

# Supporting Information

## Palladium-catalyzed *N*-arylation of (hetero)aryl chlorides with pyrroles and their analogues

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## 1. General Information

$^1\text{H}$  NMR spectra were recorded on Bruker 600 MHz spectrometer and the chemical shifts were reported in parts per million ( $\delta$ ) relative to internal solvent signal (7.261 ppm in  $\text{CDCl}_3$ , 2.500 ppm in  $\text{DMSO}-d_6$ , 7.160 ppm in  $\text{C}_6\text{D}_6$ ). The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet. The coupling constants,  $J$ , are reported in Hertz (Hz).  $^{13}\text{C}$  NMR spectra were obtained at Bruker 151 MHz and referenced to the internal solvent signals (central peak is 77.000 ppm in  $\text{CDCl}_3$ , 40.000 ppm in  $\text{DMSO}-d_6$ , 128.10 ppm in  $\text{C}_6\text{D}_6$ ).  $\text{CDCl}_3$ ,  $\text{DMSO}-d_6$  and  $\text{C}_6\text{D}_6$  were used as the NMR solvent. Thermo Q Exactive was used for HRMS and ESI-MS. Thermo Fisher Q Exactive (ORBITrap) was used for HRMS and APCI-MS.

Unless otherwise noted, all reagents were purchased from commercial suppliers (Energy-Chemical, Bidepharm, Heowns, or TCI) and used without further purification. Flash column chromatography was performed over silica gel 200-300. The reagents were weighed and handled in a glove box. All reactions were heated by metal sand bath (WATTCAS, LAB-500, <https://www.wattcas.com>).

## 2. Optimization of the Reaction Conditions

Table S1. Optimization of the reaction conditions <sup>a,b</sup>

$\text{1a} + \text{2a} \xrightarrow[\text{solvent, N}_2, 50\text{ }^\circ\text{C, 12 h}]{\text{Pd catalyst (0.8 mol\%), ligand (0.8 mol\%), base (1.0 equiv)}} \text{3a}$

entry	catalyst	ligand	base	solvent	yield/ <b>3a</b> /%
1	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	dioxane	n.d.
2	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	$\text{PhCF}_3$	n.d.
3	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	DMSO	n.d.
4	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	toluene	31
5	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	MTBE	40
6	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	CPME	42
7	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	THF	n.d.
8	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	<i>n</i> -heptane	51
9	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	DMF	n.d.
10	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	<i>n</i> -hexane	49
11	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	<i>c</i> -hexane	47
12	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	DMA	n.d.
13	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	MeCN	n.d.
14	$\text{Pd}(\text{acac})_2$	keYPhos	$t\text{-BuOK}$	DME	n.d.
15	$\text{Pd}(\text{P}^t\text{Bu}_3)_2$	keYPhos	$t\text{-BuOK}$	<i>n</i> -heptane	53
16	$\text{Pd}(\text{PPh}_3)_4$	keYPhos	$t\text{-BuOK}$	<i>n</i> -heptane	50
17	$\text{Pd}(\text{dba})_2$	keYPhos	$t\text{-BuOK}$	<i>n</i> -heptane	62
18	$\text{Pd}(\text{dba})_2$	keYPhos	$\text{Cs}_2\text{CO}_3$	<i>n</i> -heptane	n.d.
19	$\text{Pd}(\text{dba})_2$	keYPhos	$t\text{-BuONa}$	<i>n</i> -heptane	52
20	$\text{Pd}(\text{dba})_2$	keYPhos	$t\text{-BuOLi}$	<i>n</i> -heptane	78
21	$\text{Pd}(\text{dba})_2$	keYPhos	$\text{K}_2\text{CO}_3$	<i>n</i> -heptane	n.d.
22	$\text{Pd}(\text{dba})_2$	keYPhos	$\text{K}_3\text{PO}_4$	<i>n</i> -heptane	35
23	$\text{Pd}(\text{dba})_2$	keYPhos	$\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$	<i>n</i> -heptane	20
24	$\text{Pd}(\text{dba})_2$	keYPhos	DBU	<i>n</i> -heptane	trace
25	$\text{Pd}(\text{dba})_2$	keYPhos	NaOH	<i>n</i> -heptane	10
26	$\text{Pd}(\text{dba})_2$	keYPhos	MeOK	<i>n</i> -heptane	trace
27 <sup>c</sup>	$\text{Pd}(\text{dba})_2$	BrettPhos	$t\text{-BuOLi}$	<i>n</i> -heptane	56

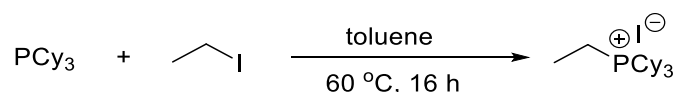
28	Pd(dba) <sub>2</sub>	XPhos	<sup>t</sup> BuOLi	<i>n</i> -heptane	52 <sup>c</sup>
29	Pd(dba) <sub>2</sub>	SPhos	<sup>t</sup> BuOLi	<i>n</i> -heptane	49 <sup>c</sup>
30	Pd(dba) <sub>2</sub>	1,10-Phen	<sup>t</sup> BuOLi	<i>n</i> -heptane	n.d.
31	Pd(dba) <sub>2</sub>	2,2-Bipyridine	<sup>t</sup> BuOLi	<i>n</i> -heptane	n.d.
32	Pd(dba) <sub>2</sub>	keYPhos	<sup>t</sup> BuOLi	<i>n</i> -heptane	78 <sup>d</sup>
33	Pd(dba) <sub>2</sub>	keYPhos	<sup>t</sup> BuOLi	<i>n</i> -heptane	79 <sup>e</sup>
34	Pd(dba) <sub>2</sub>	keYPhos	<sup>t</sup> BuOLi	<i>n</i> -heptane	81 <sup>f</sup>
35	-	keYPhos	<sup>t</sup> BuOLi	<i>n</i> -heptane	n.d. <sup>g</sup>
36	Pd(dba) <sub>2</sub>	-	<sup>t</sup> BuOLi	<i>n</i> -heptane	n.d. <sup>h</sup>
37	Pd(dba) <sub>2</sub>	keYPhos	-	<i>n</i> -heptane	n.d. <sup>i</sup>
38	Pd <sub>2</sub> (dba) <sub>3</sub>	keYPhos	<sup>t</sup> BuOK	THF	n.d. <sup>j</sup>

<sup>a</sup> Reaction conditions: **1a** (0.30 mmol), **2a** (0.45 mmol), catalyst (0.8 mol%), ligand (0.8 mol%), and base (1.0 equiv) in solvent (3.0 mL) at 70 °C for 12 hrs under N<sub>2</sub>; <sup>b</sup> Isolate yield; <sup>c</sup> catalyst (0.8 mol%), ligand (1.6 mol%); <sup>d</sup> at 50 °C; <sup>e</sup> catalyst (1.5 mol%), ligand (1.5 mol%); <sup>f</sup> **1a** (0.33 mmol), **2a** (0.30 mmol), at 50 °C; <sup>g</sup> no catalyst; <sup>h</sup> no ligand; <sup>i</sup> no base; <sup>j</sup> catalyst (0.25 mol%), ligand (0.50 mol%).

### 3. General Procedure for Starting Materials and Products

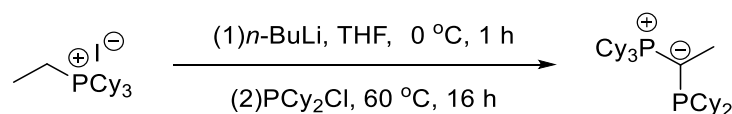
#### (a) Synthesis of ligands<sup>1</sup>

##### Synthesis of phosphonium salt 1:



Tricyclohexylphosphine (5.0 g, 17.9 mmol) and ethyl iodide (3.1 g, 19.5 mmol) were added to 30 mL of toluene. The solution was heated at 60 °C overnight and the product precipitated as a colorless solid. The precipitate was filtered off and washed with 2 x 10 mL of toluene. The solid was dried in vacuo for 10 h and the product was obtained as a colorless solid (6.1 g, 14.0 mmol, 80%).

##### Synthesis of keYPhos:



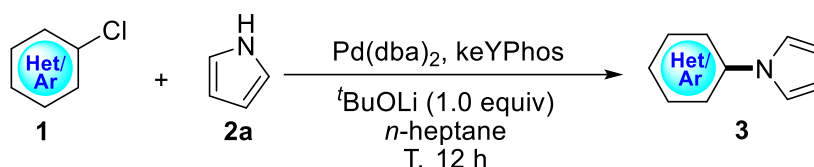
Salt 1 (4.0 g, 9.2 mmol) was placed in 30 mL of THF. The suspension was cooled down to 0 °C and 5.8 mL (9.2 mmol, 1.6 M in hexane) of a *n*-butyllithium solution was added slowly within 30 minutes until the solid was fully dissolved. Chlorodicyclohexylphosphine (2.3 g, 10.1 mmol) was added and it was stirred for 4 h while a colorless solid precipitated. The solvent was removed in vacuo and 1.2 g (10.1 mmol) <sup>t</sup>BuOK and 20 mL toluene were added to the residue and it was stirred overnight. Afterwards, the suspension was filtered over the celite and the solvent of the filtrate was removed in vacuo. The residue was suspended in 20 mL acetonitrile and it was stirred overnight. The suspension was filtered off and the solid was washed with 3 x 10 mL acetonitrile, filtered off and dried in vacuo. The **keYPhos** was obtained as a colorless solid (3.2 g, 6.3 mmol, 69%).

#### (b) Preparation of catalyst stock solution

In a glovebox containing N<sub>2</sub>, 57.5 mg of Pd(dba)<sub>2</sub> (0.10 mmol) and 50.5 mg of keYPhos (0.10 mmol) were weighed, along with 4.0 mL of THF into a dry reaction tube (15 mL). Stir the resulting mixture at room temperature for 0.5 h. The resulting palladium concentration was 0.025 mmol/mL THF, with the keYPhos ligand present at the same concentration.

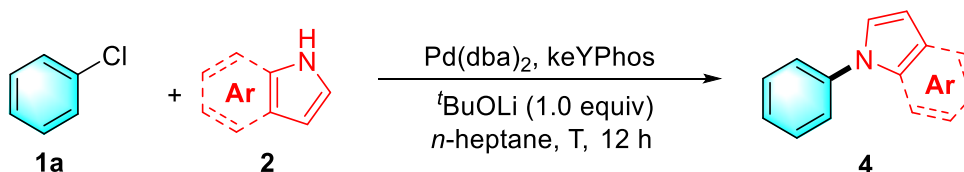
**(c) General procedure for the product 3 or 4**

**Synthesis of 3:**



In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with <sup>t</sup>BuOLi (24 mg, 0.3 mmol), aryl chlorides **1** (0.33 mmol), pyrrole **2a** (0.3 mmol), *n*-heptane (3.0 mL), and catalyst stock solution (96 uL, 0.8 mol% or 180 uL, 1.5 mol%) before being sealed with a rubber septum. The reaction mixture was stirred at 50 °C, 60 °C or 70 °C for 12 hours. After the mixture was cooled to room temperature, it was filtered directly. The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired product **3**.

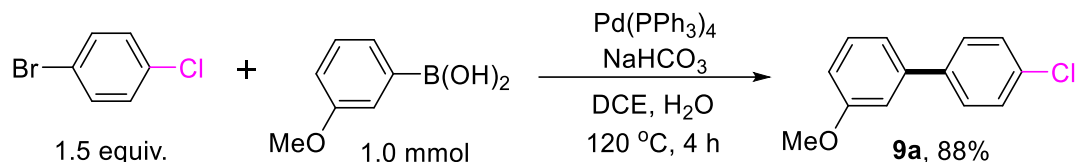
**Synthesis of 4:**



In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with <sup>t</sup>BuOLi (24 mg, 0.3 mmol), chlorobenzene **1a** (0.33 mmol), N–H heteroarenes **2** (0.3 mmol), *n*-heptane (3.0 mL), and catalyst stock solution (96 uL, 0.8 mol% or 180 uL, 1.5 mol%) before being sealed with a rubber septum. The reaction mixture was stirred at 50 °C, 60 °C, 65 °C, 70 °C, 80 °C or 90 °C for 12 hours. After the mixture was cooled to room temperature, it was filtered directly. The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired product **4**.

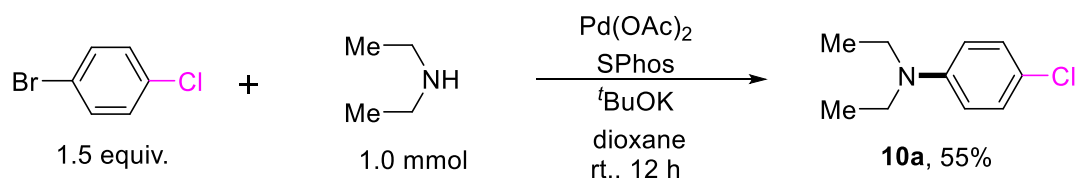
**(d) General procedure for the starting materials 9a-12a**

**Synthesis of 9a:**



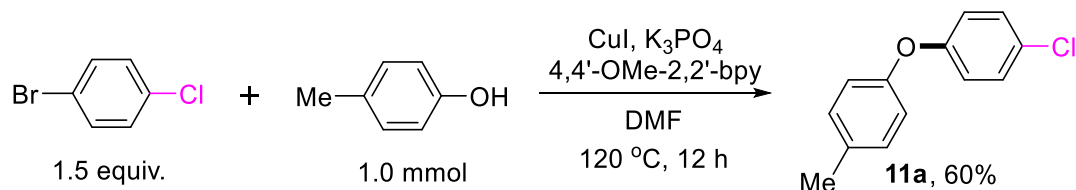
In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with  $\text{NaHCO}_3$  (168.0 mg, 2.0 equiv.), 3-methoxyphenylboronic acid (152.0 mg, 1.0 mmol), 4-bromochlorobenzene (287.2 mg, 1.5 equiv.), DCE (6.0 mL),  $\text{H}_2\text{O}$  (3.0 mL) and  $\text{Pd(PPh}_3)_4$  (115.6 mg, 10 mol%) before being sealed with a rubber septum. The reaction mixture was stirred at 120 °C for 4 hours. After the mixture was cooled to room temperature, it was filtered directly. The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired product **9a**.

#### Synthesis of 10a:



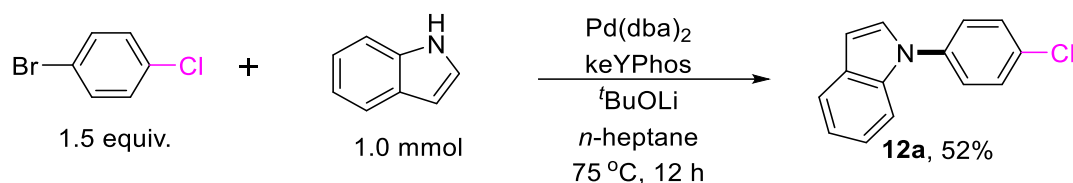
In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with  $\text{tBuOK}$  (224.4 mg, 2.0 equiv.), diethylamine (73.1 mg, 1.0 mmol), 4-bromochlorobenzene (287.2 mg, 1.5 equiv.), dioxane (9.0 mL),  $\text{Pd(OAc)}_2$  (22.7 mg, 10 mol%) and SPhos (82.1 mg, 20 mol%) before being sealed with a rubber septum. The reaction mixture was stirred at r.t. for 12 hours. After the mixture was cooled to room temperature, it was filtered directly. The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired product **10a**.

#### Synthesis of 11a:



In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with  $\text{K}_3\text{PO}_4$  (424.3 mg, 2.0 equiv.), *p*-cresol (108.1 mg, 1.0 mmol), 4-bromochlorobenzene (287.2 mg, 1.5 equiv.), DMF (9.0 mL), CuI (19.0 mg, 10 mol%) and 4,4'-dimethoxy-2,2'-bipyridine (21.6 mg, 20 mol%) before being sealed with a rubber septum. The reaction mixture was stirred at 120 °C for 12 hours. After the mixture was cooled to room temperature, it was filtered directly. The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired product **11a**.

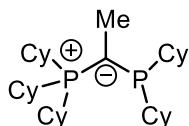
#### Synthesis of 12a:



In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with  $t\text{BuOLi}$  (80.0 mg, 1.0 equiv.), indole (117.2mg, 1.0 mmol), 4-bromochlorobenzene (287.2mg, 1.5 equiv.),  $n$ -heptane (9.0 mL), and catalyst stock solution (545  $\mu\text{L}$ ) before being sealed with a rubber septum. The reaction mixture was stirred at 75  $^\circ\text{C}$  for 12 hours. After the mixture was cooled to room temperature, it was filtered directly. The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired product **12a**.

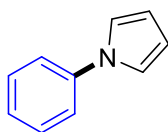
#### 4. Characterization Data of Starting Materials and Products

##### keYPhos



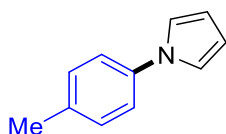
Following the general procedure, the **keYPhos** was obtained as a colorless solid (3.2 g, 6.3 mmol, 69%). The spectral data were in accordance with those reported in the literature.<sup>1</sup>  **$^1\text{H}$  NMR** (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 2.40 (q,  $J$  = 12.0, 3H), 2.29 (d,  $J$  = 12.3, 2H), 2.16 (d,  $J$  = 12.2, 2H), 2.01 (dt,  $J$  = 12.7, 6.6, 4H), 1.89 (dd,  $J$  = 13.2, 3.0, 11H), 1.79 (d,  $J$  = 11.5, 2H), 1.75 – 1.69 (m, 6H), 1.61 (dd,  $J$  = 12.5, 3.8, 5H), 1.55 – 1.43 (m, 12H), 1.36 (dd,  $J$  = 8.0, 4.5, 2H), 1.16 (s, 9H).  **$^{13}\text{C}$  NMR** (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 38.5 (dd,  $J$  = 13.8, 5.4), 33.7 (d,  $J$  = 19.7), 33.7 (dd,  $J$  = 49.3, 8.8), 33.0 (d,  $J$  = 10.0), 29.0 (d,  $J$  = 7.8), 28.6 (d,  $J$  = 11.9), 28.2 (d,  $J$  = 2.2), 27.9 (d,  $J$  = 11.0), 27.8, 27.0, 14.8 (d,  $J$  = 8.4), -1.7 (dd,  $J$  = 108.6, 20.5).  **$^{31}\text{P}$  NMR** (243 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 30.66 (d,  $J$  = 128.8), 1.06 (d,  $J$  = 128.8).

##### 1-phenyl-1*H*-pyrrole (3a)



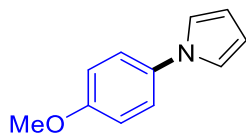
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a light brown solid in 81% (34.8 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>2</sup>  **$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.42 (m, 4H), 7.30 – 7.26 (m, 1H), 7.15 – 7.12 (m, 2H), 6.42 – 6.38 (m, 2H).  **$^{13}\text{C}$  NMR** (151 MHz,  $\text{CDCl}_3$ )  $\delta$  140.7, 129.5, 125.6, 120.5, 119.3, 110.4.

##### 1-(*p*-tolyl)-1*H*-pyrrole (3b)



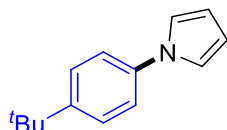
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a white crystal in 74% (34.8 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>2</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.09 (m, 2H), 6.37 (m, 2H), 2.40 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 138.5, 135.3, 130.0, 120.5, 119.3, 110.0, 20.8.

**1-(4-methoxyphenyl)-1*H*-pyrrole (3c)**



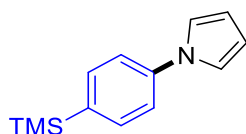
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 50:1) as a white crystal in 65% (33.9 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>2</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.33 (d, *J* = 9.0 Hz, 2H), 7.03 (m, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.35 (m, 2H), 3.85 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 157.6, 134.5, 122.2, 119.6, 114.6, 109.8, 55.5.

**1-(4-(*tert*-butyl)phenyl)-1*H*-pyrrole (3d)**



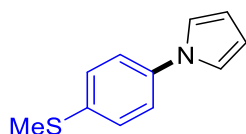
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a white crystal in 92% (55.0 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>3</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.45 (m, 2H), 7.37 – 7.34 (m, 2H), 7.10 (m, 2H), 6.37 (m, 2H), 1.38 (s, 9H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 148.6, 138.3, 126.3, 120.2, 119.4, 110.0, 34.4, 31.4.

**1-(4-(trimethylsilyl)phenyl)-1*H*-pyrrole (3e)**



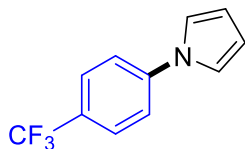
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a light white crystal in 98% (63.2 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.61 (m, 2H), 7.45 – 7.43 (m, 2H), 7.17 (m, 2H), 6.41 (m, 2H), 0.36 (s, 9H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 141.1, 137.5, 134.6, 119.7, 119.1, 110.4, 1.1. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>13</sub>H<sub>18</sub>NSi)<sup>+</sup>, 216.1203; found: 216.1190. **m.p.** = 58.6–58.9 °C.

**1-(4-(methylthio)phenyl)-1*H*-pyrrole (3f)**



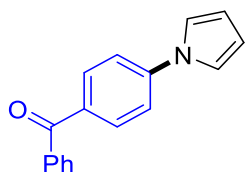
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a white solid in 90% (51.0 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>4</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.33 (s, 4H), 7.07 (m, 2H), 6.36 (m, 2H), 2.52 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 138.3, 135.4, 128.1, 121.0, 119.2, 110.4, 16.4.

**1-(4-(trifluoromethyl)phenyl)-1H-pyrrole (3g)**



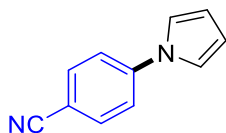
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a white crystal in 81% (51.3 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>2</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.17 – 7.15 (m, 2H), 6.44 – 6.42 (m, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 143.2, 127.4 (q, *J*<sub>C-F</sub> = 32.9 Hz), 126.8 (q, *J*<sub>C-F</sub> = 3.8 Hz), 124.0 (q, *J*<sub>C-F</sub> = 271.7 Hz) 119.9, 119.0, 111.5. **<sup>19</sup>F NMR** (565 MHz, CDCl<sub>3</sub>) δ -62.17.

**(4-(1H-pyrrol-1-yl)phenyl)(phenyl)methanone (3h)**



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a white solid in 87% (64.5 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.93 – 7.89 (m, 2H), 7.81 (dd, *J* = 10.4, 9.1 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.48 (m, 4H), 7.21 – 7.18 (m, 2H), 6.44 – 6.39 (m, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 195.3, 143.6, 137.6, 134.1, 132.3, 131.9, 129.8, 128.3, 119.1, 119.0, 111.5. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>17</sub>H<sub>14</sub>NO)<sup>+</sup>, 248.1070; found: 248.1051. **m.p.** = 153.8-154.6 °C.

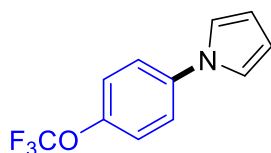
**4-(1H-pyrrol-1-yl)benzonitrile (3i)**



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 50:1) as a white crystal in 90% (45.4 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.73 – 7.70 (m, 2H), 7.50 – 7.46 (m, 2H), 7.16 – 7.12 (m, 2H), 6.42 – 6.39 (m, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 143.6, 133.7, 119.9, 118.8, 118.4, 112.1, 108.5. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>11</sub>H<sub>9</sub>N<sub>2</sub>)<sup>+</sup>, 169.0760; found: 169.0753. **m.p.** = 102.0-102.5 °C.

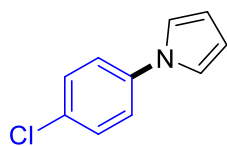
**1-(4-(trifluoromethoxy)phenyl)-1H-pyrrole (3j)**





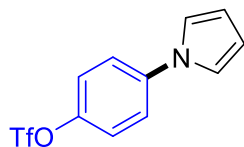
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a white solid in 71% (48.4 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.41 (m, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.10 – 7.07 (m, 2H), 6.43 – 6.40 (m, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 146.6, 139.3, 122.2, 121.5, 120.5 (q, *J*<sub>C-F</sub> = 257.2 Hz), 119.3, 110.9. **<sup>19</sup>F NMR** (565 MHz, CDCl<sub>3</sub>) δ -58.10. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>11</sub>H<sub>9</sub>F<sub>4</sub>NO)<sup>+</sup>, 228.0631; found: 228.0619. **m.p.** = 59.1-59.7 °C.

#### 1-(4-chlorophenyl)-1H-pyrrole (3k)



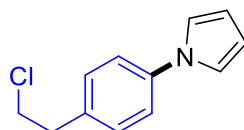
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a white crystal in 53% (28.3 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>3</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.41 – 7.38 (m, 2H), 7.35 – 7.32 (m, 2H), 7.06 (m, 2H), 6.37 (m, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 139.3, 131.0, 129.6, 121.6, 119.2, 110.8.

#### 4-(1H-pyrrol-1-yl)phenyl trifluoromethanesulfonate (3l)

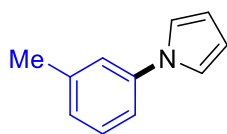


Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a yellow oil in 73% (63.7 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.47 – 7.44 (m, 2H), 7.37 – 7.34 (m, 2H), 7.09 – 7.06 (m, 2H), 6.41 – 6.38 (m, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 146.6, 140.5, 122.6, 121.6, 119.3, 118.7 (q, *J*<sub>C-F</sub> = 320.9 Hz), 111.4. **<sup>19</sup>F NMR** (565 MHz, CDCl<sub>3</sub>) δ -72.70. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>11</sub>H<sub>9</sub>F<sub>3</sub>NO<sub>3</sub>S)<sup>+</sup>, 292.0250; found: 292.0238. **m.p.** = 128.6-128.8 °C.

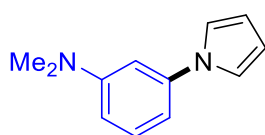
#### 1-(4-(2-chloroethyl)phenyl)-1H-pyrrole (3m)



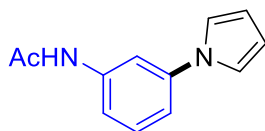
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a white solid in 92% (56.6 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.37 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.12 (m, 2H), 6.39 (m, 2H), 3.76 (t, *J* = 7.3 Hz, 2H), 3.12 (t, *J* = 7.3 Hz, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 139.5, 135.4, 129.9, 120.5, 119.2, 110.3, 44.8, 38.4. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>12</sub>H<sub>13</sub>ClN)<sup>+</sup>, 206.0731; found: 206.0722. **m.p.** = 86.4-86.9 °C.

**1-(*m*-tolyl)-1*H*-pyrrole (3n)**

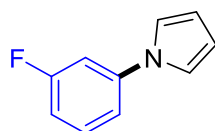
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a yellow oil in 74% (34.9 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>2</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.35 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 2.1 Hz, 2H), 7.11 (m, 2H), 6.40 (m, 2H), 2.45 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 140.7, 139.5, 129.3, 126.3, 121.2, 119.3, 117.6, 110.2, 21.4.

***N,N*-dimethyl-3-(1*H*-pyrrol-1-yl)aniline (3o)**

Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a white solid in 83% (46.3 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.29 (t, *J* = 8.1 Hz, 1H), 7.12 (m, 2H), 6.77 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.74 (t, *J* = 2.2 Hz, 1H), 6.65 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.37 (m, 2H), 3.02 (s, 6H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 151.4, 141.8, 129.9, 119.6, 109.9, 109.8, 109.0, 105.0, 40.5. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>12</sub>H<sub>15</sub>N<sub>2</sub>)<sup>+</sup>, 187.1230; found: 187.1221. **m.p.** = 135.6-135.9 °C.

***N*-(3-(1*H*-pyrrol-1-yl)phenyl)acetamide (3p)**

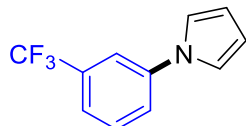
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a yellow solid in 68% (40.8 mg) yield. **<sup>1</sup>H NMR** (600 MHz, DMSO-*d*<sub>6</sub>) δ 10.09 (s, 1H), 7.83 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.23 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 1H), 6.27 (m, 2H), 2.07 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, DMSO-*d*<sub>6</sub>) δ 169.1, 141.0, 140.7, 130.4, 119.4, 116.4, 114.7, 111.0, 110.6, 24.6. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>O)<sup>+</sup>, 201.1022; found: 201.1012. **m.p.** = 110.8-111.9 °C.

**1-(3-fluorophenyl)-1*H*-pyrrole (3q)**

Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a yellow oil in 60% (29.0 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>5</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.40 (td, *J* = 8.2, 6.4 Hz, 1H), 7.21 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.14 (dt, *J* = 10.1, 2.3 Hz, 1H), 7.12 – 7.11 (m, 2H), 6.97 (tdd, *J* = 8.3, 2.4, 0.5 Hz,

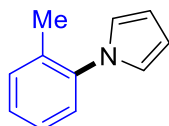
1H), 6.41 – 6.39 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 163.3 (d, *J*<sub>C-F</sub> = 246.5 Hz), 142.1 (d, *J*<sub>C-F</sub> = 10.0 Hz), 130.8 (d, *J*<sub>C-F</sub> = 9.4 Hz), 119.1, 115.7 (d, *J*<sub>C-F</sub> = 2.9 Hz), 112.2 (d, *J*<sub>C-F</sub> = 21.2 Hz), 110.9, 107.7 (d, *J*<sub>C-F</sub> = 25.0 Hz). <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -111.14.

#### 1-(3-(trifluoromethyl)phenyl)-1*H*-pyrrole (3r)



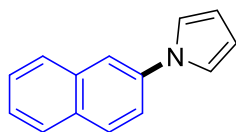
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a yellow oil in 60% (38.0 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>6</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.68 (s, 1H), 7.60 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.53 (dd, *J* = 10.2, 2.8 Hz, 1H), 7.17 – 7.14 (m, 2H), 6.45 – 6.42 (m, 2H). 123.70 (q, *J* = 272.5 Hz). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 141.1, 132.1 (q, *J*<sub>C-F</sub> = 32.7 Hz), 130.2, 123.7 (q, *J*<sub>C-F</sub> = 272.5 Hz), 123.3 (d, *J*<sub>C-F</sub> = 0.8 Hz), 122.1 (q, *J*<sub>C-F</sub> = 3.7 Hz), 119.2, 117.1 (q, *J*<sub>C-F</sub> = 3.9 Hz), 111.3. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -62.81.

#### 1-(*o*-tolyl)-1*H*-pyrrole (3s)



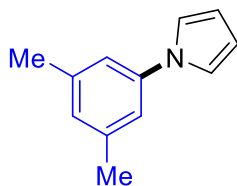
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a yellow oil in 55% (25.9 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>2</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.27 (m, 4H), 6.82 (m, 2H), 6.35 (m, 2H), 2.24 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 140.6, 133.8, 131.0, 127.4, 126.6, 126.5, 122.0, 108.7, 17.8.

#### 1-(naphthalen-2-yl)-1*H*-pyrrole (3t)



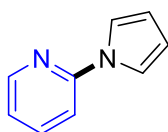
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a white solid in 75% (43.5 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>3</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.8 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.83 (d, *J* = 2.1 Hz, 1H), 7.62 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.56 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.51 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.28 – 7.26 (m, 2H), 6.48 – 6.45 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 138.1, 133.8, 131.4, 129.5, 127.7, 127.6, 126.9, 125.5, 120.1, 119.5, 117.4, 110.6.

#### 1-(3,5-dimethylphenyl)-1*H*-pyrrole (3u)



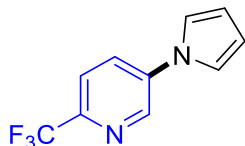
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a yellow oil in 81% (41.6 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>2</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.10 – 7.08 (m, 2H), 7.04 (s, 2H), 6.91 (d, *J* = 0.5 Hz, 1H), 6.36 – 6.34 (m, 2H), 2.38 (s, 6H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 140.7, 139.2, 127.3, 119.3, 118.5, 110.0, 21.3.

### 2-(1*H*-pyrrol-1-yl)pyridine (3x)



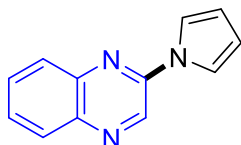
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a yellow oil in 87% (37.6 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>7</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.47 – 8.39 (m, 1H), 7.72 (ddd, *J* = 8.3, 7.4, 1.9 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.09 (ddd, *J* = 7.3, 4.9, 0.8 Hz, 1H), 6.40 – 6.36 (m, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 151.3, 148.6, 138.4, 120.1, 118.0, 111.3, 111.2.

### 5-(1*H*-pyrrol-1-yl)-2-(trifluoromethyl)pyridine (3y)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a white crystal in 52% (33.1 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.83 (d, *J* = 2.5 Hz, 1H), 7.83 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.17 – 7.14 (m, 2H), 6.47 – 6.41 (m, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 144.6 (q, *J*<sub>C-F</sub> = 35.4 Hz), 141.4, 138.8, 127.4, 121.4 (q, *J*<sub>C-F</sub> = 273.5 Hz), 121.3 (q, *J*<sub>C-F</sub> = 2.6 Hz), 118.9, 112.5. **<sup>19</sup>F NMR** (565 MHz, CDCl<sub>3</sub>) δ -67.41. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>10</sub>H<sub>8</sub>F<sub>3</sub>N<sub>2</sub>)<sup>+</sup>, 213.0634; found: 213.0623. **m.p.** = 94.2-95.0 °C.

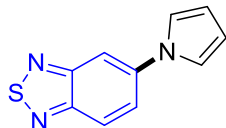
### 2-(1*H*-pyrrol-1-yl)quinoxaline (3z)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a white solid in 86% (50.4 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.03 (s, 1H), 8.06 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.97 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.74 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.72 – 7.70 (m, 2H), 7.65 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 6.47 – 6.45 (m, 2H). **<sup>13</sup>C NMR** (151 MHz,

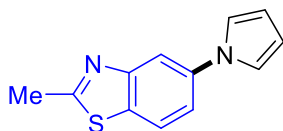
CDCl<sub>3</sub>)  $\delta$  144.8, 140.7, 140.4, 136.5, 130.9, 129.0, 128.3, 118.3, 112.7. **HRMS** (ESI)  $m/z$ : [M+H]<sup>+</sup> calcd for (C<sub>12</sub>H<sub>10</sub>N<sub>3</sub>)<sup>+</sup>, 196.0869; found: 196.0860. **m.p.** = 109.3-110.1 °C.

**5-(1*H*-pyrrol-1-yl)benzo[*c*][1,2,5]thiadiazole (3aa)**



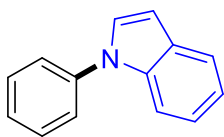
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a white crystal in 83% (50.1 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (d,  $J$  = 9.4 Hz, 1H), 7.91 (d,  $J$  = 1.9 Hz, 1H), 7.77 (dd,  $J$  = 9.4, 2.2 Hz, 1H), 7.24 – 7.21 (m, 2H), 6.46 – 6.42 (m, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  155.2, 152.8, 141.4, 124.6, 122.3, 119.5, 111.8, 109.5. **HRMS** (ESI)  $m/z$ : [M+H]<sup>+</sup> calcd for (C<sub>10</sub>H<sub>8</sub>N<sub>3</sub>S)<sup>+</sup>, 202.0433; found: 202.0424. **m.p.** = 141.0-142.1 °C.

**2-methyl-5-(1*H*-pyrrol-1-yl)benzo[*d*]thiazole (3ab).**



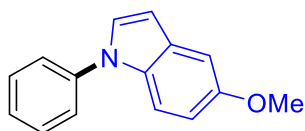
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a white crystal in 55 % (35.4 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d,  $J$  = 2.1 Hz, 1H), 7.82 (d,  $J$  = 8.5 Hz, 1H), 7.42 (dd,  $J$  = 8.5, 2.2 Hz, 1H), 7.15 (m, 2H), 6.39 (m, 2H), 2.85 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  169.0, 154.2, 139.4, 132.6, 122.0, 119.6, 118.1, 113.9, 110.6, 20.2. **HRMS** (ESI)  $m/z$ : [M+H]<sup>+</sup> calcd for (C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>S)<sup>+</sup>, 215.0637; found: 215.0627. **m.p.** = 139.6-140.2 °C.

**1-phenyl-1*H*-indole (4a)**



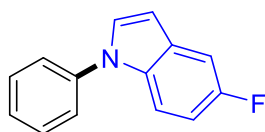
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a yellow oil in 81% (46.9 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>8</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (d,  $J$  = 7.7 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.58 (dd,  $J$  = 3.3, 1.7 Hz, 4H), 7.45 – 7.40 (m, 2H), 7.34 – 7.26 (m, 2H), 6.78 (d,  $J$  = 2.2 Hz, 1H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  139.8, 135.8, 129.5, 129.3, 127.9, 126.4, 124.3, 122.3, 121.1, 120.3, 110.5, 103.5.

**5-methoxy-1-phenyl-1*H*-indole (4b)**



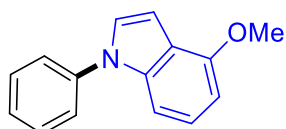
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a yellow oil in 91% (60.9 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>8</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.50 (m, 5H), 7.39 – 7.35 (m, 2H), 7.20 (d, *J* = 2.5 Hz, 1H), 6.95 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.66 (dd, *J* = 3.2, 0.6 Hz, 1H), 3.92 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 154.5, 139.9, 131.0, 129.8, 129.5, 128.3, 126.2, 123.9, 112.4, 111.3, 103.2, 102.7, 55.8.

#### 5-fluoro-1-phenyl-1H-indole (4c)



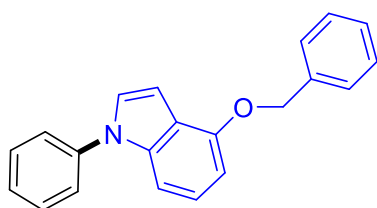
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a yellow oil in 90% (57.0 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>8</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.52 (m, 2H), 7.52 – 7.47 (m, 3H), 7.45 – 7.38 (m, 2H), 7.37 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.00 (td, *J* = 9.1, 2.5 Hz, 1H), 6.67 (dd, *J* = 3.1, 0.4 Hz, 1H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 158.1 (d, *J*<sub>C-F</sub> = 235.6 Hz), 139.6, 132.5, 129.6, 129.6 (d, *J*<sub>C-F</sub> = 10.0 Hz), 129.4, 126.6, 124.2, 111.2 (d, *J*<sub>C-F</sub> = 9.7 Hz), 110.6 (d, *J*<sub>C-F</sub> = 26.1 Hz), 105.8 (d, *J*<sub>C-F</sub> = 23.5 Hz), 103.4 (d, *J*<sub>C-F</sub> = 4.5 Hz). **<sup>19</sup>F NMR** (565 MHz, CDCl<sub>3</sub>) δ -124.12.

#### 4-methoxy-1-phenyl-1H-indole (4d)



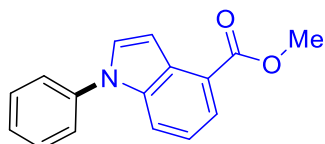
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 50:1) as a white solid in 87% (58.2 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>9</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.53 (m, 4H), 7.39 (ddd, *J* = 8.6, 5.1, 3.6 Hz, 1H), 7.29 (d, *J* = 3.3 Hz, 1H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 3.2 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 4.03 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 153.4, 139.9, 137.2, 129.5, 126.5, 126.4, 124.3, 123.1, 119.8, 103.9, 100.8, 100.2, 55.4.

#### 4-(benzyloxy)-1-phenyl-1H-indole (4e)



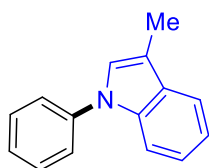
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 50:1) as a white solid in 85% (76.3 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.57 – 7.54 (m, 4H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (ddd, *J* = 8.0, 5.6, 2.6 Hz, 2H), 7.32 (d, *J* = 3.2 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.96 – 6.92 (m, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 5.32 (s, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 152.6, 139.9, 137.5, 137.3, 129.5, 128.5, 127.7, 127.3, 126.5, 126.4, 124.3, 123.1, 120.2, 104.1, 101.7, 101.0, 70.0. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>21</sub>H<sub>18</sub>NO)<sup>+</sup>, 300.1388; found: 300.1367. **m.p.** = 77.3-78.1 °C.

#### methyl 1-phenyl-1*H*-indole-4-carboxylate (4f)



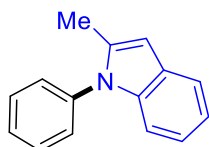
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a white crystal in 30% (22.6 mg) yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.98 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.50 – 7.47 (m, 3H), 7.42 – 7.38 (m, 1H), 7.36 (dd, *J* = 3.2, 0.5 Hz, 1H), 7.27 (dd, *J* = 9.8, 5.9 Hz, 1H), 4.03 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 167.8, 139.2, 136.7, 130.0, 129.6, 128.7, 126.9, 124.7, 123.8, 121.8, 121.5, 115.3, 104.5, 51.7. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>16</sub>H<sub>14</sub>NO<sub>2</sub>)<sup>+</sup>, 252.1019; found: 252.1007. **m.p.** = 87.7-88.6 °C.

#### 3-methyl-1-phenyl-1*H*-indole (4g)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 50:1) as a yellow solid in 86% (53.4 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>9</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.54 (m, 4H), 7.39 – 7.36 (m, 1H), 7.32 – 7.29 (m, 1H), 7.27 – 7.25 (m, 1H), 7.20 (d, *J* = 0.9 Hz, 1H), 2.47 (d, *J* = 1.1 Hz, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 140.0, 135.9, 129.7, 129.5, 125.9, 125.4, 123.9, 122.3, 119.7, 119.2, 112.8, 110.3, 9.6.

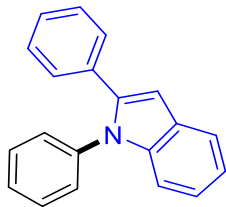
#### 2-methyl-1-phenyl-1*H*-indole (4h)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 30:1) as a yellow oil in 62% (38.5 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>9</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.59 (m, 1H), 7.56 (dt, *J* = 9.9, 1.9 Hz, 2H), 7.50 – 7.45 (m, 1H), 7.39 (dt, *J* = 8.4, 1.8 Hz, 2H), 7.19 – 7.08 (m, 3H), 6.44 (s, 1H), 2.34 (d, *J*

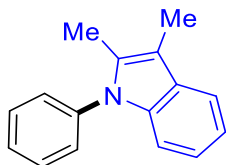
= 0.8 Hz, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 138.1, 137.9, 137.0, 129.4, 128.2, 128.0, 127.7, 121.0, 120.0, 119.5, 110.0, 101.3, 13.4.

#### 1,2-diphenyl-1*H*-indole (4i)



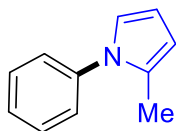
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 30:1) as a white solid in 40% (32.3 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>10</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.75 – 7.71 (m, 1H), 7.44 (dt, *J* = 10.0, 1.9 Hz, 2H), 7.39 – 7.36 (m, 1H), 7.34 (dd, *J* = 6.0, 3.3 Hz, 1H), 7.33 – 7.30 (m, 3H), 7.29 – 7.28 (m, 2H), 7.28 – 7.24 (m, 2H), 7.24 – 7.20 (m, 2H), 6.85 (d, *J* = 0.5 Hz, 1H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 140.7, 140.0, 138.5, 132.5, 129.2, 128.9, 128.2, 128.1, 128.0, 127.3, 127.2, 122.3, 120.7, 120.6, 110.7, 103.7.

#### 2,3-dimethyl-1-phenyl-1*H*-indole (4j)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 30:1) as a white solid in 81% (53.7 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>11</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.48 – 7.44 (m, 1H), 7.40 – 7.36 (m, 2H), 7.19 – 7.12 (m, 3H), 2.37 (s, 3H), 2.28 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 138.3, 137.2, 132.6, 129.3, 128.8, 128.0, 127.3, 121.1, 119.4, 117.8, 109.7, 107.9, 10.9, 8.9.

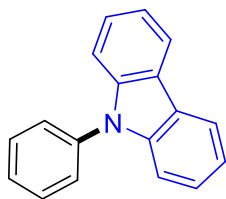
#### 2-methyl-1-phenyl-1*H*-pyrrole (4k)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a yellow solid in 53% (25.0 mg) yield. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.51 – 7.44 (m, 2H), 7.40 – 7.31 (m, 3H), 6.87 – 6.75 (m, 1H), 6.24 (t, *J* = 3.1 Hz, 1H), 6.13 – 6.05 (m, 1H), 2.26 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 140.4, 129.0, 128.9, 126.8, 125.7, 121.3, 108.1, 108.0, 12.9. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>11</sub>H<sub>12</sub>N)<sup>+</sup>, 158.0964; found: 158.0957. **m.p.** = 102.6–103.1 °C.

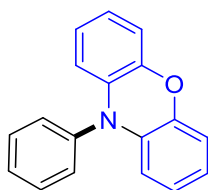
#### 9-phenyl-9*H*-carbazole (4l)





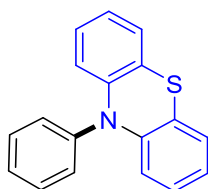
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a white crystal in 95% (69.3 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>12</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.23 (d, *J* = 7.8 Hz, 2H), 7.68 – 7.61 (m, 4H), 7.54 – 7.46 (m, 5H), 7.37 (ddd, *J* = 7.9, 5.6, 2.5 Hz, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 140.9, 137.7, 129.8, 127.4, 127.1, 125.9, 123.3, 120.3, 119.9, 109.7.

**10-phenyl-10H-phenoxazine (4m)**



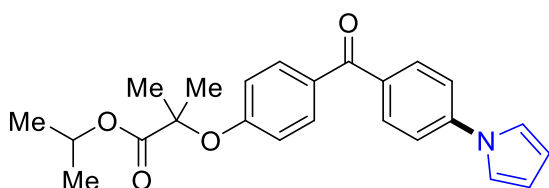
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a white crystal in 94% (73.1 mg) yield. The spectral data were in accordance with those reported in the literature.<sup>13</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.62 (dd, *J* = 10.9, 4.7 Hz, 2H), 7.51 – 7.47 (m, 1H), 7.37 (dd, *J* = 8.3, 1.1 Hz, 2H), 6.71 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.65 (dd, *J* = 10.8, 4.4 Hz, 2H), 6.61 (td, *J* = 7.7, 1.5 Hz, 2H), 5.93 (dd, *J* = 7.9, 1.5 Hz, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 143.9, 138.9, 134.4, 131.0, 130.8, 128.4, 123.2, 121.2, 115.4, 113.2.

**10-phenyl-10H-phenothiazine (4n)**



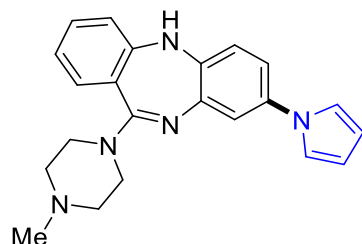
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 200:1) as a yellow solid in 98% (80.9 mg) yield; The spectral data were in accordance with those reported in the literature.<sup>13</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.61 (m, 2H), 7.51 (ddd, *J* = 4.7, 2.3, 1.1 Hz, 1H), 7.43 (dt, *J* = 8.4, 1.7 Hz, 2H), 7.06 (dd, *J* = 7.4, 1.7 Hz, 2H), 6.86 (dtd, *J* = 20.9, 7.3, 1.5 Hz, 4H), 6.25 (dd, *J* = 8.1, 1.4 Hz, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 144.2, 140.9, 130.7, 128.1, 126.7, 122.4, 120.1, 116.0, 77.2, 76.8.

**isopropyl 2-(4-(4-(1H-pyrrol-1-yl)benzoyl)phenoxy)-2-methylpropanoate (5)**



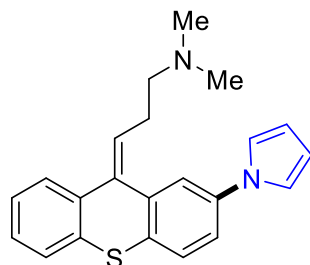
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 1:1) as a yellow solid in 88% (103.3 mg) yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.77 (t, *J* = 5.7 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.18 – 7.14 (m, 2H), 6.92 – 6.86 (m, 2H), 6.39 – 6.33 (m, 2H), 5.13 – 5.06 (m, 1H), 1.67 (s, 6H), 1.21 (d, *J* = 6.3 Hz, 6H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 193.9, 172.9, 159.4, 143.1, 134.6, 131.7, 131.5, 130.5, 119.0, 118.9, 117.1, 111.3, 79.2, 69.1, 25.2, 21.4. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>24</sub>H<sub>26</sub>NO<sub>4</sub>)<sup>+</sup>, 392.1856; found: 392.1836. **m.p.** = 107.0-108.8 °C.

**11-(4-methylpiperazin-1-yl)-8-(1*H*-pyrrol-1-yl)-5*H*-dibenzo[*b,e*][1,4]diazepine (6)**



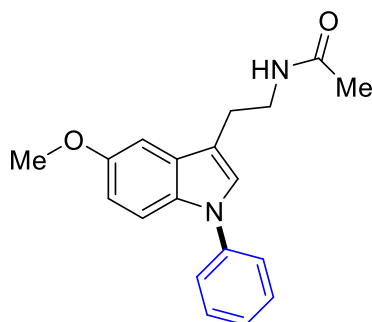
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 1:1) as a white solid in 70% (75.0 mg) yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.30 (dd, *J* = 12.4, 4.5 Hz, 2H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 7.00 (m, 2H), 6.89 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 6.28 (m, 2H), 4.99 (s, 1H), 3.50 (s, 4H), 2.53 (s, 4H), 2.35 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 162.8, 152.9, 141.4, 139.6, 137.6, 131.8, 130.3, 123.4, 122.9, 120.0, 119.7, 119.4, 119.3, 115.7, 109.7, 54.9, 46.0. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>22</sub>H<sub>24</sub>N<sub>5</sub>)<sup>+</sup>, 358.2026; found: 358.2008. **m.p.** = 105.8-106.1 °C.

**(*Z*)-3-(2-(1*H*-pyrrol-1-yl)-9*H*-thioxanthen-9-ylidene)-*N,N*-dimethylpropan-1-amine (7)**



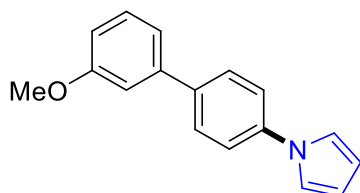
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 1:1) as a yellow solid in 86% (89.3 mg) yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.51 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.49 – 7.47 (m, 2H), 7.38 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.24 – 7.22 (m, 1H), 7.10 (m, 2H), 6.37 (m, 2H), 5.99 (t, *J* = 7.3 Hz, 1H), 2.66 (q, *J* = 7.3 Hz, 2H), 2.49 (t, *J* = 7.3 Hz, 2H), 2.24 (s, 6H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 138.9, 138.1, 136.0, 135.0, 131.5, 130.8, 130.7, 127.6, 127.0, 126.9, 125.8, 125.7, 120.6, 119.4, 119.3, 59.5, 45.4, 28.3. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>22</sub>H<sub>23</sub>N<sub>2</sub>S)<sup>+</sup>, 347.1576; found: 347.1560. **m.p.** = 100.2-100.7 °C.

***N*-(2-(5-methoxy-1-phenyl-1*H*-indol-3-yl)ethyl)acetamide (8)**



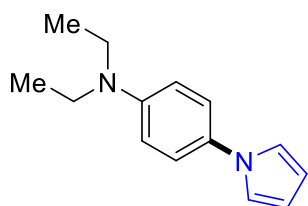
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 1:1) as a yellow solid in 85% (78.6 mg) yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.50 – 7.42 (m, 5H), 7.34 – 7.28 (m, 1H), 7.17 (s, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.07 (s, 1H), 3.88 (d, *J* = 7.1 Hz, 3H), 3.61 (dd, *J* = 12.9, 6.8 Hz, 2H), 2.98 (t, *J* = 6.9 Hz, 2H), 1.94 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 170.2, 154.3, 139.6, 131.1, 129.5, 129.2, 126.0, 125.9, 123.5, 113.7, 112.5, 111.4, 100.7, 55.8, 39.6, 25.1, 23.1. **HRMS** (ESI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>19</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>)<sup>+</sup>, 309.1598; found: 309.1584. **m.p.** = 115.2-116.3 °C.

#### 1-(3'-methoxy-[1,1'-biphenyl]-4-yl)-1H-pyrrole (9)



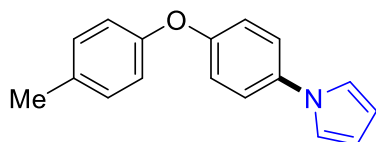
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 50:1) as a white solid in 95% (71.0 mg) yield; The spectral data were in accordance with those reported in the literature.<sup>14</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.71 – 7.66 (m, 2H), 7.52 – 7.48 (m, 2H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.25 (dd, *J* = 7.9, 7.4 Hz, 1H), 7.21 – 7.19 (m, 1H), 7.19 (m, 2H), 6.99 – 6.94 (m, 1H), 6.44 (m, 2H), 3.92 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 160.0, 141.6, 139.9, 138.2, 129.8, 128.1, 120.5, 119.3, 119.2, 112.7, 112.6, 110.5, 55.2.

#### *N,N*-diethyl-4-(1H-pyrrol-1-yl)aniline (10)



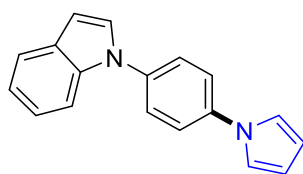
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a yellow solid in 72% (46.3 mg) yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.27 (dd, *J* = 7.9, 1.0 Hz, 2H), 7.00 (m, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 6.33 (m, 2H), 3.40 (q, *J* = 7.1 Hz, 4H), 1.21 (t, *J* = 7.1 Hz, 6H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 146.2, 130.2, 122.6, 119.8, 112.2, 109.1, 44.5, 12.5. **HRMS** (APCI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>14</sub>H<sub>19</sub>N<sub>2</sub>)<sup>+</sup>, 215.1543; found: 215.1541. **m.p.** = 116.5-117.1 °C.

#### 1-(4-(*p*-tolylloxy)phenyl)-1H-pyrrole (11)



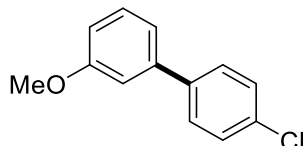
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a white solid in 68% (50.8 mg) yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.34 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.08 – 7.07 (m, 1H), 7.06 (m, 3H), 7.00 – 6.96 (m, 2H), 6.37 (m, 2H), 2.38 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 155.6, 154.7, 136.1, 133.1, 130.3, 122.0, 119.6, 119.2, 119.0, 110.1, 20.7. **HRMS** (APCI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>17</sub>H<sub>16</sub>NO)<sup>+</sup>, 250.1226; found: 250.1224. **m.p.** = 98.0-98.9 °C.

#### 1-(4-(1H-pyrrol-1-yl)phenyl)-1H-indole (12)



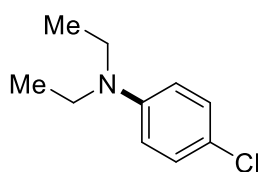
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a yellow solid in 90% (69.7 mg) yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.54 (m, 4H), 7.39 (d, *J* = 3.2 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.30 – 7.25 (m, 1H), 7.20 (m, 2H), 6.78 (d, *J* = 3.1 Hz, 1H), 6.48 (m, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 138.9, 137.2, 135.8, 129.2, 127.8, 125.3, 122.5, 121.4, 121.2, 120.5, 119.3, 110.8, 110.3, 103.8. **HRMS** (APCI) *m/z*: [M+H]<sup>+</sup> calcd for (C<sub>18</sub>H<sub>15</sub>N<sub>2</sub>)<sup>+</sup>, 259.1230; found: 259.1228. **m.p.** = 115.9-116.8 °C.

#### 4'-chloro-3-methoxy-1,1'-biphenyl (9a)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 100:1) as a colorless oil in 88% (191.9 mg) yield; The spectral data were in accordance with those reported in the literature.<sup>15</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.54 – 7.51 (m, 2H), 7.43 – 7.40 (m, 2H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.15 (ddd, *J* = 7.6, 1.5, 0.9 Hz, 1H), 7.11 – 7.09 (m, 1H), 6.92 (ddd, *J* = 8.2, 2.5, 0.7 Hz, 1H), 3.88 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 160.0, 141.5, 139.5, 133.5, 129.9, 128.8, 128.4, 119.4, 112.9, 112.8, 55.3.

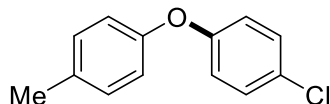
#### 4-chloro-*N,N*-diethylaniline (10a)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 20:1) as a yellow oil in 55% (100.7 mg) yield; The spectral data were in accordance with

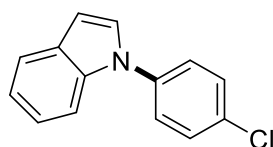
those reported in the literature.<sup>16</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.17 – 7.13 (m, 2H), 6.61 – 6.57 (m, 2H), 3.33 (q, *J* = 7.1 Hz, 4H), 1.15 (t, *J* = 7.1 Hz, 6H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 146.4, 129.0, 120.0, 112.9, 44.5, 12.4.

#### 1-chloro-4-(*p*-tolxyloxy)benzene (11a)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 1:1) as a white solid in 60% (130.8 mg) yield; The spectral data were in accordance with those reported in the literature.<sup>17</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.29 – 7.25 (m, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.97 – 6.86 (m, 4H), 2.35 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 156.5, 154.3, 133.3, 130.3, 129.6, 127.7, 119.5, 119.1, 20.7.

#### 1-(4-chlorophenyl)-1*H*-indole (12a)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc = 50:1) as a yellow oil in 52% (118.1 mg) yield; The spectral data were in accordance with those reported in the literature.<sup>18</sup> **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.48 – 7.44 (m, 2H), 7.31 (d, *J* = 3.3 Hz, 1H), 7.26 (ddd, *J* = 8.2, 6.8, 1.1 Hz, 1H), 7.23 – 7.19 (m, 1H), 6.72 (dd, *J* = 3.3, 0.7 Hz, 1H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 138.3, 135.7, 131.9, 129.7, 129.3, 127.7, 125.5, 122.6, 121.2, 120.6, 110.2, 104.0.

## 5. Gram-Scale Experiments

In a glovebox, a flame-dried reaction tube (150 mL) equipped with a magnetic stir bar was charged with <sup>t</sup>BuOLi (400 mg, 5 mmol), chlorobenzene **1** (5.5 mmol), carbazole **21** (5.0 mmol), *n*-heptane (50 mL), Pd(dba)<sub>2</sub> (12.9 mg, 1.5 mol%), and keYPhos (11.4 mg, 1.5 mol%) before being sealed with a rubber septum. The reaction mixture was stirred at 60 °C for 24 hours. After the mixture was cooled to room temperature, the mixture was directly filtered. The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired product **41** (1.12 g, 92%).

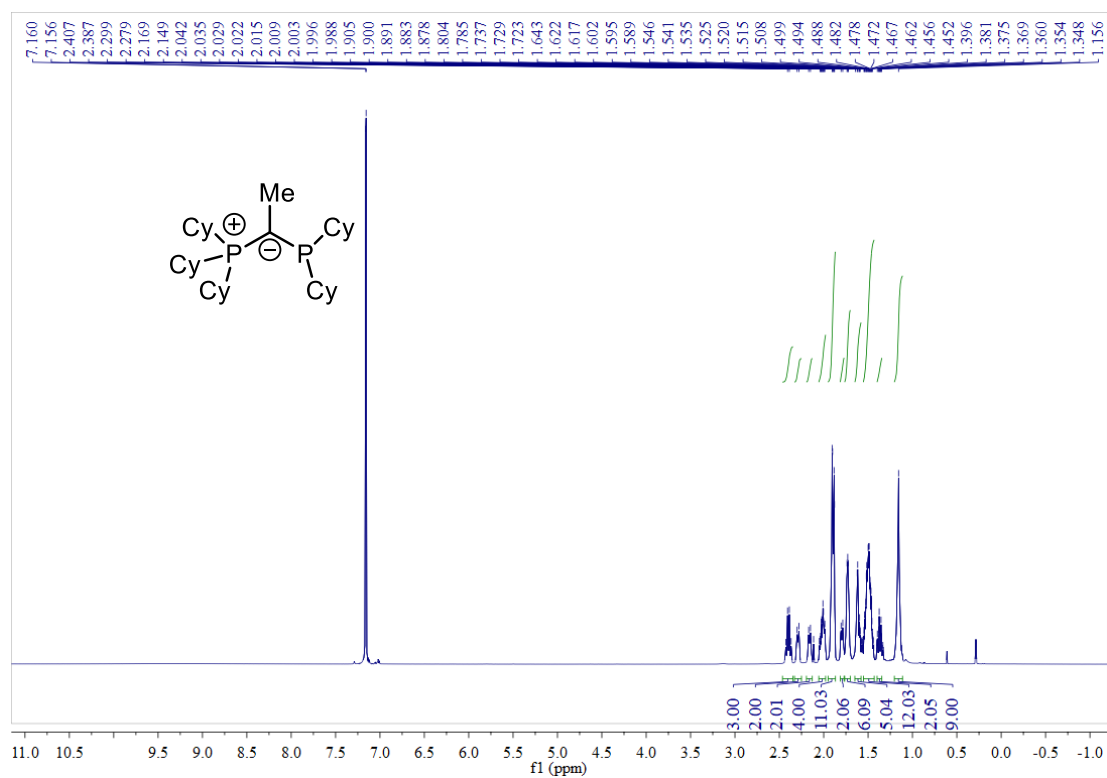
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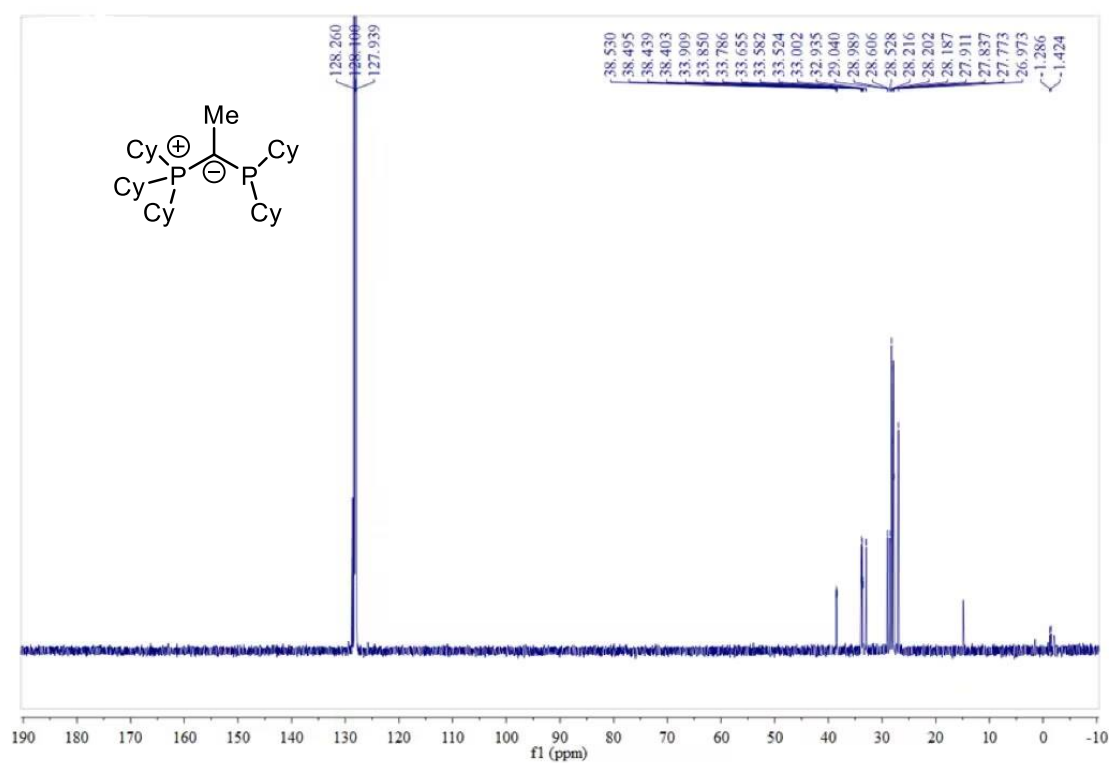
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## NMR Spectra of Starting Materials and Products

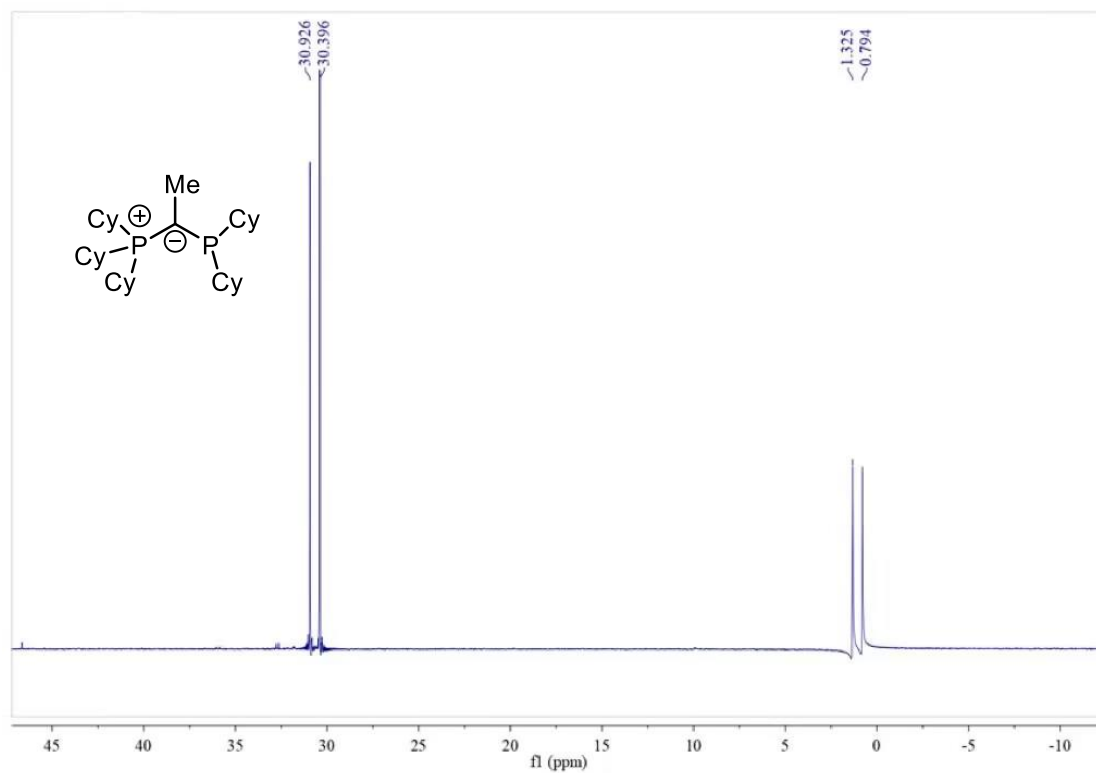
### $^1\text{H}$ NMR (600 MHz, $\text{C}_6\text{D}_6$ ) Spectrum of **keYPhos**



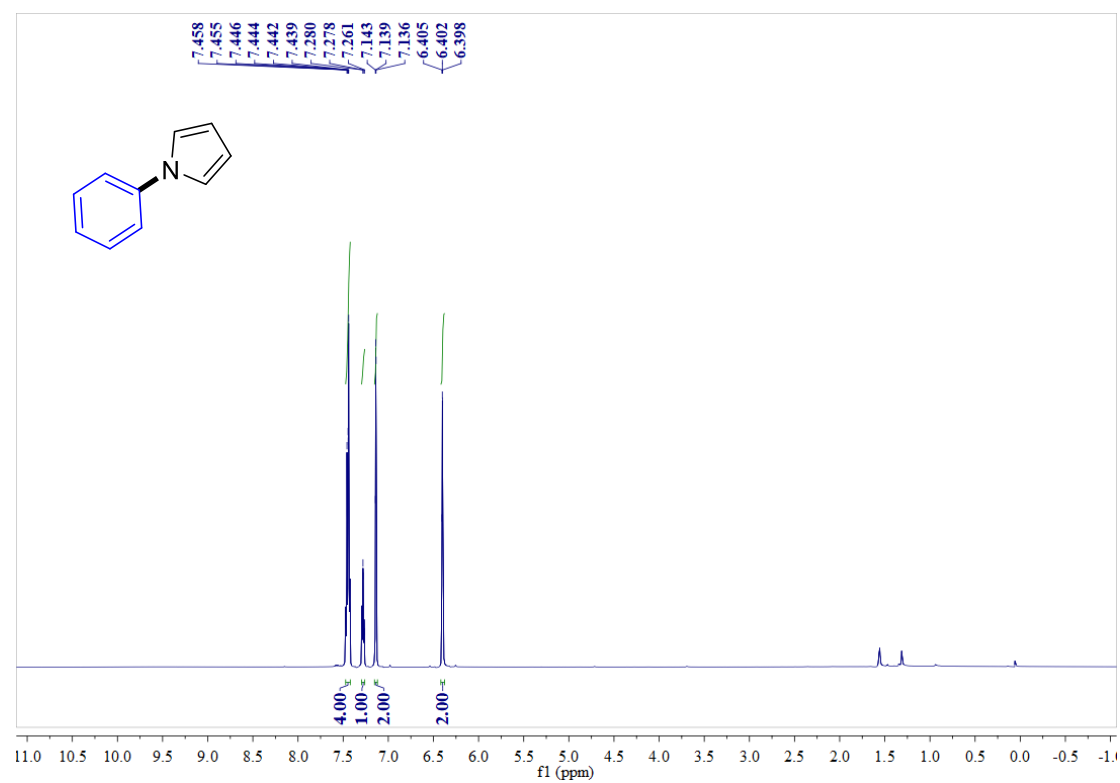
### $^{13}\text{C}$ NMR (151 MHz, $\text{C}_6\text{D}_6$ ) Spectrum of **keYPhos**



$^{31}\text{P}$  NMR(243 MHz,  $\text{C}_6\text{D}_6$ ) Spectrum of **keYPhos**

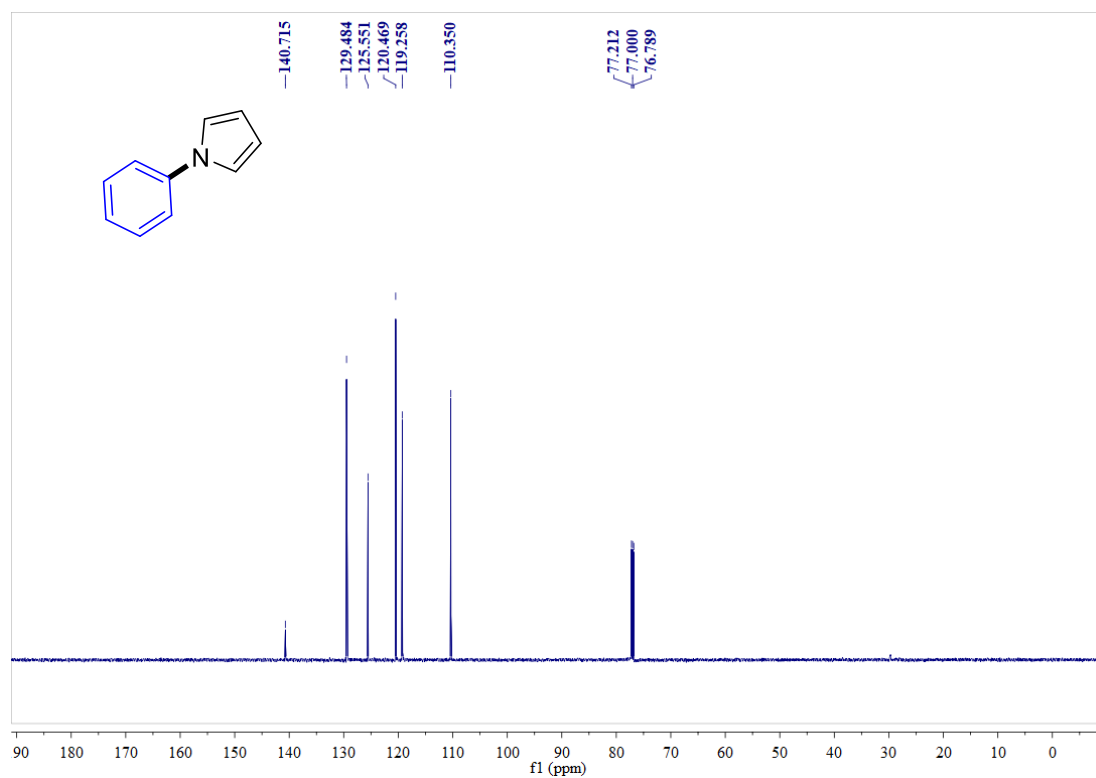


$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3a**

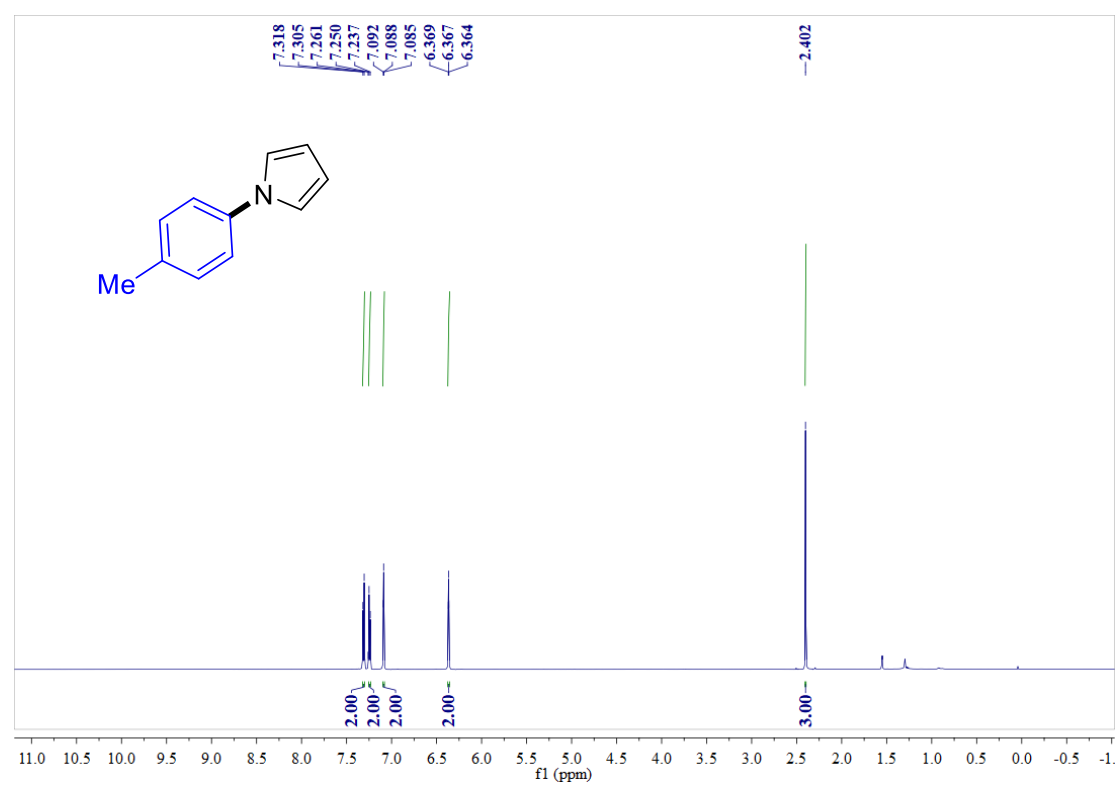




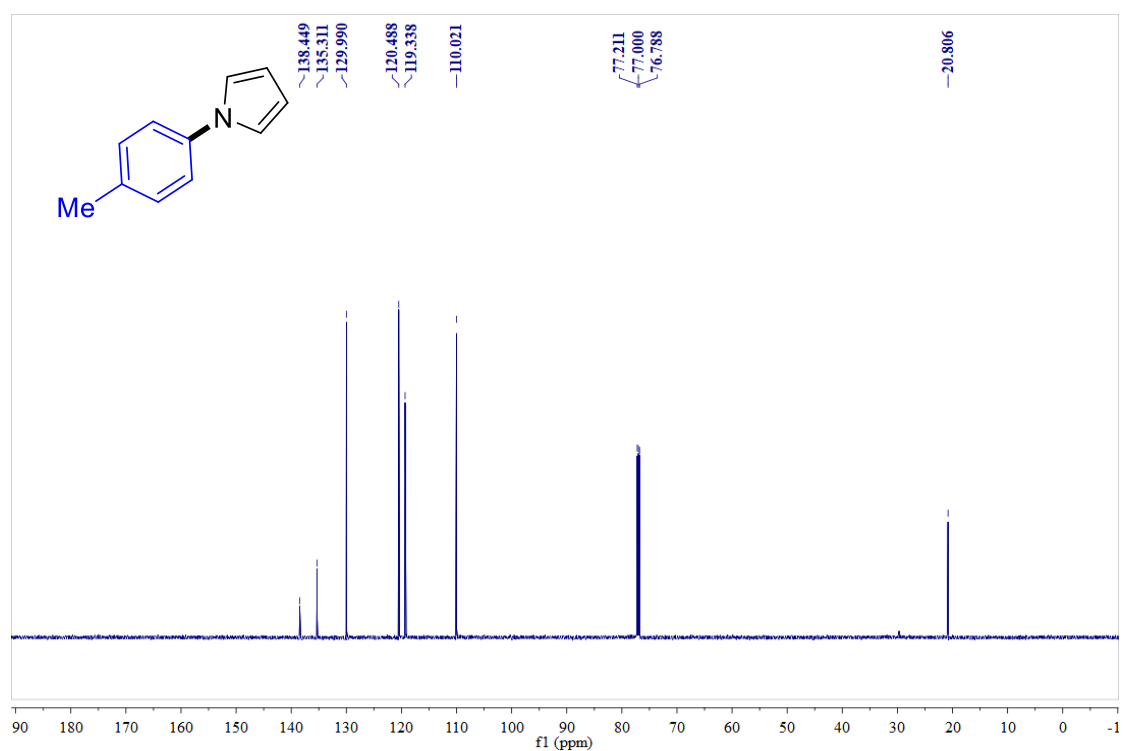
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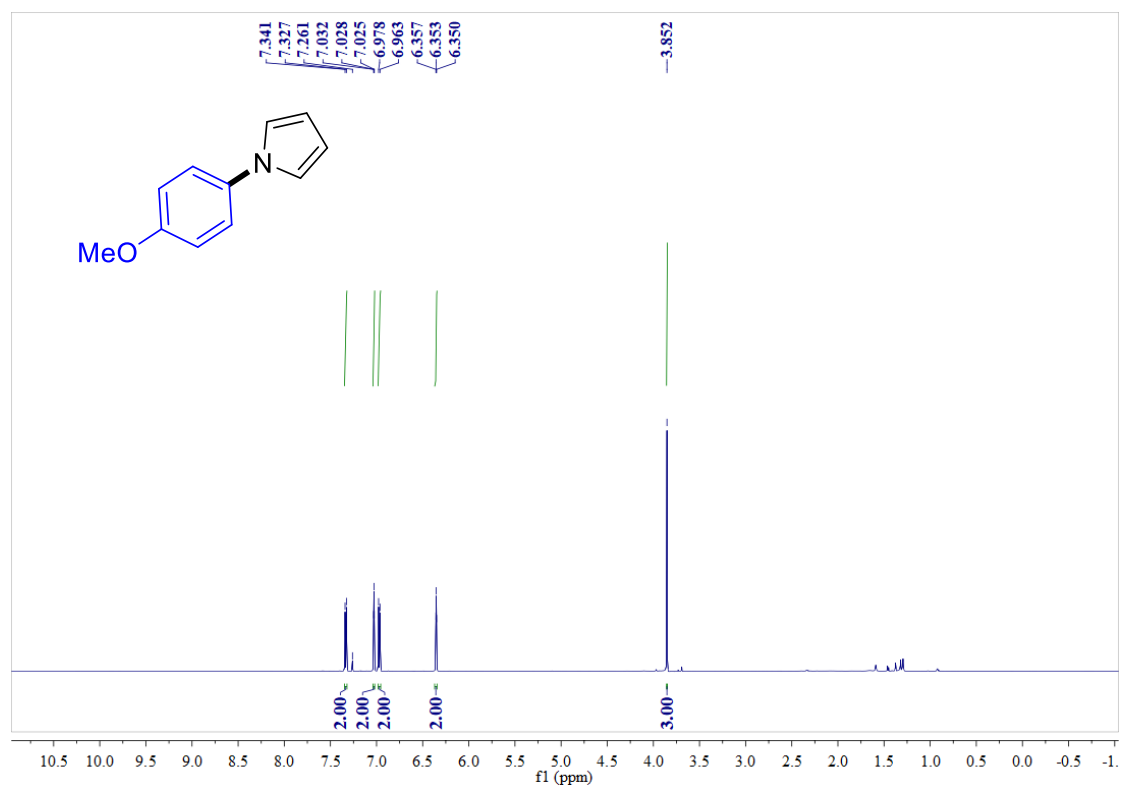
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3b**



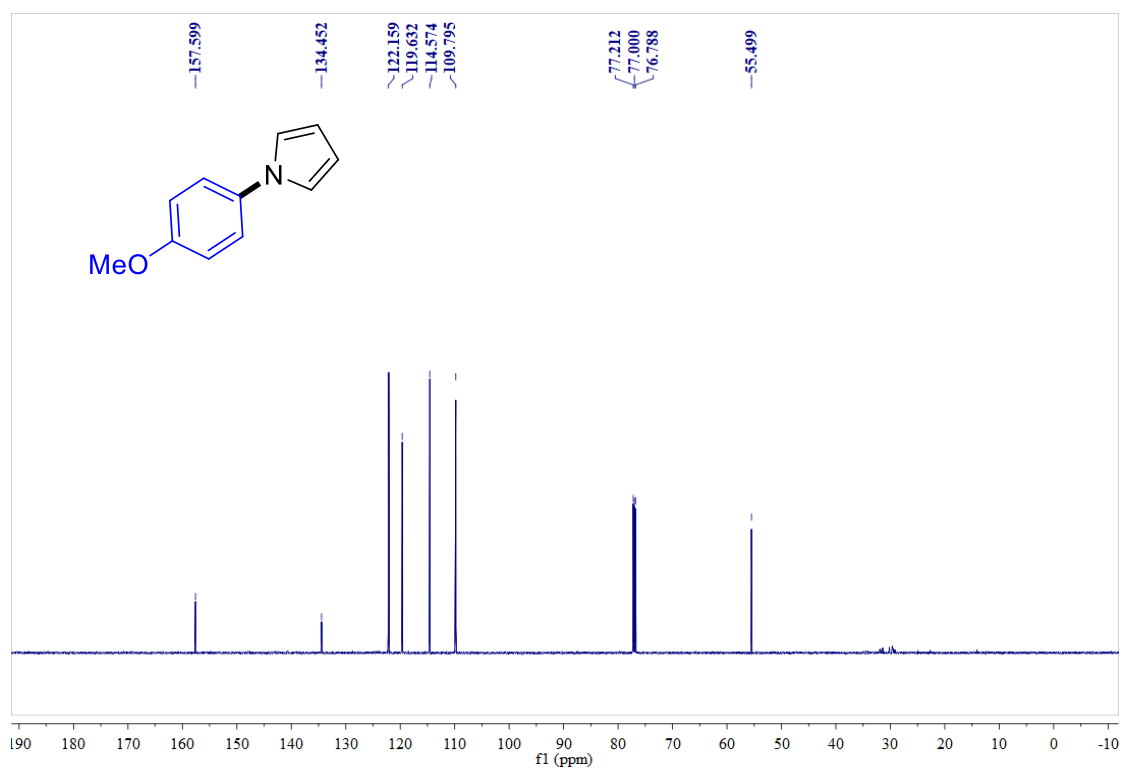
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **3b**



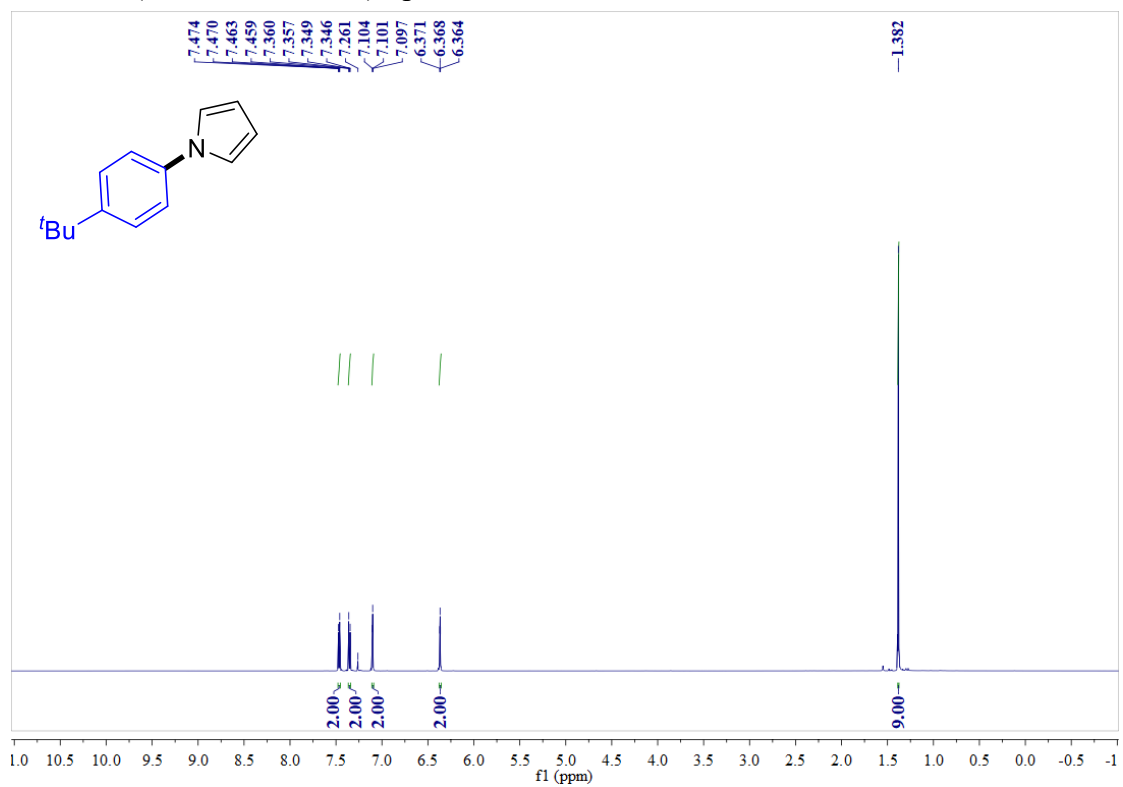
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **3c**



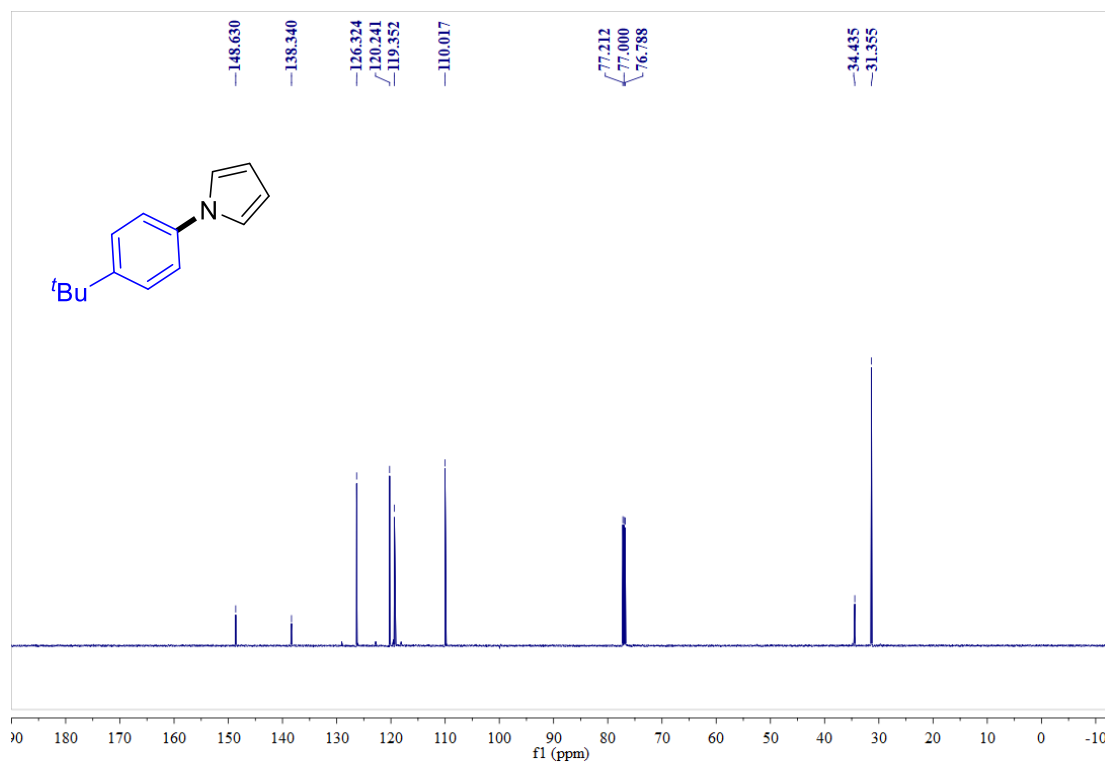
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **3c**



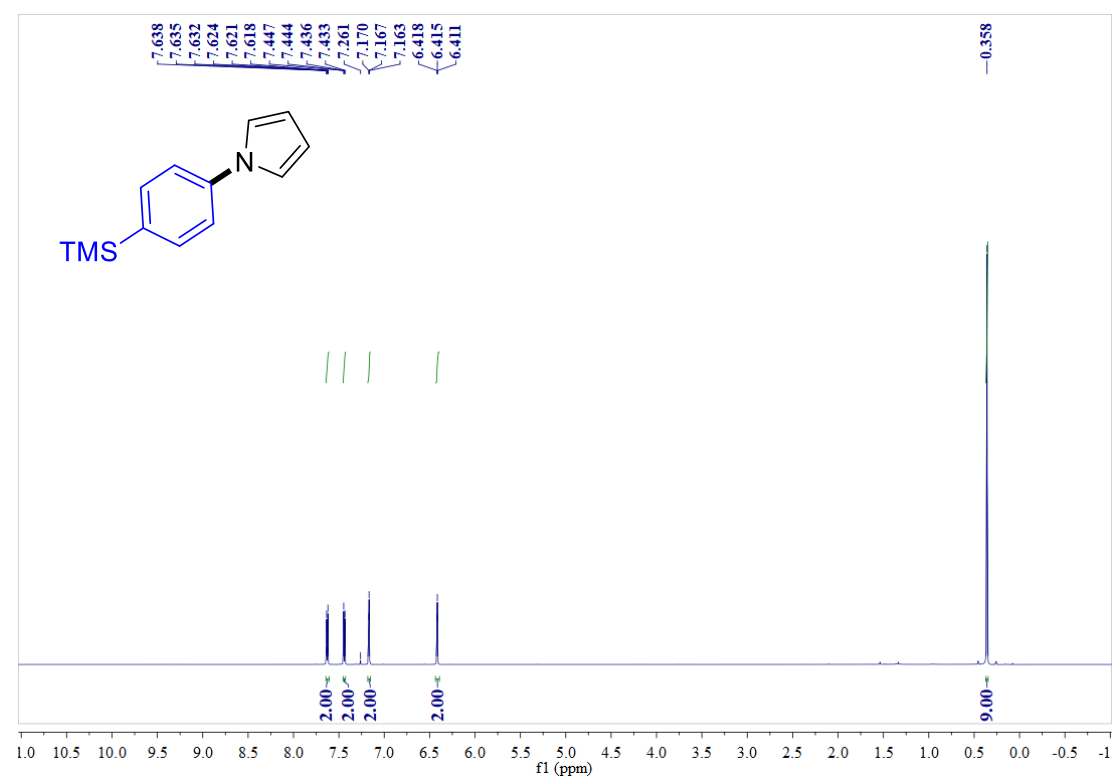
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3d**



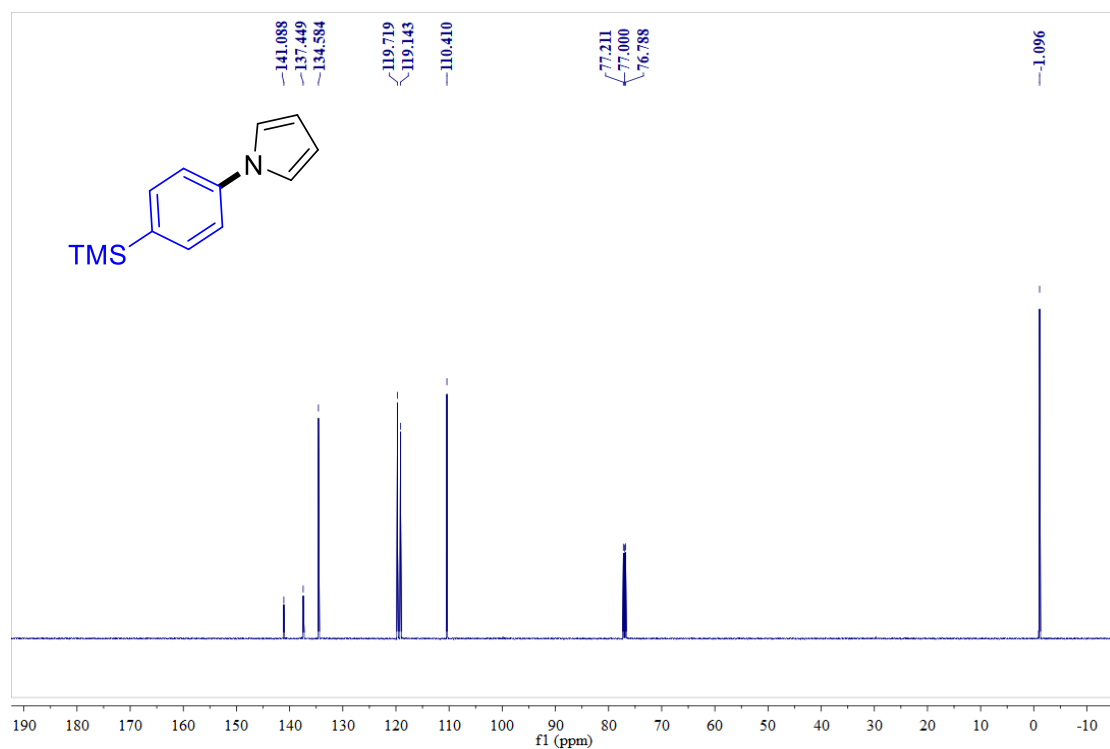
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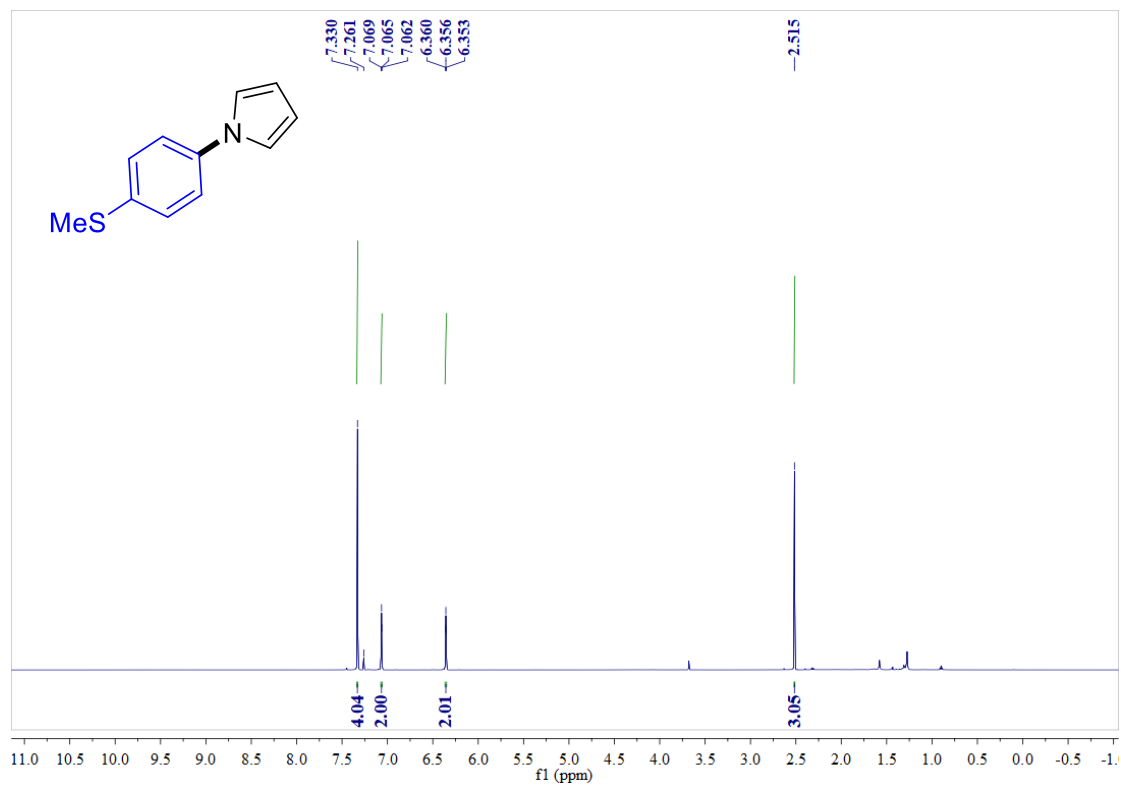
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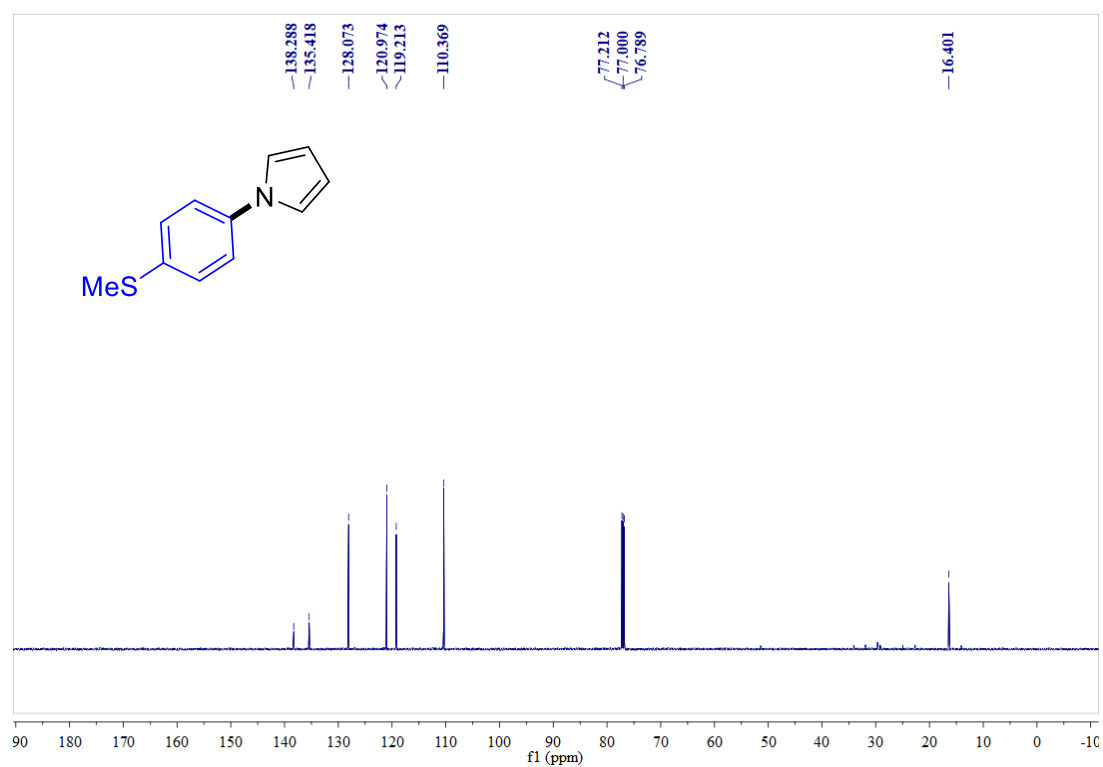
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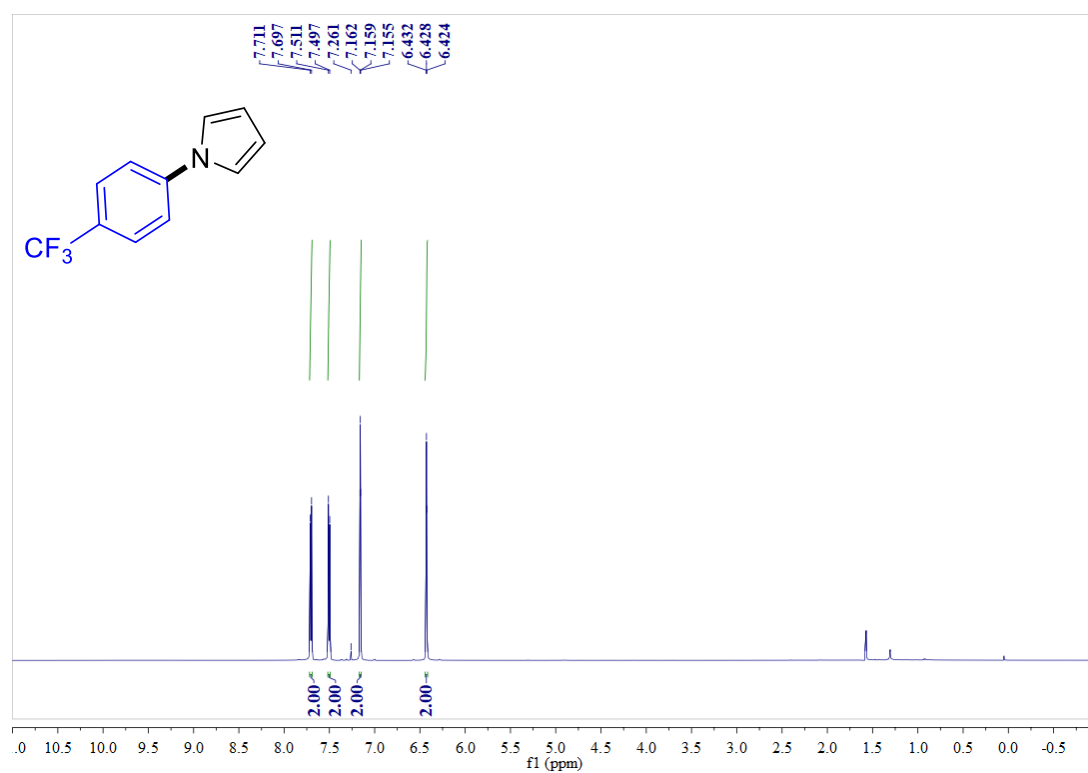
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3f**



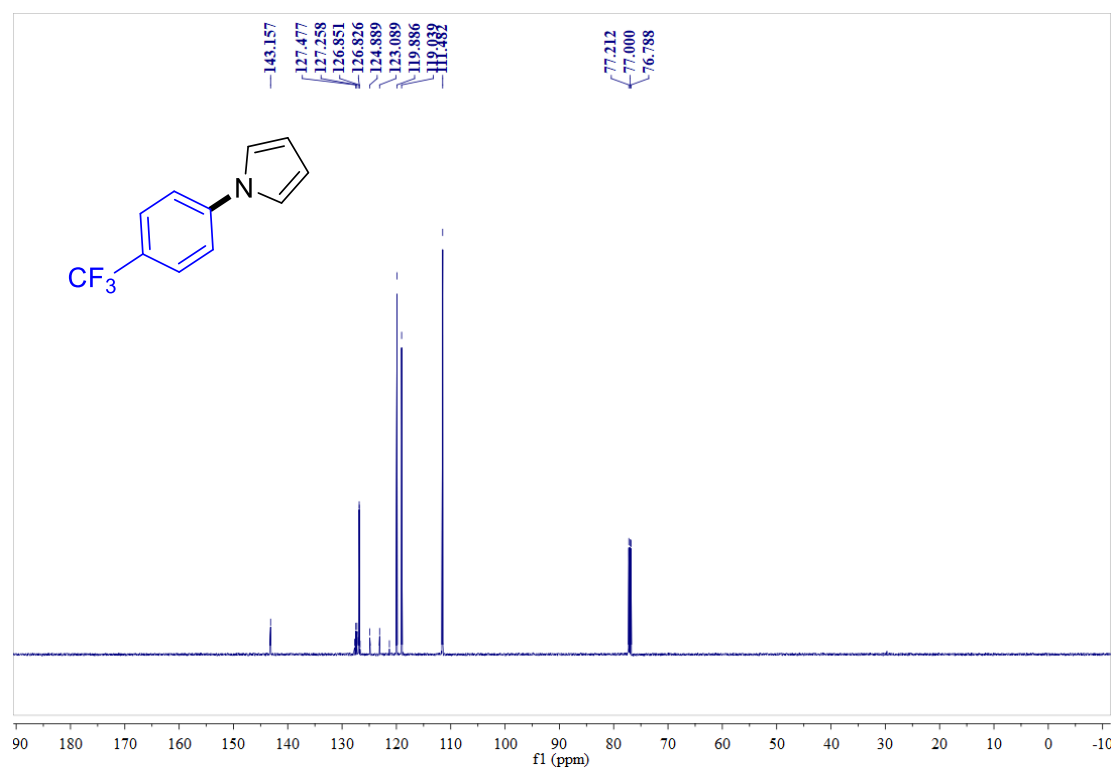
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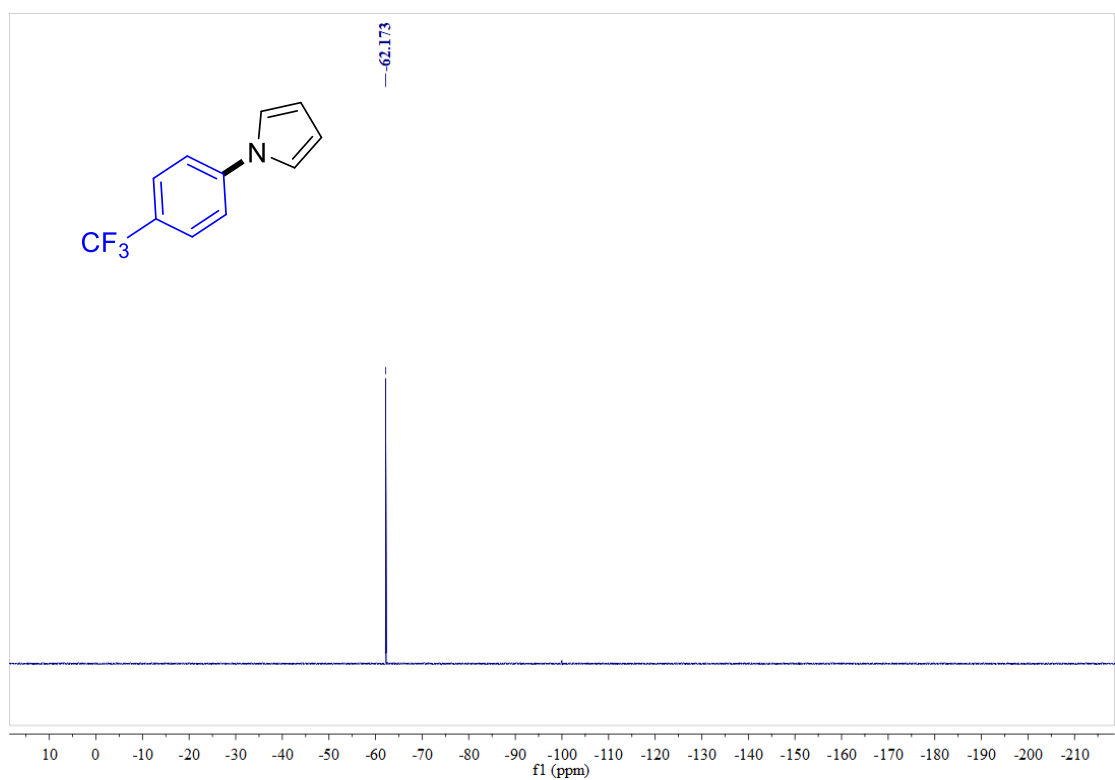
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3g**



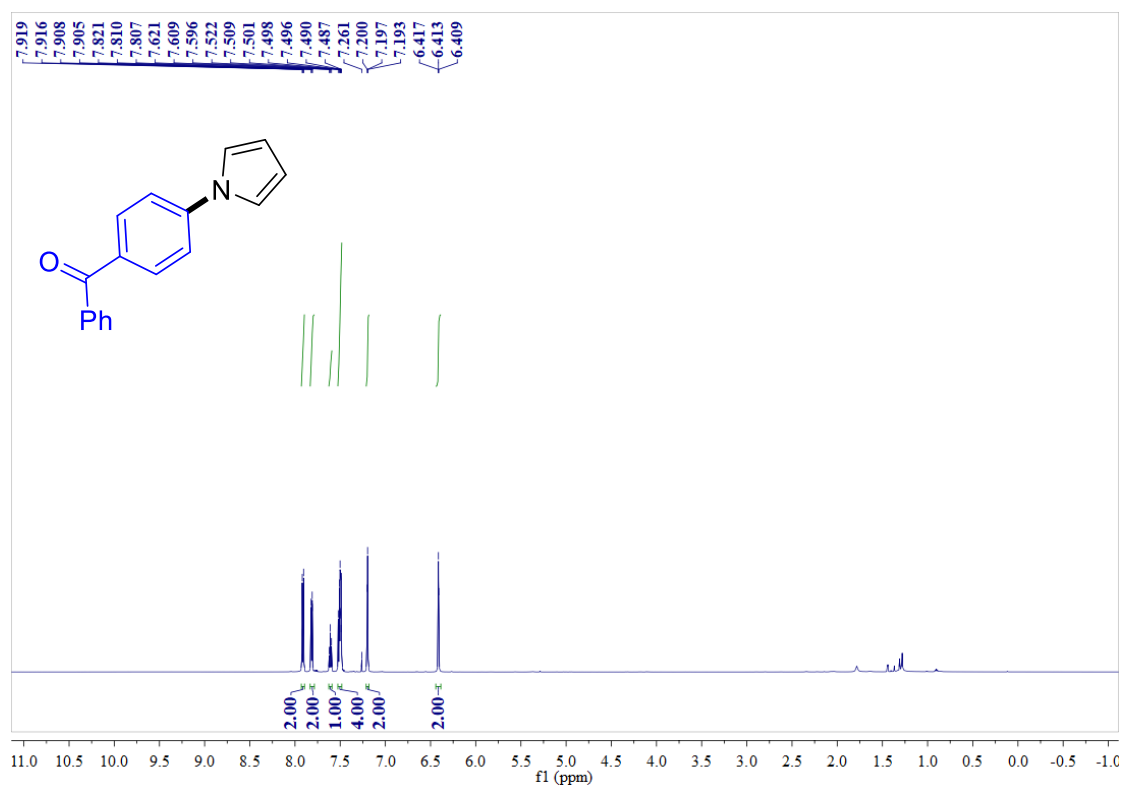
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **3g**



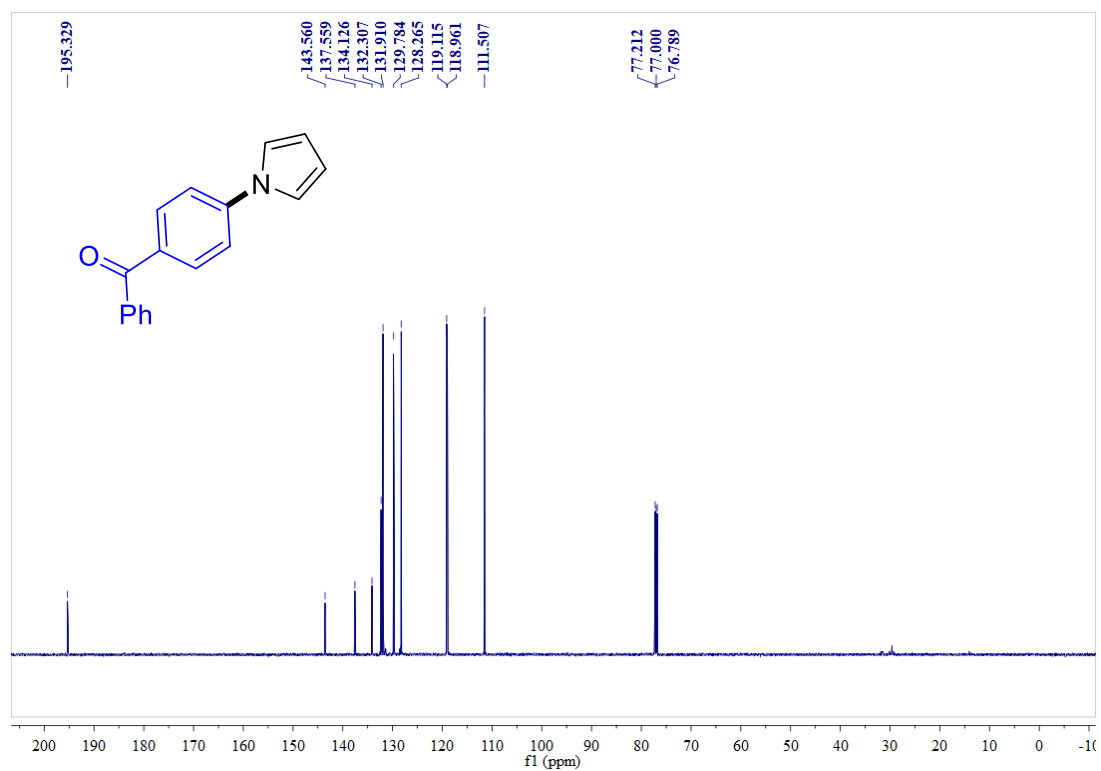
<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) Spectrum of **3g**



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3h**

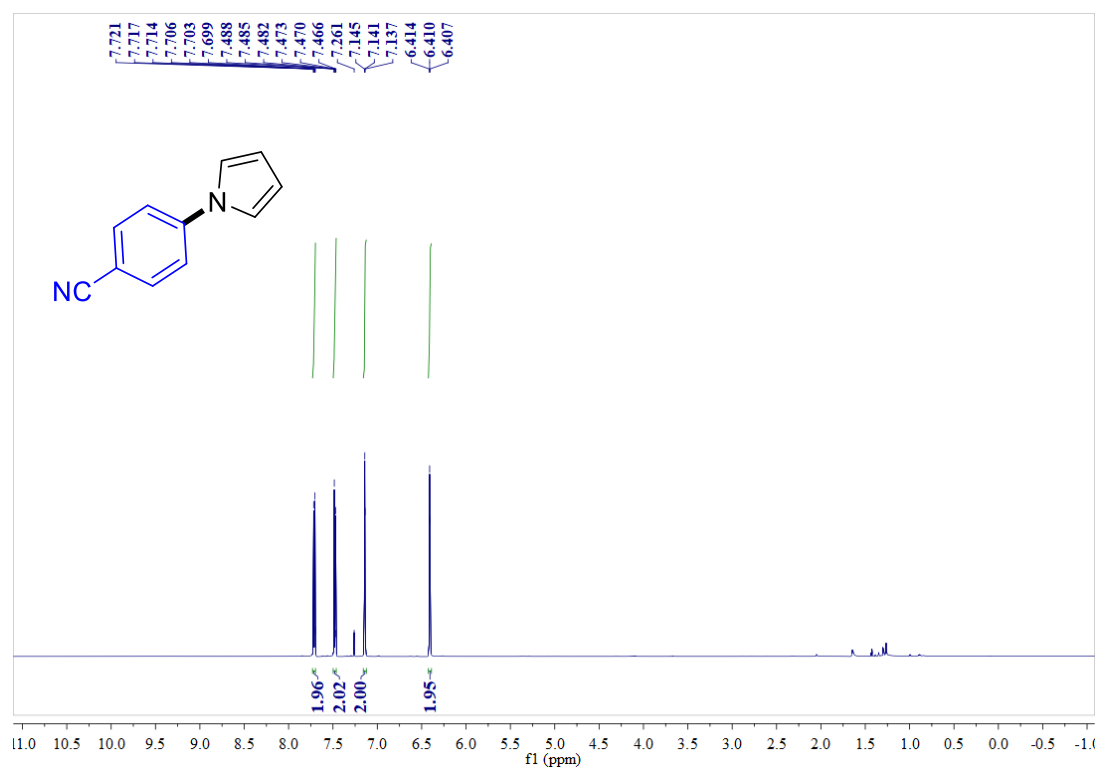


$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **3h**

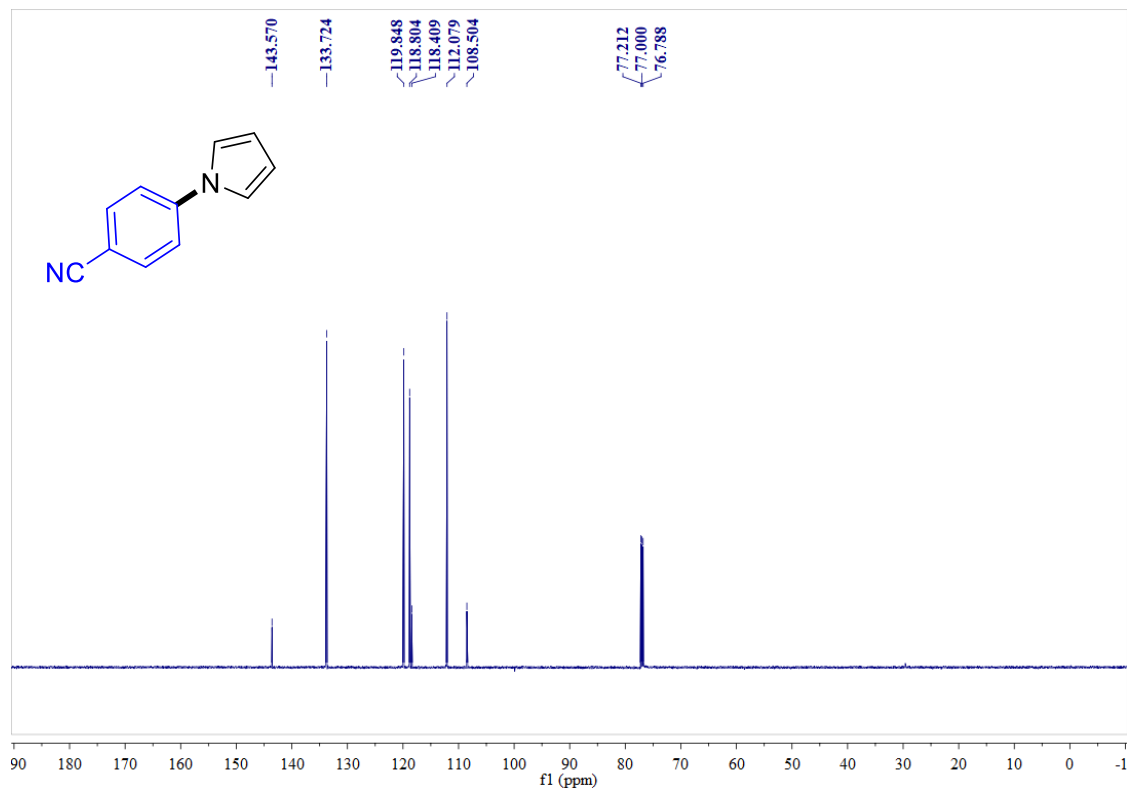




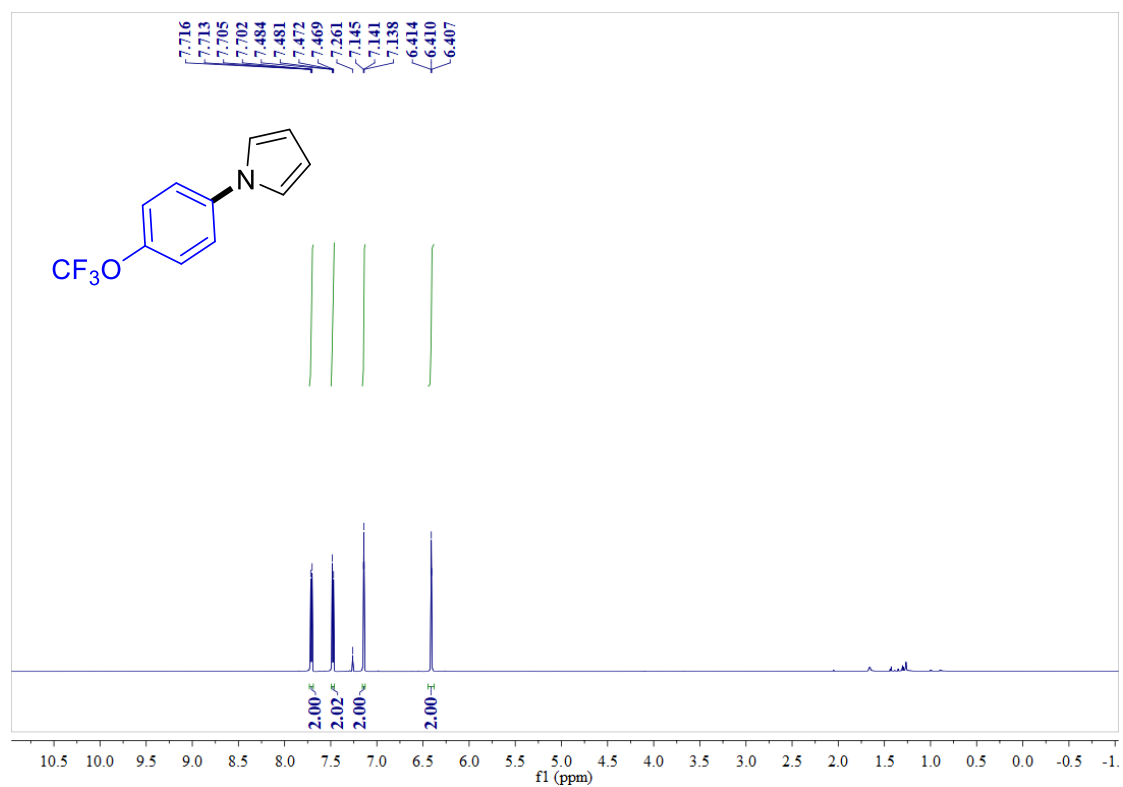
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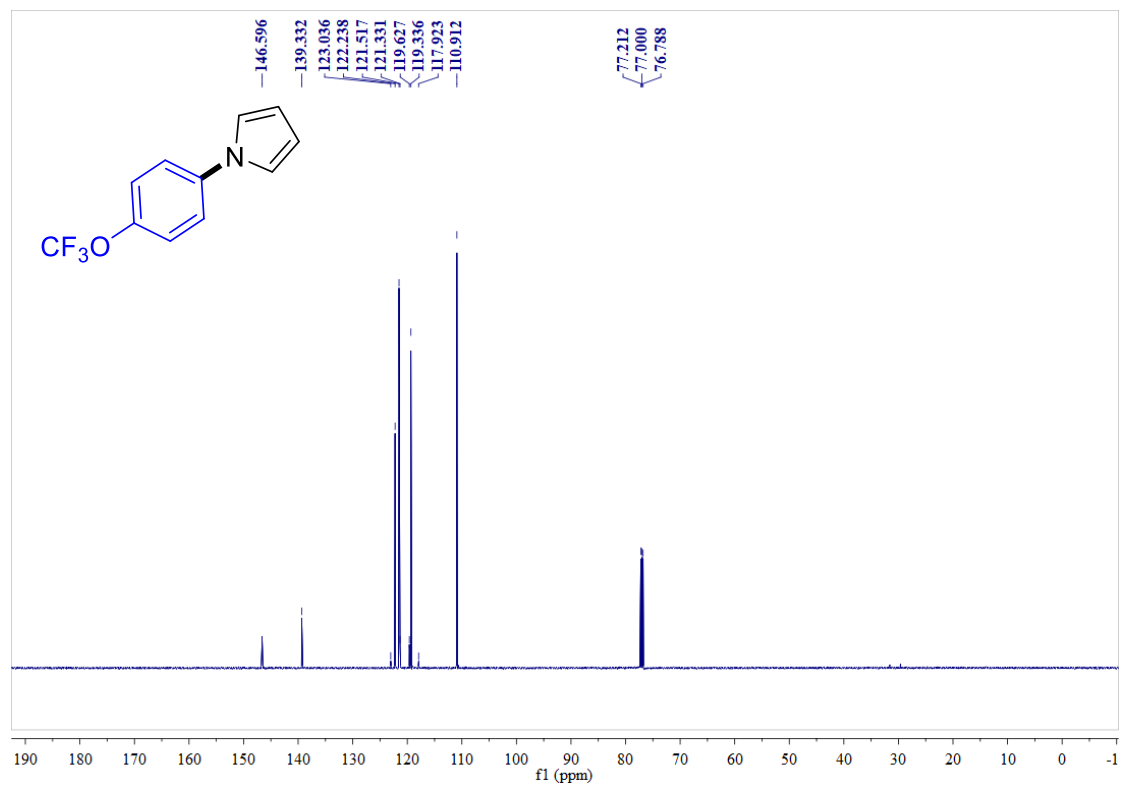
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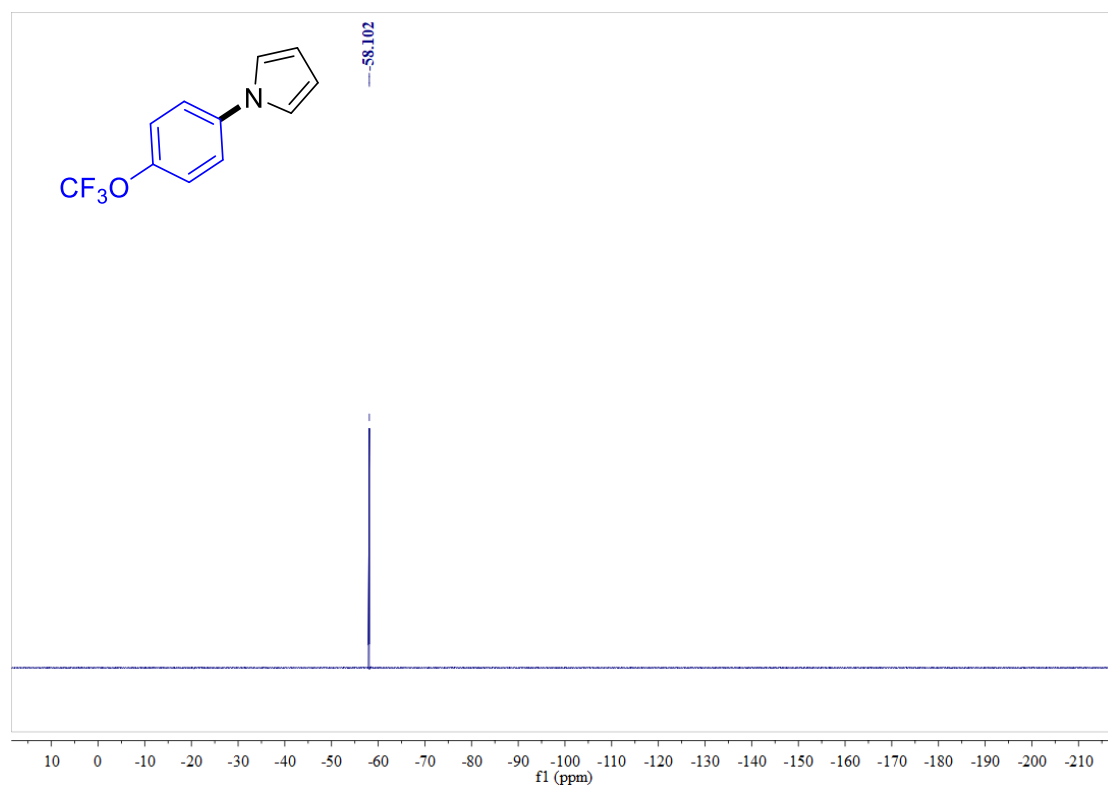
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **3j**



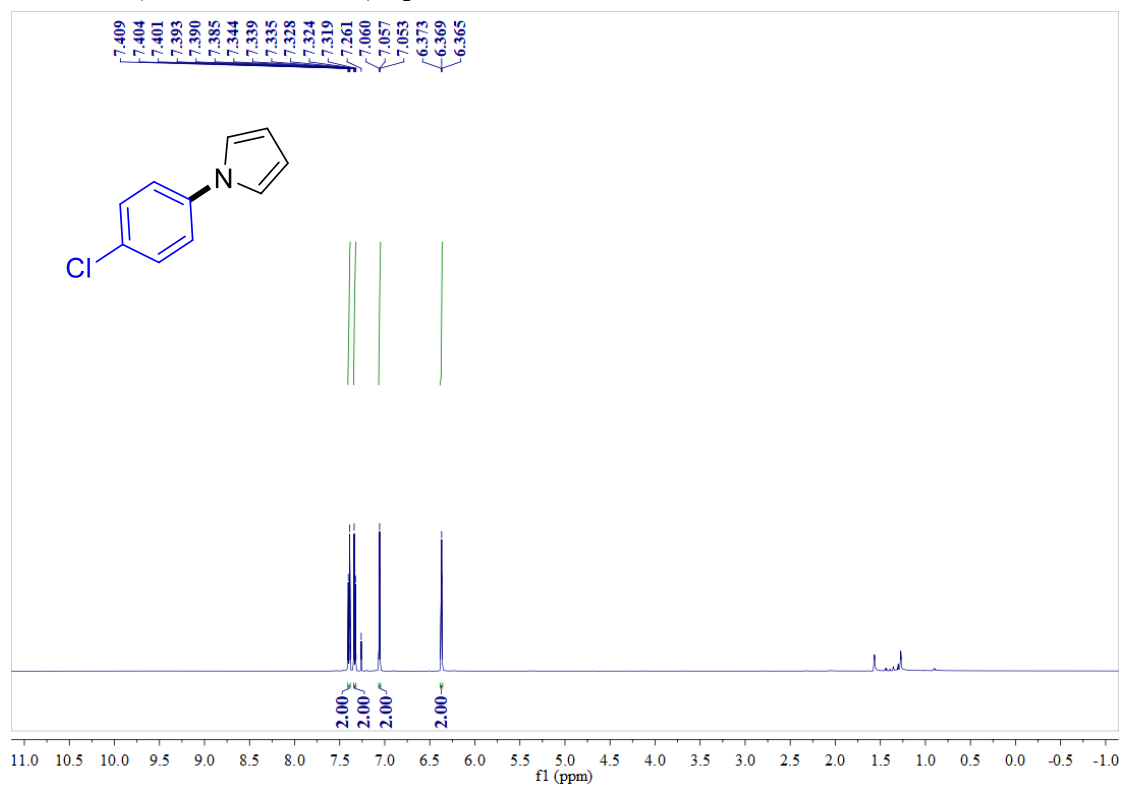
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **3j**



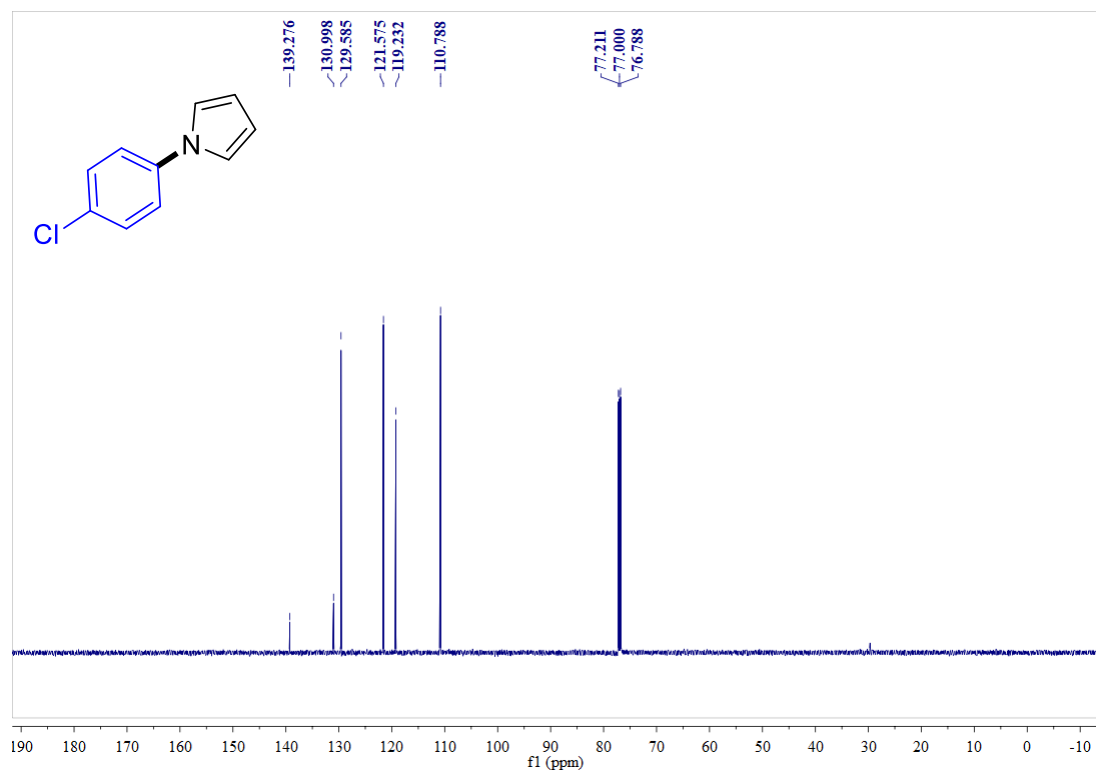
$^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ ) Spectrum of **3j**



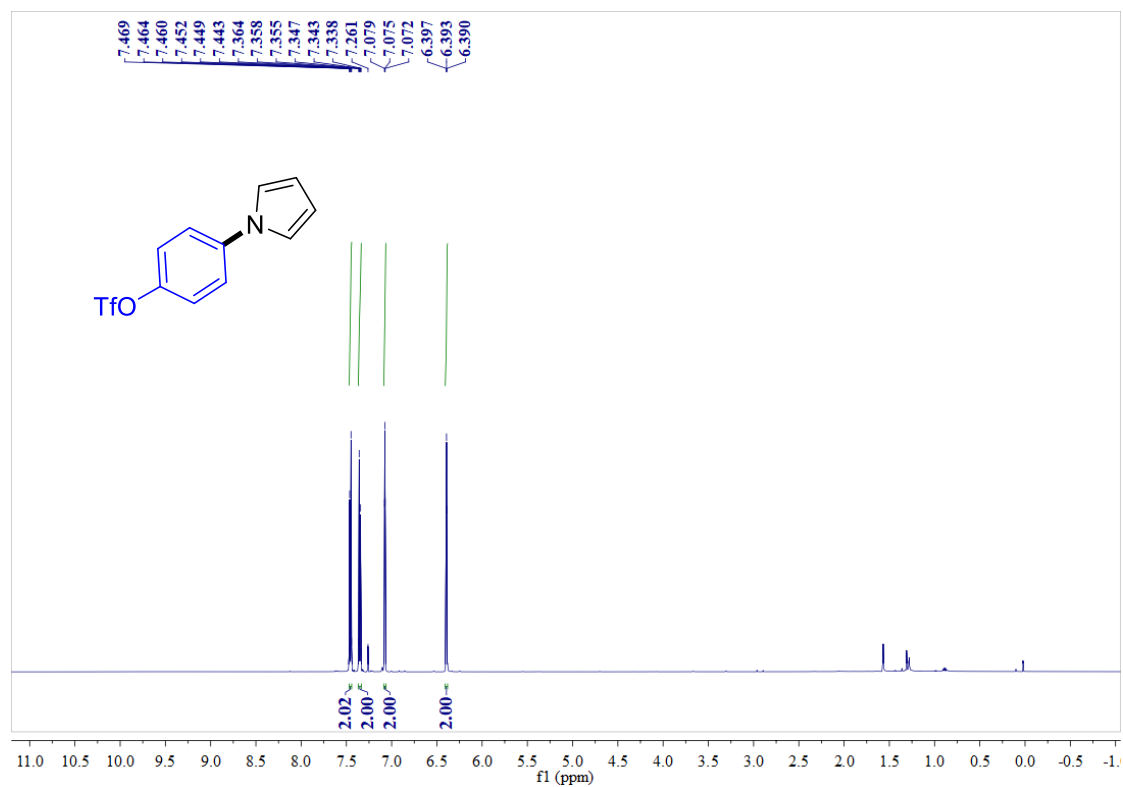
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3k**



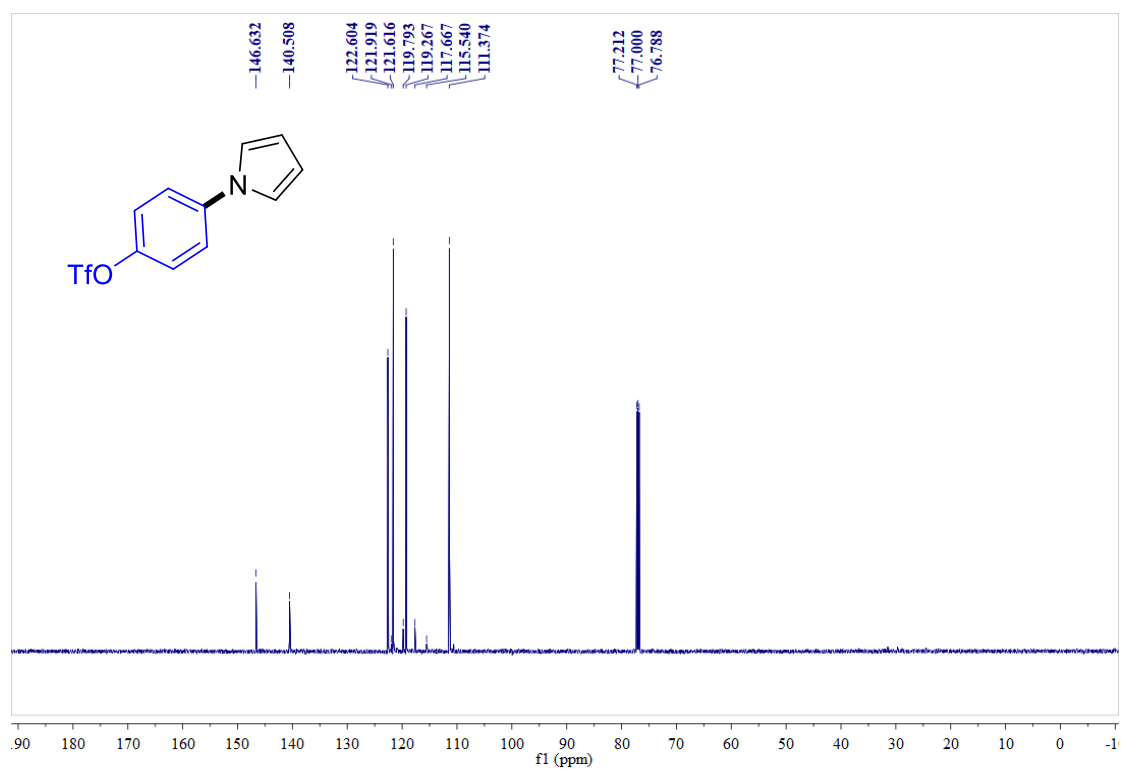
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **3k**



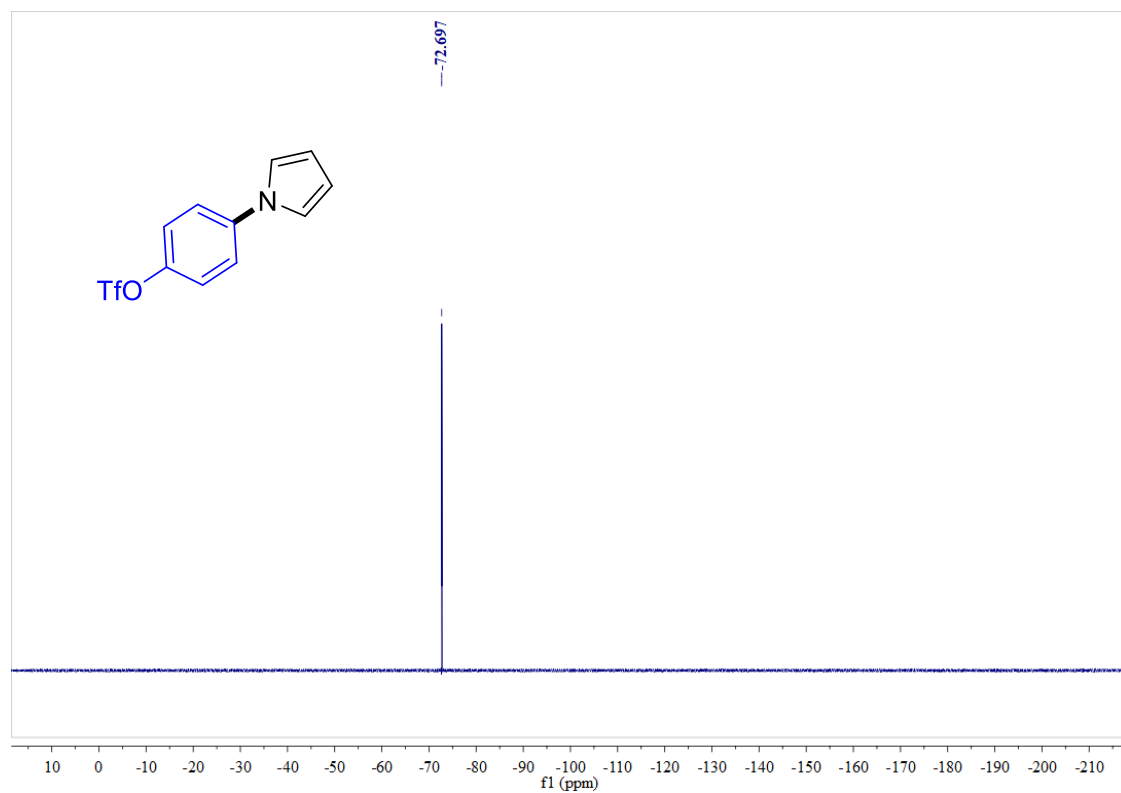
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3l**



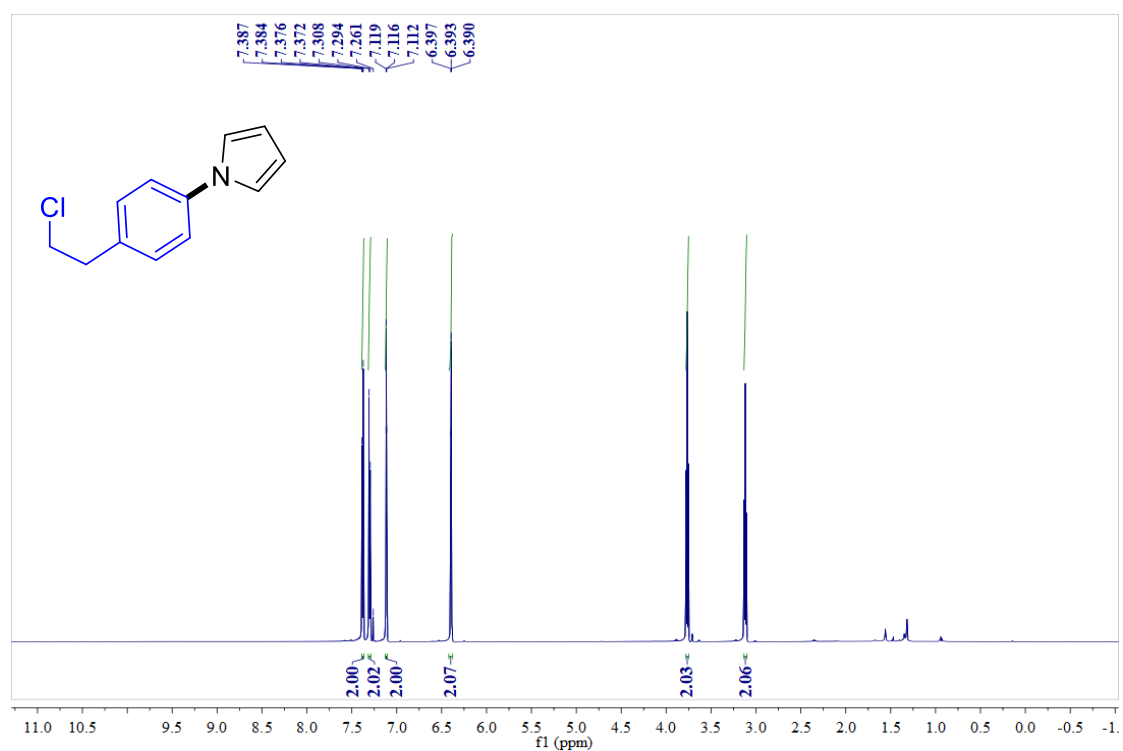
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **3l**



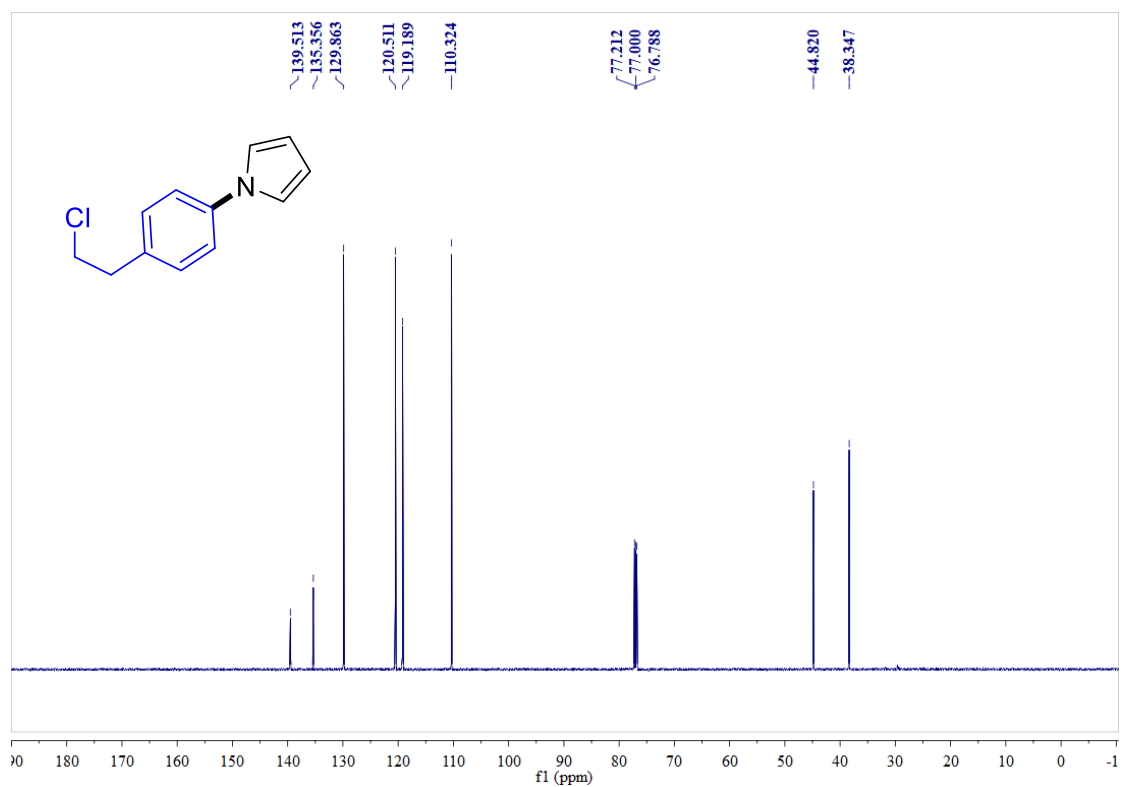
$^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ ) Spectrum of **3l**



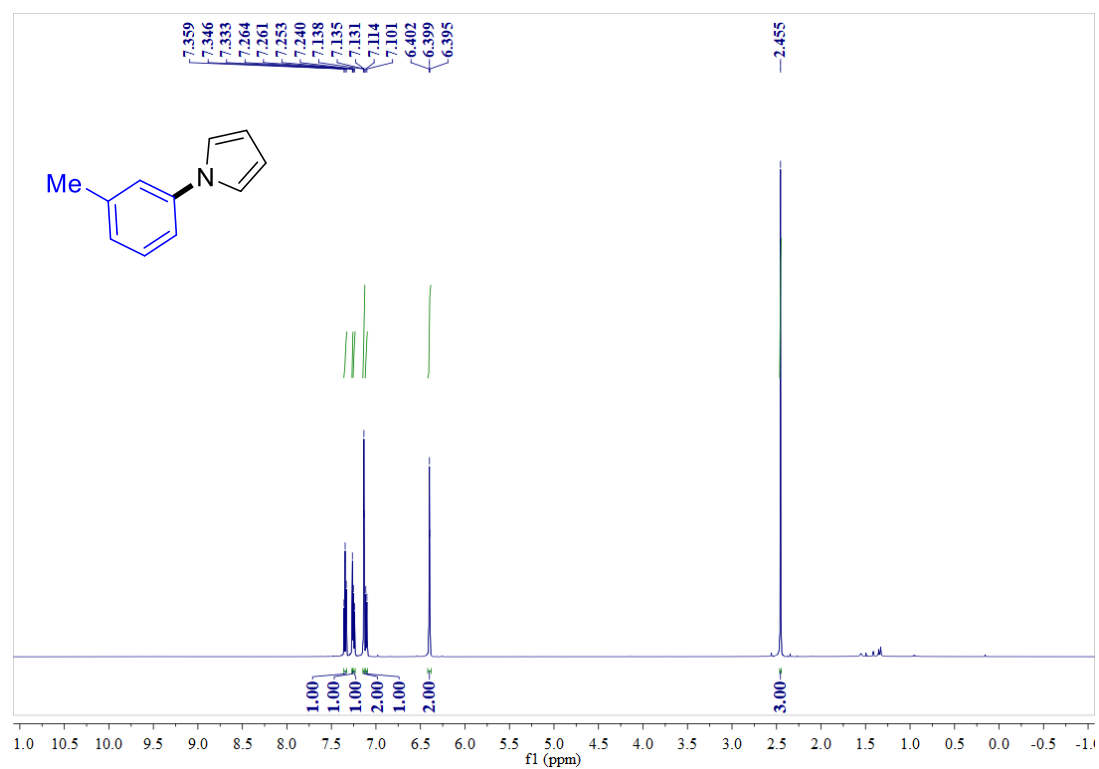
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **3m**



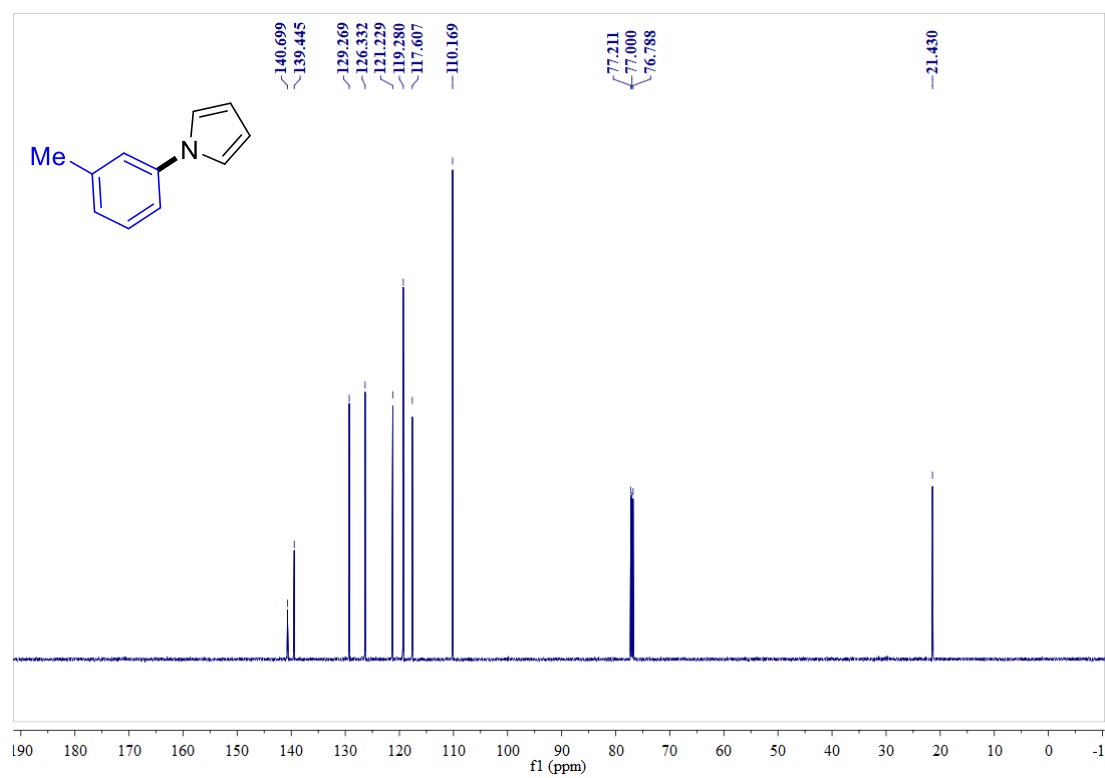
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **3m**



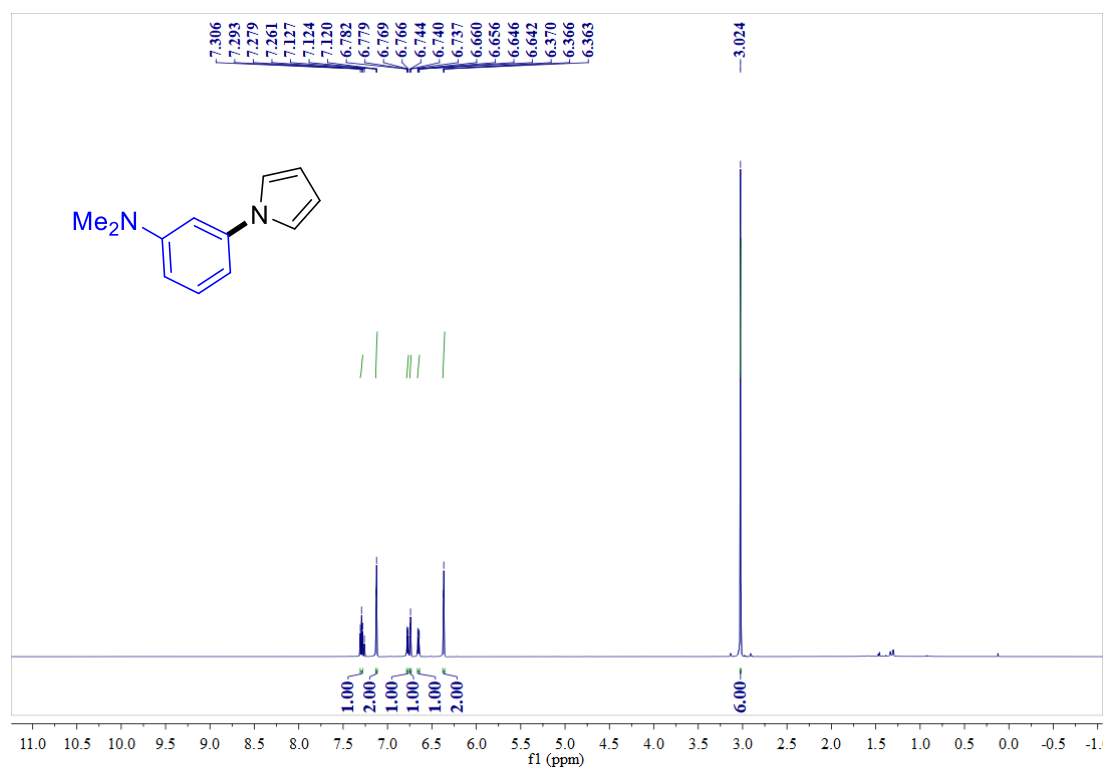
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3n**



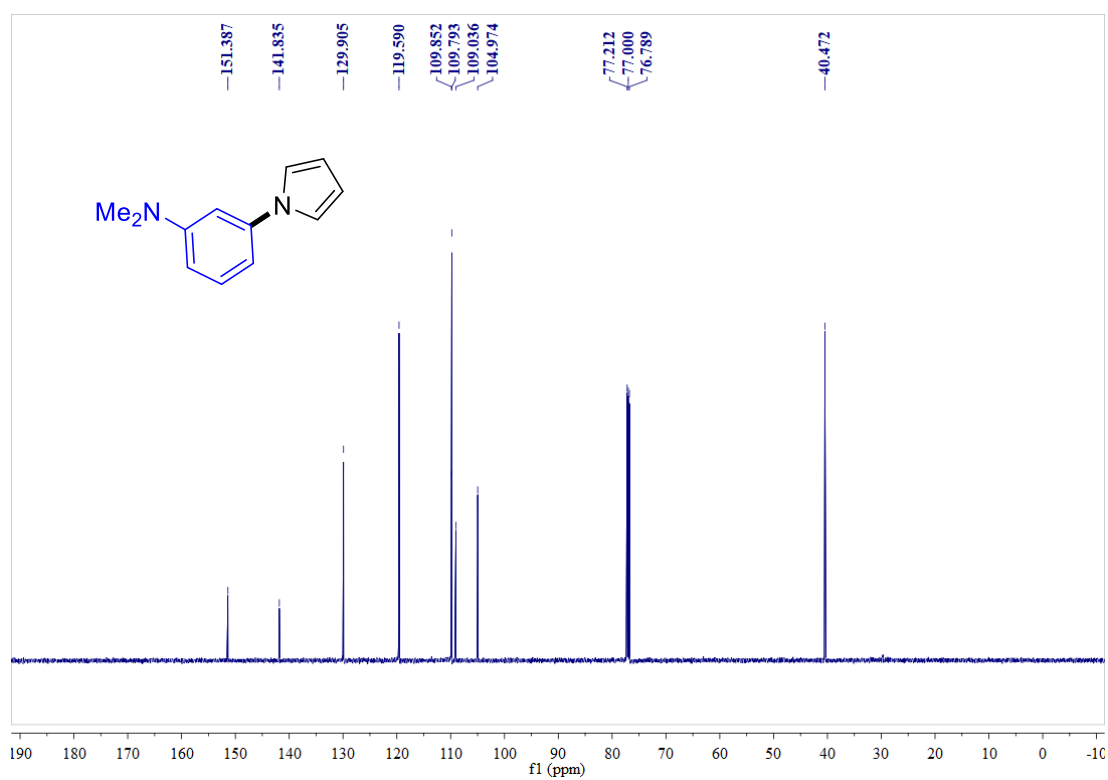
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **3n**



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3o**

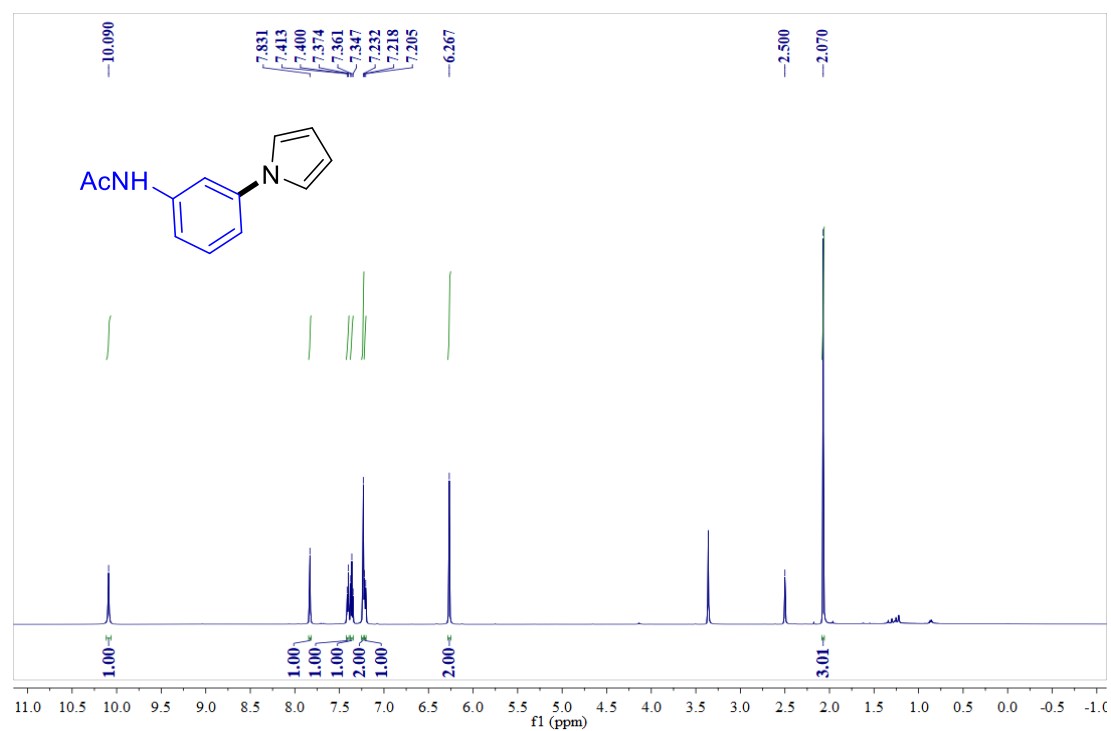


$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **3o**

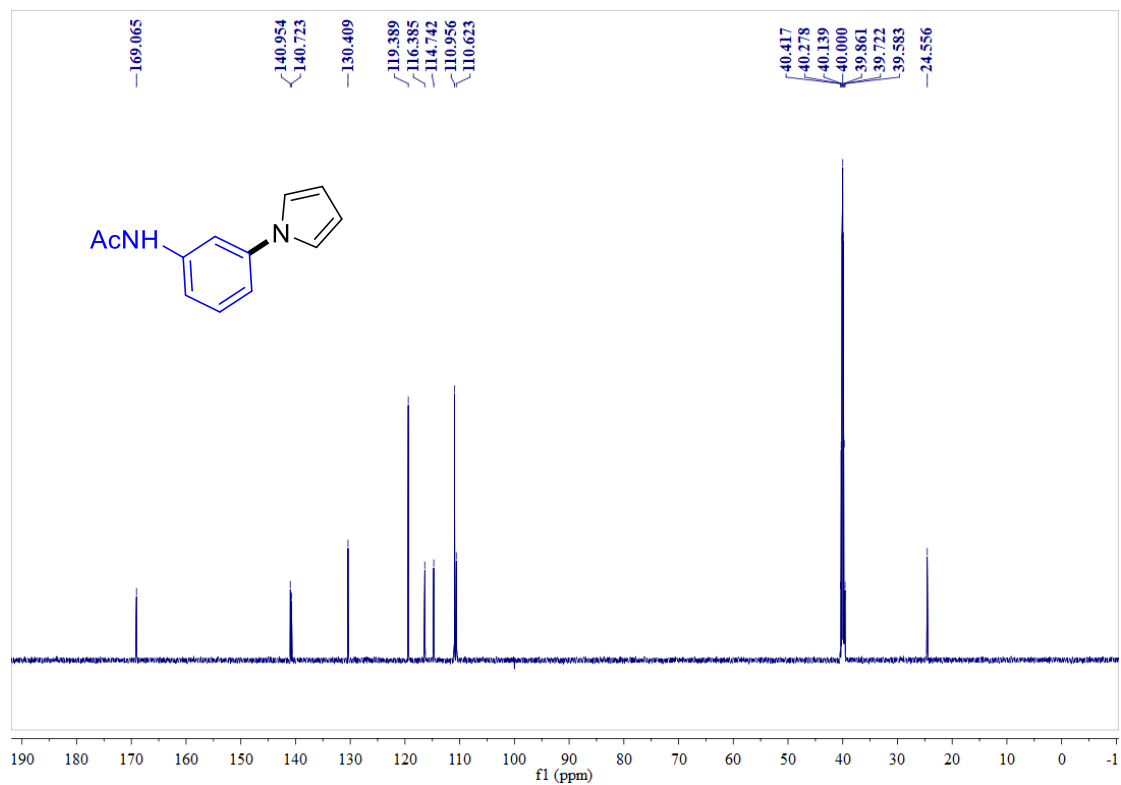




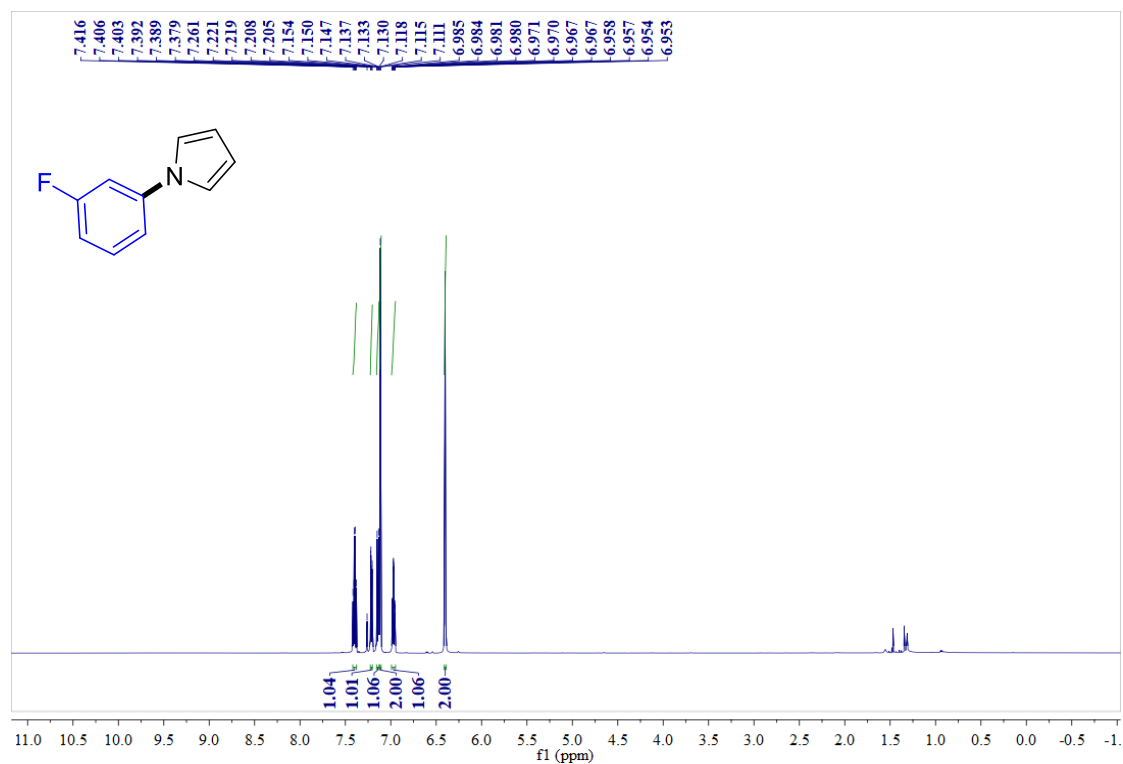
$^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ ) Spectrum of **3p**



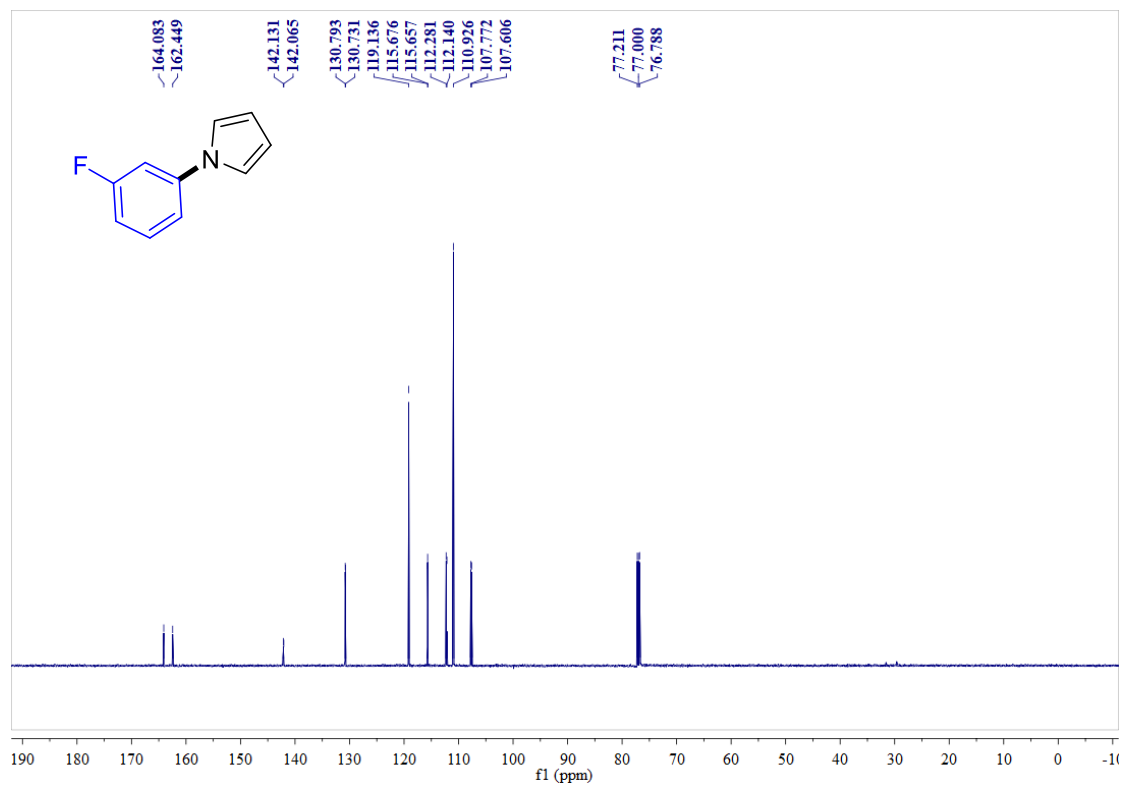
$^{13}\text{C}$  NMR (151 MHz,  $\text{DMSO}-d_6$ ) Spectrum of **3p**



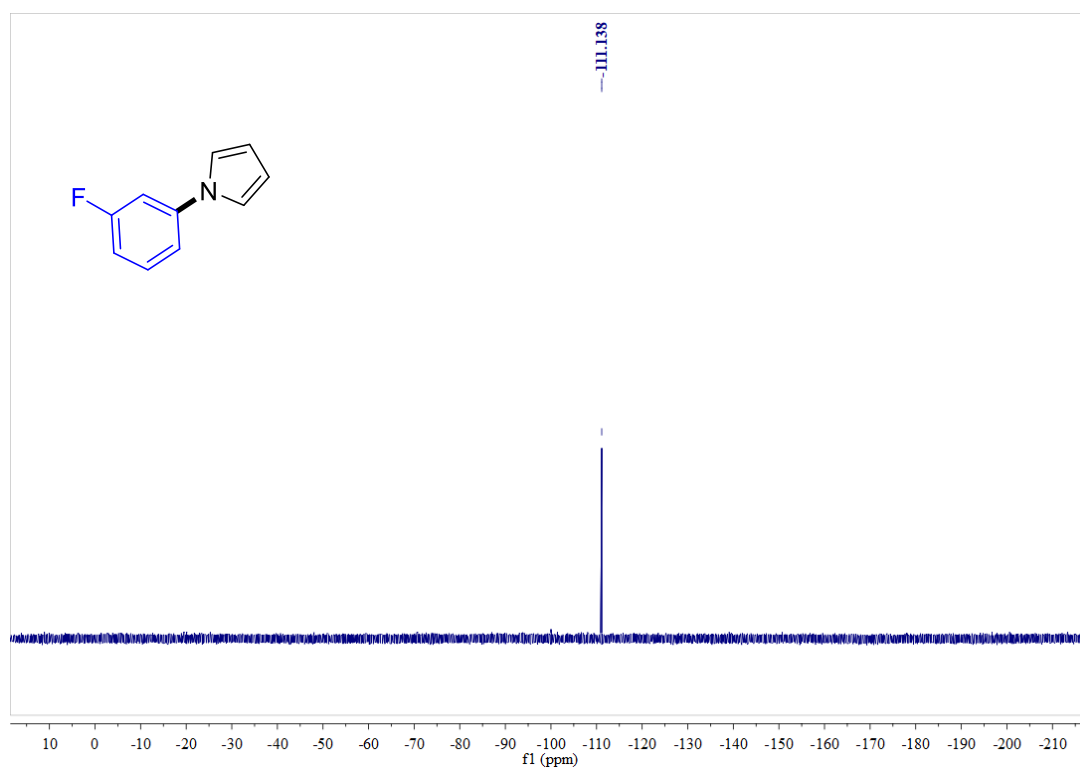
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **3q**



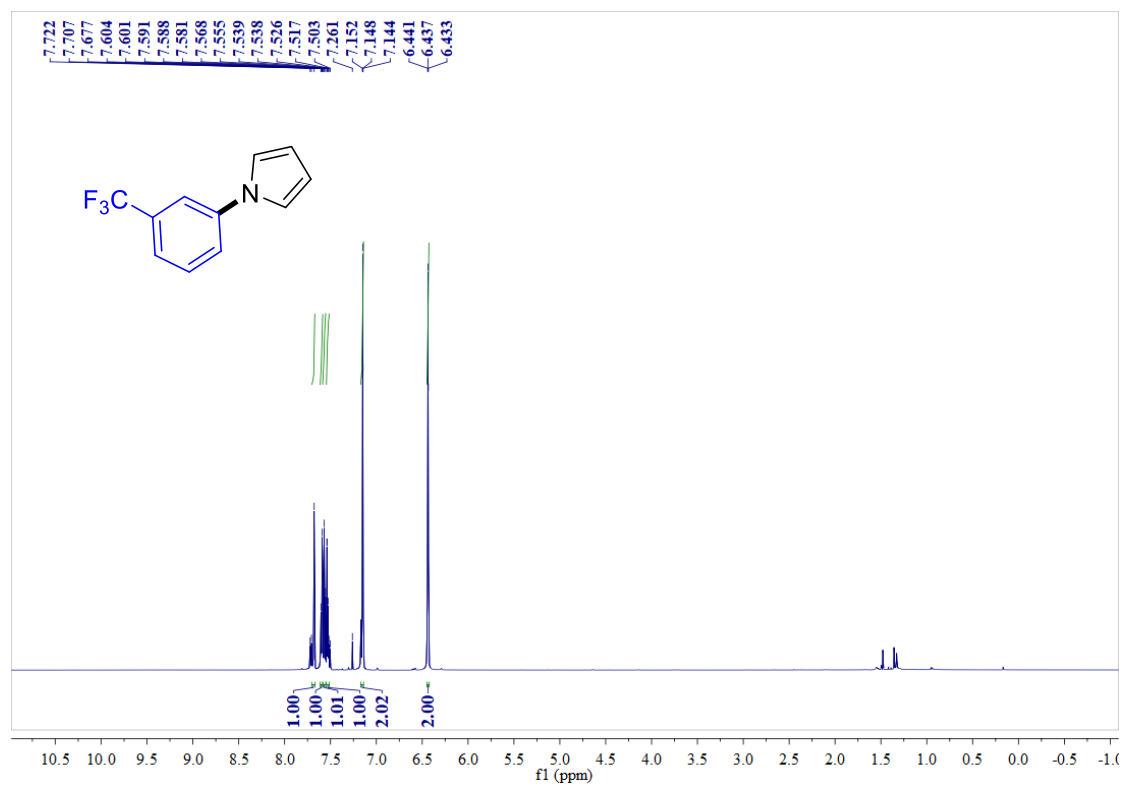
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **3q**



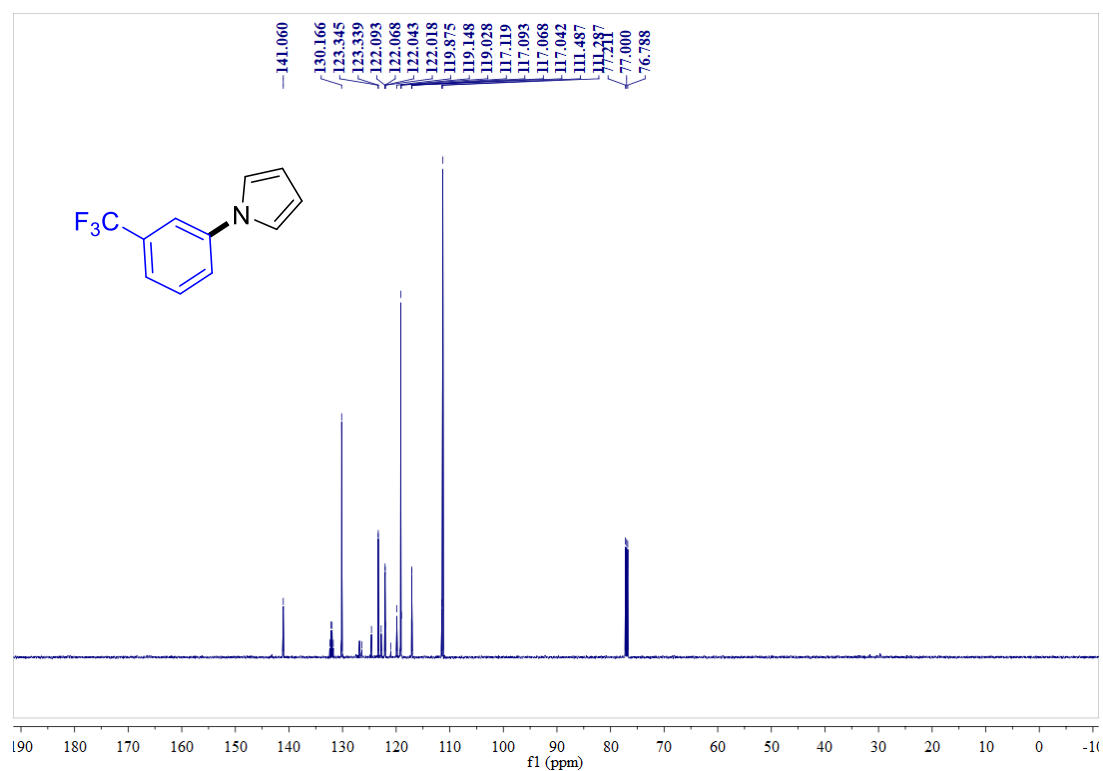
$^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ ) Spectrum of **3q**



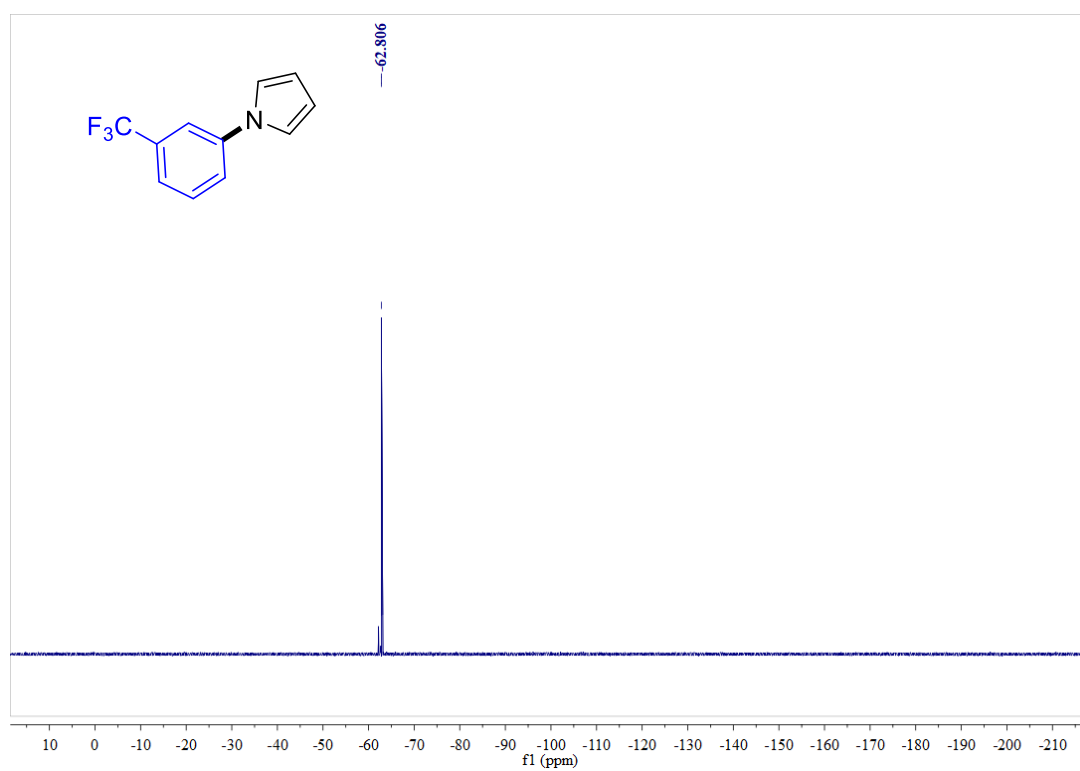
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3r**



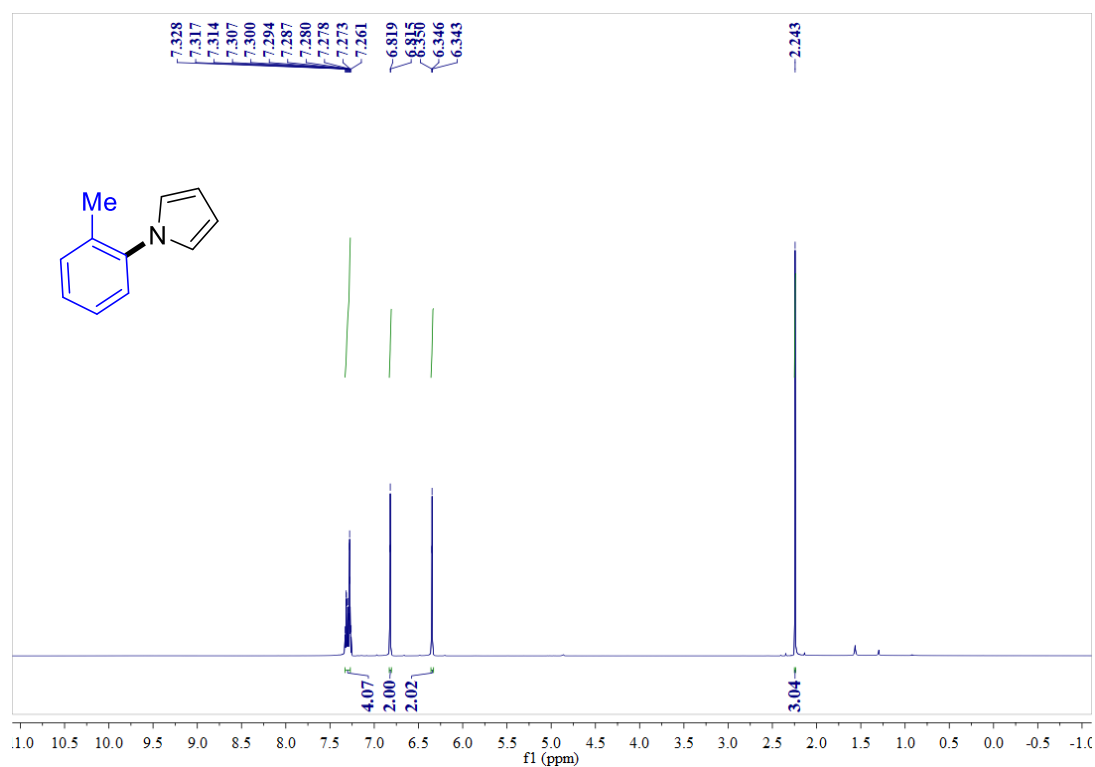
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **3r**



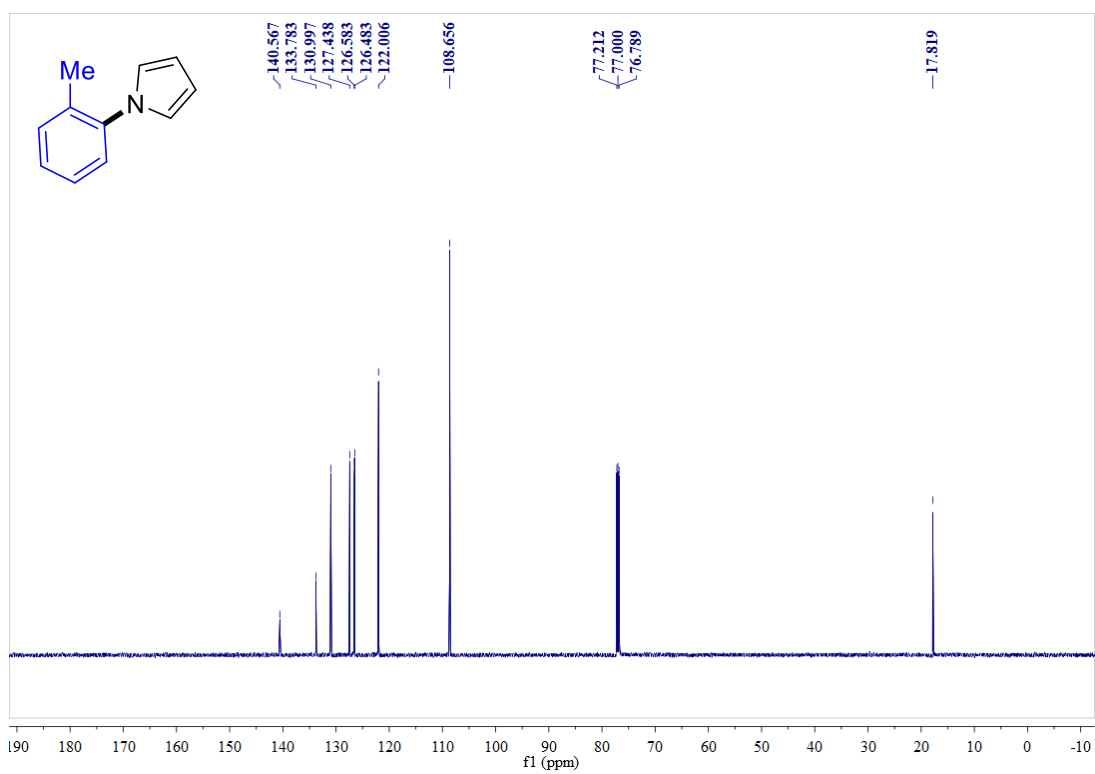
$^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ ) Spectrum of **3r**



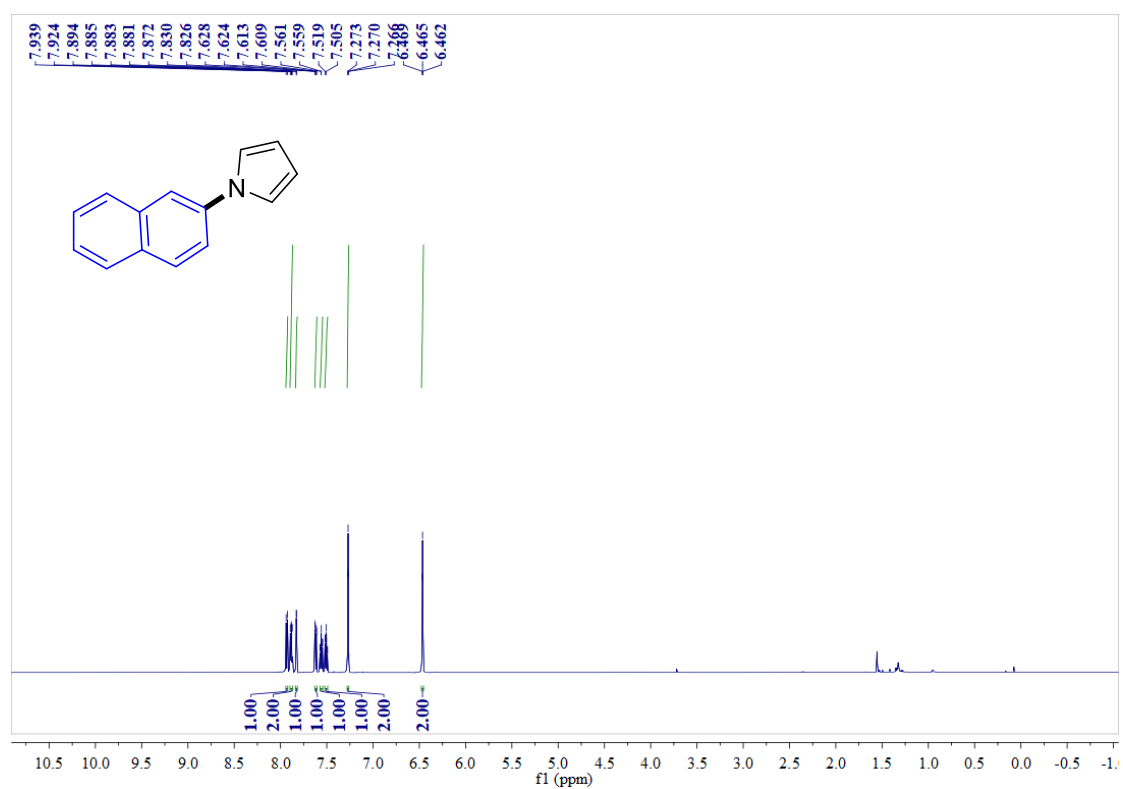
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **3s**



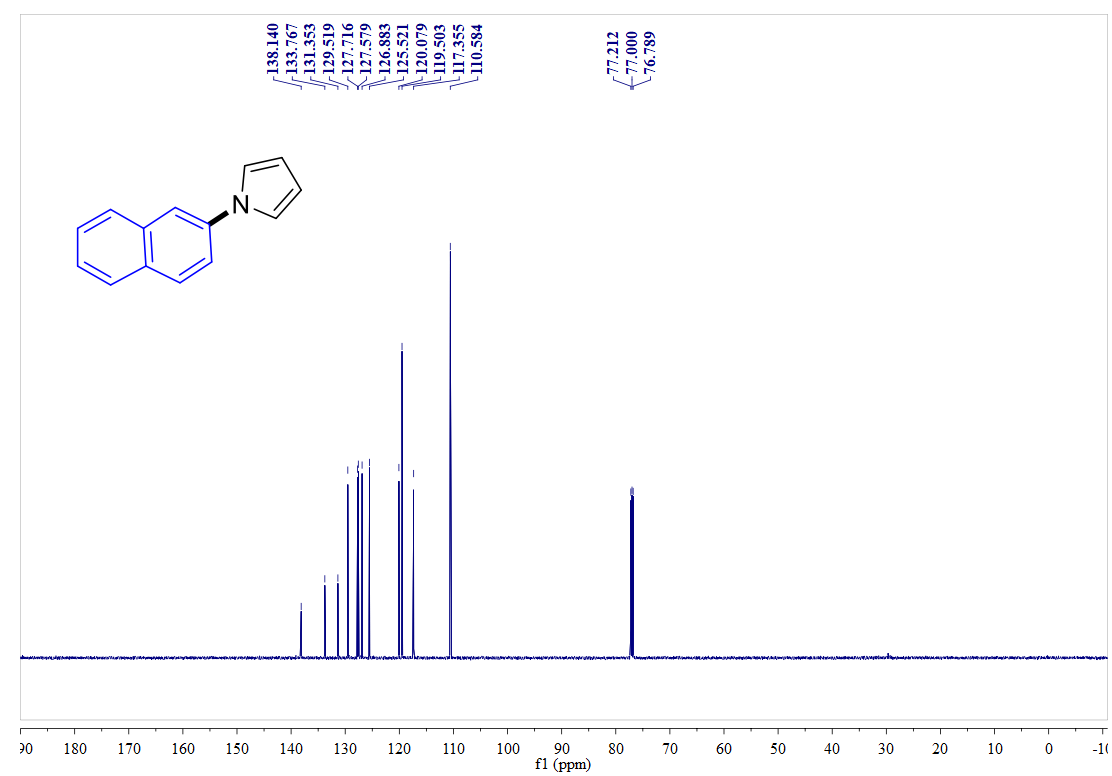
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **3s**



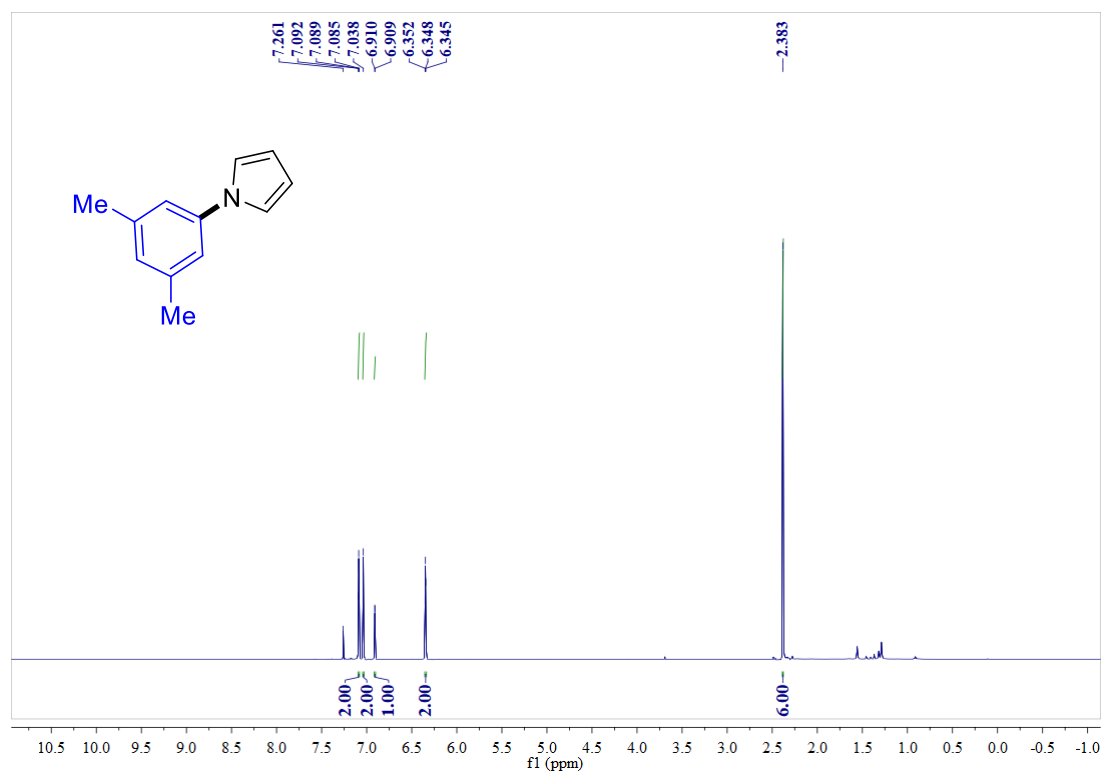
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **3t**



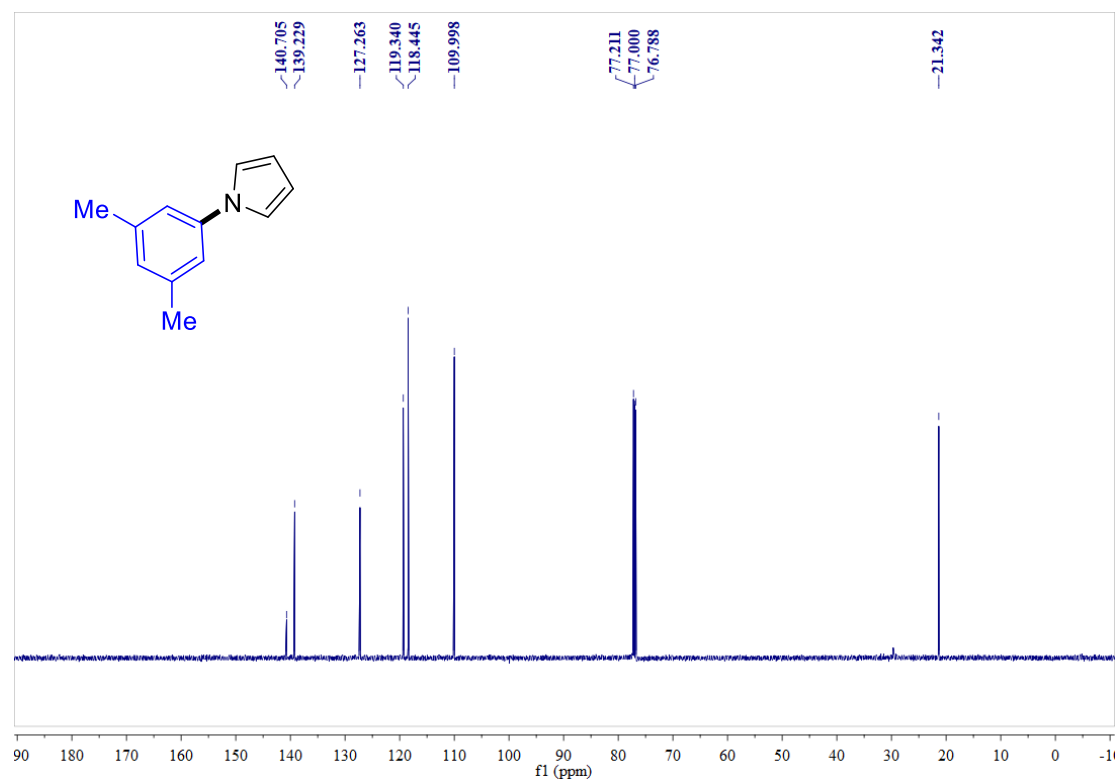
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **3t**



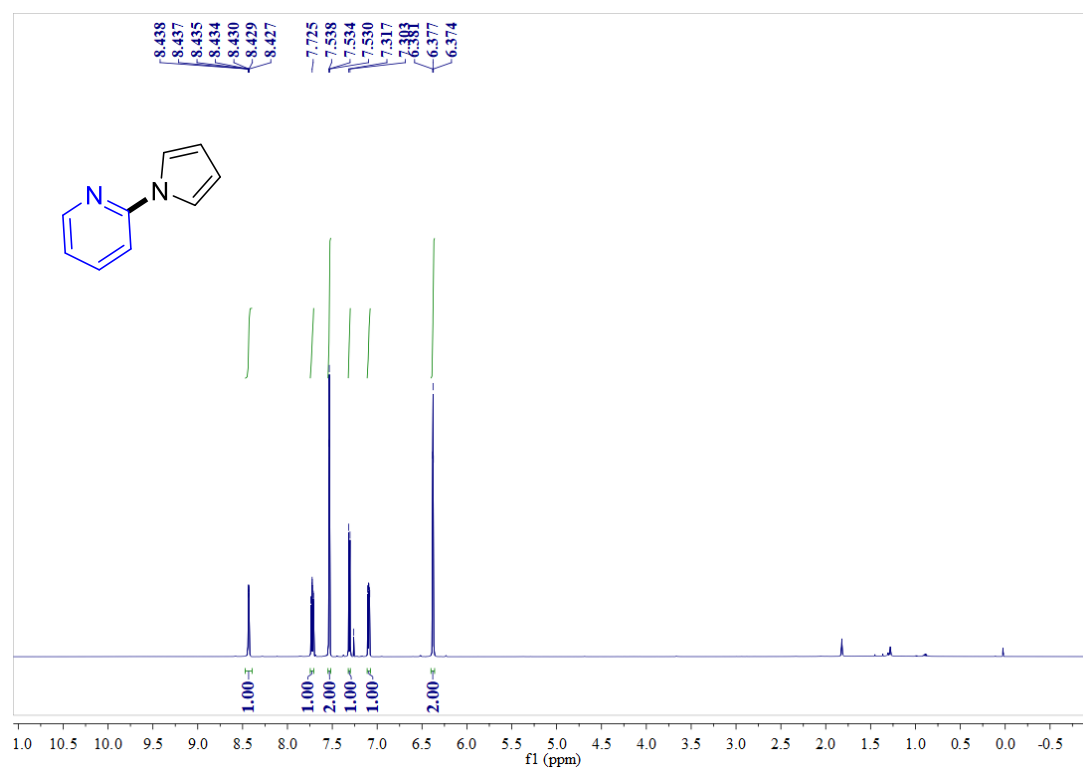
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3u**



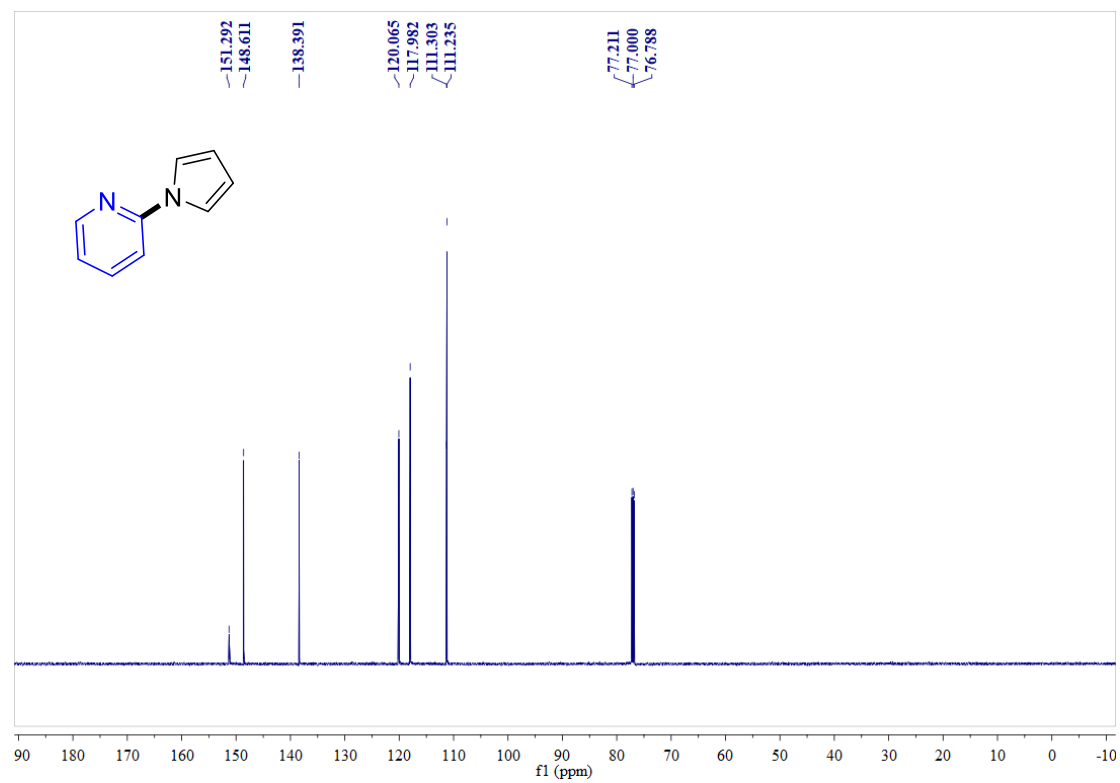
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **3u**



<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **3x**

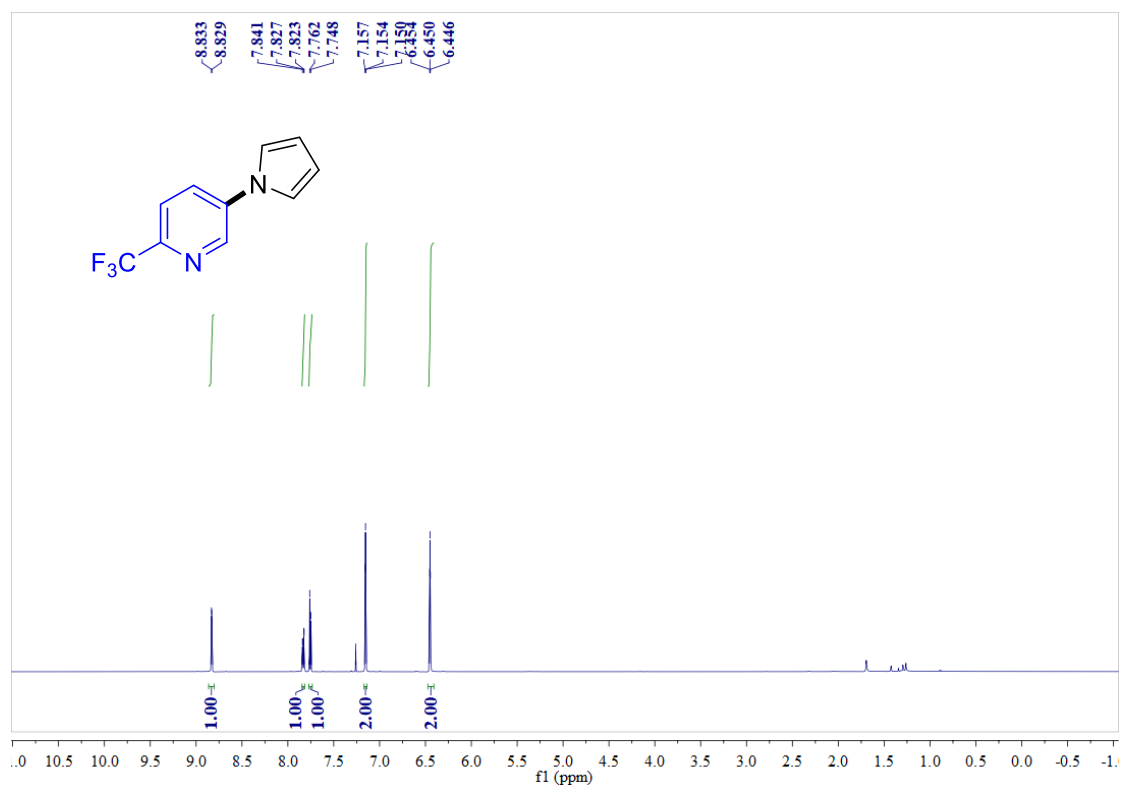


<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **3x**

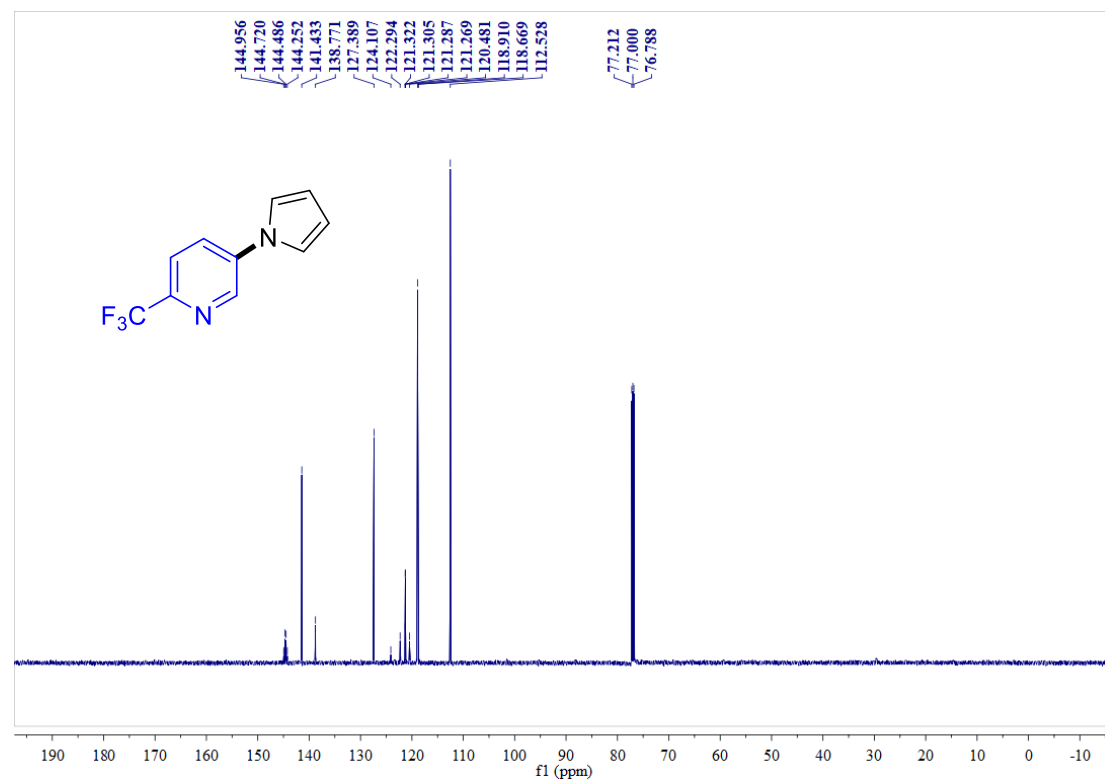




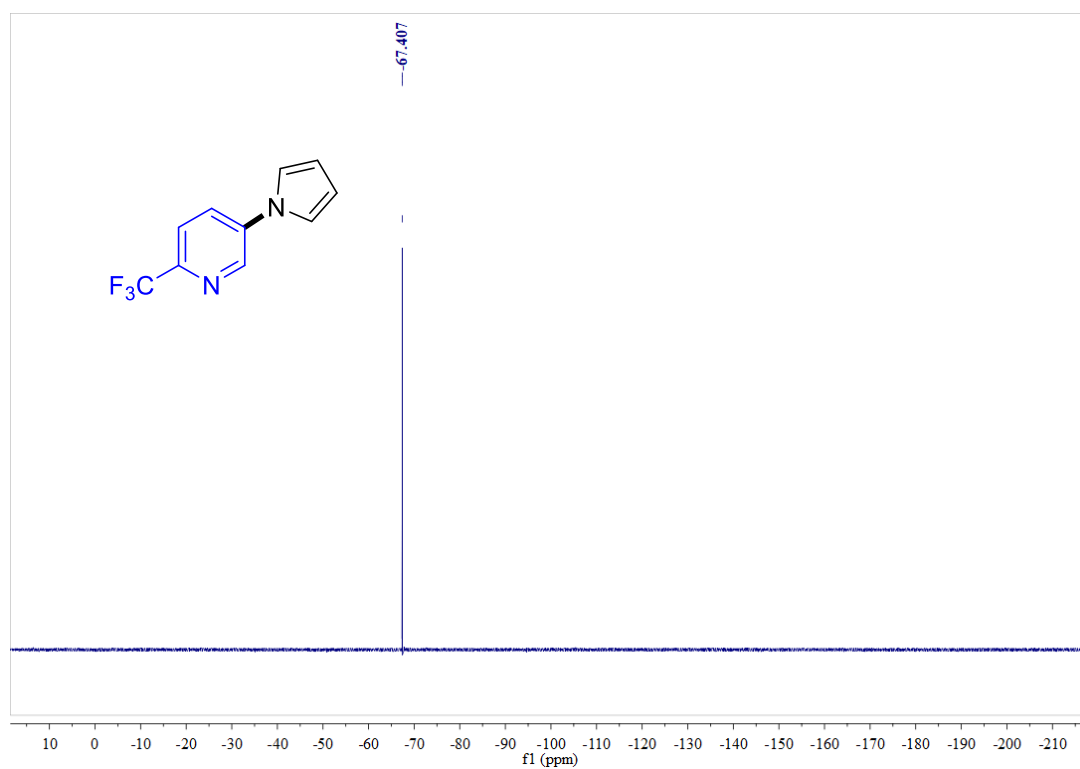
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **3y**



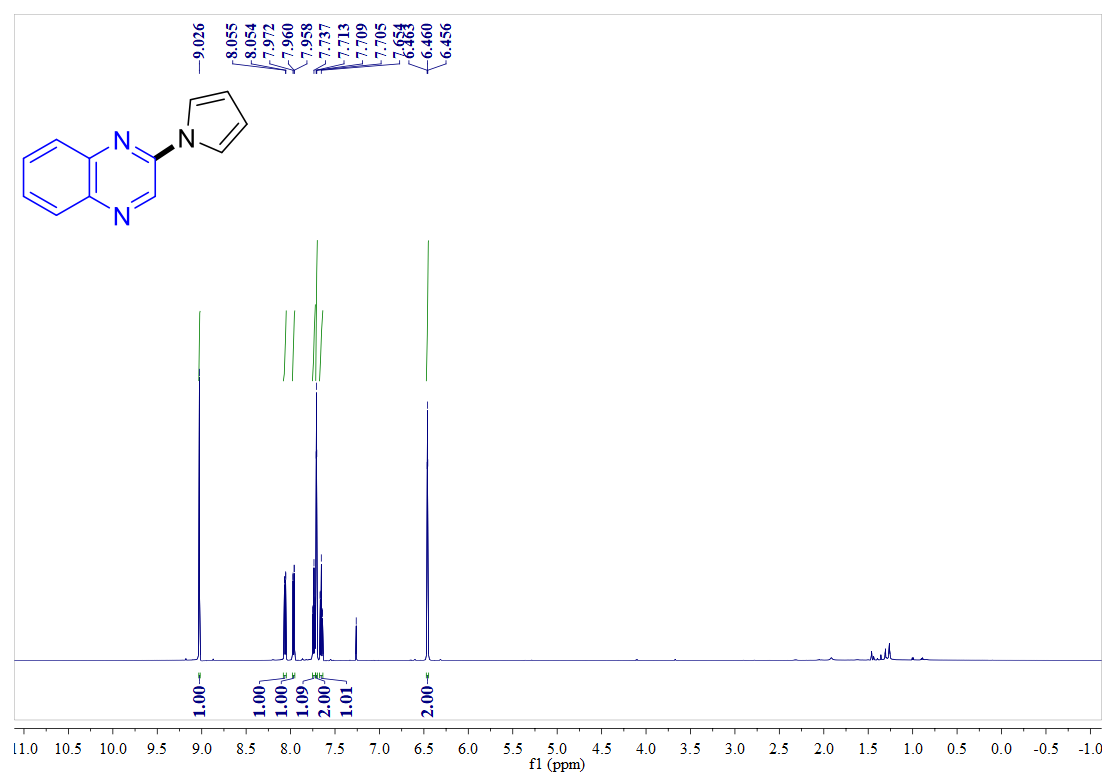
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **3y**



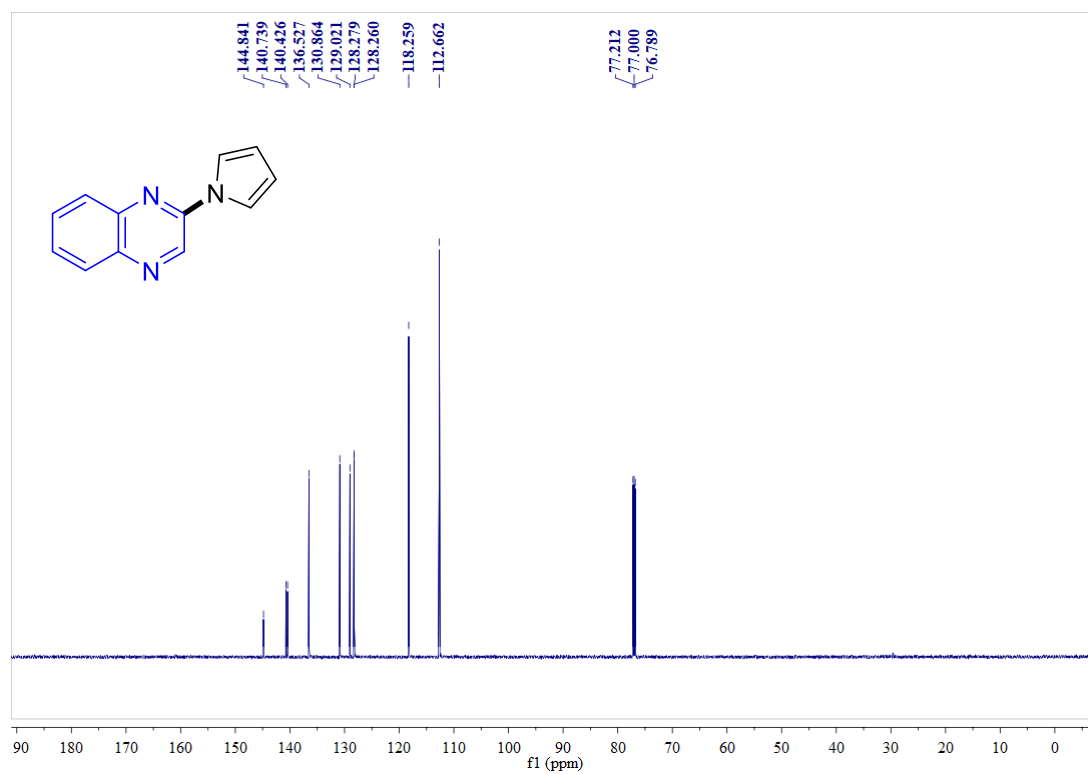
$^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ ) Spectrum of **3y**



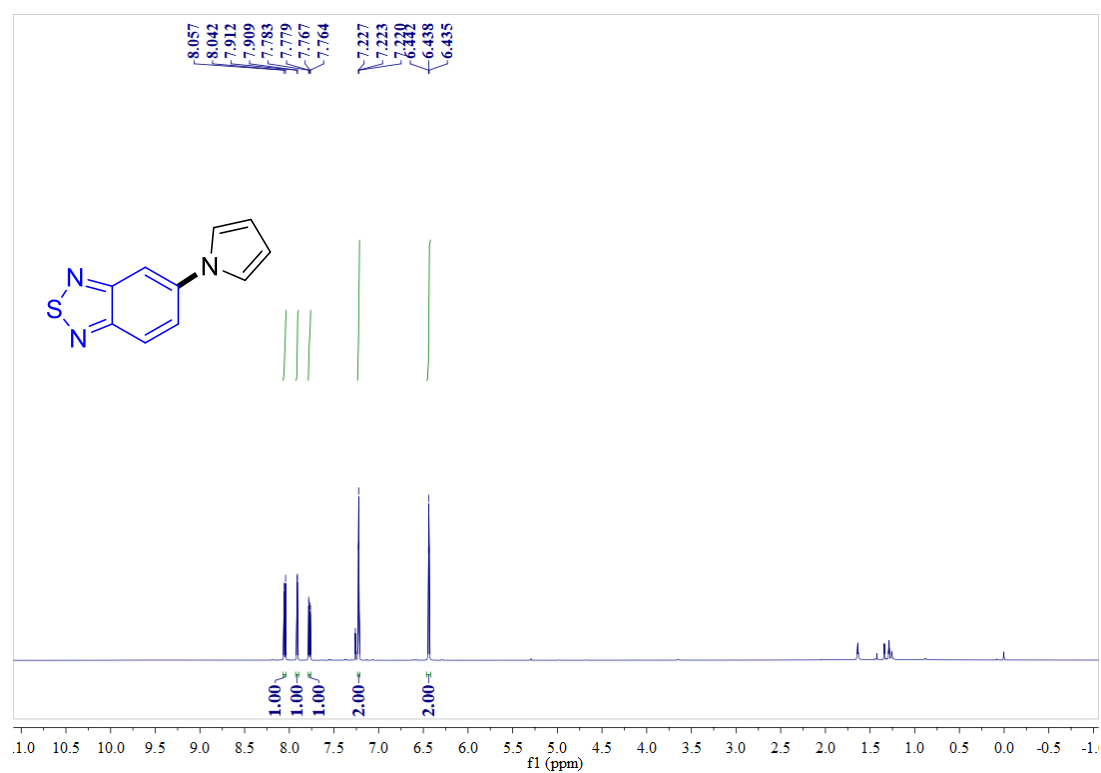
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3z**



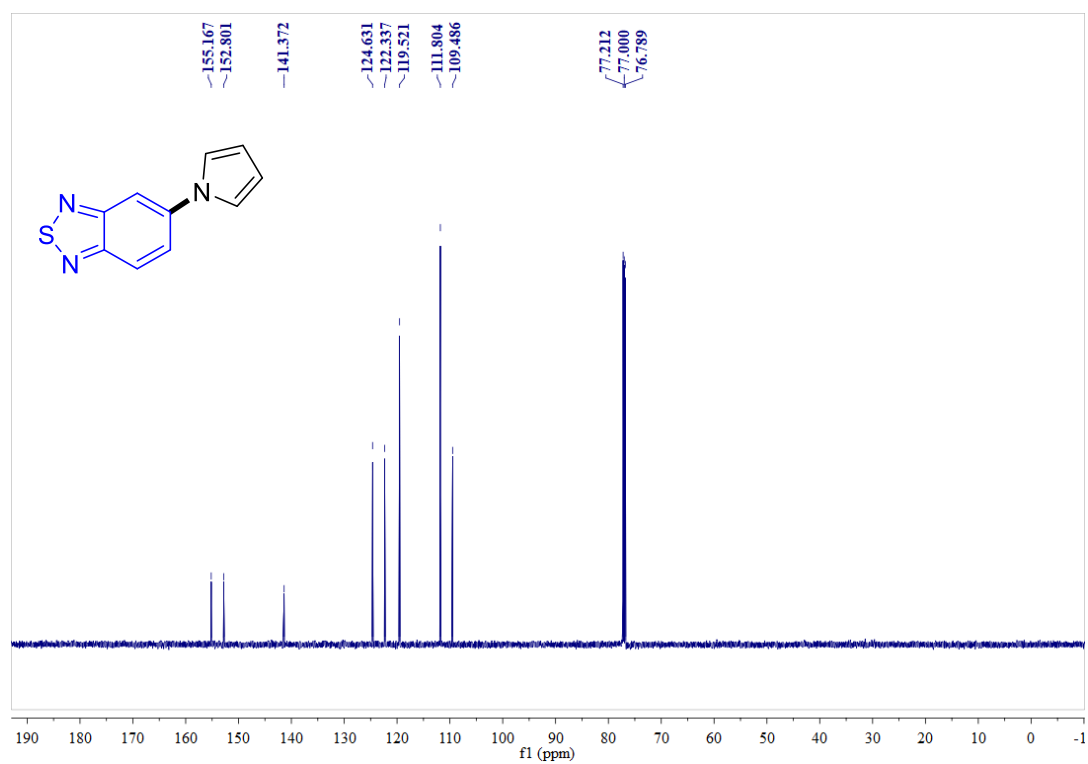
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **3z**



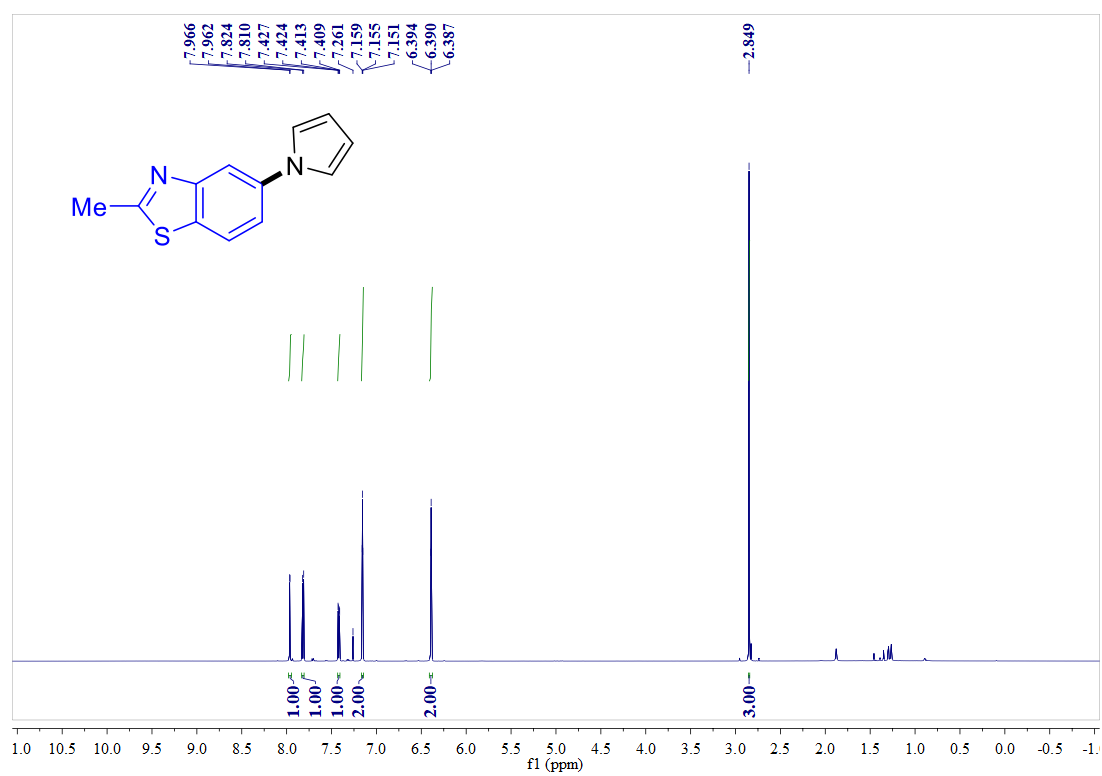
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3aa**



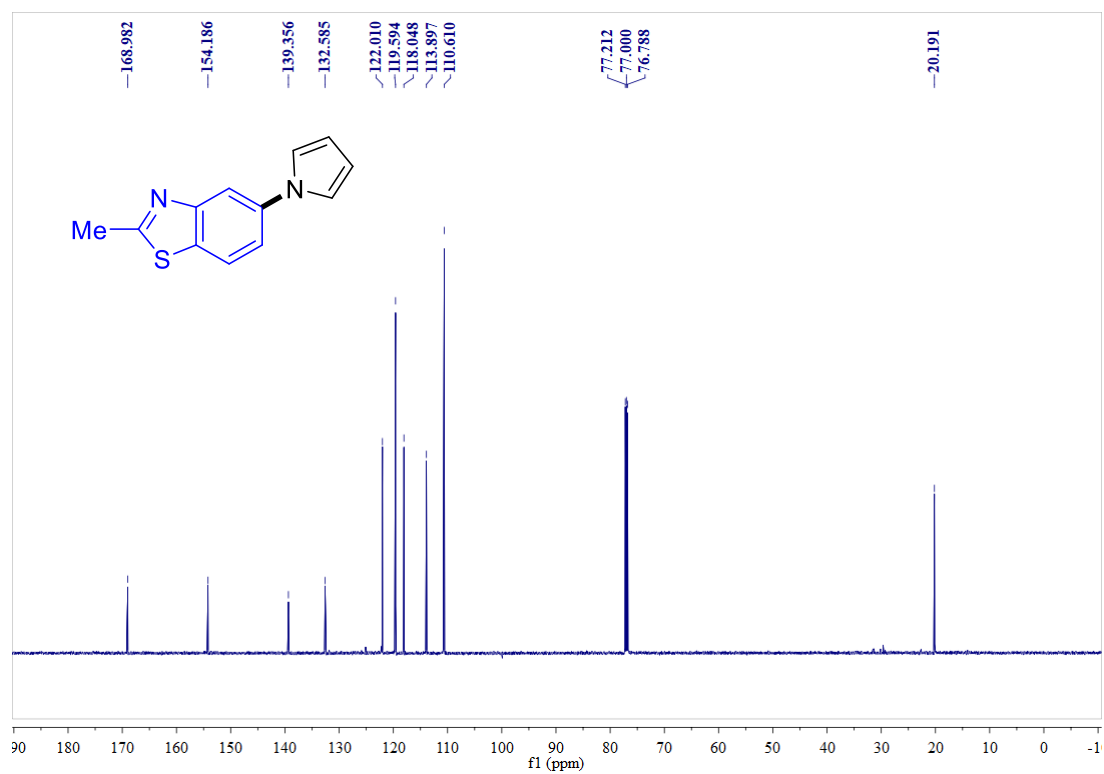
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **3aa**



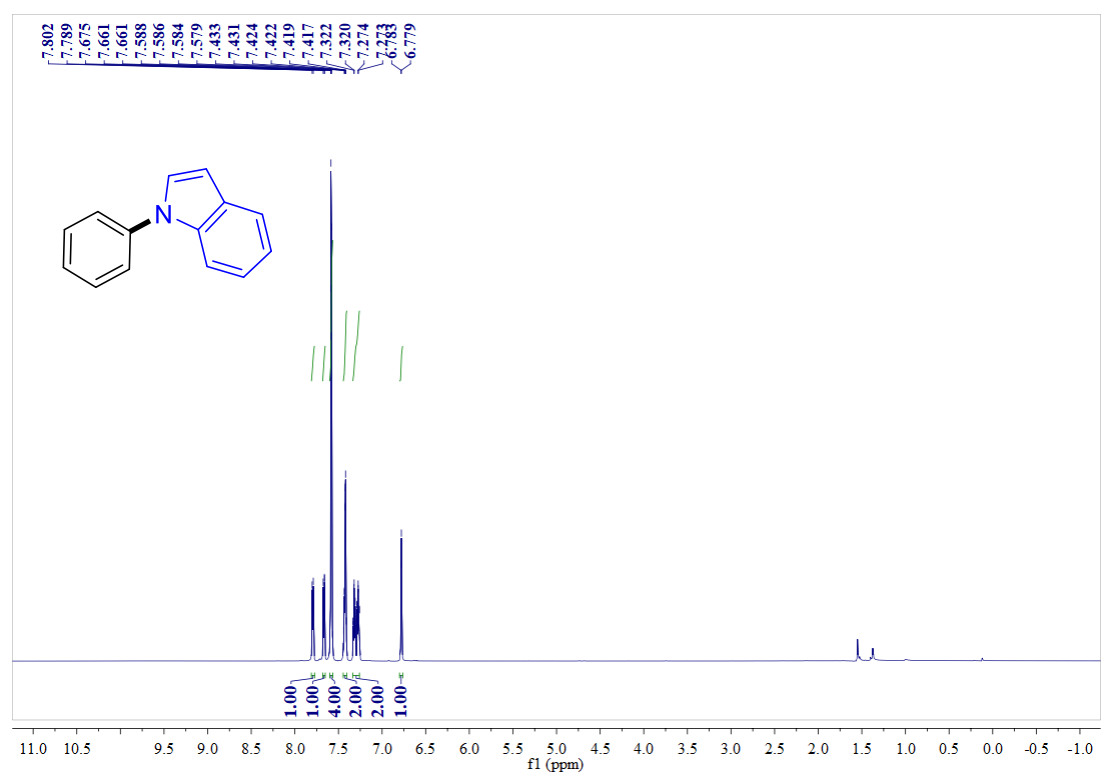
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **3ab**



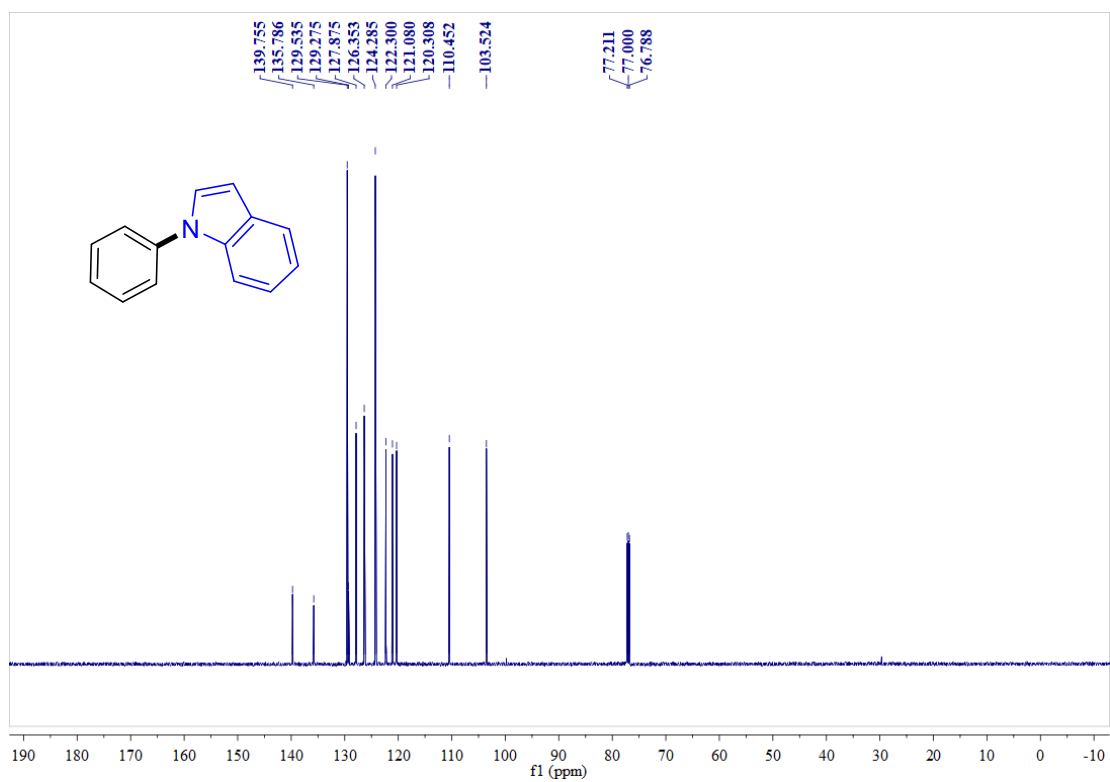
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **3ab**



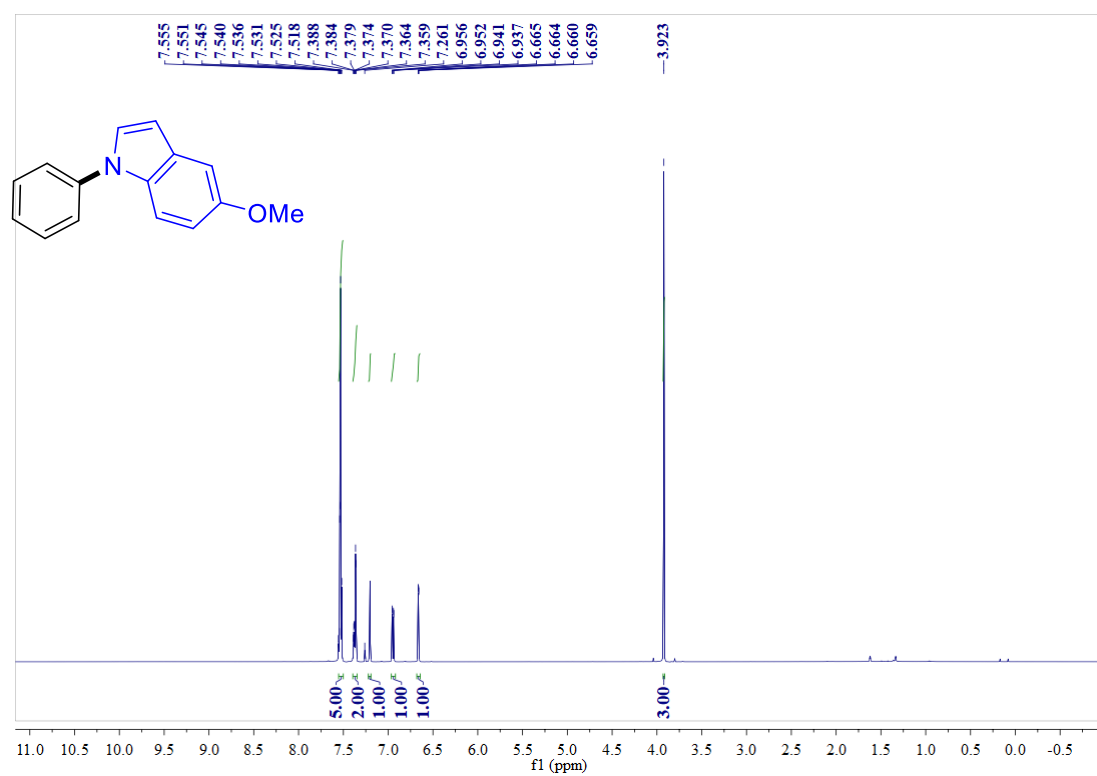
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **4a**



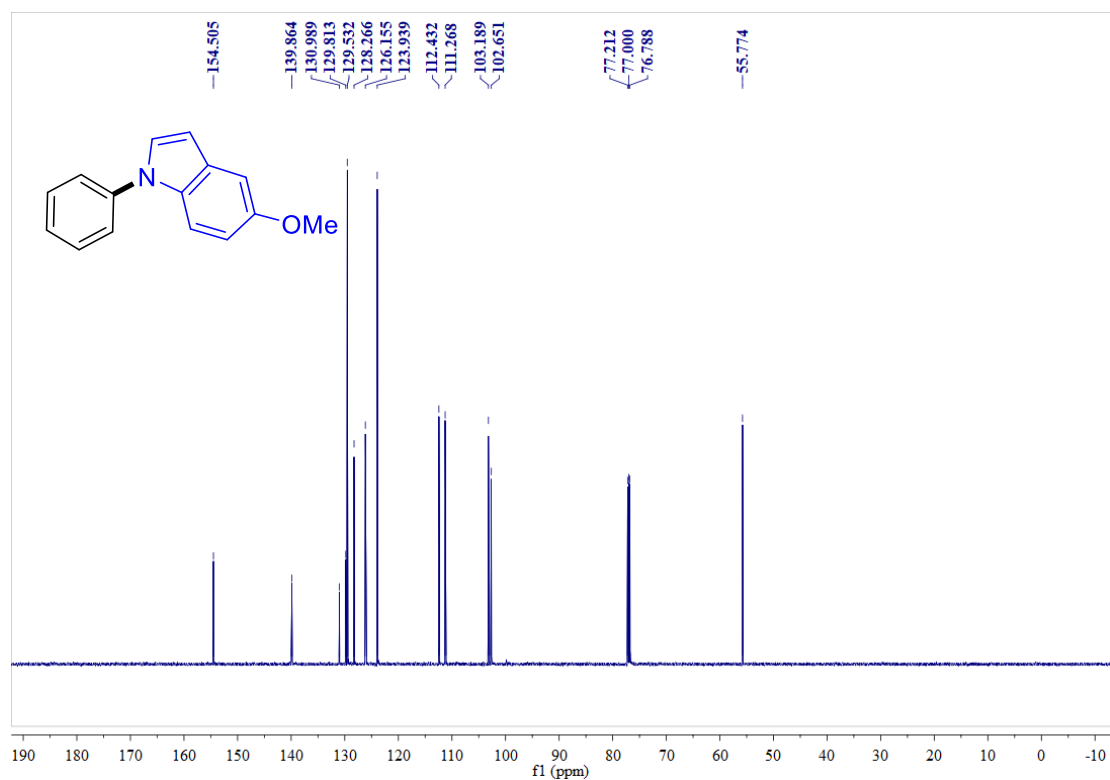
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **4a**



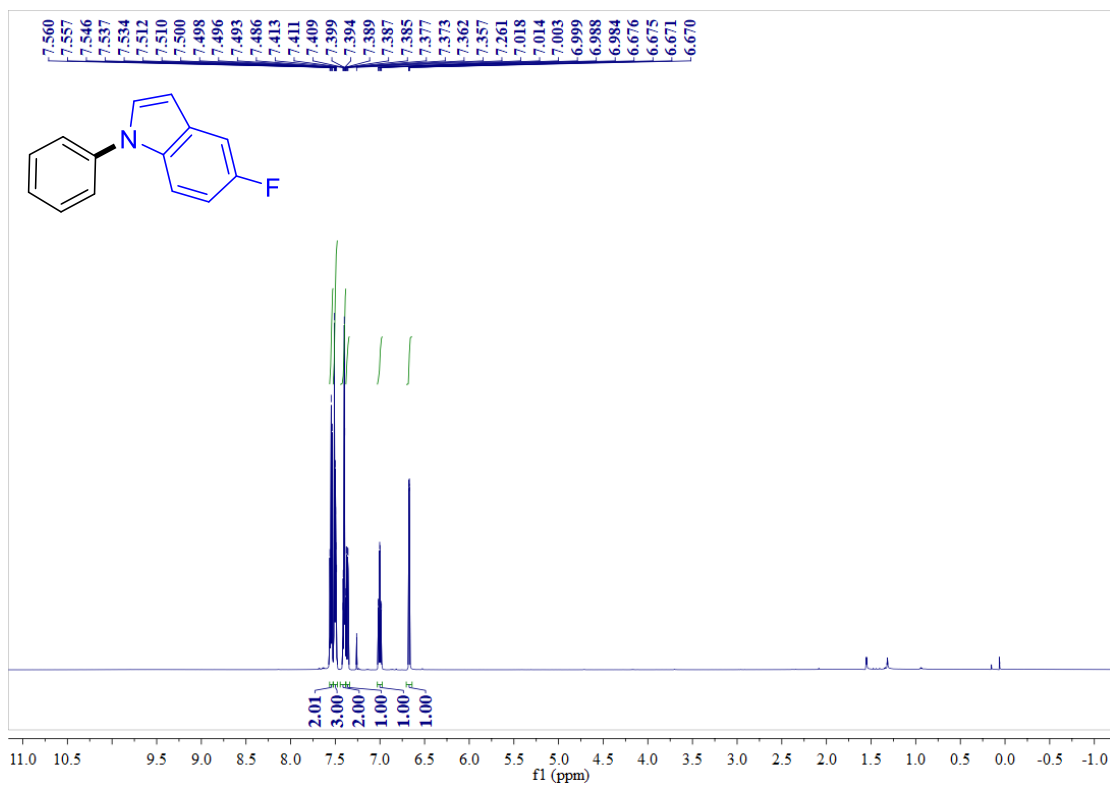
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **4b**



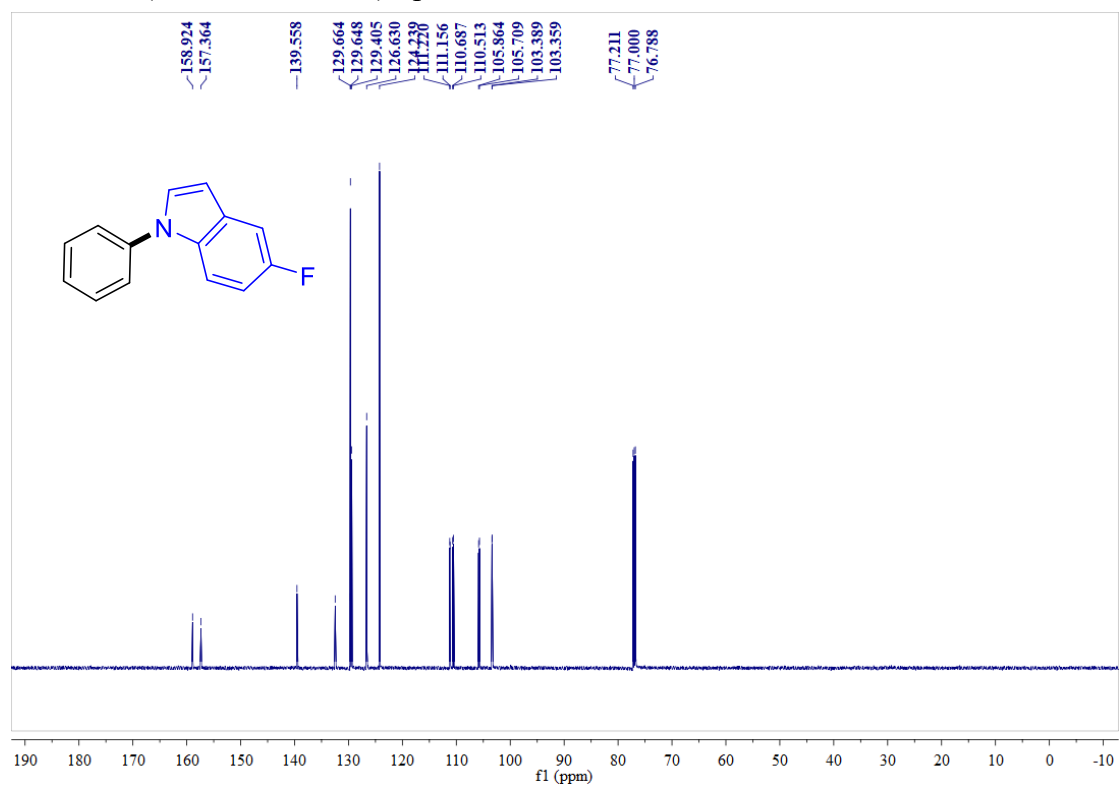
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **4b**



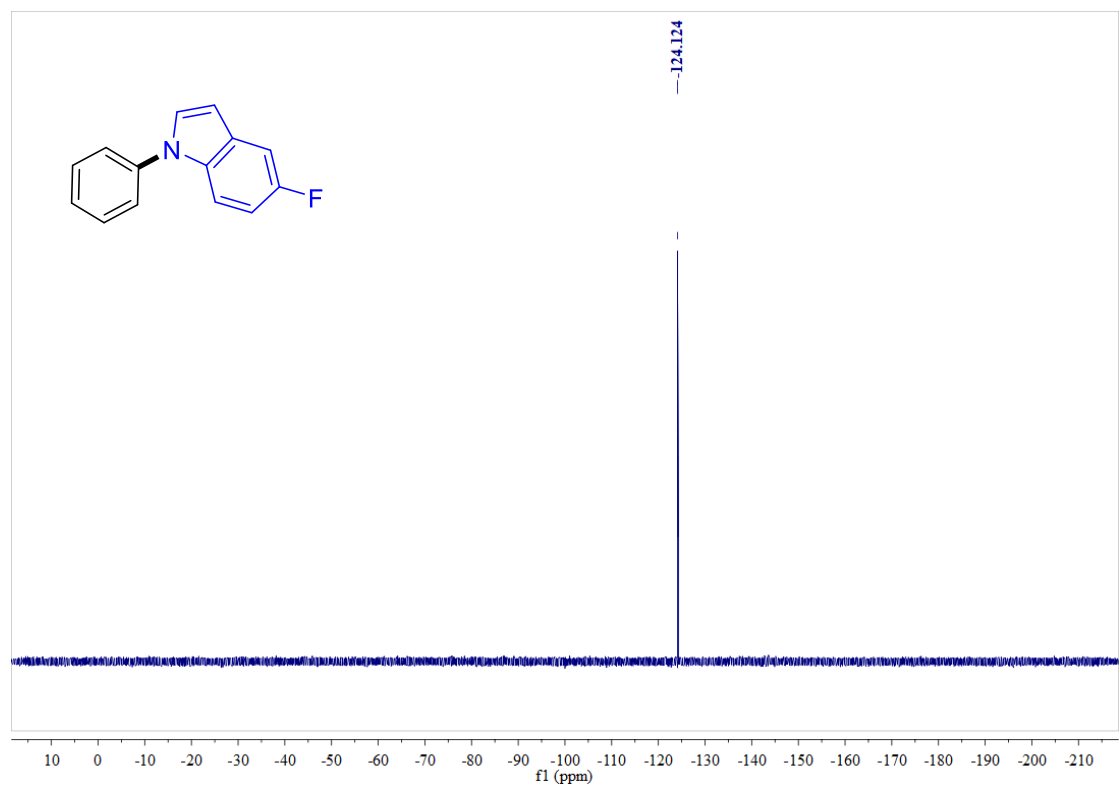
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **4c**



$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **4c**

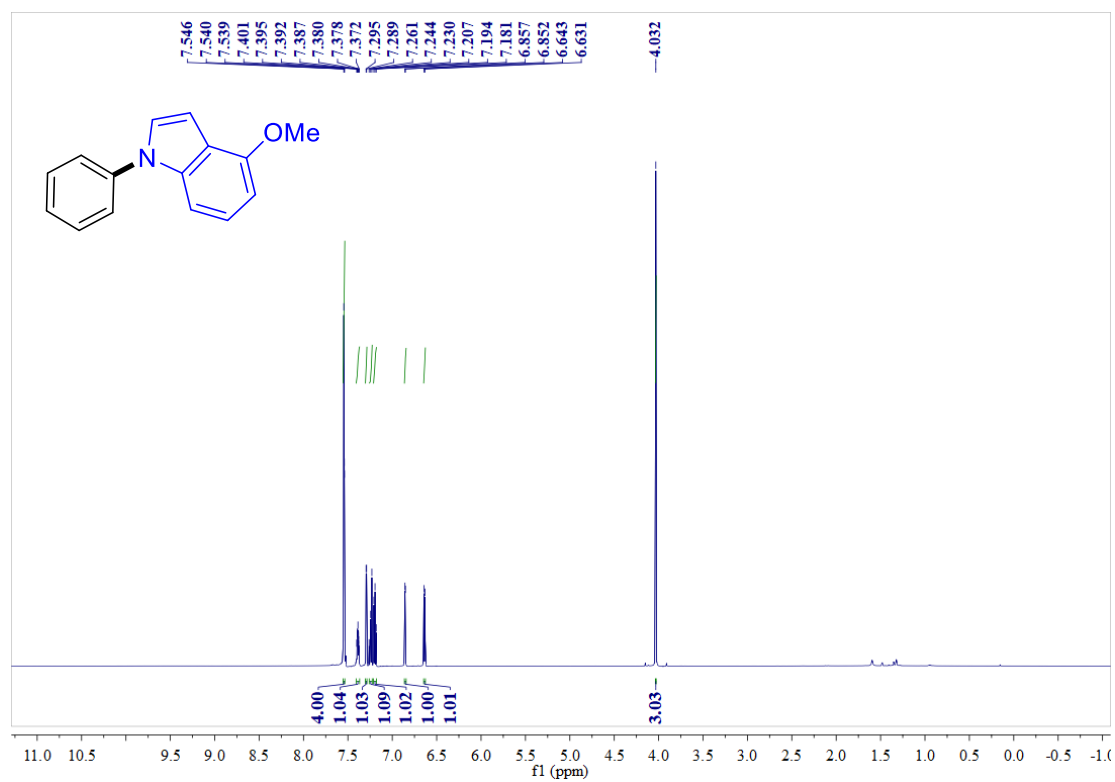


$^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ ) Spectrum of **4c**

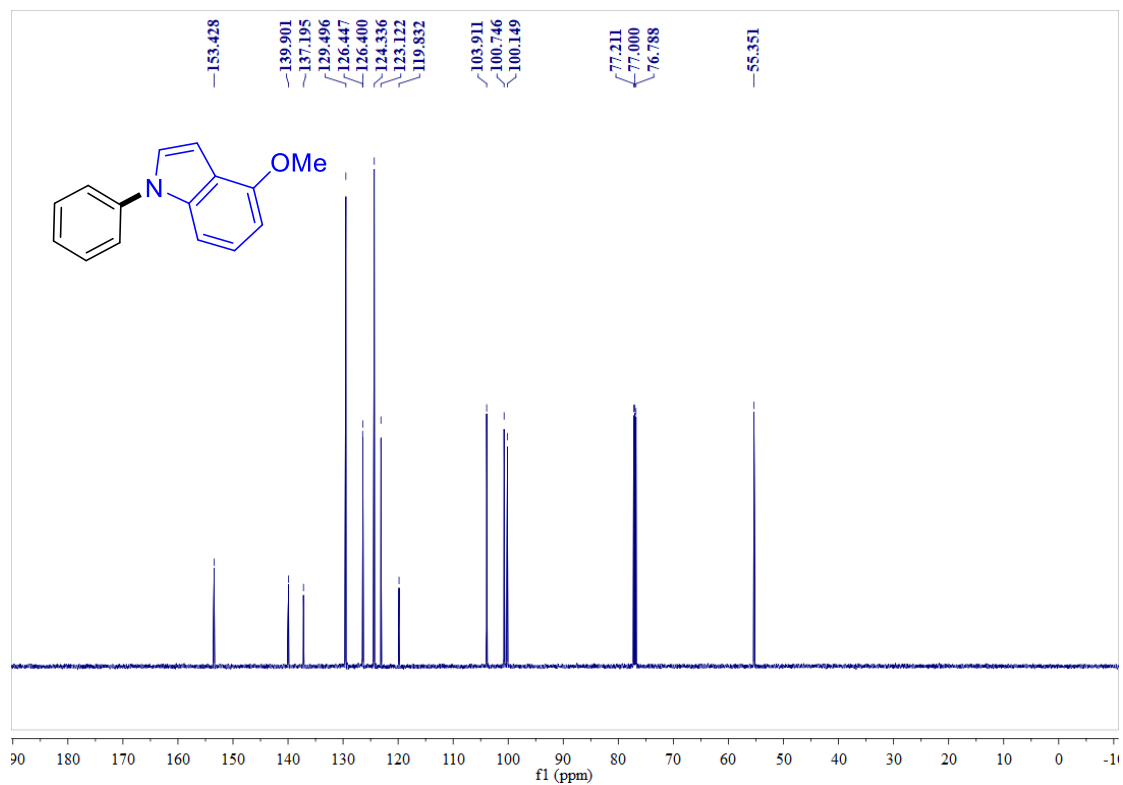




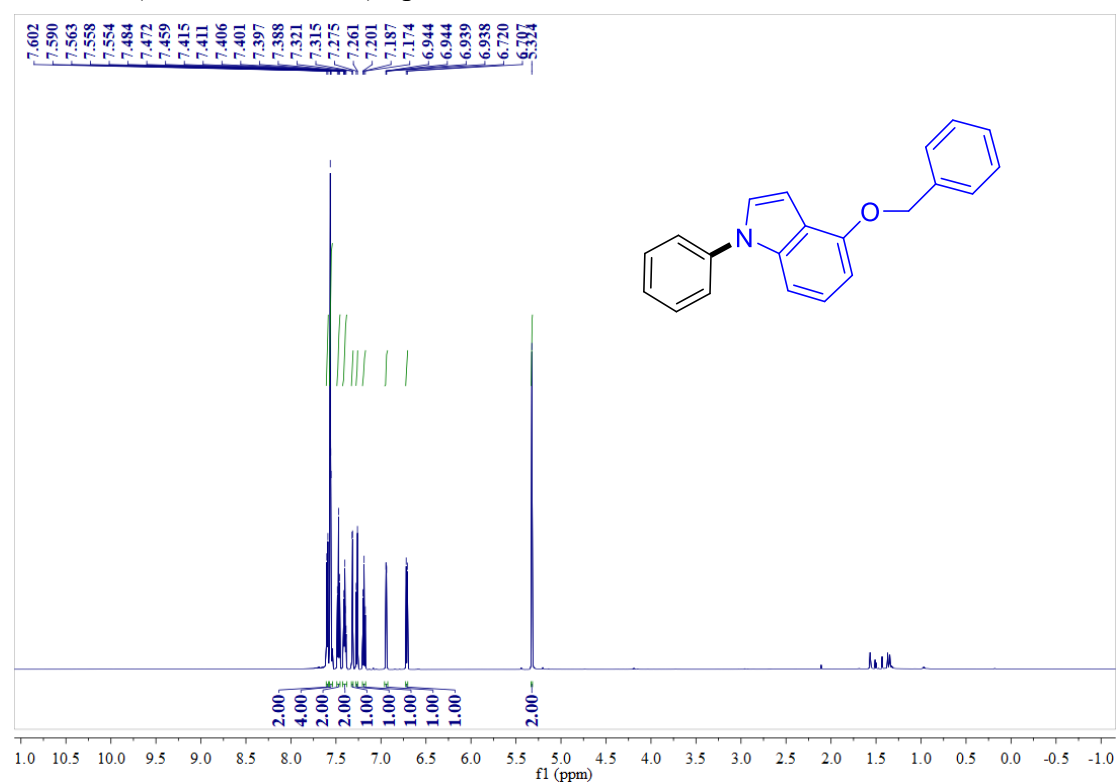
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **4d**



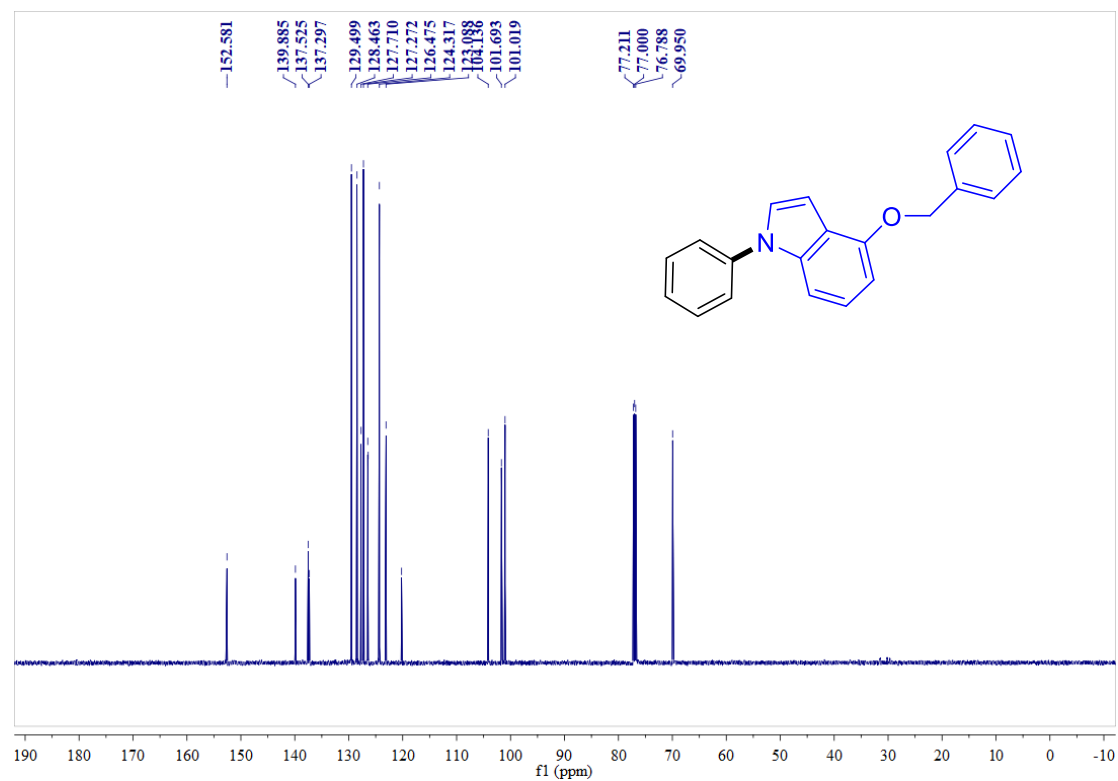
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **4d**



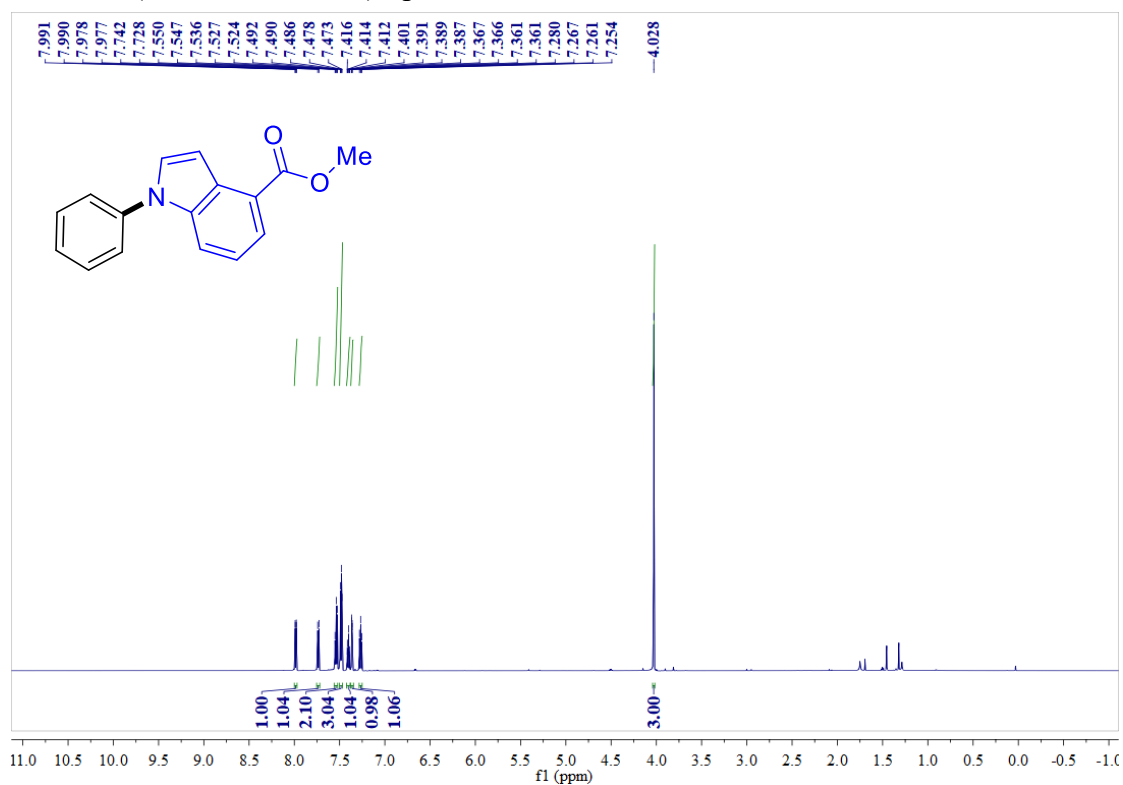
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **4e**



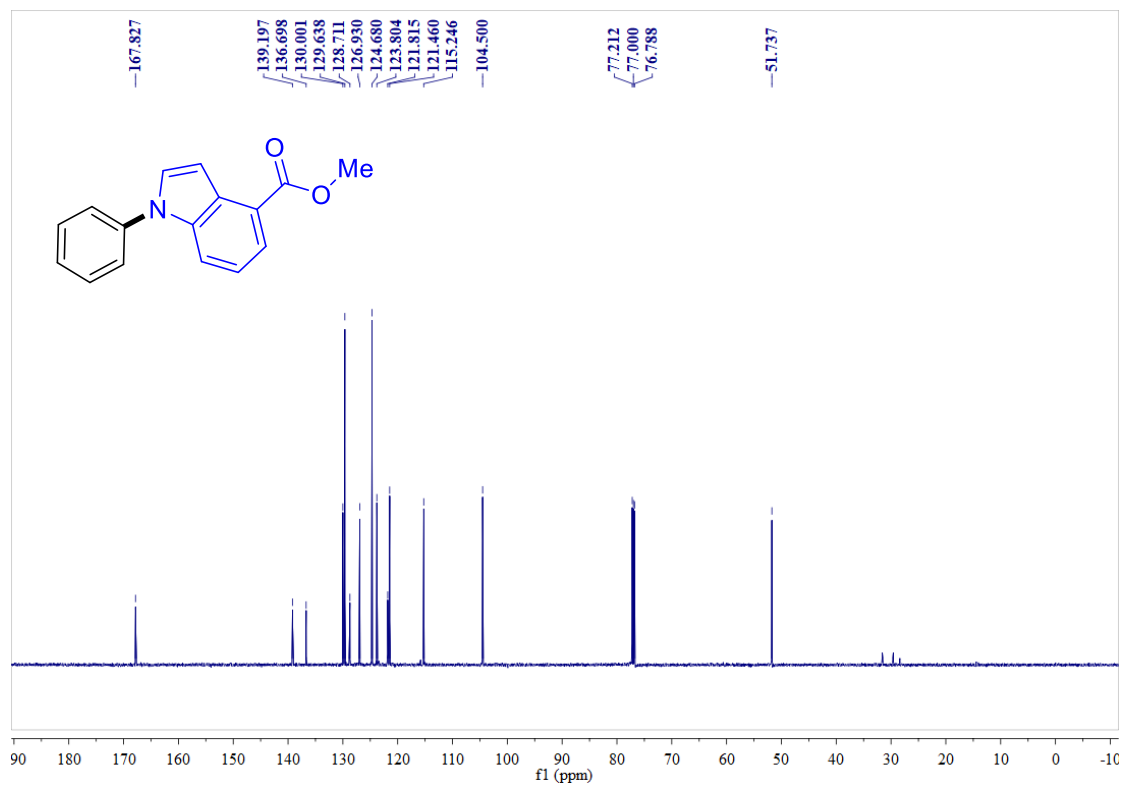
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **4e**



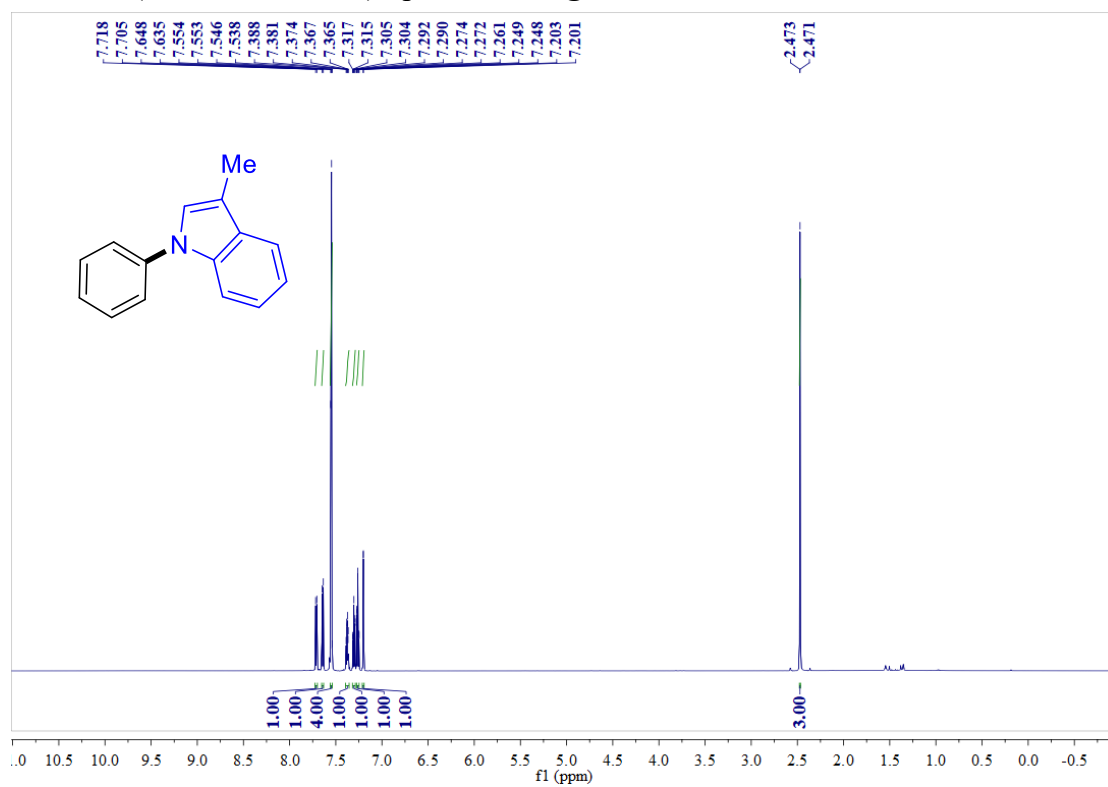
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **4f**



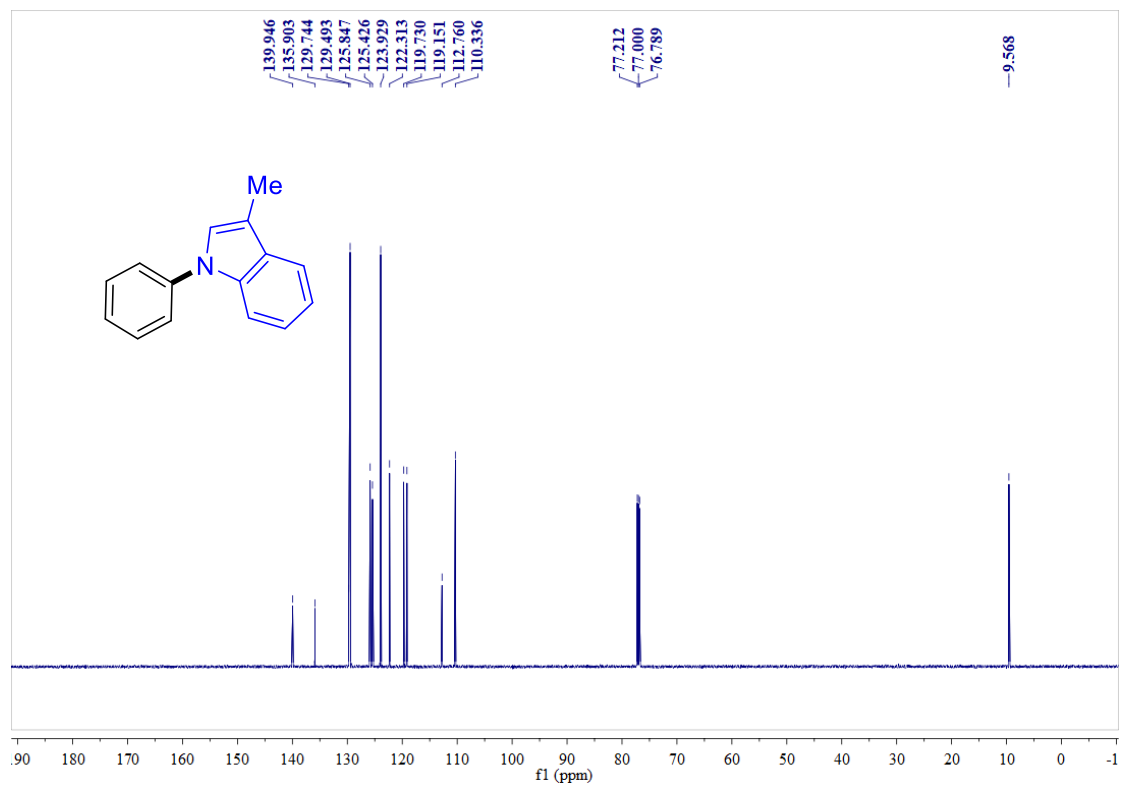
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **4f**



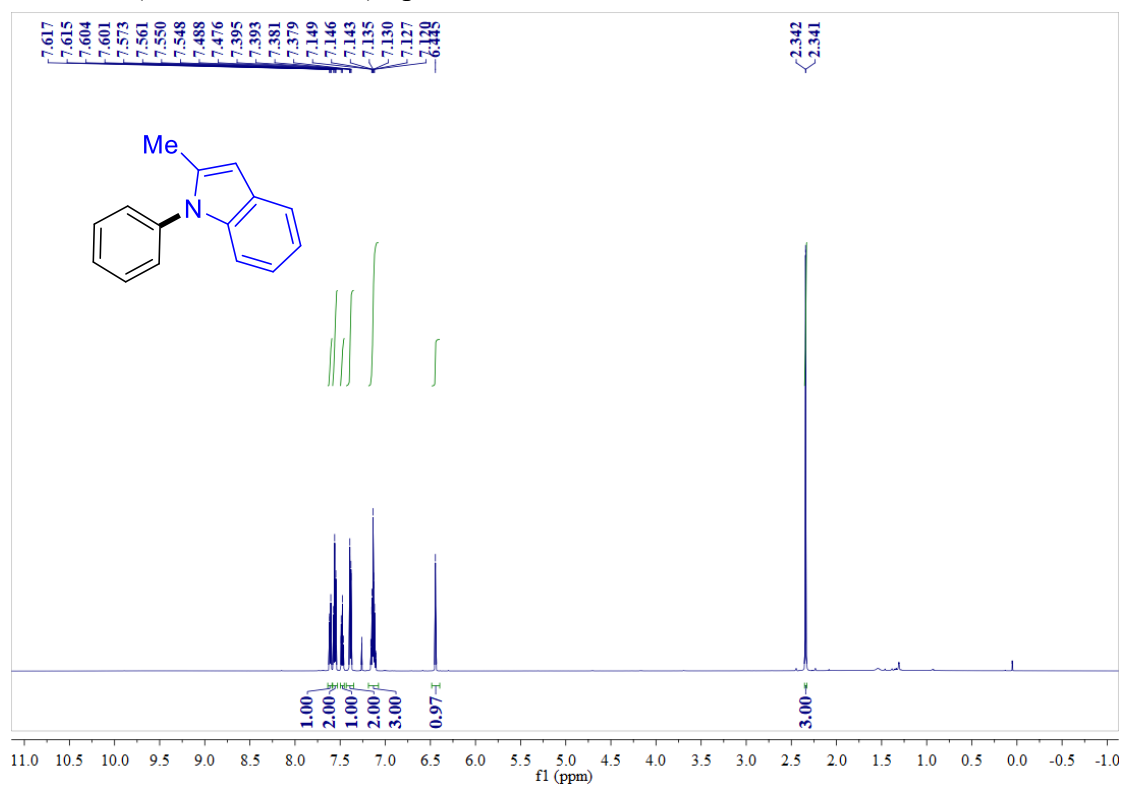
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **4g**



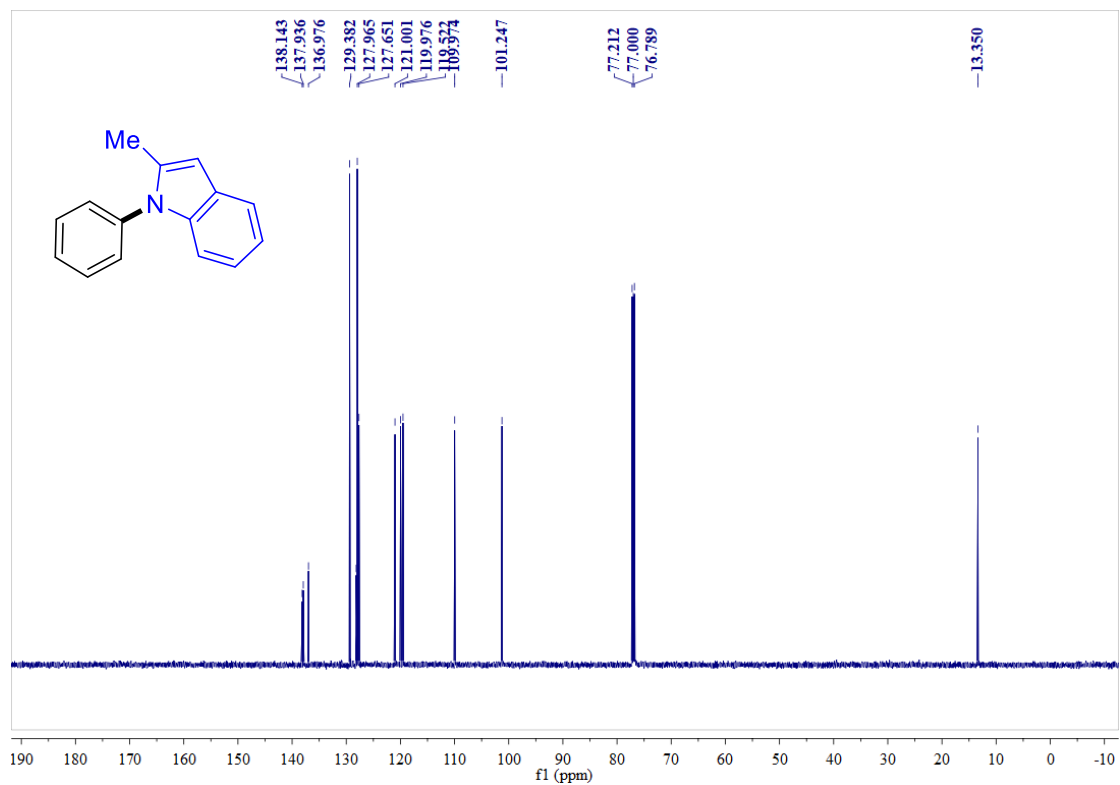
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **4g**



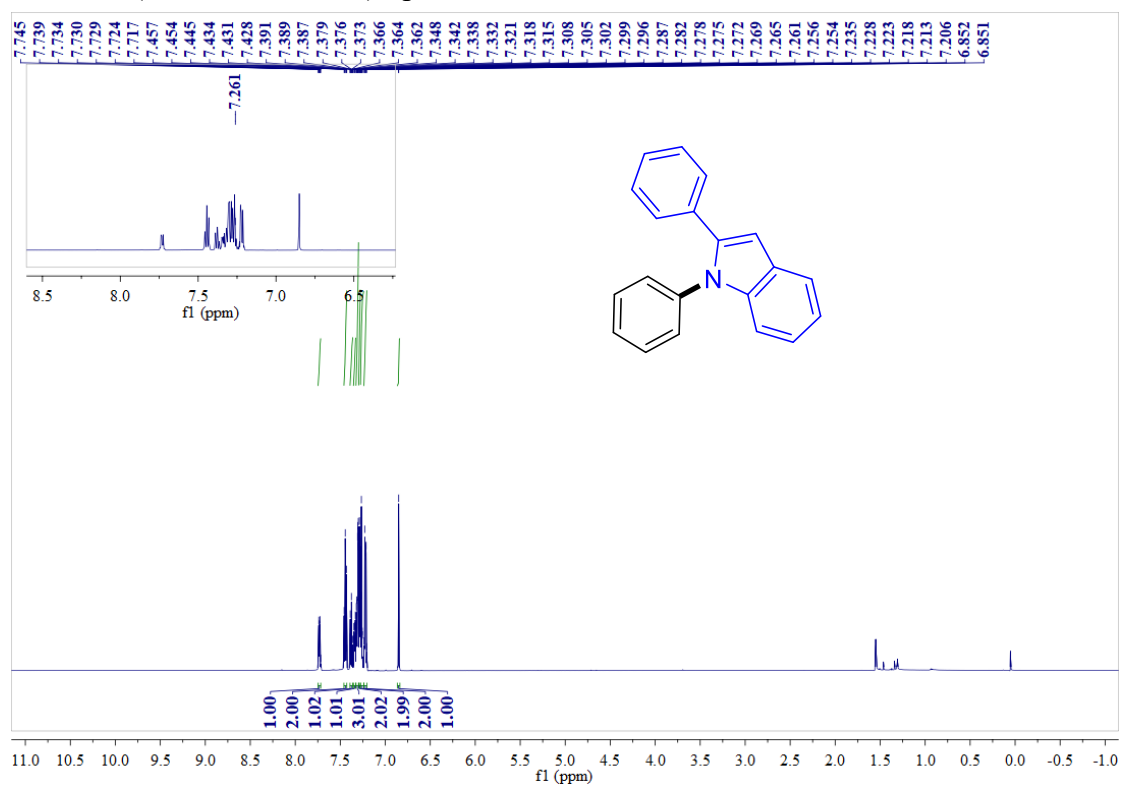
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **4h**



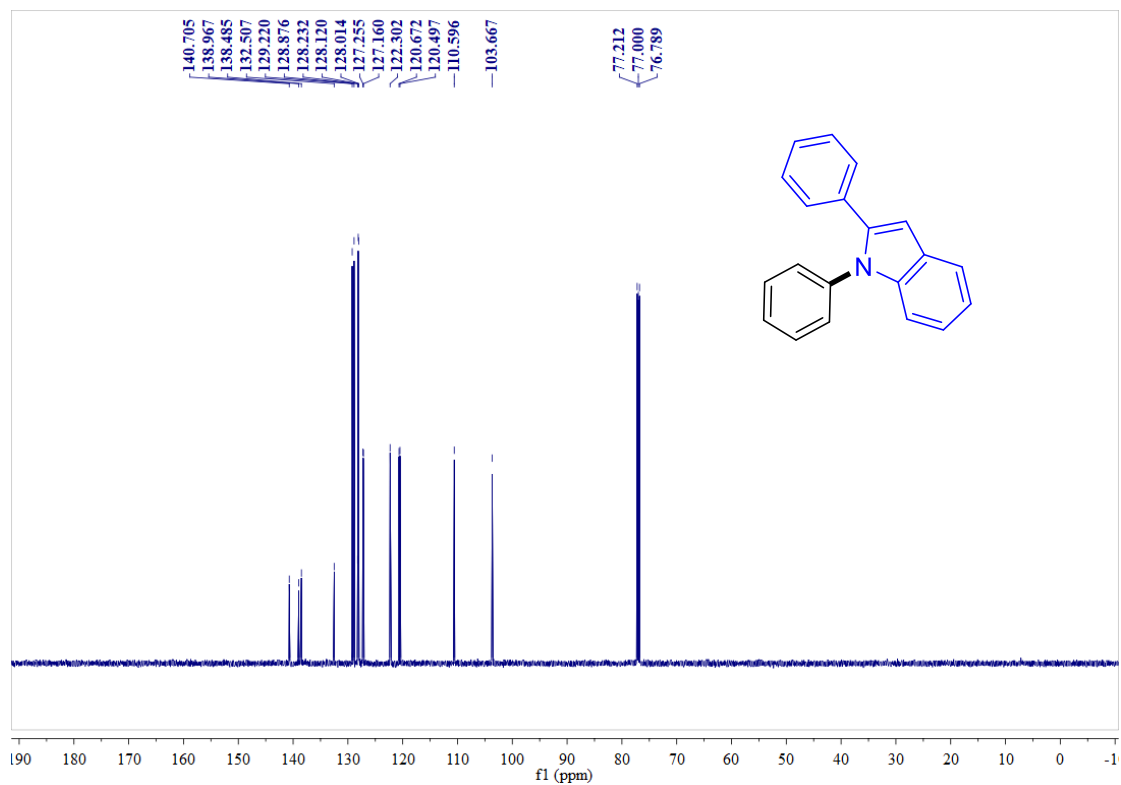
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **4h**



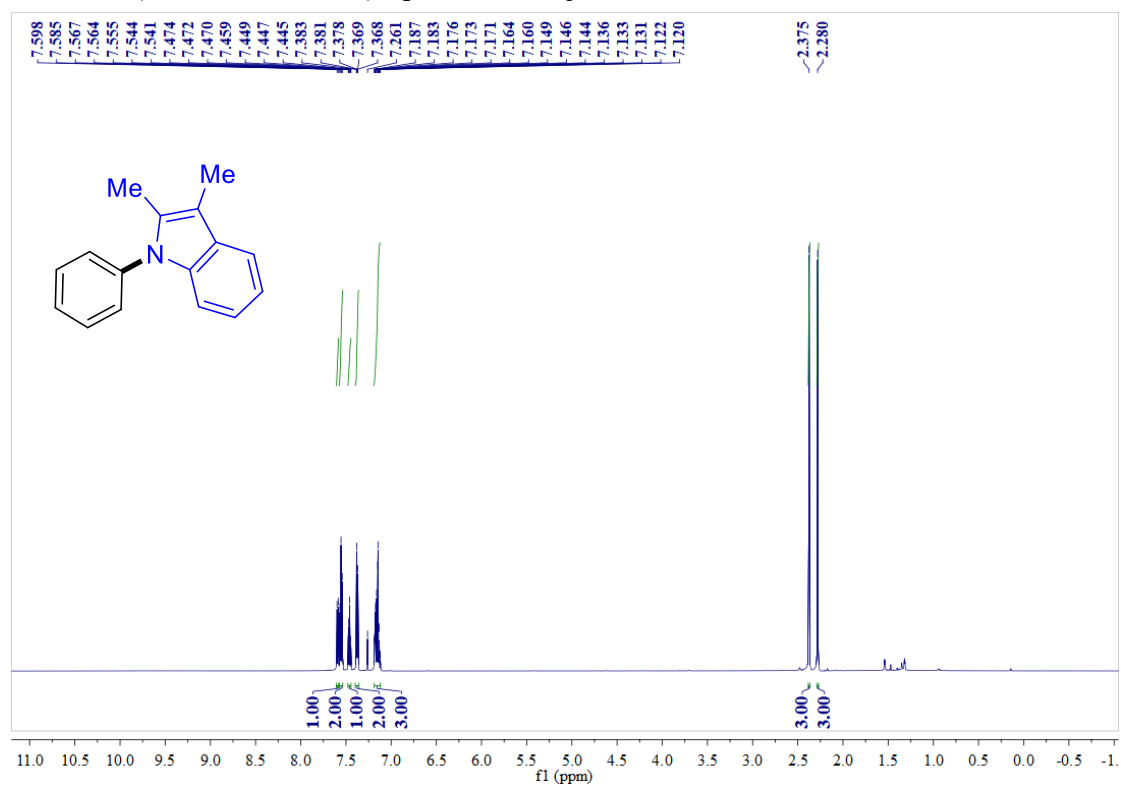
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **4i**



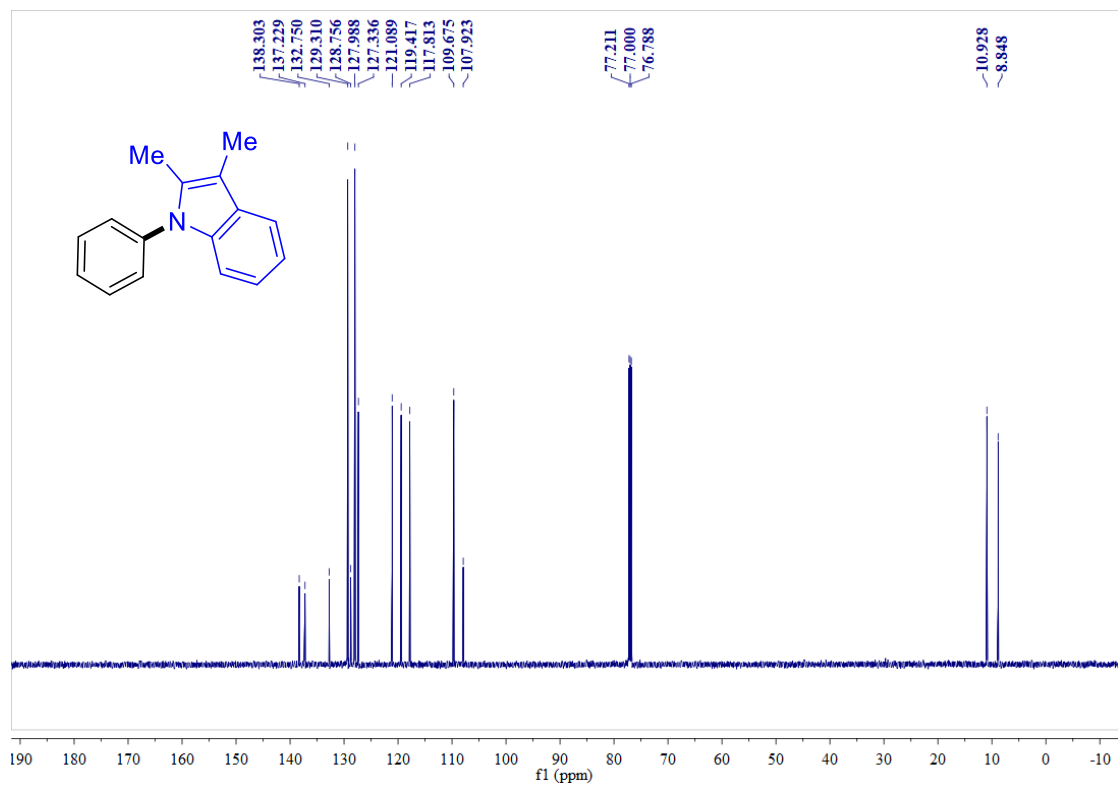
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **4i**



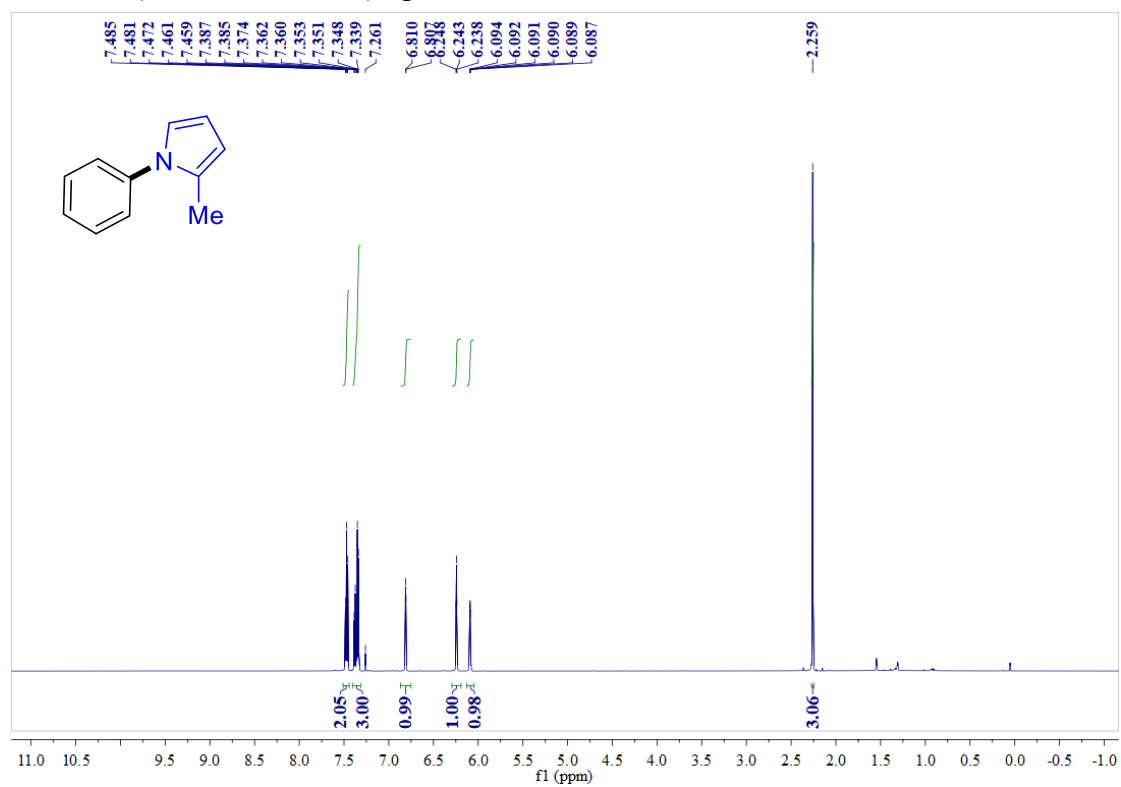
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **4j**



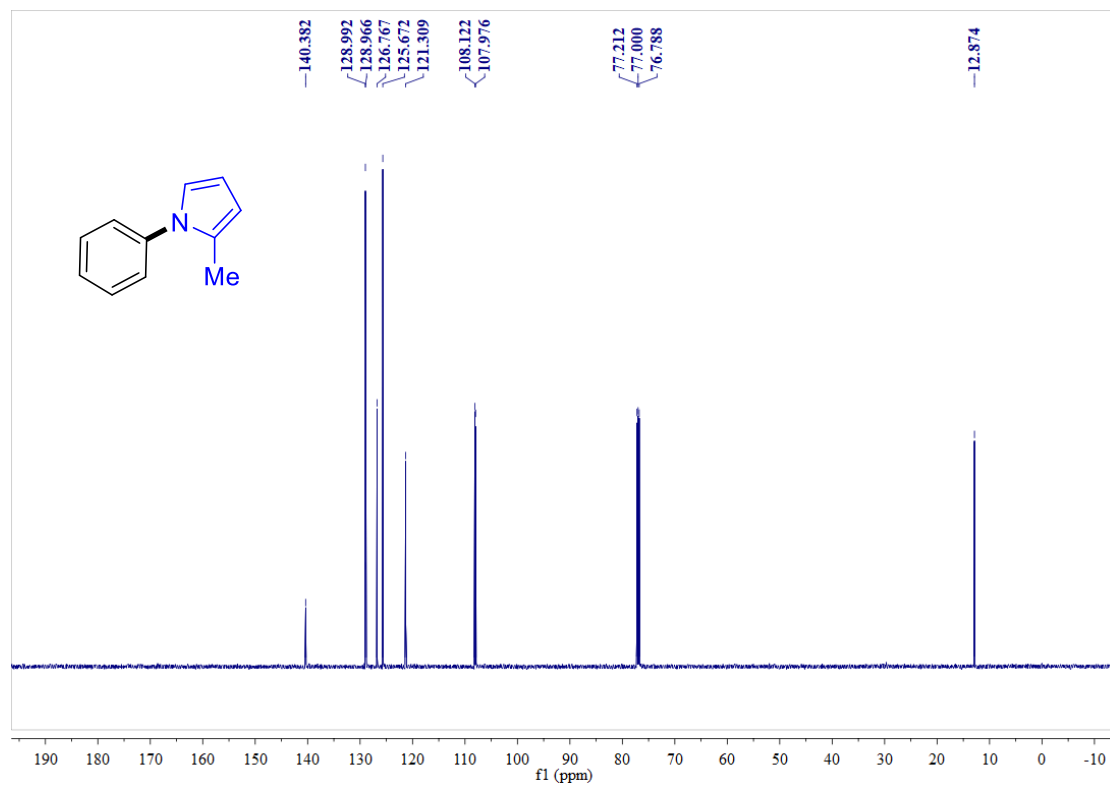
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **4j**



<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **4k**

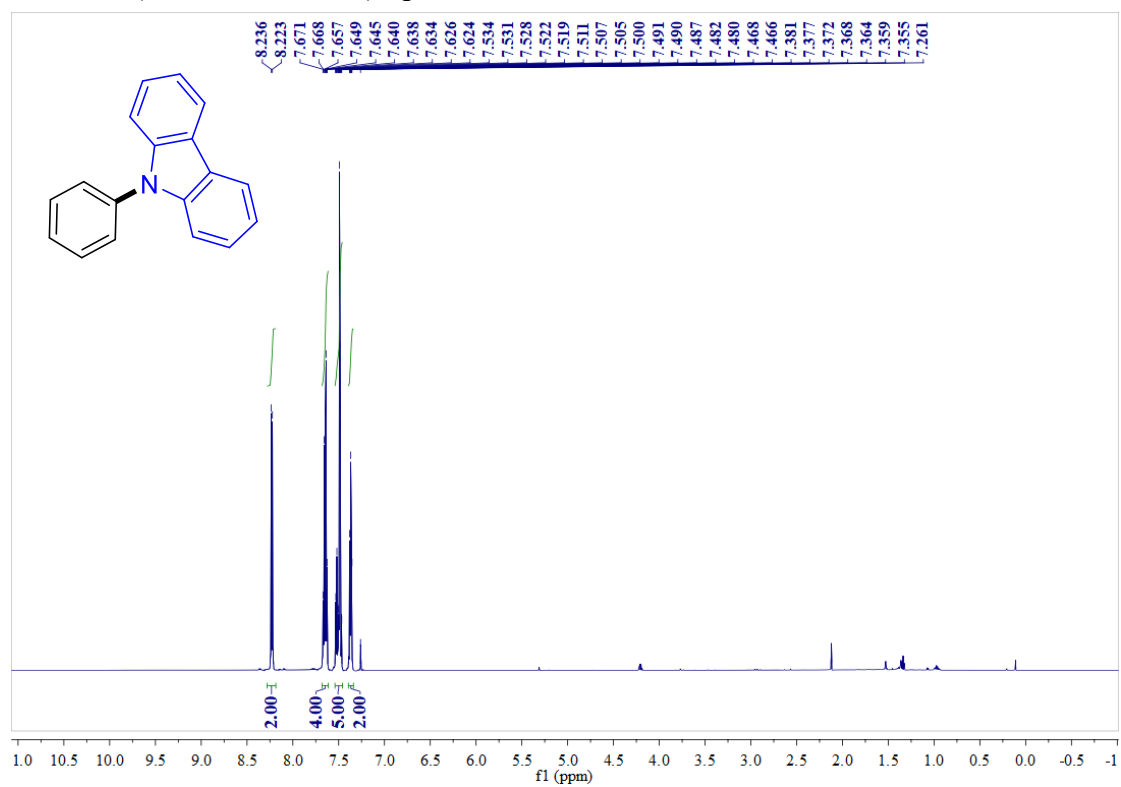


<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **4k**

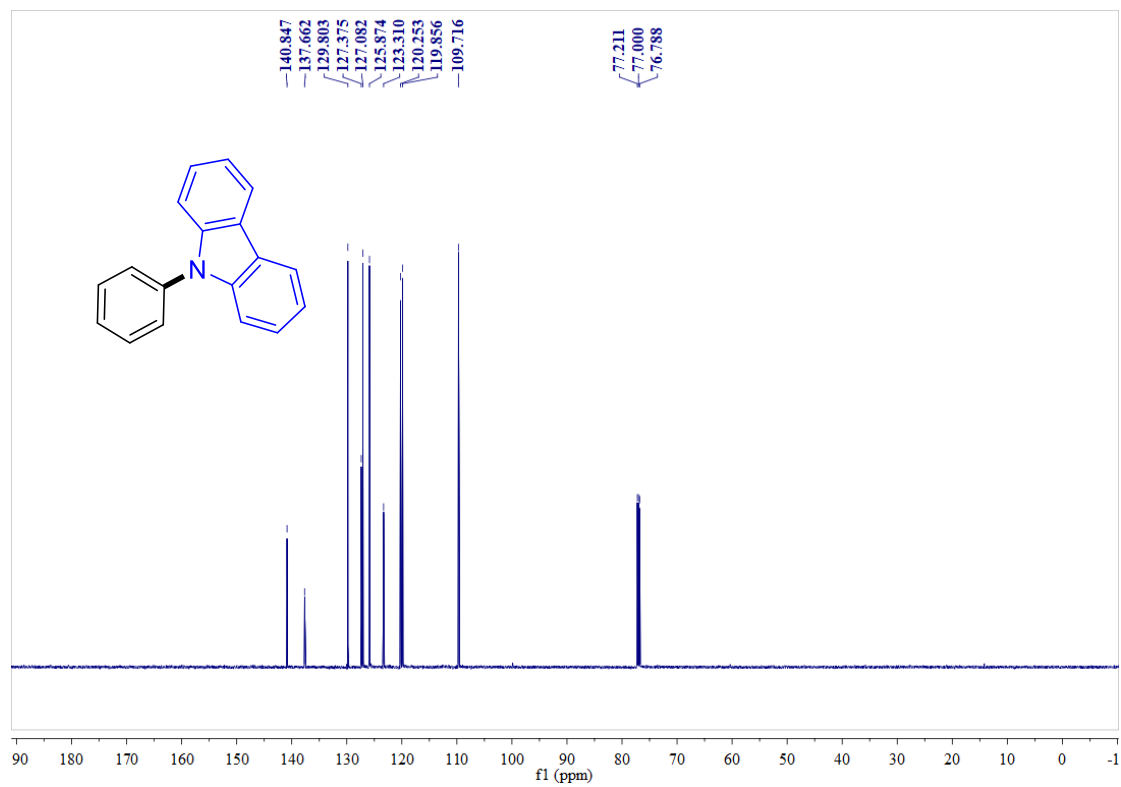




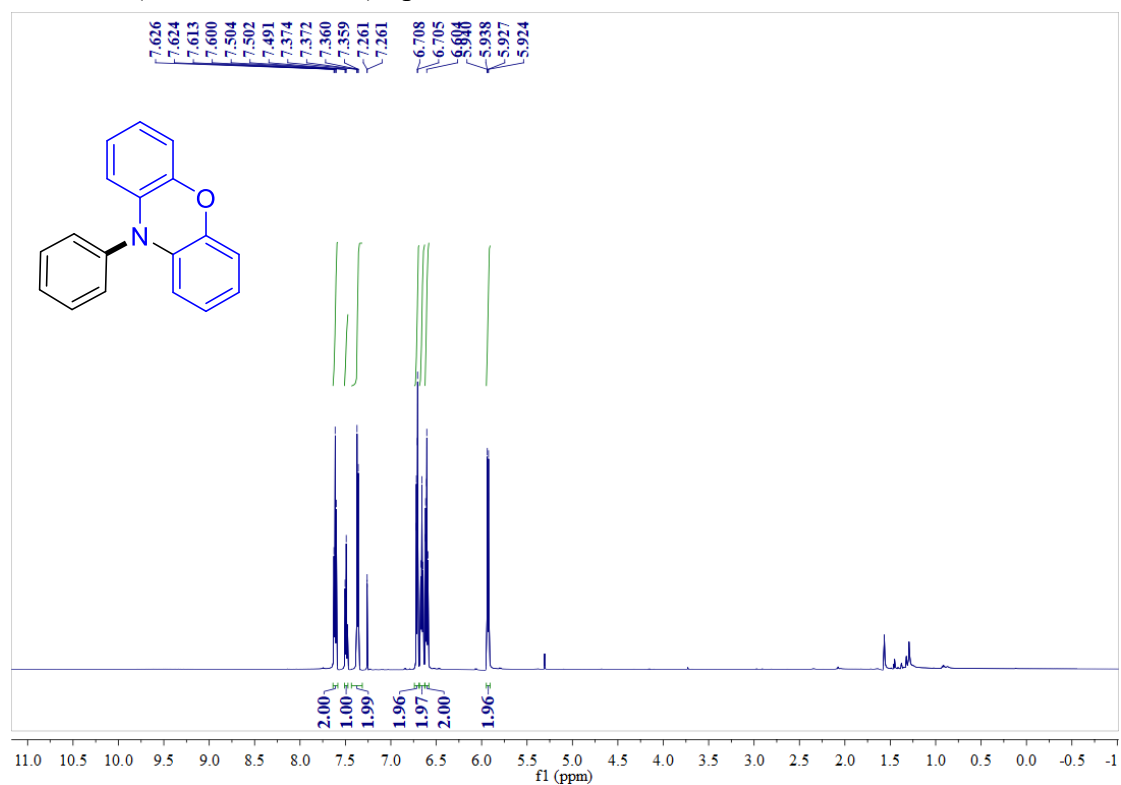
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **4l**



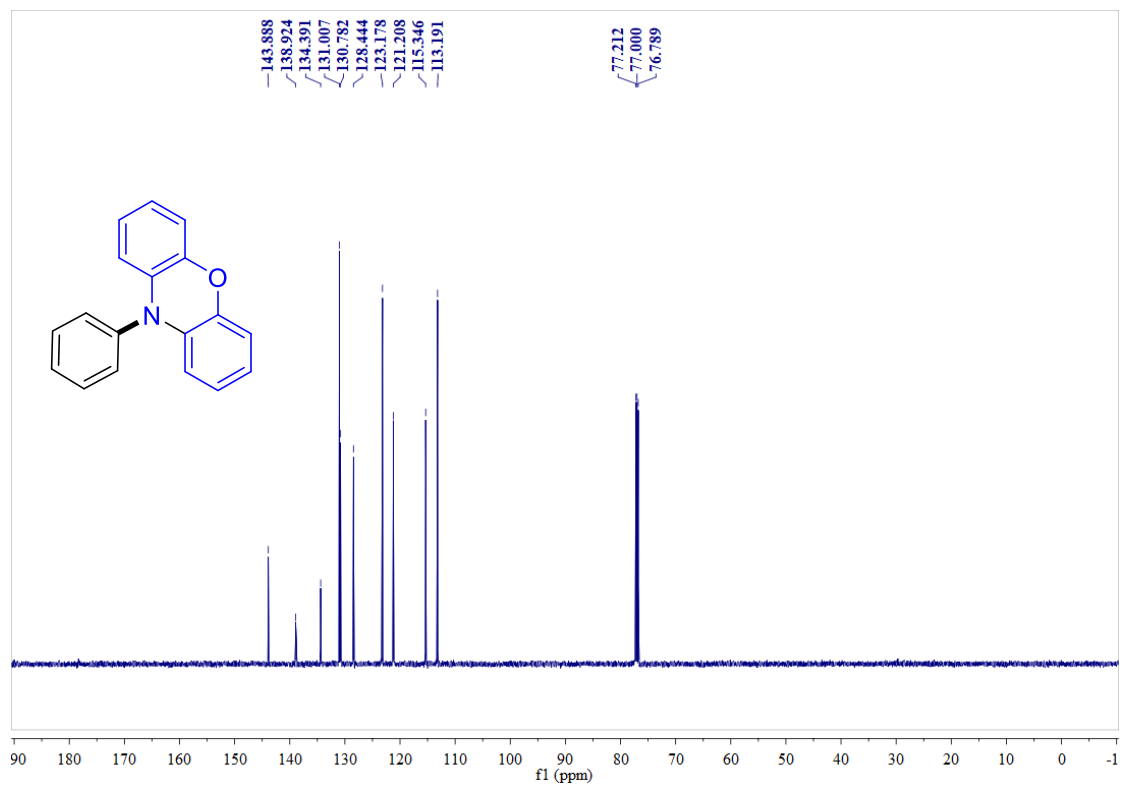
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **4l**



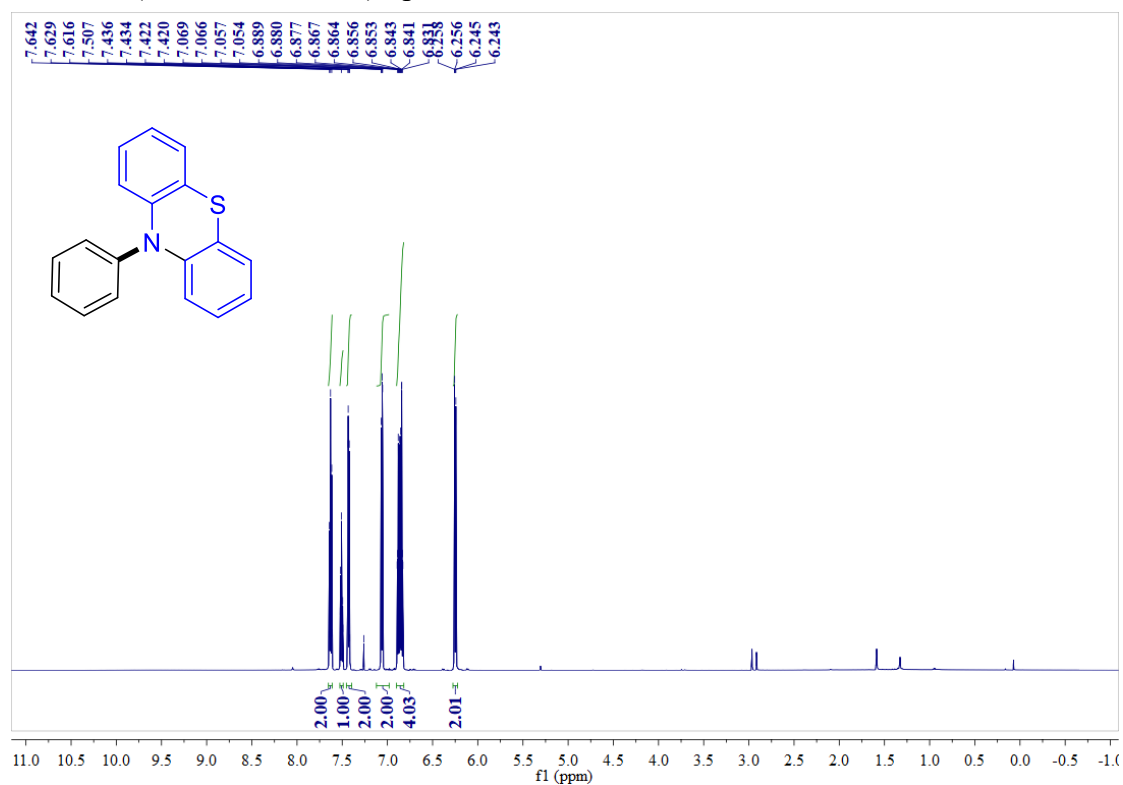
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **4m**



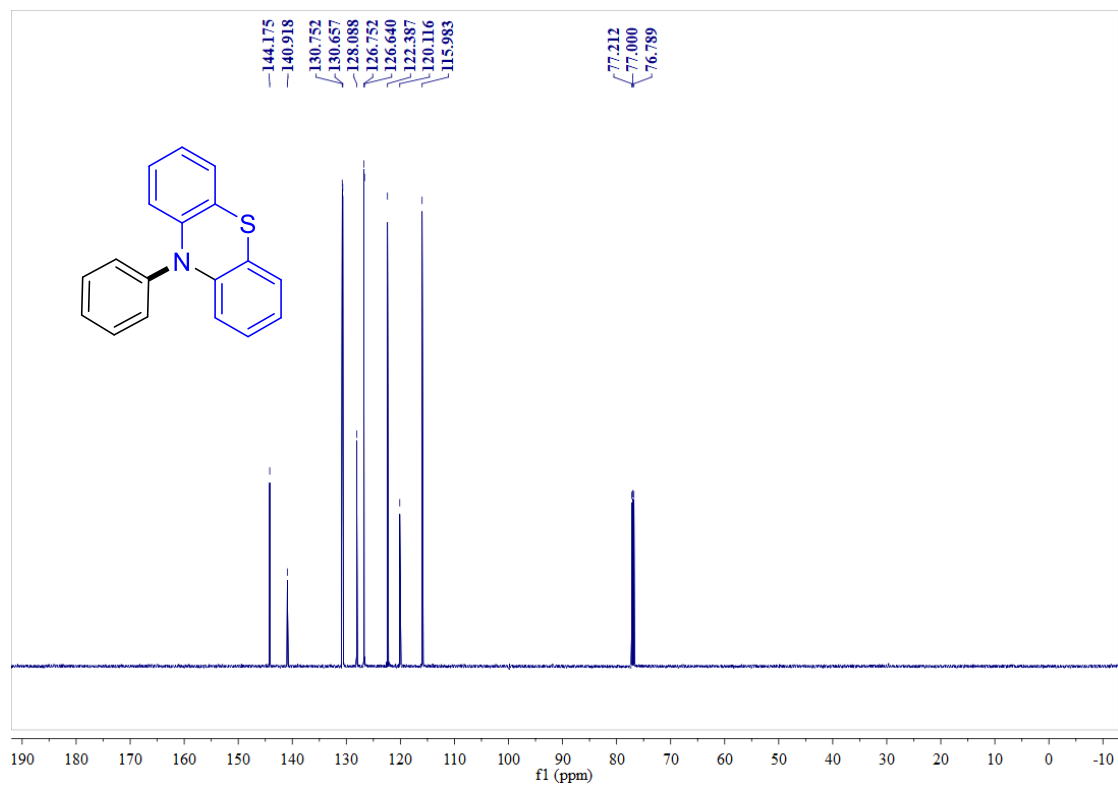
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **4m**



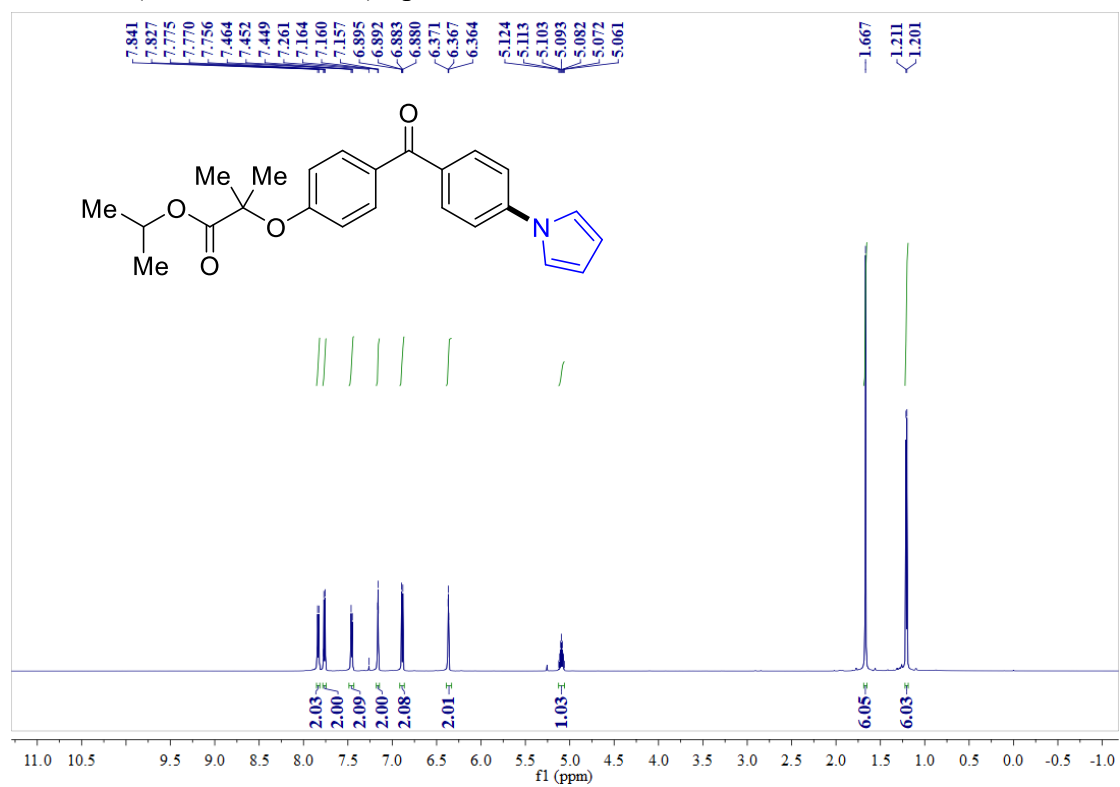
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **4n**



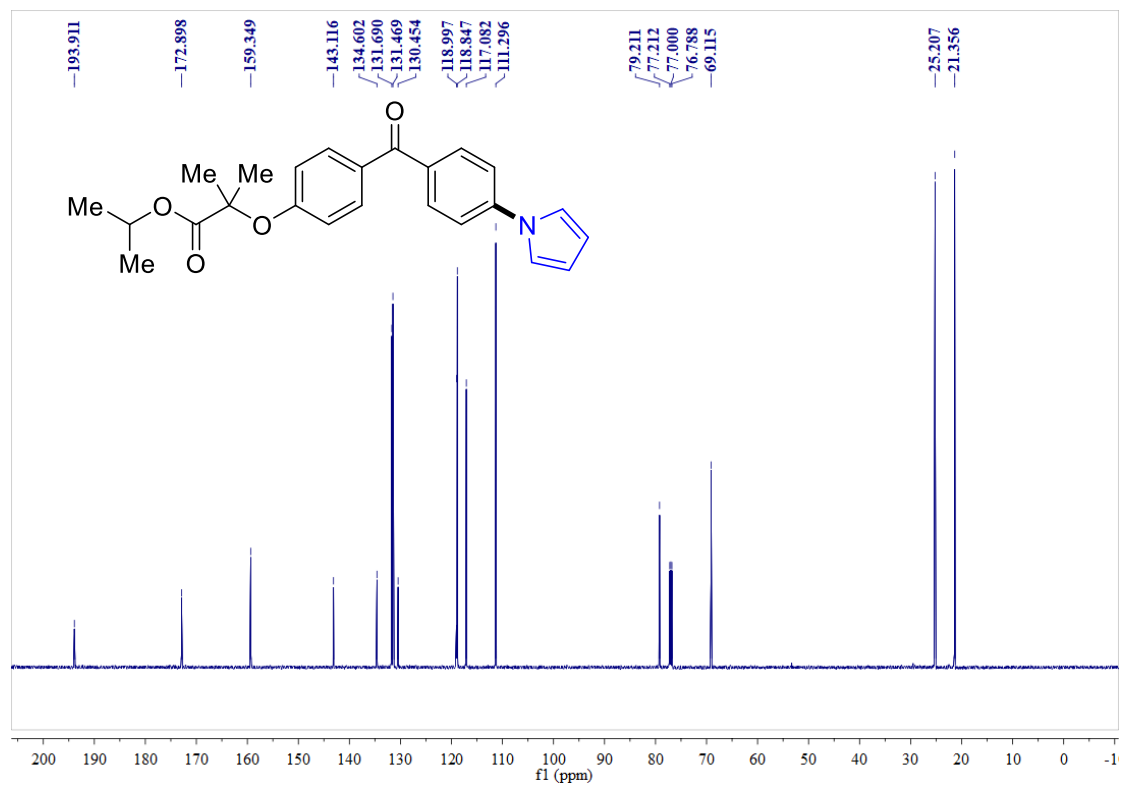
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **4n**



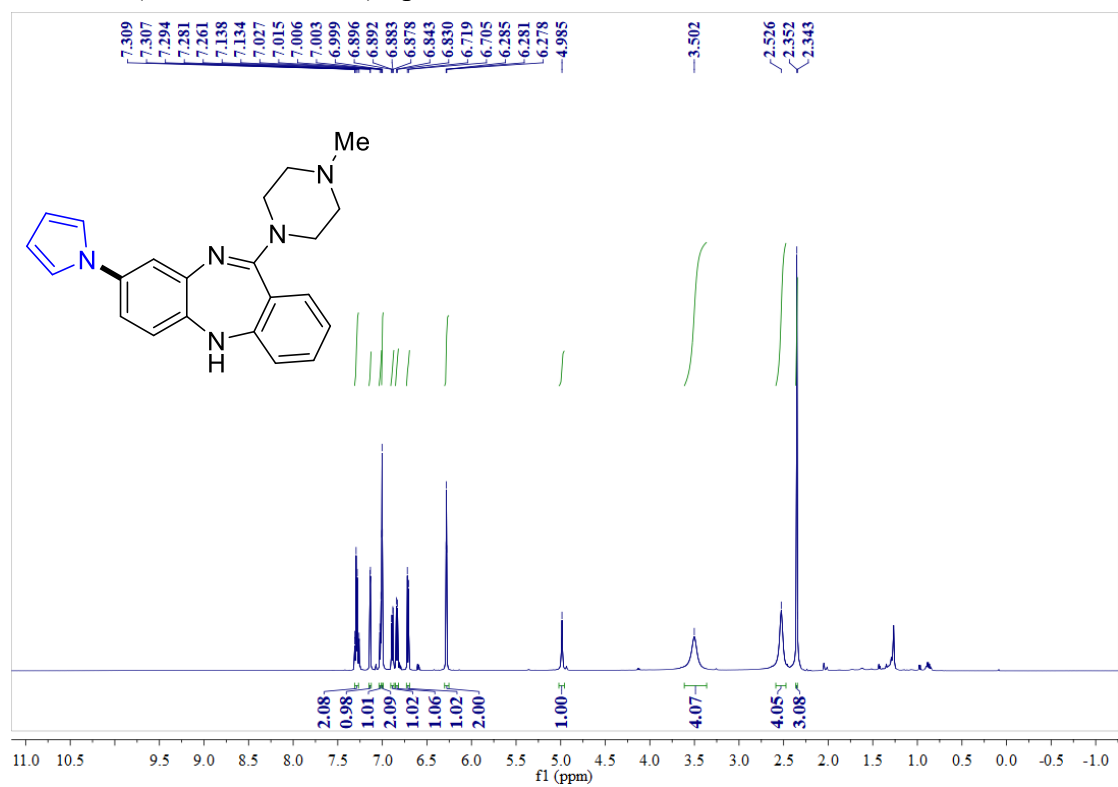
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **5**



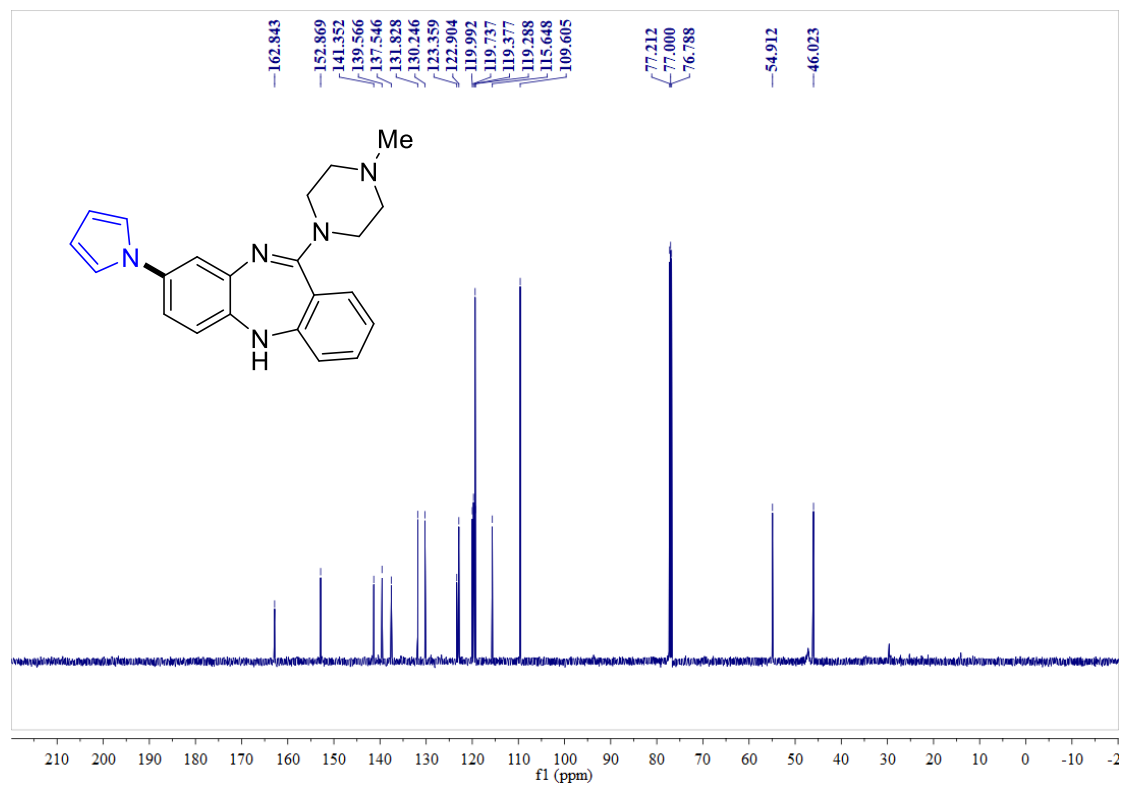
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **5**



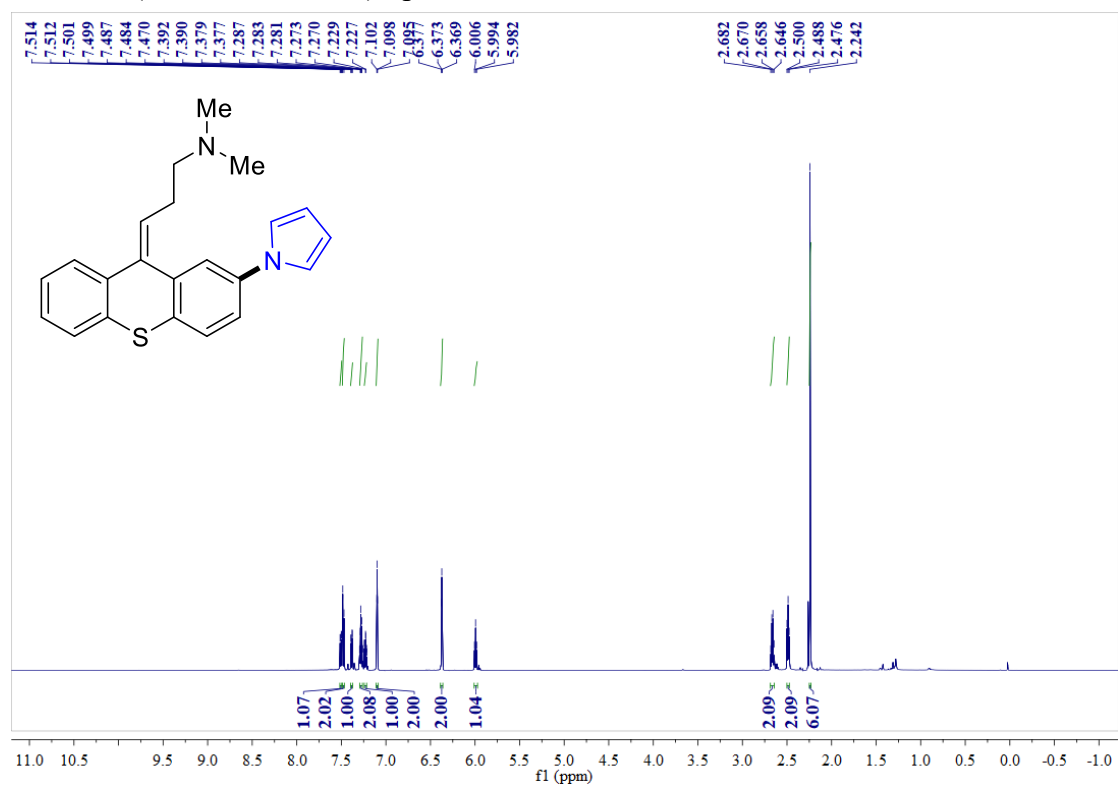
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **6**



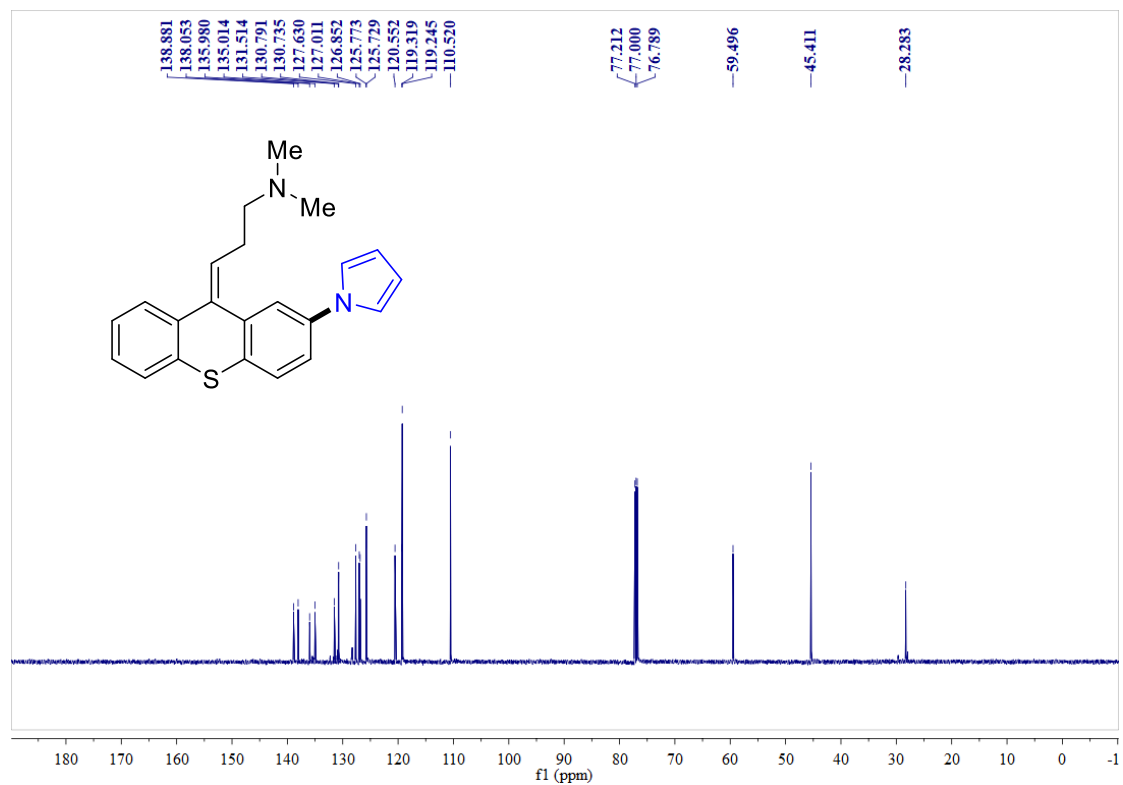
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **6**



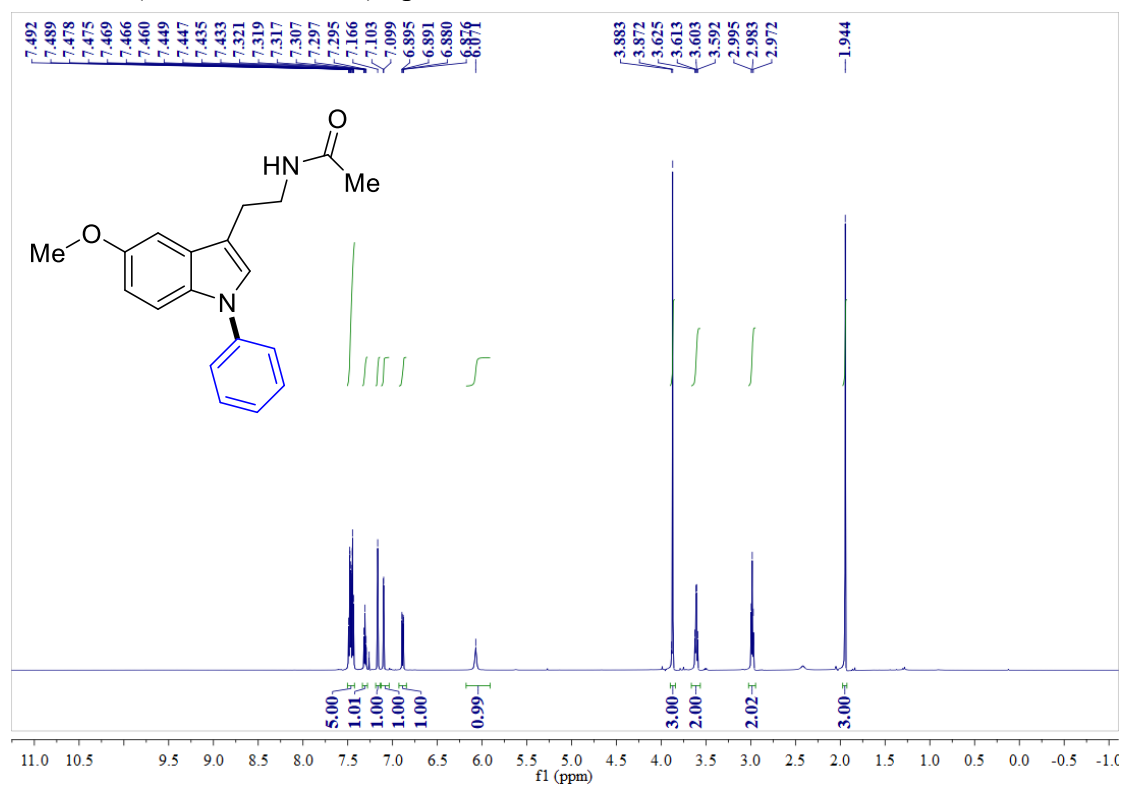
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of 7



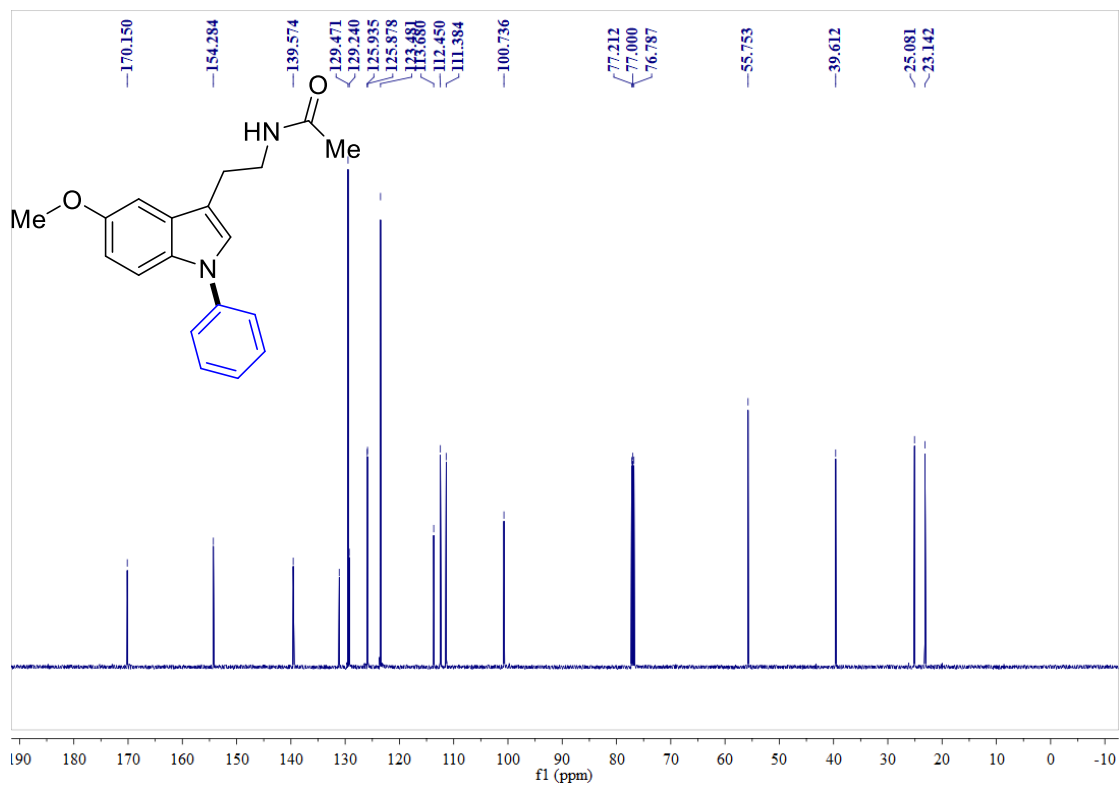
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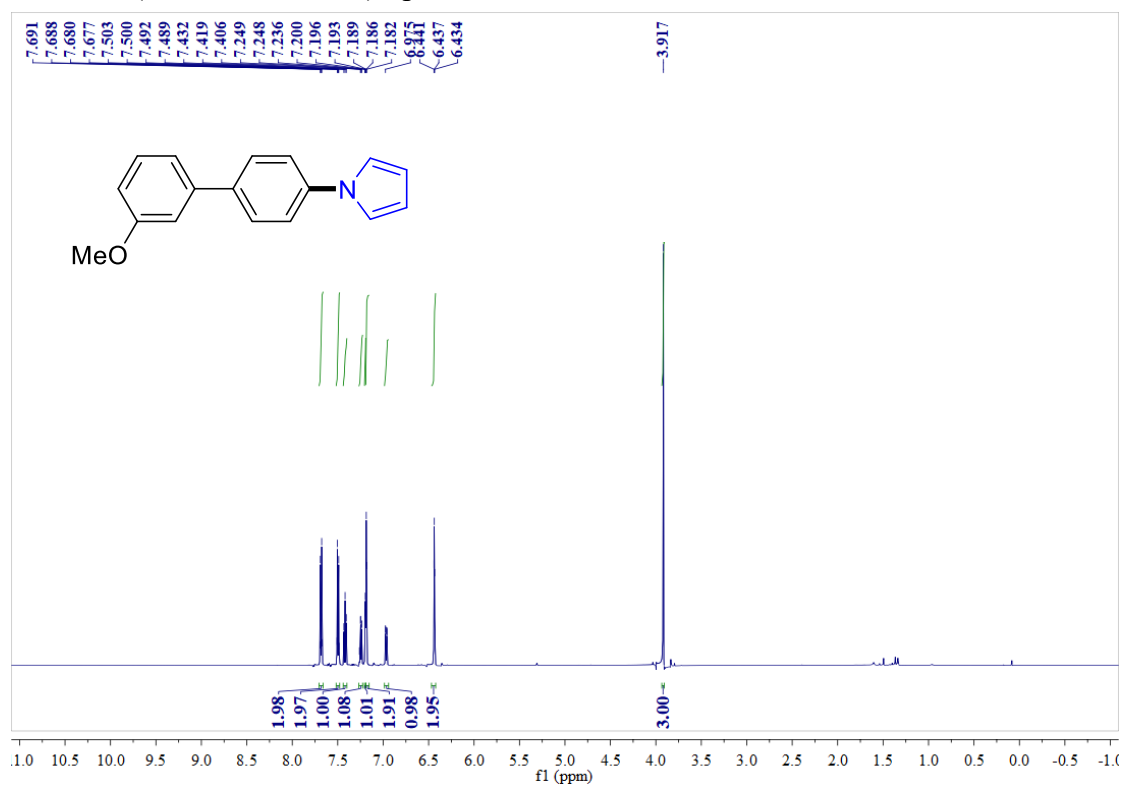
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **8**



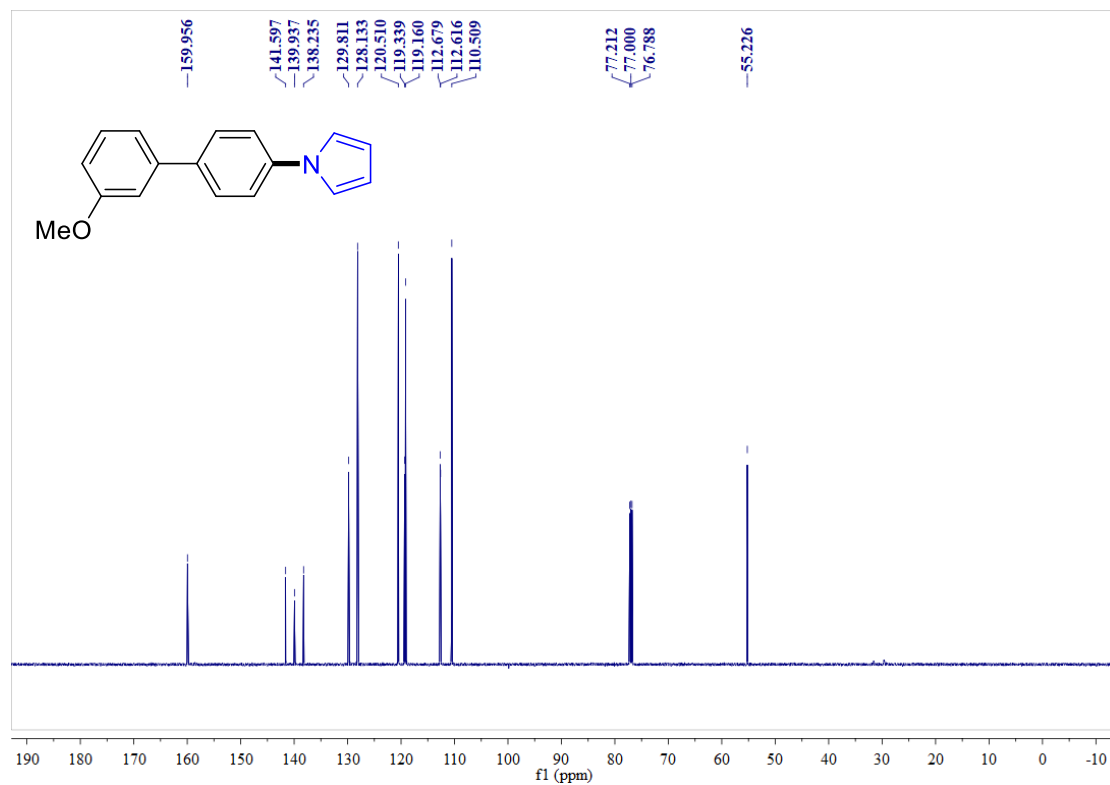
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **8**



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **9**

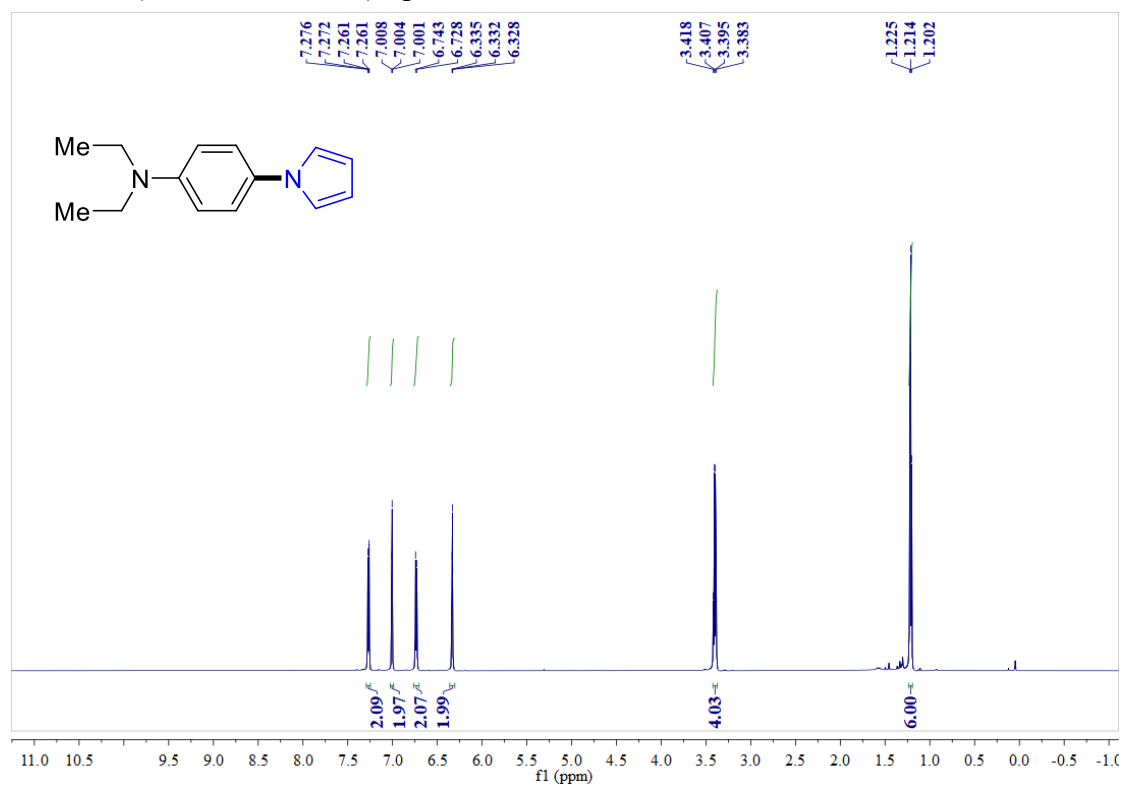


$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **9**

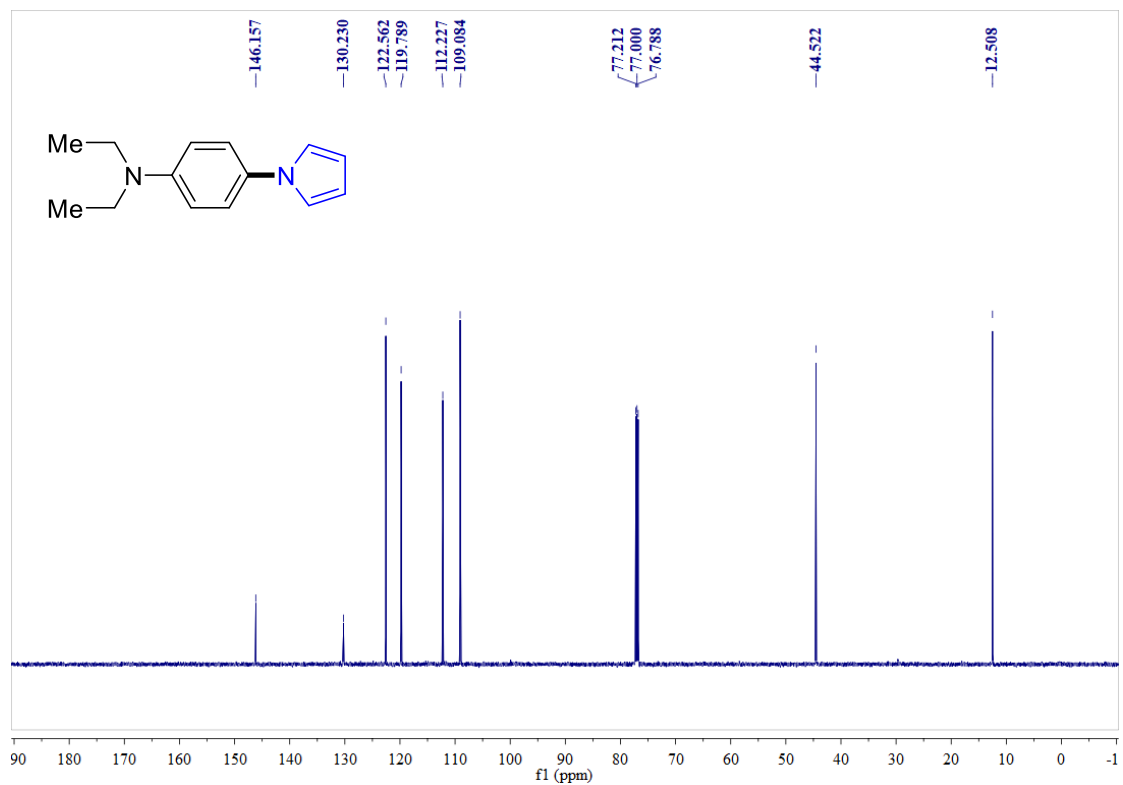




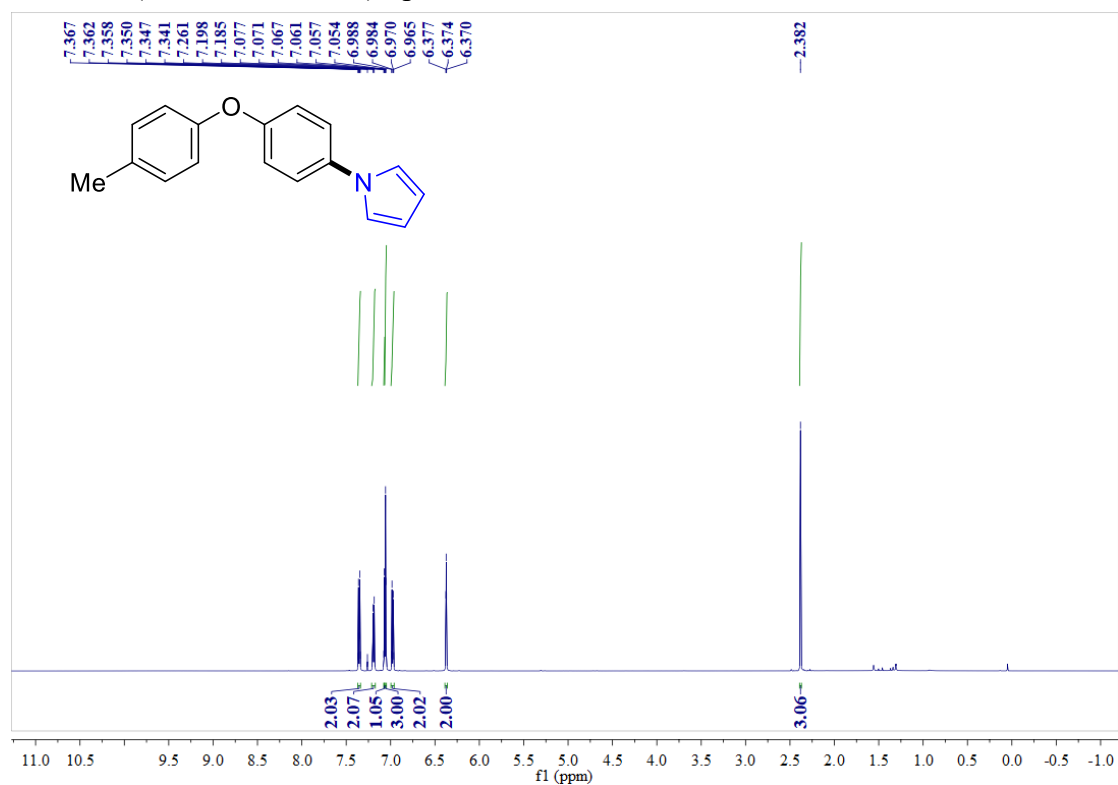
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **10**



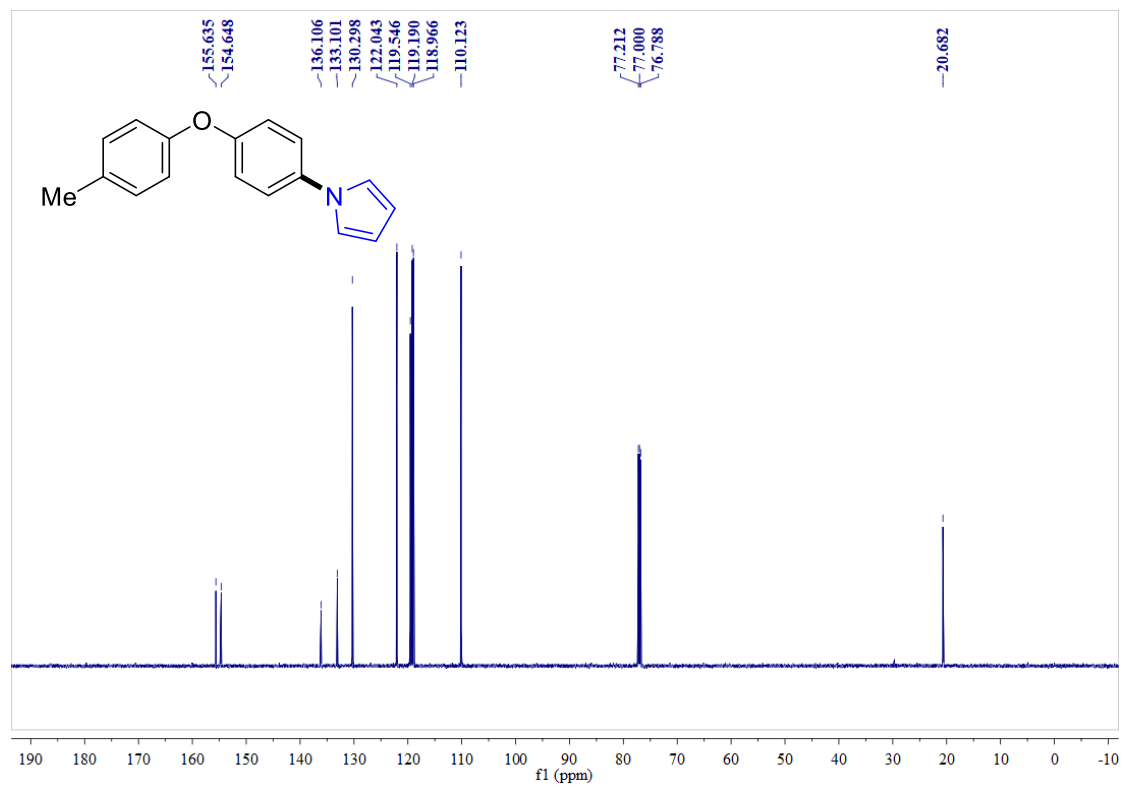
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **10**



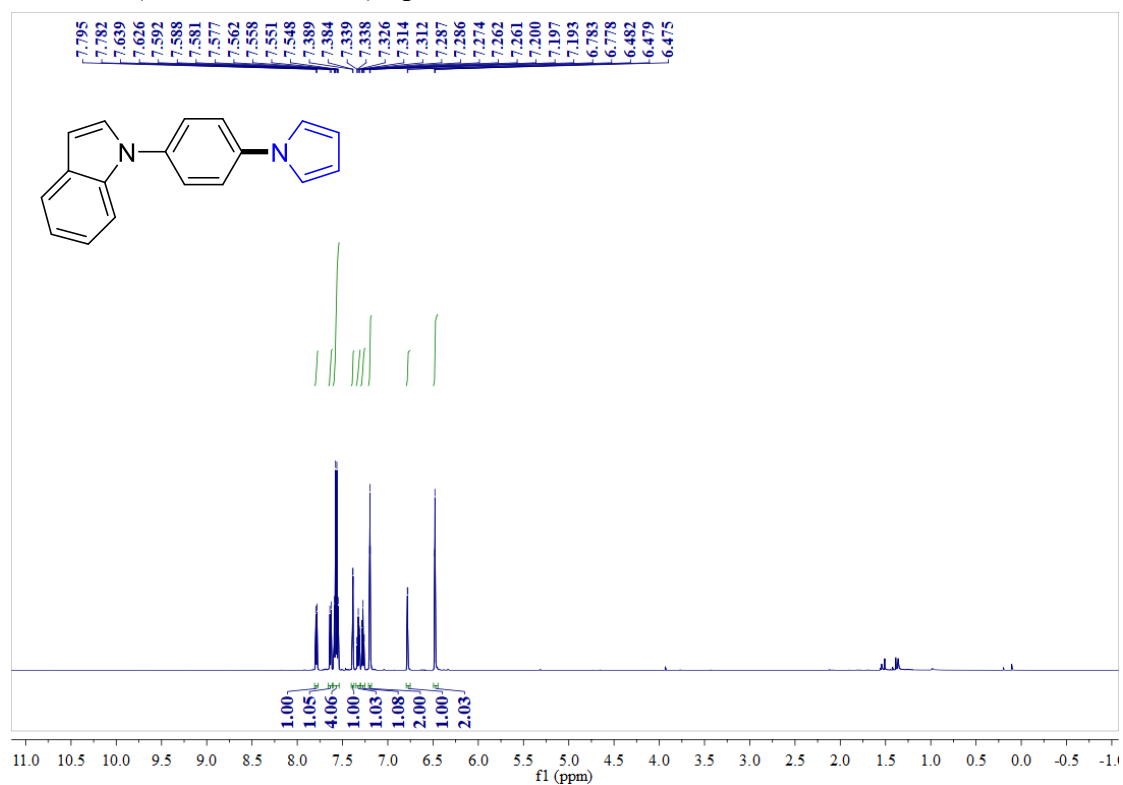
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **11**



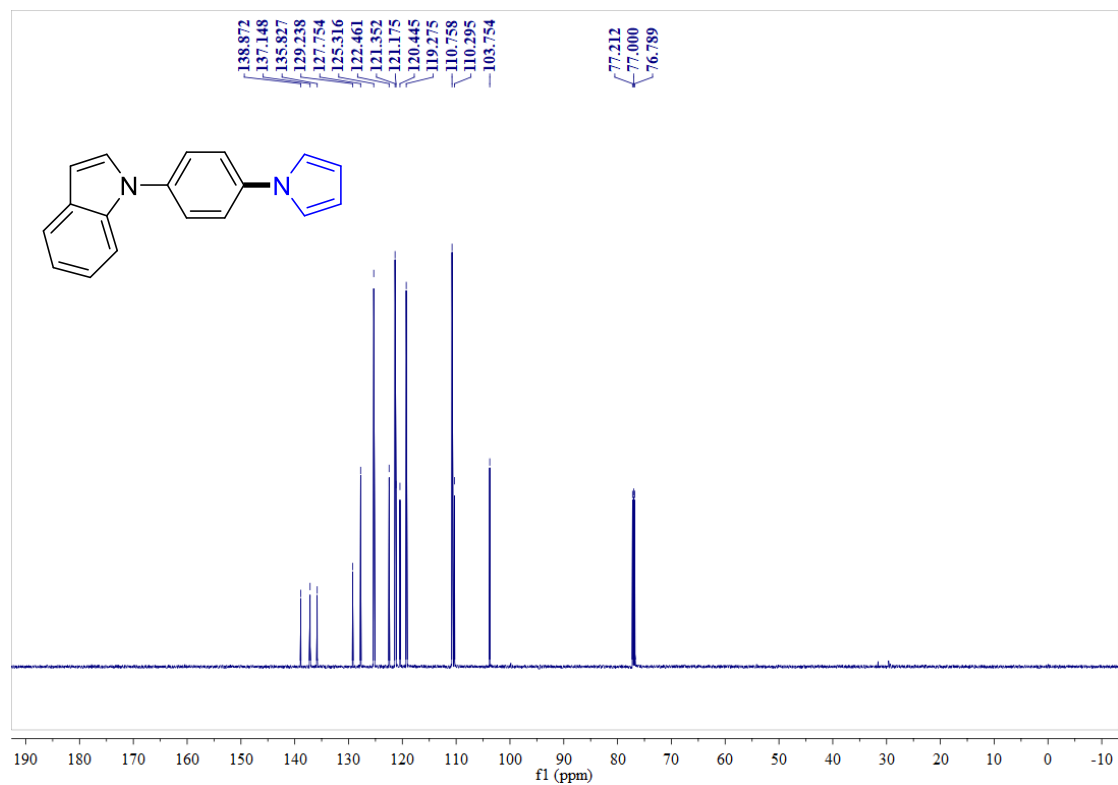
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **11**



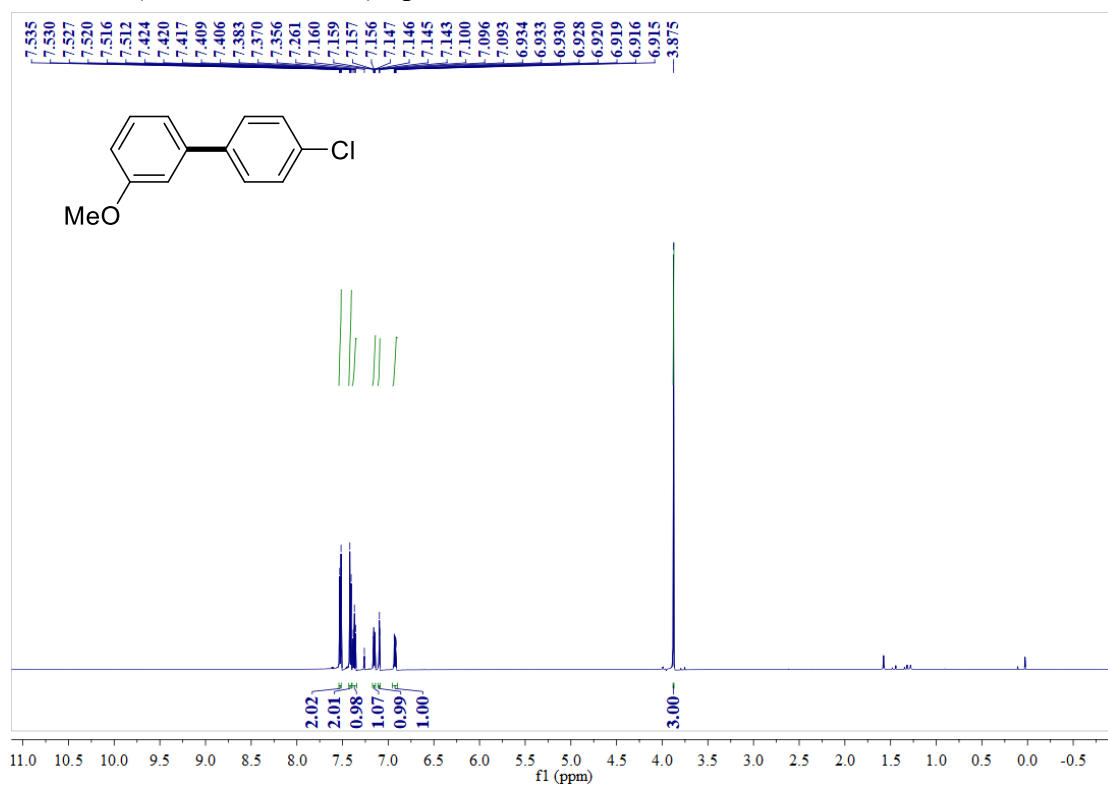
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **12**



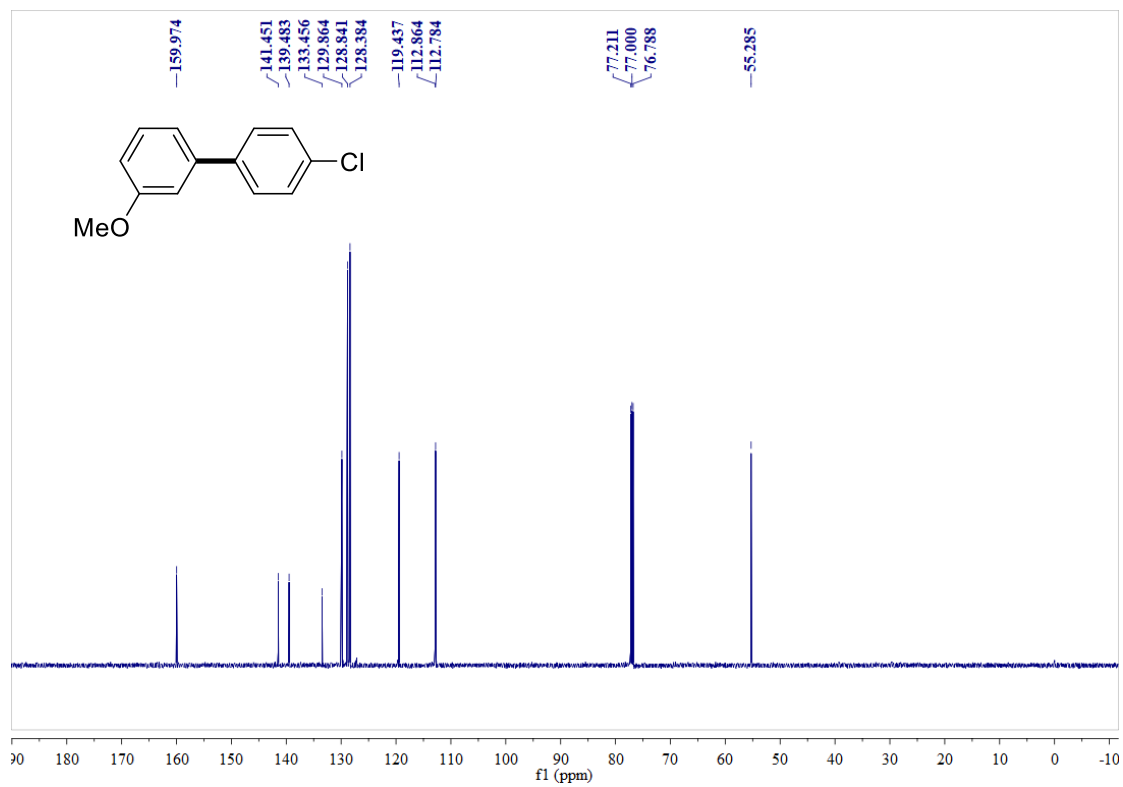
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **12**



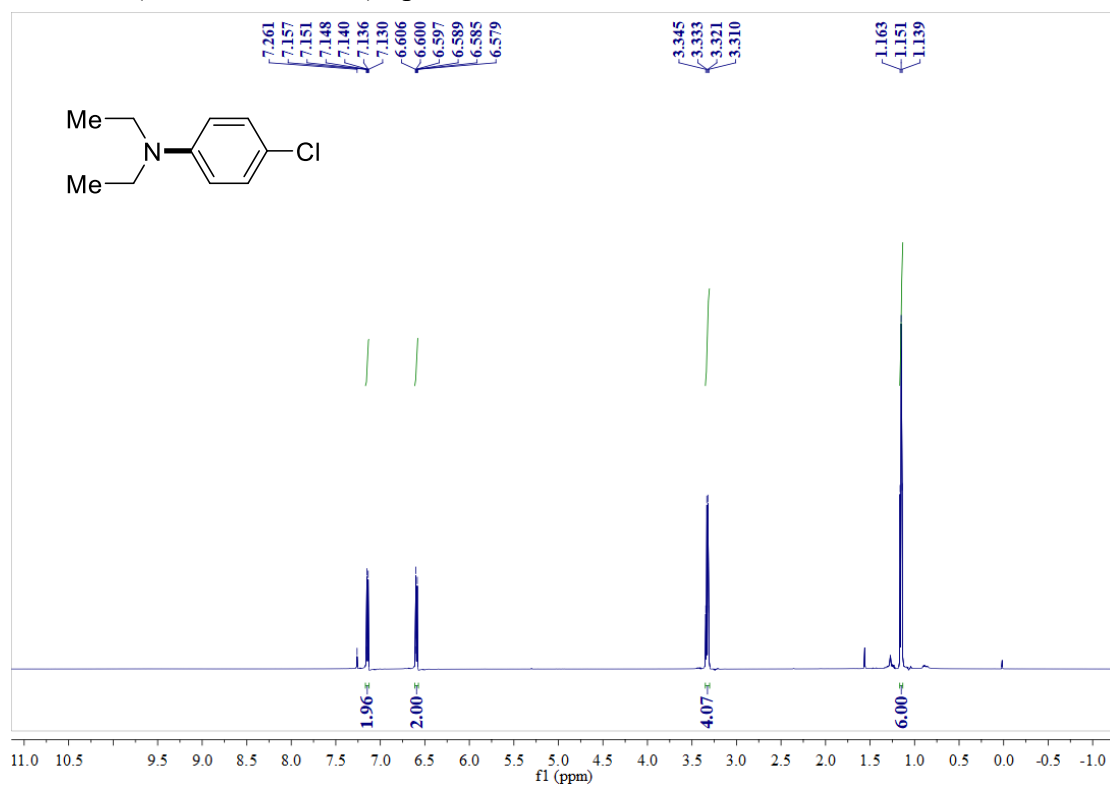
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **9a**



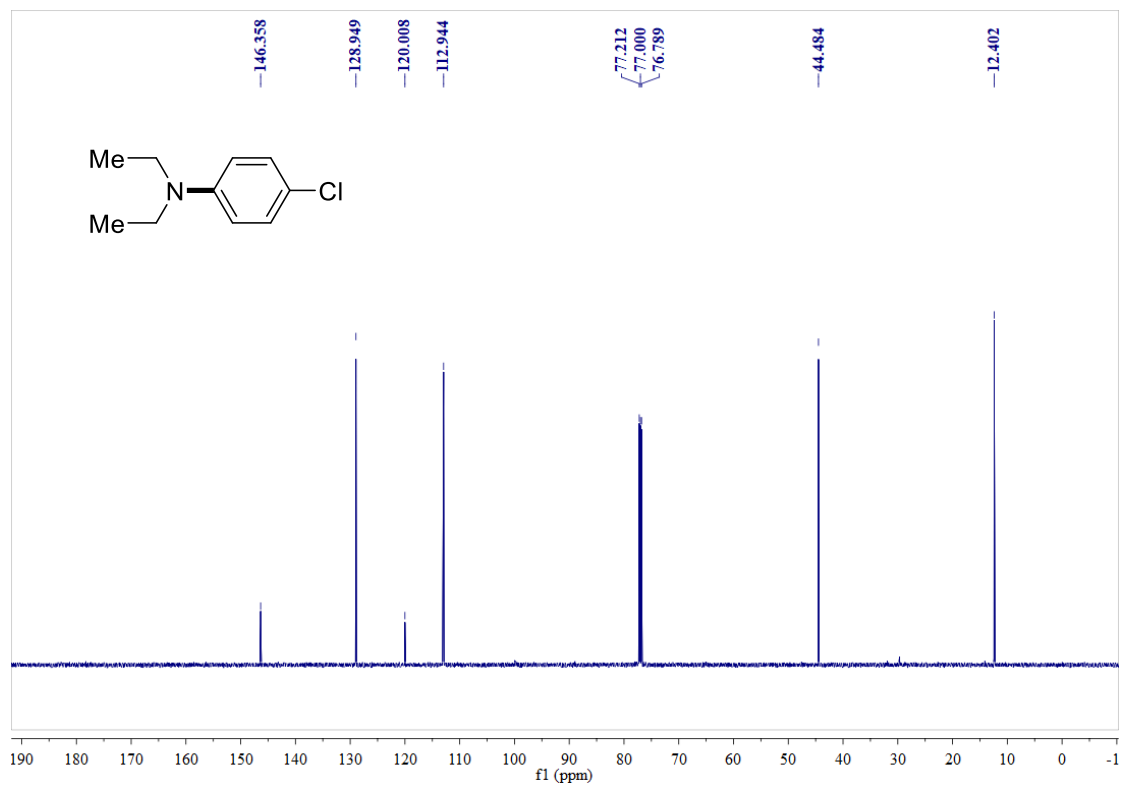
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **9a**



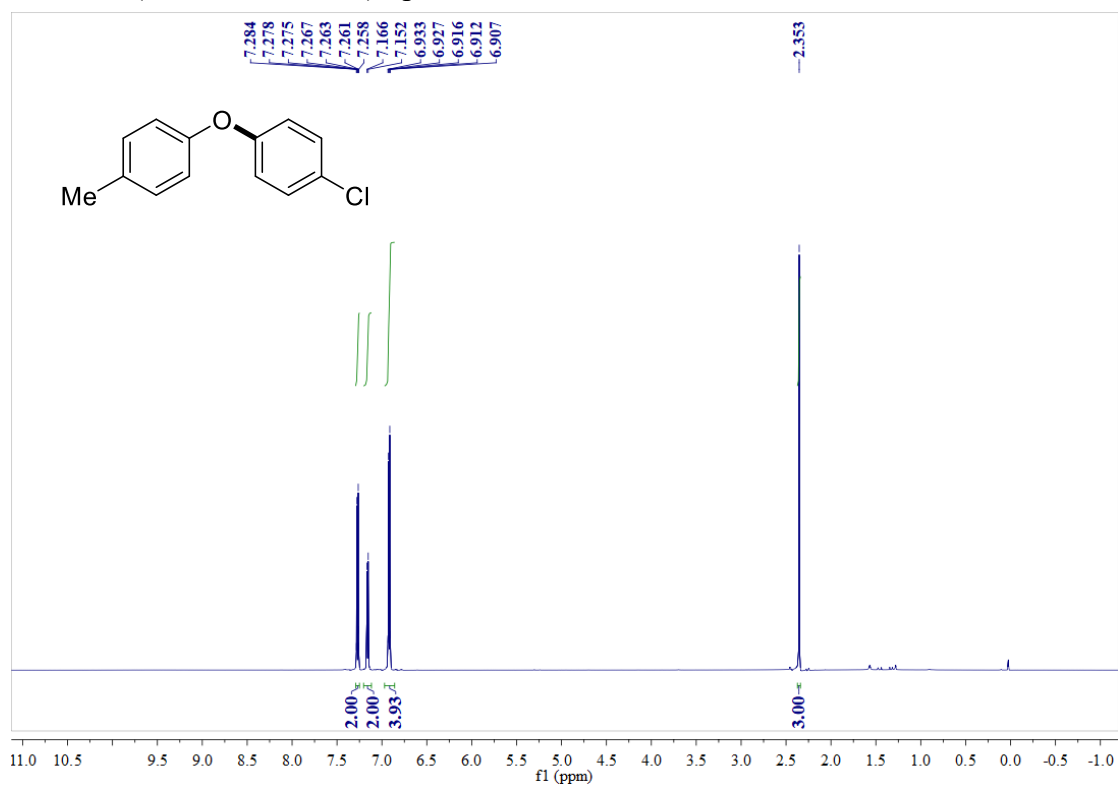
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **10a**



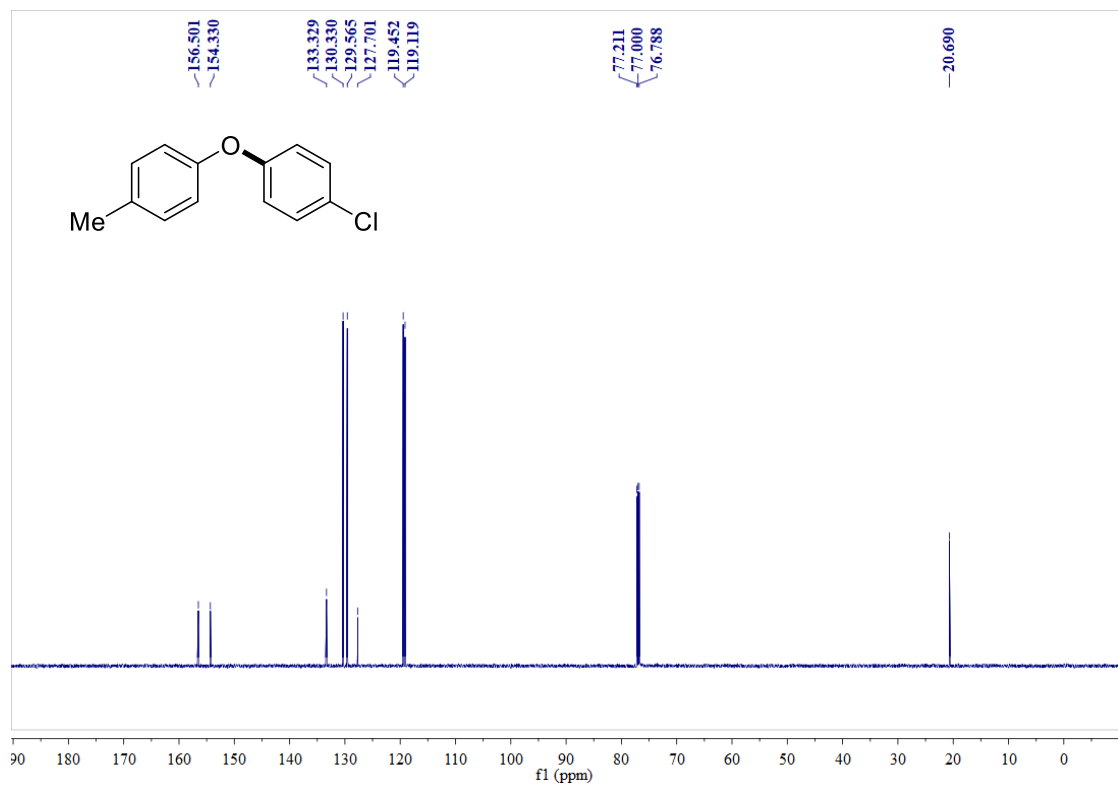
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **10a**



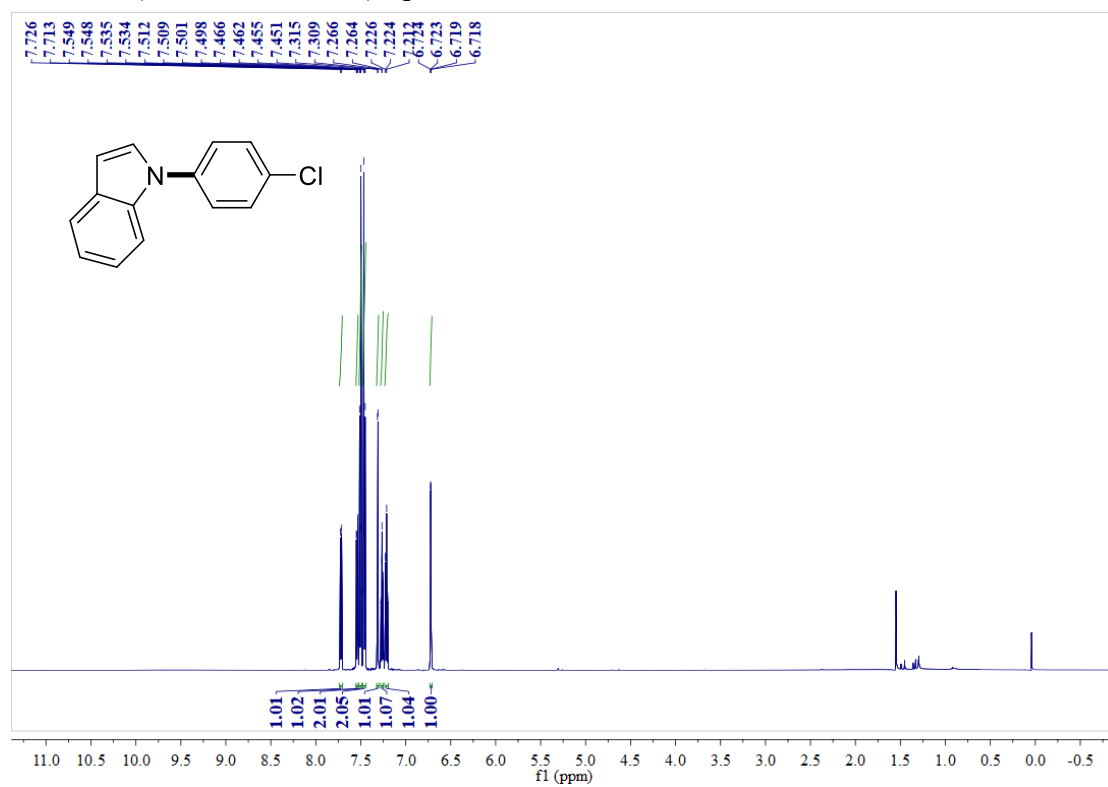
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) Spectrum of **11a**



<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) Spectrum of **11a**



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) Spectrum of **12a**



$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) Spectrum of **12a**

