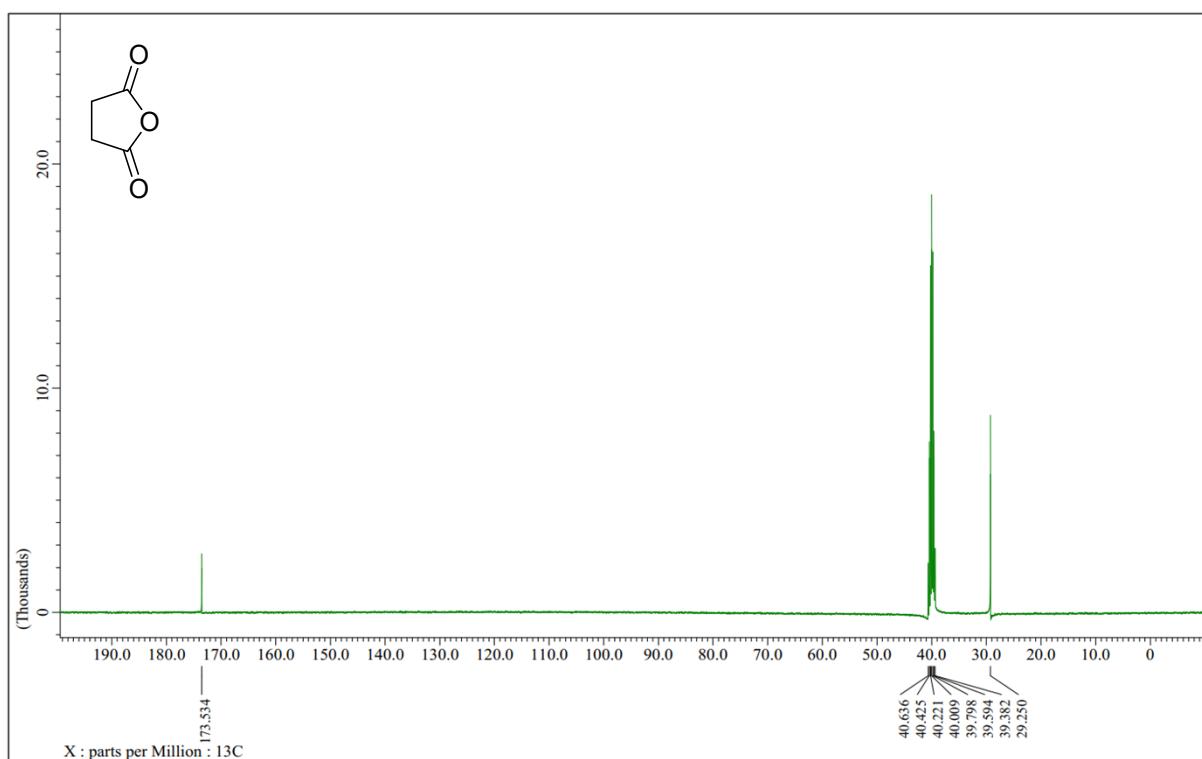


<sup>13</sup>C NMR spectrum of 2-(3,5-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (**5q**)

**dihydrofuran-2,5-dione (6)**

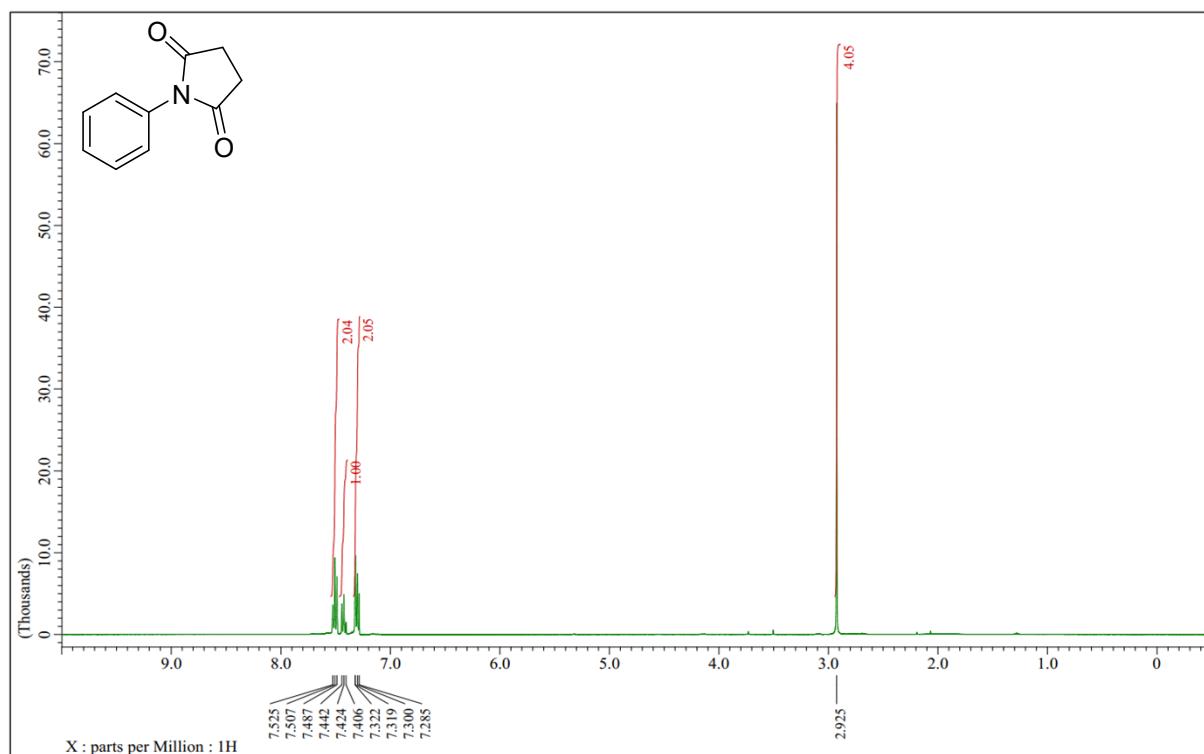


<sup>1</sup>H NMR spectrum of dihydrofuran-2,5-dione (6)

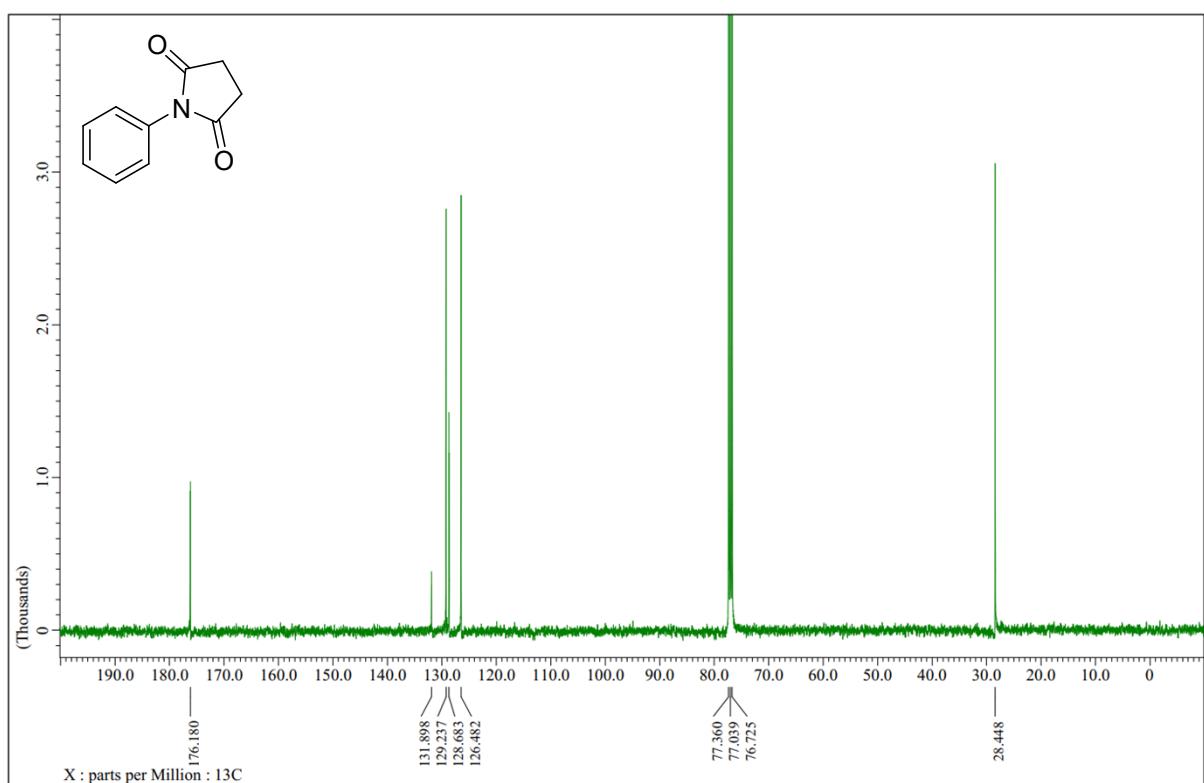


<sup>13</sup>C NMR spectrum of dihydrofuran-2,5-dione (6)

### 1-phenylpyrrolidine-2,5-dione (7)



<sup>1</sup>H NMR spectrum of 1-phenylpyrrolidine-2,5-dione (7)



<sup>13</sup>C NMR spectrum of 1-phenylpyrrolidine-2,5-dione (7)