

Supporting Information

## **Extended isoindigo core: synthesis and applications as solution-processable n-OFETs materials in ambient conditions**

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## Experimental

### General

All glassware was completely dried before use. Chemicals and solvents were purchased from commercial suppliers or purified by standard techniques. TLC plates were observed by exposure to UV light and/or immersion in a phosphomolybdic acid staining solution followed by drying. Column chromatography was carried out using silicagel 200 – 300 mesh.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were collected on a Bruker AVANCE-III 600 MHz with tetramethylsilane (TMS) as an internal standard at 298K using  $\text{CDCl}_3$  or  $d_6$ -DMSO as the solvents. The coupling constants  $J$  are given in Hz. The IR spectra were observed with Nicolet 6700 FTIR Spectrometer. Cyclic voltammetry (CV) curves were recorded on an electrochemistry workstation (CHI660D, Chenhua Shanghai) at a potential scan rate of  $0.1 \text{ V s}^{-1}$  in an anhydrous argon-saturated chloroform solution ( $10^{-3} \text{ mol L}^{-1}$ ) containing  $0.1\text{M}$  tetrabutylammonium hexafluorophosphate ( $n\text{-Bu}_4\text{NPF}_6$ ) at rt, using a three-electrode system, with glassy carbon electrode as the working electrode, Pt as counter electrode and a Ag/AgCl as the reference electrode. The potential of reference electrode in chloroform was identified by using ferrocene as internal standard. The UV-vis spectra were recorded with a Hitachi U-4100 UV-vis spectrophotometer in an anhydrous chloroform solution ( $10^{-5}\text{mol L}^{-1}$ ). Thermogravimetric analysis (TGA) was carried out using a Q500 TGA analyzer, in which the samples were heated at rate of  $10^\circ\text{C}/\text{min}$  from 30 to  $600 \text{ }^\circ\text{C}$  in a nitrogen flow of  $60 \text{ mL}/\text{min}$ . HRMS were investigated on a Bruker Maxis UHR TOF. XRD patterns were investigated with Rigaku D/MAX-2500 X-ray diffractometer. AFM patterns were collected with Digital Instrument NanoScopeIIIa.

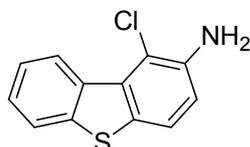
### Device fabrication and characterization.

Top-gate/bottom-contact FET devices were fabricated using  $n^{++}\text{-Si}/\text{SiO}_2$  (300 nm) substrates. The gold source and drain bottom electrodes (with Ti as the adhesion layer) were patterned by photolithography on the  $\text{SiO}_2$  surface. The substrates were treated by using ultrasonication in acetone, cleaning agent, deionized water (twice), and isopropanol. The treated substrates were dried under vacuum at  $80 \text{ }^\circ\text{C}$ . The thin films of the small molecules were deposited on the substrates by spin-coating using DCB solutions ( $10 \text{ mg}/\text{mL}$ ) at 1500 rpm for 60 s. After OFET thin films were deposited, a CYTOP solution (CTL809M:CT-solv180 = 3:1) was spin-coated onto the semiconducting layer at 2000 rpm for 60s resulting in a dielectric layer of 500 nm

thick. The CYTOP layer was then cross-linked at 100 °C for 1 h. A layer of Al (50 nm) were then evaporated onto the dielectric layer by thermal evaporation as gate electrodes. The OFET devices had a channel ratio of width to length ( $W/L=20$ ). The performance of the OFETs were investigated on a probe stage using a Keithley 4200 parameter analyzer in atmosphere (humidity 50-60%). The carrier mobility,  $\mu$ , was calculated from the data in the saturated regime according to the equation  $I_{SD} = (W/2L) C_i \mu (V_G - V_T)^2$ , where  $I_{SD}$  is the drain current in the saturated regime.  $W$  and  $L$  are the semiconductor channel width and length, respectively.  $C_i$  ( $C_i = 3.5\text{nF}$ ) is the capacitance per unit area of the gate dielectric layer.  $V_G$  and  $V_T$  are the gate voltage and threshold voltage, respectively.  $V_G - V_T$  of the devices were determined from the relationship between the square root of  $I_{SD}$  and  $V_G$  at the saturated regime.

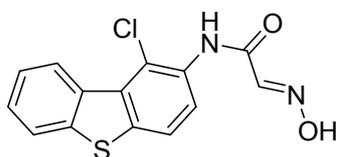
## Synthesis Details:

### Synthesis of 1-chlorodibenzo[*b,d*]thiophen-2-amine (2a).



To the solution of dibenzo[*b,d*]thiophen-2-amine (199mg, 1.0mmol, 1.0 equiv.) in MeCN (10 mL) at 60°C was added *N*-chlorosuccinimide (147 g, 1.1mmol, 1.1 equiv.) in one portion. The mixture was heated to reflux for half an hour. The reaction was quenched by water and extracted with ethyl acetate for 3 times. The combined organic phases were dried with sodium sulfate anhydrous. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel; eluent: PE (Petroleum ether):EA(ethyl acetate) = 10:1) to afford 2a as a white solid (185mg, 79 %). mp 117-118 °C. IR (KBr,  $\text{cm}^{-1}$ ): 3428 ( $\text{NH}_2$ ), 3347, 3199, 1614, 1472, 806, 731.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$ : 8.99-8.98 (m, 1H, Ar), 7.83-7.81 (m, 1H, Ar), 7.55-7.53 (d, 1H,  $J=8.3\text{Hz}$ , Ar), 7.46-7.45 (m, 2H, Ar), 6.96-6.94 (d, 1H,  $J=8.3\text{Hz}$ , Ar), 4.20 (s, 2H,  $\text{NH}_2$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$ : 140.83, 140.64, 134.99, 132.25, 130.41, 126.53, 125.63, 123.99, 122.60, 121.54, 115.86, 114.73. HRMS (ESI): calcd for  $[\text{C}_{12}\text{H}_8\text{ClNS} + \text{H}]^+$ : 234.0139, found: 234.0158.

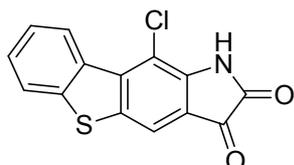
### Synthesis of (*E*)-*N*-(1-chlorodibenzo[*b,d*]thiophen-2-yl)-2-(hydroxyimino)-acetamide (3a).



To a 30 mL of EtOH/  $\text{H}_2\text{O}$  solution (v:v =1:1), was added 1-chlorodibenzo[*b,d*]thiophen-2-amine (234 mg, 1.0 mmol, 1.0 equiv.), anhydrous  $\text{Na}_2\text{SO}_4$  (1.14 g, 8.0 mmol, 8.0 equiv.), Chloral hydrate (246 mg, 1.5 mmol, 1.5 equiv.), hydroxylamine hydrochloride (242 mg, 3.5 mmol, 3.5 equiv.) and conc. HCl (0.2 mL, 2.4 mmol, 2.4 equiv.). The mixture was heated to reflux and stirred for 2 hours. Then the mixture was cooled to room temperature. The precipitate was collected by filtration and washed with water. After drying at 50 °C in vacuum oven over night, the crude was

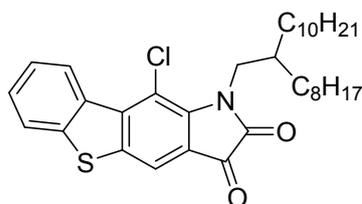
recrystallized in ethyl acetate. 214 mg (70 % yield) of product was obtained. mp 240-241 °C. IR (KBr, cm<sup>-1</sup>): 3349 (NH), 3154, 3041, 1663 (C=O), 1530, 815, 732.1H NMR (CDCl<sub>3</sub>, 600 MHz) δ: 12.42 (s, 1H, NH), 9.86(s, 1H, OH), 8.97-8.96 (d, 1H, *J*=7.9Hz, Ar), 8.12-8.11 (d, 1H, *J*=7.9Hz, Ar), 8.08-8.06 (d, 1H, *J*=8.4Hz, Ar), 7.96-7.94 (d, 1H, *J*=8.4Hz, Ar), 7.75 (s, 1H, N=CH), 7.62-7.57 (m, 2H, Ar). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz) δ: 161.14, 143.93, 140.23, 137.81, 134.43, 132.41, 131.63, 127.97, 125.62, 125.33, 124.79, 123.73, 123.57, 122.37. HRMS (ESI): calcd for [C<sub>14</sub>H<sub>9</sub>ClN<sub>2</sub>O<sub>2</sub>S + H]<sup>+</sup>: 305.0146, found: 305.0146.

**Synthesis of 10-chloro-1*H*-benzo[4,5]thieno[2,3-*f*]indole-2,3-dione (4a).**



(*E*)-*N*-(1-chlorodibenzo[*b,d*]thiophen-2-yl)-2-(hydroxyimino)acetamide (1.53 g, 5.0 mmol, 1.0 equiv.) was added in small portions with constant stirring at 50°C to 80% H<sub>2</sub>SO<sub>4</sub> (12.25 g, 50 mmol, 2.4 equiv.). The resulting deep red solution was heated to 80 °C for 2 hours and then cooled to room temperature. The mixture was poured into 10-12 times amount of crushed ice, and after 1 hour the precipitate was collected by filtration and washed with water. The crude product was dried at 50 °C in vacuum oven overnight, The crude product can be used in the next step without further purification.

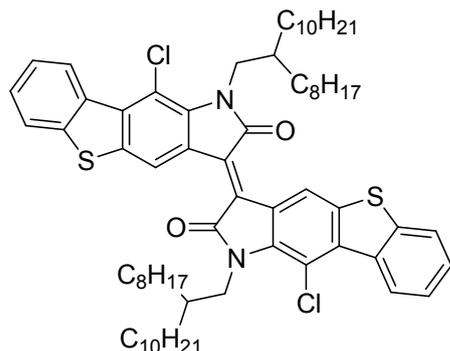
**Synthesis of 10-chloro-1-(2-octyldodecyl)-1*H*-benzo[4,5]thieno[2,3-*f*]indole-2,3-dione (5a).**



Anhydrous potassium carbonate (345 mg, 2.5 mmol, 5.0 equiv. ) was added to a 10 mL of anhydrous DMF containing 10-chloro-1*H*-benzo[4,5]thieno[2,3-*f*]indole- 2,3-dione (144 mg, 0.5mmol, 1.0 equiv. ) in a 25-mL, one-necked, round-bottomed flask and allowed to stir at room temperature for 15 min. 9-(Bromomethyl) nonadecane (361mg, 1 mmol, 2 equiv. ) was then injected and the mixture was stirred at 80°C for 10 hours. Water (9.0 mL) was added to quench the reaction and the suspension was extracted with dichloromethane. The combined organic phases were dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography silica gel; (eluent: PE:EA= 15:1) to afford 10-chloro-1-(2-octyldodecyl)-1*H*-benzo[4,5]thieno [2,3-*f*]indole-2,3-dione as a red solid (114mg, 40%, two-step yield). mp 116-117 °C. IR (KBr, cm<sup>-1</sup>): 3069, 2924, 2853, 1735 (C=O), 1608, 735. 1H NMR (CDCl<sub>3</sub>, 600 MHz) δ: 9.11-9.09 (d, 1H, *J*=8.4Hz, Ar), 7.98 (s, 1H, Ar), 7.88-7.87 (d, 1H, *J*=8.4 Hz, Ar), 7.60-

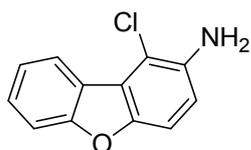
7.58 (m, 1H, Ar), 7.53-7.51 (m, 1H, Ar), 4.14-4.12 (d, 2H,  $J=7.6\text{Hz}$ , N-CH<sub>2</sub>), 2.07-2.04 (m, 1H, CH), 1.37-1.22 (m, 32H, CH<sub>2</sub>), 0.88-0.84 (m, 6H, CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$ :182.49, 159.58, 143.14, 142.94, 139.42, 135.50, 134.62, 128.79, 127.22, 124.97, 123.08, 119.14, 118.97, 113.79, 46.90, 37.78, 37.74, 31.91, 31.88, 31.80, 30.91, 30.88, 30.06, 29.76, 29.65, 29.62, 29.58, 29.53, 29.35, 29.30, 26.18, 26.15, 22.70, 22.67, 22.65, 14.13, 14.11, 14.08. HRMS (APCI): calcd for [C<sub>34</sub>H<sub>46</sub>ClNO<sub>2</sub>S + H]<sup>+</sup>: 568.3011, found: 568.3019.

**Synthesis of (*E*)-10,10'-dichloro-1,1'-bis(2-octyldodecyl)-[3,3'-bibenzo[4,5]thieno[2,3-*f*]indolylidene]-2,2'(1*H*,1'*H*)-dione (C20-DBTII).**



A solution of hexaethyltriaminophosphine (56  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv.) in dichloromethane (1.0 mL) was added dropwise to a solution of compound 10-chloro-1-(2-octyldodecyl)-1*H*-benzo[4,5]thieno[2,3-*f*]indole-2,3-dione (114 mg, 0.2 mmol, 1.0 equiv.) in the same solvent (4.0 mL) at  $-78^\circ\text{C}$  with bubbling of dry argon for 2 min. The reaction mixture was then allowed to warm to room temperature. The reaction mixture was evaporated under reduced pressure to dryness and the residue is treated with 10 mL of acetonitrile to give a precipitate. The solid was collected by filtration, washed with ethyl acetate, and dried under reduced pressure to give the pure red product (*E*)-10,10'-dichloro-1,1'-bis(2-octyldodecyl)-[3,3'-bibenzo [4,5]thieno[2,3-*f*]indolylidene]-2,2'(1*H*,1'*H*)-dione (101 mg, 92%). IR (KBr,  $\text{cm}^{-1}$ ): 3123, 2925, 2853, 1693 (C=O), 1593, 735. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 9.65 (s, 1H, Ar), 9.01-8.99 (d, 1H,  $J=8.2\text{Hz}$ , Ar), 7.85-7.84 (d, 1H,  $J=8.2\text{Hz}$ , Ar), 7.50-7.48 (m, 1H, Ar), 7.45-7.43 (m, 1H, Ar), 4.15-4.14 (d, 2H,  $J=7.5\text{Hz}$ , N-CH<sub>2</sub>), 2.06-2.04 (m, 1H, CH), 1.34-1.21 (m, 32H, CH<sub>2</sub>), 0.88-0.83 (m, 6H, CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$ : 168.48, 142.29, 138.34, 135.29, 134.97, 134.69, 132.51, 127.36, 126.52, 124.20, 123.57, 122.73, 111.45, 46.63, 37.84, 37.81, 31.91, 31.89, 31.82, 30.97, 30.14, 29.79, 29.69, 29.65, 29.63, 29.59, 29.37, 29.34, 26.22, 22.69, 22.67, 22.64, 14.12, 14.09, 14.08. HRMS (APCI): calcd for [C<sub>68</sub>H<sub>92</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> + H]<sup>+</sup>: 1103.6050, found: 1103.6055.

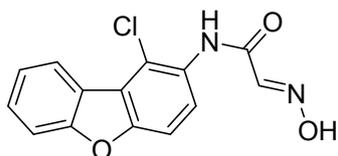
**Synthesis of 1-chlorodibenzo[*b,d*]furan-2-amine (2b).**



To the solution of dibenzo[*b,d*]furan-2-amine (199mg, 1.0mmol, 1.0 equiv.) in MeCN (10 mL) at  $60^\circ\text{C}$  was added *N*-chlorosuccinimide (147 g, 1.1mmol, 1.1 equiv.) in one portion. The mixture was heated to reflux and stirred for half an hour. The reaction

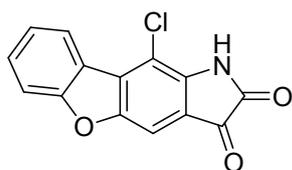
was quenched by water and extracted with ethyl acetate for 3 times. The combined organic phase was dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel; eluent: PE:EA = 10:1) to afford 1-chlorodibenzo[*b,d*]furan-2-amine as a white solid (131 g, 60 %). The mixture can be used in the next step without further purification.

**Synthesis of (*E*)-*N*-(1-chlorodibenzo[*b,d*]furan-2-yl)-2-(hydroxyimino)acetamide (3b).**



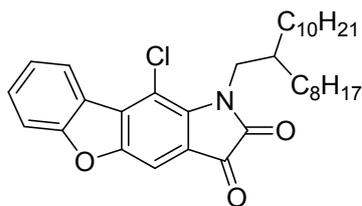
To a 30 mL of H<sub>2</sub>O solution containing 1-chlorodibenzo[*b,d*]furan-2-amine (218mg, 1.0mmol, 1.0 equiv.), were added Na<sub>2</sub>SO<sub>4</sub> (1.14 g, 8.0mmol, 8.0 equiv.), Chloral hydrate (246mg, 1.5 mmol, 1.5 equiv.), hydroxylamine hydrochloride (242mg, 3.5 mmol, 3.5 equiv.) and conc. HCl (0.2 mL, 2.4mmol, 2.4 equiv.) in sequence. The resulting mixture was heated to reflux and stirred for 2 hours. Then the mixture was cooled to room temperature. The precipitate was collected by filtration and washed with water. After drying at 50 °C in vacuum oven overnight, the crude was recrystallized in ethyl acetate. 231mg (80 %) of product was obtained. mp 226 °C. IR (KBr, cm<sup>-1</sup>): 3351, 3166, 3049, 1666 (C=O), 1553, 1047, 746. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ: 12.36 (1H, s, NH), 9.87 (1H, s, OH), 8.37-8.36 (1H, d, *J*=7.8Hz, Ar), 7.86-7.85 (1H, d, *J*=8.7Hz, Ar), 7.80-7.79 (1H, d, *J*=7.8Hz, Ar), 7.77-7.75 (1H, d, *J*=8.7Hz, Ar), 7.73 (1H, s, N=CH), 7.65-7.63 (1H, m, Ar), 7.51-7.49 (1H, m, Ar). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz) δ: 161.28, 156.35, 153.71, 143.91, 130.42, 129.02, 126.20, 124.08, 122.87, 122.81, 122.25, 112.45, 111.05. HRMS (ESI): calcd for [C<sub>14</sub>H<sub>9</sub>ClN<sub>2</sub>O<sub>3</sub>+Na]<sup>+</sup>: 311.0194, found: 311.0195.

**Synthesis of 10-chloro-1*H*-benzo[4,5]furan[2,3-*f*]indole-2,3-dione (4b).**



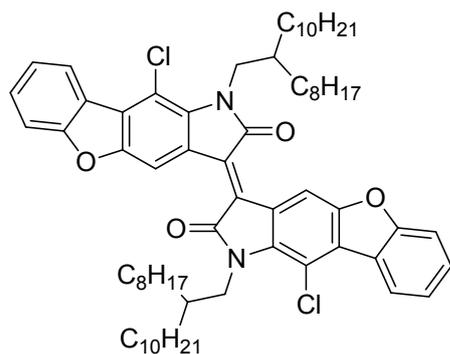
(*E*)-*N*-(1-chlorodibenzo[*b,d*]furan-2-yl)-2-(hydroxyimino)acetamide (1.45 g, 5.0 mmol, 1.0 equiv.) was added in small portions with constant stirring at 50 °C to an 80% H<sub>2</sub>SO<sub>4</sub> aqueous solution (12.25 g, 50 mmol, 10 equiv.). The resulting deep red solution was heated to 80 °C for 2 hours and then cooled to room temperature. The mixture was poured into 10-12 times amount of crushed ice, After 1 hour the precipitate was collected by filtration and washed with water. The crude product was dried in vacuum oven over night and could be used in the next step without further purification.

**Synthesis of 10-chloro-1-(2-octyldodecyl)-1*H*-benzo[4,5]furan[2,3-*f*]indole-2,3-dione (5b).**



Anhydrous potassium carbonate (345mg, 2.5 mmol, 5.0 equiv. ) was added to a 10 ml of anhydrous DMF containing 10-chloro-1*H*-benzo[4,5]furan[2,3-*f*]indole-2,3-dione (136mg, 0.5mmol, 1.0 equiv. ) in a 25-mL, one-necked, round-bottomed flask and allowed to stir at room temperature for 15 min. 9-(bromomethyl)nonadecane (361mg, 1 mmol, 2 equiv. ) was then injected and the mixture was stirred at 80°C for 10 hours. Water (9.0 mL) was added to quench the reaction and the suspension was extracted by dichloromethane. The combined organic phase was dried with sodium sulfate anhydrous. The solvent was removed under reduced pressure and the crude product was purified by column chromatography silica gel (eluent: PE:EA = 15:1) to afford 10-chloro-1-(2-octyldodecyl)-1*H*-benzo[4,5]furan[2,3-*f*]indole-2,3-dione as a red solid (96mg, 35%, two-step yield). mp 136-137 °C. IR (KBr, cm<sup>-1</sup>): 2925, 2853, 1735 (C=O), 1622, 1107, 757. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)δ: 8.47-8.46 (d, 1H, *J*=7.9Hz, Ar), 7.75 (s, 1H, Ar), 7.64-7.60 (m, 2H, Ar), 7.45-7.43 (m, 1H, Ar), 4.10-4.09 (d, 2H, *J*=7.5Hz, N-CH<sub>2</sub>), 2.07-2.04 (m, 1H, CH), 1.39-1.23 (m, 32H, CH<sub>2</sub>), 0.88-0.85 (m, 6H, CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz) δ: 182.62, 159.64, 158.31, 151.87, 142.13, 131.42, 130.29, 124.16, 123.79, 123.05, 118.84, 112.22, 111.22, 108.21, 46.49, 37.64, 37.61, 31.90, 31.88, 31.80, 30.90, 30.87, 30.05, 29.75, 29.64, 29.62, 29.58, 29.53, 29.34, 29.29, 26.17, 26.14, 22.69, 22.66, 22.64, 14.12, 14.10, 14.08. HRMS (APCI): calcd for [C<sub>34</sub>H<sub>46</sub>ClNO<sub>3</sub> + H]<sup>+</sup>:552.3239, found: 552.3249.

**Synthesis of (*E*)-10,10'-dichloro-1,1'-bis(2-octyldodecyl)-[3,3'-bibenzo[4,5]furan[2,3-*f*]indolylidene]-2,2'-(1*H*,1'*H*)-dione (C20-DBFII).**



A solution of hexaethyltriaminophosphine (56 μL, 0.2 mmol, 1.0 equiv.) in dichloromethane (1.0 mL) was added dropwise to a solution of 10-chloro-1-(2-octyldodecyl)-1*H*-benzo[4,5]furan[2,3-*f*]indole-2,3-dione (114 mg, 0.2 mmol, 1.0 equiv.) in dichloromethane (4.0 mL) at -78°C with bubbling of dry argon for 2 min. The reaction mixture was then allowed to warm to room temperature. The solvent was evaporated under reduced pressure and the residue is treated with 10 ml of acetonitrile to form a precipitate. The solid was collected by filtration, washed with ethyl acetate, and dried at 50 °C in vacuum oven to give the pure red product (*E*)-10,10'-dichloro-

1,1'-bis(2-octyldodecyl)-[3,3'-bibenzo[4,5]furan[2,3-*f*]indolylidene]-2,2'(1H,1'H)-dione(101 mg, 92%). IR (KBr,  $\text{cm}^{-1}$ ): 3128, 2924, 2853, 1694 (C=O), 1174, 745.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$ : 9.40 (s, 1H, Ar), 8.34-8.33 (d, 1H,  $J=7.9\text{Hz}$ , Ar), 7.55-7.54 (d, 1H,  $J=7.9\text{Hz}$ , Ar), 7.52-7.49 (m, 1H, Ar), 7.36-7.34 (m, 1H, Ar), 4.00-3.99 (d, 2H, 7.3Hz, N- $\text{CH}_2$ ), 2.03-2.01 (m, 1H, CH), 1.33-1.22 (m, 32H,  $\text{CH}_2$ ), 0.88-0.84 (m, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$ : 168.34, 157.66, 151.58, 136.75, 133.26, 128.58, 126.46, 123.91, 123.41, 123.37, 122.90, 111.93, 111.76, 108.36, 46.17, 37.81, 37.78, 31.91, 31.89, 31.86, 30.98, 30.13, 29.82, 29.68, 29.64, 29.59, 29.36, 29.33, 26.24, 22.69, 22.66, 22.65, 14.11, 14.08. HRMS (APCI): calcd for  $[\text{C}_{68}\text{H}_{92}\text{Cl}_2\text{N}_2\text{O}_4+\text{H}]^+$ : 1071.6507, found: 1071.6473.

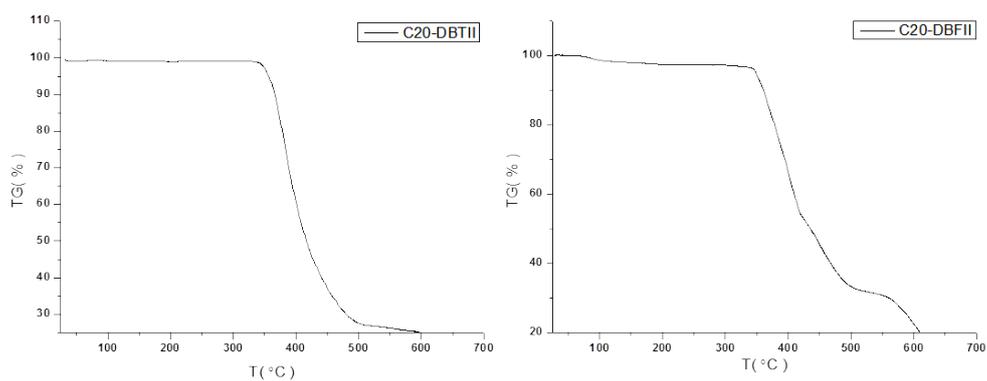


Fig. S1. TGA curve of C20-DBTII (left) and C20-DBFII (right).

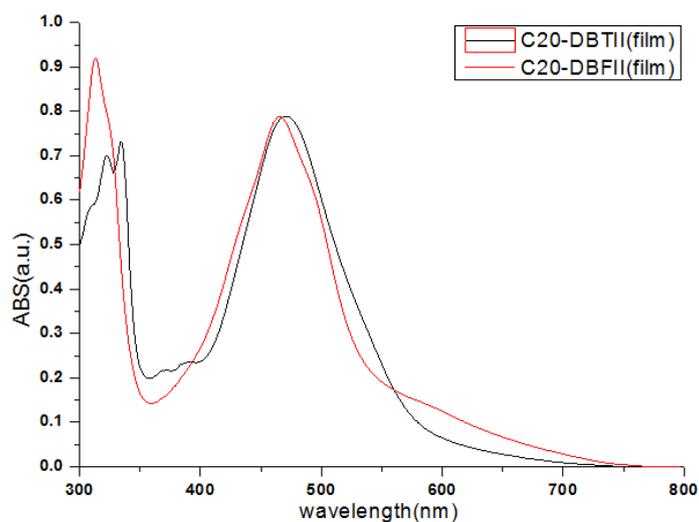


Fig. S2. Normalized UV-vis absorption of C20-DBTII and C20-DBFII in thin film state.

Table. S1. The 4 lowest excited energies (nm) of C20-DBTII and C20-DBFII in chloroform solution(TDDFT(B3LYP/6-31+G\*)).

Compounds		S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>
<b>C20-DBTII</b>	EE <sup>a</sup> (nm)	613.3	605.7	519.8	419.4
	OS <sup>b</sup>	(0.04)	(0.00)	(1.22)	(0.00)
	Main contribution <sup>c</sup>	H <sup>d</sup> →L <sup>e</sup> (98.3%)	H-1→L (98.3%)	H-2→L (99.1%)	H-3→L (91.1%)
<b>C20-DBFII</b>	EE (nm)	582.9	555.0	497.9	413.8
	OS	(0.31)	(0.00)	(0.97)	(0.00)
	Main contribution	H→L (88.3%)	H-1→L (98.5%)	H-2→L (88.3%)	H-3→L (96.0%)

<sup>a</sup>: Excited Energy; <sup>b</sup>: Oscillator Strength; <sup>c</sup>: Main Contribution; <sup>d</sup>: HOMO; <sup>e</sup>: LUMO.

Table. S2. Calculated energy level of C20-DBTII and C20-DBFII (TDDFT(B3LYP/6-31+G\*)).

Compounds	$E_{\text{LUMO}}$ (eV)	$E_{\text{HOMO}}$ (eV)	$E_{\text{HOMO-1}}$ (eV)	$E_{\text{HOMO-2}}$ (eV)	$E_{\text{HOMO-3}}$ (eV)	$E_{\text{HOMO-LUMO}}^{\text{gap}}$ (eV)
<b>C20-DBTII</b>	-3.44	-5.98	-6.04	-6.18	-6.84	2.54
<b>C20-DBFII</b>	-3.43	-6.03	-6.28	-6.35	-6.83	2.60

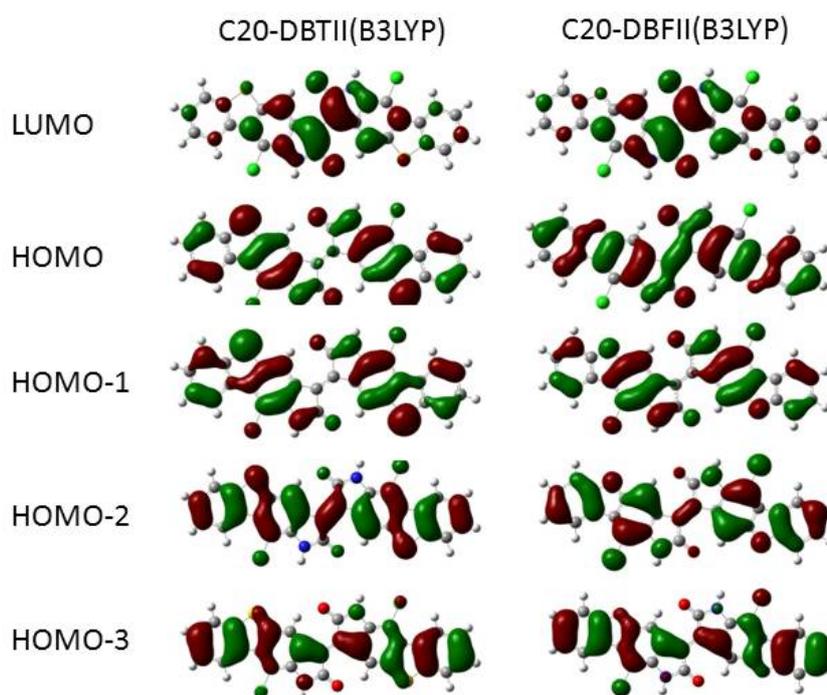


Figure S3. Molecular orbitals of compounds C20-DBTII and C20-DBFII(TDDFT(B3LYP/6-31+G\*).

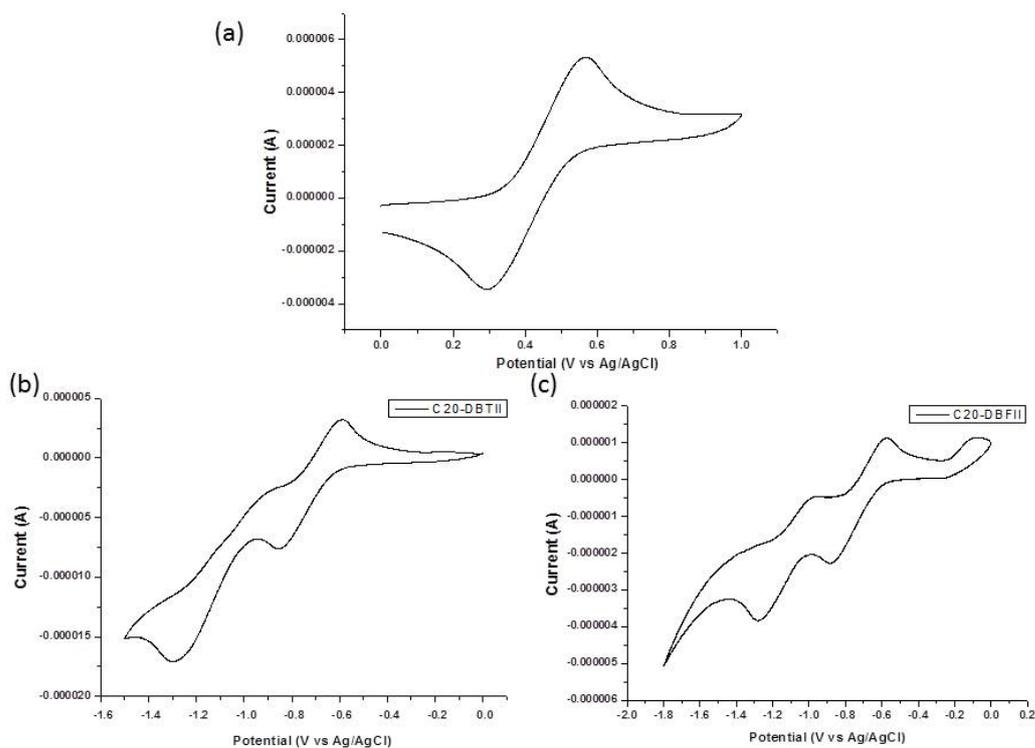


Figure S4. Cyclic Voltammery of 10<sup>-3</sup>mol L<sup>-1</sup> ferrocene (a), C20-DBTII (b) and C20-DBFII (c) in chloroform (electrolyte: NBU<sub>4</sub>PF<sub>6</sub>, 0.1 M, Ag/AgCl as the reference electrode, scan rate: 0.1 V/s).

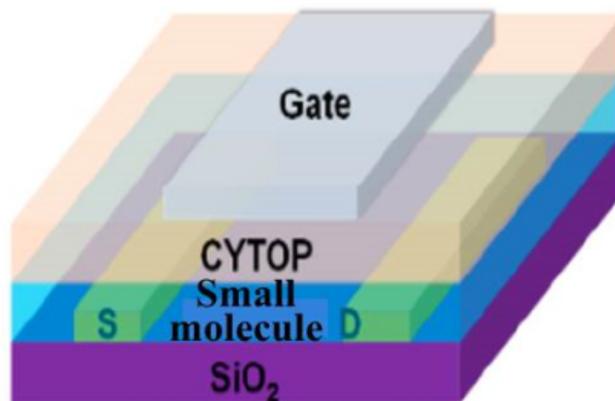


Figure S5. Top-gate/bottom-contact device configuration used in this study.

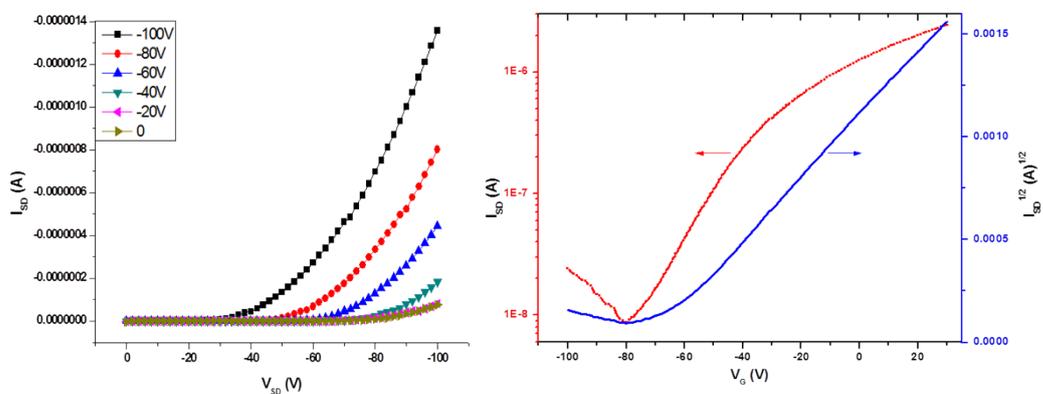
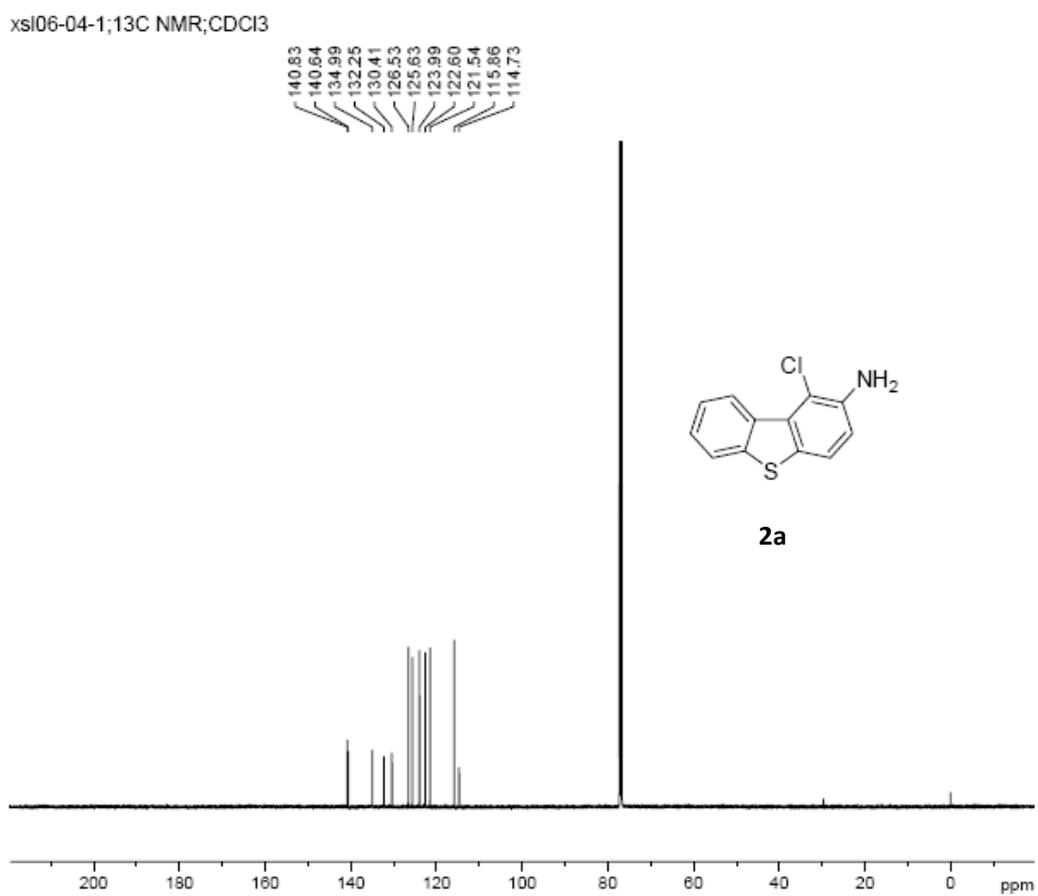
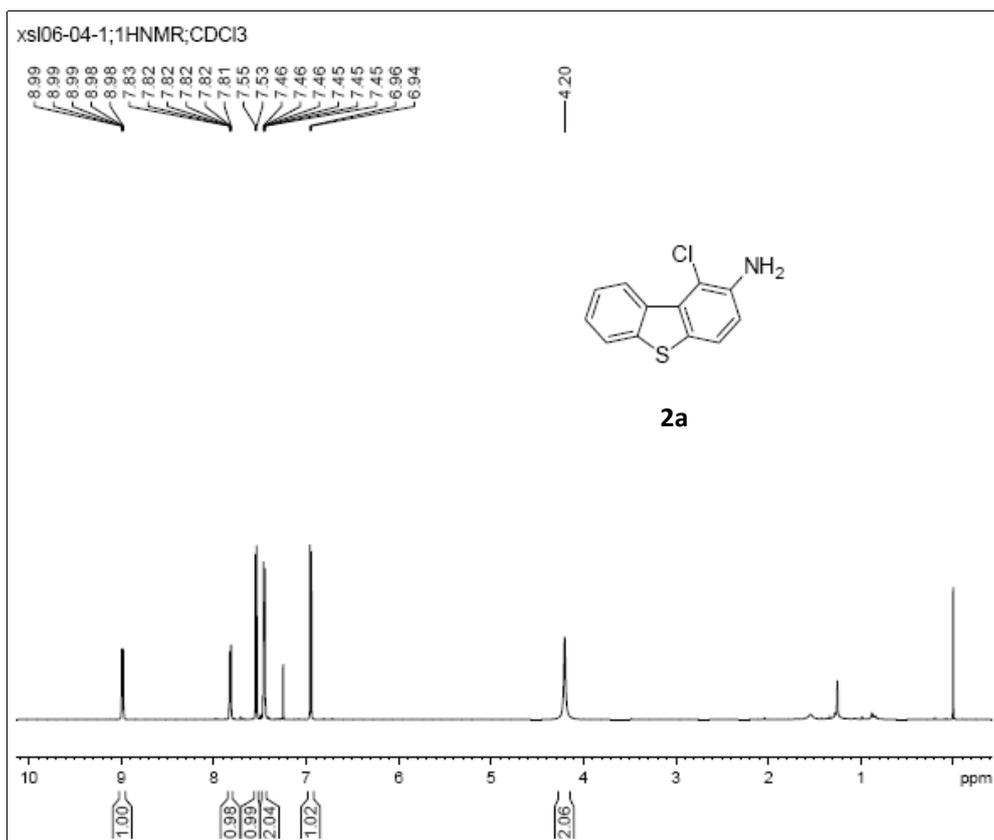
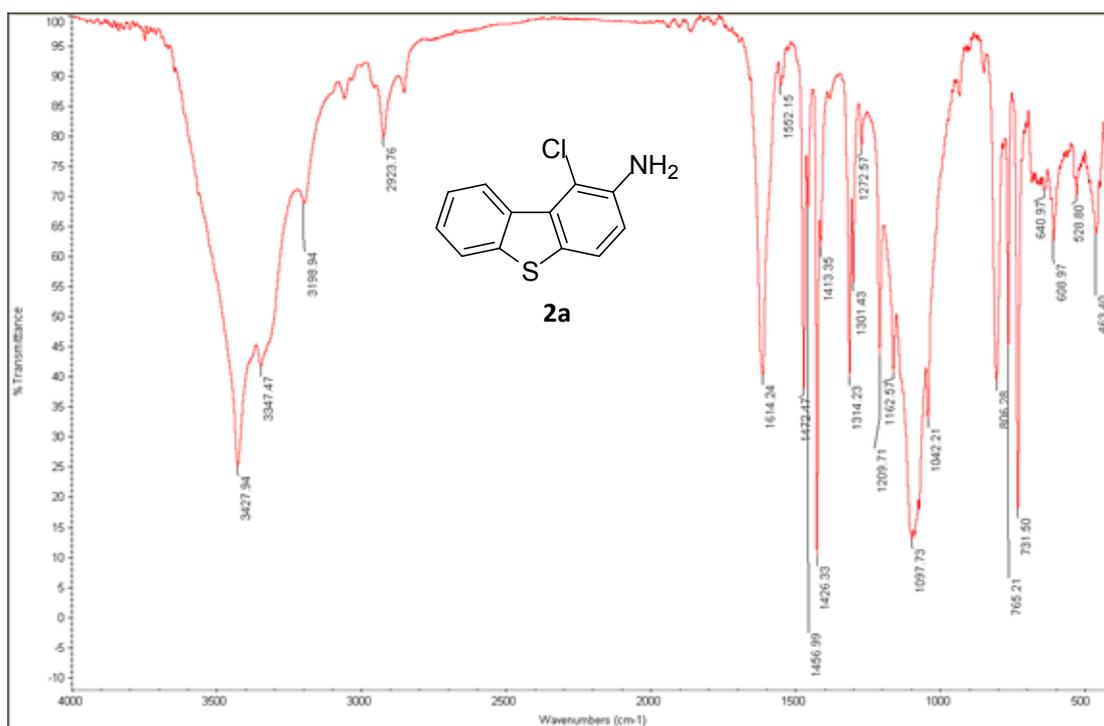
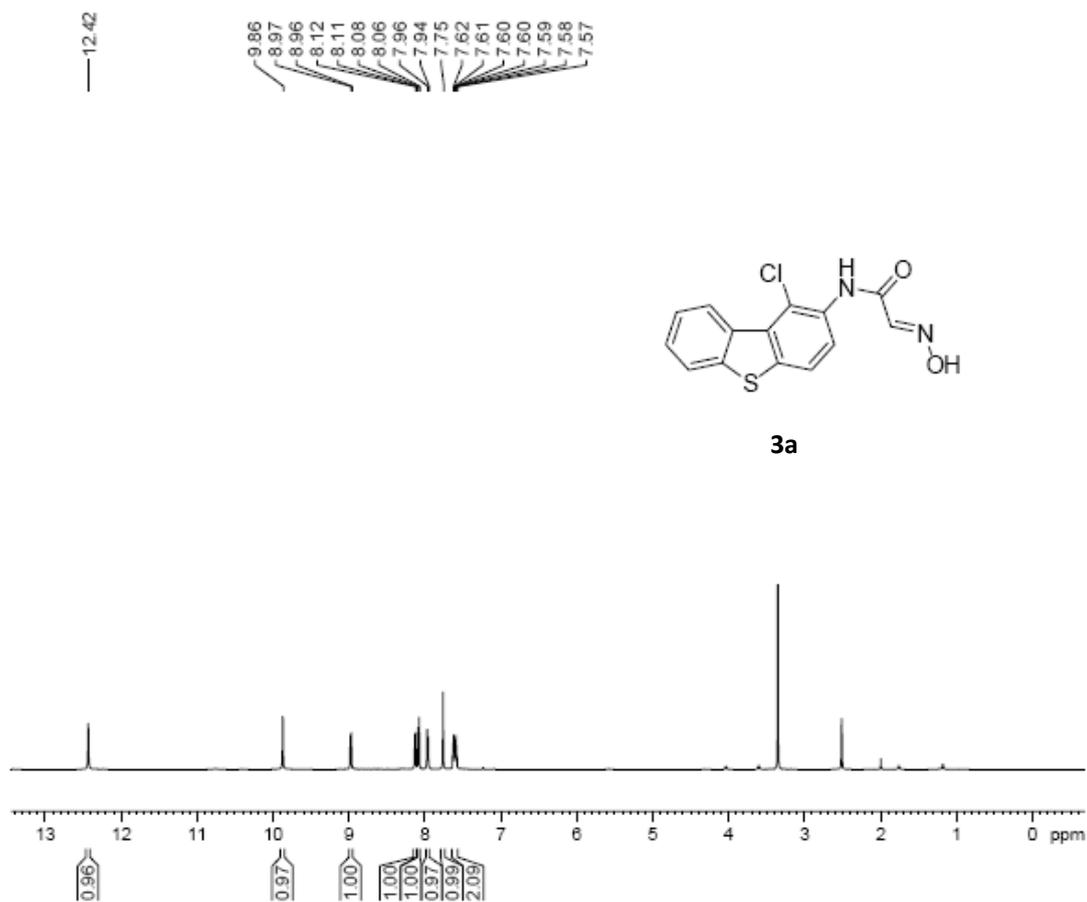


Figure S6. Output (left) and transfer (right) characteristics of hole mobility of C20-DBTII device measured in ambient conditions.

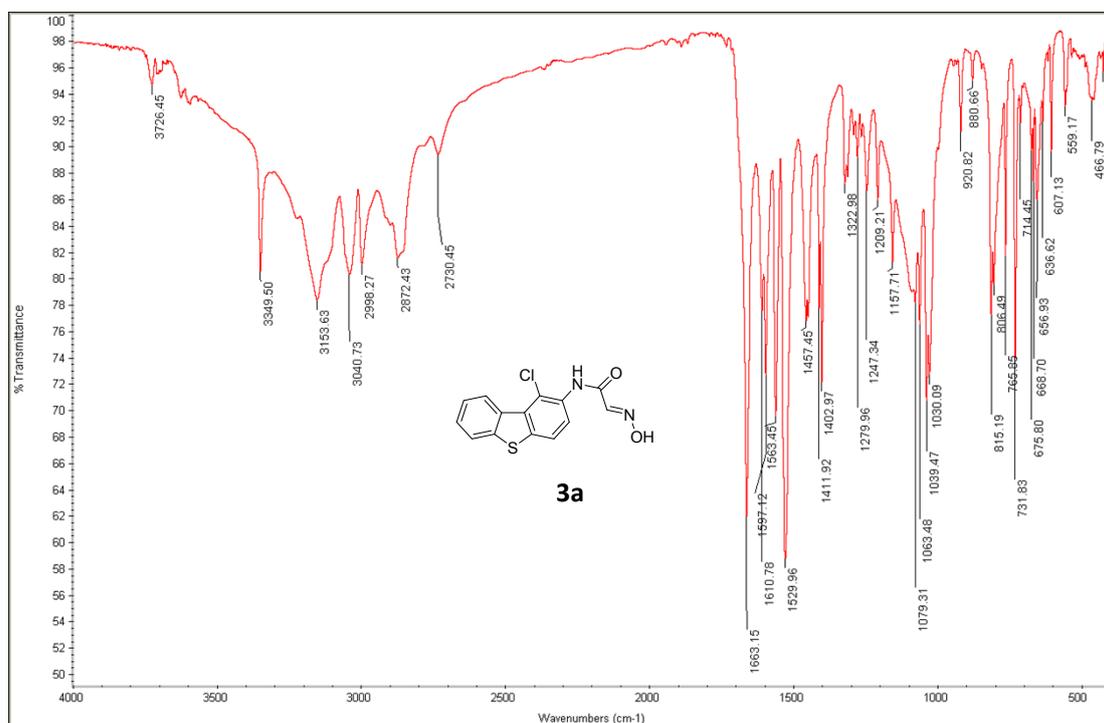
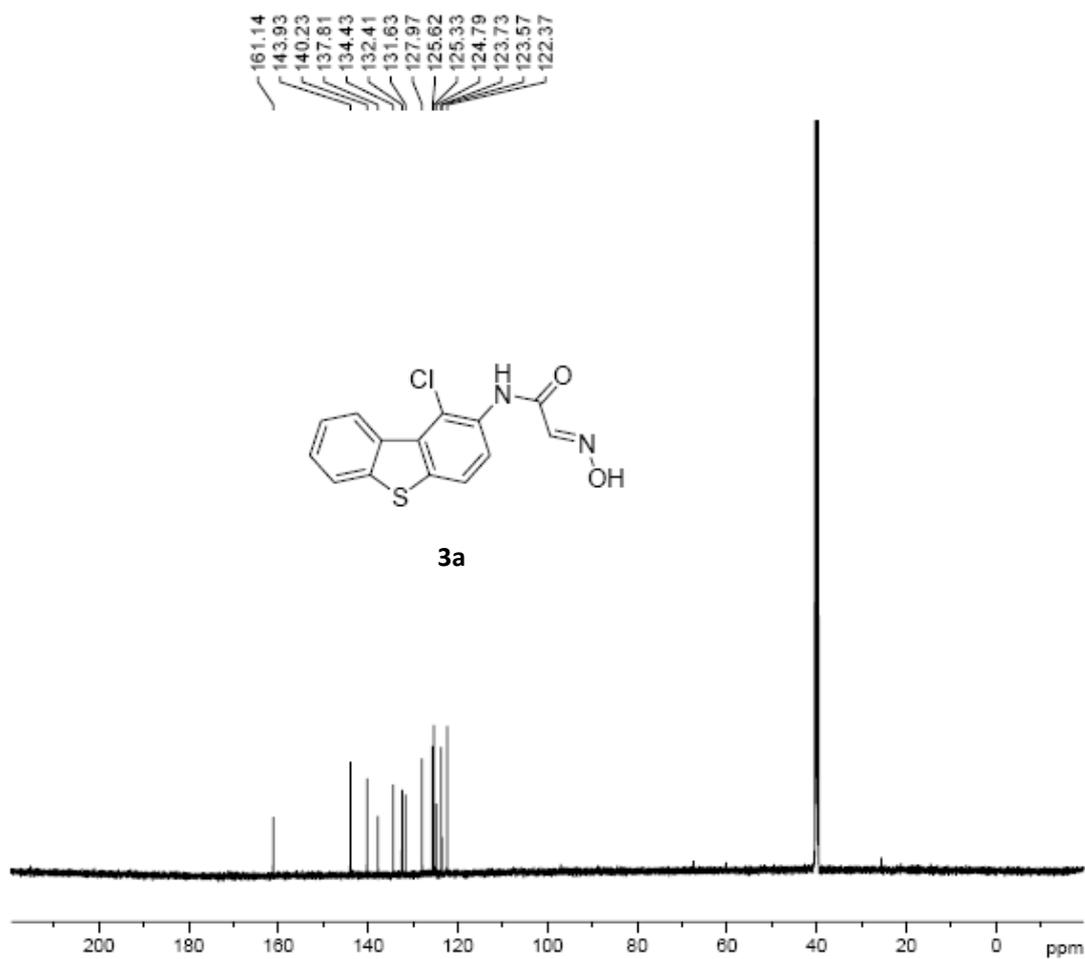




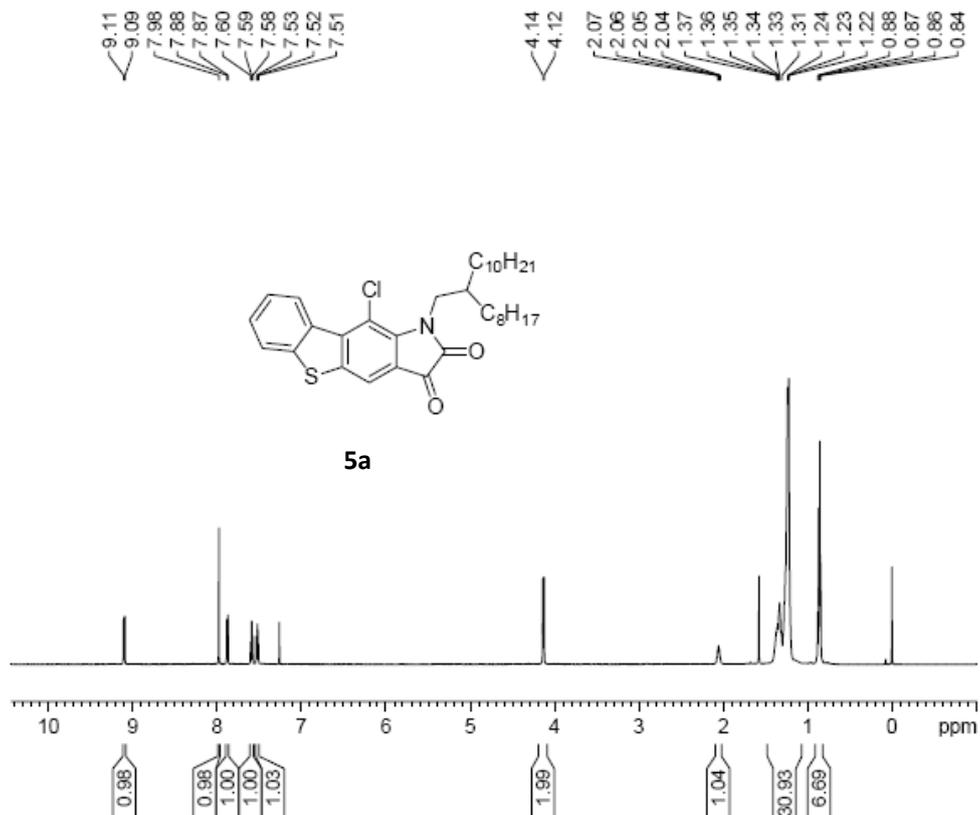
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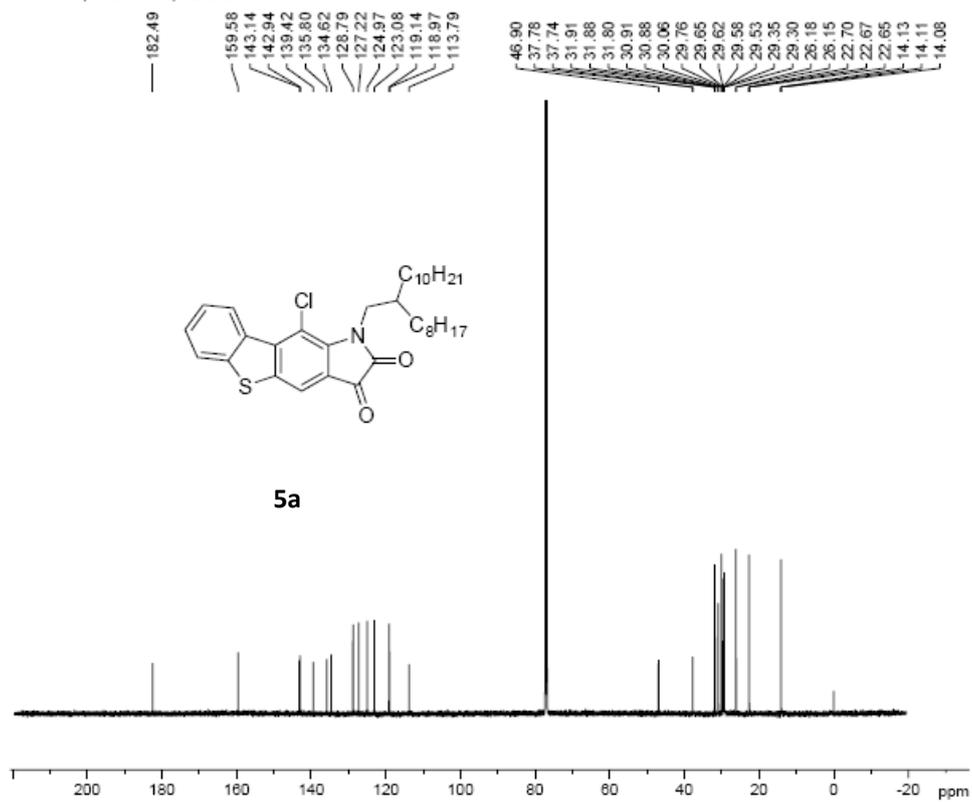
xsl04-53-1;13CNMR,DMSO

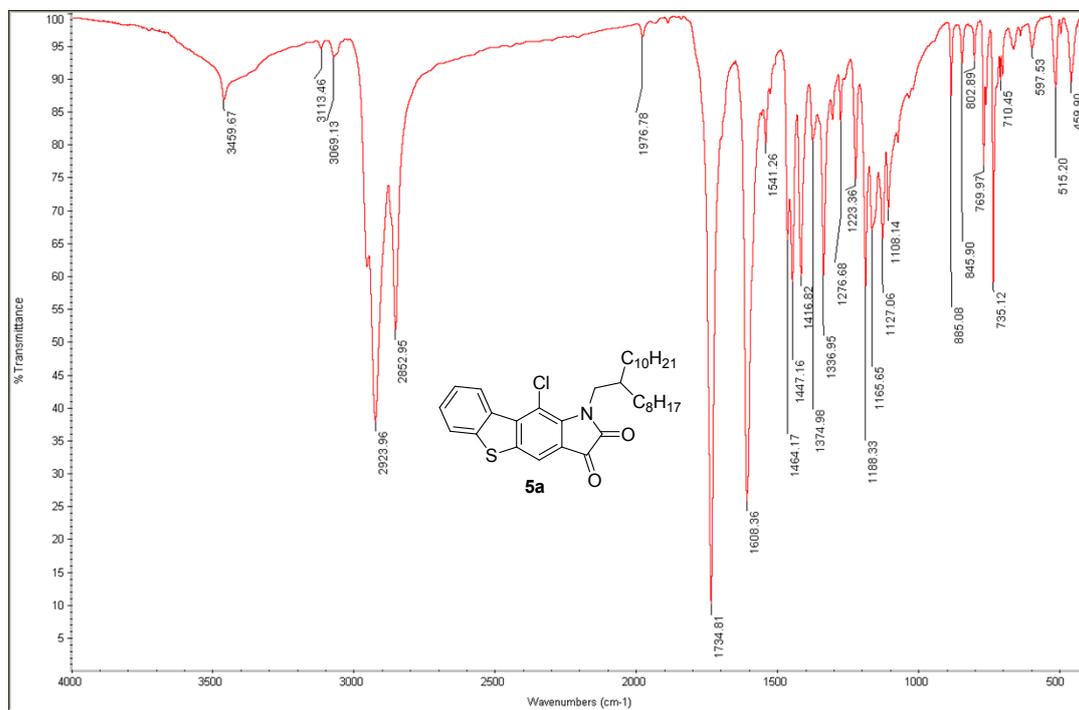


xsl05-79;1HNMR;CDCl3

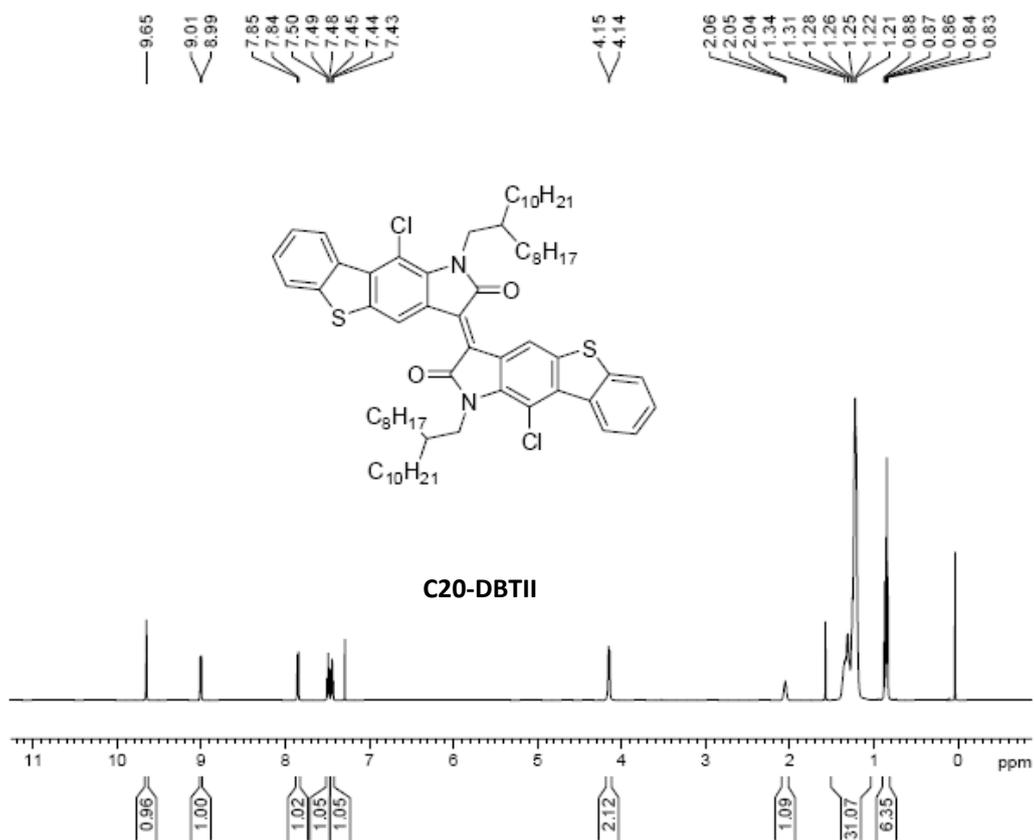


xsl05-79;13C NMR;CDCl3

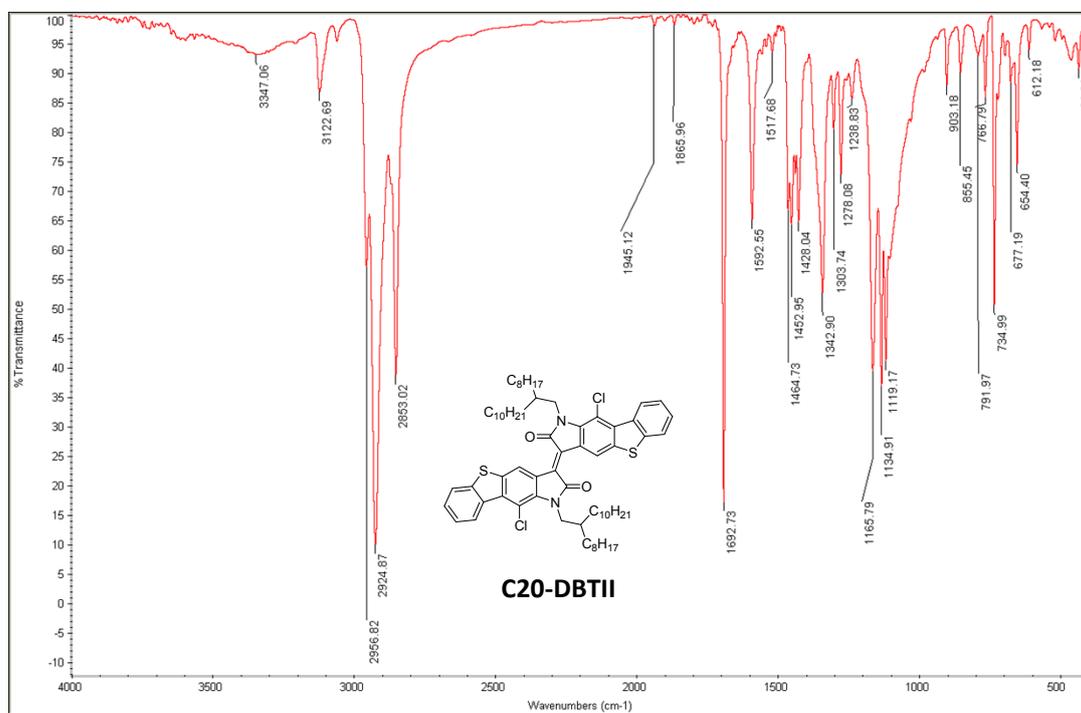
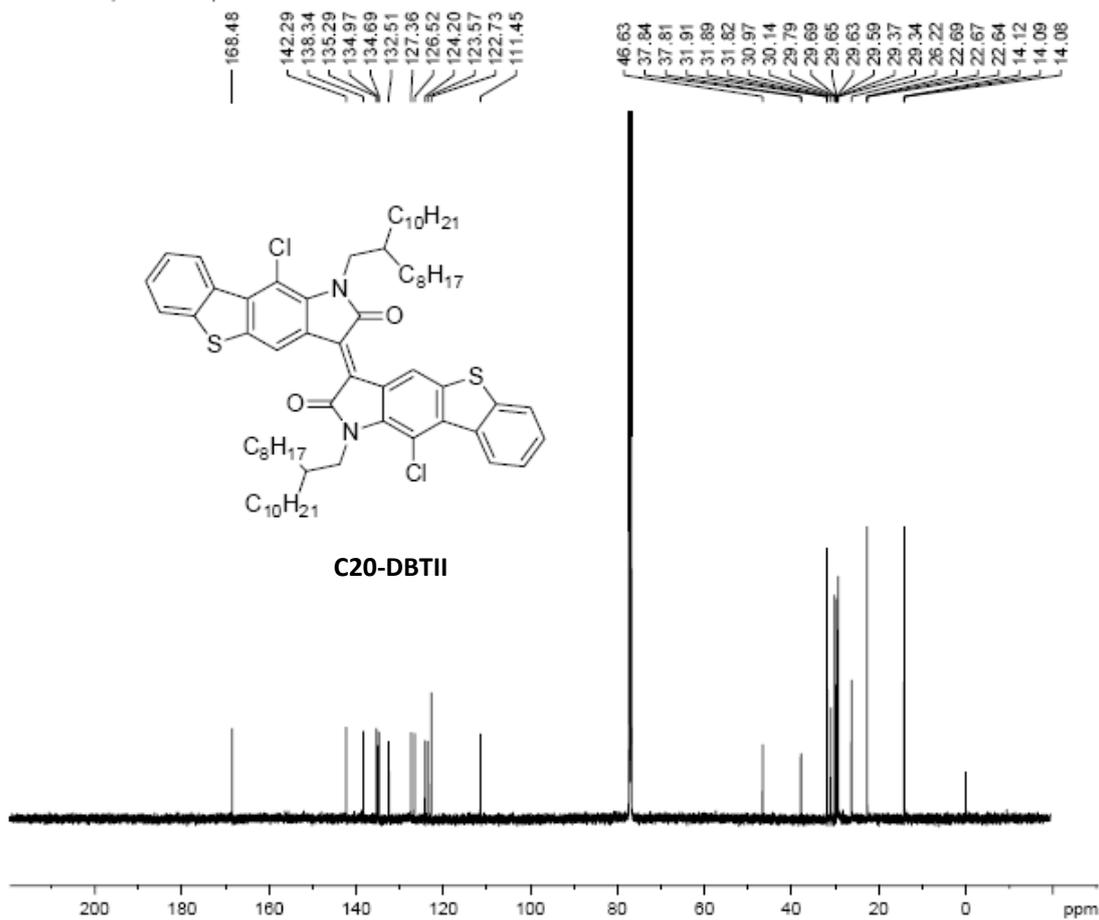




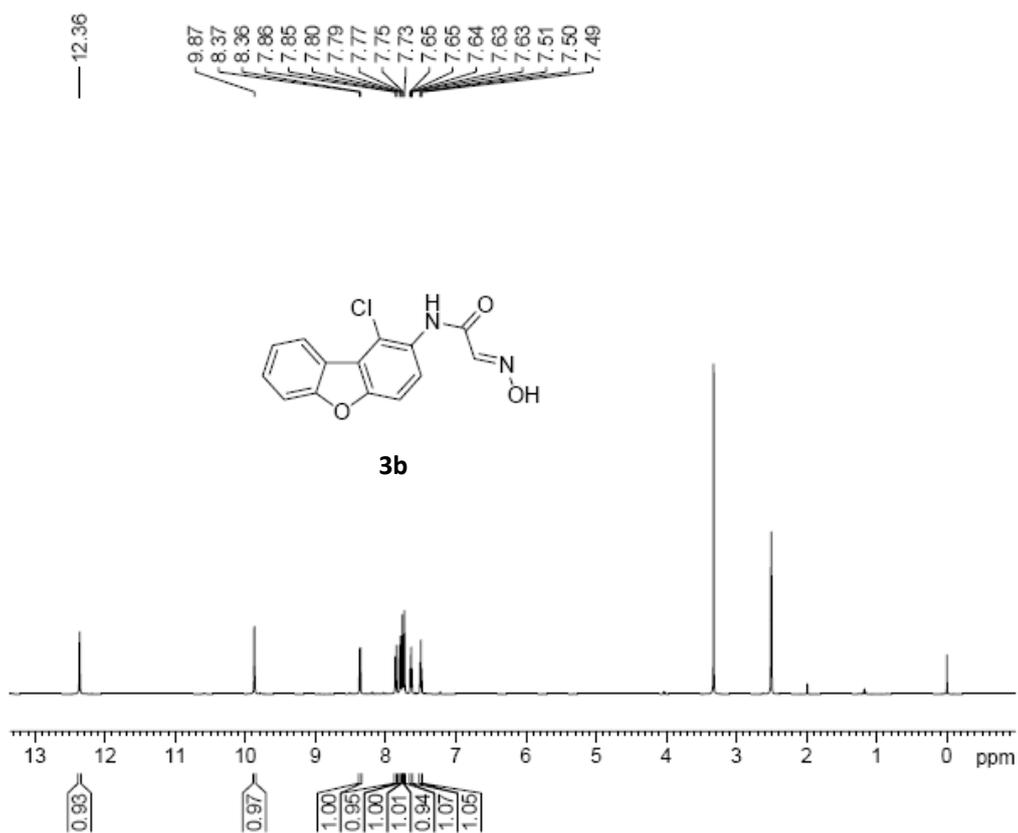
xs106-02-1; <sup>1</sup>H NMR; CDCl<sub>3</sub>



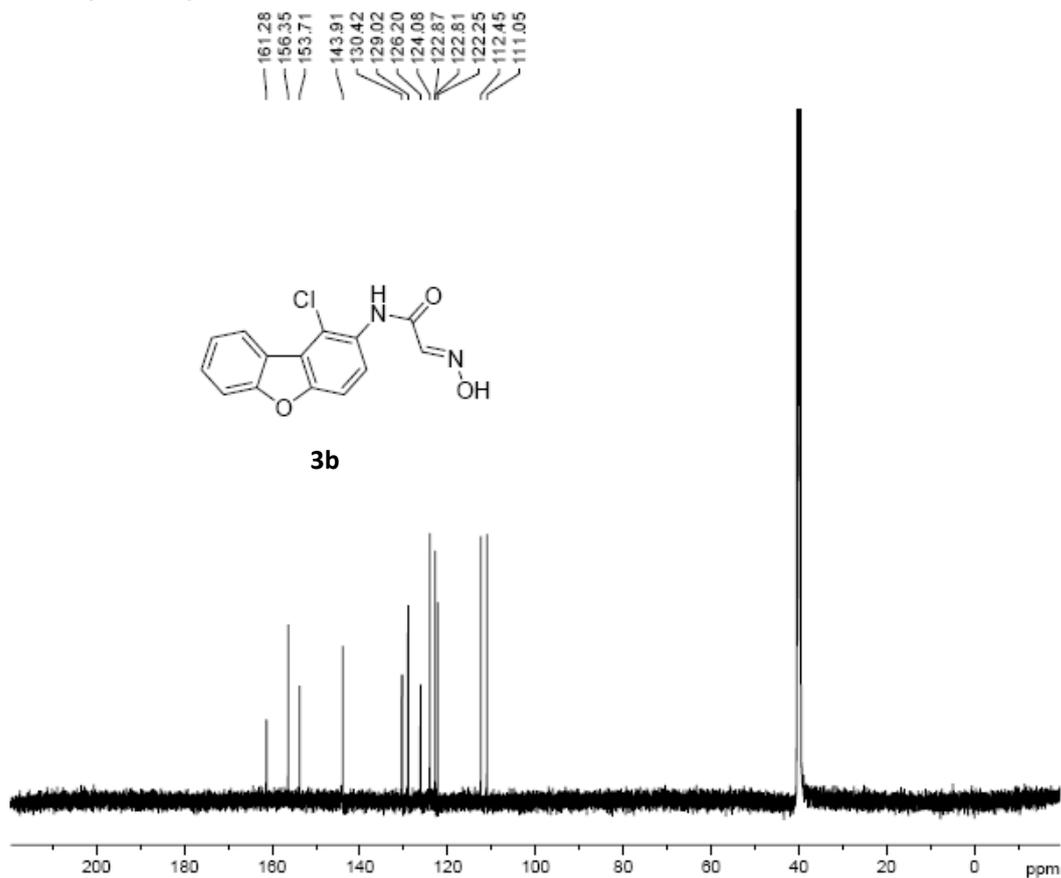
xsl06-02-1;13C NMR;CDCl3

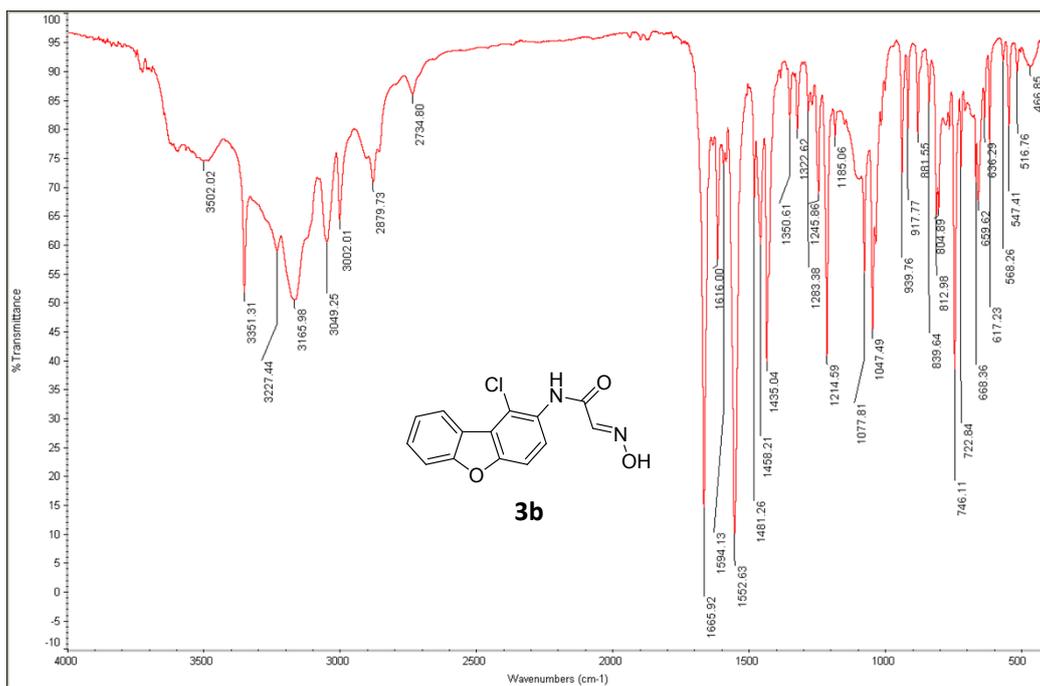


xsl06-61;1H NMR;DMSO

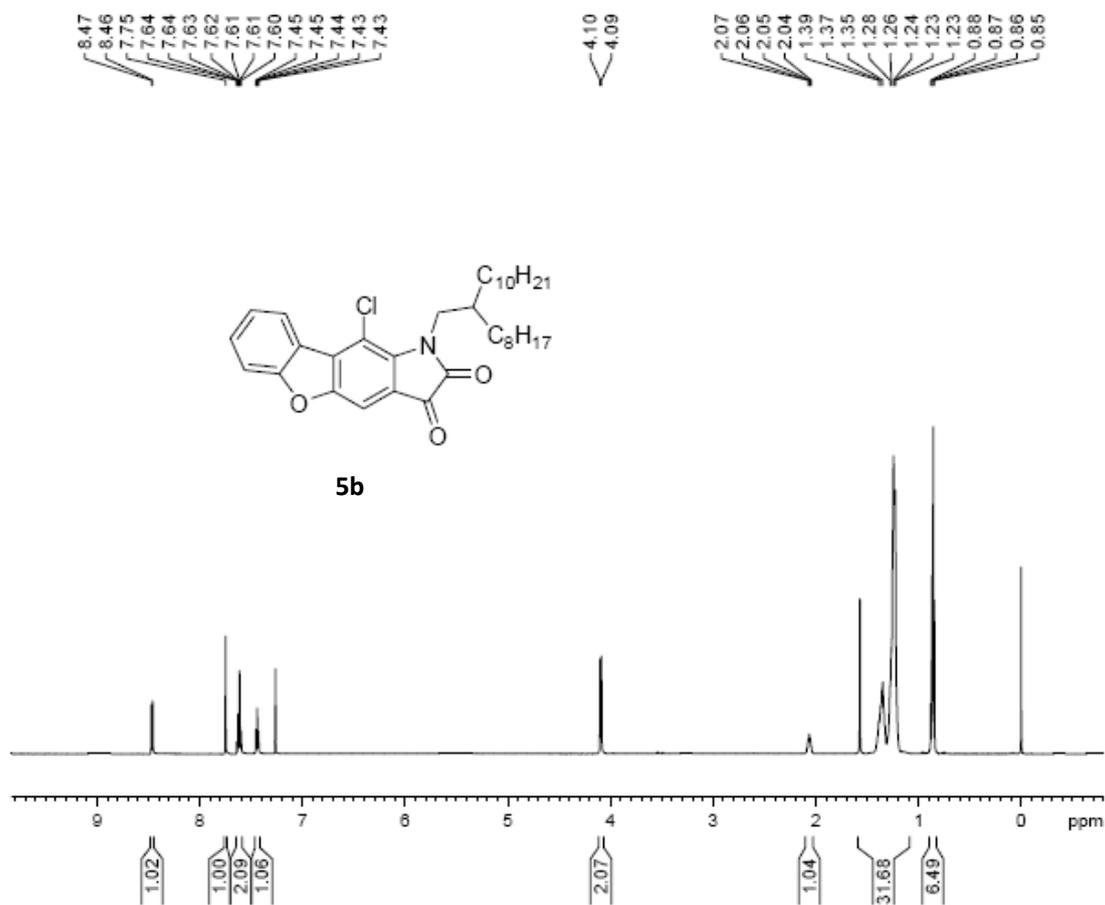


xsl06-61;13C NMR;DMSO

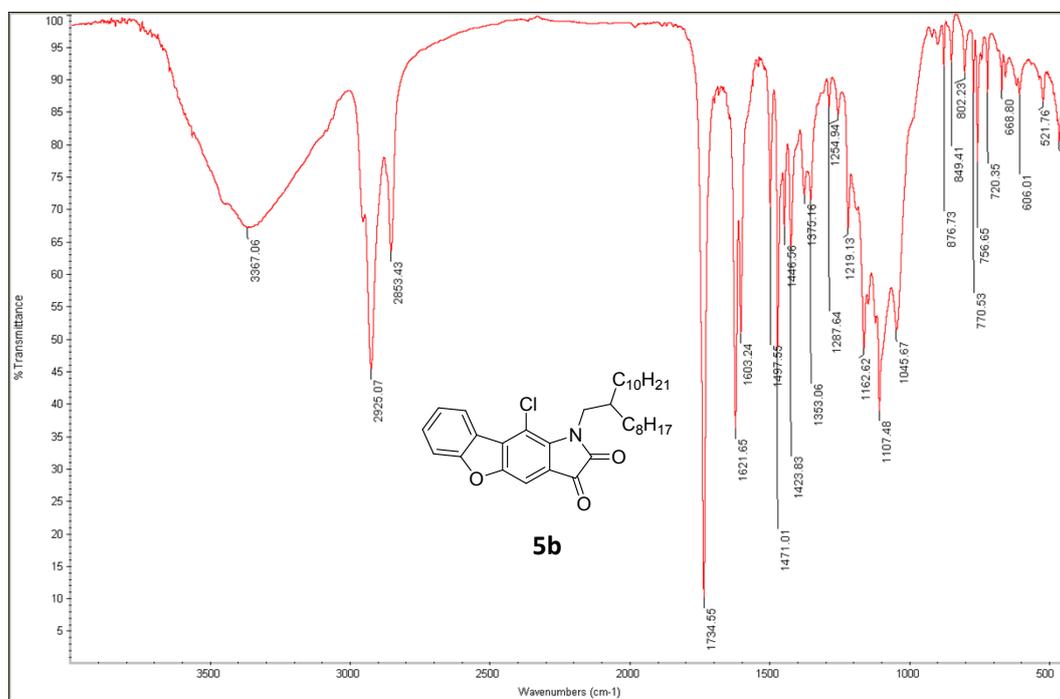
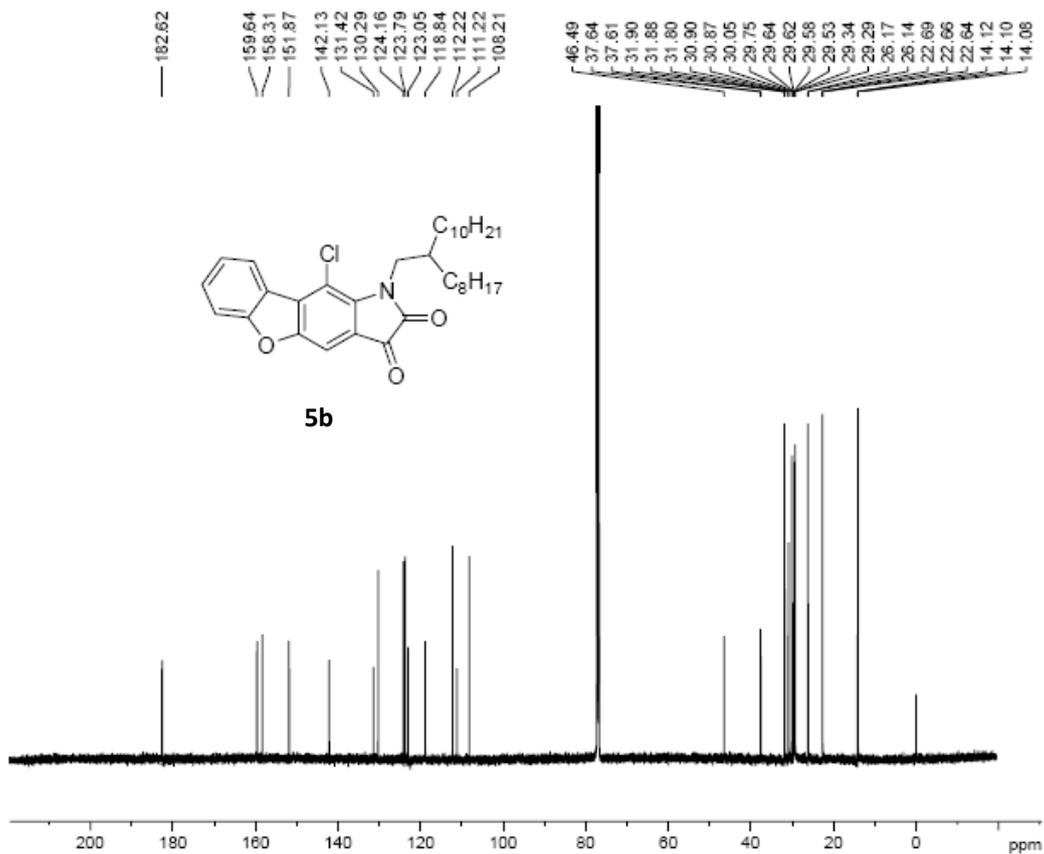




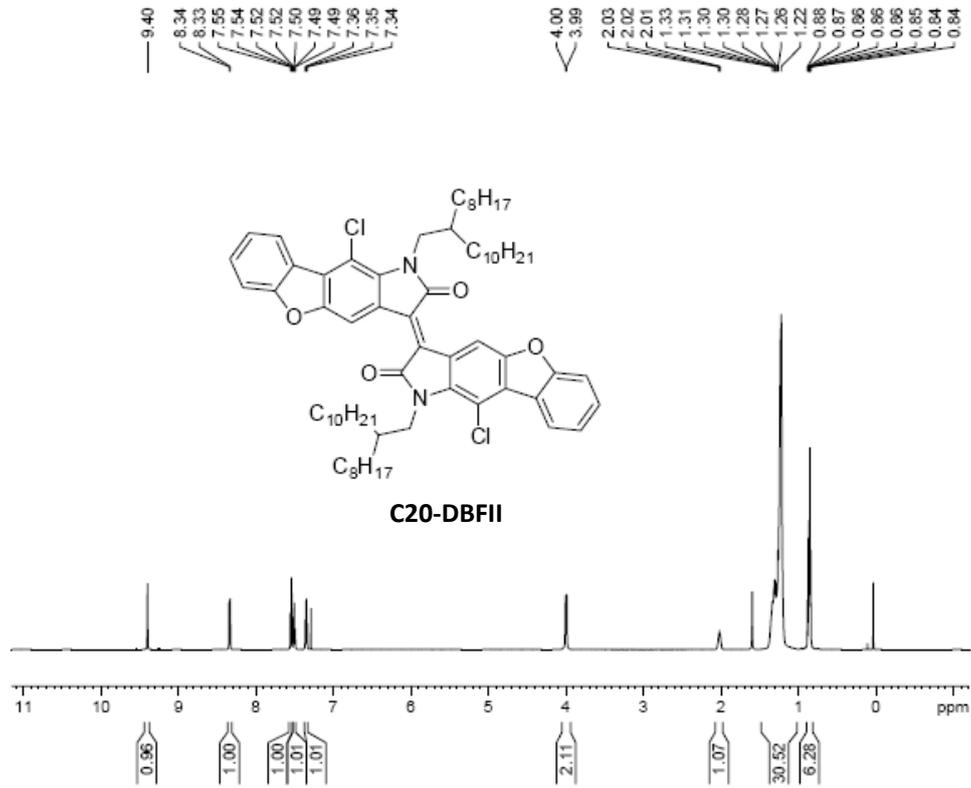
xsl06-41-x;1HNMR;CDCl3



xsl06-41-x; <sup>13</sup>C NMR; CDCl<sub>3</sub>



xs106-DBFII;1H NMR;CDCl3



xs106-44-s;13C NMR;CDCl3

