

## Extended isoindigos as building blocks for developing D-A-type conjugated polymers

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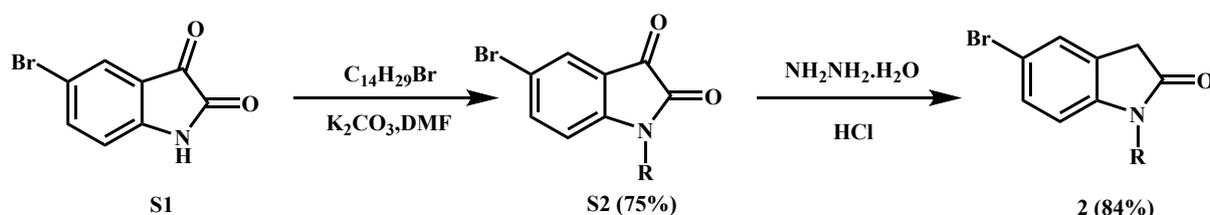
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### Materials and instrumentation

All the chemicals are reagent grade and are used as purchased. Moisture-sensitive reactions are performed under an inert atmosphere of dry nitrogen with dried solvents. Reactions are monitored by thin-layer chromatography (TLC) using Merck 60 F254 aluminium-coated plates and the spots are visualized under ultraviolet (UV) light. Column chromatography is carried out on silica gel (60–120 mesh as well as 100–200 mesh). NMR spectra are recorded on a Bruker Avance-III 400 spectrometer in CDCl<sub>3</sub> and DMSO-D<sub>6</sub>. The high resolution mass spectra are recorded on Xevo G2-XS QTOF Mass Spectrometer. Molecular weights of the

polymer samples are measured with Agilent 1260 Infinity GPC instrument, equipped with RI detector. Polystyrene is used as a calibration standard. Polymer samples (~5 mg) are dissolved in THF (~5 mL) and are filtered through a 0.2  $\mu$  filter. The analysis is done using THF as an eluent at a flow rate of 1-2 mL/min.

## Experimental procedure of intermediate compounds



### Scheme S1 Synthesis of 5-bromo-1-tetradecylindolin-2-one

Compound **S1** was synthesized according to the modified literature procedure reported by Li et al<sup>1,2</sup> while compound **2** was synthesized according to the modified literature procedure reported by Bura et al<sup>3</sup>.

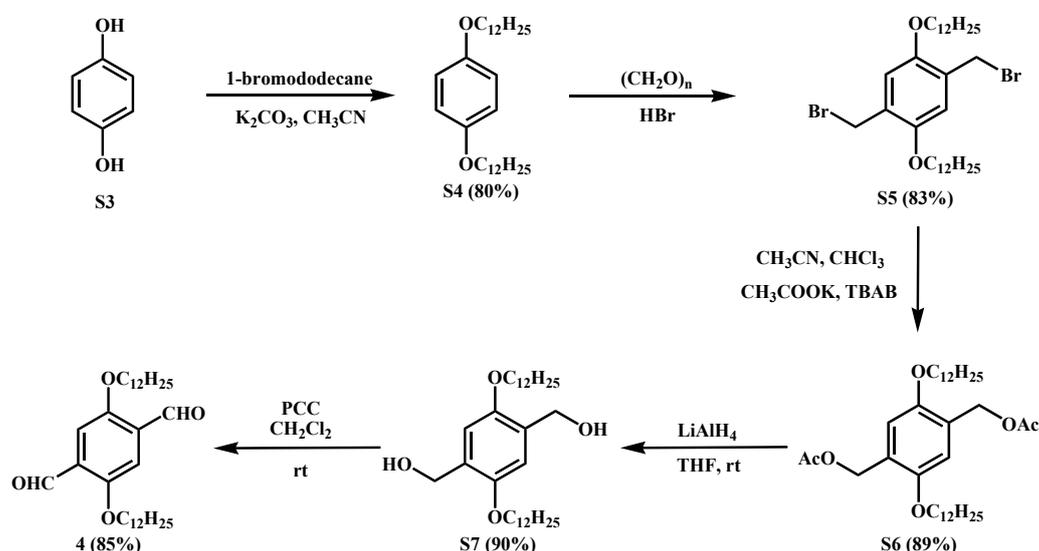
**Synthesis of compound S2:** 5-Bromoisatin (2g, 8.84 mmol) and potassium carbonate ( $\text{K}_2\text{CO}_3$ ) (5.48g, 39.7 mmol) was added to 20 mL anhydrous DMF under nitrogen atmosphere and reaction mixture was stirred at 60 °C for 10-15 min. To this stirred solution tetradecyl bromide (4.2 g, 15.47 mmol) was added in a dropwise manner. After that reaction mixture was allowed to stir at 80 °C for 3h, after cooling to room temperature reaction mixture was poured into water and extracted with ethyl acetate. The combined organic layer was washed with water and dried over  $\text{Na}_2\text{SO}_4$  and solvent was evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel and pure product was eluted using 10% ethyl acetate-petroleum ether mobile phase.

**Compound S2:** Dark orange solid. (1.83g, 49%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.67 (d,  $J_3 = 1.2$  Hz, 1H), 6.79 (d,  $J_2 = 7.6$  Hz, 1H), 6.82 (dd,  $J_2 = 7.6$  Hz,  $J_3 = 1.2$  Hz, 1H), 3.70–3.74 (t,  $J_2 = 7.2$  Hz, 2H), 1.65–1.73 (m, 2H), 1.29–1.34 (m, 18H), 0.85–0.89 (t,  $J_2 = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.57, 157.49, 149.88, 140.60, 128.30, 118.87, 116.51, 111.98, 40.56, 29.77, 29.58, 29.32, 26.99, 22.82, 14.26.

**Synthesis of compound 2:** Compound **S2** (1.5g, 3.55mmol) and hydrazine hydrate 99% (8.88g, 177.5mmol) was taken in a two necked round bottom flask and refluxed at 140 °C for 1 h. After cooling to room temperature the reaction mixture was poured into water and extracted with ethyl acetate, washed with water and dried over anhydrous sodium sulphate the

solvent was evaporated under reduced pressure. To the resulting crude, 20mL of 6N aqueous hydrochloric acid is added and resulting mixture was heated at 60 °C for 3h. The reaction mixture was poured in to 200 mL of water and extracted with ethyl acetate. Combined organic layer was washed with water, brine dried over anhydrous sodium sulphate and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel and pure product was eluted using 40% ethyl acetate-petroleum ether as mobile phase.

**Compound 2:** Pale yellow solid. (1.24g, 84%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.39 (d, J<sub>2</sub> = 8.0 Hz, 1H), 7.26 (s, 1H), 6.768 (d, J<sub>2</sub> = 8.0 Hz, 1H), 3.65–3.68 (t, J<sub>2</sub> = 7.6 Hz, 2H), 3.51 (s, 2H), 1.62–1.66 (m, 2H), 1.25–1.32 (m, 18H), 0.86–0.90 (t, J<sub>2</sub> = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 174.31, 143.86, 130.74, 127.74, 127.79, 122.21, 114.78, 109.77, 40.32, 29.80, 20.51, 27.09, 22.85, 14.28.



**Scheme S2** Synthesis of 2,5-bis(hydroxymethyl)benzene-1,4-dialdehyde

Compound **4** was synthesised according to the modified literature procedure reported by Doddi *et al*<sup>4</sup>.

**Synthesis of compound S4:** 1,4-hydroxybenzene (5g ,45mmol) and potassium hydroxide (KOH) (7.63g ,136mmol) was added to 50 mL acetonitrile under nitrogen atmosphere and the reaction mixture was stirred at room temperature for 10 min. To this stirred solution dodecyl bromide (32.4g, 135mmol) was added and the reaction mixture was allowed to refluxed for 12h. After completion of reaction the reaction mixture was poured in to 200 mL of water and extracted with ethyl acetate. The combined organic phase was washed with water dried over

anhydrous sodium sulphate and solvent was evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel and the pure product was eluted using 10% ethyl acetate-petroleum ether as mobile phase.

**Compound S4:** White solid. (16g, 84%)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.84(s, 4H), 3.91(t,  $J_3=8\text{Hz}$ , 2H) 1.28-1.80(m, 41H), 0.88-0.91(m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.29, 115.48, 68.75, 32.01, 29.75, 29.73, 29.69, 29.68, 29.53, 29.51, 29.49, 29.44, 26.15, 22.78, 14.21.

**Synthesis of compound S5:** In a two necked round bottom flask compound **S4** (1.45g, 3.30mmol) paraformaldehyde (0.21g, 7mmol) in acetic acid (20 mL) and HBr (1.40 mL) was added in one portion. The reaction mixture was heated at 80 °C for 12h. After the completion of reaction, the reaction mixture was poured in to water and extracted with chloroform. combined organic phase was washed with water dried over anhydrous sodium sulphate and Solvent was removed under reduced pressure and crude was purified by column chromatography over silica gel and pure product was eluted using 10% ethyl acetate- petroleum ether as mobile phase.

**Compound S5:** White solid. (1.33g, 83%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.85(s, 2H), 4.52(s, 4H), 3.98(t,  $J_3=8\text{ Hz}$ , 4H), 1.86-1.28(m, 40H) 0.88-0.91(m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.70, 127.56, 115.42, 114.70, 69.06, 31.93, 29.68, 29.65, 29.61, 29.38, 28.74, 26.09, 22.70, 14.13.

**Synthesis of compound S6:** In a two necked round bottom flask compound **S5** (2.2g, 3.4mmol), potassium acetate (1.03g, 10.4mmol) and tetra n-butyl ammonium bromide (0.17g, 0.26mmol) in chloroform (25 mL) and acetonitrile (50ml) was added and the reaction mixture was allowed to refluxed for 12h. After cooling to room temperature the resulting mixture was poured in to 200 mL of water and extracted with chloroform. The combined Organic layer was washed with water and dried over anhydrous sodium sulphate. The pure product was obtained by removal of solvent under reduced pressure.

**Compound S6:** Colourless solid (1.95g, 100%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.88(s, 2H), 5.14(s, 4H), 3.94(t,  $J_2=12\text{Hz}$ , 4H), 1.21-2.01(m, 21H), 0.88-0.91(m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.9, 153.2, 151.0, 125.4, 115.4, 112.6, 68.95, 61.80, 31.92, 29.35, 26.07, 24.29, 22.69, 21.06, 19.81, 14.11.

**Synthesis of compound S7:** Compound S6 (1.95g, 5.62mmol) and lithium aluminium hydride (LiAlH<sub>4</sub>) (0.85g, 22.4mmol) was added in dry THF under nitrogen atmosphere and the reaction mixture was stirred at room temperature for 2h. After completion of the reaction excess of LiAlH<sub>4</sub> was quenched by ethyl acetate at 0 °C and the resulting mixture was poured in to water and extracted with chloroform. The combined organic layer was washed with water and dried over anhydrous sodium sulphate. The pure product was obtained by removal of solvent under reduced pressure.

**Compound S7:** Colourless solid. (1.52g, 98%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.88(s, 2H), 5.14(s, 4H), 3.94(t, J<sub>2</sub>=12Hz, 4H), 1.21-2.10(m, 20H), 0.88-0.91(m, 4H).

**Synthesis of compound 4:** Compound S7 (1.52g, 3.04mmol) and pyridinium chlorochromate (PCC) (2.49g, 11.5mmol) was added in 20 mL dichloromethane (DCM) and the reaction mixture was stirred for 2h at room temperature. After completion of reaction, the reaction mixture was directly added on the silica gel column and the product was obtained with high fluorescence.

**Compound 4:** (1.27g, 90%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.53(s, 2H), 7.43(s, 2H), 4.07(t, J<sub>3</sub>=12Hz, 4H), 1.27-1.87(m, 21H), 0.87-0.90(m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 189.56, 155.21, 129.18, 111.52, 31.29, 29.68, 29.66, 29.61, 29.58, 29.39, 29.34, 29.05, 26.03, 22.73, 24.18.

## NMR spectra

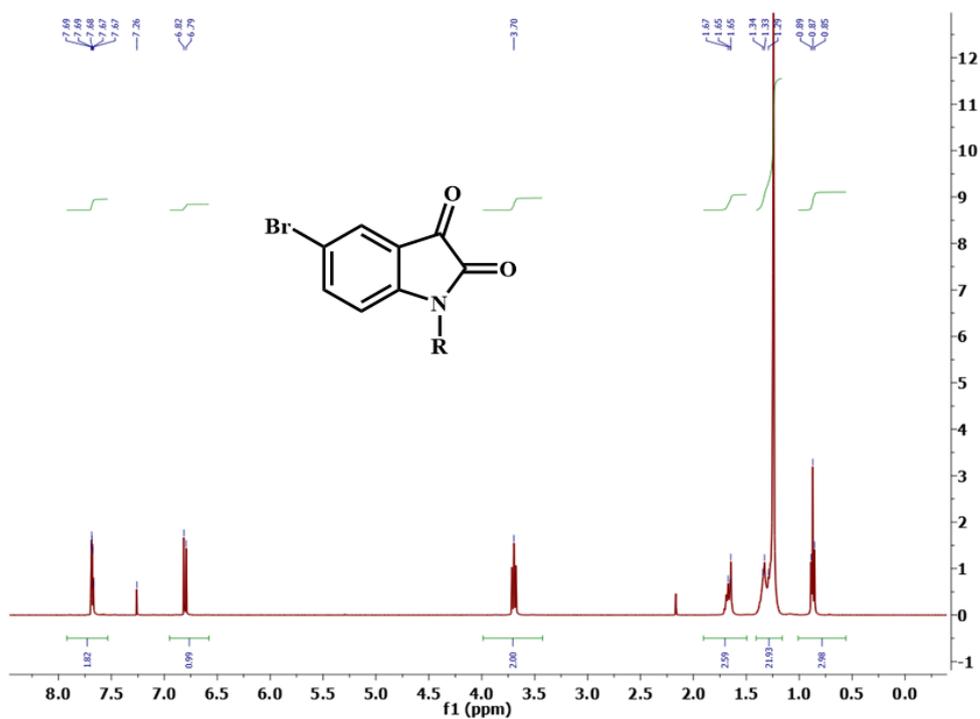


Figure S1: <sup>1</sup>H NMR spectra of compound S2

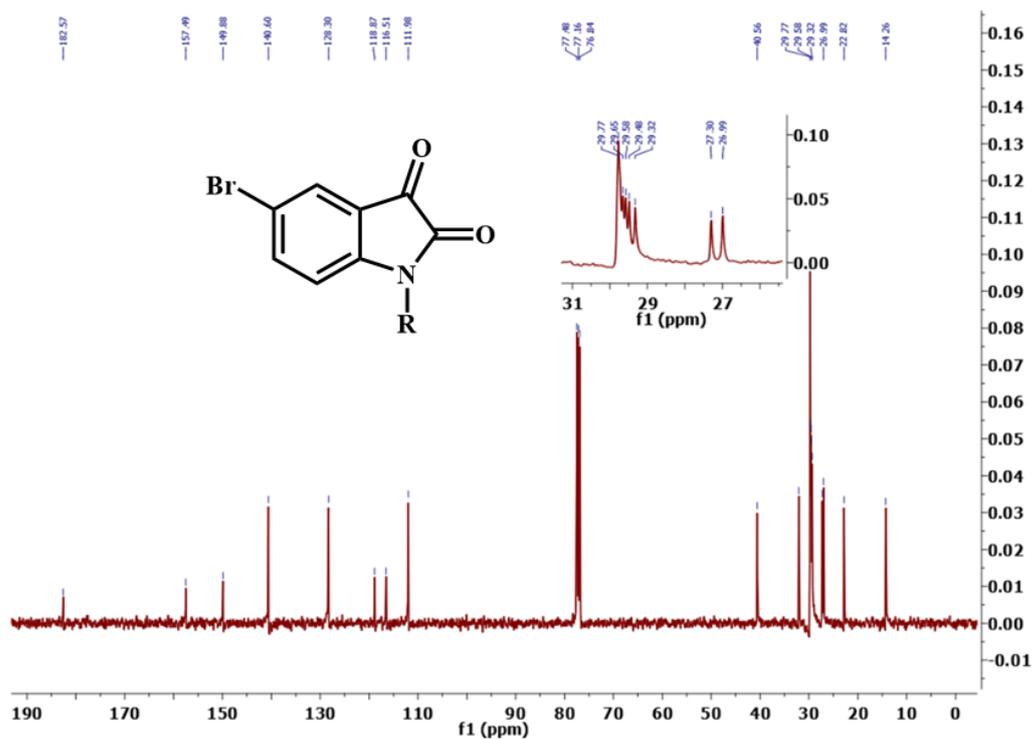


Figure S2: <sup>13</sup>C NMR spectra of compound S2

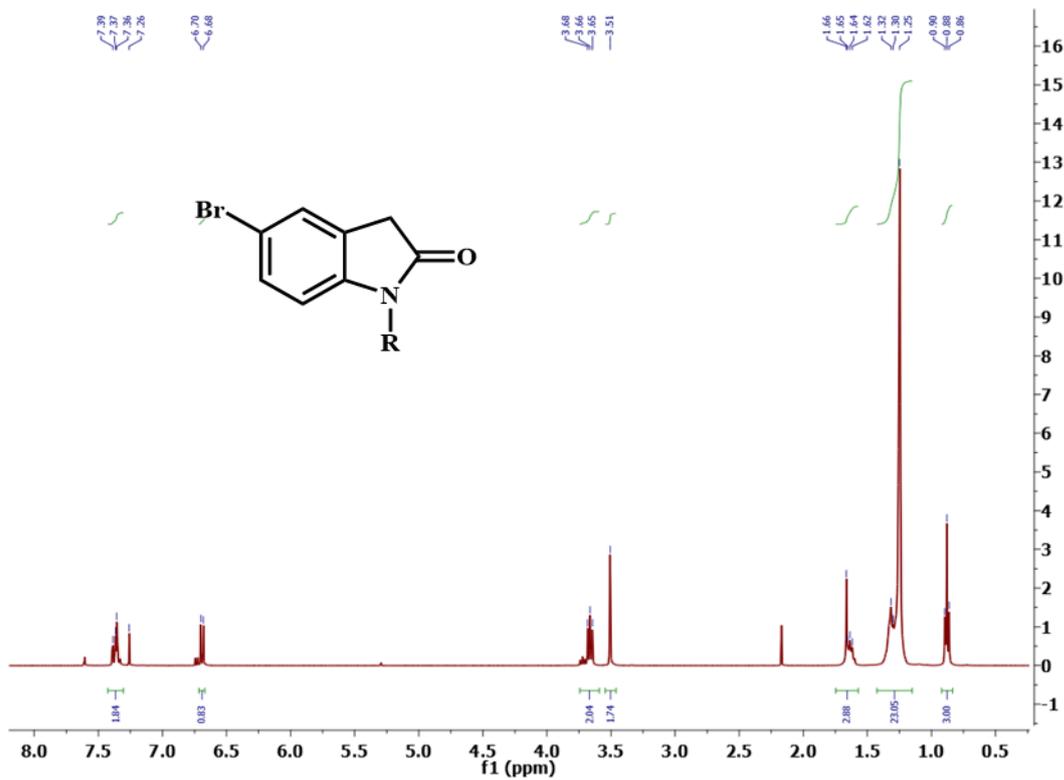


Figure S3:  $^1\text{H}$  NMR spectra of compound 2

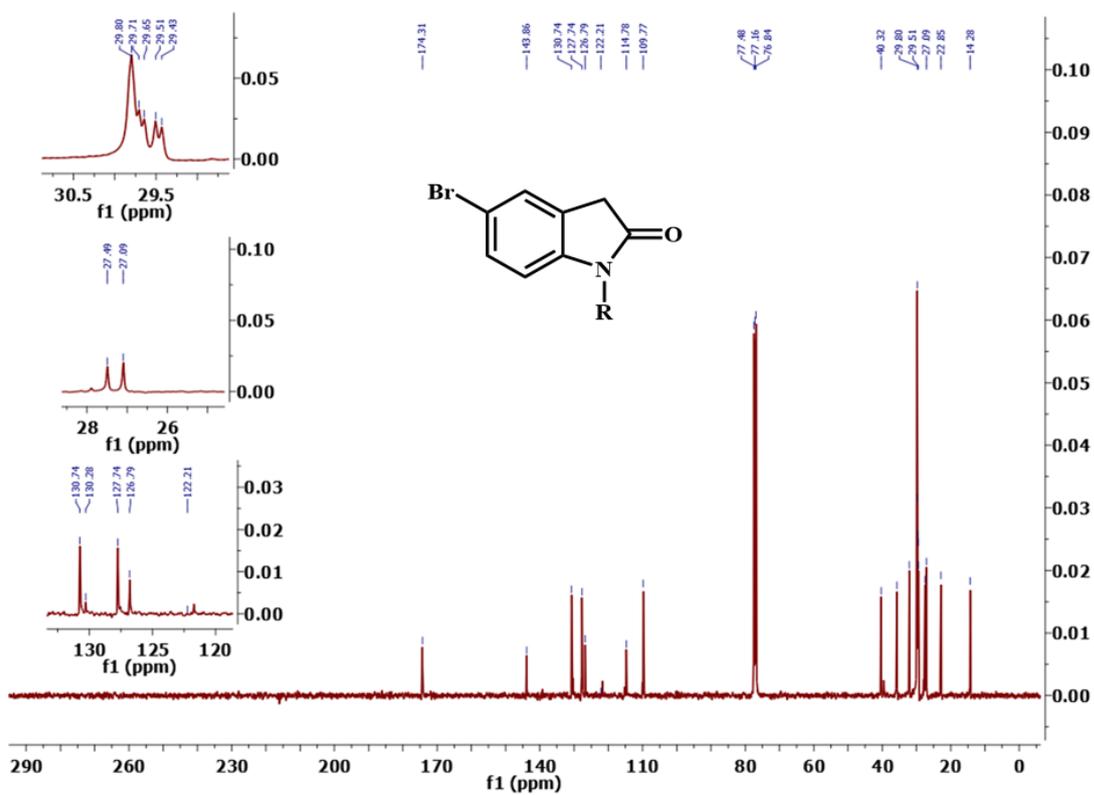


Figure S4:  $^{13}\text{C}$  NMR spectra of compound 2

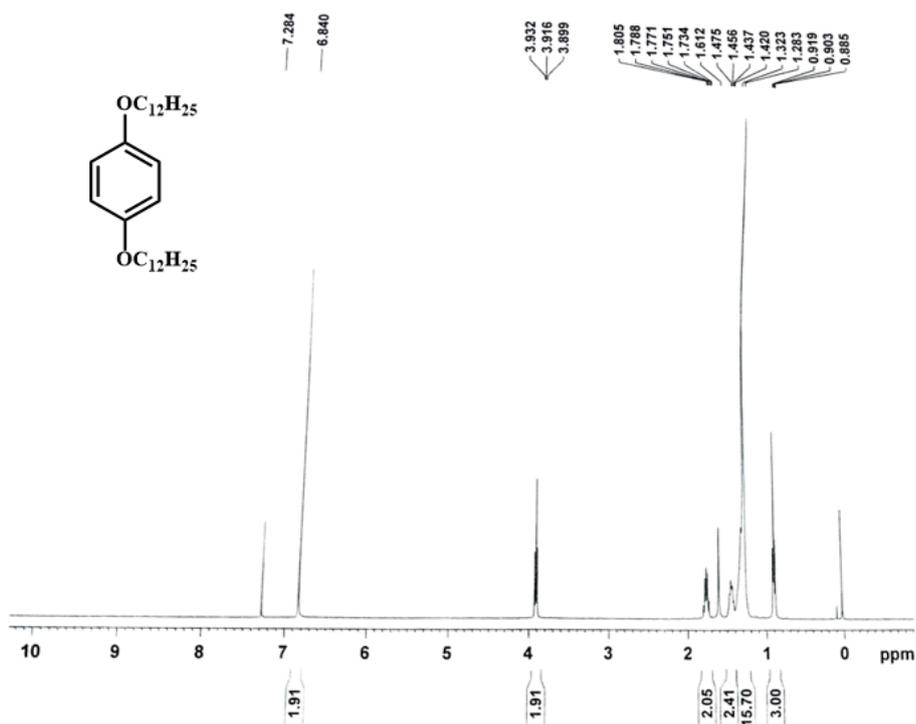


Figure S5: <sup>1</sup>H NMR spectra of compound S4

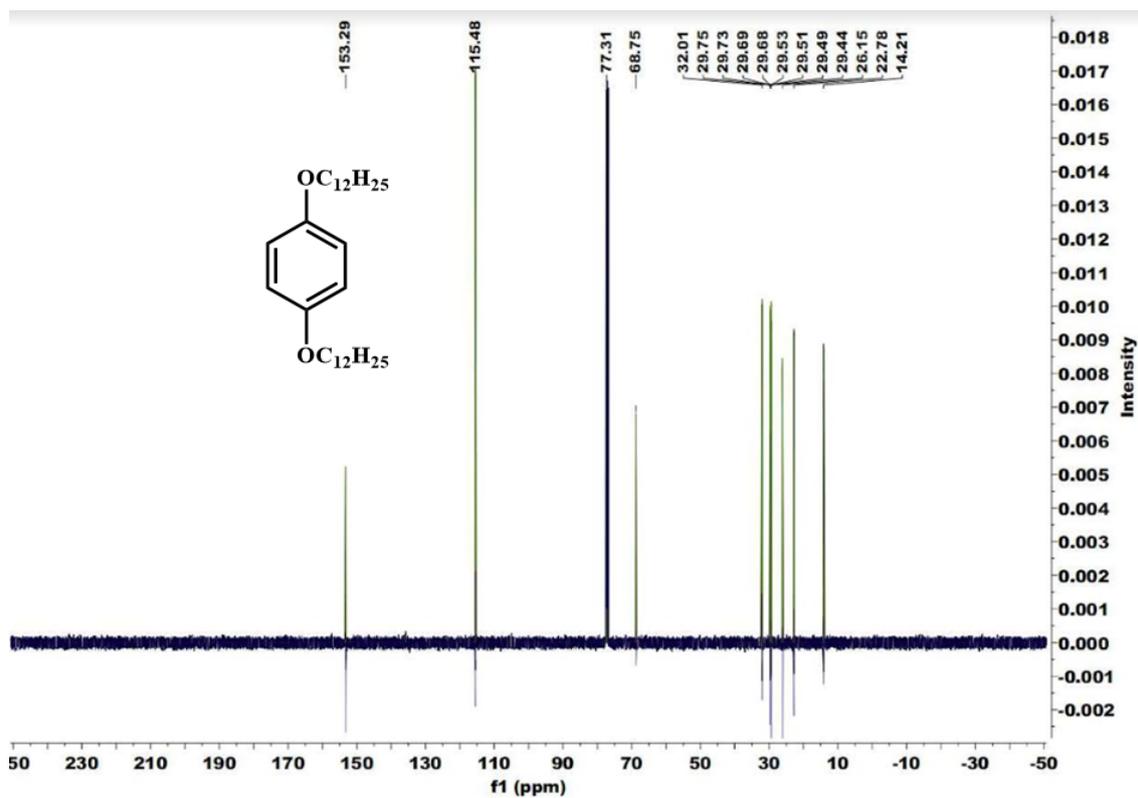


Figure S6: <sup>13</sup>C NMR spectra of compound S4

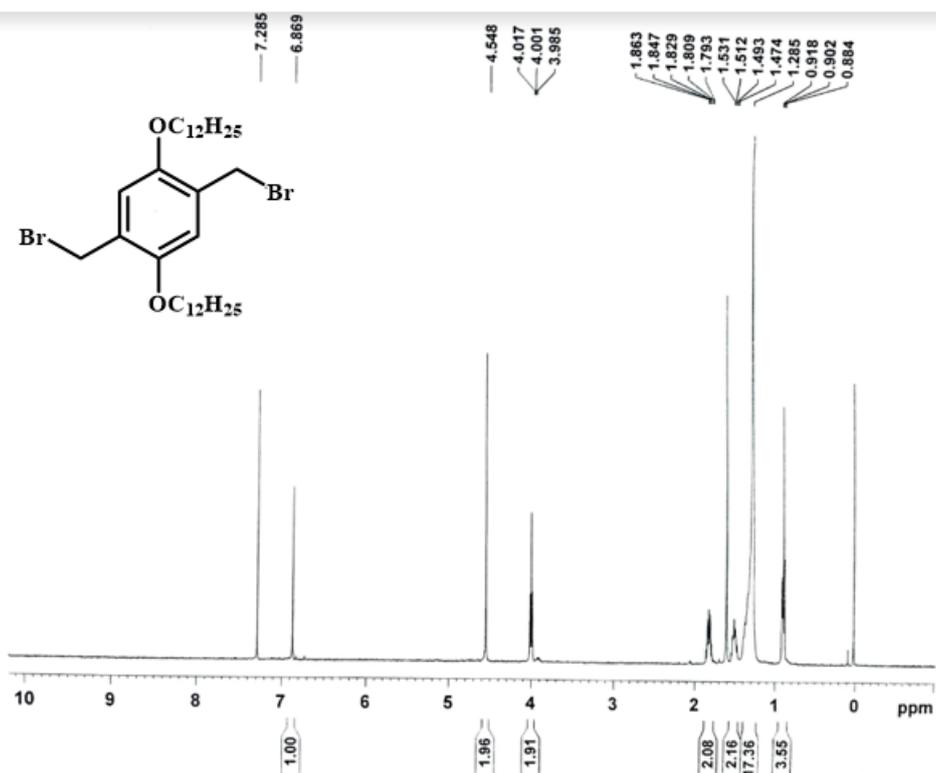


Figure S7: <sup>1</sup>H NMR spectra of compound S5

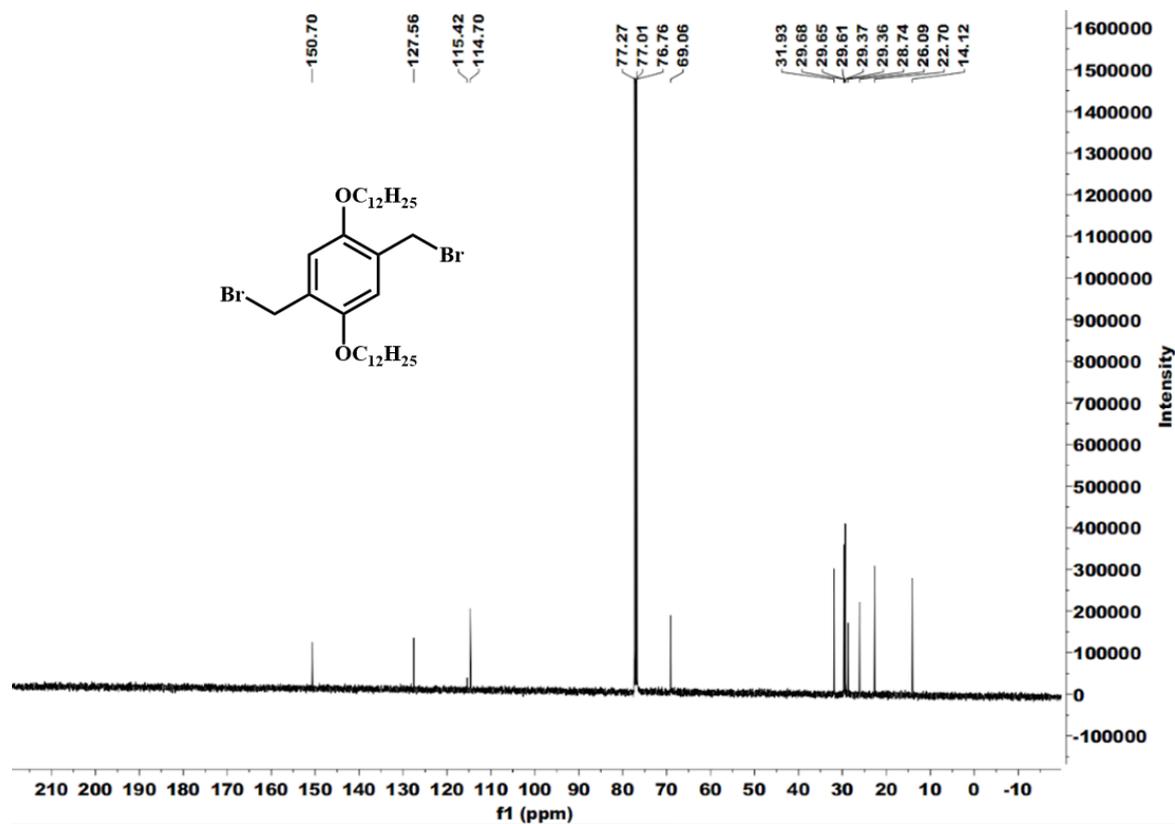


Figure S8: <sup>13</sup>C NMR spectra of compound S5

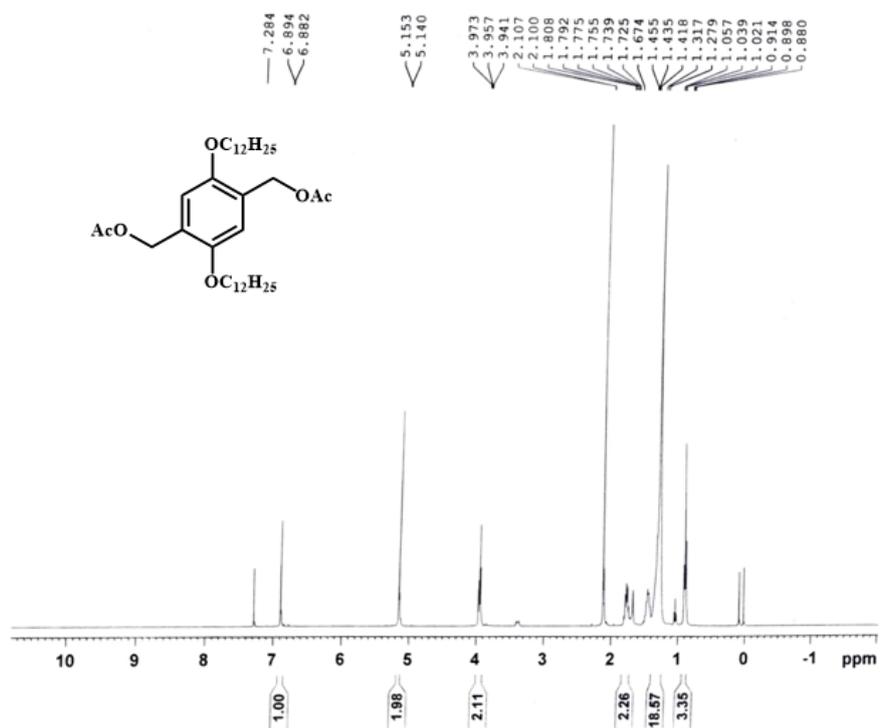


Figure S9:  $^1\text{H}$  NMR spectra of compound S6

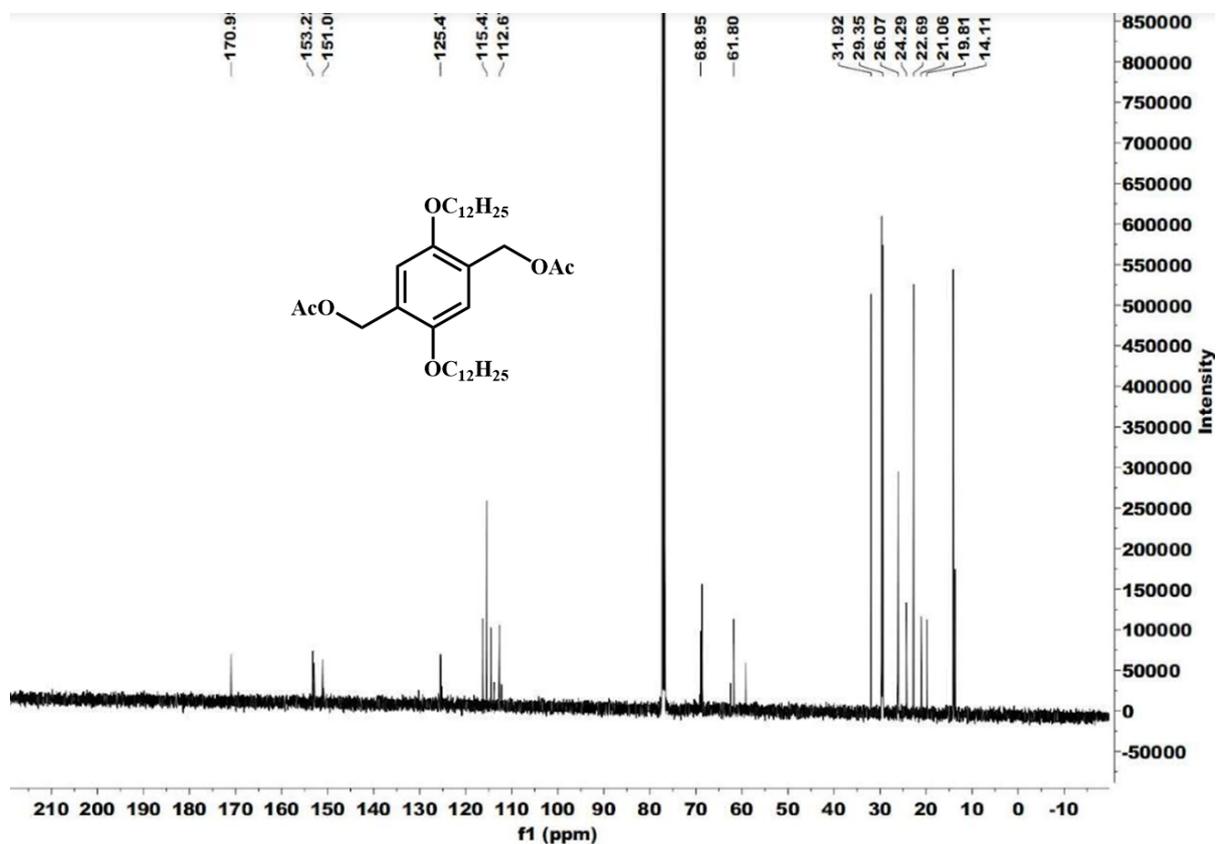


Figure S10:  $^{13}\text{C}$  NMR spectra of compound S6

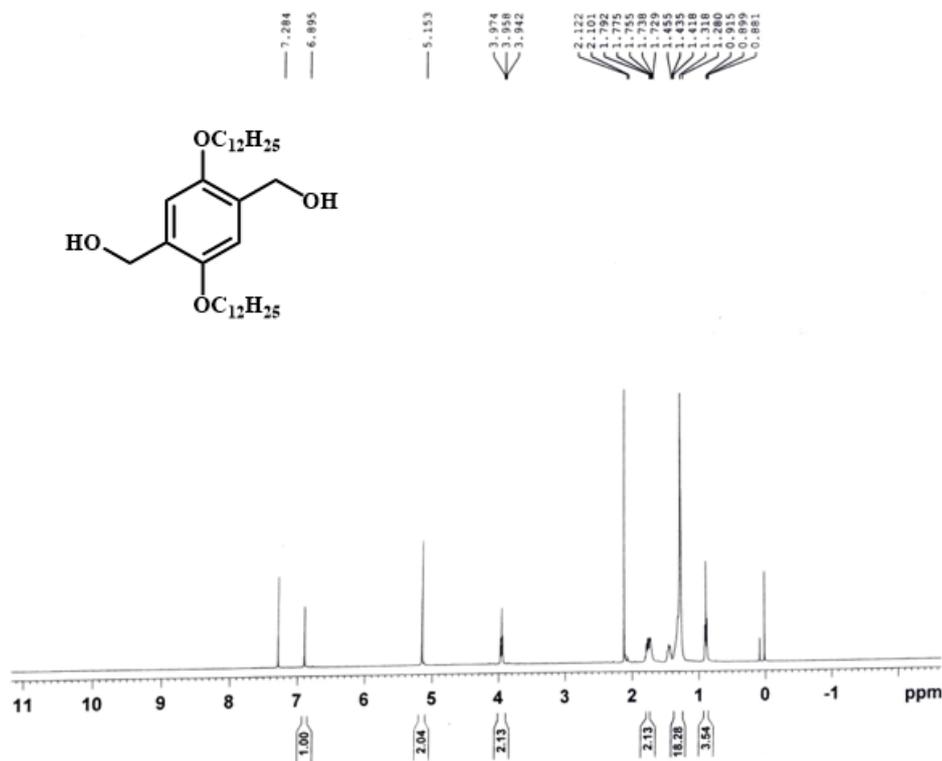


Figure S11: <sup>1</sup>H NMR spectra of compound S7

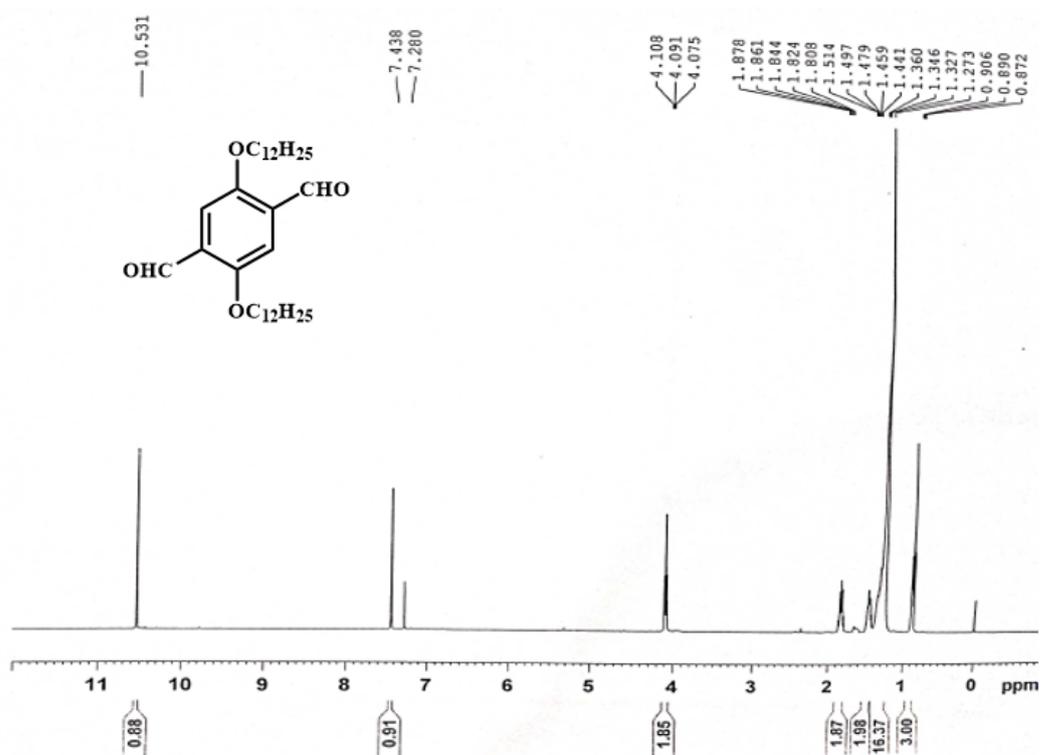


Figure S12: <sup>1</sup>H NMR spectra of compound 4

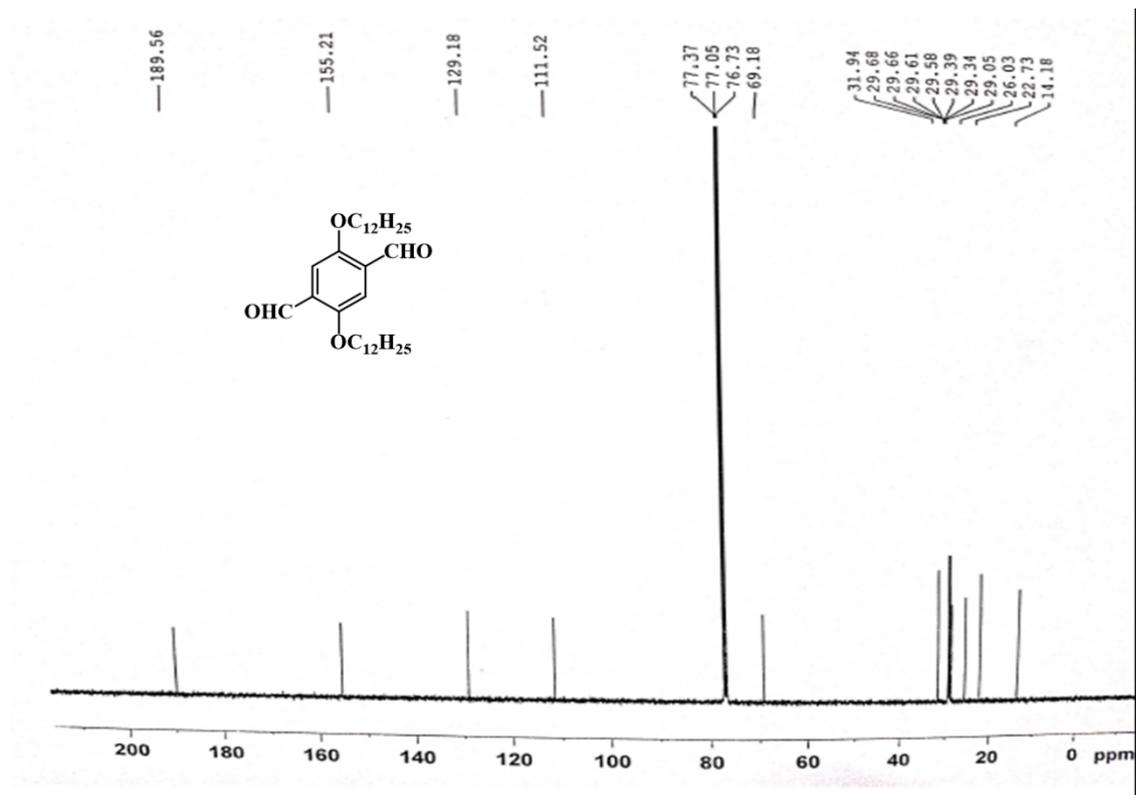


Figure S13:  $^{13}\text{C}$  NMR spectra of compound 4

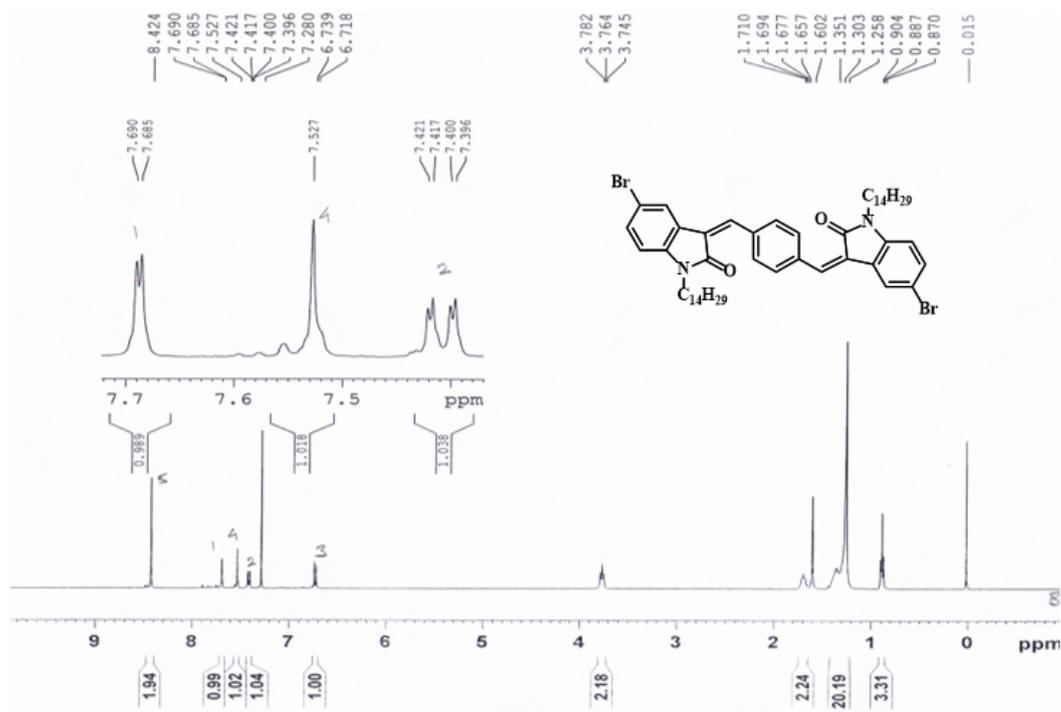


Figure S14:  $^1\text{H}$  NMR spectra of compound 3

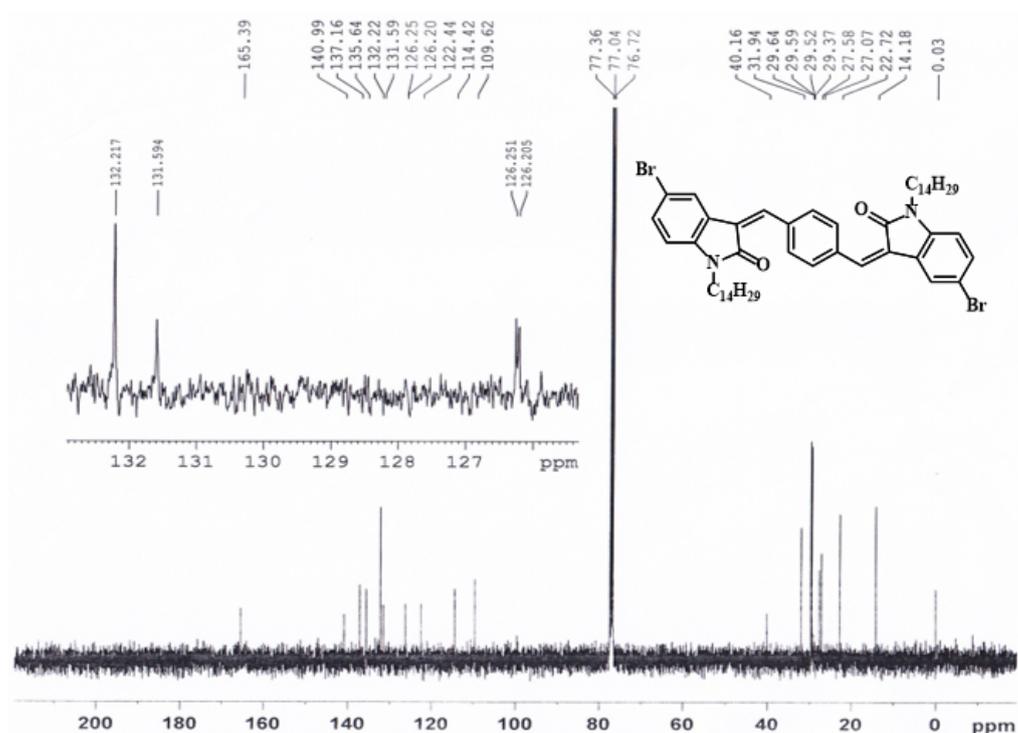


Figure S15:  $^{13}\text{C}$  NMR spectra of compound 3

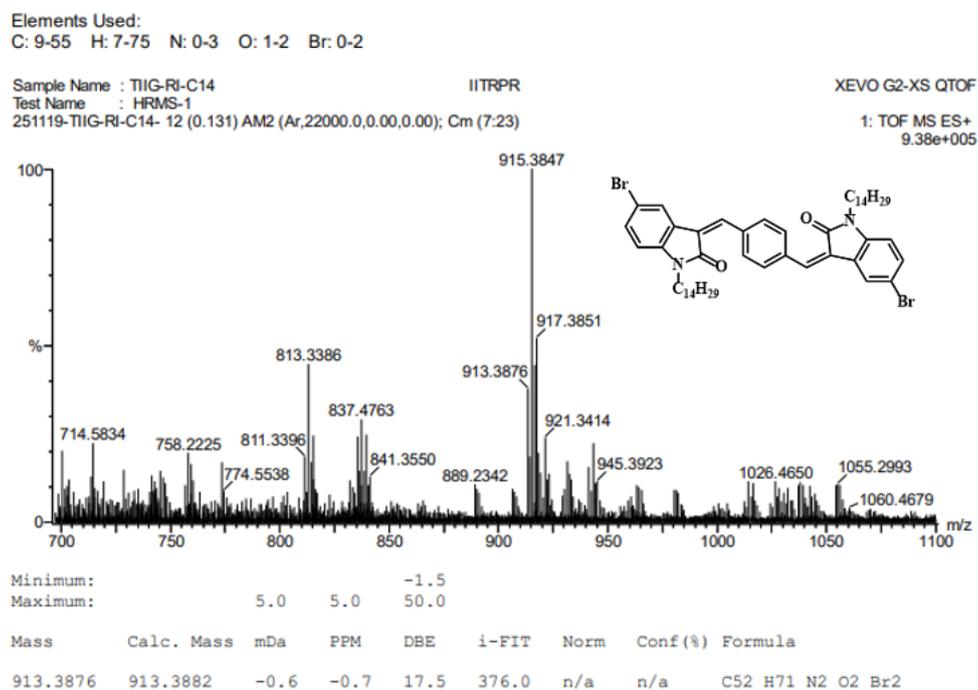


Figure S16: HR-MS spectra of compound 3

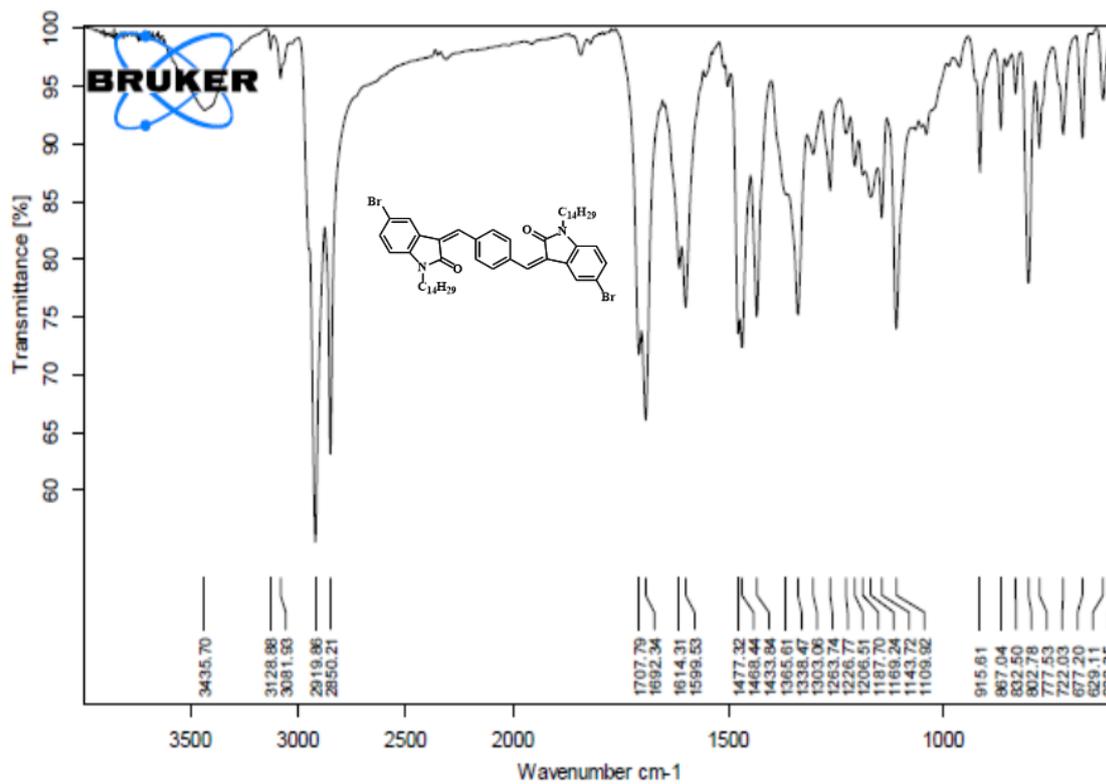


Figure S17: IR spectrum (KBr pellet) of compound 3

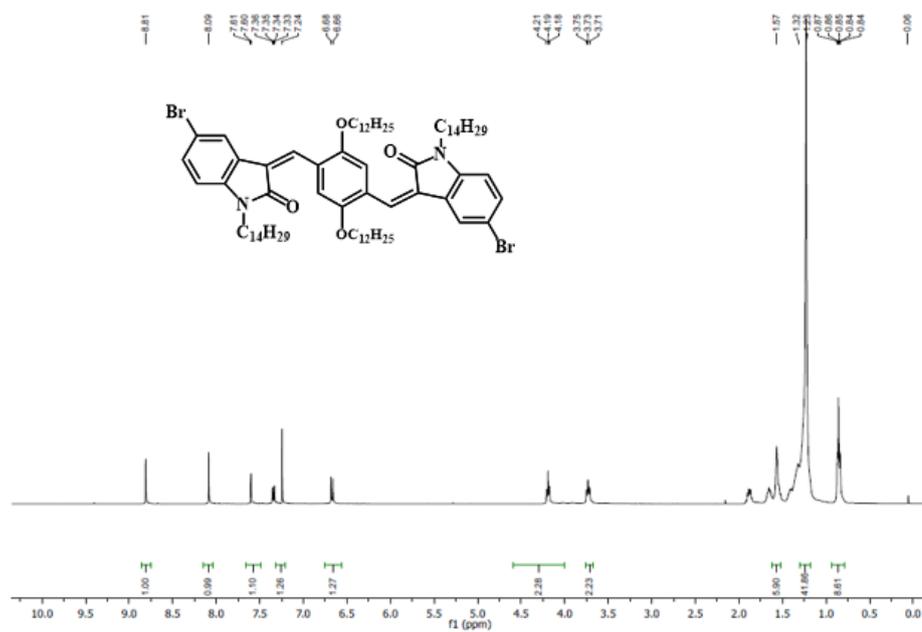


Figure S18:  $^1\text{H}$  NMR spectra of compound 5

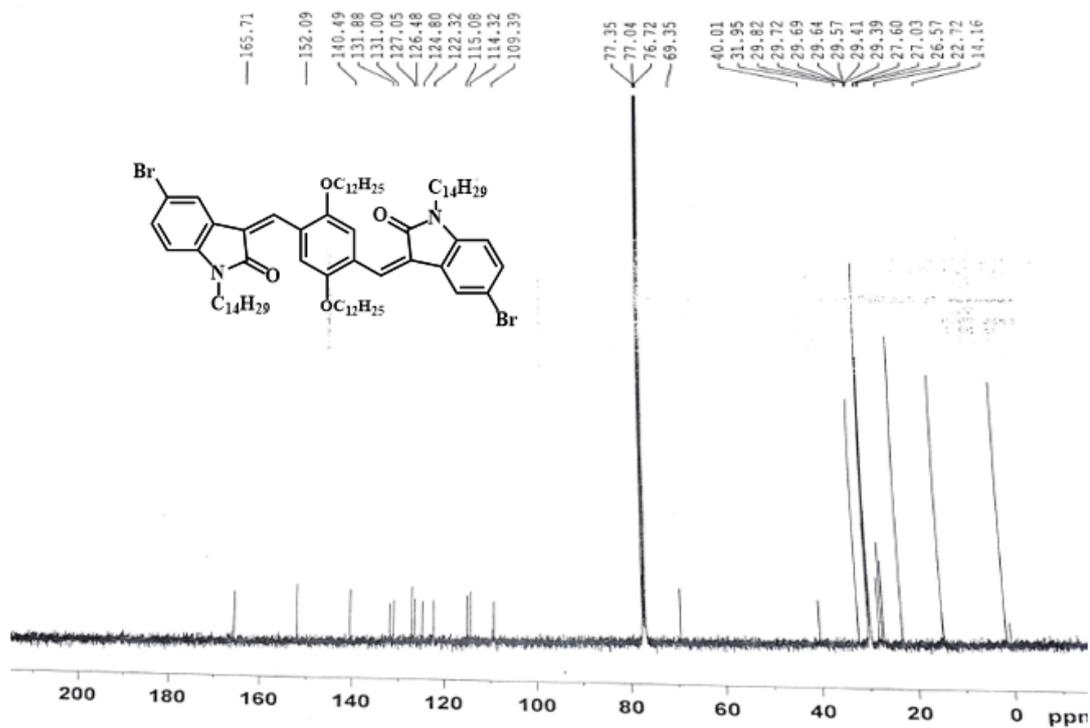


Figure S19: <sup>13</sup>C NMR spectra of compound 5

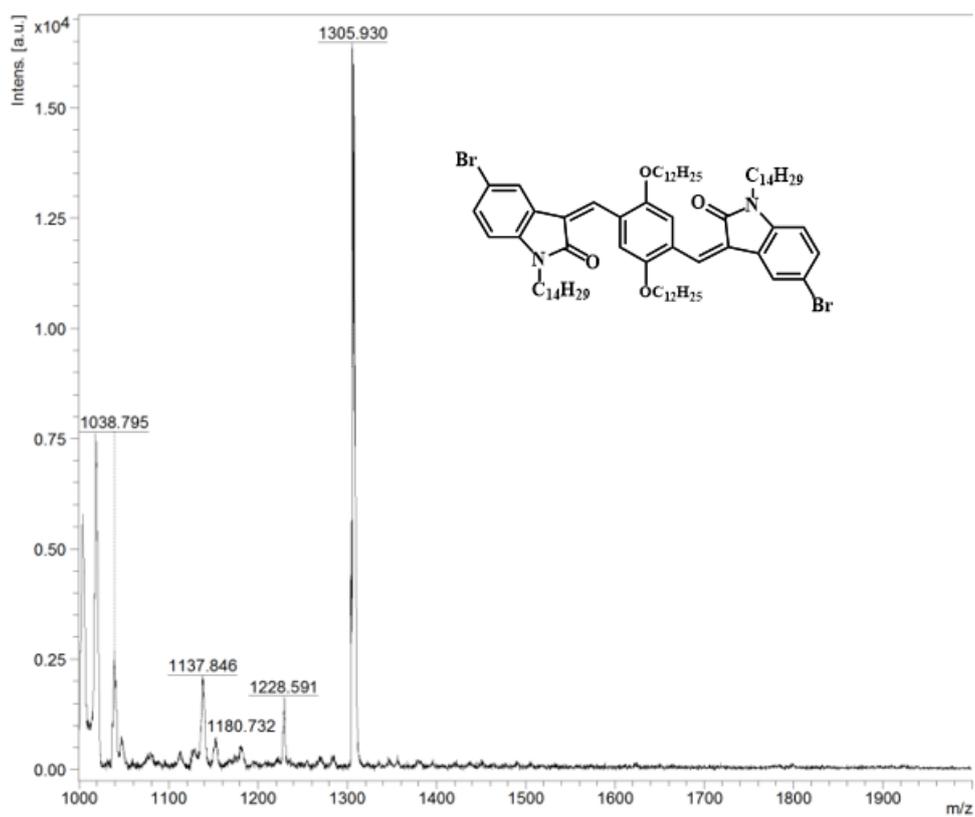


Figure S20: MALDI-TOF spectra of compound 5



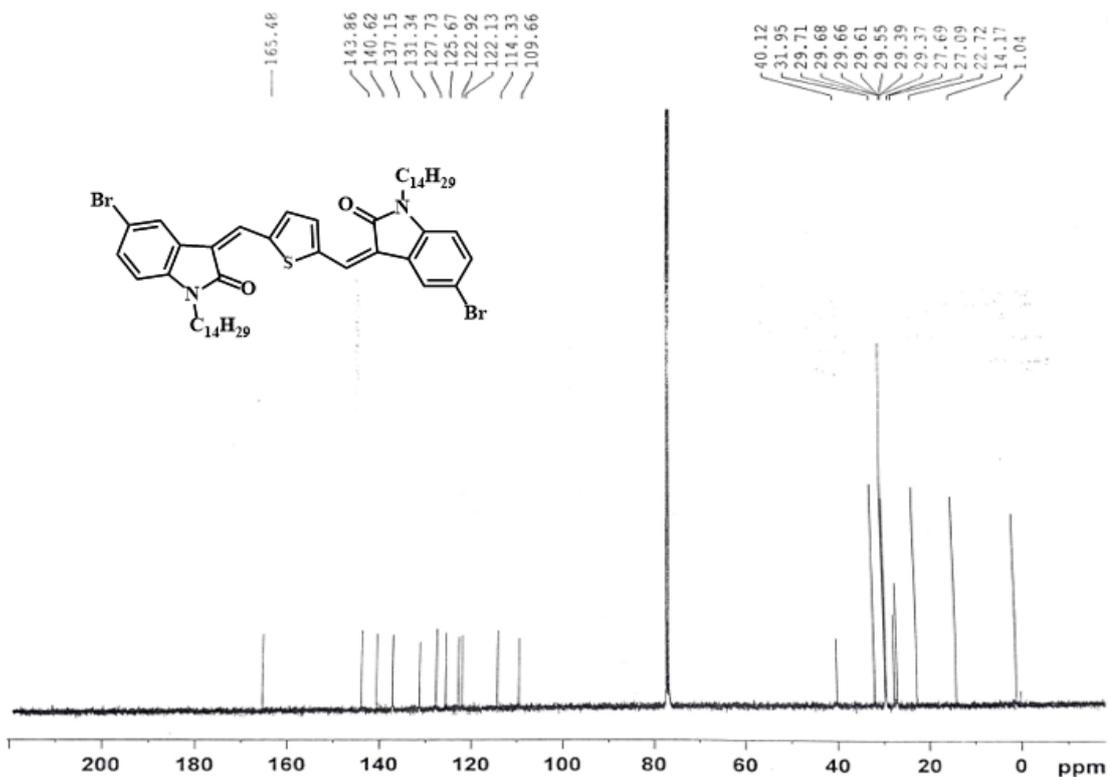


Figure S23: <sup>13</sup>C NMR spectra of compound 7

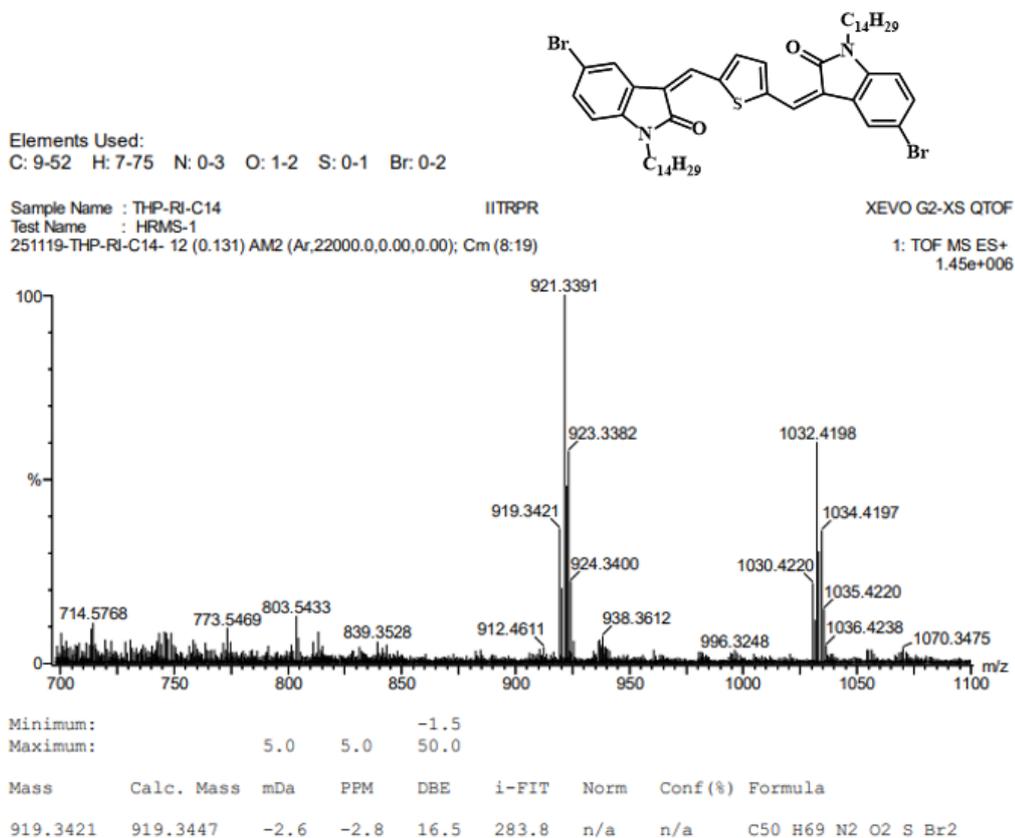


Figure S24: HR-MS spectra of compound 7

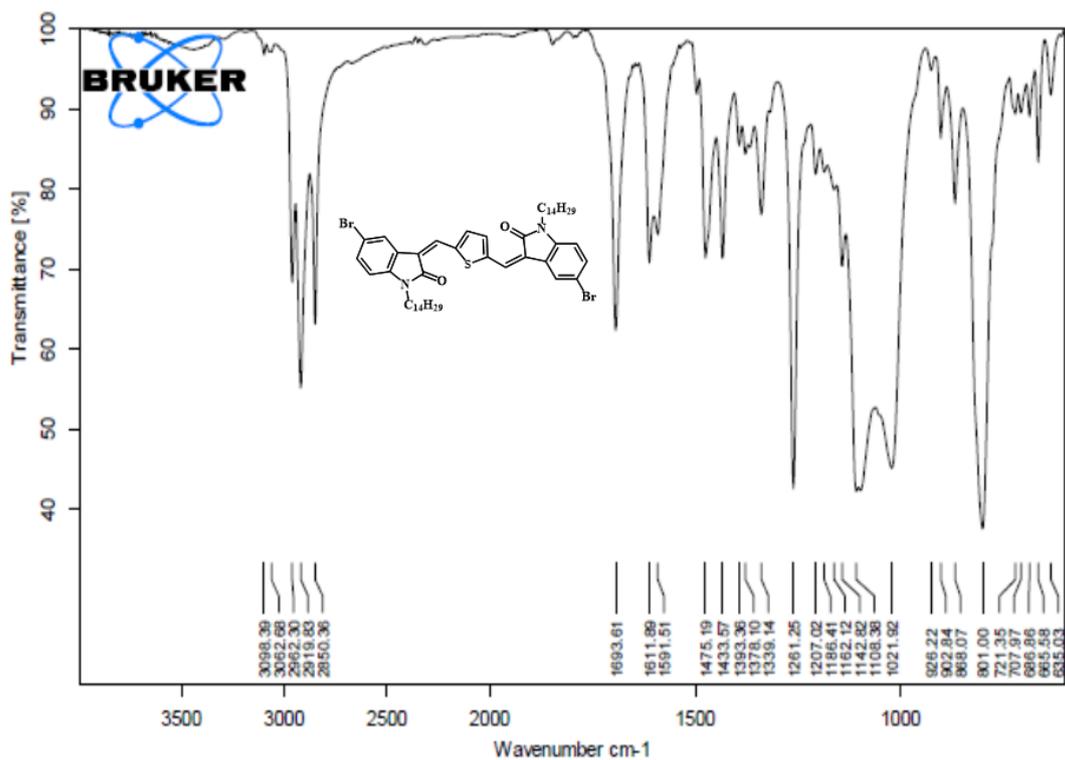


Figure S25: IR spectrum (KBr pellet) of compound 7

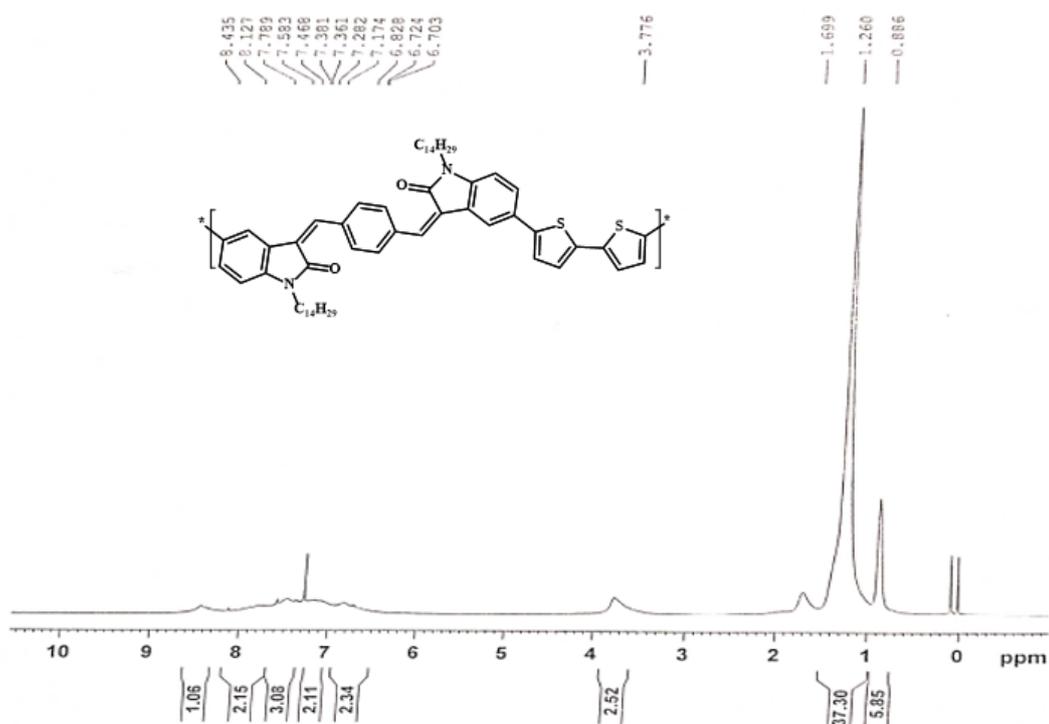


Figure S26: <sup>1</sup>H NMR spectra of P-1

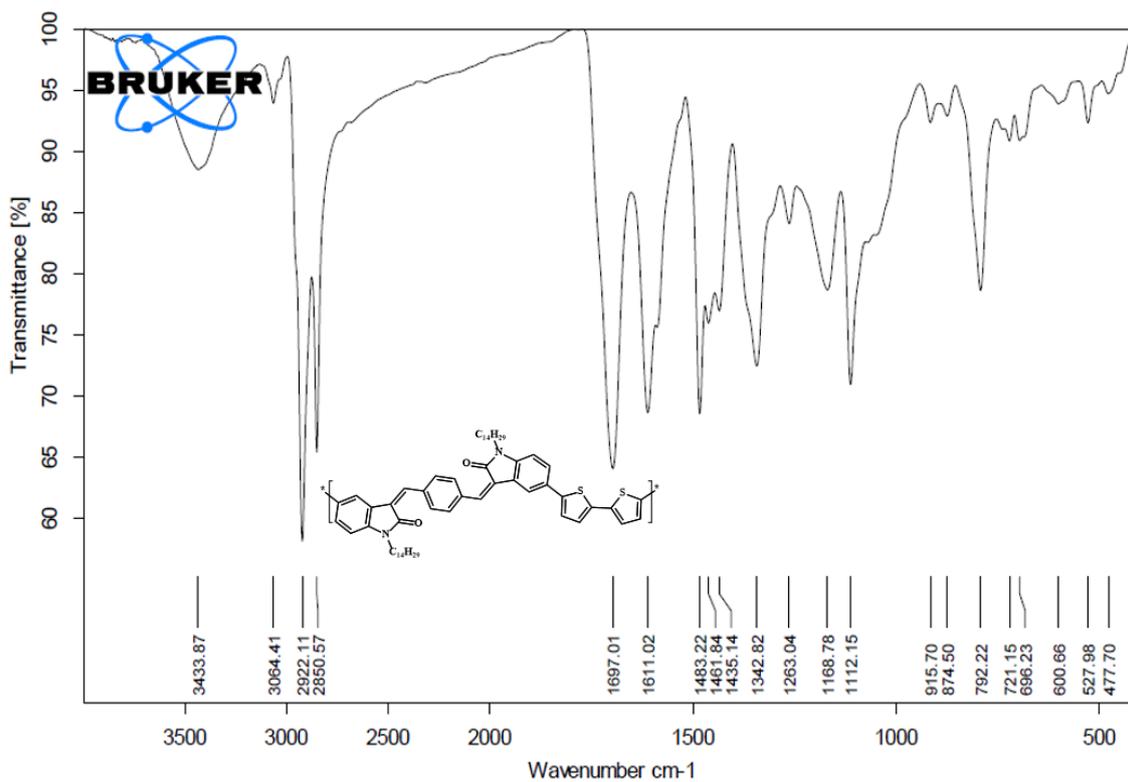
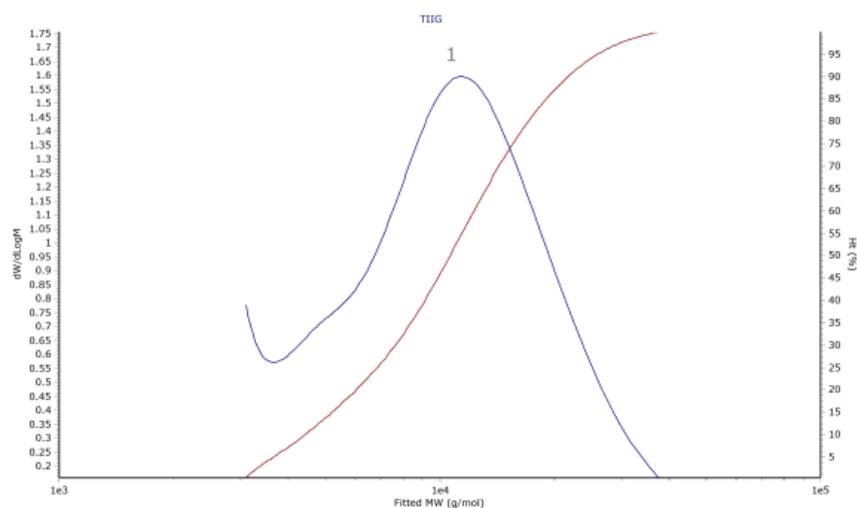


Figure S27: IR spectrum (KBr pellet) of polymer P-1



## Results

Analysed by  
Comments

Applied Chem at 16:53:44 on 17 November 2021

### Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	11475	8672	12054	15978	19808	15405	1.39

Figure S28: GPC analysis data of polymer P-1

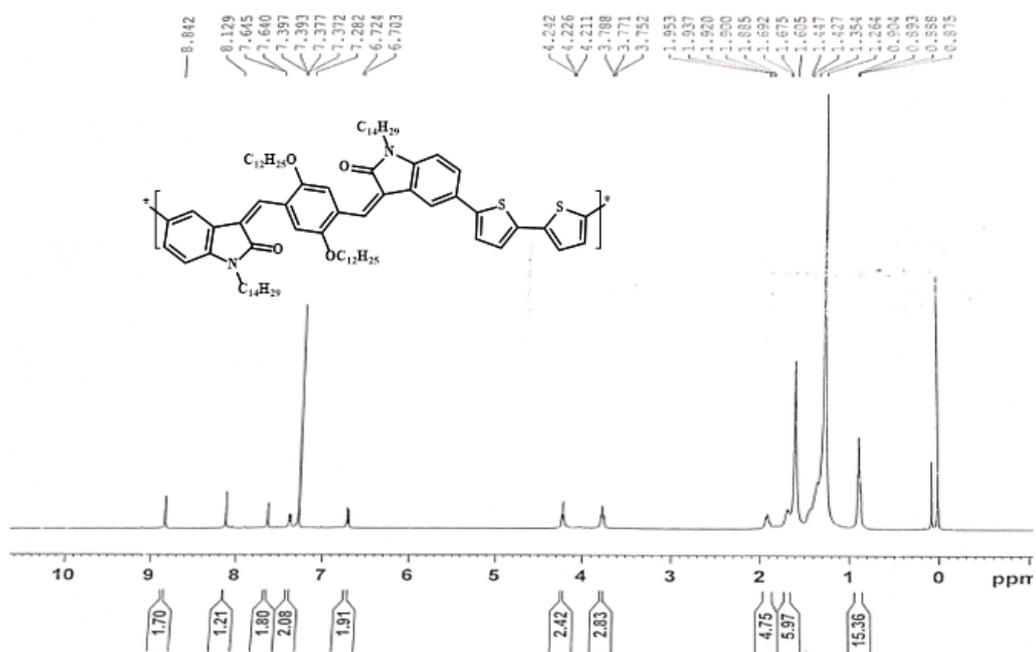


Figure S29:  $^1\text{H}$  NMR spectra of polymer P-2

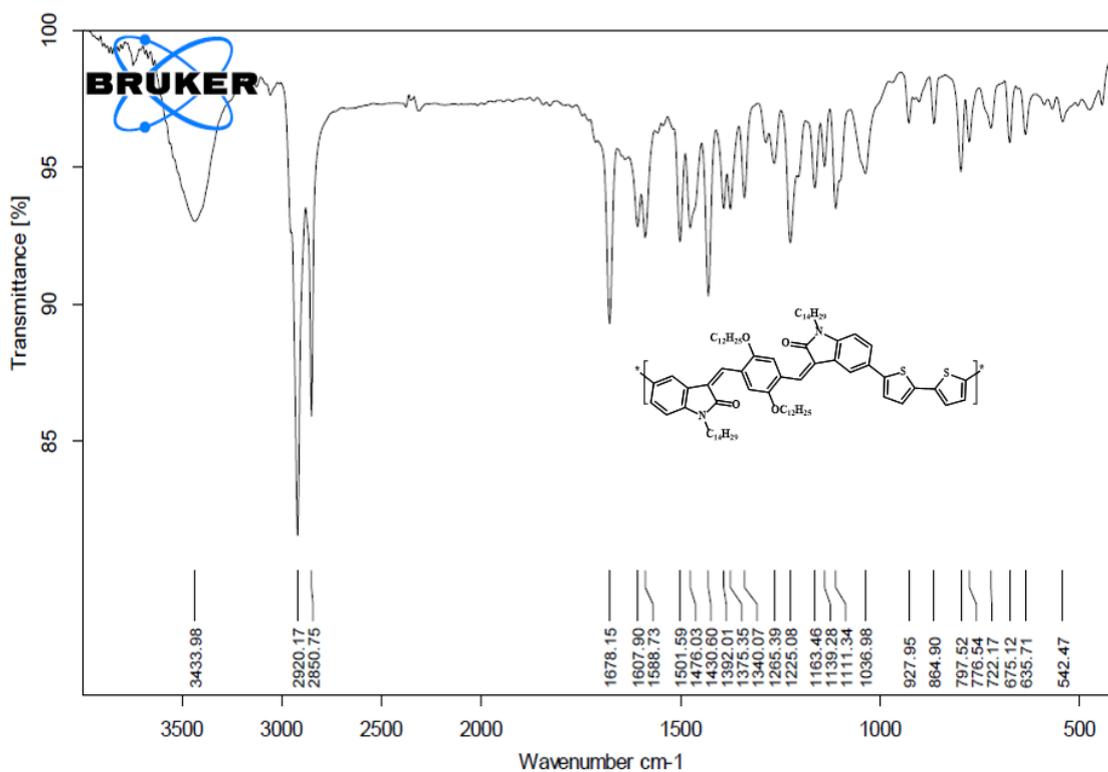
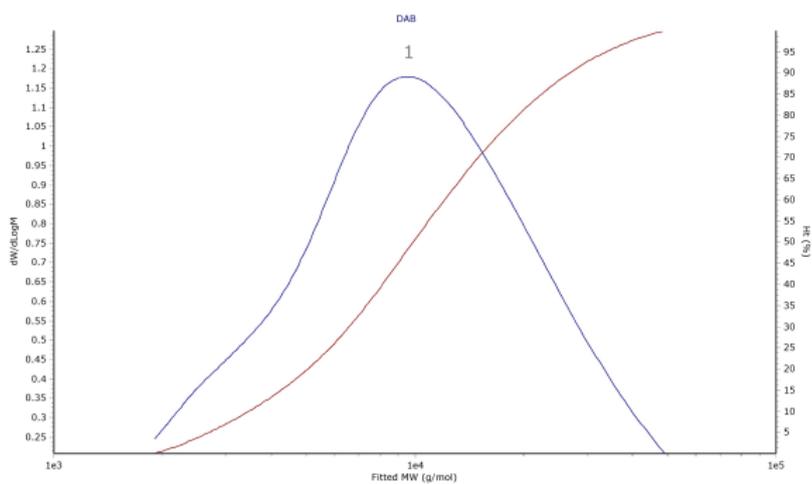


Figure S30: IR spectrum (KBr pellet) of polymer P-2



### Results

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#### Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	9788	7458	12827	20095	27033	19037	1.72

Figure S31: GPC analysis data of polymer P-2

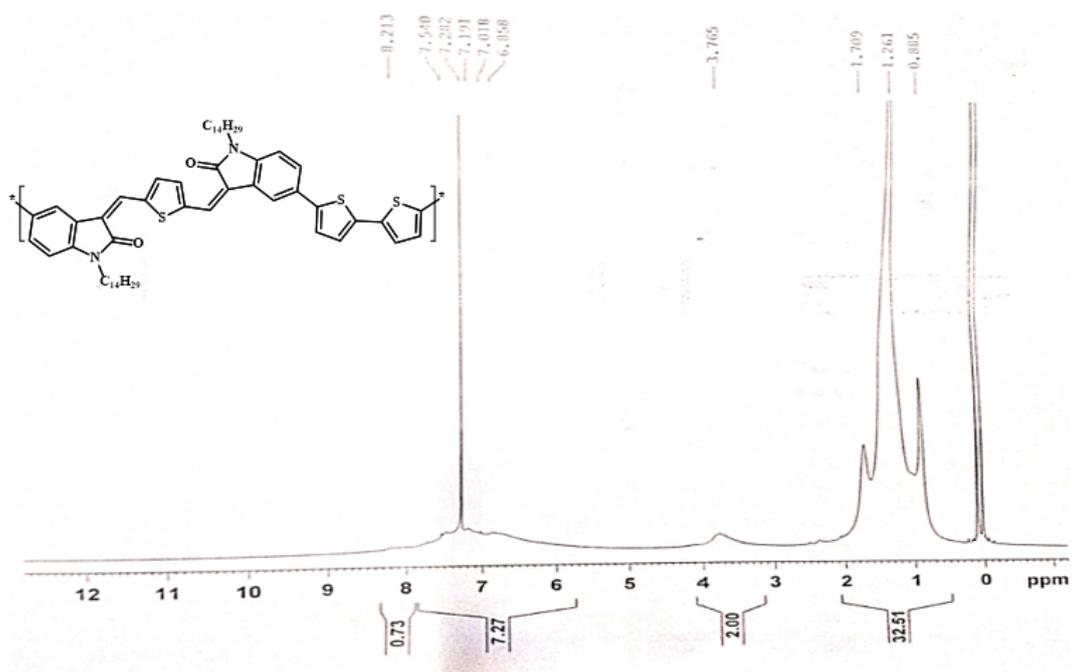


Figure S32:  $^1\text{H}$  NMR spectra of polymer P-3

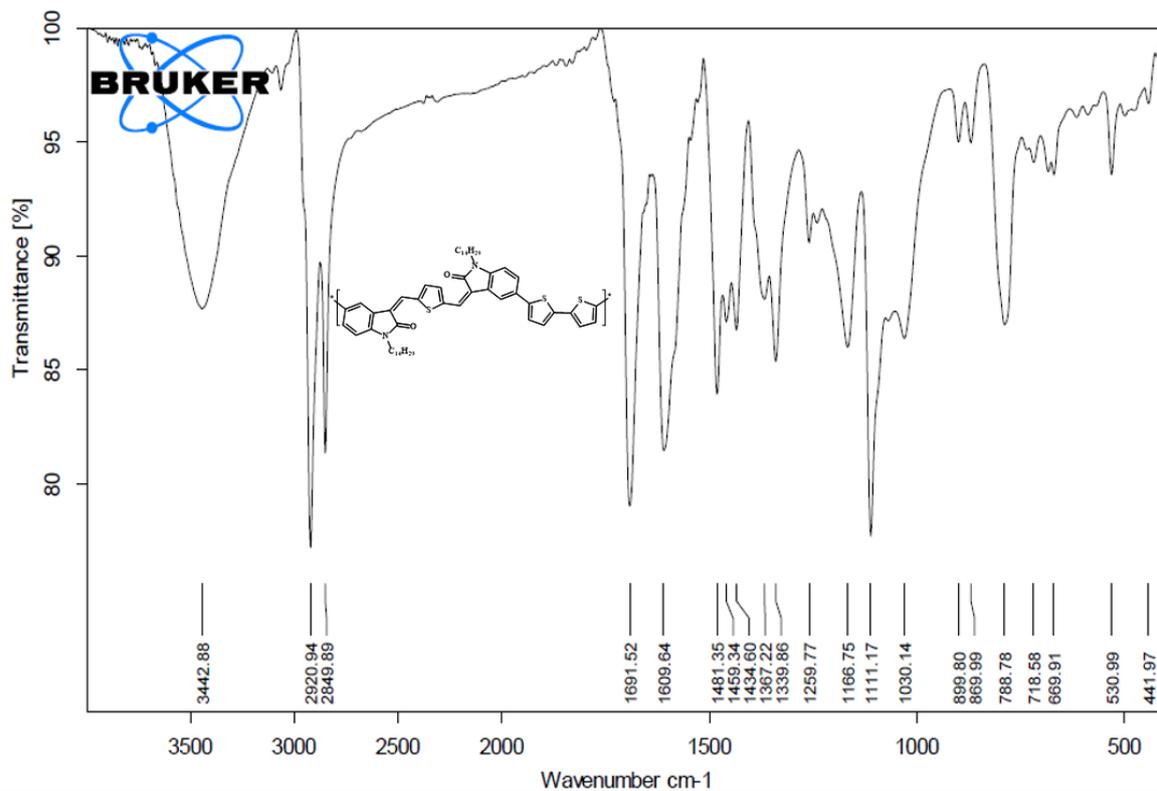
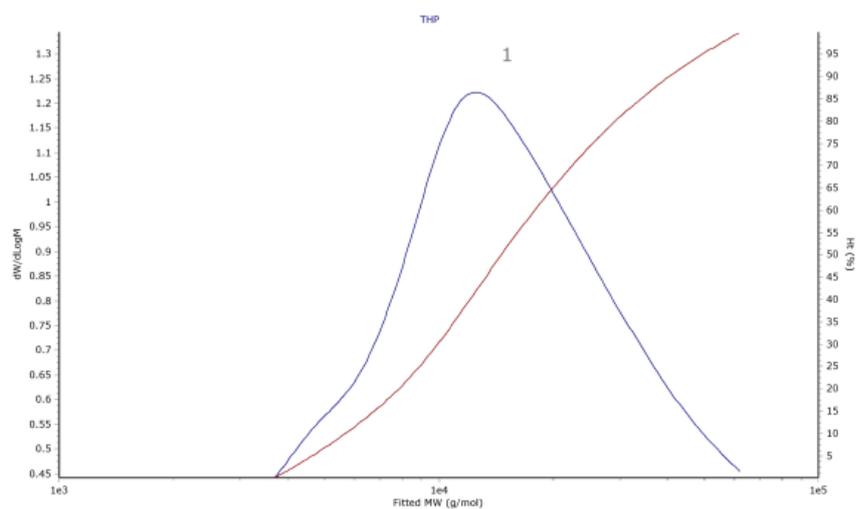


Figure S33: IR spectrum (KBr pellet) of polymer P-3



### Results

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#### Molecular Weight Averages

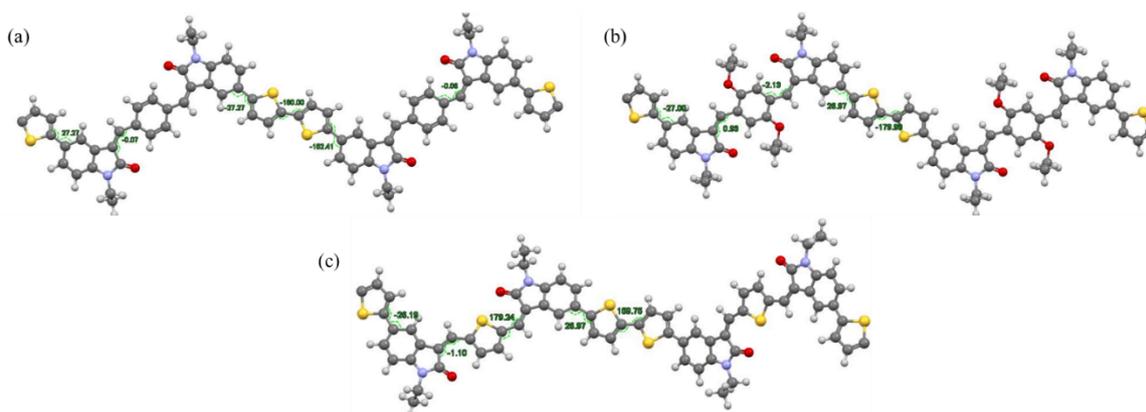
Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	12734	11793	19091	28902	37759	27502	1.619

Figure S34: GPC analysis data of polymer P-3

## Computational Studies

Compounds	HOMO	LUMO
3		
5		
7		

**Figure S35:** DFT (B3LYP/6-31G(d)) calculated structures, HOMO and LUMO of model polymer **3**, **5** and **7**, respectively



**Figure S36:** Optimised structure of  $\pi$ -extended isoindigo based conjugated polymer (a) **P-1**, (b) **P-2** and (c) **P-3** with their dihedral angles

## References:

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- 2 V. Chahal, S. NIRWAN and R. Kakkar, *Med. Chem. Commun.*, 2019, **10**, 351–368.
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- 4 S. Doddi, B. Ramakrishna, Y. Venkatesh and P. R. Bangal, *RSC Adv.*, 2015, **5**, 56855–56864.