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# Supporting Information:

# Divergence in CH-alkylation of indoles under Mn-catalysis

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## Contents

## 1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Toluene was refluxed over sodium/benzophenone followed by distillation under an argon atmosphere and was stored over sodium metal wire. Metal complexes and other chemicals used in this work were obtained from commercial sources and used without additional purification. Thin layer chromatography (TLC) was performed using silica gel pre-coated aluminum foil and was visualized on UV light at 254 nm or under iodine. Column chromatography was performed with $SiO_2$ (Silicycle Siliaflash F60 230-400 mesh) and active neutral aluminum oxide (50-260 mesh). $^{1}H$ NMR (200, 400 or 500 MHz), $^{13}C\{^{1}H\}$ NMR (126 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relatives to the residual signals of this solvent [δ 7.26 for $^{1}H$(chloroform-d), δ 77.00 for $^{13}C\{^{1}H\}$ (chloroform-d). Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was carried out using an HP-5 column (30 m, 0.25 mm, 0.25μ). Mass spectra were obtained on GCMS-QP 5000 instruments with ionization voltages of 70 eV. High-resolution mass spectra (HRMS) were obtained on a high-resolution mass spectra (HRMS) by fast atom bombardment (FAB) using a double-focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double-focusing mass analyzer) and Electrospray ionization mass spectra (ESI-MS) were recorded on an Agilent Mass Spectrometer (6200 series TOF/6500 series Q-TOF B.08.00), by infusing samples directly into the source using a manual method. The spray voltage was set at 4.2 kV and the capillary temperature at 80 °C. The composition of gases ($H_2$, m/z = 2; HD, m/z = 3 and $D_2$, m/z = 4) were determined using an online MS with an OmniStarTM Gas Analysis System GSD 320 (Pfeiffer) quadrupole mass spectrometer apparatus. The GC-MS analysis was recorded on an Agilent 7890B GC system equipped with a 5977B MSD Mass analyzer.

## 2. Experimental Section

### 2.1. General procedure for the synthesis of Mn(I)-PNP (*Mn-1 to Mn-4)* complexes

In a three-necked round-bottom flask (100 mL) under an argon atmosphere, Mn $(CO)_5Br$ (1.0 eq.) was suspended in toluene. Then, the PNP ligands (1.05 eq.) were added at room temperature. The resultant mixture was stirred for 10-15 minutes. Followed by stirring, the reaction mixture was kept at 100 °C for 16 h. After the completion of 16 h, the mixture was cooled down to room temperature and the removal of the solvent under reduced pressure resulted in the formation of a yellow solid. Further washing of this solid with n-octane (3×10 mL) and drying under a high vacuum provide the corresponding manganese complex (**Mn-1 to Mn-4**) in 90-95% yield. The complex was characterized using $^{1}H$ and $^{31}P$ NMR spectroscopy and the data obtained were well correlated with the literature reported.[S1]

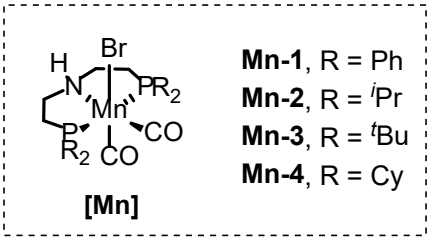



**Chart S1**. Mn-complexes used for the present study.

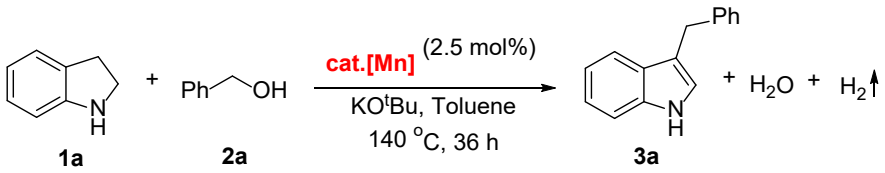
### 2.2. Synthesis of complex Mn-5:

The nitrogen-based tridentate ligand, 2,6-bis(morpholinomethyl)-pyridine (Py-$N^3$) was synthesized based on the previous report.[S2]The new $N^3$-manganese (II) pincer complex **5** was synthesized using Py-N3 ligand according to the procedure described in the literature and the complex was characterized using the state of the art analytical methods.[S3]

### 2.3. Optimization of Reaction Conditions

All the optimization studies were performed using molecularly defined complexes. Notably, in situ formed Mn-complexes did not provide concordant results.

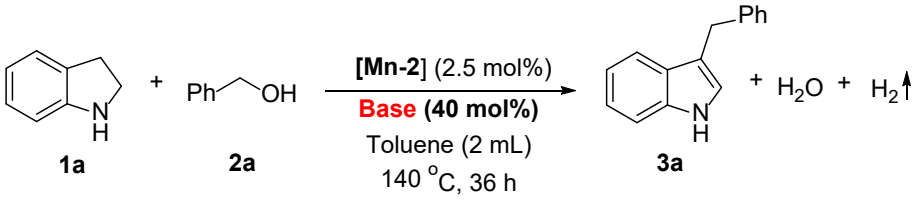
**Table S1:** Screening of manganese Complexes.[a]




| Entry | Mn Complexes | Yield of 3a (%)[b] |
|---|---|---|
| 1 | Mn-1 | 84 |
| 2 | **Mn-2** | **88** |
| 3 | Mn-3 | 72 |
| 4 | Mn-4 | 80 |
| 5 | Mn-5 | NR |

[a]Reaction conditions: Indoline **1a** (67 µL, 0.60 mmol), benzyl alcohol **2a** (93 µL, 0.90 mmol), KO$^t$Bu (27 mg, 40 mol%), Mn-complex (2.5 mol%), toluene (2 mL) in an open argon atmosphere for 36 h. NR = No reaction. [b]Yield of the isolated product.

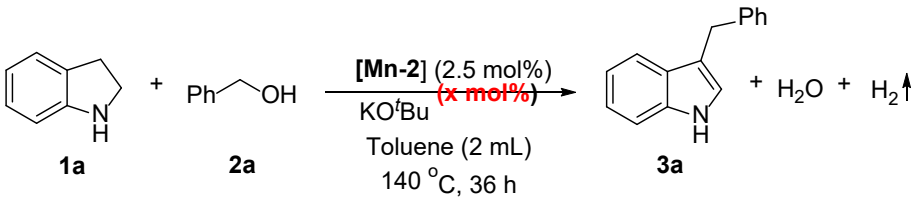
**Table S2:** Screening of Base.[a]




| Entry | Base (40 mol %) | Yield of 3a (%)[b] |
|---|---|---|
| 1 | KO$^t$Bu | **88** |
| 2 | LiO$^t$Bu | ND |
| 3 | NaO$^t$Bu | 19[c] |
| 4 | KHMDS | 22[c] |
| 5 | $Cs_2CO_3$ | 71 |

[a]Reaction conditions: Indoline **1a** (67 µL, 0.60 mmol), benzyl alcohol **2a** (93 µL, 0.90 mmol), Base (40 mol %), cat.**[Mn-2]** (2.5 mol%), toluene (2 mL) in open Argon atmosphere for 36 h. [b]Yield of the isolated product. [c]Yields of product **3a** were determined by GC using *m*-xylene as an internal standard, ND = not detected.

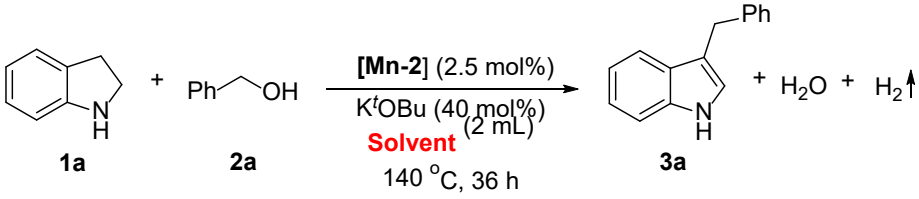
**Table S3:** Screening of Amount of Base.[a]




| Entry | KO$^t$Bu (x mol %) | Yield of **3a** (%)[b] |
|---|---|---|
| 1 | 10 | 20 |
| 2 | 20 | 43 |
| 3 | 40 | 88 |
| 4 | 50 | 89 |
| 5 | 100 | 71[c] |

[a]Reaction conditions: Indoline **1a** (67 µL, 0.60 mmol), benzyl alcohol **2a** (93 µL, 0.90 mmol), KO$^t$Bu (**x** mol %), cat. **[Mn-2]** (2.5 mol%), toluene (2 mL) in open Argon atmosphere for 36 h. [b]Yield of the isolated product. [c]Formation of BIM was also observed (~10%).

**Table S4:** Screening of Solvent.[a]




| **Entry** | **Solvent** | **Yield of 3a (%)**[b] |
|---|---|---|
| 1 | Diphenyl ether | 70 |
| 2 | n-Octane | 42 |
| 4 | 1,4-Dioxane | 29 |
| 5 | Toluene | 84 (**88**)[c] |

[a]Reaction conditions: Indoline **1a** (67 µL, 0.60 mmol), benzyl alcohol **2a** (93 µL, 0.90 mmol), KO$^t$Bu (27 mg, 40 mol%), cat.**[Mn-2]** (2.5 mol%), solvent (2 mL) in open Argon atmosphere for 36 h. [b]Yield of the isolated product. [c]Yields of product **3a** were determined by GC using *m*-xylene as an internal standard.

### 2.4. General procedure for the C3-alkylation of indoline with primary alcohol using Mn(I)-PNP complex

In an oven-dried screw cap reaction tube (15 mL), indoline (67 μL, 0.60 mmol), benzyl alcohol derivatives (0.90 mmol), KO$^t$Bu (27 mg, 40 mol%), cat. [**Mn-2**] (2.5 mol%), and toluene (2 mL) were added in a gentle stream of argon. Then the reaction mixture was stirred with a magnetic stirring bar at 140 $^o$C (oil-bath temperature) for 36 hours. After completion of the reaction the crude mixture was filtered through a celite filter and washed with ethyl acetate (3×5 mL), followed by the solvent being removed under vacuum, and finally, the residue was purified by silica gel column chromatography (230- 400 mesh size) using petroleum-ether and ethyl acetate as an eluent to give C3-alkylated indoline product.

### 2.5. General procedure for the C3-alkylation of indole with primary alcohol using Mn(I)-PNP complex.

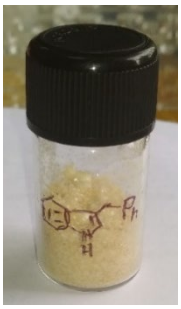
In an oven-dried screw cap reaction tube (15 mL), indole (0.60 mmol), benzyl alcohol derivatives (0.90 mmol), KO$^t$Bu (27 mg, 40 mol%), cat. [**Mn-2**] (2.5 mol%), and toluene (2 mL) were added in a gentle stream of argon. Then the reaction mixture was stirred with a magnetic stirring bar at 140 $^o$C (oil-bath temperature) for 36 hours. After completion of the reaction the crude mixture was filtered through a celite filter and washed with ethyl acetate (3×5 mL), followed by the solvent being removed under vacuum, and finally, the residue was purified by silica gel column chromatography (230- 400 mesh size) using petroleum-ether and ethyl acetate as eluent to C3-alkylated indole product.

### 2.6 General procedure for synthesis of bis(3-indolyl)methanes from indoles and alcohols using Mn(II)-NNN complex

To an oven-dried schlenk tube, indole (0.5 mmol, 1 eq.), alcohol (0.5 mmol, 1 eq.), cat. **[Mn-5]** catalyst (3 mol%), KO$^t$Bu (0.25 mmol, 50 mol%), and toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 130 °C (oil-bath temperature) for 24 h. Then, the reaction was quenched with water (2 mL) and extracted with dichloromethane/ethyl acetate (3x4 mL). The combined organic layer was dried over anhydrous $Na_2SO_4$ and the solvent

was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

### 2.7. Gram scale synthesis



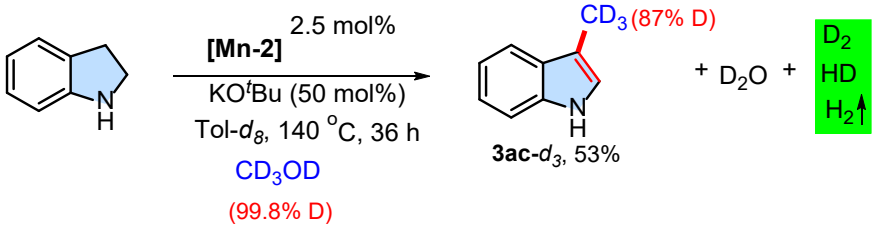
To demonstrate the practical utility of the present Mn-catalyzed synthesis of 3-alkyl-1*H*-indole derivatives, a larger-scale synthesis has been performed. To a 100 mL oven-dried seal tube, indoline (672 µL, 6.0 mmol), benzyl alcohol (931 µL, 9.0 mmol), KO$^t$Bu (269 mg, 40 mol%), cat. [**Mn-2**] (2.5 mol%), 20 mL of dry toluene were added under a continuous flow of argon gas. Then, the reaction tube was placed in a preheated oil bath temperature maintained at 140 °C (oil-bath temperature) with constant stirring. After 44 h, the reaction mixture was cooled to room temperature, water (15 mL) was added to dilute the mixture, and extracted with dichloromethane (3 × 10 mL). The resultant organic layer was dried over anhydrous $Na_2SO_4$, and the solvent was evaporated under reduced pressure. The crude residue was purified further by silica gel (230–400 mesh) column chromatography using a mixture of petroleum ether and EtOAc as the eluent (20:3 ratio).

### 2.8. Synthesis of Deuterated benzyl alcohol 2a-$d_2$

To an oven-dried 10 mL screw-capped vial, commercially available Ru-MACHO (3 mol%), benzyl alcohol (1 mmol), NaOH (0.20 mmol, 20 mol%), and deuterium oxide (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 120 $^o$C (oil-bath temperature) for 24 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous $Na_2SO_4$ and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using Petroleum ether/EtOAc = 95:5 as an eluting system to give deuterated benzyl alcohol **2a**-$d_3$ (94% deuterated).[S4]

## 2.9. Deuterium labeling experiments ($D_2$ and HD gas detection)

### 2.9.1 C3-methylation of indoline using deuterated MeOH($d_4$)



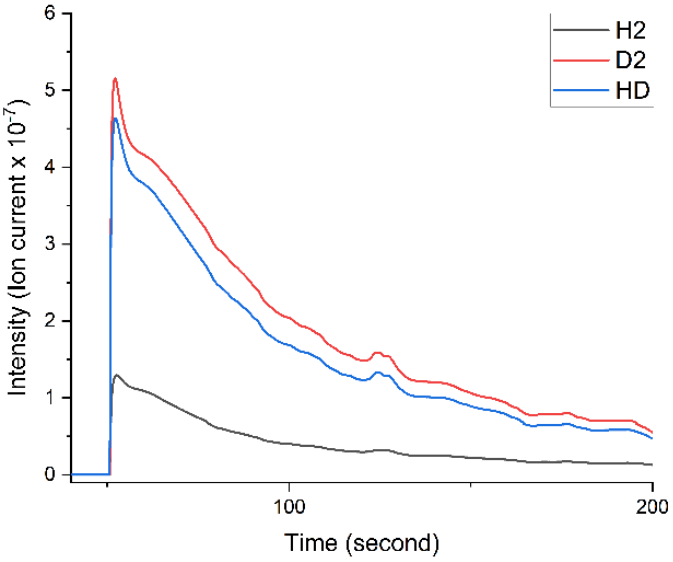




**Fig S1**. $D_2$, HD and $H_2$ gas detection by gasometer (from indoline and MeOH-$d_4$ reaction).

**Reaction conditions:** Indoline **1a** (0.25 mmol), Methanol-$d_4$ (1.25 mmol), KO$^t$Bu (40 mol%), cat. [**Mn-2**] (2.5 mol%), toluene-$d_8$ (1.5 mL), glass tube with aluminum PTFE cap, argon atmosphere, 140°C for 36 h.

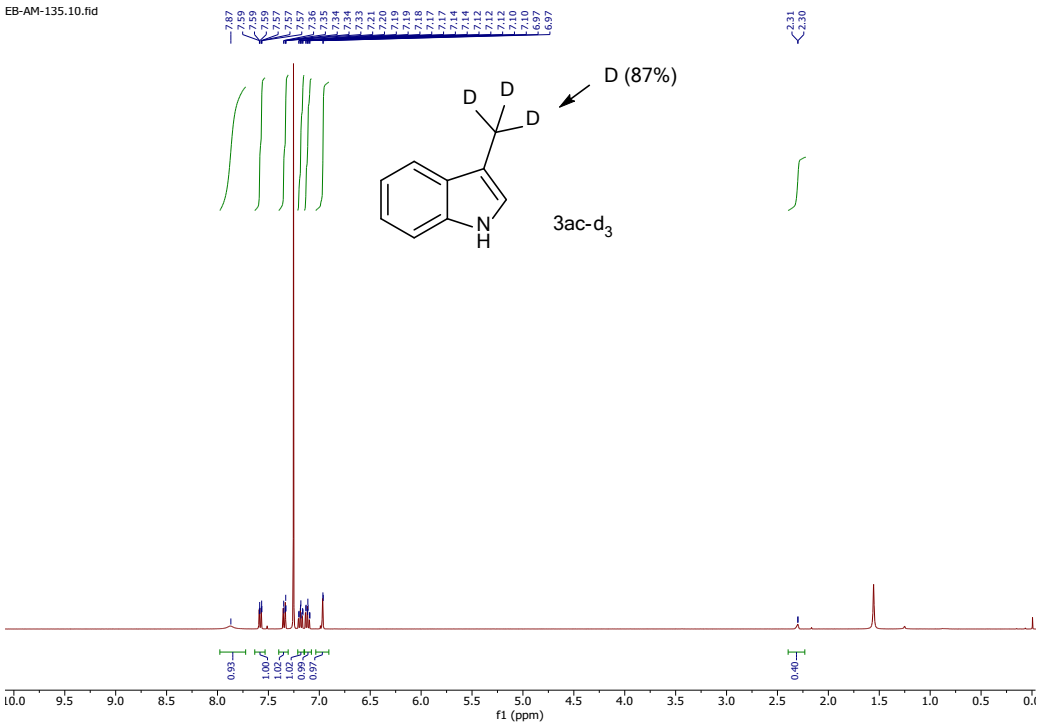



**Fig S2.** $^{1}$H NMR of **3ac**-$d_3$

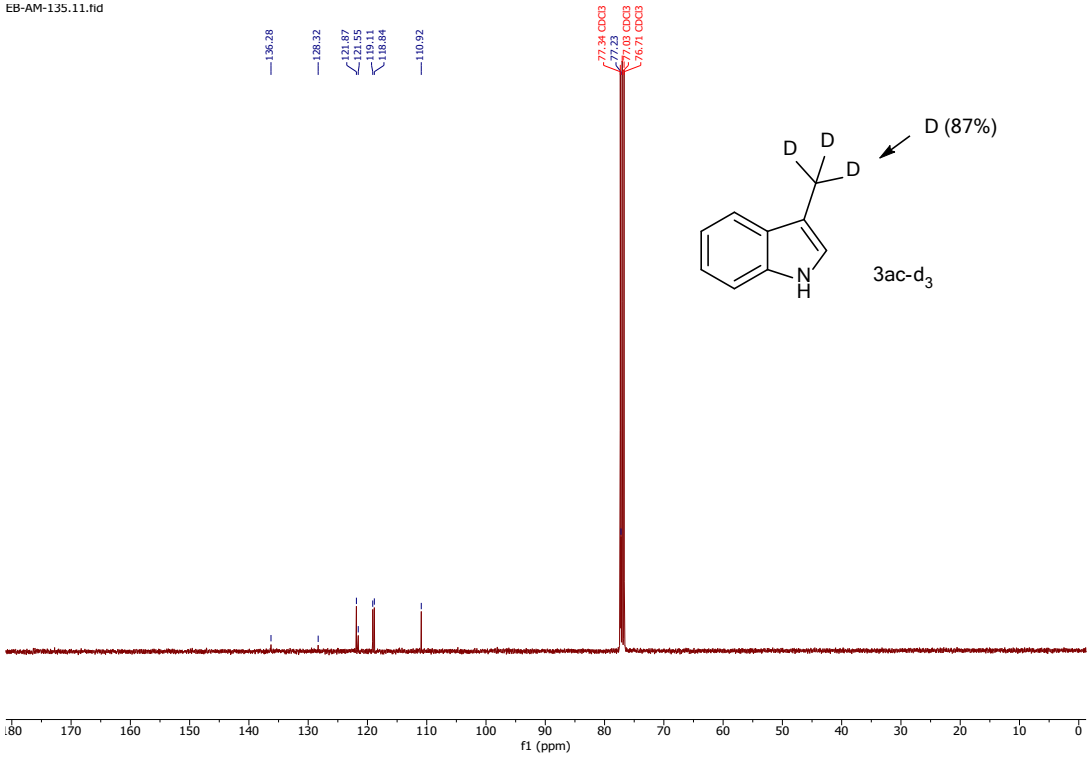



**Fig S3.** $^{13}$C NMR of **3ac**-$d_3$

### 2.9.2 C3-ethylation of indoline using deuterated EtOH($d_6$)

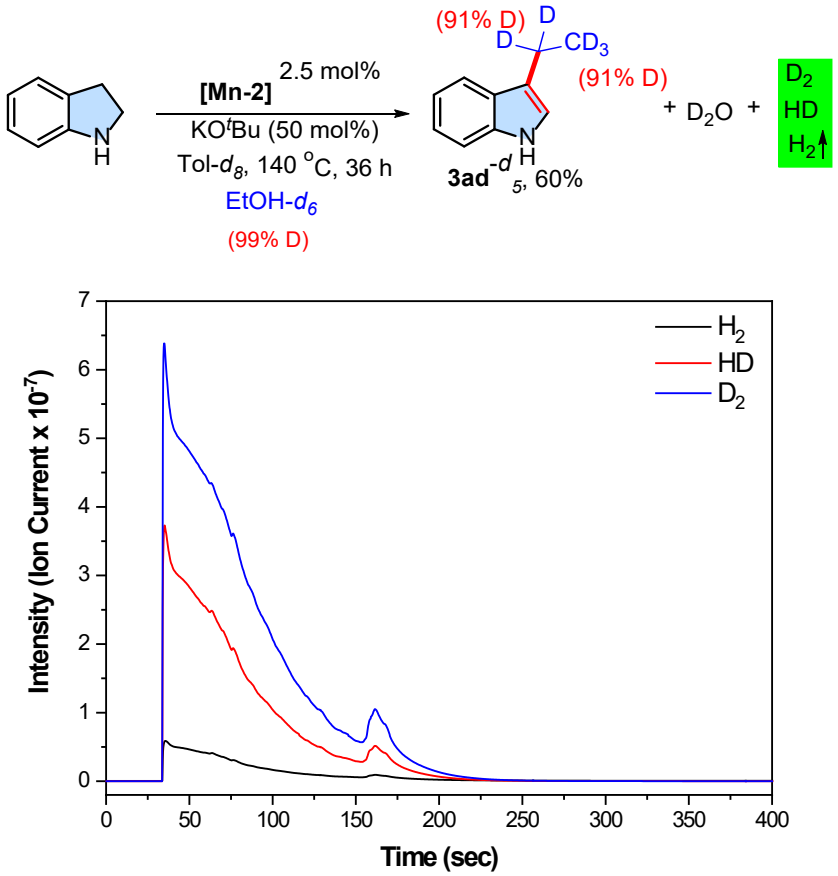



**Fig S4**. $D_2$, HD and $H_2$ gas detection by gasometer (from Indoline and EtOH-$d_6$ reaction).

**Reaction Conditions:** Indoline (0.25 mmol), ethanol-$d_6$ (1.25 mmol), KO$^t$Bu (50 mol%), cat. [**Mn-2**] (2.5 mol%), toluene (1.5 mL), glass tube with aluminum PTFE cap, argon atmosphere, 140 °C for 36 h.

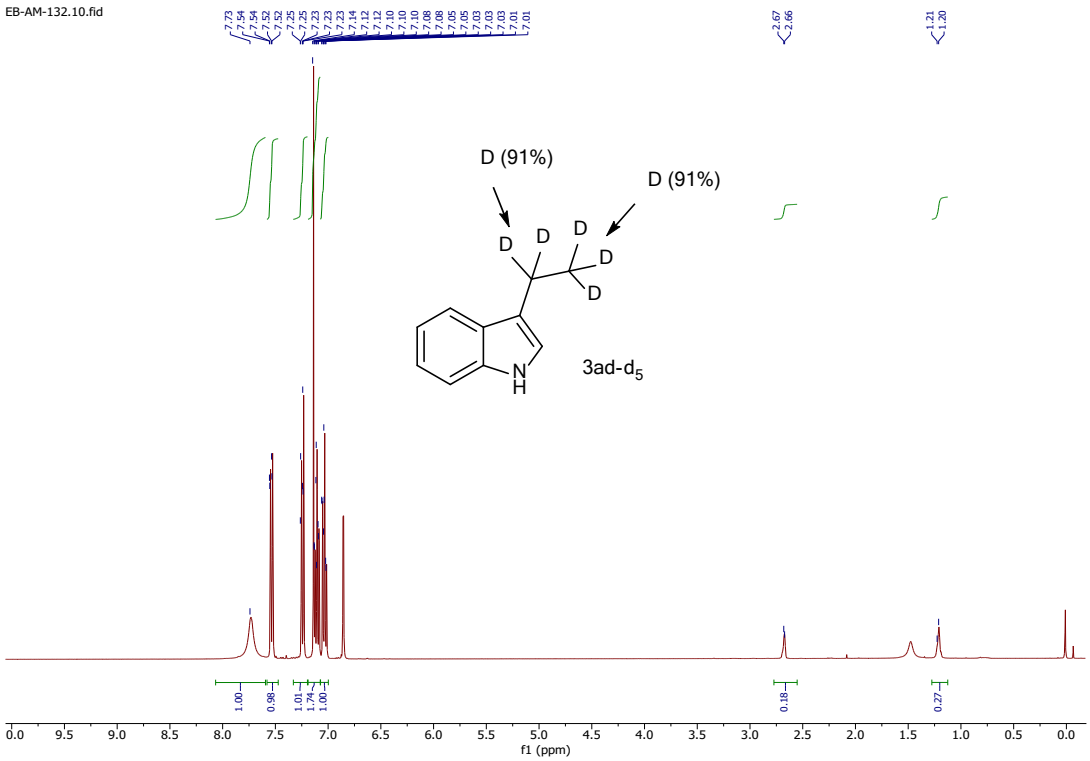



**Fig S5.** $^{1}$H NMR of **3ad-$d_5$**

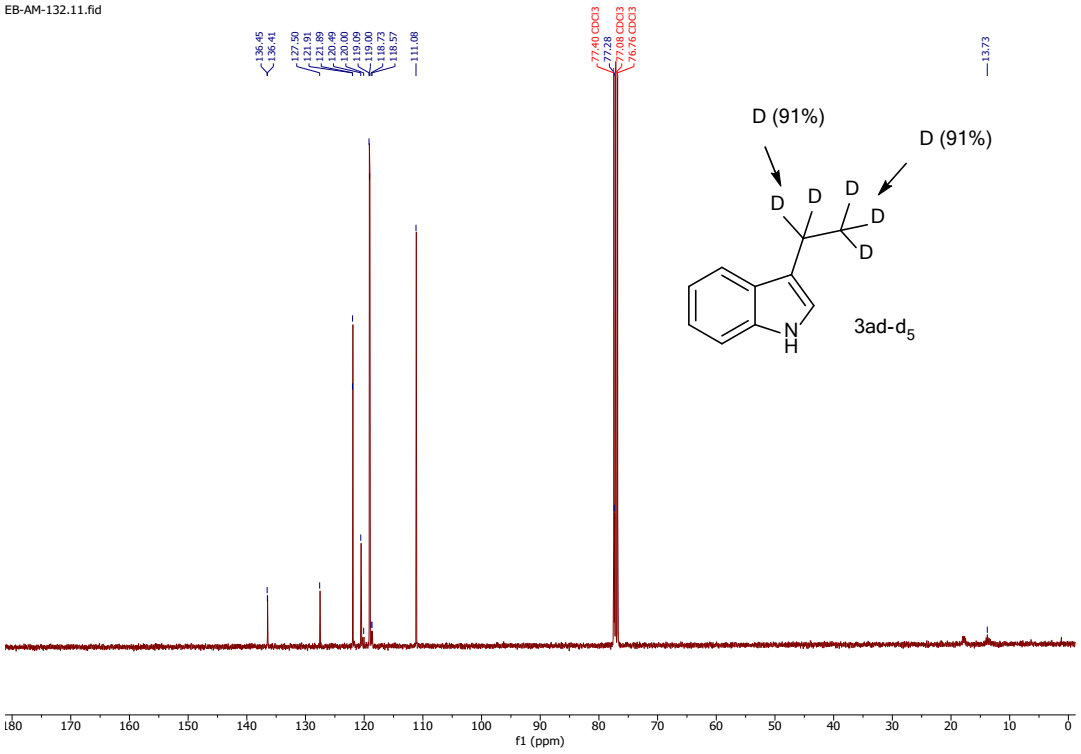
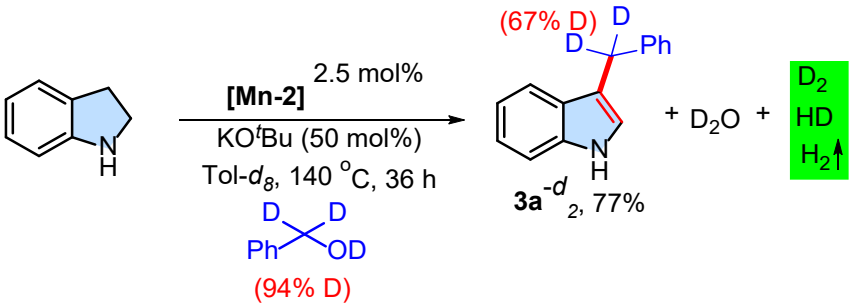



**Fig S6.** $^{13}$C NMR of **3ad-$d_5$**

### 2.9.3 C3-benzylation of indoline using deuterated $PhCH_2OH$-($d_3$)



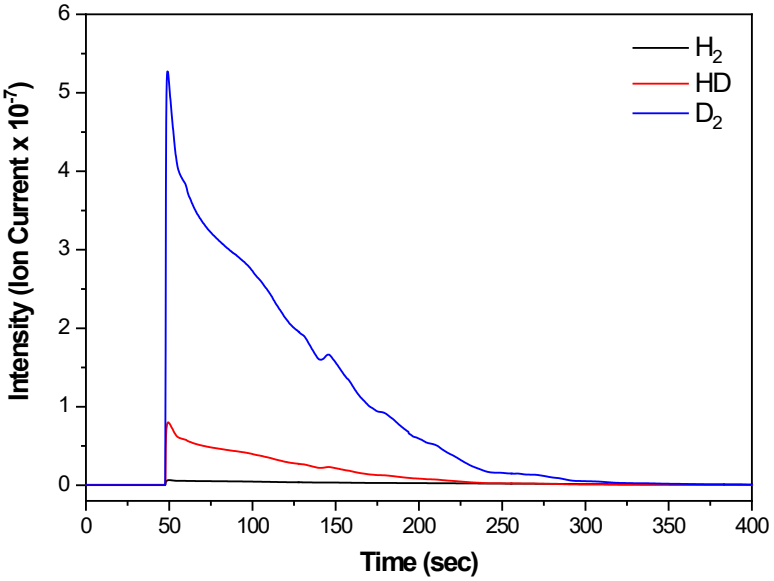




**Fig S7**: $D_2$, HD and $H_2$ gas detection by gasometer (from Indole and Benzyl alcohol-$d_2$ reaction).

**Reaction Conditions:** Indole **1a** (0.25 mmol), Benzyl alcohol **2a**-$d_3$ (0.375 mmol), KO$^t$Bu (40 mol%), cat. [**Mn-2**] (2.5 mol%), toluene (2 mL), glass tube with aluminum PTFE cap, argon atmosphere, 140°C for 36 h.

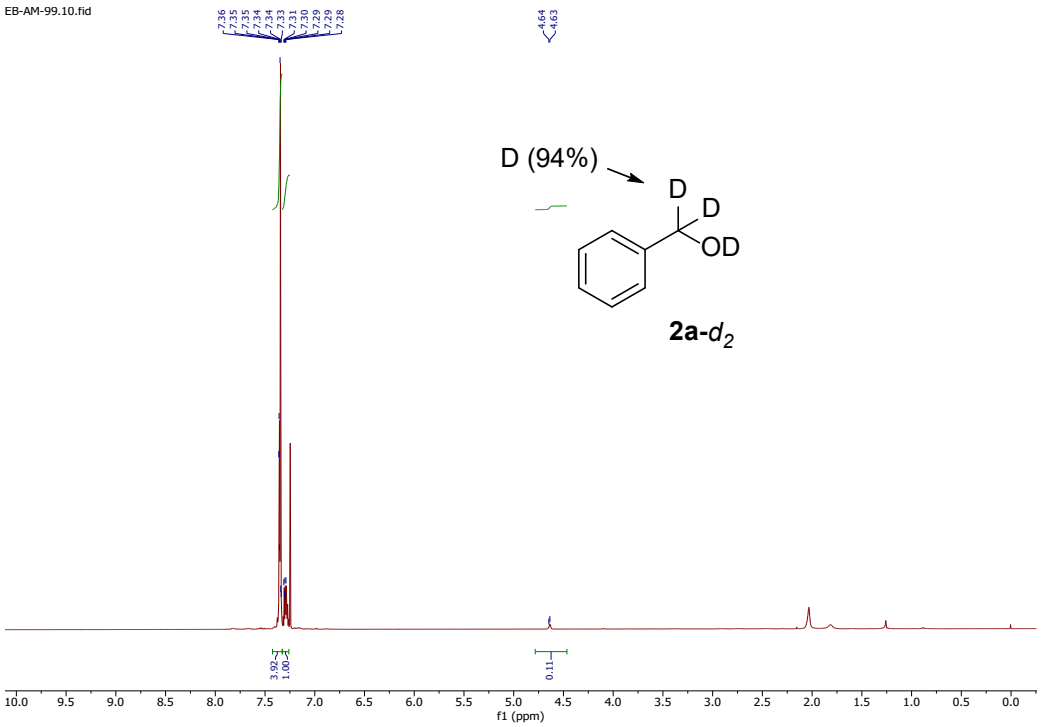



**Fig S8.** $^1$H NMR of **2a**-$d_2$

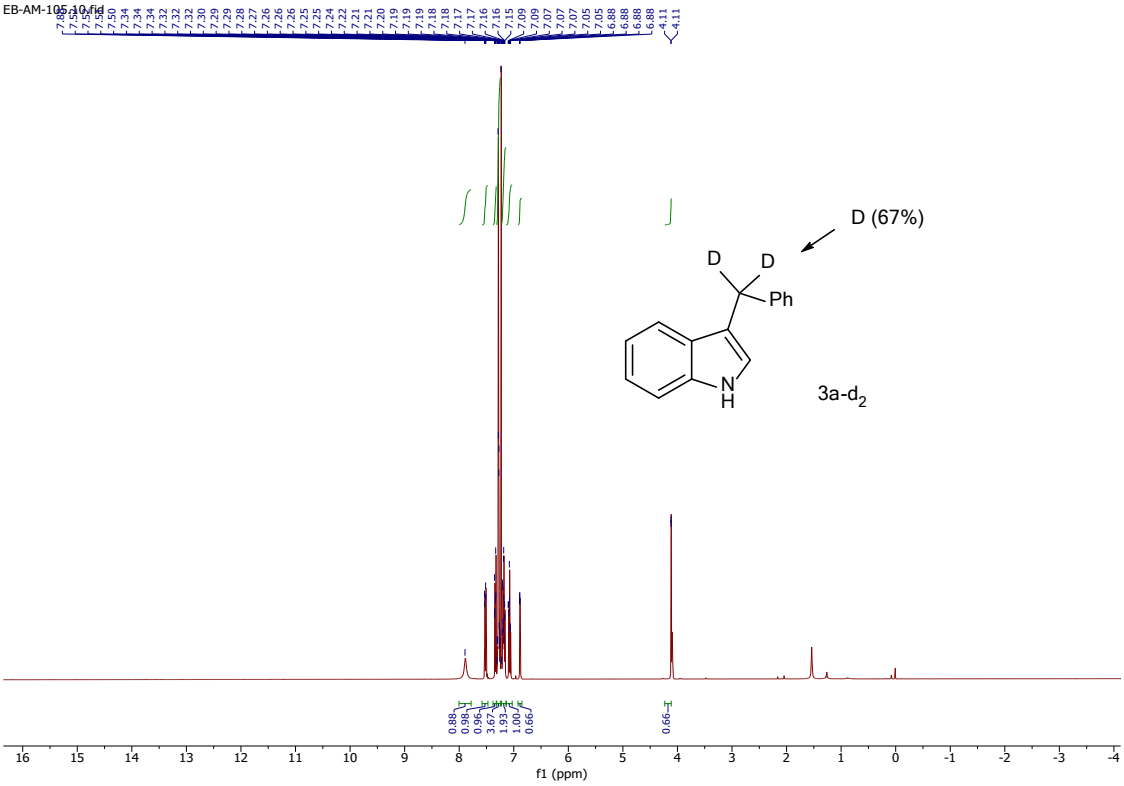



**Fig S9.** $^1$H NMR of **3a**-$d_2$

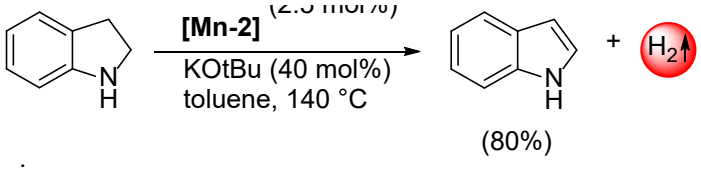

We have determined the qualitative composition of gases ($H_2$, m/z = 2; HD, m/z = 3 and $D_2$, m/z = 4) using an on-line MS with an OmniStarTM Gas Analysis System GSD 320 (Pfeiffer) quadrupole mass spectrometer apparatus.

**Fig S10**. Photograph of OmniStarTM Gas Analysis System GSD 320 (Pfeiffer) quadrupole mass spectrometer apparatus used for the analysis of gases based on following their masses.

## 3. Mechanistic Investigation

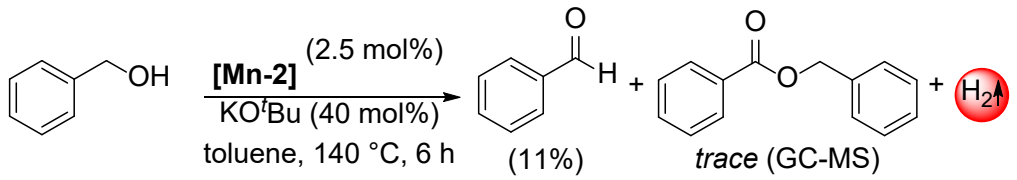
### 3.1 Dehydrogenation pathway

In an oven-dried screw cap reaction tube (15 mL), indoline (67 µL, 0.60 mmol), KO$^t$Bu (27 mg, 40 mol%), cat. [**Mn-2**] (2.5 mol%), and toluene (2 mL) was added in a gentle stream of argon. Then the reaction mixture was stirred with a magnetic stirring bar at 140 °C for 36 h. After completion of the reaction, the crude mixture was filtered through a celite filter and washed with ethyl acetate, followed by the solvent being removed under vacuum and finally the residue was purified by silica gel column chromatography (230–400 mesh size) using petroleum-ether and ethyl acetate as an eluent to give the corresponding indole with 80% yield.




**Scheme S1**. Mn-catalyzed dehydrogenation of indoline.

In an oven-dried screw cap reaction tube (15 mL), benzyl alcohol (0.90 mmol), KO$^t$Bu (27 mg, 40 mol%), cat. [**Mn-2**] (2.5 mol%), and toluene (2 mL) were added in a gentle stream of argon. Then the reaction mixture was stirred with a magnetic stirring bar at 140 °C for 6 h. After completion of the reaction, the crude mixture was filtered through a celite filter and washed with ethyl acetate. The crude reaction was analysed using GC and GC-MS.




**Scheme S2**. Mn-catalyzed dehydrogenation of benzyl alcohol.

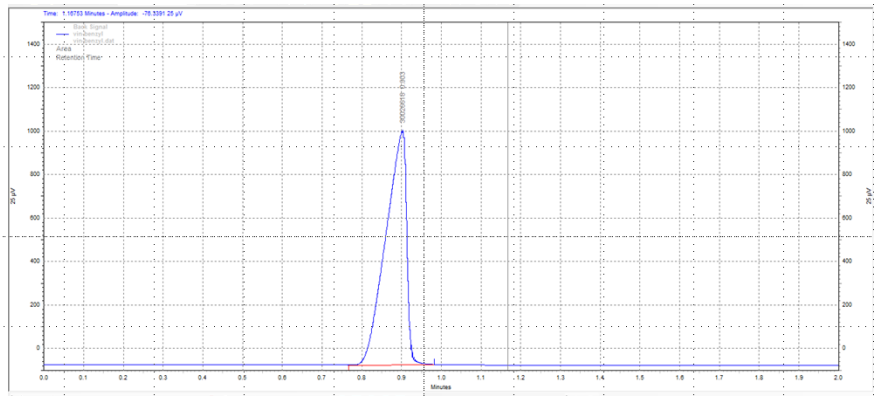
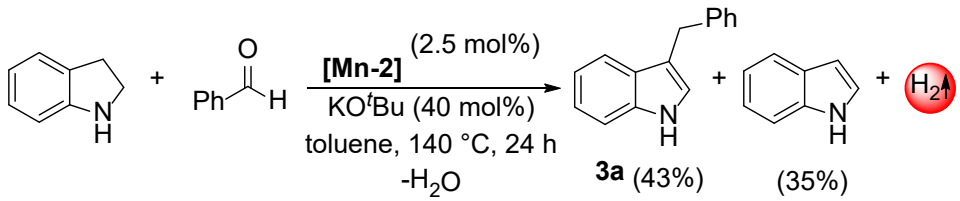


**Fig S17.** Detection of molecular hydrogen using gas phase GC analysis.

### 3.2 C-C Bond Formation

To an oven-dried Schlenk tube, indoline (0.5 mmol, 1 eq.), benzaldehyde (0.9 mmol, 1 eq.), KO$^t$Bu (0.2 mmol, 40 mol%), cat. [**Mn-2**] (2.5 mol%), and toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 140 °C for 24 h. Then, the reaction was quenched with water (2 mL) and extracted with dichloromethane/ethyl acetate (3 x 4 mL).

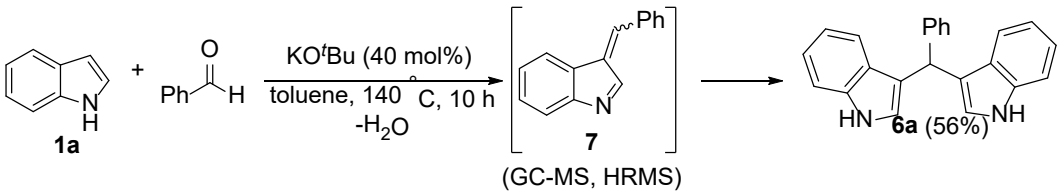
The combined organic layer was dried over anhydrous $Na_2SO_4$ and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system to give the desired C3-benzylated product 3a in 43% and indole as a dehydrogenative byproduct in 35% of isolated yield.




**Scheme S3**. Mn-catalyzed C-C bond-forming reaction.

### 3.3. Intermediate detection

To an oven-dried Schlenk tube, indole (0.5 mmol, 1 eq.), benzaldehyde (0.9 mmol, 1 eq.), KO$^t$Bu (0.2 mmol, 40 mol%) and toluene (1 mL) was added under a gentle stream of argon. The reaction mixture was kept for stirring at 140 °C for 10 h. further without quenching the reaction GCMS and HRMS samples were prepared for analysis (Figs S18 and S19). Further addition of [**Mn-5**] (3 mol %) catalyst in the same reaction and kept for stirring for another 24 h. The reaction was quenched with water (2 mL) and extracted with dichloromethane/ethyl acetate (3 x 4 mL). The combined organic layer was dried over anhydrous $Na_2SO_4$ and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system to give the desired bis(indole)methane (BIMs) **6a** in 56% yield.




**Scheme S4**. Detection of intermediate.

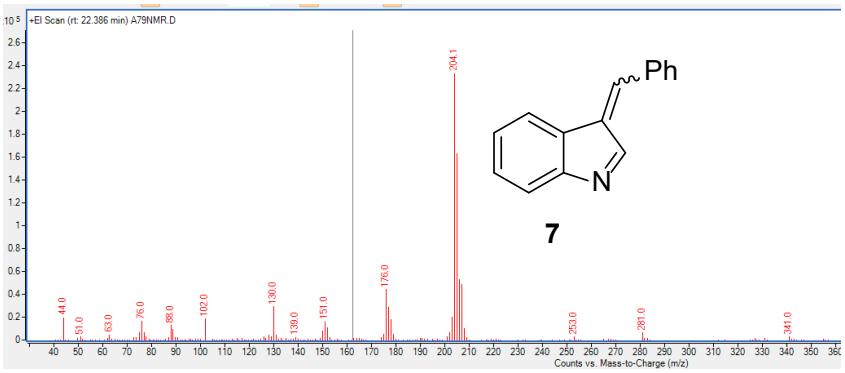



**Fig S11**. GC-MS spectrum of intermediate **7.**

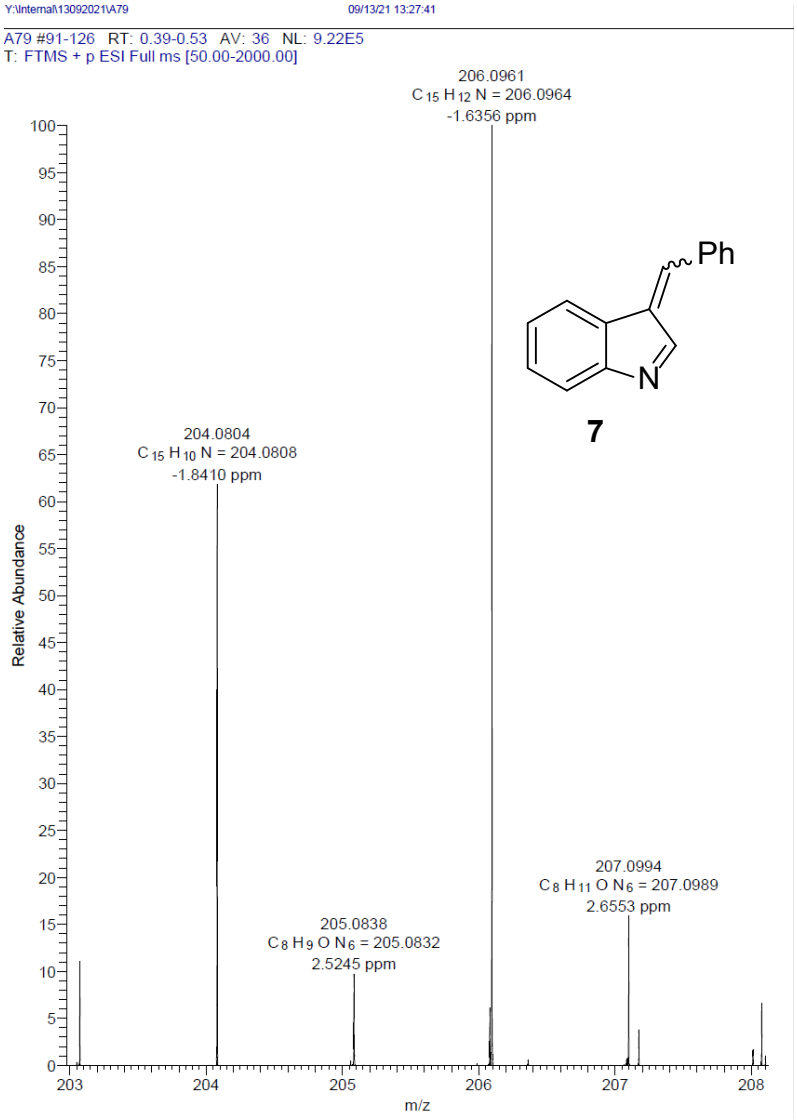


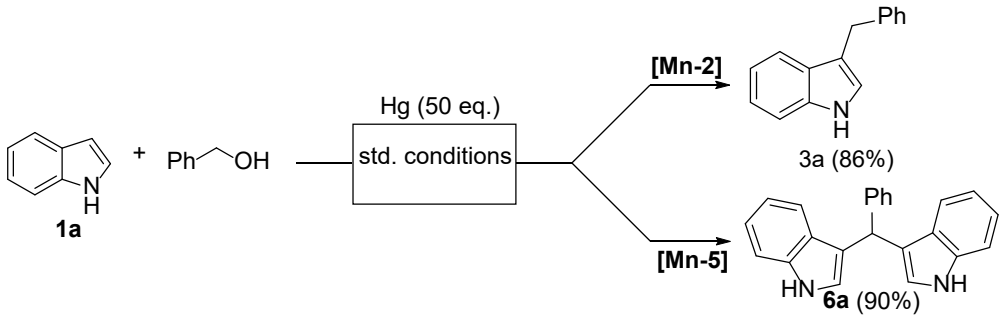

**Fig S12.** HRMS spectrum of intermediates **7**.

### 3.4. Nature of [Mn] Species: Homogeneous nature

#### 3.4.1 Mercury Test

To an oven-dried Schlenk tube, indole (0.5 mmol, 1 eq.), benzyl alcohol (0.9 mmol, 1 eq.), KO$^t$Bu (0.2 mmol, 40 mol%), cat.**[Mn-2]** or **[Mn-5]** and toluene (2 mL), Mercury (50 eq, 25 mmol) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 140 °C for 36 h. The reaction was quenched with water (2 mL) and extracted with dichloromethane/ethyl acetate (3 x 4 mL). The combined organic layer was dried over anhydrous $Na_2SO_4$ and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column

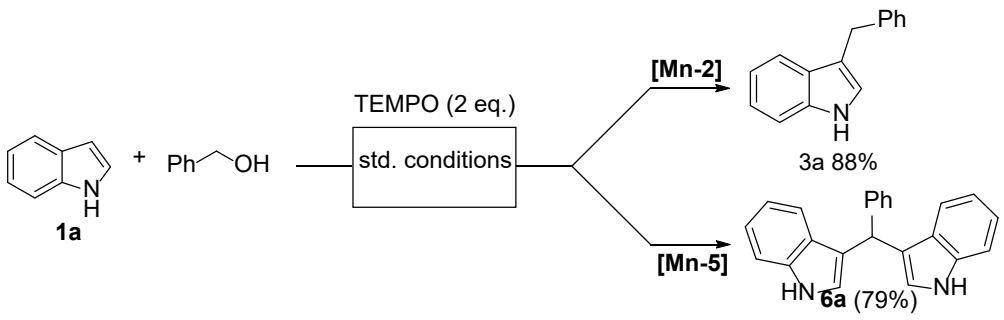
chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system to give the desired **3a** in 86% (in the case of **[Mn-2]**) and **6a** in 90% (in the case of **[Mn-5]**) of isolated yields, respectively.




**Scheme S5.** Homogeneous nature on Mn-species.

### 3.4.2 Radical trapping experiments

To an oven-dried Schlenk tube, indole (0.5 mmol, 1 eq.), benzyl alcohol (0.9 mmol, 1 eq.), KO$^t$Bu (0.2 mmol, 40 mol%), cat.**[Mn-2]** or **[Mn-5]** and toluene (2 mL), TEMPO (2 eq, 1 mmol) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 140 °C for 36 h. The reaction was quenched with water (2 mL) and extracted with dichloromethane/ethyl acetate (3x4 mL). The combined organic layer was dried over anhydrous $Na_2SO_4$ and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system to give the desired **3a** (in the case of **[Mn-2]**) in 88% and **6a** (in the case of **[Mn-5]**) in 79% of isolated yields, respectively.




**Scheme S6**. Radical trapping experiment.

## 4. Kinetic Studies

### 4.1 Kinetic profile for the formation of product 3a

To an oven dried 15 mL screw cap pressure tube, indoline (67 μL, 0.6 mmol, 1 eq.), benzyl alcohol (93 μL, 0.9 mmol, 1.5 eq.), **[Mn]-2** catalyst (2.5 mol%), KO$^t$Bu (27 mg, 40 mol %), mesitylene (84 μL, 0.6 mmol, 1 eq.) as an internal standard, and toluene (2 mL) were added under a gentle stream of argon to make up the total volume of the reaction mixture to 2.0 mL. The reaction mixture was kept for stirring at 140 °C for 6 h. Exactly the same reactions were kept and at regular intervals (12 h, 18 h, 24 h, 30 h, 36 h) the reaction mixtures were cooled to ambient temperature, and an aliquot of mixture was analysed using GC.

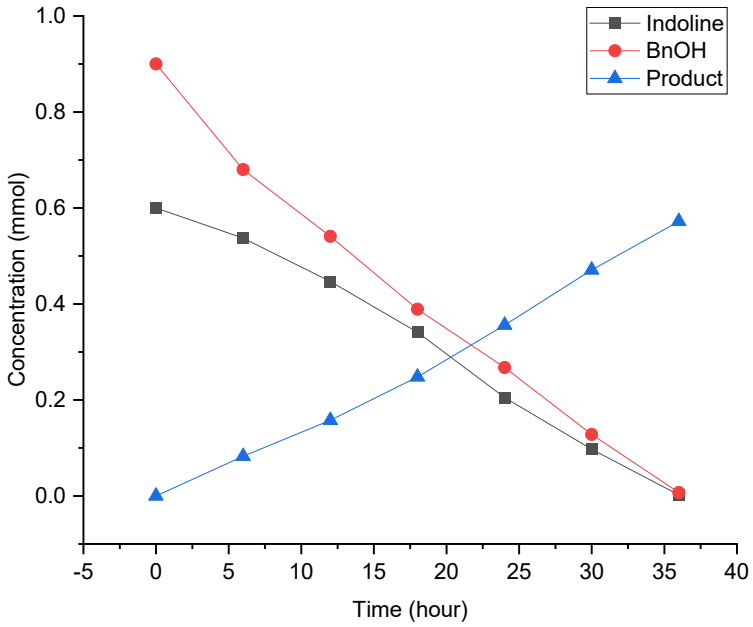



**Fig S13**. Kinetic profiles of **[Mn-2]** catalysed double AD/BH reaction of indoline (**1a**) and benzyl alcohol (**2a**).

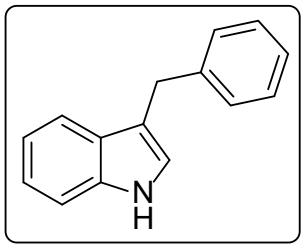
| Time (h) | Concentration of Indoline (mmol) | Concentration of Benzyl alcohol (mmol) | Concentration of Product (mmol) |
|---|---|---|---|
| 0 | 0.6 | 0.9 | 0 |
| 6 | 0.537 | 0.68 | 0.0827 |
| 12 | 0.447 | 0.541 | 0.1578 |
| 18 | 0.341 | 0.389 | 0.248 |
| 24 | 0.205 | 0.2675 | 0.356 |
| 30 | 0.0972 | 0.128 | 0.471 |
| 36 | 0.0021 | 0.0071 | 0.572 |

### 5.2 Kinetic profile for the formation of product 6a

To an oven-dried schlenk tube, indole (0.5 mmol, 1 eq.), benzyl alcohol (0.5 mmol, 1 eq.), cat.[**Mn-5**] catalyst (3 mol%), KO$^t$Bu (0.3 mmol, 40 mol%), mesitylene (1.0 mmol, 1 eq.) as an internal standard, and toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 130 °C. After completion of 0.5 h, the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with

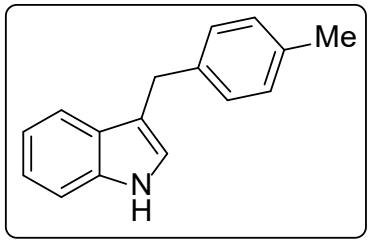
methanol and subjected to gas chromatographic analysis. The concentration of the product 3,3'-((phenyl)methylene)bis(1*H*-indole) (**6a**) was determined with respect to the mesitylene internal standaA The similar set of reactions was performed to collect the reaction mixture after completion of 1 h, 2 h, 4 h, 6 h, 8 h, 10 h, 13 h, 16 h, and 20 h. All the GC samples were diluted with methanol and subjected to GC analysis. The data was used to draw the concentration of the product (M) *vs* time (hours) plot (). The data represented was taken from the average of two independent set of experiments.

## 5. Characterization data



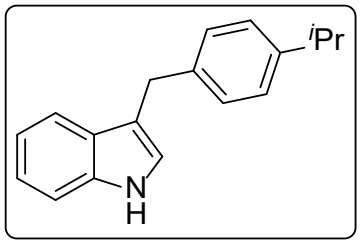
**3-benzyl-1*H*-indole (3a)**

White solid (109 mg, 88%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.82 (br. s, 1H), 7.62-7.75 (m, 1H), 7.16-7.53 (m, 8H), 6.87-7.04 (m, 1H), 4.27 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 141.2, 136.3, 128.6, 128.3, 127.3, 125.8, 122.3, 121.9, 119.3, 119.0, 115.5, 111.0, 77.6, 76.4, 31.5 ppm; HRMS (ESI) m/z calculated for $C_{15}H_{14}N$ $[M-H]^+$ 208.1121; found 208.1126.



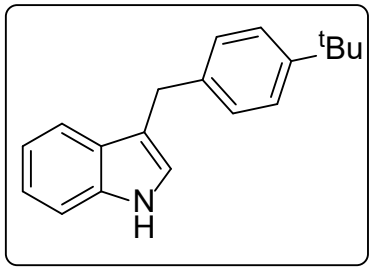
**3-(4-methylbenzyl)-1*H*-indole (3b)**

White solid (102 mg, 77%); $^1$H NMR ($CDCl_3$, 400 MHz); δ 7.75 (d, $J$ = 7.6 Hz, 2H), 7.18-7.53 (m, 7H), 6.86-7.03 (m, 1H), 4.27 (s, 2H), 2.53 (s, 3 H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 138.1, 136.3, 135.2, 129.0, 128.5, 127.4, 122.2, 121.9, 119.2, 119.1, 115.8, 111.0, 77.6, 76.4, 31.0, 20.9 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{16}N$ $[M-H]^+$ 222.1277; found 222.1284.



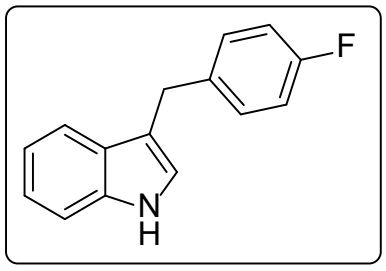
**3-(4-isopropylbenzyl)-1*H*-indole (3c)**

White solid (124.mg, 83%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.76 (br., s, 1H), 7.53 (d, $J$ = 7.9 Hz, 1H), 7.28 (d, $J$ = 8.1 Hz, 1H), 7.03-7.24 (m, 6H), 6.74-6.90 (m, 1H), 4.06 (s, 2H), 2.75-2.95 (m, 1H), 1.16-1.32 (m, 6H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 146.3, 138.5, 136.4, 128.5, 127.5, 126.3, 122.3, 121.9, 119.2, 119.1, 115.9, 111.0, 77.3, 76.7, 33.7, 31.1, 24.1 ppm; HRMS (ESI) m/z calculated for $C_{18}H_{18}N$ $[M-H]^+$ 248.1439; found 248.1429.



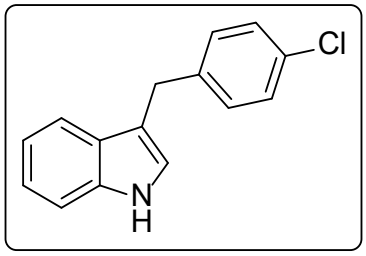

**3-(4-(*tert*-butyl)benzyl-1*H*-indole (3d)**

White solid (130 mg, 82%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.68 (br., s, 1H), 7.48-7.58 (m, 1H), 7.23-7.31 (m, 3H), 7.11-7.22 (m, 3H), 7.03-7.10 (m, 1H), 6.75-6.85 (m, 1H), 4.05 (s, 2H), 1.28 (s, 9H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 148.6, 138.1, 136.3, 128.2, 127.5, 125.2, 122.3, 121.9, 119.2, 119.1, 115.8, 111.0, 77.3, 76.7, 34.3, 31.4, 30.9 ppm; HRMS (ESI) m/z calculated for $C_{19}H_{22}N$ $[M+H]^+$ 264.1752; found 264.1754.



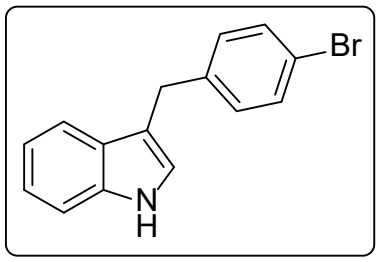

**3-(4-fluorobenzyl)-1*H*-indole (3e)**

White solid (49 mg, 36%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.96 (br., s, 1H), 7.45-7.50 (m, 1H), 7.36 (dt, $J$ = 8.1, 0.9 Hz, 1H), 7.16-7.25 (m, 3H), 7.05-7.10 (m, 1H), 6.92-6.99 (m, 2H), 6.87-6.92 (m, 1H), 4.08 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 164.2, 161.7, 143.9, 143.8, 136.4, 129.7, 129.6, 127.3, 124.3, 124.2, 122.4, 122.1, 119.5, 119.0, 115.6, 115.4, 114.9, 112.9, 112.6, 111.1, 77.3, 76.7, 31.3 ppm; HRMS (ESI) m/z calculated for $C_{15}H_{13}NF$ $[M+H]^+$ 226.1032; found 226.1022.



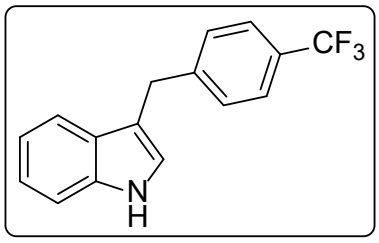

**3-(4-chlorobenzyl)-1*H*-indole (3f)**

White solid (71.mg, 49%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.67 (br. s, 1H), 7.36 (d, $J$ = 7.8 Hz, 1H), 6.89-7.28 (m, 7H), 6.64-6.76 (m, 1H), 3.94 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$,101 MHz): δ 139.6, 136.4, 131.5, 129.9, 128.4, 127.2, 122.3, 122.1, 119.4, 119.0, 115.1, 111.1, 77.6, 76.4, 30.9 ppm; HRMS (ESI) m/z calculated for $C_{15}H_{12}NCl$ $[M]^+$ 241.0658; found 241.0651.




**3-(4-bromobenzyl)-1*H*-indole (3g)**

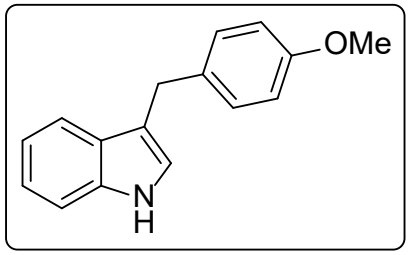
White solid (91.mg, 53%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.84 (br., s, 1H), 6.90-7.49 (m, 8H), 6.70-6.85 (m, 1H), 3.97 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 139.2, 135.4, 130.3, 129.4, 127.6, 127.3, 121.2, 118.6, 118.4, 118.1, 114.0, 110.1, 76.6, 76.0, 30.0 ppm. HRMS (ESI) m/z calculated for $C_{15}H_{13}NBr$ $[M+H]^+$ 286.0231; found 286.0222.




**3-(4-(trifluoromethyl)benzyl)-1*H*-indole (3h)**

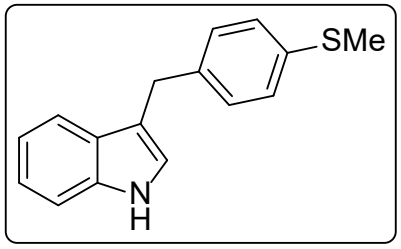
Needle like crystalline white solid (119.mg, 72%); $^{1}$H NMR ($CDCl_3$,400 MHz): δ 8.03 (br. s, 1H), 7.56 (d, $J$ = 8.0 Hz, 2H), 7.51 (d, $J$ = 8.0 Hz, 1H), 7.41 (dd, $J$= 8.0, 5.0 Hz, 3H), 7.24 (t, $J$ = 7.6

Hz, 1H), 7.08-7.16 (m, 1H), 6.94-7.01 (m, 1H), 4.21 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 145.3, 136.4, 128.9, 127.2, 125.2, 122.4, 122.3, 119.6, 118.9, 114.7, 111.2, 77.3, 76.7, 31.4 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{13}F_3N$ $[M+H]^+$ 276.0995; found 276.0999.



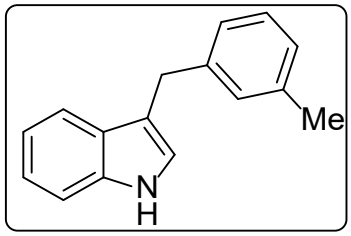

**3-(4-methoxybenzyl)-1*H*-indole (3i)**

Dark green liquid (91.mg, 64%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.90 (br. s., 1H), 7.72 (d, $J$ = 7.6 Hz, 1H), 7.20-7.49 (m, 5H), 6.91-7.09 (m, 3H), 4.23 (s, 2H), 3.93 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 157.7, 136.3, 133.3, 129.5, 127.3, 122.2, 121.8, 119.2, 119.0, 115.9, 113.7, 111.0, 77.6, 76.4, 55.1, 30.6 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{15}NO$ $[M]^+$ 237.1154; found 237.1141.



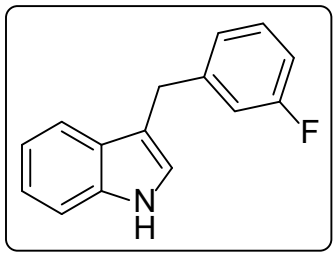

**3-(4-(methylthio)benzyl)-1*H*-indole (3j)**

White solid (106.mg, 70%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.84 (br. s, 1H), 7.63-7.75 (m, 1H), 7.19-7.49 (m, 7H), 6.86-7.01 (m, 1H), 4.23 (s, 2H), 2.60 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 138.2, 136.2, 135.2, 129.1, 127.2, 126.9, 122.3, 121.9, 119.2, 118.9, 115.2, 111.0, 77.6, 76.4, 30.9, 16.0 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{16}NS$ $[M+H]^+$ 254.1003; found 254.0996.



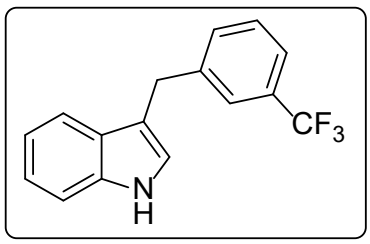

**3-(3-methylbenzyl)-1*H*-indole (3k)**

Colorless liquid (108.mg, 81%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.86 (m, 2H), 7.15-7.53 (m, 7H), 6.88-7.04 (m, 1H), 4.31 (s, 2H), 2.55 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 141.1, 137.8, 136.3, 129.4, 128.2, 127.3, 126.6, 125.7, 122.3, 121.8, 119.2, 119.0, 115.6, 111.0, 77.6, 76.4, 31.4, 21.3 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{16}N$ $[M+H]^+$ 222.1283; found 222.1273.



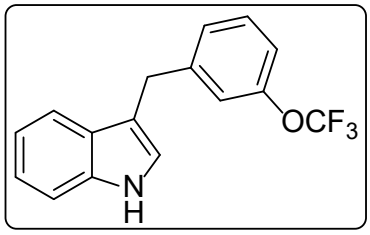

**3-(3-fluorobenzyl)-1*H*-indole (3l)**

White solid (57mg, 42%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.94 (br., s, 1H), 7.48 (d, $J$ = 7.9 Hz, 1H), 7.31-7.38 (m, 1H), 7.14-7.26 (m, 2H), 7.02-7.12 (m, 2H), 6.90-6.99 (m, 2H), 6.82-6.90 (m, 1H), 4.10 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 164.2, 161.7, 143.9, 143.8, 136.4, 129.7, 129.6, 127.3, 124.3, 124.2, 122.4, 122.1, 119.5, 119.0, 115.6, 115.4, 114.9, 112.9, 112.6, 111.1, 77.3, 76.7, 31.3 ppm; HRMS (ESI) m/z calculated for $C_{15}H_{13}NF$ $[M+H]^+$ 226.1032; found 226.1022.



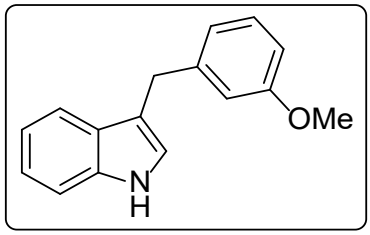

**3-(3-(trifluoromethyl)benzyl)-1*H*-indole (3m)**

White solid (114.mg, 69%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.71 (br., s, 1H), 7.45 (br., s, 1H), 7.27-7.41 (m, 3H), 7.15-7.26 (m, 2H), 6.93-7.14 (m, 2H), 6.65-6.79 (m, 1H), 4.02 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$ ,101 MHz): δ 142.1, 136.4, 132.0, 128.7, 127.2, 125.3, 122.8, 122.5, 122.2, 119.5, 118.9, 114.7, 111.2, 77.3, 76.7, 31.4 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{13}F_3N$ $[M-H]^+$ 276.0995; found 276.1004.




**3-(3-(trifluoromethoxy)benzyl)-1*H*-indole (3n)**

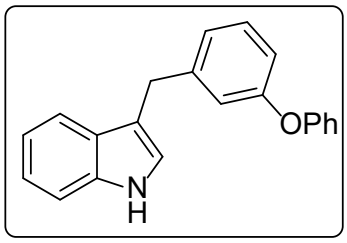
White solid (103.mg, 59%); $^1$H NMR ($CDCl_3$,400MHz): δ 7.82 (br., s, 1H), 7.43-7.55 (m, 1H), 7.14-7.36 (m, 4H), 7.02-7.14 (m, 3H), 6.84 (s, 1H), 4.07 (br., s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 147.4, 139.9, 136.4, 129.8, 127.2, 122.4, 122.2, 120.8, 119.5, 119.0, 115.1, 111.2, 77.3, 76.7, 30.9 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{13}ONF_3$ $[M+H]^+$ 292.0949; found 292.0951.




**3-(3-methoxybenzyl)-1*H*-indole (3o)**

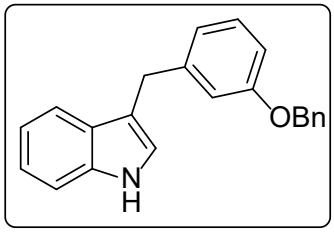
White solid (101.mg, 71%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.80 (br. s, 1H), 7.36-7.56 (m, 1H), 7.17-7.30 (m, 1H), 6.92-7.17 (m, 3H), 6.72-6.86 (m, 3H), 6.65 (dd, $J$ = 8.0, 2.4Hz, 1H), 4.00 (s, 2H), 3.66 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ = 157.2, 136.2, 129.8, 129.6, 127.6, 127.0, 122.4, 121.7, 120.4, 119.2, 119.1, 114.9, 111.0, 110.2, 77.6, 76.4, 55.3, 25.1 ppm; HRMS (ESI)

m/z calculated for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1232; found 238.1216.



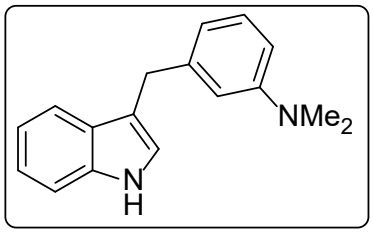

**3-(3-phenxybenzyl)-1*H*-indole (3p)**

Fade white solid (120.mg, 67%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.88 (br., s, 1H), 7.49 (d, $J$ = 8.0 Hz, 1H), 7.25-7.38 (m, 3H), 7.13-7.25 (m, 2H), 7.01-7.12 (m, 3H), 6.93-7.00 (m, 3H), 6.86-6.93 (m, 1H), 6.81 (dd, $J$ = 8.1, 2.1 Hz, 1H), 4.07 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 157.3, 157.1, 143.3, 136.4, 129.6, 129.5, 127.3, 123.7, 123.0, 122.3, 122.0, 119.4, 119.4, 119.1, 118.7, 116.4, 115.3, 111.1, 77.3, 76.7, 31.5 ppm; HRMS (ESI) m/z calculated for $C_{21}H_{18}ON$ $[M+H]^+$ 300.1388; found 300.1375.



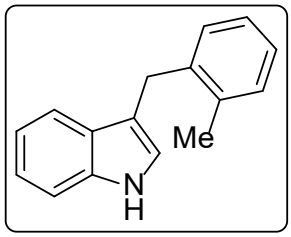

**3-(3-benzyloxy)benzyl)-1*H*-indole (3q)**

White solid (143.mg, 76%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.72 (br.,s, 1H), 7.36-7.49 (m, 1H), 7.15-7.34 (m, 6H), 6.90-7.15 (m, 3H), 6.62-6.88 (m, 4H), 4.89 (s, 2H), 3.97 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$,101 MHz): δ 159.0, 143.1, 137.2, 136.5, 129.4, 128.7, 128.0, 127.7, 127.6, 122.5, 122.1, 121.6, 119.5, 119.2, 115.6, 112.3, 111.2, 77.8, 77.2, 76.5, 70.0, 31.7 ppm; HRMS (ESI) m/z calculated for $C_{22}H_{20}NO$ $[M+H]^+$ 314.1545; found 314.1536.



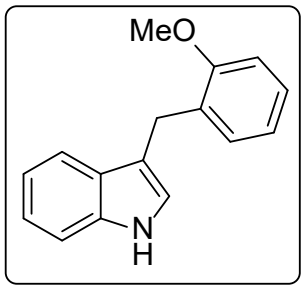

**3-((1*H*-indol-3-yl)methyl)-*N*,*N*-dimethylaniline (3r)**

Brown viscous liquid (113.mg, 75%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.77 (br., s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.24 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.09-7.18 (m, 2H), 7.01-7.09 (m, 1H), 6.76-6.82 (m, 1H), 6.70 (br., s, 1H), 6.65 (d, *J* = 7.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 4.05 (s, 2H), 2.87 (s, 6H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ = 150.7, 142.0, 136.3, 129.0, 127.5, 122.3, 121.8, 119.2, 119.1, 117.4, 116.0, 113.3, 111.0, 110.4, 77.3, 76.7, 40.6, 32.0 ppm; HRMS (ESI) m/z calculated for $C_{17}H_{19}N_2$ $[M+H]^+$ 251.1548; found 251.1545.



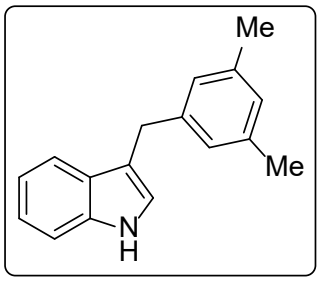

**3-(2-methylbenzyl)-1*H*-indole (3s)**

Colorless liquid (80.mg, 60%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.85 (br. s., 1H), 7.61-7.79 (m, 1H), 7.17-7.55 (m, 7H), 6.70-6.89 (m, 1H), 4.21 (s, 2H), 2.47 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 139.0, 136.4, 136.3, 130.1, 129.3, 127.4, 126.1, 125.9, 122.4, 121.9, 119.2, 118.9, 114.9, 111.0, 77.6, 76.4, 29.2, 19.4 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{16}N$ $[M-H]^+$ 222.1277; found 222.1286.



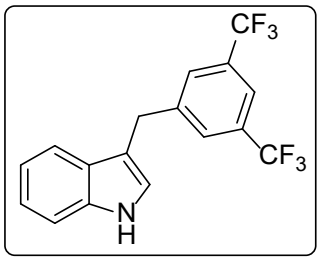

**3-(2-methoxybenzyl)-1*H*-indole (3t)**

Yellowish liquid (90.mg, 63%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.85 (br., s, 1H), 7.66-7.78 (m, 1H), 7.16-7.49 (m, 5H), 6.88-7.09 (m, 3H), 4.25 (s, 2H), 3.98 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$,101 MHz): δ 157.4, 136.5, 130.1, 129.8, 127.8, 127.2, 122.7, 121.9, 120.6, 119.4, 119.3, 115.2, 111.2, 110.4, 77.9, 77.2, 76.6, 55.5, 25.3 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1232; found 238.1215.



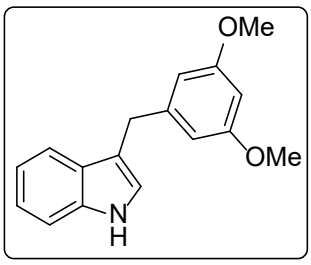

**3-(3,5-dimethylbenzyl)-1*H*-indole (3u)**

Faint yellow viscous liquid (135.mg, 96%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.93 (m, 2H), 7.28-7.55 (m, 3H), 7.07-7.27 (m, 3H), 6.90-7.04 (m, 1H), 4.29 (s, 2H), 2.52 (s, 6H) ppm$^{13}$C NMR ($CDCl_3$, 101 MHz): δ 141.1, 137.7, 136.2, 127.5, 127.3, 126.5, 122.3, 121.8, 119.2, 119.0, 115.6, 111.0, 77.6, 76.4, 31.3, 21.2 ppm; HRMS (ESI) m/z calculated for $C_{17}H_{18}N$ $[M+H]^+$ 236.1439; found 236.1430.



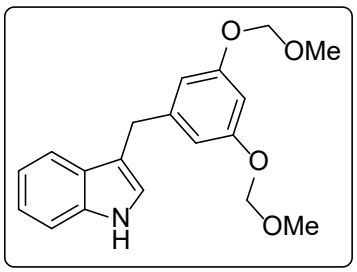

**3-(3,5-bis(trifluoromethyl)benzyl)-1*H*-indole (3v)**

White solid (127 mg, 62%); $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 7.75 (s, 1H), 7.46 (tt, *J* = 1.9, 0.8 Hz, 1H), 7.41–7.29 (m, 2H), 7.23 (ddt, *J* = 9.0, 8.1, 0.8 Hz, 2H), 7.14–7.06 (m, 1H), 6.99 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.75 (dt, *J* = 2.1, 1.0 Hz, 1H), 4.04 (s, 2H).ppm; $^{13}$C NMR ($CDCl_3$ ,101 MHz) δ 141.11, 135.4, 131.0, 129.6, 127.7, 126.1, 124.3, 121.8, 121.4, 118.5, 117.8, 113.6, 110.1, 30.3 ppm; HRMS (ESI) m/z calculated for $C_{17}H_{10}NF_6$ $[M-H]^+$ 342.0717; found 342.0706.



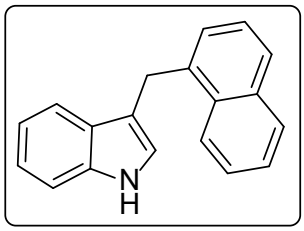

**3-(3,4-dimethoxybenzyl)-1H-indole (3w)**

Brown liquid (107.mg, 57%); $^1$H NMR ($CDCl_3$ ,400 MHz): δ 7.93 (br., s, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.13-7.25 (m, 1H), 6.89-7.13 (m, 2H), 6.58-6.79 (m, 4H), 3.95 (s, 2H), 3.68 (s, 3H), 3.72 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$,101 MHz): δ 148.6, 147.0, 136.3, 133.8, 127.2, 122.2, 121.8, 120.5, 119.1, 118.9, 115.6, 112.0, 111.1,, 77.6, 76.4, 55.6, 31.1 ppm; HRMS (ESI) m/z calculated for $C_{17}H_{16}NO_2$ $[M-H]^+$ 266.1181; found 266.1174.



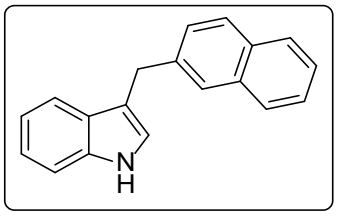

**3-(3,5-bis(methoxymethoxy)benzyl-1*H*-indole (3x)**

Colorless liquid (153.mg, 78%); $^1$H NMR ($CDCl_3$,400 MHz): δ 7.89 (br., s, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 6.87-7.26 (m, 3H), 6.65-6.83 (m, 1H), 6.42-6.63 (m, 3H), 5.00 (s, 4H), 3.93 (s, 2H), 3.33 (s, 6H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 158.3, 144.1, 136.5, 127.5, 122.6, 122.0, 119.4, 119.2, 115.1, 111.2, 110.4, 102.5, 94.6, 77.8, 77.2, 76.6, 56.1, 31.8 ppm; HRMS (ESI) m/z calculated for $C_{19}H_{22}NO_4$ $[M+H]^+$ 328.1549; found 328.1538.



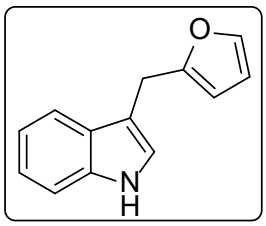

**3-(naphthalene-1-ylmethyl)-1*H*-indole (3y)**

White crystalline solid (100.mg, 65%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.13-8.32 (m, 1H), 7.84-8.10 (m, 2H), 7.77 (d, *J* = 7.1 Hz, 2H), 7.45 - 7.68 (m, 4H), 7.17-7.44 (m, 3H), 6.59-6.77 (m, 1H), 4.66 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 136.7, 136.2, 133.8, 132.1, 128.6, 127.4, 126.8, 126.6, 125.7, 125.6, 125.4, 124.3, 122.8, 122.0, 119.3, 118.9, 115.2, 111.1, 77.6, 76.4, 28.8 ppm. HRMS (ESI) m/z calculated for $C_{19}H_{16}N$ $[M+H]^+$ 258.1283; found 258.1276.



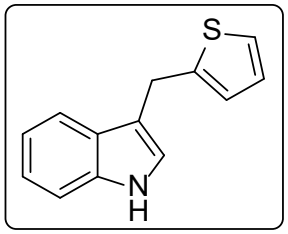
**3-(napthalen-2-ylmethyl)-1*H*-indole (3z)**

White solid (122.mg, 79%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.90 (m, 5H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.18-7.39 (m, 4H), 6.87-7.17 (m, 2H), 6.71-6.83 (m, 1H), 4.17 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$,101 MHz): δ 138.8, 136.5, 133.7, 132.2, 127.9, 127.7, 126.7, 125.9, 125.2, 122.5, 122.1, 119.5, 119.2, 115.8, 111.1, 77.7, 77.1, 76.5, 31.9 ppm; HRMS (ESI) m/z calculated for $C_{19}H_{15}N$ $[M]^+$ 257.1204; found 257.1194.



**3-(furan-2-ylmethyl)-1*H*-indole (3aa)**

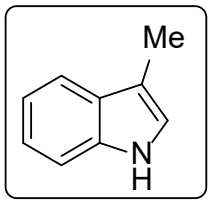
Light green solid (62.mg, 52%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.78 (br. s, 1H), 7.48 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.17-7.31 (m, 2H), 6.96-7.17 (m, 2H), 6.83-6.95 (m, 1H), 6.19 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.85-6.02 (m, 1H), 3.91-4.11 (m, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 155.5, 141.6, 136.9, 127.8, 122.9, 122.7, 120.0, 119.6, 113.2, 111.7, 110.9, 106.3, 78.3, 77.6, 25.0 ppm; HRMS (ESI) m/z calculated for $C_{13}H_{11}NO$ $[M]^+$ 197.0841; found 197.0826.



**3-(thiophen-2-ylmethyl)-1*H*-indole (3ab)**

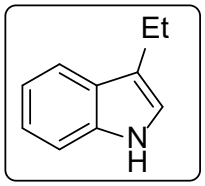
Brown solid (59.mg, 46%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.97 (m, 2H), 6.96-7.34 (m, 4H), 6.67-6.95 (m, 3H), 4.13-4.38 (m, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 144.6, 136.2, 126.9,

126.6, 124.6, 124.1, 123.3, 122.3, 122.0, 121.8, 120.6, 119.7, 119.3, 118.9, 114.9, 111.1, 111.0, 102.3, 77.6, 76.4, 25.8 ppm; HRMS (ESI) m/z calculated for $C_{13}H_{10}NS$ $[M-H]^+$ 212.0534; found 212.0629.



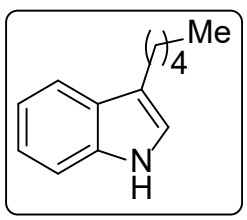

**3-methyl-1*H*-indole (3ac)**

Pale solid (45.mg, 57%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.82 (m, 2H), 6.98-7.31 (m, 3H), 6.79 (dd, *J* = 2.0, 1.0 Hz, 1H), 2.30 (d, *J* = 1.0 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 136.1, 128.2, 121.7, 121.6, 119.0, 118.7, 111.5, 110.9, 77.6, 76.4, 9.6 ppm; HRMS (ESI) m/z calculated for $C_9H_9N$ $[M]^+$ 131.0735; found 131.0729.



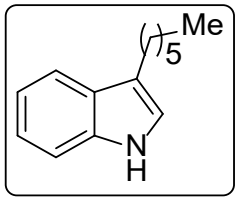

**3-ethyl-1*H*-indole (3ad)**

Brown viscous liquid (56.mg, 64%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.78 (br. s, 1H), 7.42-7.60 (m, 1H), 7.20-7.33 (m, 1H), 6.95-7.19 (m, 2H), 6.80-6.93 (m, 1H), 2.72 (q, *J* =7.5, 0.9 Hz, 2H), 1.05-1.35 (t, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101MHz): δ 136.4, 127.4, 121.9, 120.4, 119.0, 118.9, 118.8, 111.0, 77.3, 77.2, 76.7, 18.3, 14.4 ppm; HRMS (ESI) m/z calculated for $C_{10}H_{12}N$ $[M+H]^+$146.0970; found 146.0963.



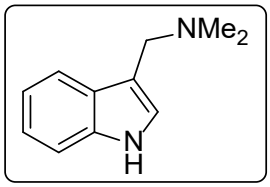

**3-pentyl-1*H*-indole (3ae)**

Colorless liquid (60 mg, 53%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.81 (br., s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.31 (dt, *J* = 8.1, 0.8 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.06-7.13 (m, 1H), 6.86-6.97 (m, 1H), 2.74 (t, *J* = 7.7 Hz, 2H), 1.65-1.78 (m, 2H), 1.34-1.43 (m, 4H), 0.82-0.95 (m, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 136.6, 127.9, 122.1, 121.3, 119.3, 117.5, 111.3, 77.6, 77.3, 32.2, 30.2, 25.4, 22.9, 14.4 ppm; HRMS (ESI) m/z calculated for $C_{13}H_{18}N$ $[M+H]^+$ 188.1439; found 188.1432.



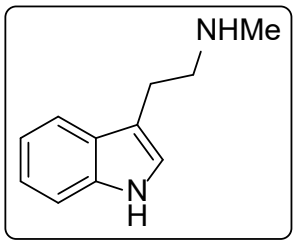

**3-hexyl-1*H*-indole (3af)**

Pale brown liquid (59.mg, 49%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.82 (s, 1H), 7.54 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.27 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.10 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.03 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 6.89 (dd, *J* = 2.2, 1.1 Hz, 1H), 2.74–2.59 (m, 2H), 1.64 (p, *J* = 7.4 Hz, 2H), 1.32 (ddd, *J* = 10.0, 8.5, 4.7, 1.9 Hz, 2H), 1.27–1.18 (m, 6H), 0.84–0.78 (m, 4H) ppm; . $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 136.3, 127.6, 121.8, 120.9, 119.0, 117.2, 111.0, 31.8, 30.1, 29.3, 25.1, 22.7, 14.1 ppm; HRMS (ESI) m/z calculated for $C_{14}H_{20}N$ $[M+H]^+$ 202.1596; found 202.1587.



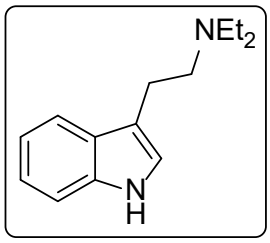

**1-(1*H*-indol-3-yl)-N,N-dimethylmethanamine (3ag)**

Pale white solid (66 mg, 63%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.73 (s, 1H), 7.82–7.45 (m, 1H), 7.36–7.25 (m, 1H), 7.21–7.07 (m, 2H), 7.03 (d, *J* = 2.4 Hz, 1H), 3.65 (s, 2H), 2.30 (s, 6H) ppm.; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 136.2, 127.9, 123.9, 121.8, 119.4, 119.1, 112.8, 111.1, 54.4, 45.2 ppm; HRMS (ESI) m/z calculated for $C_{11}H_{15}N_2$ $[M+H]^+$ 175.1235; found 175.1229.



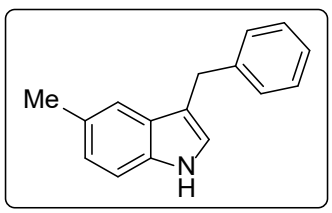

**2-(1*H*-indol-3-yl)-N-methylethan-1-amine (3ah)**

Pale white solid (70 mg, 67%). HRMS (ESI) m/z calculated for $C_{11}H_{15}N_2$ [M-H]$^+$ 175.1230; found 175.1238. (N.B. This compound was purified by column chromatography using silica gel (230-400 mesh) with eluent MeOH:EtOAc = 1:9, After column purification GC-MS analysis of the compound showed some mixture of undetermined compound).



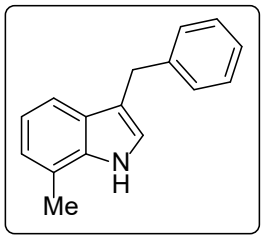

**N,N-diethyl-2-(1*H*-indol-3-yl)ethan-1-amine (3ai)**

Pale white solid (65 mg, 50%); $^1$H NMR ($CD_3OD$, 400 MHz): δ 7.47 (d, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.99 (s, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 3.22 (d, *J* = 7.6 Hz, 4H), 2.56 (d, *J* = 7.3 Hz, 4H), 0.90 (d, *J* = 7.2 Hz, 6H) ppm; $^{13}$C NMR ($CD_3OD$, 101 MHz) δ 137.0, 126.7, 123.4, 122.0, 121.0, 120.8, 119.3, 118.6, 118.4, 118.0, 117.4, 110.9, 73.8, 57.3, 32.2, 9.5 ppm; HRMS (ESI) m/z calculated for $C_{14}H_{21}N_2$ [M+H]$^+$ 217.1699; found 217.1697. (N.B. This compound was purified by column chromatography using silica gel (230-400 mesh) with eluent MeOH:EtOAc = 1:9)



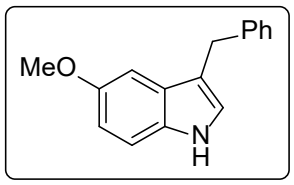

**3-benzyl-5-methyl-1*H*-indole (4a)**

White solid (112mg, 84%); $^1$H NMR ($CDCl_3$, 400 MHz *d*): δ 7.78 (s, 1H), 7.35–7.13 (m, 7H), 7.00 (d, *J* = 9.6 Hz, 1H), 6.82 (s, 1H), 4.08 (s, 2H), 2.41 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 141.3, 134.8, 128.7, 128.6, 128.3, 127.7, 125.8, 123.7, 122.5, 118.7, 115.3, 110.7, 31.5, 21.5 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{16}N$ $[M+H]^+$ 222.1283; found 222.1276.



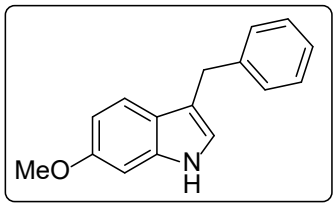

**3-benzyl-7-methyl-1*H*-indole (4b)**

Greenish solid (72 mg, 54%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.72 (s, 1H), 7.42–7.33 (m, 1H), 7.25–7.18 (m, 5H), 7.16–7.11 (m, 1H), 7.11–7.04 (m, 1H), 7.04–6.97 (m, 1H), 4.05 (s, 2H), 2.33 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 141.7, 135.3, 131.7, 130.3, 128.3, 128.3, 125.7, 121.0, 119.2, 118.4, 110.2, 30.1, 11.8 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{16}N$ $[M+H]^+$ 222.1283; found 222.1276.



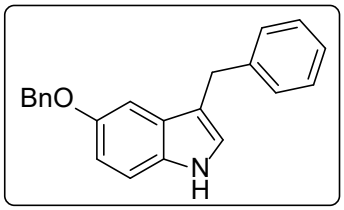

**3-benzyl-5-methoxy-1*H*-indole (4c)**

Brown liquid (108 mg, 76%) $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.77 (s, 1H), 7.33–7.10 (m, 6H), 6.93 (d, J = 2.5 Hz, 1H), 6.86–6.71 (m, 2H), 4.05 (s, 2H), 3.77 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 153.9, 141.2, 131.6, 128.7, 128.4, 127.9, 125.9, 123.3, 115.4, 112.1, 111.9, 101.1, 55.9, 31.7 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{16}ON$ $[M+H]^+$ 238.1232; found 238.1227.



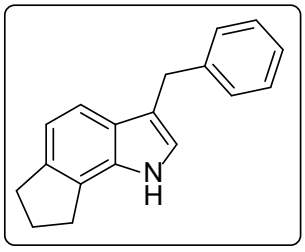

**3-benzyl-6-methoxy-1*H*-indole (4d)**

White solid (114mg, 80%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.81 (s, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.29–7.24 (m, 4H), 7.22–7.15 (m, 1H), 6.82 (dd, *J* = 16.4, 2.1 Hz, 2H), 6.77–6.68 (m, 1H), 4.07 (s, 2H), 3.83 (s, 3H).ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 156.5, 141.2, 128.6, 128.3, 125.8, 121.0, 119.7, 115.8, 109.2, 94.6, 55.7, 31.6 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{16}ON$ $[M+H]^+$ 238.1232; found 238.1229.



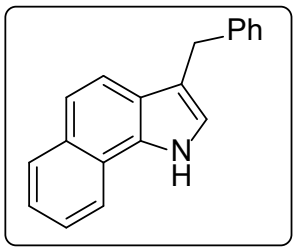

**3-benzyl-5-(benzyloxy)-1*H*-indole (4e)**

Yellow solid (115mg, 77%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.75 (s, 1H), 7.48–7.39 (m, 2H), 7.39–7.31 (m, 2H), 7.31–7.21 (m, 5H), 7.21–7.12 (m, 2H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 5.02 (s, 2H), 4.03 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz) δ 153.1, 141.2, 137.7, 131.8, 128.7, 128.6, 128.5, 128.4, 127.9, 127.7, 125.9, 123.3, 115.5, 112.9, 111.8, 102.8, 71.0, 31.6 ppm; HRMS (ESI) m/z calculated for $C_{22}H_{20}ON$ $[M+H]^+$ 314.1545; found 314.1538.



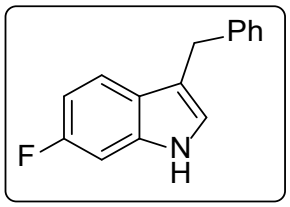

**3-benzyl-1,6,7,8-tetrahydrocyclopenta[g]indole (4f)**

White solid (93 mg, 63%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.67 (s, 1H), 7.34–7.21 (m, 5H), 7.21–7.12 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 2.5 Hz, 1H), 4.09 (s, 2H), 3.01 (dt, *J* = 11.3, 7.4 Hz, 4H), 2.27–2.10 (m, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 141.4, 138.5, 128.6, 128.2, 125.7, 125.4, 121.5, 117.2, 116.3, 116.3, 33.0, 31.8, 29.8, 25.4 ppm; HRMS (ESI) m/z calculated for $C_{18}H_{18}N$ $[M+H]^+$ 248.1439; found 248.1432.



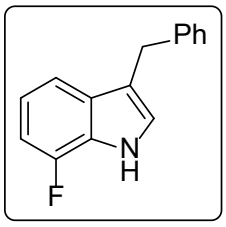

**3-benzyl-1*H*-benzo[g]indole (4g)**

White solid (79 mg, 51%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 8.59 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.65–7.09 (m, 9H), 6.93 (s, 1H), 4.18 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz) δ 141.4, 131.0, 130.4, 128.9, 128.70, 125.9, 125.4, 123.9, 123.3, 121.8, 120.6, 120.3, 119.4, 117.4, 77.2, 31.6 ppm; HRMS (ESI) m/z calculated for $C_{19}H_{16}N$ $[M+H]^+$ 258.1283; found 258.1276.




**3-benzyl-6-fluoro-1*H*-indole (4h)**

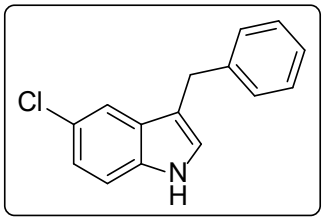
Colorless liquid (93 mg, 69%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.80 (s, 1H), 7.37 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.32–7.22 (m, 4H), 7.19 (d, *J* = 6.0 Hz, 1H), 6.97 (dd, *J* = 9.7, 2.3 Hz, 1H), 6.88–6.74 (m, 2H), 4.06 (d, *J* = 1.0 Hz, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 140.9, 136.4, 128.7, 128.4, 126.0, 124.1, 122.6, 119.9, 115.9, 108.2, 108.0, 97.5, 77.3, 31.6 ppm; HRMS (ESI) m/z calculated for $C_{15}H_{13}NF$ $[M+H]^+$ 226.1032; found 226.1029.




**3-benzyl-7-fluoro-1*H*-indole (4i)**

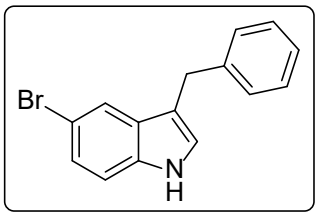
Colorless liquid (76 mg, 56%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 8.07 (s, 1H), 7.30–7.23 (m, 5H), 7.23–7.15 (m, 2H), 6.96 (td, J = 7.9, 4.8 Hz, 1H), 6.92–6.83 (m, 2H), 4.09 (d, J = 1.0 Hz, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 150.8, 140.8, 128.6, 128.4, 126.0, 124.8, 123.0, 119.6, 116.7,

116.6, 115.0, 107.0, 106.8, 77.2, 31.6 ppm; HRMS (ESI) m/z calculated for $C_{15}H_{13}NF$ $[M+H]^+$ 226.1032; found 226.1029.



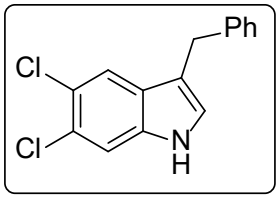

**3-benzyl-5-chloro-1H-indole (4j)**

Yellowish solid (102 mg, 70%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.93 (s, 1H), 7.47 (d, $J$ = 1.9 Hz, 1H), 7.34–7.16 (m, 6H), 7.12 (dd, $J$ = 8.6, 2.0 Hz, 1H), 6.91 (s, 1H), 4.05 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz) δ 140.7, 134.7, 128.6, 128.5, 128.4, 126.1, 125.1, 123.7, 122.3, 118.6, 115.6, 112.1, 31.4 ppm; HRMS (ESI) m/z calculated for $C_{15}H_{13}ClN$ $[M+H]^+$ 242.0731; found 242.0546.




**3-benzyl-5-bromo-1*H*-indole (4k)**

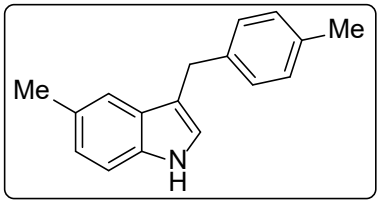
Pale yellow solid (131 mg, 76%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.95 (s, 1H), 7.63 (s, 1H), 7.36–7.10 (m, 7H), 6.89 (s, 1H), 4.05 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz) δ 140.7, 135.0, 129.2, 128.6, 128.4, 126.1, 124.9, 123.6, 121.7, 115.5, 112.7, 112.5, 31.3 ppm; HRMS (ESI) m/z calculated for $C_{15}H_{11}NBr$ $[M-H]^+$ 284.0075; found 284.0068.




**3-benzyl-5,6-dichloro-1*H*-indole (4l)**

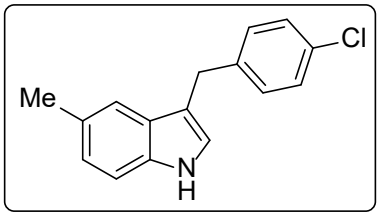
White Solid (109.mg, 66%) 1H NMR ($CDCl_3$, 400 MHz): δ 7.94 (s, 1H), 7.54 (s, 1H), 7.42 (s, 1H), 7.32–7.18 (m, 6H), 6.92 (dt, J = 2.2, 1.0 Hz, 1H), 4.03 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101

MHz) δ 140.3, 135.1, 128.5, 128.5, 127.2, 126.2, 125.9, 124.2, 123.4, 120.2, 115.7, 112.5, 77.2, 31.3 ppm; HRMS (ESI) m/z calculated for $C_{15}H_{12}NCl_2$ $[M+H]^+$ 276.0347; found 276.0158.



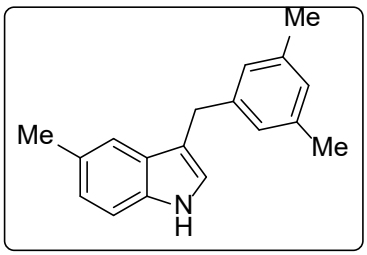

**5-methyl-3-(4-methylbenzyl)-1*H*-indole (5a)**

White solid (114 mg, 81%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.73 (s, 1H), 7.31 (dd, *J* = 1.8, 1.0 Hz, 1H), 7.23–7.13 (m, 3H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.99 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.80 (dd, *J* = 2.3, 1.1 Hz, 1H), 4.03 (s, 2H), 2.41 (s, 3H), 2.30 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 138.3, 135.2, 134.8, 129.0, 128.5, 127.7, 123.6, 122.5, 118.7, 115.5, 110.7, 31.1, 21.5, 21.0 ppm; HRMS (ESI) m/z calculated for $C_{17}H_{18}N$ $[M+H]^+$ 236.1439; found 236.1434.



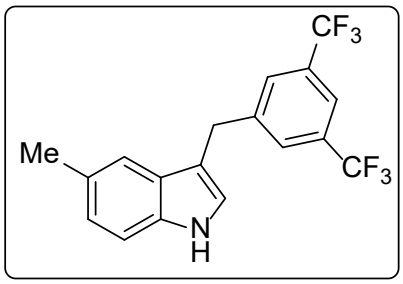

**3-(4-chlorobenzyl)-5-methyl-1*H*-indole (5b)**

Brown solid (115.mg, 75%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.88 (br., s, 1H), 7.27-7.29 (m, 1H), 7.25-7.26 (m, 3H), 7.23-7.25 (m, 1H), 7.22-7.23 (m, 1H), 7.19-7.21 (m, 2H), 6.99-7.04 (m, 1H), 6.85-6.89 (m, 1H), 4.05 (s, 2H), 1.8 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 139.8, 129.9, 128.7, 128.6, 128.4, 128.3, 123.8, 122.5, 118.7, 118.6, 114.7, 110.8, 77.3, 77.2, 76.7, 30.9, 21.5 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{15}NCl$ $[M+H]^+$ 256.0893; found 256.0887.



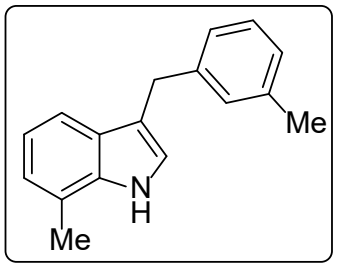

**3-(3,5-dimethylbenzyl)-5-methyl-1*H*-indole (5c)**

Greenish solid (126 mg, 84%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.74 (br., s, 1H), 7.33 (s, 1H), 7.15-7.25 (m, 1H), 6.99 (d, $J$ = 8.3 Hz, 1H), 6.89 (s, 2H), 6.73-6.85 (m, 2H), 3.99 (s, 2H), 2.42 (s, 3H), 2.25 (s, 6H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 141.5, 138.0, 135.0, 128.8, 128.1, 127.8, 126.8, 123.8, 122.8, 119.0, 115.7, 111.0, 77.6, 77.3, 31.6, 21.8, 21.6 ppm; HRMS (ESI) m/z calculated for $C_{18}H_{20}N$ $[M+H]^+$ 250.1596; found 250.1591.



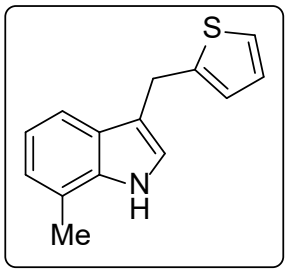

**3-(3,5-bis(trifluoromethyl)benzyl)-5-methyl-1*H*-indole (5d)**

Greenish solid (156 mg, 73%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.94 (br., s, 1H), 7.72 (s, 3H), 7.19-7.31 (m, 2H), 7.04 (d, $J$ = 8.3 Hz, 1H), 6.81-6.96 (m, 1H), 4.19 (s, 2H), 2.42 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 143.9, 134.8, 131.6, 129.1, 127.2, 124.8, 124.1, 122.7, 122.1, 120.1, 118.2, 113.1, 111.0, 77.3, 76.7, 31.3, 21.4 ppm; HRMS (ESI) m/z calculated for $C_{18}H_{14}NF_6$ $[M+H]^+$ 358.1030; found 358.1026.



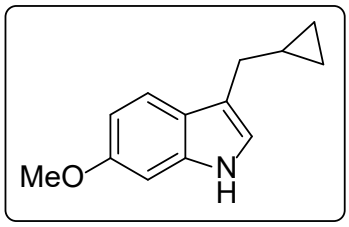

**2-methyl-3-(3-methylbenzyl)-1*H*-indole (5e)**

Yellow solid (88.mg, 62%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.72 (br., s, 1H), 7.39 (d, $J$ = 7.8 Hz, 1H), 7.19-7.25 (m, 1H), 7.05-7.14 (m, 2H), 6.97-7.04 (m, 3H), 6.94 (d, $J$ = 7.1 Hz, 1H), 4.01 (s, 2H), 2.32 (br., s, 3H), 2.26 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 141.6, 137.7, 135.2, 131.6, 129.0, 128.1, 126.4, 125.3, 120.9, 119.6, 119.2, 118.3, 110.6, 110.1, 77.3, 76.7, 30.0, 21.4, 11.7 ppm; HRMS (ESI) m/z calculated for $C_{17}H_{18}N$ $[M+H]^+$ 236.1439; found 236.1432.



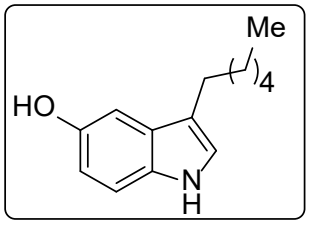

**2-methyl-3-(thiophen-2-ylmethyl)-1*H*-indole (5f)**

Dark brown solid (79.mg, 58%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.79 (br., s, 1H), 7.45 (d, $J$ = 7.5 Hz, 1H), 7.27 (d, $J$ = 7.9 Hz, 1H), 7.08-7.19 (m, 1H), 7.00-7.07 (m, 2H), 6.84-6.90 (m, 1H), 6.75-6.82 (m, 1H), 4.22 (s, 2H), 2.40 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ = 145.5, 137.3, 135.2, 131.5, 128.4, 126.6, 124.0, 123.1, 121.1, 119.3, 118.2, 110.1, 77.3, 77.2, 76.7, 24.6, 11.7 ppm; HRMS (ESI) m/z calculated for $C_{14}H_{14}NS$ $[M]^+$ 228.0841; found 228.0846.



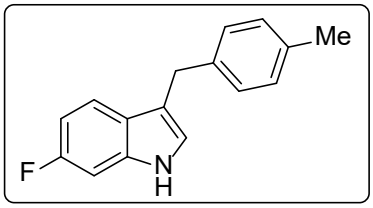

**3-(cyclopropylmethyl)-6-methoxy-1*H*-indole (5g)**

Rock salt solid (85.mg, 70%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.57 (br., s, 1H), 7.28 (d, $J$ = 8.6 Hz, 1H), 6.69-6.82 (m, 1H), 6.53-6.67 (m, 2H), 3.63 (s, 3H), 2.44 (d, $J$ = 6.8 Hz, 2H), 0.78-0.99 (m, 1H), 0.23-0.43 (m, 2H), 0.01 (q, $J$ = 4.8 Hz, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 156.4, 137.0, 122.1, 120.0, 119.6, 116.5, 109.1, 94.6, 77.3, 76.7, 55.7, 30.0, 11.1, 4.8 ppm; HRMS (ESI) m/z calculated for $C_{13}H_{16}ON$ $[M+H]^+$ 202.1232; found 202.1221.



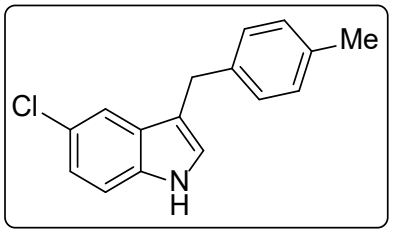

**3-hexyl-1*H*-indol-5-ol (5h)**

Viscous colorless liquid (74 mg, 57%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.76 (br., s, 1H), 7.12-7.23 (m, 1H), 7.00 (d, $J$ = 2.5 Hz, 1H), 6.86-6.97 (m, 1H), 6.75 (dd, $J$ = 8.6, 2.4 Hz, 1H), 4.63 (br., s, 1H), 2.66 (t, $J$ = 7.6 Hz, 2H), 1.56-1.83 (m, 3H), 1.22-1.44 (m, 6H), 0.77-0.97 (m, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 149.0, 131.7, 128.3, 122.2, 116.6, 111.6, 111.5, 103.6, 77.3, 76.7, 31.8, 30.0, 29.3, 25.2, 22.7, 14.1 ppm; HRMS (ESI) m/z calculated for $C_{14}H_{20}ON$ $[M+H]^+$ 218.1545; found 218.1538.



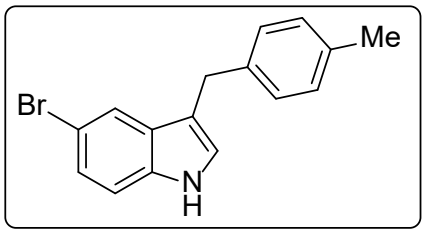

**6-fluoro-3-(4-methylbenzyl)-1*H*-indole (5i)**

White solid (103 mg, 72%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.83 (br., s, 1H), 7.38 (dd, $J$ = 8.6, 5.4 Hz, 1H), 7.03-7.18 (m, 4H), 6.98 (dd, $J$ = 9.6, 2.3 Hz, 1H), 6.77-6.87 (m, 2H), 4.02 (s, 2H), 2.30 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 161.2, 158.8, 137.8, 135.4, 129.0, 128.5, 124.0, 122.4, 119.9, 116.1, 108.1, 97.4, 77.3, 76.7, 31.1, 21.0 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{14}NF$ $[M]^+$ 239.1189; found 239.1106.



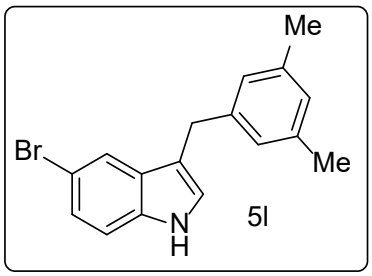

**5-chloro-3-(4-methylbenzyl)-1*H*-indole (5j)**

Green liquid (114 mg, 74%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.90 (s, 1H), 7.47 (d, $J$ = 2.0 Hz, 1H), 7.24–7.19 (m, 1H), 7.17–7.05 (m, 5H), 6.96–6.78 (m, 1H), 4.00 (s, 2H), 2.31 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$,101 MHz): δ 137.6, 135.5, 134.8, 129.1, 128.5, 125.1, 123.7, 122.3, 121.2, 118.6, 115.9, 112.1, 30.9, 21.0 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{15}NCl$ $[M+H]^+$ 256.0893; found 256.0886.



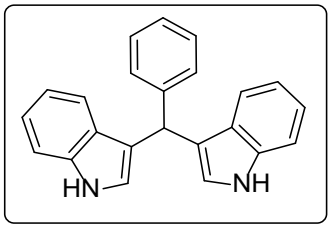

**5-bromo-3-(4-methylbenzyl)-1*H*-indole (5k)**

Colorless liquid (139 mg, 77%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.98 (s, 1H), 7.64 (d, *J* = 1.8 Hz, 1H), 7.30–7.18 (m, 3H), 7.17–7.05 (m, 4H), 6.91 (dd, *J* = 2.3, 1.2 Hz, 1H), 4.01 (s, 2H), 2.32 (s, 3H).ppm; $^{13}$C NMR ($CDCl_3$,101 MHz): δ 137.5, 135.5, 135.0, 129.2, 129.1, 128.4, 124.8, 123.4, 121.7, 115.8, 112.6, 112.4, 30.9, 21.0 ppm; HRMS (ESI) m/z calculated for $C_{16}H_{15}NBr$ $[M+H]^+$ 300.0382; found 300.0395.




**5-bromo-3-(3,5-dimethylbenzyl)-1*H*-indole (5l)**

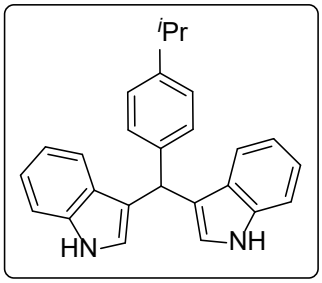
Brown liquid (151.mg, 80%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.93 (br., s, 1H), 7.66 (s, 1H), 7.12-7.30 (m, 2H), 6.76-6.93 (m, 4H), 3.96 (s, 2H), 2.26 (s, 6H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 140.5, 137.9, 135.0, 129.3, 127.7, 126.4, 124.8, 123.5, 121.7, 115.7, 112.6, 112.4, 77.3, 76.7, 31.1, 21.3 ppm; HRMS (ESI) m/z calculated for $C_{17}H_{17}NBr$ $[M+H]^+$ 314.0544; found 314.0536.




**3,3'-(Phenylmethylene)bis(1H-indole) (6a)**

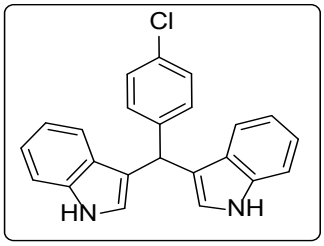
Red solid, 93% (74.63 mg) isolated yield. $^{1}$H NMR (500 MHz, $CDCl_3$): δ ppm ppm 7.86 (br s, 2 H), 7.42 (d, *J* = 8.1 Hz, 2 H), 7.35-7.38 (m, 4 H), 7.28-7.32 (m, 2H), 7.17-7.26 (m, 3 H), 7.01-7.05 (m, 2 H), 6.64 (dd, *J* = 2.4, 0.9 Hz, 2 H), 5.91 (s, 1 H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ ppm 144.0,

136.6, 128.7, 128.2, 127.0, 126.1, 123.6, 121.9, 119.9, 119.6, 119.2, 111.0, 40.1. HRMS (ESI) m/z calcd for $C_{23}H_{17}N_2$ $[M-H]^+$: 321.1392, found: 321.1393.



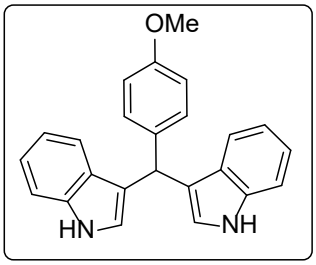

**3,3'-((4-Isopropylphenyl)methylene)bis(1H-indole) (6b)**

Red solid, 95% (86.4 mg) isolated yield. $^1$H NMR (400 MHz, $CDCl_3$): δ ppm 7.88 (br s, 2 H), 7.41 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.25-7.27 (m, 2 H), 7.16 (t, *J* = 7.8 Hz, 2 H), 7.13 (d, *J* = 8.1 Hz, 2 H), 7.00 (t, *J* = 7.5 Hz, 2 H), 6.66 (d, *J* = 1.9 Hz, 2 H), 5.86 (s, 1 H), 2.88 (quint, *J* = 6.9 Hz, 1 H), 1.24 (d, *J* = 6.9 Hz, 6 H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ ppm 146.4, 141.2, 136.6, 128.5, 127.1, 126.2, 123.5, 121.8, 120.0, 119.9, 119.1, 111.0, 39.7, 33.6, 24.0. HRMS (ESI) m/z calcd for $C_{26}H_{23}N_2$ $[M-H]^+$: 363.1861, found: 363.1862



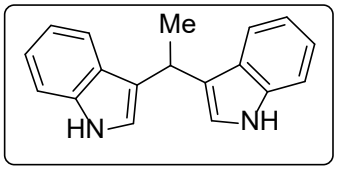

**3,3'-((4-Chlorophenyl)methylene)bis(1H-indole) (6c)**

Orange solid, 91% (80.7 mg) isolated yield. $^1$H NMR (400 MHz, $CDCl_3$): δ ppm 7.86 (br s, 2 H), 7.28 (d, *J* = 8.6 Hz, 4 H), 7.15-7.20 (m, 4 H), 7.10 (t, *J* = 7.6 Hz, 2 H), 6.94 (t, *J* = 7.5 Hz, 2 H), 6.56 (br s, 2 H), 5.78 (s, 1 H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ ppm 142.5, 136.7, 131.8, 130.0, 128.3, 126.9, 123.6, 122.1, 119.8, 119.3, 119.2, 111.1, 39.6. HRMS (ESI) m/z calcd for $C_{23}H_{16}ClN_2$ $[M-H]^+$: 355.1002, found: 355.1002.



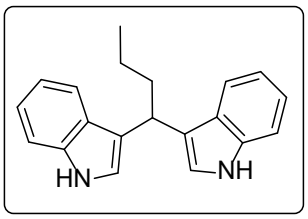

**3,3'-((4-Methoxyphenyl)methylene)bis(1H-indole) (6d)**

Orange solid, 60% (52.6 mg) isolated yield. $^{1}$H NMR (400 MHz, $CDCl_3$): δ ppm 7.90 (br s, 2 H), 7.40 (d, *J* = 8.0 Hz, 2 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 7.25-7.27 (m, 2 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 7.01 (t, *J* = 7.6 Hz, 2 H), 6.82-6.84 (m, 2 H), 6.65 (d, *J* = 1.9 Hz, 2 H), 5.85 (s, 1 H), 3.79 (s, 3 H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ ppm 157.9, 136.7, 136.2, 129.6, 127.0, 123.5, 121.9, 120.0, 119.2, 113.5, 111.0, 55.2, 39.3. HRMS (ESI) m/z calcd for $C_{24}H_{19}N_2O$ $[M-H]^+$: 351.1497, found: 351.1496.



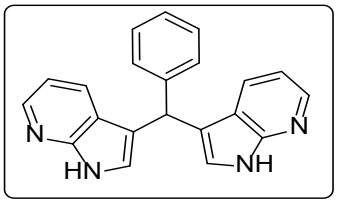

**3,3'-(ethane-1,1-diyl)bis(1H-indole) (6f)**

White solid, 15% (10.0 mg) isolated yield. $^{1}$H NMR (400 MHz, $CDCl_3$): δ ppm 7.89 (br s, 2 H), 7.60 (d, *J* = 8.0 Hz, 2 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 7.16-7.20 (m, 2 H), 7.04-7.08 (m, 2 H), 6.93 (d, *J* = 1.1 Hz, 2 H), 4.70 (q, *J* = 7.1 Hz, 1 H), 1.83 (d, *J* = 7.1 Hz, 3 H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ ppm 136.6, 126.9, 121.7, 121.6, 121.2, 119.7, 119.0, 111.0, 28.1, 21.7. LCMS (ESI) m/z for $C_{18}H_{17}N_2$ $[M+H]^+$: 261.0.



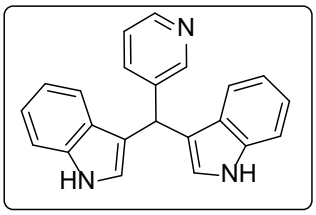

**3,3'-(Butane-1,1-diyl)bis(1H-indole) (6g)**

Brown solid, 61% (43.7 mg) isolated yield. $^{1}$H NMR (400 MHz, $CDCl_3$): δ ppm 7.83 (br s, 2 H), 7.65 (d, *J* = 8.1 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.17-7.21 (m, 2 H), 7.06-7.10 (m, 2 H), 6.96 (d, *J* = 2.0 Hz, 2 H), 4.53 (t, *J* = 7.4 Hz, 1 H), 2.21-2.27 (m, 2 H), 1.45-1.50 (m, 2 H), 1.00 (t, *J* = 7.4 Hz, 3 H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ ppm 136.5, 127.1, 121.6, 121.4, 120.5, 119.6, 118.9, 111.0, 38.1, 33.6, 21.4, 14.2. HRMS (ESI) m/z calcd for $C_{20}H_{19}N_2$ $[M-H]^+$: 287.1548, found: 287.1547.



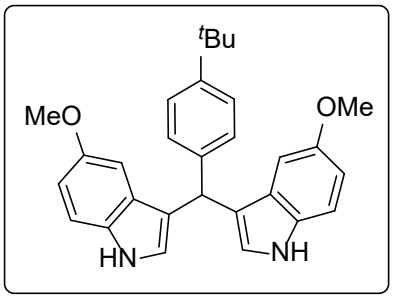

**3,3'-(Phenylmethylene)bis(1H-pyrrolo[2,3-*b*]pyridine) (6h)**

Colourless solid, 65% (52.8 mg) isolated yield. $^{1}$H NMR (400 MHz, DMSO-d6): δ ppm 11.42 (br s, 2 H), 8.16 (d, *J* = 3.9 Hz, 2 H), 7.60 (dd, *J* = 7.8, 1.3 Hz, 2 H), 7.36 (d, *J* = 7.3 Hz, 2 H), 7.28 (t, *J* = 7.5 Hz, 2 H), 7.17-7.21 (m, 1 H), 6.98 (d, *J* = 2.1 Hz, 2 H), 6.92 (dd, *J* = 7.9, 4.6 Hz, 2 H), 5.86 (s, 1 H). $^{13}$C NMR (100.6 MHz, DMSO-d6): δ ppm 148.9, 144.1, 142.5, 128.3, 127.2, 126.2, 123.9, 118.8, 116.5, 114.9, 38.9. HRMS (ESI) m/z calcd for $C_{21}H_{17}N_4$ $(M+H)^+$: 325.1453, found: 325.1444.



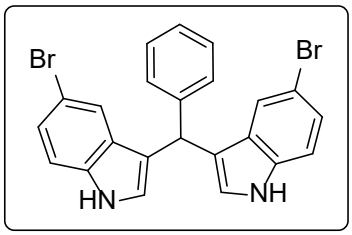

**3,3'-(Pyridin-3-ylmethylene)bis(1H-indole) (6i)**

Pink solid, 70% (56.5 mg) isolated yield. $^{1}$H NMR (400 MHz, DMSO-d6): δ ppm 10.90 (br s, 2 H), 8.61 (s, 1 H), 8.39 (d, *J* = 3.8 Hz, 1 H), 7.70 (d, *J* = 7.6 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.28-7.30 (m, 3 H), 7.05 (t, *J* = 7.4 Hz, 2 H), 6.87-6.89 (m, 4 H), 5.91 (s, 1 H). $^{13}$C NMR (101 MHz, DMSO-d6): δ ppm 149.6, 147.2, 140.3, 136.6, 135.7, 126.4, 123.7, 123.3, 121.1, 119.0, 118.4, 117.2, 111.6, 37.1. HRMS (ESI) m/z calcd for $C_{22}H_{18}N_3$ $[M+H]^+$: 324.1501, found: 324.1494.



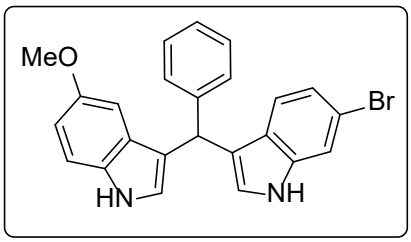

**3,3'-((4-(tert-Butyl)phenyl)methylene)bis(5-methoxy-1H-indole) (6j)**

Red solid, 85% (92.8 mg) isolated yield. $^1$H NMR (400 MHz, $CDCl_3$): δ ppm 7.81 (br s, 2 H), 7.27-7.32 (m, 4 H), 7.23 (d, *J* = 8.5 Hz, 2 H), 6.82-6.85 (m, 4 H), 6.69 (br s, 2 H), 5.76 (s, 1 H), 3.70 (s, 6 H), 1.32 (s, 9 H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ ppm 153.6, 148.7, 140.8, 131.8, 128.3, 127.6, 125.0, 124.3, 119.5, 111.8, 111.6, 102.0, 55.8, 39.8, 34.4, 31.4. HRMS (ESI) m/z calcd for $C_{29}H_{29}O_2N_2$ $[M-H]^+$: 437.2229, found: 437.2224.



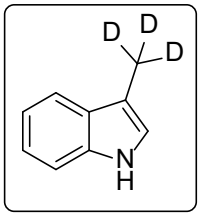

**3,3'-(Phenylmethylene)bis(5-bromo-1H-indole) (6k)**

Orange solid, 68% (80.9 mg) isolated yield. $^1$H NMR (400 MHz, DMSO-d6): δ ppm 11.07 (br s, 2 H), 7.43 (d, *J* = 2.0 Hz, 2 H), 7.33-7.35 (m, 4 H), 7.27-7.31 (m, 2 H), 7.17-7.21 (m, 1 H), 7.16 (dd, *J* = 8.6, 1.9 Hz, 2 H), 6.89 (d, *J* = 2.0 Hz, 2 H), 5.86 (s, 1 H). $^{13}$C NMR (100.6 MHz, DMSO-d6): δ ppm 144.3, 135.3, 128.4, 128.2, 126.1, 125.3, 123.5, 121.2, 117.7, 113.6, 110.9, 38.9. HRMS (ESI) m/z calcd for $C_{23}H_{15}Br_2N_2$ $[M-H]^+$: 476.9602, found: 476.9604.



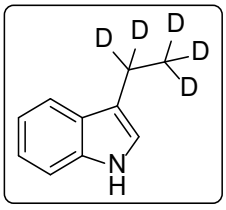

**6-Bromo-3-((5-methoxy-1H-indol-3-yl)(phenyl)methyl)-1H-indole (6l)**

Red solid, 54% (58.5 mg) isolated yield. $^1$H NMR (400 MHz, $CDCl_3$): δ ppm 7.88 (br s, 1 H), 7.83 (br s, 1 H), 7.47 (d, *J* = 1.5 Hz, 1 H), 7.28-7.35 (m, 4 H), 7.21-7.25 (m, 3 H), 7.10 (dd, *J* = 8.4 Hz, 1.7 Hz, 1 H), 6.86 (dd, *J* = 8.7 Hz, 2.4 Hz, 1 H), 6.82 (d, *J* = 2.4 Hz, 1 H), 6.61-6.62 (m, 2 H), 5.80 (s, 1 H), 3.72 (s, 3 H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ ppm 153.7, 143.6, 137.4, 131.8, 128.6, 128.3, 127.3, 126.3, 125.9, 124.3, 124.2, 122.5, 121.2, 119.7, 119.0, 115.4, 113.9, 111.9, 111.8, 101.8, 55.8, 40.1. HRMS (ESI) m/z calcd for $C_{24}H_{18}BrN_2O$ $[M-H]^+$: 429.0603, found: 429.0597.



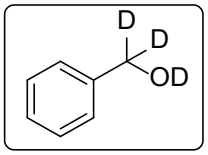

**3-(methyl-d3)-1H-indole (3ac-*d*$_3$)**

White solid (18 mg, 52%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.87 (s, 1H), 7.58 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.40–7.31 (m, 1H), 7.19 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.12 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.97 (d, *J* = 1.3 Hz, 1H).ppm; $^{13}$C NMR ($CDCl_3$,101 MHz): δ 136.2, 128.3, 121.8, 121.5, 119.1, 118.8, 110.9, 77.2 ppm; HRMS (ESI) m/z calculated for $C_9H_7D_3N$ $[M+H]^+$ 135.1002; found 135.1007.



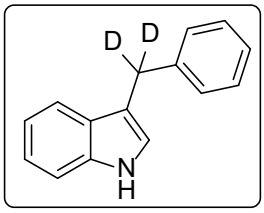

**3-(ethyl-d5)-1H-indole (3ad-*d*$_5$)**

White solid (23 mg, 60%); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.73 (s, 1H), 7.53 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.32–7.19 (m, 1H), 7.18–7.06 (m, 2H), 7.03 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H) ppm; $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 136.4, 136.4, 127.5, 121.9, 121.8, 120.4, 119.0, 119.0, 118.7, 118.5, 111.0, 77.2 ppm; HRMS (ESI) m/z calculated for $C_{10}H_7D_5N$ $[M+H]^+$ 151.1284; found 151.1277



**phenylmethan-d2-ol-d (5-DBA)**

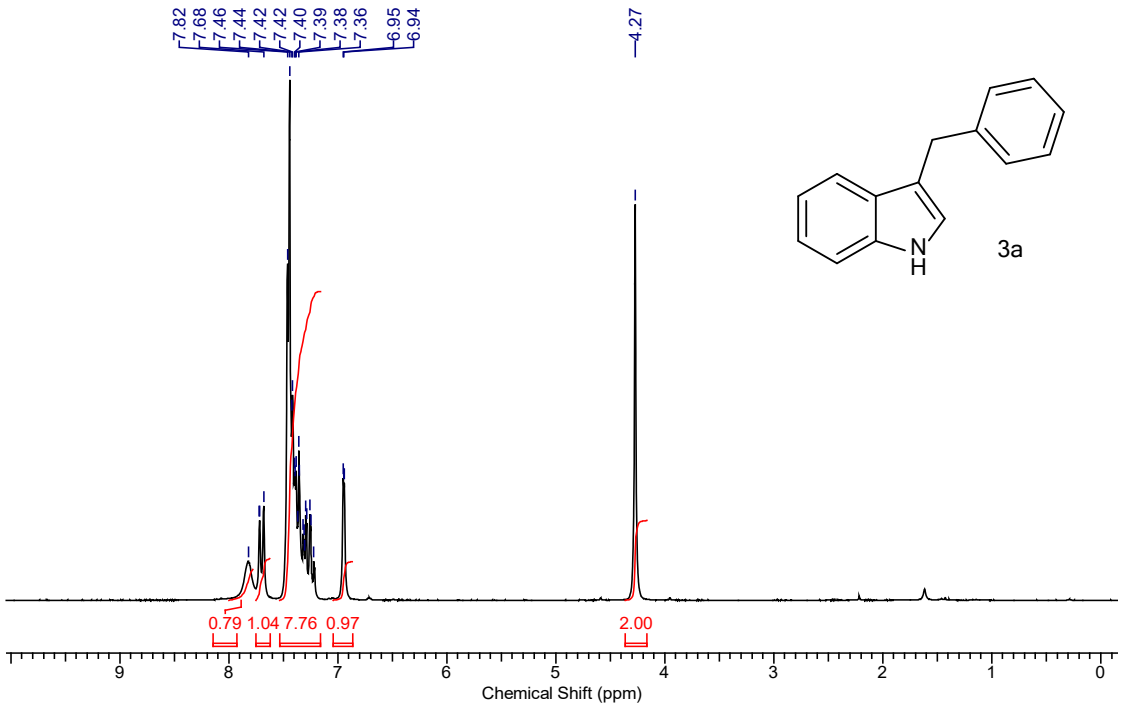
White solid (100 mg, 90%); $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.35 (d, $J$ = 4.0 Hz, 4H), 7.32–7.26 (m, 1H). $^{13}$C NMR ($CDCl_3$,101 MHz): δ 140.7, 128.5, 127.6, 127.0 ppm; HRMS (ESI) m/z calculated for $C_7H_3D_3O$ $[M]^+$ 111.0763; found 111.0804



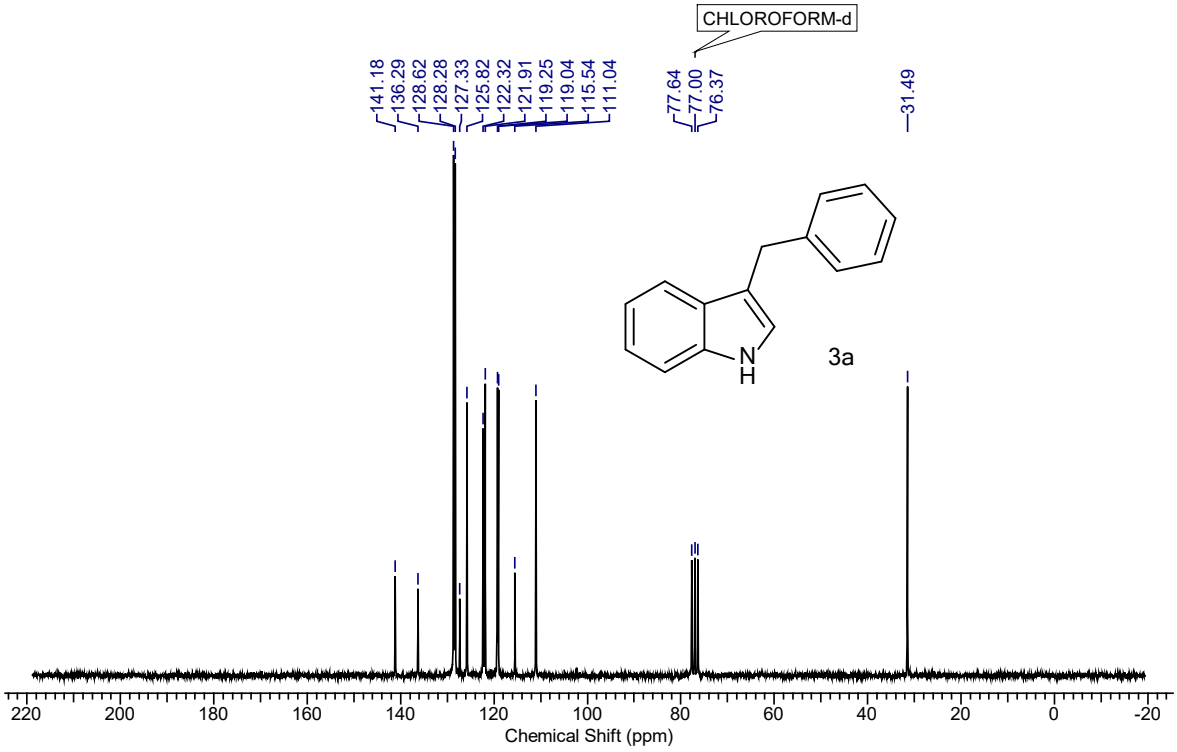

**3-(phenylmethyl-d2)-1H-indole (3a-$d_2$)**

White solid (40 mg, 77%); 1H NMR ($CDCl_3$, 400 MHz): δ 7.88 (s, 1H), 7.51 (dd, $J$ = 7.9, 1.1 Hz, 1H), 7.33 (dt, $J$ = 8.1, 1.0 Hz, 1H), 7.30–7.23 (m, 4H), 7.18 (ddt, $J$ = 8.2, 6.9, 1.8 Hz, 2H), 7.07 (ddd, $J$ = 8.0, 7.0, 1.0 Hz, 1H), 6.88 (dd, $J$ = 2.3, 0.9 Hz, 1H), 4.11 (d, $J$ = 0.8 Hz, 1H) ppm; HRMS (ESI) m/z calculated for $C_{15}H_{11}D_2N$ $[M]^+$ 209.1174; found 209.1194.

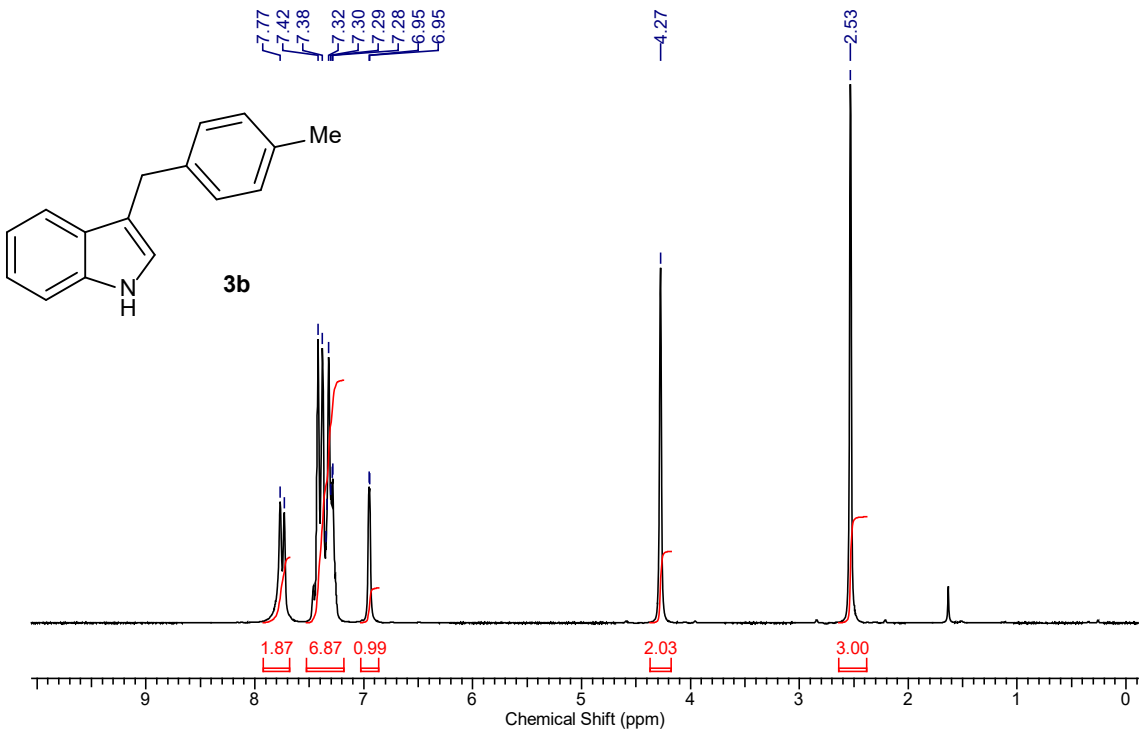
# 6. Copy of NMR Spectra



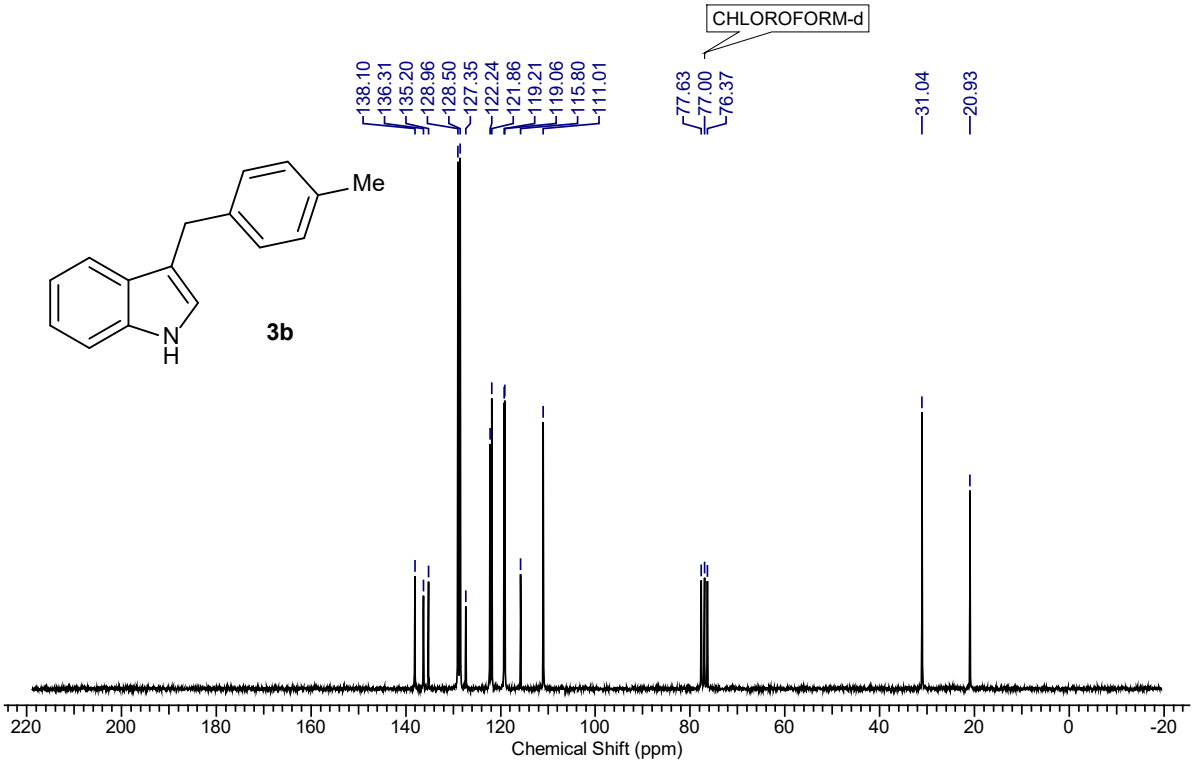

$^{1}$H NMR of **3a**



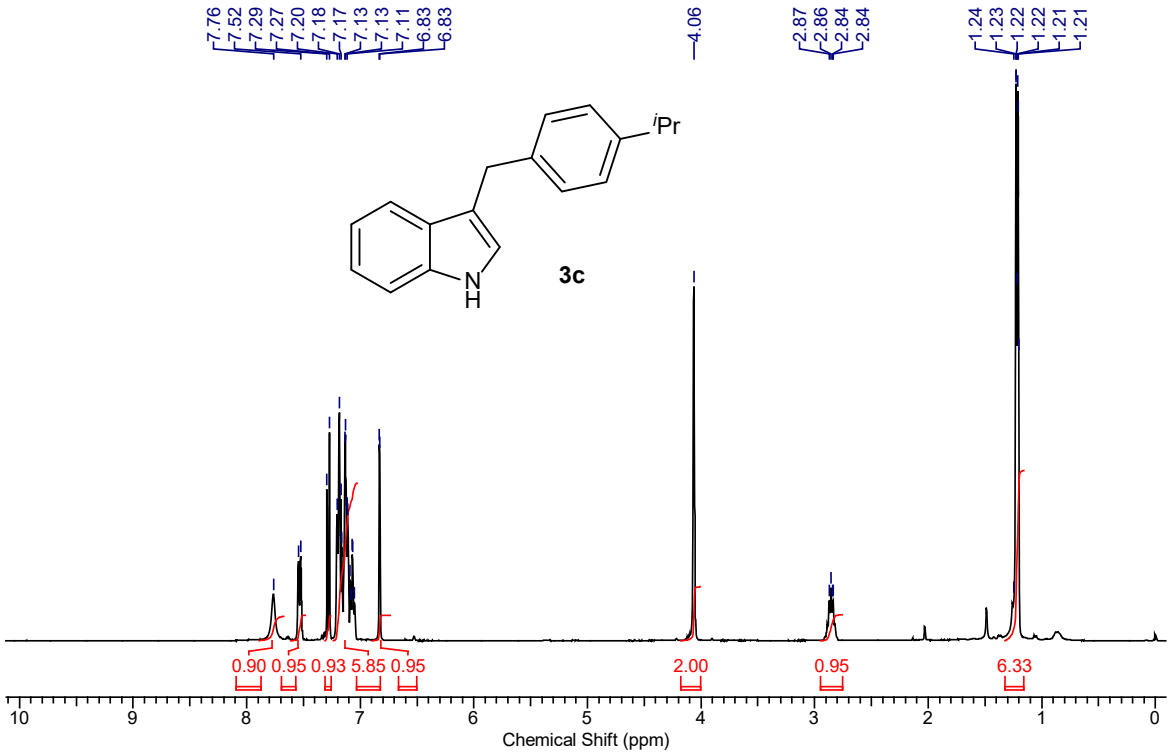

$^{13}$C NMR of **3a**



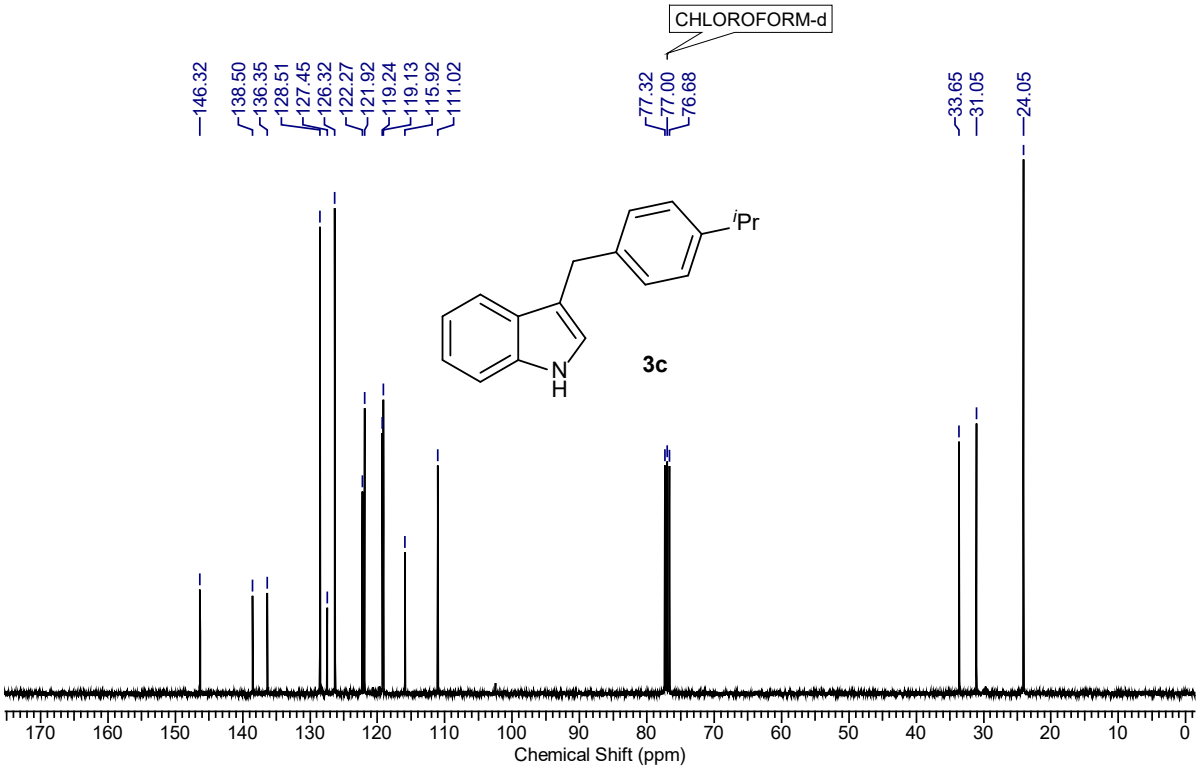

$^{1}$H NMR of **3b**



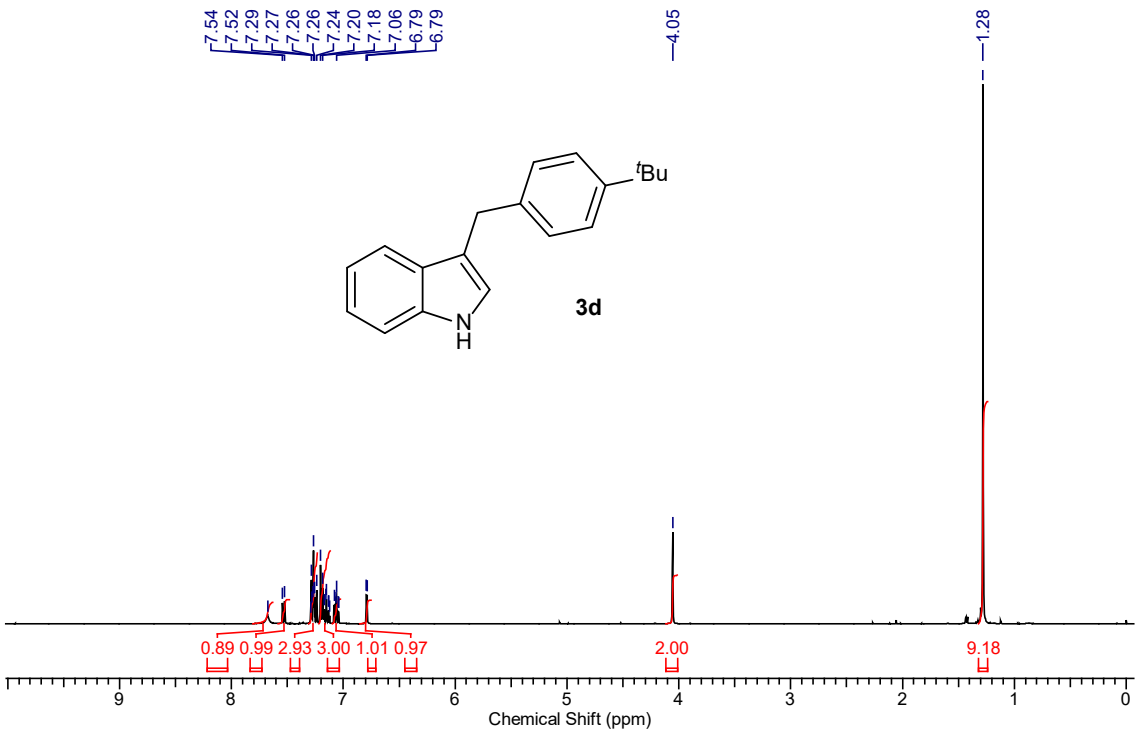

$^{13}$C{$^{1}$H} NMR of **3b**



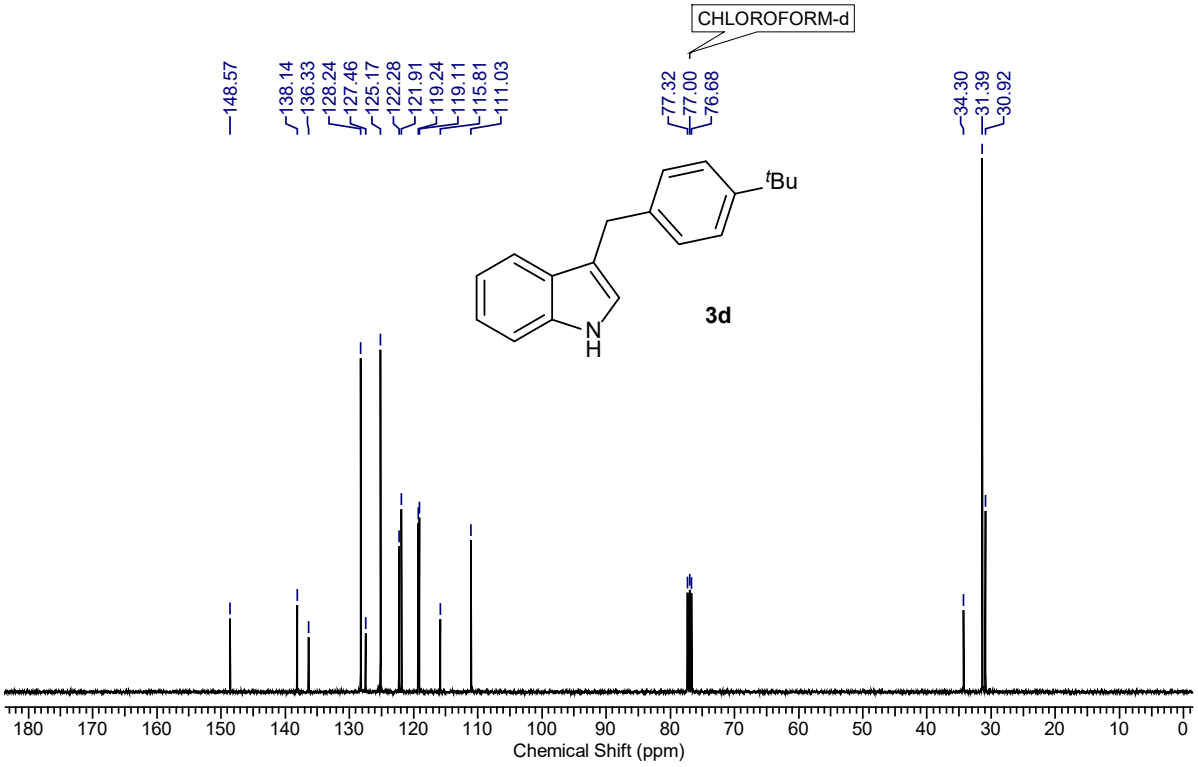

$^{1}$H NMR of **3c**



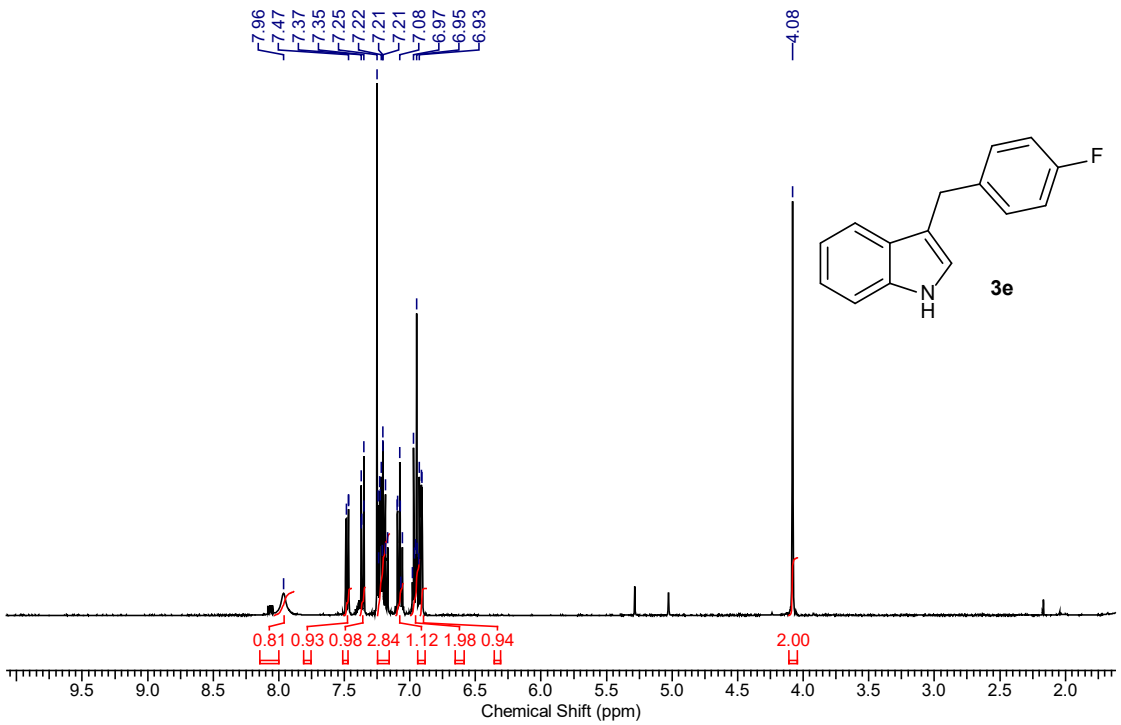

$^{13}$C{$^{1}$H} NMR of **3c**



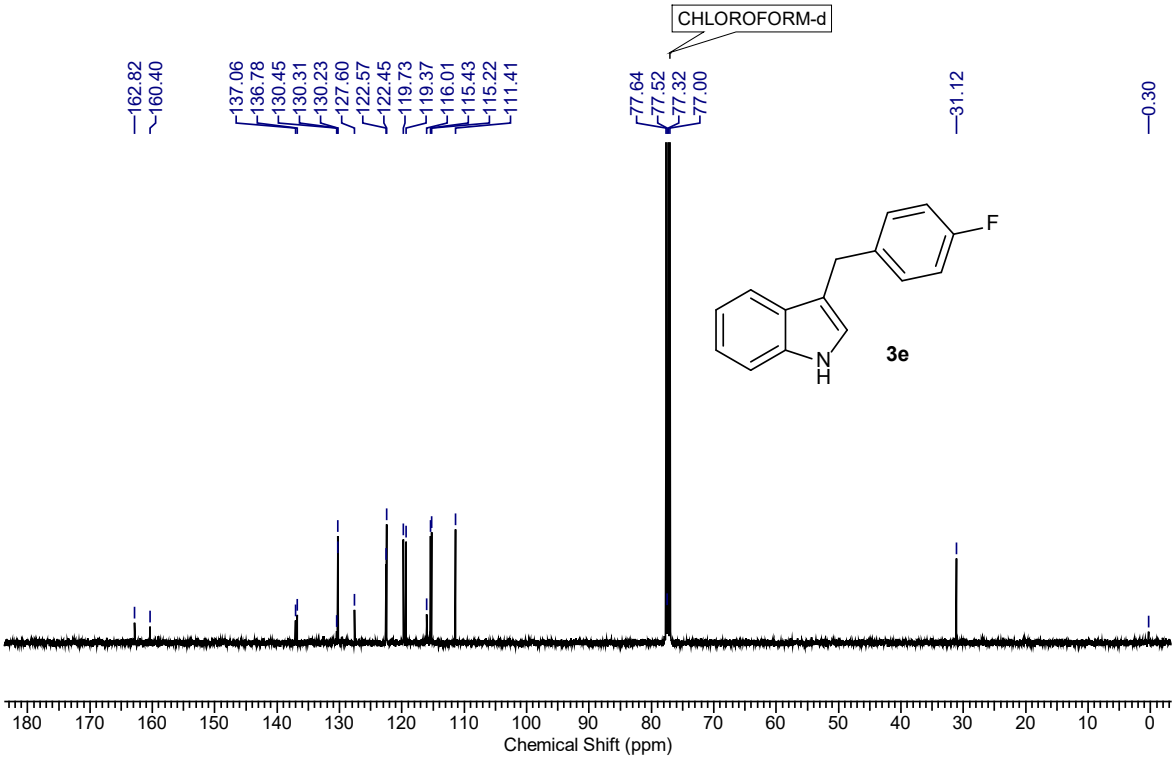

$^{1}$H NMR of **3d**



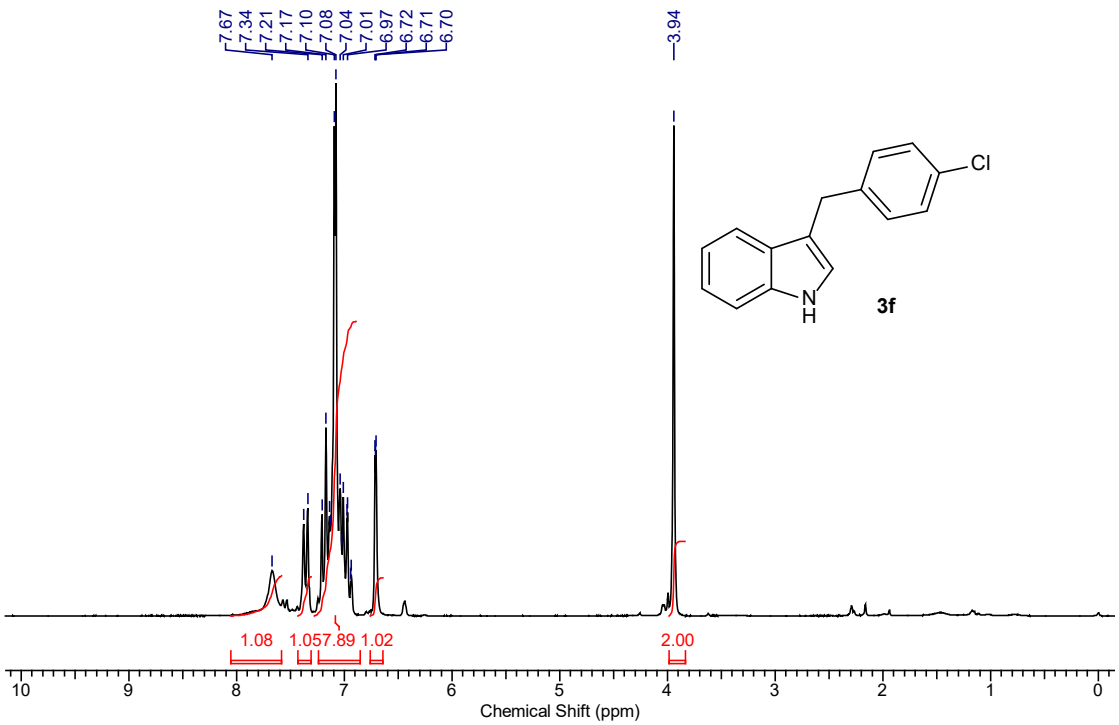

$^{13}$C{$^{1}$H} NMR of **3d**



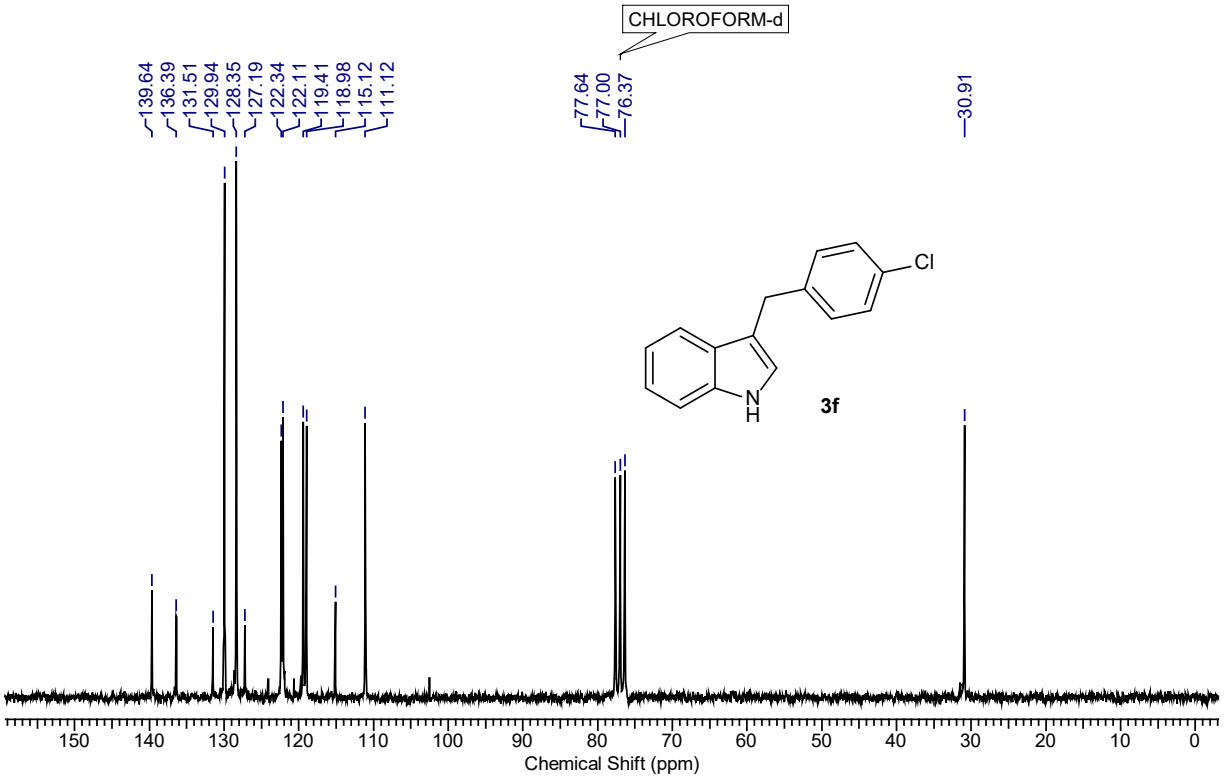

$^{1}$H NMR of **3e**



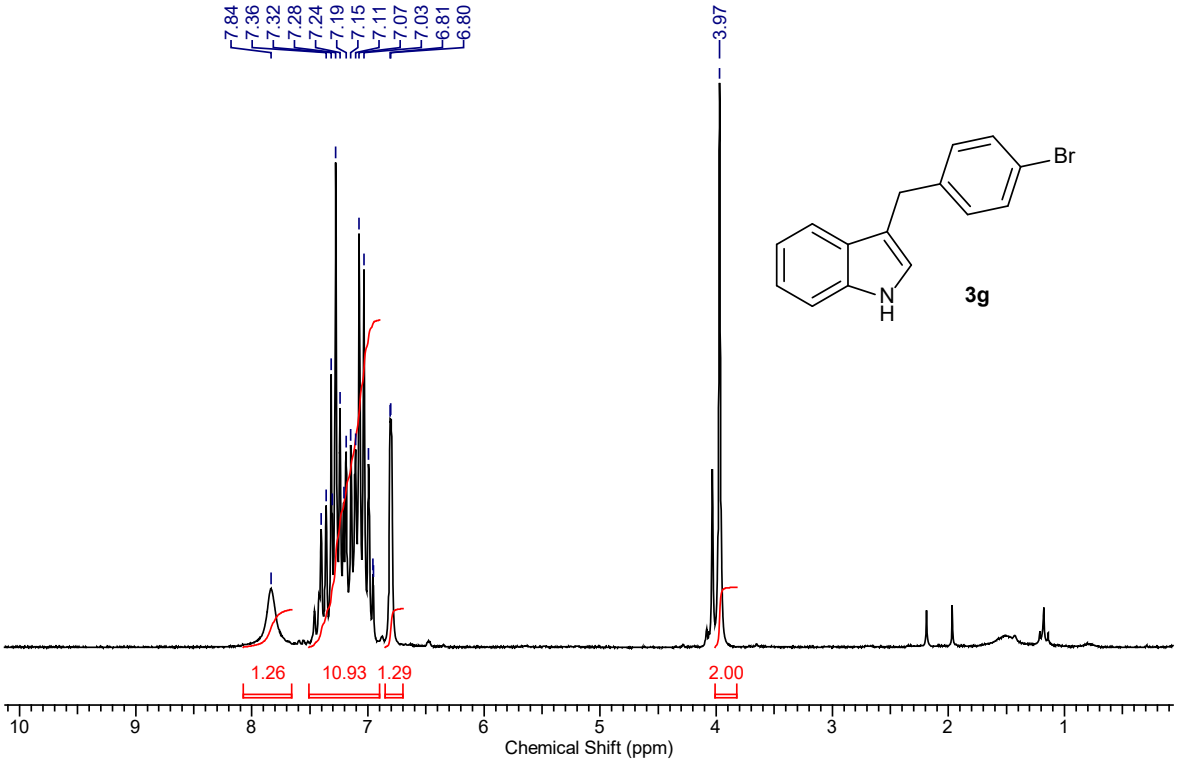

$^{13}$C{$^{1}$H} NMR of **3e**



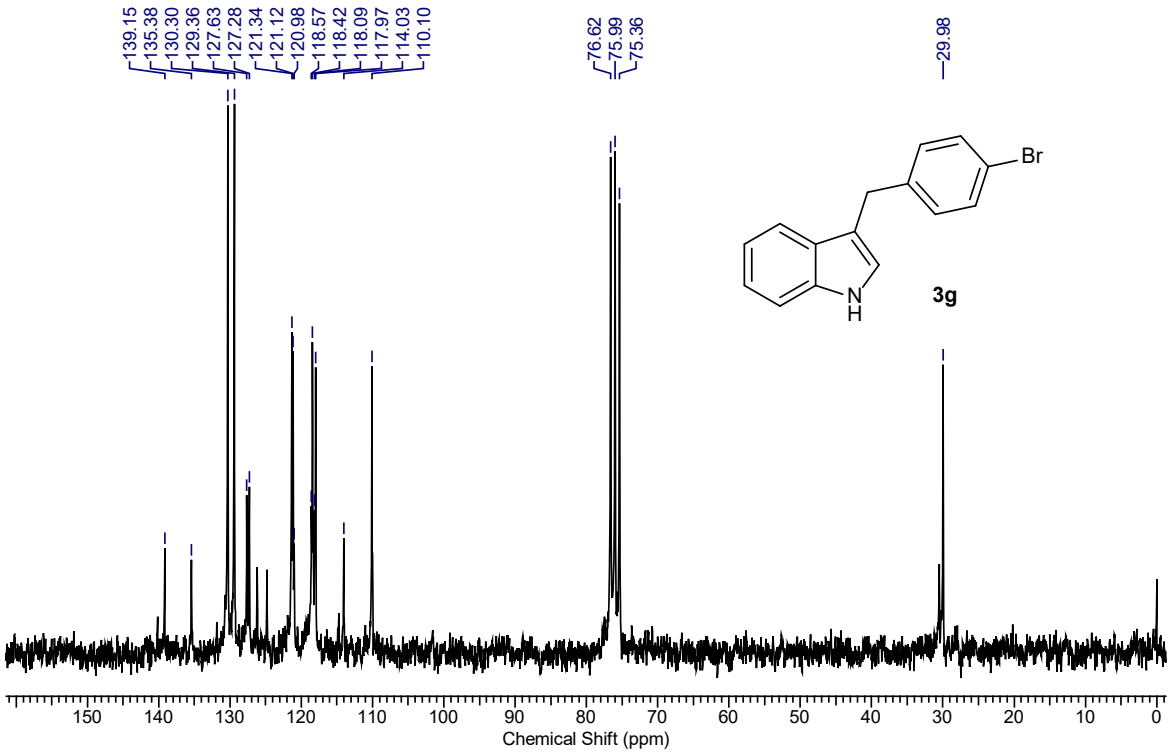

$^{1}$H NMR of **3f**



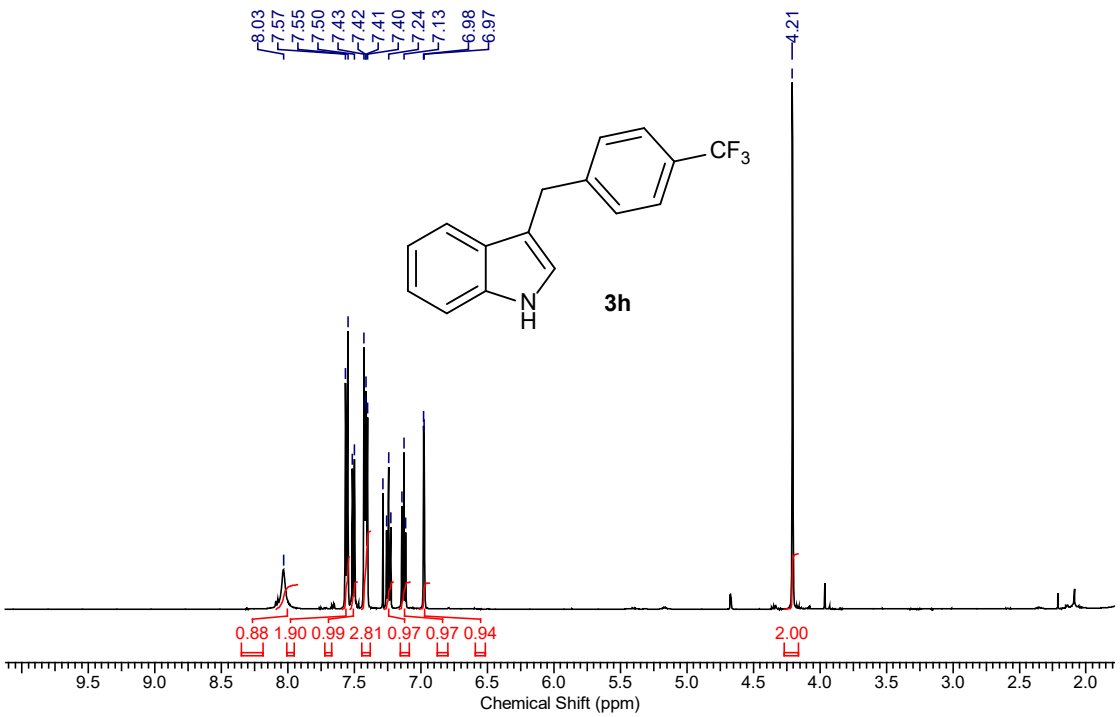

$^{13}$C{$^{1}$H} NMR of **3f**



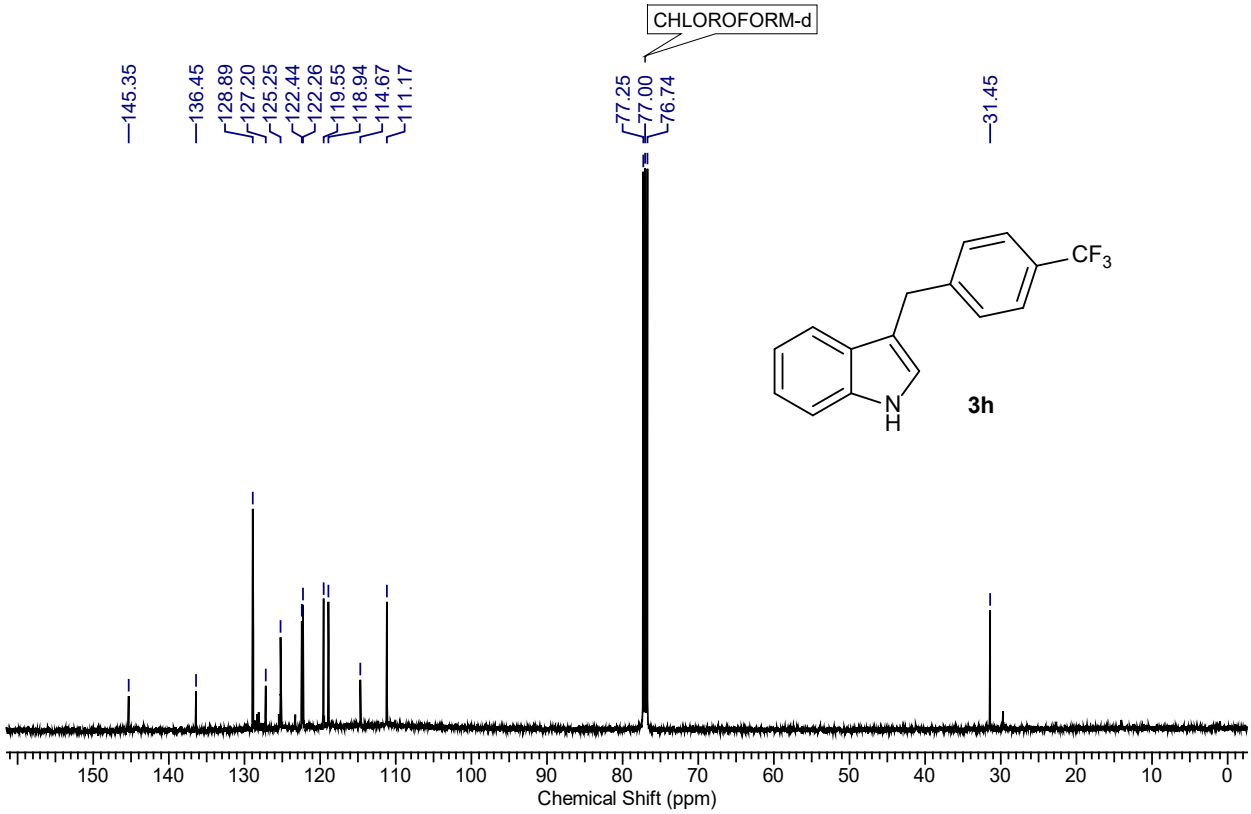

$^{1}$H NMR of **3g**



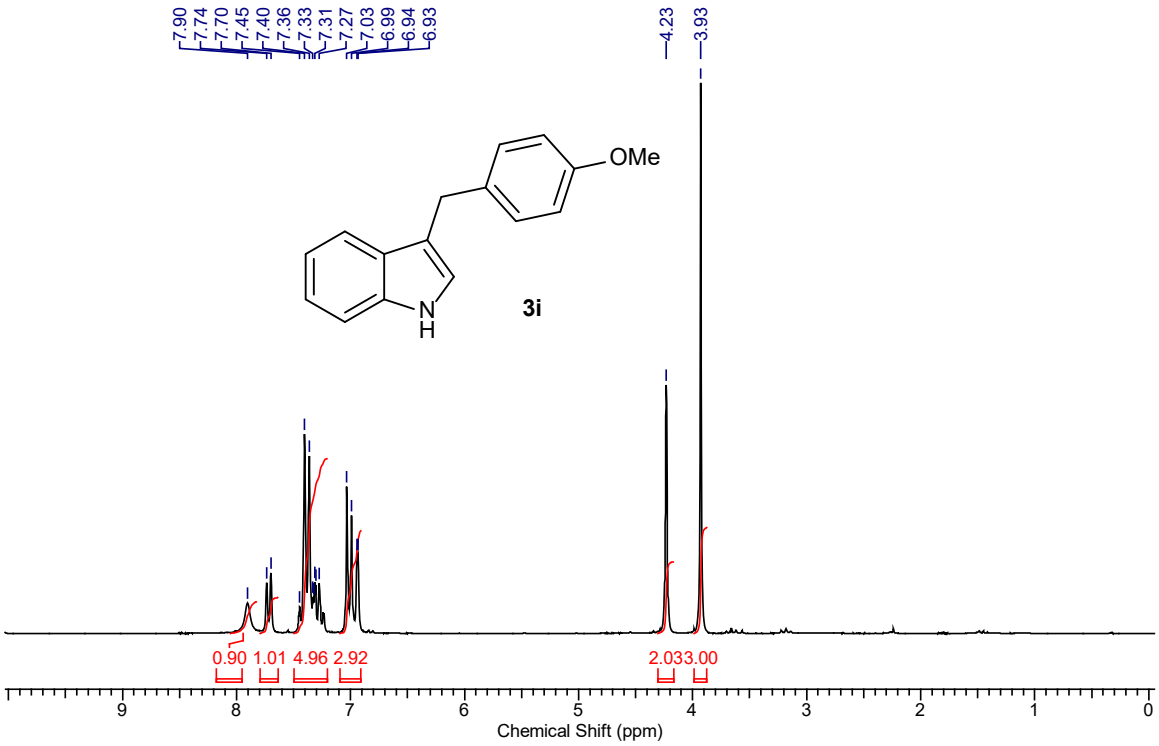

$^{13}$C{$^{1}$H} NMR of **3g**



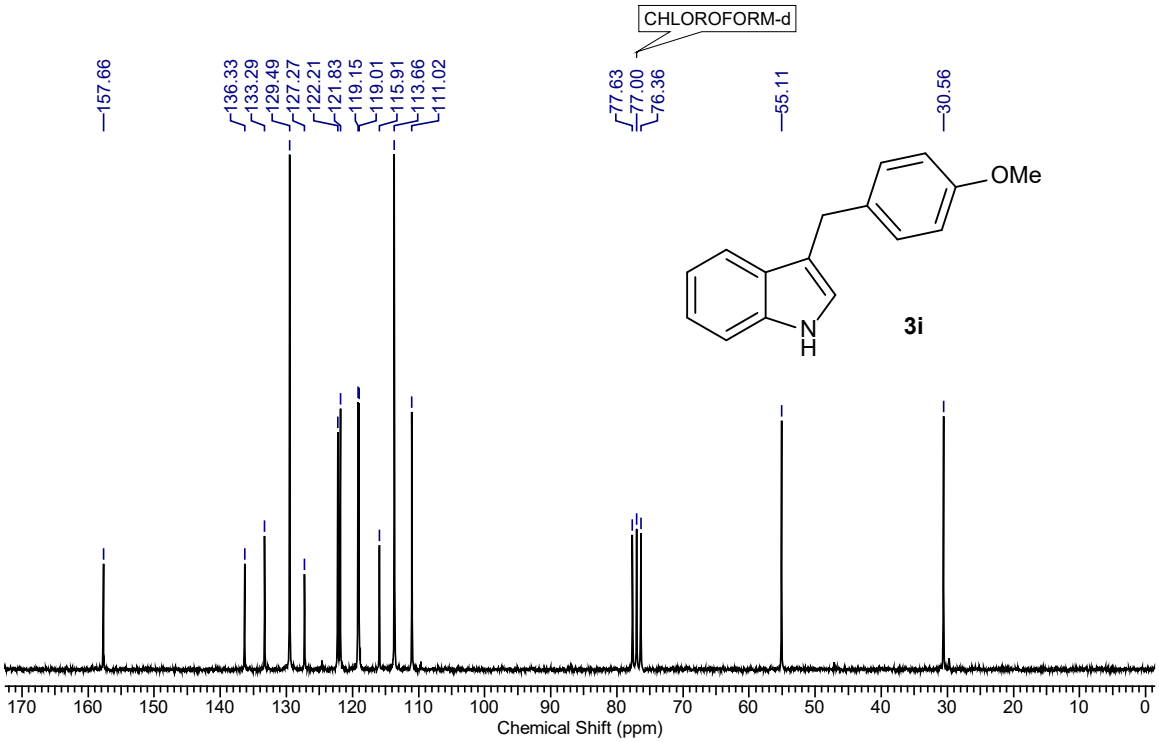

$^{1}$H NMR of **3h**



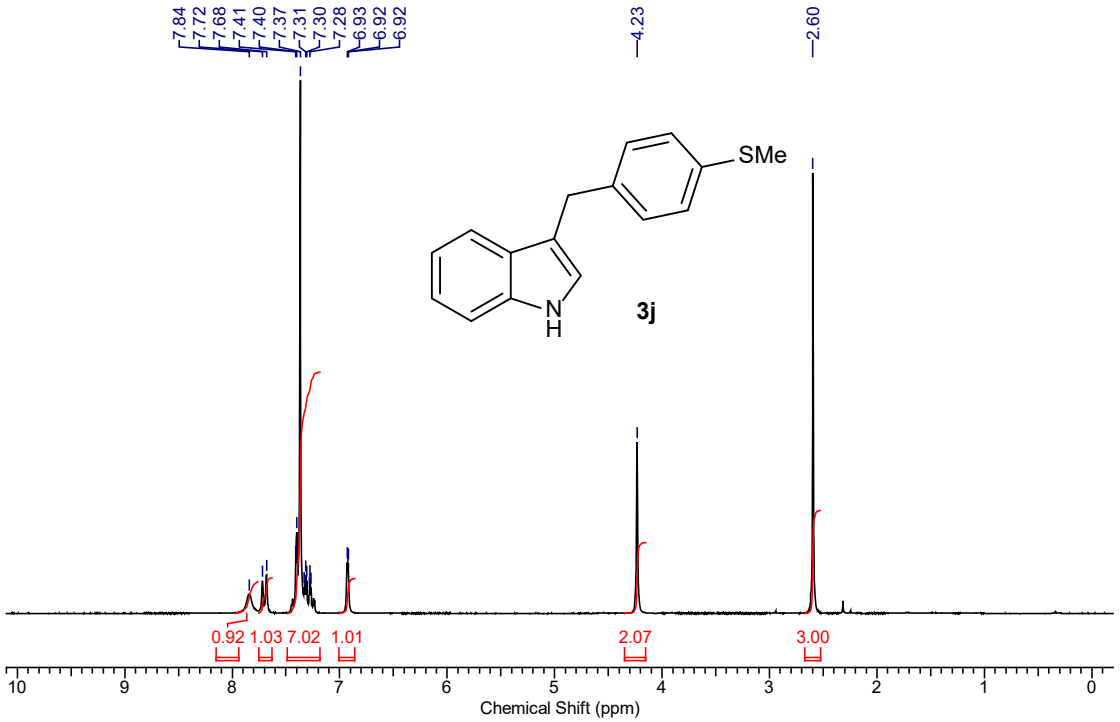

$^{13}$C{$^{1}$H} NMR of **3h**



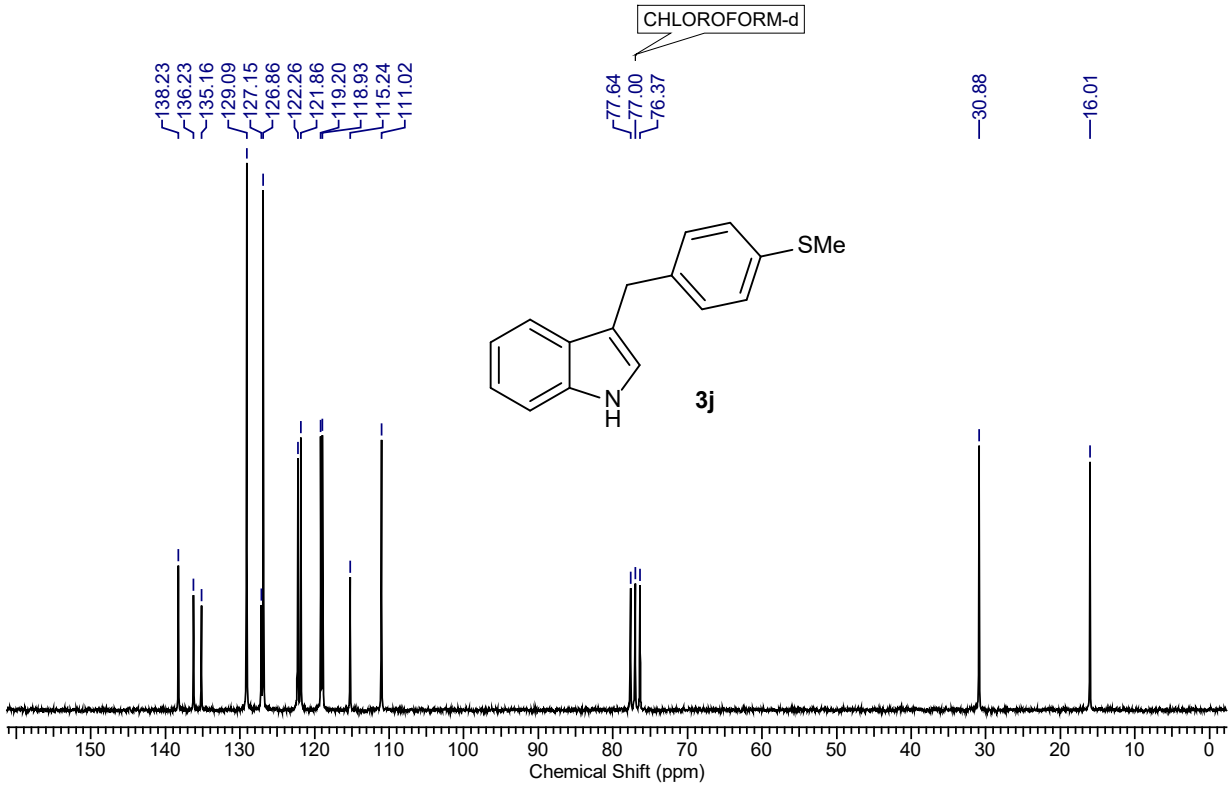

$^{1}$H NMR of **3i**



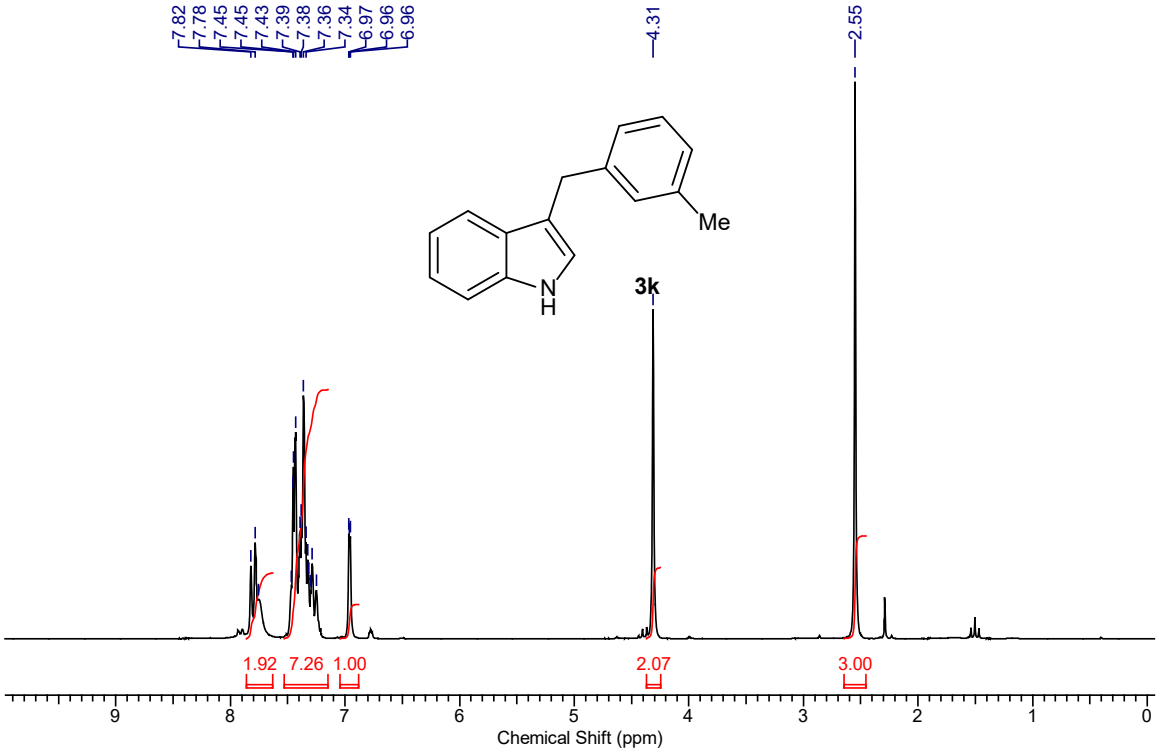

$^{13}$C{$^{1}$H} NMR of **3i**



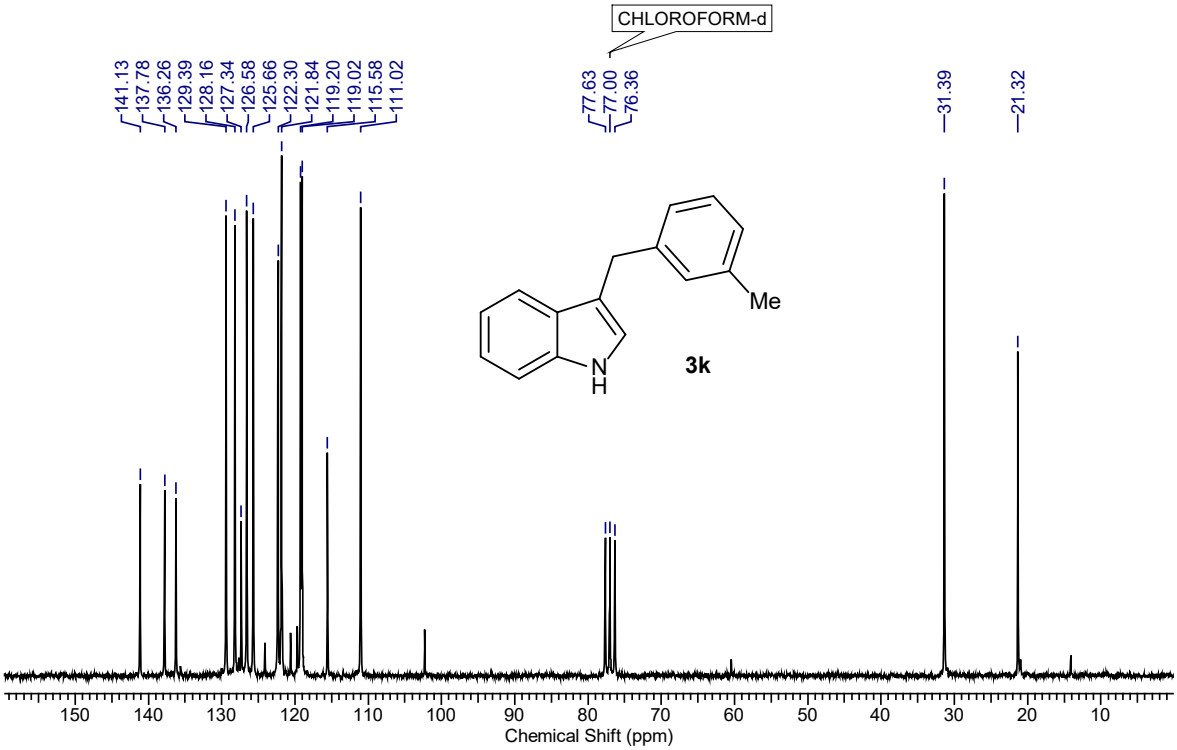

$^{1}$H NMR of **3j**



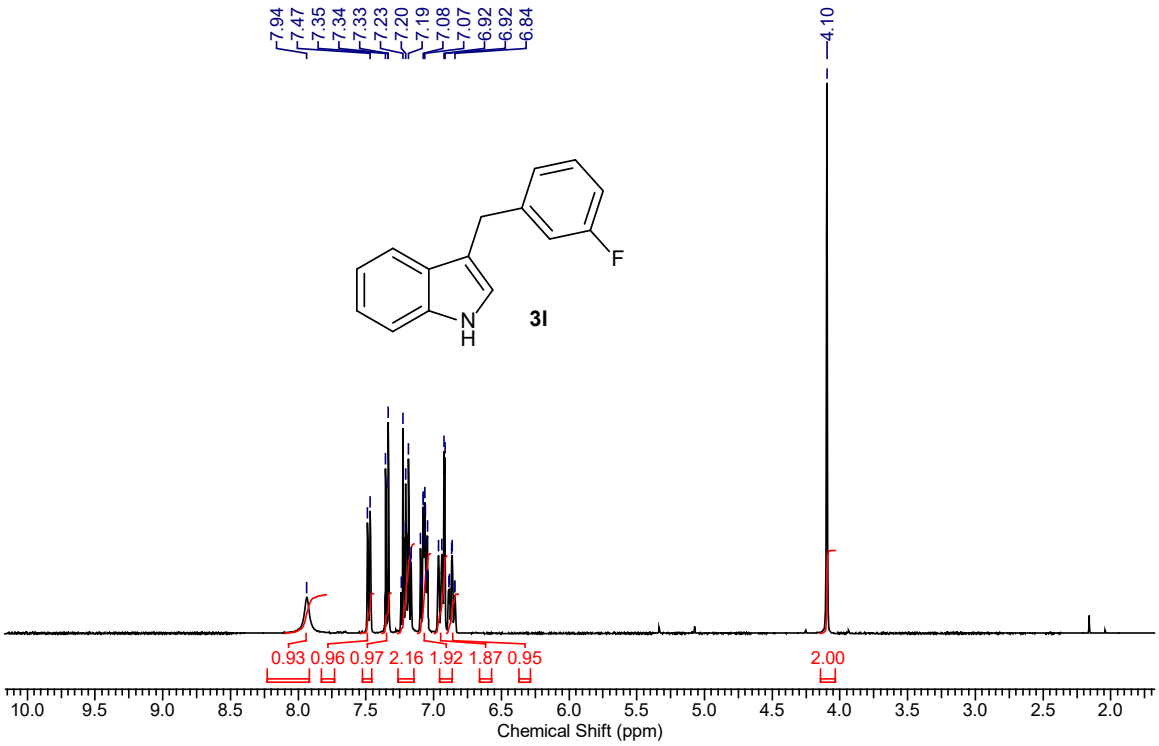

$^{13}$C{$^{1}$H} NMR of **3j**



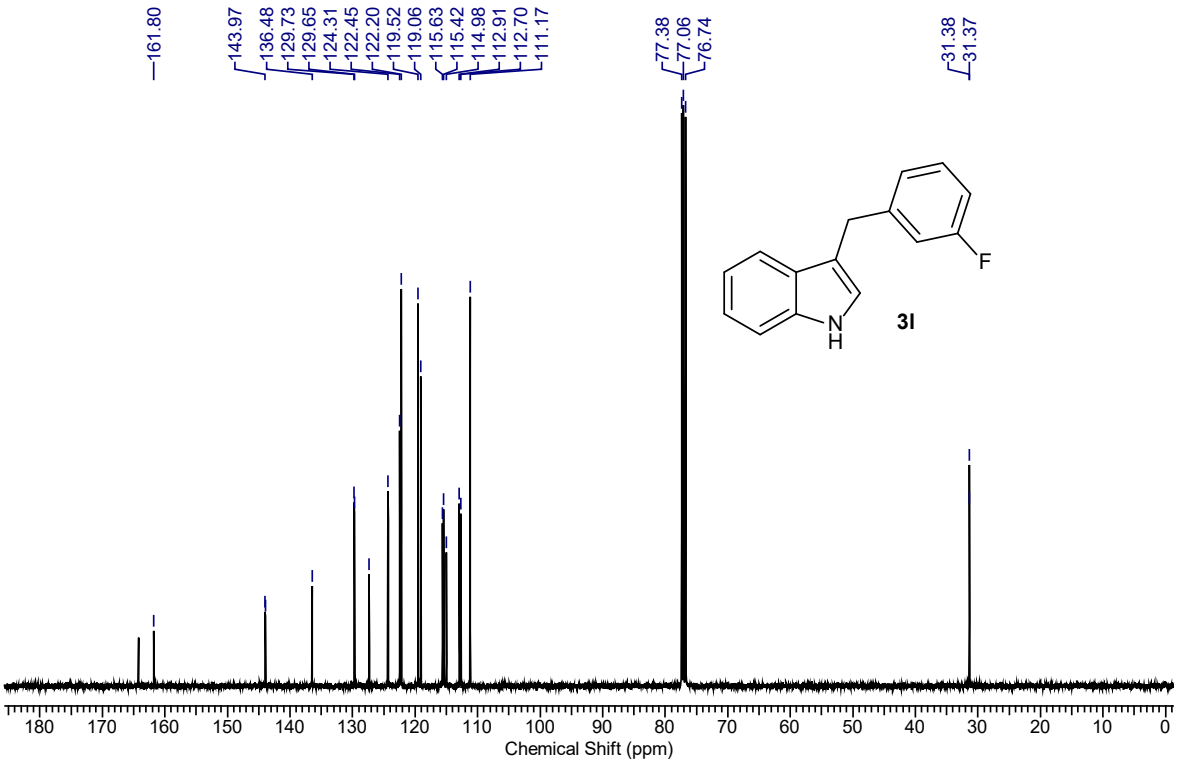

$^{1}$H NMR of **3k**



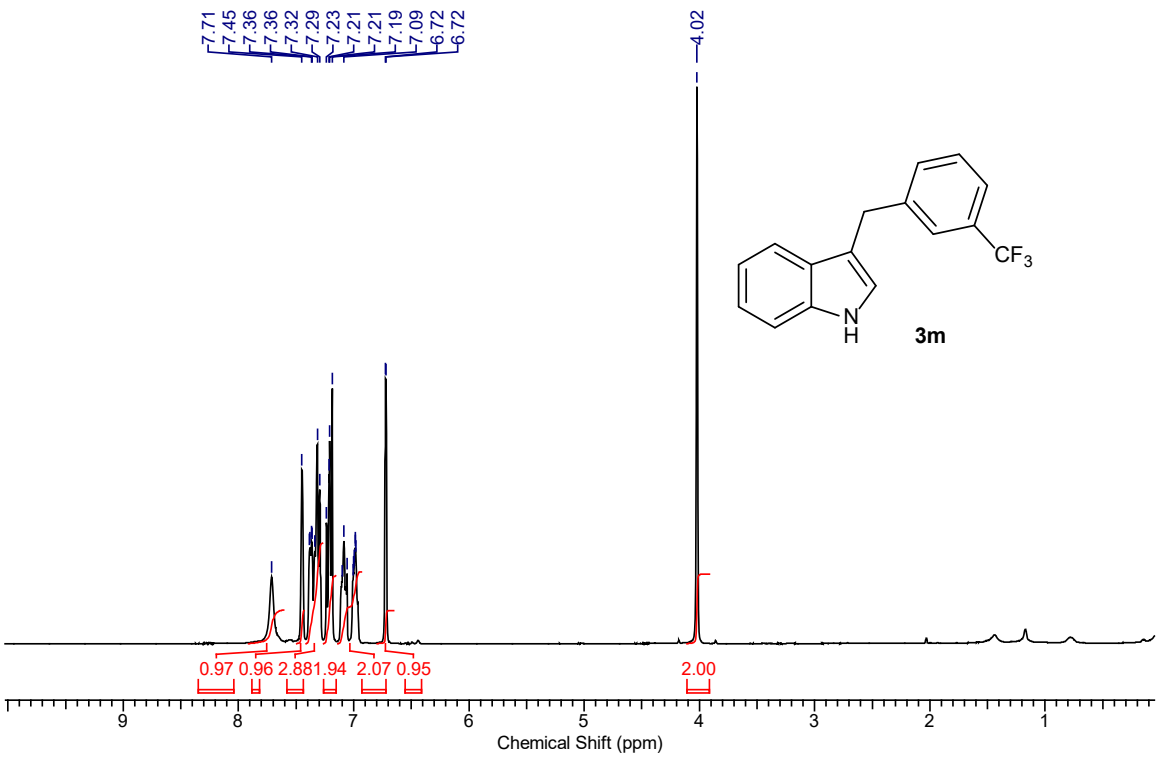

$^{13}$C{$^{1}$H} NMR of **3k**



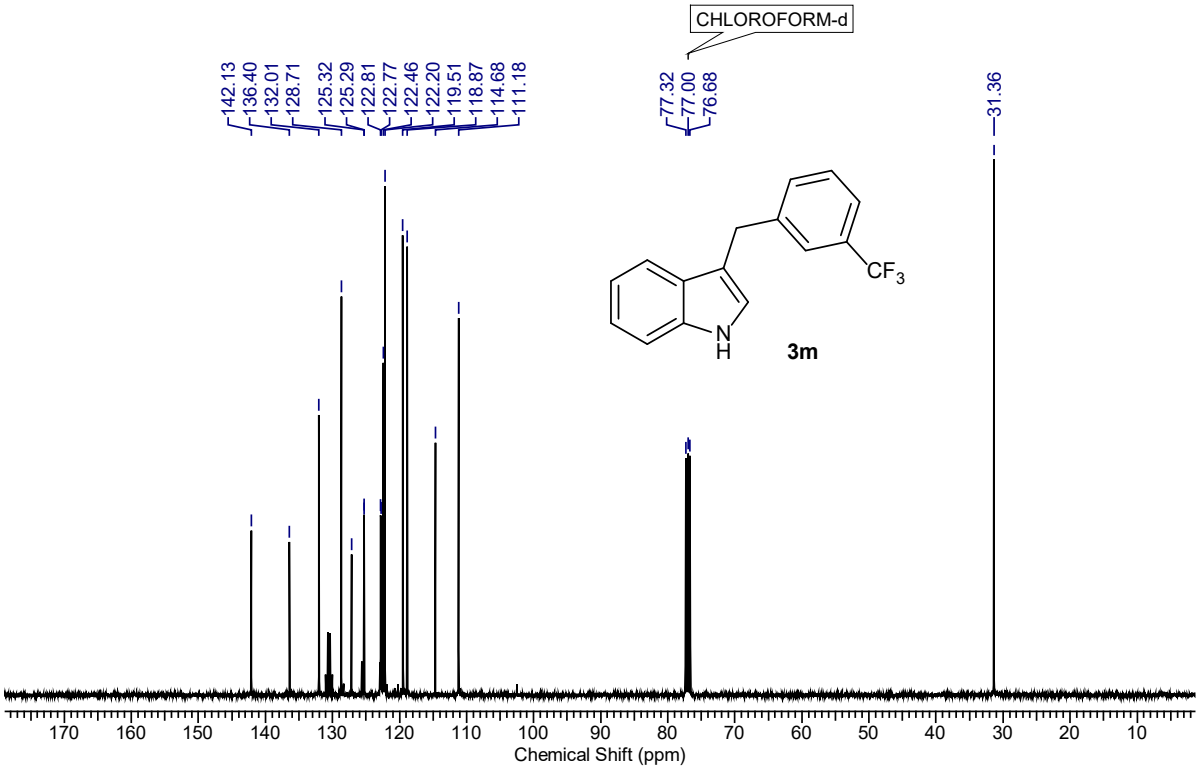

$^{1}$H NMR of **3l**



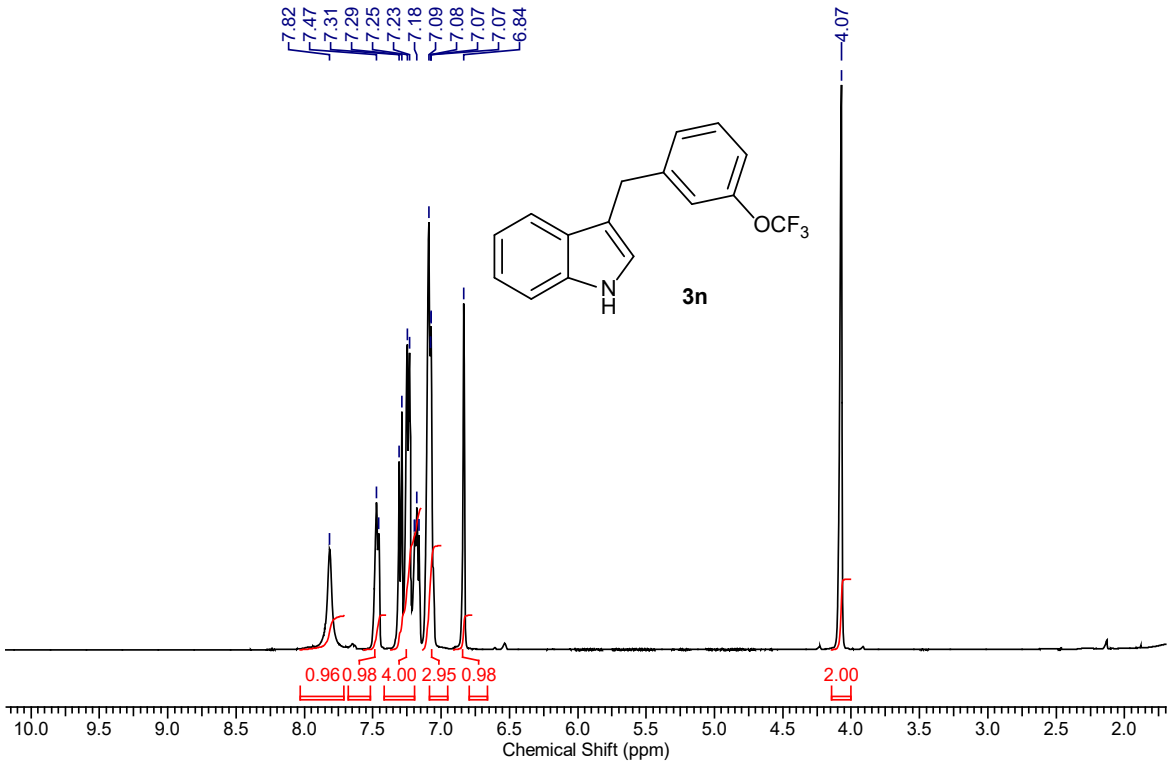

$^{13}$C{$^{1}$H} NMR of **3l**



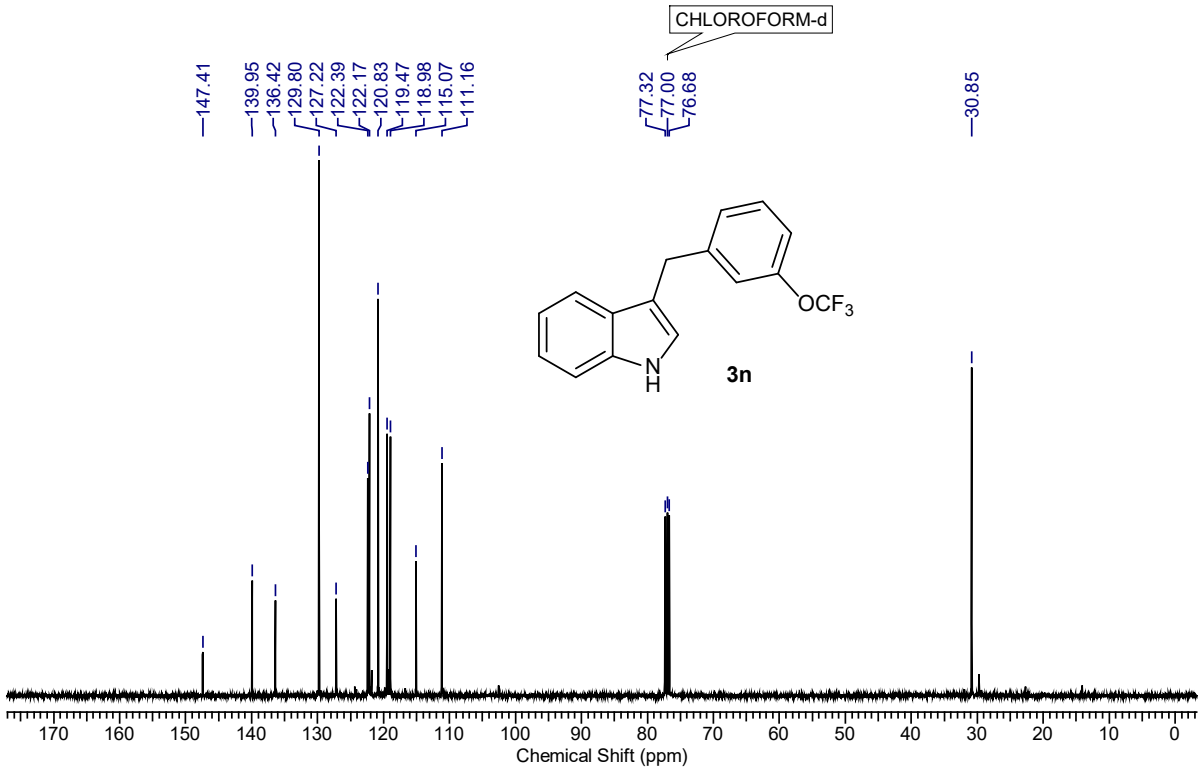

$^{1}$H NMR of **3m**



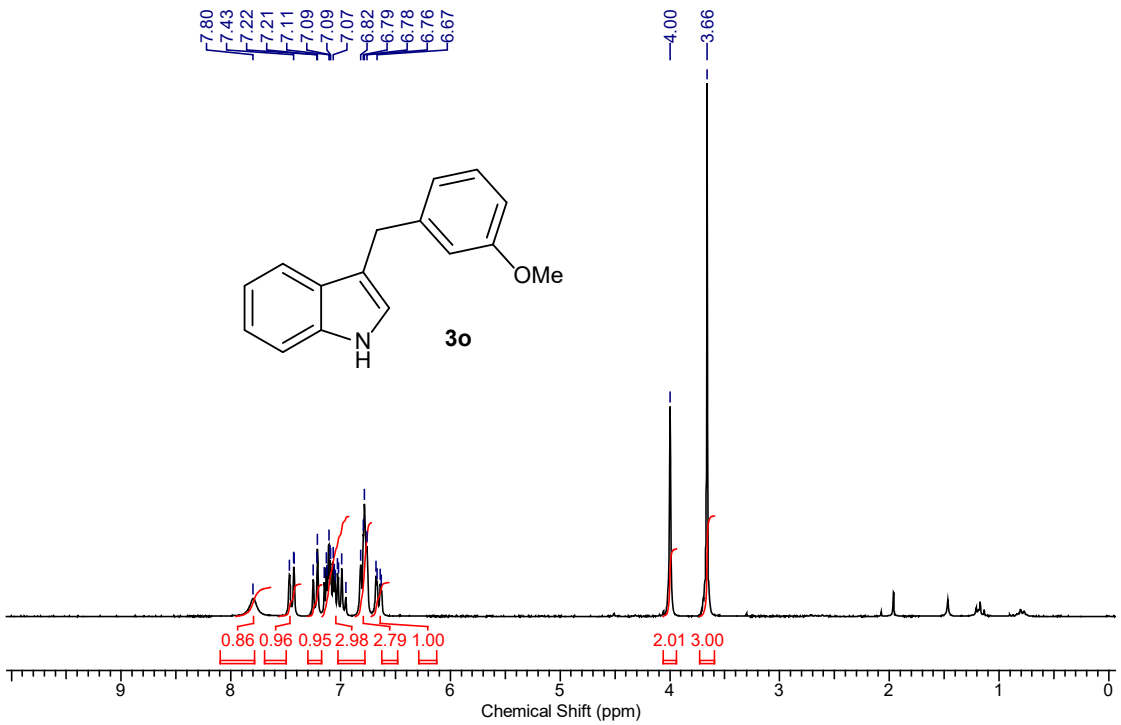

$^{13}$C{$^{1}$H} NMR of **3m**



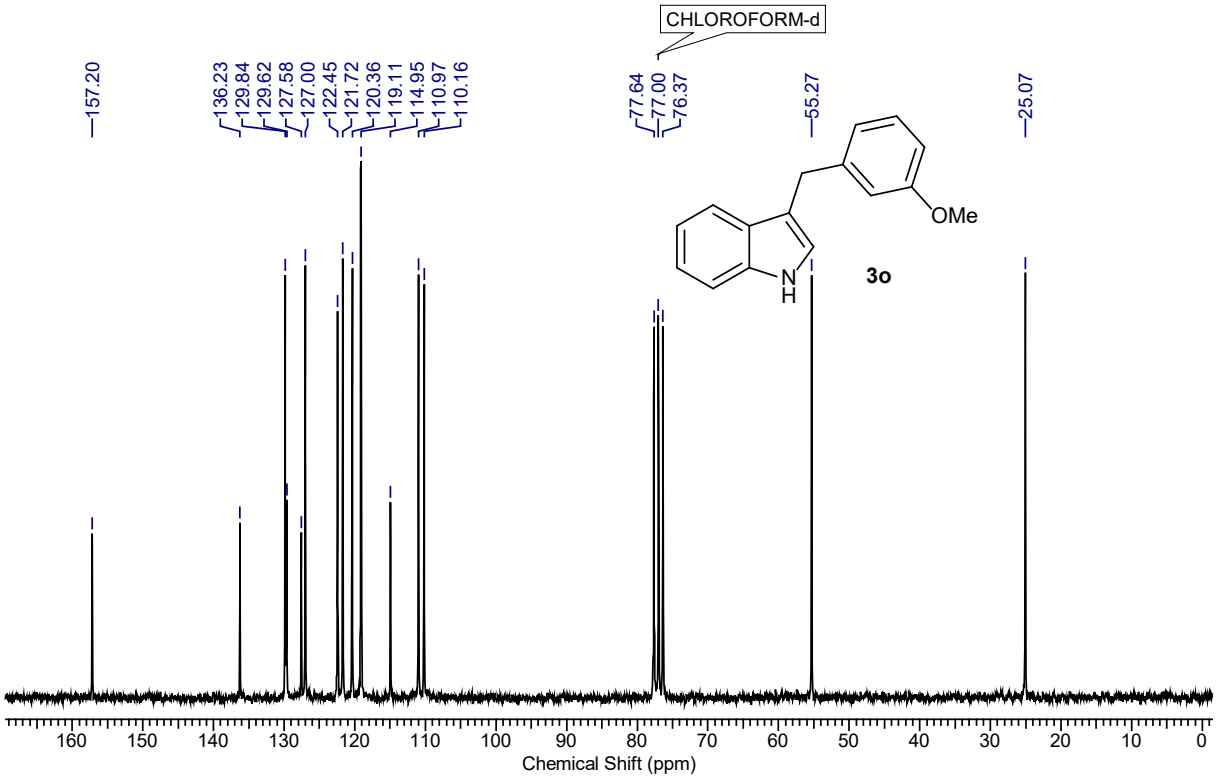

$^{1}$H NMR of **3n**



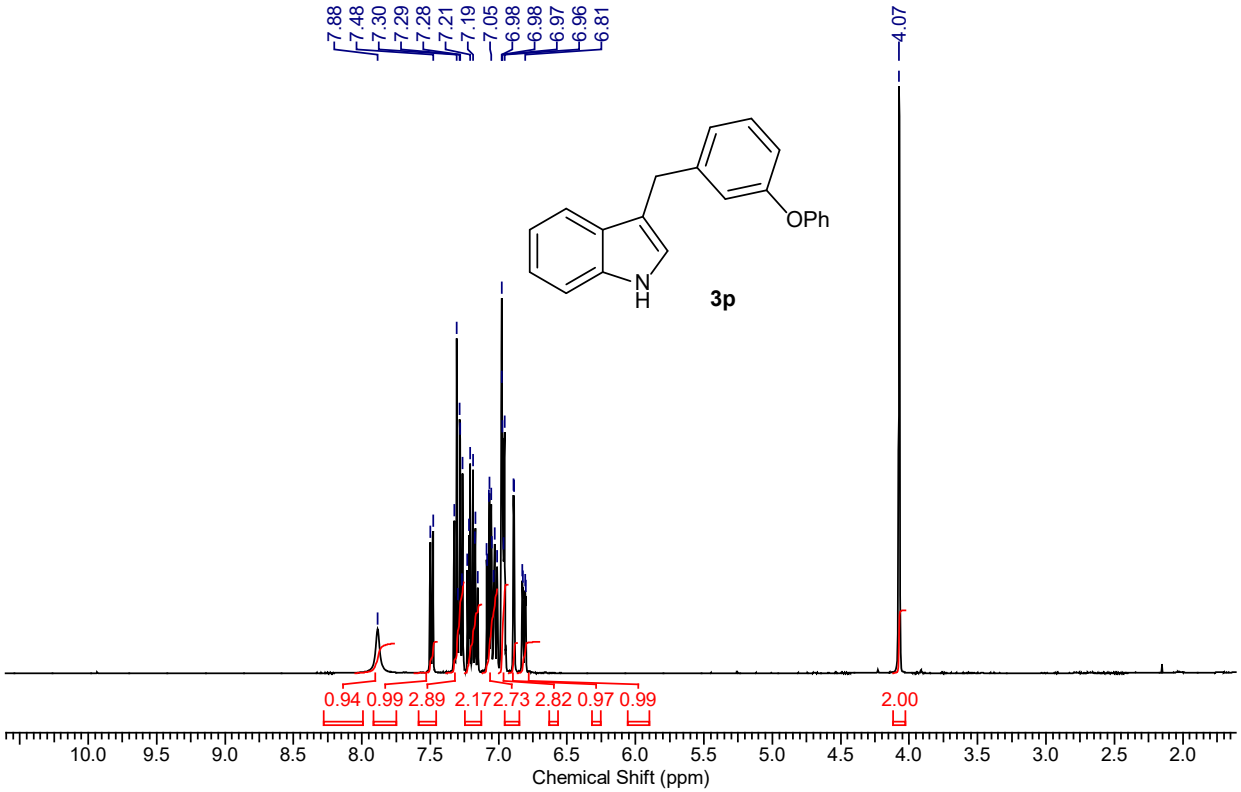

$^{13}$C{$^{1}$H} NMR of **3n**



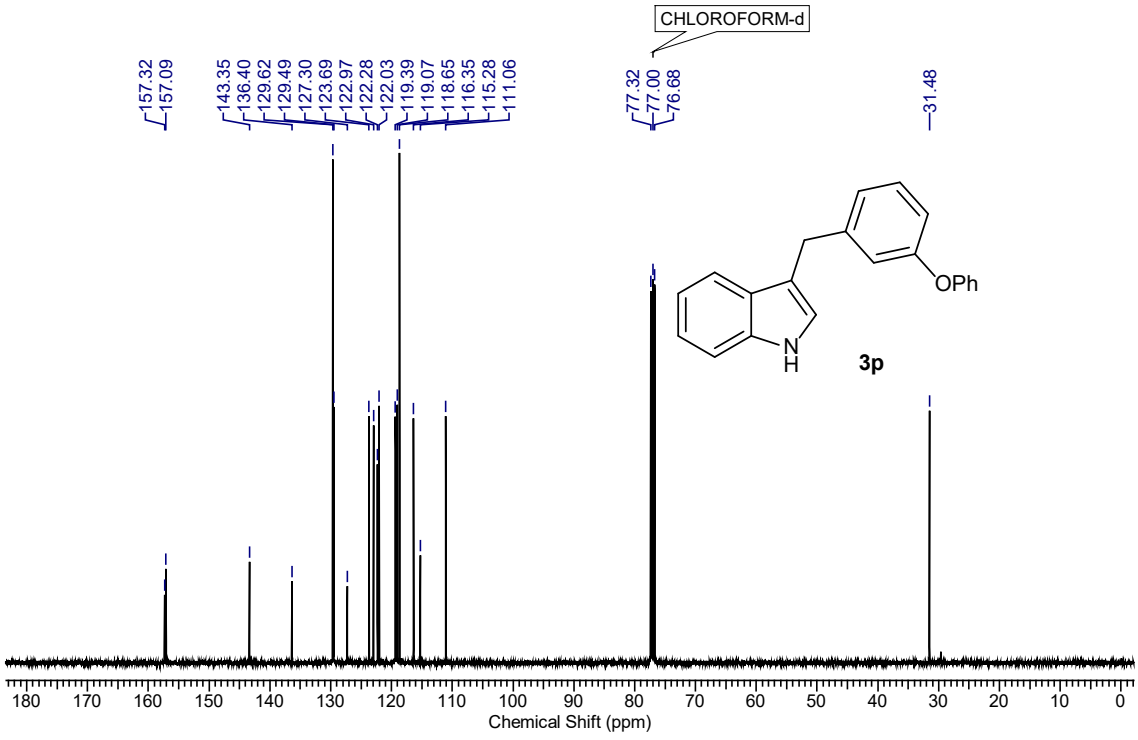

$^{1}$H NMR of **3o**



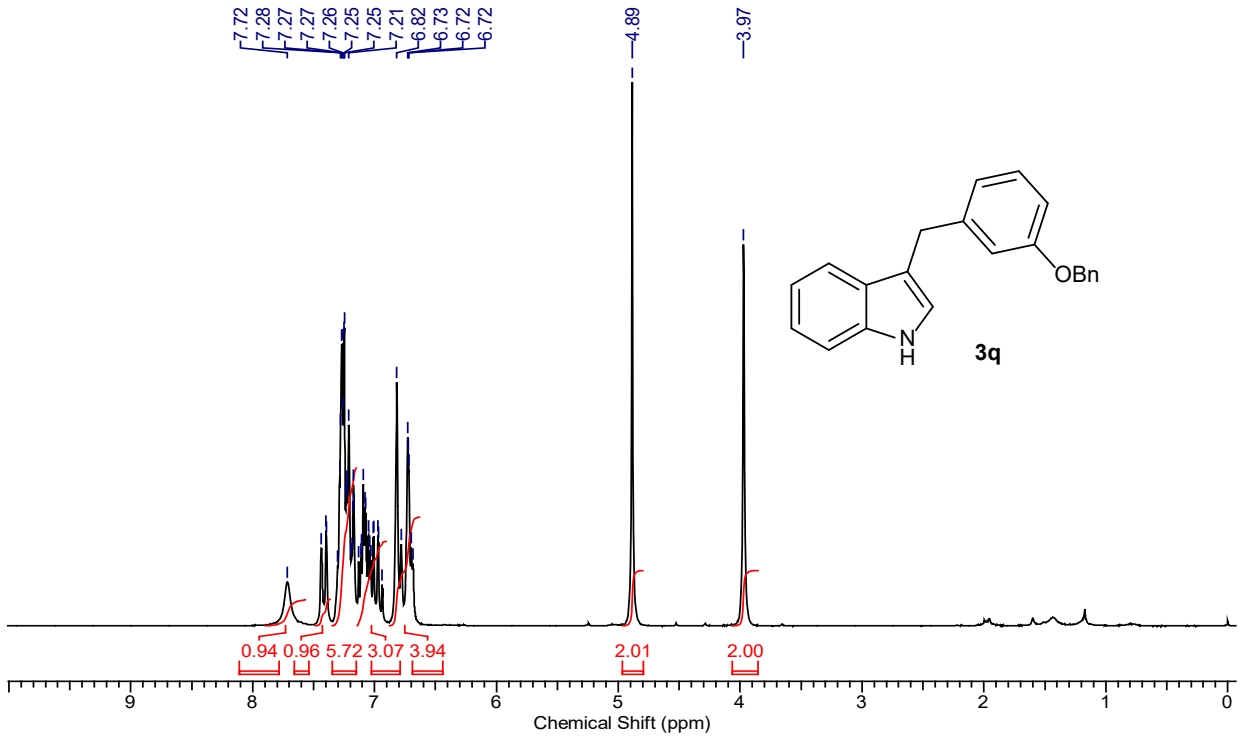

$^{13}$C{$^{1}$H} NMR of **3o**



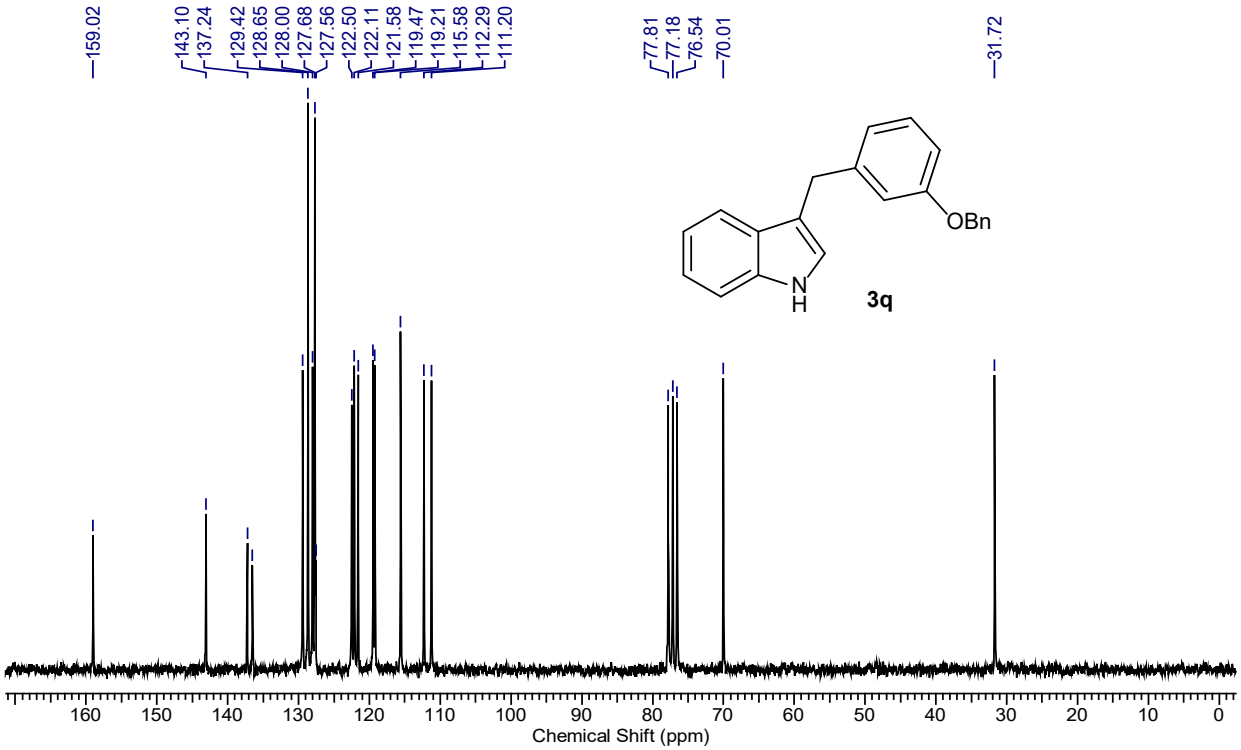

$^{1}$H NMR of **3p**



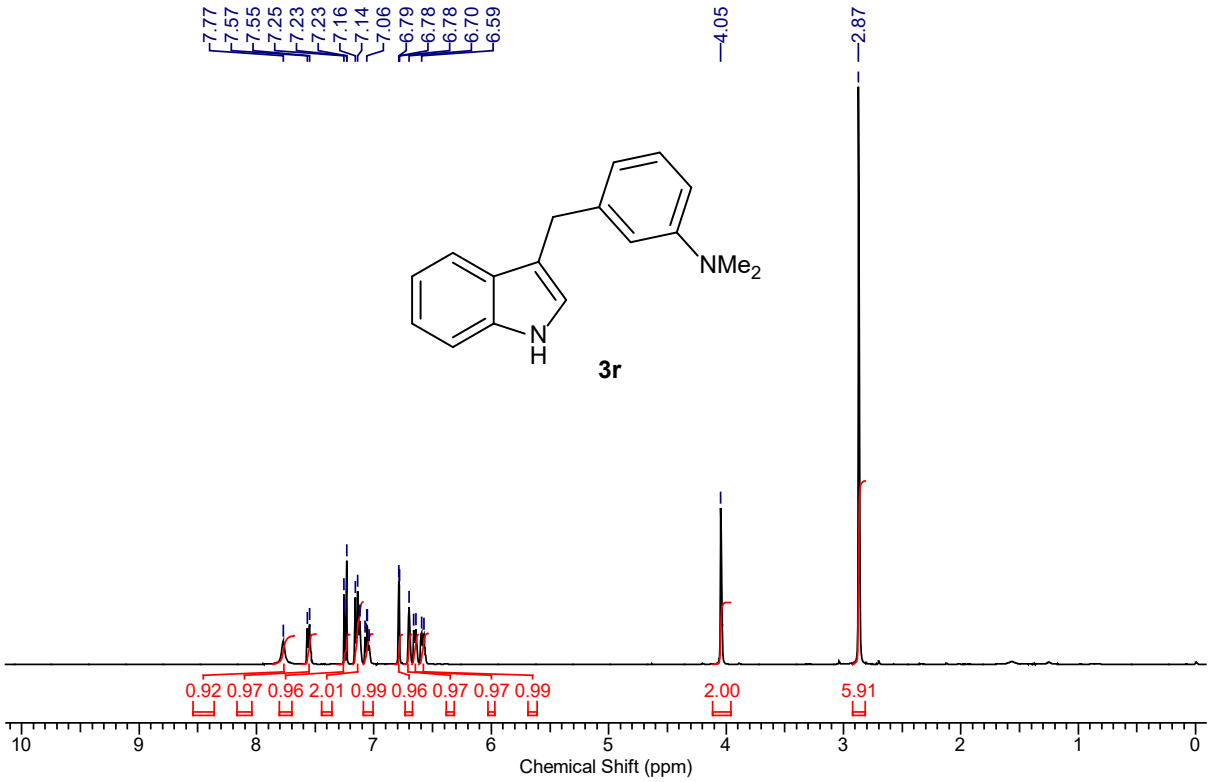

$^{13}$C{$^{1}$H} NMR of **3p**



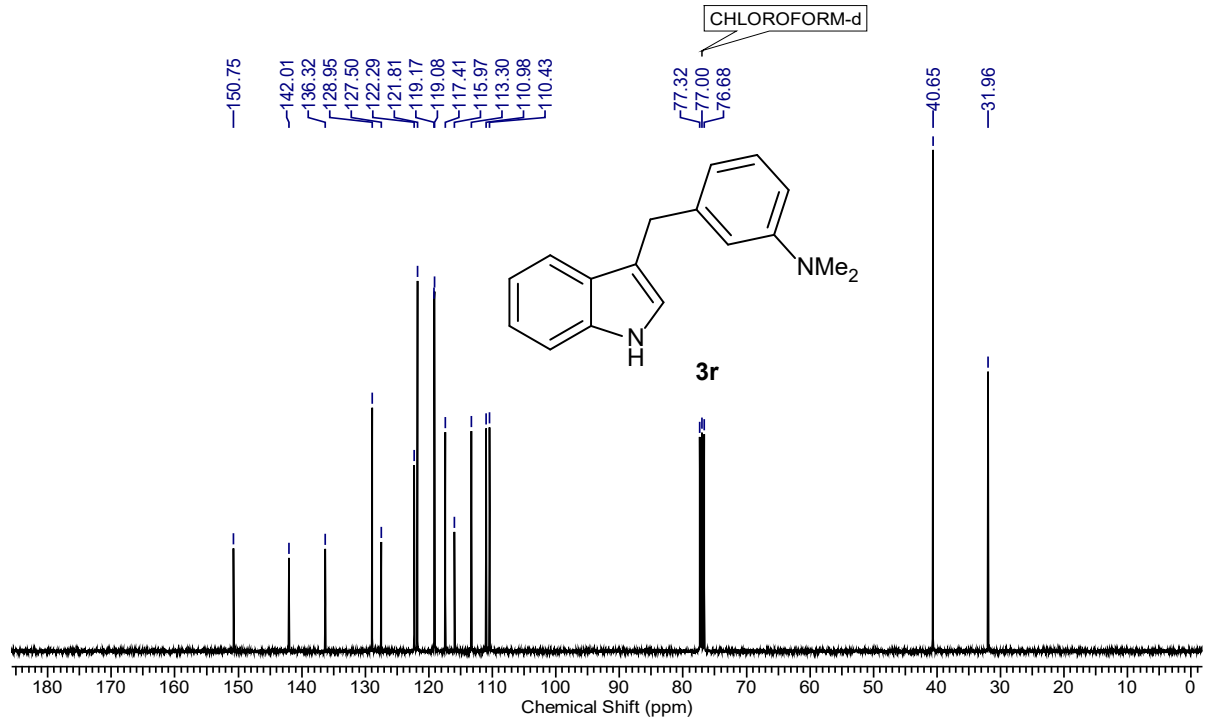

$^{1}$H NMR of **3q**



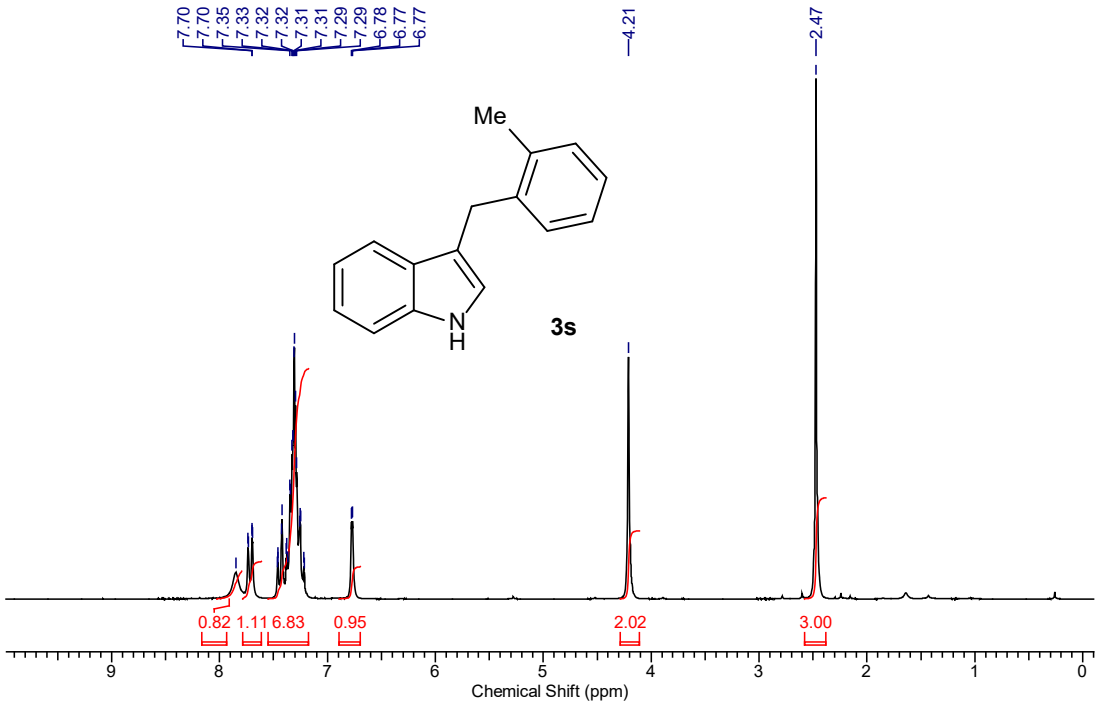

$^{13}$C{$^{1}$H} NMR of **3q**



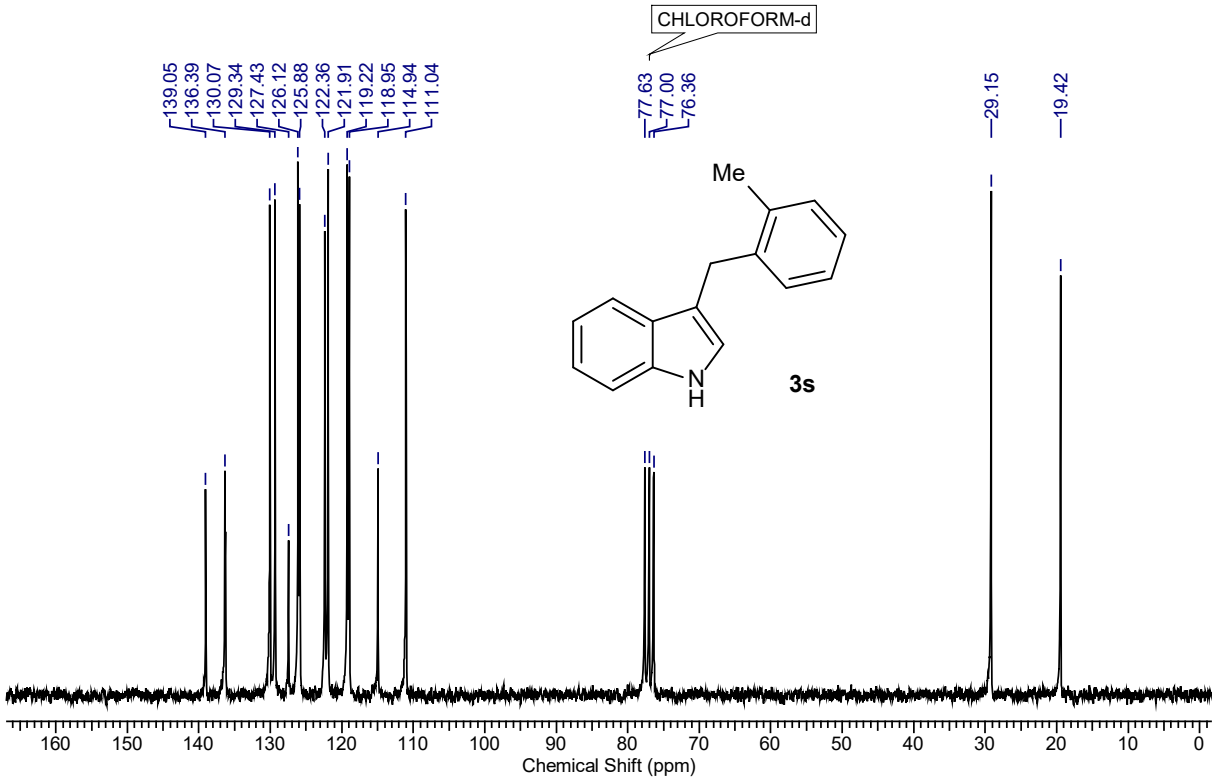

$^{1}$H NMR of **3r**



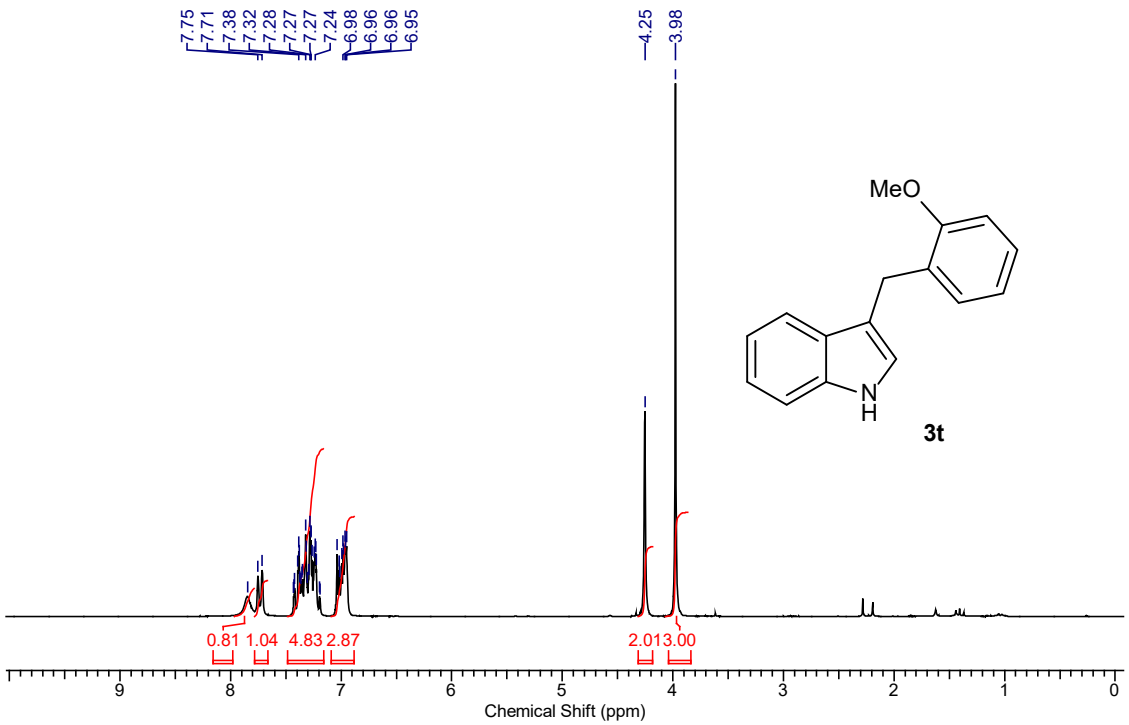

$^{13}$C{$^{1}$H} NMR of **3r**



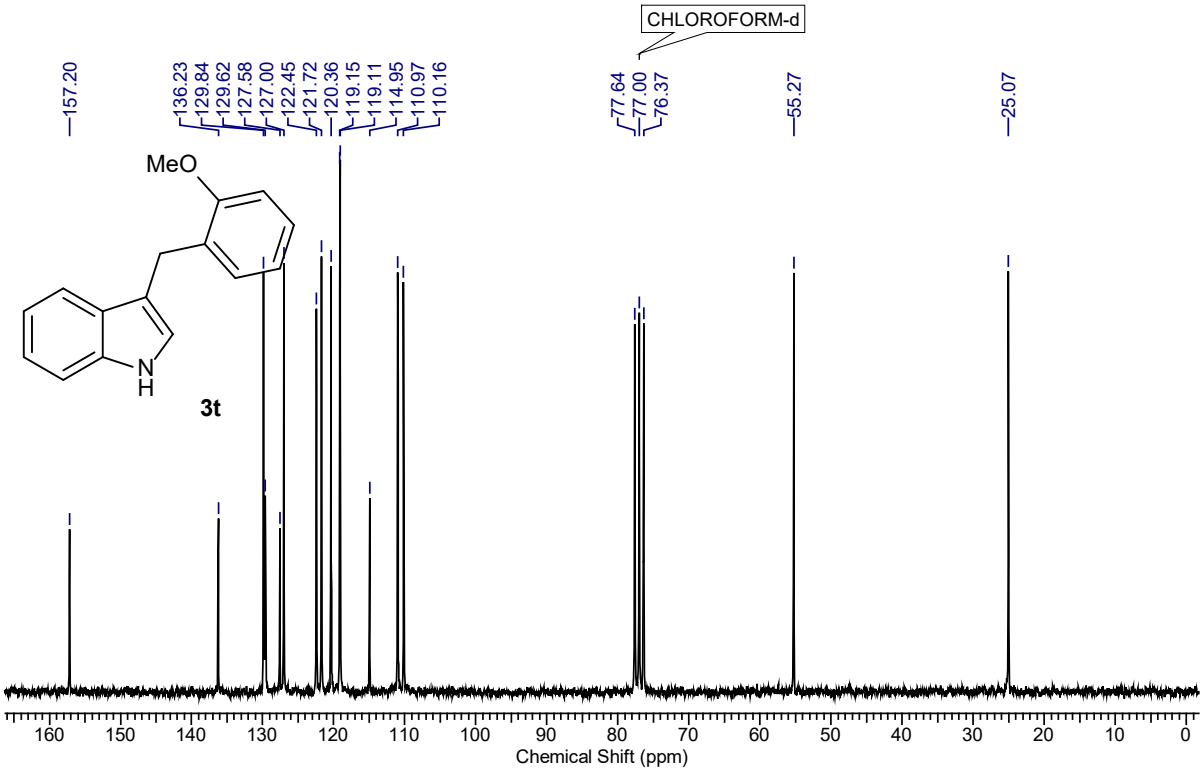

$^{1}$H NMR of **3s**



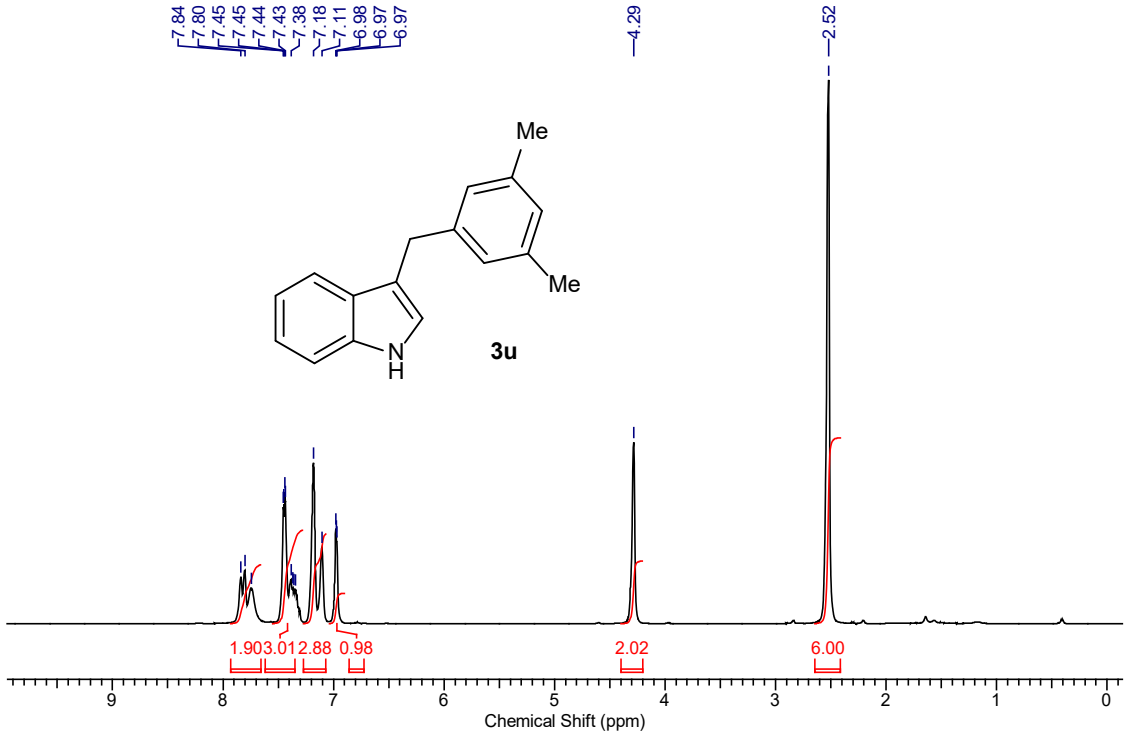

$^{13}$C{$^{1}$H} NMR of **3s**



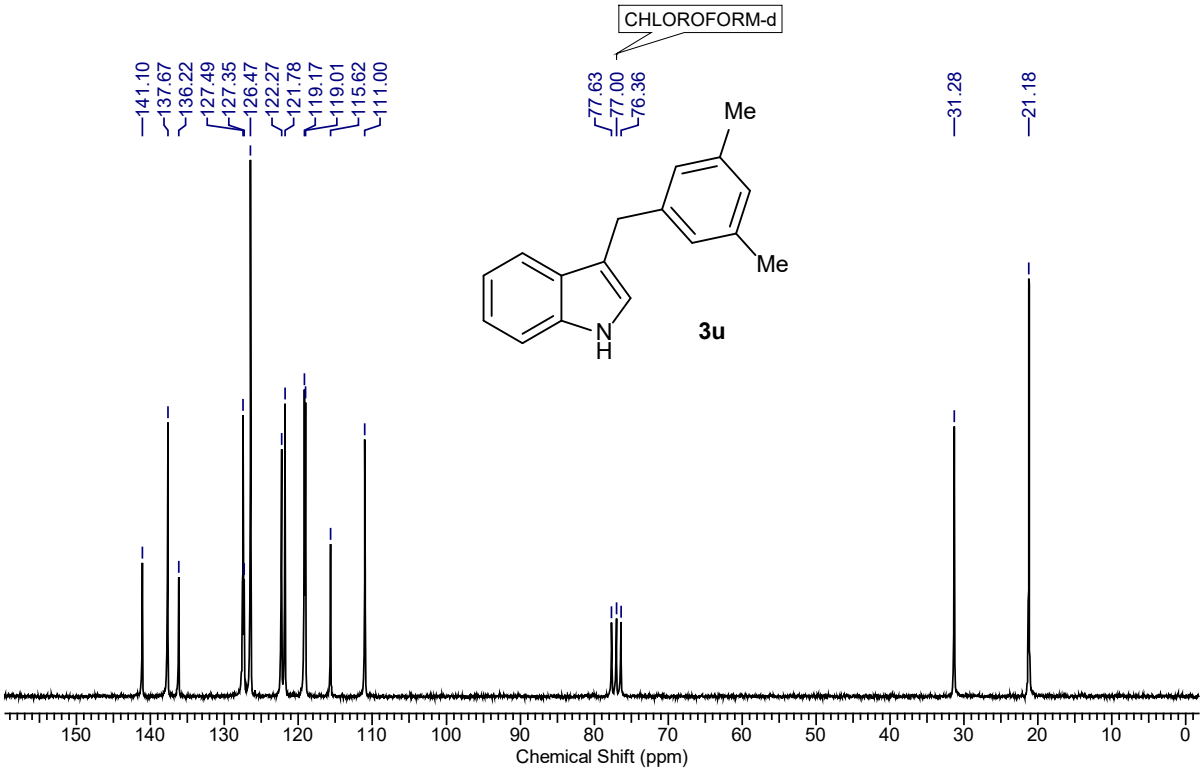

$^{1}$H NMR of **3t**



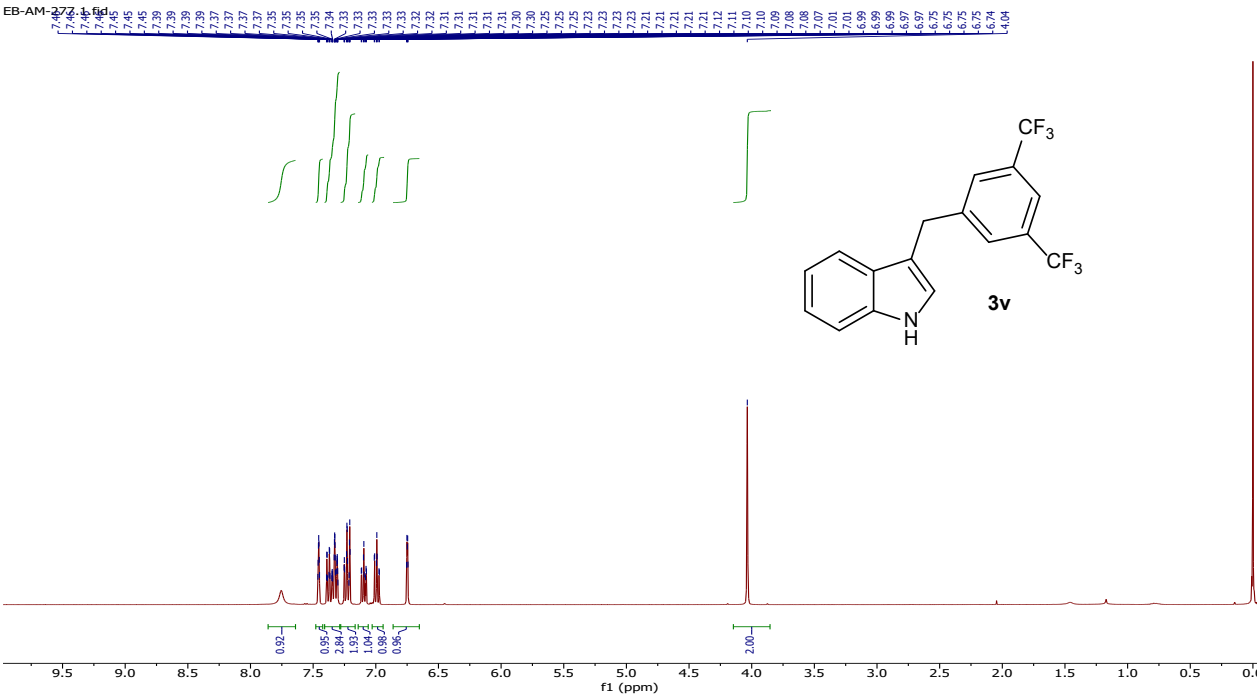

$^{13}$C{$^{1}$H} NMR of **3t**



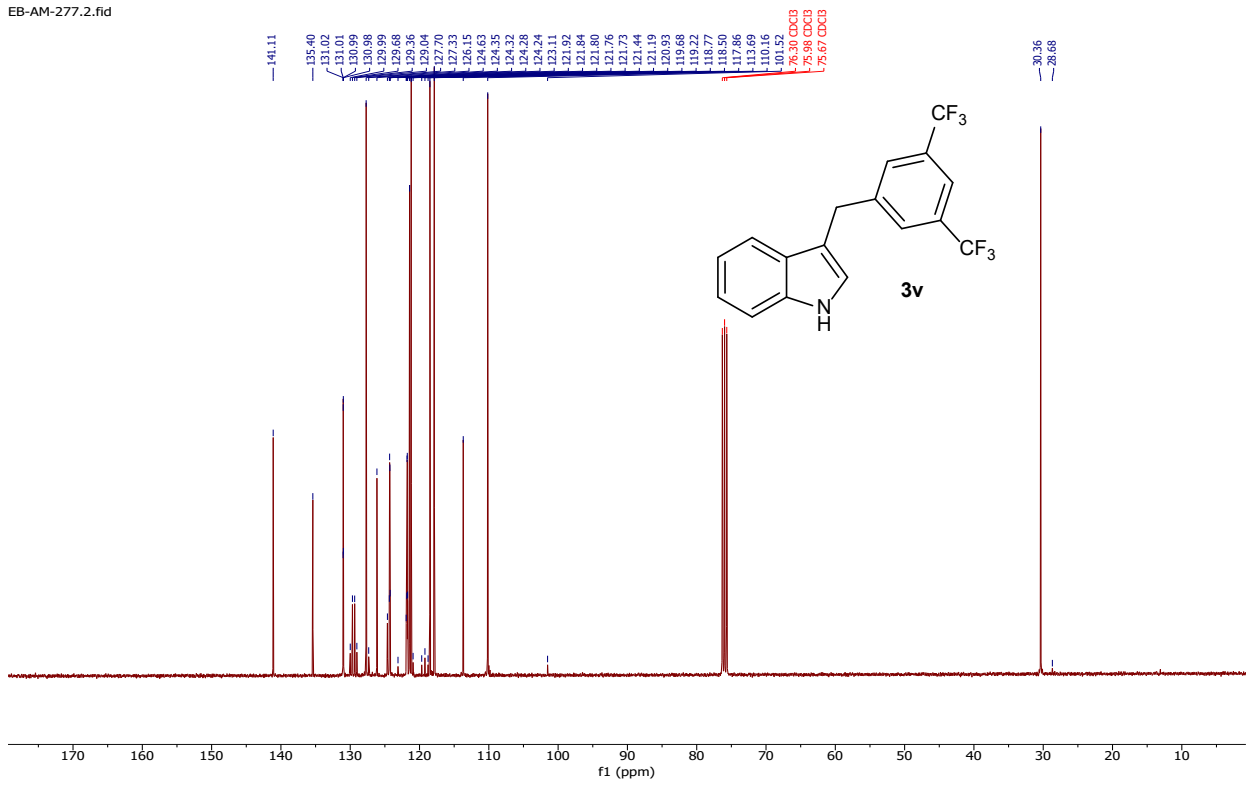

$^{1}$H NMR of **3u**



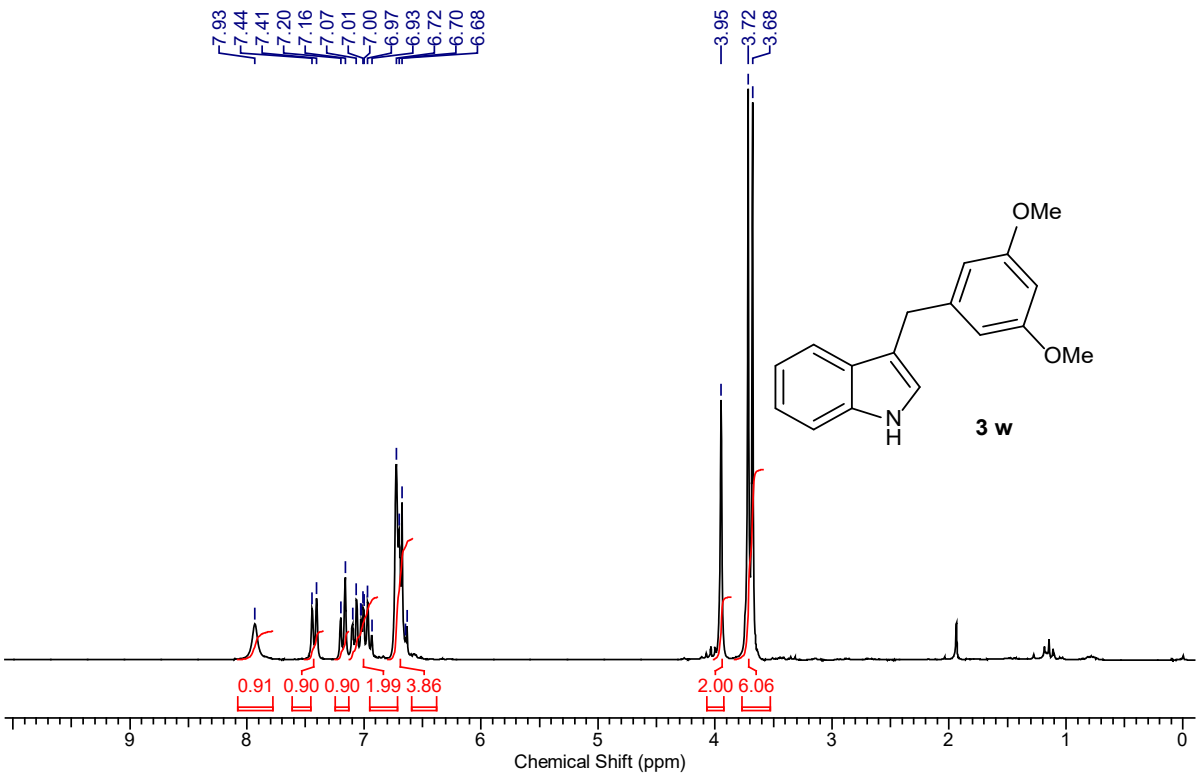

$^{13}$C{$^{1}$H} NMR of **3u**



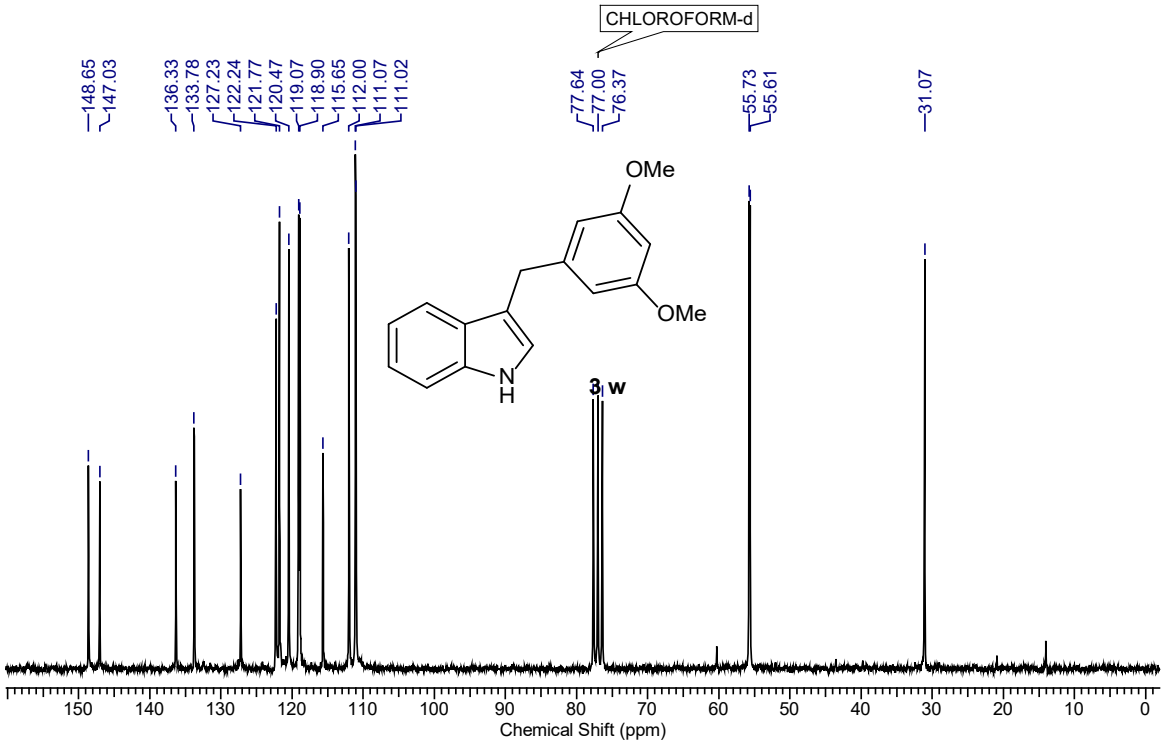

$^{1}$H NMR of **3v**



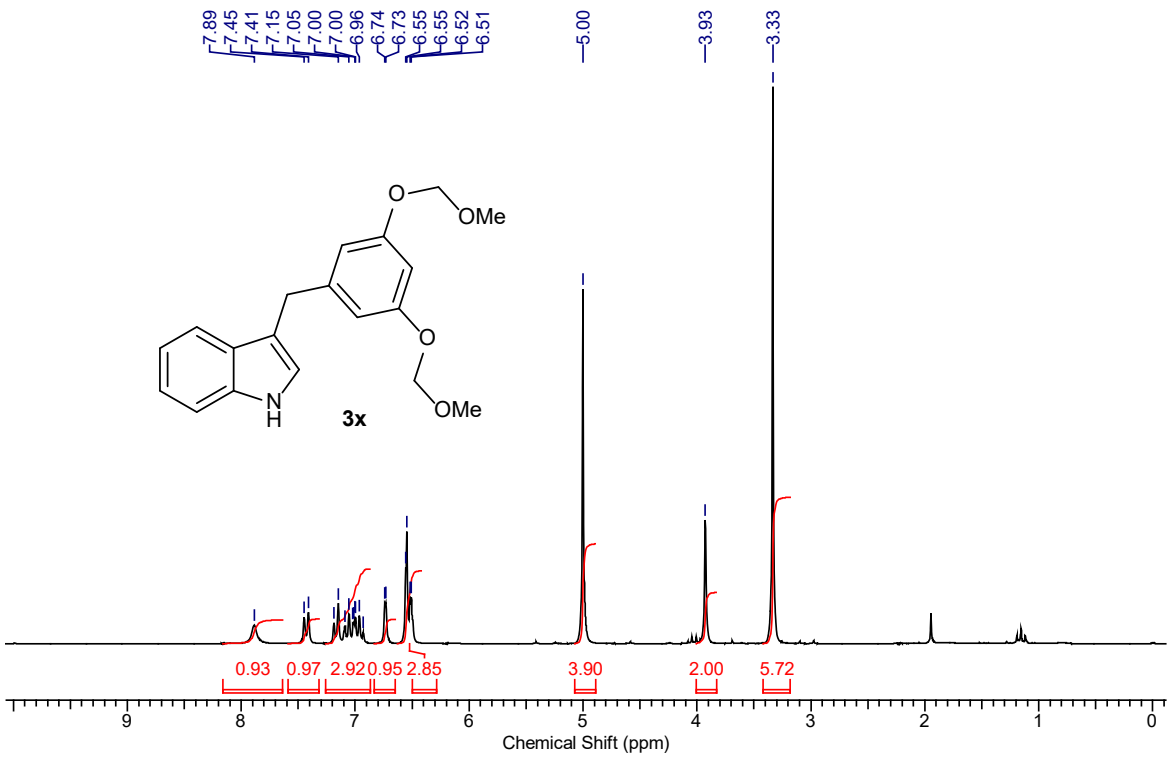

$^{13}$C{$^{1}$H} NMR of **3v**



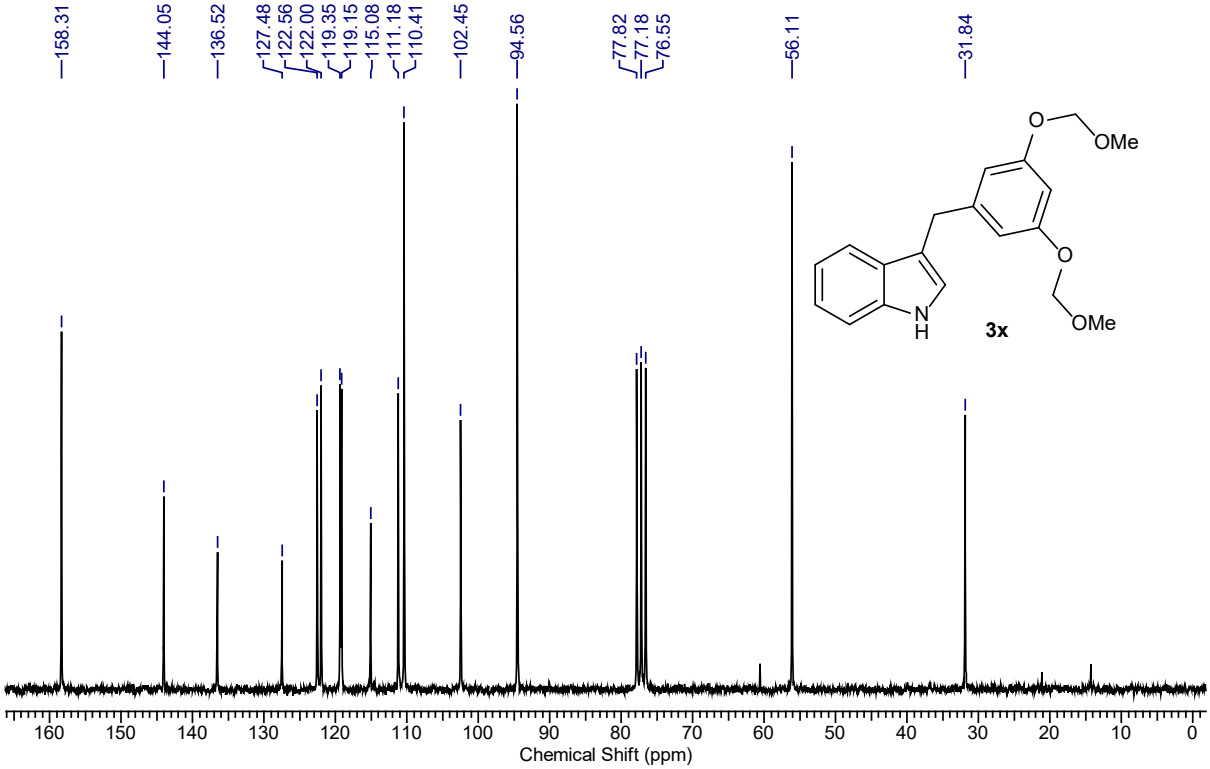

$^{1}$H NMR of **3w**



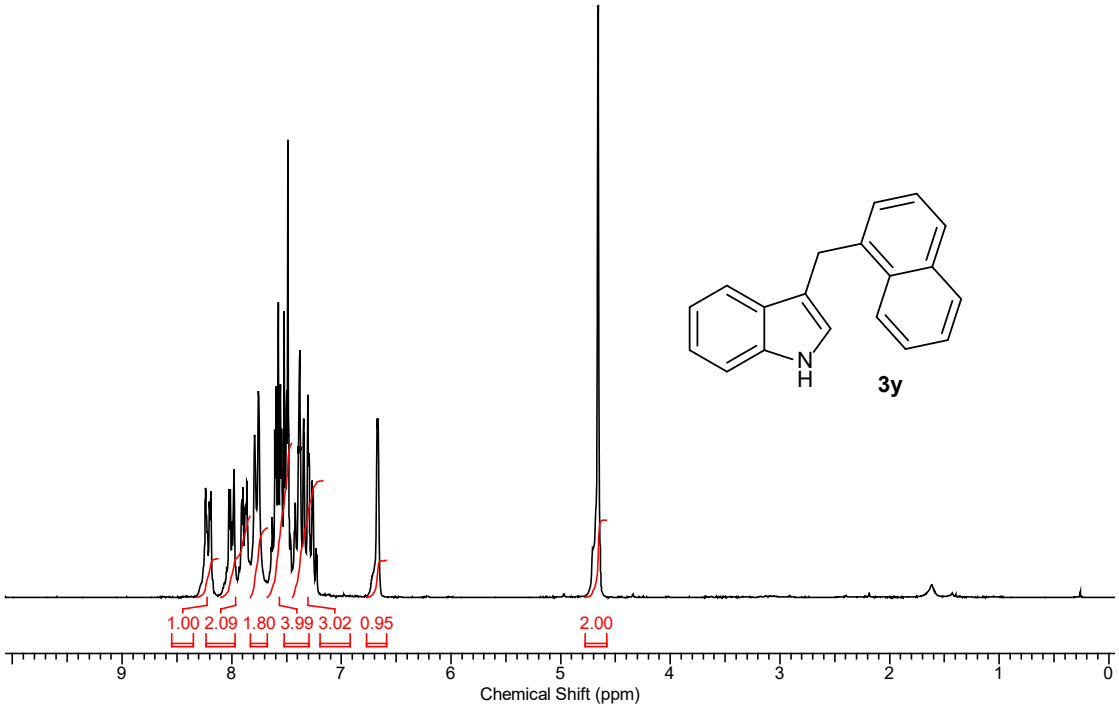

$^{13}$C{$^{1}$H} NMR of **3w**



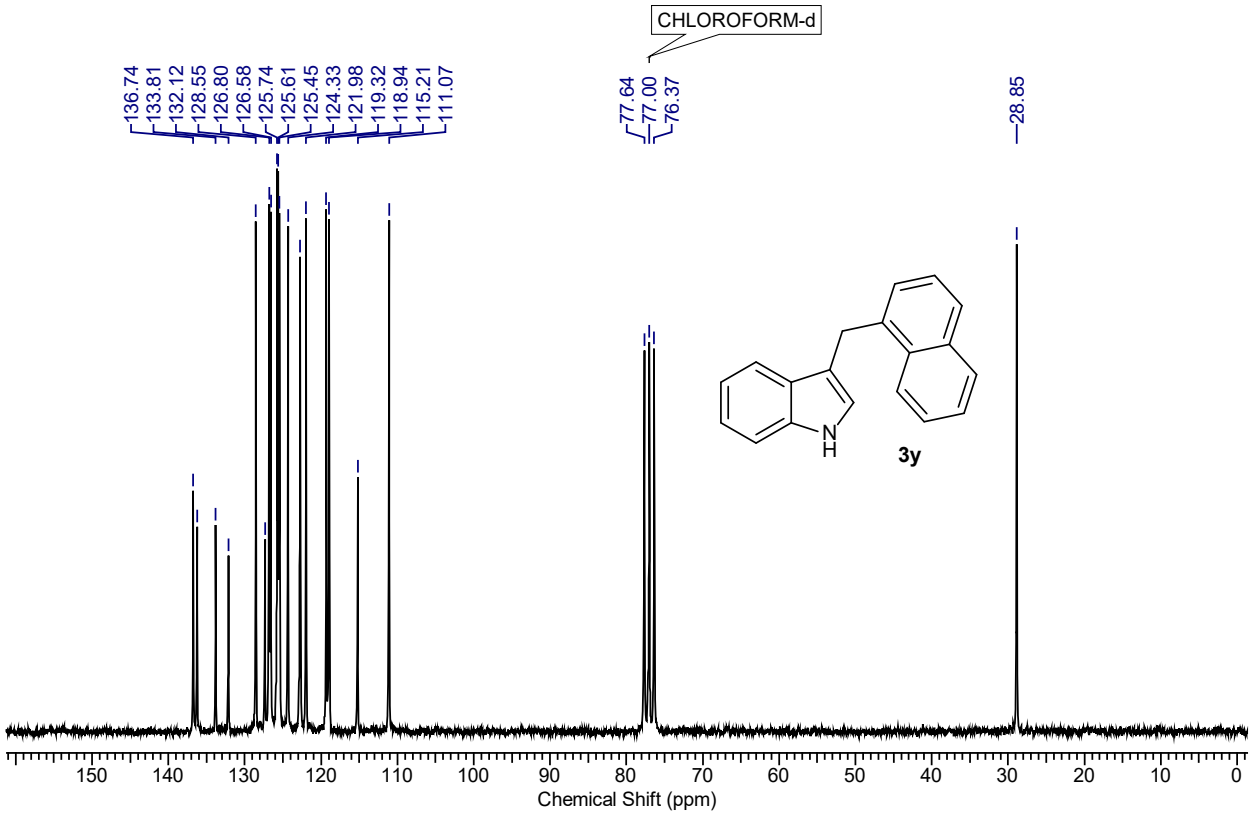

$^{1}$H NMR of **3x**



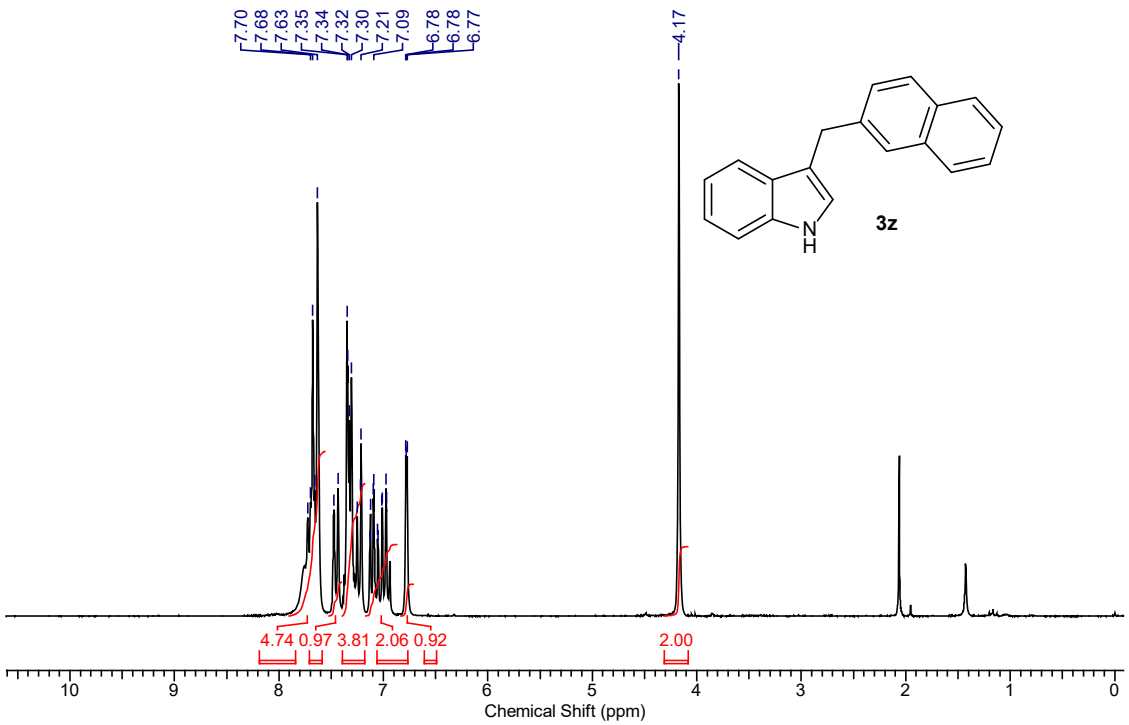

$^{13}$C{$^{1}$H} NMR of **3x**



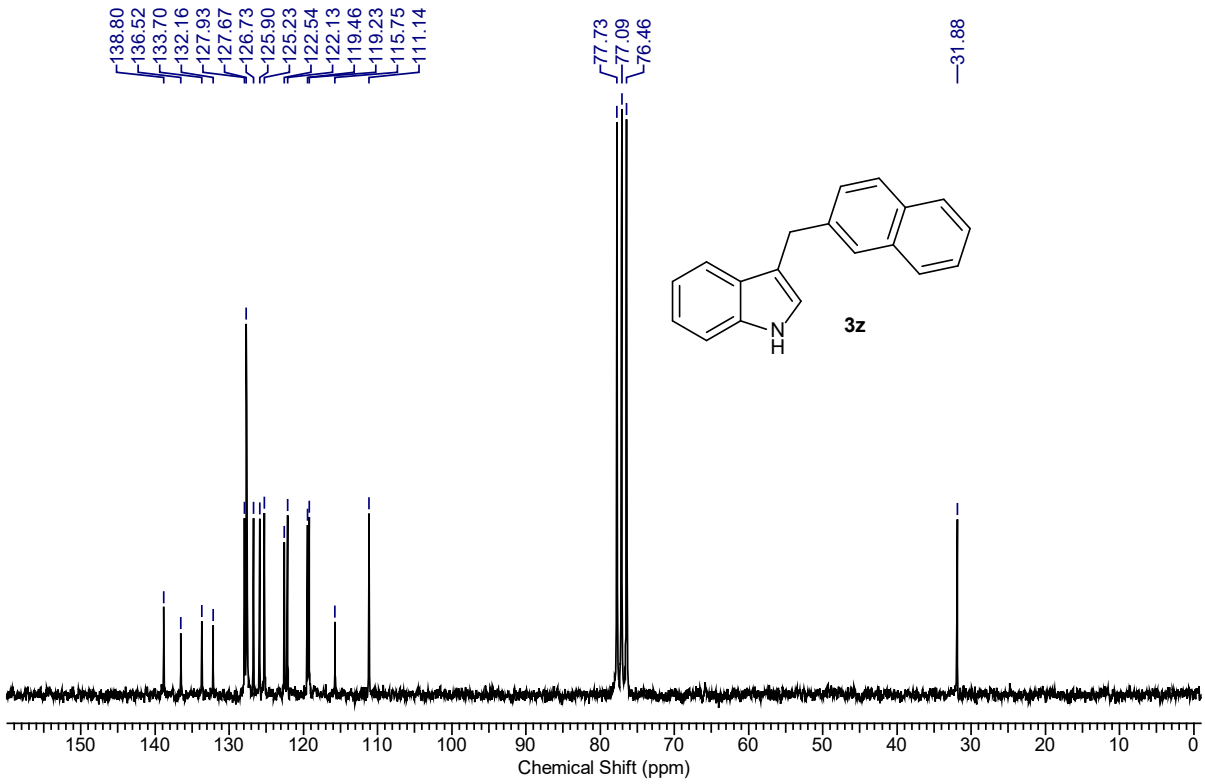

$^{1}$H NMR of **3y**



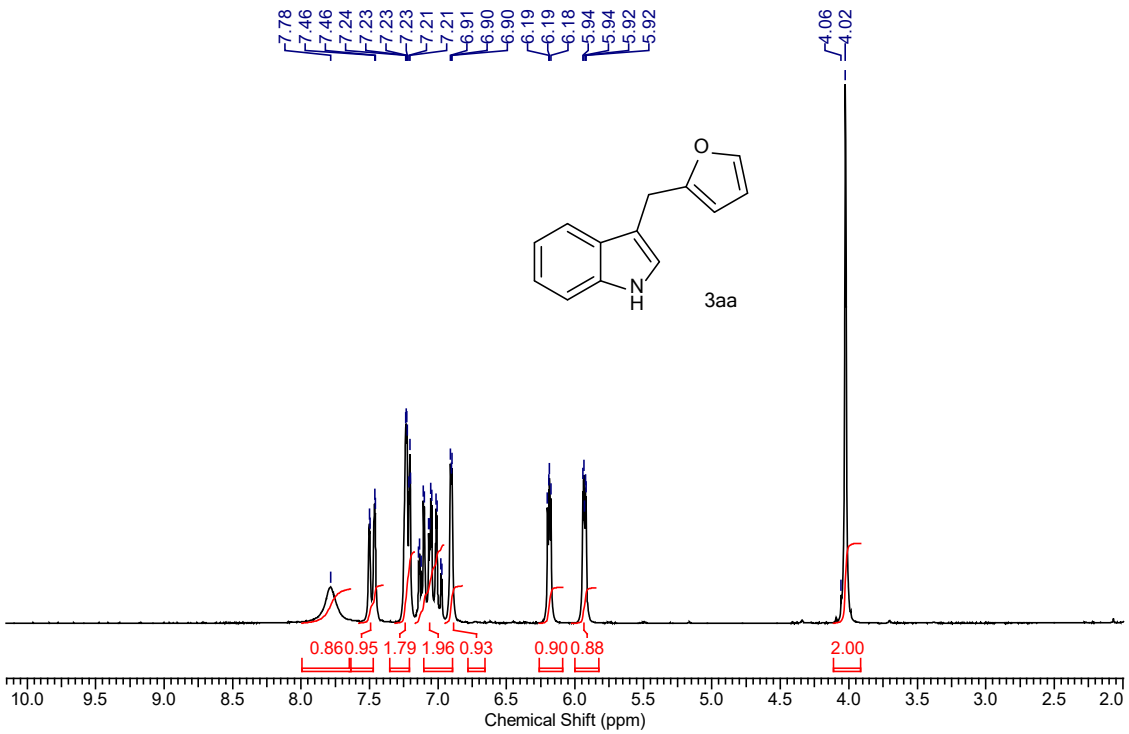

$^{13}$C{$^{1}$H} NMR of **3y**



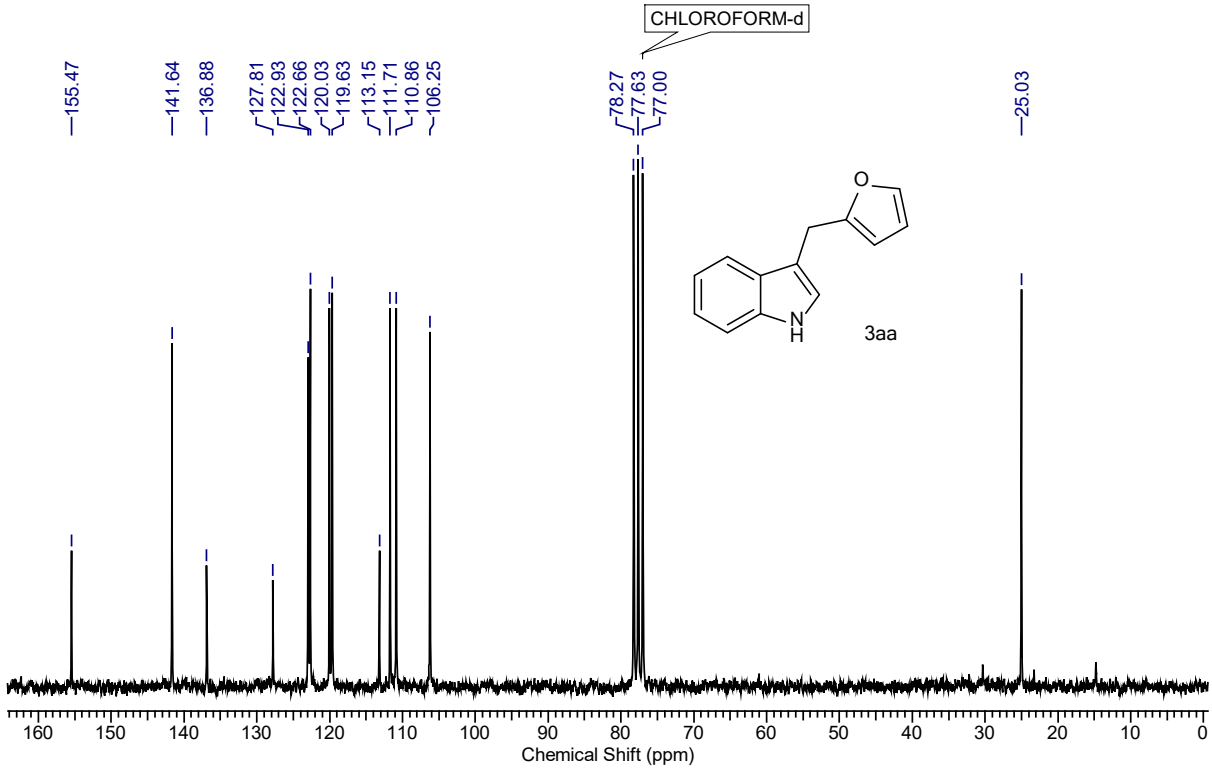

$^{1}$H NMR of **3z**



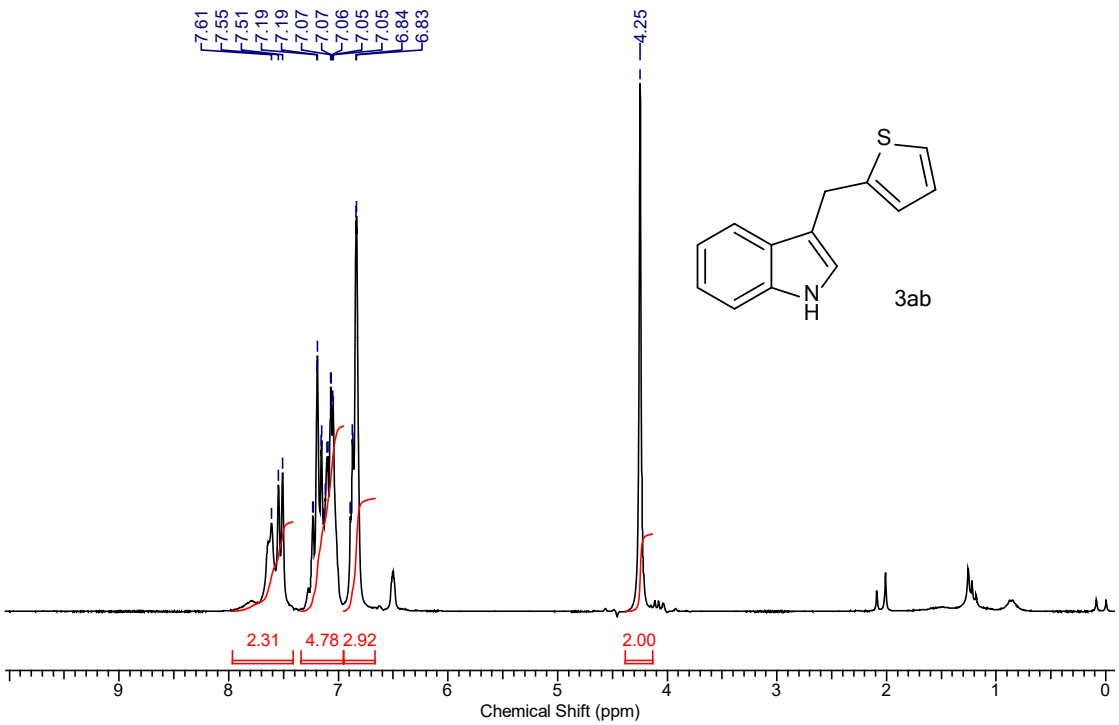

$^{13}$C{$^{1}$H} NMR of **3z**



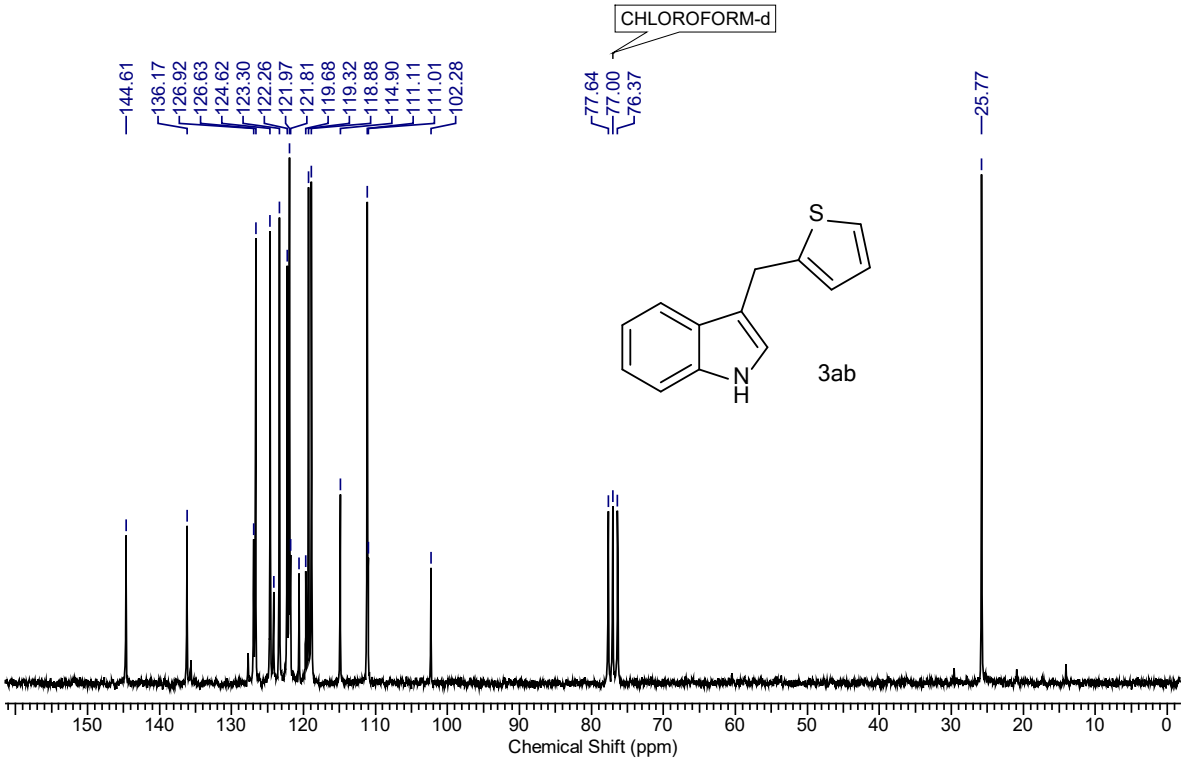

$^{1}$H NMR of **3aa**



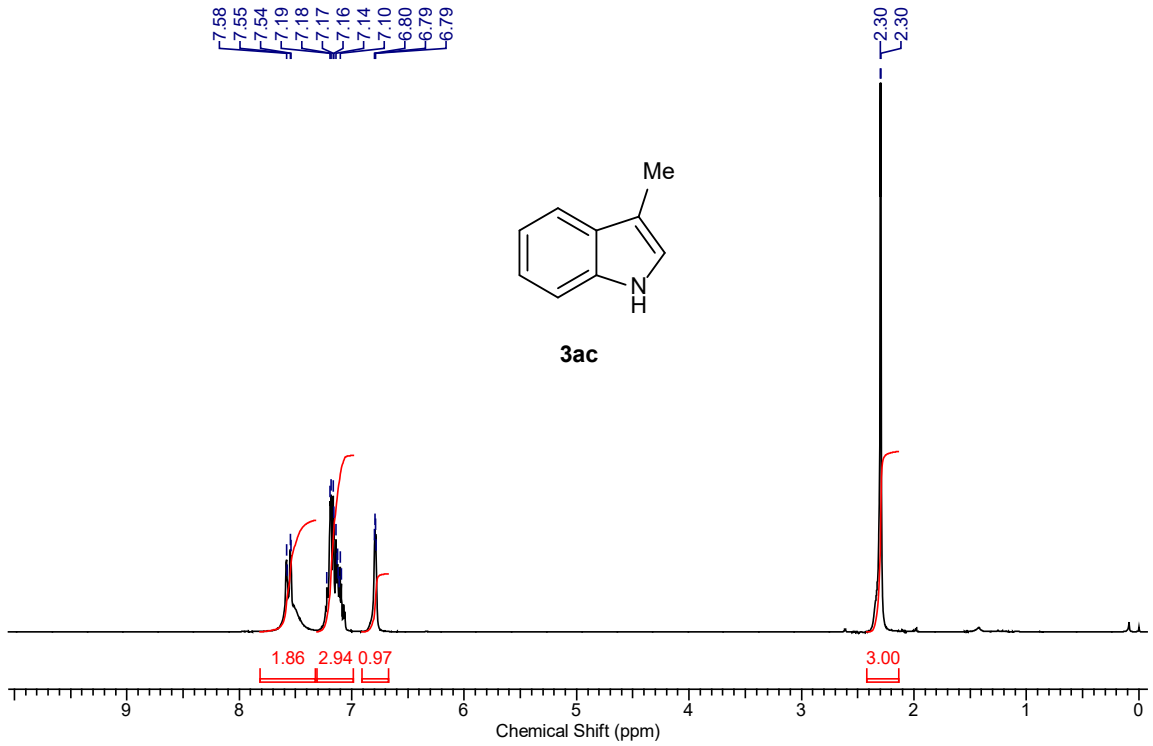

$^{13}$C{$^{1}$H} NMR of **3aa**



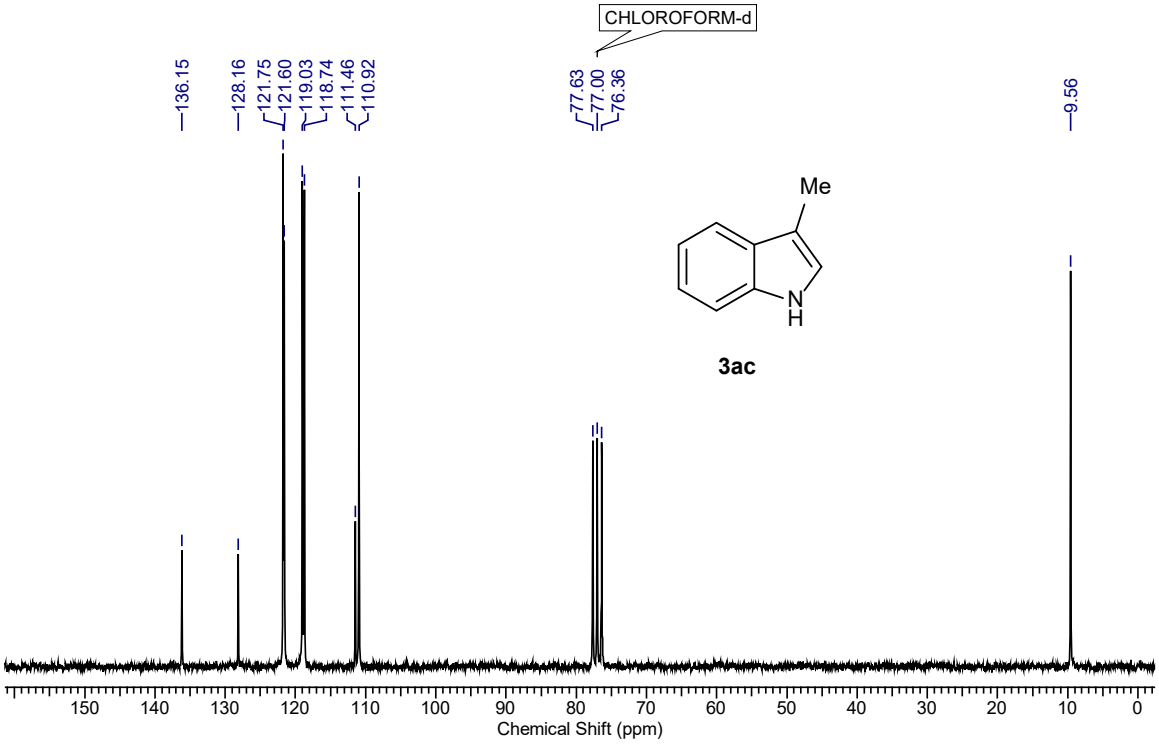

$^{1}$H NMR of **3ab**



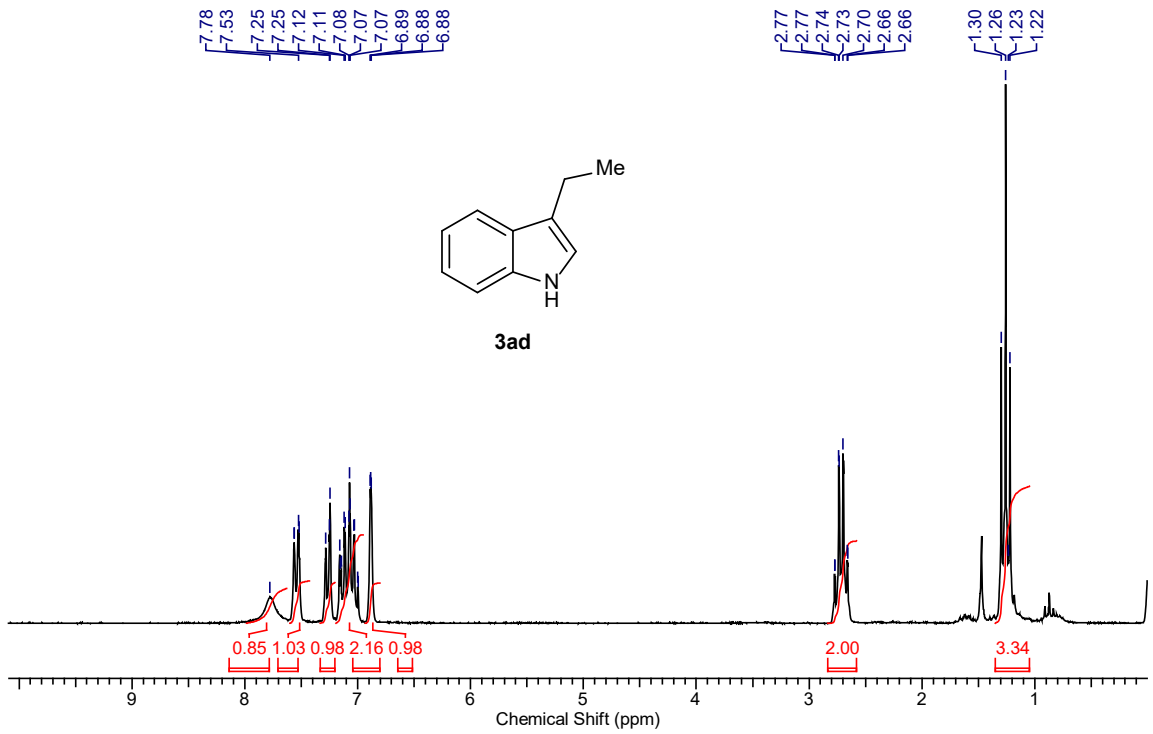

$^{13}$C{$^{1}$H} NMR of **3ab**



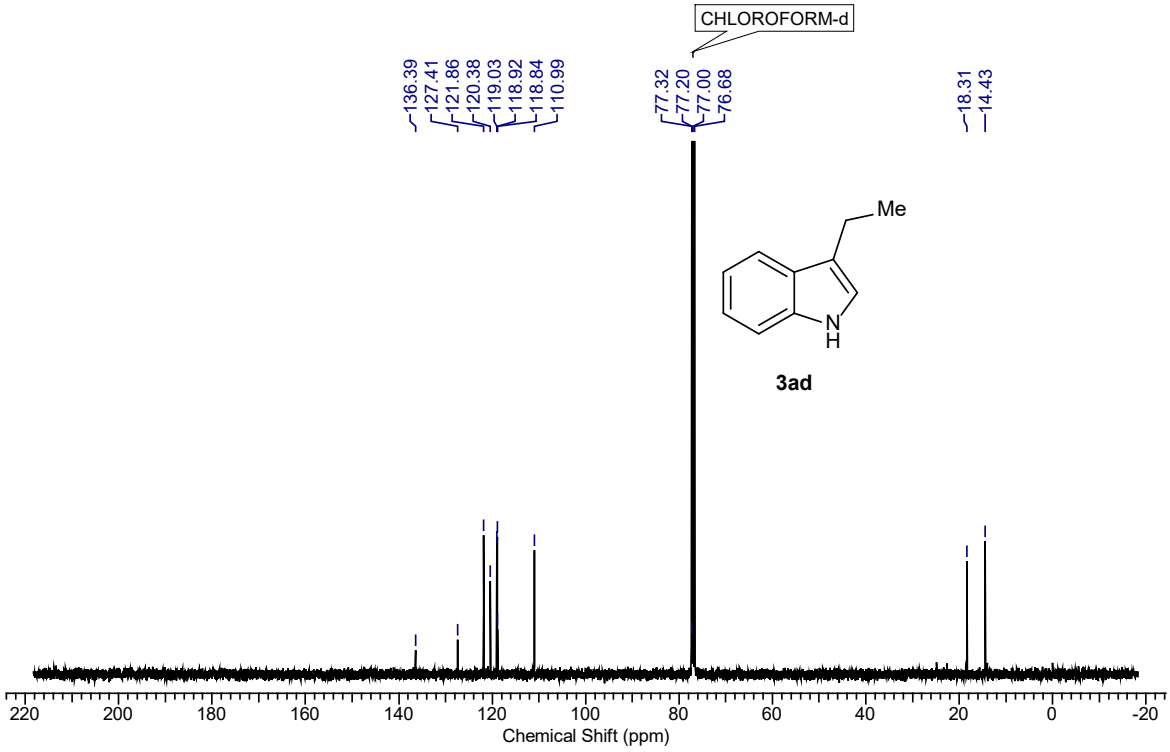

$^{1}$H NMR of **3ac**



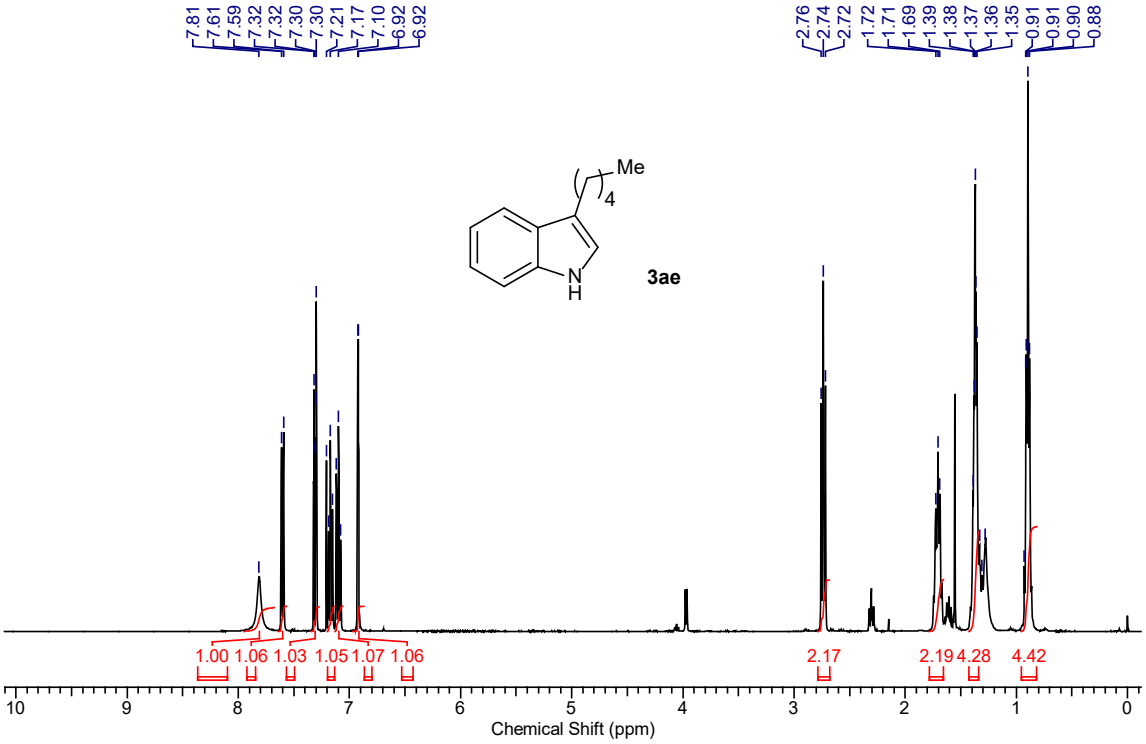

$^{13}$C{$^{1}$H} NMR of **3ac**



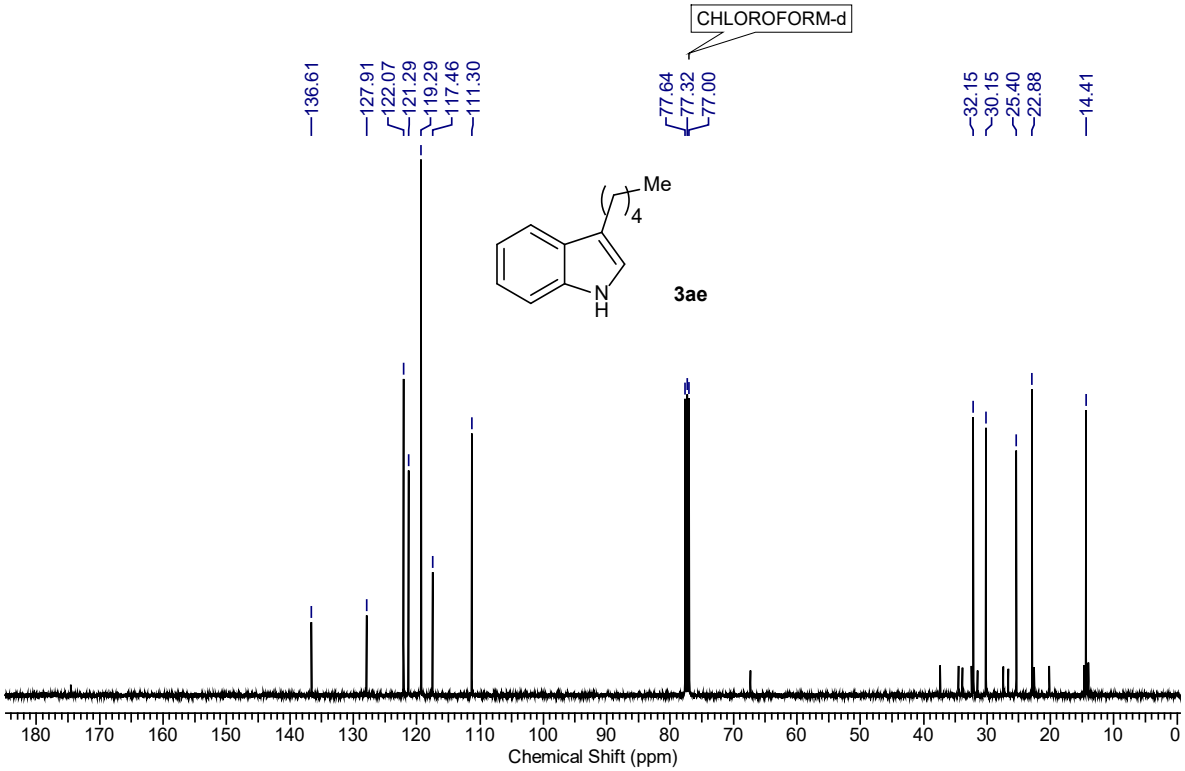

$^{1}$H NMR of **3ad**



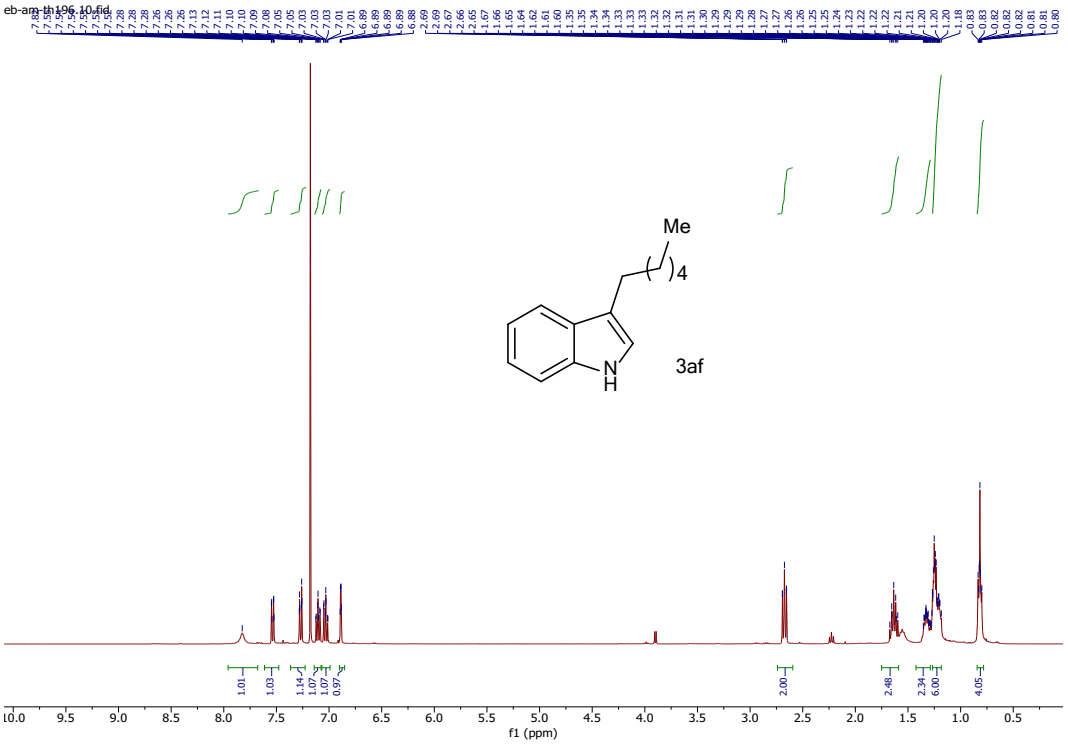

$^{13}$C{$^{1}$H} NMR of **3ad**



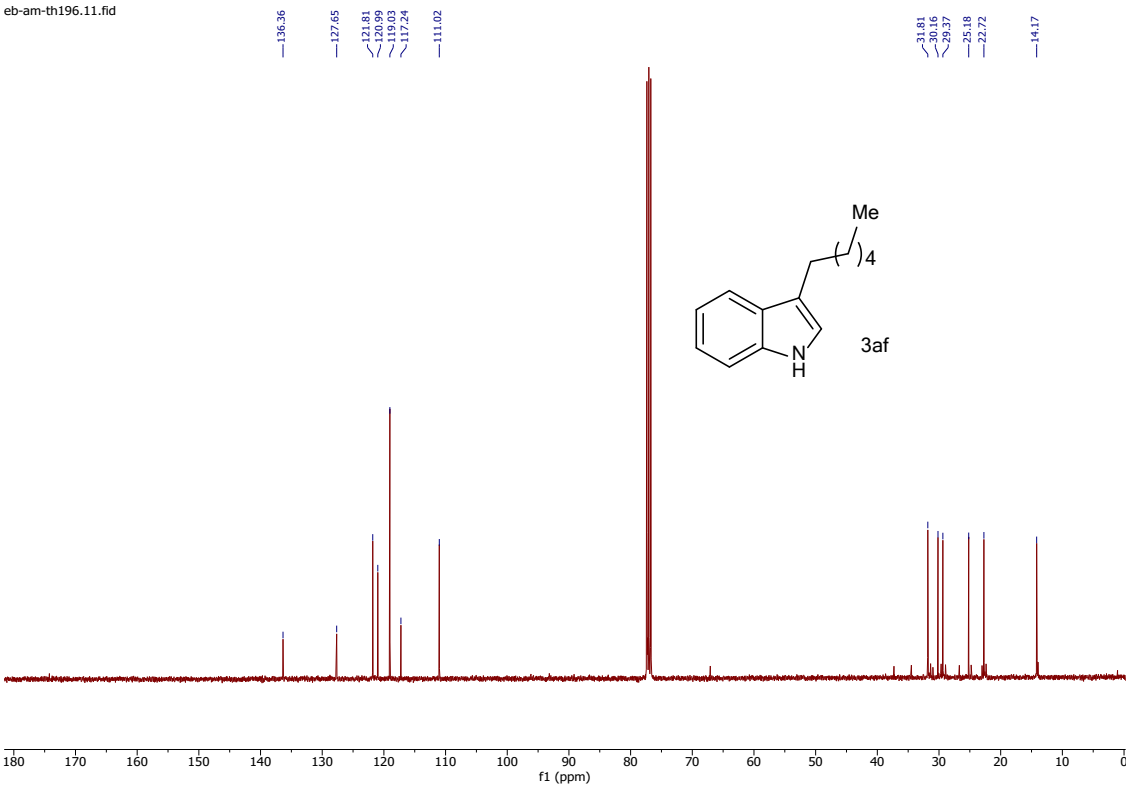

$^{1}$H NMR of **3ae**



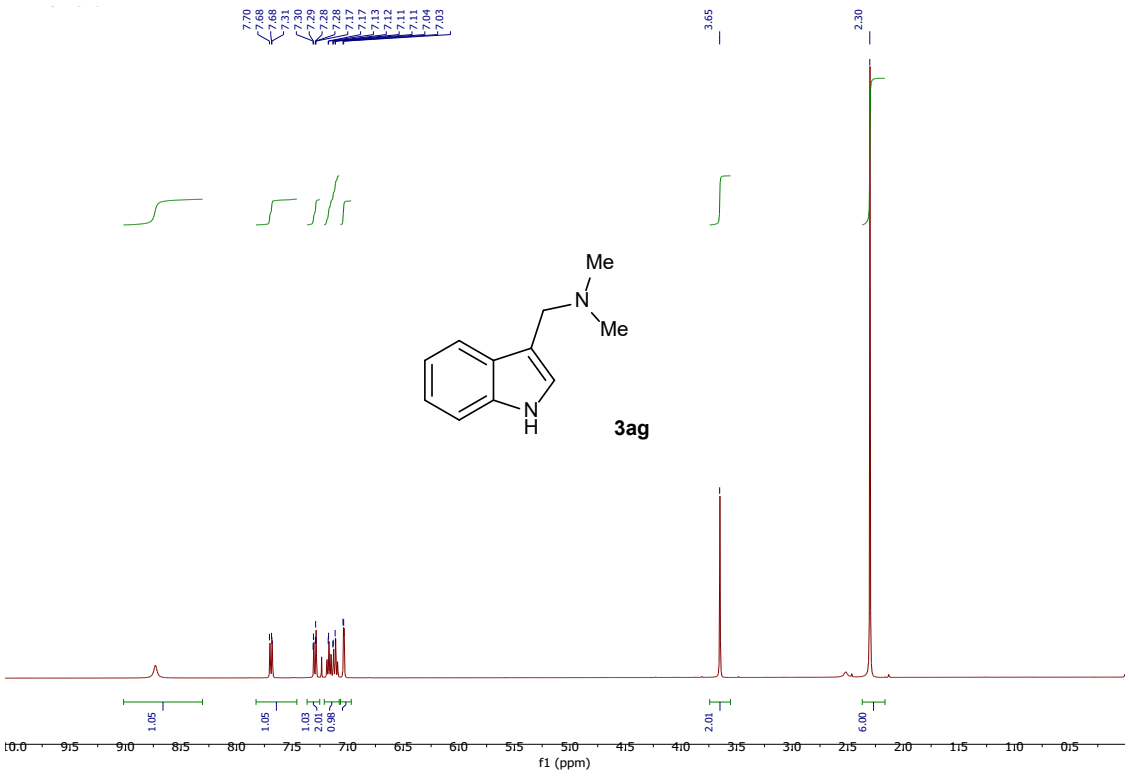

$^{13}$C{$^{1}$H} NMR of **3ae**



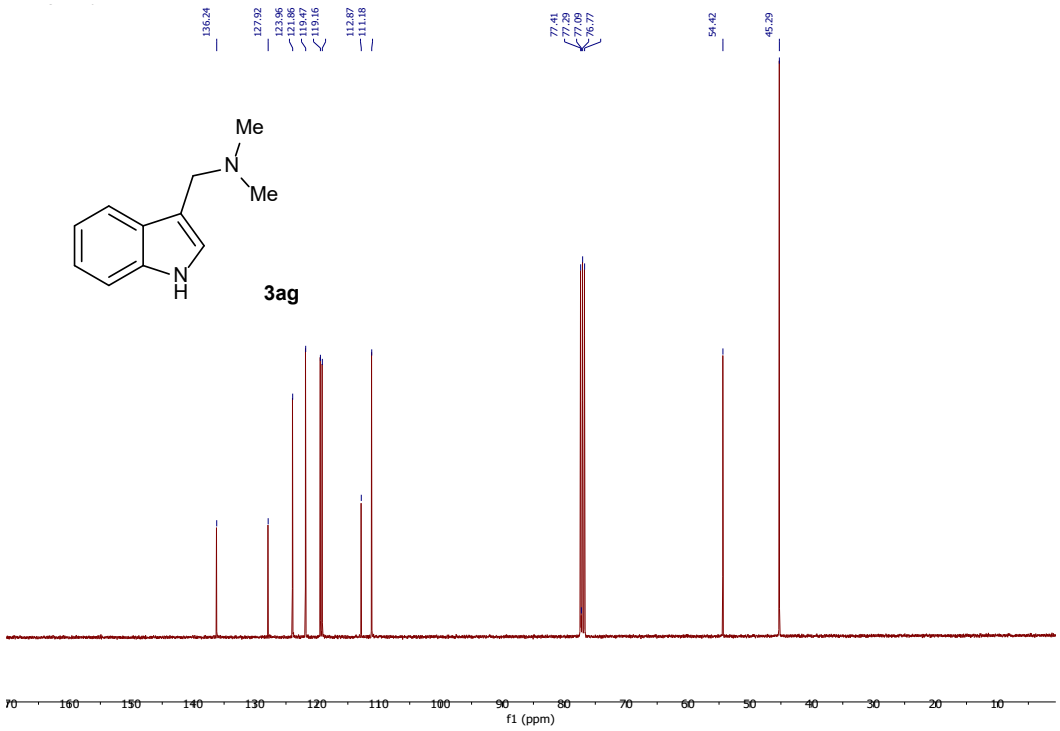

$^{1}$H NMR of **3af**



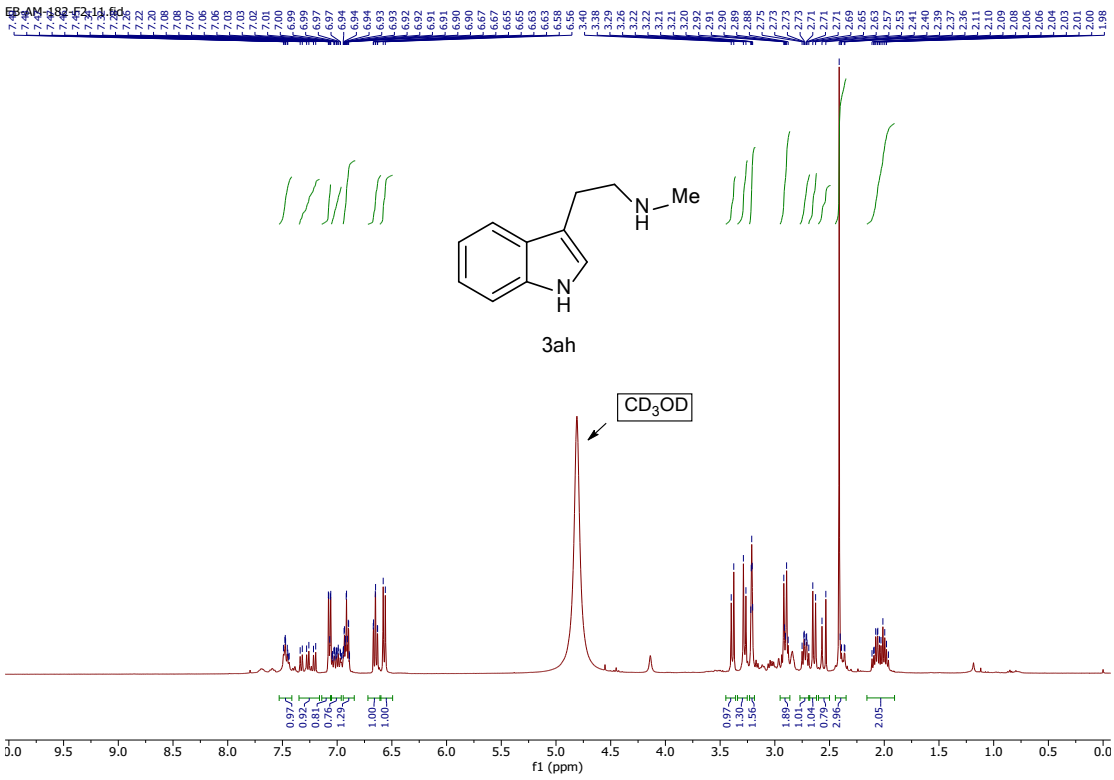

$^{13}$C{$^{1}$H} NMR of **3af**



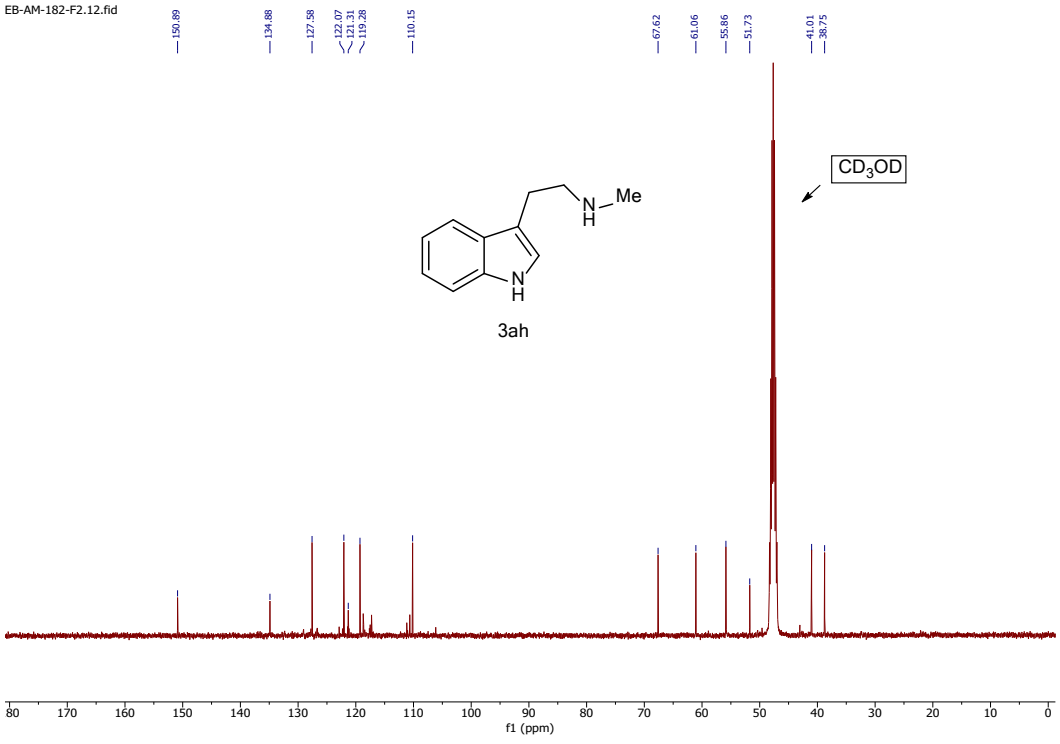

$^{1}$H NMR of **3ag**



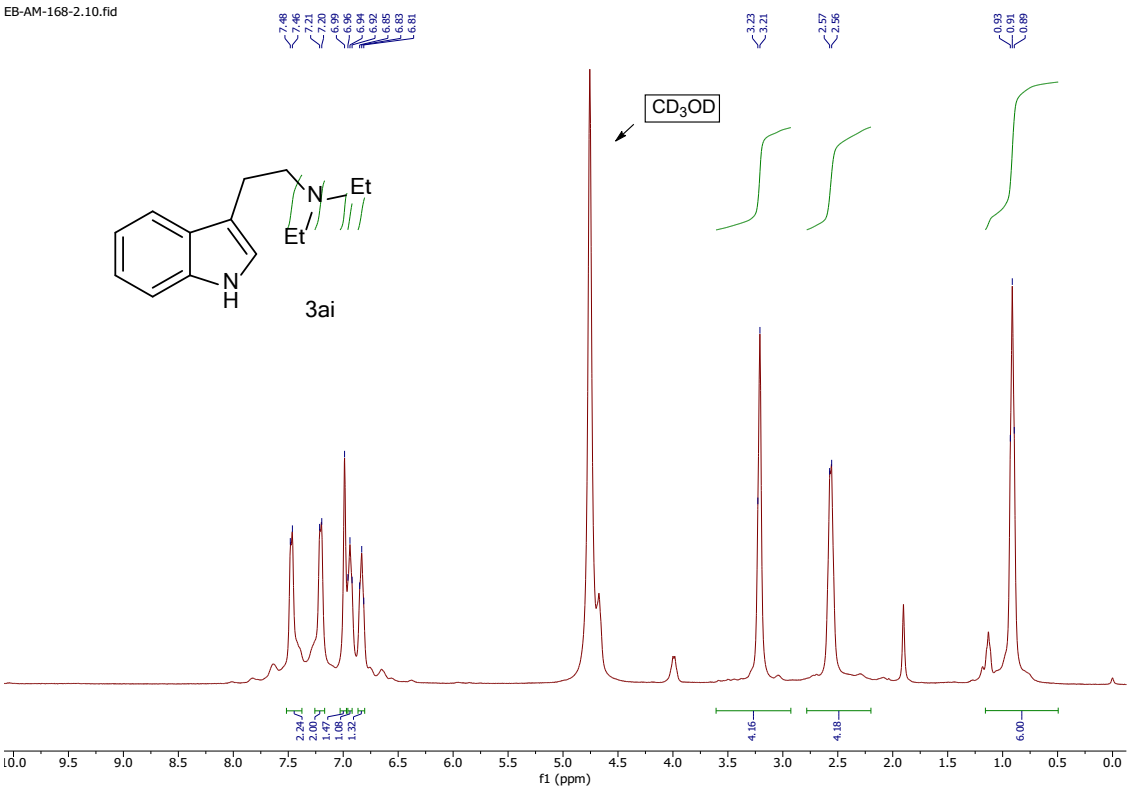

$^{13}$C{$^{1}$H} NMR of **3ag**



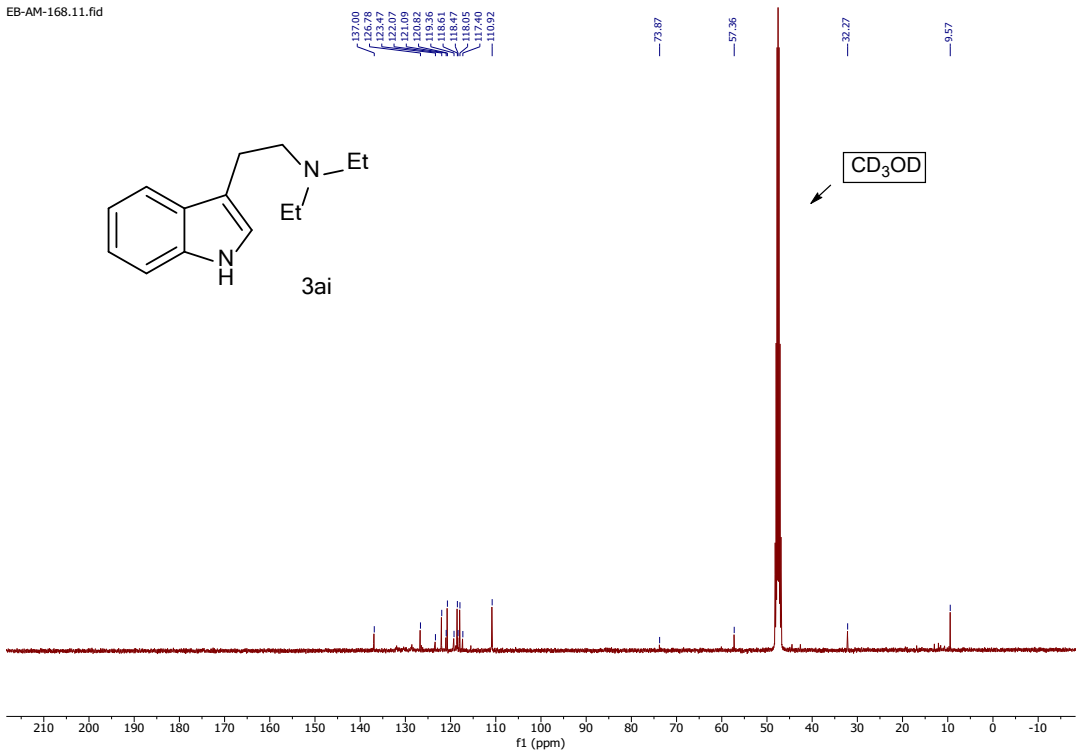

$^{1}$H NMR of **3ah** (Crude mixture).



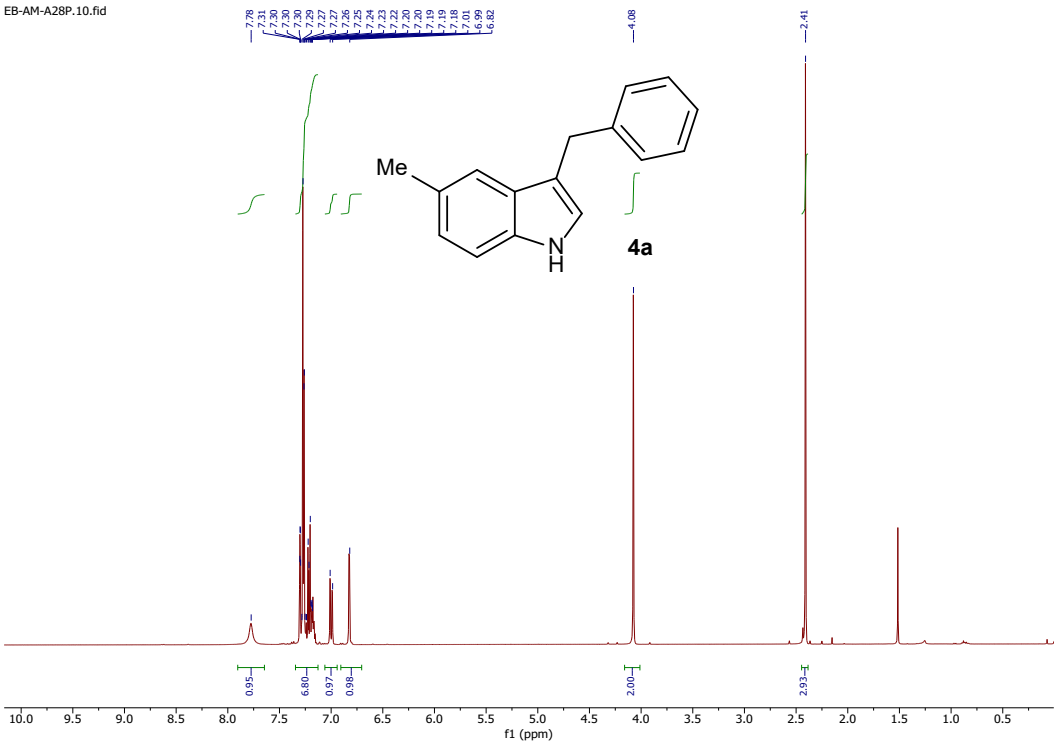

$^{13}$C{$^{1}$H} NMR of **3ah** (Crude mixture).



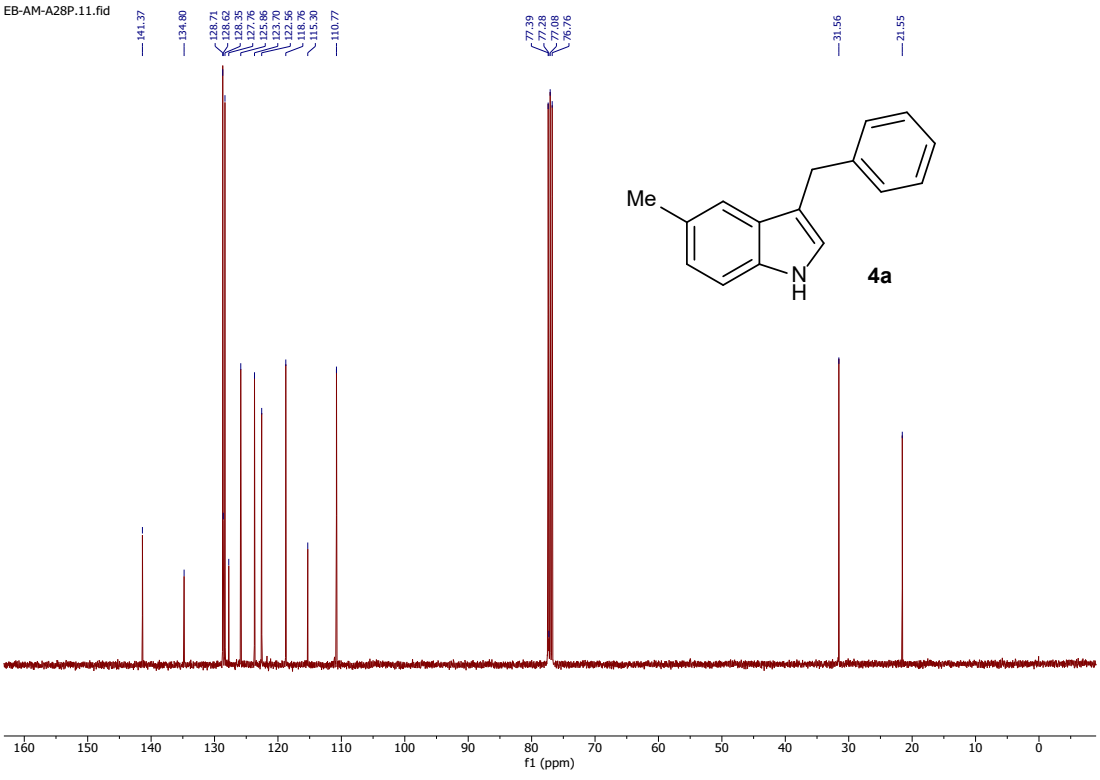

$^{1}$H NMR of **3ai**



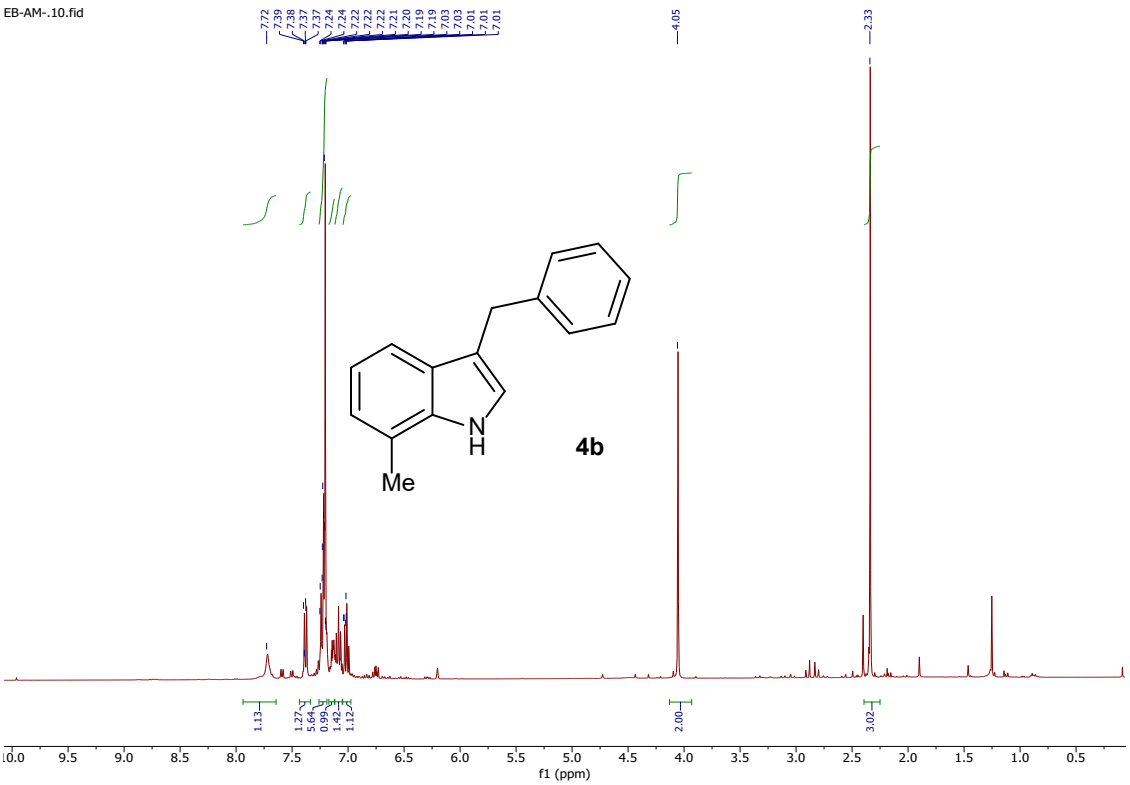

$^{13}$C{$^{1}$H} NMR of **3ai**



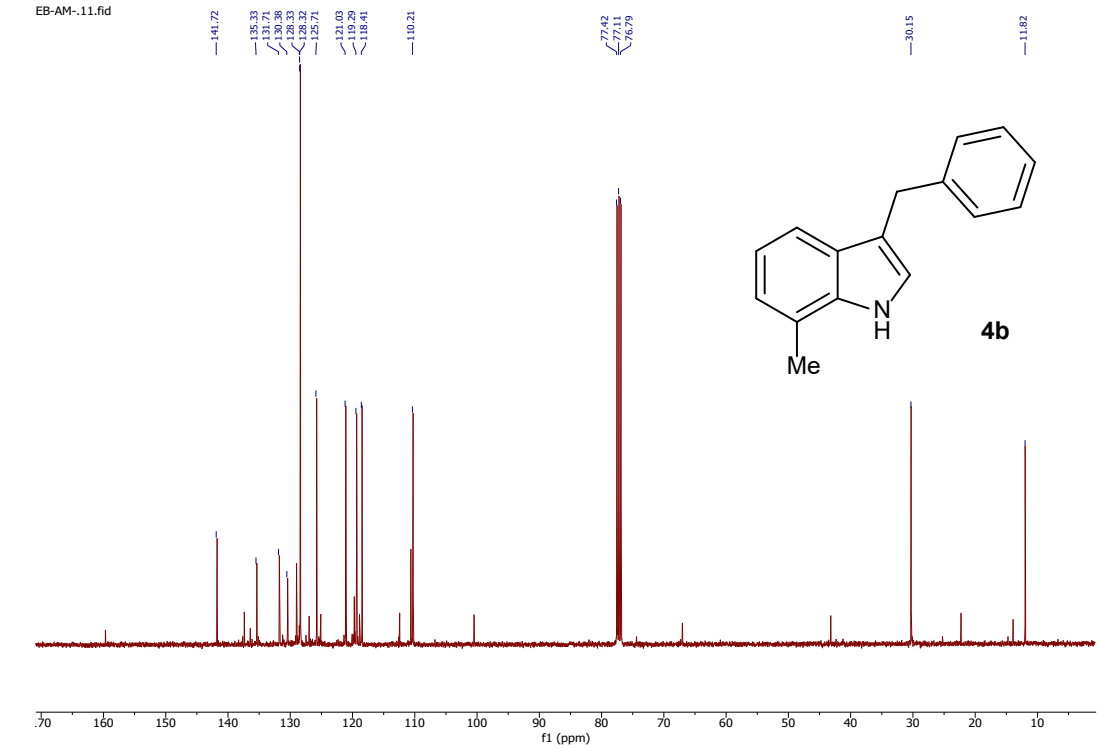

$^{1}$H NMR of **4a**



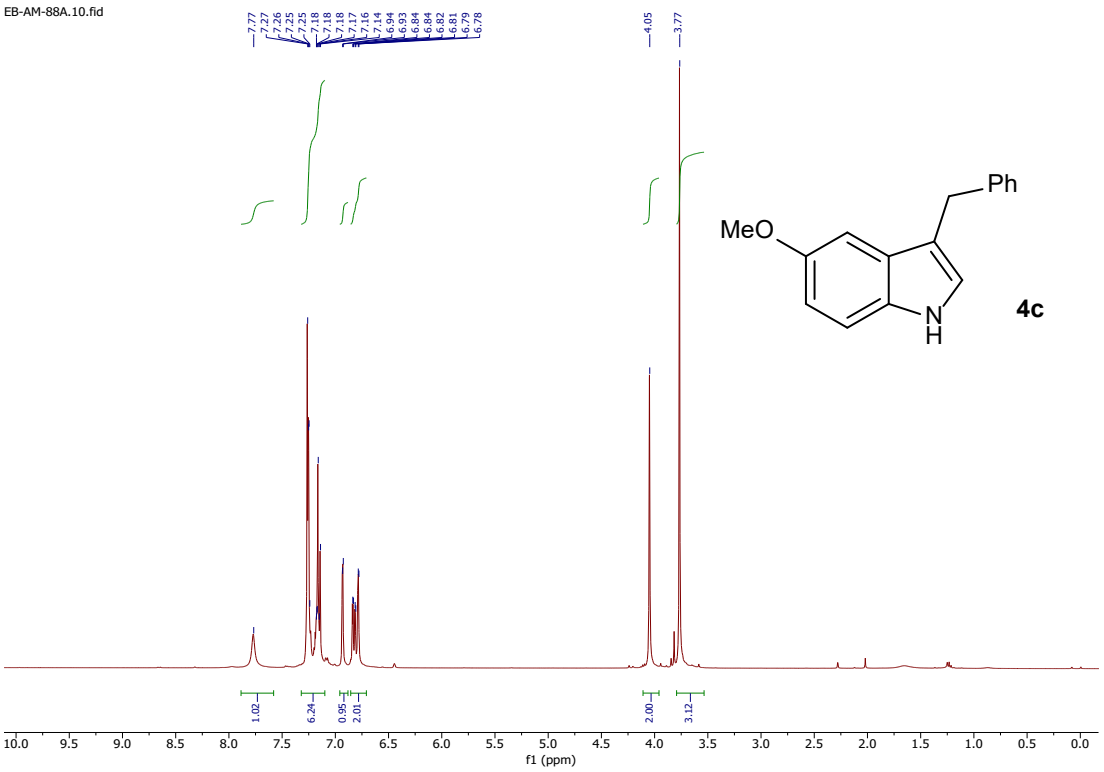

$^{13}$C{$^{1}$H} NMR of **4a**



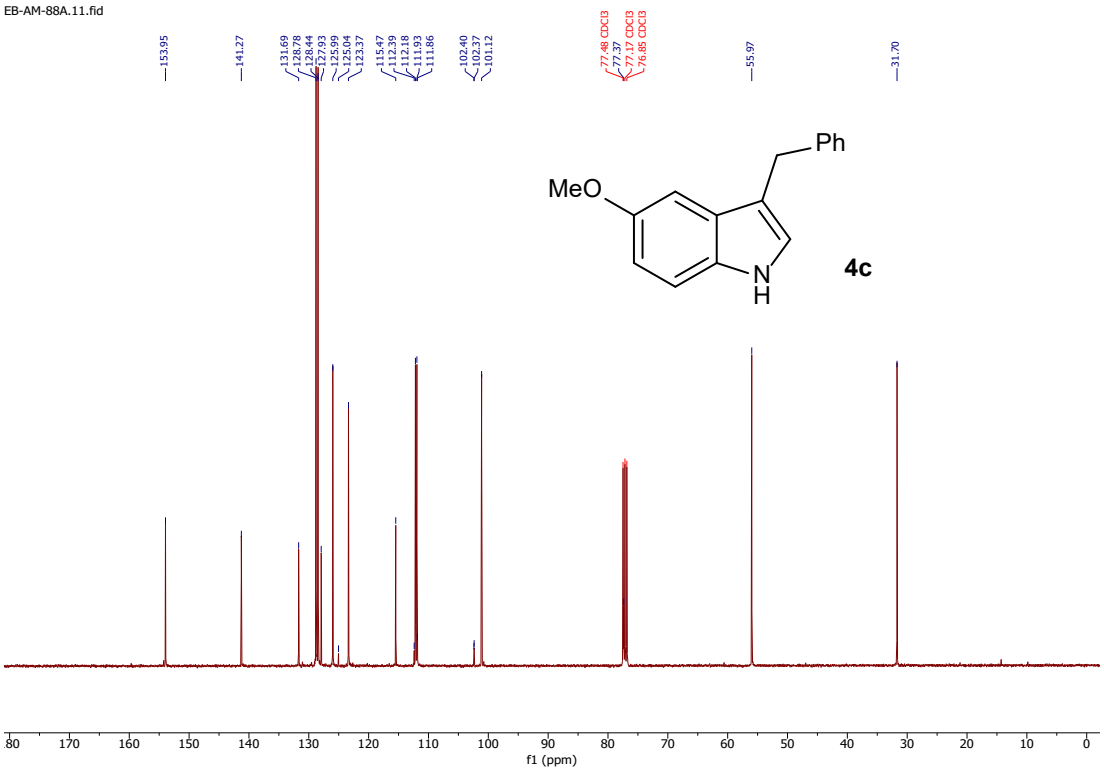

$^{1}$H NMR of **4b**



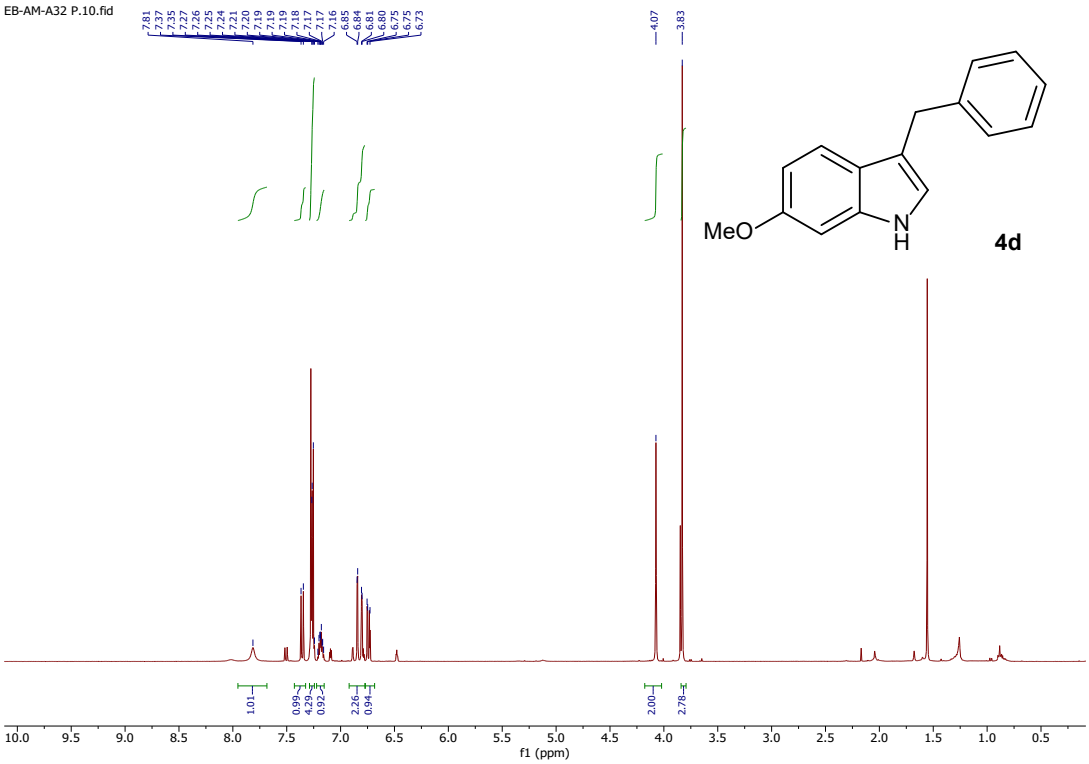

$^{13}$C{$^{1}$H} NMR of **4b**



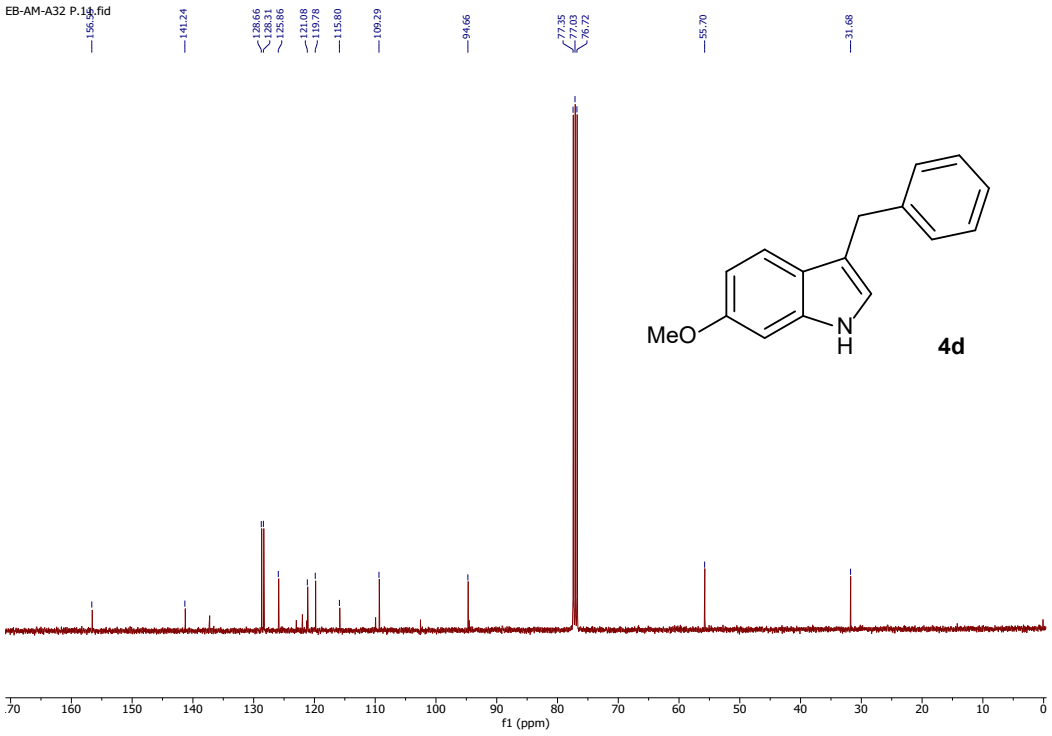

$^{1}$H NMR of **4c**



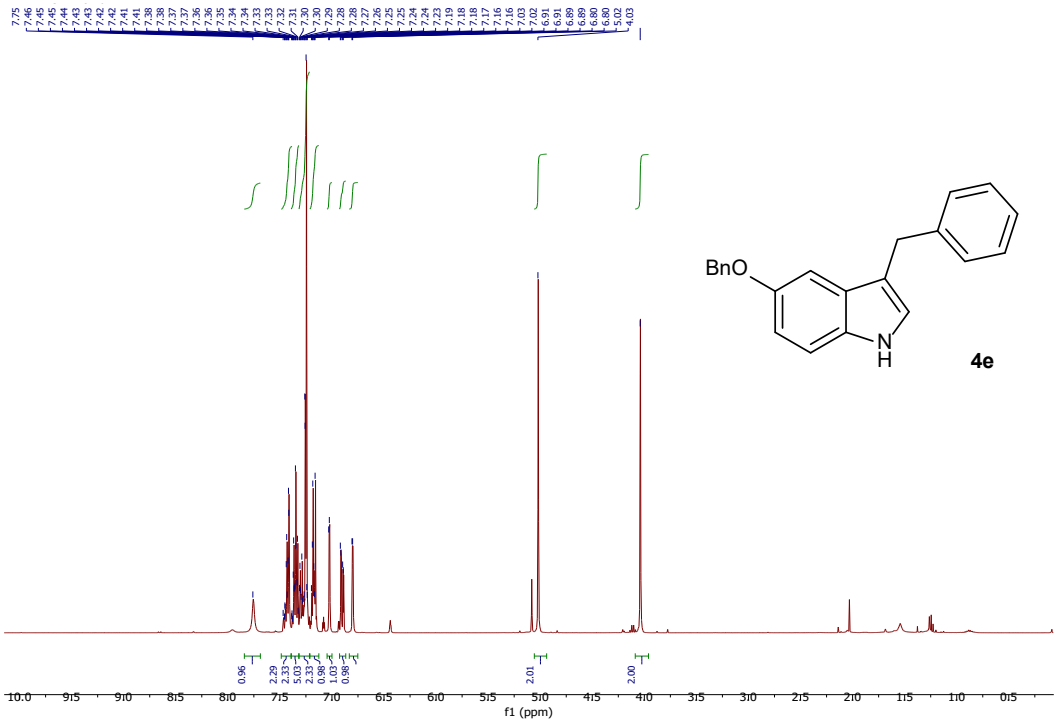

$^{13}$C{$^{1}$H} NMR of **4c**



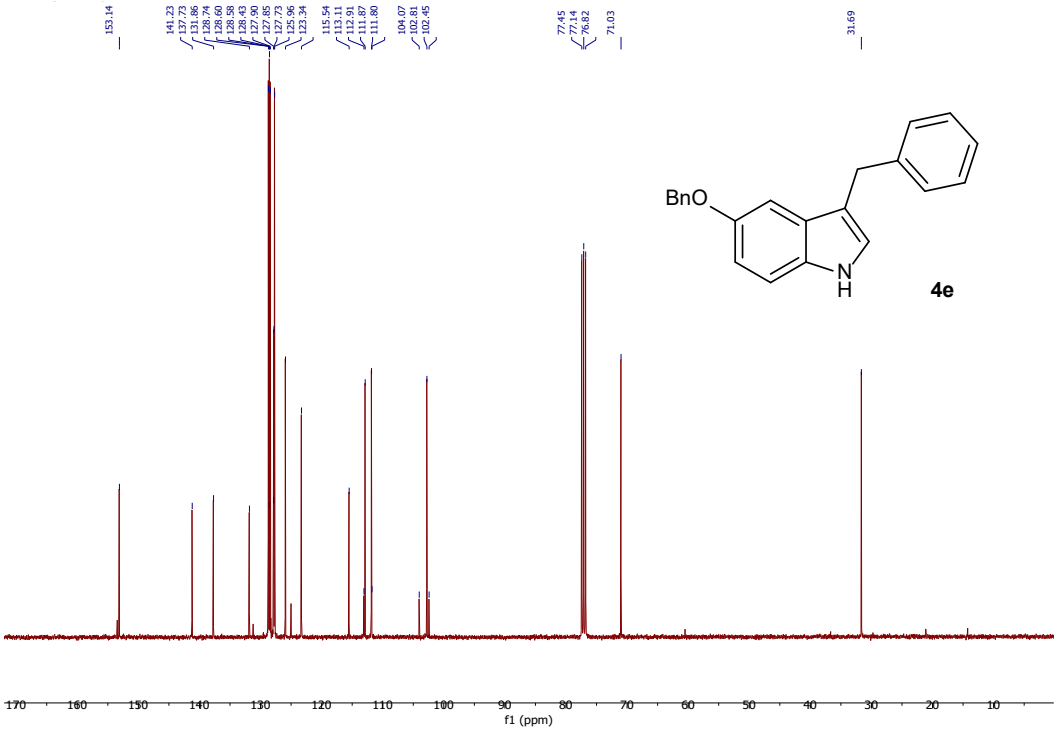

$^{1}$H NMR of **4d**



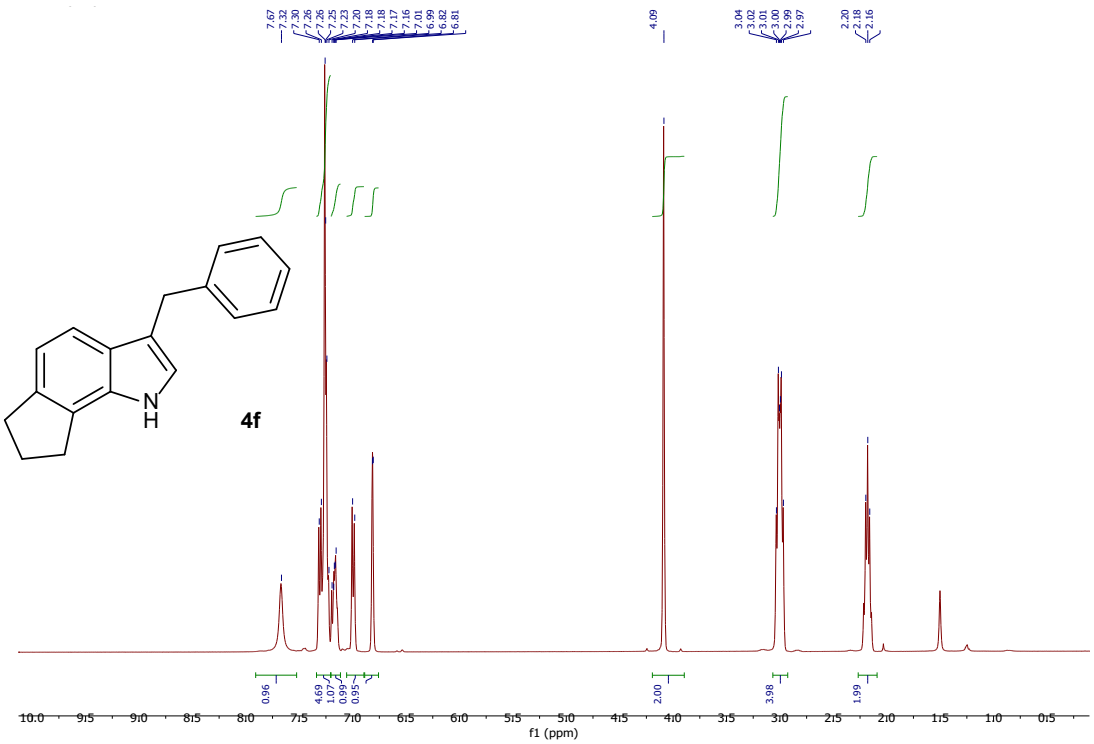

$^{13}$C{$^{1}$H} NMR of **4d**



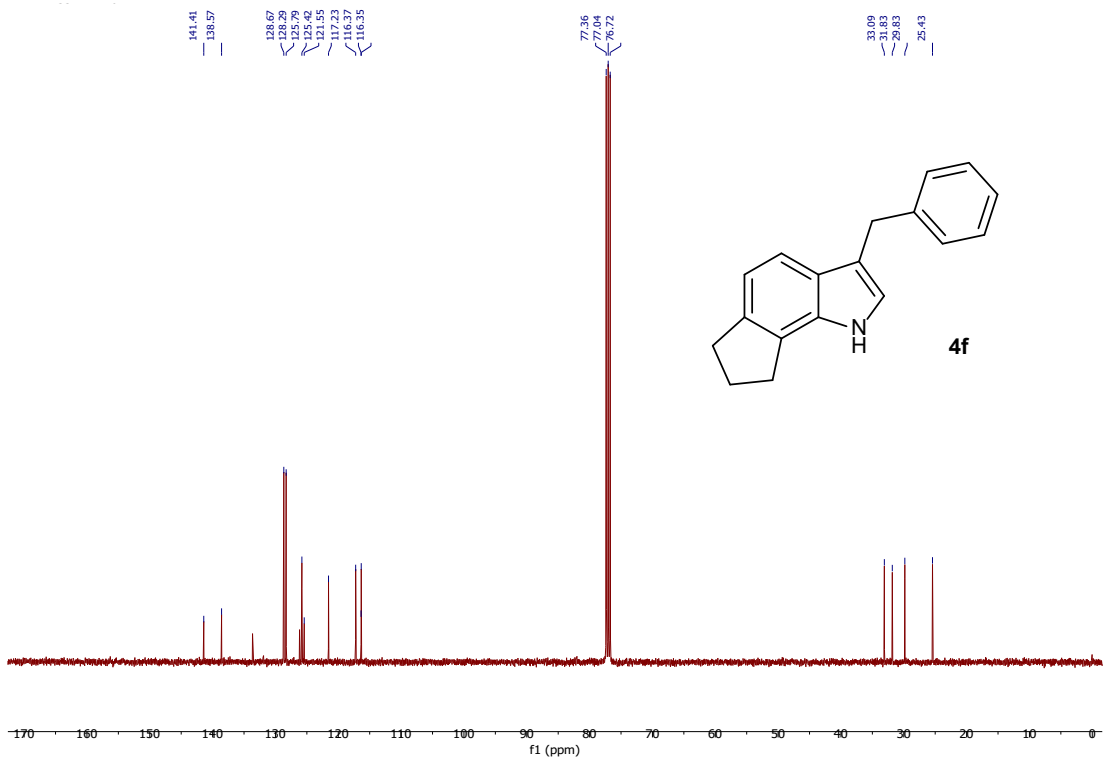

$^{1}$H NMR of **4e**



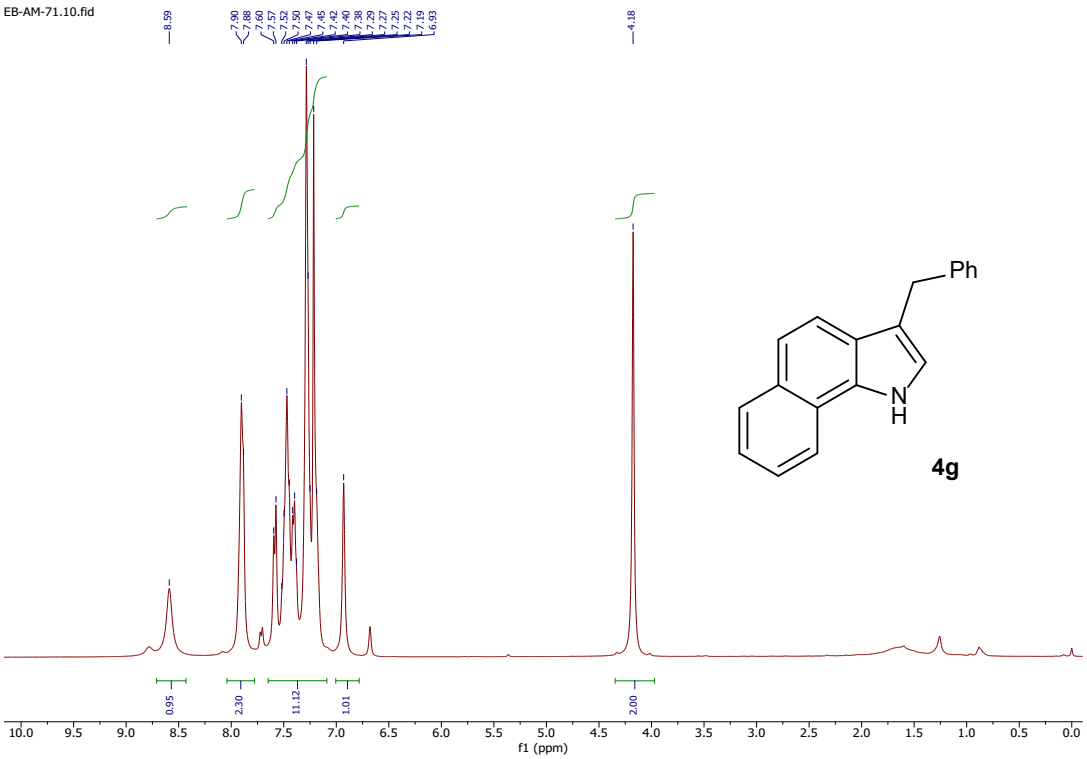

$^{13}$C{$^{1}$H} NMR of **4e**



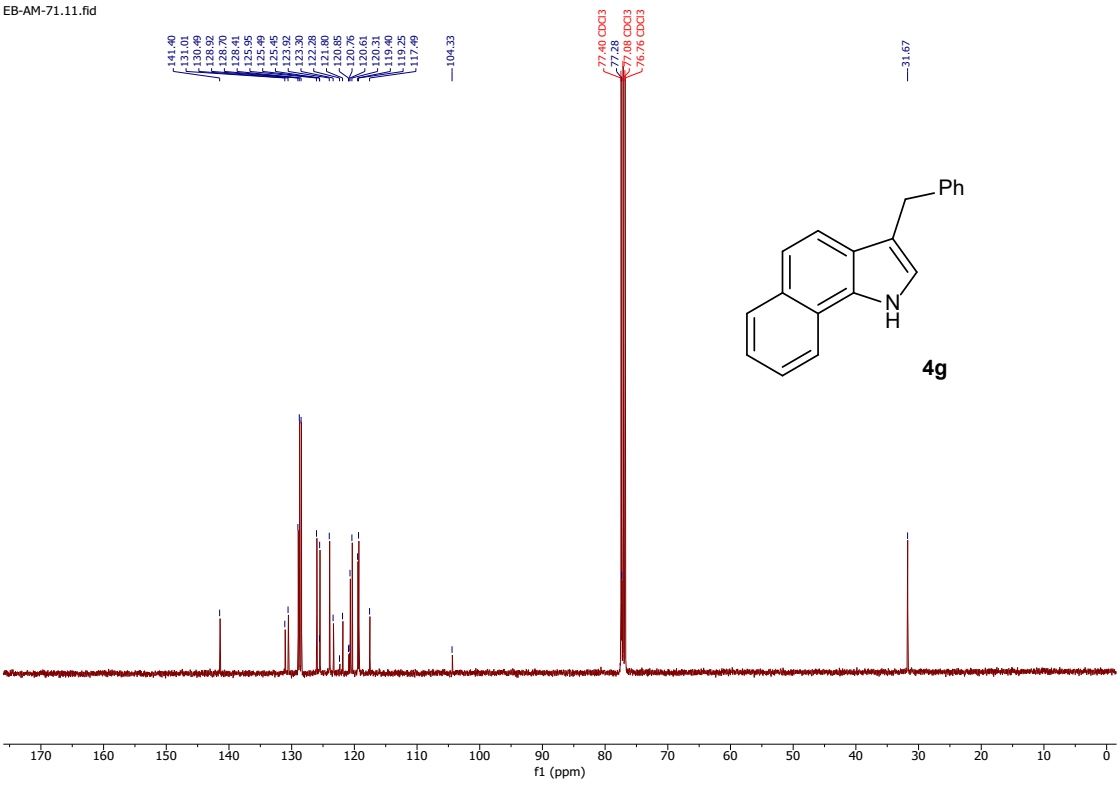

$^{1}$H NMR of **4f**



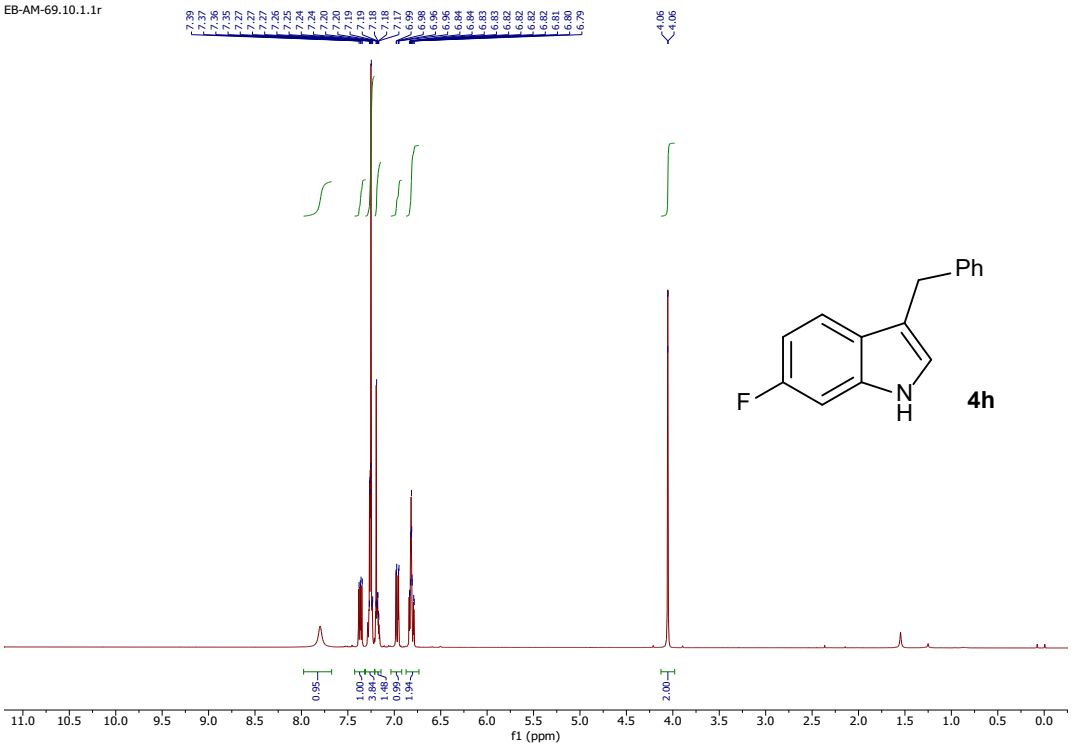

$^{13}$C{$^{1}$H} NMR of **4f**



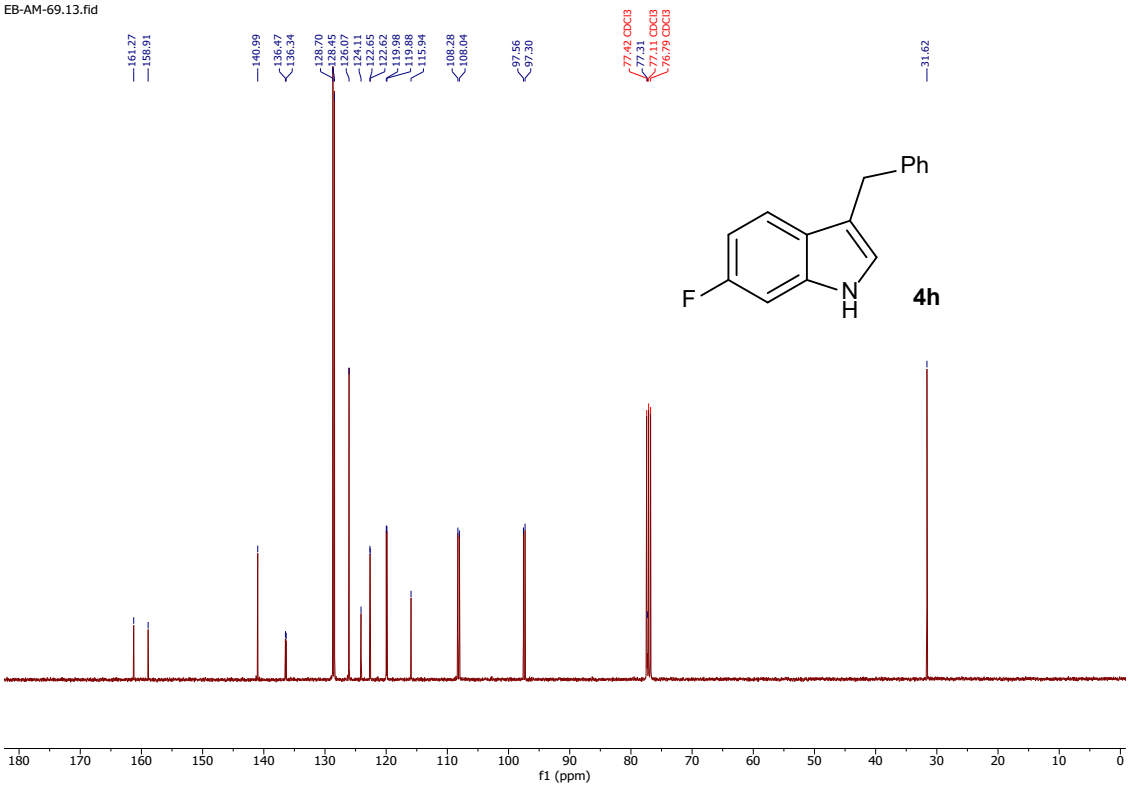

$^{1}$H NMR of **4g**



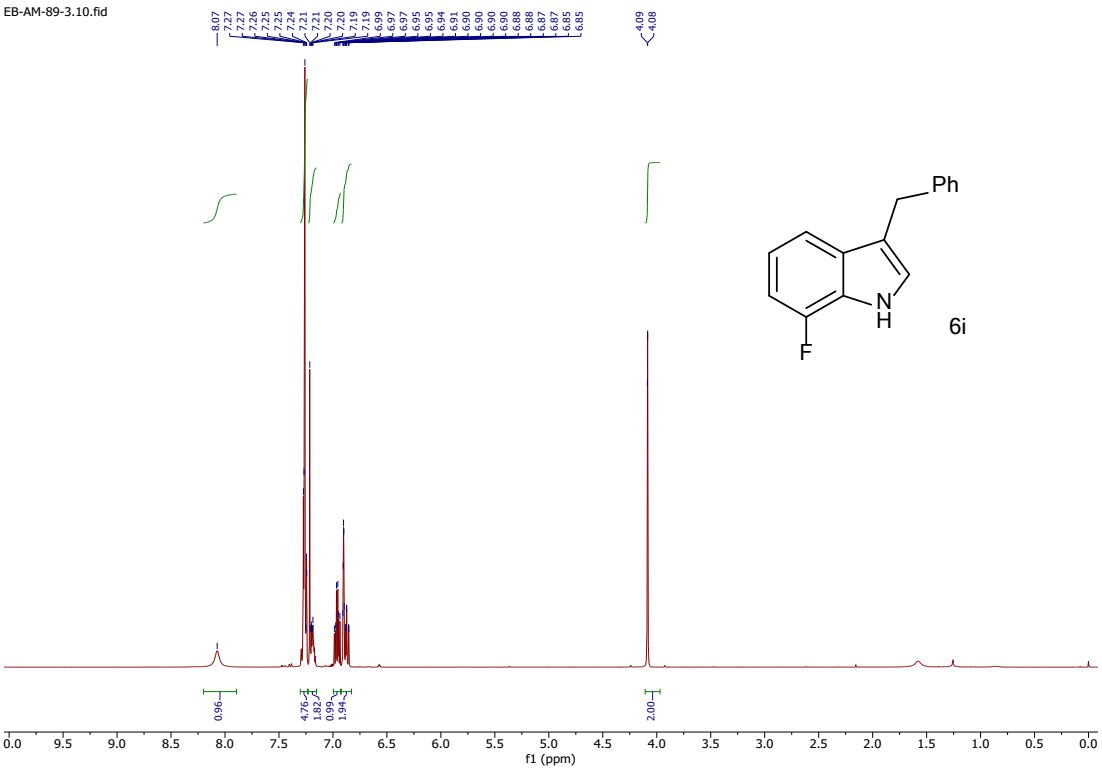

$^{13}$C{$^{1}$H} NMR of **4g**



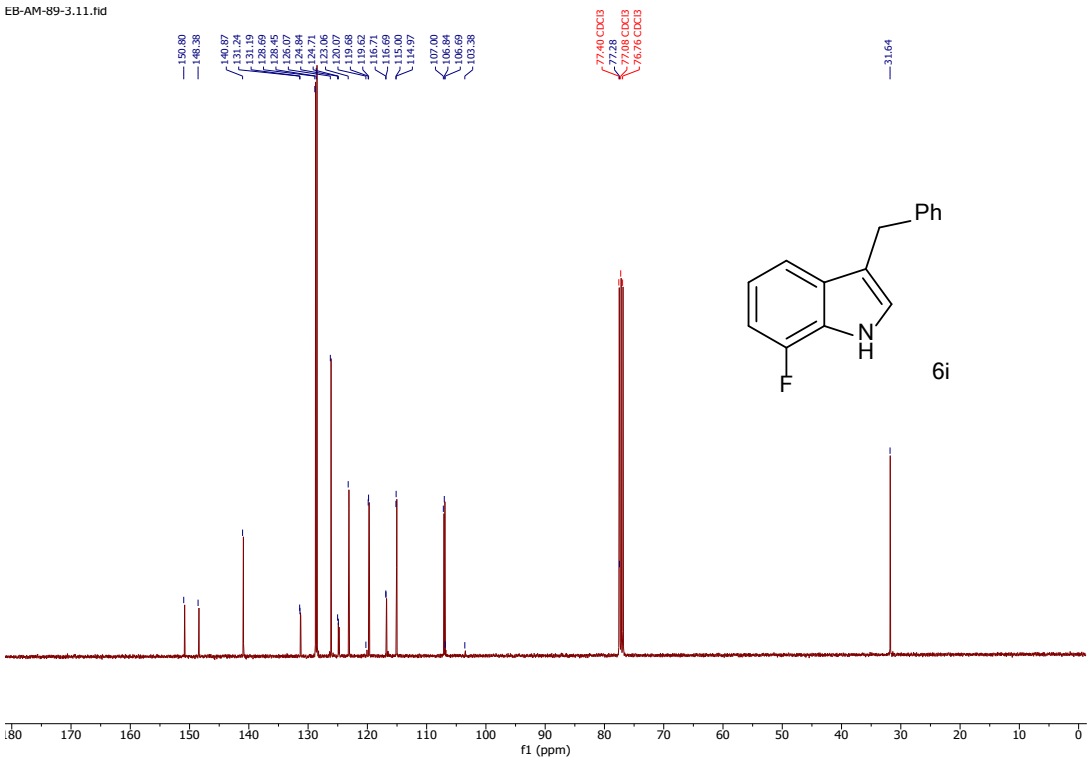

$^{1}$H NMR of **4h**



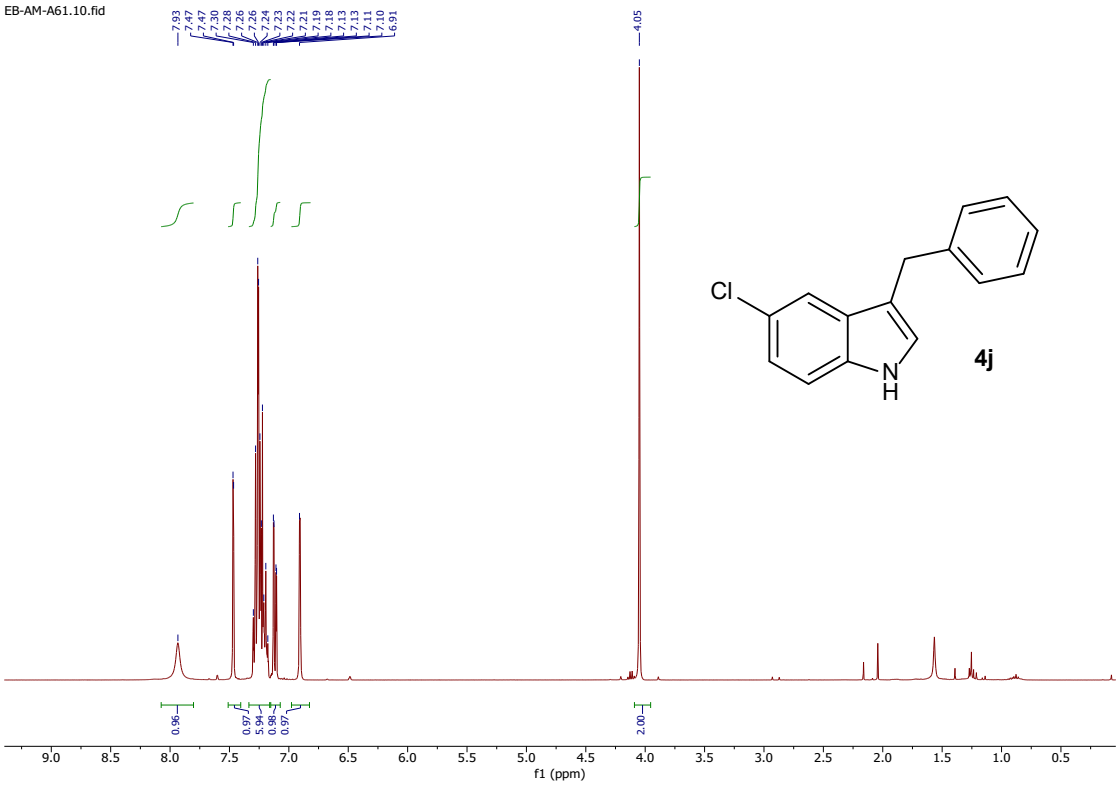

$^{13}$C{$^{1}$H} NMR of **4h**



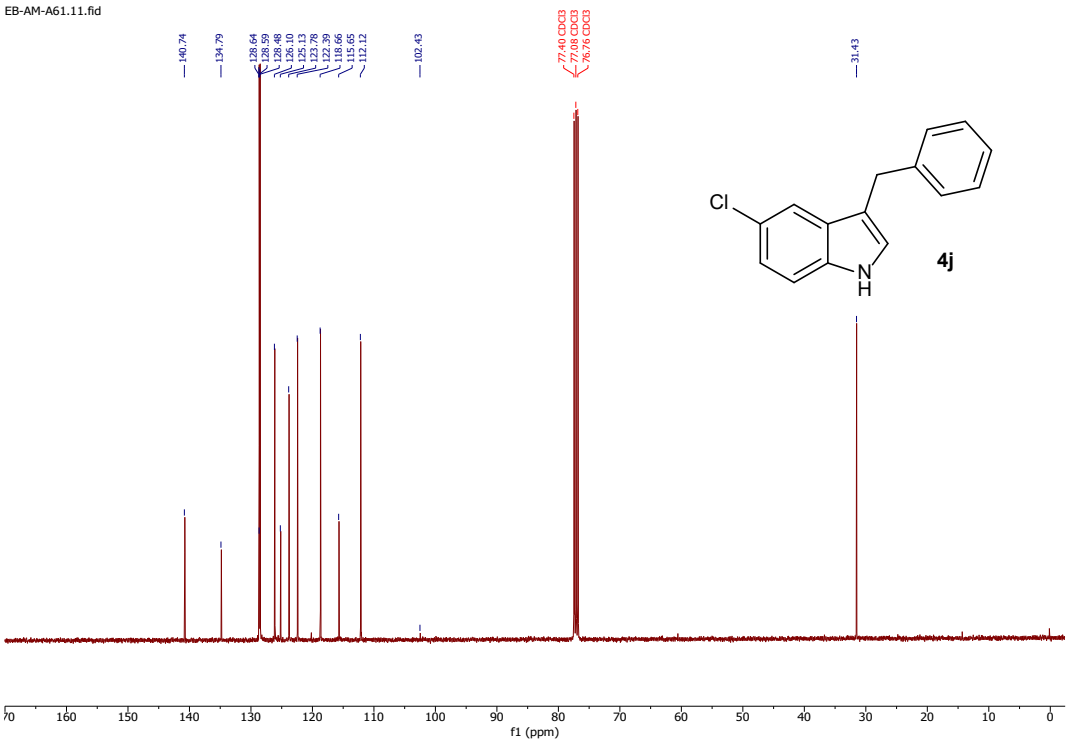

$^{1}$H NMR of **4i**



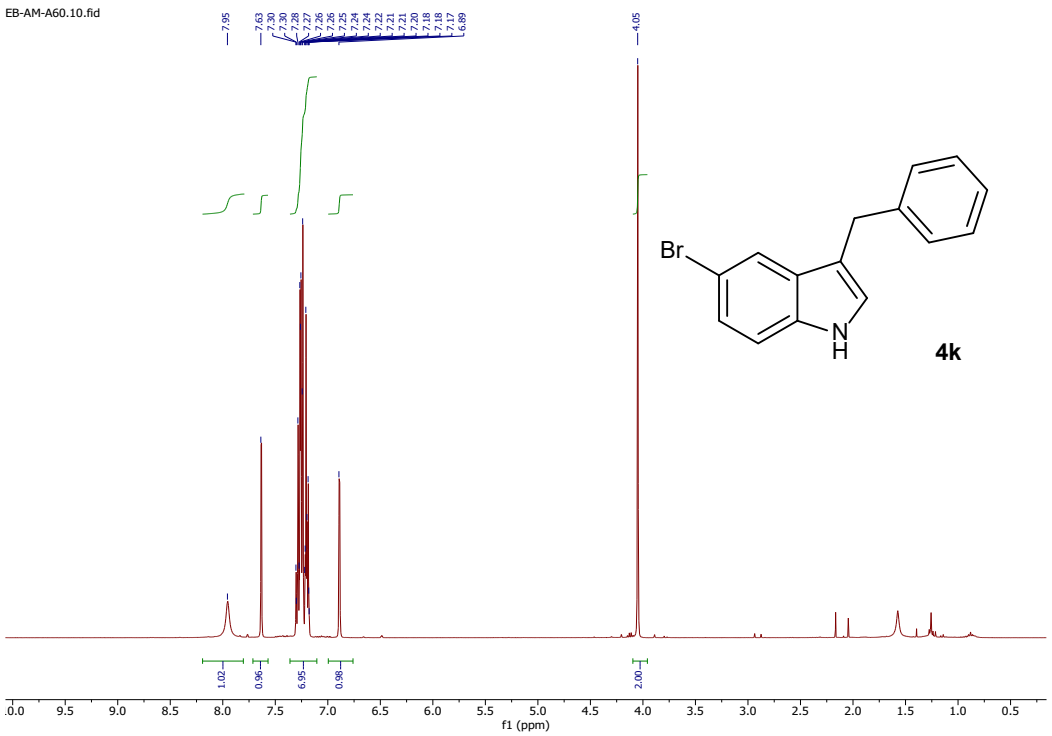

$^{13}$C{$^{1}$H} NMR of **4i**



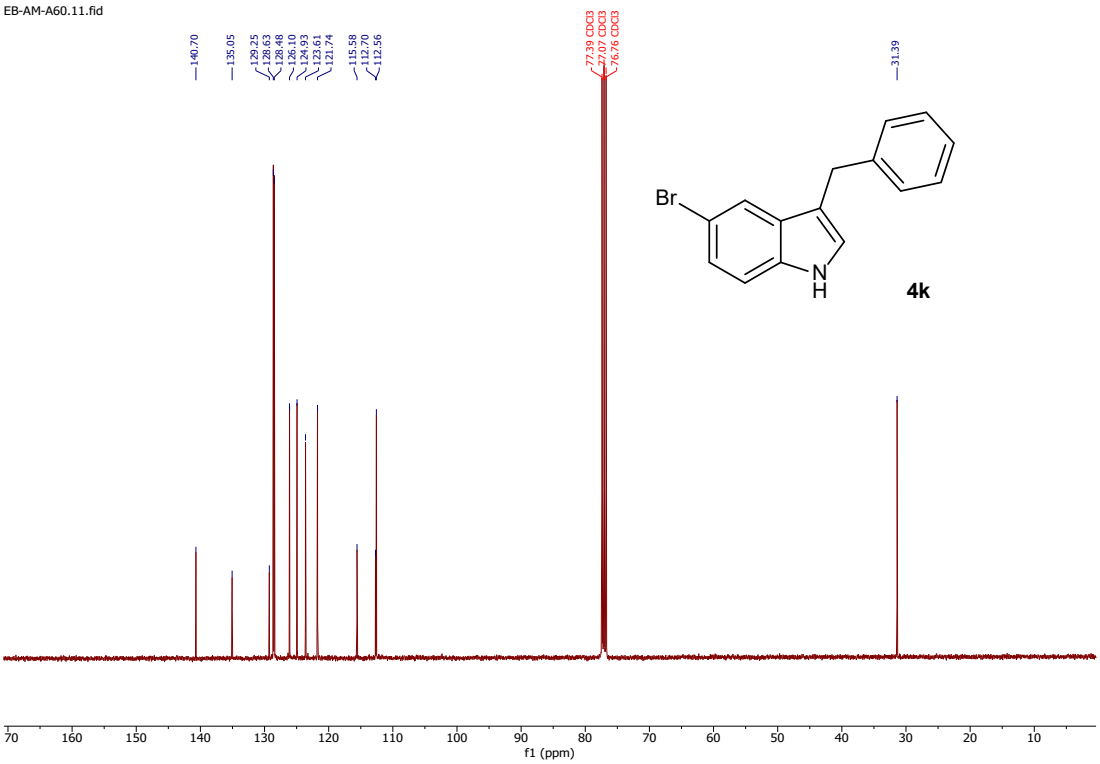

$^{1}$H NMR of **4j**



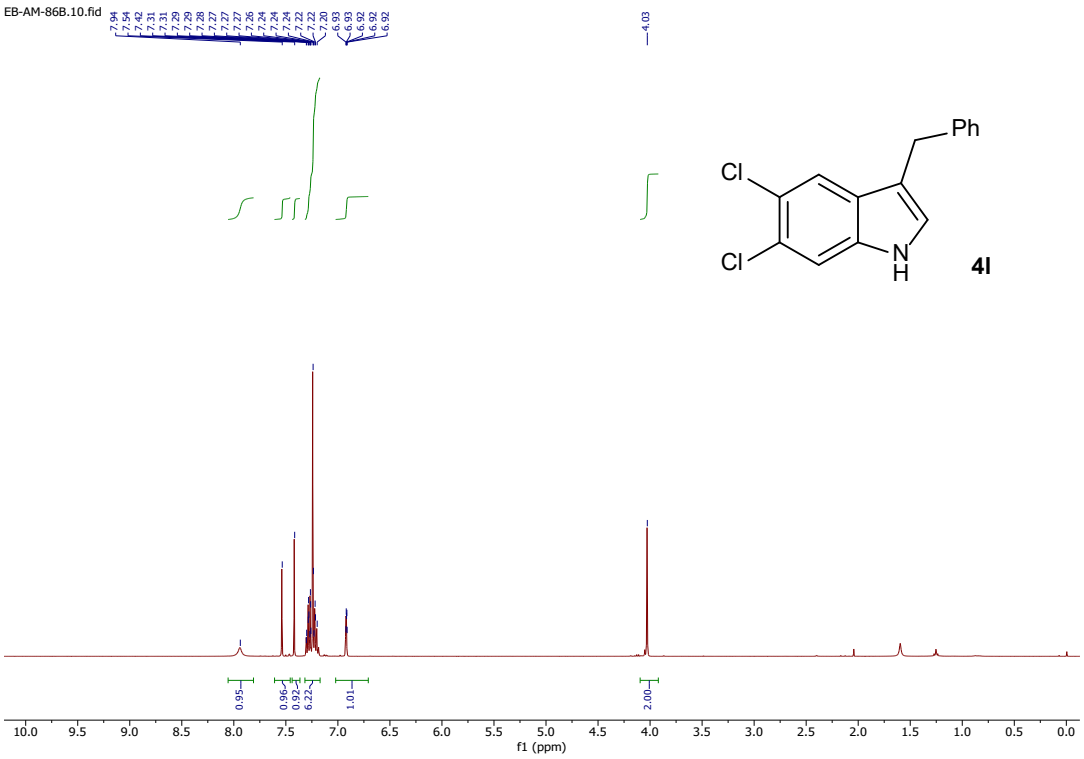

$^{13}$C{$^{1}$H} NMR of **4j**



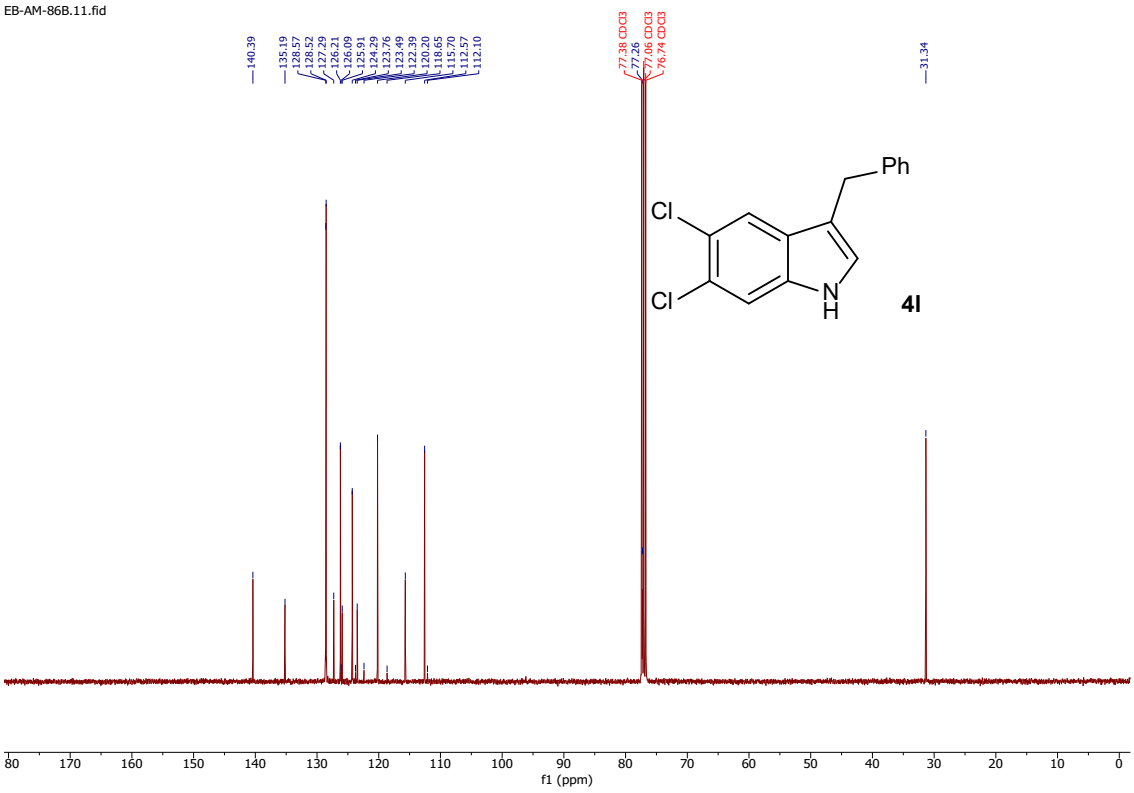

$^{1}$H NMR of **4k**



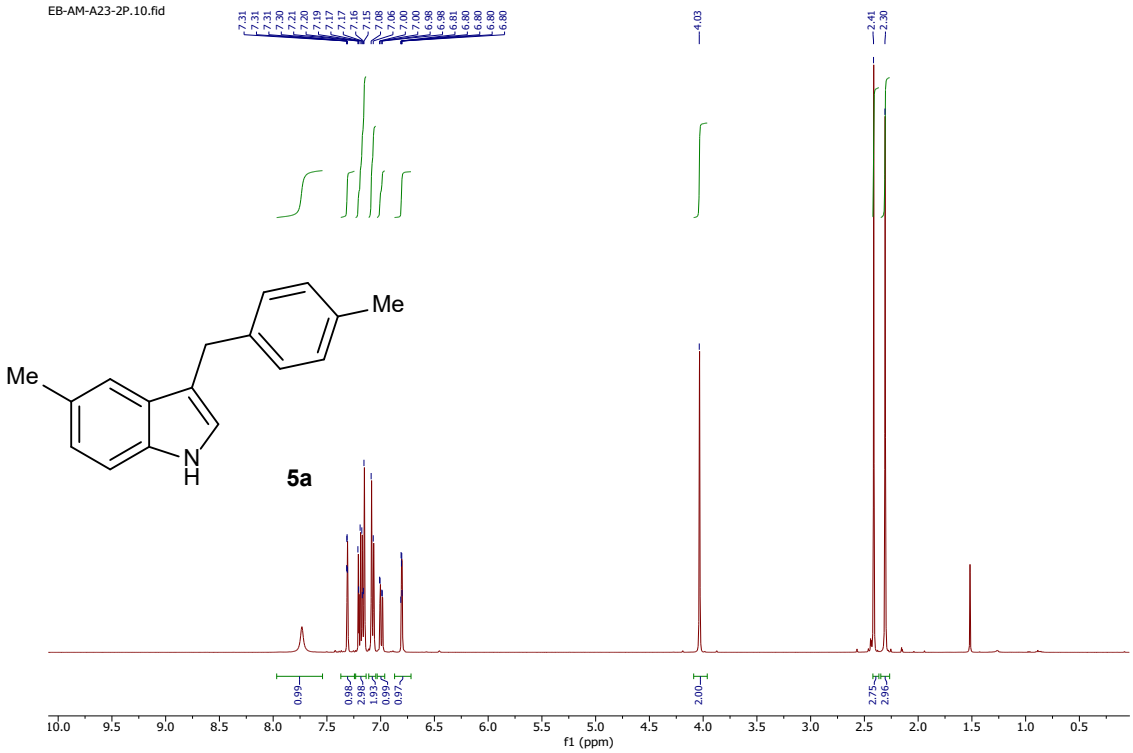

$^{13}$C{$^{1}$H} NMR of **4k**



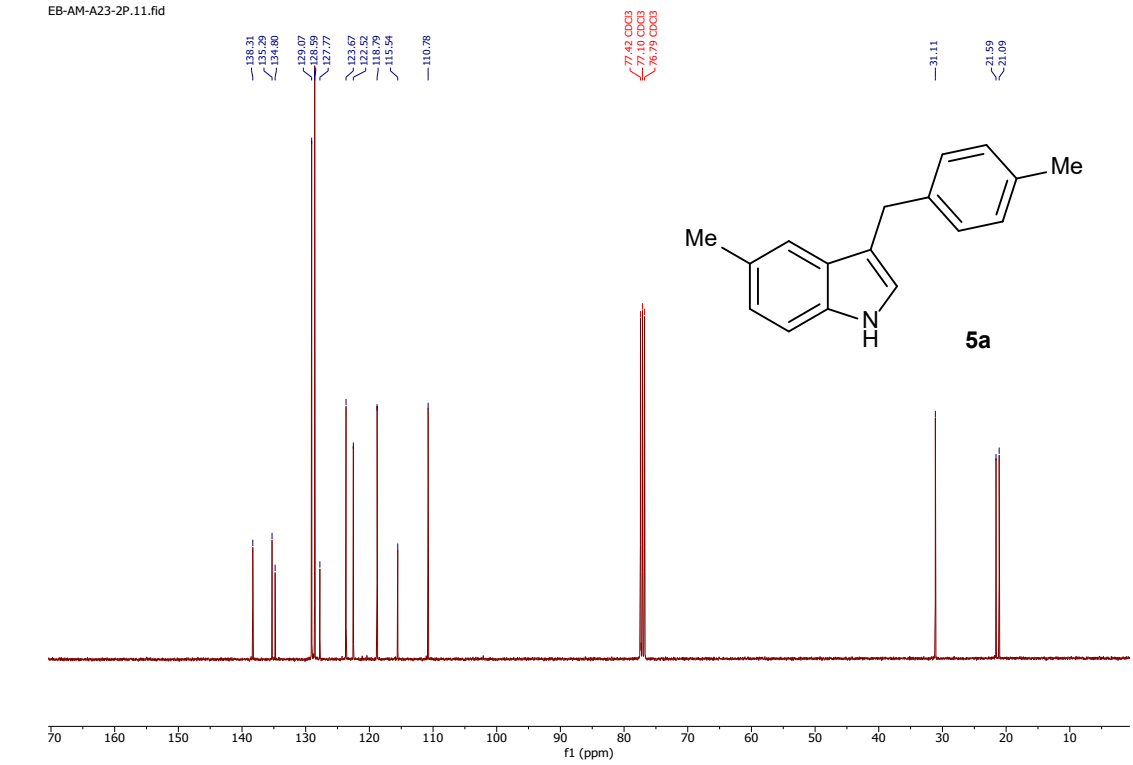

$^{1}$H NMR of **4l**



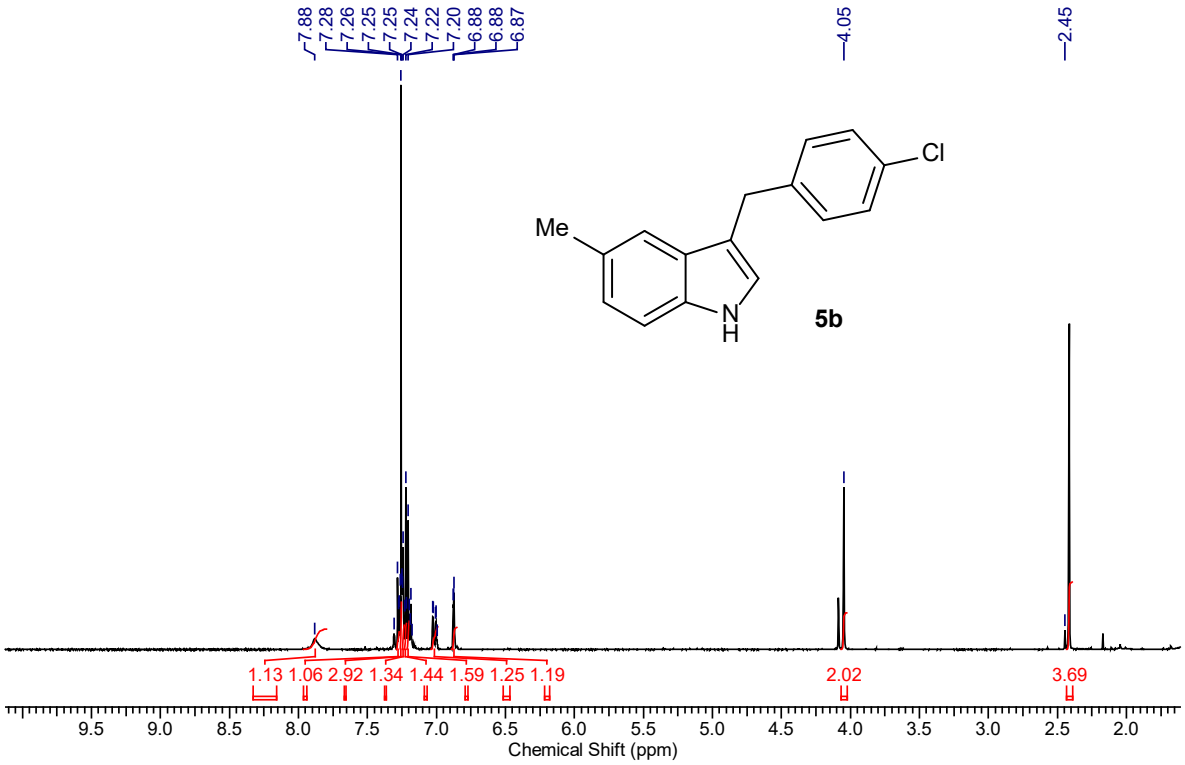

$^{13}$C{$^{1}$H} NMR of **4l**



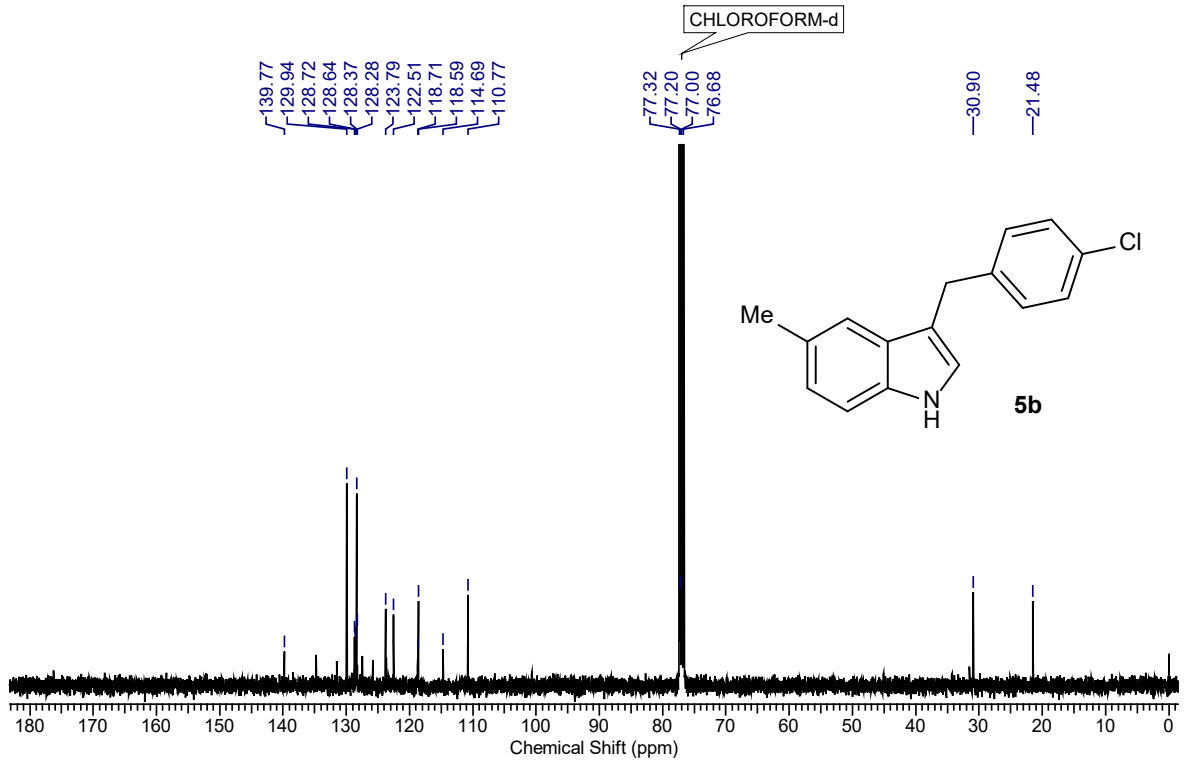

$^{1}$H NMR of **5a**



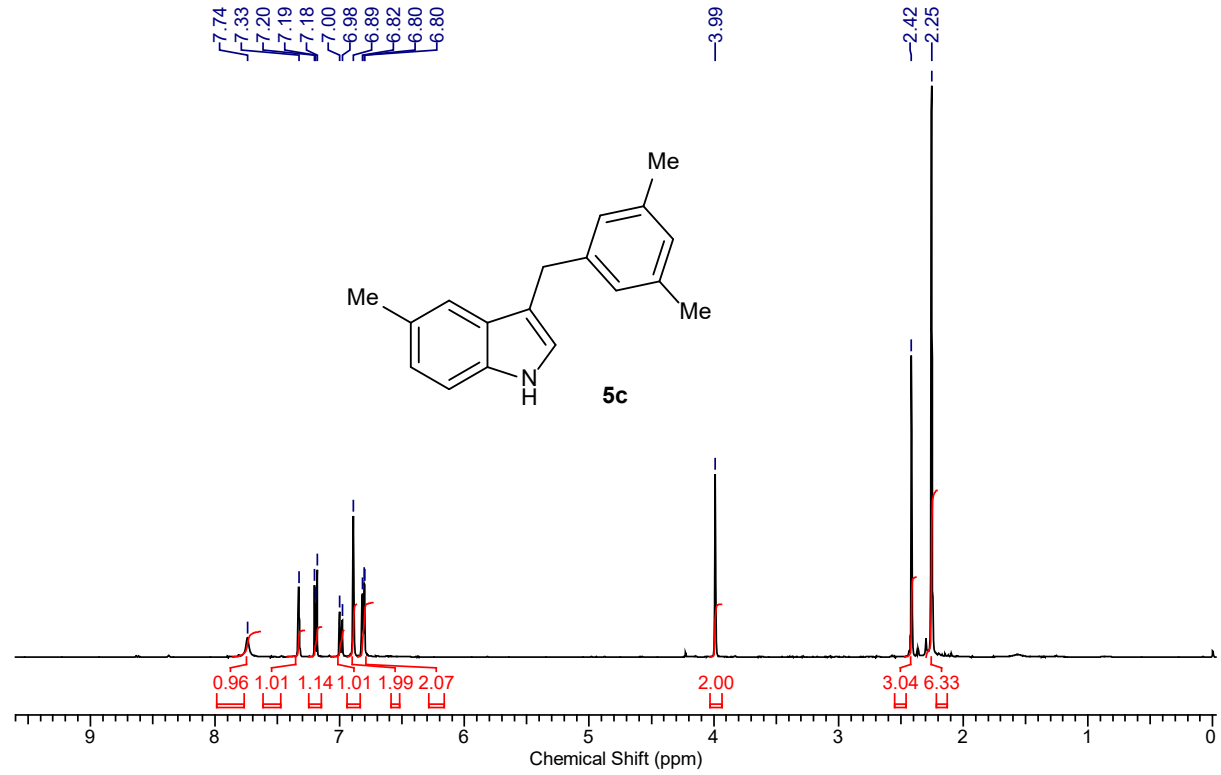

$^{13}$C{$^{1}$H} NMR of **5a**



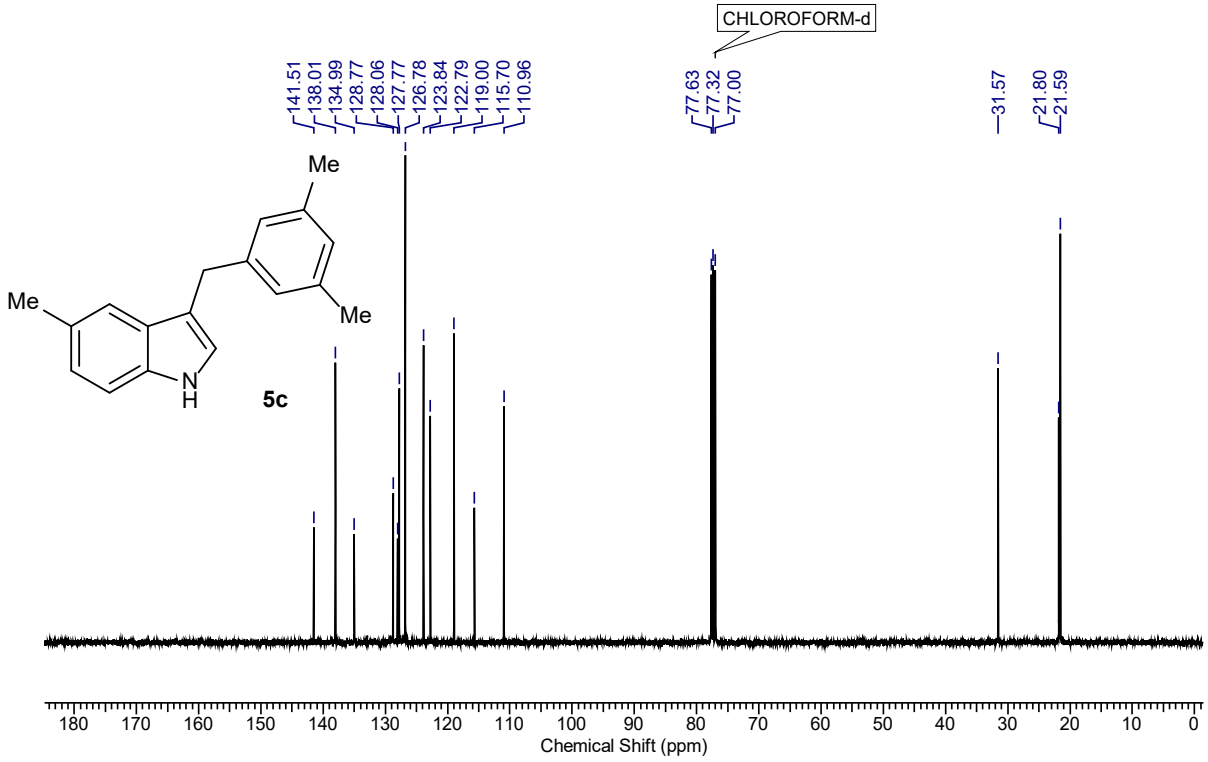

$^{1}$H NMR of **5b**



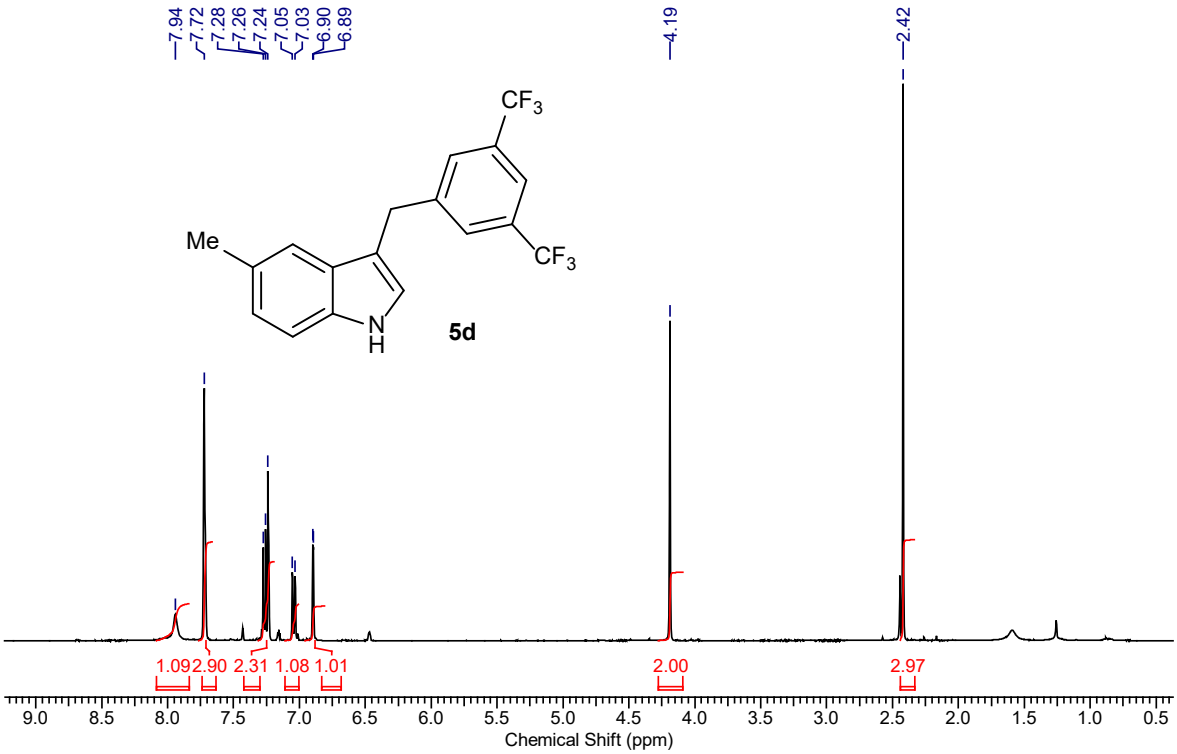

$^{13}$C{$^{1}$H} NMR of **5b**



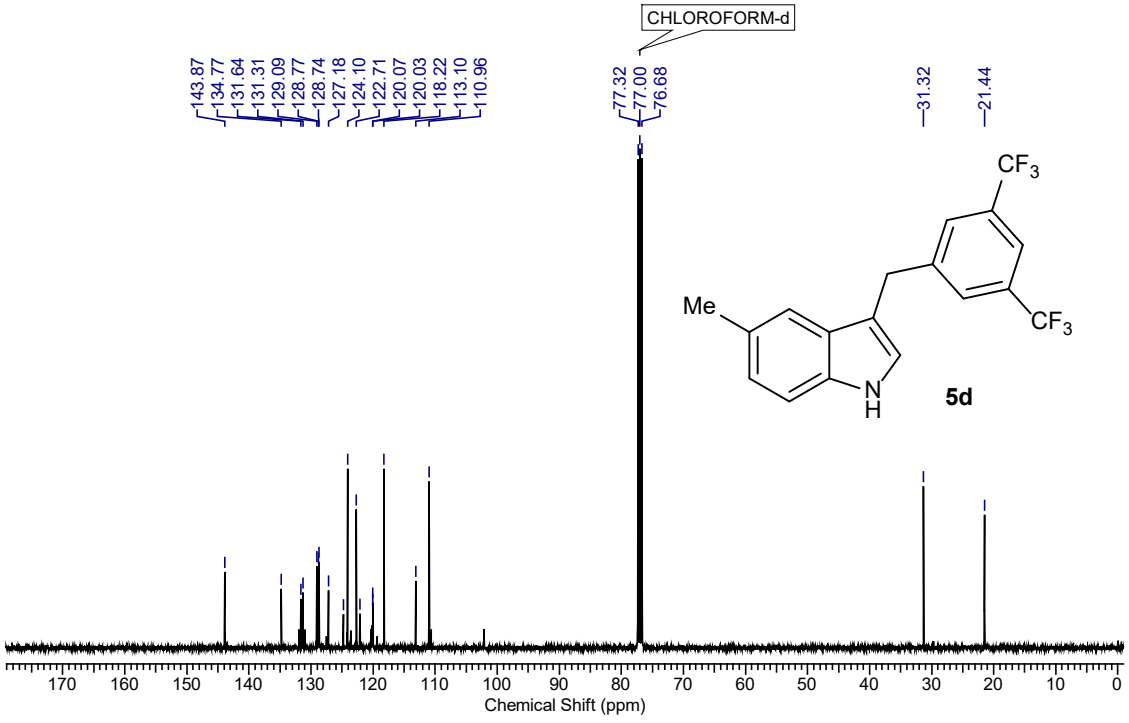

$^{1}$H NMR of **5c**



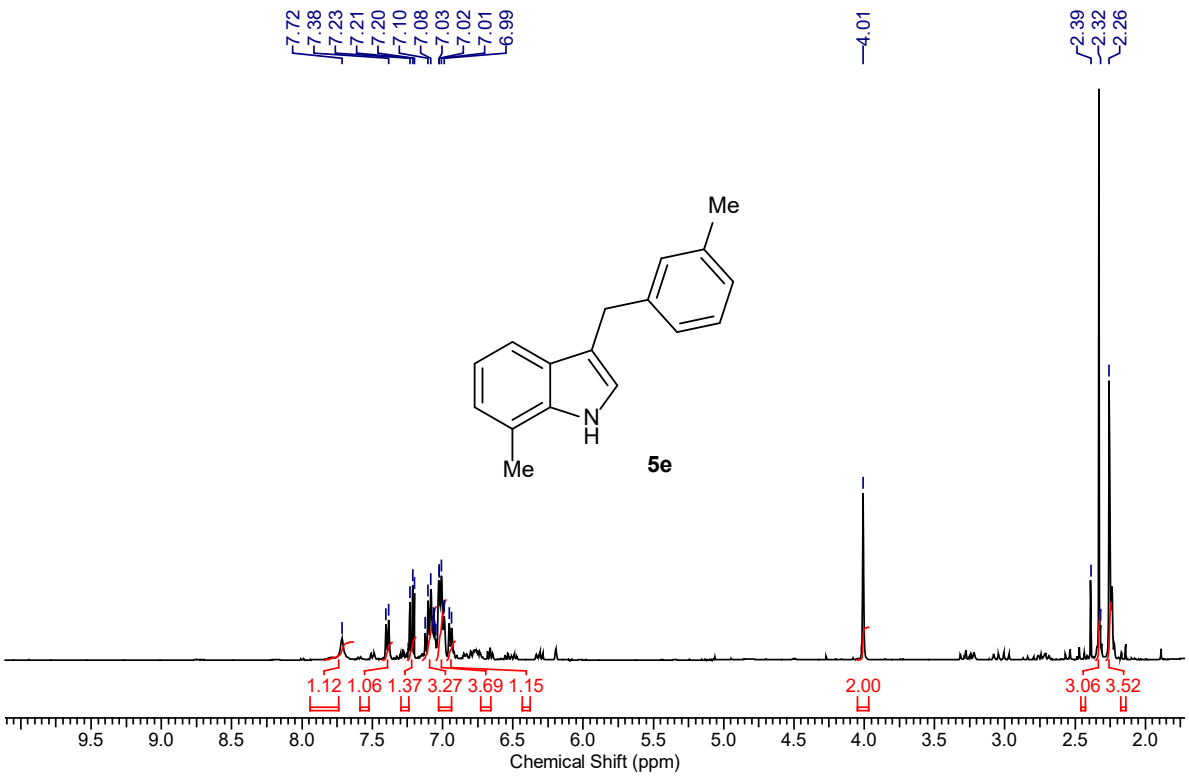

$^{13}$C{$^{1}$H} NMR of **5c**



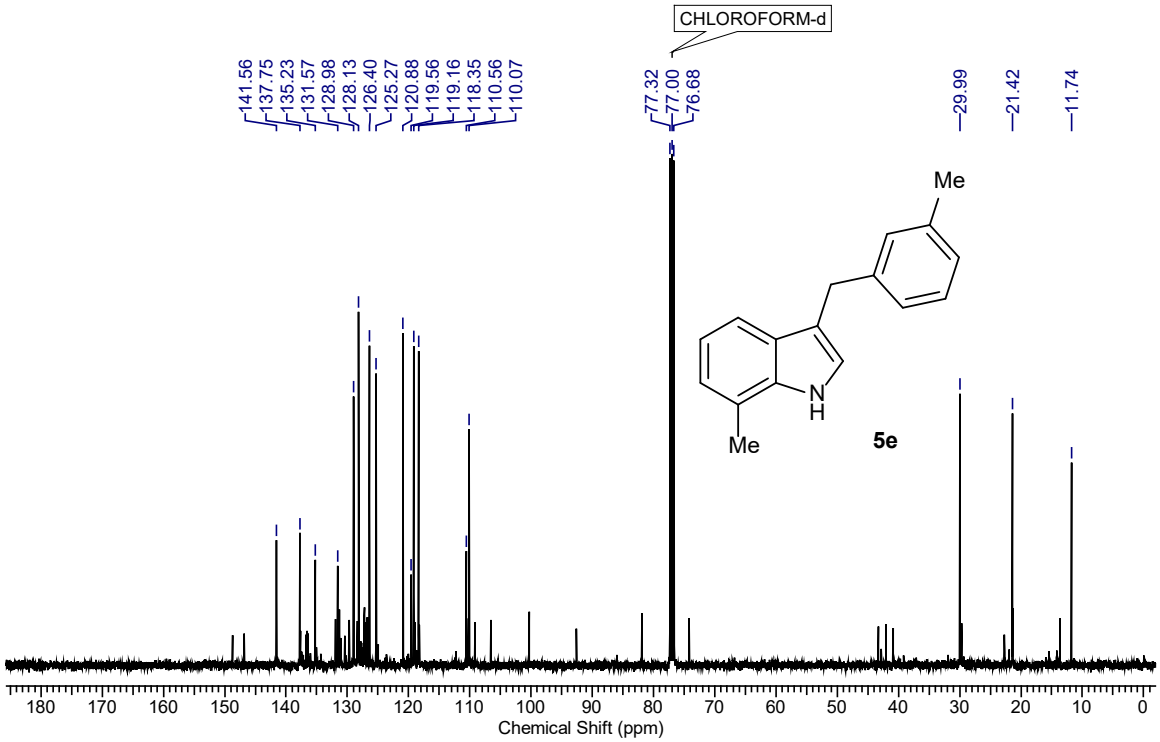

$^{1}$H NMR of **5d**



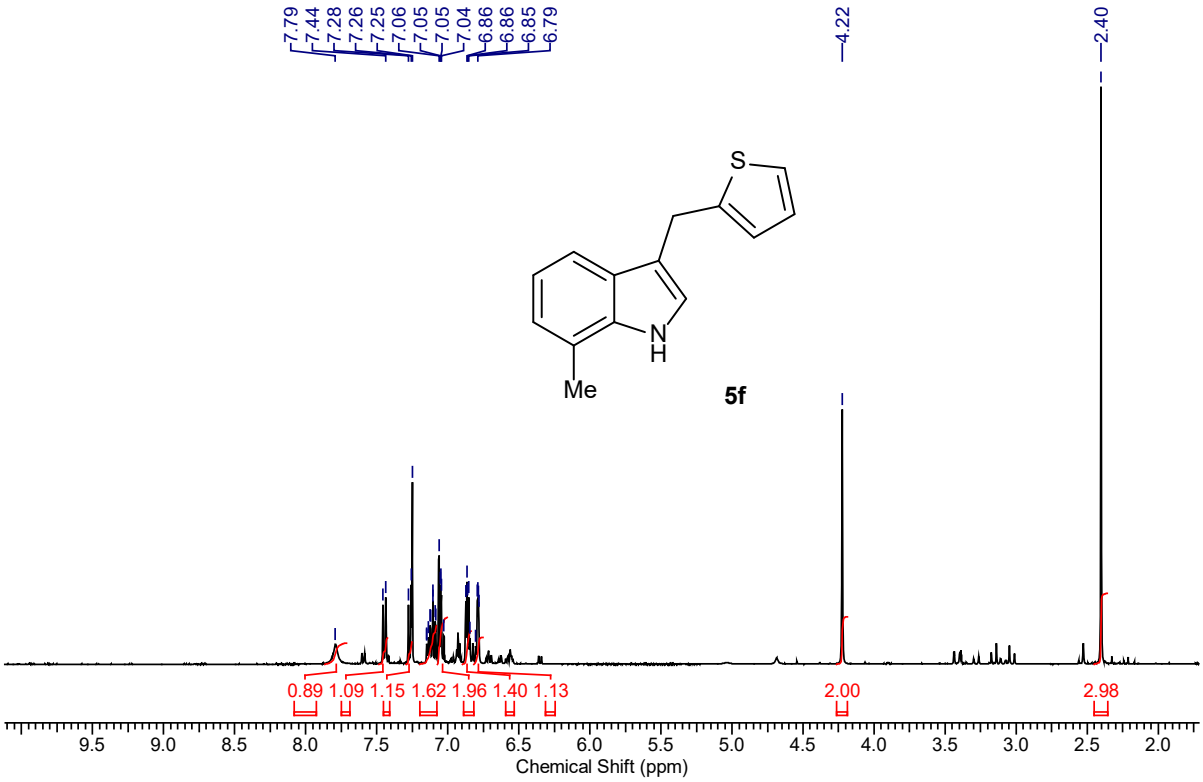

$^{13}$C{$^{1}$H} NMR of **5d**



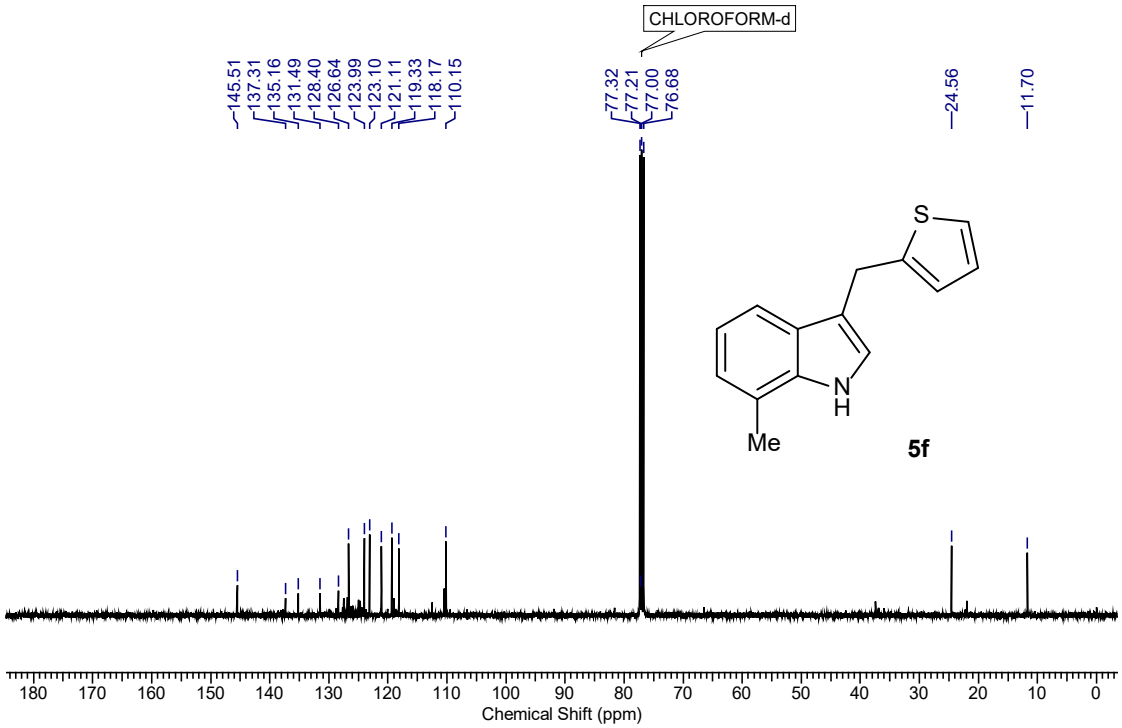

$^{1}$H NMR of **5e**



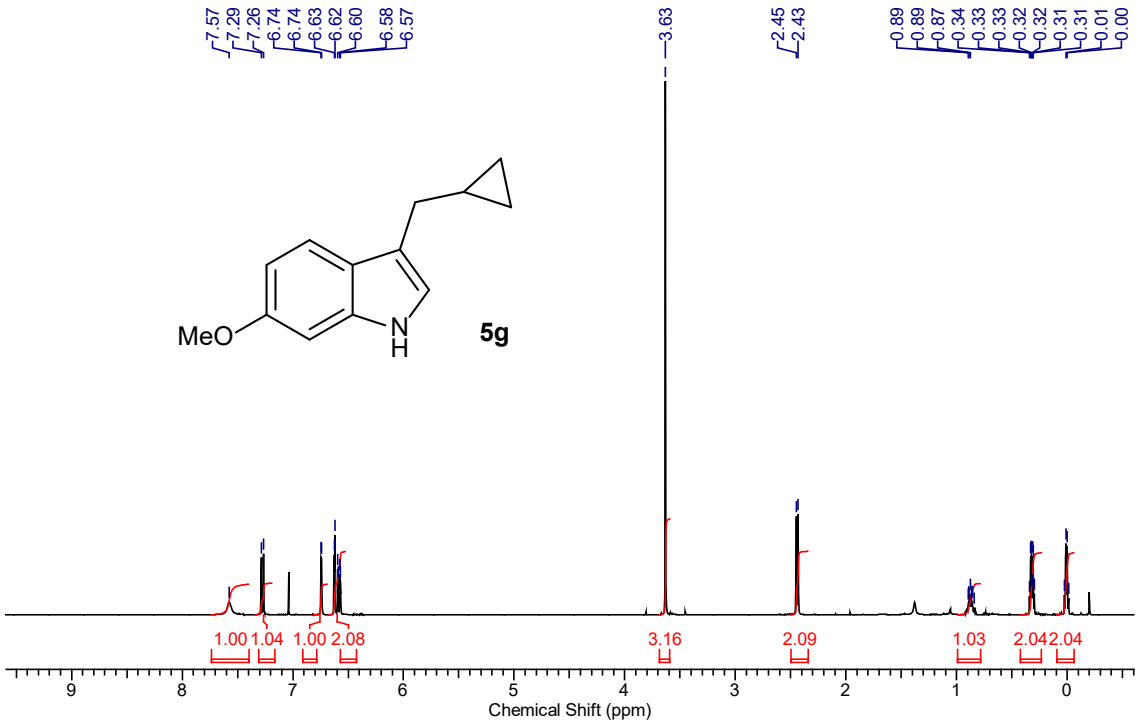

$^{13}$C{$^{1}$H} NMR of **5e**



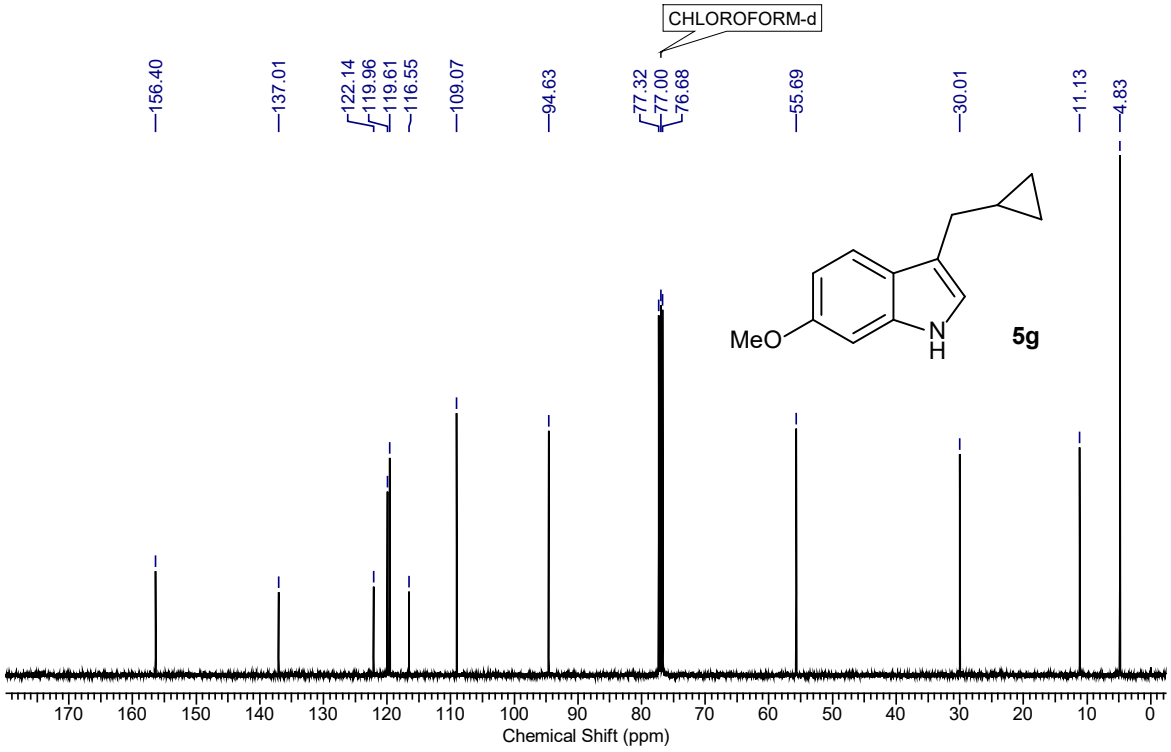

$^{1}$H NMR of **5f**



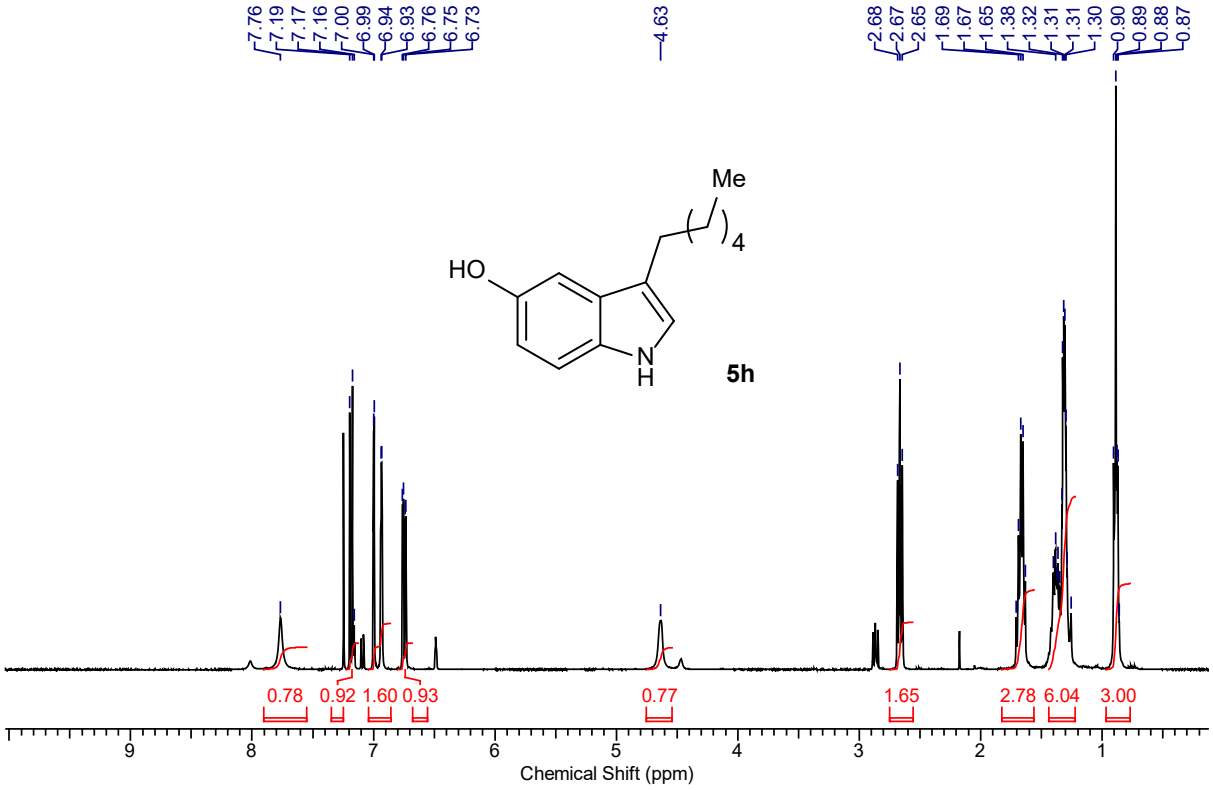

$^{13}$C{$^{1}$H} NMR of **5f**



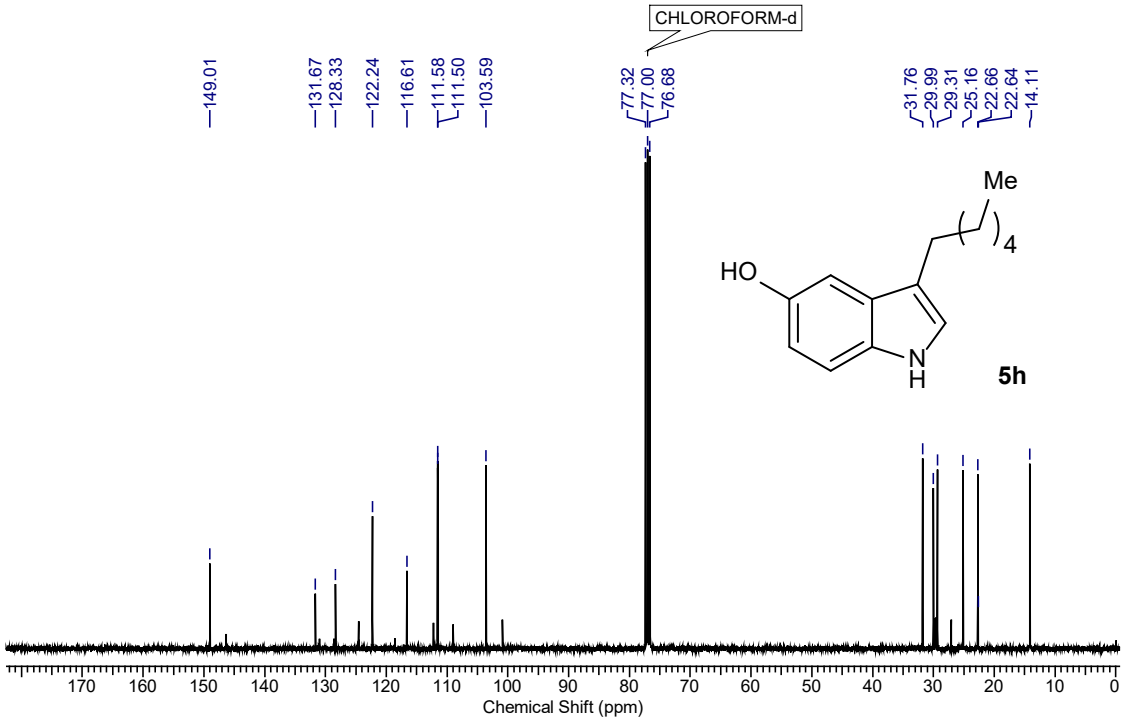

$^{1}$H NMR of **5g**



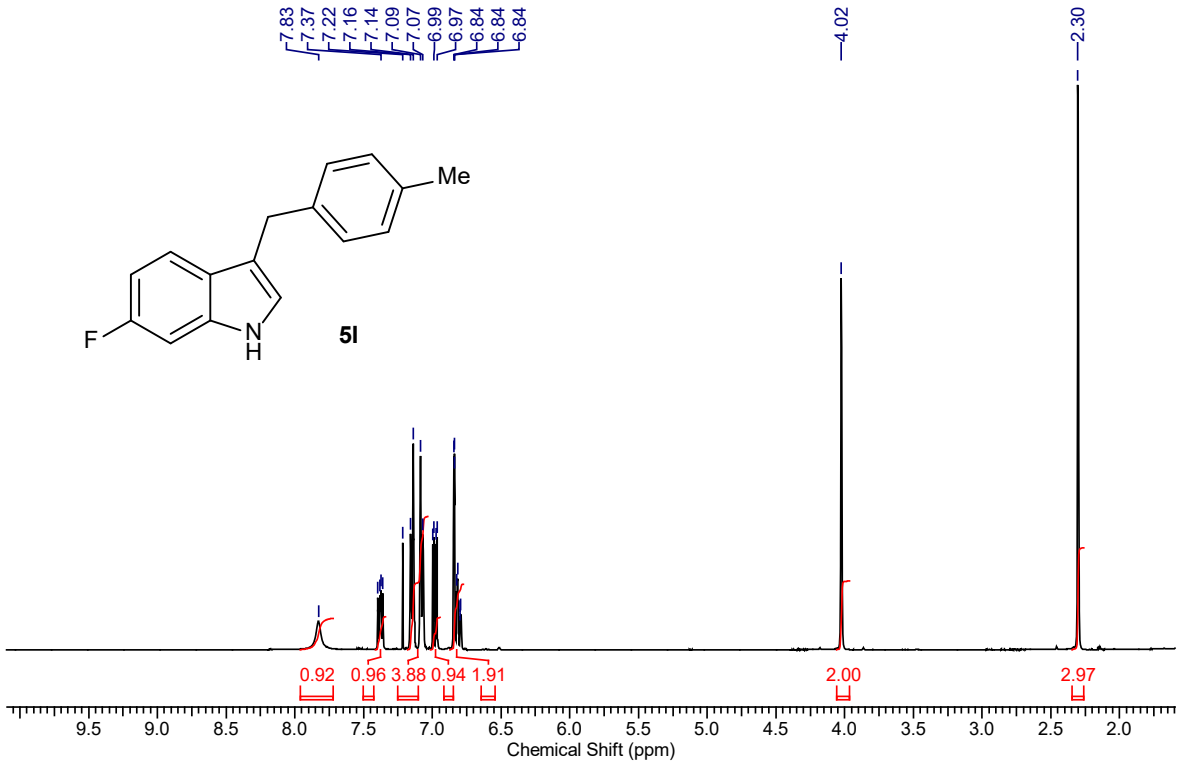

$^{13}$C{$^{1}$H} NMR of **5g**



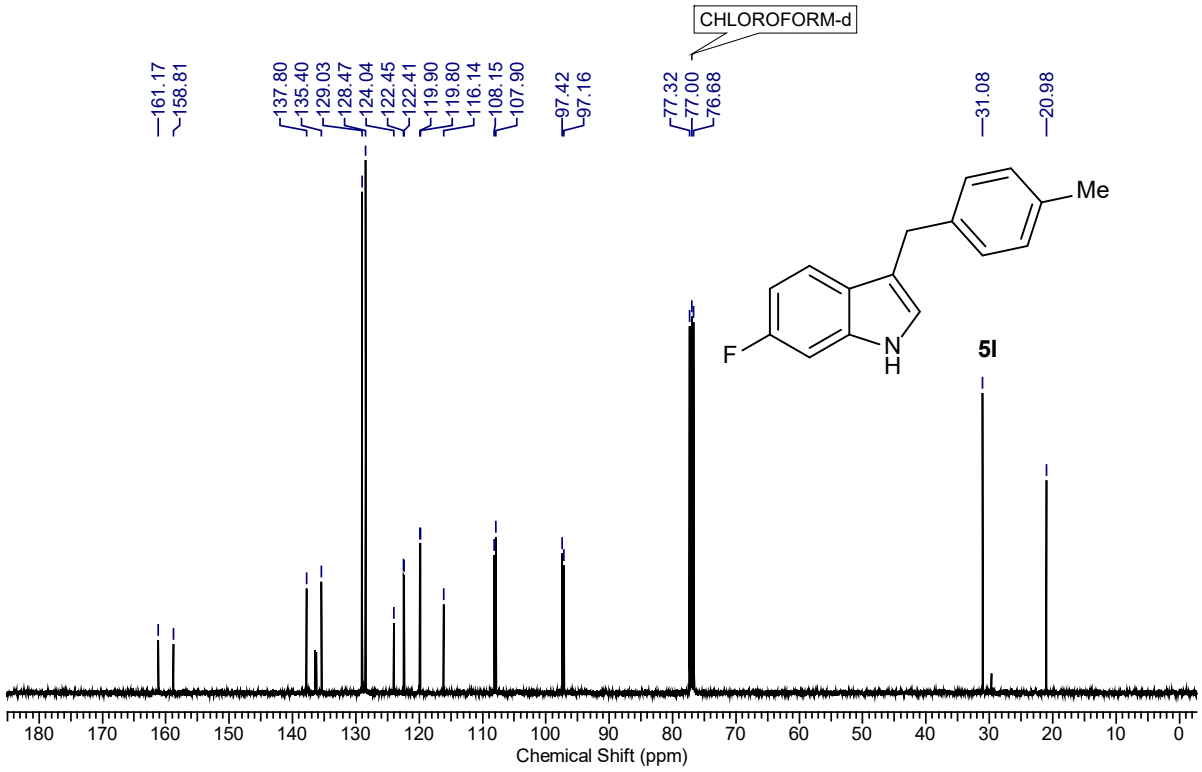

$^{1}$H NMR of **5h**



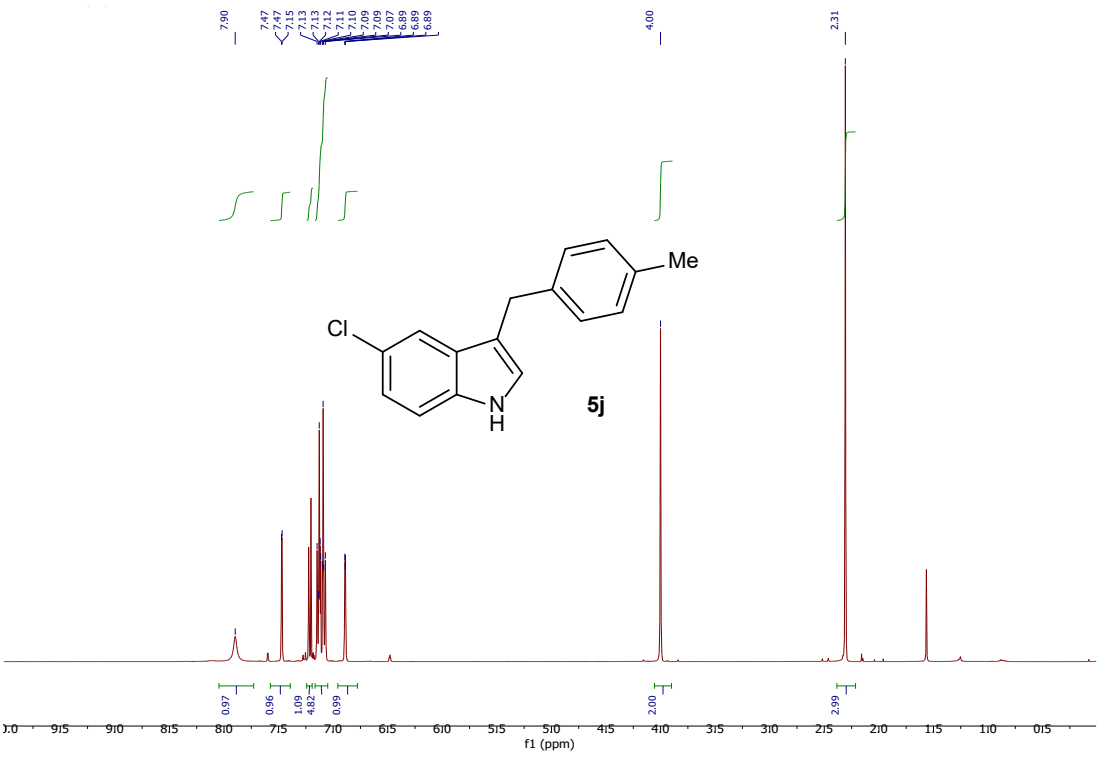

$^{13}$C{$^{1}$H} NMR of **5h**



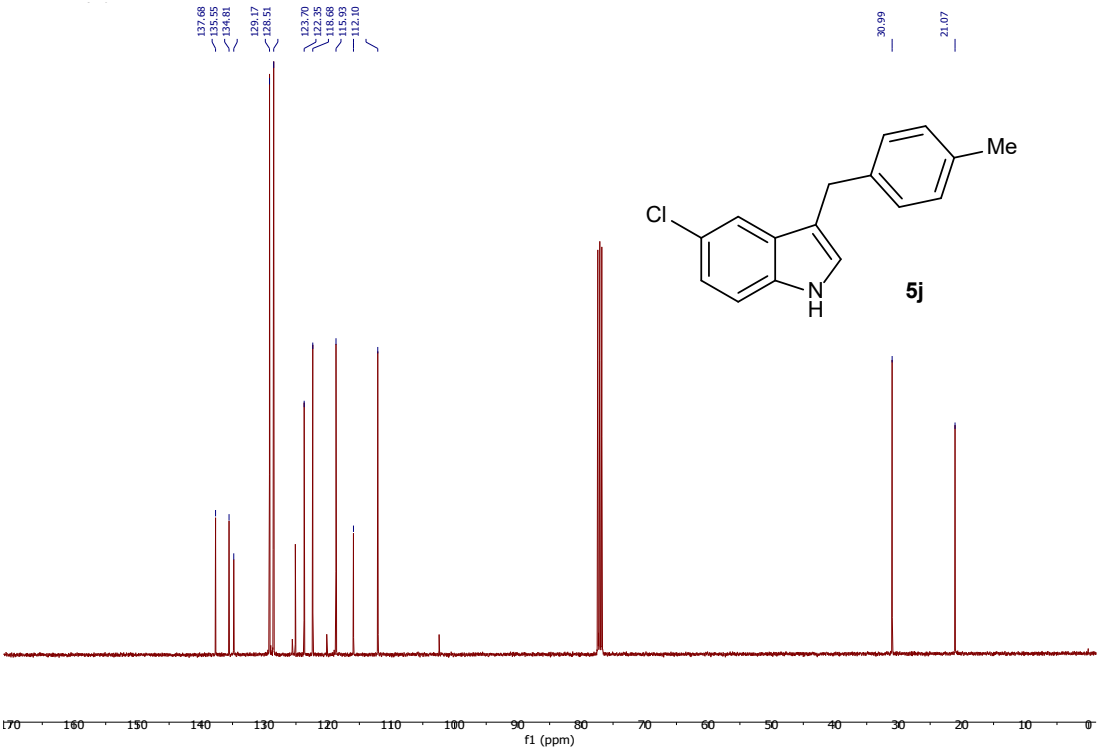

$^{1}$H NMR of **5i**



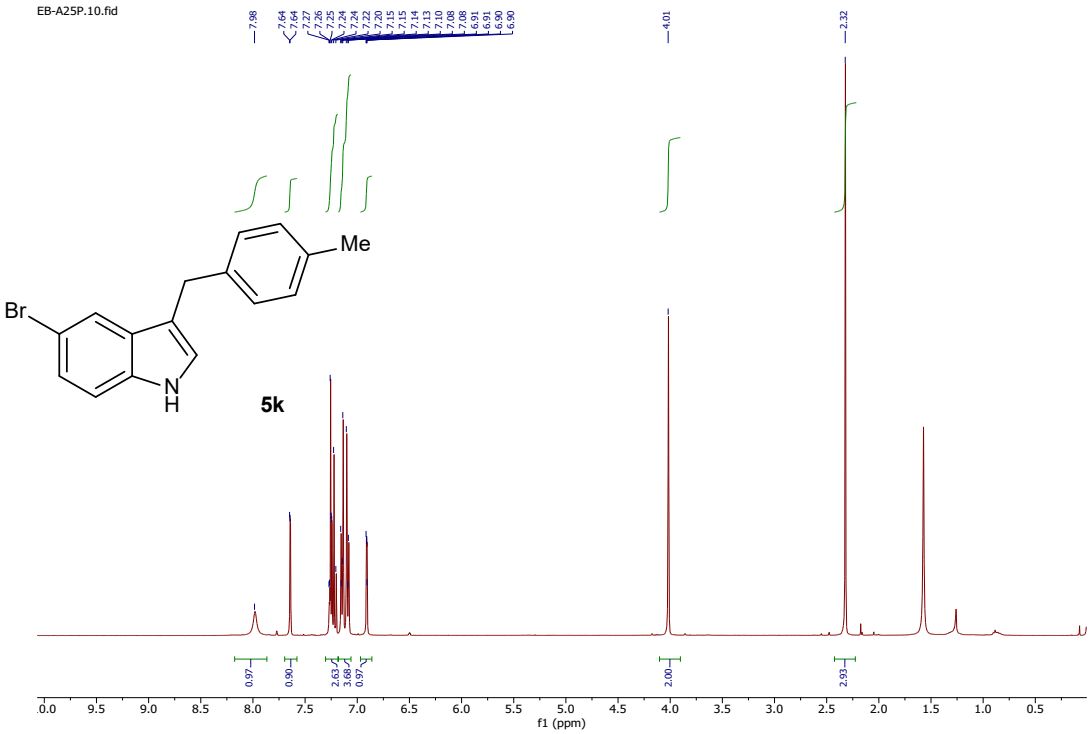

$^{13}$C{$^{1}$H} NMR of **5i**




$^{1}$H NMR of **5j**




$^{13}$C{$^{1}$H} NMR of **5j**

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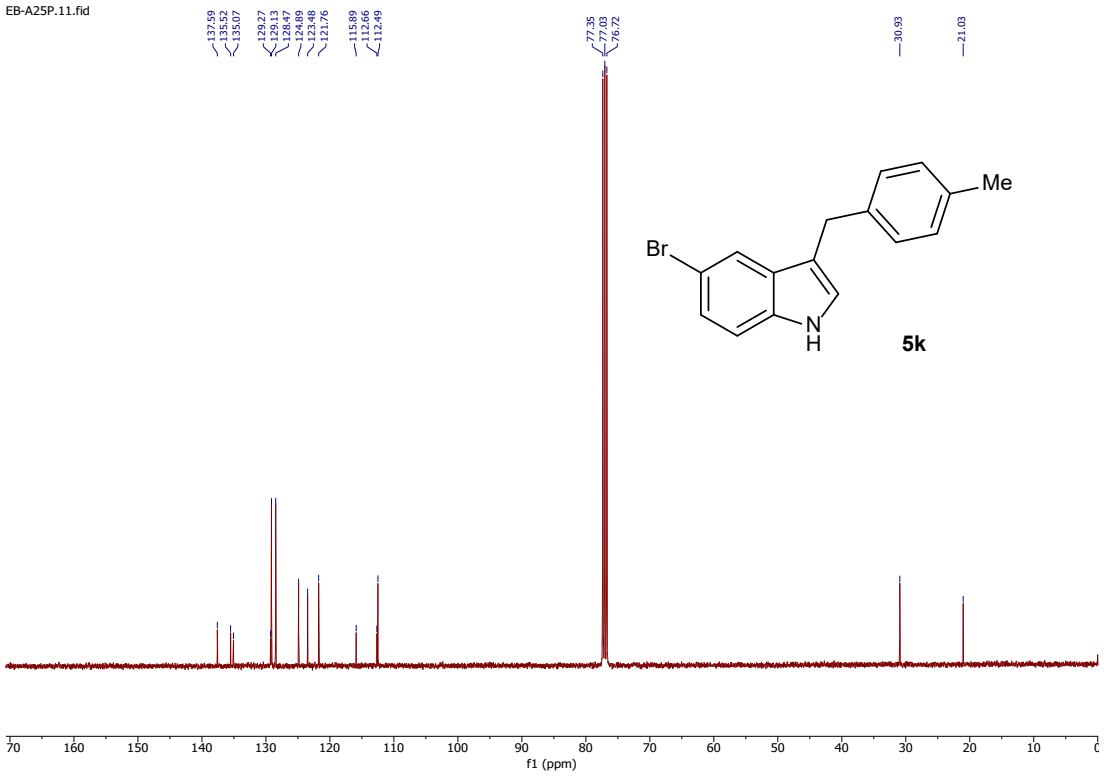


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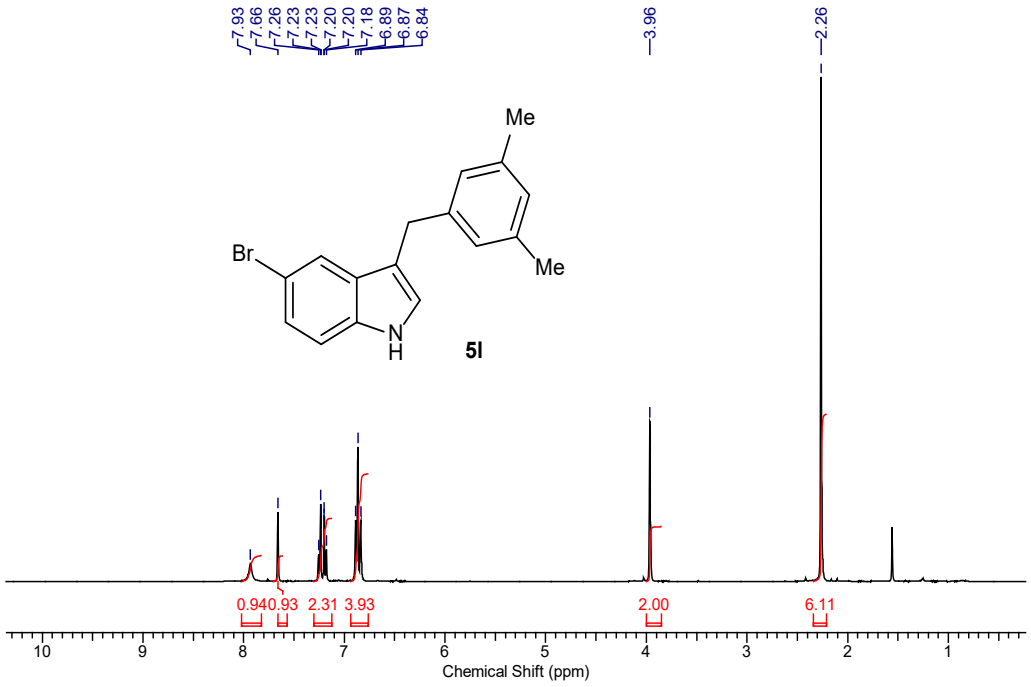
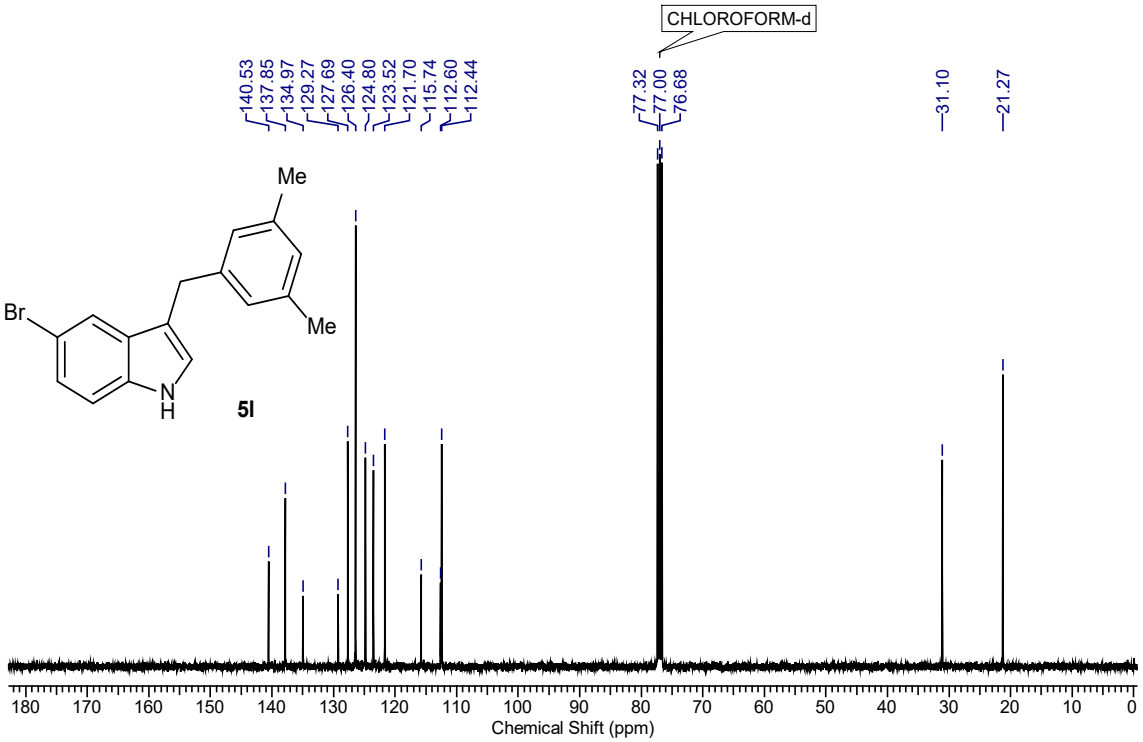
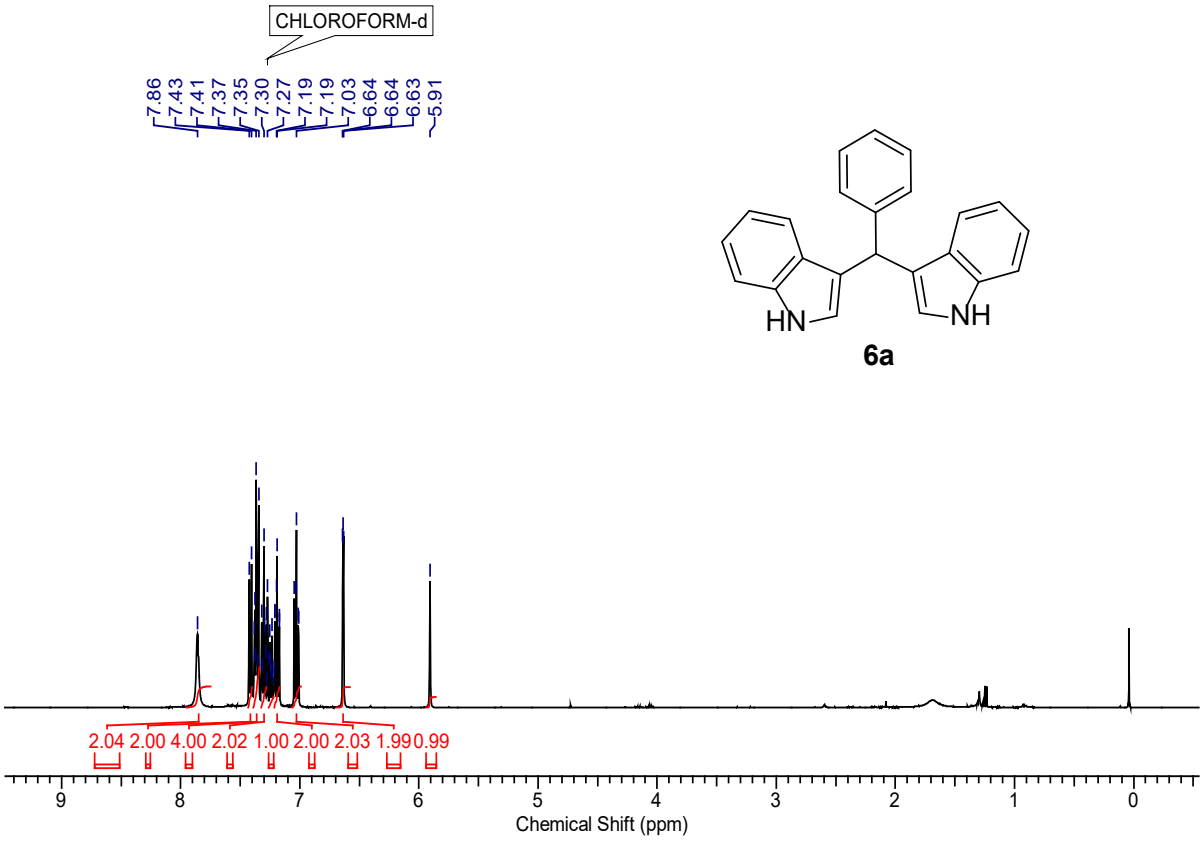


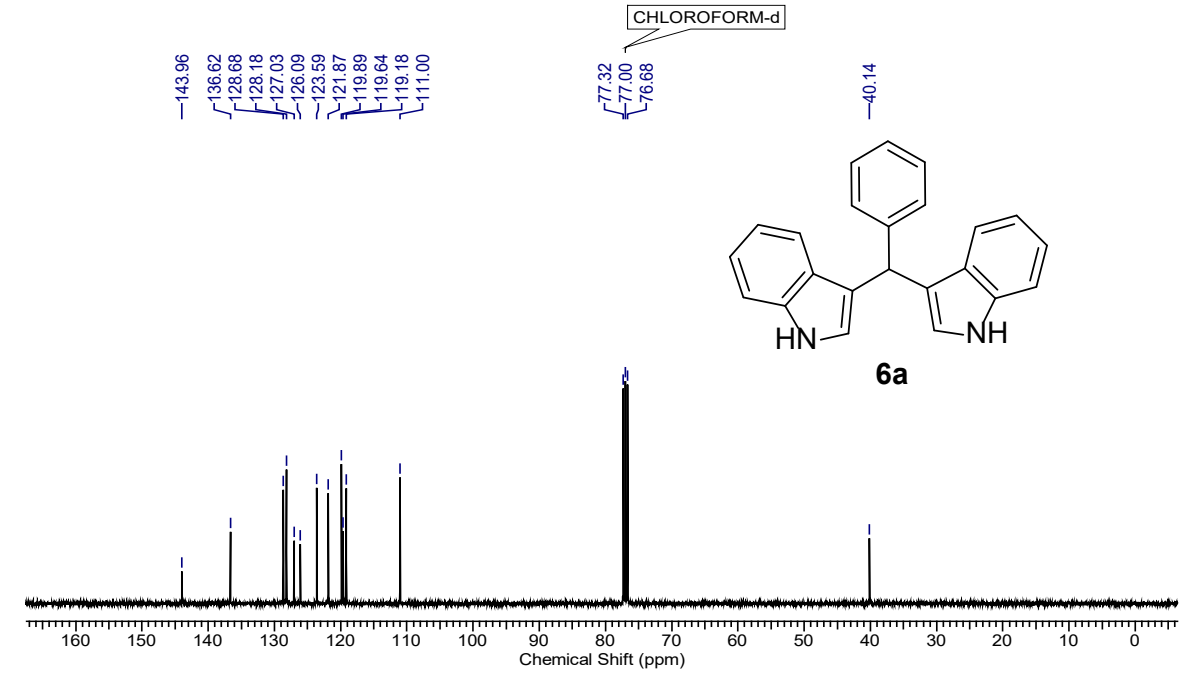

$^{1}$H NMR of **5l**



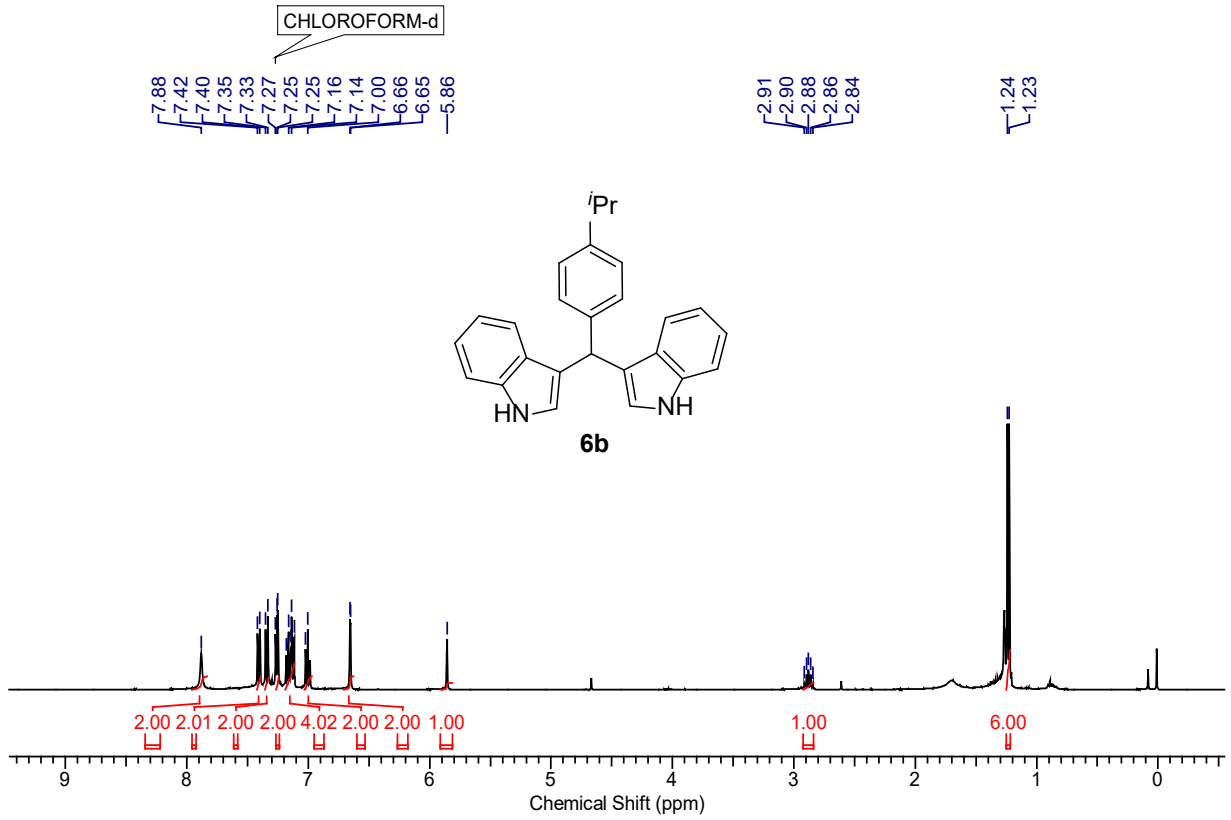

$^{13}$C{$^{1}$H} NMR of 5l




$^{1}$H NMR of **6a**




$^{13}$C NMR of **6a**

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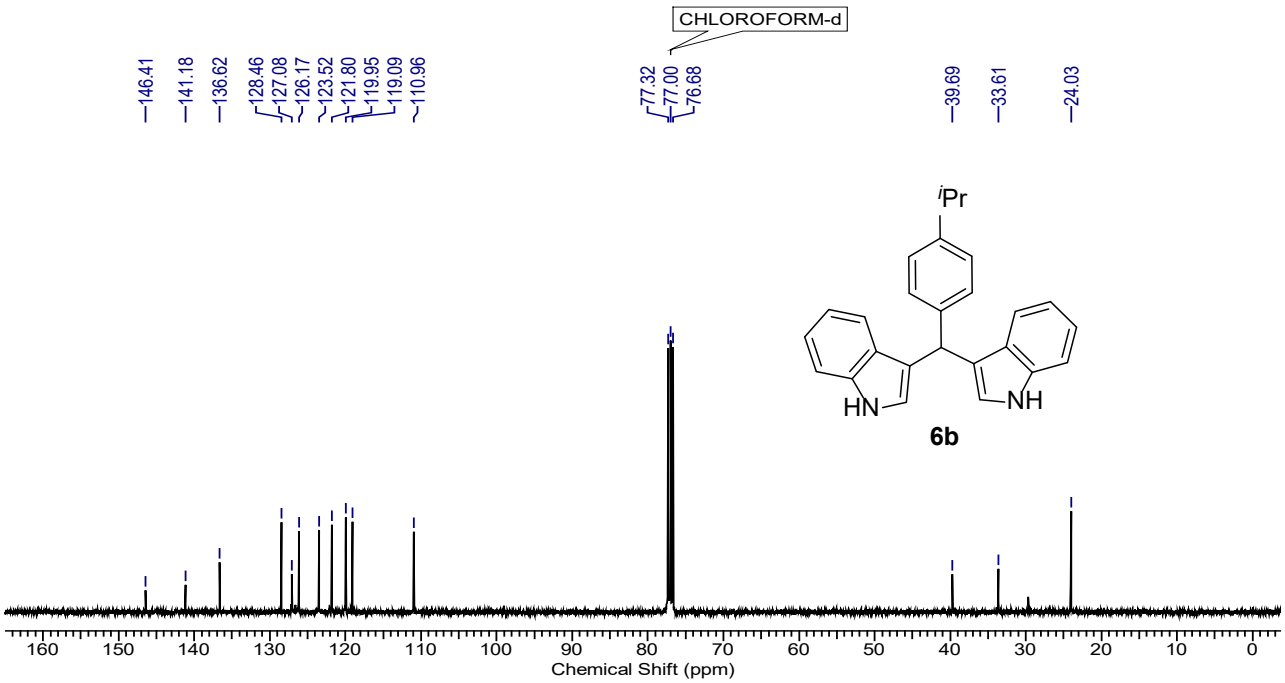
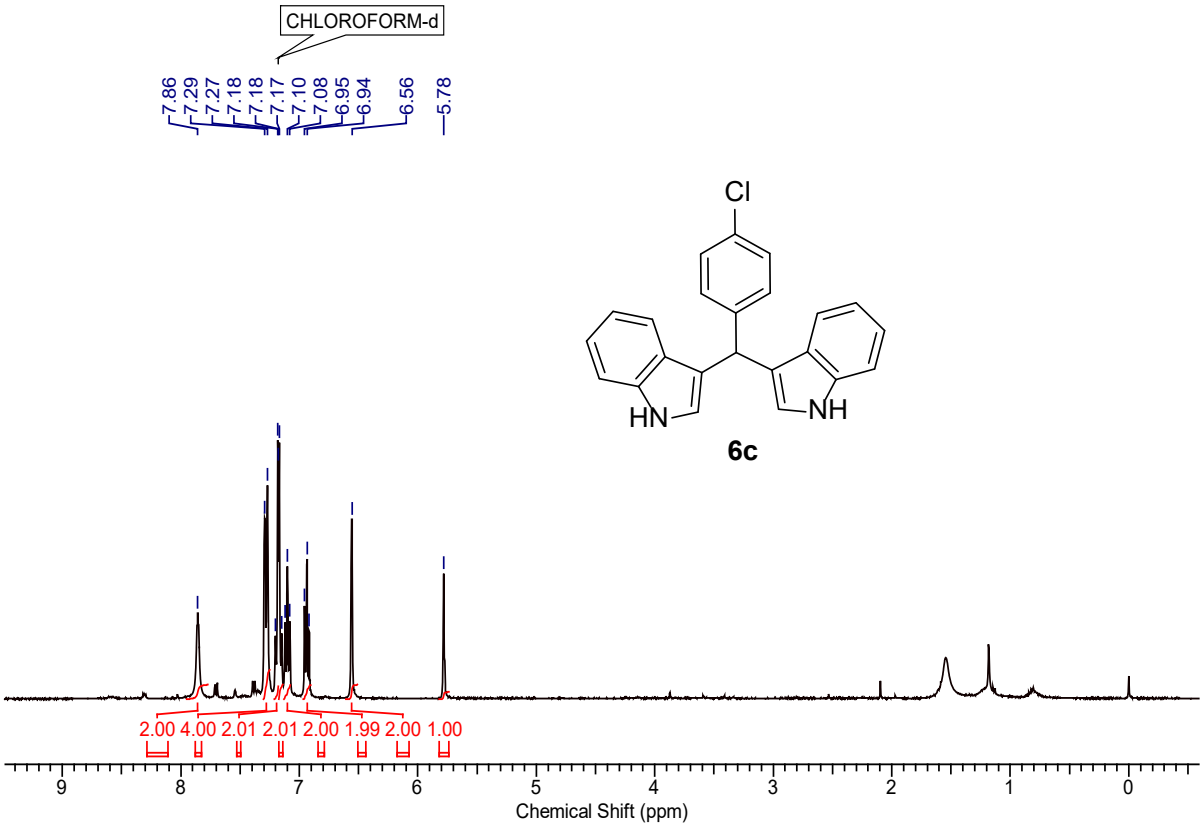
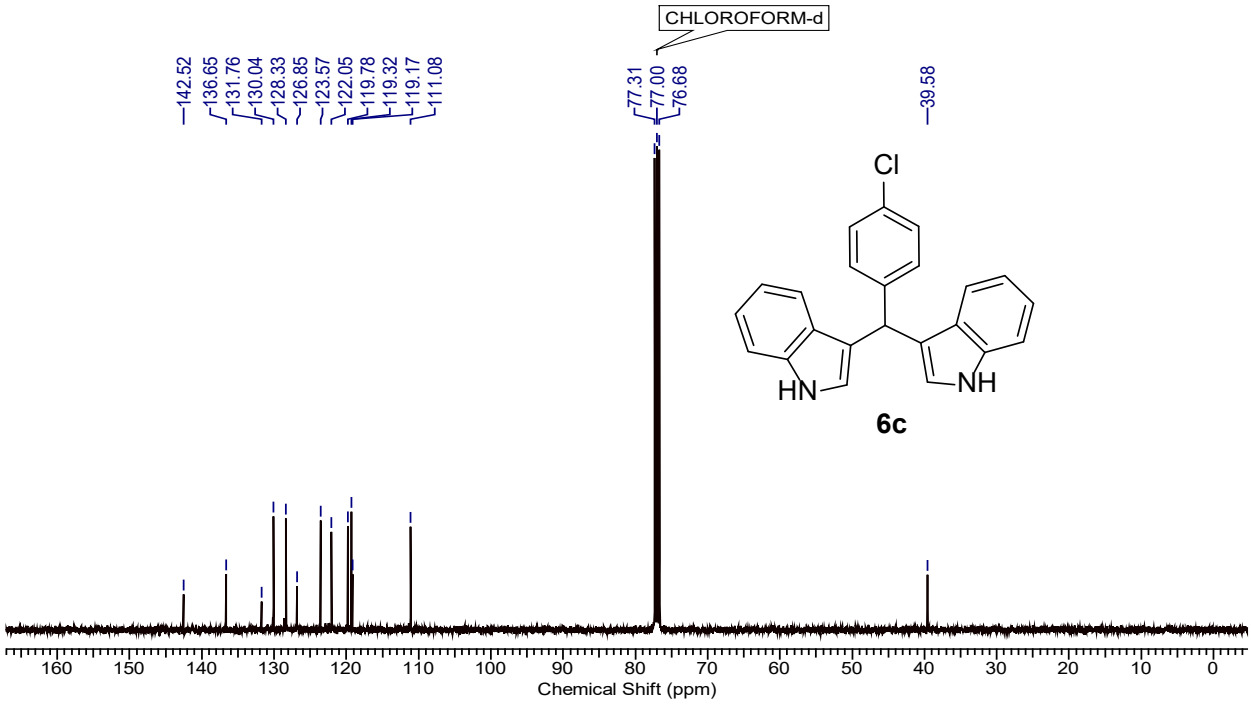


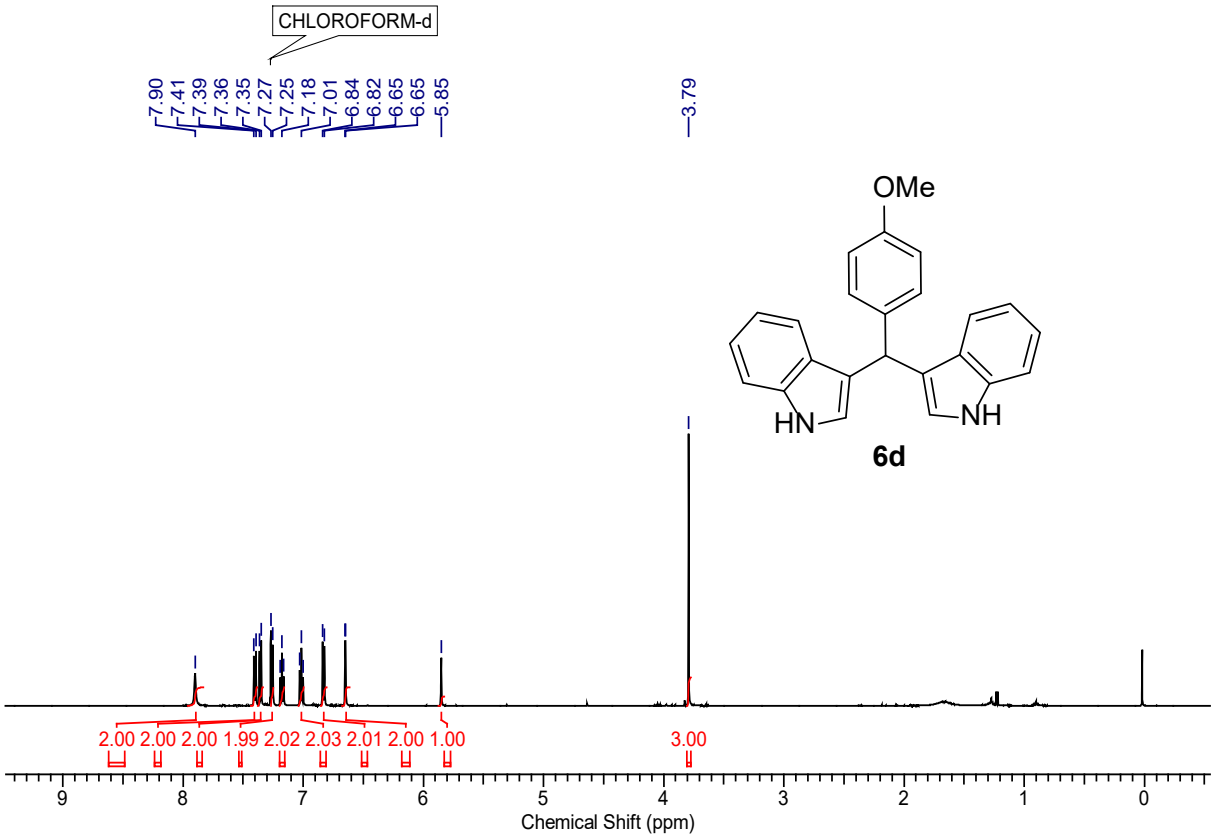

$^{13}$C NMR of **6b**



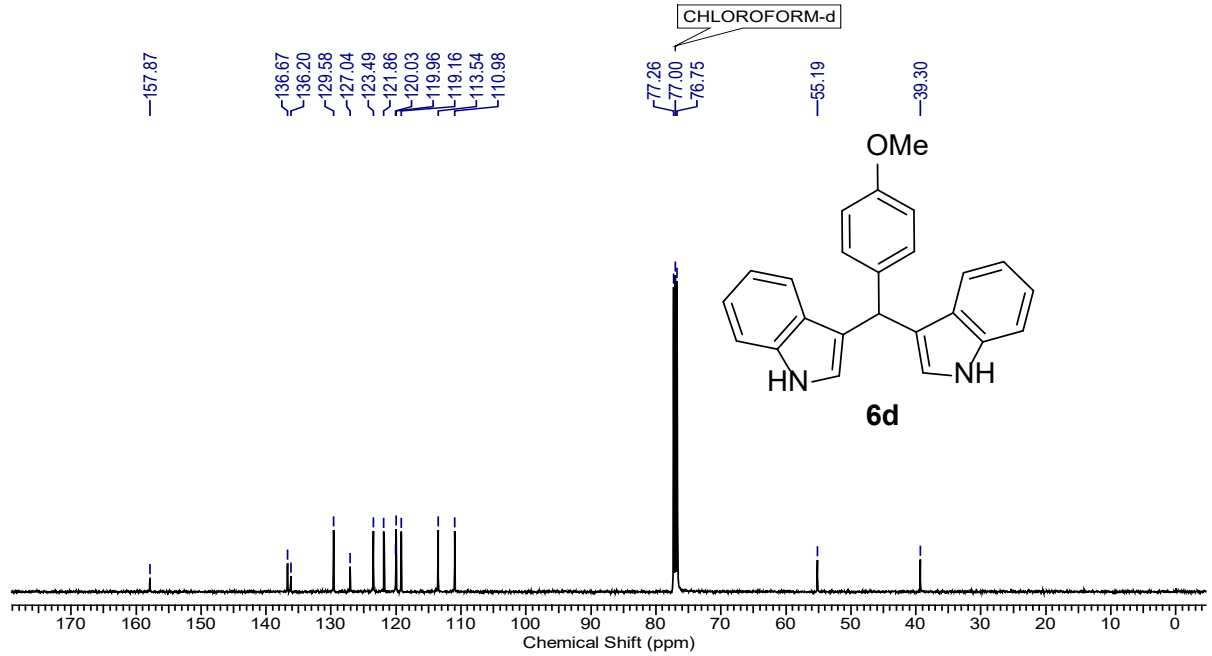

$^{1}$H NMR of **6c**



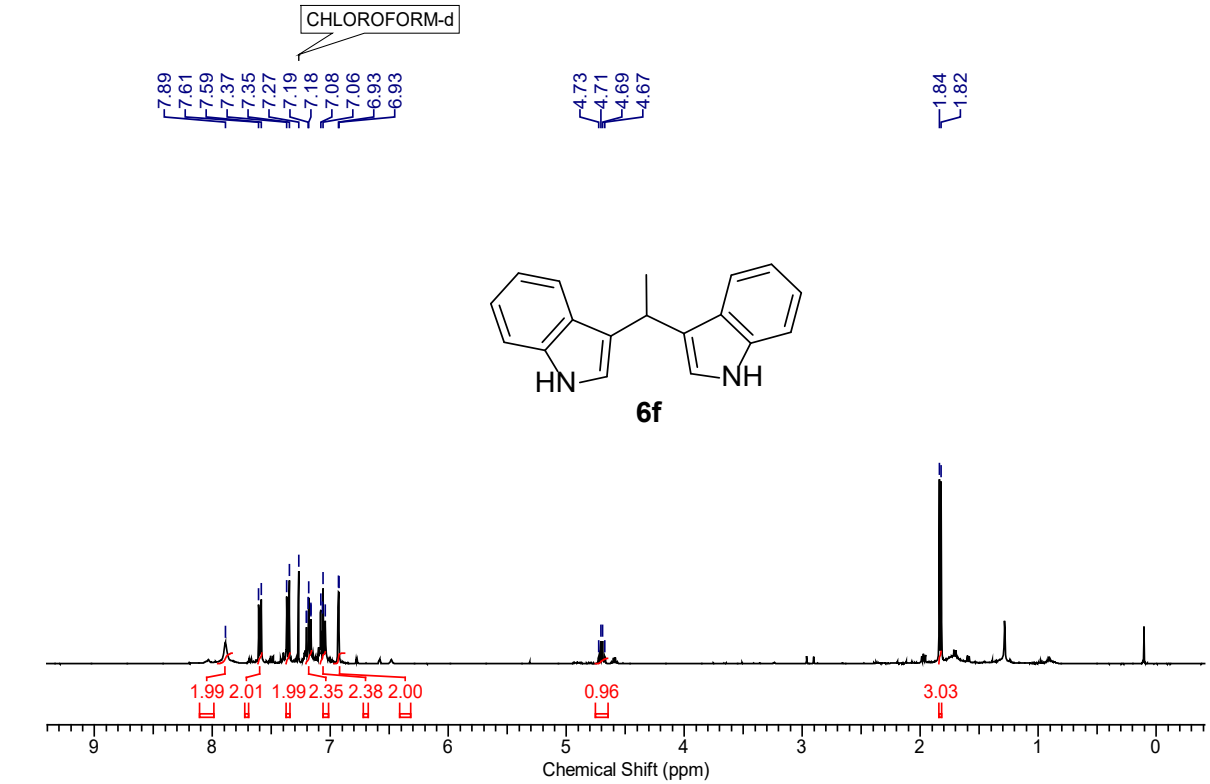

$^{13}$C NMR of **6c**



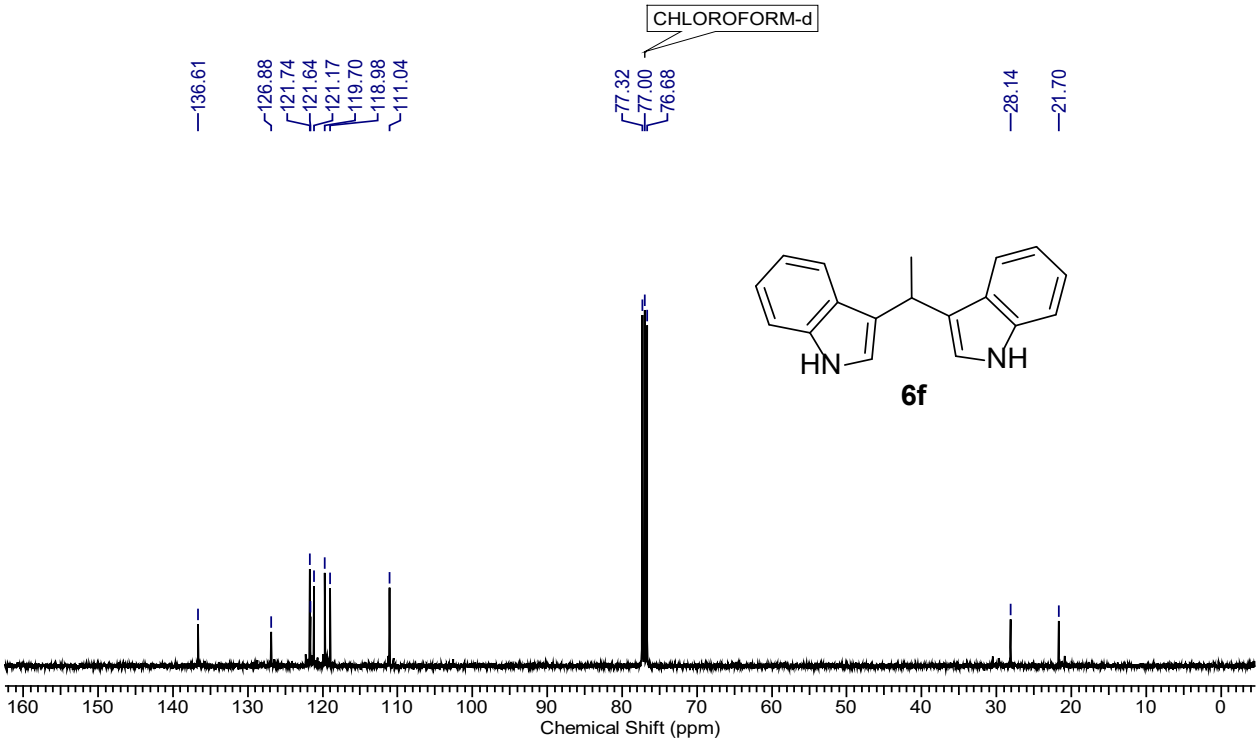

$^{1}$H NMR of **6d**



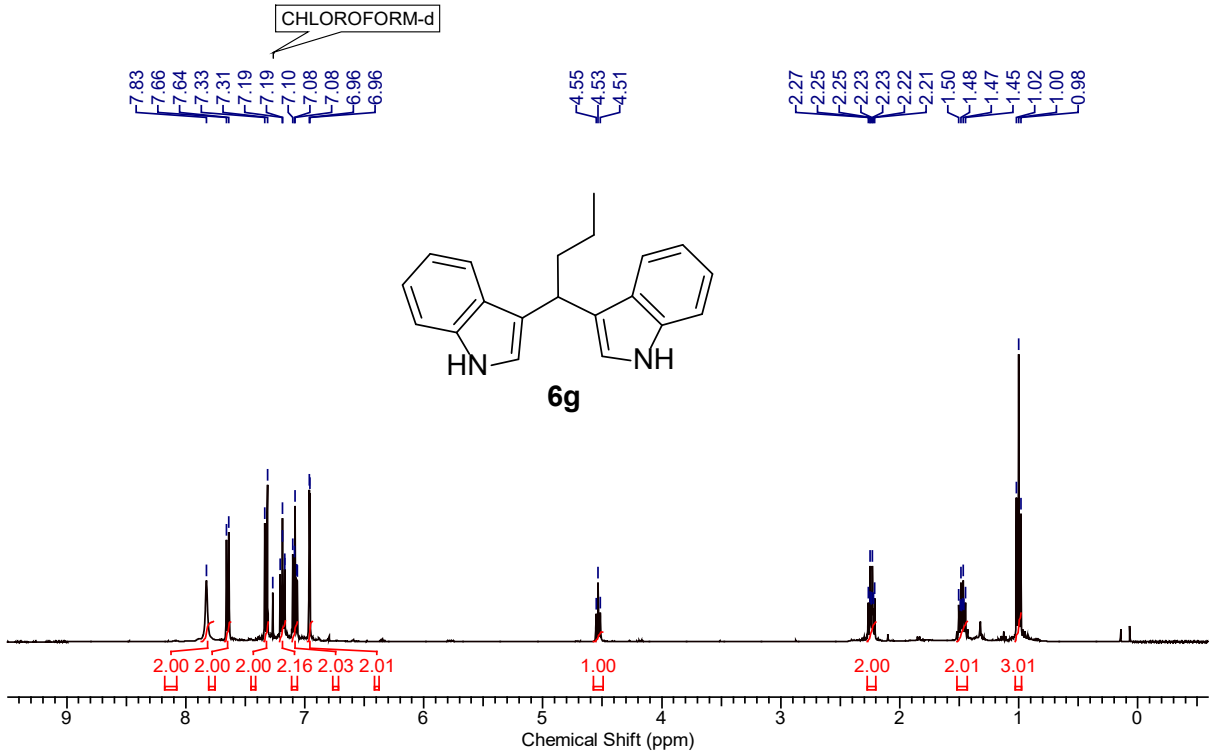

$^{13}$C NMR of **6d**



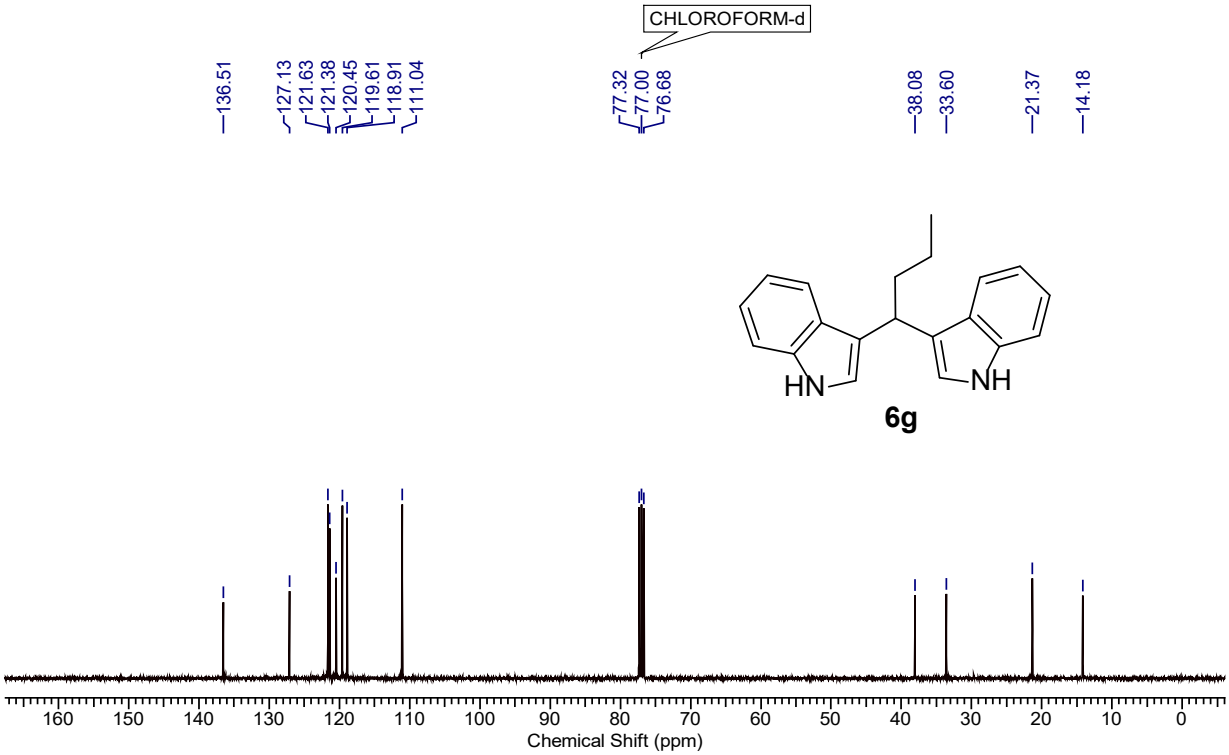

$^{1}$H NMR of **6f**




$^{13}$C NMR of **6f**




$^{1}$H NMR of **6g**

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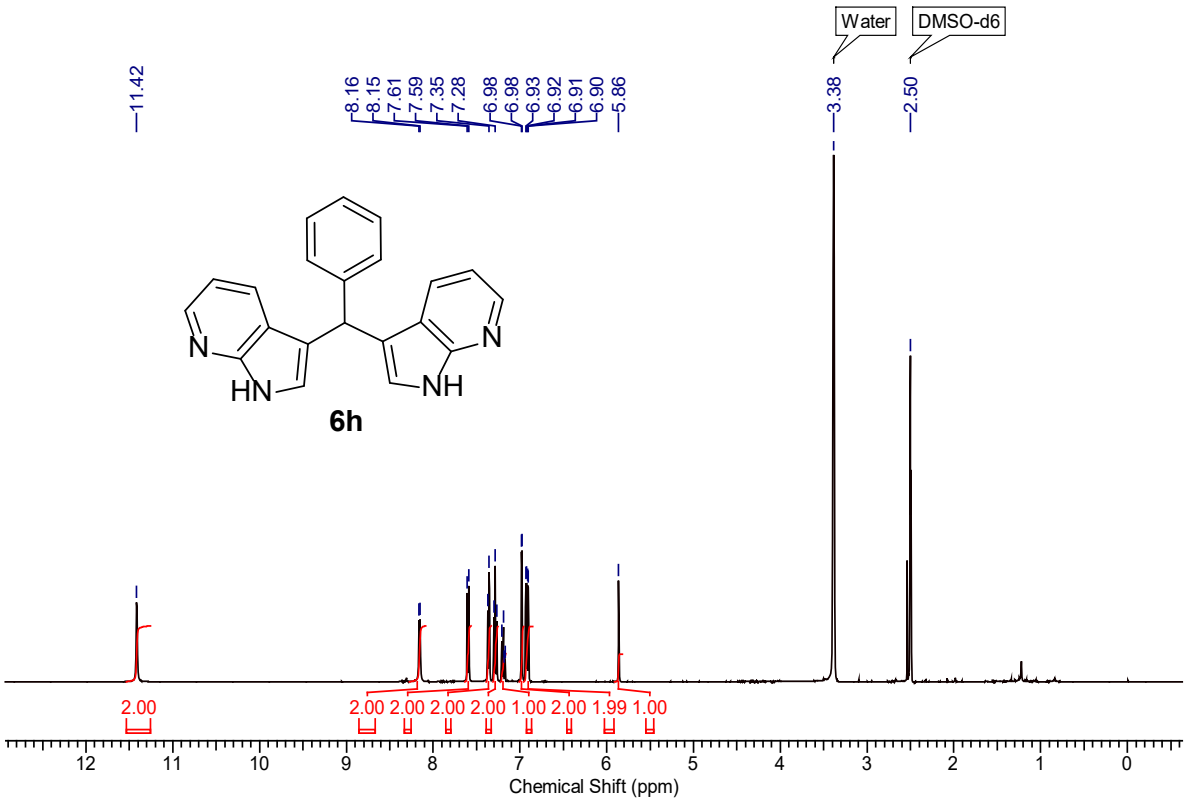


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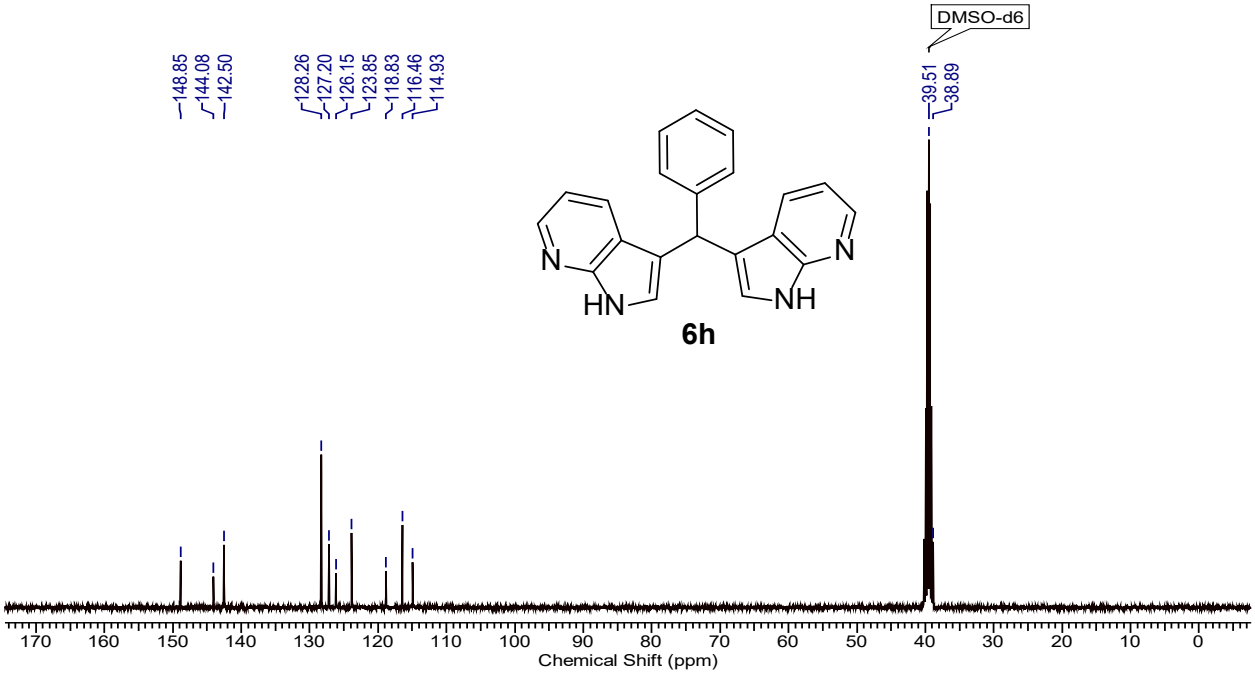
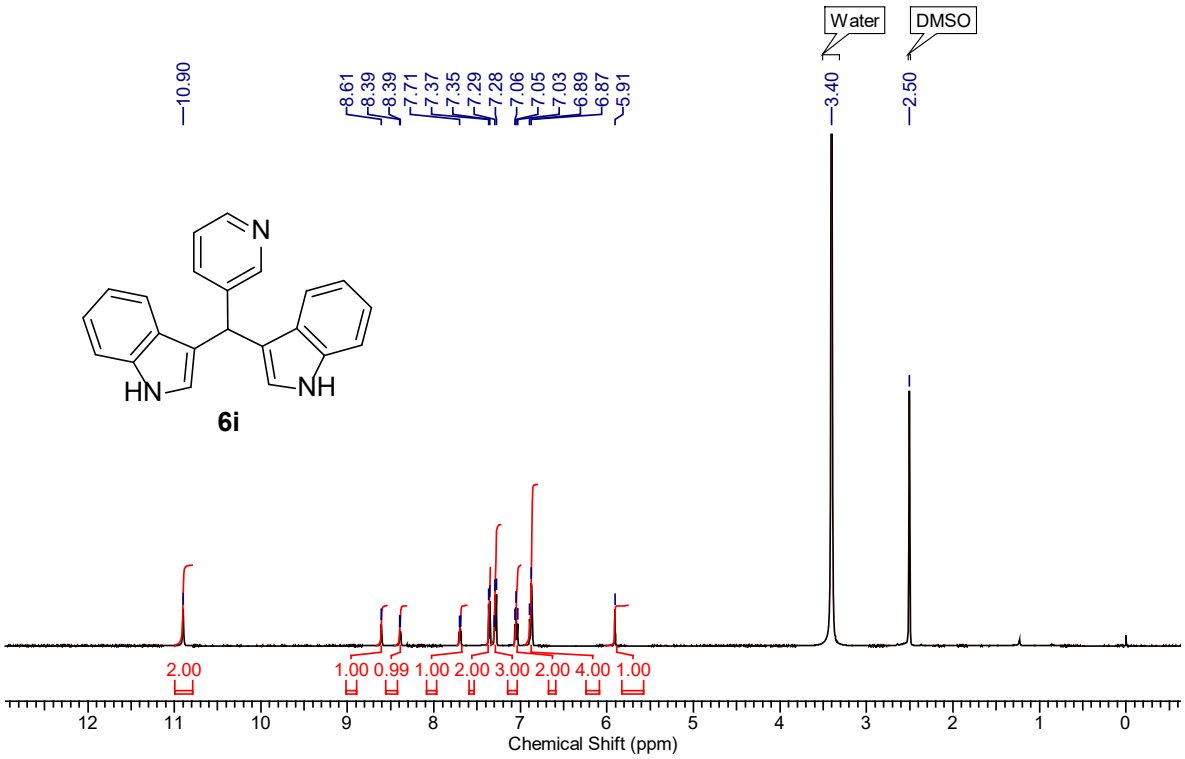
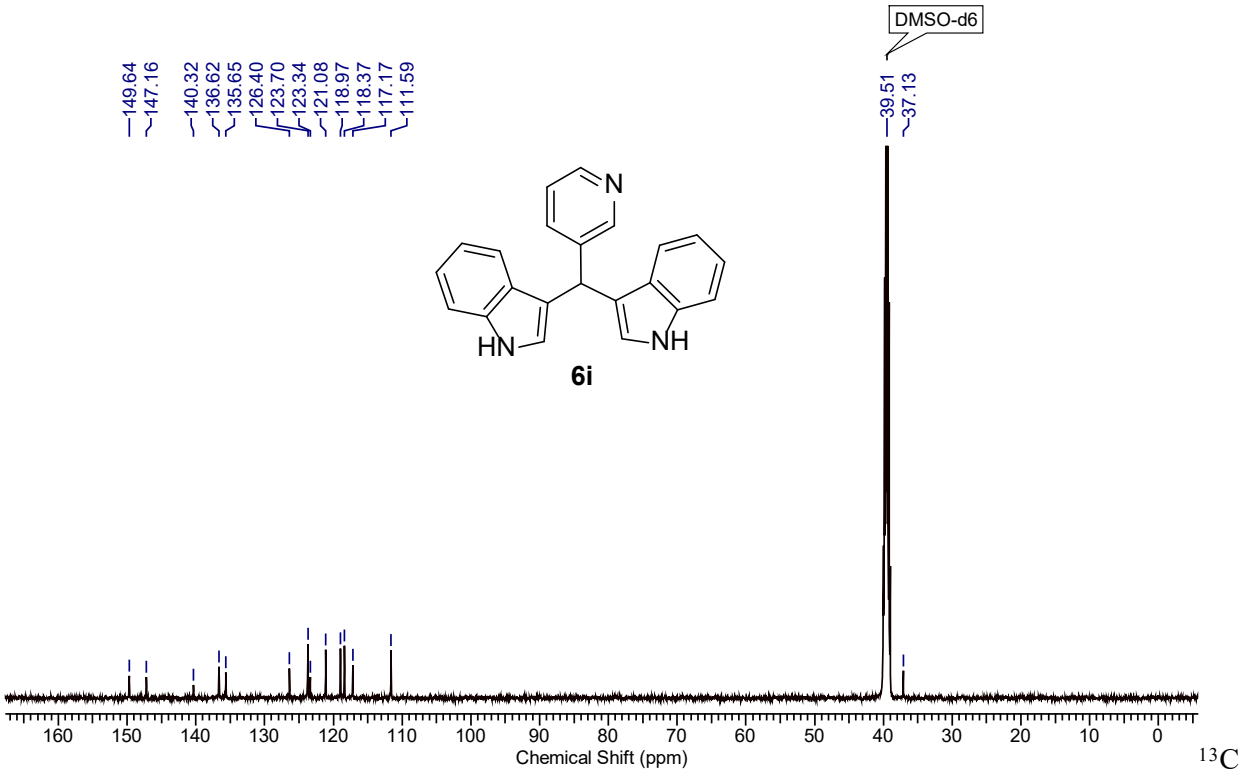


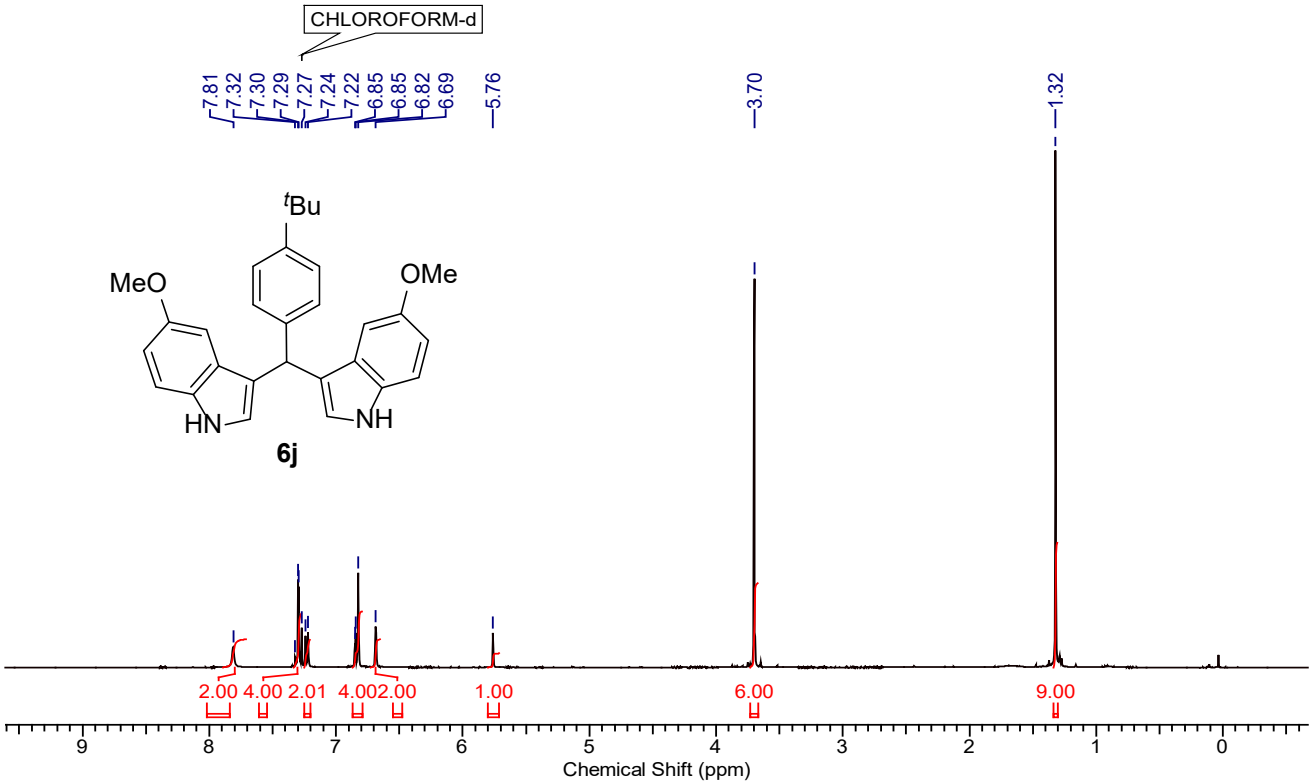

$^{13}$C NMR of **6h**




$^{1}$H NMR of **6i**




$^{13}$C NMR of **6i**

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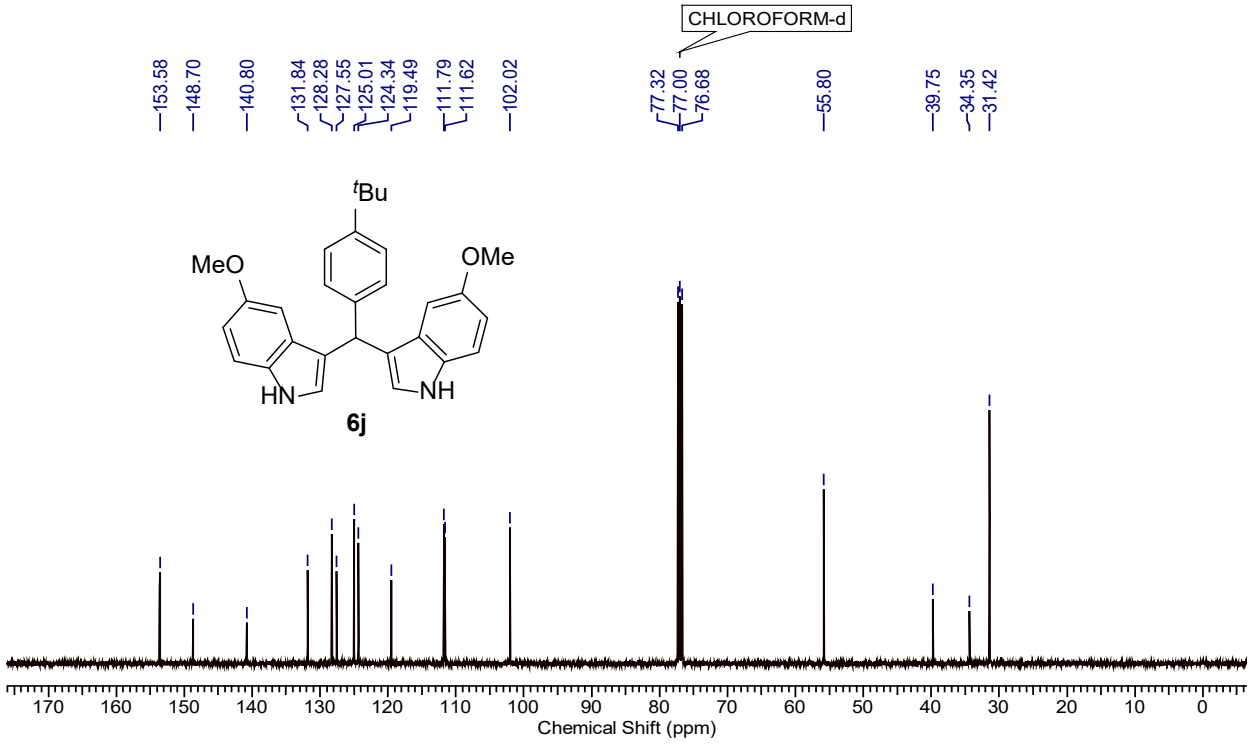


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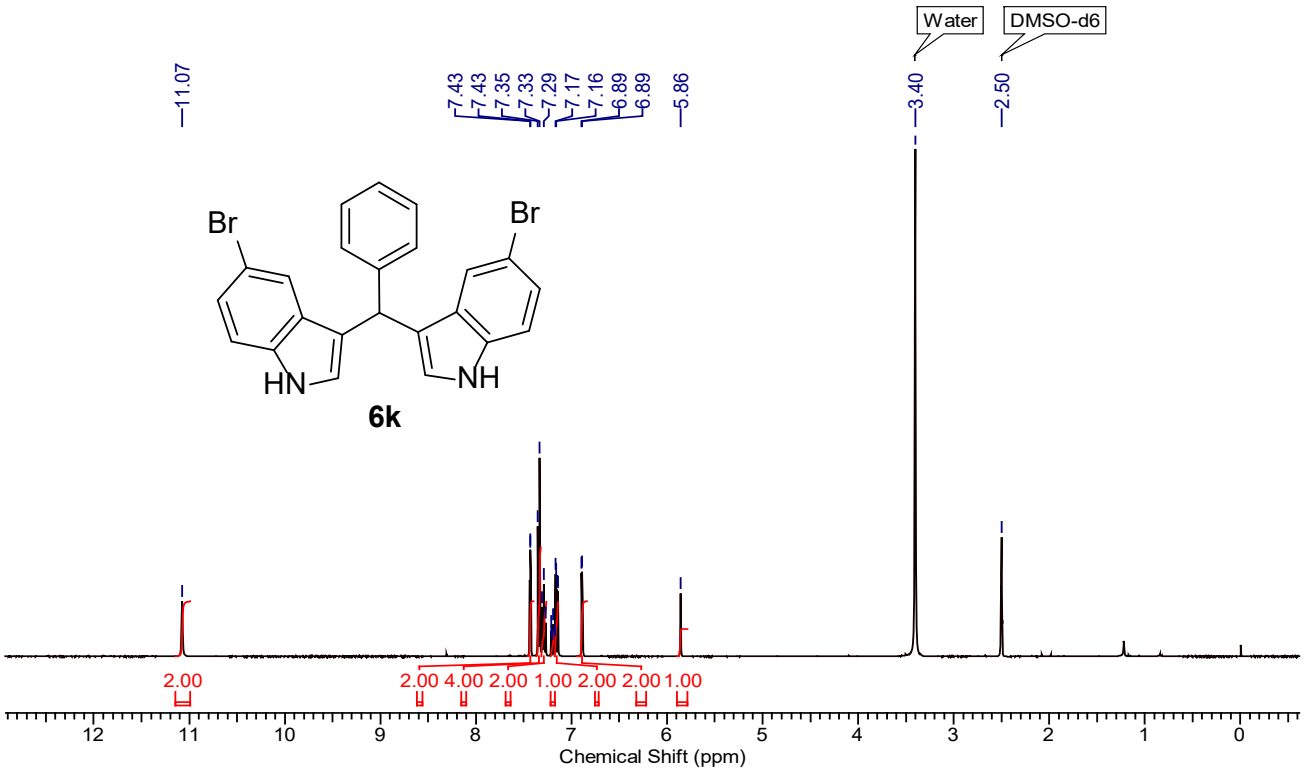
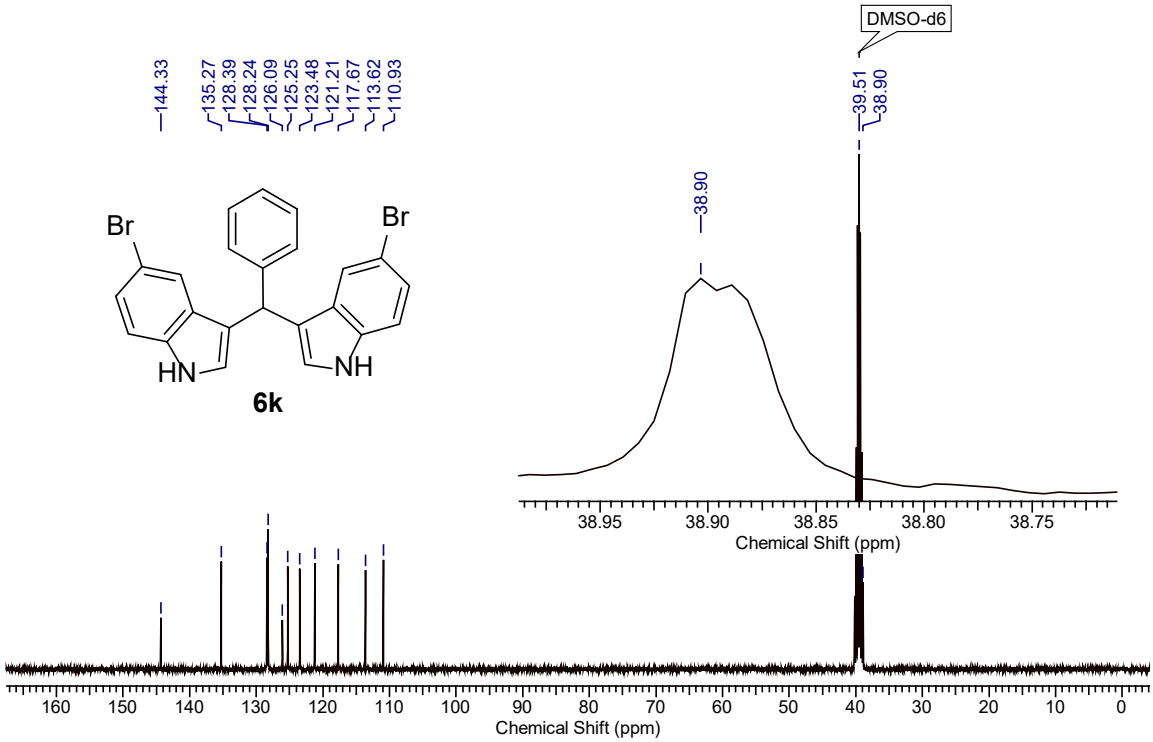



$^{1}$H NMR of **6k**

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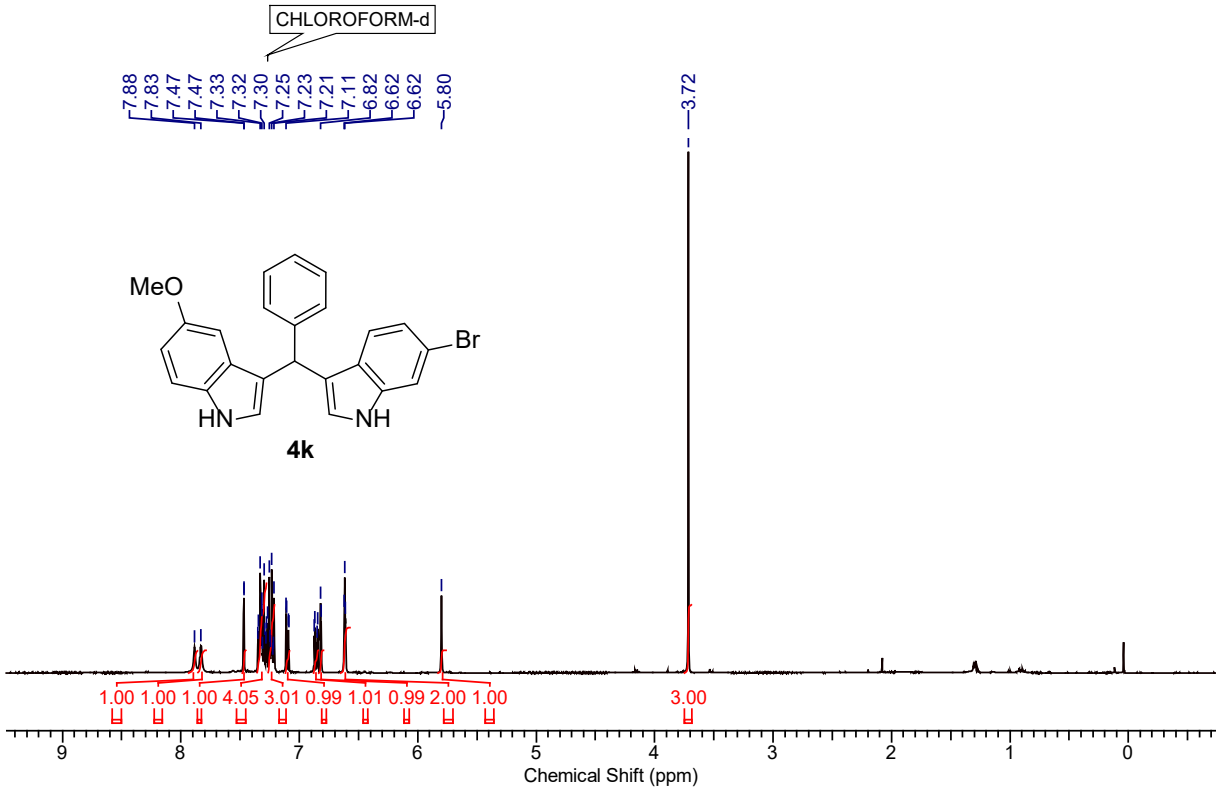
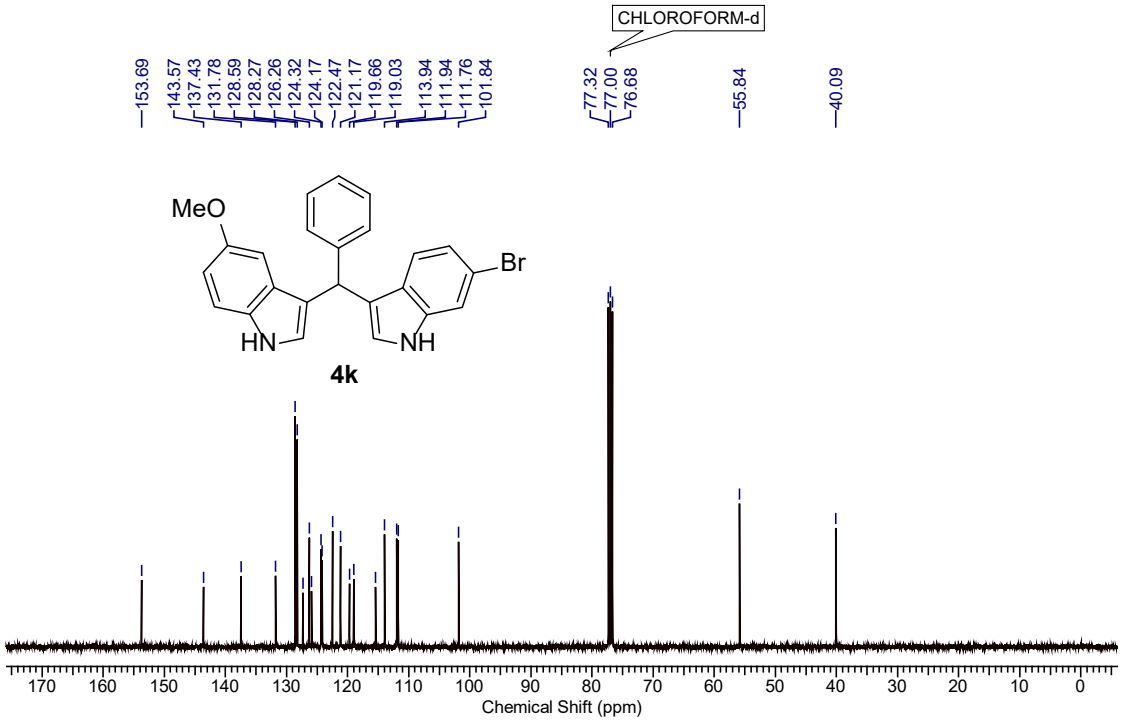



$^{1}$H NMR of **6l**

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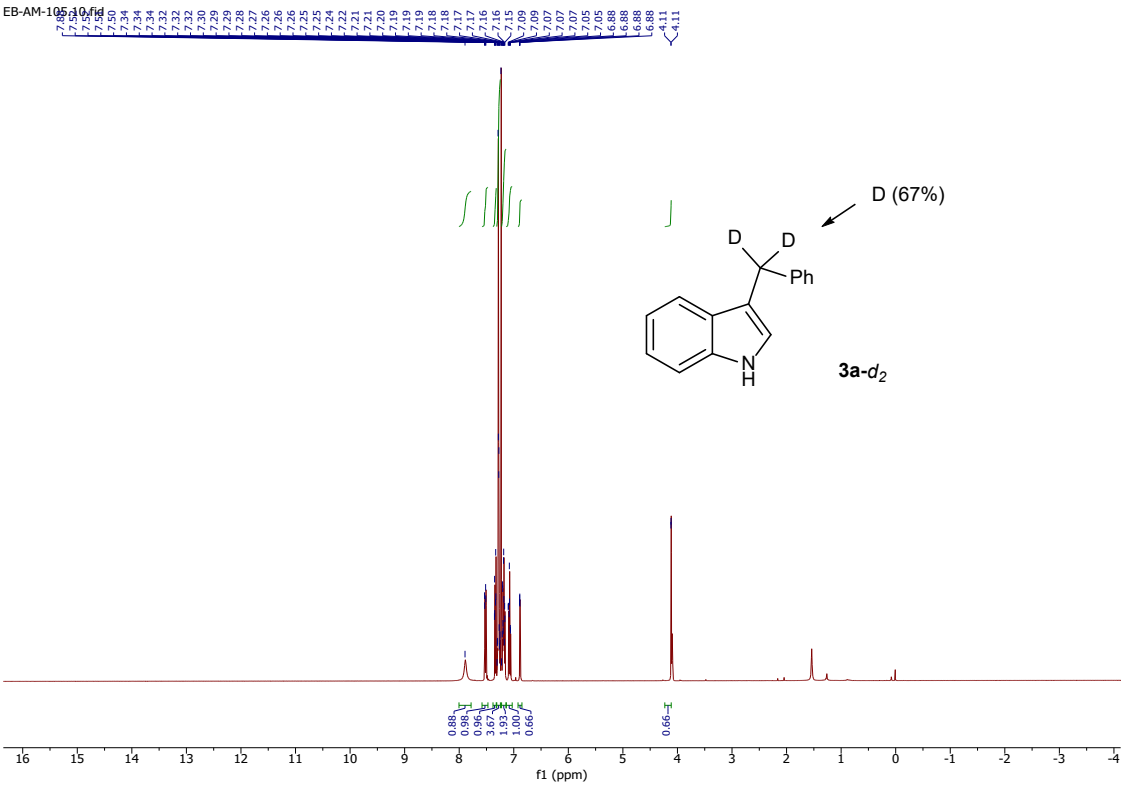
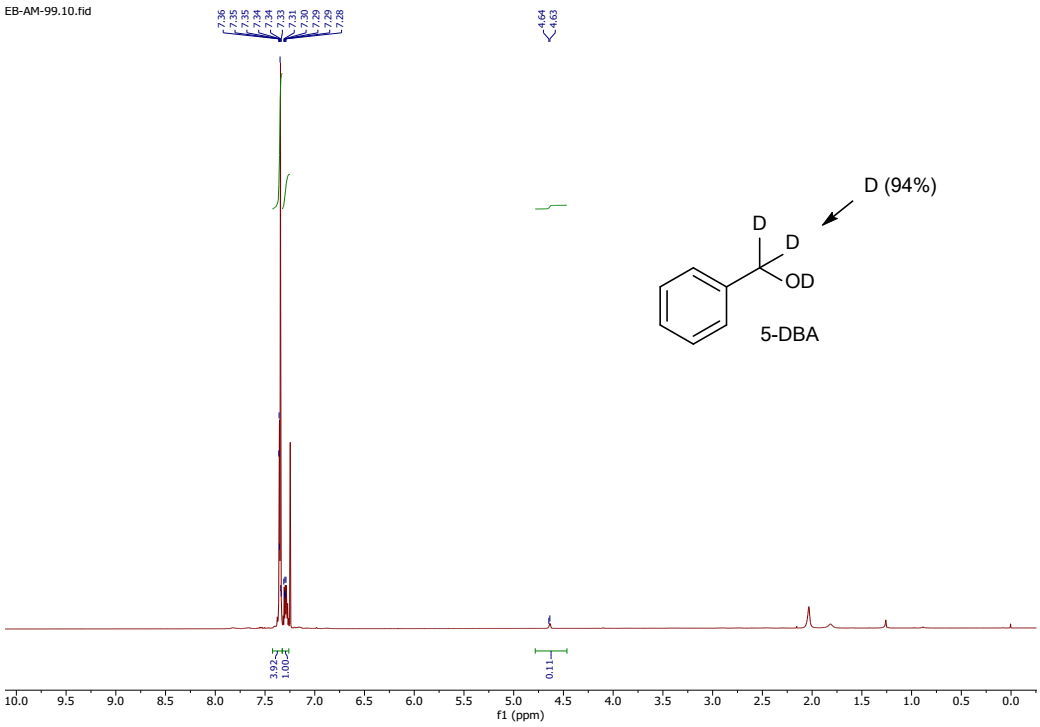
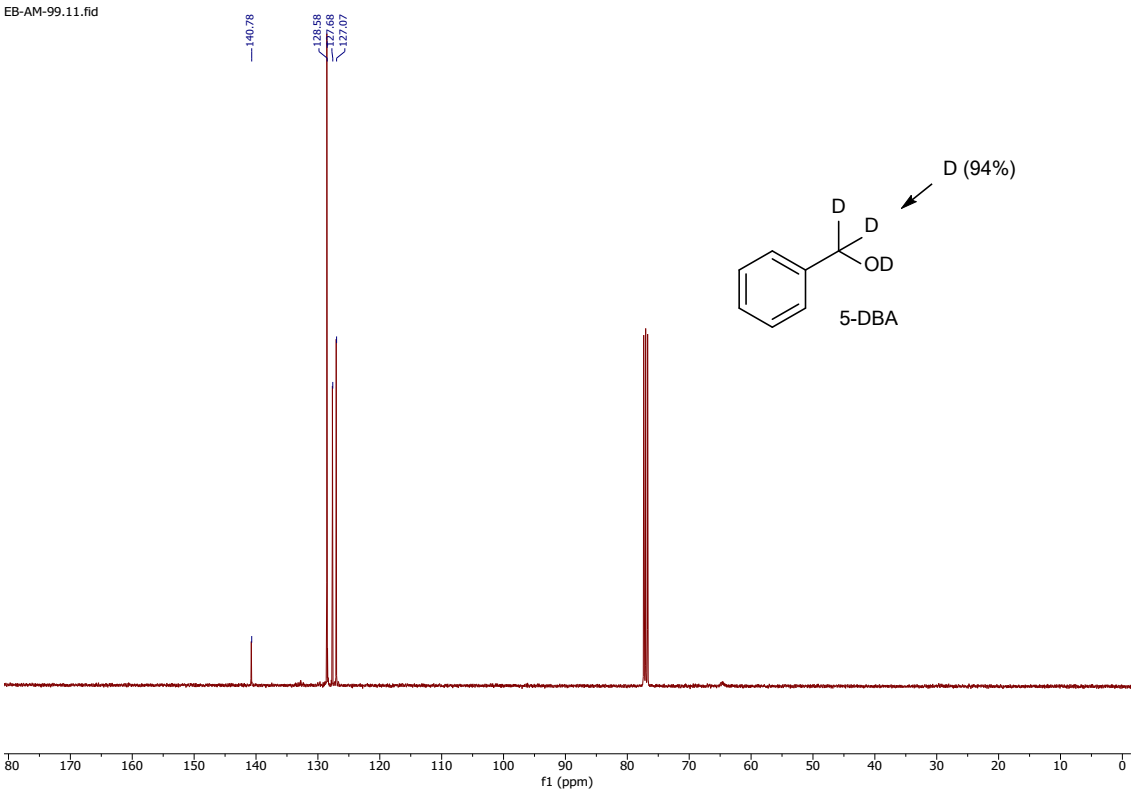


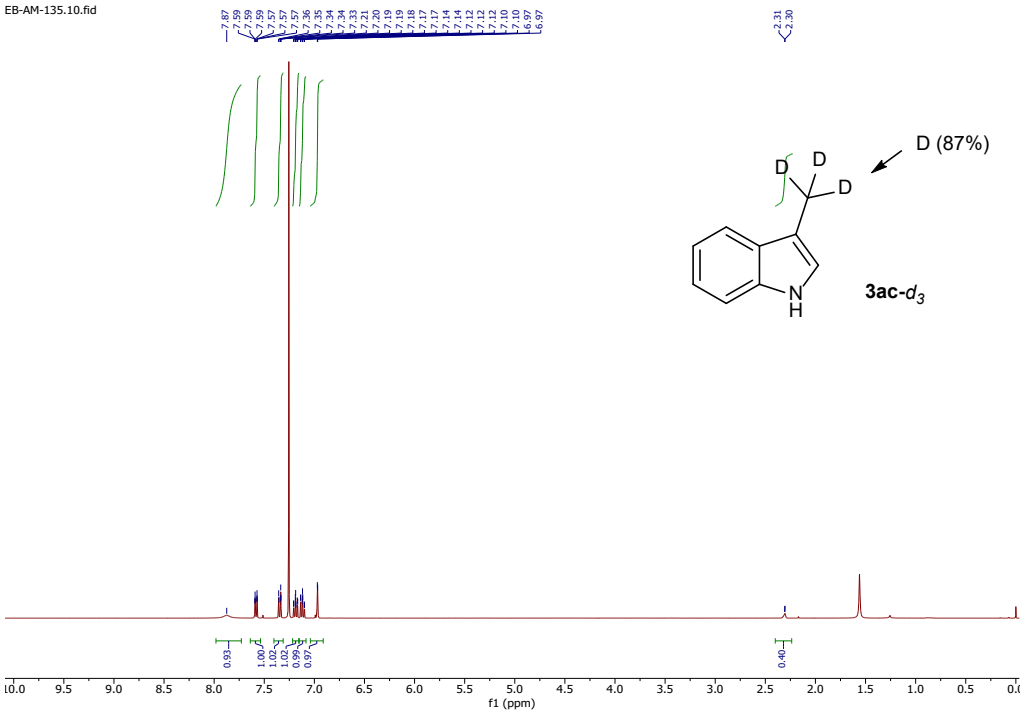

$^1$H NMR of **3a-$d_2$**



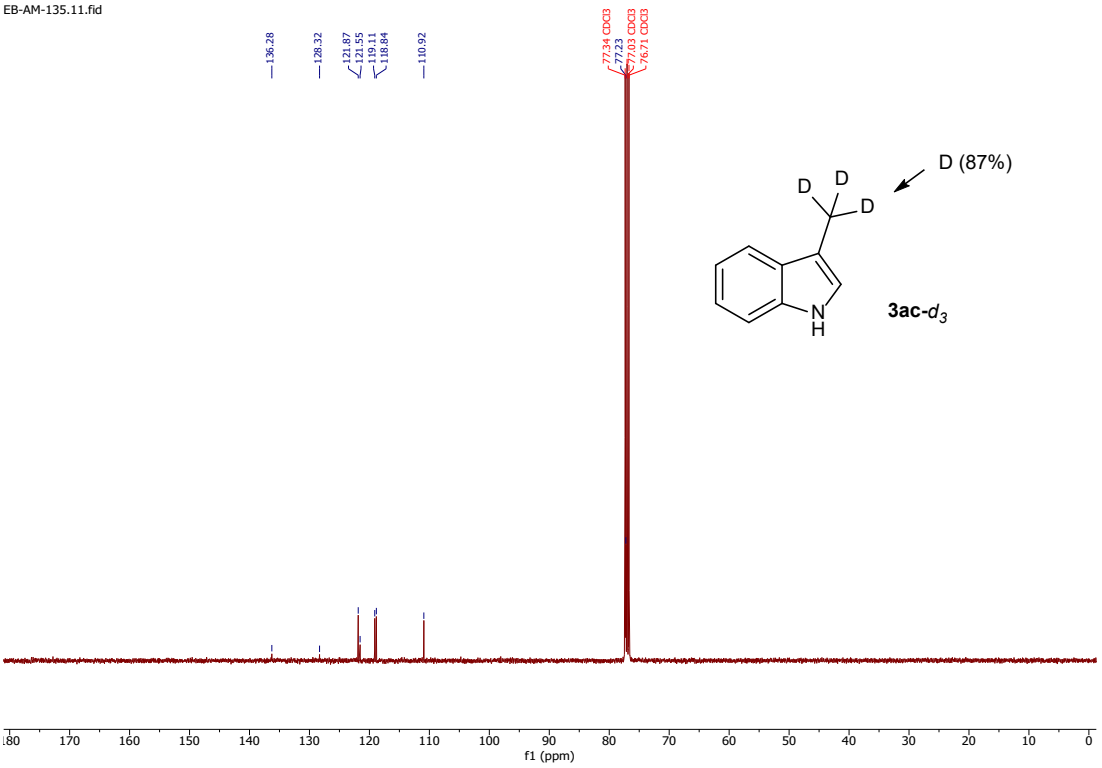

$^1$H NMR of **5-DBA**



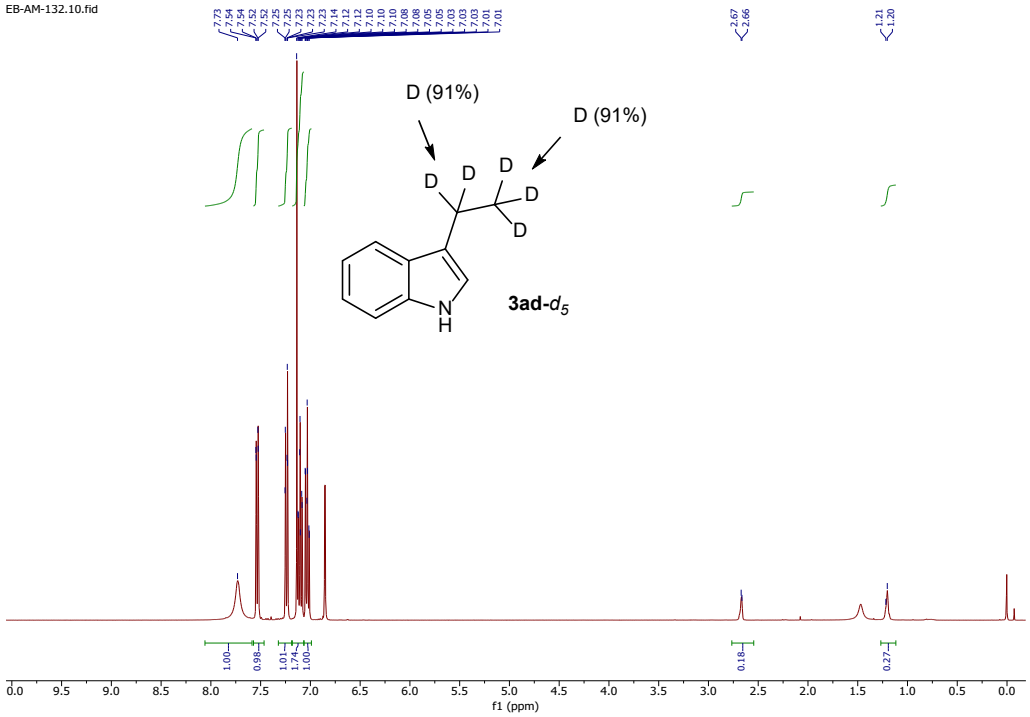

$^{13}C\{^{1}H\}$ NMR of **5-DBA**



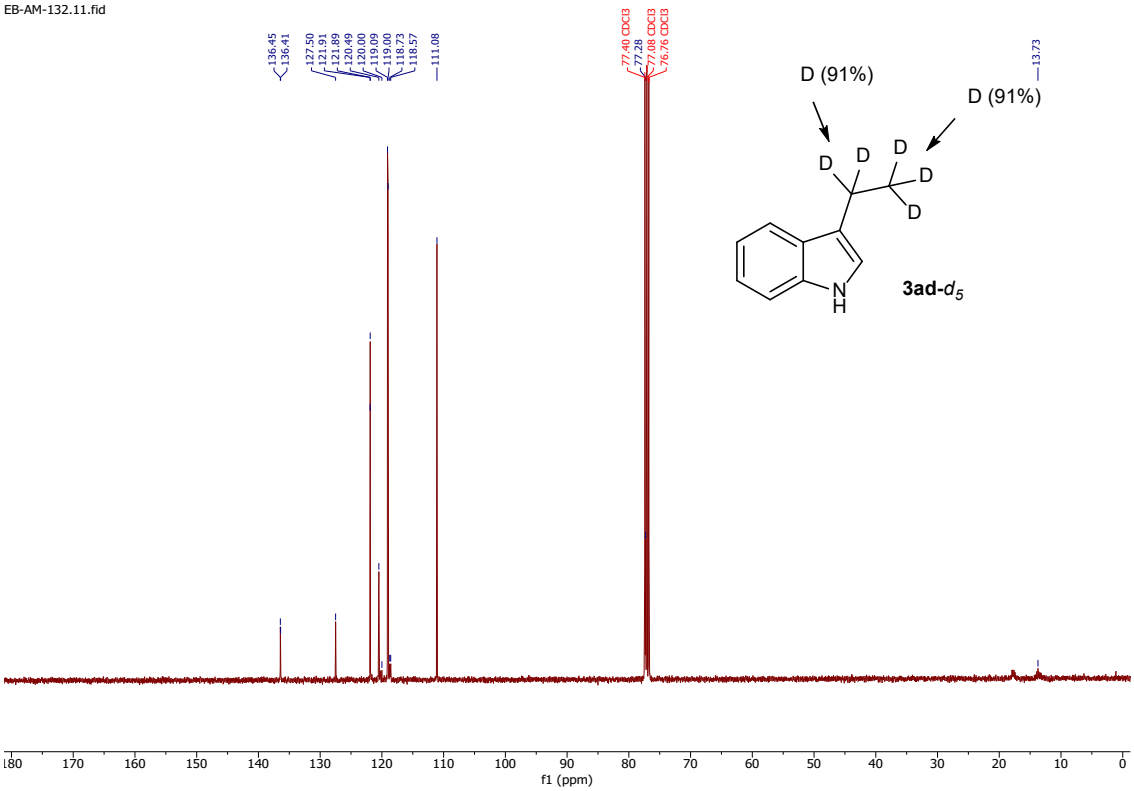

$^{1}H$ NMR of **3ac-$d_3$**




$^{13}C\{^{1}H\}$ NMR of **3ac-$d_3$**




$^{1}H$ NMR of **3ad-$d_5$**




$^{13}C\{^{1}H\}$ NMR of **3ad-$d_5$**

## 7. References

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S2. (a) S. P. Midya, J. Rana, J. Pitchaimani, A. Nandakumar, V. Madhu, and E. Balaraman, *ChemSusChem*, 2018, **11**, 3911-3916. (b) V. G. Landge, J. Pitchaimani, S. P. Midya, M. Subramanian, V. Madhu, E. Balaraman, *Catal. Sci. Technol.*, 2018, **8**, 428-433.

S3. A. Mondal (PhD Thesis, Indian Institute of Science Education and Research (IISER) Tirupati, **2022**).

S4. E. Khaskin and D. Milstein, *ACS Catal.* **2013**, *3*, 448-452.