Fabrication of an amyloid fibril-palladium nanocomposite: A sustainable catalyst for C–H activation and electrooxidation of ethanol

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Supporting Information

Contents

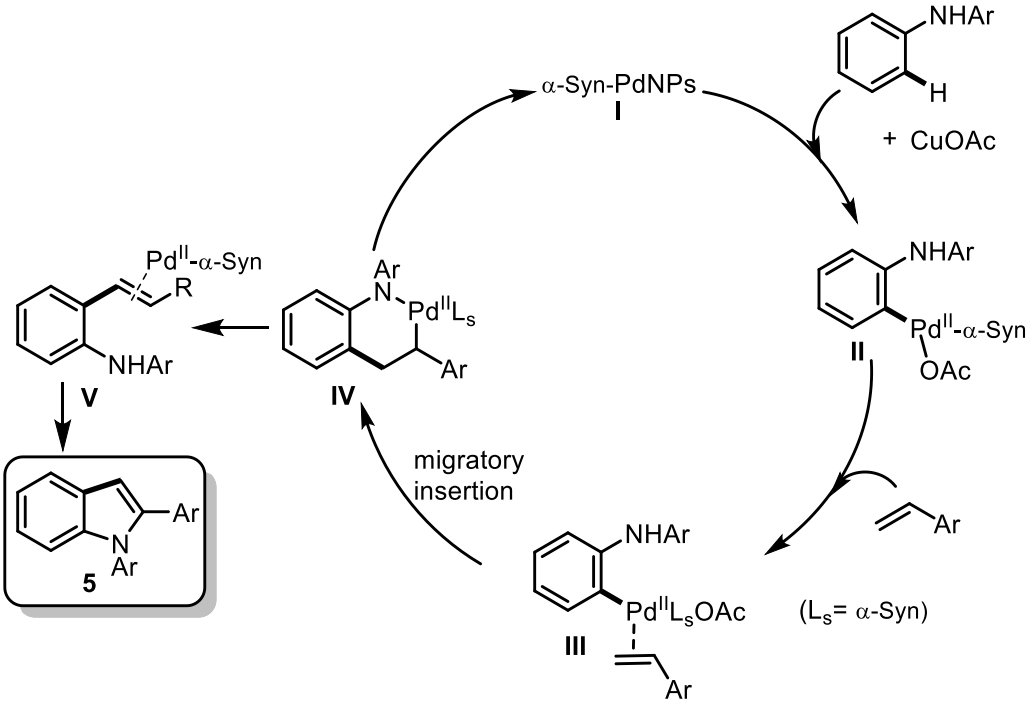
1. Supporting results:

Transmisson electron microscopy (TEM) characterization of different nanoparticles prepared using α-Syn fibrils. Pd, Cu, Pt, Au and Ag nanoparticles were prepared as explained in material and method section. The colour change was observed for all nanoparticles after reduction with $NaBH_4$. The bottles after reduction are shown in Figure S7 (a,f,k,p,u). Interestingly no agglomeration of Pd nanoparticles was observed in α-syn-PdNPs and Pd showed highly monodispersed nanoparticles (Figure S7b and S1c). Selected area electron diffraction (SAED) pattern of nanocomposites suggested face-centered cubic (fcc) structure and polycrystalline nature of palladium nanoparticles (Figure S7d) with lattice plane at (111, 200, 220 and 311). The diameter of Pd nanoparticles on fibril surface was found to *ca*. 3 nm as shown in Figure S7e. Spherical shape of nanoparticles coated on fibril was found for all metal nanocomposites. The low magnification (b,g,l,q,v) and high magnification (c,h,m,r,w) TEM images showed similar range of particle size. Interestingly, Ag showed larger particles among all metal nanoparticles. Similar SAED pattern was found for all metal nanoparticles and showed fcc crystal structure. Diameter of different nanoparticles are shown in Figure S7 (e,j,o,t,y) - Cu (*ca*. 3 nm), Pt (*ca*. 2.5 nm), Au (*ca*. 4 nm) and Ag (*ca*. 4.4 nm).

Varying the morphology of α-Syn-fibril and testing in benzofuran synthesis. Different palladium nanocomposites were prepared by varying the morphology of α-Syn-fibril as described in material and method. TEM was performed to analyse the morphology of Pd nanocomposites (Figure S10). α-Syn-PdNPs monomer showed spherical nanoparticles on amorphous monomeric protein. α-Syn-PdNPs fibril was sonicated after preparation. Short fibril with variable length was observed with spherical PdNPs coated on fibril. The α-Syn fibril digested in α-Syn-PdNPs composite using proteinase K. Partially digested fibril showed agglomerated palladium nanoparticles on fibril surface (Figure S10).

Circular dichroism (CD) spectroscopy characterization of α-Syn-PdNPs before and after reaction. We have recorded the CD spectra for freshly prepared catalyst (α-Syn-PdNPs) and recovered α-Syn-PdNPs after four turnovers. The CD spectra for both α-Syn fibril as well as the nanocomposite (α-Syn-PdNPs) showed a negative peak at 218 nm, which can be assigned for the β-sheet structure of the fibril.[1] Similar trend has been observed for a recovered α-Syn-PdNPs (after four cycle) with a slightly reduced intensity (Figure S12). This data suggest that α-Syn fibril structure is mostly unaffected even after four cycle of chemical reaction.

Plausible catalytic cycle for the formation of *N*-Arylindole. A plausible catalytic cycle is provided in Scheme S1 for the formation of *N*-arylindole.[2]



Scheme S1: Plausible mechanism for the formation of *N*-arylindole (**5**)

Electrooxidation of ethanol

The cyclic voltammetry (CV) measurements were carried out for α-Syn-PdNPs in 1 M KOH solution (without ethanol) at the scan rate of 50 mVs^{-1} to examine the electrochemical property and stability of catalyst. The Fig. S1 shows one peak in the anodic scan (forward scan) at potential −0.59 V which is associated with the formation of adsorbed OH^- and desorption of hydrogen on the Pd surface.[3] In the backward scan, two peaks were observed; one peak in the cathodic scan at potential −0.38 V is associated with the reduction of PdO to metallic Pd and another peak at potential −0.83 V is related to hydrogen adsorption.

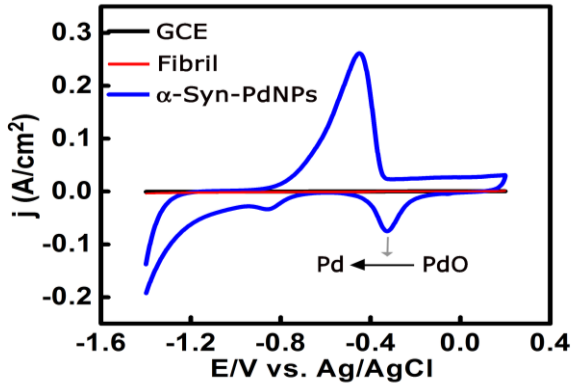


Figure S1. Cyclic voltammograms (CVs) of α-Syn-fibril and α-Syn-PdNPs on GCE in 1 M KOH at the scan rate of 50 mV s^{-1}.

Based on the results and available reports, the reaction mechanism of the reduction of PdO to metallic Pd has been dicussed below. The formation of metallic Pd to PdO and reduction of PdO to metallic Pd can be explained in four reaction steps as discussed by Feliciano-Ramos et al.[4]

$$Pd + OH^- \longrightarrow Pd{-}OH_{ads} + e^- \quad (1)$$

$$Pd{-}OH_{ads} + OH^- \longrightarrow PdO + H_2O + e^- \quad (2)$$

$$Pd{-}OH_{ads} + Pd{-}OH_{ads} \longrightarrow PdO + H_2O \quad (3)$$

$$PdO + H_2O + 2\,e^- \longrightarrow Pd + 2OH^- \quad (4)$$

The metallic Pd adsorbs OH^- and releases one e^- as given in reaction (1). Pd-OH_{ads} further adsorb the OH^- to form PdO and releases H_2O (2). Two molecules of Pd-OH_{ads} reacts to form PdO and releases H_2O (3). The bond breaking reaction of PdO to metallic Pd involves in the release of OH^- (4) which again adsorbed by the metallic Pd to form PdO in the subsequent steps in presence of 1M KOH in the cyclic voltammetry experiment.

Identification of intermediate species in ethanol oxidation: We have carried out the CVs of α-Syn-fibril and α-Syn-PdNPs in 1 M KOH + 1 M ethanol at the scan rate of 50 mV s^{-1}, which shows two well-defined characteristic current peaks in the forward and reverse potential windows. The observed peak in forward scan at -0.1V in CV is assigned for oxidation of ethanol, while the second peak in the reverse scan attributes to the oxidation of freshly adsorbed ethanol and adsorbed carbonaceous species (Fig. 5d). The assignment of peaks had been done after systematic survey of available literature.

Identifying reactive intermediates or products is key for solving mechanism of ethanol oxidation. Two commonly accepted pathways for the oxidation of ethanol using Pd based catalyst has been discussed by Wang et al.[5] In the path 1, the ethanol is partially oxidized to acetate by releasing 4 electrons or to acetaldehyde by releasing 2 electrons without the breaking of the C–C bond.

Path 1:

$$CH_3\text{-}CH_2OH + H_2O \longrightarrow CH_3\text{-}COOH + 4H^+ + 4e^-$$

$$CH_3\text{-}CH_2OH \longrightarrow CH_3\text{-}CHO + 2H^+ + 2e^-$$

In path 2, the ethanol is oxidized to a CO2 or carbonates via COads intermediate and release 12e−.

Path 2:

$$CH_3\text{-}CH_2OH + 3H_2O \longrightarrow 2CO_2 + 12H^+ + 12e^-$$

$$CH_3\text{-}CH_2OH + 5H_2O \longrightarrow 2HCO_3^- + 14H^+ + 12e^-$$

$$CH_3\text{-}CH_2OH + 5H_2O \longrightarrow 2CO_3^{2-} + 16H^+ + 12e^-$$

We have attempted to identify the intermediates formed in electrooxidation of ethanol during longer experiments (after 1000 cycle) by gas chromatography (GC). The GC data revealed the presence of other intermediate species in addition to ethanol. ^{1}H NMR of the same

sample showed the presence of traces such as acetic acid, acetaldehyde and its polymeric component (paraldehyde) in addition to ethanol. The GCMS further supported the presence of these component in the solution; ethanol (m/z: 46.01), acetaldehyde (m/z: 44.05), acetic acid (m/z: 60.04) and paraldehyde (132.16). This confirms the oxidation of ethanol in the CV experiments.

Figure S2. Gas Chromatographic data of (1M EtOH + 1M KOH) solution before CV experiments

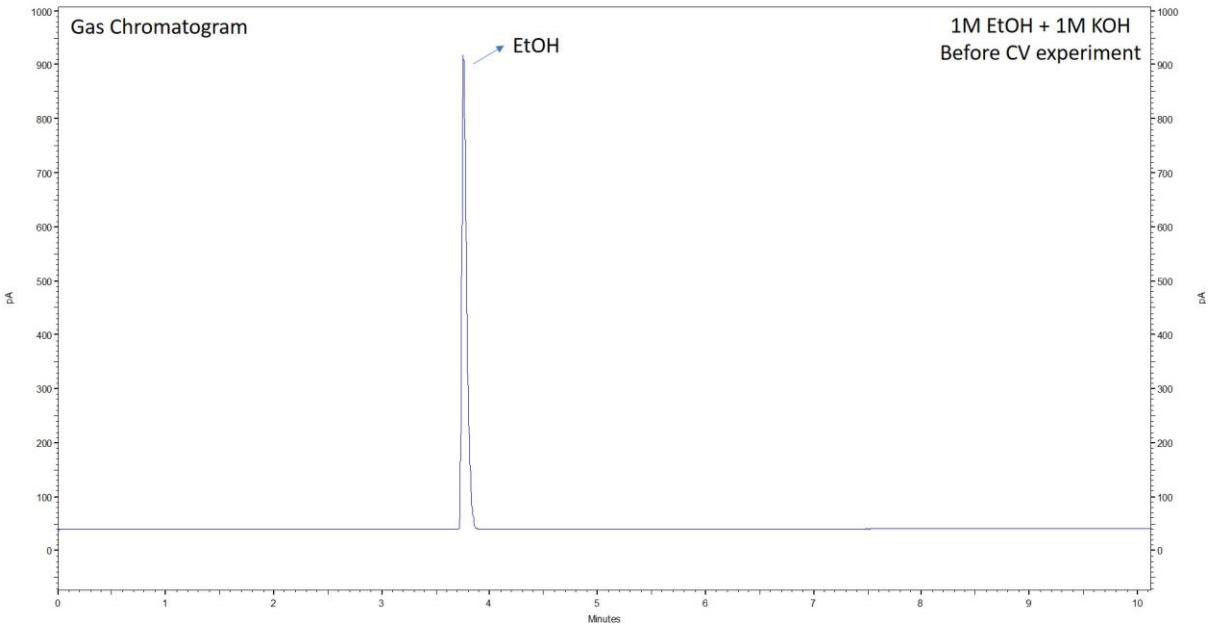


Figure S3. Gas Chromatographic data of (1M EtOH + 1M KOH) solution after CV experiments

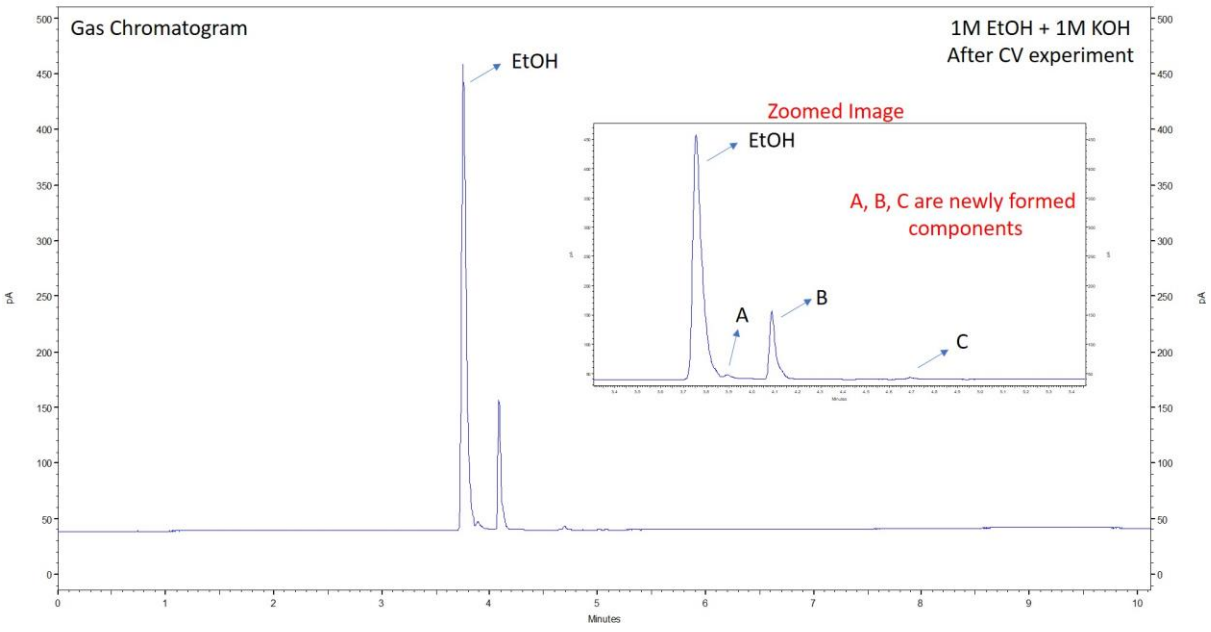
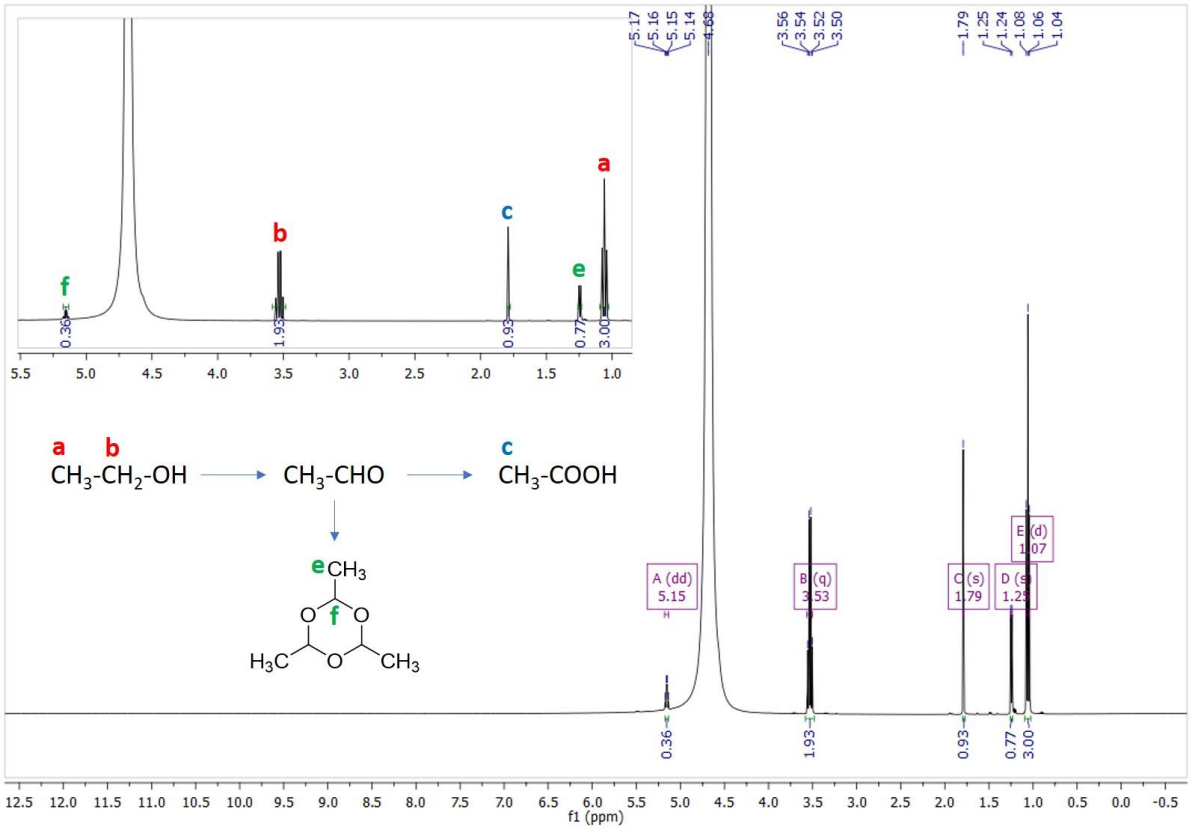
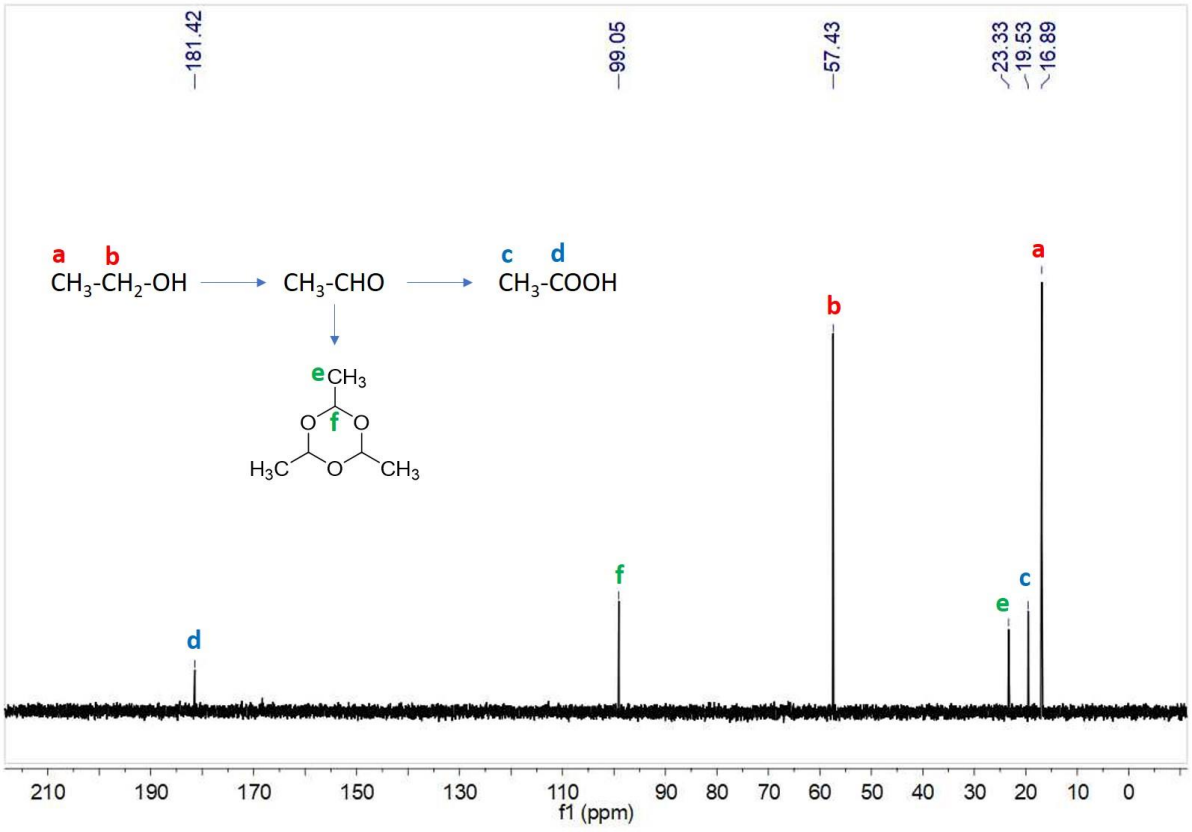


Figure S4. ^{1}H and ^{13}C NMR (D_2O) of the (1M EtOH + 1M KOH) solution after CV experiments:





2. Material and methods.

2.1 Reagent Information. Unless otherwise stated, all reactions were carried out under air atmosphere in screw cap reaction tubes. All the solvents were bought from Aldrich insure-seal bottle and were used as received. Palladium acetate was obtained as a gift from Johnson Matthey. The metal salts $CuSO_4.5H_2O$, $PtCl_4$, $HAuCl_4.3H_2O$ and $AgNO_3$ were purchased from different commercial sources like Lobachemie, Sigma and Merck. All the Phenols, diphenylamines and olefins were bought from Aldrich and Alfa-Aesar. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. A gradient elution using pet ether and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel 60F254).

2.2 Analytical Information for product characterization: All isolated compounds were characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, gas chromatography (GC) and GCMS. Representative copies of the ^{1}H NMR, ^{13}C NMR can be found in the annexure. Unless otherwise stated, all Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 MHz and 500 MHz instrument. All ^{1}H NMR experiments were reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to deuterochloroform (77.16 ppm), unless otherwise stated, and all were obtained with ^{1}H decoupling. Product yield of crude reaction mixture analysed by gas chromatography (GC) using n-decane as internal standard. All GCMS analysis was done by Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple axis detector).

2.3 α-Synuclein expression and purification: α-Synuclein (α-Syn) protein was expressed in *Escherichia coli* BL21 (DE3) strain using published protocol by Volles *et al* [6] with some modification.[7] In brief, *E. coli* cells with α-Syn gene containing plasmid (pRK 172) were grown in Luria broth. When cells reach optical density of 0.8-0.9 at 600 nm, IPTG induction was done for protein expression. After 4 hours of induction, bacterial cells were pelleted down by centrifugation (4,000 ×g, 30 minutes) and resuspended in 50 mM Tris, 150 mM NaCl, 10 mM EDTA, pH 8.0. Cells were sonicated after addition of protease inhibitor cocktail (Roche) at 40% amplitude with pulse rate of 45 pulse /minutes for 15 minutes. Then it was further heated in water bath at 95°C for 15 minutes. After heating for 15 minutes, to the supernatant, glacial acetic acid (228 µl/ml of supernatant) and 10% streptomycin sulphate solution (136 µl/ml of supernatant) was added. After 30 minutes of incubation at 4°C it was centrifuged (14,000 ×g, 30 minutes). Equal volume of saturated ammonium sulphate was added to supernatant to precipitate the protein. The resultant solution was centrifuged and pellet was resuspended in ammonium sulphate solution (saturated ammonium sulphate and water, 1:1 v/v). This was again centrifuged at (14,000 ×g, 30 minutes). Protein pellet was again dissolved in 100 mM ammonium acetate solution and vortex to dissolve the protein. Then equal volume of ethanol was added to precipitate the protein. This solution was then centrifuged after 30 minutes of incubation. This step was repeated twice. Protein solution was then resuspended in 100 mM ammonium acetate and was lyophilized to obtain dry powder. It was stored at -20°C for further use.

2.4 Fibril formation: The lyophilized protein was suspended in 20 mM Gly-NaOH buffer, pH 7.4, 0.01% sodium azide. The protein was solubilized by addition of few drops of 2N NaOH and then finally pH was adjusted to 7.4 using 2N HCl. The protein was dialyzed for 12 hours. The protein concentration was determined by UV spectrophotometer (JASCO V-650) considering the molar absorptivity (ε) of 5960 $M^{-1}cm^{-1}$ for α-Syn. Finally, protein was diluted to 300 μM and it was taken in 2 ml microfuge tube and placed into an EchoTherm model RT11 rotor (Torrey Pines Scientific, USA) at 50 r.p.m. inside a 37 °C incubator. The fibril formation was confirmed by TEM.

2.5 Preparation of Palladium, Copper, Platinum, Gold and Silver nanoparticles on α-Syn fibril: The α-Syn-fibril palladium nanoparticle composite (α-Syn-PdNPs) was prepared by adding 500 μL aqueous suspension of $Pd(OAc)_2$ (20 mM, 2.24 mg) into α-Syn- fibrils (300 μM, 500 μL) while stirring. Subsequent addition of $NaBH_4$ solution (10 mM, 100 μL) turned the entire solution into black representing formation of Pd (0). The solution was stirred for 1 hour and then centrifuged (14,000×g, 30 minutes). The pellet was lyophilized to obtain powder. Similarly, copper nanoparticles (CuNPs) from $CuSO_4.5H_2O$ (20 mM, 2.49 mg), platinum nanoparticles (PtNPs) from $PtCl_4$ (20 mM, 3.37 mg), gold nanoparticles (AuNPs) from $HAuCl_4.3H_2O$ (20 mM, 3.94 mg) and silver nanoparticles (AgNPs) from $AgNO_3$ (20 mM, 1.7 mg) were made after addition of α-Syn fibrils (300 μM, 500 μL) followed by reduction with $NaBH_4$ solution (10 mM, 100 μL). The solution was stirred for 1 hour and then centrifuged to obtain pellet, which was lyophilized to obtain solid powder. All nanoparticles were synthesized at least three times and found to be consistence. Palladium nanoparticles synthesized on α-Syn monomer in similar way, where we used α-Syn monomer instead of fibril. To obtain sonicated α-Syn-PdNPs, firstly α-Syn Pd-NPS was synthesized as described above and then sonicated (30 pulse/minute at 20 % amplitude) using probe sonicator for 10 minutes. It was then centrifuged and lyophilized to obtain dry powder. Proteinase K (PK) digested α-Syn Pd-NPs was made by digesting α-Syn-PdNPs by PK (50 μM, 12 hours). Then solution was centrifuged and lyophilized. The powder obtained was used for characterization and organic transformation.

2.6 Transmission Electron Microscopy (TEM): 10 μl samples after preparation of all nanoparticles were spotted on carbon coated copper grid (Electron Microscopy Sciences, Fort Washington, PA) and kept for 10 minutes. The excess sample was wiped out. It was washed twice with distilled water. Samples were then stained with 10 μl of 1% (w/v) uranylformate and then it was air-dried. TEM imaging was done using electron microscope (Philips CM 200) and high resolution TEM was done using FEG-TEM (FEI Tecnai). Images were acquired at 6,600X and 27,000X using the Keen View Soft imaging system. 10-12 images were taken randomly for each sample. Experiment was repeated thrice.

2.7 Fourier transform infrared (FTIR) study: FTIR of α-Syn and α-Syn Pd-NPS was done by making thin pellet of KBr containing samples by compressing the grinded KBr powder at the pressure of ~5 ton using hydraulic pressure pump. The pellet was dried under IR lamp. The IR spectra were acquired in transmittance mode in the range of 5000-500 cm^{-1} by using Bruker Vertex-80 instrument (Bruker, Germany). The resolution was set at 4 cm^{-1} and background spectra were automatically subtracted from sample.

2.8 X-ray photoelectron spectroscopy (XPS): 20µl α-Syn fibril and α-Syn-PdNPs was spotted on aluminum sheet and allowed to air dry for 2 hours. Sample was mounted and degassed over night at ultrahigh vacuum. XPS spectrum was recorded on Kratos AXIS Supra (UK) having X ray source of Monochromatic Al K-alpha.C1s peak from surface adsorbed carbon at 284.7 eV was used for internal calibration. Peak fitting and analysis was done using XPSPeak4.1.

2.9 Thermo gravimetric analysis (TGA): To determine the thermal stability of α-Syn fibril and α-Syn-PdNPs, TGA was done in Diamond TG/DTA (Perkin Elmer, USA). The sample was heated from 25 ^{o}C to 800 ^{o}C under N_2 environment at rate of 10^{o}C/minute. Weight loss was recorded with temperature and plotted.

2.10 X-ray diffraction (XRD): X-ray diffraction (XRD) analysis on α-Syn fibril and α-Syn-PdNPs was done using Smartlab Rigaku diffractometer with monochromatic Cu kα radiation (λ = 1.5406 Å) operated at voltage and current of 40 kV and 30 mA respectively. The θ-2θ scanning was done in the region of 2θ between 10° and 90°. The peaks obtained were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) file 87-0638 for palladium metal.

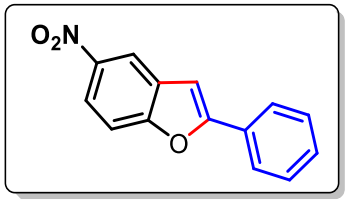
2.11 Inductive coupled plasma atomic emission spectroscopy (ICP-AES): The amount of palladium in α-Syn-PdNPs was estimated by ICP-AES (SPECTRO Analytical Instruments GmbH, Germany). 10 mg of α-Syn-PdNPs was dissolved in HNO_3 and palladium concentration in solution was obtained from standard curve of known palladium solution. The results repeated experiments showed that the 10 mg of the composite (α-Syn-PdNPs) contains 2 mg (20 wt %) of Pd.

2.12 Electrooxidation of ethanol. For electrochemical measurements, we have carried out cyclic voltammetry and chronoamperometry with a CHI1140A electrochemical workstation (CHI110, Austin, TX). All electrochemical measurements were performed at room temperature. The electrochemical experiments were carried in a three electrodes cell using a platinum wire, silver-silver chloride (Ag/AgCl), and a glassy carbon electrode (GCE) (D = 3 mm) as counter reference electrodes and the working electrode, respectively. Before starting the experiment, the GCE was properly polished with alumina powder (successively 1,0.3 and 0.05 µm) for 5 min respectively. After each polishing step, the washing of electrode was done with Milli Q water and then cleaned in an ultrasonic bath using ethanol and water. After cleaning of the electrode, 5 µl of α-Syn-PdNPs composite was carefully dropped onto the active surface of the electrode and allowed to dry at room temperature. 1M KOH was used as the supporting electrolyte during the electrochemical measurement. Further, to remove the dissolved oxygen in the electrolyte, nitrogen gas was purged for 10 minutes before electrochemical measurement. The important parameter of a catalyst on which the electrocatalytic activity is strongly dependent evaluated the existing electrochemical active surface area (ECSA). The ECSA of α-Syn-PdNPs composite was calculated from the area of reduction peak of PdO in the cyclic voltammetry (CV) in 1M KOH solution at the scan rate of 50 mVs^{-1}. The ECSA (m^2 per g_{Pd}) value was calculated according to the following Equation (1)**.** [8,9]

$$ECSA = \frac{Q}{m \times C \times v}$$

Where Q is the Coulombic charge corresponding to the reduction peak area of PdO (mC), which can be obtained from the area integral of Figure 5a and *m* is the mass of Pd loading (mg) which is 9.5μg in α-Syn-PdNPs composites. C is the charge required for electro-reduction of a PdO single layer (405 mC/cm^2_{pd}) and *v* is the scan rate.

2.13 *α*-Syn-PdNPs Catalyzed Benzofuran Synthesis from corresponding Phenols and Olefins (General Procedure A). To a dried screw cap reaction tube that charged with a magnetic stir-bar, phenol (1 mmol), *α*-Syn-PdNPs (7.5 mol%), 1,10-phenanthroline monohydrate (15 mol%), V_2O_5 (1.25 mmol), NaOAc (0.75 mmol) and olefin (0.5 mmol) were added. Then 1,2-dichloroethane (DCE) solvent (4 mL) was added and the reaction tube was closed with the screw cap. The reaction tube was heated at 110 ^oC for 24 h under vigorous stirring. Then the reaction mixture was cooled and quenched with ethyl acetate. After centrifuging, the reaction mixture was filtered (repeated thrice by washing with ethyl acetate) and combined organic portions were evaporated under reduced pressure. The residue was purified by column chromatography using silica gel (100-200 mesh size) and petroleum-ether/ ethyl acetate as the eluent.

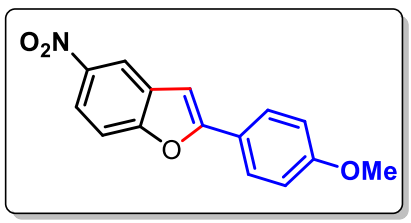


5-nitro-2-phenylbenzofuran (4a): Compound **4a** was synthesized by general procedure A using 4-nitrophenol (1 mmol) and styrene (0.5 mmol) as the substrates. Pure product was obtained as light orange solid in 91%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 2.3 Hz, 1H), 8.21 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.49 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.12 (s, 1H) ppm.

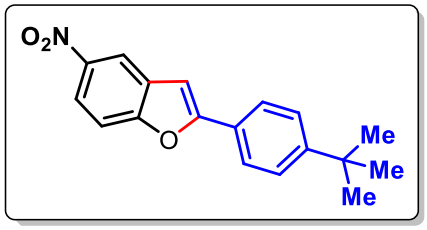
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.40, 157.75, 144.47, 129.82, 129.76, 129.31, 129.15, 125.41, 120.24, 117.39, 111.55, 101.73 ppm.

GC-MS (m/z): 239.3 $[M]^+$.

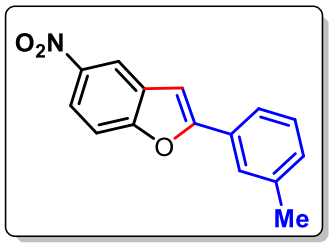


5-nitro-2-(4-methoxyphenyl)benzofuran (4b): Compound **4b** was synthesized by general procedure A using 4-nitrophenol (1 mmol) and 4-methoxystyrene (0.5 mmol) as the substrates.

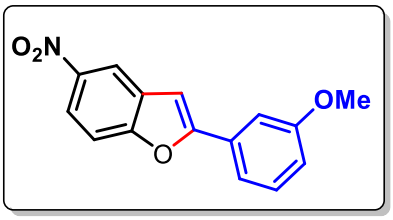
Pure product was obtained as yellow solid in 78%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:2).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 1.7 Hz, 1H), 8.18 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.9 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.98 (s, 1H), 3.88 (s, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.97, 159.58, 157.65, 144.45, 130.12, 127.01, 122.09, 119.77, 116.98, 114.63, 111.30, 100.04, 55.57 ppm.
GC-MS (m/z): 269.4 $[M]^+$.



2-(4-(tert-butyl)phenyl)-5-nitrobenzofuran (4c): Compound **4c** was synthesized by general procedure A using 4-nitrophenol (1 mmol) and 4-*tert*-butylystyrene (0.5 mmol) as the substrates. Pure product was obtained as yellow solid in 62%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 2.3 Hz, 1H), 8.20 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.08 (s, 1H), 1.37 (s, 9H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.69, 157.76, 153.31, 144.46, 129.95, 126.58, 126.13, 125.27, 120.03, 117.24, 111.48, 101.11, 35.05, 31.34 ppm.
GC-MS (m/z): 295.1 $[M]^+$.



5-nitro-2-(3-methylphenyl)benzofuran (4d): Compound **4d** was synthesized by general procedure A using 4-nitrophenol (1 mmol) and 3-methylystyrene (0.5 mmol) as the substrates. Pure product was obtained as yellow solid in 86%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.3 Hz, 1H), 8.19 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.08 (s, 1H), 2.44 (s, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.60, 157.71, 144.44, 138.89, 130.64, 129.79, 129.21, 129.04, 125.97, 122.60, 120.12, 117.30, 111.46, 101.58, 21.59 ppm.
GC-MS (m/z): 253.3 $[M]^+$.

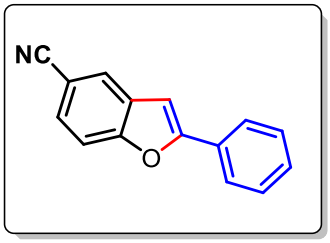


2-(3-methoxyphenyl)-5-nitrobenzofuran (4e): Compound **4e** was synthesized by general procedure A using 4-nitrophenol (1 mmol) and 3-methoxystyrene (0.5 mmol) as the substrates. Pure product was obtained yellow solid in 75%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.2 Hz, 1H), 8.22 – 8.19 (m, 1H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.10 (s, 1H), 6.97 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.90 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.16, 159.19, 157.69, 144.46, 130.53, 130.25, 129.69, 120.27, 117.93, 117.40, 115.55, 111.55, 110.71, 102.04, 55.56 ppm.

GC-MS (m/z): 269.5 $[M]^+$.

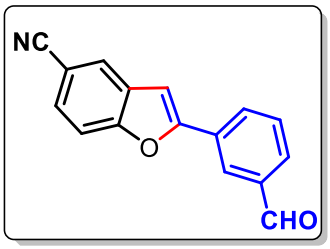


5-cyano-2-phenylbenzofuran (4f): Compound **4f** was synthesized by general procedure A using 4-cyanophenol (1 mmol) and styrene (0.5 mmol) as the substrates. Pure product was obtained as white solid in 88%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 10.4, 9.1 Hz, 3H), 7.59 – 7.53 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.42 (dd, *J* = 8.4, 6.2 Hz, 1H), 7.03 (s, 1H) ppm.

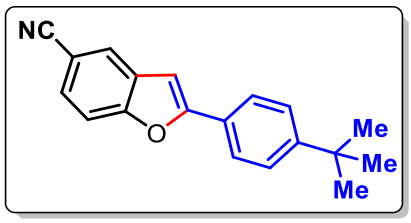
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.49, 156.57, 130.01, 129.68, 129.40, 129.11, 127.98, 125.86, 125.38, 119.59, 112.40, 107.02, 100.86 ppm.

GC-MS (m/z): 219.3 $[M]^+$.

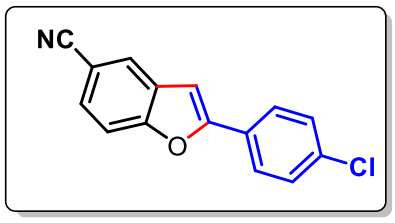


5-cyano-2-(3-formylphenyl)benzofuran (4g): Compound **4g** was synthesized by general procedure A using 4-cyanophenol (1 mmol) and 3-vinylbenzaldhyde (0.5 mmol) as the substrates. Pure product was obtained as light white solid in 66%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

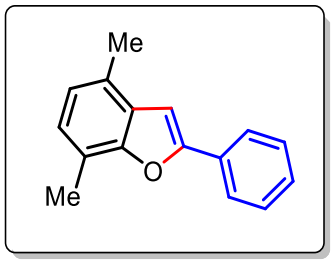
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.46 (s, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.04 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.33 (s, 1H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 191.73, 156.90, 156.71, 137.19, 130.79, 130.72, 130.52, 129.95, 129.73, 128.60, 126.28, 126.16, 119.39, 112.64, 107.46, 102.23 ppm.
GC-MS (m/z): 247.5 $[M]^+$.



2-(4-(tert-butyl)phenyl)benzofuran-5-carbonitrile (4h): Compound **4h** was synthesized by general procedure A using 4-cyanophenol (1 mmol) and 4–*tert*-butyl styrene (0.5 mmol) as the substrates. Pure product was obtained as light white solid in 60%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 1.0 Hz, 1H), 7.81 – 7.79 (m, 2H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.54 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.01 (d, *J* = 0.7 Hz, 1H), 1.37 (s, 9H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.78, 156.58, 153.15, 130.20, 127.78, 126.67, 126.09, 125.71, 125.24, 119.70, 112.35, 106.95, 100.25, 35.03, 31.34 ppm.
GC-MS (m/z): 275.5 $[M]^+$.



5-cyano-2-(4-chlorophenyl)benzofuran (4i): Compound **4i** was synthesized by general procedure A using 4-cyanophenol (1 mmol) and 4-chlorostyrene (0.5 mmol) as the substrates. Pure product was obtained as light-yellow solid in 55%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:2).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.05 (s, 1H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.61, 135.66, 129.91, 129.45, 128.29, 127.94, 126.64, 126.02, 119.50, 112.50, 107.28, 101.34 ppm.
GC-MS (m/z): 253.6 $[M]^+$.

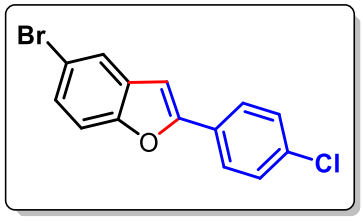


4,7-dimethyl-2-phenylbenzofuran (4j): Compound **4j** was synthesized by general procedure A using 2,5-dimethylphenol (1 mmol) and styrene (0.5 mmol) as the substrates. Pure product was obtained as colourless oil in 54%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.37 – 7.32 (m, 1H), 7.04 (s, 1H), 6.96 (dd, *J* = 22.9, 7.4 Hz, 2H), 2.55 (s, 3H), 2.52 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.18, 153.76, 130.96, 128.88, 128.59, 128.42, 128.25, 125.23, 124.95, 123.26, 118.75, 100.45, 18.50, 14.97 ppm.

GC-MS (m/z): 222.6 $[M]^+$.

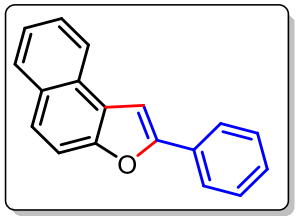


5-bromo-2-(4-chlorophenyl)benzofuran (4k): Compound **4k** was synthesized by general procedure A using 4-bromophenol (1 mmol) and 4-chlorostyrene (0.5 mmol) as the substrates. Pure product was obtained as white solid in 66%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.70 (s, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.38 (s, 2H), 6.94 (s, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.26, 153.80, 135.03, 131.21, 129.29, 128.58, 127.56, 126.44, 123.73, 116.32, 112.79, 101.21, 77.41, 77.16, 76.91 ppm.

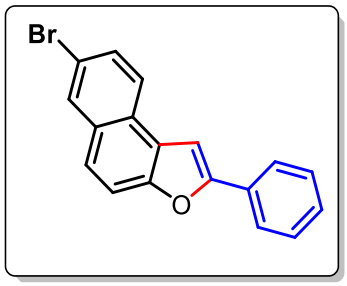
GC-MS (m/z): 307.2 $[M]^+$.



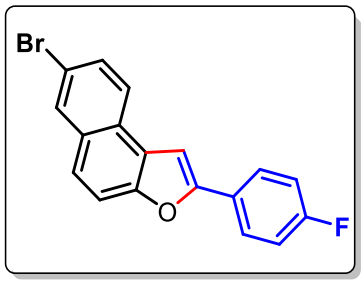
2-phenylnaphtho[2,1-b]furan (4l): Compound **4l** was synthesized by general procedure A using 2-naphthol (1 mmol) and styrene (0.5 mmol) as the substrates. Pure product was obtained as light-yellow solid in 76%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.2 Hz, 1H), 7.95 (dd, *J* = 7.8, 6.5 Hz, 3H), 7.75 – 7.69 (m, 2H), 7.63 – 7.58 (m, 1H), 7.54 – 7.52 (m, 1H), 7.49 (d, *J* = 7.3 Hz, 3H), 7.36 (t, *J* = 7.4 Hz, 1H) ppm.

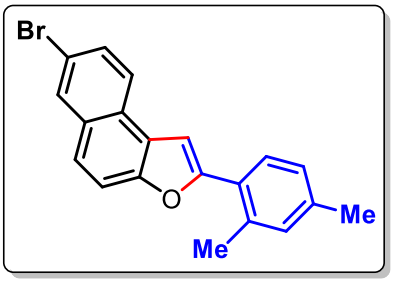
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.06, 152.51, 131.81, 130.96, 130.49, 129.55, 129.04, 128.67, 126.18, 125.34, 124.89, 124.25, 118.38, 113.48, 100.35 ppm.
GC-MS (m/z): 244.7 $[M]^+$.



7-bromo-2-phenylnaphtho[2,1-b]furan (4m): Compound **4m** was synthesized by general procedure A using 6-bromo-2-naphthol (1 mmol) and styrene (0.5 mmol) as the substrates. Pure product was obtained as creamy white solid in 90%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 1.9 Hz, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.93 – 7.90 (m, 2H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.66 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.48 (dd, *J* = 8.8, 6.6 Hz, 3H), 7.37 (t, *J* = 7.4 Hz, 1H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.10, 152.54, 131.85, 130.99, 130.53, 129.58, 129.05, 128.69, 126.22, 125.35, 124.91, 124.80, 124.26, 118.39, 113.50, 100.37 ppm.
GC-MS (m/z): 323.8 $[M]^+$.



7-bromo-2-(4-fluorophenyl)naphtho[2,1-b]furan (4n): Compound **4n** was synthesized by general procedure A using 6-bromo-2-naphthol (1 mmol) and 4-fluorostyrene (0.5 mmol) as the substrates. Pure product was obtained as creamy white solid in 79%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.0 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.70 (dd, *J* = 8.9, 0.6 Hz, 1H), 7.66 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.41 (s, 1H), 7.17 (t, *J* = 8.7 Hz, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 164.02, 155.20, 152.51, 131.86, 131.01, 129.63, 126.78, 126.72, 126.17, 125.31, 124.78, 124.31, 118.46, 116.27, 116.09, 113.43, 100.10 ppm.
GC-MS (m/z): 341.5 $[M]^+$.

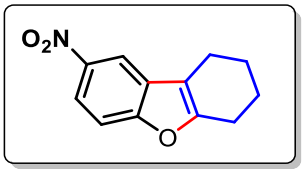


7-bromo-2-(2,4-dimethylphenyl)naphtho[2,1-b]furan (4o): Compound **4o** was synthesized by general procedure A using 6-bromo-2-naphthol (1 mmol) and 2,4-dimethylstyrene (0.5 mmol) as the substrates. Pure product was obtained as creamy white solid in 87%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (400 MHz, CDCl3) δ 8.10 (d, *J* = 1.8 Hz, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.65 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.29 (s, 1H), 7.15 (d, *J* = 6.5 Hz, 2H), 2.62 (s, 3H), 2.39 (s, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$) δ 156.09, 151.90, 138.64, 135.56, 132.29, 131.74, 130.94, 129.44, 128.11, 127.15, 127.09, 126.20, 125.32, 124.70, 123.95, 118.22, 113.43, 103.37, 22.09, 21.35 ppm.

GC-MS (m/z): 351.5 $[M]^+$.

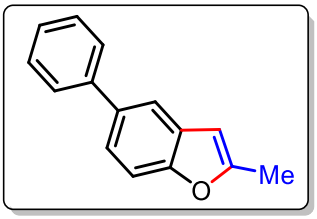


8-nitro-1,2,3,4-tetrahydrodibenzo[*b,d*]furan (4p): Compound **4p** was synthesized by general procedure A using 4-nitrophenol (1 mmol) and cyclohexene (0.5 mmol) as the substrates. Pure product was obtained as light-yellow solid in 65%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.33 (d, *J* = 2.3 Hz, 1H), 8.14 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.44 (d, *J* = 9.0 Hz, 1H), 2.77 (tt, *J* = 6.3, 1.9 Hz, 2H), 2.66 (tt, *J* = 6.0, 2.0 Hz, 2H), 2.01 – 1.94 (m, 2H), 1.91 – 1.85 (m, 2H) ppm.

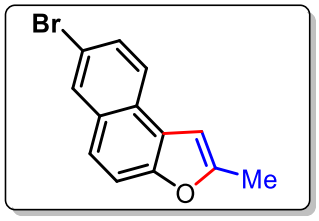
^{13}C NMR (101 MHz, CDCl$_3$) δ 157.98, 157.58, 129.51, 119.20, 115.07, 114.13, 111.07, 23.57, 22.79, 22.47, 20.36 ppm.

GC-MS (m/z): 217.1 $[M]^+$.



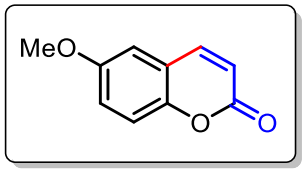
2-methyl-5-phenylbenzofuran (4q): Compound **4q** was synthesized by general procedure A using 4-phenylphenol (1 mmol) and allyl chloride (0.5 mmol) as the substrates. Pure product

was obtained as white solid in 58%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:2).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.64 (d, *J* = 1.4 Hz, 1H), 7.62 (s, 1H), 7.48 – 7.43 (m, 4H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.43 (s, 1H), 2.49 (d, *J* = 0.8 Hz, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.30, 154.54, 142.04, 136.27, 129.88, 128.83, 127.56, 126.86, 122.87, 118.81, 110.84, 102.94, 14.27 ppm.
GC-MS (m/z): 208.6 $[M]^+$.



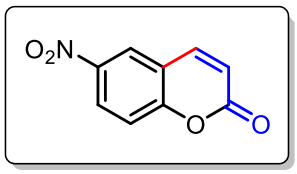
7-bromo -2-methylnaphtho[*2,1-b*]furan (4r): Compound **4r** was synthesized by general procedure A using 6-bromo-2-naphthol (1 mmol) and allyl bromide (0.5 mmol) as the substrates. Pure product was obtained as orange semi solid in 61%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:2).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.9 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 1.5 Hz, 1H), 7.59 (s, 1H), 7.53 (d, *J* = 8.9 Hz, 1H), 6.82 (s, 1H), 2.56 (s, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.45, 152.13, 131.63, 130.80, 129.21, 125.96, 125.32, 124.46, 122.91, 117.94, 113.24, 101.77, 14.35 ppm.
GC-MS (m/z): 261.2 $[M]^+$.

2.14 *α*-Syn-PdNPs Catalyzed Coumarin Synthesis from corresponding Phenols and acrylates (General Procedure B). To a dried screw cap reaction tube that charged with a magnetic stir-bar, phenol (1 mmol), *α*-Syn-PdNPs (10 mol%), 1,10-phenanthroline monohydrate (20 mol%), V_2O_5 (1.25 mmol), NaOAc (0.75 mmol), Molecular sieves (4Å, 130 mg) and acrylate (0.5 mmol) were added. Then 1,2-dichloroethane (DCE) solvent (4 mL) was added and the reaction tube was closed with the screw cap. The reaction tube was heated at 110 ^oC for 24 h under vigorous stirring. Then the reaction mixture was cooled and quenched with ethyl acetate. The mixture was filtered through celite pad and evaporated under reduced pressure. The residue was purified by column chromatography using silica gel (100-200 mesh size) and petroleum-ether/ ethyl acetate as the eluent.



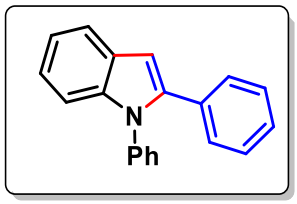
6-methoxy-2*H*-chromen-2-one (4s): Compound **4s** was synthesized by general procedure B using 4-methoxyphenol (1 mmol) and methylacrylate (0.5 mmol) as the substrates. Pure product was obtained as white solid in 82%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 80:20).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 9.5 Hz, 1H), 7.22 (d, *J* = 9.5 Hz, 1H), 7.06 (dd, *J* = 9.1, 2.9 Hz, 1H), 6.87 (d, *J* = 2.9 Hz, 1H), 6.38 (d, *J* = 9.5 Hz, 1H), 3.81 (s, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.12, 156.21, 148.59, 143.33, 119.58, 119.29, 118.00, 117.21, 110.16, 55.96 ppm.
GC-MS (m/z): 176.6 $[M]^+$.



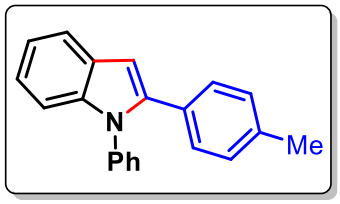
6-nitro-2H-chromen-2-one (4t): Compound **4t** was synthesized by general procedure B using 4-nitrophenol (1 mmol) and methylacrylate (0.5 mmol) as the substrates. Pure product was obtained as white solid in 65%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 80:20).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 2.5 Hz, 1H), 8.41 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.80 (d, *J* = 9.7 Hz, 1H), 7.47 (d, *J* = 9.0 Hz, 1H), 6.59 (d, *J* = 9.7 Hz, 1H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.97, 157.72, 144.22, 142.33, 126.79, 123.89, 119.02, 118.95, 118.26 ppm.
GC-MS (m/z): 191.2 $[M]^+$.

2.15 *α*-Syn-PdNPs Catalyzed *N*-Arylindole synthesis from corresponding diphenylamine and styrenes (General Procedure C). To a dried screw cap reaction tube that charged with a magnetic stir-bar, amine (1 mmol), ***α*-**Syn-PdNPs (0.025 mmol) and 1,10-phenanthroline monohydrate (0.05 mmol), CuOAc (2 equiv) and olefin (0.25 mmol) were added. Then 1,2-dichloroethane (DCE) solvent (4 mL) was added and the reaction tube was closed with the screw cap. The reaction tube was heated at 130 ^oC for 24 h under vigorous stirring. Then the reaction mixture was cooled and quenched with ethyl acetate. After centrifuging, the reaction mixture was filtered (repeated thrice by washing with ethyl acetate) and combined organic portions were evaporated under reduced pressure. The residue was purified by column chromatography using silica gel (100-200 mesh size) and petroleum-ether/ ethyl acetate as the eluent.

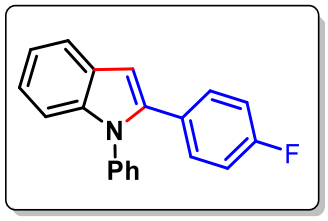


1,2-diphenyl-1H-indole (5a): Compound **5a** was synthesized by general procedure C using diphenylamine (1 mmol) and styrene (0.25 mmol) as the substrates. Pure product was obtained as white crystalline solid in 87%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 1H), 7.33 – 7.29 (m, 2H), 7.26 – 7.23 (m, 1H), 7.22 – 7.13 (m, 8H), 7.11 – 7.07 (m, 2H), 6.72 (d, *J* = 0.6 Hz, 1H) ppm.

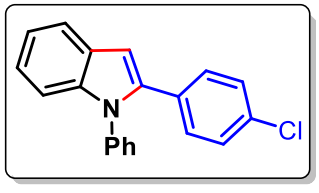
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.87, 139.14, 138.65, 132.67, 129.38, 129.04, 128.40, 128.28, 128.18, 127.42, 127.32, 122.47, 120.84, 120.66, 110.76, 103.83 ppm.
GC-MS (m/z): 269.7 $[M]^+$.



1-phenyl-2-p-tolyl-1H-indole (5b): Compound **5b** was synthesized by general procedure C using diphenylamine (1 mmol) and 4-methylstyrene (0.25 mmol) as the substrates. Pure product was obtained as white crystalline solid in 72%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 1H), 7.44 – 7.40 (m, 2H), 7.37 – 7.33 (m, 1H), 7.30 – 7.27 (m, 2H), 7.25 (d, *J* = 1.2 Hz, 1H), 7.18 – 7.15 (m, 4H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 0.7 Hz, 1H), 2.32 (s, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.02, 139.08, 138.77, 137.28, 129.78, 129.38, 129.04, 128.92, 128.45, 128.23, 127.29, 122.27, 120.77, 120.53, 110.70, 103.38, 21.33 ppm.
GC-MS (m/z): 283.6 $[M]^+$.



2-(4-fluorophenyl)-1-phenyl-1H-indole (5c): Compound **5c** was synthesized by general procedure C using diphenylamine (1 mmol) and 4-fluorostyrene (0.25 mmol) as the substrates. Pure product was obtained as white crystalline solid in 65%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.34 (dd, *J* = 6.0, 3.2 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 3H), 7.23 (dd, *J* = 6.0, 3.1 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 6.81 (s, 1H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.25, 161.29, 139.82, 139.07, 138.46, 130.73, 130.66, 129.47, 128.85, 128.82, 128.32, 128.18, 127.46, 122.57, 120.93, 120.65, 115.44, 115.27, 110.76, 103.74 ppm.
GC-MS (m/z): 287.3 $[M]^+$.

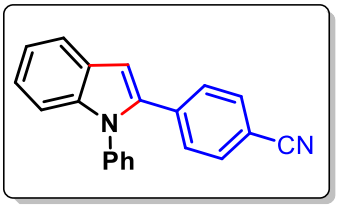


2-(4-chlorophenyl)-1-phenyl-1H-indole (5d): Compound **5d** was synthesized by general procedure C using diphenylamine (1 mmol) and 4-chlorostyrene (0.25 mmol) as the substrates. Pure product was obtained as white crystalline solid in 67% yield. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 6.1, 2.7 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (dd, *J* = 8.4, 6.3 Hz, 1H), 7.33 – 7.31 (m, 1H), 7.28 (dd, *J* = 5.4, 3.2 Hz, 2H), 7.25 – 7.21 (m, 6H), 6.84 (s, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.54, 139.22, 138.38, 133.44, 131.15, 130.14, 129.55, 128.56, 128.26, 128.14, 127.55, 122.76, 121.00, 120.75, 110.79, 104.12 ppm.

GC-MS (m/z): 303.9 $[M]^+$.

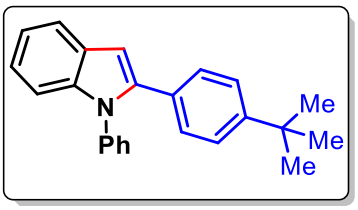


4-(1-phenyl-1H-indol-2-yl)benzonitrile (5e): Compound **5e** was synthesized by general procedure C using diphenylamine (1 mmol) and 4-vinylbenzonitrile (0.25 mmol) as the substrates. Pure product was obtained as white crystalline solid in 59%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 1H), 7.53 – 7.50 (m, 2H), 7.48 – 7.44 (m, 2H), 7.43 – 7.39 (m, 1H), 7.37 – 7.34 (m, 2H), 7.31 – 7.28 (m, 1H), 7.25 (d, *J* = 1.5 Hz, 1H), 7.24 (d, *J* = 1.5 Hz, 1H), 7.23 – 7.20 (m, 1H), 6.92 (d, *J* = 0.7 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.78, 138.50, 138.16, 137.16, 132.12, 129.78, 129.07, 128.06, 127.92, 123.61, 121.34, 121.17, 118.94, 110.97, 110.67, 105.84 ppm.

GC-MS (m/z): 294.6 $[M]^+$.

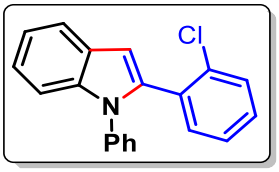


2-(4-tert-butylphenyl)-1-phenyl-1H-indole (5f): Compound was **5f** synthesized by general procedure B using diphenylamine (1 mmol) and 4-tert-butylstyrene (0.25 mmol) as the substrates. Pure product was obtained as white crystalline solid in 61%. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 1H), 7.49 – 7.45 (m, 2H), 7.42 – 7.38 (m, 1H), 7.32 (dd, *J* = 8.9, 3.9 Hz, 5H), 7.27 (d, *J* = 1.9 Hz, 1H), 7.25 – 7.21 (m, 3H), 6.85 (s, 1H), 1.35 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.40, 140.93, 139.18, 138.83, 129.69, 129.36, 128.58, 128.47, 128.27, 127.30, 125.24, 122.26, 120.75, 120.53, 110.70, 103.48, 34.66, 31.40 ppm.

GC-MS (m/z): 325.8 $[M]^+$.

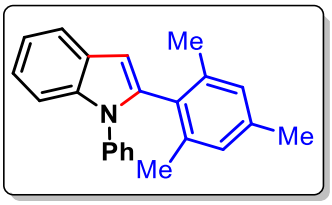


2-(2-chlorophenyl)-1-phenyl-1H-indole (5g): Compound **5g** was synthesized by general procedure B using diphenylamine (1 mmol) and 3-chlorostyrene (0.25 mmol) as the substrates. Pure product was obtained as white crystalline solid in 67% yield. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 1H), 7.40 – 7.36 (m, 2H), 7.34 (dt, *J* = 6.6, 1.1 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.25 – 7.21 (m, 5H), 7.18 (td, *J* = 7.4, 1.4 Hz, 1H), 6.79 (s, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.13, 137.93, 137.52, 134.53, 133.02, 132.19, 129.77, 129.53, 129.08, 128.10, 127.65, 127.07, 126.36, 122.64, 120.94, 120.79, 110.77, 105.45 ppm.

GC-MS (m/z): 303.9 $[M]^+$.

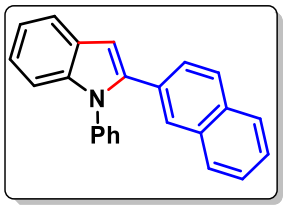


2-mesityl-1-phenyl-1H-indole (5h): Compound **5h** was synthesized by general procedure B using diphenylamine (1 mmol) and 2,4,6-trimethylstyrene (0.25 mmol) as the substrates. Pure product was obtained as white crystalline solid in 65% yield. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 1H), 7.40 – 7.38 (m, 1H), 7.32 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 7.20 – 7.16 (m, 4H), 6.82 (s, 2H), 6.51 (d, *J* = 0.7 Hz, 1H), 2.26 (s, 3H), 2.04 (s, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.96, 138.31, 138.25, 138.14, 129.57, 128.96, 128.70, 128.02, 126.78, 121.71, 120.50, 120.45, 110.74, 103.97, 29.85, 21.26, 20.76 ppm.

GC-MS (m/z): 311.4 $[M]^+$.



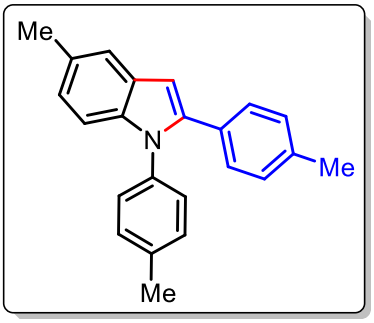
2-(naphthalen-2-yl)-1-phenyl-1H-indole (5i): Compound **5i** was synthesized by general procedure B using diphenylamine (1 mmol) and 2-vinylnaphthalene (0.25 mmol) as the substrates. Pure product was obtained as white crystalline solid in 69% yield. Isolated by

column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.74 – 7.67 (m, 3H), 7.47 – 7.44 (m, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.33 (m, 3H), 7.32 – 7.30 (m, 2H), 7.23 – 7.20 (m, 2H), 6.94 (d, *J* = 0.7 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.81, 139.28, 138.70, 133.31, 132.53, 130.14, 129.47, 128.46, 128.24, 128.20, 128.00, 127.74, 127.39, 126.87, 126.38, 126.28, 122.59, 120.91, 120.72, 110.79, 104.33 ppm.

GC-MS (m/z): 319.5 $[M]^+$.

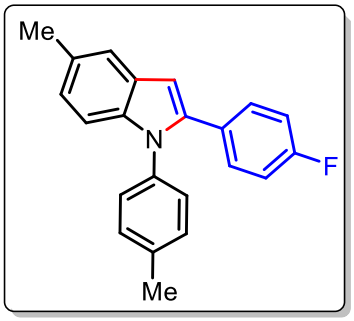


5-methyl-1,2-di-p-tolyl-1H-indole (5j): Compound **5j** was synthesized by general procedure B using di-*p*-tolylamine (1 mmol) and 4-methylstyrene (0.25 mmol) as the substrates. Pure product was obtained as white crystalline solid in 63% yield. Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.23 – 7.18 (m, 3H), 7.17 – 7.12 (m, 4H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.69 (s, 1H), 2.47 (s, 3H), 2.41 (s, 3H), 2.32 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.04, 137.68, 137.05, 136.92, 136.33, 130.03, 129.96, 129.89, 128.99, 128.83, 128.62, 127.88, 123.72, 120.12, 110.44, 102.72, 21.53, 21.33, 21.30 ppm.

GC-MS (m/z): 311.7 $[M]^+$.



2-(4-fluorophenyl)-5-methyl-1-(*p*-tolyl)-1H-indole (5k): Compound **5k** was synthesized by general procedure B using di-p-tolylamine (1 mmol) and 4-fluoroostyrene (0.25 mmol) as the substrates. Pure product was obtained as white crystalline solid in 60% yield. Isolated by

column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.27 – 7.21 (m, 4H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.13 – 7.10 (m, 2H), 7.02 (dd, *J* = 8.4, 1.4 Hz, 1H), 6.98 – 6.93 (m, 2H), 6.68 (s, 1H), 2.49 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.42, 160.96, 139.88, 137.65, 137.17, 136.01, 130.65, 130.57, 130.06, 129.08, 129.05, 128.47, 127.86, 124.02, 120.22, 115.40, 115.19, 110.51, 103.03, 21.53, 21.29.

GC-MS (m/z): 315.6 $[M]^+$.

2.16 Catalyst recovering and recycling. The recyclability of the catalyst was examined for both benzofuran and *N*-arylindole synthesis under standard reaction conditions. The isolation of the α-Syn-PdNPs catalyst was attempted after a reaction between 4-nitrophenol and styrene. After completion of the first cycle (95% GC yield), the reaction mixture was cooled to room temperature, the catalyst was recovered by centrifuging the reaction mixture and filtration. After vacuum drying of the catalyst was used in the 2nd run under the same reaction conditions as the first (92% yield). Run 3 to 4 took a slightly longer time for completion (30h). Good catalytic activity remained up to the 4 cycles.

After first cycle, the filtrate was subjected to ICP-AES measurement to estimate the amount of Pd leached out from catalyst. The ICP measurement revealed that the presence of negligible amount of Pd in the filtrate.

Further, the recovery of the catalyst was also tested from the reaction between diphenylamine and styrene. The catalyst was recovered by simple filtration and reused up to 3 cycles. All these results revealed the stability of the nanocomposite and firm deposition of PdNPs on the α-Syn fibril.

Reaction conditions for the synthesis of benzofuran:

Run 1: 4-nitrophenol (1 mmol) and styrene (0.5 mmol) using α-Syn-PdNPs (7.5 mol %), 1,10-phenanthroline (15 mol %), V_2O_5 (2.5 equiv), and NaOAc (1.5 equiv) in DCE (4 mL) at 110 ºC for 24 h. After reaction completion, the mixture was cooled, centrifuged and filtered (GC Yield, 95%).

Run 2: 4-nitrophenol (1 mmol) and styrene (0.5 mmol) was loaded in the same reaction tube (above mentioned, Run 1) and DCE (4 mL) was added and performed reaction at 110 ºC for 24 h (GC Yield, 92%).

Run 3: 4-nitrophenol (1 mmol) and styrene (0.5 mmol), along with 1,10-phenanthroline (15 mol %), V_2O_5 (1 equiv), and NaOAc (0.5 equiv) was added in DCE (4 mL) (in above mentioned, Run 2) and performed reaction at 110 ºC for 30 h (GC Yield, 92%).

Run 4: 4-nitrophenol (1 equiv), styrene (0.5 equiv) was added in DCE (4 mL) (in above mentioned, Run 2) and performed reaction at 110 ºC for 30 h (GC Yield, 90%).

Reaction conditions for the synthesis of *N*-aryindole:

Run 1: diphenylamine (1 mmol), styrene (0.25 mmol), α-Syn-PdNPs (10 mol%), 1,10-phenanthroline (20 mol%) and CuOAc (2 equiv) in 4 mL $ClCH_2CH_2Cl$ (DCE) at 130 ºC for 24 h. After reaction completion, the mixture was cooled, centrifuged and filtered (GC Yield, 92%).

Run 2: Diphenylamine (1 mmol), styrene (0.25 mmol) were loaded in the same reaction tube (above mentioned, Run 1) and DCE (4 mL) was added and performed reaction at 130 ºC for 24 hours (GC Yield, 89%).

Run 3: Diphenylamine (1 mmol) and styrene (0.25 mmol) along with CuOAc (1 equiv) were added in DCE (4 mL) (in above mentioned, Run 2) and performed reaction at 130 ºC for 30 hours (GC Yield, 86%).

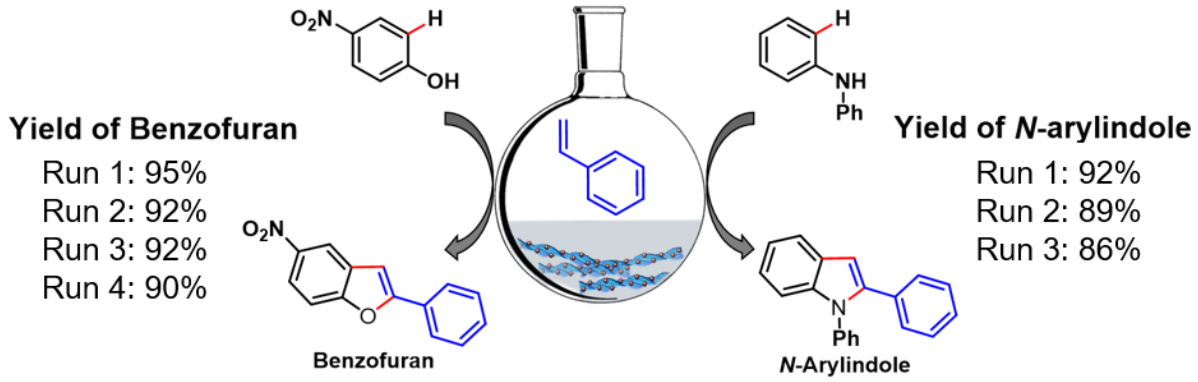
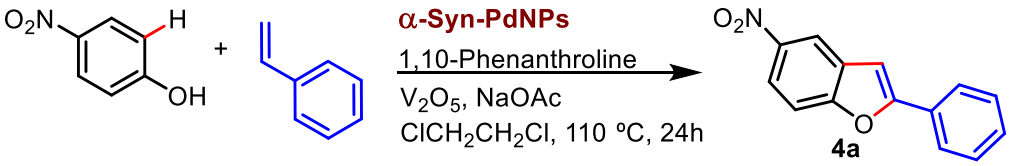


Figure S5. α-Syn-PdNPs shown to be recyclable. The composite was recovered after each reaction cycle and reused for next reaction cycle.

Table S1: Yield of benzofuran and Pd nanoparticle size in different cycles



Run/Cycle	Yield of benzofuran 4a (%)	Pd nanoparticle size (nm)
1	95	3
2	92	3.4
3	92	3.6
4	90	3.9

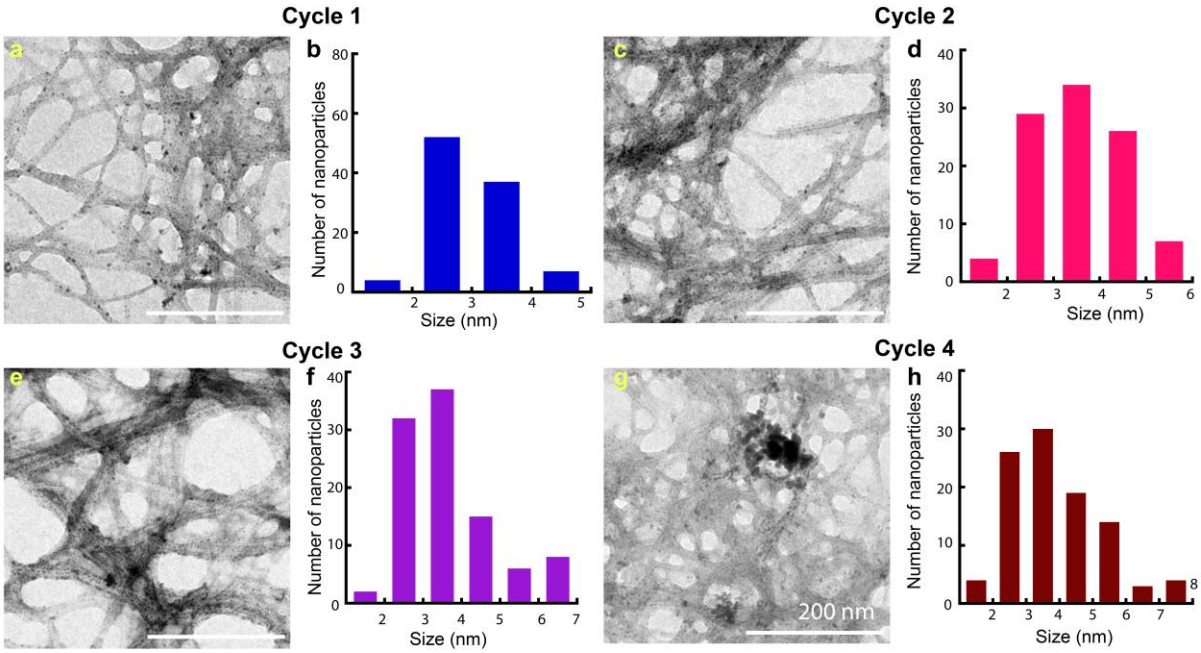


Figure S6. Particle size distribution histogram of the recovered catalyst up to four cycles

3. Supporting Figures:

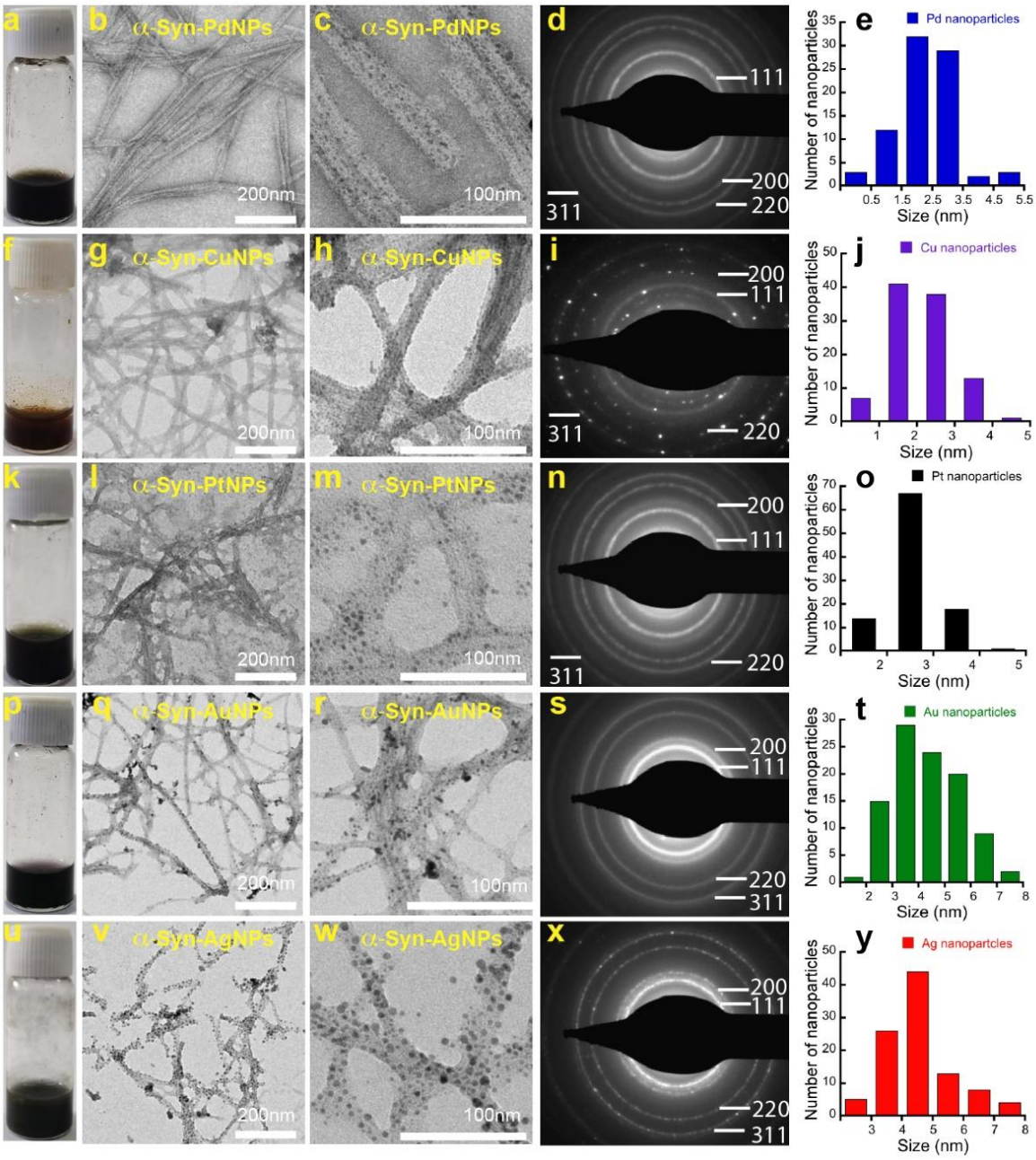


Figure S7. TEM characterization of Pd, Cu, Pt, Au and Ag nanocomposite of α-Syn-fibrils. Visual observation of nanocomposites (a,f,k,p,u). Morphology of different metal nanocomposites at low magnification (b,g,l,q,v) and high magnification (c,h,m,r,w) with α-Syn fibrils. Electron diffraction pattern of nanocomposite (d,i,n,s,x). Size distribution of Pd, Cu, Pt, Au and Ag nanoparticles in their respective nanocomposite (e,j,o,t,y).

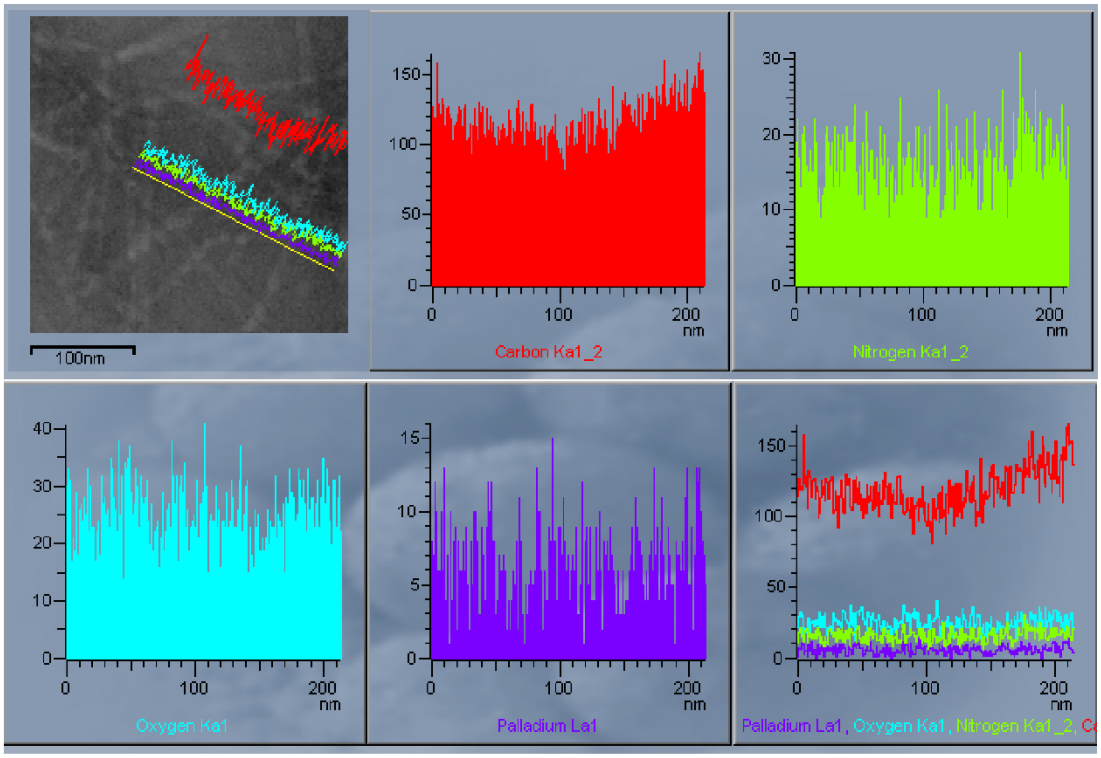


Figure S8. Line mapping on single fibril containing α-Syn-PdNPs showing abundance of carbon, nitrogen, oxygen and pallidum on single fibril.

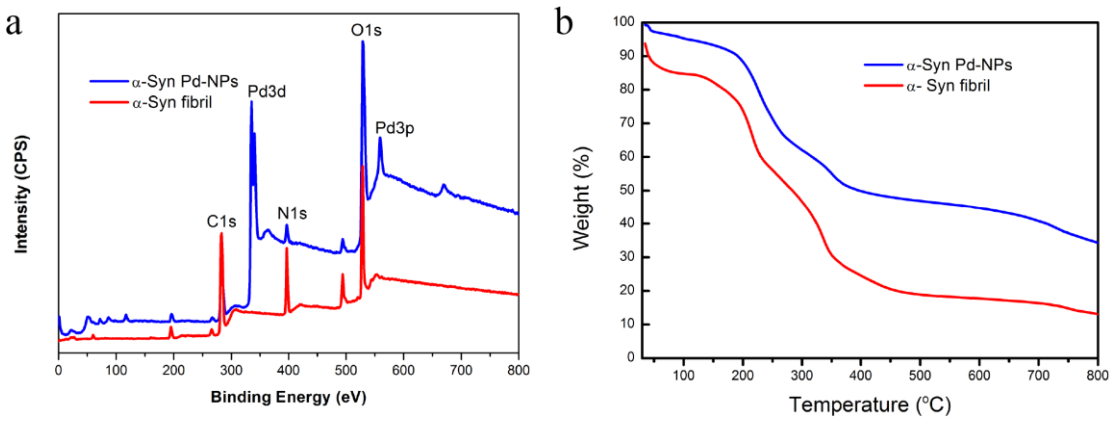


Figure S9. a) XPS survey spectra of α-Syn fibril and α-Syn-PdNPs confirming presence of palladium in composite. C, N and O peaks were observed from fibril whereas additional Pd peaks was observed in α-Syn-PdNPs composite. b) Thermogavimatric analysis of α-Syn fibril and α-Syn-PdNPs from 25° C to 800 ° C.

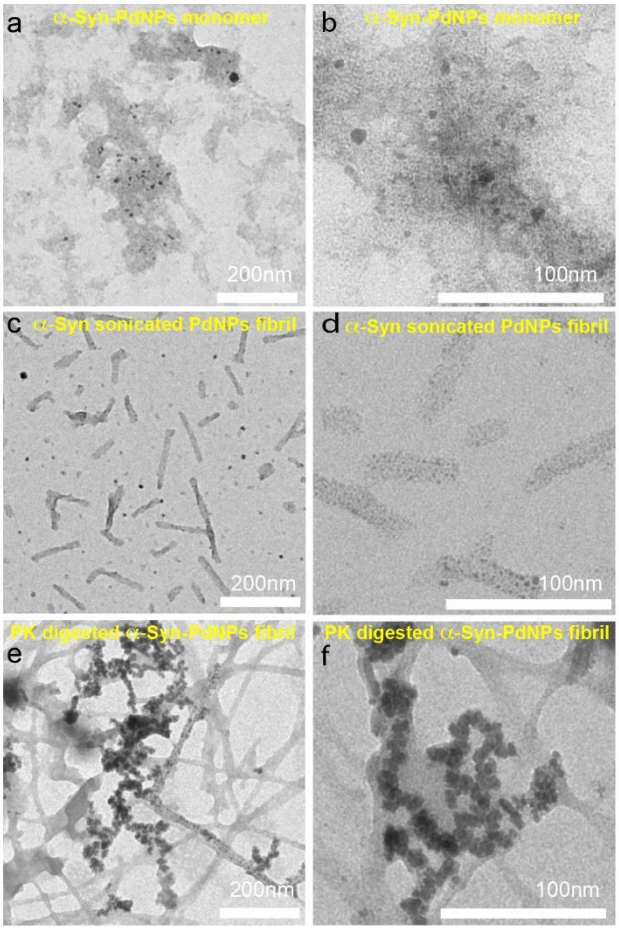


Figure S10. Morphology of different catalyst as visualized by TEM. α-Syn-PdNPs monomer (a, b), sonicated α-Syn-PdNPs (c, d) and Proteinase K digested α-Syn-PdNPs (e, f).

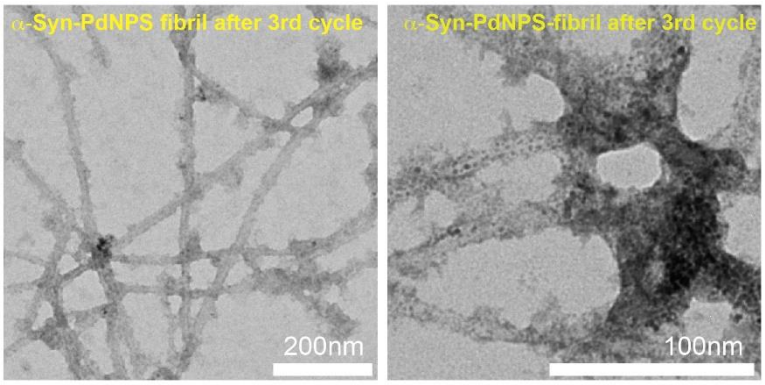


Figure S11. Morphology of recovered α-Syn-PdNPs after 3rd cycle from N-arylindole synthesis observed by TEM.

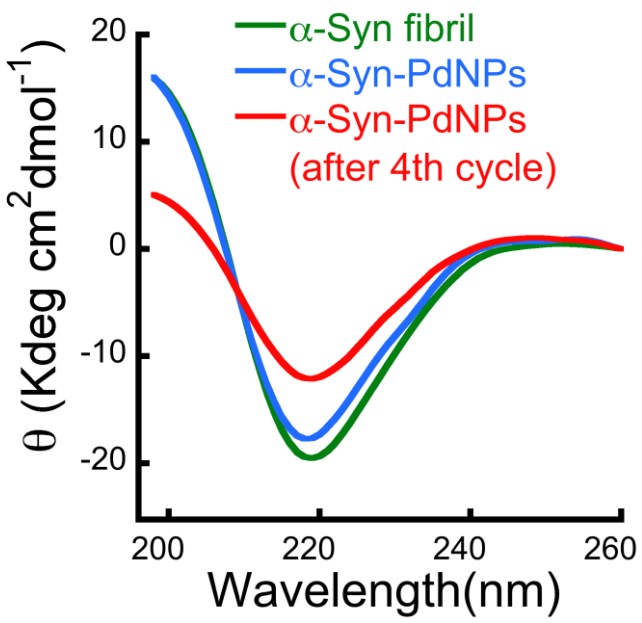


Figure S12: Circular Dichroism (CD) spectra showing negative band at 218 nm for both α-Syn fibril and α-Syn-PdNPs which correspond to β-sheet structure of protein/amyloid. Recovered α-Syn-PdNPs (after four cycle) also shows similar pattern with a slightly reduced intensity.

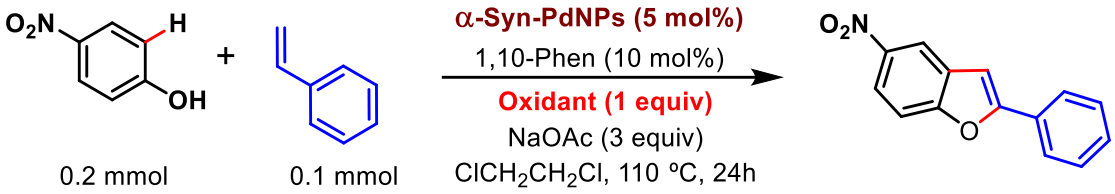
4. Supporting Tables

Table S2: Review of reported palladium nanoparticle based electrooxidation of ethanol

Catalysts	Electrolyte	Pd loading ($\mu g/cm^2$)	ECSA (m^2/g_{Pd})	Mass Current density ($A/mg_{Pd\ cm^2}$)	References
α-Syn-PdNPs	**1 M KOH + 1 M Ethanol**	**9.5**	**160.6**	**9.4**	**This Work**
PdCo nanotube	1 M KOH + 1M Ethanol	23.4	50.13	1.15	[10]
$Pd_{50}Ag_{50}$	1 M KOH + 1 M EtOH	1.25	32.81	1.97	[11]
Pd_7/Ru_1 bimetallic nanodendrites	1 M KOH +1 M NaOH	56.62	1.587	1.15	[12]
PdPt nanowires	1 M KOH +0.5 M NaOH	71.4	-	0.94	[13]
Pd–PEDOT/GE nanocomposites	1 M KOH + 1 M Ethanol	86	13.2	0.458	[14]
Pd/C	1 M KOH + 1 M Ethanol	-	39	0.019	[15]

Table S3. Optimization by varying oxidant for the synthesis of benzofuran

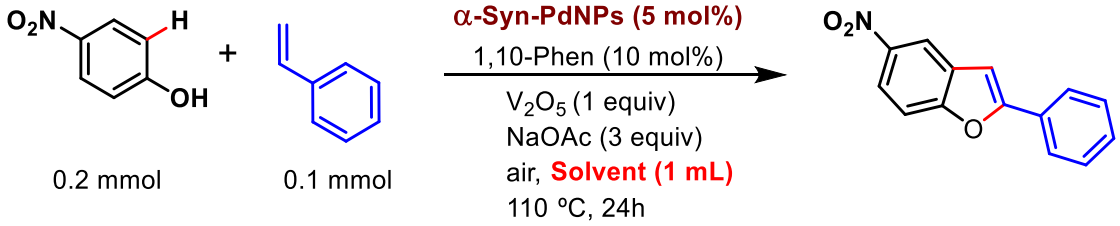
(Reactions were carried out by having styrene as a limiting reagent).



Entry	Oxidant (1 equiv)	GC Yield (%)
1	$Cu(OAc)_2.H_2O$	12
2	1,4-benzoquinone	28
3	Ag_2CO_3	15
4	AgOAc	8
5	Cu_2O	10

6	CuO	25
7	CuOAc	42
8	**V_2O_5**	**48**
9	$K_2S_2O_8$	20
10	Oxone	5
11	Ag_2SO_4	28
12	1,4-Naphthoquinone	8

Table S4. Optimization of solvent for the synthesis of benzofuran

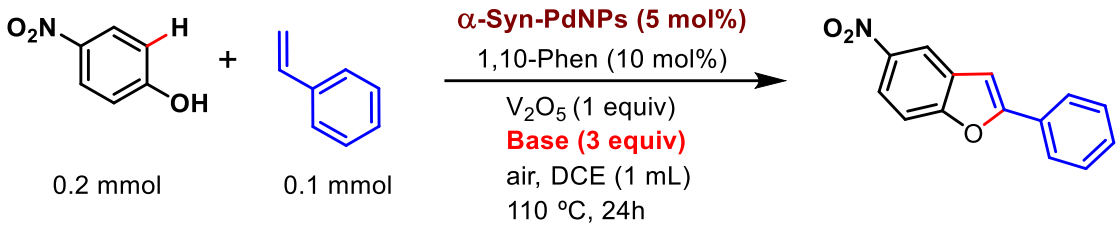


Entry	Solvent (1 mL)	GC Yield (%)
1	**DCE**	**48**
2	H_2O	25
3	CH_3CN	12
4	1,4-dioxane	n.d.
5	Toluene	28
6	AmOH	10
7	TFE	n.d.
8	HFIP	20
9	DMF	8
10	DMSO	15
11	THF	n.d.

12	EtOH	n.d.
13	M-Xylene	5

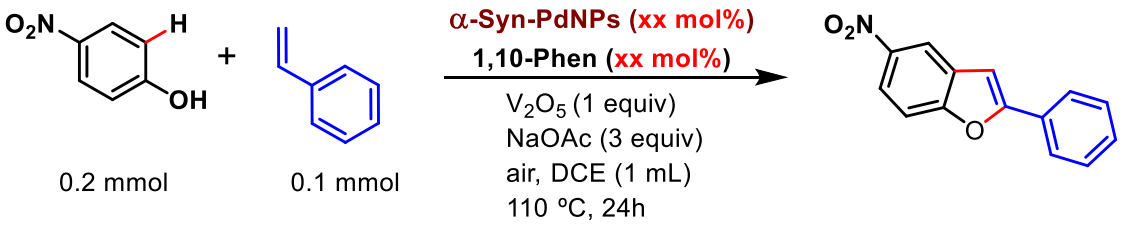
n.d. means not detected

Table S5. Optimization by varying base for the synthesis of benzofuran



Entry	Base	GC Yield (%)
1	Nil	15
2	**NaOAc**	**48**
3	$NaHCO_3$	42
4	Na_2HPO_4	23
5	$KHCO_3$	40
6	Na^tBu	28
7	KH_2PO_4	15
8	NH_4OAc	nd
9	DBU	30

Table S6. Optimization by varying the amount of catalyst and ligand



Entry	Amount of catalyst (*α*-Syn-PdNPs)	Amount of ligand	GC Yield (%)
1	5 mol%	10 mol%	48
2	**7.5 mol%**	**15 mol%**	**59**
3	10 mol%	20 mol%	59

4	15 mol%	30 mol%	42
5	20 mol%	30 mol%	38

Table S7. Ligand optimization for the synthesis of benzofuran

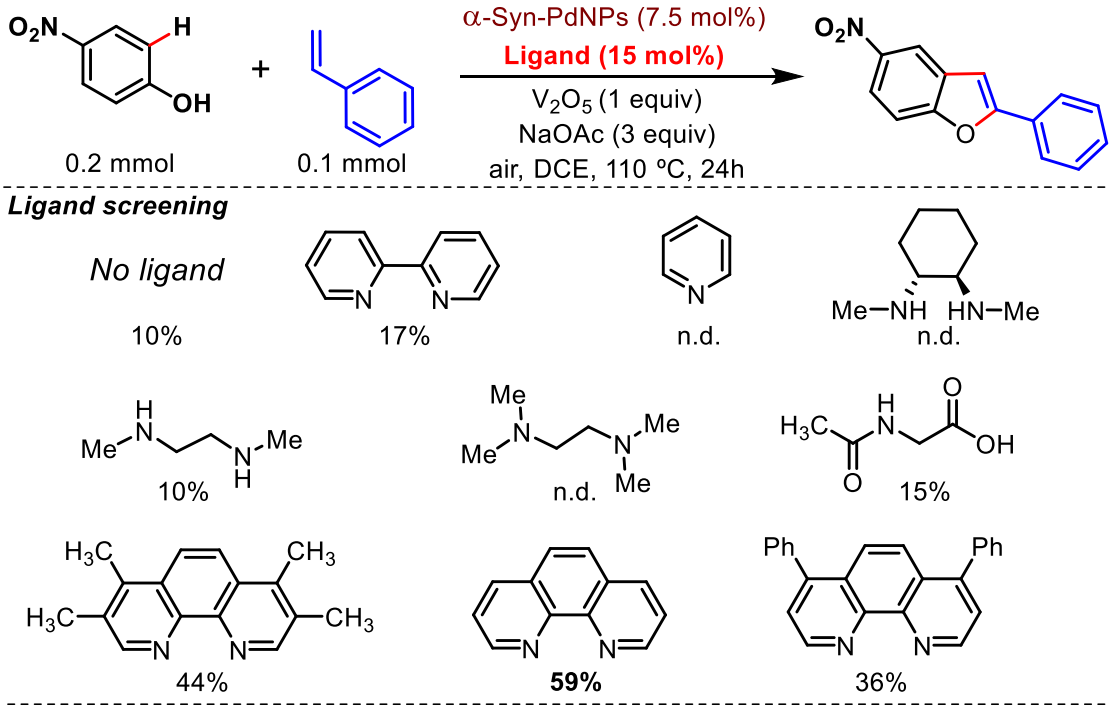
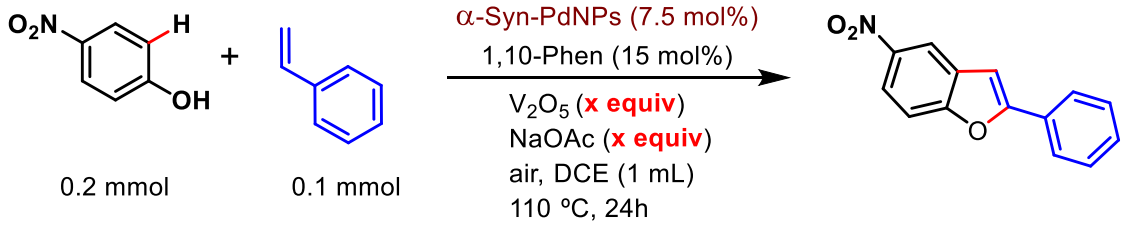


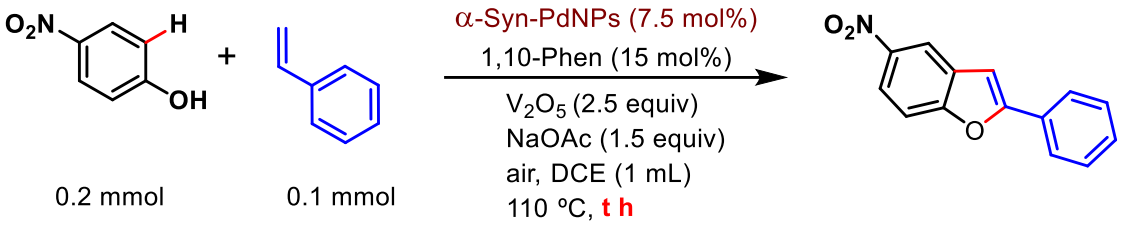
Table S8. Optimization by varying the amount of oxidant and base for the synthesis of benzofuran



Entry	Equivalent of NaOAc	Equivalent of V_2O_5	GC Yield (%)
1	1.0	1.0	42
2	2.0	1.0	47
3	3.0	1.0	59
4	3.0	1.5	65
5	3.0	2.0	84

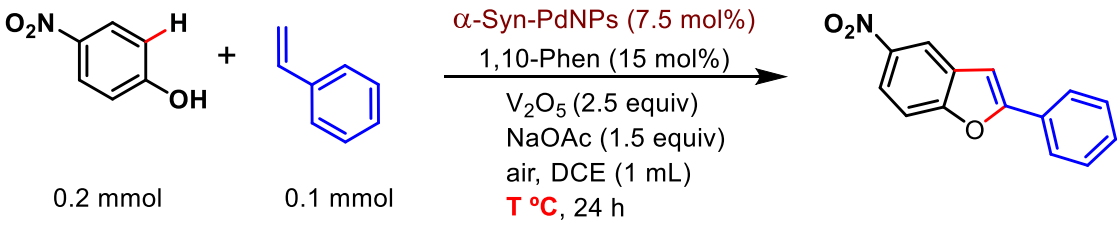
6	2.0	2.5	92
7	**1.5**	**2.5**	**95**
8	1.0	3.0	91

Table S9. Time optimization for the synthesis of benzofuran



Entry	Time (h)	GC Yield (%)
1	12	58
2	**24**	**95**
3	36	83
4	48	52

Table S10. Temperature optimization for the synthesis of benzofuran

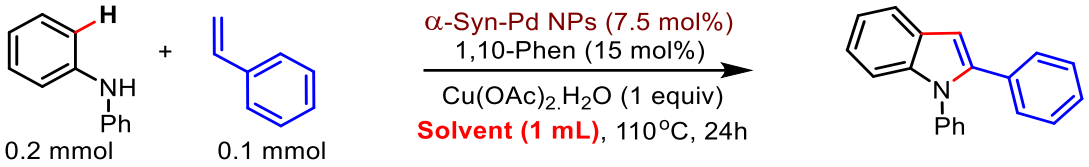


Entry	Temperature (°C)	GC Yield (%)
1	70	20
2	80	28
3	90	40
4	100	87
5	**110**	**95**
6	120	90

7	130	72

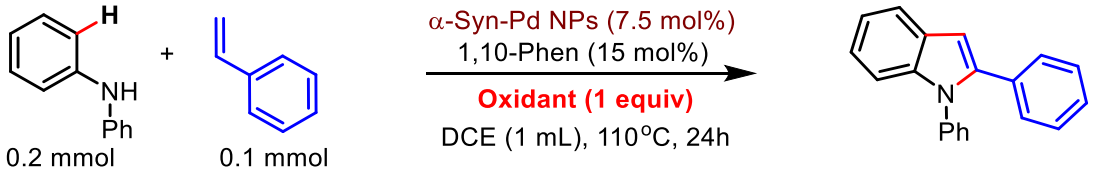
Table S11. Optimization by varying solvent for the synthesis of *N*-arylindole

(Reactions were carried out by having styrene as a limiting reagent).



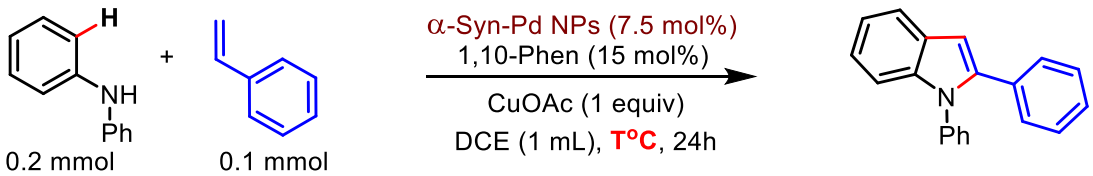
Entry	Solvent (1 mL)	GC Yield (%)
1	**DCE**	**52**
2	HFIP	28
3	TFE	40
4	Toluene	18
5	Acetic acid	30
6	Pivalic acid	12
7	1,4-dioxane	n.d.
8	DMF	n.d.
9	THF	3
10	DMSO	15
11	AmOH	n.d.
12	H_2O	15
13	CH_3CN	8
14	M-Xylene	n.d.
15	MeOH	6
16	NMP	12

Table S12. Optimization by varying oxidant for the synthesis of *N*-arylindole



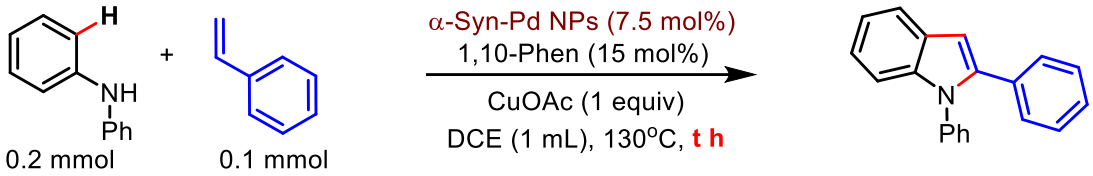
Entry	Oxidant	GC Yield (%)
1	$Cu(OAc)_2.H_2O$	52
2	**CuOAc**	**59**
3	Ag_2CO_3	n.d.
4	AgOAc	n.d.
5	Cu_2O	6
6	CuO	13
7	Ag_2SO_4	15
8	V_2O_5	22
9	$K_2S_2O_8$	n.d.
10	Oxone	n.d.
11	p-benzoquinone	n.d.
12	$PhI(OAc)_2$	n.d.
13	Nil	n.d.
14	O_2	47

Table S13. Temperature optimization for the synthesis of *N*-arylindole



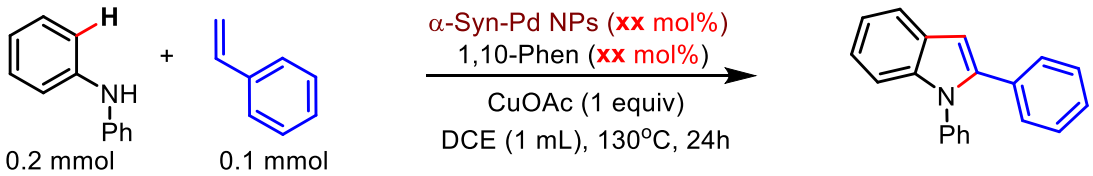
Entry	Temperature	GC Yield (%)
1	90	40
2	100	51
3	110	59
4	120	67
5	**130**	**72**
6	140	69

Table S14. Time optimization for the synthesis of *N*-arylindole



Entry	Time	GC Yield (%)
1	12 h	32
2	**24 h**	**72**
3	36 h	63
4	48h	56

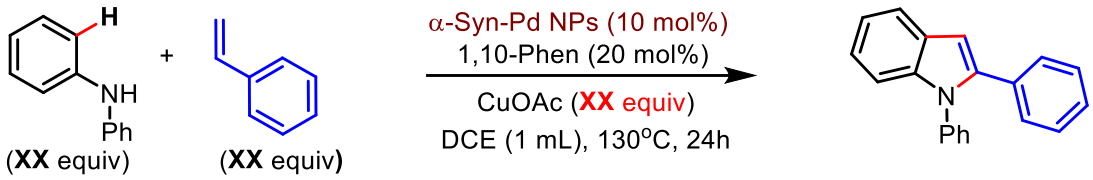
Table S15. Amount of Catalyst for the synthesis of *N*-arylindole



Entry	Amount of catalyst (*α*-Syn-PdNPs)	Amount of ligand	GC Yield (%)
1	5 mol%	10 mol%	48
2	7.5 mol%	15 mol%	72
3	**10 mol%**	**20 mol%**	**85**
4	15 mol%	30 mol%	81

5	20 mol%	30 mol%	74

Table S16. Equivalent of Diaryl amine and Styrene for the synthesis of *N*-arylindole



Entry	diphenylamine (mmol)	Styrene (mmol)	equivalent of anhyd. CuOAc	GC Yield (%)
1	0.2	0.2	1	42
2	0.2	0.1	1	85
3	0.3	0.1	2	87
4	**0.4**	**0.1**	**2**	**92**

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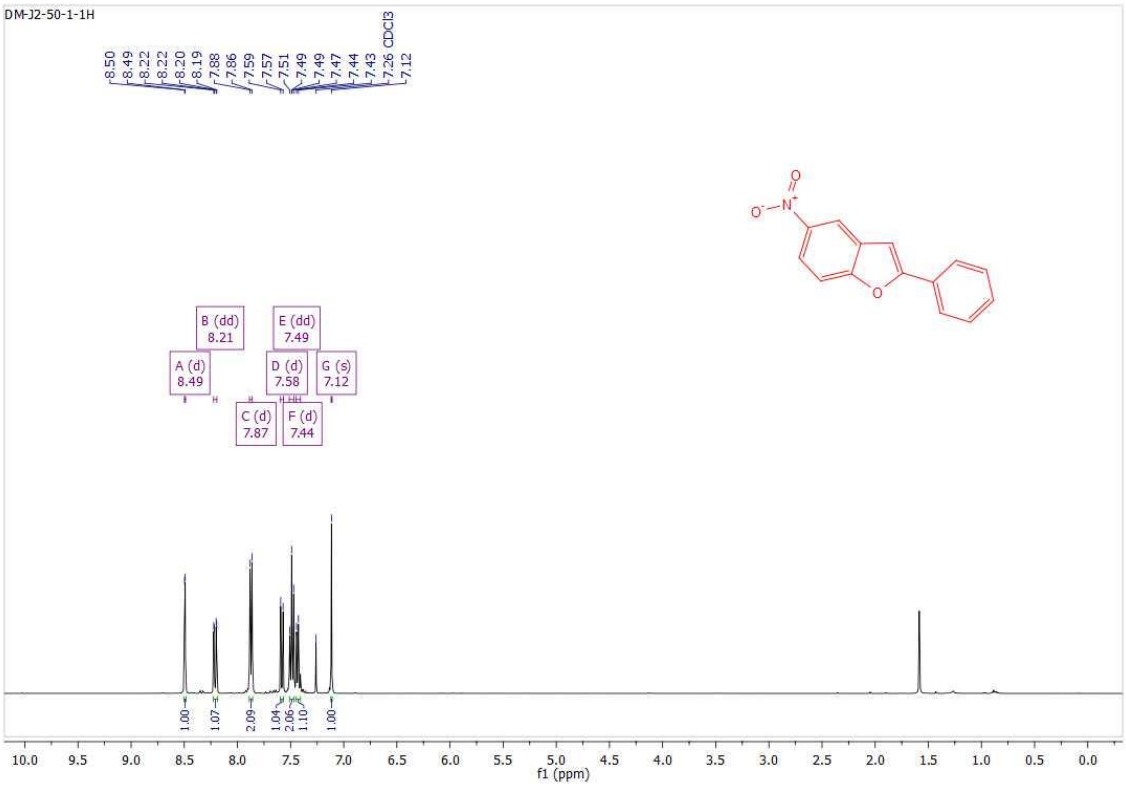
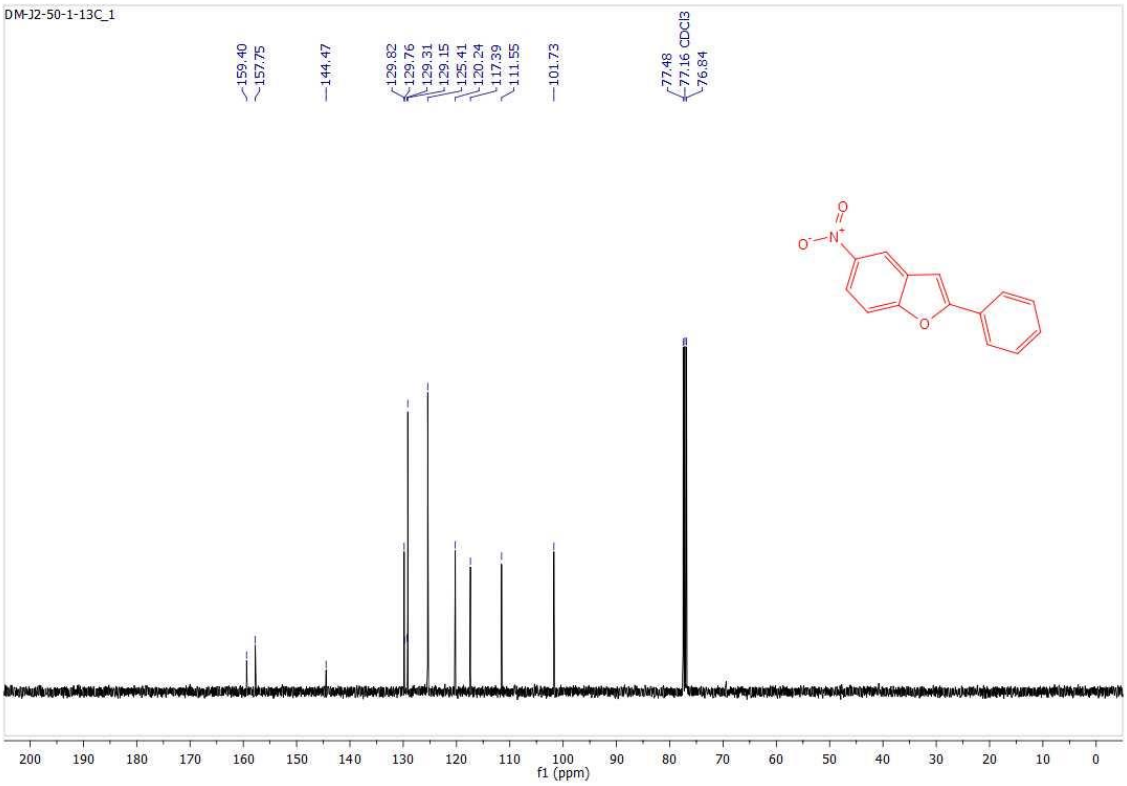
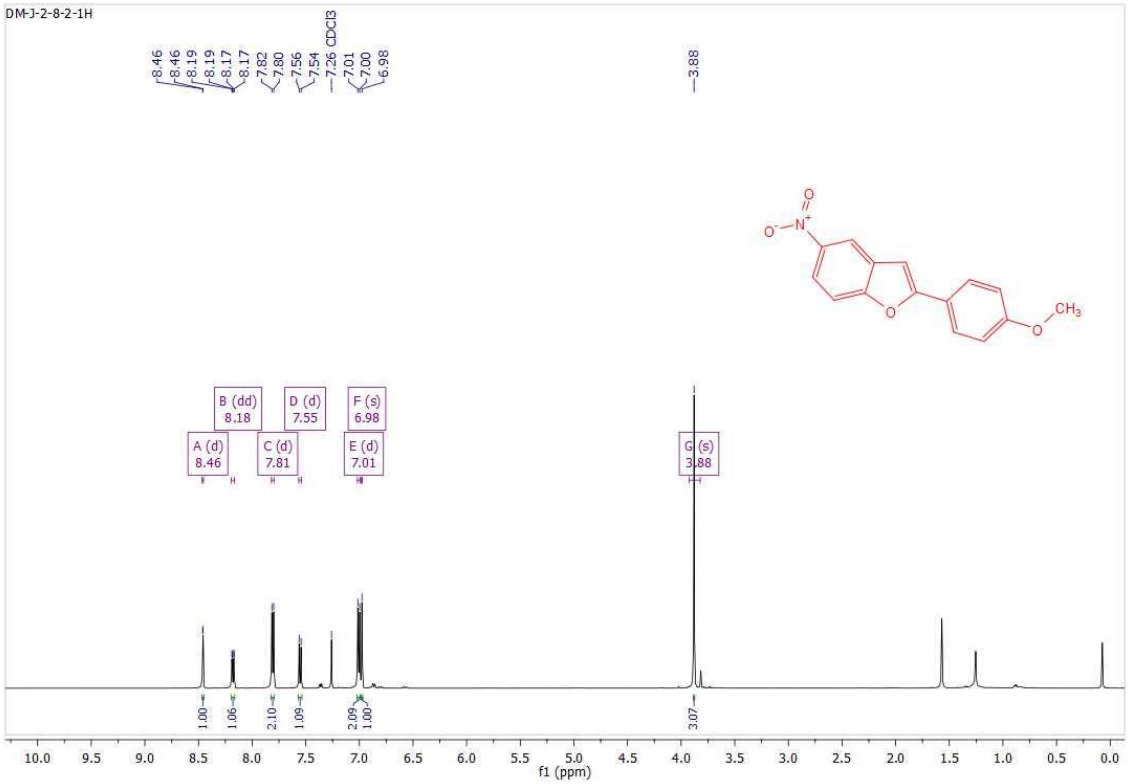
6. NMR spectra of products (Benzofuran and N-arylindole)

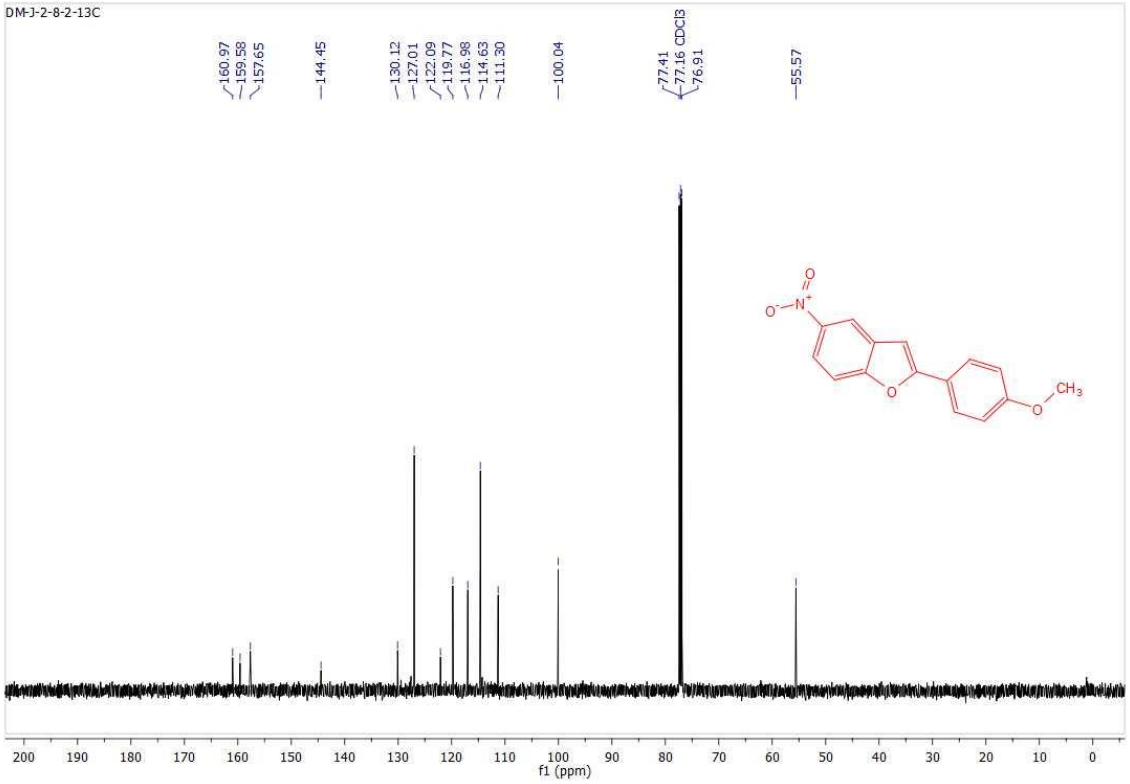
^{1}H and ^{13}C NMR of 5-nitro-2-phenylbenzofuran (4a)



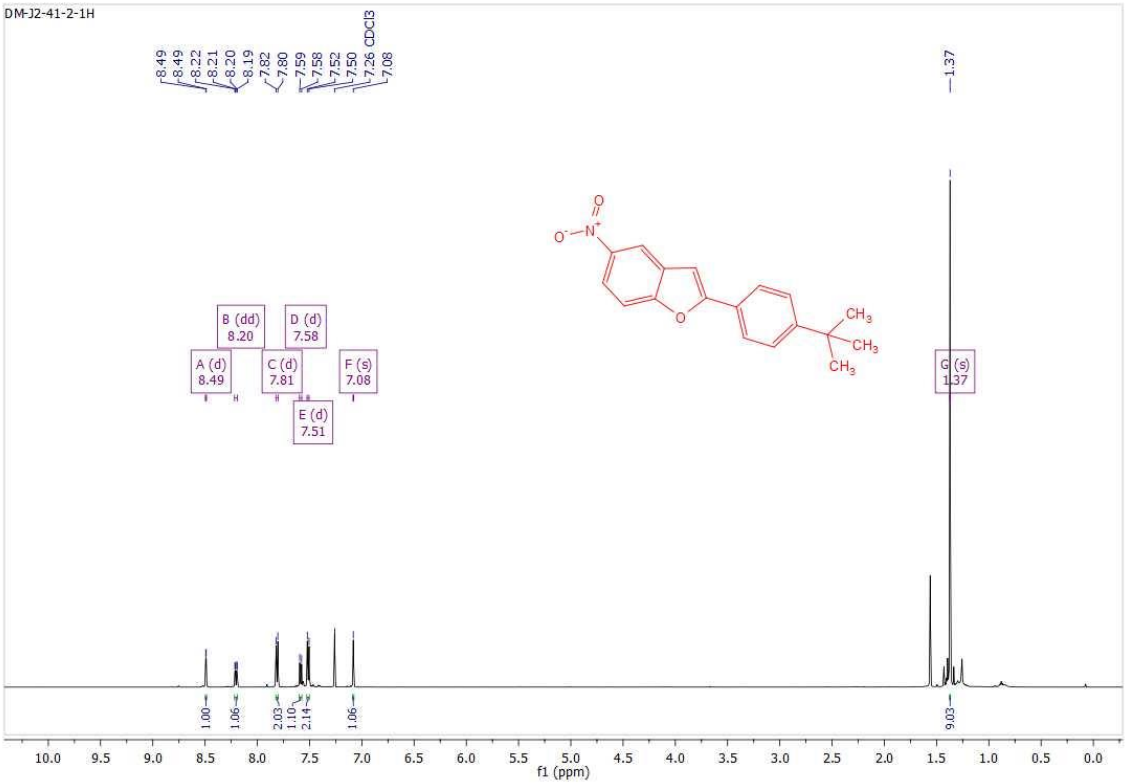


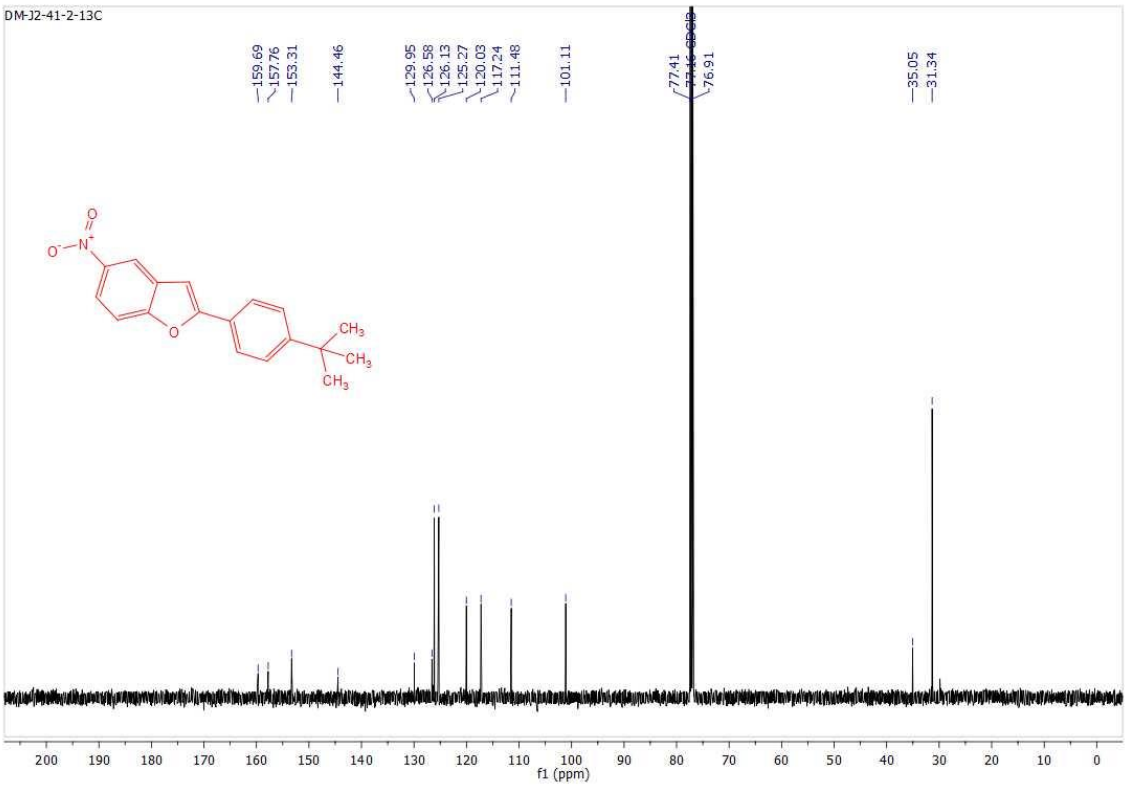
^{1}H and ^{13}C NMR of 5-nitro-2-(4-methoxyphenyl)benzofuran (4b)



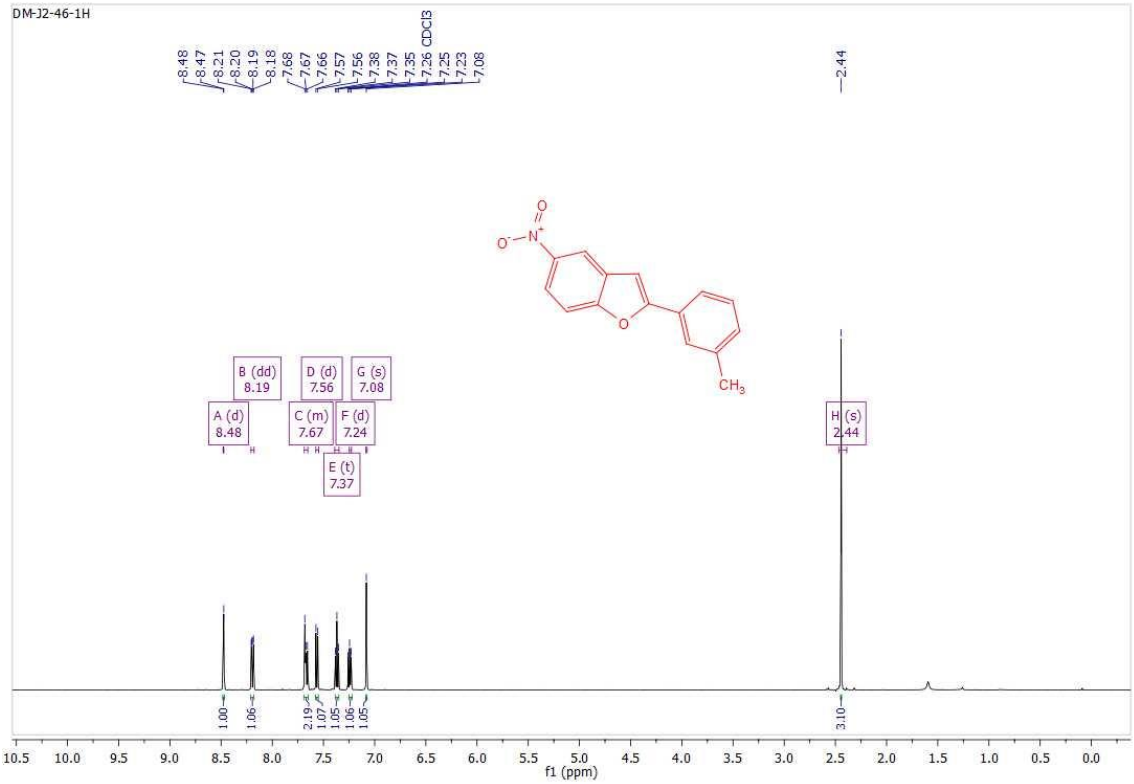


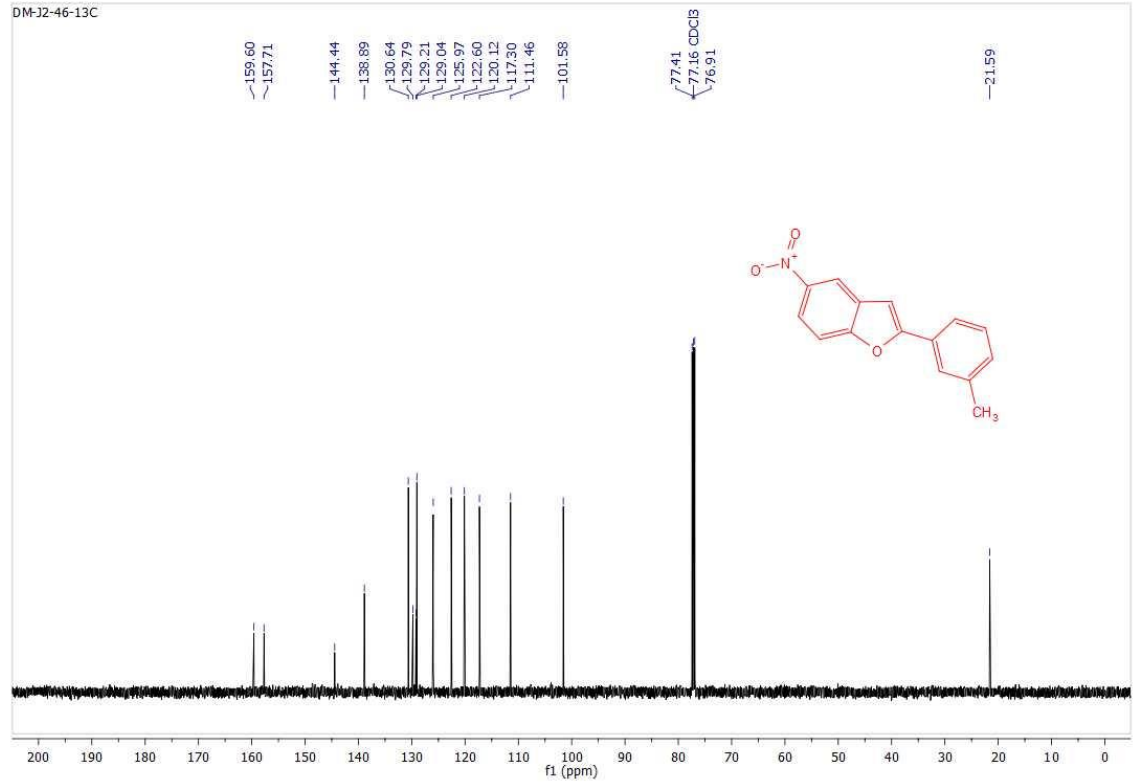
^{1}H and ^{13}C NMR of 2-(4-(tert-butyl)phenyl)-5-nitrobenzofuran (4c)



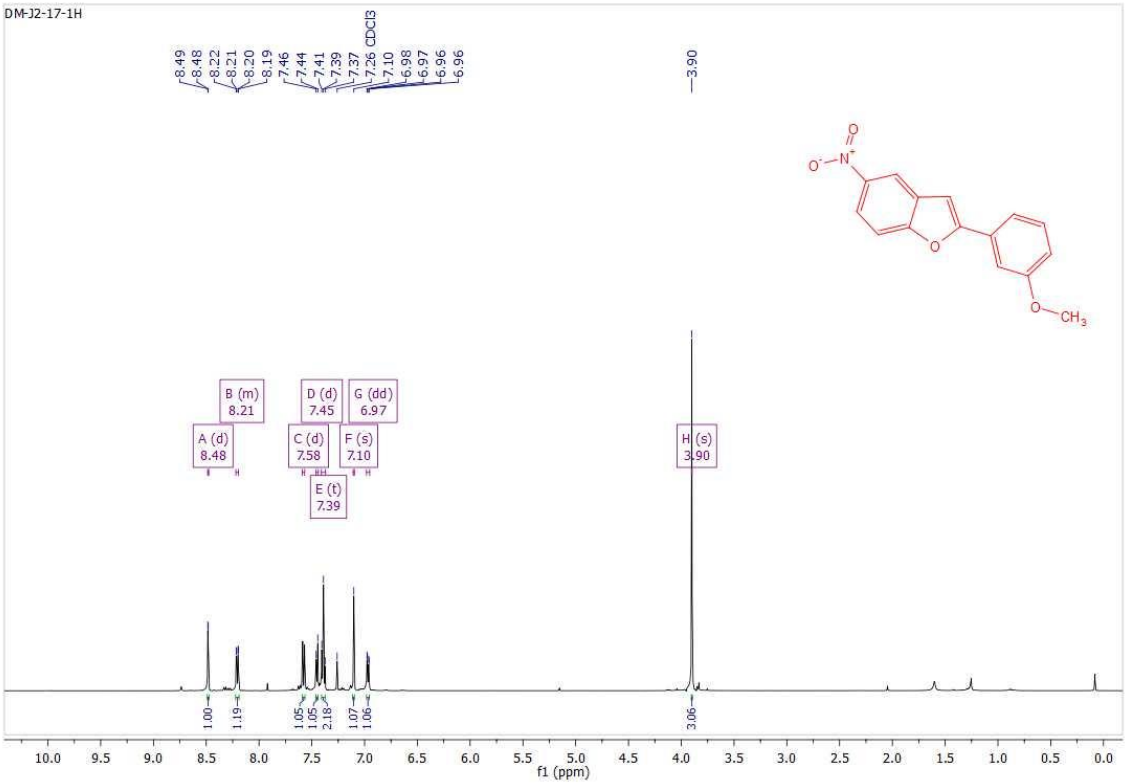


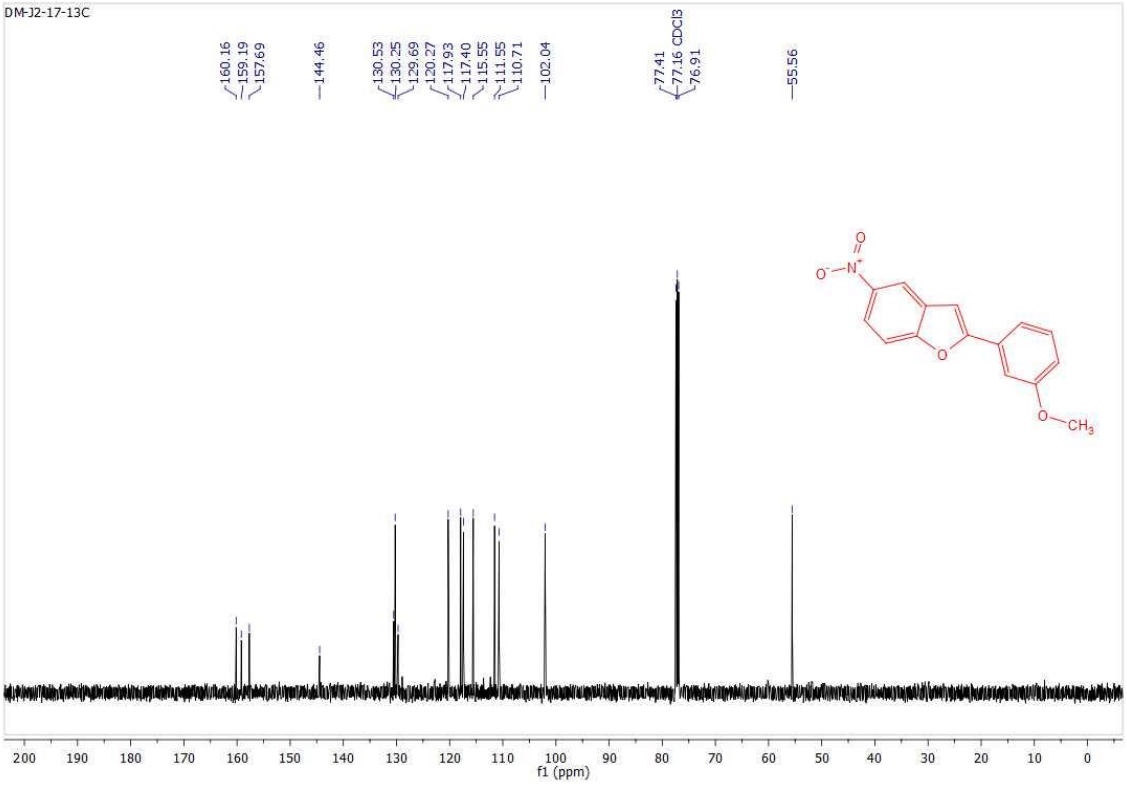
^{1}H and ^{13}C NMR of 5-nitro-2-(3-methylphenyl)benzofuran (4d)



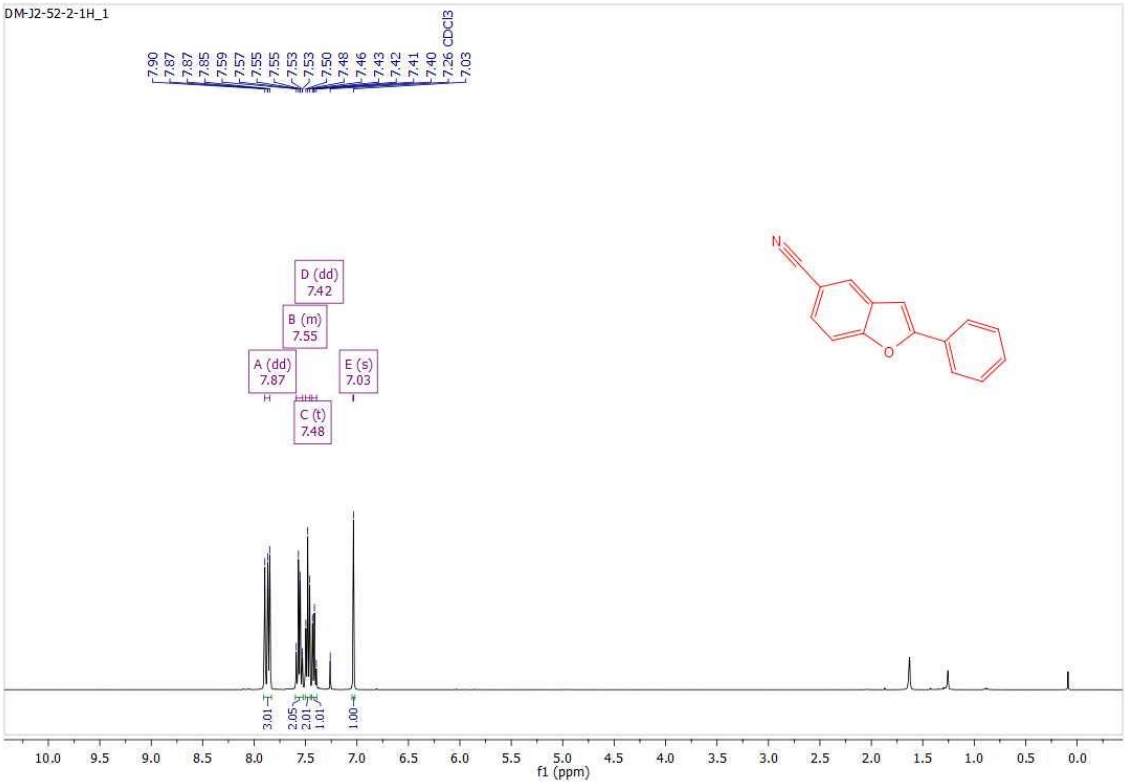


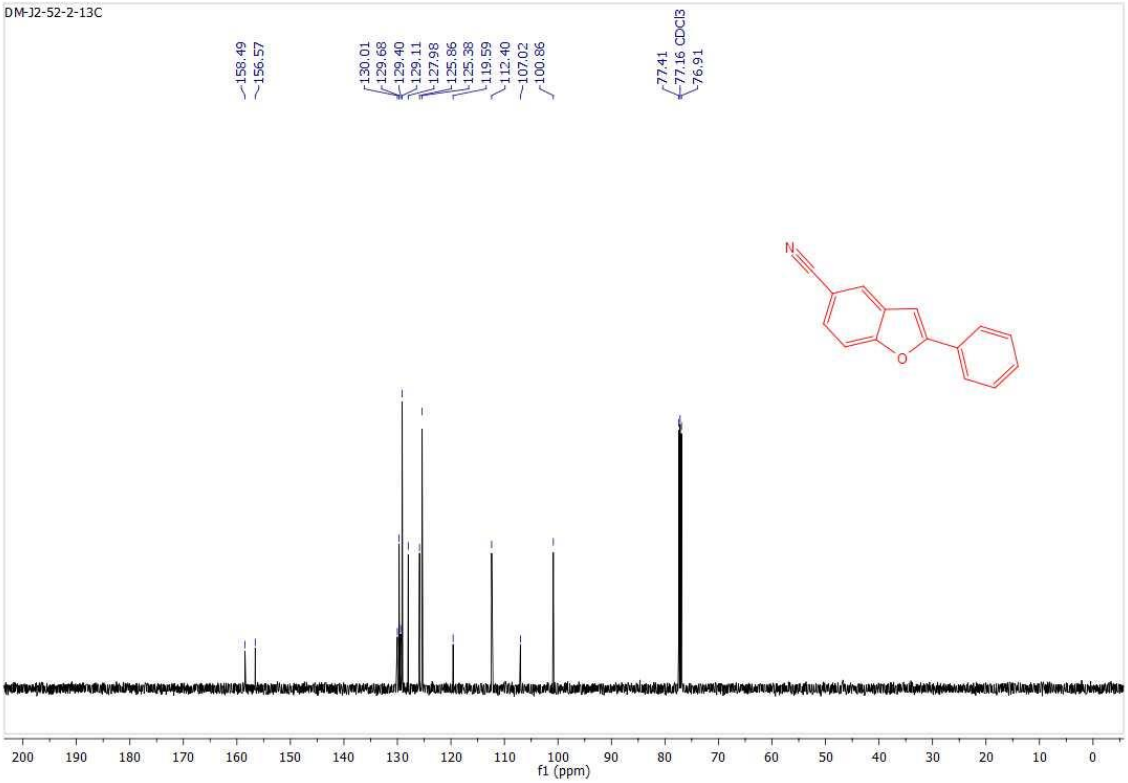
^{1}H and ^{13}C NMR of 2-(3-methoxyphenyl)-5-nitrobenzofuran (4e)



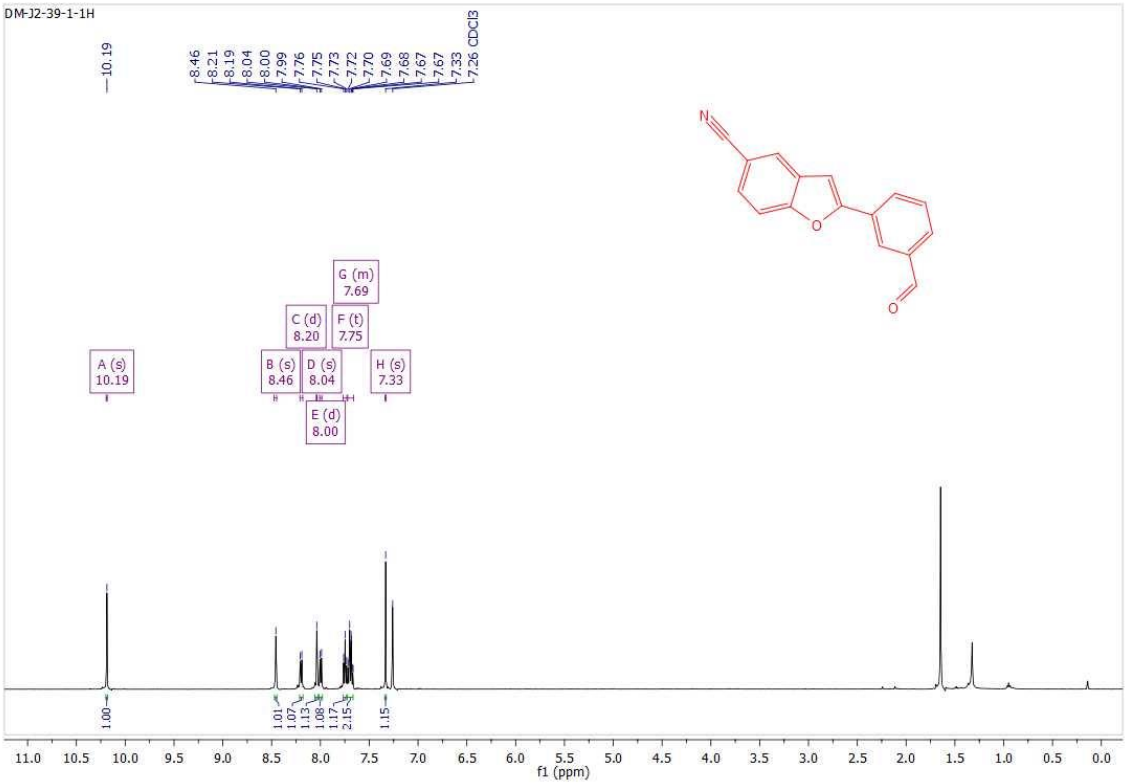


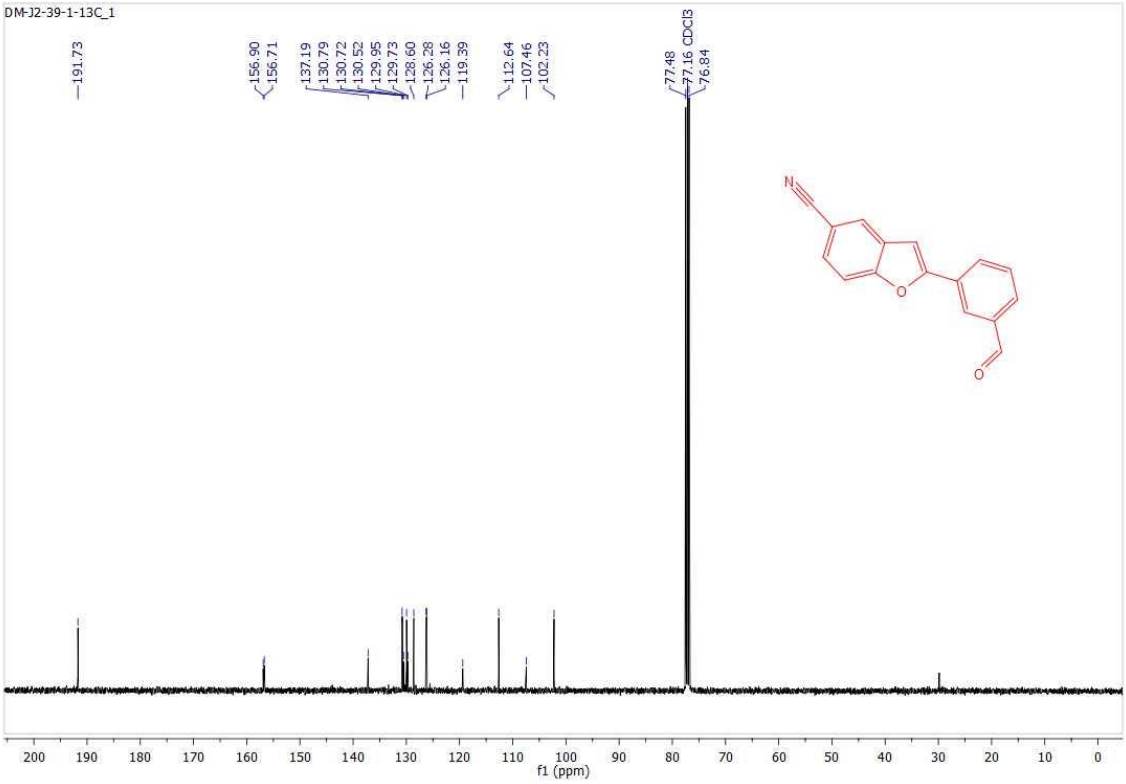
^{1}H and ^{13}C NMR of 5-cyano-2-phenylbenzofuran (4g)



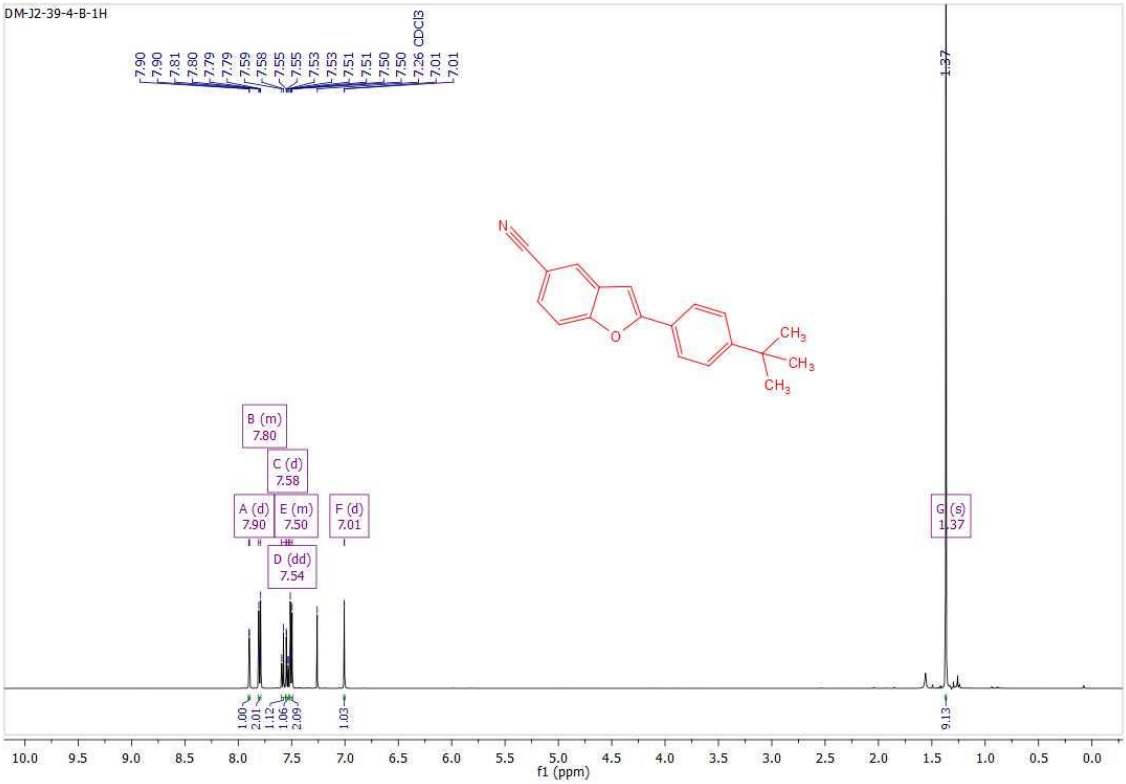


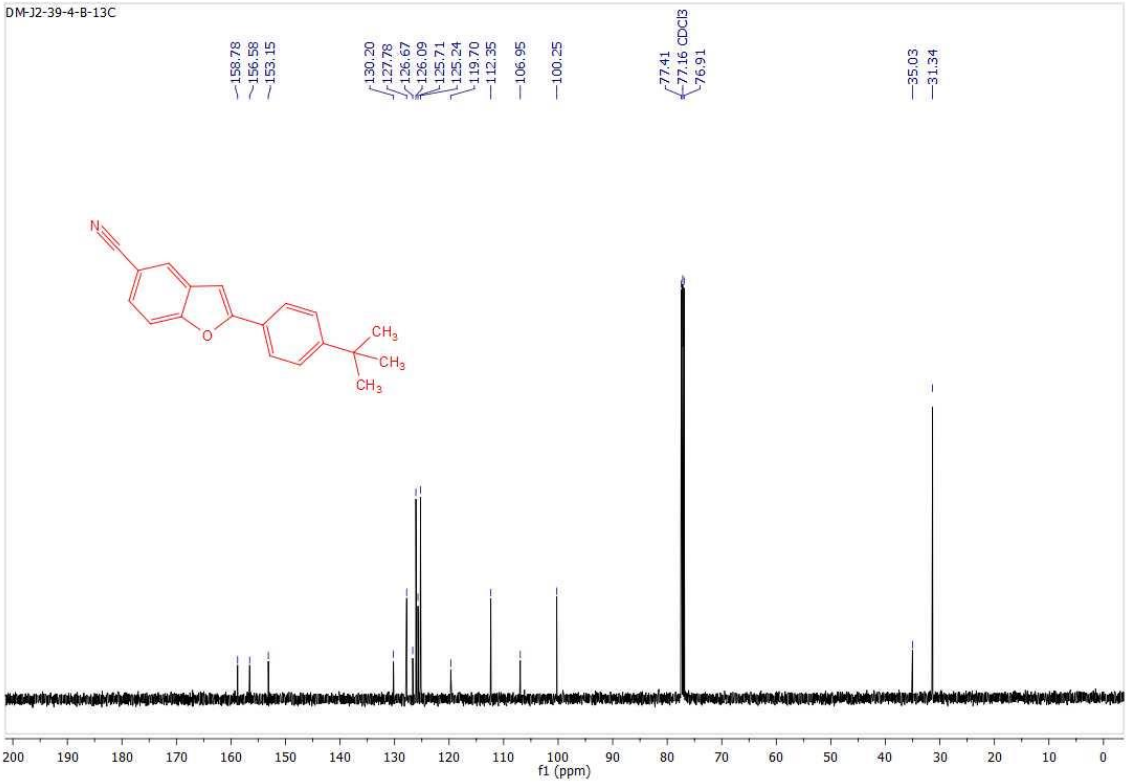
^{1}H and ^{13}C NMR of 5-cyano-2-(3-formylphenyl)benzofuran (4h)



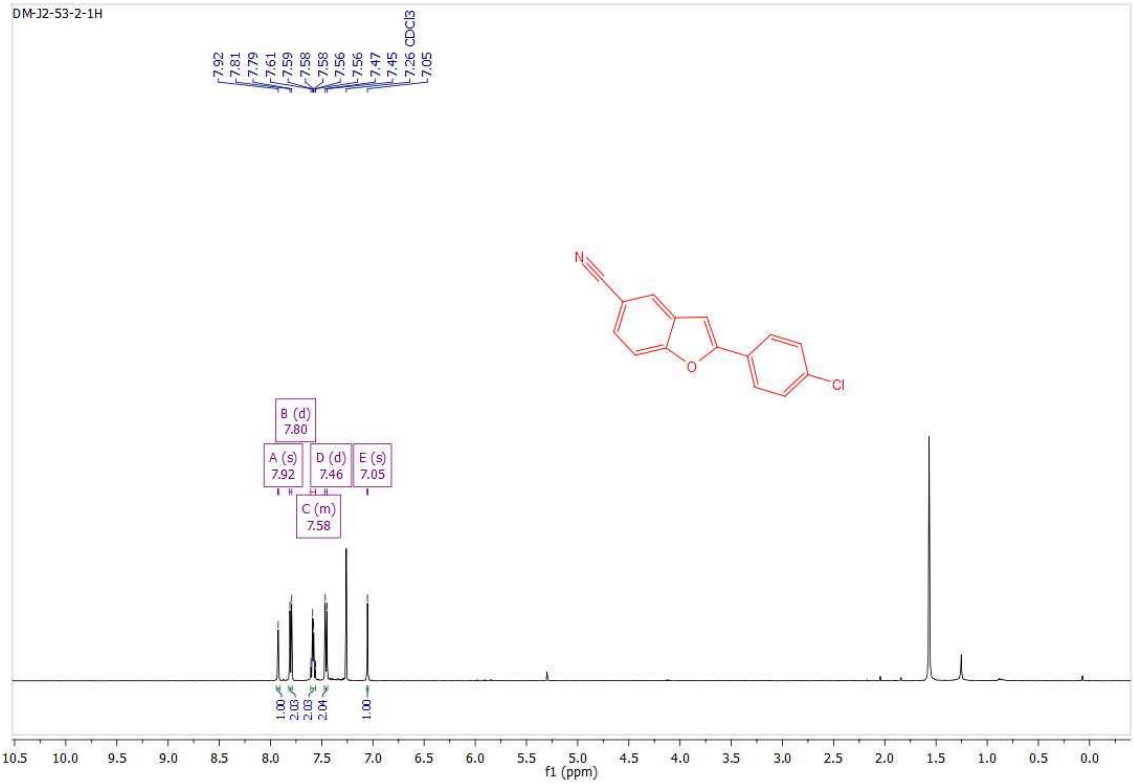


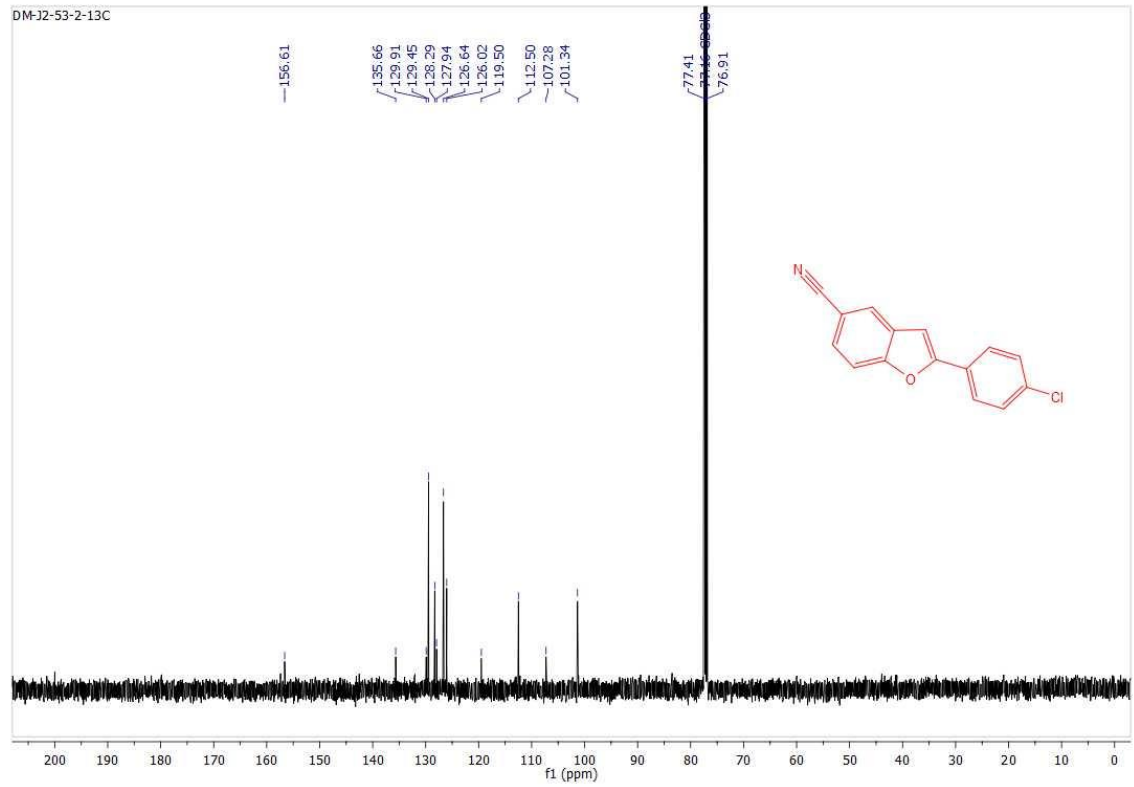
^{1}H and ^{13}C NMR of 2-(4-(tert-butyl)phenyl)benzofuran-5-carbonitrile (4i)



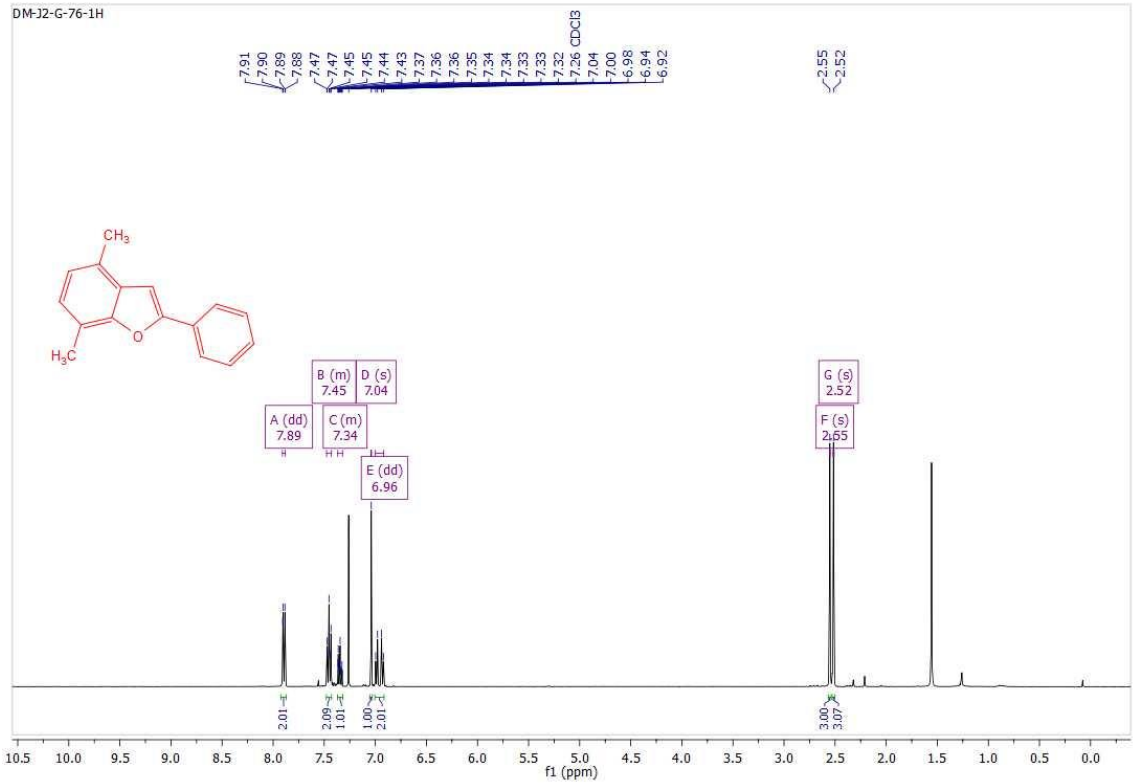


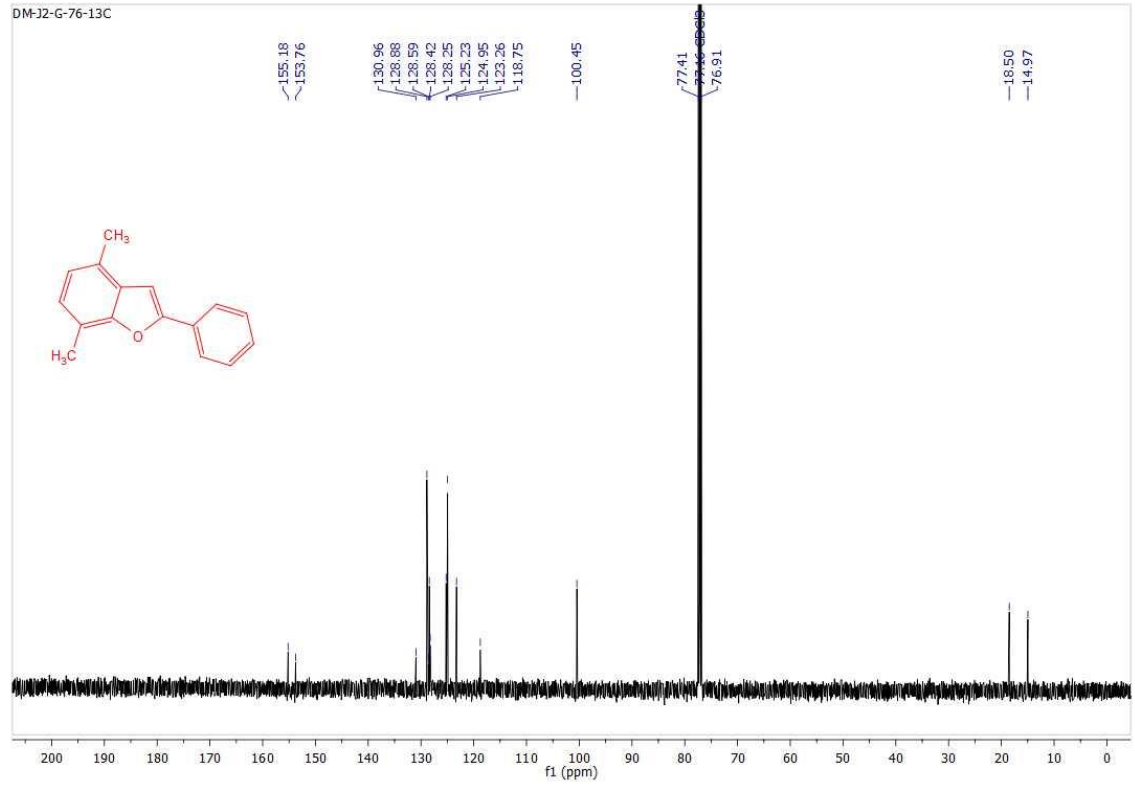
^{1}H and ^{13}C NMR of 5-cyano-2-(4-chlorophenyl)benzofuran (4j)



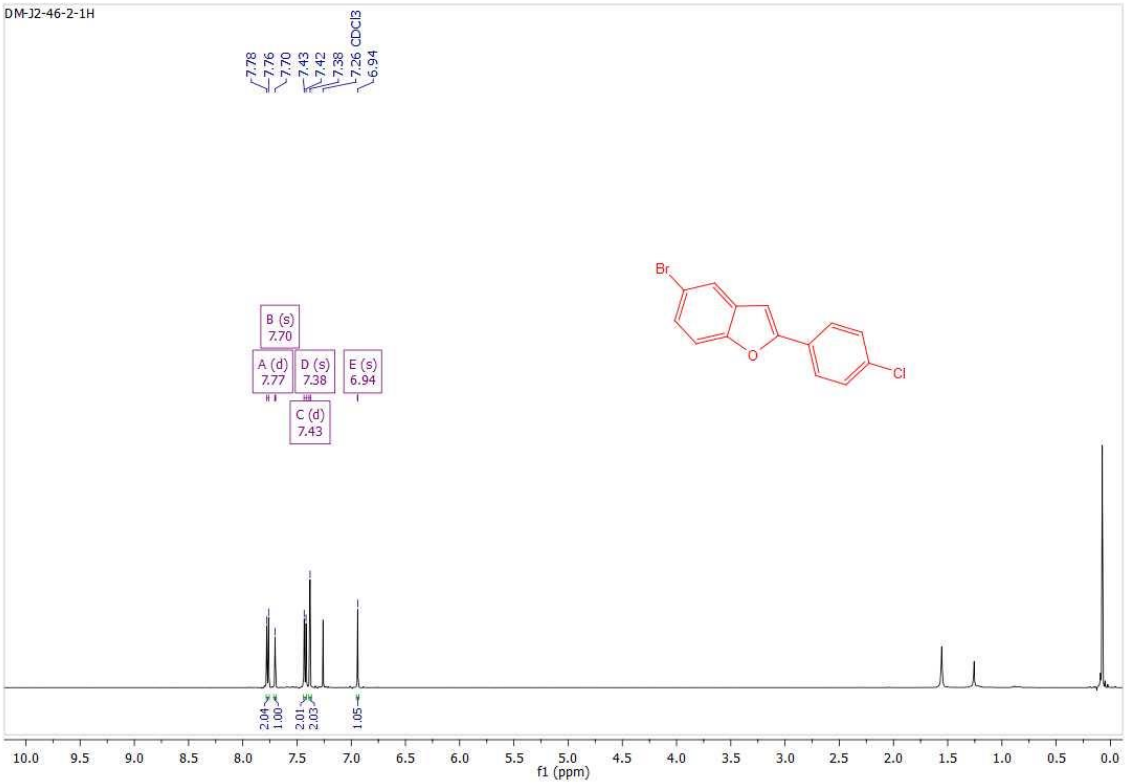


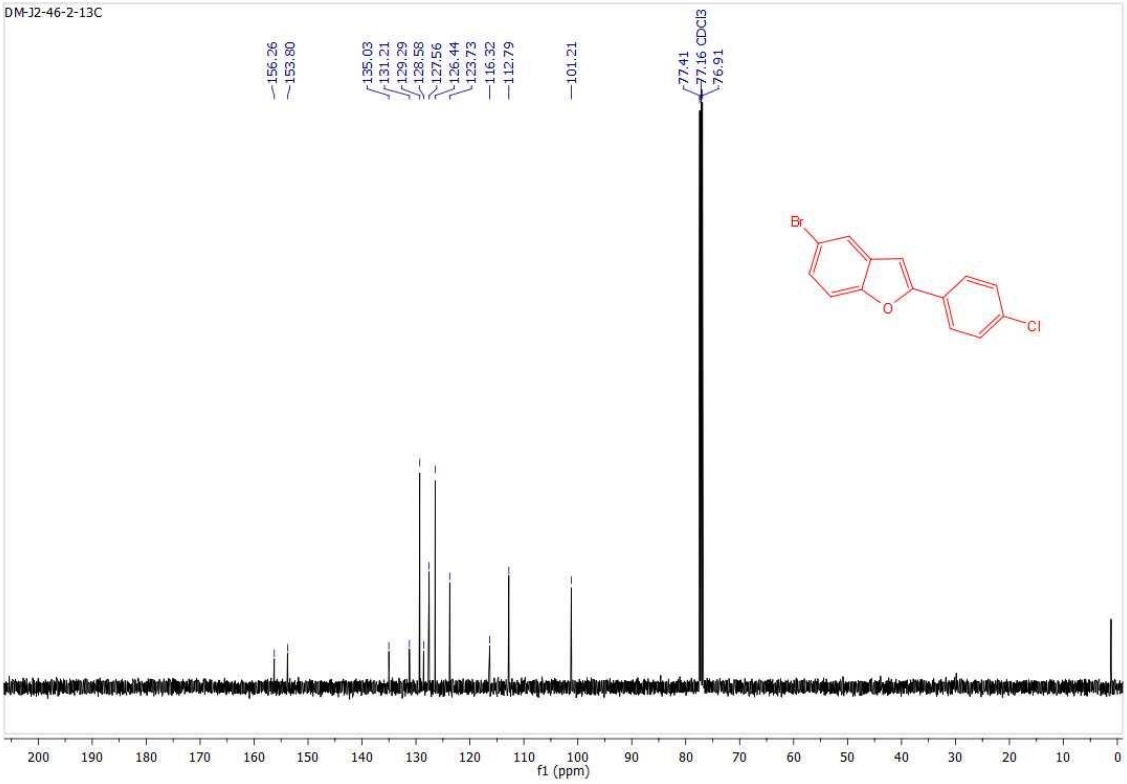
^{1}H and ^{13}C NMR of 4,7-dimethyl-2-phenylbenzofuran (4k)



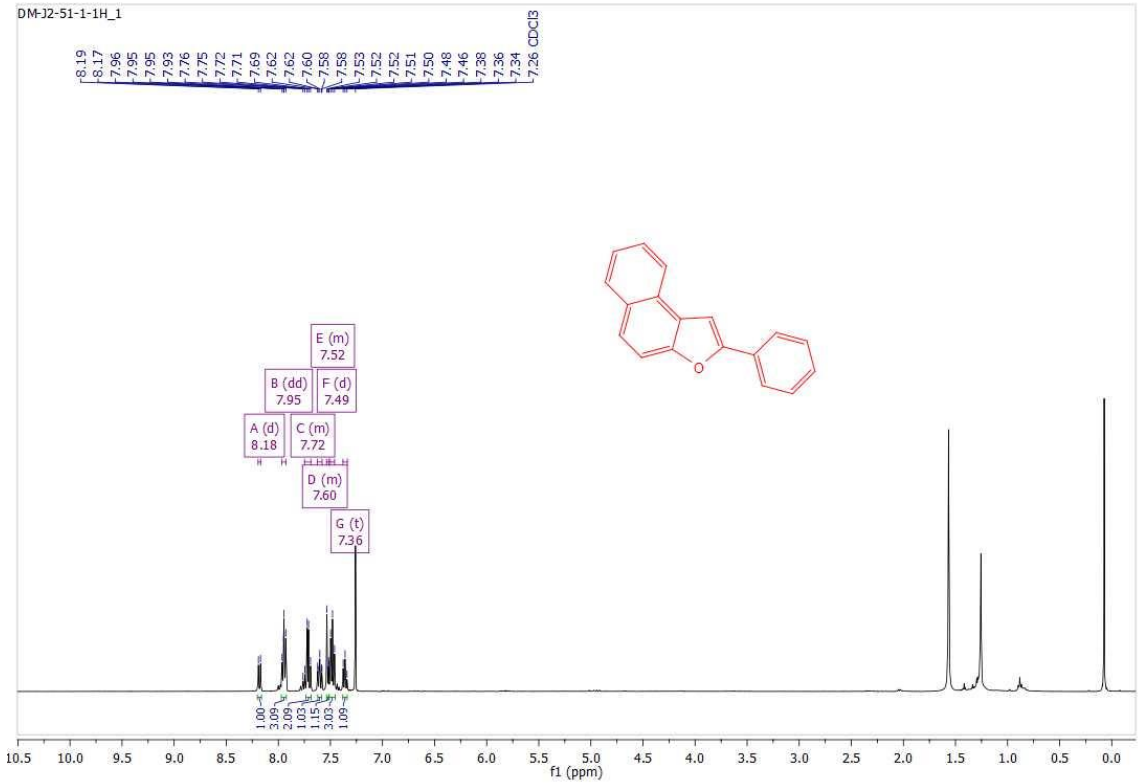


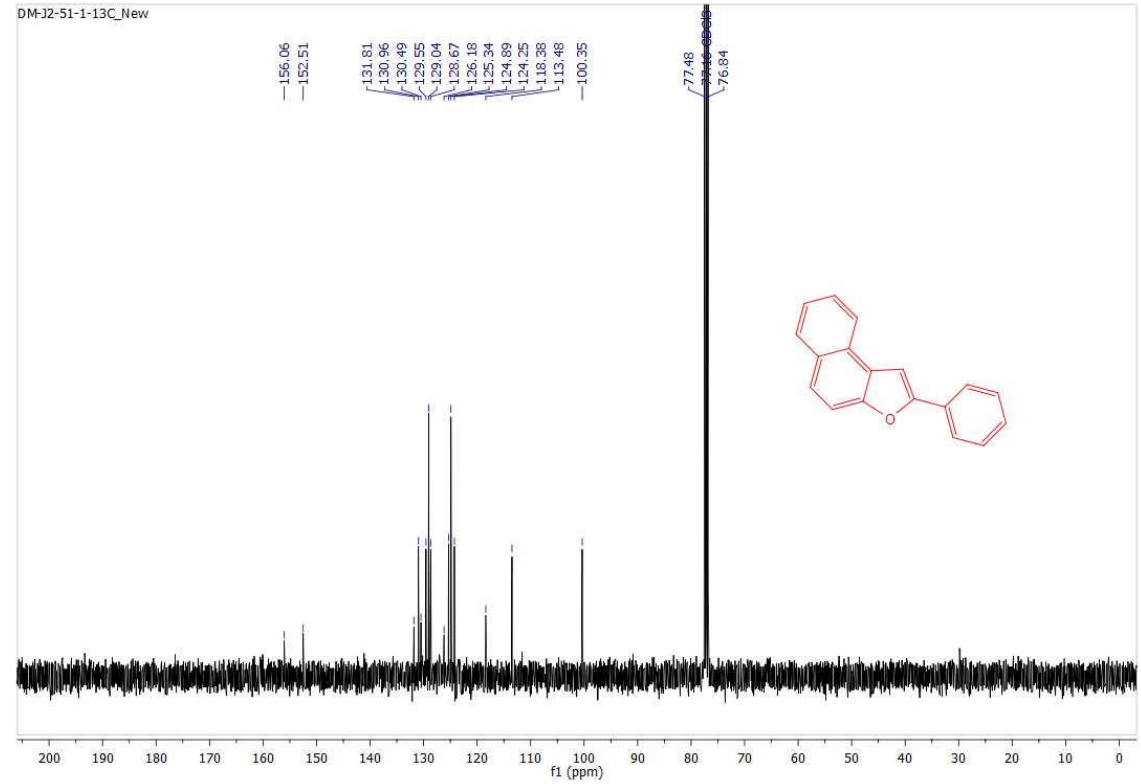
^{1}H and ^{13}C NMR of 5-bromo-2-(4-chlorophenyl)benzofuran (4l)



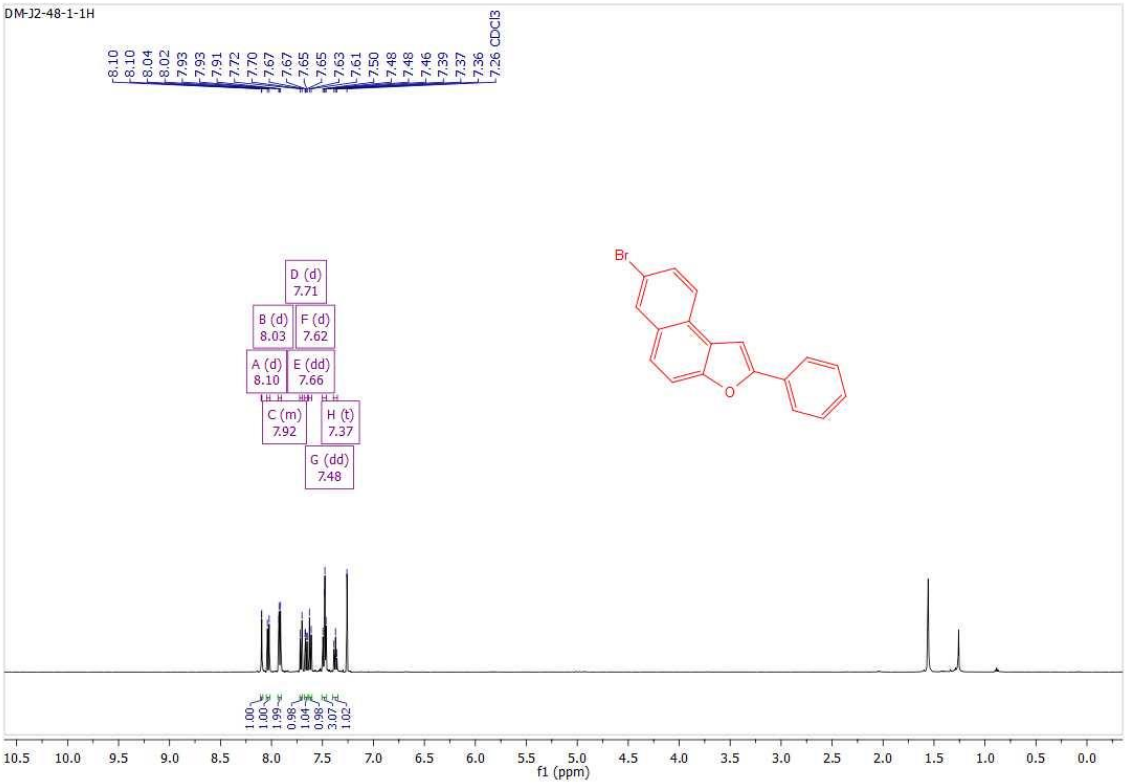


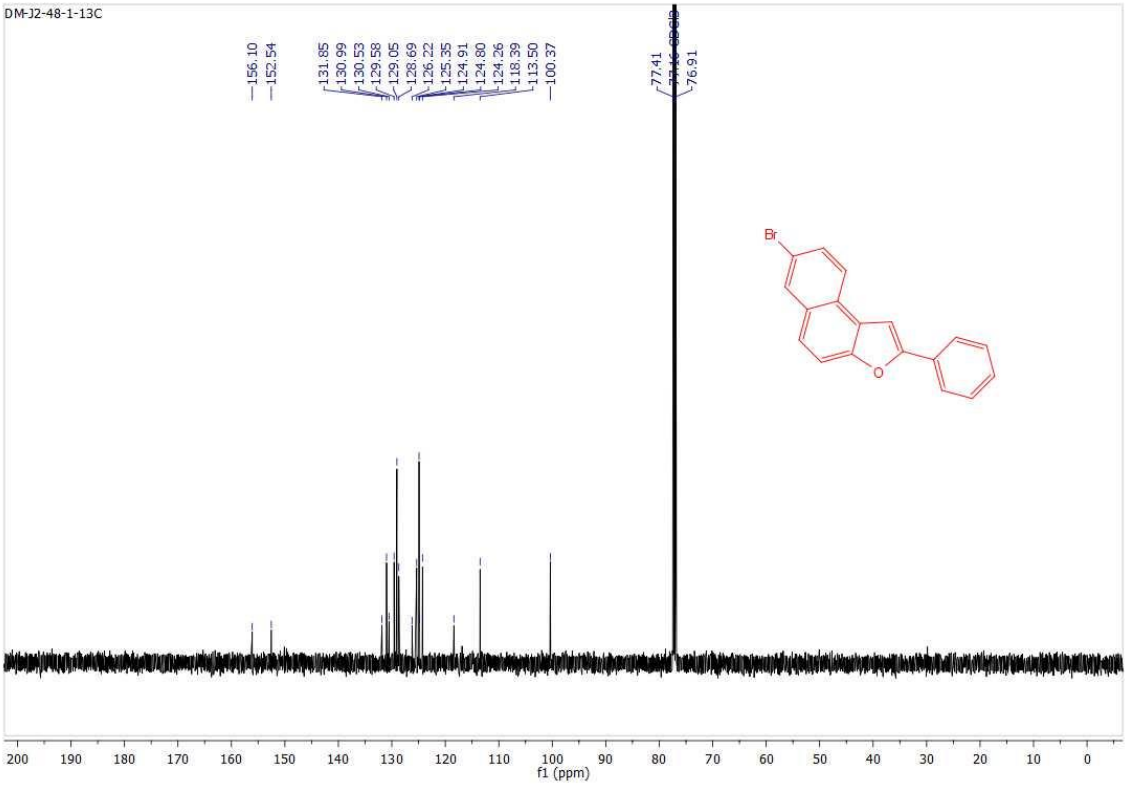
^{1}H and ^{13}C NMR of 2-phenylnaphtho[2,1-b]furan (4m)



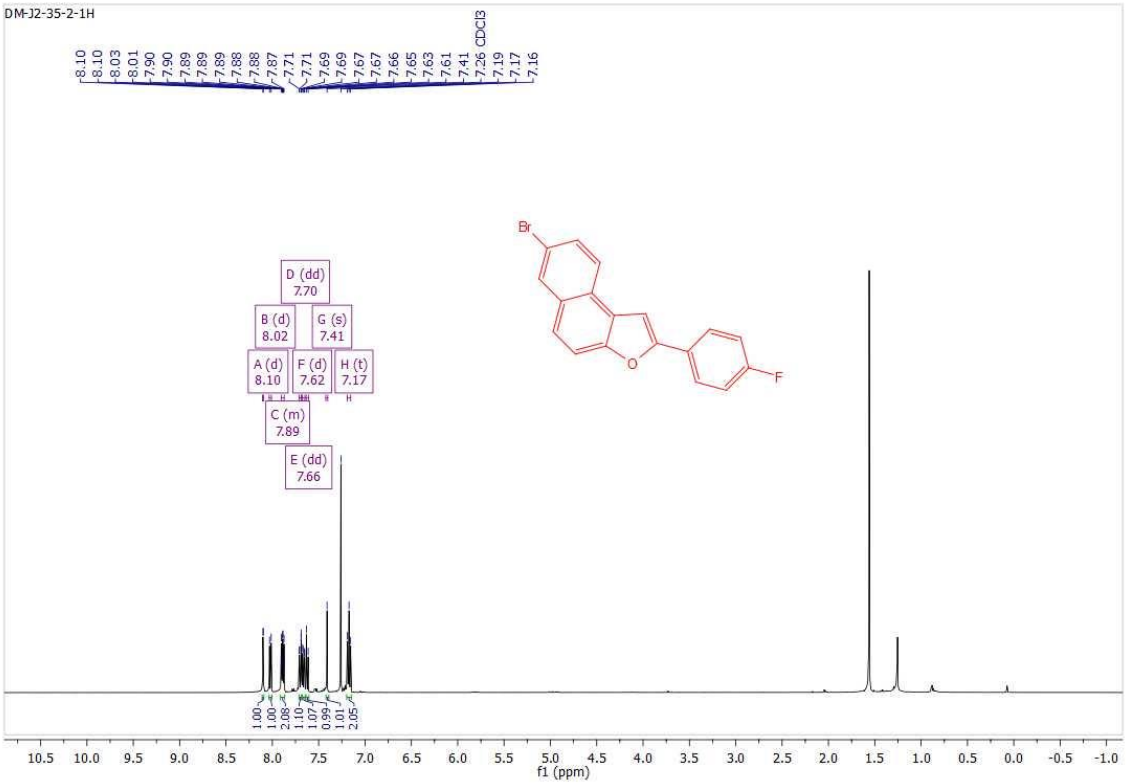


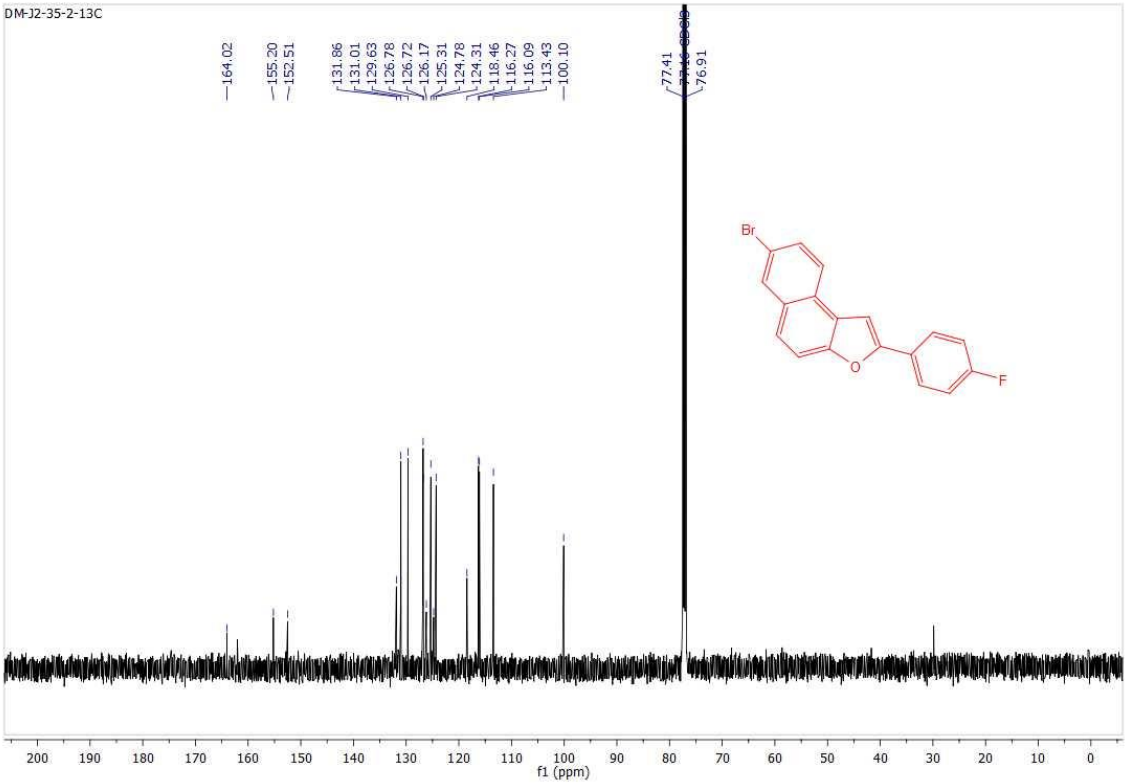
^{1}H and ^{13}C NMR of 7-bromo-2-phenylnaphtho[2,1-b]furan (4n)



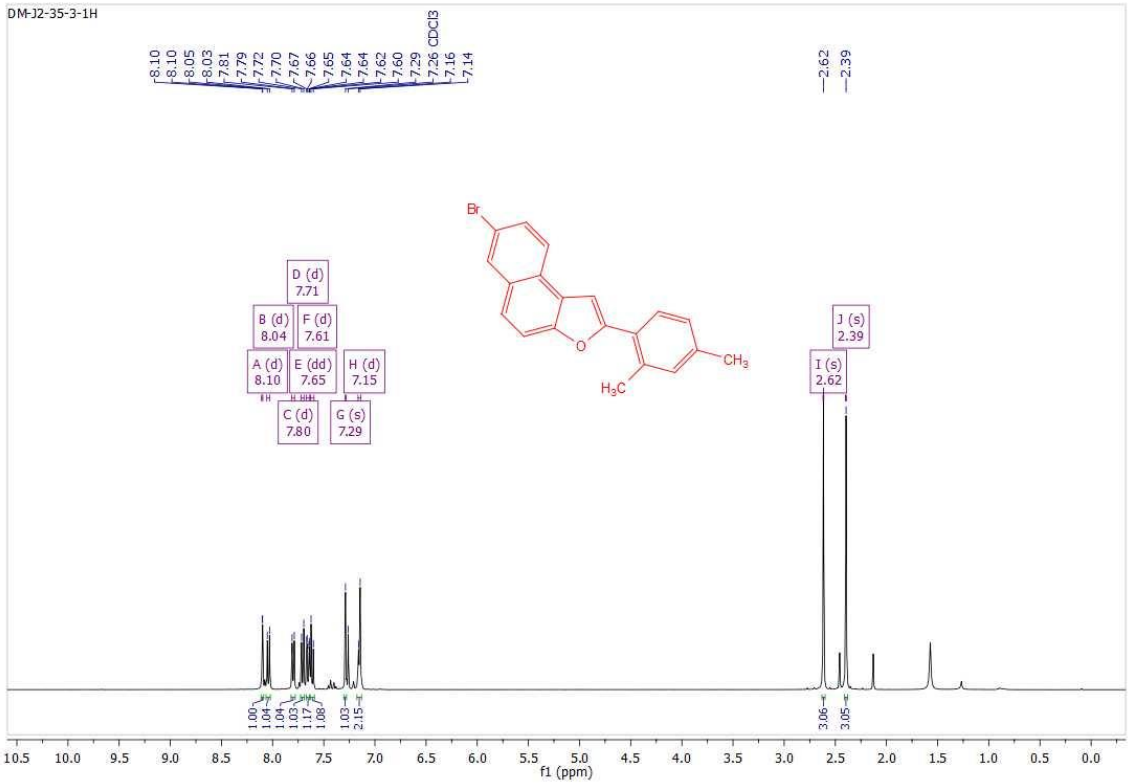


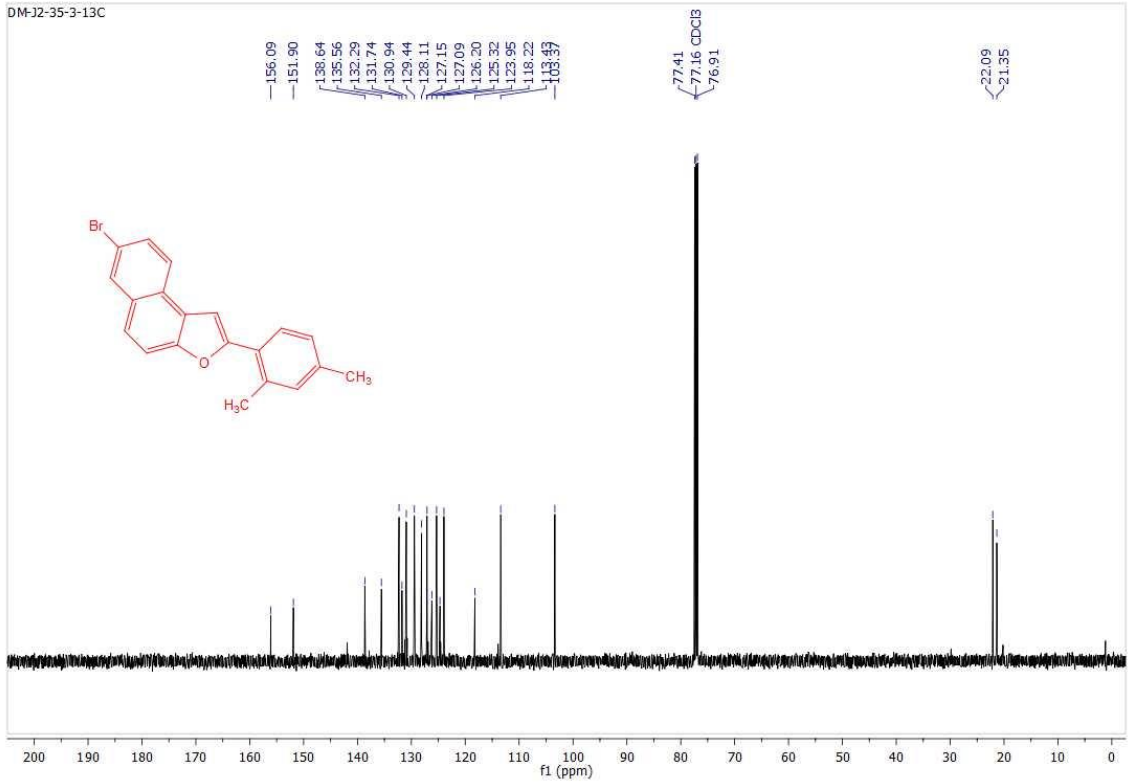
^{1}H and ^{13}C NMR of 7-bromo-2-(4-fluorophenyl)naphtho[2,1-b]furan (4o)



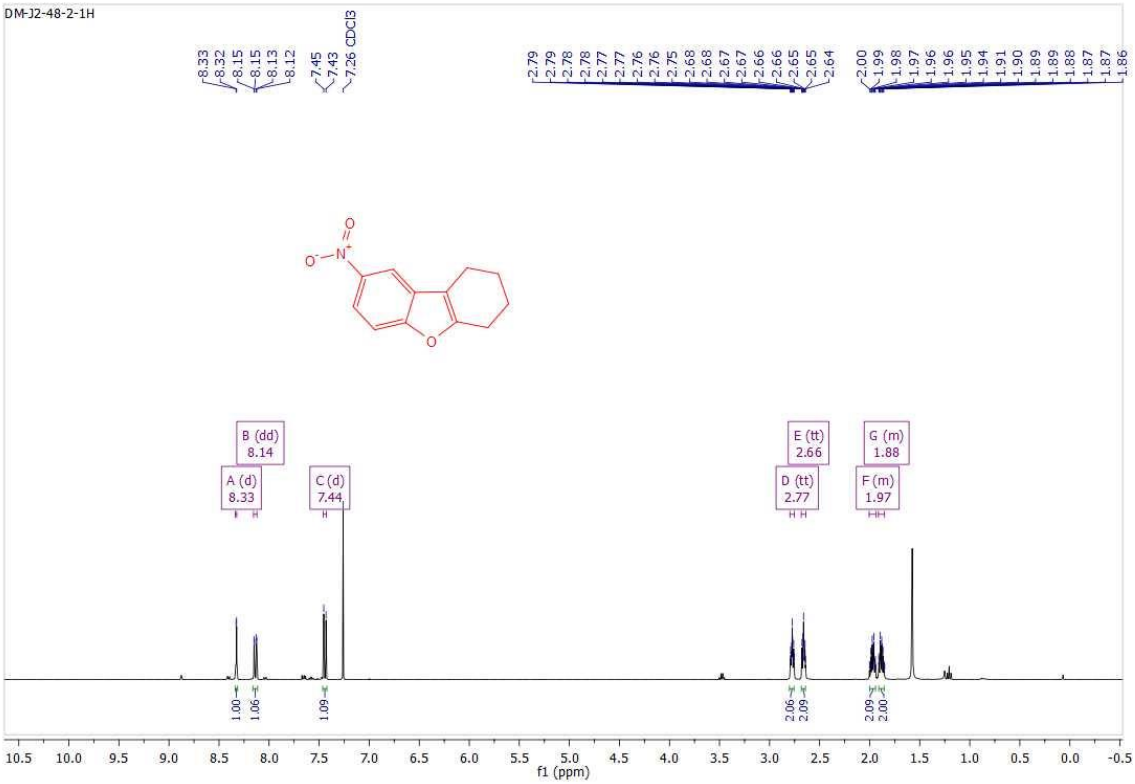


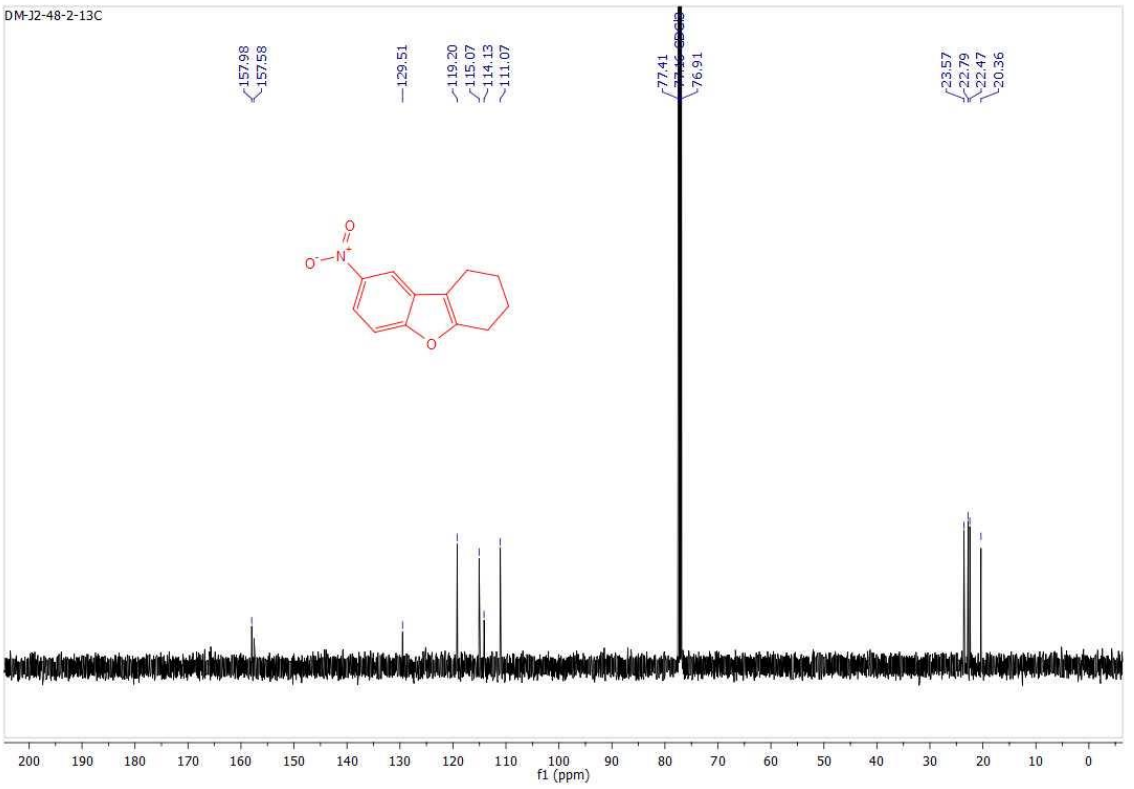
^{1}H and ^{13}C NMR of 7-bromo-2-(2,4-dimethylphenyl)naphtho[2,1-b]furan (4p)



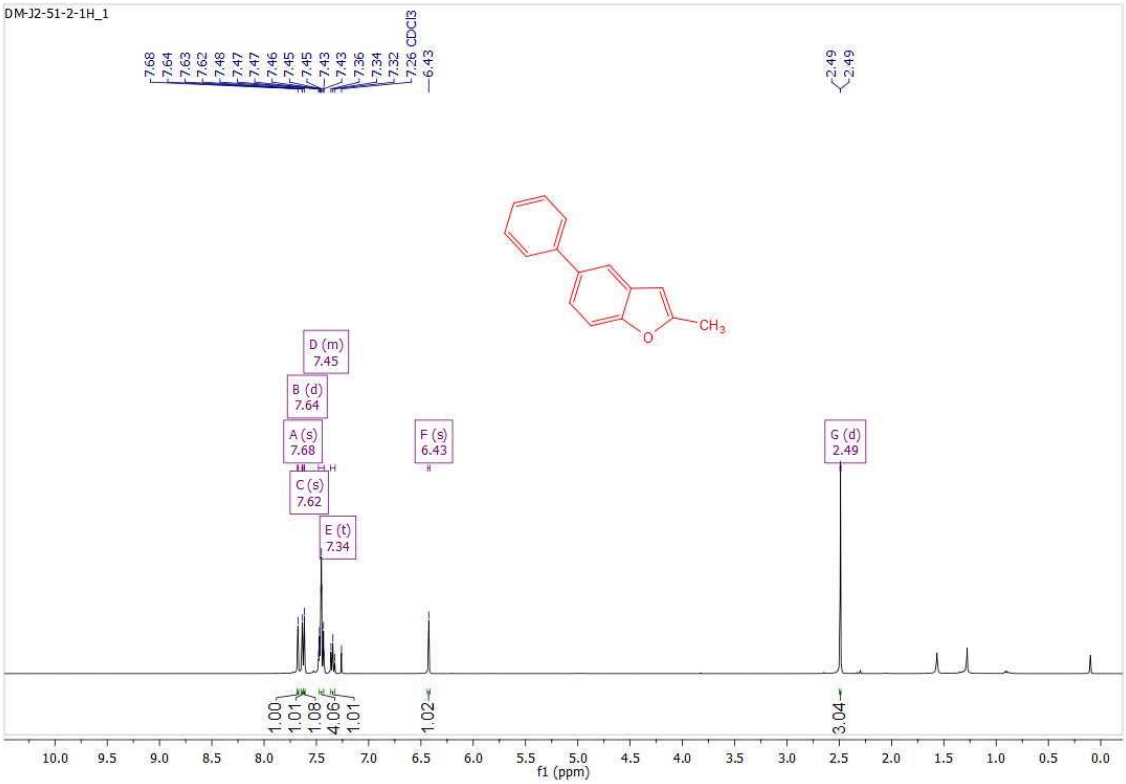


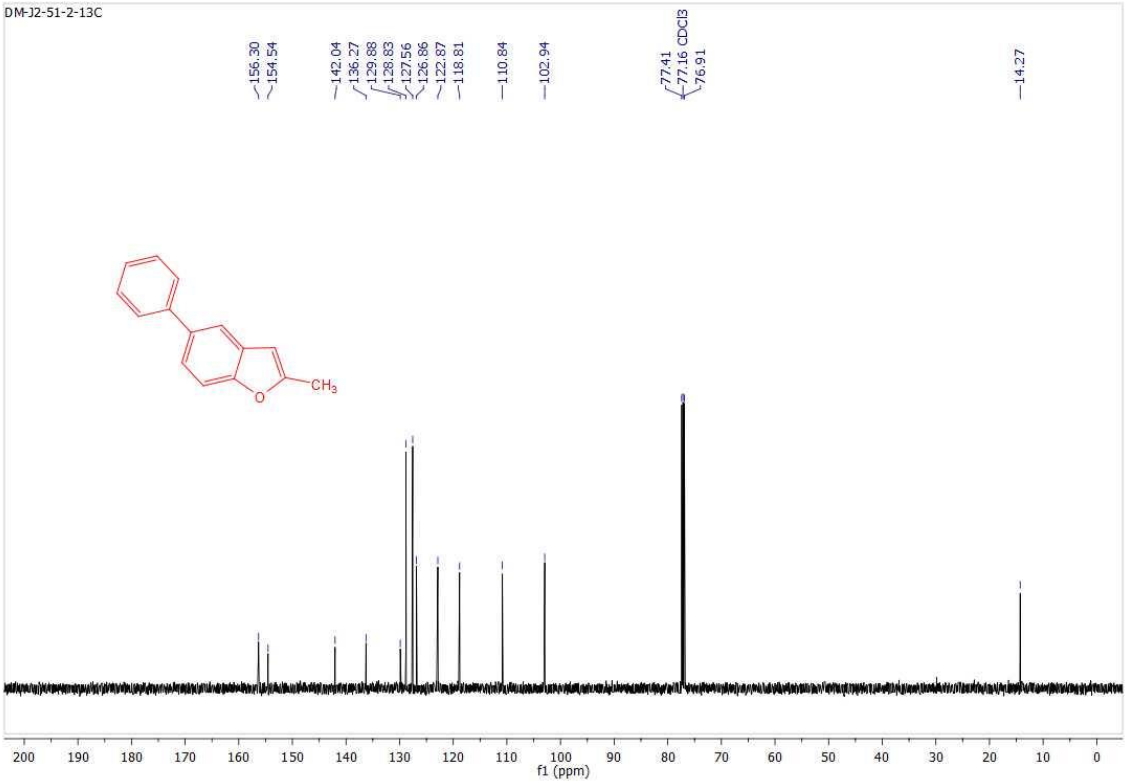
^{1}H and ^{13}C NMR of 8-nitro-1,2,3,4-tetrahydrodibenzo[*b,d*]furan (4q)



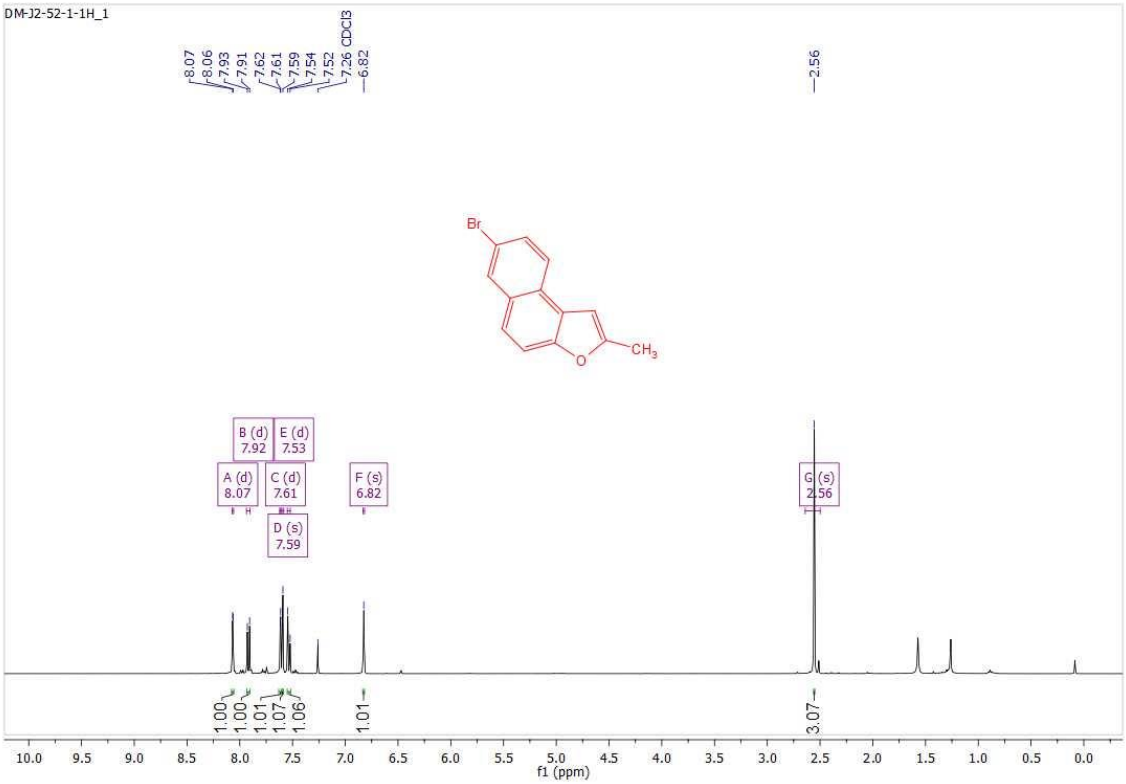


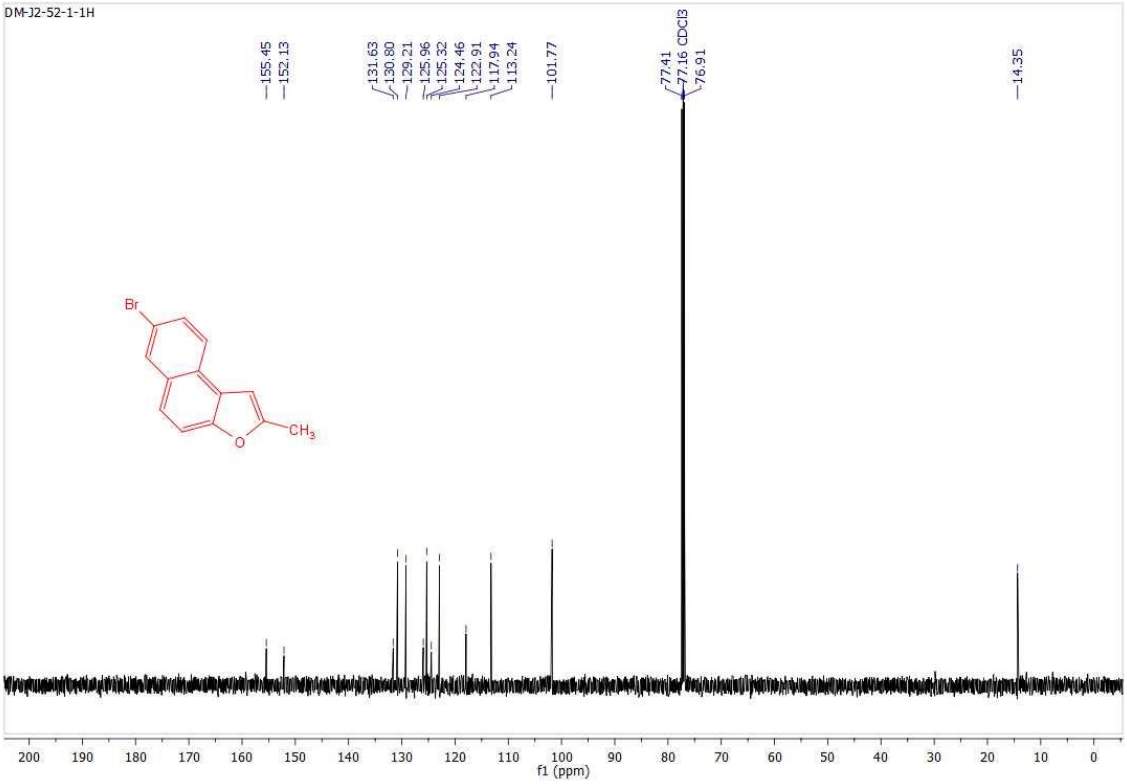
^{1}H and ^{13}C NMR of 2-methyl-5-phenylbenzofuran (4r)



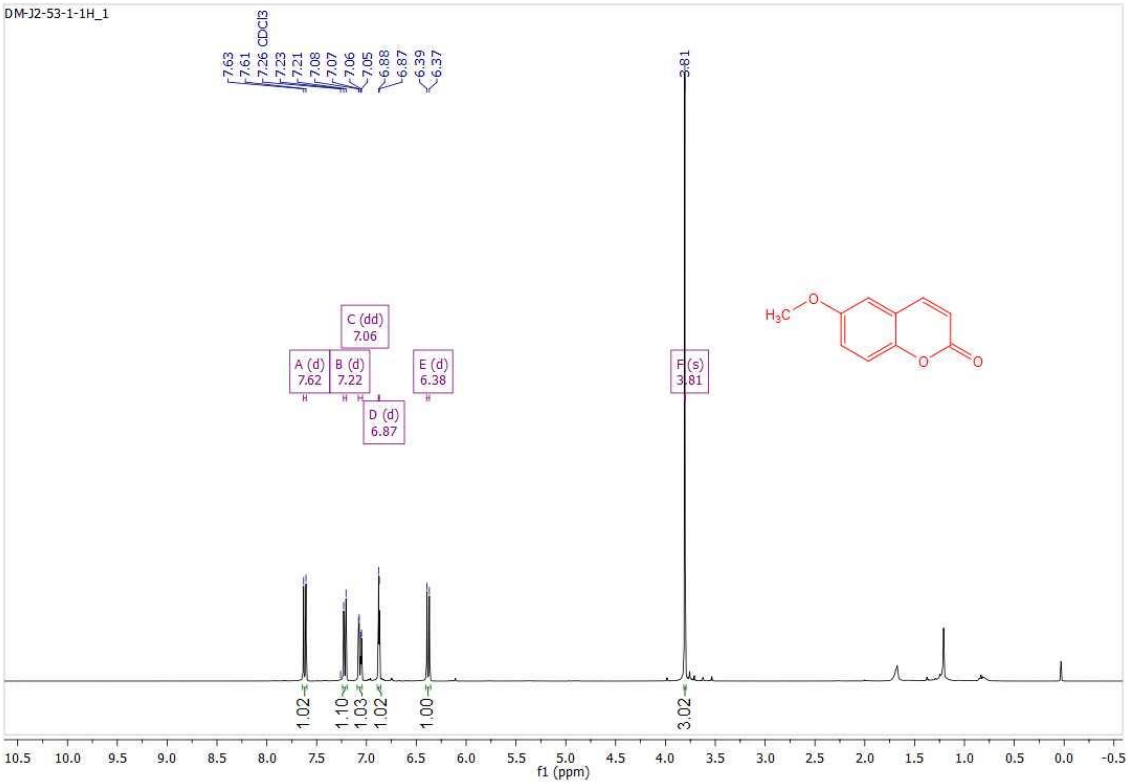


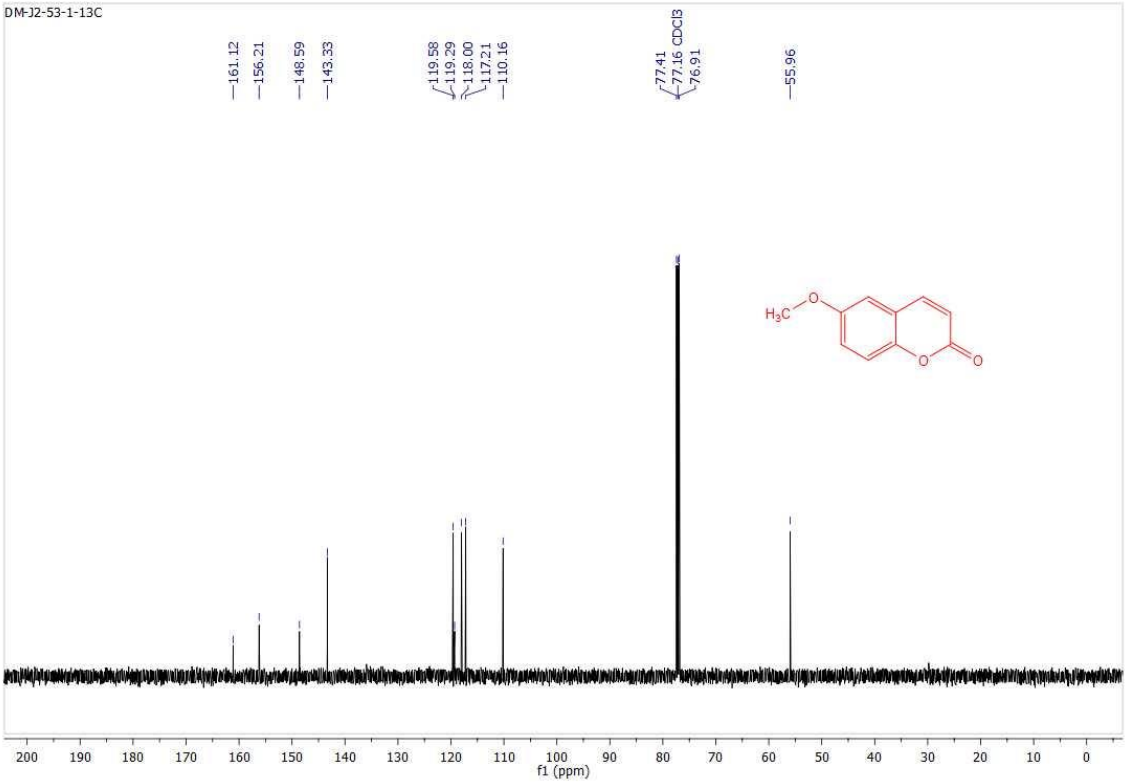
^{1}H and ^{13}C NMR of 7-bromo -2-methylnaphtho[*2,1-b*]furan (4s)



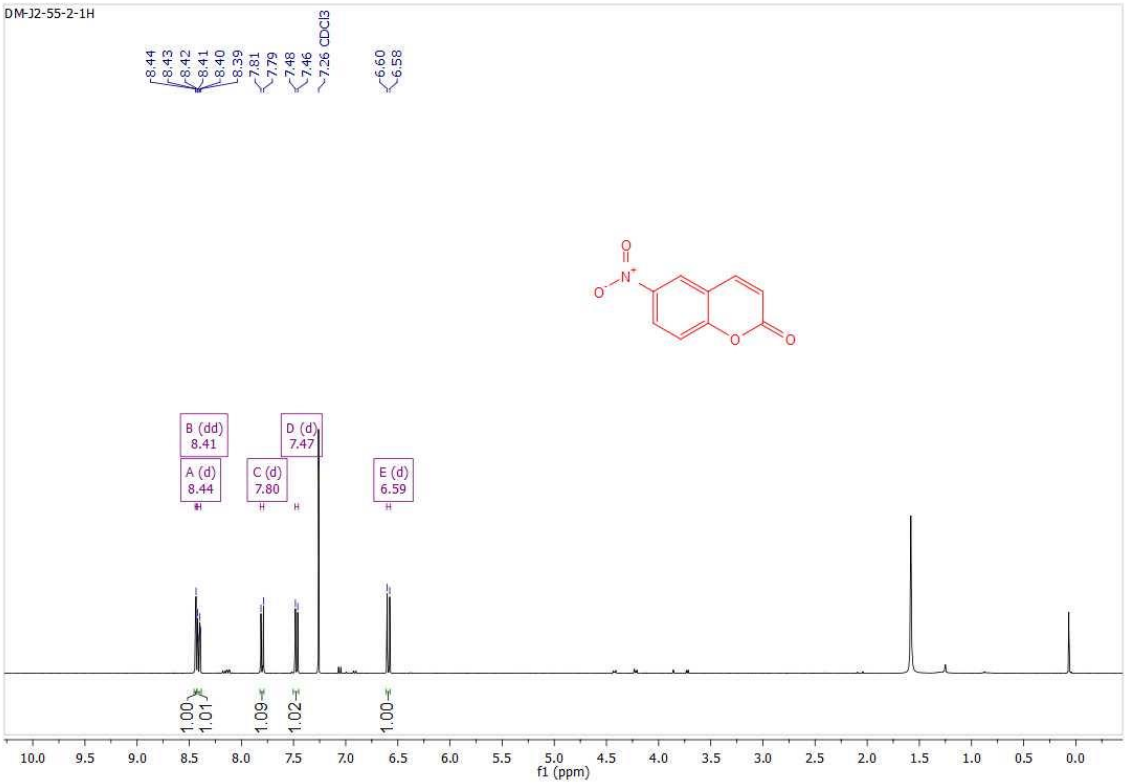


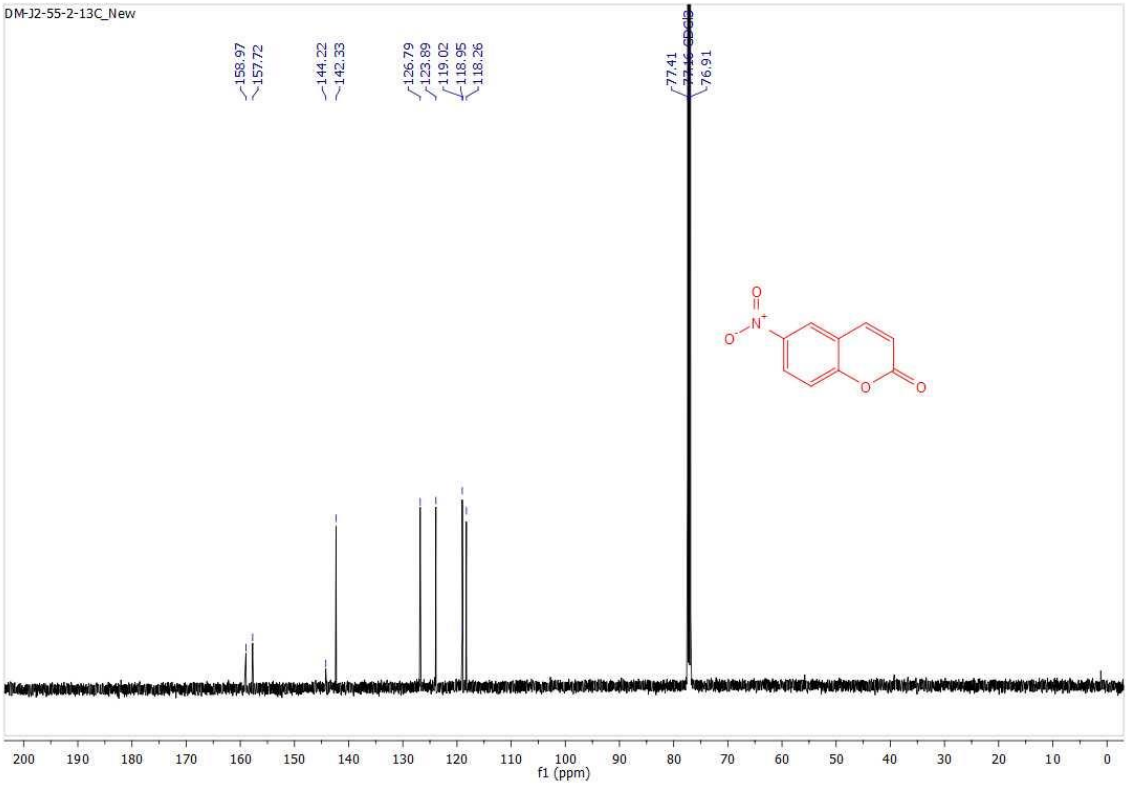
^{1}H and ^{13}C NMR of 6-methoxy-2*H*-chromen-2-one (4t)



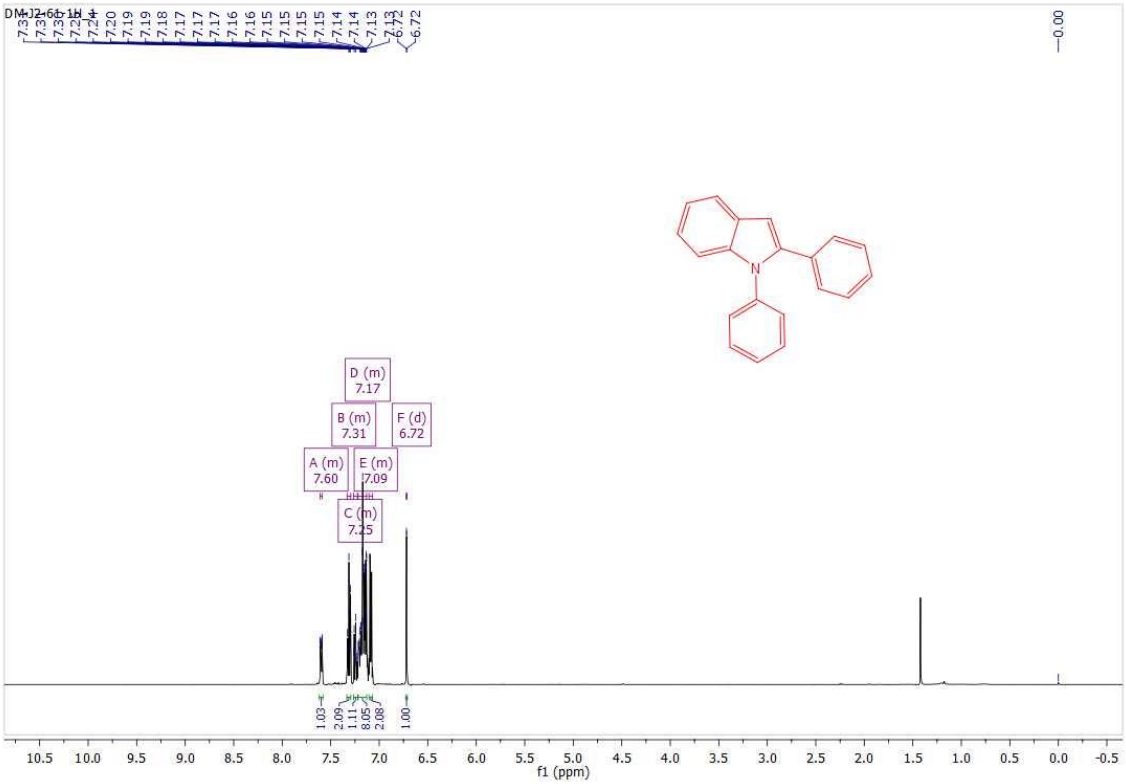


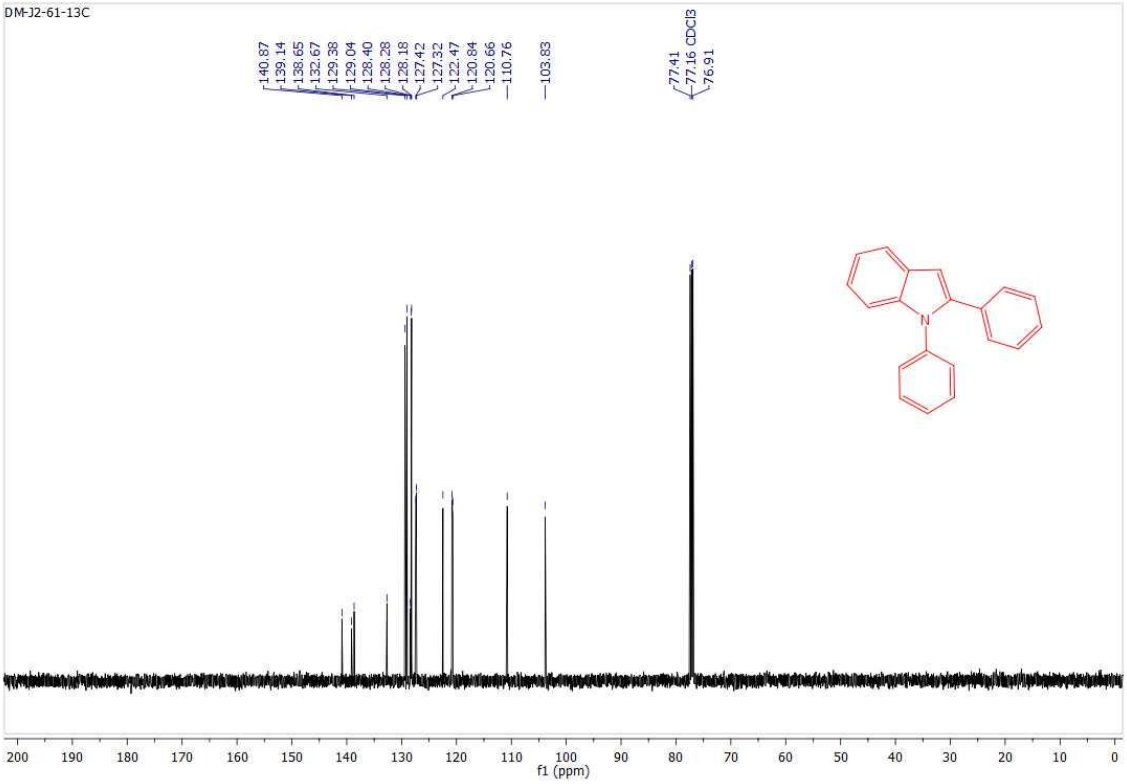
^{1}H and ^{13}C NMR of 6-nitro-2H-chromen-2-one (4u)



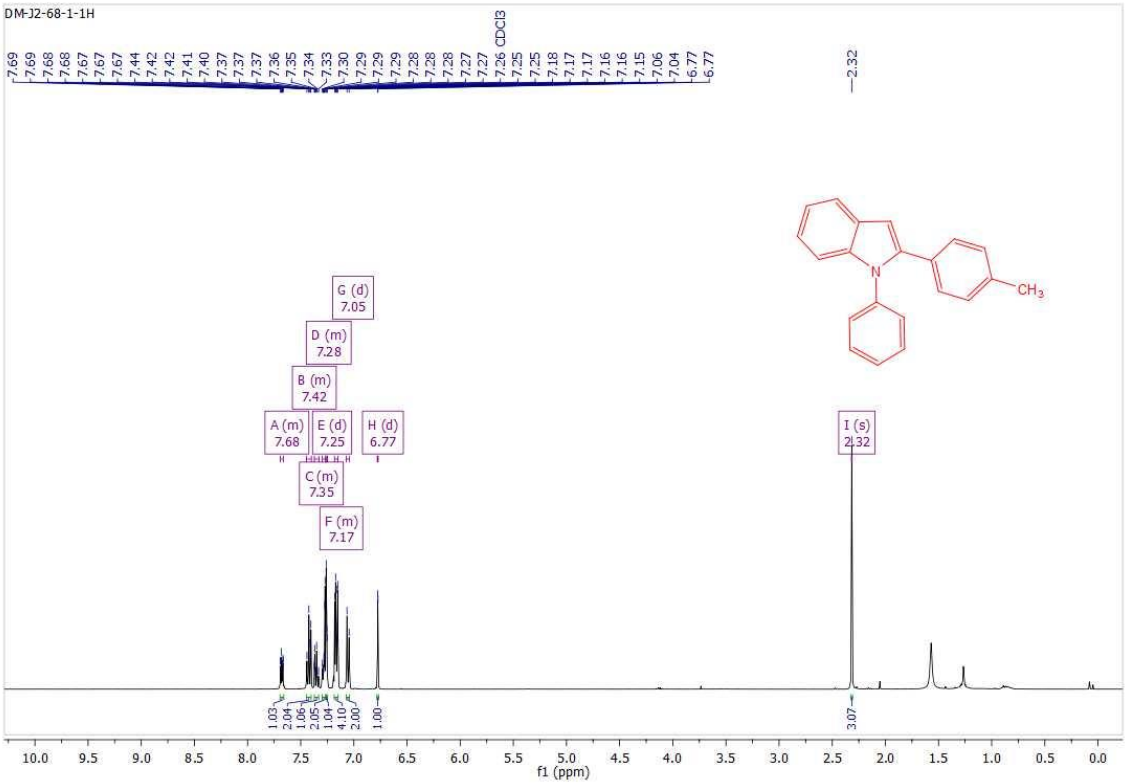


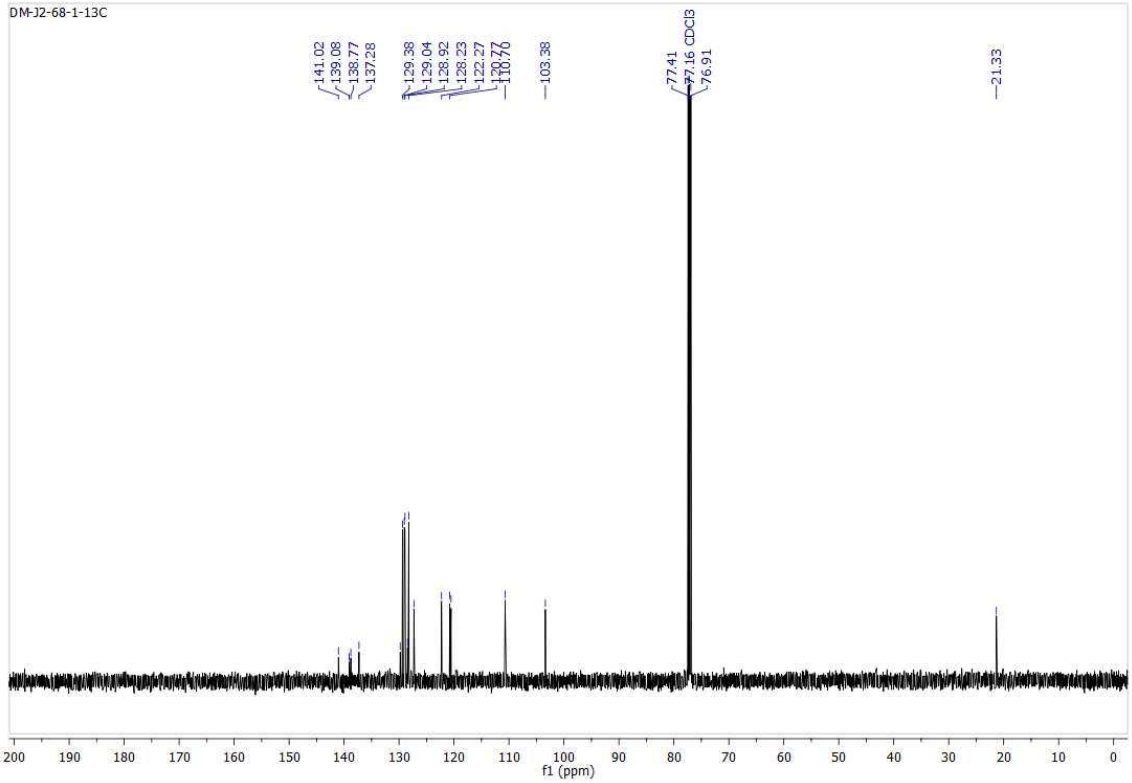
^{1}H and ^{13}C NMR of 1,2-diphenyl-1H-indole (5a)



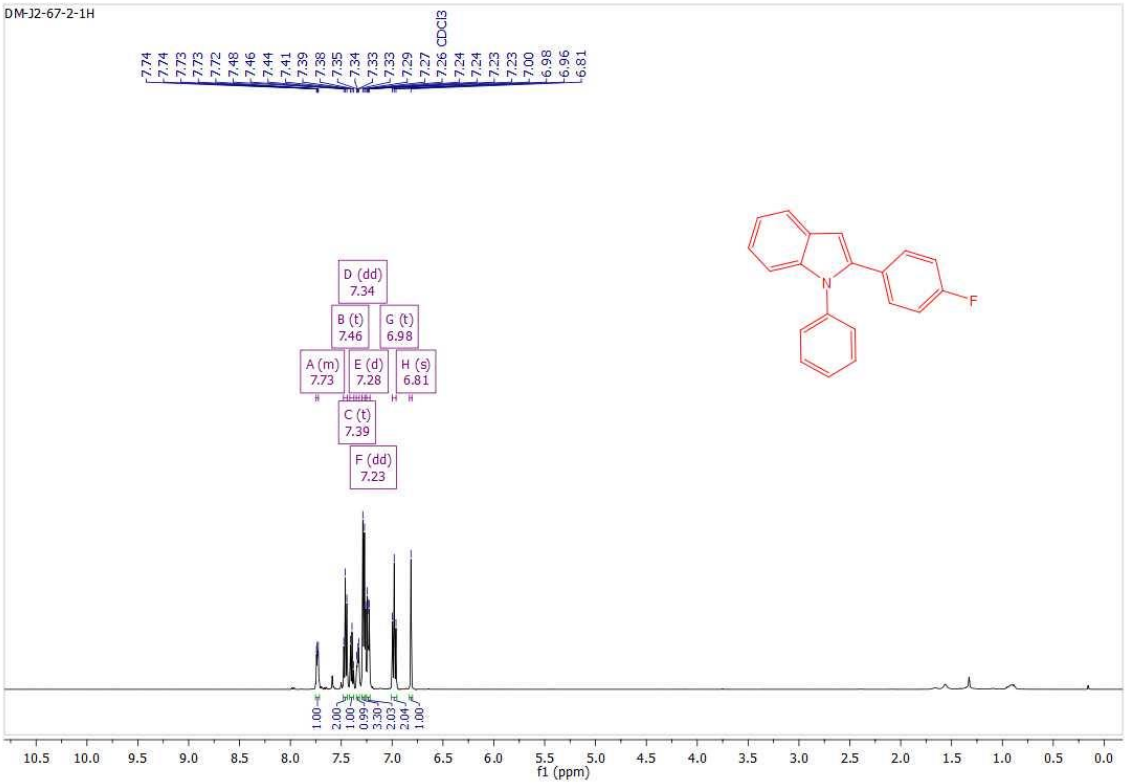


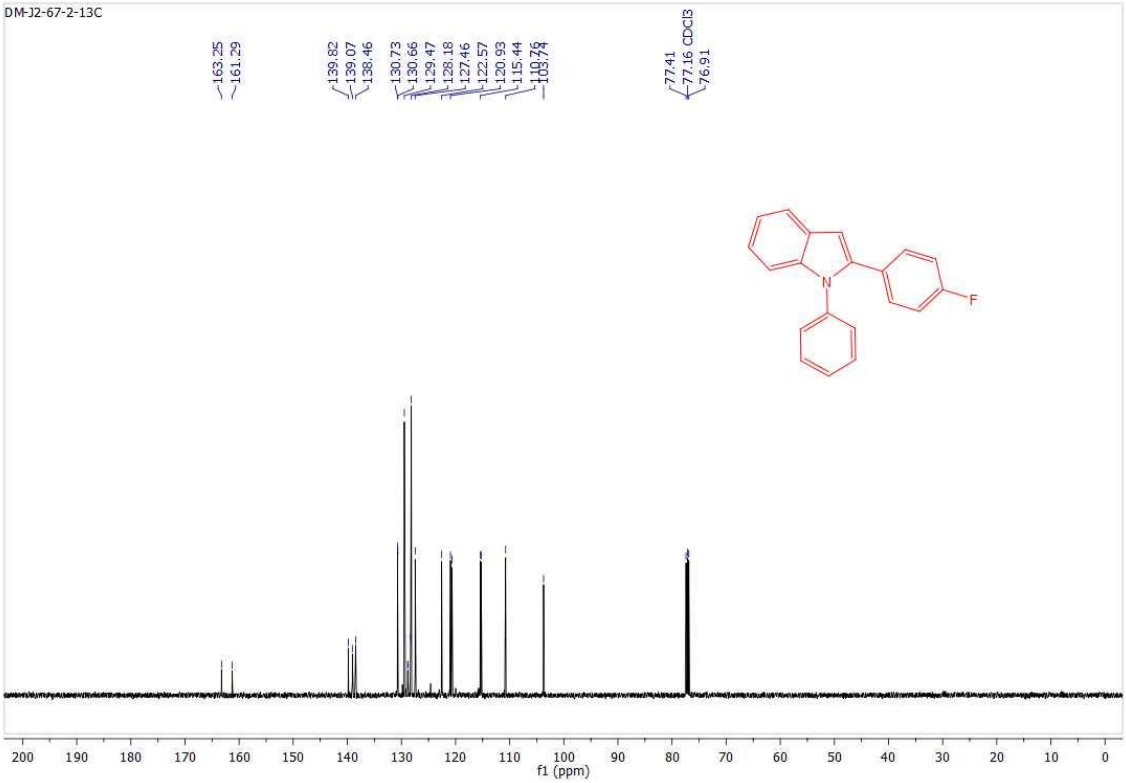
^{1}H and ^{13}C NMR of 1-phenyl-2-p-tolyl-1H-indole (5b)



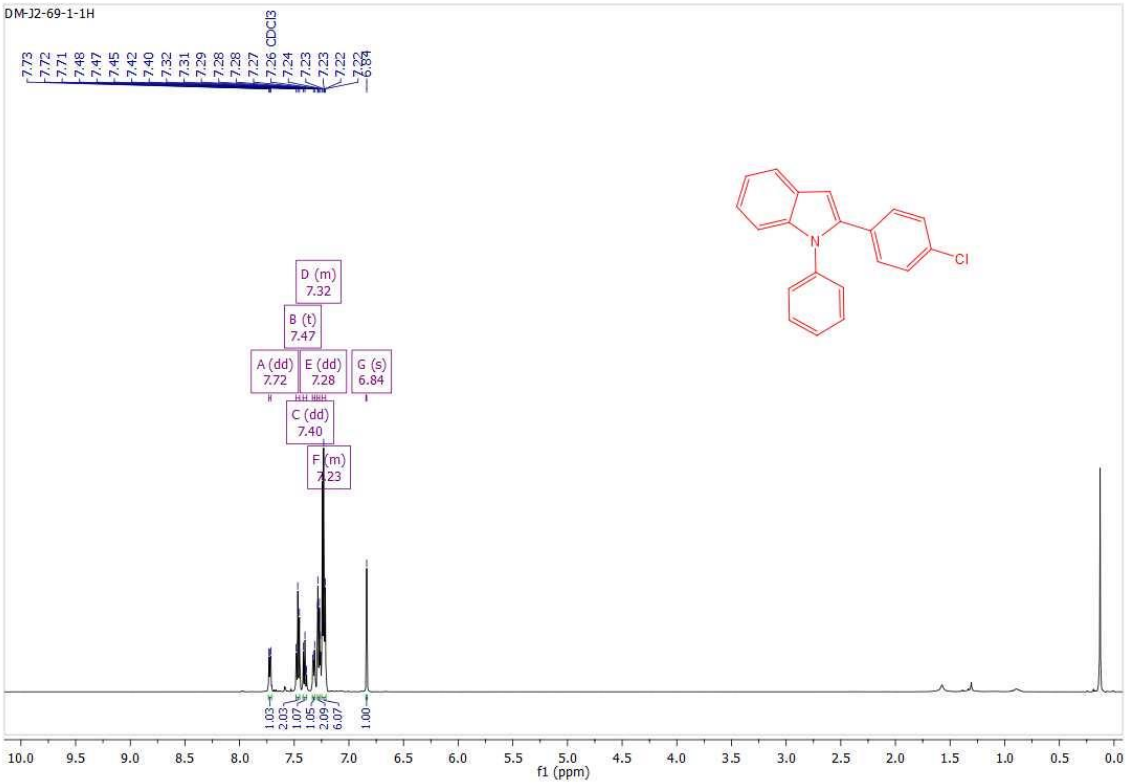


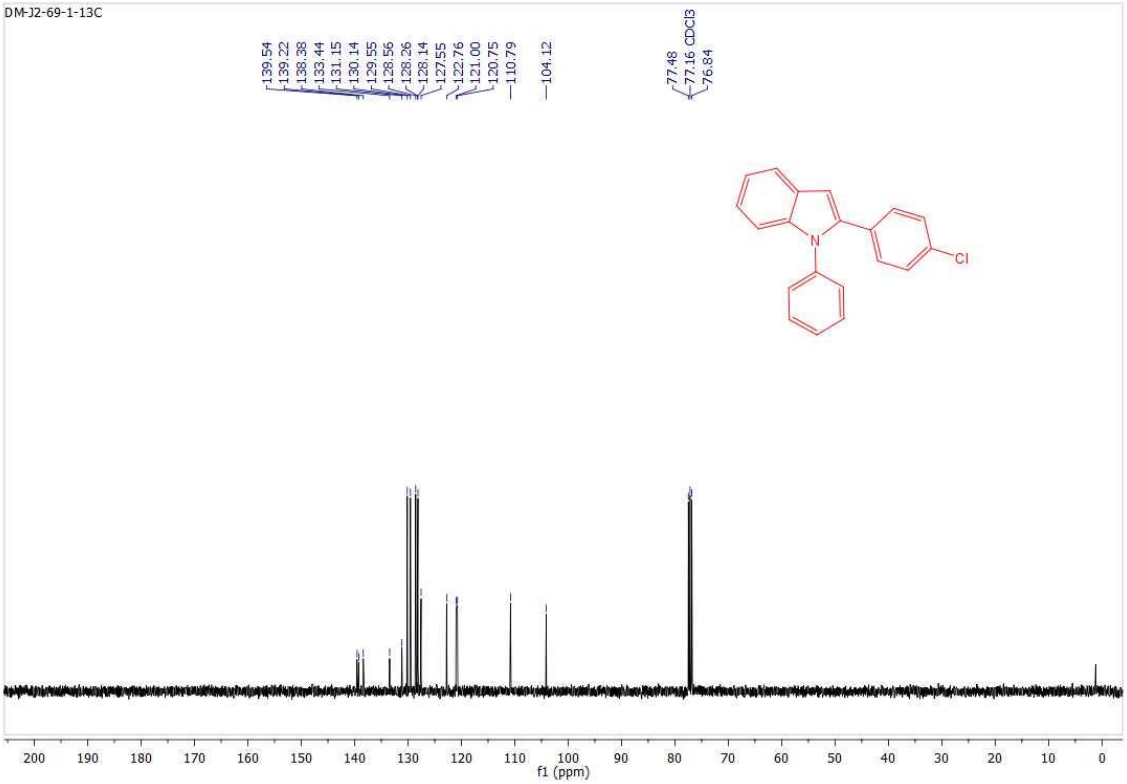
^{1}H and ^{13}C NMR of 2-(4-fluorophenyl)-1-phenyl-1H-indole (5c)



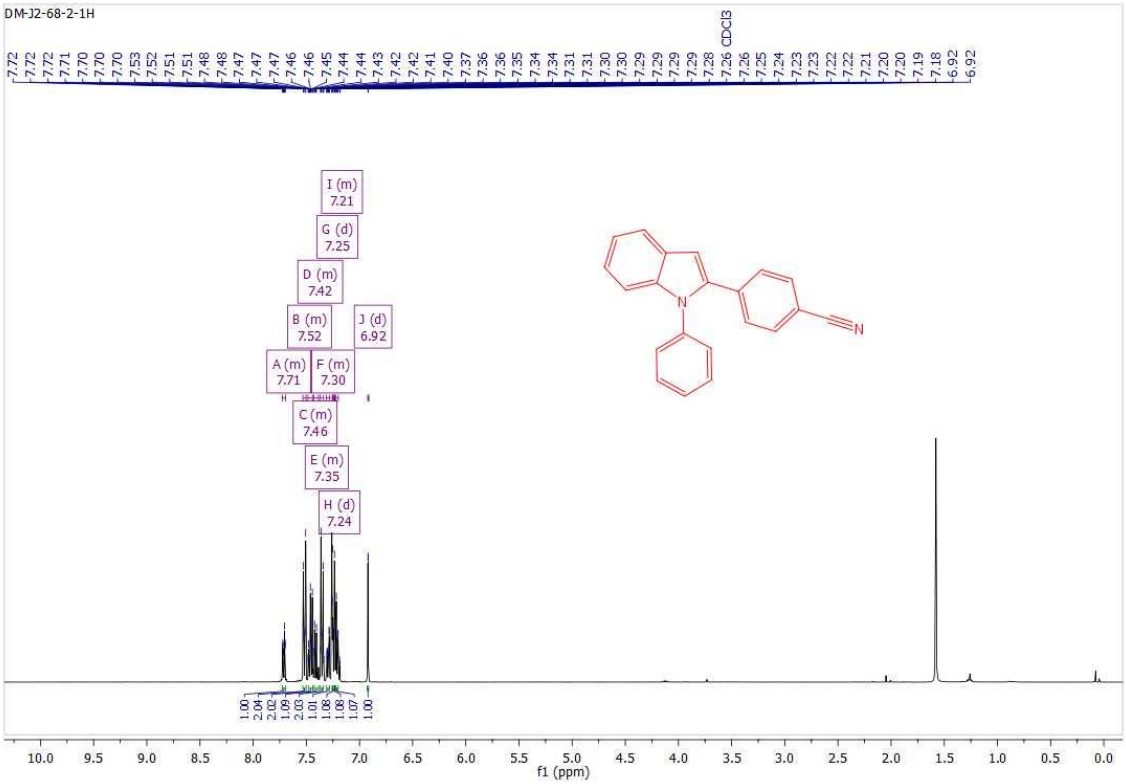


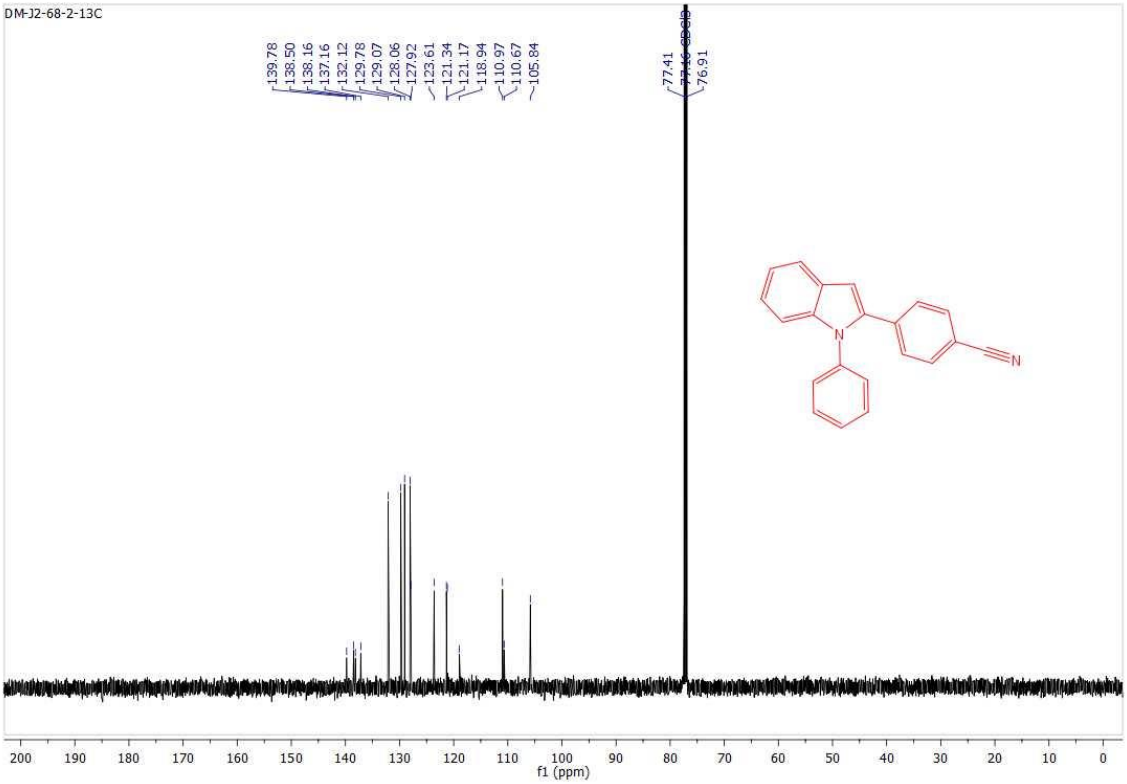
^{1}H and ^{13}C NMR of 2-(4-chlorophenyl)-1-phenyl-1H-indole (5d)



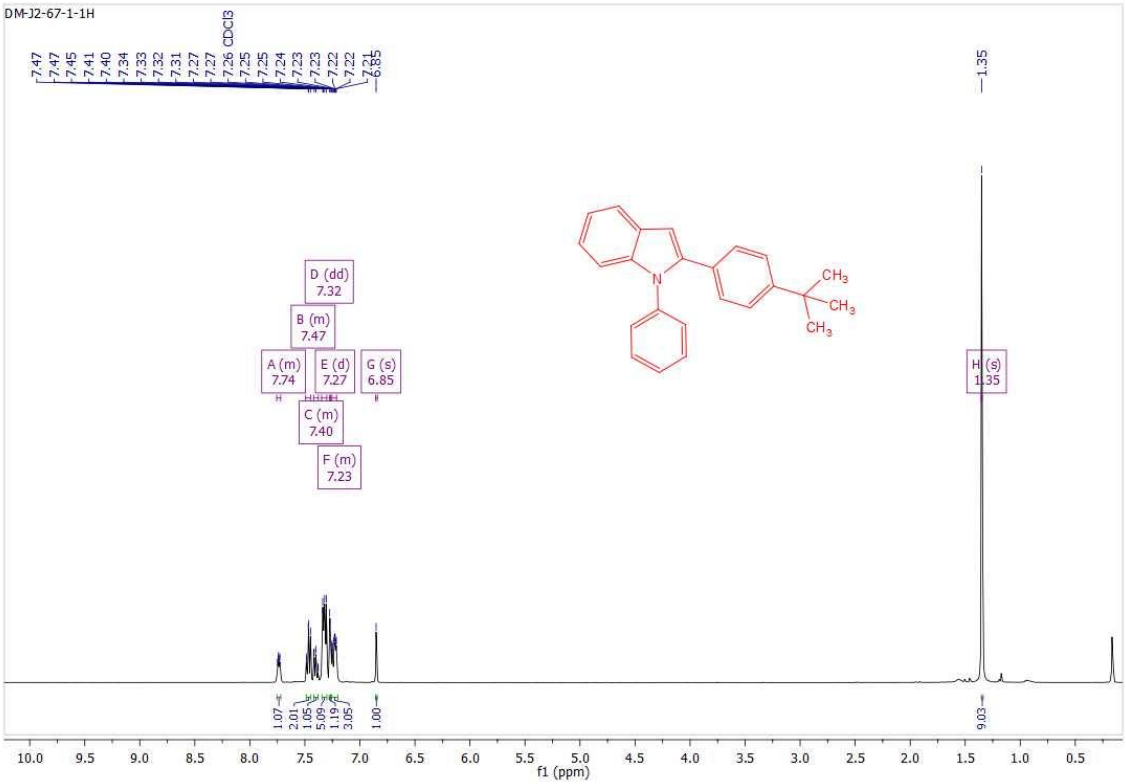


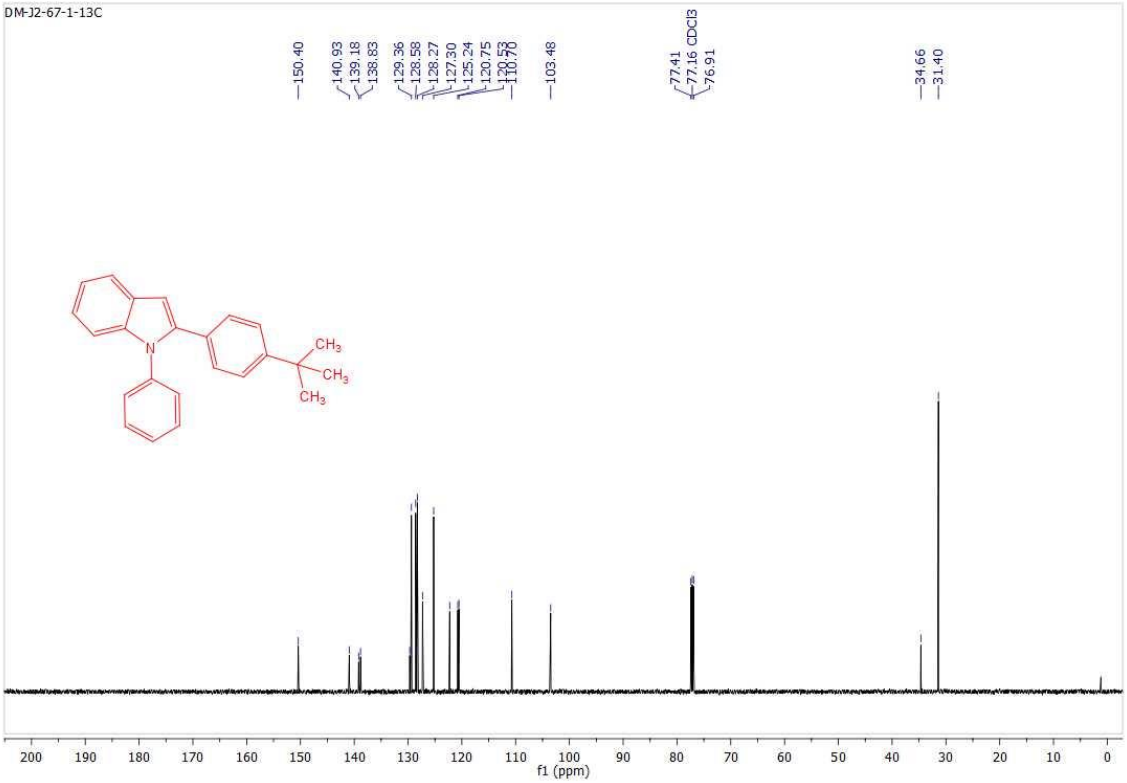
^{1}H and ^{13}C NMR of 4-(1-phenyl-1H-indol-2-yl)benzonitrile (5e)



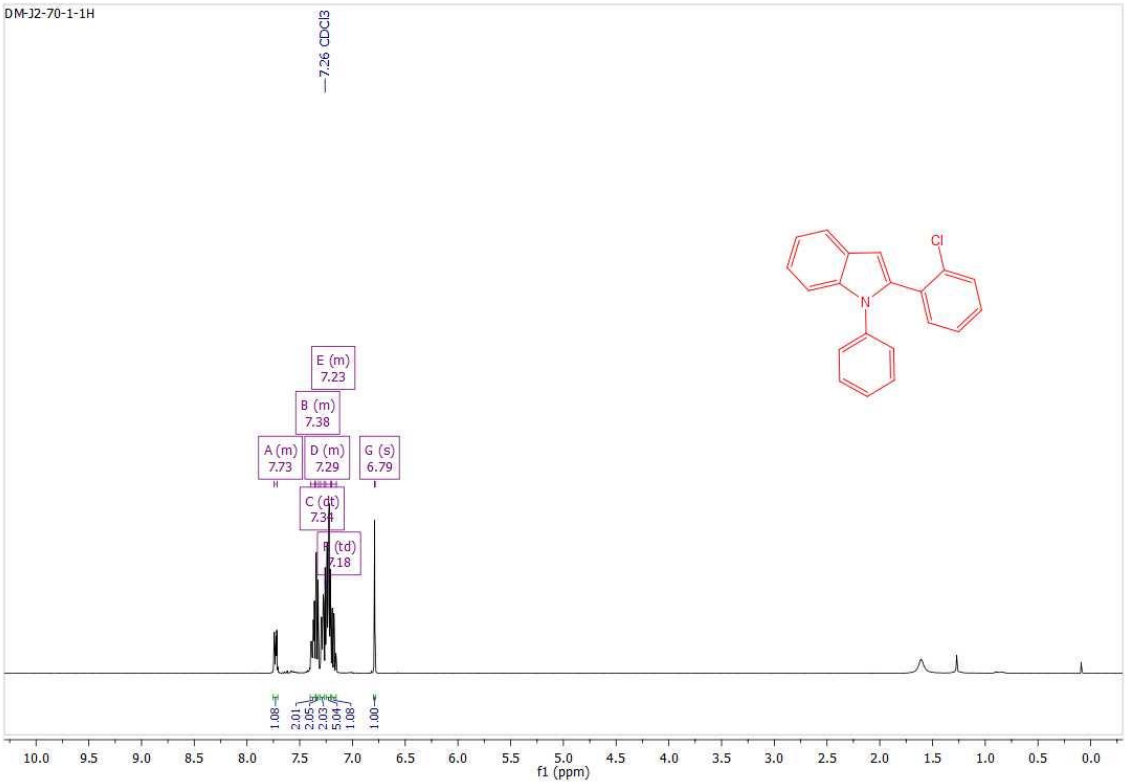


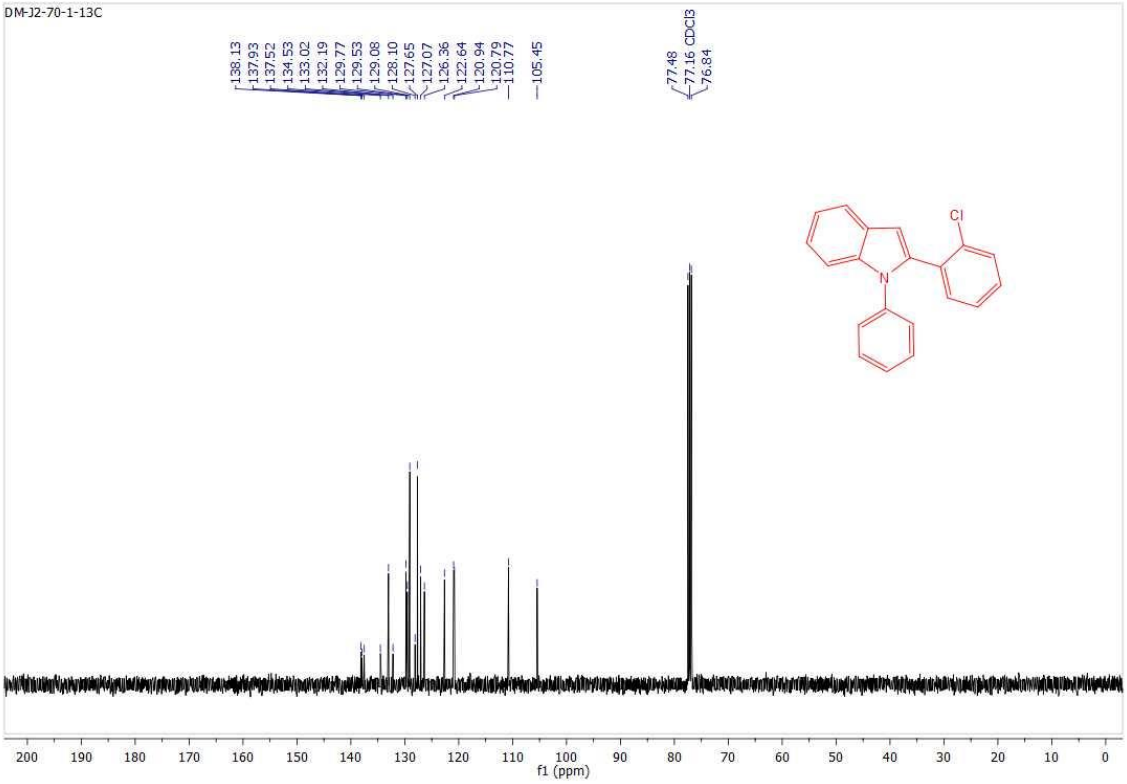
^{1}H and ^{13}C NMR of 2-(4-tert-butylphenyl)-1-phenyl-1H-indole (5f)



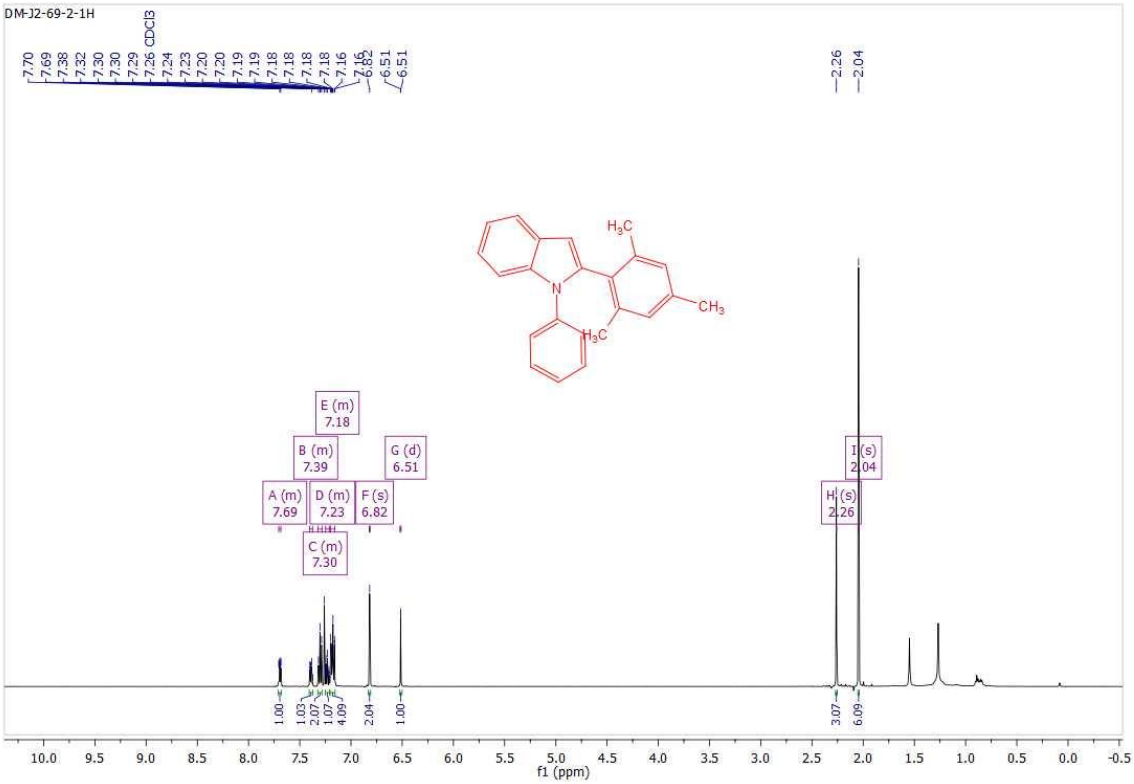


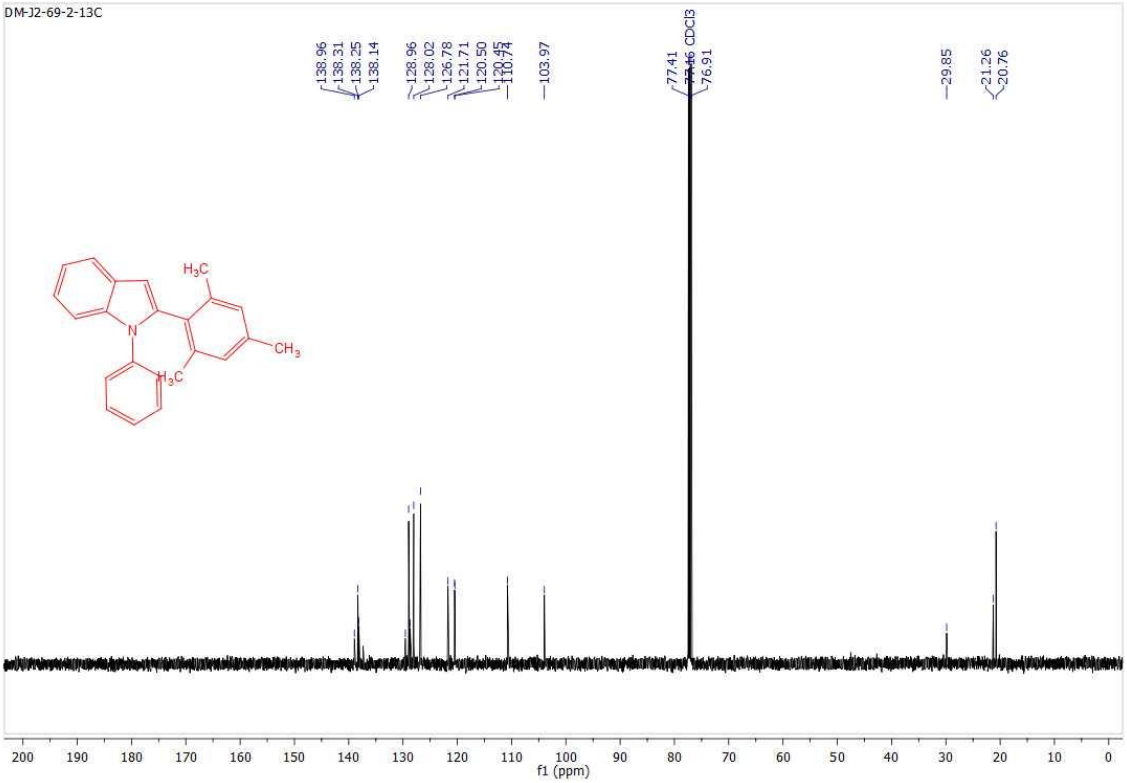
^{1}H and ^{13}C NMR of 2-(2-chlorophenyl)-1-phenyl-1H-indole (5g)



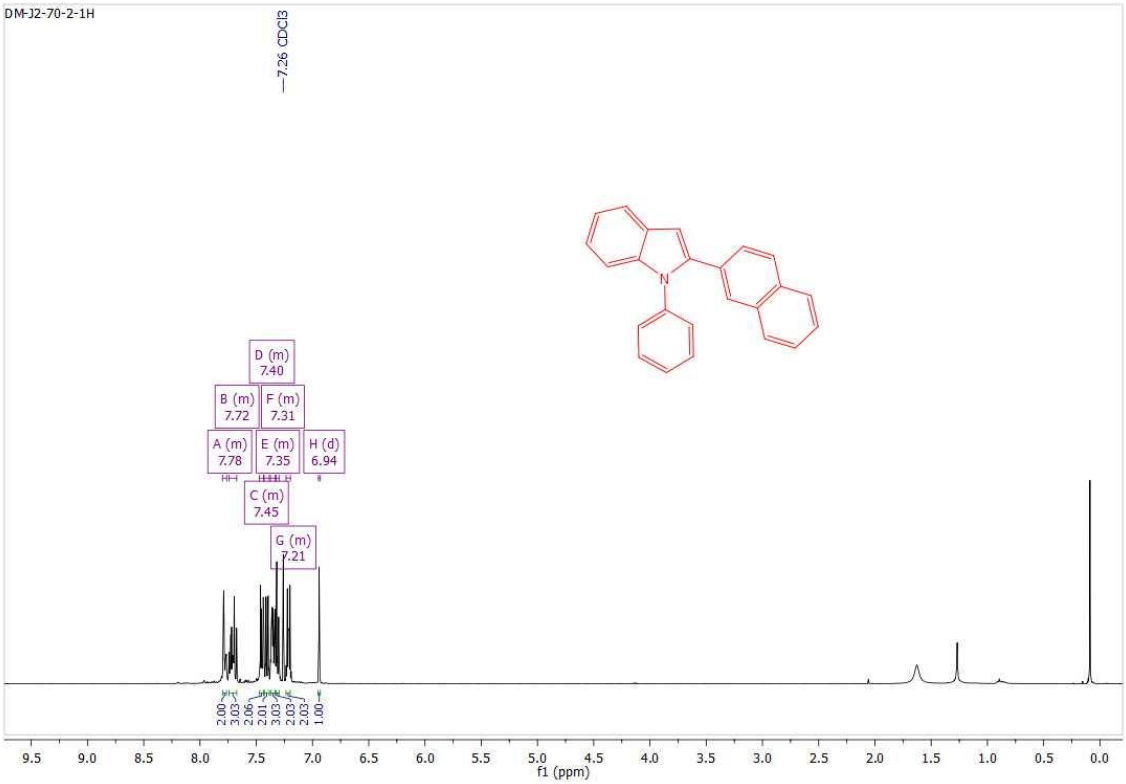


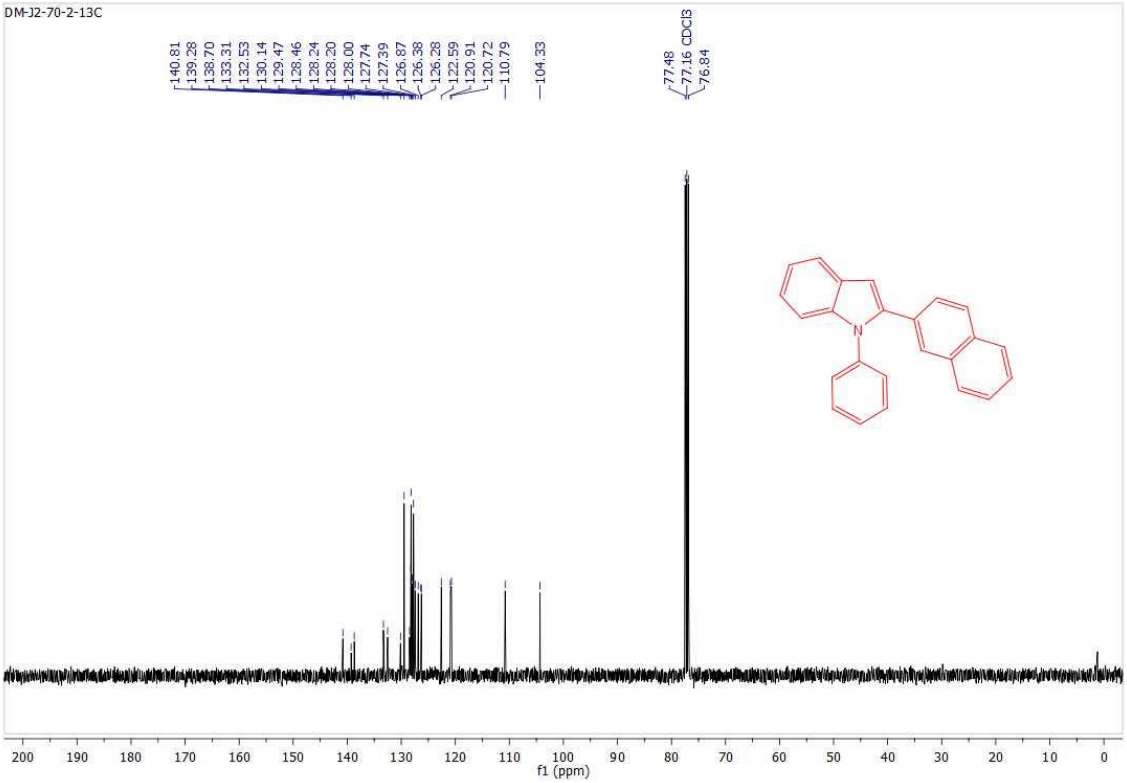
^{1}H and ^{13}C NMR of 2-mesityl-1-phenyl-1H-indole (5h)



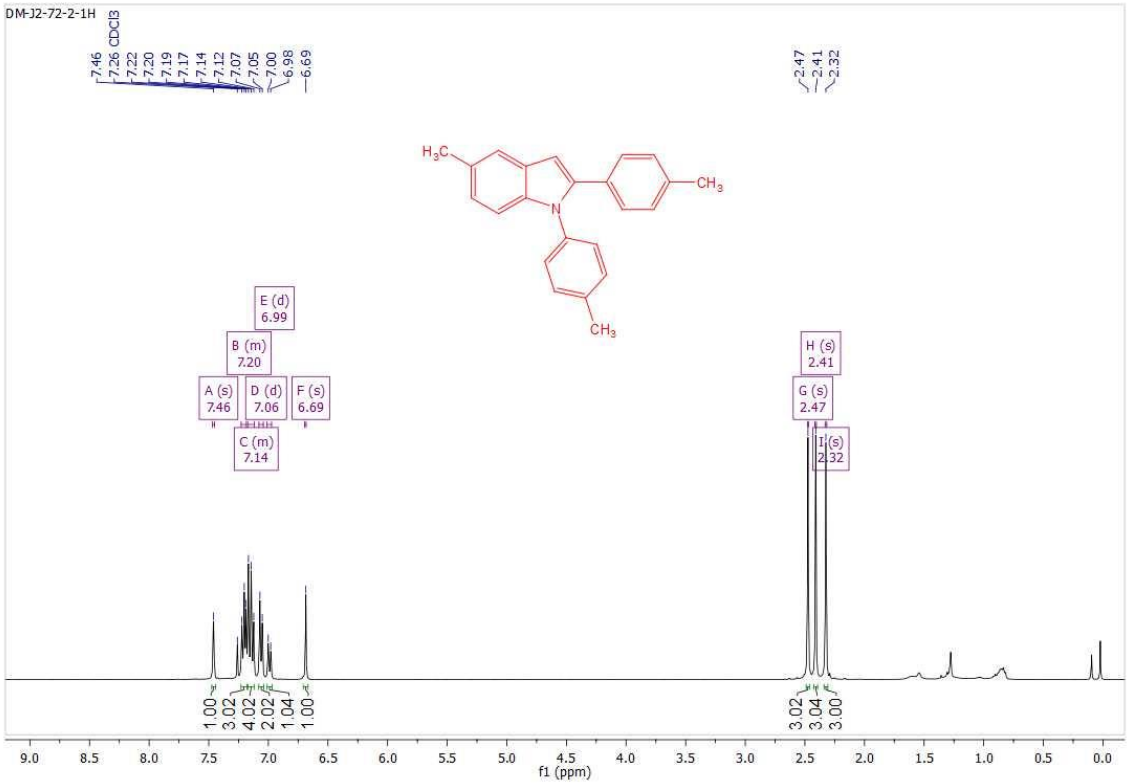


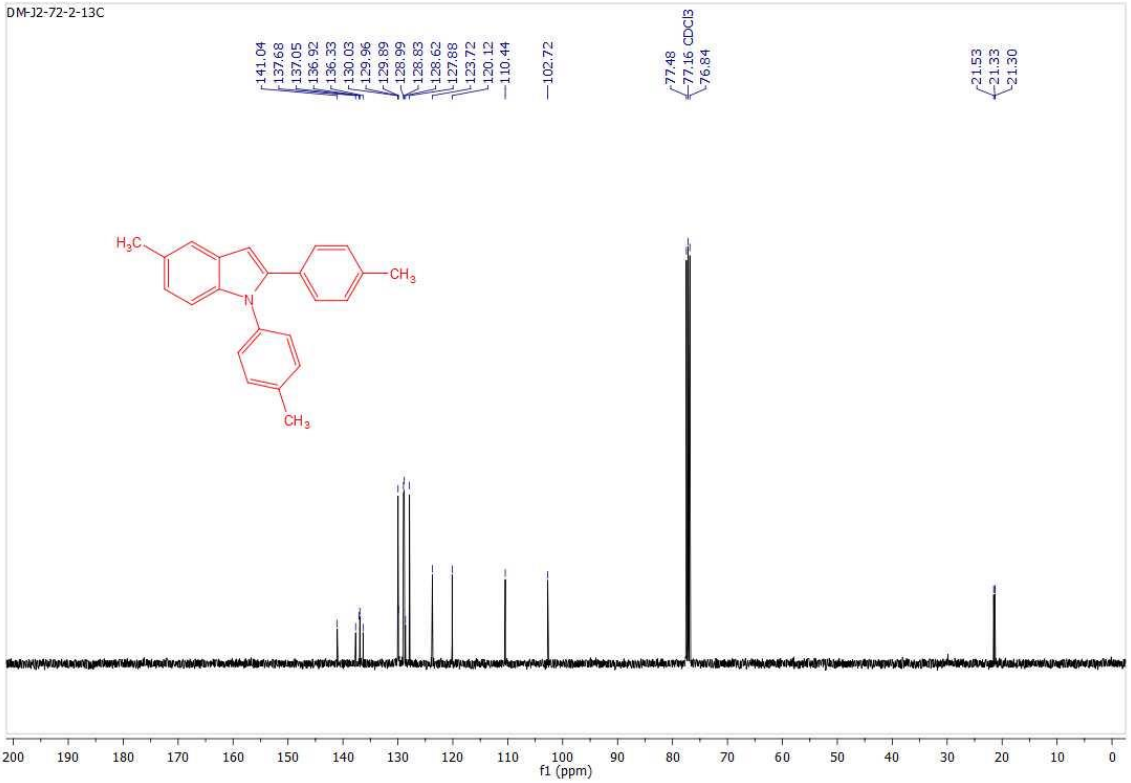
^{1}H and ^{13}C NMR of 2-(naphthalen-2-yl)-1-phenyl-1H-indole (5i)





^{1}H and ^{13}C NMR of 5-methyl-1,2-di-p-tolyl-1H-indole (5j)





^{1}H and ^{13}C NMR of 2-(4-fluorophenyl)-5-methyl-1-(p-tolyl)-1H-indole (5k)