

Synthesis of bis(indolyl)methanes under dry grinding conditions, promoted by a Lewis acid–surfactant–SiO₂-combined nanocatalyst

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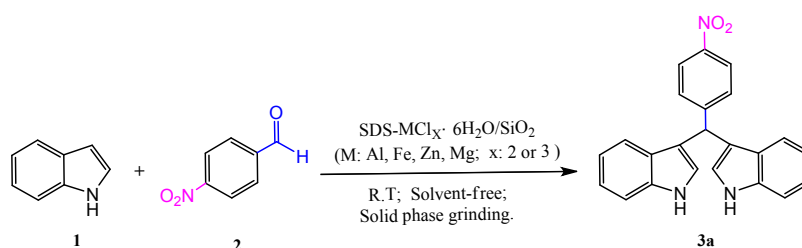
General Information	2
Experimental condition optimization	3
Experimental Procedure for Compounds 3a-3x	4
Experimental Procedure for Compounds 4a-4h and 5a	5
HRTEM, IR and TG analysis	6
The FT-IR of LASSC system	7
XRD Analysis	8
XPS Analysis and Table S1, Table S2 and Table S3	9
Experiment to obtain intermediates	11
The substrate scope of Table S4	13
The substrate scope of Table S5	14
LASSC catalytic synthesis of Schiff base	15
Characterization data for all products 3a-3v	16
Characterization data for all products 4a-4h and 5a	24
NMR spectra for all compounds 3a-3v	28
NMR spectra for all compounds 4a-4h and 5a	50
ESI-MS Organic Compounds	59
References	63

General Information

Melting points were measured with a melting point instrument and were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 400 (^1H , 400 MHz; ^{13}C , 100 MHz) instrument internally referenced to tetramethylsilane (TMS) or CDCl_3 signals. The NMR data were collected at ambient temperature and Chemical shifts are reported in parts per million (ppm) relative to the NMR solvent peaks. Data for ^1H -NMR are reported as follows: chemical shift, multiplicity (br: broad, s: singlet, d: doublet, t: triplet, m: multiplet), coupling constants, and integration. Infrared spectra were obtained with a PerkinElmer Spectrum Two. High-resolution mass-spectra (HRMS) were acquired on an Agilent 1290 Infinity separations module coupled to a 6230 time of flight (TOF) mass detector operating in ESI+ or ESI- mode. TLC was performed by using commercially prepared 200-400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. Processing of the NMR data was done using the standard Mestrenova 9.0.1 software. The powder X-ray diffraction (XRD) patterns were recorded by a Rigaku D/max-2500 X-ray diffractometer using Cu-K α radiation. Fourier transform infrared (FTIR) spectra were recorded in the range of 400-4000 cm^{-1} using a BOMEM DA-8 FT-IR spectrometer employing potassium bromide (film) pellets technique at room temperature. The morphology of the materials was obtained on JEOL JEM-2010F High Resolution Transmission Electron Microscope (HRTEM). The X-ray photoemission (XPS) spectra were performed at room temperature using a Thermo ESCALAB 250xi hemispherical electron energy analyser. Elemental analysis was conducted on a PerkinElmer 2400 elemental analyzer. Thermal gravimetric (TG) analysis was conducted on a TG-DSC instrument (TGA5500) under a N_2 atmosphere at a heating rate of 10 $^\circ\text{C}/\text{min}$ from 25 to 700 $^\circ\text{C}$. The ball mill model is YXQM-4L planetary ball mill (Changsha Miqi Instrument Equipment Co., Ltd., China). The were heated using a MM823LA6-NS for Microwave oven (China Midea Electric Company; Output power 540W).

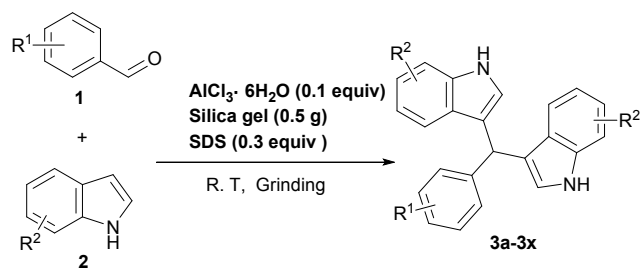
Materials: All reagents were used as received from commercial sources and all of the analytically pure. The benzaldehyde was re-distilled and purified.

Experimental condition optimization



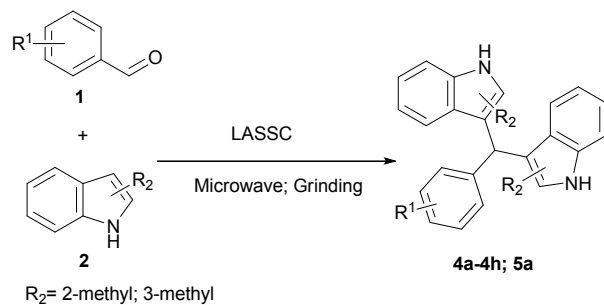
The mixture of indole **1** (2.0 mmol), 4-nitrobenzaldehyde **2** (1.0 mmol), sodium dodecyl sulfate (SDS: 0.3 mmol), Lewis acid metal salt (MCl_x·6H₂O: 0.1 mmol; M= Al, Fe, Zn, Mg; x:2 or 3) and column chromatography silica gel (0.5g; 300-400 mesh) in agate mortar was grinded at room temperature without solvent under air for 20-50 min. After the reaction is completed, the reaction mixture was dissolved in ethyl acetate (10mL) and filtered. The filtrate was concentrated, and the residue was purified with silica gel chromatography (Petroleum ether / EtOAc =3:1) to give product **3a**. The filtered solid mixture was dried for and then used for the next reaction.

Experimental Procedure for Compounds **3a-3x**.



The mixture of aromatic aldehyde **1** (1.0 mmol), indole compound **2** (2.0 mmol), SDS: 0.3 mmol, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$: 0.1 mmol and column chromatography silica gel 0.5 g (300-400 mesh) in agate mortar was grinded at room temperature without solvent under air for 10-45 min. After the reaction is completed, the reaction mixture was dissolved in ethyl acetate (10mL) and filtered. The filtrate was concentrated, and the residue was purified with silica gel chromatography (Petroleumether / EtOAc =2:1-5:1) to give product **3a-3x**.

Experimental Procedure for Compounds 4a-4h and 5a



The mixture of aromatic aldehyde or aromatic ketone **1** (1.0 mmol), 2-methylindole or 3-methylindole **2** (2.0 mmol), SDS: 0.3mmol, $AlCl_3 \cdot 6H_2O$:0.1 mmol and column chromatography silica gel 0.5 g (300-400 mesh) in agate mortar was grinded at room temperature without solvent under microwave for 3-10 min. After the reaction is completed, the reaction mixture was dissolved in ethyl acetate (10mL) and filtered. The filtrate was concentrated, and the residue was purified with silica gel chromatography (Petroleumether/EtOAc =1:1-3:1) to give product **4a-4h** and **5a**.

HRTEM , IR and TG analysis

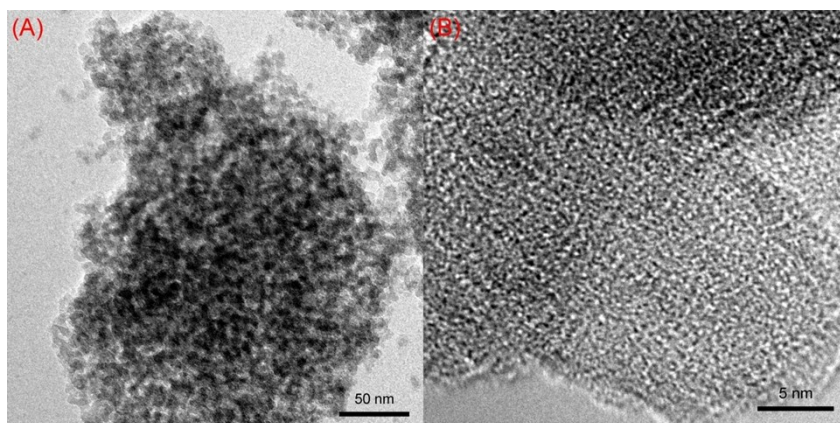


Fig. S1 The HRTEM after 10 cycles of LASSC catalyst recycling.

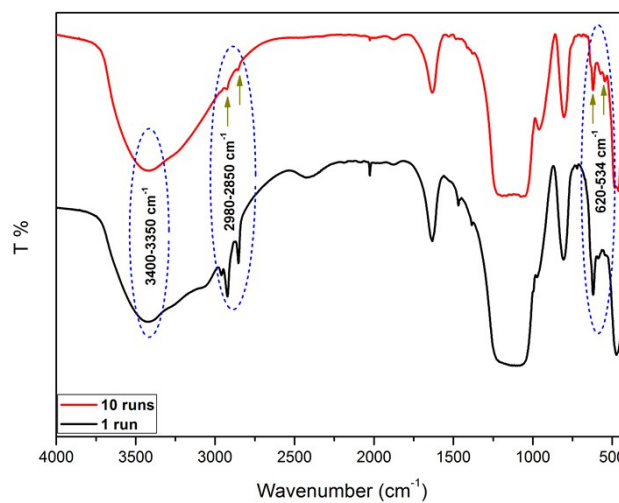


Fig. S2 The FT-IR for catalyst reuse.

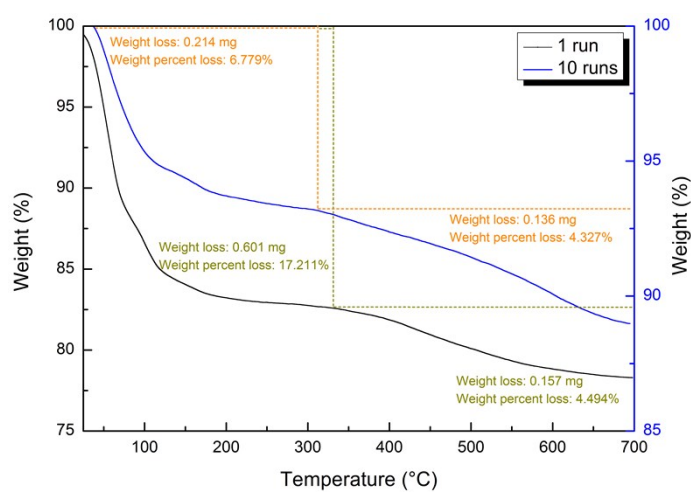


Fig. S3 TG curve after 1 and 10 cycles of LASSC catalyst (25-700°C)

The FT-IR LASSC system.

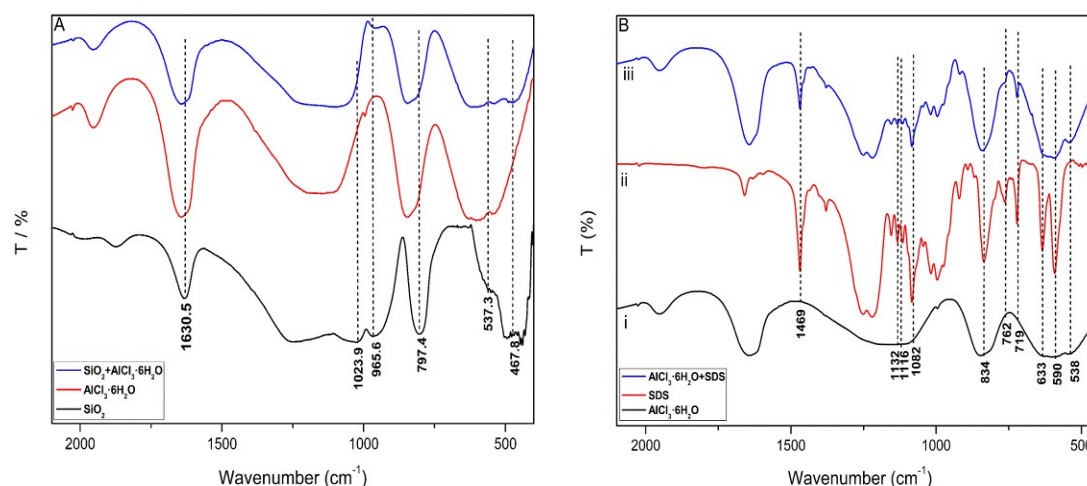


Fig. S4 FT-IR images of each component of LASSC catalytic system (A and B).

FT-IR characterization has proven to be a powerful technique for the study of components and structure of catalyst including organic segments. As seen from Fig. S4-A, it is that a large amount of inter-layer water molecules are present in the silica. 1630.5 cm^{-1} represents the H-O-H bending vibration absorption peak; 1023.9 cm^{-1} is the asymmetric stretching vibration absorption peak of the Si-O-Si bond; 965.6 cm^{-1} and 797.4 cm^{-1} correspond to the Si-OH stretching vibration peak and the Si-O characteristic peak, respectively.¹ The mixture of SiO_2 and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was solid phase milled, and the infrared spectrum showed a slight change. The apparent disappearance of the absorption peak at 1023.9 cm^{-1} and the decrease in the peak intensity at 965.6 cm^{-1} are attributed to the loss of the Si-O-Si group and the change of the Si-OH group. In addition, changes have occurred, representing Si-O-Al and Si-O characteristic peaks at 537.3 cm^{-1} and 467.8 cm^{-1} , respectively. The peak here is significantly enhanced after grinding, which also indicates that crystalline aluminum chloride and silica form a Si-O-Al functional group by hydroxyl dehydration. This has occurred to some extent by chemical bonding, with a large amount of hydroxyl groups on the surface.

The spectrum of SDS shows bands at 590 cm^{-1} , and 633 cm^{-1} corresponding to the bending vibration of SO_3^- , and peaks at 1082, 1116, and 1132 cm^{-1} ascribing to the stretching vibration of SO_3^- .² However, Fig. S4-B shows a weak characteristic peak at the position of 538 cm^{-1} , but no characteristic peak appears at 590 and 633 cm^{-1} , and other positions such as 1082, 1116, and 1132 cm^{-1} all exhibit characteristic peaks representing SO_3^- . The position and intensity of SO_3^- was found to be very sensitive to the changes of chemical environments caused by metal ions coordination. Comparing FT-IR spectra of SDS (Fig. S4-B-ii and S4-B-iii), we found that the bending and stretching vibration of SO_3^- degenerated obviously, and positions changed greatly. This is attributed to the coordination of the SDS in the catalyst system with the Al atoms in the crystalline aluminum chloride by hydrogen bonding.

XRD Analysis

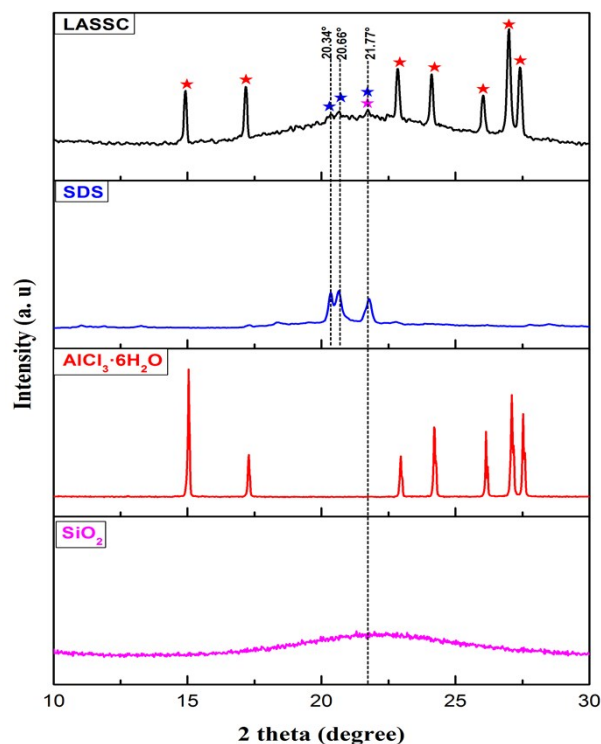


Fig. S5 The XRD analysis of LASSC catalytic system.

Fig. S5 is an XRD analysis of the components of the LASSC catalytic system. The strong reflections of SDS were observed at lower diffraction angles at $2\theta = 20.34^\circ$, 20.66° and 21.77° , corresponding to 0.436nm, 0.429nm and 0.408nm calculated by Bragg's law, respectively. By comparison, it was found that the peak intensity of SiO_2 was at 22.76° , which almost coincided with 21.77° of SDS. It is worth noting that the intensity of the diffraction peaks disappeared significantly at 20.34 and 20.66 in the LASSC system. Due to the interaction of SDS with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in the LASSC system, the hydration state of the SDS is increased, resulting in a decrease in the layer spacing of the catalyst network. It has been generally known that crystalline phases of SDS all have similar bilayer structures, in which the dodecylsulfate molecules are stacked in a head to head, tail to tail mode, alternating alkyl chains and sulfate head-group.³ Also, in view of the layered structure of the SDS, the LASSC catalyst composition exhibits lattice fringes and spacing on the nanometer scale. By calculating its lattice spacing to be 0.211 nm, it is approximately equal to the monolayer structure of SDS. The mass ratio of SDS, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and SiO_2 in the LASSC system is about 3:1:25. Such a small amount but very excellent catalytic performance, thanks to the nanostructure and catalytic properties of LASSC. The excellent catalytic properties are also manifested in the multiple cycle life of the catalyst.

XPS Analysis

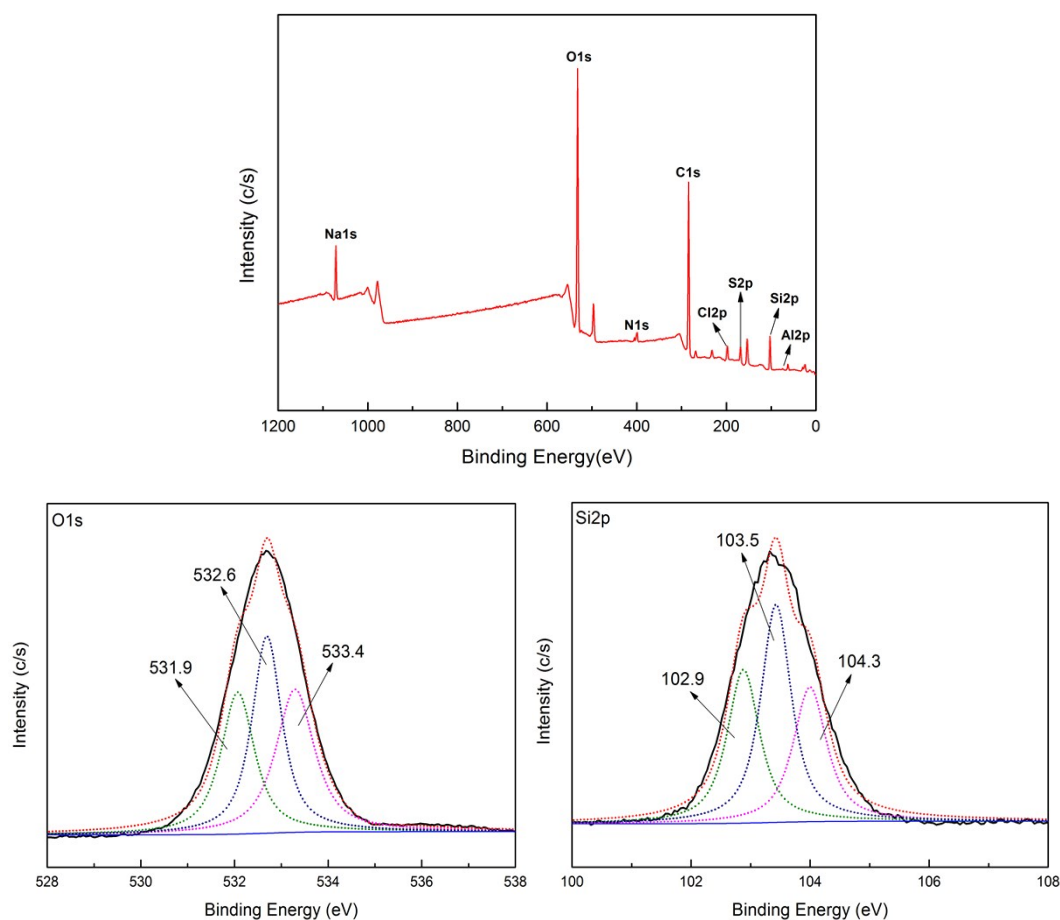


Fig. S6 XPS spectra of LASSC (including Si and O).

The O1s spectra measured consist of peaks at 531.9 eV, 532.6 eV and 533.4 eV, corresponding to O1s in sulfate, -O-H and SiO₂, respectively. These results indicate that the nanomaterial has SiO₂ as a carrier and an organic sulfonate SDS supported on its surface. The peak of Si2p is at 103.5 eV, which is in agreement with Si2p in SiO₂ (103.6 eV).⁴⁻⁵ In XPS spectrum of LASSC, two peaks of Si2p appear at 102.9 eV and 104.3 eV, respectively. As hydroxyl is electron withdrawing group, the binding energy of Si2p in -Si-OH on the particle surface shifts to 104.3 eV. The higher intensity Si2p peak at 102.9 eV is attributed to the interaction of the hydroxyl group on the surface of SiO₂ with AlCl₃·6H₂O, where the group Si-O-Al is a strong donor group, so the binding energy is lower than that of pure SiO₂ (103.5 eV). As the amount of -OH is greatly reduced after the reaction of -Si-OH with -Al-OH, the peak of -Si-OH becomes weak. The peak appearing at 104.3 eV of lower binding energy is considered to be an overlap of the Si2p peak (103.5 eV) of SiO₂ and the residual -Si-OH (104.3 eV). The peak areas of the two are nearly equal, indicating that AlCl₃·6H₂O is uniformly dispersed on the surface of SiO₂. And using SiO₂ as a carrier, SDS and AlCl₃·6H₂O are tightly fixed on their surface. It can be concluded that the SDS and AlCl₃·6H₂O is interacted to SiO₂ surface

via chemical bond. According to the results of IR and XPS, we can further affirm that the SDS and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is bonded to the surface of SiO_2 .

Table S1 The conventional LASCs catalyst preparation of each component.

LASCs	Dosage of each component	LASSC (This work)
$^7\text{Sc}(\text{DS})_3$	SDS(11.6mmol)+Water(50mL) $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$ (3.85mmol)+Water(50mL) Water for washing (250mL).	SDS (0.3mmol; 87 mg); $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (0.1mmol; 24 mg); SiO_2 (50 mg); Solvent free; Cycle more than 10 times.
$^8\text{Ce}(\text{DS})_3$	SDS(11.6mmol)+Water(50mL) $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (3.85mmol)+Water(50mL) Water for washing (250mL)	
$^9\text{Fe}(\text{DS})_3$	SDS(11.6mmol)+Water(80mL) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.85mmol)+Water(20mL) Water for washing (250mL)	

Table S2 Catalysis of different Lewis acids in aqueous phase.

Entry ^a	Lewis acid	Surfactant	Solvent	Time (min)	Yield (%) ^b
1	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	SDS	H_2O	20	93.5
2	$\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$	SDS	H_2O	180	Trace
3	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	SDS	H_2O	180	No reaction
¹⁰ 4	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	SDS	H_2O	15	90

^aReaction condition: Lewis acid (0.1mmol); Surfactant (0.3mmol); H_2O (3mL); LAS: Linear alkylbenzene sulfonates; TLC tracking (n-hexane: acetone =3:1); ^bIsolated yields.

Table S3 Elemental analysis of fresh catalyst and catalyst after recycling of LASSC catalyst system.

Catalyst	C content (%)	H content (%)	S content (%)	Other content (%)
1 run	1.612	2.593	1.727	94.068
10 runs	1.597	2.583	1.283	94.537

Experiment to obtain intermediates

The mixture of 4-nitrobenzaldehyde **1** (1.0 mmol), indole **2** (2.0 mmol), and column chromatography silica gel 0.5 g (300-400 mesh) in agate mortar was grinded at room temperature without solvent under air for 35-50 min. After the reaction is completed, the reaction mixture was dissolved in ethyl acetate (10mL) and filtered. The filtrate was concentrated, and the residue was purified with silica gel chromatography (Petroleumether / EtOAc =3:1) to give product **3b** and reaction intermediate (Marked as **A**).

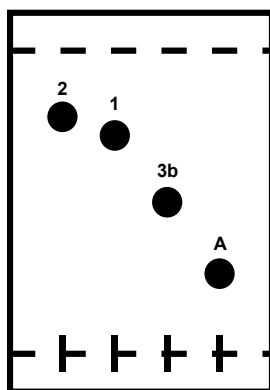


Fig. S7 The thin layer chromatography plate for intermediates.

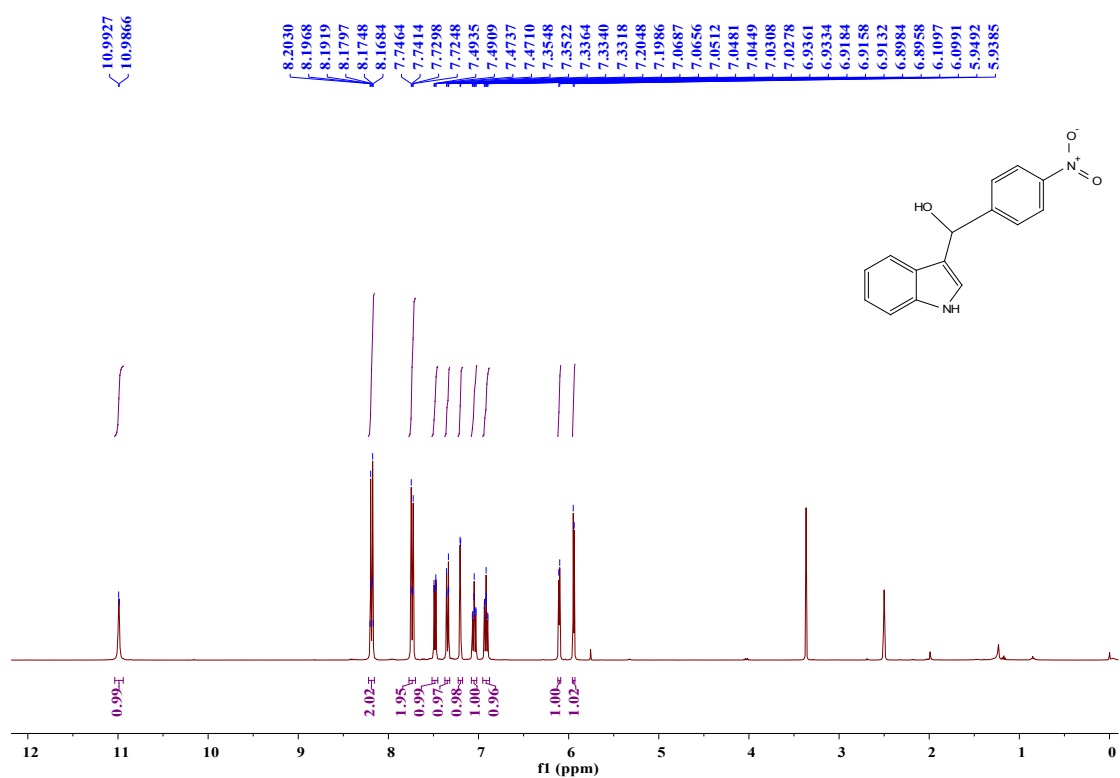
(**1**: 4-nitrobenzaldehyde; **2**: Indole; **3b**: Target product; **A**: Intermediate product)

Fig. S7 is a thin layer chromatography plate for obtaining an intermediate experiment. After the reaction reached equilibrium, the reaction materials **1** and **2** did not completely react. However, we obtained both the target product **3b** and the intermediate **A**. By the purification treatment, the target product **3b** was obtained in a yield of 11 %; at the same time, a stable pale yellow reaction intermediate **A** was obtained in a yield of 10 %. The structure was further confirmed by NMR and FT-IR. This is the first time to obtain the target product and intermediate in the "one-pot" reaction by delaying the reaction time and rate, which provides favorable evidence for the reaction catalytic mechanism. It has been proved by experiments that the intermediate we obtained is a tertiary alcohol structure. This is consistent with the literature synthesis.⁶

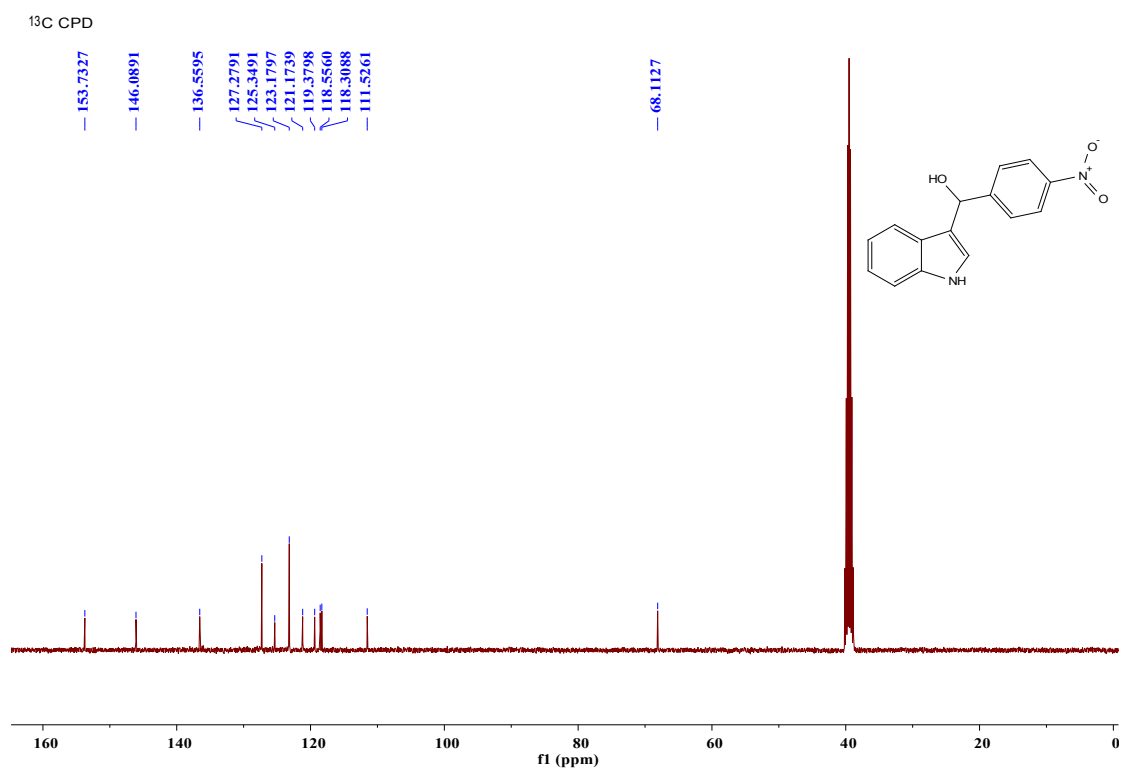
(1H-indol-3-yl)(4-nitrophenyl)methanol (Marked as **A**)

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.04 – 10.94 (m, 1H), 8.22 – 8.16 (m, 2H), 7.77 – 7.70 (m, 2H), 7.52 – 7.45 (m, 1H), 7.37 – 7.32 (m, 1H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.05 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 6.92 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.10 (d, *J* = 4.3 Hz, 1H), 5.94 (d, *J* = 4.3 Hz, 1H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 153.7, 146.1, 136.6, 127.3(2C), 125.4, 123.2, 123.18(2C), 121.17, 119.4, 118.6, 118.3, 111.5, 68.1. **IR** (KBr) ν_{max} 3404.6, 2923.6, 2852.8, 1705.1, 1604.4, 1518.0, 1346.2, 1106.0, 742.4, 620.1 cm⁻¹.

The NMR of reaction intermediate (Marked as A)

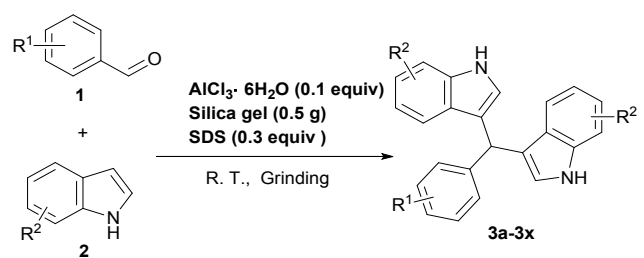


¹H NMR spectrum of compound A



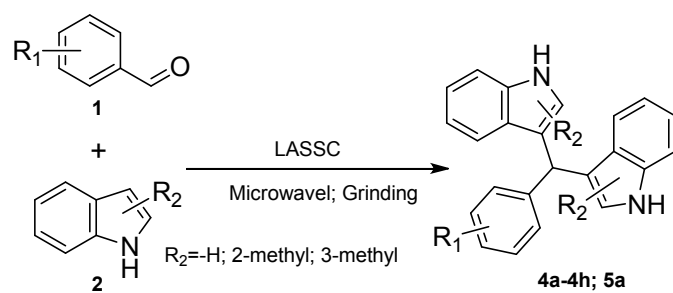
¹³C NMR spectrum of compound A

The substrate scope of Table S4



Entry ^a	R ¹	R ²	Product	Time (min)	Yield ^b (%)
1	H	H	3a	25	95
2	4-NO ₂	H	3b	20	99
3	3-NO ₂	H	3c	25	98
4	2-NO ₂	H	3d	30	71
5	4-F	H	3e	25	98
6	4-Cl	H	3f	15	97
7	4-Br	H	3g	28	94
8	4-Me	H	3h	20	96
9	4-MeO	H	3i	20	97
10	4-(CH ₃) ₂ N	H	3j	30	36
11	2-Cl	H	3k	30	57
12	2-Cl; 4-Cl	H	3l	18	98
13	3-OH; 4-OH	H	3m	30	63
14	3-MeO; 4-MeO	H	3n	29	97
15	4-NO ₂	6-NO ₂	3o	30	93
16	4-NO ₂	6-F	3p	18	95
17	4-NO ₂	6-Br	3q	28	95
18	4-NO ₂	6-Cl	3r	25	88
19	4-NO ₂	5-Br	3s	27	89
20	4-NO ₂	6-CN	3t	35	78
21	4-NO ₂	6-MeOOC	3u	35	74
22	4-NO ₂	6-OCH ₃	3v	40	46
23	4-NO ₂	6-HO	3w	40	0
24	4-NO ₂	6-NH ₂	3x	40	0

The substrate scope of Table S5

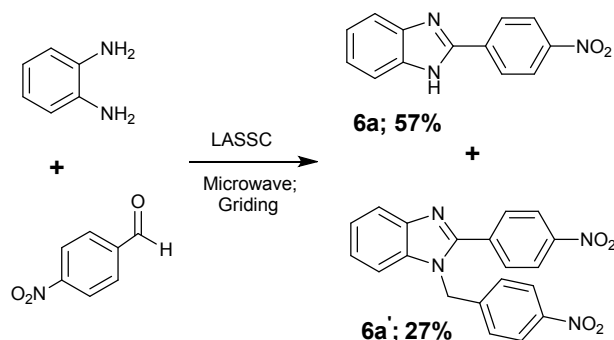


Entry ^a	R^1	R^2	Product	Time (min)	Yield ^b (%)
1	4-NO ₂	H	4a	4	95
2	3-NO ₂	H	4b	4	95
3	2-NO ₂	H	4c	5	89
4	4-CN	H	4d	4	86
5	4-C ₆ H ₅	H	4e	5	83
6	4-(CH ₃) ₂ N	H	4f	8	46
7	3-OH; 4-OH	H	4g	10	63
8 ^c	4-NO ₂	H	4h	5	17
9 ^d	4-NO ₂	3-Me	5a	10	60
10 ^e	4-NO ₂	1-Me	5b	10	0

^aReaction conditions: **1** (1.0 mmol); **2** (2.0 mmol); LASSC; Microwave, 540W; Solvent-free. ^bIsolated yields.

^c*p*-nitroacetophenone; ^d3-Methylindole; ^e1-methylindole.

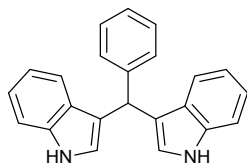
LASSC catalytic synthesis of Schiff base



Scheme S1. Synthesis of Schiff base by LASSC.

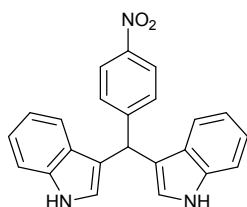
The mixture of *o*-phenylenediamine **1** (1.0 mmol), *p*-nitrobenzaldehyde **2** (1.0 mmol), SDS: 0.3mmol, AlCl₃·6H₂O: 0.1 mmol and column chromatography silica gel 0.5 g (300-400 mesh) in agate mortar was grinded at room temperature without solvent under microwave (540W) for 8 min. After the reaction is completed, the reaction mixture was dissolved in ethyl acetate (10mL) and filtered. The filtrate was concentrated, and the residue was purified with silica gel chromatography (Petroleumether / EtOAc =1:2) to give product **6a** and **6a'**.

Characterization data for all products 3a-3v



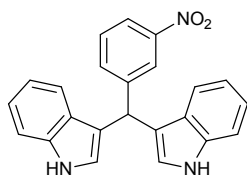
3,3'-(phenylmethylene)bis(1*H*-indole) (3a)

Pink solid (95%); mp=91.8-92.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 2.4 Hz, 2H), 7.47 – 7.44 (m, 2H), 7.42 – 7.34 (m, 2H), 7.35 – 7.27 (m, 4H), 7.28 – 7.18 (m, 3H), 7.07 (ddd, *J* = 8.0, 6.7, 1.3 Hz, 2H), 6.48 (dd, *J* = 2.4, 1.0 Hz, 2H), 5.92 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 144.2, 136.7, 128.8, 128.4, 127.1, 126.3, 123.8, 122.0, 120.0, 119.6, 119.3, 111.3, 40.3. IR (thin film) ν_{max} 3412.0; 3056.1; 2921.8; 2850.8; 1616.7; 1455.7; 1339.2; 1287.9; 1250.2; 744.7.



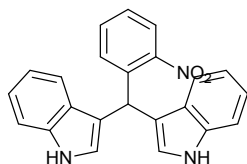
3,3'-((4-nitrophenyl)methylene)bis(1*H*-indole) (3b)

Yellow solid (99%); mp=236.4-237.9 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.99 (d, *J* = 2.5 Hz, 2H), 8.15 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.36 (dd, *J* = 34.0, 8.0 Hz, 4H), 7.07 (t, *J* = 7.6 Hz, 2H), 6.97 – 6.84 (m, 4H), 6.05 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 153.6, 146.2, 137.1, 129.9, 126.8, 124.4, 123.9, 121.60, 119.4, 118.9, 117.2, 112.1, 40.0. IR (thin film) ν_{max} 3419.8; 2945.4; 2922.8; 1656.4; 1535.2; 1517.2; 1346.2; 1275.5; 1260.7; 764.1.



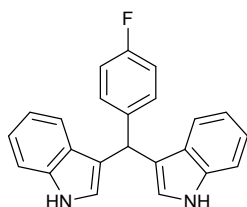
3,3'-((3-nitrophenyl)methylene)bis(1*H*-indole) (3c)

Light pink solid (98 %); mp=254.9-255.4 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.95 (d, *J* = 2.5 Hz, 2H), 8.17 (t, *J* = 2.0 Hz, 1H), 8.06 (ddd, *J* = 8.2, 2.4, 1.0 Hz, 1H), 7.84 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 7.34 (dd, *J* = 26.1, 8.0 Hz, 4H), 7.10 – 7.01 (m, 2H), 6.94 – 6.83 (m, 4H), 6.07 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 148.2, 147.9, 137.1, 135.6, 130.1, 126.8, 124.4, 123.1, 121.6, 121.5, 119.4, 118.9, 117.4, 112.1, 39.5. IR (thin film) ν_{max} 3428.6; 2923.7; 2852.6; 1656.4; 1557.8; 1526.4; 1349.4; 1287.1; 1259.7; 763.9.



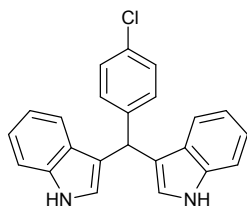
3,3'-((2-nitrophenyl)methylene)bis(1*H*-indole) (3d)

Yellow solid (71%); mp= 138.9-140.4 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.92 (s, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.51 (dt, *J* = 39.1, 7.6 Hz, 2H), 7.38 (dd, *J* = 14.4, 7.9 Hz, 3H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.88 (t, *J* = 7.5 Hz, 2H), 6.77 (s, 2H), 6.40 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 149.5, 137.7, 136.6, 132.5, 130.6, 127.5, 126.4, 124.2, 124.0, 121.2, 118.6, 118.5, 116.0, 111.7, 34.1. IR (thin film) ν_{max} 3407.7; 2920.4; 2854.1; 1606.9; 1540.1; 1522.4; 1353.3; 1260.6; 747.5.



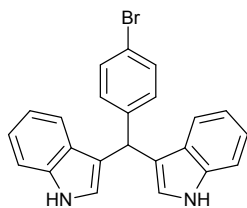
3,3'-((4-fluorophenyl)methylene)bis(1*H*-indole) (3e)

Light pink solid (98%); mp=101.5-103.9 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 2H), 7.37 (t, *J* = 8.0 Hz, 4H), 7.33 – 7.27 (m, 2H), 7.23 – 7.13 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 2H), 7.00 – 6.92 (m, 2H), 6.62 (d, *J* = 2.2 Hz, 2H), 5.88 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 136.7, 130.1, 130.0, 126.9, 123.5, 122.0, 119.8, 119.5, 119.3, 115.0, 114.8, 111.1, 39.4. IR (thin film) ν_{max} 3410.4; 2922.6; 2854.1; 1647.5; 1456.5; 1341.8; 1278.9; 1263.4; 1221.8; 1158.8; 1095.8; 1024.5; 748.1.



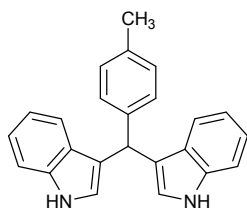
3,3'-((4-chlorophenyl)methylene)bis(1*H*-indole) (3f)

Pink solid (97 %); mp=83.5-85.7 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (s, 2H), 7.37 (d, *J* = 8.2 Hz, 4H), 7.25 (d, *J* = 5.1 Hz, 4H), 7.18 (t, *J* = 7.7 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.63 (s, 2H), 5.86 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 142.6, 136.7, 131.8, 130.1, 128.4, 126.9, 123.6, 122.1, 119.8, 119.4, 119.2, 111.2, 39.6. IR (thin film) ν_{max} 3412.7; 2925.5; 2853.9; 1617.0; 1474.5; 1337.4; 1281.8; 1251.9; 787.2; 744.0; 787.2.



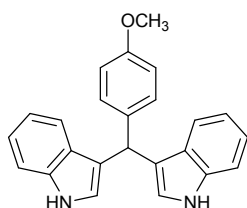
3,3'-((4-bromophenyl)methylene)bis(1*H*-indole) (3g)

Dark pink solid (94%); mp=110.1-113.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.81 – 7.71 (m, 2H), 7.45 (d, *J* = 2.2 Hz, 2H), 7.43 (d, *J* = 2.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.28 – 7.21 (m, 3H), 7.10 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 2H), 6.57 (d, *J* = 2.3 Hz, 2H), 5.89 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 143.1, 136.7, 131.4, 130.6, 126.9, 123.8, 122.2, 120.0, 119.9, 119.4, 119.0, 111.3, 111.2, 39.7. IR (thin film) ν_{max} 3413.2; 3054.8; 2925.2; 2853.2; 1618.0; 1485.2; 1337.9; 1264.2; 1230.3; 785.0; 746.3; 703.1; 597.8.



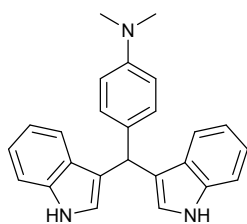
3,3'-((p-tolyl)methylene)bis(1*H*-indole) (3h)

Yellow solid (96%); mp=95.8-97.2 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.81 (d, *J* = 2.5 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.25 (dd, *J* = 14.9, 7.9 Hz, 4H), 7.07 (s, 1H), 7.06 – 7.00 (m, 3H), 6.89 – 6.82 (m, 2H), 6.81 (d, *J* = 2.3 Hz, 2H), 5.78 (s, 1H), 2.25 (s, 3H). ¹H NMR (100 MHz, DMSO-*d*₆) δ 142.4, 137.1, 135.1, 129.1, 128.7, 127.1, 124.0, 121.3, 119.7, 118.7, 118.6, 111.9, 39.8, 21.1. IR (thin film) ν_{max} 3414.2; 3052.5; 2921.3; 2856.5; 1618.2; 1452.2; 1415.4; 1285.6; 1255.2; 742.9.



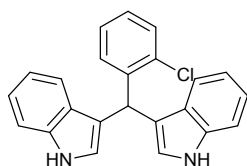
3,3'-((4-methoxyphenyl)methylene)bis(1*H*-indole) (3i)

Orange solid (97%); mp=184.8-186.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.79 (m, 2H), 7.40 (dd, *J* = 7.9, 1.0 Hz, 2H), 7.35 (dt, *J* = 8.1, 0.9 Hz, 2H), 7.27 (s, 1H), 7.25 (d, *J* = 2.2 Hz, 1H), 7.18 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 2H), 7.02 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H), 6.87 – 6.78 (m, 2H), 6.63 (dd, *J* = 2.5, 1.1 Hz, 2H), 5.85 (s, 1H), 3.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.9, 136.7, 136.2, 129.6, 127.1, 123.5, 121.9, 120.0, 112.0, 119.2, 113.6, 111.0, 55.2, 39.3. IR (thin film) ν_{max} 3412.7; 3054.7; 2927.8; 2835.7; 1609.7; 1456.1; 1338.0; 1252.7; 1226.7; 1174.7; 1092.3; 1028.3; 1009.9; 746.9.



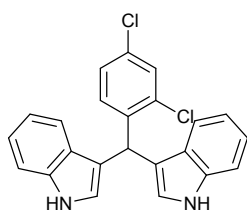
4-(di(1*H*-indol-3-yl)methyl)-*N,N*-dimethylaniline (3j)

White solid (36%); mp= 181.5-183.7°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.77 (d, *J* = 2.5 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.07 – 6.98 (m, 2H), 6.85 (t, *J* = 7.5 Hz, 2H), 6.79 (d, *J* = 2.3 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 5.71 (s, 1H), 2.82 (s, 6H). ¹³C NMR (100MHz, DMSO-*d*₆) δ 148.7, 136.6, 132.8, 128.7, 126.7, 123.4, 120.8, 119.3, 118.8, 118.0, 112.3, 111.4, 40.3, 38.8. IR (thin film) ν_{max} 3400.7;2920.9;2854.1;1646.6; 1456.9; 1347.7;1270.1;1260.9;1205.2; 749.8.



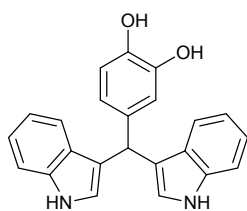
3,3'-(2-chlorophenyl)methylenebis(1*H*-indole) (3k)

Red solid (57%); mp=95.7-97.8°C; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 2.8 Hz, 2H), 7.57 – 7.41 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.15 (m, 4H), 7.19 – 7.03 (m, 3H), 6.52 (d, *J* = 2.3 Hz, 2H), 6.43 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 141.4, 136.7, 134.0, 130.4, 129.6, 127.7, 127.0, 126.8, 124.0, 122.1, 119.9, 119.4, 118.2, 111.3, 36.7. IR(thin film) ν_{max} 3413.8; 3056.3; 2925.0; 2853.5;1617.8; 1456.2;1337.3;1264.2;1230.7;794.2; 701.8;742.3.



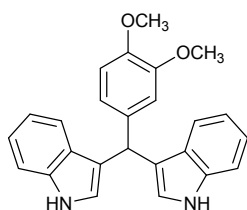
3,3'-(2,4-dichlorophenyl)methylenebis(1*H*-indole) (3l)

Pink solid (98%); mp=105.4-106.8°C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 2H), 7.45 (d, *J* = 2.1 Hz, 1H), 7.37 (dt, *J* = 8.3, 1.2 Hz, 4H), 7.19 (ddd, *J* = 8.3, 7.0, 1.1 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.04 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 2H), 6.63 (q, *J* = 1.1 Hz, 2H), 6.28 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 140.0, 136.7, 134.6, 132.4, 131.2, 129.3, 127.0, 126.8, 123.8, 122.2, 119.7, 119.4, 117.8, 111.2, 36.3. IR(thin film) ν_{max} 3414.3;2922.8;2854.1;1633.9; 1346.4; 1290.0; 1217.1; 797.7;747.9; 703.8.



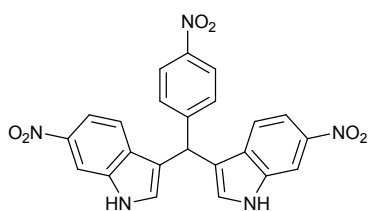
4-(di(1*H*-indol-3-yl)methyl)benzene-1,2-diol (3m)

Light pink solid (63%); mp=191.3-191.5°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.77 (s, 2H), 8.64 (s, 2H), 7.31 (dd, *J* = 25.4, 8.1 Hz, 4H), 7.03 (t, *J* = 7.5 Hz, 2H), 6.86 (t, *J* = 7.5 Hz, 2H), 6.79 (s, 2H), 6.72 (s, 1H), 6.63 (s, 2H), 5.64 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 144.7, 143.2, 136.6, 136.0, 126.7, 123.4, 120.8, 119.3, 119.1, 118.7, 118.1, 115.8, 115.1, 111.4. 39.5. IR (thin film) ν_{max} 3434.8; 3267.5; 2924.7; 2855.3; 1656.2; 1517.2; 1345.6; 1274.1; 1235.4; 1106.0; 1007.5; 761.2.



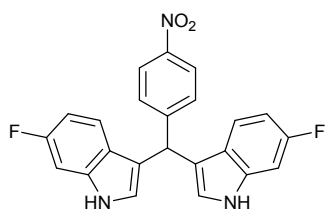
3,3'-((3,4-dimethoxyphenyl)methylene)bis(1*H*-indole) (3n)

Yellow solid (97%); mp=186.6-188.5°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.80 (d, *J* = 2.4 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.06 – 6.98 (m, 3H), 6.86 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 2H), 6.84 – 6.78 (m, 4H), 5.77 (s, 1H), 3.70 (s, 3H), 3.64 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 148.9, 147.4, 134.0, 137.1, 127.2, 124.0, 121.3, 120.6, 119.7, 118.9, 118.6, 113.0, 112.0, 111.9, 55.9. 39.8. IR (thin film) ν_{max} 3407.7; 2924.2; 2852.1; 1690.4; 1338.2; 1264.3; 1137.1; 1025.5; 1093.4; 1137.1; 743.0. ESI-MS Expected C₂₅H₂₂N₂O₂: 382.17; Observed 381.1363.



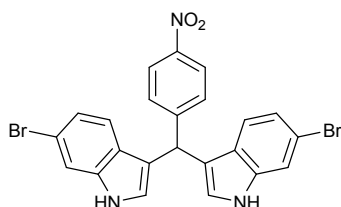
3,3'-((4-nitrophenyl)methylene)bis(6-nitro-1*H*-indole) (3o)

Dark yellow solid (93%); mp=225.8-226.4°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.88 – 11.73 (m, 2H), 8.40 – 8.30 (m, 2H), 8.19 (d, *J* = 8.3 Hz, 2H), 7.86 – 7.77 (m, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 2.6 Hz, 2H), 6.26 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 152.1, 146.6, 142.5, 135.5, 131.4, 131.3, 129.9, 124.2, 119.5, 118.1, 114.3, 109.0. 39.0. IR (thin film) ν_{max} 3422.1; 2921.4; 2851.0; 1655.2; 1540.0; 1514.9; 1469.4; 1343.1; 1290.2; 1260.5; 1041.0; 1025.9; 1015.9; 763.6. ESI-MS Expected C₂₃H₁₅N₃O₆: 457.10; Observed 456.0614.



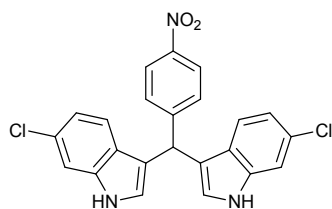
3,3'-((4-nitrophenyl)methylene)bis(6-fluoro-1H-indole) (3p)

Dark yellow solid (95%); mp=221.8-222.3 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.04 (d, *J* = 2.4 Hz, 2H), 8.20 – 8.12 (m, 2H), 7.63 – 7.56 (m, 2H), 7.25 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.14 (dd, *J* = 10.1, 2.4 Hz, 2H), 6.89 (d, *J* = 2.3 Hz, 2H), 6.76 (ddd, *J* = 9.7, 8.7, 2.4 Hz, 2H), 6.02 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 158.85 (d, *J* = 234.3 Hz), 152.66, 145.86, 136.42 (d, *J* = 12.7 Hz), 129.43, 124.51 (d, *J* = 3.4 Hz), 123.51, 123.20, 119.87 (d, *J* = 10.3 Hz), 116.76, 106.99 (d, *J* = 24.3 Hz), 97.54 (d, *J* = 25.4 Hz). 39.7. IR (thin film) ν_{max} 3423.6; 2924.7; 2852.8; 1612.0; 1455.9; 1344.5; 1256.1; 1228.2; 1139.6; 1118.1; 1091.1; 749.8. ESI-MS Expected C₂₃H₁₅F₂N₃O₂ : 403.11; Observed 402.0796.



3,3'-((4-nitrophenyl)methylene)bis(6-bromo-1H-indole) (3q)

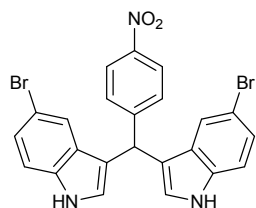
Light pink solid (95%); mp=187.5-188.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.6 Hz, 2H), 8.04 (s, 2H), 7.54 (d, *J* = 1.5 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.21 – 7.04 (m, 4H), 6.65 (d, *J* = 2.0 Hz, 2H), 5.91 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 150.9, 146.7, 137.4, 129.4, 125.4, 124.1, 123.7, 123.1, 120.7, 118.1, 116.1, 114.3, 39.9. IR (thin film) ν_{max} 3418.3; 2922.4; 2854.1; 1647.3; 1555.2; 1514.2; 1457.1; 1344.6; 1275.5; 1204.8; 783.8; 749.4; 708.6; 583.8. ESI-MS Expected C₂₃H₁₅Br₂N₃O₂: 522.95; Observed 521.9375.



3,3'-((4-nitrophenyl)methylene)bis(6-chloro-1H-indole) (3r)

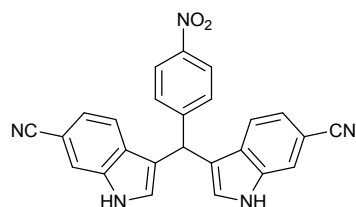
Yellow solid (88%); mp=156.2-159.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.09 (m, 2H), 8.12 – 8.03 (m, 2H), 7.49 – 7.42 (m, 2H), 7.36 (d, *J* = 1.8 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.98 (dd, *J* = 8.5, 1.8 Hz, 2H), 6.68 – 6.62 (m, 2H), 5.91 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 151.2, 146.6, 137.0, 129.5, 128.3, 125.1, 124.3, 123.8, 120.4, 120.4, 118.0, 111.4, 40.0. IR (thin film) ν_{max} 3430.3;

2997.5; 2924.9; 1594.4; 1454.6;1345.5;1242.8;1225.6;1098.0;1061.8;779.9;747.9; 706.6. **ESI-MS**
Expected $C_{23}H_{15}Cl_2N_3O_2$: 435.05; Observed 434.0167.



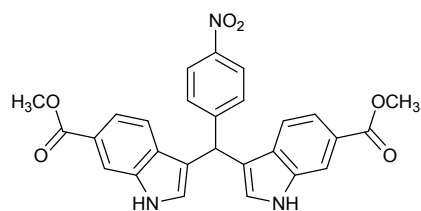
3,3'-((4-nitrophenyl)methylene)bis(5-bromo-1H-indole) (3s)

Orange solid (89%); mp=115.0-117.2°C; 1H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.12 (m, 2H), 8.14 – 8.09 (m, 2H), 7.48 – 7.40 (m, 4H), 7.28 (t, J = 1.4 Hz, 4H), 6.65 (dd, J = 2.5, 1.1 Hz, 2H), 5.86 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 146.7, 135.3, 129.4, 128.2, 125.4, 124.8, 123.9, 121.9, 117.4, 113.0, 112.9, 39.8. **IR** (thin film) ν_{max} 3428.7; 3022.5; 2924.7; 2852.7; 1595.2; 1550.9; 1516.1; 1457.9;1344.8;1263.1;1231.2;1211.8;794.3;779.7;746.5;702.4.



3,3'-((4-nitrophenyl)methylene)bis(1H-indole-6-carbonitrile) (3t)

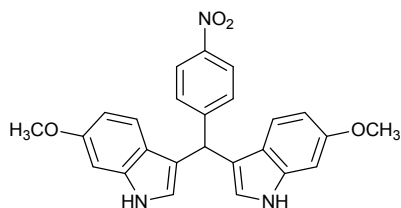
White solid (78%); mp=202.4-203.7°C; 1H NMR (400 MHz, $DMSO-d_6$) δ 11.70 – 11.57 (m, 2H), 8.15 (d, J = 8.4 Hz, 2H), 7.91 (s, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.24 (t, J = 5.5 Hz, 4H), 6.18 (s, 1H). ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 152.3, 146.5, 135.8, 129.9, 129.7, 129.0, 124.1, 121.8, 121.0, 120.4, 117.8, 117.1, 103.1, 39.0. **IR**(thin film) ν_{max} 3387.0; 1538.4 (NH); 2975.1;2220.1; 2922.8;2854.1;1552.3; 1538.4; 1552.3; 1457.7; 1346.9; 1275.6; 1260.6; 1228.5; 745.4. **ESI-MS** Expected $C_{25}H_{15}N_5O_2$: 417.12; Observed 416.1487.



dimethyl 3,3'-((4-nitrophenyl)methylene)bis(1H-indole-6-carboxylate) (3u)

Light yellow solid (74%); mp=228.5-229.3°C; 1H NMR (400 MHz, $DMSO-d_6$) δ 11.41 (d, J = 2.6 Hz, 2H), 8.21 – 8.14 (m, 2H), 8.07 – 8.02 (m, 2H), 7.65 – 7.58 (m, 2H), 7.52 (dd, J = 8.4, 1.5 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.17 (dd, J = 2.6, 0.8 Hz, 2H), 6.15 (s, 1H), 3.83 (s, 6H). ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 167.7, 152.8, 146.4, 136.3, 130.2, 129.9, 128.4, 124.1, 122.7, 119.7, 119.2, 117.5, 114.2, 52.2, 39.4. **IR**(thin film) ν_{max} 3351.4;2923.7;2351.9;1711.9; 1648.6 ; 1550.8;

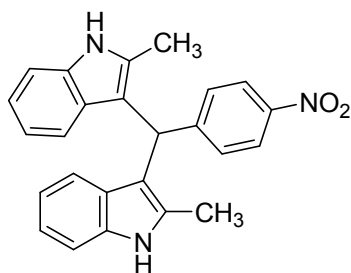
1518.4; 1435.8; 1330.9; 1248.9; 1217.1; 1087.5; 1023.3; 777.4. **ESI-MS** Expected $C_{27}H_{21}N_3O_6$: 483.14; Observed 482.1021.



3,3'-((4-nitrophenyl)methylene)bis(6-methoxy-1*H*-indole) (3v)

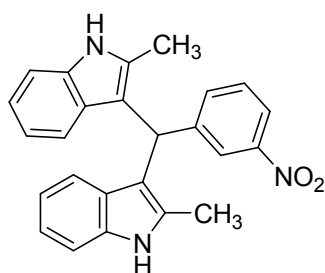
Brown solid (46%); mp=112.8-114.2°C; **¹H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.05 (m, 2H), 7.99 – 7.86 (m, 2H), 7.52 – 7.42 (m, 2H), 7.19 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 2.3 Hz, 2H), 6.69 (dd, J = 8.7, 2.2 Hz, 2H), 6.58 – 6.52 (m, 2H), 5.88 (s, 1H), 3.82 (s, 6H). **¹³C NMR** (100 MHz, $CDCl_3$) δ 156.6, 152.0, 146.5, 137.4, 129.5, 123.6, 122.4, 121.1, 120.2, 118.1, 109.5, 94.7, 55.7, 40.3. **IR** (thin film) ν_{max} 3410.6; 2923.5; 2849.3; 1628.2; 1536.0; 1515.9; 1452.2; 1345.2; 1260.2; 1232.5; 1159.3; 1058.0; 1026.2. **ESI-MS** Expected $C_{25}H_{21}N_3O_4$: 427.15; Observed 426.1174.

Characterization data for all products 4a-4h and 5a



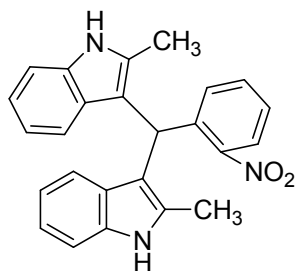
3,3'-((4-nitrophenyl)methylene)bis(2-methyl-1H-indole) (4a)

Yellow solid (95%); **¹H NMR** (400 MHz, DMSO-*d*₆) δ 10.90 (s, 2H), 8.24 – 8.12 (m, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.72 (t, *J* = 7.5 Hz, 2H), 6.09 (s, 1H), 2.12 (s, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 152.9, 145.7, 135.1, 132.6, 129.8, 127.9, 123.3, 119.8, 118.3, 118.2, 110.9, 110.5, 39.1, 12.0. **IR** (thin film) ν_{max} 3398.9; 2919.1; 1548.9; 1516.0; 1343.9; 1287.8; 1260.9; 747.9.



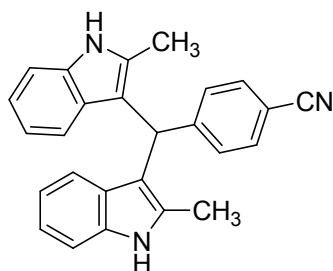
3,3'-((3-nitrophenyl)methylene)bis(2-methyl-1H-indole) (4b)

Yellow solid (95%); **¹H NMR** (400 MHz, DMSO-*d*₆) δ 10.91 (s, 2H), 8.16 – 8.08 (m, 1H), 8.05 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.73 (t, *J* = 7.5 Hz, 2H), 6.15 (s, 1H), 2.15 (s, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 147.7, 147.0, 135.5, 135.2, 132.6, 129.5, 127.9, 122.9, 121.0, 119.8, 118.2, 111.0, 110.6, 38.3, 12.0, 11.9. **IR** (thin film) ν_{max} 3393.3; 2919.3; 2878.5; 1645.9; 1548.8; 1525.5; 1459.9; 1345.9; 749.3



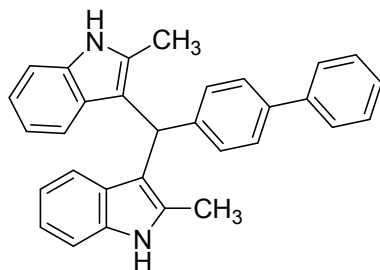
3,3'-((2-nitrophenyl)methylene)bis(2-methyl-1H-indole) (4c)

Yellow solid (89%); **¹H NMR** (400 MHz, DMSO-*d*₆) δ 10.87 (s, 2H), 7.85 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.57 (td, *J* = 7.6, 1.5 Hz, 1H), 7.49 (td, *J* = 7.6, 1.5 Hz, 1H), 7.29 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.92 (ddd, *J* = 8.1, 6.6, 1.5 Hz, 2H), 6.79 – 6.67 (m, 4H), 6.61 (s, 1H), 2.06 (s, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 150.1, 137.8, 135.0, 132.7, 132.4, 130.5, 128.1, 127.7, 124.5, 119.8, 118.3, 117.7, 110.6, 109.8, 33.9, 11.6. **IR** (thin film) ν_{max} 3400.3; 2917.9; 2780.0; 1523.3; 1318.2; 1260.8; 749.8.



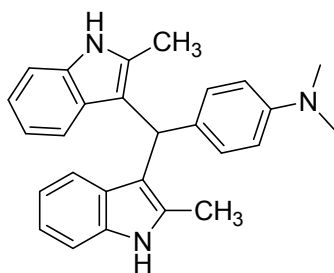
4-(bis(2-methyl-1H-indol-3-yl)methyl)benzonitrile (4d)

Yellow solid (86%); **¹H NMR** (400 MHz, DMSO-*d*₆) δ 10.86 (d, *J* = 5.7 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 6.92 (t, *J* = 7.4 Hz, 2H), 6.81 (d, *J* = 7.9 Hz, 2H), 6.72 (t, *J* = 7.4 Hz, 2H), 6.03 (d, *J* = 5.4 Hz, 1H), 2.10 (d, *J* = 5.3 Hz, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 150.5, 135.1, 132.5, 131.9, 129.7, 127.9, 119.7, 119.1, 118.3, 118.2, 110.9, 110.5, 108.5, 38.8, 11.9. **IR** (thin film) ν_{max} 3396.9; 2918.8; 2778.0; 1459.9; 748.4.



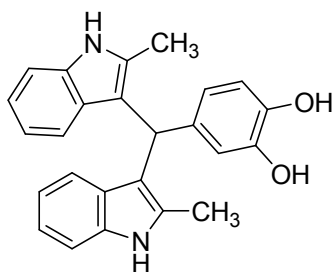
3,3'-([1,1'-biphenyl]-4-ylmethylene)bis(2-methyl-1H-indole) (4e)

Yellow solid (83%); **¹H NMR** (400 MHz, DMSO-*d*₆) δ 10.80 (s, 2H), 7.71 – 7.63 (m, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.1 Hz, 2H), 7.29 – 7.23 (m, 2H), 6.92 (t, *J* = 7.3 Hz, 4H), 6.77 – 6.68 (m, 2H), 6.00 (s, 1H), 2.14 (s, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 143.7, 140.0, 137.4, 135.1, 132.1, 129.3, 128.9, 128.3, 127.1, 126.4, 126.1, 119.6, 118.6, 118.0, 112.1, 110.4, 38.3, 12.0. **IR** (thin film) ν_{max} 3400.4; 2917.7; 1485.8; 1459.7; 1324.3; 742.6; 712.4.



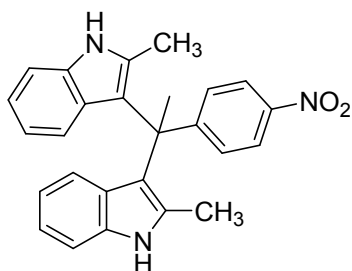
4-(bis(2-methyl-1H-indol-3-yl)methyl)-N,N-dimethylaniline (4f)

Yellow solid (46%); **¹H NMR** (400 MHz, DMSO-*d*₆) δ 10.68 (s, 2H), 7.24 – 7.17 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.93 – 6.84 (m, 4H), 6.68 (dd, *J* = 8.2, 6.8 Hz, 2H), 6.65 – 6.57 (m, 2H), 5.81 (s, 1H), 2.83 (s, 6H), 2.07 (s, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 148.6, 135.0, 131.8, 131.7, 129.1, 128.4, 119.4, 118.6, 117.8, 112.9, 112.2, 110.2, 40.3, 37.6, 11.95. **IR** (thin film) *v*_{max} 3387.8; 2918.4; 2771.4; 1275.4; 1270.1; 1260.9; 760.1; 750.1.



4-(bis(2-methyl-1H-indol-3-yl)methyl)benzene-1,2-diol (4g)

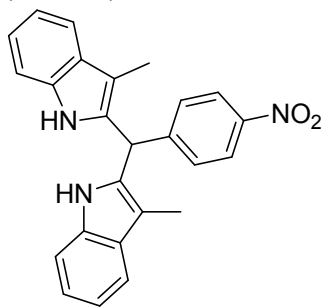
Yellow solid (99.8%); **¹H NMR** (400 MHz, DMSO-*d*₆) δ 10.69 (s, 2H), 8.62 (d, *J* = 26.0 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.93 – 6.82 (m, 4H), 6.69 (t, *J* = 7.5 Hz, 2H), 6.65 – 6.58 (m, 2H), 6.49 – 6.41 (m, 1H), 5.75 (s, 1H), 2.07 (s, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 144.7, 143.1, 135.1, 135.0, 131.8, 128.4, 119.4, 118.7, 117.8, 116.3, 115.1, 112.9, 110.2, 37.9, 12.0. **IR** (thin film) *v*_{max} 3398.4; 2919.5; 2779.5; 1459.9; 1275.9; 748.7.



3,3'-(1-(4-nitrophenyl)ethane-1,1-diyl)bis(2-methyl-1H-indole) (4h)

Yellow solid (17%); **¹H NMR** (400 MHz, DMSO-*d*₆) δ 10.83 (s, 2H), 8.16 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 2H), 6.78 (d, *J* = 8.2 Hz, 2H), 6.69 (t, *J* = 7.6 Hz, 2H), 2.49 (s, 3H), 1.74 (s, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 157.7,

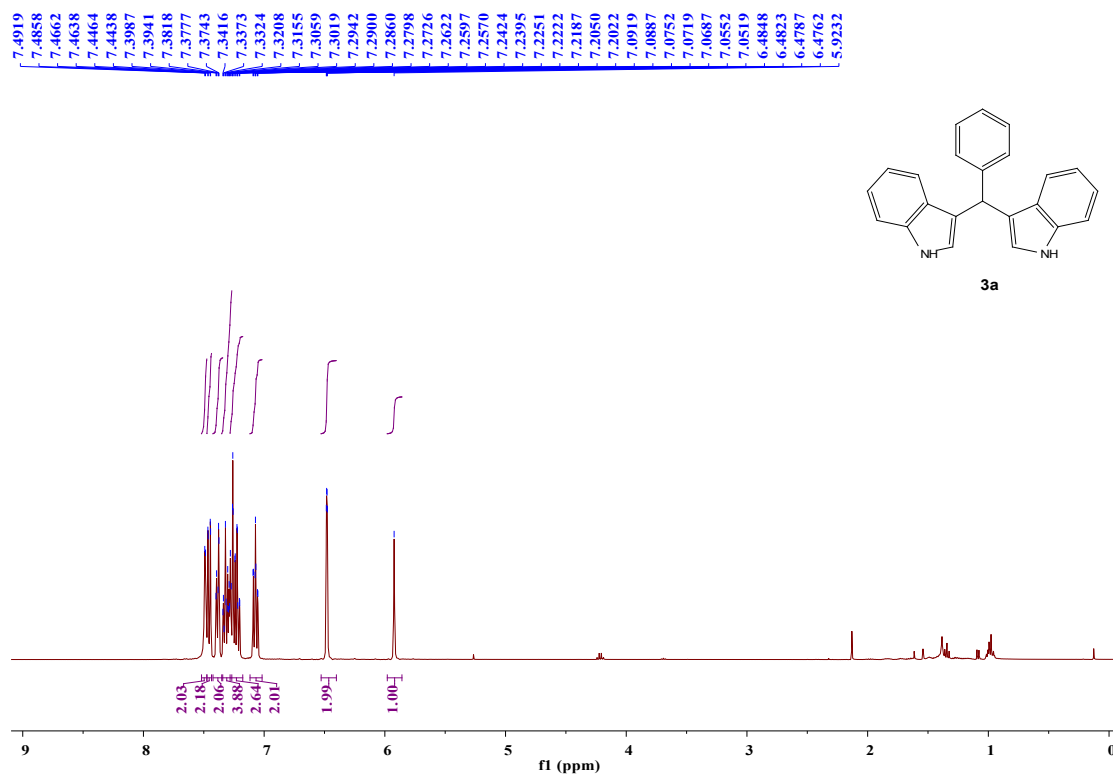
145.4, 135.0, 132.0, 129.5, 127.8, 122.8, 120.2, 119.6, 118.0, 116.5, 110.4, 44.8, 31.5, 13.6. **IR** (thin film) $\nu_{\max}$ 3398.7; 2923.5; 2880.5; 1659.2; 1563.2; 1458.2; 1263.7; 741.9.



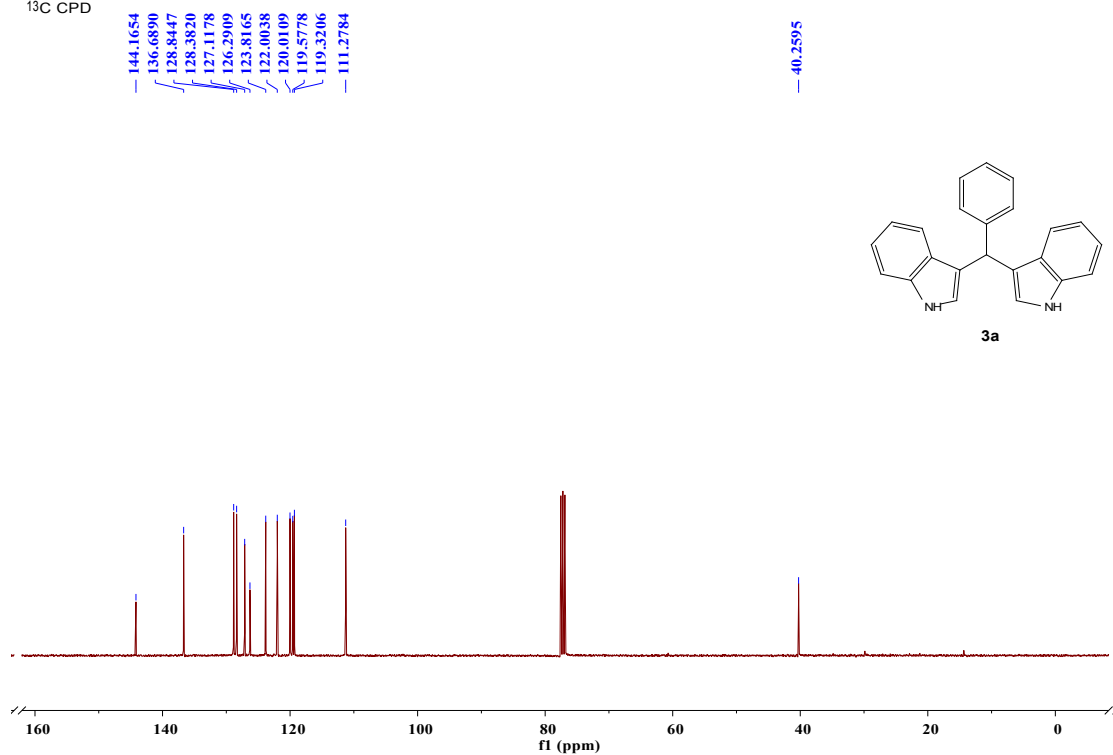
2,2'-((4-nitrophenyl)methylene)bis(3-methyl-1H-indole) (5a)

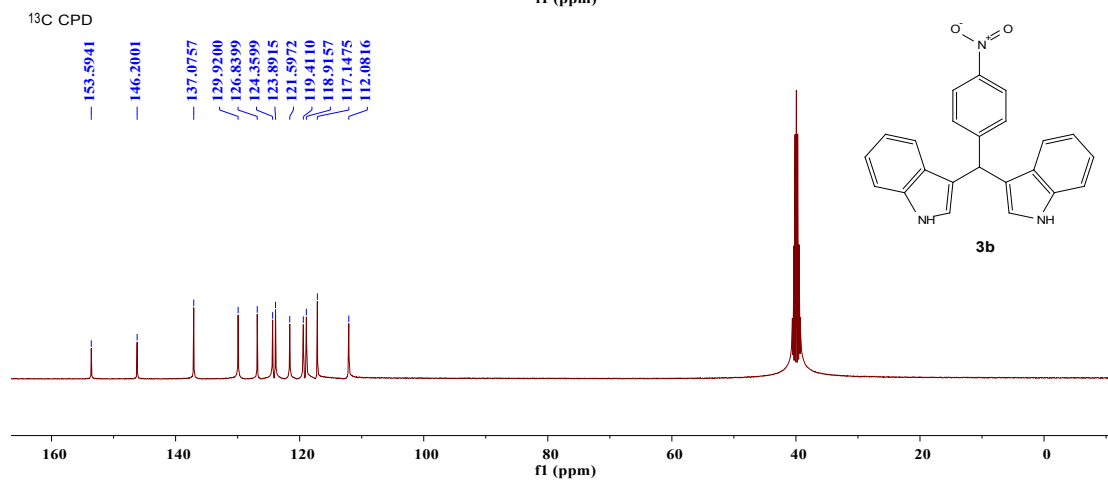
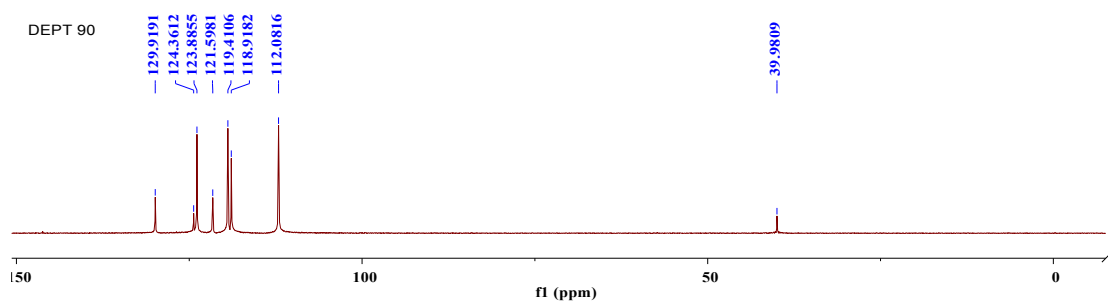
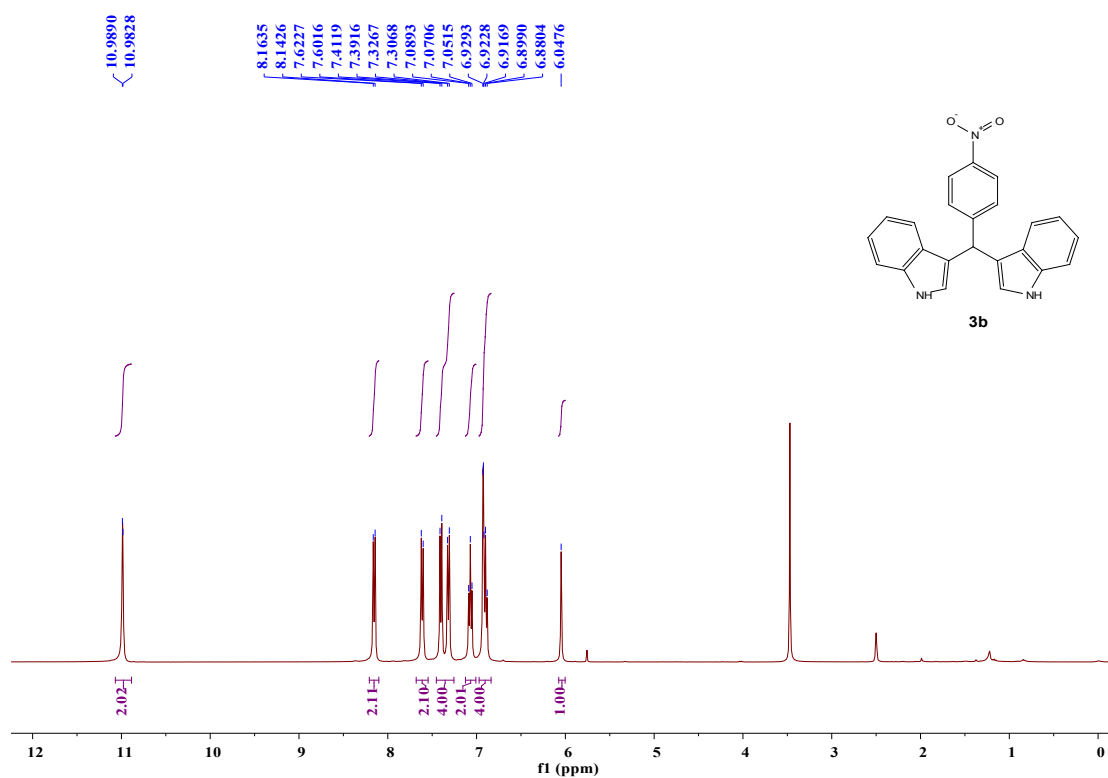
Yellow solid (60%); **¹H NMR** (400 MHz, DMSO-*d*₆) δ 10.50 (d, J = 6.1 Hz, 2H), 8.33 – 8.18 (m, 2H), 7.45 (dt, J = 13.9, 6.8 Hz, 4H), 7.32 (t, J = 7.2 Hz, 2H), 7.02 (dq, J = 26.6, 6.7, 5.4 Hz, 4H), 6.24 (d, J = 5.9 Hz, 1H), 2.17 (d, J = 6.1 Hz, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 149.1, 146.3, 135.7, 133.1, 129.7, 128.5, 123.7, 121.0, 118.4, 118.0, 111.2, 107.3, 40.1, 8.5. **IR** (thin film) $\nu_{\max}$ 3395.9; 2919.9; 2878.2; 1646.4; 1613.6; 1554.1; 1458.7; 742.4.

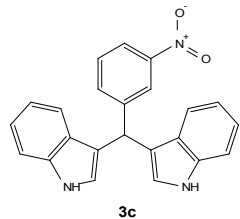
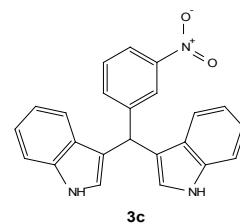
NMR spectra for all compounds **3a-3v**

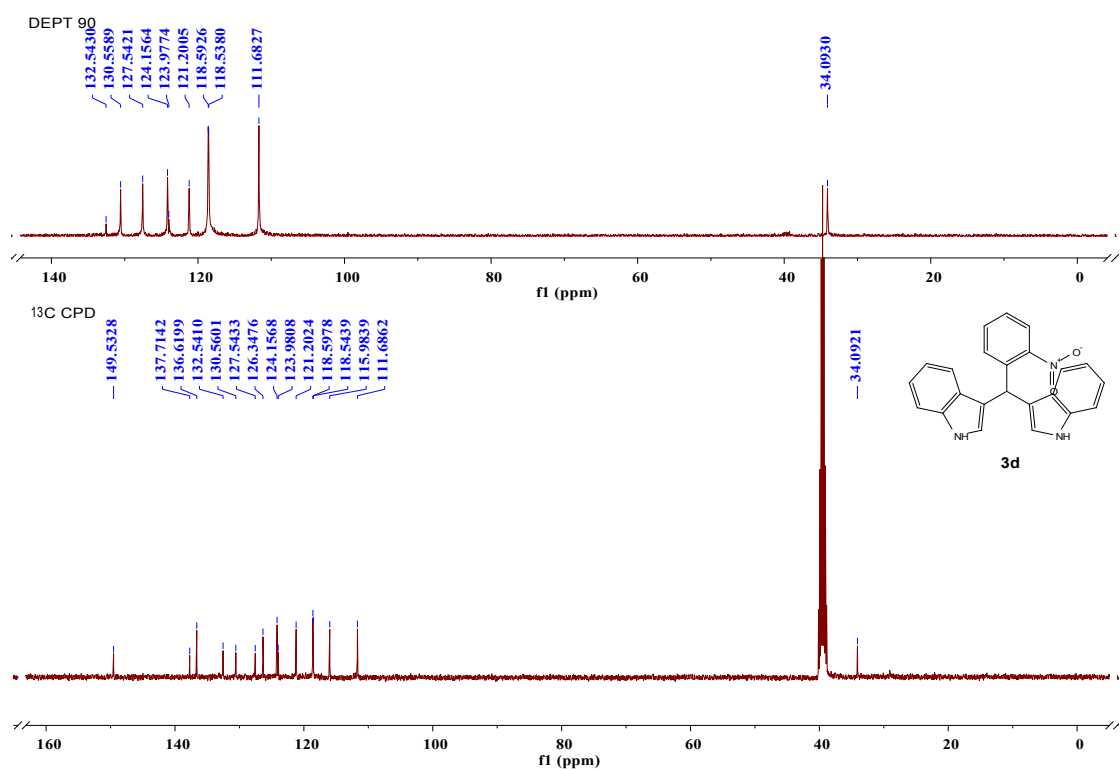
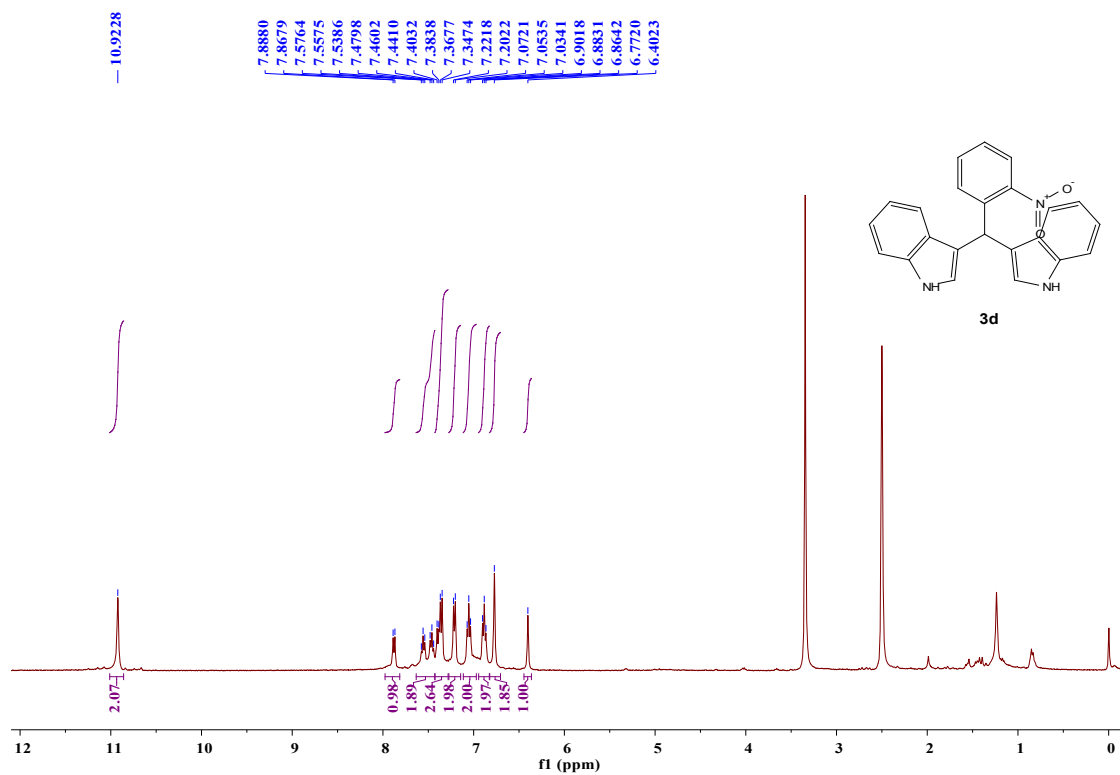


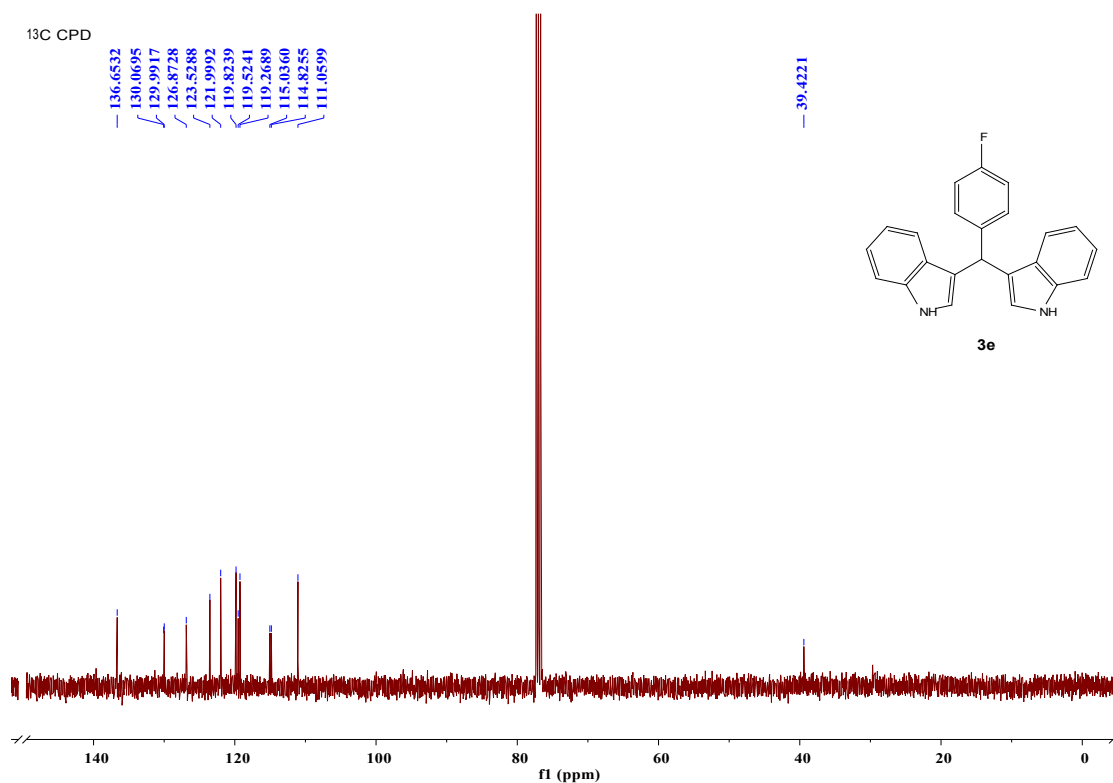
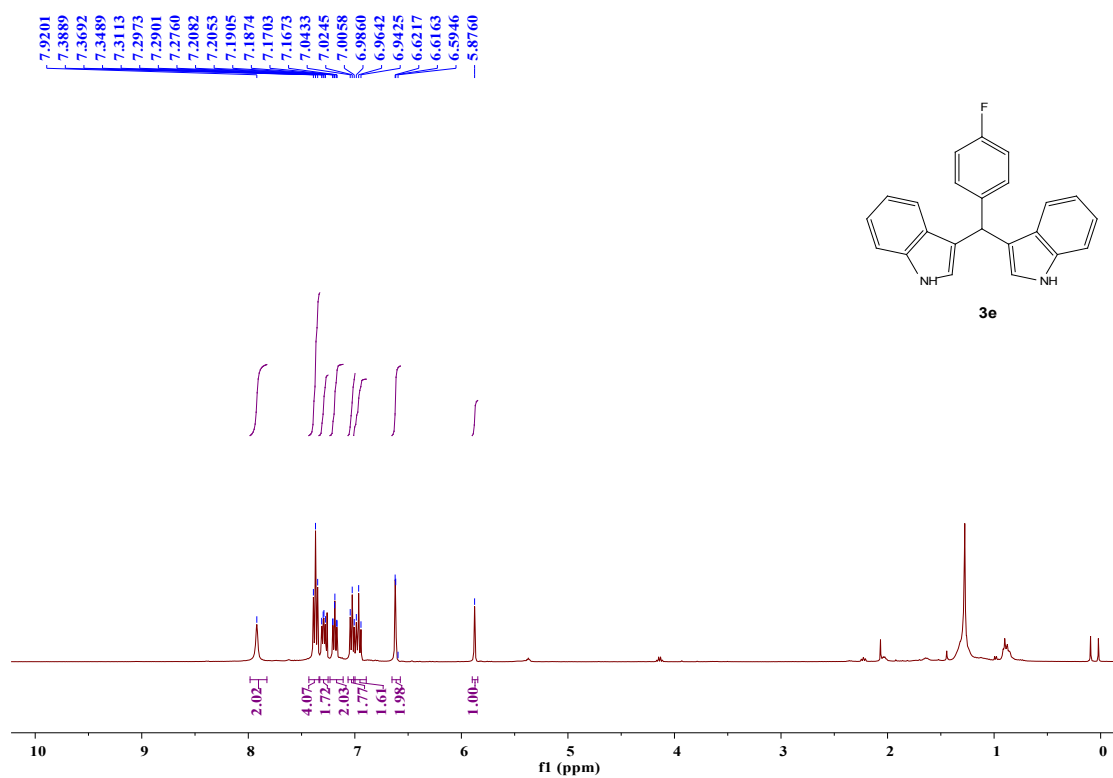
¹³C CPD

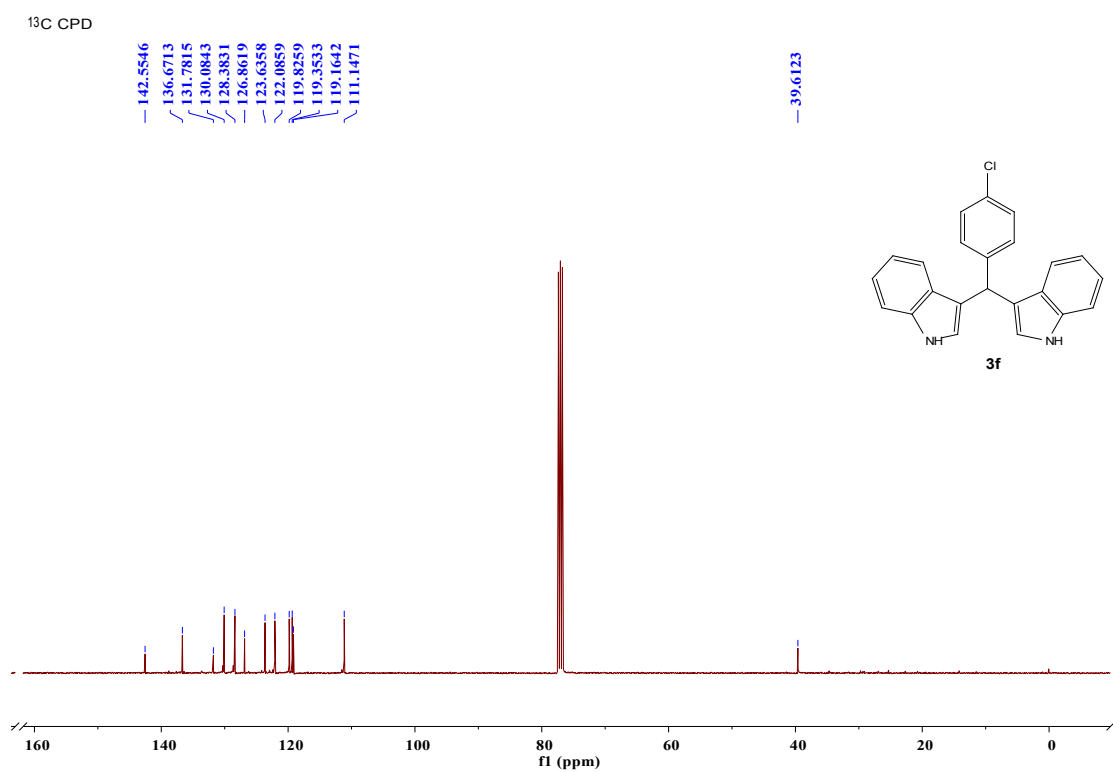
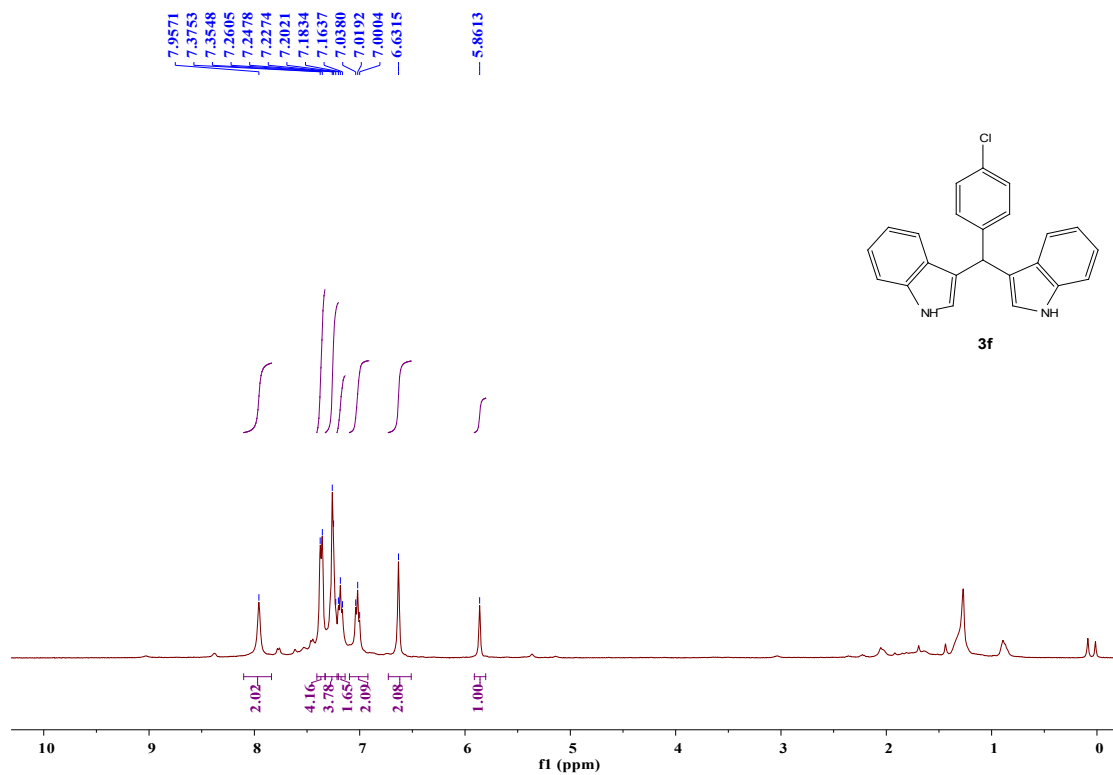


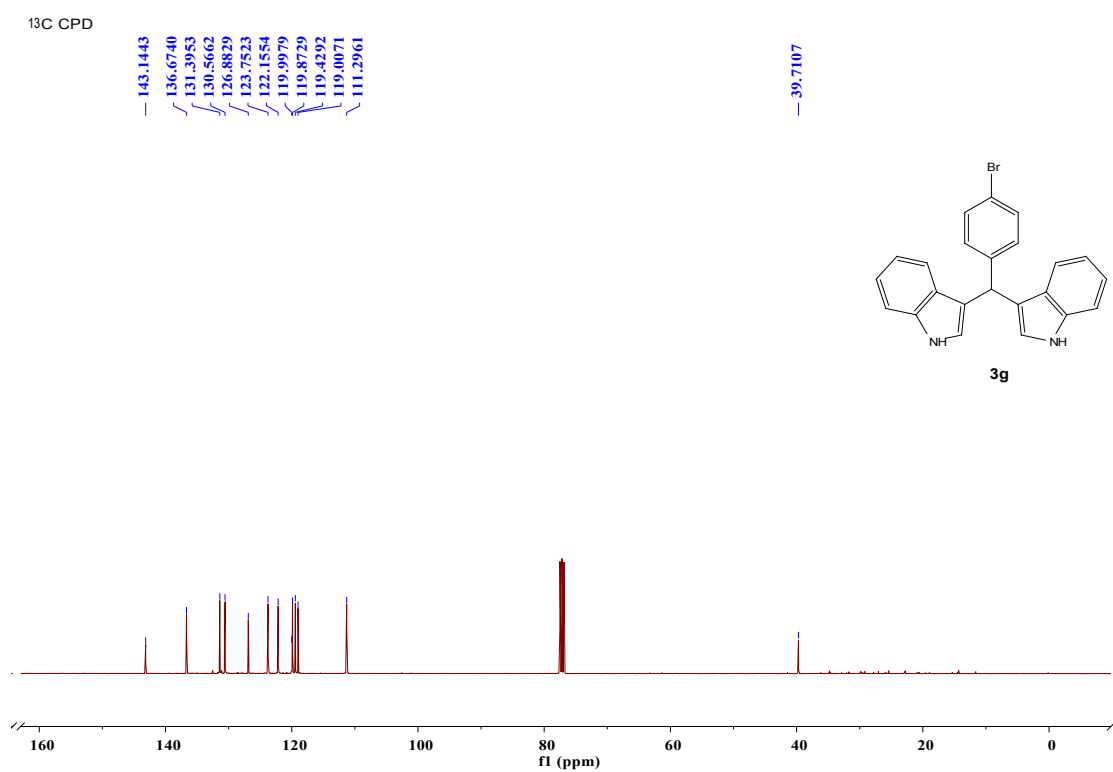
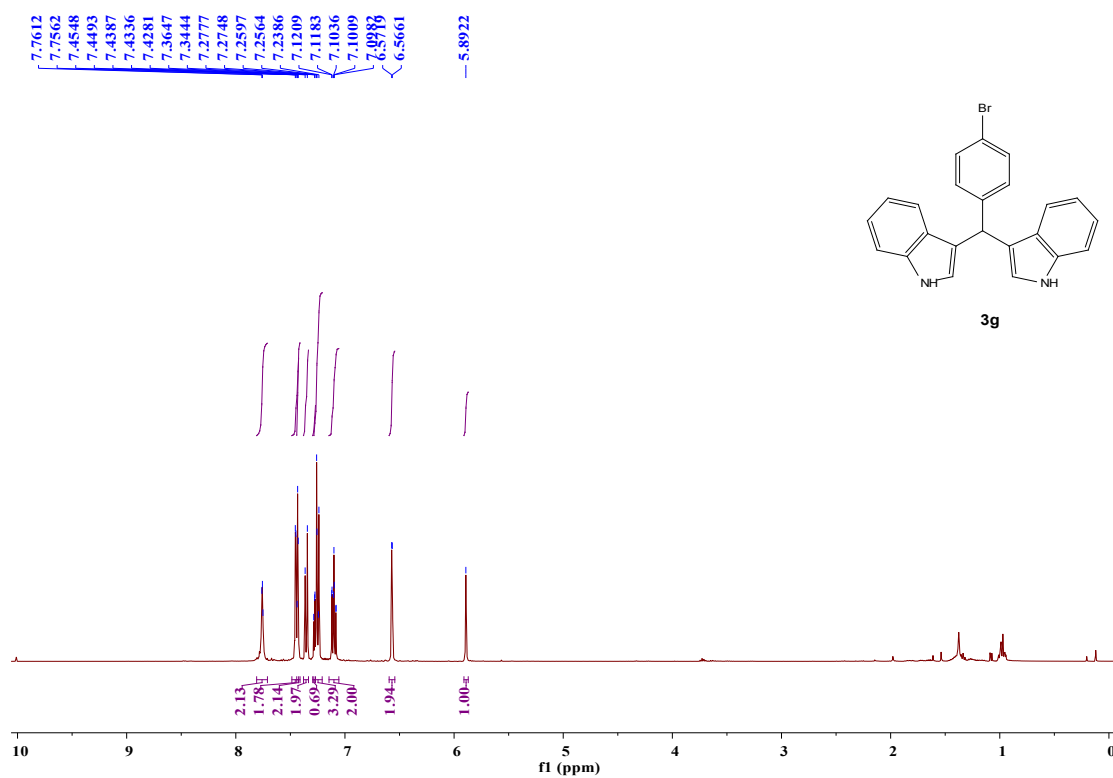


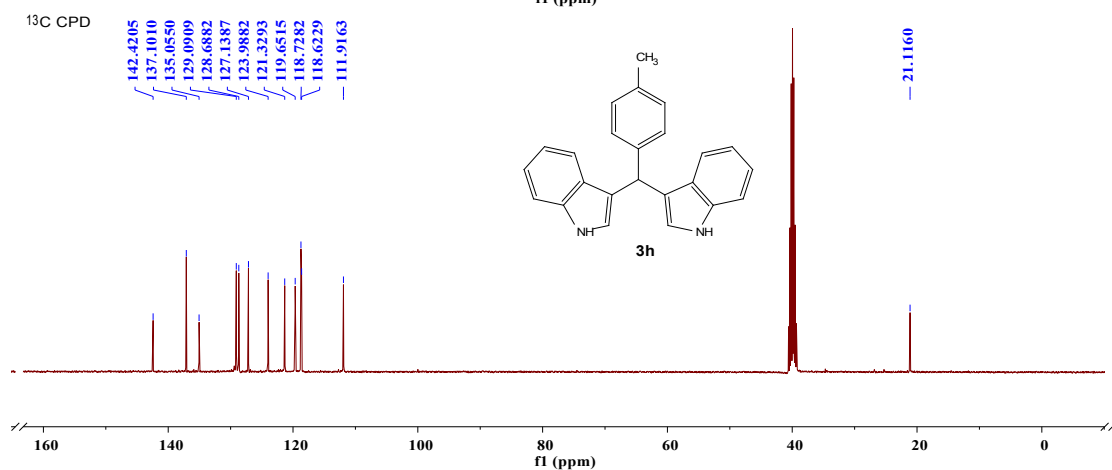
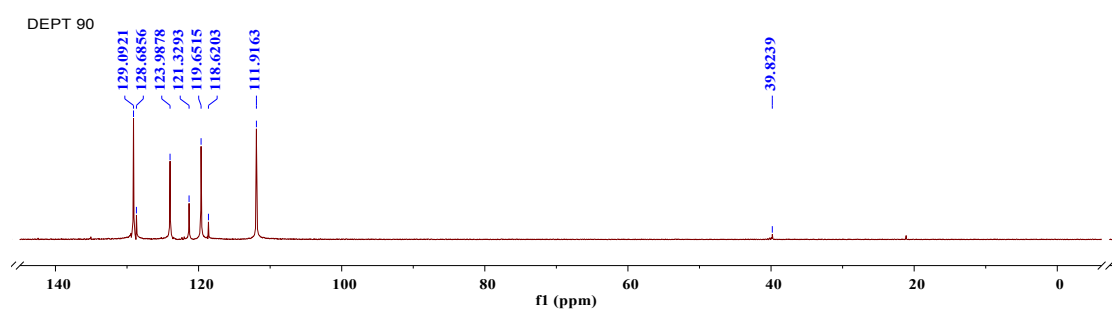
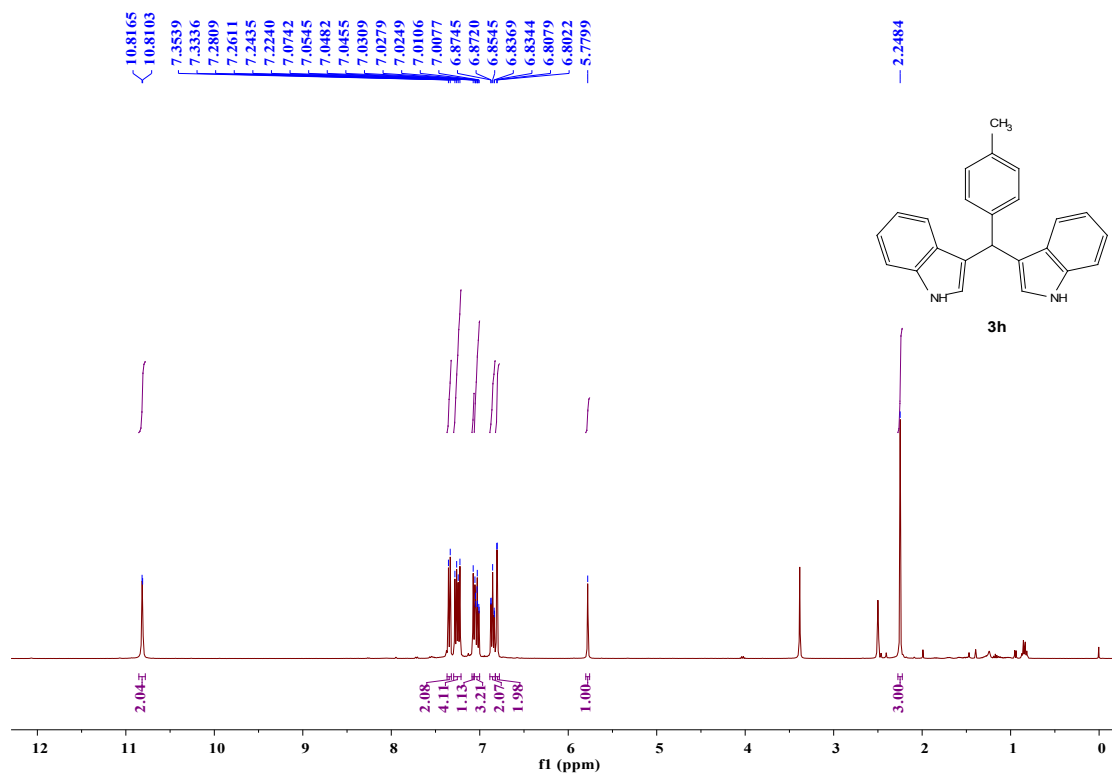


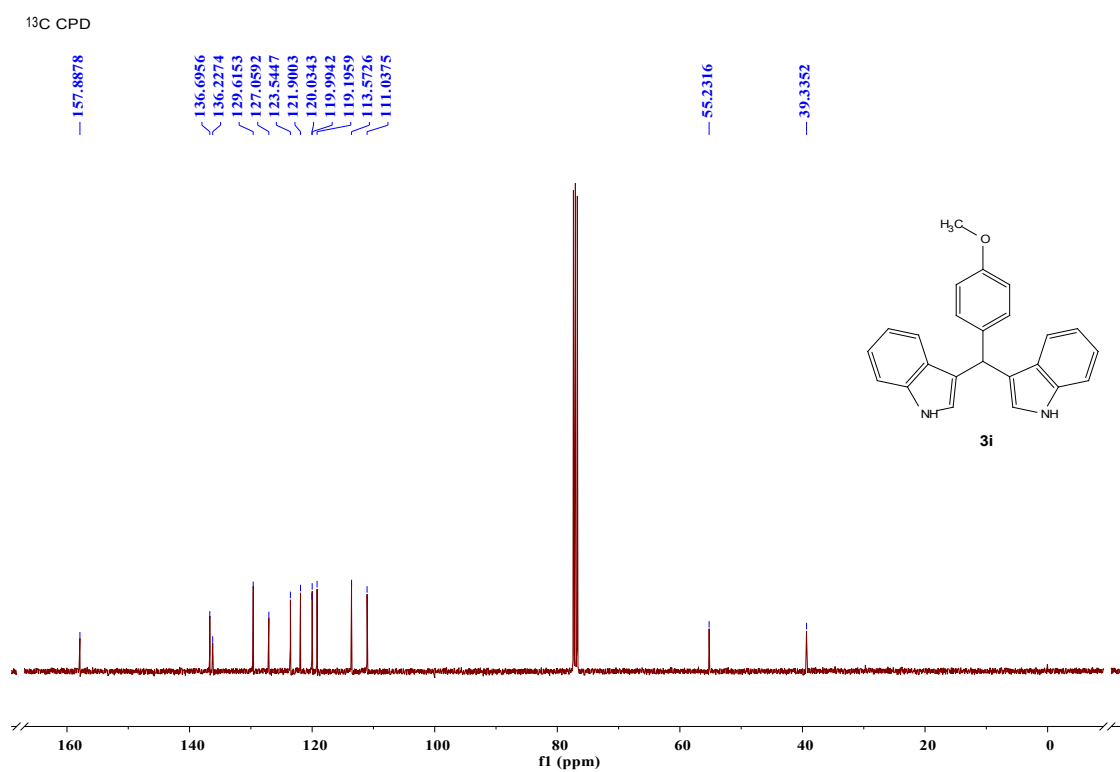
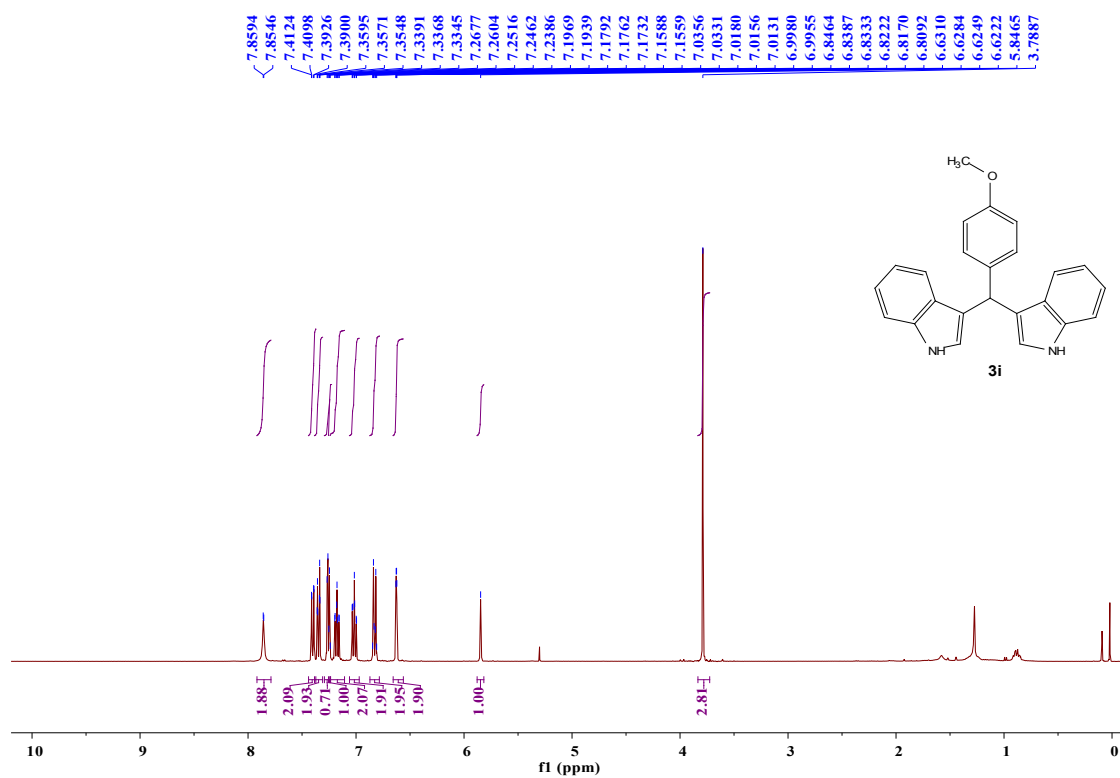


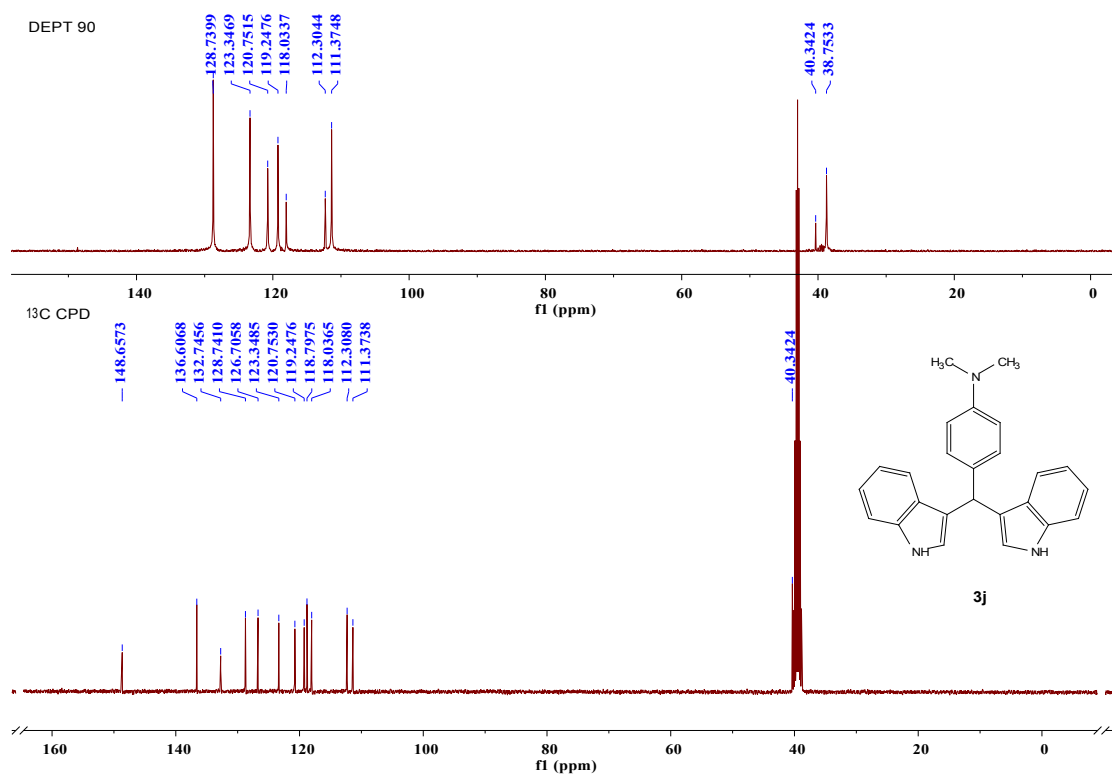
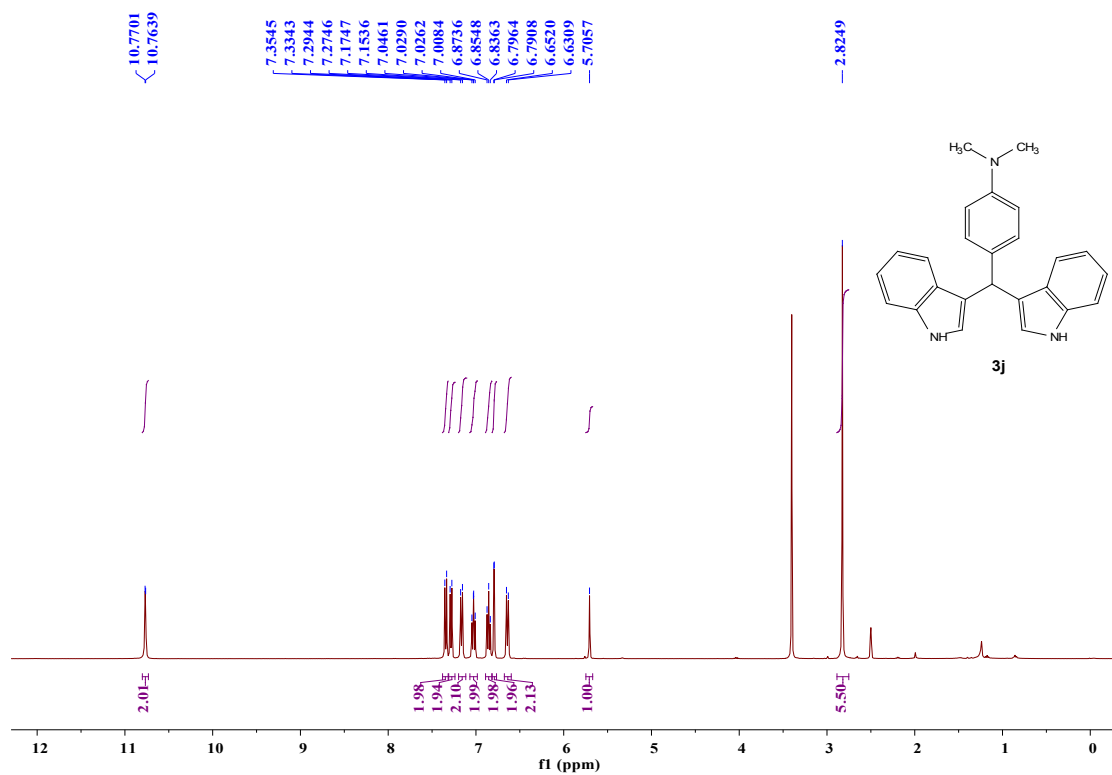


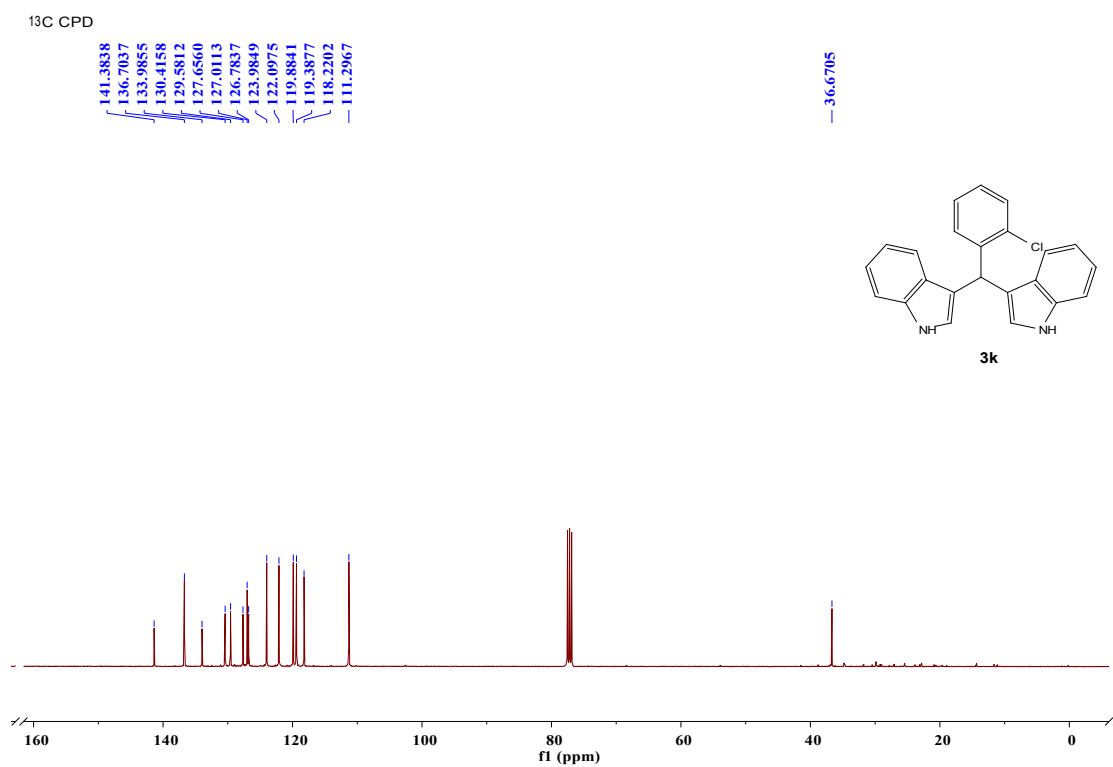
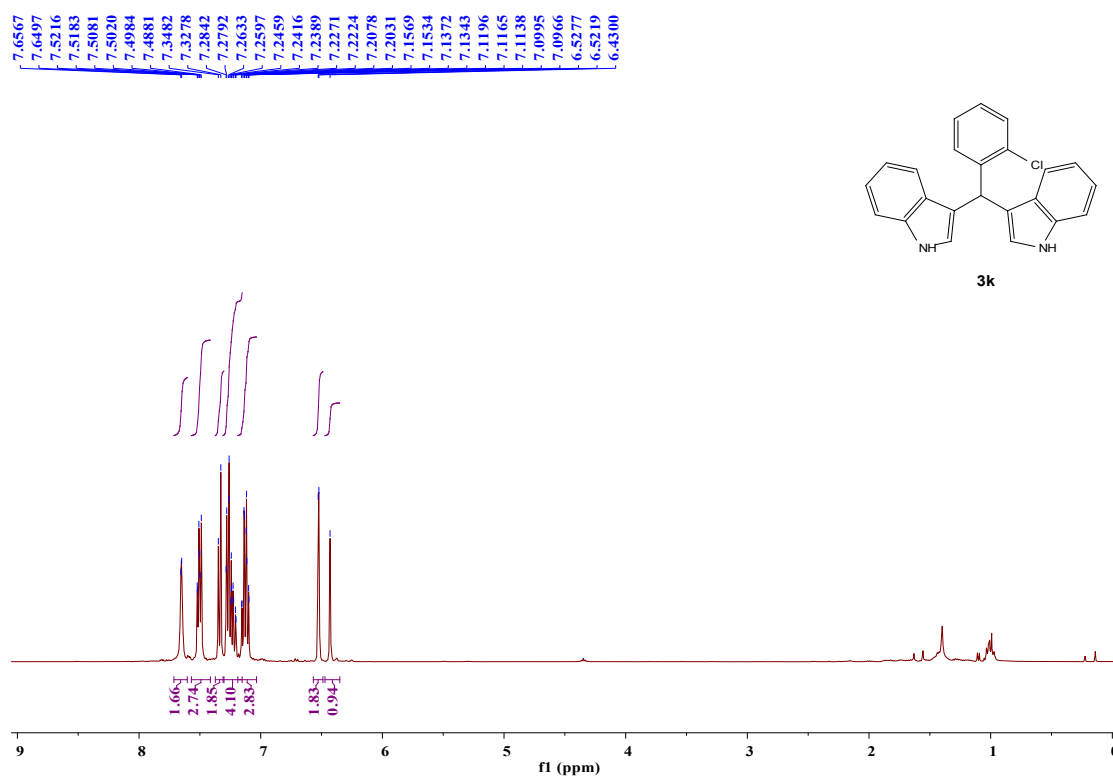


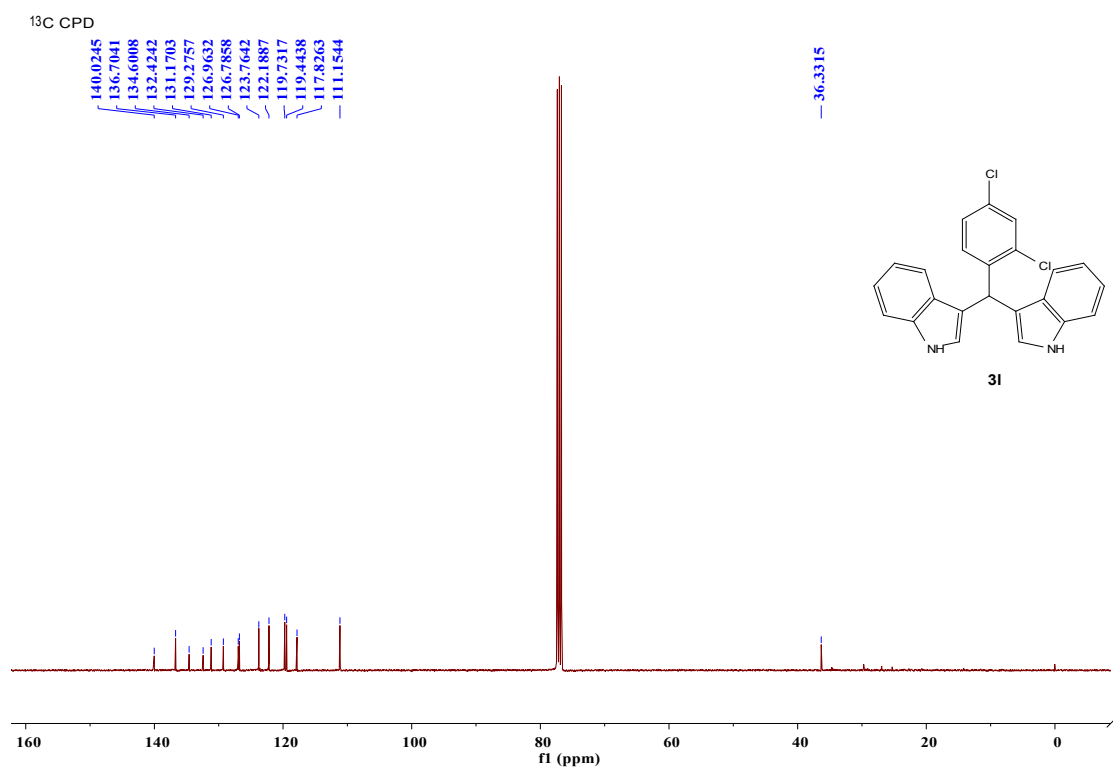
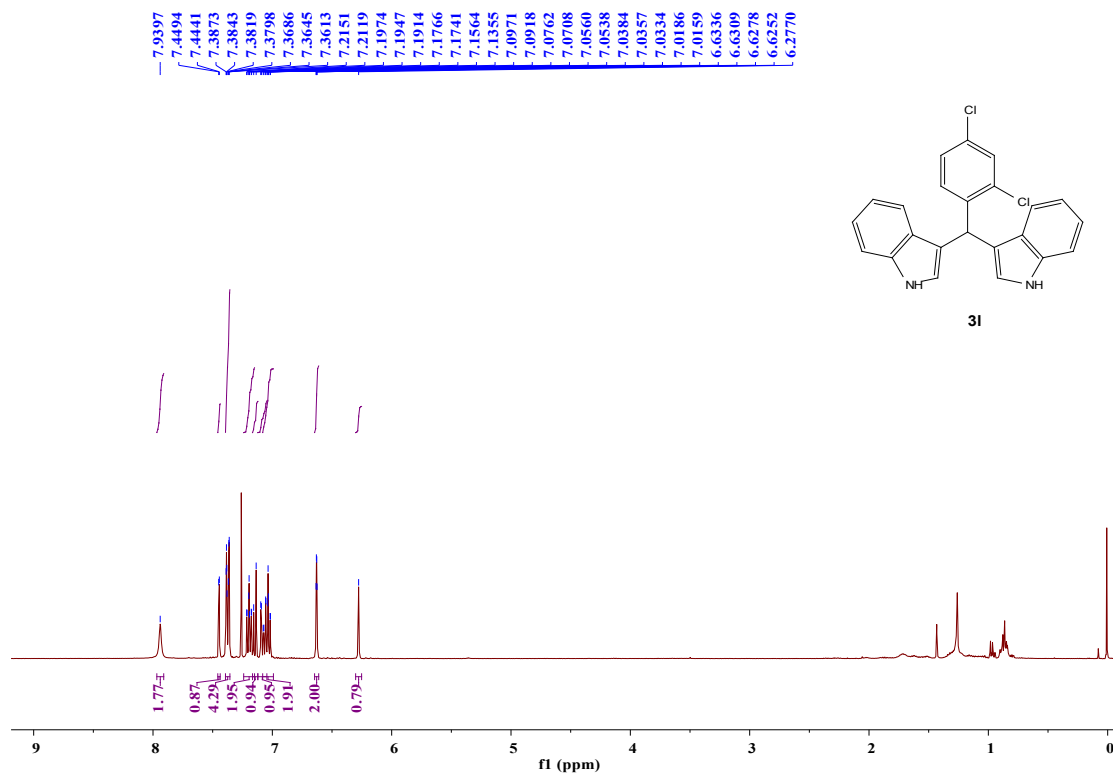


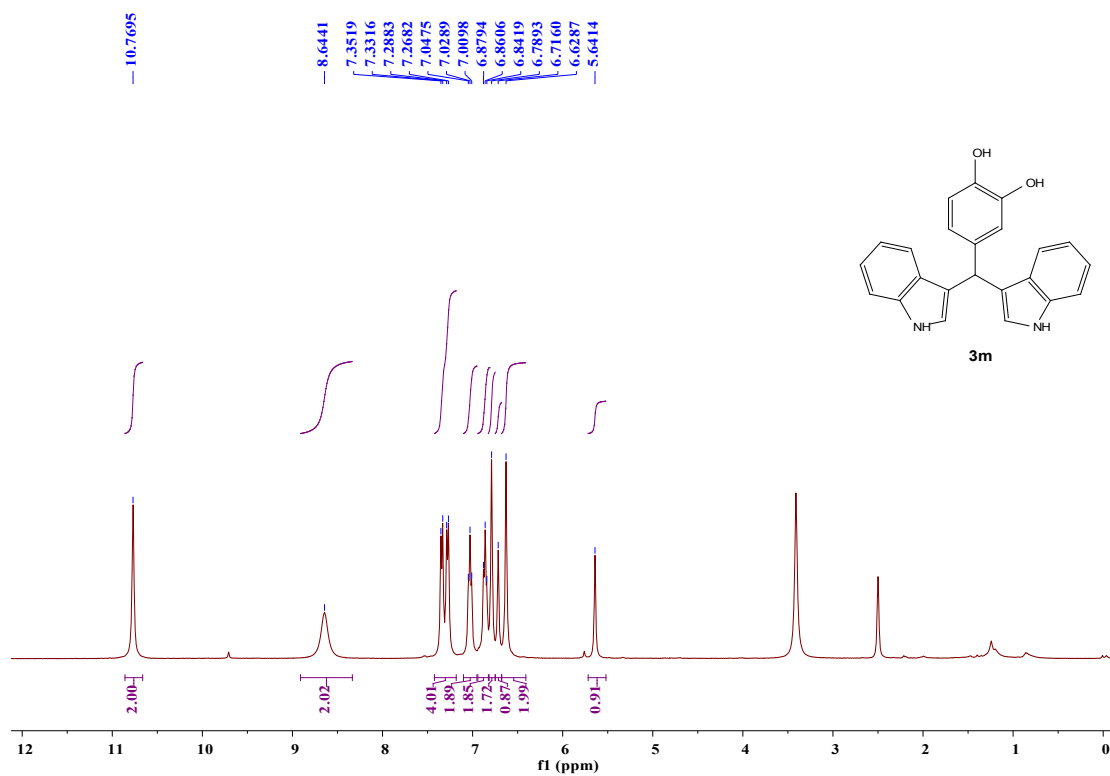
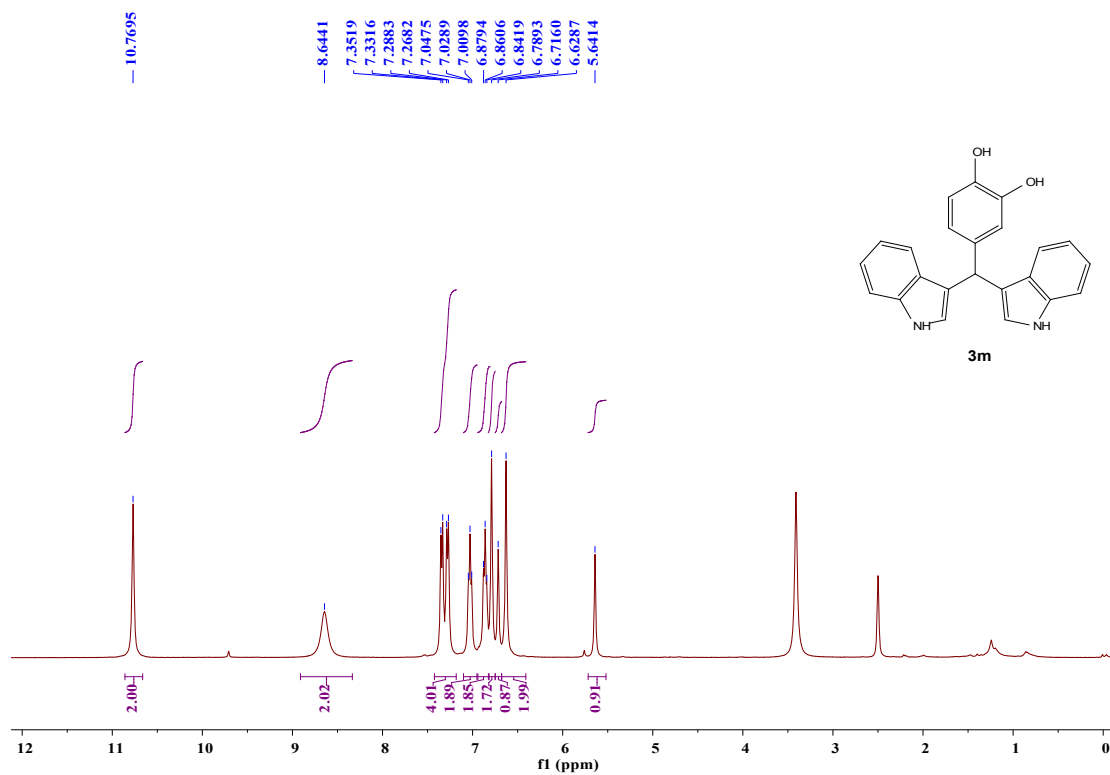


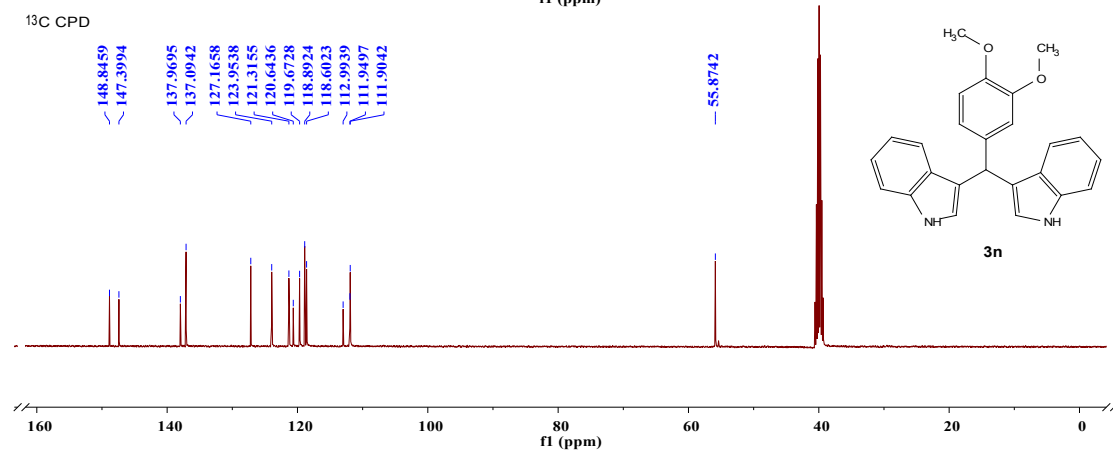
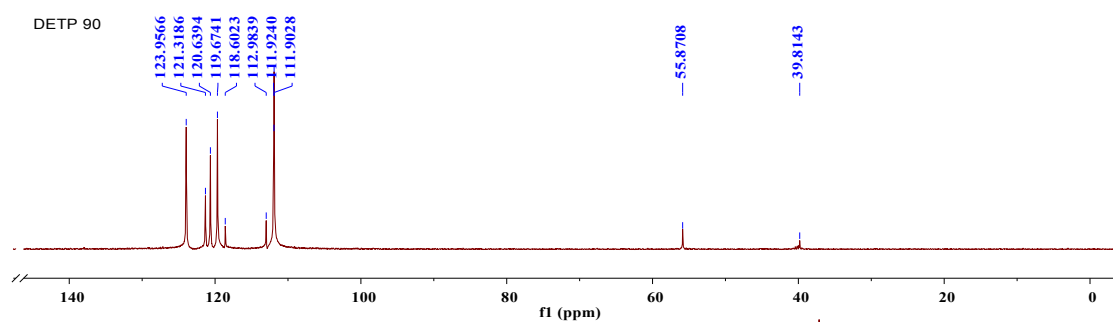
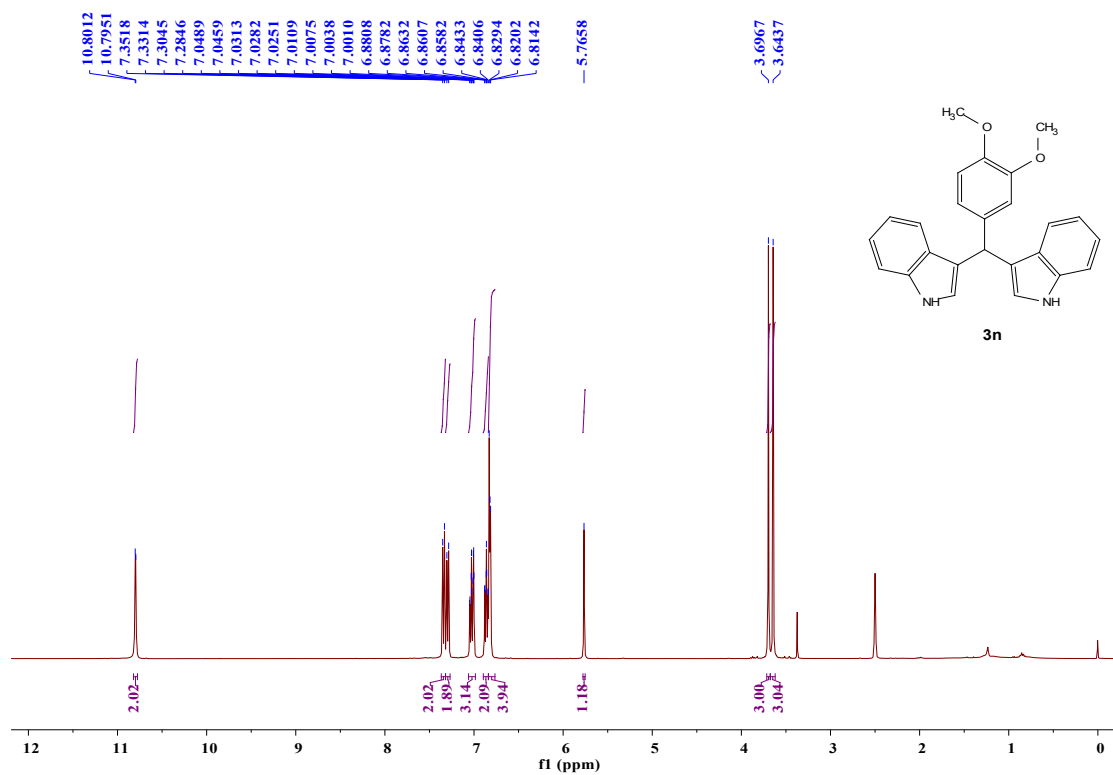


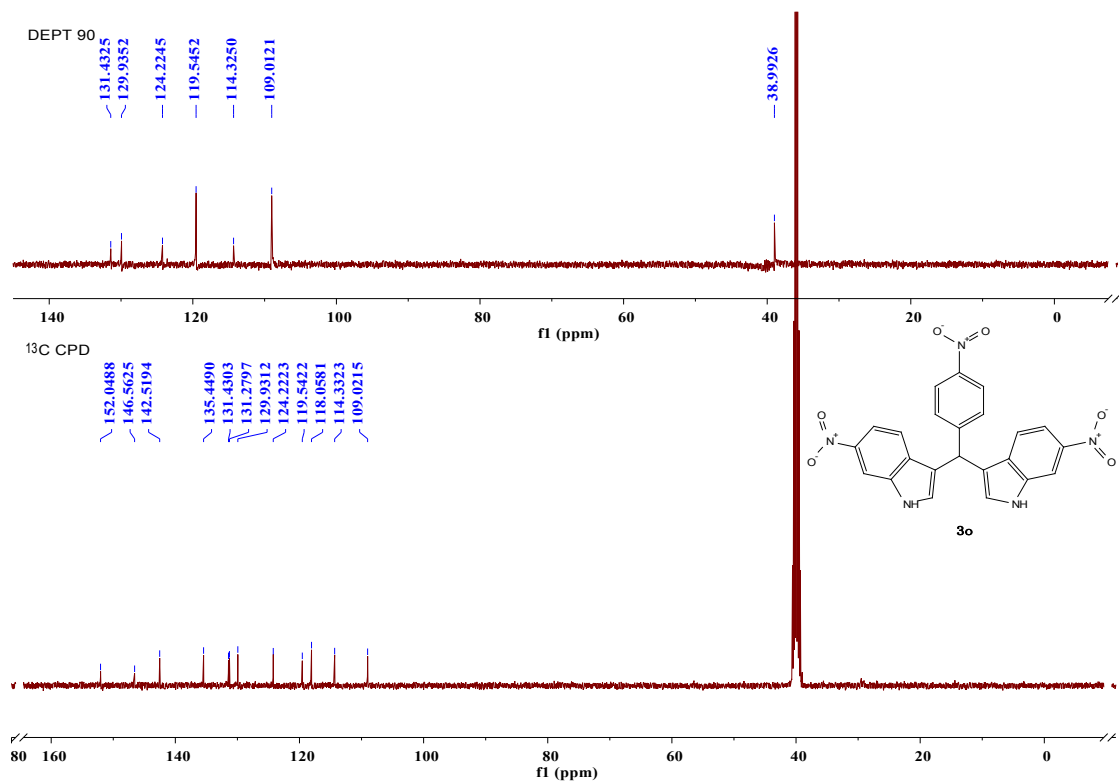
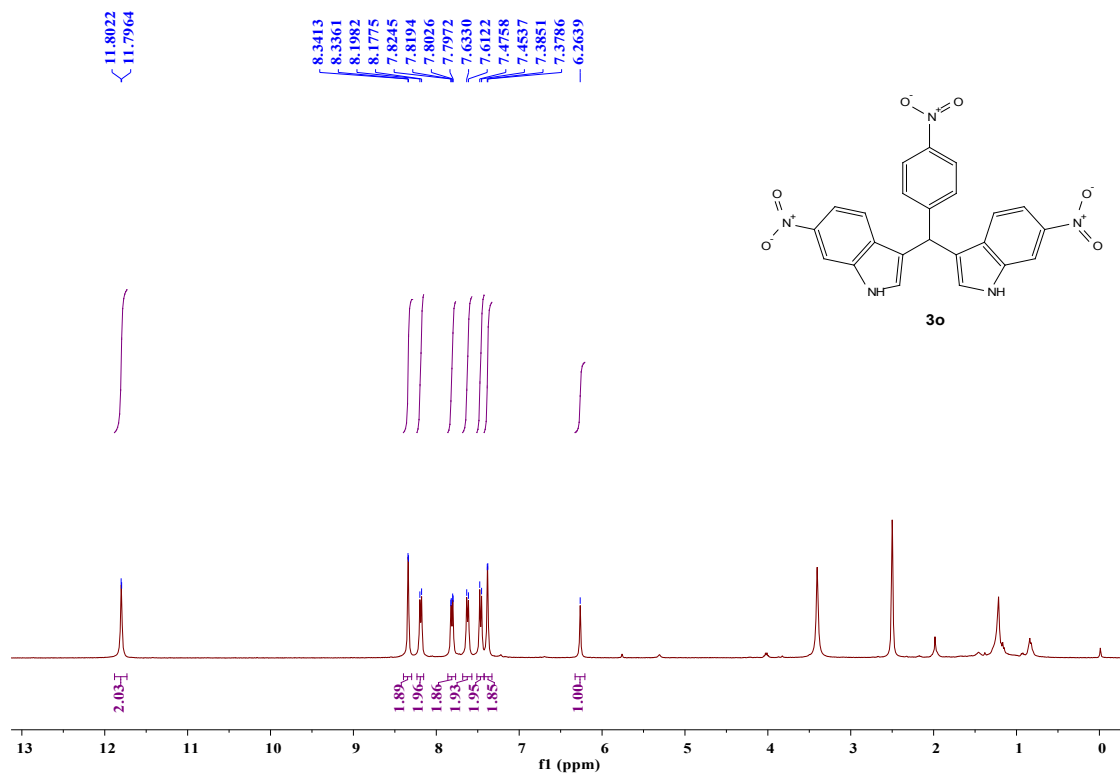


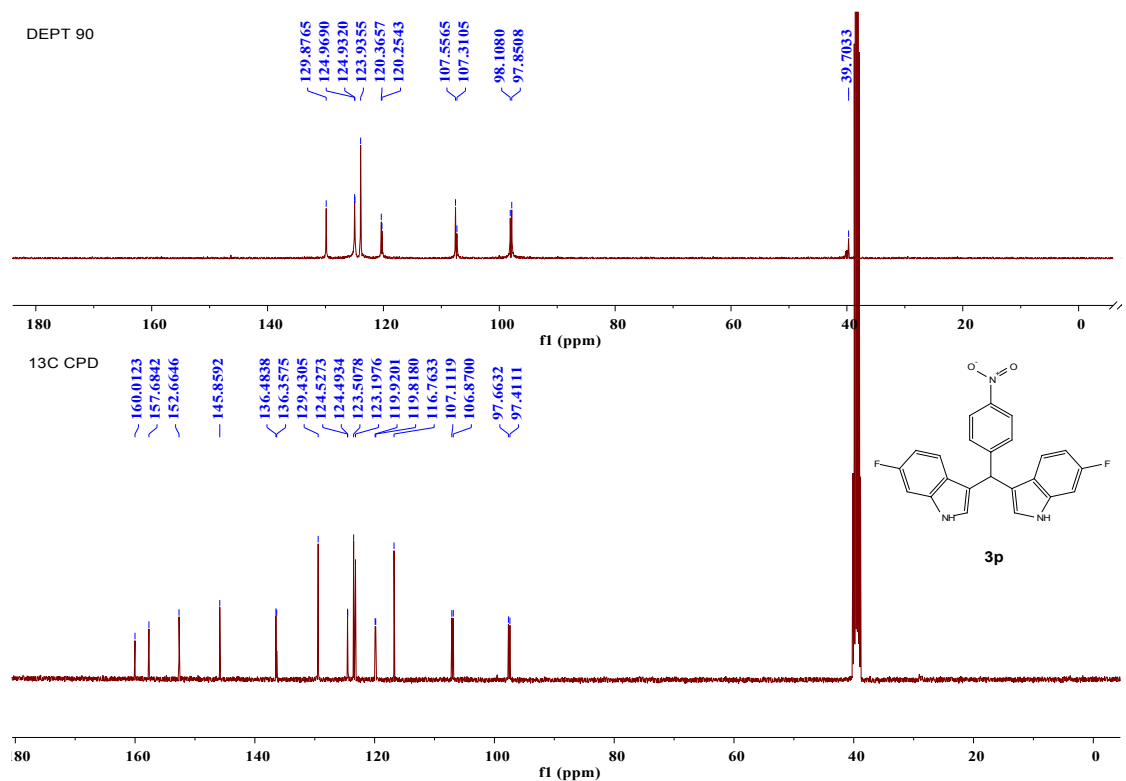
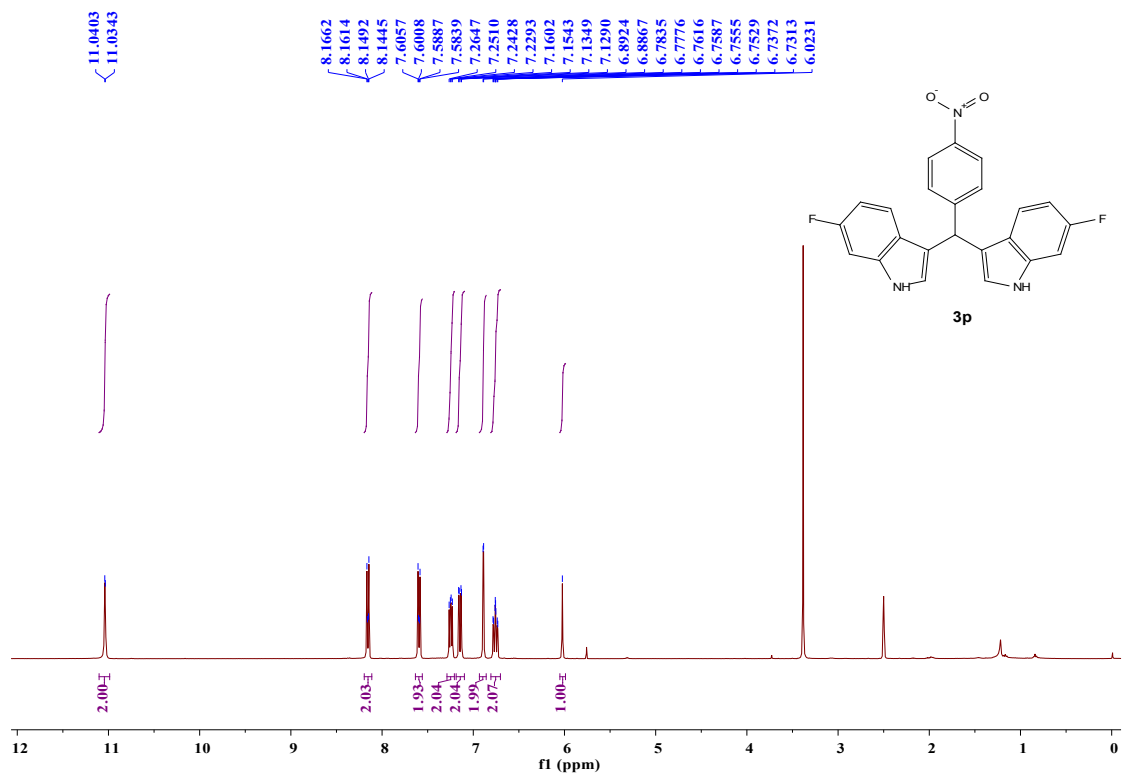


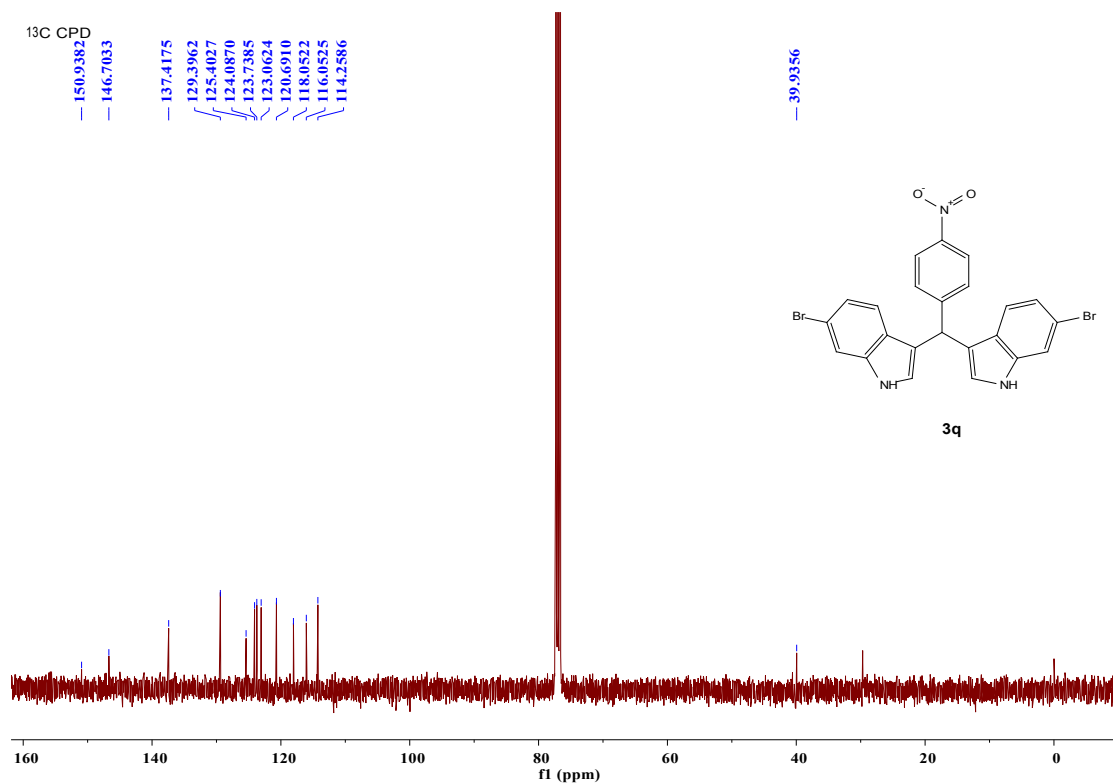
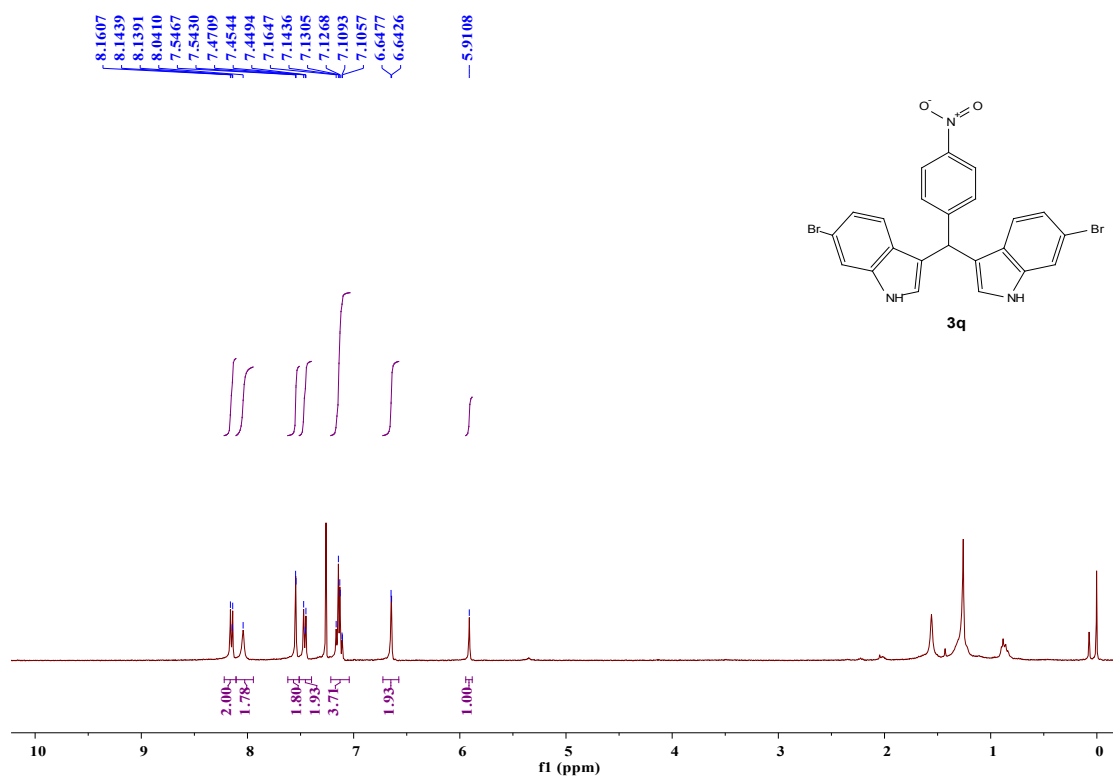


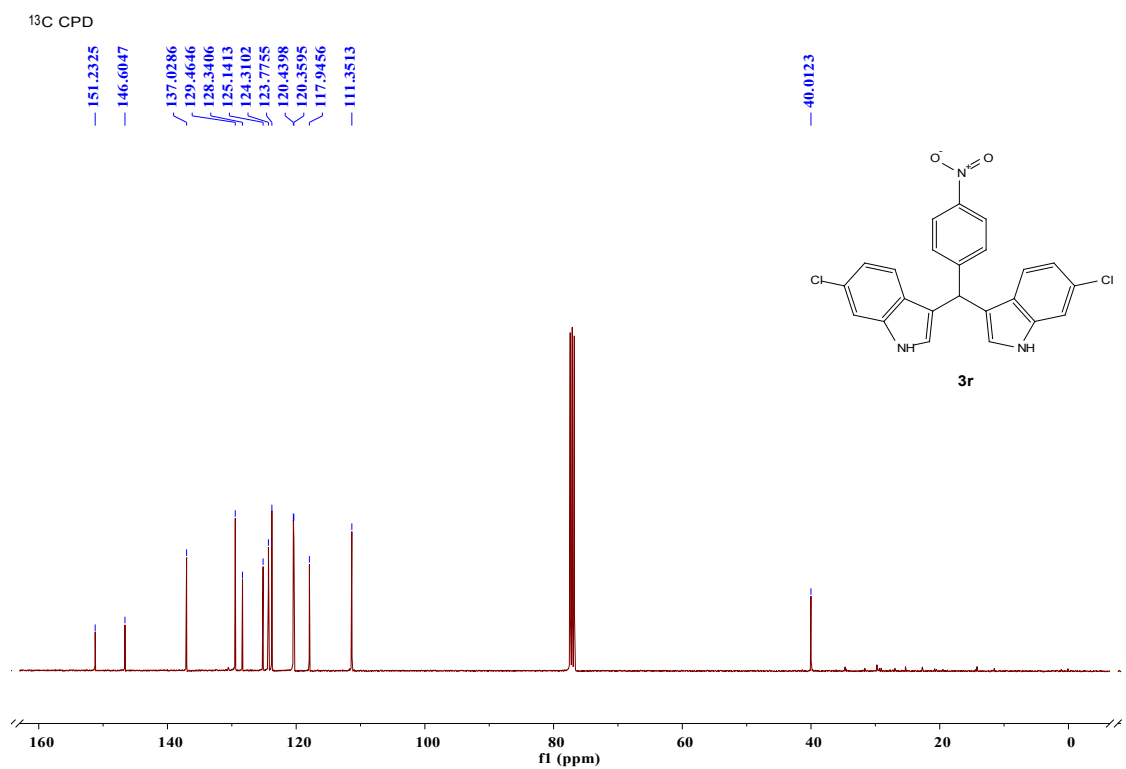
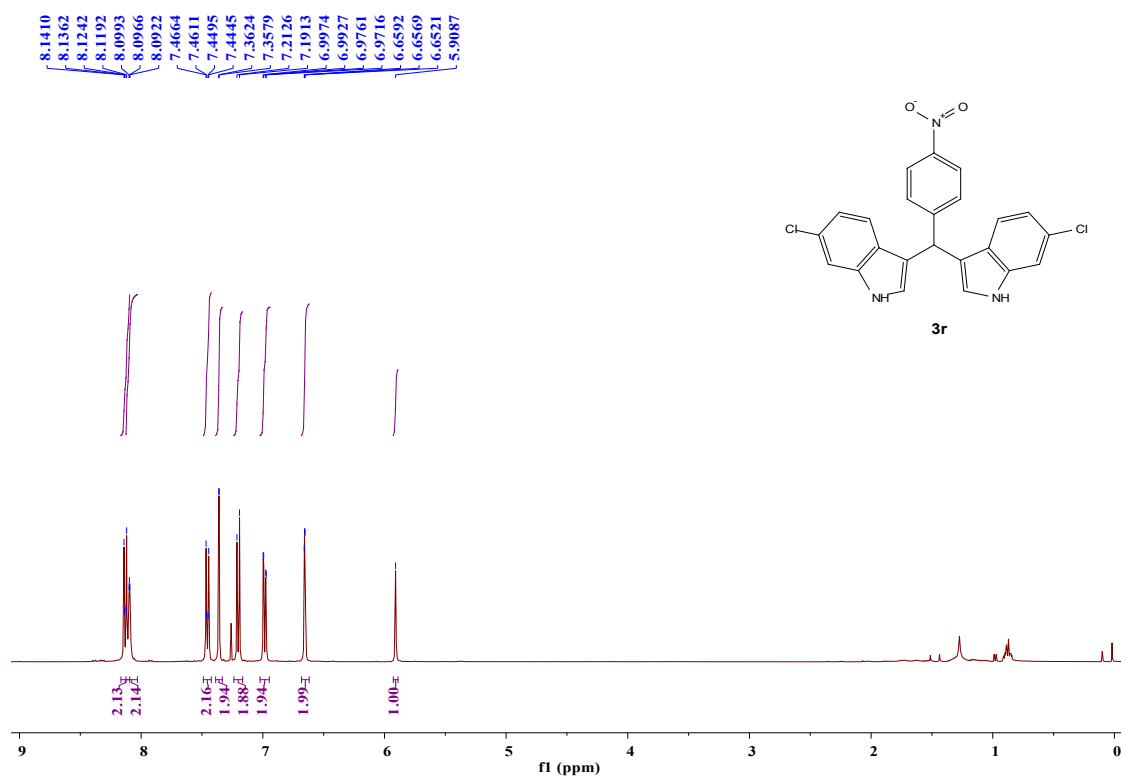


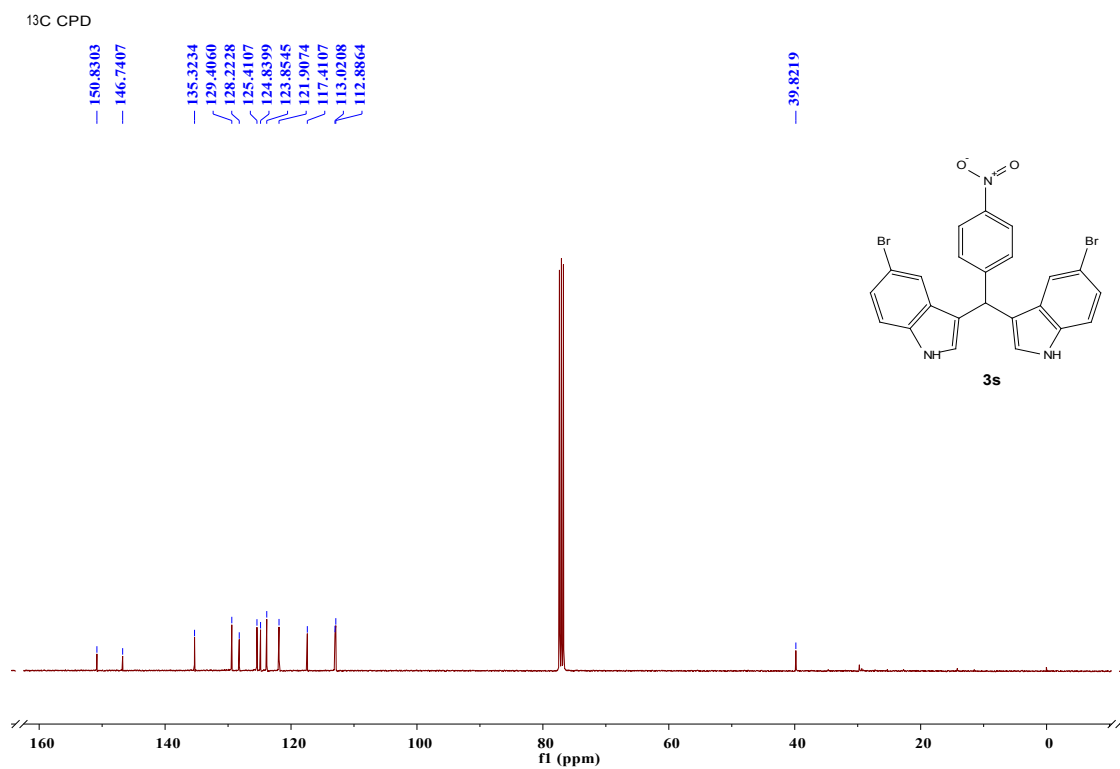
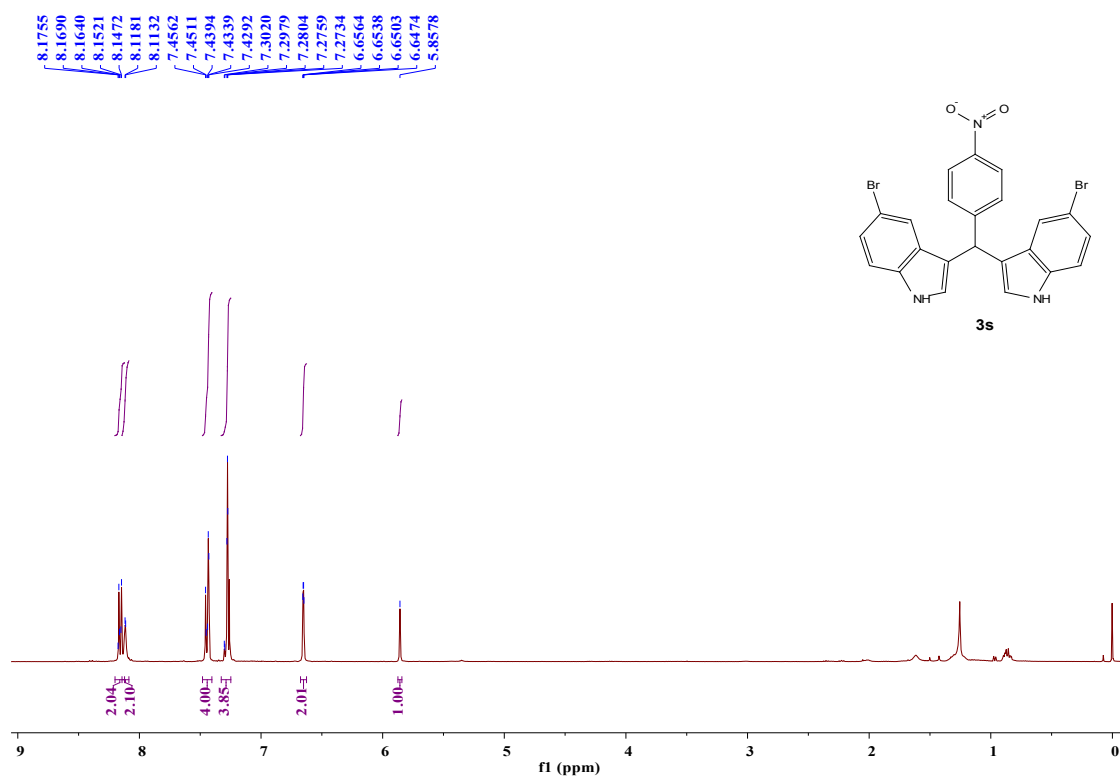


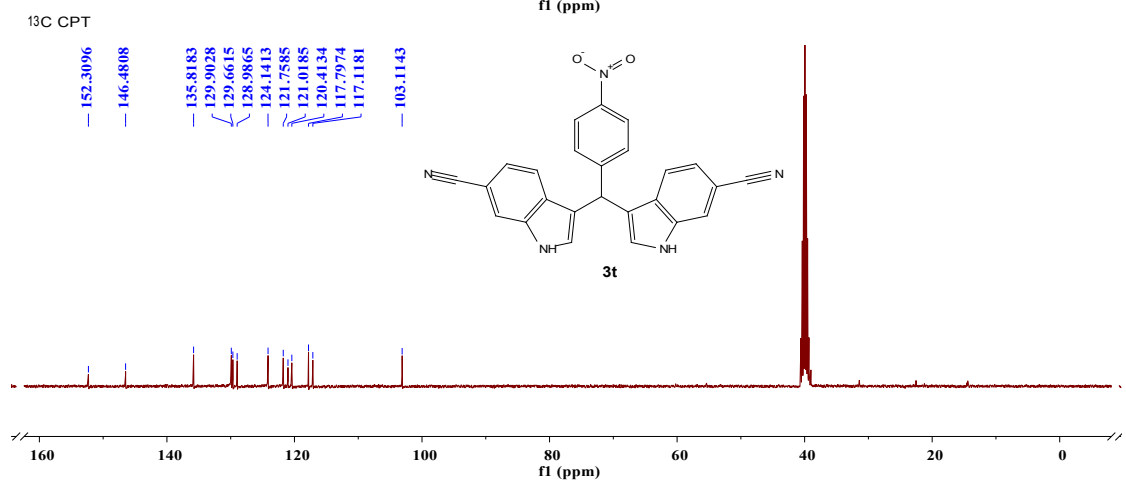
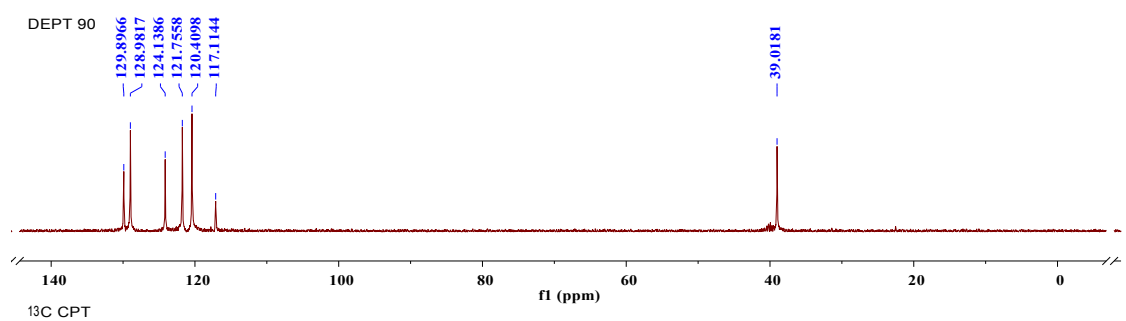
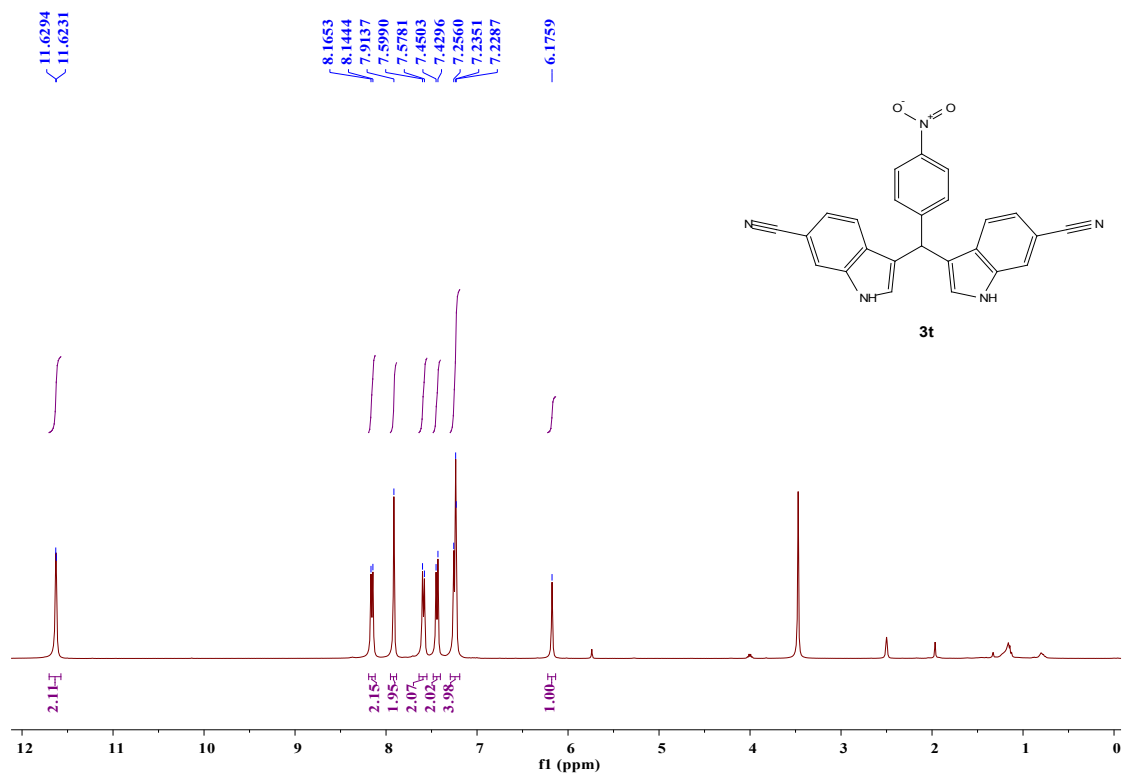


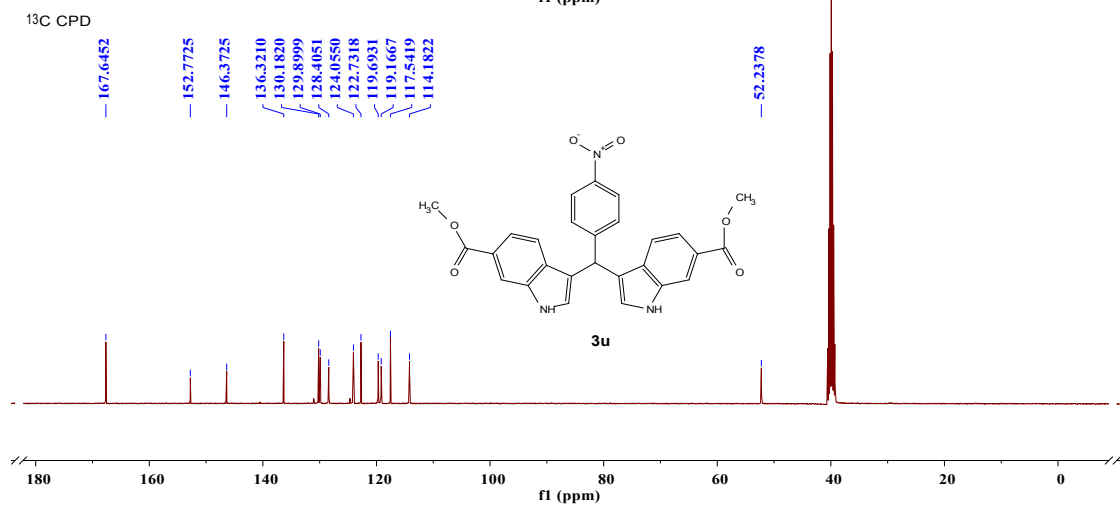
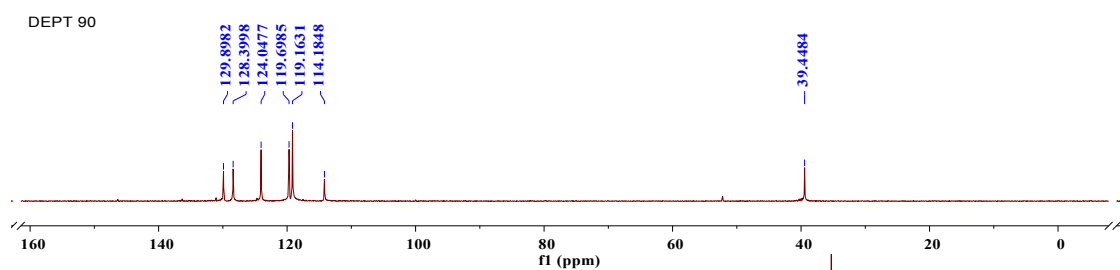
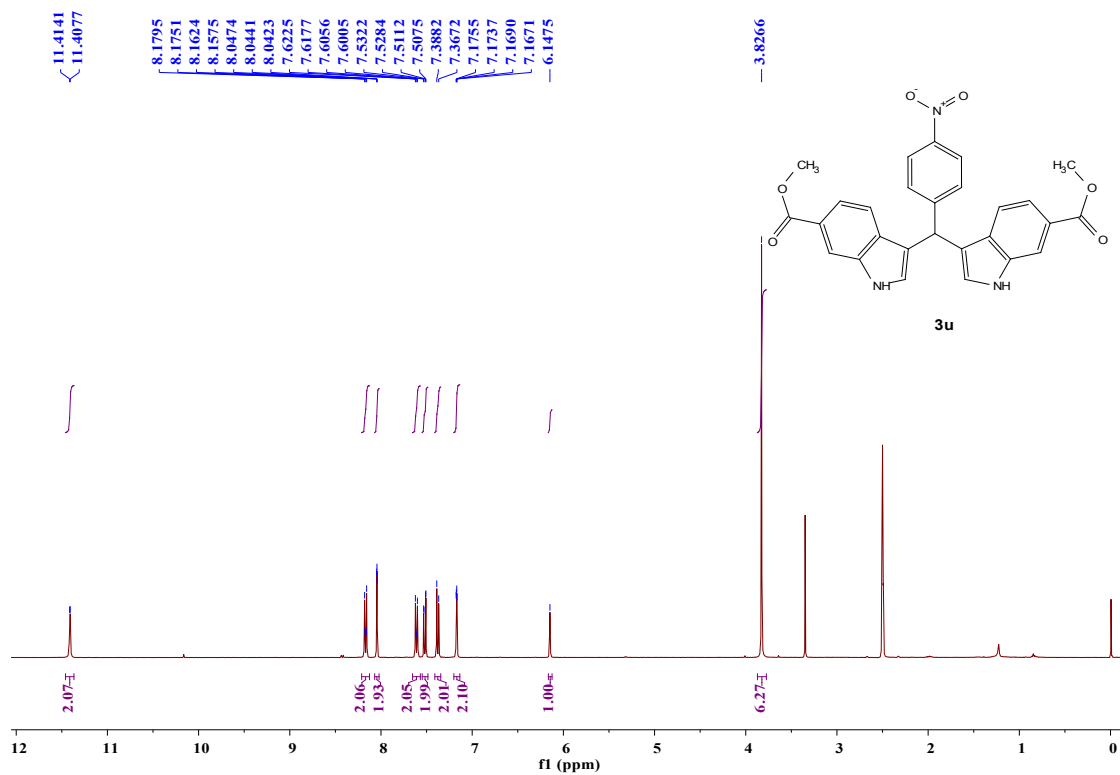


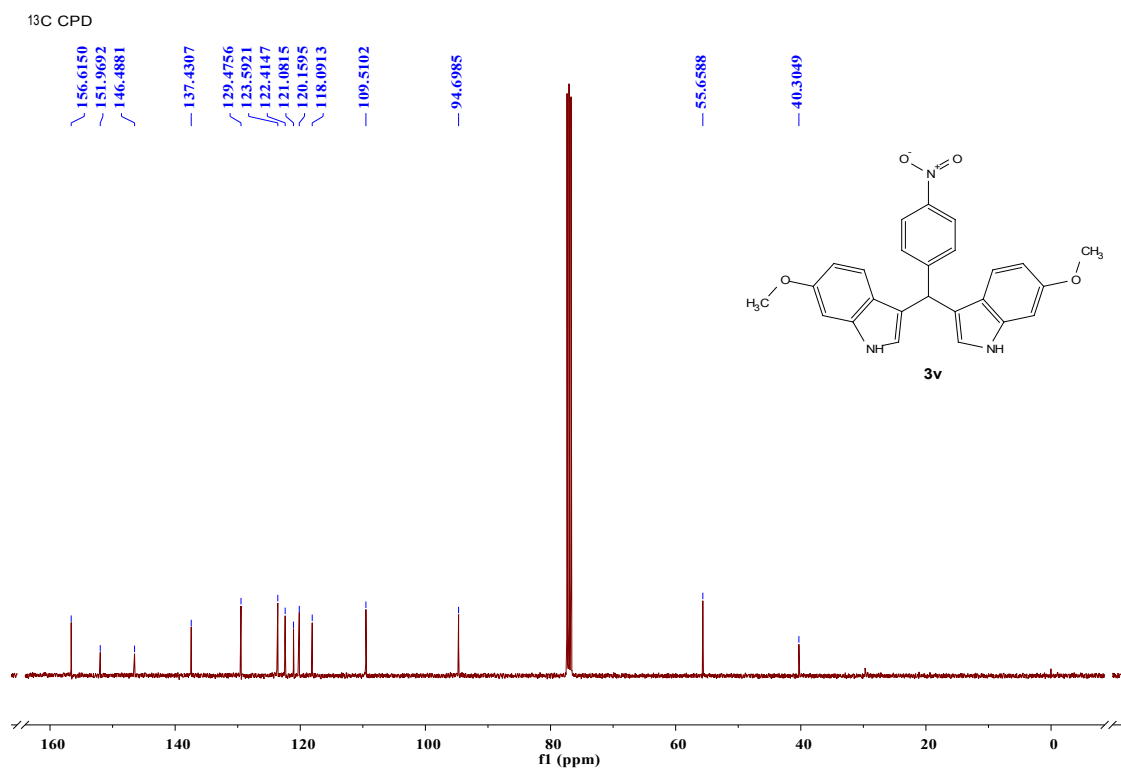
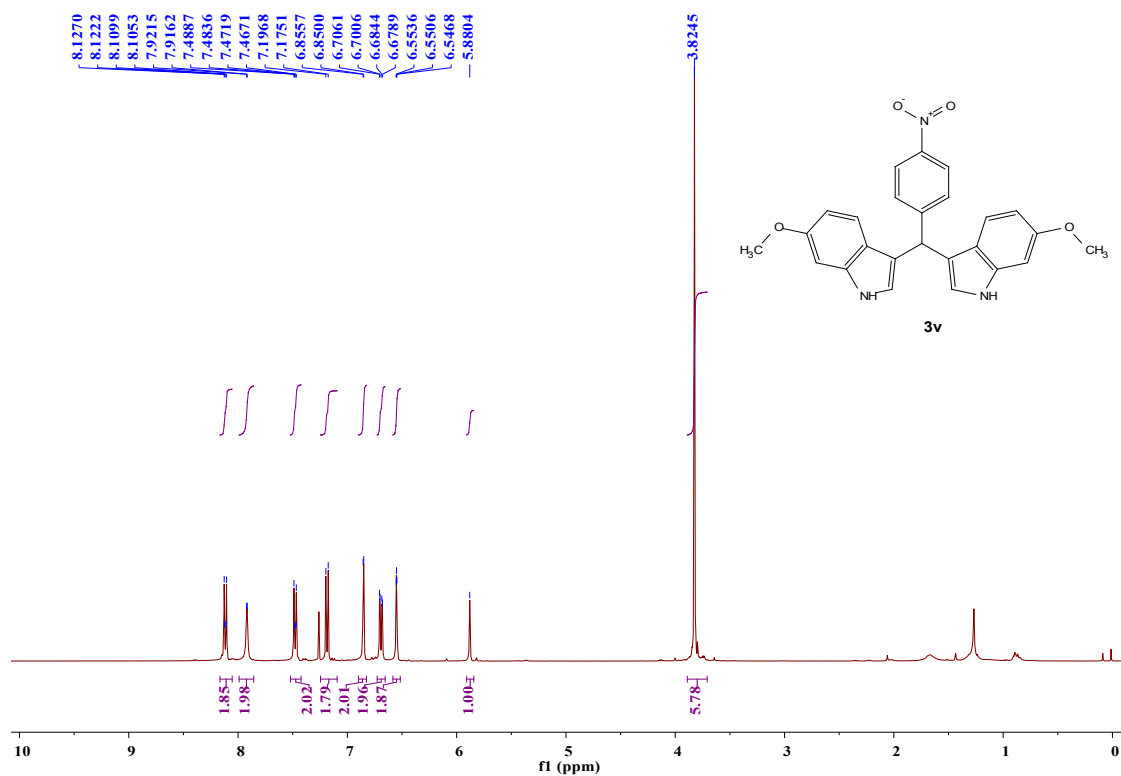




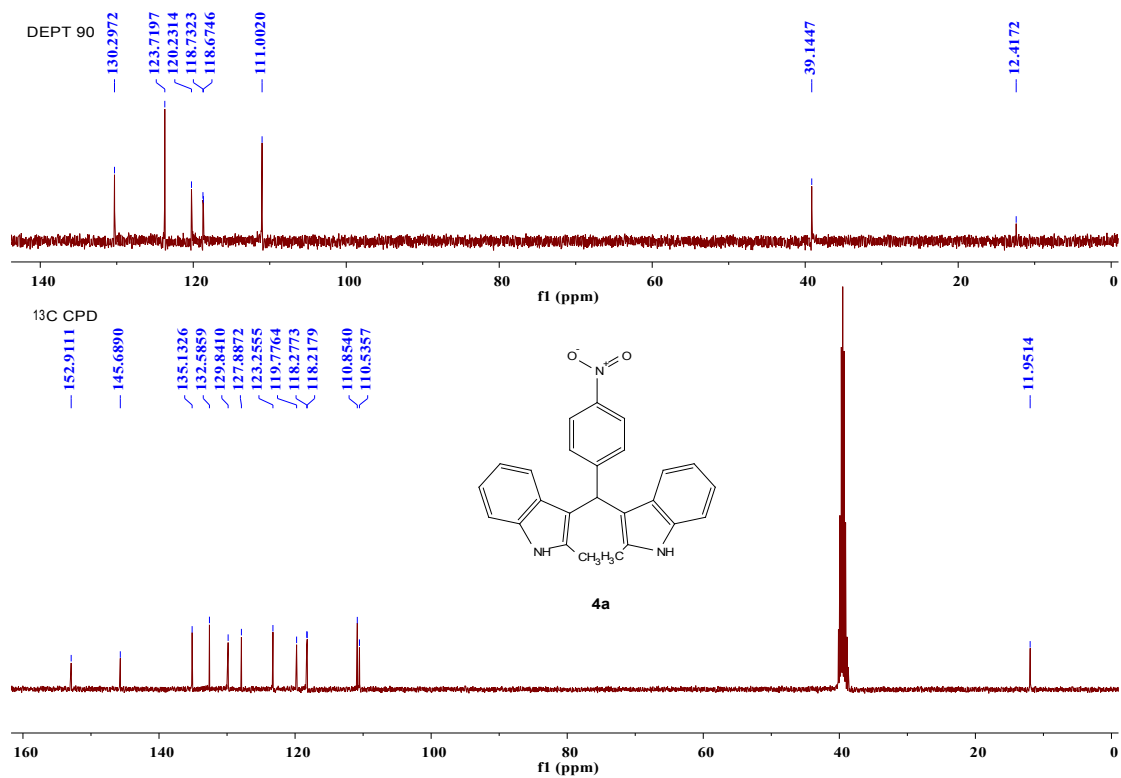
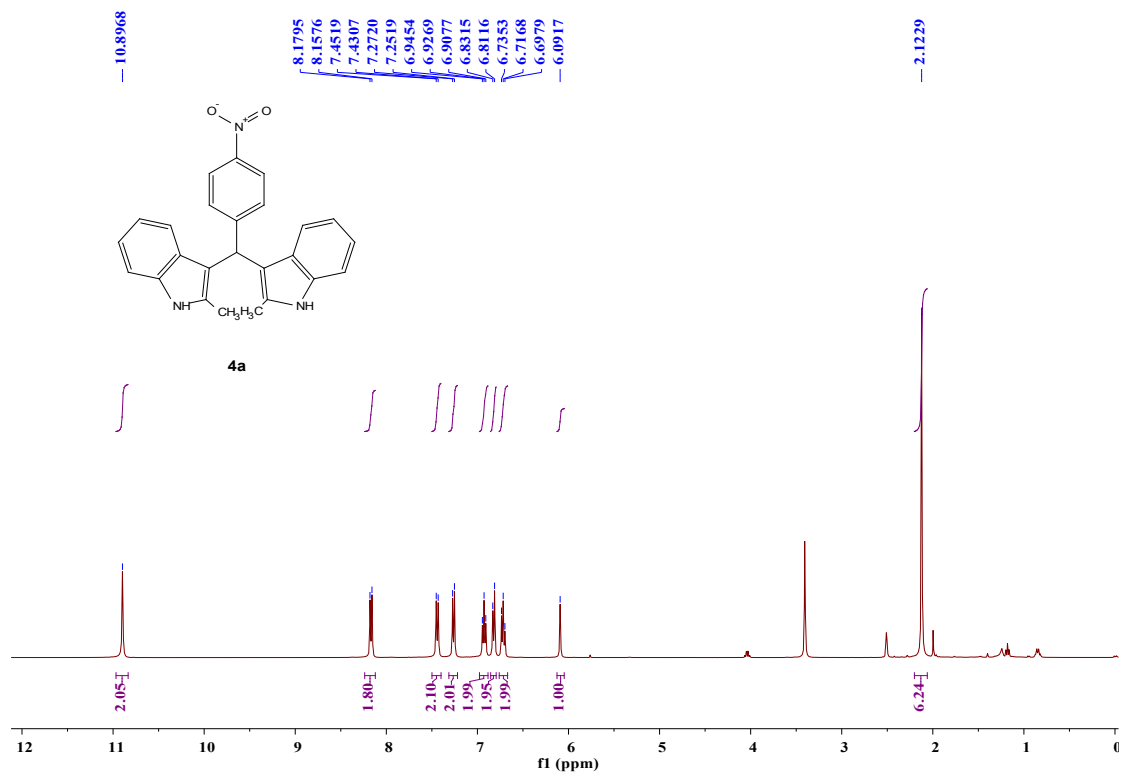


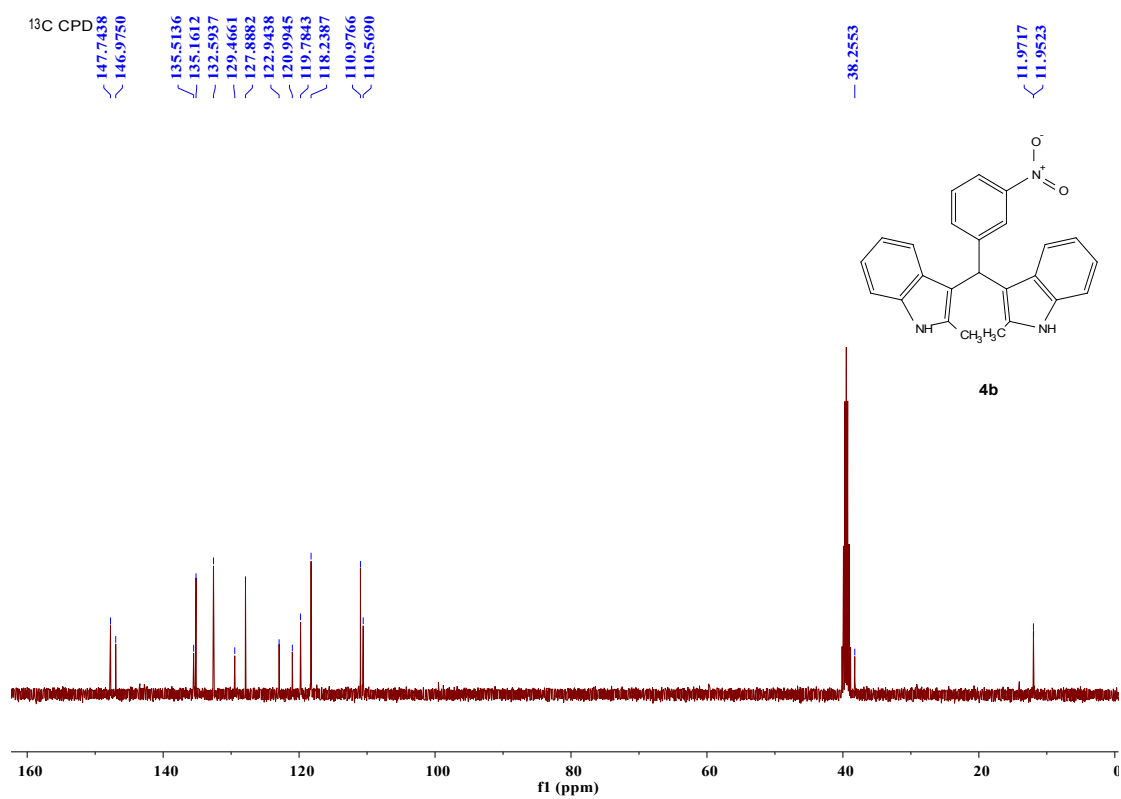
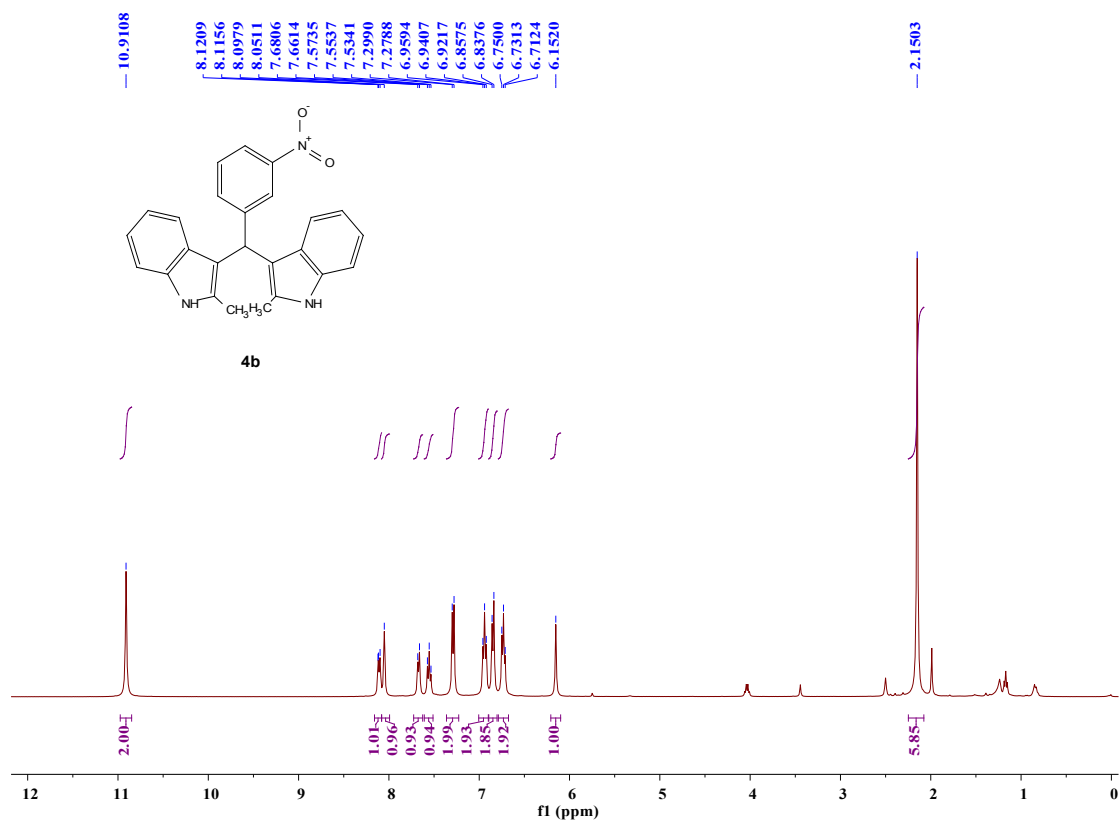


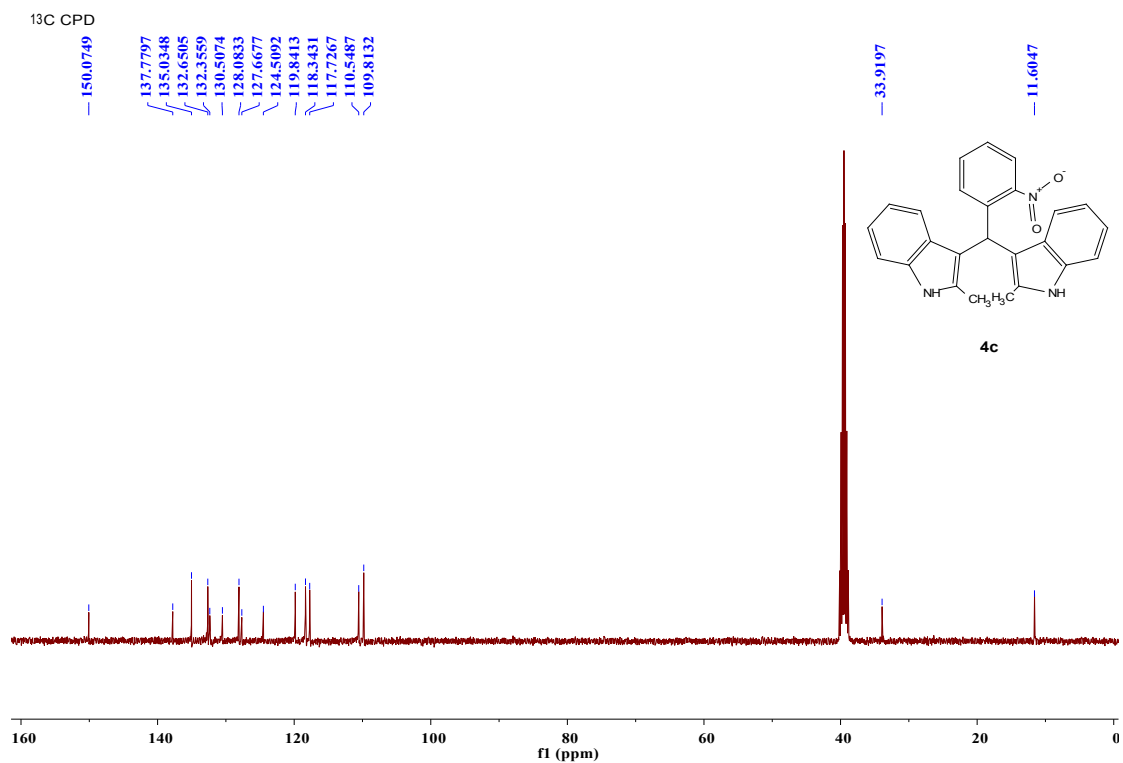
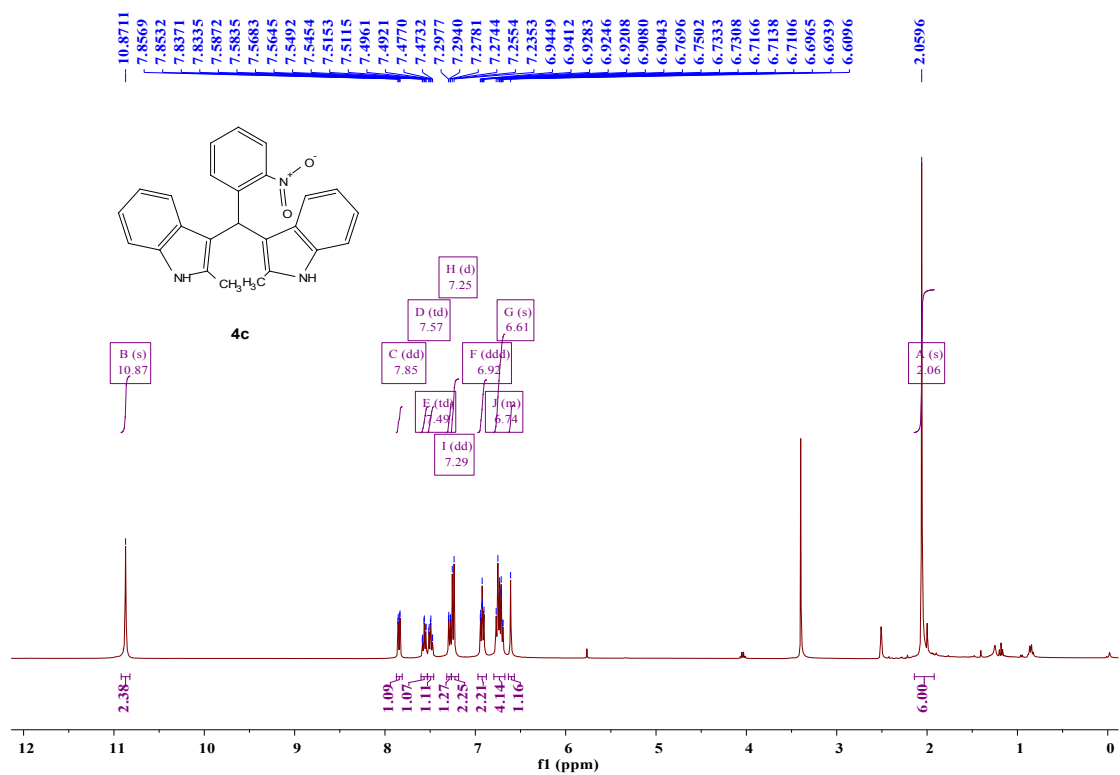


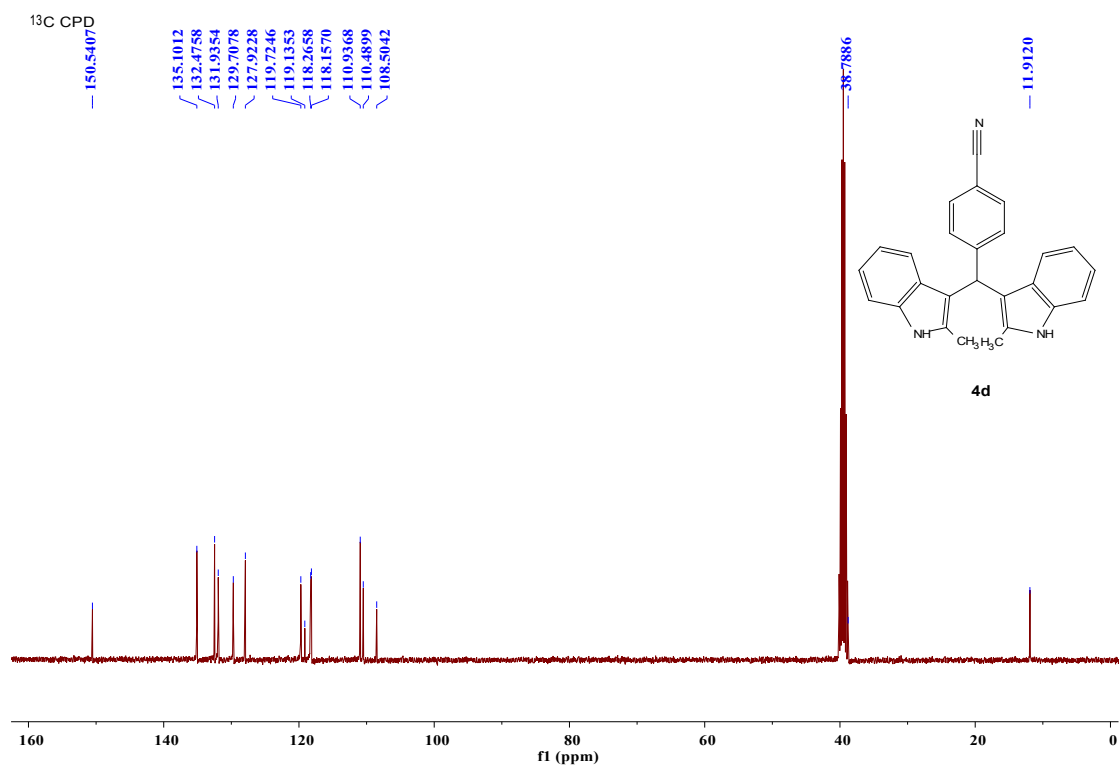
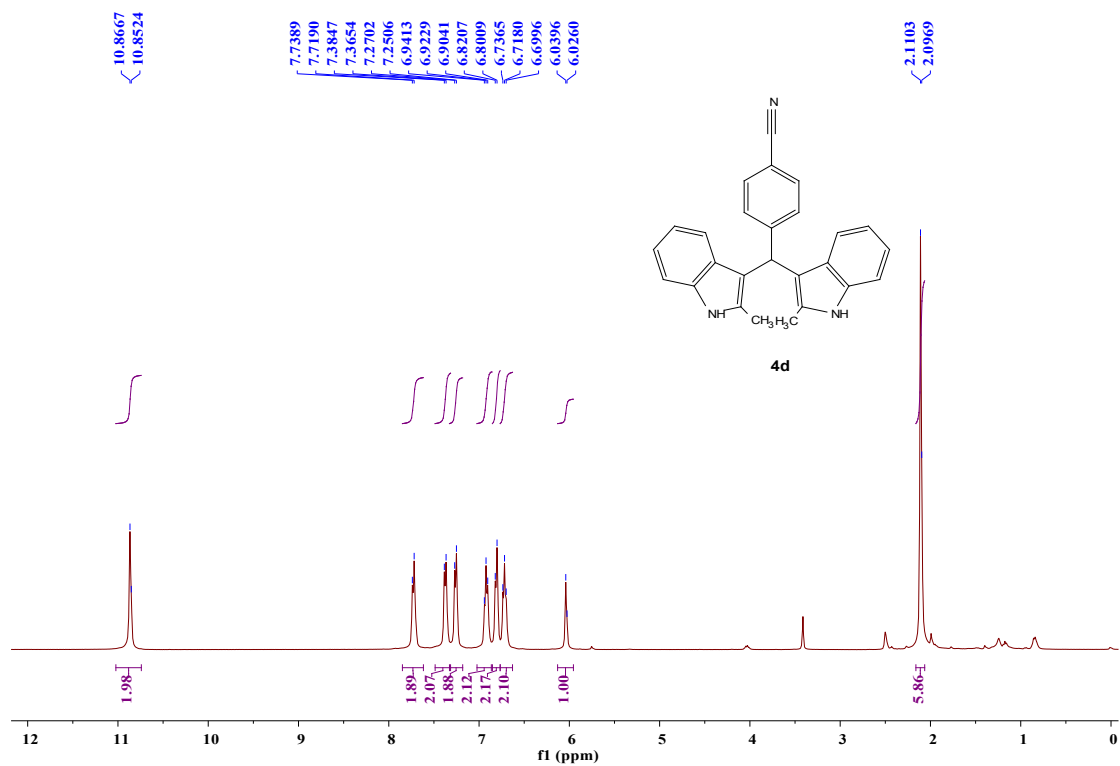


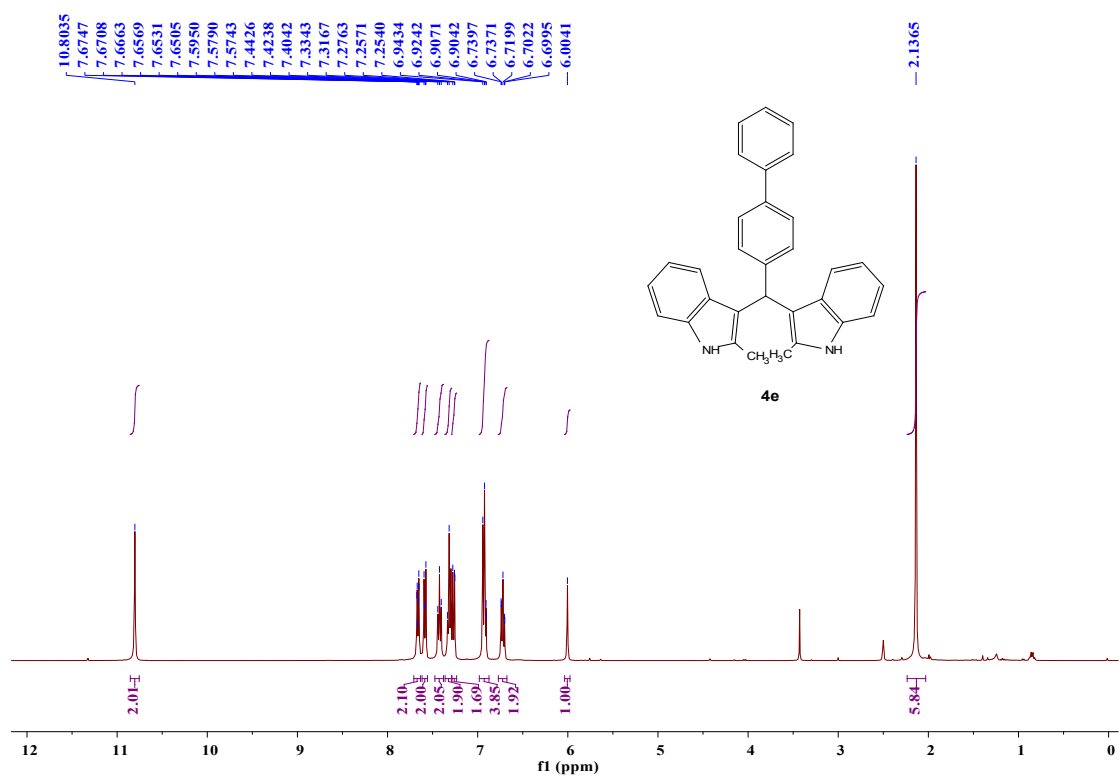
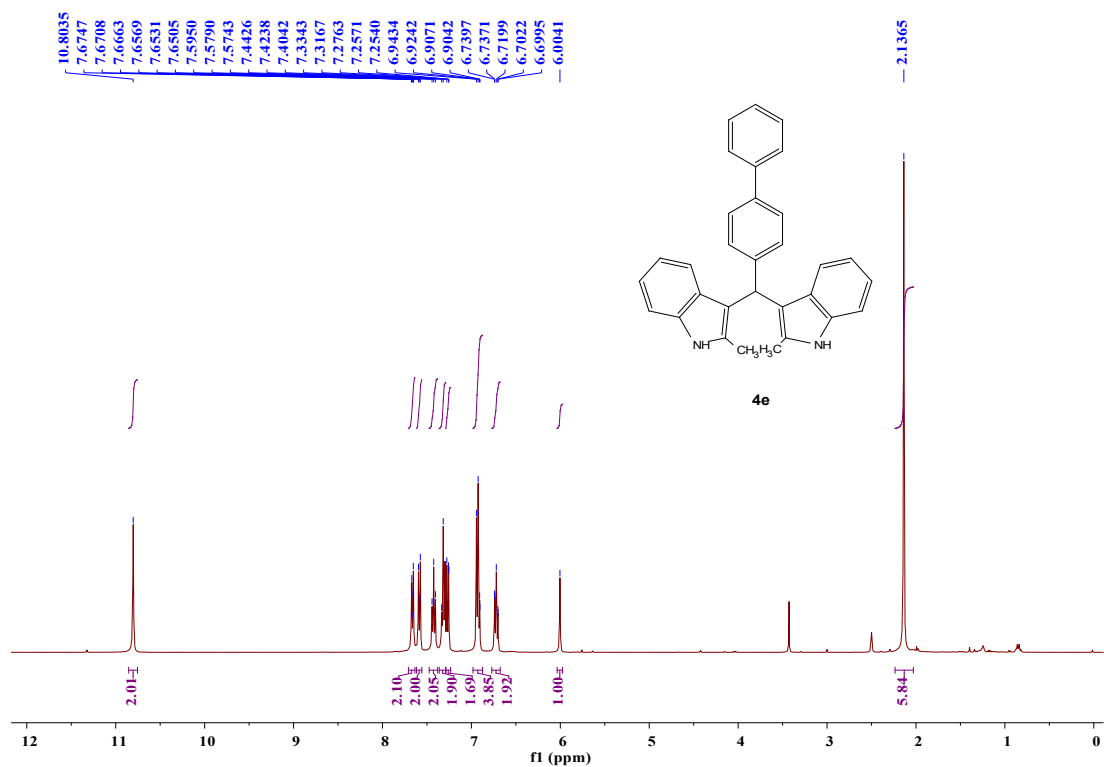
NMR spectra for all compounds **4a-4h** and **5a**

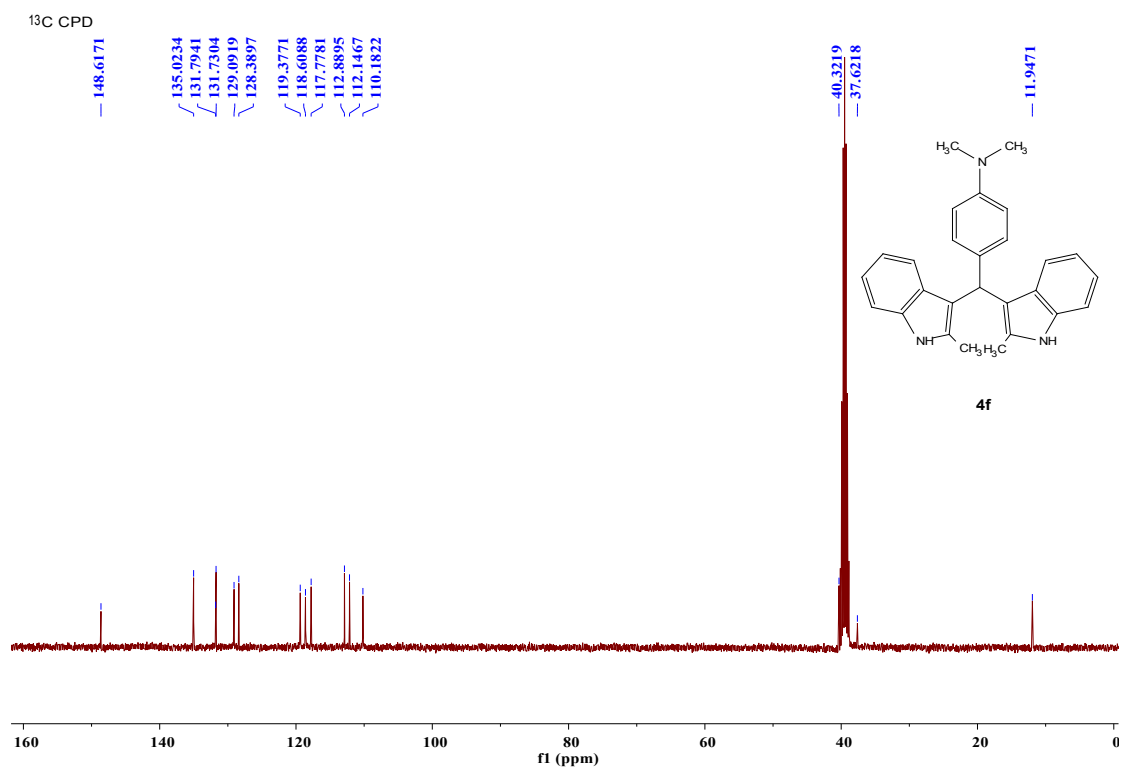
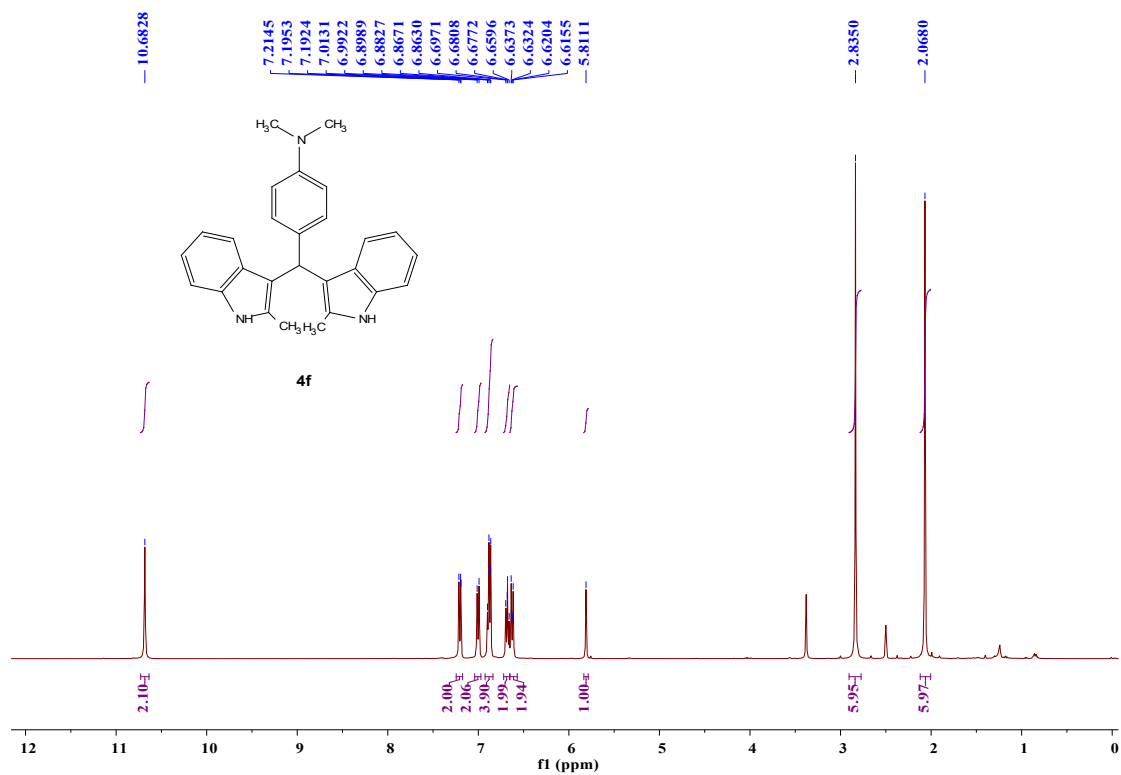


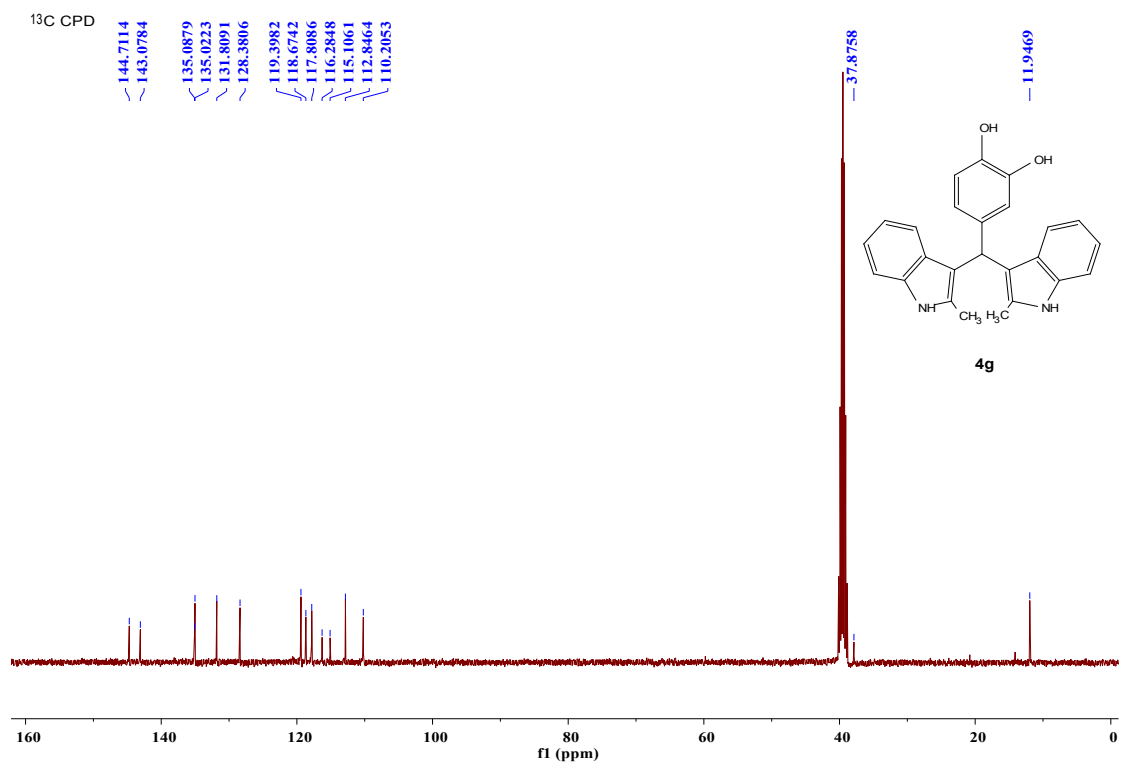
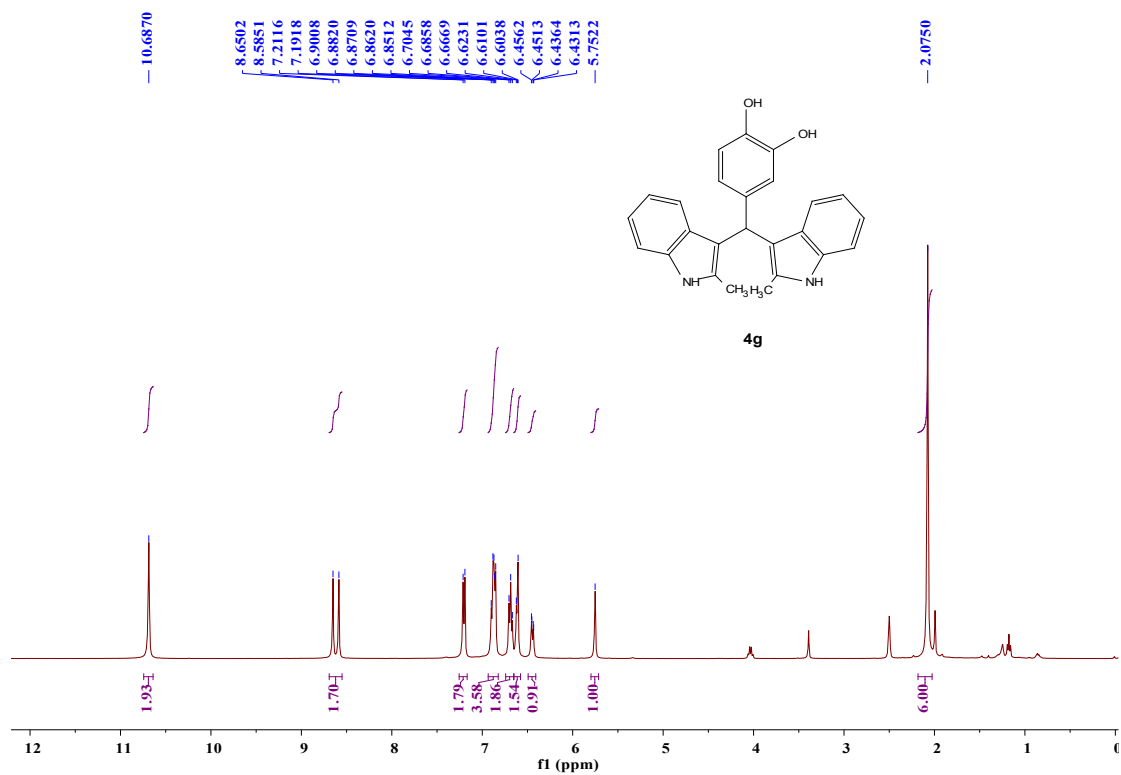


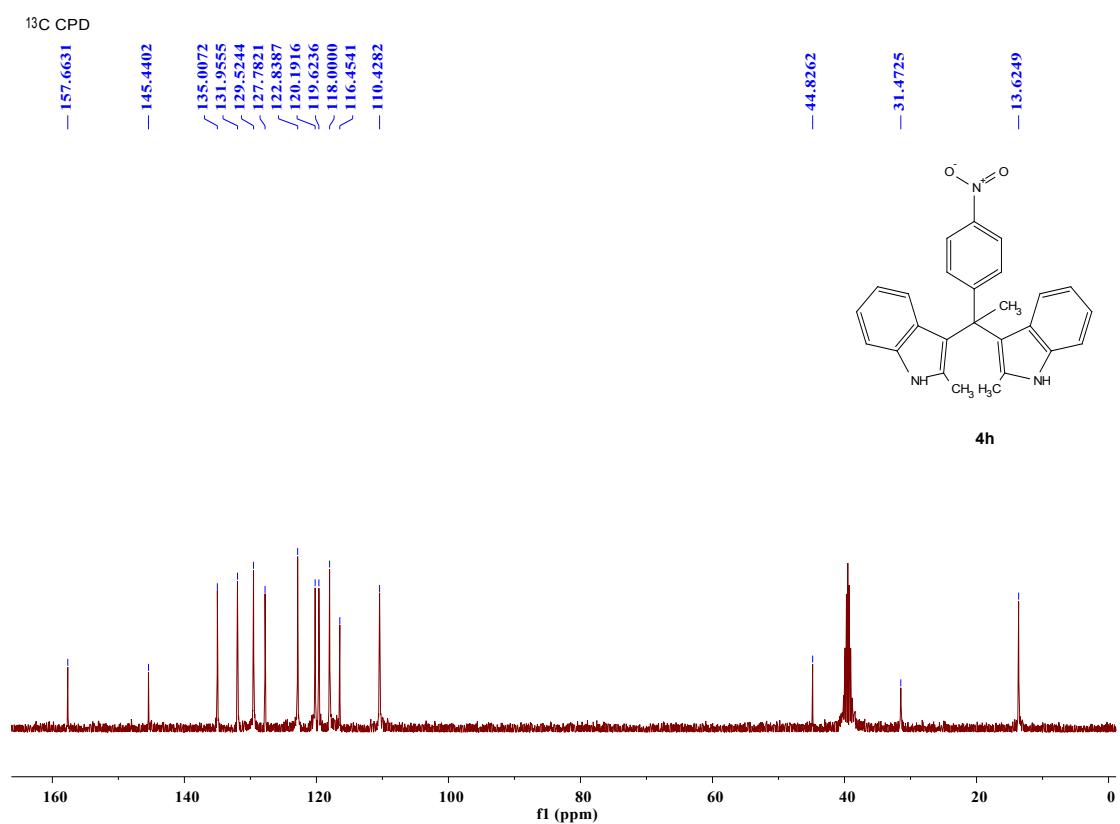
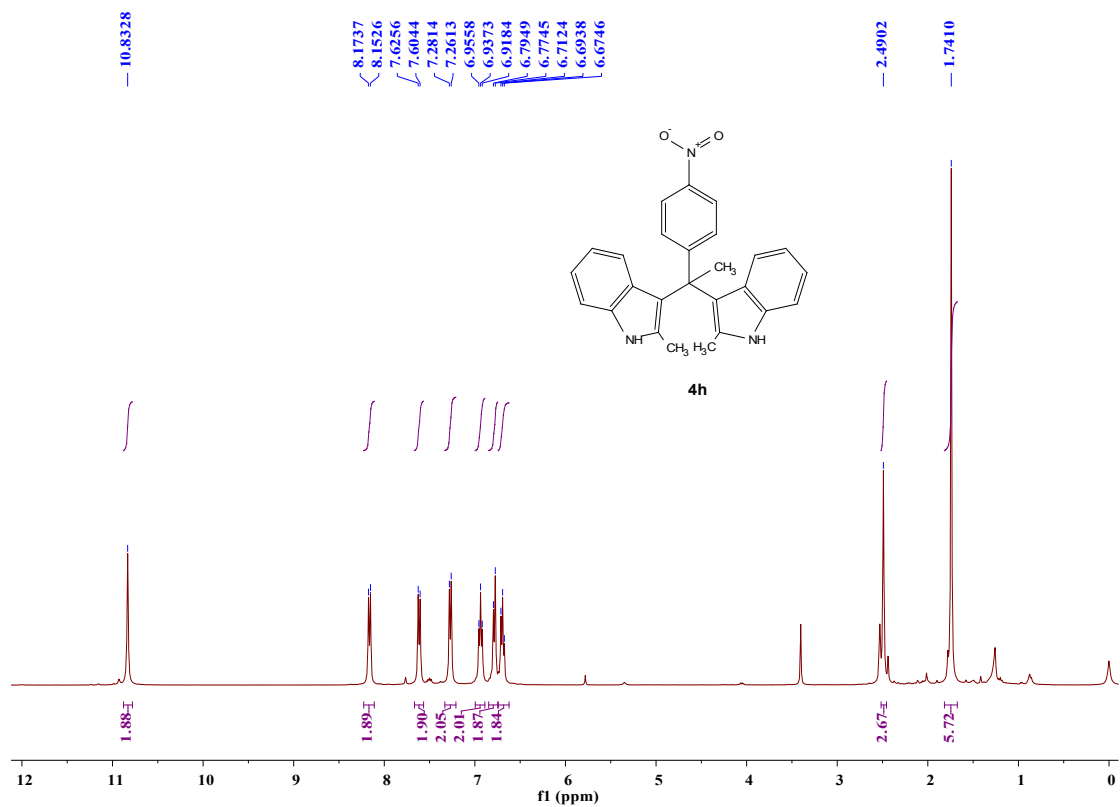


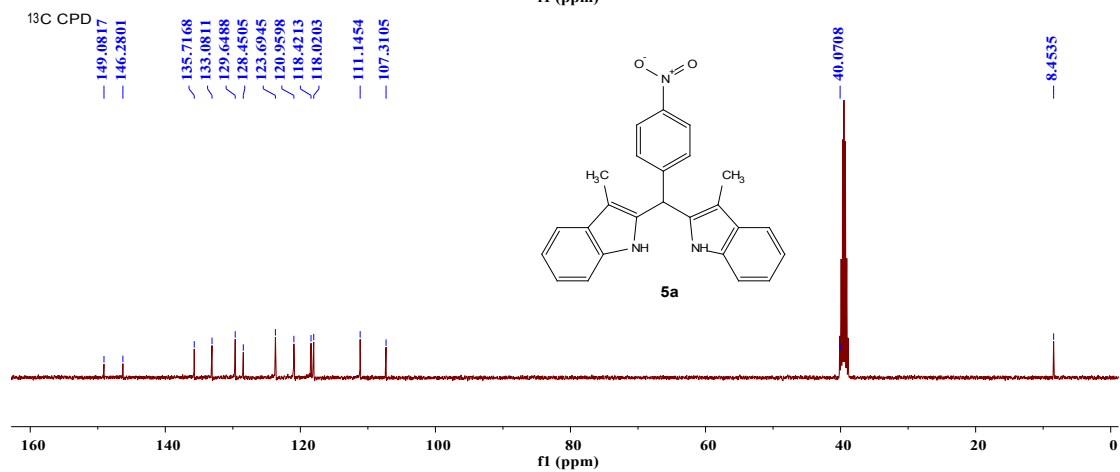
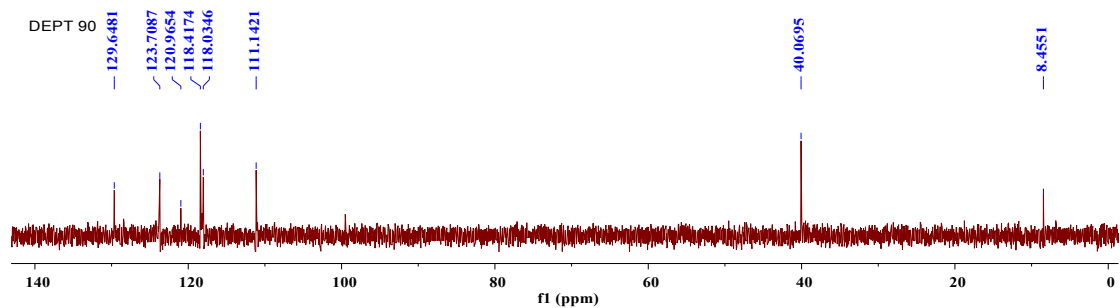
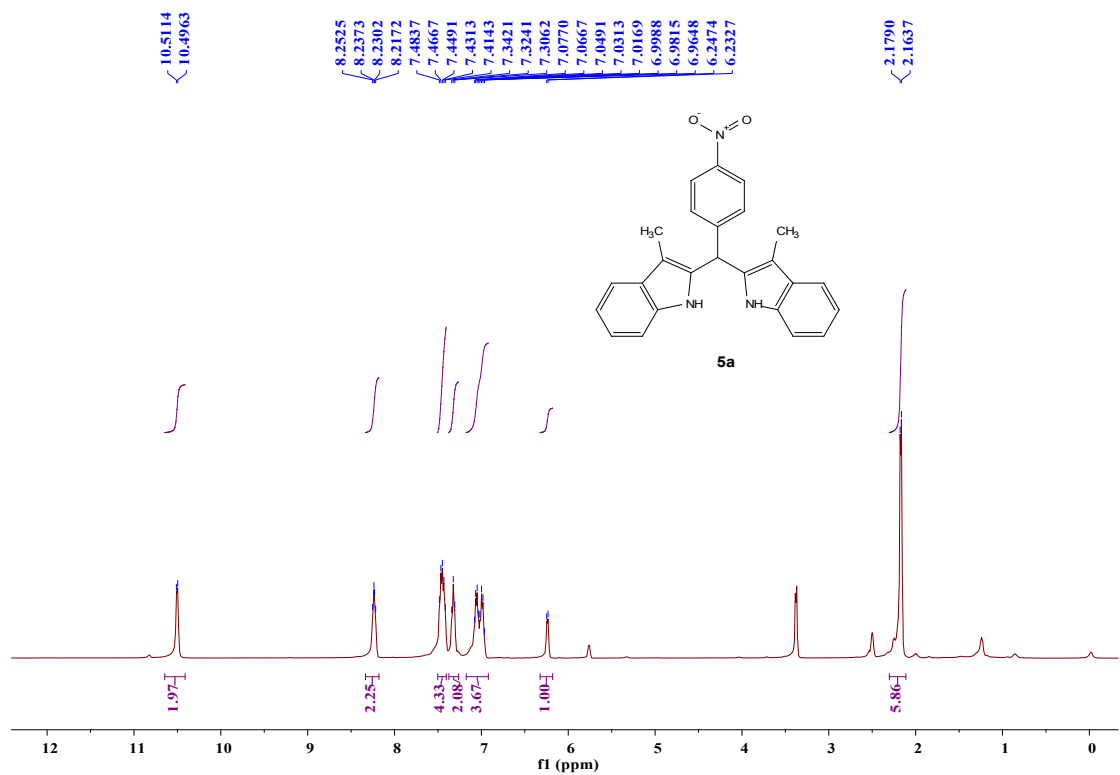






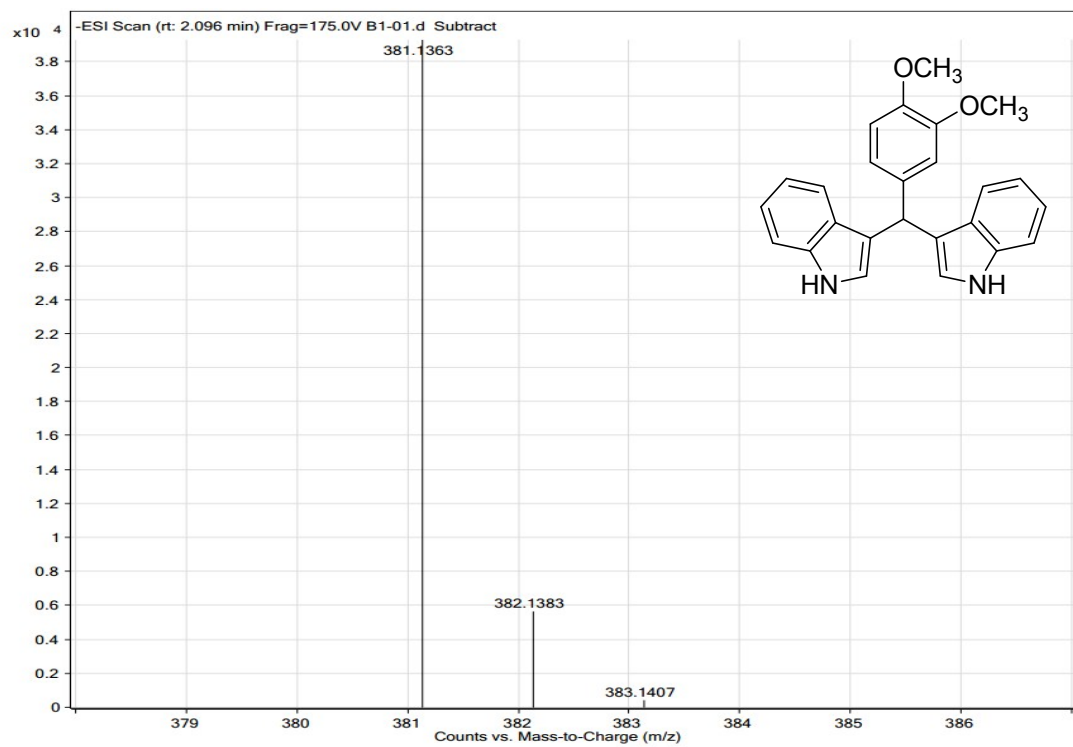




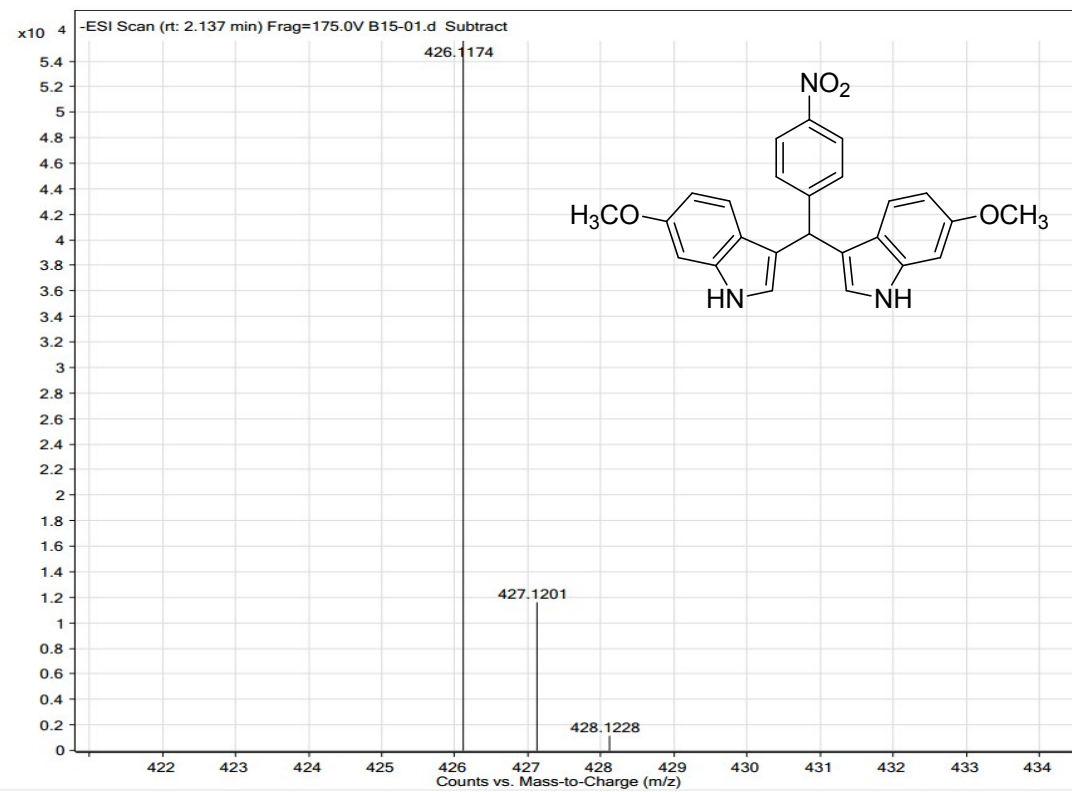


ESI-MS Organic Compounds

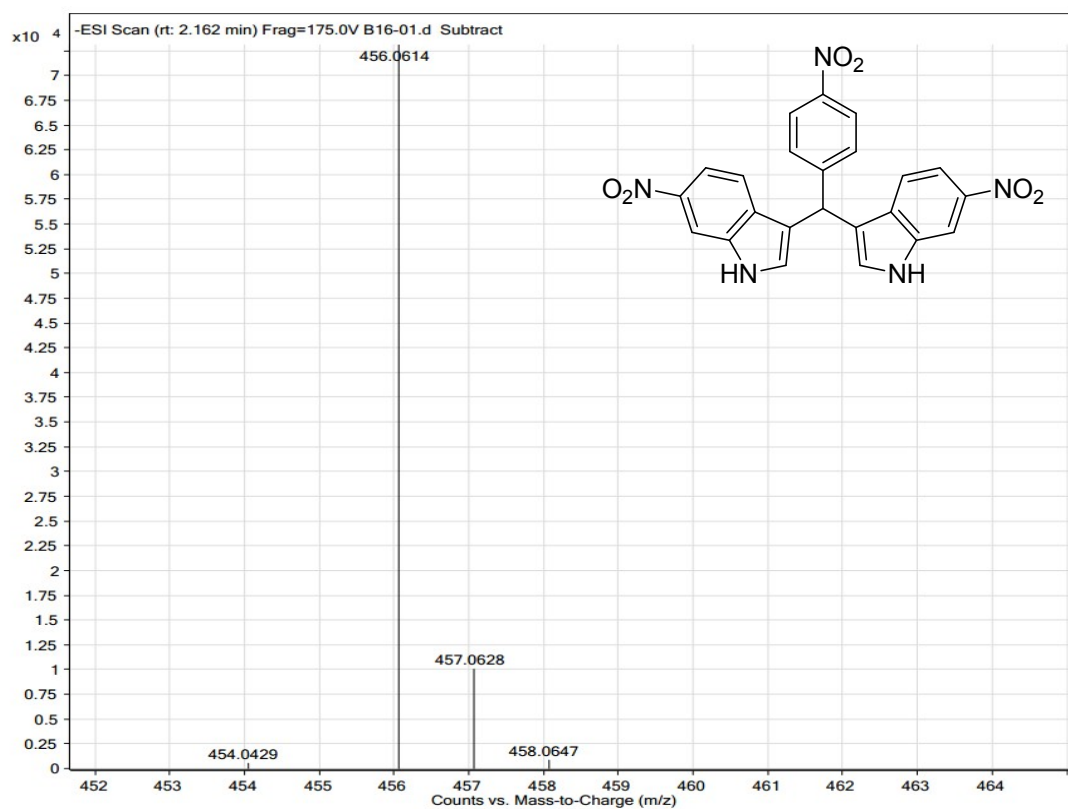
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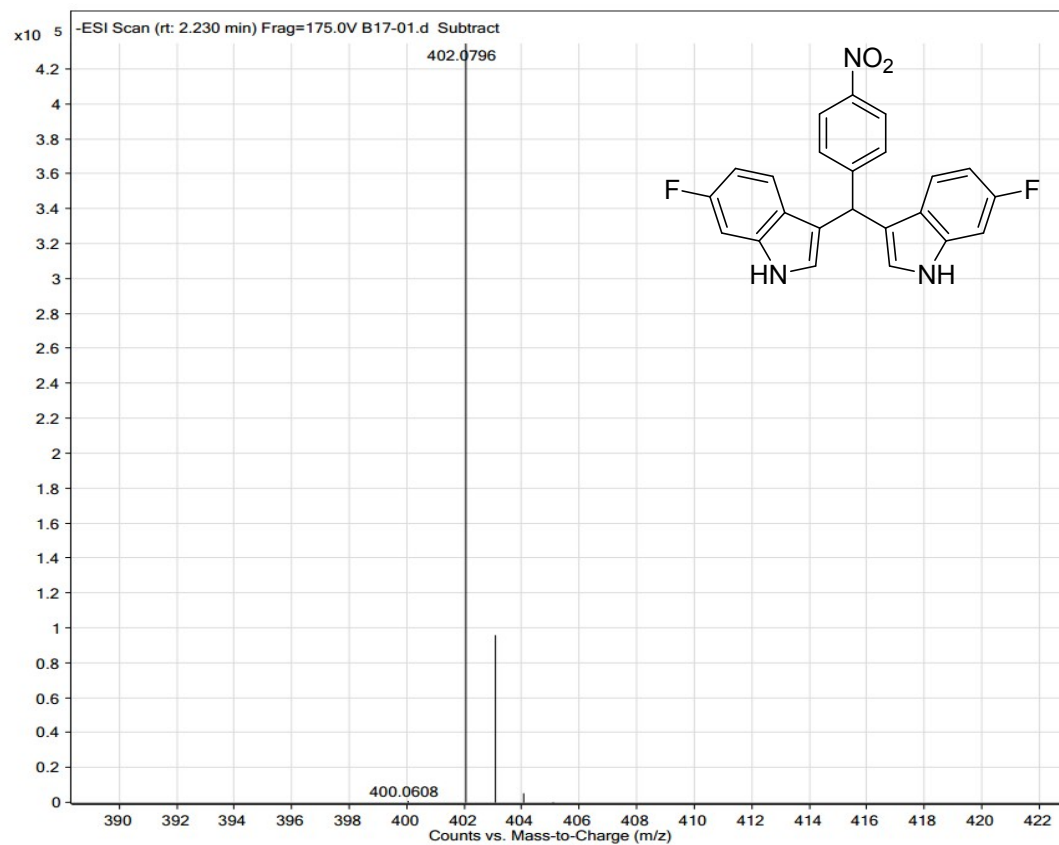
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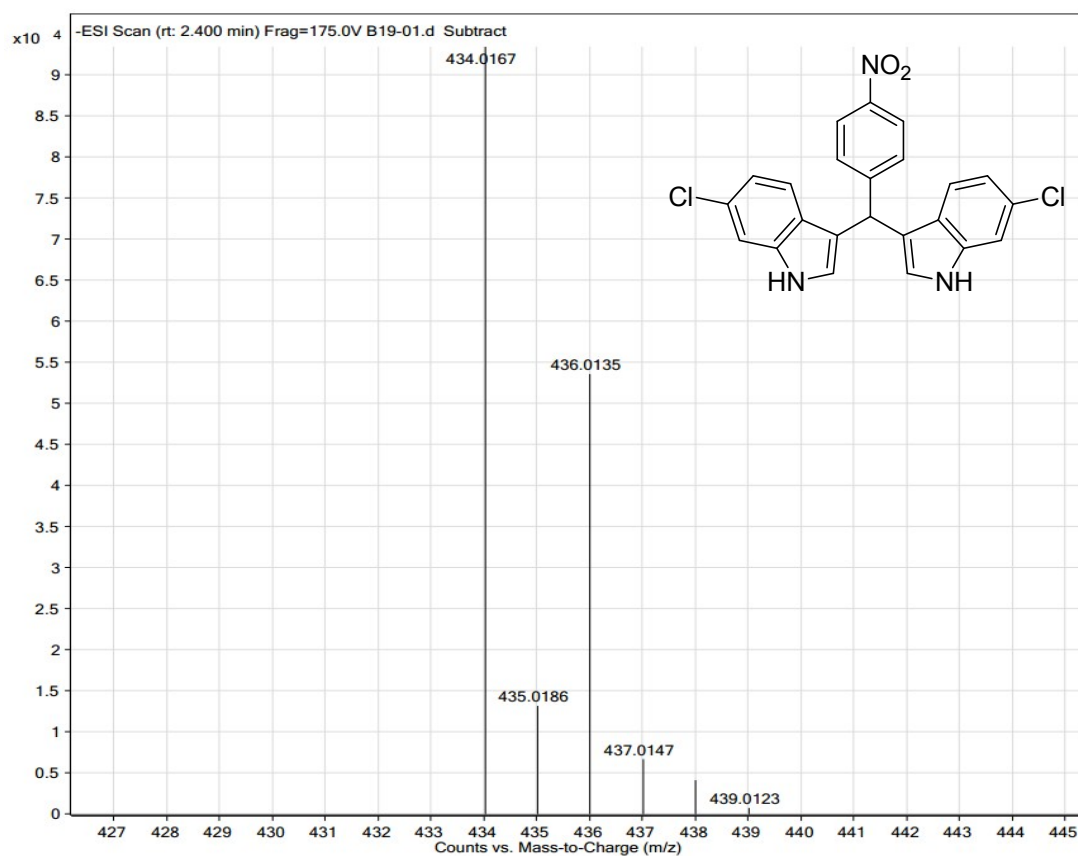
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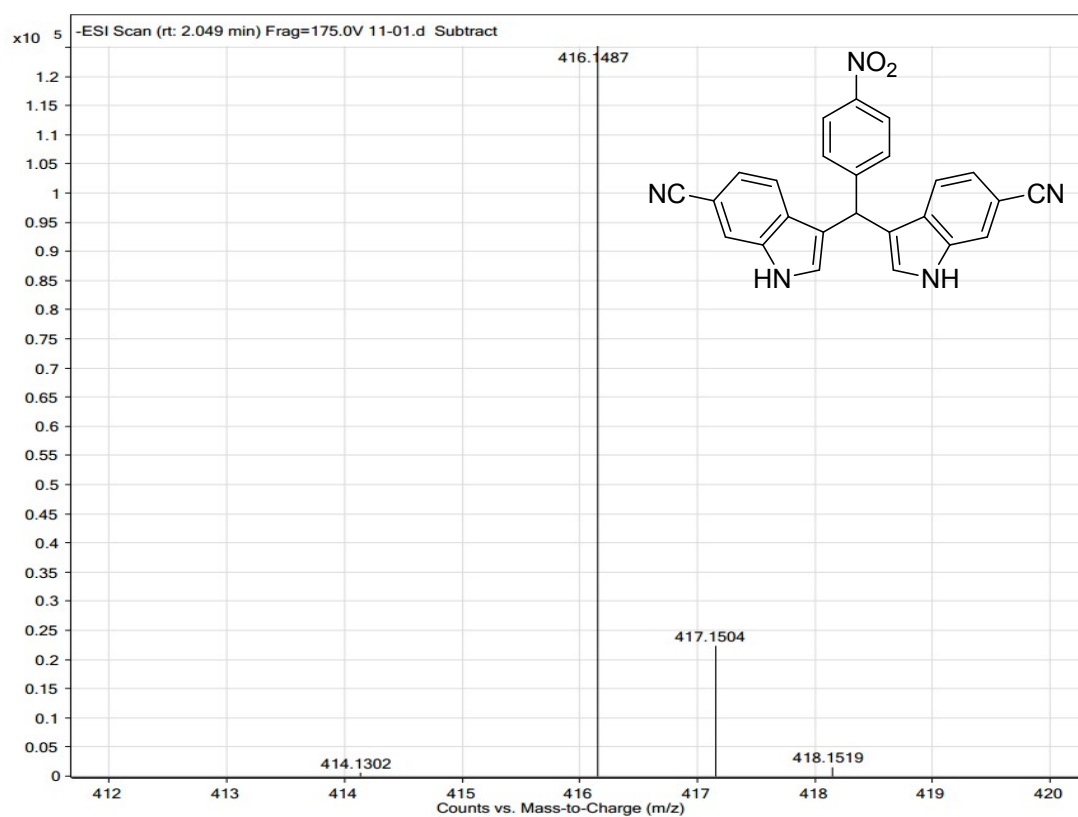
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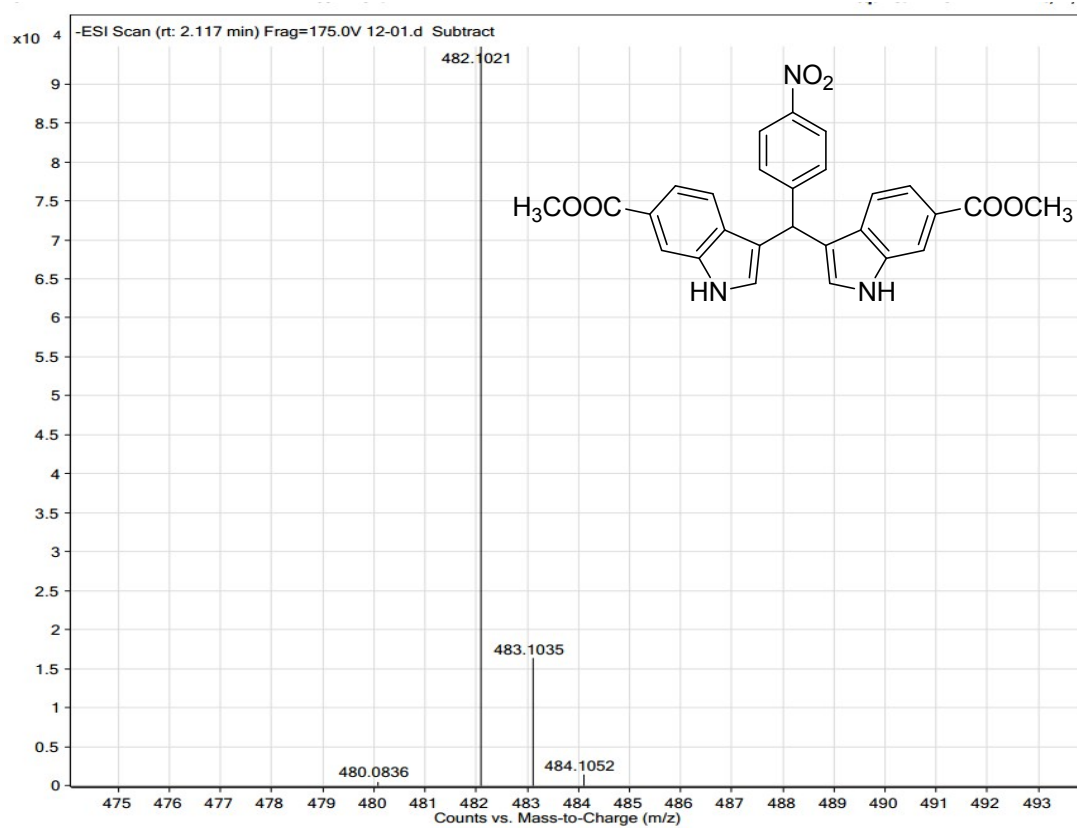
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3u



3v



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