Synthesis and Study of Donor-Acceptor Conjugated Polymers based on Isoindigo units *via* Metal Free Aldol Polymerization Strategy

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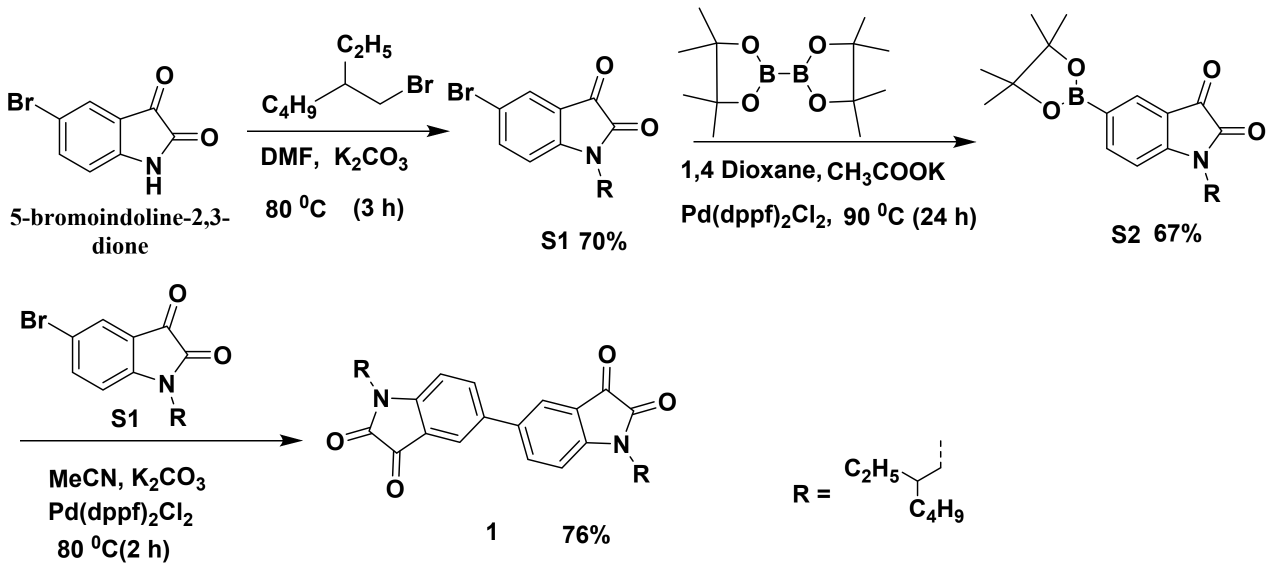
CONTENTS

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 progress was 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 1,1'-Bis(2-ethylhexyl)-[5,5'-biindoline]-2,2',3,3'-tetraone (1)



Scheme S1 Synthesis of 1,1'-bis(2-ethylhexyl)-[5,5'-biindoline]-2,2',3,3'-tetraone (**1**) from 5-bromoindoline-2,3-dione.

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

5-Bromo-1-(2-ethylhexyl)indoline-2,3-dione (**S1**): Under nitrogen atmosphere, 5-bromoisatin (2.0g, 8.84 mmol) and anhydrous potassium carbonate (5.492g, 39.8 mmol) were dissolved in dry DMF (18 mL) and heated for 10 minutes at 50 °C. After adding ethylhexyl bromide (2.73 mL, 15.4 mmol), the reaction mixture was stirred at 80 °C 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 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 pet ether.

5-Bromo-1-(2-ethylhexyl)indoline-2,3-dione (**S1**): Orange red solid (2.45g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.71 (dd, J_1= 7.2 Hz, J_2= 2 Hz, 2H), 6.80-6.82 (dd, 1H, J_1 = 8 Hz, J_2 = 1.6 Hz), 3.56-3.62 (t, 2H), 1.72-1.81 (s, 1H), 1.28-1.43 (m, 8H), 0.90-0.96 (m, 6H). IR (KBr, cm^{-1}): 2959, 2927, 2864, 1732, 1605, 1471, 1467, 1438, 1326, 1182, 825, 711, 468.

1-(2-Ethylhexyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indoline-2,3-dione (**S2**): In dry two-necked round bottom flask, a mixture of 1,4 dioxane (20 mL), compound **S1** (1.0g, 2.9 mmol), bis(pinacolato)diborane (1.12g, 4.4 mmol), and potassium acetate (0.580g, 5.9 mmol) was taken. After degassing for 30 minutes with sparging nitrogen, catalyst, $Pd(PPh_3)_2Cl_2$ (0.103g, 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 pet ether to get red oil.

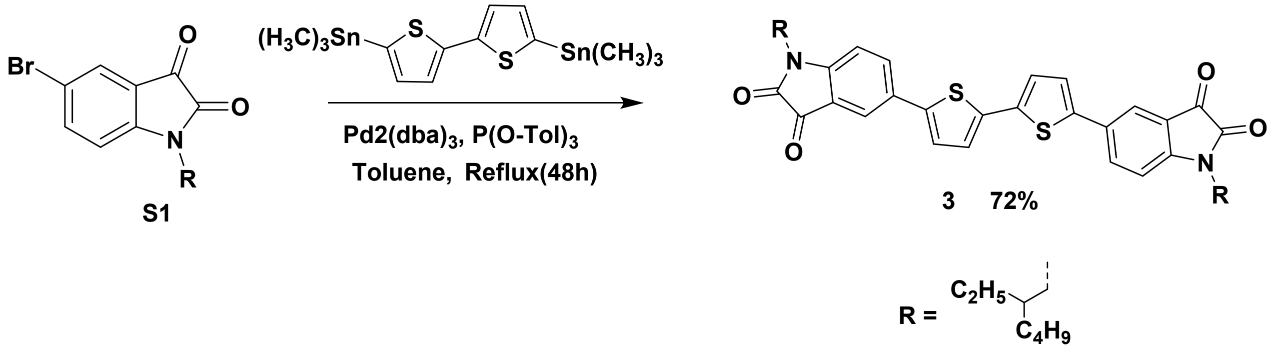
1-(2-Ethylhexyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indoline-2,3-dione (**S2**): Orange red liquid (0.81g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.06 (d, J = 0.8 Hz, 1H), 8.01-8.03 (dd, J_1 = 8 Hz, J_2 = 1.2 Hz, 1H), 6.87-6.89 (d, J = 8 Hz, 1H), 3.61-3.64 (m, 2H), 1.78 (s, 1H), 1.35 (s, 12H), 1.27-1.33 (m, 8H) 0.87-0.95 (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.

1,1'-Bis(2-ethylhexyl)-[5,5'-biindoline]-2,2',3,3'-tetraone (**1**)

Compound **S2** (0.860g, 2.5 mmol) and compound **S1** (1.10g, 2.88mmol) were dissolved in 45 mL acetonitrile and the reaction mixture was stirred for 5 minutes. 2 M K_2CO_3 (0.84g, 6.1 mmol) solution was added to the reaction mixture, followed by 30 minutes of nitrogen purging. The catalyst, [Pd(dppf)$_2$Cl$_2$] (0.10g, 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 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 eluent.

1,1'-Bis(2-ethylhexyl)-[5,5'-biindoline]-2,2',3,3'-tetraone (**1**): Brown red solid (1.0g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.78 (m, 4H), 6.99-7.01 (d, J_1= 8 Hz, 2H), 3.65-3.68 (m, 4H), 1.84-1.87 (m, 2H), 1.26-1.46 (m, 16H), 0.92-0.99 (m, 12H). ^{13}C NMR (100MHz, $CDCl_3$): δ 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 5,5'-([2,2'-bithiophene]-5,5'-diyl)bis(1-(2-ethylhexyl)indoline-2,3-dione) (**3**) from compound **S1**

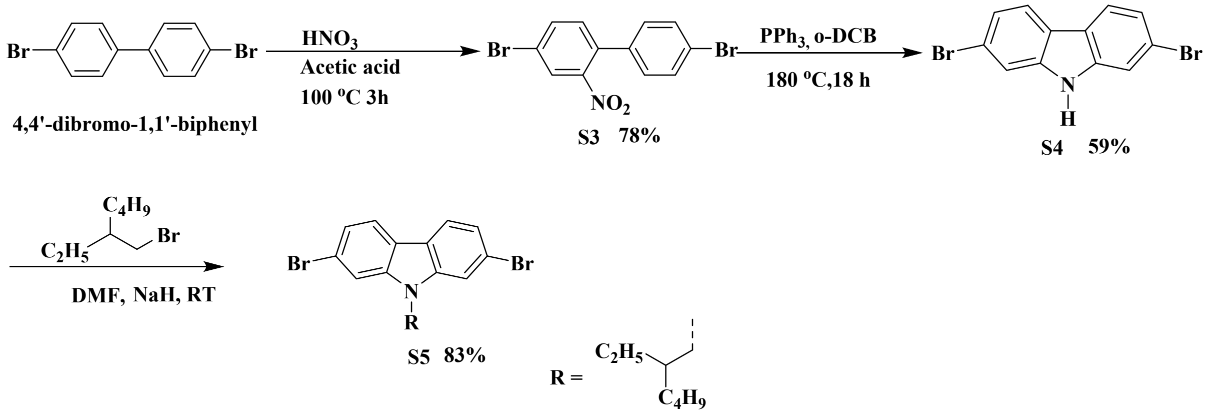
Compound **3** was synthesized according to the modified literature procedure.[3]

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

Compound **S1** (0.604g, 1.79 mmol) was taken in two neck round bottom flask and adissolved in 30 mL toluene. 5,5'-Bis(trimethylstannyl)-2,2'-bithiophene (0.400g, 0.814 mmol), $Pd_2(dba)_3$ (0.074g, 0.081 mmol), and $P(o\text{-}tol)_3$ (0.318g, 0.651 mmol) were added into the reaction mixture under nitrogen atmosphere. The reaction mixture was stirred for 24 hours at 110 °C, cooled down to room temperature, water and dichloromethane were added. The organic extract was washed with water and then dried over with anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by silica gel chromatography with eluent 40% DCM in petroleum ether as an eluent to give compound **3** as a black solid (0.600g, 72.2 %).

5,5'-([2,2'-Bithiophene]-5,5'-diyl)bis(1-(2-ethylhexyl)indoline-2,3-dione) **(3):** Brown solid (0.600g, 72.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.84 (m, 4H), 7.18-7.22 (dd, J_1= 12.8 Hz, J_2= 3.6 Hz, 4H), 6.93-6.95 (d, J_1= 8 Hz, 2H), 3.64-3.68 (m, 4H), 1.83-1.85 (m, 2H), 1.27-1.45 (m, 16H), 0.91-0.99 (m, 12H). ^{13}C NMR (100MHz, $CDCl_3$): 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.

Compound **S5** was synthesized according to the modified literature procedure.[4–6]

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

In a 250 mL two necked round bottom flask, 4,4'-dibromo- biphenyl (4g, 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 into water and subsequently extracted with DCM. The organic layer was then washed successively with water and dried over Na_2SO_4. The compound **S3** was obtained by evaporation of solvent under reduced pressure.

4,4'-Dibromo-2-nitro-1,1'-biphenyl **(S3):** Yellow solid (3.60g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.88-7.90 (d, J = 8.4, 2H), 7.58–7.59 (d, J = 1.6 Hz, 2H), 7.37-7.39 (dd, J_1 = 8 Hz, J_2 = 1.6 Hz, 2H).

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

4,4'-Dibromo-2-nitro-1,1'-biphenyl (**S3**) (6g, 16.8 mmol) and PPh_3 (11g, 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.

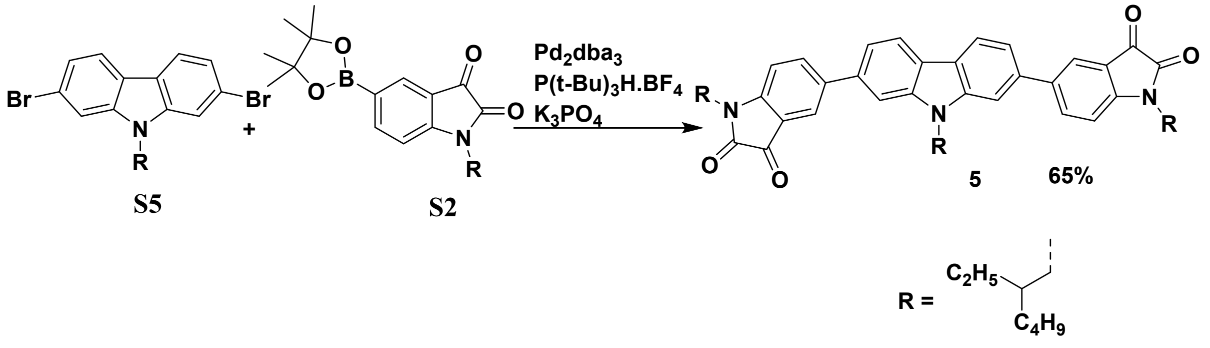
2,7-Dibromocarbazole (**S4**): White solid (3.25g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.06 (d, J = 2 Hz, 1H), 7.77- 7.80 (dd, J = 8.4 Hz, J = 2 Hz, 1H), 7.60 (s, 1H), 7.57-7.58 (d, J = 2 Hz, 1H), 7.31-7.33 (d, J = 8.4 Hz, 1H), 7.17-7.19 (dd, J = 1.6 Hz, J = 6.4 Hz, 2H).

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

In a 100 mL two necked round bottom flask, compound **S4** (5g, 15.4 mmol) in DMF (50 mL) was taken. To this reaction mixture, NaH (60% w/w suspension in mineral oil) (865mg, 21.6 mmol) was added. After 1 hour, 2-ethylhexyl bromide *(3*.83g, 19.84 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 into 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.

2,7-Dibromo-9-(2-ethylhexyl)-9*H*-carbazole (**S5**): White solid (7.0g, 83%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.90-7.92 (d, J = 8.4 Hz, 2H), 7.52 (s, 2H), 7.34-7.37 (dd, J_1 = 8.2 Hz, J_2 = 1.2 Hz, 2H), 4.06-4.08 (d, J = 6 Hz, 2H), 1.99-2.09 (m, 1H), 1.24–1.41 (m, 24H), 0.86–0.91 (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 5,5'-(9-(2-ethylhexyl)-9*H*-carbazole-2,7-diyl) bis(1-(2-ethylhexyl) indoline-2,3-dione) **(5)** from compound **S5.**

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

Compound **S5** (0.500g, 1.14 mmol), compound **S2** (0.951g, 2.47 mmol) and $Pd_2(dba)_3$ (47mg, 0.052 mmol), $P(t\text{-}Bu)_3 .BF_4$ (62mg, 0.216 mmol) were added into clean and dry two neck round bottom flask under nitrogen atmosphere. Then THF (40 ml) and potassium phosphate (1.7g, 2M) were added by injection in sequence. The reaction mixture was stirred at 80 °C for 24 hours. After cooling down, the mixture was poured into water, organic layer was extracted with dichloromethane, dried over anhydrous Na_2SO_4, and purified by silica gel column chromatography using 50% Ethyl acetate in petroleum ether.

5,5'-(9-(2-ethylhexyl)-9*H*-carbazole-2,7-diyl)bis(1-(2-ethylhexyl)indoline-2,3-dione) **(5):** Dark red solid (0.60g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-8.18 (d, J= 8 Hz, 2H), 7.94-7.97 (m, 4H), 7.52 (s, 2H), 7.42-7.44 (dd, J = 8 Hz, J = 1.2 Hz, 2H), 7.01-7.03 (d, J = 8.0 Hz, 2H), 4.25-4.29 (m, 2H), 3.67-3.70 (m, 4H), 2.09 (s, 1H), 1.88– 1.89 (d, 2H), 1.27-1.46 (m, 32H), 0.88-1.01 (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.

Compound **9** was synthesized using the modified reported literature process.[7,8]

5-Bromoindolin-2-one **(7)**

5-Bromoisatin (2.50 g, 11.0 mmol) was dissolved in methanol (20 mL). Following this, hydrazine monohydrate (1.5 mL, 31 mmol) was introduced, and the resulting mixture was stirred at reflux for 1 hour. Subsequently, the reaction mixture was cooled to 0 °C, subjected to suction filtration to get a bright yellow solid. This yellow solid was combined with a solution of sodium ethoxide in ethanol. Sodium metal (0.97 g, 42 mmol) had been dissolved in absolute ethanol (25 mL) to form the sodium ethoxide solution. The reaction mixture was then stirred at reflux temperature in air for 0.5 hours. The resultant mixture was poured over ice and acidified to pH 1 with dilute hydrochloric acid. The resulting solid was collected *via* suction filtration and dried under high vacuum, yielding compound **7** as a beige solid.

5-bromoindolin-2-one **(7)**: Beige solid (1.84 g, 78.4% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.51 (s, 1H), 7.38-7.35 (d, J= 11.2 Hz, 2H), 6.76-6.77 (d, J= 5.2 Hz, 1H), 3.51 (s, 2H).

(*E*)-5,5'-Dibromo-[3,3'-biindolinylidene]-2,2'-dione **(8)**

5-Bromoisatin (1.23 g, 5.44 mmol) and compound **7** (1.16 g, 5.47 mmol) were suspended in glacial acetic acid (35 mL). Following this, concentrated hydrochloric acid (0.25 mL) was added and the reaction mixture was stirred at reflux temperature for a duration of 18 hours. The mixture was then cooled to room temperature and subjected to suction filtration. The resulting solid was washed with water, ethanol and ethyl acetate before being dried under high vacuum.

(*E*)-5,5'-Dibromo-[3,3'-biindolinylidene]-2,2'-dione **(8):** Blackish red solid (1.98 g, 86.7% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.13 (s, 2H), 7.30-7.31 (d, J= 1.6 Hz, 2H), 7.53-7.58 (dd, J_1= 2H$_Z$, J_2 = 8.4 H$_Z$, 2H), 6.82-6.84 (d, J= 8 Hz, 2H).

(*E*)-5,5'-Dibromo-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione **(9)**
Compound **8** (2.10 g, 5.00 mmol) and K_2CO_3 (6.91g, 52.2 mmol) were suspended in dry DMF (100 mL). 2-Hexyldecylbromide (3.34 g, 10.9 mmol) was added into the reaction mixture and the reaction mixture was stirred at 100 °C for 20 hours. After completion of the reaction, the reaction mixture was poured over ice and subjected to extraction with Et_2O. The combined organic layers were washed successively with H_2O, brine and then dried over anhydrous Na_2SO_4. Subsequently, the solvent was concentrated under reduced pressure, yielding the crude product. Purification of the crude product was accomplished through silica gel column chromatography using 60% dichloromethane in petroleum ether. The solvent was evaporated under reduced pressure to get the desired product as a red solid (1.37 g, 31.3% yield).

(*E*)-5,5'-Dibromo-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione **(9)**: Red solid (1.37g, 31.3% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41-9.41 (d, J= 1.6 Hz, 2H), 7.48-7.50 (dd, J_1= 2 Hz, J_2= 8.4 Hz, 2H), 6.70-6.80 (d, J= 8.4 Hz, 2H), 3.74-3.78 (t, J= 7.2 Hz, 4H), 2.19 (m, 4H), 1.62-1.68 (m, 35H), 0.86-0.93 (m, 12H).

Spectral data of intermediate compounds and monomers

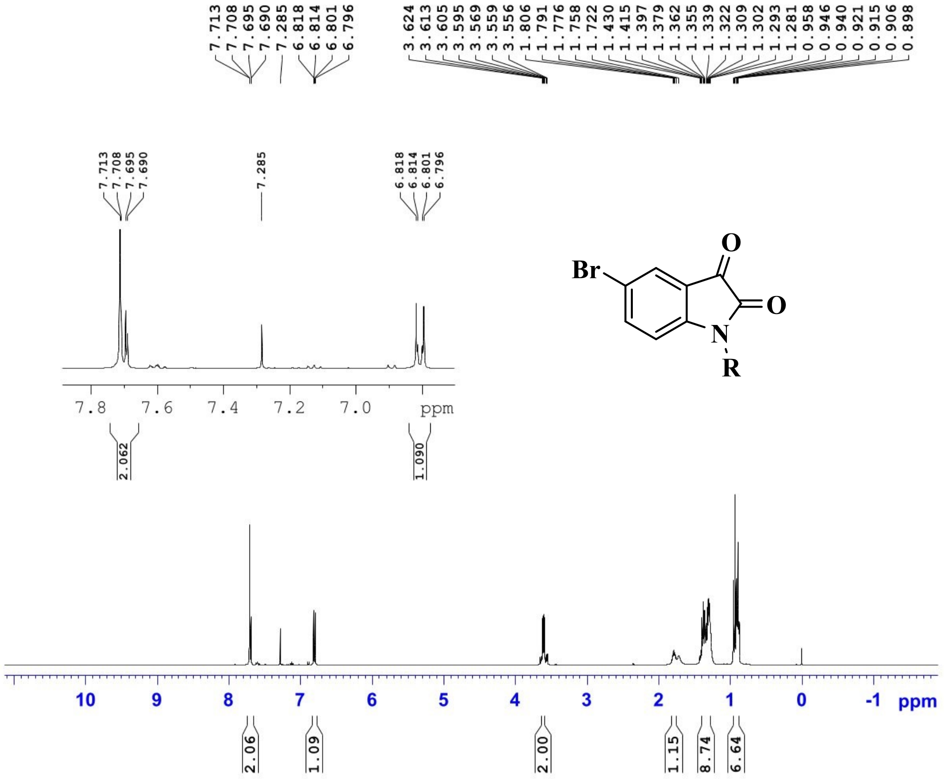


Figure **S1**: ^{1}H NMR spectra of compound S**1**

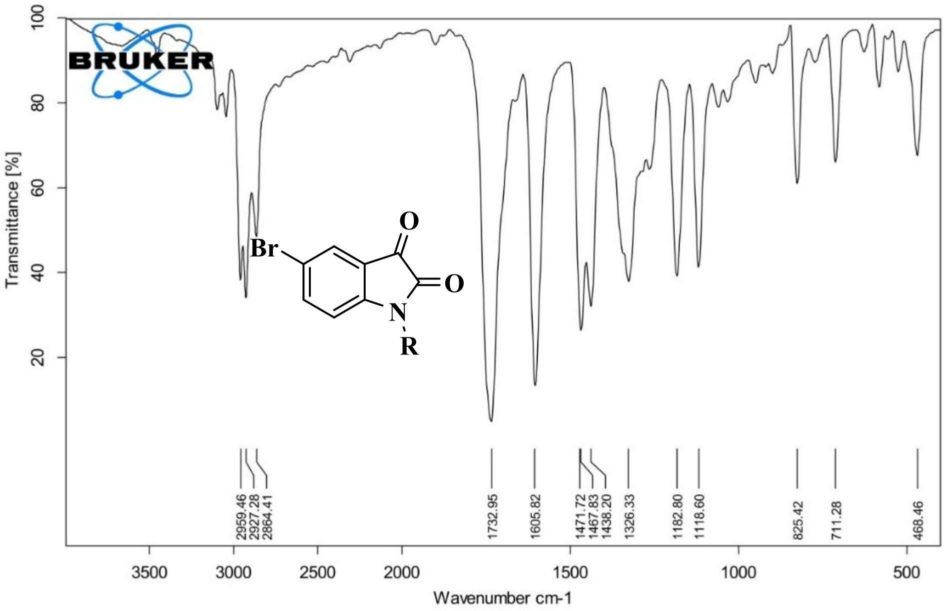


Figure **S2**: IR spectrum (KBr pellet) of compound **S1**

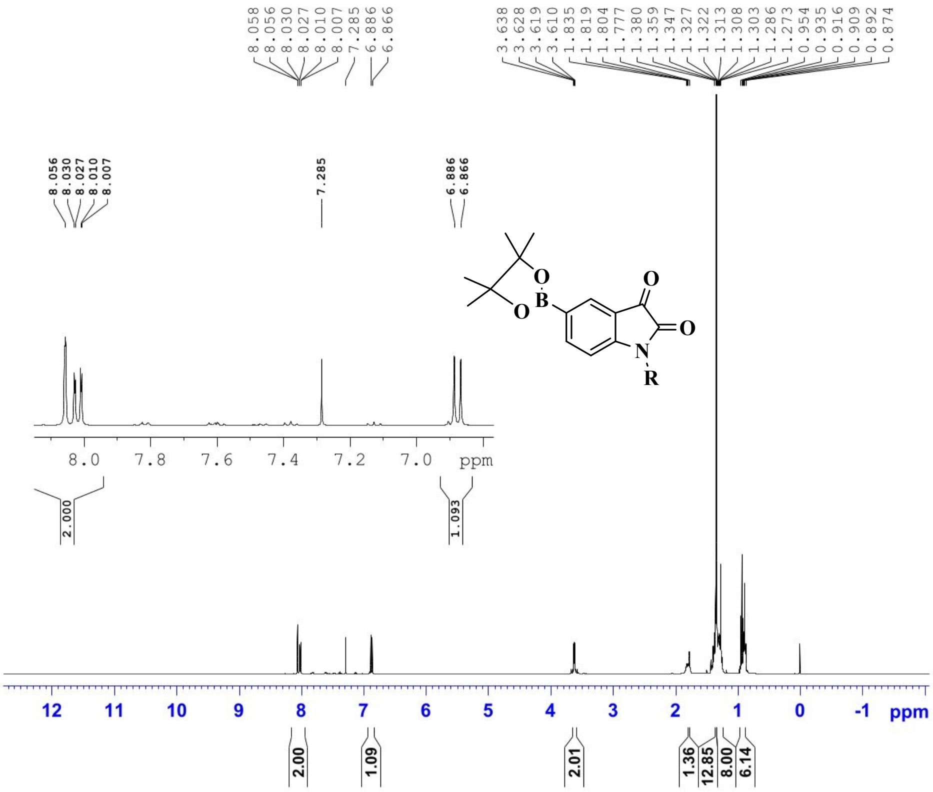


Figure **S3**: ^{1}H NMR spectra of compound S**2**

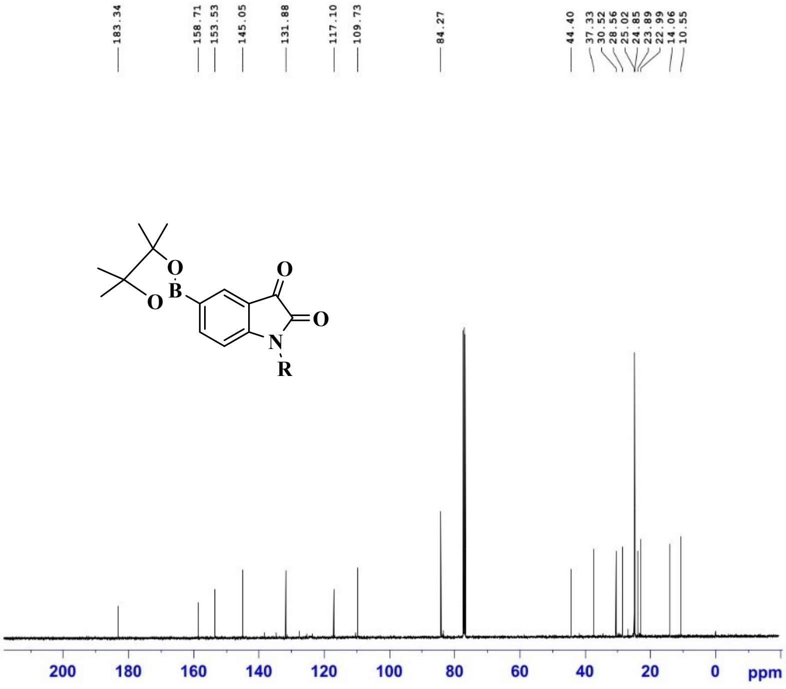


Figure **S4**: ^{13}C NMR spectra of compound **S2**

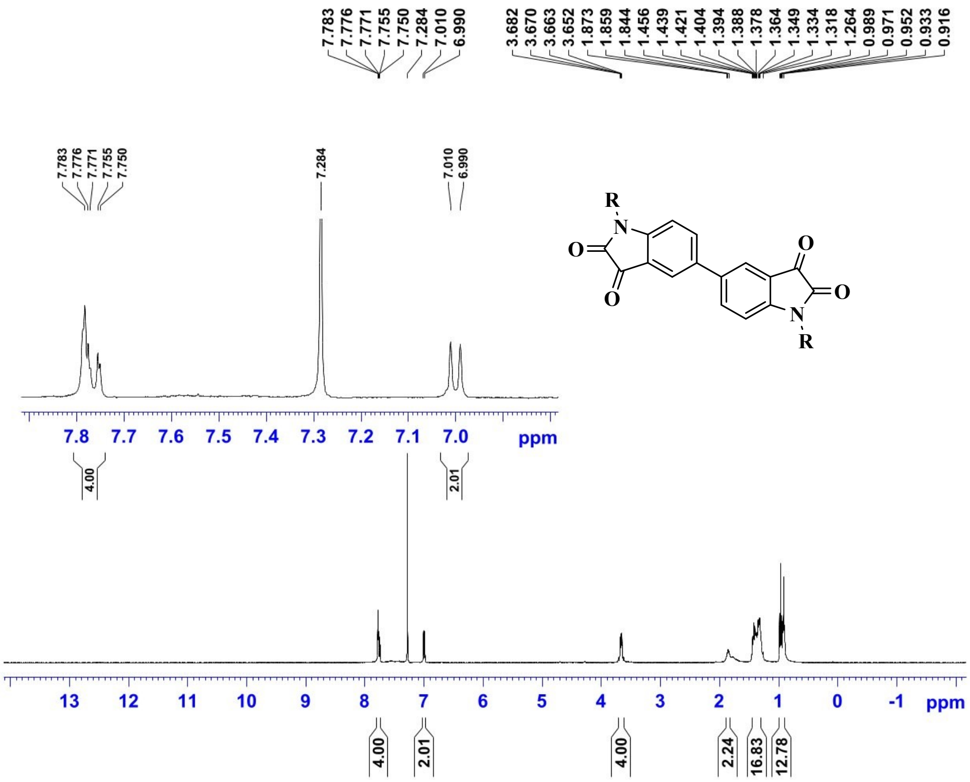


Figure **S5**: ^{1}H NMR spectra of compound **1**

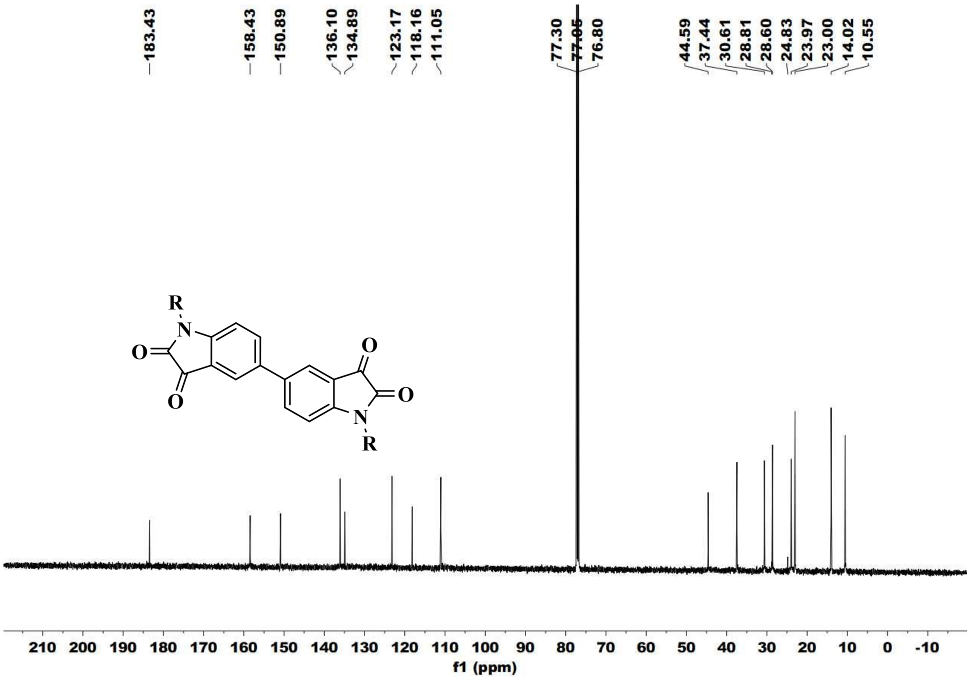
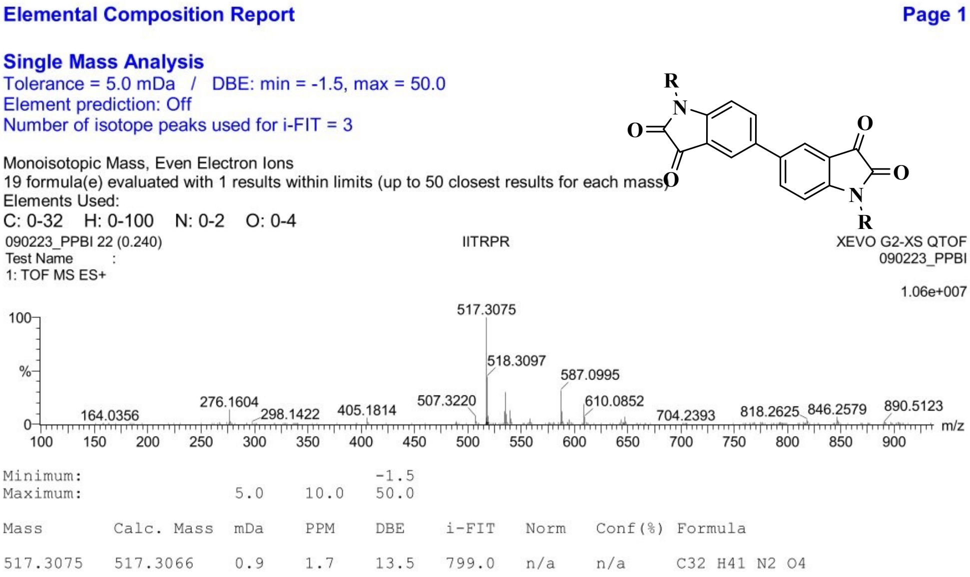


Figure **S6**: ^{13}C NMR spectra of compound **1**



Elemental Composition Report Page 1

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-32 H: 0-100 N: 0-2 O: 0-4
090223_PPBI 22 (0.240) IITRPR XEVO G2-XS QTOF
Test Name :
090223_PPBI
1: TOF MS ES+
1.06e+007

```
Minimum:                               -1.5
Maximum:               5.0     10.0    50.0

Mass       Calc. Mass  mDa     PPM     DBE     i-FIT   Norm   Conf(%)  Formula

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Figure **S7:** HR-MS data of compound **1**

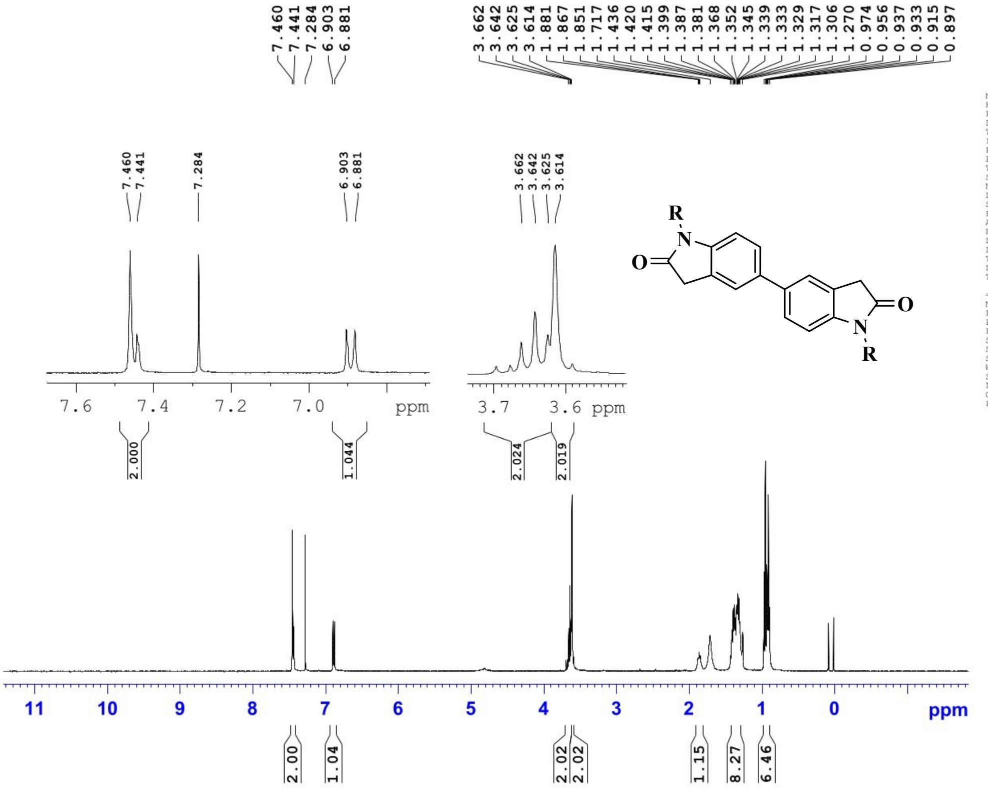


Figure **S8**: ^{1}H NMR spectra of compound **2**

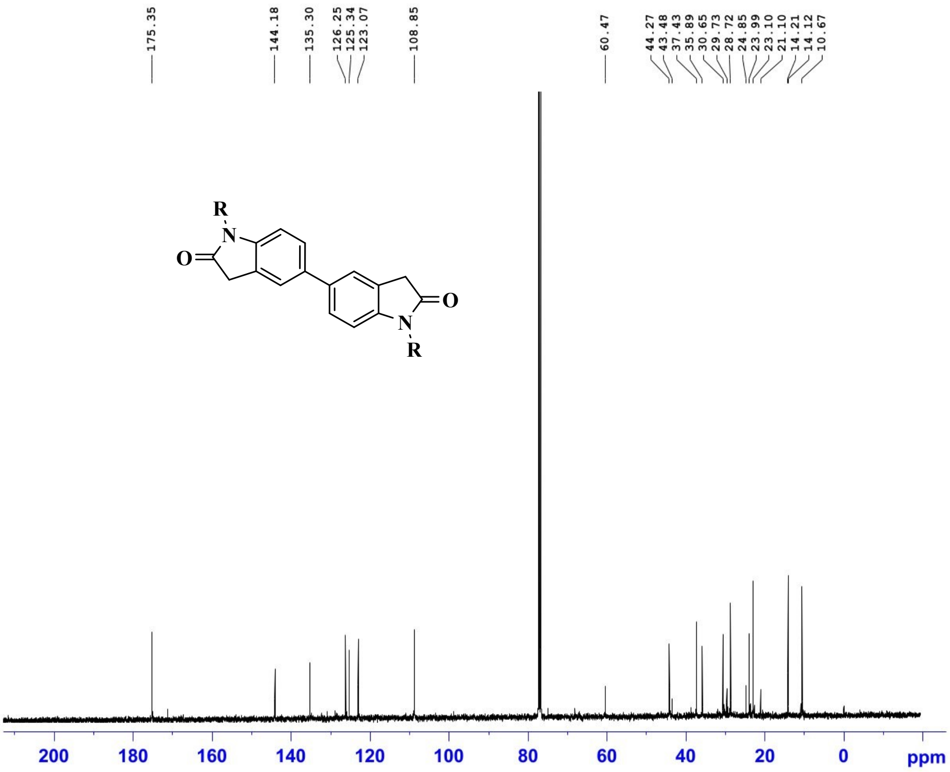
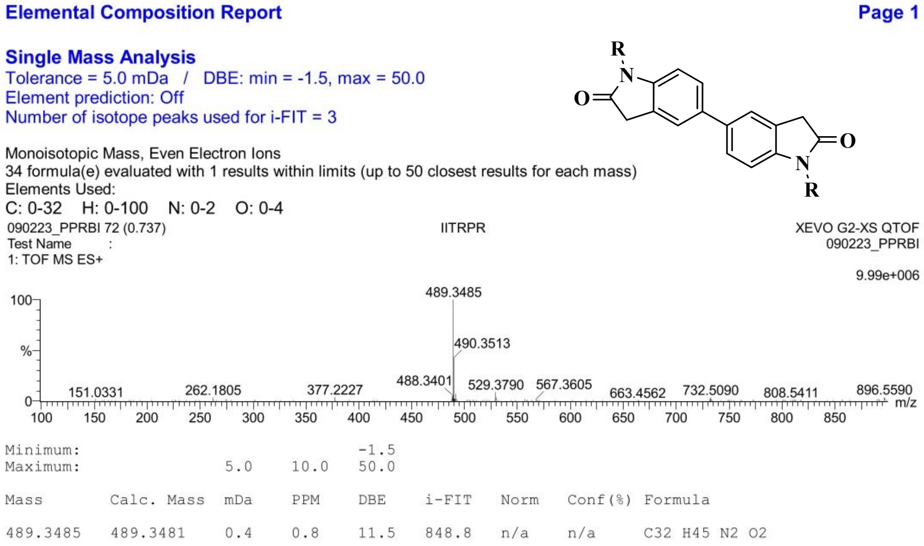


Figure **S9**: ^{13}C NMR spectra of compound **2**



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
34 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-32 H: 0-100 N: 0-2 O: 0-4

090223_PPRBI 72 (0.737) IITRPR XEVO G2-XS QTOF
Test Name : 090223_PPRBI
1: TOF MS ES+ 9.99e+006

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Minimum:                              -1.5
Maximum:                  5.0    10.0  50.0

Mass       Calc. Mass   mDa    PPM    DBE    i-FIT   Norm   Conf(%)  Formula

489.3485   489.3481     0.4    0.8    11.5   848.8   n/a    n/a      C32 H45 N2 O2
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Figure **S10:** HR-MS data of compound **2**

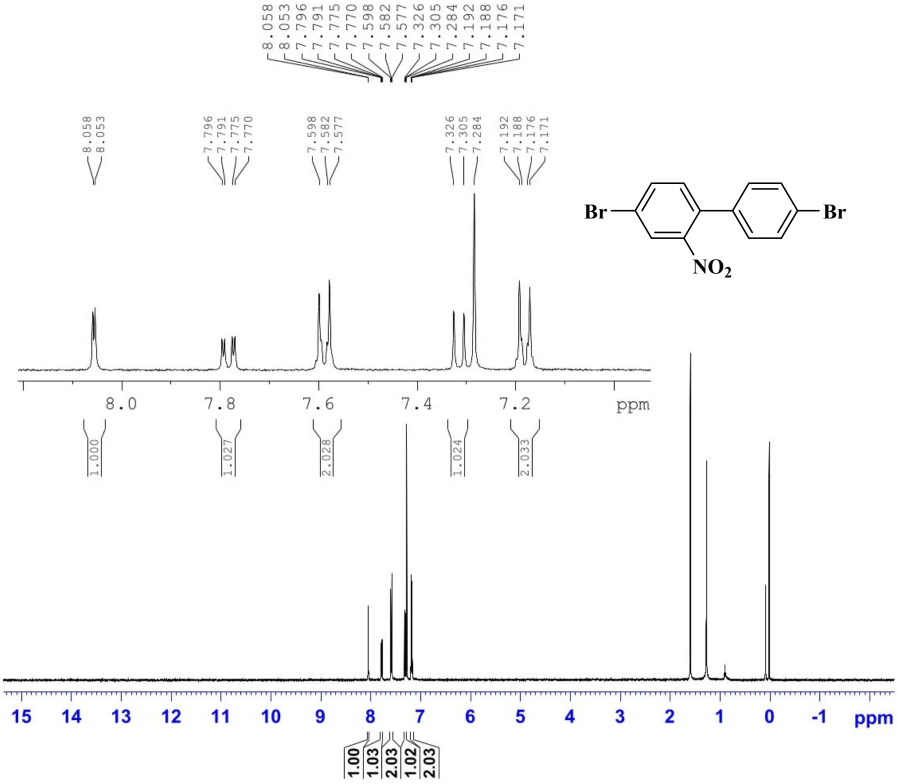


Figure S11: ^{1}H NMR spectra of compound **S3**

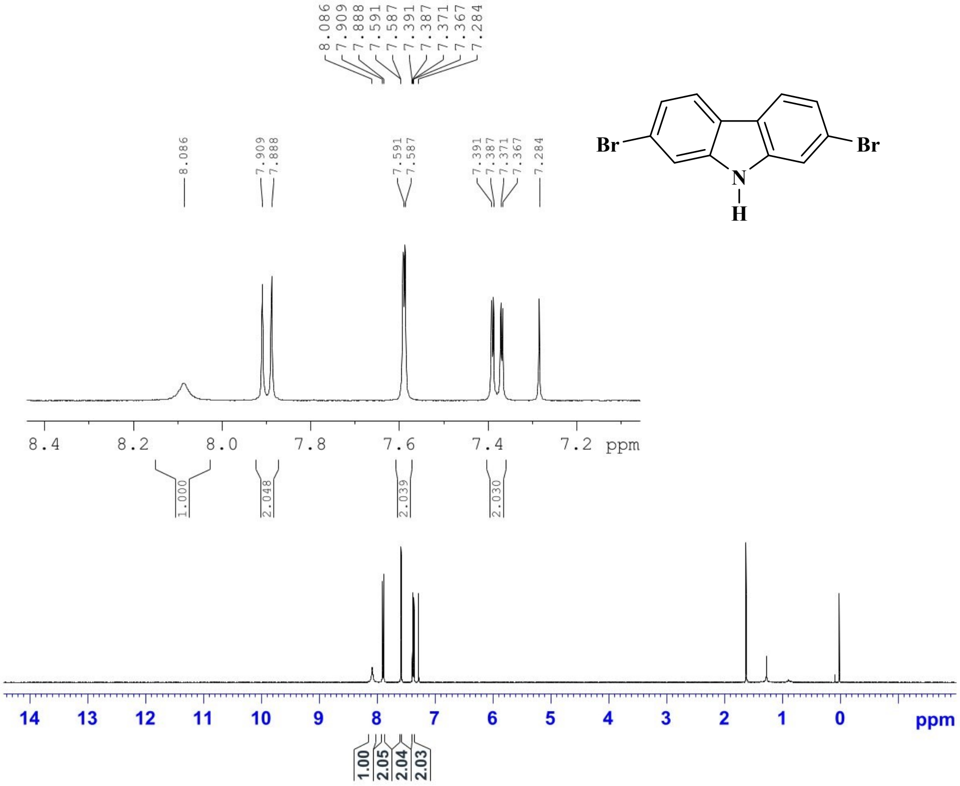


Figure S12: ^{1}H NMR spectra of compound **S4**

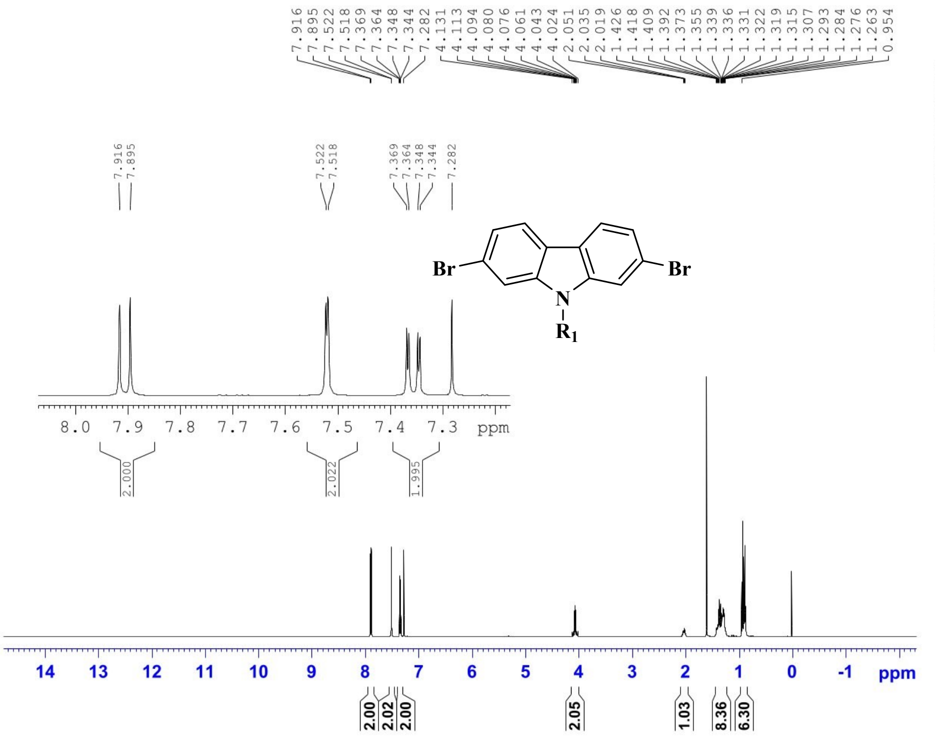


Figure S13: ^{1}H NMR spectra of compound **S5**

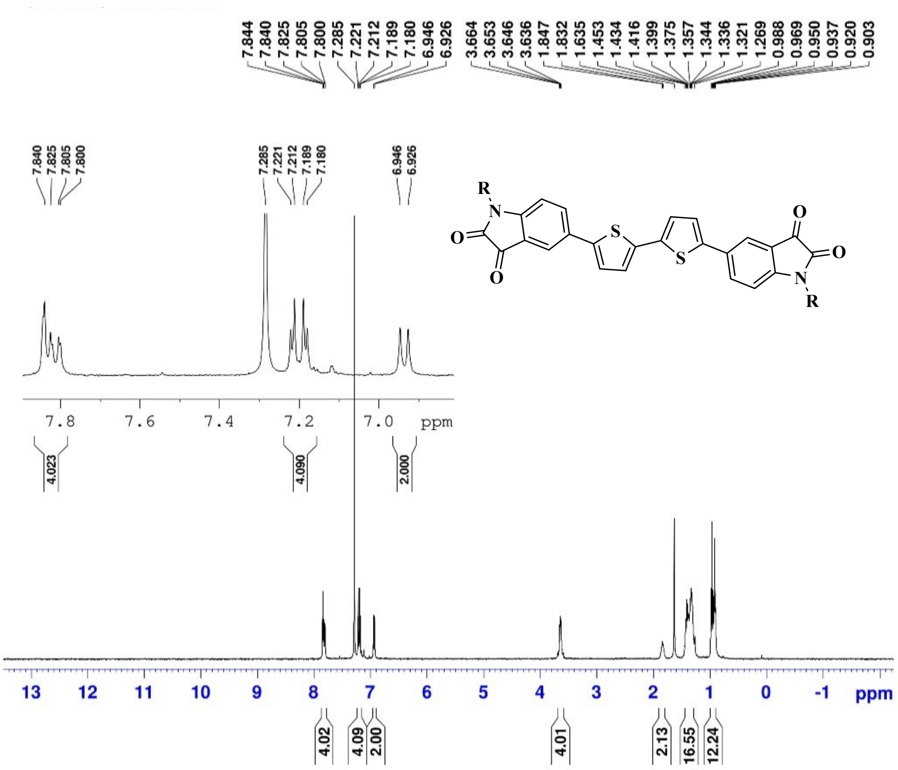


Figure **S14**: ^{1}H NMR spectra of compound **3**

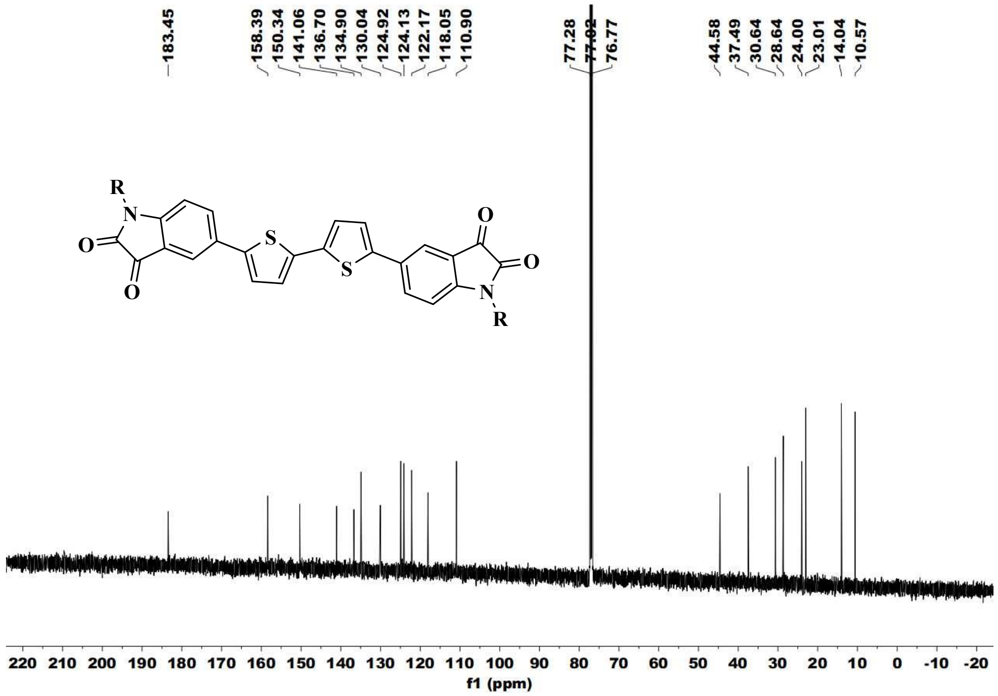
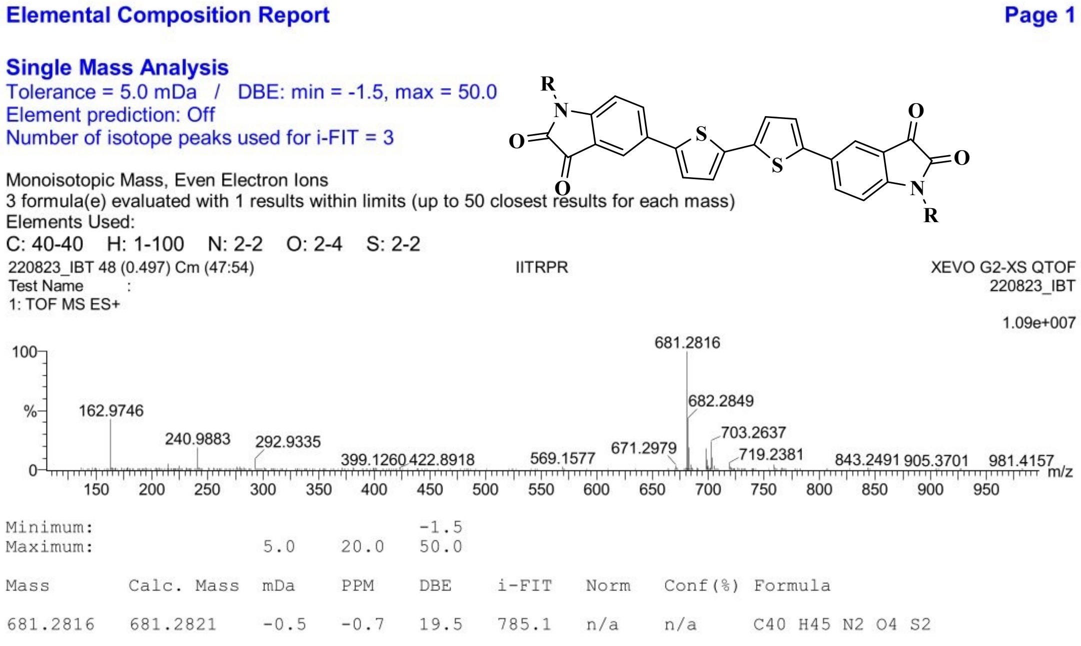


Figure **S15**: ^{13}C NMR spectra of compound **3**



Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 40-40 H: 1-100 N: 2-2 O: 2-4 S: 2-2

220823_IBT 48 (0.497) Cm (47:54) IITRPR XEVO G2-XS QTOF

Test Name : 220823_IBT

1: TOF MS ES+ 1.09e+007

```
Minimum:                               -1.5
Maximum:                5.0     20.0    50.0

Mass        Calc. Mass  mDa     PPM     DBE     i-FIT   Norm    Conf(%)  Formula

681.2816    681.2821    -0.5    -0.7    19.5    785.1   n/a     n/a      C40 H45 N2 O4 S2
```

Figure **S16:** HR-MS data of compound **3**

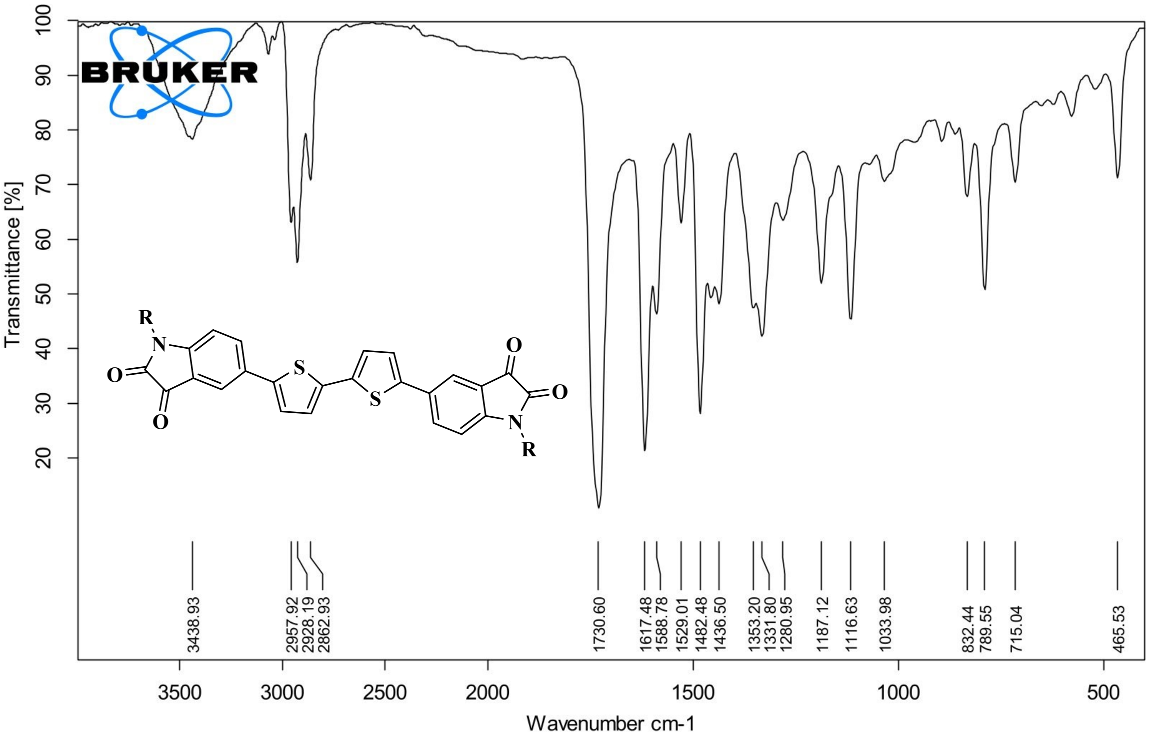


Figure **S17**: IR spectrum (KBr pellet) of compound **3**

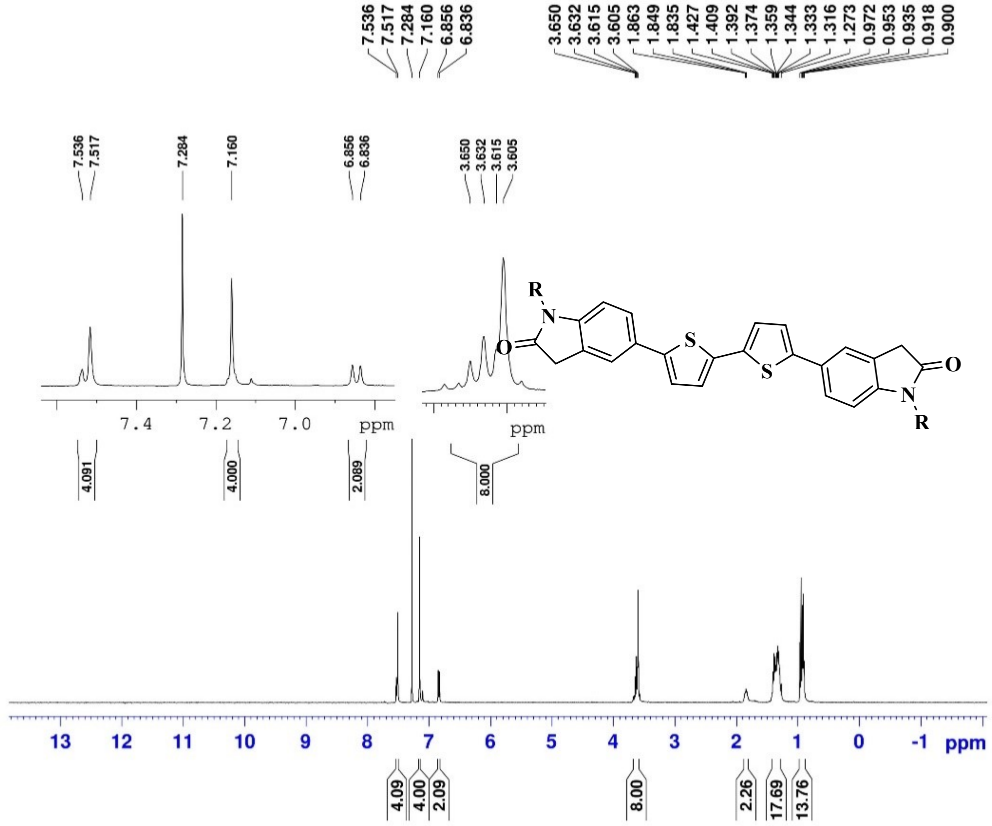


Figure **S18**: ^{1}H NMR spectra of compound **4**

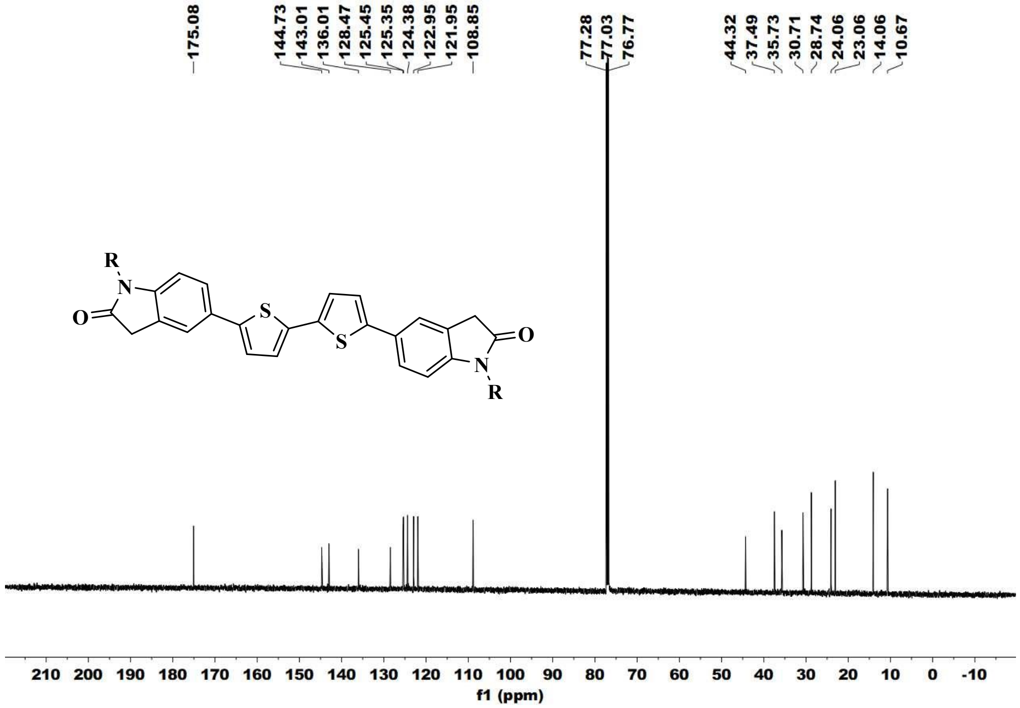
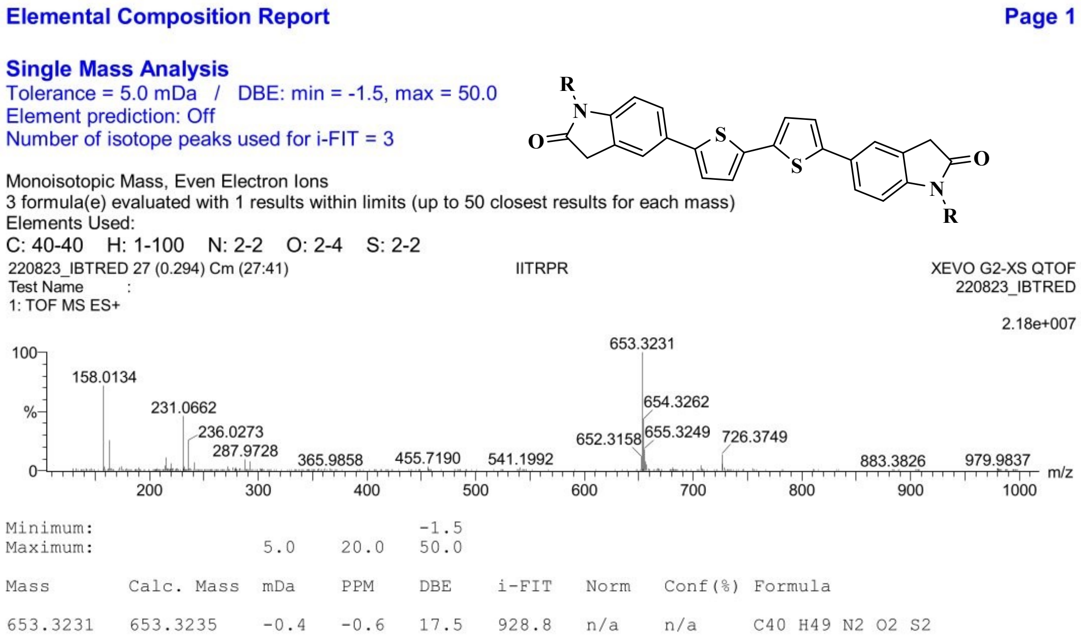


Figure **S19**: ^{13}C NMR spectra of compound **4**



Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 40-40 H: 1-100 N: 2-2 O: 2-4 S: 2-2

220823_IBTRED 27 (0.294) Cm (27:41) IITRPR XEVO G2-XS QTOF
Test Name : 220823_IBTRED
1: TOF MS ES+

```
Minimum:                                  -1.5
Maximum:                    5.0    20.0   50.0

Mass       Calc. Mass   mDa    PPM    DBE    i-FIT   Norm   Conf(%)  Formula

653.3231   653.3235     -0.4   -0.6   17.5   928.8   n/a    n/a      C40 H49 N2 O2 S2
```

Figure **S20:** HR-MS data of compound **4**

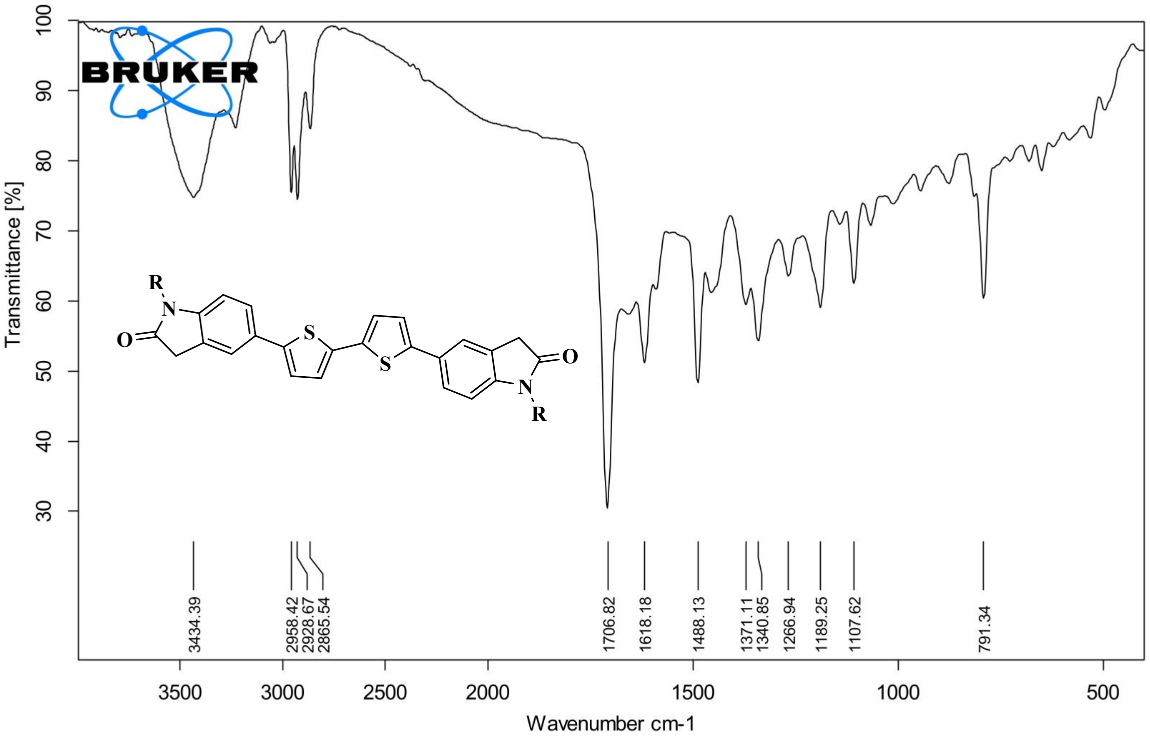


Figure **S21**: IR spectrum (KBr pellet) of compound **4**

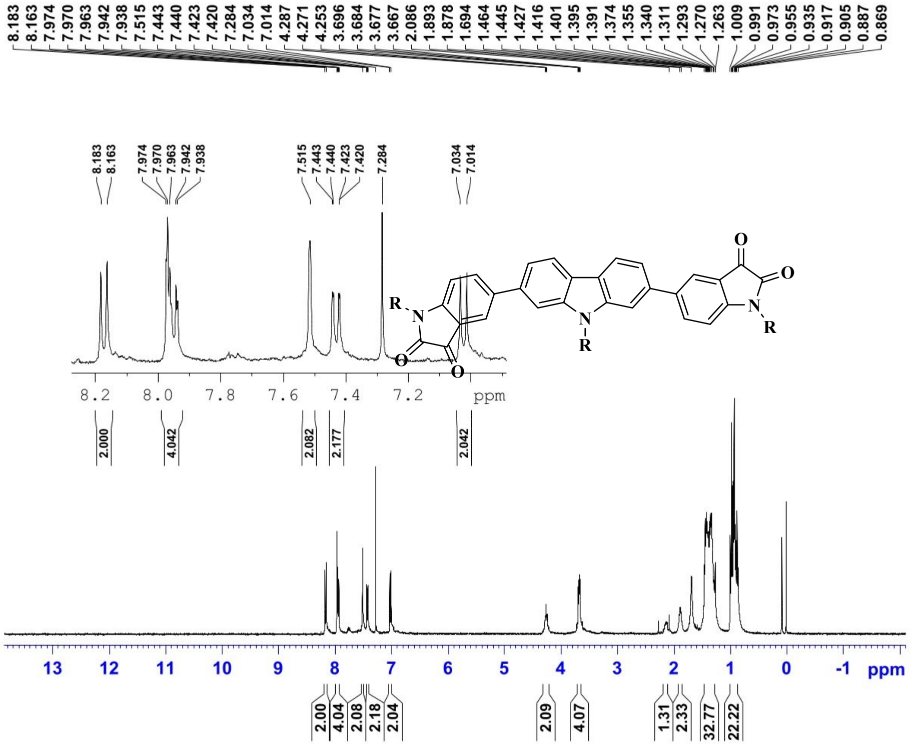


Figure **S22**: ^{1}H NMR spectra of compound **5**

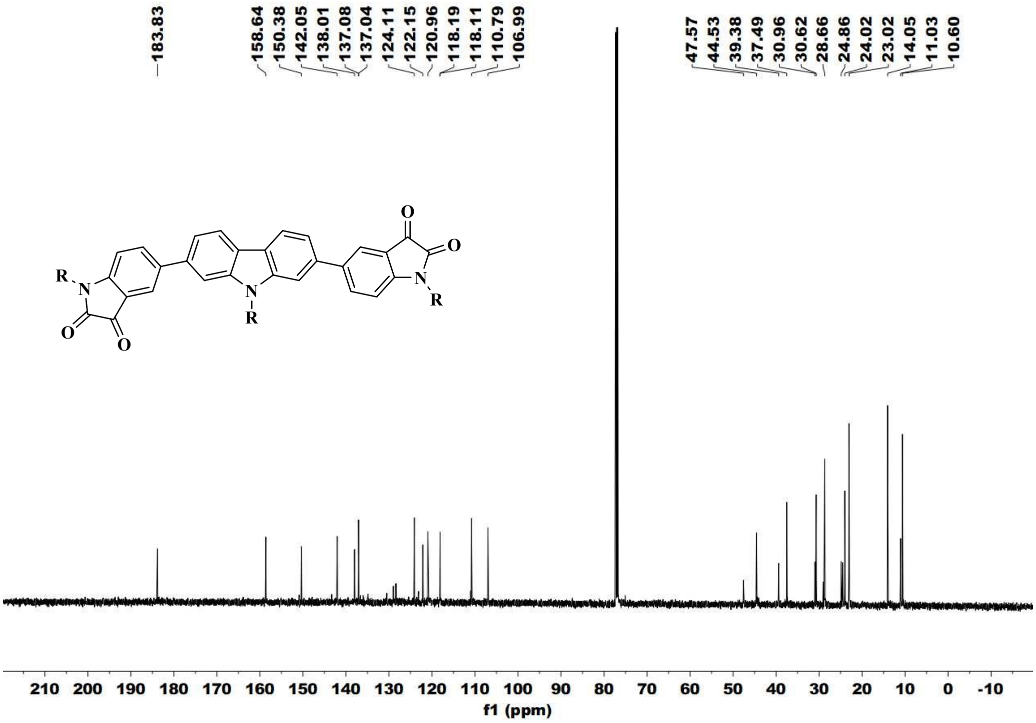
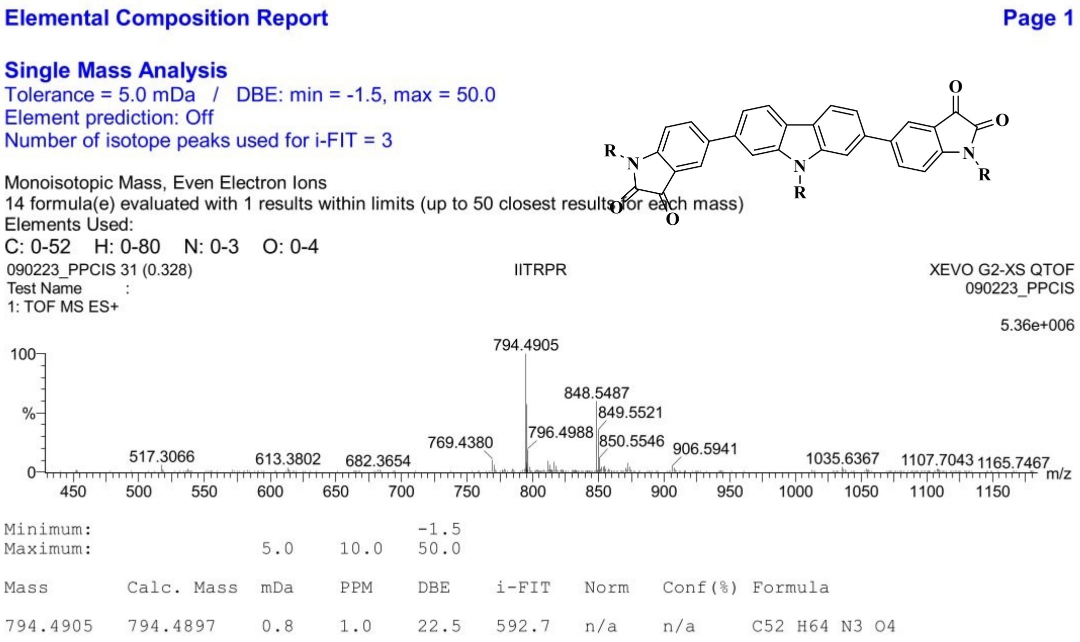


Figure **S23**: ^{13}C NMR spectra of compound **5**



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
14 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-52 H: 0-80 N: 0-3 O: 0-4

090223_PPCIS 31 (0.328) IITRPR XEVO G2-XS QTOF
Test Name : 090223_PPCIS
1: TOF MS ES+

```
Minimum:                            -1.5
Maximum:                5.0   10.0  50.0

Mass       Calc. Mass  mDa   PPM   DBE    i-FIT  Norm   Conf(%) Formula

794.4905   794.4897    0.8   1.0   22.5   592.7  n/a    n/a     C52 H64 N3 O4
```

Figure **S24**: ^{13}C NMR spectra of compound **5**

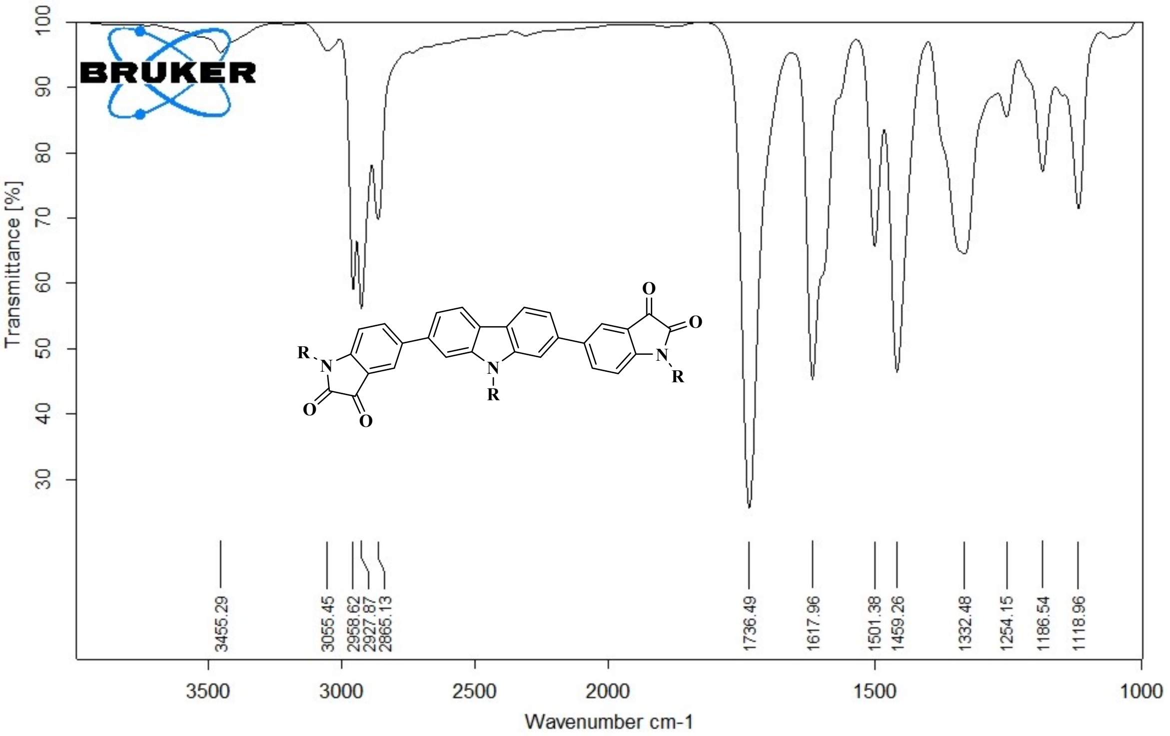


Figure **S25**: IR spectrum (KBr pellet) of compound **5**

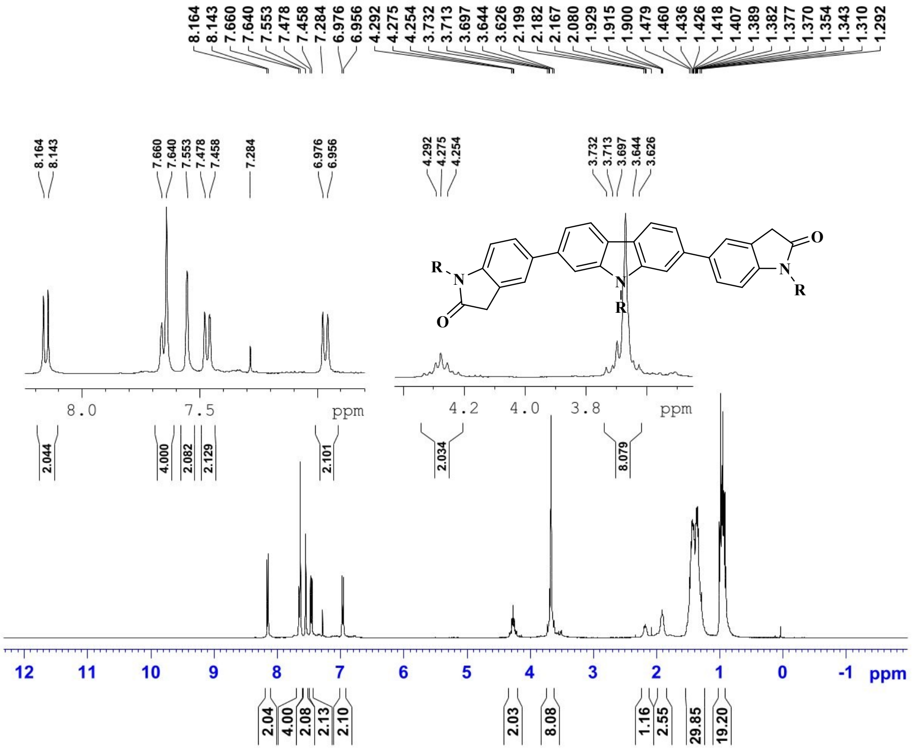


Figure **S26**: ^{1}H NMR spectra of compound **6**

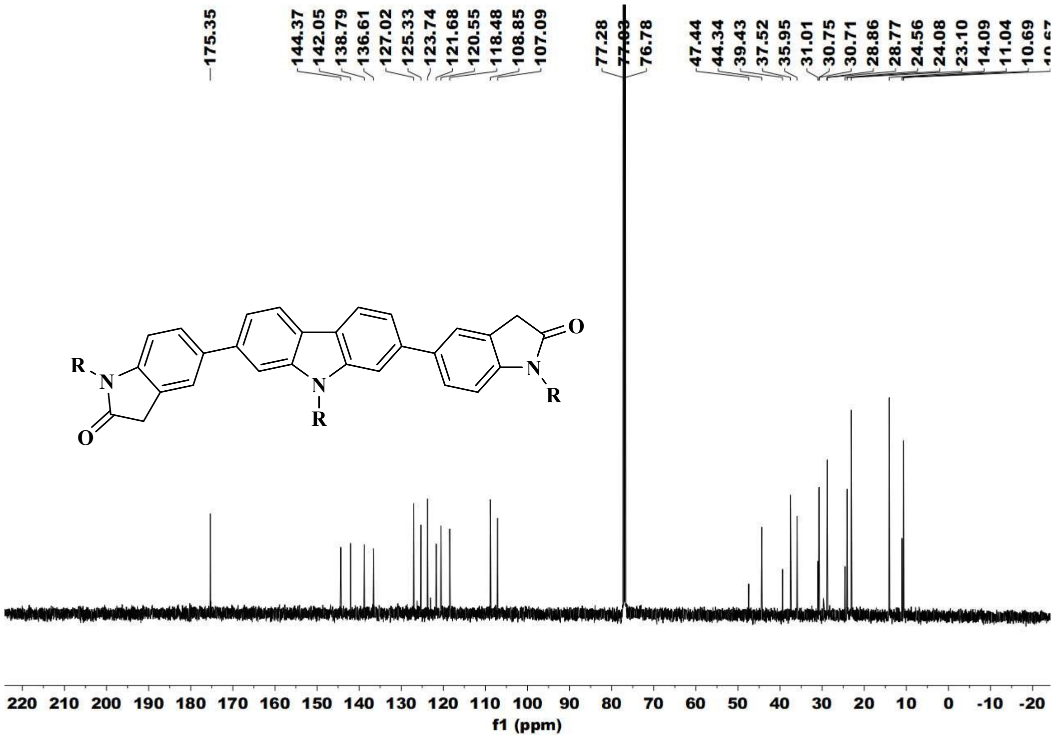
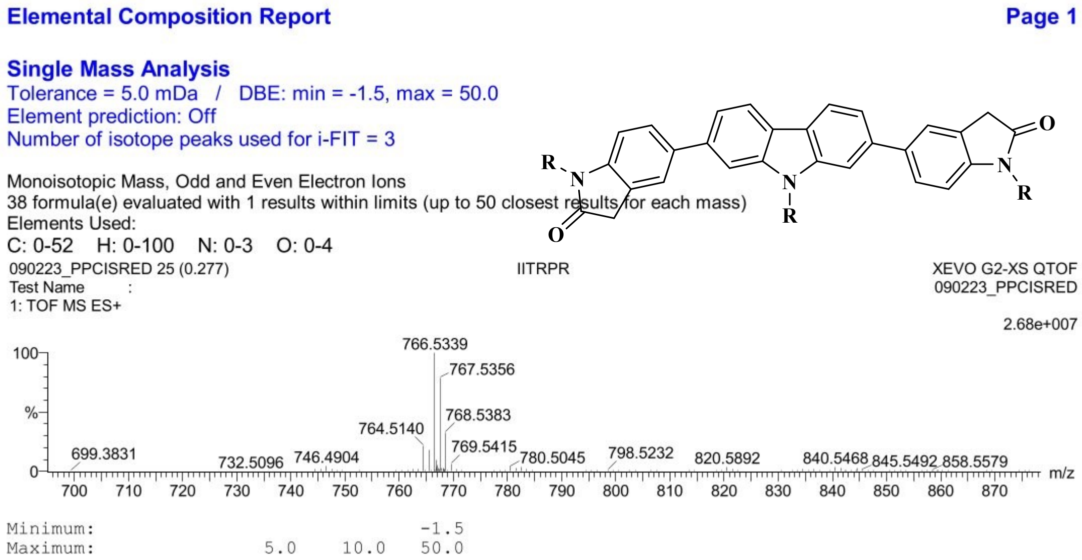


Figure **S27**: ^{13}C NMR spectra of compound **6**



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
38 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-52 H: 0-100 N: 0-3 O: 0-4

090223_PPCISRED 25 (0.277) IITRPR XEVO G2-XS QTOF
Test Name : 090223_PPCISRED
1: TOF MS ES+

```
Minimum:                        -1.5
Maximum:            5.0   10.0  50.0
```

Figure **S28:** HR-MS data of compound **6**

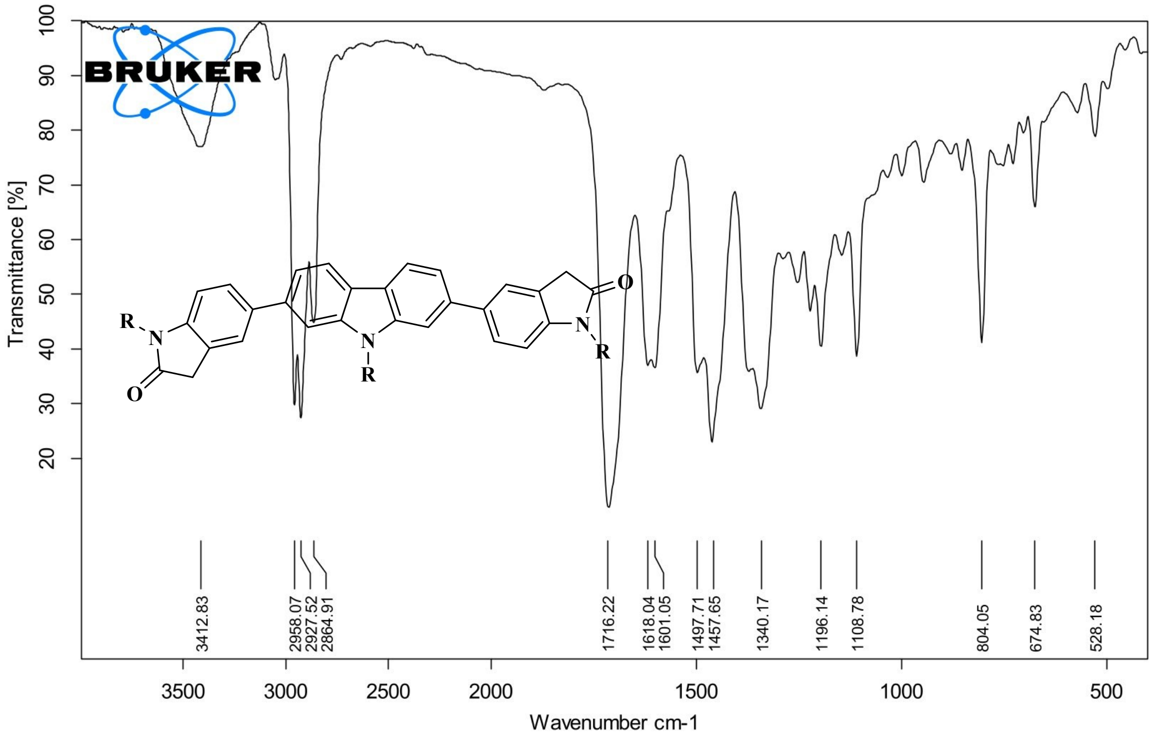


Figure S29: IR spectrum (KBr pellet) of compound **6**

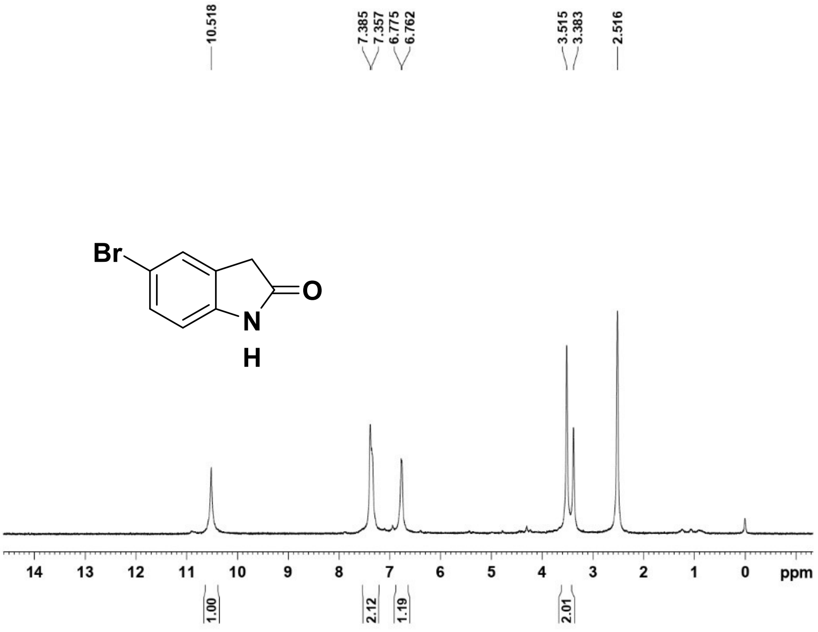


Figure **S30**: ^{1}H NMR spectra of compound **7**

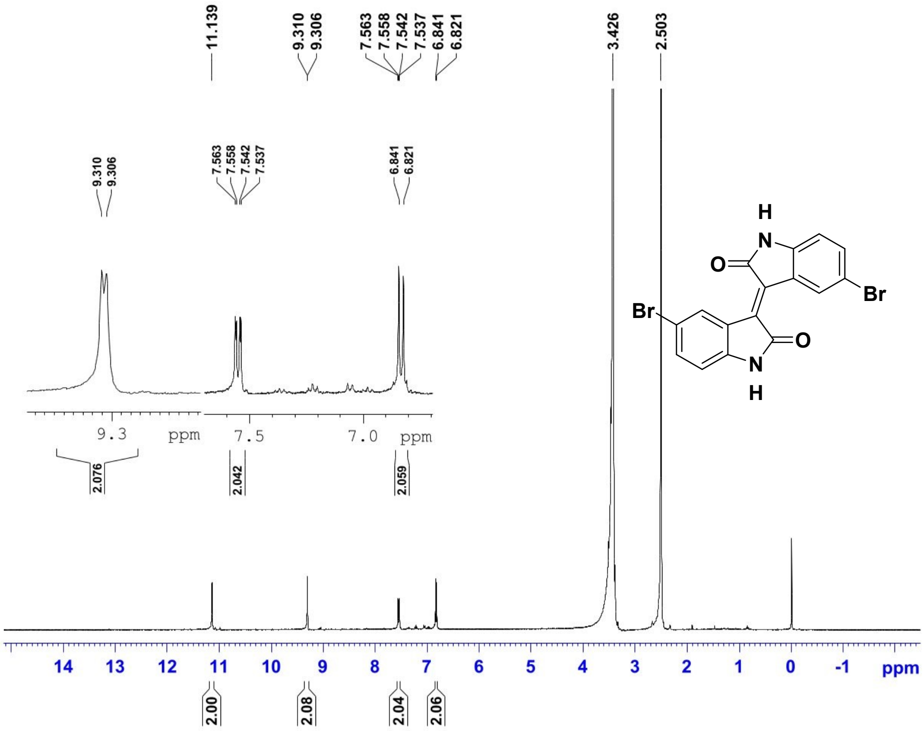


Figure **S31**: ^{1}H NMR spectra of compound **8**

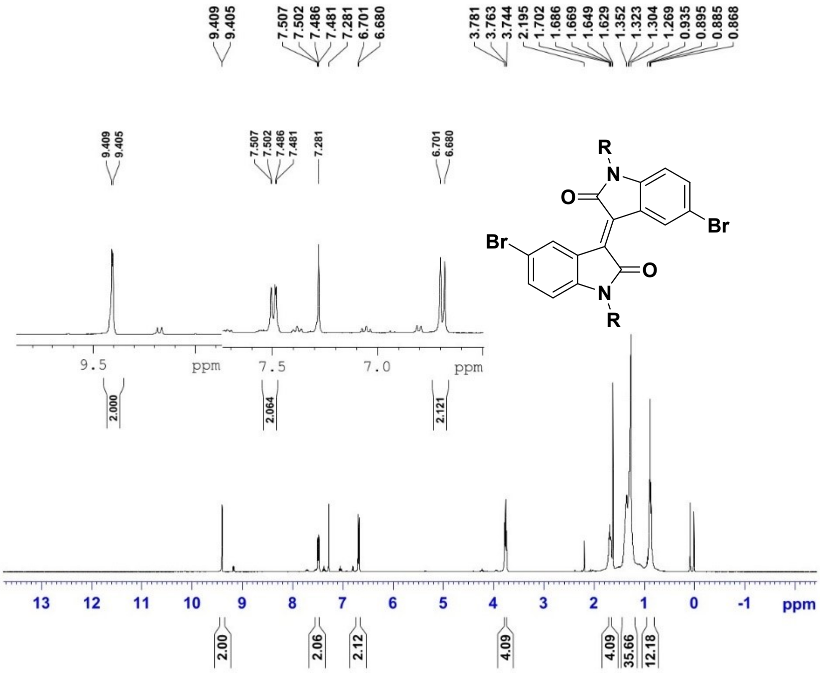


Figure **S32**: ^{13}C NMR spectra of compound **9**

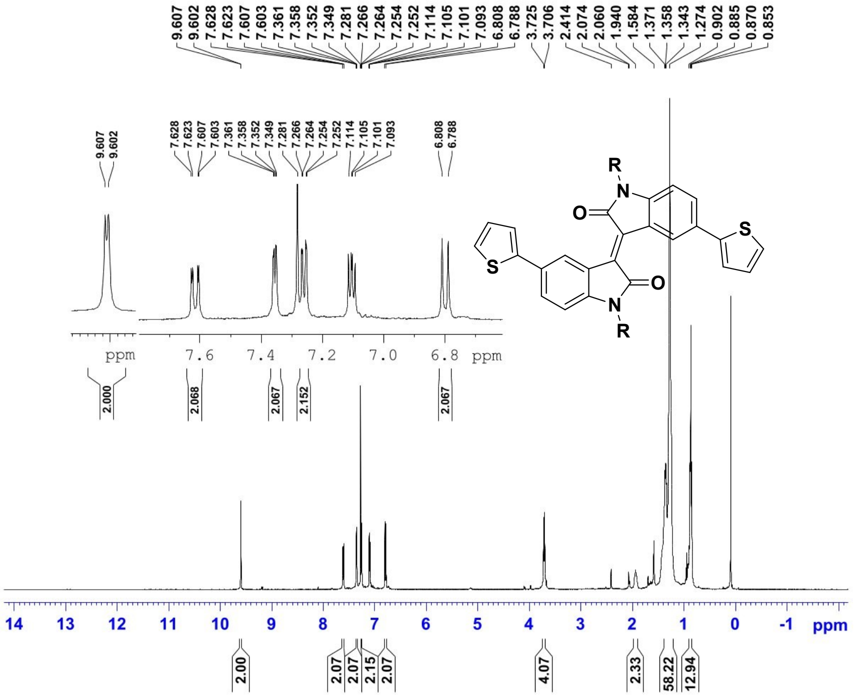


Figure **S33**: ^{1}H NMR spectra of compound **10**

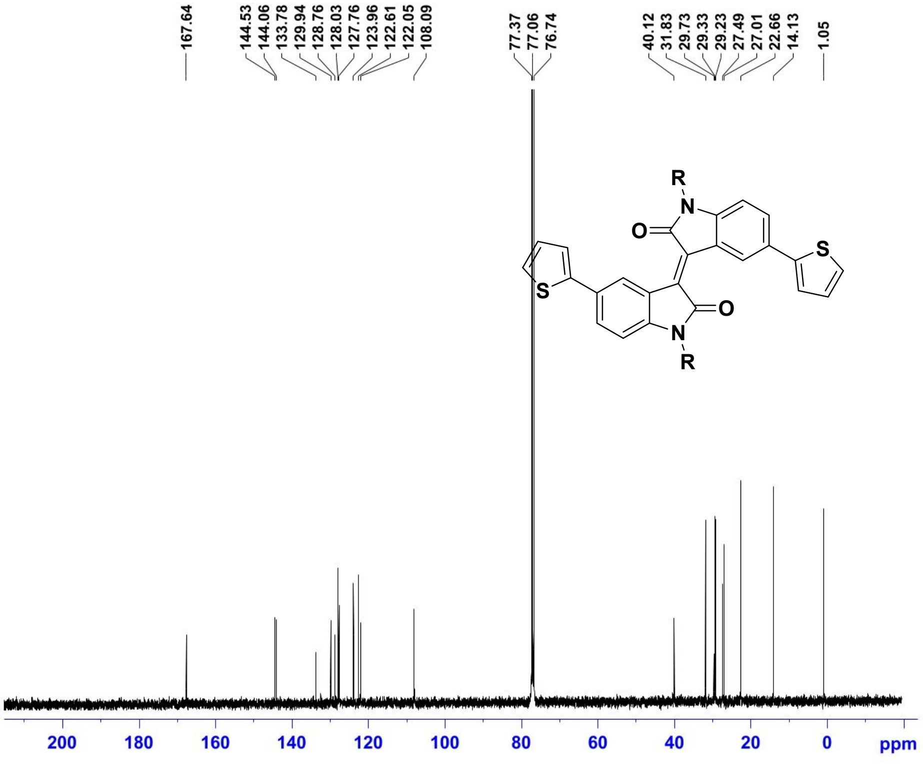


Figure **S34**: ^{13}C NMR spectra of compound **10**

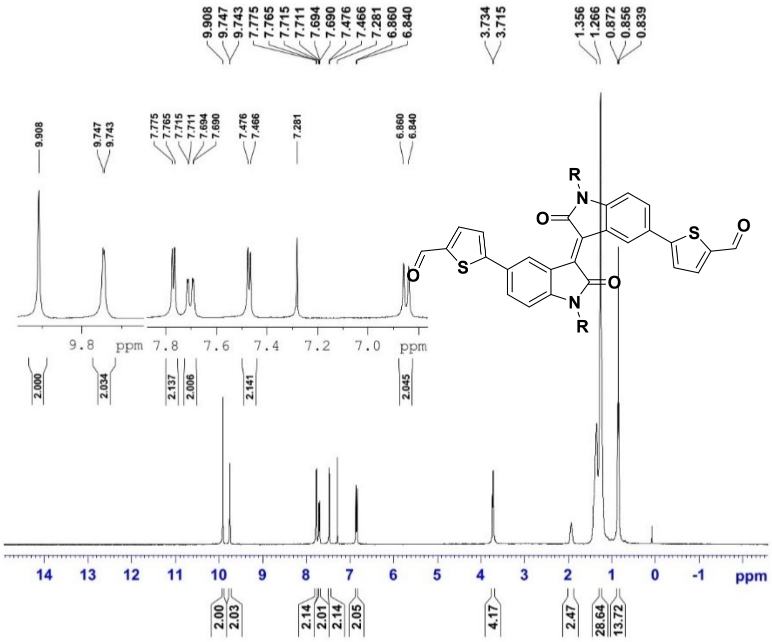


Figure **S35**: ^{1}H NMR spectra of compound **11**

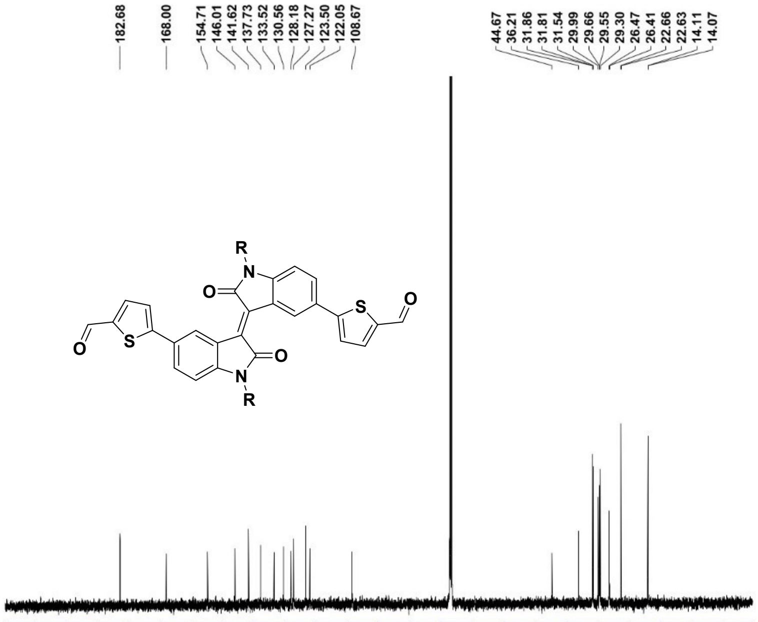


Figure **S36**: ^{13}C NMR spectra of compound **11**

Spectral data of polymers

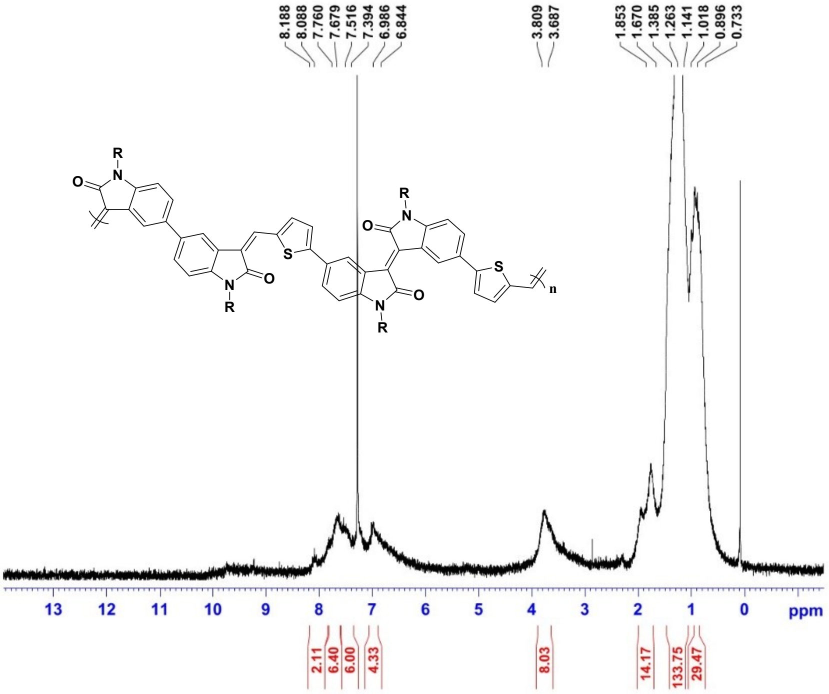


Figure S37: ^{1}H NMR spectra of polymer **AIRI**

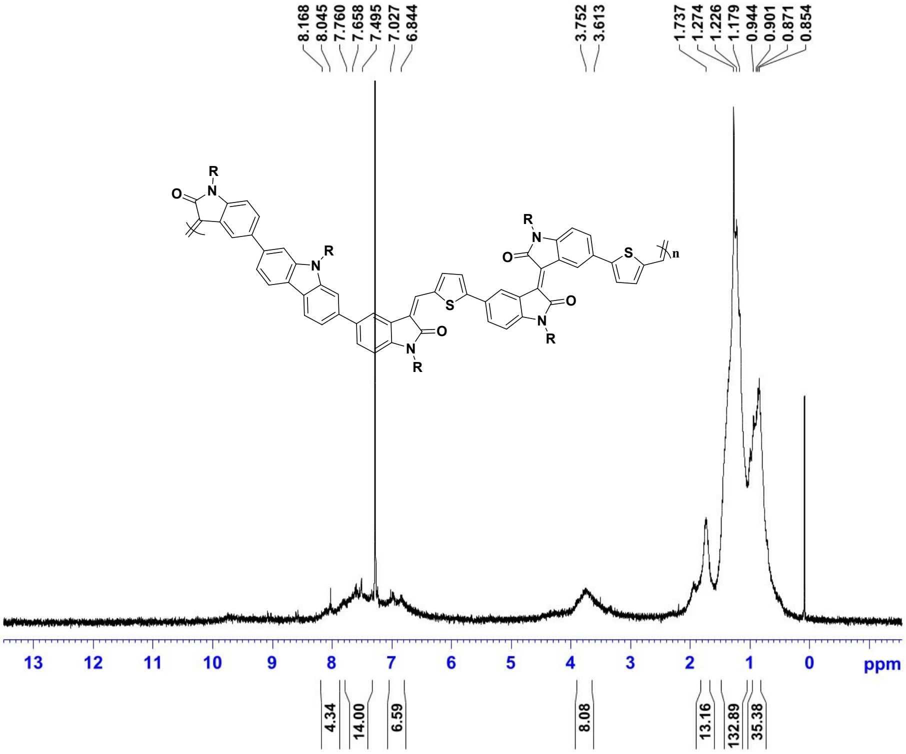


Figure S38: ^{1}H NMR spectra of polymer **AICRI**

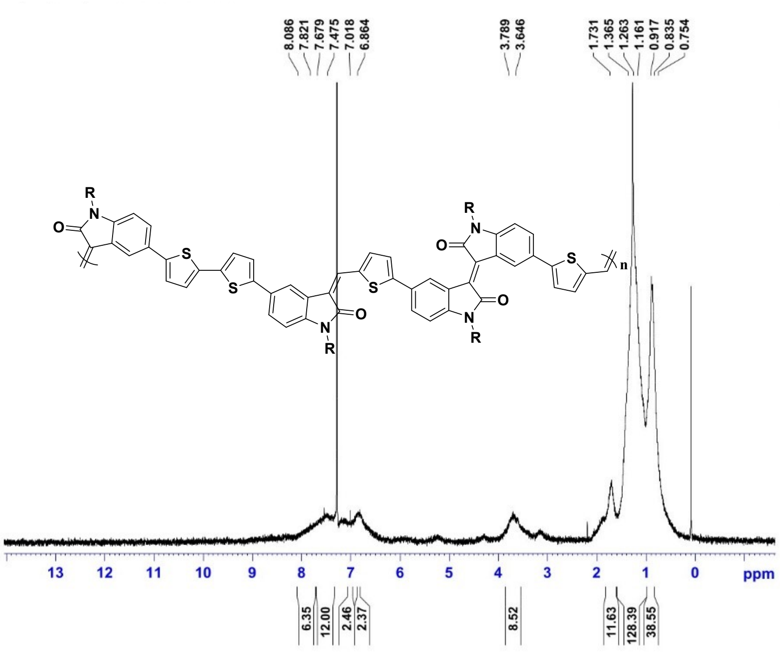


Figure S39: ^{1}H NMR spectra of polymer **AITRI**

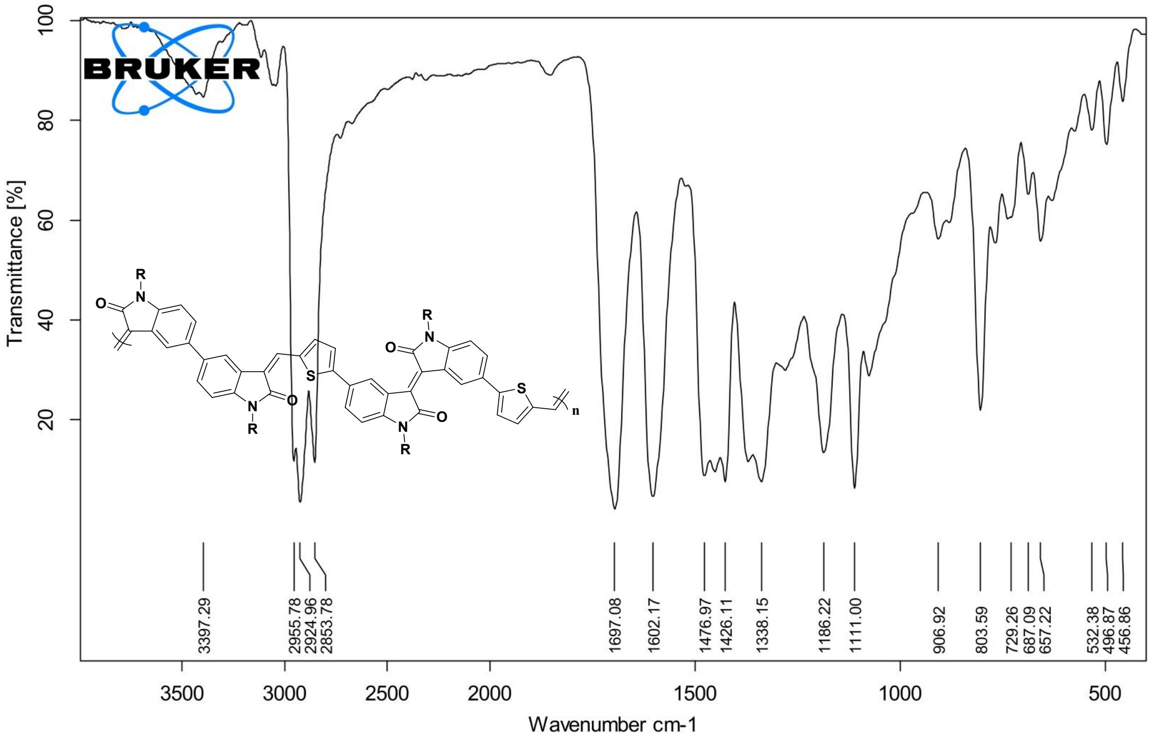


Figure **S40**: IR spectrum (KBr pellet) of polymer **AIRI**

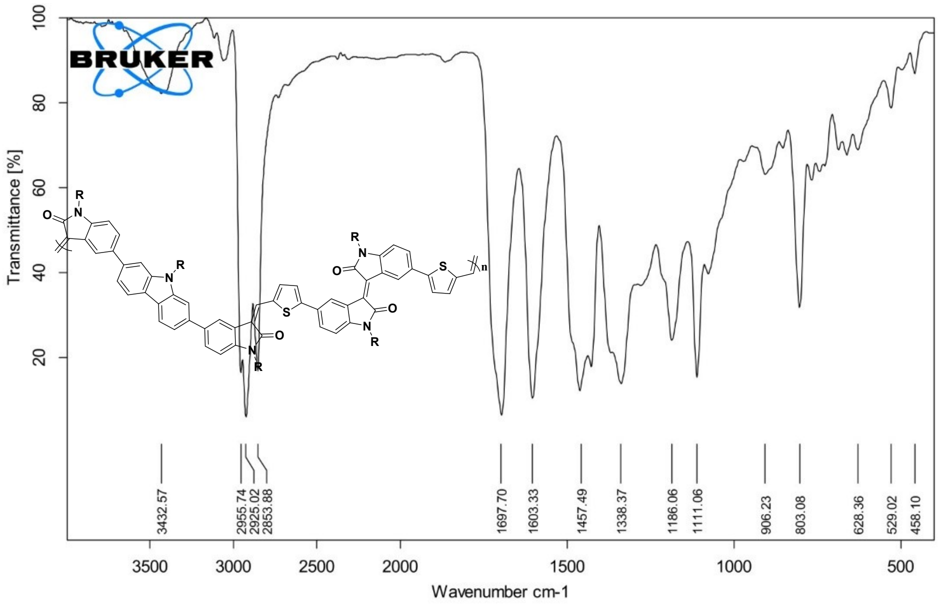


Figure **S41**: IR spectrum (KBr pellet) of polymer **AICRI**

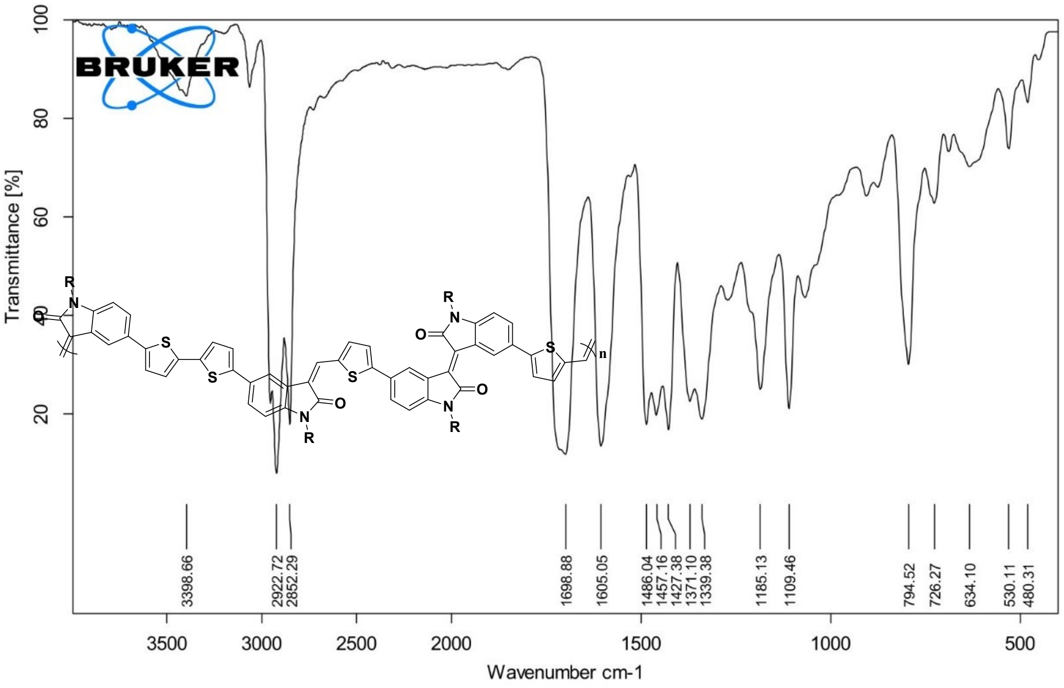


Figure **S42**: IR spectrum (KBr pellet) of polymer **AITRI**

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