Supporting Information for

Diazaisoindigo Conjugated Polymers for High Performance N-type and Ambipolar Thin Film Transistors Application

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1. TGA of Polymers

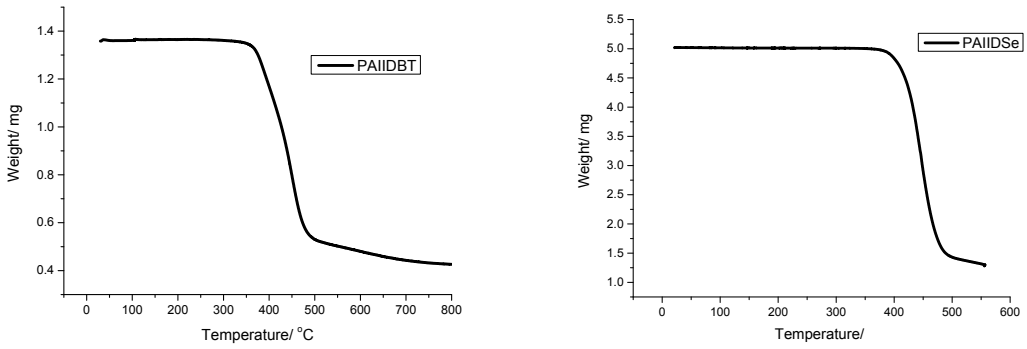


Figure S1: Thermal gravimetric analysis (TGA) of polymer **PAIIDBT** (Td: 375 °C) and **PAIIDSe** (Td: 410 °C) recorded at 30 °C /min in a nitrogen atmosphere.

2. DSC of Polymers

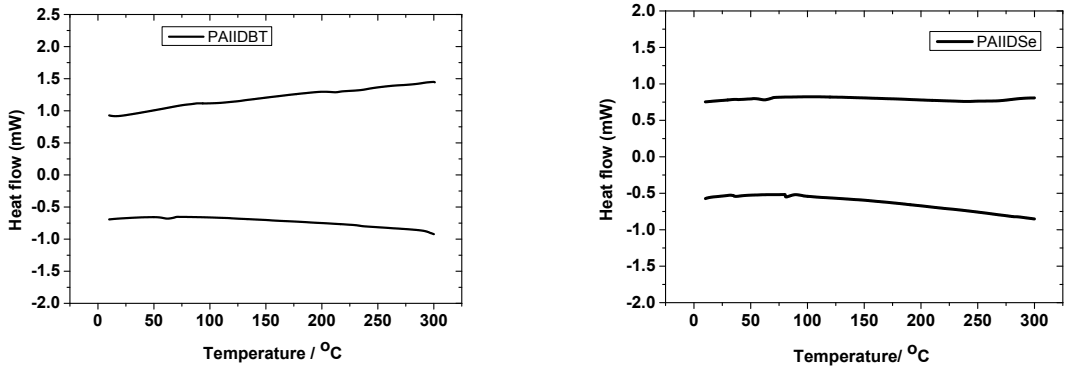


Figure S2: DSC traces of **PAIIDBT** and **PAIIDSe** recorded at 10°C /min from 0 to 300 °C (the tiny peaks of both polymers are from instrument artefact).

3. The X-ray crystal structure of 5.

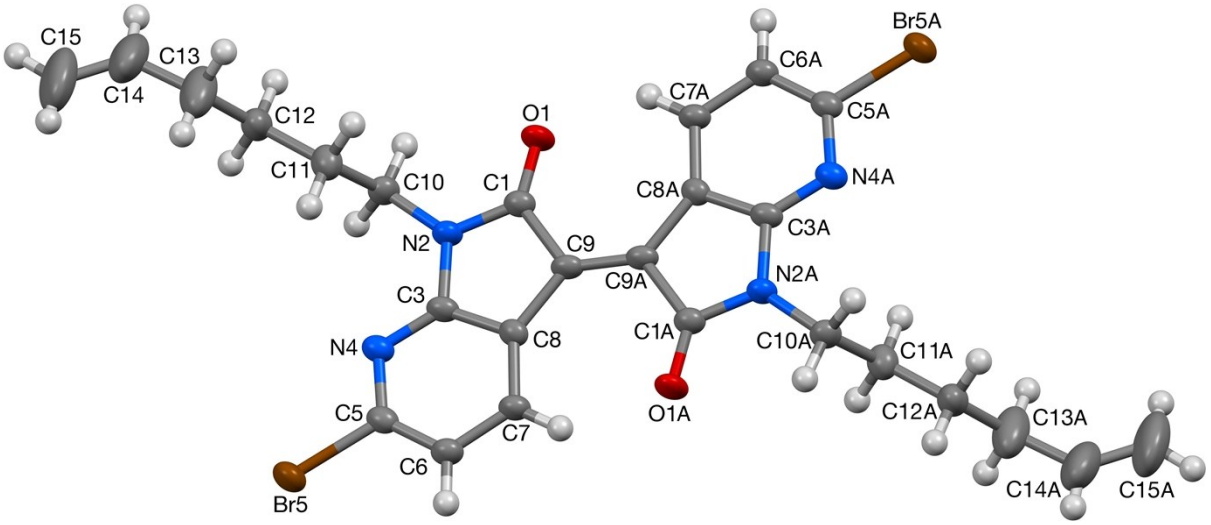


Figure S3: The crystal structure of **5** (50% probability ellipsoids).

Crystal data for **5**: $C_{26}H_{26}Br_2N_4O_2$, M = 586.33, triclinic, P-1 (no. 2), a = 4.7412(3), b = 7.7243(6), c = 16.8734(14) Å, α = 95.985(7), β = 90.633(6), γ = 92.942(6)°, V = 613.69(8) Å^3, Z = 1 [C_i symmetry], D_c = 1.587 g cm^{-3}, μ(Cu-Kα) = 4.441 mm^{-1}, T = 173 K, orange platy needles, Agilent Xcalibur PX Ultra A diffractometer; 2331 independent measured reflections (R_{int} = 0.0403), F^2 refinement,[X1] R_1(obs) = 0.0417, wR_2(all) = 0.1021, 1968 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 147°], 154 parameters.

[CCDC 1483575 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

[X1] (a) SHELXTL, Bruker AXS, Madison, WI; (b) SHELX-97, G.M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112-122; (c) SHELX-2013, http://shelx.uni-ac.gwdg.de/SHELX/index.php

4. Temperature –dependent UV-vis absorption of polymers.

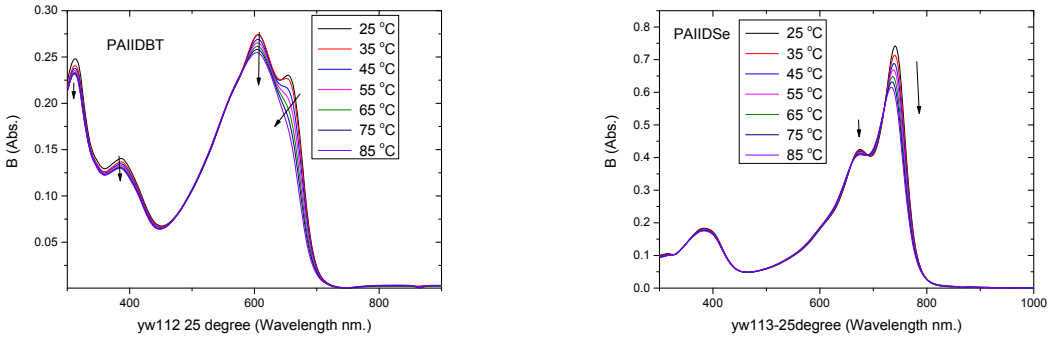


Figure S4: Temperature –dependent UV-vis absorption of **PAIIDBT** and **PAIIDSe** in dilute chlorobenzene solution.

5. DFT model of polymers

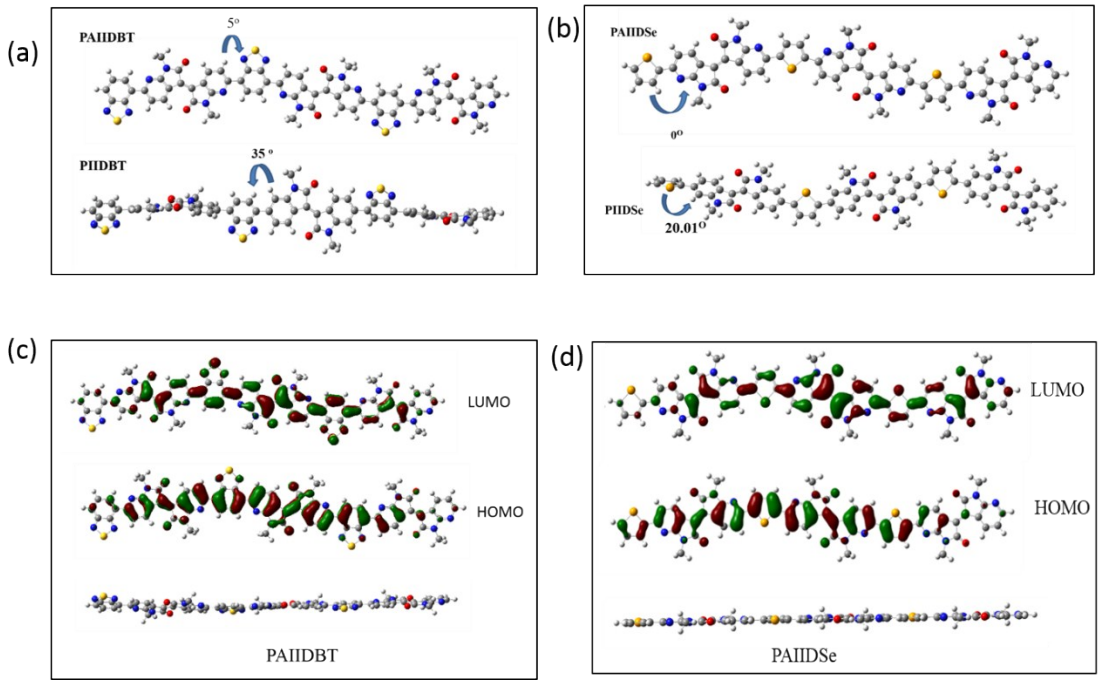


Figure S5: Face on DFT images of the **PAIIDBT** and **PIIDBT** (a); Face on DFT images of the **PAIIDSe** and **PIIDSe** (b); LUMO, HOMO and side-on DFT images of the minimum-

energy conformation of the trimmers **PAIIDBT** (c) and **PAIIDSe** (d) at the B3LYP/6-31G (d,p) level. Alkyl chains were substituted for methyl groups.

6. OFETs Characterization

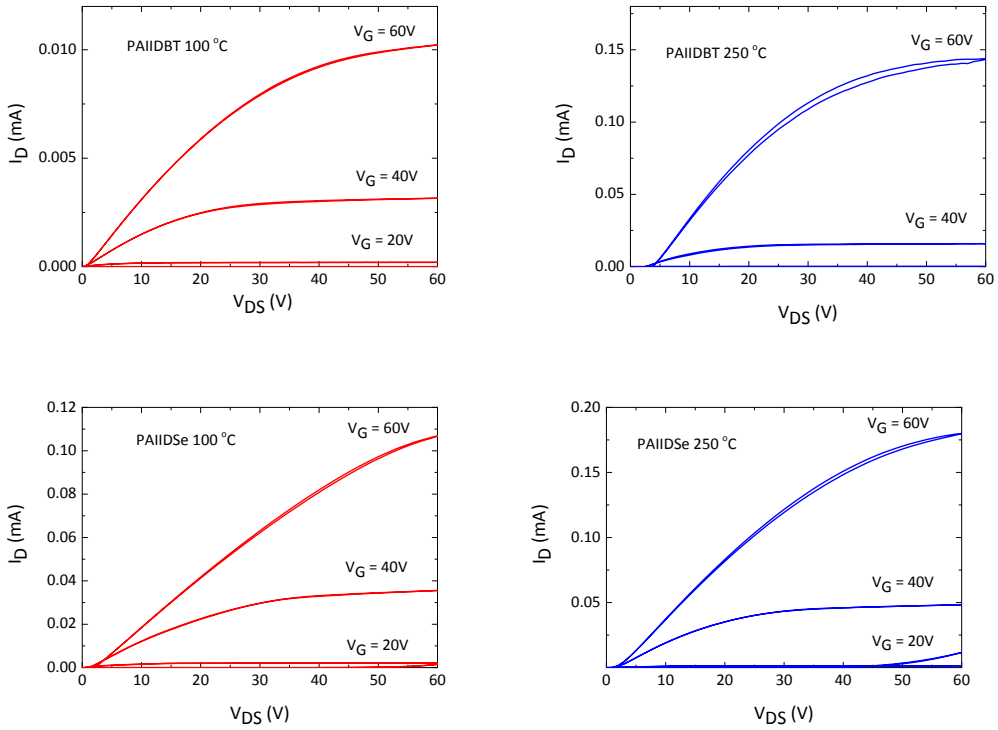
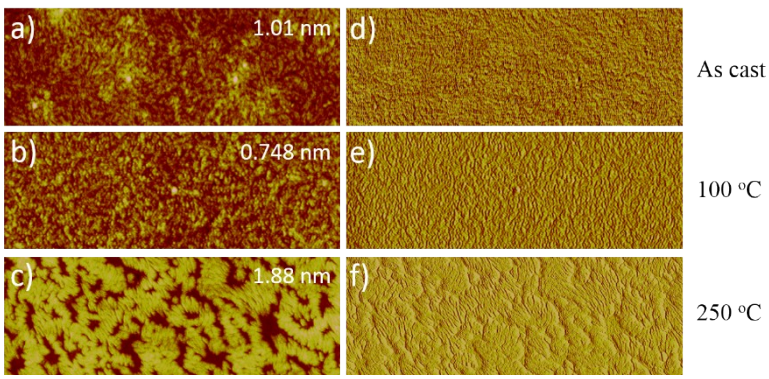


Figure S6: Output characteristics of **PAIIDBT** (a, b) and **PAIIDSe** (c, d) annealed at 100 °C and 250 °C.

7. AFM Characterization



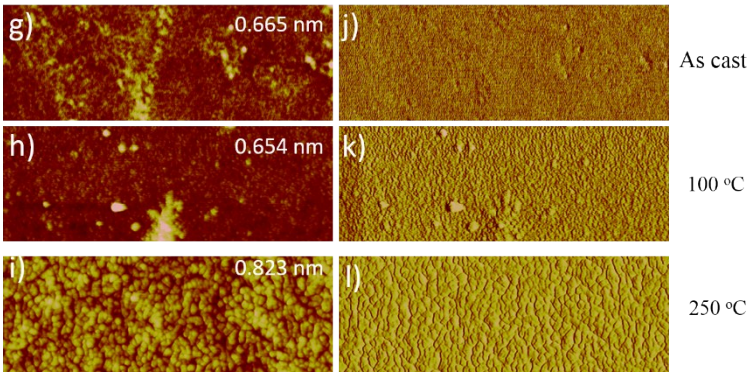
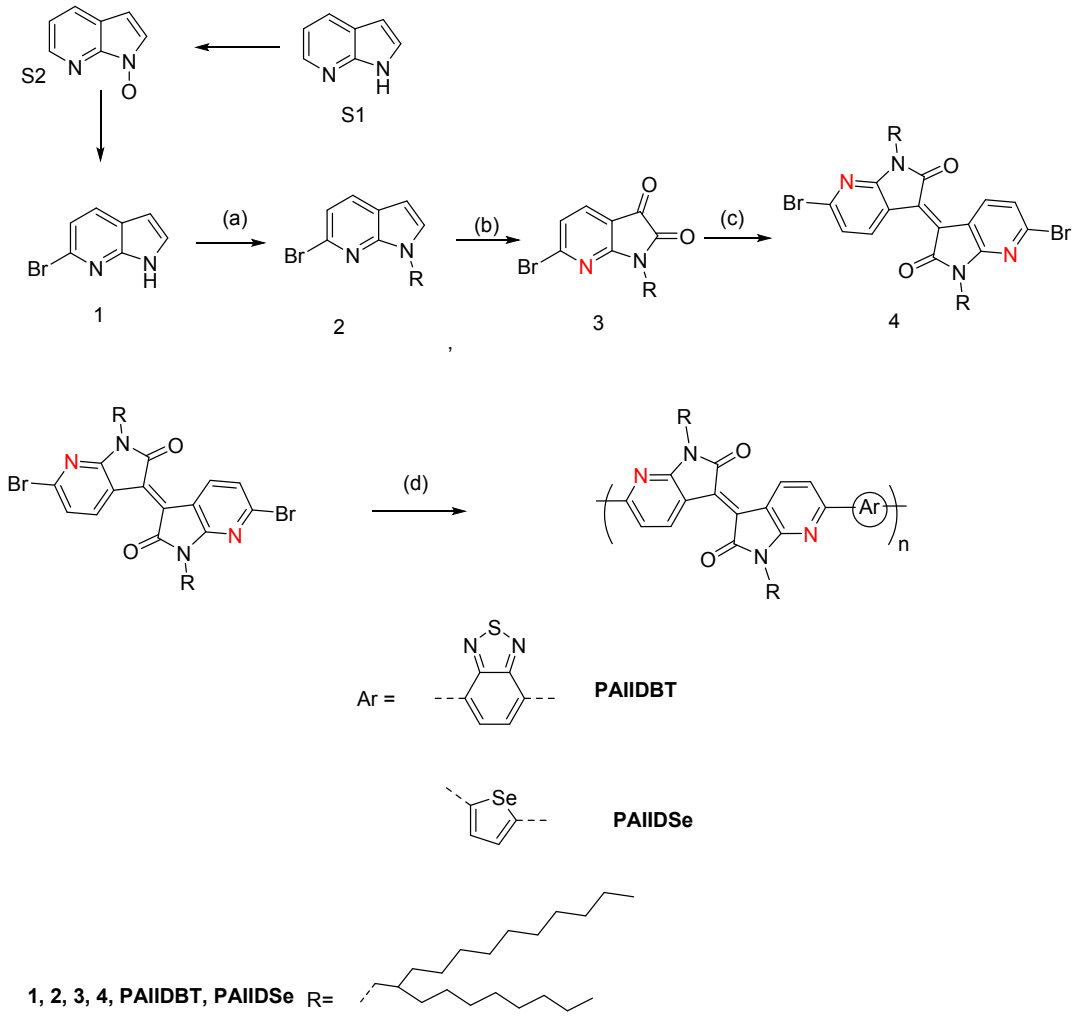


Figure S7: AFM topography (a,b,c) and phase (d,e,f) images of **PAIIDBT**, and AFM topography (g,h,i) and phase (j,k,l) images of **PAIIDSe**, as cast and after annealing at 100 °C and 250 °C. Scan size: 5 µm × 5 µm.

8. Experimental details



7-azaindole **S1** was purchased from Fluorochem LTD. **S2** and **1** were prepared according to the literature. [1, 2]

[1] S. W. Schneller, J.-K Luo, *J. Org. Chem.* **1980**, *45*, 4045-4048.

[2] S. Minakata, M. Komatsu, Y. Ohshiro. *Synthesis* **1992**, 661-663.

Compounds 2

Compound **1** (1.11g, 5.6 mmol) was dissolved in dry DMF (30 mL), hydride sodium (290 mg, 60 % in oil) was added to the solution at room temperature and stir for another 45 mins, 1-bromo octyldodecyl (2.4 g, 6.67mmol) or 1-bromo hexane (v = 0.68 mL, 6.67 mmol) DMF was then added slowly to above mixtures, and the mixture stir overnight. Water was slowly added to quench the reaction until no obvious bubble, extract with ethyl estate for three times, dried with magnesium sulphate, and the solvent was removed with reduced vacuum, the reside was purified with silicon chromgraphy with DCM to afford a light yellow oil for compounds **2** (2.2 g, 78 %) . Compound **2**: ^{1}H NMR (400 MHz, Chloroform-d) δ 7.75 (d, J= 8.2 Hz, 1H), 7.19 (d, J= 8.1 Hz, 1H), 7.16 (d, J= 3.5 Hz, 1H), 6.45 (d, J= 3.4 Hz, 1H), 4.18-4.16 (m, 2H), 1.96-1.99 (m, 1H), 1.30-1.22 (m, 36H), 0.91-0.90 (m, 6H) . ^{13} C NMR (100 MHz, Chloroform-d) δ 147.46, 134.52, 130.60, 128.32, 119.08, 118.91, 99.64, 48.32, 38.81, 31.93, 31.39, 29.92, 29.64, 29.56, 29.52, 29.35, 26.29, 14.13. HRMS (ESI, pos. mode): Calculated for C27H45BrN2: 476.2766, $[M+H]^+$, found: 477.2849.

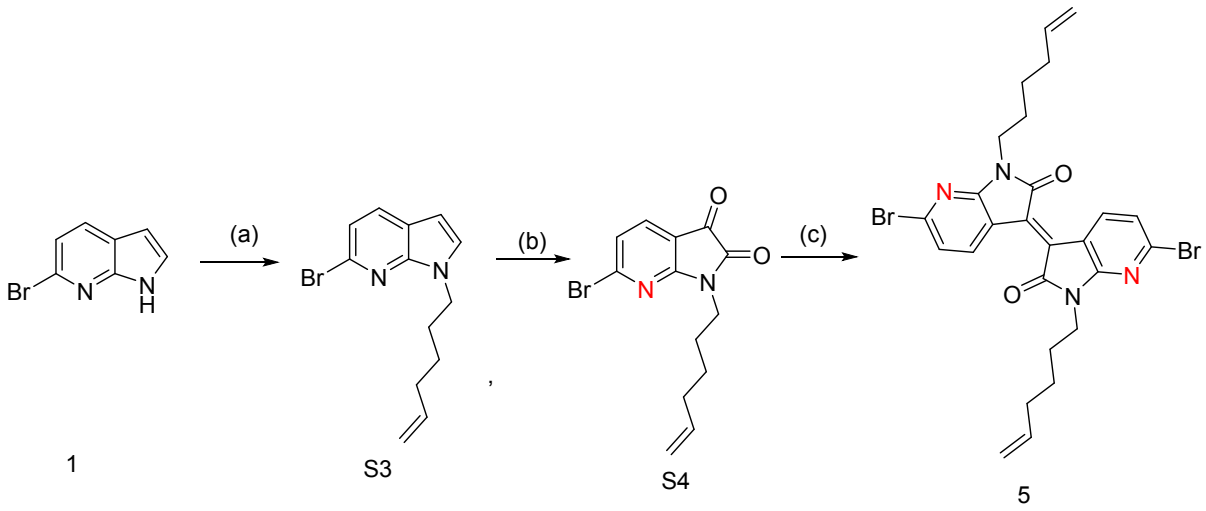
Compound **3**

Chromium trioxide (90 mg, 0.91 mmol) in 0.3 ml water was added to a solution of compound **2** (200 mg, 0.39 mmol) in 4 ml AcOH at room temperature for 2 h, the reaction mixture was extracted with chloroform, and the organic phase was collected and dried with magnesium sulphate, solvent was removed by the reduced pressure, purified by column chromatography to afford a bright yellow solid for **3** (175 mg, 88 %). Compound **3**: 1H NMR (400 MHz, Methylene Chloride-d2) δ 7.68 (d, J = 7.7 Hz, 1H), 7.31 (d, J = 7.7 Hz, 1H), 3.74-3.72 (m, 2H), 2.02-1.99(m, 1H), 1.34-1.30 (m, 35 H), 0.93-0.90 (m, 6H). ^{13} C NMR (100 MHz, Chloroform-d) δ 181.01, 164.51, 158.48, 149.82, 133.86, 123.17, 110.32, 43.64, 31.90, 31.37, 29.89, 29.63, 29.60, 29.55, 26.12, 22.67, 13.86. Cal MS (MALDI-TOF, CHCl3): calculated for C27H43BrN2O2: 506.3, found: 505.0.

Compound **4**

A soln of P(NEt2)3 (0.11 mL, 0.78 mmol) in CHCl3 (2 mL) was added dropwise to a solution of appropriate 1-alkylisatin (200 mg, 0.39 mmol) in (4 mL) CHCl3 at –60 °C under bubbling dry argon for 2 min. The mixture was allowed to warm to r.t, and then reflux for overnight. After cooled down, the reaction mixture was purified with silicon column choromgraphy with the eluting (DCM) to afford compound **4** (60 mg, 31%) as a bright red solid. Compound **4**: ^{1} H NMR (400 MHz, Chloroform-d) δ 9.32 (d, J= 8.3 Hz, 2H), 7.20 (d, J= 8.3 Hz, 2H), 3.78 (m, 4H), 2.06 (m, 2H), 1.31-1.26 (m, 64H), 0.91-0.87 (m, 12H). ^{13} C NMR (100 MHz, Chloroform-d) δ 167.76, 158.15, 143.79, 138.97, 131.30, 121.82, 114.30, 109.99, 43.76, 31.93, 31.42, 29.98, 29.68, 29.64, 29.37, 26.16, 22.70, 14.13.

MS (MALDI-TOF, $CHCl_3$): Calculated for C54H86Br2N4O2, 980.5, $[M+H]^+$, found: 981.8.



Compound **S3** has been synthesized according to the similar procedure with **2** (89 %).

Compound **S3**: ^{1}H NMR (400 MHz, Chloroform-d) δ 7.75 (d, J = 8.1 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 3.6 Hz, 1H), 6.45 (d, J = 3.5 Hz, 1H), 5.95 – 5.62 (m, 1H), 5.15 – 4.77 (m, 2H), 4.28 (m, 2H), 2.43 – 1.98 (m, 2H), 1.97 – 1.79 (m, 2H), 1.58 – 1.30 (m, 2H). ^{13} C NMR (100 MHz, Chloroform-d) δ 147.03, 138.24, 134.55, 130.74, 127.92, 99.78, 44.41, 33.24, 29.70, 26.00. HRMS (ESI, pos. mode): Calculated for C13H15BrN2: 278.0419, $[M+H]^{+}$, found: 279.0497.

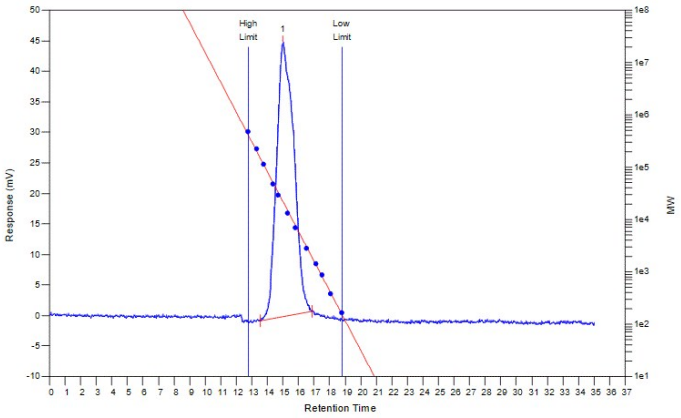
Compound **S4** has been synthesized according to the similar procedure with **3** (61 %).

Compound **S4**: 1H NMR (400 MHz, Methylene Chloride-d2) δ 7.66 (d, J = 7.7 Hz, 1H), 7.29 (d, J = 7.7 Hz, 1H), 5.86-5.76 (m, 1H), 5.07 – 4.97 (m, 2H), 3.87– 3.84 (m, 2H), 2.27-2.11 (m, 2H), 1.82 – 1.76 (m, 2H), 1.53 – 1.47 (m, 2H).). 13 C NMR (100 MHz, Methylene Chloride-d2) δ 180.81, 164.11, 158.10, 150.15, 138.04, 133.99, 123.31, 115.07, 110.28, 39.38, 33.12, 26.86, 25.97. HRMS (ESI, pos. mode): Calculated for C13H13BrN2O2+MeOH: 340.0423, $[M+MeOH]^{+}$, found: 341.0523.

Compound **5** has been synthesized according to the similar procedure with **4** (39 %).

Compound **5**: ^{1}H NMR (400 MHz, Chloroform-d) δ 9.31 (d, J = 8.3 Hz, 1H), 7.22 (d, J = 8.3 Hz, 1H), 5.82 (m, 1H), 5.21 – 4.82 (m, 2H), 3.91 (m, 2H), 2.34 – 1.94 (m, 2H), 1.93 – 1.64 (m, 2H), 1.54 – 1.41 (m, 2H). ^{13} C NMR (100 MHz, Chloroform-d) δ 167.49, 157.79, 143.84, 139.11, 138.28, 131.42, 121.96, 114.91, 114.48, 39.41, 33.25, 27.06, 26.01. MS (MALDI-TOF, CHCl3): Calculated for C26H26Br2N4O2, 584.0423, found, 584.3.

PAIIDBT

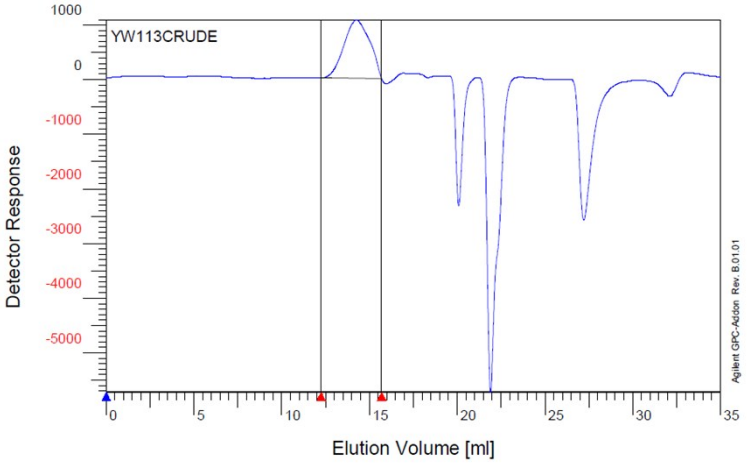


Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	22091	13974	21765	32144	44880	20446	1.55754

PAIIDSe



Mn :	9.6163e4	g/mol
Mw :	1.9374e5	g/mol
Mz :	3.7394e5	g/mol
Mv :	0.000000	g/mol
D :	2.0147e0	
[n]:	0.000000	ml/g
Vp :	1.4256e1	ml
Mp :	1.4146e5	g/mol
A :	1.8119e3	ml*V
10%	4.2987e4	g/mol
30%	8.1805e4	g/mol
50%	1.3350e5	g/mol
70%	2.1553e5	g/mol
90%	4.1899e5	g/mol

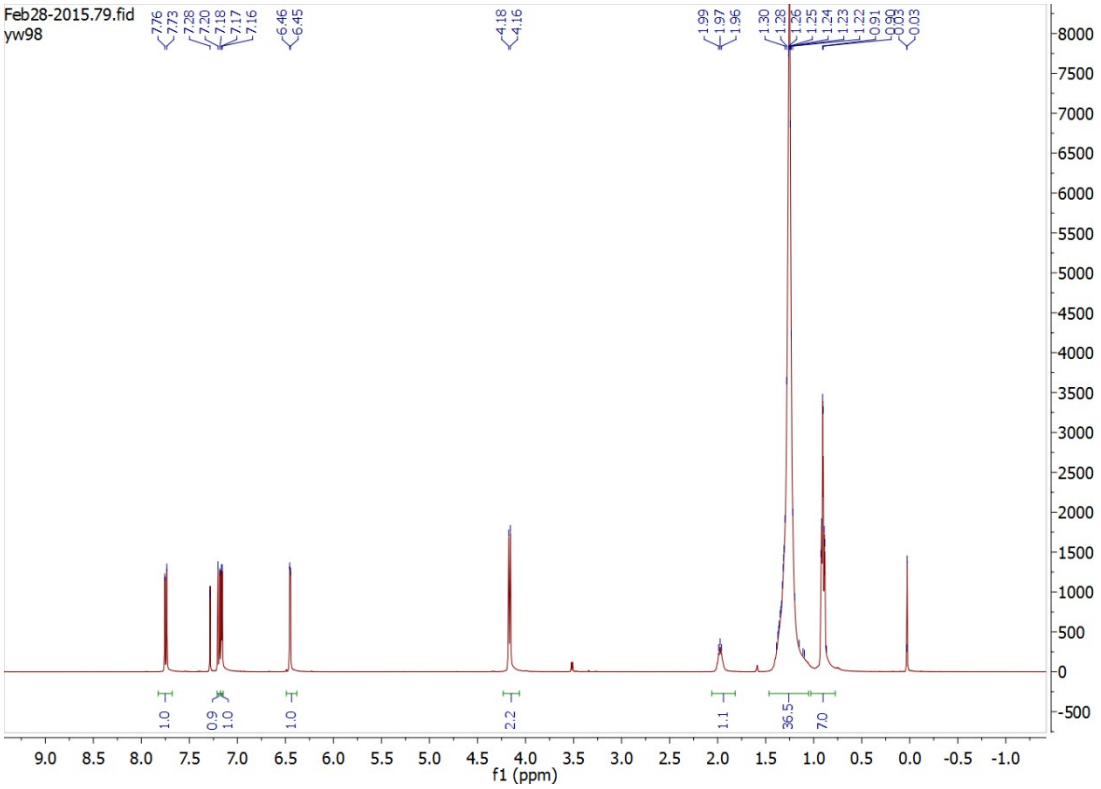


Figure S8: ^{1}H NMR of compound **2** in Chloroform-d at room temperature.

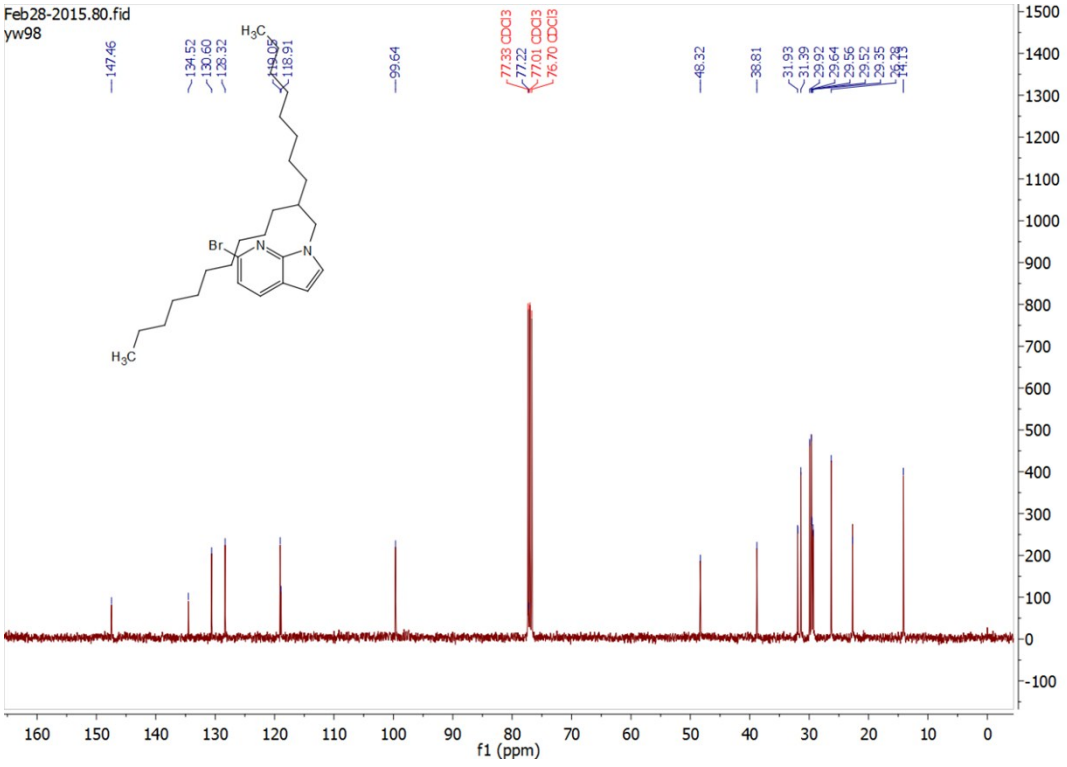


Figure S9: ^{13}C NMR of compound **2** in Chloroform-d at room temperature.

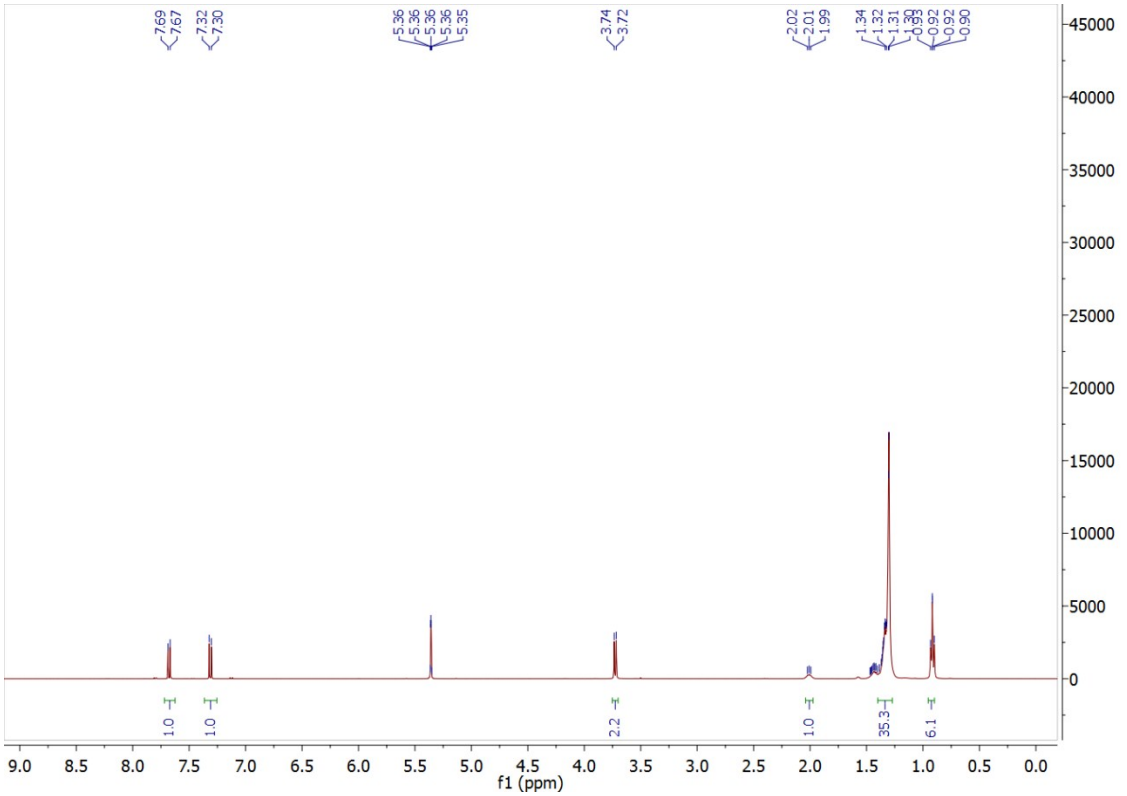


Figure S10: [1]H NMR of compound **3** in dichloromethane-d at room temperature.

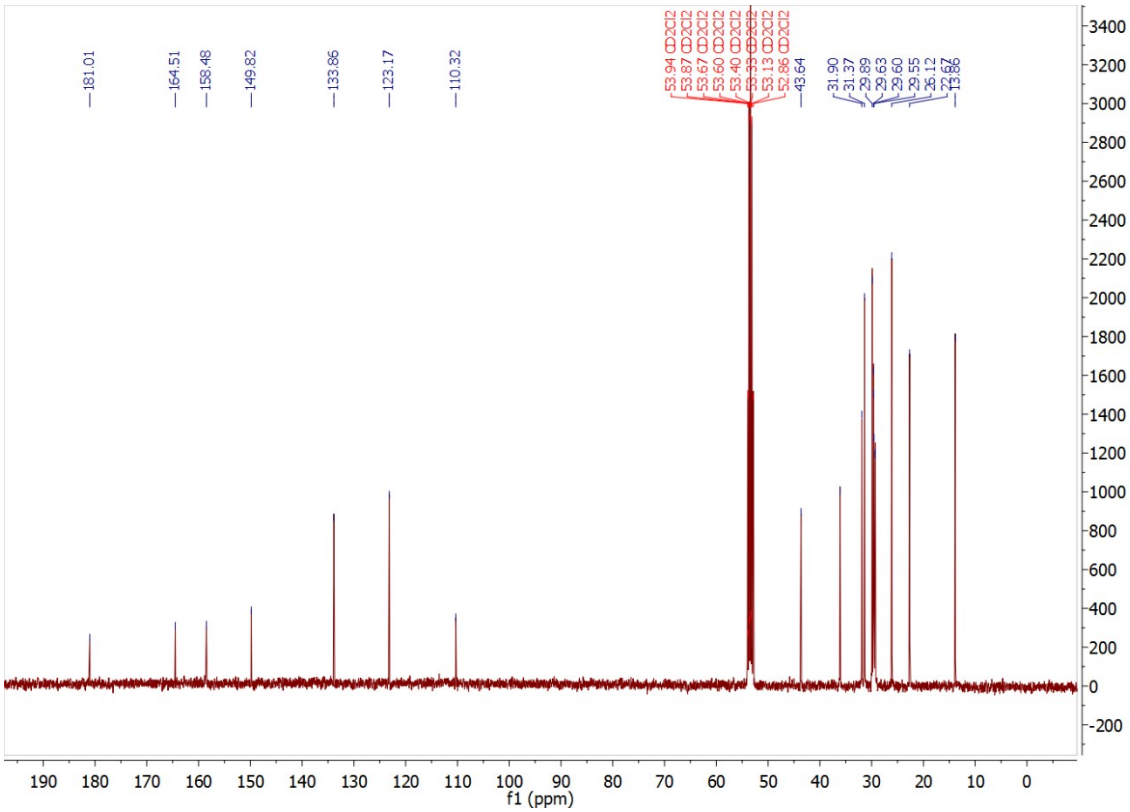


Figure S11: [13]C NMR of compound **3** in dichloromethane-d at room temperature.

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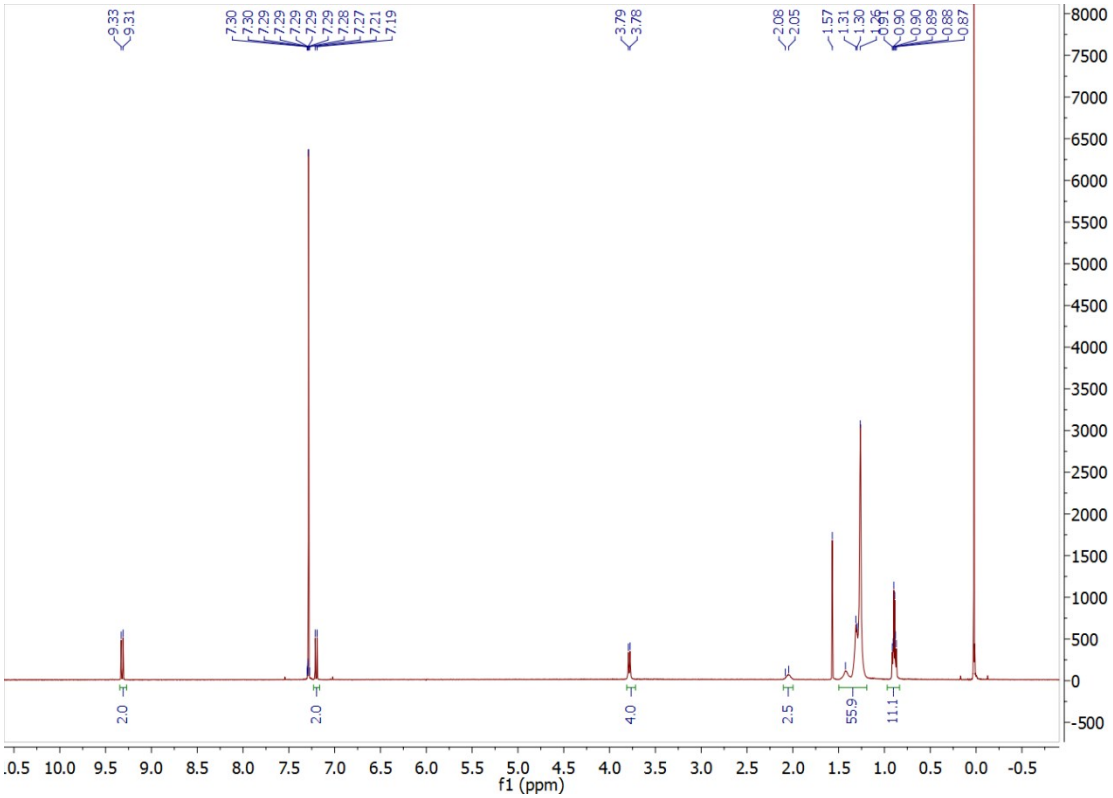

Figure S12: [1]H NMR of compound **4** in Chloroform-d at room temperature.

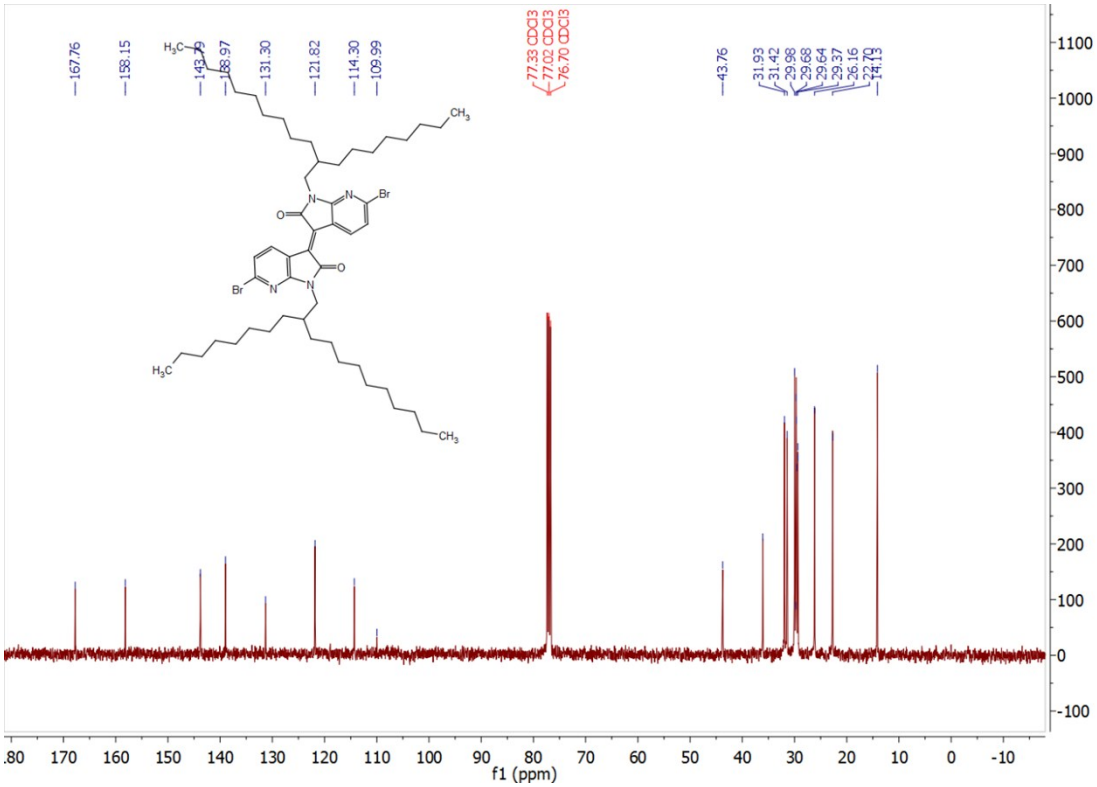

Figure S13: ^{13}C NMR of compound **4** in Chloroform-d at room temperature.

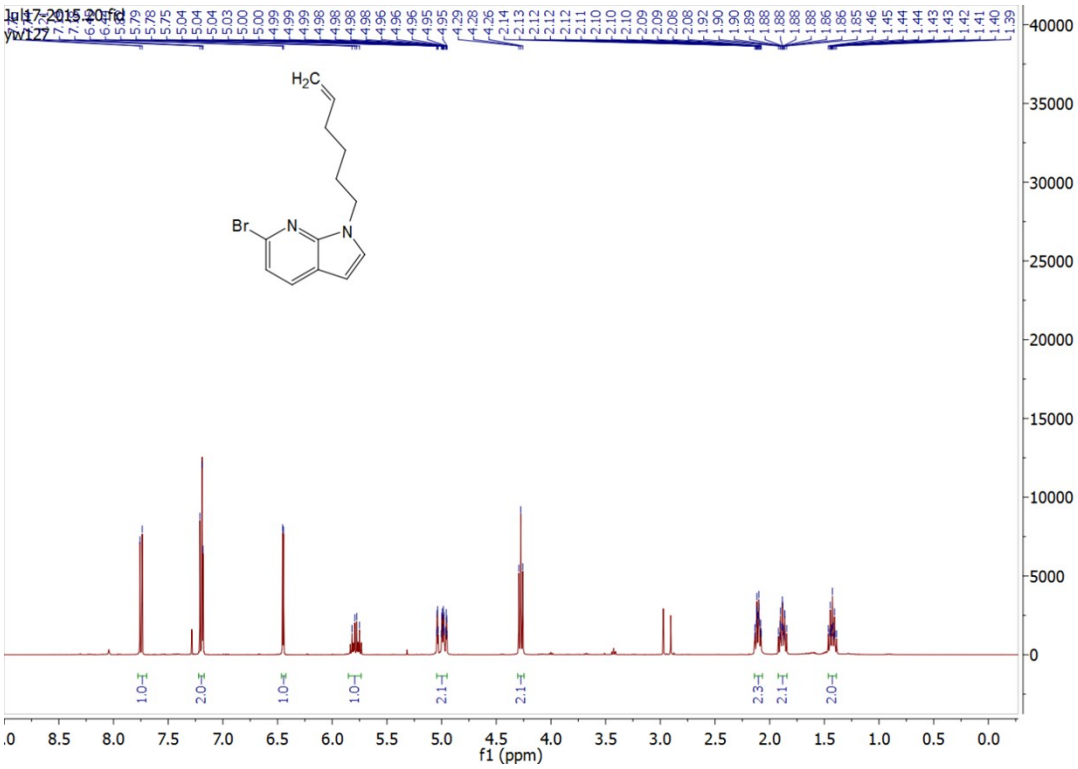

Figure S14: ^{1}H NMR of compound **S3** in Chloroform-d at room temperature.

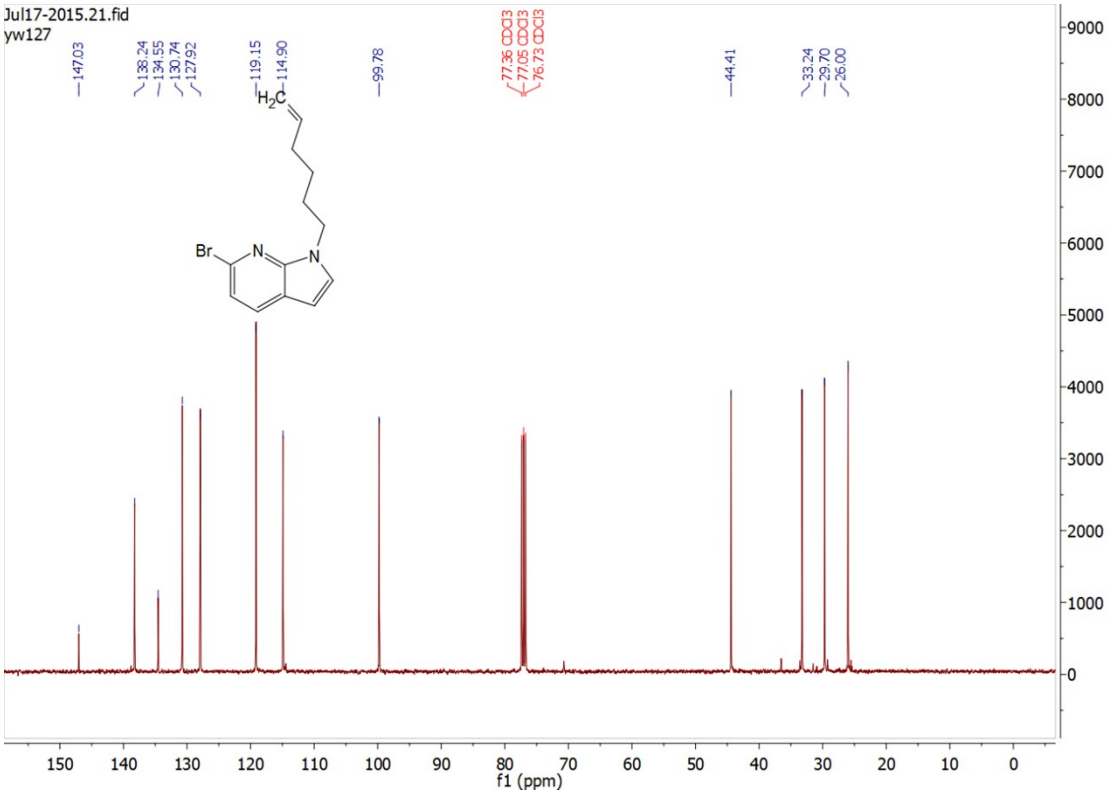

Figure S15: ^{13}C NMR of compound **S3** in Chloroform-d at room temperature.

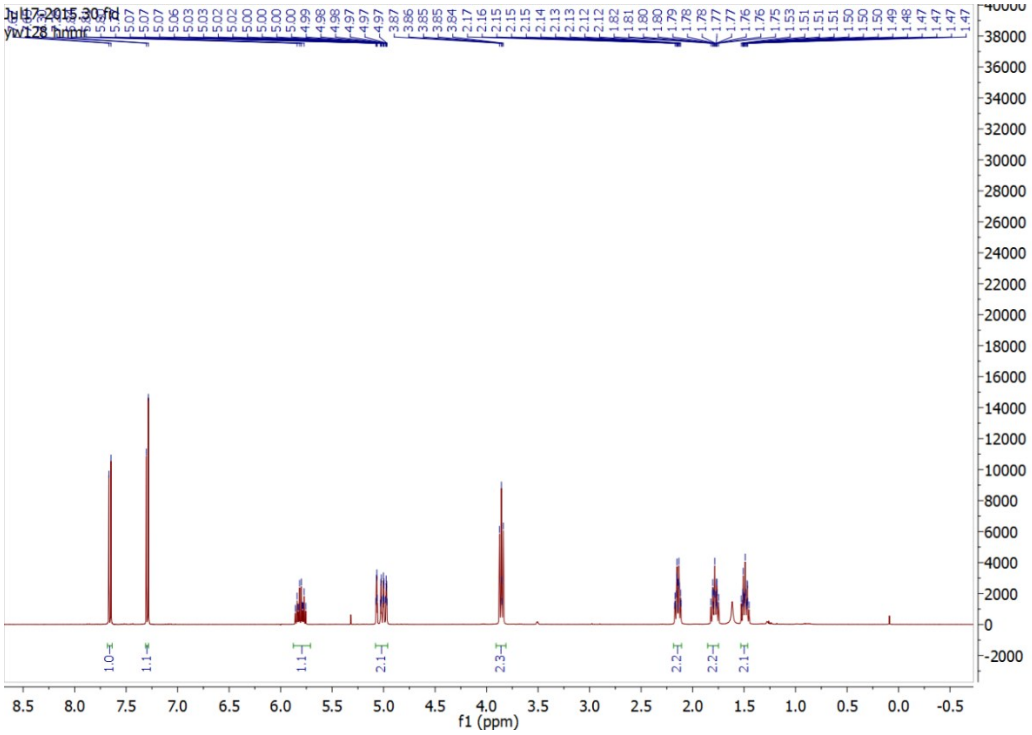

Figure S16: ^{1}H NMR of compound **S4** in Chloroform-d at room temperature.

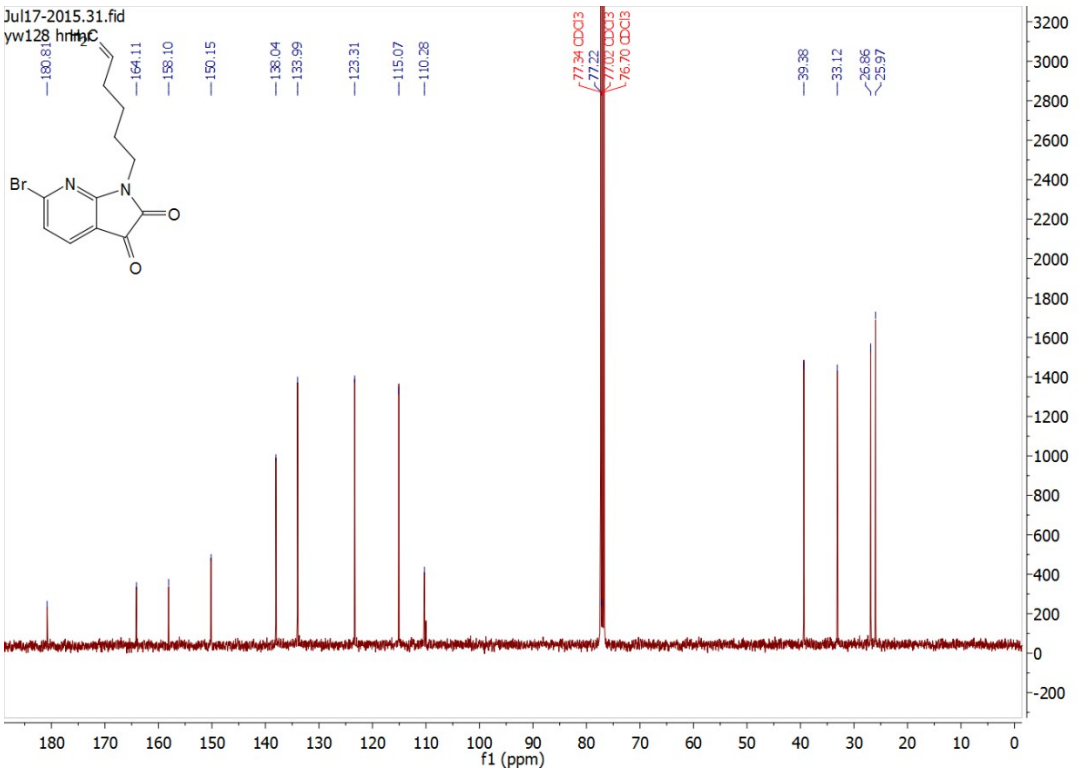

Figure S17: ^{13}C NMR of compound **S4** in Chloroform-d at room temperature.

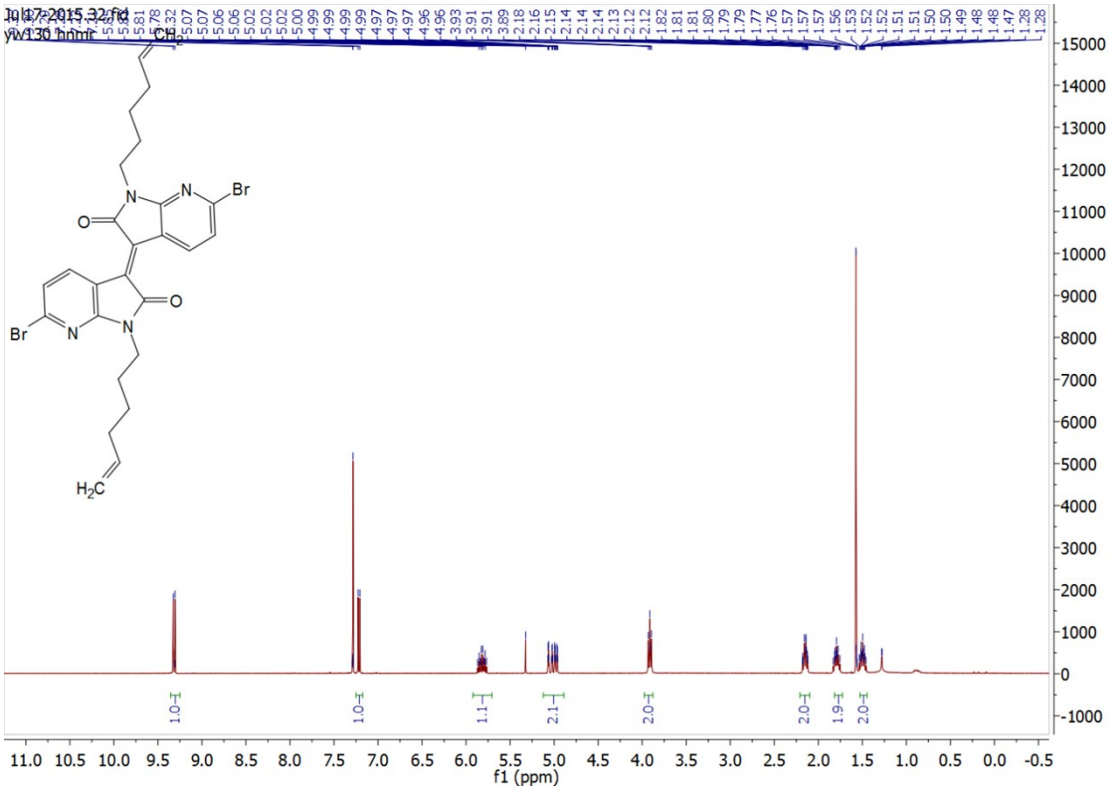

Figure S18: ^{1}H NMR of compound **5** in Chloroform-d at room temperature.

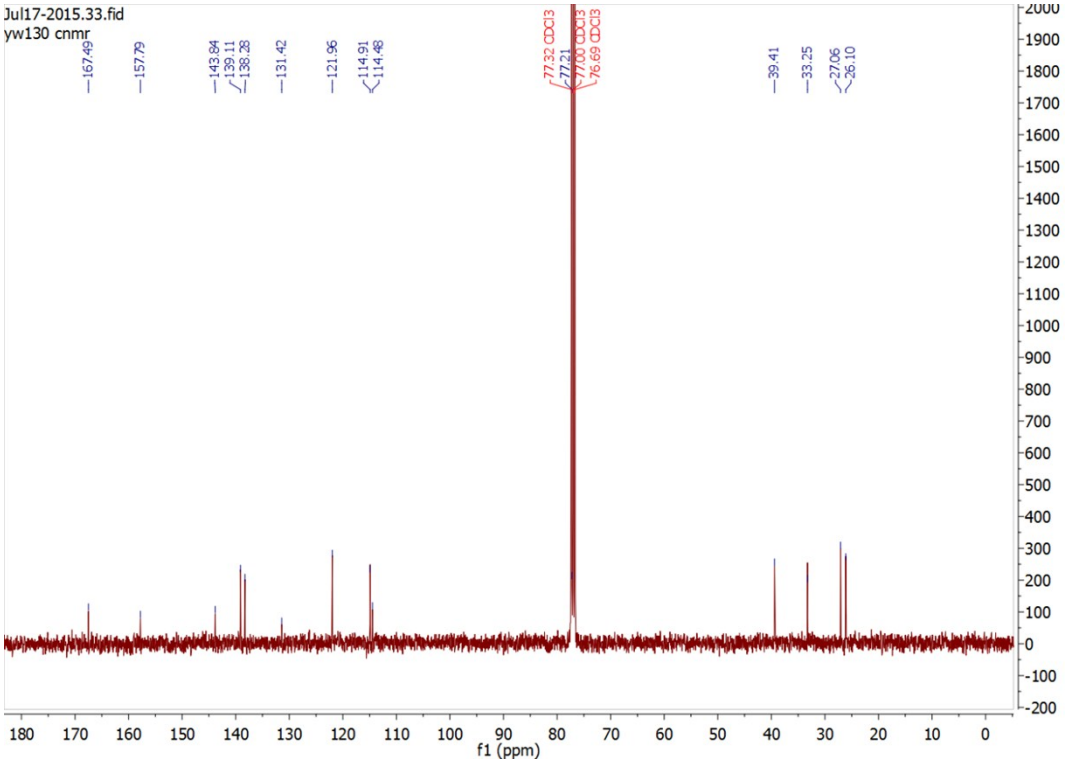

Figure S19: ^{13}C NMR of compound **5** in Chloroform-d at room temperature.

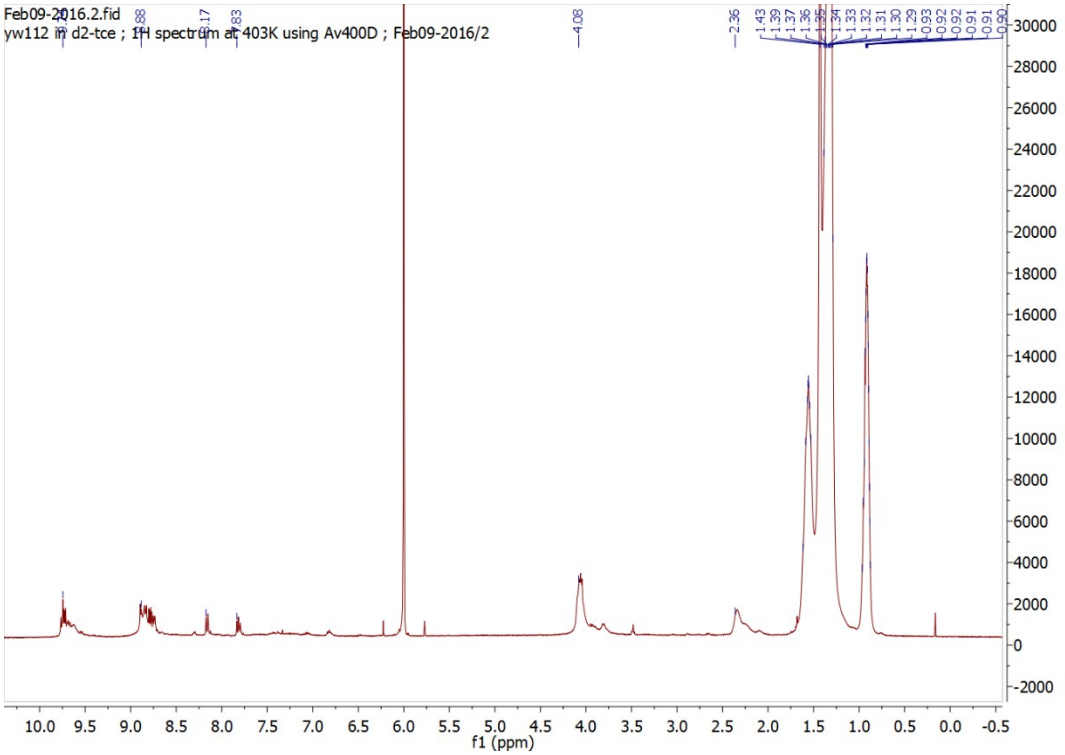

Figure S20: ^{1}H NMR of **PAIIDBT** in d2-TCE at 393 K.

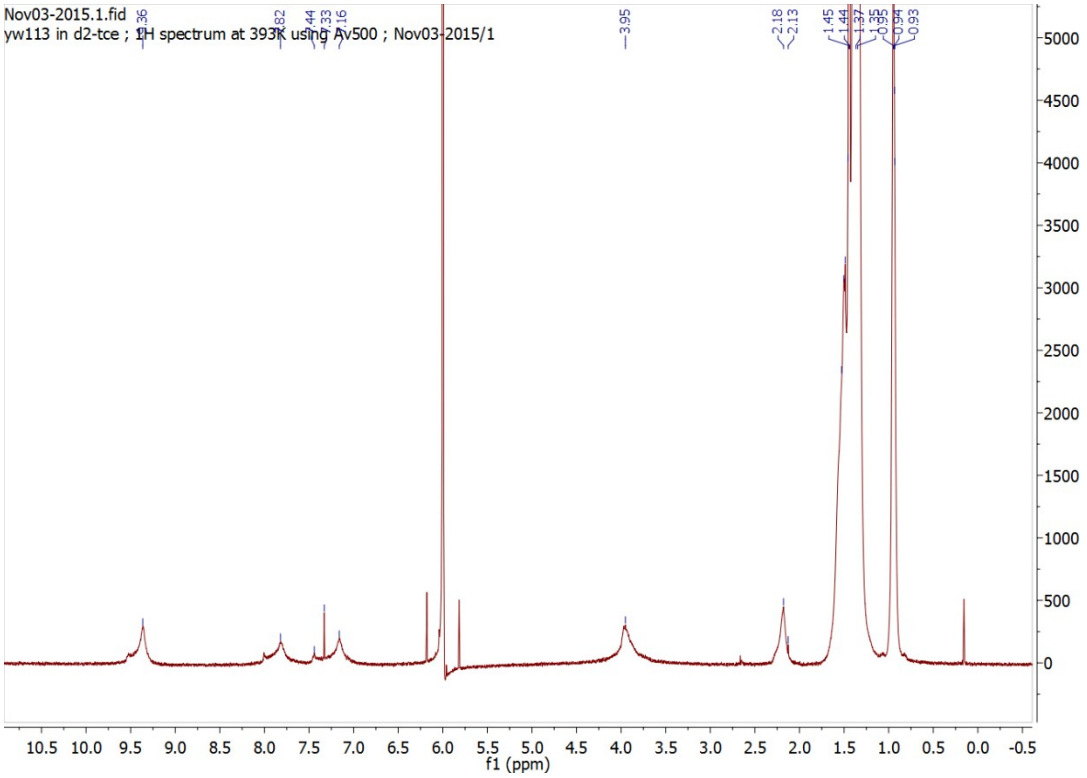

Figure 21: 1H NMR of PAIIDSe in d2-TCE at 393 K.