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Electronics Supplementary Information

New triphenylamine organic dyes containing dithieno[3,2-b:2',3'-d]pyrrole (DTP) units for iodine-free dye-sensitized solar cells

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1. Materials and instruments

The synthetic routes for dyes XS54–57 are shown in Scheme S1-4. 3,3'-dibromo-2,2'-bithiophene, n-butyllithium, $Pd(PPh_3)_4$, $Pd_2(dba)_3$, $SnBu_3Cl$, t-ButONa, BINAP and cyanocertic acid were purchased from Energy Chemical (China). 4–tertpyridine (TBP) and 0.1 M Lithium bis–(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from Aldrich. *N*,*N*-Dimethylformamide was dried over and distilled from CaH_2 under an atmosphere of nitrogen. Phosphorus oxychloride was freshly distilled before use. Dichloromethane was distilled from calcium hydride under nitrogen atmosphere. All other solvents and chemicals used in this work were analytical grade and used without further purification.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM–300 or AM–400 spectrometer. The reported chemical shifts were against TMS. High resolution mass spectra were obtained with a Micromass GCT–TOF mass spectrometer.

2. Photophysical and electrochemical measurements

The absorption spectra of the dyes either in solution or on the adsorbed TiO_2 films were measured by HITACHI U-3310 spectrophotometer. Fluorescence measurements were carried out with a HITACHI F-4500 fluorescence spectrophotometer.

Cyclic voltammetry (CV) measurements for XS54-57 sensitized films were performed on a Zennium electrochemical workstation (ZAHNER), with sensitized electrodes as the working electrode, Pt–wires as the counter electrode, and an Ag/AgCl electrode as the reference electrode at a scan rate of 50 mV s^{-1}. Tetrabutylammonium perchlorate (TBAP, 0.1 M) and MeCN were used as supporting electrolyte and solvent, respectively. The measurements were calibrated using ferrocene as standard.

3. Fabrication of DSCs

The TiO_2 paste (particle size, 20 nm) consisting of 18 wt.% TiO_2, 9 wt.% ethyl cellulose and 73 wt.% terpineol was firstly prepared,[S1] which was printed on a conducting glass (Nippon Sheet Glass, Hyogo, Japan, fluorine–doped SnO_2 over layer, sheet resistance of 10 Ω/sq) using a screen printing technique. Different thickness of the TiO_2 films (5 and 14 μm) were obtained by selection of screen mesh size and repetition of printing and the active area of cells is 0.156 cm^2. The film was dried in air at 120 °C for 30 min and calcined at 500 °C for 30 min under flowing oxygen before cooling to room temperature. The heated electrodes were impregnated with a 0.05 M titanium tetrachloride solution in a water–saturated desiccator at 70 °C for 30 min and sintered again to give a mesoscopic TiO_2 film. The TiO_2 electrode was stained by immersing it into a dye solution containing 300 μM sensitizers (DCM–Ethanol 1:4) for 24 h at room temperature. Then the sensitized–electrode was rinsed with dry ethanol and dried by a dry air flow. Note that, devices fabricated using 150 μM dyes solution yield comparable performance to those of the 300 μM dyes solution.

Pt catalyst was deposited on the FTO glass by coating with a drop of H_2PtCl_6 solution (40 mM in ethanol) with the heat treatment at 395 °C for 15 min to give photoanode. The dye–covered TiO_2 electrode and Pt–counter electrode were assembled into a sandwich type cell by a 25 μm–thick Surlyn (DuPont) hot–melt gasket and sealed up by heating. The cobalt electrolyte is composed of 0.25 M $[Co(II)(phen)_3](PF_6)_2$, 0.05 M $[Co(III)(phen)_3](PF_6)_3$, 0.5 M 4–tertpyridine (TBP) and 0.1M LiTFSI in acetonitrile, whereas the iodine electrolyte is composed of 0.6 M 1,2–dimethyl–3–n–propylimidazolium iodide (DMPImI), 0.1 M LiTFSI, 0.03 M I_2, and 0.5 M tertbutylpyridine in acetonitrile.

[S1] Ito, S.; Murakami, T. N.; Comte, P.; Liska, P.; Grätzel, C.; Nazeeruddin,M. K.; Grätzel, M. *Thin Solid Films*, 2008, **516**, 4613.

4. Characterization of DSCs

The photocurrent–voltage (*J*–*V*) characteristics of the solar cells were carried out using a Keithley 2400 digital source meter controlled by a computer and a standard AM1.5 solar simulator–Oriel 91160–1000 (300W) SOLAR SIMULATOR 2 x 2 BEAM. The light intensity was calibrated by an Oriel reference solar cell. A metal mask with an aperture area of 0.2 cm^2 was covered on a testing cell during all measurements. The action spectra of monochromatic incident photon–to–current conversion efficiency (IPCE) for solar cell were performed by using a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTECH, USA). We estimated the short circuit current density of cells based on the four dyes by integrating the IPCE values versus the sun AM1.5G spectrum, which are slightly lower than the measured short circuit photocurrent density and that calculated from the overlap integral of the IPCE curve with the standard AM1.5G solar emission spectra, implying that there existed a spectral mismatch between our solar simulating system and the standard AM1.5G irradiation. Similar phenomena have been reported by other groups.[S2] In addition, the integration is performed only from 400 to 800 nm. The contribution from wavelength shorter than 400 nm is ignored, so that the calculated current may be underestimated. However, in view of the same conditions in the test, our approach is reliable for fair evaluation of the photovoltaic performance of the four dyes discussed in this work.

[S2] (a) Wang, Z; Koumura, N; Cui, Y; Takahashi, M; Sekiguchi, H; Mori, A; Kubo, T; Furube, A; Hara, K. *Chem. Mater.* **2008**, *20*, 3993. (b) Liu, W. H.; Wu, I. C.; Lai, C. H.; Lai, C. H.; Chou, P. T.; Li, Y. T.; Chen, C. L.; Hsu, Y. Y.; Chi, Y. *Chem. Commun.* **2008**, 5152.

Charge densities at open circuit and intensity modulated photovoltage spectroscopy (IMVS) were performed on a Zennium electrochemical workstation (ZAHNER, Germany), which includes a green light emitting diode (LED, 532 nm) and the corresponding control system. The intensity-modulated spectra were measured at room temperature with light intensity ranging from 5 to 75 W m^{-2}, in modulation frequency ranging from 0.1 Hz to 10 kHz, and with modulation amplitude less than 5% of the light intensity.

Charge densities at open-circuit, measured by charge extraction technique,[S3] were used to compare the conduction band positions in different DSCs. The IMVS is used to measure the time constants for charge recombination at open circuit (τ_{oc}), which can be obtained by fitting either the real or imaginary part of the IMVS response (eq 1 and 2).[S4,S5]

$$re(\Delta V_{oc}) = \frac{X_1}{1+(\omega\tau_{oc}^{re})^2} \quad (1)$$

$$im(\Delta V_{oc}) = -\frac{X_2\omega\tau_{oc}^{im}}{1+(\omega\tau_{oc}^{im})^2} \quad (2)$$

Where $im(\Delta V_{oc})$ is the imaginary modulation of the photopotential (ΔV_{oc}), $re(\Delta V_{oc})$ is the real modulation of the photopotential (ΔV_{oc}), X_1, X_2, τ_{oc}^{re} and τ_{oc}^{im} are the fit parameters, ω is the circular frequency of the light modulation.

[S3] Duffy, N. W.; Peter, L. M.; Rajapakse, R. M. G.; Wijayantha, K. G. U. *J. Phys. Chem. B*, 2000, **104**, 8916–8919.

[S4] Schlichthörl, G.; Huang, S. Y.; Sprague, J.; Frank, A. J. *J. Phys. Chem. B*, 1997, **101**, 8141–8155.

[S5] G. Schlichtho1rl, N. G. Park, and A. J. Frank, *J. Phys. Chem. B*, 1999, **103**, 782-791.

5. Computational Methods

The geometrical structures of the four dyes were optimized by performed density functional theory (DFT) calculations and time-dependent DFT (TDDFT) calculations of the excited states at the B3LYP/6-31+G(d) level with the Gaussian 03W program package.[S6]

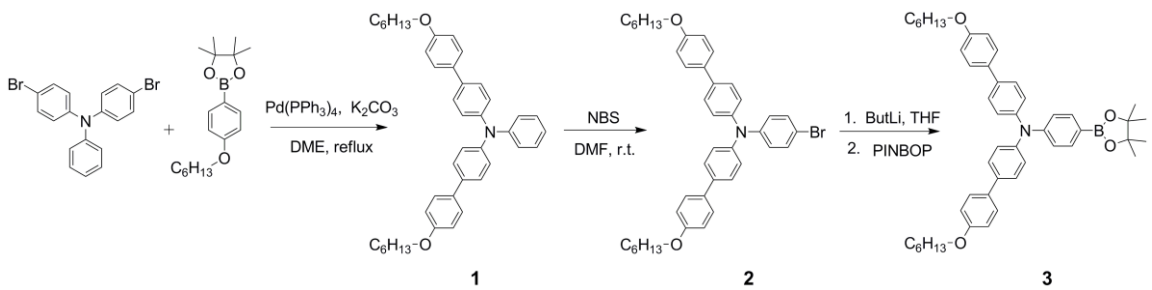
[S6] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03*; Revision C.01 ed.; Gaussian, Inc.: Wallingford CT, 2004.

6. Experimental procedures

Compounds **5**, **9a** and **9b** were prepared according to a slightly modified literature procedure starting from 3,3'-dibromo-2,2'-bithiophene.[S7] Dihexylcyclopentadithiophene was synthesized according to the literature.[S8]

[S7] Patigul Imin, Mokhtar Imit, and Alex Adronov, *Macromolecules*, 2011, **44**, 9138–9145.

[S8] Gregory L. Gibson, Theresa M. McCormick, and Dwight S. Seferos, *J. Am. Chem. Soc.*, 2012, **134**, 539−547.



Scheme S1. Synthetic route to compound **3**.

Synthesis of Compound 1

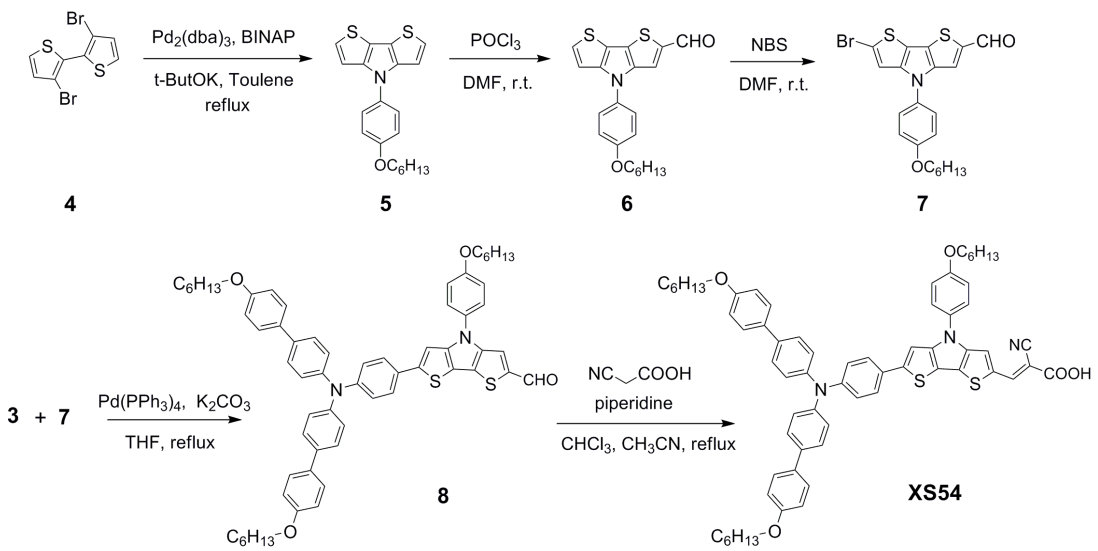
To a 100 mL two-neck round-bottom flask, 45 mL 1, 2-dimethoxyethane, compound of 4-bromo-N-(4-bromophenyl)-N-phenylbenzenamine (2.02 g, 5 mmol), 2-(4-(henyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dixaborolane (3.35 g, 11 mmol), $Pd(PPh_3)_4$ (289 mg, 0.25 mmol) and K_2CO_3 (4.14 g, 30 mmol, 2M) were added. The mixture was refluxed overnight under argon. After cooling to room temperature, H_2O and ethyl acetate were added. The organic layer was separated and dried in $MgSO_4$. The solvent was evaporated and the remaining crude product was purified by column chromatography to give a colorless oil of compound **1** (2.16 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.7 Hz, 4H), 7.43 (d, *J* = 8.7 Hz, 4H), 7.27-7.22 (m, 2H), 7.15-7.13 (m, 6H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 4H), 3.97 (t, *J* = 6.5 Hz, 4H), 1.82-1.75 (m, 4H), 1.50-1.45 (m, 4H), 1.37-1.32 (m, 8H), 0.91 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 147.8, 146.5, 135.3, 133.1, 129.4, 127.7, 127.4, 124.4, 124.3, 122.9, 114.9, 68.2, 31.7, 29.4, 25.9, 22.7, 14.2. HRMS (ESI) calcd for $C_{42}H_{48}NO_2$ ($M+H^+$): 598.3685, found: 589.3696.

Synthesis of Compound 2

N-bromosuccinimide (NBS, 0.94 g, 5.25 mmol), dissolved in dimethylformamide (DMF, 10 mL) was added dropwise at room temperature to a stirred DMF (10 mL) solution of compound **1** (2.99 g, 5 mmol). After the addition, the mixture was stirred overnight. Ice water was added to terminate the reaction and the product was extracted with ethyl acetate. The combined organic layers were washed with water and dried with anhydrous $MgSO_4$. The solvent was evaporated and the remaining crude product was purified by column chromatography to give a pale oil of **2** (3.2 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.8 Hz, 4H), 7.44 (d, *J* = 8.8 Hz, 4H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 4H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.94(d, *J* = 8.8 Hz, 4H), 3.98 (d, *J* = 6.6 Hz, 4H), 1.83-1.76 (m, 4H), 1.51-1.43 (m, 4H), 1.37-1.32 (m, 8H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 146.7, 145.9, 135.8, 132.9, 132.2, 127.7, 127.5, 125.2, 124.6, 114.8, 68.1, 31.6, 29.3, 25.8, 22.7, 14.1. HRMS (ESI) calcd for $C_{42}H_{47}NO_2Br$ ($M+H^+$): 677.2823, found: 677.2816.

Synthesis of Compound 3

To a solution of compound **2** (0.5mmol, 338 mg) in dry THF, n-BuLi (0.6 mmol, 2.4 M in hexane) was added dropwise at -78℃ under argon. The mixture was stirred at -78 ℃ for two hours and 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (0.6 mmol, 112 mg) was added via a syringe. The reaction was kept at room temperature overnight. Saturated NH_4Cl was added to terminate the reaction, and the product was extracted with ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent is evaporated under vacuum and the remaining crude product was carried on to next step without further purification.



Scheme S2. Synthetic route to XS54.

Synthesis of Compound 5

To a 100 mL two-neck round-bottom flask under argon atmosphere, dry toluene (30 mL), $Pd_2(dba)_3$ (0.15 mmol, 137 mg) and 2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BINAP, 0.45 mmol, 280 mg) were added. The base *t*-BuONa (9 mmol, 864 mg) and 3,3'-dibromo-2,2'-bithiophene **4** (3 mmol, 965 mg) were then added consecutively. After five minutes, 4-(hexyloxy)aniline (3.9 mmol, 753 mg) was added and the reaction mixture was allowed to reflux overnight. When the reaction mixture was cooled to room temperature, water was added to terminate the reaction and the product was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated and the remaining crude product was purified by column chromatography to give desired compound **5**: off-white flakes (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.8 Hz, 2H), 7.14 (d,

J = 5.3 Hz, 2H), 7.08 (d, *J* = 5.3 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 1.85-1.79 (m, 2H), 1.53-1.47 (m, 2H), 1.40-1.34 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 144.5, 132.9, 124.4, 123.3, 116.3, 115.5, 112.1, 68.5, 31.7, 29.4, 25.9, 22.7, 14.1. HRMS (ESI) calcd for $C_{20}H_{22}NOS_2$ ($M+H^+$): 356.1143, found: 356.1139.

Synthesis of Compound 6

$POCl_3$ (1.1 mmol, 169 mg) was added dropwise to dry DMF (3 mL) at 0 ℃. The reaction was kept at 0 ℃ for 30 minutes and the dry DMF (5 mL) solution of compound **5** (1 mmol) was added via a syringe. After the addition, the mixture was stirred overnight at room temperature. Ice water was added to terminate the reaction, and the product was extracted with ethyl acetate. The combined organic layers were washed with water and dried with anhydrous $MgSO_4$. The solvent was evaporated and the remaining crude product was purified by column chromatography to give desired compound **6**: yellow solid (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.85 (s, 1H), 7.71 (s, 1H), 7.47-7.43 (m, 2H), 7.39 (d, *J* = 5.4 Hz, 1H), 7.09-7.05 (m, 3H), 4.03 (t, *J* = 6.5 Hz, 2H), 1.87-1.80 (m, 2H), 1.54-1.47 (m, 2H), 1.40-1.35 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.0, 158.2, 148.6, 144.0, 140.5, 131.5, 128.7, 124.7, 124.4, 120.6, 116.2, 115.7, 111.9, 68.5, 31.6, 29.2, 25.7, 22.6, 14.0. HRMS (ESI) calcd for $C_{21}H_{22}NO_2S_2$ ($M+H^+$): 384.1092, found: 384.1091.

Synthesis of Compound 7

N-bromosuccinimide (NBS, 196 mg, 1.1 mmol), dissolved in DMF (5 mL) was added dropwise at room temperature to a stirred DMF (5 mL) solution of compound **6** (1 mmol). After the addition, the mixture was stirred overnight. Ice water was added and the product was extracted with ethyl acetate. The combined organic layers were washed with water and dried with anhydrous $MgSO_4$. The solvent was evaporated and the remaining crude product was purified by column chromatography to give desired compound **7**: yellow solid (95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.67 (s, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.12 (s, 1H), 7.05 (d, *J* = 8.8 Hz, 2H), 4.03 (t, *J* = 6.5 Hz, 2H), 1.87-1.80 (m, 2H), 1.54-1.47 (m, 2H), 1.40-1.35 (m, 4H), 0.93 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.9,

158.5, 146.2, 143.1, 140.8, 131.0, 124.8, 123.9, 120.4, 116.2, 115.8, 115.3, 68.5, 31.6, 29.2, 25.7, 22.6, 14.1. HRMS (ESI) calcd for $C_{21}H_{21}NO_2S_2Br$ ($M+H^+$): 462.0197, found: 462.0194.

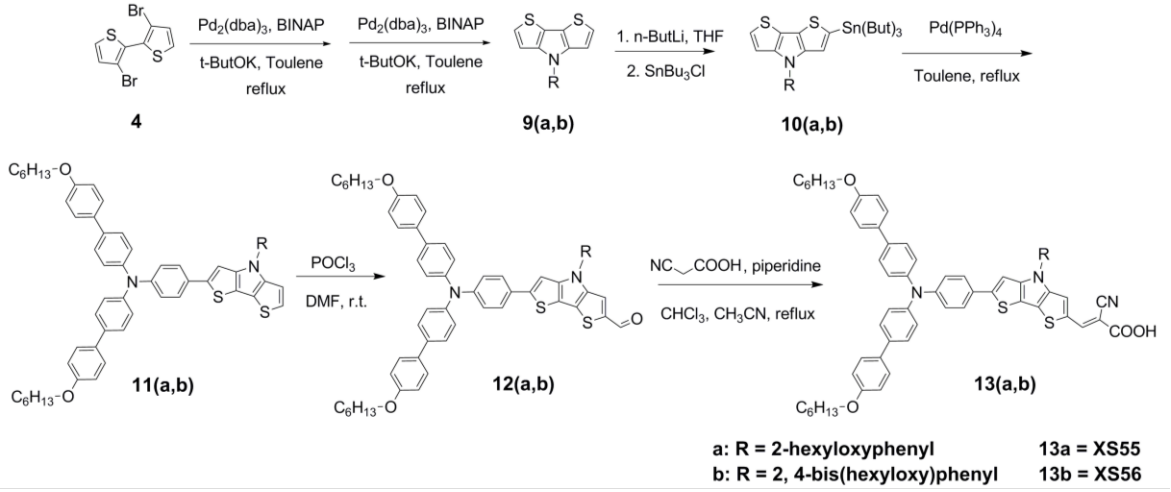
Synthesis of Compound 8

To a 100 mL two-neck round-bottom flask, 25 mL THF, compound of **3** (0.5 mmol), aldehyde **7** (0.2 mmol), $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol), K_2CO_3 (276 mg, 2 mmol, 2M), were added. The mixture was refluxed overnight under argon. After cooling to room temperature, H_2O and ethyl acetate were added. The organic layer was separated and dried in $MgSO_4$. The solvent was evaporated and the remaining crude product was purified by column chromatography to give desired aldehydes **8**: yellow solid (94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.65 (s, 1H), 7.51-7.463 (m, 12H), 7.19-7.17 (m, 5H), 7.13 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 4H), 4.03 (t, *J* = 6.5 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 4H), 1.87- 1.76 (m, 6H), 1.52-1.44 (m, 6H), 1.39-1.33 (m, 12H), 0.94-0.90 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.8, 158.6, 158.3, 149.1, 147.9, 147.8, 145.8, 143.6, 140.2, 136.0, 132.8, 131.4, 128.4, 127.7, 127.5, 126.6, 124.9, 124.8, 123.3, 120.3, 115.7, 114.8, 114.7, 106.5, 68.5, 68.1, 31.6, 31.5, 29.3, 29.2, 25.8, 25.7, 22.6, 14.1. HRMS (ESI) calcd for $C_{63}H_{67}N_2O_4S_2$ ($M+H^+$): 979.4542, found: 979.4609.

Synthesis of XS54

To a stirred solution of compound **8** (0.2 mmol) and cyanoacetic acid (0.3 mmol) in acetonitrile (8 mL) was added chloroform (4 mL) and piperidine (0.6 mmol). The reaction mixture was refluxed for 8 hours. Additional cyanocertic acid (0.2 mmol) and piperdine (0.4 mmol) were added. The mixture was refluxed continued for 8 hours and then acidified with 1 M hydrochloric acid aqueous solution (30 mL). The crude product was extracted into CH_2Cl_2, washed with water, and dried over anhydrous $MgSO_4$. After removing solvent under reduced pressure, the residue was purified by column chromatography to give desired product, **XS54**: red power (96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.88 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.61-7.54 (m, 11H), 7.14-7.10 (m, 6H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 4H), 4.04 (t, *J* = 6.4 Hz, 2H), 3.97 (t, *J* = 6.4 Hz, 4H), 1.77-1.68 (m, 6H), 1.49-1.42 (m, 6H), 1.33-1.30 (m, 12H), 0.91-0.87 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 158.1,

150.2, 149.1, 146.1, 135.9, 135.8, 135.6, 135.4, 135.1, 134.7, 132.8, 131.7, 129.2, 127.9, 126.8, 125.2, 123.7, 123.4, 123.1, 122.7, 115.8, 115.2, 68.0, 31.6, 29.4, 29.3, 25.8, 22.6, 14.0, 13.9. HRMS (ESI) calcd for $C_{66}H_{68}N_3O_5S_2$ ($M+H^+$): 1046.4601, found: 1046.4667.



Scheme S3. Synthetic routes to XS55 and XS56.

Synthesis of Compound 9a and 9b

The **9a,b** were synthesized according to the procedure for synthesis of **5**.

9a: off-white crystal (72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, *J* =7.9 Hz, *J* = 1.6 Hz, 1H), 7.35-7.30 (m, 1H), 7.1-7.02 (m, 4H), 6.90 (d, *J* = 5.2 Hz, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 1.60-1.53 (m, 2H), 1.19-1.11(m, 6H), 0.79 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 145.3, 128.6, 128.2, 126.9, 122.4, 120.9, 115.9, 113.9, 113.1, 68.9, 31.4, 29.0, 25.5, 22.5, 14.0. HRMS (ESI) calcd for $C_{20}H_{22}NOS_2$ ($M+H^+$): 356.1143, found: 356.1141.

9b: off-white crystal (68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.31 (m, 3H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 2.5 Hz, 1H), 6.64 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H), 4.03 (t, *J* = 6.4 Hz, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 1.78-1.71 (m, 2H), 1.47-1.44 (m, 2H), 1.37-1.30 (m, 4H), 1.13-1.08 (m, 6H), 0.9 (t, *J* = 6.9 Hz, 3H), 0.75 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 154.5, 145.7, 127.8, 123.8, 120.8, 114.9, 113.2, 106.3, 101.6, 68.7, 68.3, 31.5, 31.2, 29.2, 28.9, 25.7, 25.3, 22.6, 22.4, 14.4, 14.2. HRMS (ESI) calcd for $C_{26}H_{34}NO_2S_2$ ($M+H^+$): 456.2031, found: 456.2036.

Synthesis of compound 10a and 10b

To a solution of compound **9(a, b**) (0.7 mmol) in dry THF, n-BuLi (0.84 mmol, 2.4 M in hexane) was added dropwise at -78℃ under argon. The mixture was stirred at -78 ℃ for two hours and $SnBu_3Cl$ (0.84 mmol, 274 mg) was added via a syringe. The reaction was kept at room temperature overnight. Saturated NH_4Cl was added to terminate the reaction, and the product was extracted with ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent is evaporated under vacuum and the remaining crude product was used to the synthesis of **11(a, b)** without further purification.

Synthesis of compound 11a and 11b

To a 50 mL two-neck round-bottom flask, toluene (20 mL), $Pd(PPh_3)_4$ (40 mg, 0.035 mmol), compound of **2** (474 mg, 0.7 mmol) and **10(a, b)** were added. The mixture was refluxed overnight under nitrogen. The solvent was evaporated and the remaining crude product was purified by column chromatography to yield **11a** and **11b**.

11a: light yellow oil (41% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.48 (m, 11H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 4H), 7.17-7.09 (m, 6H), 6.99 (d, *J* = 8.4 Hz, 4H), 6.94 (d, *J* = 5.2 Hz, 1H), 4.04-3.99 (m, 6H), 1.88-1.81 (m, 4H), 1.66-1.59 (m, 2H), 1.52-1.39 (m, 12H), 1.24-1.16 (m, 6H), 0.97-0.80 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 153.4, 146.6, 146.1, 145.6, 144.9, 141.2, 135.5, 132.9, 130.1, 128.5, 128.3, 127.7, 127.4, 127.0, 126.1, 124.5, 124.1, 122.5, 121.0, 116.4, 114.9, 114.8, 113.9, 113.0 ,108.4, 69.0, 68.1, 31.7, 31.5, 29.3, 29.1, 25.8, 25.7, 22.7, 22.5, 14.1, 14.0. HRMS (ESI) calcd for $C_{62}H_{67}N_2O_3S_2$ ($M+H^+$): 951.4593, found: 951.4556.

11b: light yellow oil (44% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.47 (m, 10H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 4H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 5.2 Hz, 1H), 7.07 (s, 1H), 6.98 (d, *J* = 8.5 Hz, 4H), 6.88 (d, *J* = 5.2 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 6.59 (dd, *J* = 8.5 Hz, *J* = 2.4 Hz, 1H), 4.01-4.0 (m ,6H), 3.95 (t, *J* = 6.4 Hz, 2H), 1.89-1.79 (m, 6H), 1.61-1.57 (m, 2H), 1.56-1.49 (m, 6H), 1.40-13.6 (m, 14H), 1.21-1.14 (m, 6H), 0.97-0.92 (m,

9H), 0.79 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 158.5, 154.6, 146.5, 146.1, 146.0, 145.3, 141.0, 135.4, 133.0, 130.2, 127.7, 127.4, 126.1, 124.5, 124.1, 122.4, 121.5, 115.8, 114.8, 114.4, 112.7, 108.1, 105.2, 101.5, 68.9, 68.4, 68.1, 31.6, 31.5, 31.4, 30.2, 29.3, 29.0, 25.8, 25.6, 22.6, 22.4, 14.1, 14.0. HRMS (ESI) calcd for $C_{68}H_{79}N_2O_4S_2$ ($M+H^+$): 1051.5481, found: 1051.5402.

Synthesis of compound 12a and 12b

The product was synthesized according to the procedure for the synthesis of compound **6**.

12a: yellow solid (84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.50-7.45 (m, 12H), 7.43-7.39 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 4H), 7.15-7.10 (m, 4H), 7.05 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 4H), 4.0-3.97 (m, 6H), 1.83-1.76 (m, 4H), 1.58-1.53 (m, 2H), 1.49-1.44 (m, 4H), 1.37-1.33 (m, 8H), 1.18-1.13 (m, 2H), 1.11-1.08 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 6H), 0.75 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.8, 158.6, 153.4, 149.9, 147.7, 147.0, 145.8, 144.3, 139.8, 135.9, 132.9, 129.2, 128.7, 127.7, 127.5, 127.3, 127.0, 126.5, 124.9, 123.4, 121.5, 121.1, 114.8, 114.7, 113.9, 107.6, 69.0, 68.1, 31.6, 31.4, 29.3, 29.0, 25.8, 25.7, 22.6, 22.4, 14.1, 13.9. HRMS (ESI) calcd for $C_{63}H_{67}N_2O_4S_2$ ($M+H^+$): 979.4542, found: 979.4512.

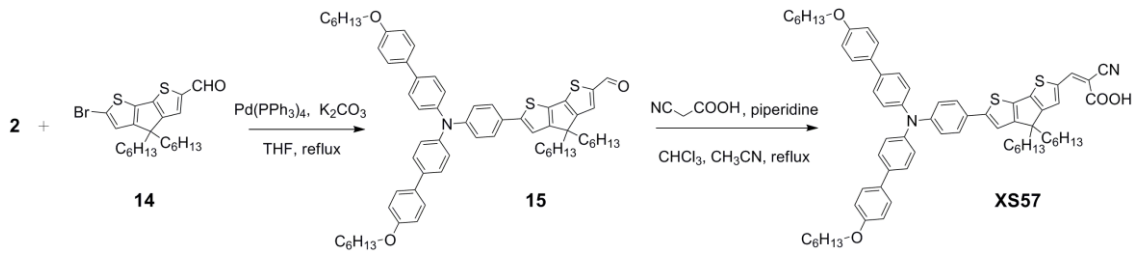
12b: yellow solid (82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.51-7.46 (m, 11H), 7.36-7.33 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 4H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.02 (s, 1H), 6.95 (d, *J* = 8.5 Hz, 4H), 6.67 (d, *J* = 2.4 Hz, 1H), 6.59 (dd, *J* = 8.5 Hz, *J* = 2.4 Hz, 1H), 4.04-3.93 (m, 8H), 1.87-1.77 (m, 6H), 1.54-1.44 (m, 8H), 1.40-1.33 (m, 12H), 1.15-1.09 (m, 6H), 0.95-0.90 (m, 9H), 0.74 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.7, 160.1, 158.6, 154.7, 150.4, 147.6, 146.9, 145.9, 144.7, 139.6, 135.9, 132.9, 128.8, 127.7, 127.5, 126.5, 124.9, 124.5, 123.4, 120.2, 114.8, 114.3, 107.4, 105.4, 101.4, 68.9, 68.5, 68.1, 31.9, 31.6, 31.5, 31.3, 29.7, 29.3, 29.2, 28.9, 25.8, 25.6, 22.6, 22.4, 10.0, 13.9. HRMS (ESI) calcd for $C_{69}H_{79}N_2O_5S_2$ ($M+H^+$): 1079.5431, found: 1079.5442.

Synthesis of XS55 and XS56

The products were synthesized according to the procedure for the synthesis of compound **XS54**.

XS55: red power (95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.2 (s, 1H), 7.68 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.55-7.44 (m, 10H), 7.34-7.31 (m, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 4H), 7.0 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 4H), 4.04-4.03 (m, 2H), 3.94 (t, *J* = 6.4 Hz,4H), 1.74-1.67 (m, 4H), 1.49-1.38 (m, 6H), 1.32-1.30 (m, 8H), 1.11-0.99 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 6H), 0.66 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 153.5, 150.2, 149.1, 147.6, 146.2, 146.1, 145.0, 135.9, 135.7, 134.7, 134.3, 132.8, 129.4, 127.9, 127.7, 127.3, 127.1, 126.7, 125.1, 123.8, 123.7, 122.7, 121.2, 119.5 115.3, 114.9, 114.1, 108.7, 68.9, 68.0, 31.5, 31.4, 29.3, 29.1, 25.8, 25.7, 22.6, 22.5, 13.91, 13.89. HRMS (ESI) calcd for $C_{66}H_{68}N_3O_5S_2$ ($M+H^+$): 1046.4601, found: 1046.4663.

XS56: red power (81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.82 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.56-7.52 (m, 8H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.30 (s, 1H), 7.09 (d, *J* = 8.4 Hz, 4H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 4H), 6.83 (s, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 4.05-3.93 (m, 8H), 1.76-1.67 (m, 6H), 1.43-1.41 (m, 8H), 1.32-1.30 (m, 12H), 1.06-0.99 (m, 6H), 0.89-0.66 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 162.2, 160.5, 156.4, 152.5, 149.4, 149.1, 148.7, 147.6, 147.5, 137.6, 137.3, 136.2, 135.1, 134.3, 130.7, 129.6, 129.4, 129.2, 128.4, 126.8, 126.6, 125.3, 124.2, 121.6, 116.8, 116.1, 109.9, 107.4, 103.2, 70.0, 69.5, 61.9, 45.6, 33.0, 32.8, 31.2, 30.8, 30.5, 27.3, 27.25, 27.2, 24.13, 24.1, 24.0, 15.45, 15.43, 15.39. HRMS (ESI) calcd for $C_{72}H_{80}N_3O_6S_2$ ($M+H^+$): 1146.5488, found: 1146.5448.



Scheme S4. Synthetic route to XS57.

Synthesis of Compound 15

To a 100 mL two-neck round-bottom flask, 25 mL 1, 2-dimethoxyethane, compound of **2** (0.5 mmol) and **14** (0.2 mmol), $Pd(PPh_3)_4$ (0.02 mmol), K_2CO_3 (276 mg, 2 mmol, 2 M), were added. The mixture was refluxed overnight under argon. After cooling to room temperature, H_2O and ethyl acetate were added. The organic layer was separated and dried in $MgSO_4$. The

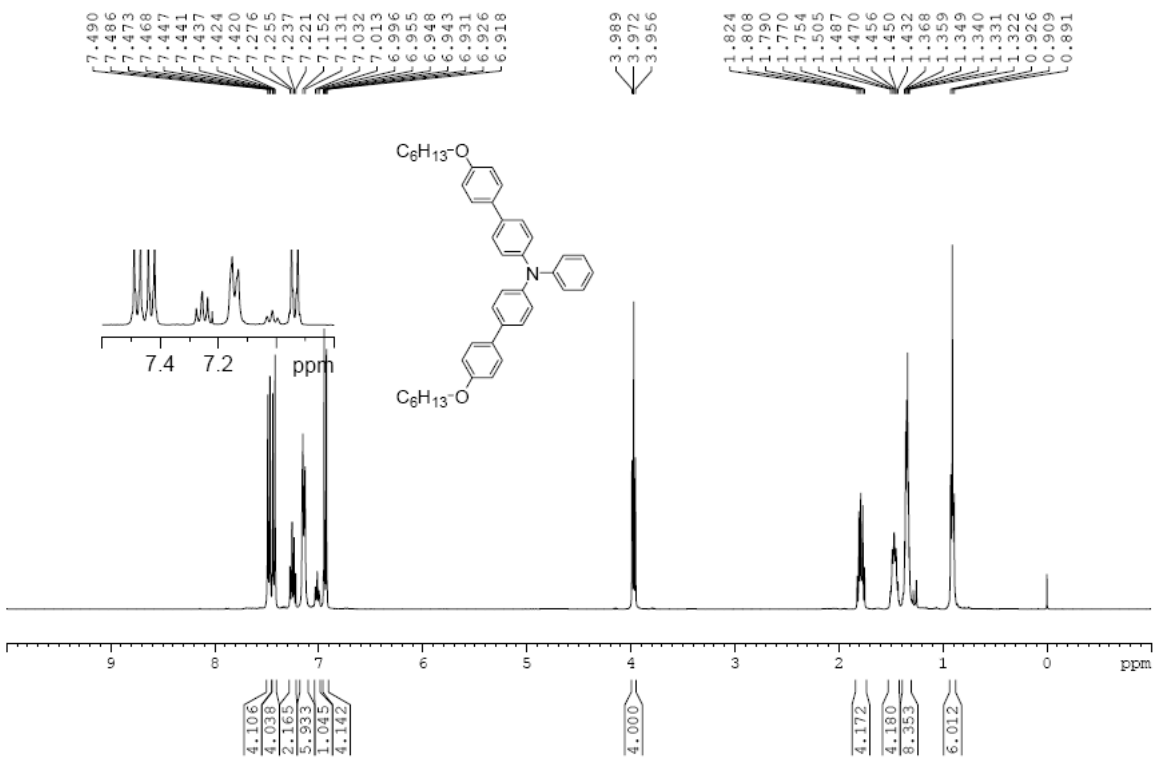
solvent was evaporated and the remaining crude product was purified by column chromatography to give a yellow solid **15** (58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.55-7.47 (m, 11H), 7.21-7.17 (m, 5H), 7.17 (d, *J* = 4.6 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 4H), 4.0 (t, *J* = 6.5 Hz, 4H), 1.95-1.77 (m, 8H), 1.52-1.44 (m, 4H), 1.39-1.33 (m, 8H), 1.22-1.15 (m, 12H), 0.99-0.90 (m, 10H), 0.82 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.4, 163.6, 158.6, 157.4, 149.5, 148.2, 147.7, 145.8, 142.9, 135.9, 133.9, 132.8, 129.9, 128.3, 127.7, 127.5, 126.4, 124.9, 123.5, 116.7, 114.8, 68.1, 54.1, 37.8, 31.6, 31.5, 29.6, 29.3, 25.8, 24.6, 22.6, 22.5, 14.1, 14.0. HRMS (ESI) calcd for $C_{64}H_{76}NO_3S_2$ ($M+H^+$): 970.5267, found: 970.5291.

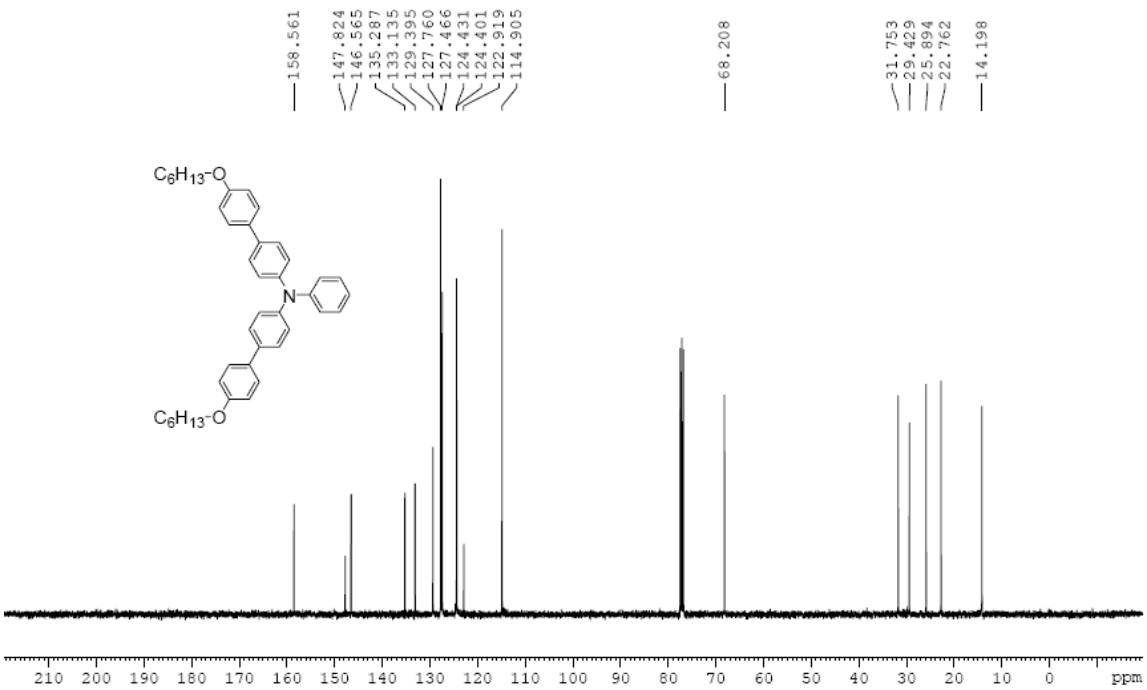
Synthesis of XS57

The product was synthesized according to the procedure for the synthesis of compound **XS54**.

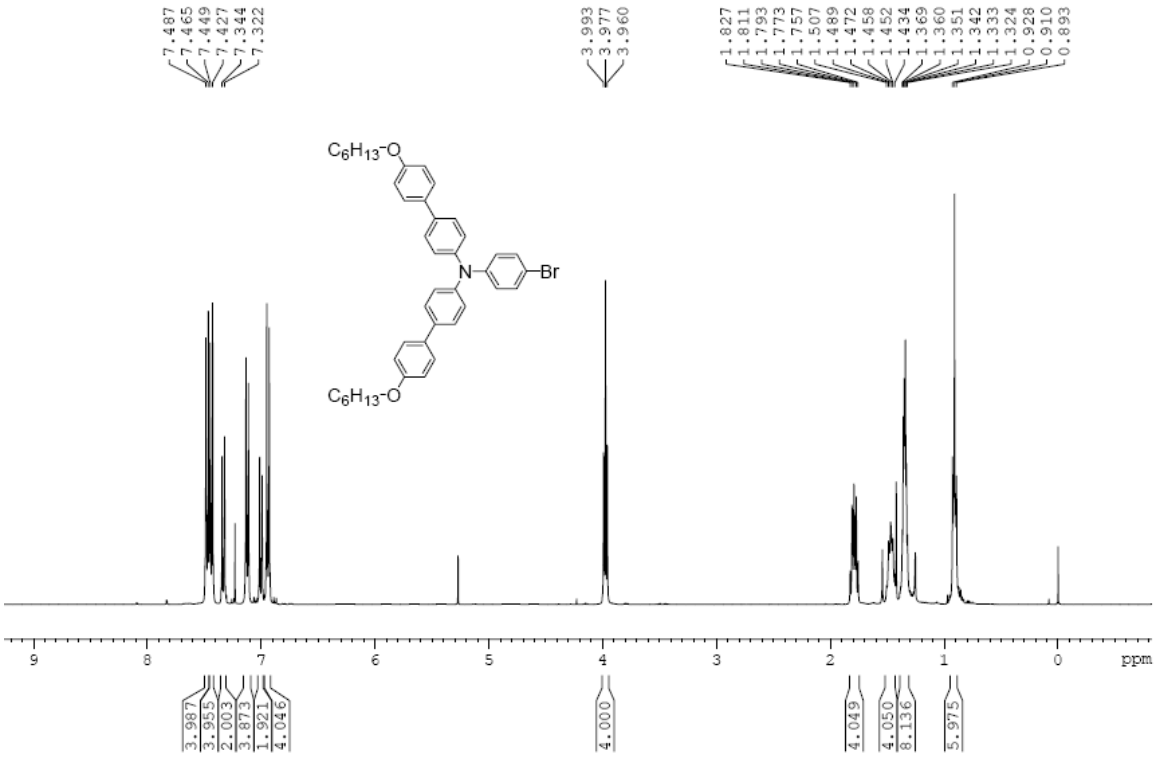
XS57: deep red power (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.96 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.60-7.55 (m, 9H), 7.12 (d, *J* = 8.4 Hz, 4H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 4H), 3.98 (t, *J* = 6.4 Hz, 4H), 1.91-1.88 (m, 4H), 1.75-1.68 (m, 4H), 1.44-1.40 (m, 12H), 0.90-0.87 (m, 10H), 0.77 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 165.9, 160.6, 159.6, 151.8, 149.9, 149.4, 148.1, 147.6, 138.5, 137.6, 135.7134.3, 133.0, 130.2, 129.4, 129.3, 128.3, 126.8, 124.2, 120.0, 119.3, 116.8, 98.5, 69.5, 55.8, 39.2, 33.1, 33.0, 31.2, 30.8, 27.3, 26.3, 24.2, 24.1, 15.5, 15.4. HRMS (ESI) calcd for $C_{67}H_{77}N_2O_4S_2$ ($M+H^+$): 1037.5325, found: 1037.5316.

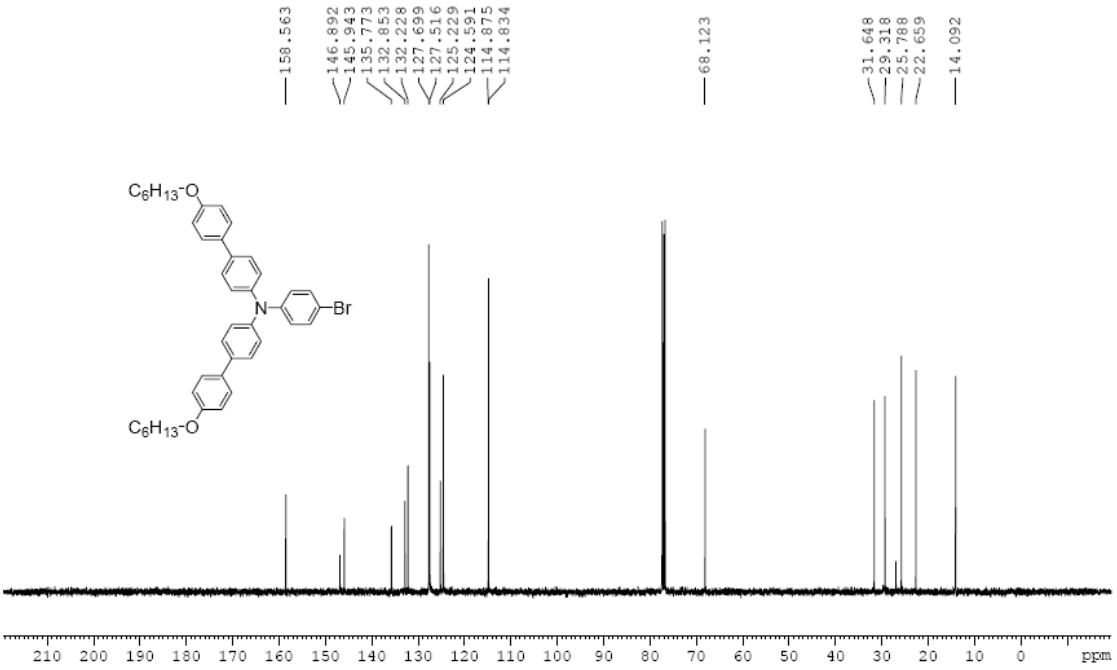
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 1



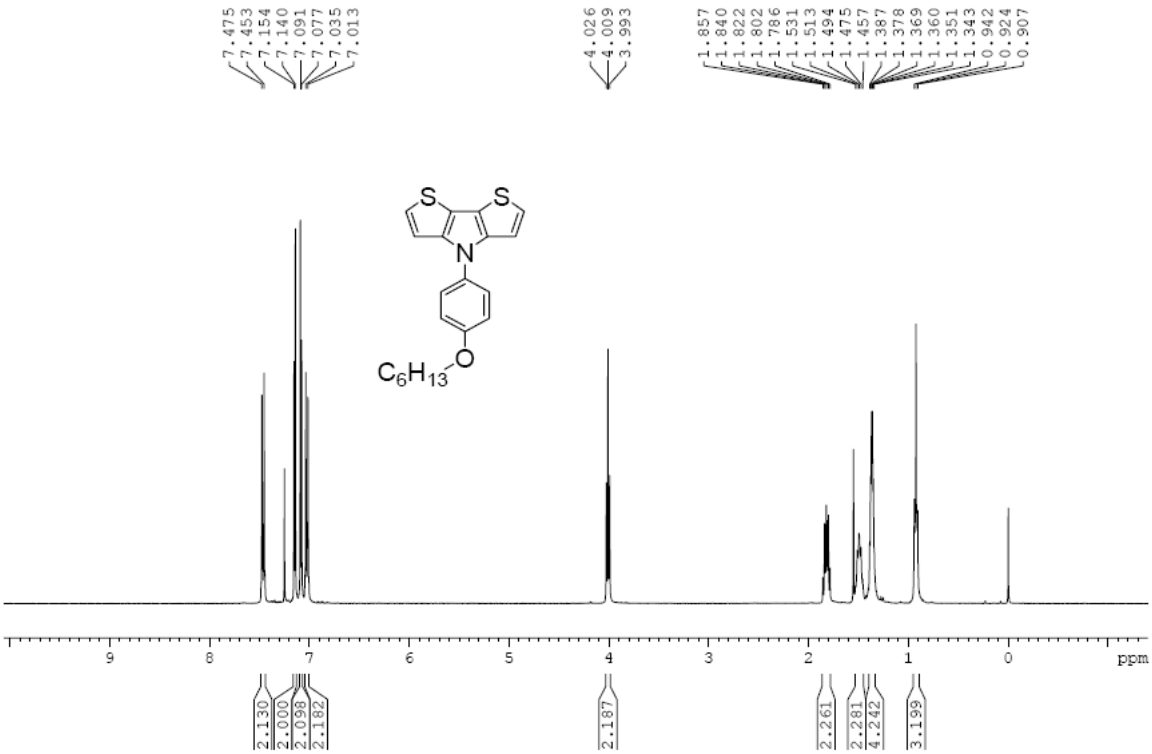


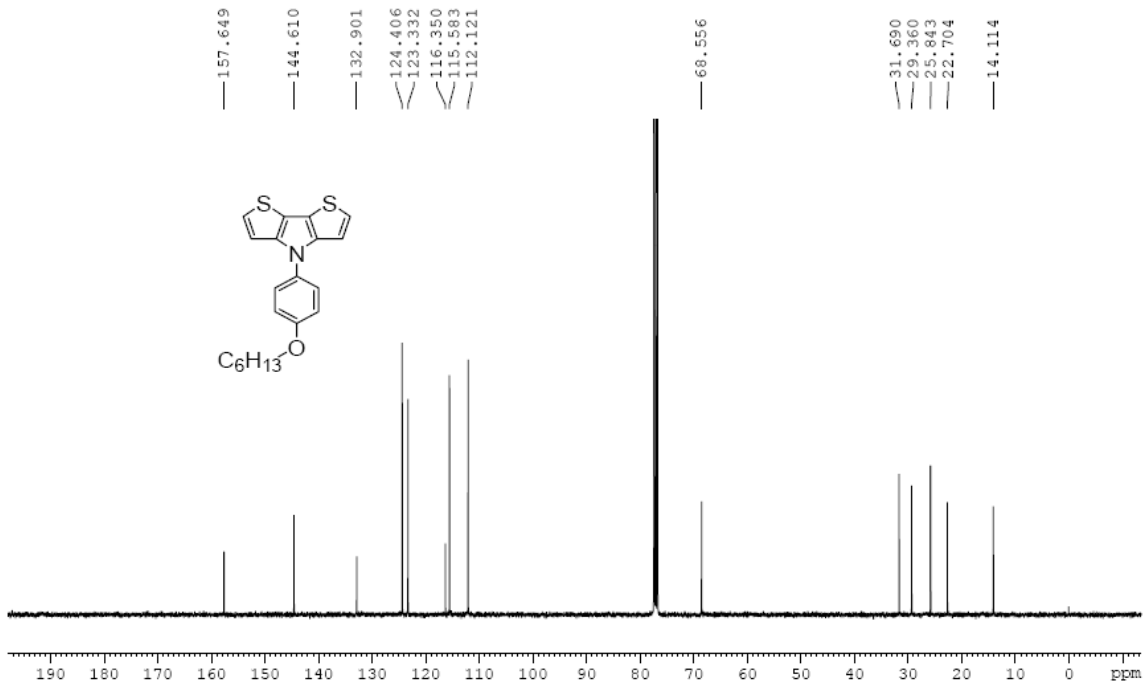
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 2



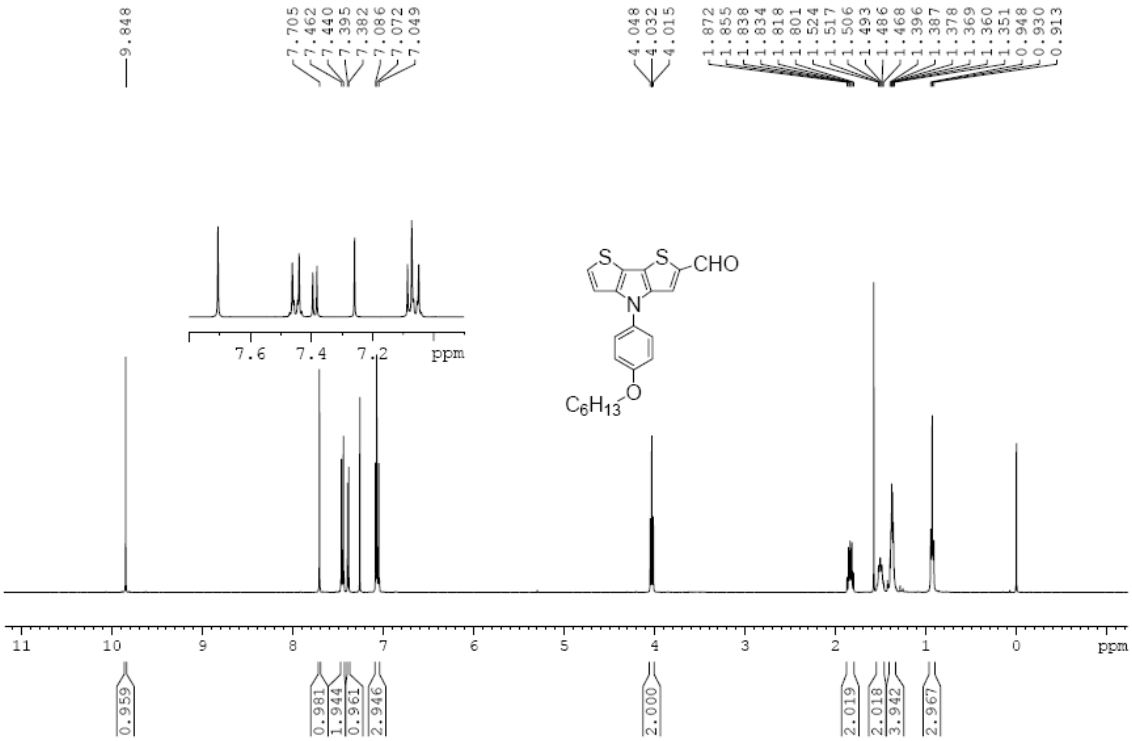


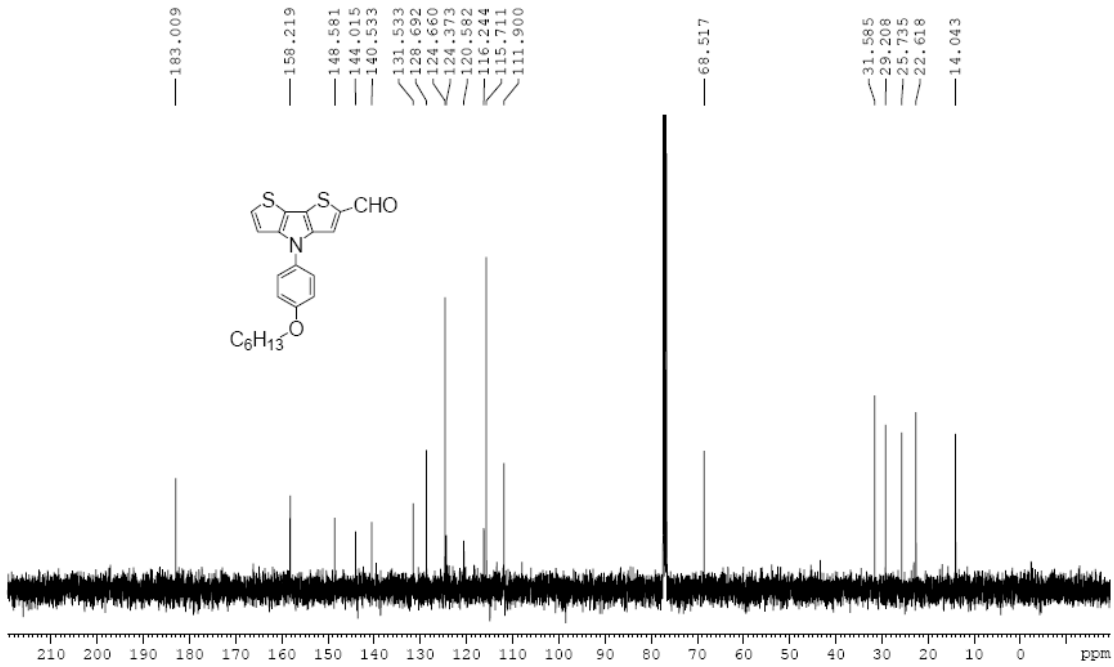
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 5



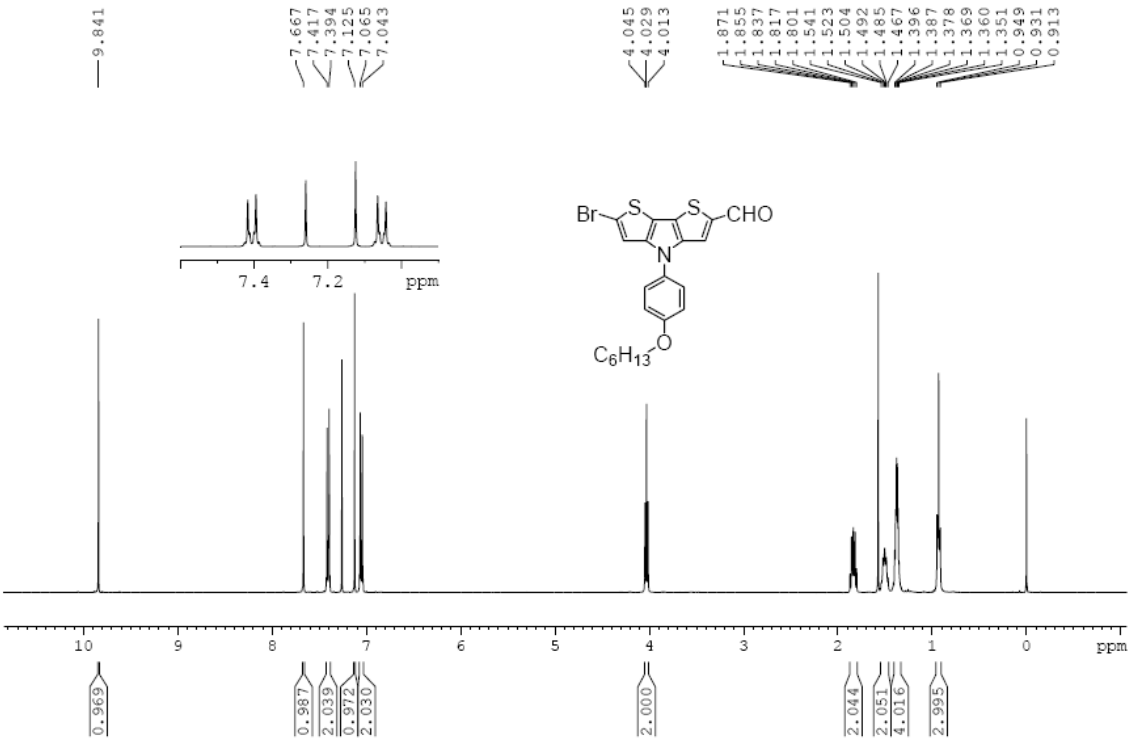


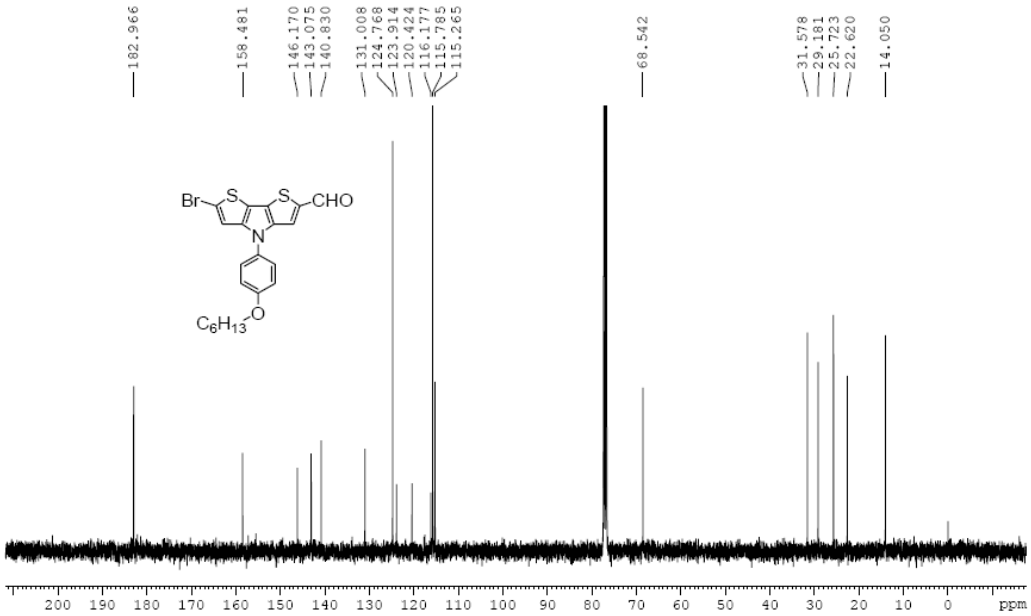
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 6



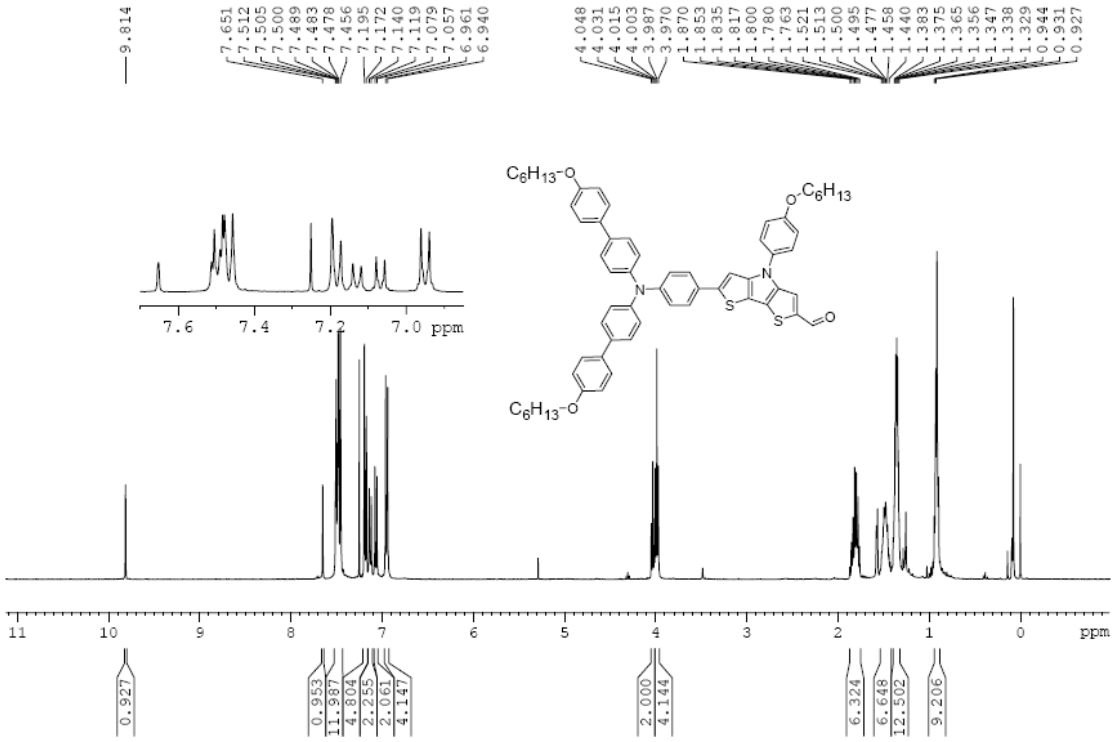


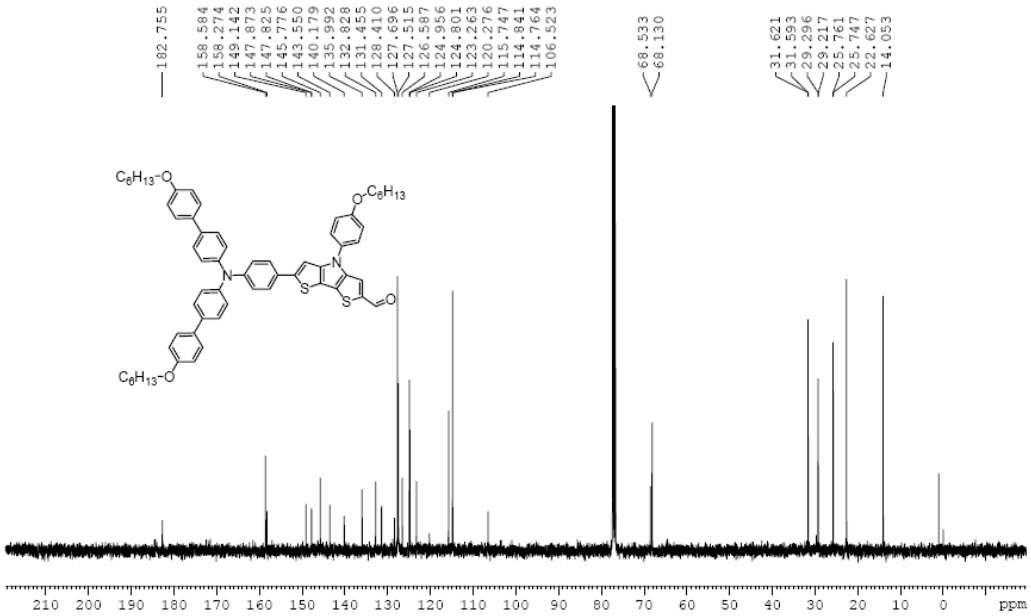
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 7



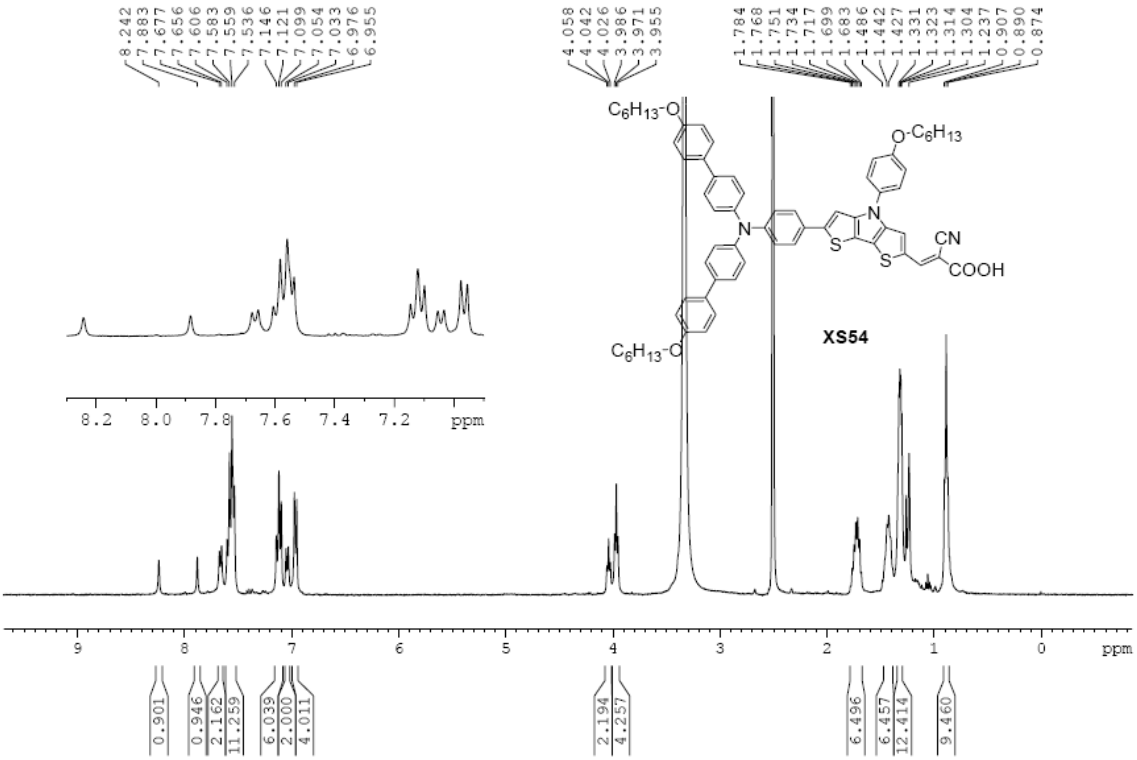


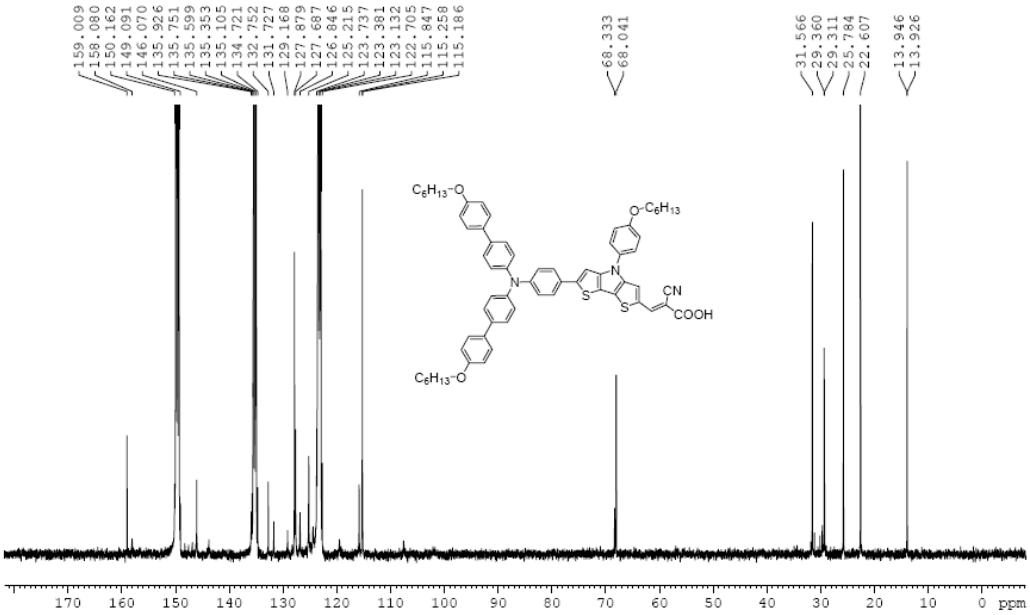
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 8



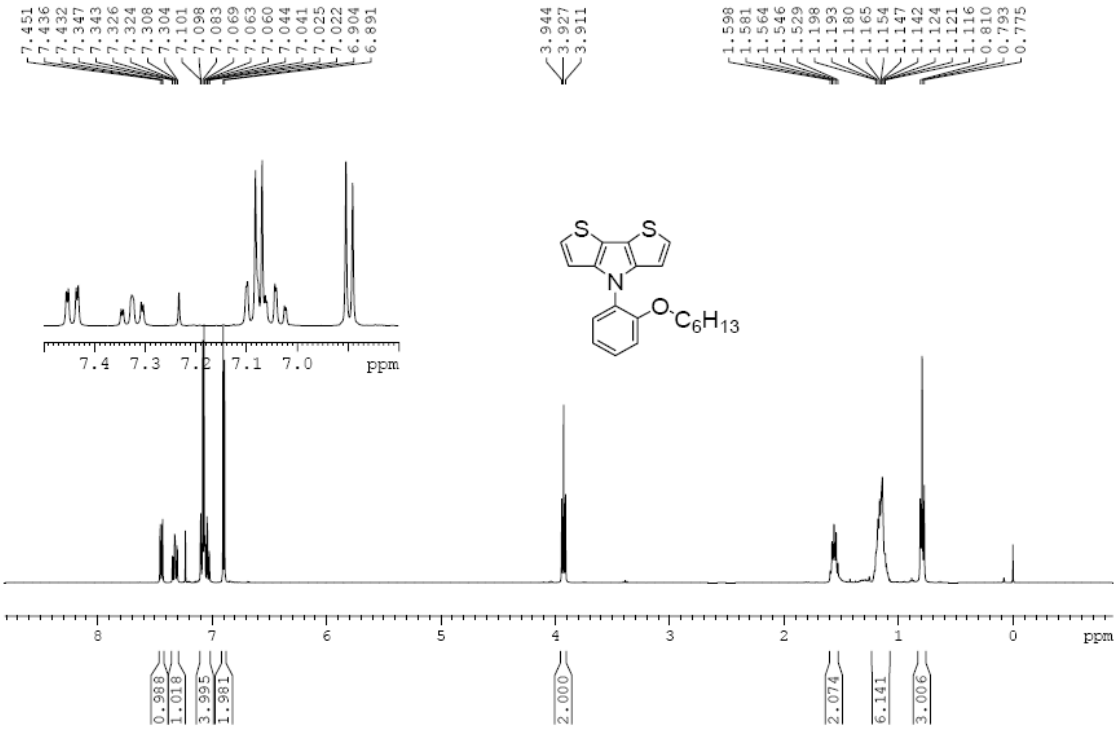


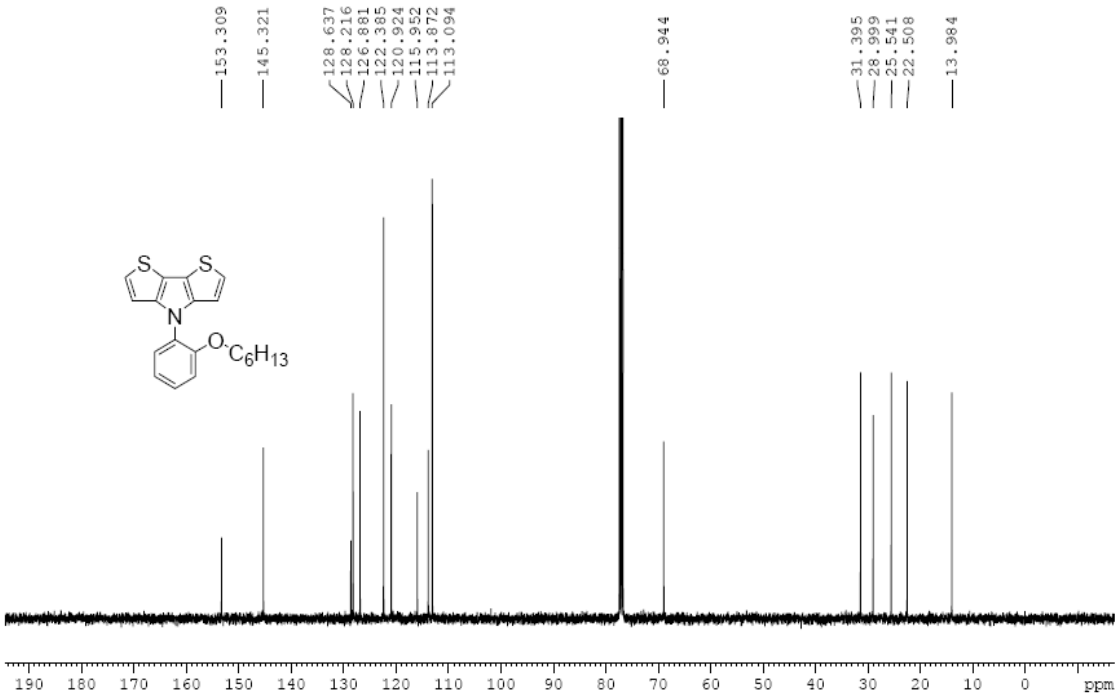
^{1}H (DMSO-d_6) and ^{13}C NMR (Pyridine-d_5) spectra of XS54



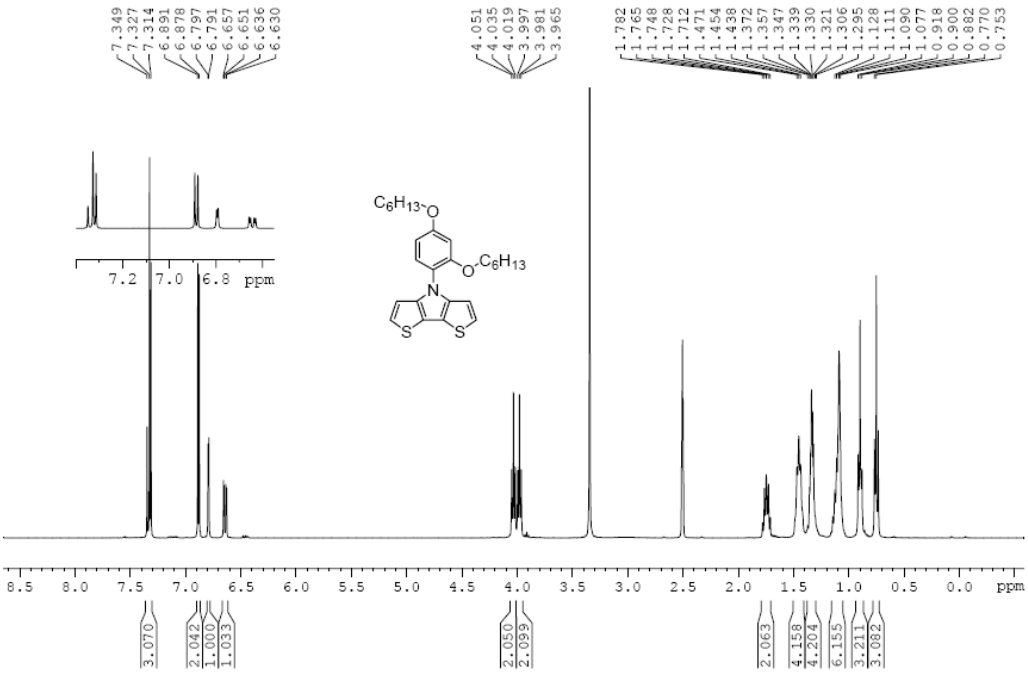


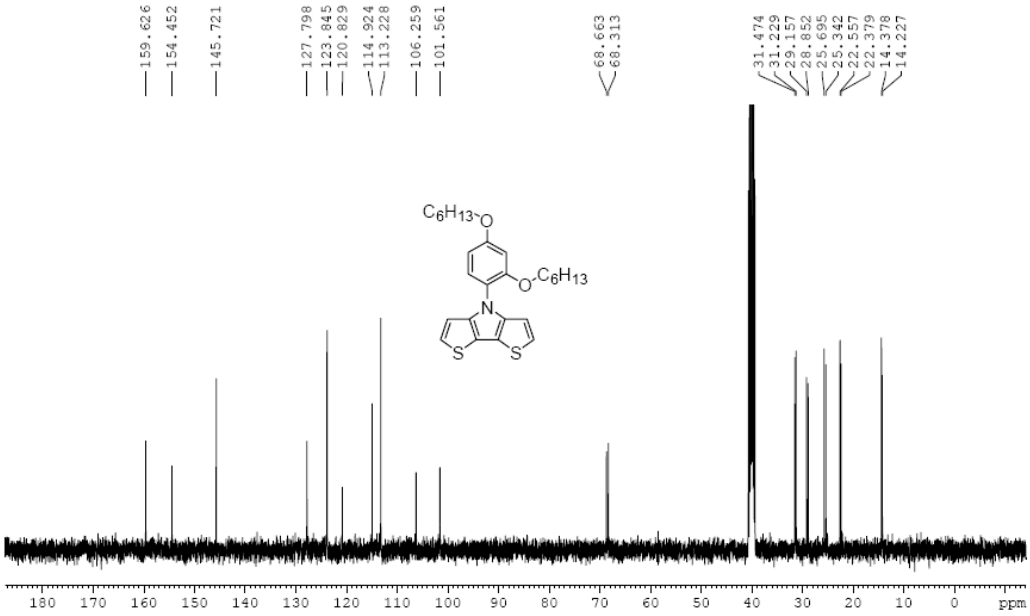
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 9a



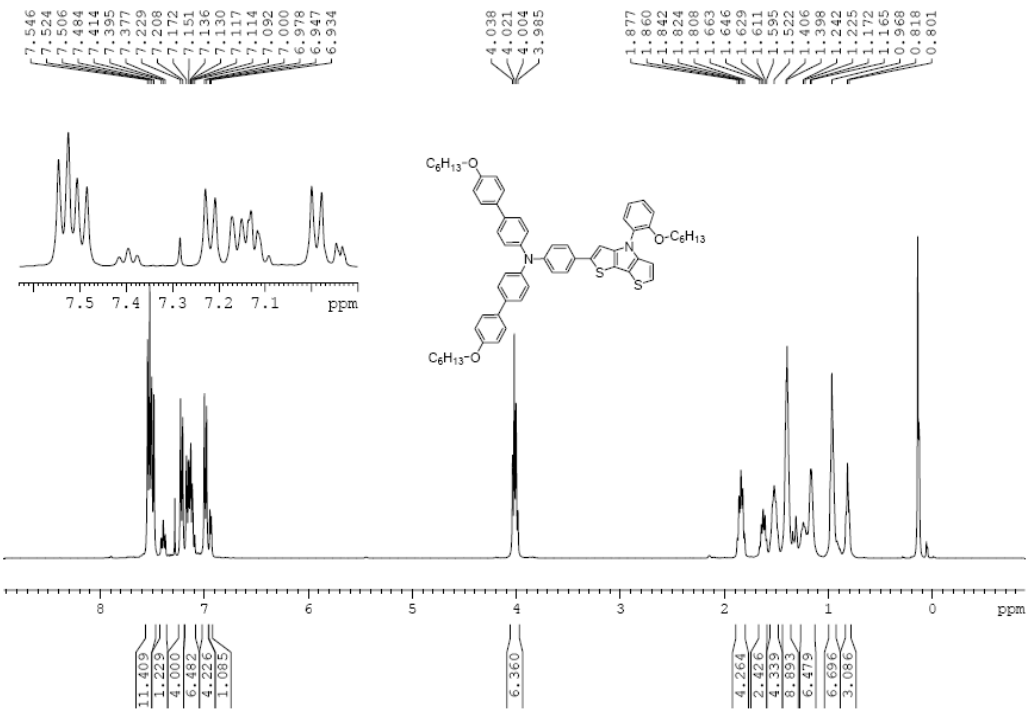


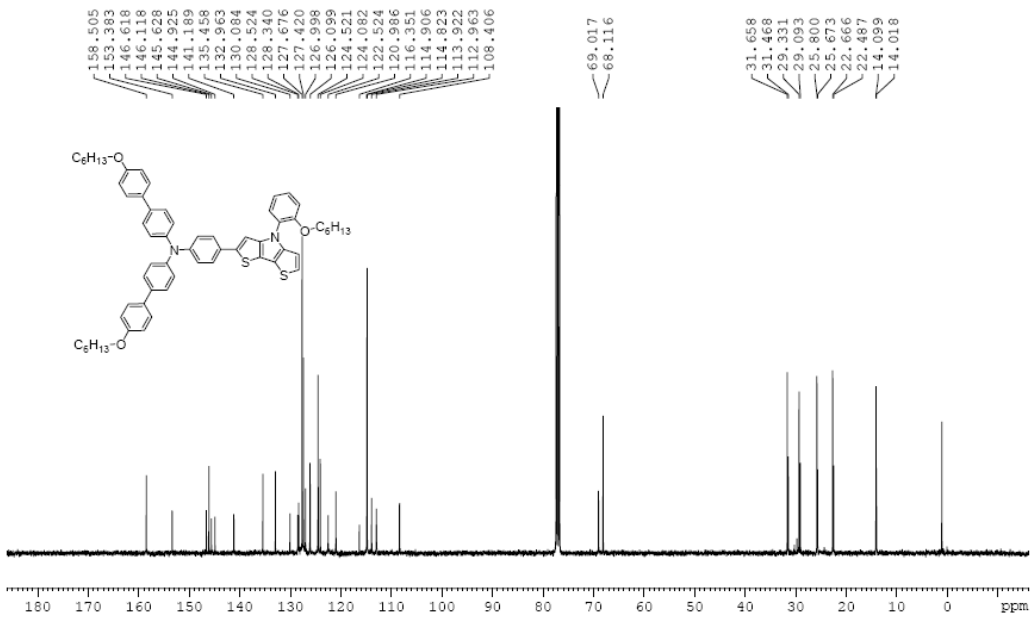
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 9b



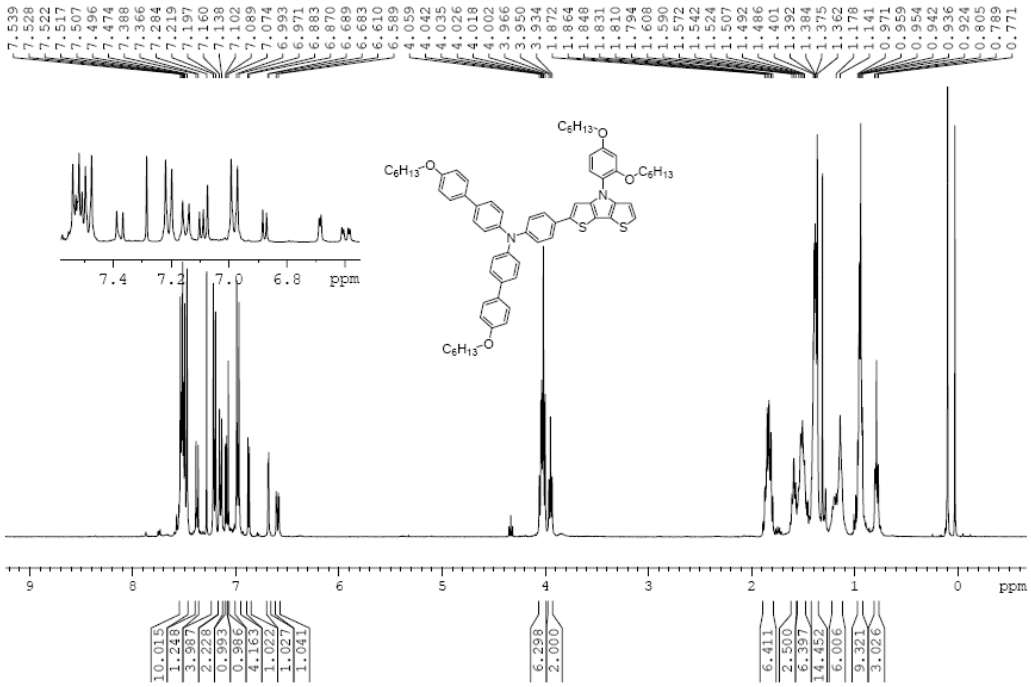


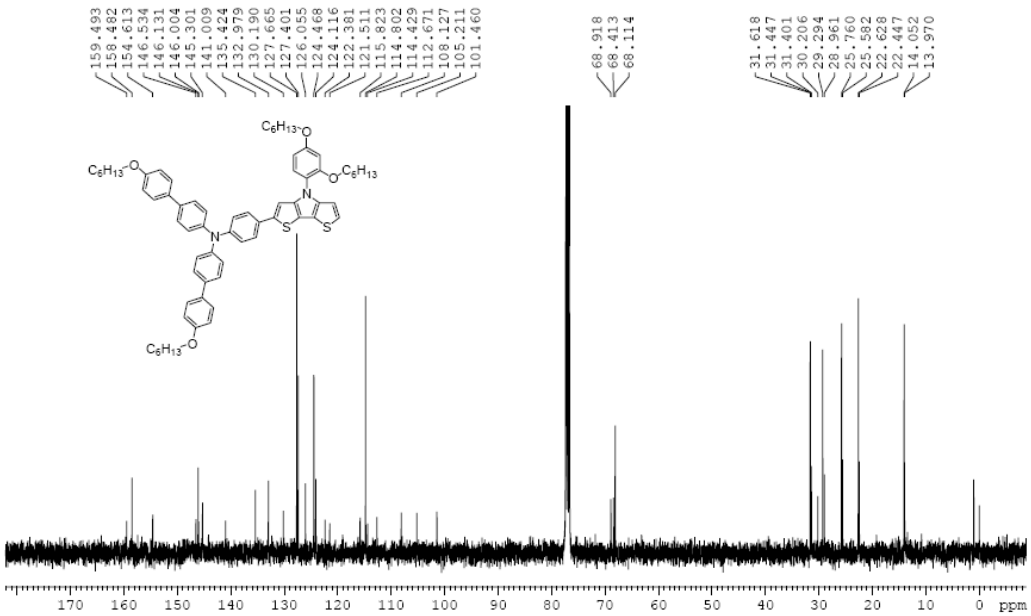
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 11a



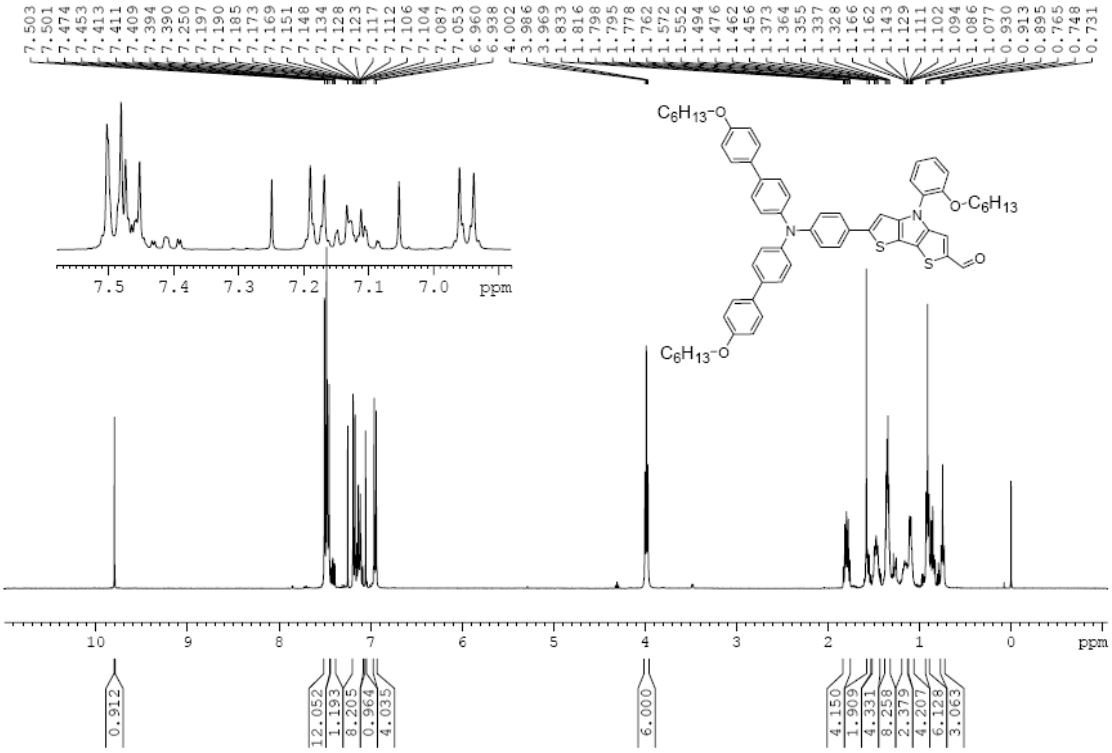


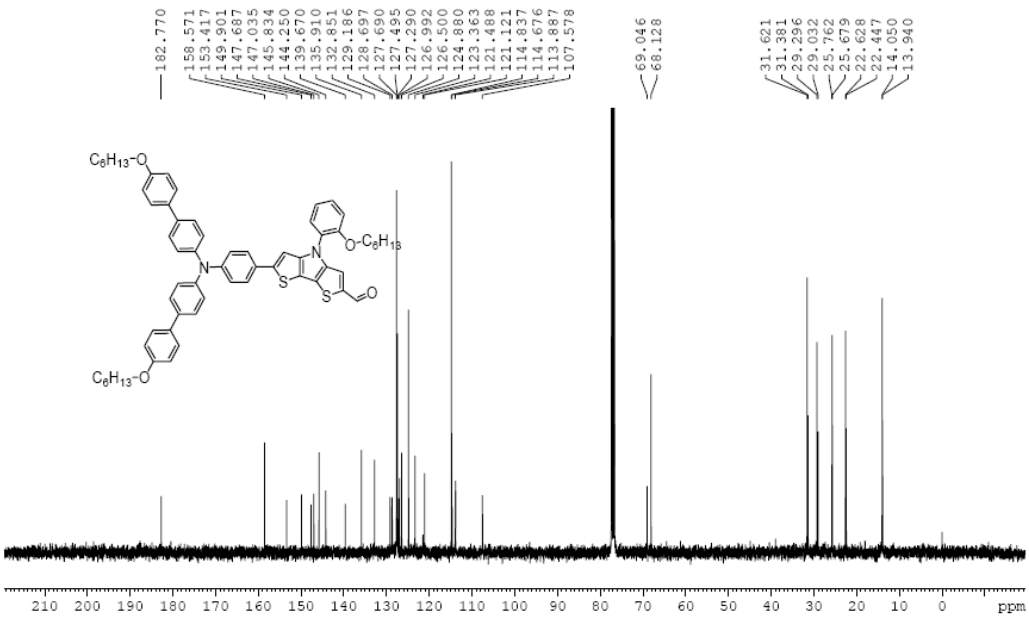
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 11b



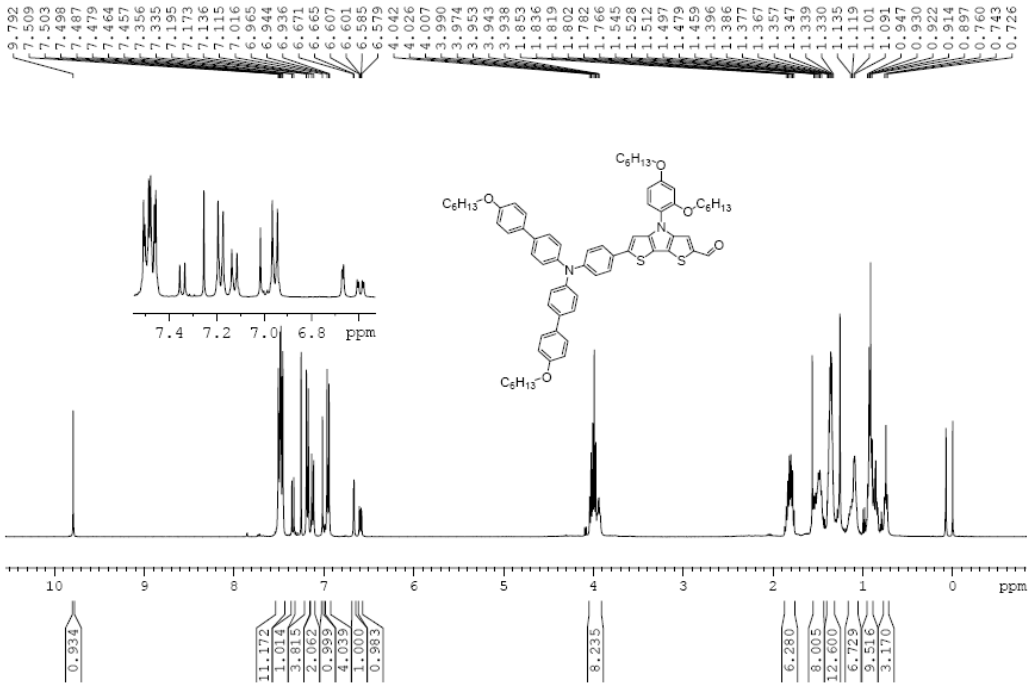


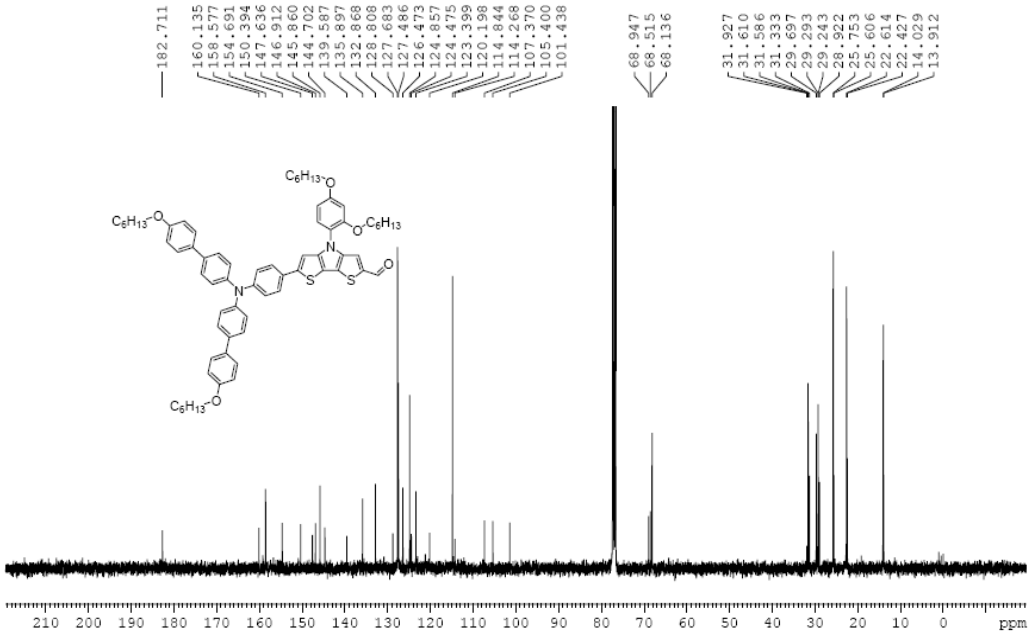
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 12a



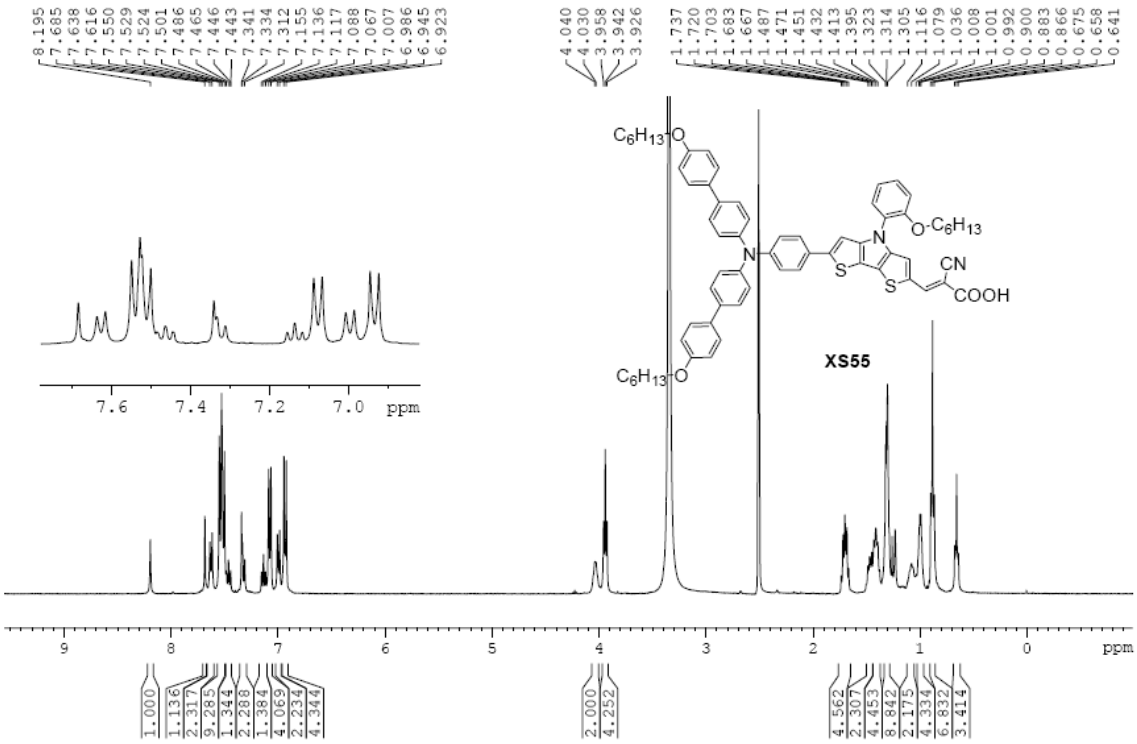


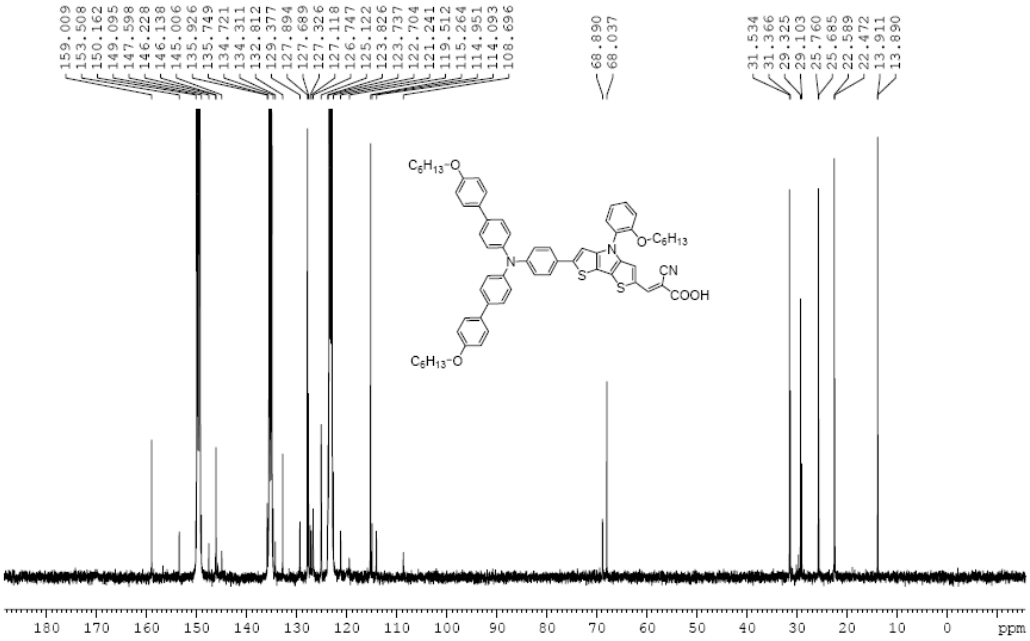
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 12b



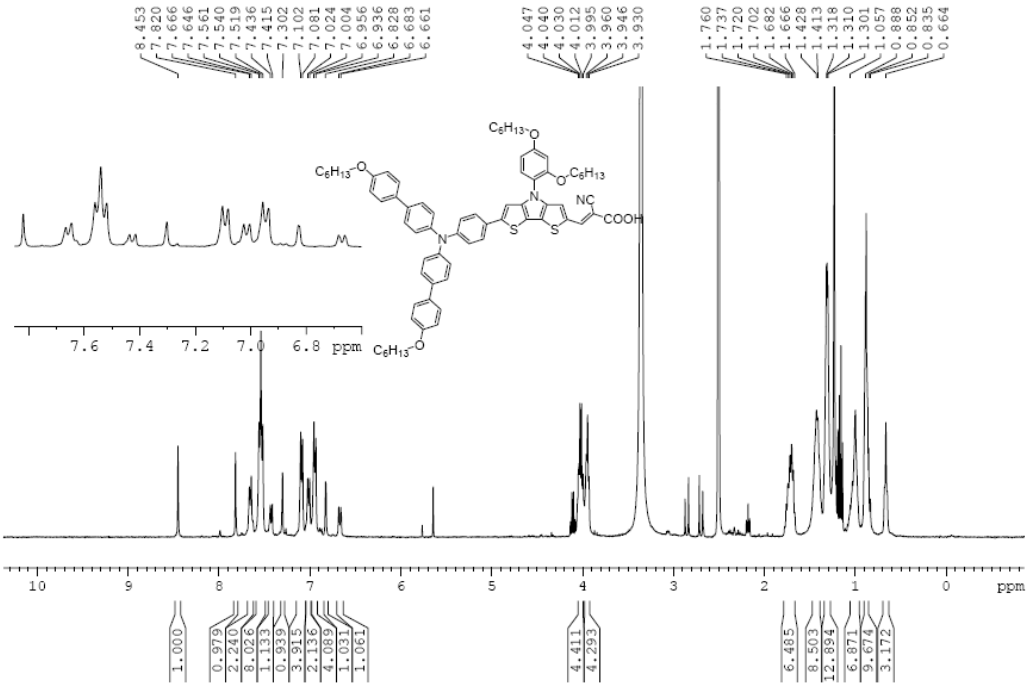


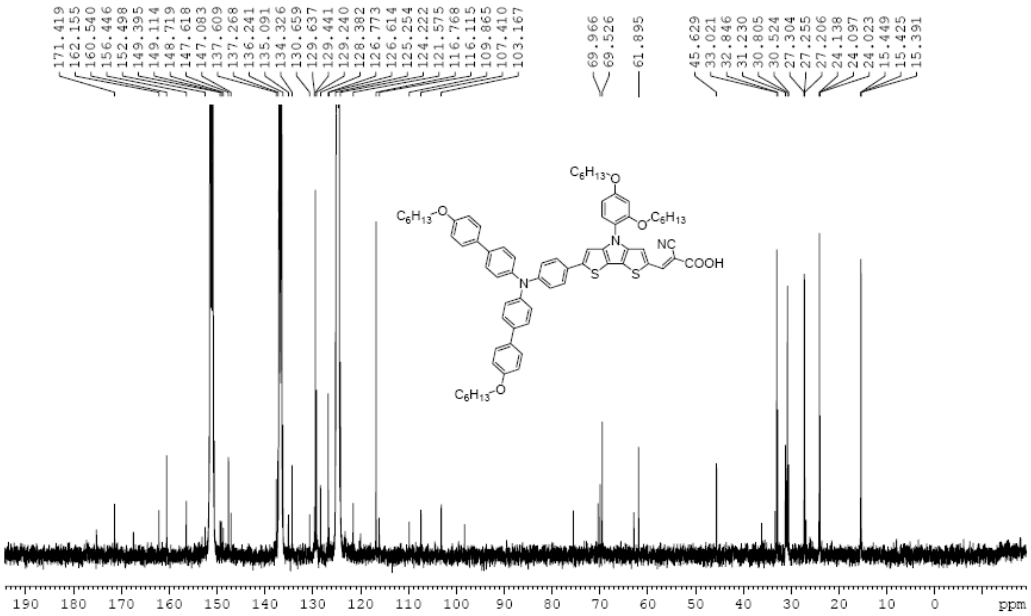
^{1}H (DMSO-d_6) and ^{13}C NMR (Pyridine-d_5) spectra of XS55



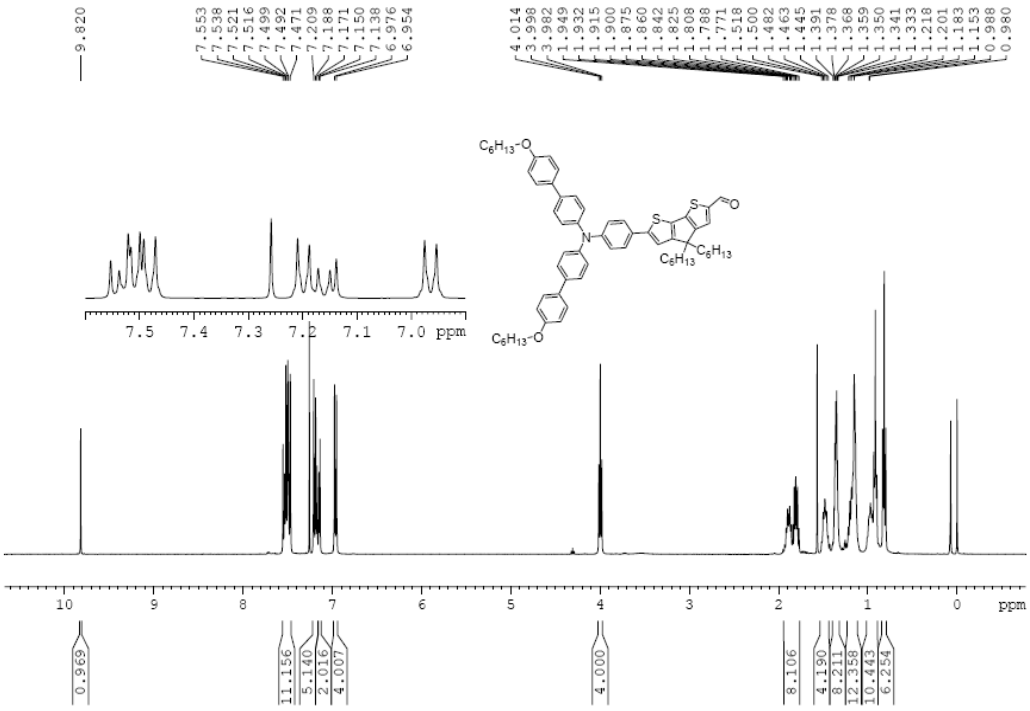


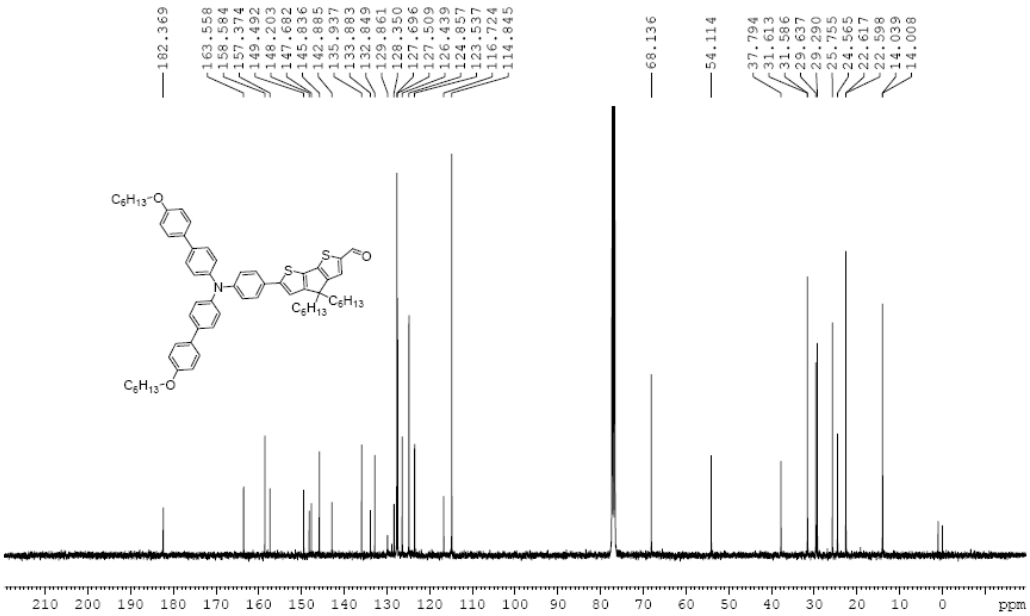
^{1}H (DMSO-d_6) and ^{13}C NMR (Pyridine-d_5) spectra of XS56



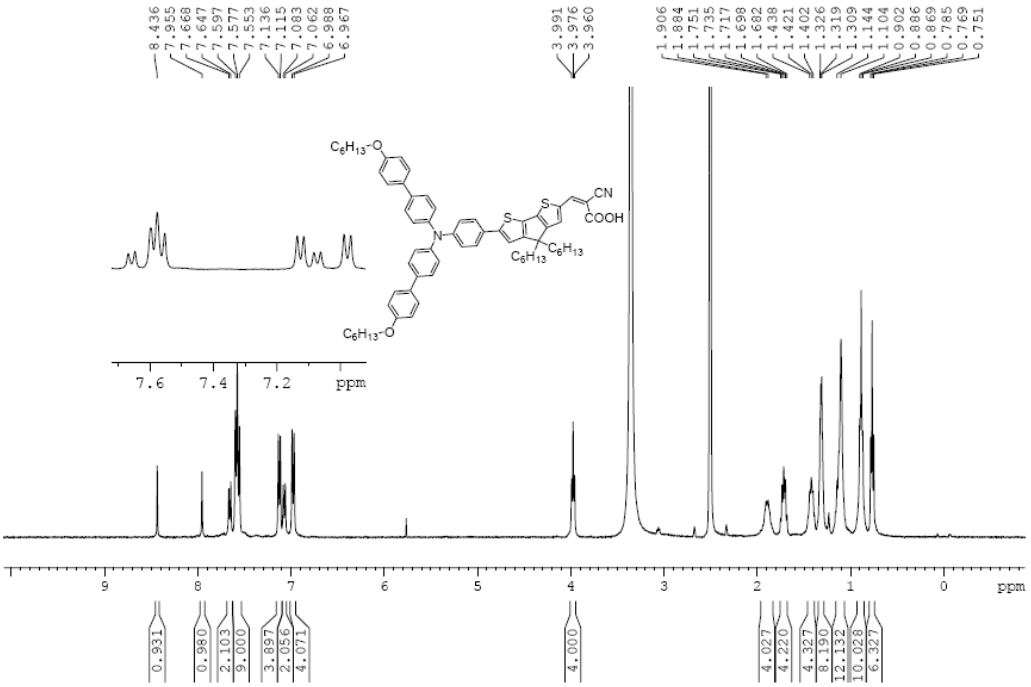


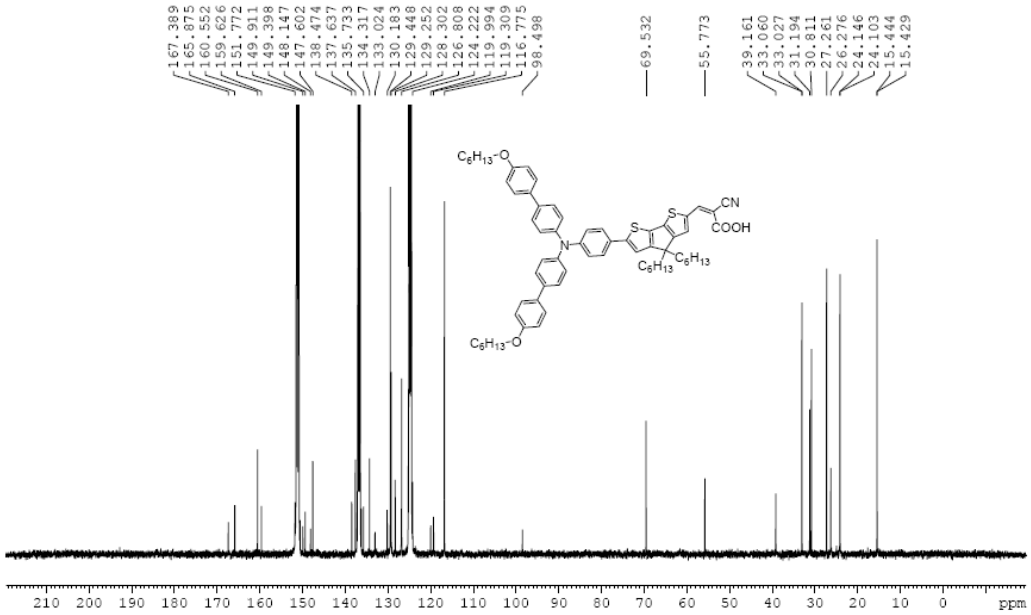
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 15





^{1}H (DMSO-d_6) and ^{13}C NMR (Pyridine-d_5) spectra of XS57





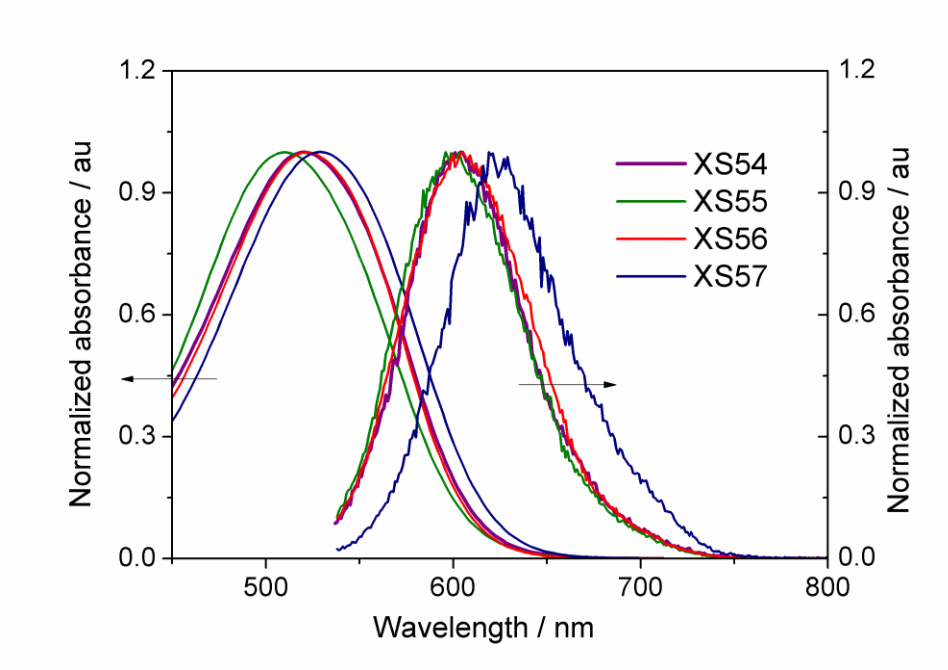


Figure S1. Normalized absorption and emission spectra of the dyes.

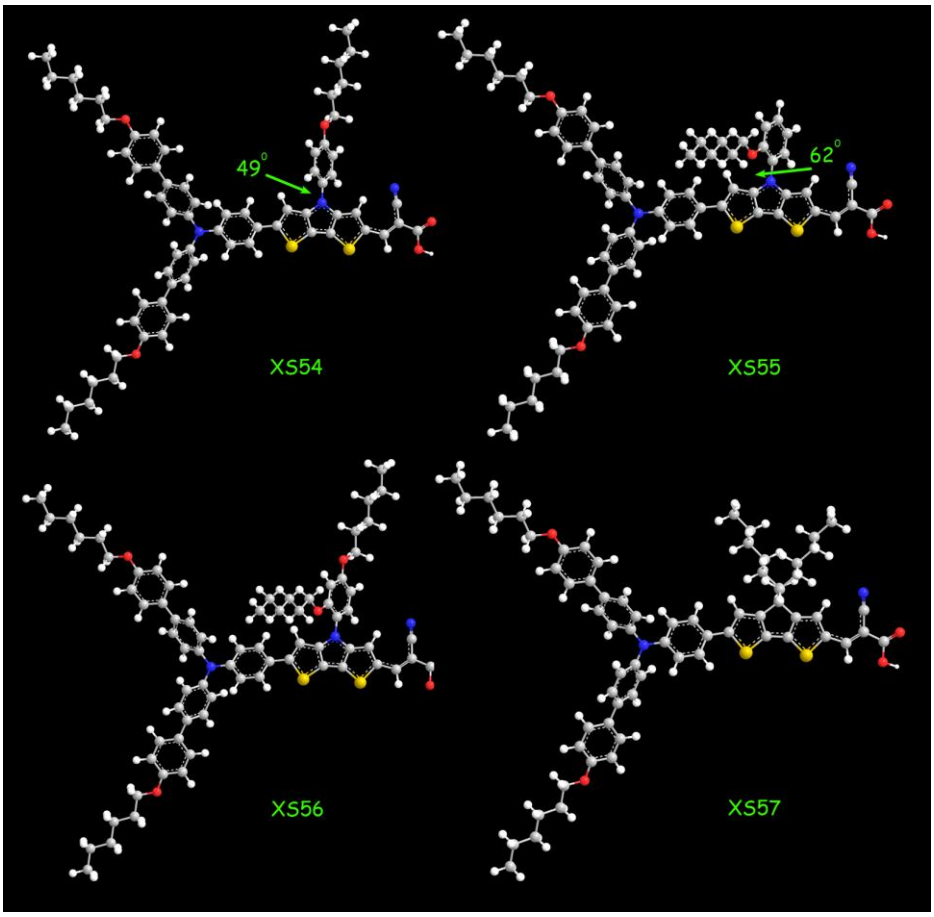


Fig. S2. Optimized geometrical configuration of the dyes.

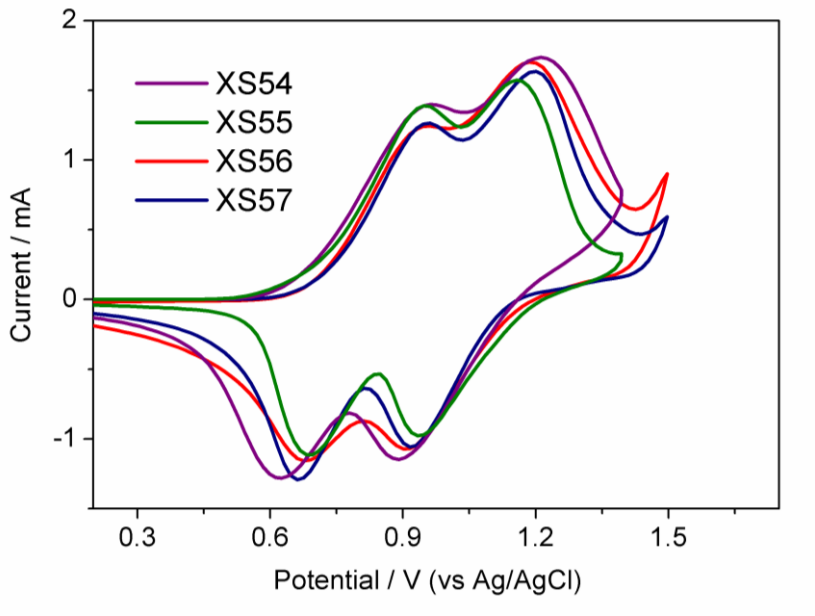


Fig. S3. Cyclic voltammograms of the dyes–loaded TiO_2 films.

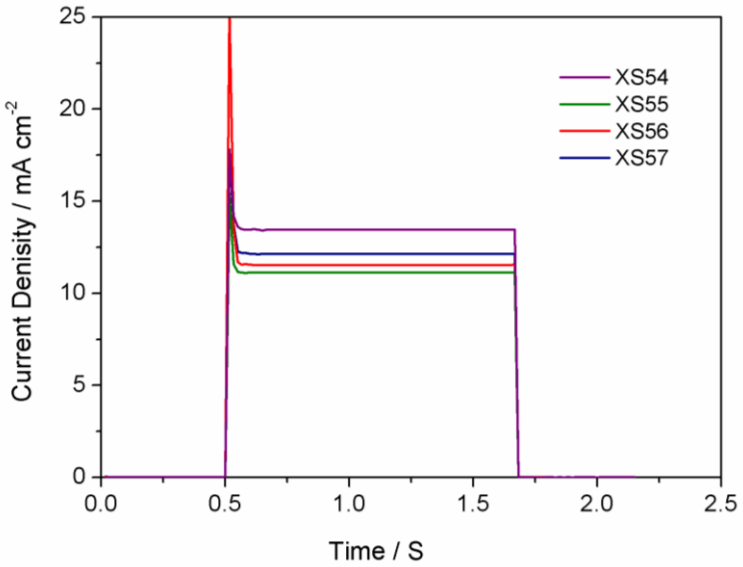


Figure S4. Photo-current dynamics as a function of light intensity for the dyes–sensitized DSCs (5 μm film) with a cobalt electrolyte.

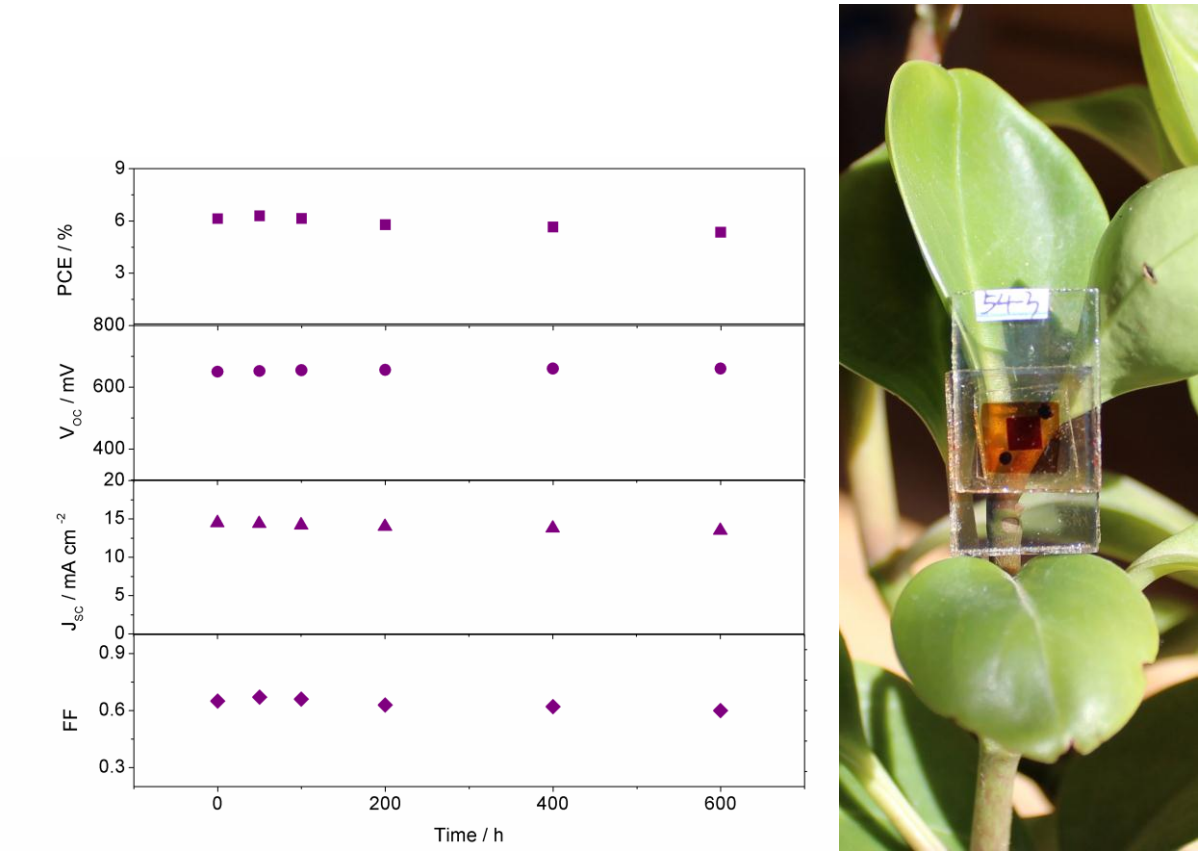


Fig. S5 Variations of photovoltaic parameters (J_{SC}, V_{OC}, FF, and PCE) with aging time for the DSC (14 μm film) based on XS54 and ionic-liquid electrolyte (0.1 M LiI, 0.4 M I_2, 0.4 M TBP in 1-methyl-3-n-propylimidazolium iodide (MPImI)) under visible-light soaking. Originally, the photovoltaic parameters were V_{OC} = 650 mV, J_{SC} = 14.5 mA cm^{-2}, FF = 0.65, and PCE = 6.13% under standard global AM 1.5 solar light conditions (100 mW cm^{-2}). The overall efficiency remained at 94% of the initial value after 200 h of visible-light soaking.

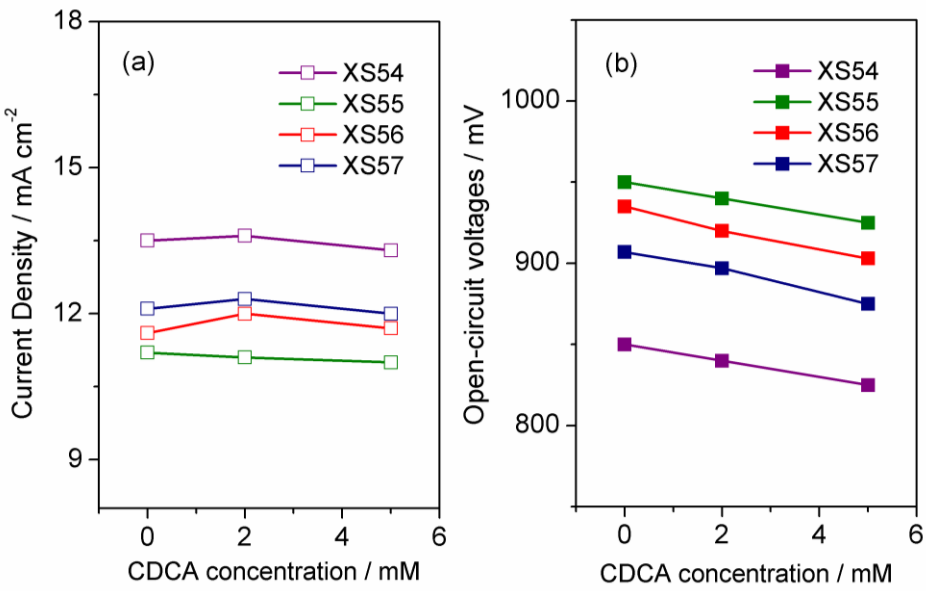


Figure S6. Dependence of J_{SC} (a) and V_{OC} (b) on the concentration of CDCA for DSCs.

Table S1. Performance of DSCs (14 μm film) employing the ionic-liquid electrolyte

dye	J_{SC} (mA cm^{-2})	V_{OC} (mV)	*FF*	PCE (%)
XS54	14.3	648	0.65	6.13
XS55	12.8	676	0.63	5.45
XS56	12.7	680	0.62	5.35
XS57	13.1	639	0.65	5.44

Table S2. Performance of DSCs (5 μm film) employing the iodide electrolyte.

dye	J_{SC} (mA cm^{-2})	V_{OC} (mV)	*FF*	PCE (%)
XS54	14.4	720	0.69	7.15
XS55	12.1	762	0.70	6.45
XS56	12.8	780	0.71	7.08
XS57	13.0	755	0.71	6.97

The results confirm that for XS54-57, the Co(II/III)tris(phen) redox couple outperforms the I^-/I_3^- redox couple for thin–film DSCs.

Table S3. Performance of DSCs (14 μm film) employing the iodine electrolyte.

dye	J_{SC} (mA cm^{-2})	V_{OC} (mV)	*FF*	PCE (%)
XS54	17.6	708	0.70	8.72
XS55	15.5	740	0.70	8.03
XS56	15.8	760	0.69	8.29
XS57	16.2	730	0.71	8.39