Synthesis and Study of Donor-Acceptor Conjugated Polymers based on Dithienopyrrolobenzothiadiazole unit *via* Metal Free Aldol Condensation Polymerization Strategy and their SCLC Hole Mobilities

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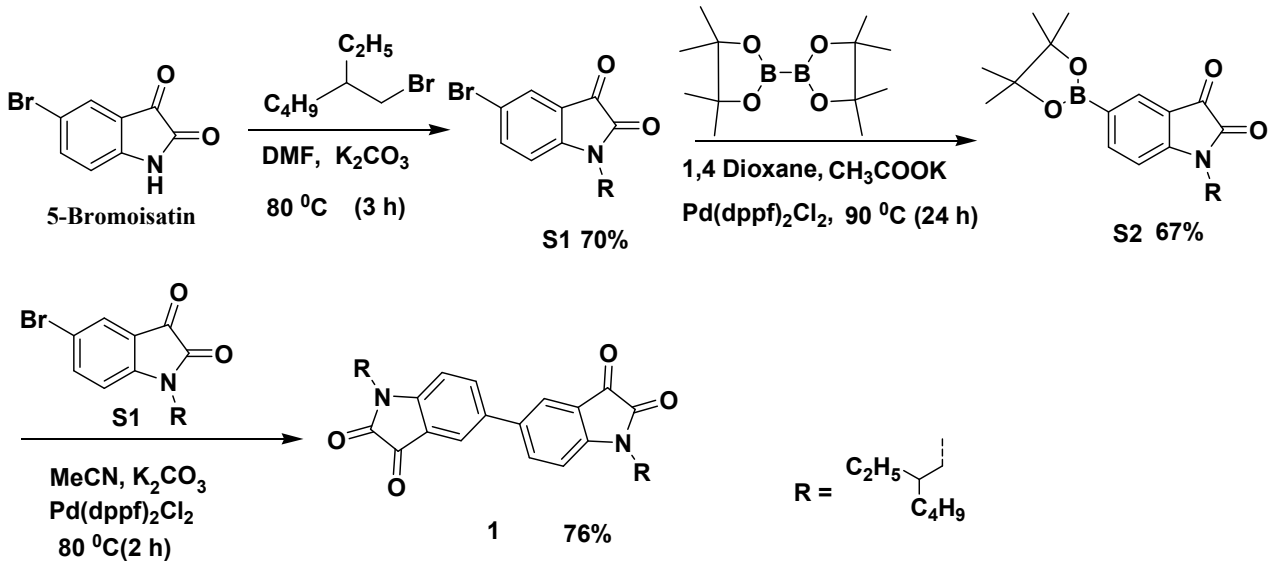
CONTENTS

Materials and Instrumentation

All the chemical were reagent grade and used as it was purchased. Moisture-sensitive reaction were carried out using dry solvents in an inert environment of dry nitrogen. Reaction were 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-D^6. High resolution mass spectra (HRMS) were recorded on Xevo G2-XS QTOF Mass Spectrometer.

Synthesis of precursor compounds 1, 3, 5 and 7

Synthesis of 1,1'-bis(2-ethylhexyl)-[5,5'-biindoline]-2,2',3,3'-tetraone (1)



Scheme S1 Synthesis of compound **1** from 5-bromoisatin

Compound **1** was synthesized according to the modified literature procedure (Scheme 1).[1,2]

Synthesis of 5-bromo-1-(2-ethylhexyl)indoline-2,3-dione (**S1**)

Under nitrogen atmosphere, 5-bromoisatin (2.0 g, 8.84 mmol) and anhydrous potassium carbonate (5.492 g, 39.8 mmol) were dissolved in dry DMF (18 mL) and heated for 10 minutes at 50 ^oC. After adding ethylhexyl bromide (2.73 mL; 15.4 mmol), the reaction mixture was stirred at 80 ^oC for 4 hours. The reaction mixture was poured into 180 mL of H_2O and then extracted with ethyl acetate. The organic fraction was washed with brine and water and dried over anhydrous Na_2SO_4. A crude product was obtained as a dark crimson oil, which was further purified by column chromatography using 5% ethyl acetate in petroleum ether.

Compound **S1**: Orange red solid (2.45g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.690-7.713 (dd, J_1= 7.2 Hz, J_2= 2 Hz, 2H), 6.796-6.818 (dd, 1H, J_1 = 8 Hz, J_2 = 1.6 Hz), 3.556-3.624 (t, 2H), 1.722-1.806 (s, 1H), 1.281-1.430 (m, 8H), 0.898-0.958 (m, 6H). IR (KBr, cm^{-1}): 2959, 2927, 2864, 1732, 1605, 1471, 1467, 1438, 1326, 1182, 825, 711, 468.

Synthesis of 1-(2-ethylhexyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indoline-2,3-dione (**S2**)

In a dry two-neck round bottom flask, a mixture of 1,4 dioxane (20 mL), compound **S1** (1.0 g, 2.9 mmol), bis(pinacolato)diborane (1.12 g, 4.4 mmol), and potassium acetate (0.580 g, 5.9 mmol) was taken. After degassing for 30 minutes with sparging nitrogen, catalyst, $Pd(PPh_3)_2Cl_2$ (0.103 g, 0.14mmol) was added and the reaction mixture was heated at 100 °C for 24 hours under a nitrogen atmosphere. The reaction mixture was then poured into 200 mL of H_2O and the organic layer was extracted with ethyl acetate. The organic layer was washed with H_2O and brine, dried over anhydrous Na_2SO_4 and concentrated to obtain red oil as the crude product. The crude product was further purified by column chromatography using 20% ethyl acetate in petroleum ether to get red oil.

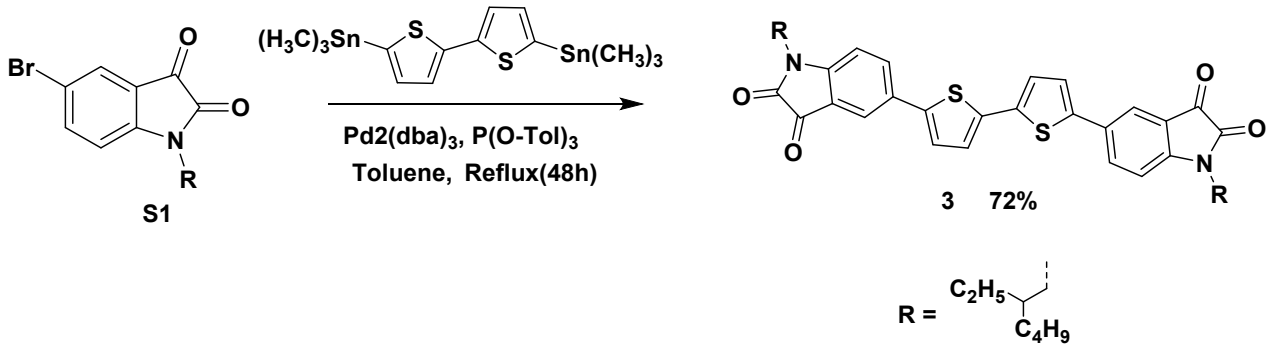
Compound **S2**: Orange red liquid (0.81g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.056-8.058 (d, J = 0.8 Hz, 1H), 8.007-8.030 (dd, J_1 = 8 Hz, J_2 = 1.2 Hz, 1H), 6.866-6.886 (d, J = 8 Hz, 1H), 3.610-3.638 (m, 2H), 1.777 (s, 1H), 1.347 (s, 12H), 1.273-1.327 (m, 8H) 0.874-0.954 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.34, 158.71, 153.53, 145.05, 131.88, 117.10, 109.73, 84.27, 44.40, 37.33, 30.52, 28.56, 25.02, 23.89, 22.99, 14.06, 10.55.

Synthesis of 1,1'-bis(2-ethylhexyl)-[5,5'-biindoline]-2,2',3,3'-tetraone (**1**)

Compound **S2** (0.860 g, 2.5 mmol) and compound **S1** (1.10 g, 2.88mmol) were dissolved in 45 mL acetonitrile and the reaction mixture was stirred for 5 minutes. 2 M K_2CO_3 (0.84 g, 6.1 mmol) solution was added to the reaction mixture, followed by 30 minutes of nitrogen purging. The catalyst, $Pd(dppf)_2Cl_2$ (0.10 g, 0.147 mmol) was added and the reaction mixture was heated at reflux temperature for 6 hours. After the completion of the reaction, 200 mL of water was added and the product was extracted with ethyl acetate. The organic layers are washed with saturated brine solution, then with water, and finally dried by adding anhydrous Na_2SO_4. After solvent evaporation, the crude product is further purified by column chromatography over silica gel using 30% ethyl acetate in petroleum ether as an eluent.

Compound **1**: Brown red solid (1.0 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.750-7.783 (m, 4H), 6.990-7.010 (d, J_1= 8 Hz, 2H), 3.652-3.682 (m, 4H), 1.844-1.873 (m, 2H), 1.264-1.456 (m, 16H), 0.916-0.989 (m, 12H). ^{13}C NMR (100MHz, $CDCl_3$): 183.43, 158.43, 150.89, 136.10, 134.89, 123.17, 118.16, 111.05, 44.59, 37.44, 30.61, 28.81, 28.66, 24.83, 23.87, 23.00, 14.02, 10.55. HRMS(ES^+): $C_{32}H_{41}N_2O_4$ requires 517.3066, found 517.3075.

Synthesis of 5,5'-([2,2'-bithiophene]-5,5'-diyl)bis(1-(2-ethylhexyl)indoline-2,3-dione) (3)



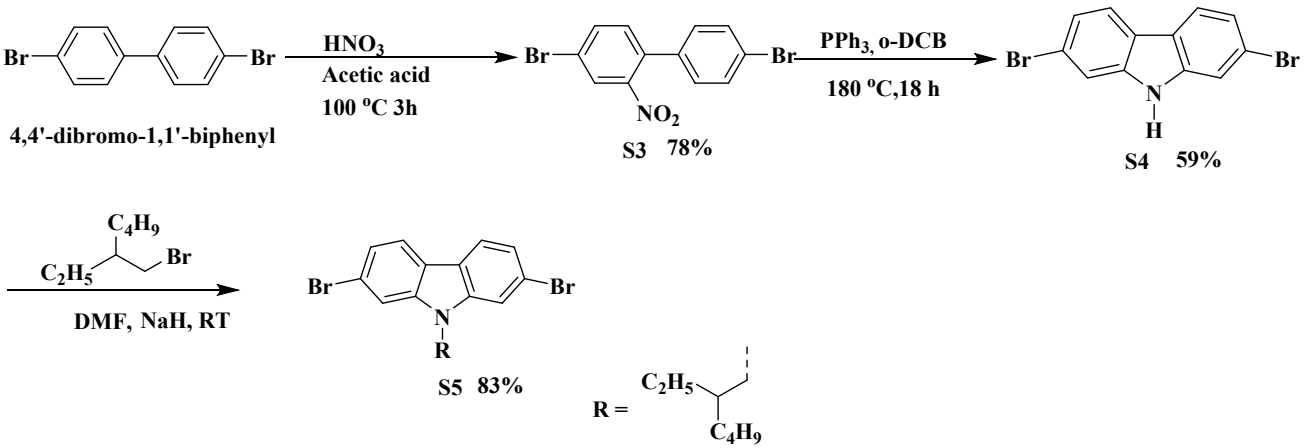
Scheme S2 Synthesis of compound **3** from compound **S1**

Compound **3** was synthesized according to the modified literature procedure.[3]

A mixture of compound **S1** (0.604 g, 1.79 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.400 g, 0.814 mmol), $Pd_2(dba)_3$ (0.074 g, 0.081mmol) and P(o-tol)$_3$ (0.318 g, 0.651 mmol) were taken 30 mL toluene in two-neck round bottom flask under nitrogen atmosphere. The mixture was stirred for 24 hours at 110 °C. After completion of the reaction, the reaction mixture was cooled down to room temperature and poured it in water followed by extraction with dichloromethane. The organic extract was washed with water and then dried with anhydrous Na_2SO_4. The crude product obtained after removal of the solvent under reduced pressure was further purified by silica gel chromatography using 40% DCM in petroleum ether as an eluent.

Compound **3:** Brown solid (0.600 g, 72.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.800-7.840 (m, 4H), 7.180-7.221 (dd, J_1= 12.8 Hz, J_2= 3.6 Hz, 4H), 6.926-6.946 (d, J_1= 8 Hz, 2H), 3.638-3.684 (m, 4H), 1.832-1.847 (m, 2H), 1.266-1.453 (m, 16H), 0.908-0.988 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): 183.45, 158.39, 150.34, 141.06, 136.70, 134.90, 130.04, 124.92, 124.13, 122.17, 118.05, 110.90, 44.58, 37.49, 30.64, 28.64, 24.00, 23.01, 14.04, 10.57. HRMS (ES^+): $C_{40}H_{45}N_2O_4S_2$ requires 681.2821, found 681.2816. IR (KBr, cm^{-1}): 3438, 2957, 2928, 2862, 1730, 1617, 1588, 1529, 1482, 1436, 1353, 1331, 1280, 1187, 1116, 1033, 832, 789, 715, 465.

Synthesis of 2,7-dibromo-9-(2-ethylhexyl)-9*H*-carbazole (S5)



Scheme S3 Synthesis of compound **S5** from 4,4'-dibromo-1,1'-biphenyl.

Synthesis of 4,4'-dibromo-2-nitro-1,1'-biphenyl **(S3)**

Compound **S3** was synthesized according to the modified literature procedure.[4–6]

In a 250 mL, two-neck 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 anhydrous Na_2SO_4. The compound **S3** was obtained by evaporation of solvent under reduced pressure.

Compound **S3:** Yellow solid (3.60 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.086 (s, 1H), 7.88-7.90 (d, J = 8.4, 2H), 7.587–7.591 (d, J = 1.6 Hz, 2H), 7.367-7.391 (dd, J_1 = 8 Hz, J_2 = 1.6 Hz, 2H).

Synthesis of 2,7-dibromocarbazole (**S4**)

Compound **S3** (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.

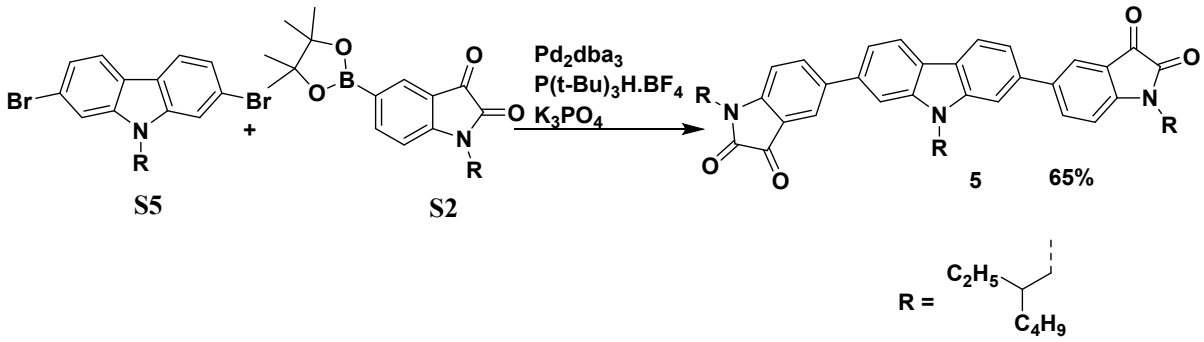
Compound **S4**: White solid (3.25 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.053-8.058 (d, J = 2 Hz, 1H), 7.770- 7.796 (dd, J = 8.4 Hz, J = 2 Hz, 1H), 7.598 (s, 1H), 7.577-7.582 (d, J = 2 Hz, 1H), 7.305-7.326 (d, J = 8.4 Hz, 1H), 7.171-7.192 (dd, J = 1.6 Hz, J = 6.4 Hz, 2H).

Synthesis of 2,7-dibromo-9-(2-ethylhexyl)-9*H*-carbazole **(S5)**

In a 100 mL, two-neck round bottom flask, compound **S4** (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, 2-ethylhexyl bromide (3.83 g, 19.84 mmol) was added and the reaction mixture was stirred at room temperature for further 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 anhydrous 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.

Compound **S5**: White solid (7.0 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.895-7.916 (d, J = 8.4 Hz, 2H), 7.520 (s, 2H), 7.344-7.368 (dd, J_1 = 8.2 Hz, J_2 = 1.2 Hz, 2H), 4.061-4.076 (d, J = 6 Hz, 2H), 1.995-2.097 (m, 1H), 1.239–1.406 (m, 24H), 0.864–0.912 (m, 6H).

Synthesis of 5,5'-(9-(2-ethylhexyl)-9*H*-carbazole-2,7-diyl)bis(1-(2-ethylhexyl)indoline-2,3-dione) (5)



Scheme S4 Synthesis of compound **5** from compound **S5**

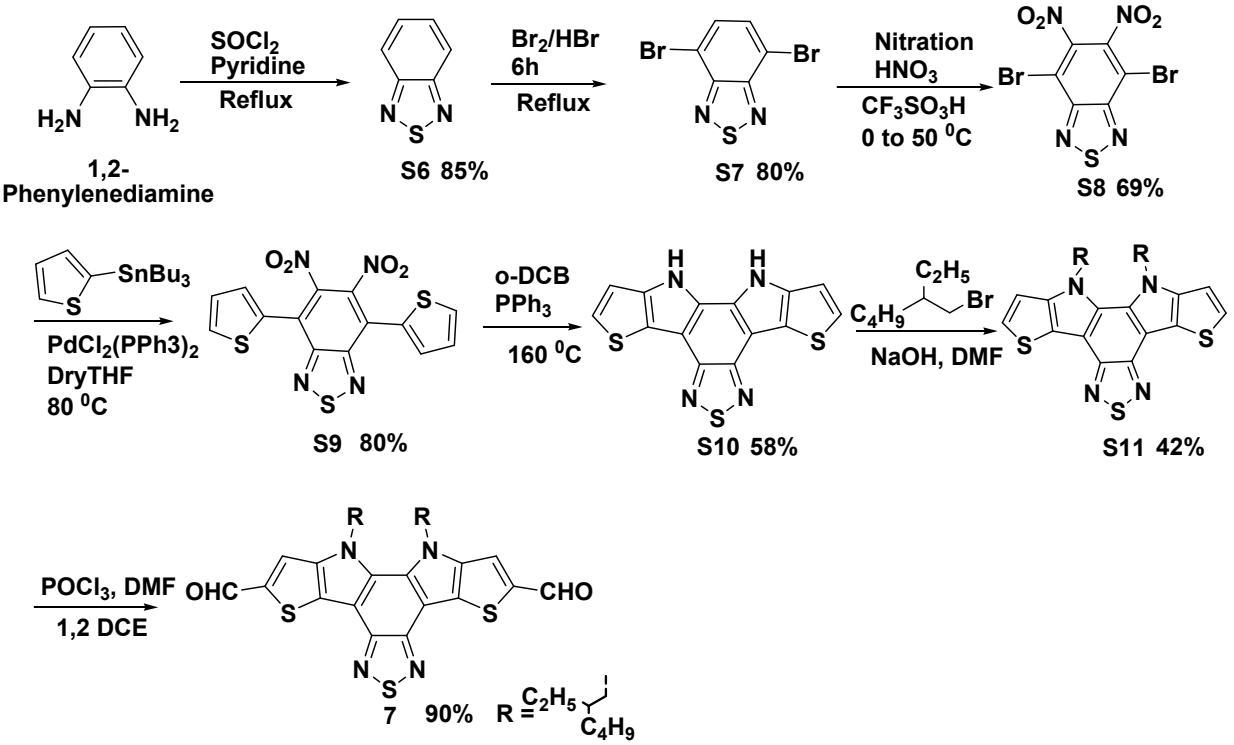
Compound **S5** was synthesized according to the modified literature procedure.[7]

Compound **S5** (0.500 g, 1.14 mmol), compound **S2** (0.951 g, 2.47 mmol) and $Pd_2(dba)_3$ (47 mg, 0.052 mmol), $P(t\text{-}Bu)_3.HBF_4$ (62 mg, 0.216 mmol) were taken into clean and dry two-neck round bottom flask under nitrogen atmosphere. THF (40 mL) and potassium phosphate (1.7 g, 2M) were added into the reaction mixture and the resultant mixture was stirred at 80 °C for 24 hours. After completion of reaction, the cold solution of the reaction mixture was poured into

water and the product was extracted with dichloromethane, dried over anhydrous Na_2SO_4, and purified by silica gel column chromatography using 50% ethyl acetate in petroleum ether.

Compound **5**: Dark red solid (0.60 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.163-8.183 (d, J= 8 Hz, 2H), 7.938-7.974 (m, 4H), 7.515 (s, 2H), 7.420-7.443 (dd, J = 8 Hz, J = 1.2 Hz, 2H), 7.014-7.034 (d, J = 8.0 Hz, 2H), 4.253-4.287 (m, 2H), 3.667-3.696 (m, 4H), 2.086 (s, 1H), 1.878– 1.893 (d, 2H), 1.270-1.464 (m, 32H), 0.879-1.009 (m, 22H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.83, 158.64, 150.36, 142.05, 138.08, 137.08, 137.04, 124.11, 122.15, 120.96, 118.19, 188.11, 110.79, 106.99, 47.57, 44.53, 39.38, 37.49, 30.96, 30.62, 28.66, 24.86, 24.02, 23.02, 14.05, 11.03, 10.60. HRMS (ES$^+$): $C_{52}H_{64}N_3O_4$ requires 794.4897, found 794.4905. IR (KBr, cm^{-1}): 3455, 3055, 2958, 2927, 2865, 1736, 1617, 1501, 1459, 1332, 1332, 1254, 1186, 1118.

Synthesis of 10,11-bis(2-ethylhexyl)-10,11-dihydro-[1,2,5]thiadiazolo[3,4-*e*]thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[3,2-*b*]indole-2,8-dicarbaldehyde from 1,2-phenylenediamine (7)



Scheme S5 Synthesis of compound **7**

Compound **7** was synthesized according to the modified literature procedure.[8]

Synthesis of 2,1,3-benzothiadiazole (**S6)**

In a three-neck, 500 mL round bottom flask, 1,2-phenylenediamine (5.0 g, 46.2 mmol), 150 mL of dichloromethane and triethylamine (19 g, 185 mmol) was added. The reaction mixture was stirred until total dissolution of the 1,2-phenylenediamine. To this stirred reaction mixture, a solution of $SOCl_2$ in a small amount of dichloromethane was added slowly and the resulting reaction mixture was refluxed for 4 hours. The solvent was removed in a rotary evaporator and resulting concentrate was diluted with 400 mL of water. The pH of the solution was adjusted to 2 by adding concentrated HCl. The crude product was purified by steam distillation. The steam distilled compound was extracted with 120 mL of dichloromethane, dried over anhydrous Na_2SO_4. The solvent was removed to get pure compound **S6**.

Compound **S6**: White solid (2.8 g, 45%); ^{1}H NMR (400 MHz, $CDCl_3$): 8.00−8.05 (dd, J_1 = 6.8 Hz, J_2 = 3.2 Hz, 1H), 7.59−7.63 (dd, J_1 = 6.8 Hz, J_2 = 3.2 Hz, 1H). ESI-Mass 135.90 [M+] (100.0%), 135.17 [M−1(-H)] (42.4%).

Synthesis of 4,7-dibromo-2,1,3-benzothiadiazole (**S7)**

In a 500 mL two-neck round bottom flask, compound **S6** (5.00 g, 37 mmol) and 75 mL of HBr (47%) were added and a reaction mixture was allowed to stir at 60 ^{o}C for 20 minutes. A solution of Br_2 (17.60 g, 110.16 mmol) in 50 mL of hydrobromic acid was added dropwise into the reaction mixture. After addition of the Br_2, the reaction mixture was refluxed for 6 hours. The reaction mixture was allowed to cool to room temperature and unreacted Br_2 was removed by addition of saturated solution of $NaHSO_3$. The crude product was filtered and washed with water and purified by silica gel column chromatography using 10% ethyl acetate in petroleum ether.

Compound **S7**: White solid (20.3 g, 94%); ^{1}H NMR (400 MHz, $CDCl_3$): 7.75 (s, 1H).

Synthesis of 4,7-dibromo-5,6-dinitro-2,1,3-benzothiadiazole (**S8)**

In a two-neck, 250 mL round bottom flask, fuming nitric acid (3.0 g; 47.6 mmol) was taken and chilled in an ice- salt bath under nitrogen atmosphere. Trifluoromethanesulfonic acid (30 g; 200 mmol) was added into this mixture and stirred it for 30 minutes. To this solution, compound **S7** (5.0 g; 17.0 mmol) was added in portion-wise over a period of 30 minutes to avoid exothermicity. The reaction mixture was further stirred at 50 °C for 8 hours, during which evolution of brisk red coloured gas was noted. After completion of the reaction, the reaction mixture was poured into ice water slowly, and then NaOH solution was added to neutralize the

excess acid. The resulting solution was filtered and rinsed with water. The pure product was obtained by recrystallization of crude product from ethanol.

Compound **S8**: Yellow beige solid (2.71 g, 83%); ^{1}H NMR (400 MHz, $CDCl_3$): No proton signals observed. ^{13}C NMR (100 MHz, $CDCl_3$): 151.3, 144.9, 110.3.

Synthesis of 5,6-dinitro-4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole (**S9)**

In a two-neck round bottom flask, compound **S8** (1.9 g; 4.95 mmol), $PdCl_2(PPh_3)_2$ (0.07 g; 0.1 mmol) and 20 mL of dried THF were degassed by purging nitrogen gas through the reaction mixture for 15 minutes. To the degassed reaction mixture, tri-*n*-butyl(thiophen-2-yl)stannane (4.25 g; 11.4 mmol) was added and the mixture was refluxed for 8 hours. After the reaction was completed, the reaction mixture was poured into water and the organic layer was extracted in DCM before being dried over anhydrous Na_2SO_4. The pure product was obtained by column chromatography over silica gel by using 20% ethyl acetate in petroleum ether as an eluent.

Compound **S9**: Orange red solid (1.54 g, 79%); ^{1}H NMR (400 MHz, $CDCl_3$): 7.76−7.77 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.53−7.54 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 7.25−7.27 (m, 1H).

Synthesis of 10,11-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2',3':4,5]pyrrolo[3,2-g]thieno[3,2-b]indole (**S10)**

In a two-neck, 250 mL round bottom flask was charged with compound **S9** (1.0 g; 2.5 mmol), PPh_3 (6.55 g; 25 mmol) and 125 mL of 1,2-dichlorobenzene (*o*-DCB) under nitrogen atmosphere. The reaction mixture was degassed by purging nitrogen gas through the reaction mixture for 10 minutes. The reaction mixture was heated to 160 °C under nitrogen atmosphere for 24 hours. After completion of a reaction, the cold reaction mixture was poured into water and extracted in ethyl acetate. The compound was purified by column chromatography using 40% ethyl acetate in petroleum ether to get a bright yellow solid.

Compound **S10**: Bright yellow solid (0.65 g, 77%); ^{1}H NMR (400 MHz, DMSO-D_6): 11.922 (s, 2H), 7.606−7.620 (d, J = 5.6 Hz, 1H), 7.424−7.437 (d, J = 5.2 Hz, 1H).

Synthesis of 10,11-bis(2-ethylhexyl)-10,11-dihydro-[1,2,5]thiadiazolo[3,4-*e*]thieno[2',3':4,5]pyrrolo[3,2-g]thieno[3,2-*b*]indole (**S11)**

In a 100 mL round bottom flask, compound **S10** (0.84 g; 2.5 mmol) was dissolved in anhydrous DMSO (90 mL). To this stirred solution KOH powder (1.73 g; 30.0 mmol) and ethyl hexyl bromide (3.0 mL; 16.25 mmol) was added and the resulting mixture was allowed to stir under

nitrogen atmosphere at 80 °C for 12 hours. After the completion of reaction, the reaction mixture was poured into water and organic layer was extracted in DCM before being dried over anhydrous Na_2SO_4. The pure product was obtained by column chromatography over silica gel by using 5% ethyl acetate in petroleum ether as an eluent.

Compound **S11**: Yellowish orange liquid (1.01 g, 71%); ^{1}H NMR (400 MHz, $CDCl_3$): 7.442−7.455 (d, J = 5.2 Hz, 2H), 7.182−7.195 (d, J = 5.2 Hz, 1H), 4.502−4.531 (m, 4H), 1.969−2.00 (m, 2H), 0.861−1.071 (m, 20H), 0.627−0.660 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): 147.64, 145.15, 132.63, 126.47, 120.98, 112.10, 110.57, 54.15, 39.28, 29.73, 29.58, 27.74, 23.05, 22.71, 13.78, 10.07, 10.04.

Synthesis of 10,11-bis(2-ethylhexyl)-10,11-dihydro-[1,2,5]thiadiazolo[3,4-*e*]thieno[2',3':4,5] pyrrolo[3,2-*g*]thieno[3,2-b]indole-2,8-dicarbaldehyde (**7)**

In a clean dry, two-neck round-bottom flask, DMF (4.21 mL, 54.3mmol) was taken and stirred it in an ice-salt bath. To this solution, $POCl_3$ (4.22 mL, 45.2 mmol) was added and stirred for an hour at 0 °C. In the resulting reaction mixture, the solution of compound **S11** (1.0 g, 1.81 mmol) in DCE (37 mL) was added dropwise with the help of a syringe through a rubber septum. The reaction mixture was stirred at room temperature for an hour and refluxed for 24 hours. After the completion of the reaction, DCE was evaporated and the crude product was washed with water and then extracted with DCM. The organic layer was then dried over anhydrous Na_2SO_4 and the DCM was evaporated to get pure solid compound.

Compound **7**: Dark yellow solid (0.90 g, 81%); ^{1}H NMR (400 MHz, $CDCl_3$): 10.046 (S, 2H), 7.861 (S, 2H), 4.555−4.581 (m, 4H), 1.994 (s, 2H), 0.993−1.267 (m, 18H), 0.907−0.981 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): 183.17, 147.49, 144.77, 144.52, 134.58, 128.29, 119.82, 112.19, 54.44, 39.65, 29.60, 27.71, 23.09, 22.70, 13.75, 10.04, 10.03. HRMS (ES^+): $C_{32}H_{39}N_2O_2S_3$ requires 606.2157, found 607.2217. IR (KBr, cm^{-1}): 3077, 2957, 2926, 2857, 1650, 1508, 1457, 1419, 1355, 1294, 1224, 1189, 1130, 1076, 863, 812, 704, 643, 503.

Spectral data of intermediate compounds and monomers

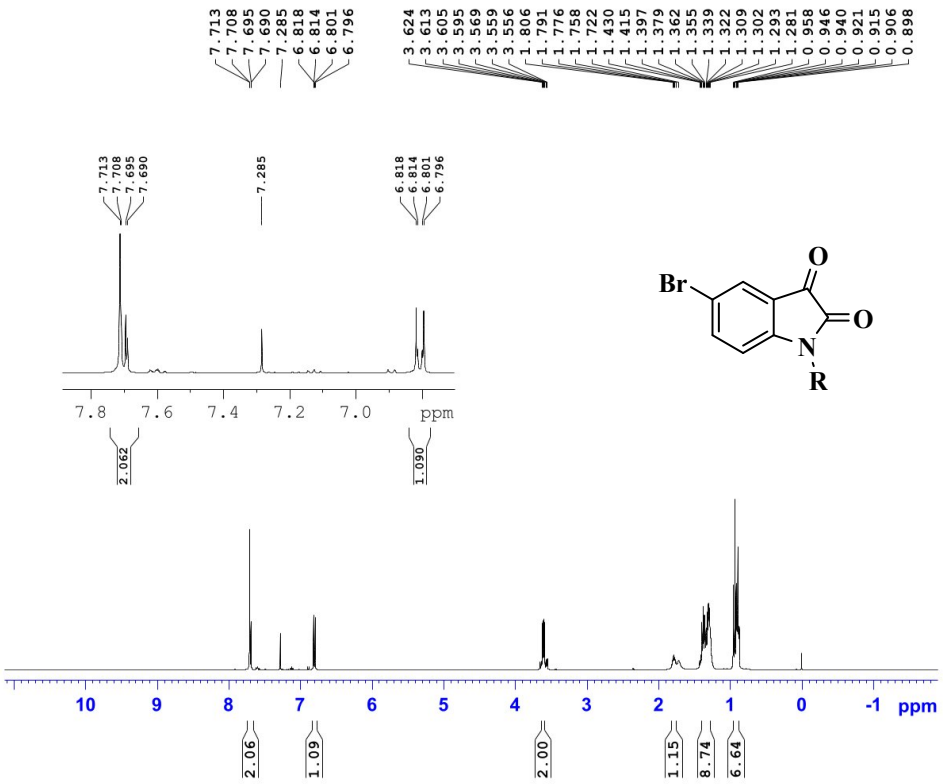


Figure **S1**: ^{1}H NMR spectra of compound S**1**

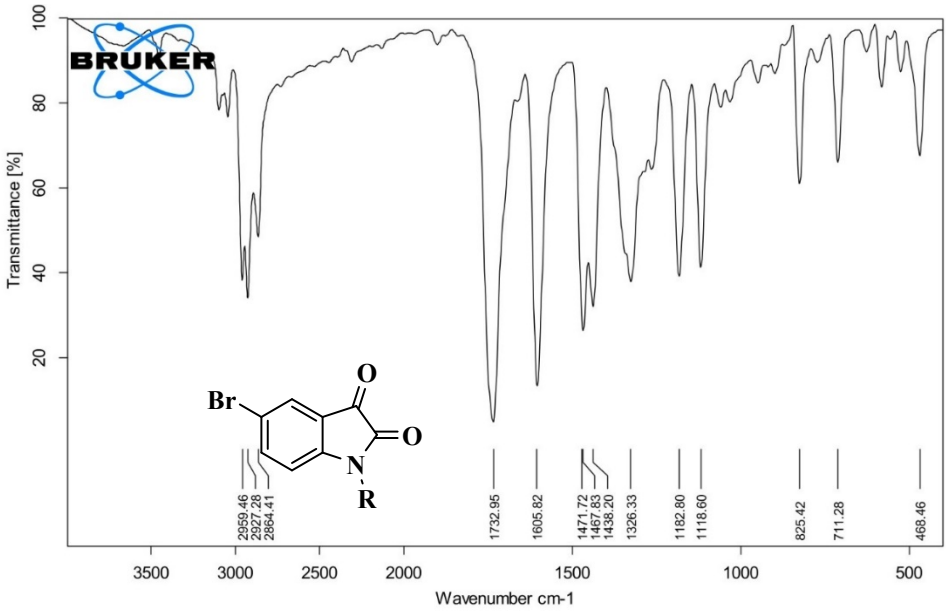


Figure **S2**: IR spectrum (KBr pellet) of compound **S1**

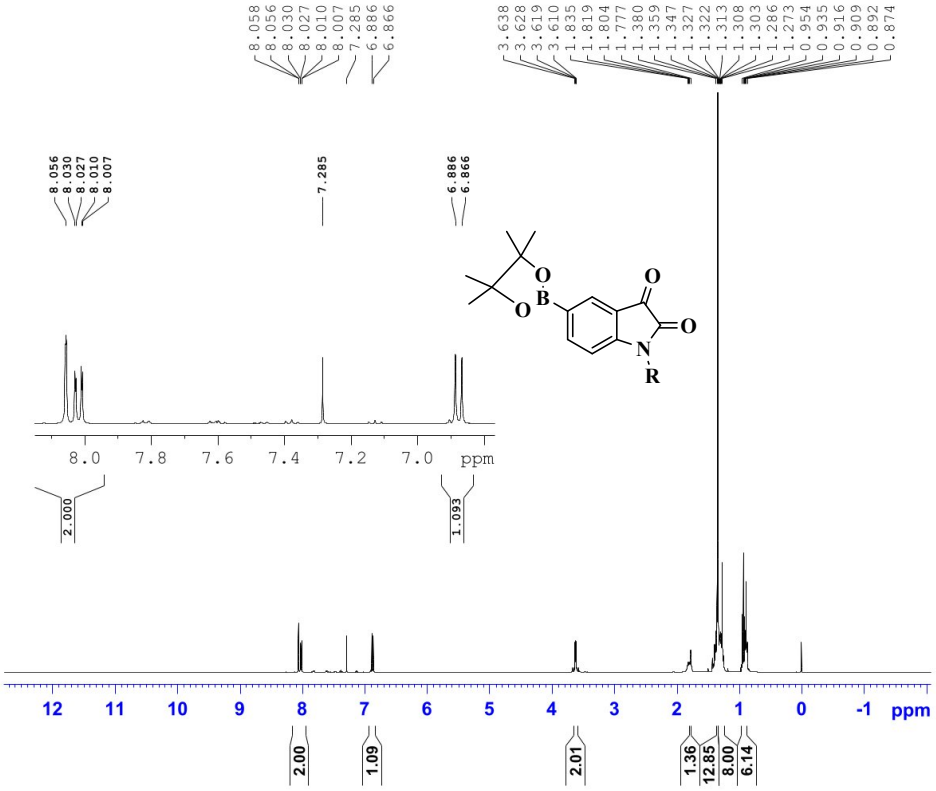


Figure **S3**: ^{1}H NMR spectra of compound S**2**

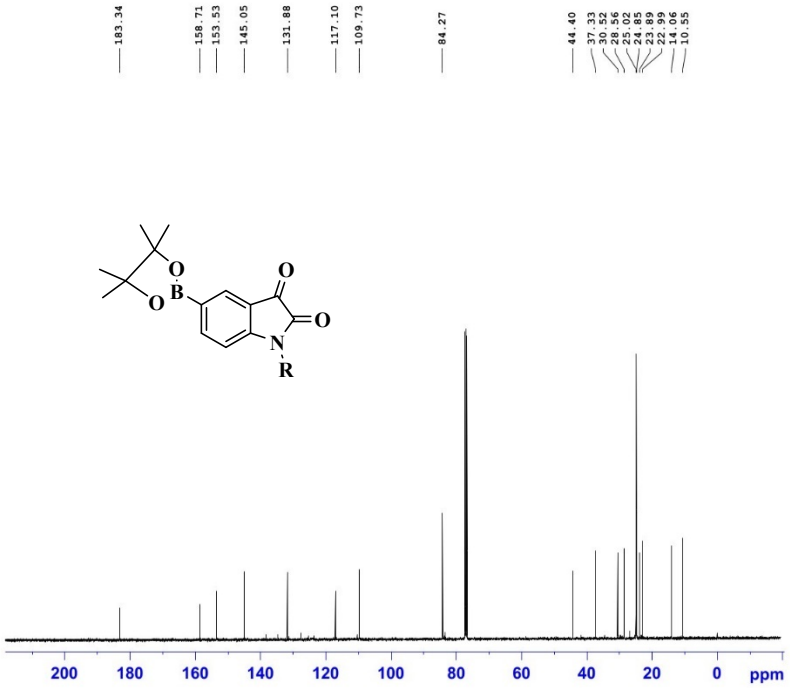


Figure **S4**: ^{13}C NMR spectra of compound **S2**

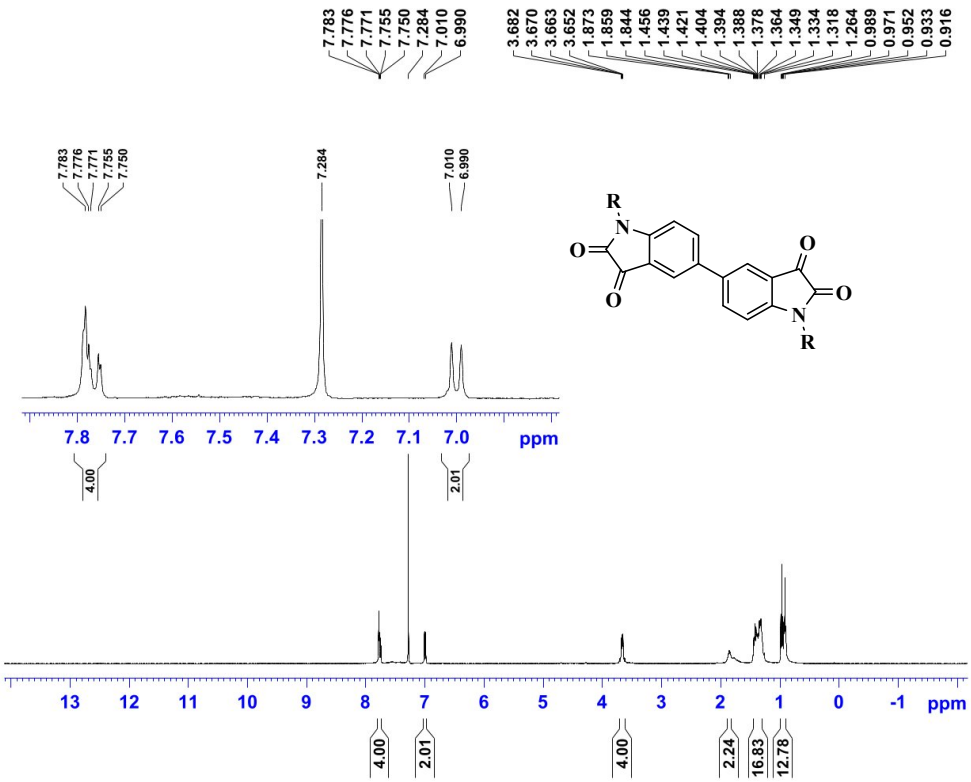


Figure **S5**: ^{1}H NMR spectra of compound **1**

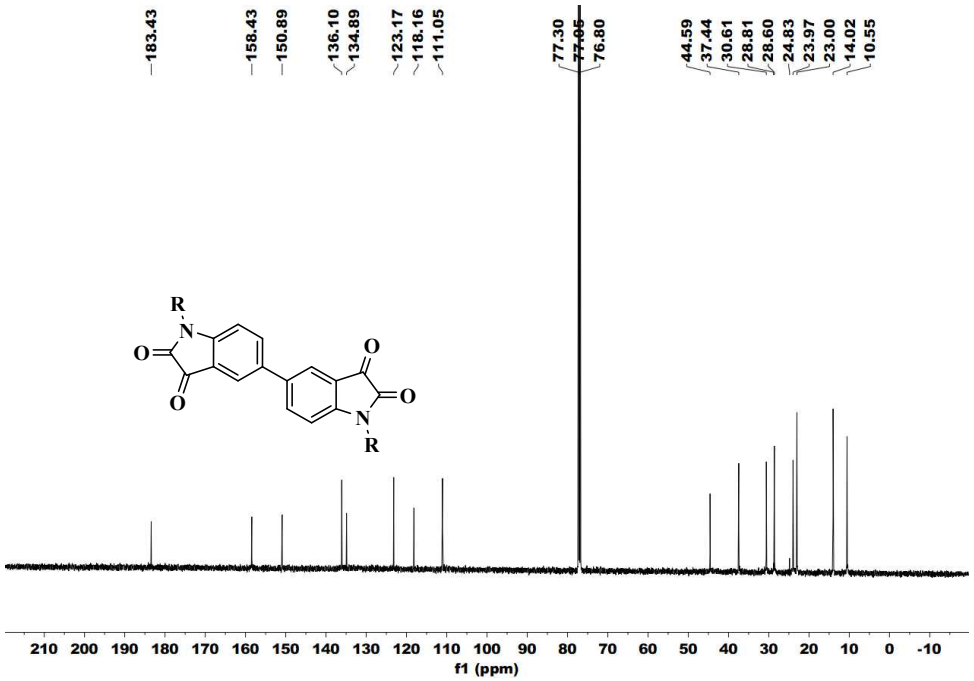


Figure **S6**: ^{13}C NMR spectra of compound **1**

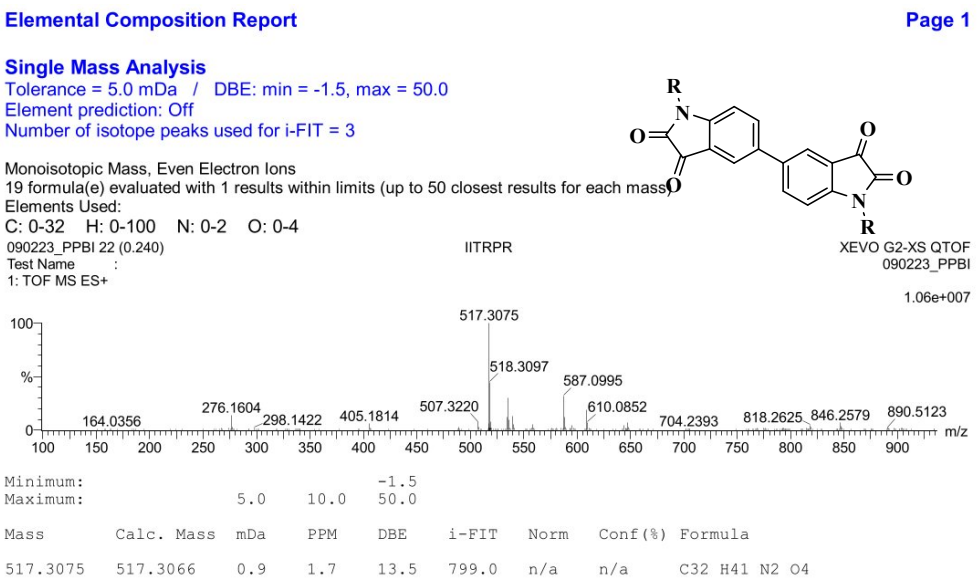


Figure **S6:** HR-MS data of compound **1**

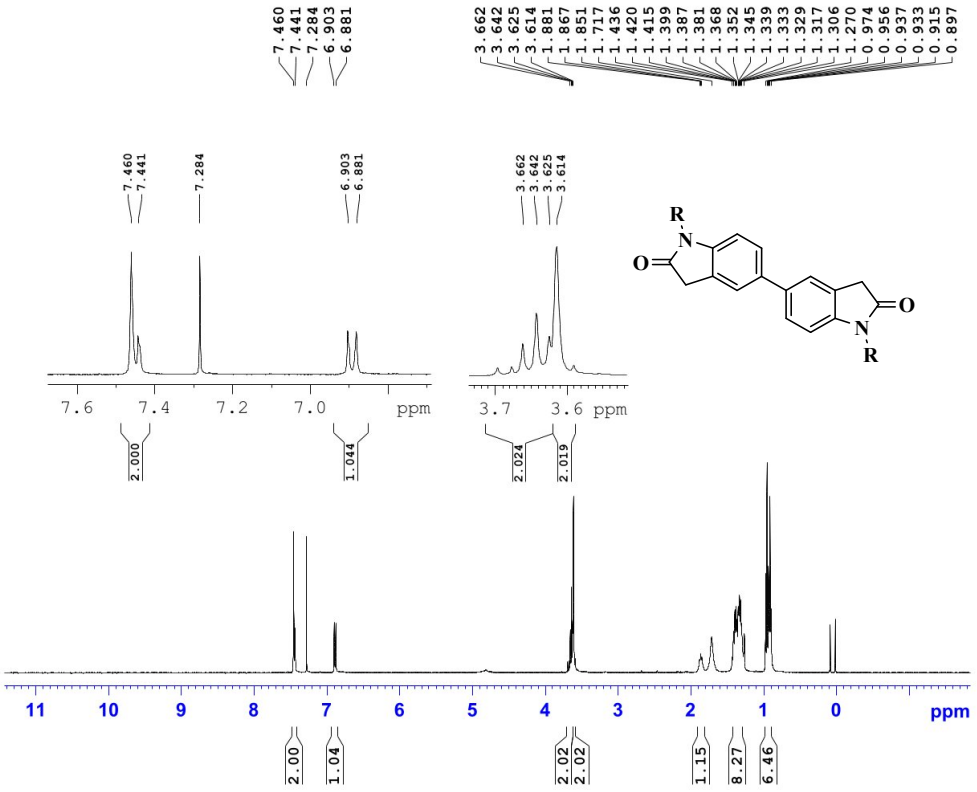


Figure **S7**: ^{1}H NMR spectra of compound **2**

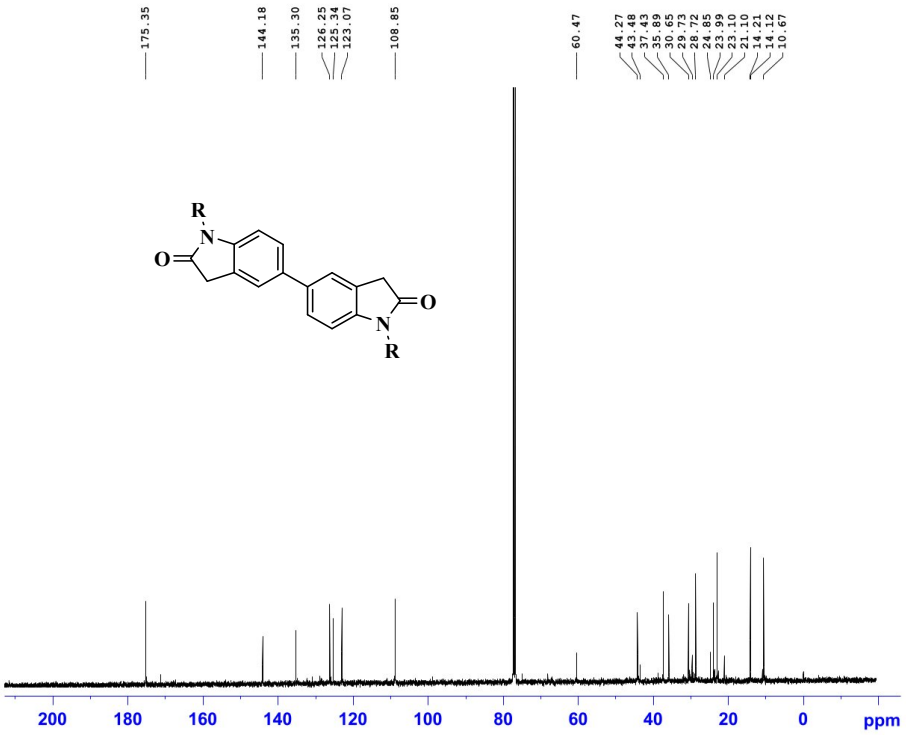


Figure **S8**: ^{13}C NMR spectra of compound **2**

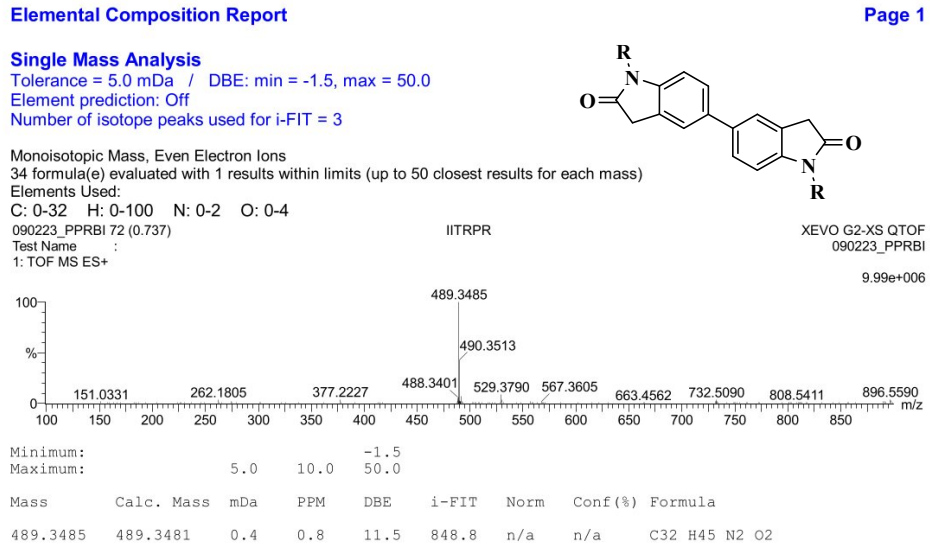


Figure **S9:** HR-MS data of compound **2**

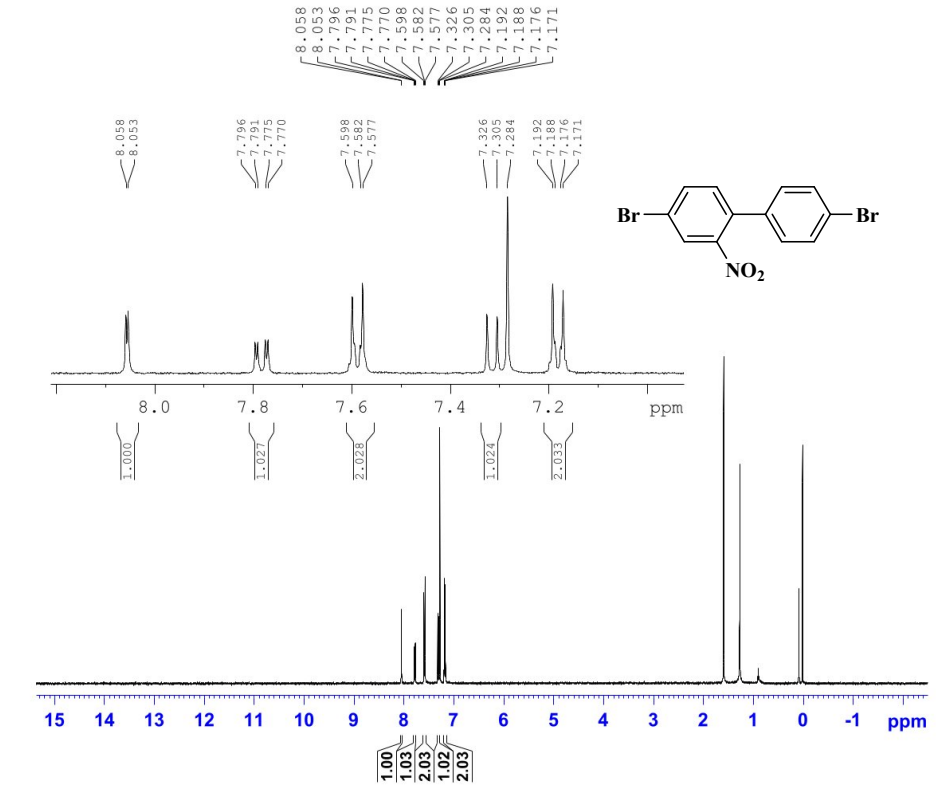


Figure S10: [1]H NMR spectra of compound **S3**

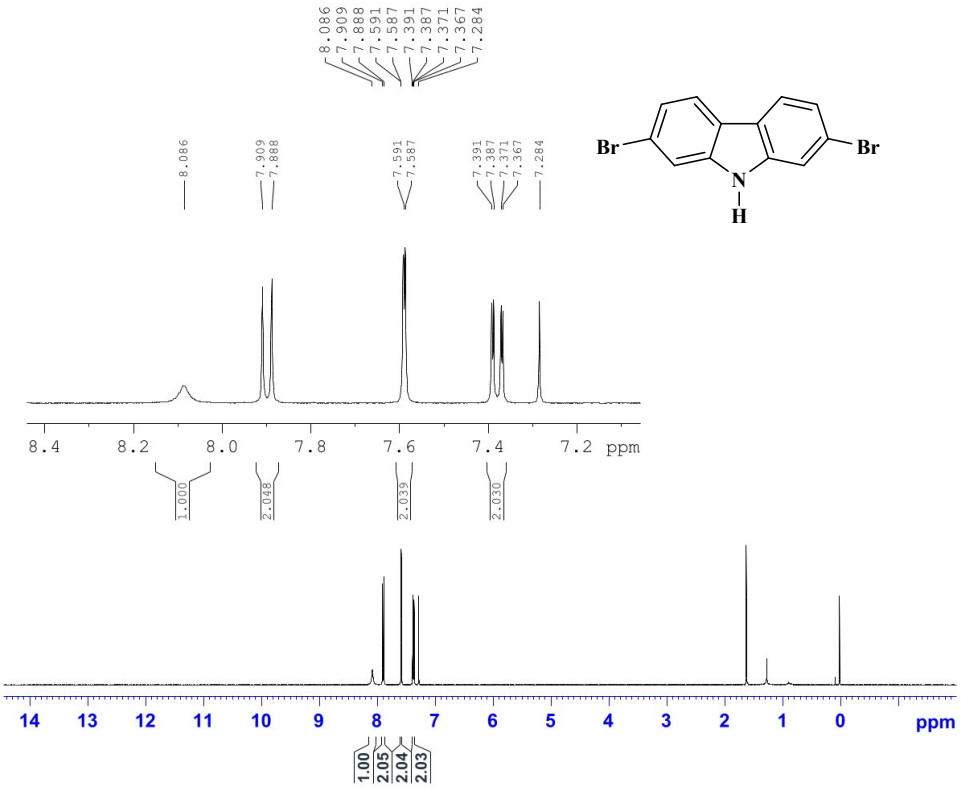


Figure S11: [1]H NMR spectra of compound **S4**

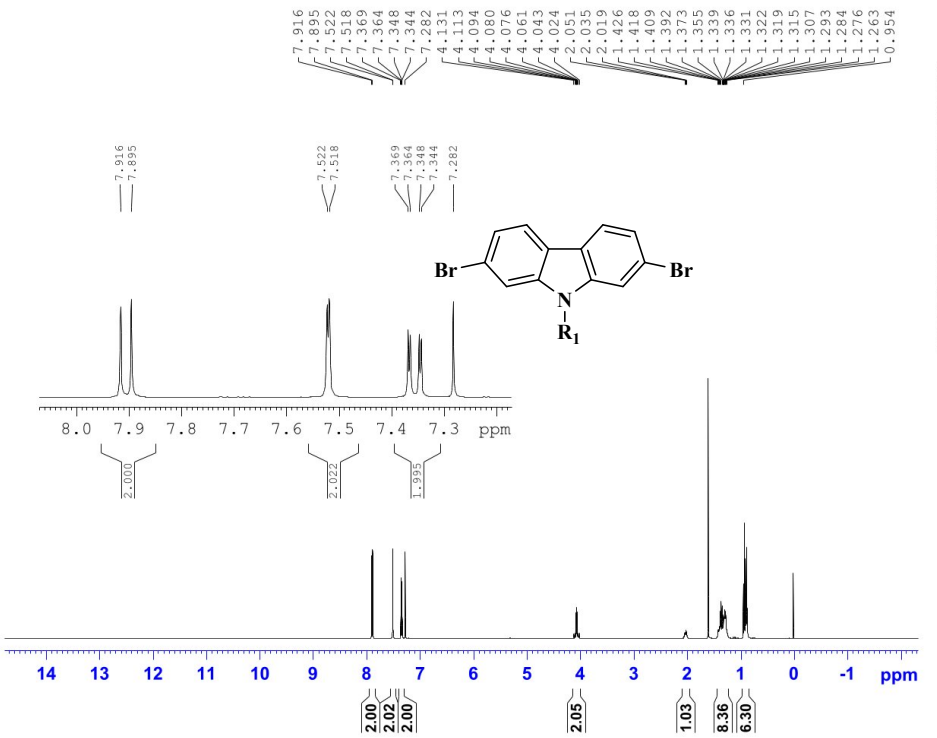


Figure S12: ^{1}H NMR spectra of compound **S5**

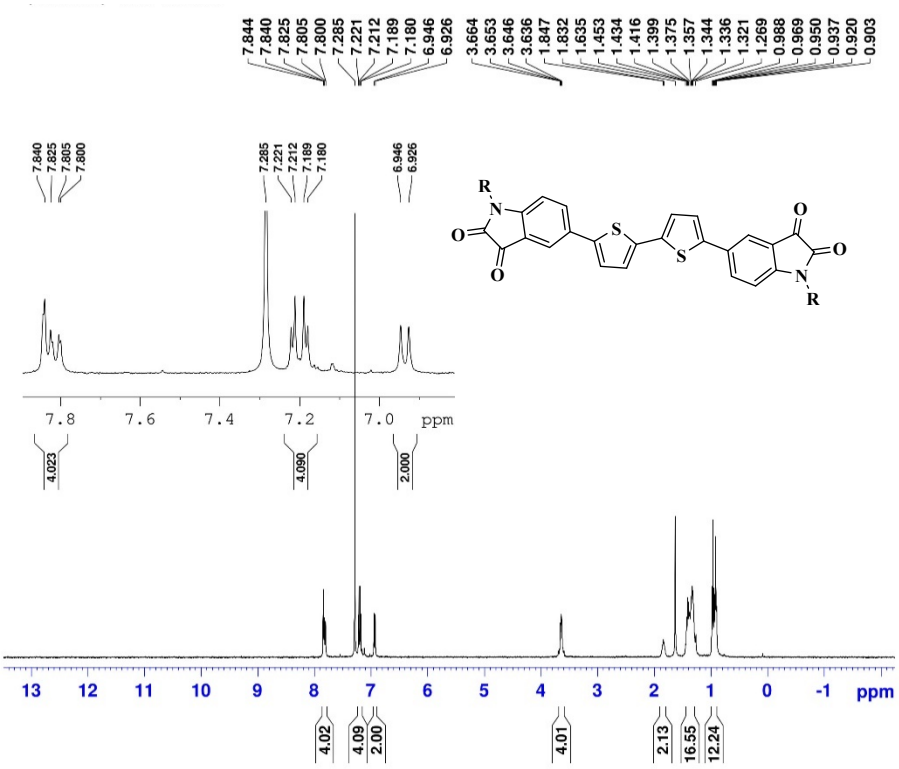


Figure **S13**: ^{1}H NMR spectra of compound **3**

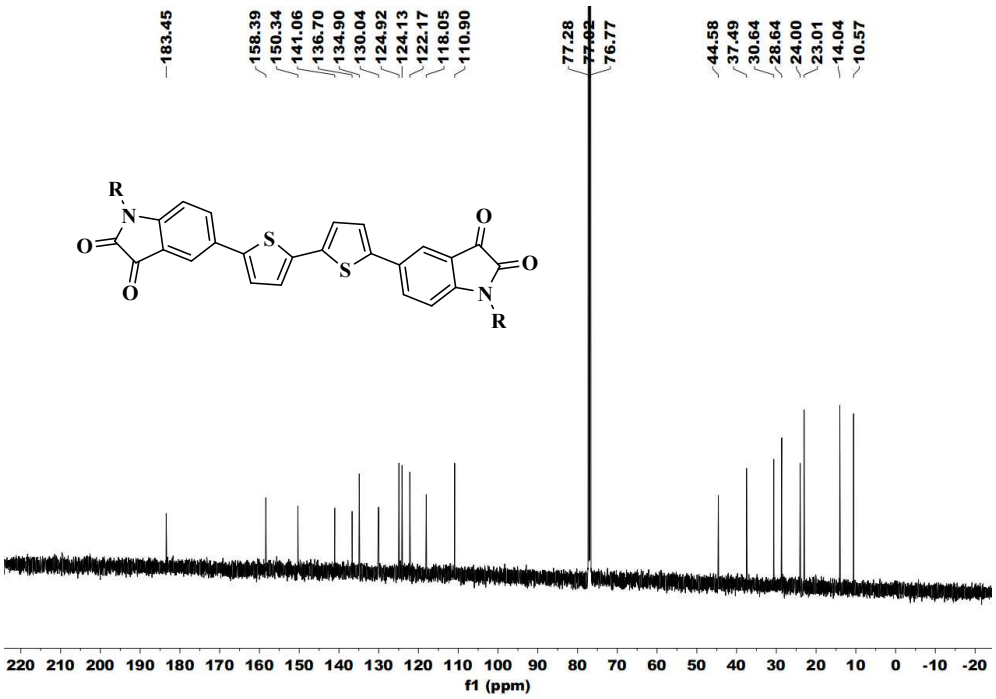


Figure **S14**: ^{13}C NMR spectra of compound **3**

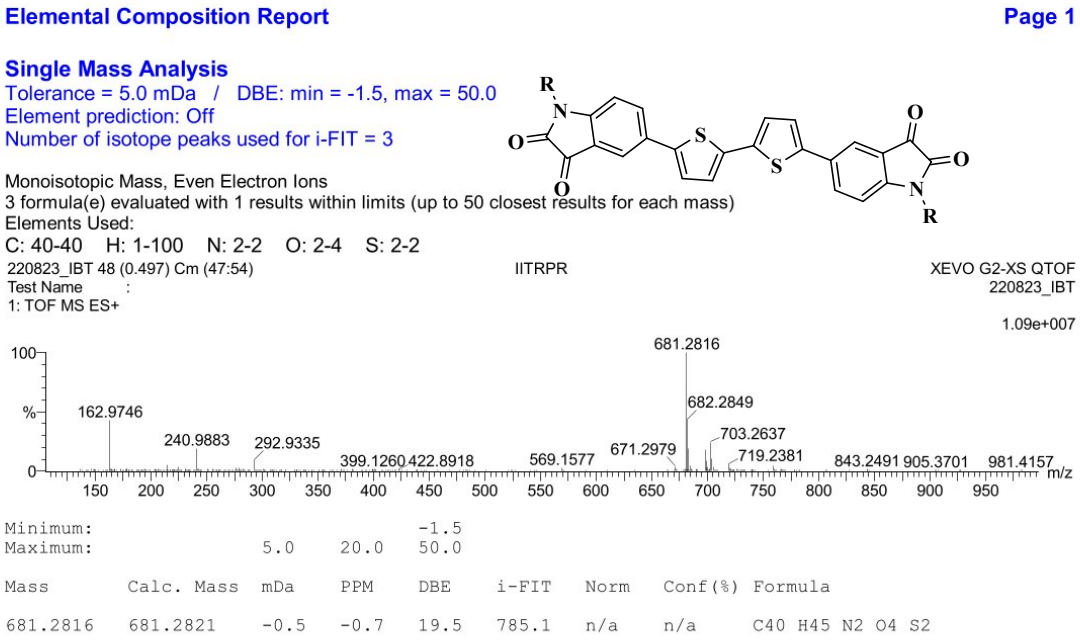


Figure **S15:** HR-MS data of compound **3**

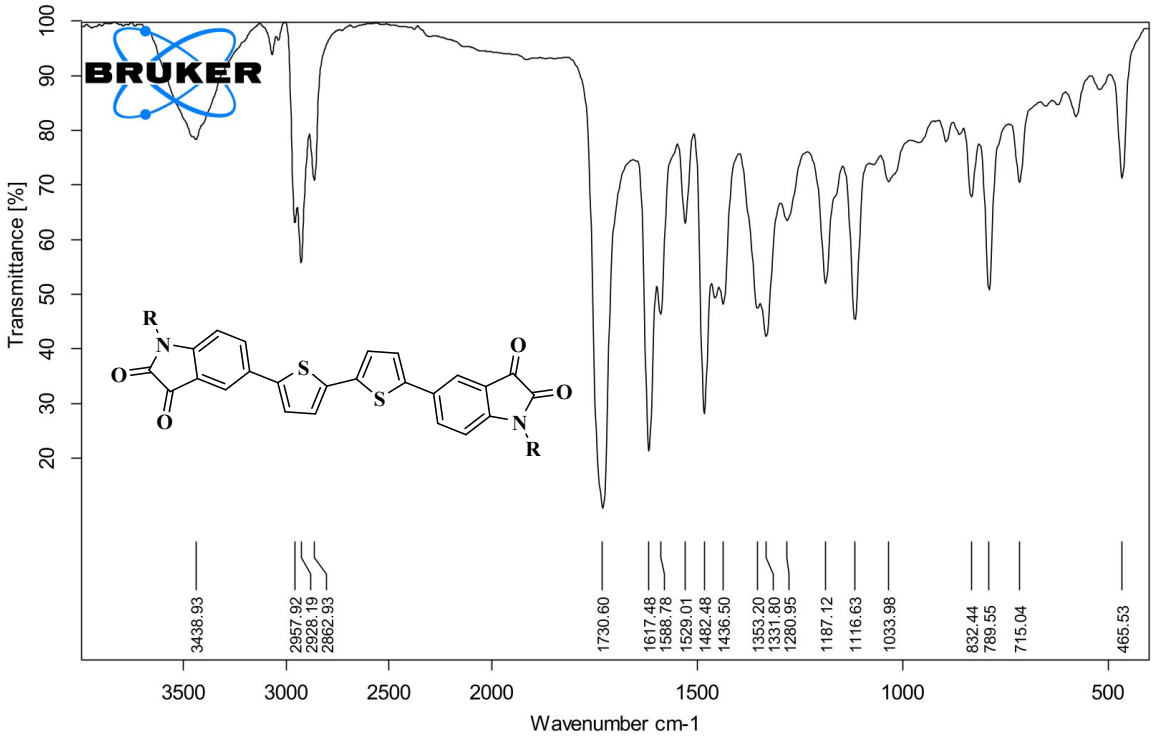


Figure **S16**: IR spectrum (KBr pellet) of compound **3**

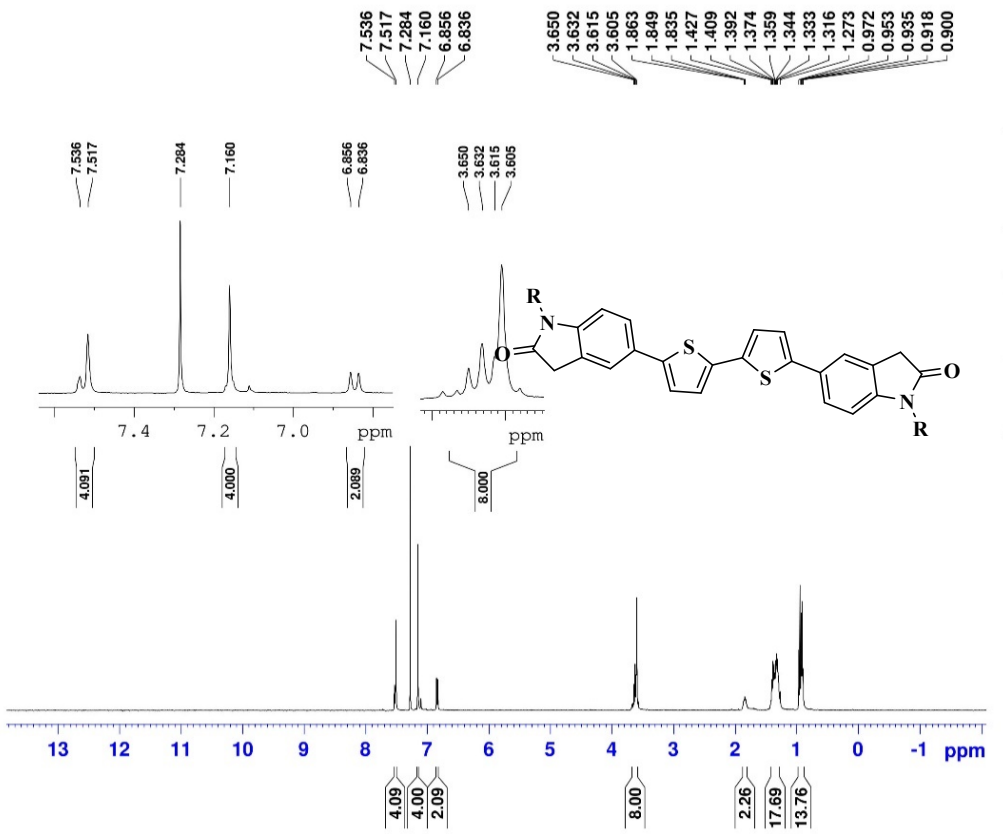


Figure **S17**: ^{1}H NMR spectra of compound **4**

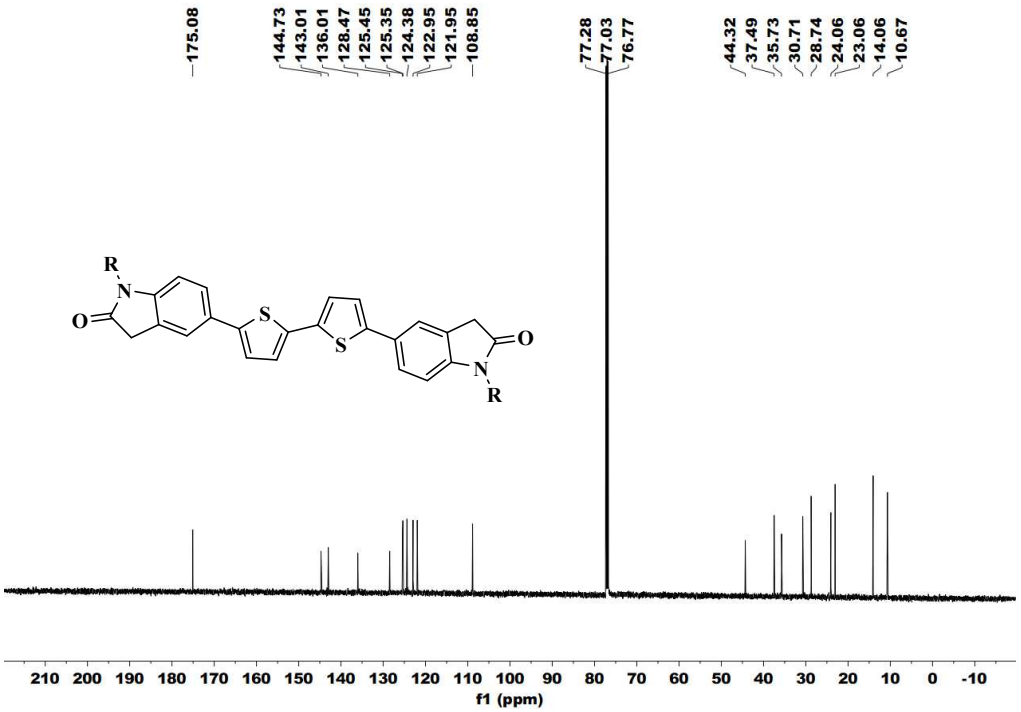


Figure **S18**: ^{13}C NMR spectra of compound **4**

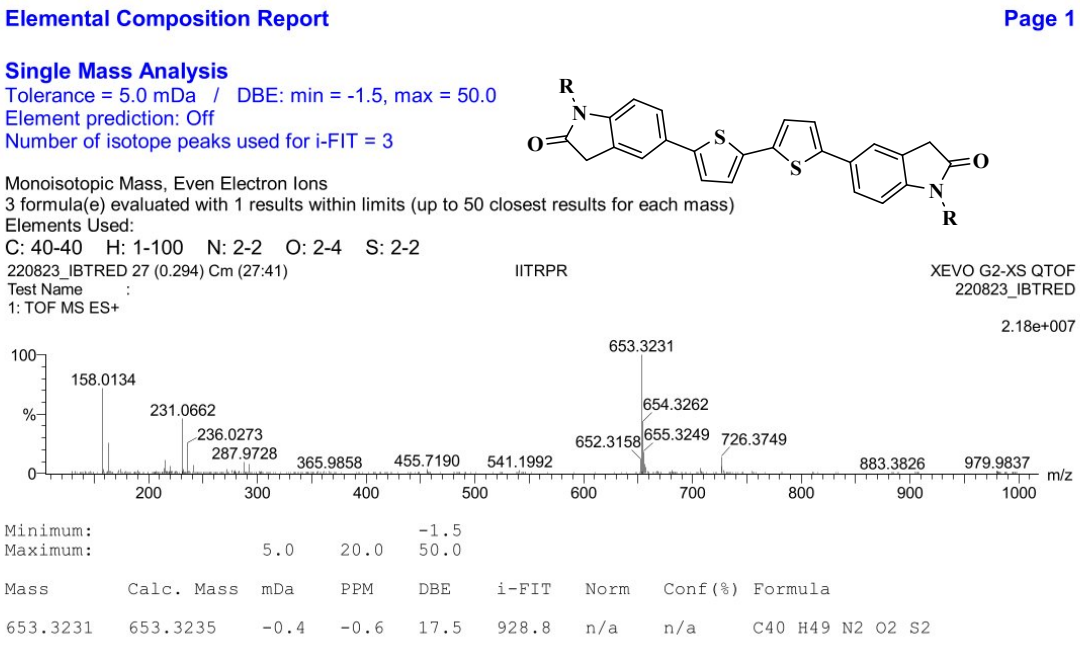


Figure **S19:** HR-MS data of compound **4**

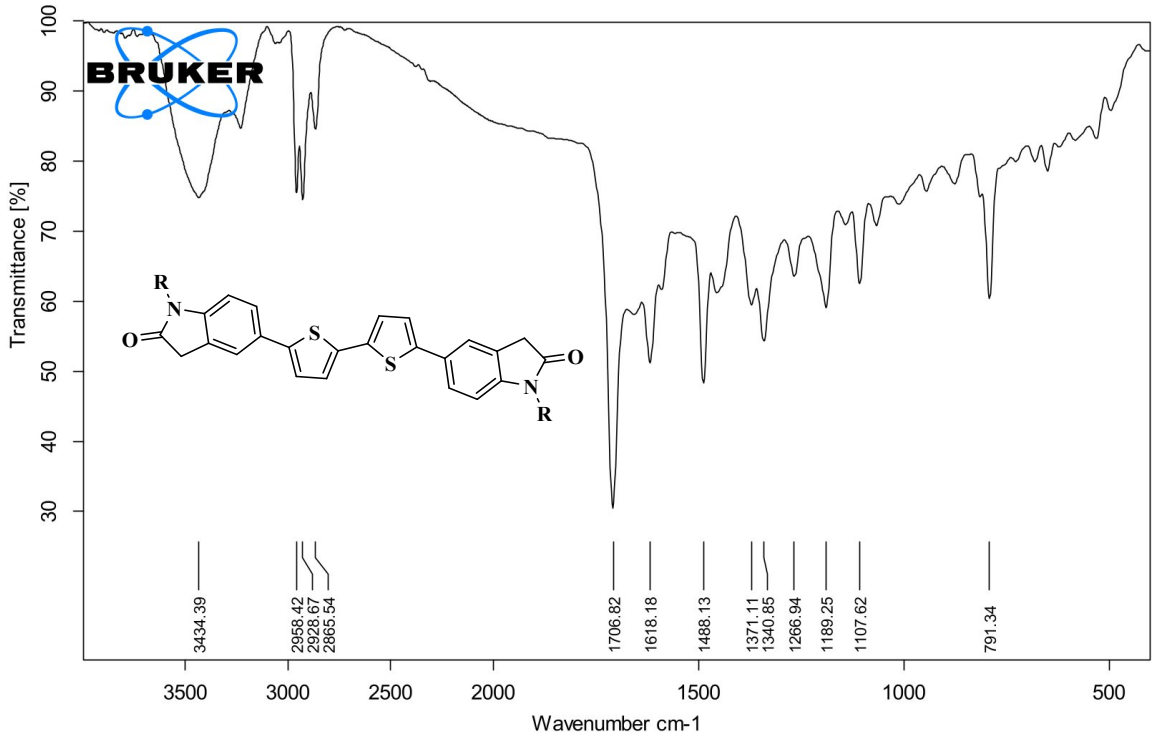


Figure **S20**: IR spectrum (KBr pellet) of compound **4**

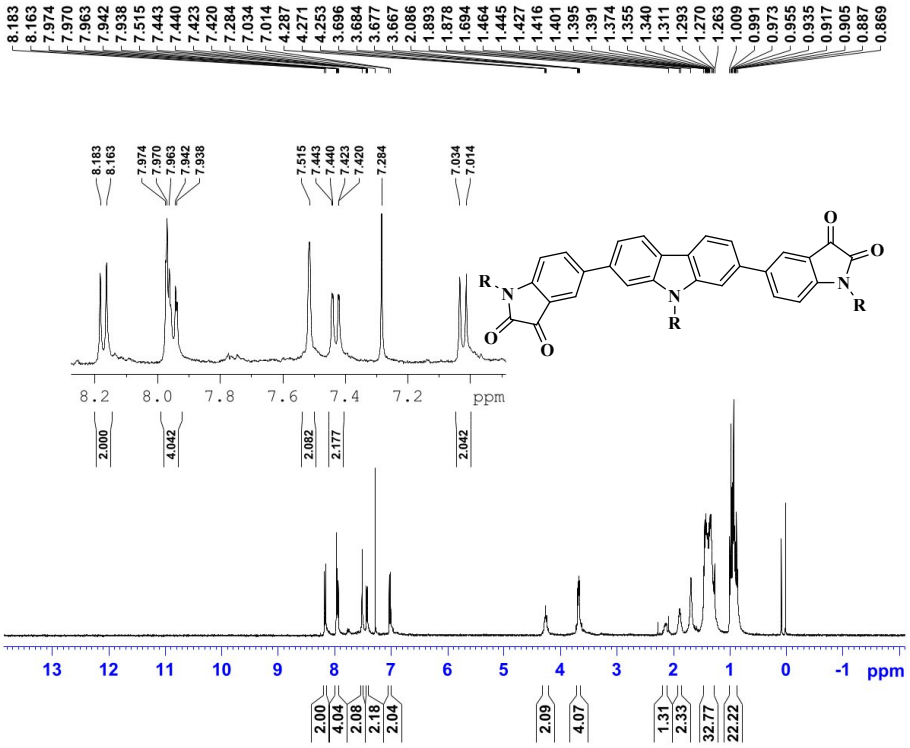


Figure **S21**: ^{1}H NMR spectra of compound **5**

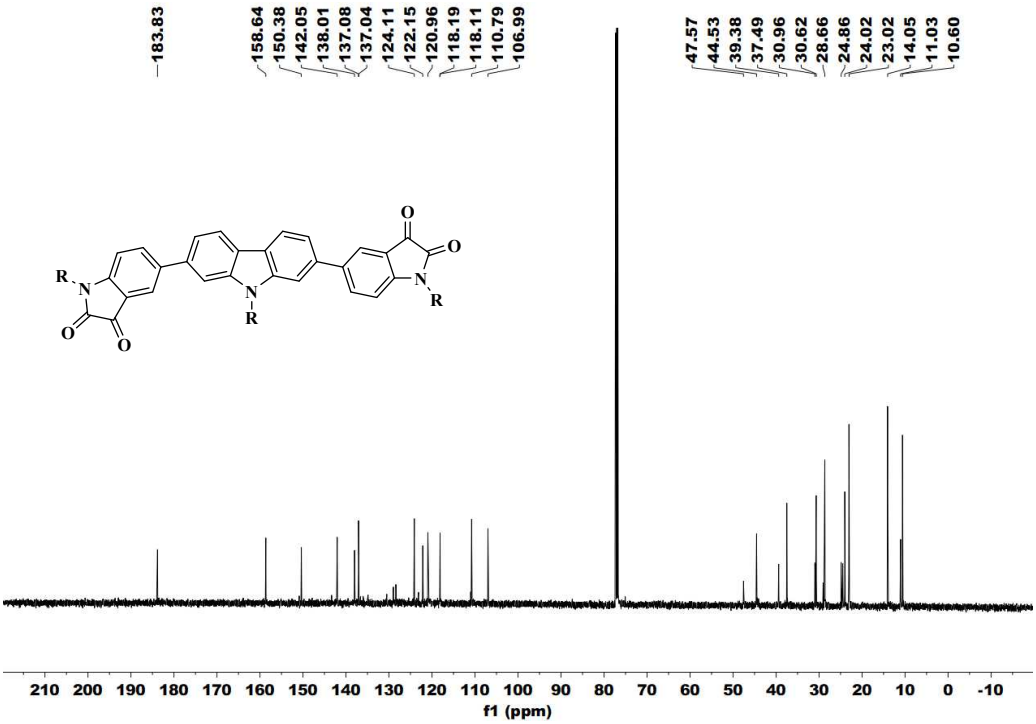


Figure **S22**: ^{13}C NMR spectra of compound **5**

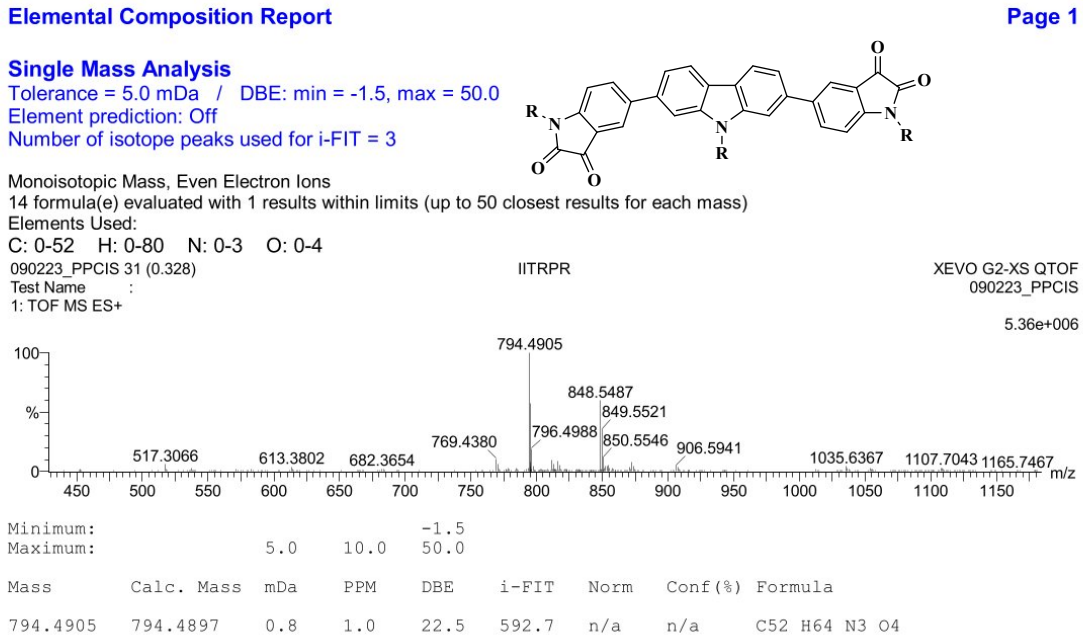


Figure **S23**: ^{13}C NMR spectra of compound **5**

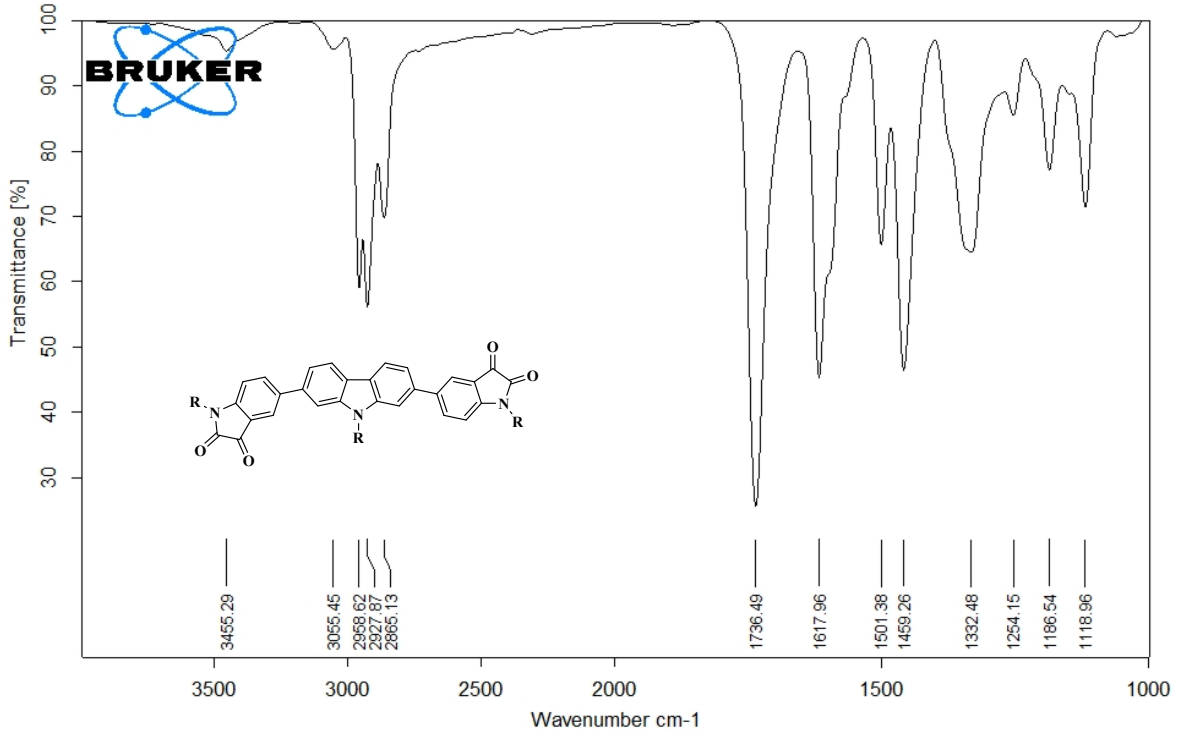


Figure **S24**: IR spectrum (KBr pellet) of compound **5**

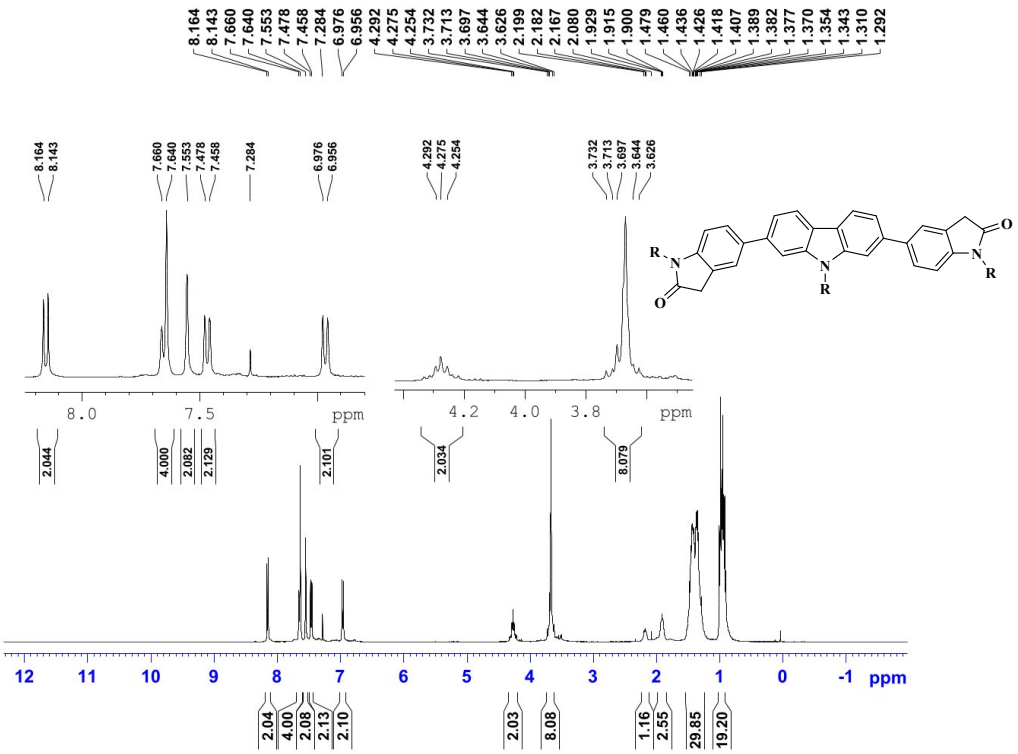


Figure **S25**: ^{1}H NMR spectra of compound **6**

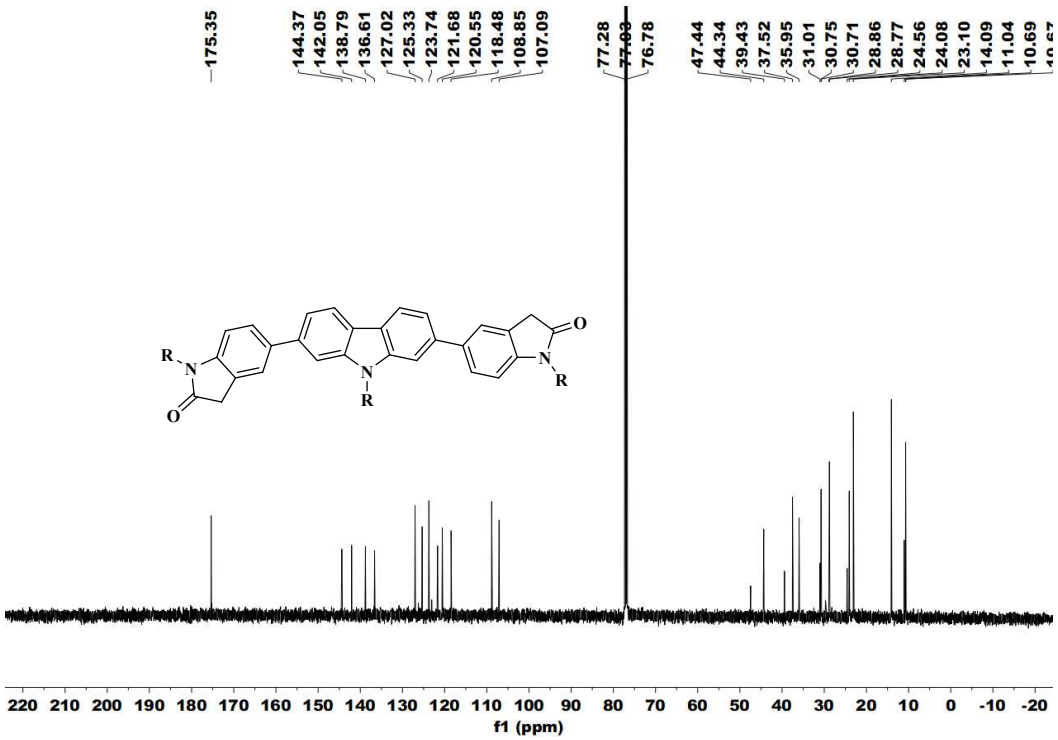


Figure **S26**: ^{13}C NMR spectra of compound **6**

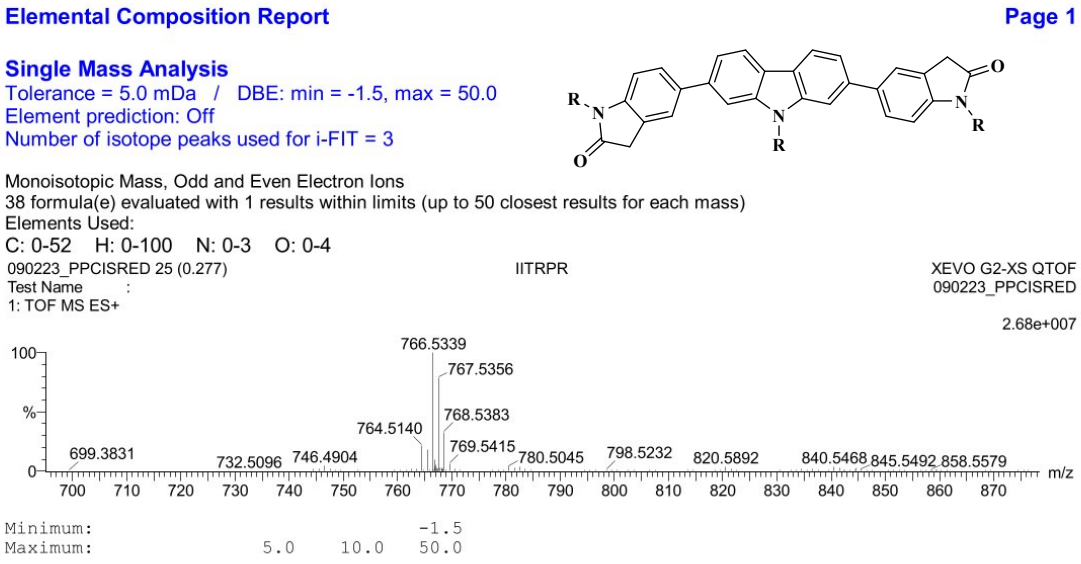


Figure **S27:** HR-MS data of compound **6**

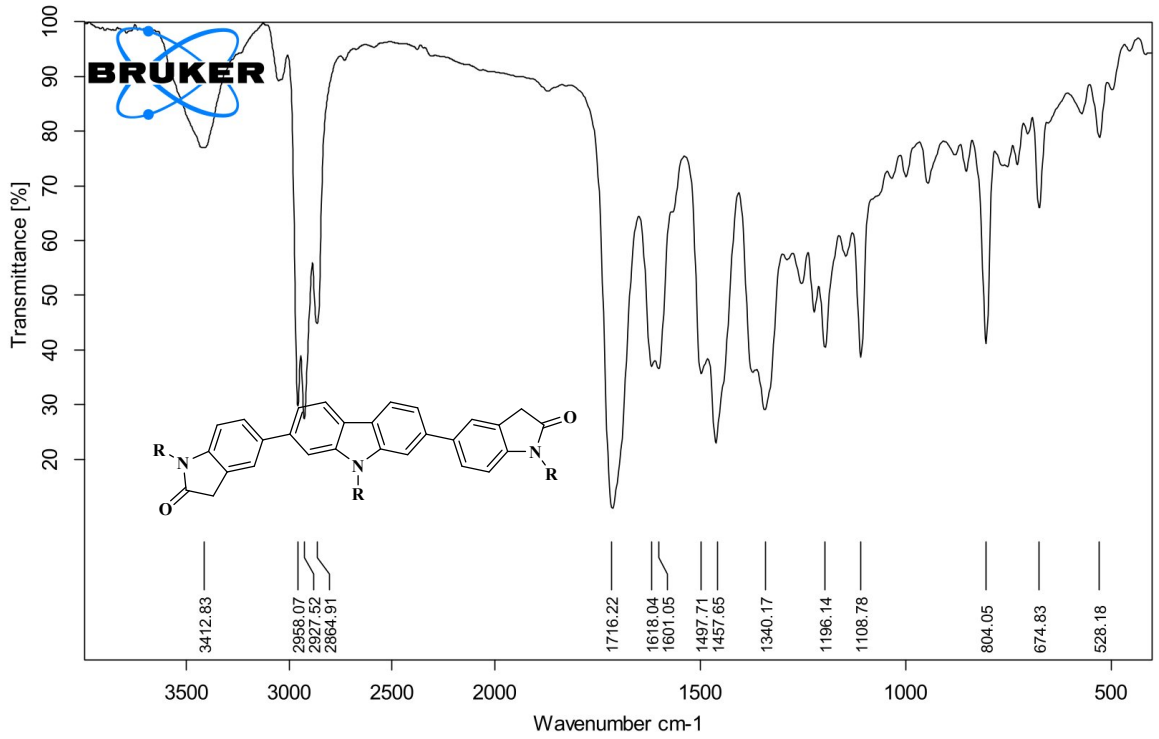


Figure S28: IR spectrum (KBr pellet) of compound **6**

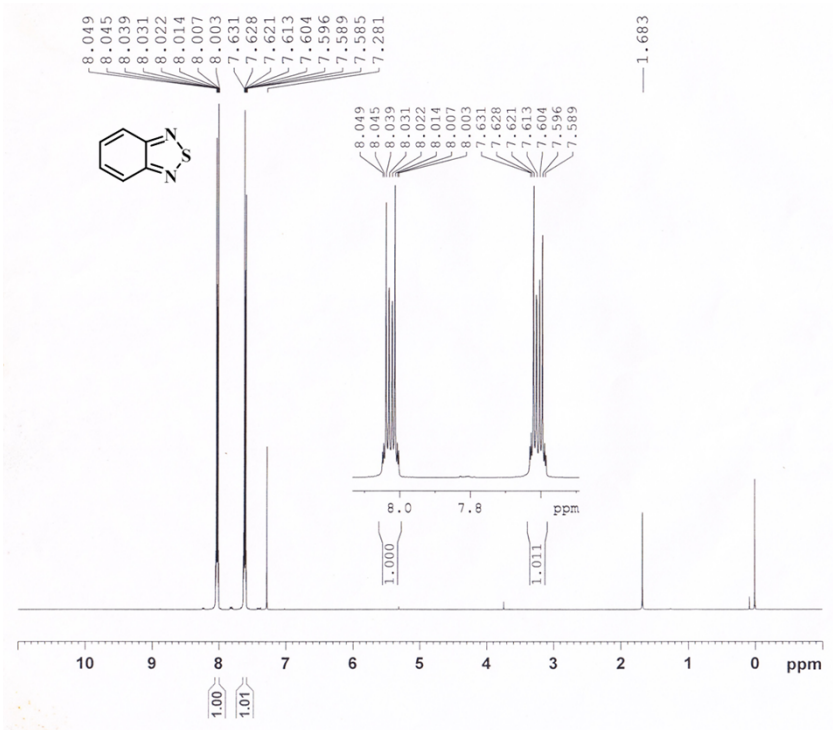


Figure **S29**: ^{1}H NMR spectra of compound **S6**

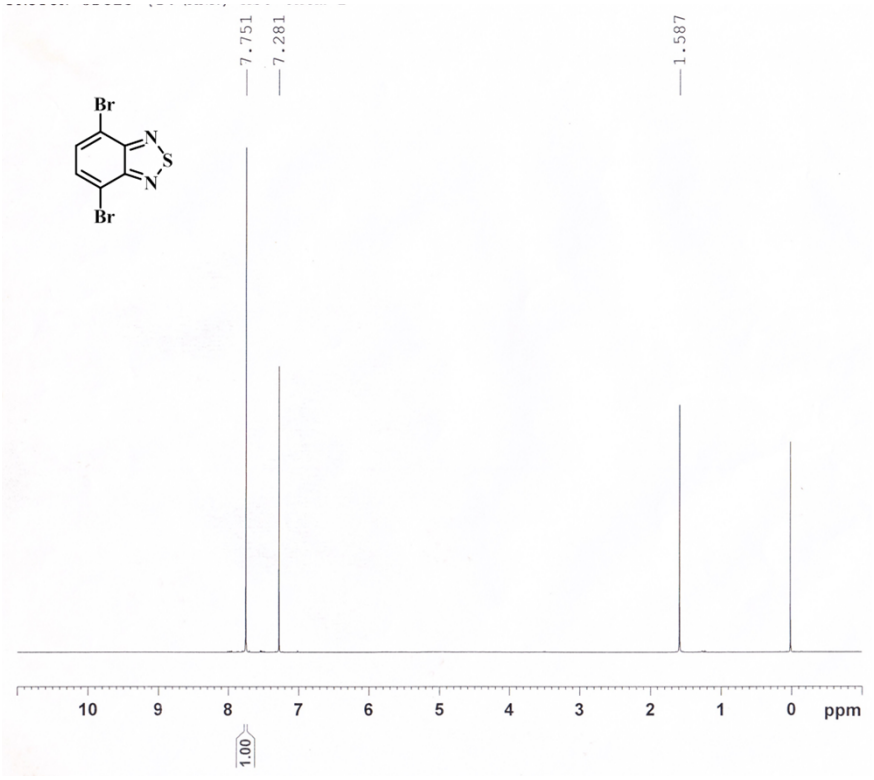


Figure **S30**: ^{1}H NMR spectra of compound **S7**

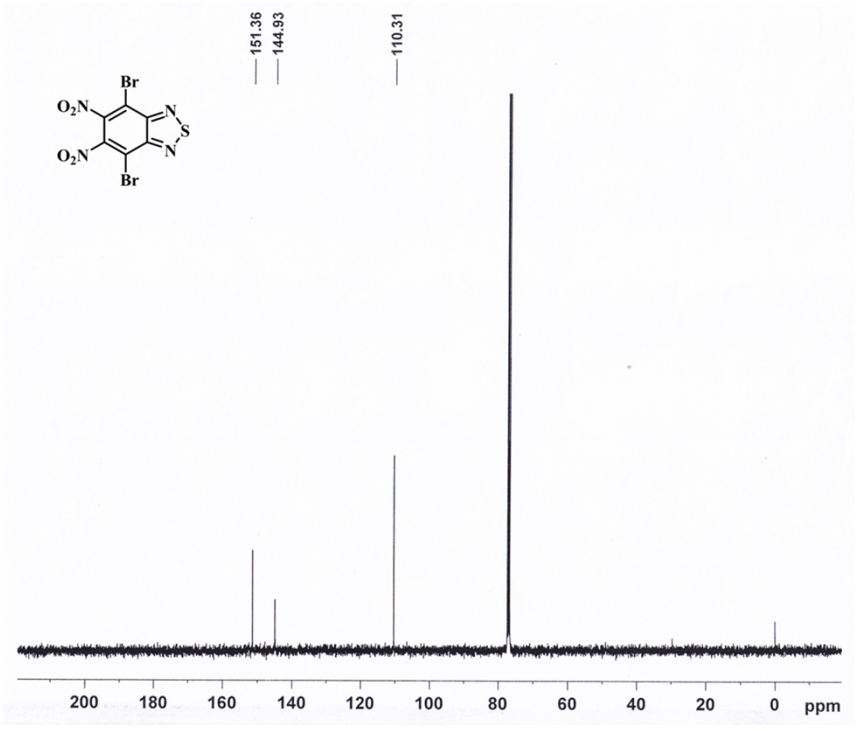


Figure **S31**: ^{13}C NMR spectra of compound **S8**

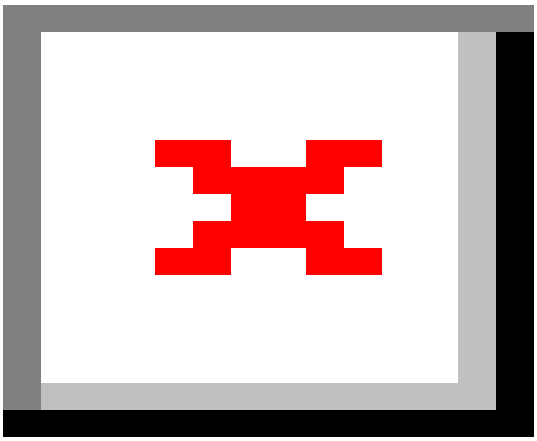


Figure **S32**: ^{1}H NMR spectra of compound **S9**

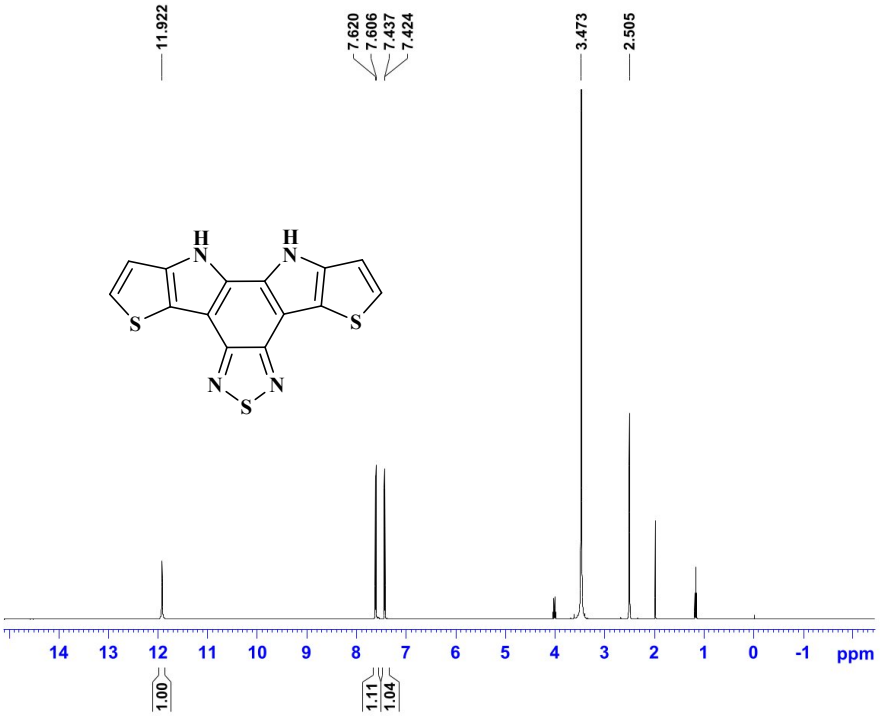


Figure **S33**: ^{1}H NMR spectra of compound **S10**

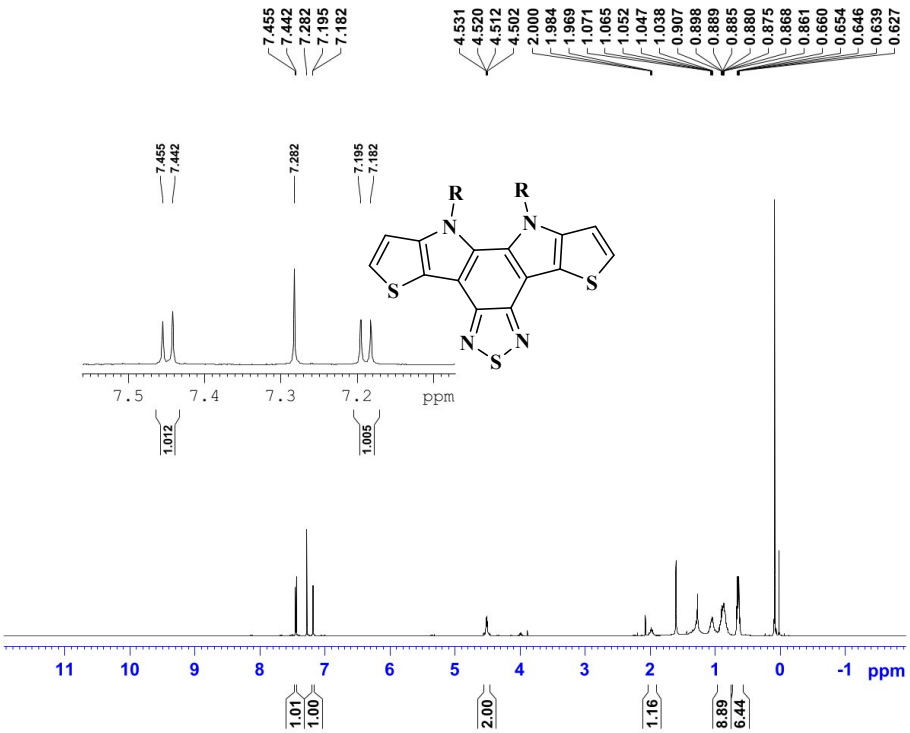


Figure **S34**: ^{1}H NMR spectra of compound **S11**

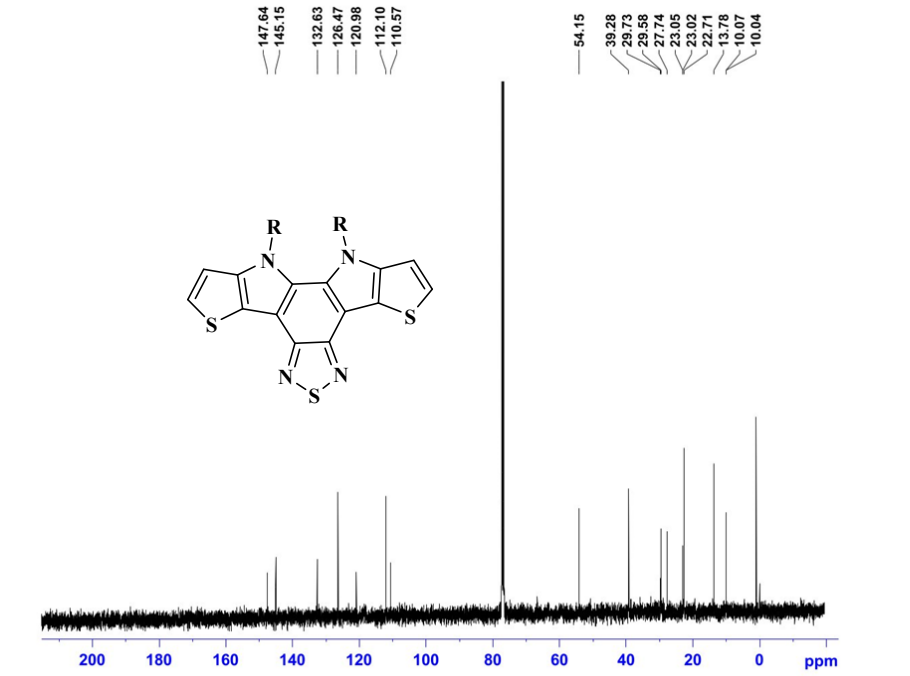


Figure **S35**: ^{13}C NMR spectra of compound **S11**

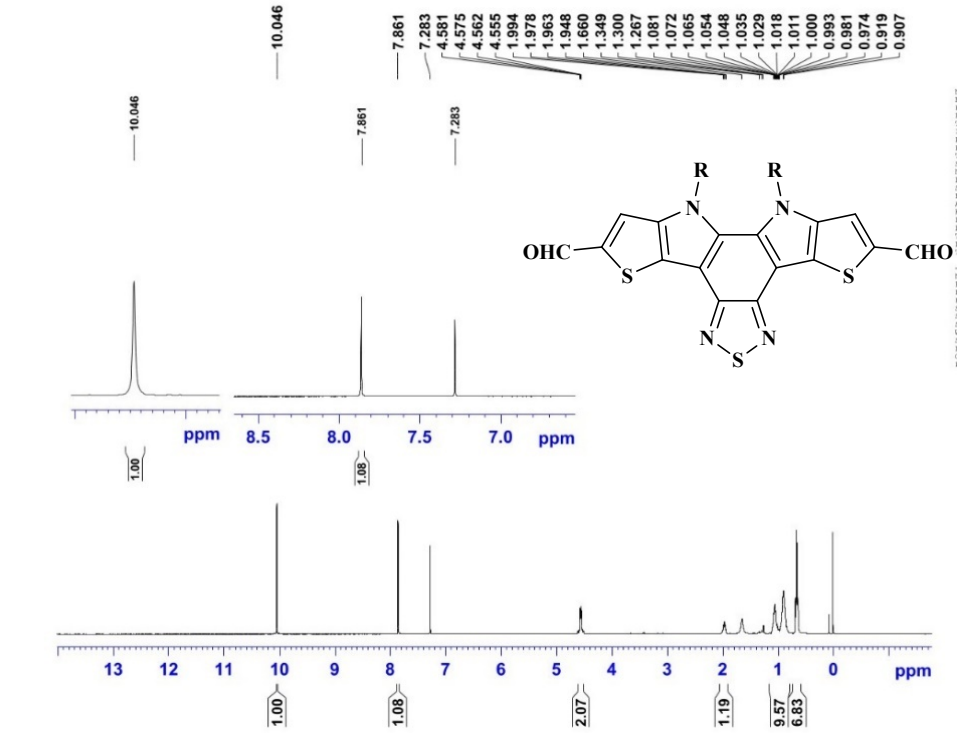


Figure **S36**: ^{1}H NMR spectra of compound **7**

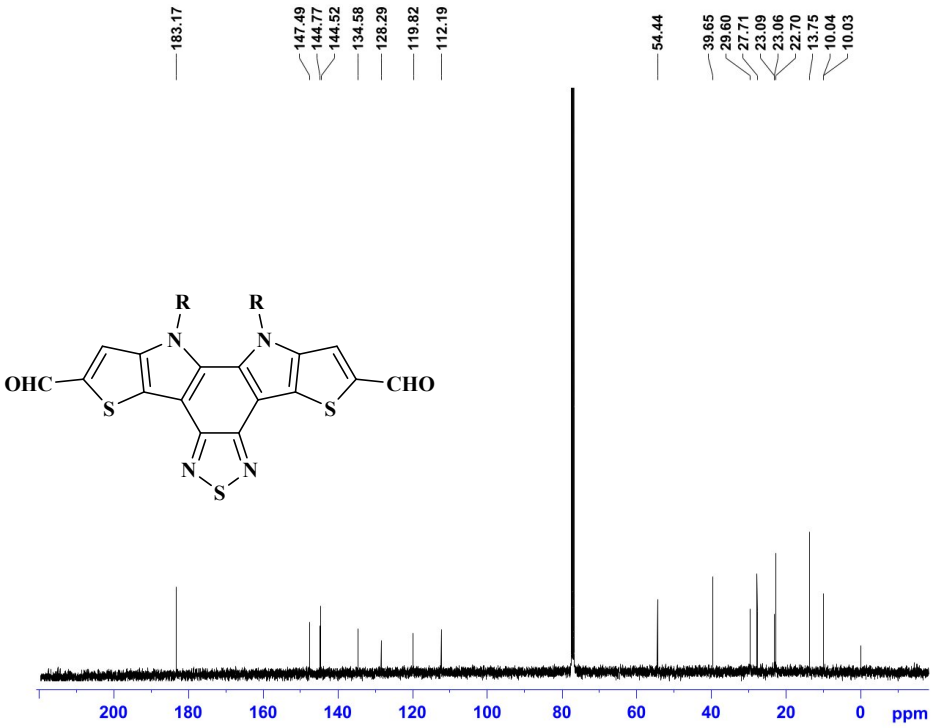


Figure **S37**: ^{13}C NMR spectra of compound **7**

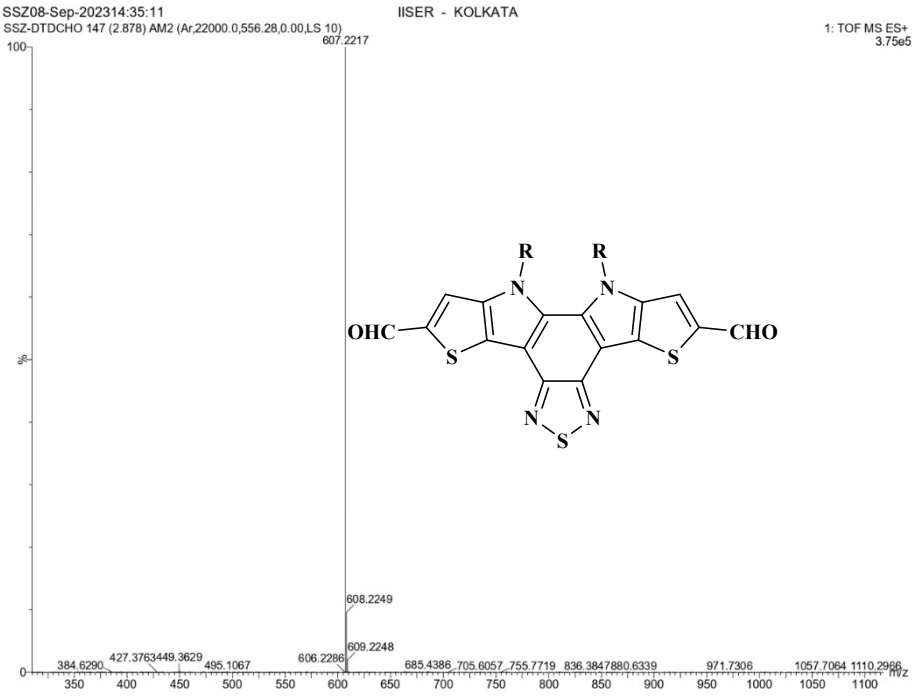


Figure **S38:** HR-MS data of compound **7**

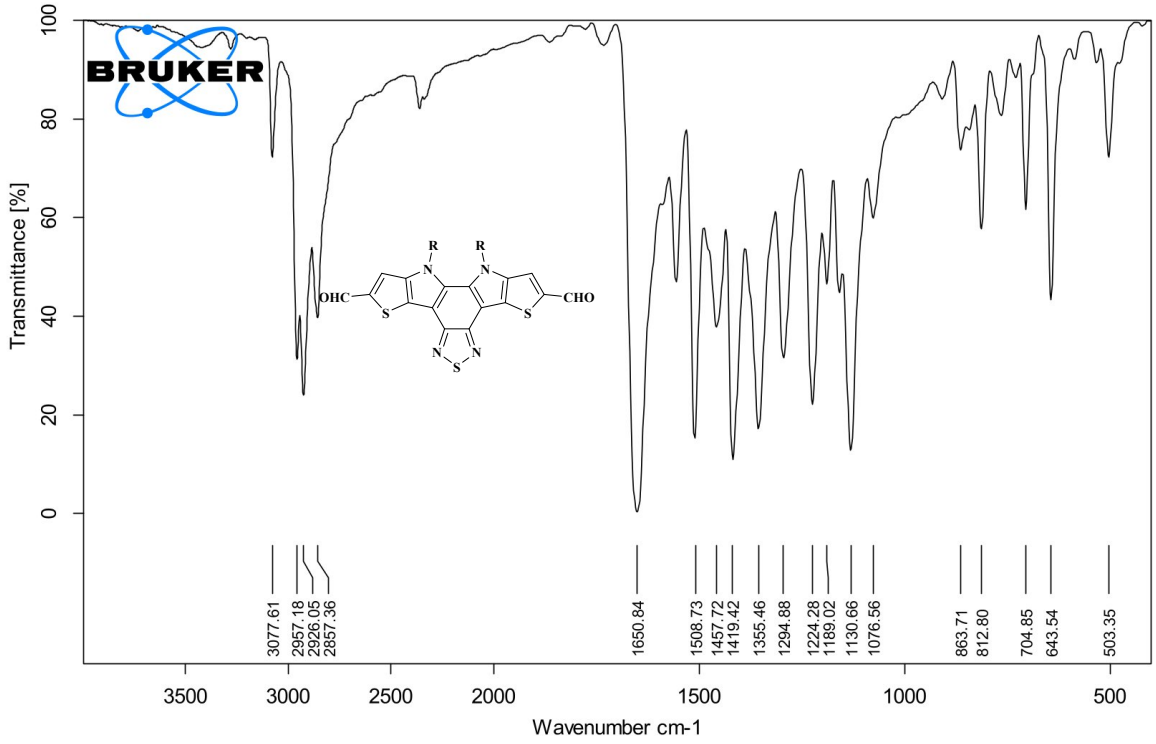


Figure **S39**: IR spectrum (KBr pellet) of compound **7**

Spectral data and GPC analysis data of polymers

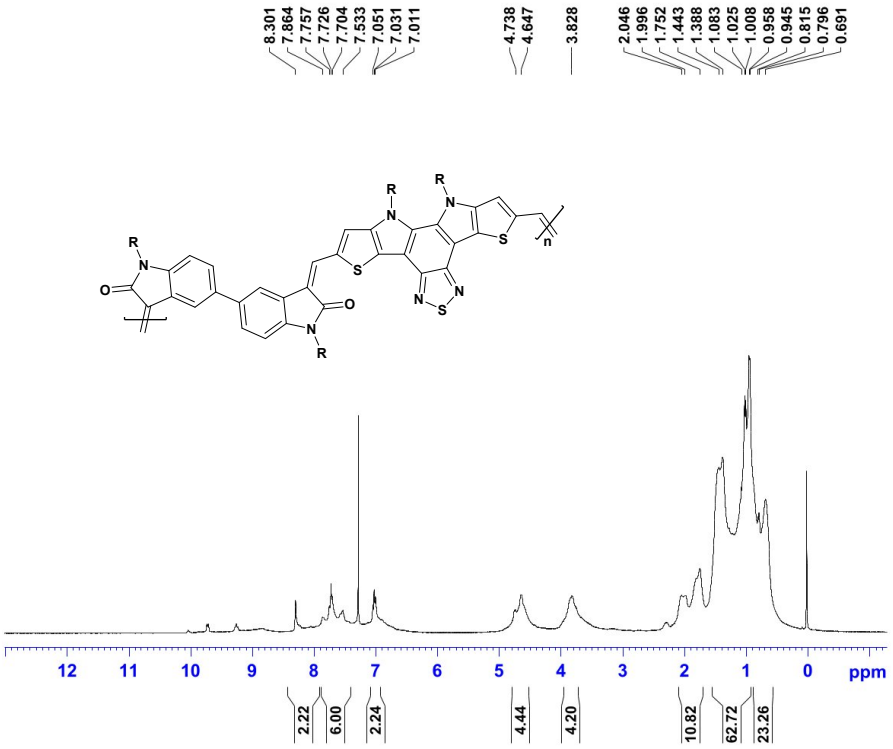


Figure S40: ^{1}H NMR spectra of polymer **ADRI**

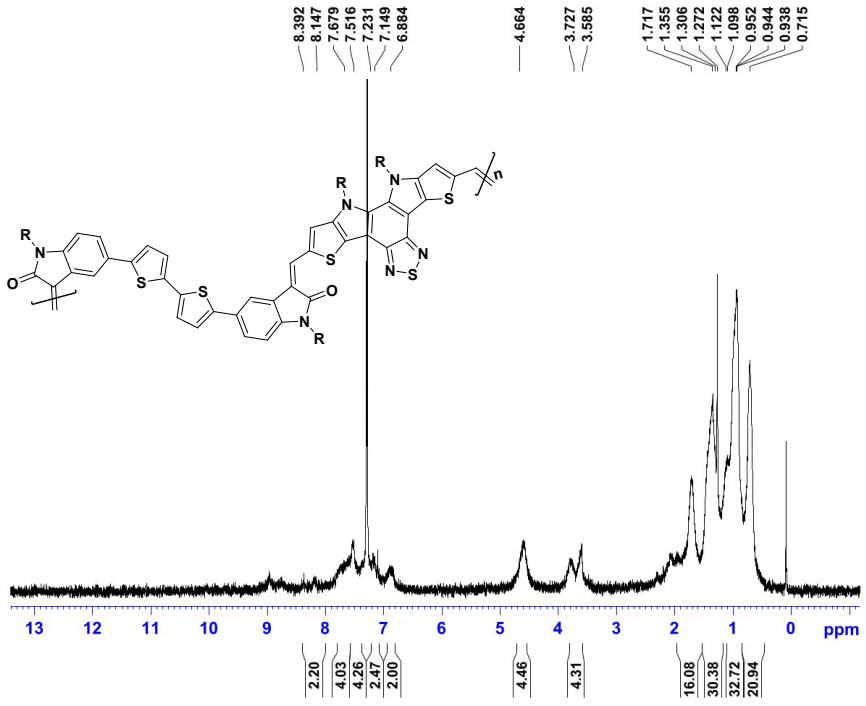


Figure S41: ^{1}H NMR spectra of polymer **ADTRI**

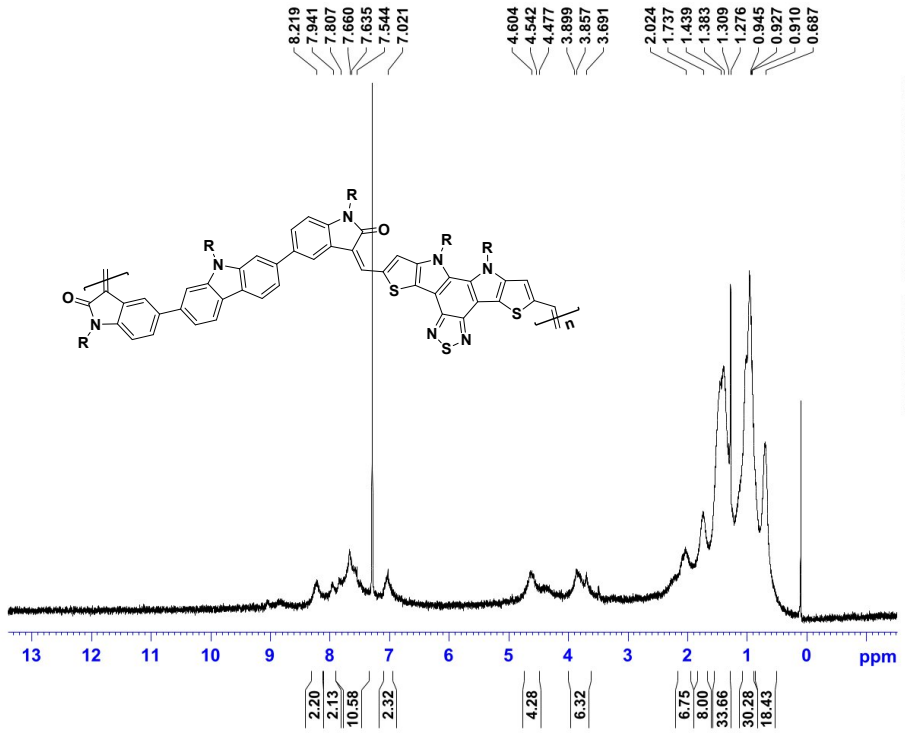


Figure S42: [1]H NMR spectra of polymer **ADCRI**

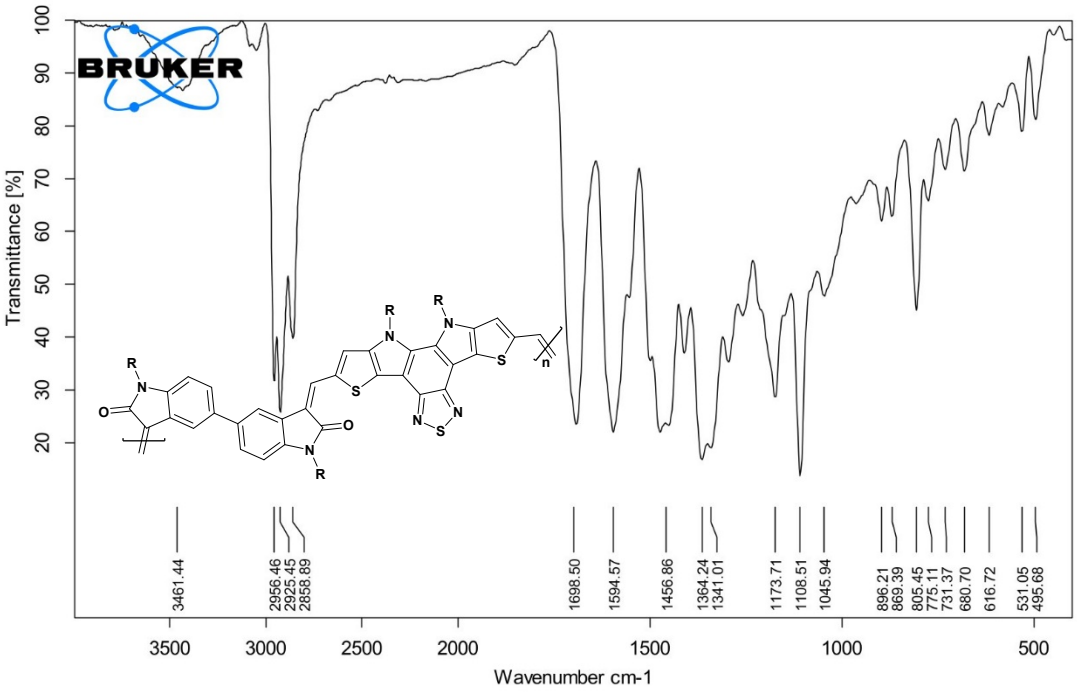


Figure **43**: IR spectrum (KBr pellet) of polymer **ADRI**

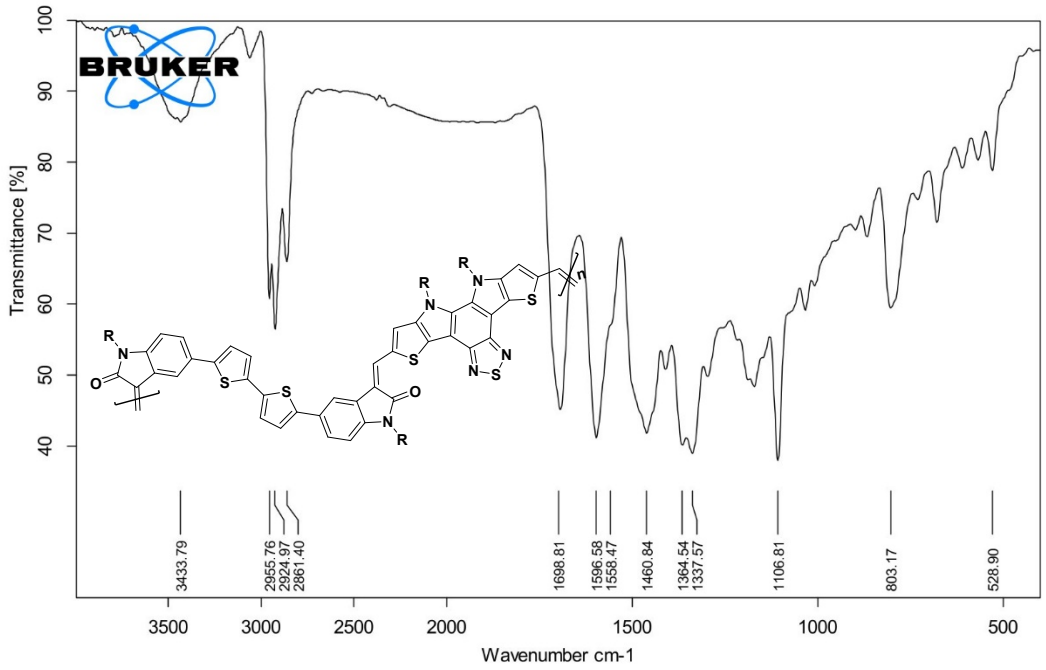


Figure **44**: IR spectrum (KBr pellet) of polymer **ADTRI**

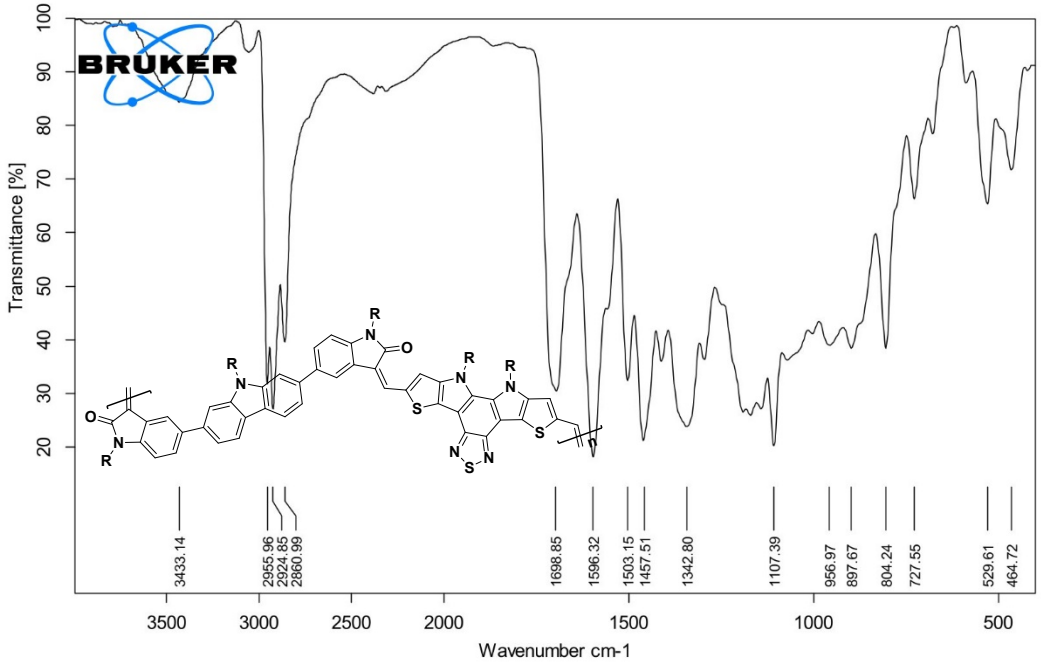
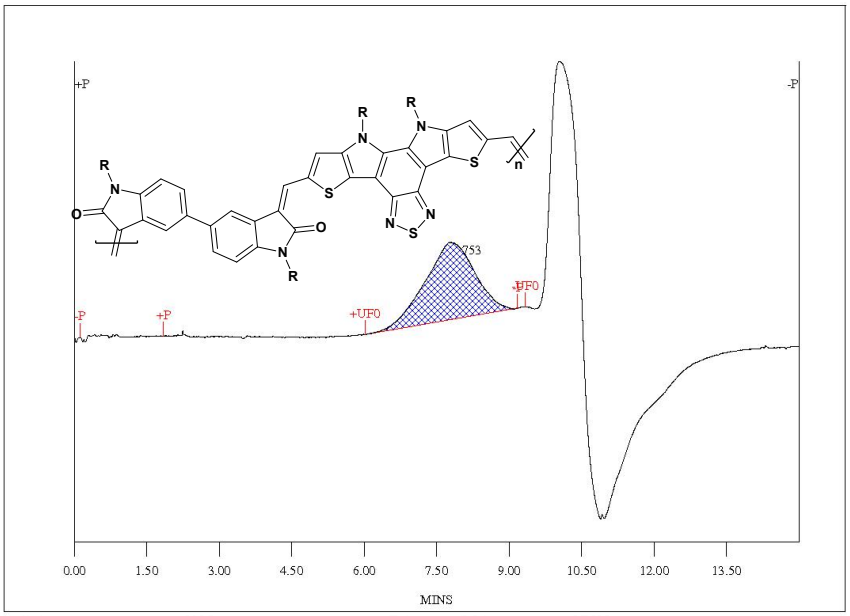


Figure **45**: IR spectrum (KBr pellet) of polymer **ADCRI**

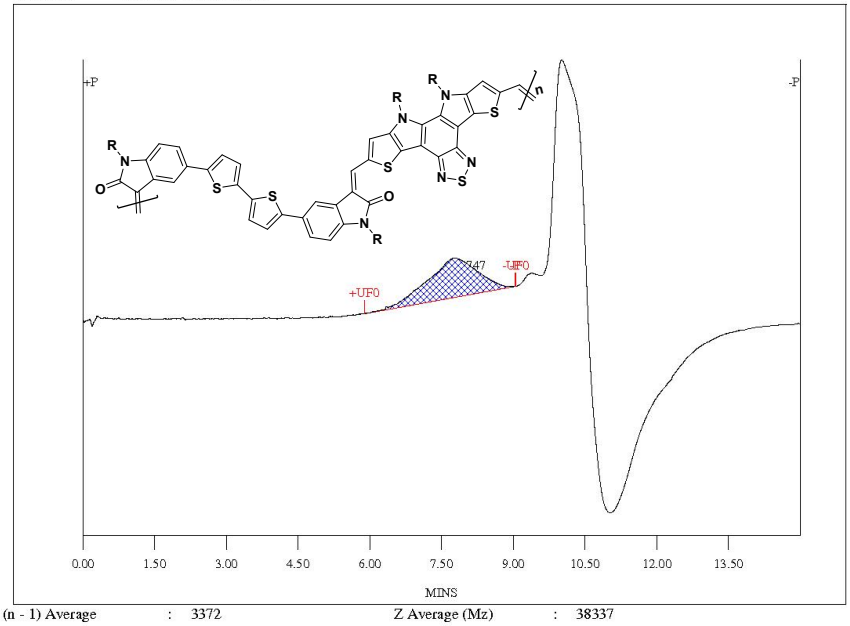


(n - 1) Average : 3025 Z Average (Mz) : 27633
Number Average (Mn) : 5694 (Z + 1) Average : 51309
Weight Average (Mw) : 12436 PolyDispersity (Mw/Mn) : 2.184
Total Area : 6.9942432e+004 (microvolt seconds)

Peak Molecular Weight Report

Peak	Component	RT	Area	%Area	PMwt	Mw	Mn	Mw/Mn	StartMw	EndMw
1		7.753	69942.4	100.000	8009.8	12436.1	5693.9	2.1841	199190.0	479.0

Figure S46: GPC Analysis report of polymer **ADRI**

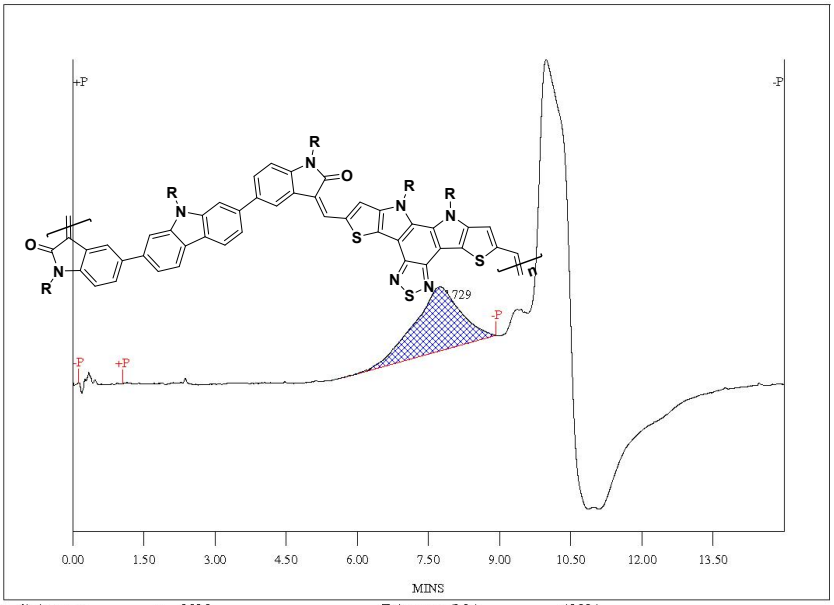


(n - 1) Average : 3372 Z Average (Mz) : 38337
Number Average (Mn) : 6296 (Z + 1) Average : 77683
Weight Average (Mw) : 15070 PolyDispersity (Mw/Mn) : 2.393
Total Area : 4.6117452e+004 (microvolt seconds)

Peak Molecular Weight Report

Peak	Component	RT	Area	%Area	PMwt	Mw	Mn	Mw/Mn	StartMw	EndMw
1		7.747	46117.5	100.000	8107.0	15070.3	6296.4	2.3935	261596.1	794.2

Figure S47: GPC Analysis report of polymer **ADTRI**



(n - 1) Average	: 3686	Z Average (Mz)	: 42884
Number Average (Mn)	: 6859	(Z + 1) Average	: 105745
Weight Average (Mw)	: 16053	PolyDispersity (Mw/Mn)	: 2.340
Total Area	: 7.4675149e+004 (microvolt seconds)		

Peak Molecular Weight Report

Peak	Component	RT	Area	%Area	PMwt	Mw	Mn	Mw/Mn	StartMw	EndMw
1		7.729	74675.1	100.000	8374.8	16052.9	6858.9	2.3404	402797.2	988.0

Figure S48: GPC Analysis report of polymer **ADCRI**

References

1 P. R. Patel, Y. G. Kapdi, S. S. Soni, S. S. Zade and A. L. Patel, *New J. Chem.*, 2024, **48**, 7007-7019.

2 Y. W. Huang, Y. C. Lin, J. S. Li, W. C. Chen and C. C. Chueh, *J. Mater. Chem. C*, 2021, **9**, 9473–9483.

3 Y. Jiang, J. Chen, Y. Sun, Q. Li, Z. Cai, J. Li, Y. Guo, W. Hu and Y. Liu, *Adv. Mater.*, 2019, **31**, 1–7.

4 F. Dierschke, A. C. Grimsdale and K. Müllen, *Synthesis (Stuttg).*, 2003, 2470–2472.

5 H. Wang, P. Cheng, Y. Liu, J. Chen, X. Zhan, W. Hu, Z. Shuai, Y. Li and D. Zhu, *J. Mater. Chem.*, 2012, **22**, 3432–3439.

6 H. Li, S. Sun, T. Salim, S. Bomma, A. C. Grimsdale and Y. M. Lam, *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 250–260.

7 Y. Yu, N. Xue, C. Xiao, M. K. Ravva, Y. Guo, L. Wu, L. Zhang, Z. Li, W. Yue and Z. Wang, *Fan, H.; Huang, D.; Yuan, D.; Di, C. Accept. Artic. Chem. C*, 2019, **7**, 12263–12269.

8 V. S. Kadam, P. A. Bhatt, H. K. Machhi, S. S. Soni, S. S. Zade and A. L. Patel, *Nano Select*, 2020, **1**, 491–498.