

Electronic supporting information

Functional Phenylethynylene Side Arm Polyaryleneethynylene Conjugated Polymers; Optical and Electrochemical Behavior for Enrichment of Electronic Application

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1) Materials and Methods.

4-Bromophenyle acetonitrile, hydroquinone, 1,4-dibromo-2-nitrobenzene, potassium iodide, potassium fluoride, potassium carbonate, potassium hydroxide, sodium hydroxide, sodium nitrile, concentrated sulfuric acid, Fe-powder, acetic acid (AcOH), triethylamine, tetrahydrofuran were purchased from Avra chemical lab and Fisher scientific. Trimethylsilylethynylene, 1-bromooctane, 1-bromododecane, potassium periodate, thiophene aldehyde, bis-triphenyl phosphine palladium (II) dichloride or $\text{Pd}(\text{PPh}_3)\text{Cl}_2$, tetrakis triphenyl phosphine palladium (0) or $\text{Pd}(\text{PPh}_3)_4$, copper (I) iodide or Cu(I)I were purchased from Sigma-Aldrich.

The FTIR spectra of the CPs were recorded in the form of KBr pellet by PerkinElmer Two model (FT-IR C101375) spectrophotometer. The UV-visible spectra of the monomer and polymers were recorded in JASCO-V670, UV-visible spectrophotometer. The Fluorescence spectra were recorded on (FP - 8200) JASCO fluorescence spectrophotometer, the slit width was 5 nm for both excitation and emission. Gel permeation chromatography for copolymers was recorded in THF solution using a Shimadzu instrument equipped with 510 pump, SPD-20A, UV-vis-254 detector and 7725 Rheodyne injector. The column used was phenogel 00H-646-K0 (phenomenex, Hyderabad, India). The mobile phase was THF at a flow rate of 1 mL / min. The molecular weight (MW) and polydispersity index (PDI) of the polymer samples were calculated on the basis of known MW polystyrene calibration. Bruker 300 MHz and 500 MHz Nuclear Magnetic Resonance (NMR) spectroscopy instrument was used for ^1H , ^{13}C and DEPT-135 NMR spectra were recorded for structural identification. Powder X-ray diffraction of the polymers were recorded in PANalytical X'pert Pro diffractometer using $\text{Cu K}\alpha$ (1.54 Å) radiation and flat plate configuration at room temperature. Cyclic voltammetry experiments were carried out using multichannel auto lab MAC 80038 instrument with NOVA software using three electrode configuration

with oxygen free acetonitrile solution in presence of tetra-n-butylammoniumhexafluoro phosphate (100 mmol) as electrolyte solution, working electrode, counter electrode and reference electrode used were as follows: platinum electrode, platinum plate and Ag / Ag⁺ (0.01 M AgNO₃ in Acetonitrile) electrode. The polymer sample was dissolved in THF solution, the soluble polymer sample was coated on the bottom surface of the working electrode. The uncontrolled thickness and aggregation of dried modified working electrode were used in an electrochemical analysis. The ferrocene / ferrocenium (Fc / Fc⁺) redox couple as an external standard. The energy level of the Fc / Fc⁺ was presumed at -4.8 eV at vacuum. The half-wave potential (E_{1/2}) of the Fc / Fc⁺ redox couple was calculated by using anodic (E anodic potential) and cathodic (E cathodic potential) peak potential according to the equation (1).

$$\text{Ferrocene / Ferrocenium (Fc / Fc}^+\text{) } E_{1/2, \text{Fc, Fc}^+} = E_{\text{ap}} + E_{\text{cp}} / 2 \quad (1)$$

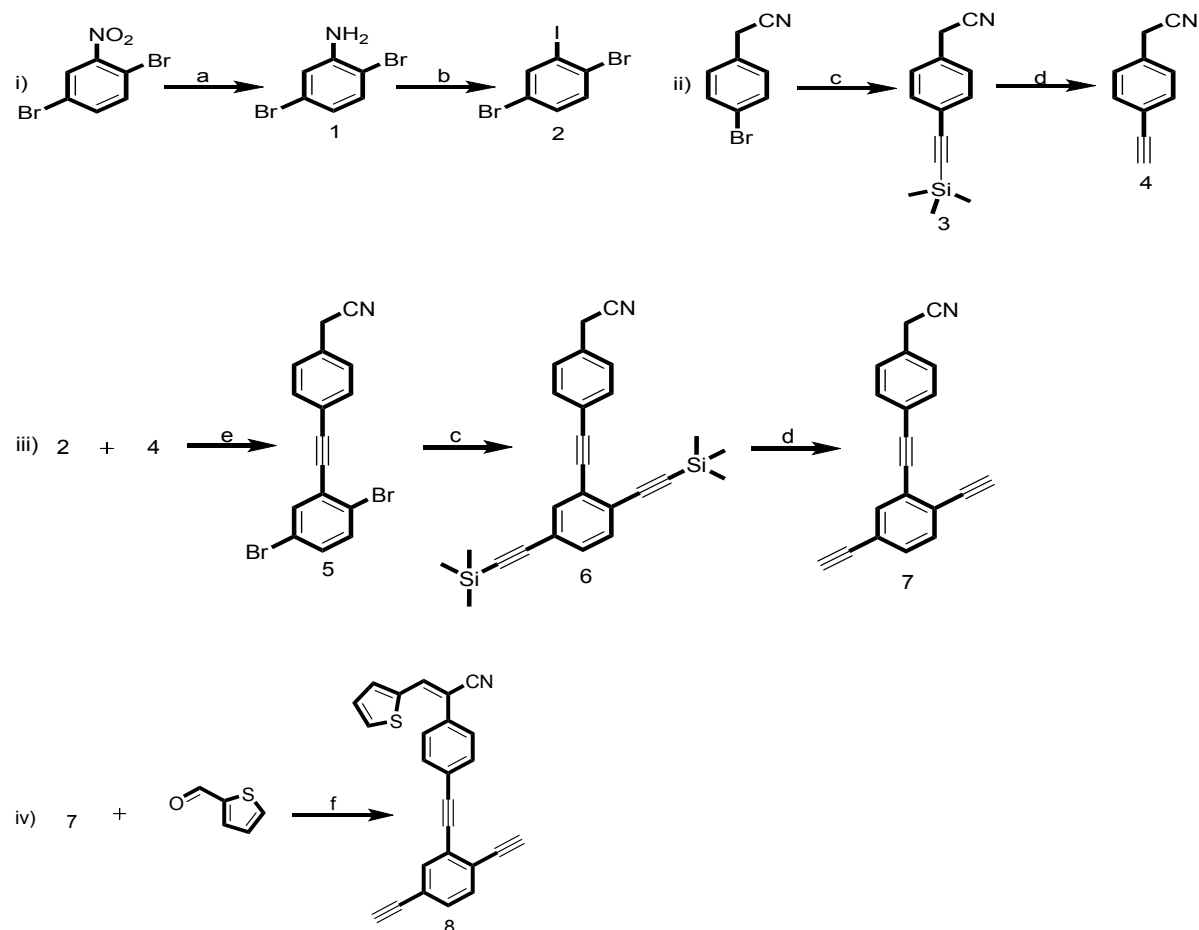
The half -wave potential of Fc / Fc⁺ was determined by 0.05 V by using the equation. The synthesis of CPs with optical energy gap was calculated using onset value of thin film UV-vis spectra and substituted in 1240 / λ onset. The HOMO energy level of the polymers were calculated by using the equation (2) and the LUMO energy level was calculated from optical energy gap and HOMO energy level values using the equation 3.

$$\text{HOMO} = E_{\text{HOMO}} = - [4.8 - E_{1/2, \text{Fc, Fc}^+} + E_{\text{Ox, onset}}] \quad (2)$$

$$\text{LUMO} = E_{\text{LUMO}} = [E_{\text{HOMO}} + E_{\text{g, opt}}] \quad (3)$$

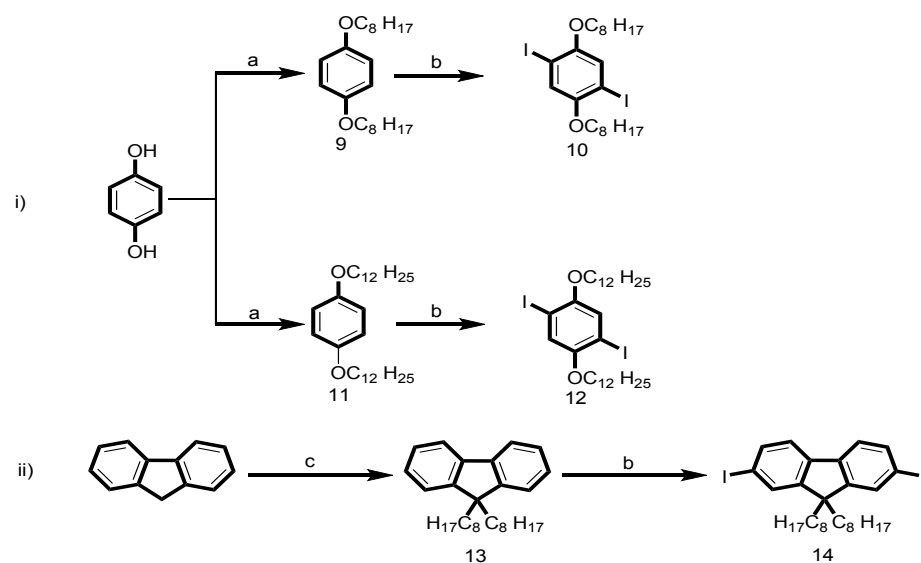
2) Synthesis scheme of diethynylene and diiodo monomers.

a) Reaction scheme of synthesis of diethynylene monomers.



Outline procedure ESI a: (a) Fe powder, AcOH, EtOH, H₂O (b) Con. HCl, NaNO₂, KI, 0 ° C (C) Pd(PPh₃)Cl₂, Cu(I)I, triethylamine (TEA), THF, 80 ° C (d) KF, MeOH, THF, Room temperature condition (RT) (e) Pd(PPh₃)Cl₂, Cu(I)I, TEA, THF, RT condition (f) NaOH, EtOH, THF, RT condition.

b) Reaction scheme of 2, 5-bis-alkoxy and 9, 9'-bis-octyle substituted iodinated arylene Monomers (10, 12 and 14)



Outline procedure ESI b: (a) n-bromo octane or n-bromododecane, dried K_2CO_3 , $80^\circ C$ (b) $AcOH$, H_2O , KIO_4 , I_2 , H_2SO_4 , $70^\circ C$ (c) n-bromo octane, KOH , $DMSO$, RT condition.

3) Experimental procedure.

Synthesis of 2,5-dibromoaniline (compound-1)¹⁻³

Dry three necked 1L round bottomed (Rb) flask was fitted with the controlled mechanical stirrer and reflux condenser. The Rb was charged with the mixture of 1,4-dibromo-2-nitrobenzene (10 g, 35 mmol), methanol 600 mL, acetic acid 60 mL and deionized water 10 mL. After reaching the homogeneous mixture, the iron powder (20 g, 357 mmol) was added to the above reaction mixture under constant stirring. The reaction mixture was maintained with constant stirring for overnight at $70^\circ C$ with and the progress of the reaction was monitored using TLC plates. After the completion of the reaction the crude reaction product was filtered through celite bed followed by concentration of liquid portion under reduced pressure. A pure product of compound-1 was obtained by recrystallization of the crude solid product using methanol. Yield: 8.72 g (87 %). 1NMR (500 MHz, $CDCl_3$): δ 7.17 (t, 1H, $J = 7.5$ Hz), 6.82 (s, 1H), 6.65 (d, 1H, $J = 10$ Hz) and 4.06 (s, 2H).

Synthesis of 1, 4-dibromo-2-iodobenzene (compound-2)¹⁻³

250 mL two necked Rb was charged with (10 g, 40 mmol) of compound-1 and 52 mL of con. HCl and water (1:1) reaction mixture was stirred at 80 ° C for 30 min. The reaction temperature was brought to RT, the Rb was kept in an ice bath maintained at 0 ° C and the reaction mixture was stirred to obtain homogenous form. After that, the cold aqueous sodium nitrite (4.1 g, 59.7 mmol) solution was added slowly under constant stirring and kept for 30 min at 0 ° C. The final reaction mixture was transferred to another 250 mL Rb containing aqueous potassium iodide (9.91 g, 59.7 mmol) solution maintained at 0 ° C using an ice bath. The whole reaction mixture was allowed to reach RT with constant stirring for 6 h. Then the product mixture resulted was poured into crushed ice water and the crude product obtained was extracted using dichloromethane. The organic layer was washed with 5 % aqueous NaOH solution followed by water wash for three times and dried over anhydrous sodium sulfate. For the pure product, the crude product of compound-2 was purified by column chromatography using petroleum ether as eluent. Yield: 9.75 g (67.6 %). ¹NMR (300 MHz, CDCl₃): δ 7.97 (d, 1H, *J* = 1.5 Hz), 7.44 (d, 1H, *J* = 8.7 Hz) and 7.31 (dd, 1H, *J*₁ = 8.7 Hz, *J*₂ = 1.8 Hz).

Synthesis of 2-trimethylsilylethynyl phenylacetonitrile (compound-3)⁴⁻⁸.

Ultra-clean dry three necked Rb having Teflon coated magnetic bar was charged with 4-bromophenyleacetonitrile (4 g, 20 mmol), Pd(PPh₃)₂Cl₂ (0.216 g, 0.3 mmol) and Cu(I)I (0.058 g, 0.3 mmol). The above reaction setup was de-oxygenated by using high vacuum pump followed by refilling of dry N₂ gas followed by the addition of dry THF 20 mL and the dry TEA by using syringe. Trimethylesilyl acetylene (3.02 g, 31 mmol) was dissolved in dry THF solvent and then slowly added to the above reaction mixture for 30 min. Finally, the whole reaction system was deoxygenated and back filled with dry N₂ gas with the reaction system being maintained at 75 to

80 ° C overnight. After the completion of the reaction the reaction mass was filtered through celite bead then concentrated and dissolved in DCM followed by work up with aqueous ammonium chloride solution, brine solution and distilled water (more than two times). The separated organic layer was dried with anhydrous sodium sulfate and then concentrated under vacuum condition. The crude product of was purified with silica column chromatography by using n-hexane and DCM (9.8 : 0.2 percentage) as eluent. The pure yellow colored scales like the compound-3 solid product was collected and preserved for further analysis. Yield: 4.07 g (93.1 %). ¹NMR (500 MHz, CDCl₃): δ 7.34 (d, 2H, *J* = 10Hz), 7.13 (d, 2H, *J* = 10Hz), 3.61 (s, 2H), and 0.13 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) 132.7, 130.2, 127.9, 123.3, 117.5, 104.2, 95.4, 23.6, 0.02, 0.01 and -0.04.

Synthesis of 4-ethynylphenylacetonitrile (compound-4).

700 mL of THF and methanol with the ratio of (1:1) was added with compound-3 (5 g, 23.4 mmol) in 1lit Rb under constant stirring and then potassium fluoride was (2.04 g, 35 mmol) added to the above reaction mixture. The reaction was stirred for 90 min and monitored by TLC. The concentrated crude product was dissolved in DCM and washed with deionized water followed by dried with anhydrous sodium sulfate. The final concentrated crude liquid product was purified by using column chromatography. The eluent as hexane with DCM (9.5: 0.5). The yellow colored liquid like compound-4 product obtained was collected. Yield: 3.1 g, (95.3 %). ¹NMR (300 MHz, CDCl₃): δ 7.50 (d, 2H, *J* = 7.8Hz), 7.29 (d, 2H, *J* = 7.8Hz), 3.75 (s, 2H), and 3.11 (s, 1H). ¹³C NMR (75 MHz, CDCl₃): 132.8, 130.6, 128.0, 122.1, 117.4, 82.9, and 23.5. DEPT-135 (CDCl₃) 132.8, 128.0, 82.8, 78.2, and 23.5.

Synthesis of 2-(4-((2,5-dibromophenyl)ethynyl) phenyl)acetonitrile (compound-5)

The compound-5 was synthesized using the compound-2 (5 g, 13.8 mmol) and compound-4 (1.85 g, 13.1 mmol) as the halogen and ethynyl source precursor materials respectively. The procedure and work up method were same as for the compound-3. The reaction condition was maintained for 12 h at RT. After column purification, the compound-5 pure yellow solid product obtained was collected. Yield: 4.4 g (88 %). ¹NMR (300 MHz, CDCl₃): δ 7.68 (s, 1H), 7.6 (d, 2H, *J* = 6.6Hz), 7.47 (d, 1H, *J* = 8.4Hz), 7.71 (q, 3H, *J* = 18Hz), and 3.80 (s, 2H). ¹³C NMR (75 MHz, CDCl₃): 135.7, 133.8, 132.7, 132.5, 130.7, 128.1, 127.0, 124.3, 122.5, 120.7, 117.2, 94.2, 87.6, and 23.7.

Synthesis of 2-(4-((2,5bis ((trimethylsilyl) ethynyl) phenyl) ethynyl) phenyl) acetonitrile (compound-6)

The corresponding compound-5 (3.9 g, 10.3 mmol) was treated with the trimethylsilylacetylene (2.24 g, 22.8 mmol) in the presence of precursor materials were used for the synthesis of compound-6. The reaction mixture was maintained at 75 to 80 ° C for 24 h and the reaction was monitored by TLC. The procedure and work up method was used same as those adopted for compound-3. After the purification of the column, the pure yellow colored scale like product compound-6 obtained was collected. Yield: 3.5 g, (82.3 %). ¹NMR (300 MHz, CDCl₃): δ 7.43 (s, 1H), 7.36 (d, 2H, *J* = 8.1Hz), 7.24 (d, 1H, *J* = 8.1Hz), 7.17-7.12 (m, 3H), 3.58 (s, 2H), 0.08 (s, 9H), and 0.065 (s, 9H).

Synthesis of 2-(4-((2, 5-diethynylphenyl) ethynyl) phenyl) acetonitrile (compound 7)

The compound-7 was synthesized by deprotection method, using compound-6 (3.54 g, 8.6 mmol) and potassium fluoride (0.75 g, 12.9 mmol) in presence of 490 mL of THF and methanol

(1:1 ratio). The whole reaction mass was stirred for more than 2h at RT and monitored by using TLC. The procedure and work up method were used same as those adopted for the compound-4. After purification of column diethynyl yellow colored product compound-7 obtained was collected and preserved. Yield: 1.8 g (82 %). FTIR (KBr, cm^{-1}): 3000-3070, 1594, 1509, 14580, 1415, 3296, 2218. ^1NMR (300 MHz, CDCl_3): δ 7.65 (s, 1H), 7.5 (s, 1H), 7.56 (d, 2H, $J = 9\text{Hz}$), 7.48 (d, 1H, $J = 7.8\text{Hz}$), 7.40 (d, 1H, $J = 9\text{Hz}$), 7.31 (d, 2H, $J = 9\text{Hz}$), 3.77 (s, 2H), 3.47 (s, 1H), and 3.12 (s, 1H). ^{13}C (75 MHz, CDCl_3): 135.2, 132.6, 132.5, 131.5, 130.4, 128.0, 126.2, 124.9, 122.8, 122.7, 117.4, 93.2, 87.7, 83.0, 87.7, 83.0, 82.2, 81.6, 79.7, and 23.6. HR-MS (m/z) calculated for $\text{C}_{20}\text{H}_{11}\text{N}$, 266.0969; Founded, 266.3158.

Synthesis of 2-(4-((2,5-diethynylphenyl)ethynyl)phenyl)-3-(thiophen-2-yl)acrylonitrile (compound-8).

Three necked dry 100 mL Rb with Teflon coated magnetic pellet charged with compound-7 (200 mg, 0.75 mmol) and 2-thiophenealdehyd (92 mg, 0.0082 mmol) with the 3 mL volume of 1:1 ratio of ethanol and THF. The reaction mixture was kept in an ice bath with constant stirring followed by slow addition of sodium hydroxide (44 mg) solution. The color change was observed from yellowish orange to dark blue color and then it was monitored by TLC. After the completion of the reaction product resulted was poured into ice water and then extracted with DCM. The organic layer was washed with water for several times and then dried over anhydrous sodium sulfate. Further, the organic layer of compound-8 was concentrated and then purified by column chromatography. Yield: 0.270 g (85 %). FTIR (KBr, cm^{-1}): 3050, 1594, 1518, 1481, 1414, 3298, 2216. ^1NMR (300 MHz, CDCl_3): δ 7.70 (d, 4H, $J = 10.2\text{Hz}$), 7.64-7.58 (m, 4H), 7.5 (d, 1H, $J = 7.8\text{Hz}$), 7.41 (d, 1H, $J = 7.8\text{Hz}$), 7.17 (t, 1H, $J = 4.5\text{Hz}$), 3.48 (s, 1H), and 3.2 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3): 137.8, 135.2, 134.5, 134.0, 132.8, 132.6, 132.4, 131.5, 130.6, 128.0, 126.2,

125.5, 124.9, 123.4, 122.7, 117.8, 107.5, 93.5, 88.8, 83.0, 82.2, 81.6, 79.7, and 29.7. HR-MS (m/z) calculated for $C_{25}H_{13}NS$, 360.08470, Found value m/z , 360.0846.

Synthesis of 1,4-bis (octyloxy) benzene (compound 9).⁹⁻¹¹

The 500 mL three neck RB fitted with a controlled mechanical stirrer. The RB charged with hydroquinone (15 g, 136 mmol) in the presence of DMF under constant stirring maintained at 50 °C. Powdered anhydrous potassium carbonate (94 g, 680 mmol) was added in portions for 30 min. The 1-bromooctane (52.61 g, 272 mmol) was slowly added to above reaction mixture. The reaction mixture was increased up to 80 °C and was maintained for 24 h with vigorous stirring. After the completion of the reaction, the crude mixture was poured into crushed ice water. Later the organic solid material obtained was extracted with ethyl acetate and then the organic layer was washed with brine solution followed by water for several times. The organic layer of was dried with anhydrous sodium sulfate and then concentrated under reduced pressure. The compound-9 was purified by using silica column. Yield: 30.4 g, (66.7 %) ¹NMR (300 MHz, $CDCl_3$): δ 6.80 (s, 4H), 3.88 (t, 4H), 1.8 (q, 4H, $J=13.8$ Hz), 1.43-1.29 (m, H₂₀), and 0.88(m, 6H). ¹³C NMR (75 MHz, $CDCl_3$): 153.3, 115.4, 71.0, 68.7, 31.9, 29.8, 29.5, 29.4, 29.3, 29.1, 22.7, and 14.1.

Synthesis of 1,4-diiodo-2,5-bis(octyloxy)benzene (compound 10).^{12, 13}

500 mL three necked Rb was charged with compound-9 (9.5 g, 28 mmol), acetic acid 70 mL, deionized water 9.5 mL. Then iodine powder (8.5 g, 34 mmol) and potassium periodate (7.8 g, 34 mmol) were added pinch by pinch to the reaction mixture over a period of 30 min. Once the homogeneous phase of the reaction mixture was reached the concentrated sulfuric acid 2.2 mL was added. The whole reaction mixture was kept for 24 h at 70 to 75 °C. After the completion of reaction, it was kept idle to reach RT and then the crude product obtained was quenched with

crushed ice water. The crude product obtained was extracted with ethyl acetate. The organic layer was washed with deionized water for several times and then dried over anhydrous sodium sulfate. The organic layer was concentrated then the crude solid product of compound 10 was recrystallized with ethanol, the pure white product was obtained. Yield: 11.2 g (67.6 %). ^1NMR (500 MHz, CDCl_3): δ 7.2(s, 2H), 3.95 (t, 4H, $J = 7.5\text{Hz}$), and 1.83-0.95 (m, 30H). ^{13}C NMR (75 MHz, CDCl_3): 153.0, 122.8, 86.2, 70.1, 31.8, 29.3, 29.2, 29.2, 26.0, 22.7, and 14.0.

Synthesis of 1,4-bis (dodecyloxy) benzene (compound 11).

For the synthesis of compound-11, the same procedure and precursor materials were used as compound-9. At that same time, the aliphatic chain precursor of 1-bromo dodecane (67.8 g, 272 mmol) was used instead of 1-bromo octane. The crude compound-12 obtained was purified by silica column. Yield: 31.46 g, (51.7 %). ^1NMR (500 MHz, CDCl_3): δ 6.84 (s, 4H), 3.92 (t, 4H, $J = 7\text{Hz}$), 1.76 (q, 4H, $J = 14.75\text{Hz}$), and 1.29-0.89 (m, 42H)

Synthesis of 1,4-bis(dodecyloxy)-2,5-diiodobenzene (compound 12)

The compound-12 was synthesized using compound- 11 (10 g, 22.4 mmol), acetic acid 73.7 mL, deionized water 10 mL. Then iodine powder (6.8 g, 26.8 mmol) and potassium periodate (6.16 g, 26.8 mmol) and concentrated sulfuric acid 2.4 mL. The compound-10 reaction procedure was followed. The crude solid product was recrystallized with ethanol and the pure white colored product was obtained (compound-12). Yield: 8.3 g, (53.1 %). ^1NMR (300 MHz, CDCl_3): δ 7.17 (s, 2H), 3.92 (t, 4H, $J = 7\text{Hz}$), 1.84-1.75 (m, 4H), 1.57-1.27 (m, 36H), and 0.89-0.86 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3): 171.2, 64.7, 31.9, 29.6, 29.6, 29.5, 29.3, 29.2, 28.6, 25.9, 22.7, 21.0, and 14.1.

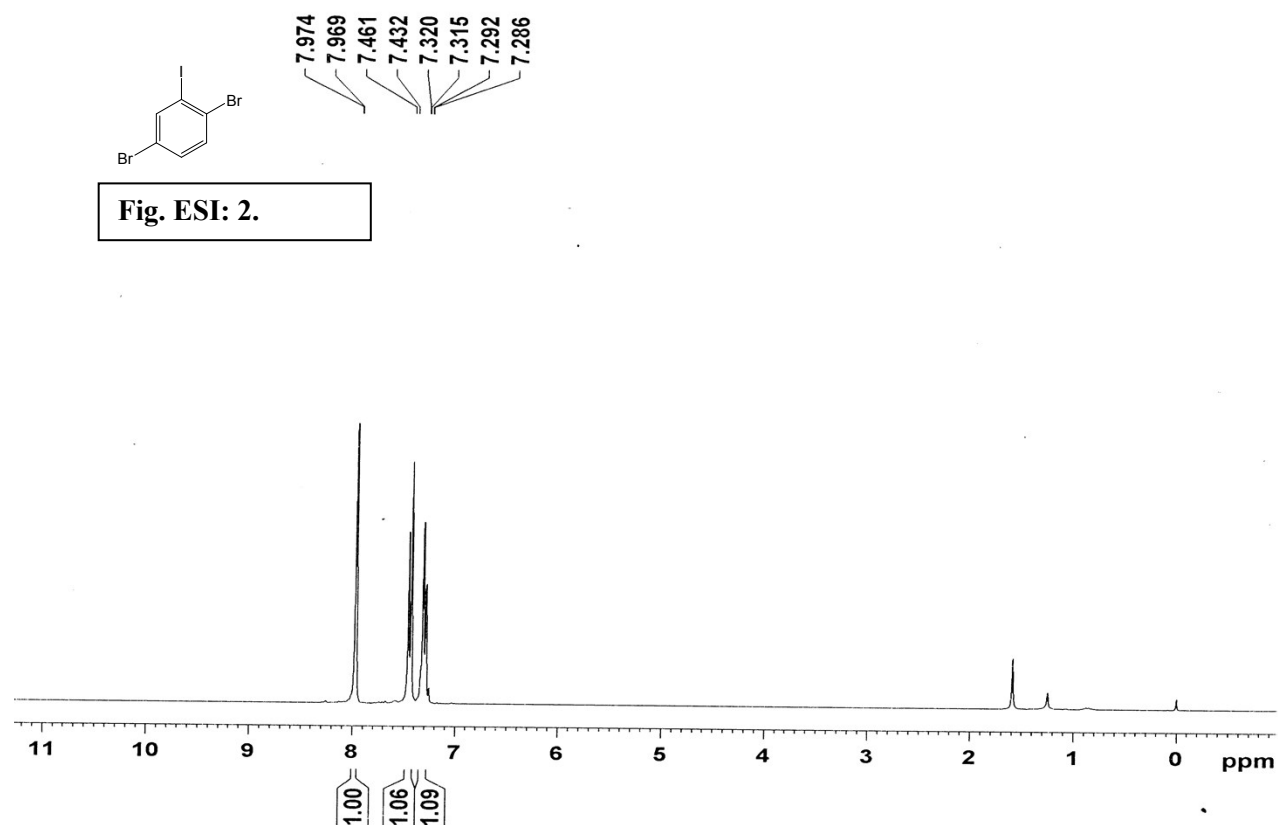
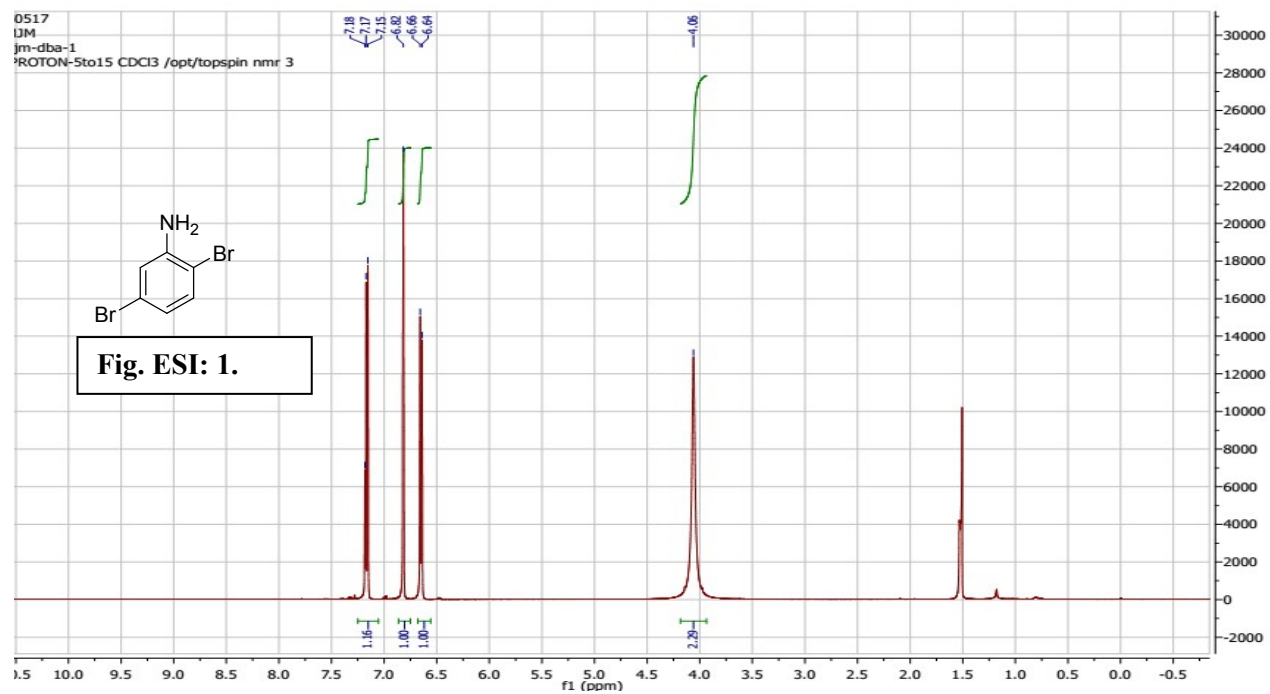
Synthesis of 9, 9-dioctyl-9H-fluorene (compound 13).¹⁴

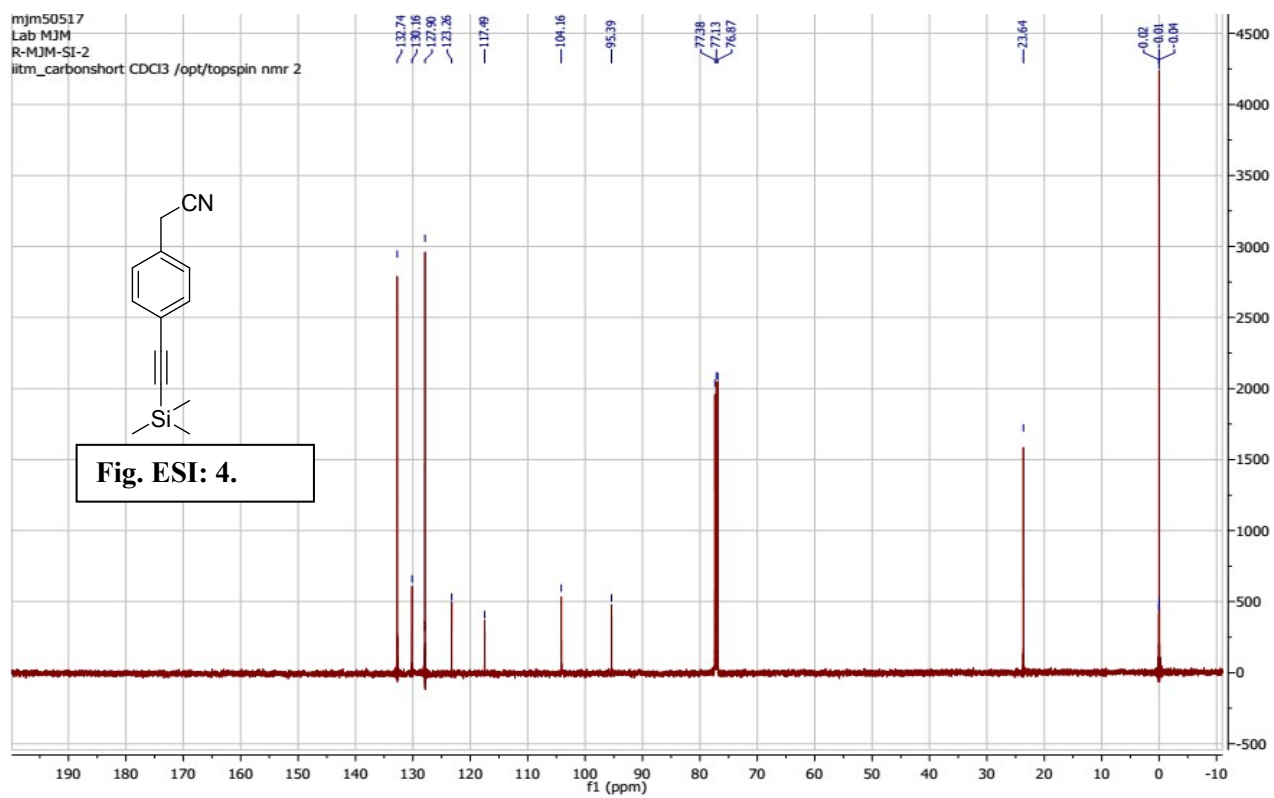
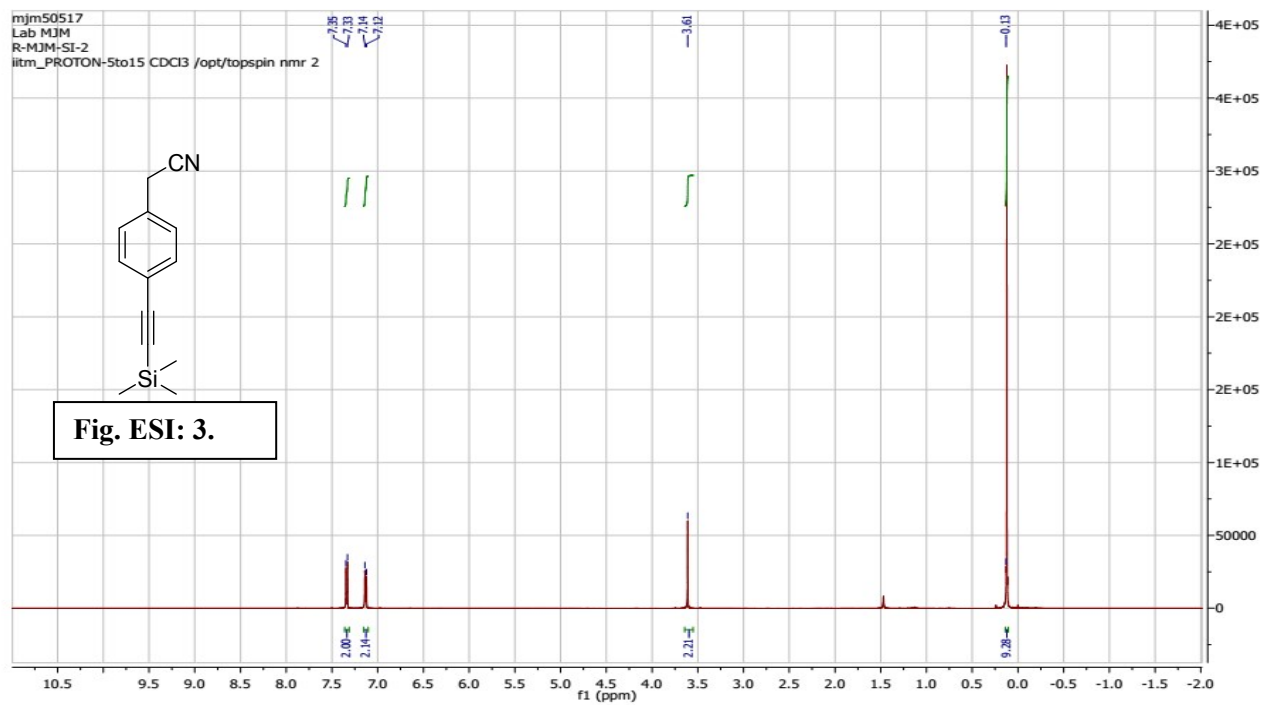
The 9H-fluorene (10 g, 60 mmol) with DMSO was added in 500 mL three necked Rb. The potassium hydroxide (17 g, 0.3 mol) and the small pinch of potassium iodide were added to the above reaction mixture. The reaction mixture was under constant stirring for 10 min and then 1-bromo octane (24 g, 0.126 mmol) was added slowly. Then the reaction mixture was stirred for overnight at RT. The crude product obtained was transferred into crushed ice water and then extracted with ethyl acetate followed by washing of organic layer with brine and water for several times. The separated organic layer was dried over anhydrous sodium sulfate and then concentrated. The concentrated compound-13 crude product was purified by column chromatography. The colorless oily product was collected. Yield: 26.1 g (65.3 %). ¹NMR (300 MHz, CDCl₃): δ 7.68 (t, 2 H, *J* = 2.9 Hz), 7.30 (q, 6 H, *J* = 8.1 Hz), 1.95 (q, 4H, *J* = 10.1Hz), 1.25-0.785 (m, 26 H), and 0.61 (s, 4 H). ¹³C NMR (75 MHz, CDCl₃): 150.7, 141.2, 127.0, 126.7, 122.9, 119.7, 55.0, 40.4, 31.8, 30.1, 29.8, 29.3, 23.8, 22.6, and 14.1.

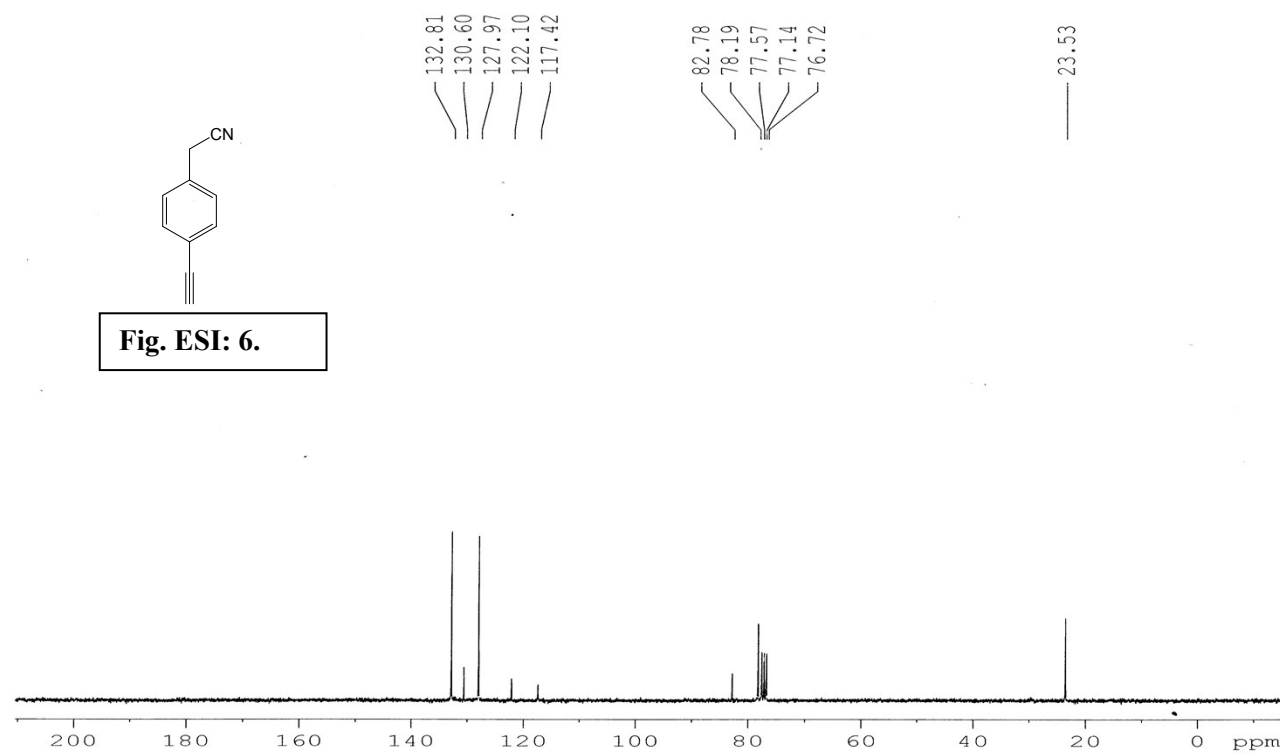
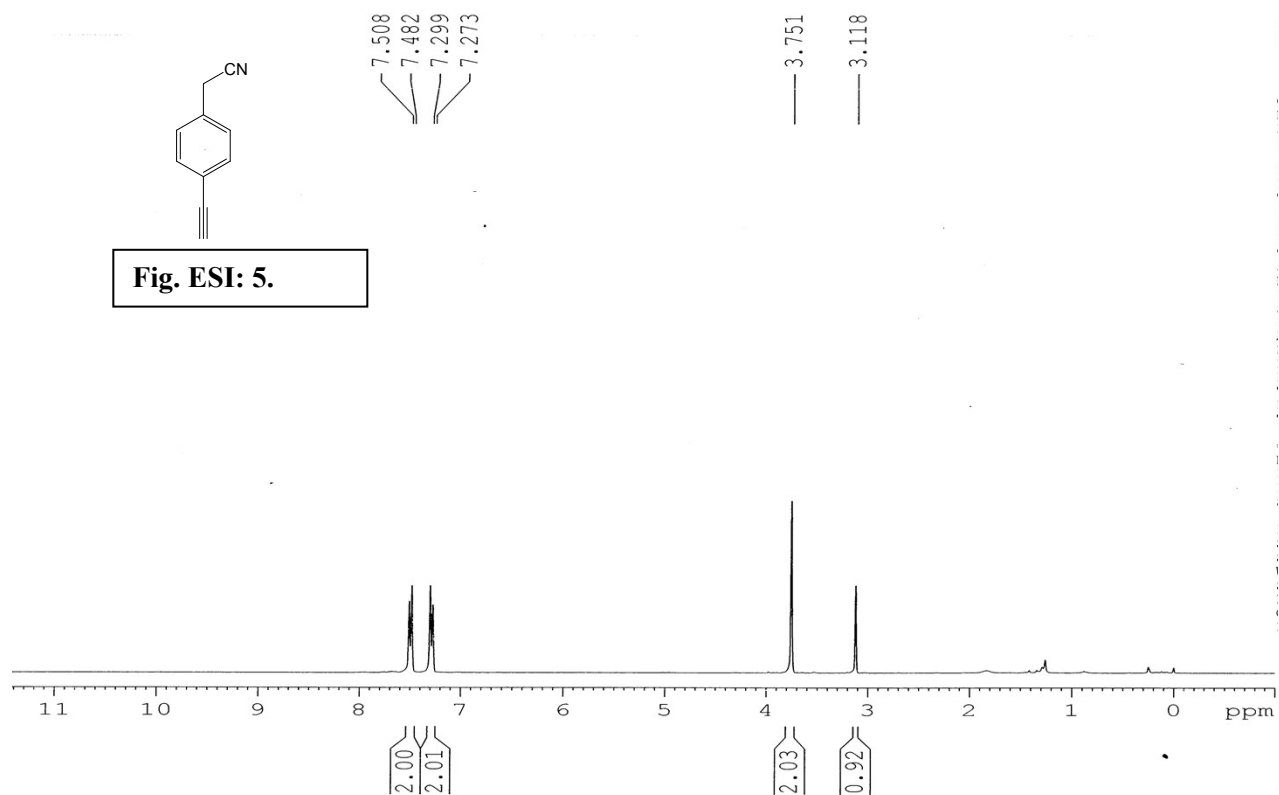
Synthesis of 2,7-diiodo-9,9-dioctyl-9H-fluorene (compound-14)

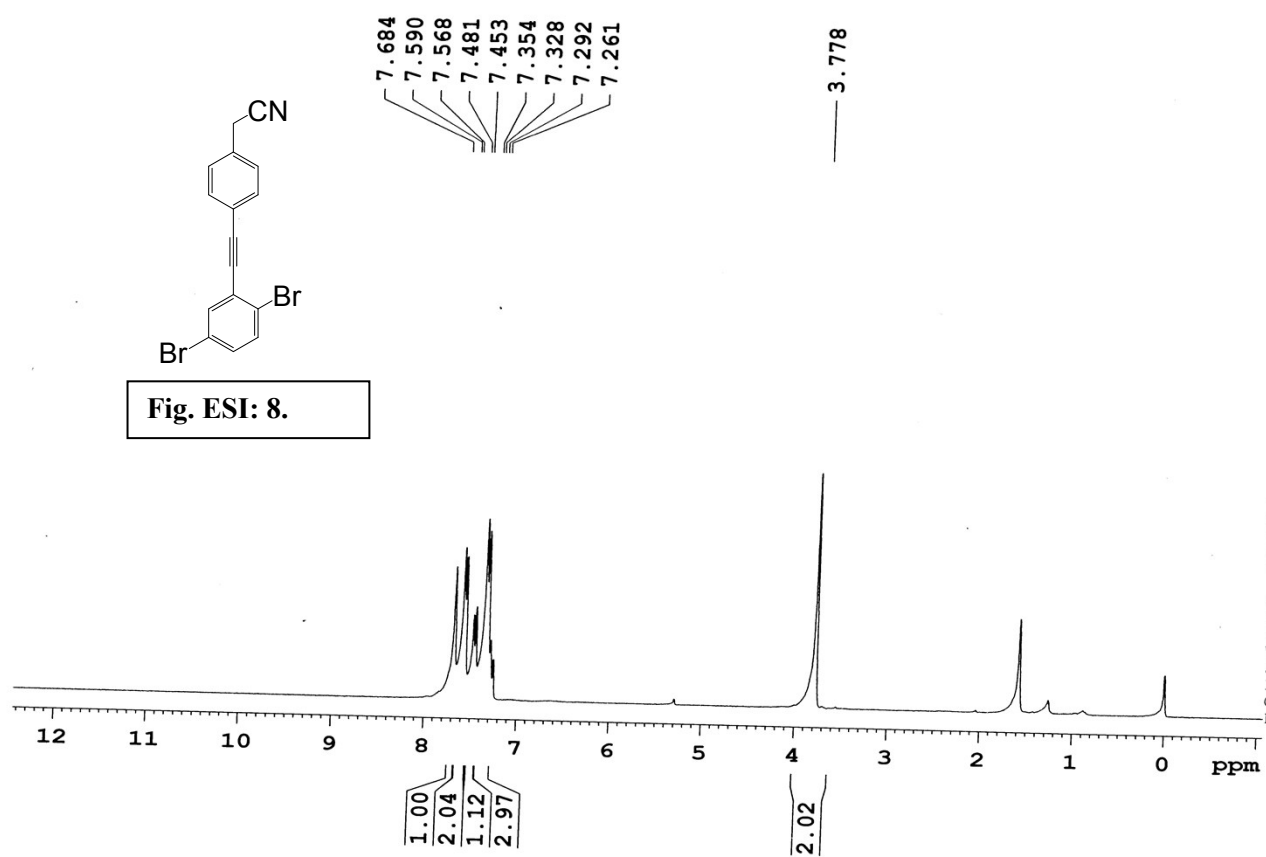
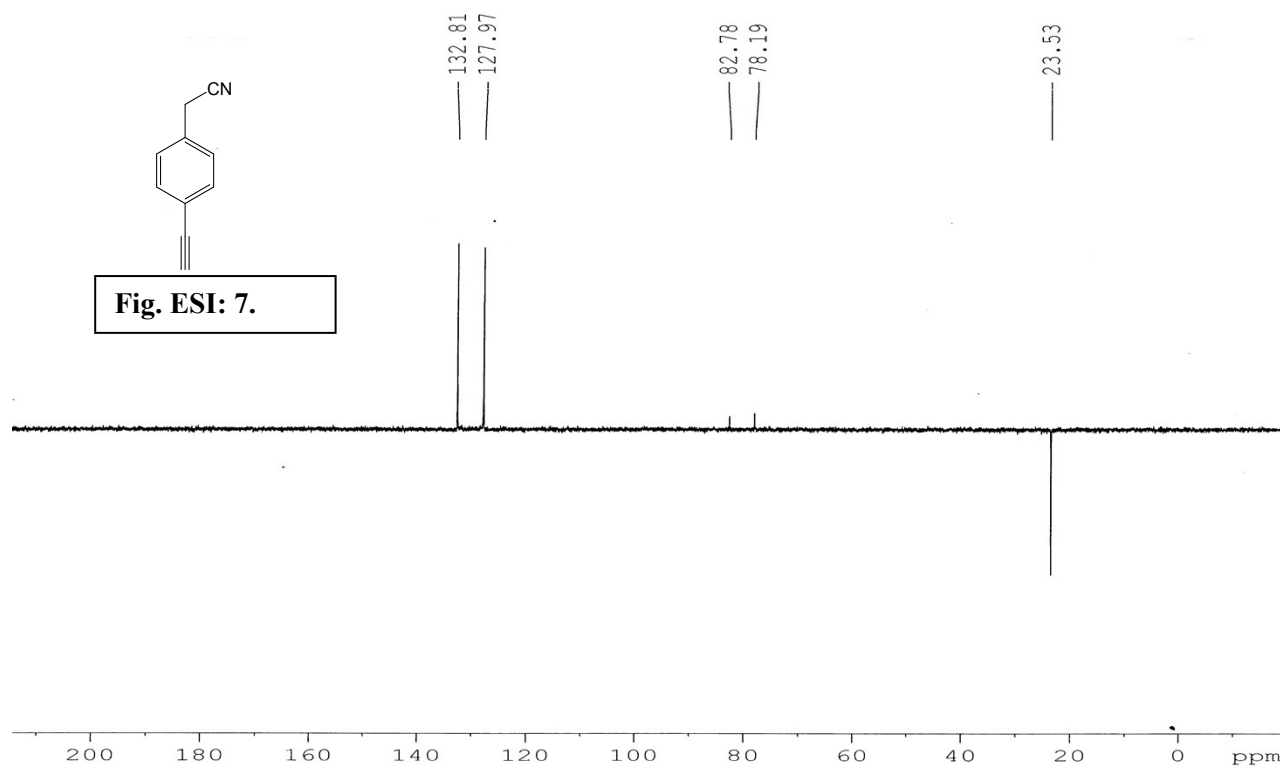
The compound-14 was synthesized using compound-13 (10 g, 25.6 mmol), acetic acid 73.7 mL, and deionized water 10ml. Then iodine powder (7.8 g, 30.7 mmol) and potassium periodate (7.061 g, 30.7 mmol) and concentrated sulfuric acid 2.4 mL. The procedure was adopted same of compound-10. The light orange pure solid product of compound-14 obtained was collected after the recrystallization in ethanol. Yield: 8.3 g, (53.1 %). ¹NMR (300 MHz, CDCl₃): δ 7.45 (d, 4H, *J* = 8.7 Hz), 7.20 (d, 2H, *J* = 7.8 Hz), 1.71 (q, 4H, *J* = 9.45 Hz), 1.068-0.66 (m, 26 H), and 0.64 (s, 4 H). ¹³C NMR (75 MHz, CDCl₃) 152.5, 139.8, 136.1, 132.1, 121.6, 93.3, 55.6, 40.2, 31.8, 29.9, 29.3, 29.2, 23.7, and 14.2.

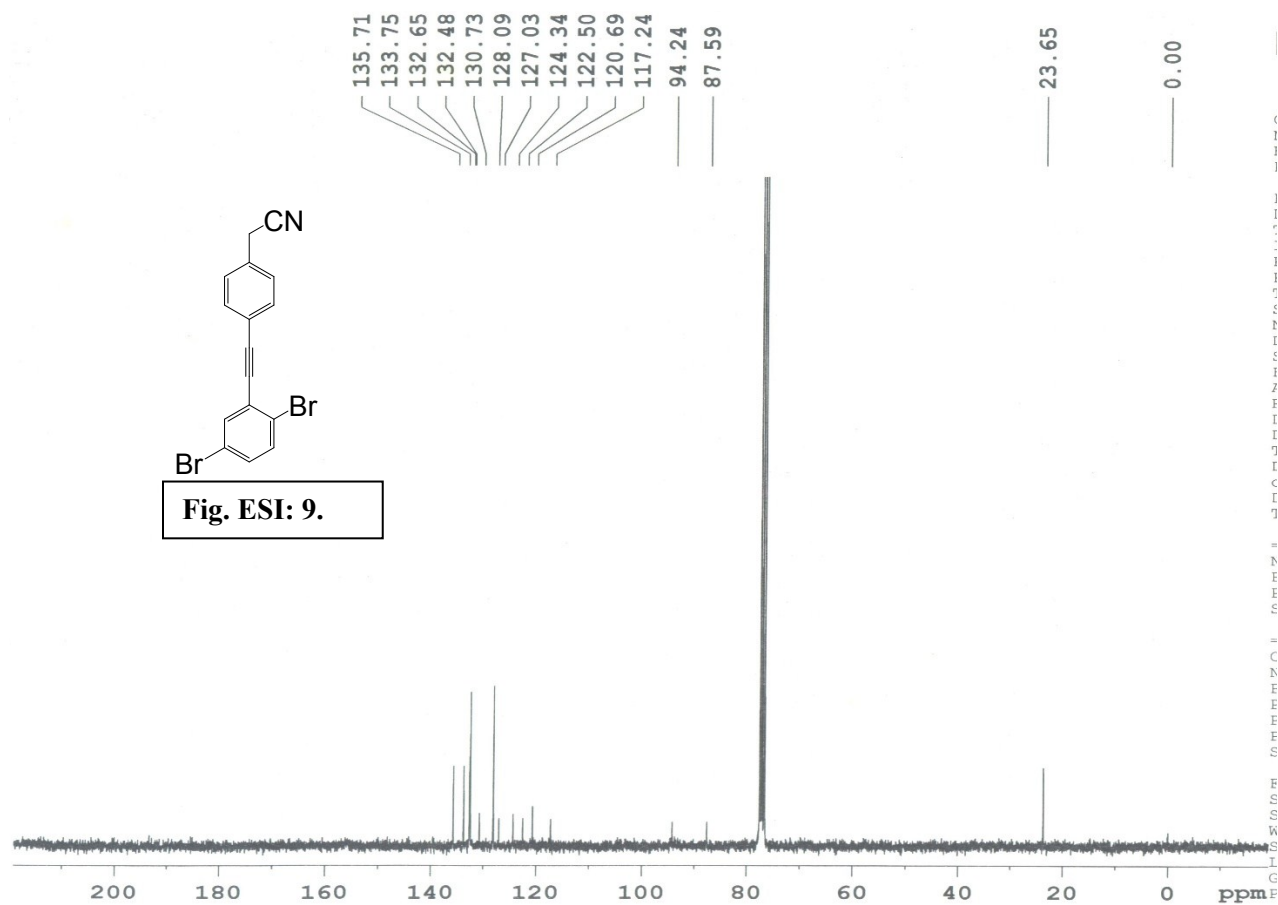
4) ^1H , ^{13}C and DEPT-135 NMR spectra for the compounds.

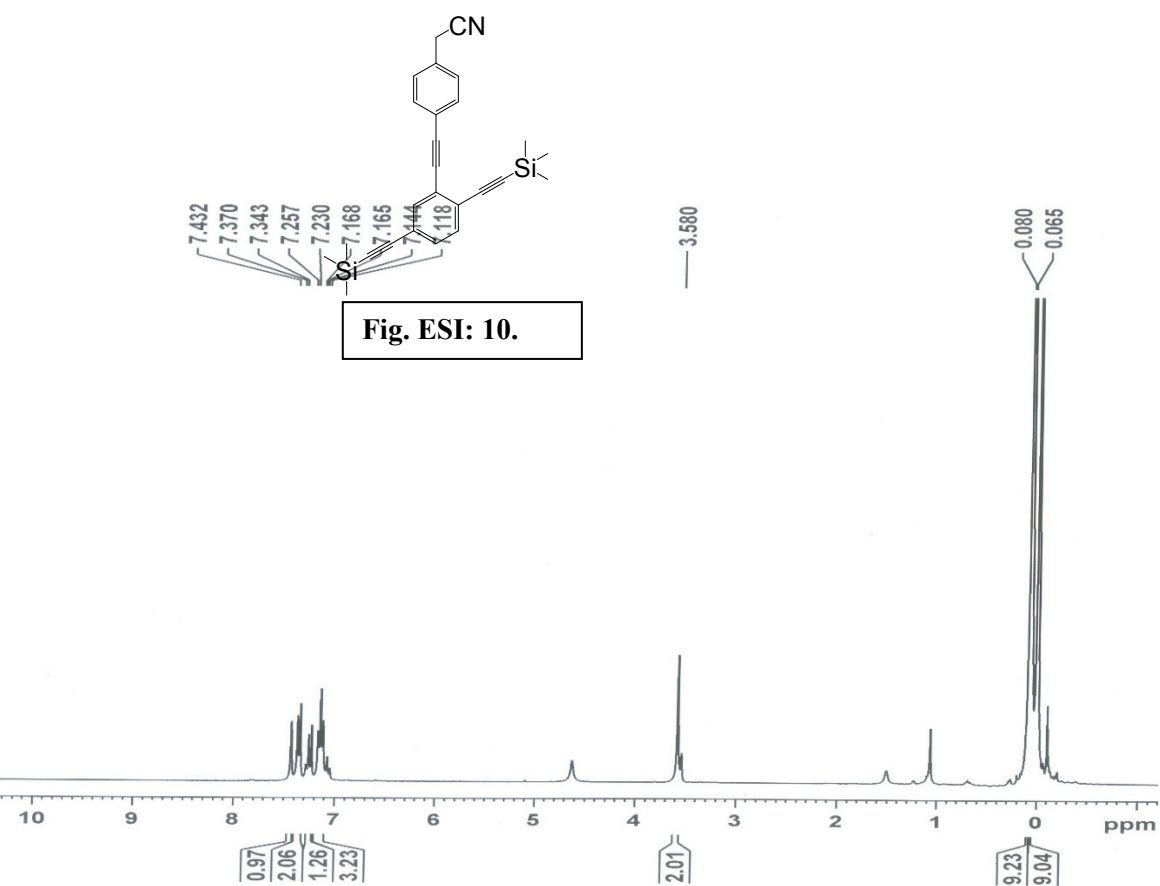


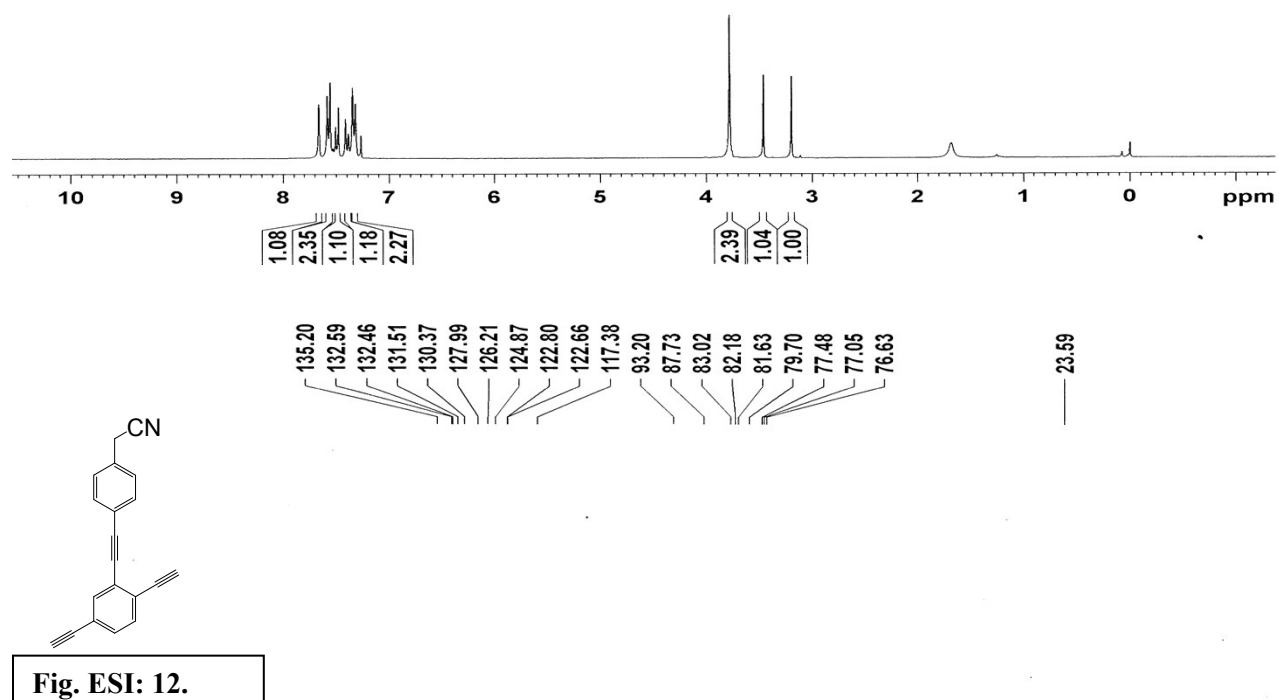
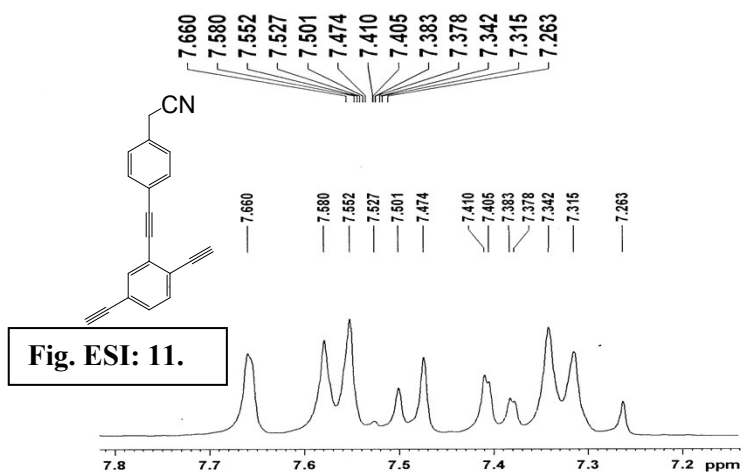












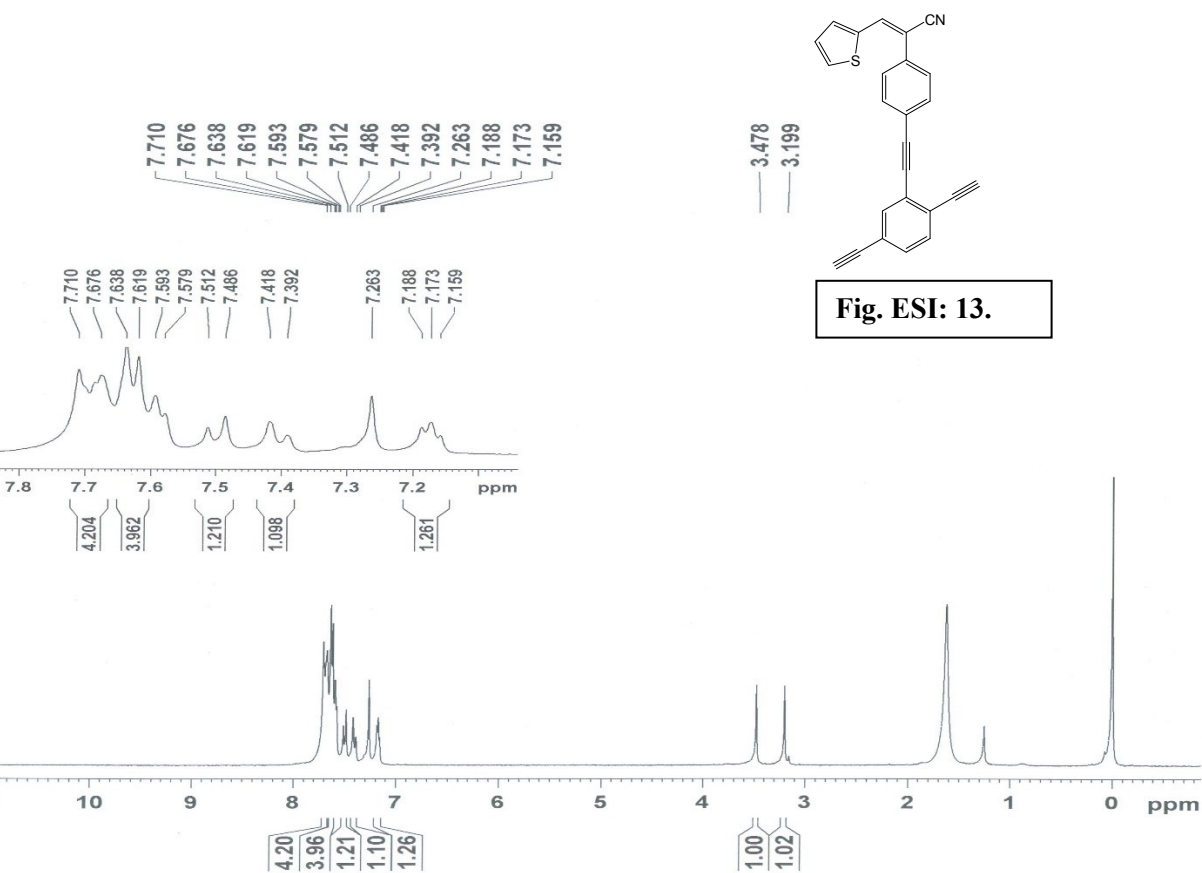
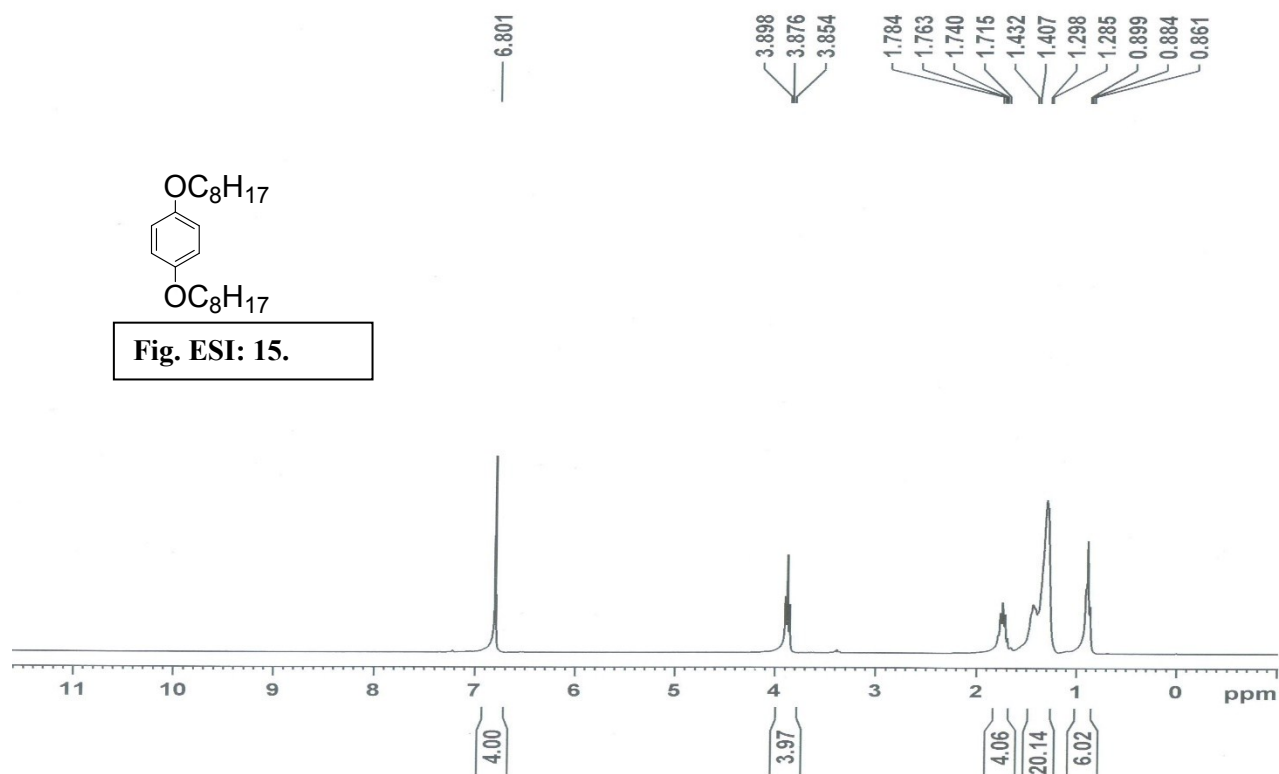
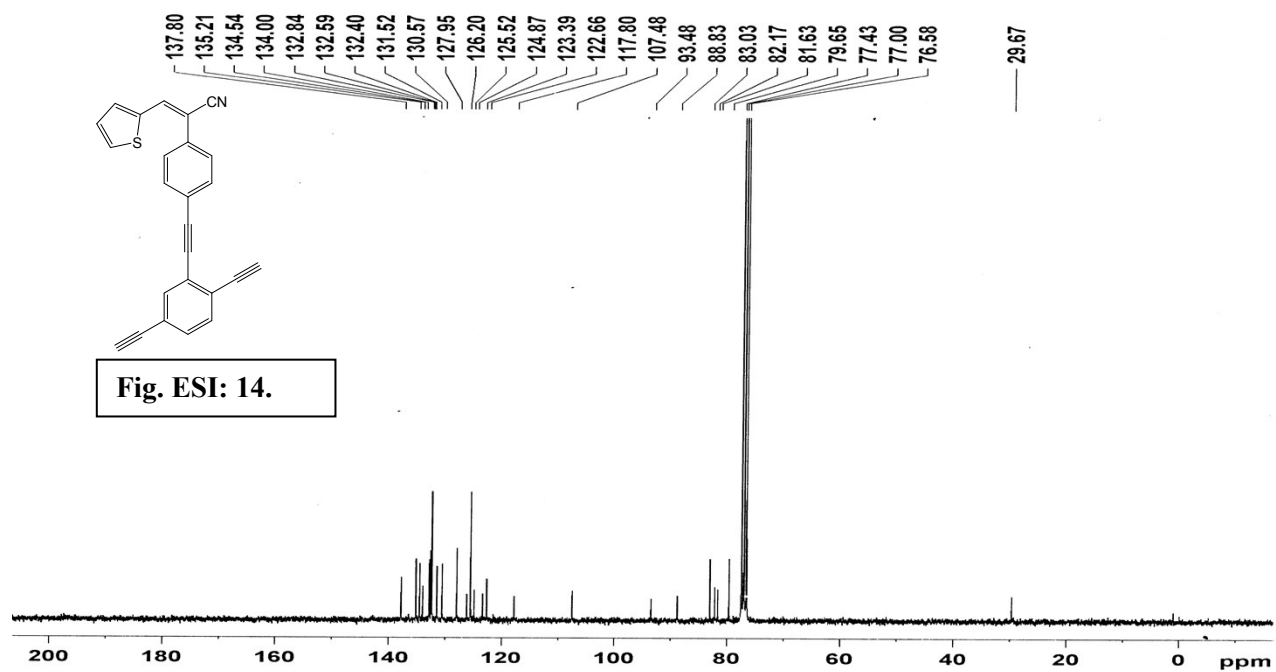
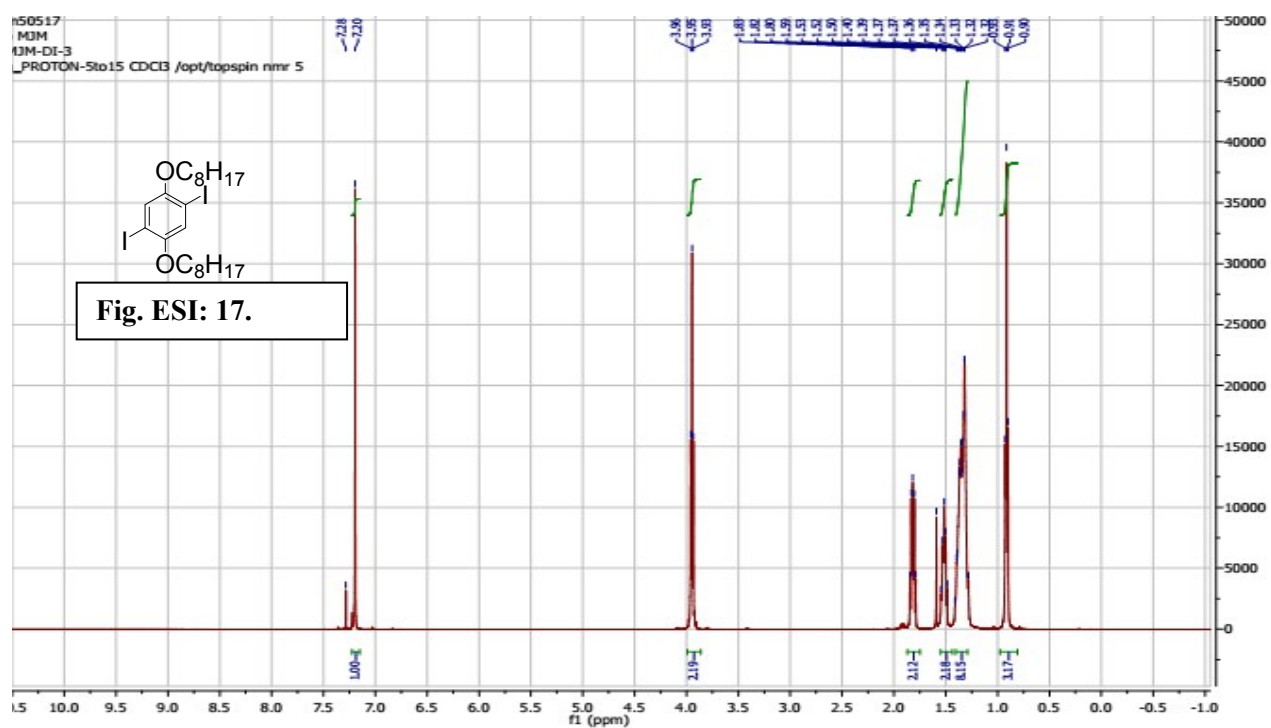
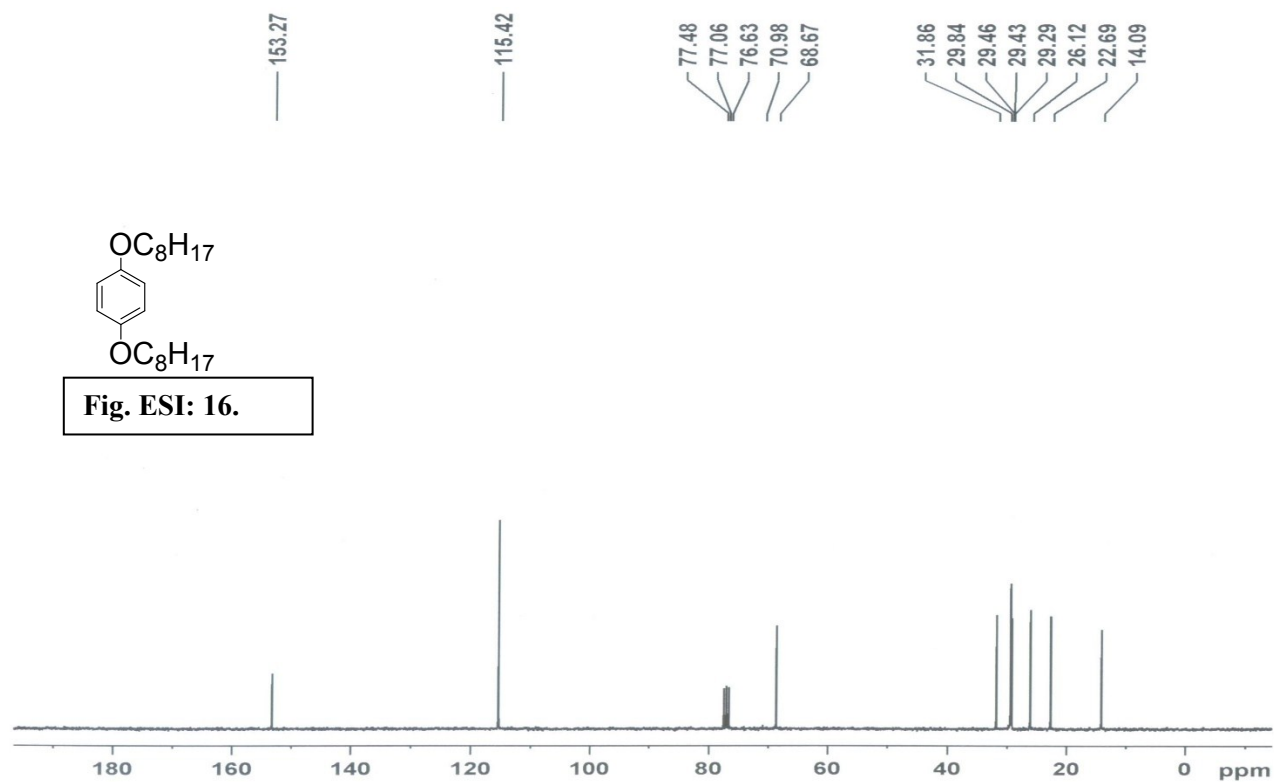
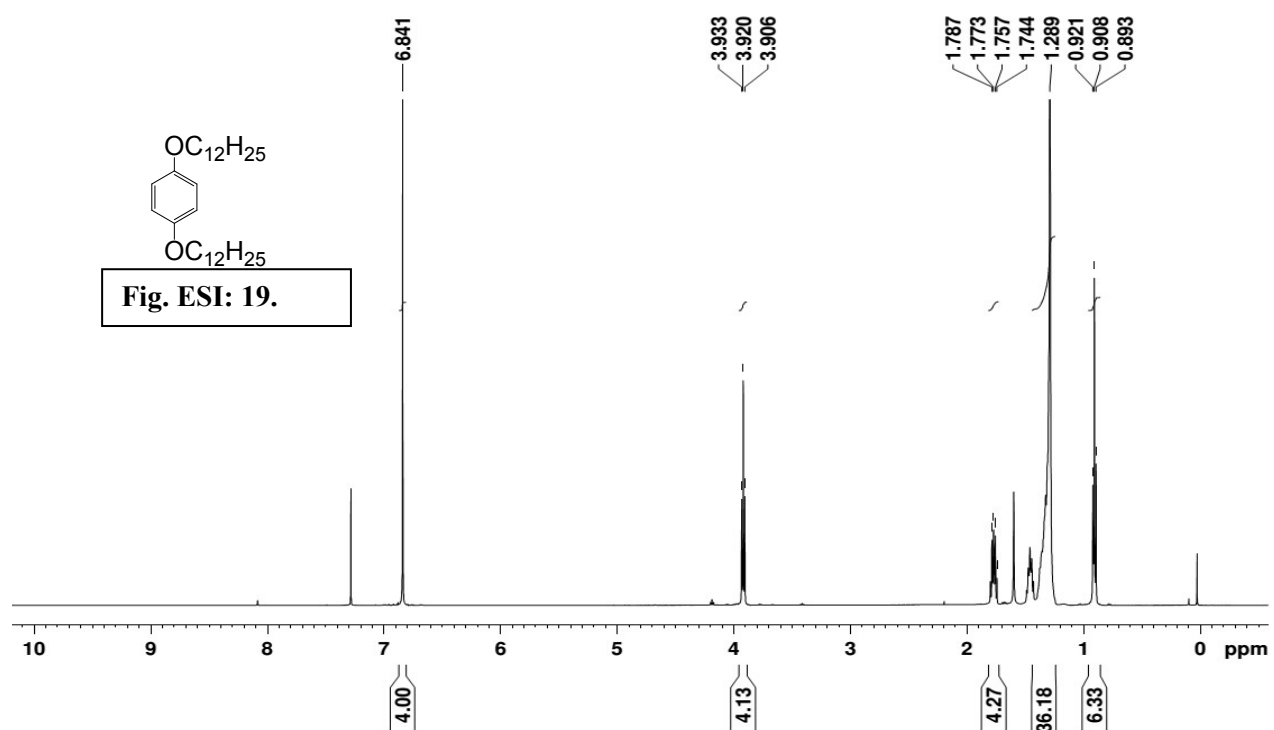
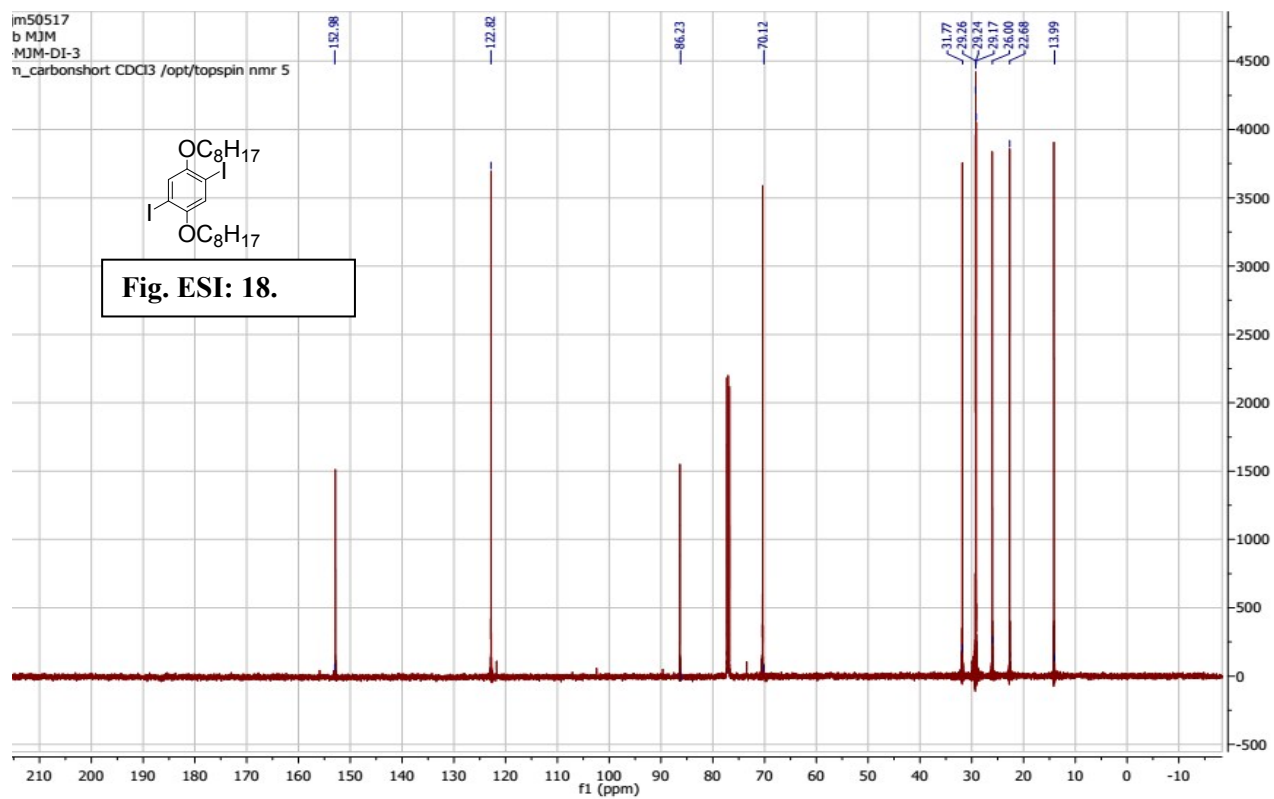
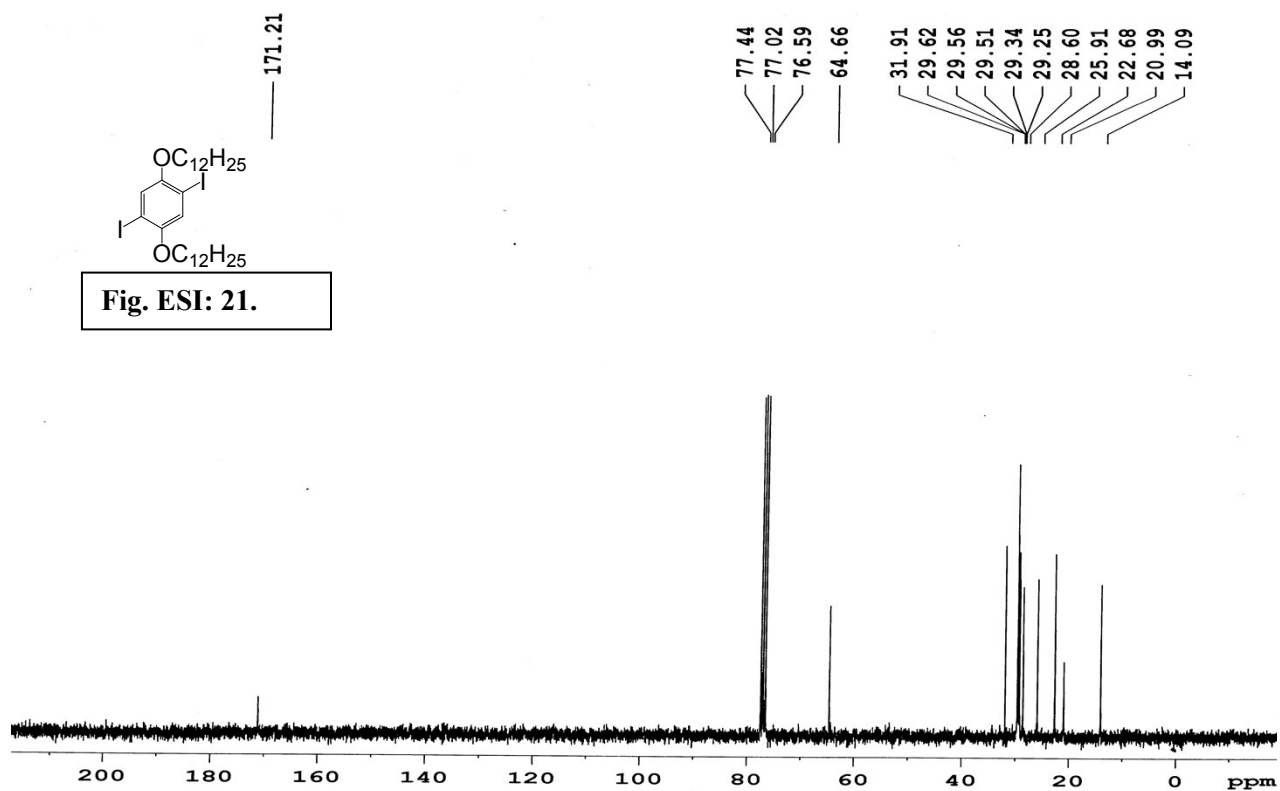
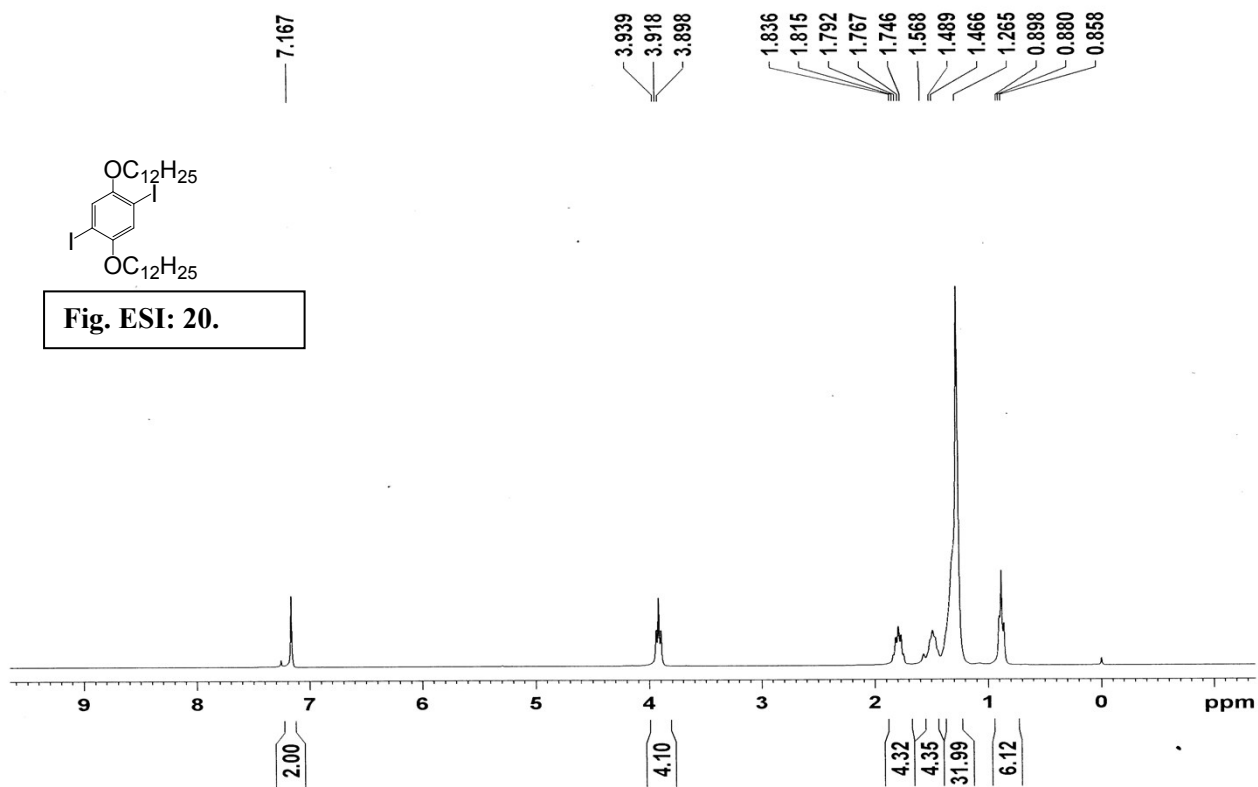


Fig. ESI: 13.









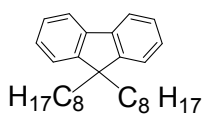
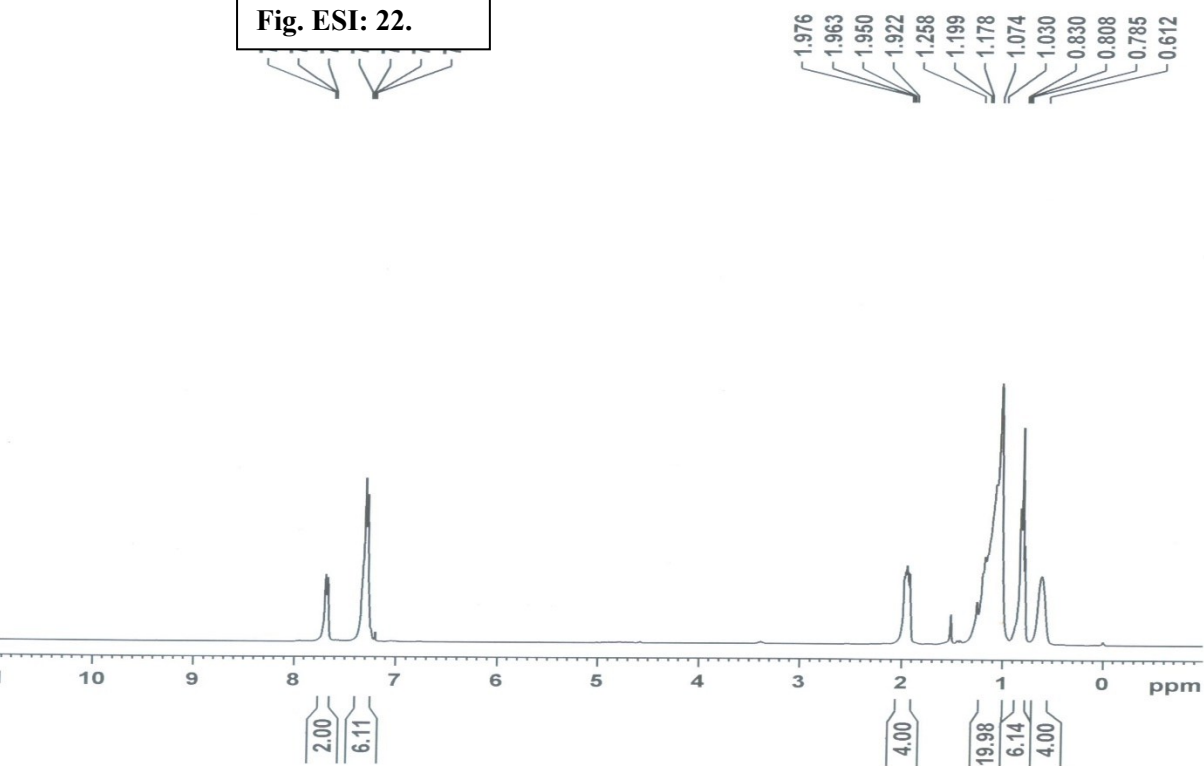


Fig. ESI: 22.



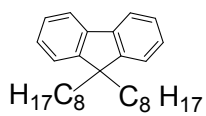
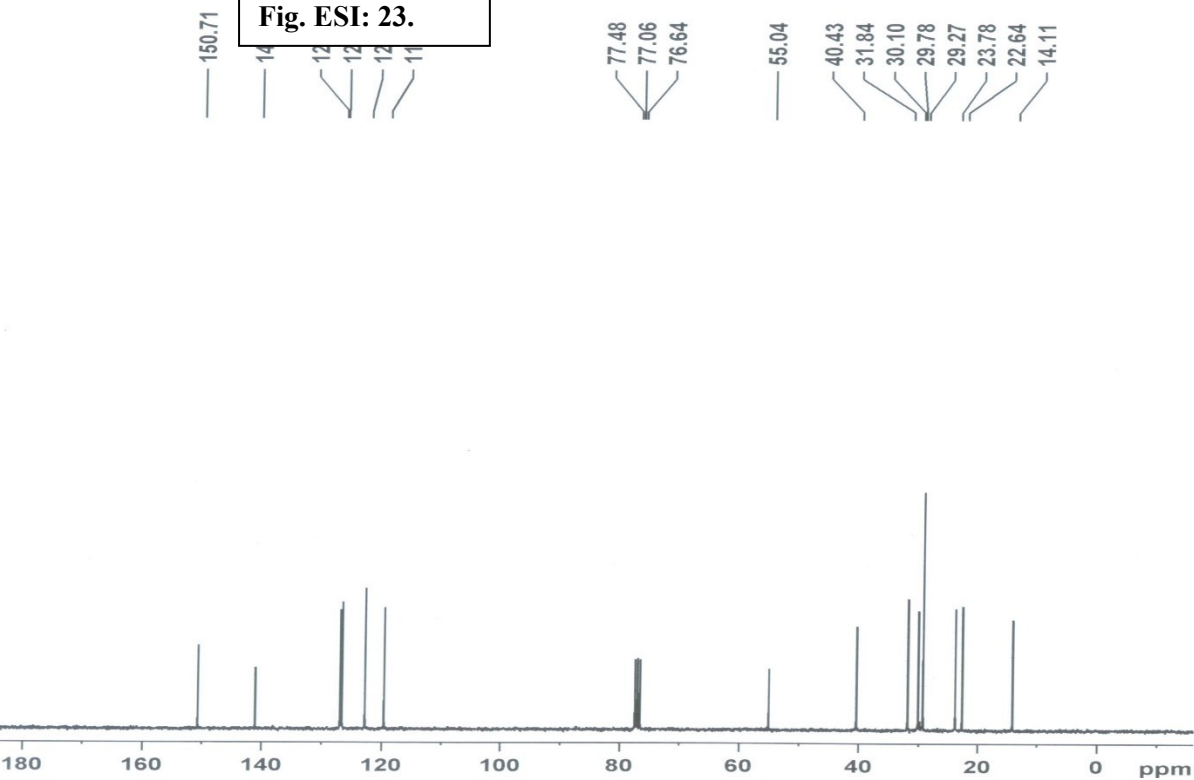


Fig. ESI: 23.



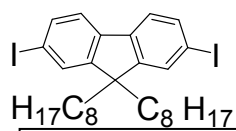
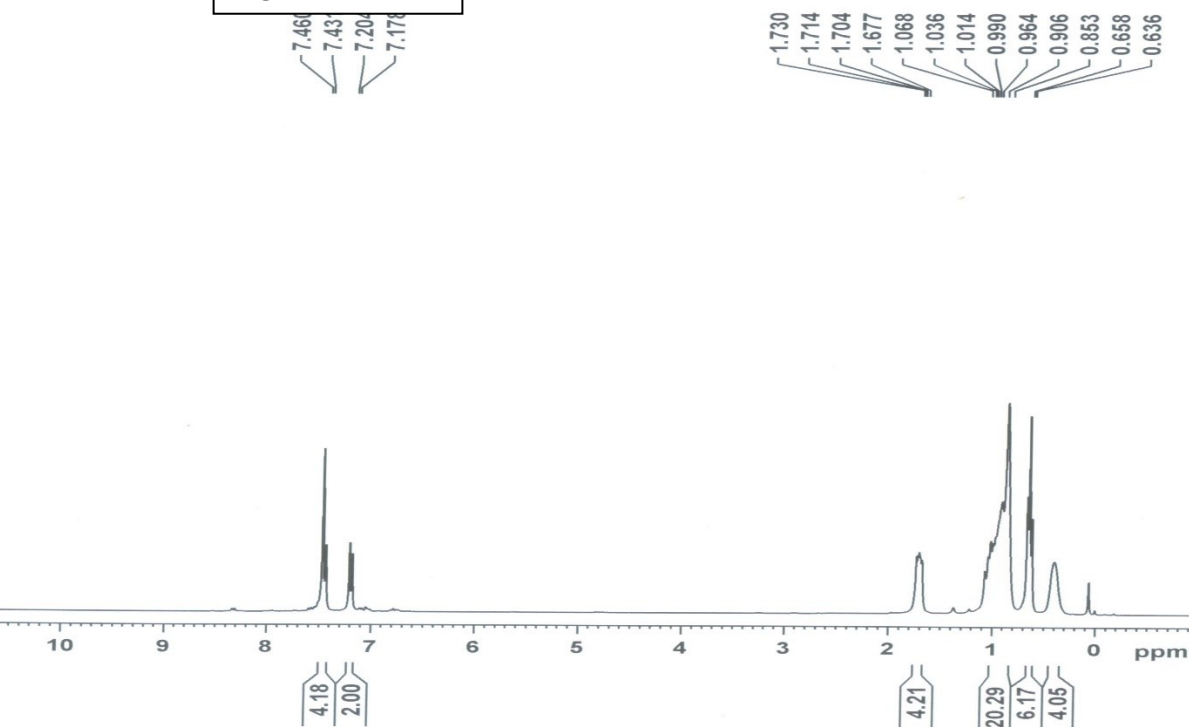


Fig. ESI: 24.



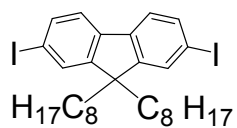
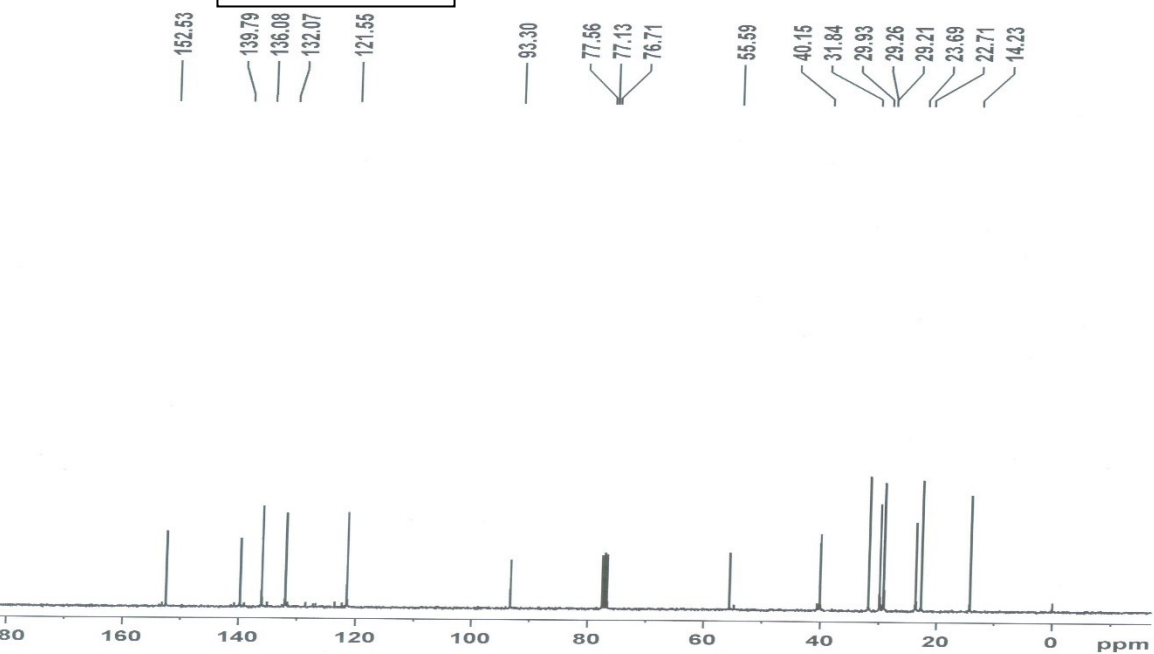
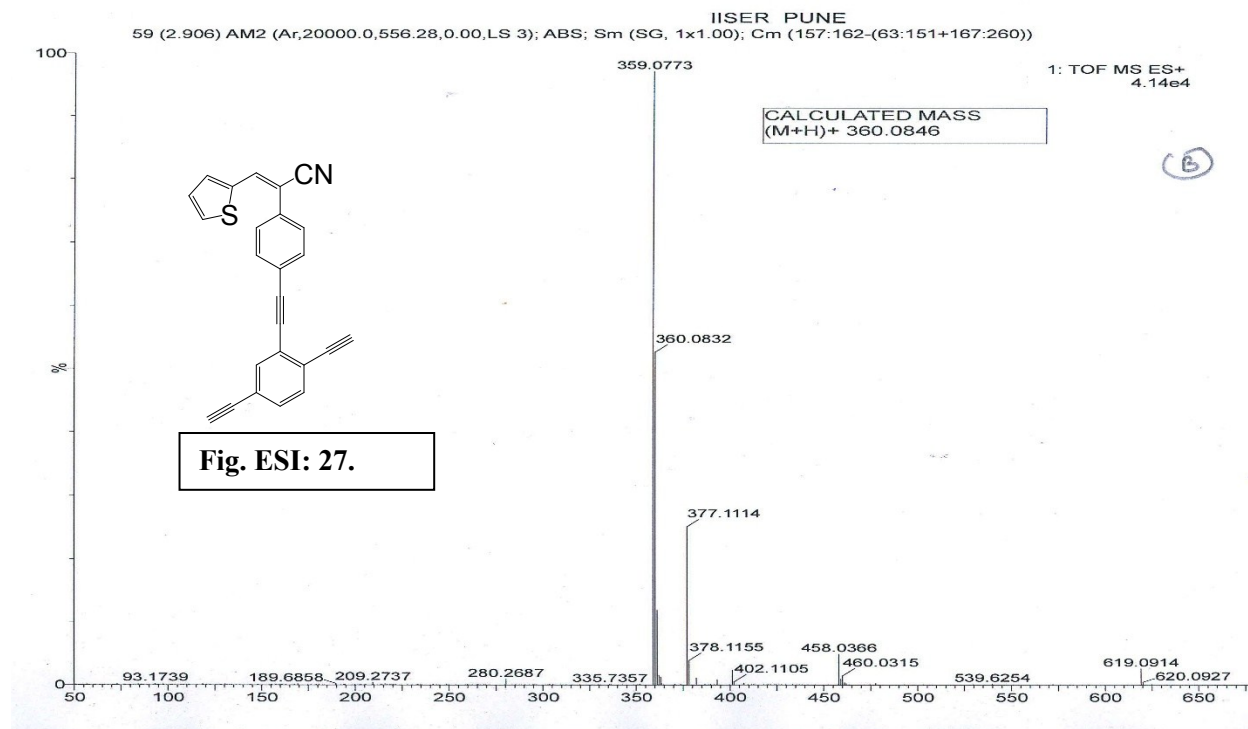
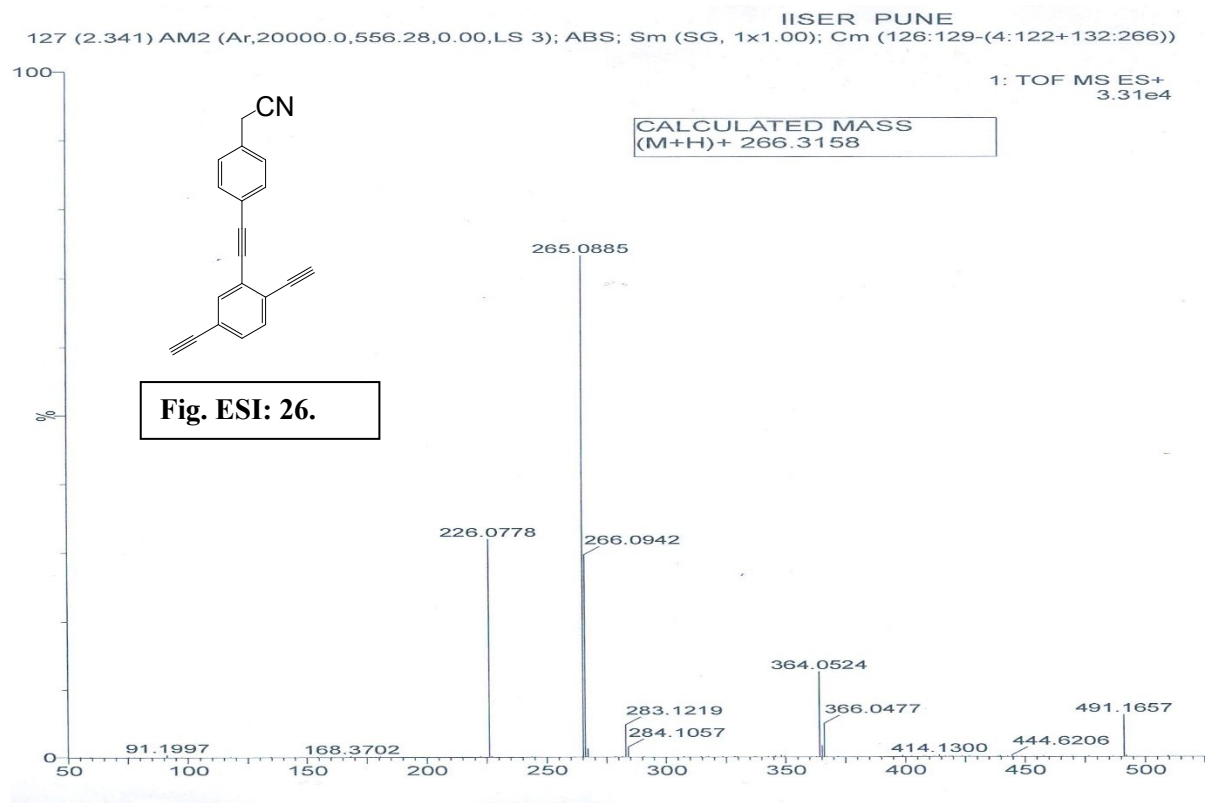


Fig. ESI: 25.



5) HRMS analysis.



6) Thin film UV-visible spectra.

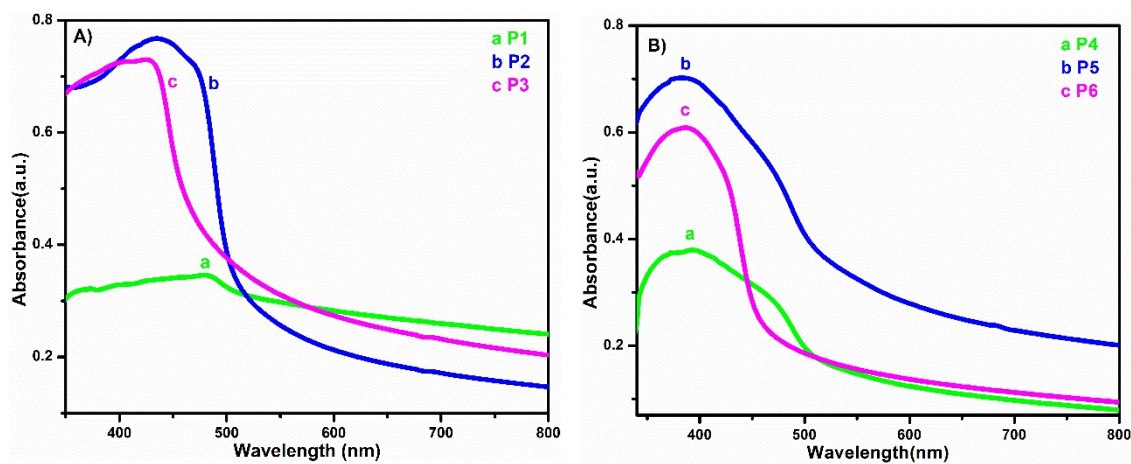


Fig. ESI: 28. Solid state (thin film) absorption spectra of CPs: A) P₁, P₂ and P₃. B) P₄, P₅ and P₆.

7) Low angle X-ray diffraction pattern

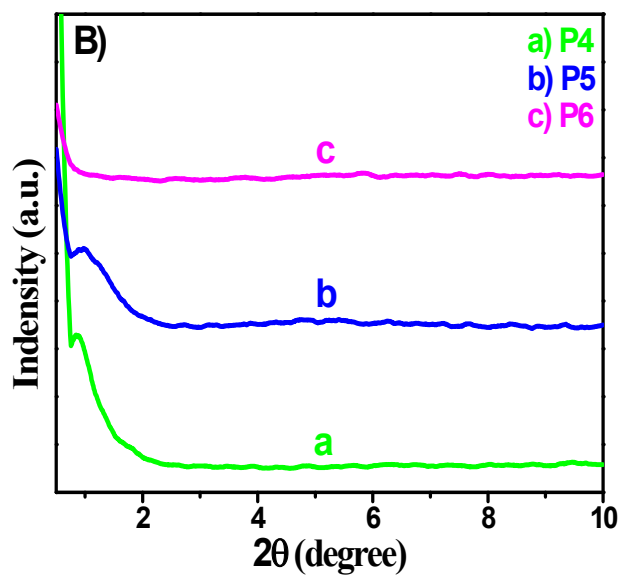
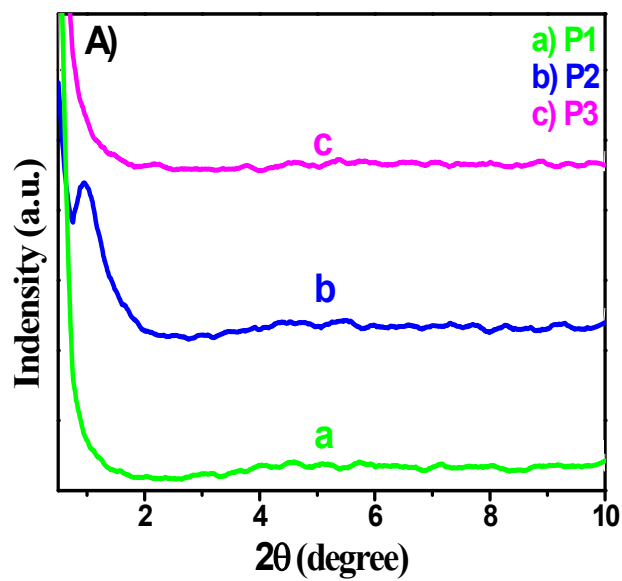


Fig. ESI: 29. Low angle X-ray diffraction pattern of synthesis PAE CPs: A) P₁, P₂ and P₃. B) P₄, P₅ and P₆.

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