

Supporting Information

Graphene oxide supported nickel(II) complex as a reusable nano catalyst for the synthesis of bis(indolyl)methanes

Gautam Kumar, Ananya Srivastava, Vinod P. Singh*

Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi-221005,
India

*Corresponding author email address: singvp@yahoo.co.in, Phone No: +919450145060

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1. Experimental procedures

Synthesis of graphene oxide (GO)

GO was synthesized by the modified Hummers' method. In a typical procedure, 0.5 g of graphite powder and 2.0 g of sodium nitrate were taken in a round bottom flask and added 18 mL cold (below 5 °C) concentrated H₂SO₄ in it. The mixture was stirred continuously for 1 h and keeping the temperature below 5 °C on ice bath. Thereafter, 3 g of potassium permanganate was added gradually and reaction was continued for another 2 h at a temperature below 5 °C. The mixture was then heated to 35 °C for 30 min and 40 mL of deionised water (DI) was added to it slowly while increasing temperature. It was kept at 100 °C for 15 min, diluted with 70 mL of DI water and cooled to room temperature. The colour of the suspension changed to bright yellow after adding 10 mL of H₂O₂ (35%). The suspension was filtered and washed with 400 mL of 5% HCl twice followed by further washing with 200 mL of DI water for 3 times. Finally, the precipitate was dried in the vacuum desiccator for at least 5 days before further use.

General procedure for synthesis of bis(indolyl)methanes

Indole (0.220 g, 1.88 mmol), benzaldehyde (0.100 g, 0.943 mmol) and GO-APH-Ni(II) (2 wt%) were taken in a round bottom flask. The contents were stirred for 1 h at 60 °C. Reaction was monitored through TLC. After completion of reaction, reaction mixture was extracted with dichloromethane, dried over anhydrous sodium sulphate and concentrated at reduced pressure. The products were purified through the column chromatography and yields were recorded. The synthesized bis(indolyl)methanes (3a-3j) were characterized by ¹H and ¹³C NMR spectra.

Synthesis of APH-Ni(II) complex

The Ni(II) complex of APH was synthesized by reacting 50 mL methanolic solution of (CH₃COO)₂Ni.4H₂O (1 mmol) with 50 mL methanolic solution of APH (1 mmol) in a round bottom flask and stirring the reaction mixture on a magnetic stirrer at room temperature for 2 h. The APH-Ni(II) complex was precipitated as yellow solid. The product was filtered, washed several times with methanol and dried in desiccator over anhydrous calcium chloride at room temperature.

Yield (80%). ¹H NMR (500 MHz, DMSO-d₆) δ 11.07 (1H, OH), 8.10-7.14 (12H, Ar-H), 6.45 (2H, NH₂). IR (cm⁻¹, KBr): ν(O-H) 3157 broad, ν(C=N) 1586, ν(C-O) 1362, ν(N-N) 1030; HRMS calculated for C₂₀H₁₇ClN₃NiO₃: m/z (M+H⁺) 442.5216; found 442.8682; UV-Vis (nm, DMF): 502, 365.

2. ¹H NMR and ¹³C NMR data of bis(indolyl)methanes

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

¹H NMR (500 MHz, CDCl₃) δ 7.82 (s, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.30 (dd, 8.0 Hz, 4H), 7.23 (dd, *J* = 12.4, 5.3 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 2H), 6.58 (s, 2H), 5.89 (s, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 144.16, 136.78, 128.84, 128.33, 127.17, 126.23, 123.75, 121.98, 120.02, 119.71, 119.29, 111.17, 77.42, 77.16, 76.91, 65.99.

2-(di(1H-indol-3-yl)methyl)phenol (**3b**)

¹H NMR (500 MHz, DMSO-d₆) δ 10.97 (s, 1H), 10.85 (s, 1H), 8.72 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 3H), 6.98 (t, *J* = 7.6 Hz, 4H), 6.86 (d, *J* = 7.8 Hz, 2H).

¹³C NMR (126 MHz, DMSO-d₆) δ 189.17, 171.48, 153.02, 141.42, 138.88, 137.65, 129.83, 125.20, 124.90, 121.90, 121.81 – 121.69, 119.56, 113.96, 110.13, 107.11.

Methyl 4-(di(1H-indol-3-yl)methyl)benzoate (**3c**)

¹H NMR (500 MHz, CDCl₃) δ 7.93 (s, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.23 (s, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.62 (s, 2H), 5.82 (s, 1H), 3.77 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.96, 136.82, 136.39, 129.67, 127.16, 123.63, 121.89, 120.04, 119.20, 113.64, 111.11, 77.36, 77.10, 76.85, 55.28, 39.42.

3,3'-(naphthalen-1-ylmethylene)bis(1H-indole) (**3d**)

¹H NMR (500 MHz, DMSO-d₆) δ 10.74 (s, 2H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.34 – 7.28 (m, 3H), 7.22 (d, *J* = 8.3 Hz, 3H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.80 (t, *J* = 7.5 Hz, 2H), 6.69 (s, 2H), 6.58 (s, 1H).

¹³C NMR (126 MHz, DMSO-d₆) δ 137.18, 129.08, 127.11, 126.34, 126.09 – 125.68, 124.77, 121.41, 119.48, 118.78, 118.21, 112.04, 40.55, 40.38, 40.22, 40.05, 39.88, 39.72, 39.55.

3,3'-(anthracen-9-ylmethylene)bis(1H-indole) (**3e**)

¹H NMR (500 MHz, CDCl₃) δ 8.63 (d, *J* = 9.1 Hz, 2H), 8.43 (s, 1H), 8.00 (s, 2H), 7.89 (s, 2H), 7.41 (s, 1H), 7.36 (s, 2H), 7.31 (d, *J* = 8.1 Hz, 3H), 7.10 (t, *J* = 8.2 Hz, 5H), 6.86 (t, *J* = 7.6 Hz, 2H), 6.79 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 136.65, 135.22, 132.02, 129.21, 127.37, 124.72, 124.01, 121.92, 120.07, 119.27, 119.00, 111.04, 77.34, 77.08, 76.83, 35.14.

3,3'-((4-bromophenyl)methylene)bis(1H-indole) (**3f**)

¹H NMR (500 MHz, CDCl₃) δ 7.96 (s, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 4H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.63 (s, 2H), 5.83 (s, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 143.47, 136.87, 131.40, 130.66, 127.01, 123.98, 122.04, 119.91, 119.34, 118.90, 111.47, 77.59, 77.34, 77.08, 66.08.

Methyl 4-(di(1H-indol-3-yl)methyl)benzoate (3g)

^1H NMR (500 MHz, CDCl_3) δ 8.03 (s, 2H), 7.95 (d, $J = 8.1$ Hz, 2H), 7.40 (d, $J = 8.3$ Hz, 2H), 7.36 (d, $J = 7.9$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 7.17 (t, $J = 7.6$ Hz, 2H), 7.01 (t, $J = 7.4$ Hz, 2H), 6.57 (s, 2H), 5.92 (s, 1H), 3.89 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 167.52, 149.85, 136.82, 129.75, 128.90, 128.11, 126.98, 123.86, 122.07, 119.78, 119.36, 118.65, 111.33, 77.44, 77.19, 76.93, 52.12.

4-(di(1H-indol-3-yl)methyl)benzene-1,3-diol (3h)

^1H NMR (500 MHz, DMSO-d_6) δ 10.61 (s, 2H), 9.11 (s, 1H), 8.89 (s, 1H), 7.27 (d, $J = 8.2$ Hz, 2H), 7.20 (d, $J = 7.9$ Hz, 2H), 6.96 (t, $J = 7.5$ Hz, 2H), 6.82 – 6.74 (m, 3H), 6.65 (s, 2H), 6.27 (s, 1H), 6.05 – 6.01 (m, 1H), 5.99 (s, 1H).

3,3'-(pyridin-3-ylmethylene)bis(1H-indole) (3i)

^1H NMR (500 MHz, DMSO-d_6) δ 10.85 (s, 2H), 8.57 (s, 1H), 8.34 (s, 1H), 7.66 (d, $J = 7.6$ Hz, 1H), 7.33 (d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 3H), 7.01 (t, $J = 7.5$ Hz, 2H), 6.86 – 6.82 (m, 4H), 5.87 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 150.11, 147.63, 140.81, 137.13, 136.16, 126.90, 124.19, 123.84, 121.59, 119.47, 118.88, 117.67, 112.08, 60.30, 40.47, 40.30, 40.14, 39.97, 39.80, 39.64, 39.47.

3,3'-(furan-2-ylmethylene)bis(1H-indole) (3j)

^1H NMR (500 MHz, CDCl_3) δ 7.89 (s, 2H), 7.60 (d, $J = 7.9$ Hz, 2H), 7.40 (s, 1H), 7.25 (d, $J = 5.6$ Hz, 4H), 7.14 (t, $J = 6.4$ Hz, 2H), 6.71 (s, 2H), 6.36 (s, 1H), 6.14 (d, $J = 2.7$ Hz, 1H), 6.03 (s, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 157.51, 141.37, 136.72, 12s 6.92, 123.59, 121.97, 119.77, 119.41, 116.89, 111.61, 110.46, 106.81, 77.71, 77.45, 77.19, 60.84.

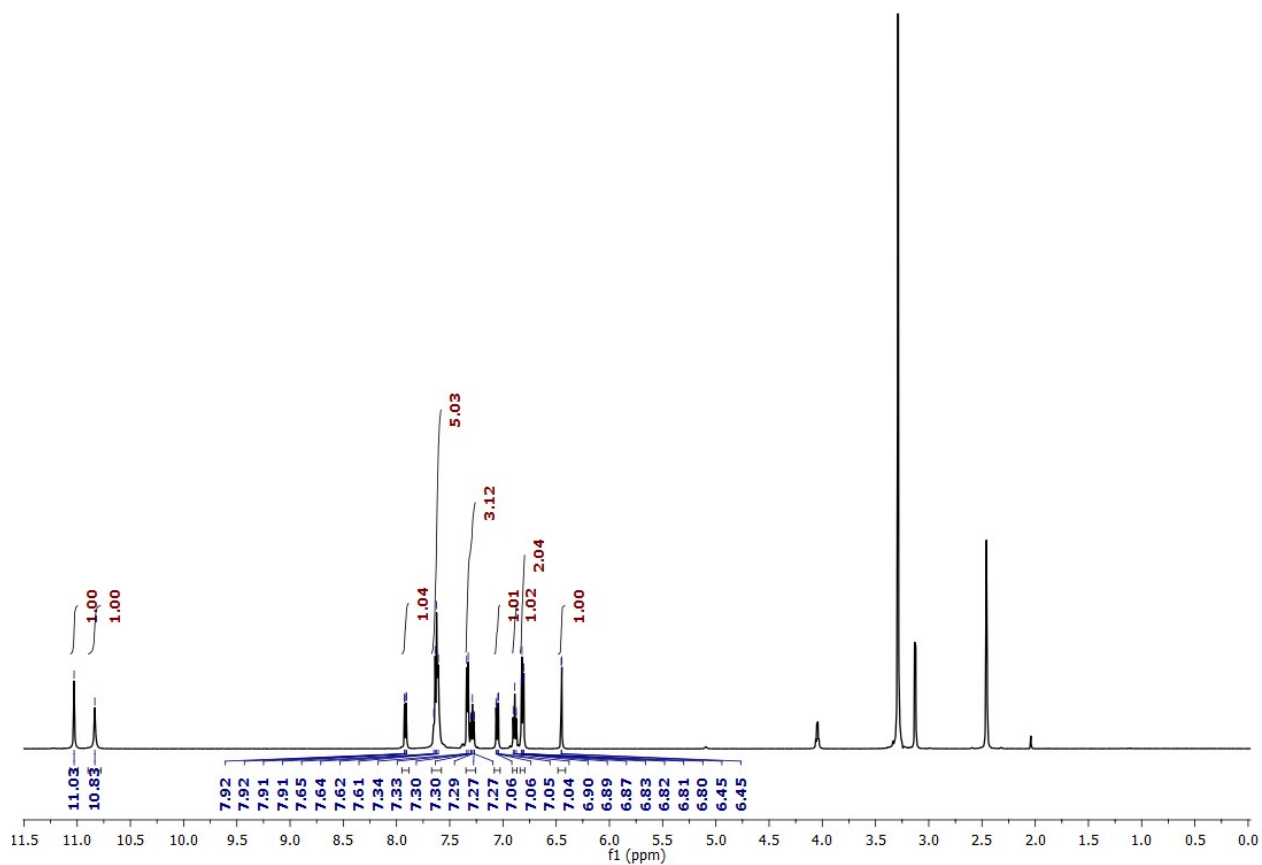


Fig. S1. ¹H NMR spectrum of APH

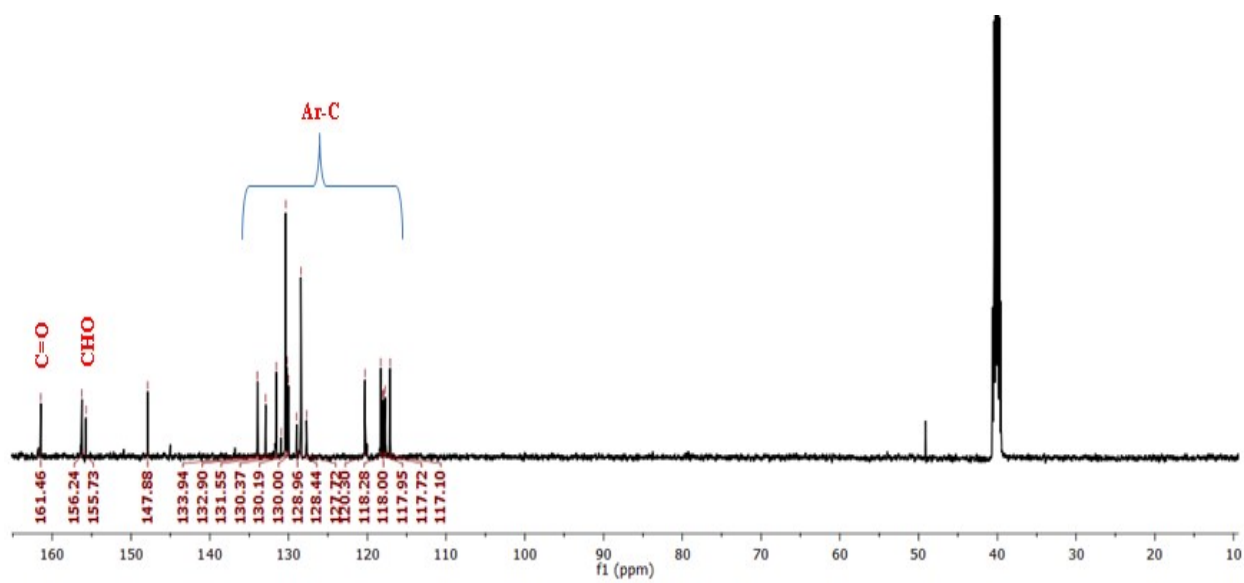


Fig. S2. ¹³C NMR spectrum of APH

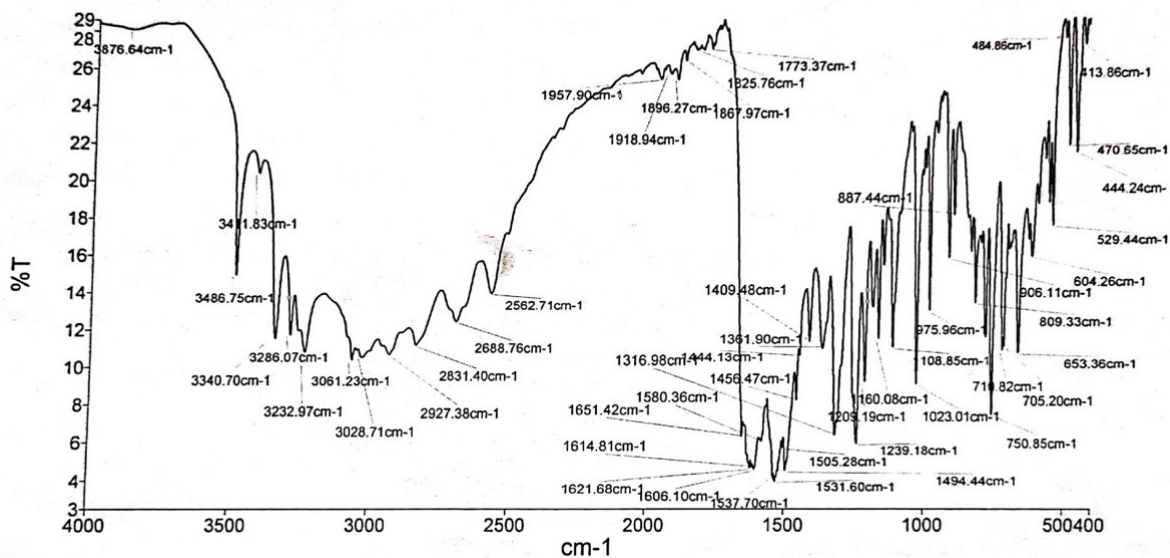


Fig. S3. FT-IR spectrum of APH

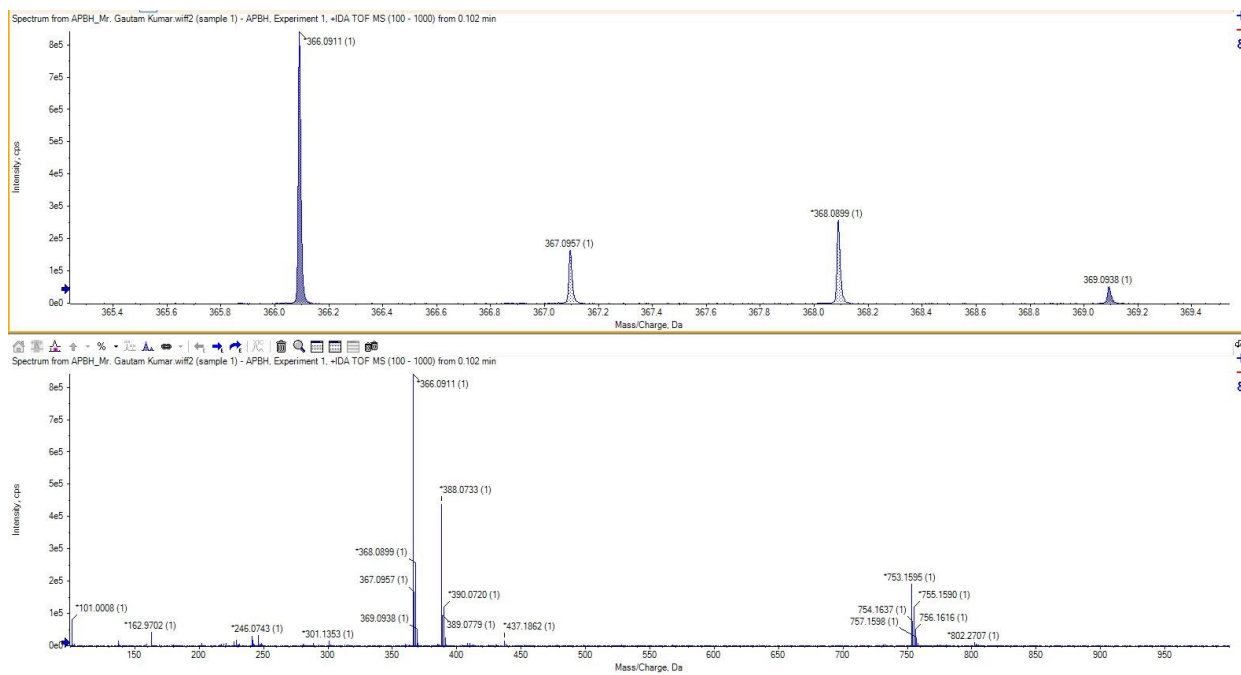


Fig. S4. HRMS spectrum of APH

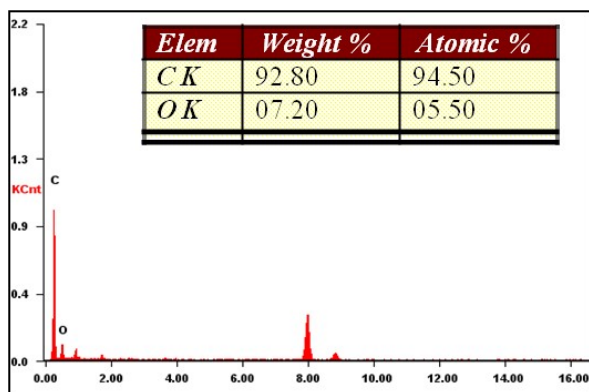


Fig. S5. EDX spectrum of GO

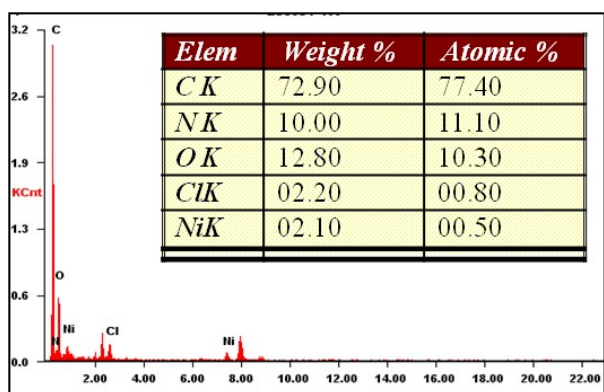


Fig. S6. EDX spectrum of GO-APH-Ni(II)

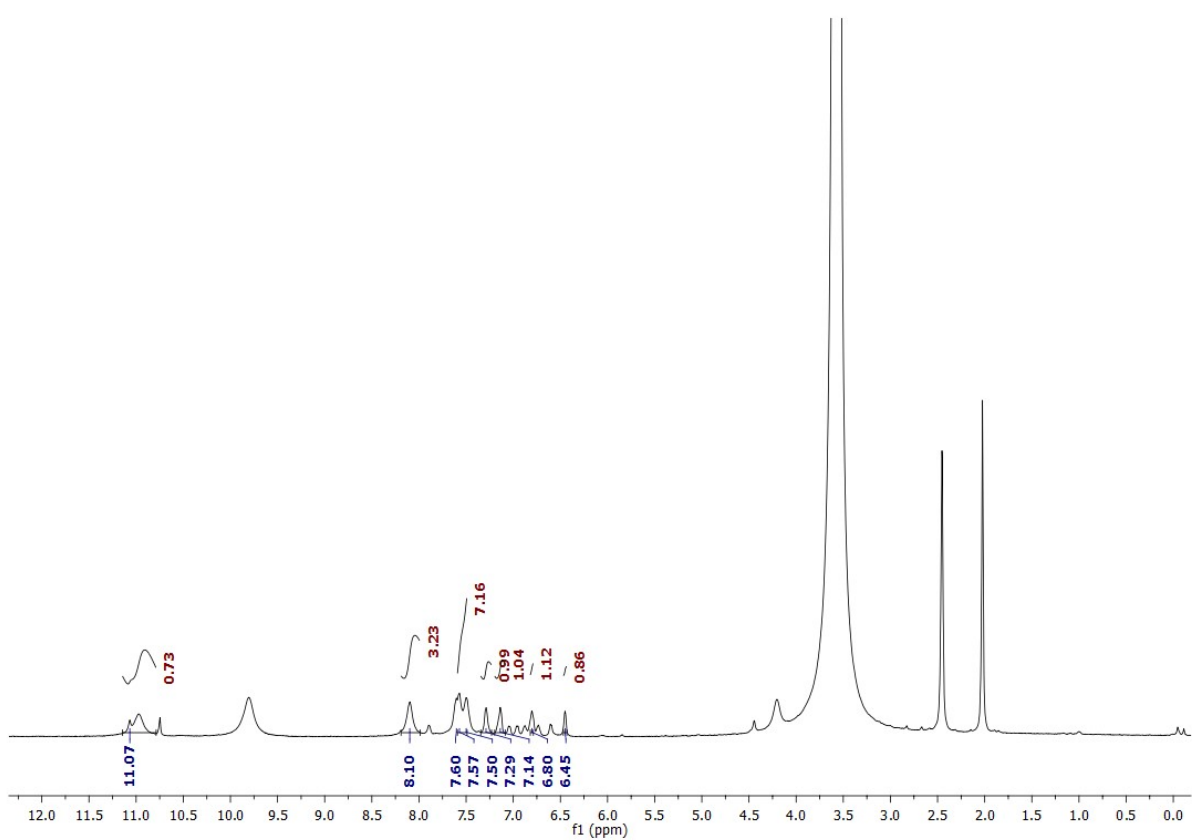


Fig. S7. ^1H NMR spectrum of APH-Ni(II)

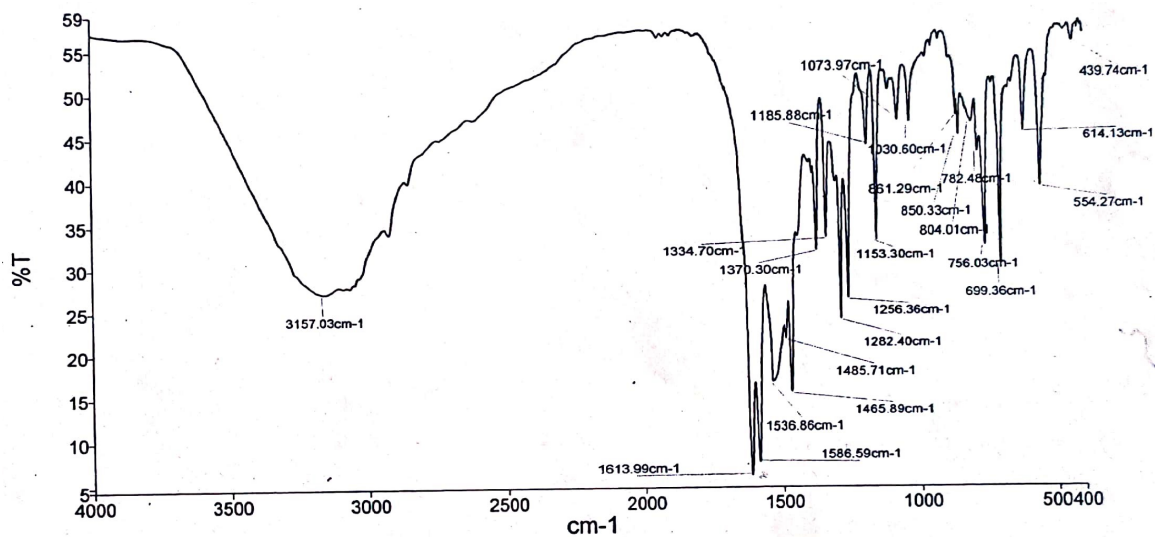


Fig. S8. FT-IR spectrum of APH-Ni(II)

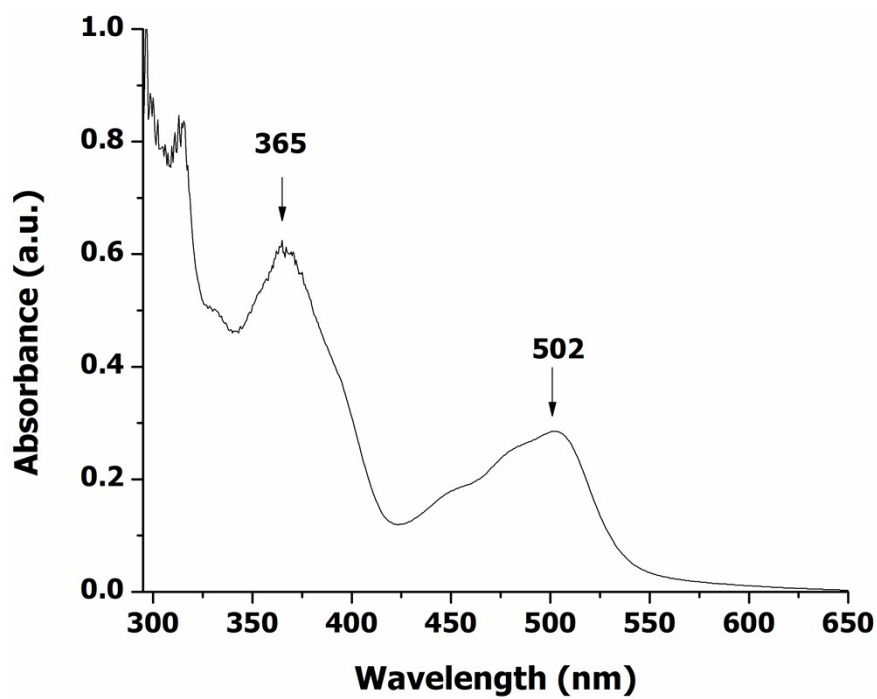


Fig. S9. UV-Vis spectrum of APH-Ni(II)

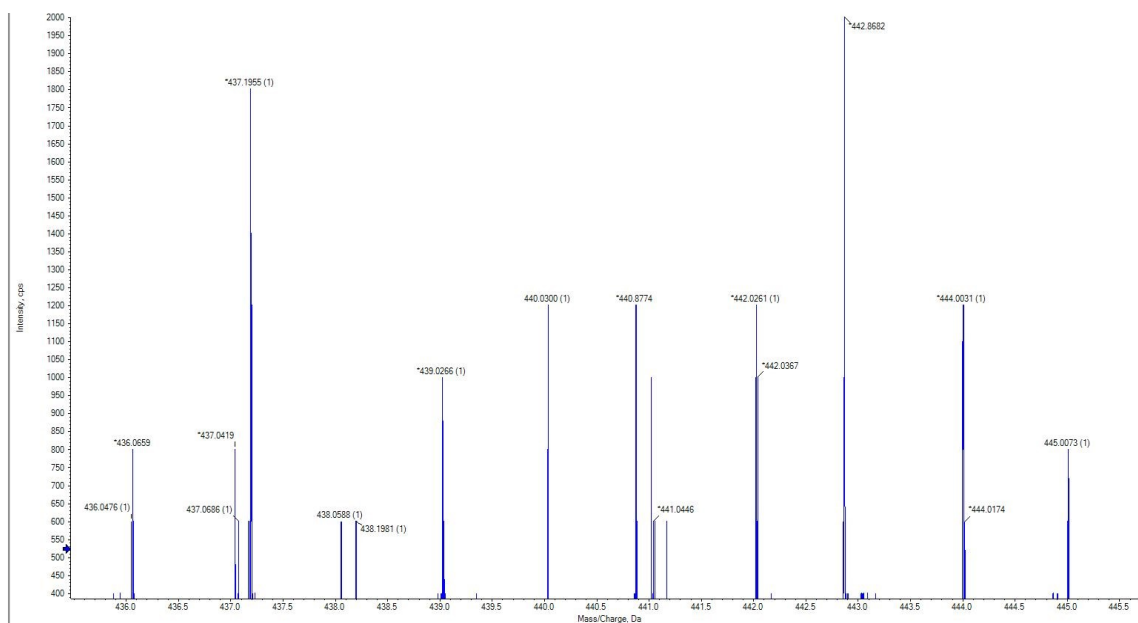


Fig. S10. HRMS spectrum of APH-Ni(II)

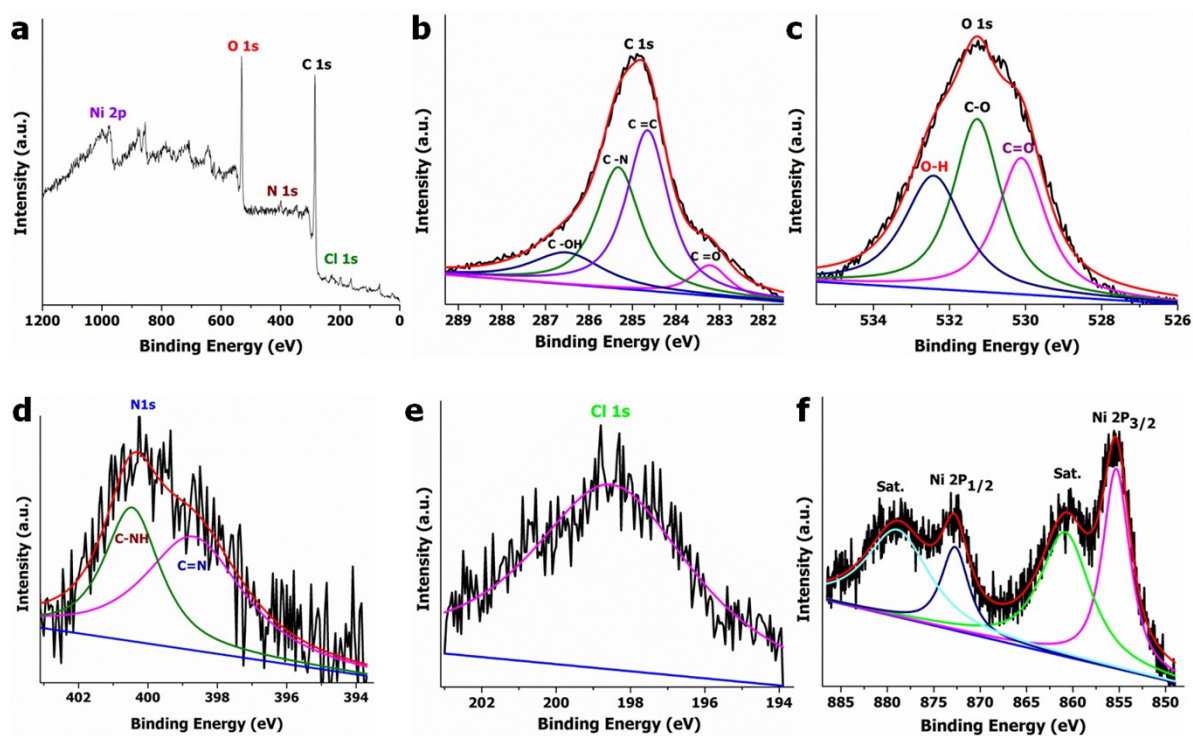


Fig. S11. XPS spectra of reused GO-APH-Ni(II) after sixth cycle.

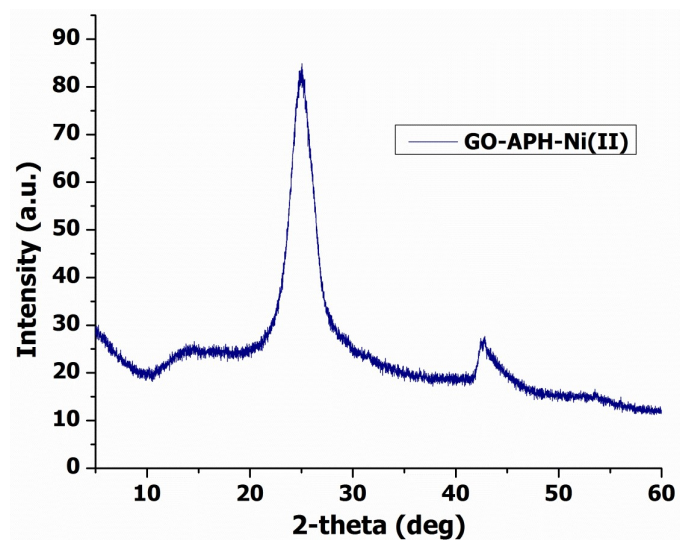


Fig. S12. Powder XRD spectrum of reused GO-APH-Ni(II) after sixth cycle.

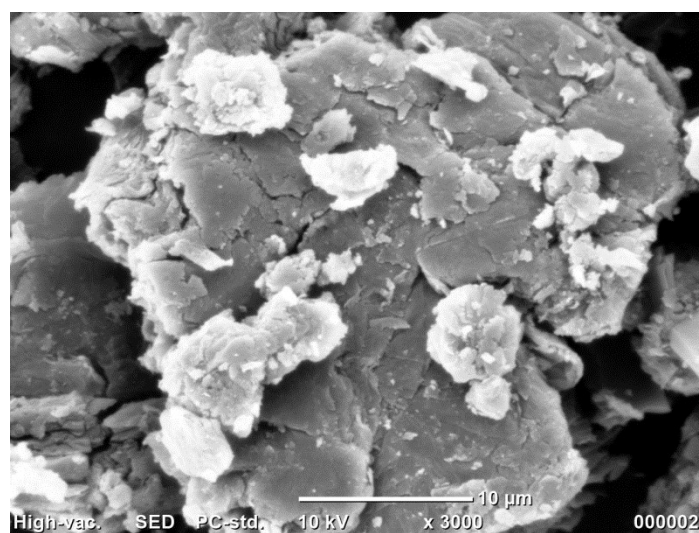
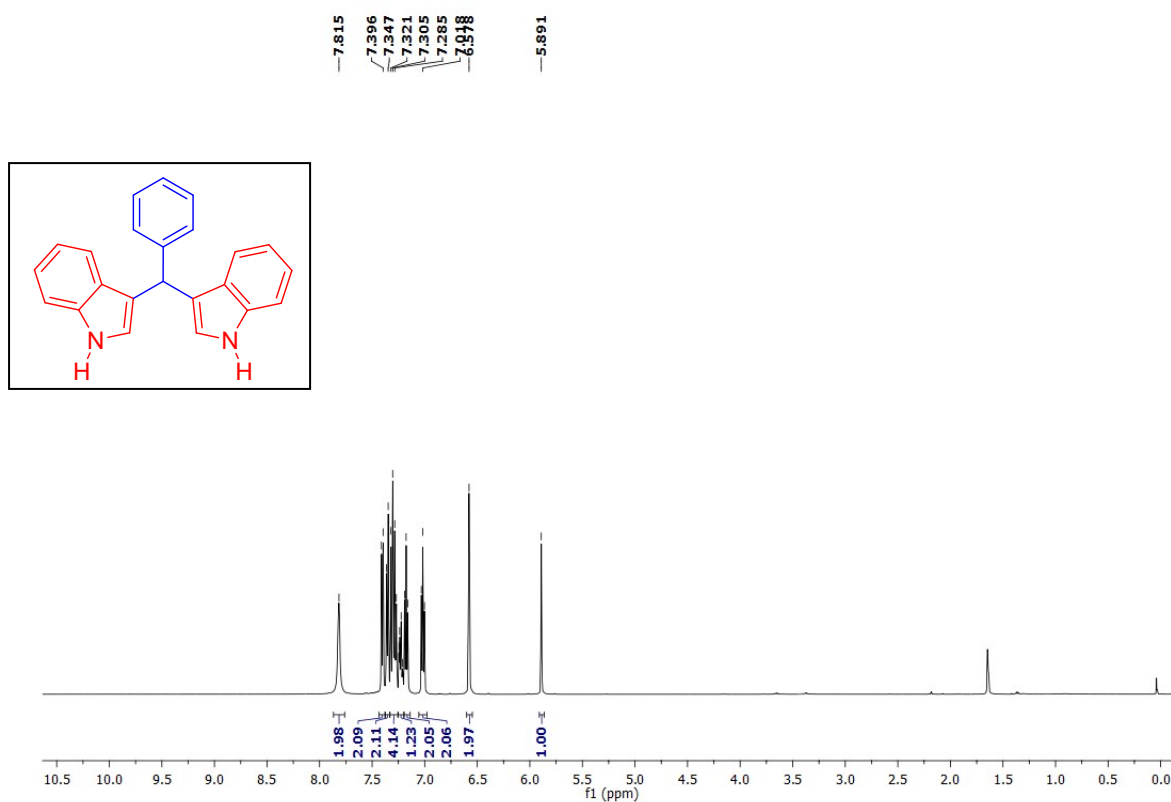
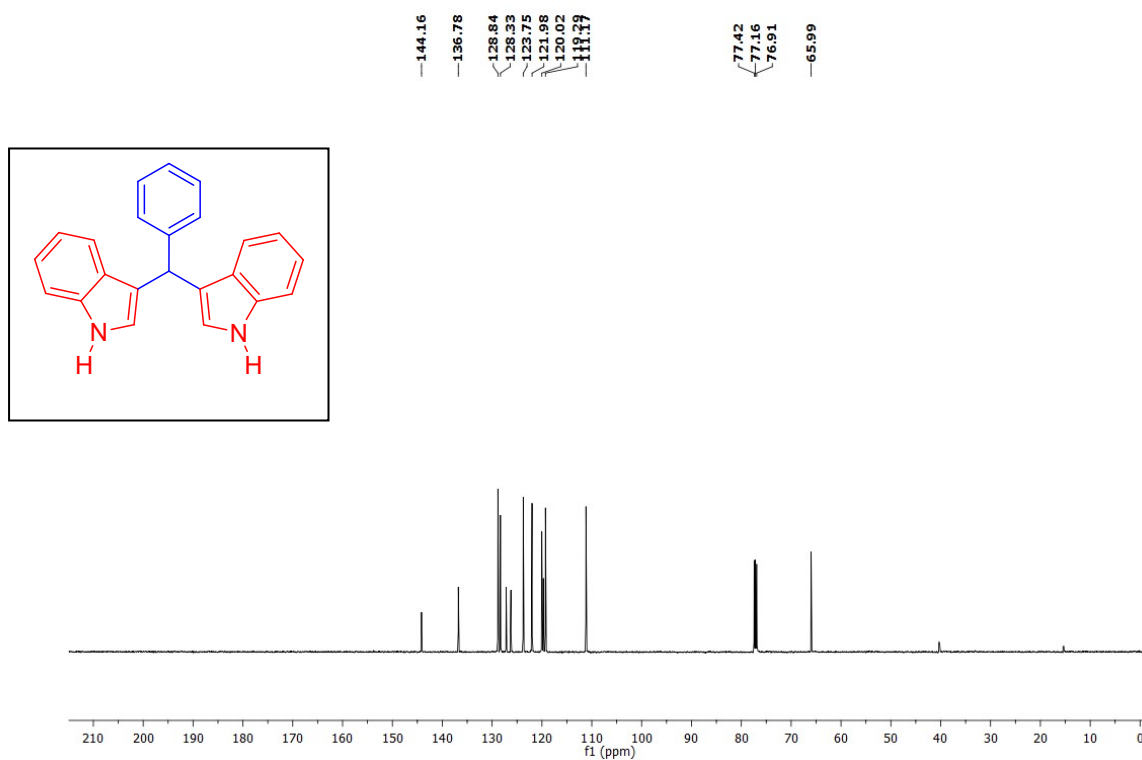


Fig. S13. SEM image of reused GO-APH-Ni(II) after sixth cycle.

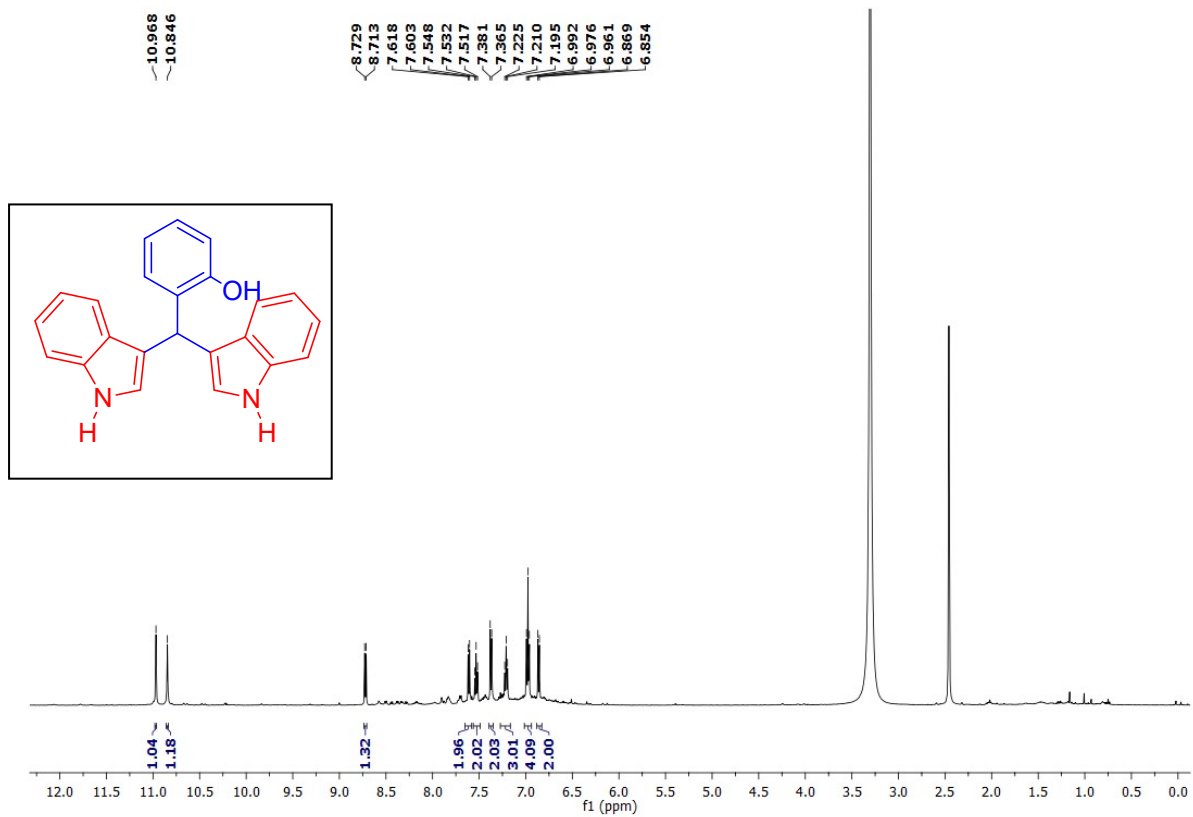
3. ^1H NMR and ^{13}C NMR spectra of bis(indolyl)methanes



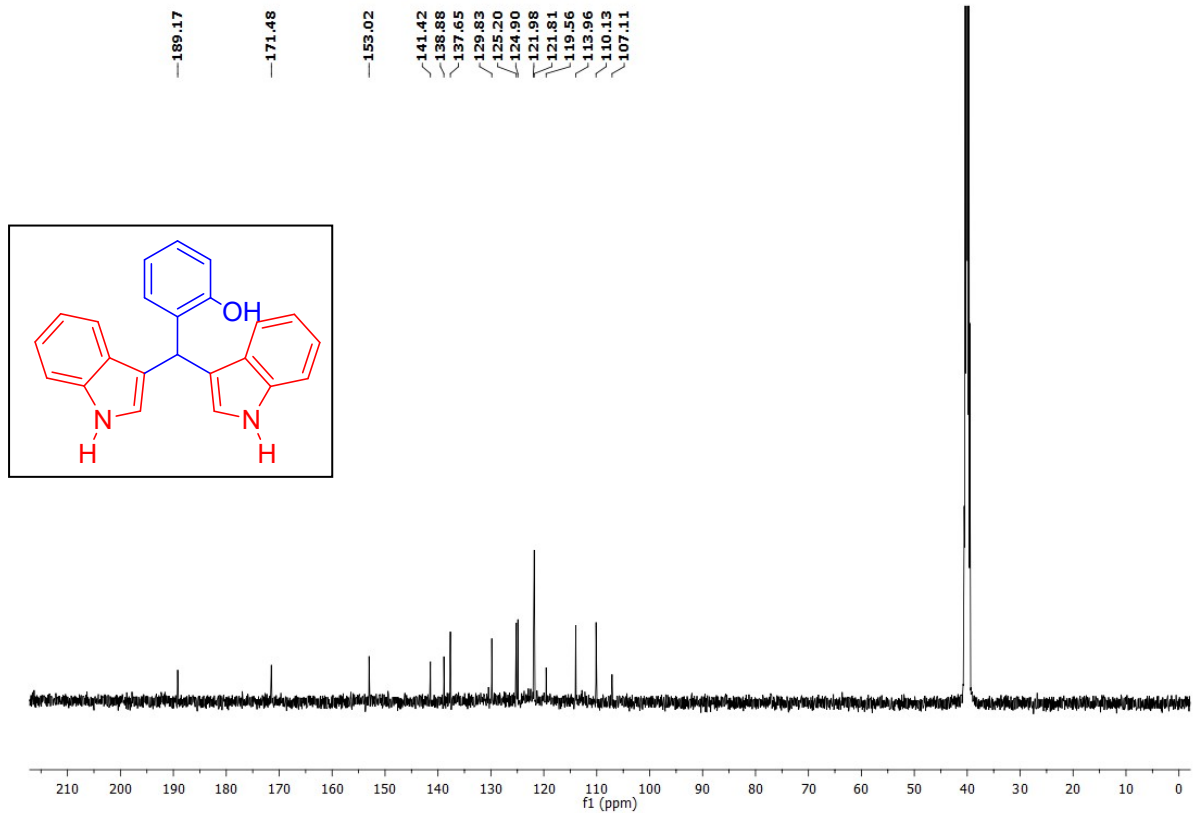
Spectrum 1. ^1H NMR of 3a



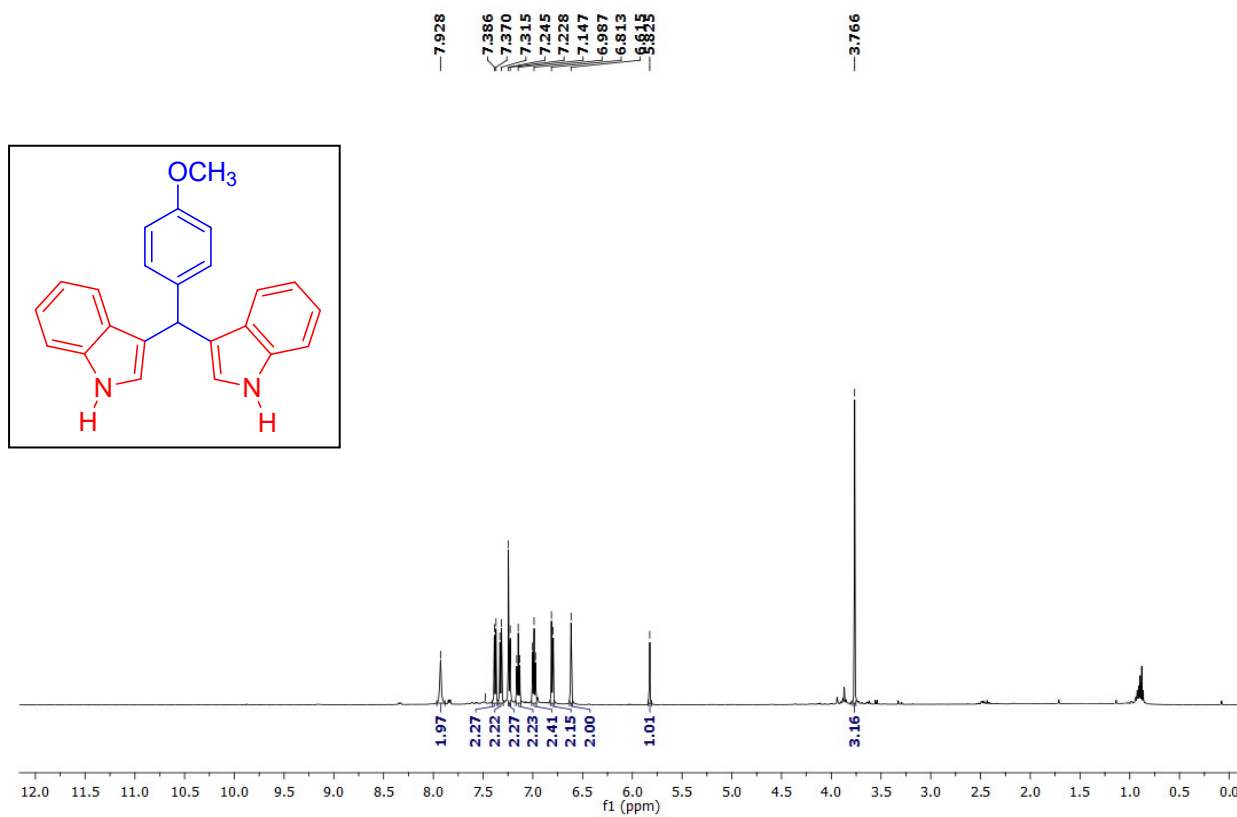
Spectrum 2. ^{13}C NMR of 3a



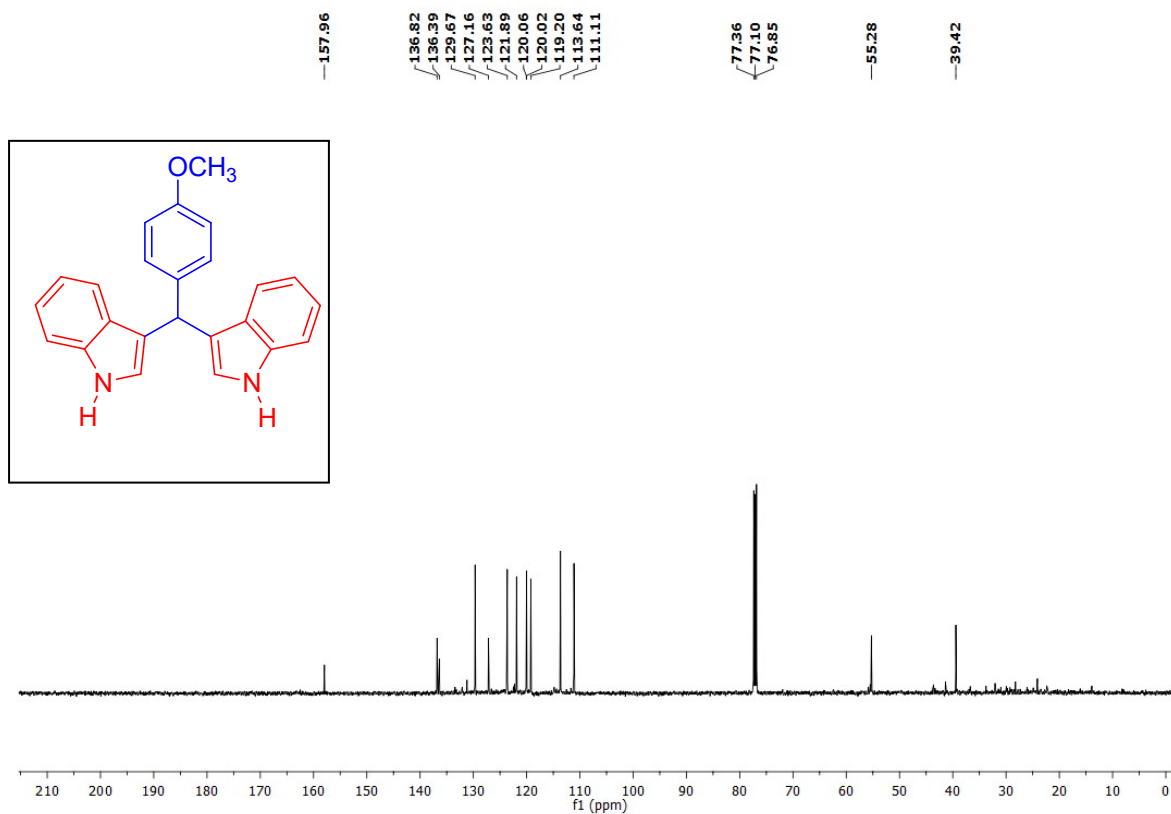
Spectrum 3. ¹H NMR of 3b



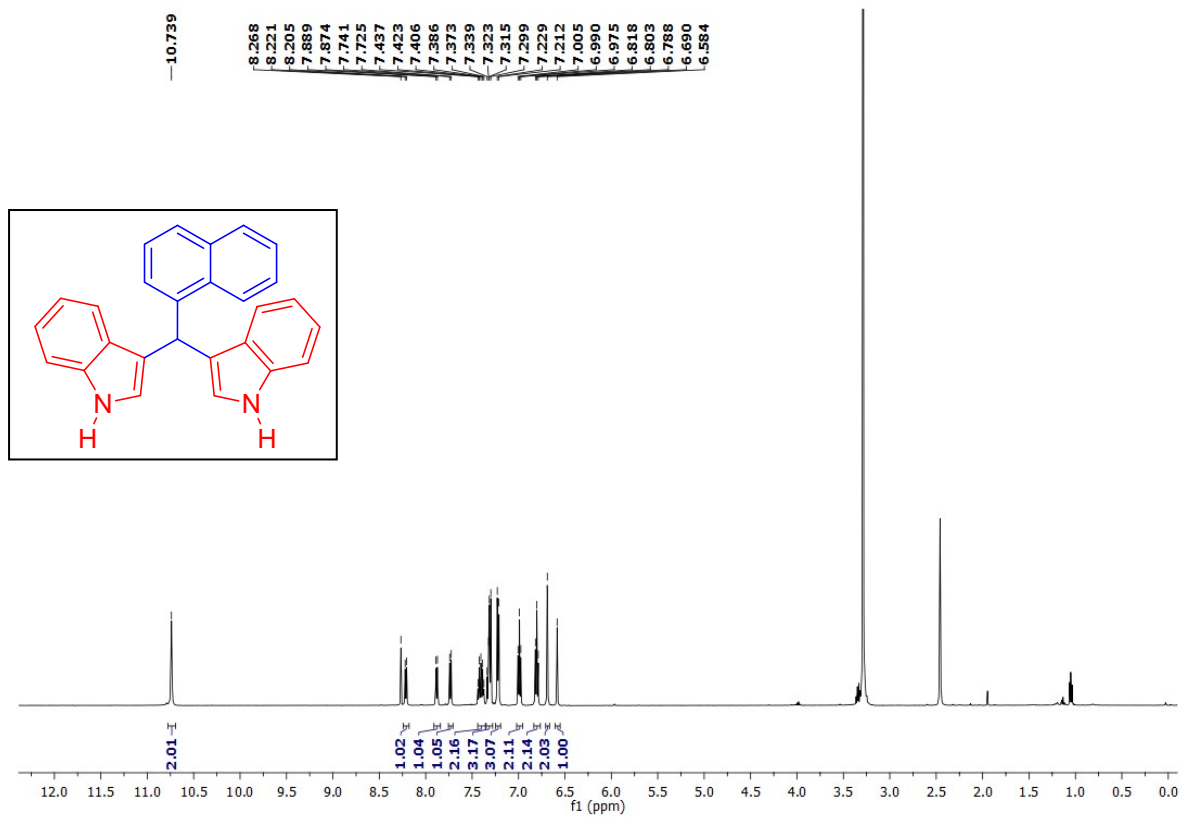
Spectrum 4. ¹³C NMR of 3b



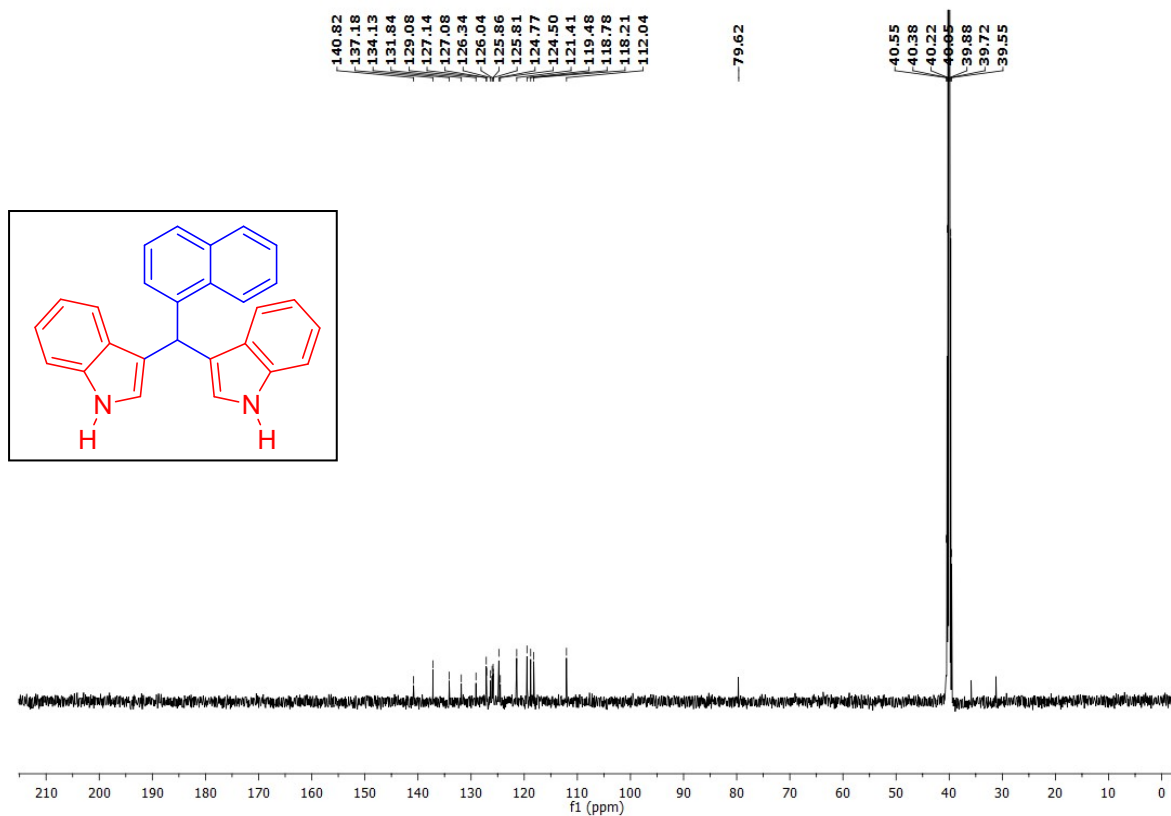
Spectrum 5. ¹H NMR of 3c



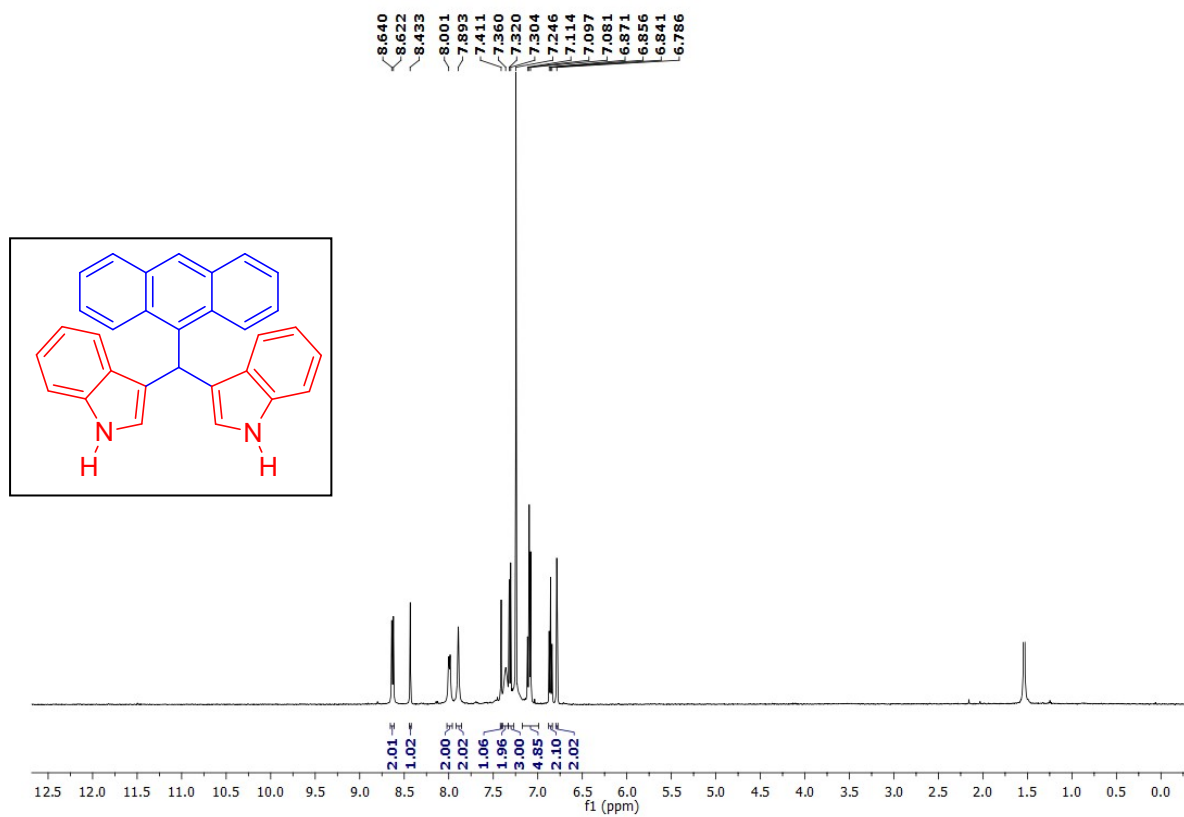
Spectrum 6. ¹³C NMR of 3c



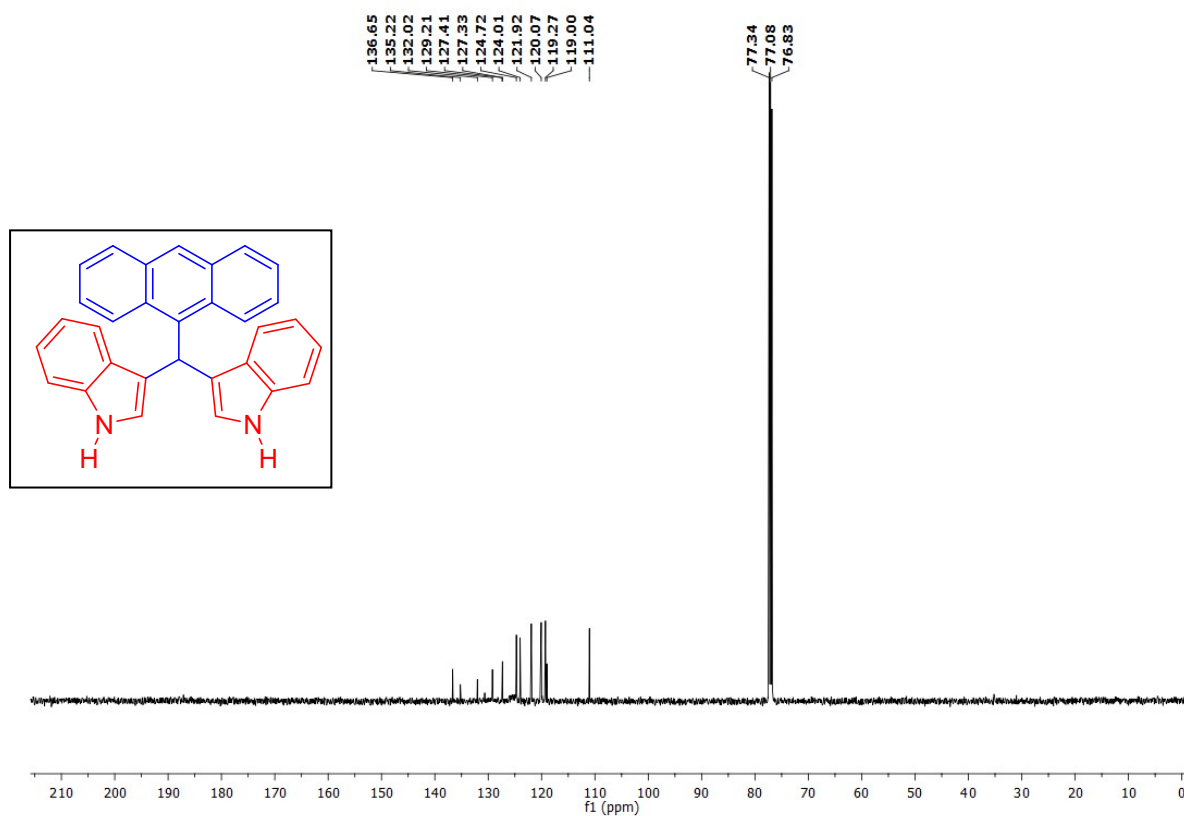
Spectrum 7. ^1H NMR of 3d



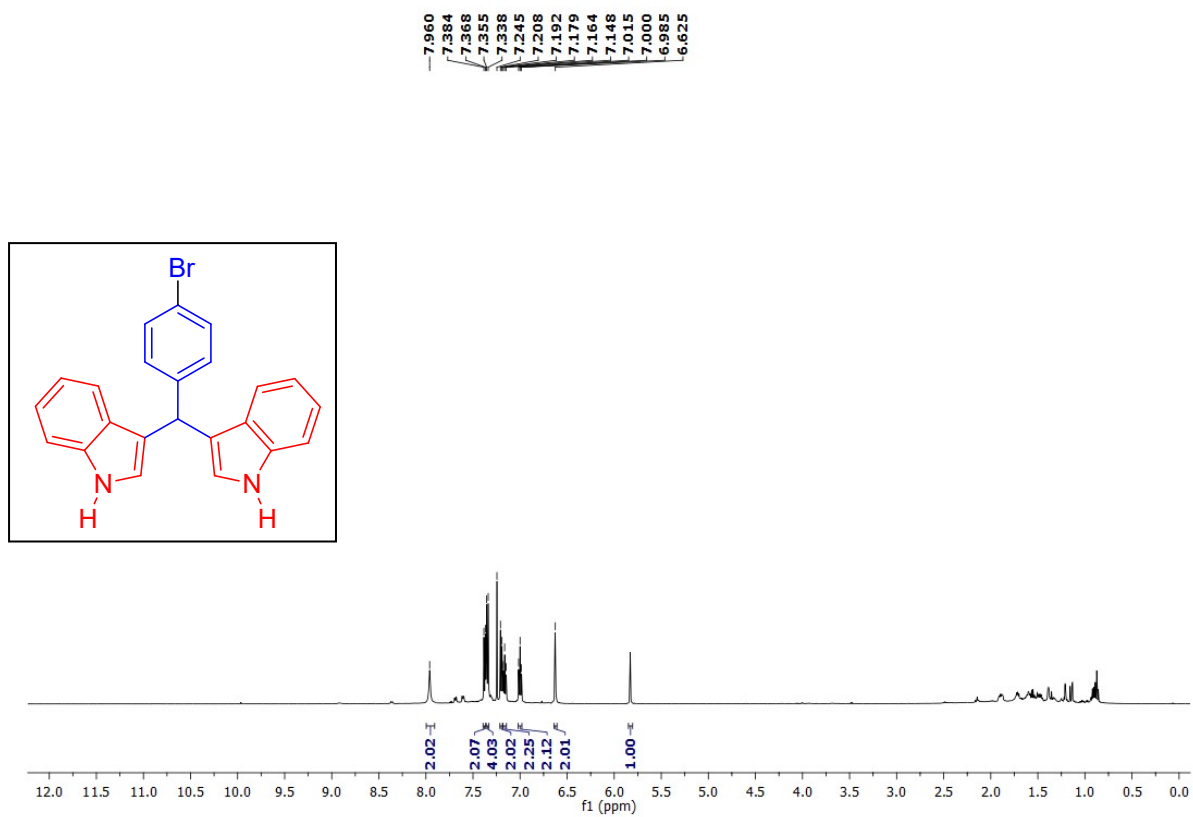
Spectrum 8. ^{13}C NMR of 3d



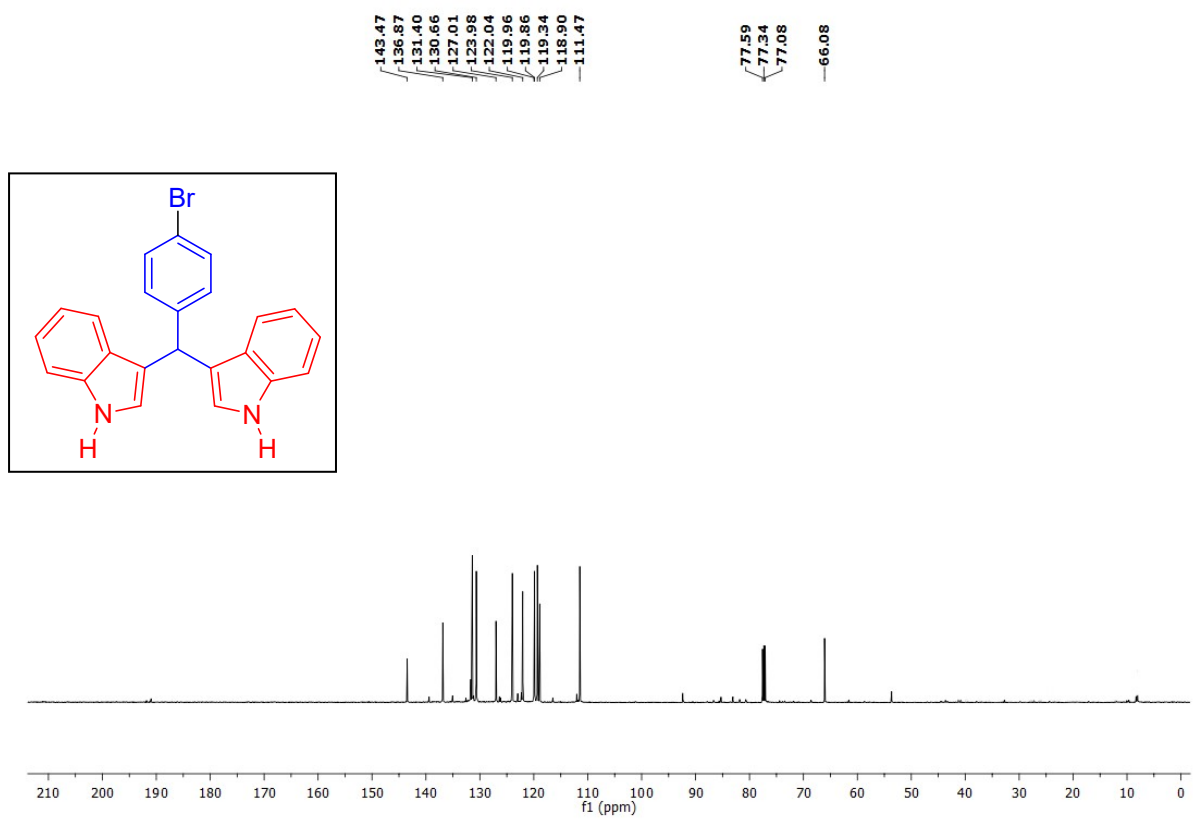
Spectrum 9. ¹H NMR of 3e



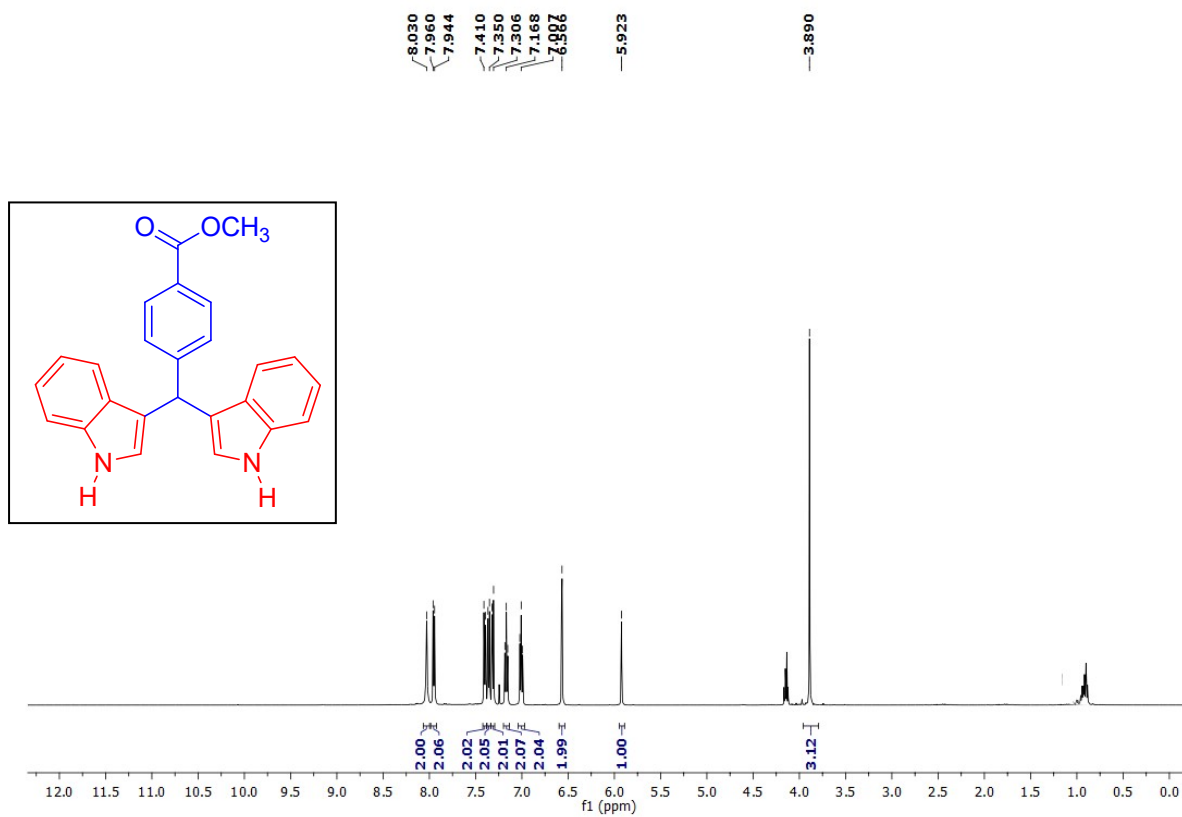
Spectrum 10. ¹³C NMR of 3e



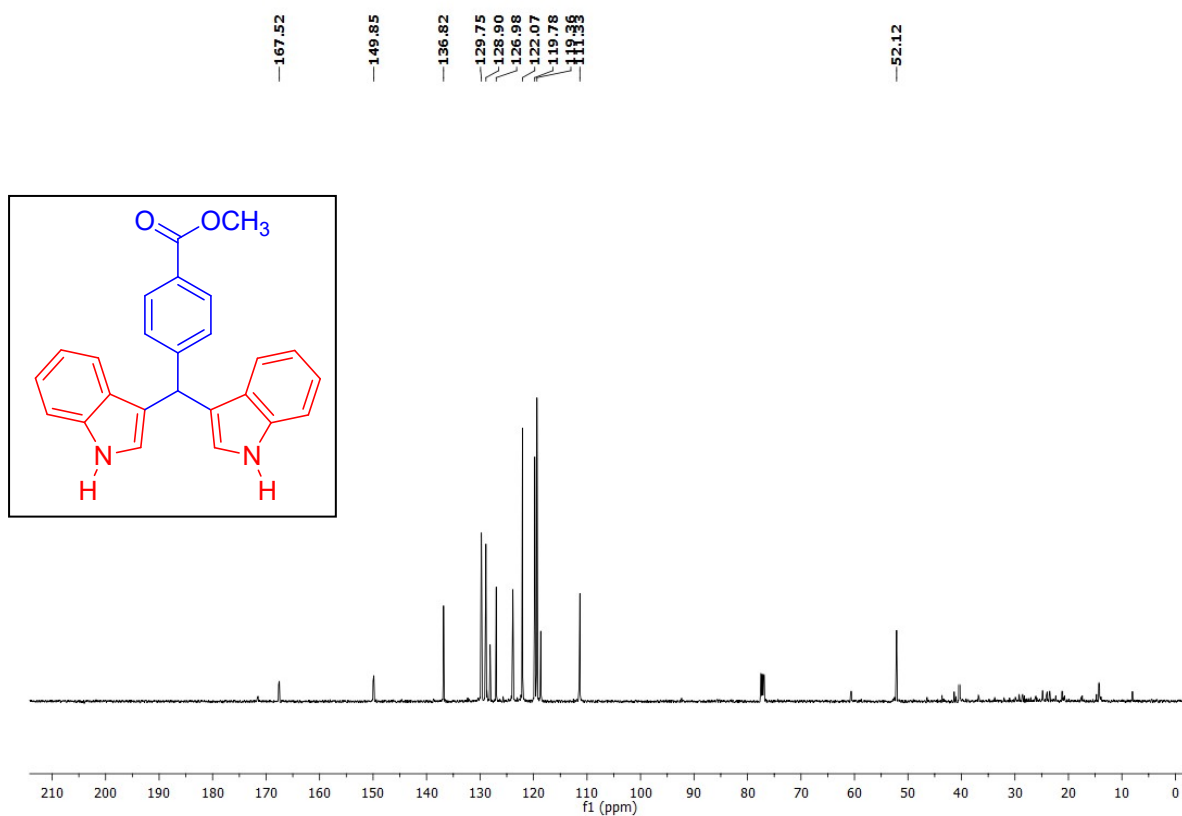
Spectrum 11. ¹H NMR of 3f



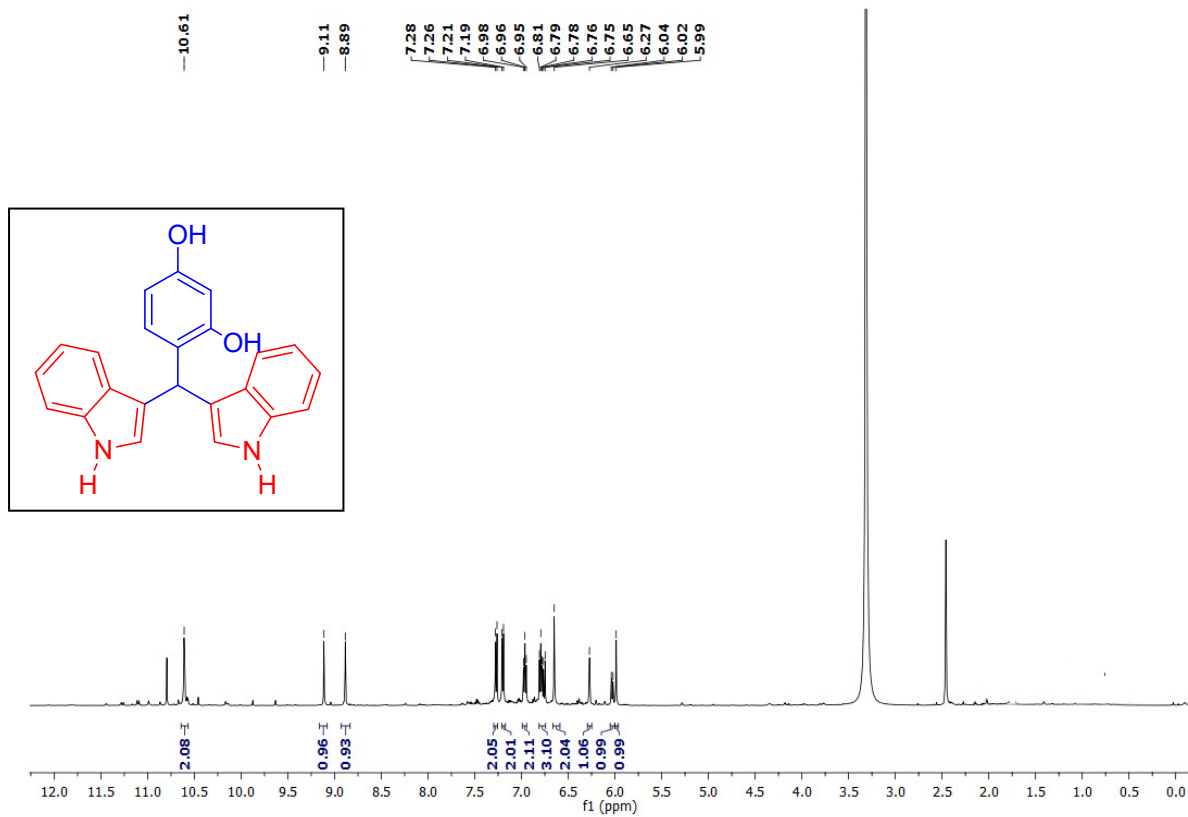
Spectrum 12. ¹³C NMR of 3f



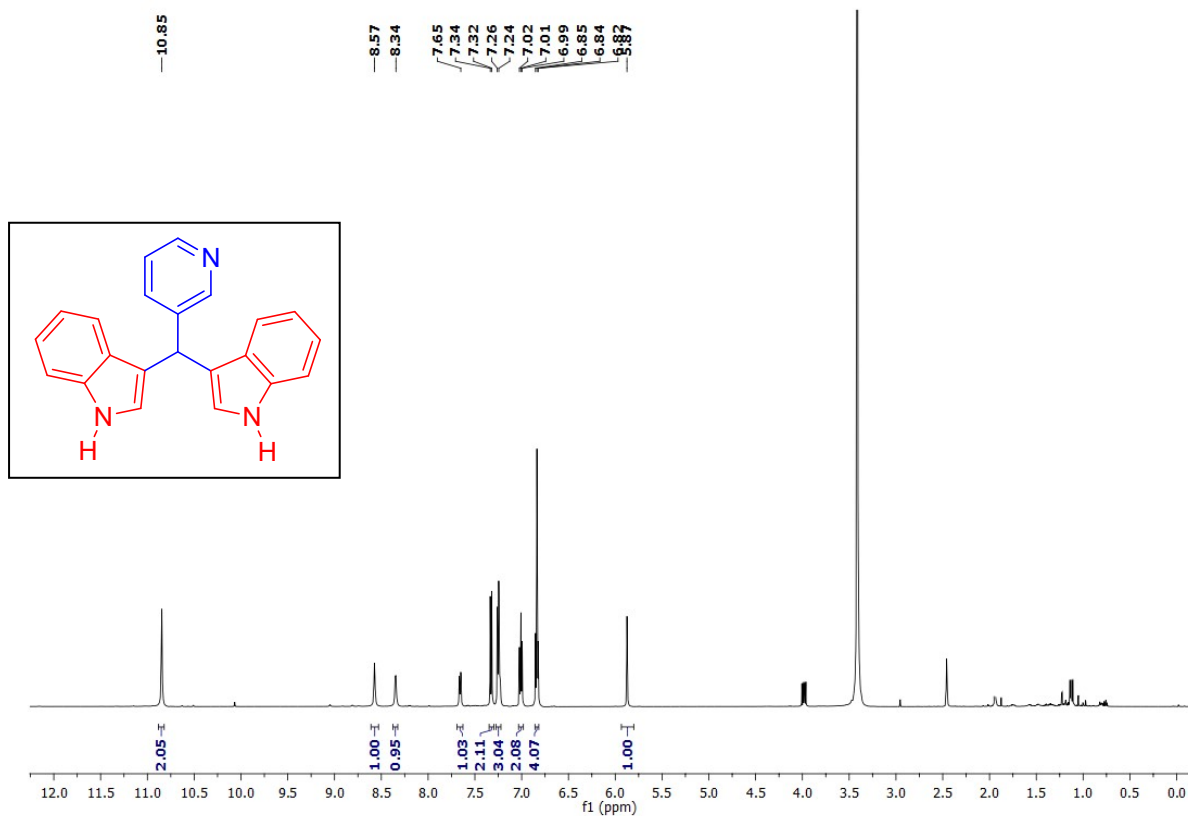
Spectrum 13. ¹H NMR of 3g



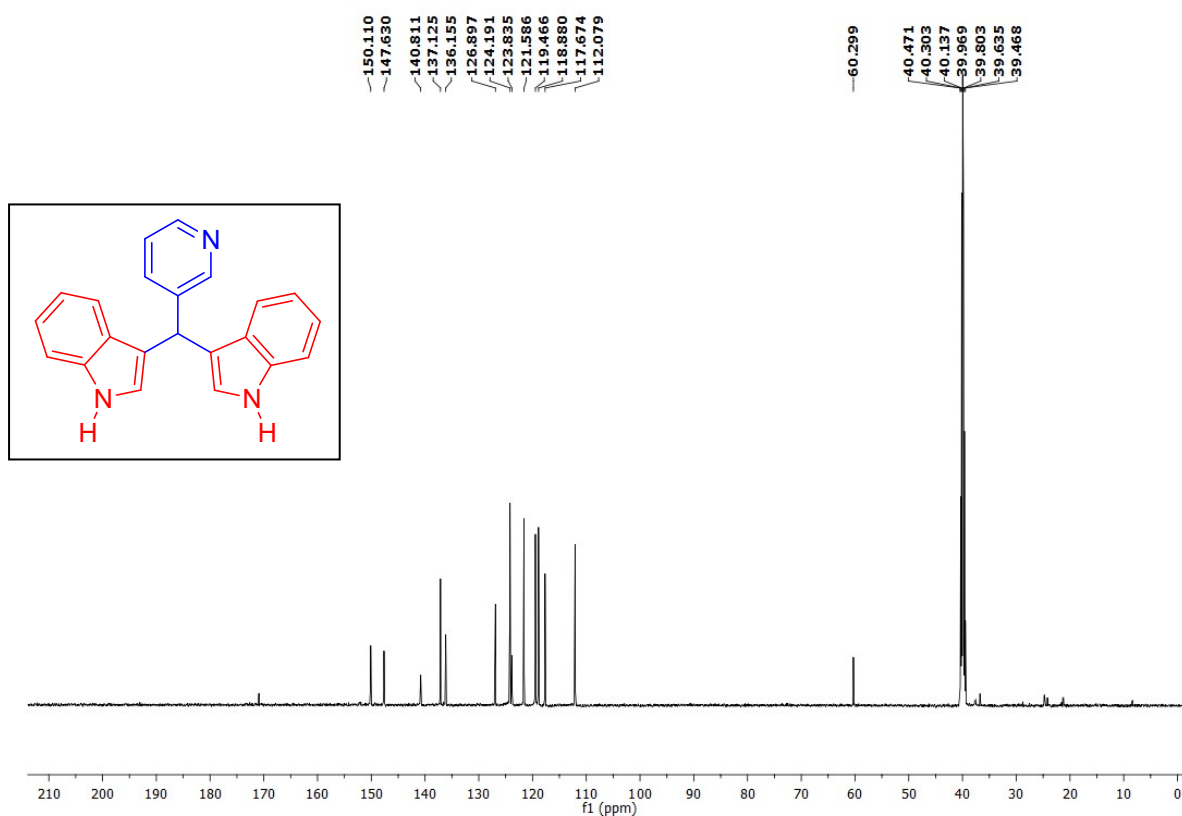
Spectrum 14. ¹³C NMR of 3g



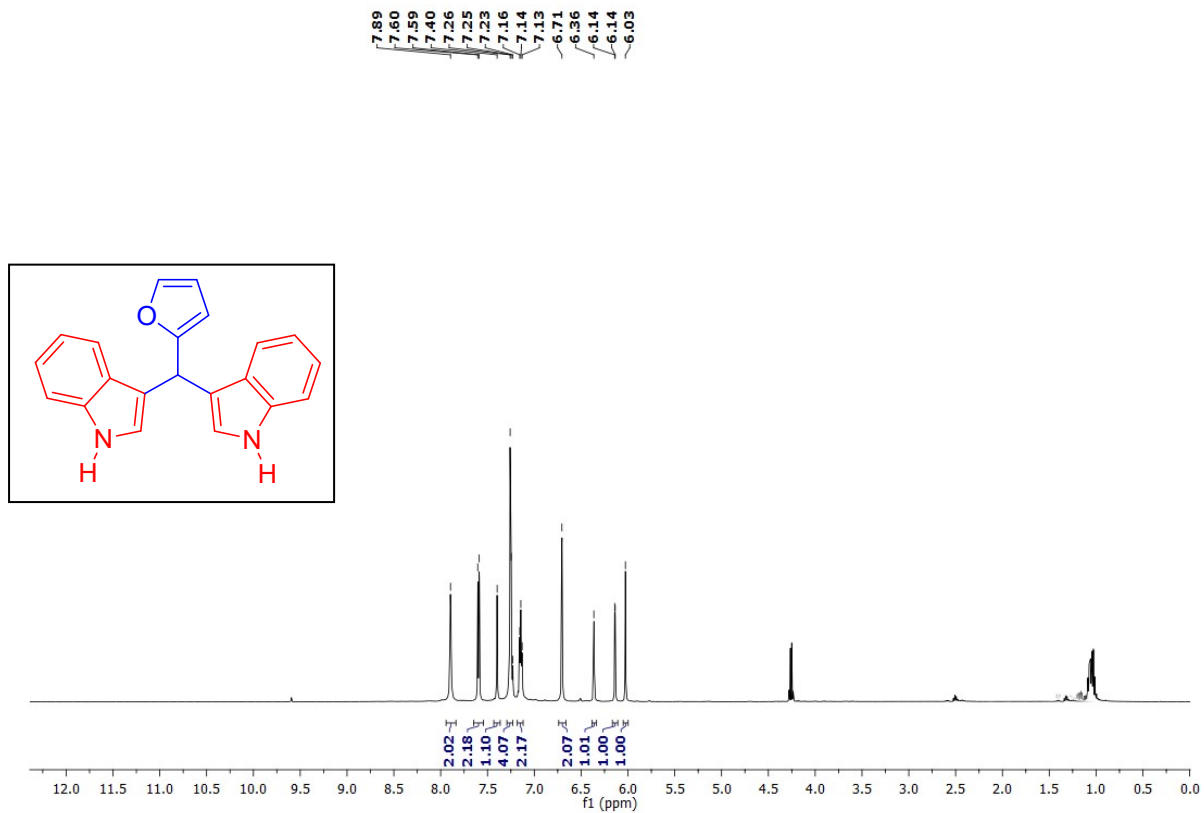
Spectrum 15. ¹H NMR of 3h



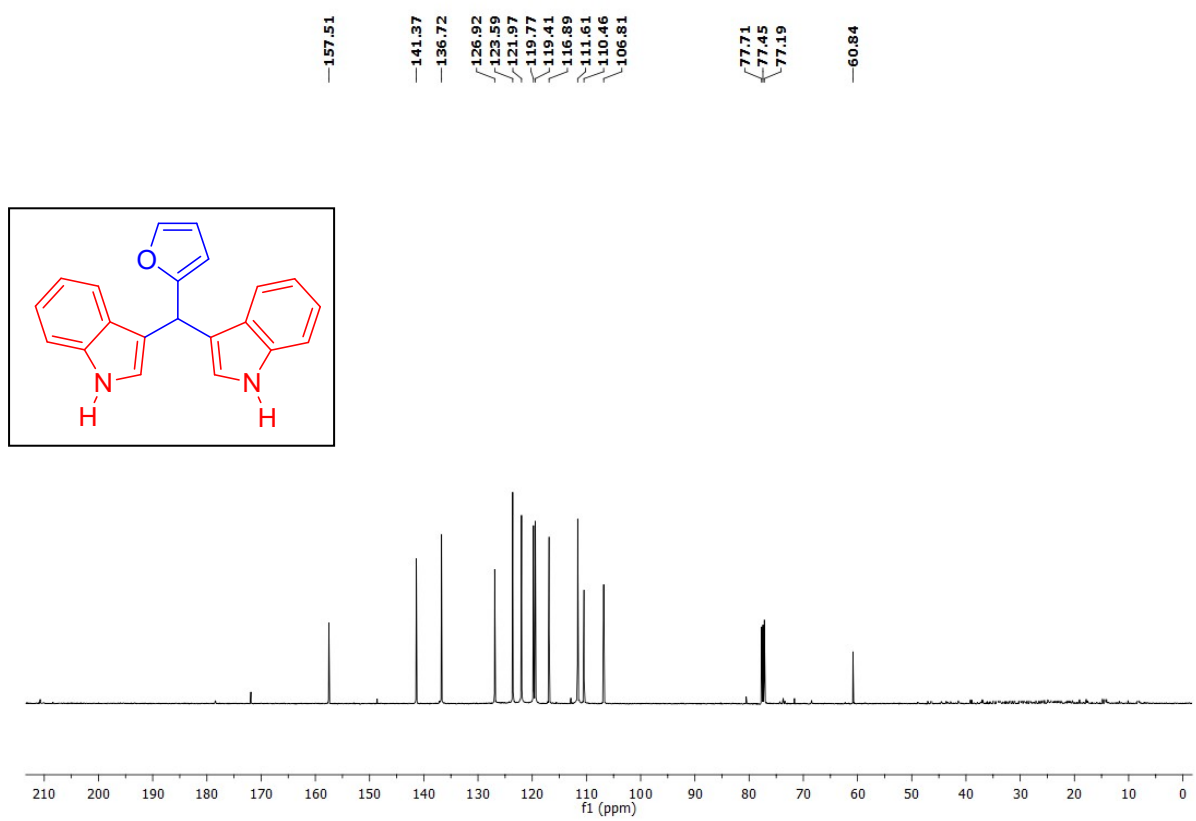
Spectrum 16. ¹H NMR of 3i



Spectrum 17. ^{13}C NMR of 3i



Spectrum 18. ^1H NMR of 3j



Spectrum 19. ^{13}C NMR of **3j**