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Synthesis and Study of Donor-Acceptor Conjugated Polymers *via* Metal Free Aldol Condensation Polymerization Strategy

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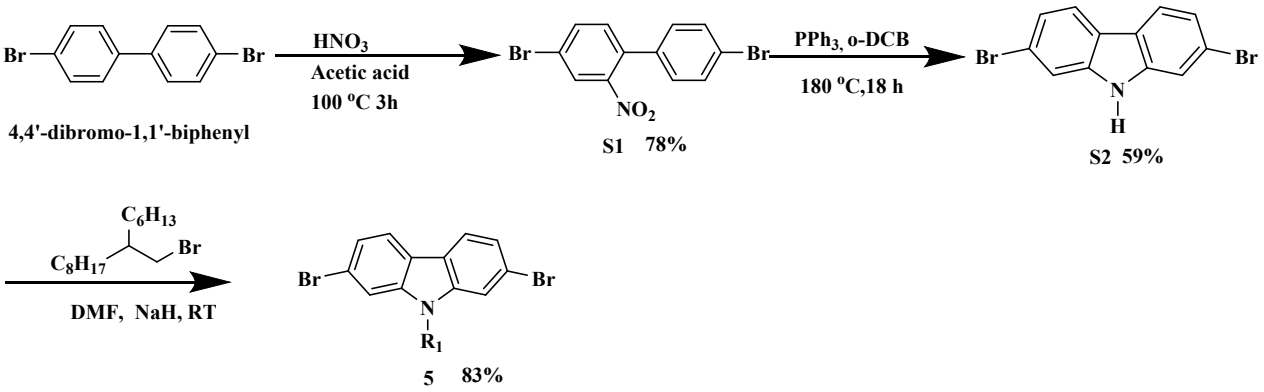
CONTENTS

Sr No	Contents	Page No
1	Materials and Instrumentation	**S1**
2	Synthesis of 2,7-dibromo-9-(2-hexyldecyl)-carbazole (**5**)	**S2-S3**
3	Synthesis of 2,7-dibromo-9,9-didodecyl-9*H*-fluorene (**8**)	**S3-S4**
4	Synthesis of 2,8-dibromo-5,11-dioctyl-5,11-dihydroindolo[3,2-b] carbazole (**11**)	**S4-S5**
5	Spectral data of intermediate compounds and monomers	**S6-S23**
6	Spectral data and GPC analysis data of polymers	**S24-S28**
7	References	**S29**

Materials and Instrumentation

All the chemical is reagent grade and is used exactly as it was purchased. Moisture-sensitive processes are carried out using dried solvents in an inert environment of dry nitrogen. Reaction are monitored by thin-layer chromatography (TLC) using Merck 60 F254 aluminum-coated plates. Synthesized compounds were purified by column chromatography using Silica gel (60-120 mesh and 100-200 mesh). NMR spectra were recorded on a Bruker Avance-III 400 spectrometer, NMR in $CDCl_3$ and DMSO-D6. High resolution mass spectra (HRMS) were recorded on Xevo G2-XS QTOF Mass Spectrometer.

Synthesis of 2,7-dibromo-9-(2-hexyldecyl)-carbazole (5)



Scheme S1 Synthesis of compound 5 from 4,4'-dibromo-1,1'-biphenyl

Compound **5** was synthesized according to the modified literature procedure[1–3]

Synthesis of 4,4'-dibromo-2-nitro-1,1'-biphenyl (**S1**)

In a 250 mL two necked round bottom flask, 4,4'-dibromo- biphenyl (4 g, 12.82 mmol) in glacial AcOH (60 mL) was taken and heated at 100 °C. To this solution fuming HNO_3 (100%, 18.5 mL) and H_2O (1.5 mL) was added. The reaction mixture was stirred at 100 °C for 30 minutes and then allowed to cool to room temperature. The resultant reaction mixture was poured in to water and subsequently extracted with DCM. The organic layer was then washed successively with water and dried over Na_2SO_4. The compound **S1** was obtained by evaporation of solvent under reduced pressure.

4,4'-Dibromo-2-nitro-1,1'-biphenyl (**S1**): Yellow solid (3.60 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.086 (s, 1H), 7.89 (d, J = 8.4, 2H), 7.58 (d, J = 1.6 Hz, 2H), 7.38 (dd, J_1 = 8 Hz, J_2 = 1.6 Hz, 2H).

Synthesis of 2,7-dibromocarbazole (**S2**)

4,4'-Dibromo-2-nitro-1,1'-biphenyl (**S1**) (6 g, 16.8 mmol) and PPh_3 (11 g, 42.0 mmol) were dissolved in *o*-dichlorobenzene (35 mL) under nitrogen atmosphere and refluxed for 24 hours. After the completion of reaction, the solvent was evaporated and the crude product was purified by column chromatography over silica gel by using 20% ethyl acetate in petroleum ether.

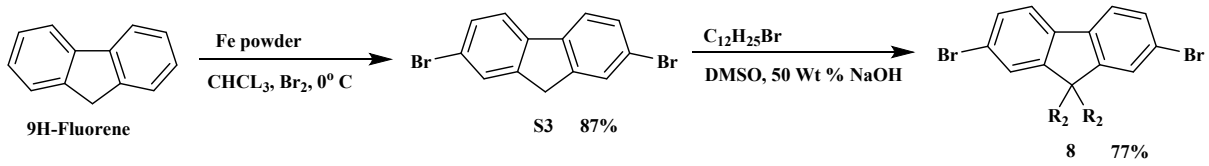
2,7-Dibromocarbazole (**S2**): White solid (3.25 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 2 Hz, 1H), 7.78 (dd, J = 8.4 Hz, J = 2 Hz, 1H), 7.598 (s, 1H), 7.57 (d, J = 2 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.18 (dd, J = 1.6 Hz, J = 6.4 Hz, 2H).

Synthesis of 2,7-dibromo-9-(2-hexyldecyl)-carbazole (**5**)

In a 100 mL two necked round bottom flask, 2,7-dibromocarbazole (**S2**) (5 g, 15.4 mmol) in DMF (50 mL) was taken. To this reaction mixture, NaH (60% w/w suspension in mineral oil) (865 mg, 21.6 mmol) was added. After 1 hour, 7-(bromomethyl) pentadecane (6.11 g, 20 mmol) was added and the reaction mixture was stirred at room temperature for more 20 hours under nitrogen atmosphere. After the completion of the reaction, the reaction mixture was poured in water and the product was extracted in ethyl acetate. Organic fraction was washed with brine and dried over Na_2SO_4, followed by solvent distillation under reduced pressure. The resultant crude product was subjected to the column chromatography over silica gel by using 5% ethyl acetate in petroleum ether to get desired pure product.

2,7-Dibromo-9-(2-hexyldecyl)-carbazole (**5**): Colourless liquid (7.0 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.4 Hz, 2H), 7.520 (s, 2H), 7.35 (dd, J_1 = 8.2 Hz, J_2 = 1.2 Hz, 2H), 4.06 (d, J = 6 Hz, 2H), 1.99-2.00 (m, 1H), 1.23–1.40 (m, 24H), 0.86–0.91 (m, 6H).

Synthesis of 2,7-dibromo-9,9-didodecyl-9*H*-fluorene (8)



Scheme S2 Synthesis of compound 8 from 9*H*-Fluoene.

Compound **8** was synthesized according to the modified literature procedure.[4]

Synthesis of 2,7-dibromo-9*H*-fluorene (**S3**)

In a dry 100 mL two necked round bottom flask, fluorene (4.1 g, 25.0 mmol) was taken in $CHCl_3$ (40 mL) and cool it to 0 °C. In this cold solution Fe-powder (140 mg, 2.50 mmol) and Br_2 (2.69 mL, 52.2 mmol) in $CHCl_3$ (20 mL) was added, subsequently. After that the reaction mixture was allowed to achieved the room temperature and stirred for 3 hours. The reaction mixture was poured in to the water and washed with sodium thiosulfate until the red color disappeared. The aqueous layer was extracted with ethyl acetate and the combined organic layers were dried over Na_2SO_4. The solid compound was further purified by column chromatography on silica gel by using 10% ethyl acetate in petroleum ether as an eluent.

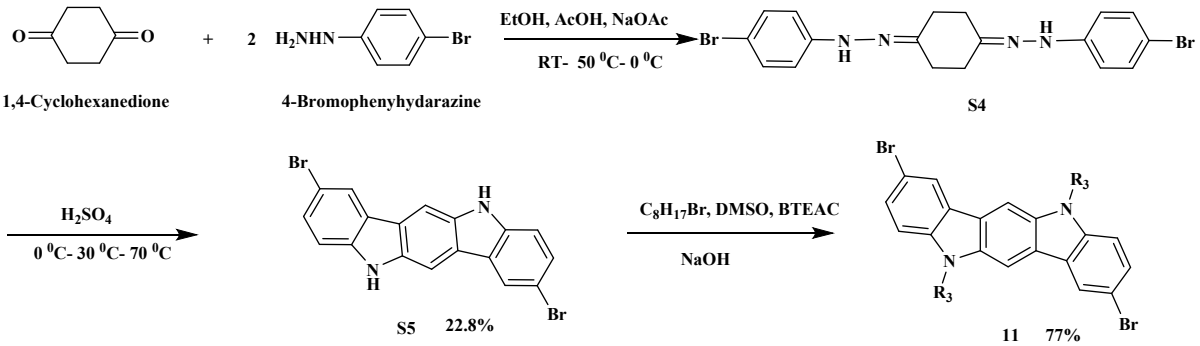
2,7-Dibromo-9*H*-fluorene (**S3**): White solid (7.0 g, 86%) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69(d, J = 0.8 Hz, 2H), 7.62 (d, J = 8 Hz, 2H), 7.52 (dd, J_1= 0.8 Hz, J_2= 0.8 Hz, 2H), 3.89 (s, 2H).

Synthesis of 2,7-dibromo-9,9-didodecyl-9*H*-fluorene (**8**)

2,7-Dibromofluorene (**S3**) (2 g, 6.17 mmol) in 20 mL toluene was taken in dry two necked round bottom flask under nitrogen atmosphere. To this reaction mixture, tetrabutylammonium bromide (0.2 g, 0.6 mmol) and NaOH (2 mL,50% W/V aqueous solution) was added. The resultant reaction mixture was further stirred for 1 hour and the followed by the addition of 1-bromododecane (2.63 g, 13.6 mmol). The reaction mixture was further heated at 90 °C for 24 hours. After completion of the reaction, the reaction mixture was poured in distilled water and the product was extracted with ethyl acetate. Organic fraction was washed with brine and dried over Na_2SO_4. The crude product was obtained by solvent evaporation under reduced pressure. The crude product was further subjected to the column chromatography over silica gel by using 5% ethyl acetate in petroleum ether as an eluent to get the pure desired product.

2,7-Dibromo-9,9-didodecyl-9*H*-fluorene (**8**): (2.57 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.54 (dd, J_1 = 8 Hz, J_2 = 0.8 Hz, 2H), 7.48 (dd, J_1 = 4.4 Hz, J_2 = 1.2 Hz, 2H), 7.46 (s, 2H) 1.90 – 1.94 (m, 4H), 1.10 – 1.31 (m, 36H), 0.87-0.90 (m, 6H), 0.592 (m, 4H).

Synthesis of 2,8-dibromo-5,11-dioctyl-5,11-dihydroindolo[3,2-b] carbazole (11)



Scheme S3 Synthesis of compound 11 from 1,4-cyclohexanedione.

Compound **11** was synthesized according to the modified literature procedure[5,6]

Synthesis of 2,8-dibromo-5,11-dihydroindolo[3,2-*b*] carbazole (**S5**)

In 250 mL two necked round bottom flask, 4-bromophenylhydrazine hydrochloride (10 g, 44.84 mmol) dissolved in 100 mL of ethanol. In this resultant solution sodium acetate (11 g, 134 mmol) was added and the reaction mixture was stirred for 15 minutes at room temperature

Subsequently, 25 mL solution of 1,4-cyclohexandione (2.5 g, 22.32 mmol) in ethanol and 20 mL of acetic acid was added and the reaction mixture was further heated for 1 hour at 50 °C and then the reaction mixture was cool to 0 °C. The light-yellow solid of cyclohexane-1,4-dionebis[(4-bromophenyl) hydrazone] (**S4**) was precipitated out which further separated by filtration and washed with water and dried. The crude compound **S4** was added into a mixture of AcOH (40 mL) and H_2SO_4 (7 mL) in dry two necked round bottom flask. The reaction mixture was stirred at 10 °C for 20 minutes and further stirred at 30 °C for more 20 minutes. Subsequently, the reaction mixture was heated at 70 °C for another 1 hour. The reaction mixture was further stirred at room temperature for 24 hours.The product was filtered, washed with methanol and water, and then stirred in 100 mL of boiling methanol for 30 minutes. The solid product was separated by filtration and dried to get pure compound **S5**.

2,8-Dibromo-5,11-dihydroindolo[3,2-*b*] carbazole (**S5**): Brown solid (1.89 gm, 23%). ^{1}H NMR (DMSO-d^6): δ 11.33 (s, 2H), 8.50 (s, 2H), 8.24 (s, 2H), 7.62 (dd, J1 = 8.8 Hz, J2 = 2 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100MHz, DMSO-d^6): 140.3, 135.5, 128.4, 124.8, 123.4, 122.7, 112.8, 110.1, 101.7.

Synthesis of 2,8-dibromo-5,11-dioctyl-5,11-dihydroindolo[3,2-*b*] carbazole (**11**)

2,8-Dibromo-5,11-dihydroindolo[3,2-*b*] carbazole (**S5**) (0.5 g, 1.2 mmol) in 20 mL DMSO was taken in dry two necked round bottom flask of 50 mL capacity and the reaction mixture was stirred under nitrogen atmosphere. In this solution benzyl triethylammonium chloride (30 mg, 1.3 mmol), and 50% aq. NaOH solution (2 mL) was added. Subsequently, 1-bromoctane (0.51 g, 2.6 mmol) was added and the resultant mixture was stirred at room temperature for 1 hour followed by further stirring at 50 °C for 4 hours. The reaction mixture was then poured into 200 mL of methanol and the precipitated yellow solid was filtered and washed with water, DMF, methanol and acetone, subsequently. The desired compound **11** was obtained by drying.

2-Dibromo-5,11-dioctyl-5,11-dihydroindolo[3,2-*b*] carbazole (**11**): Green solid (0.60 g,77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J=1.6 Hz, 2H), 7.95 (s, 2H), 7.56 (dd, J = 8,8 Hz, J = 1.6 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 4.34-4.38 (t, 4H), 1.90– 1.94 (t, 4H), 1.26-1.43(m, 8H), 0.87 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$):140.35, 136.28, 128.44, 124.37, 123.01, 122.22, 110.63, 109.86, 53.47, 43.48, 31.84, 29.44, 29.23, 28.77, 27.39, 22.65, 14.18, 14.12, 11.49.

Spectral data of intermediate compounds and monomers

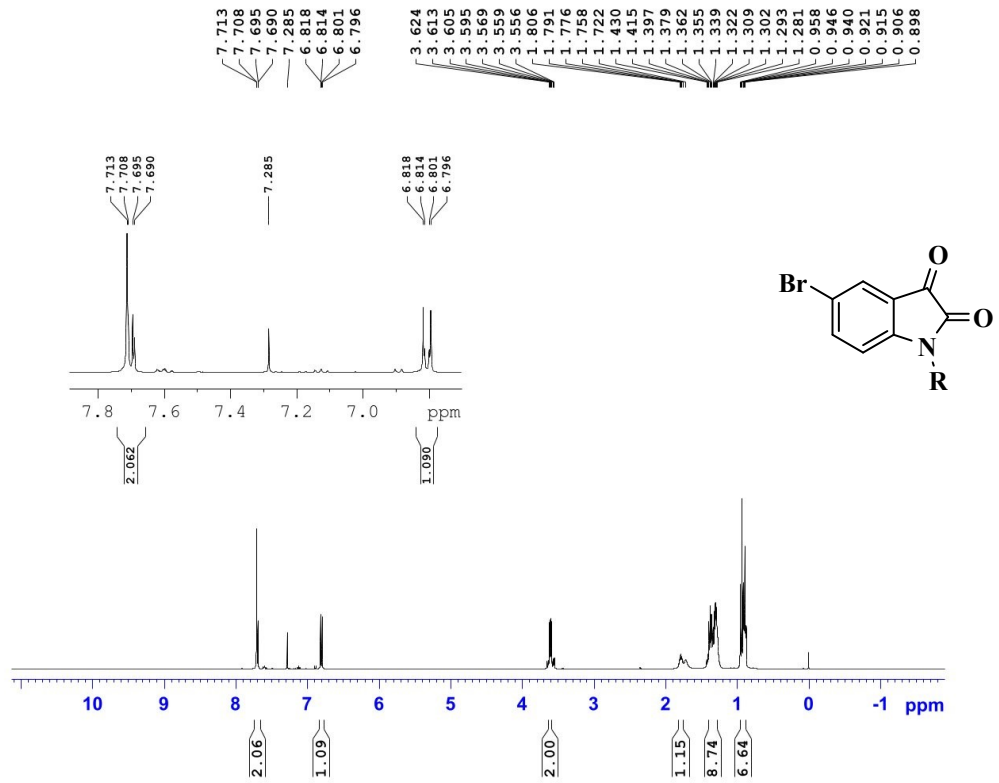


Figure S1 ^{1}H NMR spectra of compound **1**

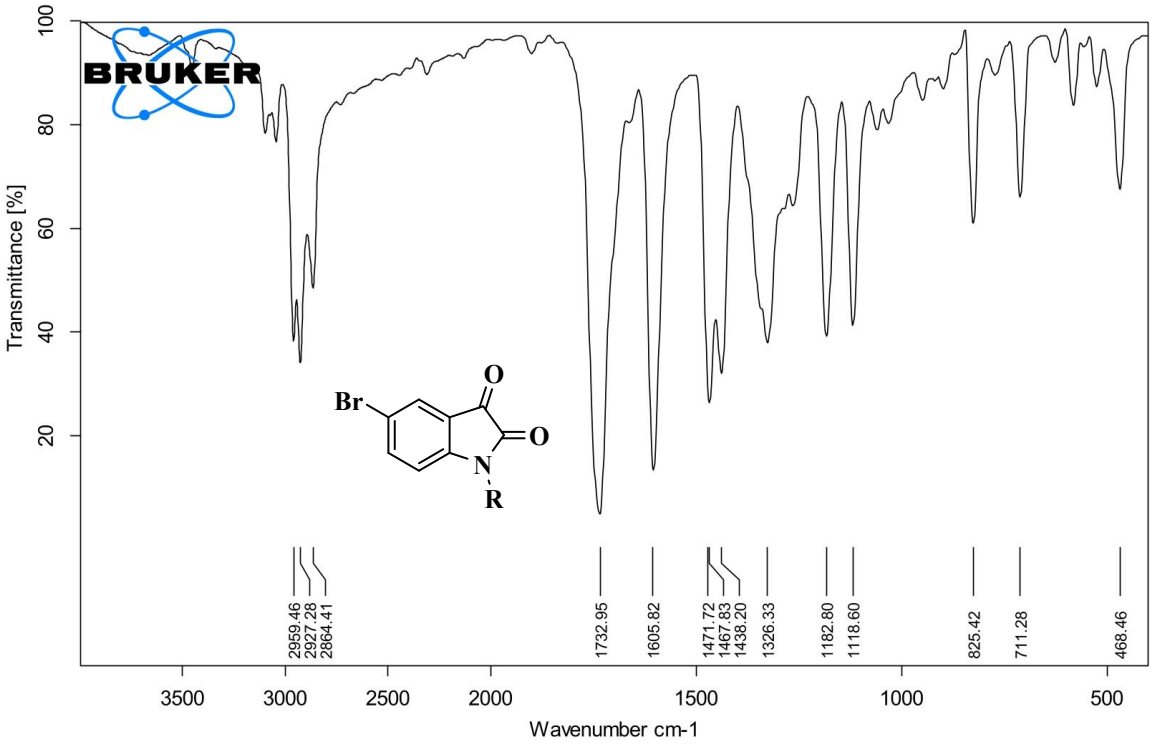


Figure S2 IR spectrum (KBr pellet) of compound **1**

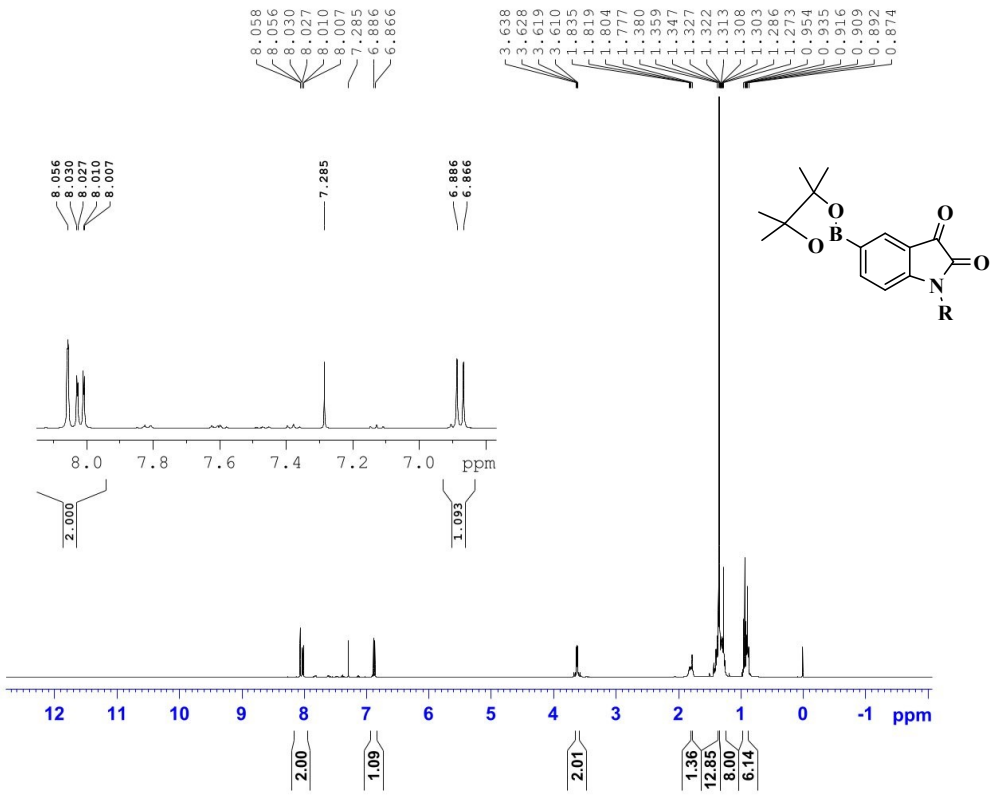


Figure S3 ^{1}H NMR spectra of compound **2**

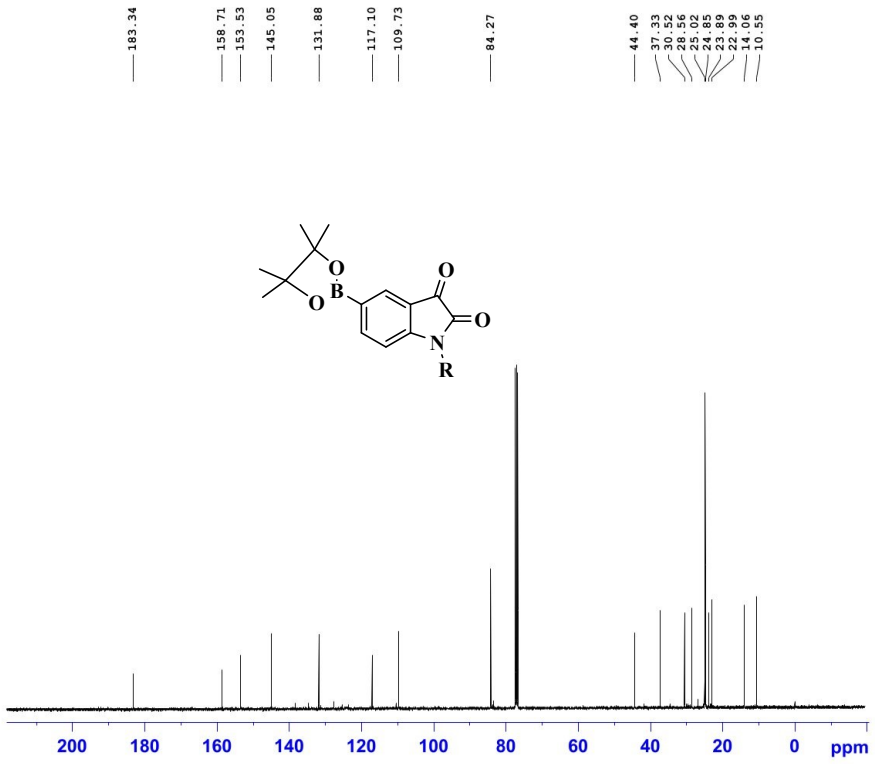


Figure S4 ^{13}C NMR spectra of compound **2**

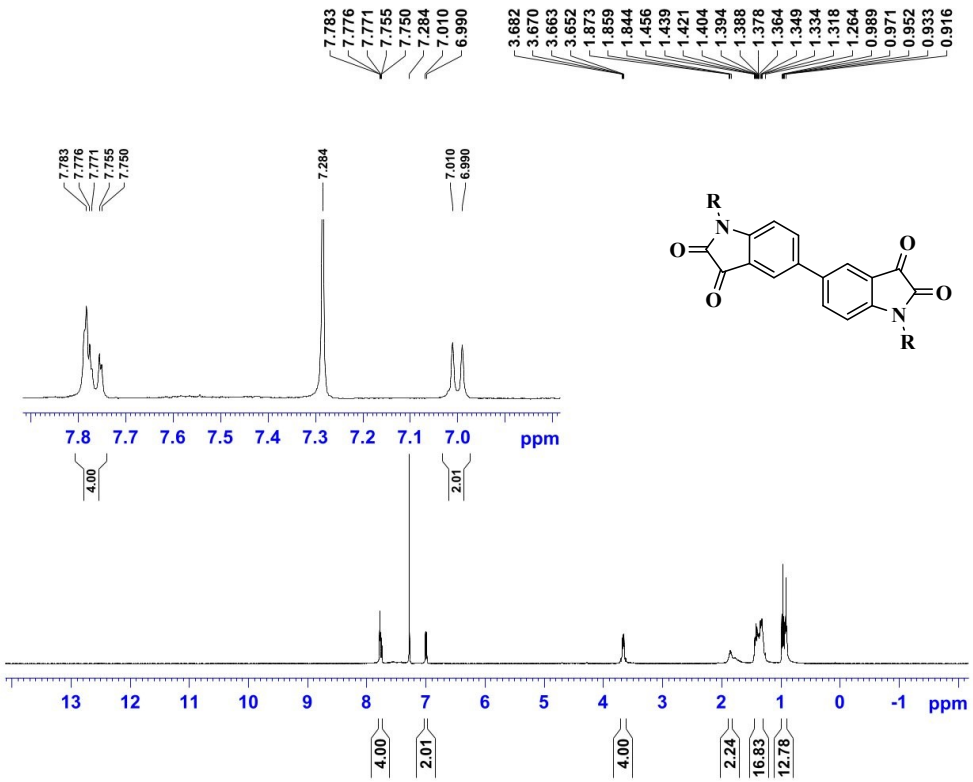


Figure S5 ^{1}H NMR spectra of compound **3**

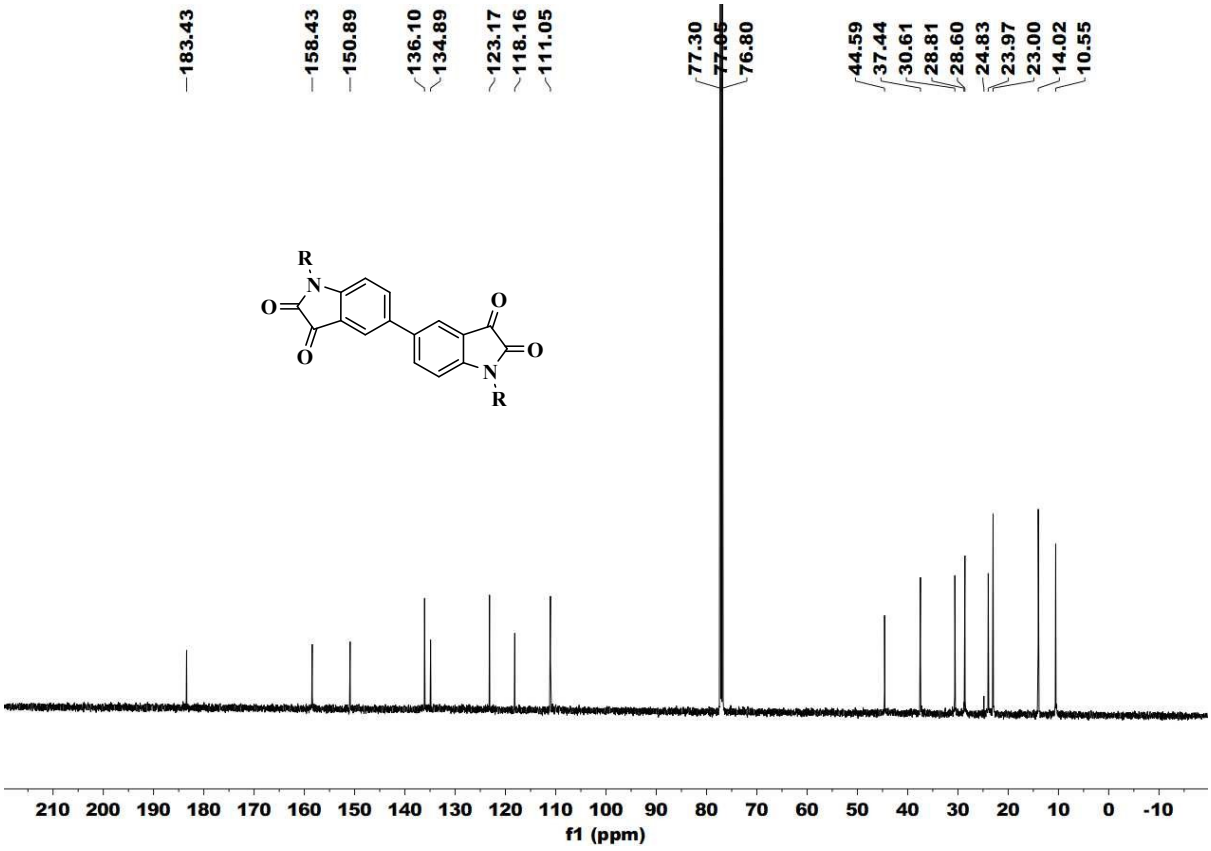


Figure S6 ^{13}C NMR spectra of compound **4**

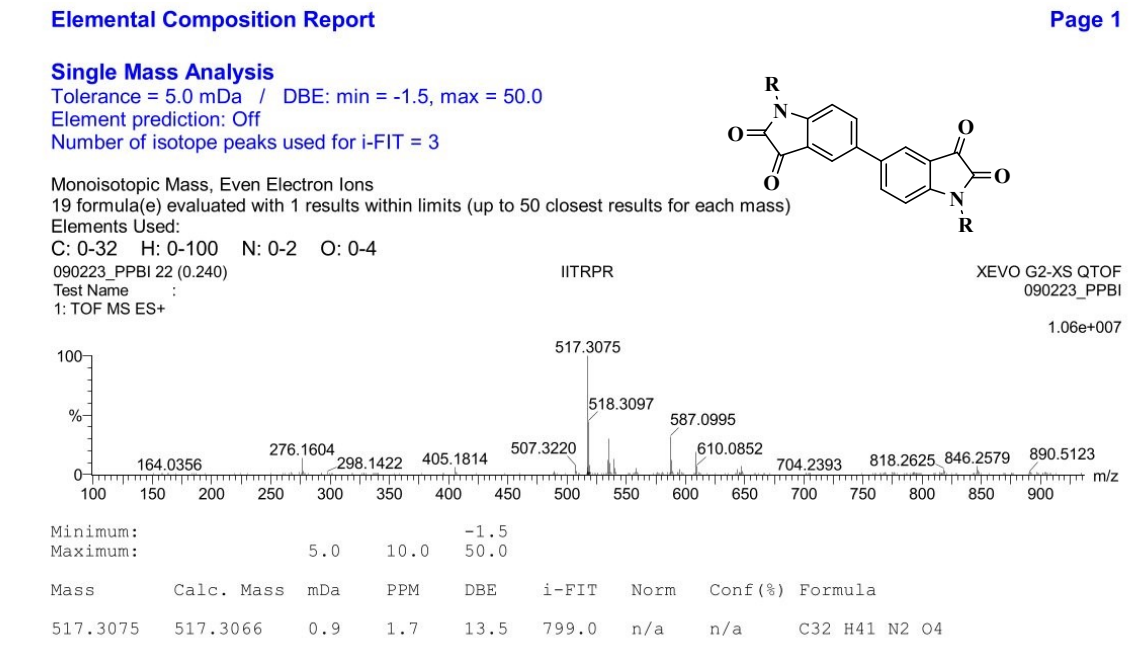


Figure S7 HR-MS data of compound **3**

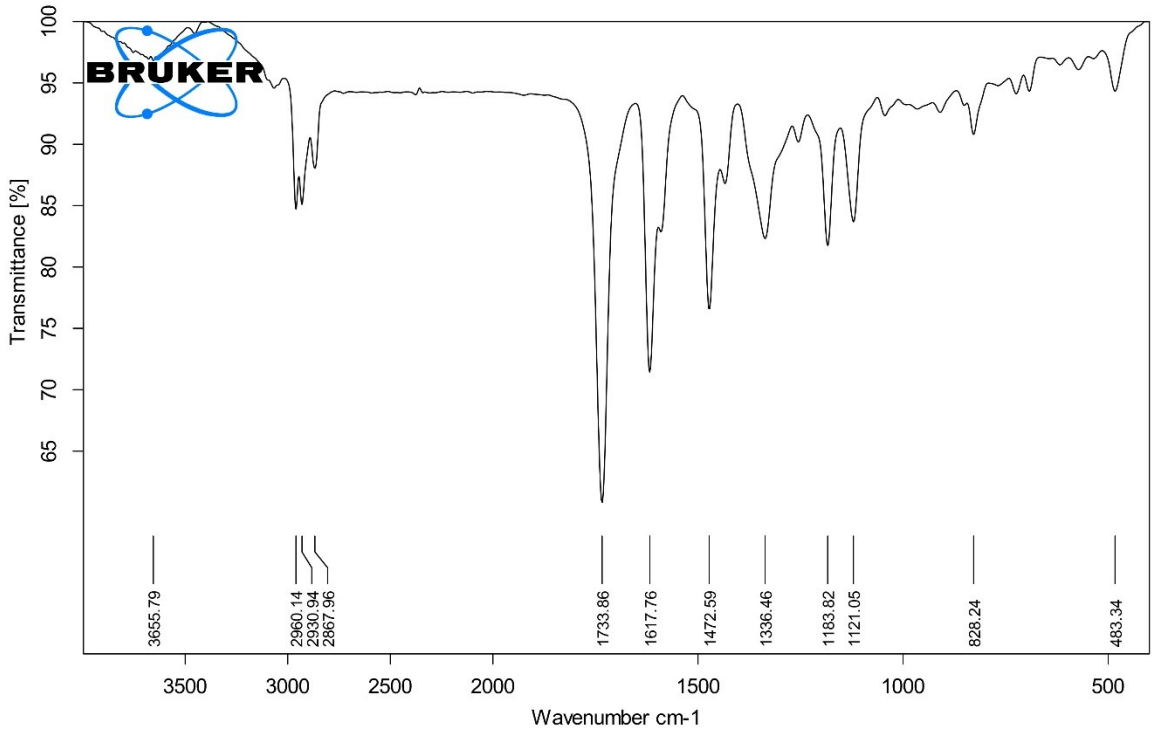


Figure S8 IR spectrum (KBr pellet) of compound **3**

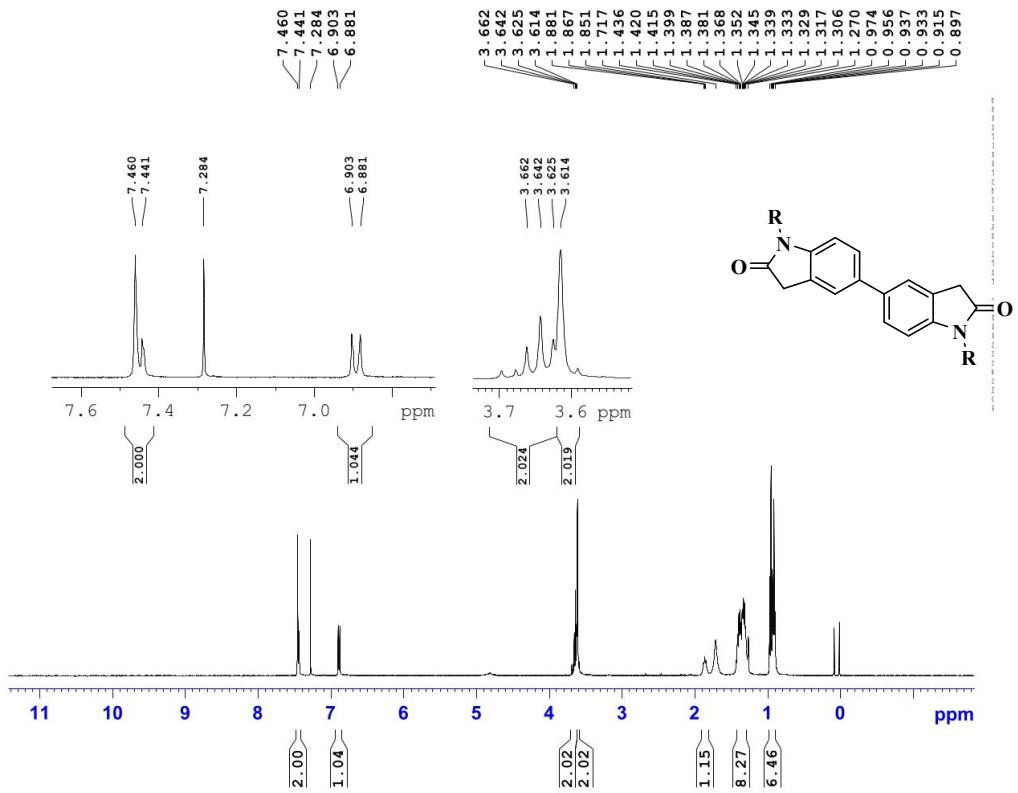


Figure S9 [1]H NMR spectra of compound **4**

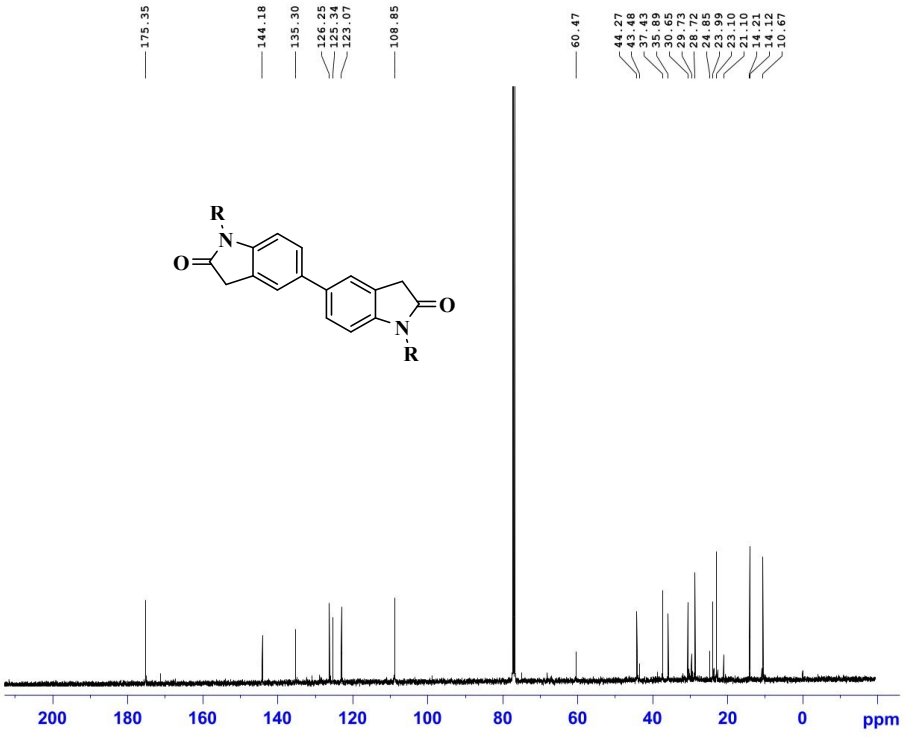


Figure S10 [13]C NMR spectra of compound **4**

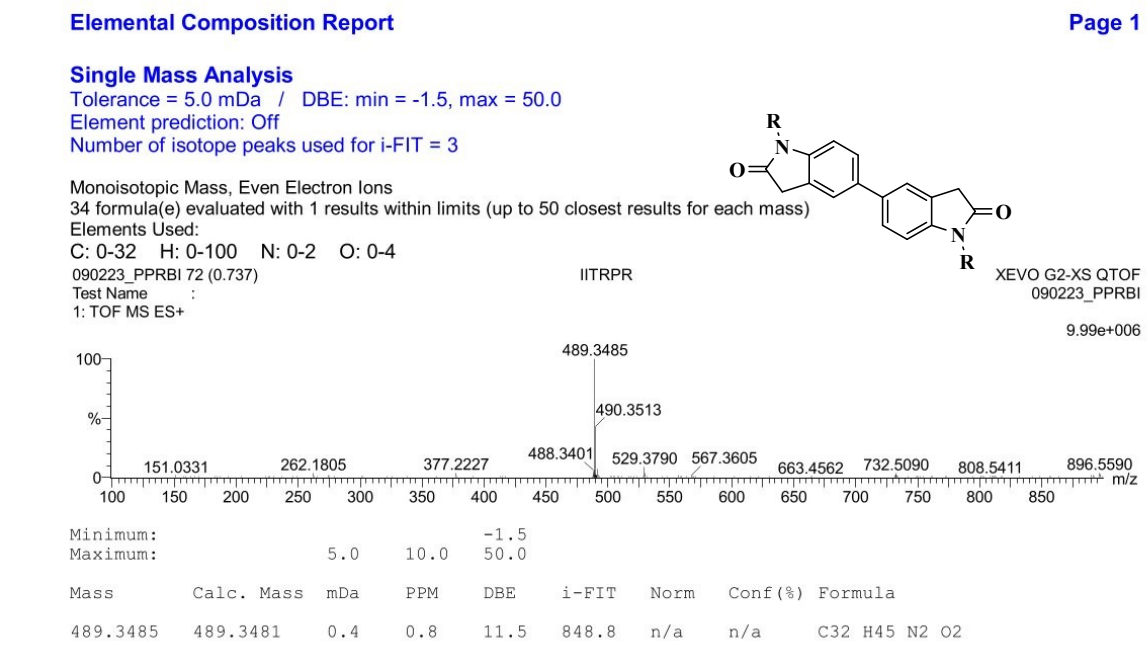


Figure S11 HR-MS data of compound **4**

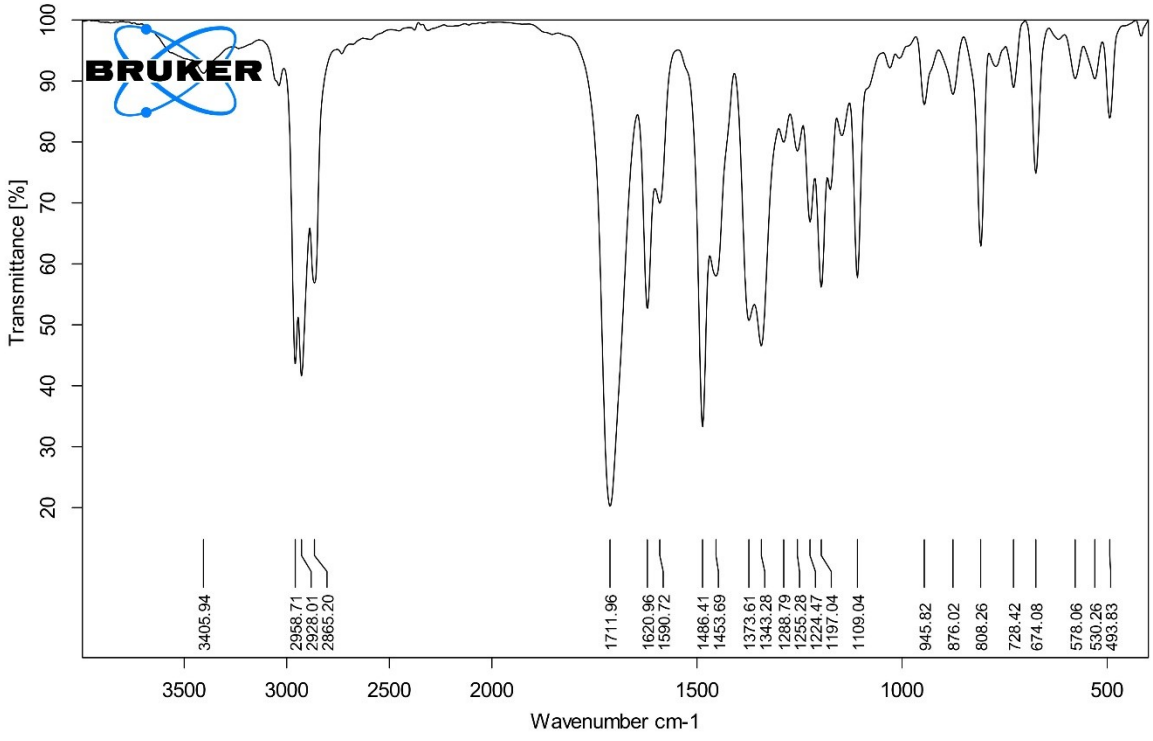


Figure S12 IR spectrum (KBr pellet) of compound **4**

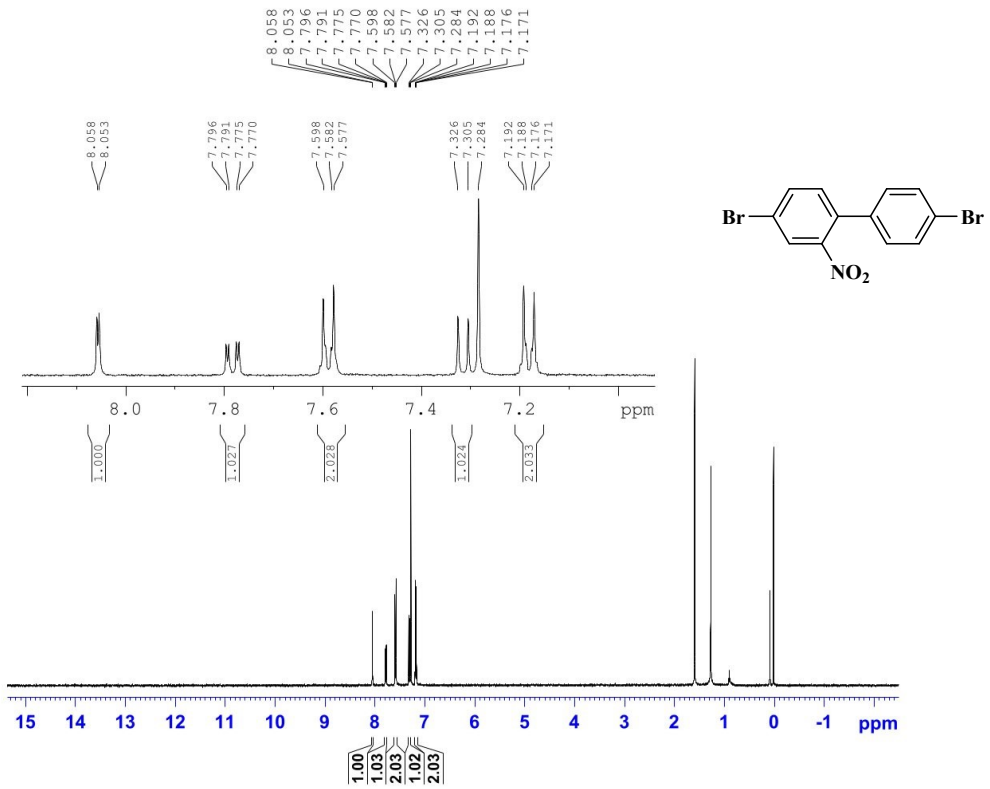


Figure S13 [1]H NMR spectra of compound **S1**

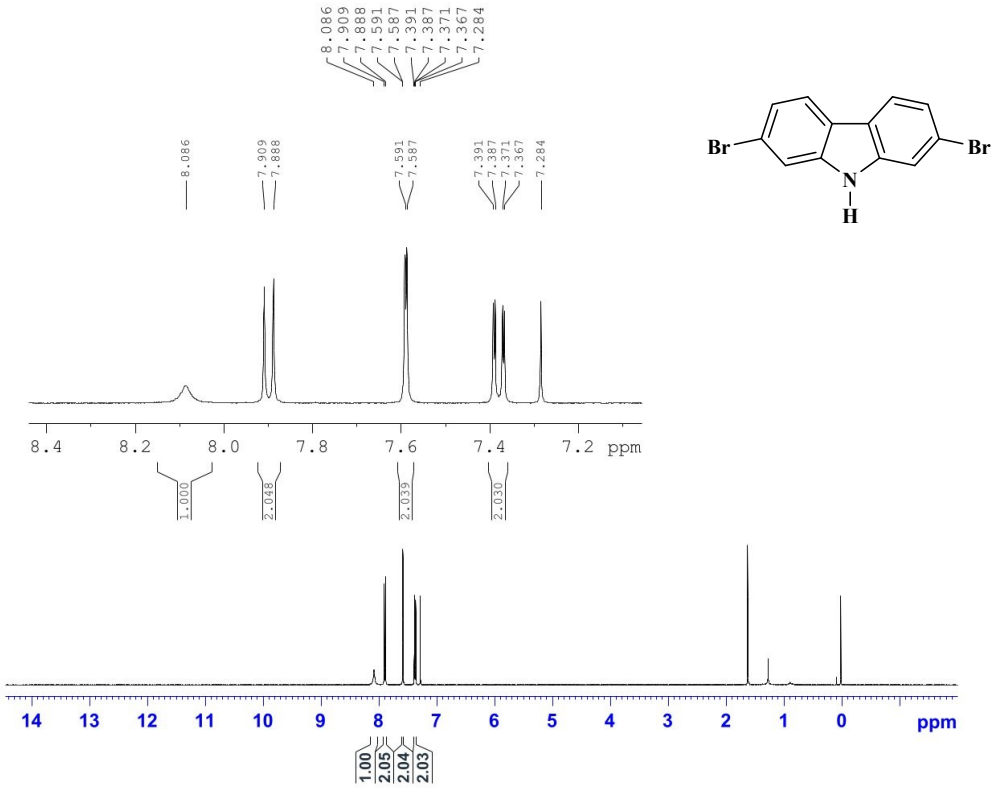


Figure S**14** [1]H NMR spectra of compound **S2**

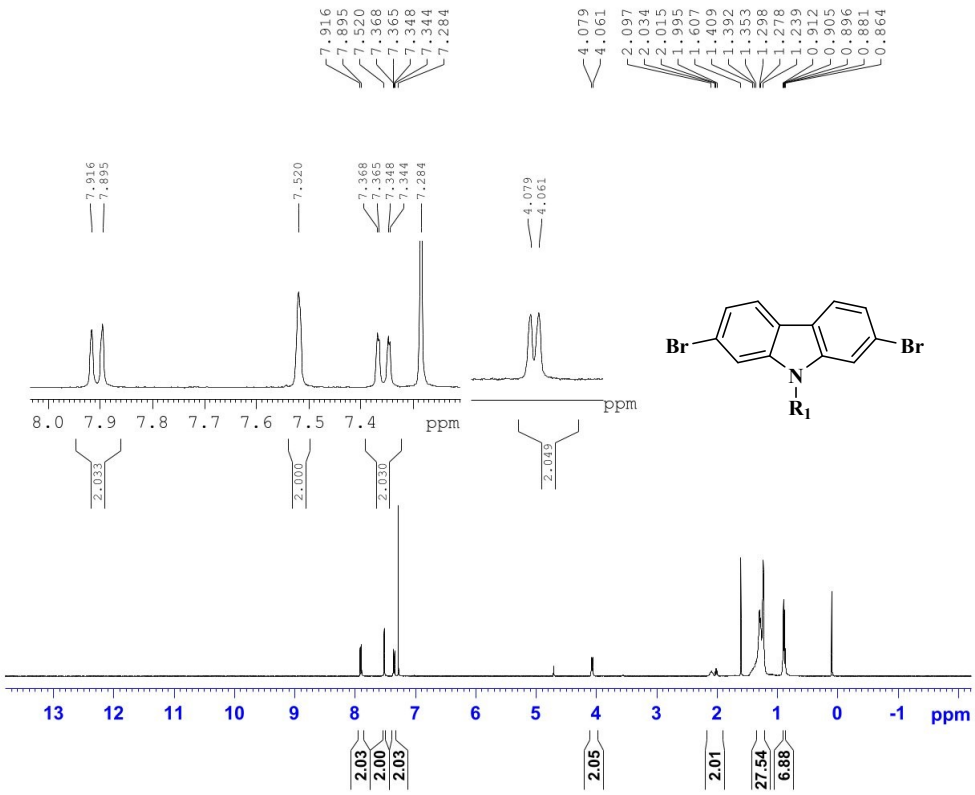


Figure S15 [1]H NMR spectra of compound **5**

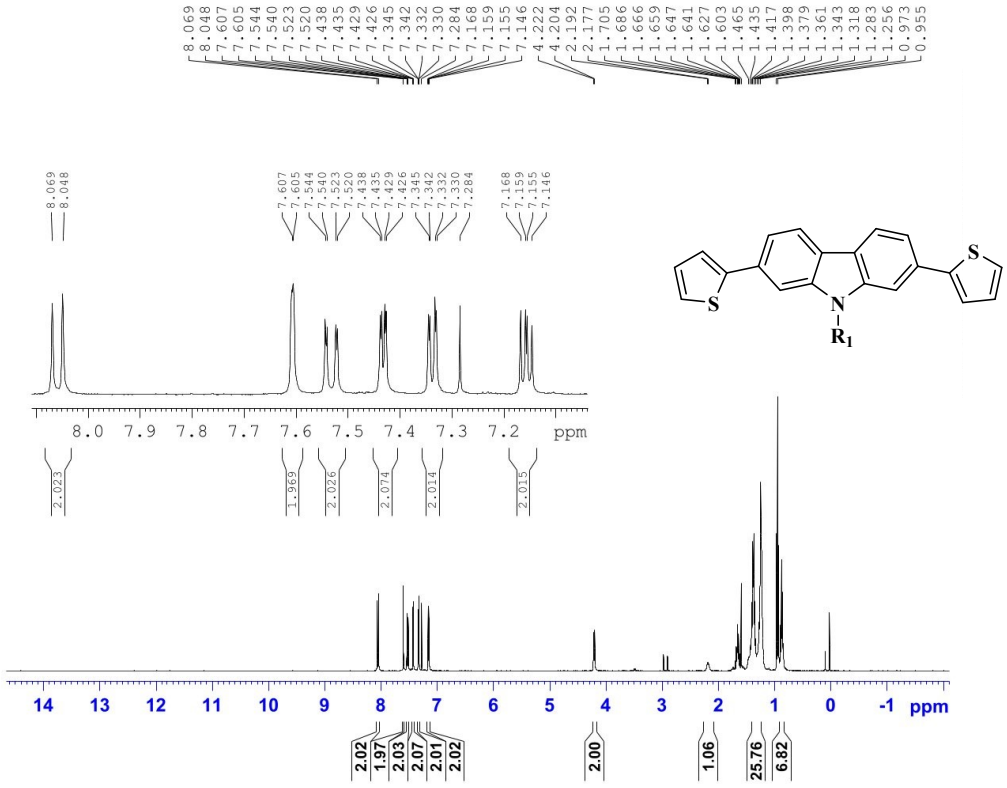


Figure S16 [1]H NMR spectra of compound **6**

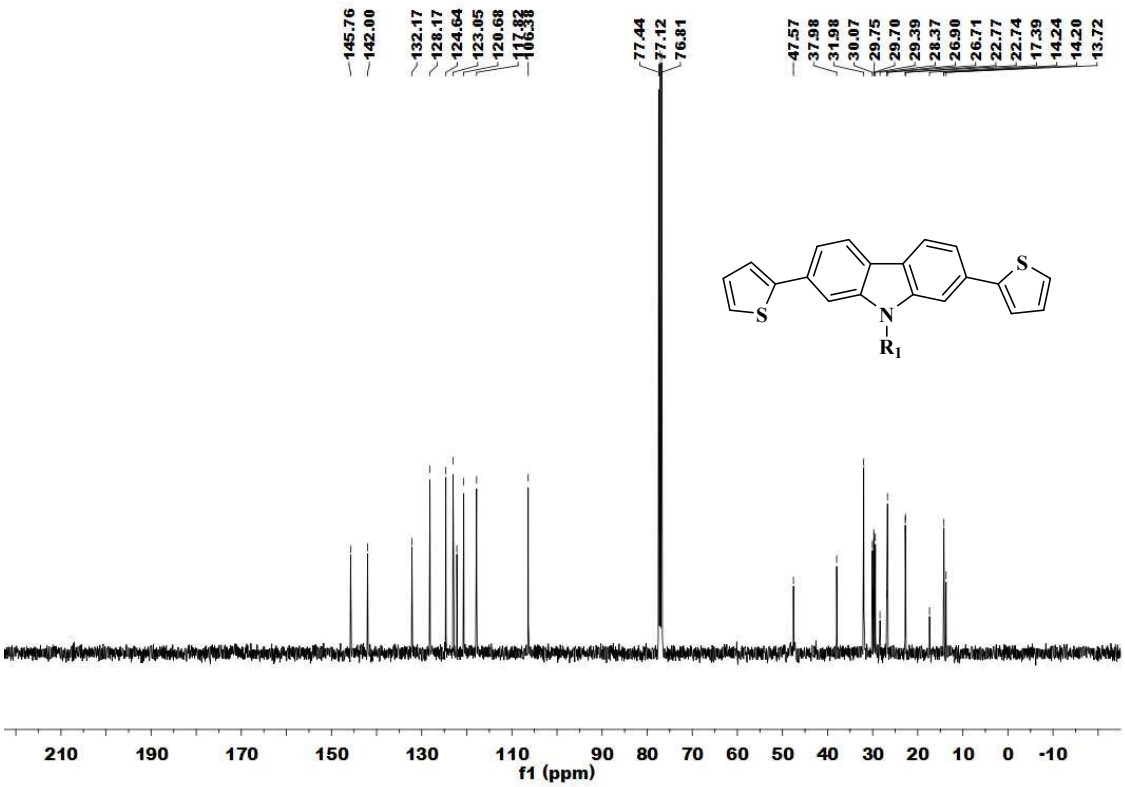


Figure S17 ^{13}C NMR spectra of compound **6**

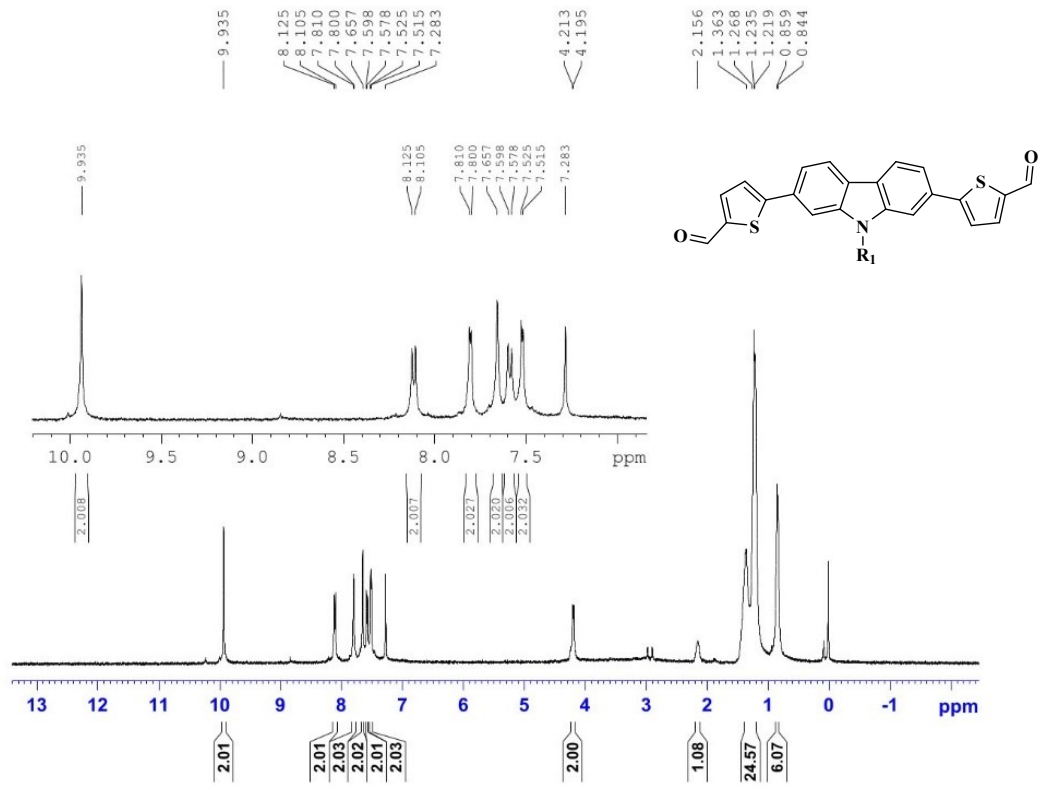


Figure S18 ^{1}H NMR spectra of compound **7**

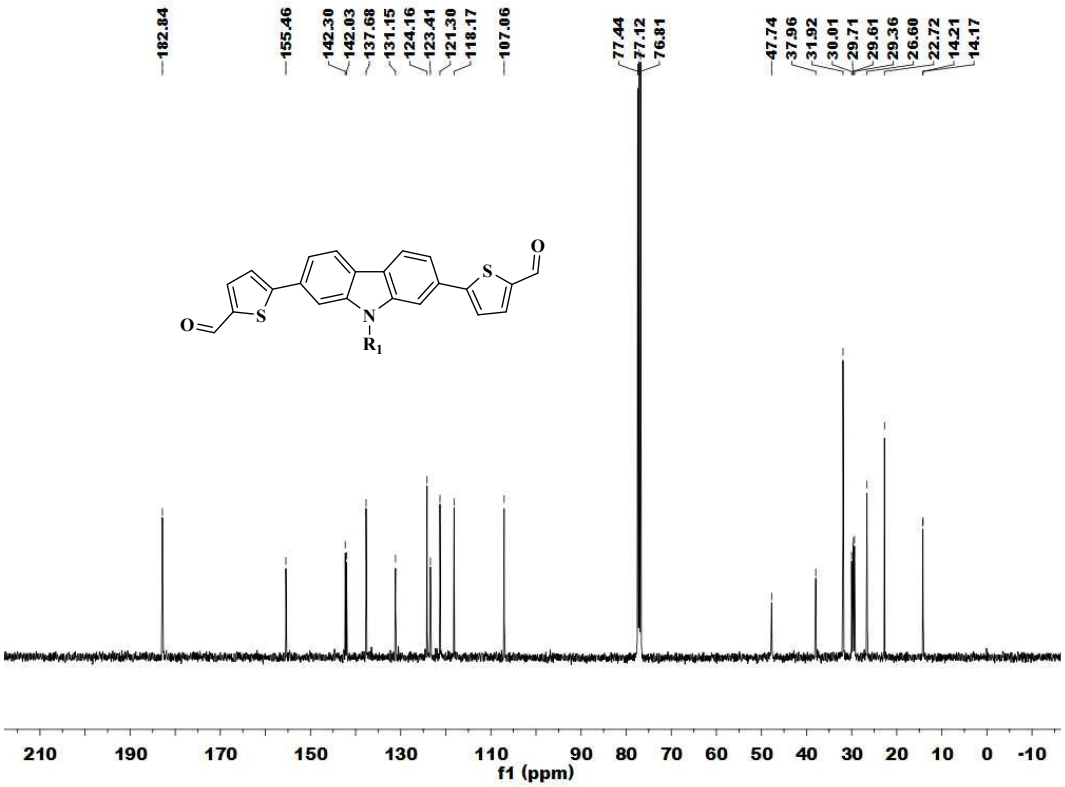


Figure S19 ^{13}C NMR spectra of compound **7**

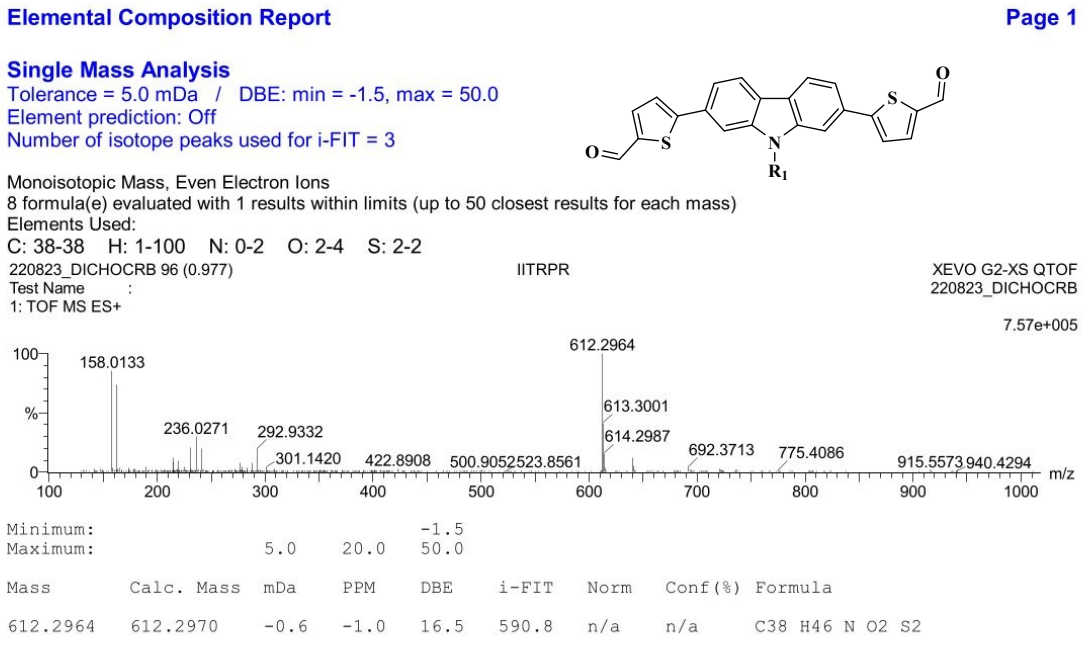


Figure S20 HR-MS data of compound **7**

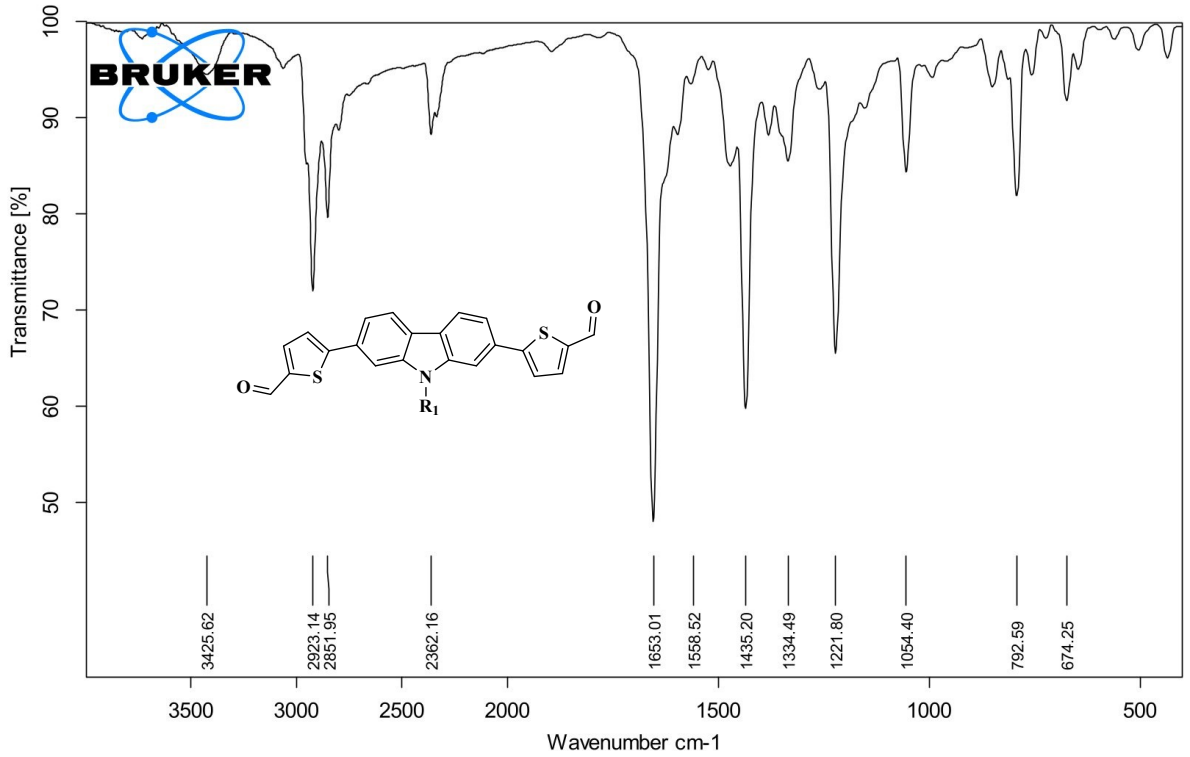


Figure S21 IR spectrum (KBr pellet) of compound **7**

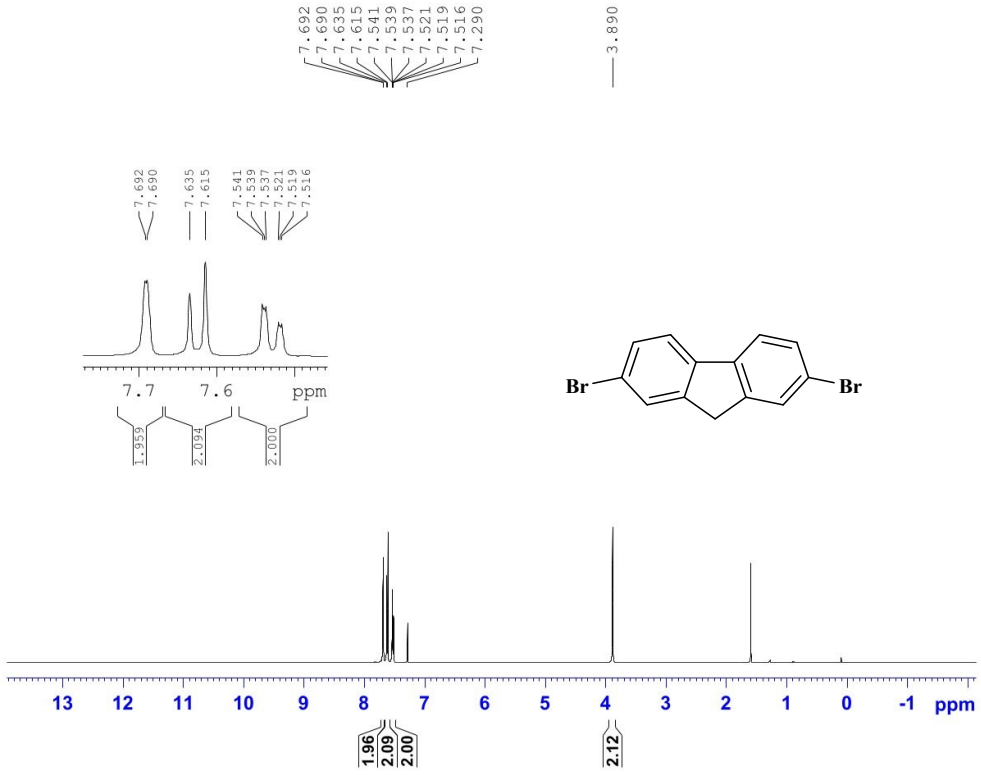


Figure S22 [1]H NMR spectra of compound **S3**

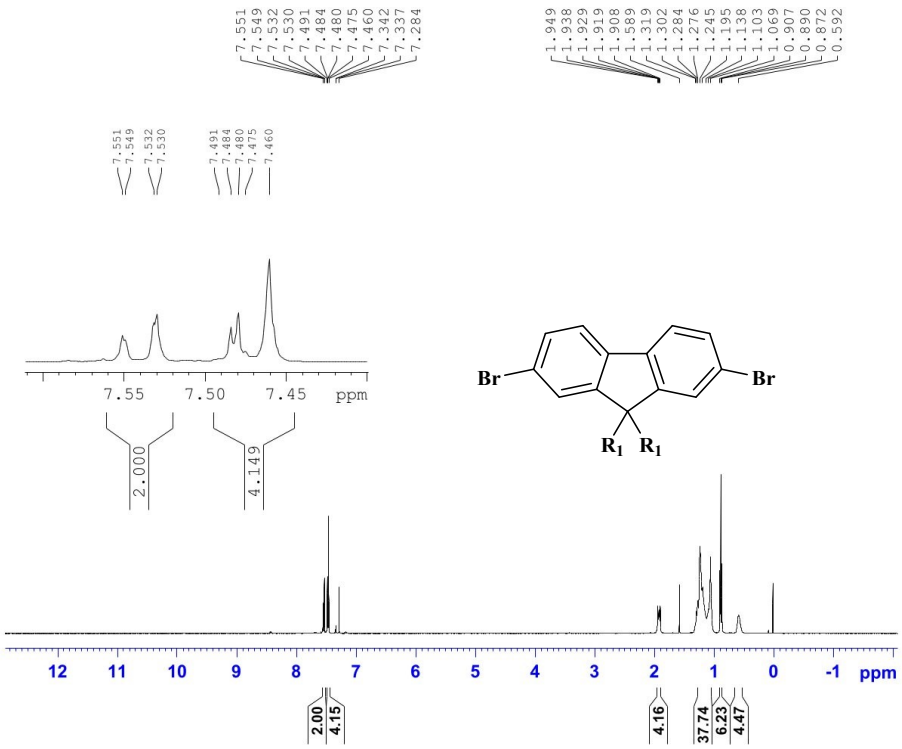


Figure S**23** [1]H NMR spectra of compound **8**

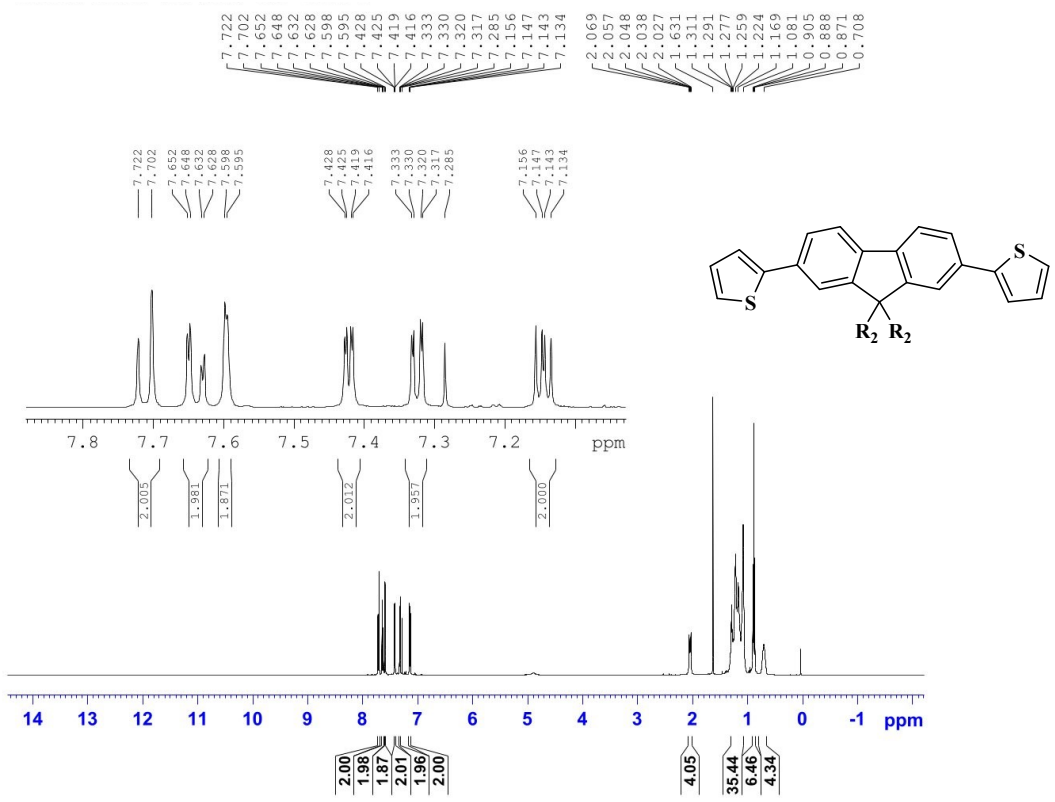


Figure S24 [1]H NMR spectra of compound **9**

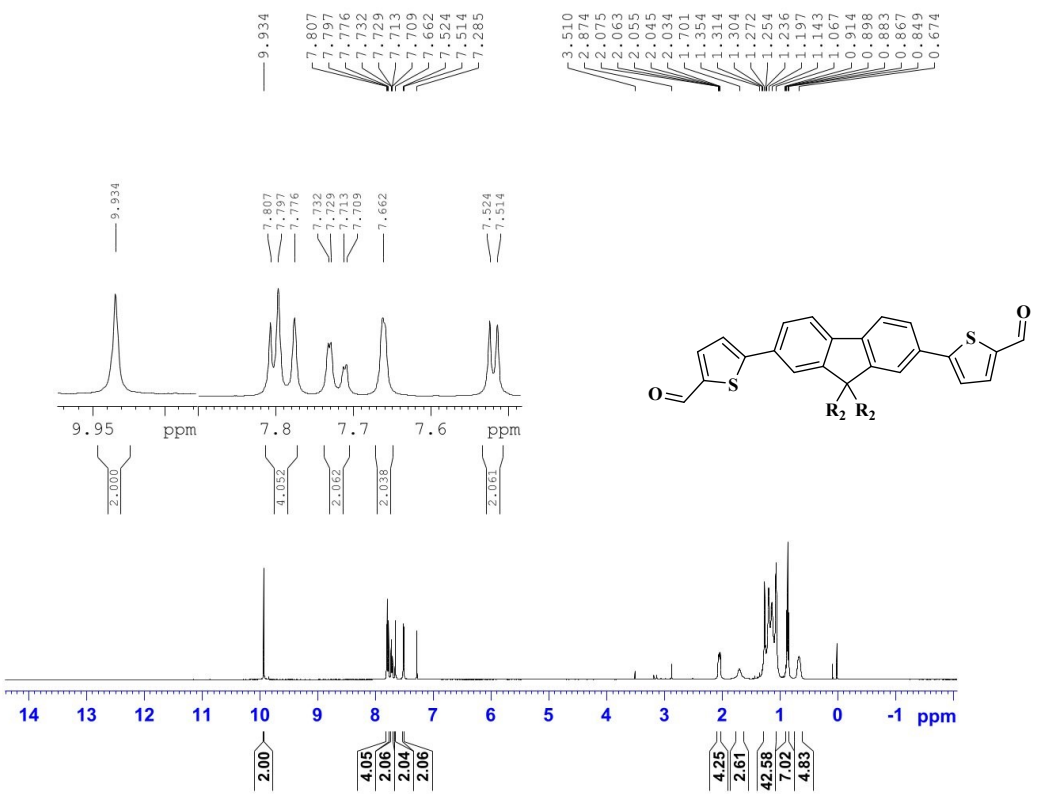


Figure S25 [1]H NMR spectra of compound **10**

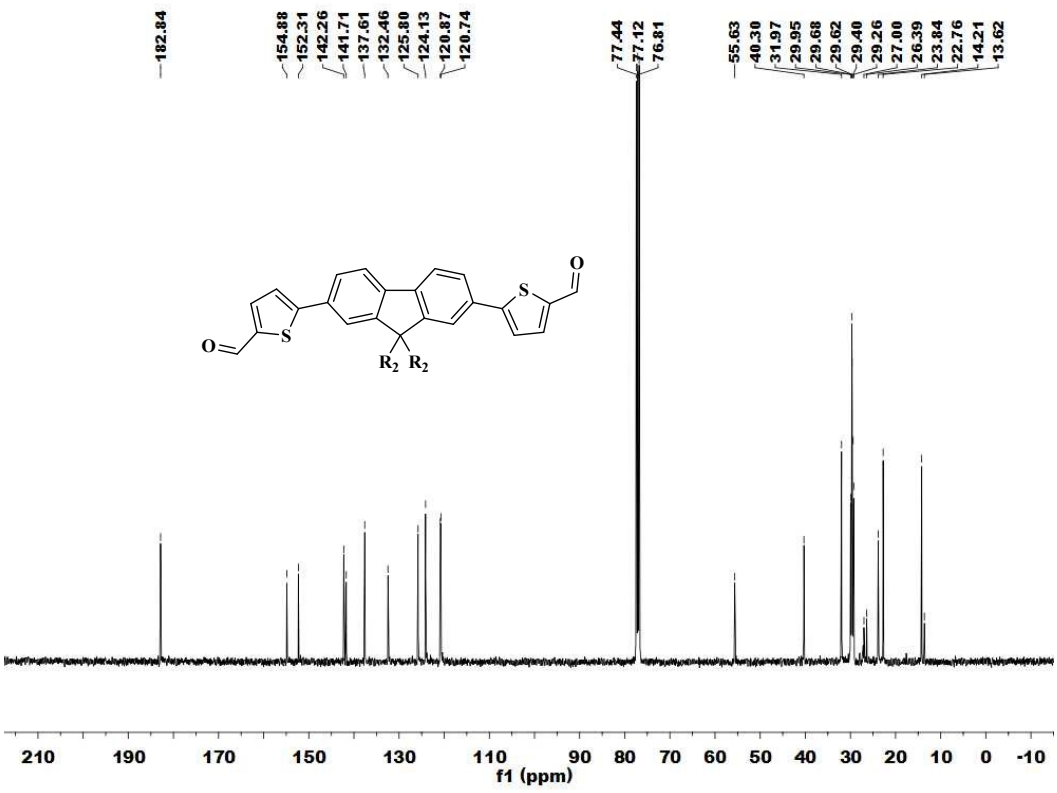


Figure S26 [13]C NMR spectra of compound **10**

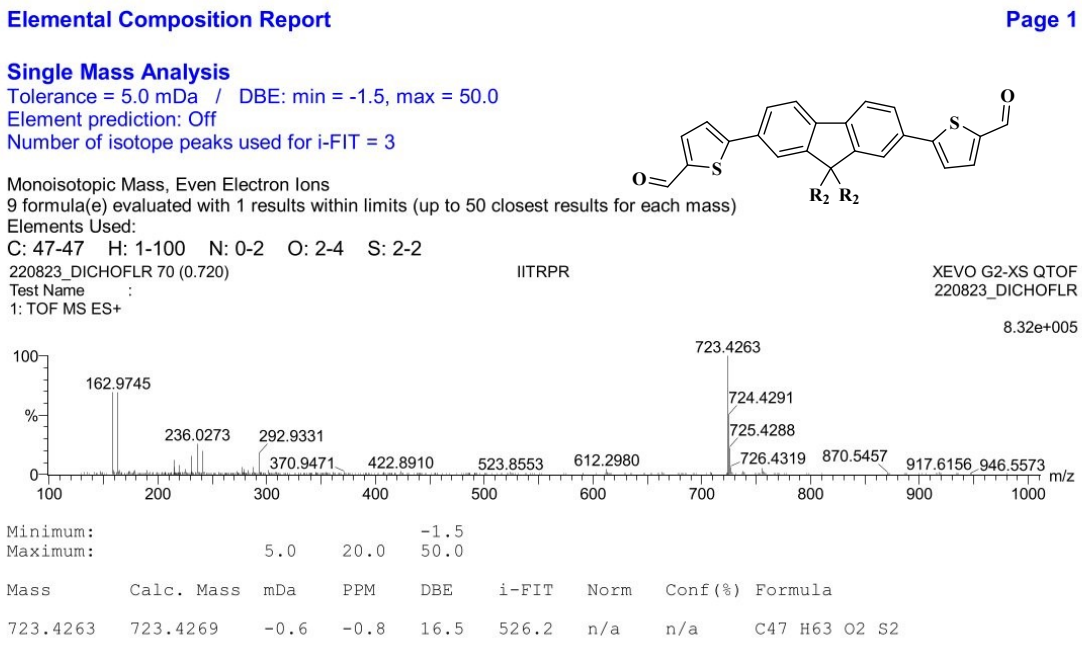


Figure S27 HR-MS data of compound **10**

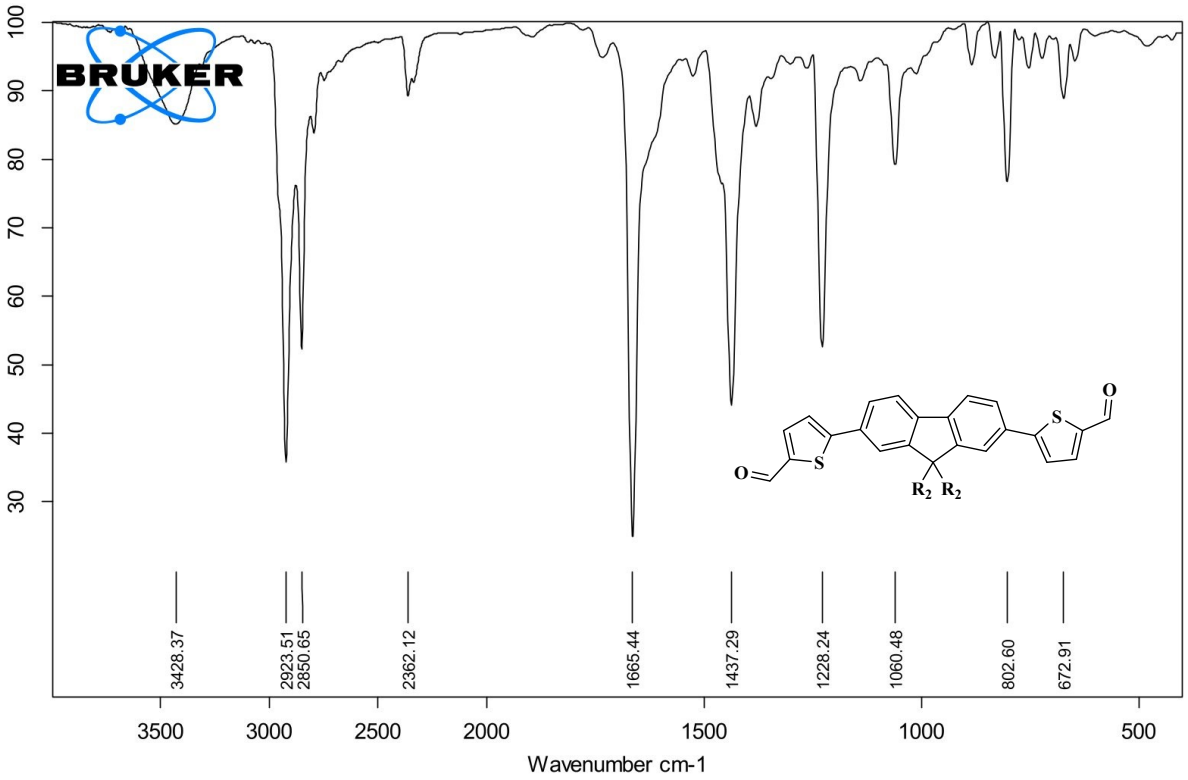


Figure S28 IR spectrum (KBr pellet) of compound **10**

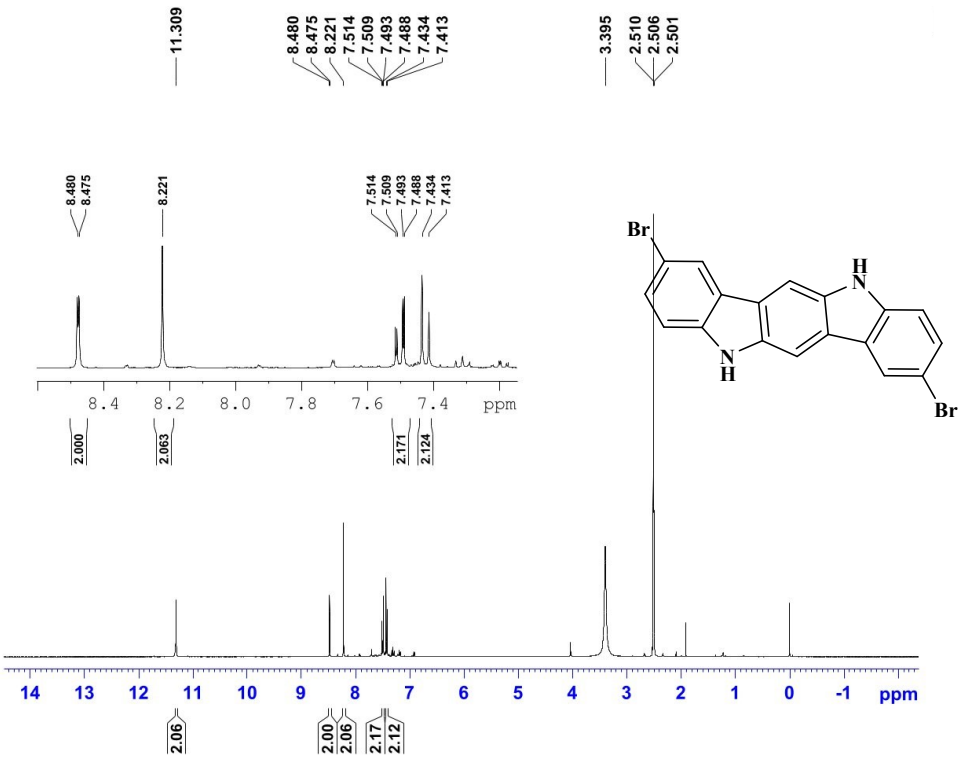


Figure S29 ^{1}H NMR spectra of compound **S5**

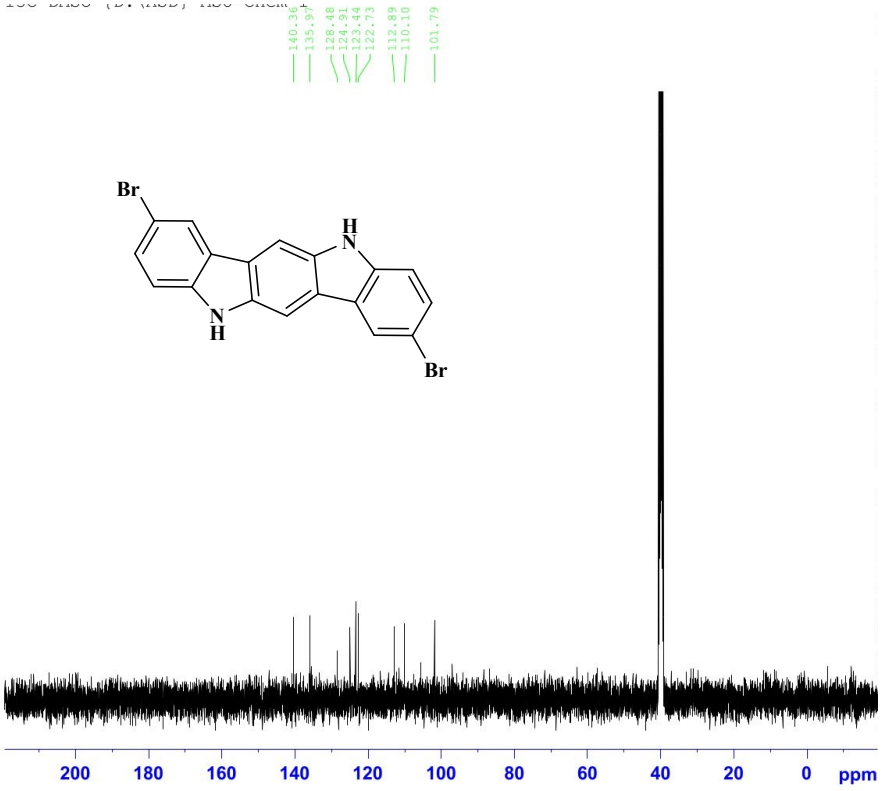


Figure S30 ^{13}C NMR spectra of compound **S5**

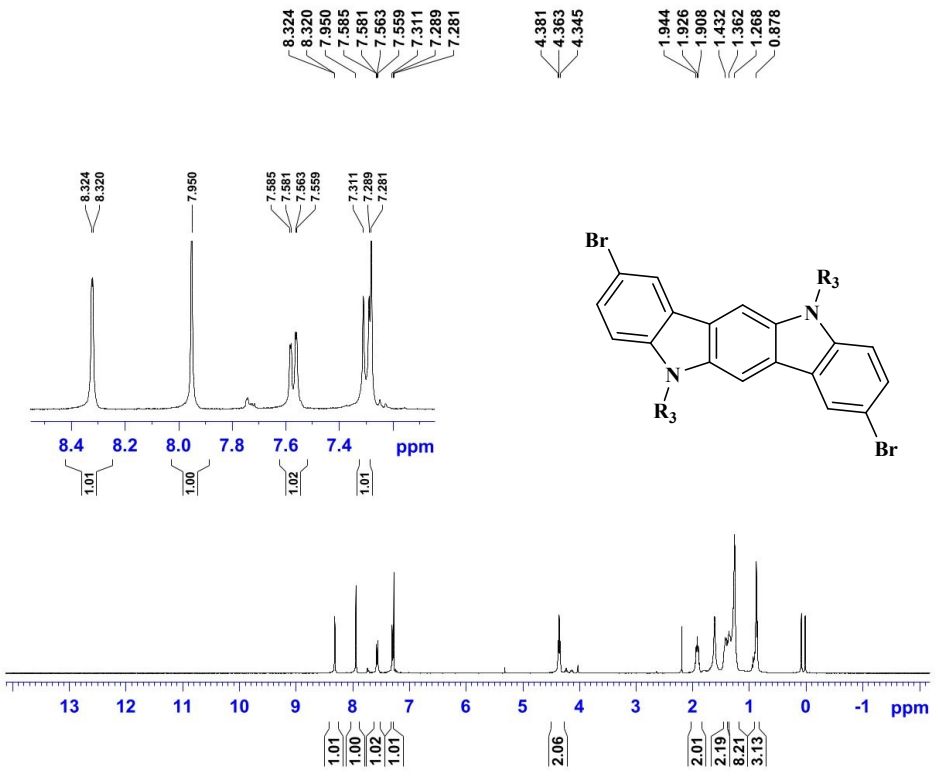


Figure S31 ^{1}H NMR spectra of compound **11**

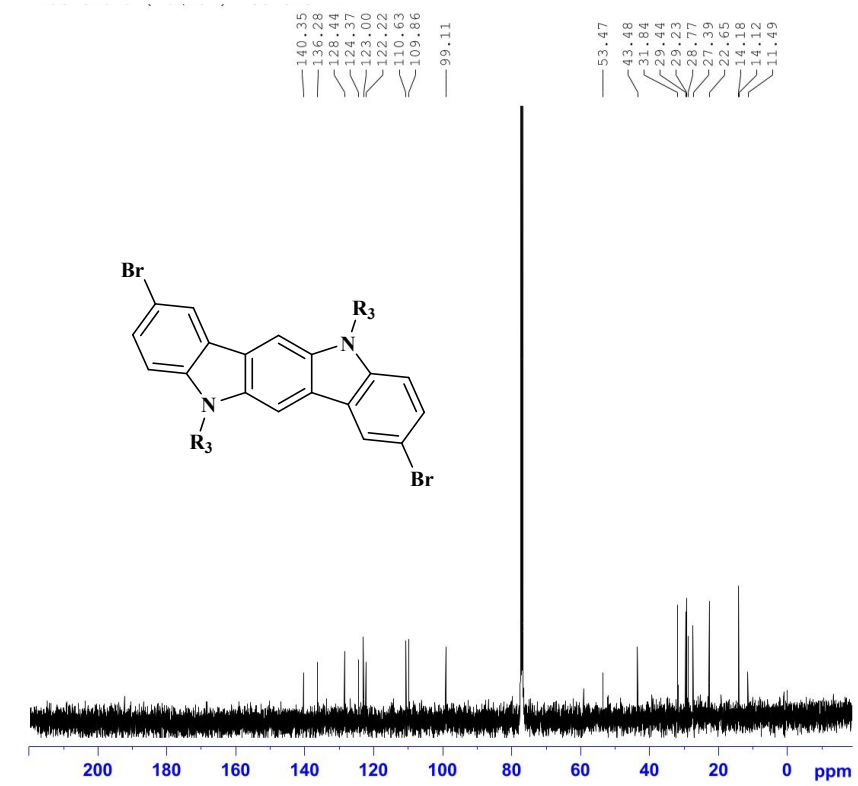


Figure S32 ^{13}C NMR spectra of compound **11**

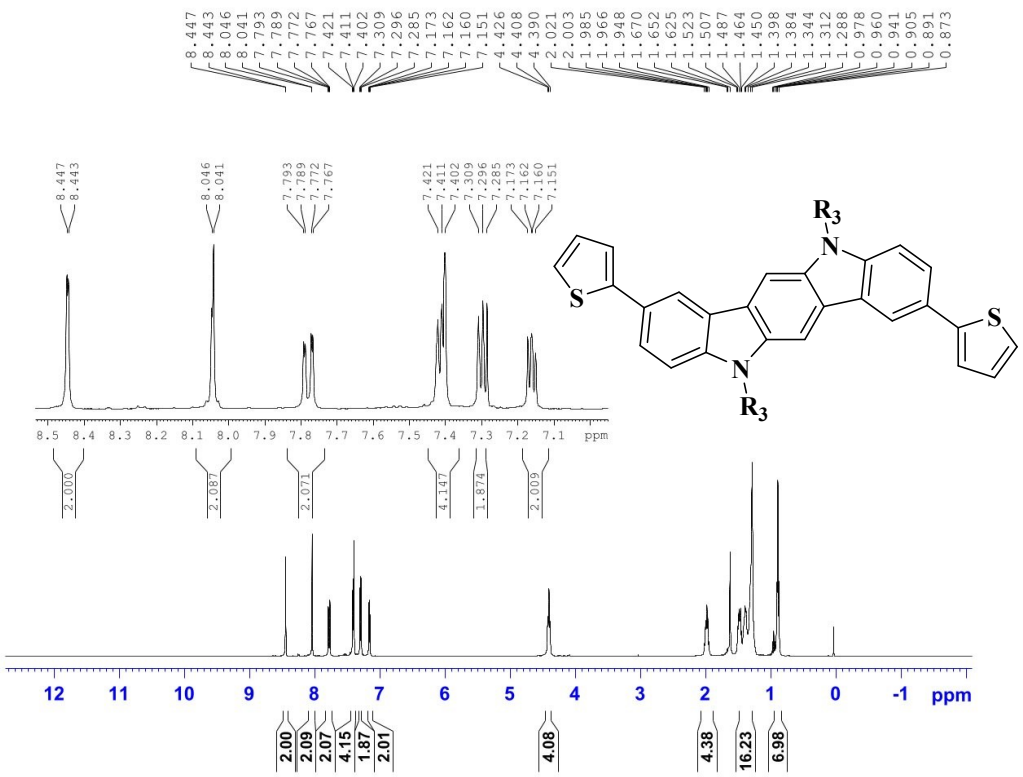


Figure S33 [1]H NMR spectra of compound **12**

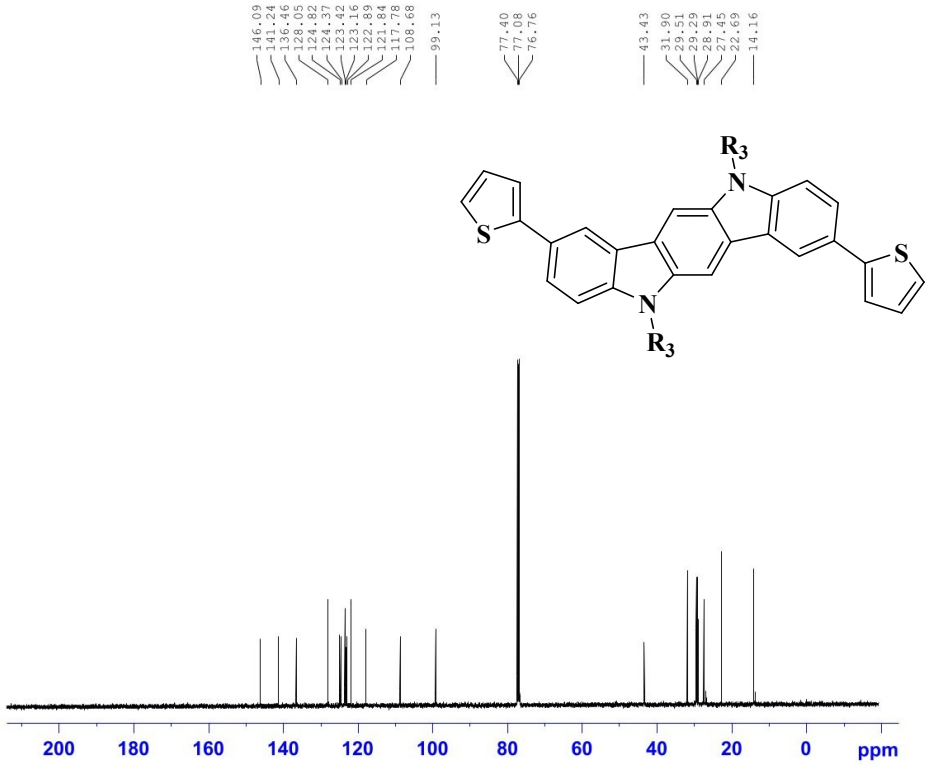


Figure S34 [13]C NMR spectra of compound **12**

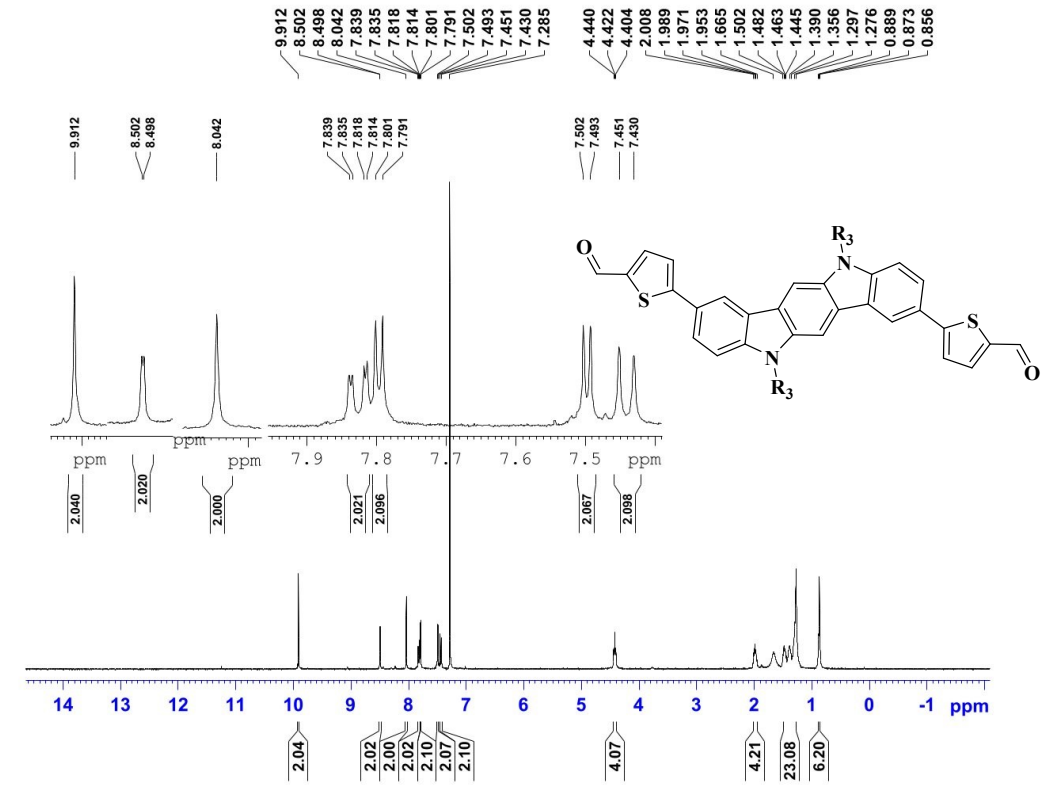


Figure S35 ^{1}H NMR spectra of compound **13**

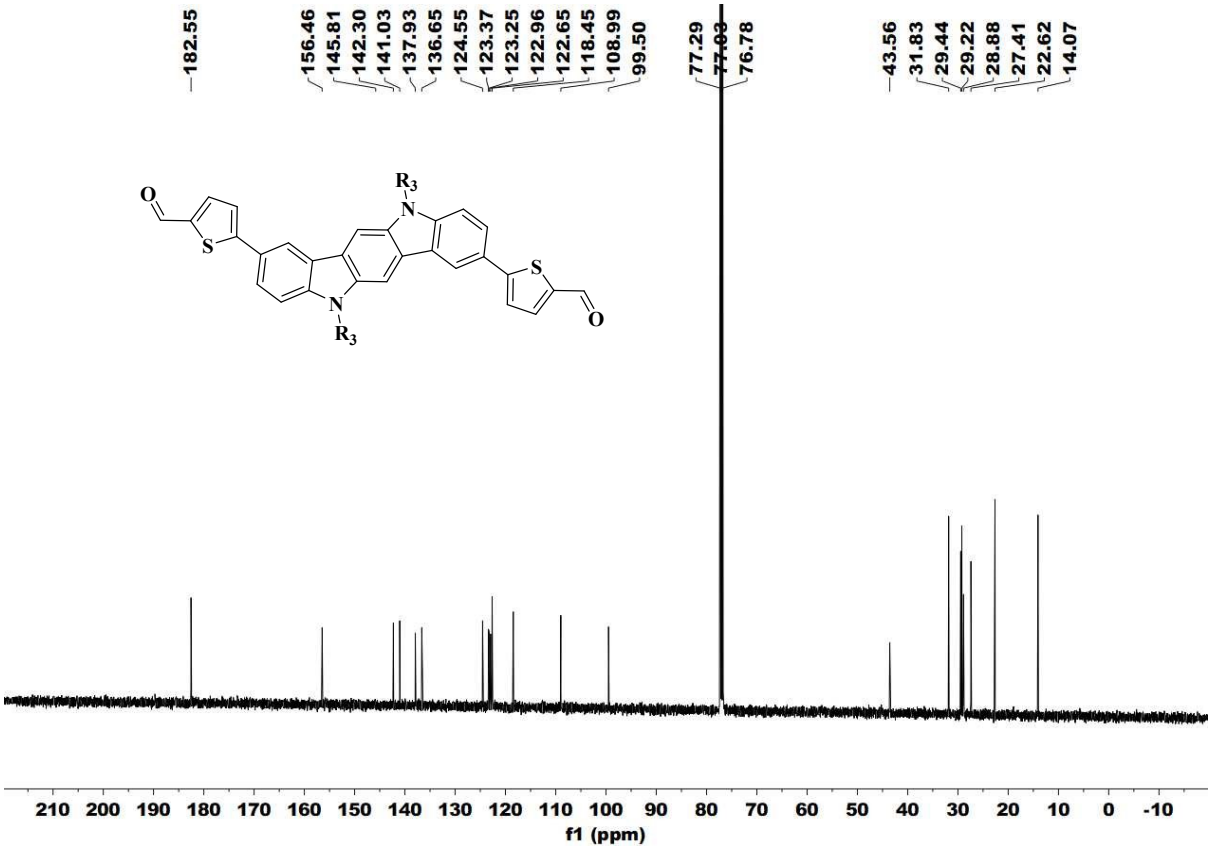


Figure S36 ^{13}C NMR spectra of compound **13**

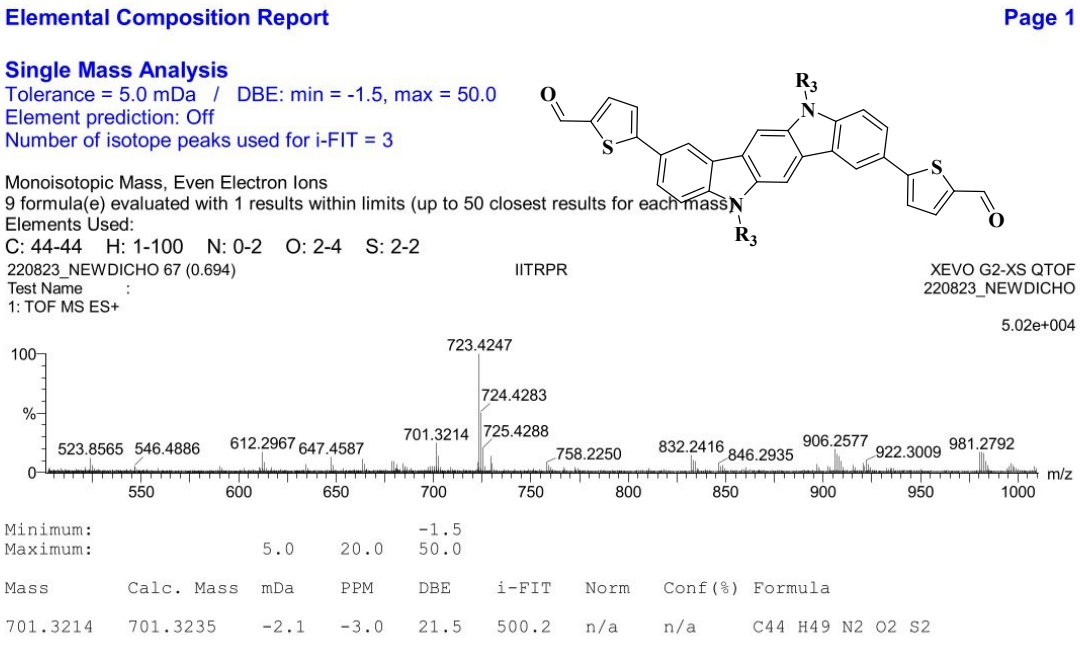


Figure S37 HR-MS data of compound **13**

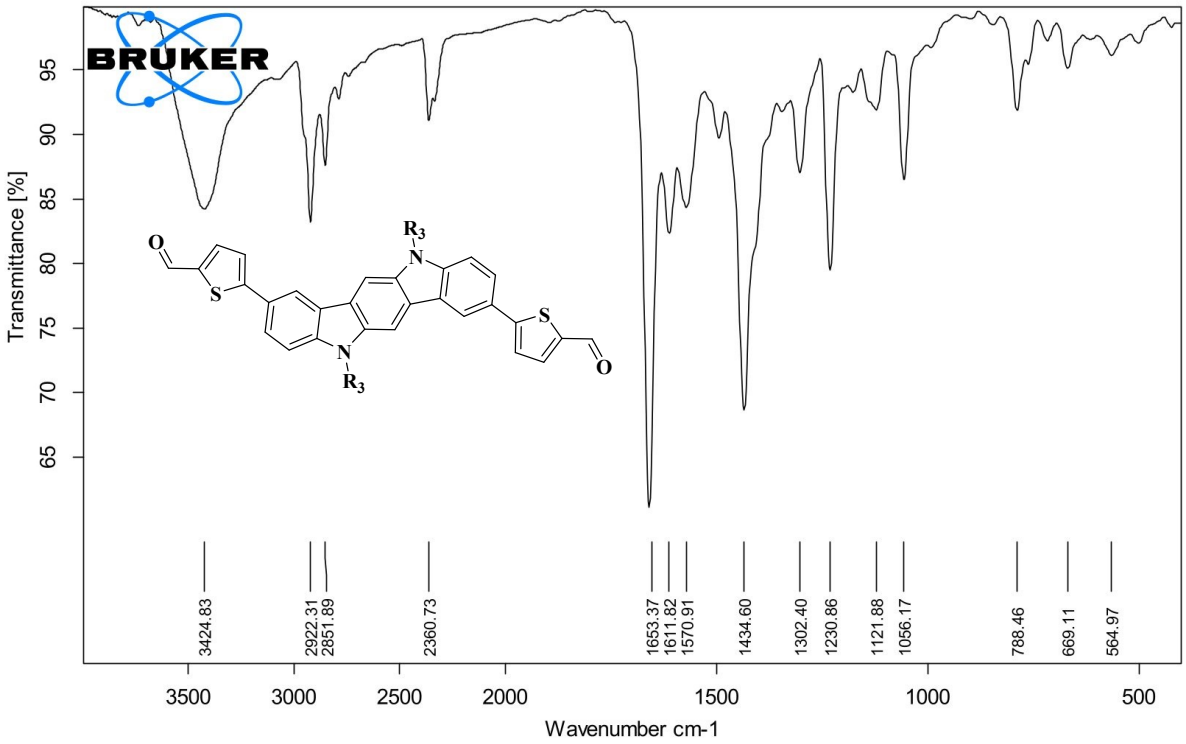


Figure S38 IR spectrum (KBr pellet) of compound **13**

Spectral data and GPC analysis data of polymers

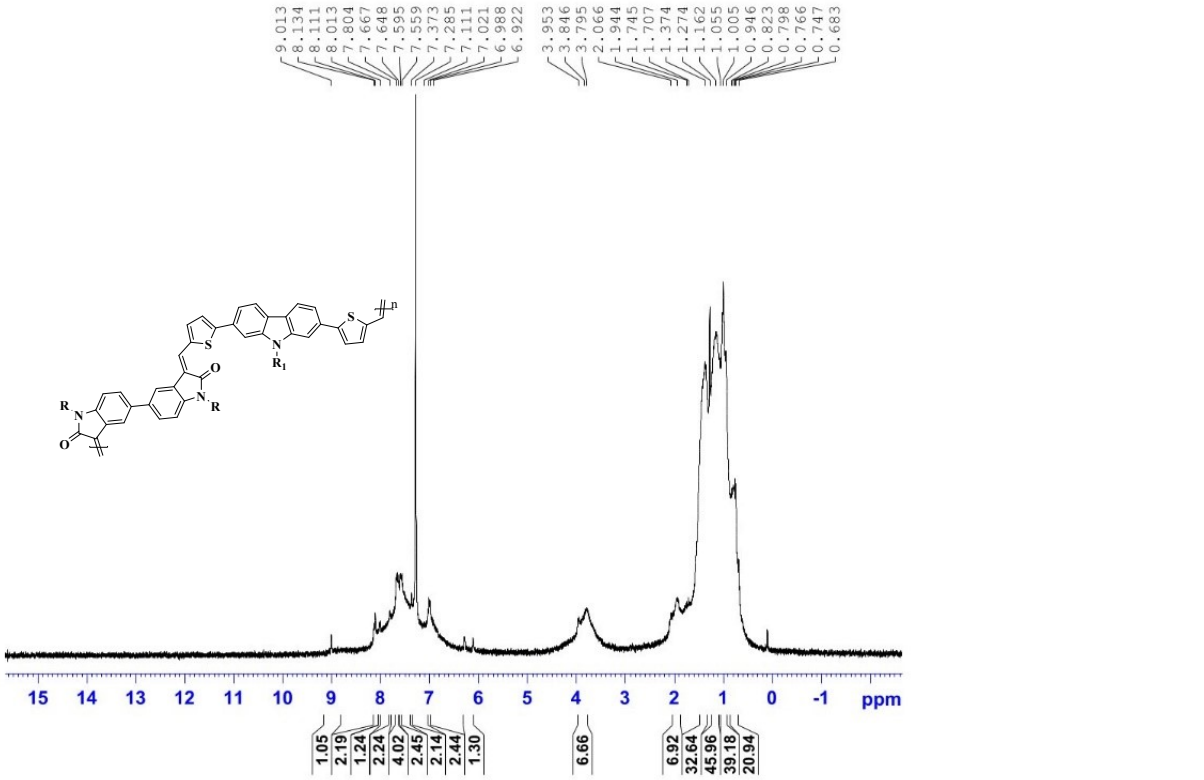


Figure S39 [1]H NMR spectra of polymer **ACRBI**

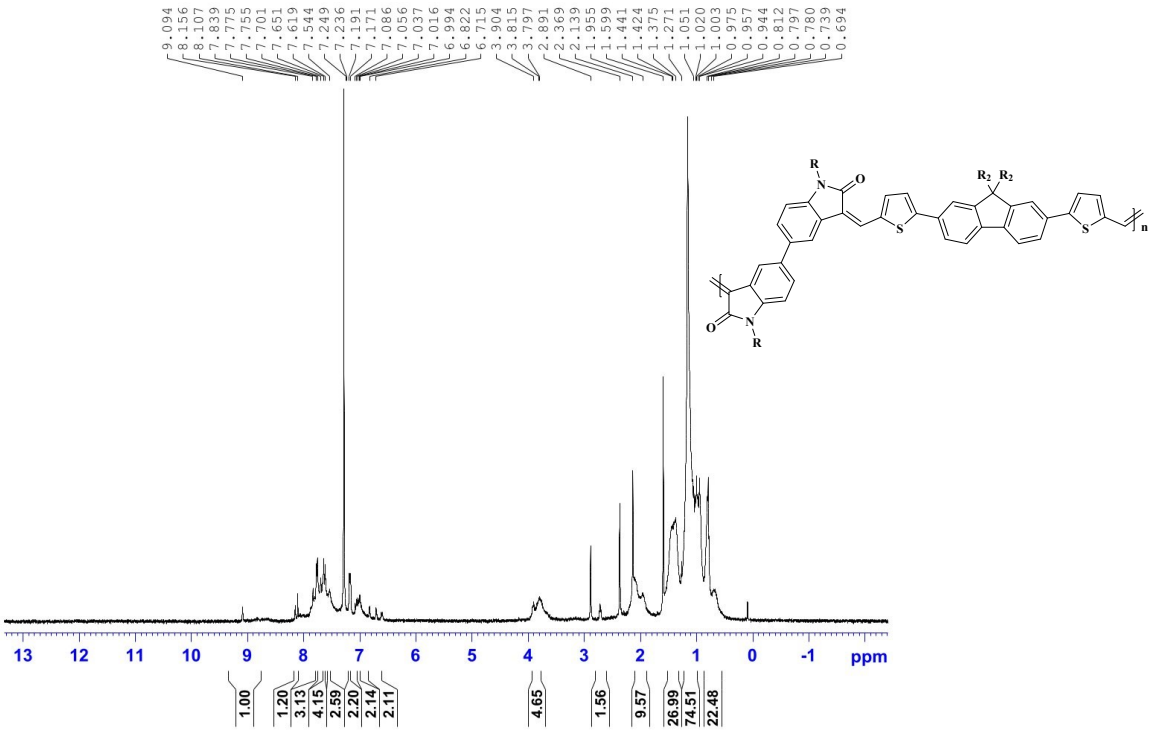


Figure S40 [1]H NMR spectra of polymer **AFRBI**

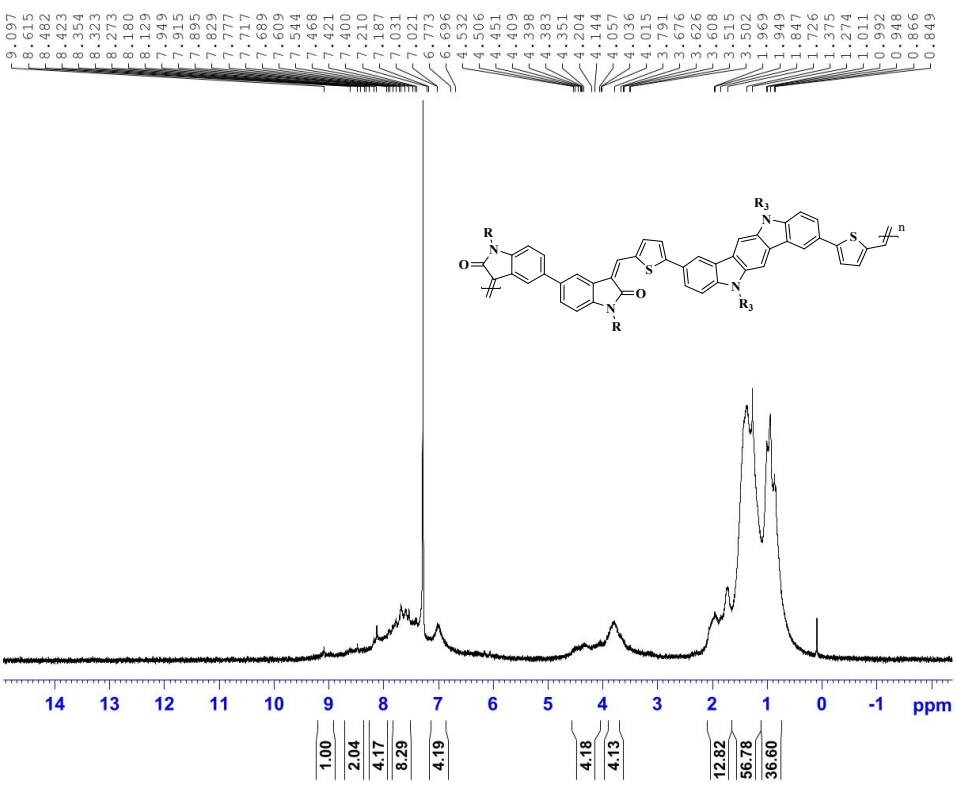


Figure S41 ^{1}H NMR spectra of polymer **AICRBI**

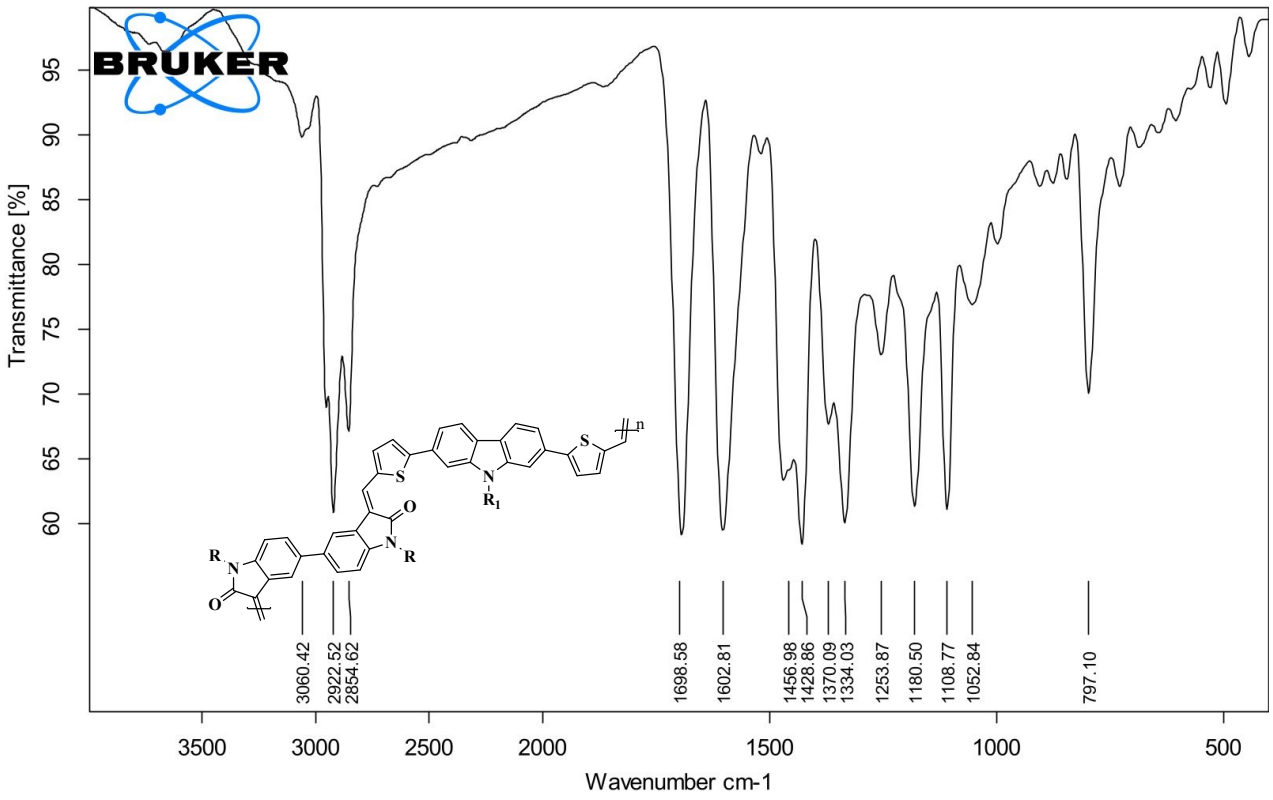


Figure S42: IR spectrum (KBr pellet) of compound **ACRBI**

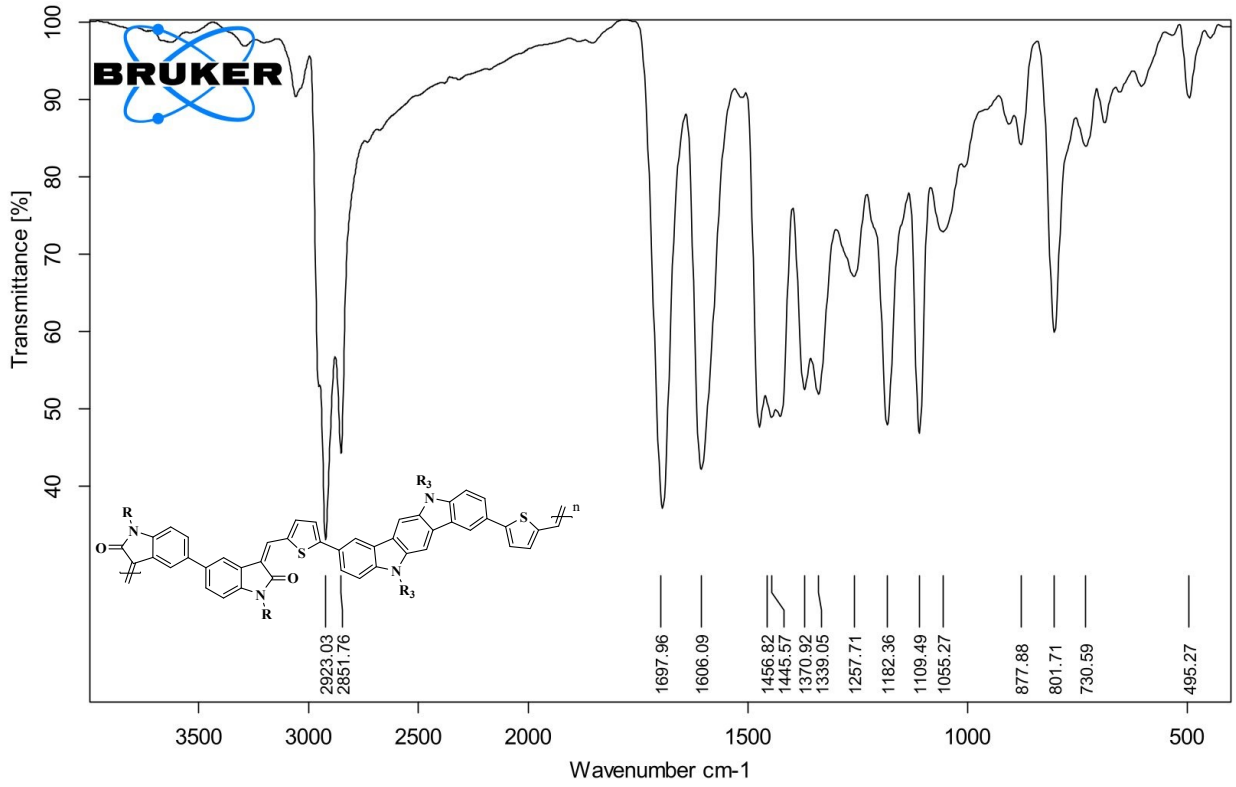


Figure S43 IR spectrum (KBr pellet) of compound **AFRBI**

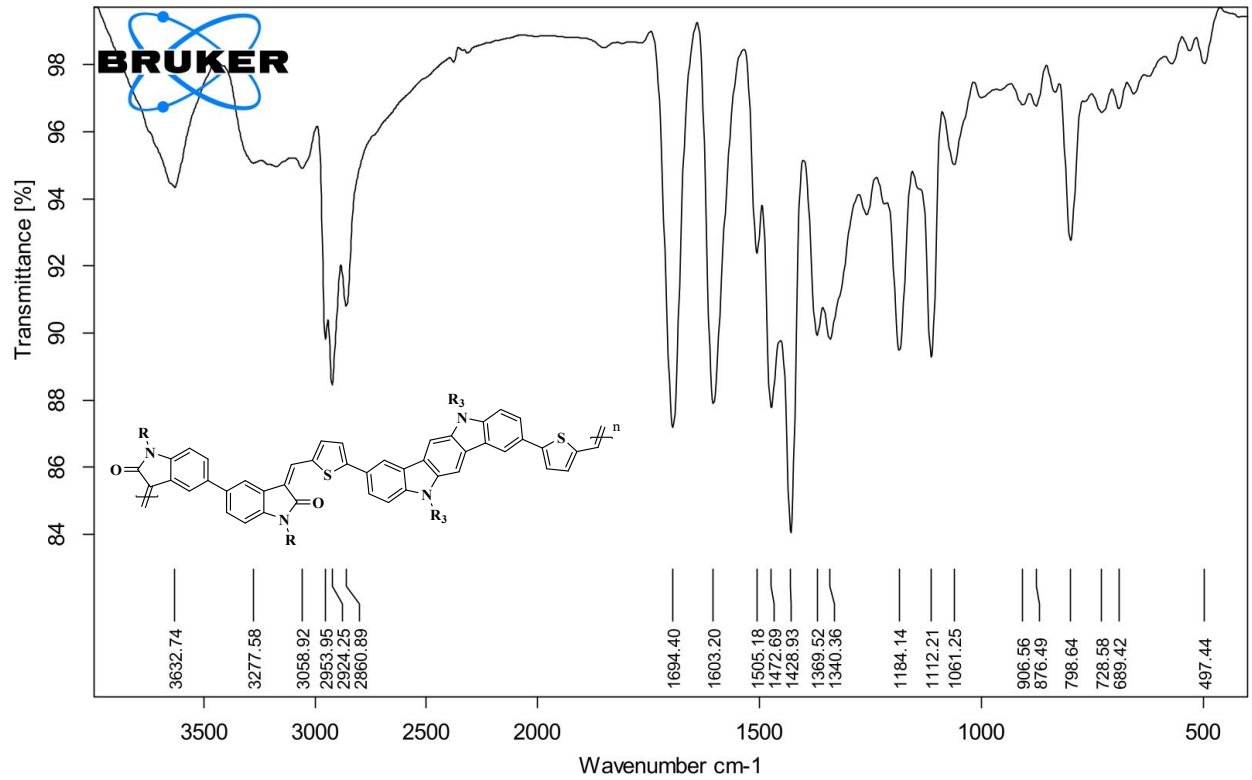
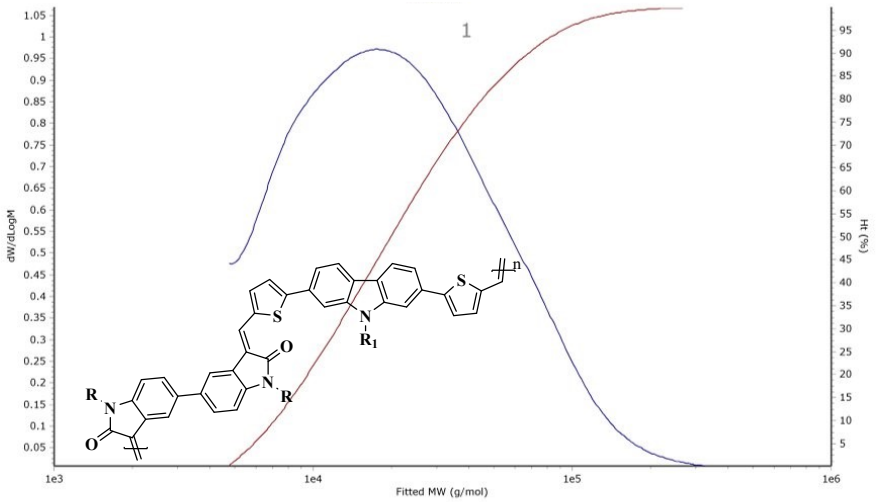


Figure S44 IR spectrum (KBr pellet) of compound **AICRBI**



Results

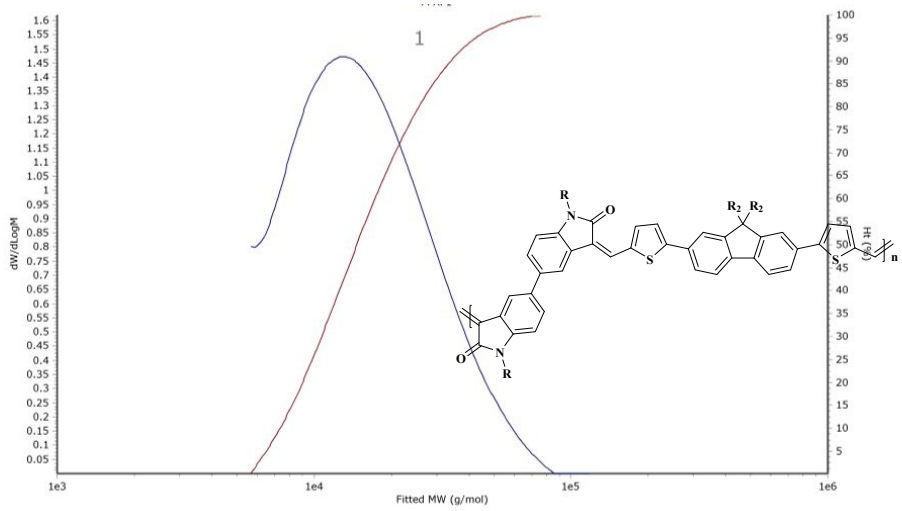
Analysed by
Comments

Applied Chem at 17:25:25 on 11 April 2023

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	18782	15422	30751	63503	109874	57685	1.994

Figure S45 GPC Analysis report of polymer **ACRBI**



Results

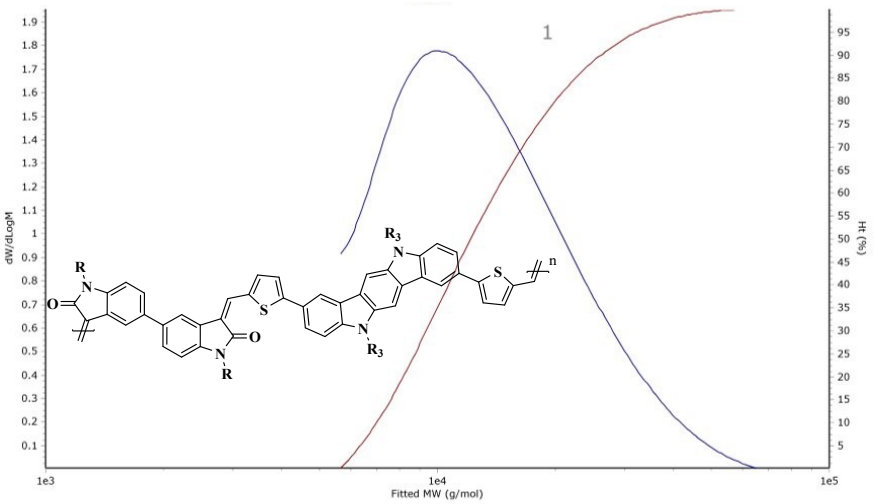
Analysed by
Comments

Applied Chem at 17:12:20 on 11 April 2023

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	13256	13235	18238	25824	34902	24567	1.378

Figure S46 GPC Analysis report of polymer **AFRBI**



Results

Analysed by: Applied Chem at 16:54:36 on 11 April 2023

Comments

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	10184	11556	14755	19617	25755	18787	1.277

Figure S47 GPC Analysis report of polymer **AICRBI**

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