

# Orthometallated Pd(II) C<sup>N</sup>S Pincer Complexes Catalyzed Sustainable Synthesis of Bis(indolyl)methanes via Acceptorless Dehydrogenative Coupling of Alcohols

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## 1. Materials and methods

Chemically pure and analar grade reagents were used for all the reactions. Commercially available  $[\text{PdCl}_2(\text{PPh}_3)_2]$ , Phenyl isothiocyanate, benzhydrazide derivatives,  $\text{CDCl}_3$ ,  $\text{DMSO-d}_6$ , Indole, 5-methoxy indole and various alcohols was used as supplied from sigma aldrich. The solvents were freshly distilled before use following the standard procedures.<sup>1</sup> Melting point was recorded in the Boetie micro heating table and is uncorrected. The elemental analysis of carbon, hydrogen, nitrogen and sulphur were performed at Sophisticated Test and Instrumentation Centre (STIC), Cochin University of Science and Technology, Kochi. Infrared spectra of complexes were recorded in KBr pellets with a Perkin–Elmer 597 spectrophotometer in the range of  $4000\text{--}400\text{cm}^{-1}$ . The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded in  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  with Bruker 400 MHz instrument using TMS as internal reference.

### X-ray crystallographic data collection

Single crystals of complex **1** was grown by slow evaporation of a chloroform in methanol (2:1) solution at room temperature. The data collection was carried out using a Bruker AXS Kappa APEX II single crystal X-ray diffractometer using monochromated  $\text{Mo-K}\alpha$  radiation ( $k\lambda = 0.71073 \text{ \AA}$ ). Data was collected at 296 K. The absorption corrections were performed by the multi-scan method using SADABS software.<sup>3</sup> Corrections were made for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS 97) and refined by full-matrix least squares on F<sup>2</sup> using SHELXL 97.<sup>4</sup> All non-hydrogen atoms were refined anisotropically and the hydrogen atoms in these structures were located from the difference Fourier map and constrained to the ideal positions in the refinement procedure. The unit cell parameters were determined by the method of difference vectors using reflections scanned from three different zones of the reciprocal lattice. The intensity data were measured using  $\omega$  and  $\phi$  scan with a frame width of  $0.5^\circ$ . Frame integration and data reduction were performed using the Bruker SAINT-Plus (Version 7.06a) software.<sup>5</sup> Figure 1 was drawn with ORTEP and the structural data have been deposited at the Cambridge Crystallographic Data Centre: CCDC **2066887**.

**2. Table S1. Crystal data and structure refinement for complex Pd1**

<b>Crystal data</b>	<b>Pd1</b>
Empirical formula	C <sub>32</sub> H <sub>26</sub> N <sub>3</sub> OPPdS
Formula weight	637.99
Colour	yellow
CCDC number	2066887
Temperature(K)	295(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.8480(4)
b/Å	11.6412(5)
c/Å	14.0807(6)
α/°	71.591(4)
β/°	74.372(4)
γ/°	75.139(4)
Volume/Å <sup>3</sup>	1448.84(12)
Z	2
Crystal density <sub>calcd.</sub> (Mg m <sup>-3</sup> )	1.462
Absorption coefficient(μ)(mm <sup>-1</sup> )	0.798
F(000)	648.0
Radiations	Mo Kα (λ = 0.71073)
Crystal size(mm)	0.14 × 0.06 × 0.05
Theta range(°)	6.84 to 58.99
Limiting indices	-13 ≤ h ≤ 13, -13 ≤ k ≤ 16, -19 ≤ l ≤ 18
Reflections collected	17484
Data/restraints/parameters	6991/0/360
Goodness-of-fit on F <sup>2</sup>	1.044
Final R indices [I ≥ 2σ(I)]	R <sub>1</sub> = 0.0387, wR <sub>2</sub> = 0.0761
R indices (all data)	R <sub>1</sub> = 0.0387, wR <sub>2</sub> = 0.0761
Largest diff. Peak and hole (e <sup>-</sup> Å <sup>-3</sup> )	1.13/-0.65

**Table S2. Selected bond lengths (Å) and bond angles (°) for the complex Pd1**

<b>Pd1</b>	
<b>Bond lengths (Å)</b>	
S(1)Pd(1)	2.3547(9)
P(1)Pd(1)	2.2444(7)
N(1)Pd(1)	1.997(2)
C(3)Pd(1)	2.040(3)
N(1)N(2)	1.377(3)
C(1)O(1)	1.255(3)
C(8)N(3)	1.347(4)
<b>Bond angles (°)</b>	
P(1)Pd(1) S(1)	97.75(3)
N(1)Pd(1) S(1)	82.64(7)
N(1)Pd(1) P(1)	175.74(7)
N(1)Pd(1)C(3)	80.59(10)
C(8)S(1)Pd(1)	96.72(11)
C(3)Pd(1)P(1)	98.89(8)
C(1)N(1)Pd(1)	120.02(19)
N(2)C(8)N(3)	115.7(2)
O(1)C(1)N(1)	124.4(3)
C(1)N(1)Pd(1)	120.029(19)
C(1)N(1)N(2)	119.2(2)

### 3. $^1\text{H}$ & $^{13}\text{C}$ NMR spectra of the ligands L1- L3

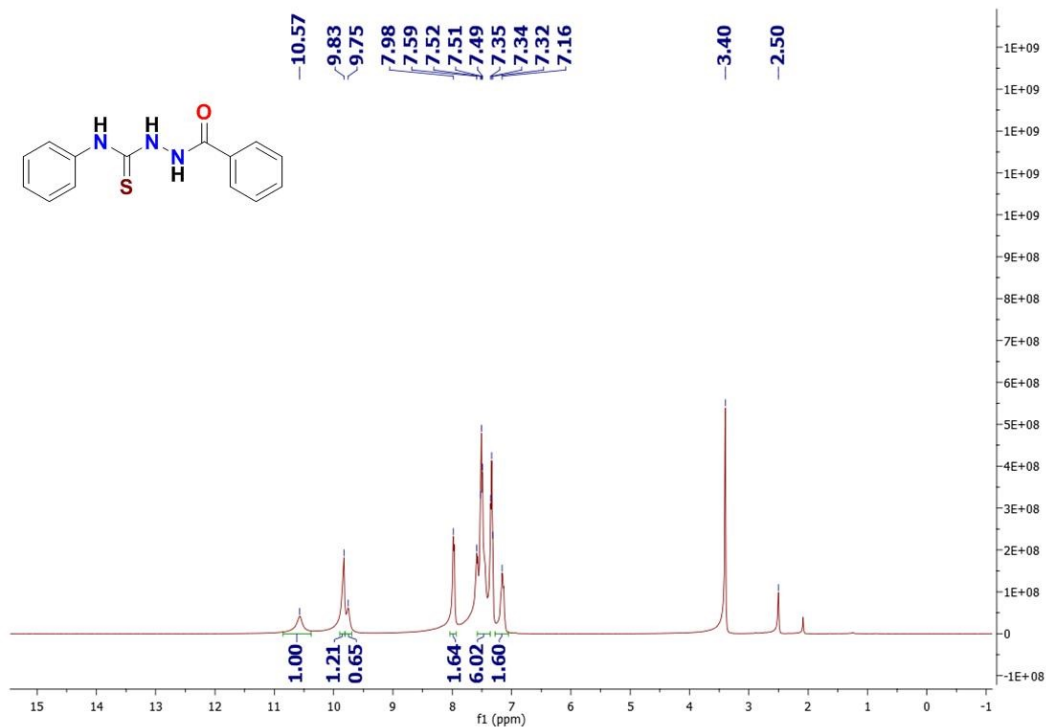


Figure 1.  $^1\text{H}$  NMR spectrum of ligand L1 in DMSO-  $\text{d}_6$  (400 MHz, 293 K)

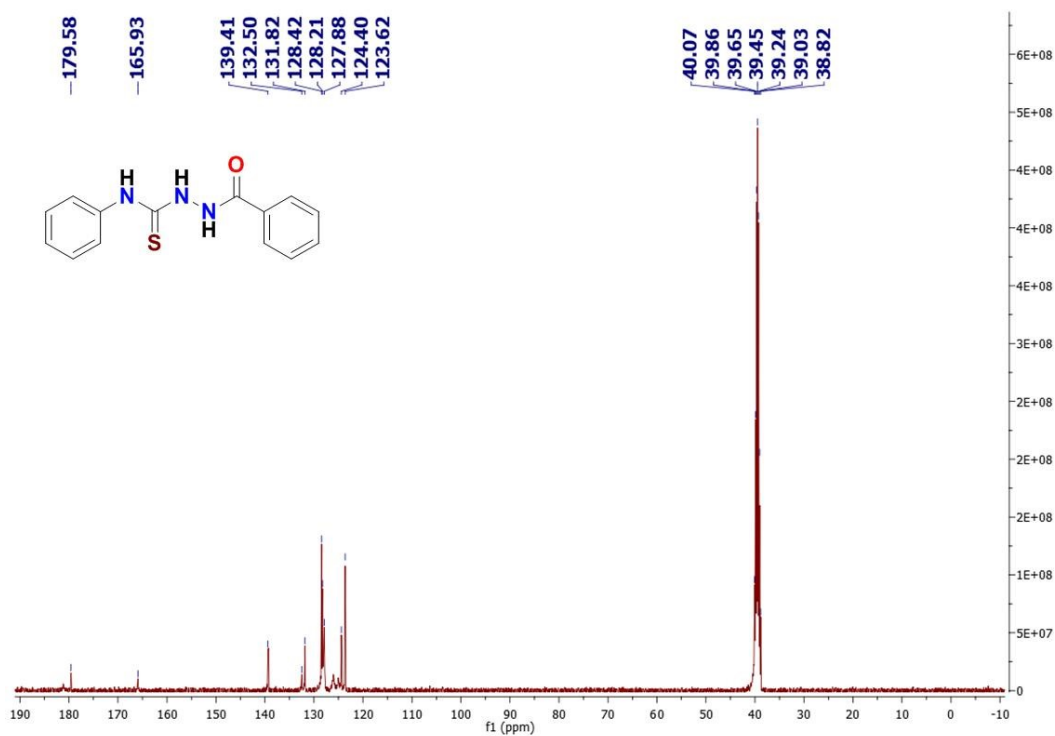
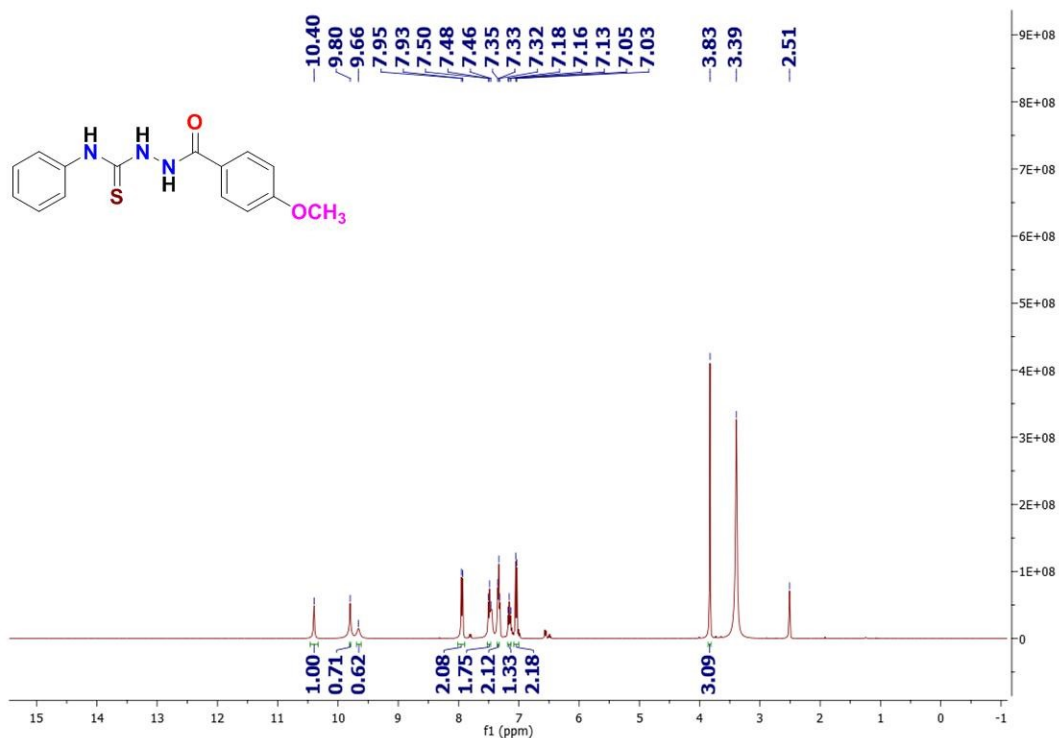
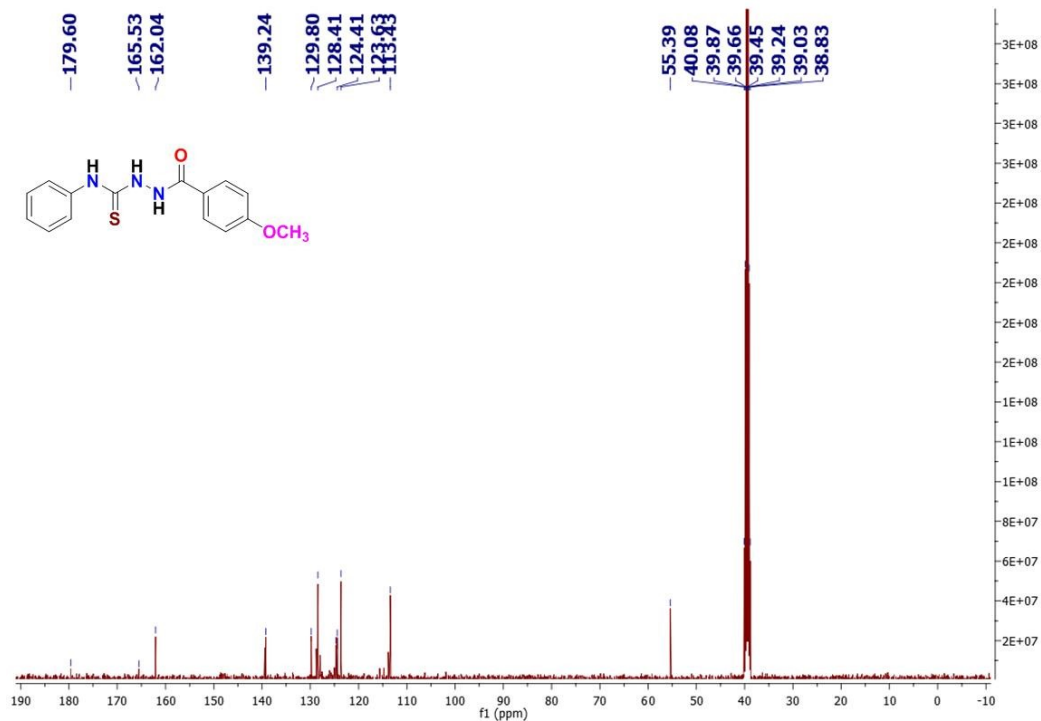


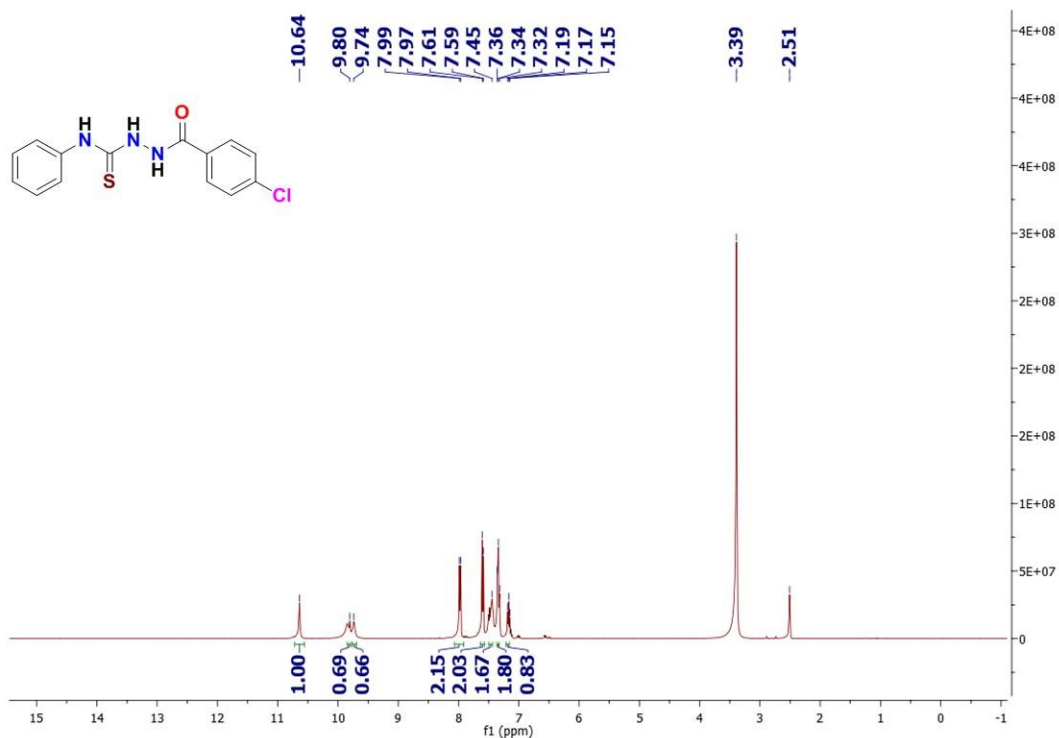
Figure 2.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of ligand L1 in DMSO-  $\text{d}_6$  (100 MHz, 293 K).



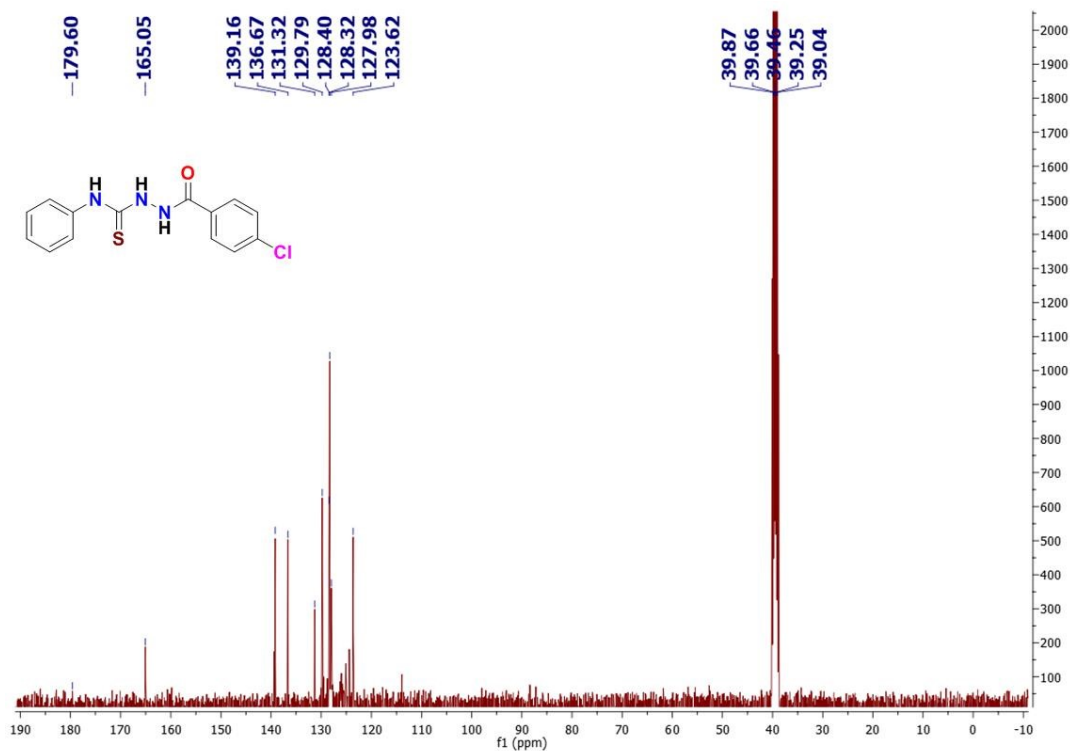
**Figure 3.**  $^1\text{H}$  NMR spectrum of ligand L2 in DMSO-  $\text{d}_6$  (400 MHz, 293 K)



**Figure 4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of ligand L2 in DMSO-  $\text{d}_6$  (100 MHz, 293 K).



**Figure 5.**  $^1\text{H}$  NMR spectrum of ligand L3 in DMSO- $\text{d}_6$  (400 MHz, 293 K).



**Figure 6.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of ligand L3 in DMSO- $\text{d}_6$  (100 MHz, 293 K).

#### 4. $^1\text{H}$ & $^{13}\text{C}$ NMR spectra of the complexes Pd1-Pd3

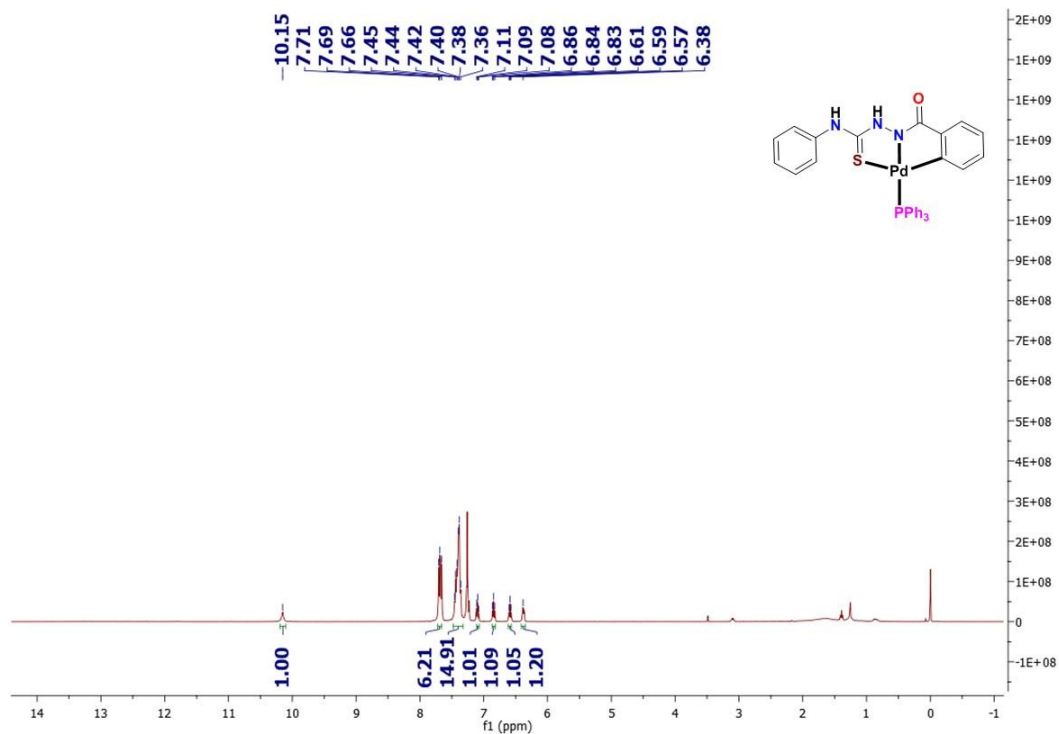


Figure 7.  $^1\text{H}$  NMR spectrum of complex Pd1 in  $\text{CDCl}_3$  (400 MHz, 293 K)

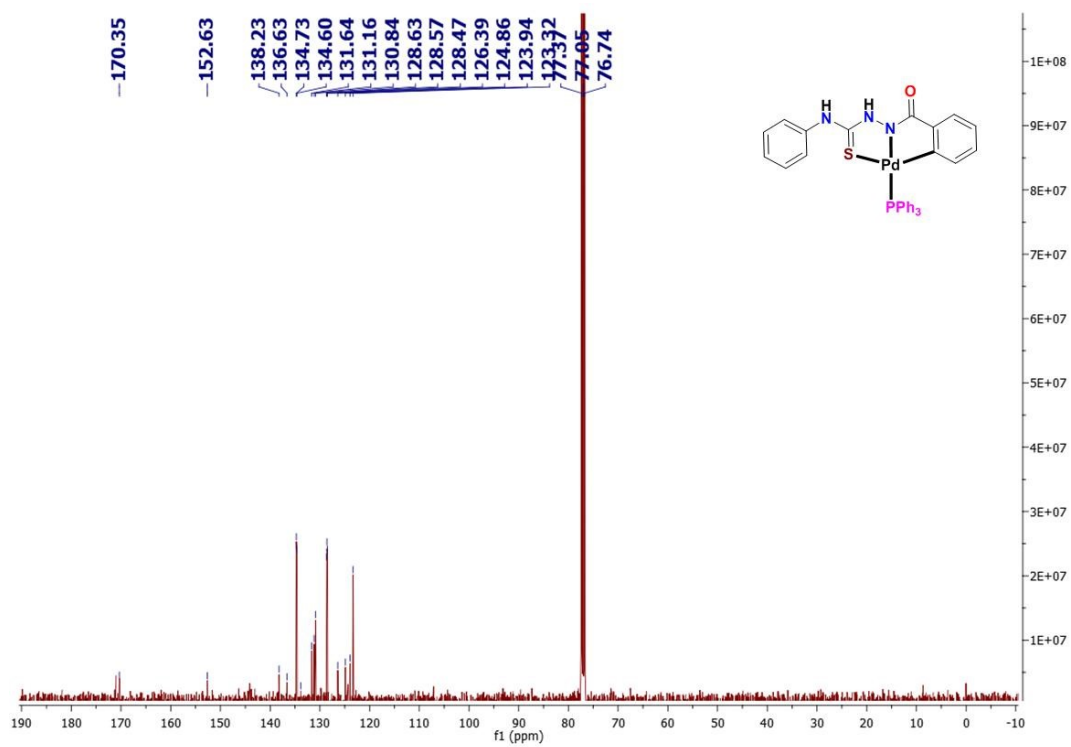


Figure 8.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex Pd1 in  $\text{CDCl}_3$  (100 MHz, 293 K)



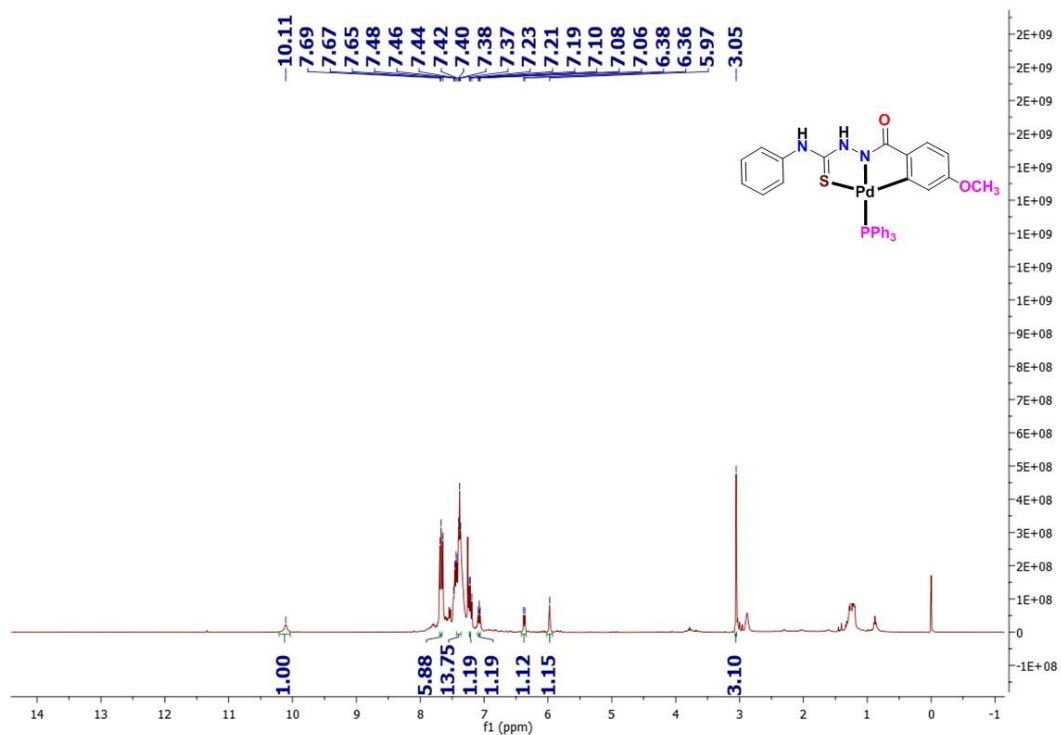


Figure 9.  $^1\text{H}$  NMR spectrum of complex Pd2 in  $\text{CDCl}_3$  (400 MHz, 293 K)

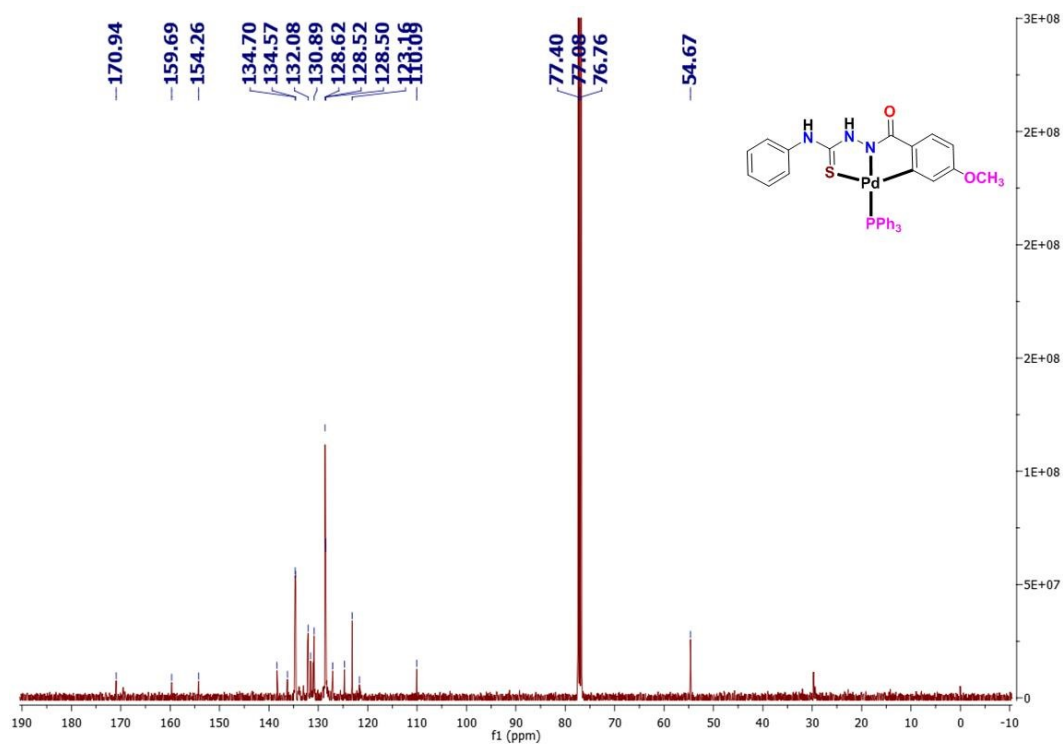
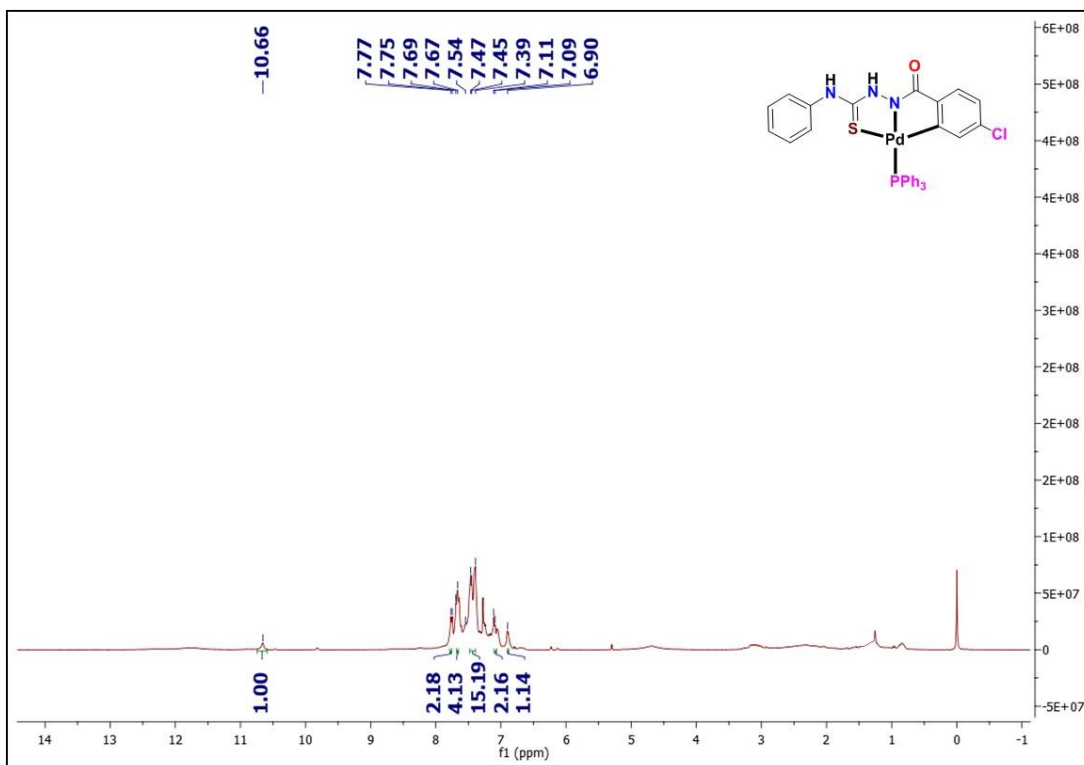
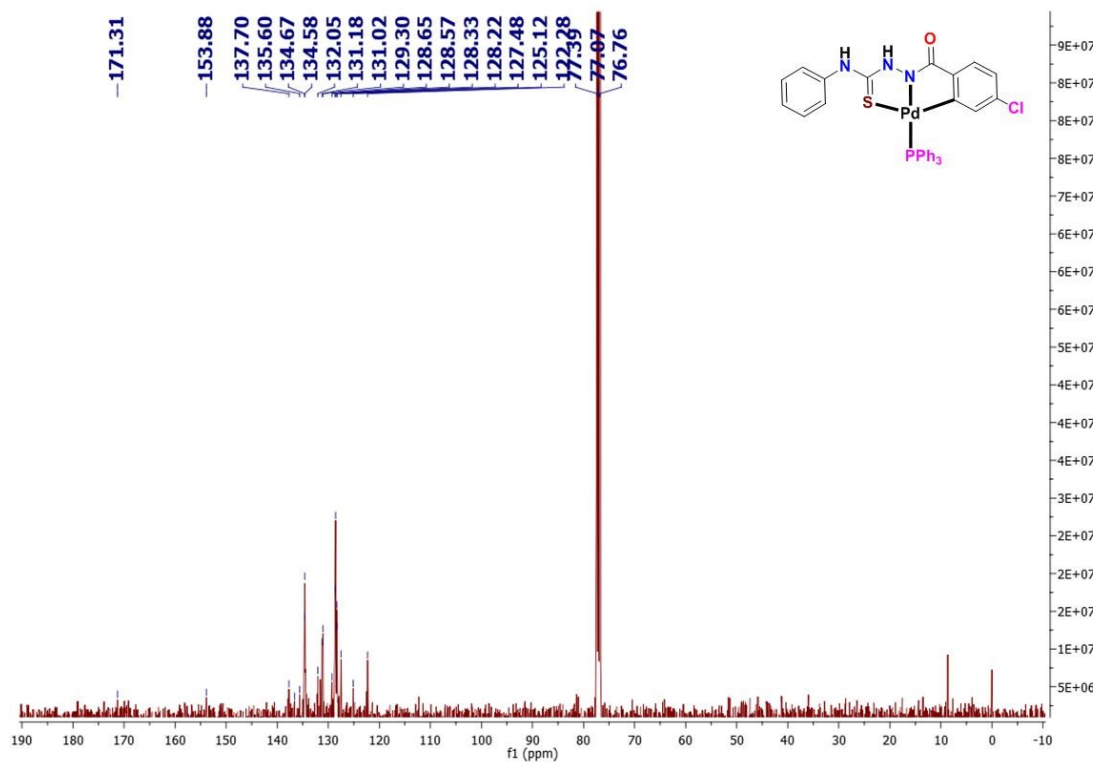


Figure 10.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex Pd2 in  $\text{CDCl}_3$  (100 MHz, 293 K)



**Figure 11.**  $^1\text{H}$  NMR spectrum of complex **Pd3** in  $\text{CDCl}_3$  (400 MHz, 293 K)

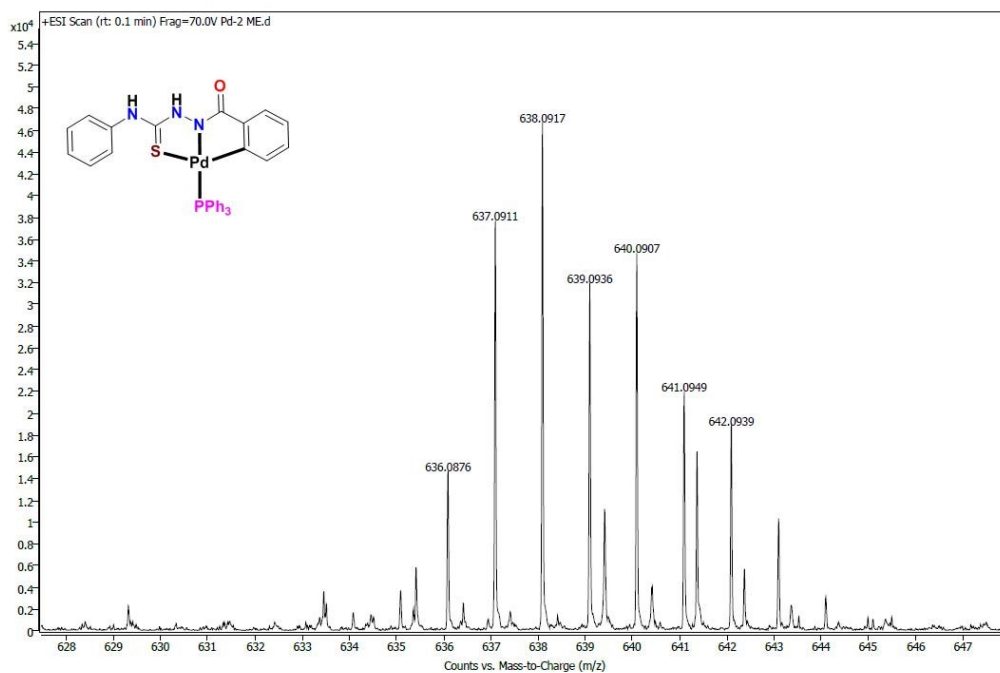


**Figure 12.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **Pd3** in  $\text{CDCl}_3$  (100 MHz, 293 K)

## 5. HRMS spectra of the complexes Pd1-Pd3

### User Spectrum Plot Report

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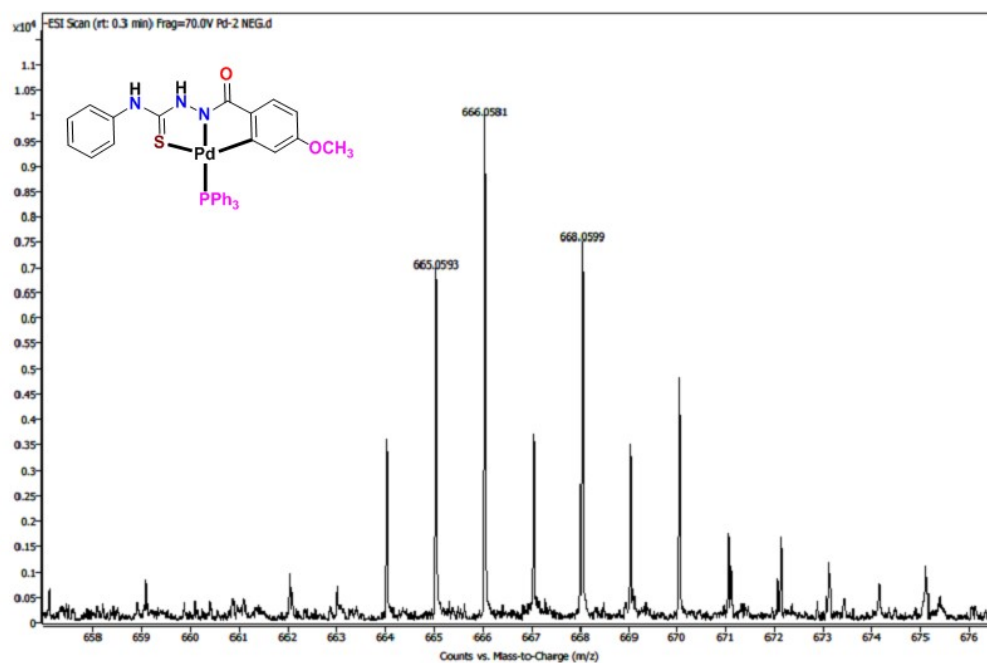
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Figure 13. HR-MS spectrum of complex Pd1

### User Spectrum Plot Report

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Figure 14. HR-MS spectrum of complex Pd2

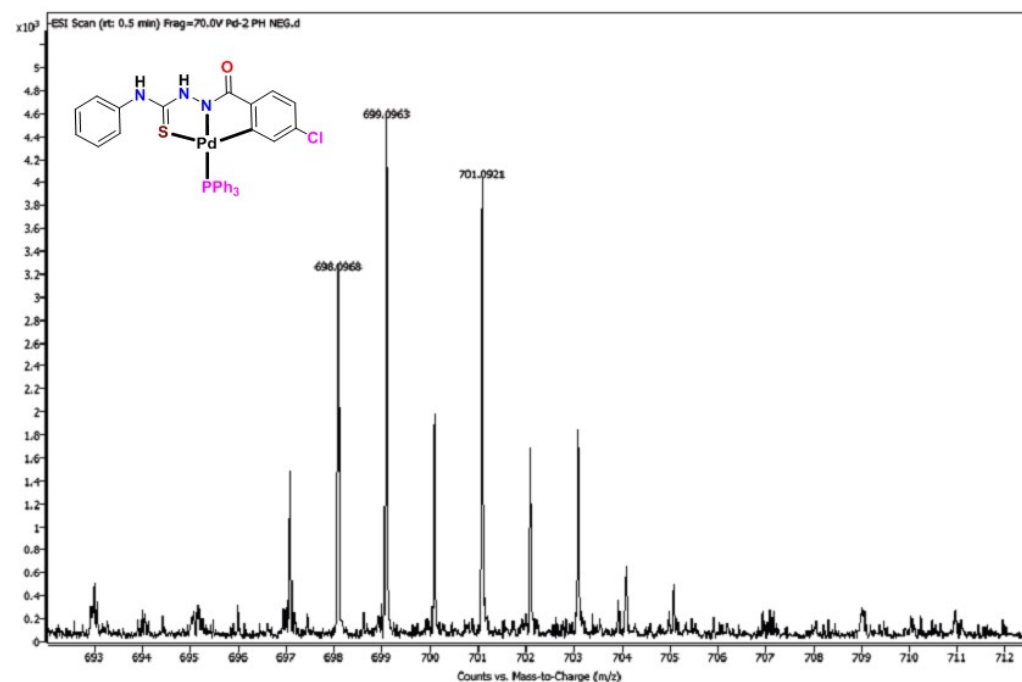


Figure 15. HR-MS spectrum of complex Pd3

## 6. HRMS spectra of the Pd alkoxy intermediate

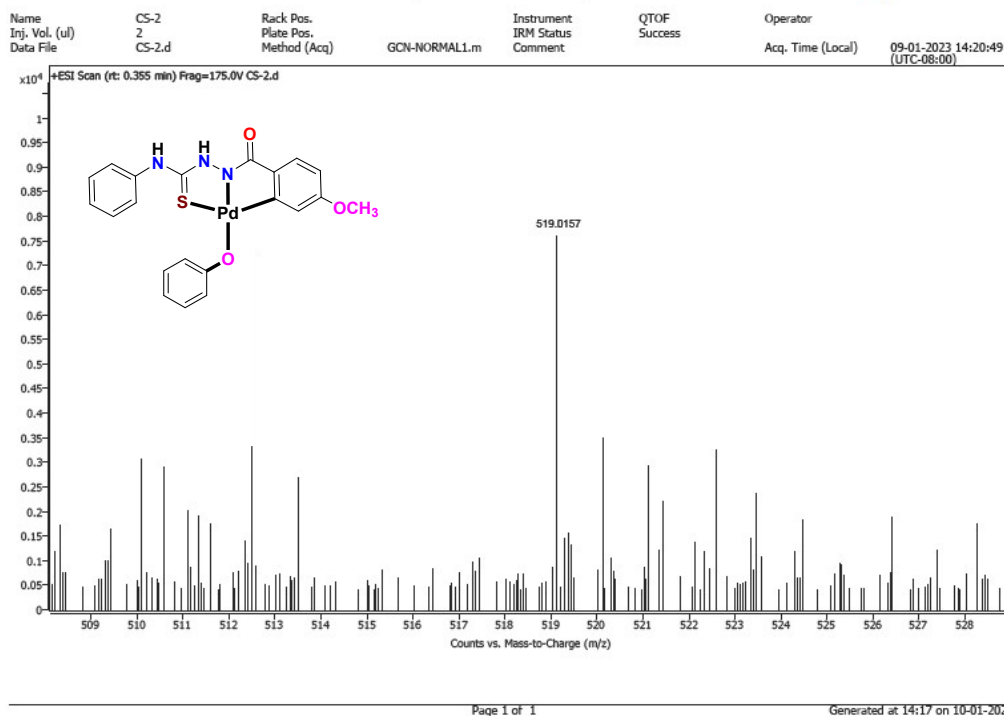


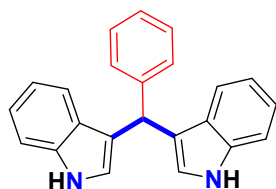
Figure 16. HR-MS spectrum of palladium alkoxy intermediate

## General Procedure for Synthesis of Bis(Indolyl)methanes

To an oven dried 50 mL round-bottom flask, indole (2 mmol), alcohol (1 mmol), **Pd2** catalyst (0.5 mol%), KO<sup>t</sup>Bu (0.50 mmol) and toluene (3 mL) were added under a gentle stream of nitrogen. The reaction mixture was kept for stirring at 110 °C (oil-bath temperature) for 18 h. Then, the reaction was quenched with water and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude mixture was purified by silica gel column chromatography using hexane/ethyl acetate as an eluting system to yield the desired bis(indolyl)methane product.

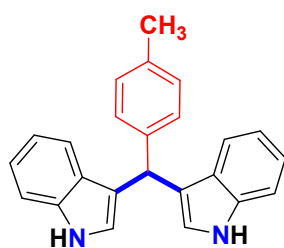
## 7. Characterization of the catalytic isolated product of bis(indolyl)methane product.

3,3'-(phenylmethylene)bis(1H-indole) (**3a**).<sup>5</sup>



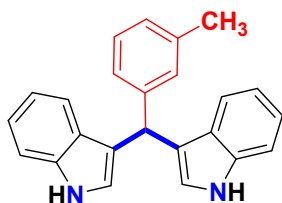
Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.11 (d, <sup>3</sup>J= 8Hz, 1H), 7.59 (s, 1H), 7.46 (d, <sup>3</sup>J= 8Hz, 1H), 7.38-7.13 (m, 10H), 6.99 (t, <sup>3</sup>J=4Hz, <sup>3</sup>J=8Hz, 2H), 6.58 (s, 2H), 5.86 (s, 1H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 144.07, 136.71, 133.73, 130.25, 128.77, 128.55, 128.28, 127.10, 126.19, 123.71, 121.95, 119.97, 119.68, 119.25, 111.12, 40.22.

3,3'-(p-tolylmethylene)bis(1H-indole) (**3b**).<sup>5</sup>



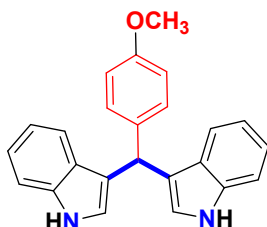
Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.81 (s, 1H), 7.37 (d, <sup>3</sup>J= 8Hz, 2H), 7.25 (d, <sup>3</sup>J= 8Hz, 2H), 7.14-7.10 (m, 5H), 6.96 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 4H), 6.52 (s, 2H), 5.80 (s, 1H), 2.24 (s, 3H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 144.10, 137.71, 136.74, 129.54, 128.14, 127.17, 126.98, 125.82, 123.74, 121.88, 119.96, 119.74, 119.21, 111.16, 40.20, 21.59.

3,3'-(*m*-tolylmethylene)bis(1H-indole) (**3c**).<sup>5</sup>



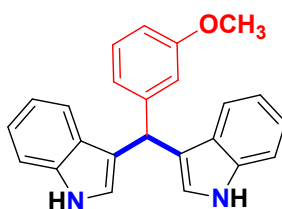
Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.73 (s, 1H), 7.36 (d, <sup>3</sup>J= 8Hz, 2H), 7.25 (d, <sup>3</sup>J= 8Hz, 2H), 7.19 (d, <sup>3</sup>J= 8Hz, 2H), 7.12 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 7.04 (d, <sup>3</sup>J= 8Hz, 2H), 6.97 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.53 (s, 2H), 5.81 (s, 1H), 2.29 (s, 3H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 141.10, 136.73, 135.55, 128.99, 128.64, 127.15, 123.66, 121.90, 120.01, 119.86, 119.22, 111.13, 39.84, 21.13.

3,3'-((4-methoxyphenyl)methylene)bis(1H-indole) (**3d**).<sup>5</sup>



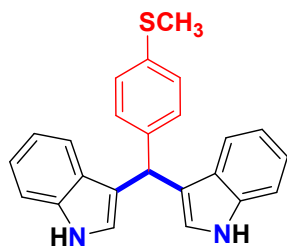
Orange solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.82 (s, 2H), 7.37 (d, <sup>3</sup>J= 8Hz, 2H), 7.30 (d, <sup>3</sup>J= 8Hz, 2H), 7.23 (d, <sup>3</sup>J= 8Hz, 2H), 7.14 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=4Hz, 2H), 6.99 (t, <sup>3</sup>J=4Hz, <sup>3</sup>J=8Hz, 2H), 6.80 (d, <sup>3</sup>J= 8Hz, 2H), 6.59 (s, 2H), 5.82 (s, 1H), 3.76 (s, 3H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 157.94, 136.75, 136.30, 129.65, 127.11, 123.57, 121.92, 120.06, 120.01, 119.22, 113.62, 111.07, 55.25, 39.37.

3,3'-((3-methoxyphenyl)methylene)bis(1H-indole) (**3e**).<sup>5</sup>



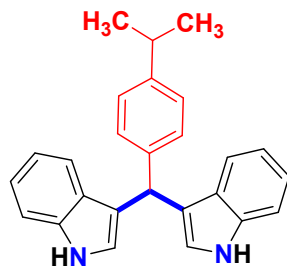
Orange solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.81 (s, 2H), 7.39 (d, <sup>3</sup>J= 8Hz, 2H), 7.30 (d, <sup>3</sup>J= 8Hz, 2H), 7.23-7.12 (m, 3H), 7.01-6.90 (m, 4H), 6.75 (d, <sup>3</sup>J= 8Hz, 1H), 6.60 (s, 2H), 5.83 (s, 1H), 3.71 (s, 3H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 159.59, 145.81, 136.70, 129.16, 127.12, 123.63, 121.92, 121.36, 119.92, 119.54, 119.24, 114.83, 111.27, 111.06, 55.14, 40.25.

3,3'-((4-(methylthio)phenyl)methylene)bis(1H-indole) (**3f**).<sup>5</sup>



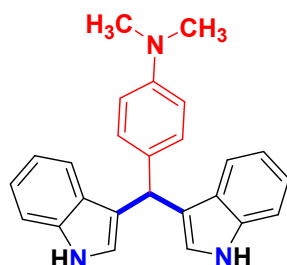
Orange solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.67 (s, 2H), 7.34 (d, <sup>3</sup>J= 8Hz, 2H), 7.25-7.19 (m, 4H), 7.13 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 4H), 6.97 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.49 (s, 2H), 5.79 (s, 1H), 2.40 (s, 3H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 141.23, 136.72, 135.60, 129.31, 127.04, 126.73, 123.70, 122.03, 119.97, 119.49, 119.32, 111.19, 39.72, 16.04.

3,3'-((4-isopropylphenyl)methylene)bis(1H-indole) (**3g**).<sup>5</sup>



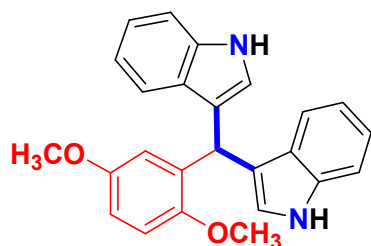
Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.49 (s, 2H), 7.35 (d, <sup>3</sup>J= 8Hz, 2H), 7.18 (d, <sup>3</sup>J= 8Hz, 4H), 7.13-7.07 (m, 4H), 6.95 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.44 (s, 2H), 5.79 (s, 1H), 2.89-2.82 (m, 1H), 1.20 (d, <sup>3</sup>J=8Hz, 6H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 146.59, 141.42, 136.72, 128.65, 127.22, 126.32, 123.71, 121.93, 120.06, 119.93, 119.24, 111.18, 39.80, 33.76, 24.18.

4-(di(1H-indol-3-yl)methyl)-N,N-dimethylaniline (**3h**).<sup>5</sup>



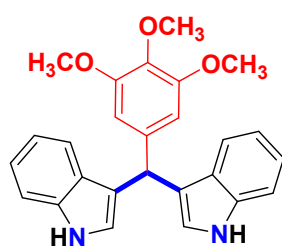
Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.83 (s, 2H), 7.31 (d, <sup>3</sup>J= 8Hz, 2H), 7.20-7.12 (m, 4H), 6.98 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.97 (d, <sup>3</sup>J=8Hz, 2H), 6.62 (s, 2H), 5.79 (s, 1H), 2.90 (s, 6H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 149.11, 136.74, 132.45, 129.29, 127.23, 123.53, 121.78, 120.46, 120.12, 119.11, 112.76, 110.97, 40.86, 39.18.

3,3'-((2,5-dimethoxyphenyl)methylene)bis(1H-indole) (**3i**).<sup>5</sup>



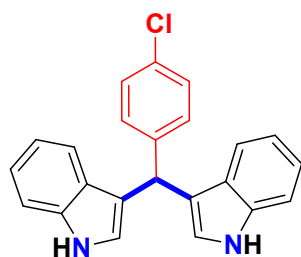
Orange solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.70 (s, 2H), 7.39 (d, <sup>3</sup>J= 8Hz, 2H), 7.22 (d, <sup>3</sup>J= 8Hz, 2H), 7.11 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.97 (t, <sup>3</sup>J=4Hz, <sup>3</sup>J=8Hz, 2H), 6.83 (d, <sup>3</sup>J= 12Hz, 1H), 6.70 (t, <sup>3</sup>J=12Hz, <sup>3</sup>J=8Hz, 2H), 6.46 (s, 2H), 6.29 (s, 1H), 3.72 (s, 3H), 3.60 (s, 3H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 153.47, 151.49, 136.75, 134.19, 127.25, 123.59, 121.75, 119.97, 119.30, 119.04, 116.95, 111.91, 111.03, 110.63, 56.65, 55.54, 32.19.

3,3'-((3,4,5-trimethoxyphenyl)methylene)bis(1H-indole) (**3j**).<sup>5</sup>



Orange solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.97 (s, 2H), 7.41 (d, <sup>3</sup>J= 8Hz, 2H), 7.35 (d, <sup>3</sup>J= 8Hz, 2H), 7.16 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 7.01 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.67 (s, 1H), 6.59 (s, 2H), 5.81 (s, 1H), 3.83 (s, 3H), 3.70 (s, 6H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 152.99, 139.88, 136.73, 127.08, 123.59, 121.96, 119.91, 119.58, 119.25, 111.08, 105.88, 60.88, 60.54, 56.04, 40.59.

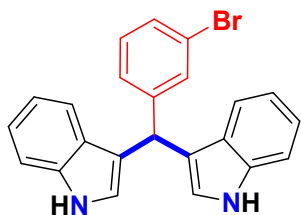
3,3'-((4-chlorophenyl)methylene)bis(1H-indole) (**3k**).<sup>5</sup>



Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.80 (s, 2H), 7.35-7.28 (m, 4H), 7.24-7.13 (m, 6H), 6.99 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.54 (s, 2H), 5.82 (s, 1H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 142.63, 136.73, 131.83, 130.83, 130.13, 128.42, 126.93, 123.68, 122.12, 119.86, 119.40, 119.19, 111.21, 39.66.

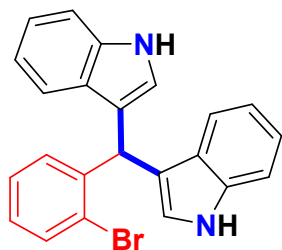


3,3'-((3-bromophenyl)methylene)bis(1H-indole) (**3l**).<sup>5</sup>



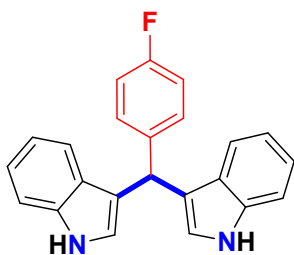
Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.80 (s, 2H), 7.47 (s, 1H), 7.36-7.29 (m, 5H), 7.24 (d, <sup>3</sup>J= 4Hz, 1H), 7.18-7.08 (m, 3H), 7.00 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.55 (s, 2H), 5.82 (s, 1H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 146.56, 136.71, 131.74, 129.89, 129.41, 127.43, 126.90, 123.73, 122.45, 122.13, 119.79, 119.43, 118.94, 111.20, 39.98.

3,3'-((2-bromophenyl)methylene)bis(1H-indole) (**3m**).<sup>5</sup>



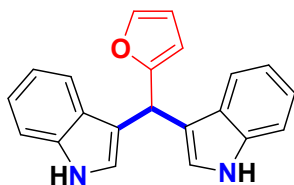
Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.56 (s, 2H), 7.50 (d, 3J= 8Hz, 1H), 7.29 (d, 3J= 8Hz, 2H), 7.17 (d, 3J= 8Hz, 2H), 7.09-6.89 (m, 7H), 6.37 (s, 2H), 6.19 (s, 1H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 143.05, 136.74, 132.92, 130.55, 127.92, 127.38, 127.06, 124.89, 123.97, 122.09, 119.93, 119.39, 118.41, 111.21, 39.59.

3,3'-((4-fluorophenyl)methylene)bis(1H-indole) (**3n**).<sup>5</sup>



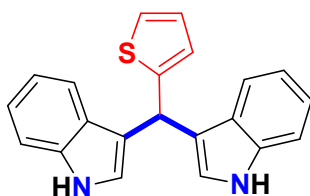
Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.70 (s, 2H), 7.33 (d, 3J= 8Hz, 2H), 7.26-7.20 (m, 4H), 7.13 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.98 (t, <sup>3</sup>J=4Hz, <sup>3</sup>J=8Hz, 2H), 6.89 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.48 (s, 2H), 5.81 (s, 1H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 162.68, 160.26, 139.78, 136.76, 130.18, 130.10, 126.99, 123.69, 122.09, 119.92, 119.54, 119.37, 115.14, 114.92, 111.25, 39.52.

3,3'-(thiophen-2-ylmethylene)bis(1H-indole) (**3o**).<sup>5</sup>



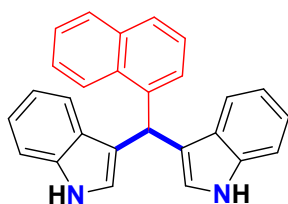
Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.87 (s, 2H), 7.46 (d, <sup>3</sup>J= 8Hz, 3H), 7.34 (d, <sup>3</sup>J= 8Hz, 2H), 7.18-7.13 (m, 2H), 7.02 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.91 (d, <sup>3</sup>J=4Hz, 2H), 6.80 (d, <sup>3</sup>J=8Hz, 2H), 6.15 (s, 1H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 172.83, 148.68, 136.61, 126.79, 126.45, 125.17, 123.63, 123.21, 122.05, 119.79, 119.71, 119.39, 111.15, 35.35.

3,3'-(furan-2-ylmethylene)bis(1H-indole) (**3p**).<sup>5</sup>



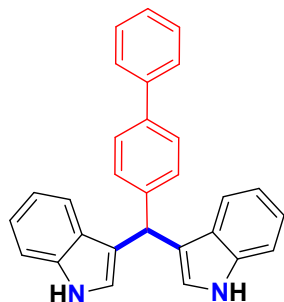
Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.80 (s, 2H), 7.45 (d, <sup>3</sup>J= 8Hz, 2H), 7.32-7.26 (m, 3H), 7.14 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 7.01 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.75 (s, 2H), 6.27 (s, 1H), 6.03 (s, 1H), 5.90 (s, 1H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 157.15, 141.27, 136.55, 126.80, 123.15, 121.99, 119.71, 119.39, 117.14, 111.21, 110.21, 106.66, 34.14.

3,3'-(naphthalen-1-ylmethylene)bis(1H-indole) (**3q**).<sup>5</sup>



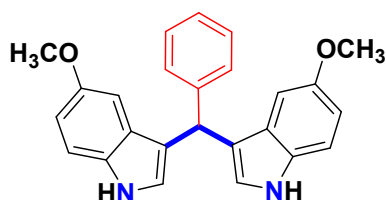
Red solid. <sup>1</sup>H NMR (400 MHz, dms<sup>o</sup>-d<sub>6</sub>) δ (ppm) 10.83 (s, 2H), 8.28 (d, <sup>3</sup>J= 8Hz, 2H), 7.92 (d, <sup>3</sup>J= 8Hz, 1H), 7.78 (d, <sup>3</sup>J= 8Hz, 1H), 7.44-7.28 (m, 7H), 7.05 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.86 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.76 (s, 2H), 6.66 (s, 1H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, dms<sup>o</sup>-d<sub>6</sub>) δ (ppm) 140.27, 136.64, 133.58, 131.30, 128.53, 126.60, 125.78, 125.50, 125.31, 124.24, 123.95, 120.87, 118.94, 118.24, 117.67, 111.50, 35.33.

3,3'-([1,1'-biphenyl]-4-ylmethylene)bis(1H-indole) (**3r**).<sup>5</sup>



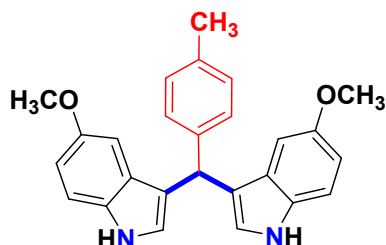
Red solid. <sup>1</sup>H NMR (400 MHz, dms<sub>o</sub>-d<sub>6</sub>) δ (ppm) 10.87 (s, 2H), 7.64 (d, <sup>3</sup>J= 8Hz, 2H), 7.58 (d, <sup>3</sup>J= 8Hz, 2H), 7.47-7.30 (m, 10H), 7.06 (t, <sup>3</sup>J=8Hz, <sup>3</sup>J=8Hz, 2H), 6.90 (d, <sup>3</sup>J=8Hz, 3H), 5.91 (s, 1H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, dms<sub>o</sub>-d<sub>6</sub>) δ (ppm) 144.30, 140.05, 137.58, 136.60, 128.82, 127.08, 126.61, 126.45, 126.32, 123.56, 120.88, 119.09, 118.19, 117.89, 111.45, 28.96.

3,3'-(phenylmethylene)bis(5-methoxy-1H-indole) (**3s**).<sup>5</sup>



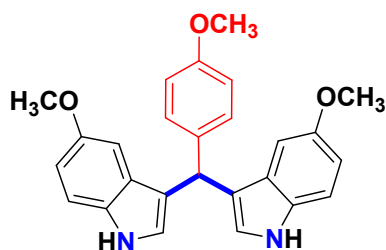
Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.82 (s, 2H), 7.34 (d, <sup>3</sup>J= 8Hz, 2H), 7.29-7.21 (m, 5H), 6.83-6.80 (m, 4H), 6.64 (s, 2H), 5.76 (s, 1H), 3.68 (s, 6H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 153.72, 143.96, 131.91, 128.75, 128.24, 127.54, 126.13, 124.46, 119.32, 111.92, 111.69, 102.02, 55.88, 40.33.

3,3'-(p-tolylmethylene)bis(5-methoxy-1H-indole) (**3t**).<sup>5</sup>



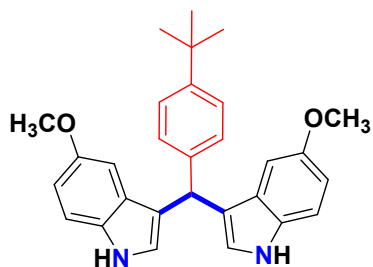
Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.78 (s, 2H), 7.23-7.17 (m, 4H), 7.06 (d, <sup>3</sup>J= 8 Hz, 2H), 6.80 (d, <sup>3</sup>J= 8 Hz, 4H), 6.61 (s, 2H), 5.71 (s, 1H), 3.68 (s, 6H), 2.30 (s, 3H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 153.66, 140.96, 135.49, 131.93, 128.95, 128.60, 127.57, 124.45, 119.49, 111.83, 111.71, 102.08, 55.91, 39.89, 21.10.

3,3'-((4-methoxyphenyl)methylene)bis(5-methoxy-1H-indole)(**3u**).<sup>5</sup>



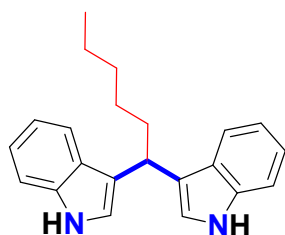
orange solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.83 (s, 2H), 7.23 (t, <sup>3</sup>J = 8 Hz, <sup>3</sup>J = 8 Hz, 4H), 6.81 (d, <sup>3</sup>J = 8 Hz, 6H), 6.62 (s, 2H), 5.71 (s, 1H), 3.77 (s, 4H), 3.69 (s, 5H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 172.06, 153.67, 136.22, 131.94, 129.64, 127.52, 124.42, 123.07, 119.63, 118.61, 113.60, 111.85, 111.70, 102.07, 55.91, 39.44.

3,3'-((4-(tert-butyl)phenyl)methylene)bis(5-methoxy-1H-indole)(**3v**).<sup>5</sup>



Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.77 (s, 2H), 7.28-7.23 (m, 4H), 7.18 (d, <sup>3</sup>J = 8 Hz, 2H), 6.80 (d, <sup>3</sup>J = 8 Hz, 4H), 6.63 (s, 2H), 5.72 (s, 1H), 3.66 (s, 6H), 1.28 (s, 9H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 153.63, 140.90, 131.90, 128.35, 127.60, 125.09, 124.43, 119.53, 111.85, 111.72, 102.07, 55.87, 39.82, 34.42, 31.49.

3,3'-((hexane-1,1-diyl)bis(1H-indole) (**3w**).



Red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.59 (s, 2H), 7.49 (d, <sup>3</sup>J = 8 Hz, 2H), 7.12 (d, <sup>3</sup>J = 8 Hz, 2H), 7.02 (t, <sup>3</sup>J = 8 Hz, <sup>3</sup>J = 8 Hz, 2H), 6.93 (t, <sup>3</sup>J = 8 Hz, <sup>3</sup>J = 8 Hz, 2H), 6.73 (s, 1H), 4.34 (t, <sup>3</sup>J = 8 Hz, <sup>3</sup>J = 4 Hz, 1H), 2.08 (dd, 2H), 1.30-1.12 (m, 6H), 0.75 (t, <sup>3</sup>J = 8 Hz, <sup>3</sup>J = 8 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 135.48, 126.09, 120.58, 120.41, 119.40, 118.57, 117.87, 110.06, 34.81, 32.91, 30.96, 26.97, 21.61, 13.10, 12.98.

### 8a. NMR spectrum of the isolated benzaldehyde intermediate

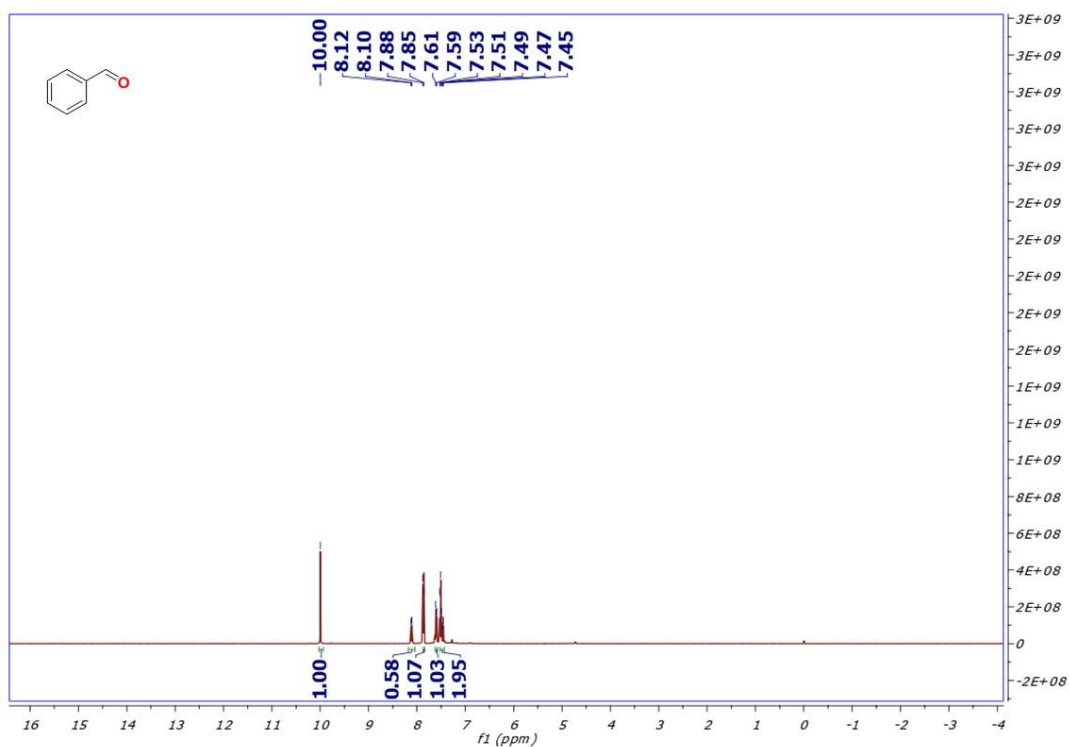


Figure 17.  $^1\text{H}$  NMR spectrum of Benzaldehyde in  $\text{CDCl}_3$  (400 MHz, 293 K)

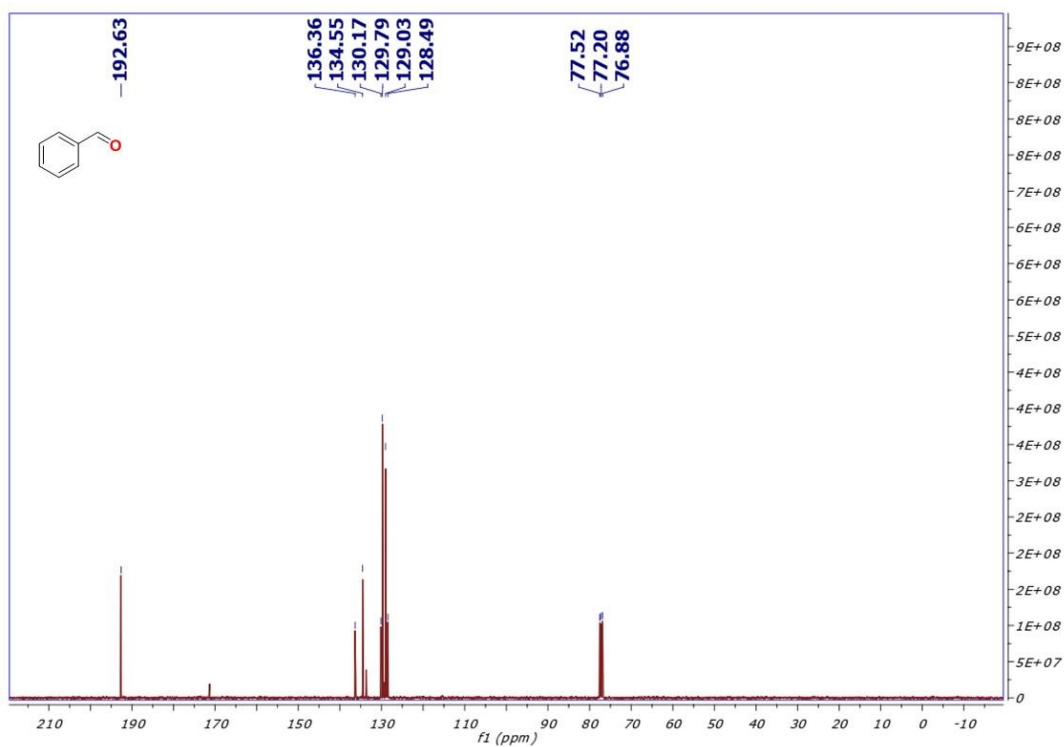


Figure 18.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of Benzaldehyde in  $\text{CDCl}_3$  (100 MHz, 293 K)

8b. NMR spectrum of the Bisindole products

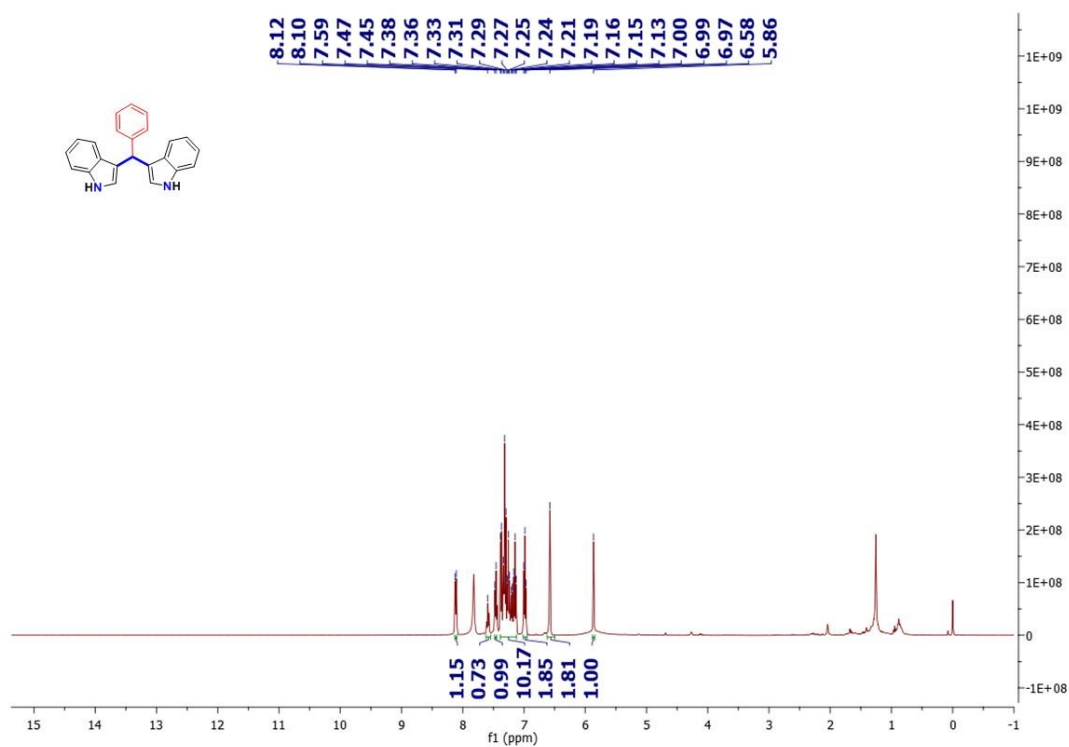


Figure 19.  $^1\text{H}$  NMR spectrum of 3a in  $\text{CDCl}_3$  (400 MHz, 293 K)

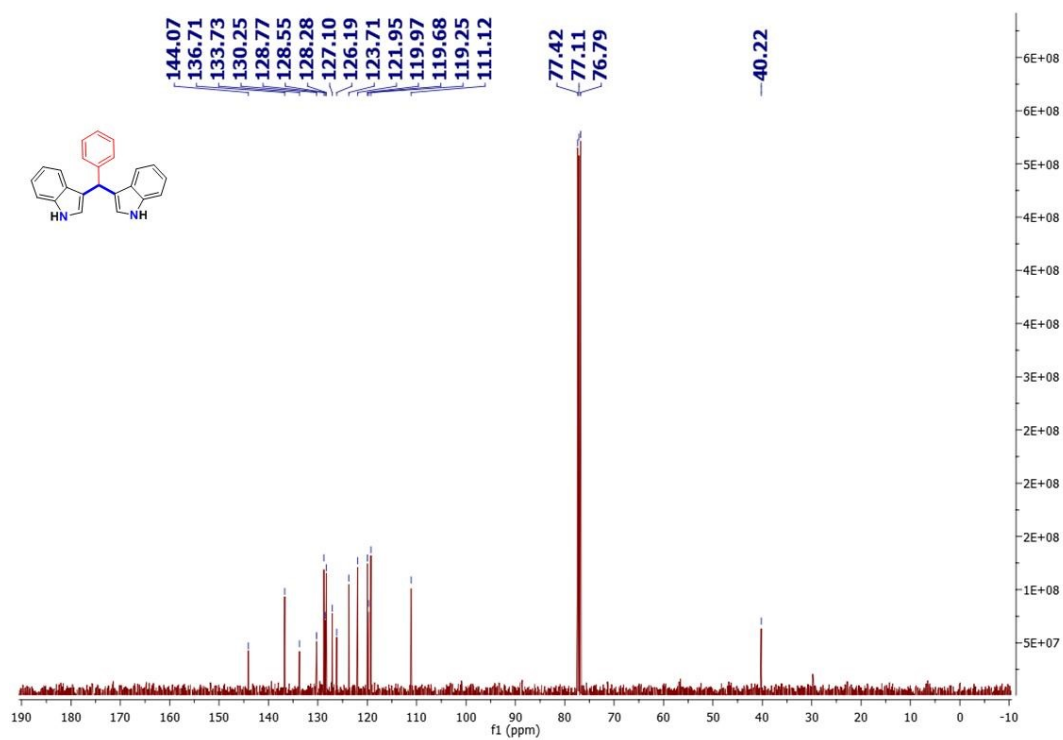


Figure 20.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3a** in  $\text{CDCl}_3$  (100 MHz, 293 K)

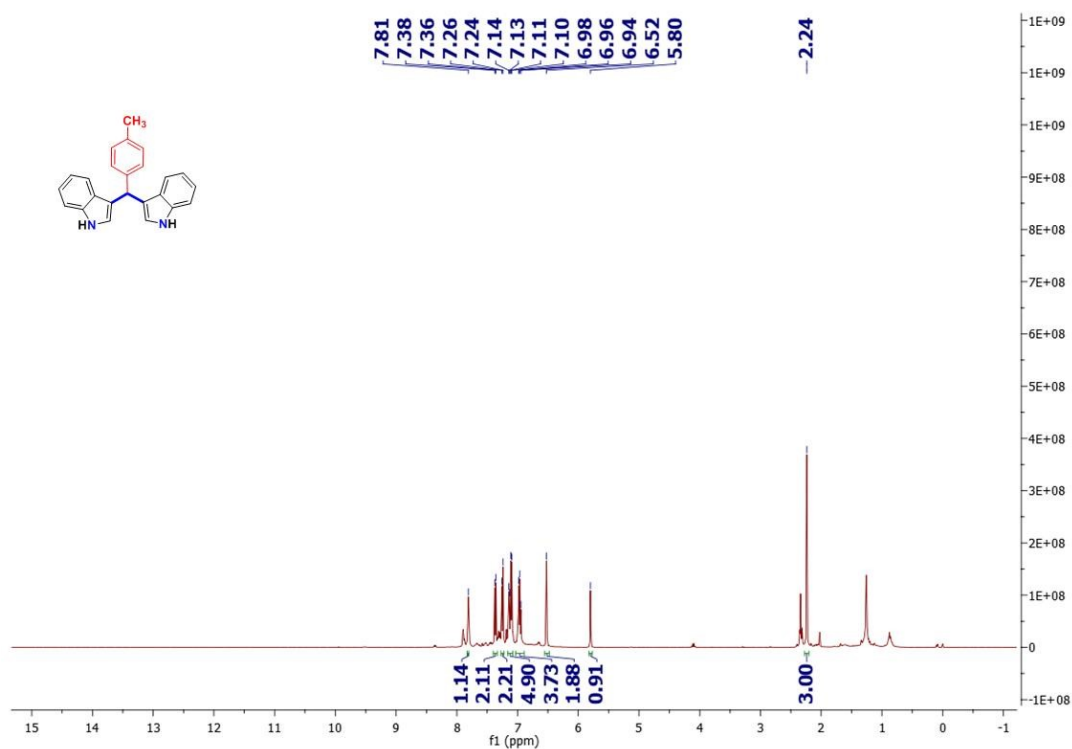
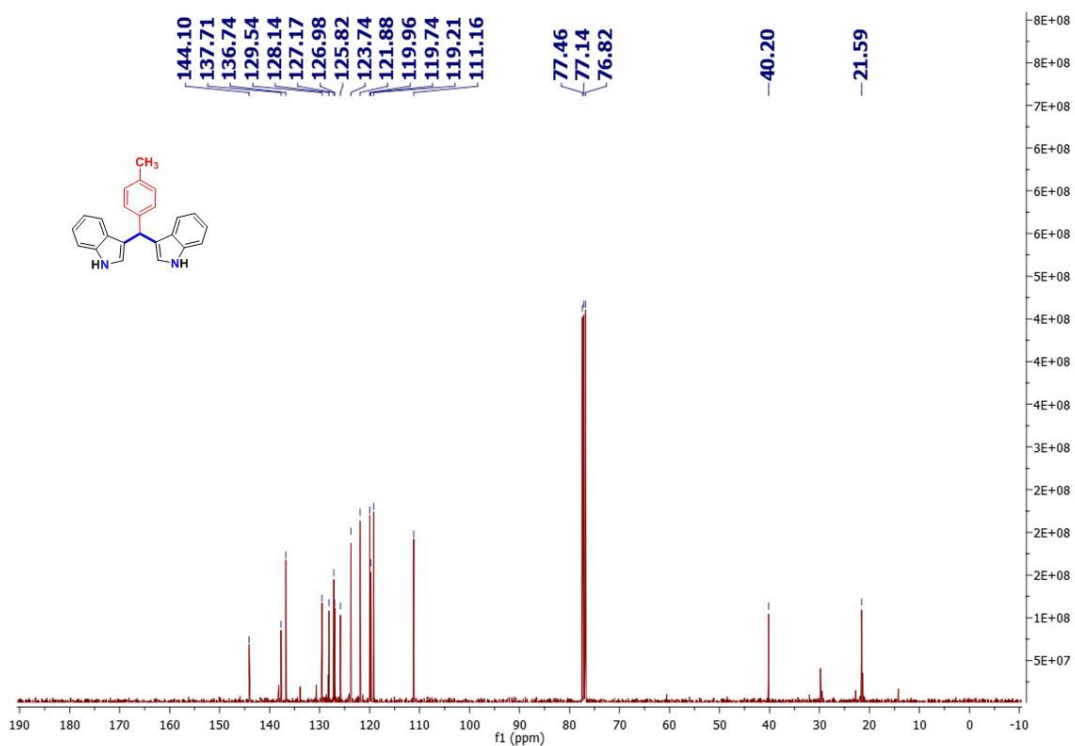
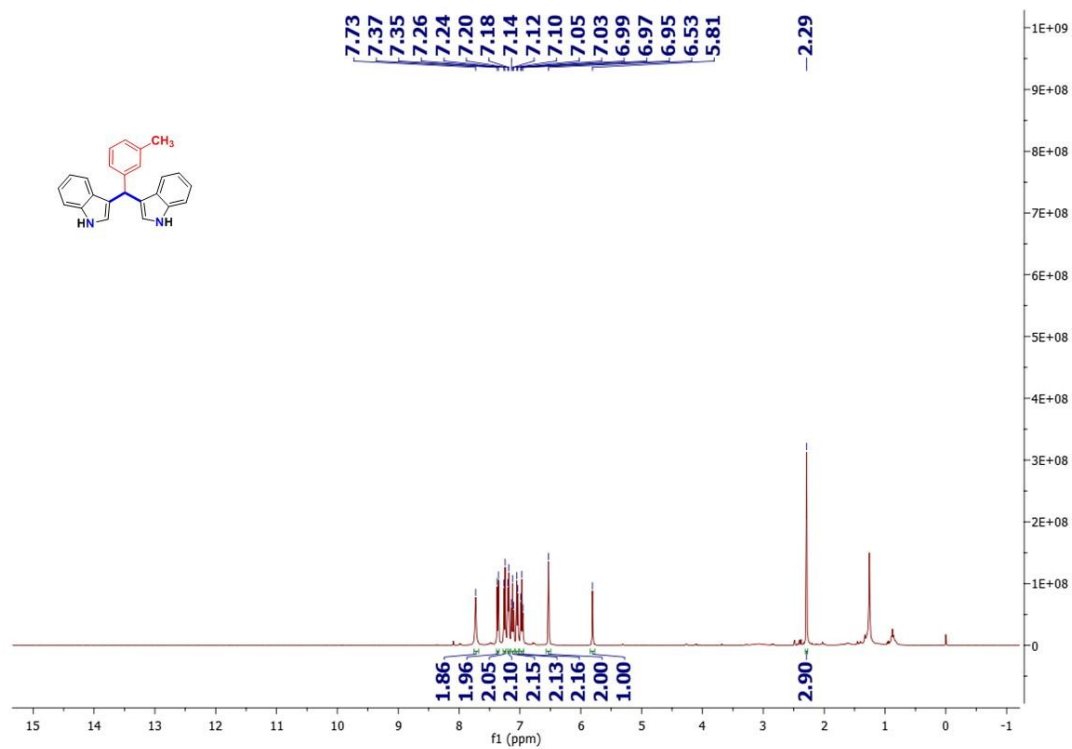


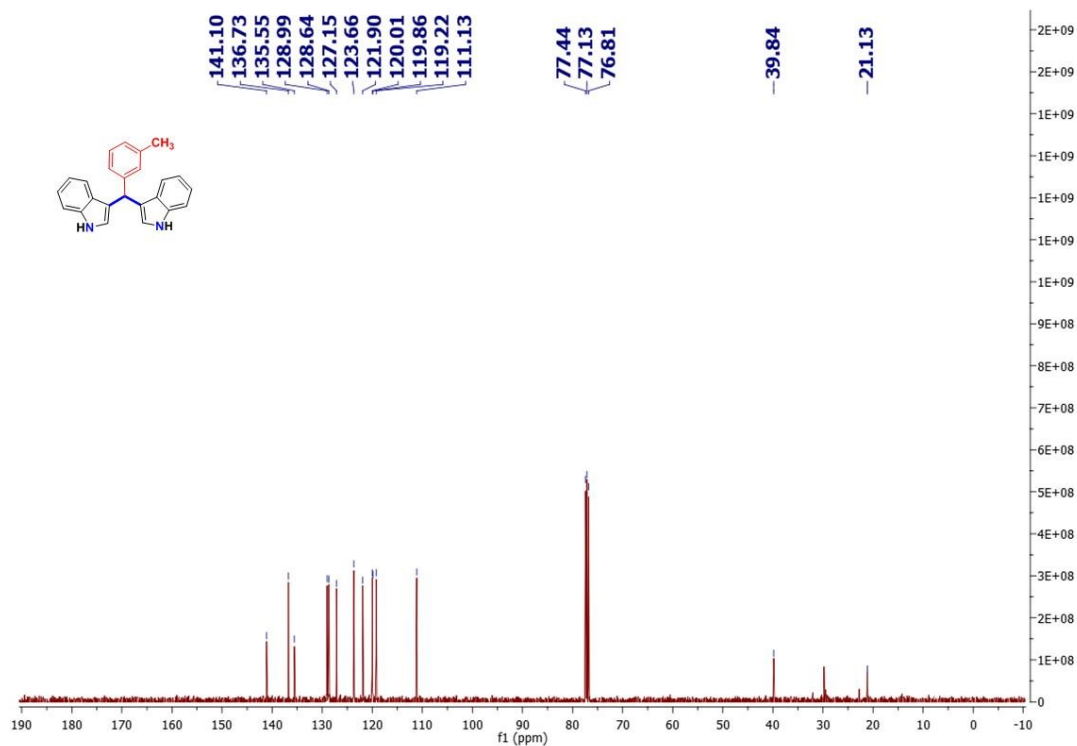
Figure 21.  $^1\text{H}$  NMR spectrum of **3b** in  $\text{CDCl}_3$  (400 MHz, 293 K)



**Figure 22.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3b** in  $\text{CDCl}_3$  (100 MHz, 293 K)



**Figure 23.**  $^1\text{H}$  NMR spectrum of **3c** in  $\text{CDCl}_3$  (400 MHz, 293 K)



**Figure 24.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3c** in  $\text{CDCl}_3$  (100 MHz, 293 K)



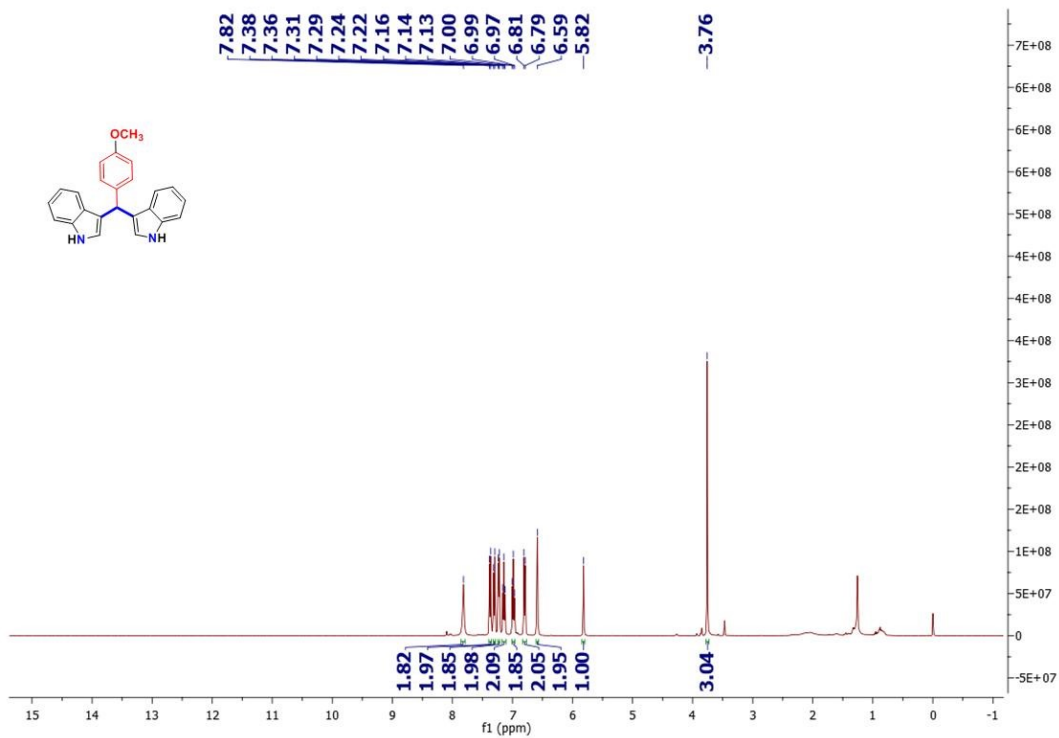


Figure 25.  $^1\text{H}$  NMR spectrum of **3d** in  $\text{CDCl}_3$  (400 MHz, 293 K)

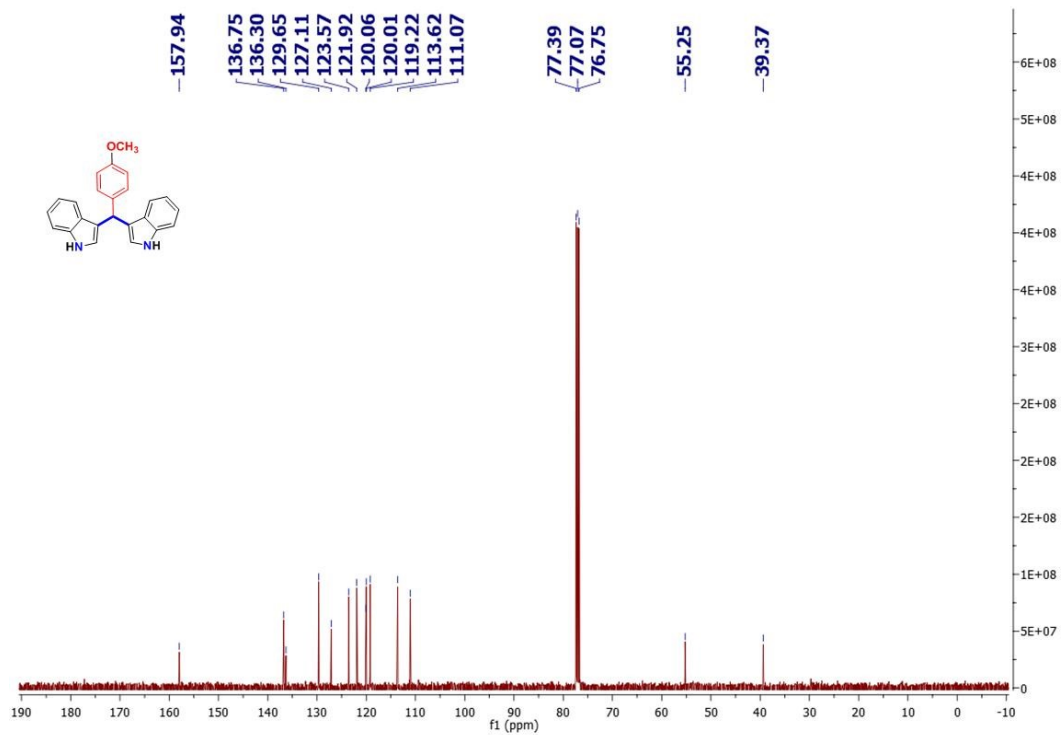


Figure 26.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3d** in  $\text{CDCl}_3$  (100 MHz, 293 K)

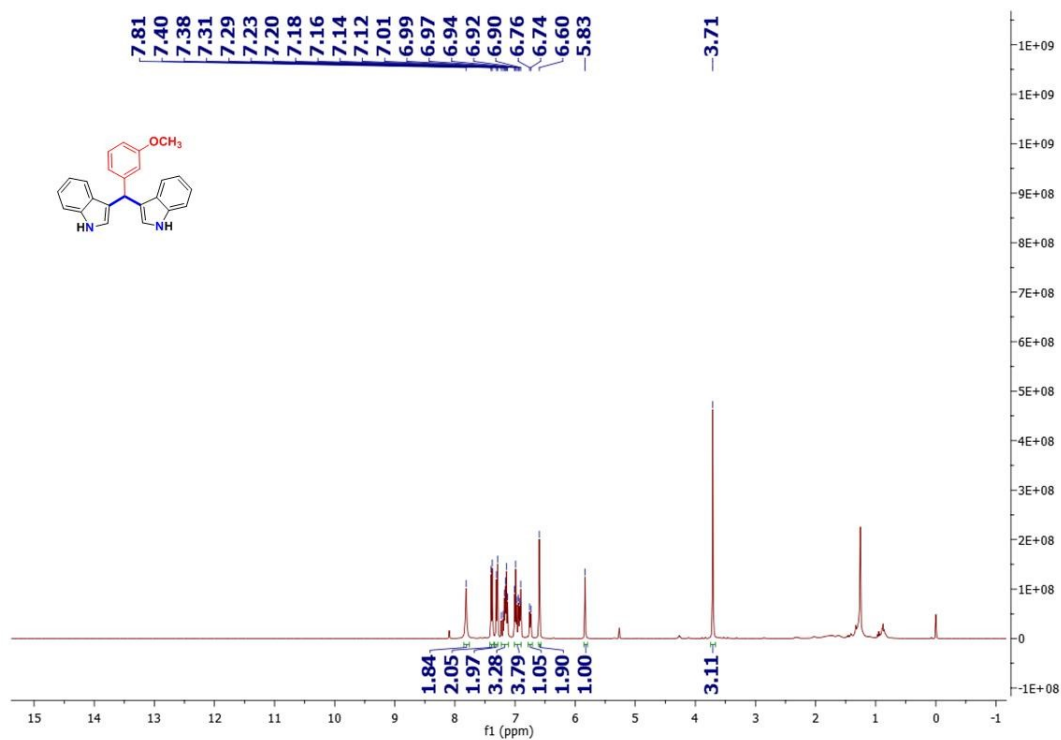


Figure 27.  $^1\text{H}$  NMR spectrum of **3e** in  $\text{CDCl}_3$  (400 MHz, 293 K)

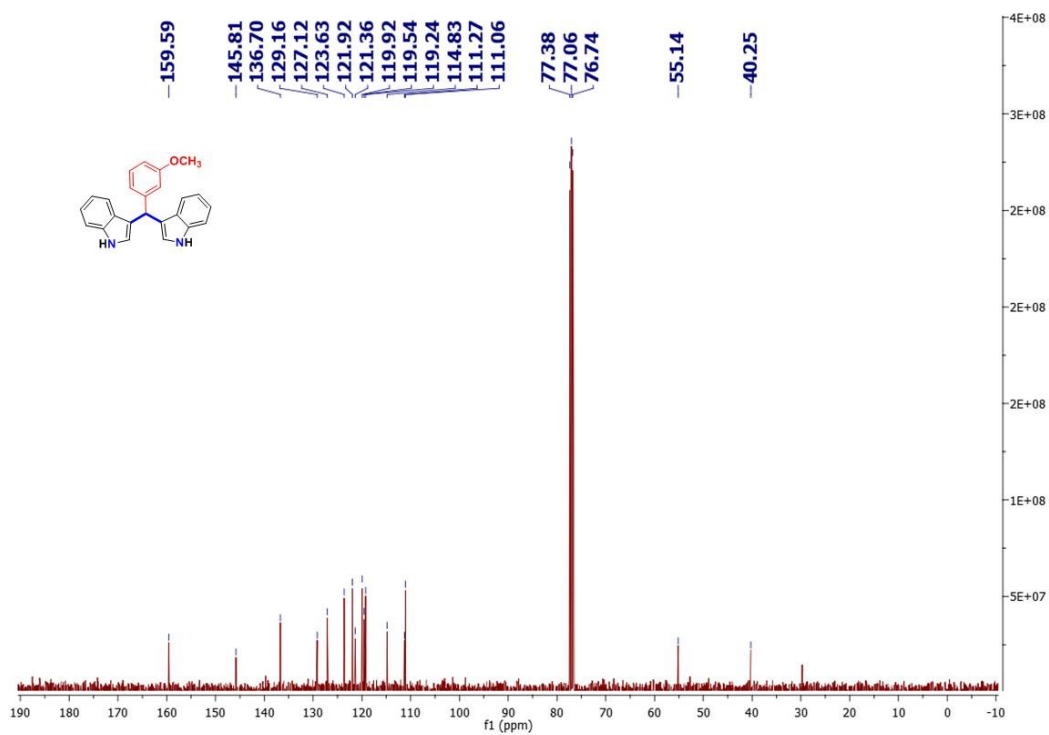
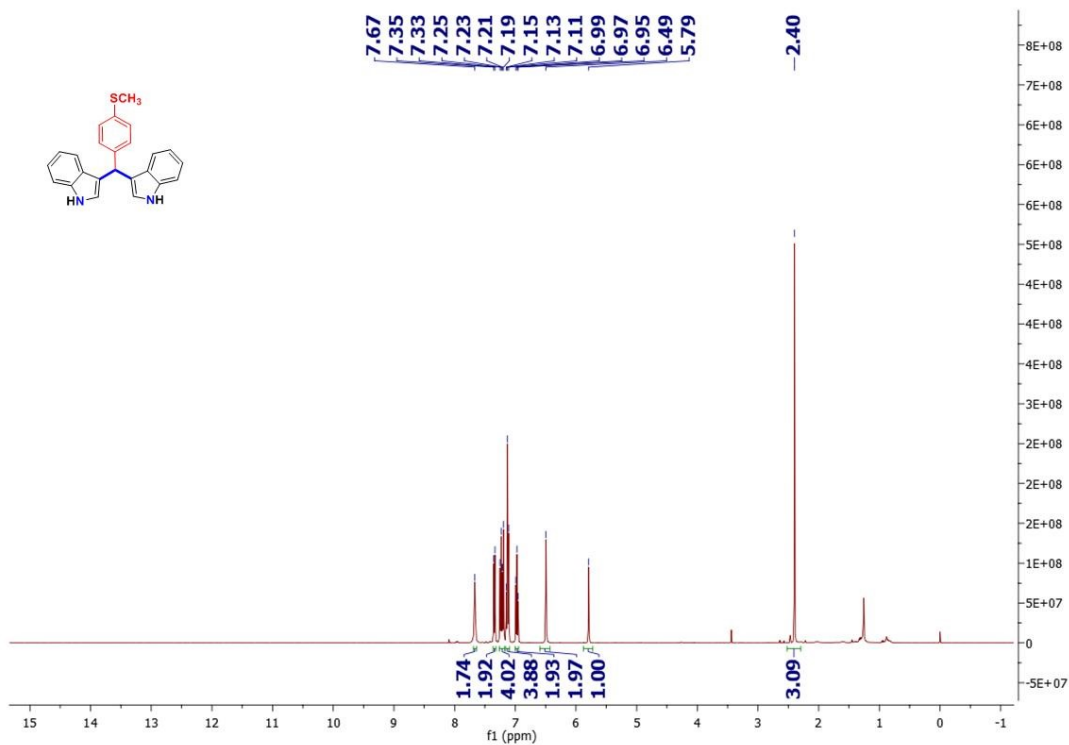
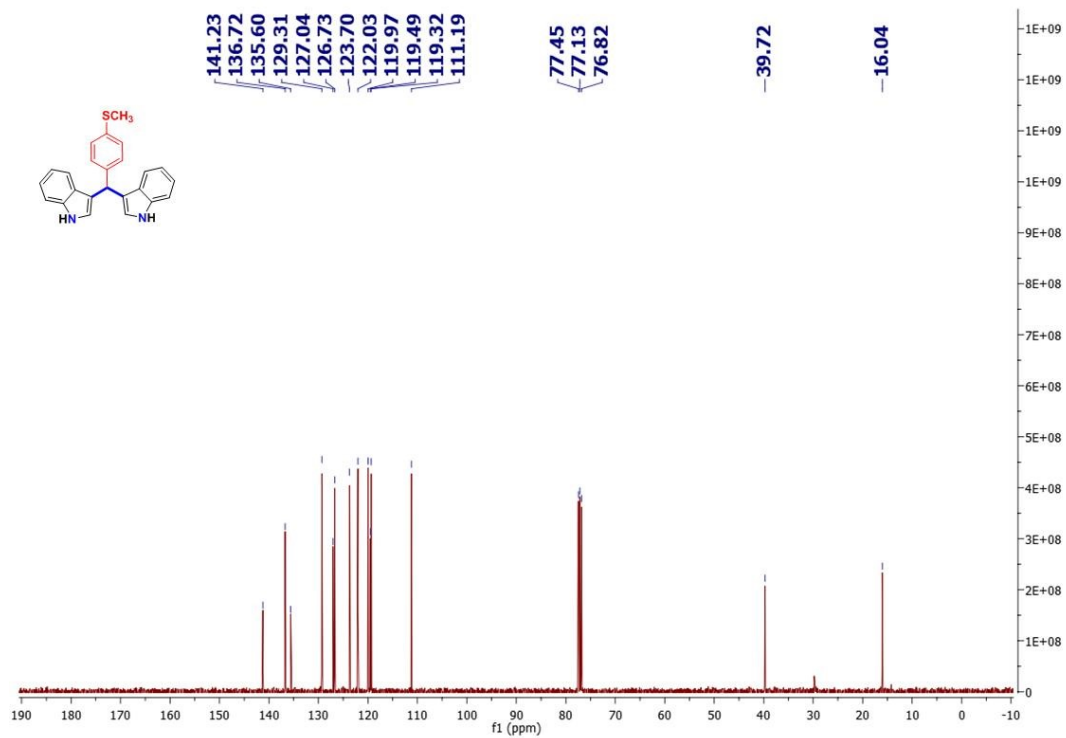


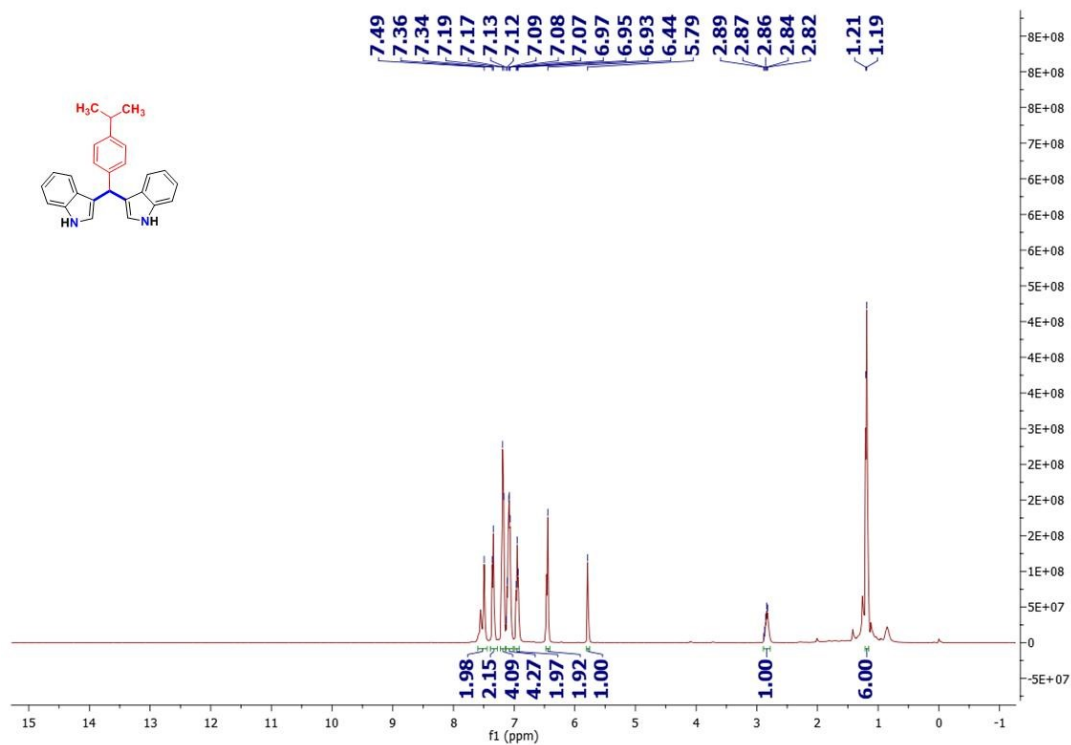
Figure 28.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3e** in  $\text{CDCl}_3$  (100 MHz, 293 K)



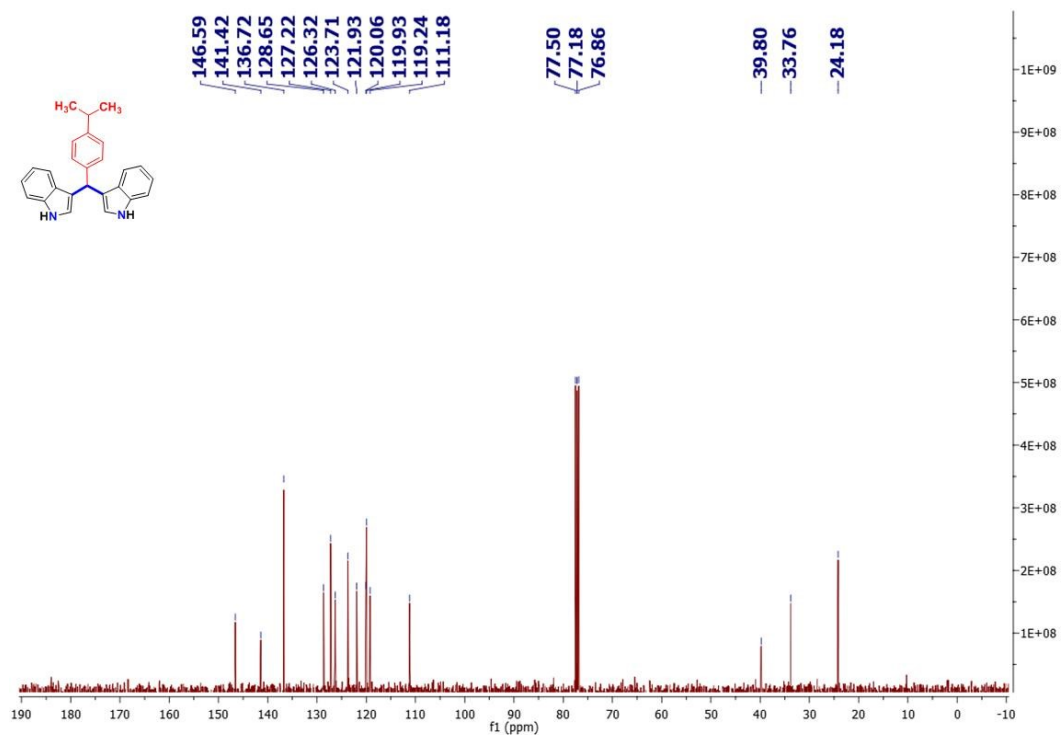
**Figure 29.**  $^1\text{H}$  NMR spectrum of **3f** in  $\text{CDCl}_3$  (400 MHz, 293 K)



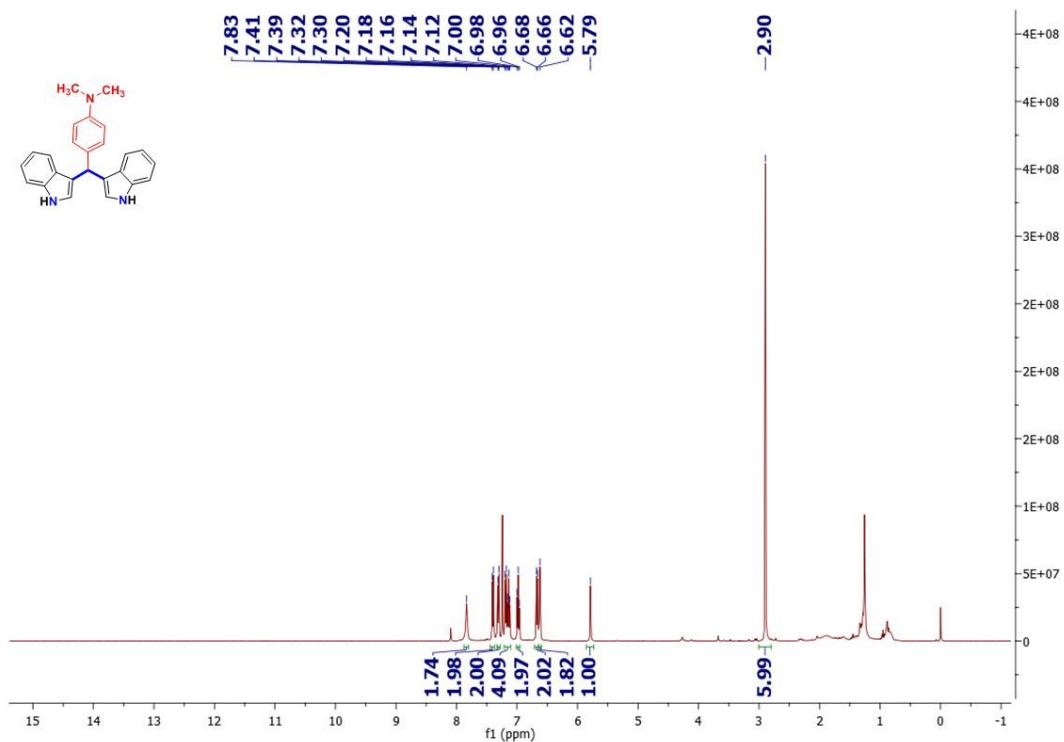
**Figure 30.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3f** in  $\text{CDCl}_3$  (100 MHz, 293 K)



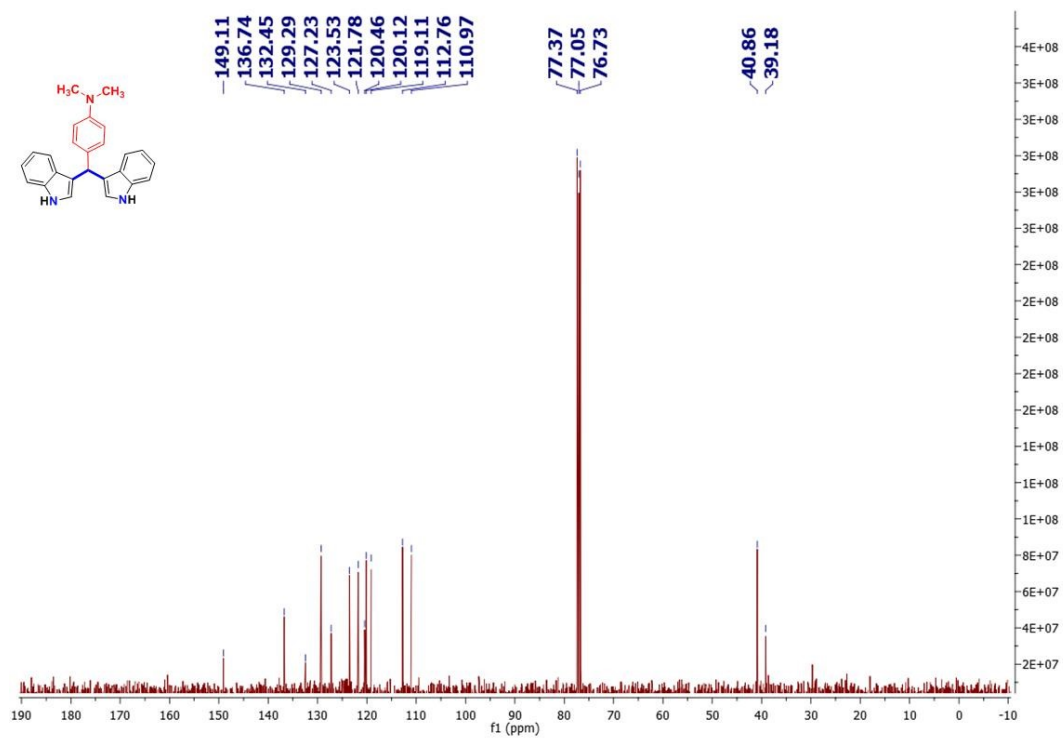
**Figure 31.**  $^1\text{H}$  NMR spectrum of **3g** in  $\text{CDCl}_3$  (400 MHz, 293 K)



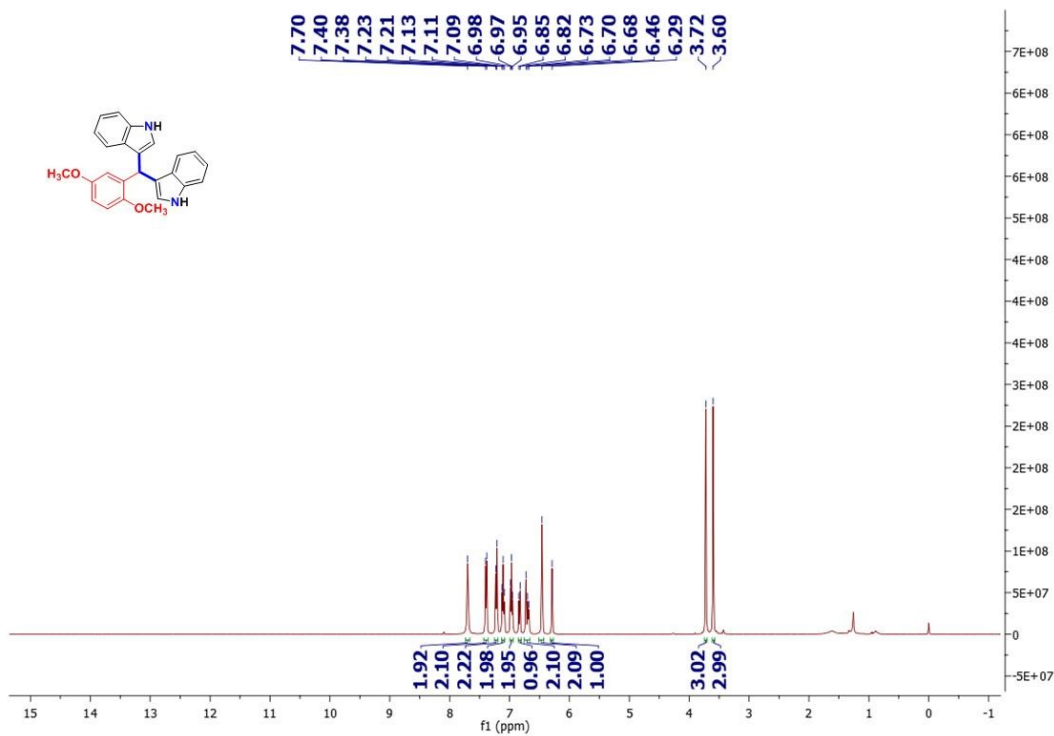
**Figure 32.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3g** in  $\text{CDCl}_3$  (100 MHz, 293 K)



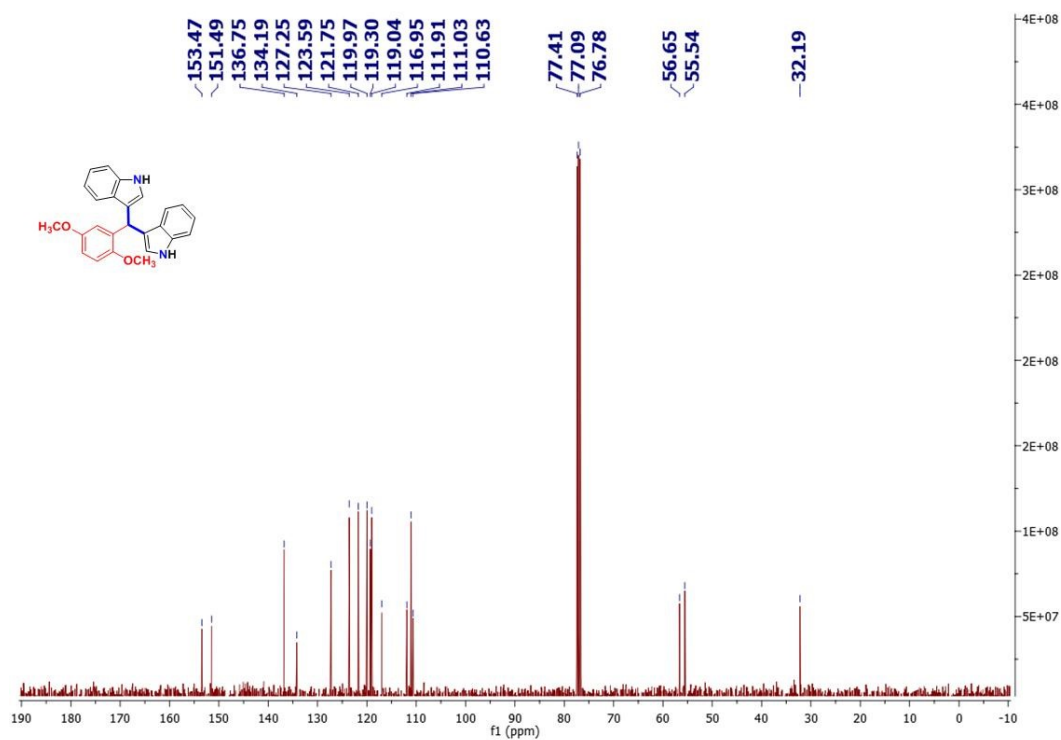
**Figure 33.**  $^1\text{H}$  NMR spectrum of **3h** in  $\text{CDCl}_3$  (400 MHz, 293 K)



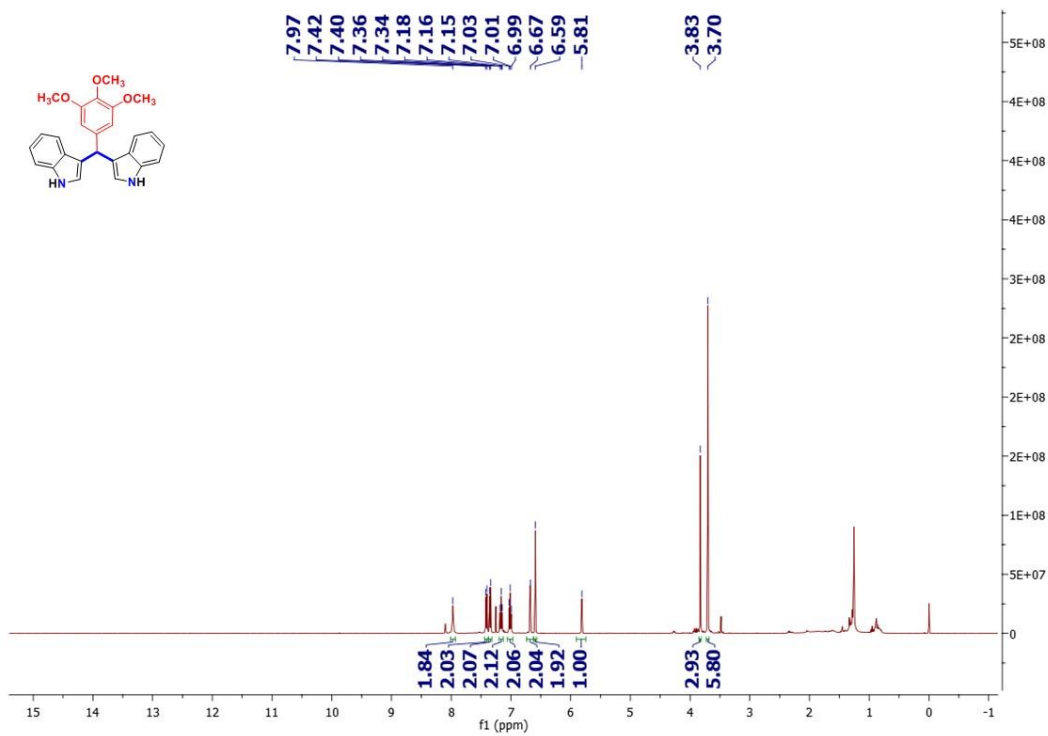
**Figure 34.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3h** in  $\text{CDCl}_3$  (100 MHz, 293 K)



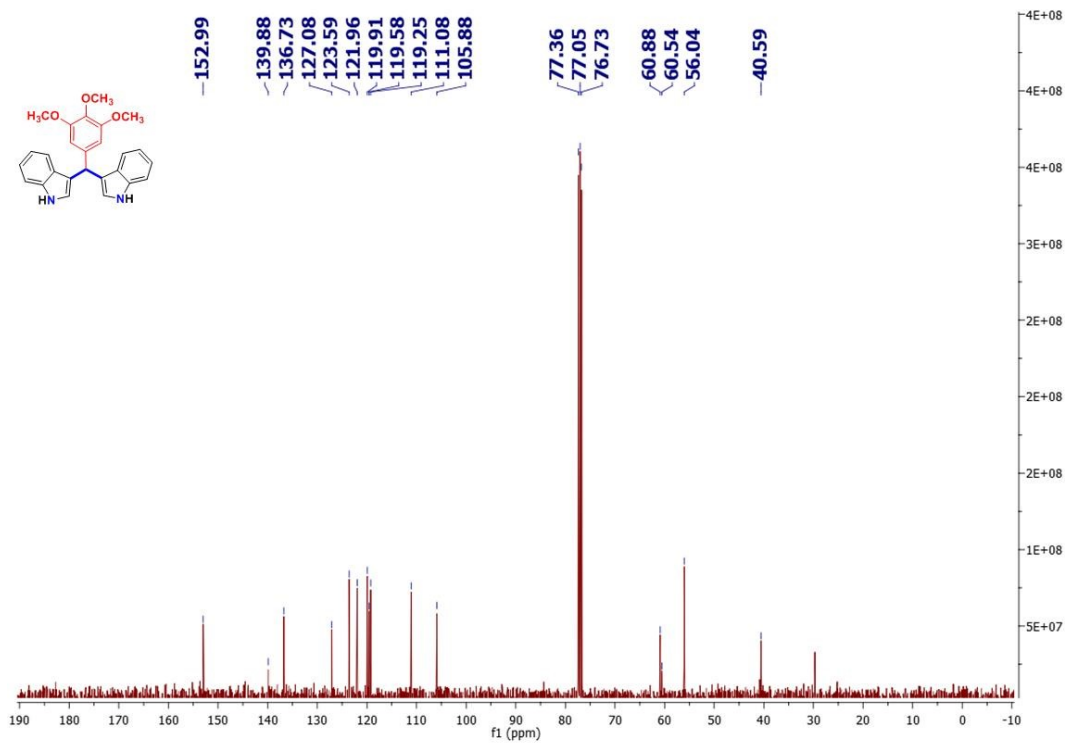
**Figure 35.**  $^1\text{H}$  NMR spectrum of **3i** in  $\text{CDCl}_3$  (400 MHz, 293 K)



**Figure 36.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3i** in  $\text{CDCl}_3$  (100 MHz, 293 K)



**Figure 37.**  $^1\text{H}$  NMR spectrum of **3j** in  $\text{CDCl}_3$  (400 MHz, 293 K)



**Figure 38.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3j** in  $\text{CDCl}_3$  (100 MHz, 293 K)

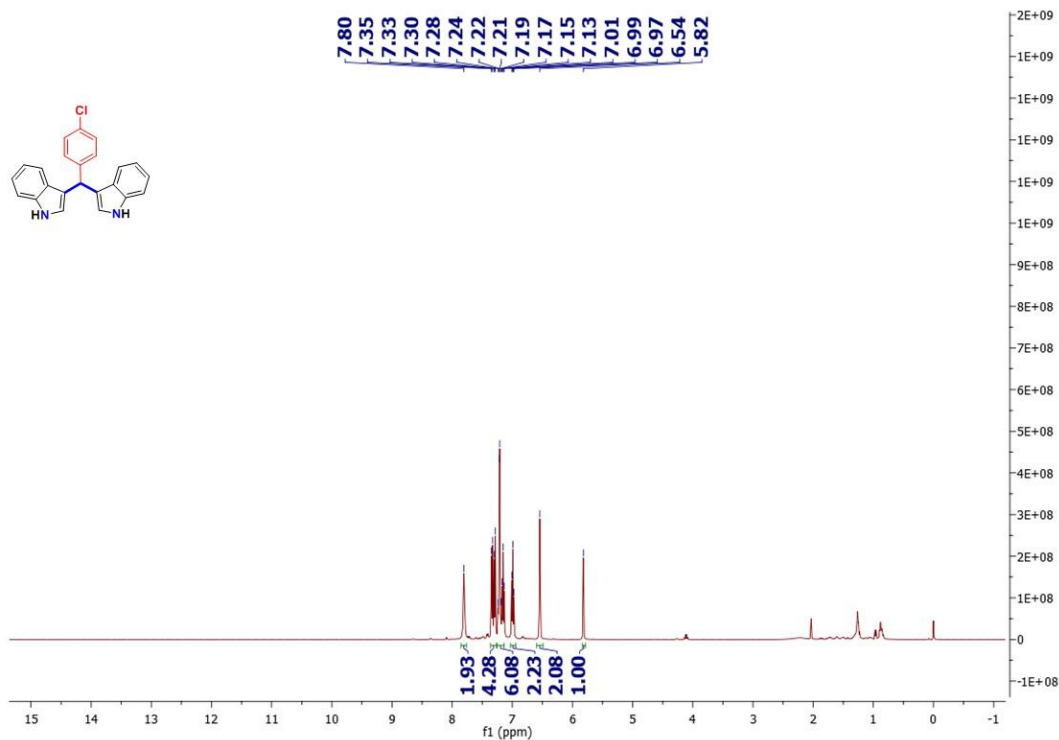


Figure 39.  $^1\text{H}$  NMR spectrum of **3k** in  $\text{CDCl}_3$  (400 MHz, 293 K)

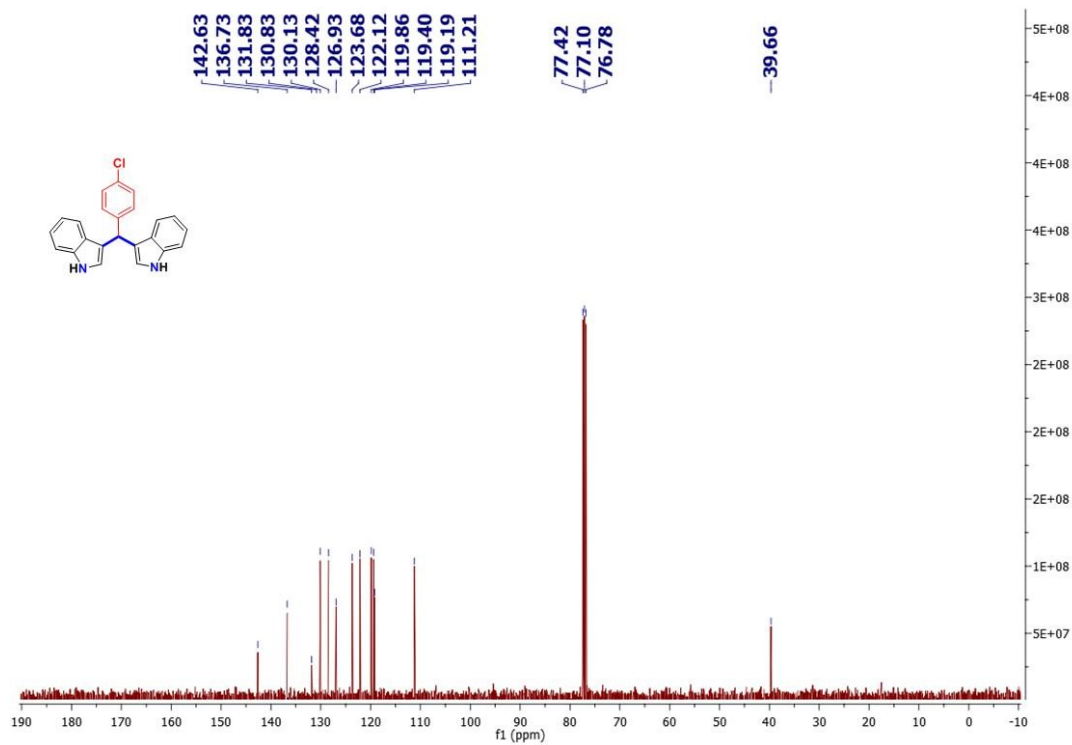
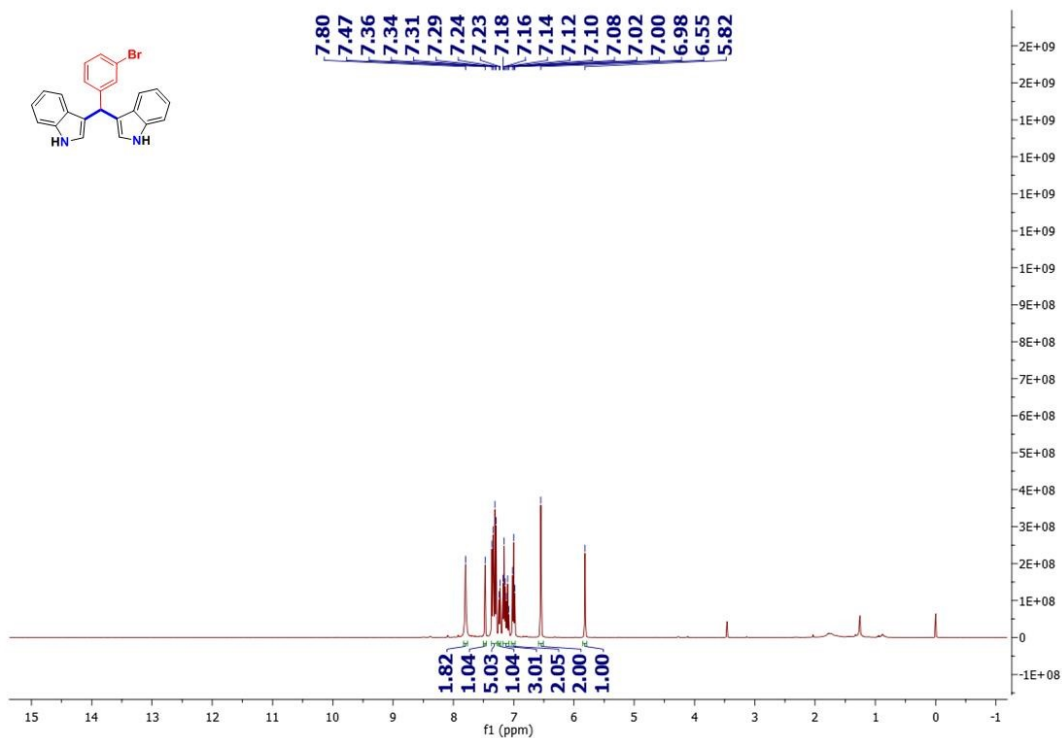
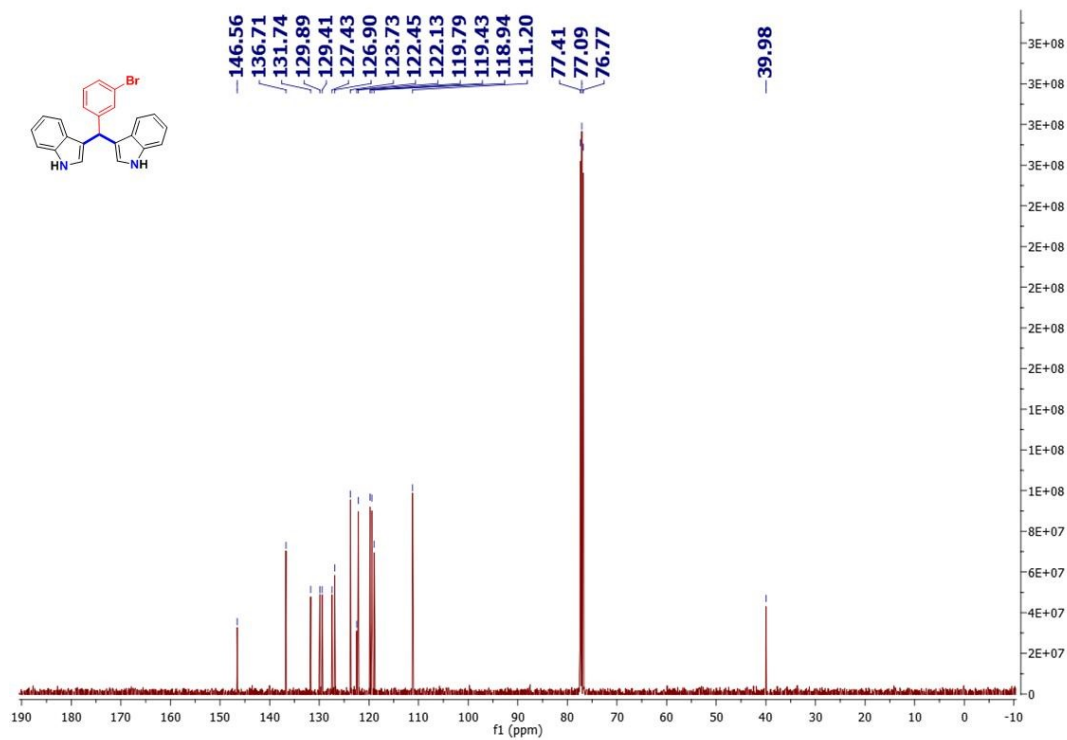


Figure 40.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3k** in  $\text{CDCl}_3$  (100 MHz, 293 K)





**Figure 41.**  $^1\text{H}$  NMR spectrum of **31** in  $\text{CDCl}_3$  (400 MHz, 293 K)



**Figure 42.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **31** in  $\text{CDCl}_3$  (100 MHz, 293 K)

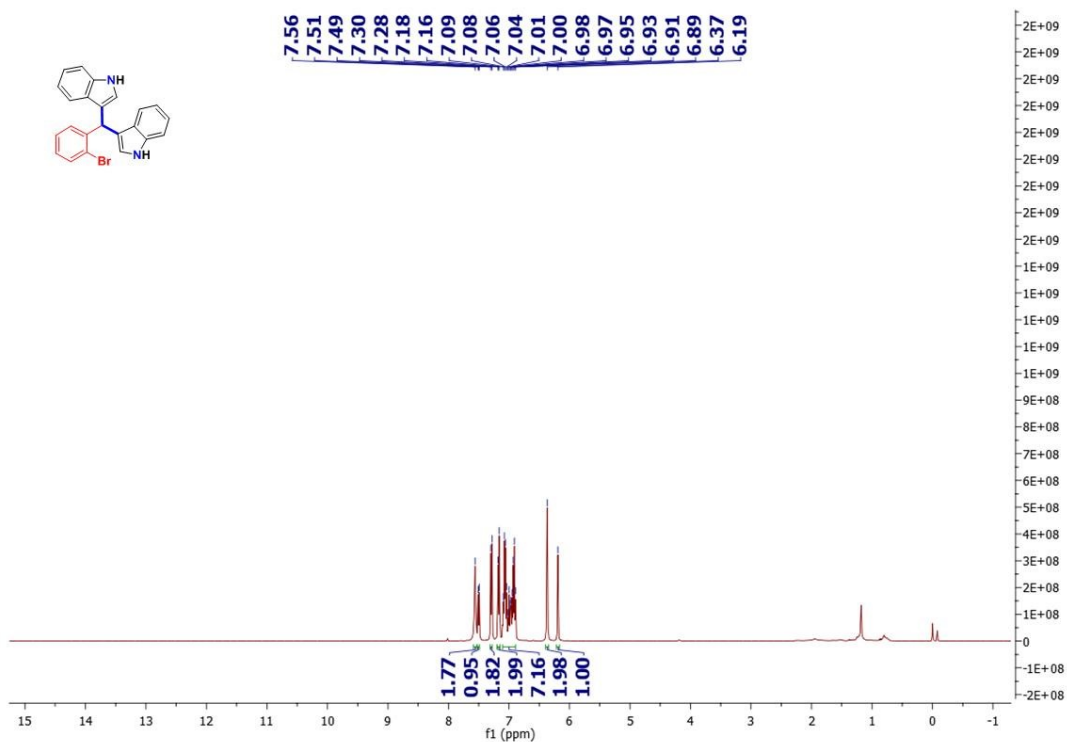


Figure 43.  $^1\text{H}$  NMR spectrum of **3m** in  $\text{CDCl}_3$  (400 MHz, 293 K)

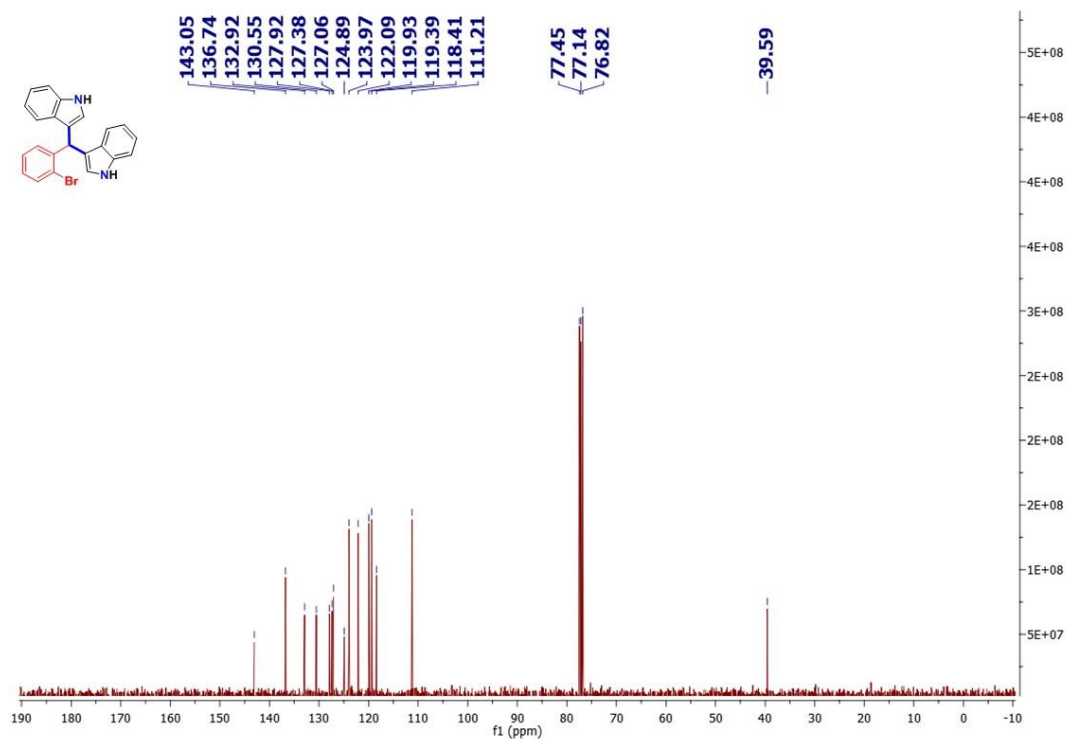


Figure 44.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3m** in  $\text{CDCl}_3$  (100 MHz, 293 K)

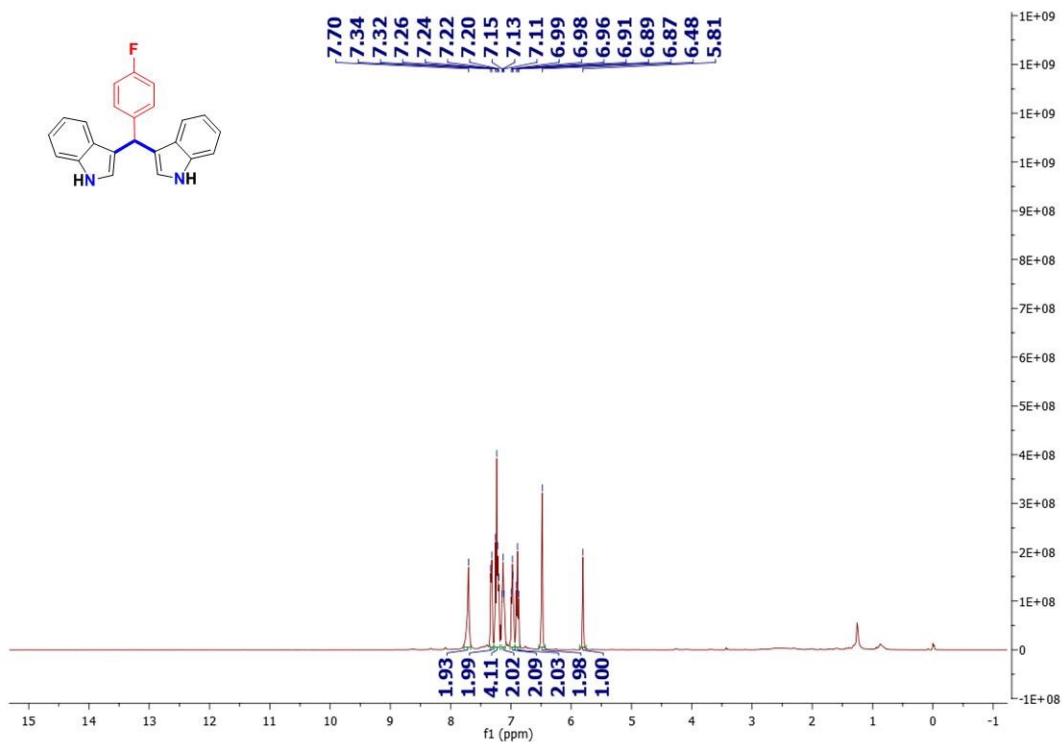


Figure 45.  $^1\text{H}$  NMR spectrum of **3n** in  $\text{CDCl}_3$  (400 MHz, 293 K).

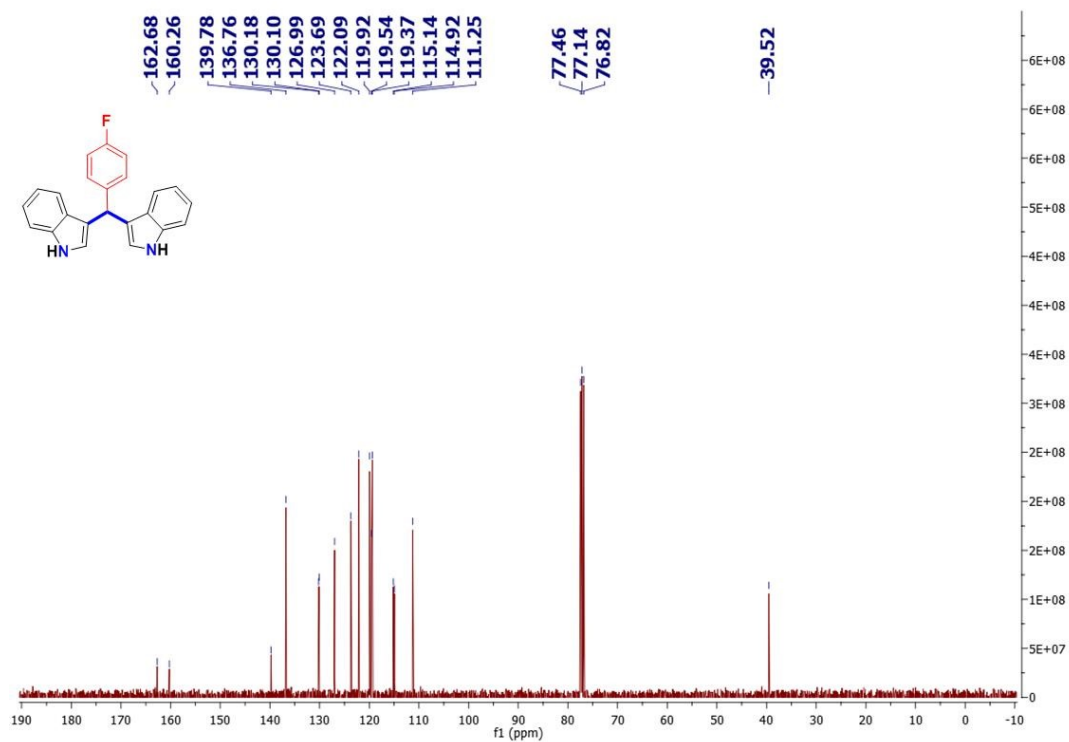
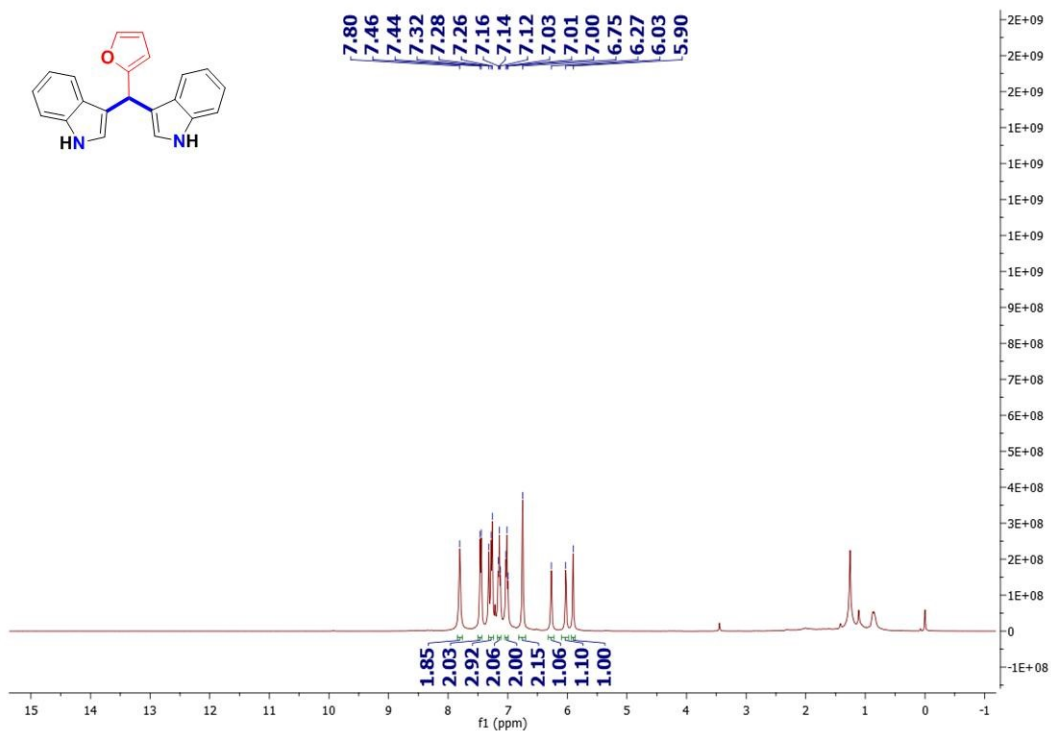
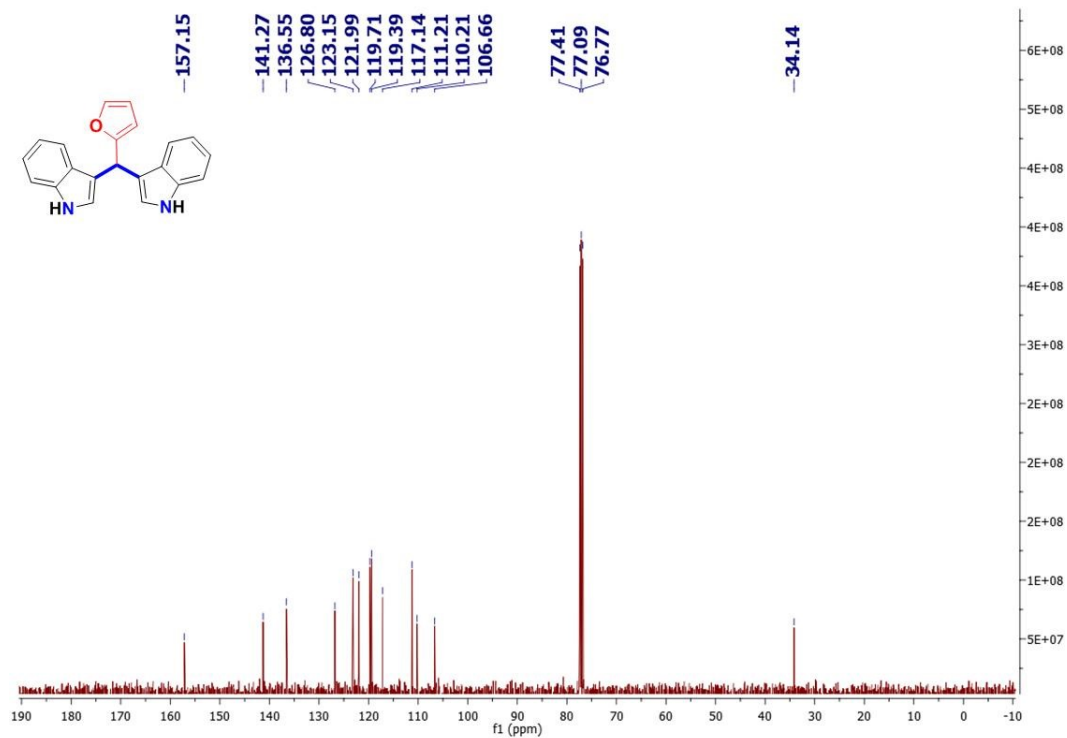


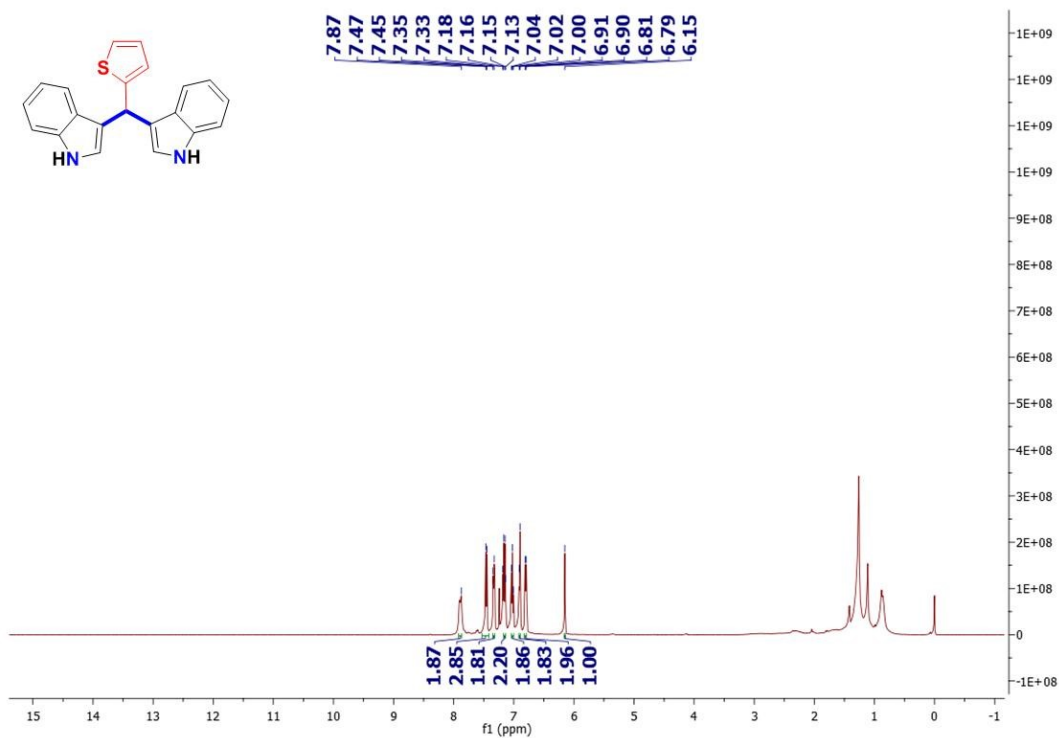
Figure 46.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3n** in  $\text{CDCl}_3$  (100 MHz, 293 K).



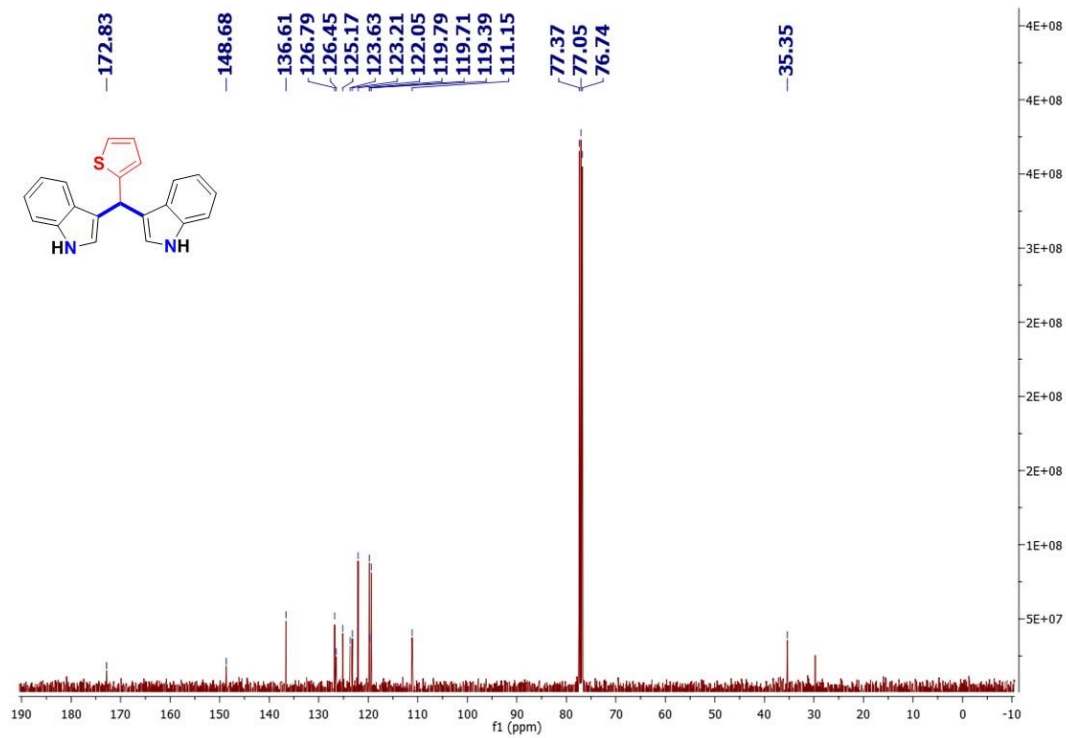
**Figure 47.** <sup>1</sup>H NMR spectrum of **3o** in CDCl<sub>3</sub> (400 MHz, 293 K)



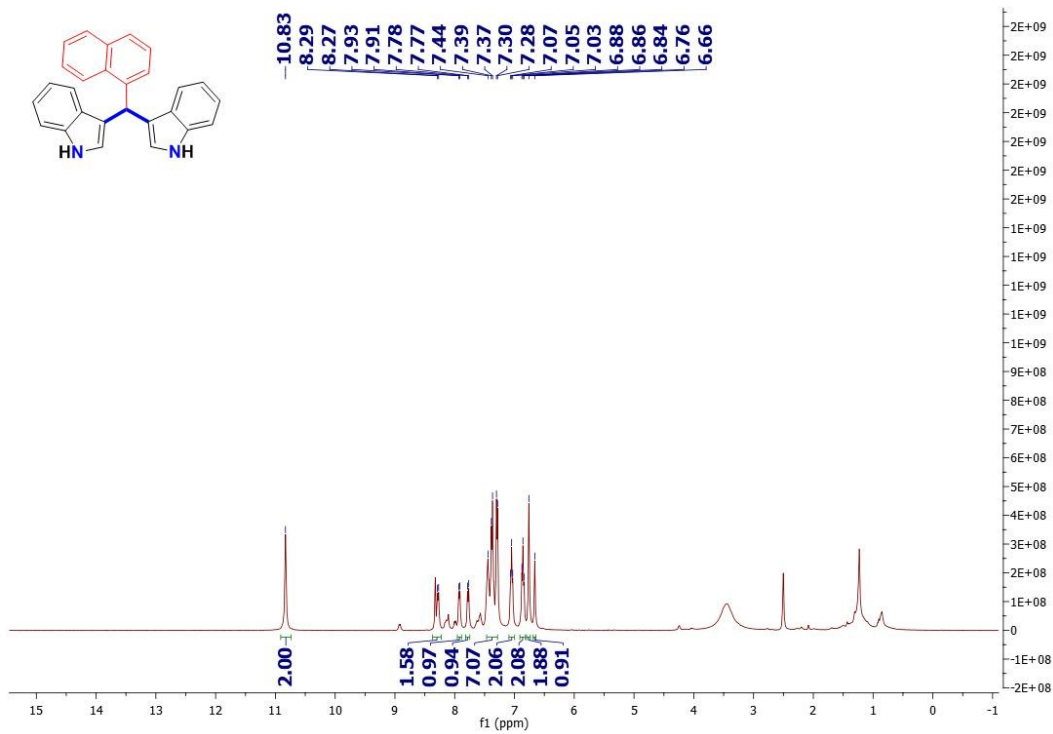
**Figure 48.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3o** in CDCl<sub>3</sub> (100 MHz, 293 K)



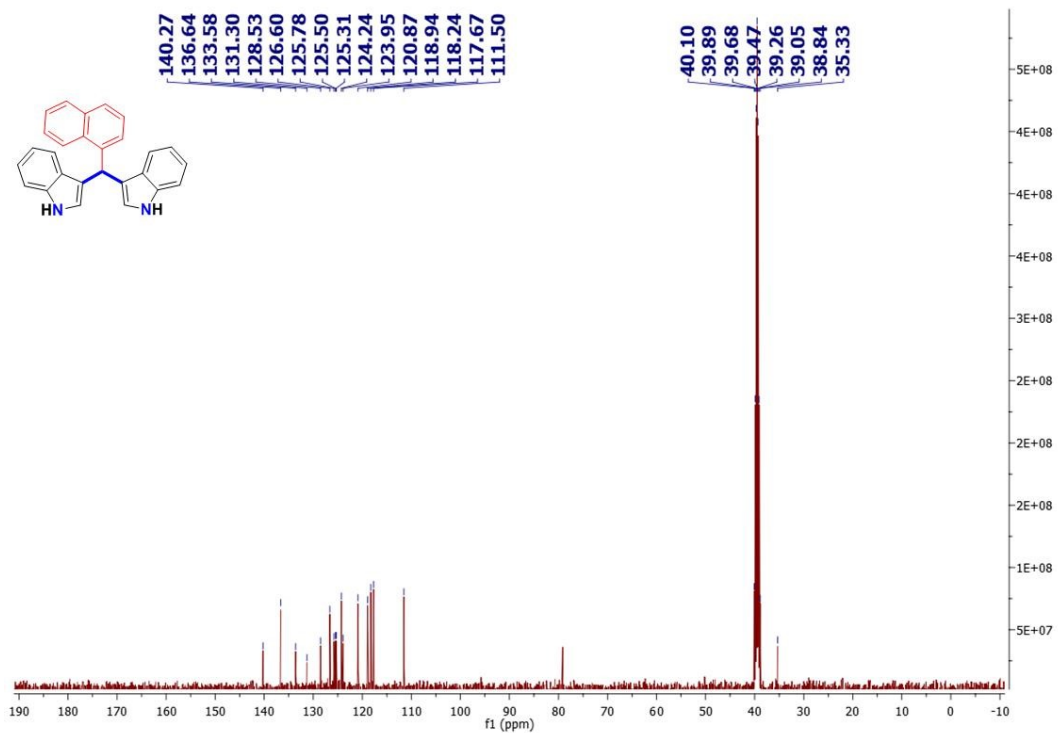
**Figure 49.** <sup>1</sup>H NMR spectrum of **3p** in CDCl<sub>3</sub> (400 MHz, 293 K)



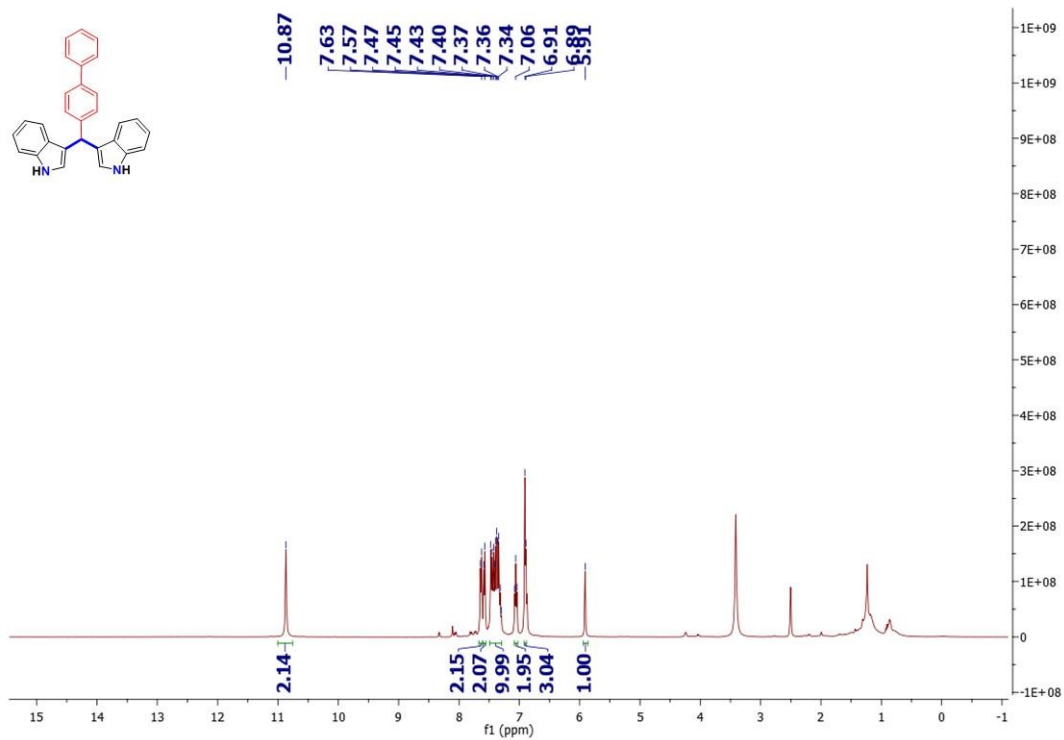
**Figure 50.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3p** in CDCl<sub>3</sub> (100 MHz, 293 K)



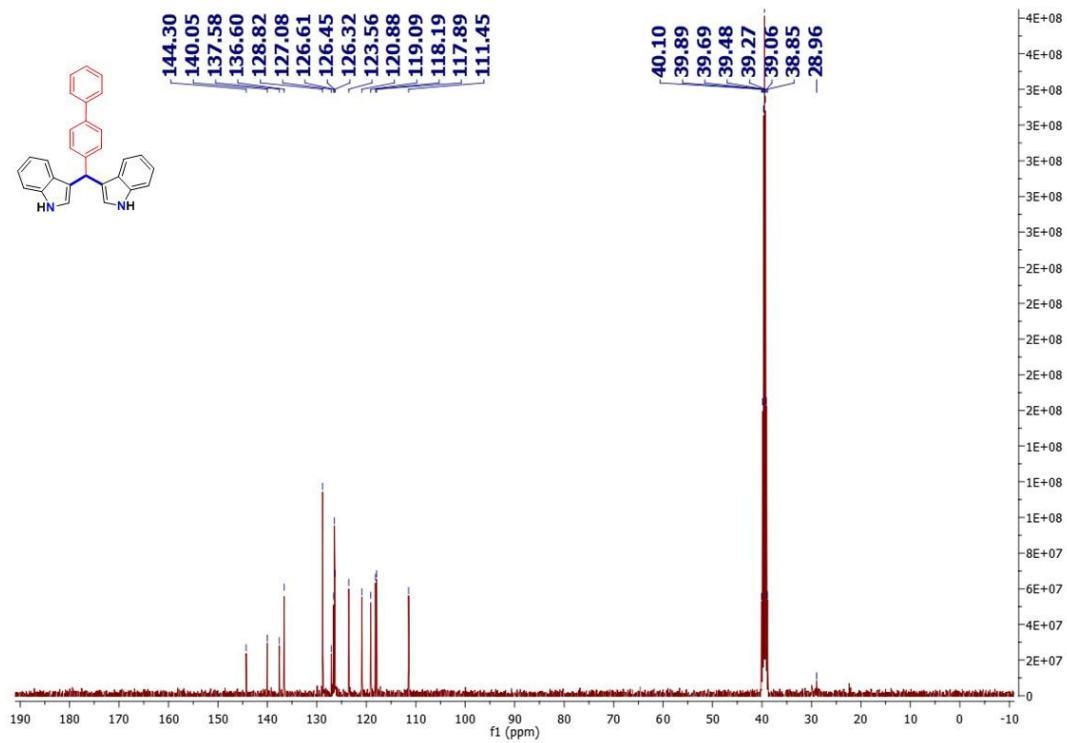
**Figure 51.**  $^1\text{H}$  NMR spectrum of **3q** in DMSO- $d_6$  (400 MHz, 293 K)



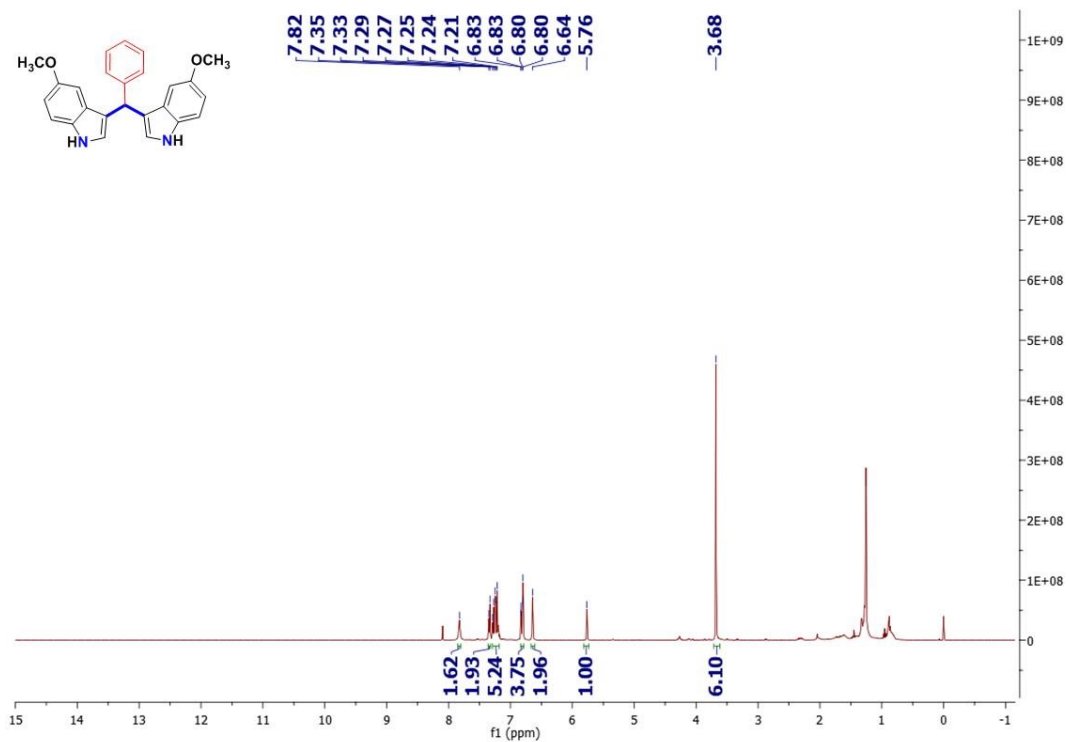
**Figure 52.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3q** in DMSO- $d_6$  (100 MHz, 293 K)



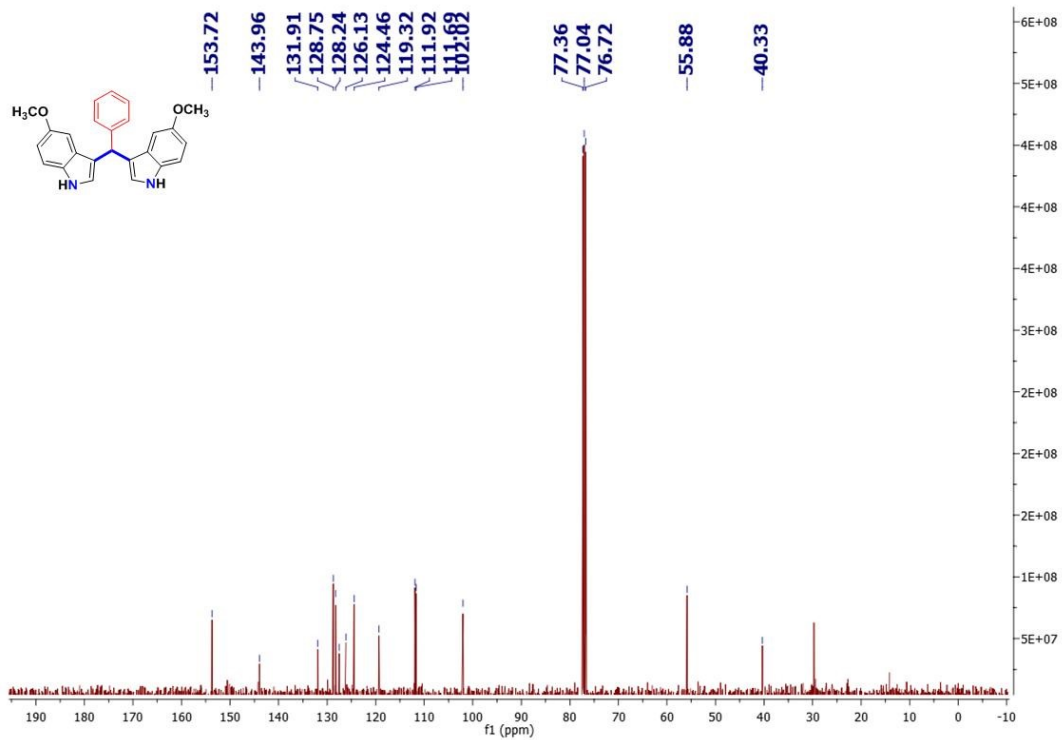
**Figure 53.**  $^1\text{H}$  NMR spectrum of **3r** in DMSO- $d_6$  (400 MHz, 293 K)



**Figure 54.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3r** in DMSO- $d_6$  (100 MHz, 293 K)

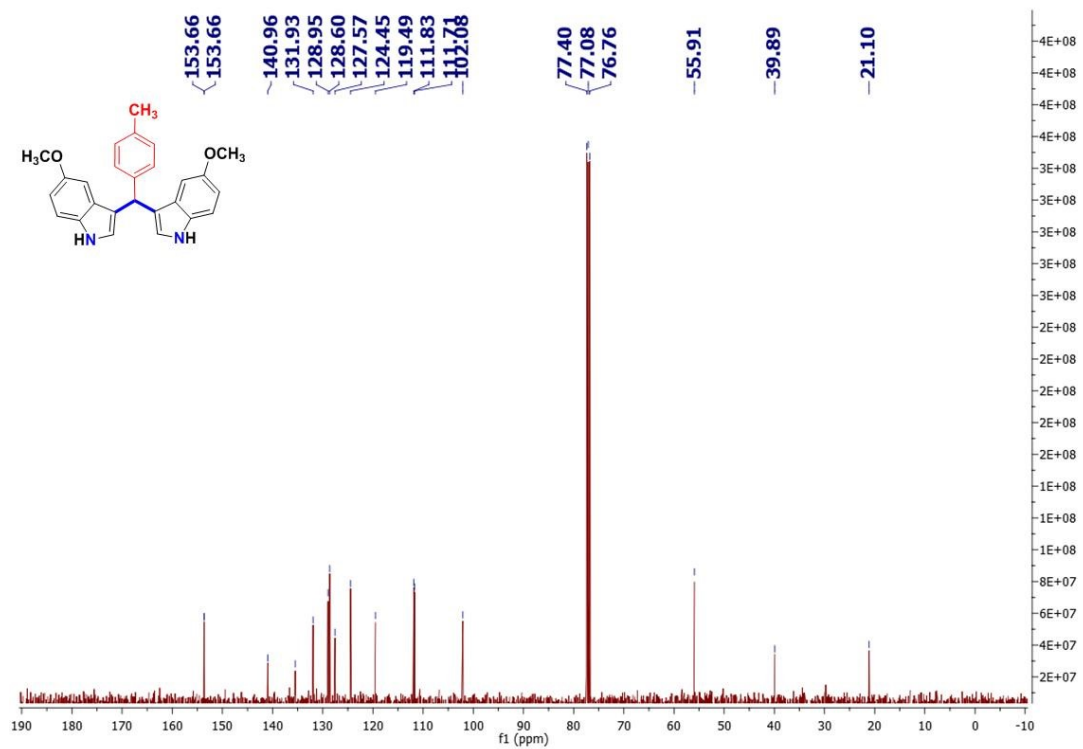
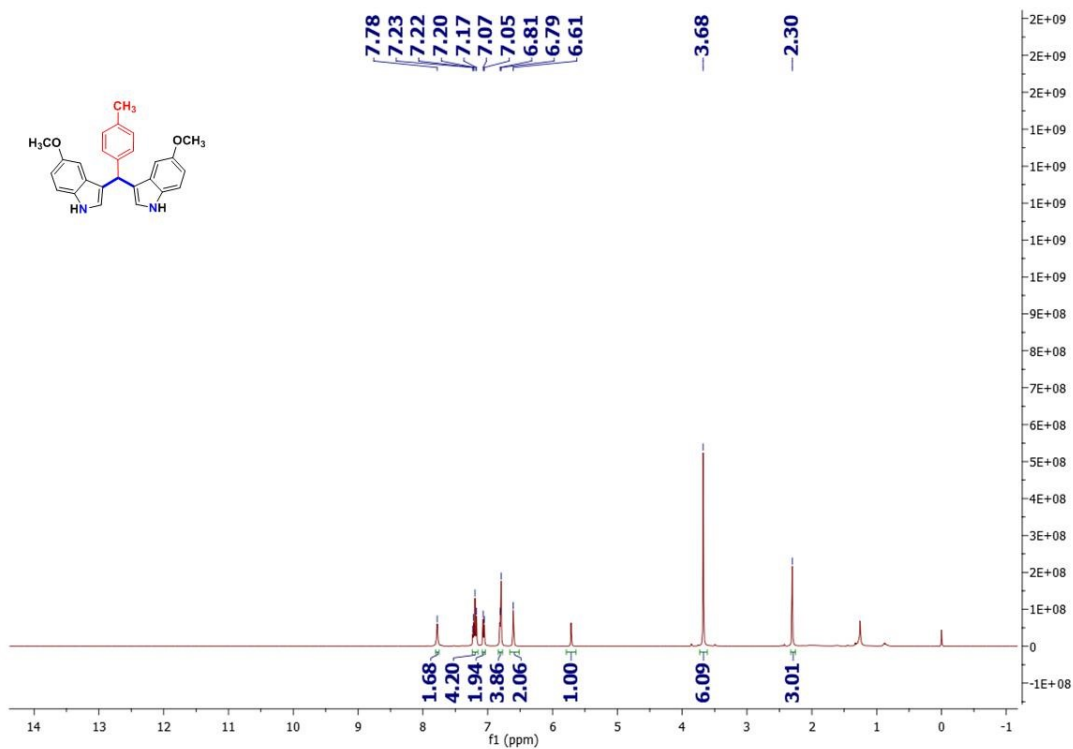


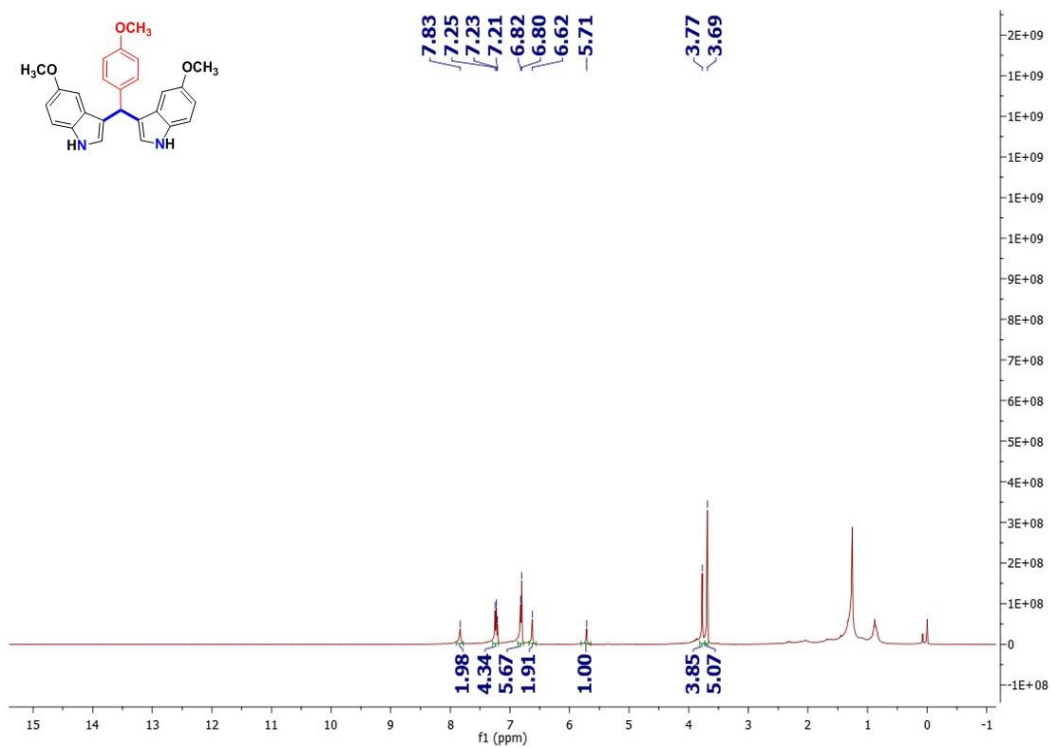
**Figure 55.** <sup>1</sup>H NMR spectrum of **3s** in CDCl<sub>3</sub> (400 MHz, 293 K)



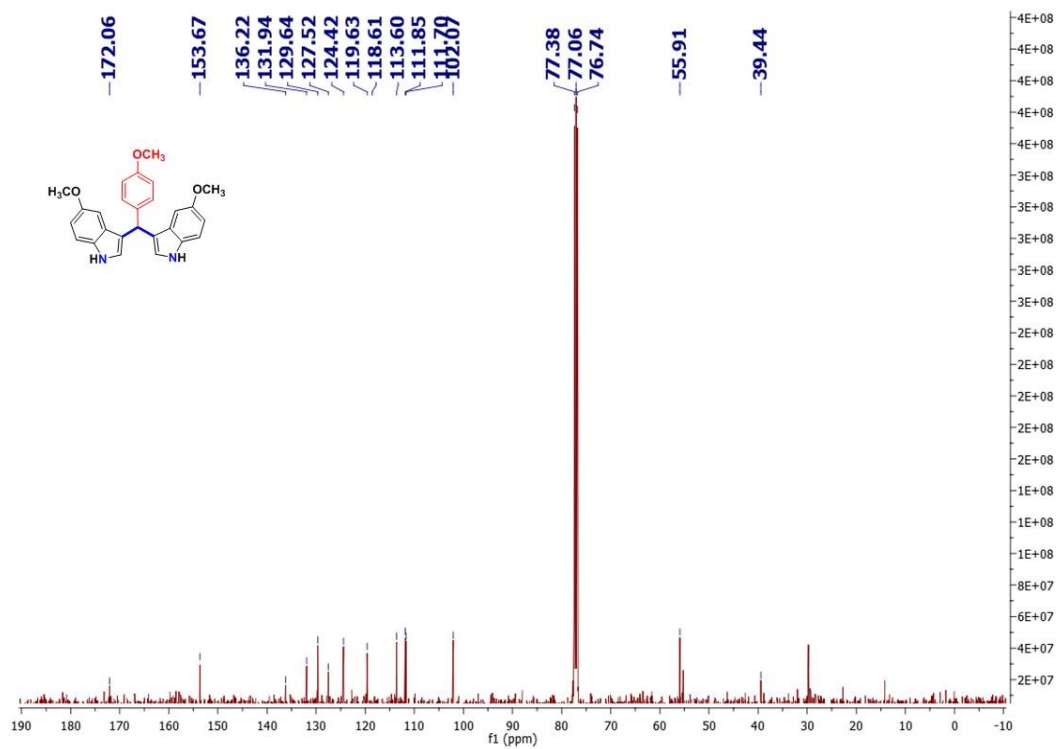
**Figure 56.** <sup>13</sup>C {<sup>1</sup>H} NMR spectrum of **3s** in CDCl<sub>3</sub> (100 MHz, 293 K)



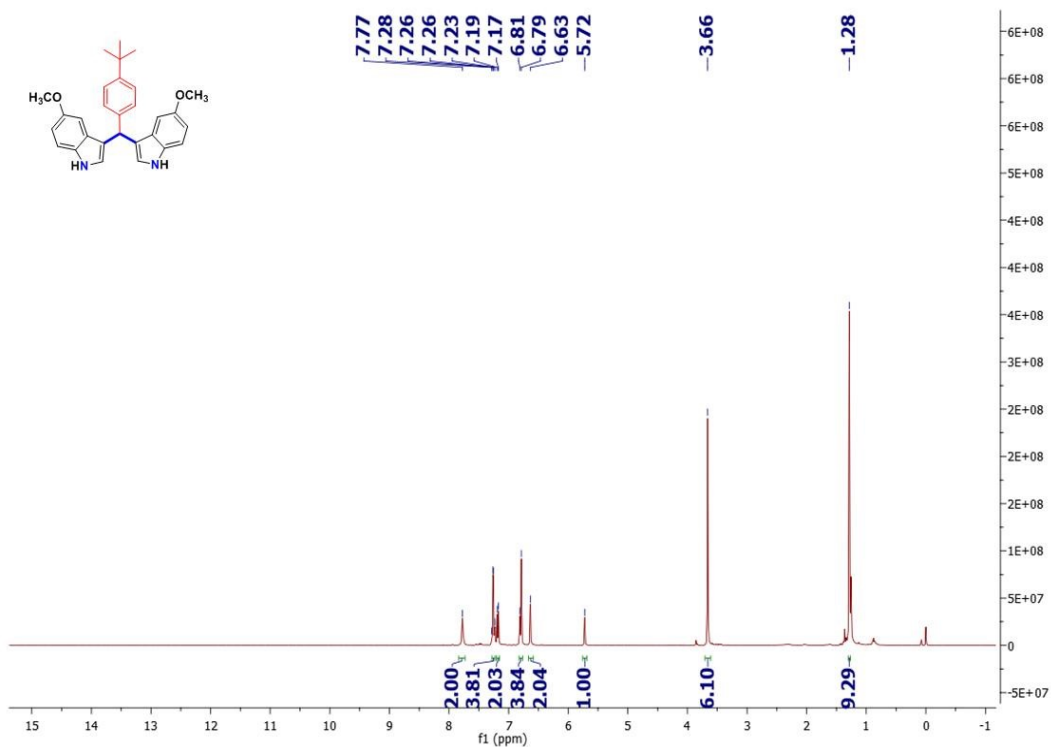




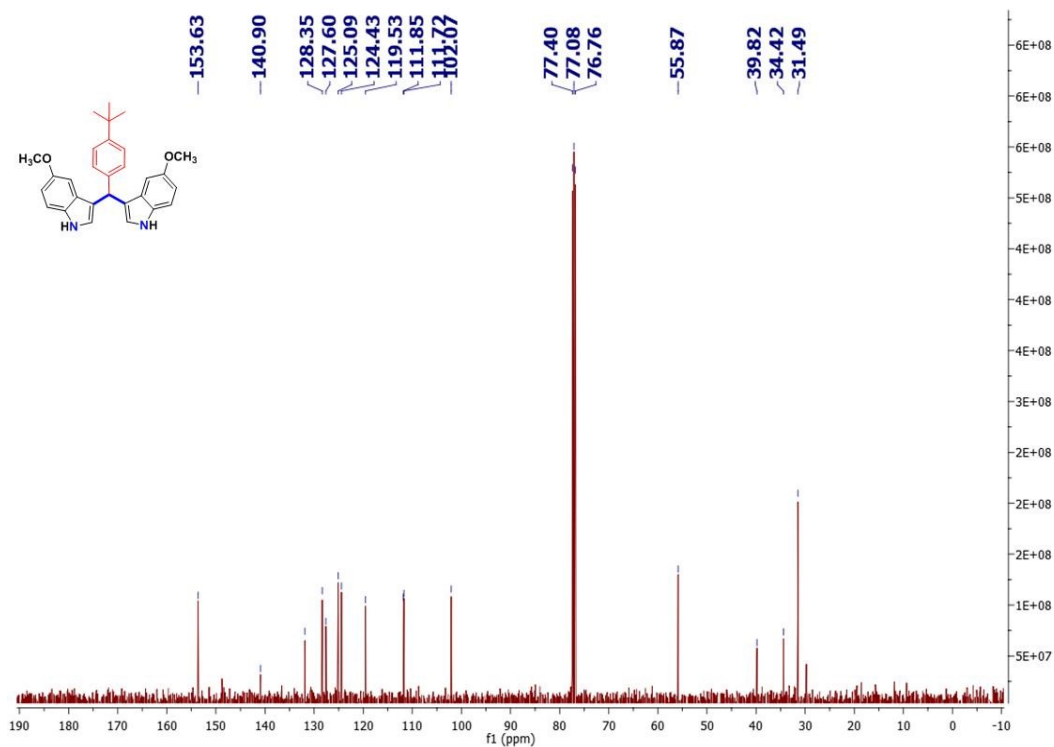
**Figure 59.**  $^1\text{H}$  NMR spectrum of **3u** in  $\text{CDCl}_3$  (400 MHz, 293 K)



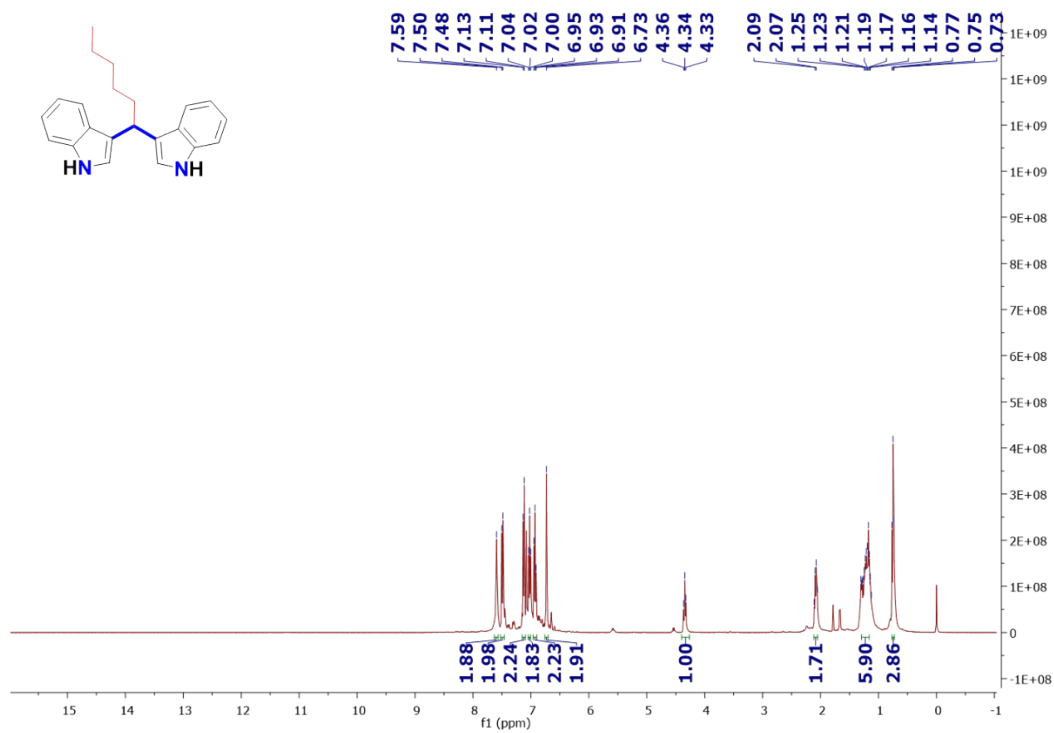
**Figure 60.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3u** in  $\text{CDCl}_3$  (100 MHz, 293 K)



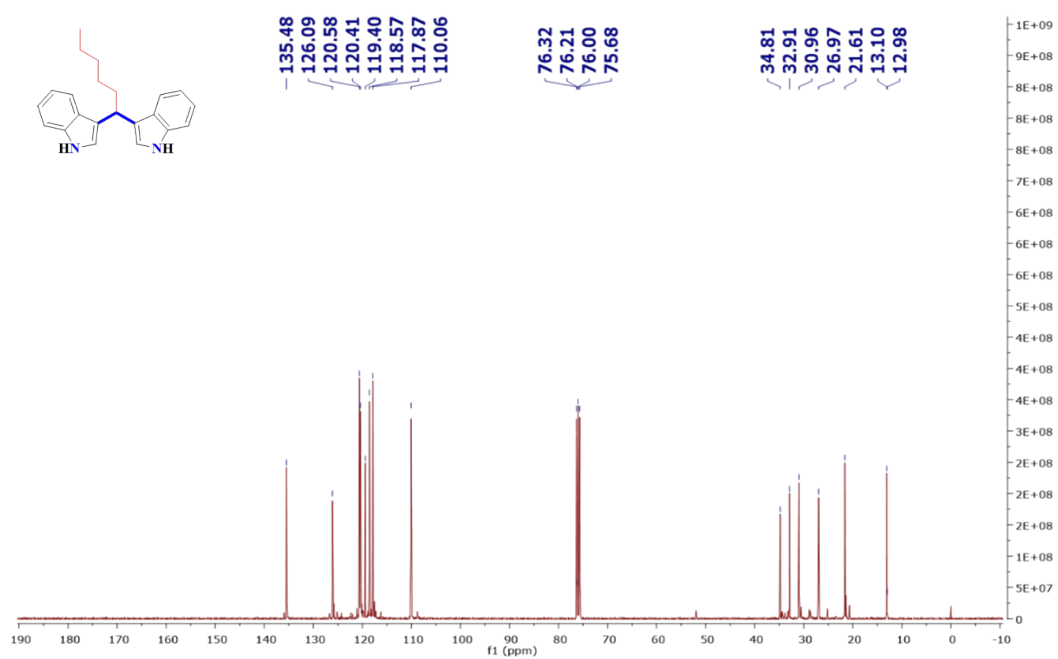
**Figure 61.** <sup>1</sup>H NMR spectrum of **3v** in CDCl<sub>3</sub> (400 MHz, 293 K)



**Figure 62.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3v** in CDCl<sub>3</sub> (100 MHz, 293 K)



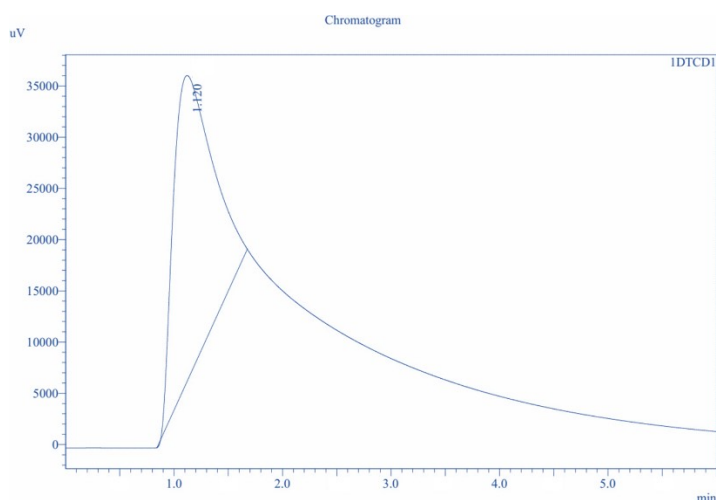
**Figure 63.** <sup>1</sup>H NMR spectrum of **3w** in CDCl<sub>3</sub> (400 MHz, 293 K)



**Figure 64.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3w** in CDCl<sub>3</sub> (100 MHz, 293 K)

## 9. Experimental confirmation for the H<sub>2</sub> liberation using GC-TCD detector

Under N<sub>2</sub> atmosphere, a mixture of Pd<sub>2</sub> catalyst (0.5 mol%), <sup>t</sup>BuOK (0.50 mmol), benzyl alcohol (1.0 mmol), and indole (2.0 mmol) was dissolved in 3 mL of toluene, and the mixture was placed in an oil bath and heated at 110 °C for 4 h. Then, the gaseous reaction mixture has been analyzed on GC-TCD detector to witness the liberation of hydrogen gas.



**Figure 65.** chromatogram for the evaluation of H<sub>2</sub>

## 10. References

1. A. I. Vogel, Test book of practical organic chemistry, Longman, London, 5<sup>th</sup> edn, 1989, 395.
2. F. H. Allen, D. Motherwell, R. Raithby, G. P. Shields and R. Taylor, New J. Chem. **1999**, 23, 25.
3. G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr. **2008**, 64, 112.
4. Bruker-Nonius (2004), APEX-II and SAINT-Plus (Version 7.06a), Bruker AXS Inc., Madison, Wisconsin, USA.
5. V. Yadav, E. Balaraman and S. B. Mhaske. Adv. Synth. Catal., 2021, 363, 4430-4439.