

# Supporting Information

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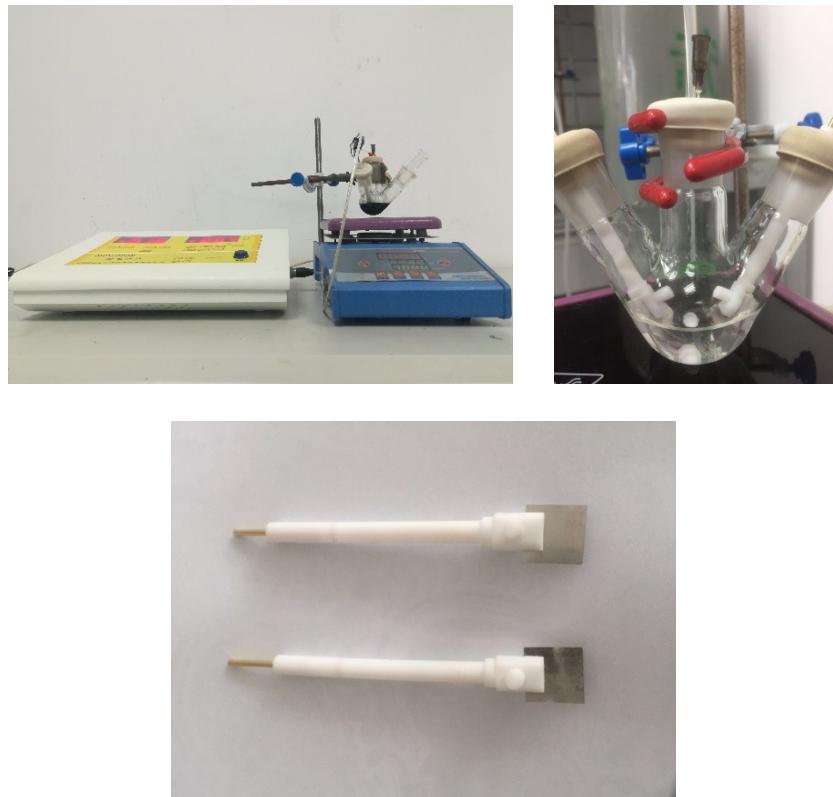
## **1. General information**

All glassware was oven dried at 85 °C for hours and cooled down for use. Acetonitrile (MeCN) was dried and distilled from calcium hydride under argon. Unless otherwise stated, materials were obtained from commercial suppliers and used without further purification. The instruments for electrochemical studies are Metrohm Autolab PGSTAT204 (made in The Netherlands) and dual display potentiostat (DJS-292B) (made in China). Both anode and cathode electrode are platinum plate electrodes ( $1.5 \times 1.5 \text{ cm}^2$ ). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp.60-90°C). Gas chromatographic analyses were performed on an Agilent GC-7820A gas chromatography instrument with FID detector for organic liquid samples.  $^1\text{H}$  and  $^{13}\text{C}$  NMR data were recorded with Bruker AVANCE III (600 MHz) spectrometers with tetramethylsilane (TMS) as the internal standard. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ( $\text{CDCl}_3 = \delta 7.26$ ;  $\text{DMSO} = \delta 2.50$ ). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ( $\text{CDCl}_3 = \delta 77.16$ ;  $\text{DMSO} = \delta 39.60$ ). GC-MS spectra were recorded on Thermo GC MS TRACE 1300.

## **2. Optimization of conditions for the electrochemical N1-allylation and C3-iodination of 1*H*-indole**

In an oven-dried undivided four-necked flask (25 mL) equipped with a stir bar (**Fig. S1**), 1*H*-indole (0.5 mmol, 1 equiv.), allyl iodide (0.55 mmol, 1.1 equiv.), and electrolyte salt were added to 10 mL  $\text{CH}_3\text{CN}$ . The flask was equipped with platinum plates ( $1.5 \times 1.5 \text{ cm}^2$ ) as both the anode and cathode and was then charged with argon.

The reaction mixture was stirred and electrolyzed under constant current mode at room temperature. After the completion of reaction, the resulted solution was analyzed by gas chromatography with *1H*-indole itself as the internal standard.

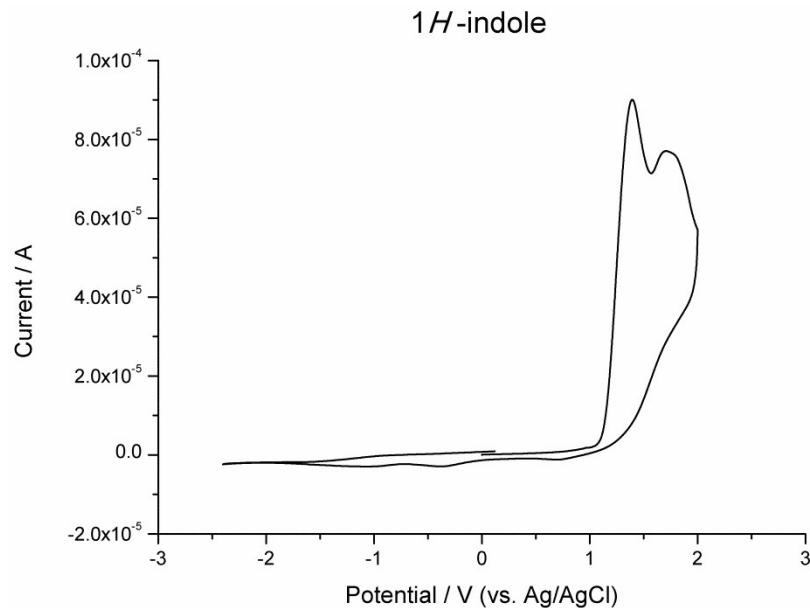


**Fig. S1: Electrosynthetic installation**

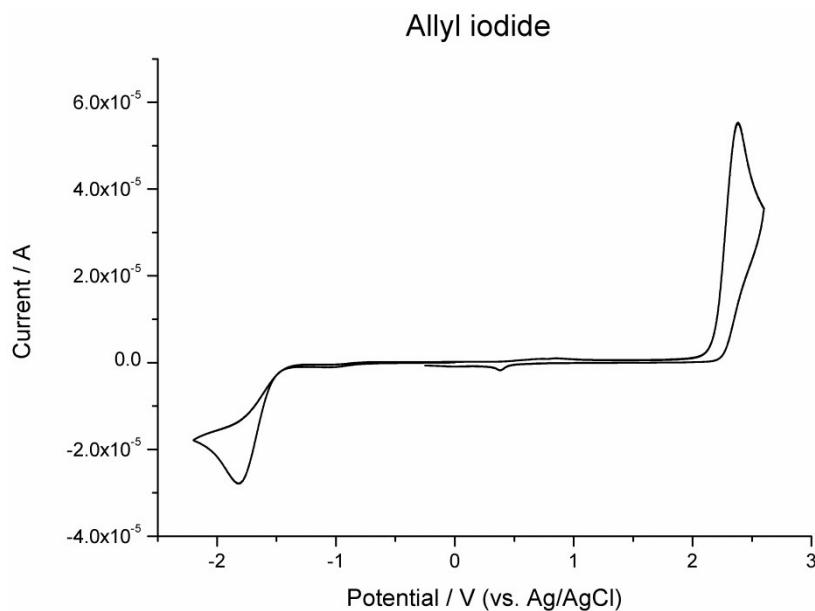
### 3. General procedure for cyclic voltammetry

The redox property of each compound was measured in anhydrous acetonitrile ( $\text{CH}_3\text{CN}$ ) containing *n*-tetrabutylammonium hexafluorophosphate ( $n\text{Bu}_4\text{NPF}_6$ ) as the supporting electrolyte. Cyclic voltammetry was carried out in conventional three-electrode electrochemical cell with Metrohm Autolab PGSTAT204 under argon at room temperature. A glassy carbon disk electrode (diameter is 2.0 mm) was used as the working electrode. A platinum plate electrode ( $1.5 \times 1.5 \text{ cm}^2$ ) was used as the counter electrode. The reference Ag/AgCl electrode was made by immersing a silver wire in a solution of saturated KCl aqueous solution, and separated from reaction by a

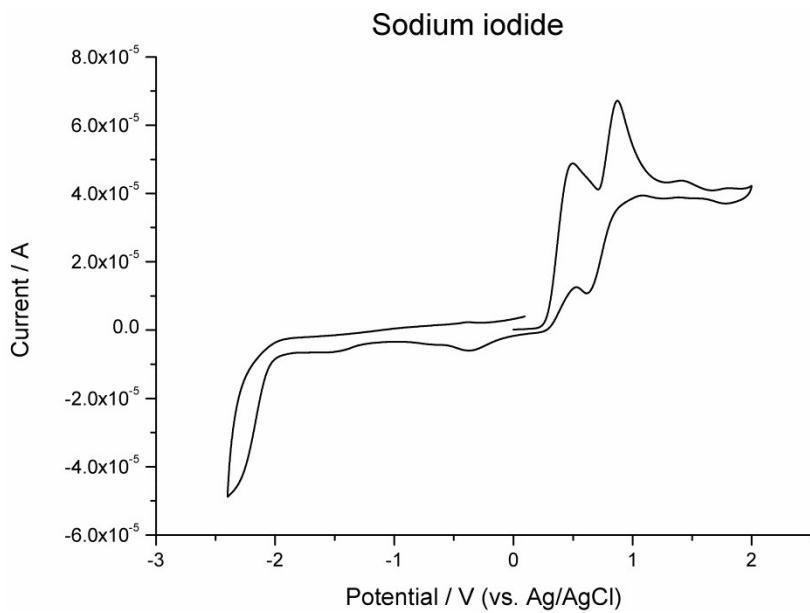
salt bridge. 10mL electrolyte solution containing 0.05 M  $n$ Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN was poured into electrochemical cell in all experiments. The concentration of sample was 0.01 M. The potential scan ranged from -2.4 to 2.2 V at a scan rate of 0.1 V/s.



**Fig. S2:** Cyclic voltammogram for 1*H*-indole



**Fig. S3:** Cyclic voltammogram for allyl iodide



**Fig. S4:** Cyclic voltammogram for sodium iodide

#### 4. General electrosynthetic procedure

In an oven-dried undivided four-necked bottle (25 mL) equipped with a stir bar, indoles (0.5 mmol), alkyl halide (0.55 mmol), sodium halide (0.25 mmol) and CH<sub>3</sub>CN (10 mL) were combined and added. The bottle was equipped with platinum plate electrodes (1.5×1.5 cm<sup>2</sup>) as both the anode and cathode and was then charged with argon. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under room temperature for 2 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The pure product was obtained by column chromatography on a silica gel column using petroleum ether.

#### 5. Gram-scale synthesis and reagent recycling procedure

In an oven-dried undivided glass cell (100 mL) equipped with a stir bar (**Fig. S5**), indole (10.0 mmol), allyl halide (11.0 mmol), electrolyte salt (5.0 mmol) and CH<sub>3</sub>CN (70 mL) were combined and added. The bottle was equipped with a platinum plate

( $2.0 \times 2.0$  cm $^2$ ) anode and platinum gauze cathode, and was then charged with argon. The reaction mixture was stirred and electrolyzed at a constant current of 32 mA. The potentiostat was operating in constant current mode under room temperature for 22.5 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on a silica gel column using petroleum ether and ethyl acetate.

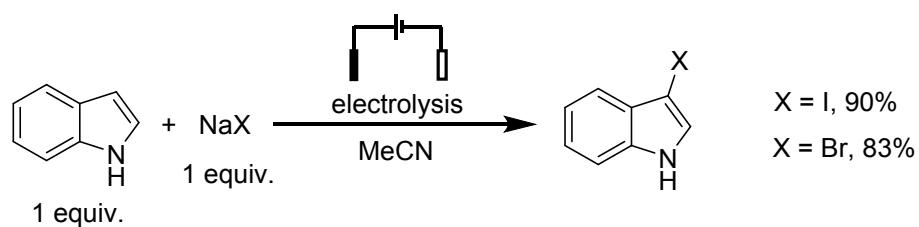


**Fig. S5:** Electrosynthetic installation for gram scale

Acetonitrile can be recycled by the rotary evaporator and then distilled for further use. Supporting electrolyte can also be recycled, after removing the solvent from the reaction mixture, diethyl ether was added to precipitate the inorganic salt (e.g. NaI). The recycled NaI is recovered at around 85% mass.

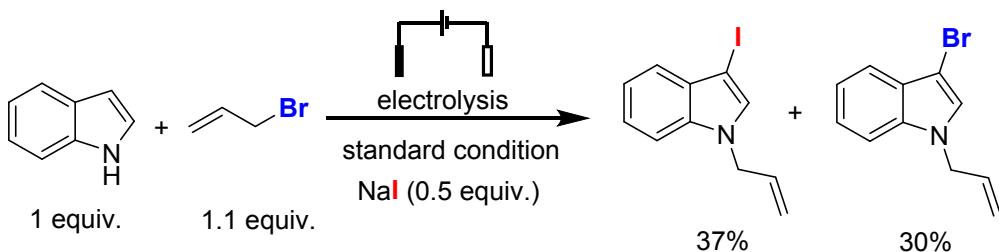
## 6. Mechanistic study

### 6.1 Electrosynthesis of 3-iodo-indole

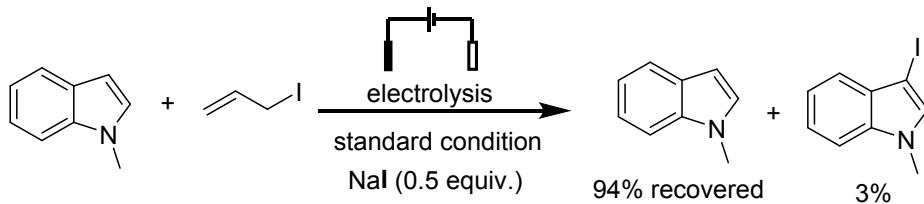


3-iodo-1*H*-indole was synthesized according to our previous reported work (*Eur. J. Org. Chem.*, 2018, 4949-4952), in an oven-dried undivided four-necked flask (25 mL) equipped with a stir bar. NaI or NaBr (2 mmol, 1 equiv.) and 1*H*-indole (2 mmol, 1 equiv.) were added to 10 mL CH<sub>3</sub>CN. The flask was equipped with platinum electrode (1.5×1.5 cm<sup>2</sup>) as both anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA at room temperature for 12 h in the argon. When the reaction was finished, the solvent was removed with a rotary evaporator. The pure product was obtained by column chromatography on silica gel.

## 6.2 Control reactions

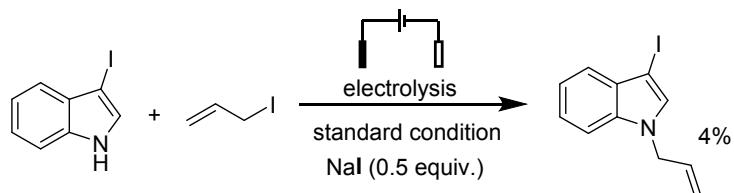


In an oven-dried undivided four-necked flask (25 mL) equipped with a stir bar, 1*H*-indole (0.5 mmol, 1 equiv.), allyl bromide (0.55 mmol, 1.1 equiv.) and sodium iodide (0.25 mmol, 0.5 equiv.) were added to 10 mL CH<sub>3</sub>CN. The flask was equipped with platinum plate electrodes (1.5×1.5 cm<sup>2</sup>) as both the anode and cathode and was then charged with argon. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under room temperature for 2 h. When the reaction was finished, the yields were determined by gas Chromatography.



In an oven-dried undivided four-necked flask (25 mL) equipped with a stir bar, 1-methyl-1*H*-indole (0.5 mmol, 1 equiv.), allyl iodide (0.55 mmol, 1.1 equiv.) and sodium iodide (0.25 mmol, 0.5 equiv.) were added to 10 mL CH<sub>3</sub>CN. The flask was

equipped with platinum plate electrodes ( $1.5 \times 1.5 \text{ cm}^2$ ) as both the anode and cathode and was then charged with argon. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under room temperature for 2 h. When the reaction was finished, the yields were determined by gas Chromatography.



In an oven-dried undivided four-necked flask (25 mL) equipped with a stir bar, 3-iodo-1*H*-indole (0.5 mmol, 1 equiv.), allyl iodide (0.55 mmol, 1.1 equiv.) and sodium iodide (0.25 mmol, 0.5 equiv.) were added to 10 mL CH<sub>3</sub>CN. The flask was equipped with platinum plate electrodes ( $1.5 \times 1.5 \text{ cm}^2$ ) as both the anode and cathode and was then charged with argon. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under room temperature for 2 h. When the reaction was finished, the yield was determined by gas Chromatography.

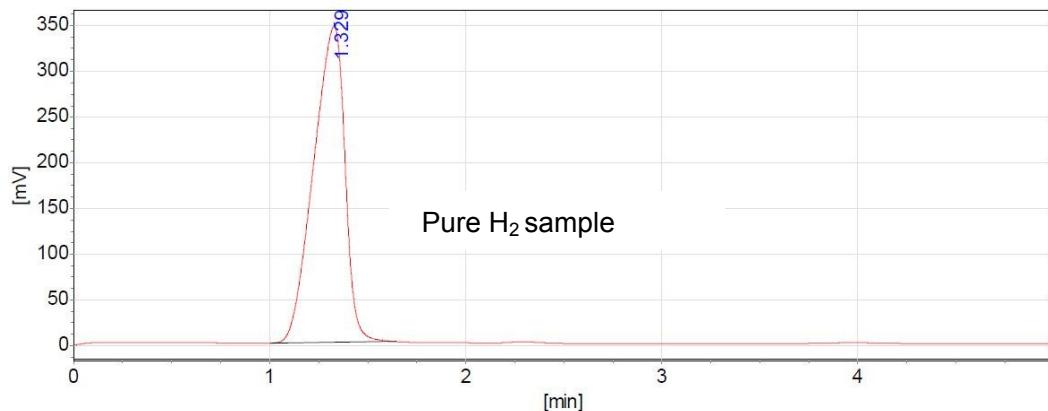
### 6.3 Detection of hydrogen-evolution



**Fig. S6: Electrosynthetic installation for the study on hydrogen-evolution**

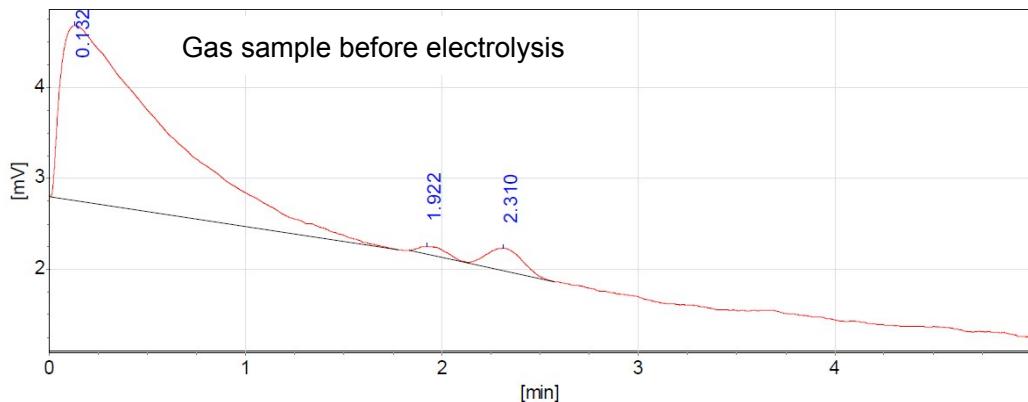
A special designed gas-tight electrochemical cell (50 mL) equipped with a stir bar (**Fig. S6**) was used for the detection of gas product during electrolysis. The cell was equipped with platinum electrode ( $1.5 \times 1.5 \text{ cm}^2$ ) as both anode and cathode. 1H-indole (0.5 mmol), allyl iodide (0.55 mmol), sodium iodide (0.25 mmol) and 25 mL anhydrous  $\text{CH}_3\text{CN}$  was added to the cell before charged with argon. All the valves were kept closed during the reaction to remain the gas tightness. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under room temperature. The gas samples were taken out though the sealed injector (1 mL, Hamilton) and then injected in to the gas chromatograph (GC-2014 with TCD detector, Shimadzu Corp., Japan) equipped with 5Å molesieve chromatographic column.

A qualitative analysis of gas product was carried out. First, the standard hydrogen sample (0.5 mL, chemical purity 99.9%) was injected to the gas chromatography showing a time of retention at 1.329 min (**Fig. S7**).



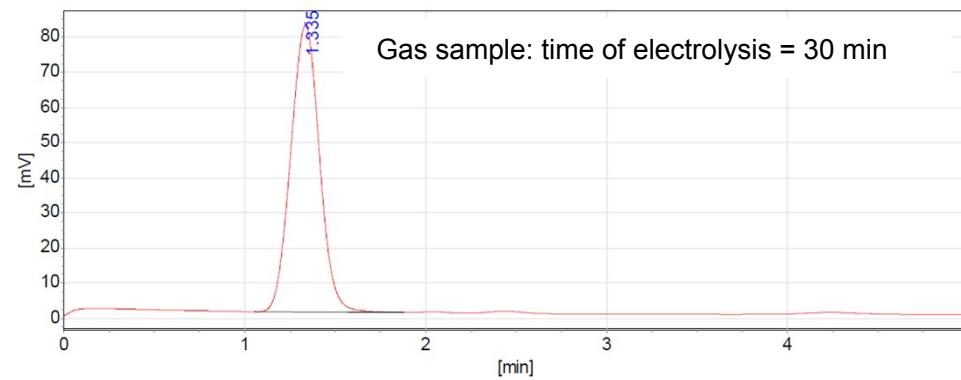
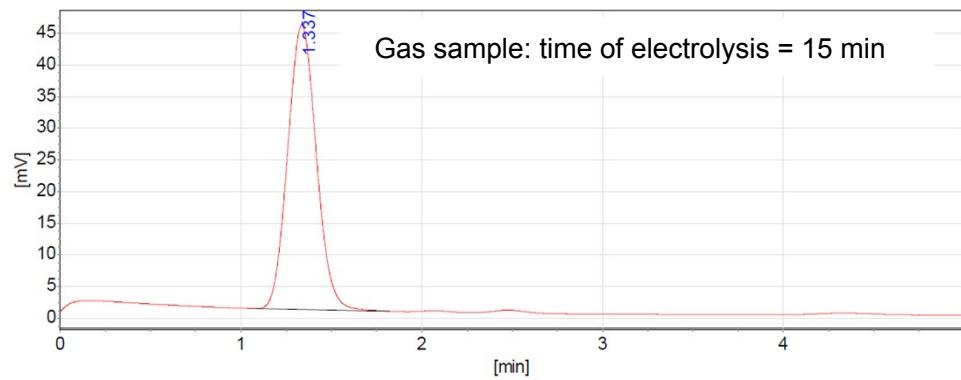
**Fig. S7: Chromatography of pure H<sub>2</sub>**

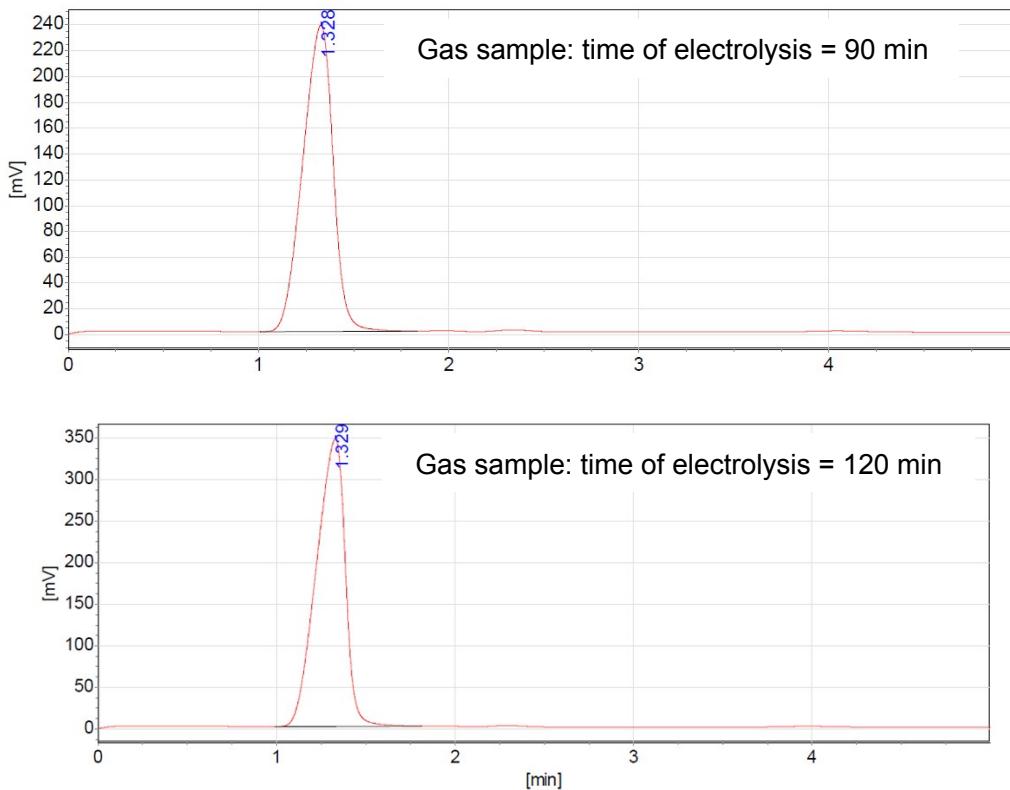
0.5 mL gas sample was taken from the electrochemical cell before electrolysis. The chromatography showed no significant peak for  $\text{H}_2$ , but only a trace amount of  $\text{N}_2$  and  $\text{O}_2$  which is probably from the residual air (**Fig. S8**).



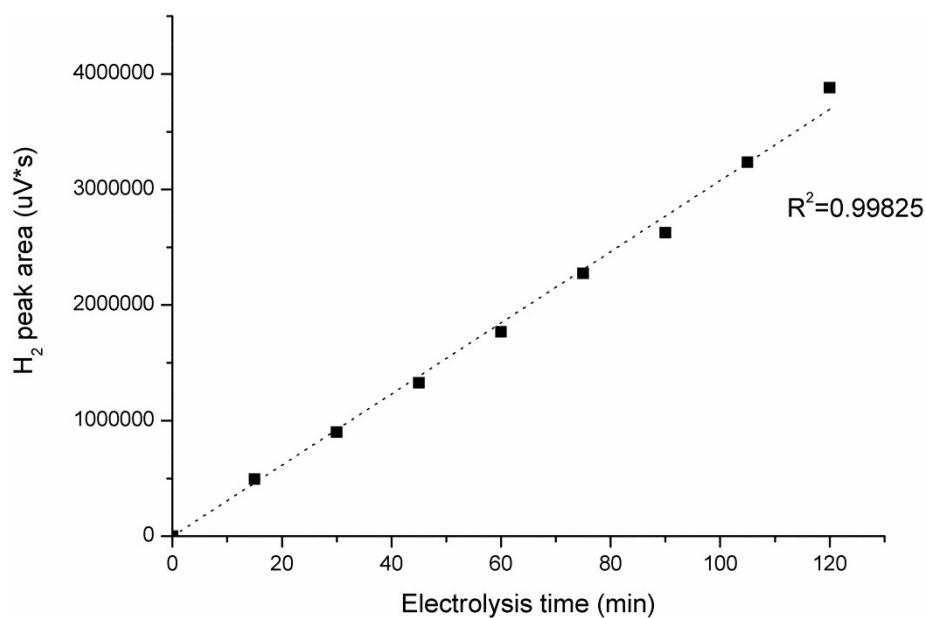
**Fig. S8: Chromatography of gas sample taken from the cell before electrolysis**

During the electrolysis, a gas sample was taken every 15 min and analyzed by gas chromatography. The chromatography of selected samples were listed as below.





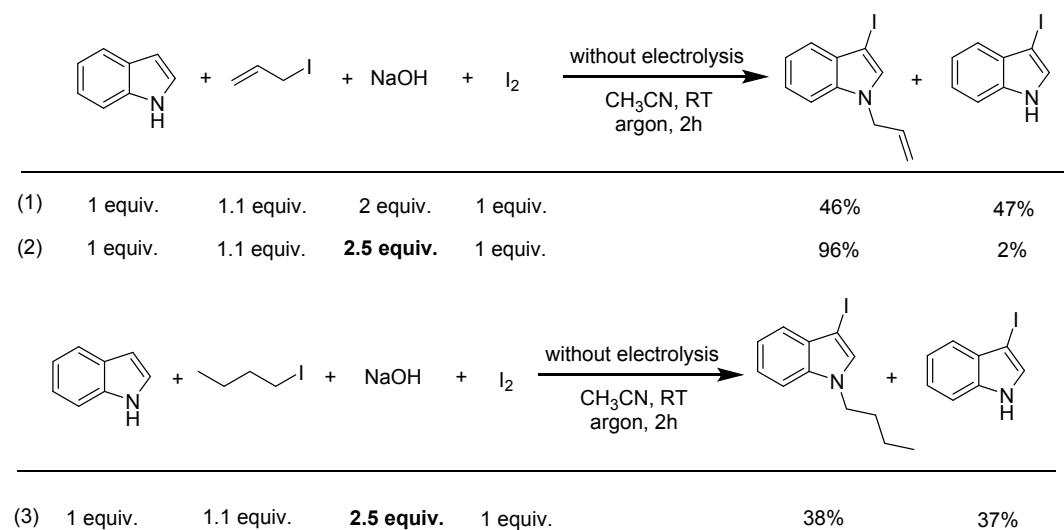
The above results indicated that without electrolysis,  $H_2$  cannot be produced. During electrolysis only one peak at around 1.33 min was observed for all the gas samples taken from the cell, we can conjecture that  $H_2$  is the sole electrogenerated gas product. By plotting the  $H_2$  peak area as a function of electrolysis time (Fig. S9), an approximate linear relation has been found, which let us conclude that  $H_2$  is generated by electrolysis (according to Faraday's the first law).



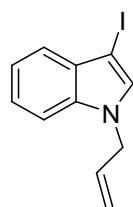
**Fig. S9 Evolution of H<sub>2</sub> (peak area of chromatography) during electrolysis**

## 7. Essay of difunctionalization without electrolysis

In an oven-dried flask (25 mL) equipped with a stir bar, indoles (0.5 mmol), alkyl halide (0.55 mmol), sodium hydroxide, molecular iodine (0.5 mmol) and CH<sub>3</sub>CN (10 mL) were combined and added. The flask was then charged with argon. The reaction mixture was stirred for 2 h. After that, the resulted solution was analyzed by gas chromatography with <sup>1</sup>H-indole itself as the internal standard. The results are summarized as below:

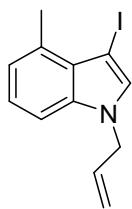


## 8. Characterization Data

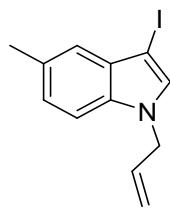


**1-allyl-3-iodo-1H-indole (3a):** yellow liquid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.45 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.26 (ddd, *J* = 8.2, 6.7, 1.1 Hz, 1H), 7.24-7.18 (m, 2H), 6.02-5.92 (m, 1H), 5.26-5.20 (m, 1H), 5.12 (ddd, *J* = 17.1, 2.8, 1.6 Hz, 1H), 4.73 (dt, *J* = 5.5, 1.6 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 136.21, 133.00,

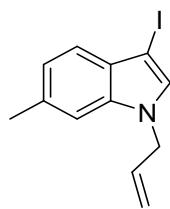
131.88, 130.60, 122.78, 121.34, 120.50, 118.04, 109.90, 55.68, 49.22. GC-MS (EI)  $m/z$  284.00 [M+H]<sup>+</sup>



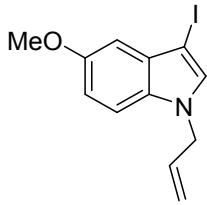
**1-allyl-3-iodo-4-methyl-1H-indole (3b):** yellow brown solid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.19 (t, 2H), 7.11 (t, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 5.99-5.92 (m, 1H), 5.24-5.21 (m, 1H), 5.13-5.09 (m, 1H), 4.69-4.67 (m, 2H), 2.88 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 136.39, 133.00, 132.96, 131.53, 126.70, 122.58, 122.17, 118.02, 108.21, 51.43, 49.14, 19.43. GC-MS (EI)  $m/z$  298.00 [M+H]<sup>+</sup>



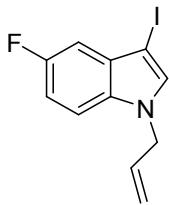
**1-allyl-3-iodo-5-methyl-1H-indole (3c):** yellow solid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.32 (d, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 7.08 (s, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.00-5.93 (m, 1H), 5.24-5.21 (m, 1H), 5.14-5.09 (m, 1H), 4.70-4.68 (m, 2H), 2.49 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 136.63, 133.17, 132.78, 131.28, 128.62, 122.35, 121.00, 117.90, 109.75, 55.48, 49.08, 21.98. GC-MS (EI)  $m/z$  297.99 [M+H]<sup>+</sup>



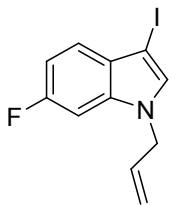
**1-allyl-3-iodo-6-methyl-1H-indole (3d):** pale yellow solid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.23 (s, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.14 (s, 1H), 7.08 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.00-5.93 (m, 1H), 5.23-5.20 (m, 1H), 5.13-5.09 (m, 1H), 4.71-4.69 (m, 2H), 2.49 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 134.67, 133.16, 131.86, 130.83, 130.03, 124.47, 120.94, 117.91, 109.66, 55.07, 49.27, 21.50. GC-MS (EI)  $m/z$  297.99 [M+H]<sup>+</sup>



**1-allyl-3-iodo-5-methoxy-1H-indole (3e):** pale yellow liquid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 (d,  $J = 8.9$  Hz, 1H), 7.15 (s, 1H), 6.90 (dd,  $J = 8.8, 2.4$  Hz, 1H), 6.87 (d,  $J = 2.4$  Hz, 1H), 6.00-5.90 (m, 1H), 5.23 (ddd,  $J = 10.3, 2.5, 1.3$  Hz, 1H), 5.12 (ddd,  $J = 17.1, 2.8, 1.6$  Hz, 1H), 4.69 (dt,  $J = 5.5, 1.6$  Hz, 2H), 3.90 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  155.08, 133.15, 132.21, 131.41, 131.12, 118.00, 113.51, 110.91, 102.57, 55.99, 54.97, 49.44. GC-MS (EI)  $m/z$  313.98 [M+H]<sup>+</sup>

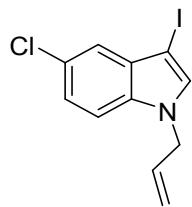


**1-allyl-5-fluoro-3-iodo-1H-indole (3f):** yellow brown solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (q,  $J = 4.3$  Hz, 2H), 7.11 (dd,  $J = 9.2, 2.5$  Hz, 1H), 6.99 (td,  $J = 9.0, 2.5$  Hz, 1H), 6.01-5.91 (m, 1H), 5.25 (dd,  $J = 10.2, 1.2$  Hz, 1H), 5.16-5.08 (m, 1H), 4.71 (dt,  $J = 5.5, 1.6$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  158.62 (d,  $J_{\text{C-F}} = 236.62$  Hz), 133.45, 132.86 (d,  $J_{\text{C-F}} = 14.04$  Hz), 131.33 (d,  $J_{\text{C-F}} = 10.42$  Hz), 118.27, 111.42 (d,  $J_{\text{C-F}} = 26.58$  Hz), 110.87 (d,  $J_{\text{C-F}} = 9.67$  Hz), 106.44 (d,  $J_{\text{C-F}} = 24.46$  Hz), 54.89 (d,  $J_{\text{C-F}} = 4.83$  Hz), 49.54.  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -123.53. GC-MS (EI)  $m/z$  301.97 [M+H]<sup>+</sup>

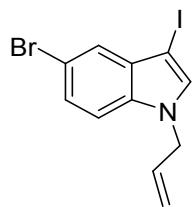


**1-allyl-6-fluoro-3-iodo-1H-indole (3g):** yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (dd,  $J = 8.7, 5.3$  Hz, 1H), 7.16 (s, 1H), 7.01-6.92 (m, 2H), 6.00-5.88 (m, 1H), 5.25 (dd,  $J = 10.3, 1.1$  Hz, 1H), 5.13 (dd,  $J = 17.1, 1.1$  Hz, 1H), 4.66 (dt,  $J = 5.5, 1.5$

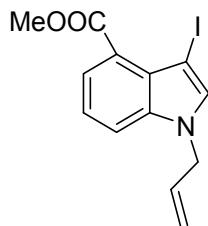
Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  160.56 (d,  $J_{\text{C-F}} = 239.64$  Hz), 136.12 (d,  $J_{\text{C-F}} = 12.23$  Hz), 132.59, 132.43 (d,  $J_{\text{C-F}} = 3.62$  Hz), 127.24, 122.44 (d,  $J_{\text{C-F}} = 10.27$  Hz), 118.33, 109.41 (d,  $J_{\text{C-F}} = 24.92$  Hz), 96.32 (d,  $J_{\text{C-F}} = 26.73$  Hz), 55.64, 49.44.  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -119.58. GC-MS (EI)  $m/z$  301.98 [M+H]<sup>+</sup>



**1-allyl-5-chloro-3-iodo-1H-indole (3h):** yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 1.4$  Hz, 1H), 7.24-7.15 (m, 3H), 5.95 (ddd,  $J = 22.5, 10.6, 5.5$  Hz, 1H), 5.25 (dd,  $J = 10.3, 1.0$  Hz, 1H), 5.11 (dd,  $J = 17.1, 0.9$  Hz, 1H), 4.71 (dt,  $J = 5.4, 1.5$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  134.80, 133.20, 132.67, 131.84, 126.57, 123.26, 120.96, 118.34, 111.10, 54.77, 49.46. GC-MS (EI)  $m/z$  318.83 [M+H]<sup>+</sup>

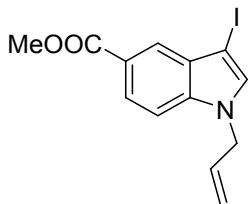


**1-allyl-5-bromo-3-iodo-1H-indole (3i):** yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 1.8$  Hz, 1H), 7.32 (dd,  $J = 8.7, 1.9$  Hz, 1H), 7.20-7.13 (m, 2H), 5.95 (ddt,  $J = 17.0, 10.6, 5.5$  Hz, 1H), 5.24 (dd,  $J = 10.3, 1.1$  Hz, 1H), 5.10 (dd,  $J = 17.1, 1.0$  Hz, 1H), 4.70 (dt,  $J = 5.4, 1.5$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  135.08, 133.05, 132.62, 132.42, 125.79, 124.05, 118.34, 114.00, 111.48, 54.67, 49.42. GC-MS (EI)  $m/z$  362.79 [M+H]<sup>+</sup>

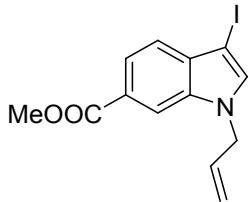


**Methyl 1-allyl-3-iodo-1H-indole-4-carboxylate (3j):** pale yellow liquid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (dd,  $J = 7.3, 0.8$  Hz, 1H), 7.45 (dd,  $J = 8.3, 0.7$  Hz, 1H),

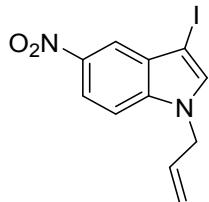
7.34 (s, 1H), 7.27-7.23 (m, 1H), 5.95 (ddt,  $J = 17.0, 10.5, 5.4$  Hz, 1H), 5.24 (dd,  $J = 10.3, 1.0$  Hz, 1H), 5.11 (dd,  $J = 17.1, 1.0$  Hz, 1H), 4.74 (dt,  $J = 5.4, 1.6$  Hz, 2H), 4.02 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  168.48, 137.04, 135.93, 132.50, 126.05, 125.63, 122.40, 121.75, 118.38, 113.20, 52.29, 52.03, 49.23. GC-MS (EI)  $m/z$  341.95 [M+H]<sup>+</sup>



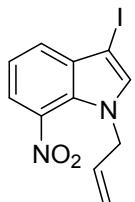
**Methyl 1-allyl-3-iodo-1H-indole-5-carboxylate (3k):** pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (d,  $J = 1.4$  Hz, 1H), 7.95 (dd,  $J = 8.7, 1.6$  Hz, 1H), 7.30 (d,  $J = 8.7$  Hz, 1H), 7.25 (s, 1H), 5.97 (ddt,  $J = 16.9, 10.6, 5.5$  Hz, 1H), 5.26 (dd,  $J = 10.3, 1.1$  Hz, 1H), 5.12 (dd,  $J = 17.1, 1.0$  Hz, 1H), 4.74 (dt,  $J = 5.5, 1.5$  Hz, 2H), 3.95 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  167.89, 138.89, 133.38, 132.49, 130.41, 124.39, 124.17, 122.75, 118.50, 109.75, 57.43, 52.12, 49.41. GC-MS (EI)  $m/z$  341.95 [M+H]<sup>+</sup>



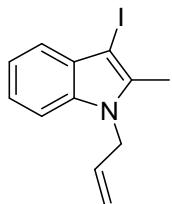
**Methyl 1-allyl-3-iodo-1H-indole-6-carboxylate (3l):** pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (s, 1H), 7.87 (dd,  $J = 8.4, 1.3$  Hz, 1H), 7.46 (d,  $J = 8.4$  Hz, 1H), 7.34 (s, 1H), 5.99 (ddt,  $J = 16.8, 10.7, 5.5$  Hz, 1H), 5.26 (dd,  $J = 10.3, 1.0$  Hz, 1H), 5.13 (dd,  $J = 17.1, 0.9$  Hz, 1H), 4.79 (dt,  $J = 5.4, 1.4$  Hz, 2H), 3.95 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  167.84, 135.58, 134.87, 134.06, 132.50, 124.51, 121.37, 121.00, 118.40, 112.16, 55.81, 52.12, 49.18. GC-MS (EI)  $m/z$  341.96 [M+H]<sup>+</sup>



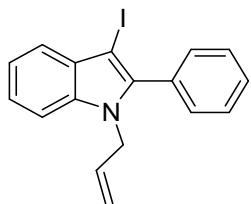
**1-allyl-3-iodo-5-nitro-1H-indole (3m):** yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (d,  $J = 2.2$  Hz, 1H), 8.14 (dd,  $J = 9.1, 2.2$  Hz, 1H), 7.34 (t,  $J = 4.5$  Hz, 2H), 6.03-5.92 (m, 1H), 5.31 (dd,  $J = 10.3, 0.8$  Hz, 1H), 5.14 (dd,  $J = 17.1, 0.8$  Hz, 1H), 4.78 (dt,  $J = 5.5, 1.5$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  142.57, 139.31, 135.20, 131.96, 130.44, 119.01, 118.92, 118.43, 110.22, 58.24, 49.72. GC-MS (EI)  $m/z$  328.96 [M+H]<sup>+</sup>



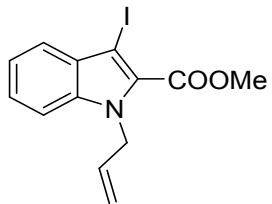
**1-allyl-3-iodo-7-nitro-1H-indole (3n):** yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (dd,  $J = 7.8, 0.7$  Hz, 1H), 7.73 (dd,  $J = 7.9, 1.0$  Hz, 1H), 7.30 (s, 1H), 7.23 (t,  $J = 7.9$  Hz, 1H), 5.85-5.75 (m, 1H), 5.14 (dd,  $J = 10.3, 1.0$  Hz, 1H), 4.92 (dd,  $J = 17.1, 0.9$  Hz, 1H), 4.87 (dt,  $J = 5.5, 1.5$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  137.10, 136.72, 135.25, 132.83, 127.79, 126.86, 121.06, 119.63, 118.48, 57.90, 52.67. GC-MS (EI)  $m/z$  328.96 [M+H]<sup>+</sup>



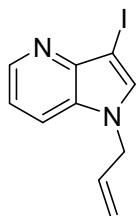
**1-allyl-3-iodo-2-methyl-1H-indole (3o):** yellow brown solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 7.6$  Hz, 1H), 7.24-7.10 (m, 3H), 5.98-5.86 (m, 1H), 5.14 (dd,  $J = 10.3, 1.0$  Hz, 1H), 4.85 (dd,  $J = 17.1, 0.9$  Hz, 1H), 4.80-4.71 (m, 2H), 2.47 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  137.65, 136.93, 132.94, 130.22, 122.14, 120.67, 120.44, 116.72, 109.46, 58.76, 46.57, 13.26. GC-MS (EI)  $m/z$  297.96 [M+H]<sup>+</sup>



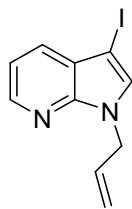
**1-allyl-3-iodo-2-phenyl-1H-indole (3p):** pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64-7.39 (m, 6H), 7.34-7.27 (m, 2H), 7.26-7.22 (m, 1H), 5.89 (ddt,  $J = 17.1, 10.2, 4.6$  Hz, 1H), 5.16 (dd,  $J = 10.4, 1.0$  Hz, 1H), 4.92 (dd,  $J = 17.1, 1.0$  Hz, 1H), 4.71-4.62 (m, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  141.75, 137.20, 133.42, 131.68, 130.86, 130.56, 129.06, 128.52, 123.08, 121.61, 120.96, 116.87, 110.67, 59.75, 47.62. GC-MS (EI)  $m/z$  359.97 [M+H]<sup>+</sup>



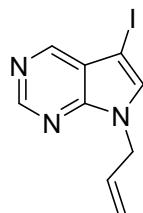
**Methyl 1-allyl-3-iodo-1H-indole-2-carboxylate (3q):** pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 8.1$  Hz, 1H), 7.39 (ddd,  $J = 8.1, 6.9, 1.1$  Hz, 1H), 7.33 (d,  $J = 8.4$  Hz, 1H), 7.26-7.22 (m, 1H), 5.98 (ddt,  $J = 17.1, 10.2, 5.1$  Hz, 1H), 5.20 (dt,  $J = 5.0, 1.6$  Hz, 2H), 5.12 (dd,  $J = 10.3, 1.2$  Hz, 1H), 4.94 (dd,  $J = 17.1, 1.2$  Hz, 1H), 3.97 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  161.75, 138.68, 133.69, 130.51, 128.38, 126.42, 124.22, 121.82, 116.63, 110.94, 67.65, 51.83, 48.17. GC-MS (EI)  $m/z$  341.94 [M+H]<sup>+</sup>



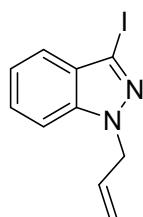
**1-allyl-3-iodo-1H-pyrrolo[3,2-b]pyridine (3r):** yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.55 (dd,  $J = 4.6, 1.2$  Hz, 1H), 7.59 (dd,  $J = 8.3, 1.2$  Hz, 1H), 7.42 (s, 1H), 7.15 (dd,  $J = 8.3, 4.6$  Hz, 1H), 6.00-5.90 (m, 1H), 5.26 (dd,  $J = 10.3, 1.0$  Hz, 1H), 5.12 (dd,  $J = 17.1, 0.9$  Hz, 1H), 4.72 (dt,  $J = 5.5, 1.4$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  146.57, 144.43, 134.78, 132.44, 129.27, 118.59, 117.54, 117.45, 58.15, 49.61. GC-MS (EI)  $m/z$  285.02 [M+H]<sup>+</sup>



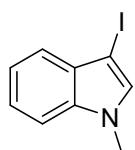
**1-allyl-3-iodo-7-azaindole (3s):** yellow brown solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 (dd,  $J = 4.7, 1.4$  Hz, 1H), 7.72 (dd,  $J = 7.9, 1.5$  Hz, 1H), 7.33 (s, 1H), 7.14 (dd,  $J = 7.9, 4.7$  Hz, 1H), 6.03 (ddt,  $J = 17.0, 10.3, 5.7$  Hz, 1H), 5.27-5.19 (m, 1H), 5.15 (ddd,  $J = 17.1, 2.8, 1.5$  Hz, 1H), 4.92 (dt,  $J = 5.7, 1.5$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  147.20, 144.18, 133.40, 131.93, 129.36, 123.25, 118.13, 116.79, 53.69, 46.89. GC-MS (EI)  $m/z$  284.96 [M+H] $^+$



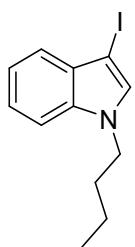
**7-allyl-5-iodo-7H-pyrrolo[2,3-d]pyrimidine (3t):** pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 (s, 1H), 8.74 (s, 1H), 7.31 (s, 1H), 5.99 (ddt,  $J = 16.9, 10.2, 5.8$  Hz, 1H), 5.28 (dd,  $J = 10.2, 1.1$  Hz, 1H), 5.17 (ddd,  $J = 17.1, 2.5, 1.5$  Hz, 1H), 4.88 (dt,  $J = 5.8, 1.5$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  152.58, 150.80, 150.35, 132.90, 132.45, 121.45, 118.98, 52.66, 46.77. GC-MS (EI)  $m/z$  286.03 [M+H] $^+$



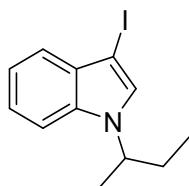
**1-allyl-3-iodo-1H-indazole (3u):** yellow liquid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 8.2$  Hz, 1H), 7.45-7.41 (m, 1H), 7.37 (d,  $J = 8.4$  Hz, 1H), 7.21 (t,  $J = 7.5$  Hz, 1H), 6.02 (ddd,  $J = 16.0, 10.8, 5.7$  Hz, 1H), 5.24 (dd,  $J = 10.3, 1.0$  Hz, 1H), 5.18 (dd,  $J = 17.1, 1.1$  Hz, 1H), 5.03 (d,  $J = 5.7$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  140.27, 132.58, 128.71, 127.57, 121.82, 121.57, 118.30, 109.58, 91.47, 52.46. GC-MS (EI)  $m/z$  284.97 [M+H] $^+$



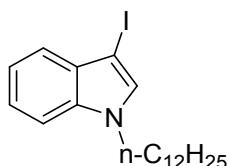
**3-iodo-1-methyl-1H-indole (3v):** yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 7.8$  Hz, 1H), 7.31-7.26 (m, 2H), 7.22-7.19 (m, 1H), 7.14 (s, 1H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  136.91, 132.86, 130.55, 122.77, 121.29, 120.39, 109.54, 54.90, 33.25. GC-MS (EI)  $m/z$  257.95 [M+H] $^+$



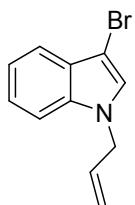
**1-butyl-3-iodo-1H-indole (3w):** pale yellow liquid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 7.9$  Hz, 1H), 7.30 (d,  $J = 8.2$  Hz, 1H), 7.27-7.22 (m, 1H), 7.21-7.14 (m, 2H), 4.10 (t,  $J = 7.1$  Hz, 2H), 1.85-1.72 (m, 2H), 1.33 (dd,  $J = 15.1, 7.5$  Hz, 2H), 0.93 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  136.22, 131.87, 130.56, 122.58, 121.35, 120.28, 109.72, 55.01, 46.60, 32.47, 20.25, 13.80. GC-MS (EI)  $m/z$  299.99 [M+H] $^+$



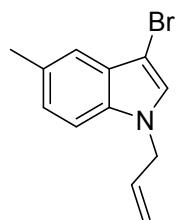
**1-(sec-butyl)-3-iodo-1H-indole (3x):** white solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 7.9$  Hz, 1H), 7.34 (d,  $J = 8.3$  Hz, 1H), 7.26-7.21 (m, 2H), 7.18 (t,  $J = 7.4$  Hz, 1H), 4.41 (dd,  $J = 14.1, 6.8$  Hz, 1H), 1.88 (dq,  $J = 13.7, 7.3$  Hz, 2H), 1.50 (d,  $J = 6.8$  Hz, 3H), 0.84 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  136.25, 130.42, 128.44, 122.44, 121.37, 120.31, 109.83, 55.62, 53.84, 30.32, 21.15, 11.05. GC-MS (EI)  $m/z$  300.00 [M+H] $^+$



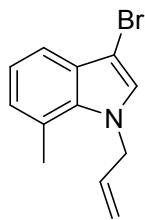
**1-dodecyl-3-iodo-1H-indole (3y):** pale yellow liquid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 7.9$  Hz, 1H), 7.31 (d,  $J = 8.2$  Hz, 1H), 7.25 (dd,  $J = 8.9, 6.2$  Hz, 1H), 7.21-7.14 (m, 2H), 4.10 (t,  $J = 7.2$  Hz, 2H), 1.86-1.77 (m, 2H), 1.34 – 1.21 (m, 18H), 0.88 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  136.22, 131.86, 130.57, 122.58, 121.36, 120.28, 109.72, 55.01, 46.93, 32.05, 30.43, 29.74, 29.69, 29.59, 29.48, 29.35, 27.06, 22.83, 14.27. GC-MS (EI)  $m/z$  412.14 [M+H] $^+$



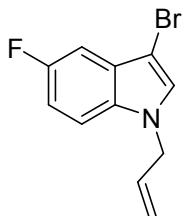
**1-allyl-3-bromo-1H-indole (5a):** pale yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J = 7.9$  Hz, 1H), 7.32 (d,  $J = 8.2$  Hz, 1H), 7.28-7.24 (m, 1H), 7.22-7.18 (m, 1H), 7.13 (s, 1H), 6.03-5.93 (m, 1H), 5.23 (dd,  $J = 10.2, 1.2$  Hz, 1H), 5.16-5.09 (m, 1H), 4.71 (dt,  $J = 5.5, 1.5$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  135.82, 133.02, 127.60, 126.84, 122.81, 120.38, 119.54, 118.03, 109.93, 90.14, 49.18. GC-MS (EI)  $m/z$  236.97 [M+H] $^+$



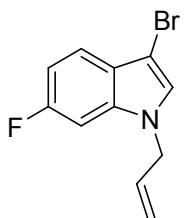
**1-allyl-3-bromo-5-methyl-1H-indole (5b):** yellow liquid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (s, 1H), 7.20 (d,  $J = 8.4$  Hz, 1H), 7.10-7.06 (m, 2H), 6.00-5.92 (m, 1H), 5.22 (dd,  $J = 10.2, 1.3$  Hz, 1H), 5.13-5.07 (m, 1H), 4.67 (dt,  $J = 5.4, 1.5$  Hz, 2H), 2.49 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  134.22, 133.13, 129.85, 127.73, 126.83, 124.48, 119.02, 117.85, 109.68, 89.47, 49.18, 21.51. GC-MS (EI)  $m/z$  250.96 [M+H] $^+$



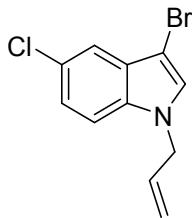
**1-allyl-3-bromo-7-methyl-1H-indole (5c):** white solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 7.9$  Hz, 1H), 7.08 (t,  $J = 7.5$  Hz, 1H), 7.04 (s, 1H), 6.97 (d,  $J = 7.1$  Hz, 1H), 6.02 (ddt,  $J = 17.1, 10.3, 4.5$  Hz, 1H), 5.17 (dd,  $J = 10.4, 0.8$  Hz, 1H), 4.98-4.86 (m, 2H), 4.82 (dd,  $J = 17.1, 0.7$  Hz, 1H), 2.67 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  134.97, 134.68, 128.47, 125.73, 121.37, 120.59, 117.69, 116.62, 90.51, 51.22, 19.52. GC-MS (EI)  $m/z$  250.97 [M+H]<sup>+</sup>



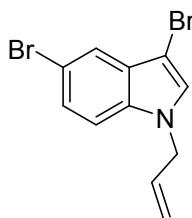
**1-allyl-3-bromo-5-fluoro-1H-indole (5d):** brown red liquid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (dt,  $J = 8.9, 3.4$  Hz, 2H), 7.16 (s, 1H), 6.99 (td,  $J = 9.1, 2.5$  Hz, 1H), 5.96 (ddd,  $J = 22.4, 10.6, 5.5$  Hz, 1H), 5.24 (d,  $J = 10.2$  Hz, 1H), 5.12 (dd,  $J = 17.1, 0.6$  Hz, 1H), 4.69 (d,  $J = 5.4$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  158.44 (d,  $J_{\text{C}-\text{F}} = 235.56$  Hz), 132.79, 132.41, 128.44, 128.04 (d,  $J_{\text{C}-\text{F}} = 10.57$  Hz), 118.22, 111.47 (d,  $J_{\text{C}-\text{F}} = 27.18$  Hz), 110.93 (d,  $J_{\text{C}-\text{F}} = 10.57$  Hz), 104.54 (d,  $J_{\text{C}-\text{F}} = 24.16$  Hz), 89.65 (d,  $J_{\text{C}-\text{F}} = 4.53$  Hz), 49.47. GC-MS (EI)  $m/z$  254.91 [M+H]<sup>+</sup>



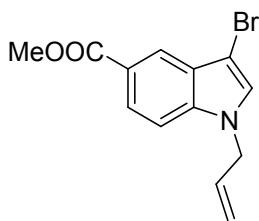
**1-allyl-3-bromo-6-fluoro-1H-indole (5e):** brown red liquid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (dd,  $J = 8.7, 5.3$  Hz, 1H), 7.10 (s, 1H), 7.05-6.90 (m, 2H), 6.00-5.89 (m, 1H), 5.25 (dd,  $J = 10.3, 1.0$  Hz, 1H), 5.12 (dd,  $J = 17.1, 1.0$  Hz, 1H), 4.64 (dt,  $J = 5.4, 1.5$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  160.52 (d,  $J_{\text{C}-\text{F}} = 240.09$  Hz), 135.77 (d,  $J_{\text{C}-\text{F}} = 12.08$  Hz), 132.57, 127.27 (d,  $J_{\text{C}-\text{F}} = 4.53$  Hz), 124.20, 120.59 (d,  $J_{\text{C}-\text{F}} = 10.57$  Hz), 118.29, 109.35 (d,  $J_{\text{C}-\text{F}} = 25.67$  Hz), 96.43 (d,  $J_{\text{C}-\text{F}} = 25.67$  Hz), 90.26, 49.38. GC-MS (EI)  $m/z$  254.93 [M+H]<sup>+</sup>



**1-allyl-3-bromo-5-chloro-1H-indole (5f):** colorless liquid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 1.8$  Hz, 1H), 7.20 (dt,  $J = 8.7, 5.3$  Hz, 2H), 7.14 (s, 1H), 5.95 (ddd,  $J = 22.5, 10.6, 5.4$  Hz, 1H), 5.25 (dd,  $J = 10.3, 0.8$  Hz, 1H), 5.10 (dd,  $J = 17.1, 0.8$  Hz, 1H), 4.68 (dd,  $J = 4.0, 1.4$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  134.25, 132.63, 128.62, 128.17, 126.39, 123.26, 119.06, 118.29, 111.13, 89.43, 49.38. GC-MS (EI)  $m/z$  270.87 [M+H]<sup>+</sup>

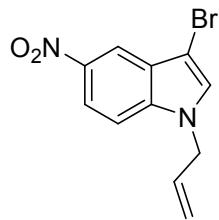


**1-allyl-3,5-dibromo-1H-indole (5g):** Fuchsia liquid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 1.8$  Hz, 1H), 7.32 (dd,  $J = 8.7, 1.9$  Hz, 1H), 7.17 (d,  $J = 8.7$  Hz, 1H), 7.12 (s, 1H), 5.95 (ddt,  $J = 16.9, 10.6, 5.4$  Hz, 1H), 5.24 (dd,  $J = 10.3, 1.1$  Hz, 1H), 5.10 (dd,  $J = 17.1, 1.0$  Hz, 1H), 4.67 (dt,  $J = 5.4, 1.5$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  134.53, 132.58, 129.21, 128.02, 125.79, 122.17, 118.30, 113.80, 111.52, 89.32, 49.35. GC-MS (EI)  $m/z$  314.81 [M+H]<sup>+</sup>

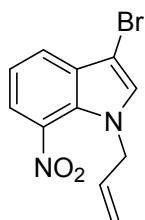


**Methyl 1-allyl-3-bromo-1H-indole-5-carboxylate (5h):** pale pink solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 (d,  $J = 1.1$  Hz, 1H), 7.95 (dd,  $J = 8.7, 1.5$  Hz, 1H), 7.32 (d,  $J = 8.7$  Hz, 1H), 7.19 (s, 1H), 5.96 (ddd,  $J = 15.8, 10.4, 5.3$  Hz, 1H), 5.26 (dd,  $J = 10.3, 0.9$  Hz, 1H), 5.12 (dd,  $J = 17.1, 0.9$  Hz, 1H), 4.72 (d,  $J = 5.5$  Hz, 2H), 3.95 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  167.89, 138.27, 132.46, 128.29, 127.29, 124.14,

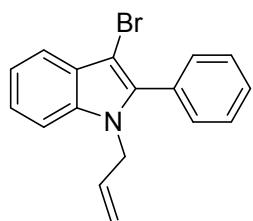
122.62, 122.60, 118.47, 109.76, 91.79, 52.12, 49.36. GC-MS (EI)  $m/z$  294.90 [M+H]<sup>+</sup>



**1-allyl-3-bromo-5-nitro-1H-indole (5i):** yellow solid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.53 (d,  $J$  = 2.2 Hz, 1H), 8.13 (dd,  $J$  = 9.1, 2.2 Hz, 1H), 7.35 (d,  $J$  = 9.1 Hz, 1H), 7.28 (s, 1H), 5.98 (ddd,  $J$  = 22.5, 10.6, 5.5 Hz, 1H), 5.30 (dd,  $J$  = 10.3, 0.6 Hz, 1H), 5.14 (dd,  $J$  = 17.1, 0.4 Hz, 1H), 4.76 (dt,  $J$  = 5.5, 1.5 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  142.38, 138.57, 131.91, 130.12, 127.17, 118.97, 118.37, 117.10, 110.23, 92.73, 49.66. GC-MS (EI)  $m/z$  281.91 [M+H]<sup>+</sup>

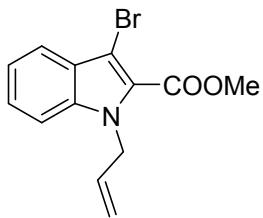


**1-allyl-3-bromo-7-nitro-1H-indole (5j):** yellow liquid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (t,  $J$  = 8.2 Hz, 2H), 7.26-7.21 (m, 2H), 5.81 (ddd,  $J$  = 22.5, 10.6, 5.5 Hz, 1H), 5.15 (dd,  $J$  = 10.3, 0.8 Hz, 1H), 4.93 (d,  $J$  = 17.1 Hz, 1H), 4.85 (dt,  $J$  = 5.4, 1.4 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  137.26, 132.82, 132.37, 131.62, 126.42, 125.88, 121.15, 119.58, 118.50, 92.03, 52.68. GC-MS (EI)  $m/z$  281.91 [M+H]<sup>+</sup>

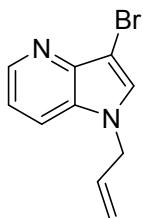


**1-allyl-3-bromo-2-phenyl-1H-indole (5k):** white solid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (d,  $J$  = 7.8 Hz, 1H), 7.52-7.43 (m, 5H), 7.33-7.21 (m, 3H), 5.93-5.84 (m, 1H), 5.16 (dd,  $J$  = 10.4, 0.9 Hz, 1H), 4.93 (dd,  $J$  = 17.2, 0.8 Hz, 1H), 4.67-4.61 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  138.07, 136.40, 133.46, 130.68, 130.55, 128.96, 128.57, 127.55, 123.06, 120.84, 119.55, 116.89, 110.60, 90.80, 47.28. GC-MS (EI)

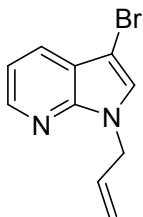
*m/z* 312.93 [M+H]<sup>+</sup>



**Methyl 1-allyl-3-bromo-1H-indole-2-carboxylate (5l):** colorless liquid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.69 (d, *J* = 8.1 Hz, 1H), 7.41-7.34 (m, 2H), 7.26-7.22 (m, 1H), 5.97 (ddt, *J* = 17.0, 10.2, 5.0 Hz, 1H), 5.18 (dd, *J* = 3.5, 1.5 Hz, 2H), 5.12 (dd, *J* = 10.3, 1.0 Hz, 1H), 4.93 (dd, *J* = 17.1, 1.0 Hz, 1H), 3.98 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 161.79, 137.87, 133.63, 126.93, 126.44, 125.03, 121.73, 121.61, 116.58, 110.81, 99.50, 51.98, 47.80. GC-MS (EI) *m/z* 294.93 [M+H]<sup>+</sup>

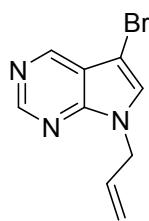


**1-allyl-3-bromo-1H-pyrrolo[3,2-b]pyridine (5m):** yellow solid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.54 (dd, *J* = 4.6, 1.3 Hz, 1H), 7.61 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.36 (s, 1H), 7.15 (dd, *J* = 8.3, 4.6 Hz, 1H), 5.99-5.90 (m, 1H), 5.25 (dd, *J* = 10.3, 1.0 Hz, 1H), 5.11 (ddd, *J* = 17.1, 2.5, 1.6 Hz, 1H), 4.70 (dt, *J* = 5.5, 1.6 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.31, 143.65, 132.38, 130.06, 129.04, 118.57, 117.57, 117.51, 90.95, 49.47. GC-MS (EI) *m/z* 238.07 [M+H]<sup>+</sup>

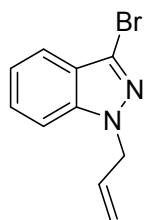


**1-allyl-3-bromo-7-azaindole (5n):** pale yellow liquid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.36 (dd, *J* = 4.7, 1.3 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.25 (s, 1H), 7.14 (dd, *J* = 7.9, 4.7 Hz, 1H), 6.02 (ddd, *J* = 15.9, 10.7, 5.7 Hz, 1H), 5.23 (dd, *J* = 10.2, 1.1 Hz, 1H), 5.14 (dd, *J* = 17.1, 1.2 Hz, 1H), 4.91 (d, *J* = 5.7 Hz, 2H). <sup>13</sup>C NMR (151 MHz,

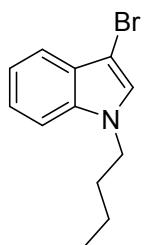
$\text{CDCl}_3$ )  $\delta$  146.51, 144.18, 133.35, 127.70, 126.84, 120.11, 118.09, 116.58, 88.47, 46.78. GC-MS (EI)  $m/z$  237.96 [M+H]<sup>+</sup>



**7-allyl-5-bromo-7H-pyrrolo[2,3-d]pyrimidine (5o):** yellow solid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.92 (d,  $J = 3.2$  Hz, 2H), 7.25 (s, 1H), 5.99 (ddt,  $J = 16.0, 10.3, 5.8$  Hz, 1H), 5.29 (dd,  $J = 10.2, 1.1$  Hz, 1H), 5.18 (dd,  $J = 17.1, 1.0$  Hz, 1H), 4.88 (dt,  $J = 5.7, 1.4$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  152.53, 149.86, 148.95, 132.41, 127.83, 119.00, 118.55, 88.35, 46.72. GC-MS (EI)  $m/z$  239.04 [M+H]<sup>+</sup>

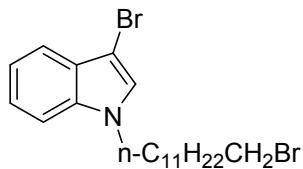


**1-allyl-3-bromo-1H-indazole (5p):** pale yellow liquid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J = 8.2$  Hz, 1H), 7.46-7.34 (m, 2H), 7.22 (ddd,  $J = 7.9, 6.8, 0.8$  Hz, 1H), 6.06-5.97 (m, 1H), 5.25 (dd,  $J = 10.3, 1.1$  Hz, 1H), 5.18 (dd,  $J = 17.1, 1.1$  Hz, 1H), 4.99 (dt,  $J = 5.7, 1.5$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  140.82, 132.48, 127.65, 124.12, 121.56, 120.69, 120.63, 118.37, 109.68, 52.35. GC-MS (EI)  $m/z$  237.96 [M+H]<sup>+</sup>



**3-bromo-1-butyl-1H-indole (5q):** pale yellow liquid;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 7.9$  Hz, 1H), 7.33 (d,  $J = 8.3$  Hz, 1H), 7.24 (d,  $J = 8.7$  Hz, 1H), 7.18 (t,  $J = 7.4$  Hz, 1H), 7.11 (s, 1H), 4.09 (t,  $J = 7.1$  Hz, 2H), 1.83-1.77 (m, 2H), 1.34 (dd,  $J = 15.1, 7.5$  Hz, 2H), 0.93 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  135.72,

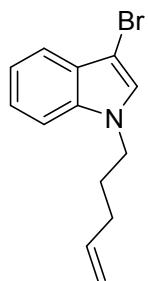
127.44, 126.81, 122.57, 120.12, 119.49, 109.75, 89.50, 46.53, 32.45, 20.25, 13.81.  
GC-MS (EI)  $m/z$  252.95 [M+H]<sup>+</sup>



**3-bromo-1-(12-bromododecyl)-1H-indole (5r):** colorless liquid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.26 (s, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 4.23-4.18 (m, 2H), 3.41 (t, *J* = 6.9 Hz, 2H), 1.89-1.81 (m, 2H), 1.79-1.72 (m, 2H), 1.46-1.35 (m, 3H), 1.32-1.19 (m, 13H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 135.80, 127.19, 122.87, 120.80, 119.07, 114.36, 109.86, 92.94, 46.13, 34.22, 32.97, 30.02, 29.61, 29.59, 29.56, 29.53, 29.39, 28.88, 28.30, 26.90. GC-MS (EI)  $m/z$  443.93 [M+H]<sup>+</sup>

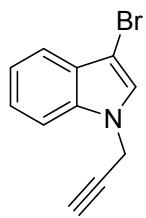


**1-benzyl-3-bromo-1H-indole (5s):** pale yellow solid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.60 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.34-7.27 (m, 4H), 7.22 (dtd, *J* = 15.8, 7.1, 1.1 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 3H), 5.29 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 136.89, 136.04, 129.02, 128.04, 127.66, 127.18, 127.07, 122.98, 120.49, 119.57, 110.03, 90.46, 50.47. GC-MS (EI)  $m/z$  286.95 [M+H]<sup>+</sup>



**3-bromo-1-(pent-4-en-1-yl)-1H-indole (5t):** colorless liquid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.26-7.22 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.11 (s, 1H), 5.78 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 5.07-5.01 (m, 2H), 4.09 (t, *J* = 7.1 Hz, 2H), 2.06 (q, *J* = 7.0 Hz, 2H), 1.92 (p, *J* = 7.2 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 137.20, 135.68, 127.47, 126.78, 122.63, 120.19, 119.52, 116.00,

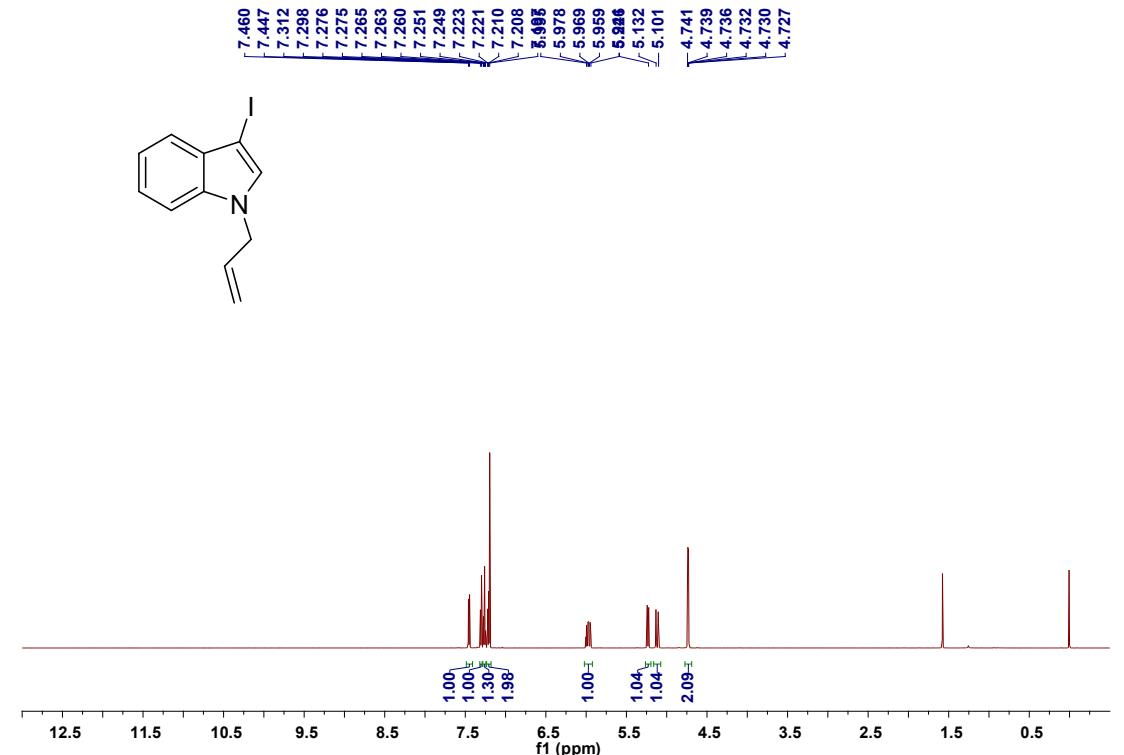
109.75, 89.66, 45.95, 30.84, 29.30. GC-MS (EI)  $m/z$  263.95 [M+H]<sup>+</sup>



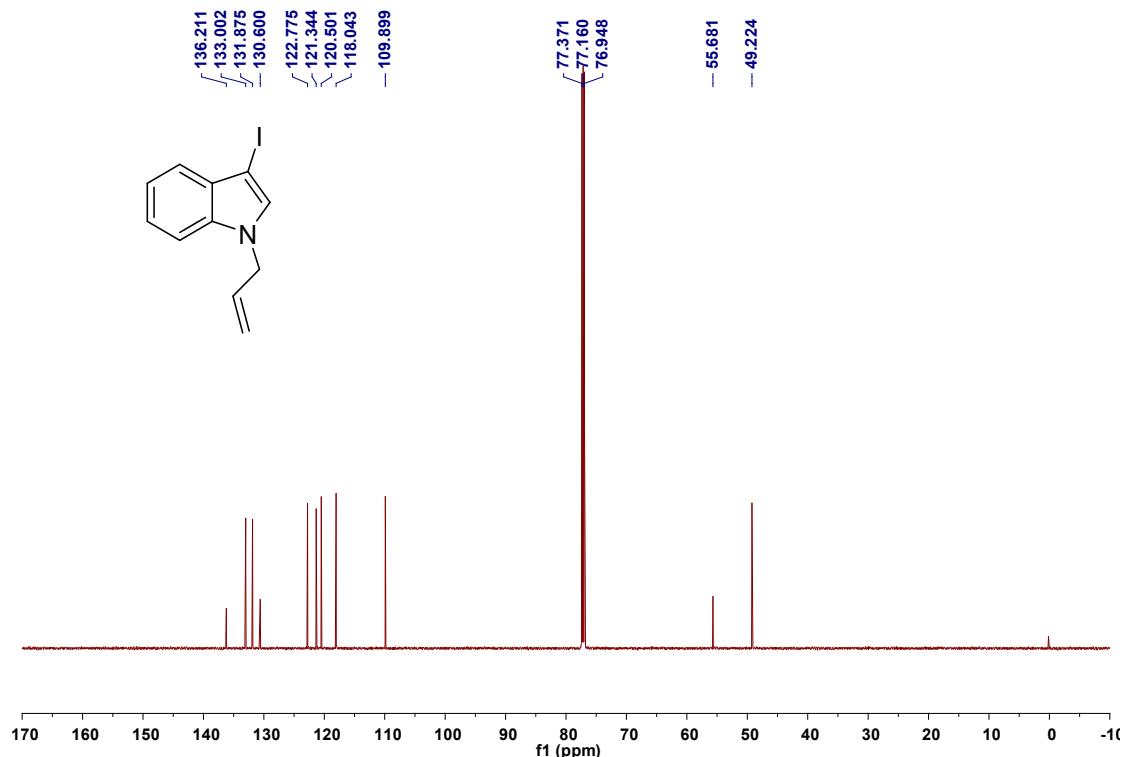
**3-bromo-1-(prop-2-yn-1-yl)-1H-indole (5u):** pale yellow solid; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.33-7.28 (m, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 4.85 (d, *J* = 2.5 Hz, 2H), 2.43 (t, *J* = 2.5 Hz, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 135.49, 127.89, 126.30, 123.18, 120.83, 119.74, 109.67, 90.95, 77.24, 74.29, 36.17. GC-MS (EI)  $m/z$  234.94 [M+H]<sup>+</sup>

## 9. NMR spectra

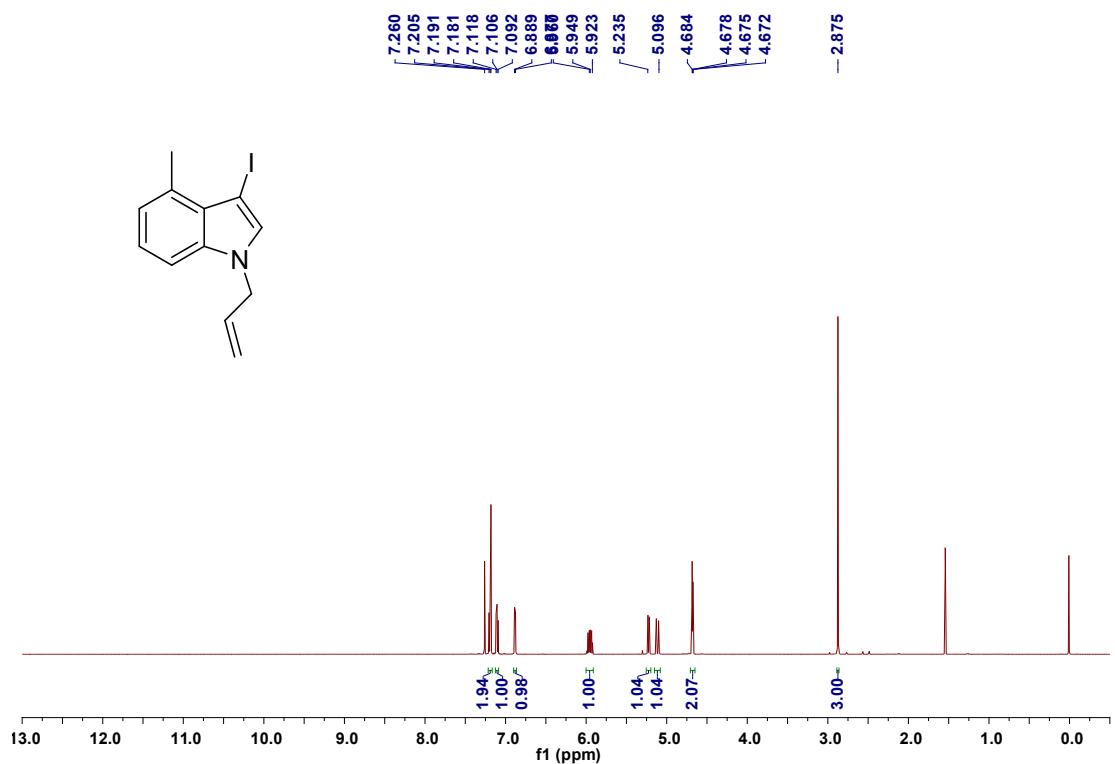
### $^1\text{H}$ NMR



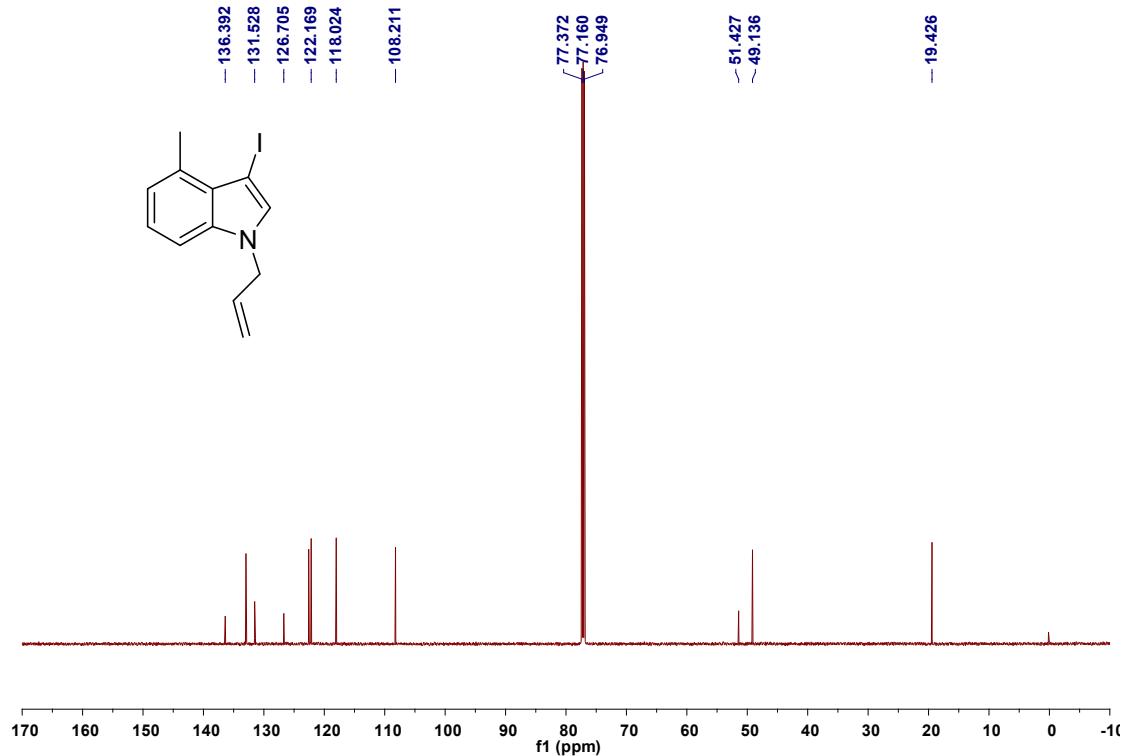
### $^{13}\text{C}$ NMR



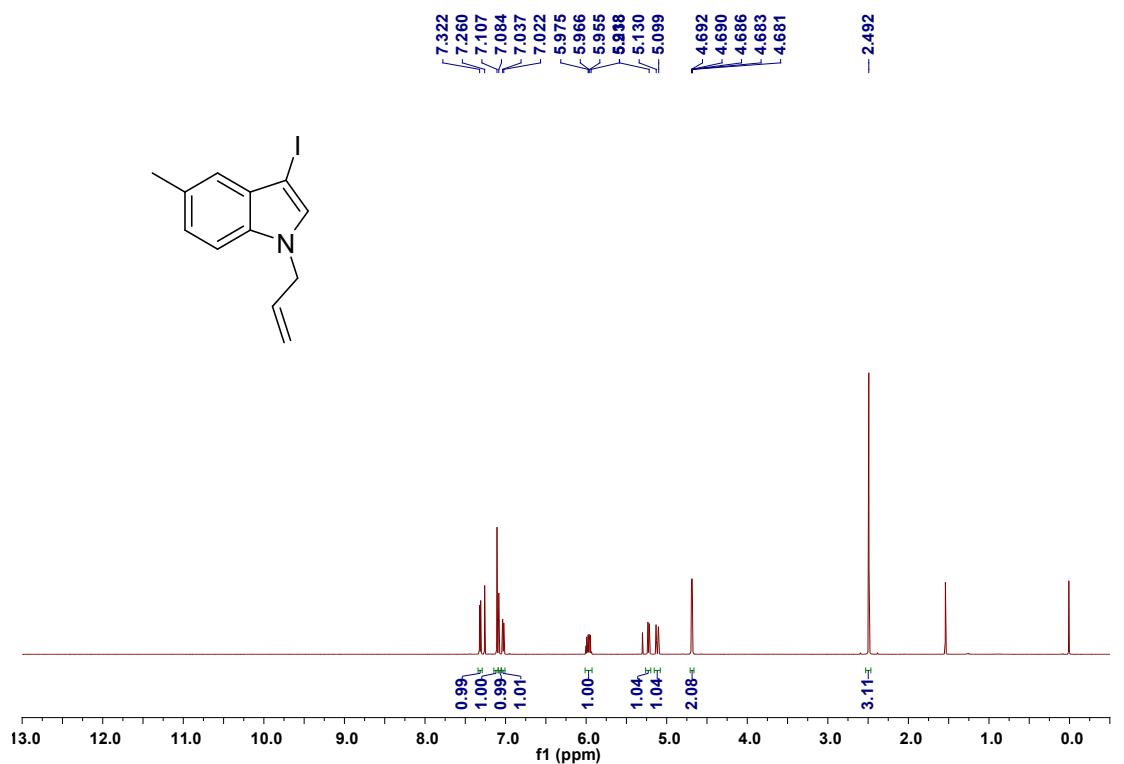
### $^1\text{H}$ NMR



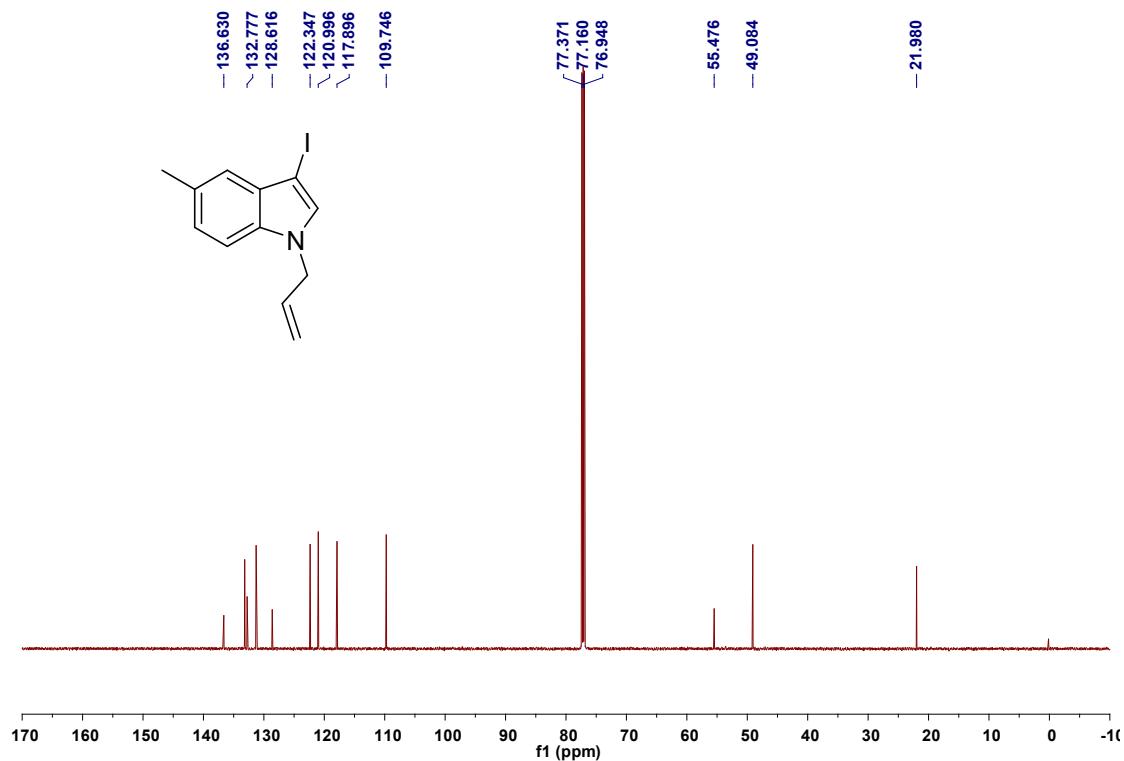
### $^{13}\text{C}$ NMR



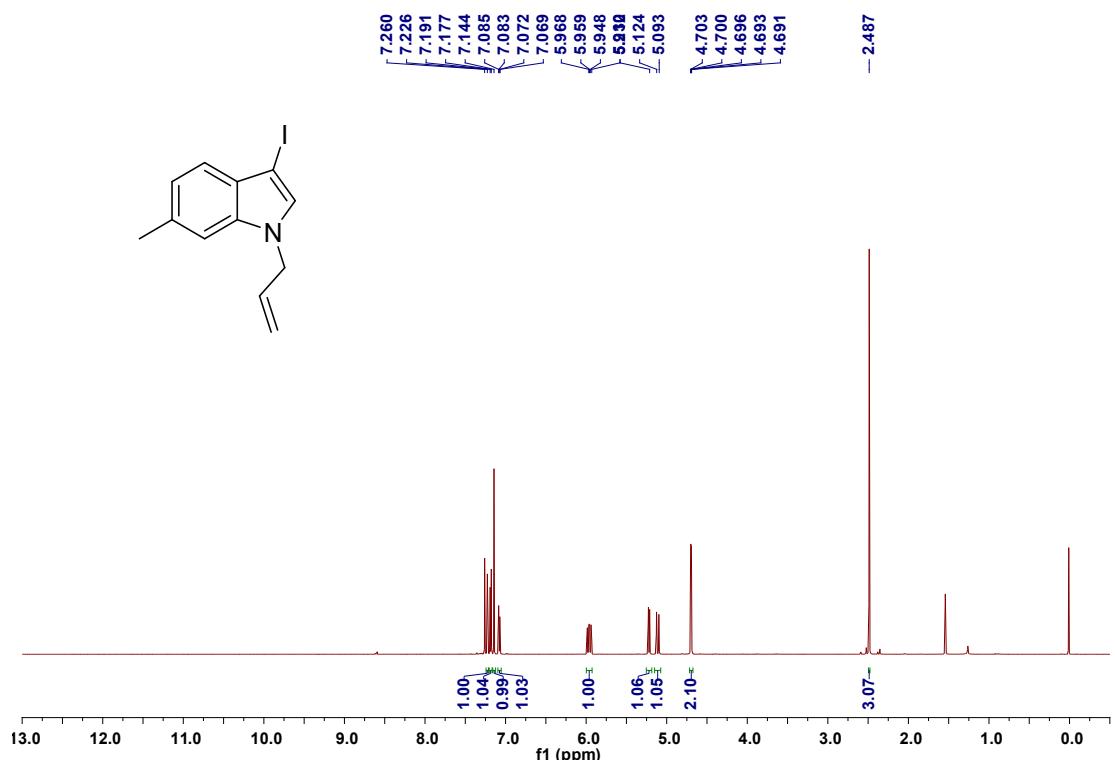
### $^1\text{H}$ NMR



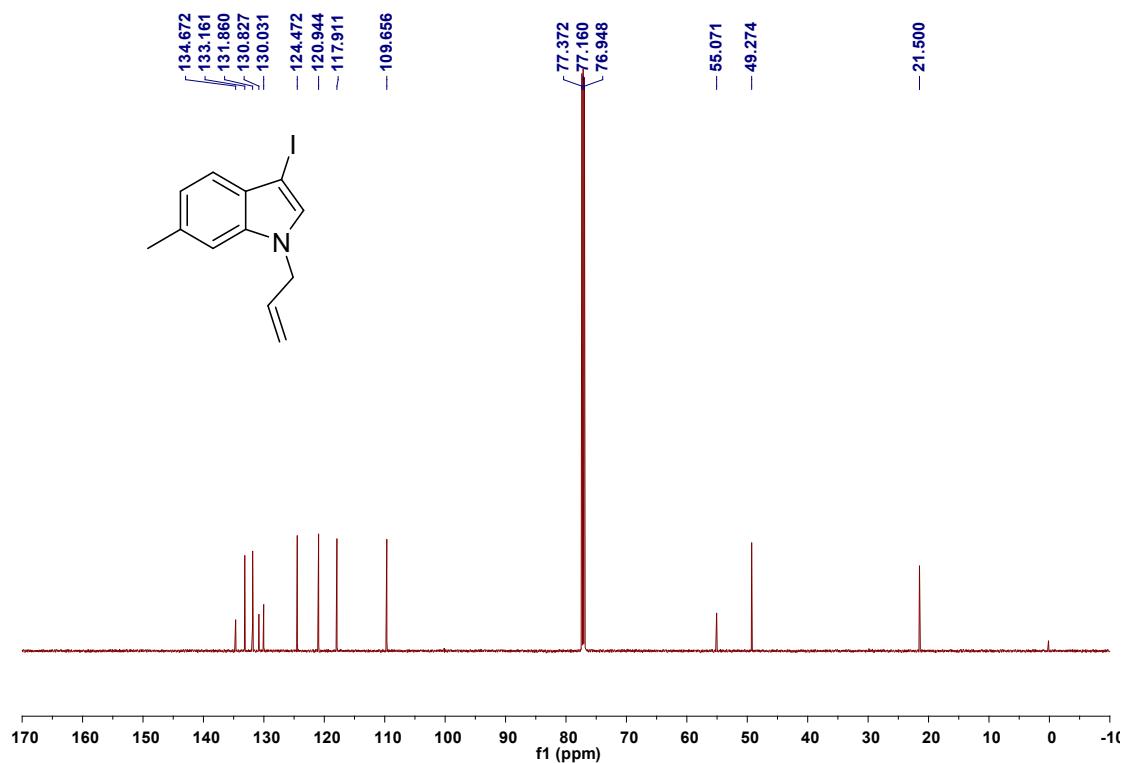
### <sup>13</sup>C NMR



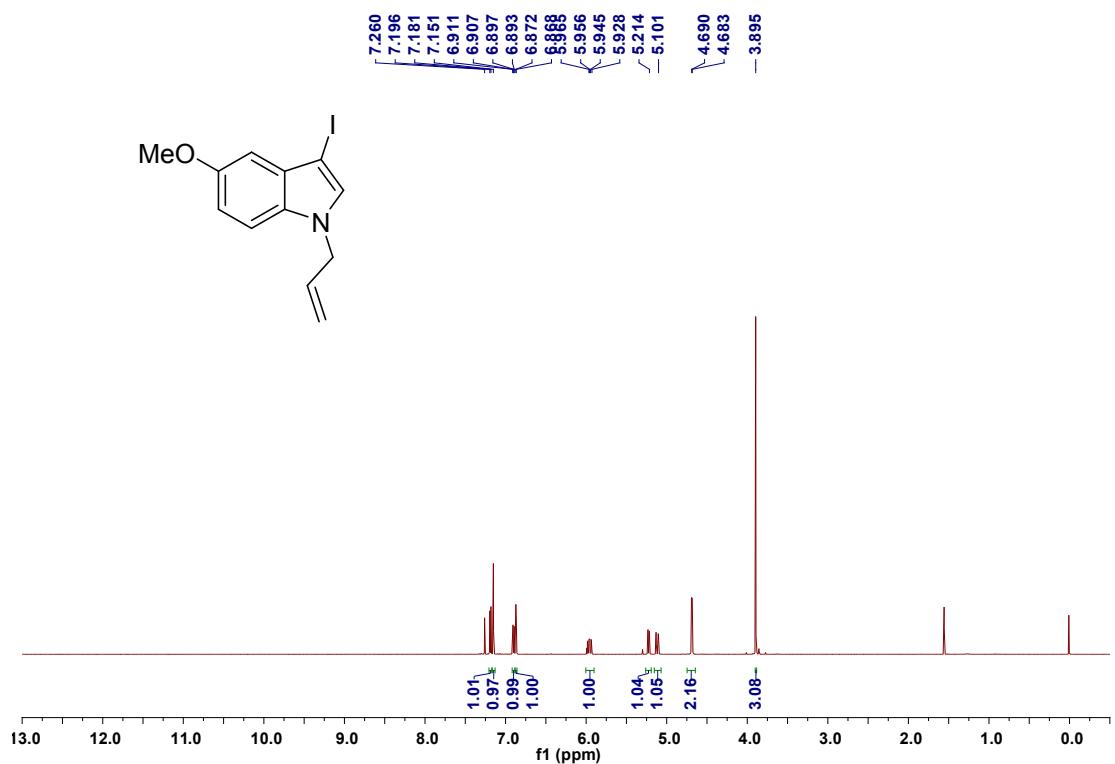
### <sup>1</sup>H NMR



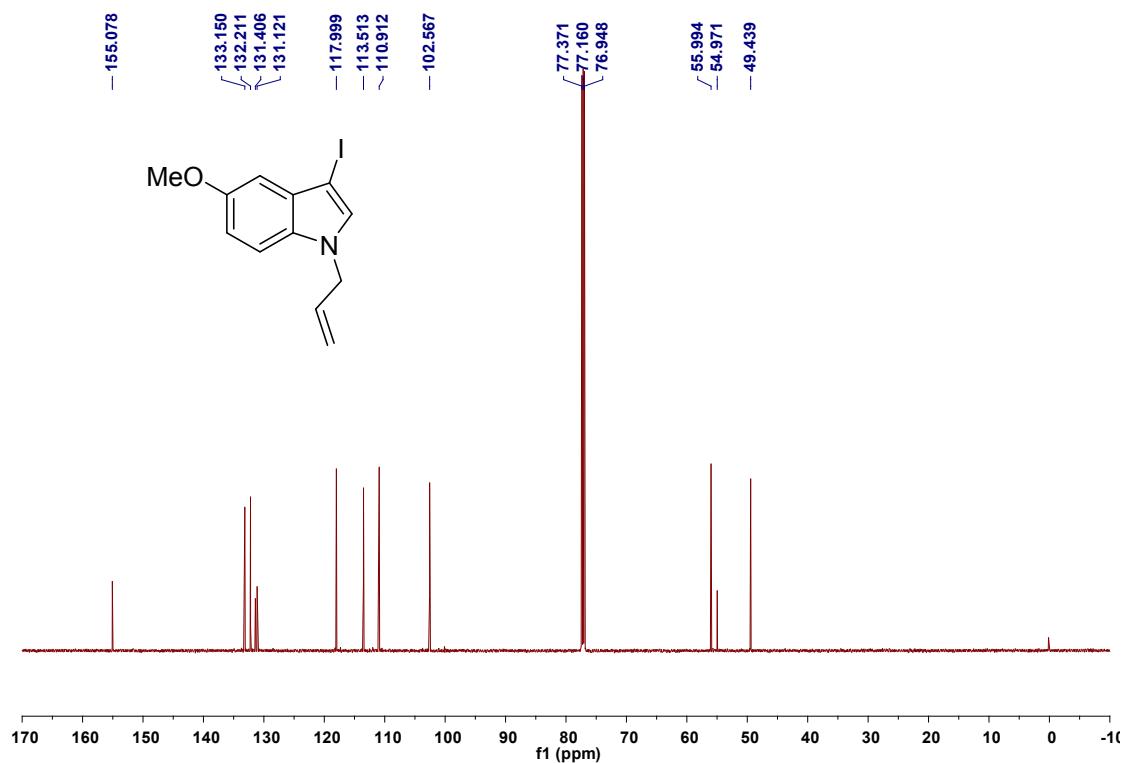
### <sup>13</sup>C NMR



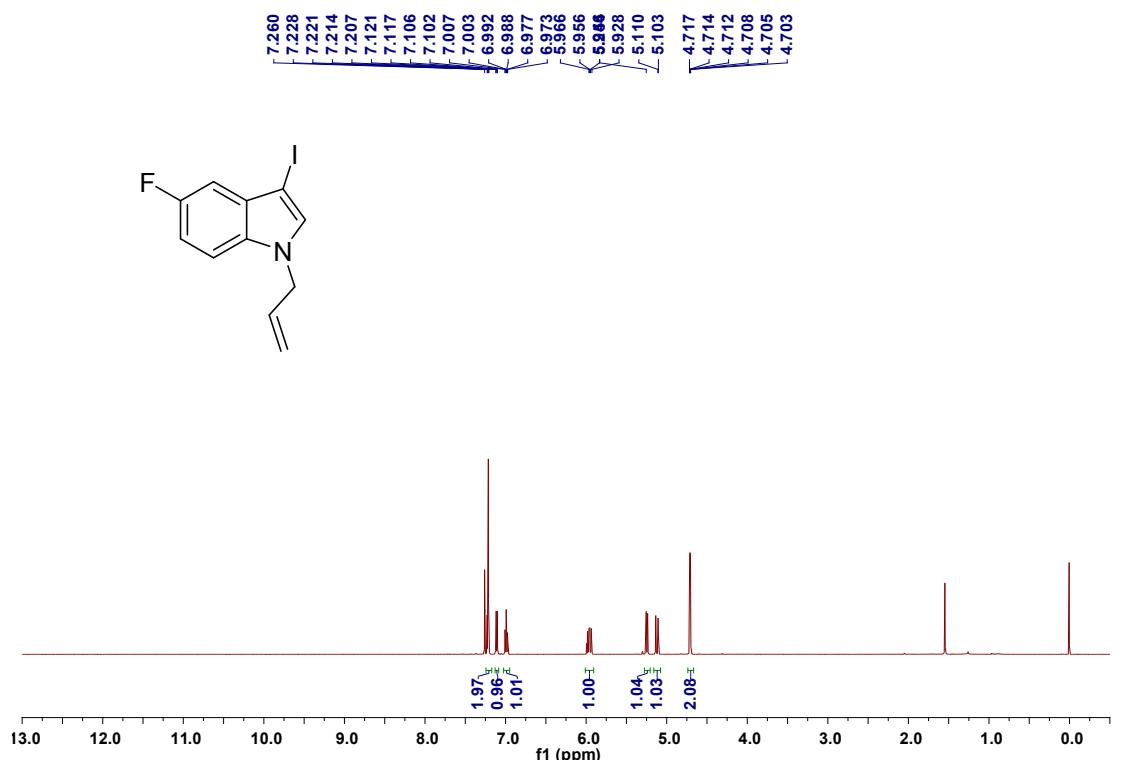
### <sup>1</sup>H NMR



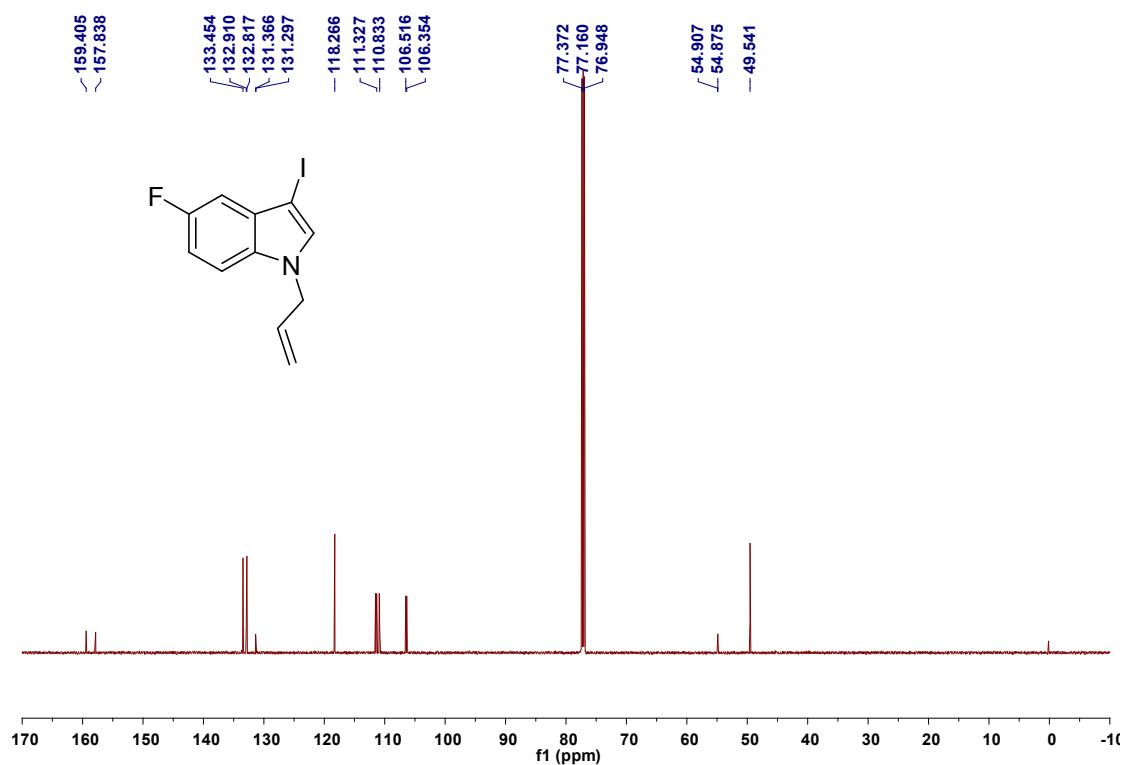
### <sup>13</sup>C NMR



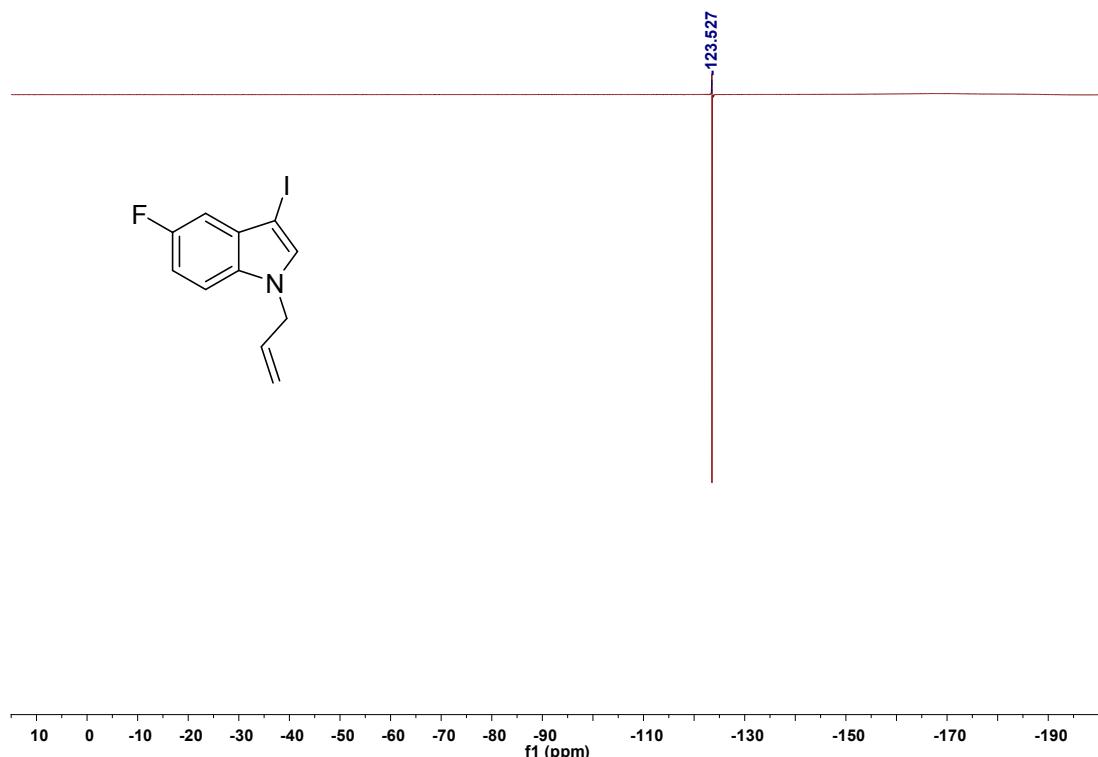
### <sup>1</sup>H NMR



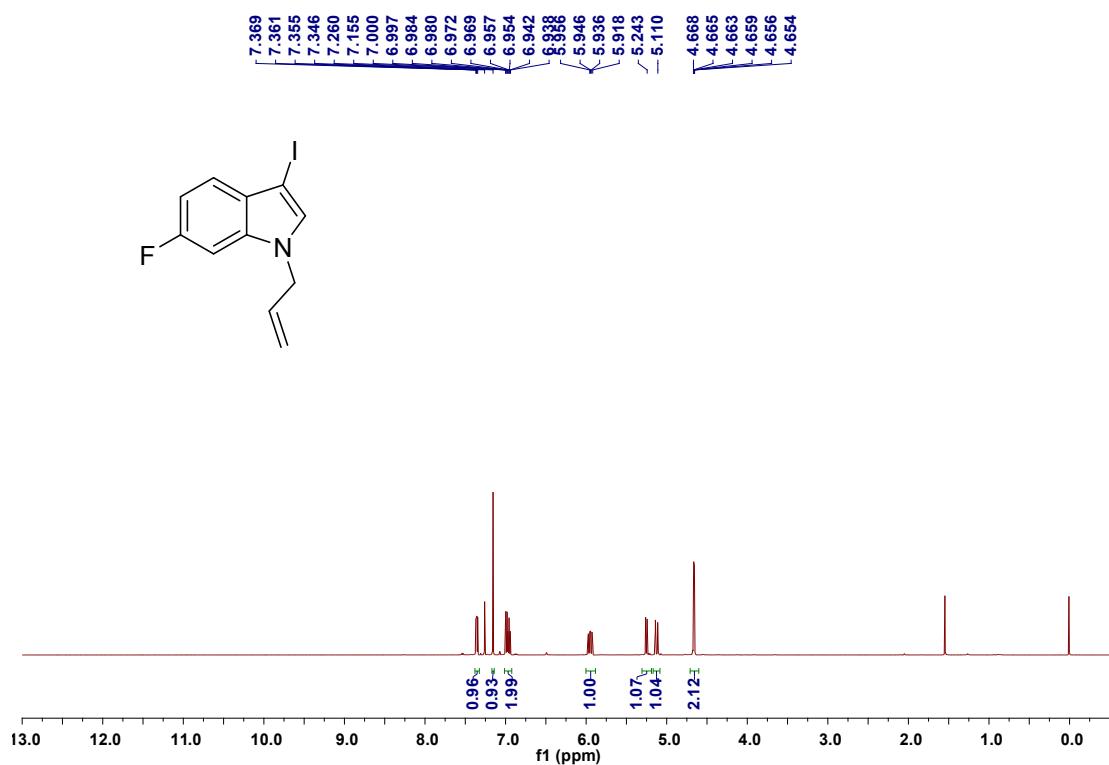
### <sup>13</sup>C NMR



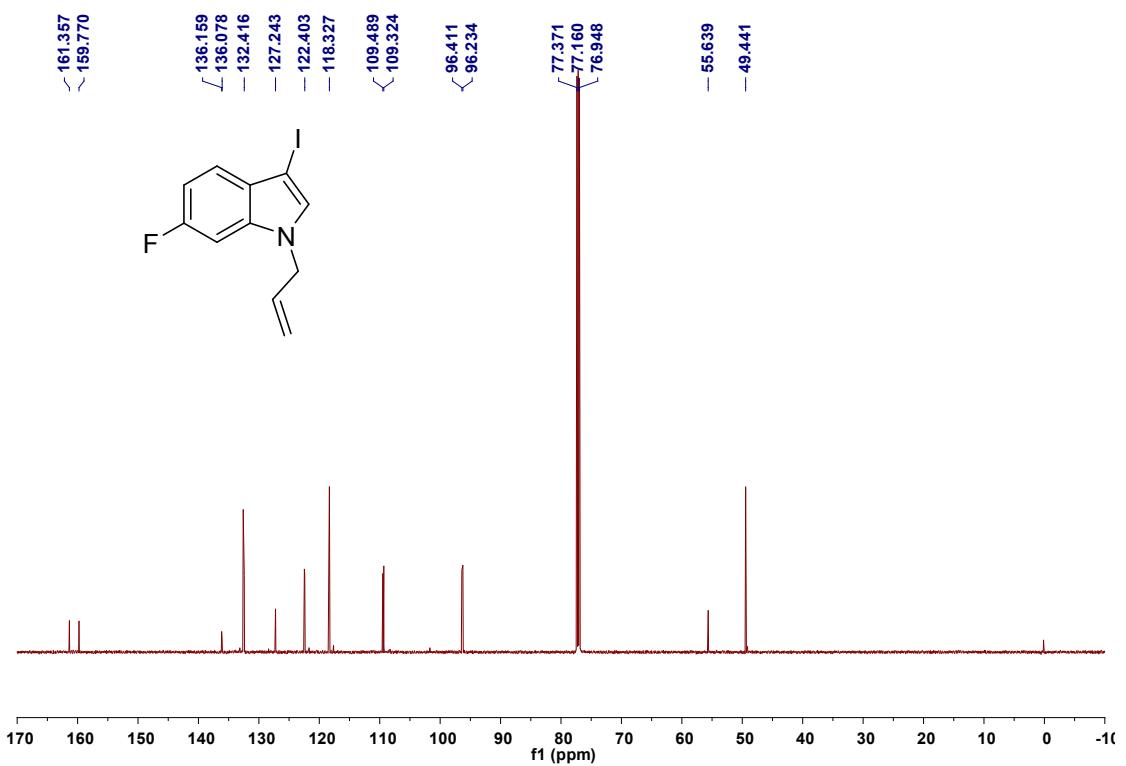
### <sup>19</sup>F NMR



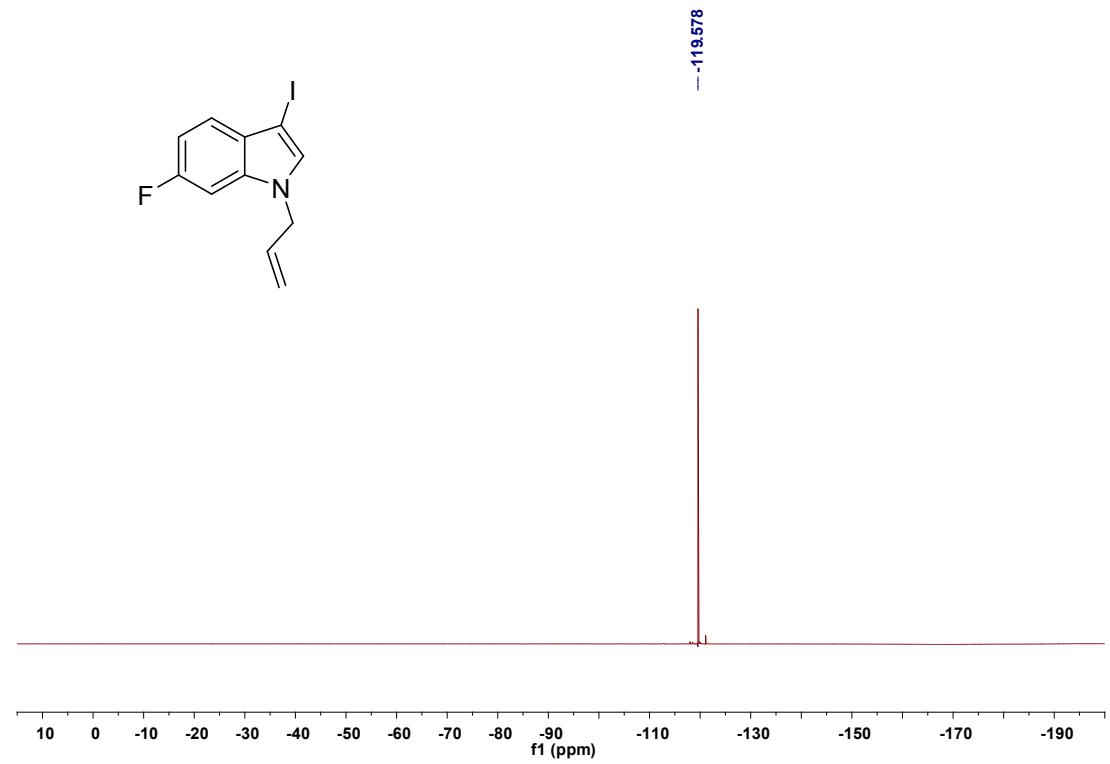
### <sup>1</sup>H NMR



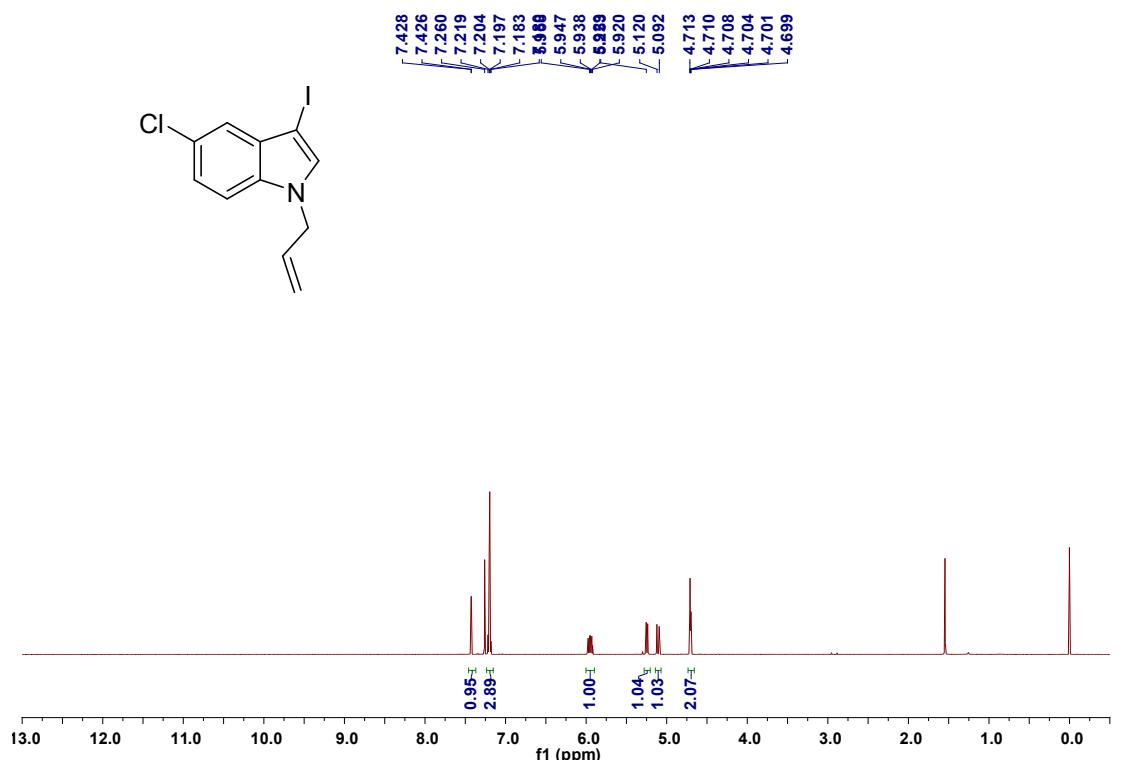
### <sup>13</sup>C NMR



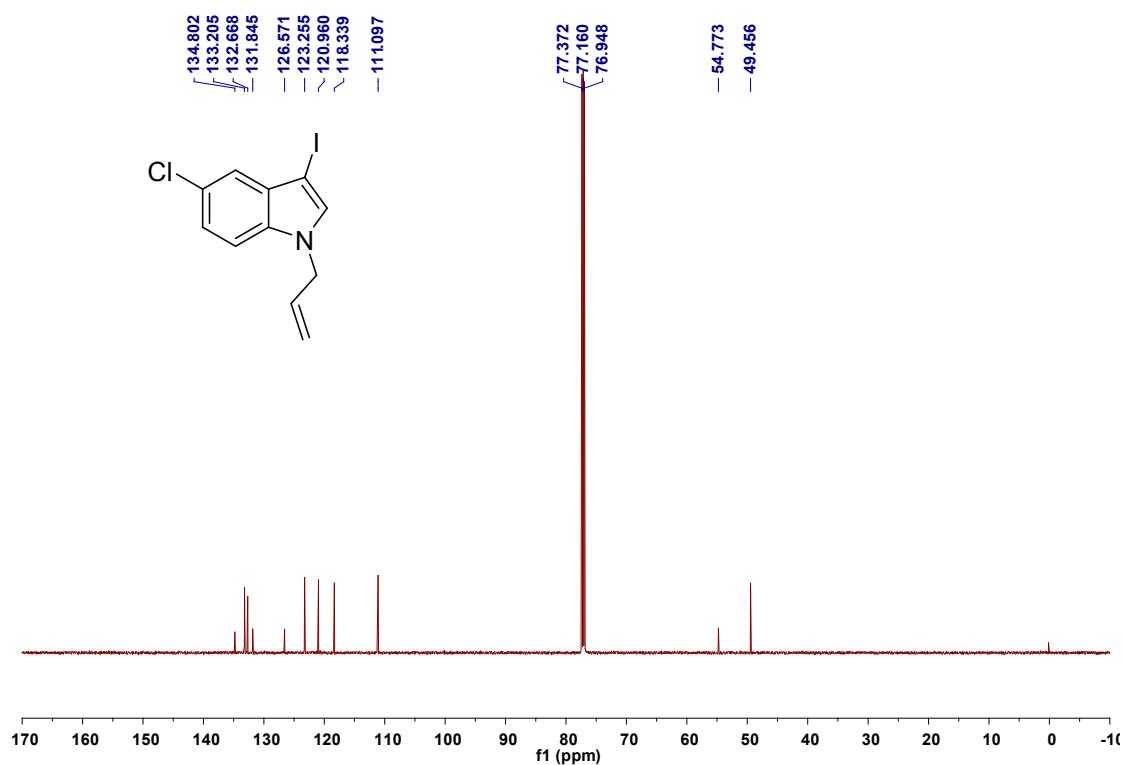
### $^{19}\text{F}$ NMR



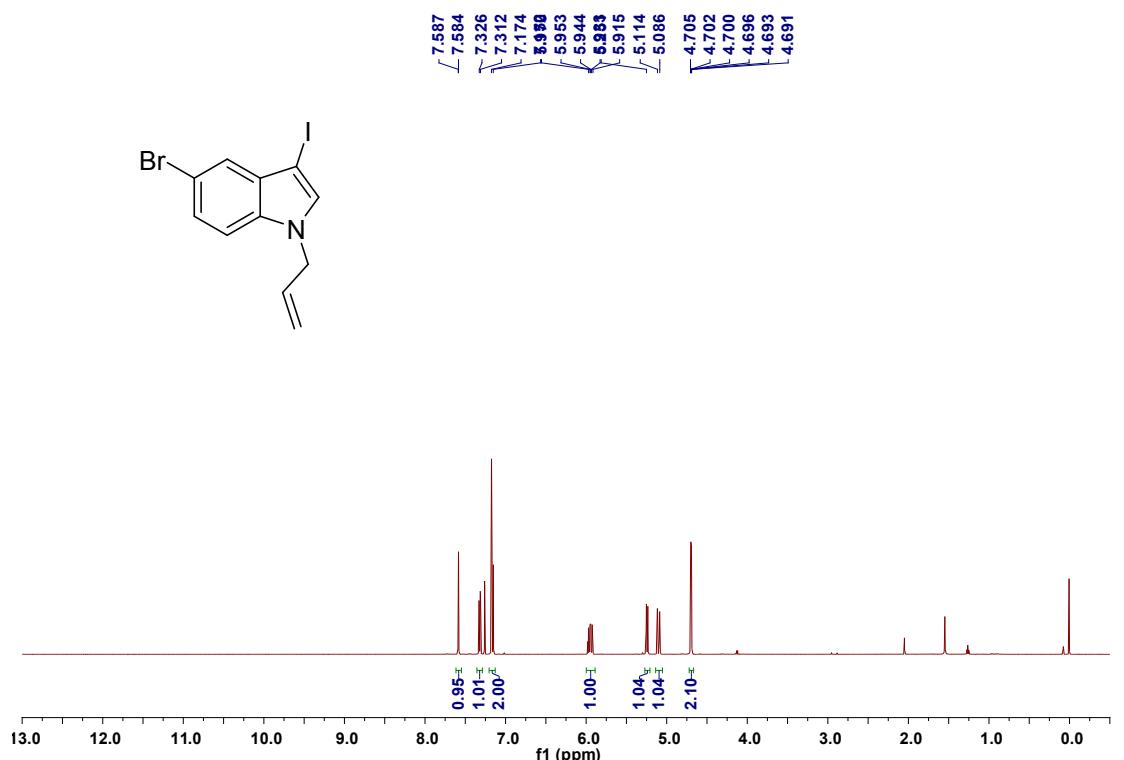
### $^1\text{H}$ NMR



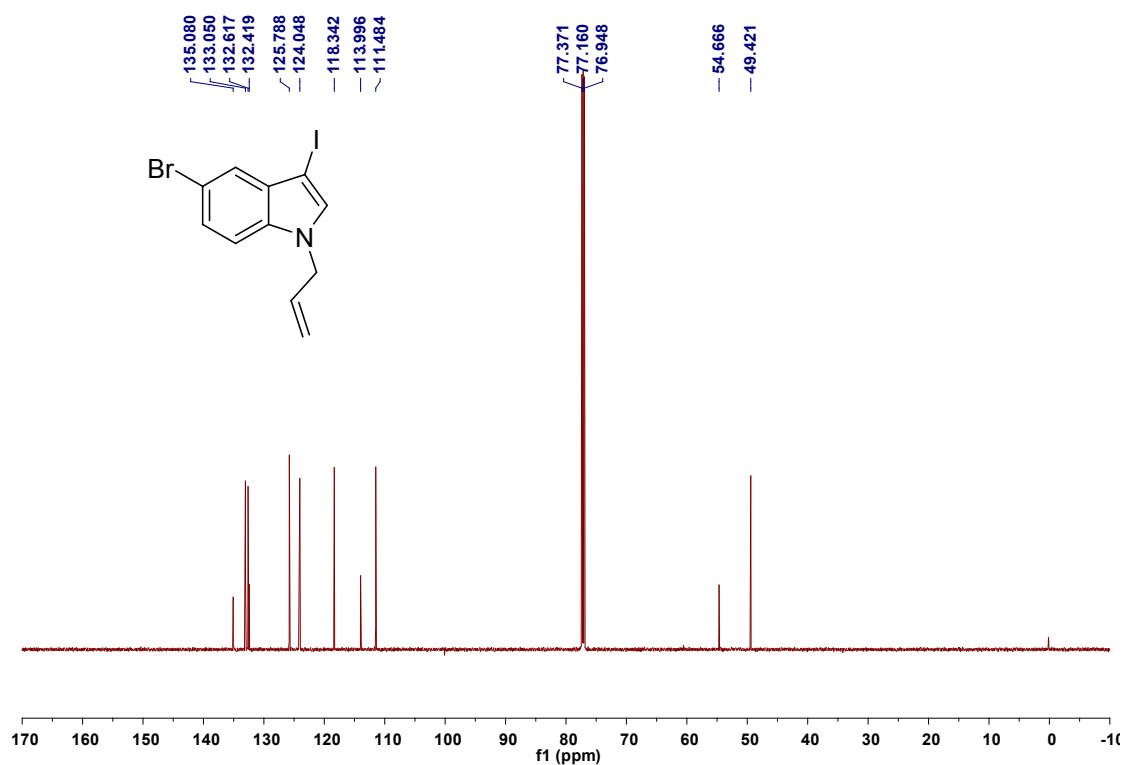
### $^{13}\text{C}$ NMR



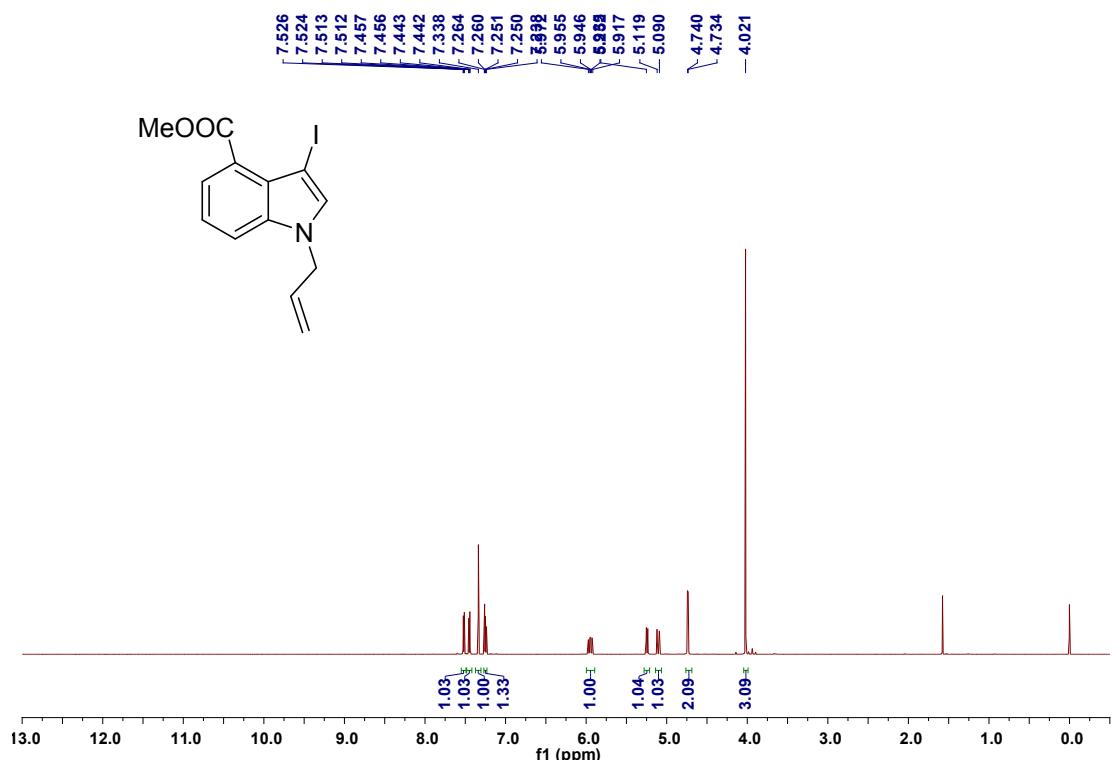
### $^1\text{H}$ NMR



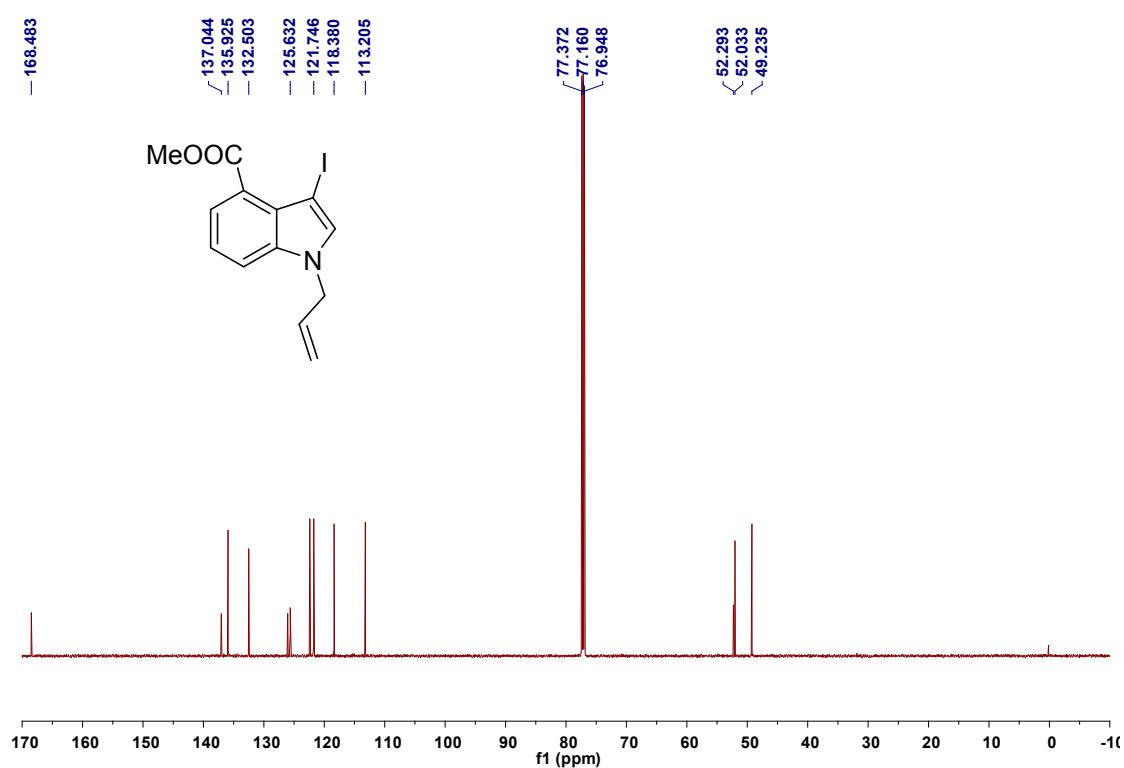
### <sup>13</sup>C NMR



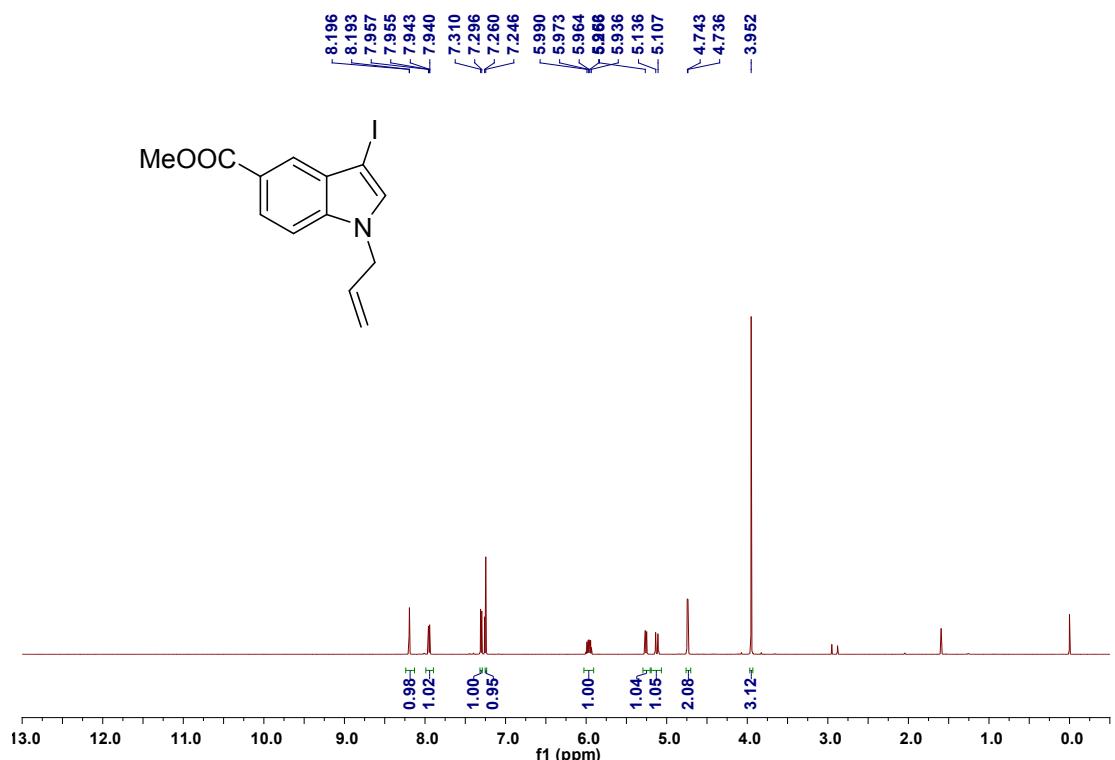
### <sup>1</sup>H NMR



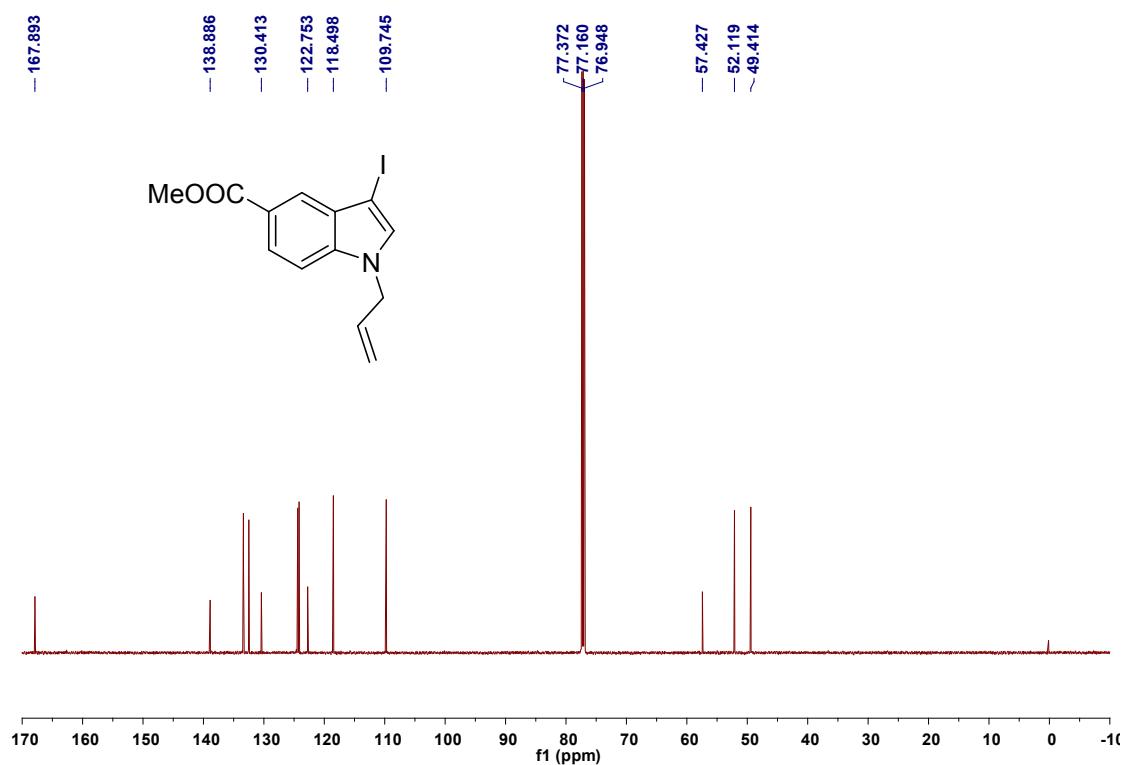
### <sup>13</sup>C NMR



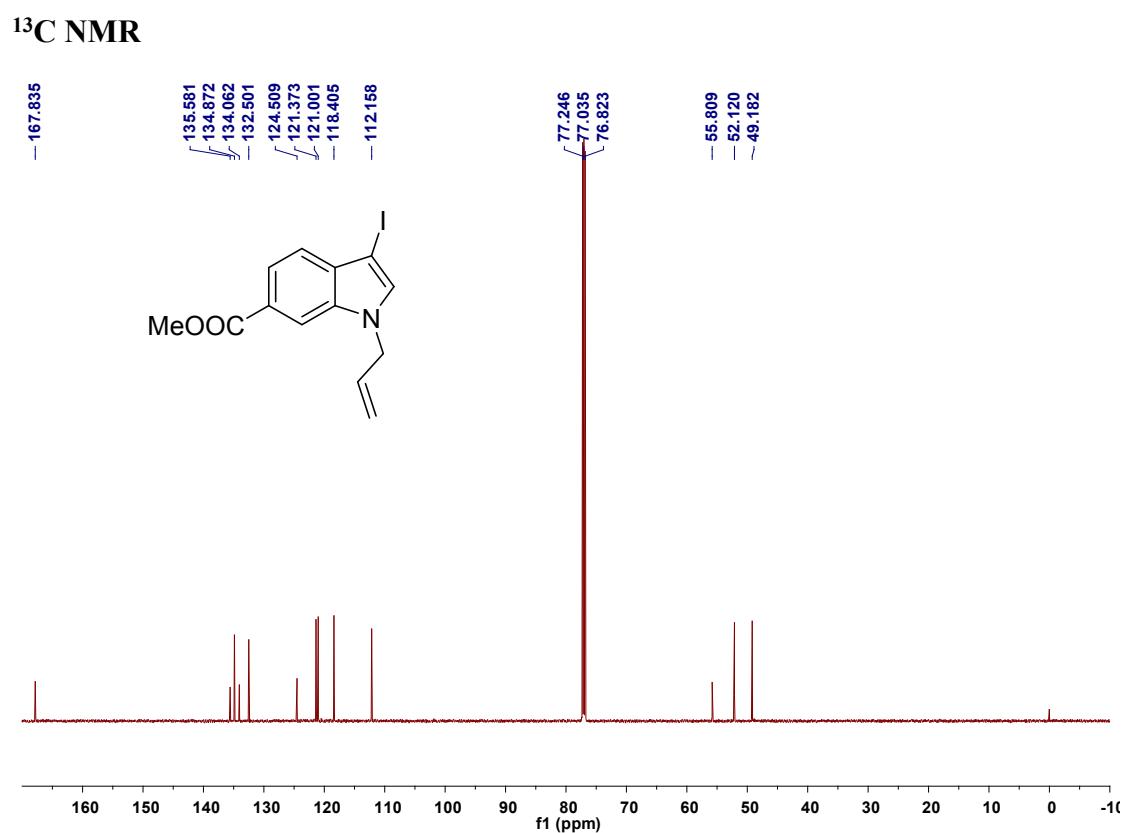
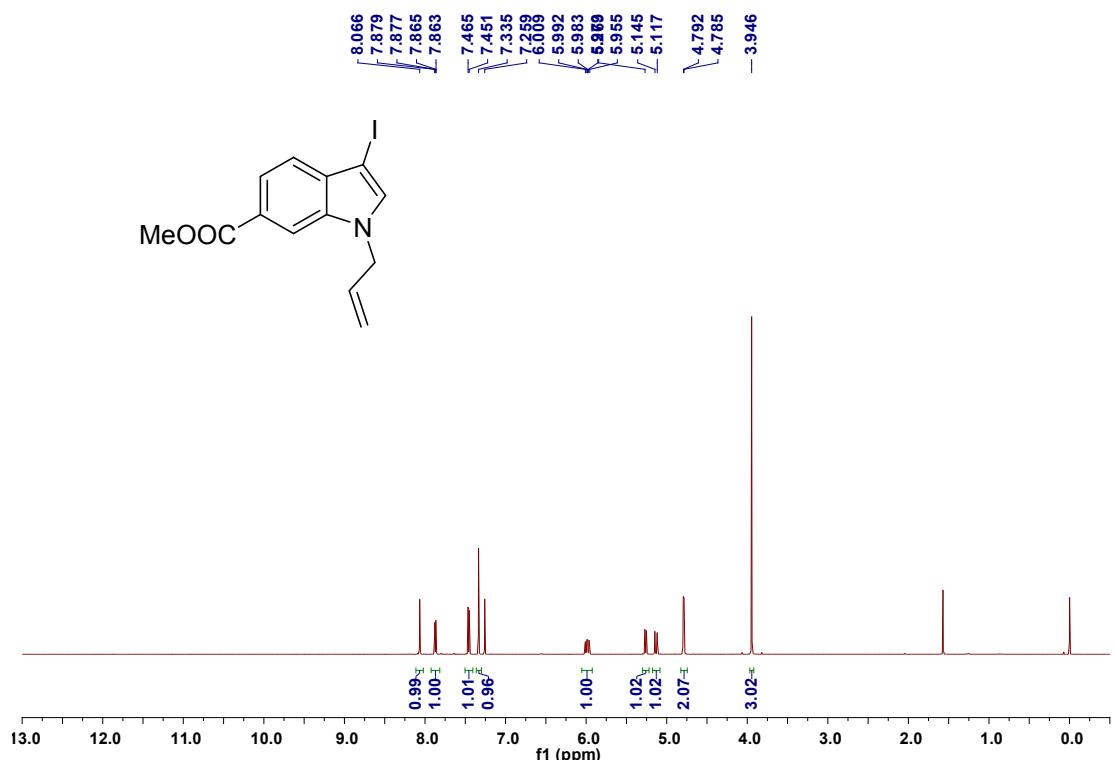
### <sup>1</sup>H NMR

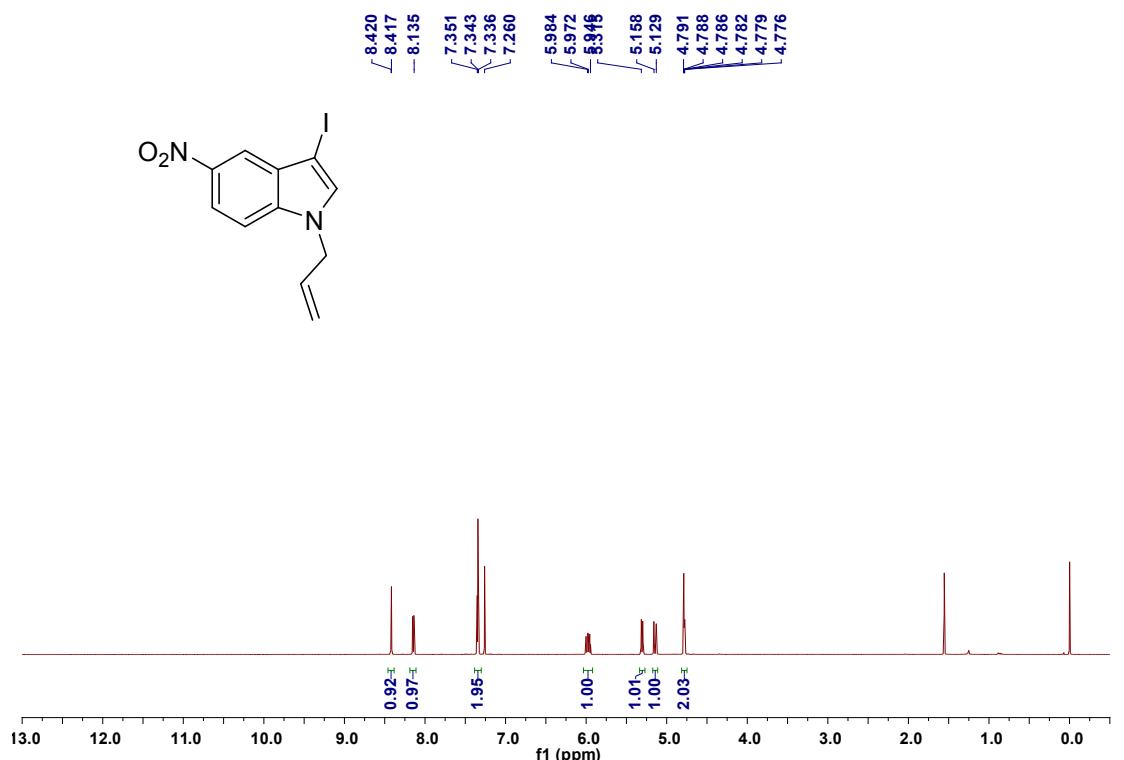


### <sup>13</sup>C NMR

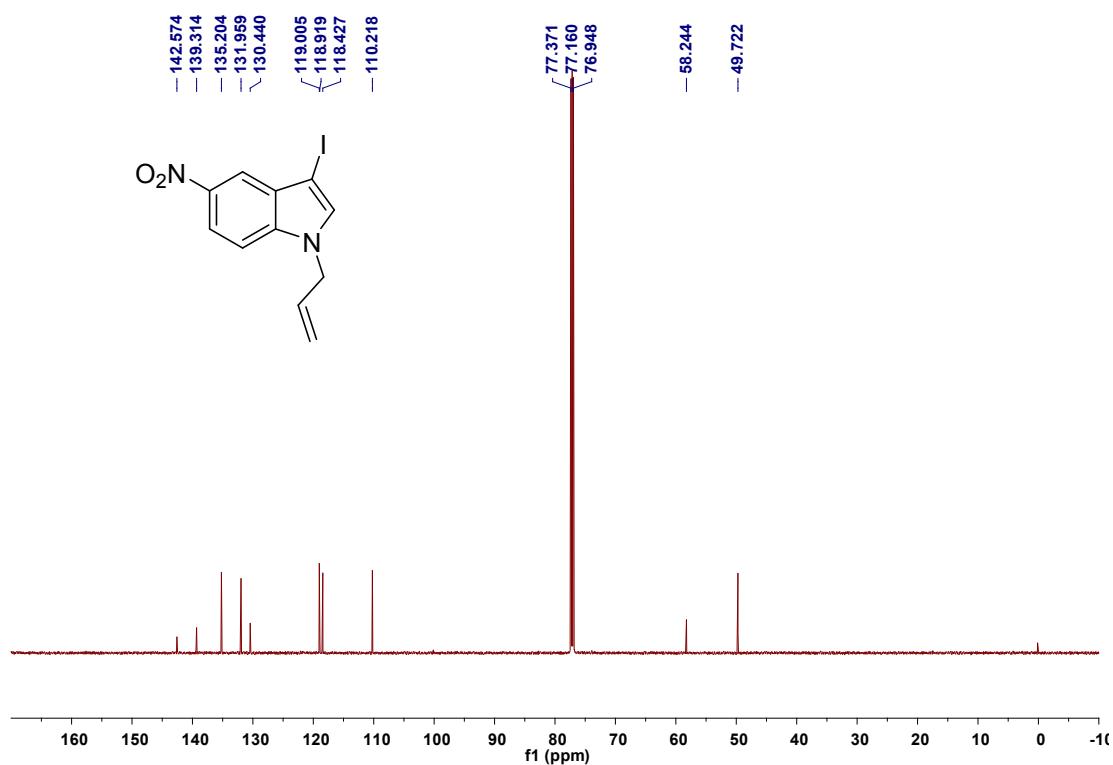


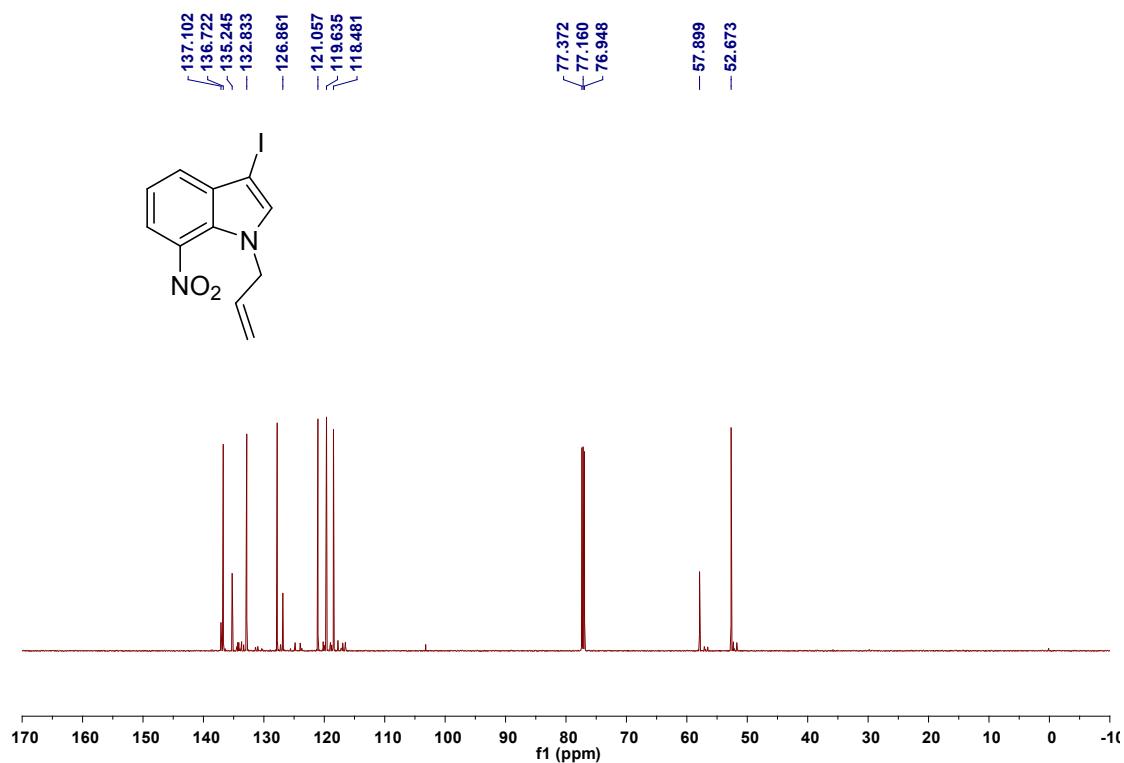
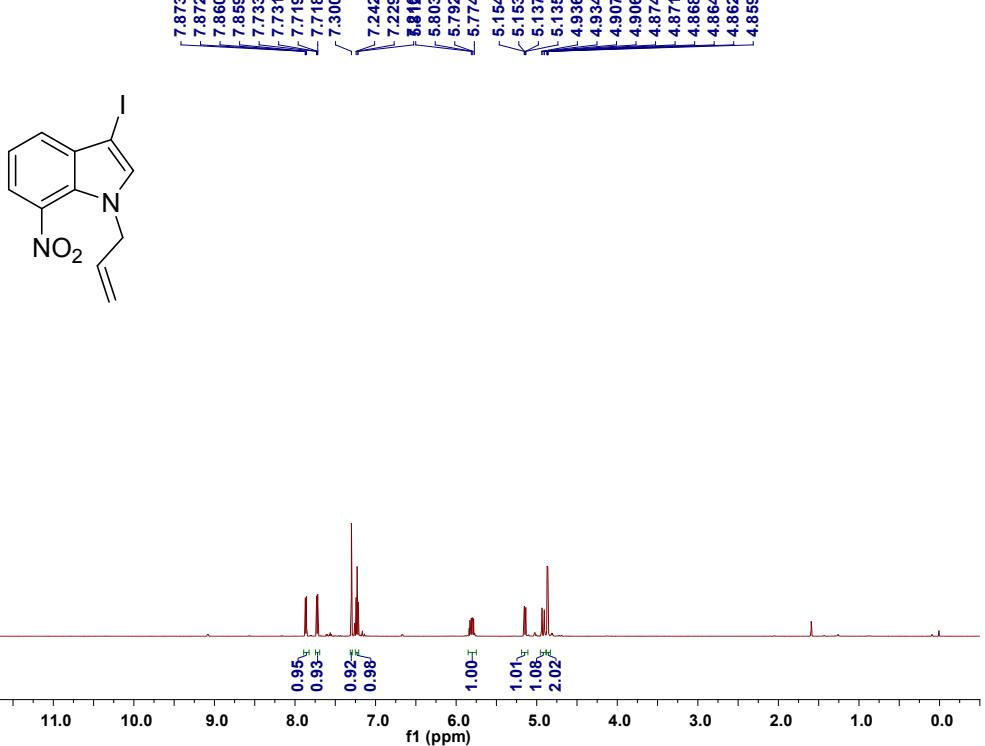
### <sup>1</sup>H NMR

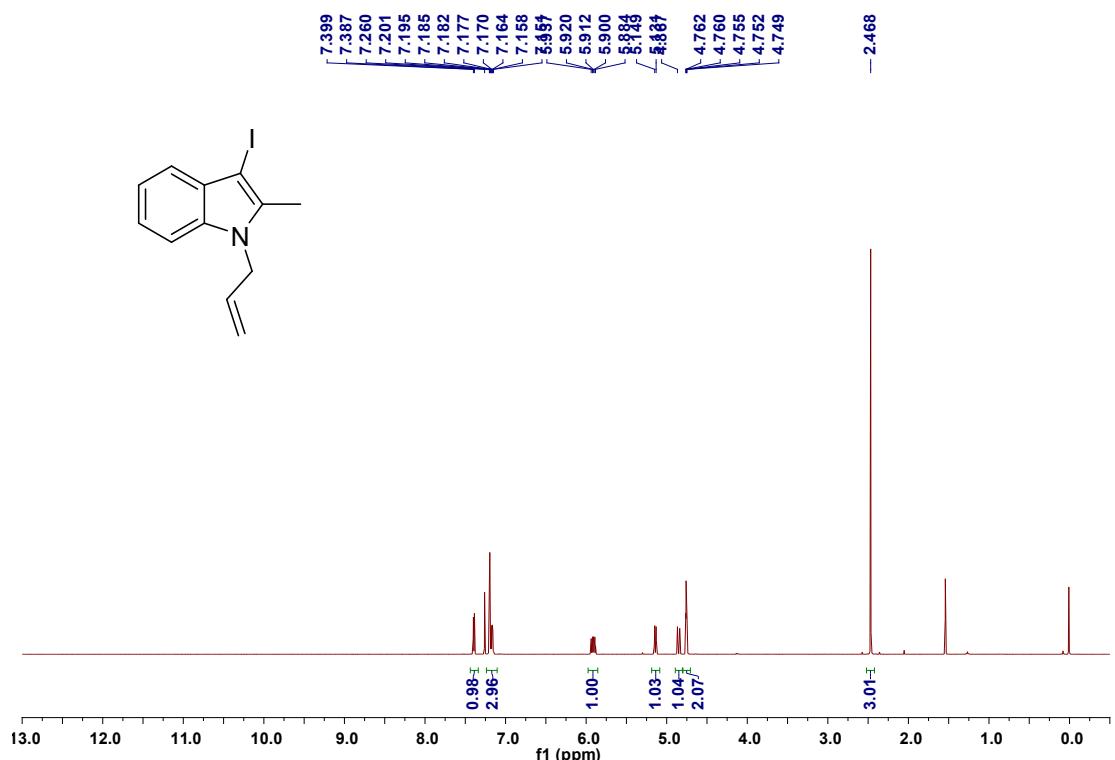




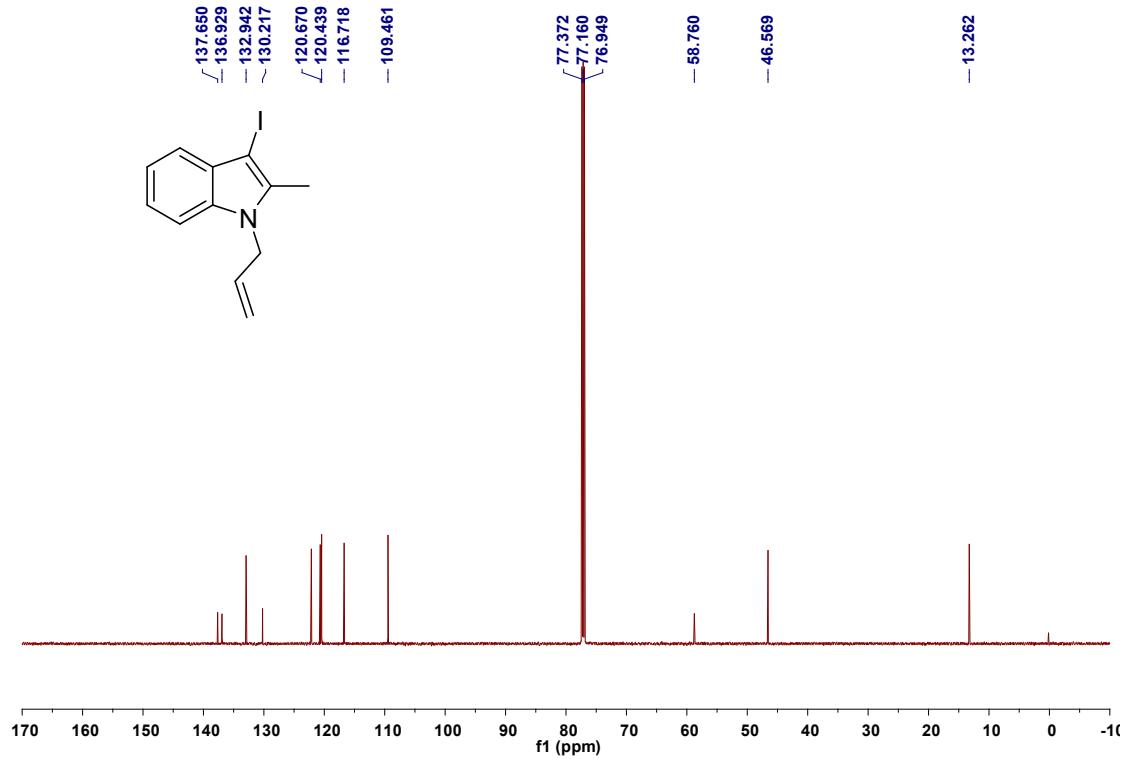
### <sup>13</sup>C NMR





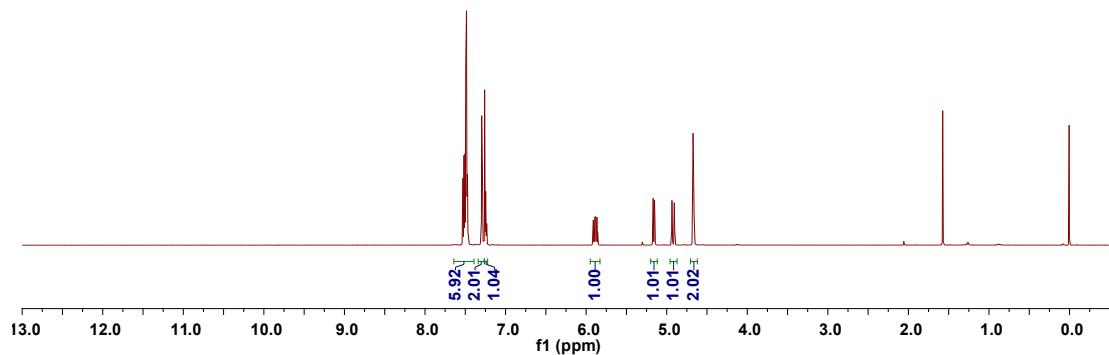
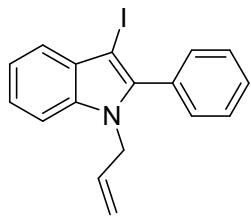


### $^{13}\text{C}$ NMR

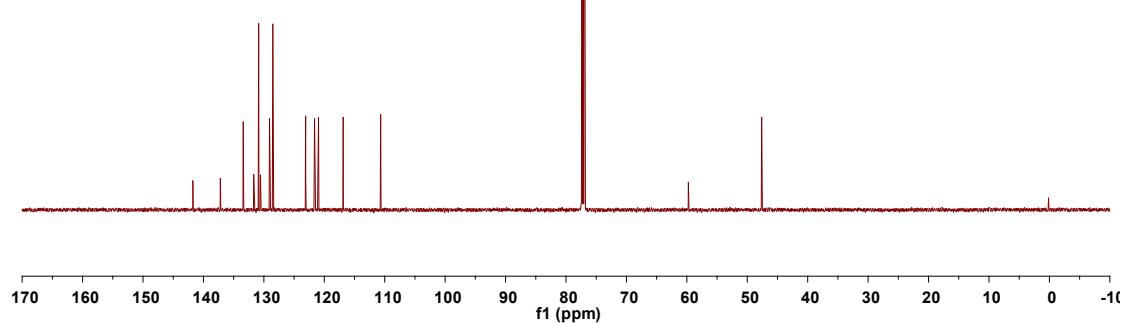
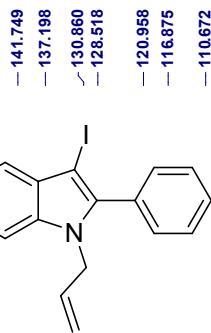


### $^1\text{H}$ NMR

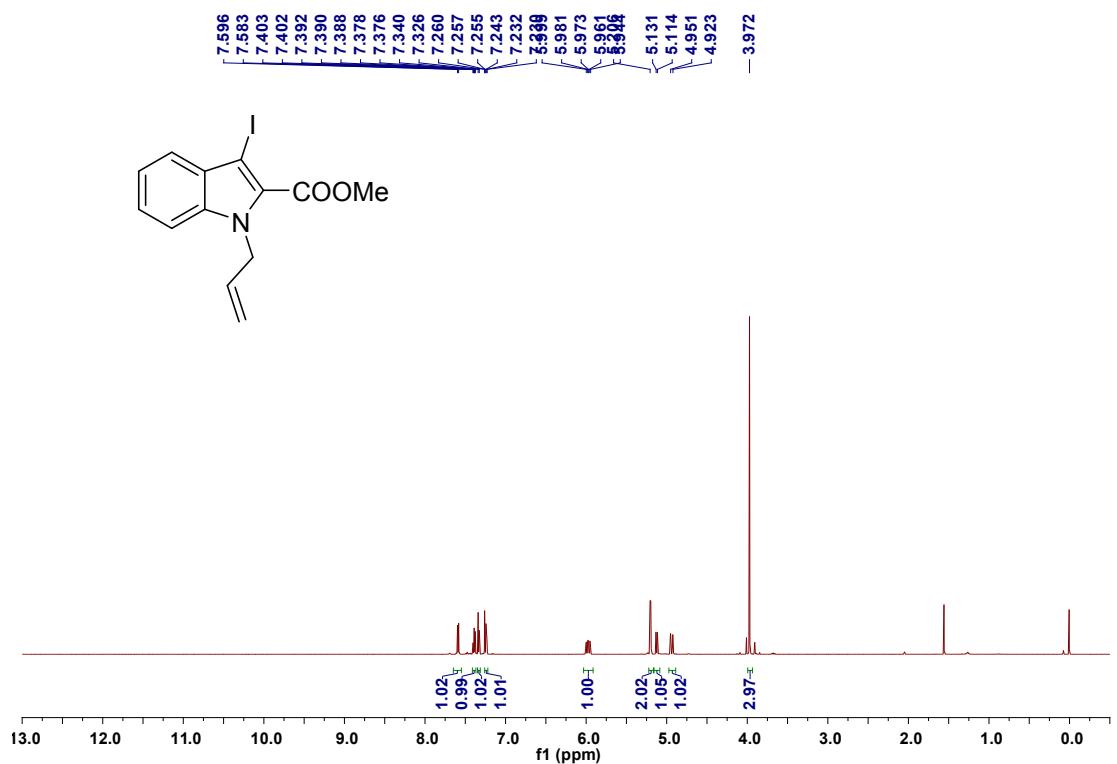
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7.517  
7.510  
7.503  
7.484  
7.485  
7.477  
7.473  
7.465  
7.462  
7.396  
7.297  
7.296  
7.293  
7.299  
7.286  
7.287  
7.275  
7.273  
7.269  
7.260  
7.259  
7.256  
7.243  
7.238  
7.234  
5.932  
5.892  
5.882  
5.887  
5.110  
5.168  
5.153  
5.181  
4.935  
4.933  
4.933  
4.936  
4.995  
4.676  
4.673  
4.689  
4.665  
4.662



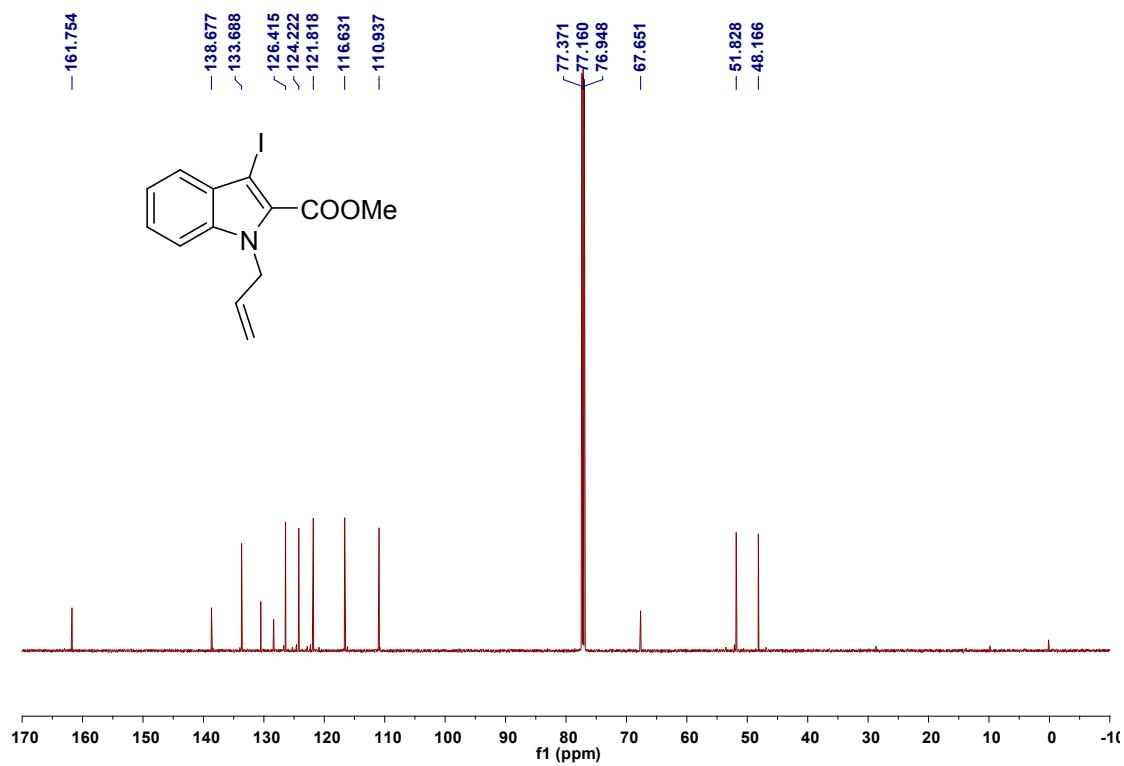
### <sup>13</sup>C NMR



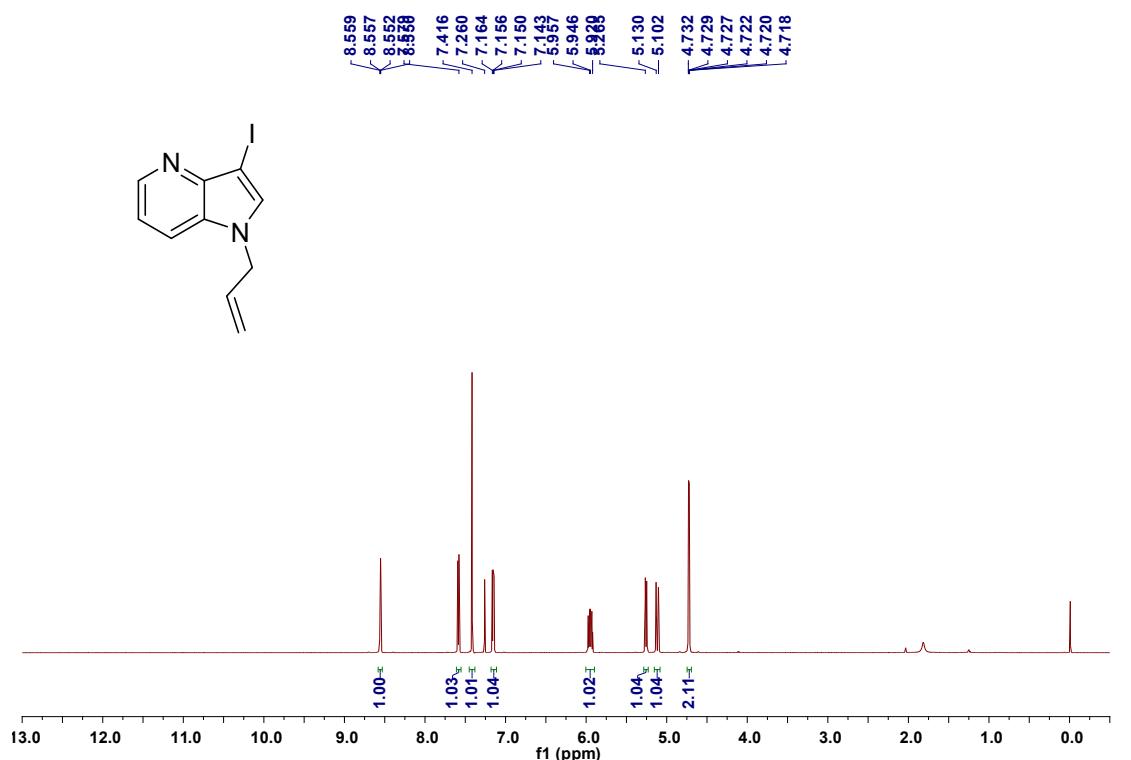
### <sup>1</sup>H NMR



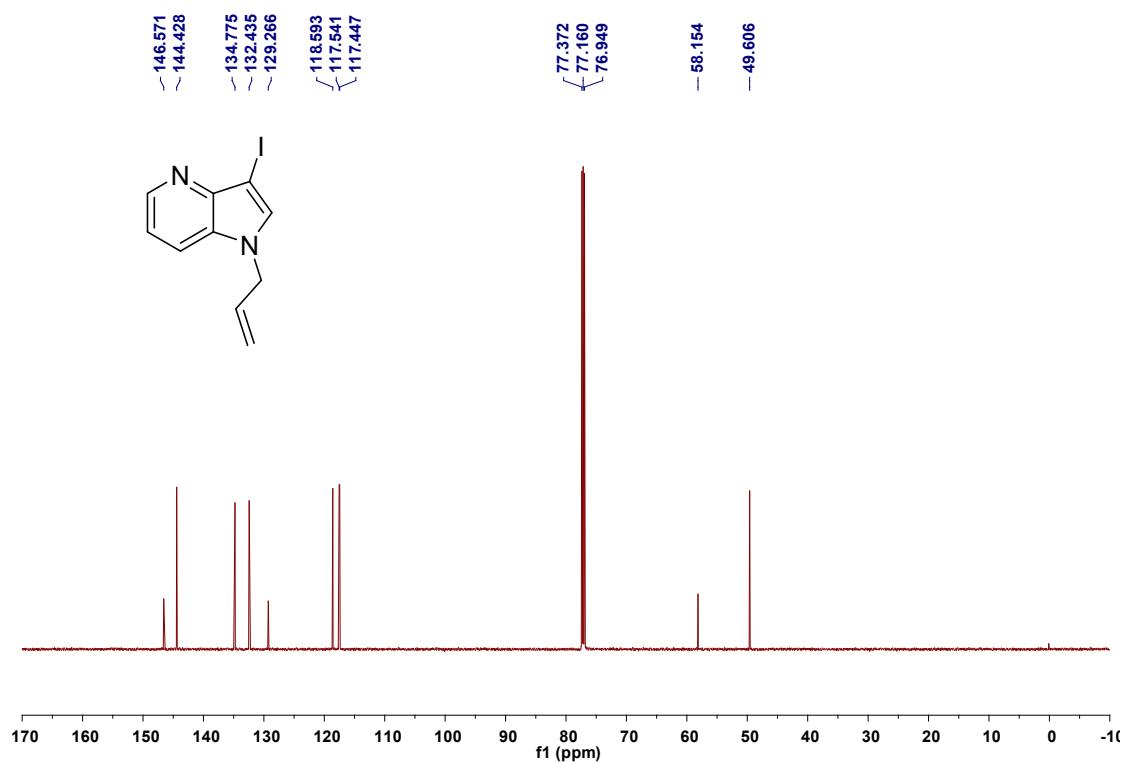
### <sup>13</sup>C NMR



### <sup>1</sup>H NMR

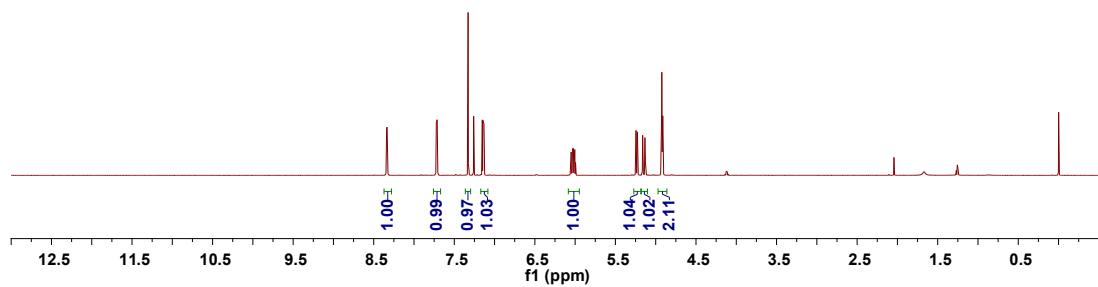
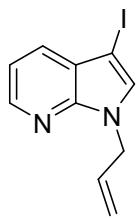


### <sup>13</sup>C NMR



### <sup>1</sup>H NMR

8.342  
8.340  
8.334  
8.333  
7.710  
7.738  
7.145  
7.139  
6.021  
6.010  
5.247  
5.245  
5.243  
5.230  
5.227  
5.225  
5.164  
5.162  
5.160  
5.157  
5.136  
5.133  
5.131  
5.129  
4.927  
4.924  
4.922  
4.917  
4.915  
4.912



### <sup>13</sup>C NMR

-147.200  
-144.180

133.395

131.933

129.364

123.253

118.131

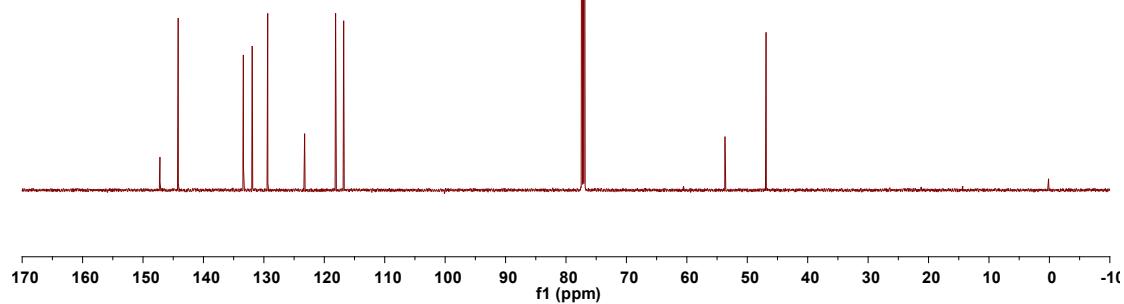
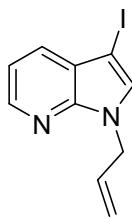
116.792

77.372

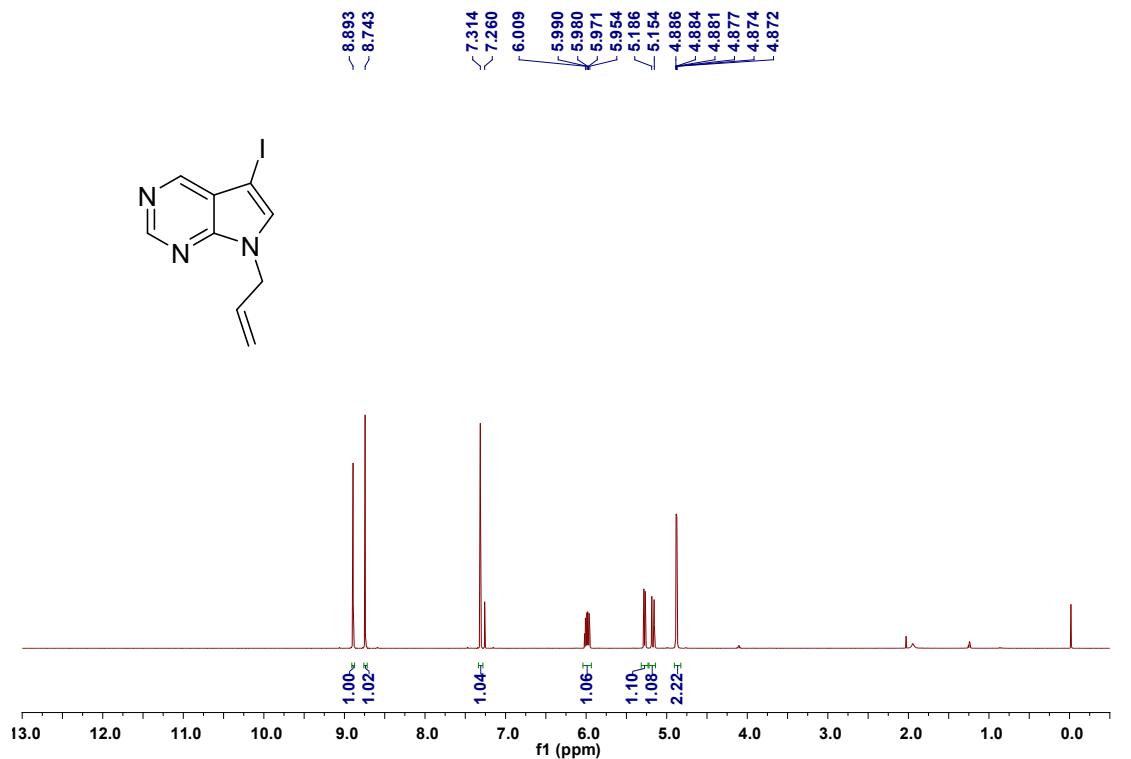
77.160

76.949

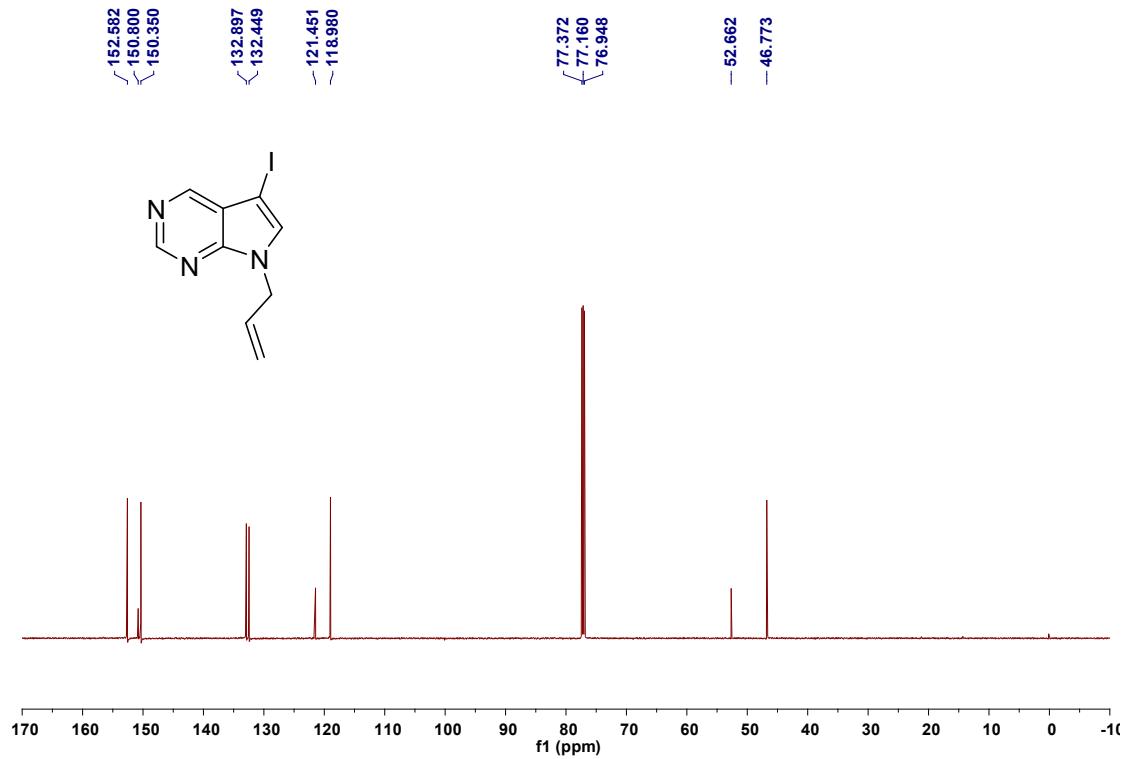
-53.689  
-46.892



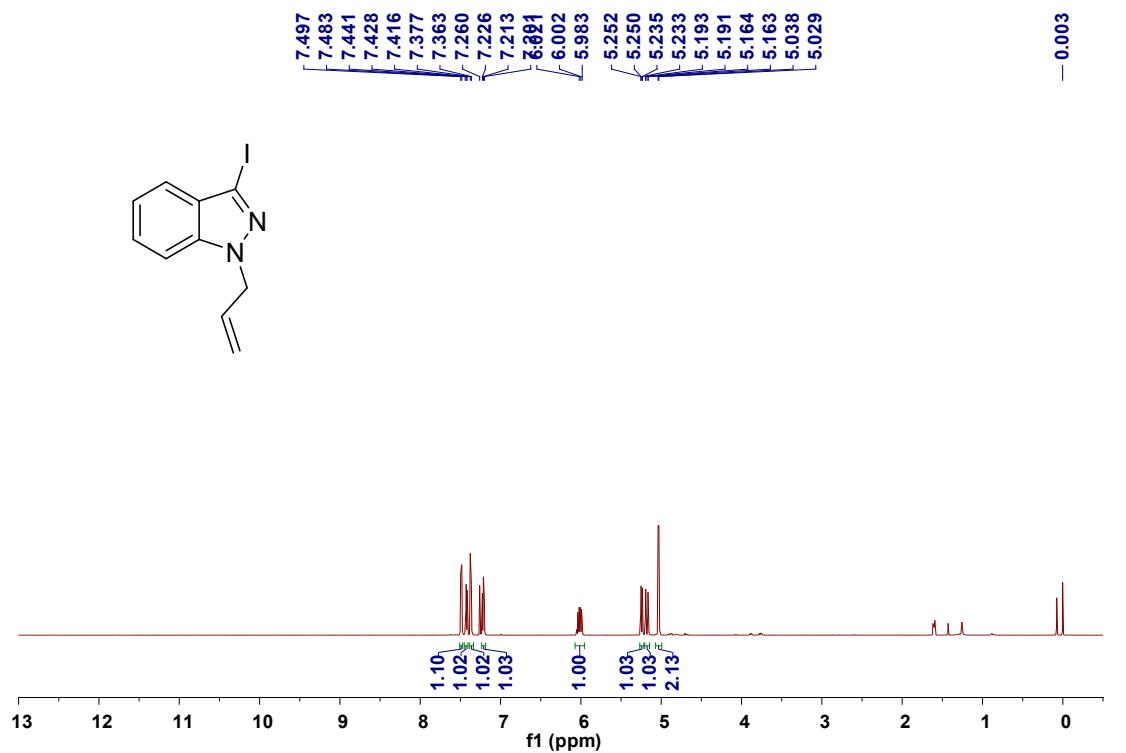
### <sup>1</sup>H NMR



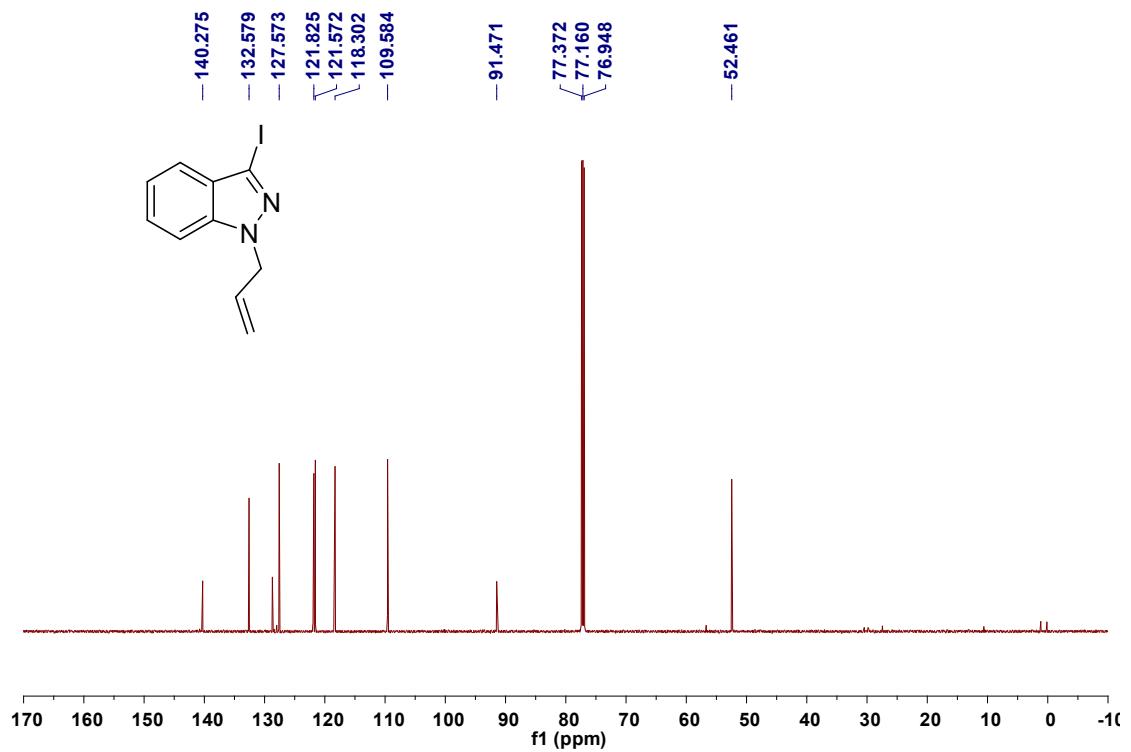
### <sup>13</sup>C NMR



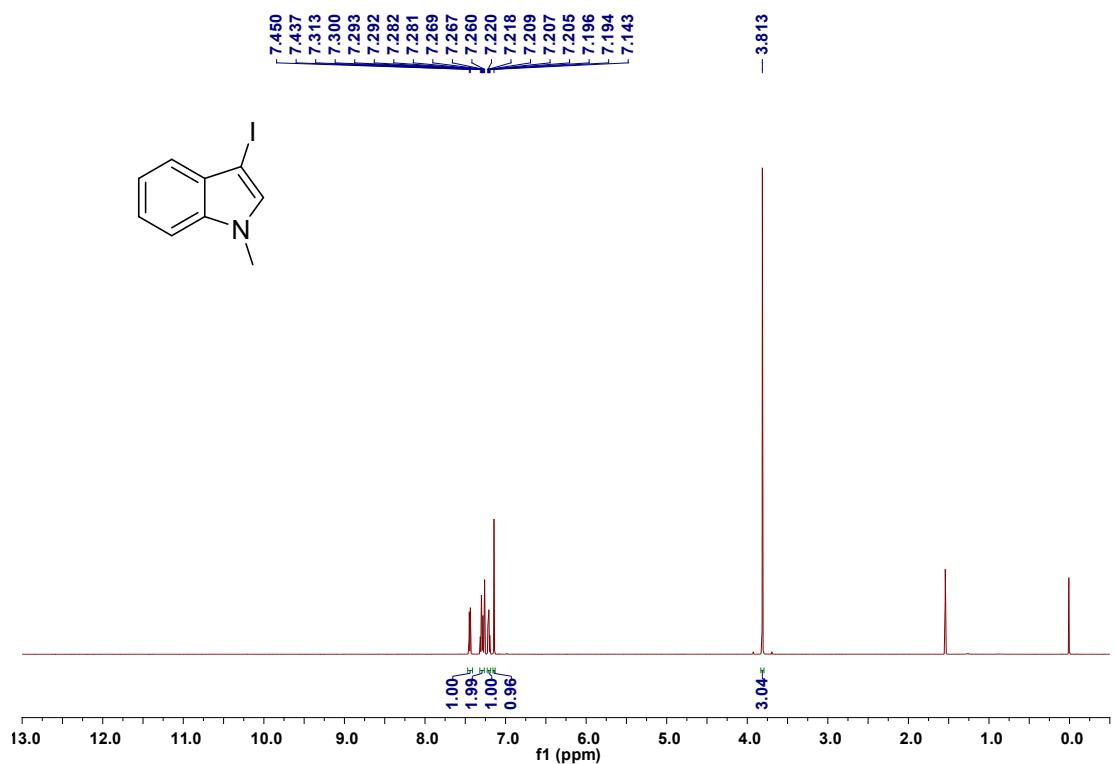
### <sup>1</sup>H NMR



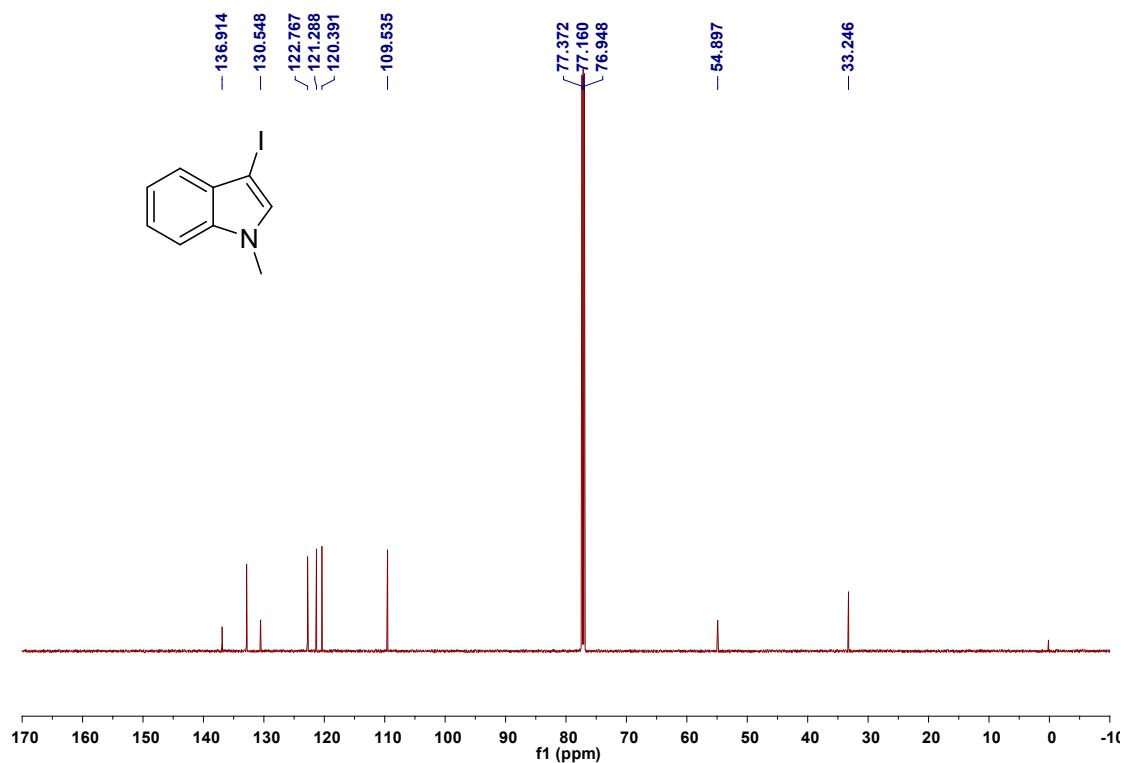
### $^{13}\text{C}$ NMR



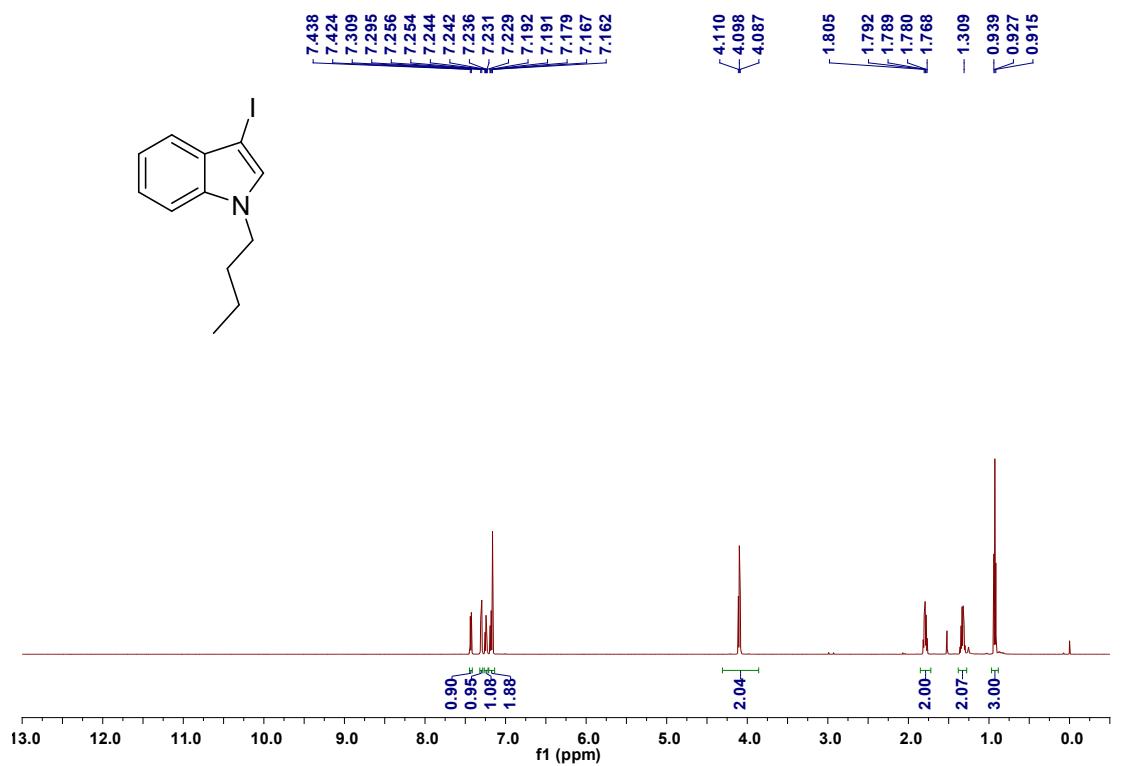
### $^1\text{H}$ NMR



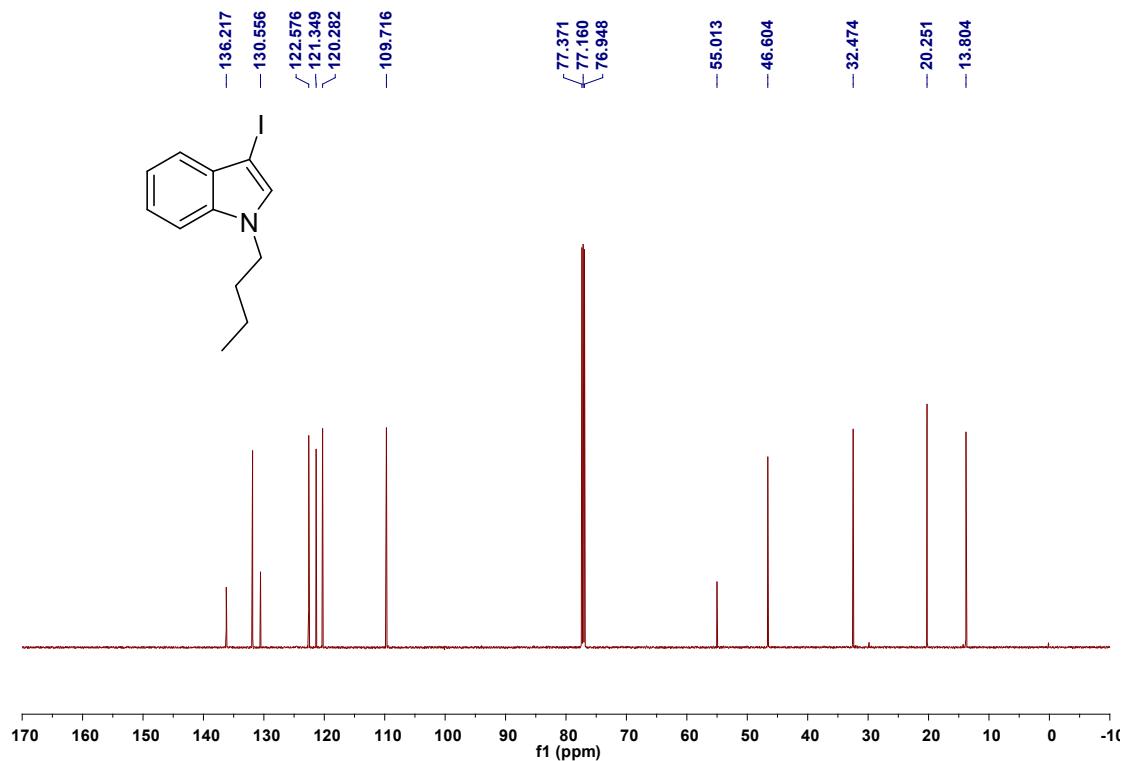
### <sup>13</sup>C NMR



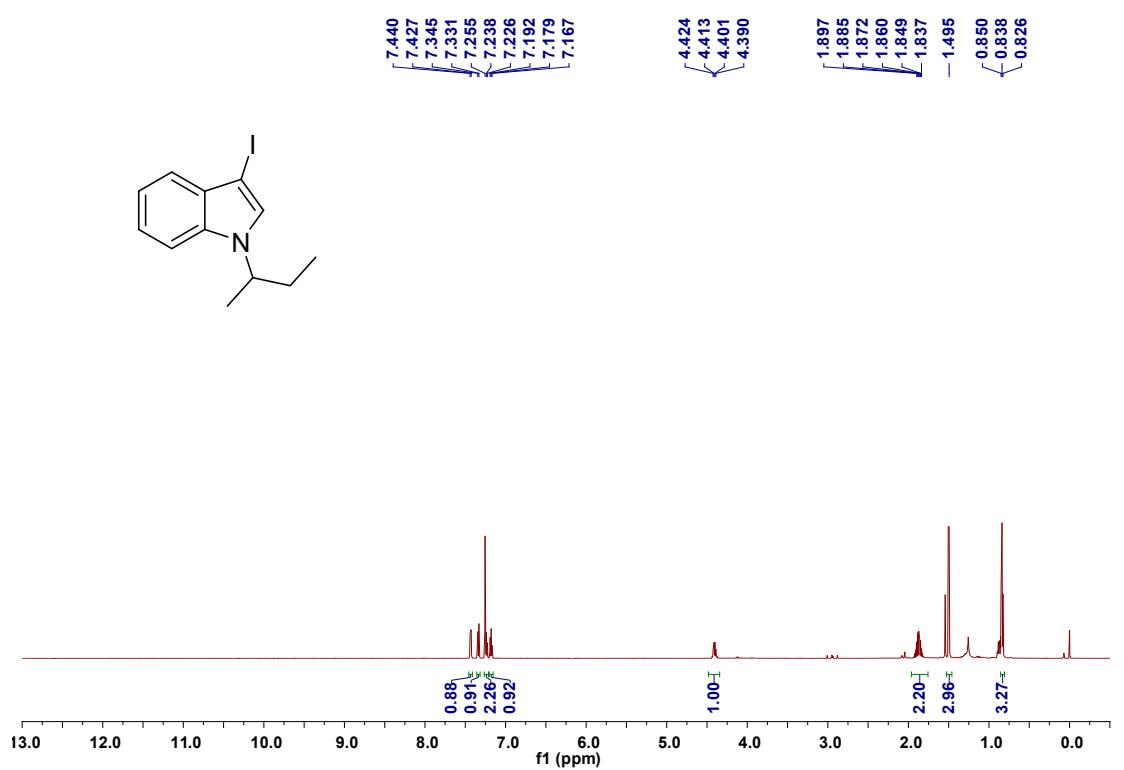
### <sup>1</sup>H NMR



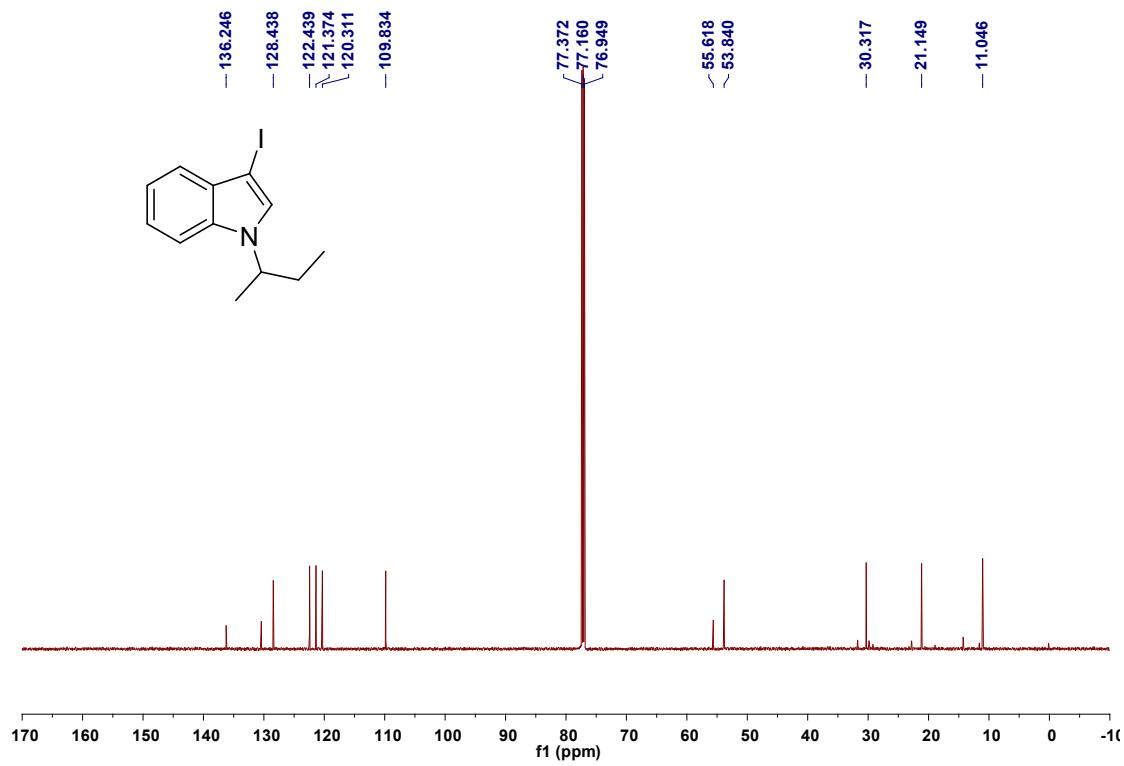
### <sup>13</sup>C NMR



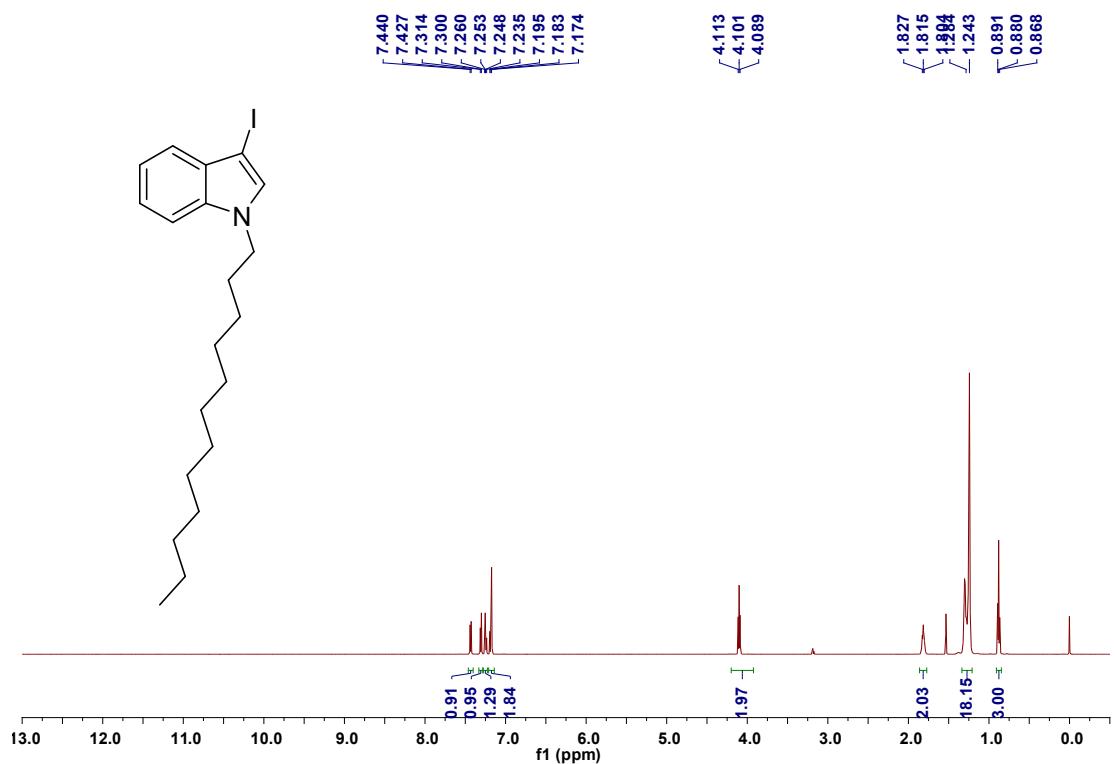
### <sup>1</sup>H NMR



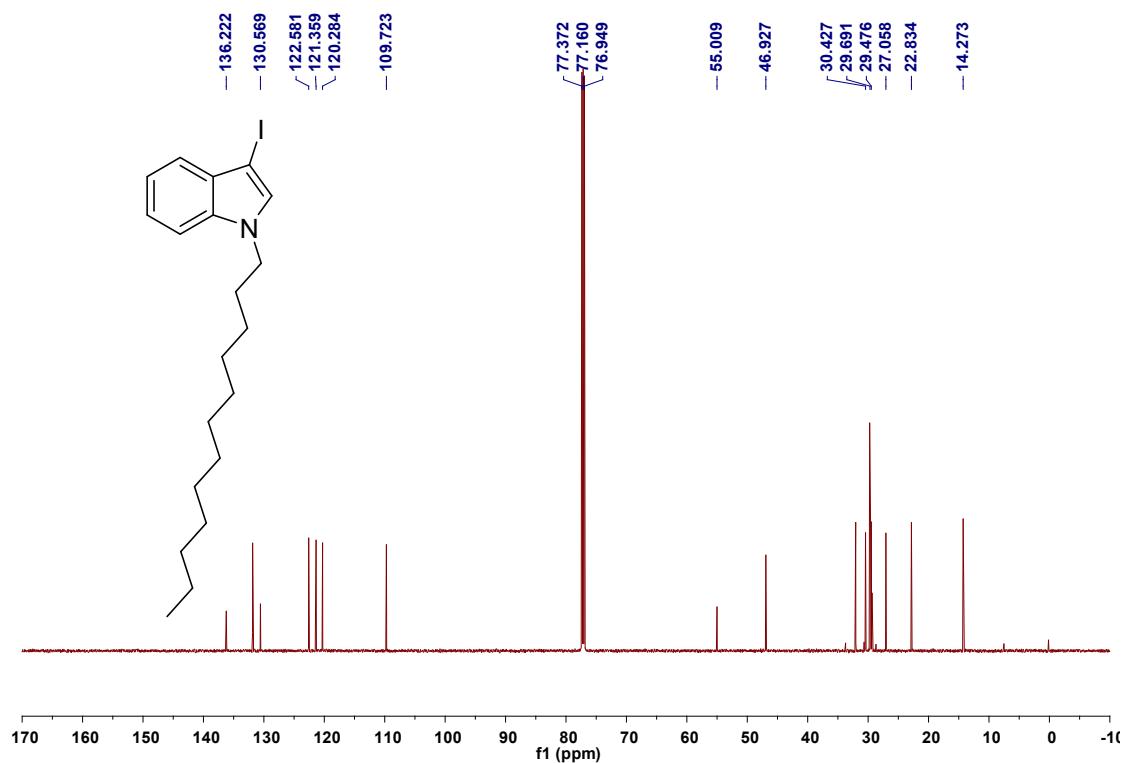
### $^{13}\text{C}$ NMR



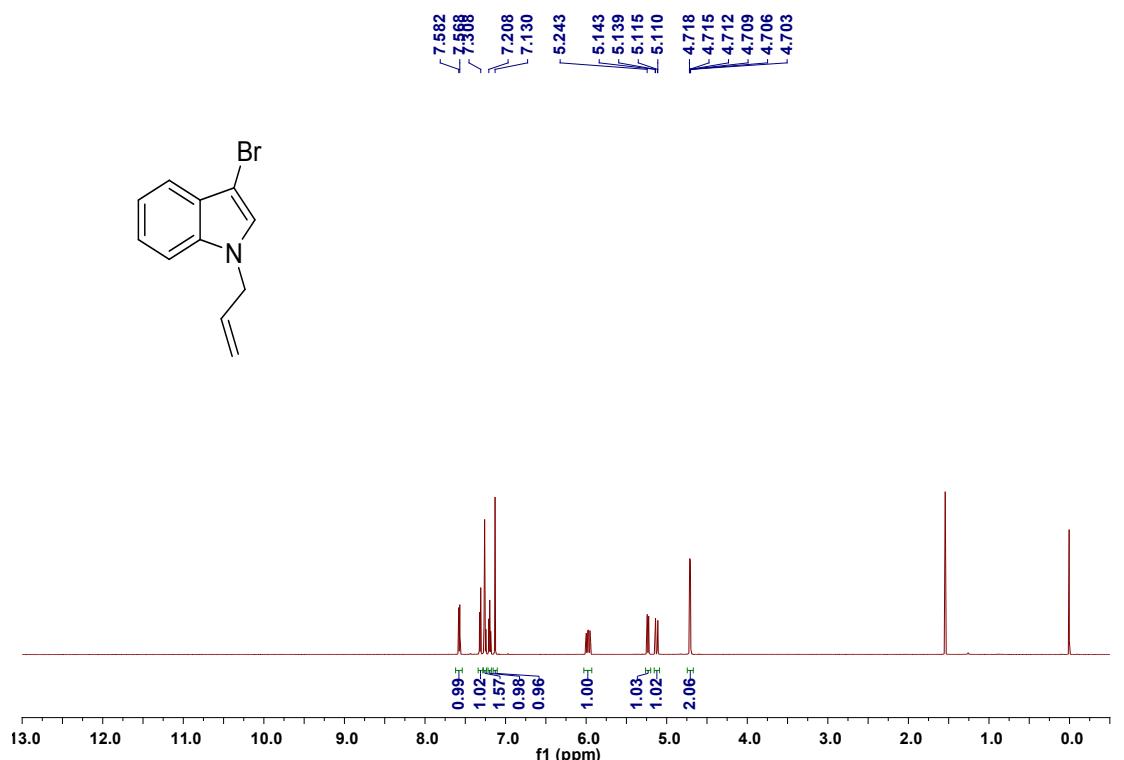
### $^1\text{H}$ NMR



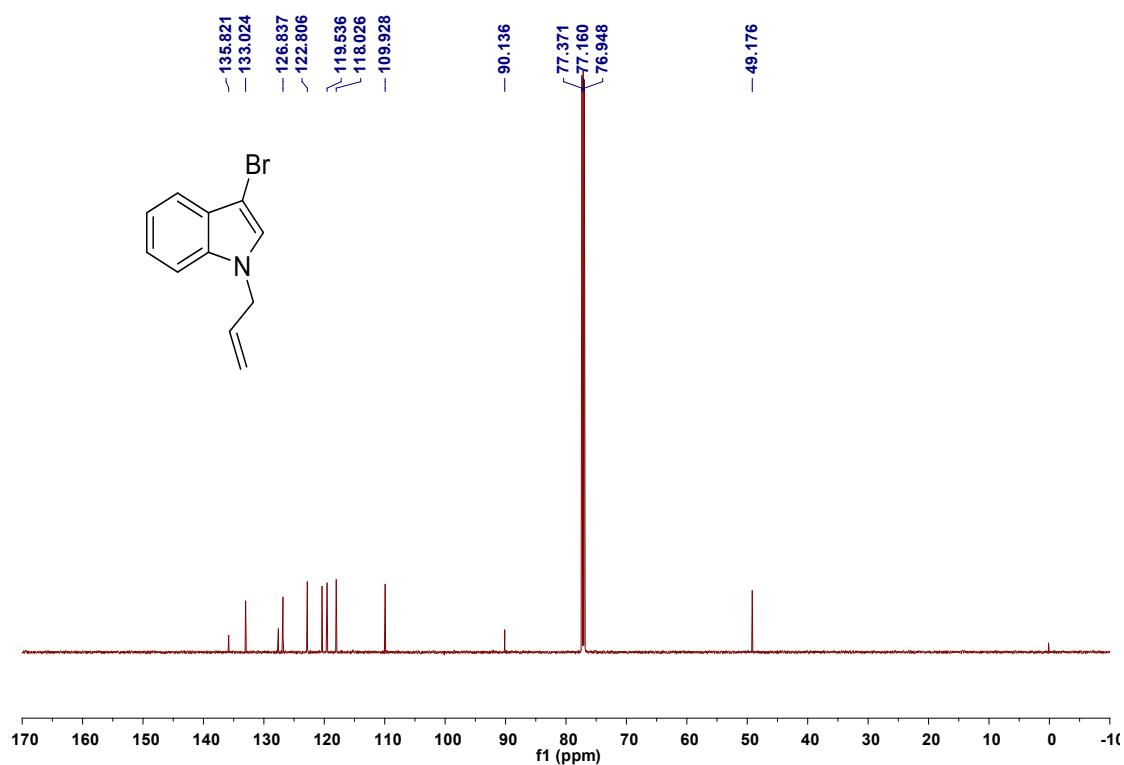
### <sup>13</sup>C NMR



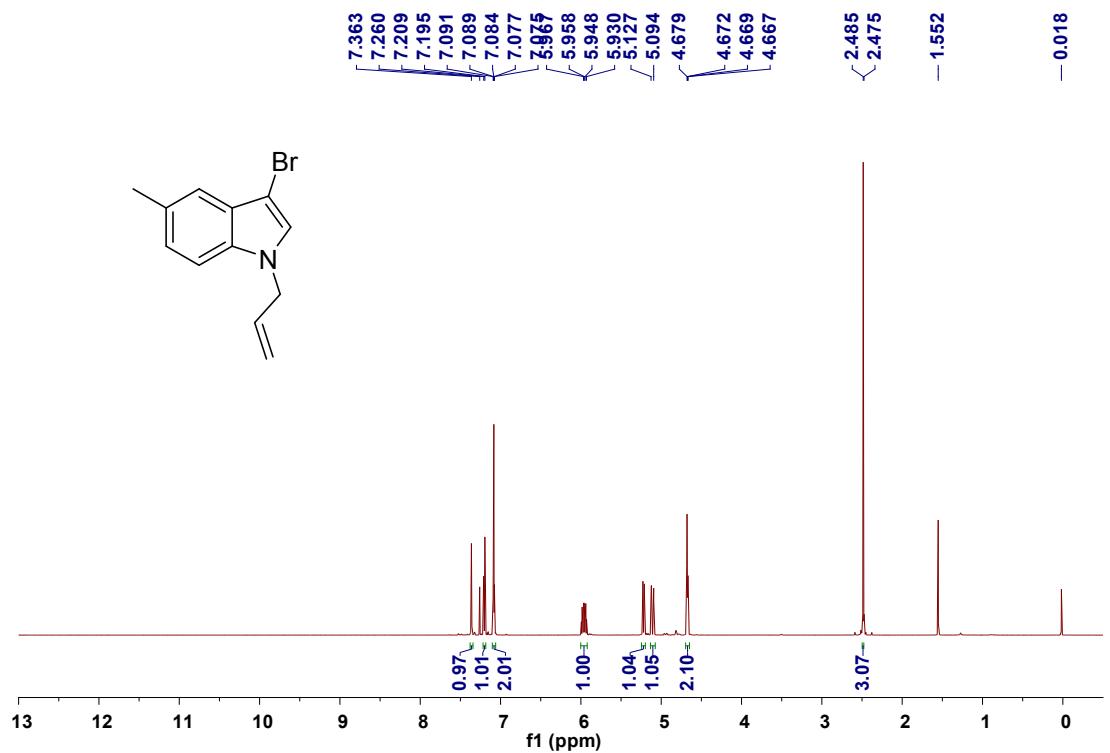
### <sup>1</sup>H NMR



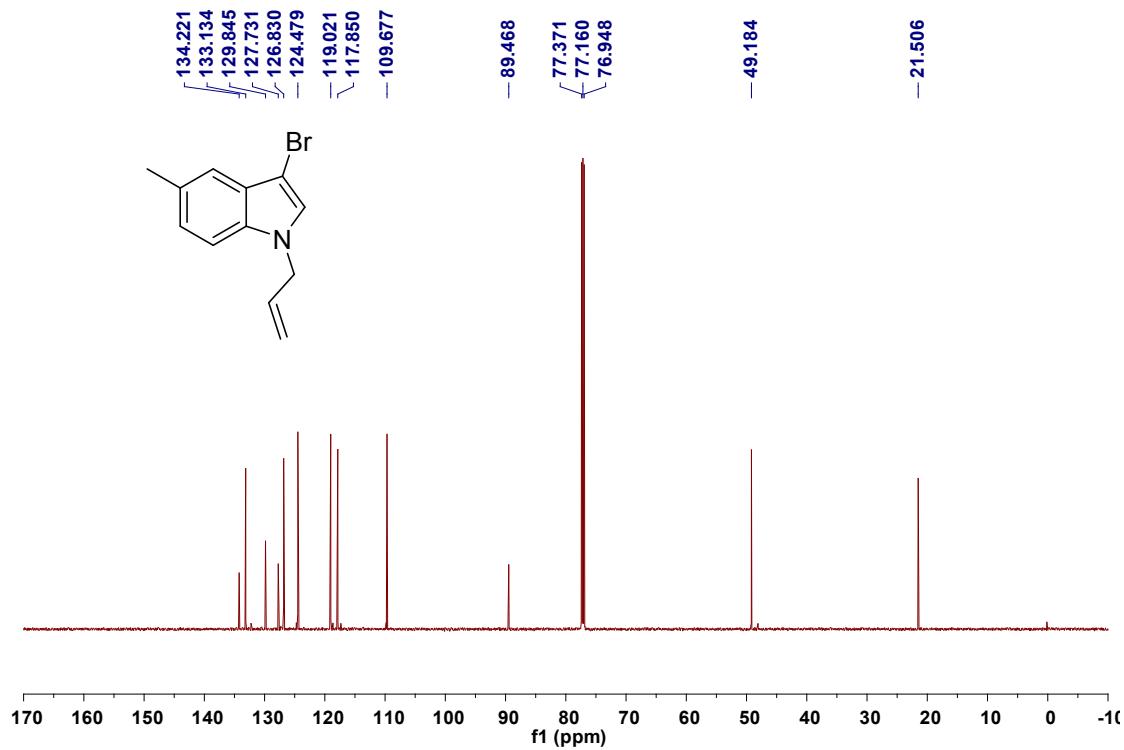
### $^{13}\text{C}$ NMR



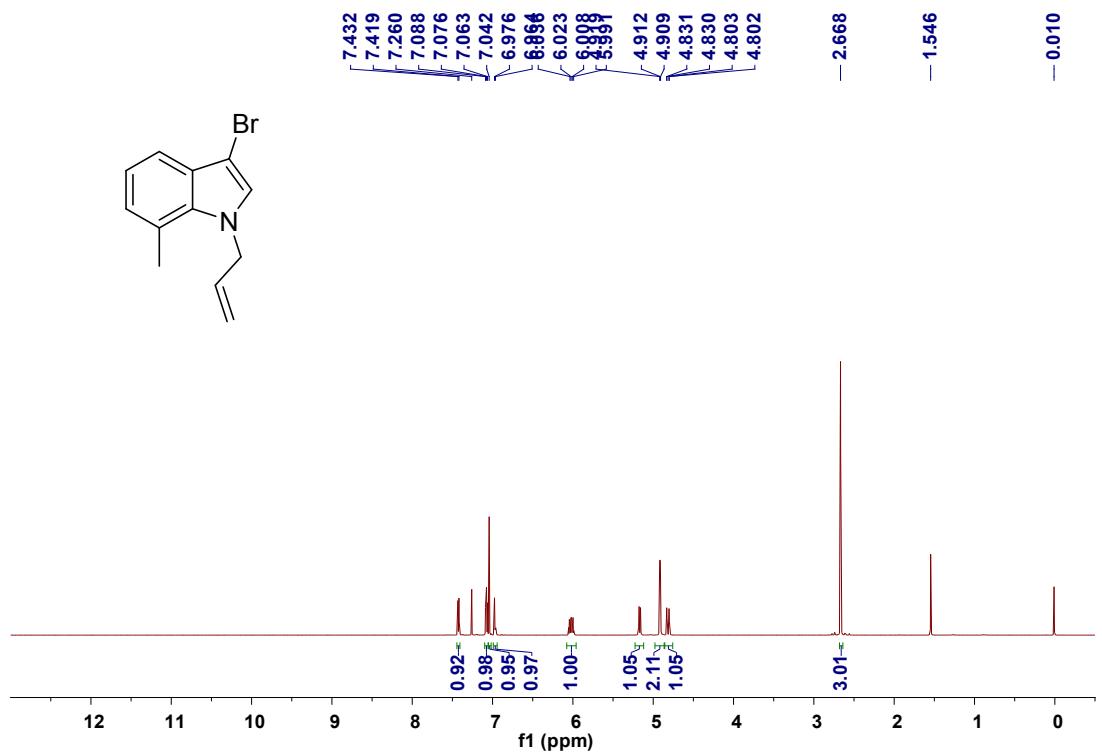
### $^1\text{H}$ NMR



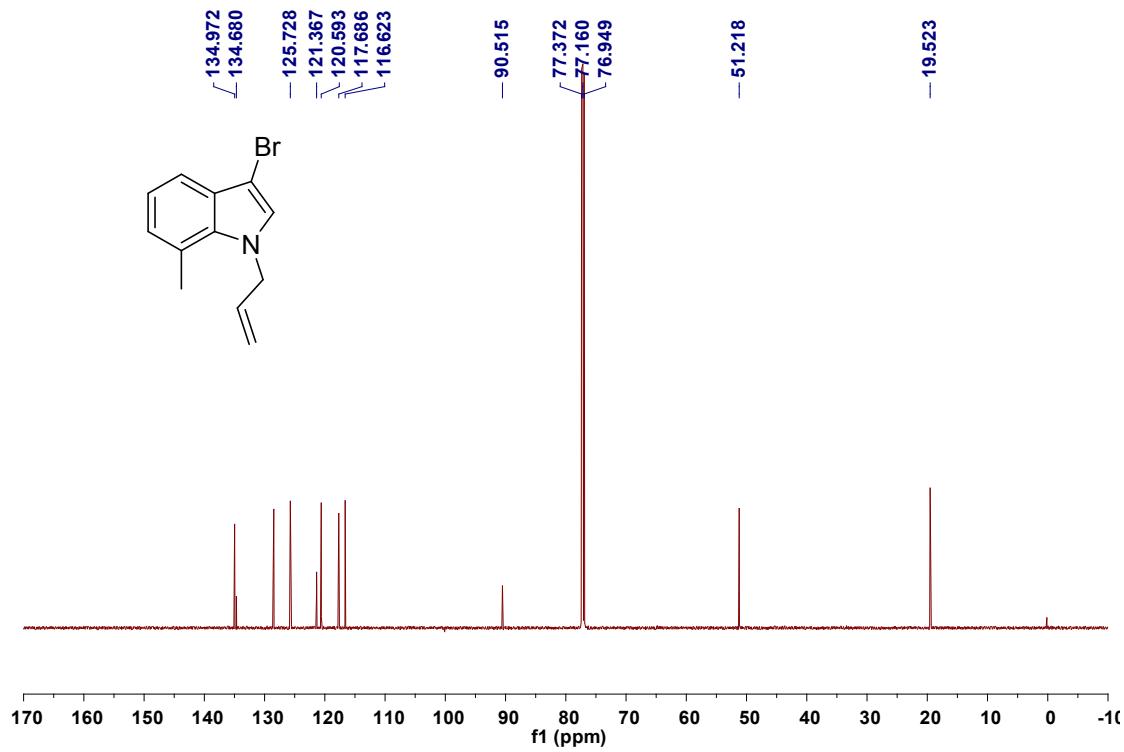
### <sup>13</sup>C NMR



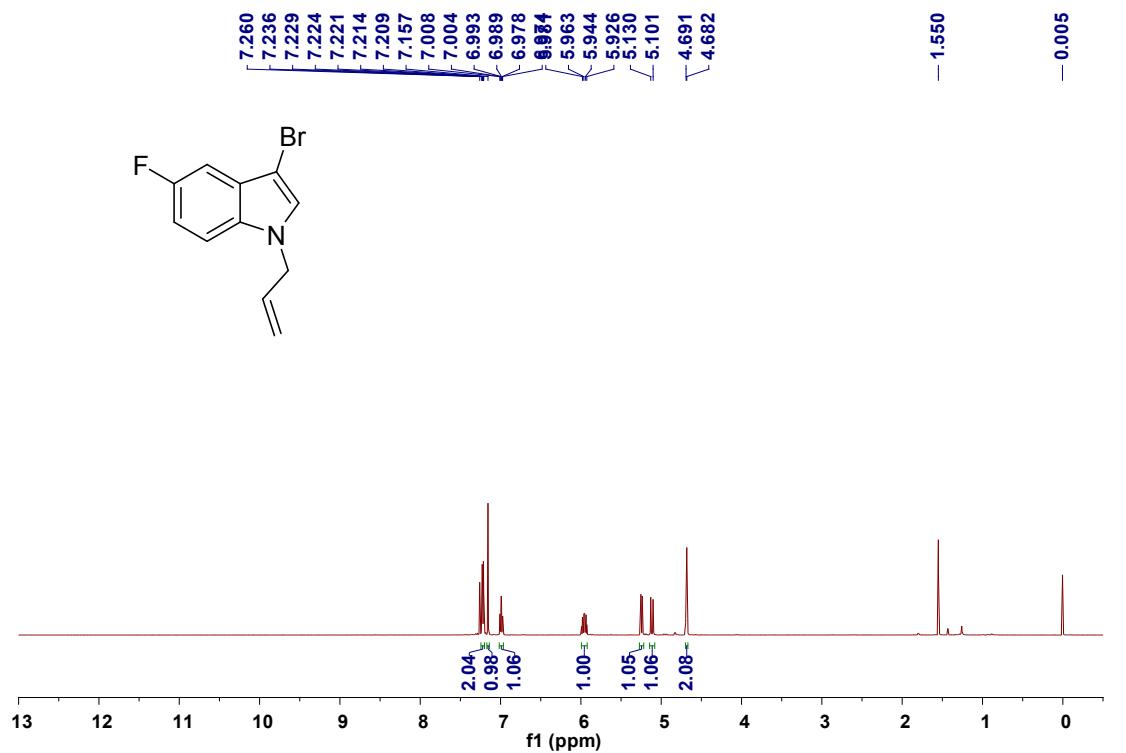
### <sup>1</sup>H NMR



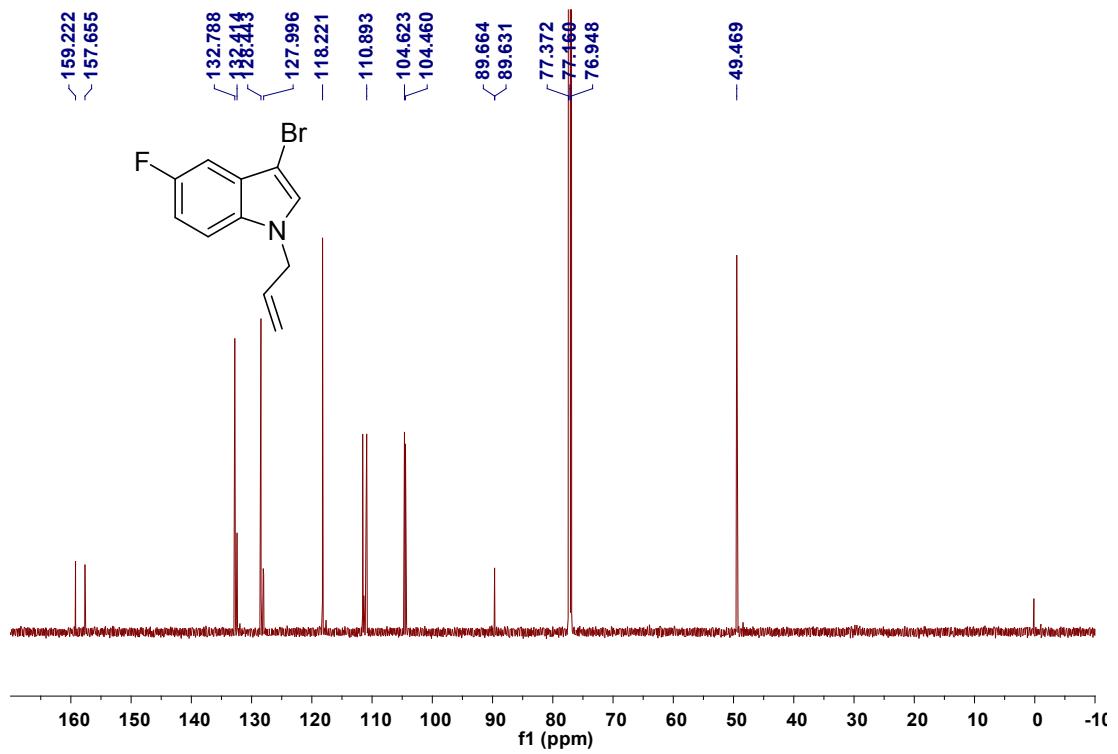
### $^{13}\text{C}$ NMR



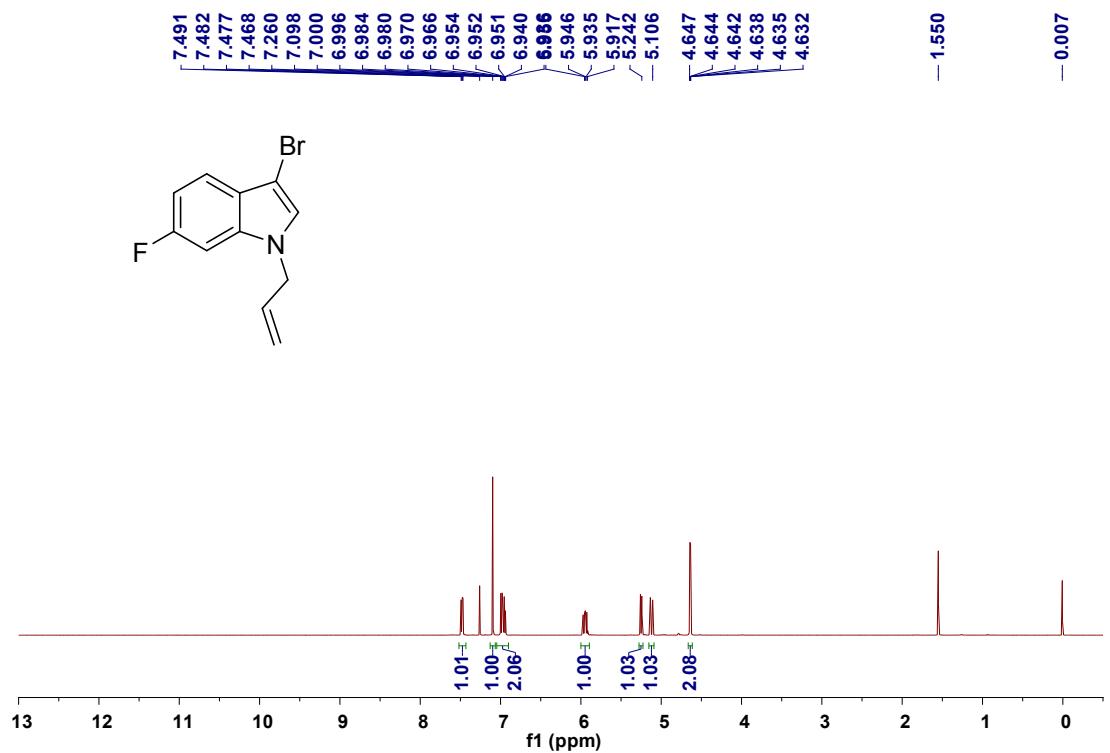
### $^1\text{H}$ NMR



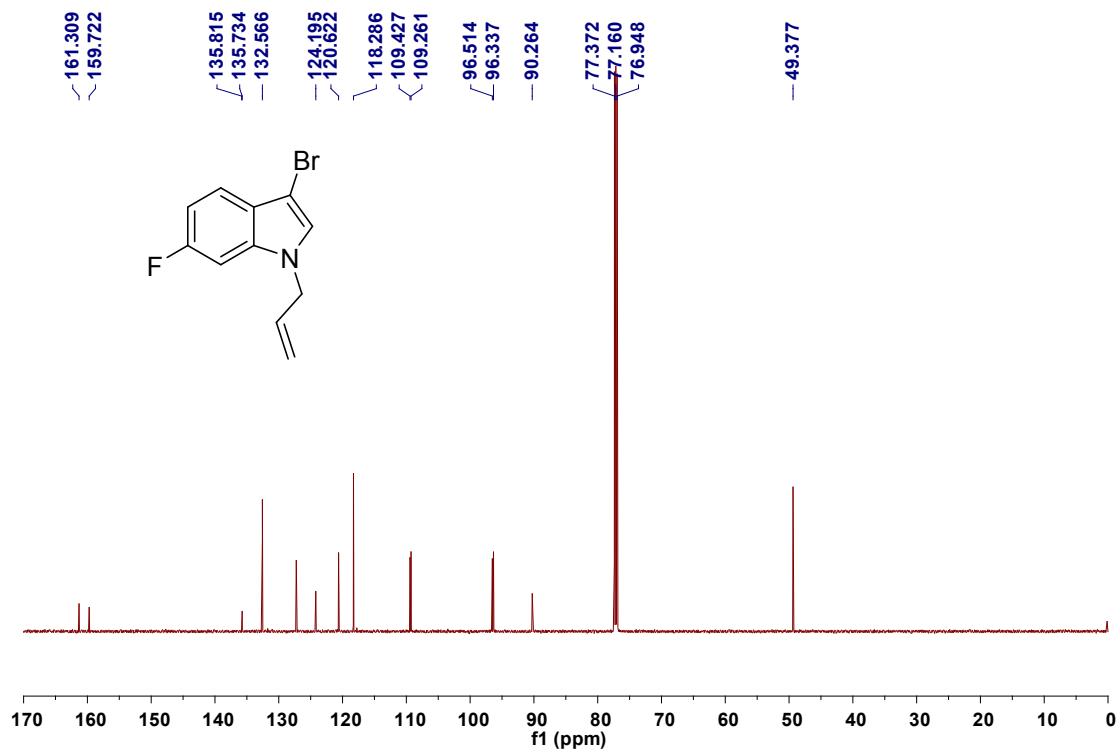
### <sup>13</sup>C NMR



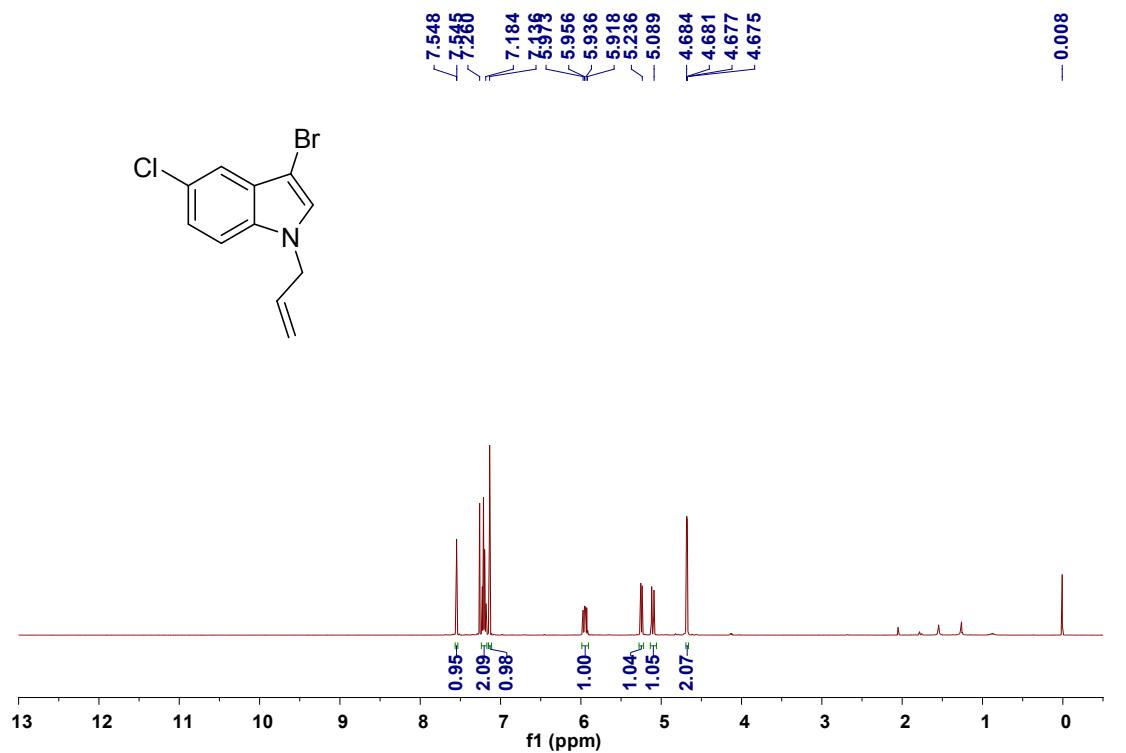
### <sup>1</sup>H NMR



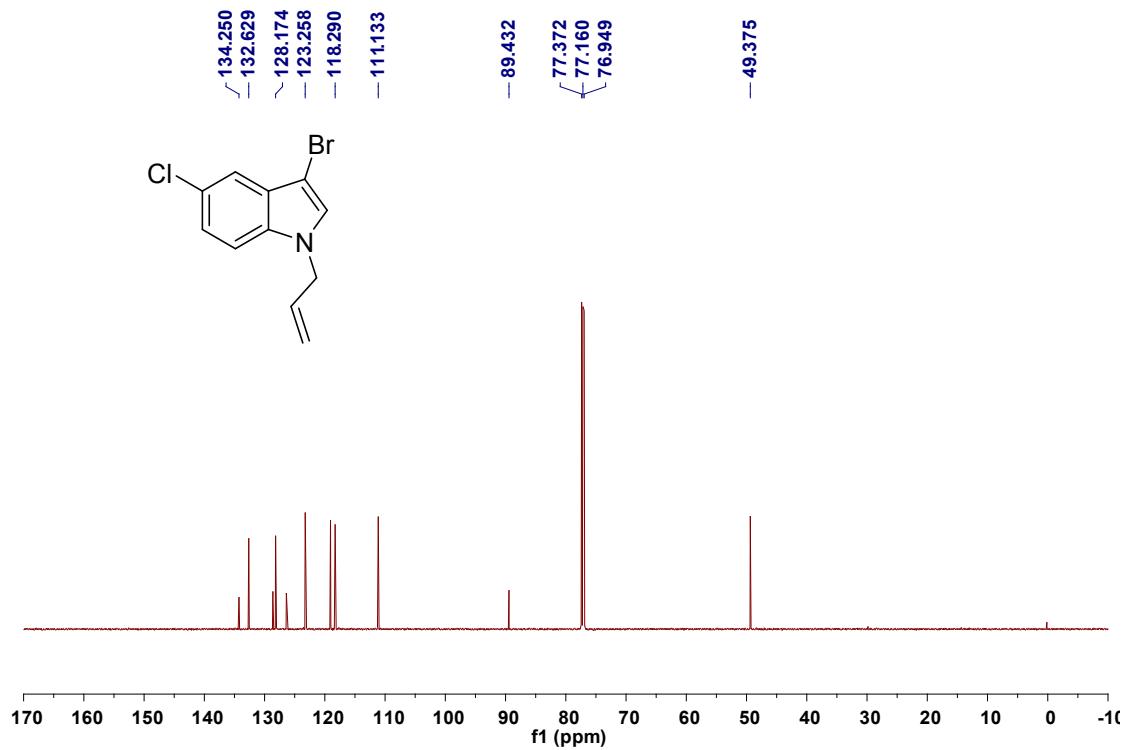
### $^{13}\text{C}$ NMR



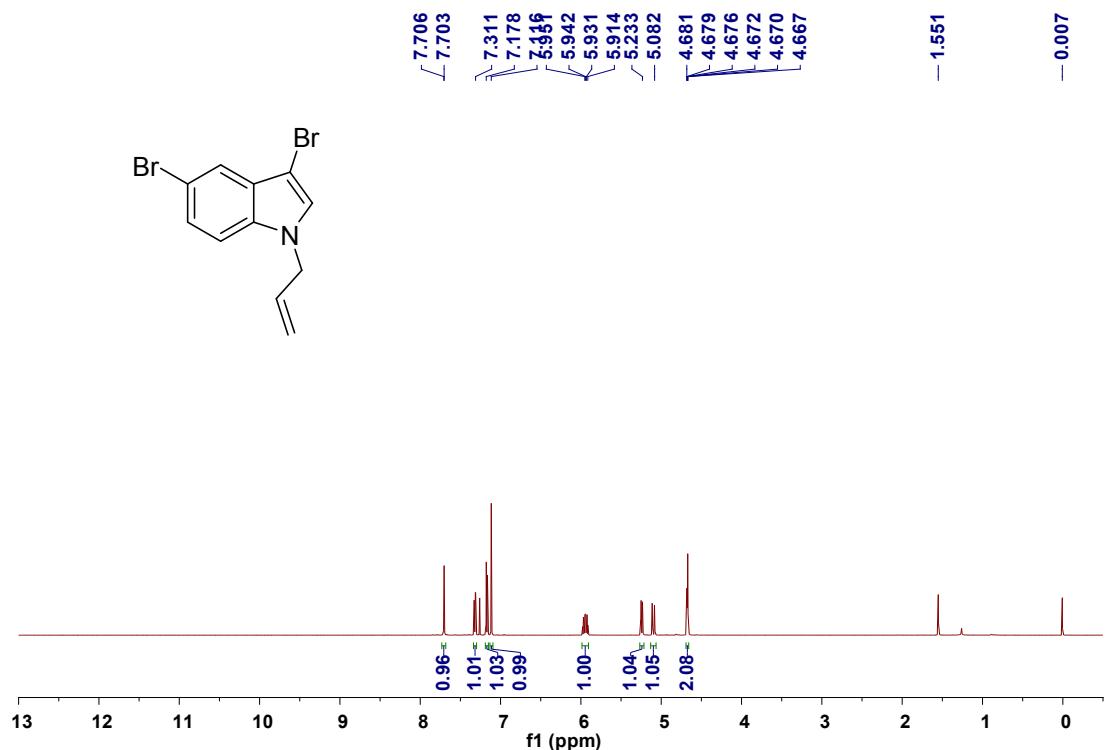
### $^1\text{H}$ NMR



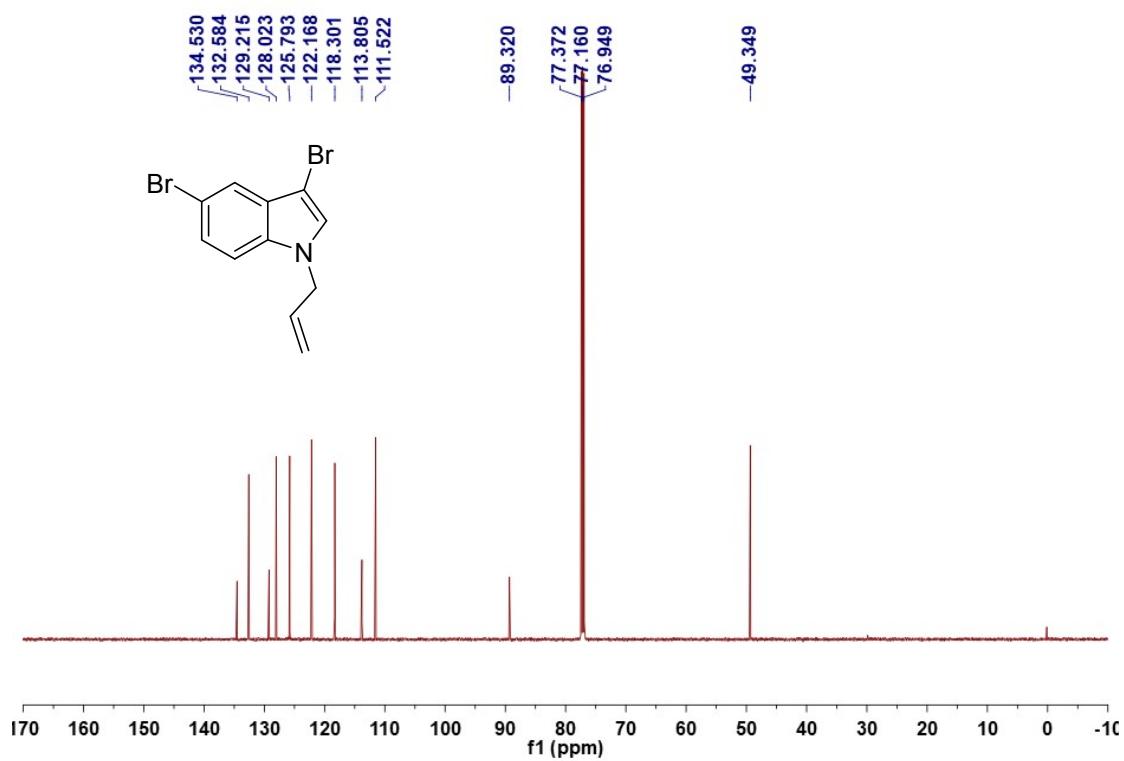
### <sup>13</sup>C NMR



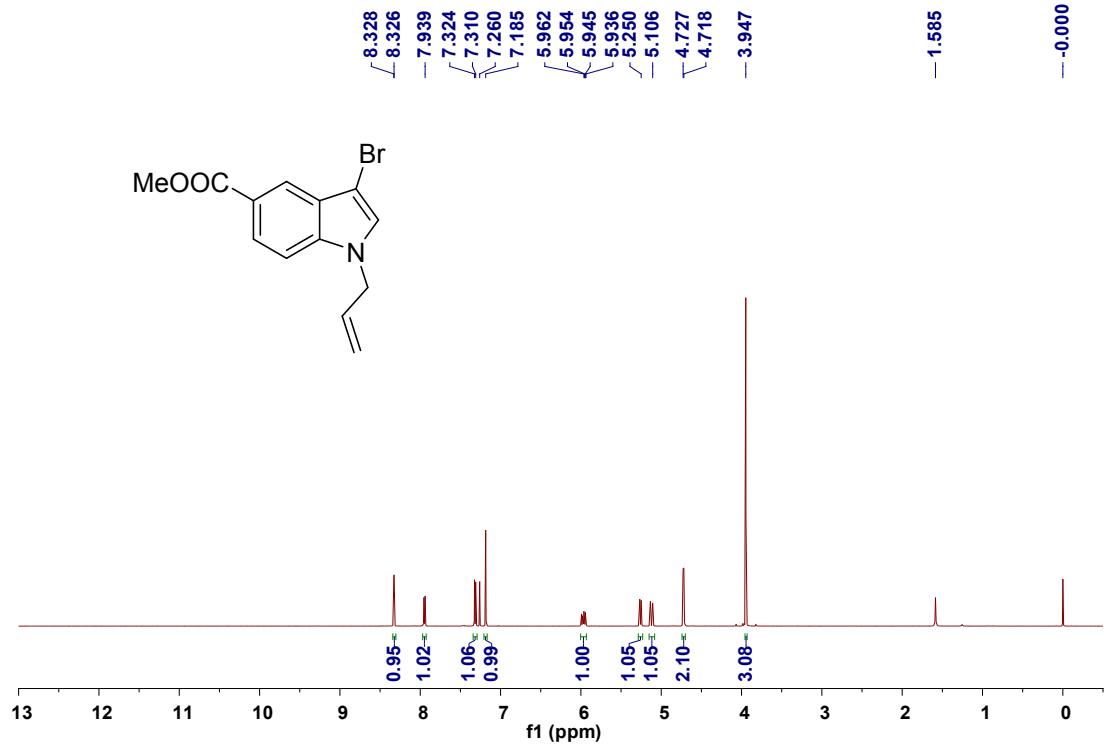
### <sup>1</sup>H NMR



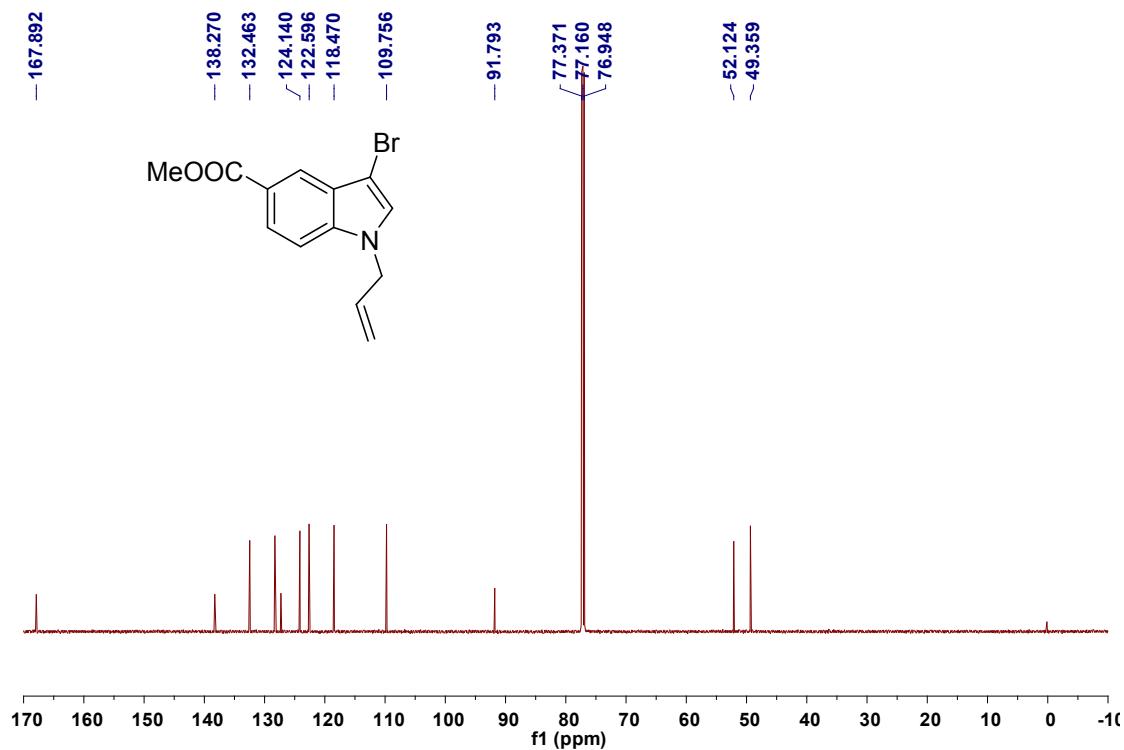
### $^{13}\text{C}$ NMR



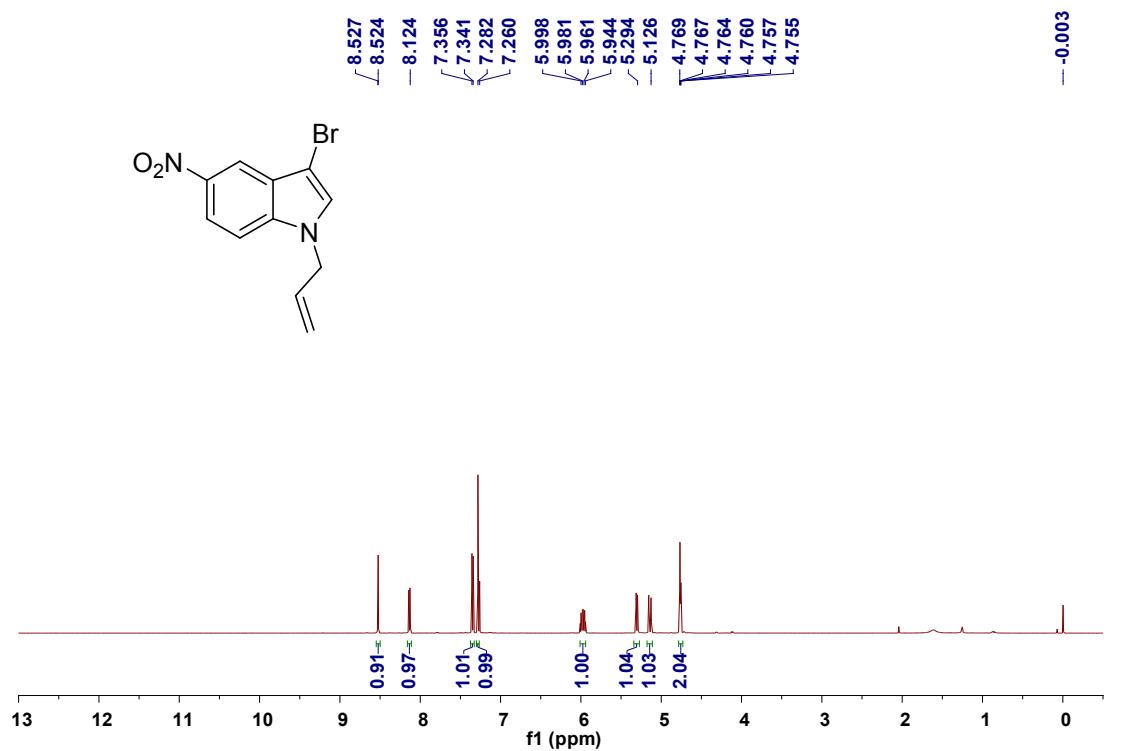
### $^1\text{H}$ NMR



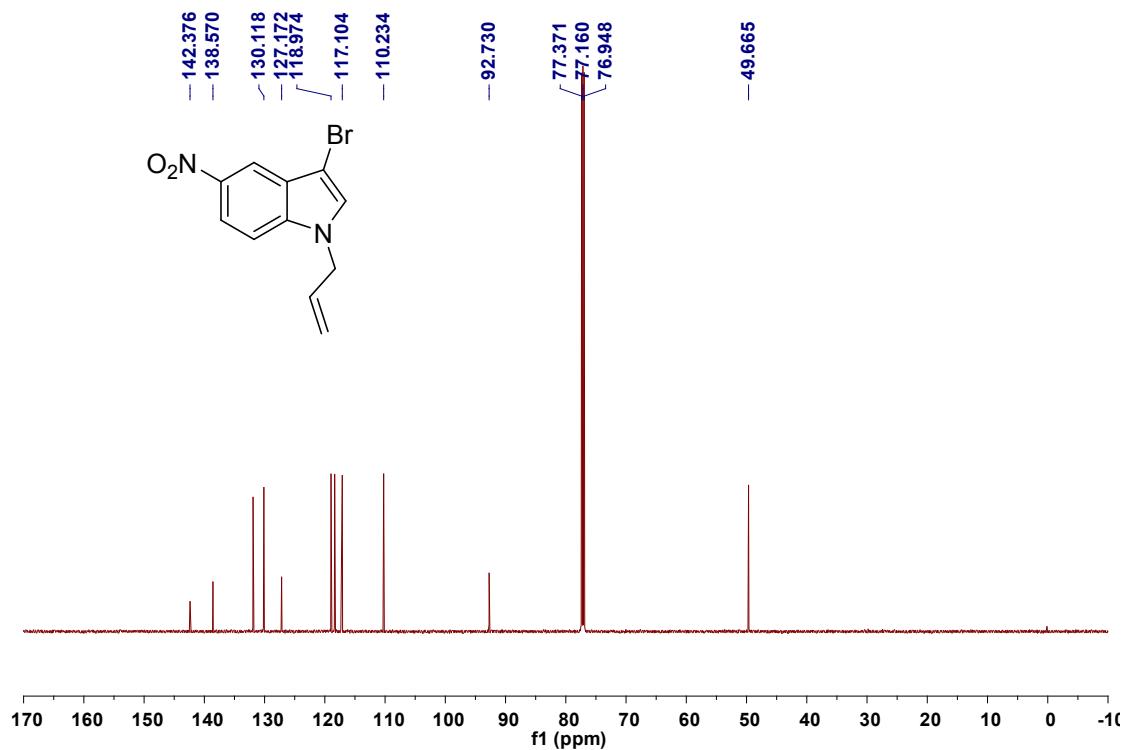
### <sup>13</sup>C NMR



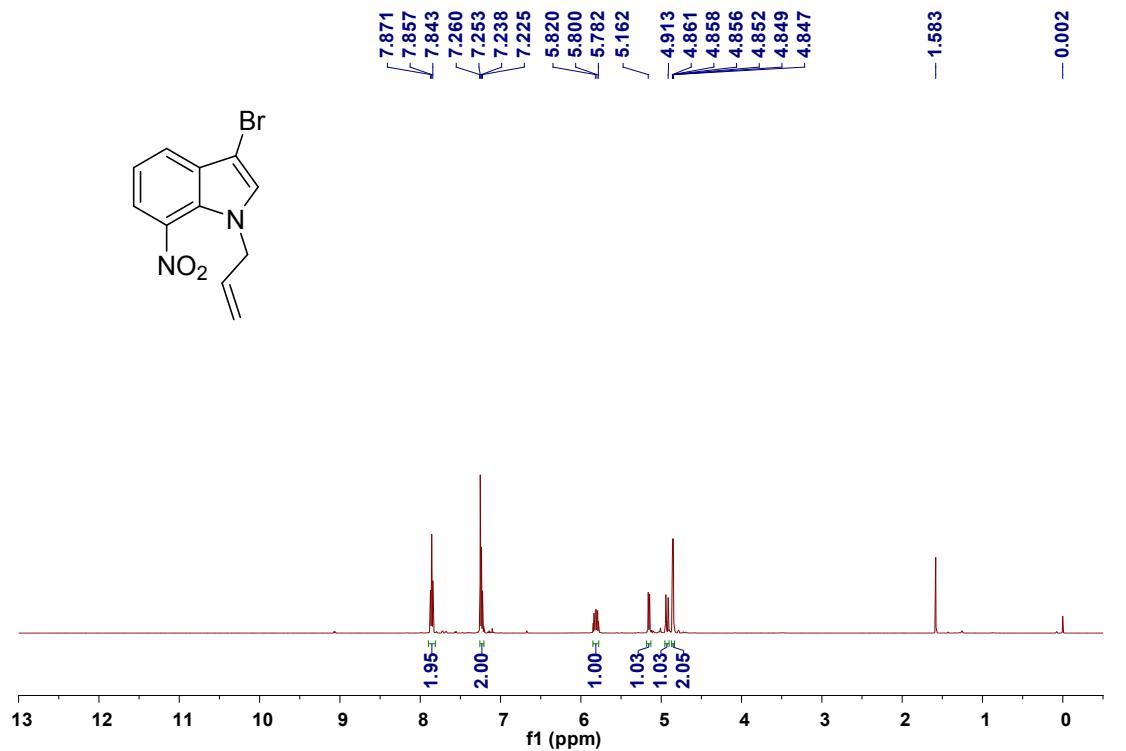
### <sup>1</sup>H NMR



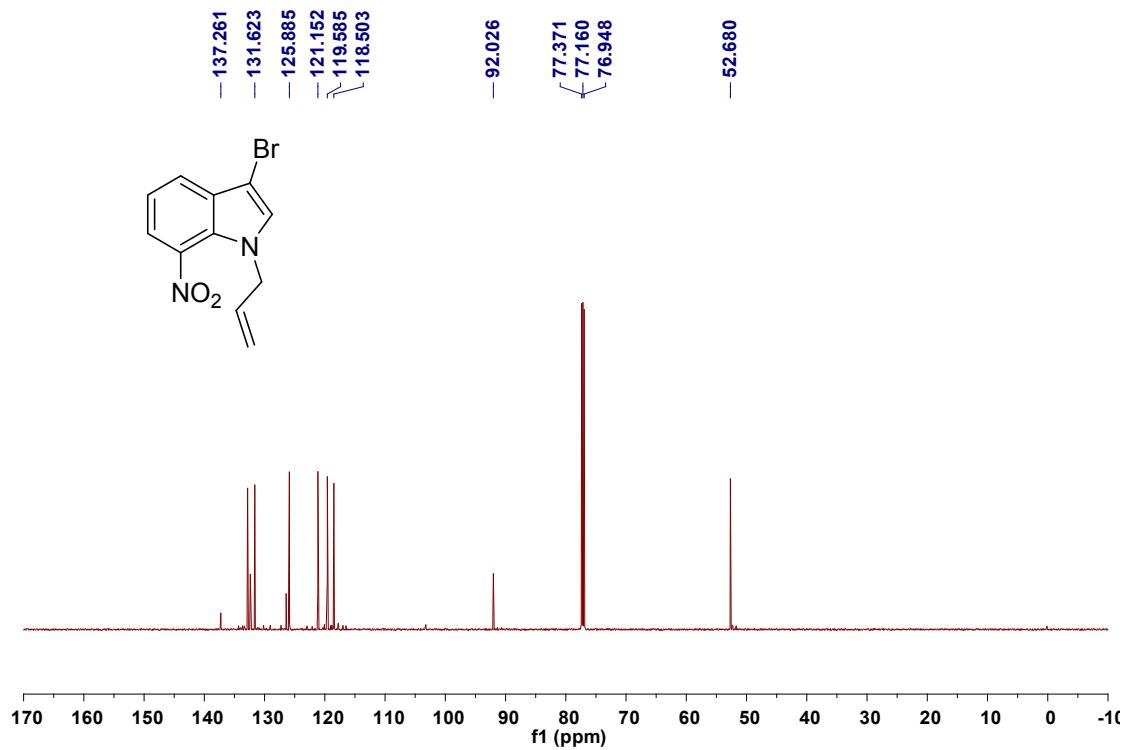
### <sup>13</sup>C NMR



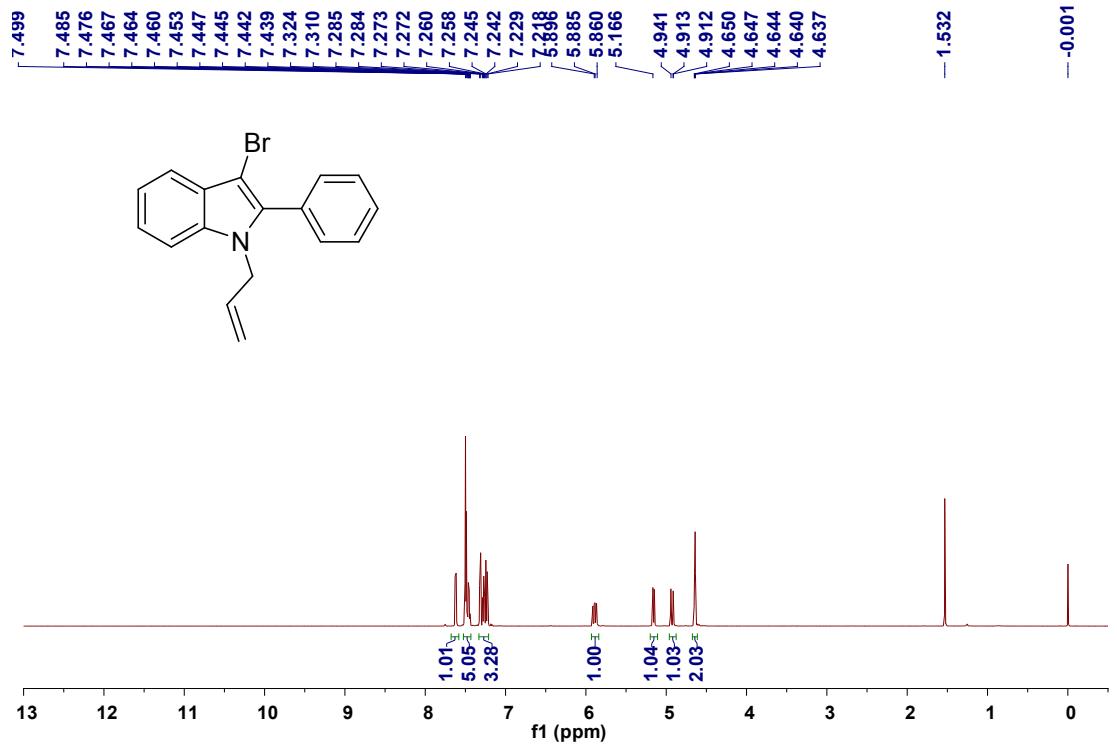
### <sup>1</sup>H NMR



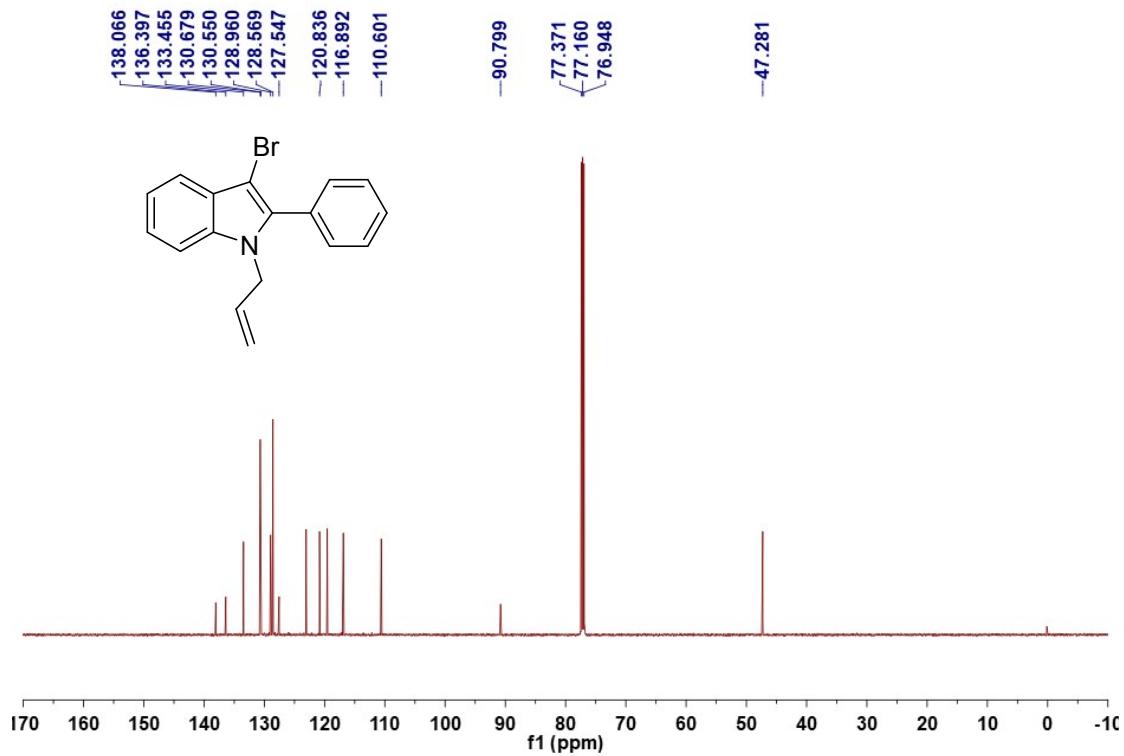
### <sup>13</sup>C NMR



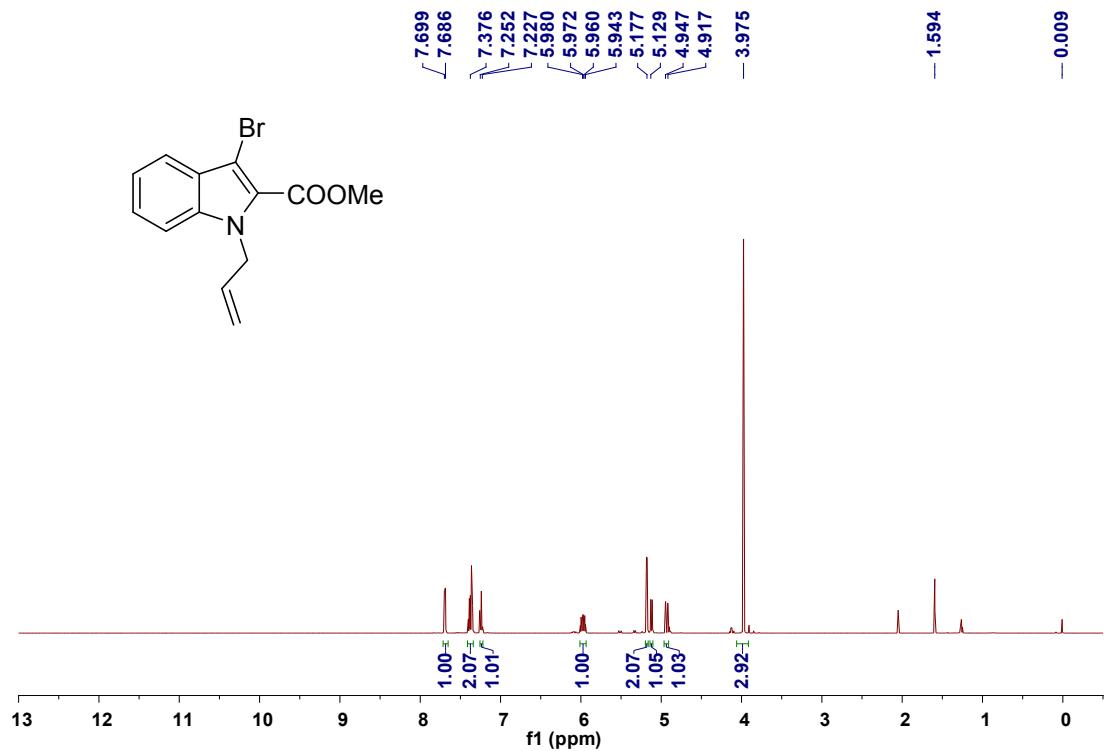
### <sup>1</sup>H NMR



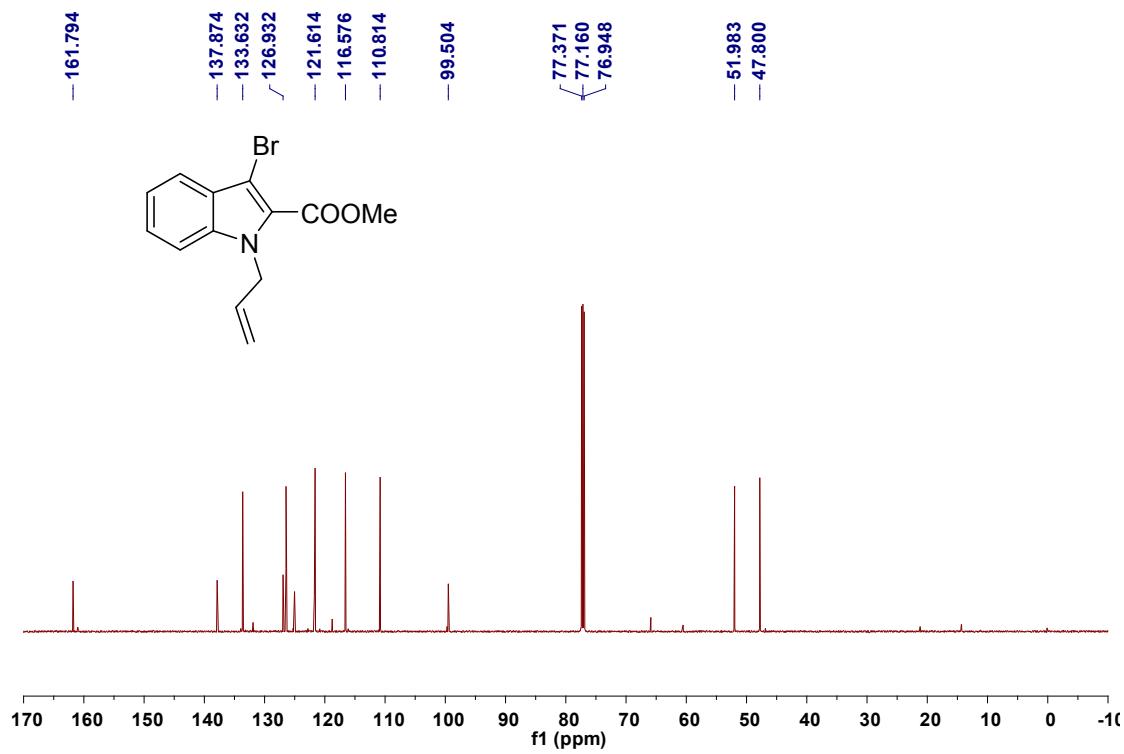
### <sup>13</sup>C NMR



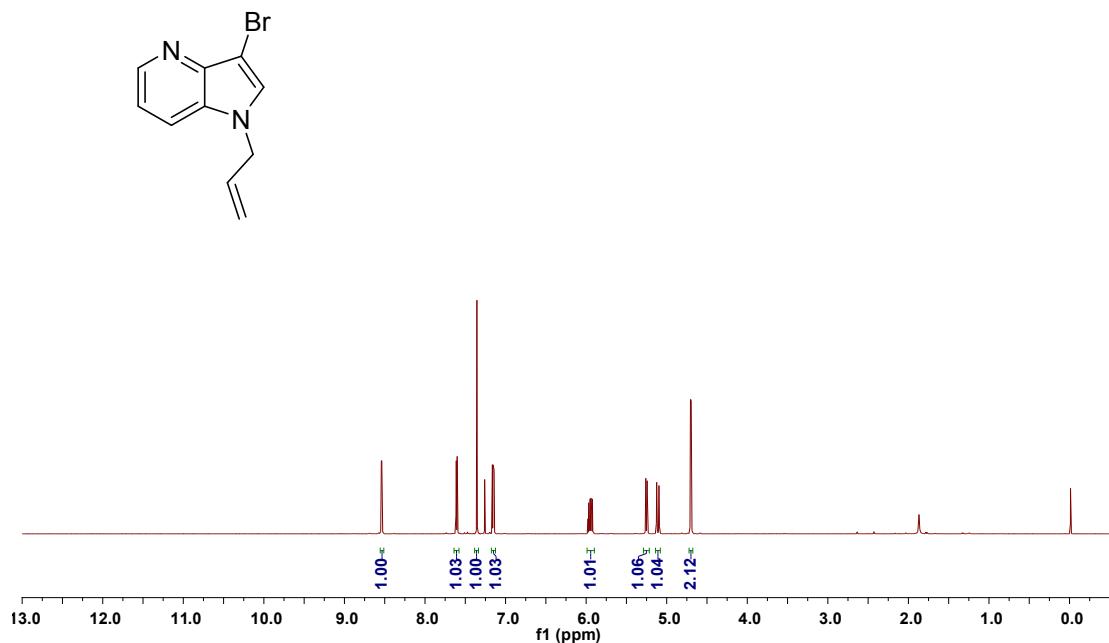
### <sup>1</sup>H NMR



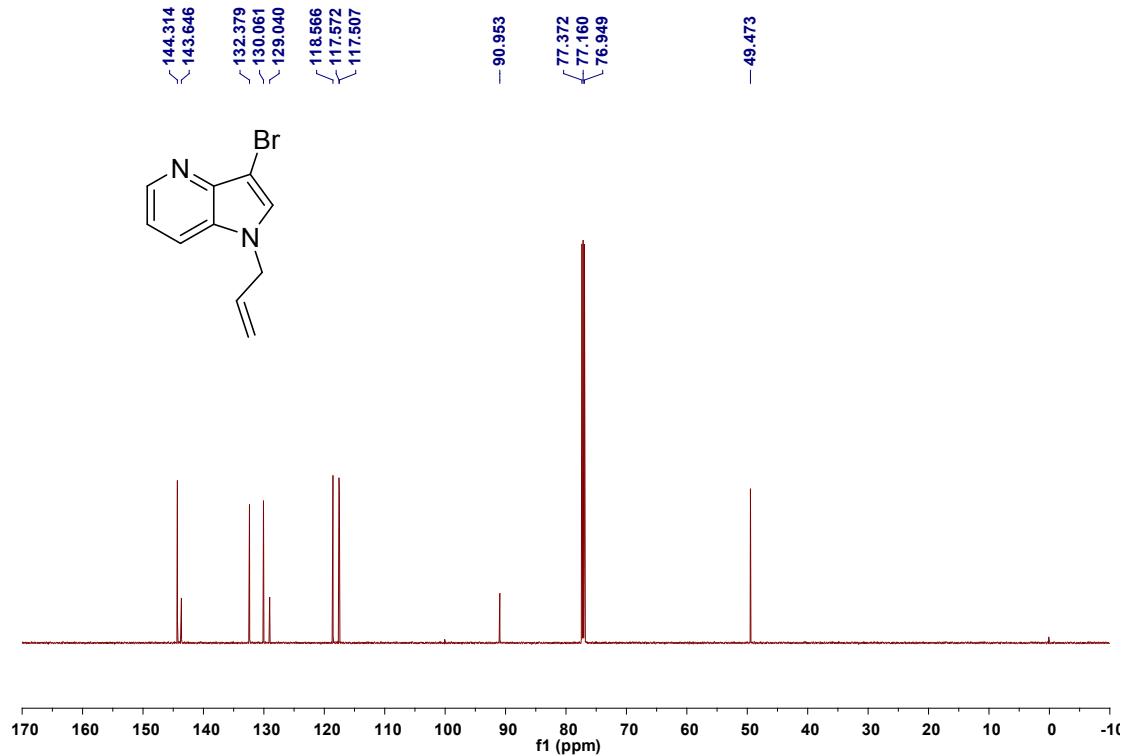
### <sup>13</sup>C NMR



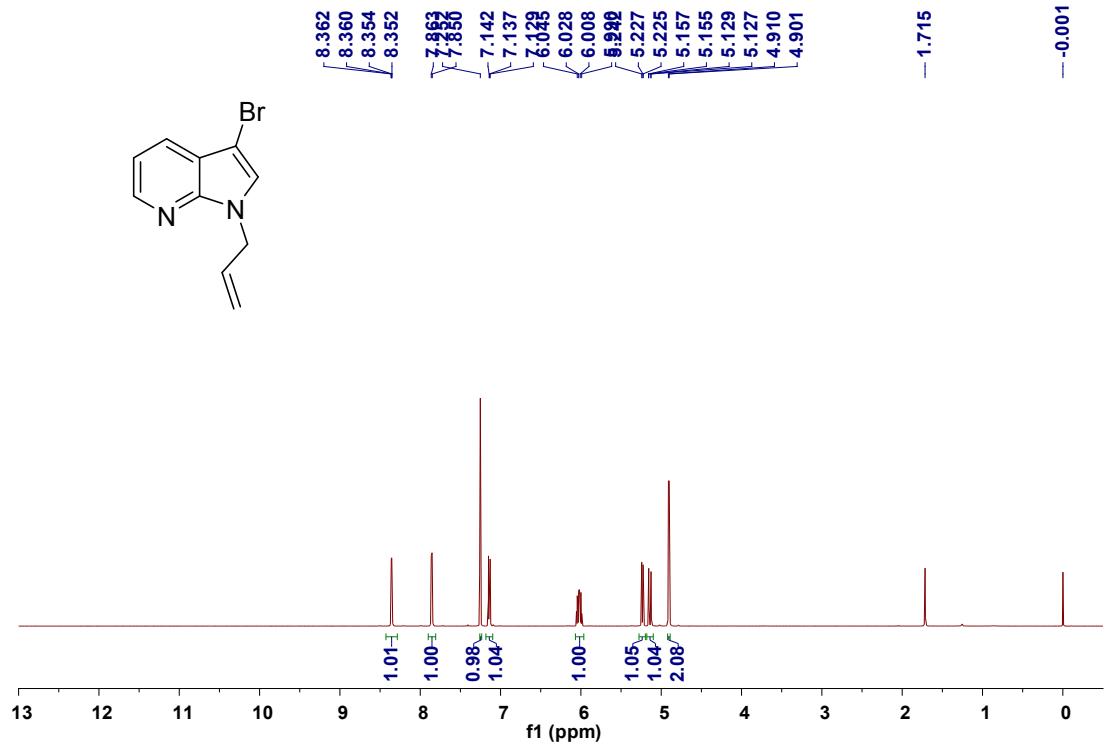
### <sup>1</sup>H NMR



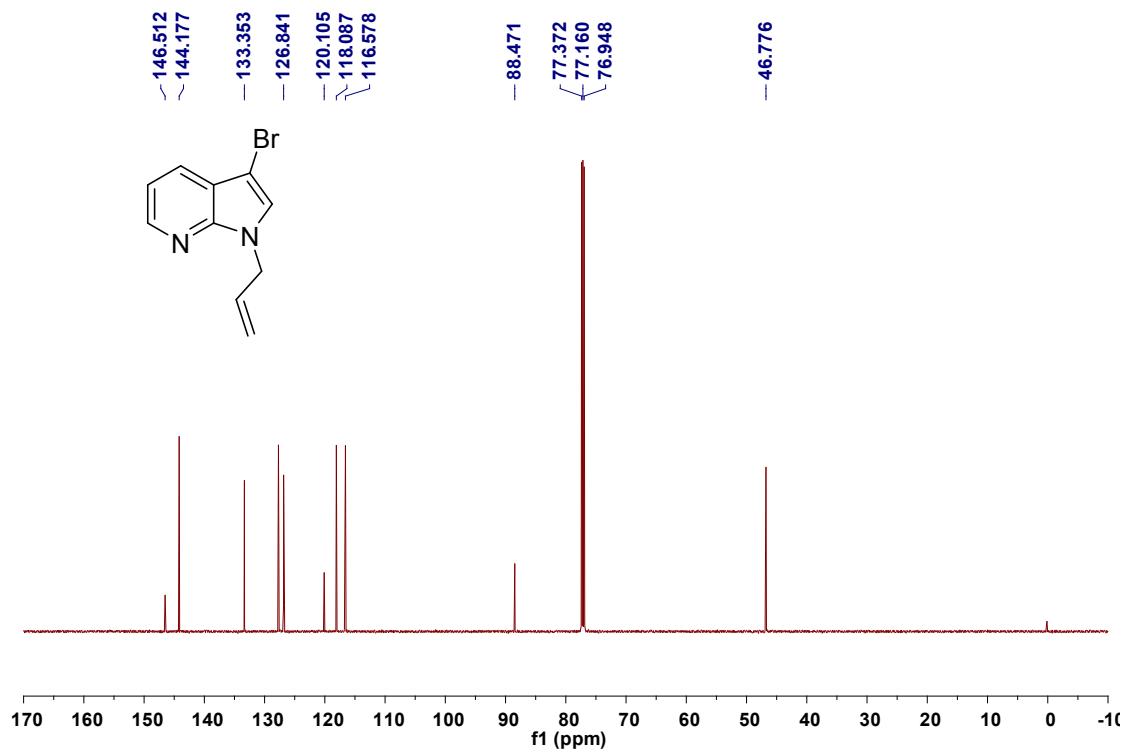
### <sup>13</sup>C NMR



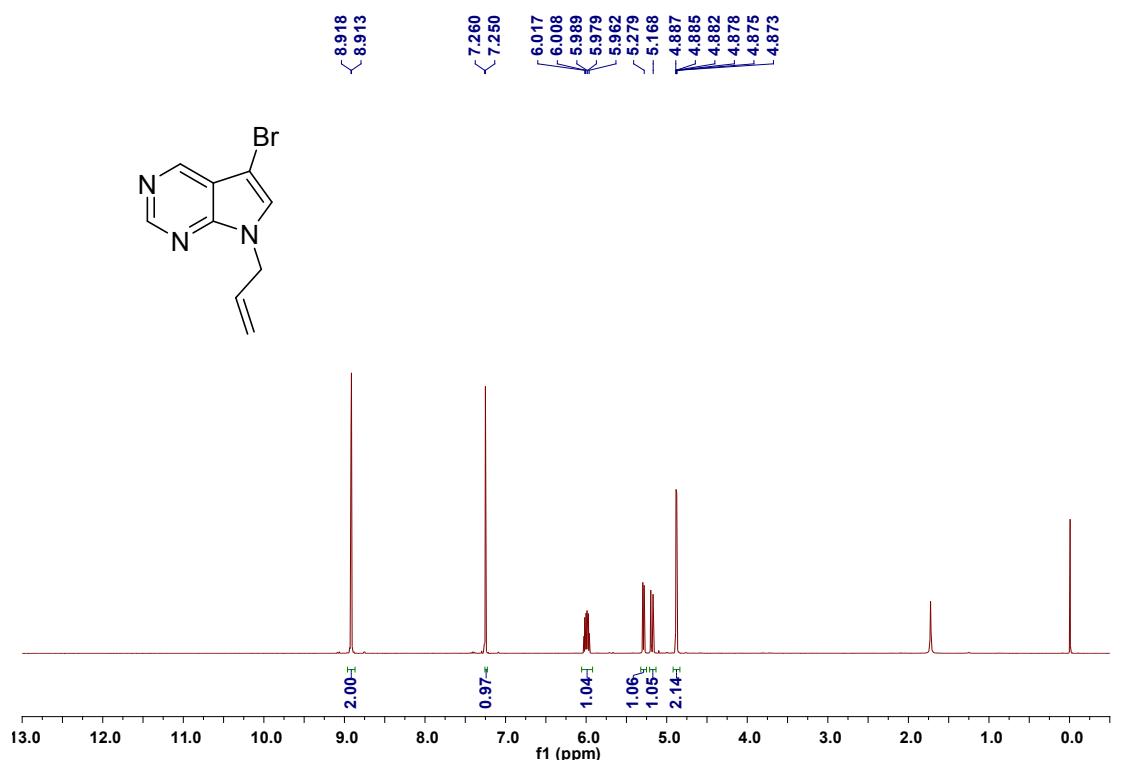
### <sup>1</sup>H NMR



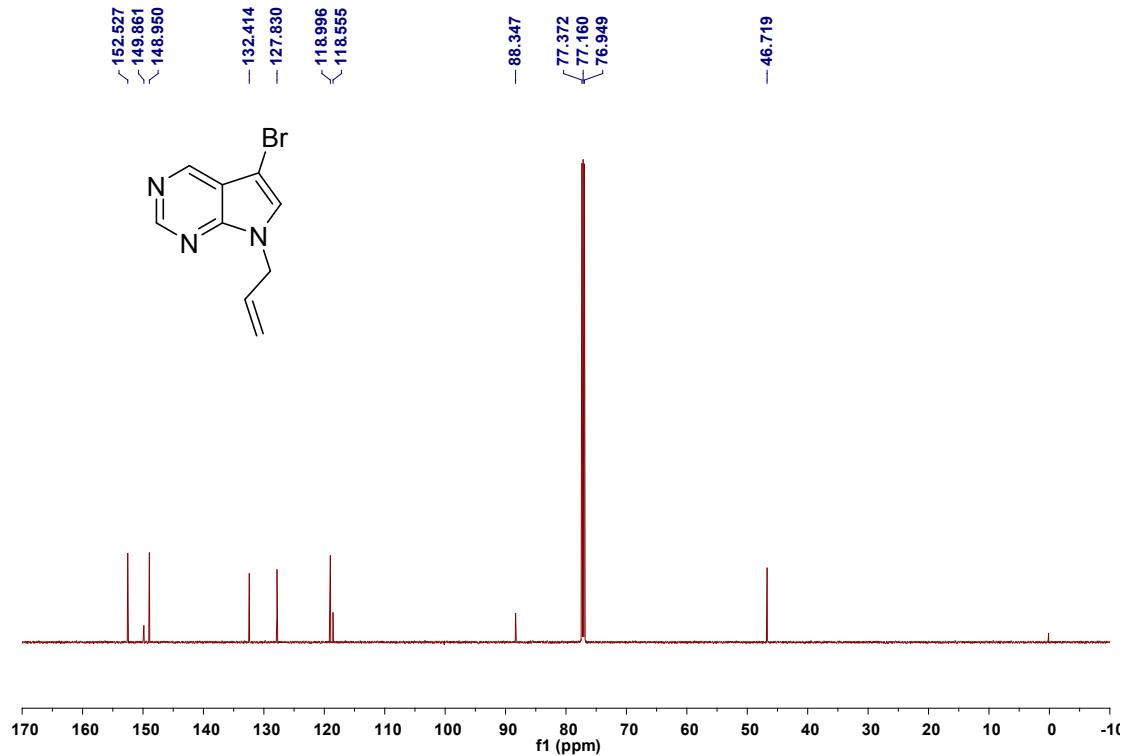
### <sup>13</sup>C NMR



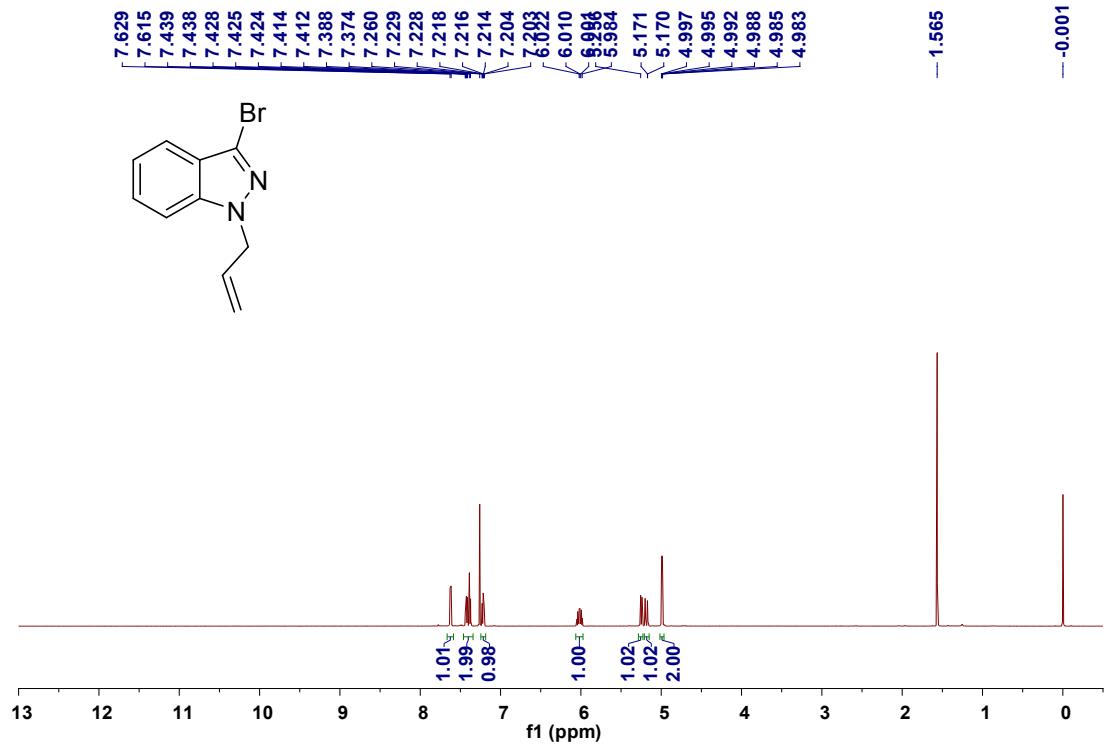
### <sup>1</sup>H NMR



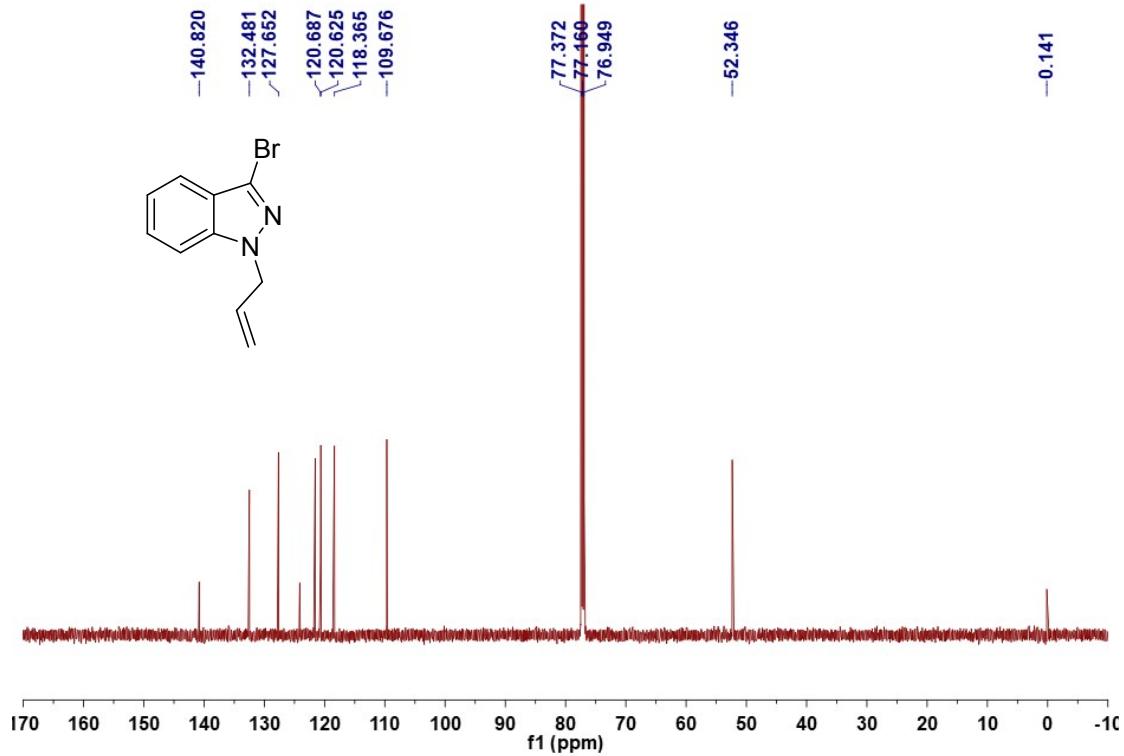
### <sup>13</sup>C NMR



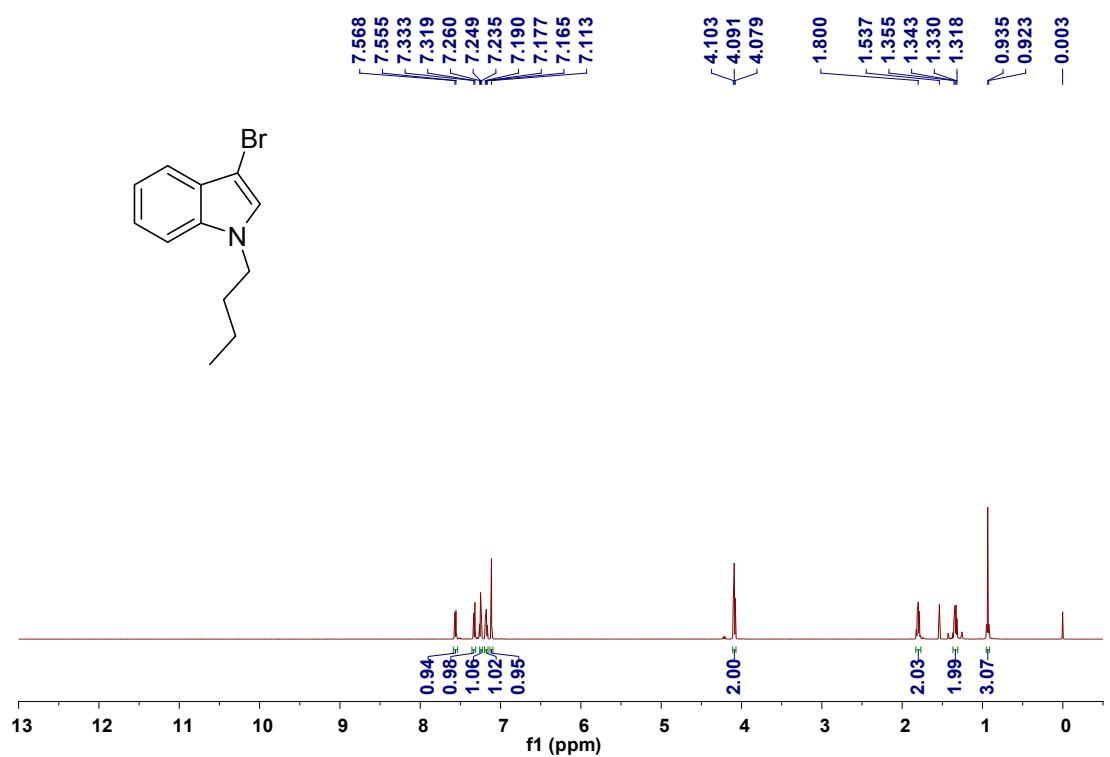
### <sup>1</sup>H NMR



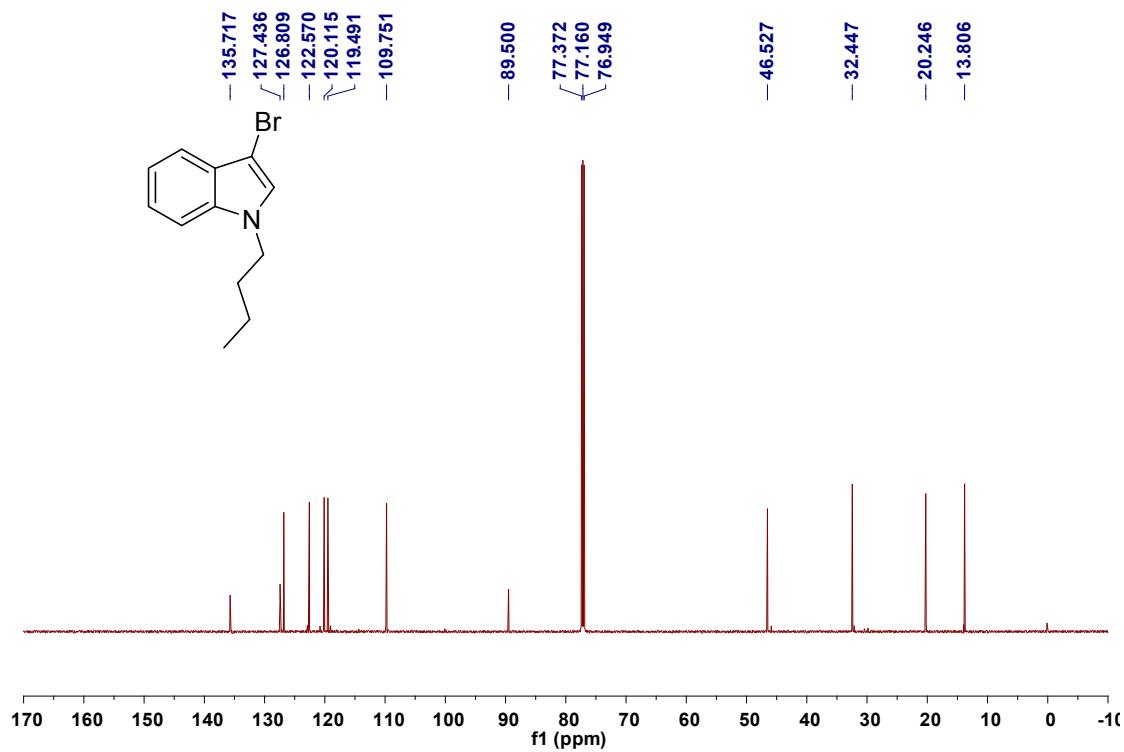
### <sup>13</sup>C NMR



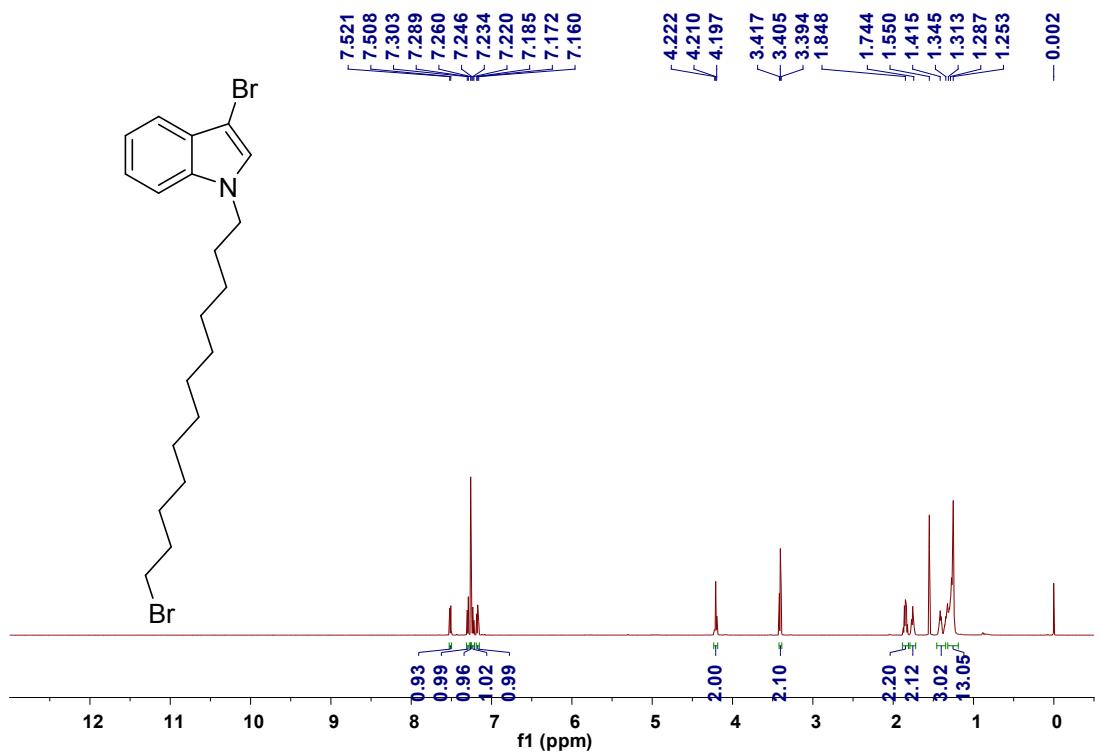
### <sup>1</sup>H NMR



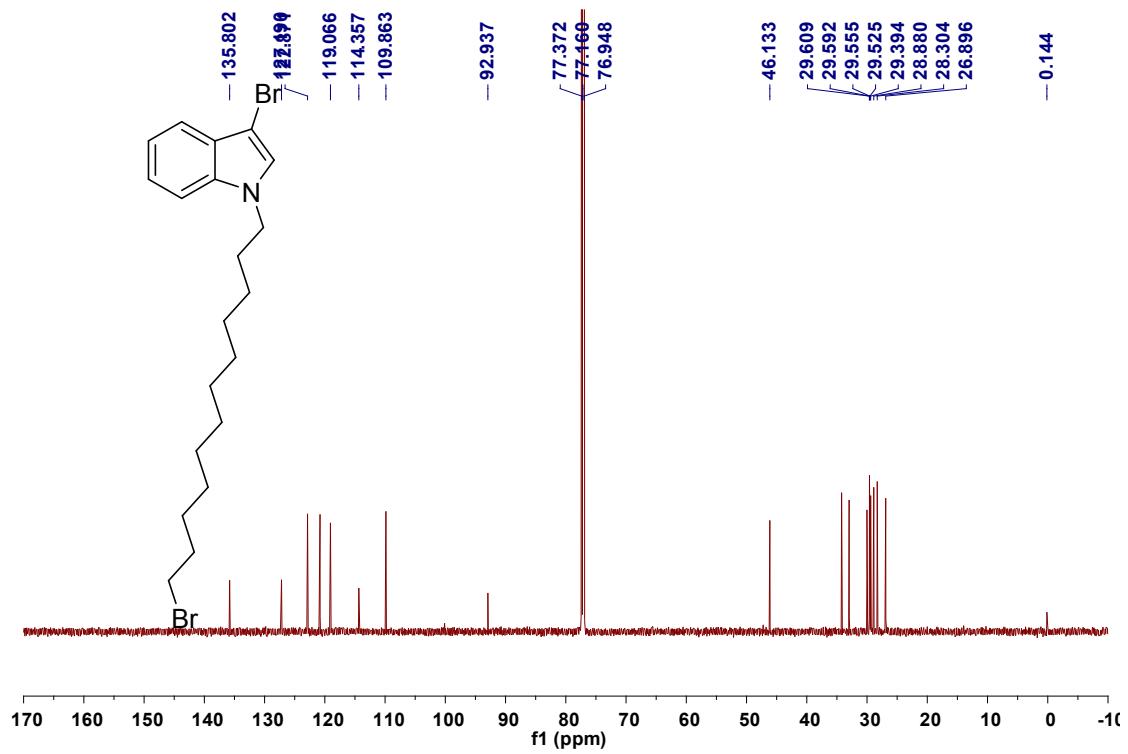
### <sup>13</sup>C NMR



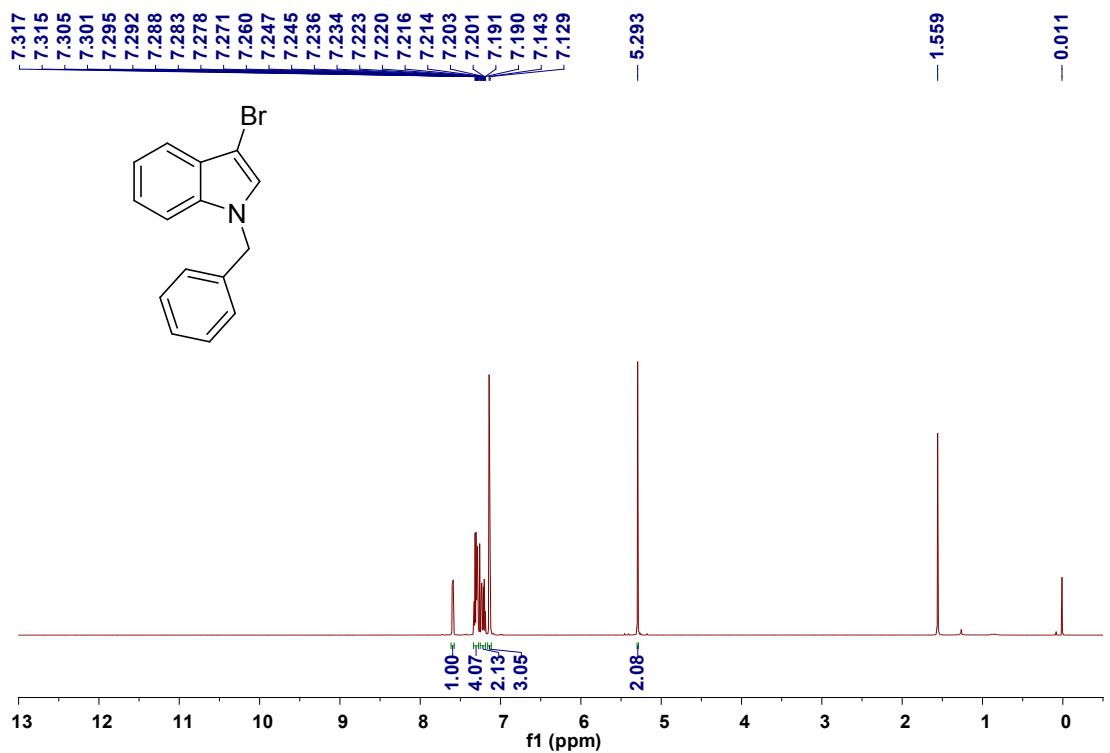
### <sup>1</sup>H NMR



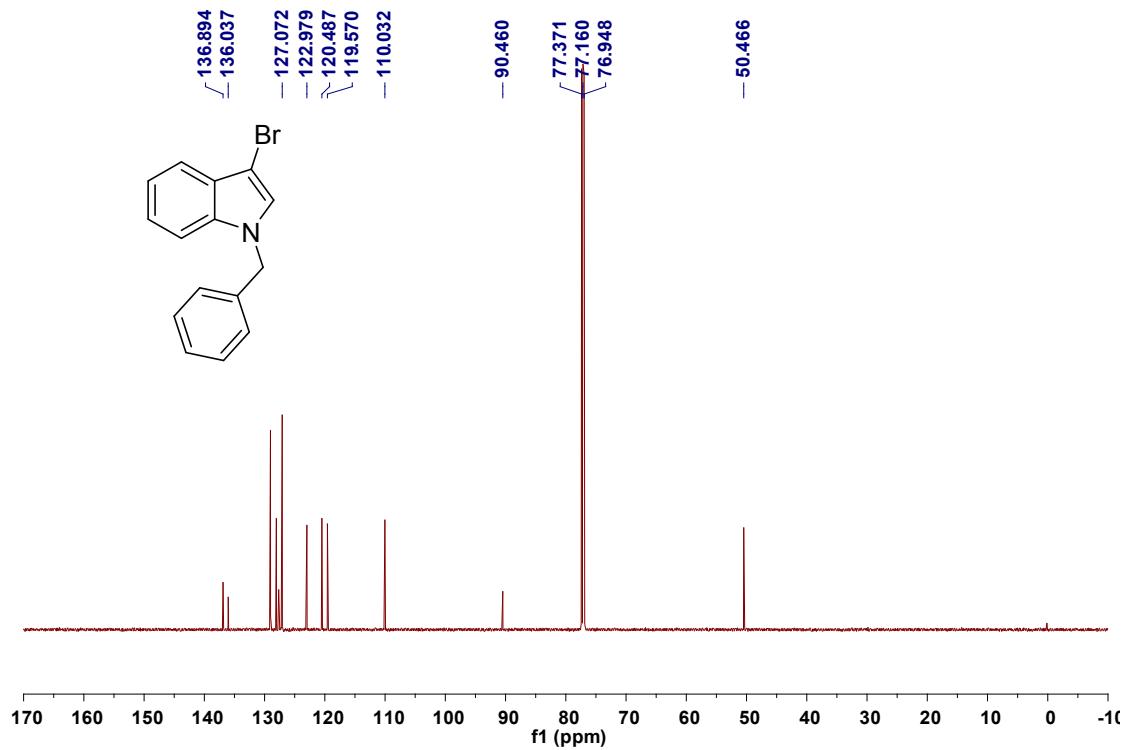
### <sup>13</sup>C NMR



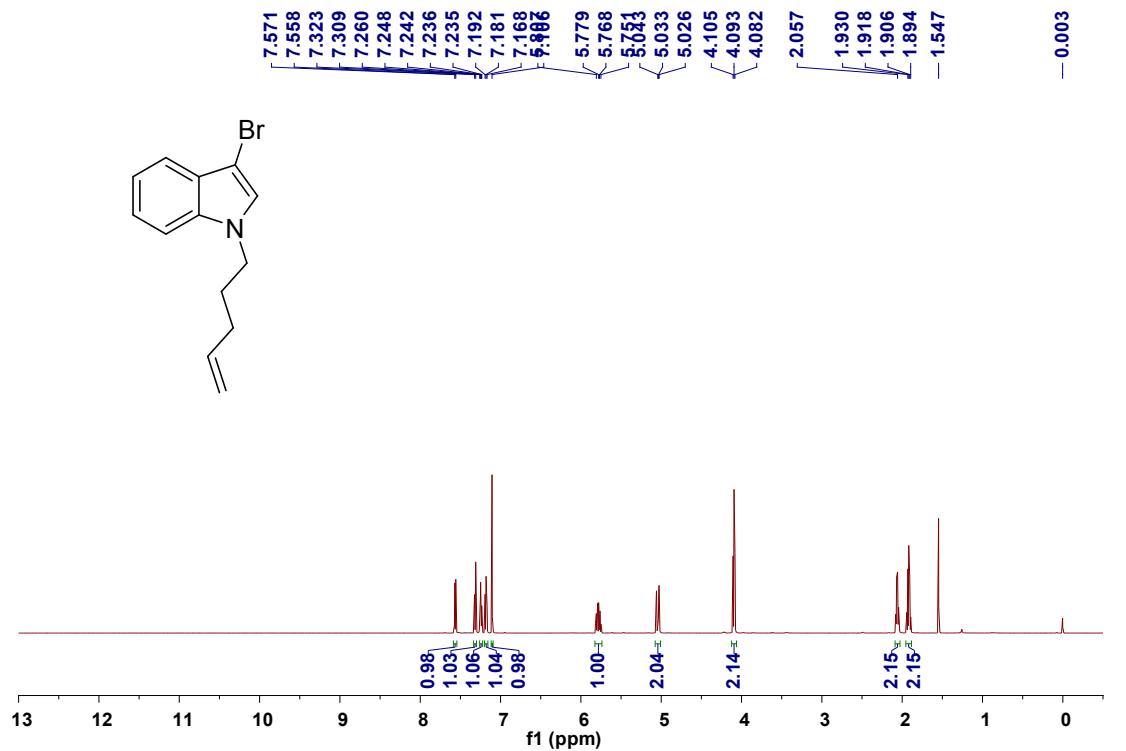
### <sup>1</sup>H NMR



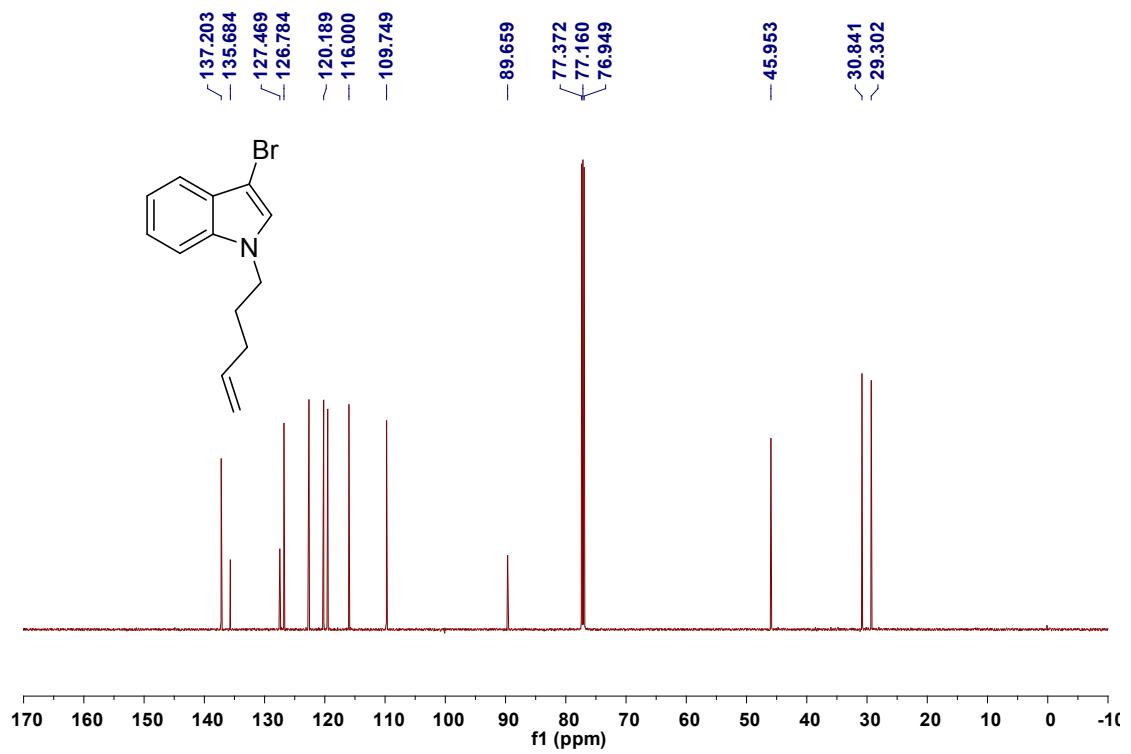
### <sup>13</sup>C NMR



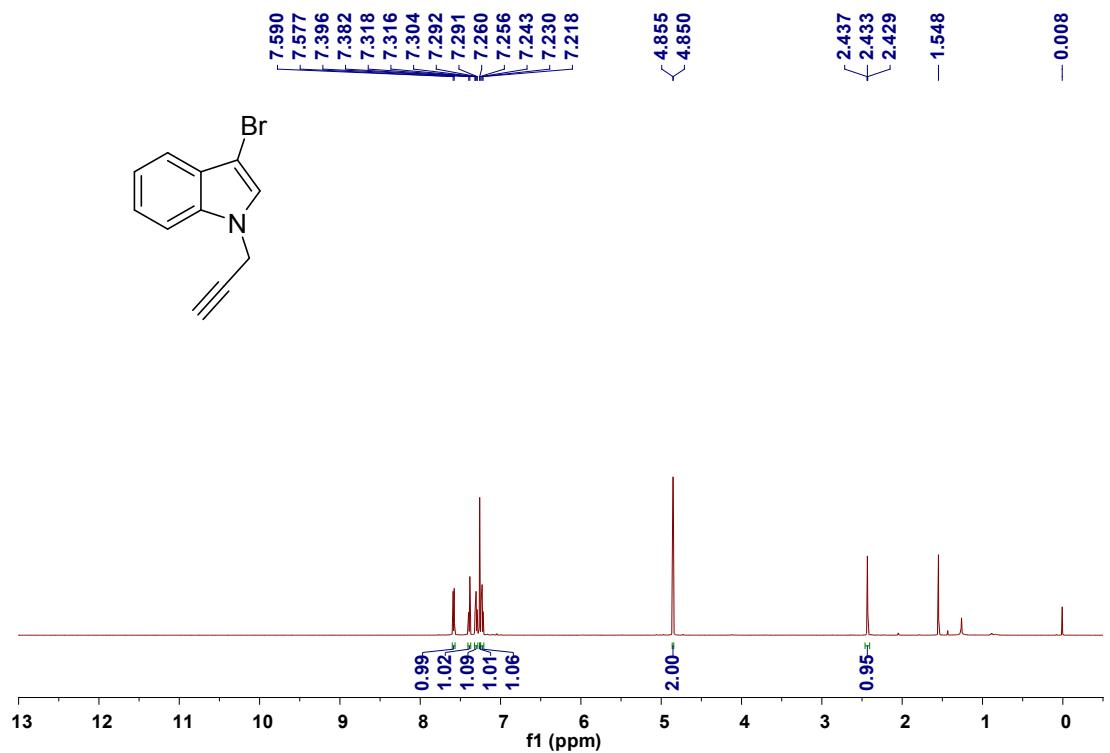
### <sup>1</sup>H NMR



### <sup>13</sup>C NMR



### <sup>1</sup>H NMR



### $^{13}\text{C}$ NMR

