

# Catalytic Asymmetric Sulfenylation of Unprotected 3-Substituted Oxindoles

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## Supporting information

### Contents:

|                                                                                           |       |
|-------------------------------------------------------------------------------------------|-------|
| 1. General remarks.....                                                                   | S-1   |
| 2. Determination of the absolute configuration and the X-ray structure of <b>3p</b> ..... | S-2   |
| 3. Procedures for chiral <i>N,N'</i> -dioxide preparation.....                            | S-2   |
| 4. Preparation of racemic <b>3a-3z</b> and <b>6a-6o</b> .....                             | S-2   |
| 5. General procedure for catalytic asymmetric sulfenylation reaction.....                 | S-2   |
| 6. Extra optimization of reaction conditions.....                                         | S-3   |
| 7. Some preliminary mechanistic studies.....                                              | S-9   |
| 8. Characterization of the new unprotected oxindoles <b>5b-5o</b> and <b>1z</b> .....     | S-12  |
| 9. Characterization of the new products.....                                              | S-14  |
| 10. References.....                                                                       | S-42  |
| 11. Copy of <sup>1</sup> H NMR and <sup>13</sup> C NMR spectra .....                      | S-43  |
| 12. Copy of CD spectra in methanol.....                                                   | S-157 |

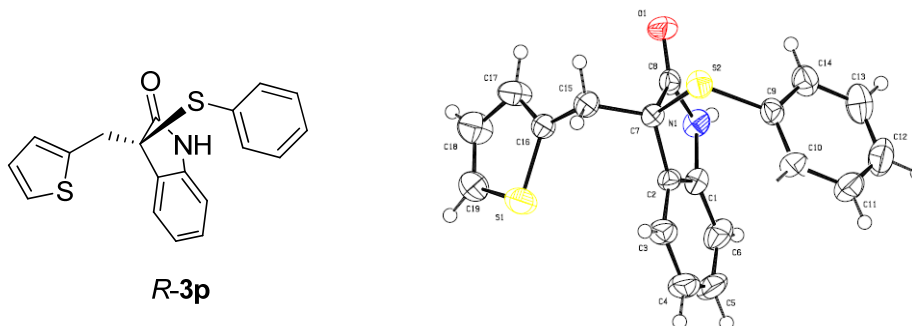
### 1. General remarks

Reactions were carried out using commercial available reagents in over-dried apparatus. CH<sub>2</sub>Cl<sub>2</sub> was dried over powdered CaH<sub>2</sub> and distilled under nitrogen just before use. CH<sub>3</sub>CCl<sub>3</sub>, CH<sub>2</sub>ClCH<sub>2</sub>Cl, CHCl<sub>3</sub>, CHCl<sub>2</sub>CHCl<sub>2</sub> and PhCl were directly distilled before use. Enantiomeric excesses (*ee*) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 23 °C with UV detector at 254 nm. Optical rotations were reported as follows: [ $\alpha$ ]<sub>D</sub><sup>25</sup> (c g/100 mL, in solvent). <sup>1</sup>H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl<sub>3</sub>,  $\delta$  = 7.26; DMSO,  $\delta$  = 2.50). Spectra were reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. <sup>13</sup>C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with

the solvent resonance as internal standard ( $\text{CDCl}_3$ ,  $\delta = 77.0$ ; DMSO,  $\delta = 39.5$ ). HRMS was recorded on a commercial apparatus (ESI Source).

## 2. Determination of the absolute configuration and X-ray structure of **3p**

The absolute configuration of the optically active sulfenylated product **3p** was determined by X-ray chromatography analysis. All other absolute configurations were assigned by comparison with the Cotton effect in the CD spectra of **3p**.



Single crystal of  $\text{C}_{19}\text{H}_{15}\text{NOS}_2$  **3p** was obtained by recrystallization in ethyl acetate. The absolute configuration of oxindole **3p** is *R*.

**Crystal data.**  $\text{C}_{19}\text{H}_{15}\text{NOS}_2$ ,  $M = 337.44$ , monoclinic,  $a = 8.5240(3)$ ,  $b = 8.2187(2)$ ,  $c = 12.2542(4)$ ,  $U = 815.60(5) \text{ \AA}^3$ ,  $T = 293(2) \text{ K}$ , space group  $P1211$ ,  $Z = 2$ .

## 3. General procedure for chiral *N,N'*-dioxide preparation

The *N,N'*-dioxide ligands **L1-L4** were synthesized by the same procedure in the literature<sup>[1]</sup>.

## 4. Preparation of racemic **3a-3z** and **6a-6o**

A reaction tube was charged with oxindole **1** or **5** (0.1 mmol), sulfenylating agent **2** (0.105 mmol, 26.8 mg, 1.05 equiv) and NaOH (0.2 mmol, 8.0 mg). Then,  $\text{CH}_2\text{Cl}_2$  (0.5 mL) were added. After stirring at 35 °C for 0.5 h, the crude racemic products **3** or **6** were obtained directly by silica gel chromatography (eluent: petroleum ether/AcOEt 3:1 to 4:1). Removal of phthalimide in the crude product with 1 N NaOH aqueous solution, following by extraction with  $\text{CH}_2\text{Cl}_2$  and flash chromatography (petroleum ether/EtOAc 2:1) afforded the pure race products.

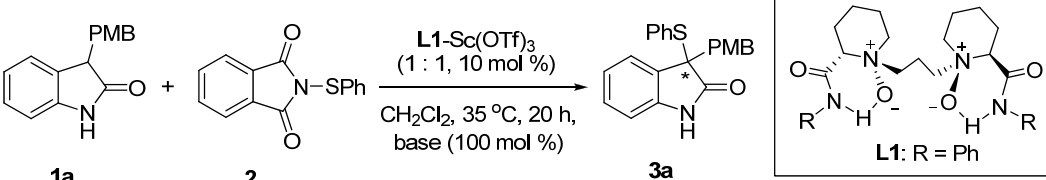
## 5. Procedures for catalytic asymmetric sulfenylation reaction

General procedure for catalytic asymmetric reaction: A dry reaction tube was charged with **L4-Sc(OTf)<sub>3</sub>** (1:1, 3–5 mol % catalyst loading), 4 Å MS (25.0 mg, activated at 500 °C for 5 h before use), and **1** or **5** (0.1 mmol) under  $\text{N}_2$  atmosphere. Then,  $\text{CH}_2\text{Cl}_2$  (2.0 mL) were added and the mixture was stirred at 35 °C for 0.5 h. Finally, *N*-(phenylthio)phthalimide **2** (0.105 mmol, 26.8 mg), and  $\text{K}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$  (10–200 mol %) were added under stirring. The reaction mixture was stirred at 35 °C for 12–72 h. The residue was purified by flash chromatography (petroleum ether/AcOEt 3:1 to 4:1) on silica gel to afford the crude product. Removal of phthalimide in the crude product with 1 N NaOH aqueous solution (5 mL), following by extraction with  $\text{CH}_2\text{Cl}_2$  and flash chromatography (petroleum ether/AcOEt 2:1) afforded the products **3** or **6**. The enantiomeric excess (*ee*) was determined by high-performance liquid chromatography (HPLC) with Chiralcel OD-H, Chiralcel AD-H, Chiralcel IA, Chiralcel IB or Chiralcel IC.

Typical procedure for the scale-up reaction: A flask (150 mL) was charged with **L4** (0.15 mmol, 97.0 mg), Sc(OTf)<sub>3</sub> (0.15 mmol, 74.0 mg), 4 Å MS (1.25 g, activated at 500 °C for 5 h before use), and **1a** (5.0 mmol, 1.267 g) under N<sub>2</sub> atmosphere. Then, CH<sub>2</sub>Cl<sub>2</sub> (100 mL) were added and the mixture was stirred at 35 °C for 0.5 h. Finally, N-(phenylthio)-phthalimide **2** (5.1 mmol, 1.34 g) and K<sub>2</sub>CO<sub>3</sub> (10.0 mmol, 1.38 g) was added under stirring. The reaction mixture was stirred at 35 °C for 20 h. The residue was purified by flash chromatography (petroleum ether/AcOEt = 3/1) on silica gel to afford the crude product. Removal of phthalimide in the crude product with 1 N NaOH aqueous solution, following by extraction with CH<sub>2</sub>Cl<sub>2</sub> and flash chromatography (petroleum ether/AcOEt = 2/1) afforded the product **3a** as a white solid (1.70 g, 94% yield, 97% ee). After a single recrystallization (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>) of the product, 82% yield with 99% ee was obtained.

## 6. Extra Optimization of reaction conditions

### A) preliminary survey of base

|  |                                    |          |                        |                     |
|------------------------------------------------------------------------------------|------------------------------------|----------|------------------------|---------------------|
| Entry <sup>a</sup>                                                                 | Base                               | Time (h) | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
| 1                                                                                  | No                                 | 20       | 0                      | -                   |
| 2                                                                                  | NaHCO <sub>3</sub>                 | 20       | 0                      | -                   |
| 3                                                                                  | Li <sub>2</sub> CO <sub>3</sub>    | 20       | 0                      | -                   |
| 4                                                                                  | Na <sub>2</sub> CO <sub>3</sub>    | 20       | 45                     | < 5                 |
| 5                                                                                  | K <sub>2</sub> CO <sub>3</sub>     | 22       | 75                     | < 5                 |
| 6                                                                                  | Cs <sub>2</sub> CO <sub>3</sub>    | 6        | 88 <sup>d</sup>        | < 5                 |
| 7                                                                                  | NaOH                               | 0.1      | 90 <sup>d</sup>        | < 5                 |
| 8                                                                                  | DMAP                               | 20       | 90 <sup>d</sup>        | < 5                 |
| 9                                                                                  | EtN( <sup>i</sup> Pr) <sub>2</sub> | 20       | 85 <sup>d</sup>        | < 5                 |

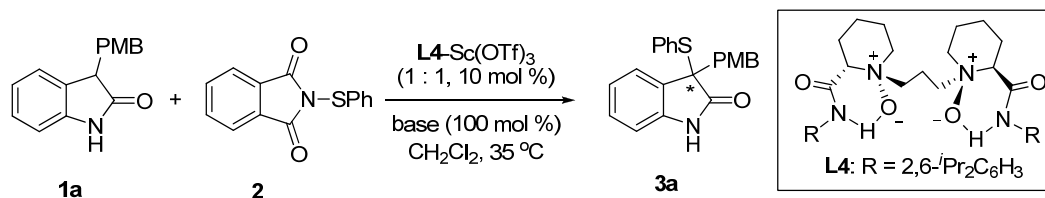
<sup>a</sup> Unless otherwise noted, all reactions were performed with **L1**-Sc(OTf)<sub>3</sub> (1:1, 10 mol %), base (0.1 mmol), **1a** (0.1 mmol, PMB = *p*-methoxybenzyl), N-(phenylthio)phthalimide **2** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) under N<sub>2</sub> at 35 °C for the indicated time. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis (Chiralcel OD-H). <sup>d</sup> **1a** was completely consumed.

### B) survey of chiral ligand

| <p> <b>1a</b> + <b>2</b> <math>\xrightarrow[\text{Na}_2\text{CO}_3 (100 \text{ mol } \%), \text{CH}_2\text{Cl}_2, 35 \text{ }^\circ\text{C}]{\text{L-Sc(OTf)}_3 (1 : 1, 10 \text{ mol } \%)}</math> <b>3a</b> + <b>4a</b> </p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                |                        |                     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|------------------------|---------------------|
| <p> <b>L1:</b> R = Ph, n = 2<br/> <b>L2:</b> R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, n = 2<br/> <b>L3:</b> R = 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, n = 2<br/> <b>L4:</b> R = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, n = 2<br/> <b>L5:</b> R = 2,4,6-<sup>i</sup>Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, n = 2<br/> <b>L6:</b> R = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, n = 1<br/> <b>L8:</b> R = Bn, n = 2<br/> <b>L9:</b> R = 1-admantyl, n = 2<br/> <b>L10:</b> R = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, n = 2<br/> <b>L7:</b> R = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub><br/> <b>L11:</b> R = 2,4,6-<sup>i</sup>Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub> </p> |                |                        |                     |
| Entry <sup>a</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | Ligand (mol %) | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
| 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <b>L1</b>      | 45                     | 0                   |
| 2                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <b>L2</b>      | 71                     | 46                  |
| 3                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <b>L3</b>      | 86 <sup>d</sup>        | 76                  |
| 4                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <b>L4</b>      | 87 <sup>d</sup>        | 94                  |
| 5                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <b>L5</b>      | 86 <sup>d</sup>        | 93                  |
| 6                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <b>L6</b>      | 58                     | 91                  |
| 7                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <b>L7</b>      | 76                     | 94                  |
| 8                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <b>L8</b>      | 25                     | 9                   |
| 9                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <b>L9</b>      | 21                     | 0                   |
| 10                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | <b>L10</b>     | 35                     | 24                  |
| 11                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | <b>L11</b>     | 30                     | 70                  |

<sup>a</sup> Unless otherwise noted, all reactions were performed with **L** (10 mol %), Sc(OTf)<sub>3</sub> (10 mol %, 4.9 mg), Na<sub>2</sub>CO<sub>3</sub> (0.1 mmol), **1a** (0.1 mmol, PMB = *p*-methoxybenzyl), N-(phenylthio)phthalimide **2** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) under N<sub>2</sub> at 35 °C for 20 h. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis (Chiralcel OD-H). <sup>d</sup> **1a** was completely consumed and about 10–15% yield of **4a** was observed.

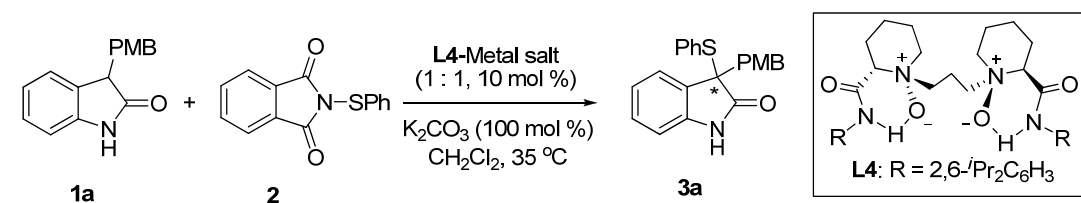
### C) the effect of base in the presence of chiral Lewis acid catalyst



| Entry <sup>a</sup> | Base                               | Time (h) | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
|--------------------|------------------------------------|----------|------------------------|---------------------|
| 1                  | No                                 | 48       | 0                      | -                   |
| 2                  | NaHCO <sub>3</sub>                 | 20       | 75                     | 94                  |
| 3                  | Li <sub>2</sub> CO <sub>3</sub>    | 20       | 65                     | 94                  |
| 4                  | Na <sub>2</sub> CO <sub>3</sub>    | 20       | 87 <sup>d</sup>        | 94                  |
| 5                  | K <sub>2</sub> CO <sub>3</sub>     | 2        | 88 <sup>d</sup>        | 94                  |
| 6                  | Cs <sub>2</sub> CO <sub>3</sub>    | 1        | 89 <sup>d</sup>        | 90                  |
| 7                  | NaOH                               | 0.1      | 85 <sup>d</sup>        | 71                  |
| 8                  | DABCO                              | 1        | 89 <sup>d</sup>        | 68                  |
| 9                  | DMAP                               | 20       | 85 <sup>d</sup>        | -16                 |
| 10                 | DBU                                | 3        | 92 <sup>d</sup>        | 19                  |
| 11                 | TMG                                | 3        | 90 <sup>d</sup>        | 2                   |
| 12                 | Pyridine                           | 20       | 50                     | 76                  |
| 13                 | Lutidine                           | 20       | 85 <sup>d</sup>        | 94                  |
| 14                 | EtN( <sup>i</sup> Pr) <sub>2</sub> | 20       | 86 <sup>d</sup>        | 89                  |

<sup>a</sup> Unless otherwise noted, all reactions were performed with **L4**-Sc(OTf)<sub>3</sub> (1:1, 10 mol %), base (0.1 mmol), **1a** (0.1 mmol, PMB = *p*-methoxybenzyl), N-(phenylthio)phthalimide **2** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) under N<sub>2</sub> at 35 °C for the indicated time. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis (Chiralcel OD-H). <sup>d</sup> **1a** was completely consumed.

#### D) survey of other Lewis acid

|  |                      |          |                        |                     |
|--------------------------------------------------------------------------------------|----------------------|----------|------------------------|---------------------|
| Entry <sup>a</sup>                                                                   | Metal salt           | Time (h) | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
| 1                                                                                    | Sc(OTf) <sub>3</sub> | 2        | 88 <sup>d</sup>        | 94                  |
| 2                                                                                    | Y(OTf) <sub>3</sub>  | 20       | 52                     | 27                  |
| 3                                                                                    | La(OTf) <sub>3</sub> | 20       | 63                     | -16                 |
| 4                                                                                    | Yb(OTf) <sub>3</sub> | 20       | 64                     | 41                  |
| 5                                                                                    | Gd(OTf) <sub>3</sub> | 20       | 54                     | 7                   |

<sup>a</sup> Unless otherwise noted, all reactions were performed with **L4**-Metal salt (1:1, 10 mol %), K<sub>2</sub>CO<sub>3</sub> (0.1 mmol), **1a** (0.1 mmol, PMB = *p*-methoxybenzyl), N-(phenylthio)phthalimide **2** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) under N<sub>2</sub> at 35 °C for the indicated time. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis (Chiralcel OD-H). <sup>d</sup> **1a** was

completely consumed.

### E) survey of solvent effects

| Entry <sup>a</sup> | Solvent                              | Time (h) | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
|--------------------|--------------------------------------|----------|------------------------|---------------------|
| 1                  | Cl <sub>3</sub> CCH <sub>3</sub>     | 12       | 87                     | 73                  |
| 2                  | CH <sub>2</sub> Cl <sub>2</sub>      | 2        | 88                     | 94                  |
| 3                  | CH <sub>2</sub> ClCH <sub>2</sub> Cl | 12       | 86                     | 90                  |
| 4                  | CHCl <sub>3</sub>                    | 12       | 69                     | 52                  |
| 5                  | PhCl                                 | 12       | 87                     | 74                  |
| 6                  | CHCl <sub>2</sub> CHCl <sub>2</sub>  | 12       | 39                     | 56                  |
| 7                  | Cl <sub>3</sub> CCH <sub>3</sub>     | 12       | 87                     | 73                  |

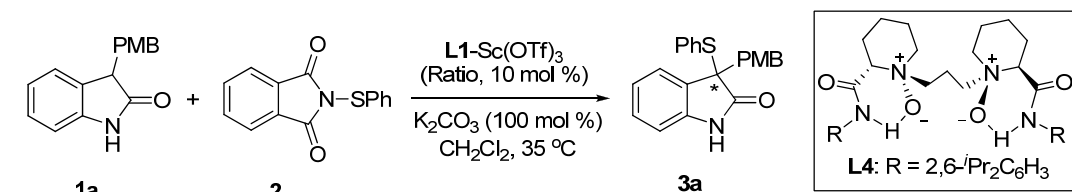
<sup>a</sup> Unless otherwise noted, all reactions were performed with **L4**-Sc(OTf)<sub>3</sub> (1:1, 10 mol %), K<sub>2</sub>CO<sub>3</sub> (0.1 mmol), **1a** (0.1 mmol, PMB = *p*-methoxybenzyl), N-(phenylthio)phthalimide **2** (0.12 mmol) in the corresponding solvent (0.5 mL) under N<sub>2</sub> at 35 °C for the indicated time. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis (Chiralcel OD-H). <sup>d</sup> **1a** was completely consumed.

### F) survey of temperature effects

| Entry <sup>a</sup> | Temperature (°C) | Time (h) | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
|--------------------|------------------|----------|------------------------|---------------------|
| 1                  | 35               | 2        | 88 <sup>d</sup>        | 94                  |
| 2                  | 25               | 12       | 85 <sup>d</sup>        | 89                  |
| 3                  | 0                | 24       | 86 <sup>d</sup>        | 81                  |

<sup>a</sup> Unless otherwise noted, all reactions were performed with **L4**-Sc(OTf)<sub>3</sub> (1:1, 10 mol %), K<sub>2</sub>CO<sub>3</sub> (0.1 mmol), **1a** (0.1 mmol, PMB = *p*-methoxybenzyl), N-(phenylthio)phthalimide **2** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) under N<sub>2</sub> at the corresponding temperature for the indicated time. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis (Chiralcel OD-H). <sup>d</sup> **1a** was completely consumed.

### G) optimization of the ratio between ligand and metal



| Entry <sup>a</sup> | Ratio (ligand : metal) | Time | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
|--------------------|------------------------|------|------------------------|---------------------|
| 1                  | 1.5 : 1                | 2    | 86 <sup>d</sup>        | 94                  |
| 2                  | 1.2 : 1                | 2    | 85 <sup>d</sup>        | 94                  |
| 3                  | 1 : 1                  | 2    | 88 <sup>d</sup>        | 94                  |
| 4                  | 0.8 : 1                | 2    | 84 <sup>d</sup>        | 94                  |

<sup>a</sup> Unless otherwise noted, all reactions were performed with **L4**-Sc(OTf)<sub>3</sub> (corresponding ratio, 10 mol %), K<sub>2</sub>CO<sub>3</sub> (0.1 mmol), **1a** (0.1 mmol, PMB = *p*-methoxybenzyl), N-(phenylthio)phthalimide **2** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) under N<sub>2</sub> at the 35 °C for the indicated time. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis (Chiralcel OD-H). <sup>d</sup> **1a** was completely consumed.

## H) screening of additive

Reaction scheme showing the screening of additive. Reagents: **L1**-Sc(OTf)<sub>3</sub> (1:1, 10 mol %), CH<sub>2</sub>Cl<sub>2</sub>, 35 °C, K<sub>2</sub>CO<sub>3</sub> (100 mol %), Additive. Product **3a** is a chiral indoline derivative. A box shows the structure of **L4**: R = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.

| Entry <sup>a</sup> | Additive | Time | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
|--------------------|----------|------|------------------------|---------------------|
| 1                  | -        | 2    | 88 <sup>d</sup>        | 94                  |
| 2                  | 3 Å MS   | 2    | 88 <sup>d</sup>        | 95                  |
| 3                  | 4 Å MS   | 2    | 89 <sup>d</sup>        | 96                  |
| 4                  | 5 Å MS   | 4    | 88 <sup>d</sup>        | 95                  |

<sup>a</sup> Unless otherwise noted, all reactions were performed with **L4**-Sc(OTf)<sub>3</sub> (1:1, 10 mol %), additive (25.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.1 mmol), **1a** (0.1 mmol, PMB = *p*-methoxybenzyl), N-(phenylthio)phthalimide **2** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) under N<sub>2</sub> at the 35 °C for the indicated time. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis (Chiralcel OD-H). <sup>d</sup> **1a** was completely consumed.

## I) survey of concentration effects

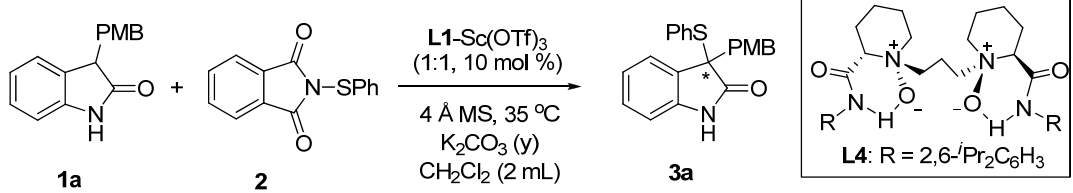
Reaction scheme showing the survey of concentration effects. Reagents: **L1**-Sc(OTf)<sub>3</sub> (1:1, 10 mol %), 4 Å MS, 35 °C, K<sub>2</sub>CO<sub>3</sub> (100 mol %), CH<sub>2</sub>Cl<sub>2</sub> (x mL). Product **3a** is a chiral indoline derivative. A box shows the structure of **L4**: R = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.

| Entry <sup>a</sup> | x (mL) | Time | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
|--------------------|--------|------|------------------------|---------------------|
| 1                  | 0.25   | 1.5  | 88 <sup>d</sup>        | 95                  |
| 2                  | 0.5    | 3    | 89 <sup>d</sup>        | 96                  |
| 3                  | 1.0    | 6    | 87 <sup>d</sup>        | 97                  |
| 4                  | 2      | 14   | 88 <sup>d</sup>        | 98                  |
| 5                  | 2.5    | 16   | 88 <sup>d</sup>        | 98                  |

<sup>a</sup> Unless otherwise noted, all reactions were performed with **L4**-Sc(OTf)<sub>3</sub> (1:1, 10 mol %), 4 Å MS (25.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.1 mmol), **1a** (0.1 mmol, PMB = *p*-methoxybenzyl), N-(phenylthio)phthalimide **2** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub>

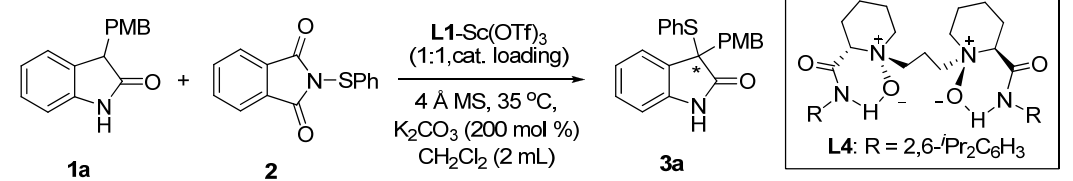
(x mL) under N<sub>2</sub> at the 35 °C for the indicated time. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis (Chiralcel OD-H). <sup>d</sup> **1a** was completely consumed.

#### J) survey of the amount of base

|  |           |      |                        |                     |
|------------------------------------------------------------------------------------|-----------|------|------------------------|---------------------|
| Entry <sup>a</sup>                                                                 | y         | Time | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
| 1                                                                                  | 200 mol % | 6    | 88 <sup>d</sup>        | 98                  |
| 2                                                                                  | 150 mol % | 10   | 87 <sup>d</sup>        | 98                  |
| 3                                                                                  | 100 mol % | 16   | 88 <sup>d</sup>        | 98                  |
| 4                                                                                  | 50 mol %  | 24   | 85 <sup>d</sup>        | 98                  |
| 5                                                                                  | 10 mol %  | 36   | 86 <sup>d</sup>        | 98                  |

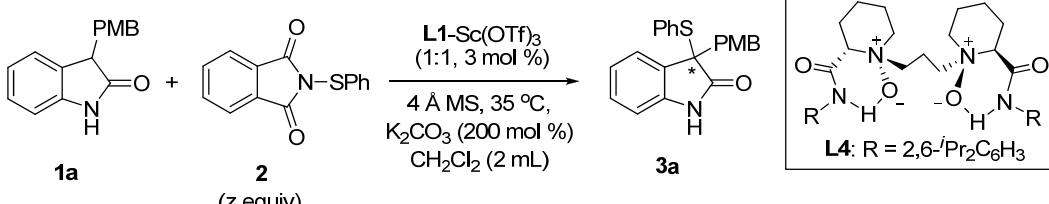
<sup>a</sup> Unless otherwise noted, all reactions were performed with **L4**-Sc(OTf)<sub>3</sub> (1:1, 10 mol %), 4 Å MS (25.0 mg), K<sub>2</sub>CO<sub>3</sub> (y), **1a** (0.1 mmol, PMB = *p*-methoxybenzyl), N-(phenylthio)phthalimide **2** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) under N<sub>2</sub> at the 35 °C for the indicated time. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis (Chiralcel OD-H). <sup>d</sup> **1a** was completely consumed.

#### K) survey of catalyst loading

|  |              |          |                        |                     |
|--------------------------------------------------------------------------------------|--------------|----------|------------------------|---------------------|
| Entry <sup>a</sup>                                                                   | Cat. loading | Time (h) | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
| 1                                                                                    | 10 mol %     | 6        | 88 <sup>d</sup>        | 98                  |
| 2                                                                                    | 5 mol %      | 6        | 86 <sup>d</sup>        | 98                  |
| 3                                                                                    | 3 mol %      | 10       | 88 <sup>d</sup>        | 97                  |
| 4                                                                                    | 2 mol %      | 14       | 87 <sup>d</sup>        | 95                  |
| 5                                                                                    | 1 mol %      | 14       | 85 <sup>d</sup>        | 92                  |

<sup>a</sup> Unless otherwise noted, all reactions were performed with **L4**-Sc(OTf)<sub>3</sub> (1:1, cat. loading), 4 Å MS (25.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.2 mmol), **1a** (0.1 mmol, PMB = *p*-methoxybenzyl), N-(phenylthio)phthalimide **2** (0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) under N<sub>2</sub> at the 35 °C for the indicated time. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis (Chiralcel OD-H). <sup>d</sup> **1a** was completely consumed.

#### L) optimization of the amount of the sulfenylating agent 2

|  |           |          |                        |                     |
|--------------------------------------------------------------------------------------|-----------|----------|------------------------|---------------------|
| Entry <sup>a</sup>                                                                   | z (equiv) | Time (h) | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
| 1                                                                                    | 1.2       | 6        | 88 <sup>d</sup>        | 98                  |
| 2                                                                                    | 1.5       | 6        | 86 <sup>d</sup>        | 98                  |
| 3                                                                                    | 2.0       | 10       | 88 <sup>d</sup>        | 97                  |
| 4                                                                                    | 2.5       | 14       | 87 <sup>d</sup>        | 95                  |
| 5                                                                                    | 3.0       | 14       | 85 <sup>d</sup>        | 92                  |

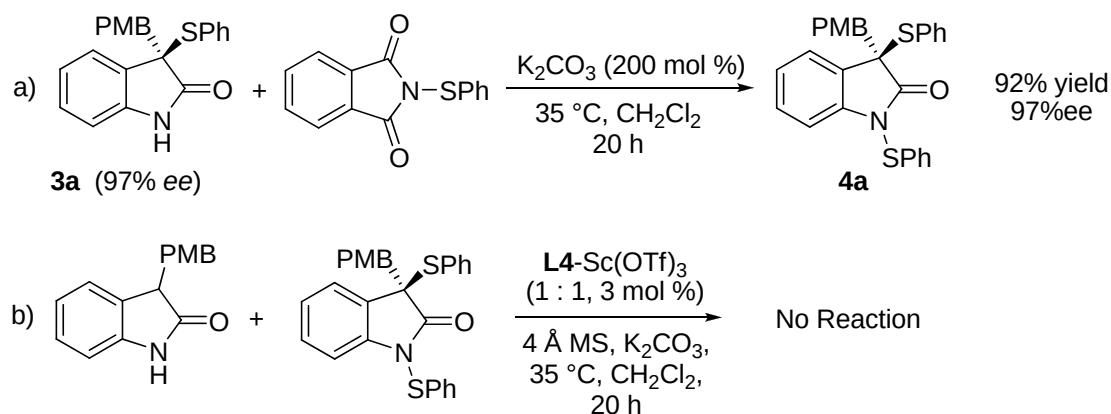


| Entry <sup>a</sup> | z (equiv.) | Time (h) | Yield <sup>b</sup> (%) | Ee <sup>c</sup> (%) |
|--------------------|------------|----------|------------------------|---------------------|
| 1                  | 2.0        | 12       | 16 <sup>d</sup>        | 97                  |
| 2                  | 1.2        | 12       | 86 <sup>d</sup>        | 97                  |
| 3                  | 1.05       | 12       | 98 <sup>d</sup>        | 97                  |
| 4                  | 1          | 12       | 95                     | 97                  |

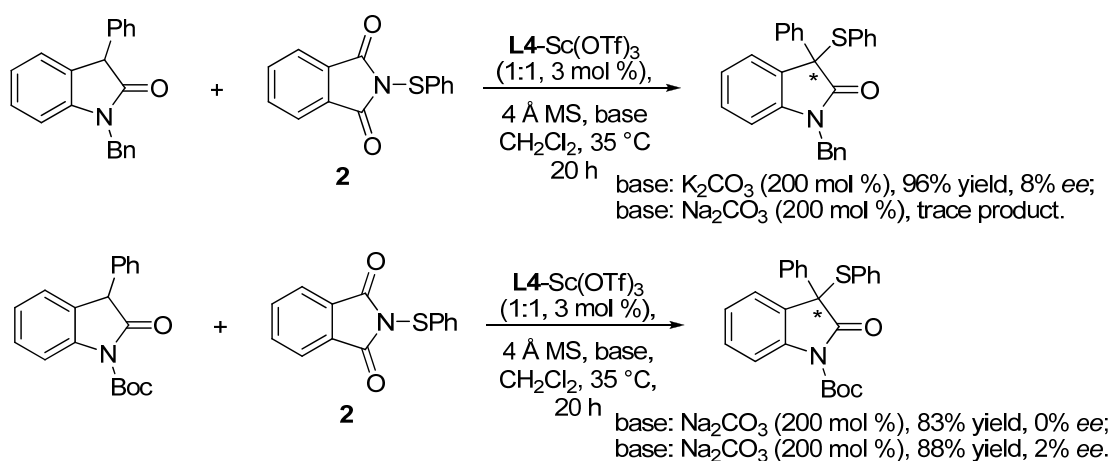
<sup>a</sup> Unless otherwise noted, all reactions were performed with **L4**-Sc(OTf)<sub>3</sub> (1:1, 3 mol %), 4 Å MS (25.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.2 mmol), **1a** (0.1 mmol, PMB = *p*-methoxybenzyl), N-(phenylthio)phthalimide **2** (z equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) under N<sub>2</sub> at the 35 °C for the indicated time. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis (Chiralcel OD-H). <sup>d</sup> **1a** was completely consumed.

## 7. Some preliminary mechanistic studies

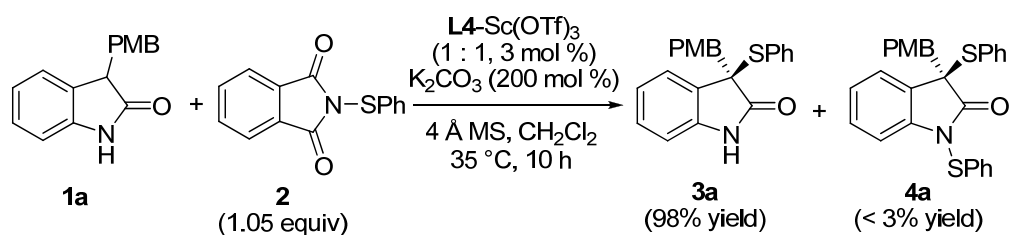
### A) Control experiments to elucidate the reaction process



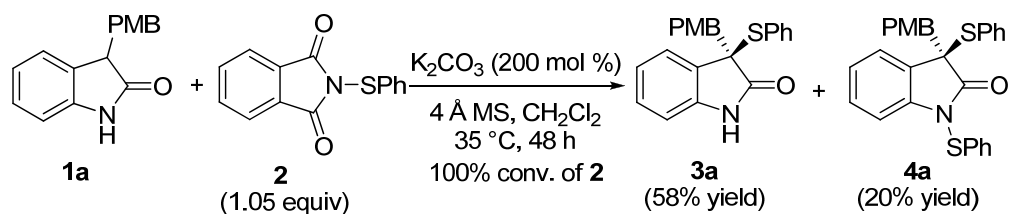
### B) Sulfenylation of the N-Bn and N-Boc protected oxindole



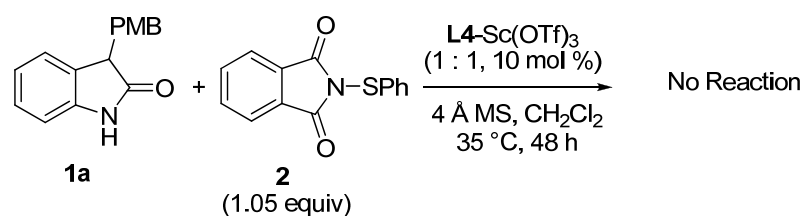
### C) Control experiments using 1a and 2 as model substrates



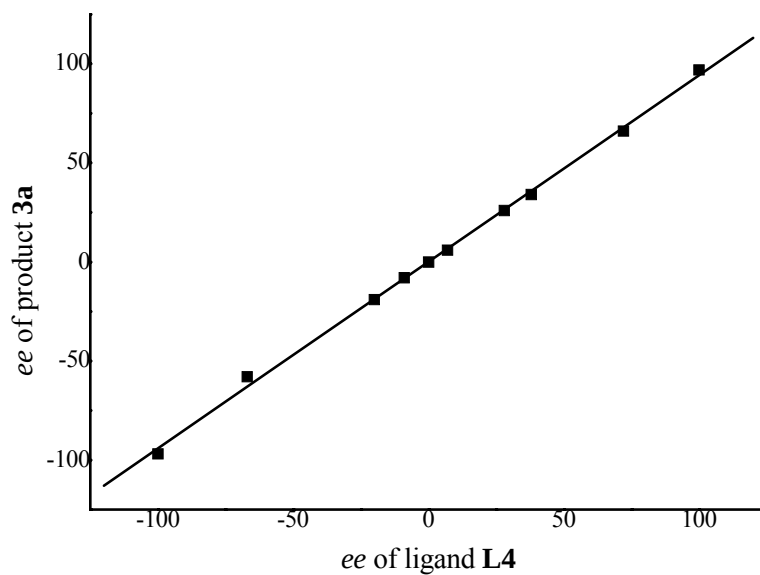
Without **L4-Sc(OTf)<sub>3</sub>**



Without Brønsted base

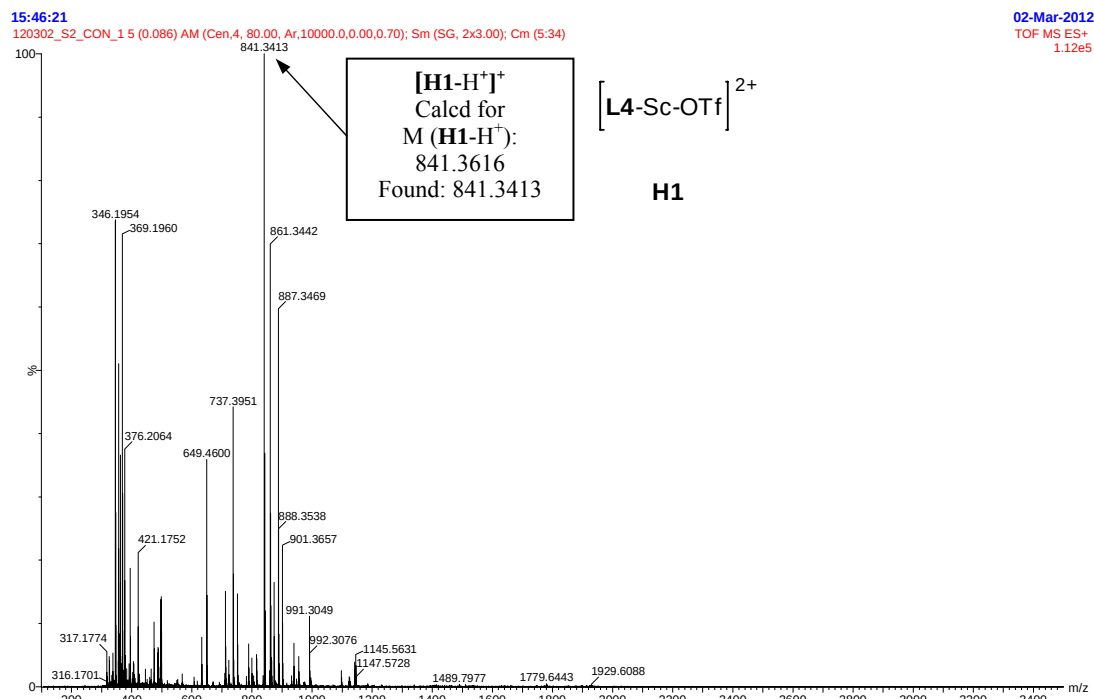


#### D) Nonlinear effect

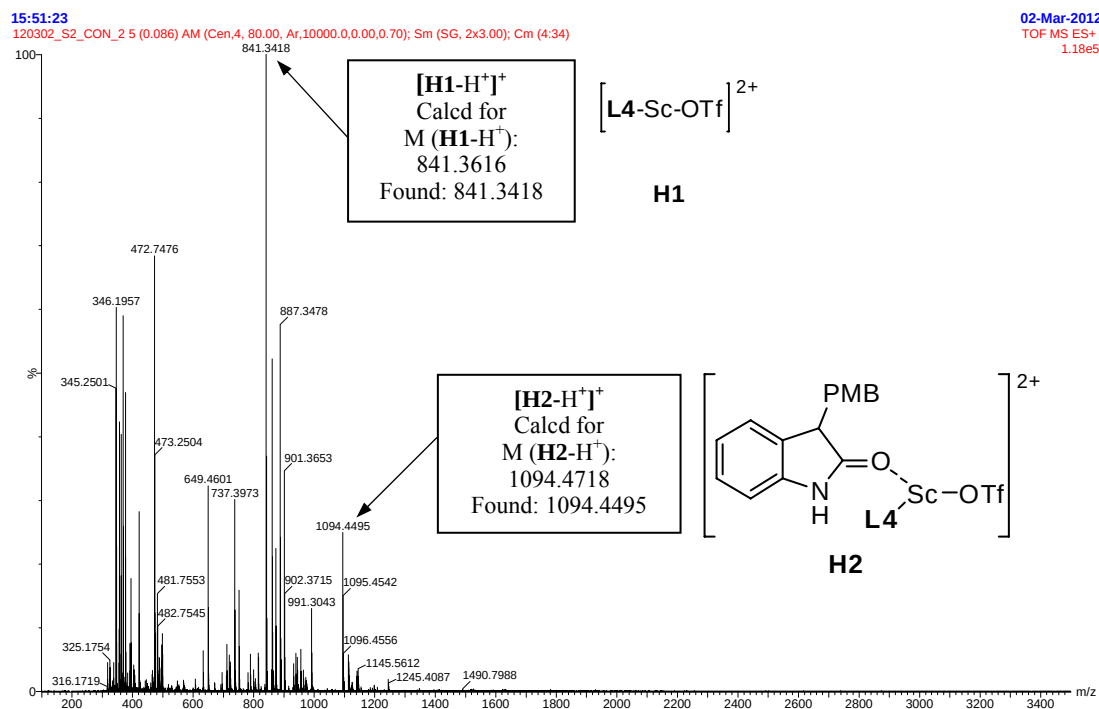


#### E) HRMS analysis

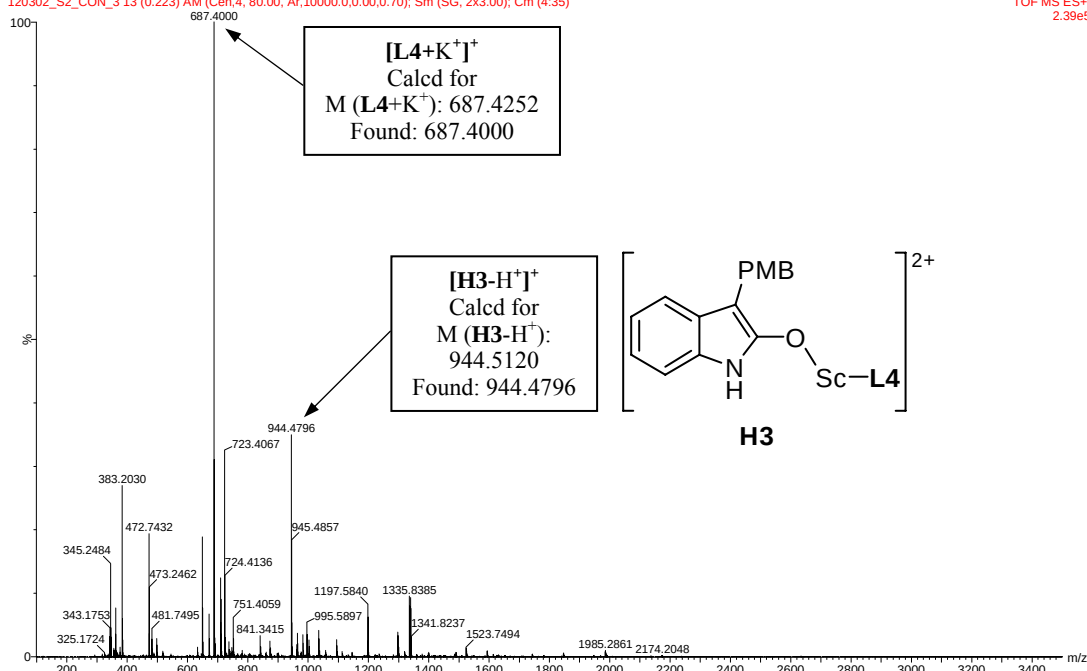
a) The mixture of **L4** and **Sc(OTf)<sub>3</sub>** (1:1)



**b) The mixture of L4, Sc(OTf)<sub>3</sub> and 1a (1:1:1)**



**c) The mixture of L4, Sc(OTf)<sub>3</sub>, 1a (1:1:1) and 200 mol % of K<sub>2</sub>CO<sub>3</sub>**



## 8. Characterization of the new unprotected oxindoles 5b-5o and 1z

### 3-o-tolyindolin-2-one (5b)

<sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  = 10.60 (s, 1H), 7.40 – 6.40 (m, 8H), 4.95 (s, 1H), 2.27 (s, 3H).

<sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  = 177.29, 142.65, 136.91, 136.20, 130.60, 129.97, 127.92, 127.18, 126.05, 124.23, 121.63, 109.34, 19.07.

### 3-m-tolyindolin-2-one (5c)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.89 (s, 1H), 7.24 (t,  $J$ =7.6, 2H), 7.11 (d,  $J$ =7.2, 2H), 7.05 – 6.97 (m, 3H), 6.94 (d,  $J$ =7.6, 1H), 4.60 (s, 1H), 2.32 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 178.89, 141.63, 138.71, 136.38, 129.85, 129.17, 128.86, 128.53, 128.35, 125.58, 125.27, 122.73, 109.98, 52.72, 21.45.

### 3-p-tolyindolin-2-one (5d)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.88 (s, 1H), 7.23 (t,  $J$  = 7.6, 1H), 7.19 – 7.06 (m, 5H), 7.02 (t,  $J$ =7.6, 1H), 6.93 (d,  $J$ =7.6, 1H), 4.60 (s, 1H), 2.33 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 178.96, 141.67, 137.44, 133.43, 129.84, 129.70, 128.36, 125.25, 122.71, 109.98, 52.37, 21.16.

### 3-(4-fluorophenyl)indolin-2-one (5e)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.81 (s, 1H), 7.29 – 7.23 (m, 1H), 7.23 – 7.16 (m, 2H), 7.12 (d,  $J$ =7.3, 1H), 7.08 – 7.00 (m, 3H), 6.95 (d,  $J$ =7.8, 1H), 4.62 (s, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 178.51, 162.35 (d,  $J$ =246.2), 141.55, 132.14, 130.15, 130.07, 129.30, 128.61, 125.28, 122.88, 116.02, 115.80, 110.11, 51.84.

### 3-(4-chlorophenyl)indolin-2-one (5f)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.10 (s, 1H), 7.32 (d,  $J$ =8.2, 2H), 7.24 (d,  $J$ =8.2, 1H), 7.16 (d,  $J$ =8.2, 2H), 7.10 (d,  $J$ =7.4, 1H), 7.04 (t,  $J$ =7.4, 1H), 6.94 (d,  $J$ =8.0, 1H), 4.61 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.45, 141.67, 134.89, 133.70, 129.87, 129.16, 129.02, 128.69, 125.24, 122.91, 110.24, 52.04.

**3-(4-methoxyphenyl)indolin-2-one (5g)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.35 (s, 1H), 7.22 (t,  $J=7.6$ , 1H), 7.17 – 6.07 (m, 3H), 7.01 (t,  $J=7.6$ , 1H), 6.92 (d,  $J=7.6$ , 1H), 6.88 (d,  $J=8.4$ , 2H), 4.58 (s, 1H), 3.78 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 179.50, 159.12, 141.78, 129.94, 129.58, 128.51, 128.34, 125.17, 122.68, 114.43, 110.16, 55.31, 52.04.

**3-(naphthalen-1-yl)indolin-2-one (5h)**

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.77 (d, 1H), 8.71 – 6.50 (m, 11H), 5.42 (d, 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 177.32, 142.67, 133.76, 130.54, 128.53, 128.04, 127.54, 126.24, 125.89, 125.60, 124.46, 121.69, 109.60, 47.55.

**3-(naphthalen-2-yl)indolin-2-one (5i)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.17 (s, 1H), 7.85 – 7.78 (m, 3H), 7.74 (s, 1H), 7.51 – 7.41 (m, 2H), 7.30 – 7.18 (m, 2H), 7.12 (d,  $J=7.6$ , 1H), 7.01 (t,  $J=7.6$ , 1H), 6.94 (d,  $J=8.0$ , 1H), 4.79 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.96, 141.75, 133.89, 133.53, 132.85, 129.69, 128.92, 128.52, 127.86, 127.78, 127.72, 126.32, 126.07, 125.34, 122.82, 110.17, 52.97.

**5-methyl-3-phenylindolin-2-one (5j)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.99 (s, 1H), 7.41 – 7.27 (m, 3H), 7.22 (d,  $J=7.2$ , 2H), 7.03 (d,  $J=7.6$ , 1H), 6.93 (s, 1H), 6.82 (d,  $J=8.0$ , 1H), 4.60 (s, 1H), 2.27 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.94, 139.19, 136.73, 132.26, 129.81, 128.98, 128.71, 128.55, 127.65, 125.93, 109.75, 52.85, 21.10.

**5-methoxy-3-phenylindolin-2-one (5k)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.49 (s, 1H), 7.40 – 7.27 (m, 3H), 7.23 (d,  $J=7.2$ , 2H), 6.85 (d,  $J=8.4$ , 1H), 6.78 (d,  $J=8.4$ , 1H), 6.73 (s, 1H), 4.61 (s, 1H), 3.74 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.34, 155.98, 136.45, 134.95, 130.90, 129.01, 128.51, 127.71, 113.25, 112.14, 110.28, 55.78, 53.12.

**5-fluoro-3-phenylindolin-2-one (5l)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.15 (s, 1H), 7.41 – 7.28 (m, 3H), 7.21 (d,  $J=7.2$ , 2H), 6.94 (t,  $J=8.0$ , 1H), 6.89 – 6.82 (m, 2H), 4.63 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.79, 159.21 (d,  $J=240.8$ ), 137.57, 135.82, 131.19 (d,  $J=8.3$ ), 129.13, 128.43, 127.96, 114.90 (d,  $J=23.6$ ), 113.12 (d,  $J=24.8$ ), 110.64 (d,  $J=8.0$ ), 53.14.

**5-chloro-3-phenylindolin-2-one (5m)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.21 (s, 1H), 7.41 – 7.28 (m, 3H), 7.24 – 7.15 (m, 3H), 7.10 (s, 1H), 6.85 (d,  $J=8.0$ , 1H), 4.62 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.59, 140.19, 135.68, 131.32, 129.16, 128.48, 128.45, 128.12, 128.01, 125.62, 111.08, 52.83.

**6-bromo-3-phenylindolin-2-one (5n)**

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.71 (s, 1H), 7.41 – 7.22 (m, 1H), 7.21 – 7.10 (m, 1H), 7.07 (s, 1H), 6.98 (d,  $J=7.4$ , 1H), 4.75 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 176.98, 144.45, 137.02, 129.38, 128.72, 128.32, 127.23, 126.55, 124.21, 120.61, 112.26, 51.37.

### 7-fluoro-3-phenylindolin-2-one (5o)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.45 (s, 1H), 7.40 – 7.27 (m, 3H), 7.22 (d,  $J$ =7.2, 2H), 7.09 – 6.96 (m, 2H), 6.93 (d,  $J$ =7.2, 1H), 4.68 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 177.27, 146.99 (d,  $J$ =244.3), 135.82, 132.12, 132.09, 129.05, 128.87 (d,  $J$ =12.1), 128.43, 127.89, 123.37 (d,  $J$ =5.9), 121.01 (d,  $J$ =3.4), 115.48 (d,  $J$ =17.1), 52.67.

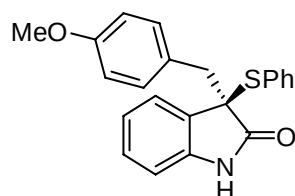
### methyl 2-(2-oxoindolin-3-yl)acetate (1z)

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.45 (s, 1H), 7.25 – 7.11 (m, 2H), 6.92 (t,  $J$ =7.6, 1H), 6.82 (d,  $J$ =7.6, 1H), 3.68 (t,  $J$ =5.7, 1H), 3.57 (s, 3H), 2.91 (ddd,  $J$ =23.8, 16.9, 5.7, 2H).

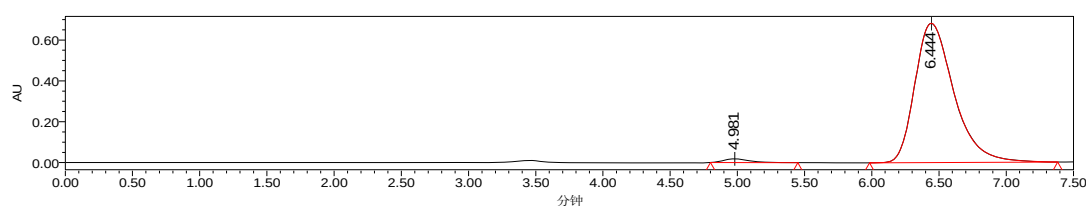
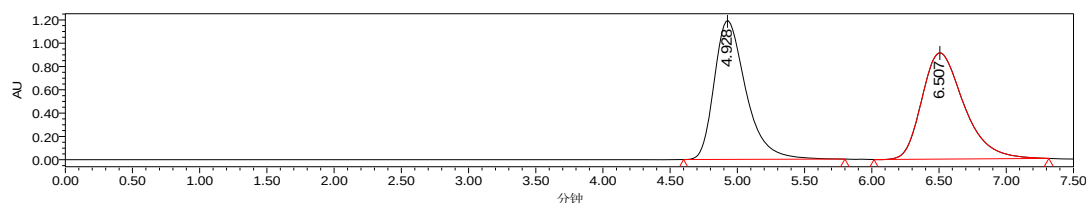
$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 177.87, 171.18, 142.82, 128.93, 127.78, 123.57, 121.17, 109.17, 51.52, 41.62, 33.48.

## 9. Characterization of the new products

### (R)-3-(4-methoxybenzyl)-3-(phenylthio)indolin-2-one (3a):



Prepared according to the general procedure (12 h). The title compound **3a** was obtained as a white solid in 98% yield. HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 6.44 min,  $t_r$  (minor) = 4.98 min,  $ee$  = 97%.  $[\alpha]_D^{25}$  = -61.6 ( $c$  = 0.68, in  $\text{CH}_2\text{Cl}_2$ ).



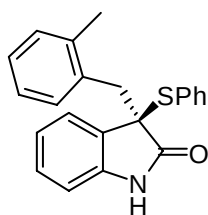
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 4.981          | 240776   | 1.72   |
| 2 | 6.444          | 13731490 | 98.28  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.37 (s, 1H), 7.45 – 7.29 (m, 1H), 7.29 – 7.15 (m, 3H), 7.14 – 6.95 (m, 4H), 6.88 (d,  $J$ =8.7, 2H), 6.60 – 6.48 (m, 3H), 3.62 (s, 3H), 3.39 (d,  $J$ =13.4, 1H), 3.32 (d,  $J$ =13.4, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.25, 158.34, 140.47, 136.51, 131.23, 129.46, 129.42, 128.66, 128.44, 126.87, 125.21, 122.29, 113.28, 109.82, 60.51, 55.00, 40.36.

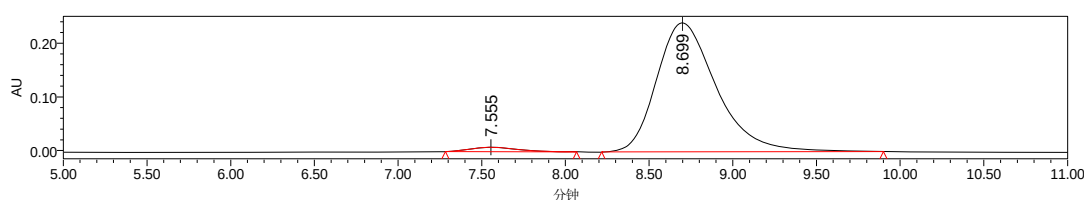
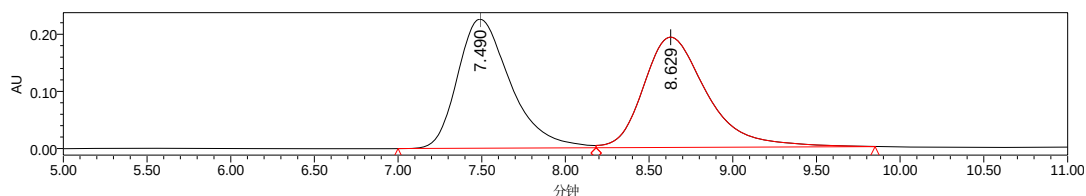
HRMS (ESI-TOF) calcd for  $\text{C}_{22}\text{H}_{19}\text{NO}_2\text{S}$  ( $[\text{M}] + \text{Na}^+$ ) = 384.1034, Found 384.1035.

**(R)-3-(2-methylbenzyl)-3-(phenylthio)indolin-2-one (3b):**



Prepared according to the general procedure (24 h). The title compound **3b** was obtained as a white solid in 91% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 8.70 min,  $t_r$  (minor) = 7.56 min,  $ee$  = 95%.  $[\alpha]_D^{25}$  = -45.4 ( $c$  = 0.63, in  $\text{CH}_2\text{Cl}_2$ ).



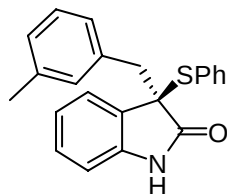
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 7.555          | 162015  | 2.65   |
| 2 | 8.699          | 5954989 | 97.35  |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.23 (s, 1H), 7.36 – 7.26 (m, 2H), 7.26 – 7.15 (m, 4H), 7.07 (t,  $J$ =7.6, 1H), 7.03 – 6.92 (m, 3H), 6.92 – 6.84 (m, 1H), 6.80 (d,  $J$ =7.6, 1H), 6.49 (d,  $J$ =7.7, 1H), 3.42 (d,  $J$ =14.0, 1H), 3.33 (d,  $J$ =14.0, 1H), 2.16 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 176.49, 141.58, 136.69, 135.91, 133.87, 130.10, 129.60, 129.44, 128.91, 128.79, 128.51, 126.70, 125.19, 125.09, 121.29, 109.22, 59.67, 36.44, 19.69.

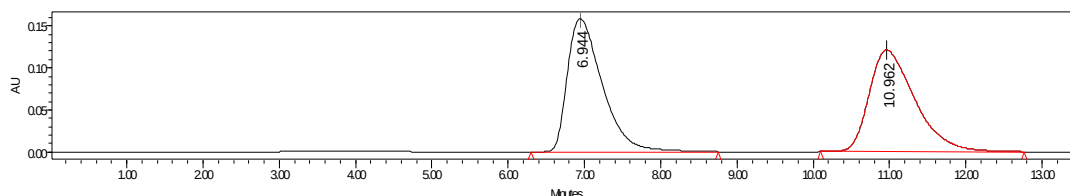
HRMS (ESI-TOF) calcd for  $\text{C}_{22}\text{H}_{19}\text{NOS}$  ( $[\text{M}] + \text{H}^+$ ) = 346.1266, Found 346.1266.

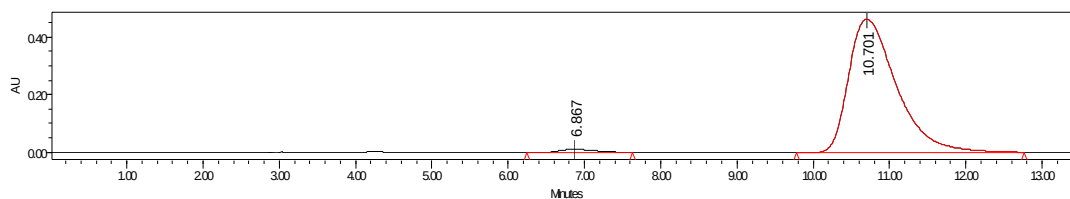
**(R)-3-(3-methylbenzyl)-3-(phenylthio)indolin-2-one (3c):**



Prepared according to the general procedure (20 h). The title compound **3c** was obtained as a white solid in 96% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 10.70 min,  $t_r$  (minor) = 6.87 min,  $ee$  = 97%.  $[\alpha]_D^{25}$  = -50.5 ( $c$  = 0.63, in  $\text{CH}_2\text{Cl}_2$ ).





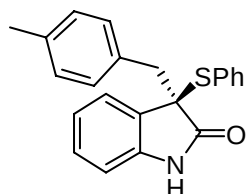
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 6.867          | 330294   | 1.62   |
| 2 | 10.701         | 20067439 | 98.38  |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.16 (s, 1H), 7.41 (d,  $J$ =7.2, 1H), 7.37 – 7.29 (m, 1H), 7.28 – 7.16 (m, 4H), 7.04 (t,  $J$ =7.5, 1H), 7.01 – 6.90 (m, 2H), 6.87 (d,  $J$ =7.5, 1H), 6.75 (s, 1H), 6.70 (d,  $J$ =7.5, 1H), 6.44 (d,  $J$ =7.5, 1H), 3.35 (d,  $J$ =13.0, 1H), 3.26 (d,  $J$ =13.0, 1H), 2.09 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 176.14, 141.51, 136.59, 135.99, 135.11, 127.57, 127.27, 126.96, 125.03, 121.28, 109.15, 59.50, 40.15, 20.87.

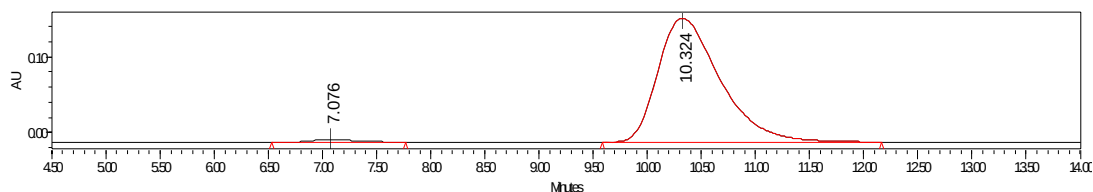
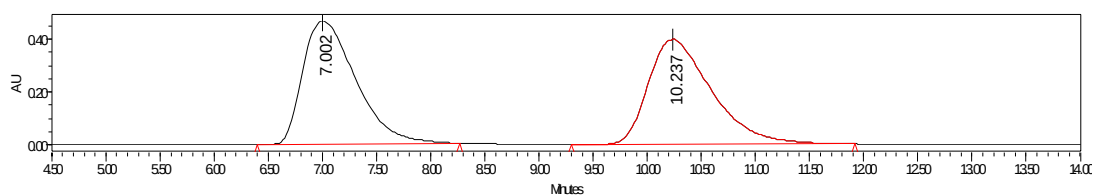
HRMS (ESI-TOF) calcd for  $\text{C}_{22}\text{H}_{19}\text{NOS}$  ( $[\text{M}] + \text{H}^+$ ) = 346.1266, Found 346.1264.

**(R)-3-(4-methylbenzyl)-3-(phenylthio)indolin-2-one (3d):**



Prepared according to the general procedure (20 h). The title compound **3d** was obtained as a white solid in 97% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 10.32 min,  $t_r$  (minor) = 7.08 min,  $ee$  = 97%.  $[\alpha]_D^{25}$  = -54.1 ( $c$  = 0.67, in  $\text{CH}_2\text{Cl}_2$ ).



|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 7.076          | 100229  | 1.51   |
| 2 | 10.324         | 6534656 | 98.49  |

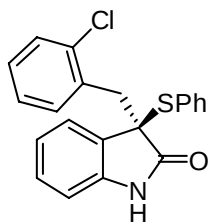
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.24 (s, 1H), 7.35 (dd,  $J$ =6.4, 2.2, 1H), 7.28 – 7.19 (m, 3H), 7.15 – 6.99 (m, 4H), 6.89 – 6.81 (m, 4H), 6.53 – 6.46 (m, 1H), 3.41 (d,  $J$ =13.3, 1H), 3.35 (d,  $J$ =13.3, 1H), 2.17 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.09, 140.40, 136.56, 136.38, 131.77, 130.10, 129.50, 129.44, 129.40, 128.66, 128.64, 128.45, 125.28, 122.27, 109.76, 60.42, 40.74, 21.05.

HRMS (ESI-TOF) calcd for  $\text{C}_{22}\text{H}_{19}\text{NOS}$  ( $[\text{M}] + \text{H}^+$ ) = 346.1266, Found 346.1259.

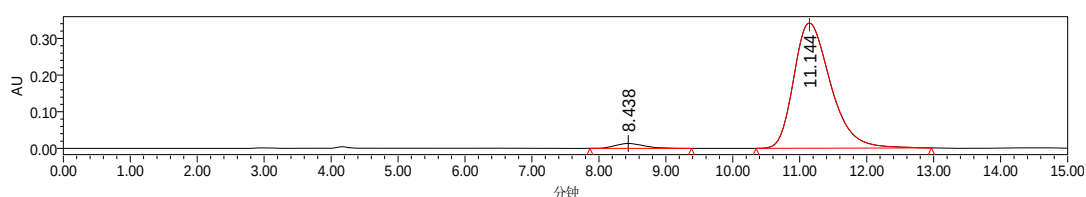
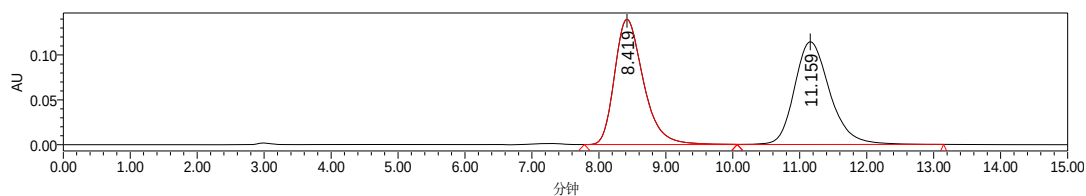


**(R)-3-(2-chlorobenzyl)-3-(phenylthio)indolin-2-one (3e):**



Prepared according to the general procedure (20 h). The title compound **3e** was obtained as a white solid in 95% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 11.14 min,  $t_r$  (minor) = 8.44 min,  $ee$  = 94%.  $[\alpha]_D^{25}$  = 29.5 ( $c$  = 0.70, in  $\text{CH}_2\text{Cl}_2$ ).



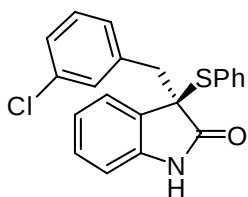
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 8.438          | 398149   | 2.96   |
| 2 | 11.144         | 13030276 | 97.04  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.58 (s, 1H), 7.33 (d,  $J$ =7.4, 1H), 7.30 – 7.22 (m, 3H), 7.22 – 7.09 (m, 4H), 7.08 – 6.91 (m, 4H), 6.54 (d,  $J$ =7.6, 1H), 3.79 (d,  $J$ =14.1, 1H), 3.58 (d,  $J$ =14.1, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.47, 140.10, 136.69, 134.59, 133.52, 131.17, 129.69, 129.49, 129.21, 128.81, 128.64, 128.47, 128.34, 126.57, 125.97, 122.27, 109.56, 60.08, 36.78.

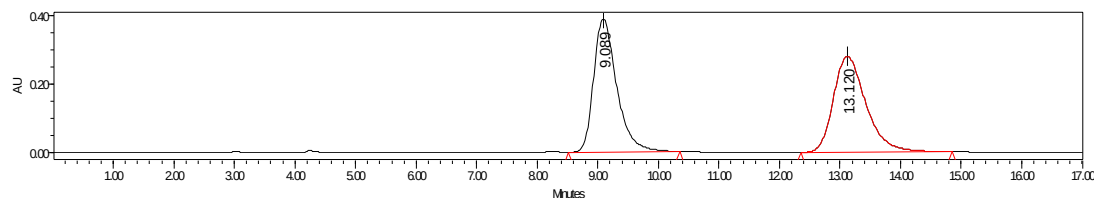
HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{16}\text{Cl}^{34,9689}\text{NOS}$  ( $[\text{M}]+\text{H}^+$ ) = 366.0719, Found 366.0717.

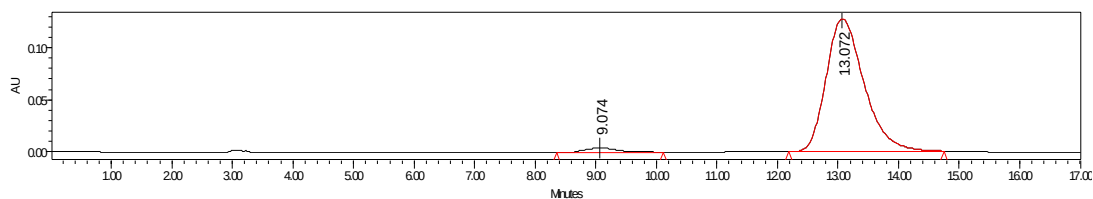
**(R)-3-(3-chlorobenzyl)-3-(phenylthio)indolin-2-one (3f):**



Prepared according to the general procedure (20 h). The title compound **3f** was obtained as a white solid in 96% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 13.07 min,  $t_r$  (minor) = 9.07 min,  $ee$  = 95%.  $[\alpha]_D^{25}$  = -46.6 ( $c$  = 0.67, in  $\text{CH}_2\text{Cl}_2$ ).





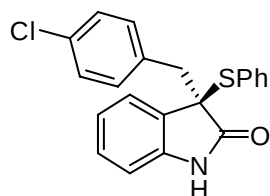
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 9.074          | 154628  | 2.71   |
| 2 | 13.072         | 5543775 | 97.29  |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.35 – 10.11 (m, 1H), 7.46 (d,  $J$ =7.3, 1H), 7.38 – 7.29 (m, 1H), 7.29 – 7.17 (m, 4H), 7.17 – 6.94 (m, 5H), 6.89 (d,  $J$ =7.2, 1H), 6.45 (d,  $J$ =7.2, 1H), 3.46 (d,  $J$ =13.0, 1H), 3.30 (d,  $J$ =13.0, 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 176.00, 141.41, 137.71, 136.02, 132.22, 129.67, 129.55, 129.16, 128.85, 128.59, 128.22, 126.69, 125.06, 121.46, 109.26, 59.37, 39.52.

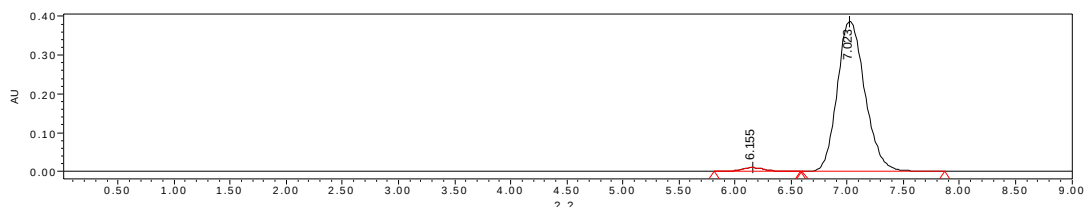
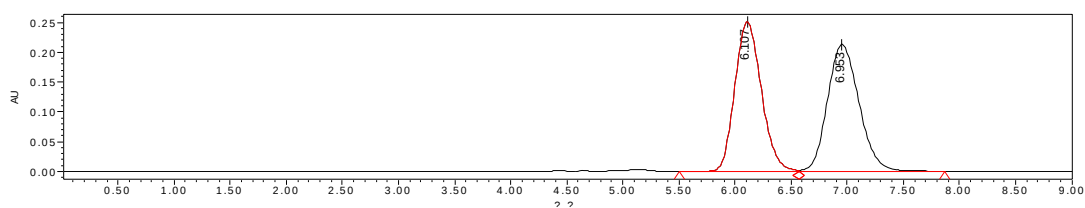
HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{16}\text{Cl}^{34,9689}\text{NOS}$  ( $[\text{M}]+\text{H}^+$ ) = 366.0719, Found 366.0713.

### (R)-3-(4-chlorobenzyl)-3-(phenylthio)indolin-2-one (3g):



Prepared according to the general procedure (12 h). The title compound **3g** was obtained as a white solid in 97% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 7.02 min,  $t_r$  (minor) = 6.16 min,  $ee$  = 96%.  $[\alpha]_D^{25}$  = -55.6 ( $c$  = 0.63, in  $\text{CH}_2\text{Cl}_2$ ).



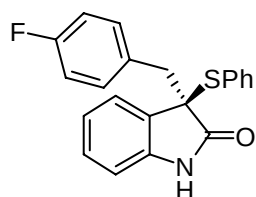
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 6.155          | 139308  | 2.06   |
| 2 | 7.023          | 6626623 | 97.94  |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.18 (s, 1H), 7.44 (d,  $J$ =7.3, 1H), 7.36 – 7.28 (m, 1H), 7.27 – 7.18 (m, 4H), 7.14 (d,  $J$ =8.4, 2H), 7.05 (t,  $J$ =7.6, 1H), 6.98 (t,  $J$ =7.6, 1H), 6.94 (d,  $J$ =8.4, 2H), 6.45 (d,  $J$ =7.6, 1H), 3.43 (d,  $J$ =13.0, 1H), 3.29 (d,  $J$ =13.0, 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 175.92, 141.35, 135.92, 134.16, 131.62, 131.35, 129.44, 129.14, 128.72, 128.49, 128.22, 127.65, 124.96, 121.39, 109.15, 59.35, 39.30.

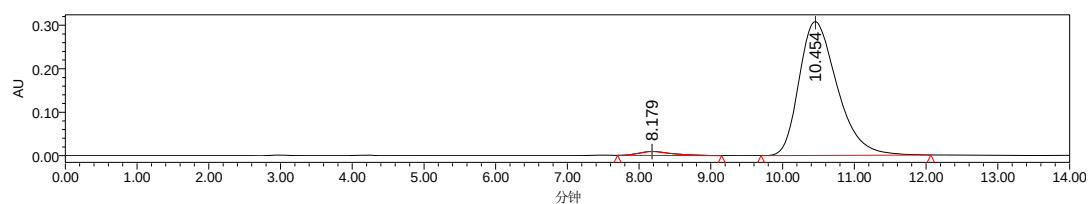
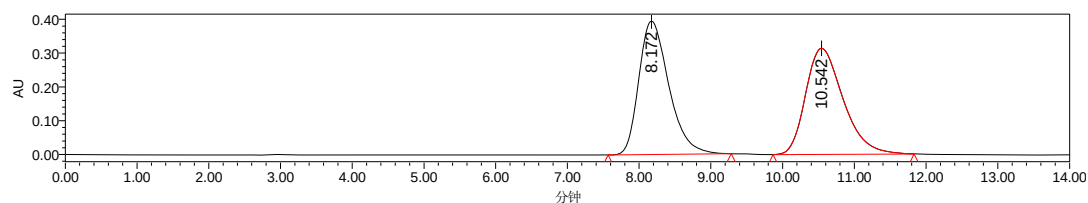
HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{16}\text{Cl}^{34,9689}\text{NOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 388.0539, Found 388.0535.

**(R)-3-(4-fluorobenzyl)-3-(phenylthio)indolin-2-one (3h)**



Prepared according to the general procedure (20 h). The title compound **3h** was obtained as a white solid in 95% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 254$  nm)  $t_r$  (major) = 10.45 min,  $t_r$  (minor) = 8.18 min,  $ee = 95\%$ .  $[\alpha]_D^{25} = -41.9$  ( $c = 0.61$ , in  $\text{CH}_2\text{Cl}_2$ ).



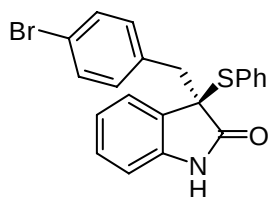
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 8.179          | 286564   | 2.46   |
| 2 | 10.454         | 11341088 | 97.54  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.31$  (s, 1H), 7.40 – 7.33 (m, 1H), 7.30 – 7.20 (m, 3H), 7.17 – 7.02 (m, 4H), 6.95 – 6.85 (m, 2H), 6.68 (t,  $J=8.6$ , 2H), 6.52 (d,  $J=7.1$ , 1H), 3.42 (d,  $J=13.4$ , 1H), 3.34 (d,  $J=13.4$ , 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 178.01$ , 161.75 (d,  $J=245.4$ ), 140.35, 136.58, 131.69 (d,  $J=8.0$ ), 130.53 (d,  $J=3.2$ ), 129.61, 129.21, 129.03, 128.86, 128.51, 125.15, 122.45, 114.78 (d,  $J=21.2$ ), 109.82, 60.32, 40.30.

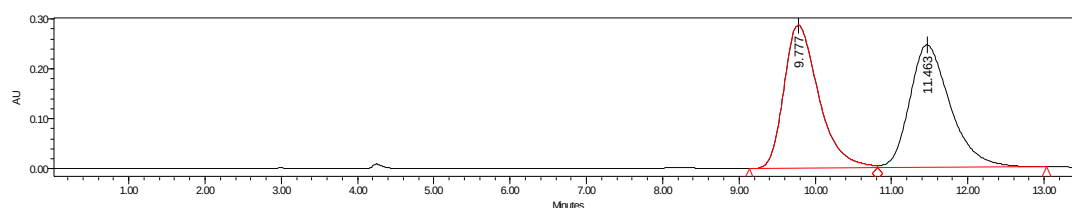
HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{16}\text{FNOS}$  ( $[\text{M}] + \text{Na}^+$ ) = 372.0834, Found 372.0823.

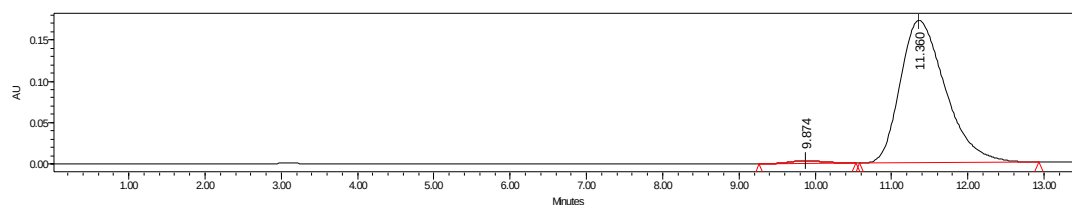
**(R)-3-(4-bromobenzyl)-3-(phenylthio)indolin-2-one (3i):**



Prepared according to the general procedure (20 h). The title compound **3i** was obtained as a white solid in 92% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda = 254$  nm)  $t_r$  (major) = 11.36 min,  $t_r$  (minor) = 9.87 min,  $ee = 97\%$ .  $[\alpha]_D^{25} = -39.9$  ( $c = 0.74$ , in  $\text{CH}_2\text{Cl}_2$ ).





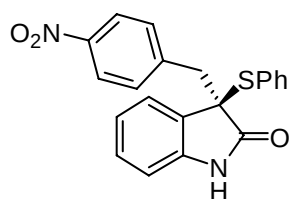
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 9.874          | 118745  | 1.64   |
| 2 | 11.360         | 7102909 | 98.36  |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.19 (s, 1H), 7.44 (d,  $J$ =7.3, 1H), 7.38 – 7.30 (m, 1H), 7.30 – 7.18 (m, 6H), 7.05 (t,  $J$ =7.6, 1H), 6.98 (t,  $J$ =7.6, 1H), 6.88 (d,  $J$ =8.3, 2H), 6.45 (d,  $J$ =7.6, 1H), 3.41 (d,  $J$ =13.0, 1H), 3.27 (d,  $J$ =13.0, 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 175.98, 141.43, 136.01, 134.64, 132.07, 130.65, 129.53, 129.21, 128.81, 128.57, 128.29, 125.04, 121.47, 120.04, 109.24, 59.35. (One peak overlaps with peaks of DMSO).

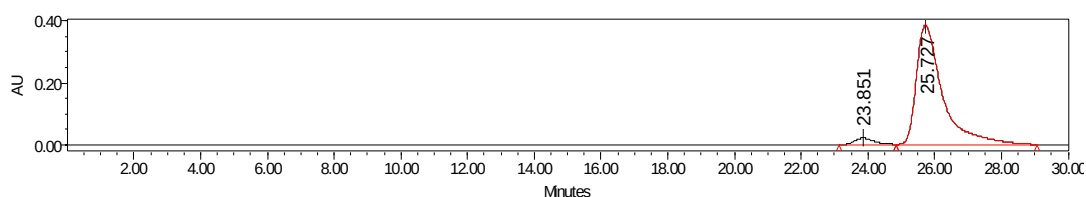
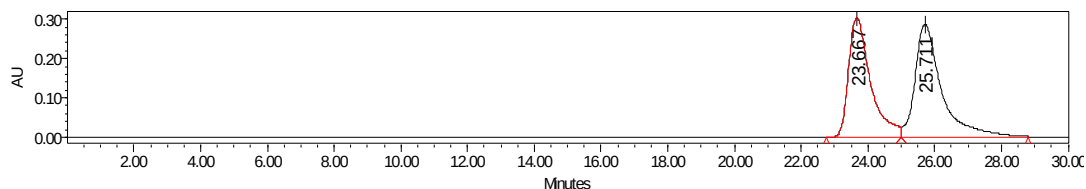
HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{16}\text{Br}^{78,9183}\text{NOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 432.0034, Found 432.0027.

**(R)-3-(4-nitrobenzyl)-3-(phenylthio)indolin-2-one (3j):**



Prepared according to the general procedure (20 h). The title compound **3j** was obtained as a white solid in 95% yield.

HPLC (Chiralcel IA, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 25.73 min,  $t_r$  (minor) = 23.85 min,  $ee$  = 92%.  $[\alpha]_D^{25}$  = -54.9 ( $c$  = 0.70, in  $\text{CH}_2\text{Cl}_2$ ).



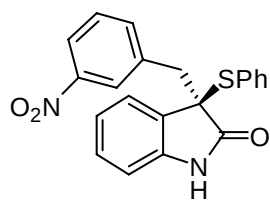
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 23.851         | 860521   | 3.96   |
| 2 | 25.727         | 20861671 | 96.04  |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.25 (s, 1H), 7.96 (d,  $J$ =8.6, 2H), 7.48 (d,  $J$ =7.4, 1H), 7.39 – 7.30 (m, 1H), 7.26 – 7.18 (m, 6H), 7.05 (t,  $J$ =7.4, 1H), 6.99 (t,  $J$ =7.4, 1H), 6.45 (d,  $J$ =7.4, 1H), 3.62 (d,  $J$ =12.9, 1H), 3.43 (d,  $J$ =12.9, 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 175.72, 146.25, 143.30, 141.27, 136.06, 131.16, 129.60, 128.93, 128.56, 127.85, 125.05, 122.76, 121.54, 109.28, 59.16, 39.54.

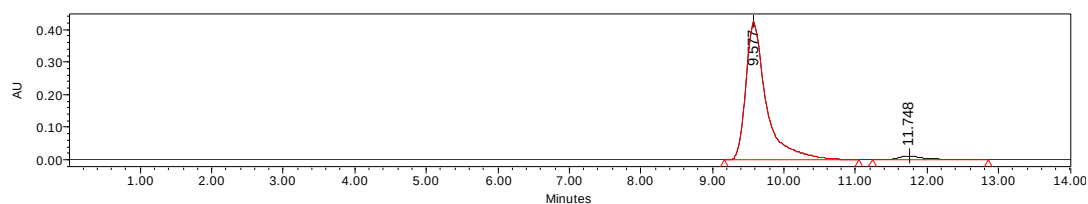
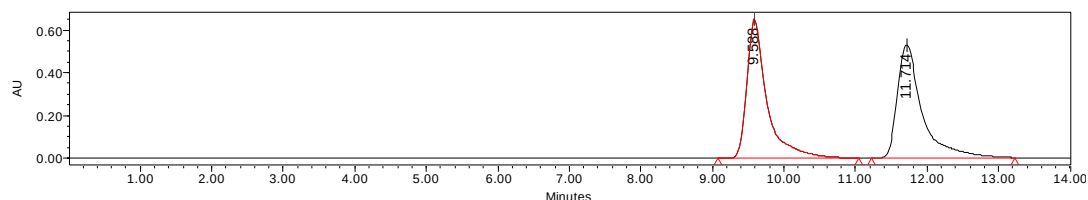
HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$  ( $[\text{M}]+\text{H}^+$ ) = 377.0960, Found 377.0953.

**(R)-3-(3-nitrobenzyl)-3-(phenylthio)indolin-2-one (3k):**



Prepared according to the general procedure (20 h). The title compound **3k** was obtained as a white solid in 94% yield.

HPLC (Chiralcel IA, hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 9.58 min,  $t_r$  (minor) = 11.75 min, *ee* = 94%.  $[\alpha]_D^{25} = -22.0$  ( $c = 0.66$ , in  $\text{CH}_2\text{Cl}_2$ ).



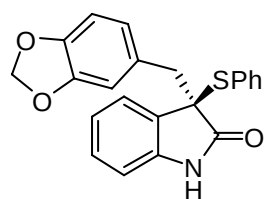
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 9.577          | 8471399 | 96.92  |
| 2 | 11.748         | 269448  | 3.08   |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.26 (s, 1H), 8.02 – 7.86 (m, 1H), 7.79 (s, 1H), 7.52 (d,  $J=7.1$ , 1H), 7.44 – 7.30 (m, 3H), 7.29 – 7.18 (m, 4H), 7.09 – 6.94 (m, 2H), 6.43 (d,  $J=7.5$ , 1H), 3.64 (d,  $J=13.0$ , 1H), 3.43 (d,  $J=13.0$ , 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 175.91, 147.03, 141.31, 137.46, 136.82, 136.04, 129.62, 129.27, 129.03, 129.00, 128.63, 127.90, 125.13, 124.43, 121.81, 121.58, 109.32, 59.29, 39.38.

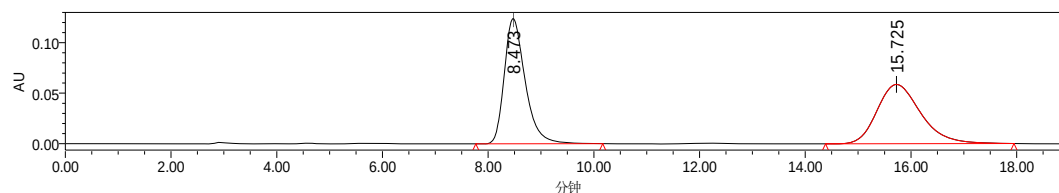
HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$  ( $[\text{M}] + \text{Na}^+$ ) = 399.0779, Found 399.0775.

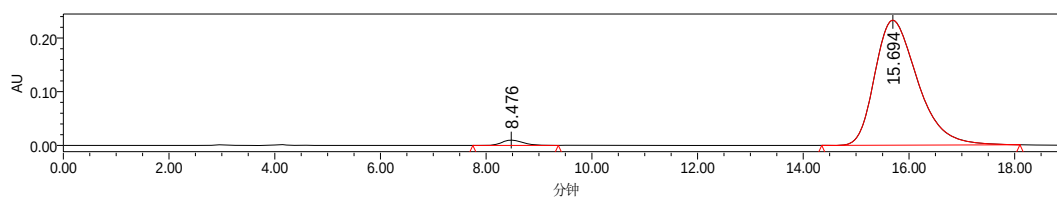
**(R)-3-(benzo[d][1,3]dioxol-5-ylmethyl)-3-(phenylthio)indolin-2-one (3l):**



Prepared according to the general procedure (20 h). The title compound **3l** was obtained as a white solid in 94% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 15.69 min,  $t_r$  (minor) = 8.48 min, *ee* = 96%.  $[\alpha]_D^{25} = -58.9$  ( $c = 0.83$ , in  $\text{CH}_2\text{Cl}_2$ ).





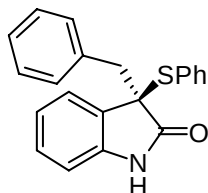
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 8.476          | 272783   | 2.04   |
| 2 | 15.694         | 13068656 | 97.96  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.33 (s, 1H), 7.41 – 7.31 (m, 1H), 7.28 – 7.18 (m, 3H), 7.17 – 6.99 (m, 4H), 6.57 – 6.51 (m, 1H), 6.50 – 6.37 (m, 3H), 5.78 (d,  $J$ =1.4, 1H), 5.74 (d,  $J$ =1.4, 1H), 3.38 (d,  $J$ =13.4, 1H), 3.30 (d,  $J$ =13.4, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.07, 147.01, 146.34, 140.42, 136.57, 129.55, 129.33, 129.25, 128.75, 128.49, 128.47, 125.16, 123.51, 122.39, 110.48, 109.87, 107.79, 100.75, 60.37, 40.79.

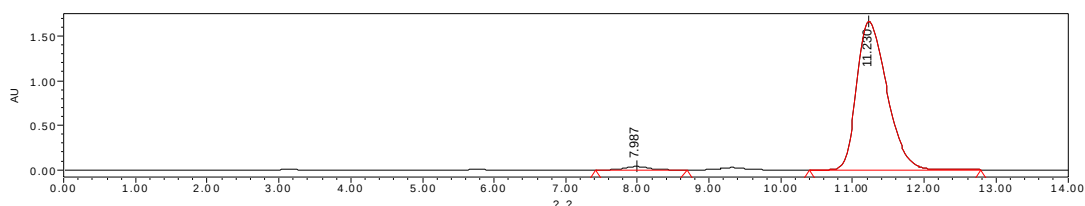
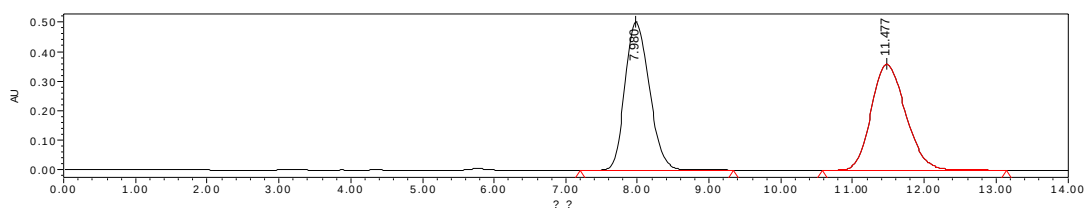
HRMS (ESI-TOF) calcd for  $\text{C}_{22}\text{H}_{17}\text{NO}_3\text{S}$  ( $[\text{M}] + \text{Na}^+$ ) = 398.0827, Found 398.0828.

**(R)-3-benzyl-3-(phenylthio)indolin-2-one (3m):**



Prepared according to the general procedure (12 h). The title compound **3m** was obtained as a white solid in 96% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 11.23 min,  $t_r$  (minor) = 7.99 min,  $ee$  = 97%.  $[\alpha]_D^{25}$  =  $-56.2$  ( $c$  = 0.61, in  $\text{CH}_2\text{Cl}_2$ ).

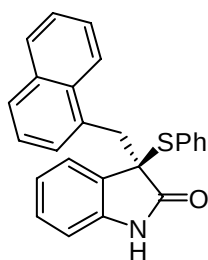


|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 7.987          | 739117   | 1.50   |
| 2 | 11.230         | 48421915 | 98.50  |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.14 (s, 1H), 7.42 (d,  $J$ =7.2, 1H), 7.36 – 7.29 (m, 1H), 7.29 – 7.15 (m, 4H), 7.08 – 6.88 (m, 7H), 6.42 (d,  $J$ =7.6, 1H), 3.41 (d,  $J$ =13.0, 1H), 3.31 (d,  $J$ =13.0, 1H).

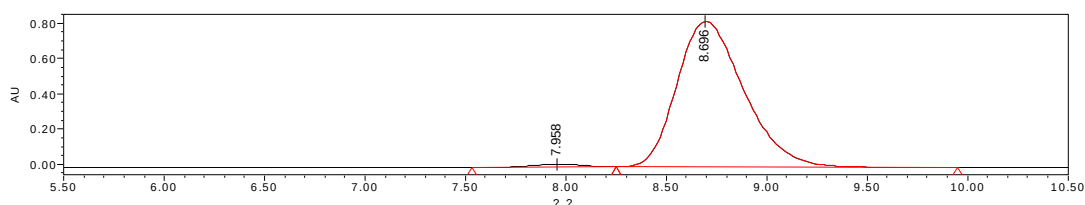
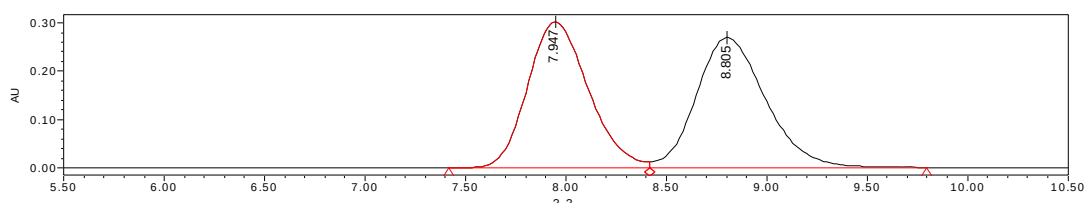
$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 176.02, 141.40, 135.90, 135.13, 129.81, 129.38, 129.28, 128.56, 128.50, 128.46, 127.64, 126.53, 124.94, 121.26, 109.05, 59.51, 40.11.

HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{17}\text{NOS}$  ( $[\text{M}] + \text{Na}^+$ ) = 354.0929, Found 354.0922.

**(R)-3-(naphthalen-1-ylmethyl)-3-(phenylthio)indolin-2-one (3n):**

Prepared according to the general procedure (12 h). The title compound **3n** was obtained as a white solid in 98% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 8.70 min,  $t_r$  (minor) = 7.96 min,  $ee$  = 97%.  $[\alpha]_D^{25}$  = -21.5 ( $c$  = 0.69, in  $\text{CH}_2\text{Cl}_2$ ).

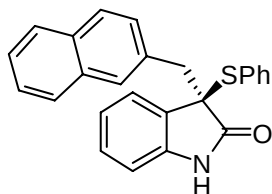


|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 7.958          | 300562   | 1.54   |
| 2 | 8.696          | 19179609 | 98.46  |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.14 (d,  $J$ =47.6, 1H), 8.19 (d,  $J$ =8.2, 1H), 7.79 (d,  $J$ =7.6, 1H), 7.68 (d,  $J$ =8.1, 1H), 7.51 – 7.40 (m, 2H), 7.40 – 7.30 (m, 2H), 7.30 – 7.20 (m, 5H), 7.13 (d,  $J$ =7.1, 1H), 6.96 (t,  $J$ =7.6, 1H), 6.83 (t,  $J$ =7.6, 1H), 6.40 (d,  $J$ =7.6, 1H), 3.94 (d,  $J$ =14.1, 1H), 3.83 (d,  $J$ =14.1, 1H).

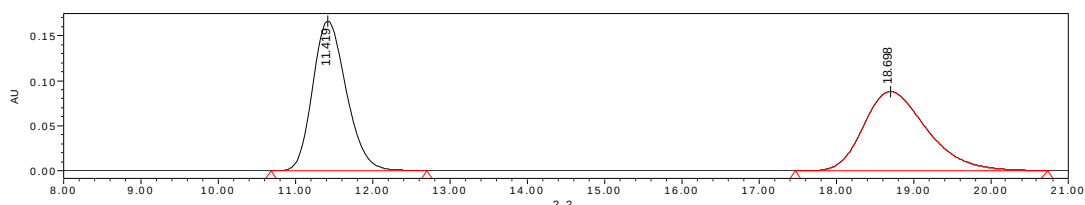
$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 176.43, 141.48, 136.04, 133.15, 131.74, 131.71, 129.52, 129.48, 128.70, 128.62, 128.54, 128.18, 127.95, 127.41, 125.52, 125.41, 124.82, 124.49, 121.13, 109.10, 59.82, 35.70.

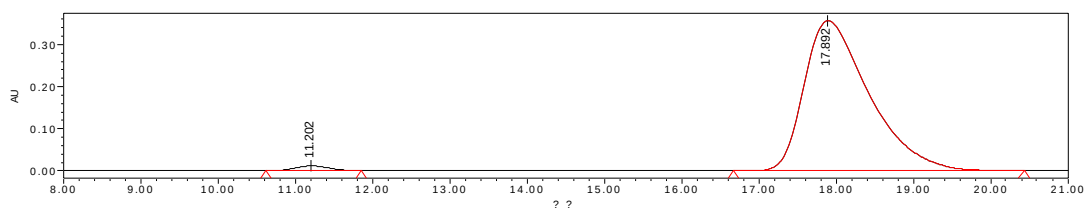
HRMS (ESI-TOF) calcd for  $\text{C}_{25}\text{H}_{19}\text{NOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 404.1085, Found 404.1079.

**(R)-3-(naphthalen-2-ylmethyl)-3-(phenylthio)indolin-2-one (3o):**

Prepared according to the general procedure (12 h). The title compound **3o** was obtained as a white solid in 95% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 17.89 min,  $t_r$  (minor) = 11.20 min,  $ee$  = 97%.  $[\alpha]_D^{25}$  = -65.2 ( $c$  = 0.66, in  $\text{CH}_2\text{Cl}_2$ ).





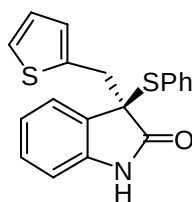
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 11.202         | 358923   | 1.70   |
| 2 | 17.892         | 20814402 | 98.30  |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.16 (s, 1H), 7.79 – 7.71 (m, 1H), 7.71 – 7.63 (m, 1H), 7.60 (d,  $J$ =8.5, 1H), 7.55 – 7.45 (m, 2H), 7.44 – 7.37 (m, 2H), 7.34 (t,  $J$ =7.0, 1H), 7.31 – 7.20 (m, 4H), 7.11 – 6.93 (m, 3H), 6.43 – 6.33 (m, 1H), 3.60 (d,  $J$ =13.0, 1H), 3.49 (d,  $J$ =13.0, 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 176.17, 141.46, 136.06, 132.95, 132.48, 131.68, 129.51, 129.38, 128.71, 128.63, 128.58, 128.55, 128.15, 127.38, 127.30, 127.00, 125.94, 125.67, 125.14, 121.38, 109.16, 59.58, 40.38.

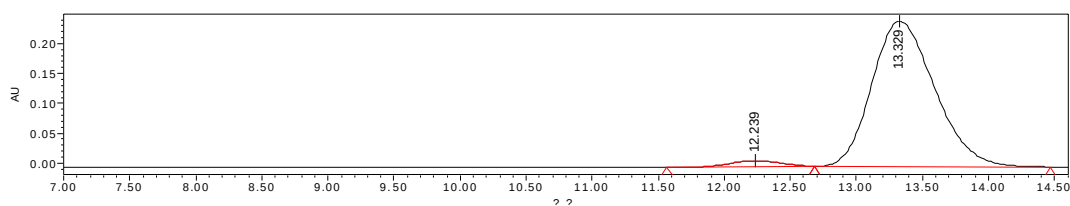
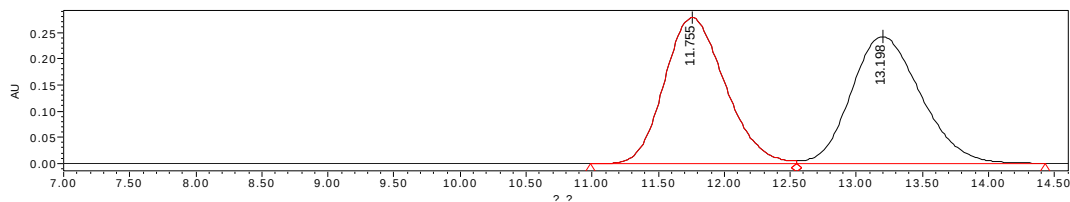
HRMS (ESI-TOF) calcd for  $\text{C}_{25}\text{H}_{19}\text{NOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 404.1085, Found 404.1077.

**(R)-3-(phenylthio)-3-(thiophen-2-ylmethyl)indolin-2-one (3p):**



Prepared according to the general procedure (20 h). The title compound **3p** was obtained as a white solid in 85% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 13.33 min,  $t_r$  (minor) = 12.24 min,  $ee$  = 94%.  $[\alpha]_D^{25}$  = –26.1 ( $c$  = 0.54, in  $\text{CH}_2\text{Cl}_2$ ).



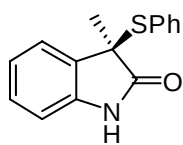
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 12.239         | 259564  | 3.13   |
| 2 | 13.329         | 8037386 | 96.87  |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.25 (s, 1H), 7.40 – 7.32 (m, 2H), 7.30 – 7.21 (m, 4H), 7.17 (d,  $J$ =5.1, 1H), 7.10 (t,  $J$ =7.6, 1H), 6.99 (t,  $J$ =7.5, 1H), 6.78 – 6.71 (m, 1H), 6.61 (d,  $J$ =3.2, 1H), 6.52 (d,  $J$ =7.6, 1H), 3.65 (d,  $J$ =14.2, 1H), 3.50 (d,  $J$ =14.2, 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 175.97, 141.91, 136.66, 136.19, 129.62, 129.09, 129.02, 128.61, 128.47, 127.29, 126.28, 125.26, 124.78, 121.51, 109.32, 58.69, 34.64.

HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{15}\text{NOS}_2$  ( $[\text{M}]+\text{Na}^+$ ) = 360.0493, Found 360.0483.

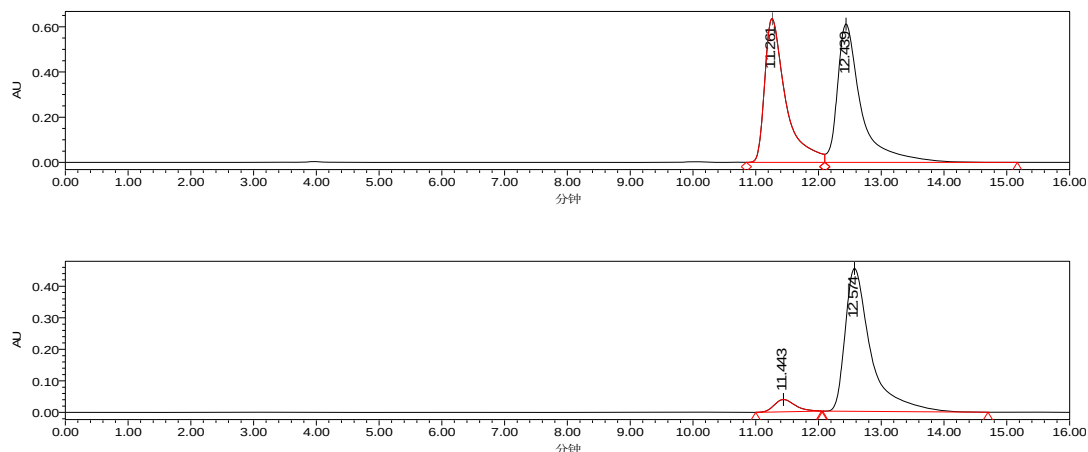


**(R)-3-methyl-3-(phenylthio)indolin-2-one (3q):**

Prepared according to the general procedure (48 h). The title compound **3q** was obtained as a white solid in 83% yield.

HPLC (Chiralcel IA, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 12.57 min,  $t_r$  (minor) = 11.44 min,  $ee$  = 87%.  $[\alpha]_D^{25} = -7.7$  ( $c$  =

0.72, in  $\text{CH}_2\text{Cl}_2$ ).

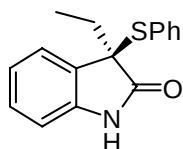


|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 11.443         | 897127   | 6.51   |
| 2 | 12.574         | 12878628 | 93.49  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.85 (s, 1H), 7.35 (d,  $J$ =7.3, 1H), 7.22 (d,  $J$ =7.3, 3H), 7.15 (t,  $J$ =7.6, 1H), 7.12 – 7.02 (m, 3H), 6.71 (d,  $J$ =7.6, 1H), 1.71 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 179.75, 139.94, 136.30, 131.96, 129.83, 129.48, 128.74, 128.40, 124.21, 122.70, 109.96, 55.19, 21.50.

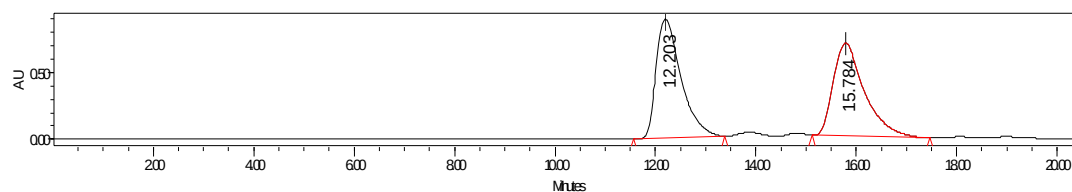
HRMS (ESI-TOF) calcd for  $\text{C}_{15}\text{H}_{13}\text{NOS}$  ( $[\text{M}] + \text{Na}^+$ ) = 278.0616, Found 278.0613.

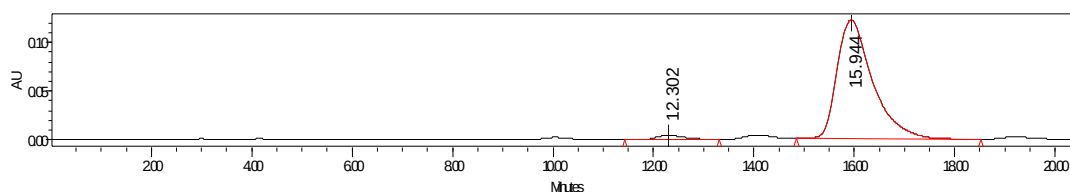
**(R)-3-ethyl-3-(phenylthio)indolin-2-one (3r):**

Prepared according to the general procedure (48 h). The title compound **3r** was obtained as a white solid in 82% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 15.94 min,  $t_r$  (minor) = 12.30 min,  $ee$  = 95%.  $[\alpha]_D^{25} = 1.1$  ( $c$  =

0.28, in  $\text{CH}_2\text{Cl}_2$ ).





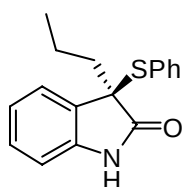
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 12.302         | 170236  | 2.74   |
| 2 | 15.944         | 6053346 | 97.26  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.95 (s, 1H), 7.32 (d,  $J$ =7.3, 1H), 7.26 – 7.18 (m, 3H), 7.15 (t,  $J$ =7.6, 1H), 7.10 – 7.02 (m, 3H), 6.71 (d,  $J$ =7.6, 1H), 2.28 – 2.07 (m, 2H), 0.76 (t,  $J$ =7.3, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 179.12, 140.80, 136.43, 129.84, 129.50, 129.38, 128.66, 128.34, 124.51, 122.62, 109.91, 60.25, 28.62, 9.34.

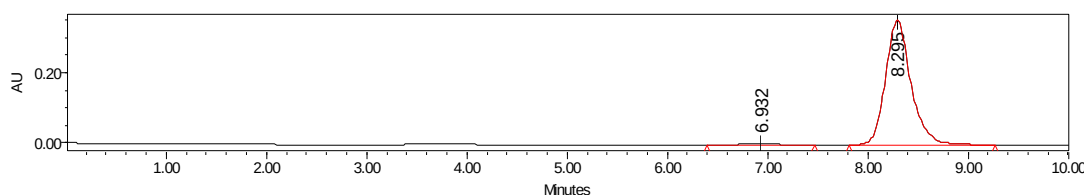
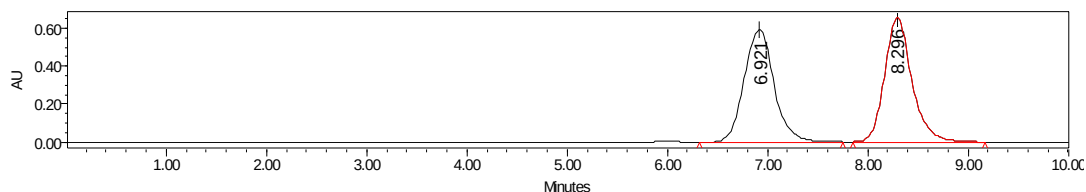
HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{15}\text{NOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 292.0772, Found 292.0764.

**(R)-3-(phenylthio)-3-propylindolin-2-one (3s):**



Prepared according to the general procedure (48 h). The title compound **3s** was obtained as a white solid in 85% yield.

HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 8.30 min,  $t_r$  (minor) = 6.93 min,  $ee$  = 97%.  $[\alpha]_D^{25}$  = 1.4 ( $c$  = 0.50, in  $\text{CH}_2\text{Cl}_2$ ).

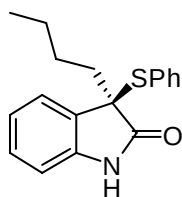


|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 6.932          | 85343   | 1.34   |
| 2 | 8.295          | 6263867 | 98.66  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.88 (s, 1H), 7.33 (d,  $J$ =7.2, 1H), 7.21 (d,  $J$ =7.2, 3H), 7.14 (t,  $J$ =7.6, 1H), 7.07 (t,  $J$ =7.2, 3H), 6.70 (d,  $J$ =7.6, 1H), 2.22 – 1.99 (m, 2H), 1.27 – 0.98 (m, 2H), 0.84 (t,  $J$ =7.2, 3H).

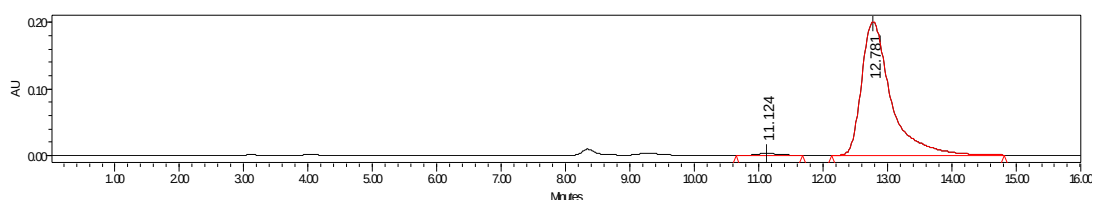
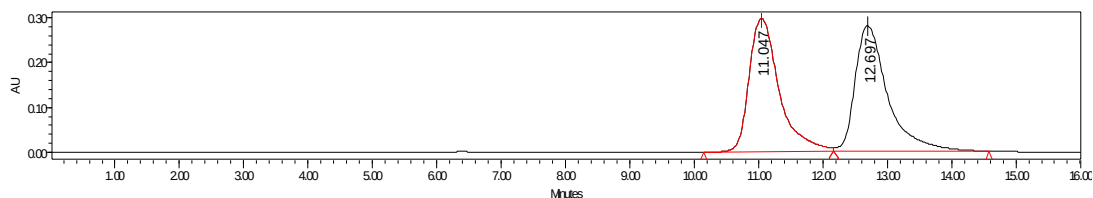
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 179.20, 140.61, 136.43, 130.27, 129.45, 129.38, 128.60, 128.33, 124.49, 122.59, 109.87, 59.60, 37.44, 18.38, 14.07.

HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{17}\text{NOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 306.0929, Found 306.0922.

**(R)-3-butyl-3-(phenylthio)indolin-2-one (3t):**

Prepared according to the general procedure (48 h). The title compound **3t** was obtained as a white solid in 89% yield.

HPLC (Chiralcel IA, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 12.78 min,  $t_r$  (minor) = 11.12 min,  $ee$  = 98%.  $[\alpha]_D^{25}$  = -3.7 ( $c$  = 0.53, in  $\text{CH}_2\text{Cl}_2$ ).

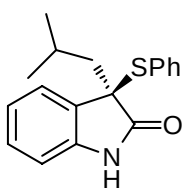


|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 11.124         | 57596   | 0.90   |
| 2 | 12.781         | 6317443 | 99.10  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.64 (s, 1H), 7.33 (d,  $J$ =7.4, 1H), 7.20 (d,  $J$ =7.2, 3H), 7.14 (t,  $J$ =7.6, 1H), 7.07 (t,  $J$ =7.4, 3H), 6.68 (d,  $J$ =7.6, 1H), 2.25 – 2.00 (m, 2H), 1.35 – 1.19 (m, 2H), 1.18 – 0.94 (m, 2H), 0.80 (t,  $J$ =7.2, 3H).

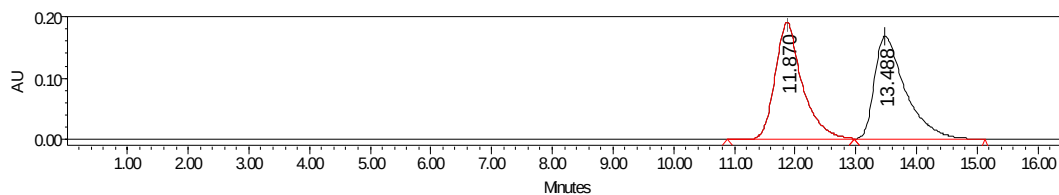
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 179.02, 140.55, 136.43, 130.29, 129.47, 129.38, 128.58, 128.32, 124.50, 122.61, 109.79, 59.58, 35.10, 26.97, 22.71, 13.77.

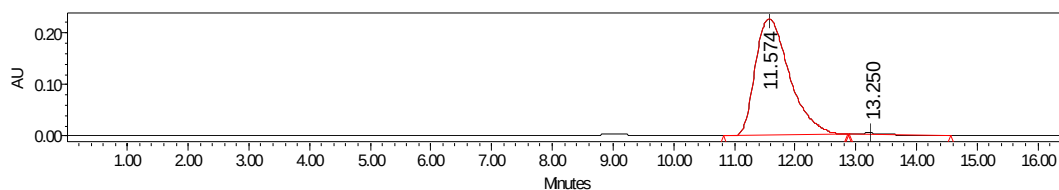
HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{19}\text{NOS}$  ( $[\text{M}] + \text{Na}^+$ ) = 320.1085, Found 320.1085.

**(R)-3-isobutyl-3-(phenylthio)indolin-2-one (3u):**

Prepared according to the general procedure (48 h). The title compound **3u** was obtained as a white solid in 91% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 11.57 min,  $t_r$  (minor) = 13.25 min,  $ee$  = 98%.  $[\alpha]_D^{25}$  = -27.7 ( $c$  = 0.74, in  $\text{CH}_2\text{Cl}_2$ ).





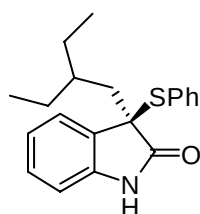
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 11.574         | 8881129 | 98.95  |
| 2 | 13.250         | 93940   | 1.05   |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.60 (s, 1H), 7.31 (d,  $J=7.3$ , 1H), 7.22 (t,  $J=7.3$ , 1H), 7.17 (d,  $J=7.3$ , 2H), 7.13 (d,  $J=7.7$ , 1H), 7.11 – 7.02 (m, 3H), 6.67 (d,  $J=7.6$ , 1H), 2.24 – 2.08 (m, 2H), 1.60 – 1.44 (m, 1H), 0.72 (d,  $J=6.6$ , 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 179.15, 140.43, 136.62, 130.15, 129.53, 129.31, 128.55, 128.29, 124.87, 122.47, 109.85, 59.21, 43.09, 26.23, 23.93, 22.69.

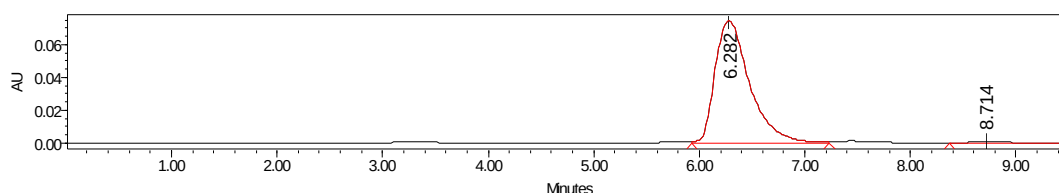
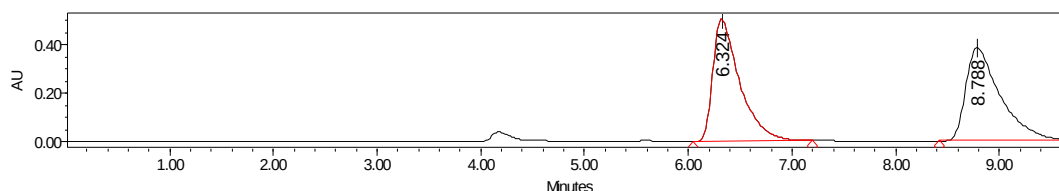
HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{19}\text{NOS}$  ( $[\text{M}] + \text{Na}^+$ ) = 320.1085, Found 320.1087.

### (R)-3-(2-ethylbutyl)-3-(phenylthio)indolin-2-one (3v):



Prepared according to the general procedure (48 h). The title compound **3v** was obtained as a white solid in 90% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 6.28 min,  $t_r$  (minor) = 8.71 min,  $ee$  = 98%.  $[\alpha]_D^{25} = -23.0$  ( $c$  = 0.64, in  $\text{CH}_2\text{Cl}_2$ ).

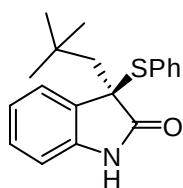


|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 6.282          | 1701784 | 99.18  |
| 2 | 8.714          | 14031   | 0.82   |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.75 (s, 1H), 7.31 (d,  $J=7.3$ , 1H), 7.21 (t,  $J=7.3$ , 1H), 7.16 (d,  $J=7.8$ , 2H), 7.12 (d,  $J=7.6$ , 1H), 7.07 (d,  $J=6.8$ , 3H), 6.64 (d,  $J=7.6$ , 1H), 2.24 – 2.08 (m, 2H), 1.24 – 1.02 (m, 5H), 0.78 – 0.58 (m, 6H).

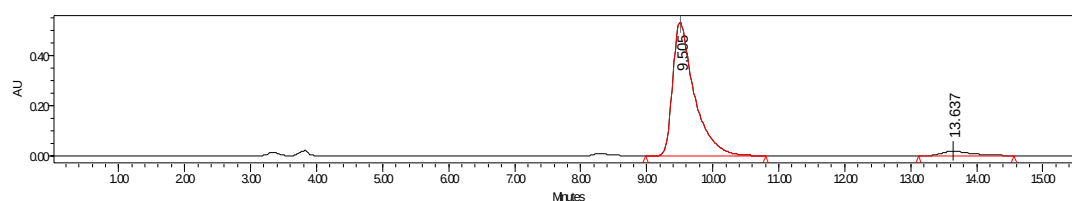
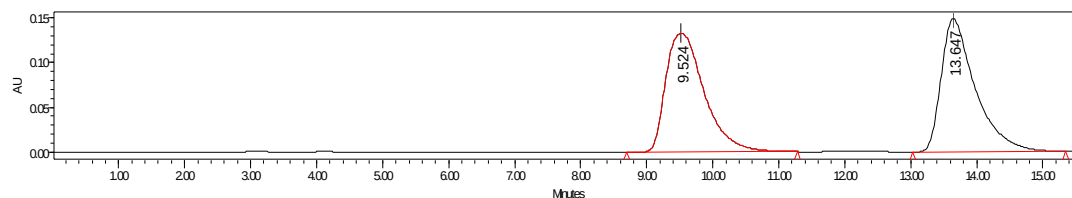
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 179.31, 140.51, 136.47, 130.20, 129.45, 129.42, 128.51, 128.27, 124.94, 122.39, 109.83, 59.67, 37.83, 37.58, 25.76, 25.13, 10.38, 9.87.

HRMS (ESI-TOF) calcd for  $\text{C}_{20}\text{H}_{23}\text{NOS}$  ( $[\text{M}] + \text{Na}^+$ ) = 348.1398, Found 348.1396.

**(R)-3-neopentyl-3-(phenylthio)indolin-2-one (3w):**

Prepared according to the general procedure (48 h). The title compound **3w** was obtained as a white solid in 90% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 9.51 min,  $t_r$  (minor) = 13.64 min,  $ee$  = 91%.  $[\alpha]_D^{25} = -18.1$  ( $c$  = 0.56, in  $\text{CH}_2\text{Cl}_2$ ).

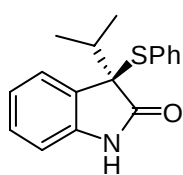


|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 9.505          | 12043888 | 95.63  |
| 2 | 13.637         | 550802   | 4.37   |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.47 (s, 1H), 7.36 (d,  $J$ =7.4, 1H), 7.23 (t,  $J$ =7.0, 1H), 7.16 – 6.96 (m, 6H), 6.63 (d,  $J$ =7.7, 1H), 2.42 (d,  $J$ =14.2, 1H), 2.23 (d,  $J$ =14.2, 1H), 0.74 (s, 9H).

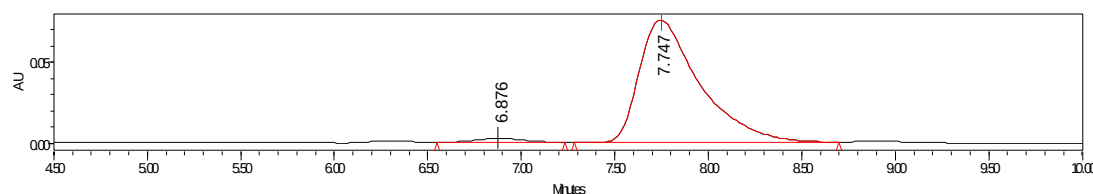
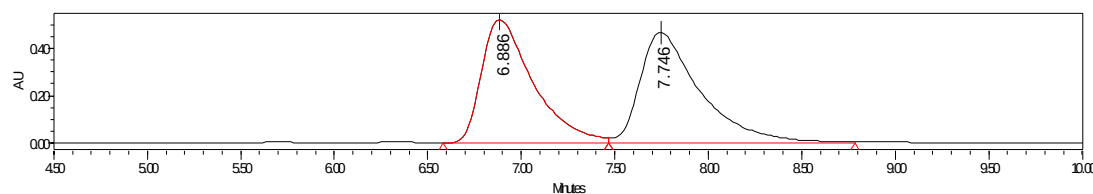
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.99, 140.09, 136.77, 130.04, 129.62, 129.04, 128.48, 128.23, 126.18, 122.06, 109.81, 59.16, 46.88, 32.74, 30.98..

HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{21}\text{NOS}$  ( $[\text{M}] + \text{Na}^+$ ) = 334.1242, Found 334.1240.

**(R)-3-isopropyl-3-(phenylthio)indolin-2-one (3x):**

Prepared according to the general procedure (48 h). The title compound **3x** was obtained as a white solid in 92% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 7.75 min,  $t_r$  (minor) = 6.88 min,  $ee$  = 95%.  $[\alpha]_D^{25} = 40.3$  ( $c$  = 0.26, in  $\text{CH}_2\text{Cl}_2$ ).



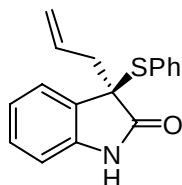
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 6.876          | 47116   | 2.71   |
| 2 | 7.747          | 1692013 | 97.29  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.86 (s, 1H), 7.43 (d,  $J$ =7.4, 1H), 7.25 – 7.09 (m, 4H), 7.09 – 6.96 (m, 3H), 6.67 (d,  $J$ =7.6, 1H), 2.48 (dt,  $J$ =13.5, 6.7, 1H), 1.28 (d,  $J$ =6.7, 3H), 0.87 (d,  $J$ =6.7, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 179.20, 140.84, 136.32, 129.65, 129.19, 128.53, 128.27, 125.57, 122.33, 109.76, 64.29, 34.02, 18.12, 17.78.

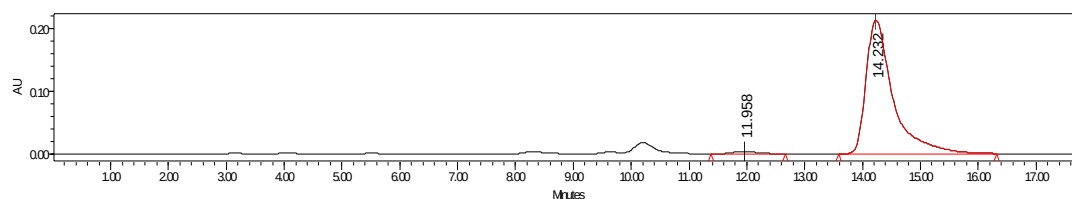
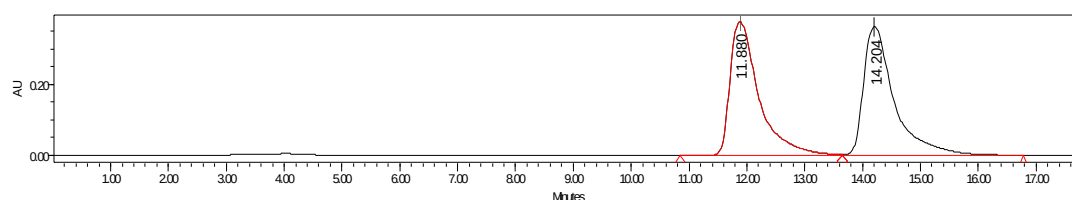
HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{17}\text{NOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 306.0929, Found 306.0927.

**(R)-3-allyl-3-(phenylthio)indolin-2-one (3y):**



Prepared according to the general procedure (48 h). The title compound **3y** was obtained as a white solid in 85% yield.

HPLC (Chiralcel IA, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 14.23 min,  $t_r$  (minor) = 11.96 min,  $ee$  = 95%.  $[\alpha]_D^{25}$  = -26.9 ( $c$  = 0.45, in  $\text{CH}_2\text{Cl}_2$ ).



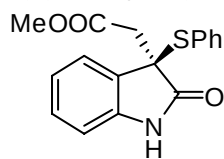
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 11.958         | 102136  | 1.45   |
| 2 | 14.232         | 6918870 | 98.55  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.76 (s, 1H), 7.35 (d,  $J$ =7.3, 1H), 7.28 – 7.18 (m, 3H), 7.14 (t,  $J$ =7.6, 1H), 7.11 – 7.00 (m, 3H), 6.69 (d,  $J$ =7.6, 1H), 5.60 – 5.42 (m, 1H), 5.07 (d,  $J$ =17.0, 1H), 4.96 (d,  $J$ =10.1, 1H), 2.86 (d,  $J$ =7.1, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.50, 140.46, 136.49, 131.18, 129.74, 129.48, 129.27, 128.76, 128.42, 124.80, 122.57, 119.81, 109.87, 58.86, 39.62.

HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{15}\text{NOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 304.0772, Found 304.0777.

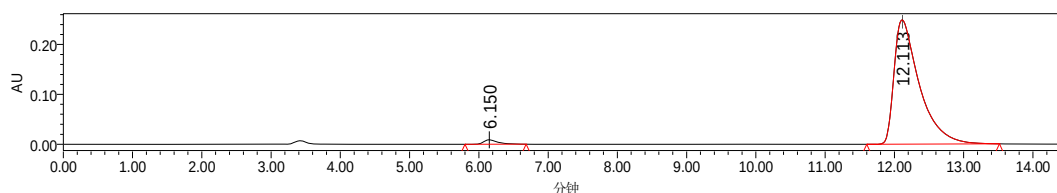
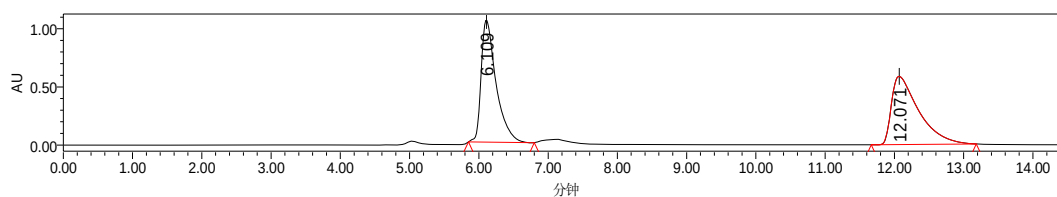
**(R)-methyl 2-(2-oxo-3-(phenylthio)indolin-3-yl)acetate (3z):**



Prepared according to the general procedure (20 h). The title compound **3z** was obtained as a white solid in 98% yield.

HPLC (Chiralcel IB, hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 12.11 min,  $t_r$  (minor) = 6.15 min,  $ee$  = 96%.  $[\alpha]_D^{25}$  =

-69.0 ( $c$  = 0.54, in  $\text{CH}_2\text{Cl}_2$ ).



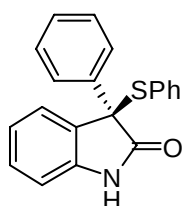
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 6.150          | 122296  | 1.90   |
| 2 | 12.113         | 6321193 | 98.10  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.54 (s, 1H), 7.38 – 7.28 (m, 3H), 7.25 – 7.12 (m, 4H), 7.02 (t,  $J$ =7.5, 1H), 6.71 (d,  $J$ =7.7, 1H), 3.46 (s, 3H), 3.33 (d,  $J$ =16.7, 1H), 3.22 (d,  $J$ =16.7, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 177.81, 169.29, 140.94, 137.24, 130.08, 129.14, 129.02, 128.58, 128.28, 123.74, 122.46, 110.01, 54.82, 51.98, 39.25.

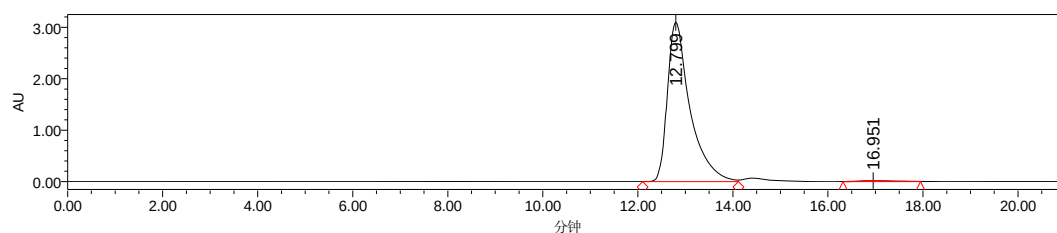
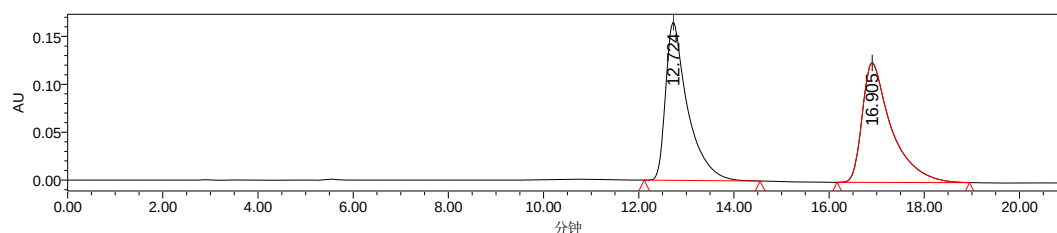
HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{15}\text{NO}_3\text{S}$  ( $[\text{M}] + \text{H}^+$ ) = 314.0851, Found 314.0851.

### 3-phenyl-3-(phenylthio)indolin-2-one (6a):



Prepared according to the general procedure (48 h). The title compound **6a** was obtained as a white solid in 95% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 12.80 min,  $t_r$  (minor) = 16.95 min,  $ee$  = 99%.  $[\alpha]_D^{25}$  = -116.8 ( $c$  = 0.45, in  $\text{CH}_2\text{Cl}_2$ ).



|   | Retention Time | Area      | % Area |
|---|----------------|-----------|--------|
| 1 | 12.799         | 102021224 | 99.29  |

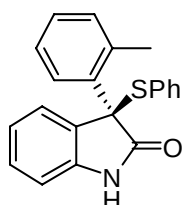
|   |        |        |      |
|---|--------|--------|------|
| 2 | 16.951 | 724468 | 0.71 |
|---|--------|--------|------|

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.53 (s, 1H), 7.70 (d,  $J$ =7.6, 2H), 7.45 – 7.30 (m, 4H), 7.24 – 7.13 (m, 4H), 7.09 (t,  $J$ =7.6, 1H), 7.03 (t,  $J$ =7.6, 2H), 6.67 (d,  $J$ =7.6, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 177.52, 140.20, 136.32, 136.06, 130.48, 129.88, 129.58, 128.89, 128.71, 128.41, 128.35, 128.09, 126.50, 122.71, 110.09, 63.00.

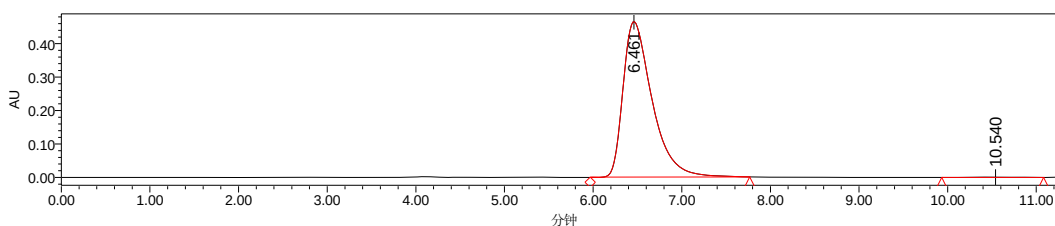
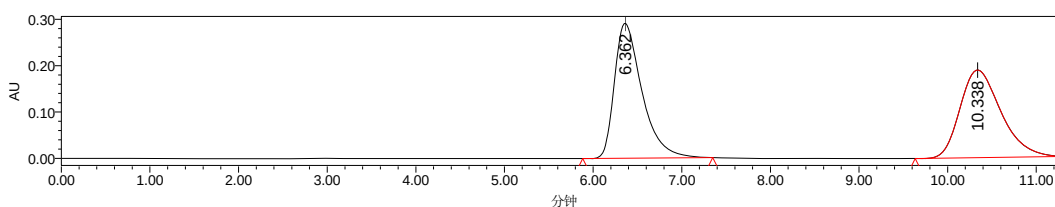
HRMS (ESI-TOF) calcd for C<sub>20</sub>H<sub>15</sub>NOS ([M]<sup>+</sup>+Na<sup>+</sup>) = 340.0772, Found 340.0771.

### 3-(phenylthio)-3-o-tolyindolin-2-one (6b):



Prepared according to the general procedure (72 h). The title compound **6b** was obtained as a white solid in 92% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 6.46 min,  $t_r$  (minor) = 10.54 min, *ee* = 99.5%.  $[\alpha]_D^{25}$  = 32.7 (*c* = 0.66, in CH<sub>2</sub>Cl<sub>2</sub>).



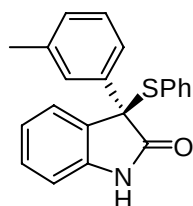
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 6.461          | 10646968 | 99.77  |
| 2 | 10.540         | 24798    | 0.23   |

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.57 (s, 1H), 8.27 (d,  $J$ =7.8, 1H), 7.38 (t,  $J$ =7.6, 1H), 7.31 – 7.22 (m, 2H), 7.19 (d,  $J$ =7.6, 2H), 7.05 – 7.15 (m, 4H), 7.03 – 6.93 (m, 2H), 6.56 (d,  $J$ =7.8, 1H), 1.83 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 177.48, 140.05, 136.64, 136.60, 134.12, 131.94, 131.13, 129.58, 129.14, 129.05, 128.71, 128.43, 128.31, 126.15, 124.83, 123.02, 109.71, 63.81, 19.92.

HRMS (ESI-TOF) calcd for C<sub>21</sub>H<sub>17</sub>NOS ([M]<sup>+</sup>+H<sup>+</sup>) = 332.1109, Found 332.1104.

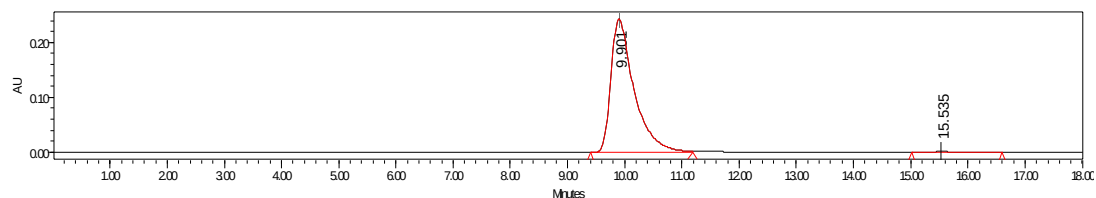
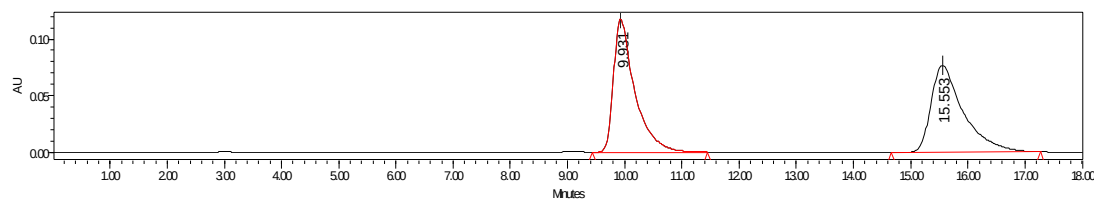
### 3-(phenylthio)-3-m-tolyindolin-2-one (6c):



Prepared according to the general procedure (48 h). The title compound **6c** was obtained as a white solid in 93% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 9.90 min,  $t_r$  (minor) = 15.54 min, *ee* = 99%.  $[\alpha]_D^{25}$  = -103.1 (*c* = 0.38, in CH<sub>2</sub>Cl<sub>2</sub>).





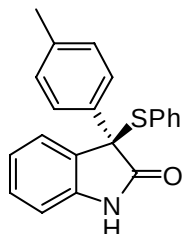
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 9.901          | 6816678 | 99.50  |
| 2 | 15.535         | 34120   | 0.50   |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.60 (s, 1H), 7.52 (s, 1H), 7.46 (d,  $J$ =7.8, 1H), 7.40 (d,  $J$ =7.3, 1H), 7.26 (t,  $J$ =7.8, 1H), 7.22 – 7.12 (m, 5H), 7.09 (t,  $J$ =7.6, 1H), 7.02 (t,  $J$ =7.5, 2H), 6.67 (d,  $J$ =7.6, 1H), 2.36 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 177.72, 140.22, 138.47, 136.31, 135.96, 130.71, 129.91, 129.54, 129.17, 128.81, 128.59, 128.38, 126.46, 125.07, 122.71, 110.07, 63.07, 21.63.

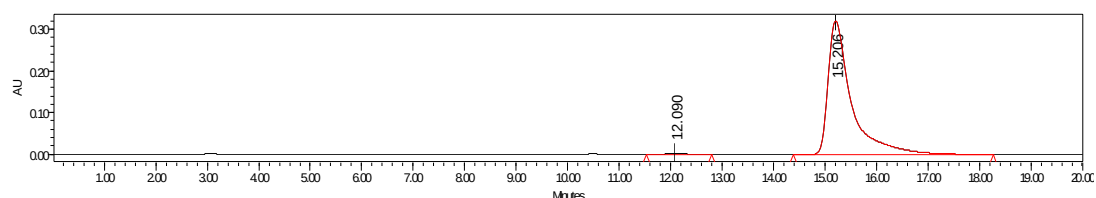
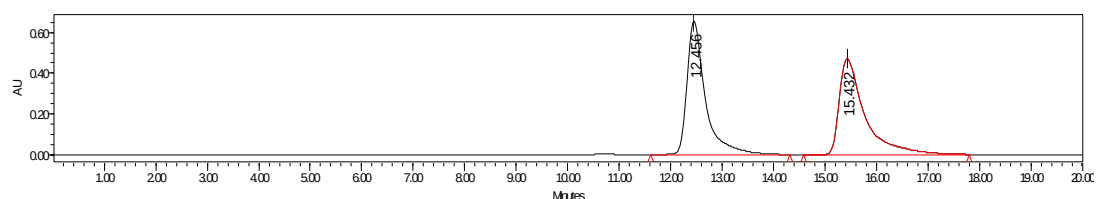
HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{17}\text{NOS}$  ( $[\text{M}] + \text{Na}^+$ ) = 354.0929, Found 354.0928.

### 3-(phenylthio)-3-p-tolylindolin-2-one (6d)



Prepared according to the general procedure (48 h). The title compound **6d** was obtained as a white solid in 94% yield.

HPLC (Chiralcel IA, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 15.21 min,  $t_r$  (minor) = 12.09 min,  $ee$  = 99%.  $[\alpha]_D^{25}$  = -114.3 ( $c$  = 0.54, in  $\text{CH}_2\text{Cl}_2$ ).



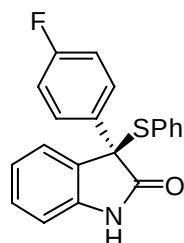
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 12.090         | 70241   | 0.70   |
| 2 | 15.206         | 9979659 | 99.30  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.64 (s, 1H), 7.58 (d,  $J$ =7.6, 2H), 7.38 (d,  $J$ =7.3, 1H), 7.23 – 7.12 (m, 6H), 7.08 (t,  $J$ =7.4, 1H), 7.02 (t,  $J$ =7.4, 2H), 6.66 (d,  $J$ =7.6, 1H), 2.34 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 177.78, 140.25, 138.22, 136.28, 133.02, 130.63, 130.01, 129.51, 129.42, 128.79, 128.38, 127.95, 126.44, 122.65, 110.10, 62.86, 21.14.

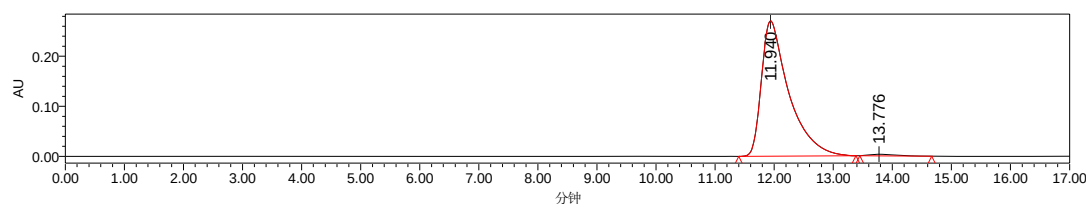
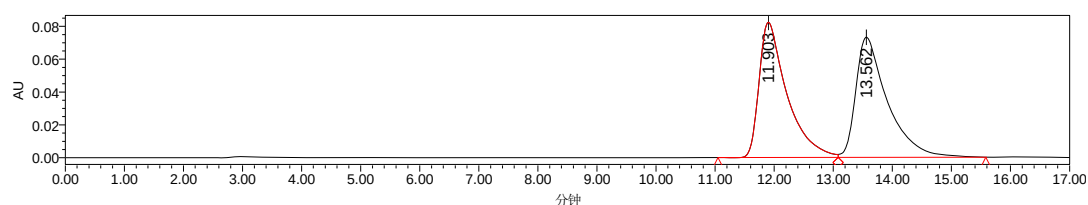
HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{17}\text{NOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 354.0929, Found 354.0931.

### 3-(4-fluorophenyl)-3-(phenylthio)indolin-2-one (6e):



Prepared according to the general procedure (48 h). The title compound **6e** was obtained as a white solid in 97% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 11.94 min,  $t_r$  (minor) = 13.78 min,  $ee$  = 98%.  $[\alpha]_D^{25}$  = -126.4 ( $c$  = 0.60, in  $\text{CH}_2\text{Cl}_2$ ).



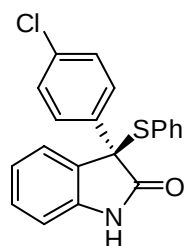
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 11.940         | 8690165 | 98.85  |
| 2 | 13.776         | 101528  | 1.15   |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.39 (s, 1H), 7.70 (dd,  $J$ =8.2, 5.5, 2H), 7.37 (d,  $J$ =7.6, 1H), 7.19 (t,  $J$ =9.6, 4H), 7.14 – 6.99 (m, 5H), 6.68 (d,  $J$ =7.6, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 177.23, 162.66 (d,  $J$ =248.3), 140.12, 136.33, 131.78, 130.13, 130.10, 130.05, 129.73, 129.70, 129.07, 128.46, 126.48, 122.81, 115.66, 115.45, 110.17, 62.22.

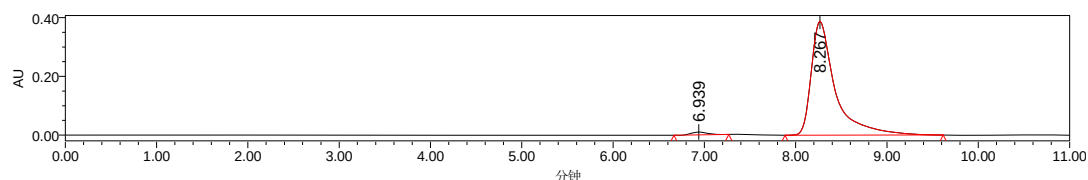
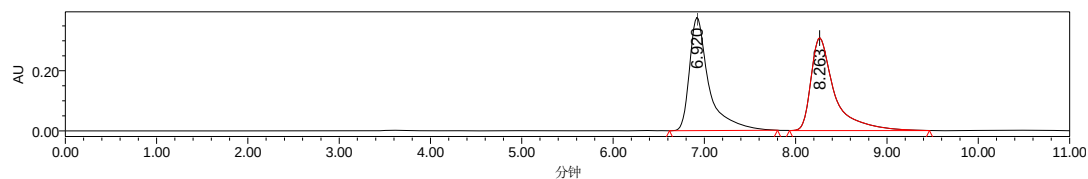
HRMS (ESI-TOF) calcd for  $\text{C}_{20}\text{H}_{14}\text{FNOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 358.0678, Found 358.0674.

### 3-(4-chlorophenyl)-3-(phenylthio)indolin-2-one (6f):



Prepared according to the general procedure (48 h). The title compound **6f** was obtained as a white solid in 91% yield.

HPLC (Chiralcel IA, hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 8.27 min,  $t_r$  (minor) = 6.94 min,  $ee$  = 97%.  $[\alpha]_D^{25}$  = -125.7 ( $c$  = 0.53, in  $\text{CH}_2\text{Cl}_2$ ).



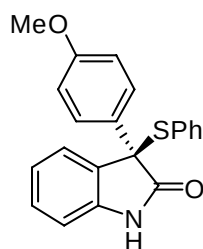
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 6.939          | 117221  | 1.63   |
| 2 | 8.267          | 7062361 | 98.37  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.31 (s, 1H), 7.66 (d,  $J$ =8.2, 2H), 7.34 (d,  $J$ =7.7, 3H), 7.24 – 7.14 (m, 4H), 7.11 (t,  $J$ =7.5, 1H), 7.05 (t,  $J$ =7.5, 2H), 6.68 (d,  $J$ =7.7, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 176.92, 140.10, 136.35, 134.54, 134.47, 129.85, 129.75, 129.64, 129.61, 129.13, 128.81, 128.49, 126.47, 122.85, 110.18, 62.29.

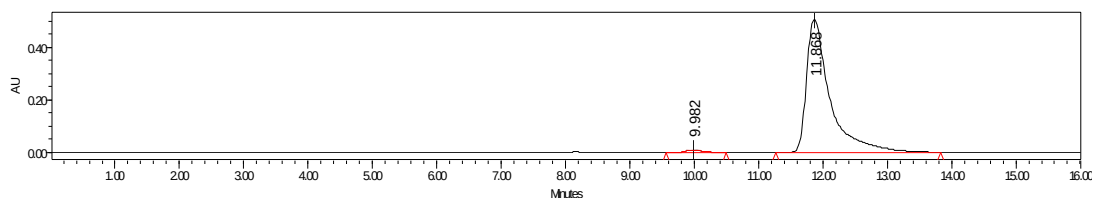
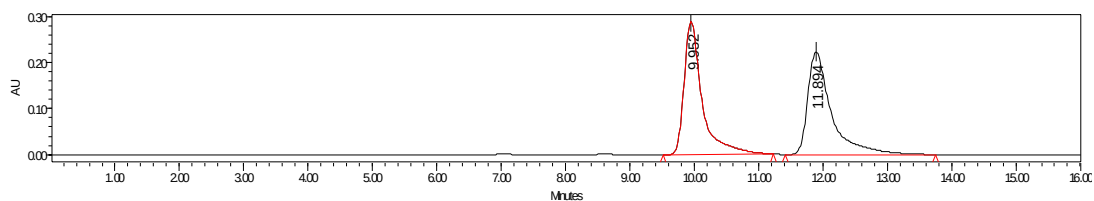
HRMS (ESI-TOF) calcd for  $\text{C}_{20}\text{H}_{14}\text{Cl}^{34.9689}\text{NOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 374.0382, Found 374.0375.

### 3-(4-methoxyphenyl)-3-(phenylthio)indolin-2-one (6g):



Prepared according to the general procedure (48 h). The title compound **6g** was obtained as a white solid in 90% yield.

HPLC (Chiralcel IA, hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 11.87 min,  $t_r$  (minor) = 9.98 min,  $ee$  = 98%.  $[\alpha]_D^{25}$  = -131.4 ( $c$  = 0.62, in  $\text{CH}_2\text{Cl}_2$ ).



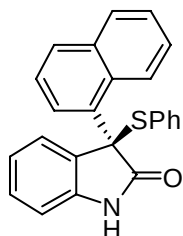
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 9.982          | 161579   | 1.24   |
| 2 | 11.868         | 12886407 | 98.76  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.50 (s, 1H), 7.63 (d,  $J$ =7.9, 2H), 7.38 (d,  $J$ =7.4, 1H), 7.17 (t,  $J$ =9.7, 4H), 7.21 – 7.13 (m, 1H), 7.03 (t,  $J$ =7.4, 2H), 6.90 (d,  $J$ =7.9, 2H), 6.67 (d,  $J$ =7.6, 1H), 3.80 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 177.69, 159.55, 140.19, 136.26, 130.54, 130.07, 129.52, 129.41, 128.81, 128.39, 127.86, 126.48, 122.64, 114.03, 110.08, 62.46, 55.35.

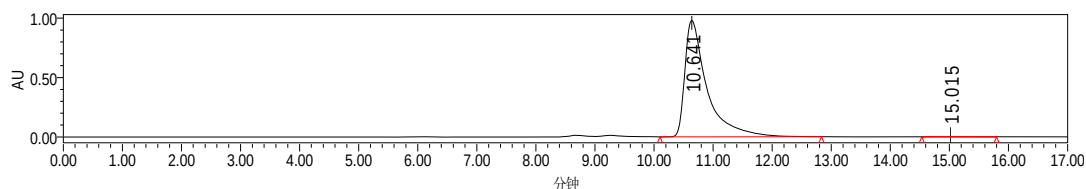
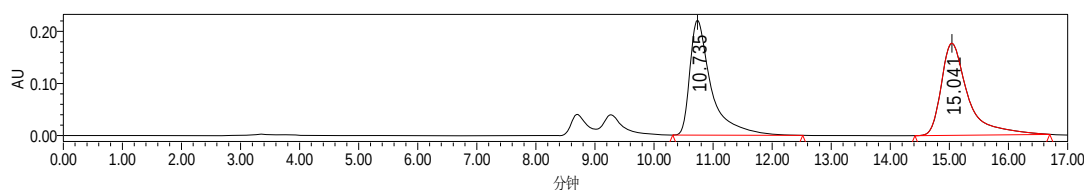
HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{17}\text{NO}_2\text{S}$  ( $[\text{M}] + \text{Na}^+$ ) = 370.0878, Found 370.0872.

### 3-(naphthalen-1-yl)-3-(phenylthio)indolin-2-one (6h):



Prepared according to the general procedure (48 h). The title compound **6h** was obtained as a white solid in 91% yield.

HPLC (Chiralcel IA, hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 10.64 min,  $t_r$  (minor) = 15.02 min,  $ee$  = 99%.  $[\alpha]_D^{25} = -8.7$  ( $c$  = 0.61, in  $\text{CH}_2\text{Cl}_2$ ).



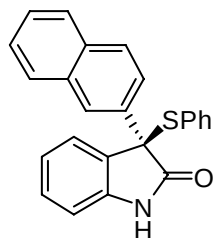
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 10.641         | 25439598 | 99.64  |
| 2 | 15.015         | 92970    | 0.36   |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.05 (s, 1H), 8.48 (d,  $J$ =7.2, 1H), 7.90 (d,  $J$ =8.2, 1H), 7.85 (d,  $J$ =8.2, 1H), 7.62 (t,  $J$ =7.8, 1H), 7.45 – 7.32 (m, 2H), 7.30 – 7.15 (m, 4H), 7.12 – 7.01 (m, 3H), 6.96 (d,  $J$ =7.4, 1H), 6.89 (t,  $J$ =7.4, 1H), 6.57 (d,  $J$ =7.8, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 178.28, 139.47, 136.74, 134.49, 132.35, 131.28, 130.91, 129.98, 129.69, 129.23, 129.08, 128.76, 128.35, 128.26, 126.51, 125.61, 125.08, 124.86, 123.94, 123.04, 110.36, 64.18.

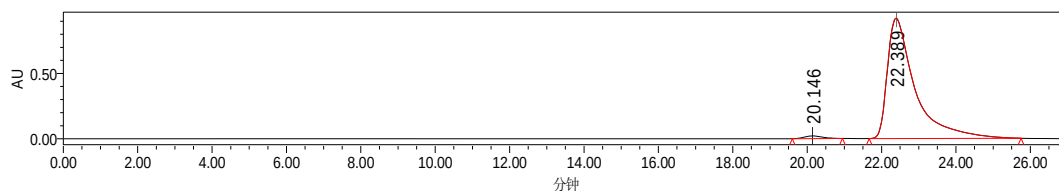
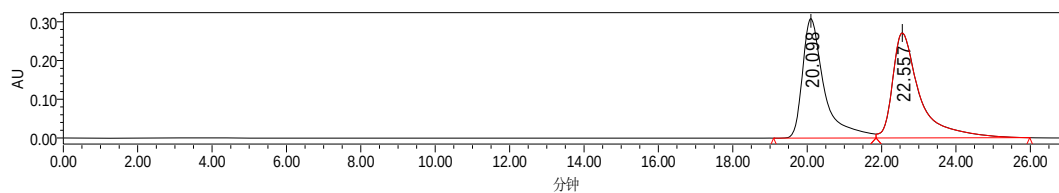
HRMS (ESI-TOF) calcd for  $\text{C}_{24}\text{H}_{17}\text{NOS}$  ( $[\text{M}] + \text{Na}^+$ ) = 390.0929, Found 390.0913.

### 3-(naphthalen-2-yl)-3-(phenylthio)indolin-2-one (6i):



Prepared according to the general procedure (48 h). The title compound **6i** was obtained as a white solid in 92% yield.

HPLC (Chiralcel IA, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 22.39 min,  $t_r$  (minor) = 20.15 min,  $ee$  = 97%.  $[\alpha]_D^{25} = -126.2$  ( $c$  = 0.54, in  $\text{CH}_2\text{Cl}_2$ ).



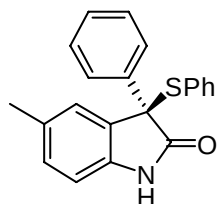
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 20.146         | 684853   | 1.42   |
| 2 | 22.389         | 47397370 | 98.58  |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.70 (s, 1H), 8.07 (s, 1H), 7.95 – 7.73 (m, 4H), 7.52 – 7.43 (m, 2H), 7.41 (d,  $J$ =7.6, 1H), 7.29 – 7.07 (m, 5H), 7.02 (t,  $J$ =7.6, 2H), 6.71 (d,  $J$ =7.6, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 177.56, 140.27, 136.36, 133.41, 133.10, 132.99, 130.52, 129.85, 129.62, 128.98, 128.53, 128.46, 128.43, 127.56, 127.41, 126.60, 126.51, 126.32, 125.70, 122.78, 110.23, 63.20.

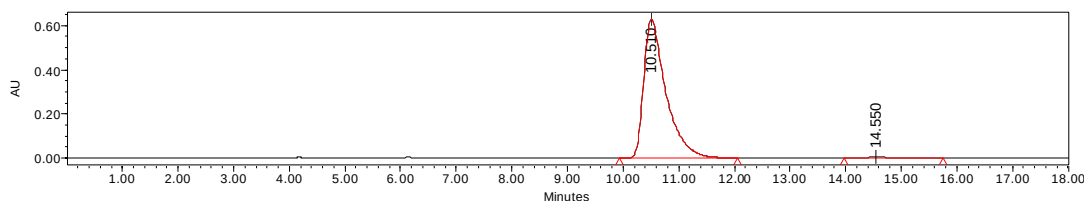
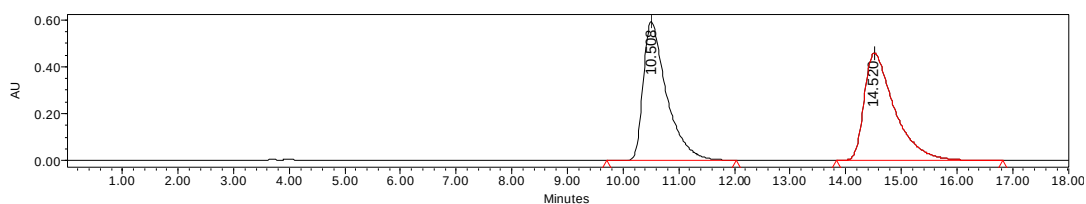
HRMS (ESI-TOF) calcd for  $\text{C}_{24}\text{H}_{17}\text{NOS}$  ( $[\text{M}] + \text{Na}^+$ ) = 390.0929, Found 390.0917.

#### 5-methyl-3-phenyl-3-(phenylthio)indolin-2-one (**6j**):



Prepared according to the general procedure (48 h). The title compound **6j** was obtained as a white solid in 90% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 10.51 min,  $t_r$  (minor) = 14.55 min,  $ee$  = 99%.  $[\alpha]_D^{25}$  =  $-48.0$  ( $c$  = 0.56, in  $\text{CH}_2\text{Cl}_2$ ).



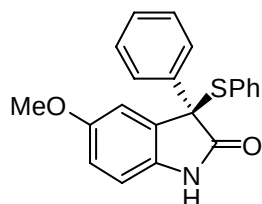
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 10.510         | 17357570 | 99.26  |
| 2 | 14.550         | 129440   | 0.74   |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.45 (s, 1H), 7.66 (d,  $J$ =7.3, 2H), 7.52 – 7.29 (m, 4H), 7.29 – 7.09 (m, 5H), 7.04 (d,  $J$ =7.8, 1H), 6.63 (d,  $J$ =7.9, 1H), 2.32 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 175.44, 138.75, 136.70, 135.36, 130.73, 130.05, 129.69, 129.43, 129.28, 128.57, 128.52, 128.01, 127.68, 126.42, 109.48, 62.18, 20.72.

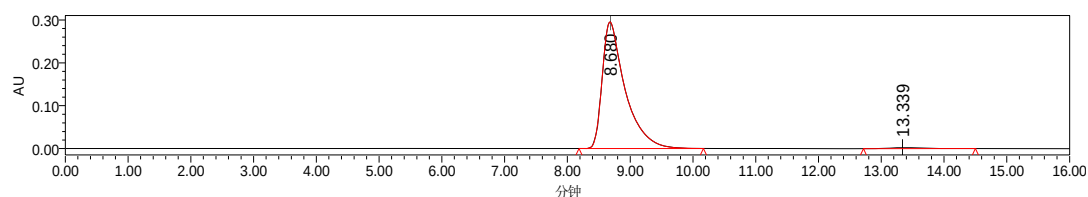
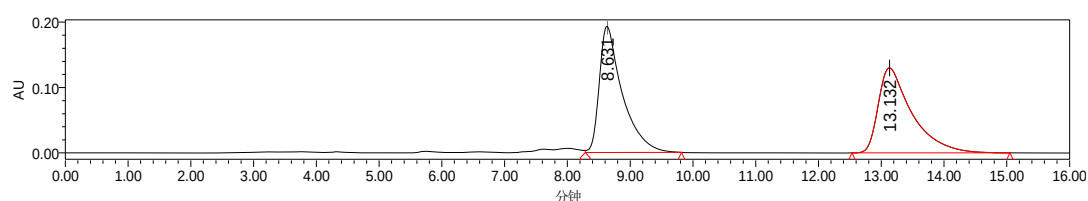
HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{17}\text{NOS}$  ( $[\text{M}+\text{H}^+]$ ) = 332.1109, Found 332.1113.

#### 5-methoxy-3-phenyl-3-(phenylthio)indolin-2-one (6k):



Prepared according to the general procedure (48 h). The title compound **6k** was obtained as a white solid in 97% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 8.68 min,  $t_r$  (minor) = 13.34 min,  $ee$  = 98%.  $[\alpha]_D^{25}$  = -37.9 ( $c$  = 0.75, in  $\text{CH}_2\text{Cl}_2$ ).



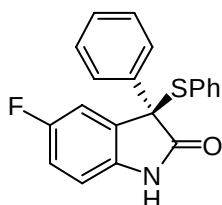
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 8.680          | 7468027 | 98.83  |
| 2 | 13.339         | 88687   | 1.17   |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.31 (s, 1H), 7.70 (d,  $J$ =7.5, 2H), 7.49 – 7.30 (m, 3H), 7.25 – 7.16 (m, 3H), 7.06 (t,  $J$ =7.4, 2H), 6.95 (s, 1H), 6.72 (d,  $J$ =8.5, 1H), 6.59 (d,  $J$ =8.5, 1H), 3.79 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 177.32, 155.86, 136.30, 136.11, 133.62, 131.70, 129.90, 129.60, 128.73, 128.47, 128.35, 128.08, 114.29, 112.62, 110.56, 63.48, 55.91.

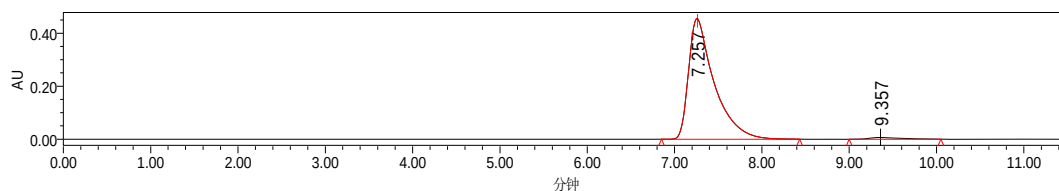
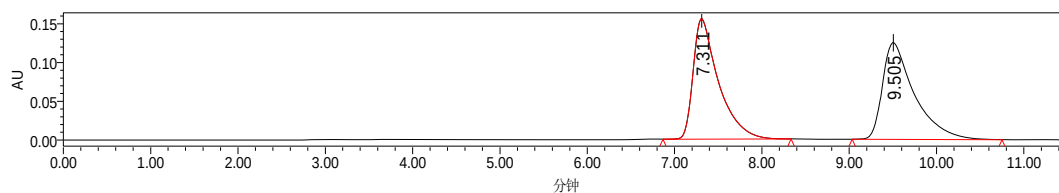
HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{17}\text{NO}_2\text{S}$  ( $[\text{M}+\text{H}^+]$ ) = 348.1058, Found 348.1053.

#### 5-fluoro-3-phenyl-3-(phenylthio)indolin-2-one (6l):



Prepared according to the general procedure (48 h). The title compound **6l** was obtained as a white solid in 93% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 85/15, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 7.26 min,  $t_r$  (minor) = 9.36 min,  $ee$  = 97%.  $[\alpha]_D^{25}$  = -130.0 ( $c$  = 0.56, in  $\text{CH}_2\text{Cl}_2$ ).



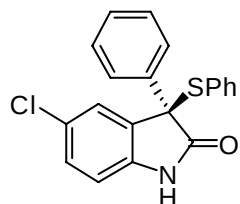
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 7.257          | 9248070 | 98.40  |
| 2 | 9.357          | 150414  | 1.60   |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.53 (s, 1H), 7.62 (d,  $J$ =7.5, 2H), 7.49 – 7.28 (m, 4H), 7.25 – 7.14 (m, 5H), 7.02 (t,  $J$ =9.0, 1H), 6.65 (dd,  $J$ =8.1, 4.2, 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 175.52, 157.90 (d,  $J$ =237.4), 137.42, 135.98, 135.56, 131.26 (d,  $J$ =8.4), 129.78, 129.50, 128.72, 128.30, 127.57, 115.55 (d,  $J$ =23.3), 113.48 (d,  $J$ =25.2), 110.64 (d,  $J$ =8.1), 62.53.

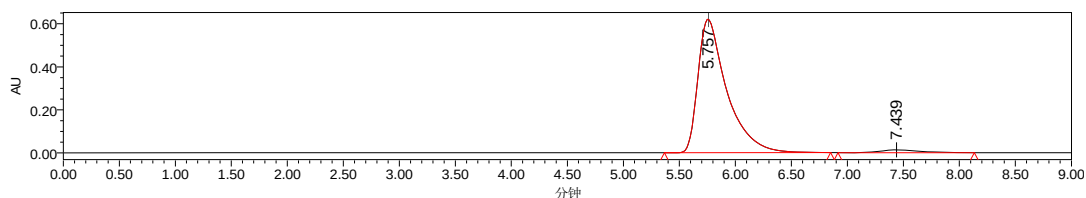
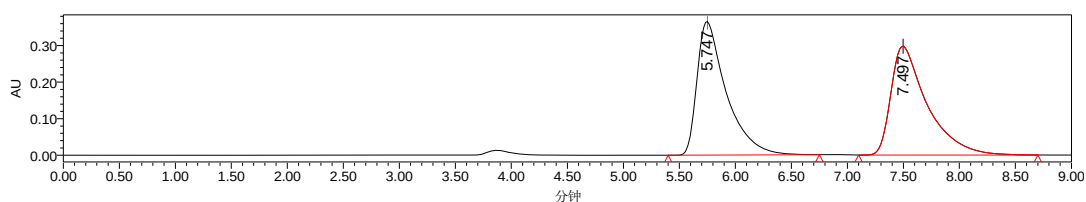
HRMS (ESI-TOF) calcd for  $\text{C}_{20}\text{H}_{14}\text{FNOS}$  ( $[\text{M}] + \text{Na}^+$ ) = 358.0678, Found 358.0677.

#### 5-chloro-3-phenyl-3-(phenylthio)indolin-2-one (6m):



Prepared according to the general procedure (48 h). The title compound **6m** was obtained as a white solid in 92% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 5.76 min,  $t_r$  (minor) = 7.44 min,  $ee$  = 95%.  $[\alpha]_D^{25}$  = -10.8 ( $c$  = 0.67, in  $\text{CH}_2\text{Cl}_2$ ).



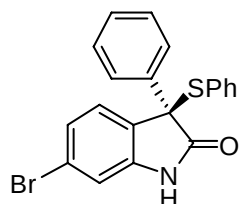
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 5.757          | 11068479 | 97.31  |
| 2 | 7.439          | 305641   | 2.69   |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.67 (s, 1H), 7.61 (d,  $J$ =7.6, 2H), 7.50 – 7.30 (m, 4H), 7.22 (t,  $J$ =7.4, 3H), 7.17 (d,  $J$ =7.6, 2H), 6.69 (d,  $J$ =8.3, 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 175.21, 140.07, 135.88, 135.57, 131.67, 129.84, 129.43, 128.94, 128.78, 128.75, 128.34, 127.57, 125.87, 125.77, 111.27, 62.26.

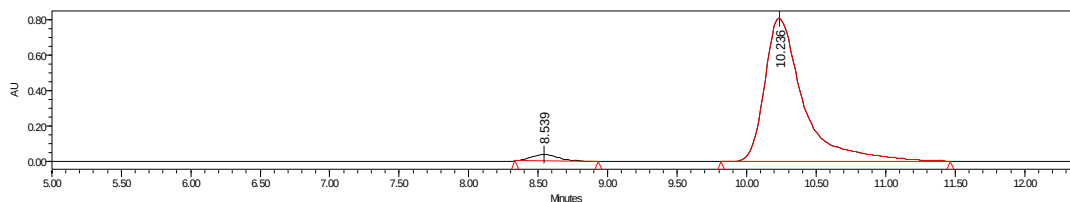
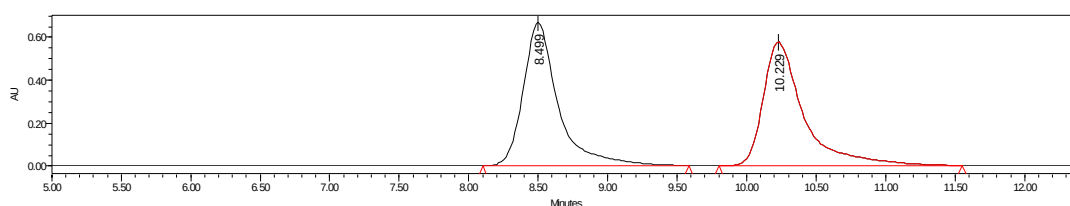
HRMS (ESI-TOF) calcd for  $\text{C}_{20}\text{H}_{14}\text{Cl}^{34.9689}\text{NOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 374.0382, Found 374.0372.

#### 6-bromo-3-phenyl-3-(phenylthio)indolin-2-one (6n):



Prepared according to the general procedure (48 h). The title compound **6n** was obtained as a white solid in 93% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 10.24 min,  $t_r$  (minor) = 8.54 min,  $ee$  = 94%.  $[\alpha]_D^{25}$  = -68.3 ( $c$  = 0.73, in  $\text{CH}_2\text{Cl}_2$ ).



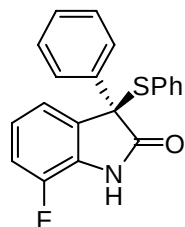
|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 8.539          | 503030   | 3.13   |
| 2 | 10.236         | 15586443 | 96.87  |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 10.65 (s, 1H), 7.60 (d,  $J$ =7.9, 2H), 7.48 – 7.10 (m, 10H), 6.82 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 175.37, 142.80, 135.88, 135.57, 129.82, 129.46, 128.94, 128.72, 128.31, 127.87, 127.56, 124.55, 121.48, 112.52, 61.91.

HRMS (ESI-TOF) calcd for  $\text{C}_{20}\text{H}_{14}\text{BrNOS}$  ( $[\text{M}]+\text{Na}^+$ ) = 417.9877, Found 417.9880.

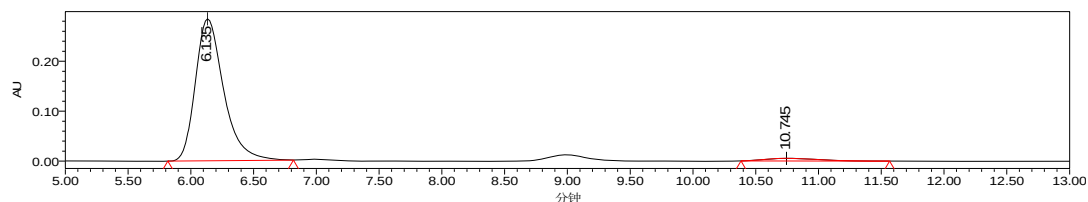
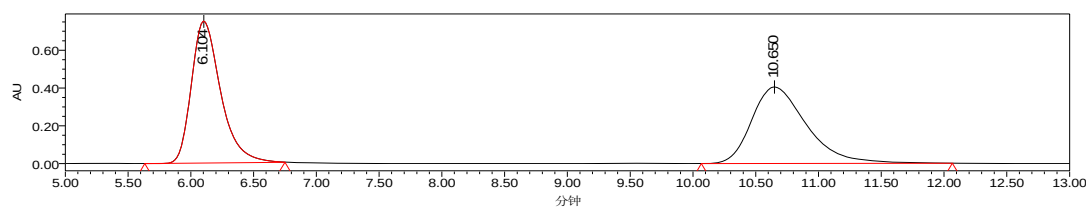
#### 7-fluoro-3-phenyl-3-(phenylthio)indolin-2-one (6o):



Prepared according to the general procedure (72 h). The title compound **6o** was obtained as a white solid in 88% yield.

HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 6.14 min,  $t_r$  (minor) = 10.75 min,  $ee$  = 93%.  $[\alpha]_D^{25}$  = -94.6 ( $c$  = 0.63, in  $\text{CH}_2\text{Cl}_2$ ).





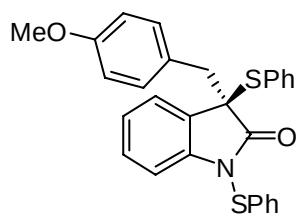
|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 6.135          | 4435926 | 96.50  |
| 2 | 10.745         | 161049  | 3.50   |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.93 (s, 1H), 7.70 (d,  $J$ =7.4, 2H), 7.44 – 7.28 (m, 3H), 7.28 – 7.16 (m, 4H), 7.13 – 7.01 (m, 3H), 6.95 (t,  $J$ =9.0, 1H).

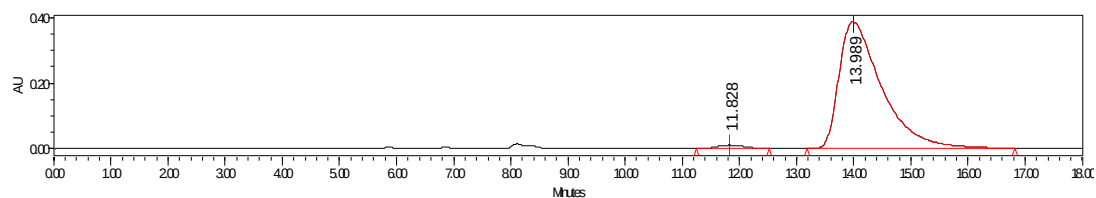
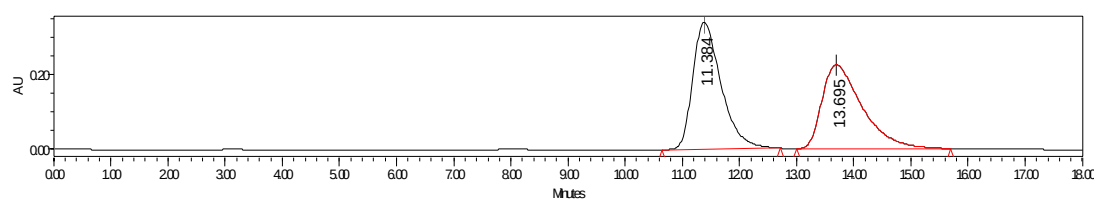
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 176.16, 146.84 (d,  $J$ =245.0), 136.34, 135.44, 133.13 (d,  $J$ =3.0), 129.87, 129.57, 128.78, 128.55, 128.04, 127.62 (d,  $J$ =12.7), 123.20 (d,  $J$ =5.9), 122.24 (d,  $J$ =3.4), 115.65 (d,  $J$ =17.0), 63.05.

HRMS (ESI-TOF) calcd for  $\text{C}_{20}\text{H}_{14}\text{FNOS}$  ( $[\text{M}] + \text{Na}^+$ ) = 358.0678, Found 358.0669.

**(R)-3-(4-methoxybenzyl)-1,3-bis(phenylthio)indolin-2-one (4a):**



HPLC (Chiralcel ODH, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 13.99 min,  $t_r$  (minor) = 11.83 min,  $ee$  = 97%.  $[\alpha]_D^{25}$  = -89.4 ( $c$  = 0.85, in  $\text{CH}_2\text{Cl}_2$ ).

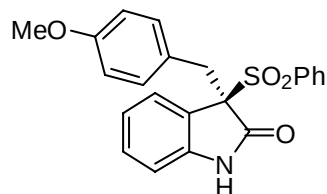


|   | Retention Time | Area     | % Area |
|---|----------------|----------|--------|
| 1 | 11.828         | 345841   | 1.69   |
| 2 | 13.989         | 20099868 | 98.31  |

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 7.76 (d,  $J$ =7.2, 1H), 7.35 (t,  $J$ =7.3, 1H), 7.28 – 6.98 (m, 9H), 6.80 (d,  $J$ =8.5, 2H), 6.69 – 6.57 (m, 3H), 6.52 (d,  $J$ =7.3, 2H), 3.64 (s, 3H), 3.59 (d,  $J$ =13.2, 1H), 3.38 (d,  $J$ =13.2, 1H).

$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 176.54, 158.11, 142.48, 136.08, 134.83, 131.19, 129.99, 129.41, 129.02, 128.69, 128.44, 128.23, 126.83, 126.35, 125.39, 124.00, 123.91, 113.34, 109.76, 60.01, 54.84.  
HRMS (ESI-TOF) calcd for  $\text{C}_{28}\text{H}_{23}\text{NO}_2\text{S}_2$  ( $[\text{M}] + \text{H}^+$ ) = 470.1248, Found 470.1247.

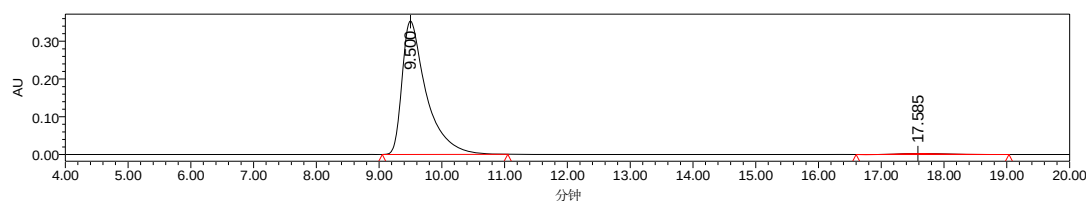
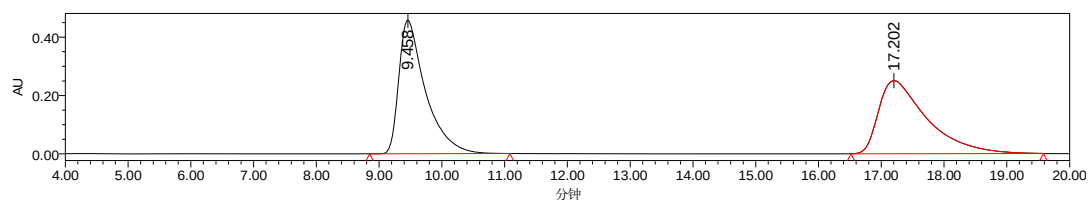
**(R)-3-(4-methoxybenzyl)-3-(phenylsulfonyl)indolin-2-one (7a)**



Prepared by oxidization of **3a** with *m*-CPBA (2.5 equiv) in  $\text{CH}_2\text{Cl}_2$ .

The title compound **7a** was purified by silica gel chromatography (petroleum ether : EtOAc = 2 : 1) to afford a white solid in 82% yield.

HPLC (Chiralcel AD-H, hexane/ *i*-PrOH = 70/30, flow rate 1.0 mL/min,  $\lambda$  = 254 nm)  $t_r$  (major) = 9.50 min,  $t_r$  (minor) = 17.59 min,  $ee$  = 97%.  $[\alpha]_D^{25}$  = -72.3 ( $c$  = 0.37, in  $\text{CH}_2\text{Cl}_2$ ).



|   | Retention Time | Area    | % Area |
|---|----------------|---------|--------|
| 1 | 9.500          | 9432240 | 98.52  |
| 2 | 17.585         | 141251  | 1.48   |

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.92 (s, 1H), 7.77 (d,  $J$ =7.2, 1H), 7.65 – 6.48 (m, 3H), 7.35 (t,  $J$ =7.3, 2H), 7.24 – 7.10 (m, 2H), 6.83 (d,  $J$ =7.4, 2H), 6.49 (t,  $J$ =7.6, 3H), 3.83 (d,  $J$ =13.3, 1H), 3.68 (d,  $J$ =13.3, 1H), 3.57 (s, 3H).

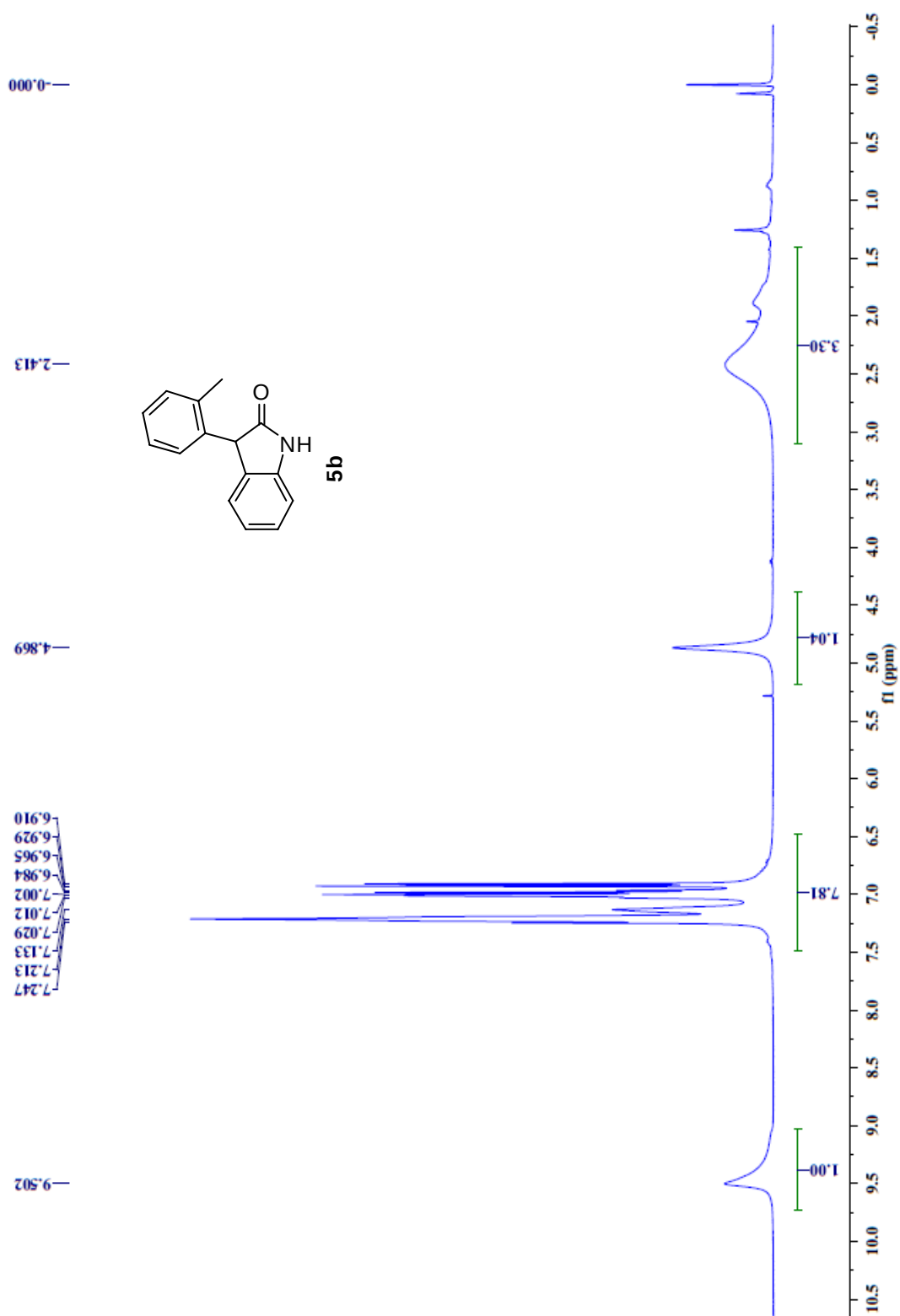
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 171.54, 158.52, 141.39, 134.96, 134.27, 131.17, 130.46, 130.30, 128.45, 127.26, 124.73, 122.89, 122.23, 113.49, 109.98, 54.95, 34.15.

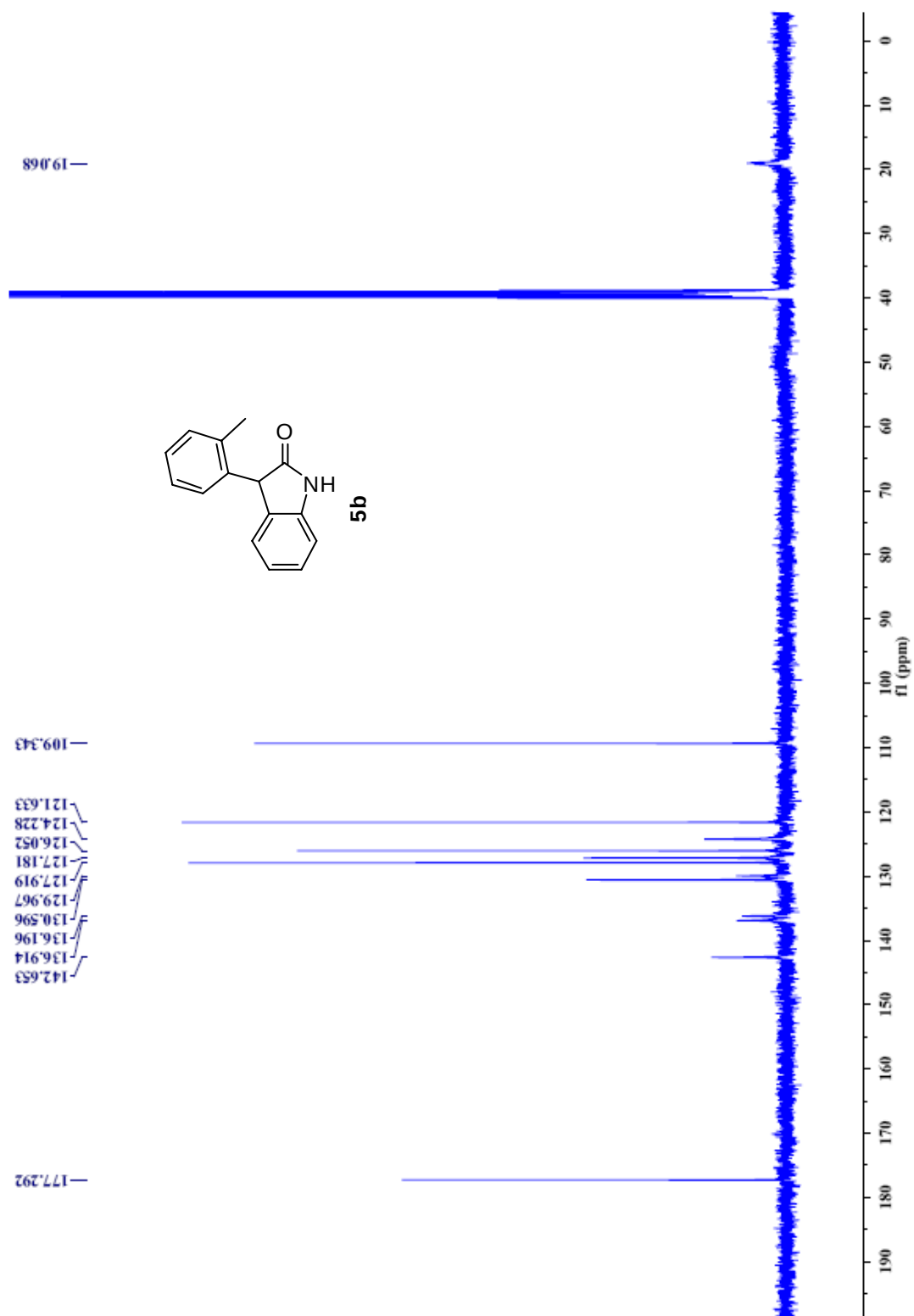
HRMS (ESI-TOF) calcd for  $\text{C}_{22}\text{H}_{19}\text{NO}_4\text{S}$  ( $[\text{M}] + \text{Na}^+$ ) = 416.0932, Found 416.0927.

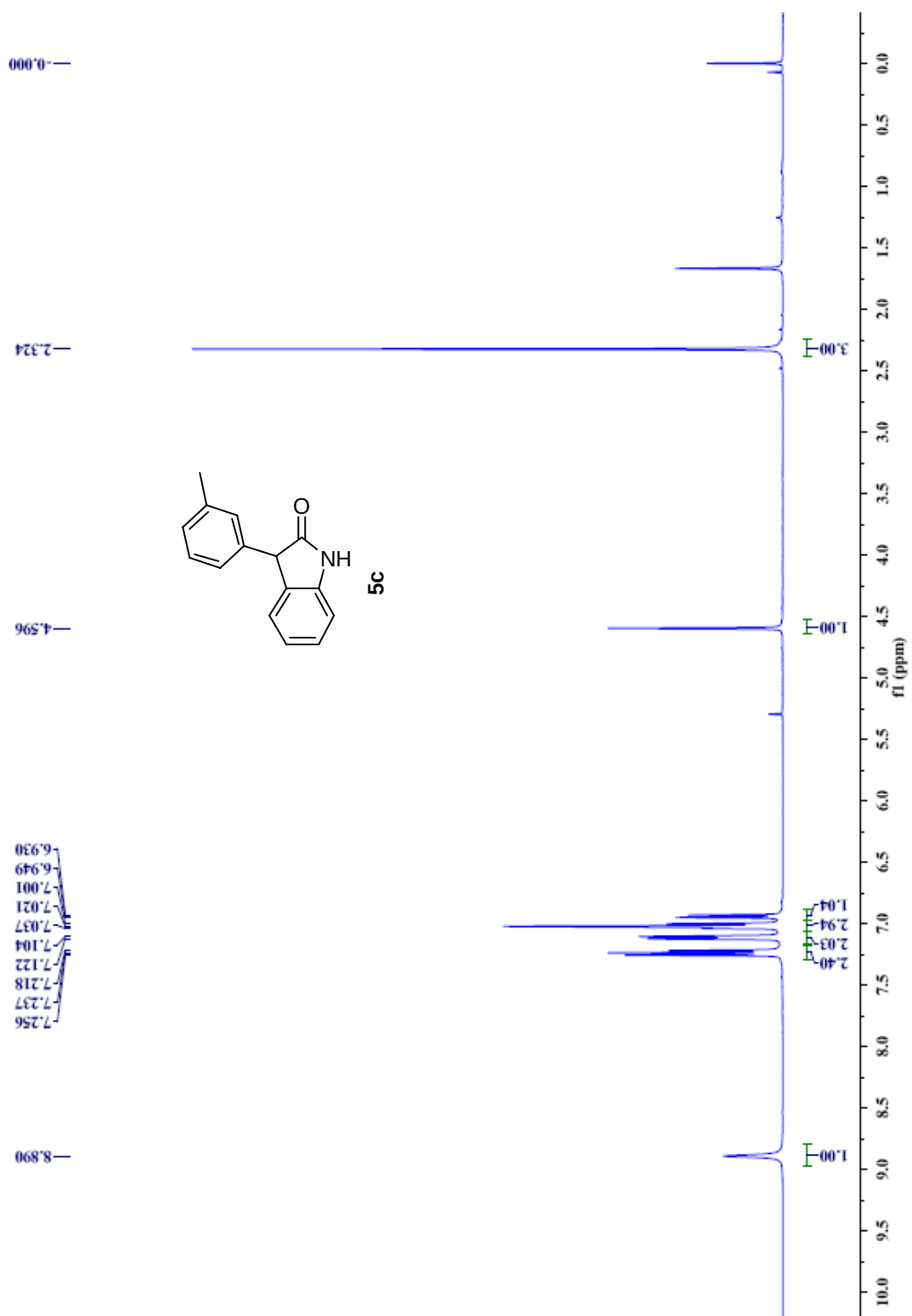
## 10. References

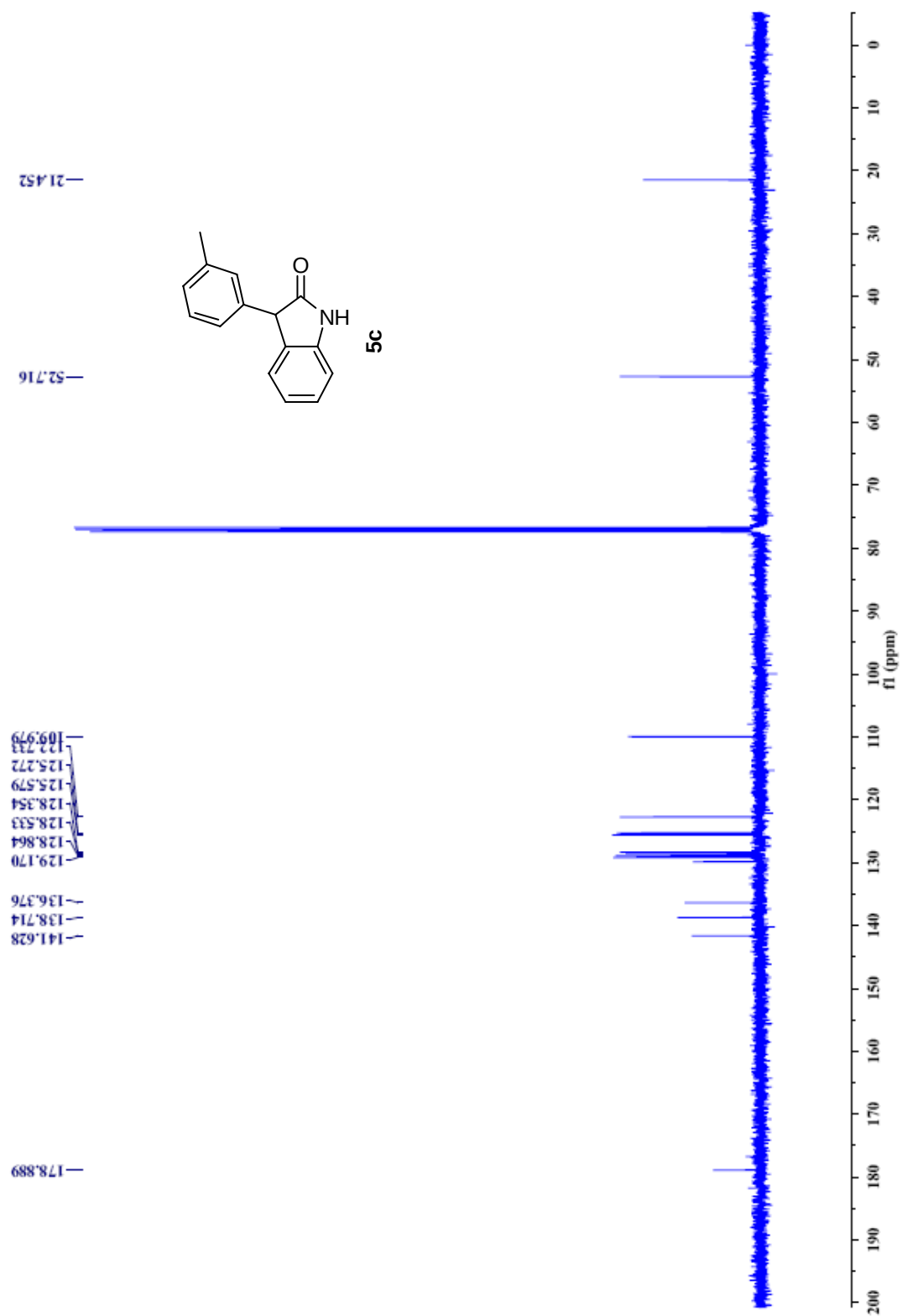
[1]. Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett*. **2005**, 2445-2448.

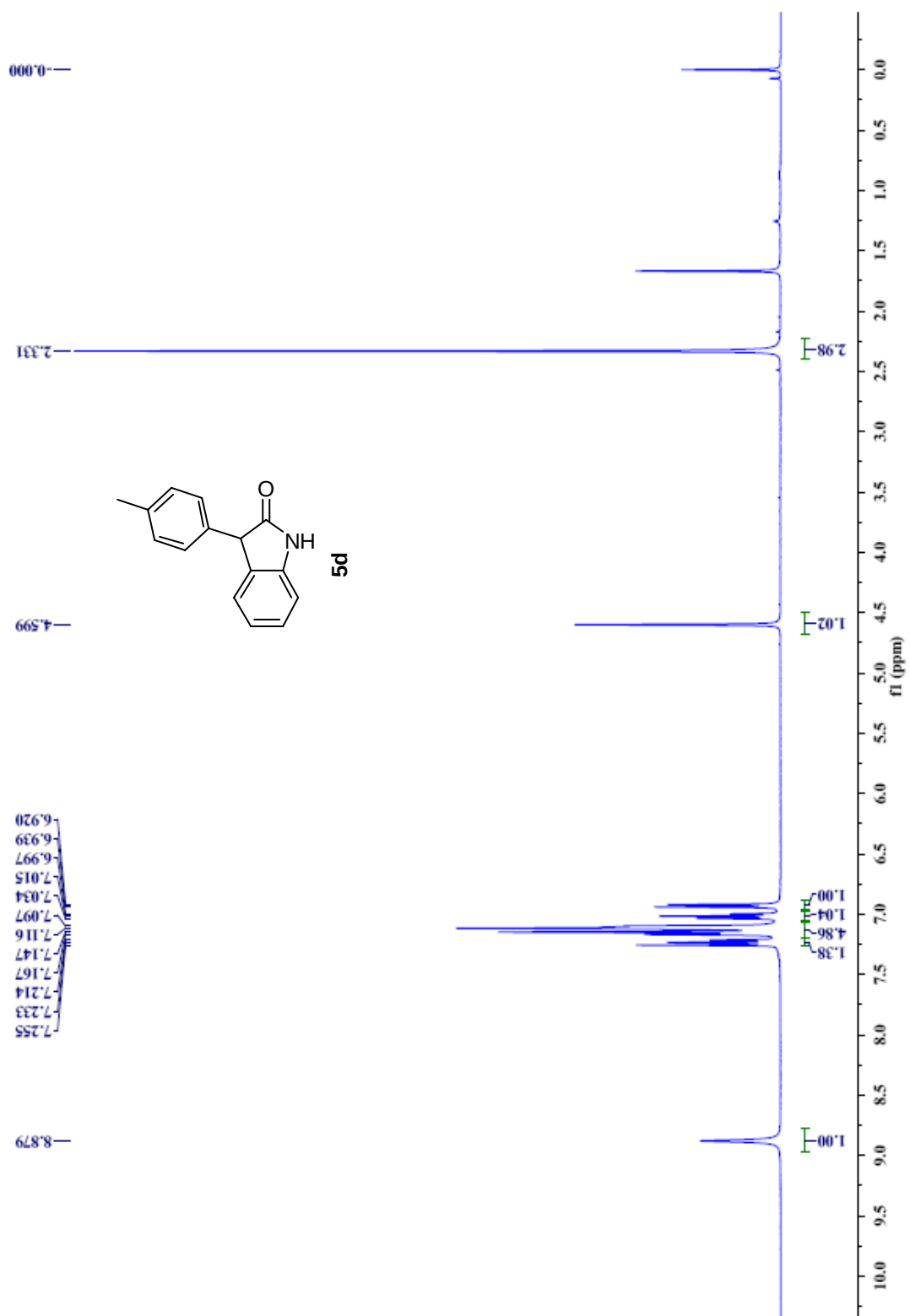
# 11. Copy of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

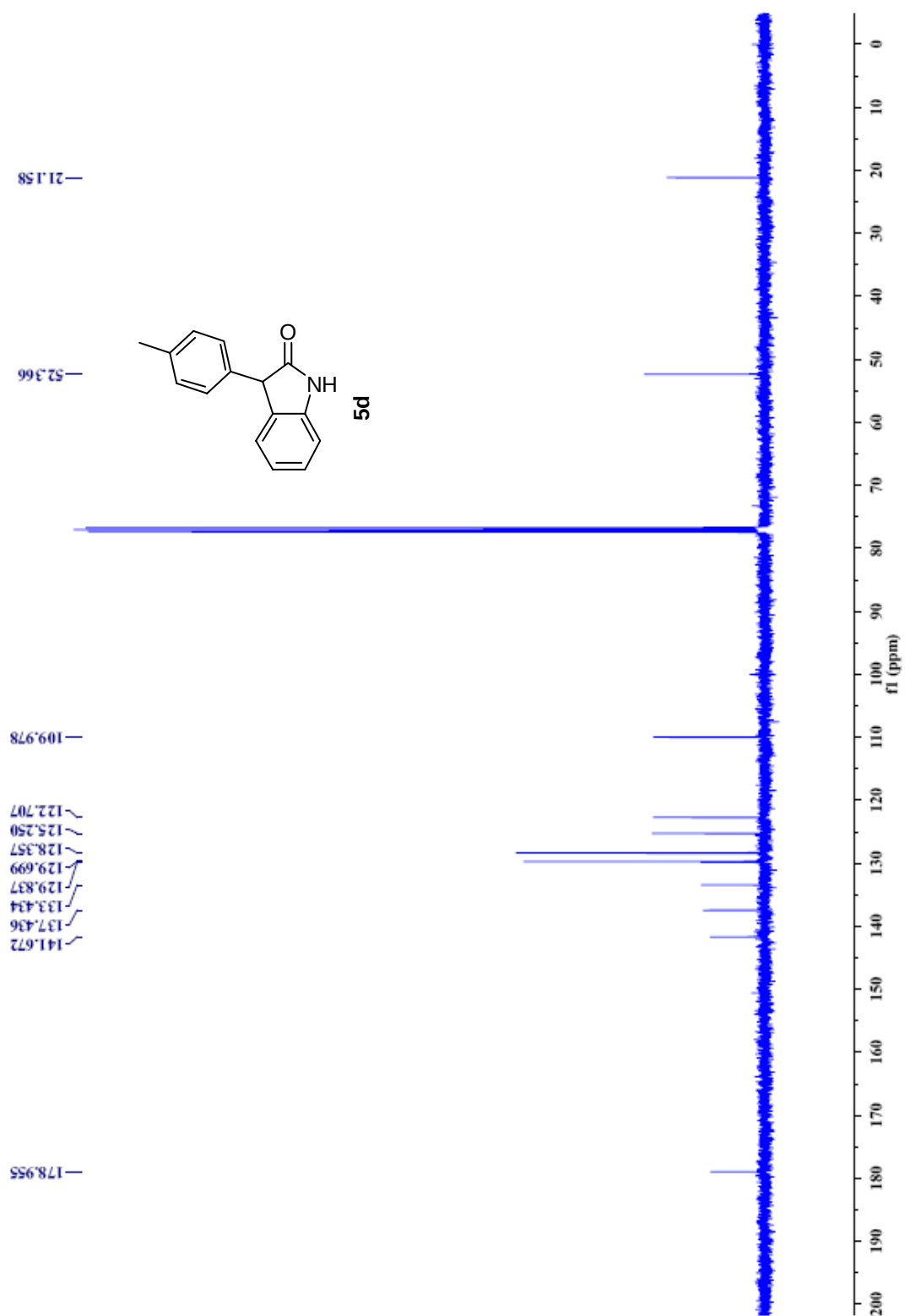




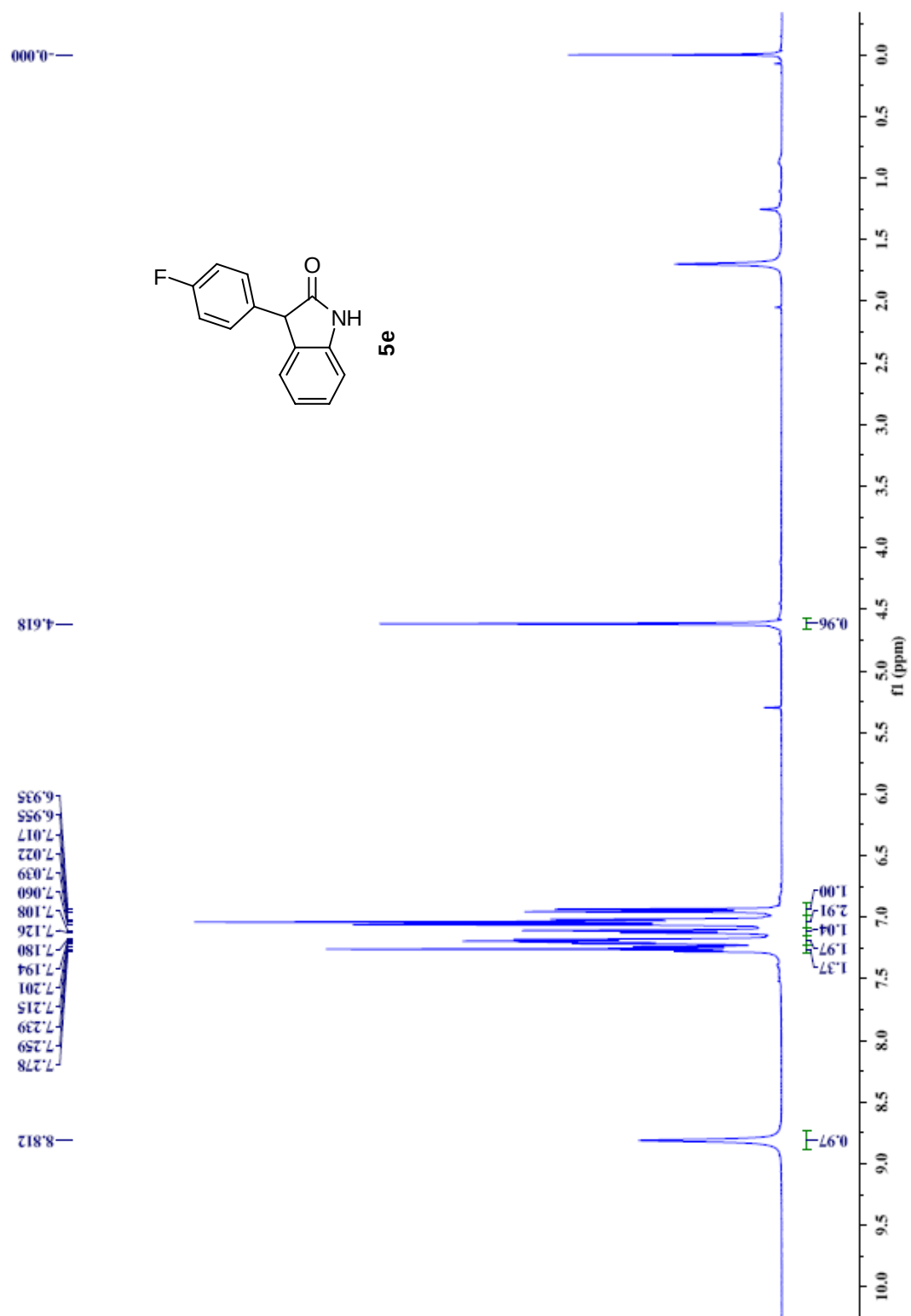


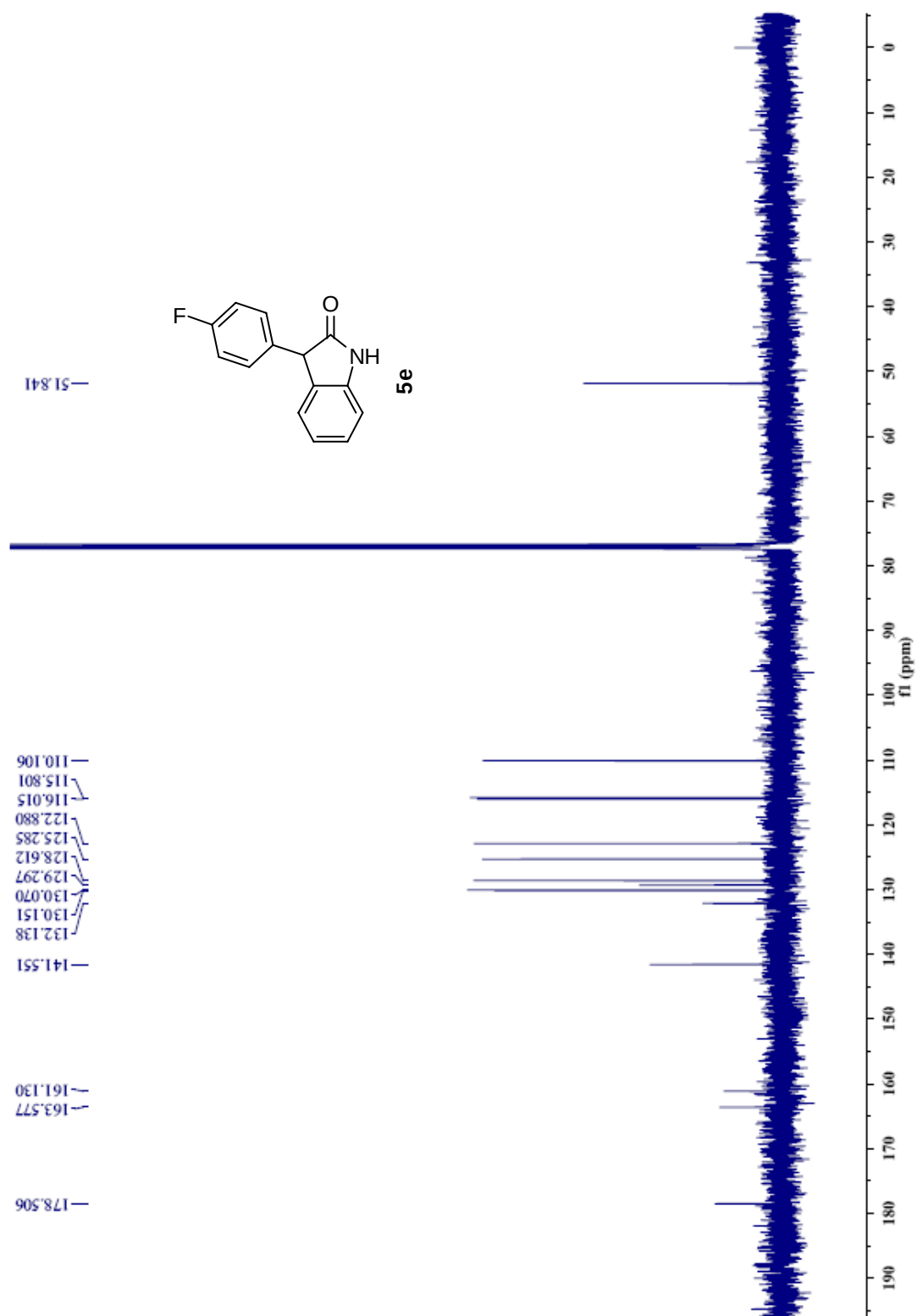


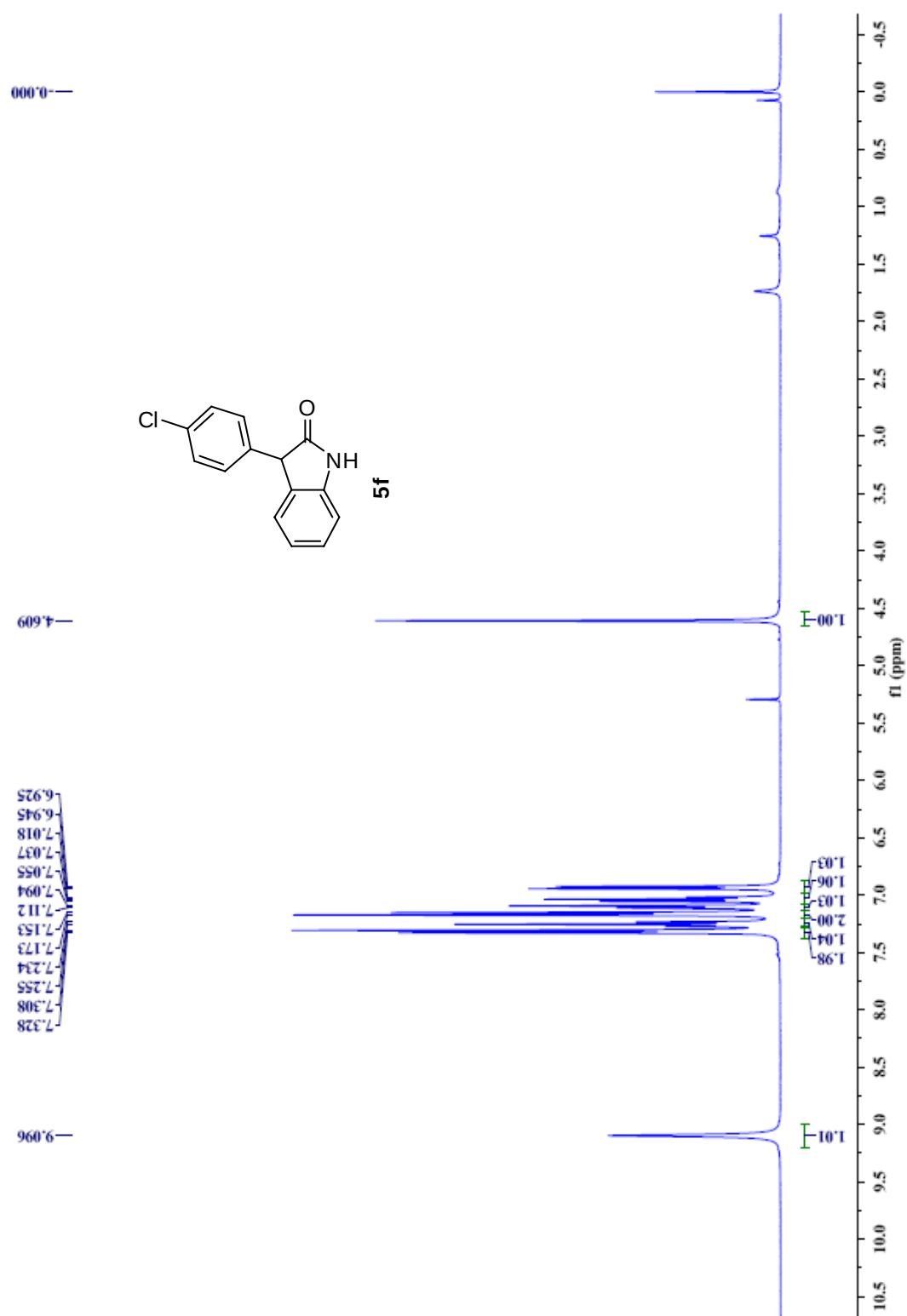


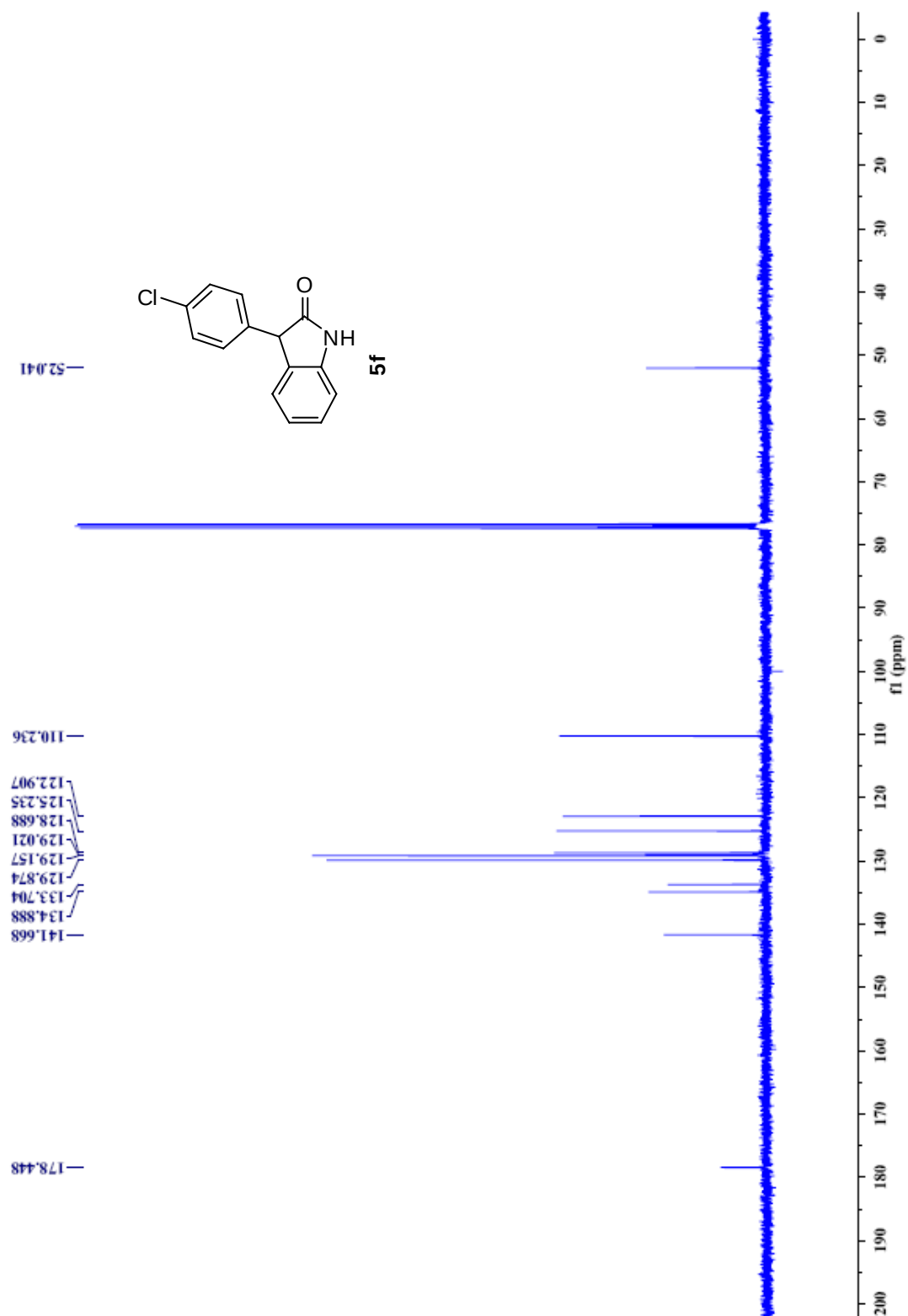


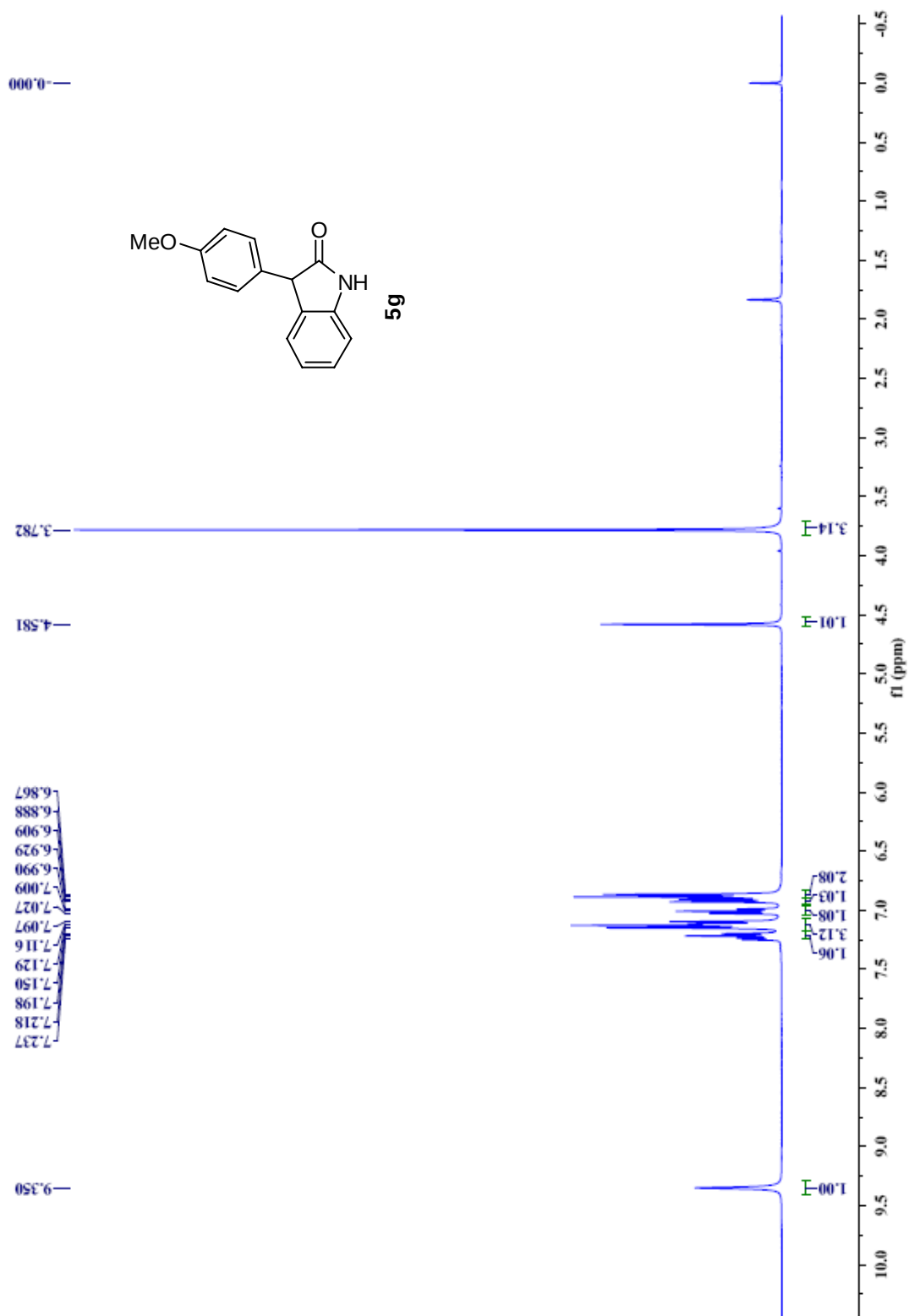


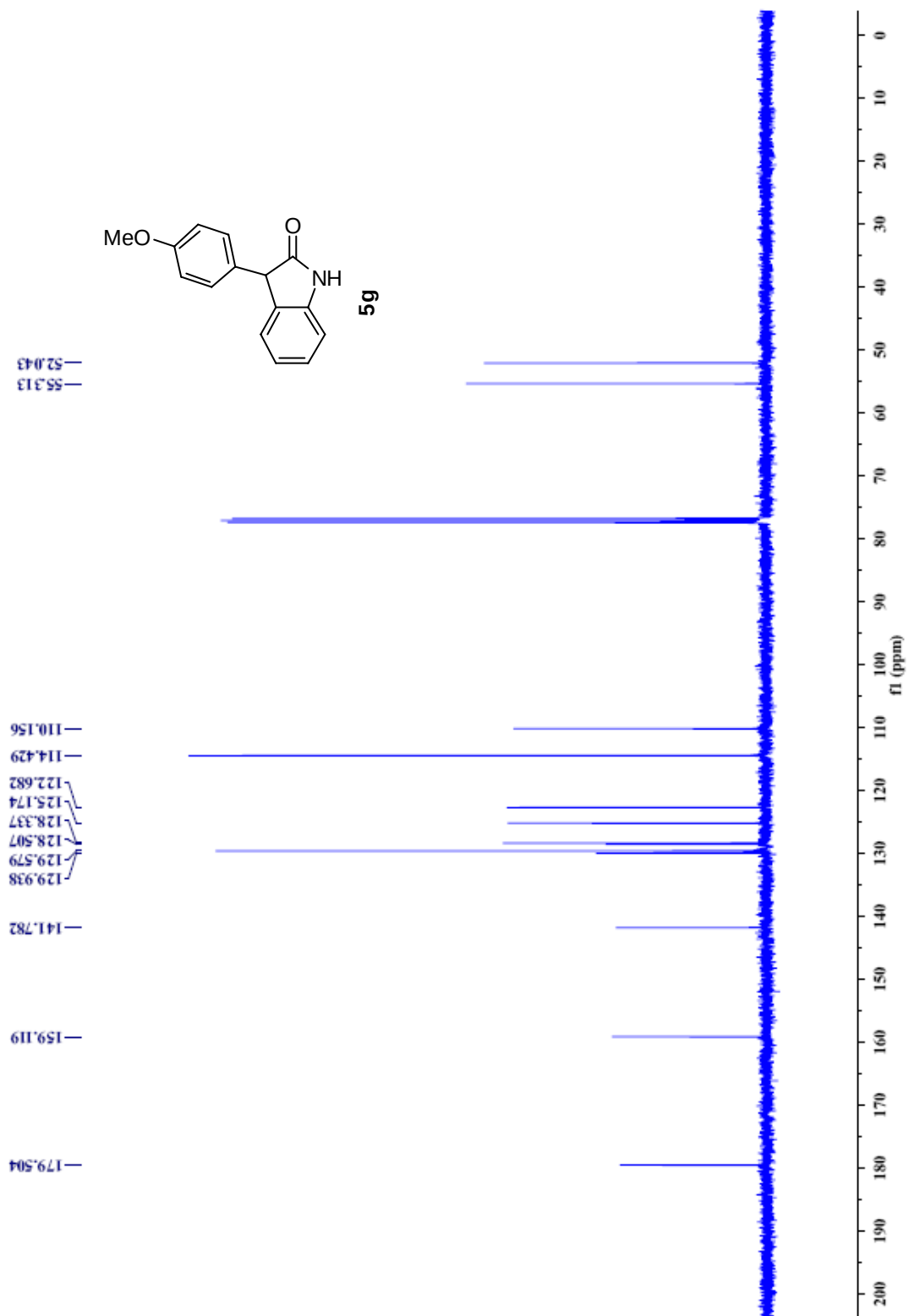


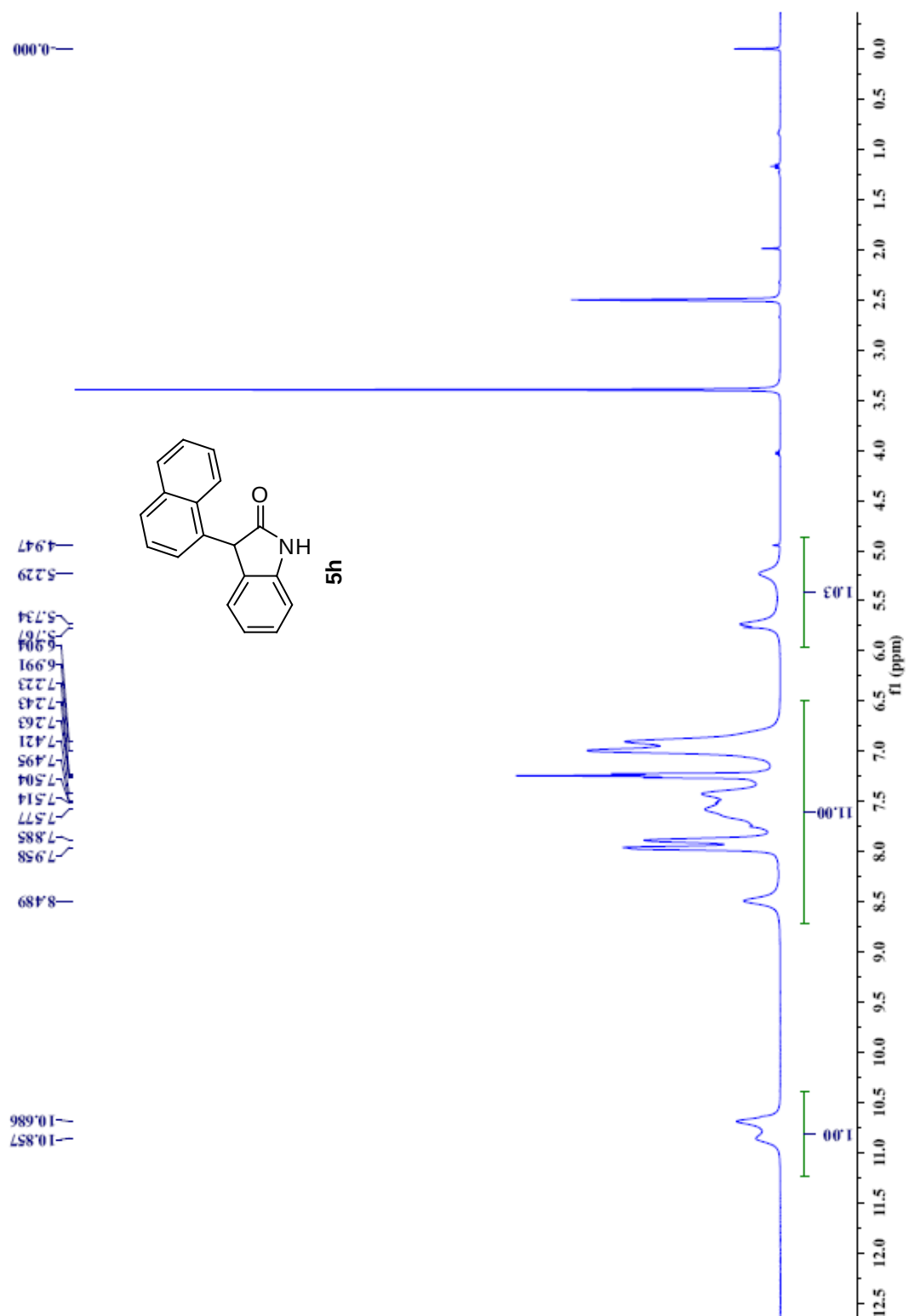


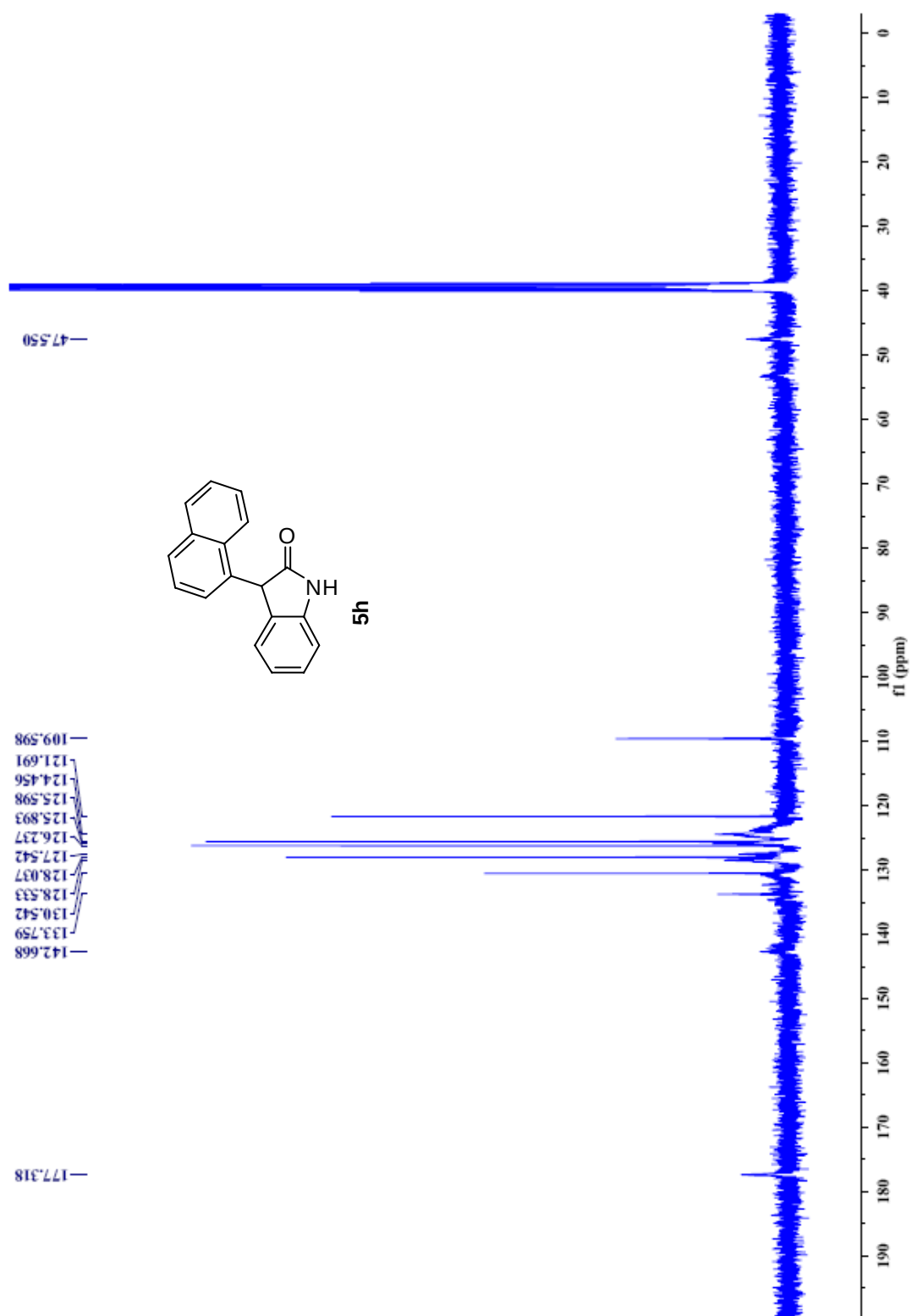




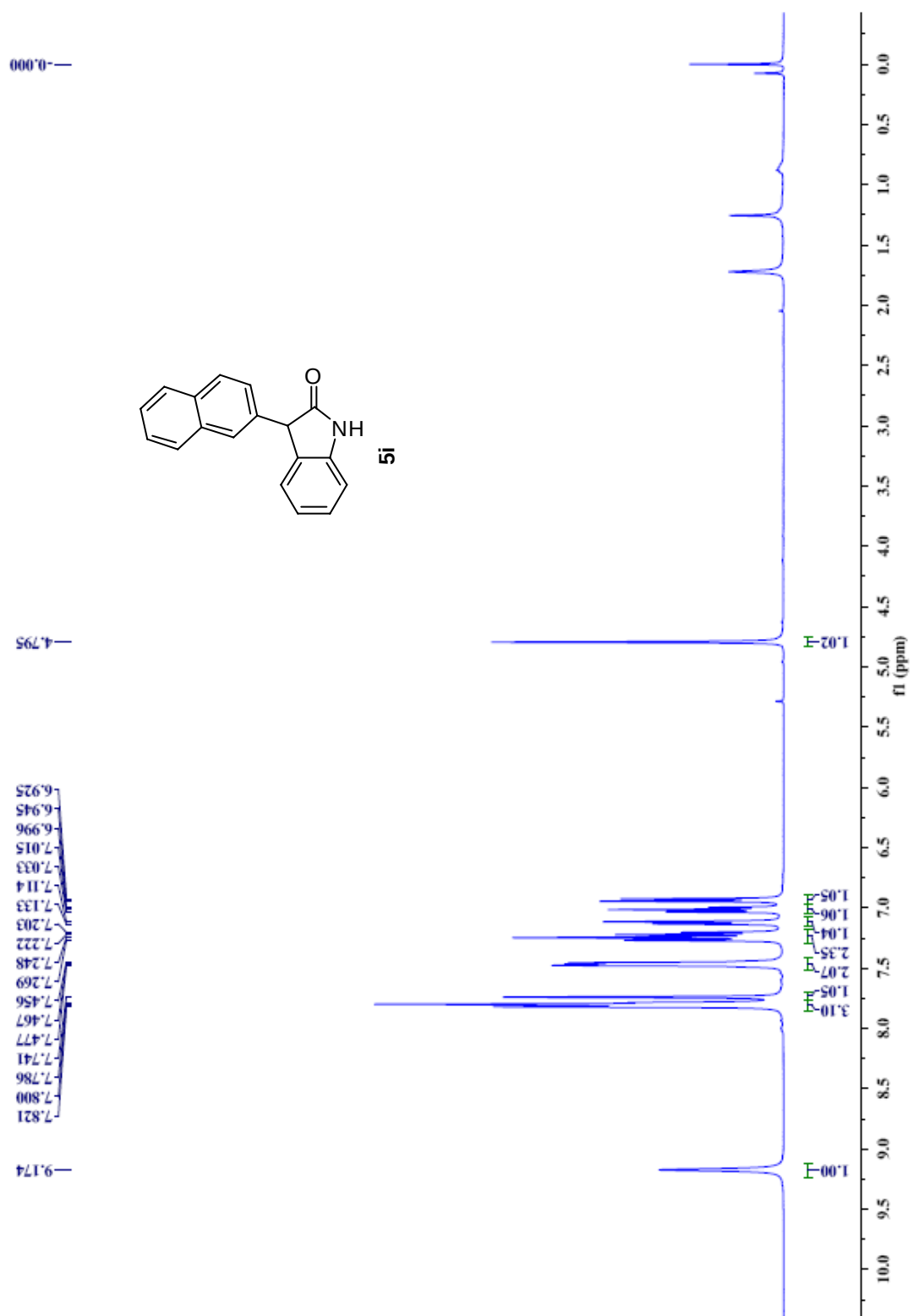


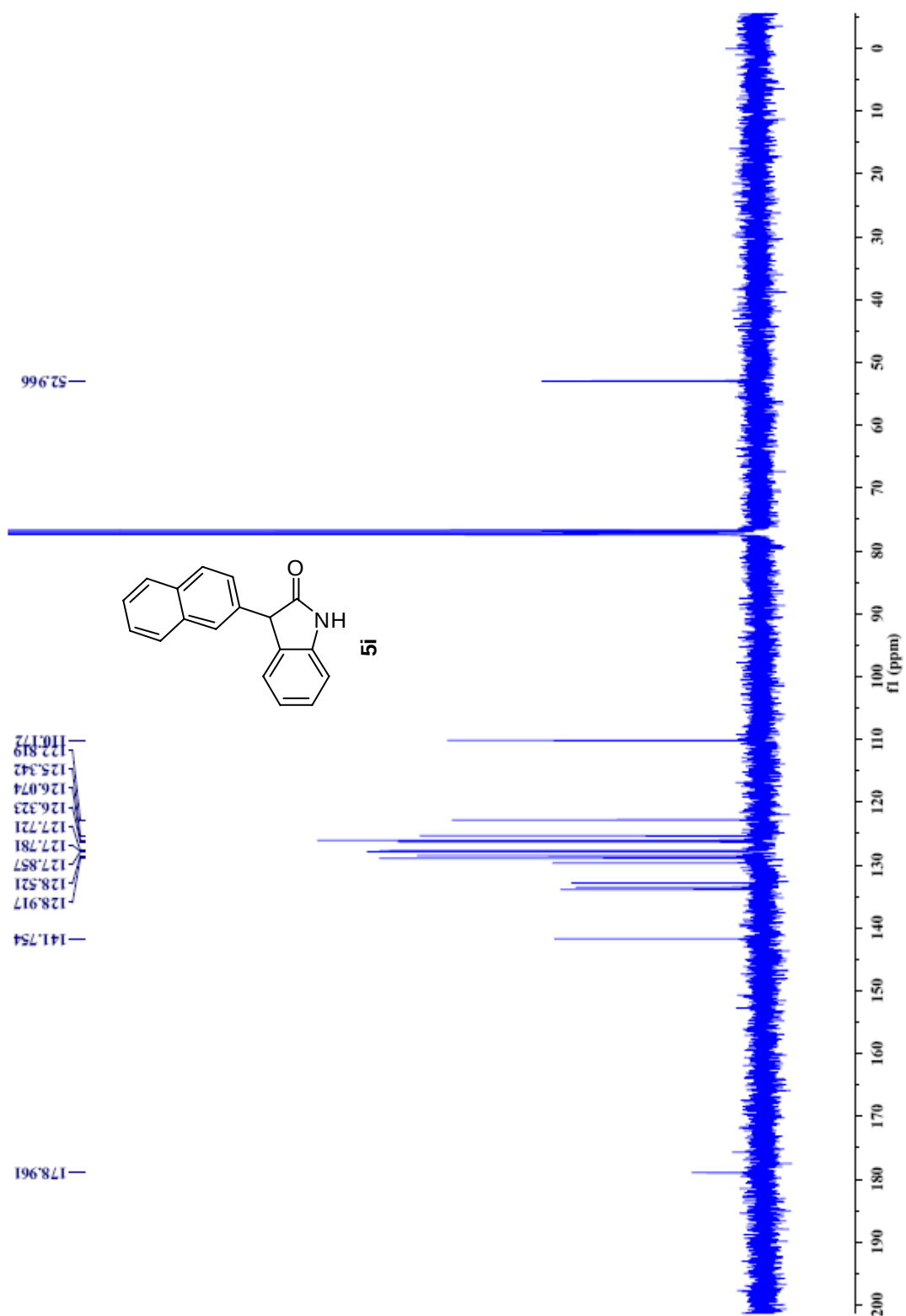


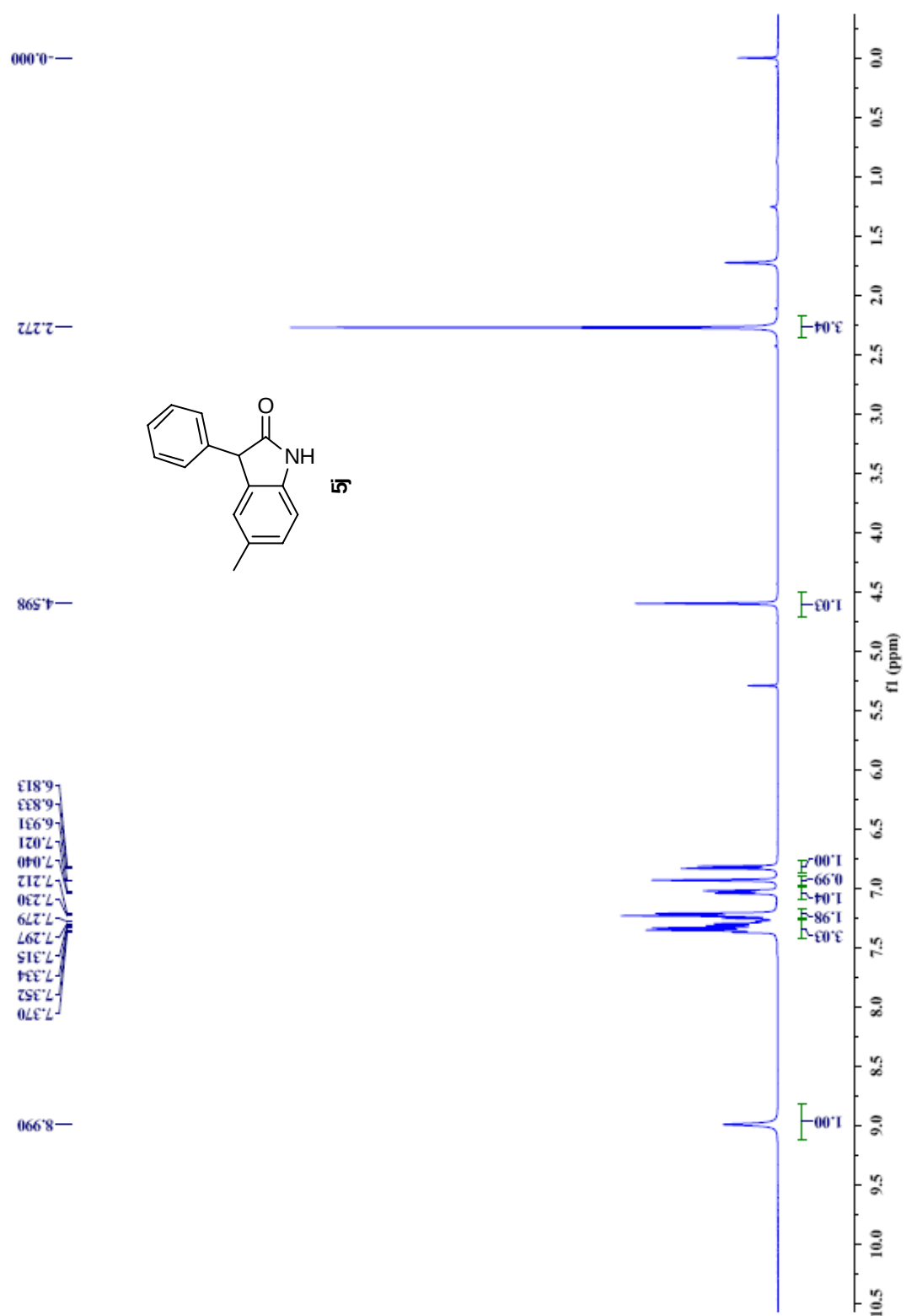


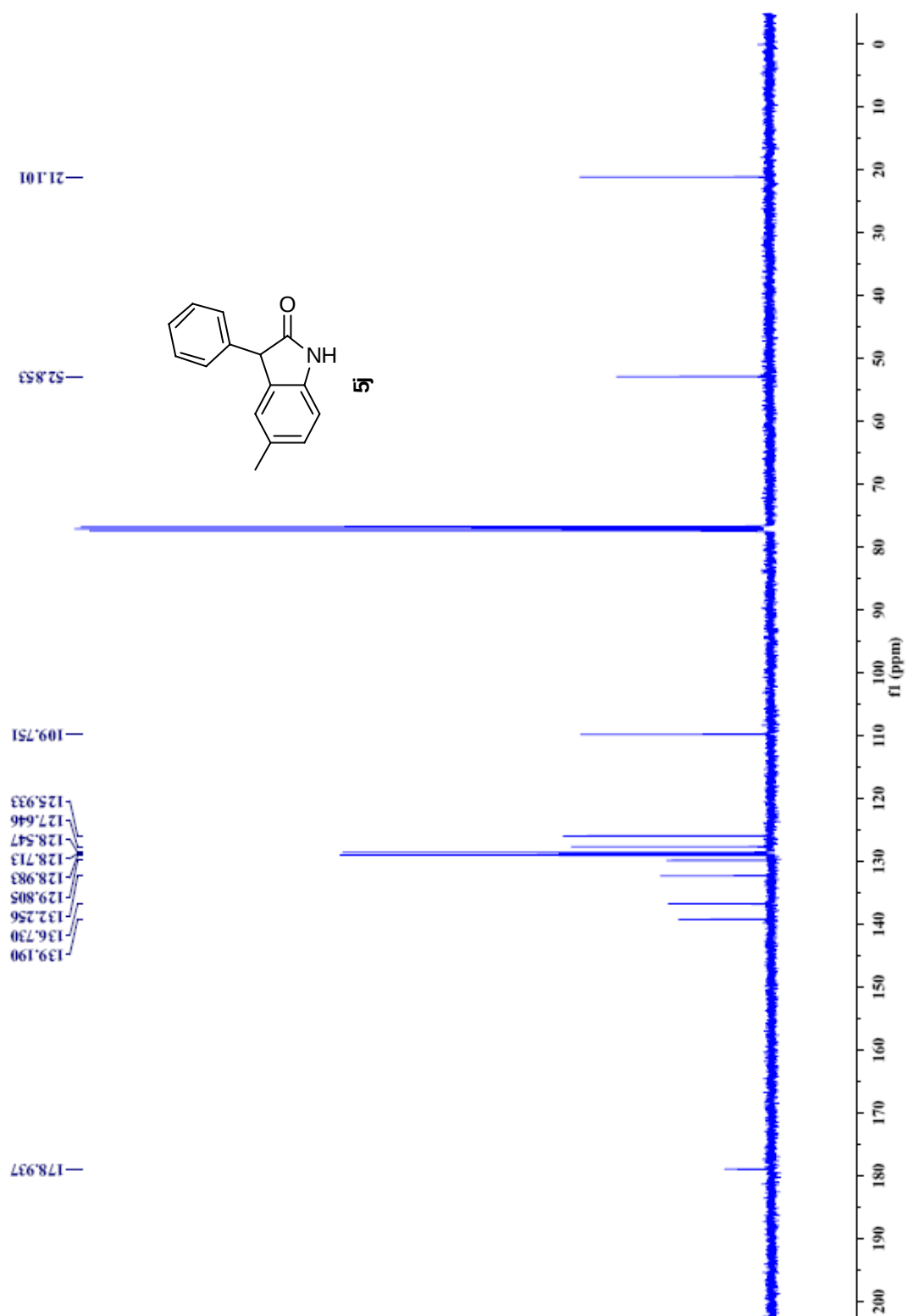


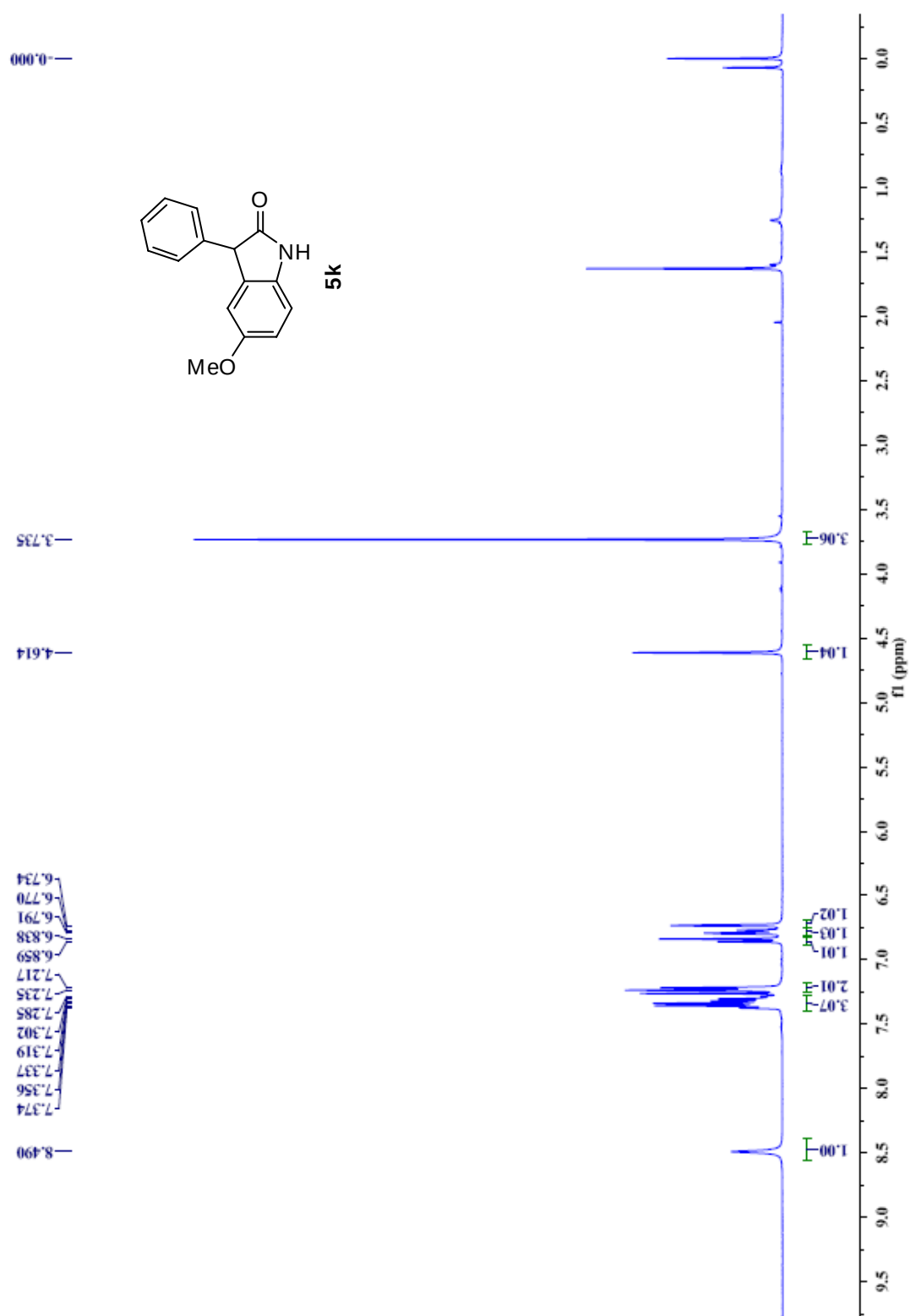


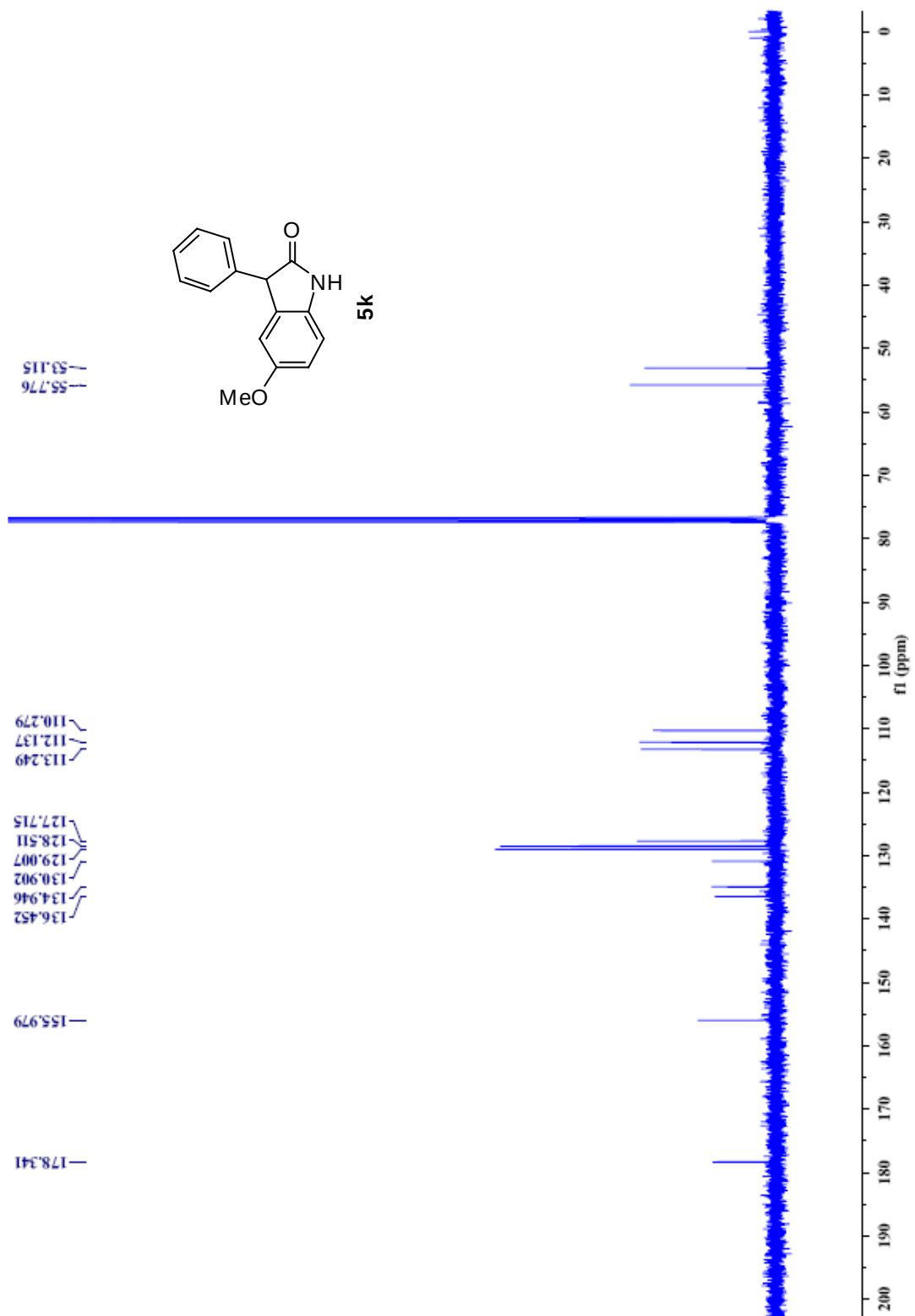


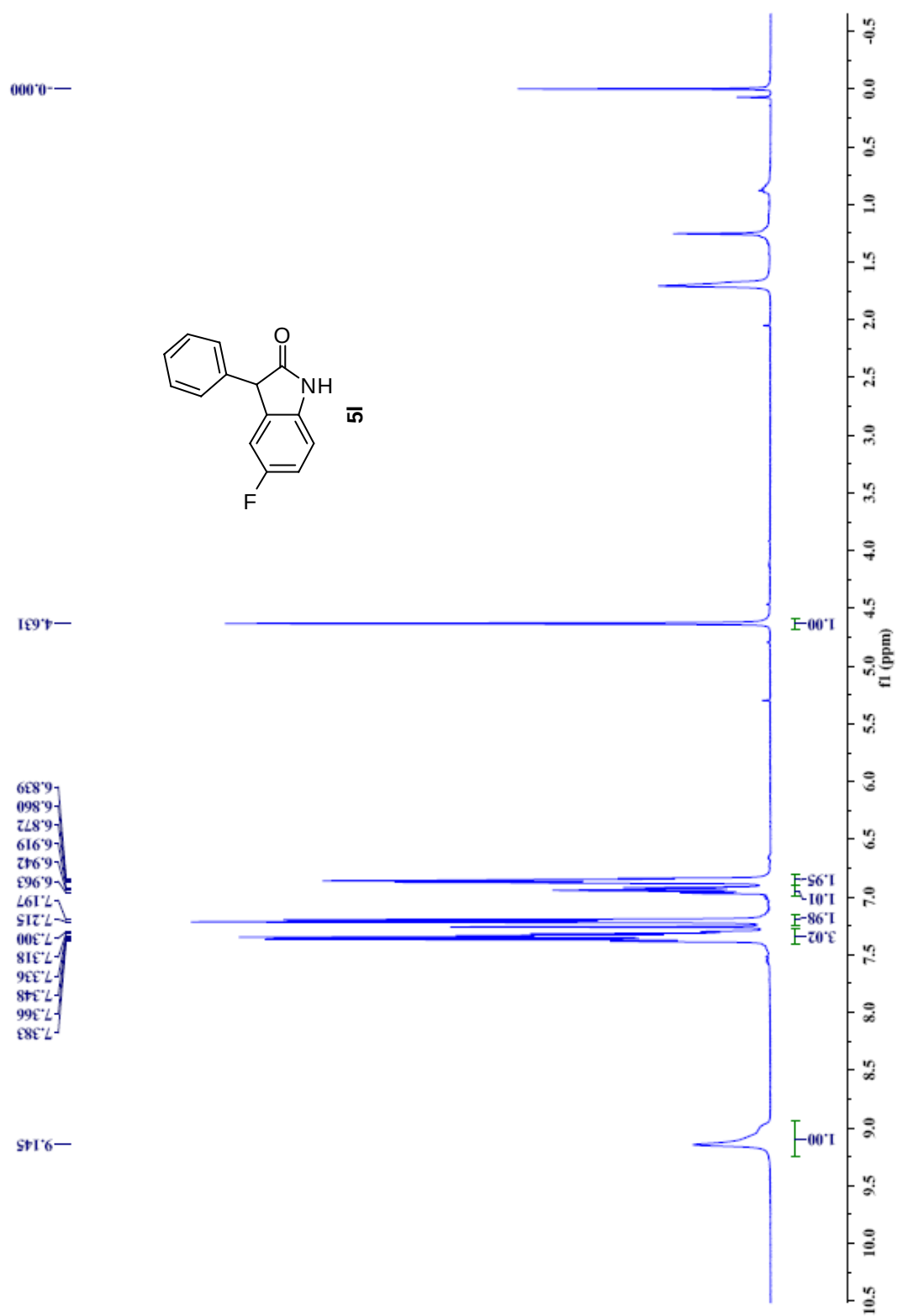


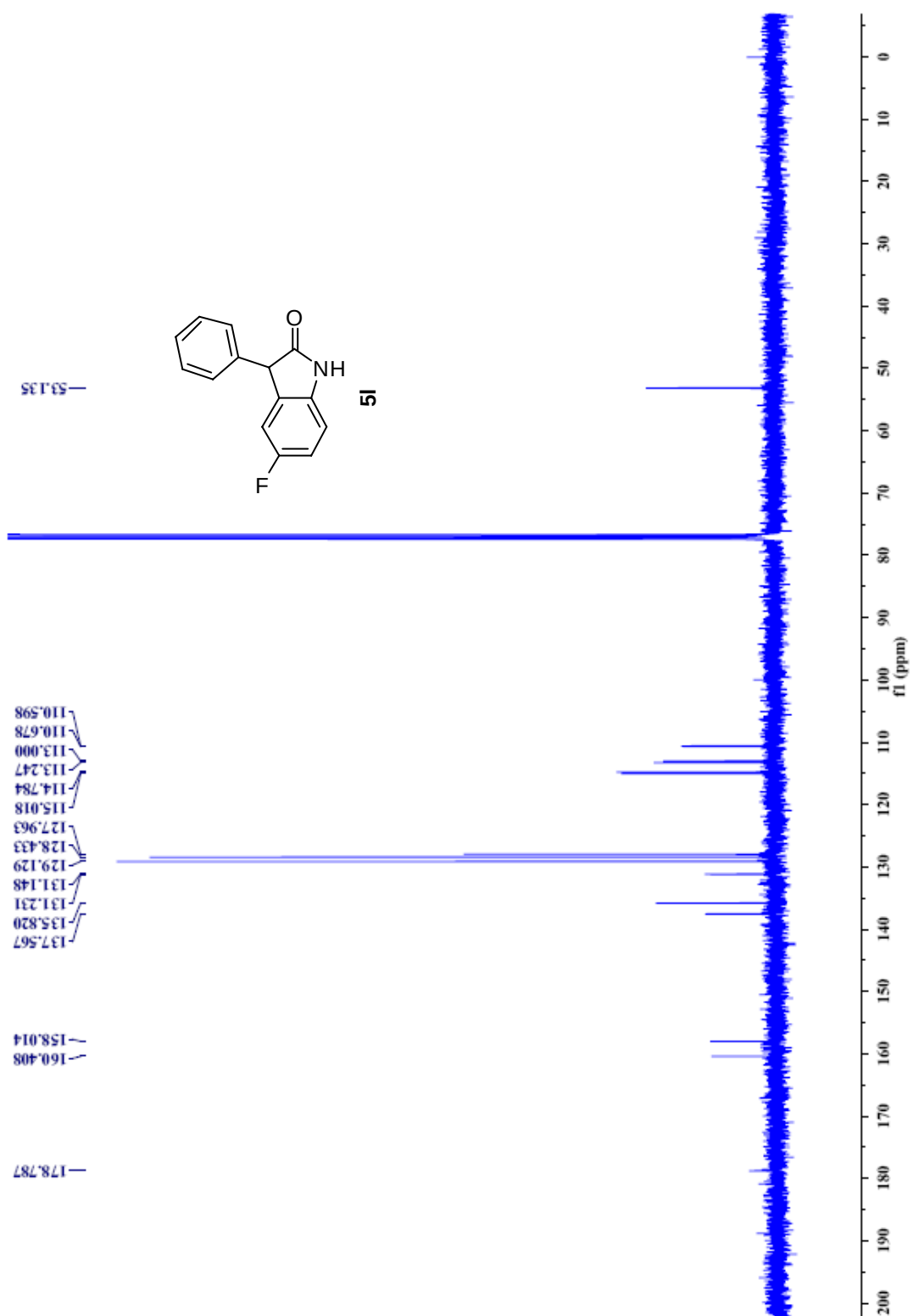




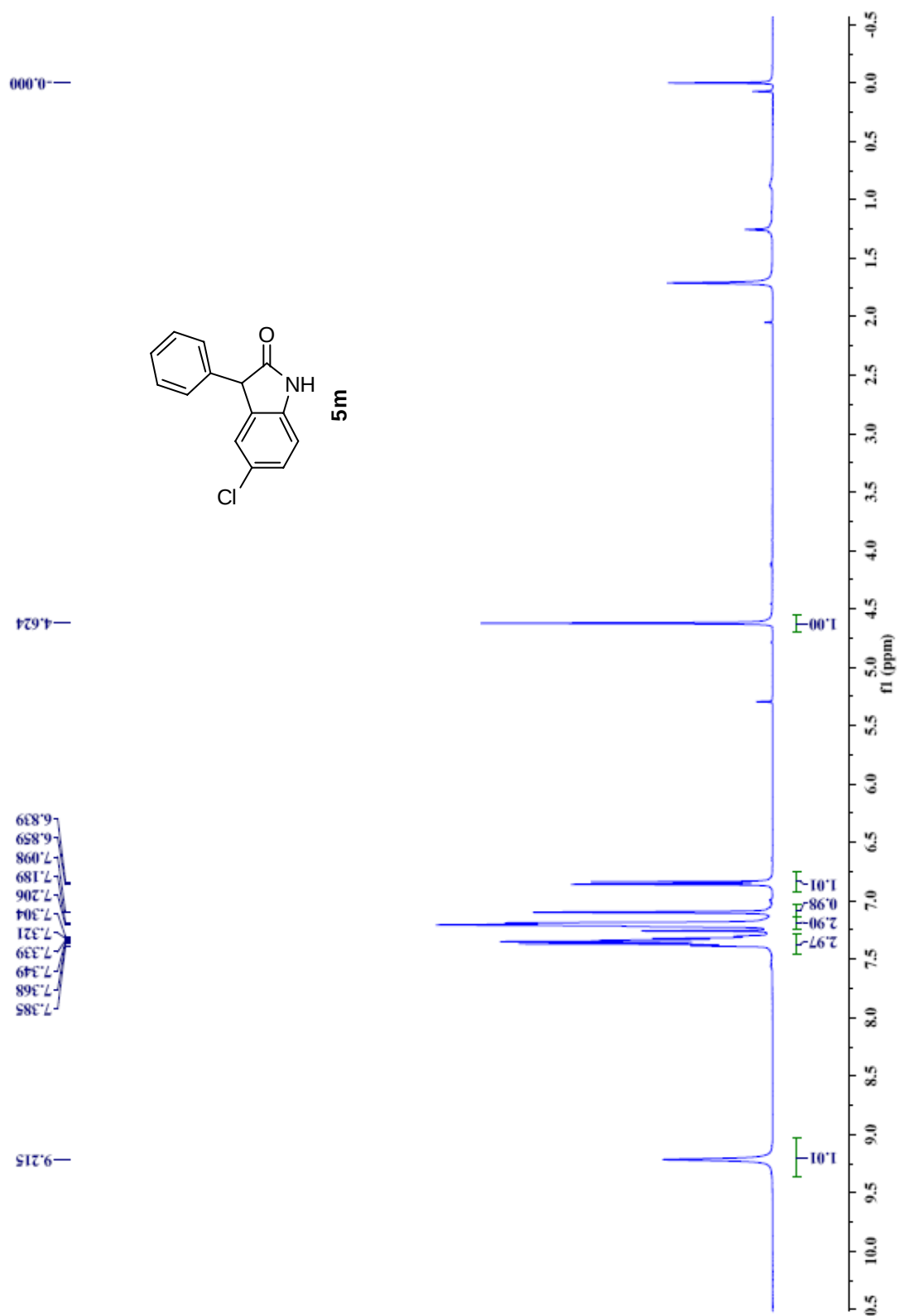


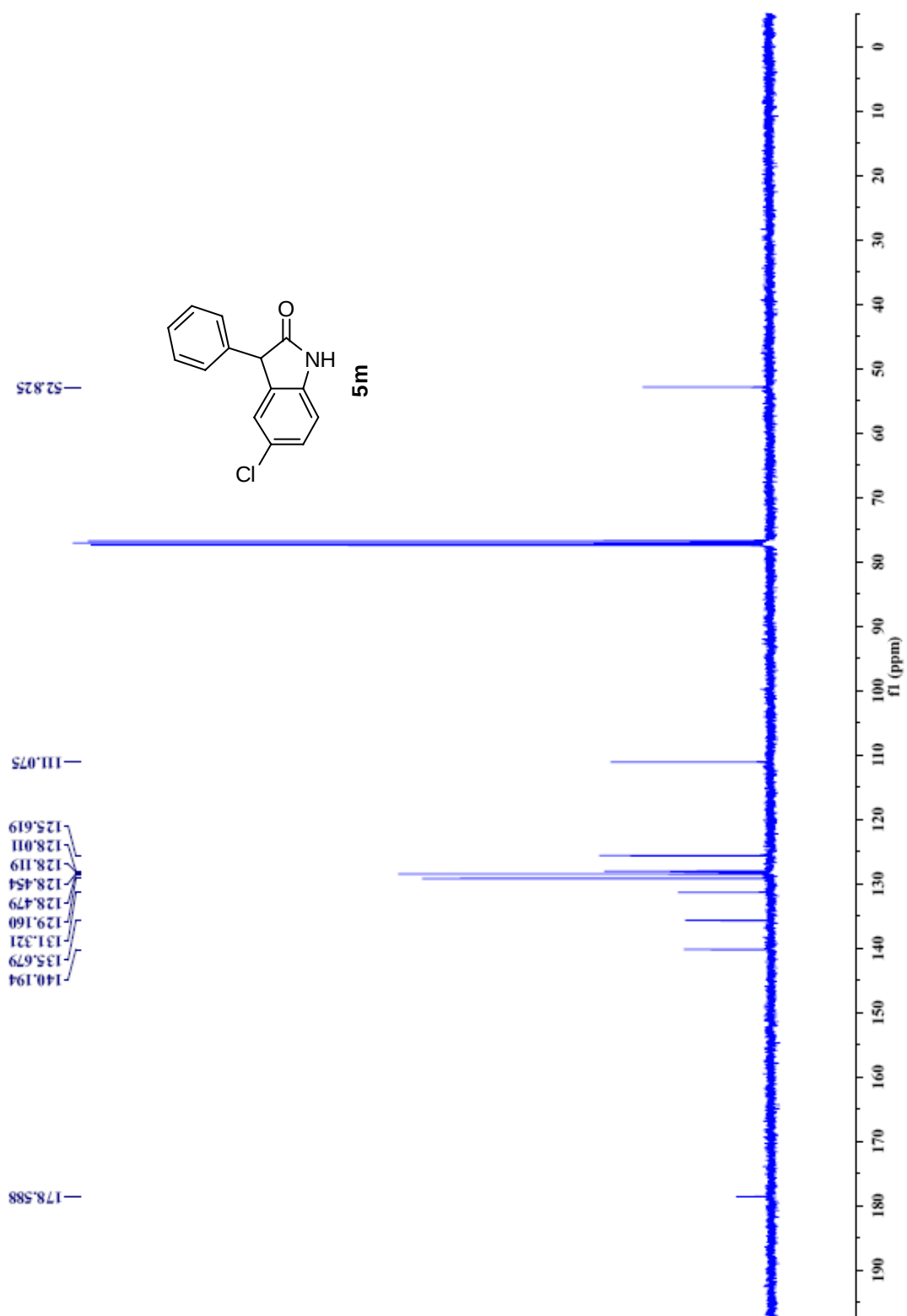


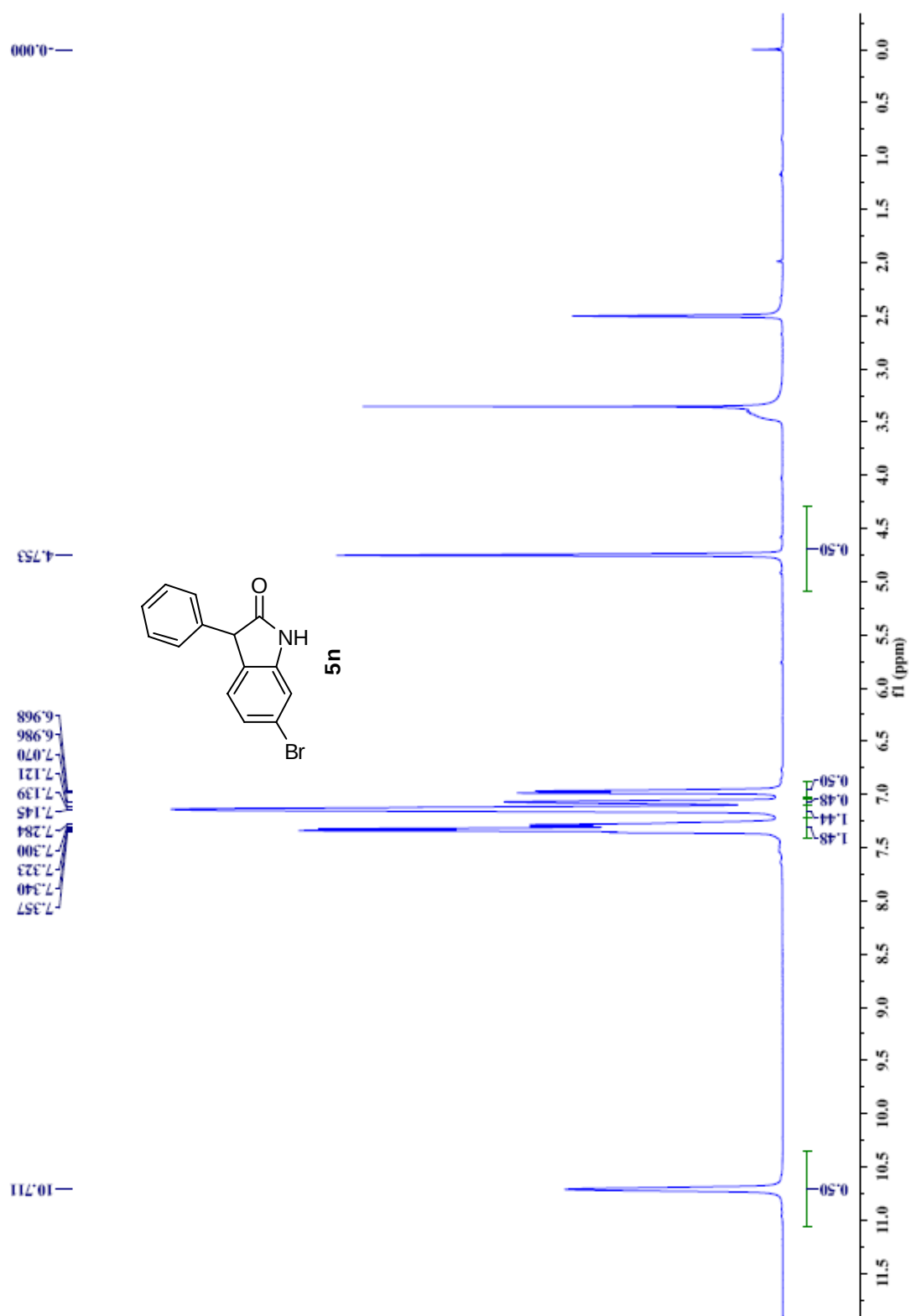


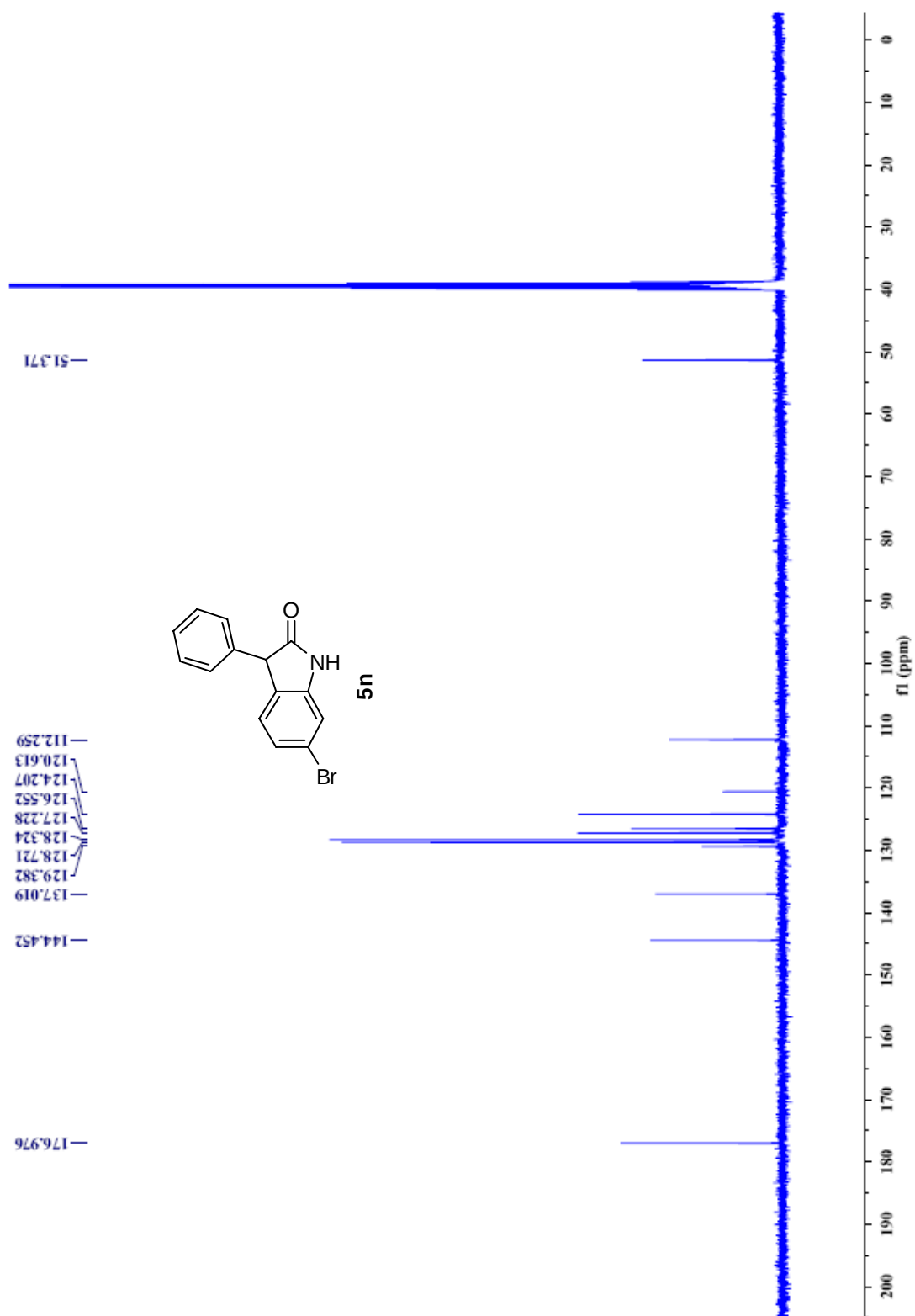


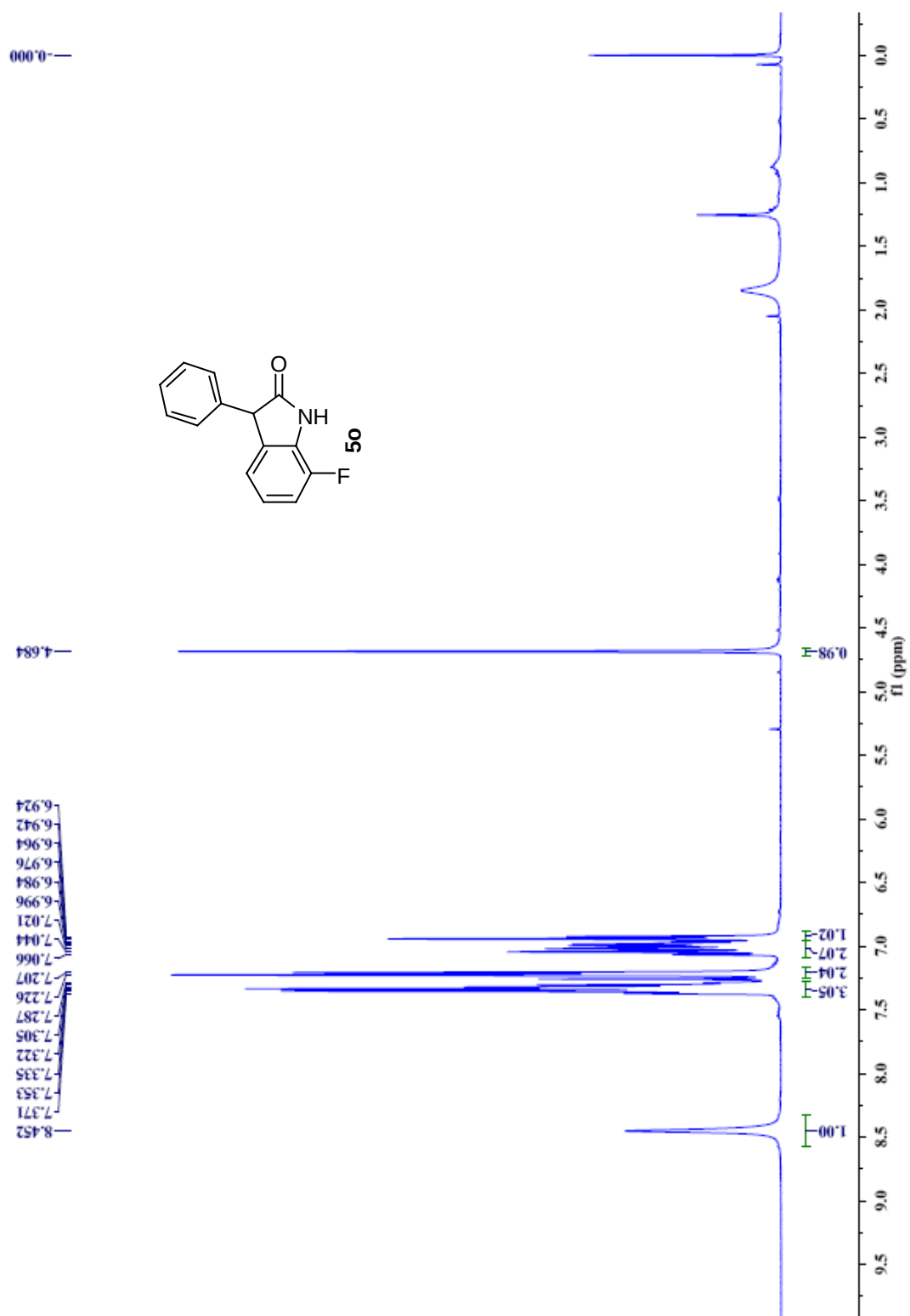


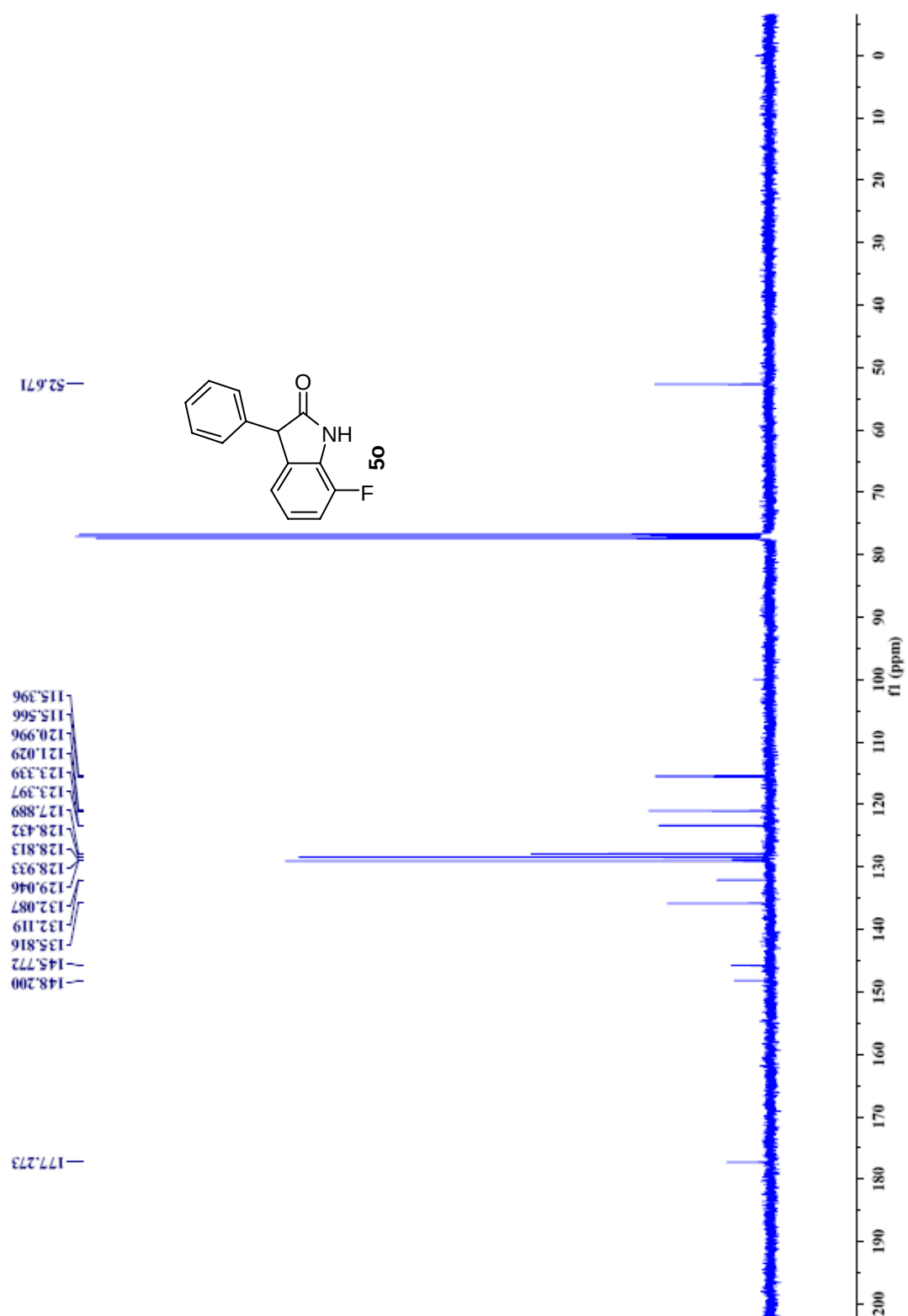


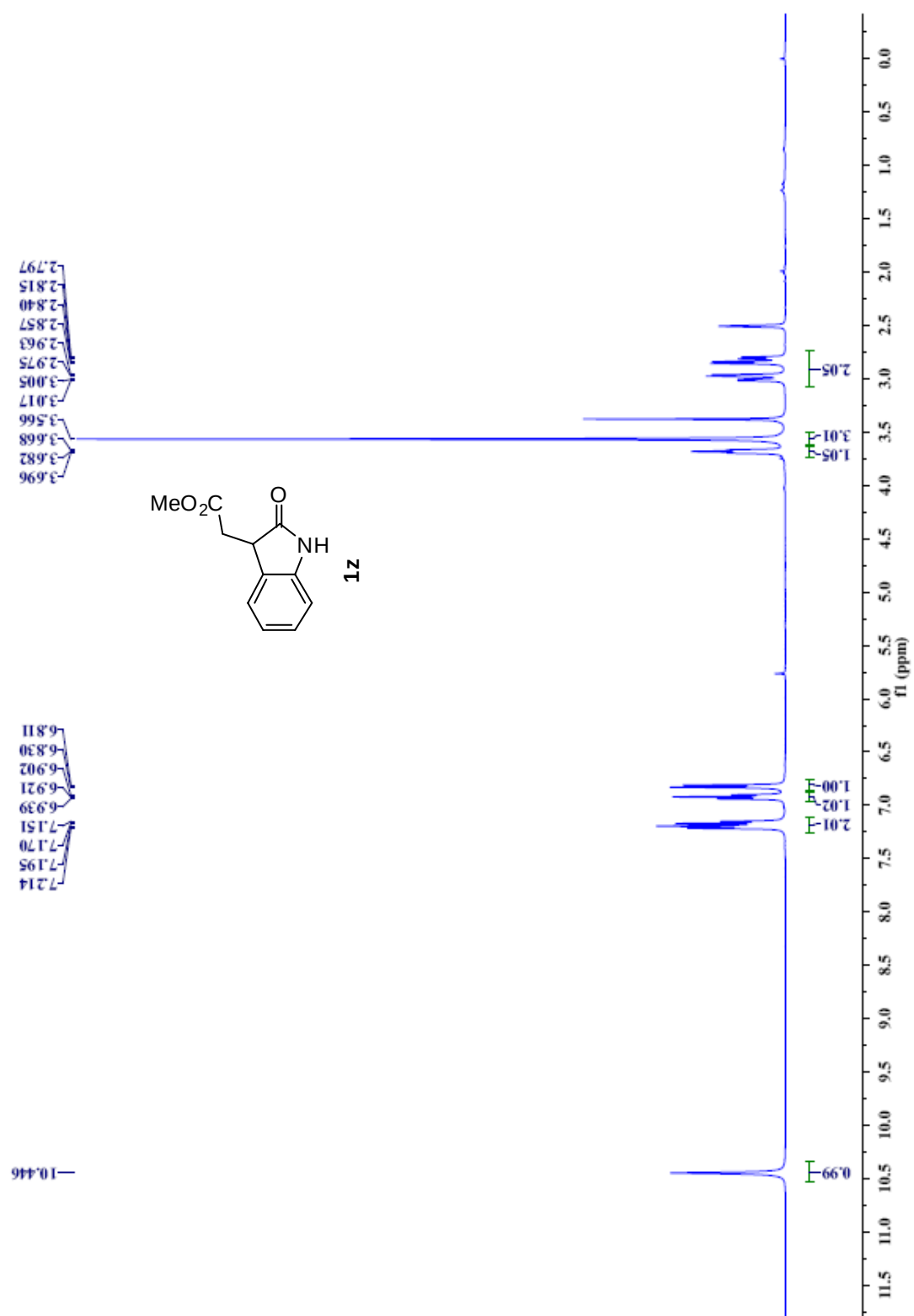


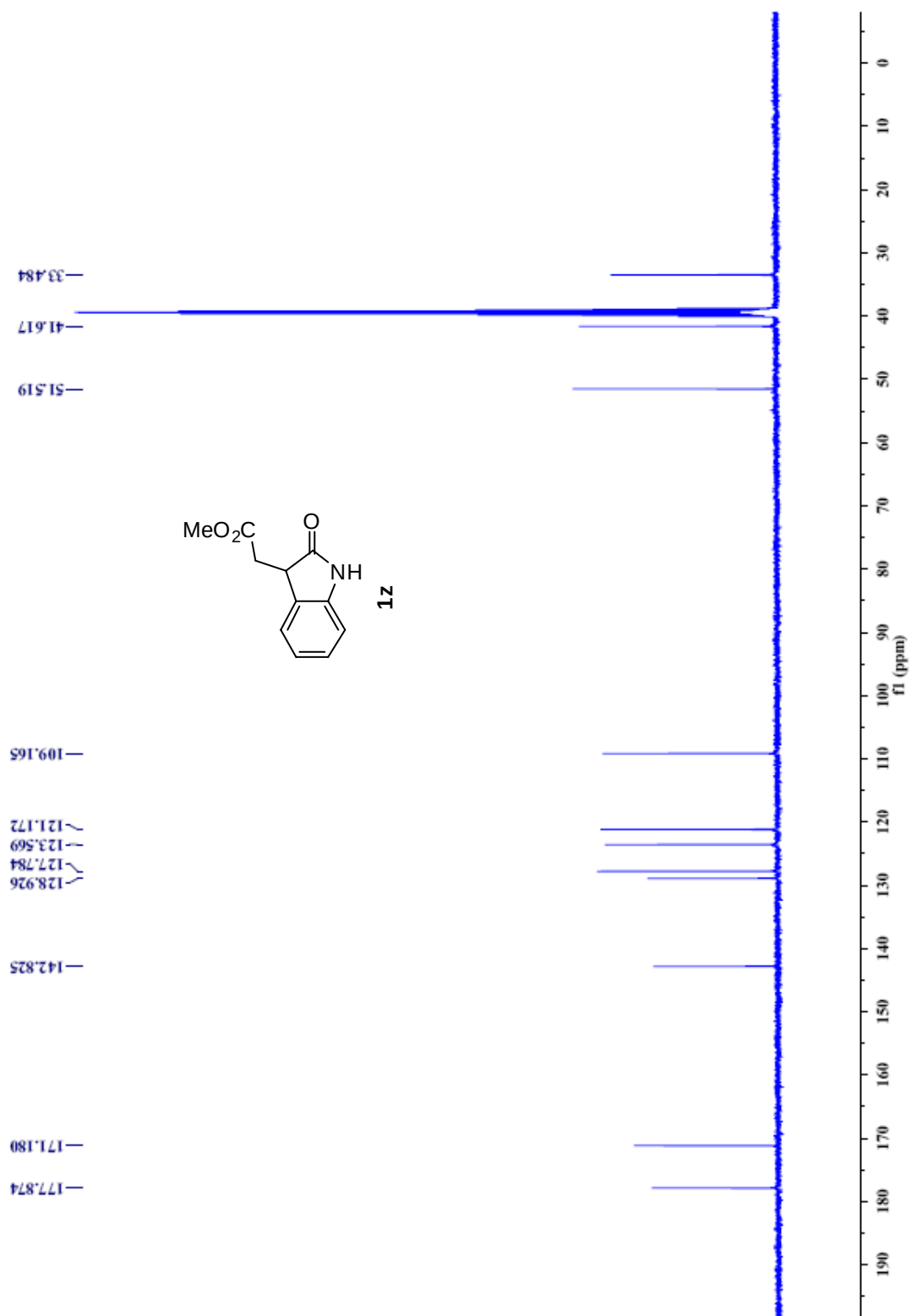




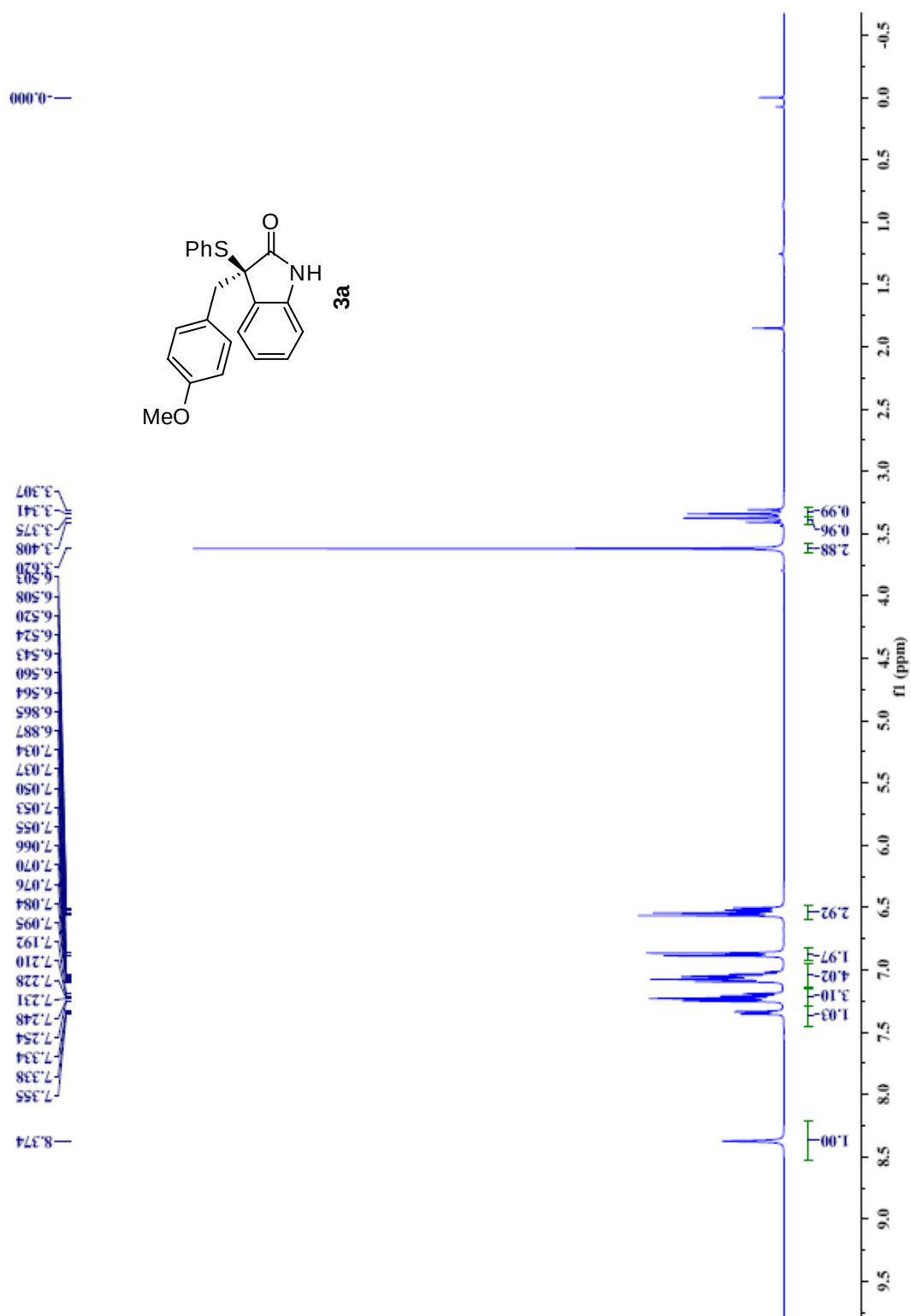


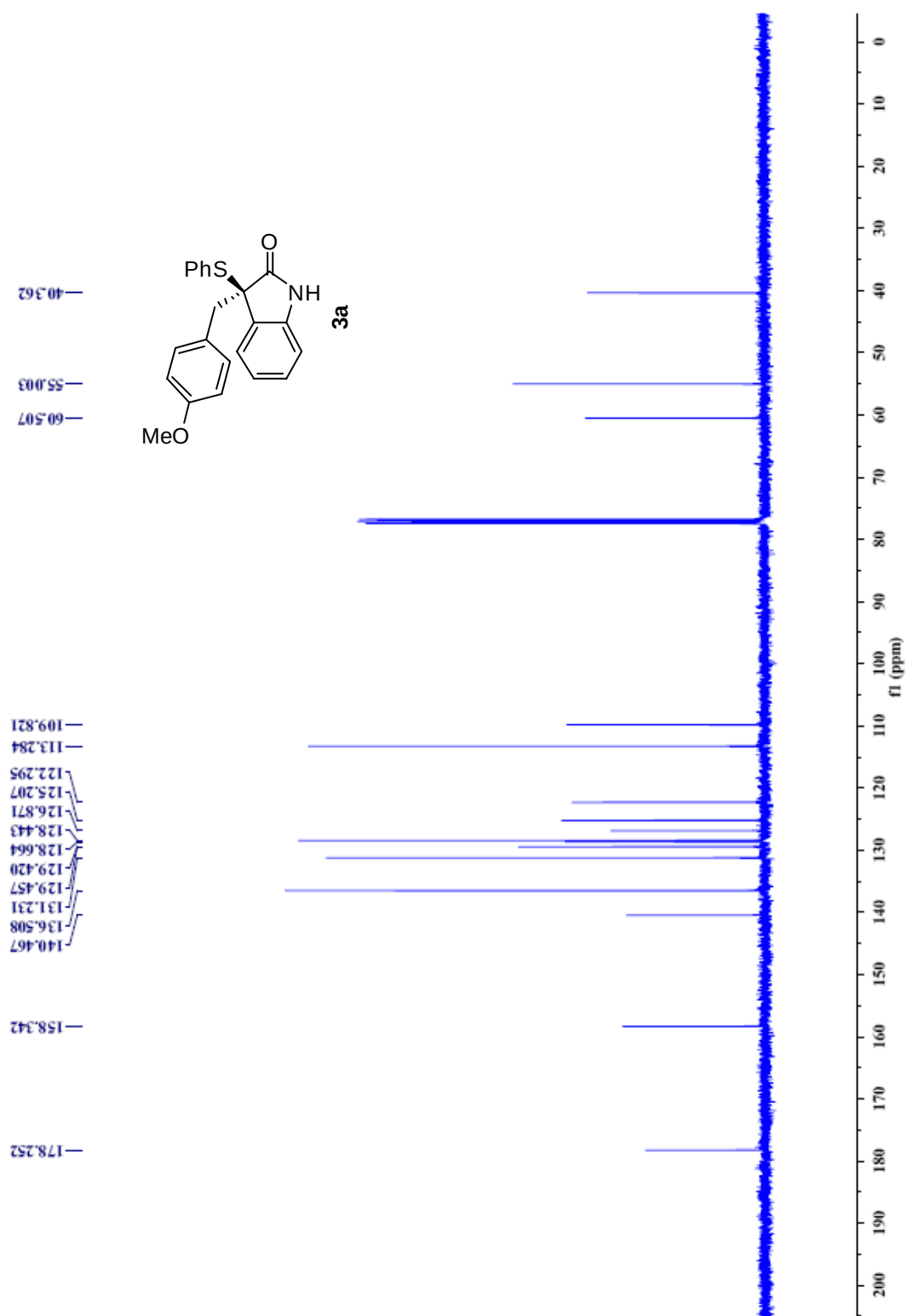


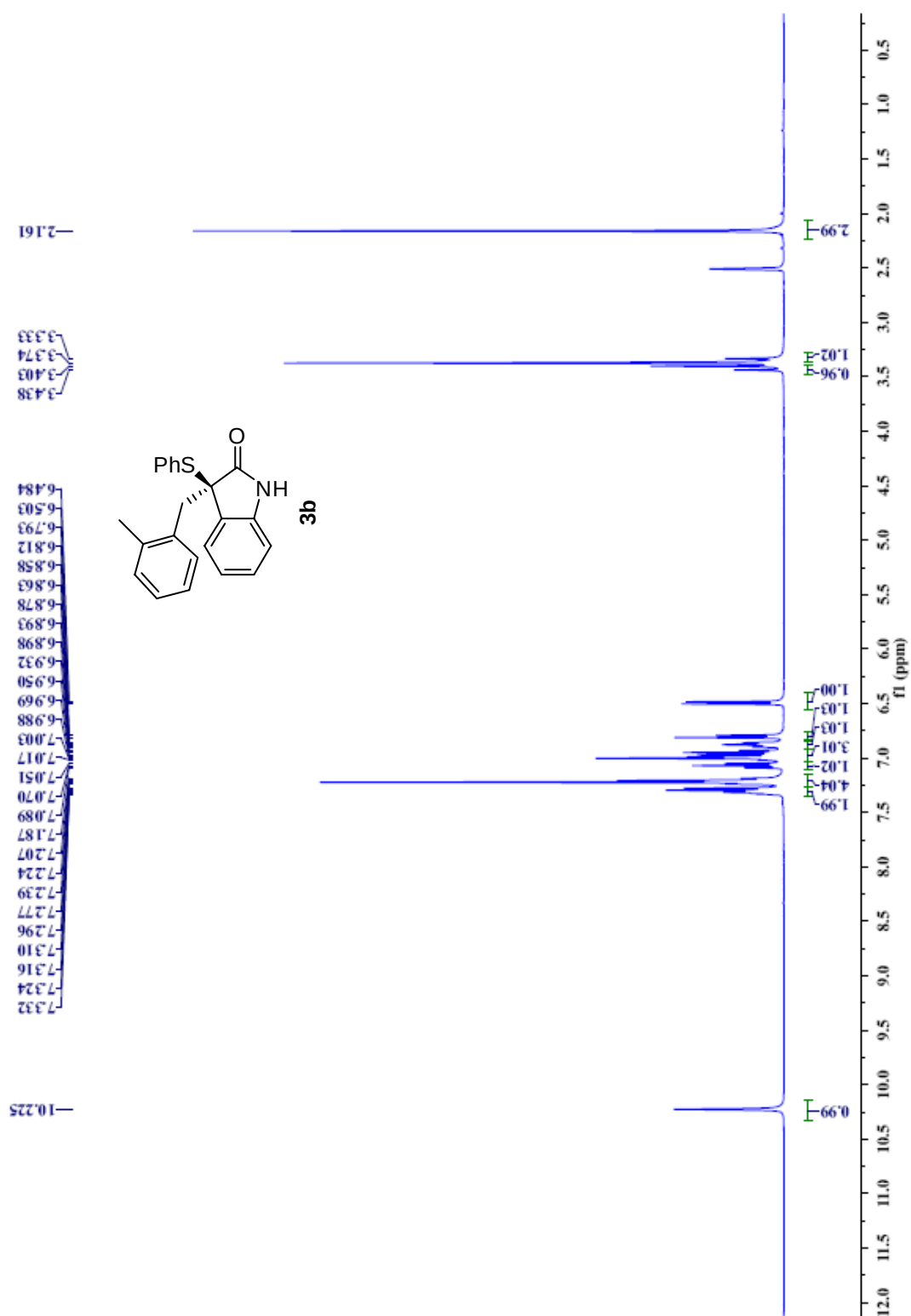


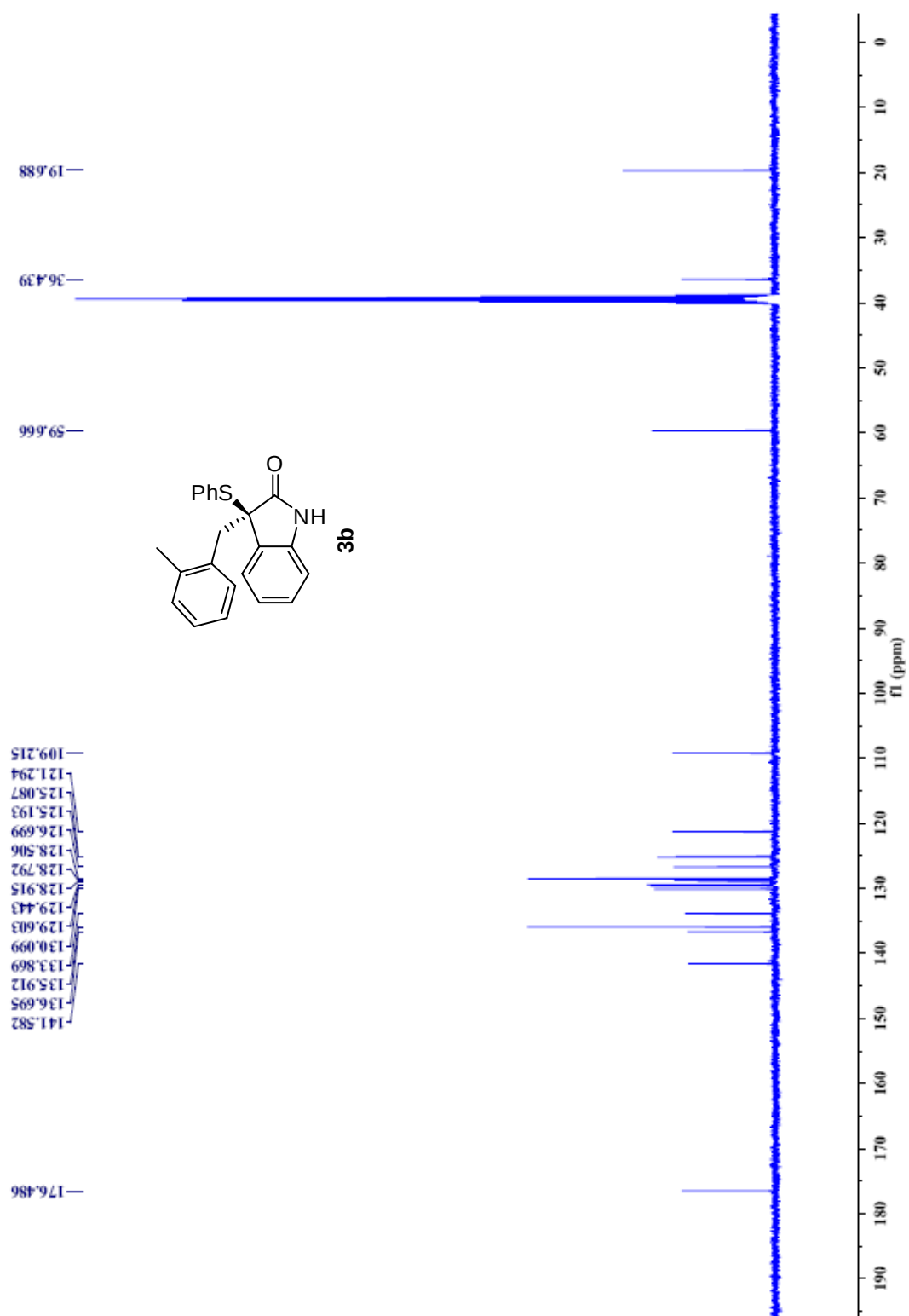


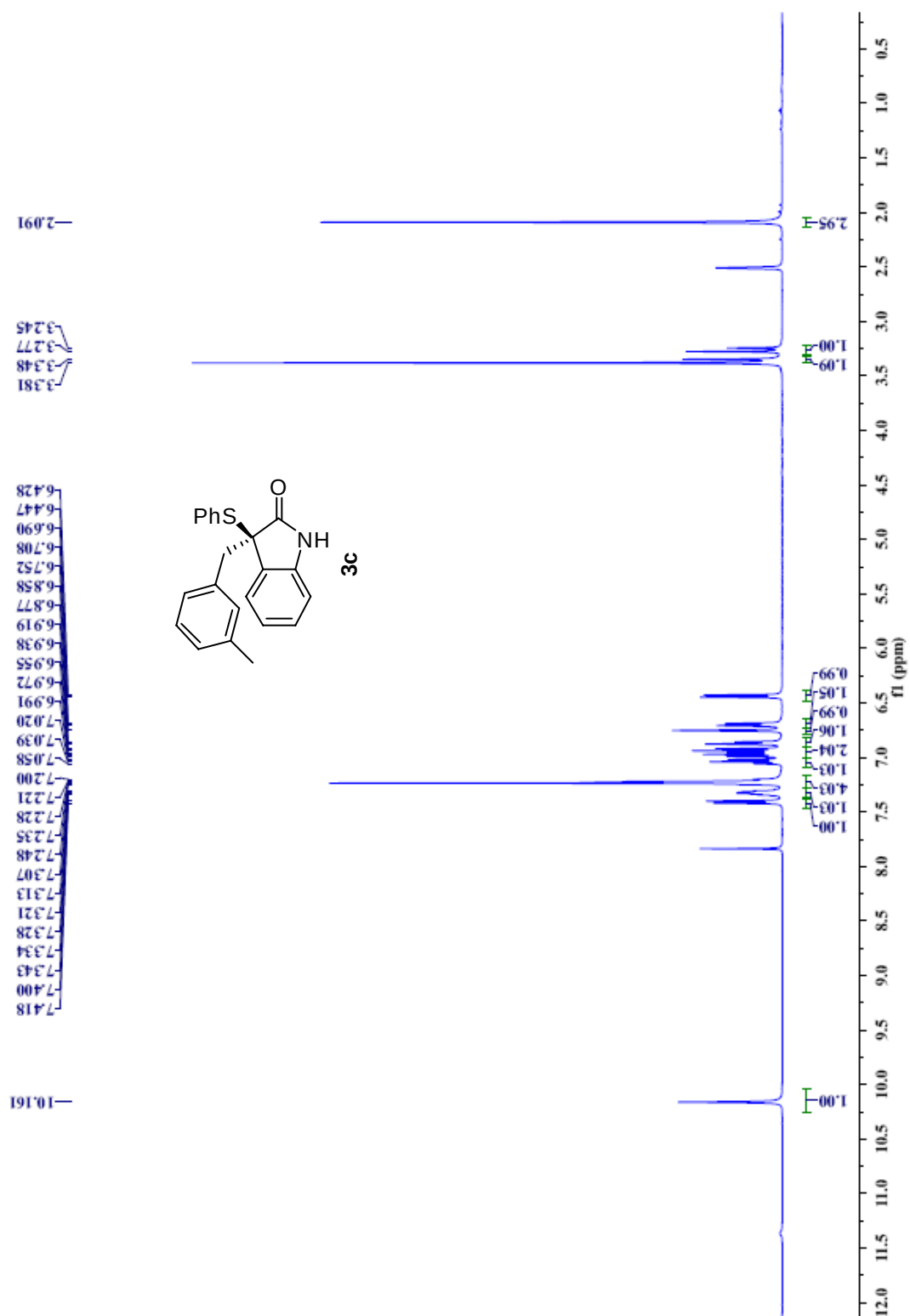


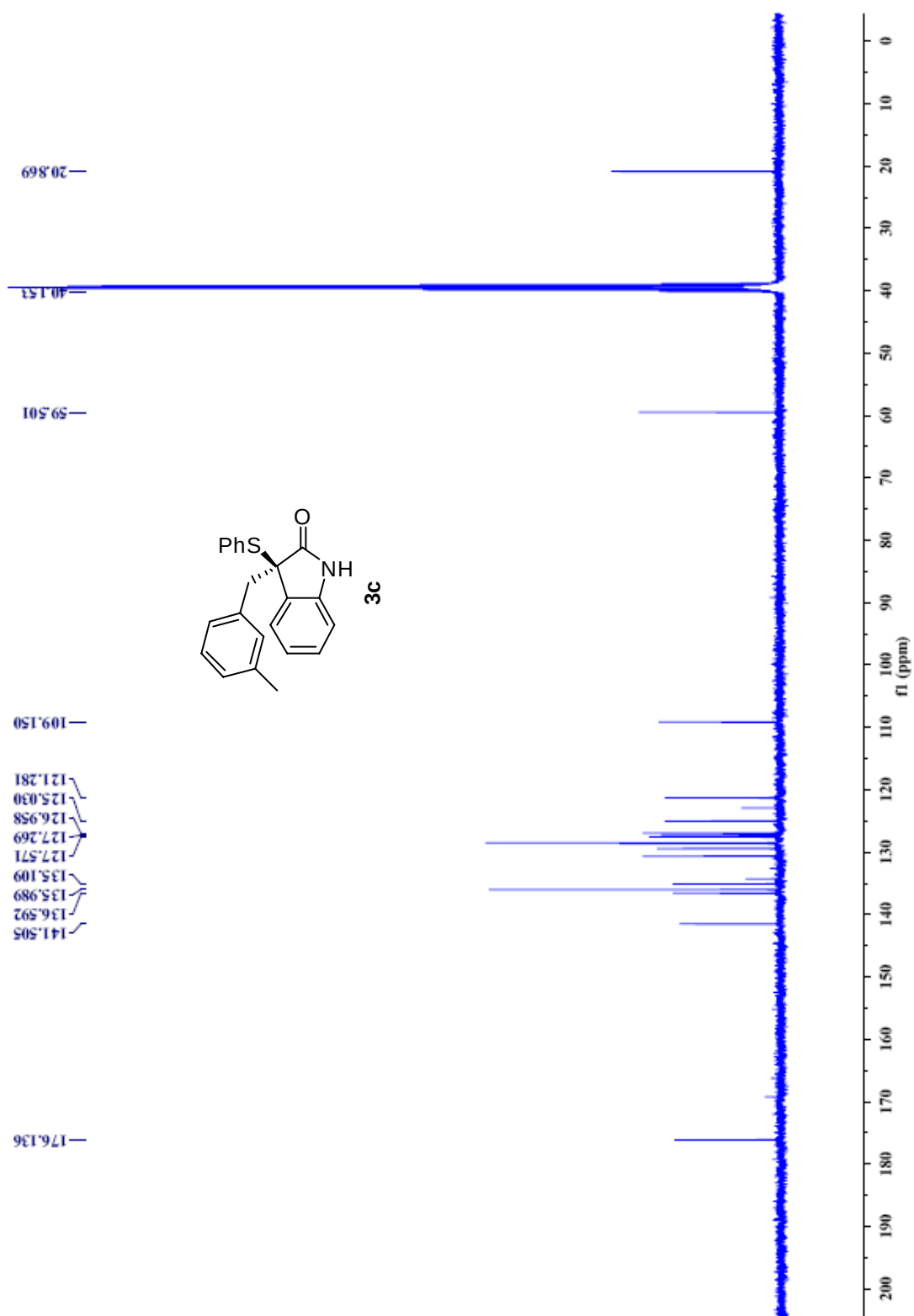


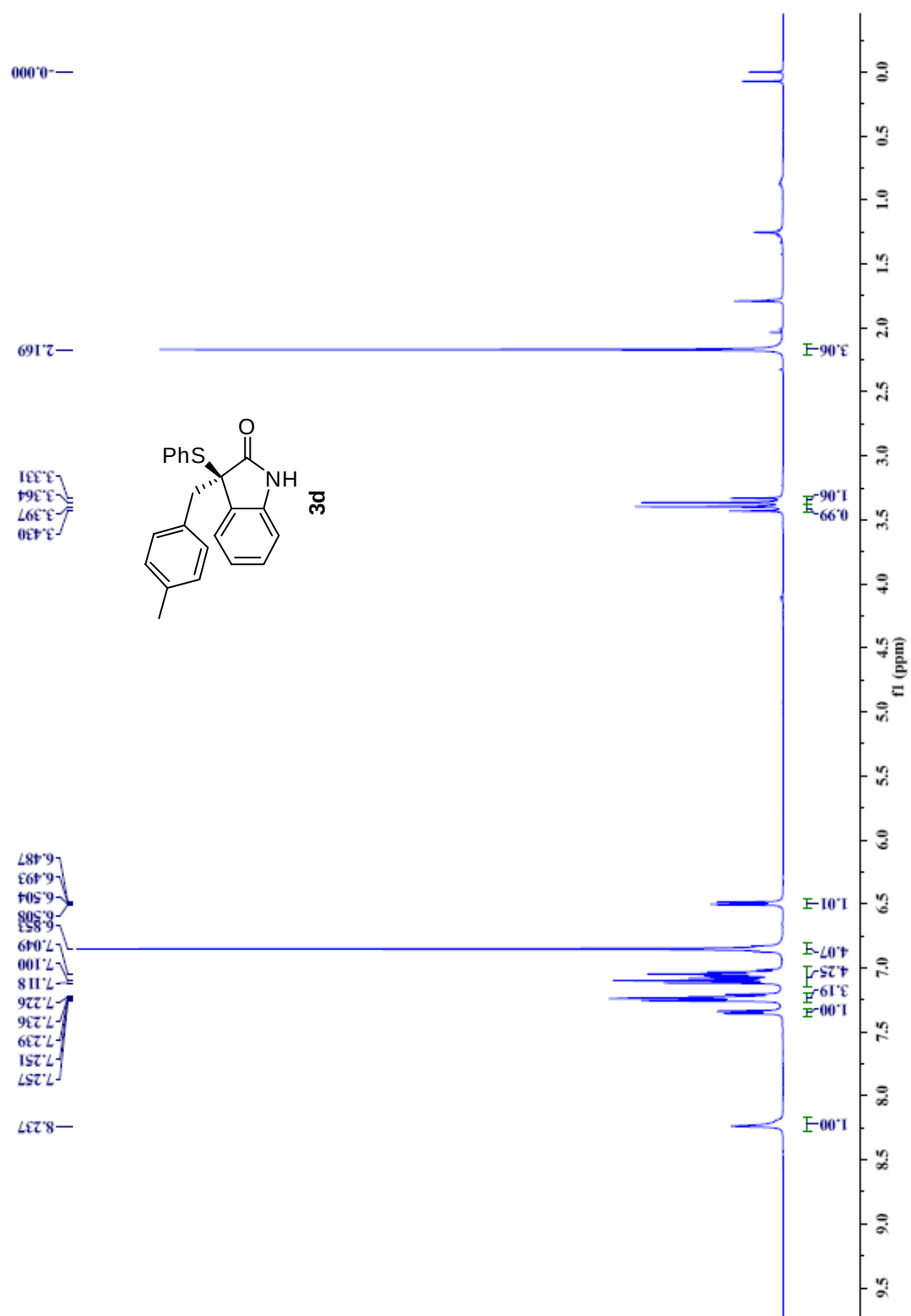


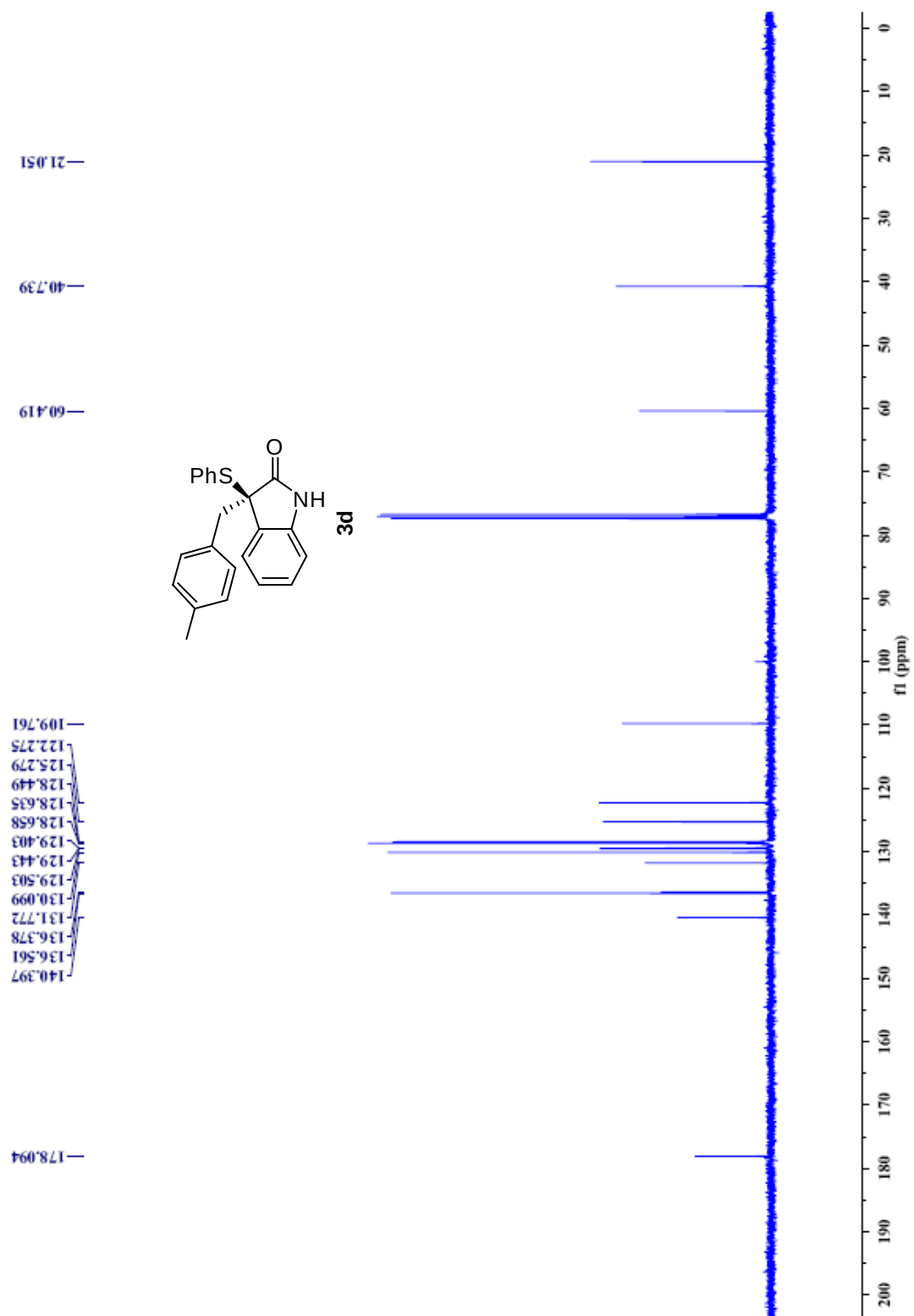




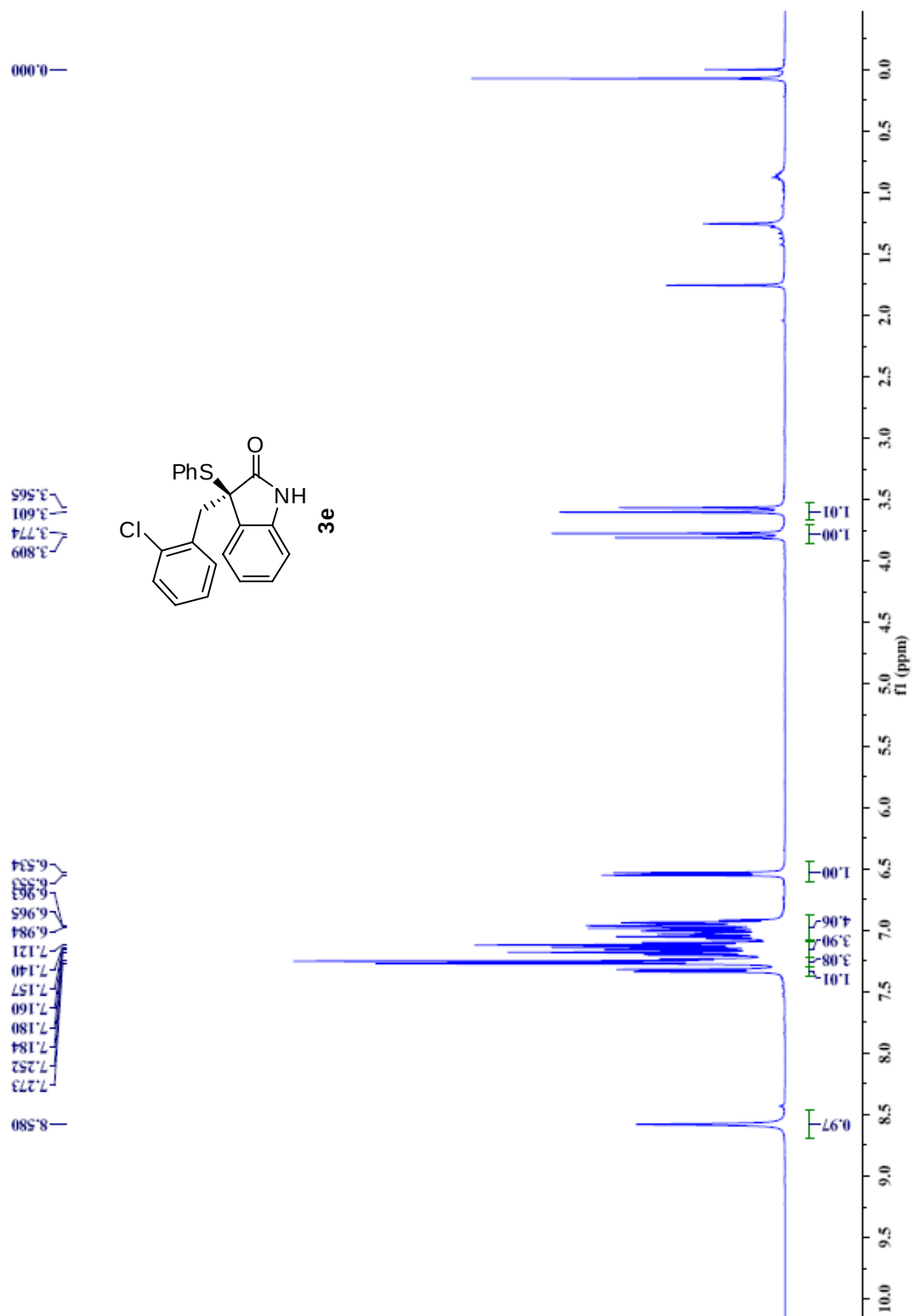


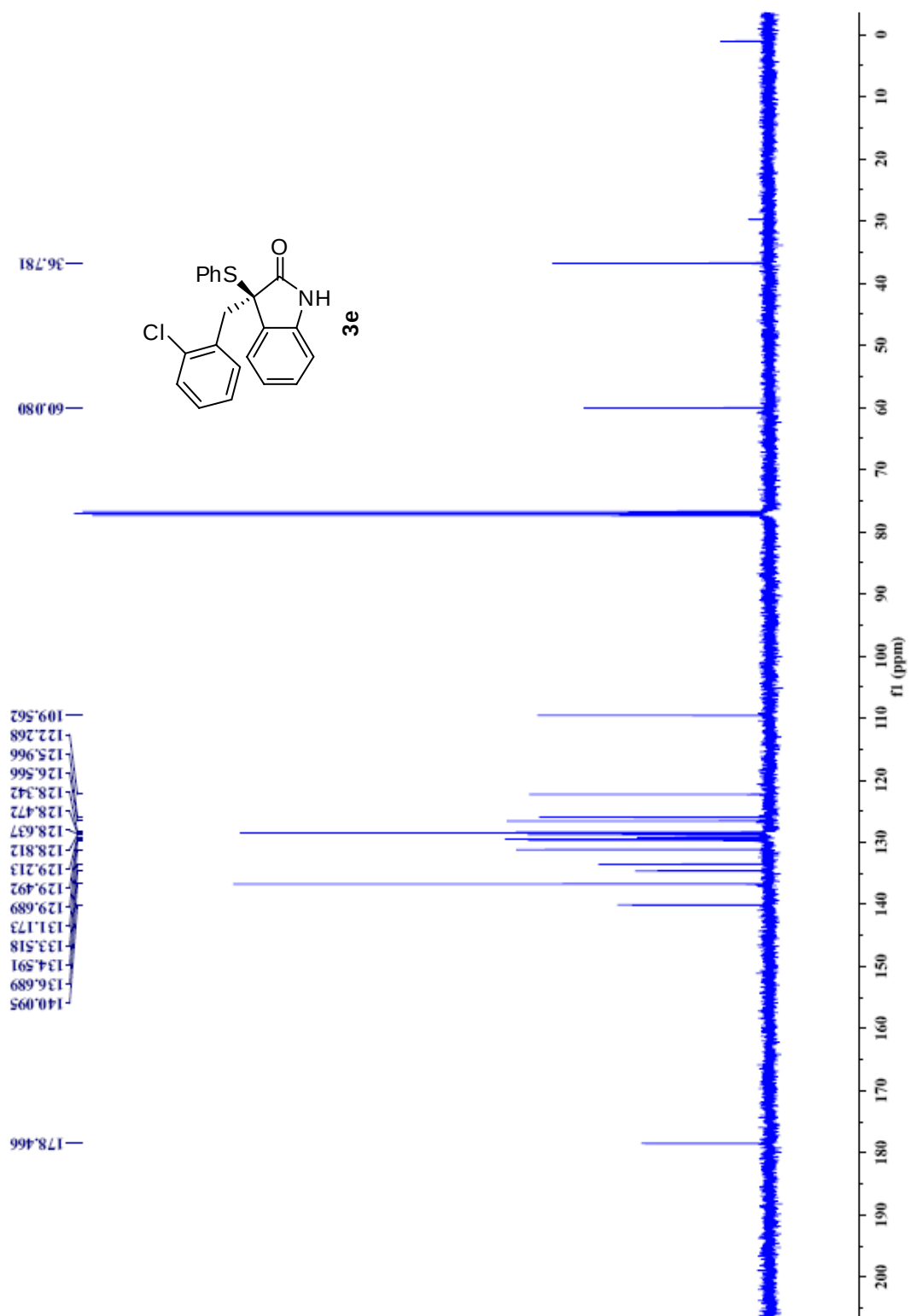


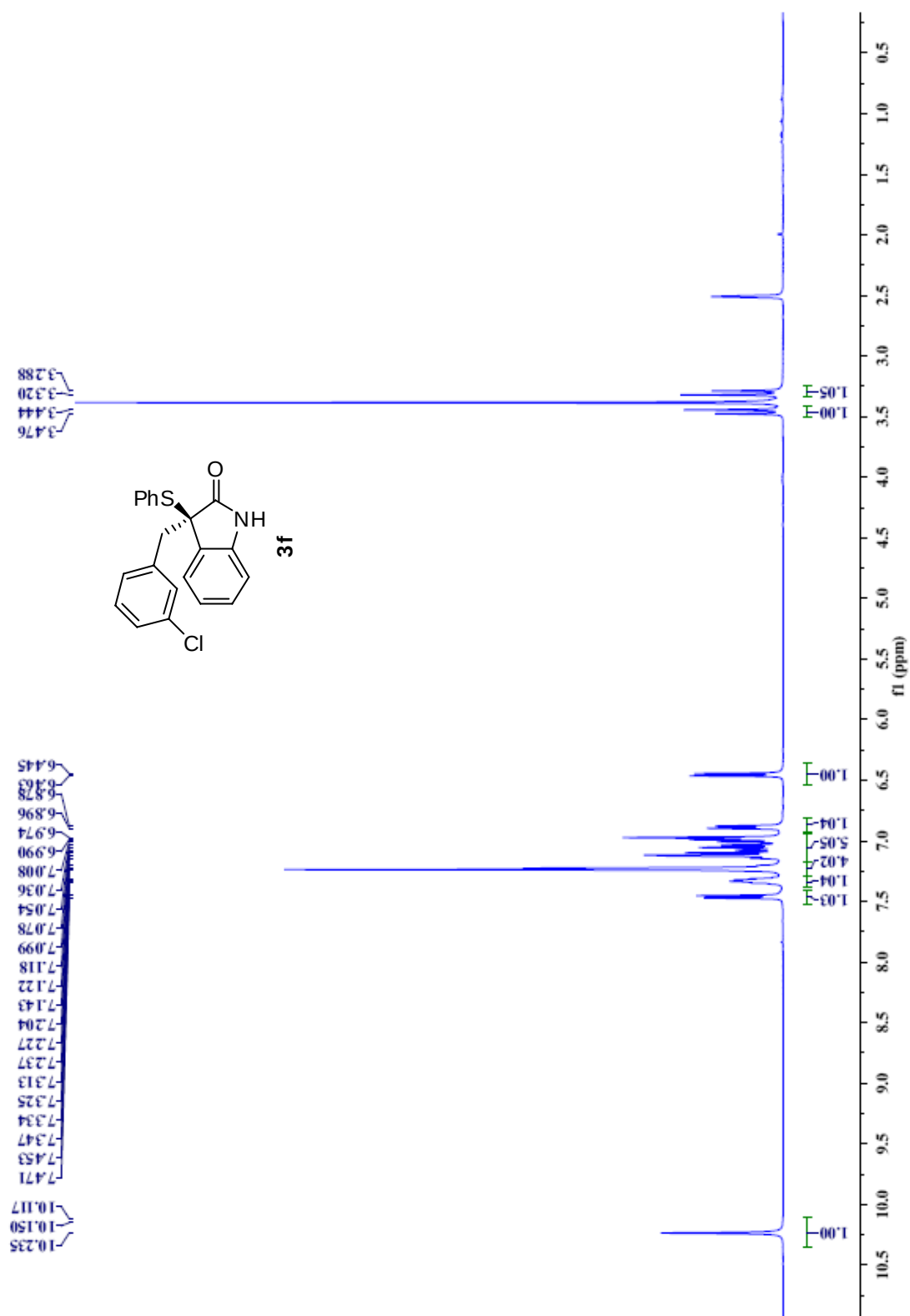


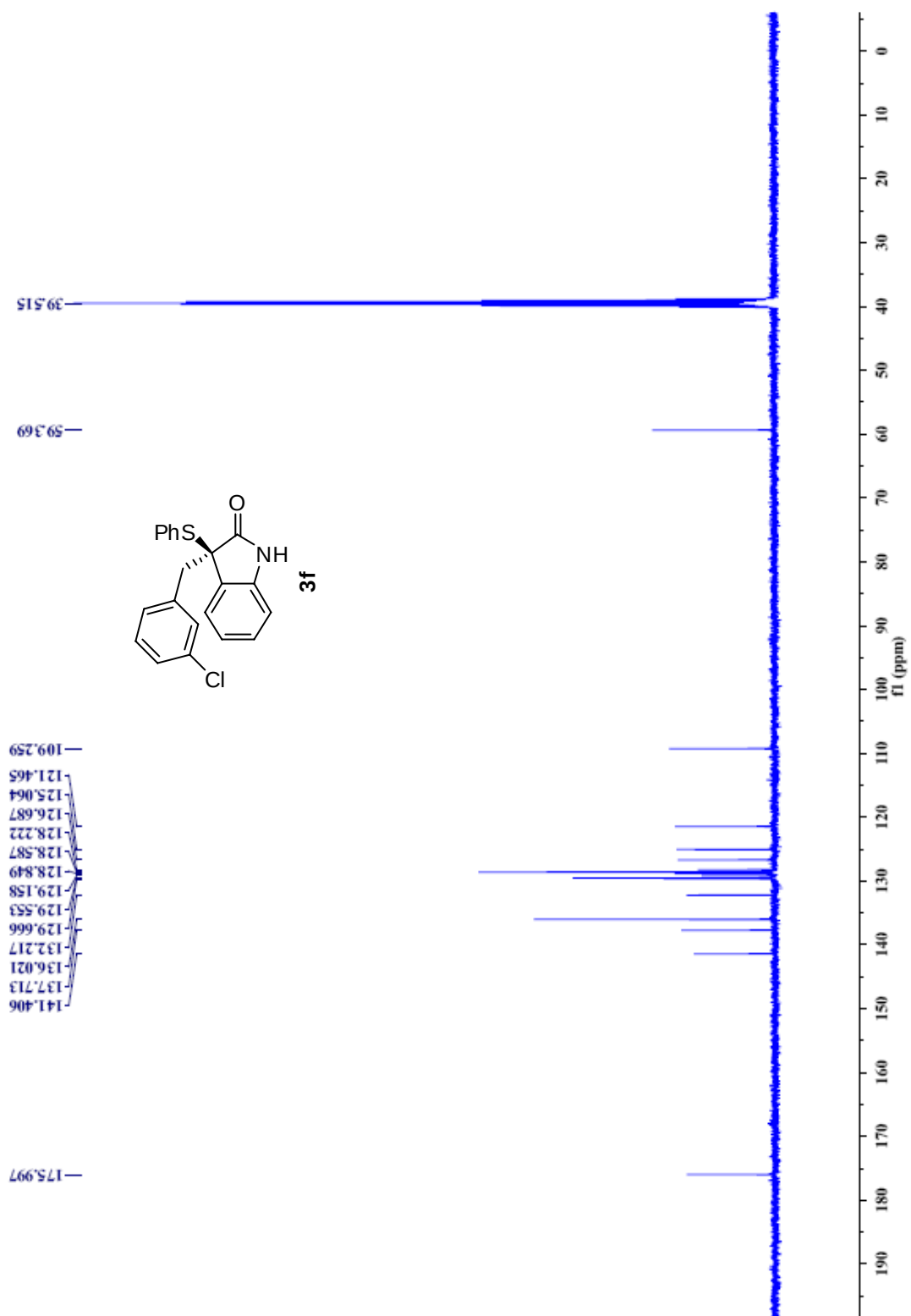


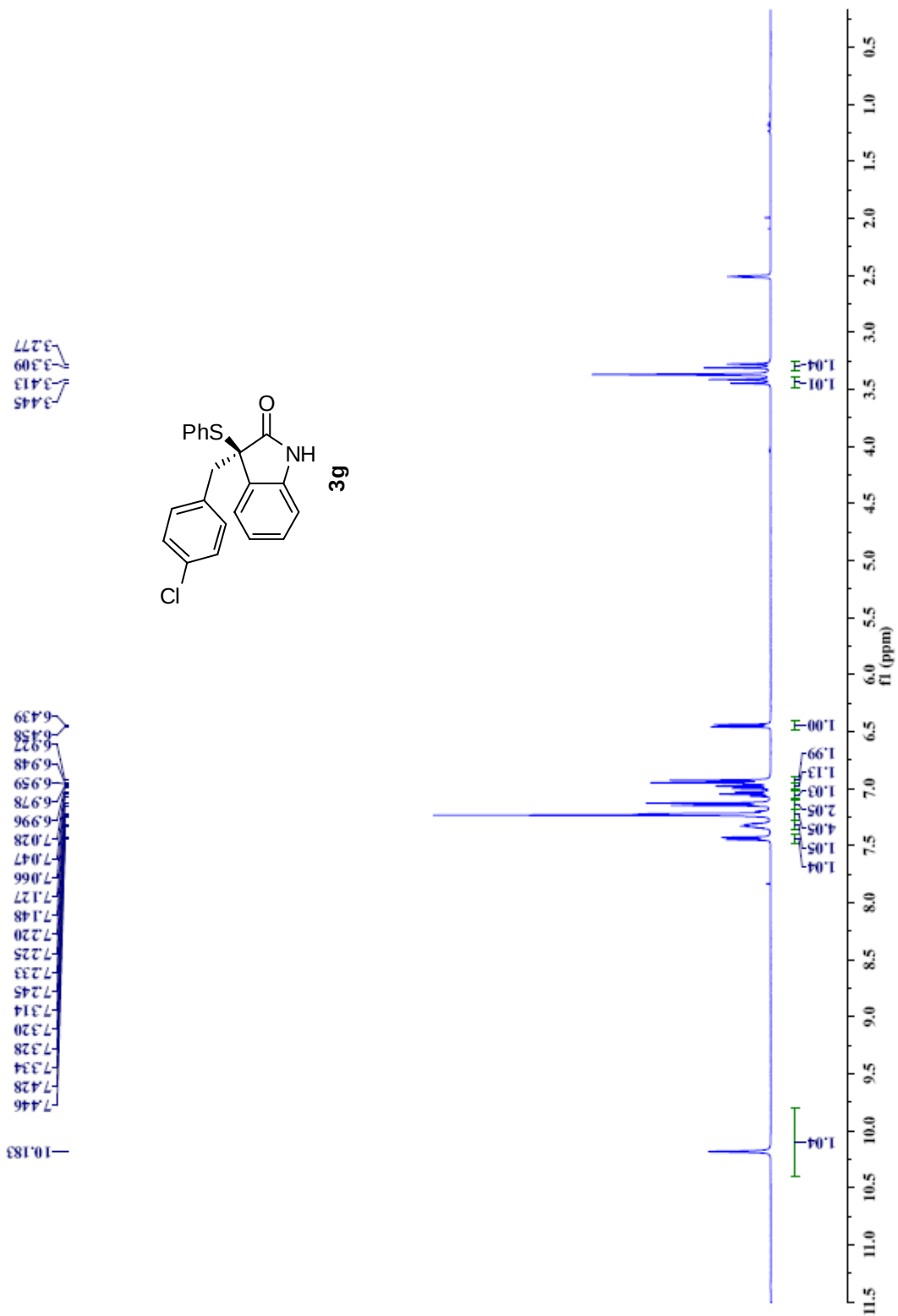


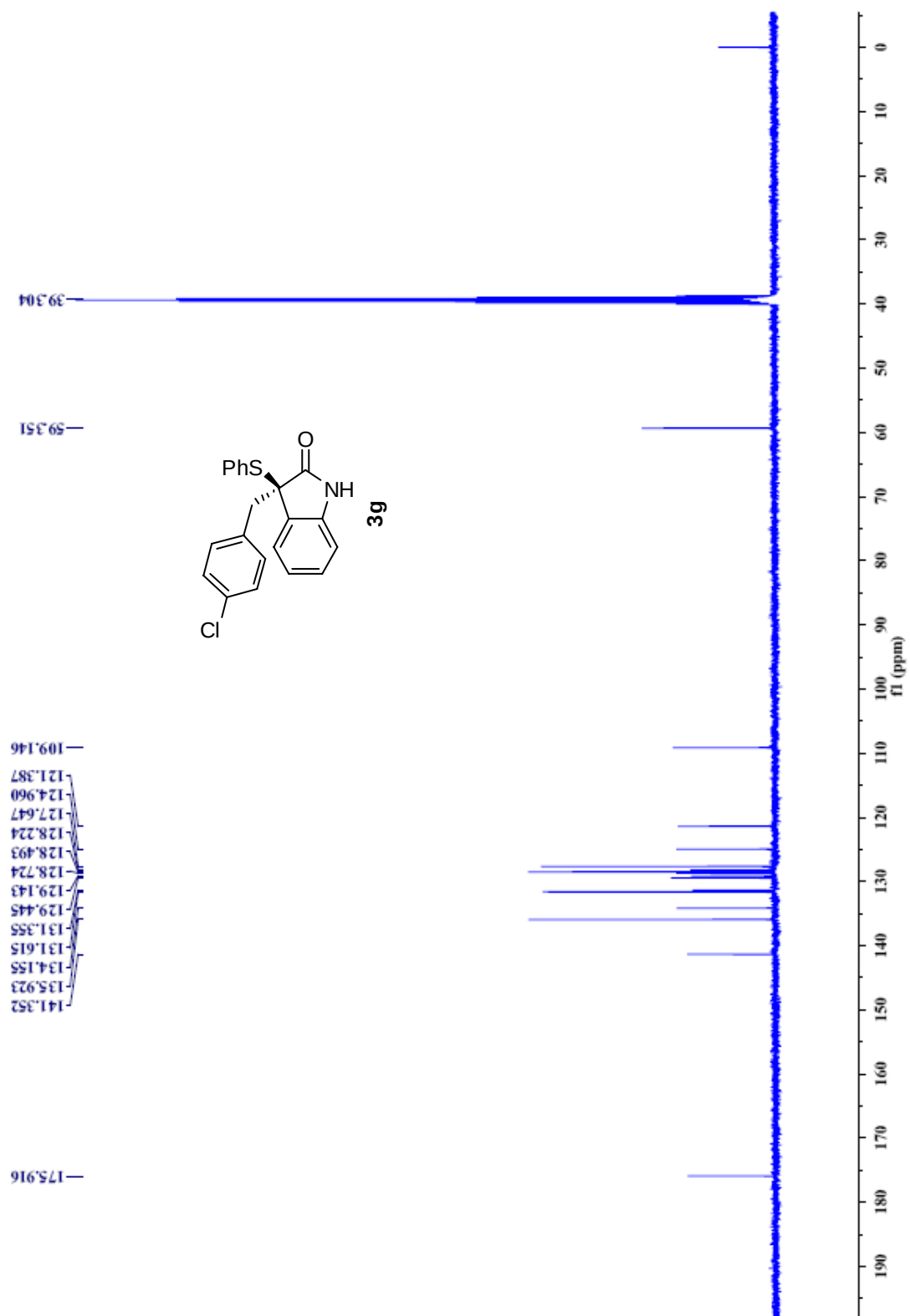


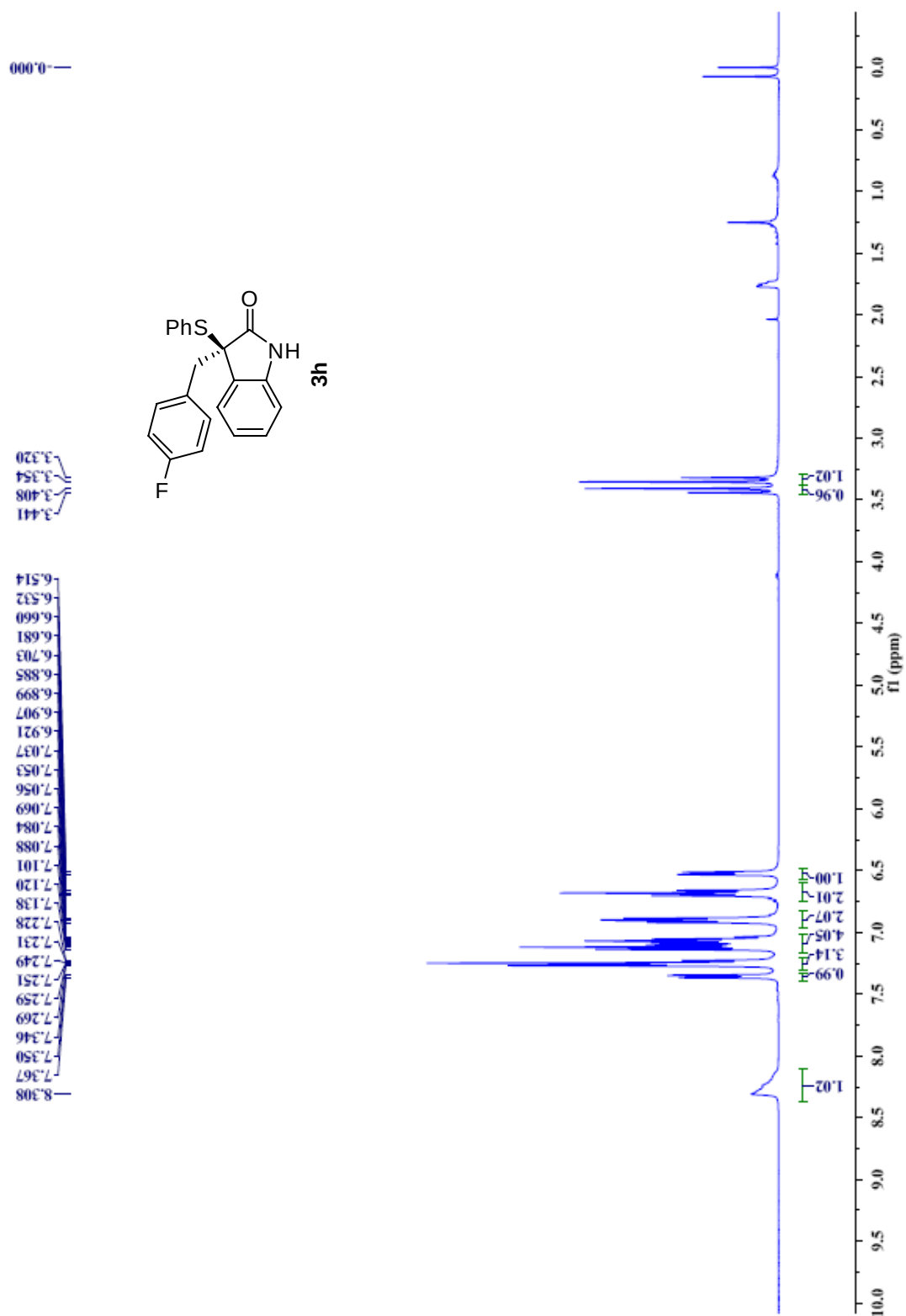


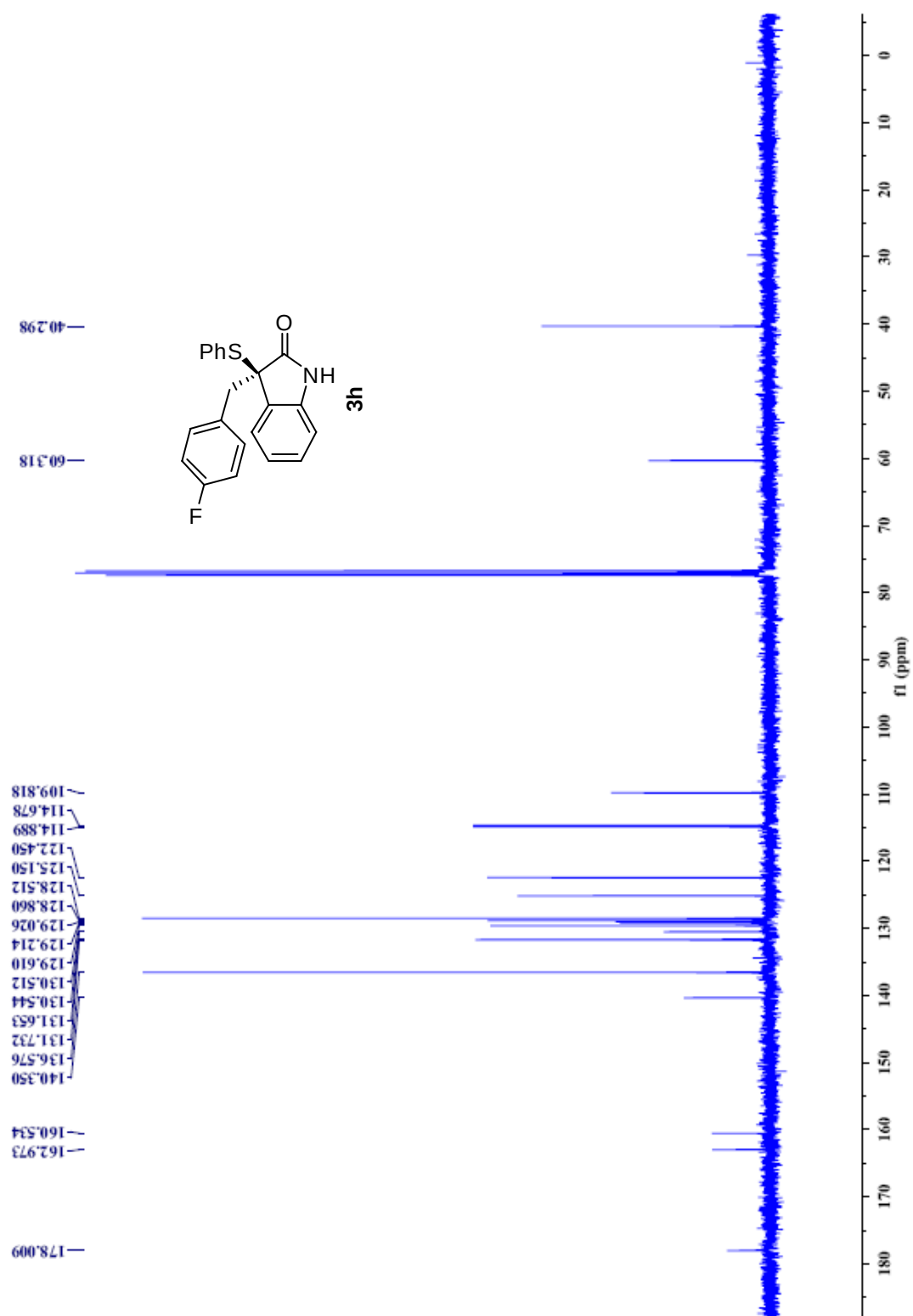




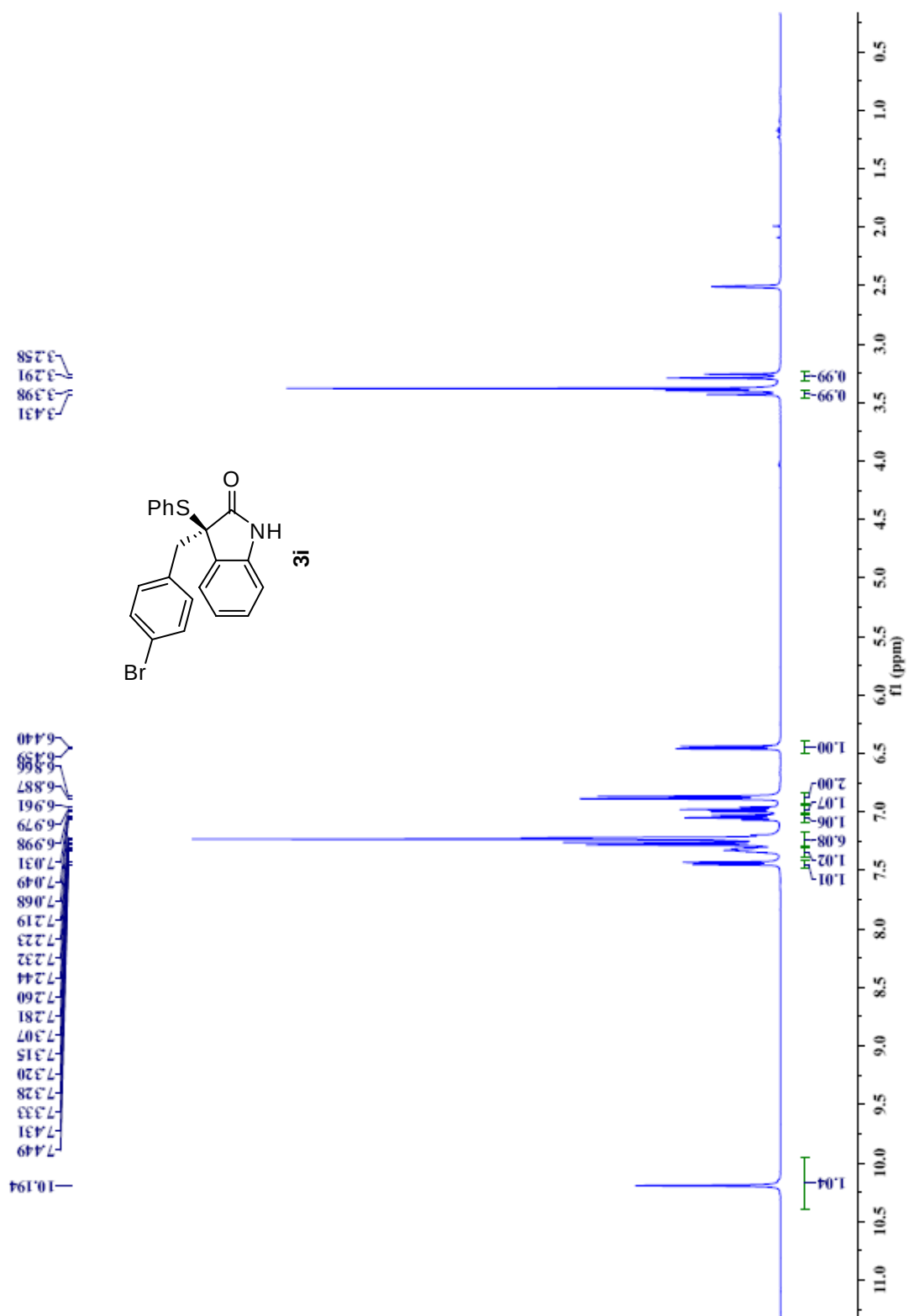


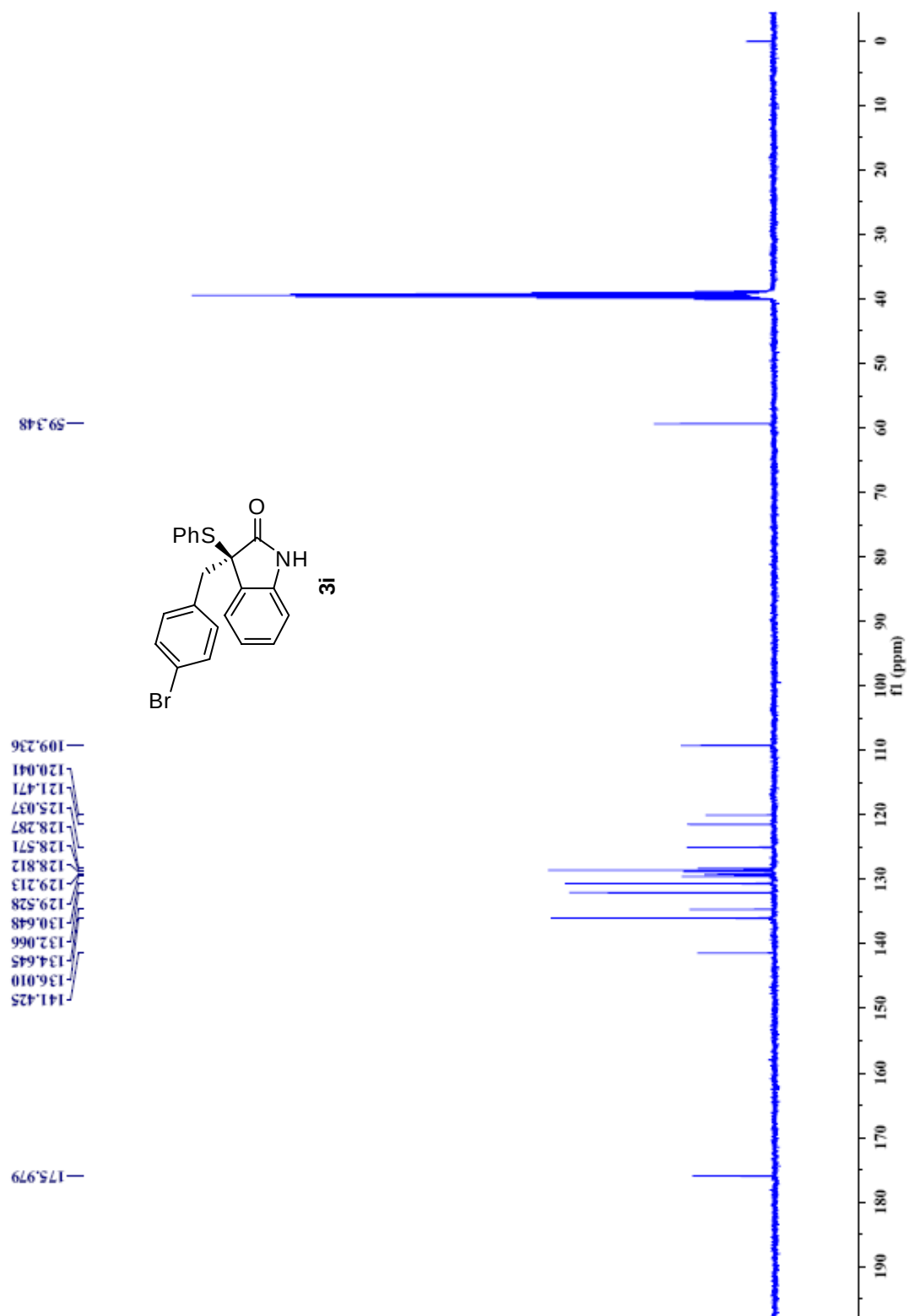


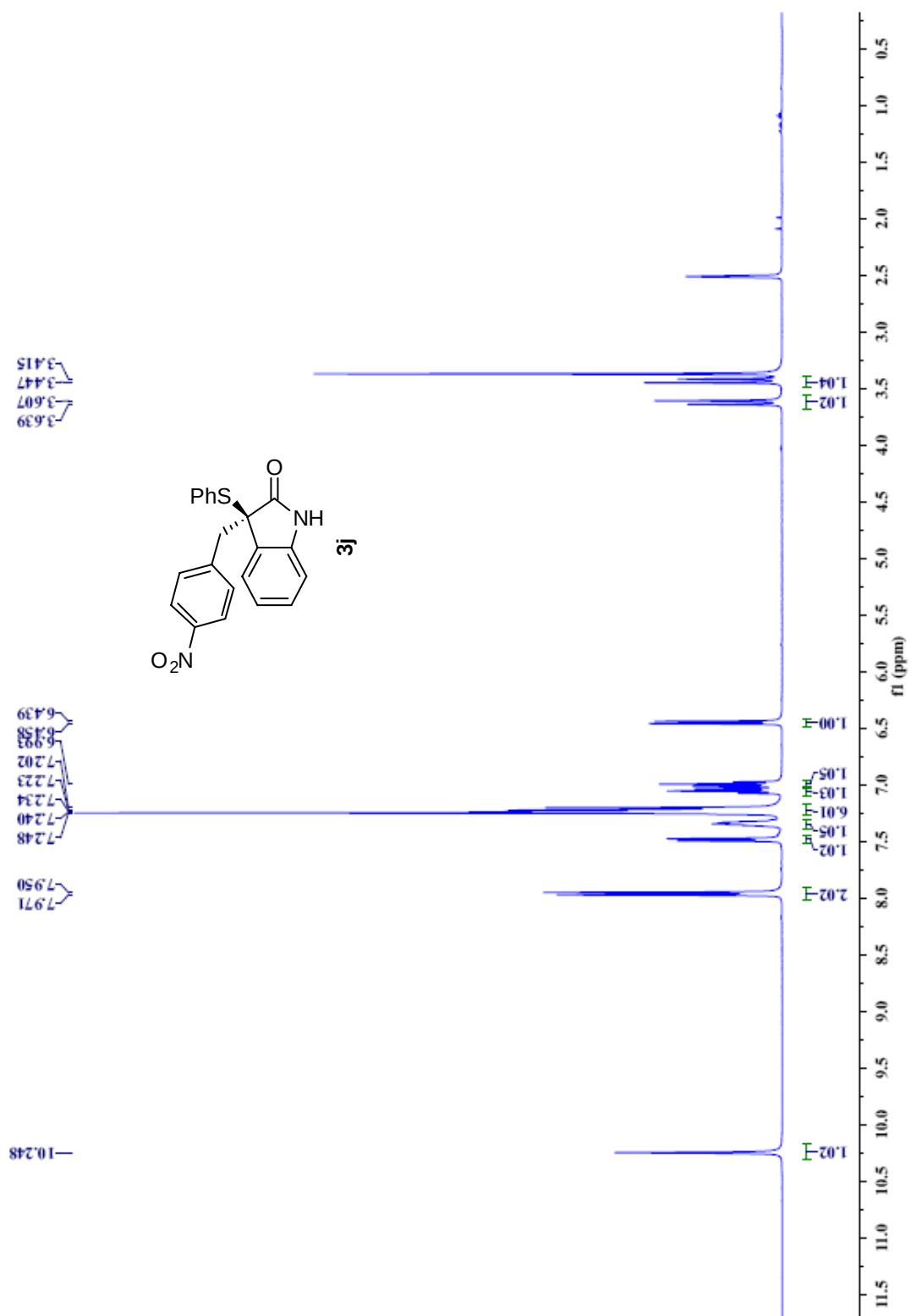


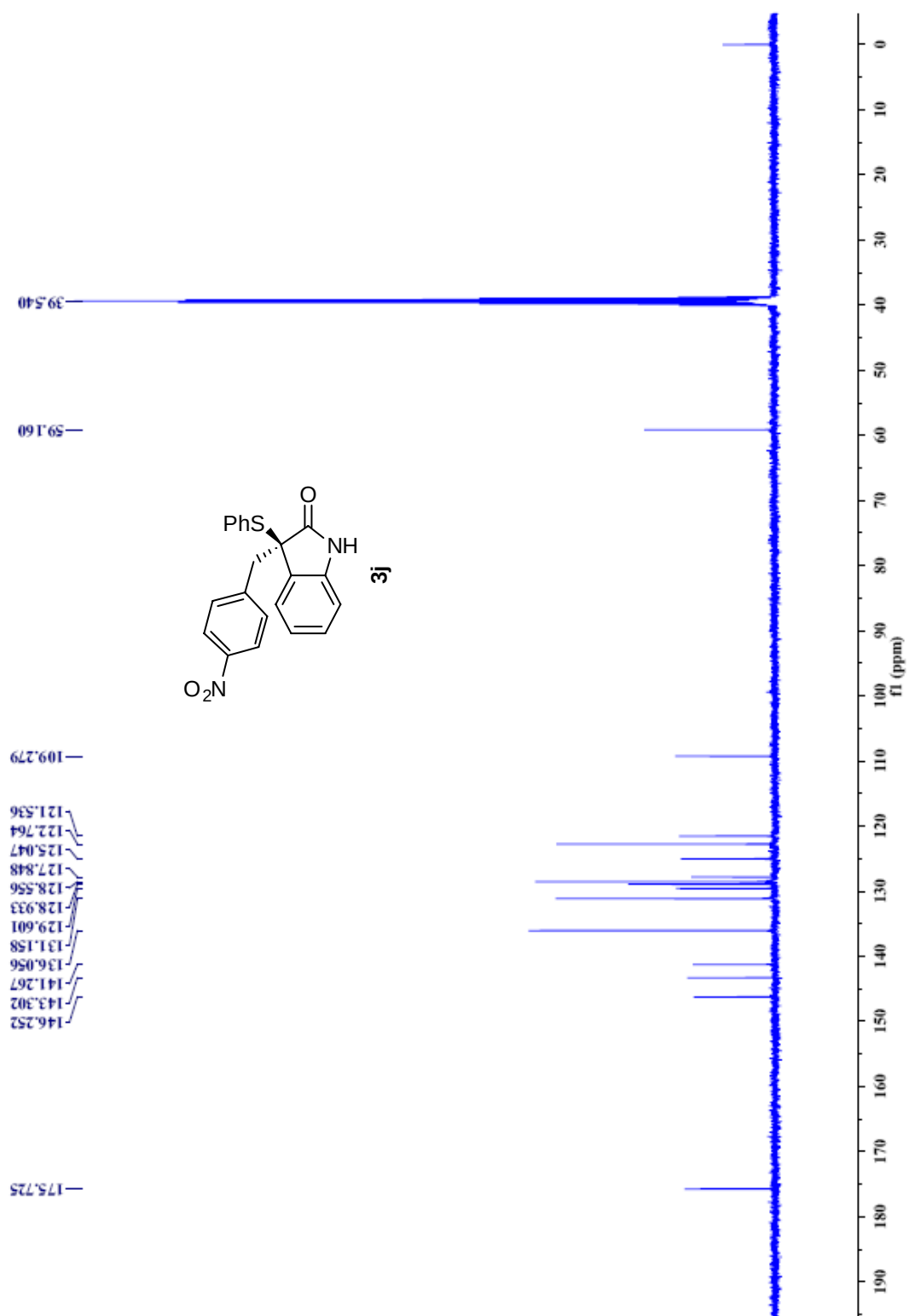


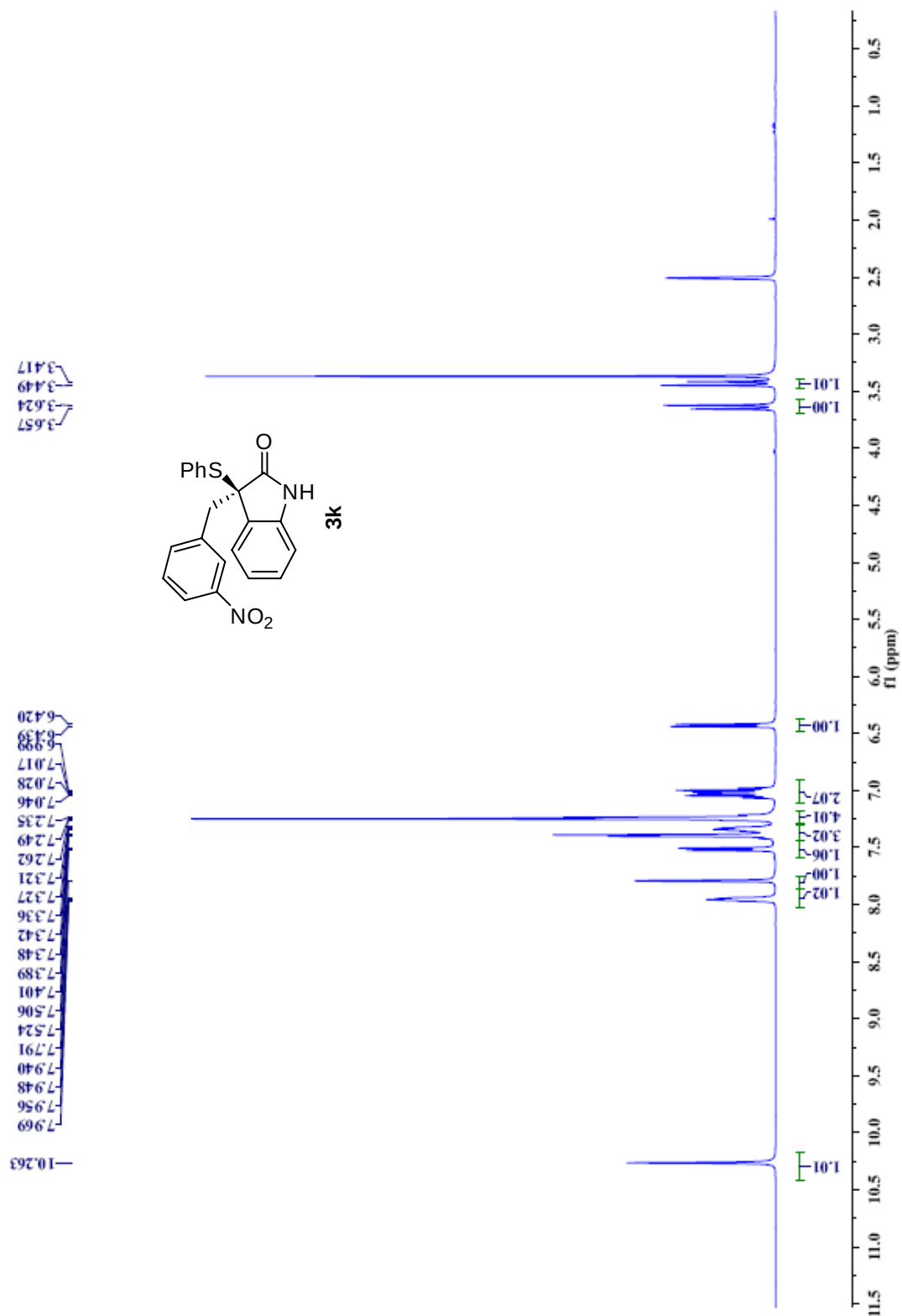


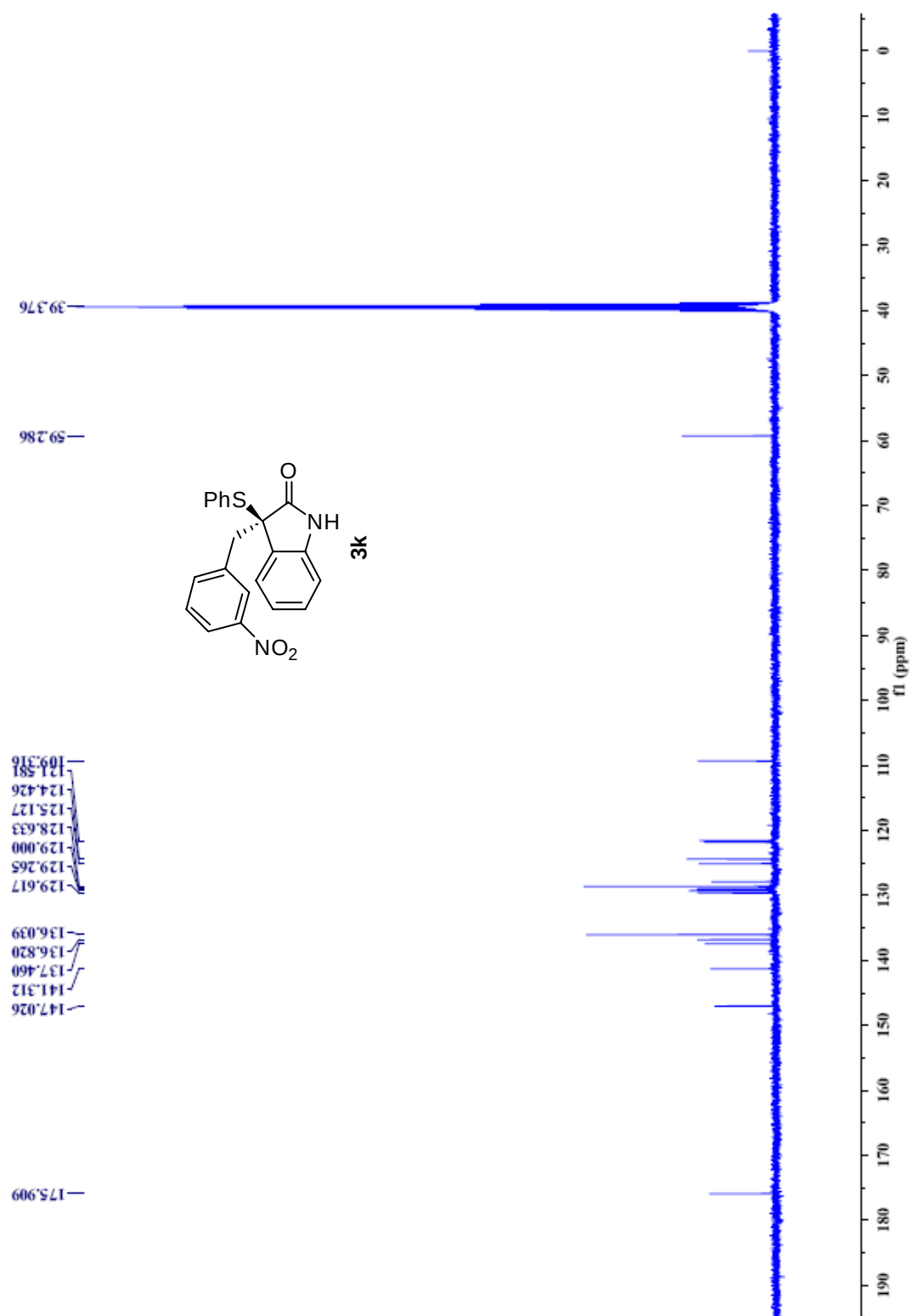


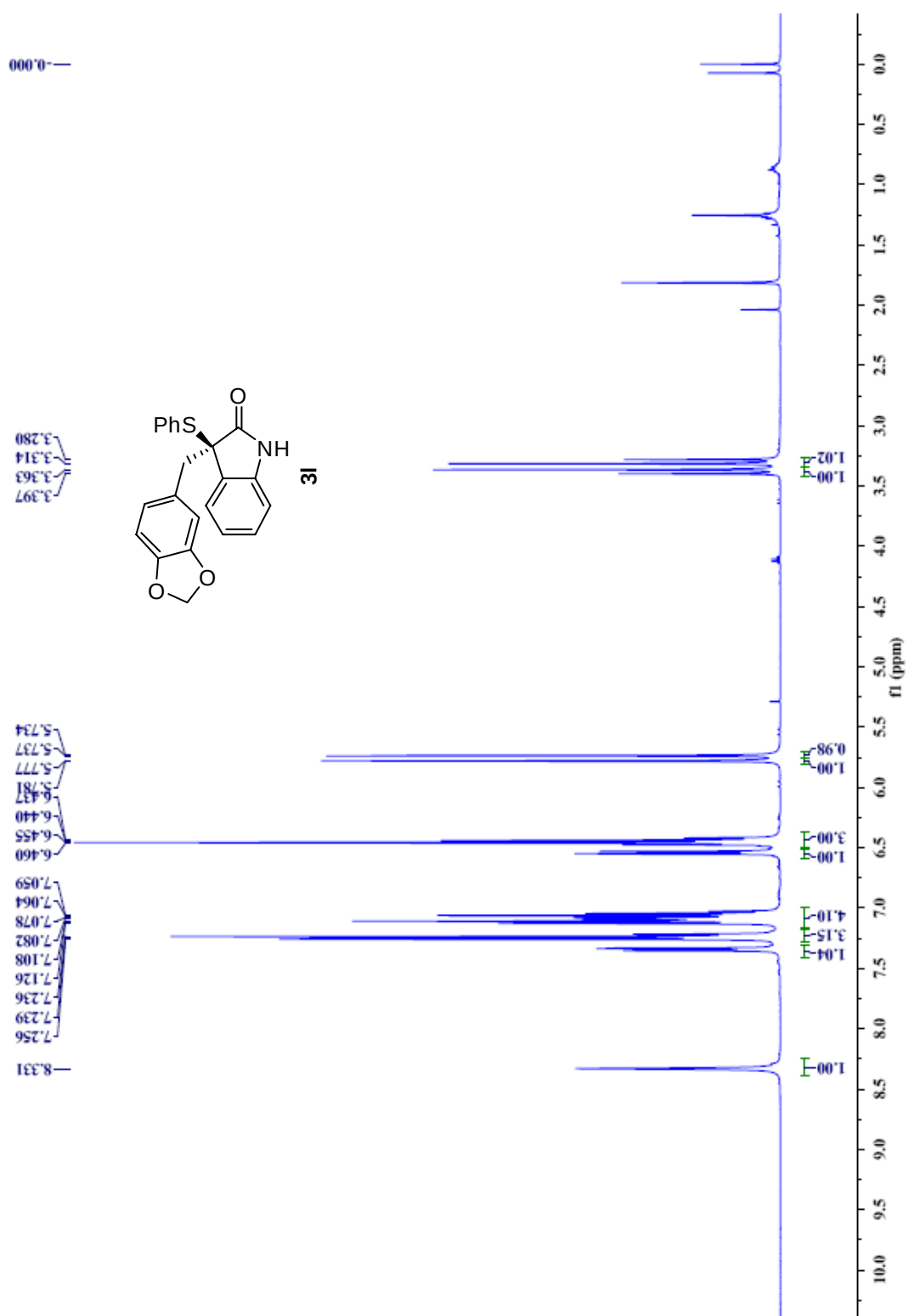


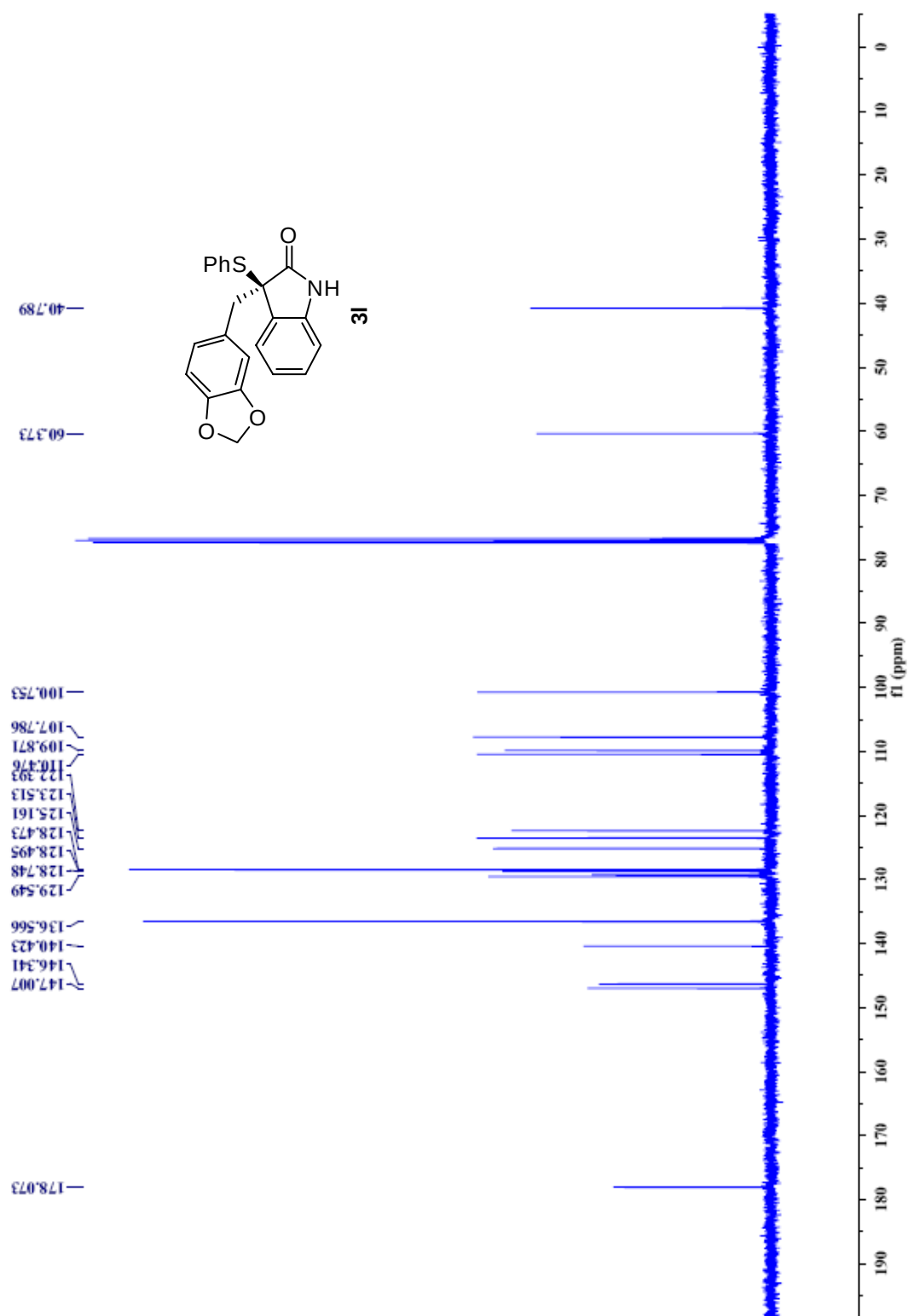




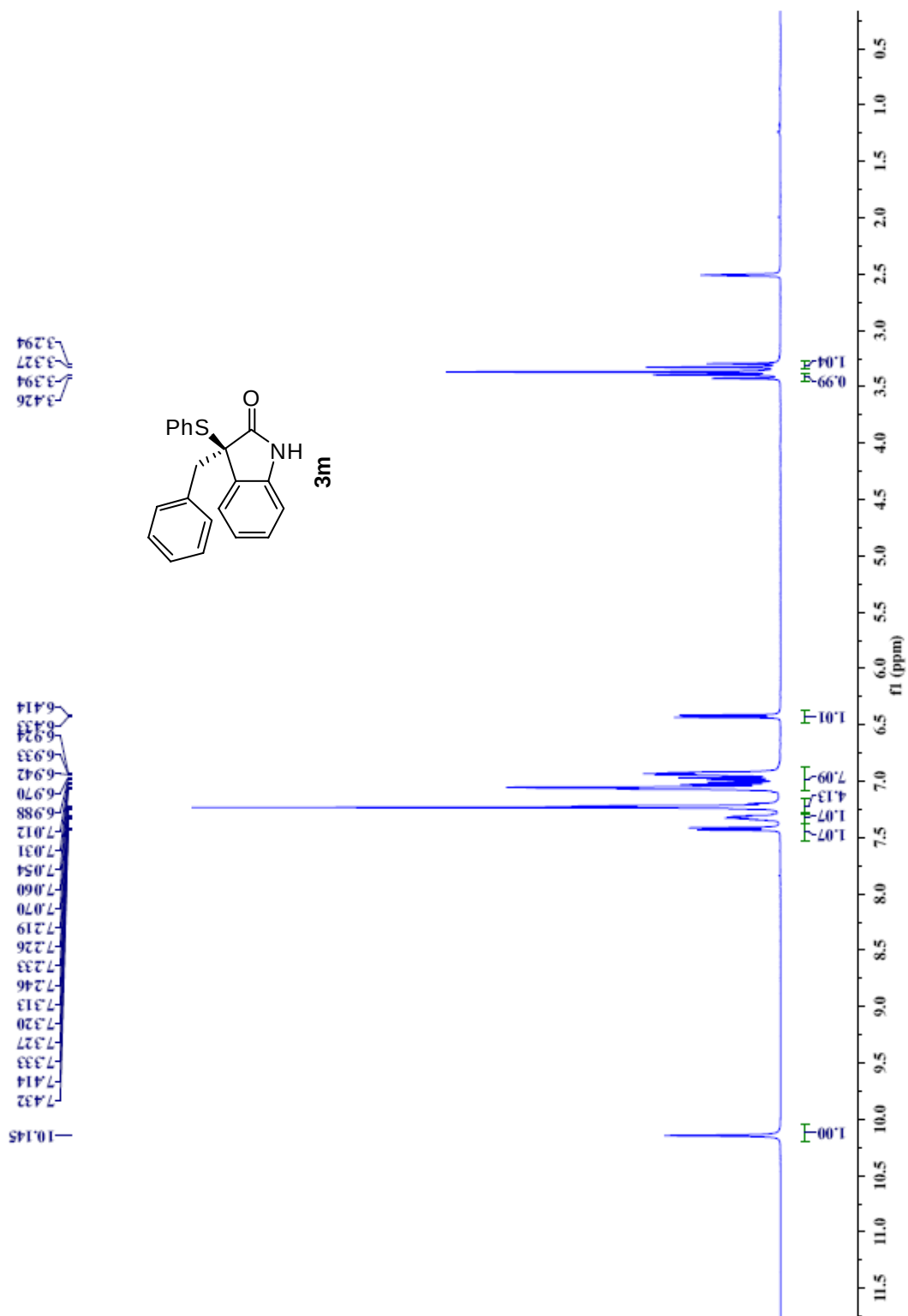


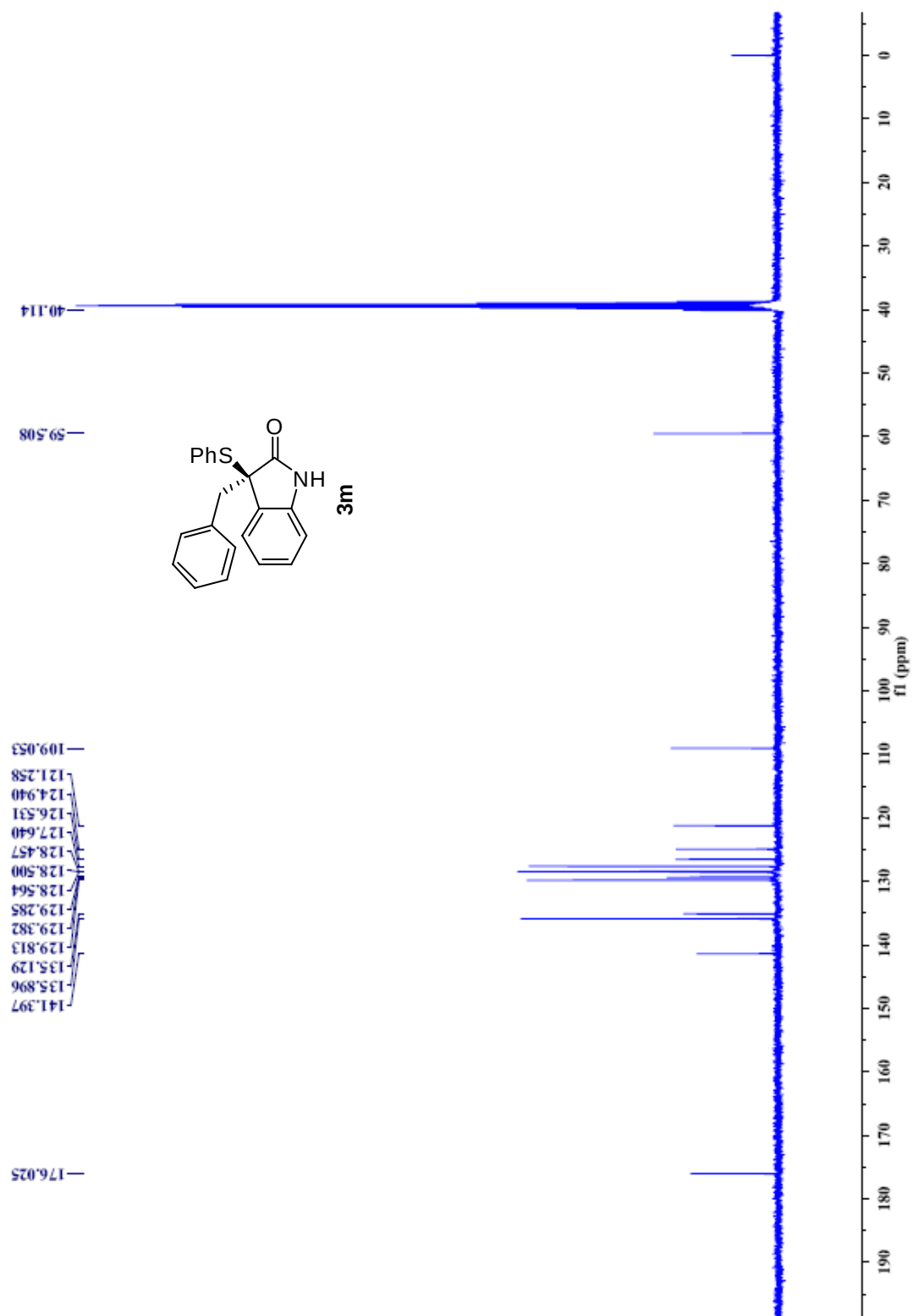


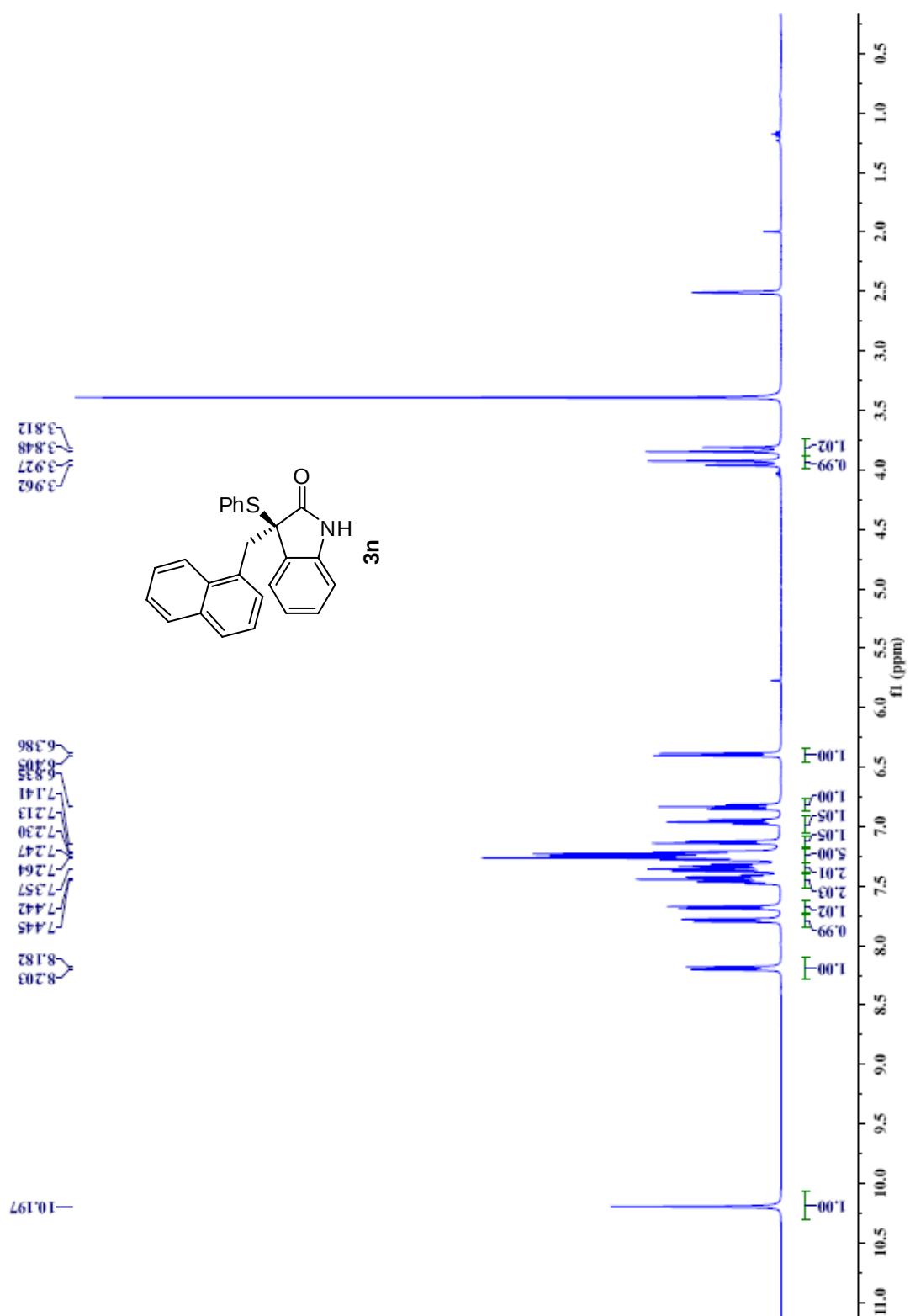


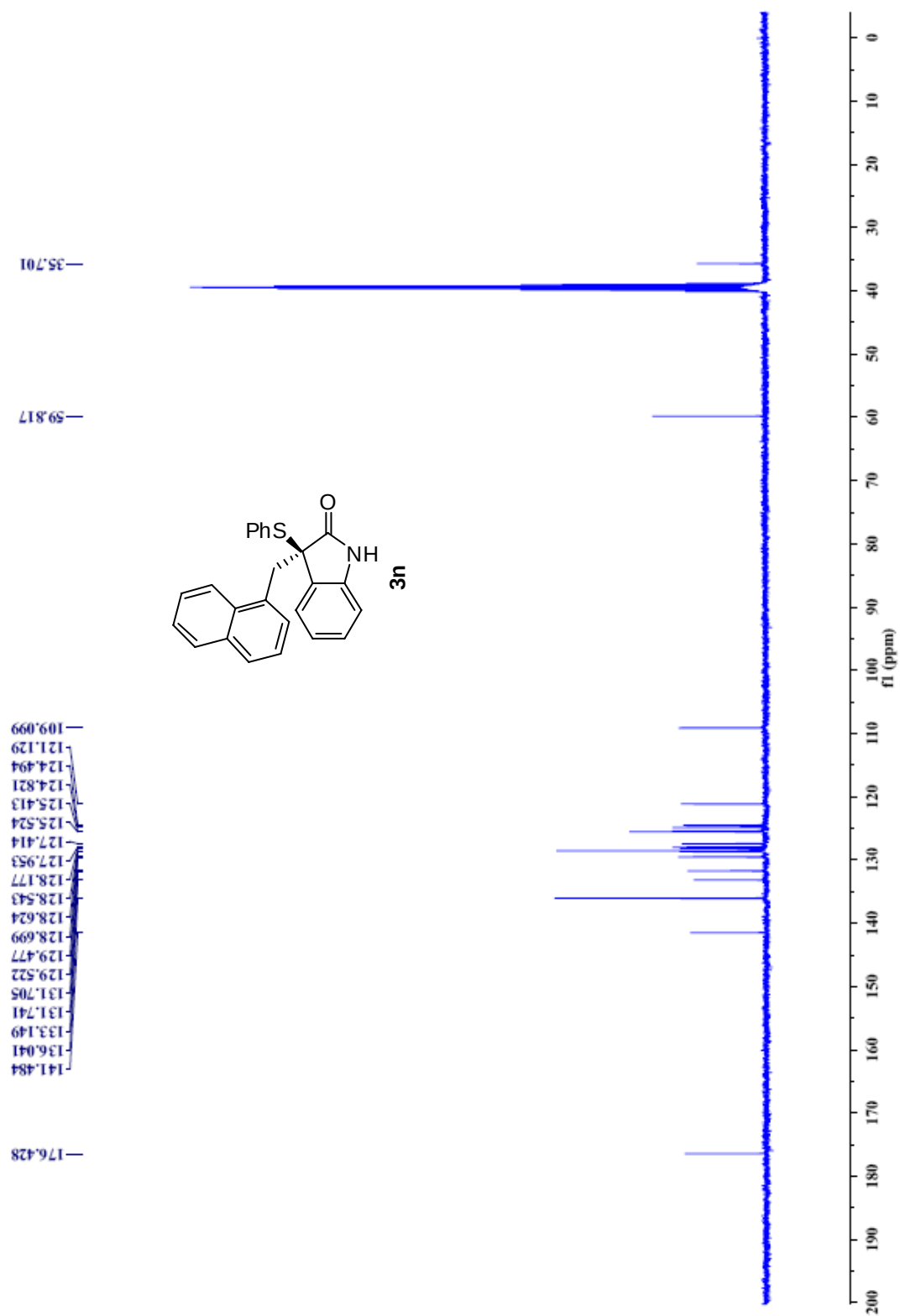


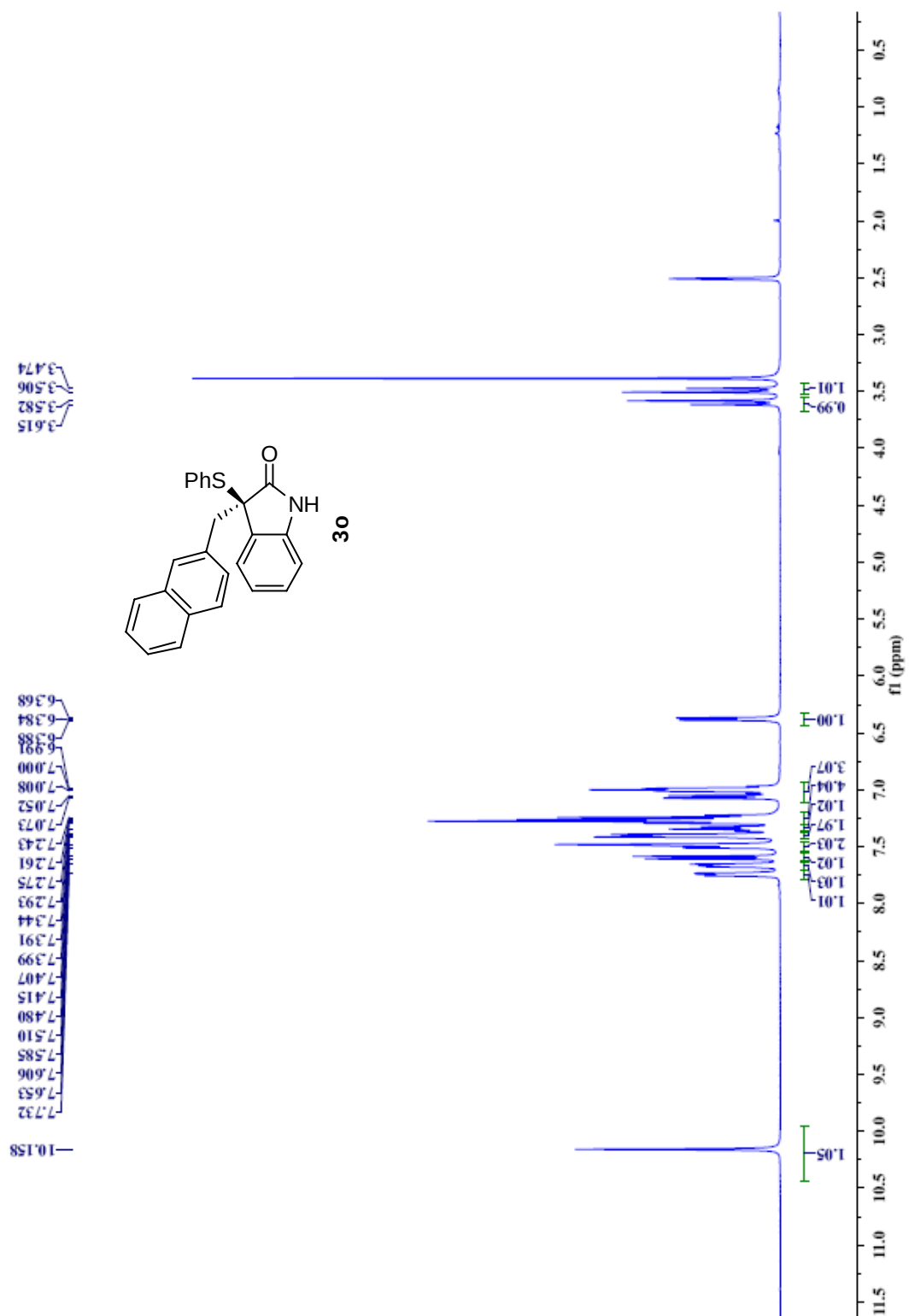


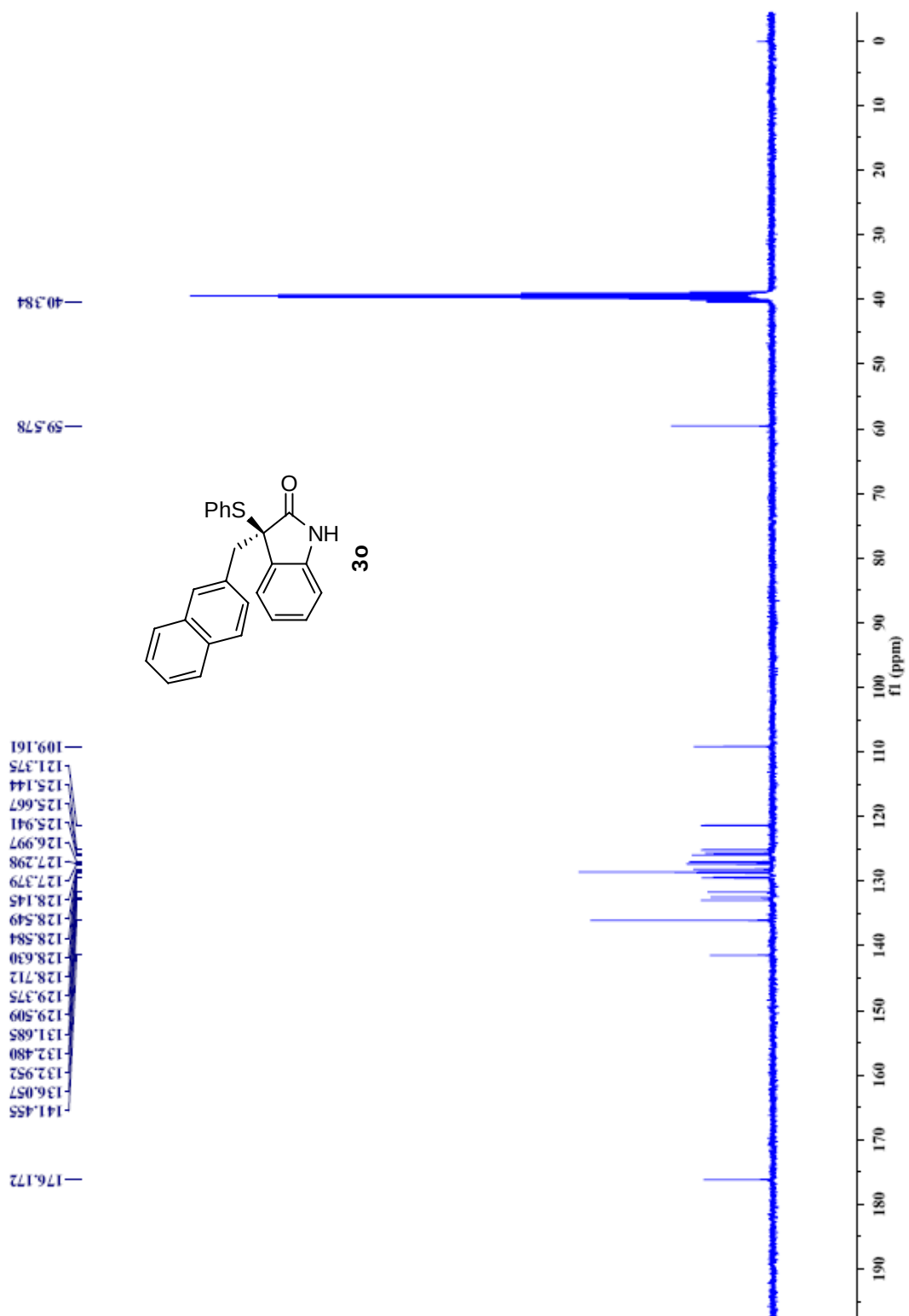


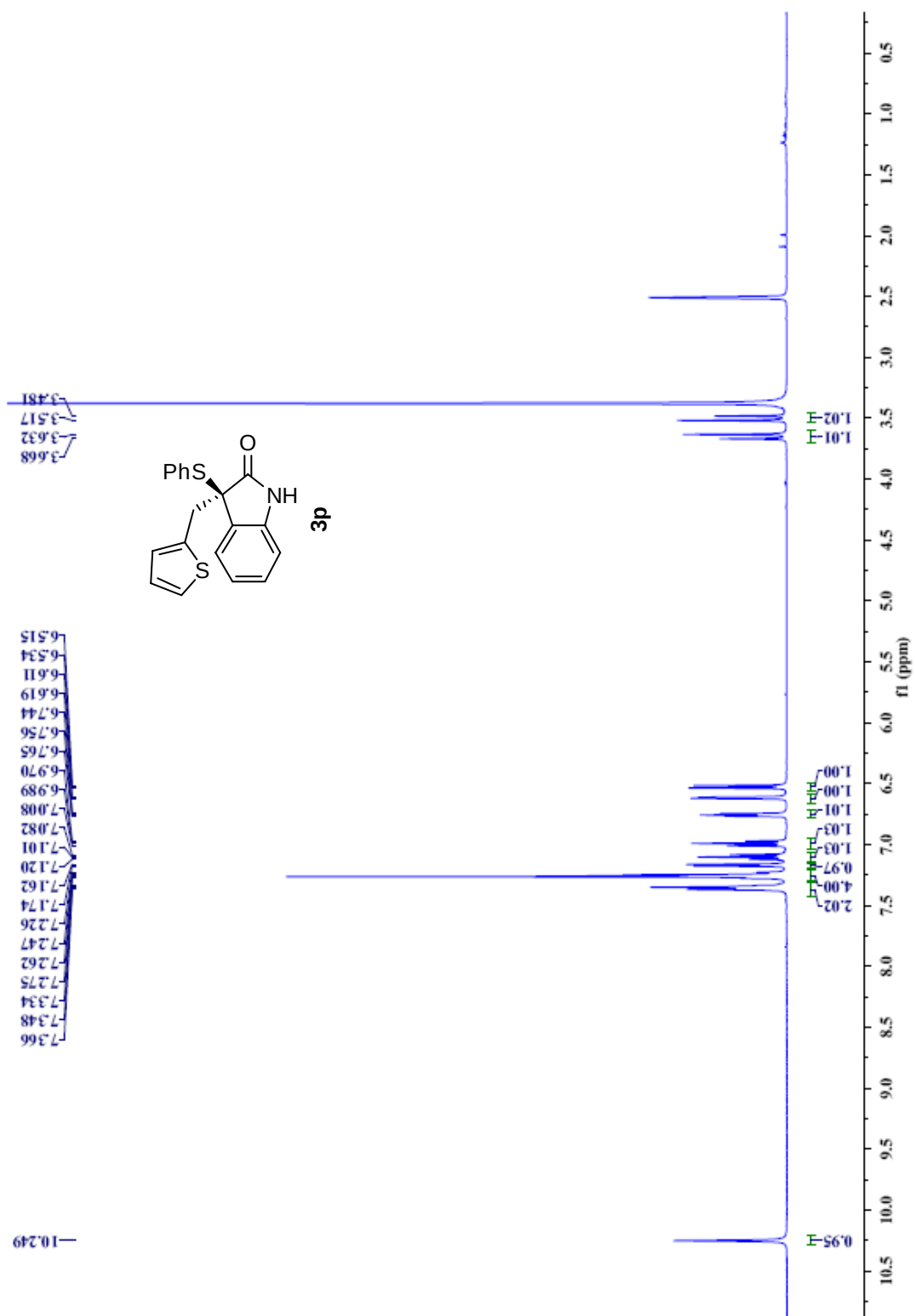


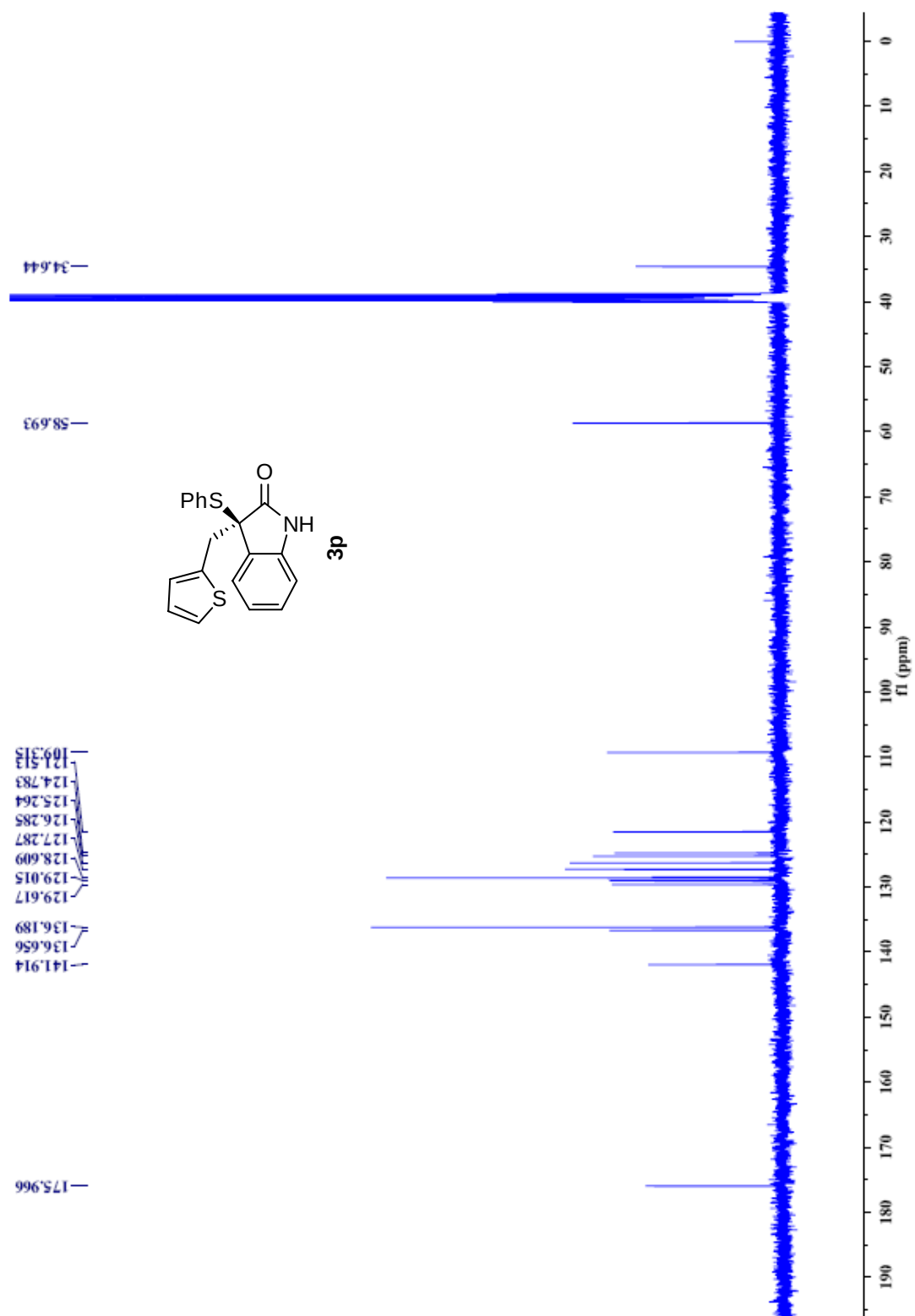




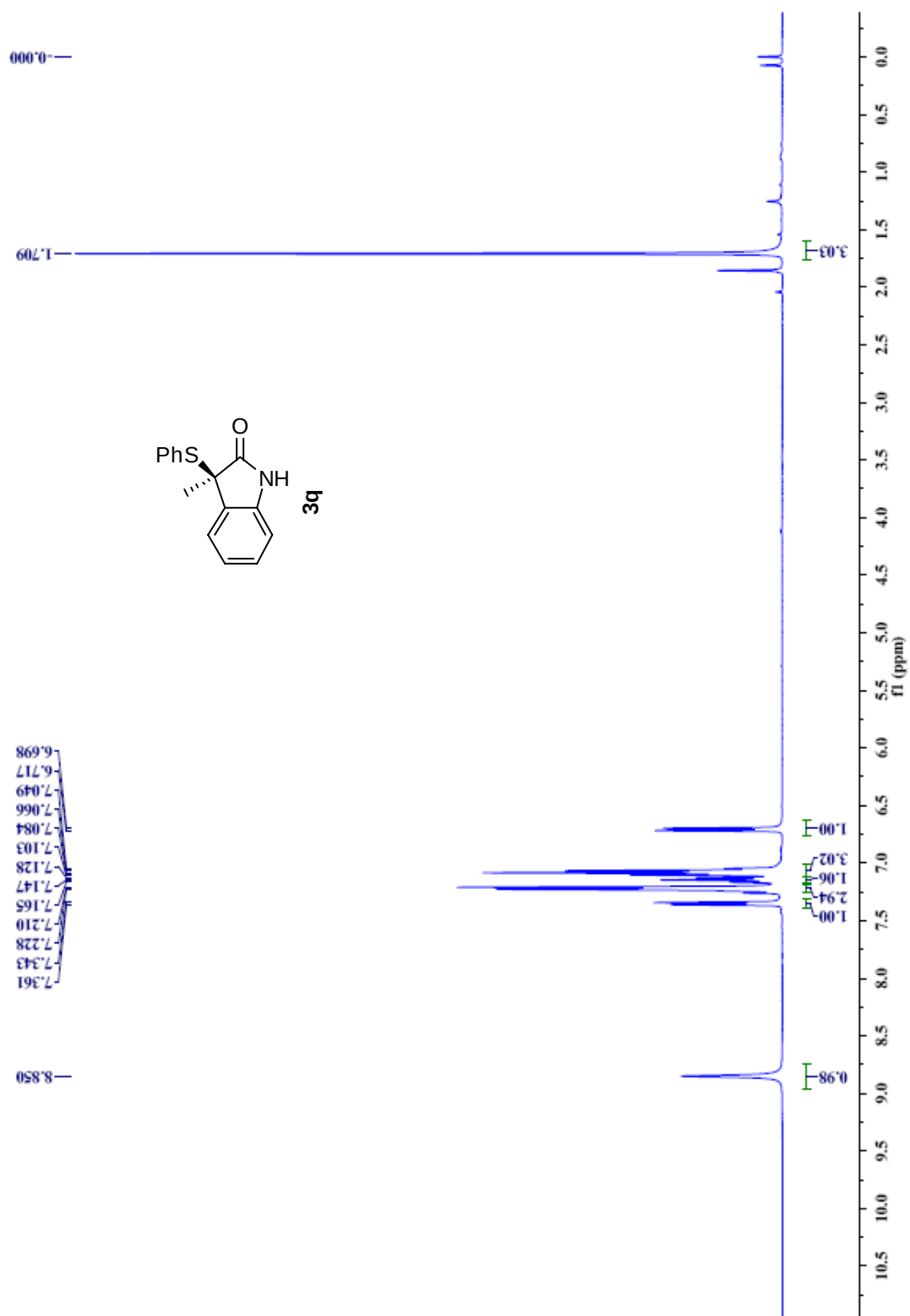


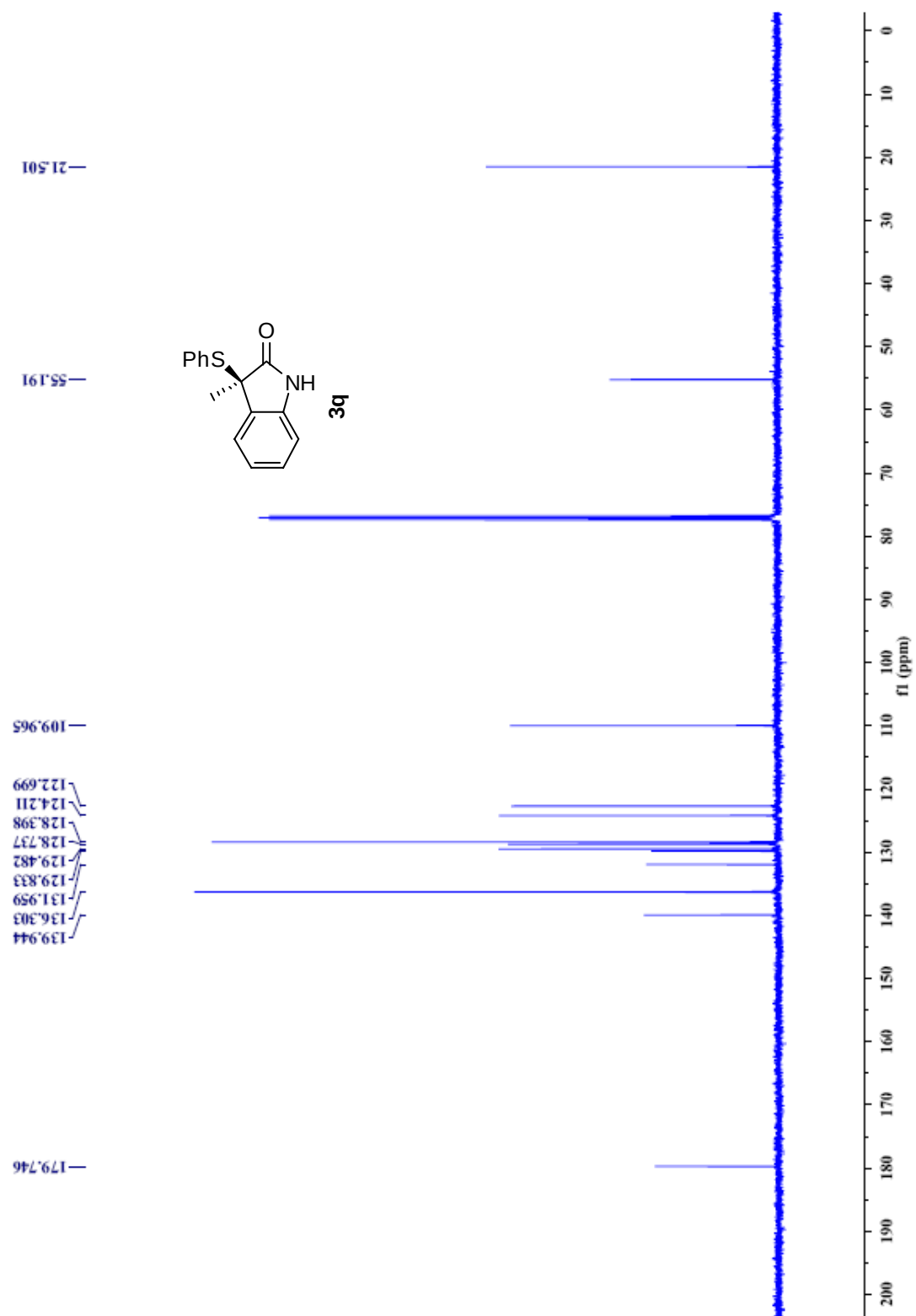


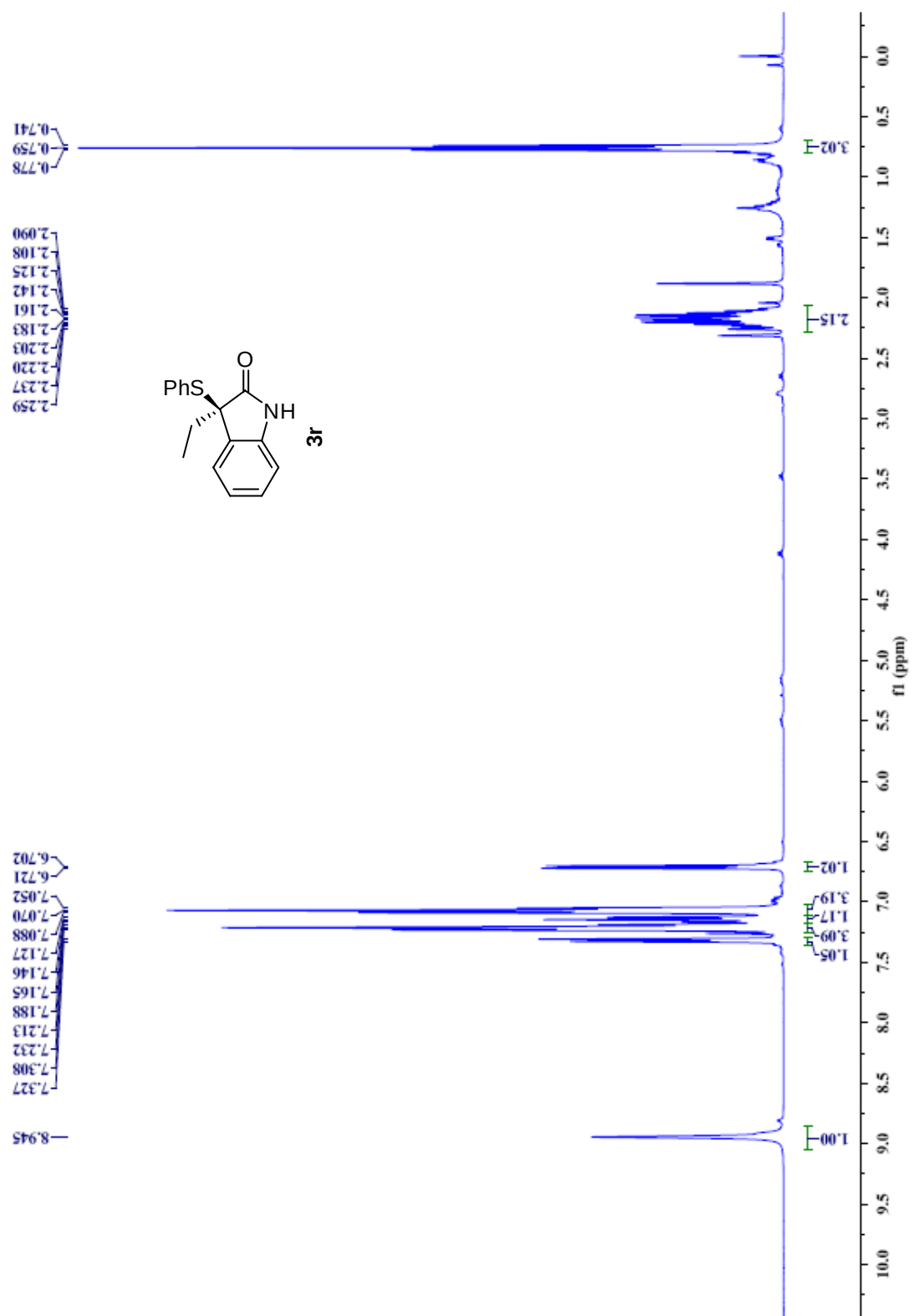


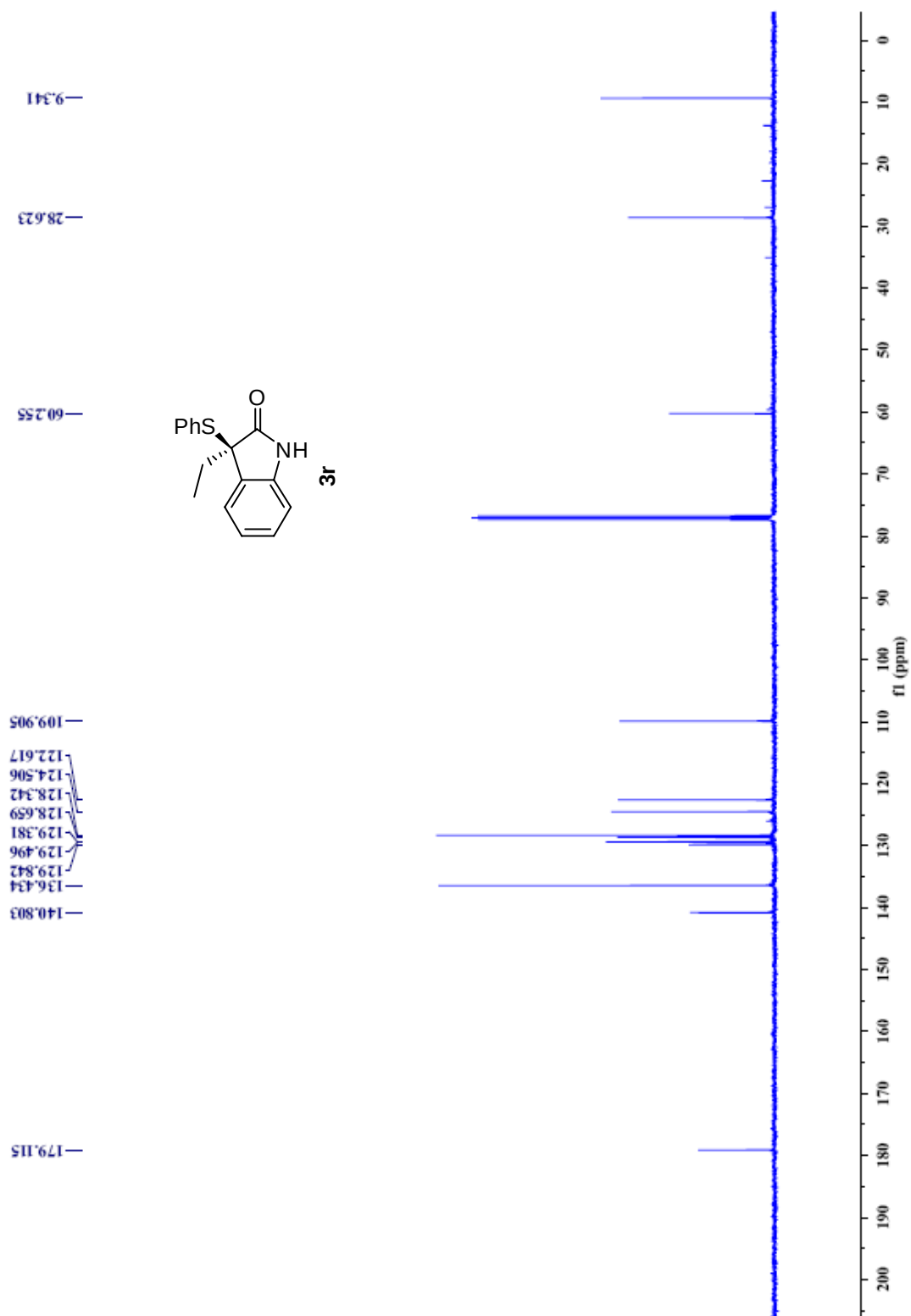


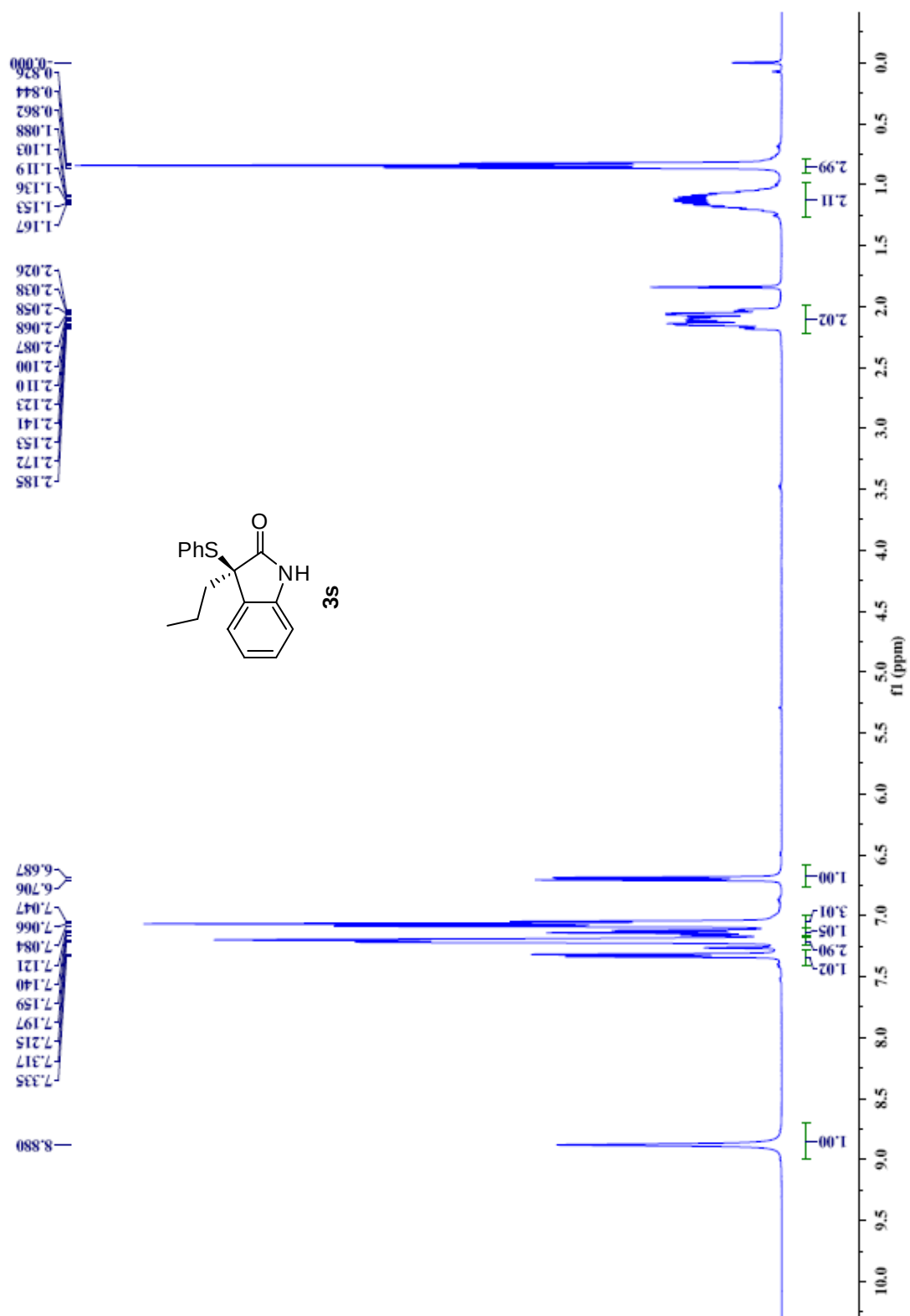


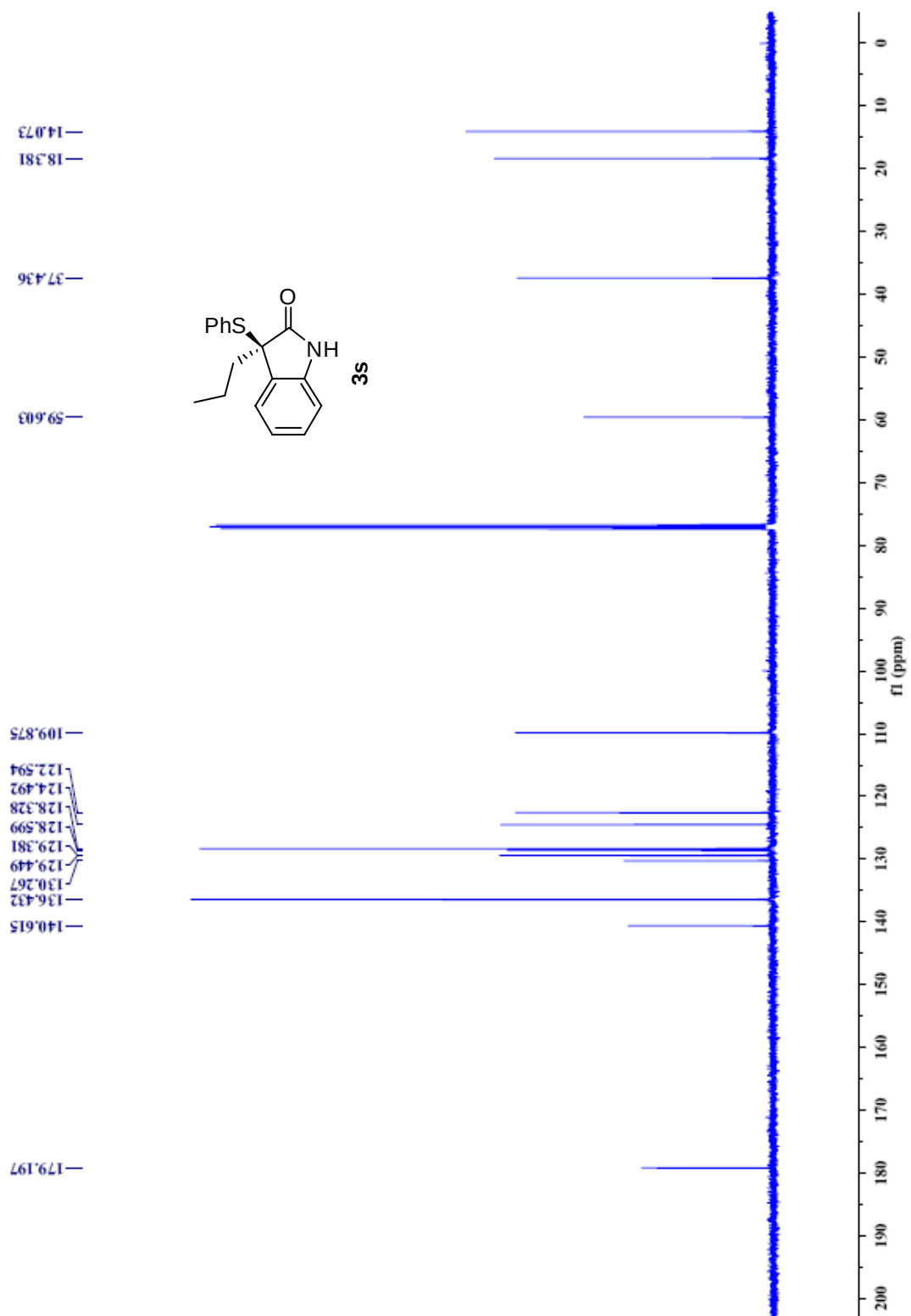


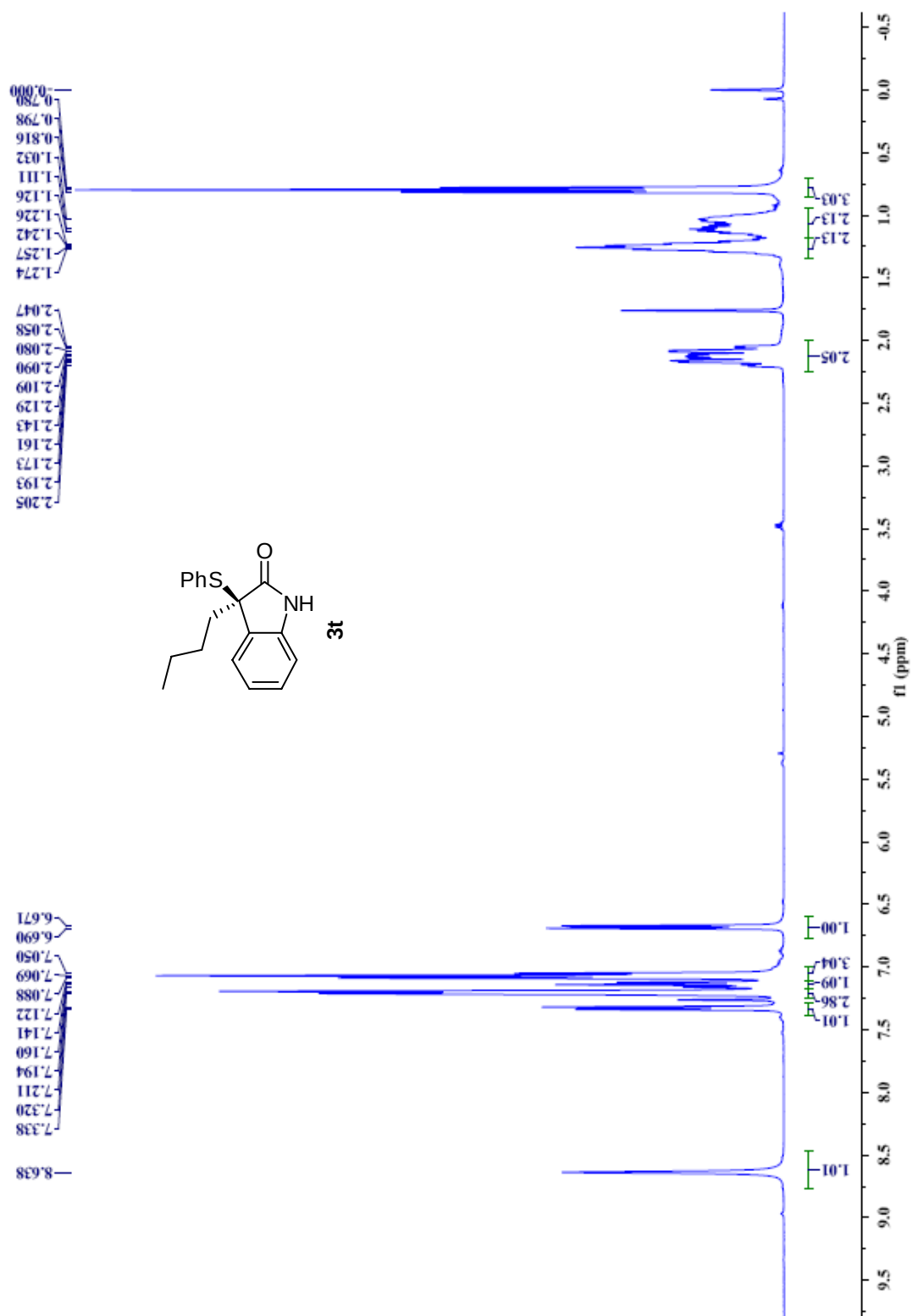


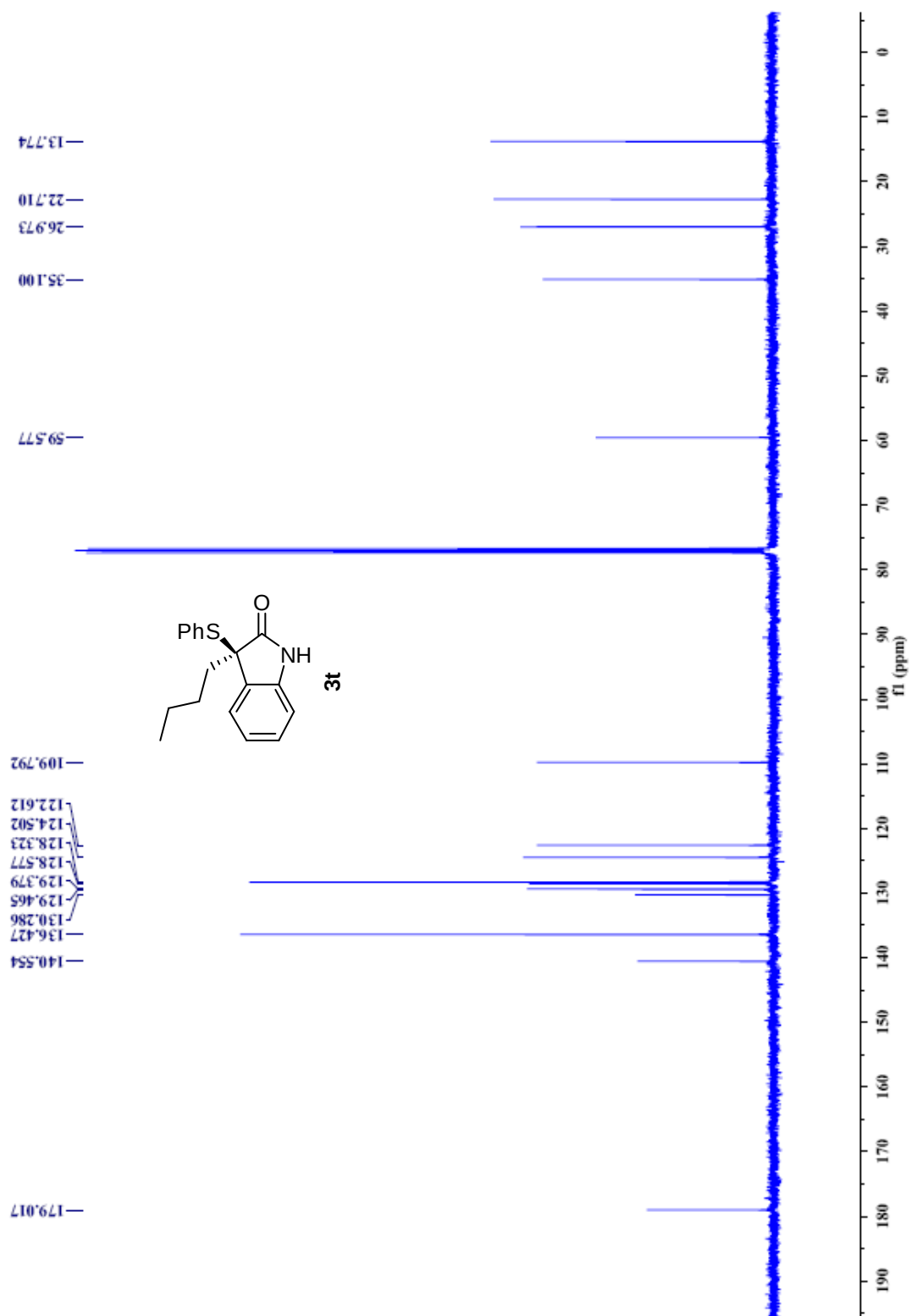




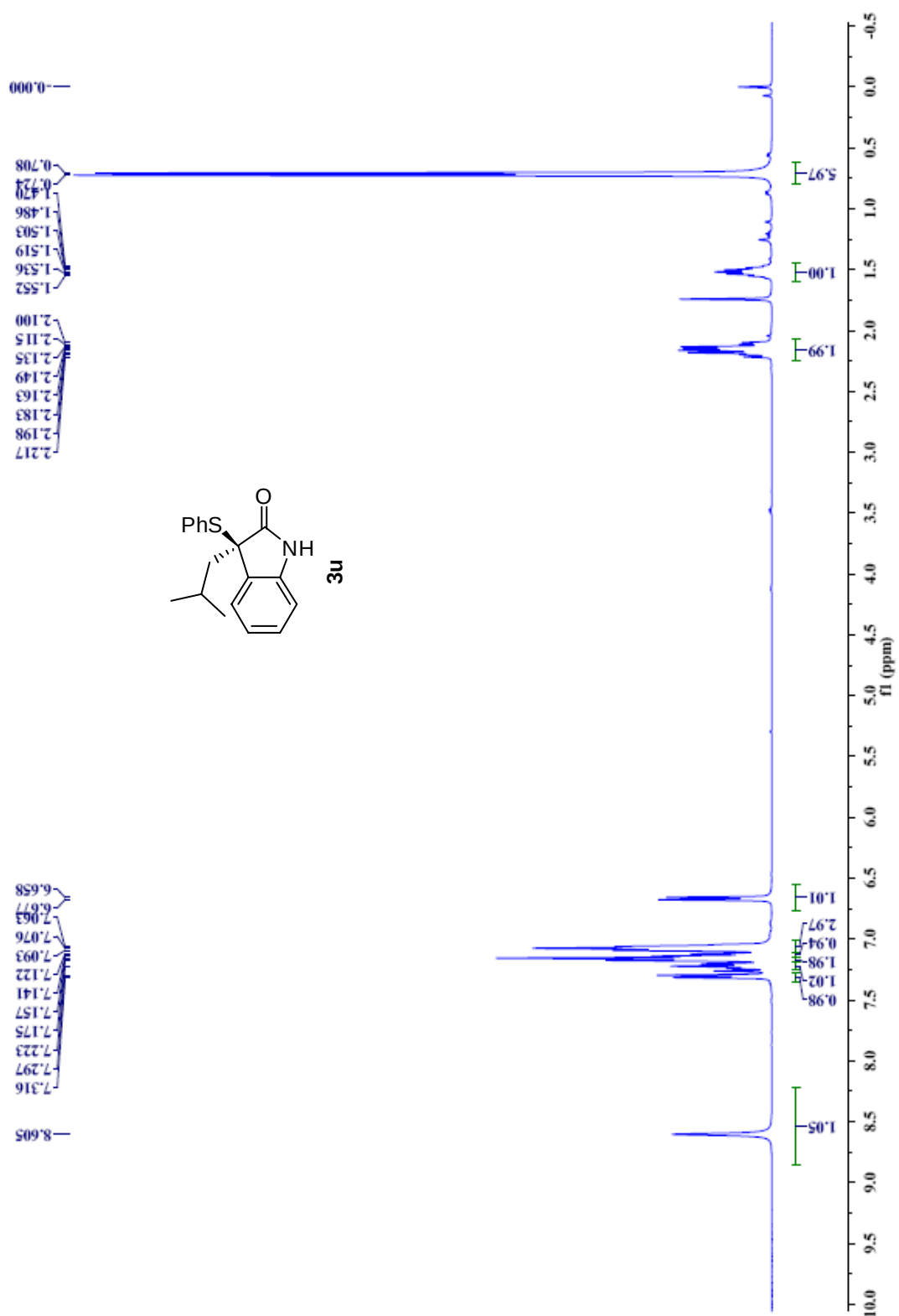


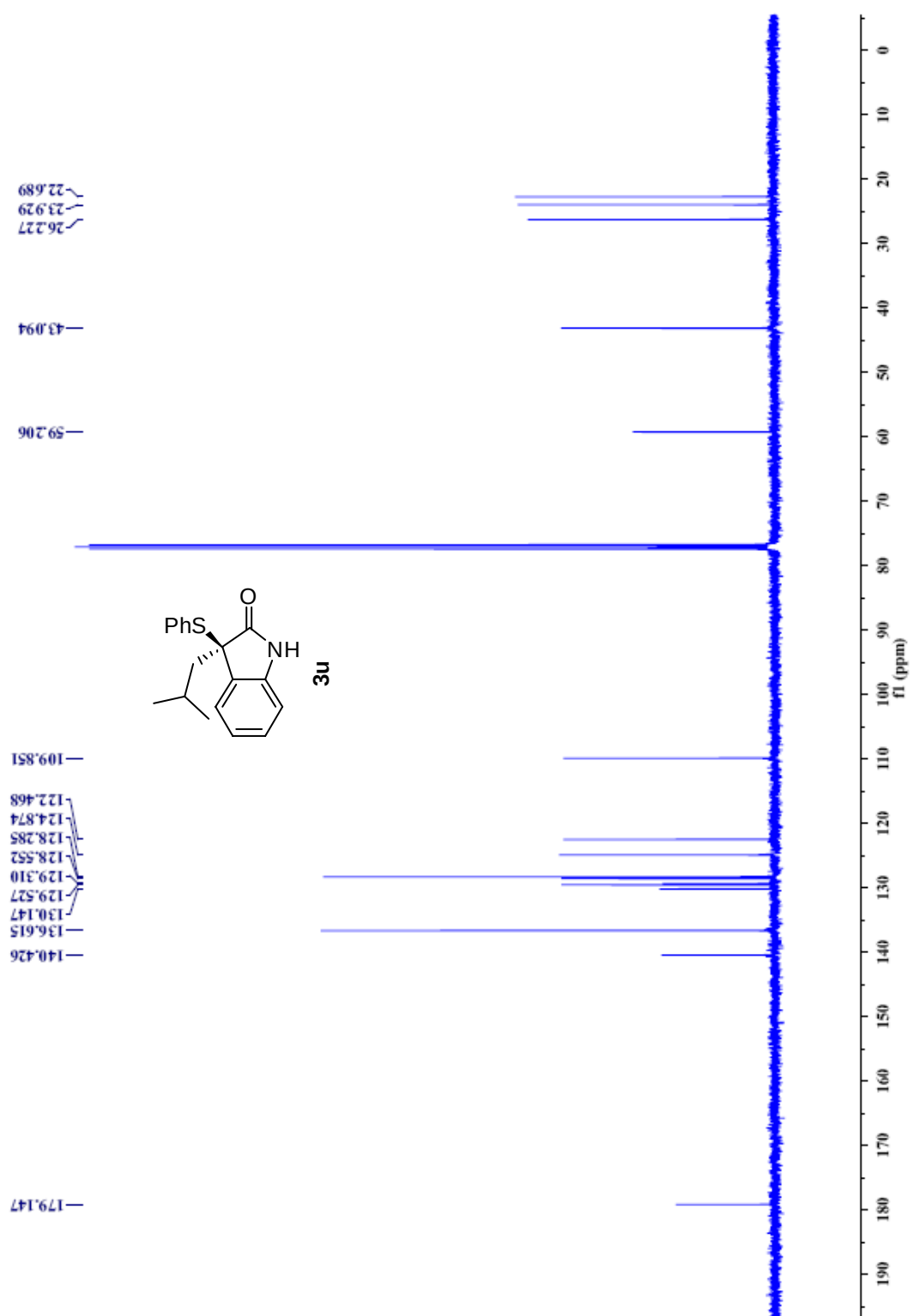


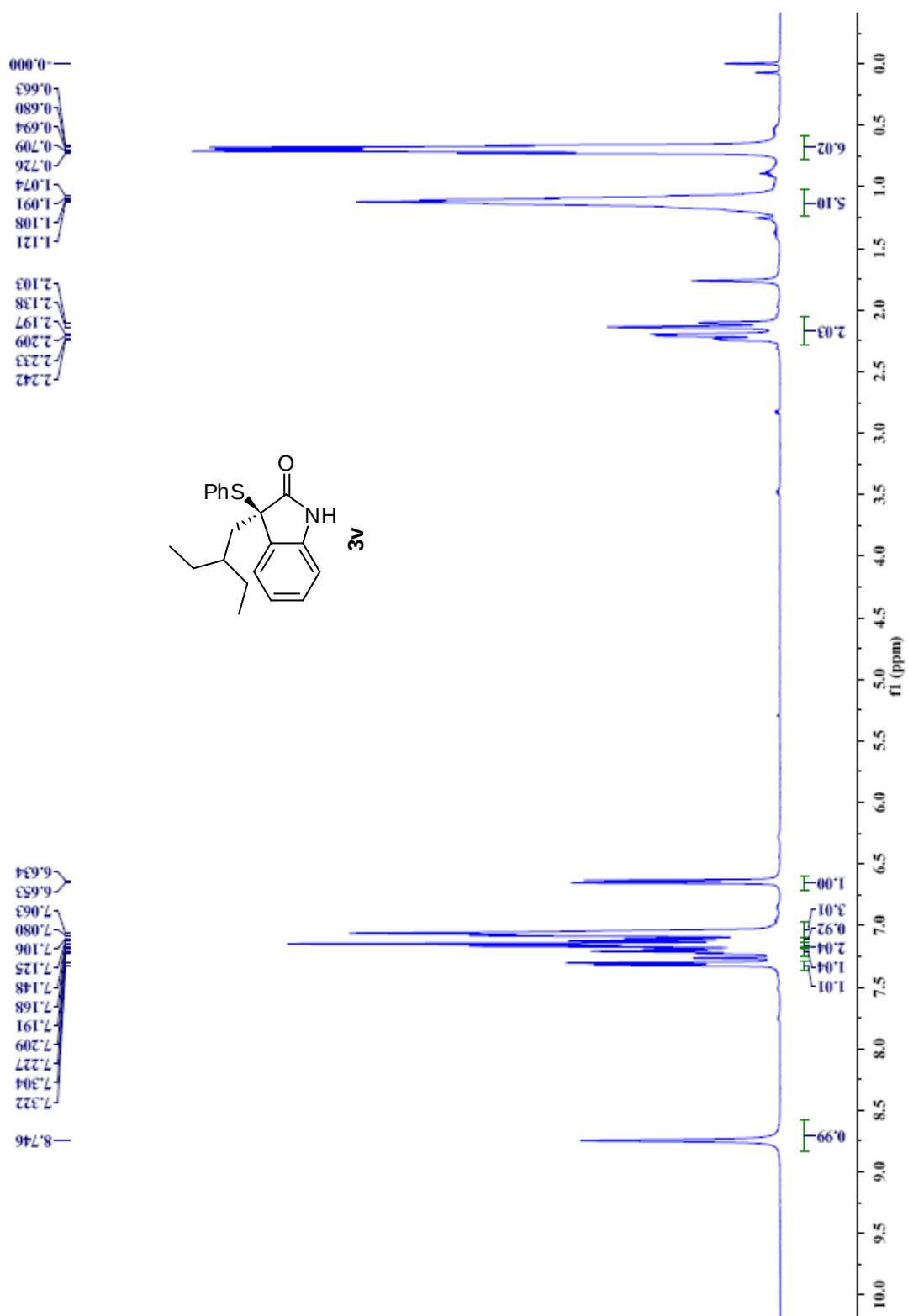


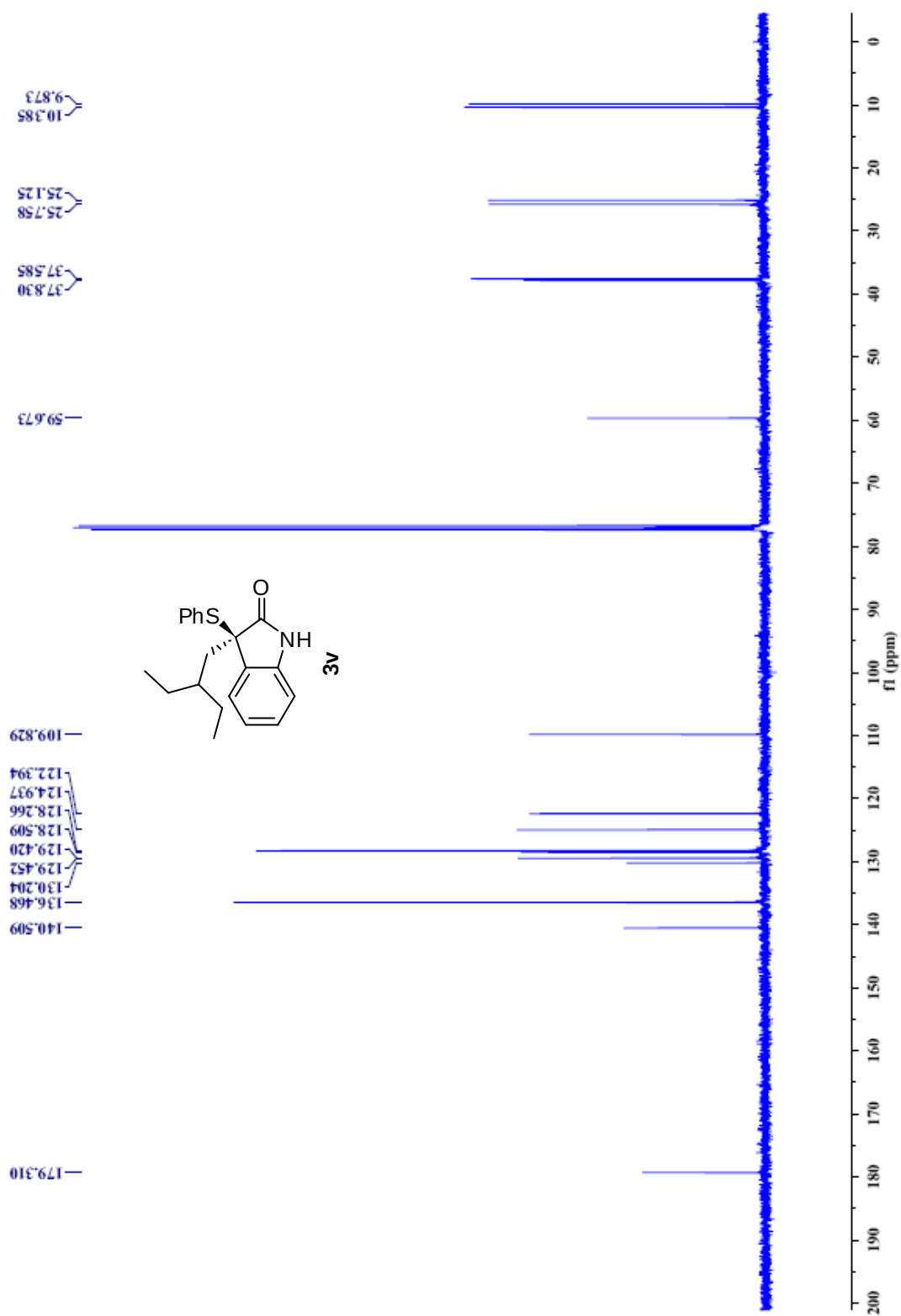


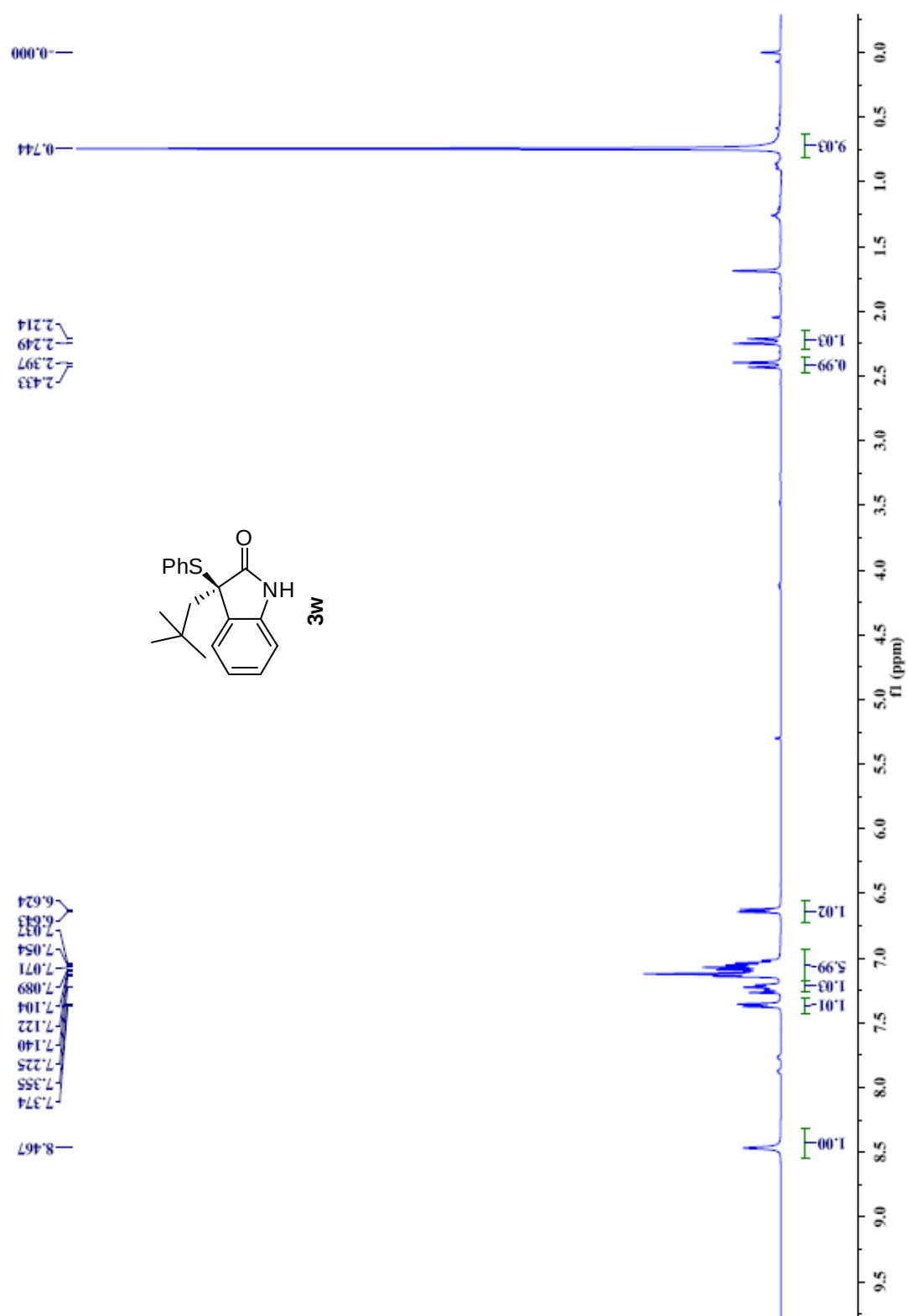


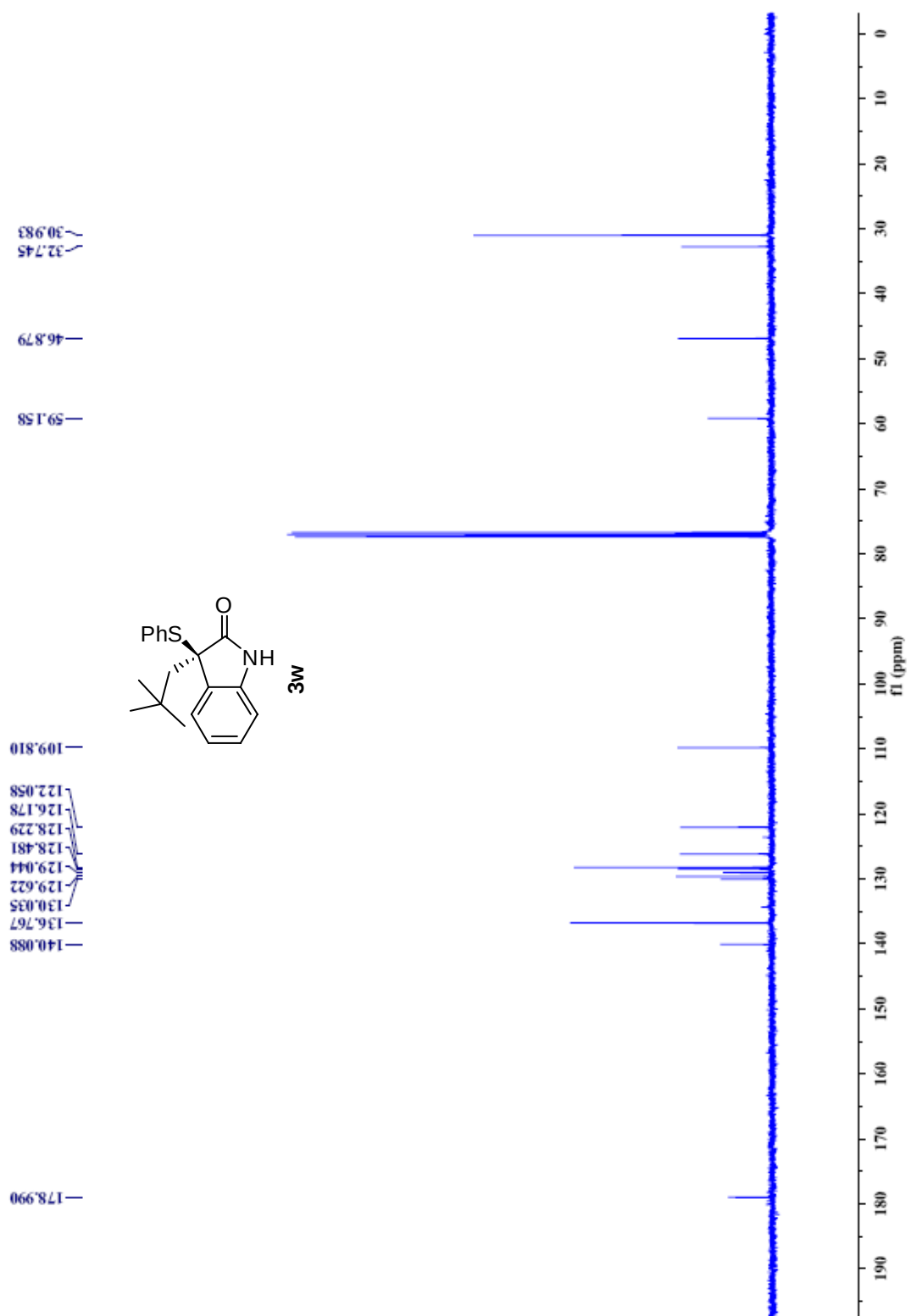


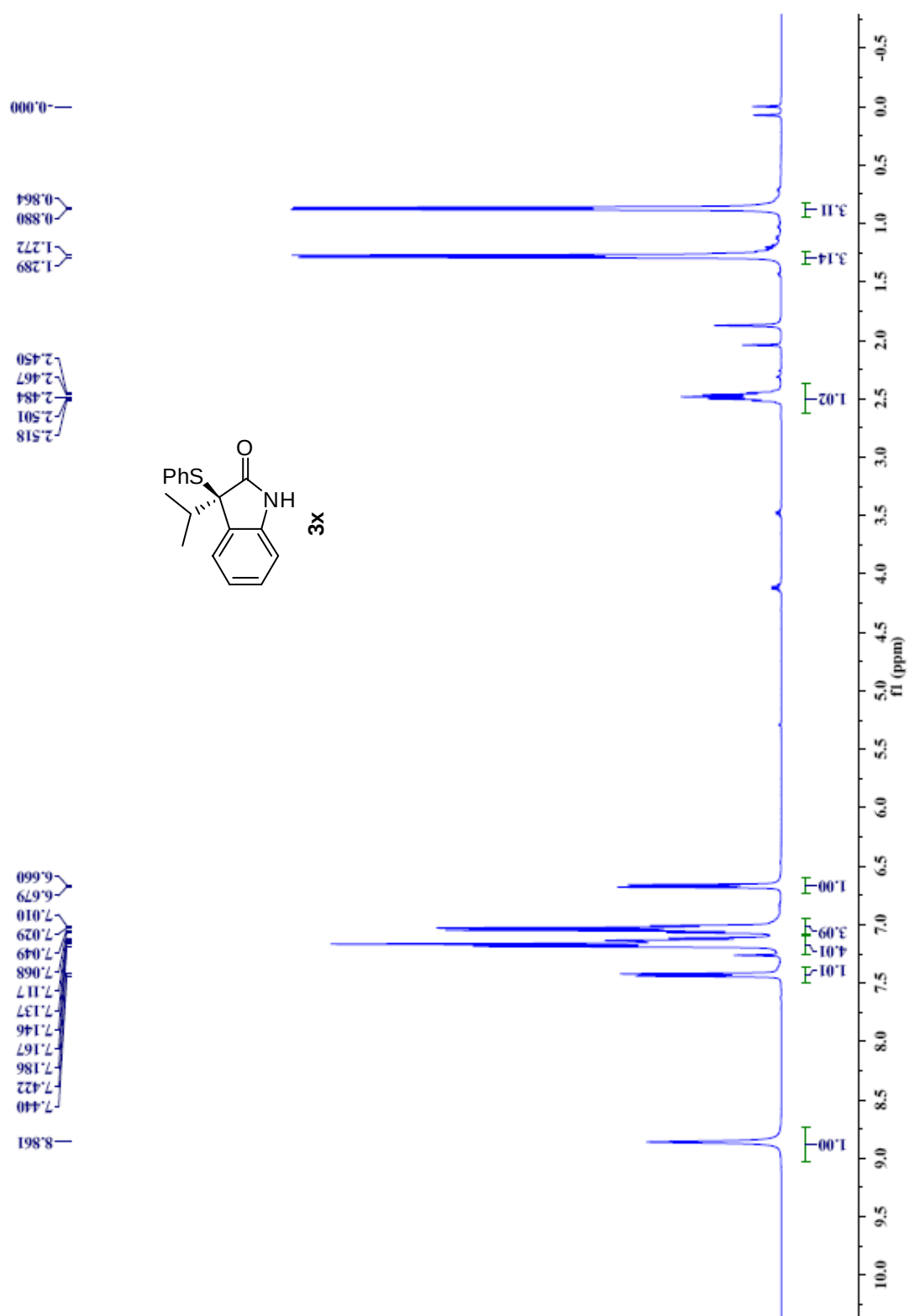


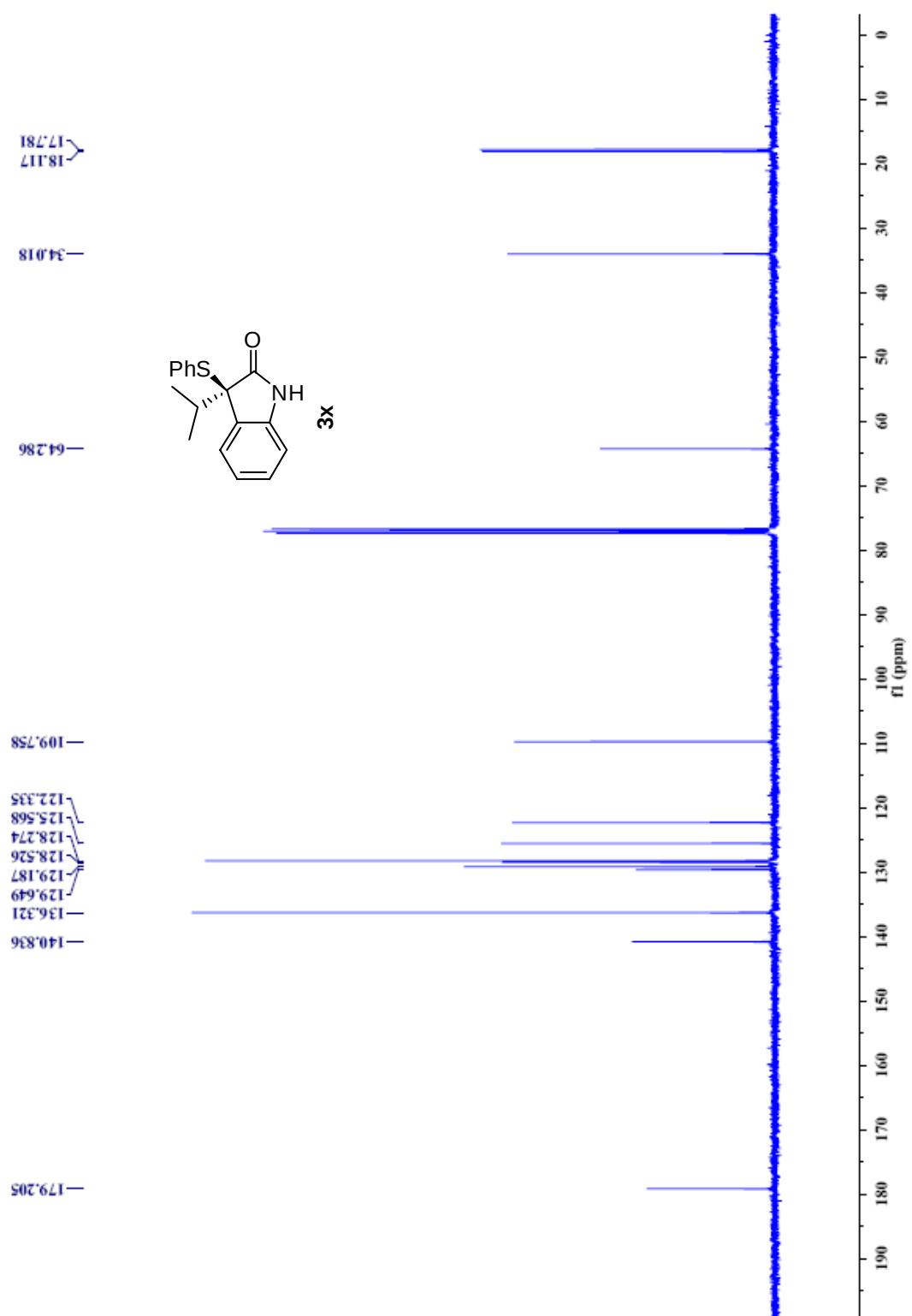




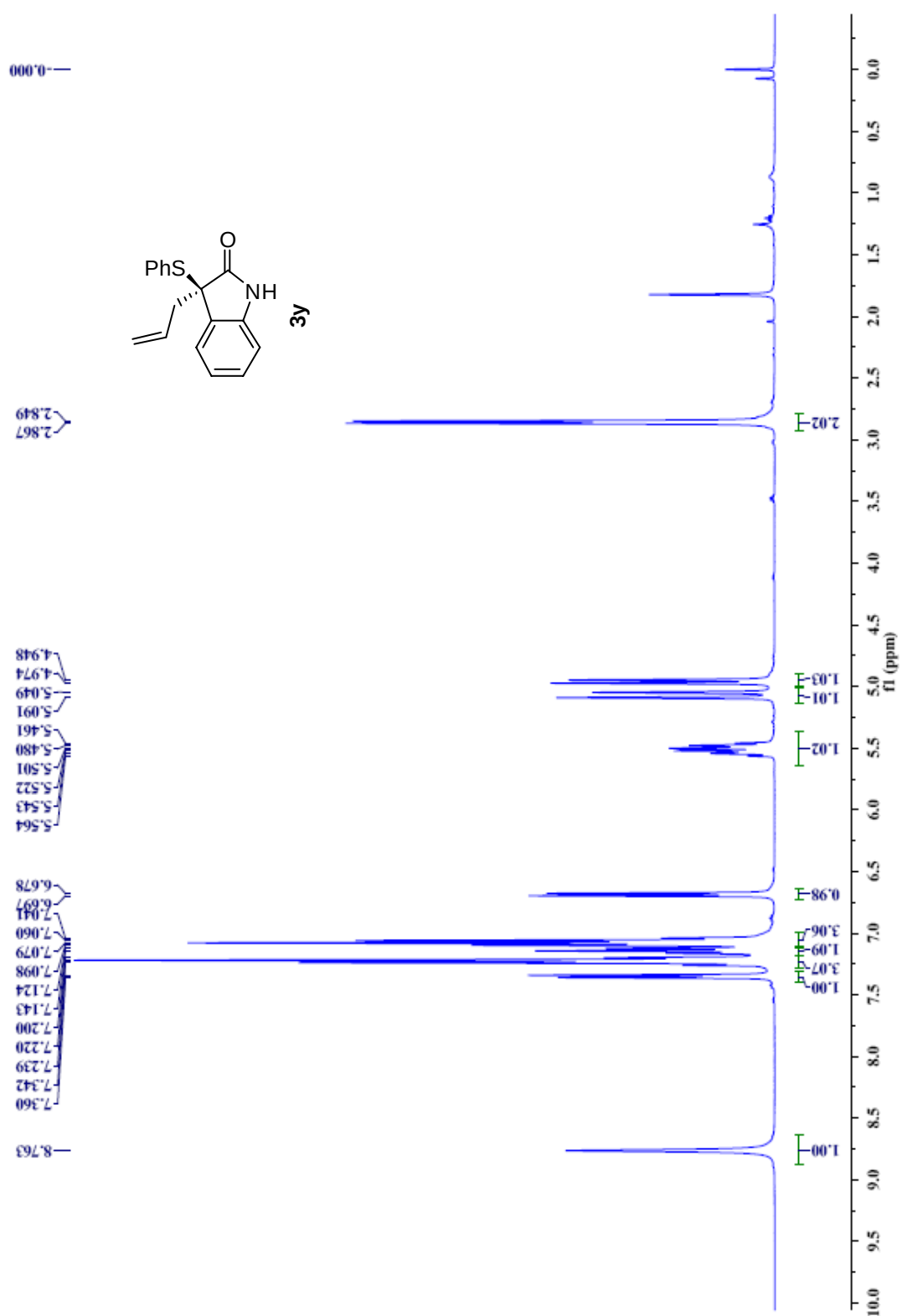


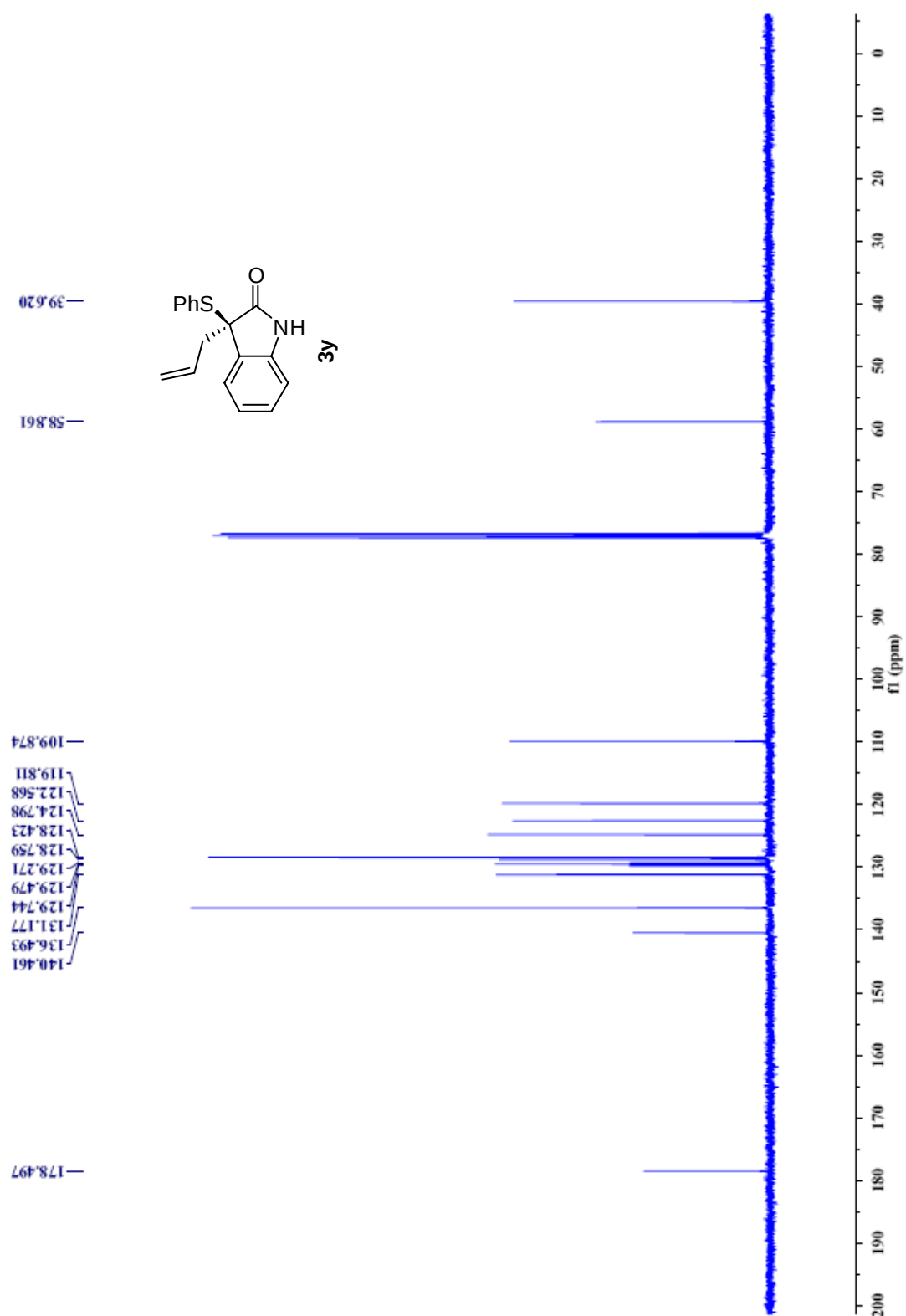


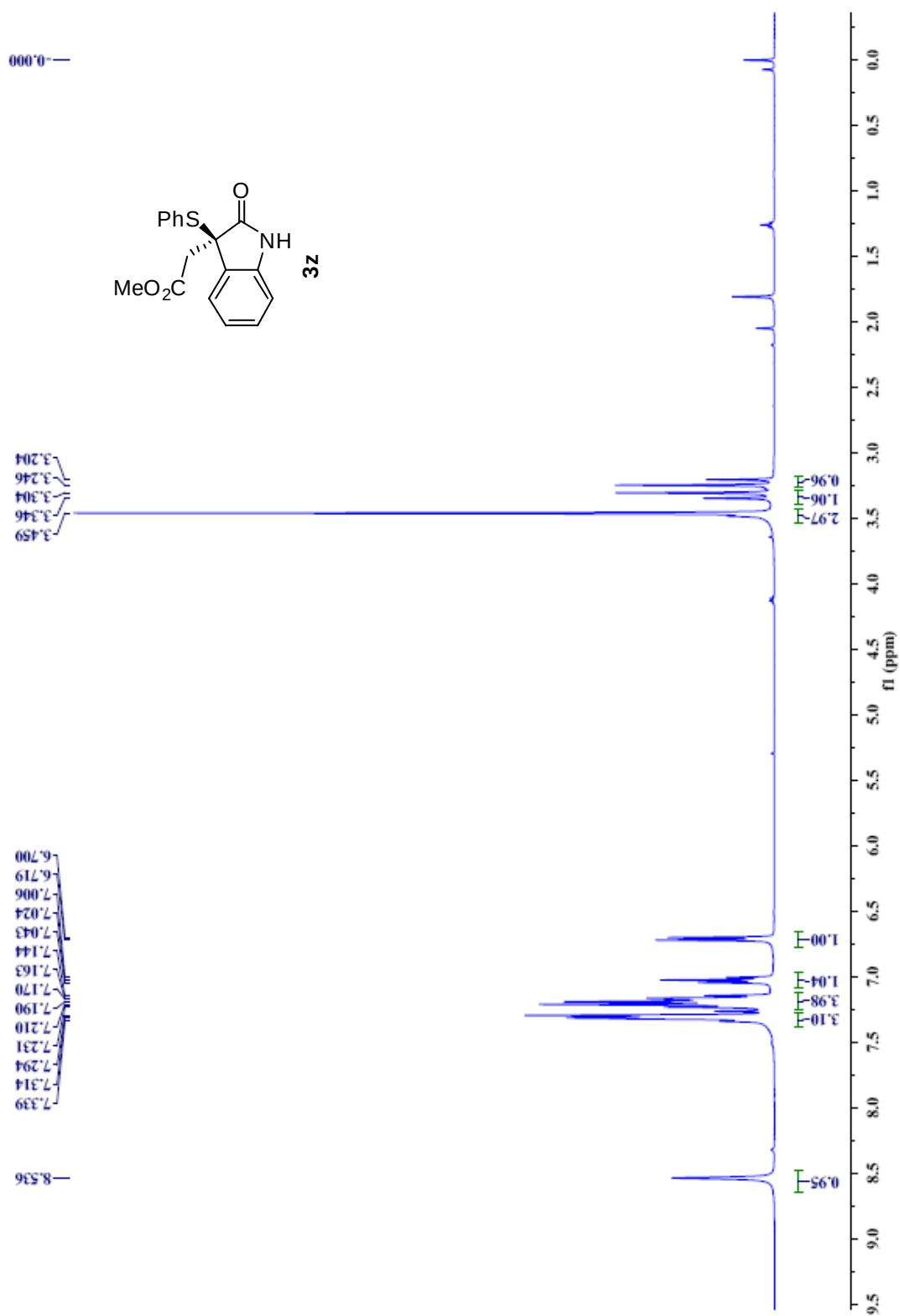


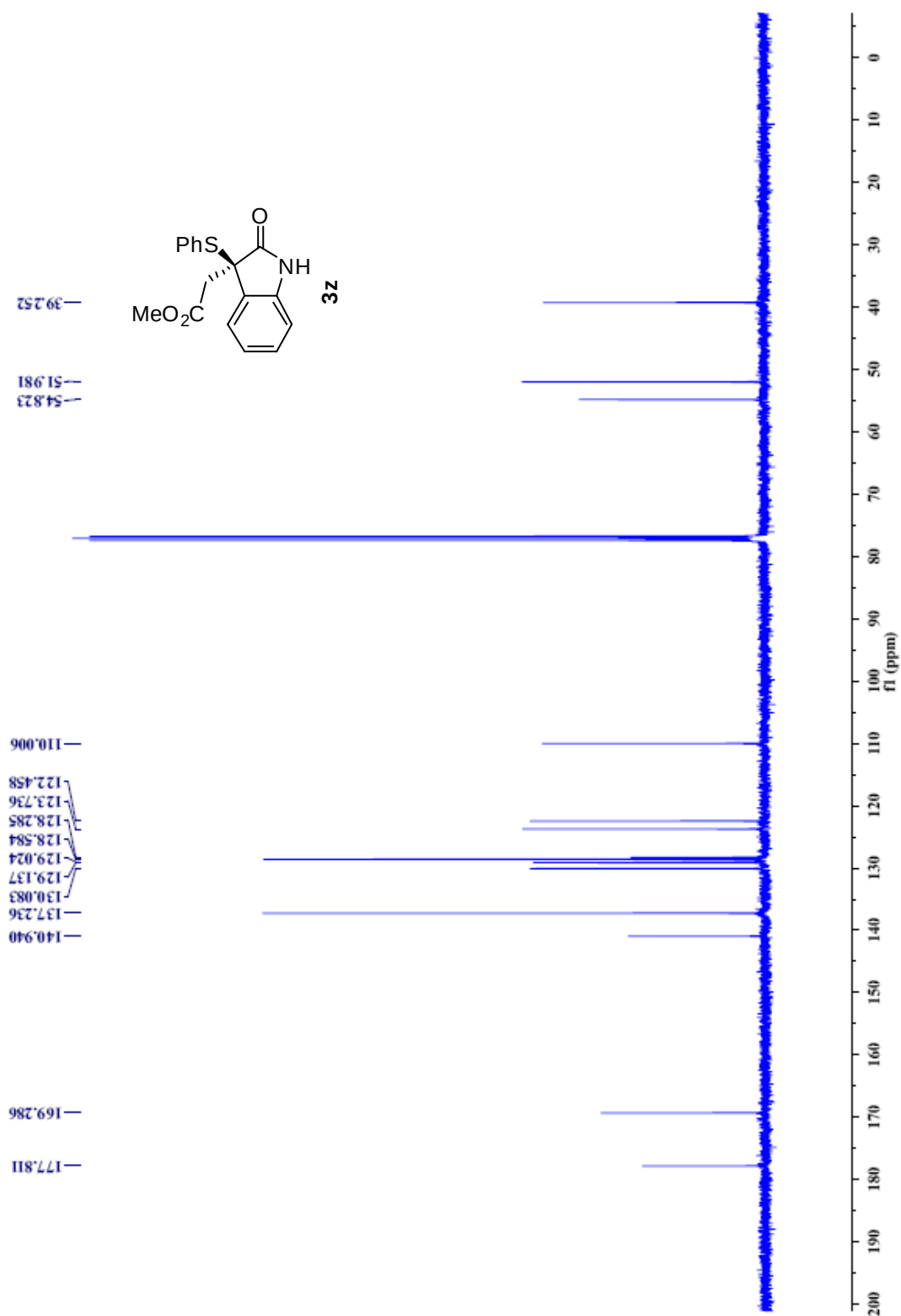


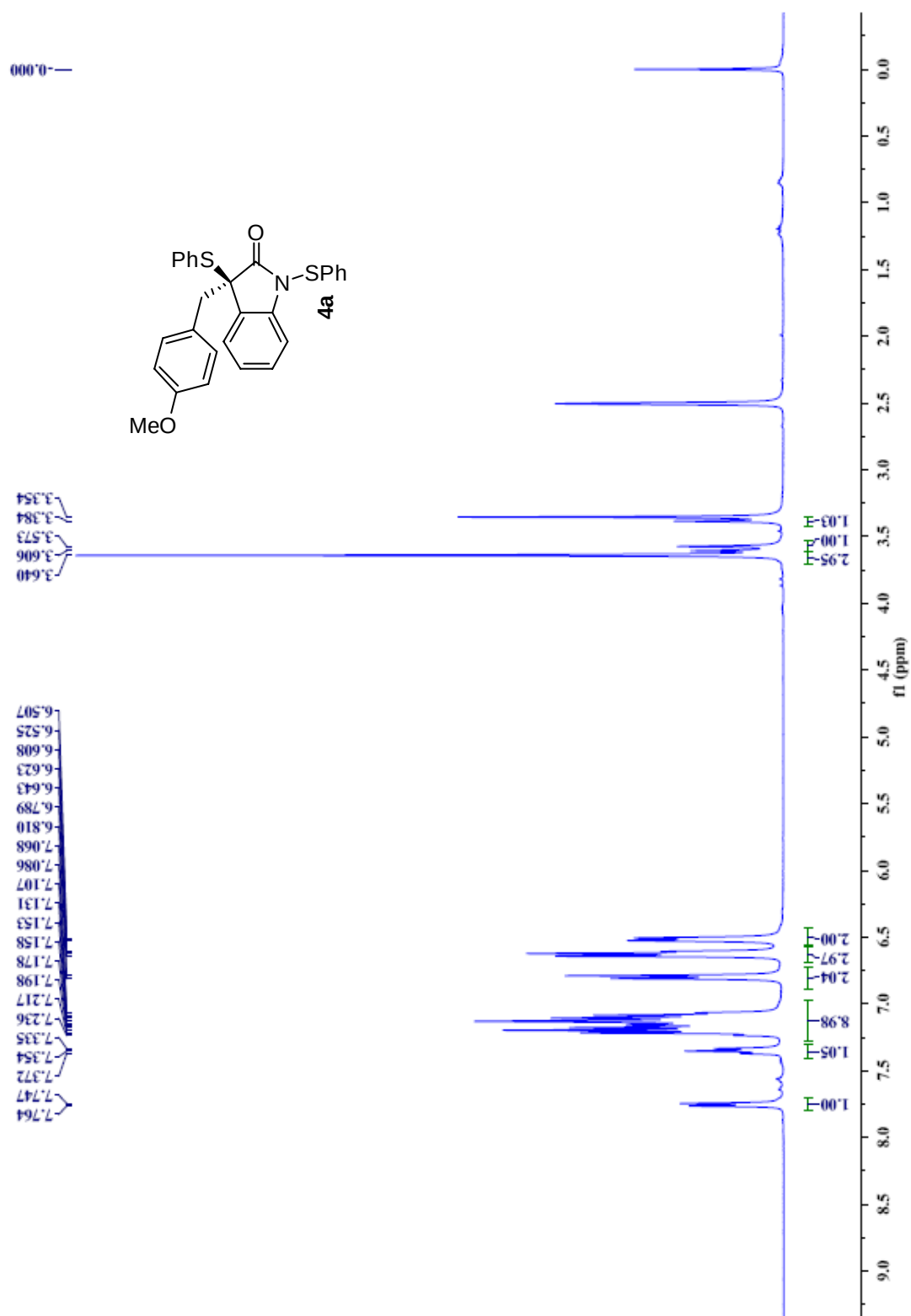


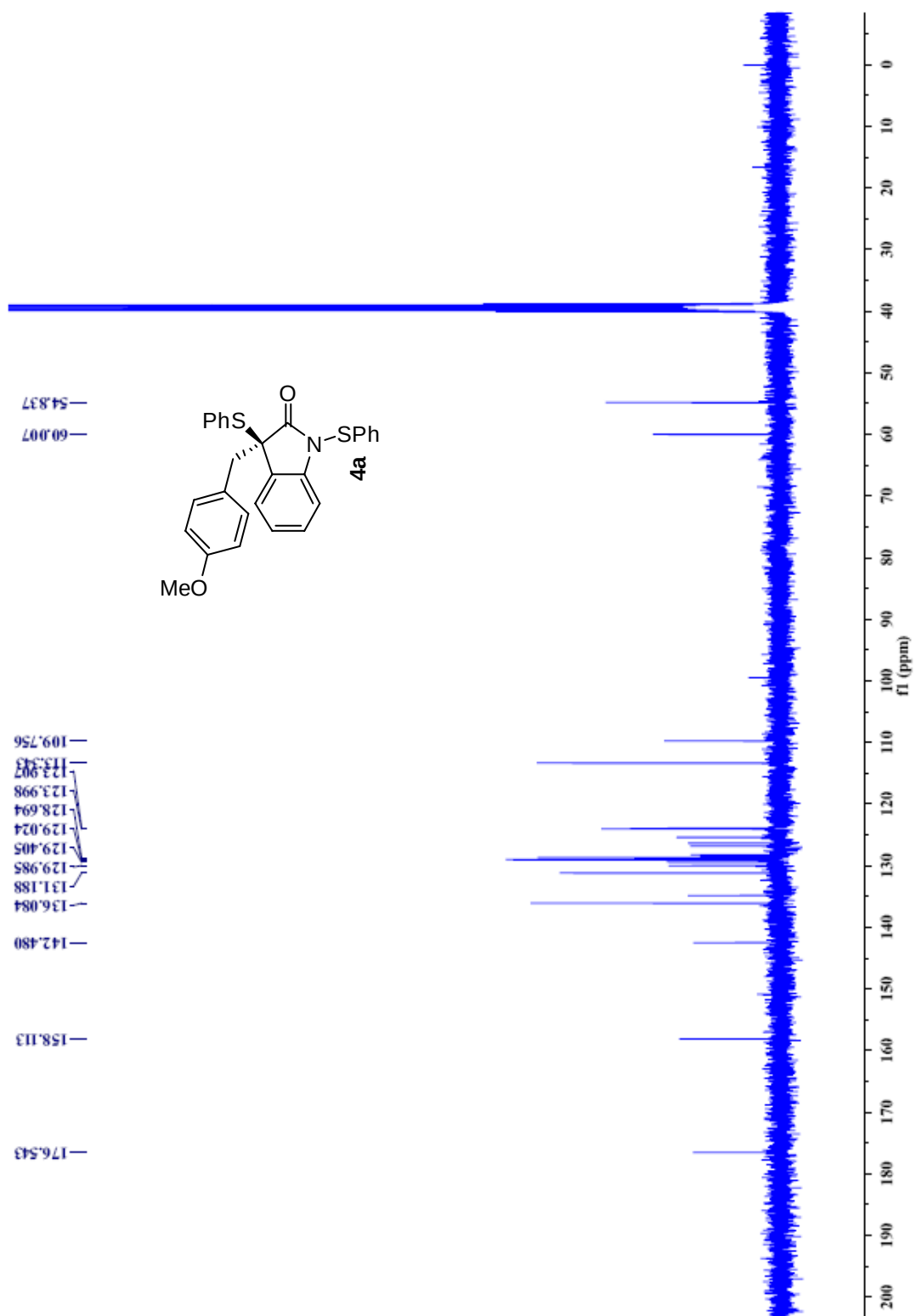


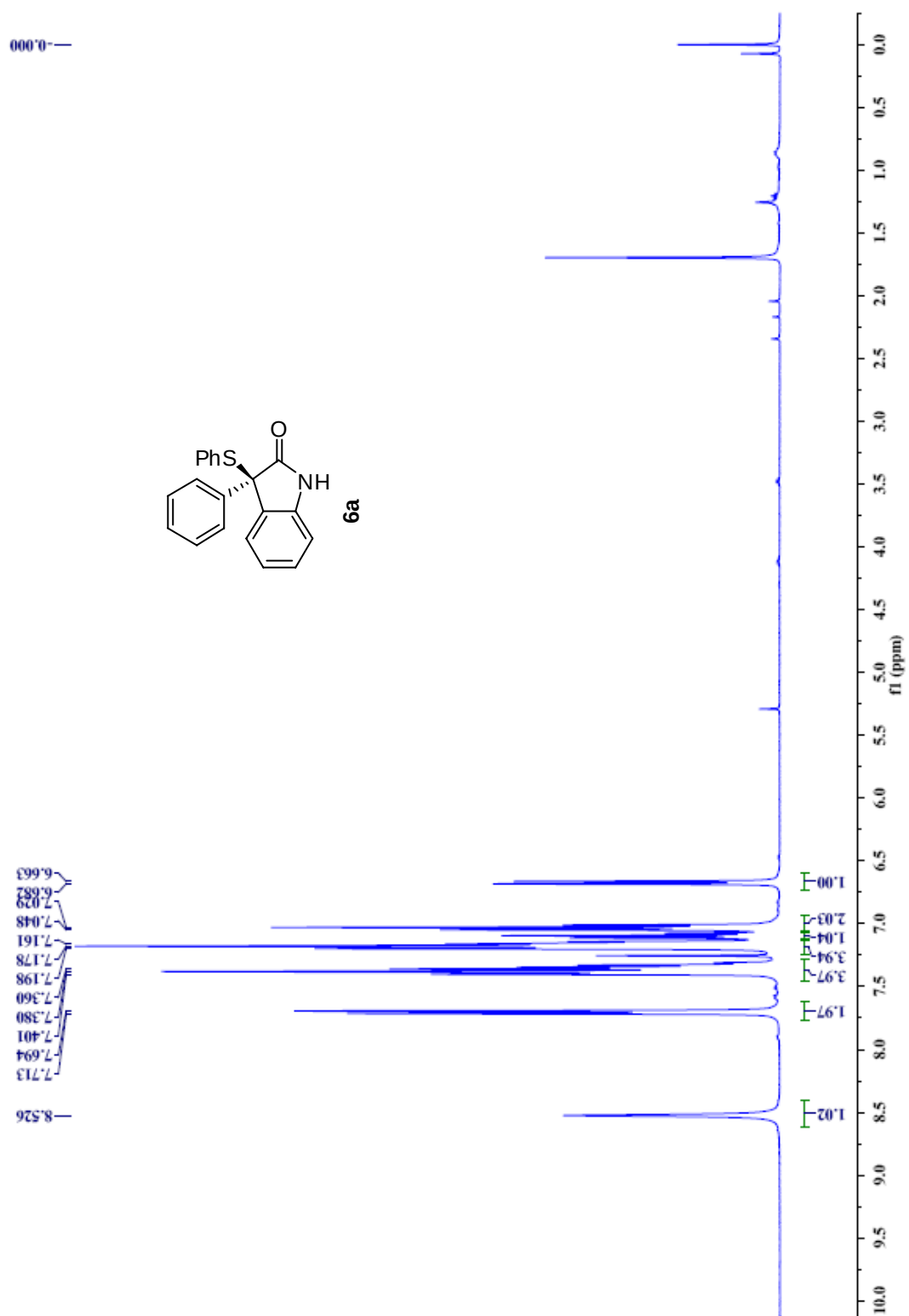


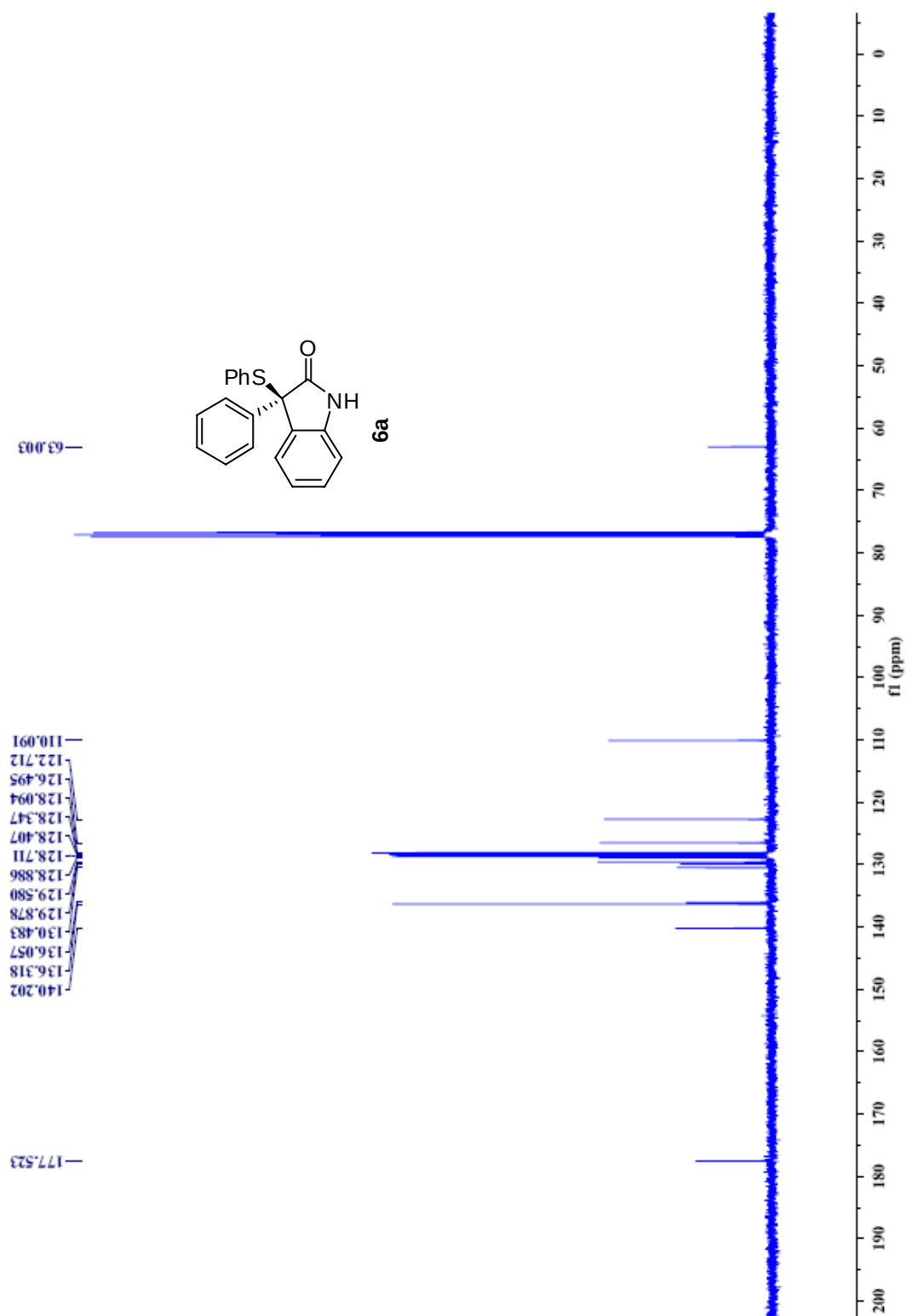




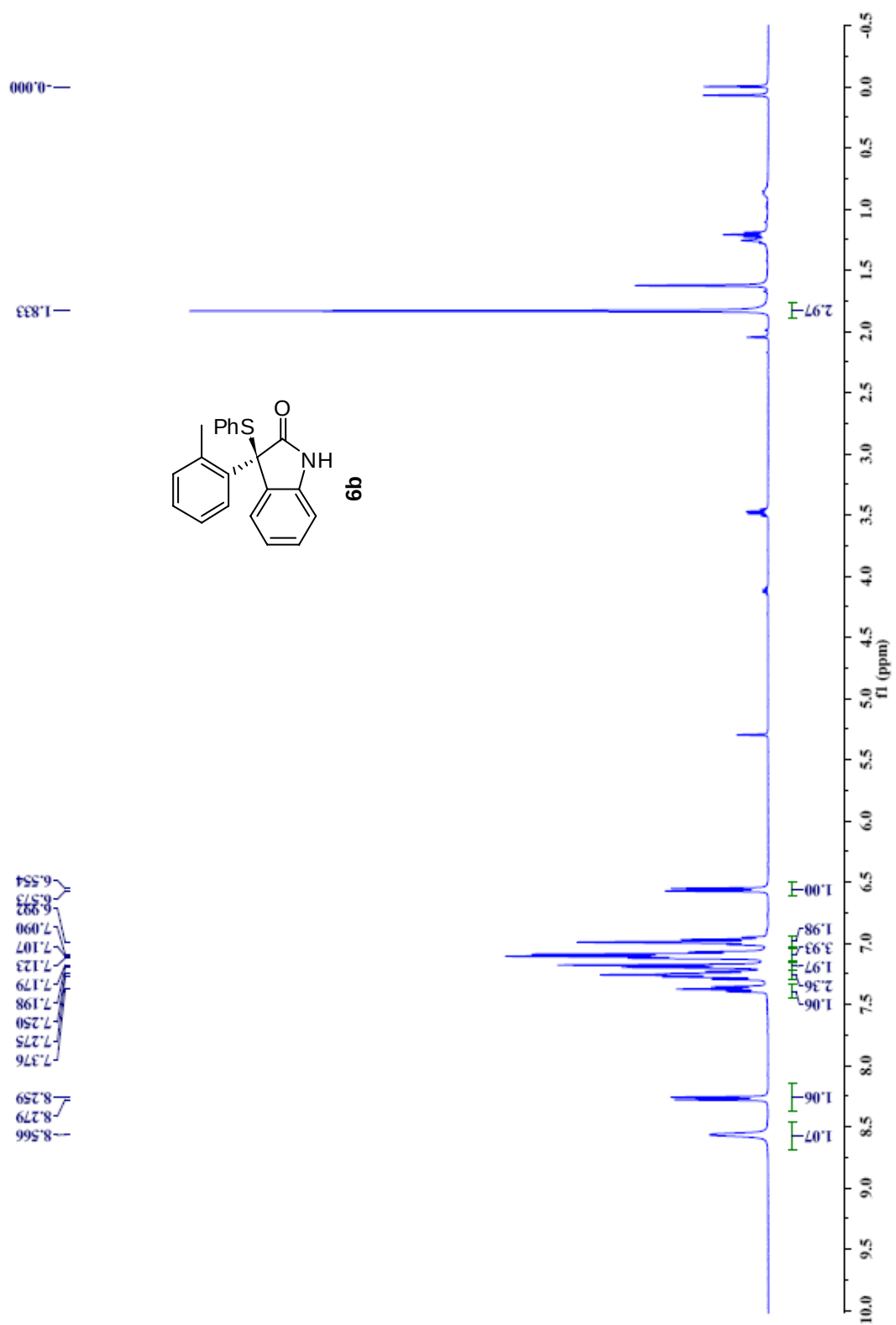


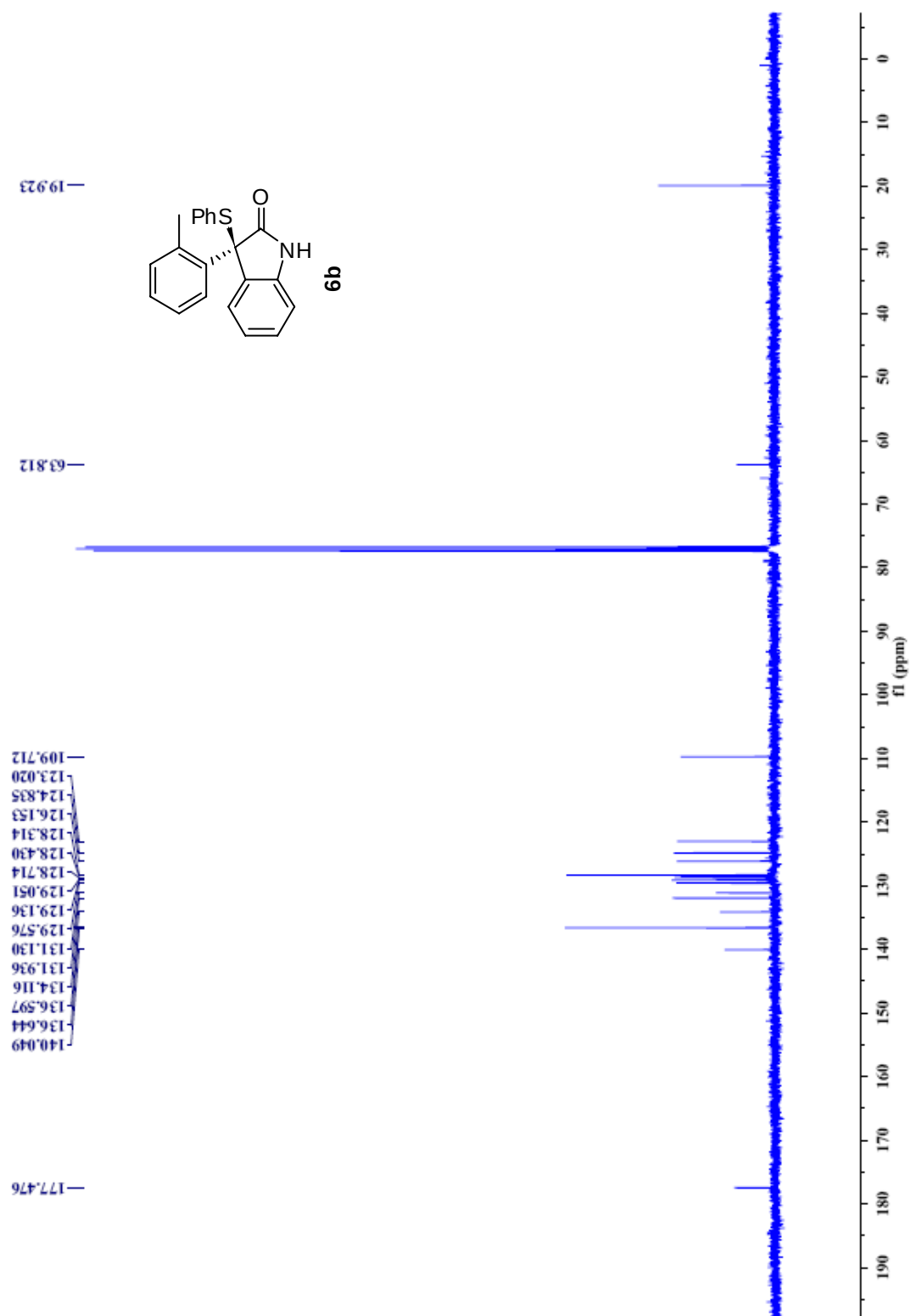


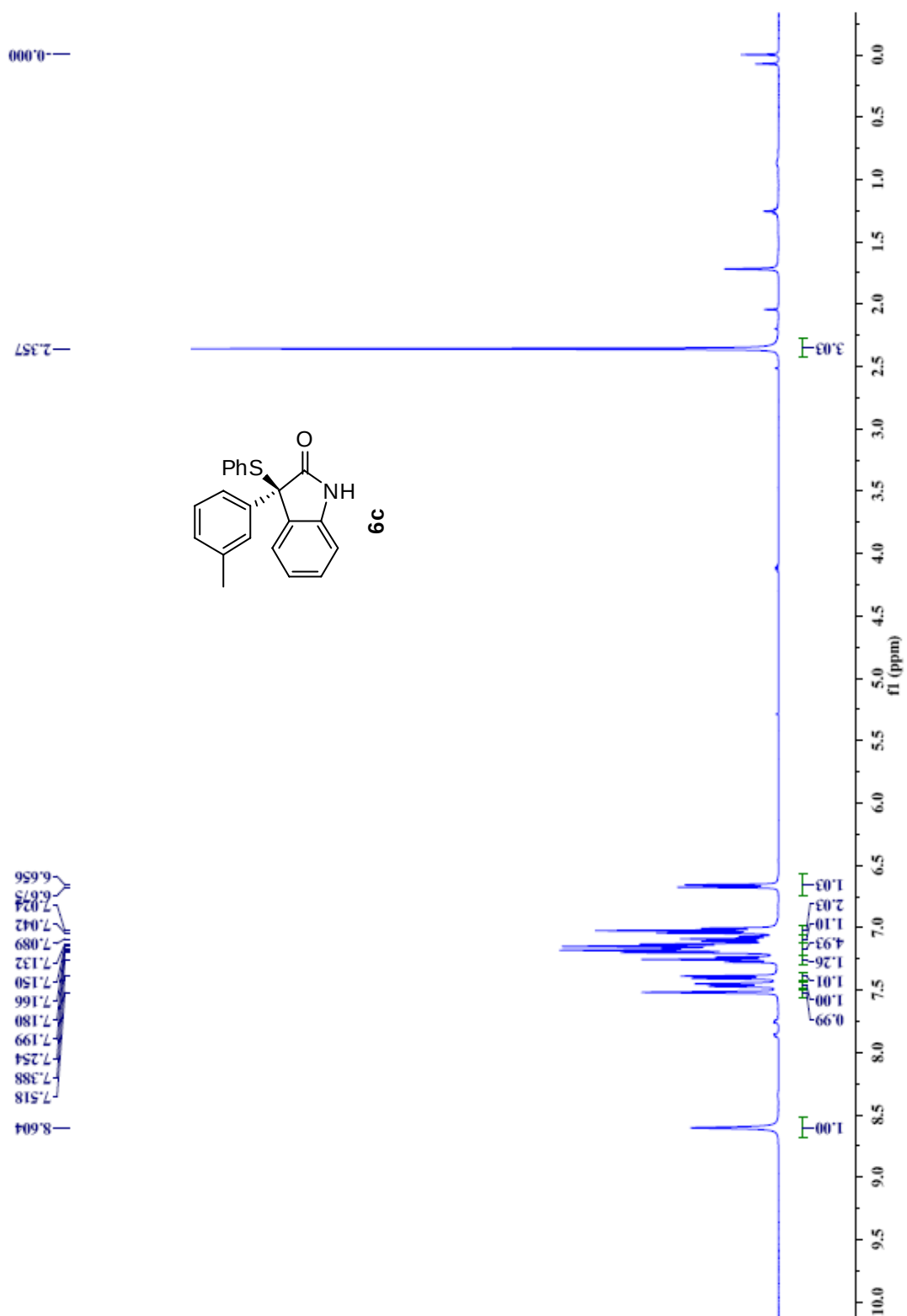


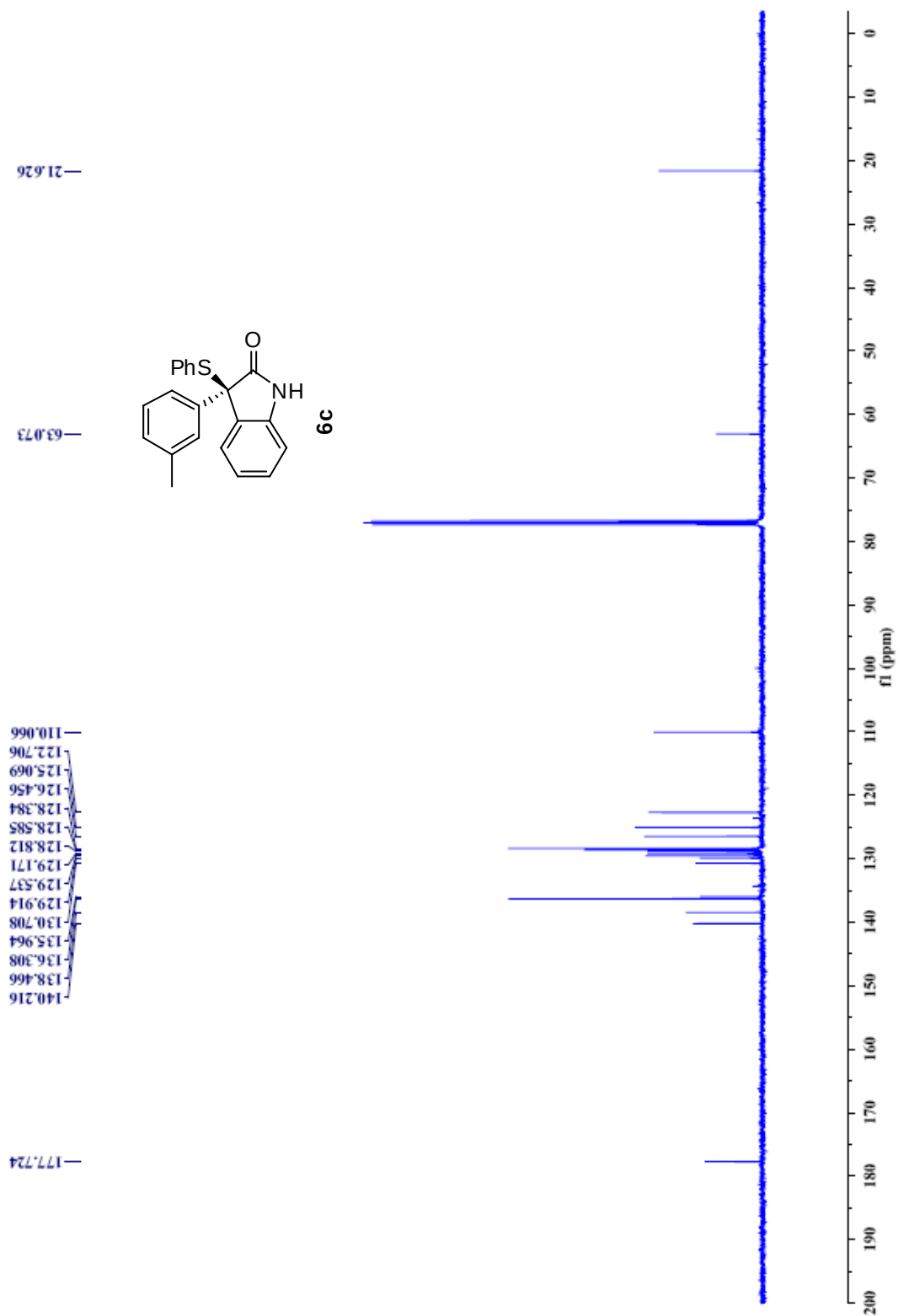


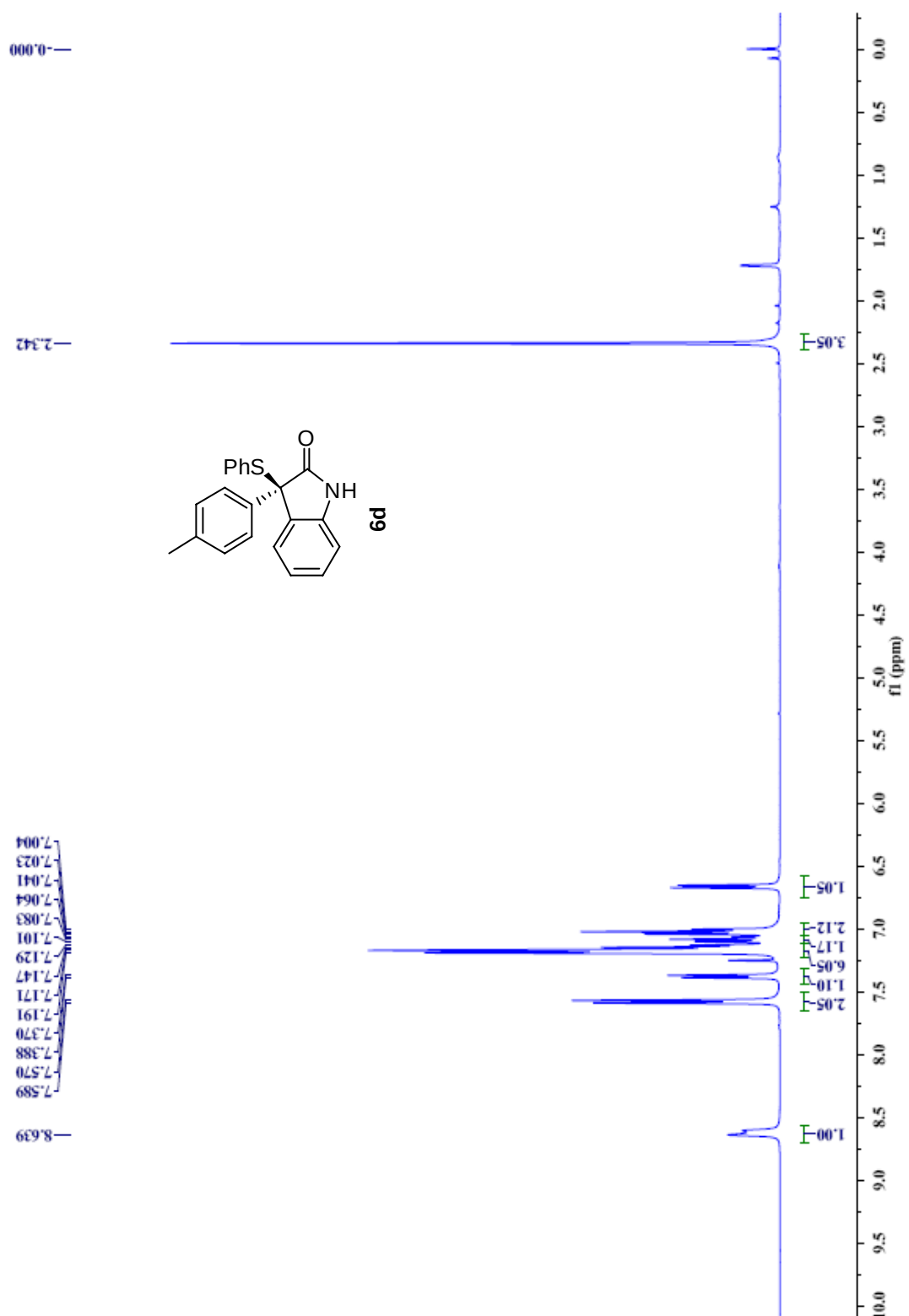


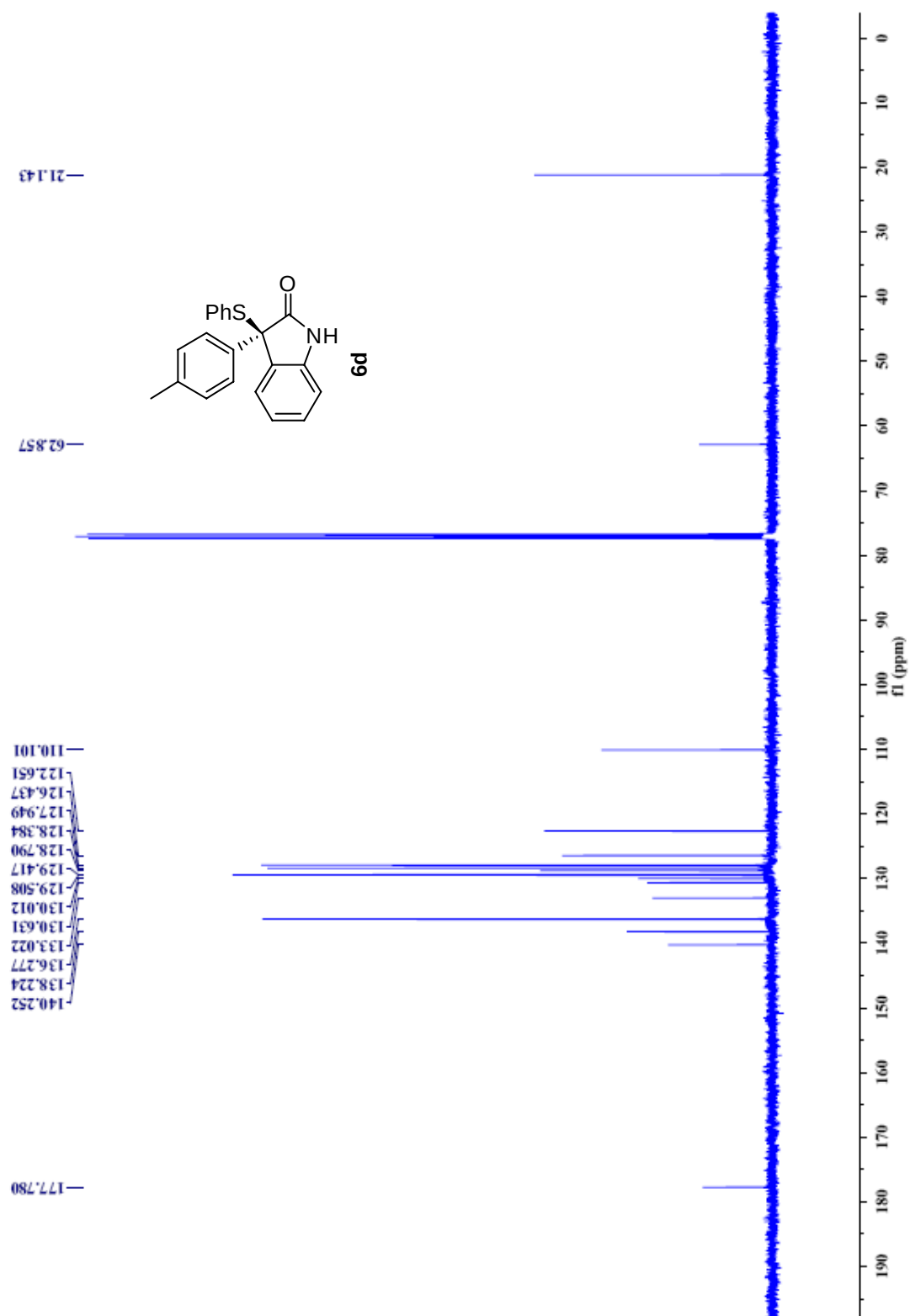


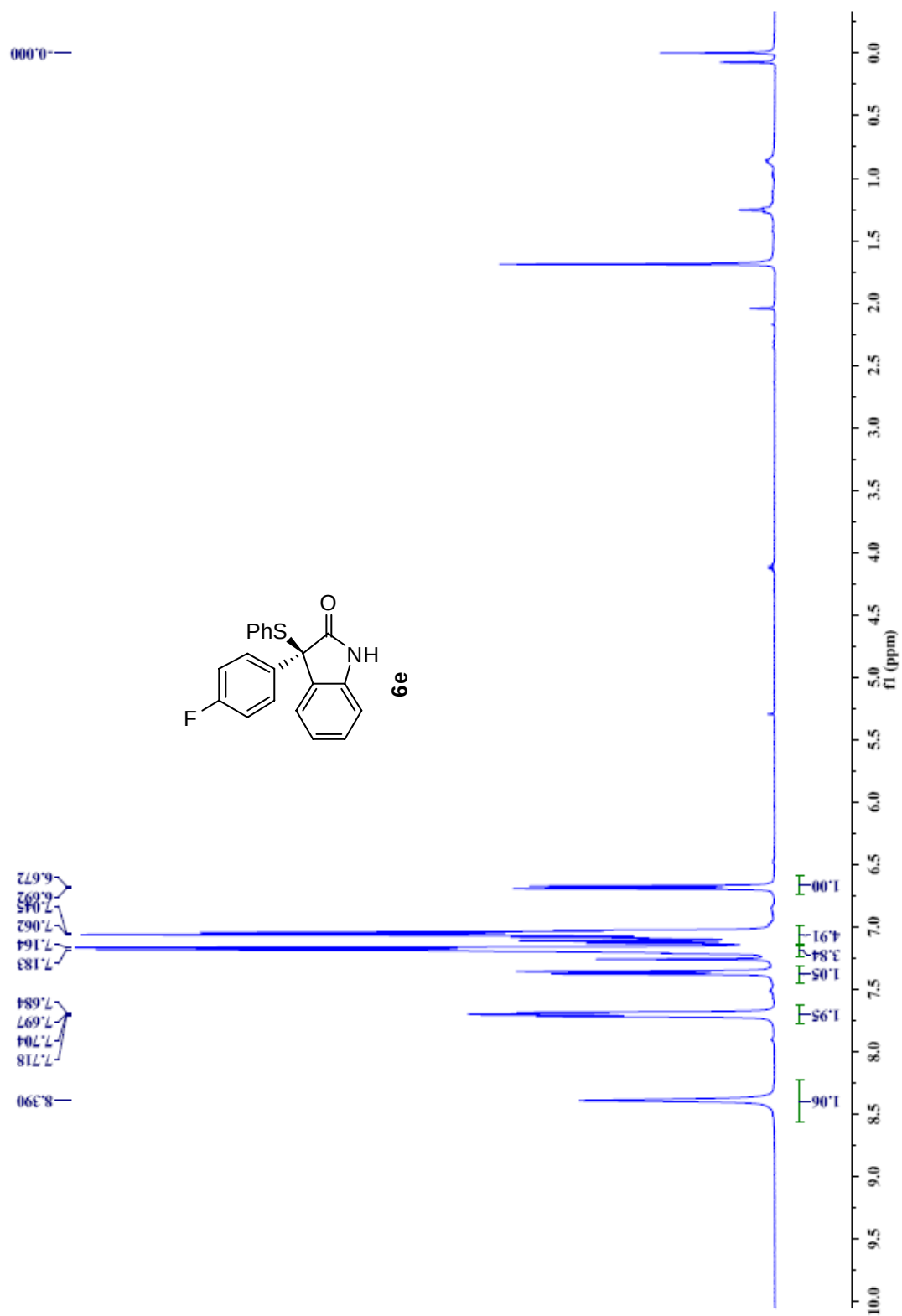


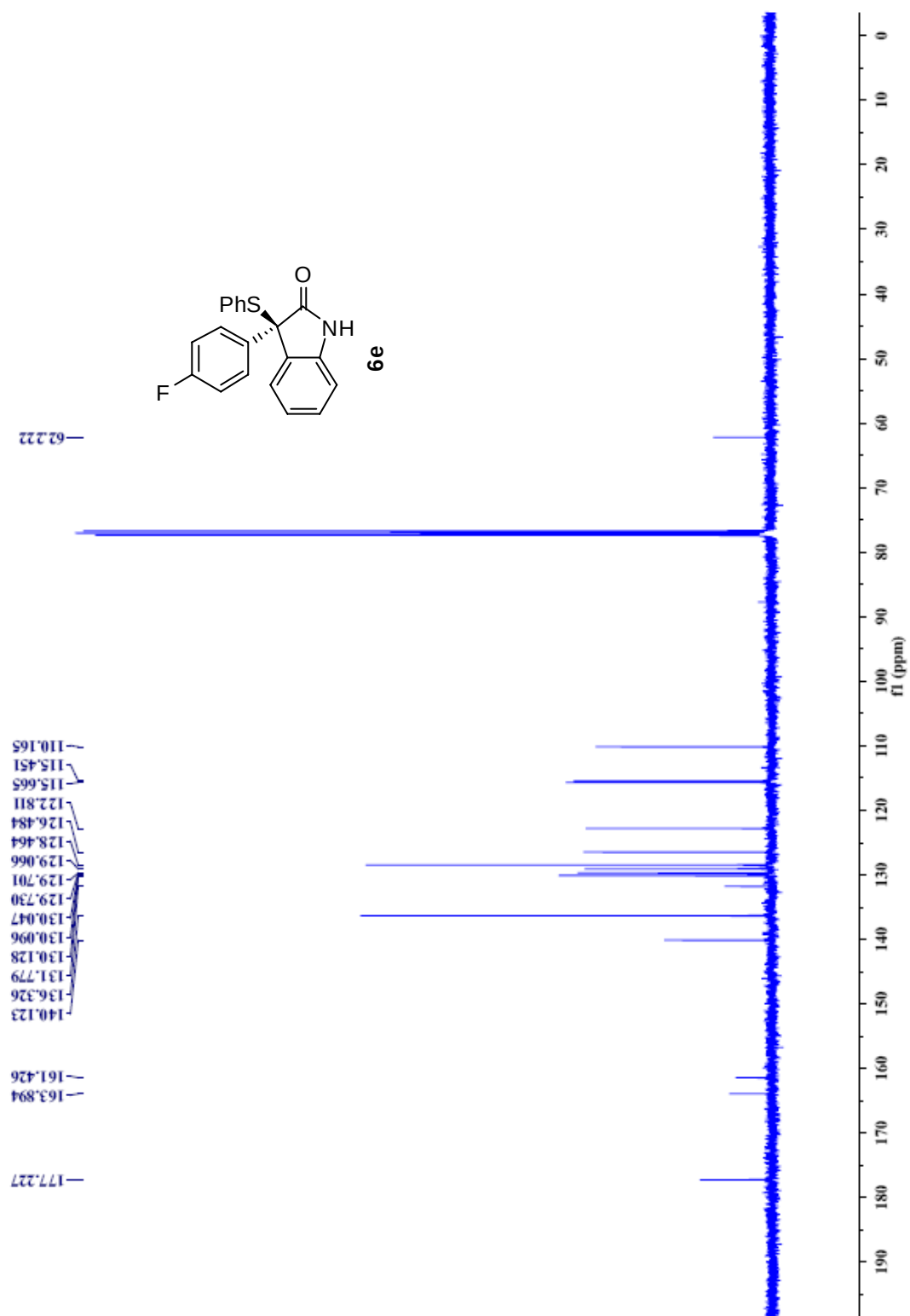






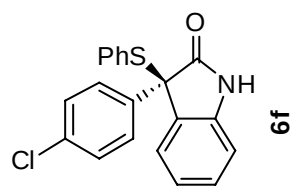




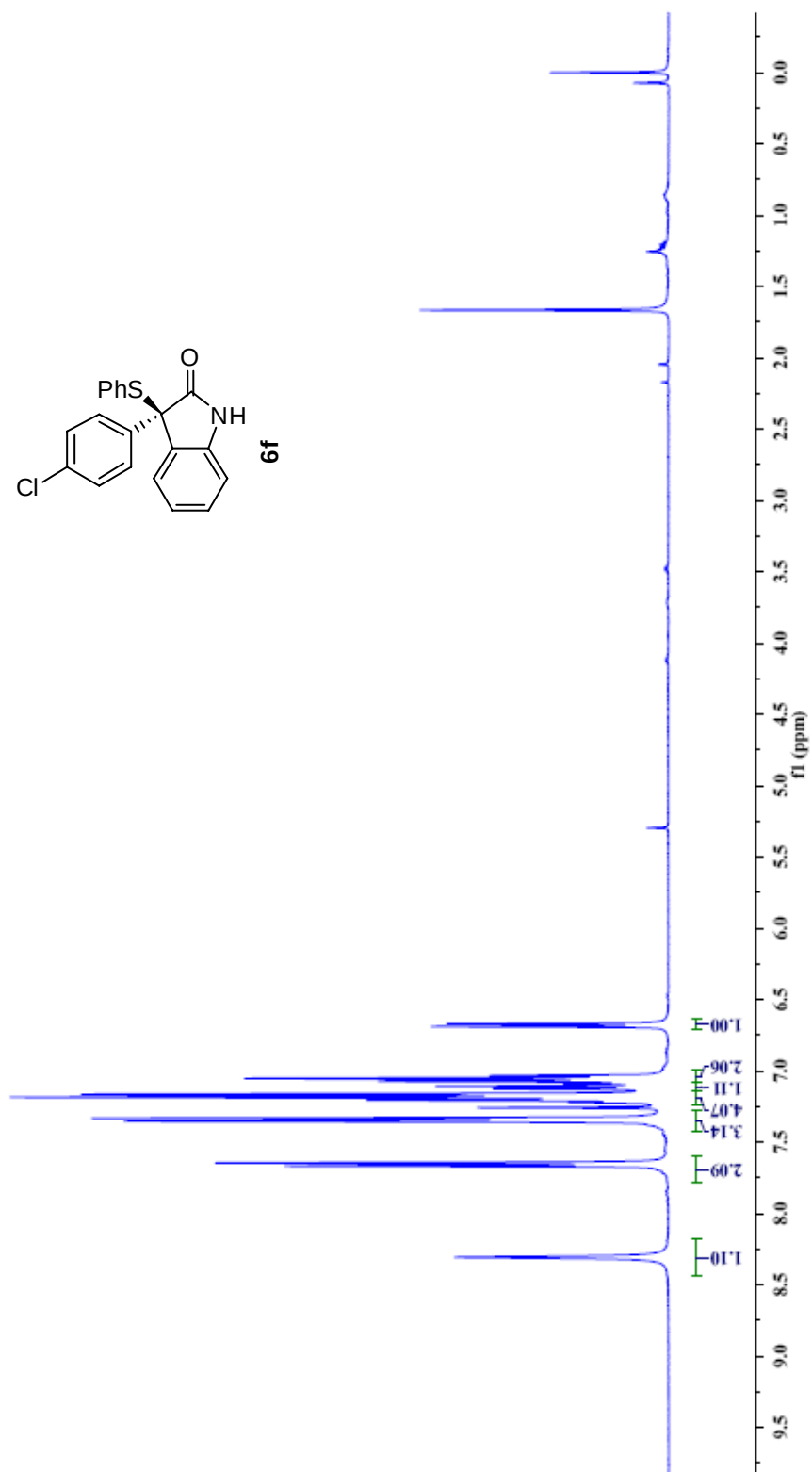


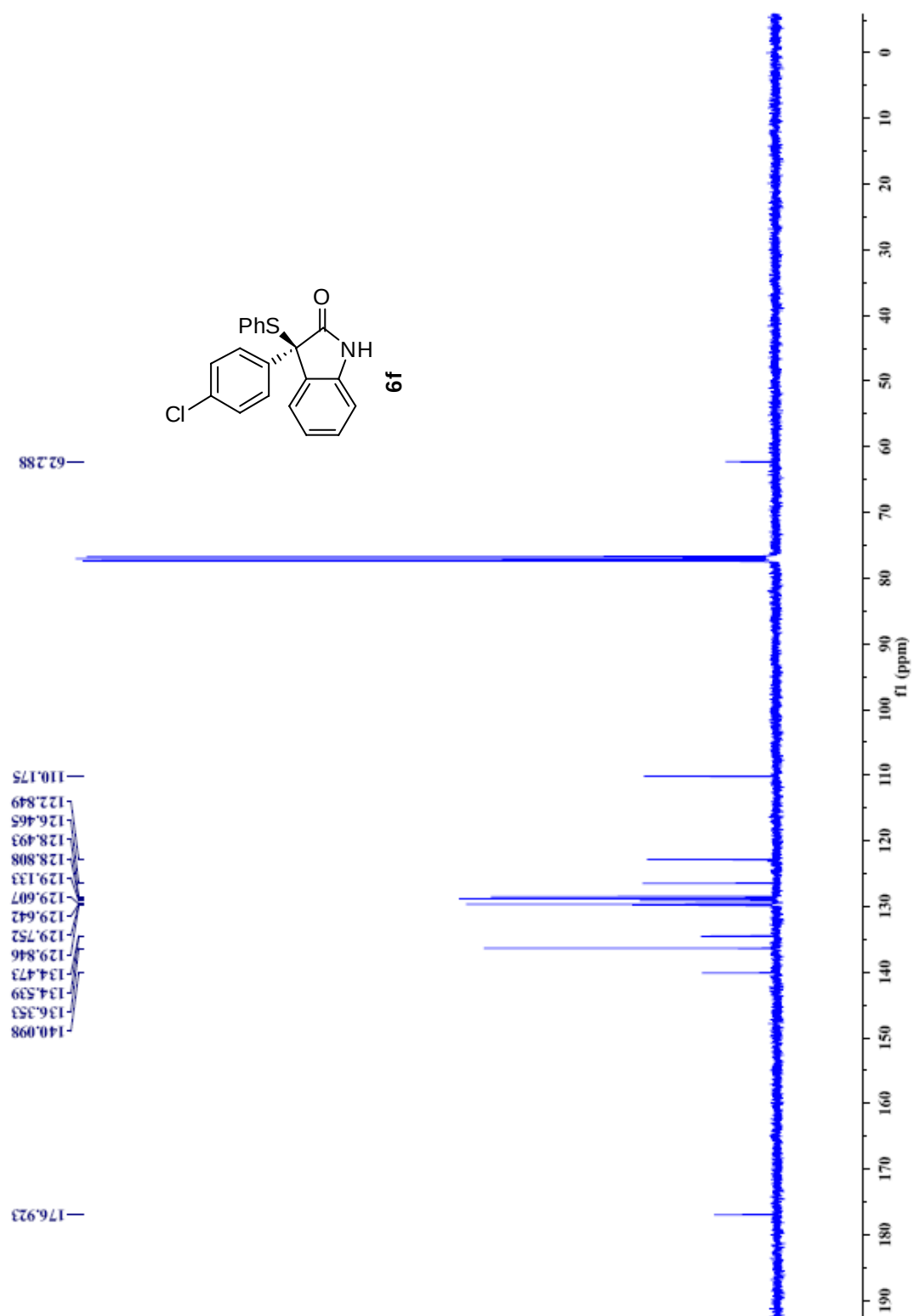


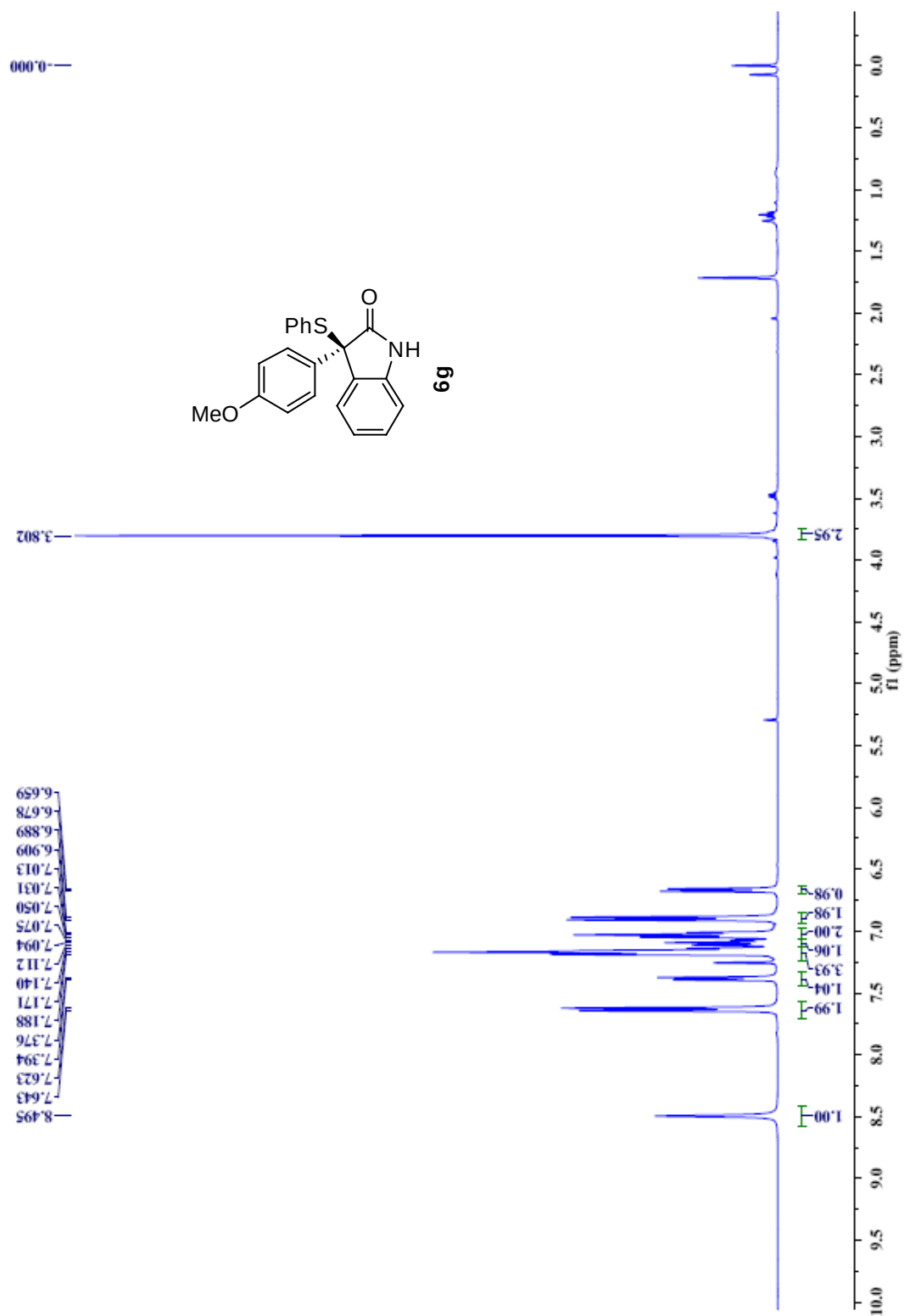
—0.000

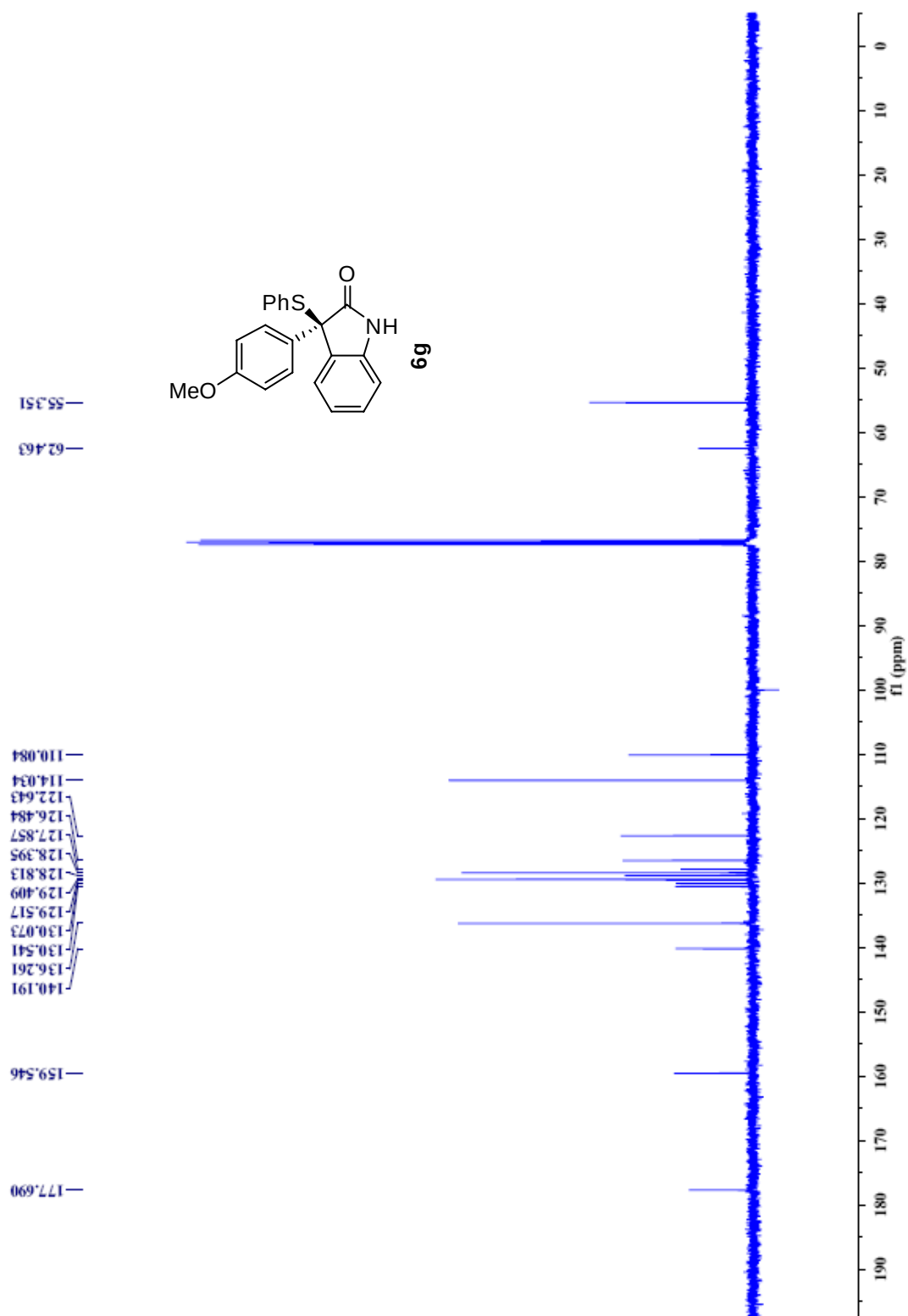


6.670  
 6.653  
 6.639  
 7.072  
 7.165  
 7.184  
 7.204  
 7.333  
 7.352  
 7.645  
 7.666  
 —8.307

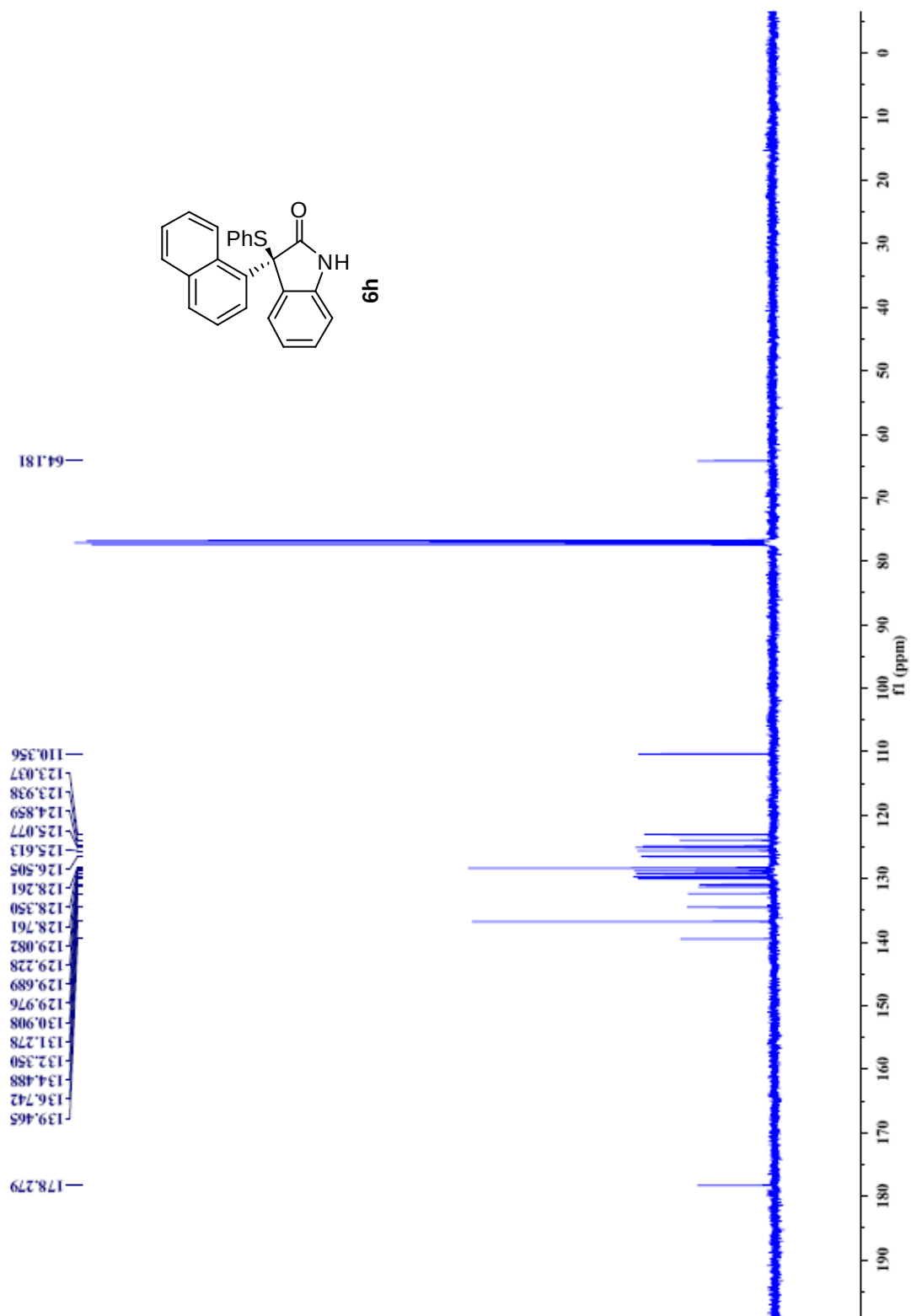


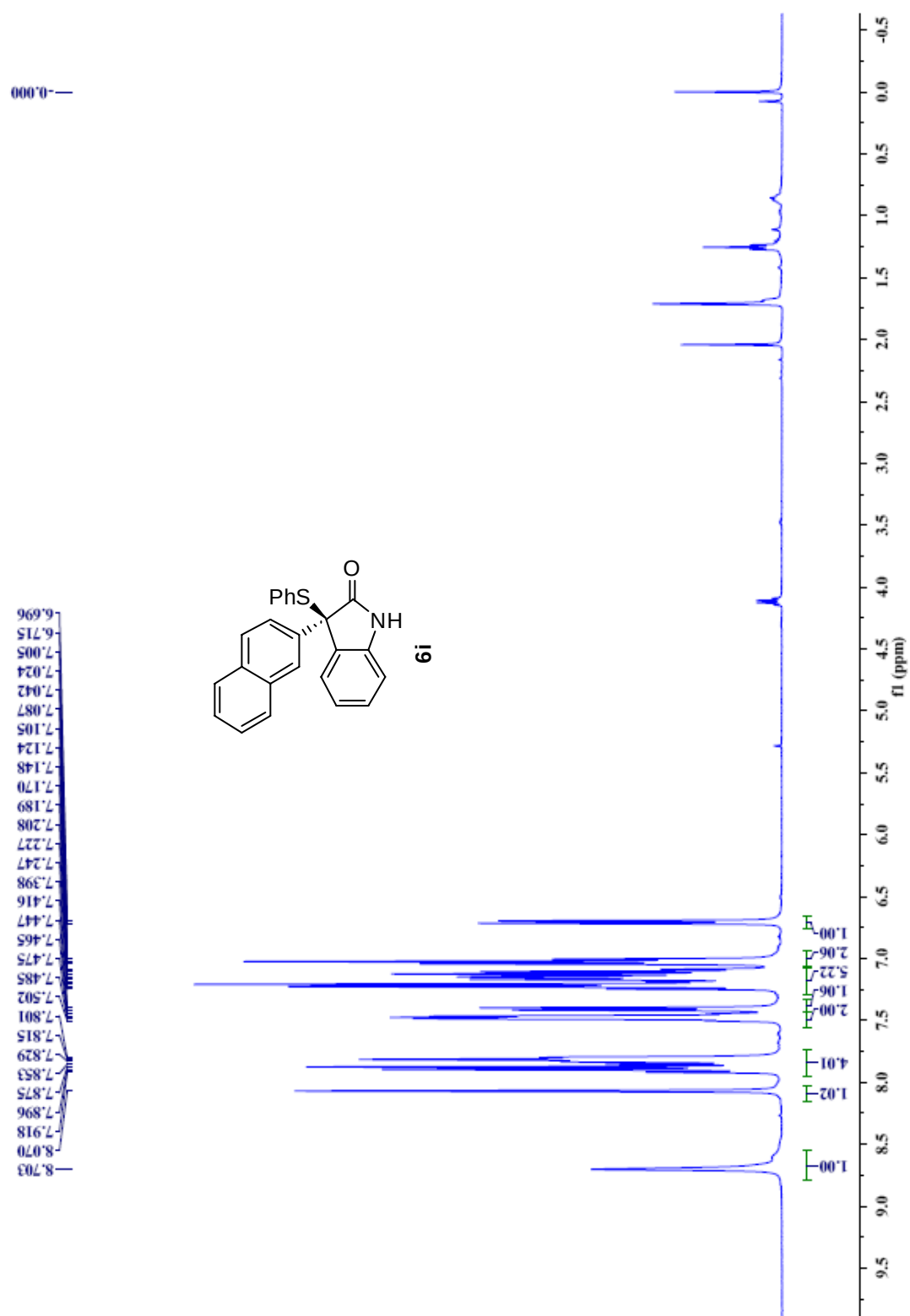


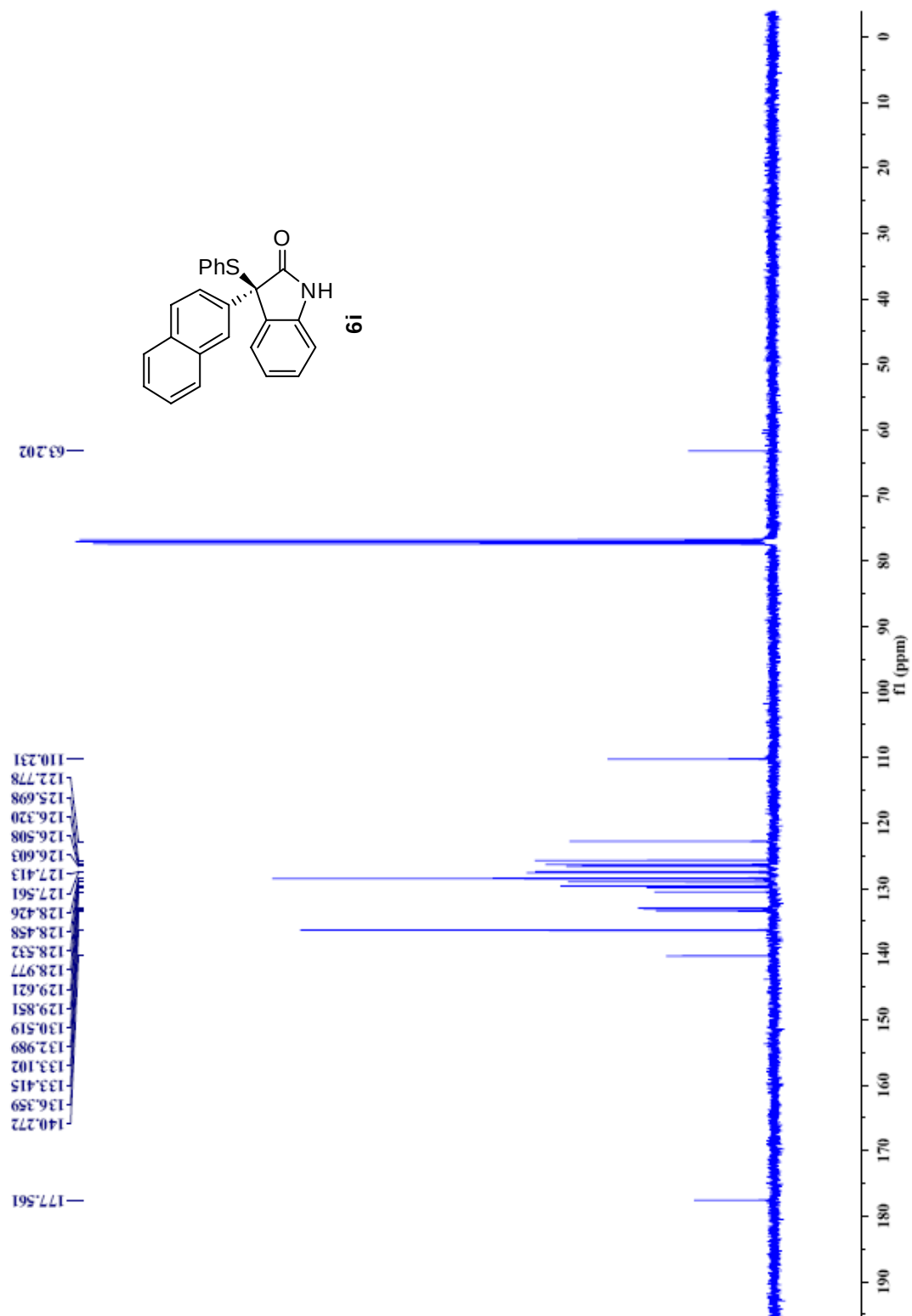






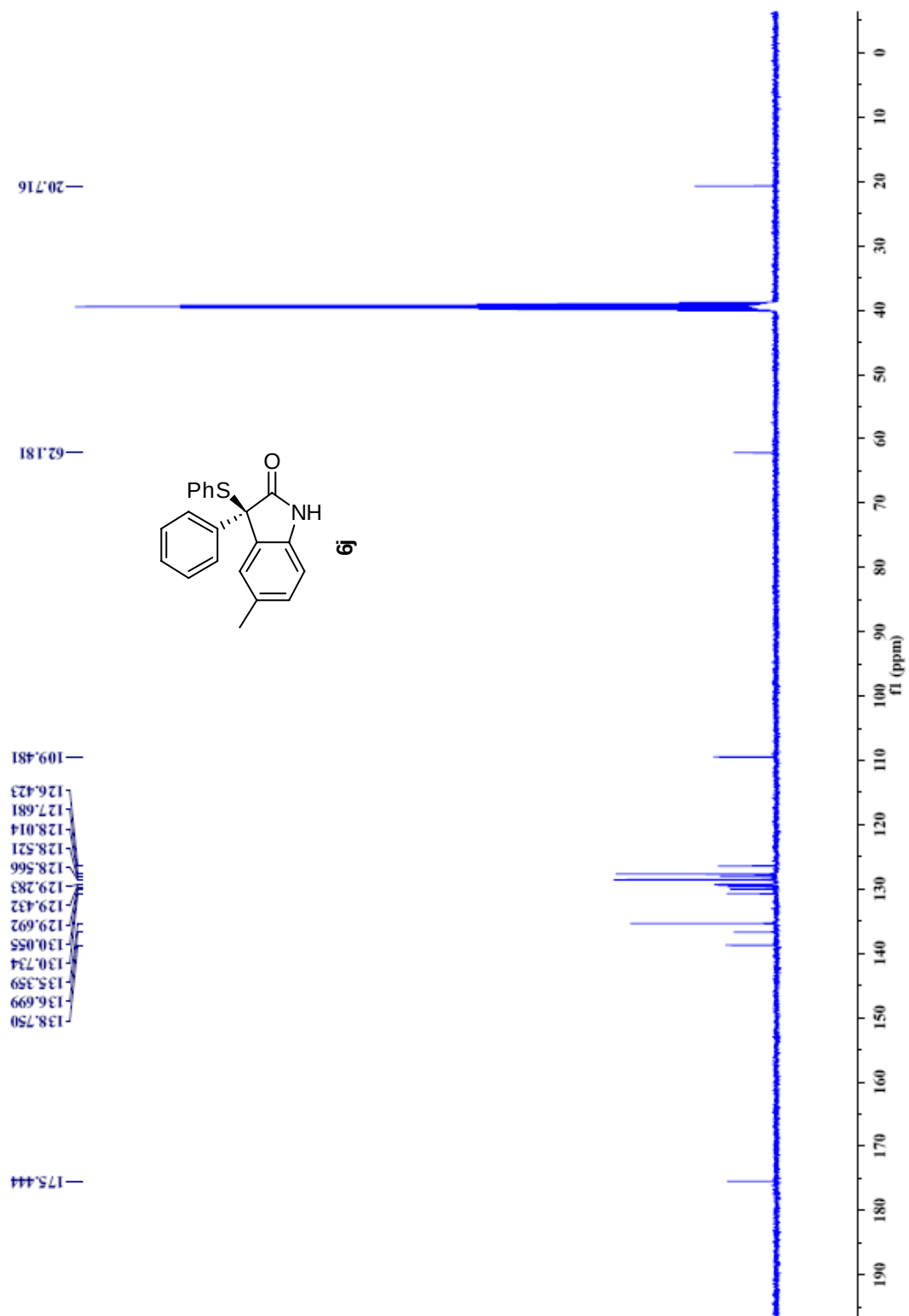


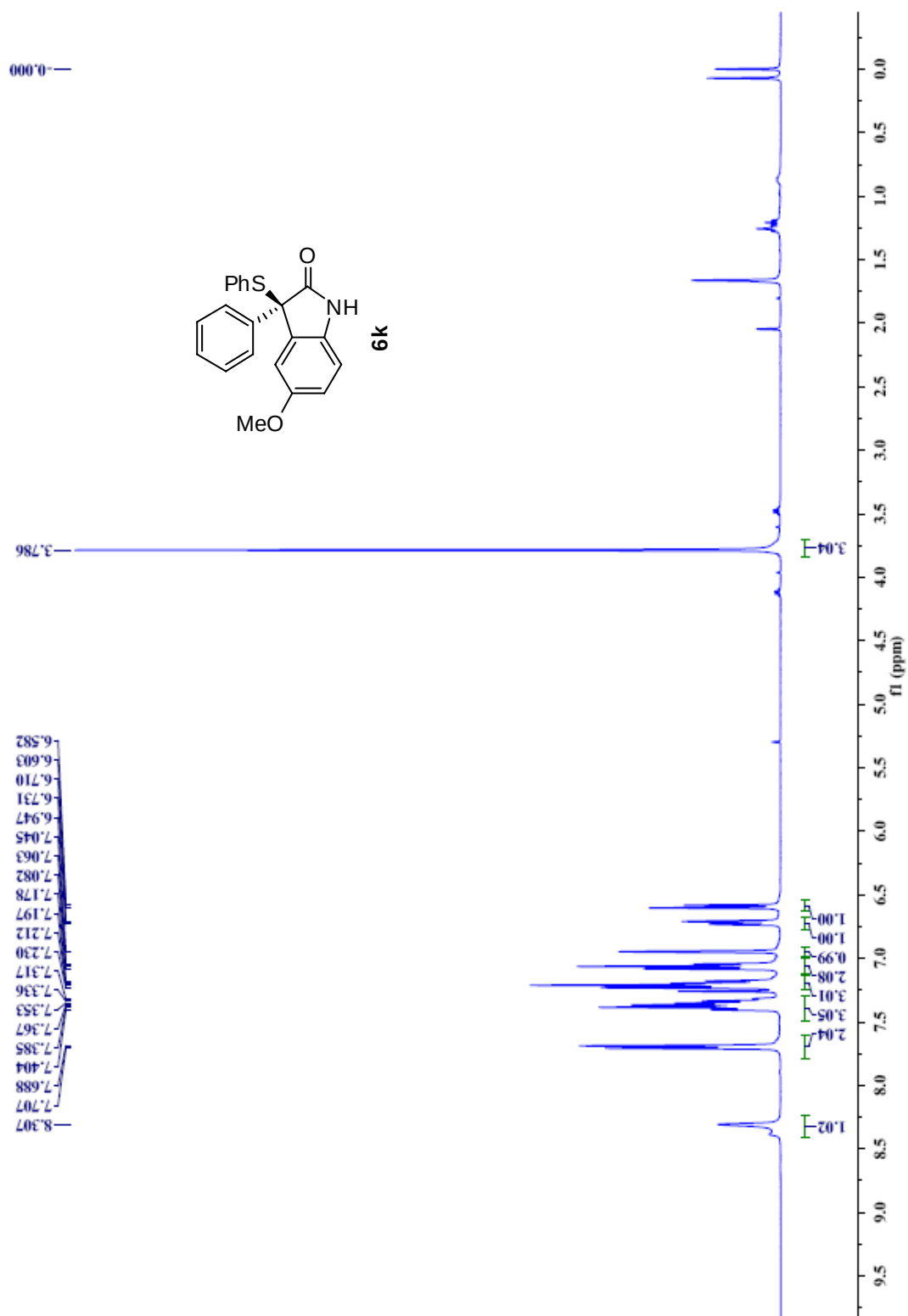


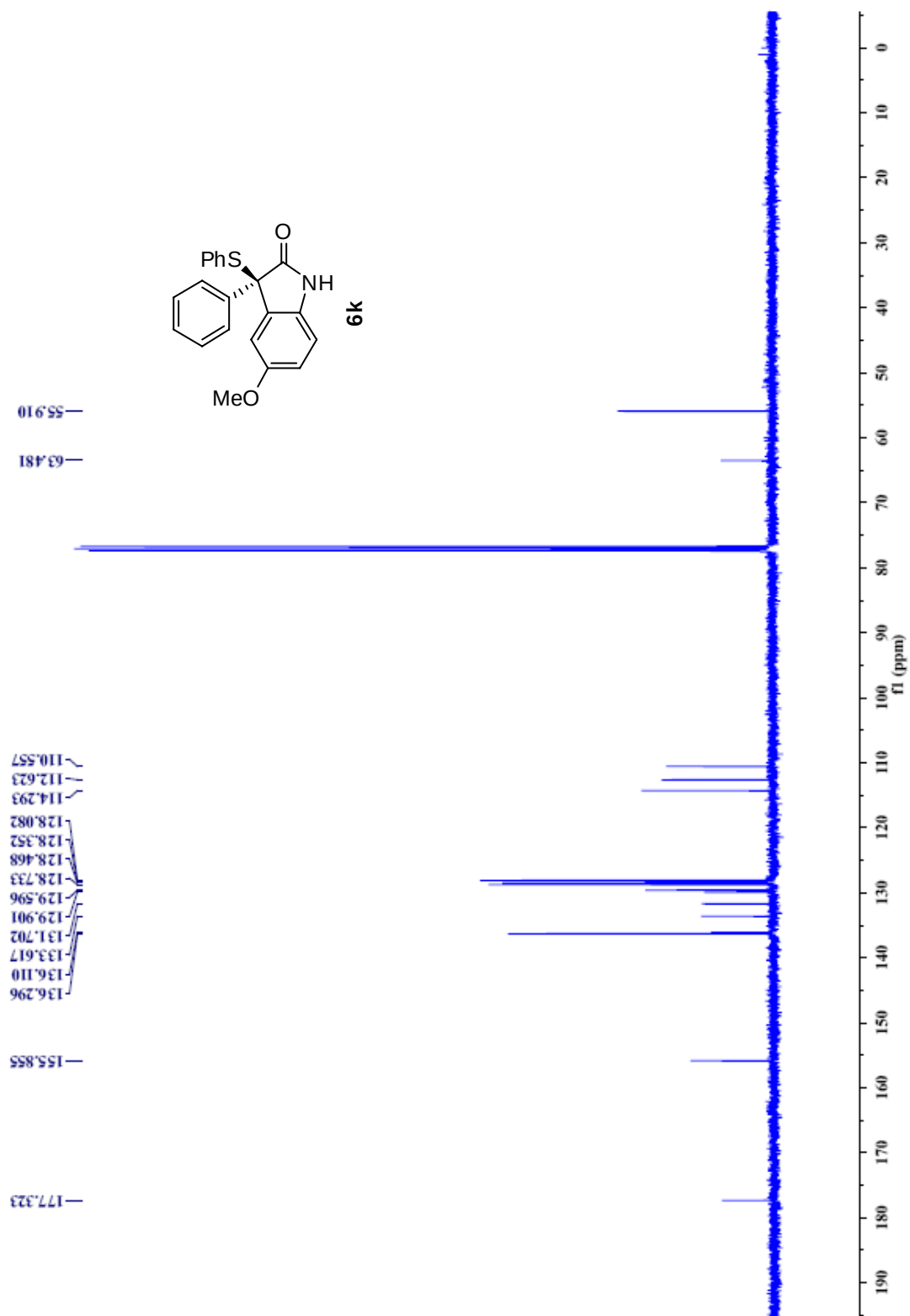


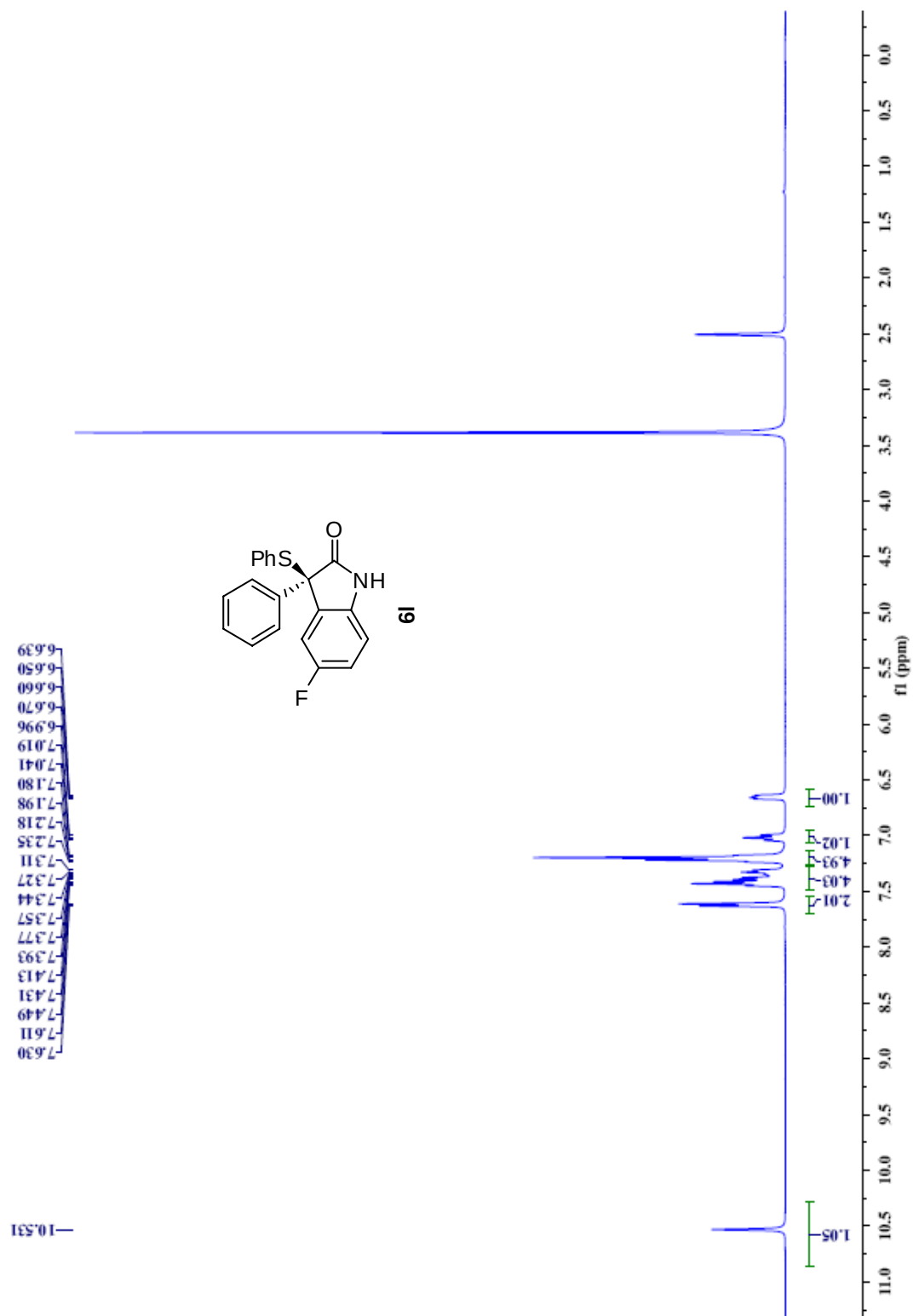


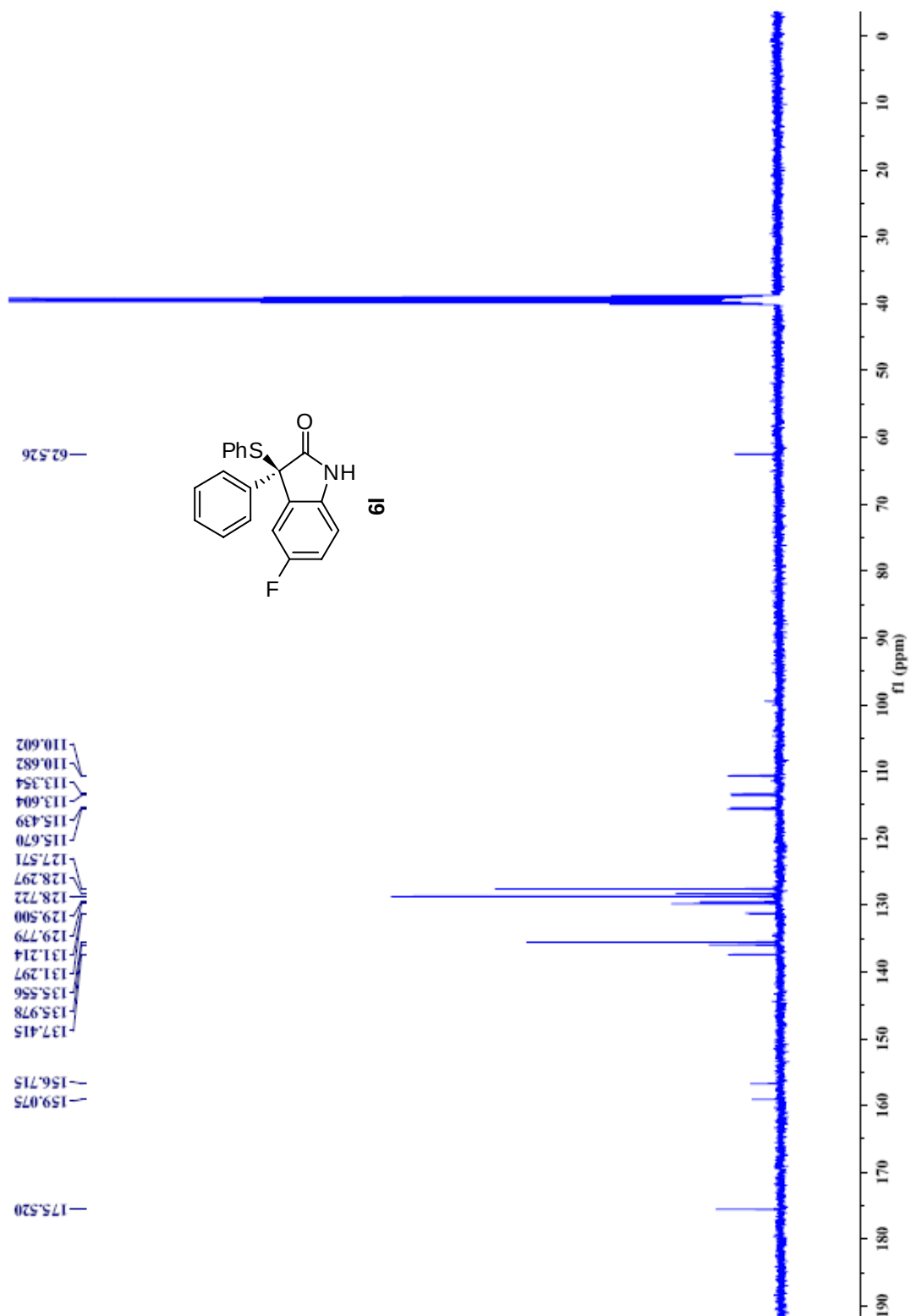


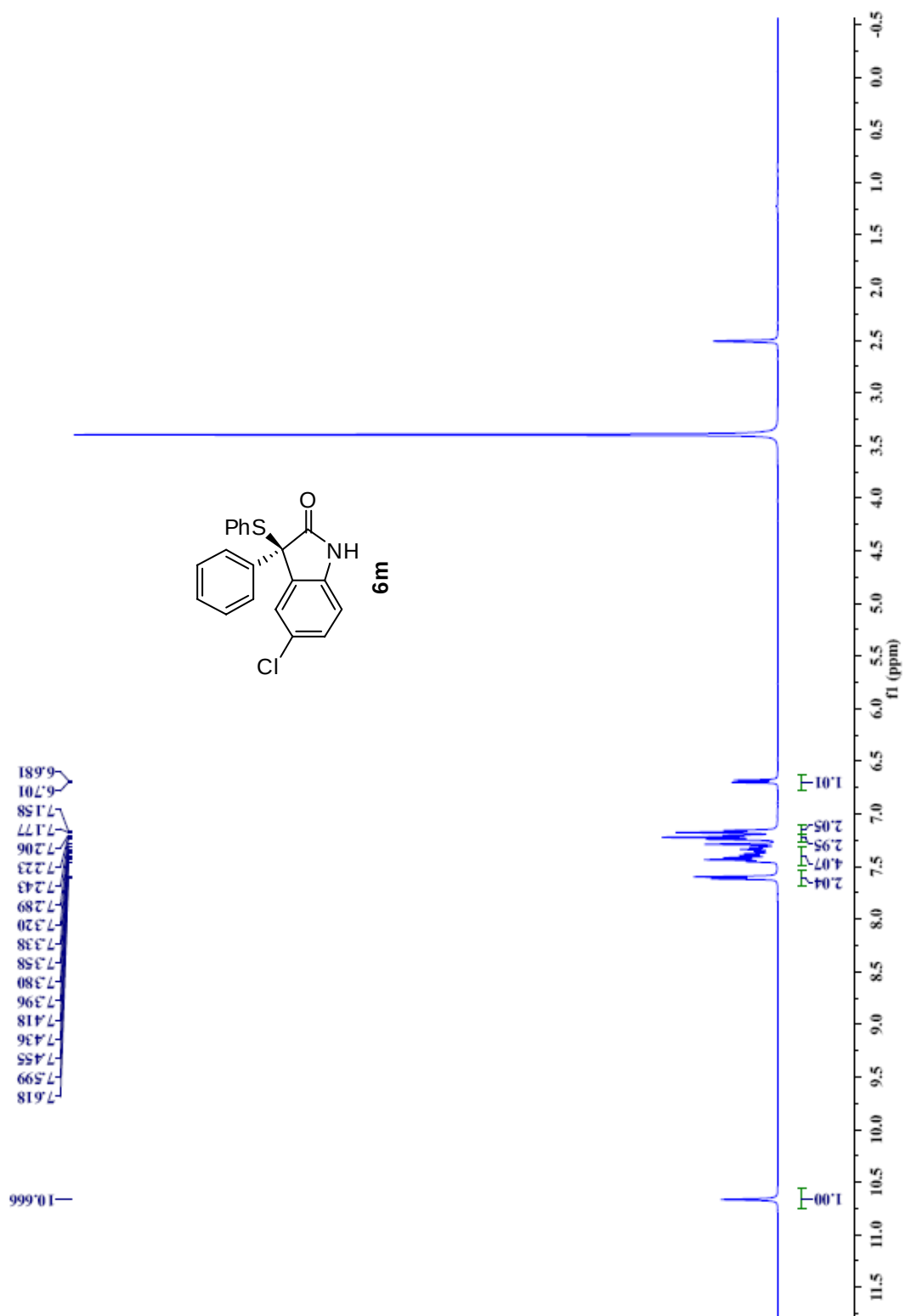


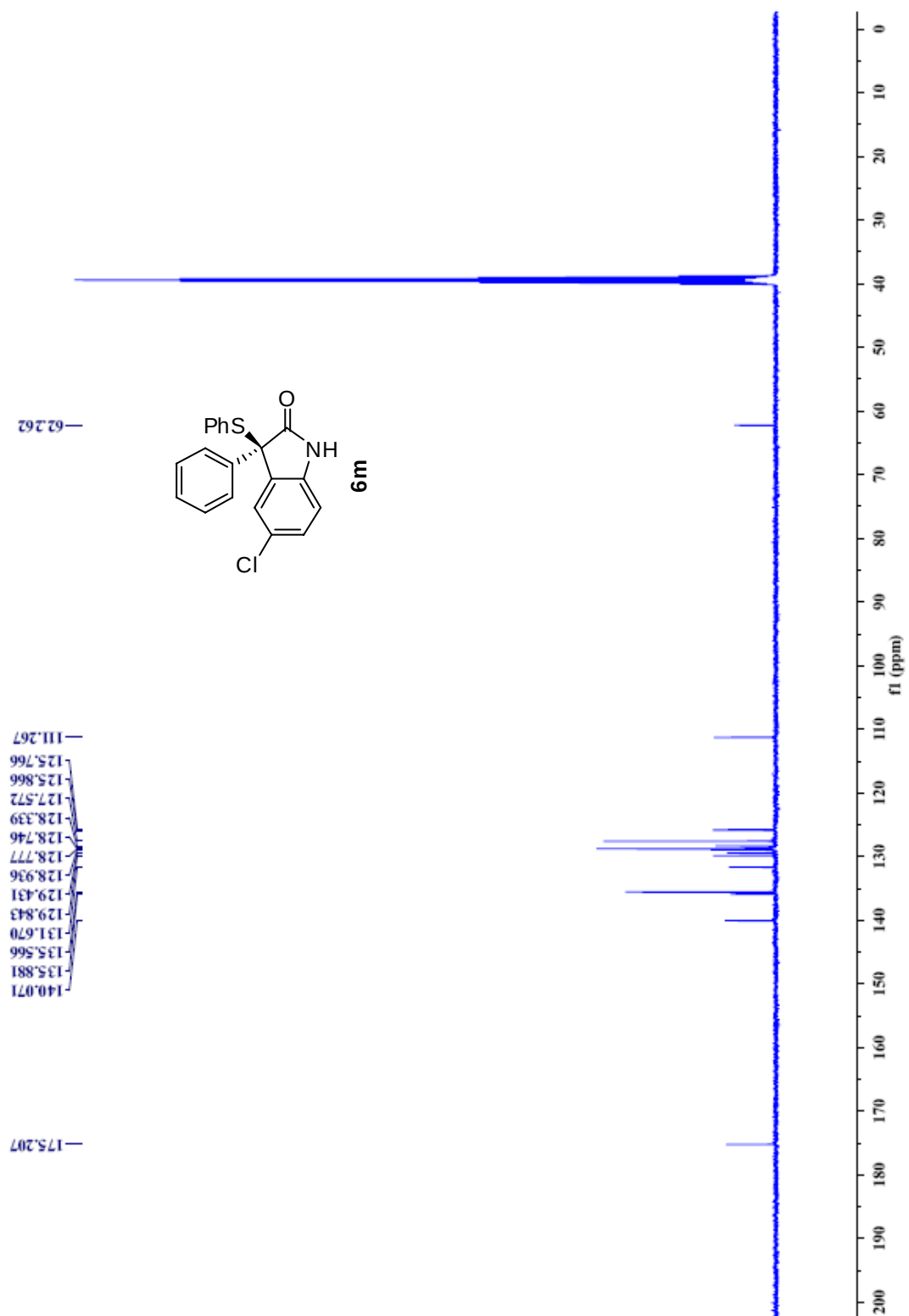




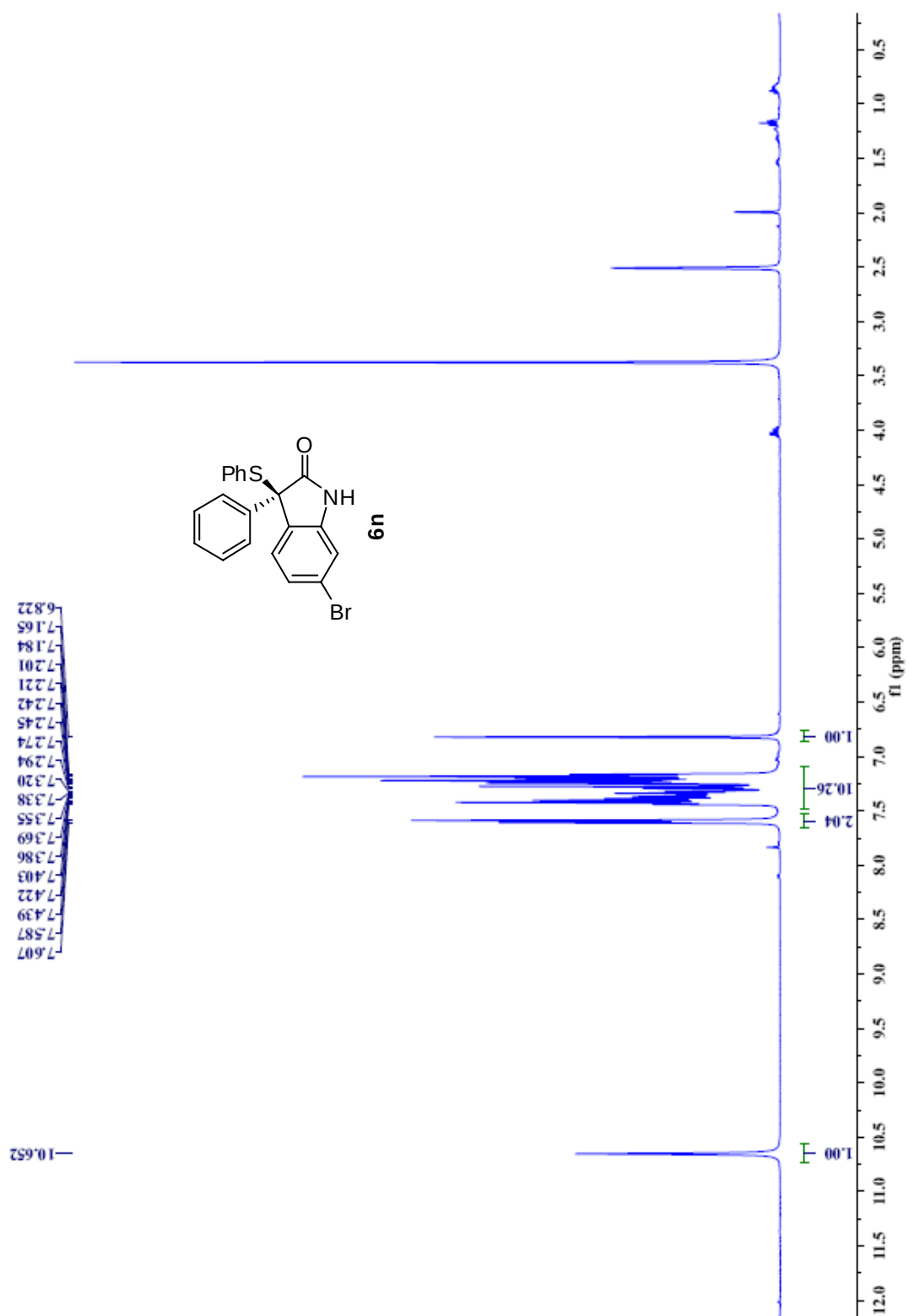


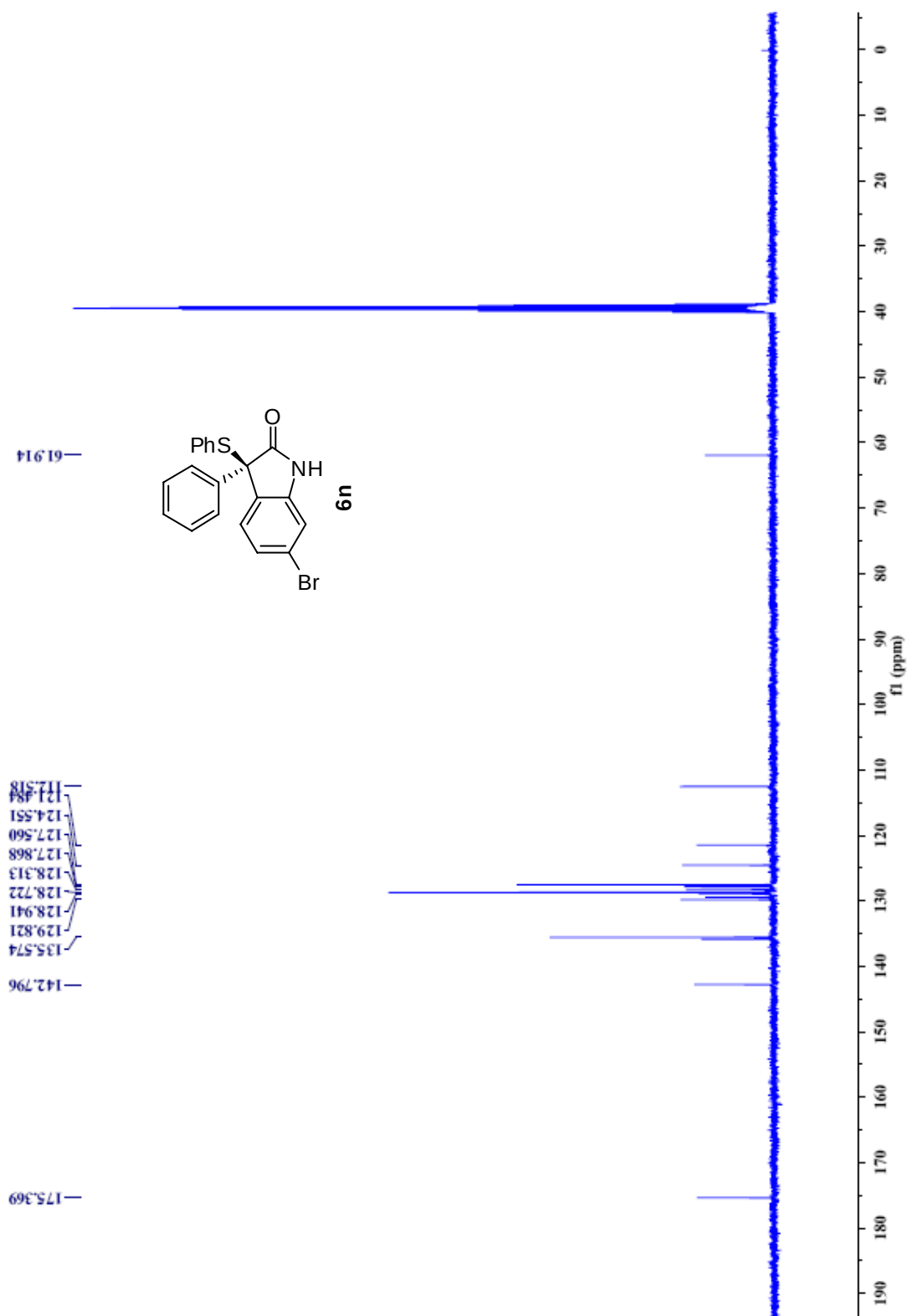


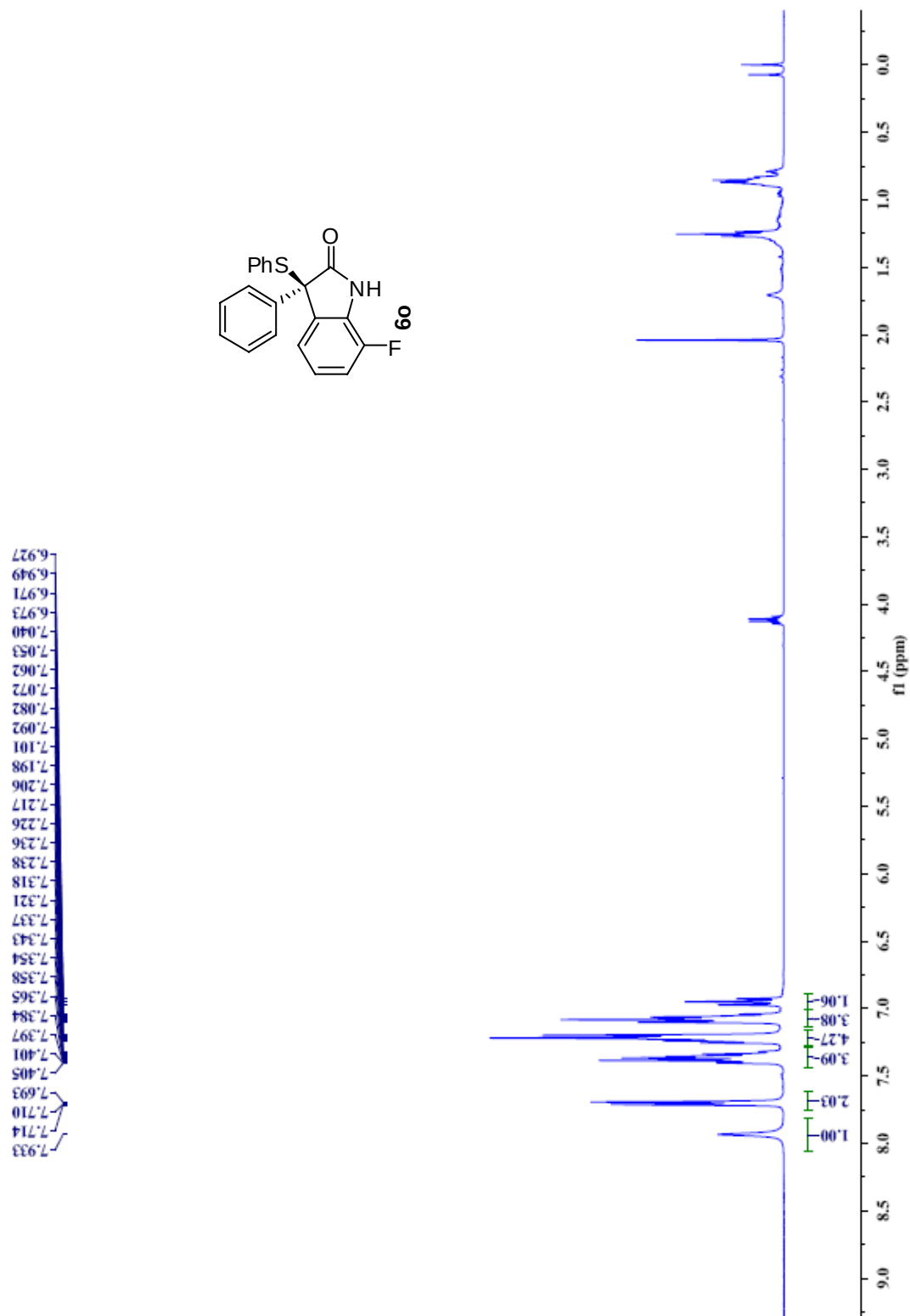


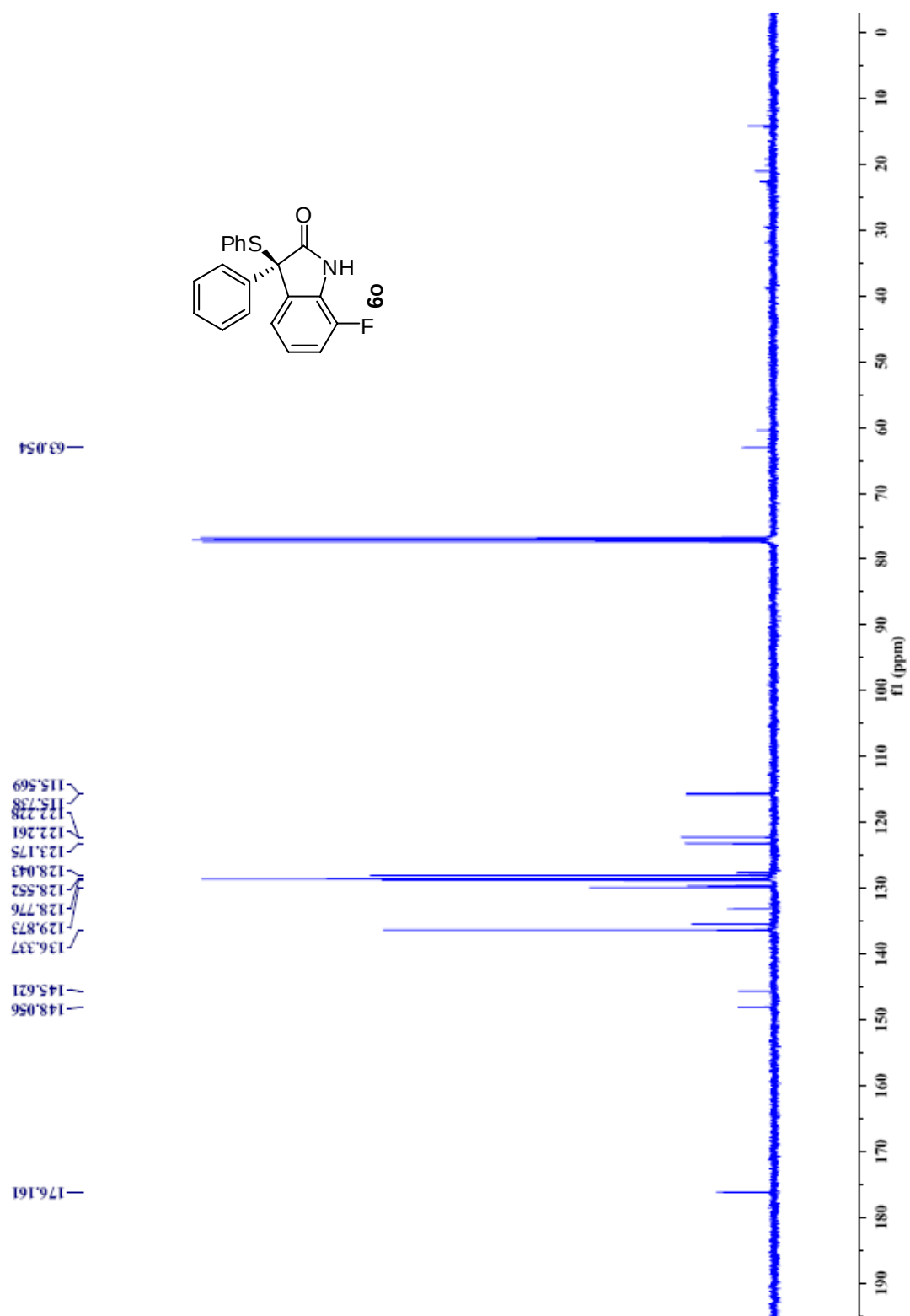






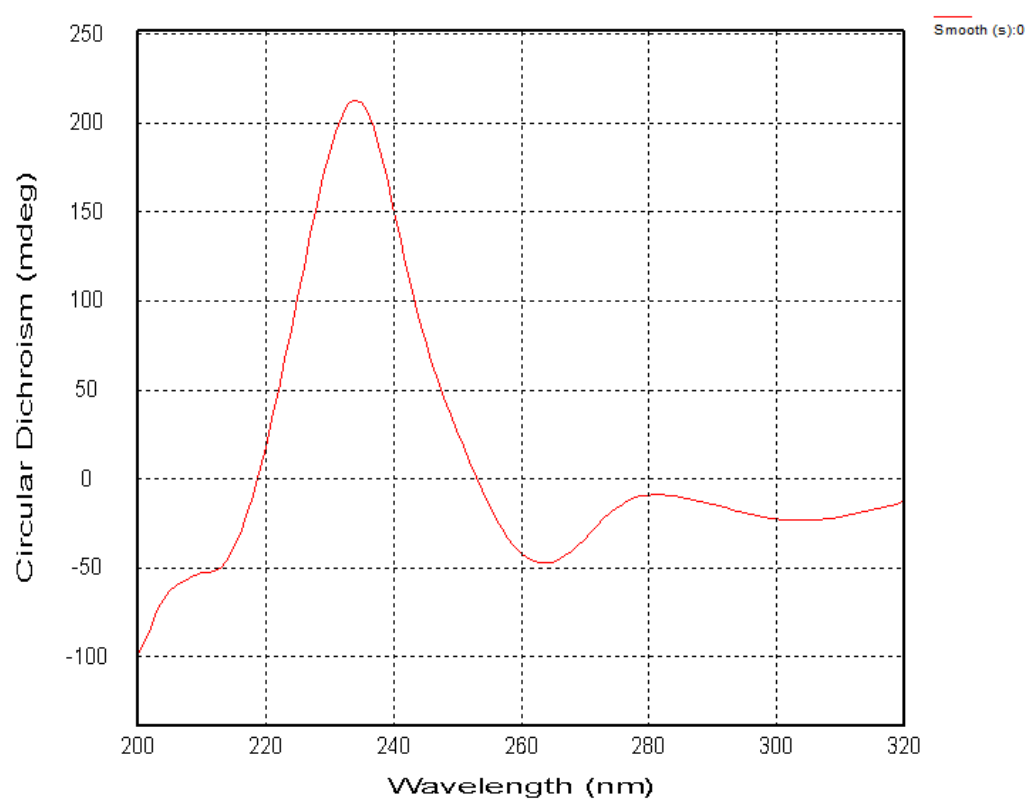




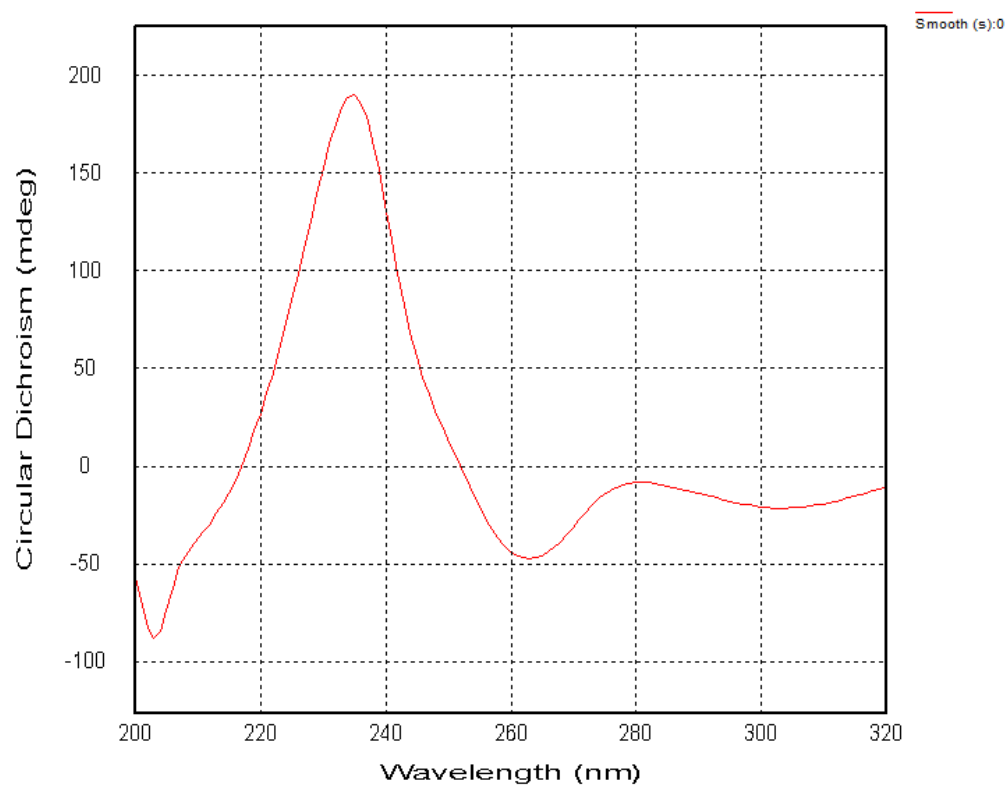


## 12. Copy of CD spectra in methanol

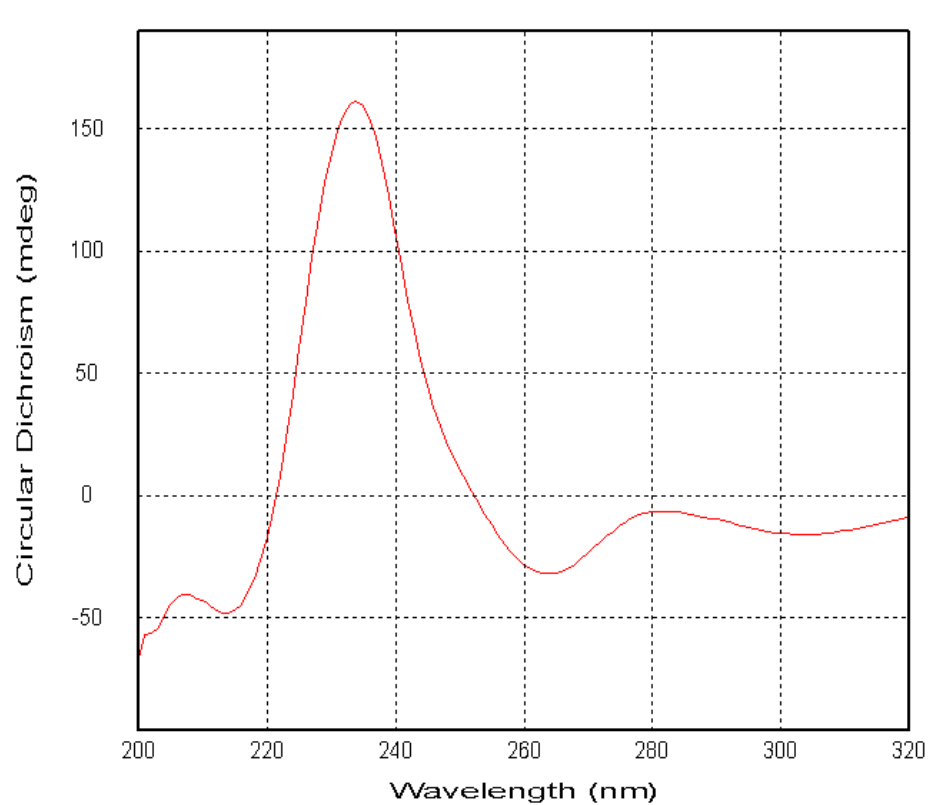
R-3p (Standard)



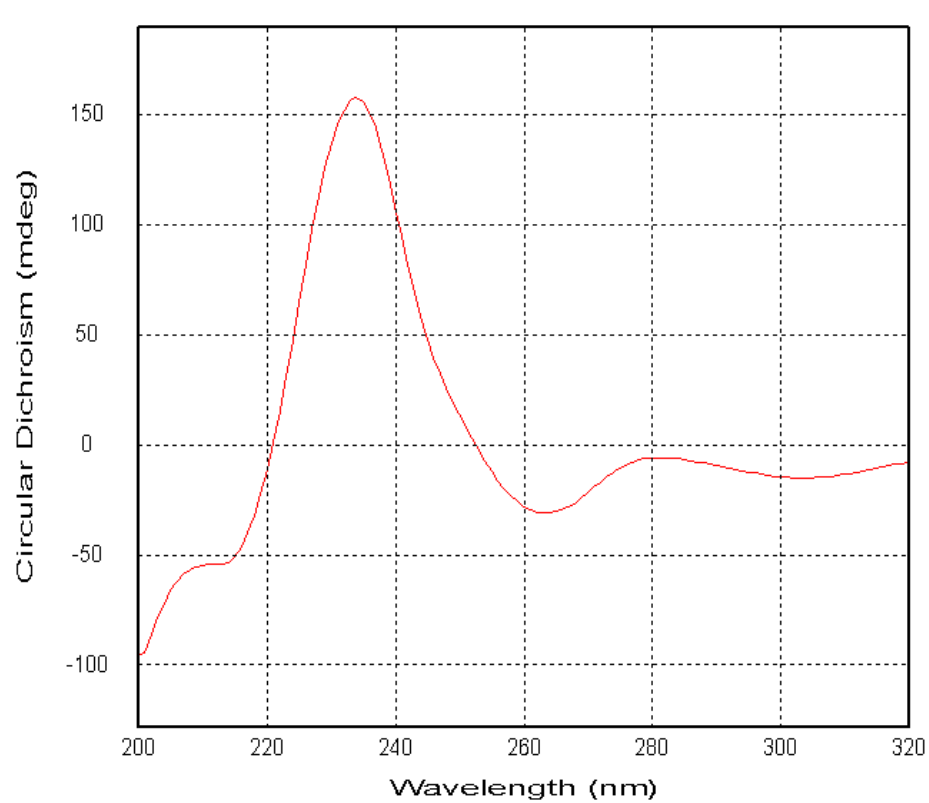
3a



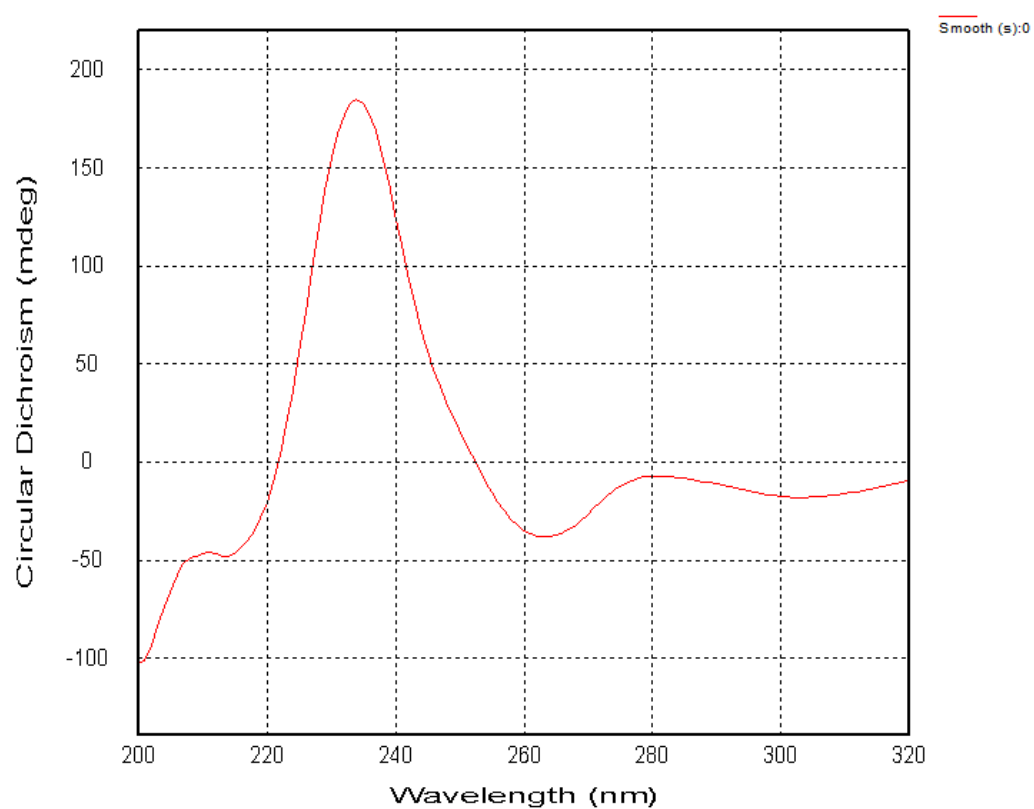
3b



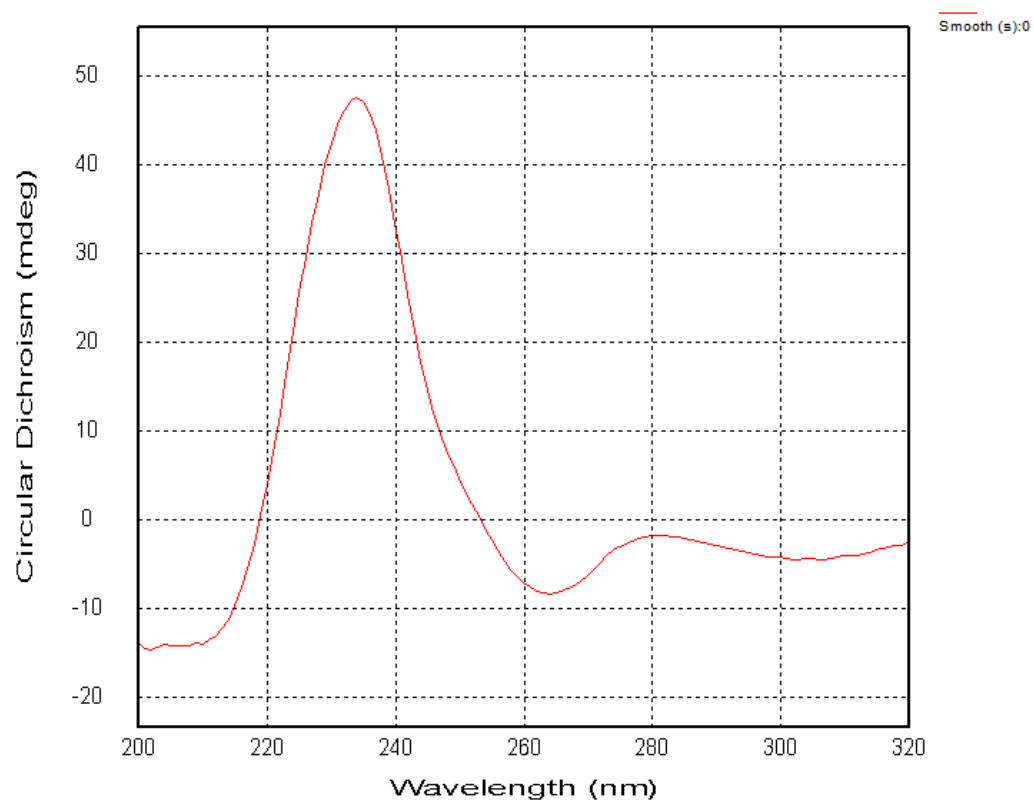
3c



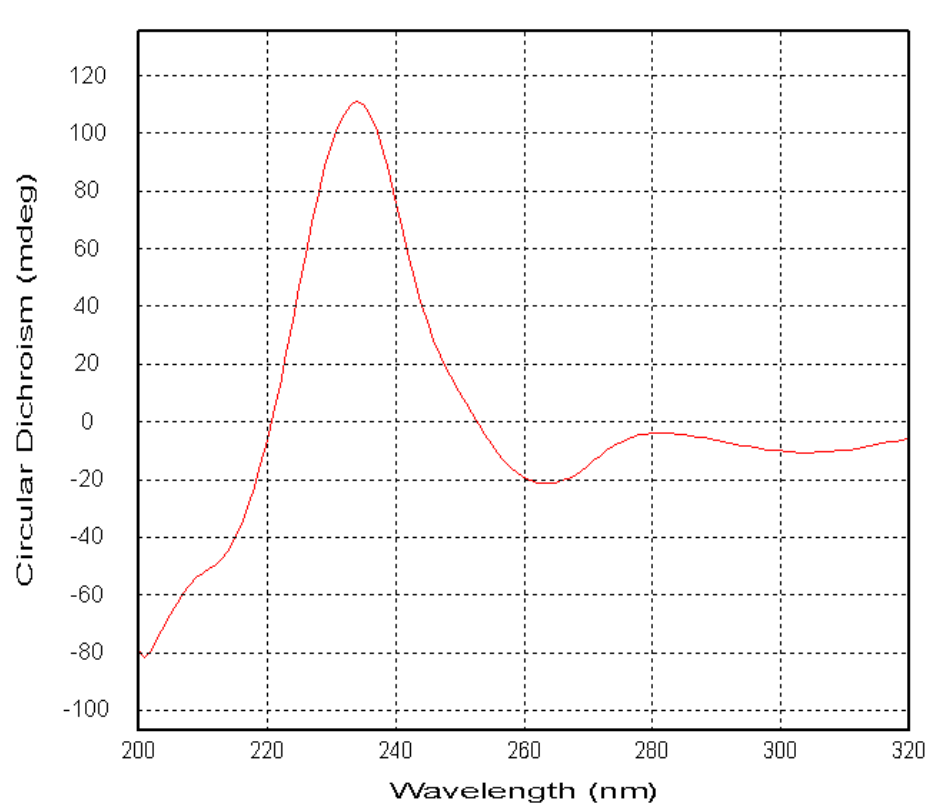
3d



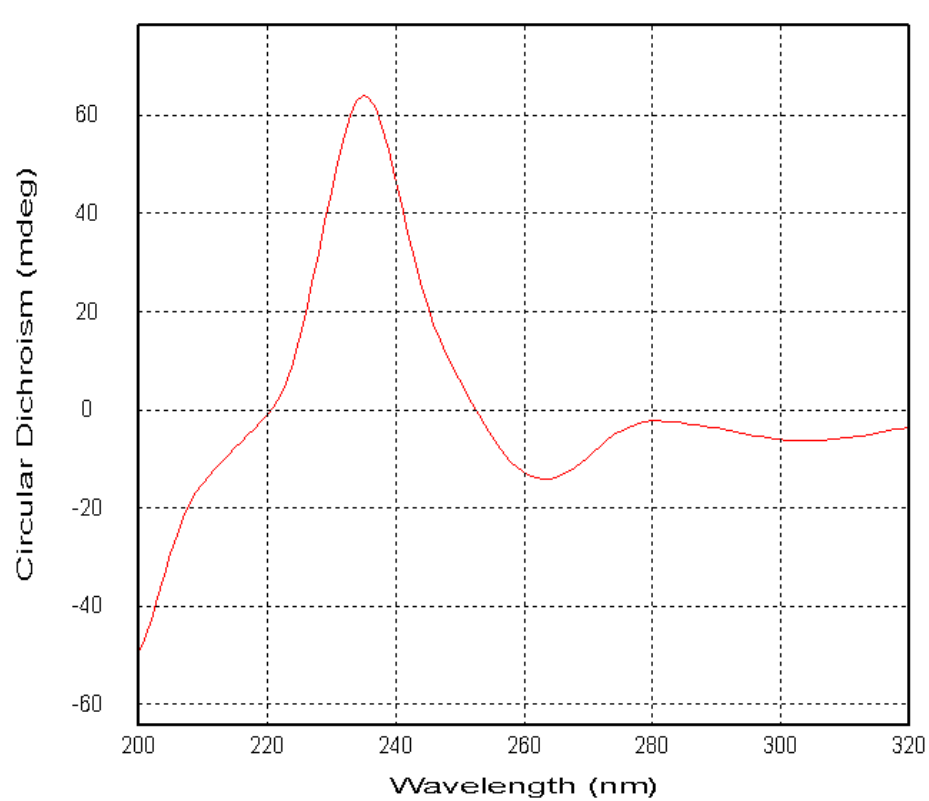
3e



3f

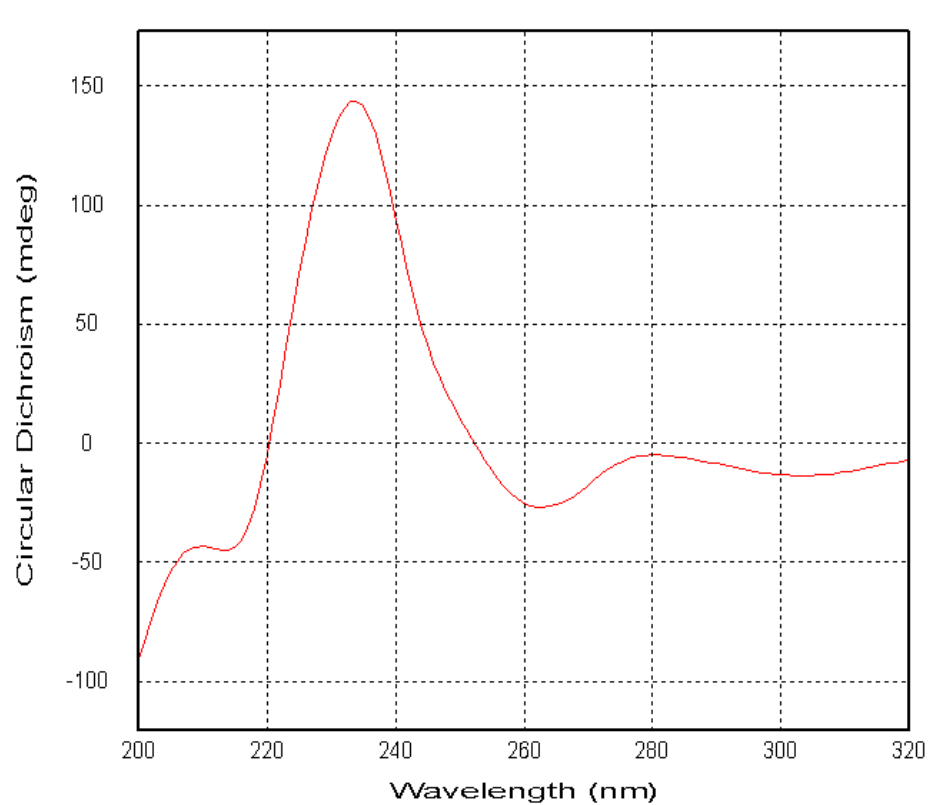


3g

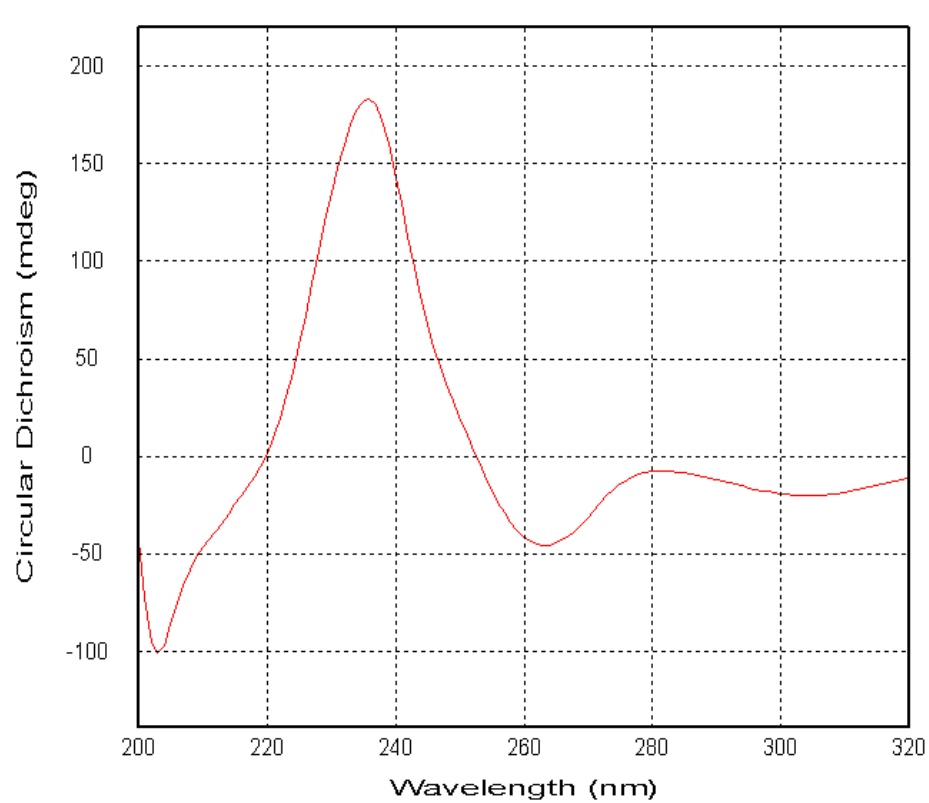




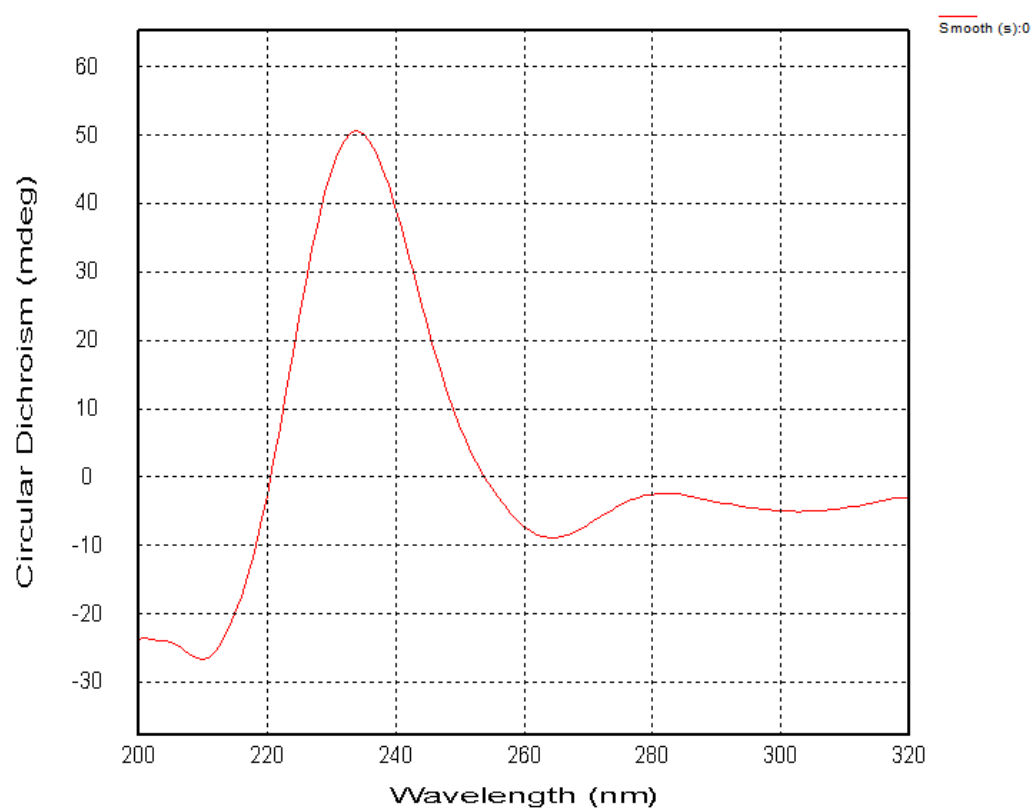
3h



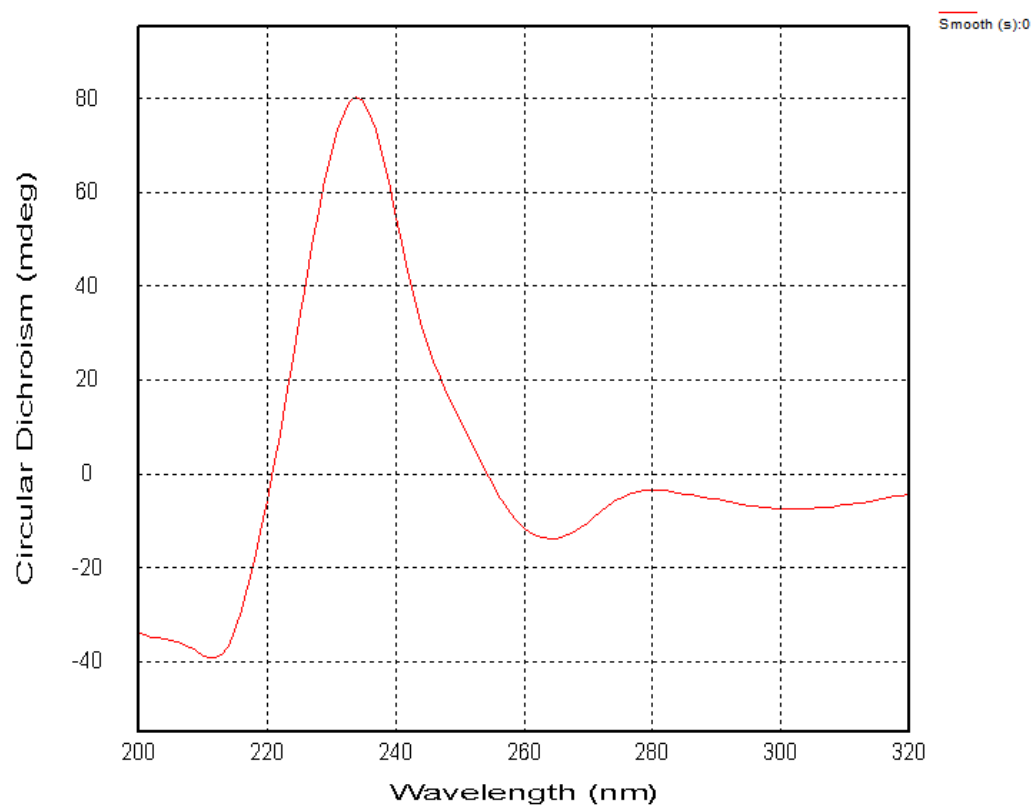
3i



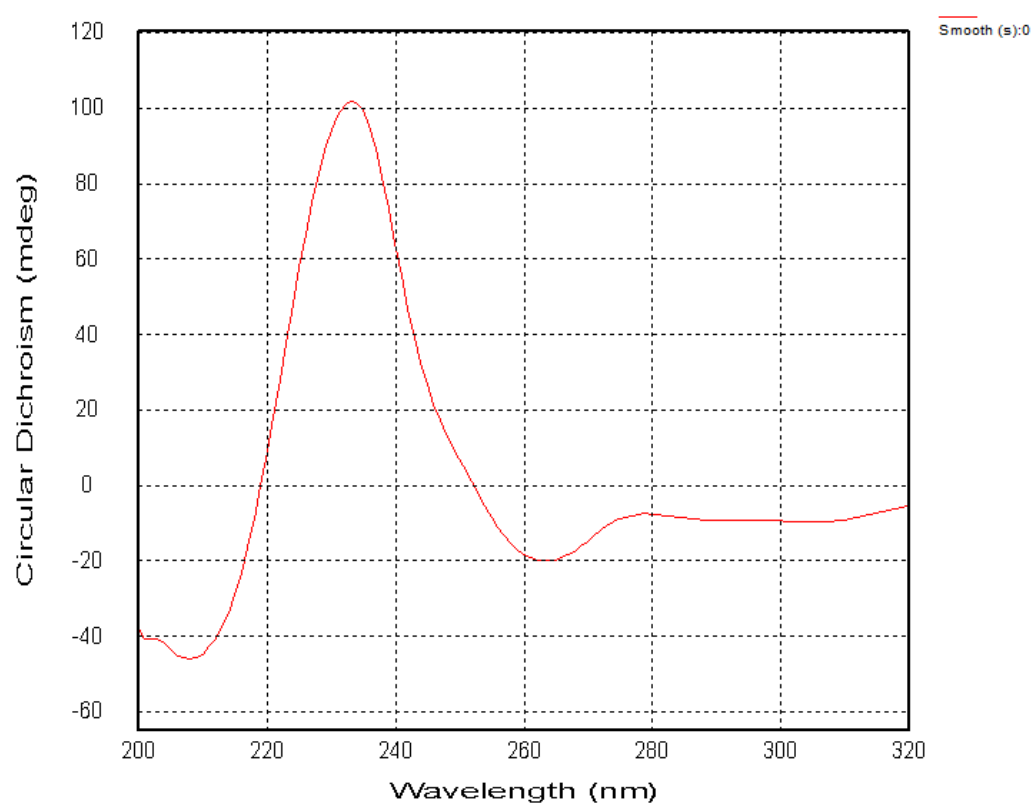
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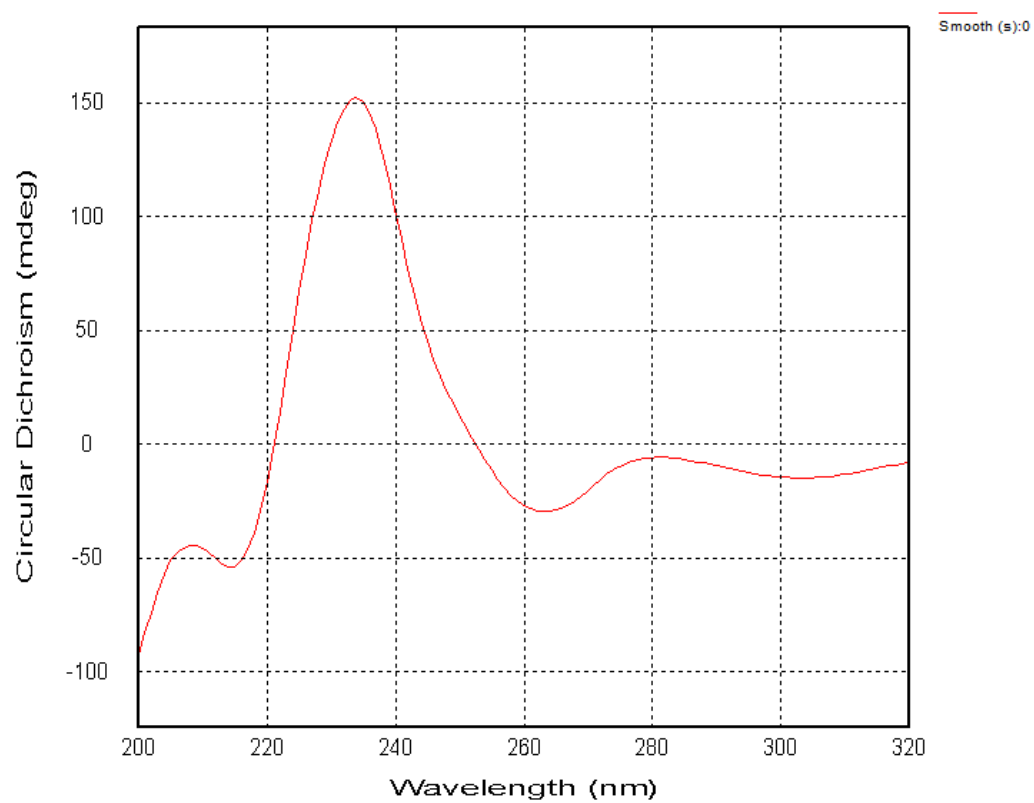
3k



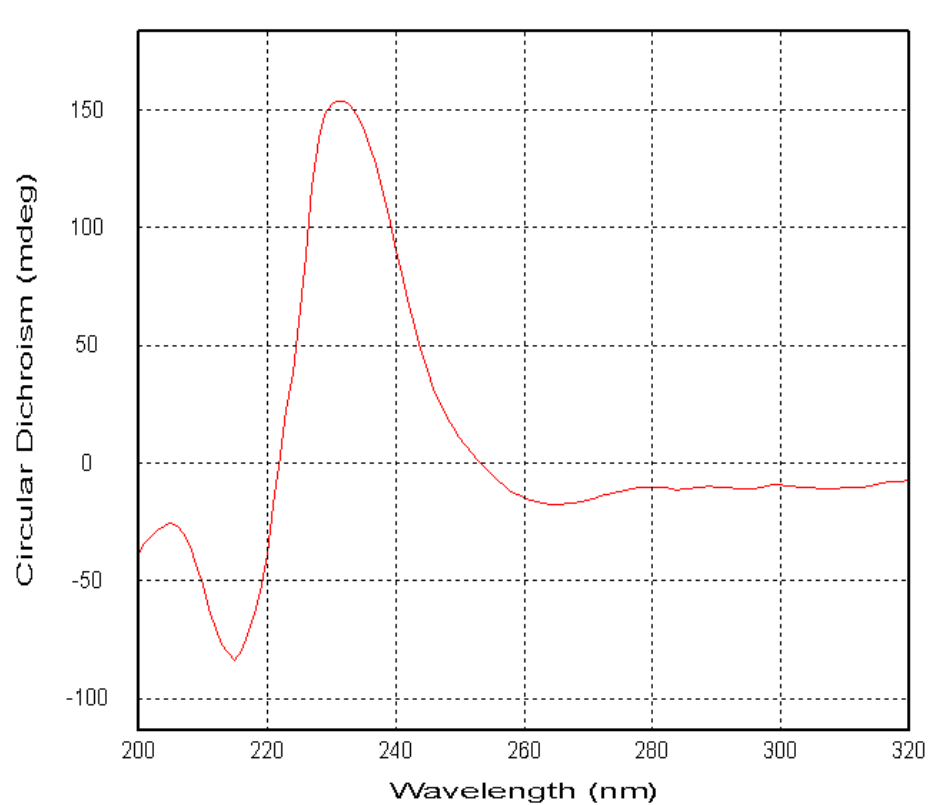
3l



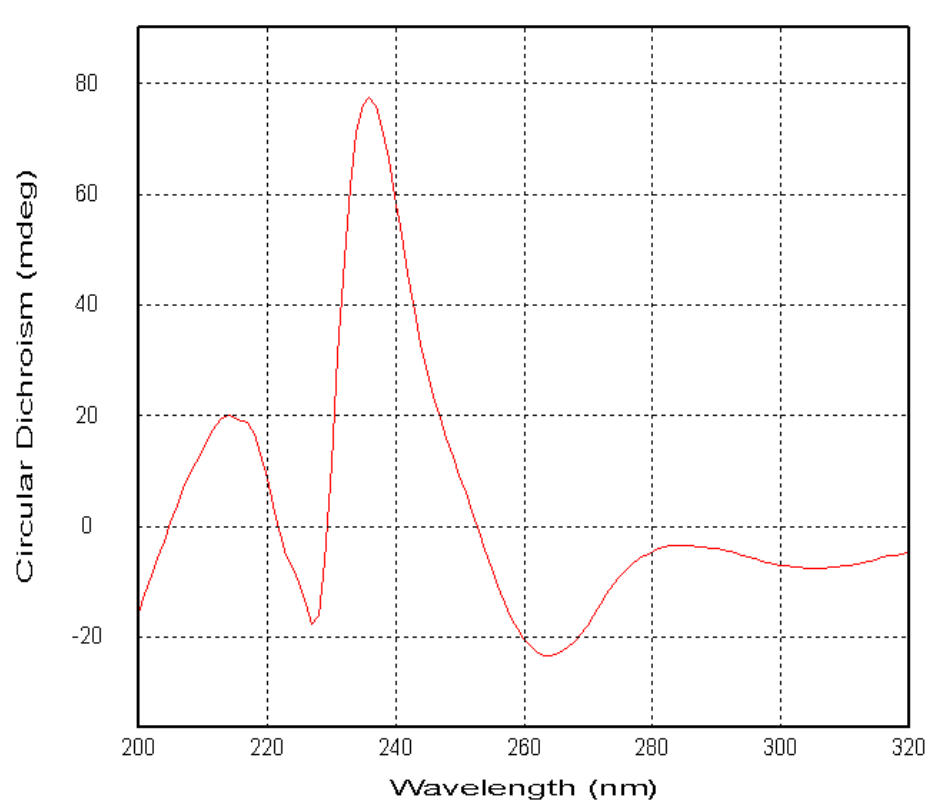
3m



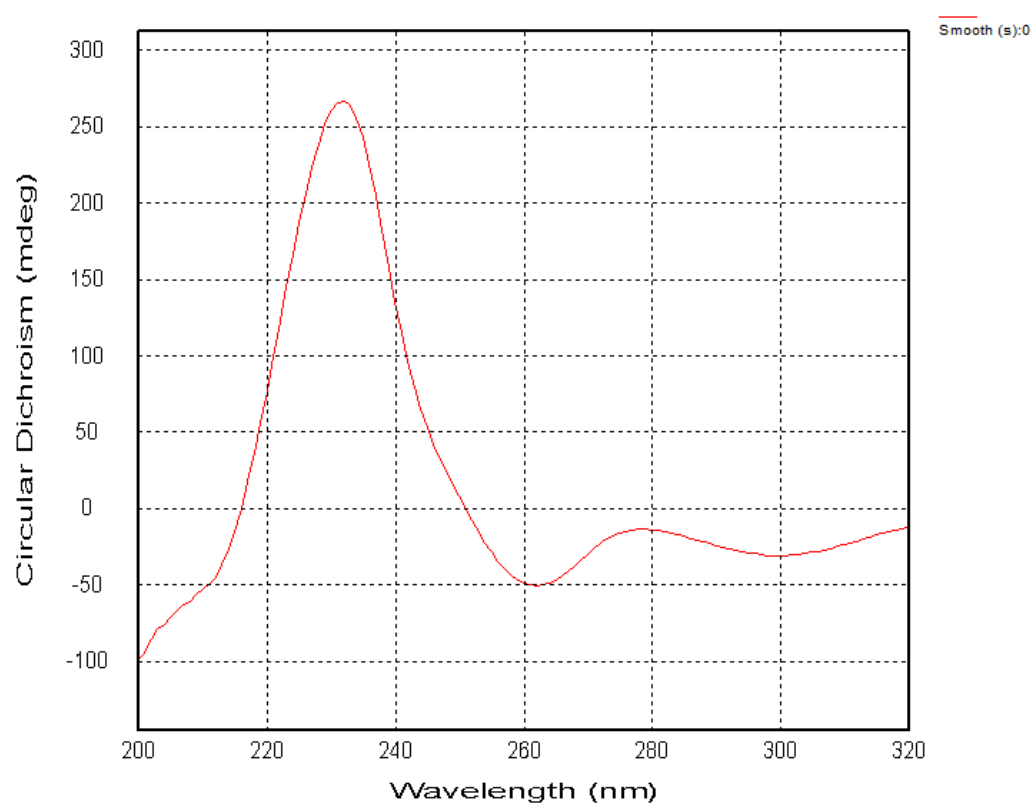
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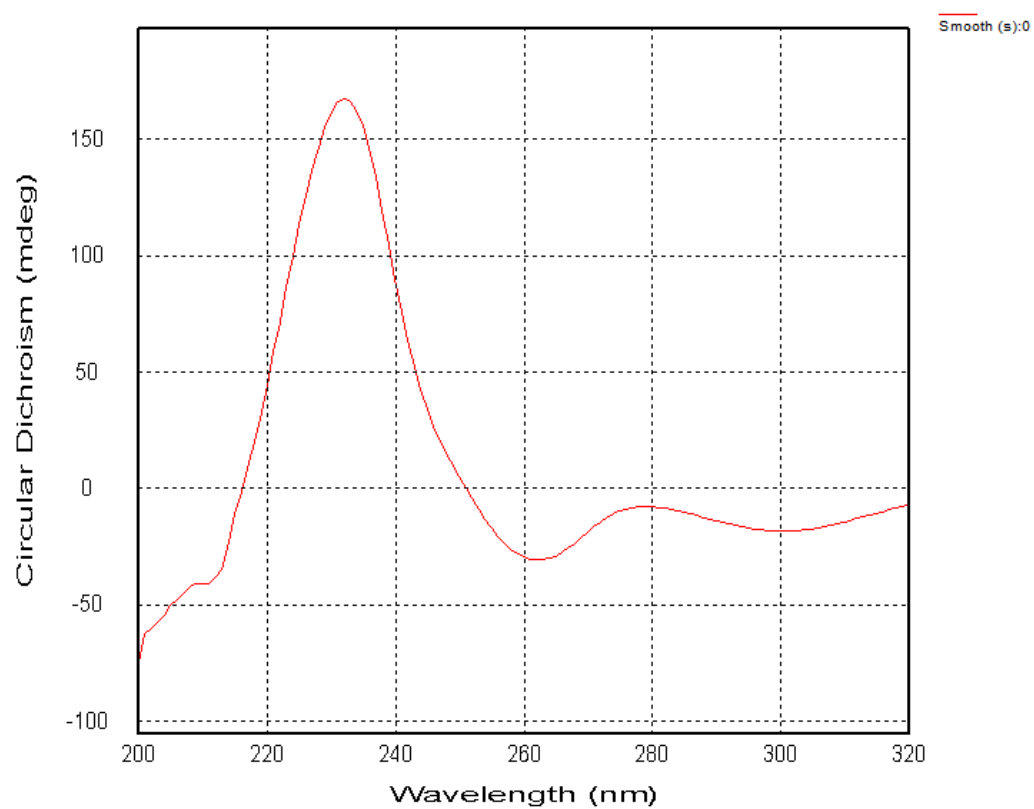
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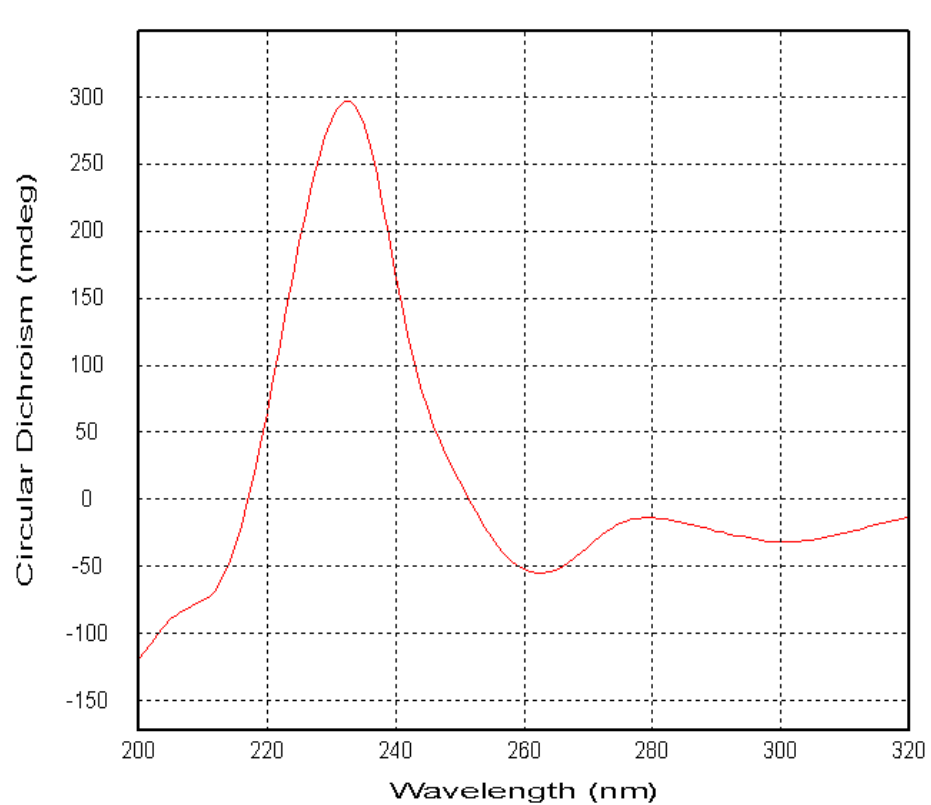
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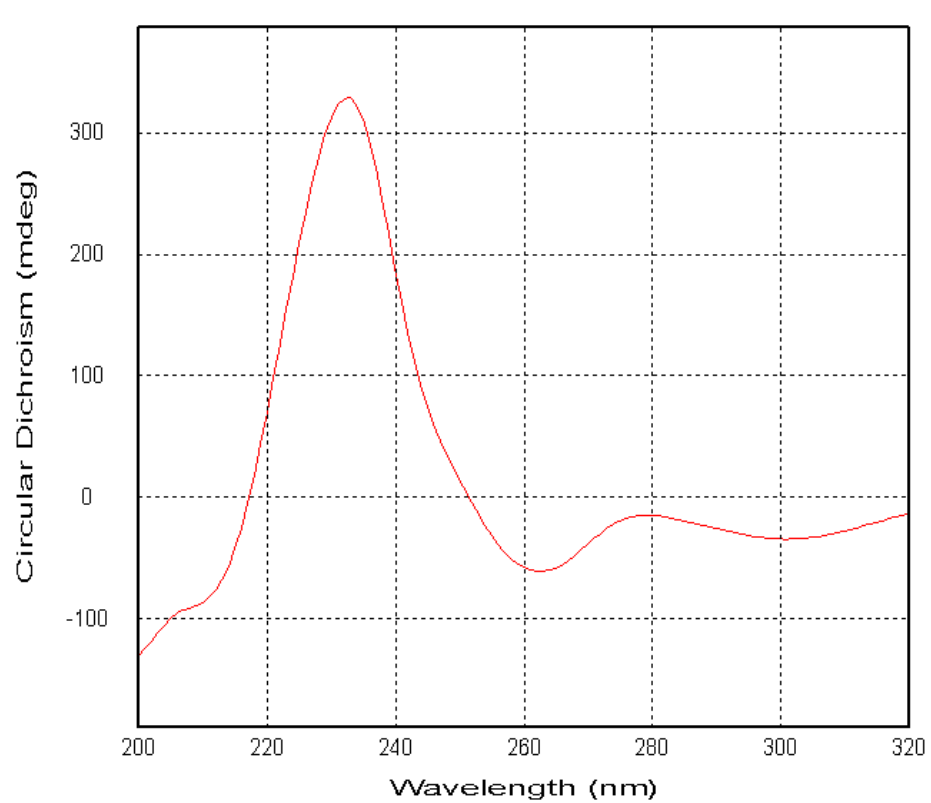
3r



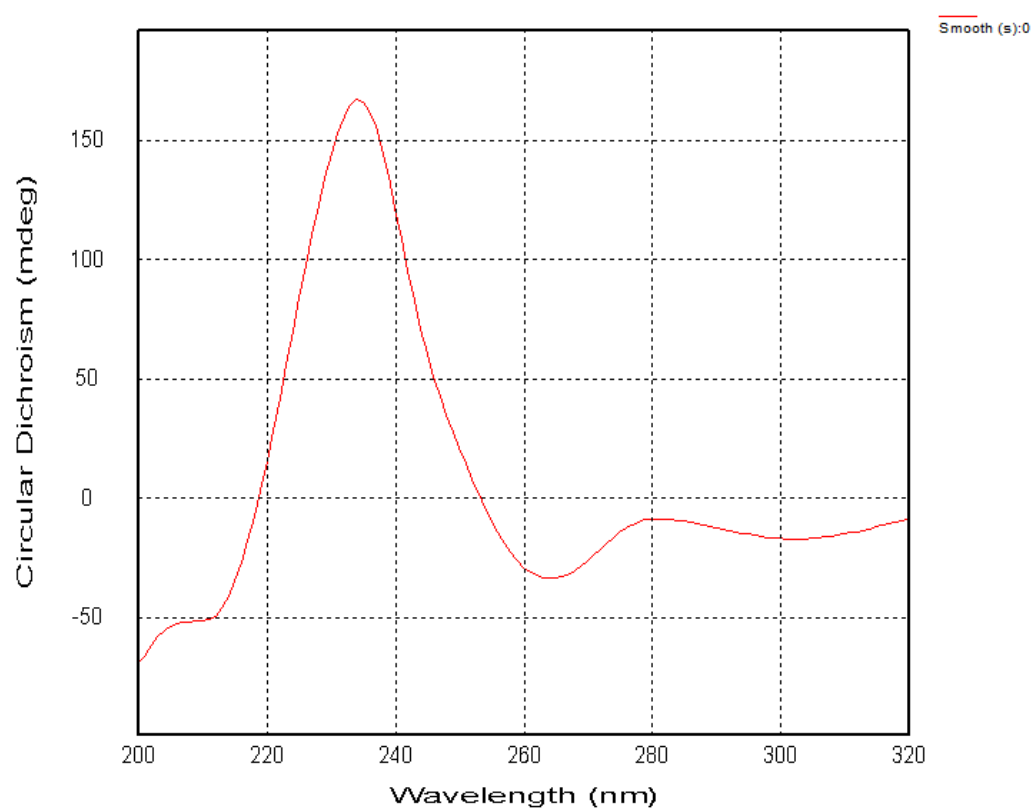
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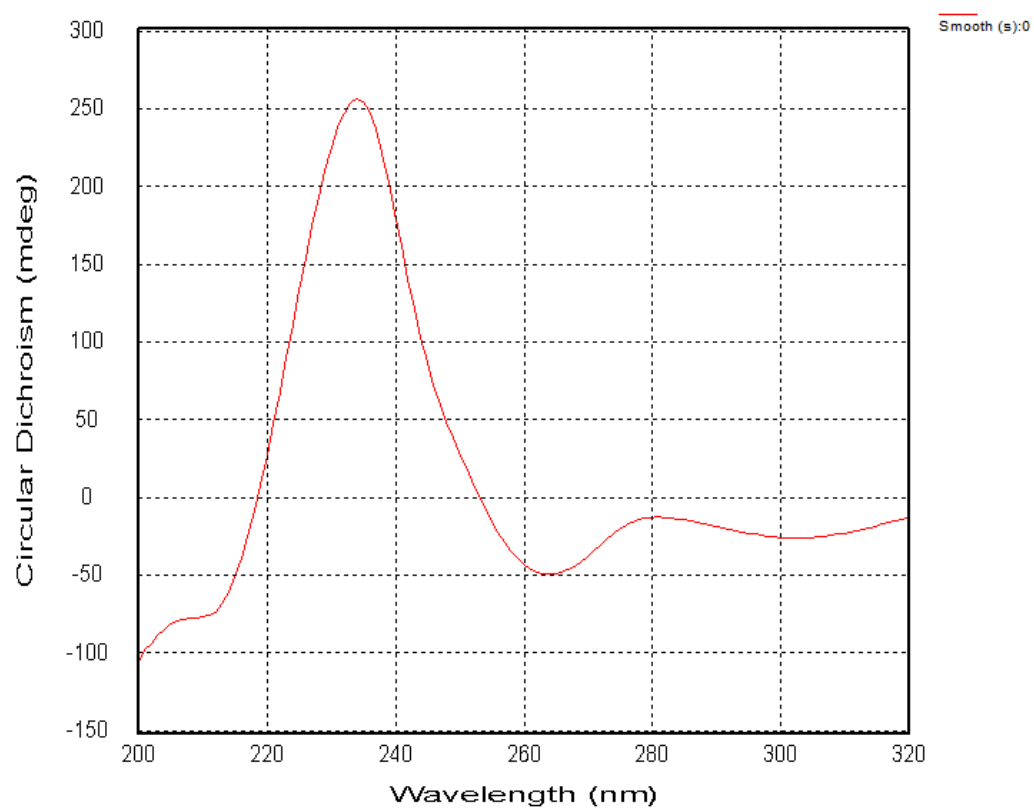
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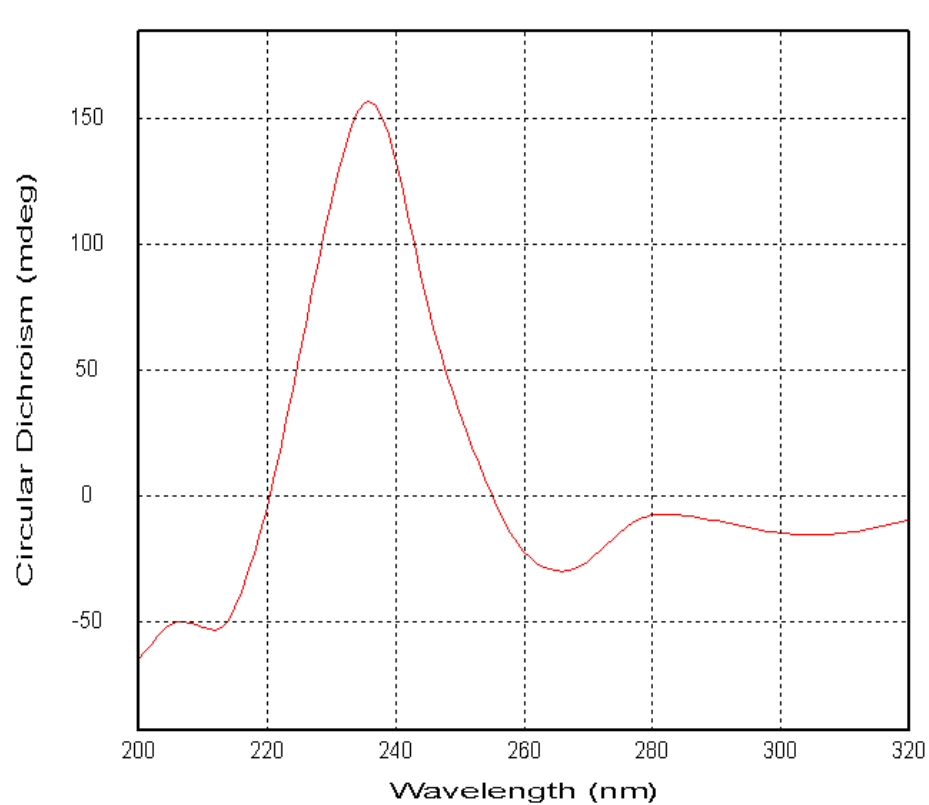
3u



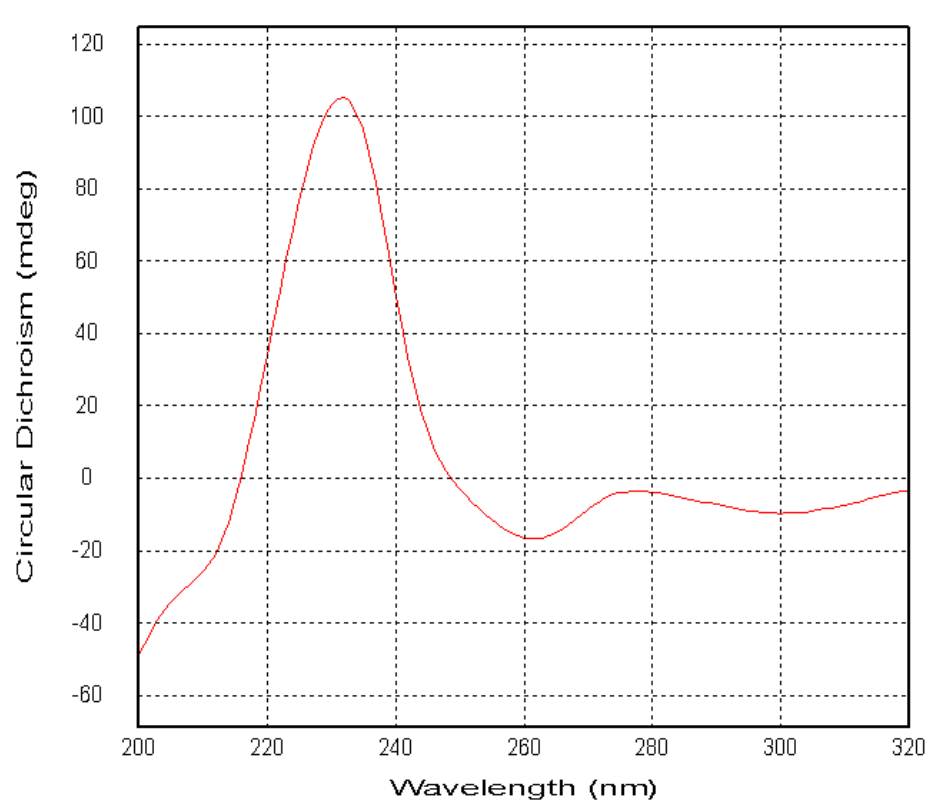
3v



3w

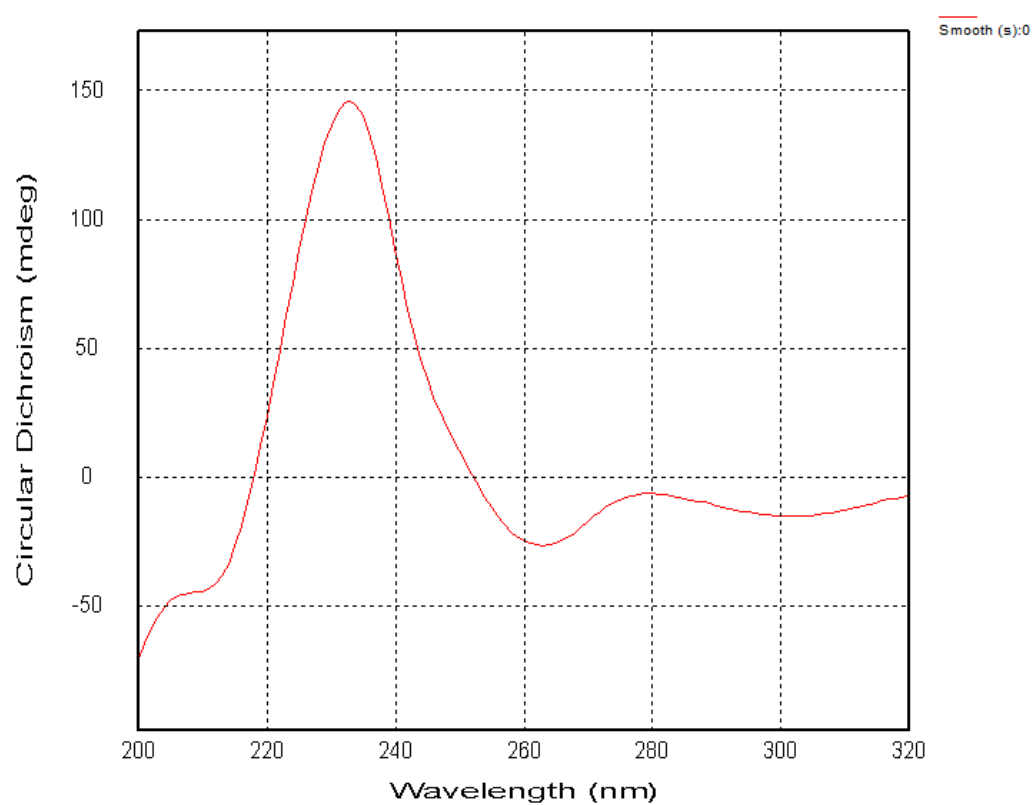


3x

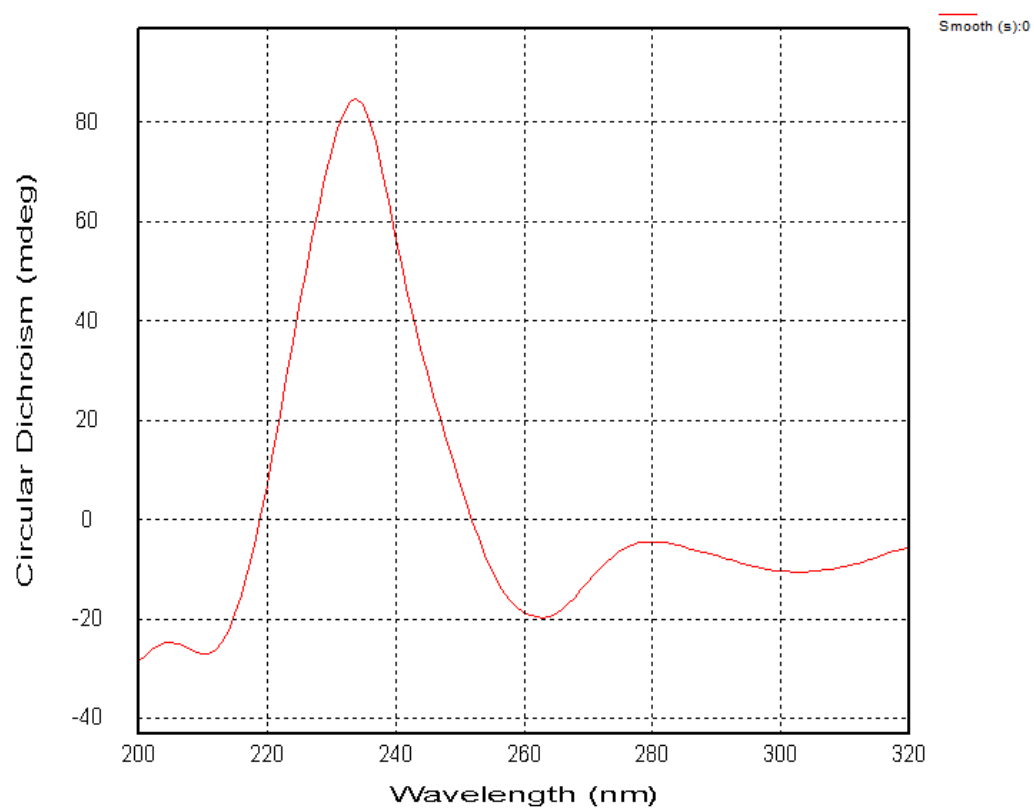




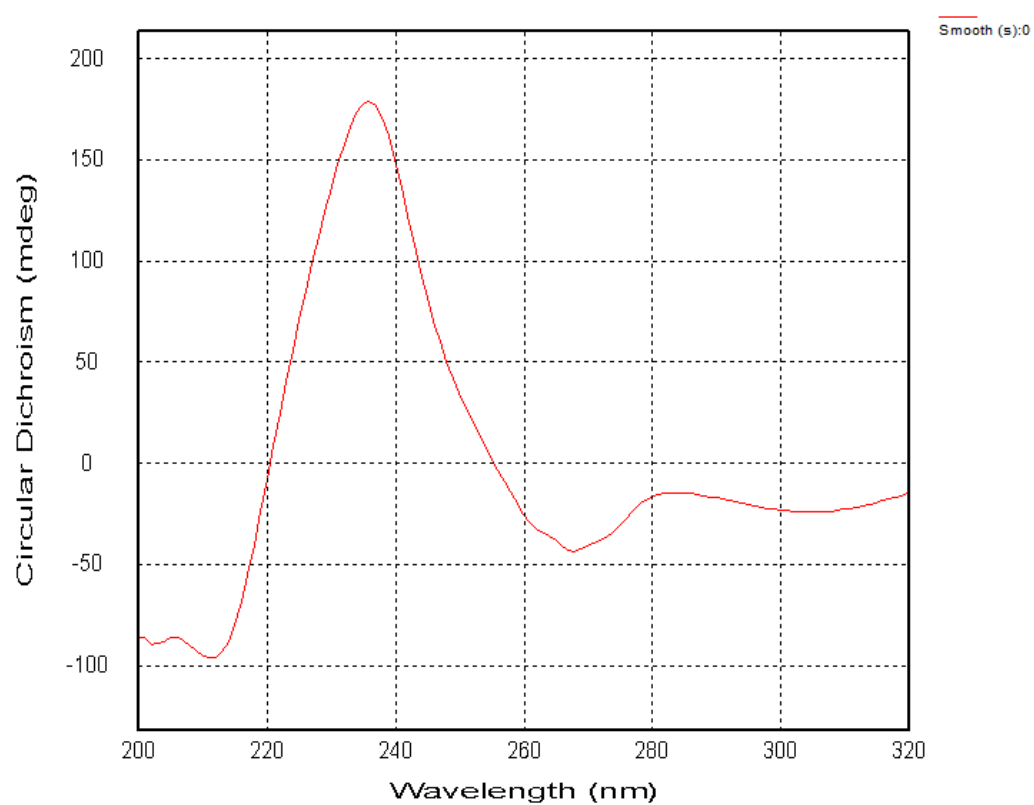
3y



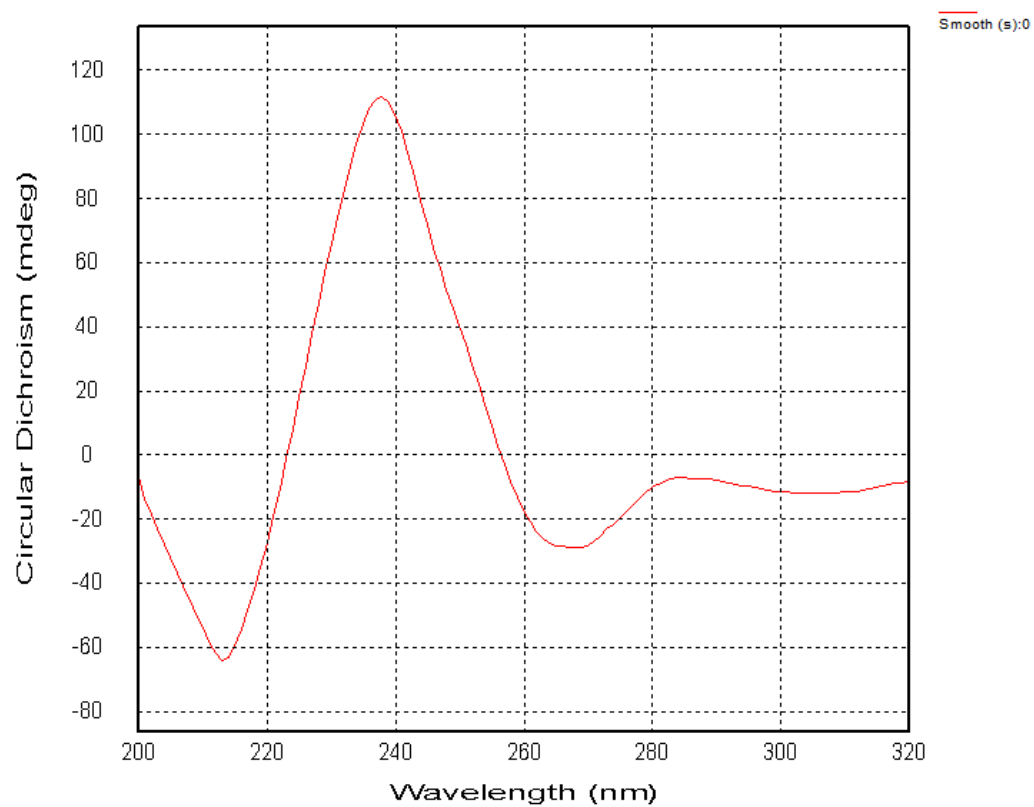
3z



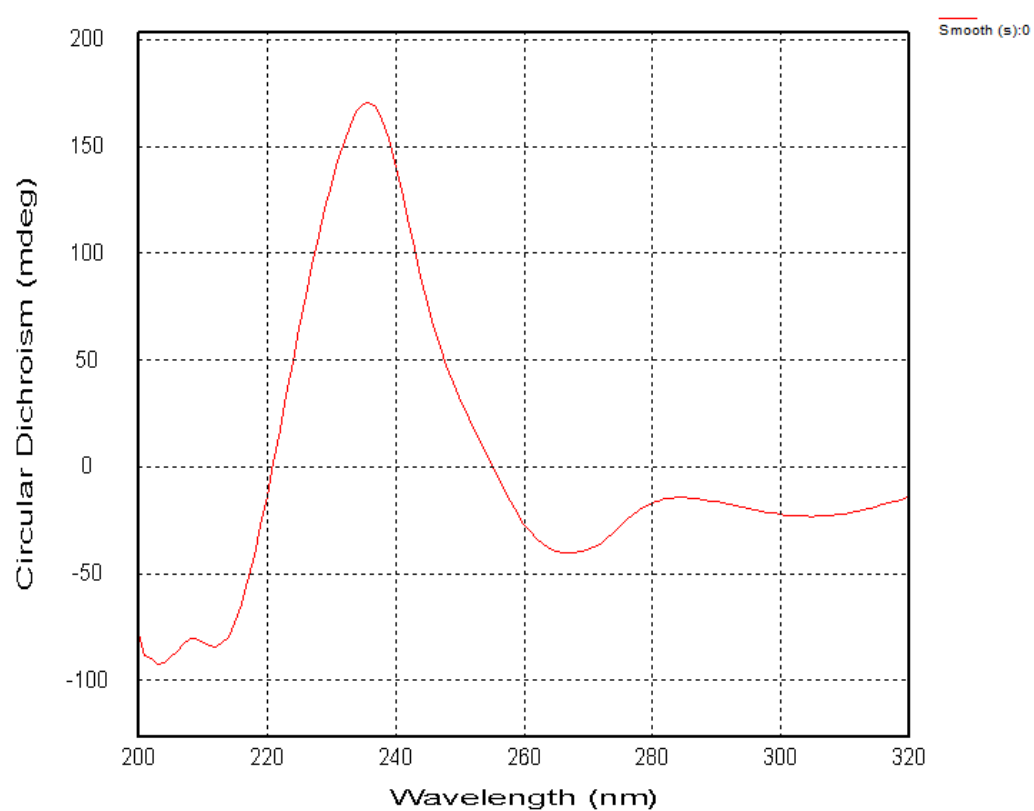
6a



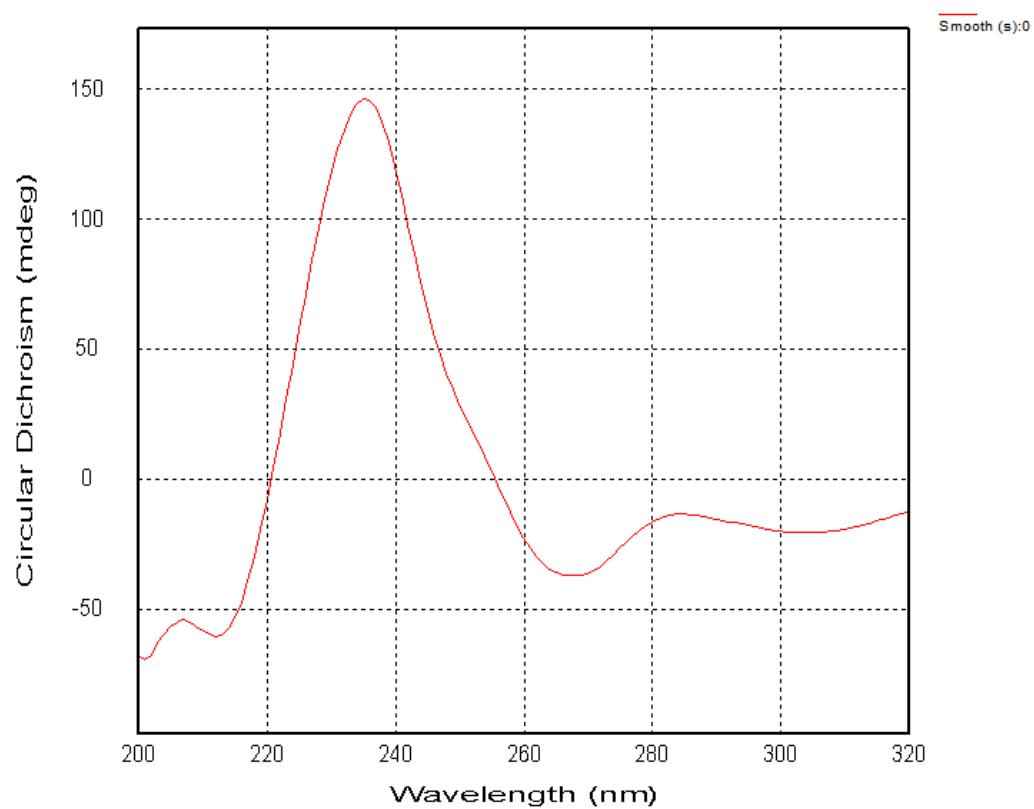
6b



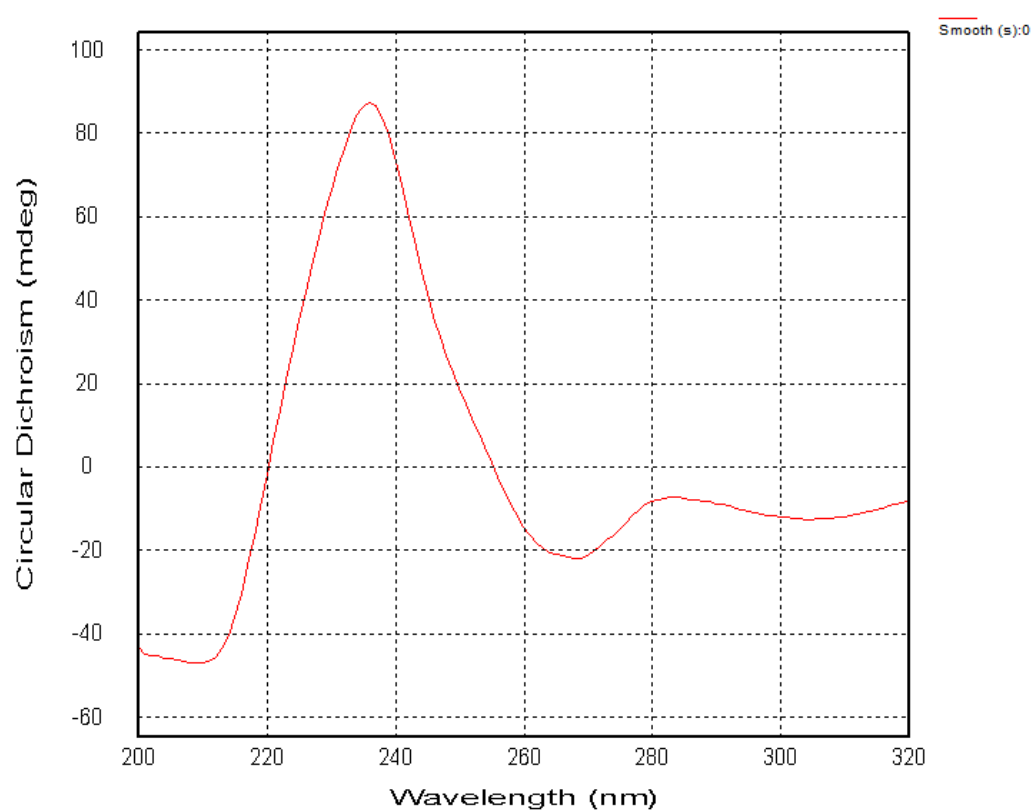
6c



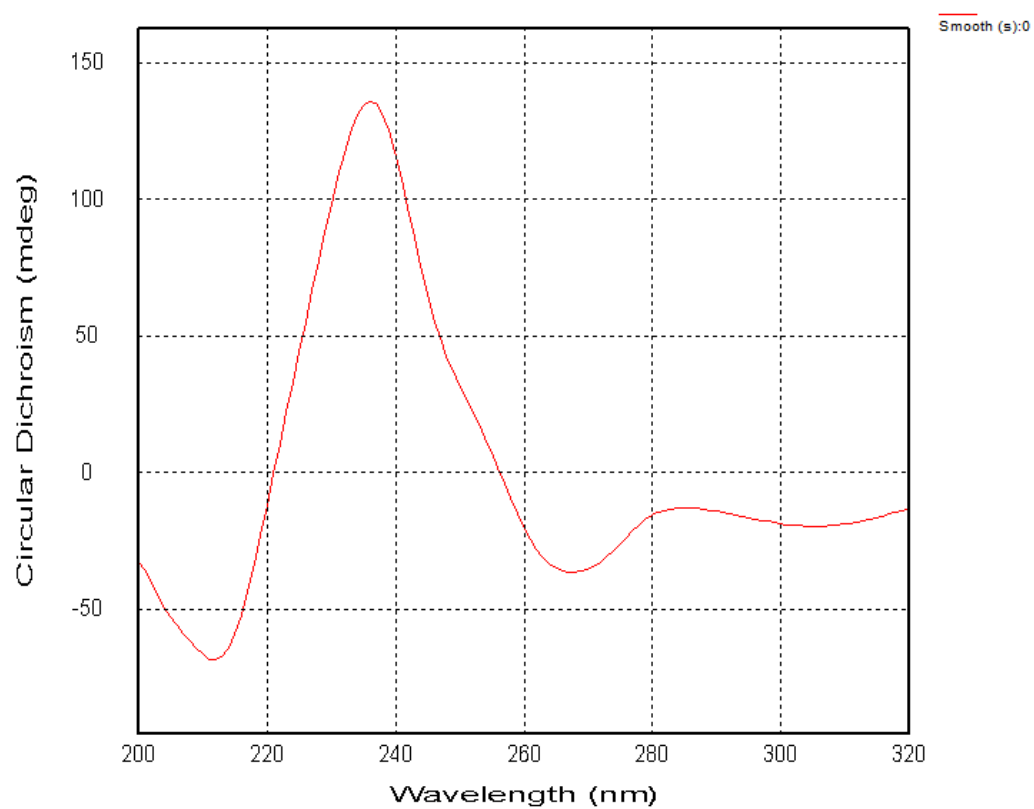
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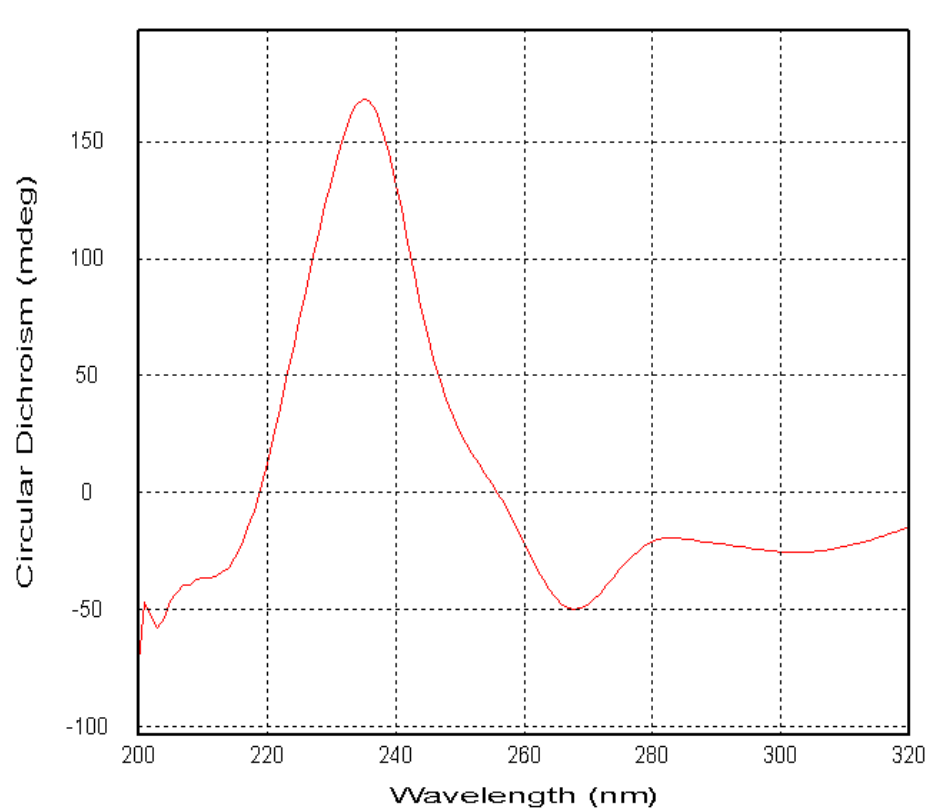
6e



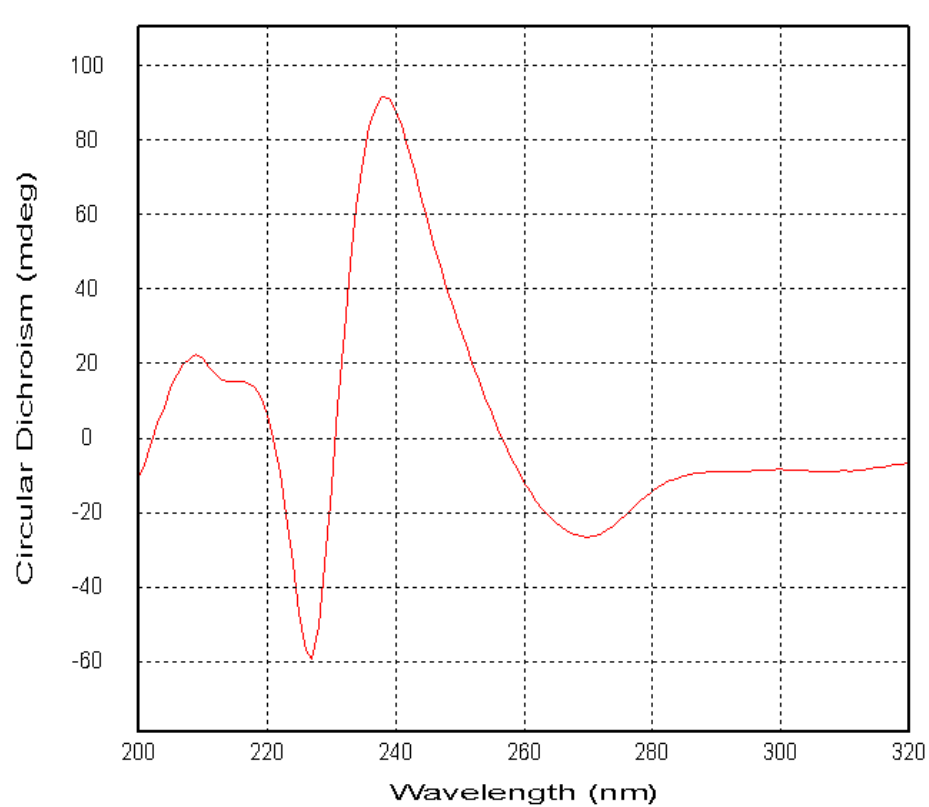
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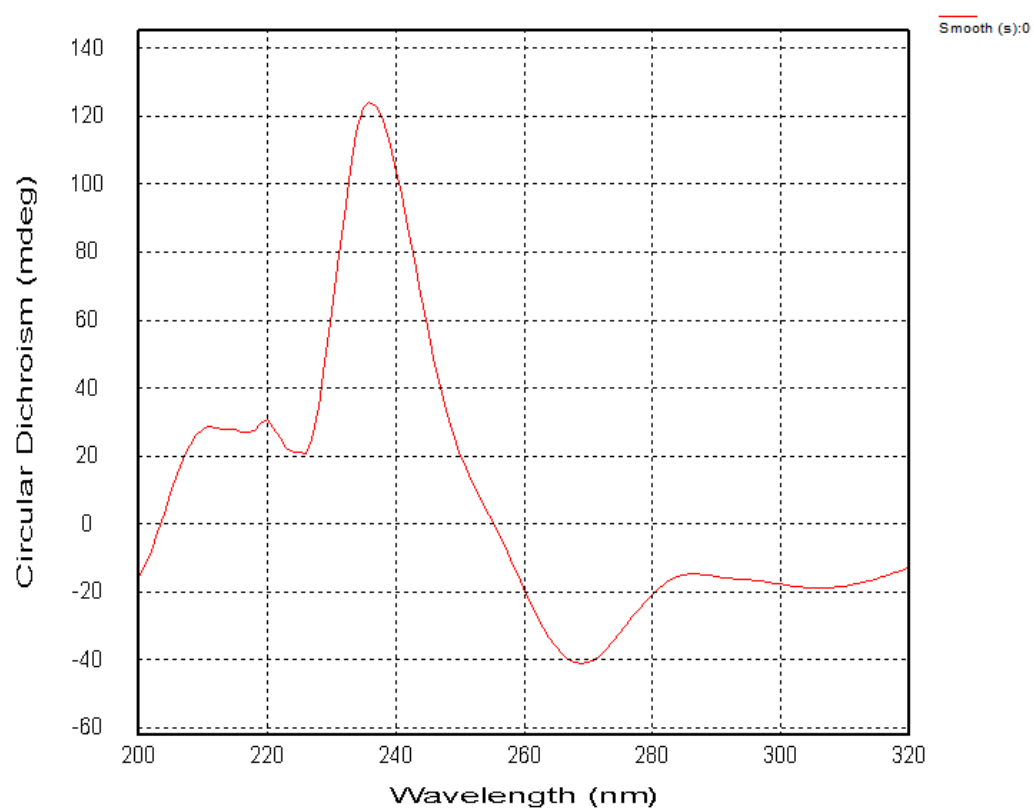
6g



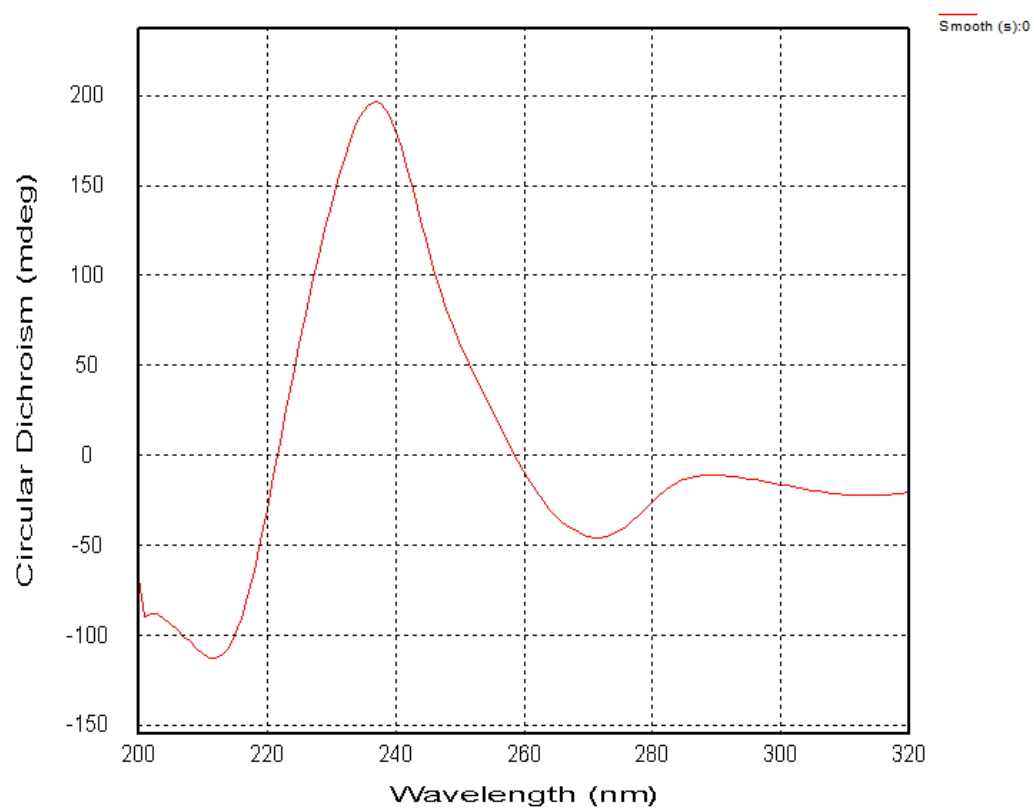
6h



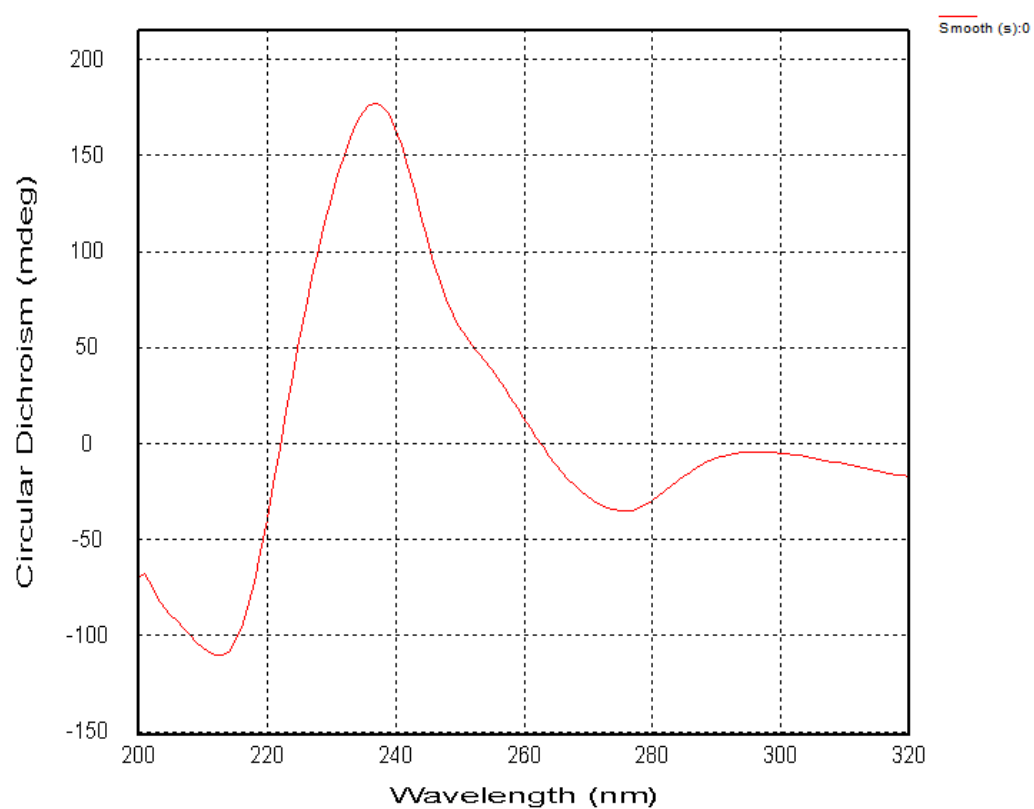
6i



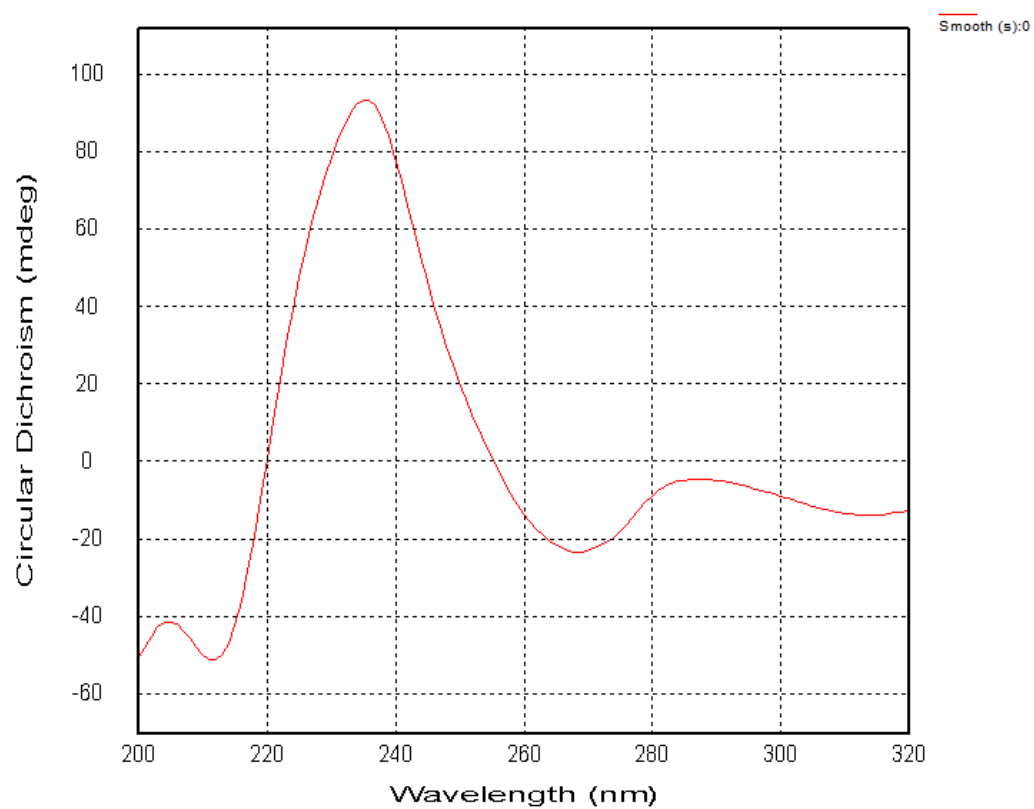
6j



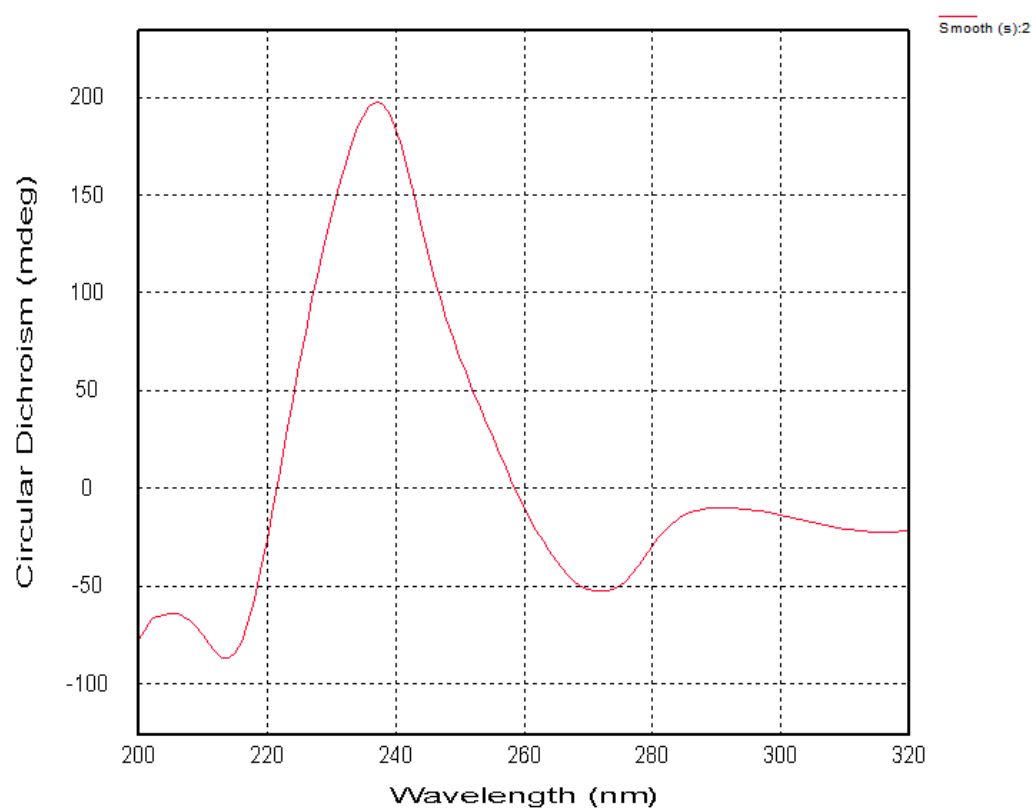
6k



6l



6m



6n

