Electronics Supplementary Information

Organic Sensitizers Featuring Thiophene Derivatives Based Donors with Improved Stability and Photovoltaic Performance

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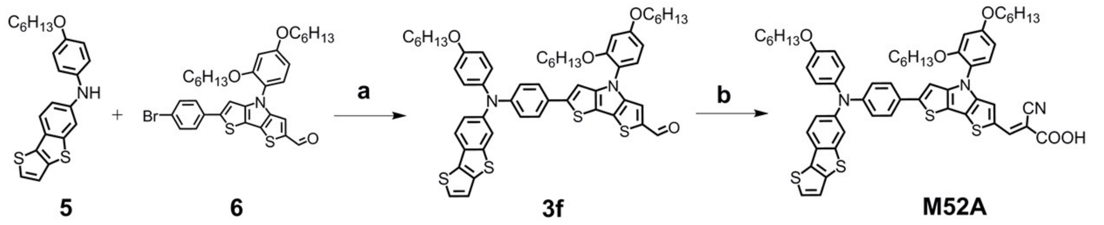


Scheme S1. Schematic routes for the M52A dye: (a) *t*-BuONa, $Pd_2(dba)_3$, Xphos, toluene, reflux 8 hours; (b) Piperidine, Cyanoacetic acid, $CHCl_3/CH_3CN$ (v/v, 1/2), reflux, 8 hours.

Synthesis of compound 3f

To a 100 mL two-neck round-bottom flask, 20 mL anhydrous toluene, compound **5** (139 mg, 0.36 mmol), compound **6** (233 mg, 0.36 mmol), anhydrous sodium tert-butoxide (105 mg, 1.08 mmol), tris(dibenzylideneacetone) dipalladium (17 mg, 0.02 mmol) and XPhos (52 mg, 0.11 mmol) were added. The mixture was refluxed for 24 hours in the dark under argon. After cooling to room temperature, H_2O and ethyl acetate were added. The organic layer was separated and dried in Na_2SO_4. The solvent was evaporated and the remaining crude product was purified by column chromatography to give desired compound **3f**: yellow powder (193 mg, yield: 56.26%). MP: 59-63 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.72 (d, *J* = 8.52 Hz, 1H), 7.54 (d, *J* = 1.68 Hz, 1H), 7.49 (s, 2H), 7.46 (d, *J* = 6.28 Hz, 2H), 7.37 (d, *J* = 8.60 Hz, 1H), 7.29 (s, 1H), 7.21 (dd, *J* = 8.60 Hz, *J* = 1.84 Hz, 1H), 7.14 (s, 1H), 7.12 (s, 1H), 7.06 (s, 1H), 7.04 (s, 1H), 7.02 (s, 1H), 6.91 (s, 1H), 6.88 (s, 1H), 6.69 (d, *J* = 2.32 Hz, 1H), 6.62 (dd, *J* = 8.60 Hz, *J* = 2.40 Hz, 1H), 4.05 (t, *J* = 6.48 Hz, 2H), 3.98 (t, *J* = 6.38 Hz, 4H), 1.89-1.78 (m, 4H), 1.40-1.37 (m, 9H), 1.30-1.26 (m, 6H), 4.05 (t, 2H), 1.16-1.12 (m, 4H), 0.98-0.92 (m, 7H), 0.77 (t, *J* = 6.04 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 182.1, 161.9, 159.5, 155.7, 154.0, 149.8, 147.5, 146.4, 144.1, 144.0, 143.5, 139.3, 138.8, 136.6, 134.1, 127.5, 127.4, 127.1, 126.9, 126.5, 125.8, 123.9, 121.4, 121.1, 120.7, 119.7, 119.5, 117.9, 114.9,113.5, 106.5, 104.7, 100.7, 68.3, 67.9, 67.7, 31.0, 30.9, 31.8, 30.7, 28.7, 28.6, 28.3, 25.2, 25.0, 22.0, 21.8, 13.5, 13.3. HRMS (EIS) cacld for $C_{55}H_{59}N_2O_4S_4$ (M+H$^+$): 939.3358, found: 939.3348.

Synthesis of compound M52A

To a stirred solution of compound **7** (193 mg, 0.21 mmol) and cyanoacetic acid (26 mg, 0.31 mmol) in acetonitrile (8 mL) was added chloroform (4 mL) and piperidine (61 μL, 0.56 mmol). The reaction mixture was refluxed for 8 hours. Additional cyanocertic acid (18 mg, 0.33 *m*mol) and piperdine (40 μL , 0.36 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 Na_2SO_4. After removing solvent under reduced pressure, the residue was purified by column chromatography to give desired product, **M52A**: red power (175mg, yield: 84.62%). MP: 92-95 ℃. ^{1}H NMR (400 MHz, $CDCl_3$+MeOD-*d*$_4$): δ 8.18 (s, 1H), 7.68 (d, *J* = 8.64 Hz, 1H), 7.49 (s, 2H), 7.43 (m, 3H), 7.31 (d, *J* = 8.84 Hz, 1H), 7.25 (d, *J* = 5.12 Hz, 1H), 7.16 (d, *J* = 8.60 Hz, 1H), 7.09 (s, 1H), 7.07 (s, 1H), 7.01 (s, 1H), 6.99 (s, 1H), 6.96 (s, 1H), 6.86 (s, 1H), 6.84 (s, 1H), 6.64 (s, 1H), 6.57 (d, *J* = 8.88 Hz, 1H), 4.00 (t, *J* = 6.56 Hz, 2H), 3.94 (t, *J* = 6.04 Hz, 4H), 1.84-1.73 (m, 4H), 1.54-1.46 (m, 6H), 1.35-1.32 (m, 6H), 1.23 (s, 4H), 1.09-1.06 (m, 4H), 0.92-0.88 (m, 6H), 1.13 (t, *J* = 6.44 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 160.2, 156.3, 154.5, 148.3, 144.5, 144.1, 139.8, 137.3, 134.7, 128.2, 127.8, 127.6, 127.5, 127.1, 126.5, 121.9, 121.7, 121.4, 120.3, 119.8, 118.7, 115.6, 114.3, 107.0, 105.4, 101.4, 68.9, 68.5, 68.3, 31.6, 31.4, 29.3, 29.3, 28.9, 25.8, 25.6, 22.6, 22.4, 14.0, 13.9. HRMS (EIS) cacld for $C_{58}H_{60}N_3O_5S_4$ (M+H$^+$): 1006.3416, found: 1006.3408.

Optical and Electrochemical Measurements.

The absorption spectra of dyes and sensitized films were measured by SHIMADZU UV-2600 spectrophotometer. Fluorescence measurements were carried out with a HITACHI F–4500 fluorescence spectrophotometer.

Cyclic voltammetry (CV) measurements for sensitized films were performed on a Zennium electrochemical workstation (ZAHNER, Germany), 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 results were calibrated using ferrocene as standard. In this work, the LUMO of these dyes were estimated from calculated from $LUMO = HOMO – E_{0–0}$. $E_{0–0}$ values were estimated from the intersections of normalized absorption and emission spectra (λ_{int}): $E_{0–0} = 1240/\lambda_{int}$.

Electrochemical impedance spectroscopy (EIS) in the frequency range from 200 mHz to 100 kHz was performed with a Zennium electrochemical workstation (ZAHNER, Germany) in the dark with the alternate current amplitude set at 10 mV.

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.

Fabrication and Characterization of DSSCs

The TiO_2 paste (particle size, 20 nm) 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. 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 fired again to give a ca. 3 μm (for cobalt cells) or 9μm (for iodine cells) thick mesoscopic TiO_2 film. The TiO_2 electrode was stained by immersing it into a 0.3 mM dye solution in a mixture of DCM/EtOH (v/v, 1:1) and kept at room temperature for 12 hours. The sensitized electrodes were then rinsed with dry ethanol and dried by a dry air flow. 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 sensitized 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 Co-bpy electrolyte, is composed of 0.25 M $[Co(II)(bpy)_3](PF_6)_2$, 0.05 M $[Co(III) (bpy)_3](PF_6)_3$, 0.5 M TBP and

0.1 M LiTFSI in acetonitrile. For comparison, an iodine electrolyte consisting of 0.6 M 1,2–dimethyl–3–n–propylimidazolium iodide (DMPImI), 0.1 M LiTFSI, 0.05 M I_2 and 0.5 M TBP in acetonitrile was formulated.

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)

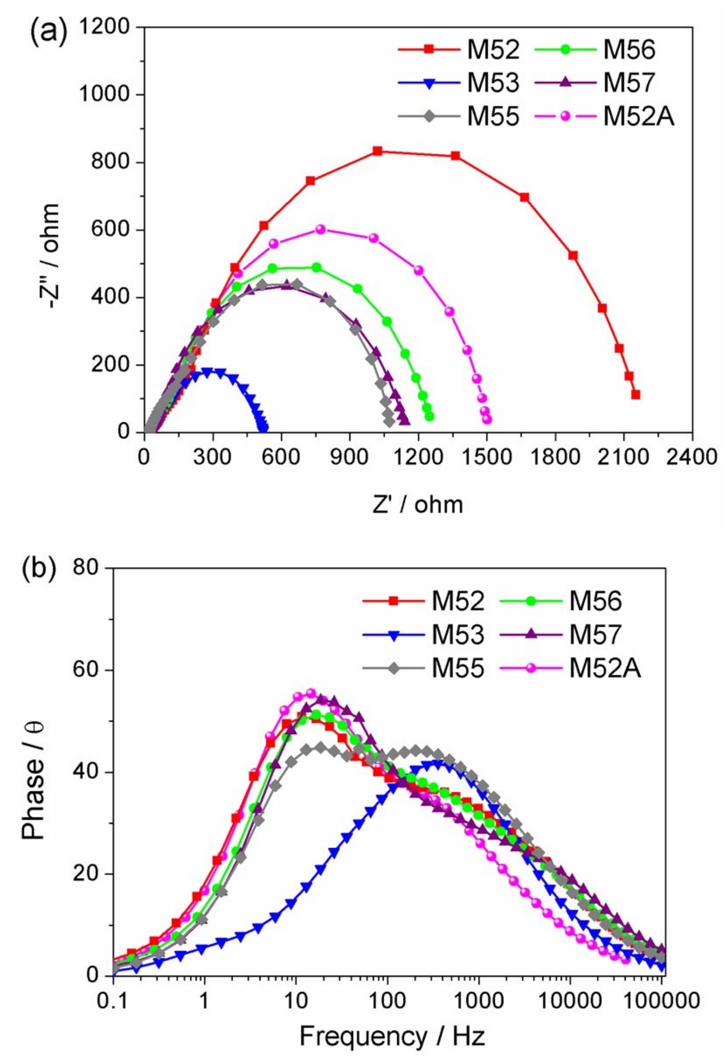


Fig. S1. EIS for DSSCs based on the studied dyes measured in the dark under -0.8 V bias displayed in the form of Nyquist plots (a) and Bode phase plots (b).

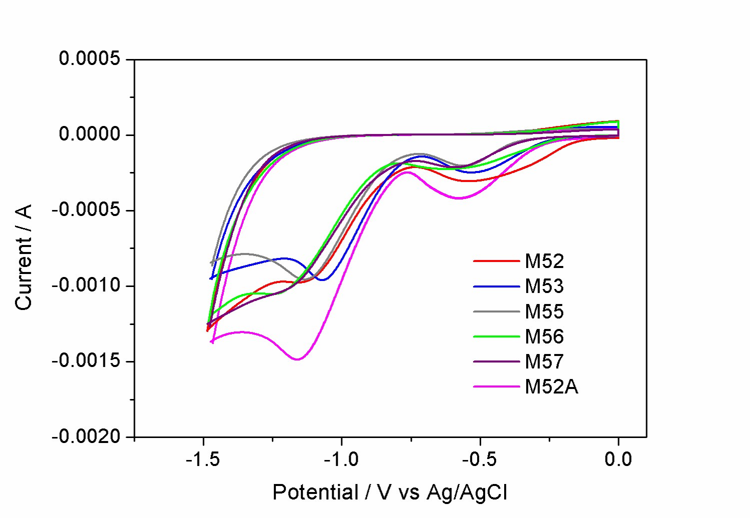


Fig. S2. CV of sensitized electrodes between 0 to -1.5 V.

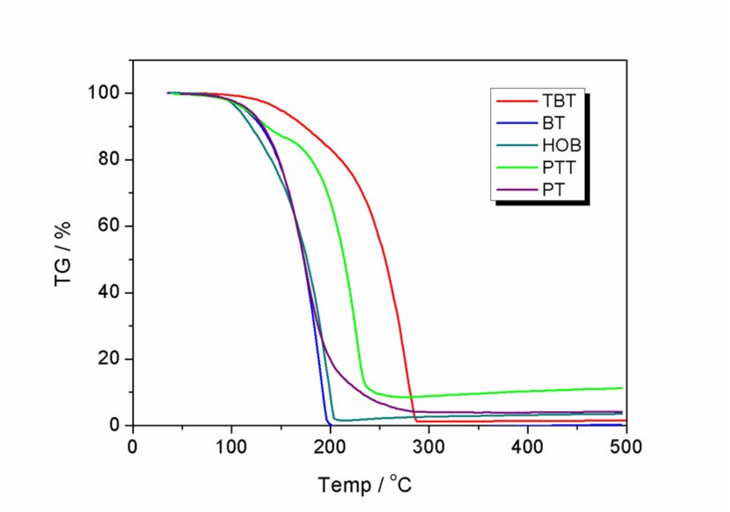


Fig. S3. Temperature-dependent TG curves of different donor units. Clearly, **TBT** is more stable than other donor units in terms of thermal stability.

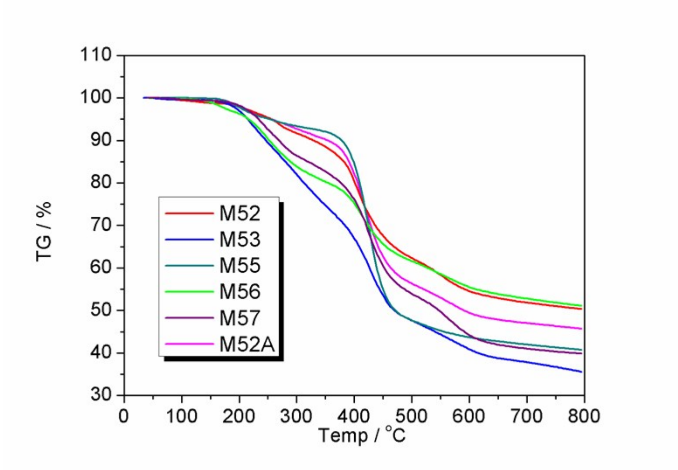


Fig. S4. Temperature-dependent TG curves of dyes.

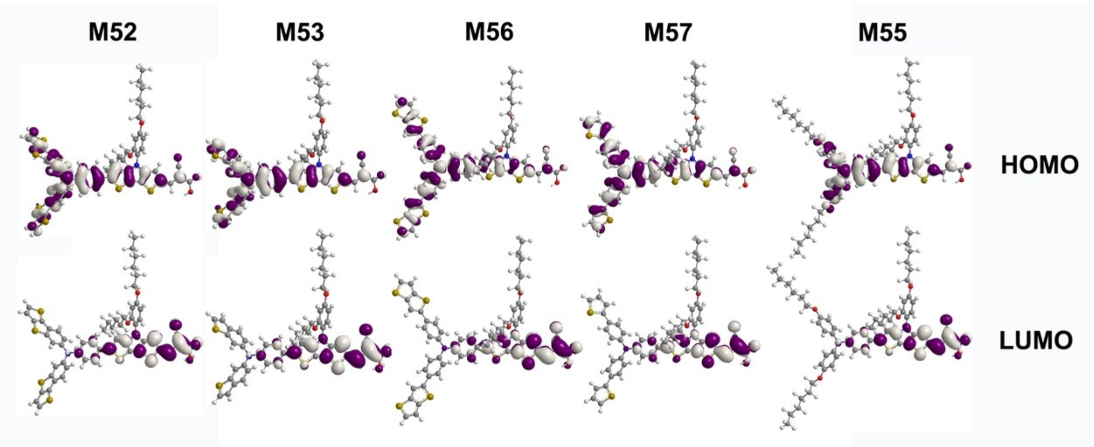
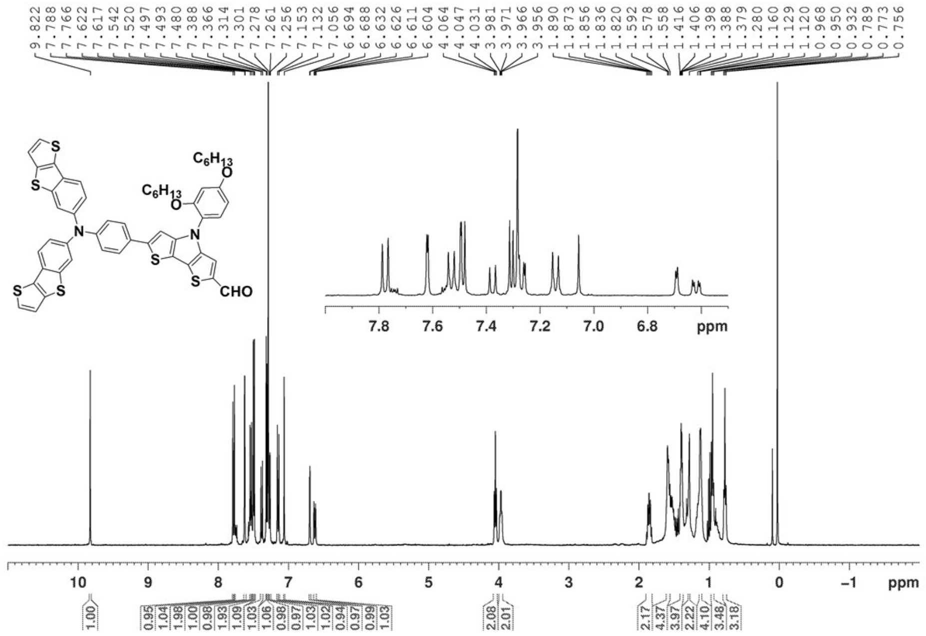
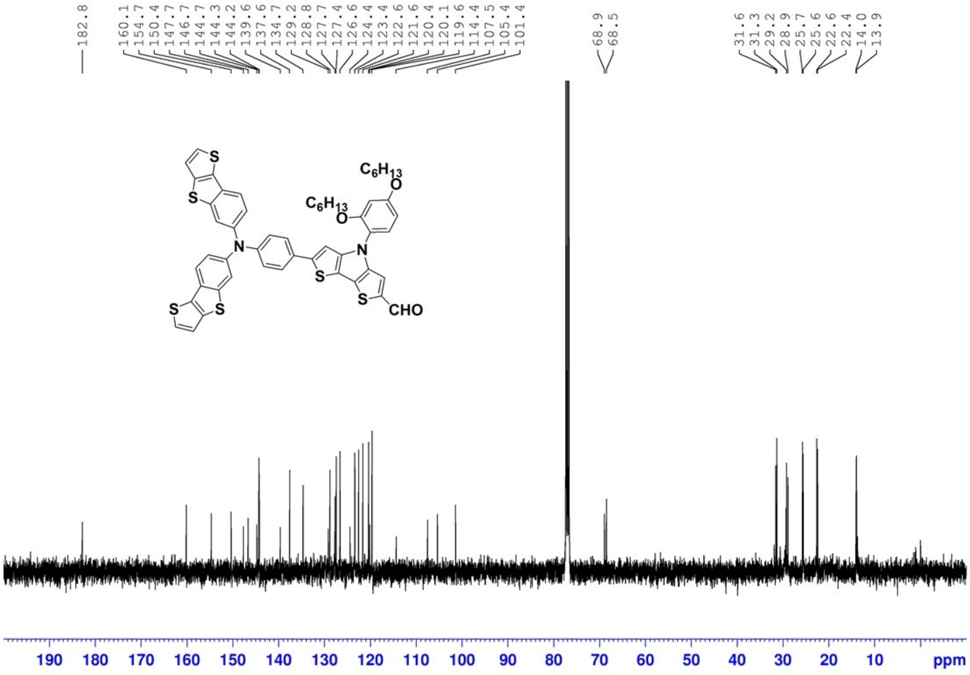


Fig. S5. Optimized geometrical configuration of the dyes.

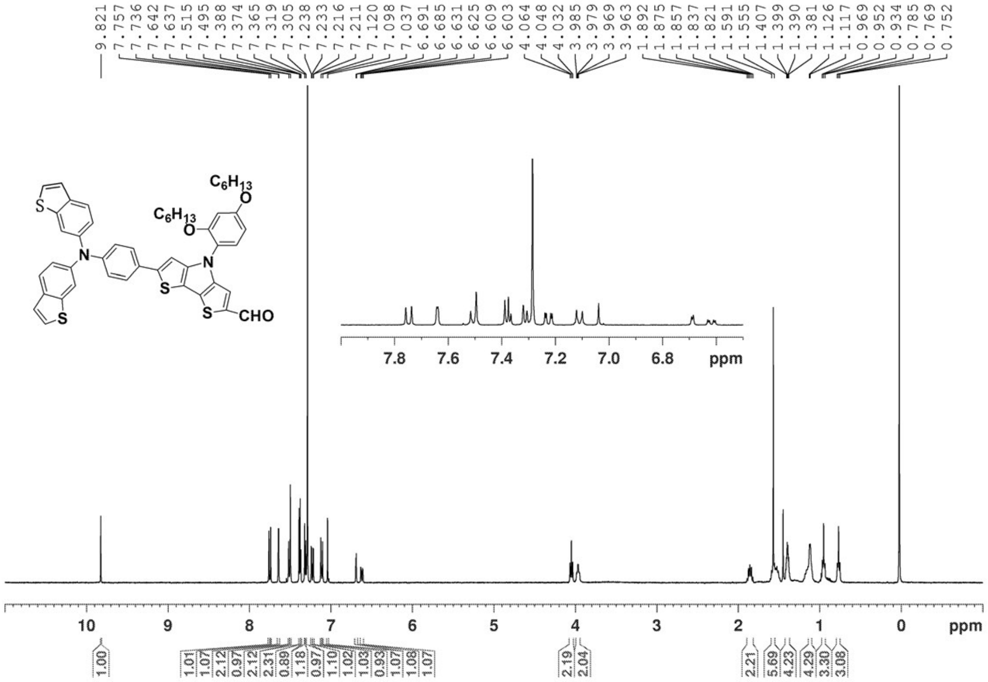
^{1}H NMR ($CDCl_3$) spectra of compound 3a



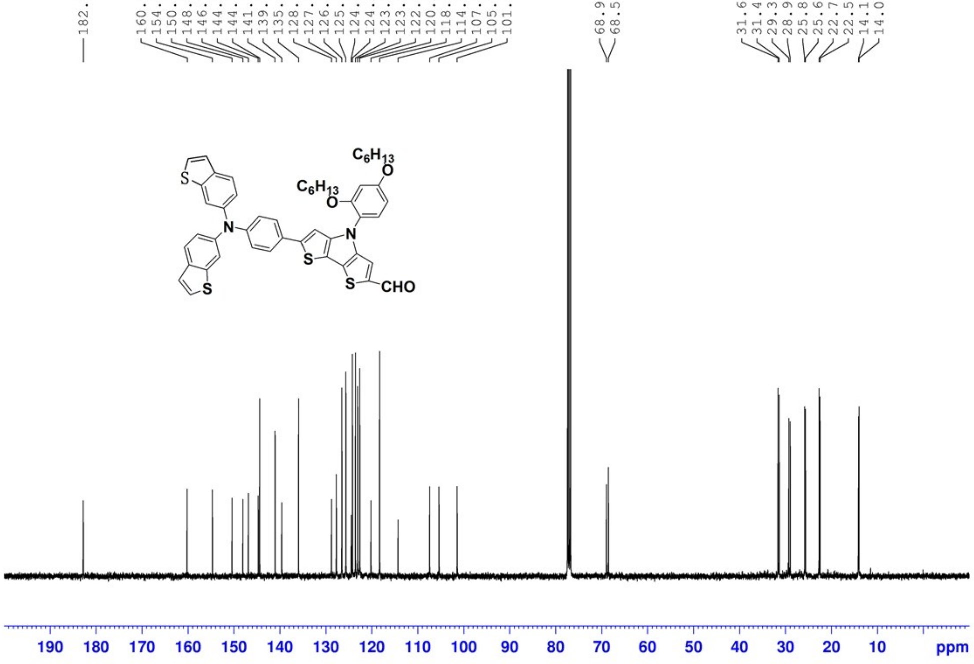
^{13}C NMR ($CDCl_3$) spectra of compound 3a



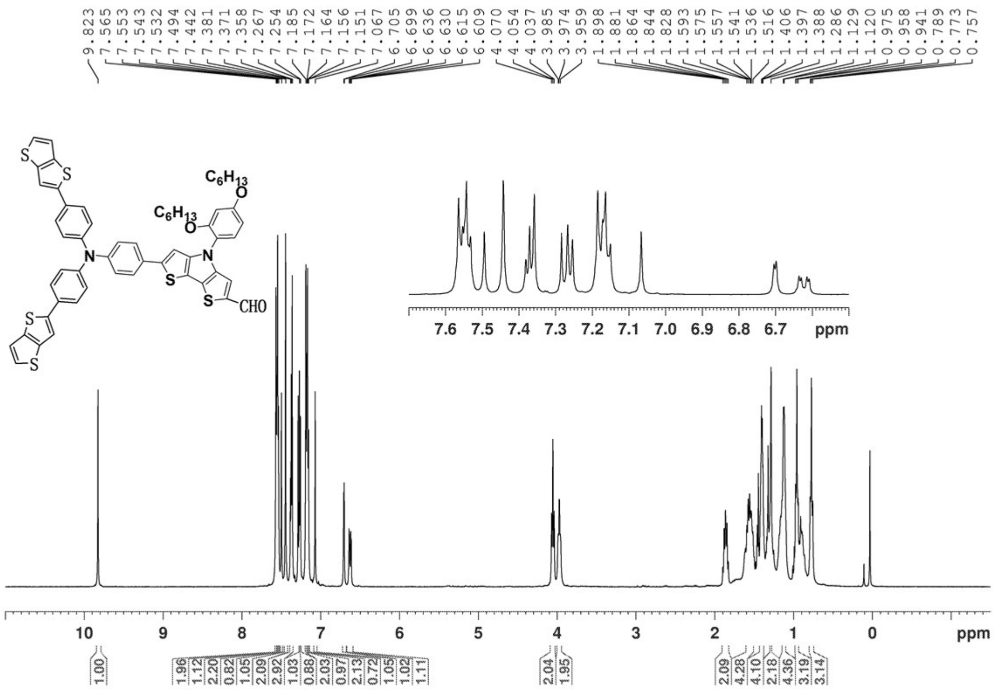
^{1}H NMR ($CDCl_3$) spectra of compound 3b



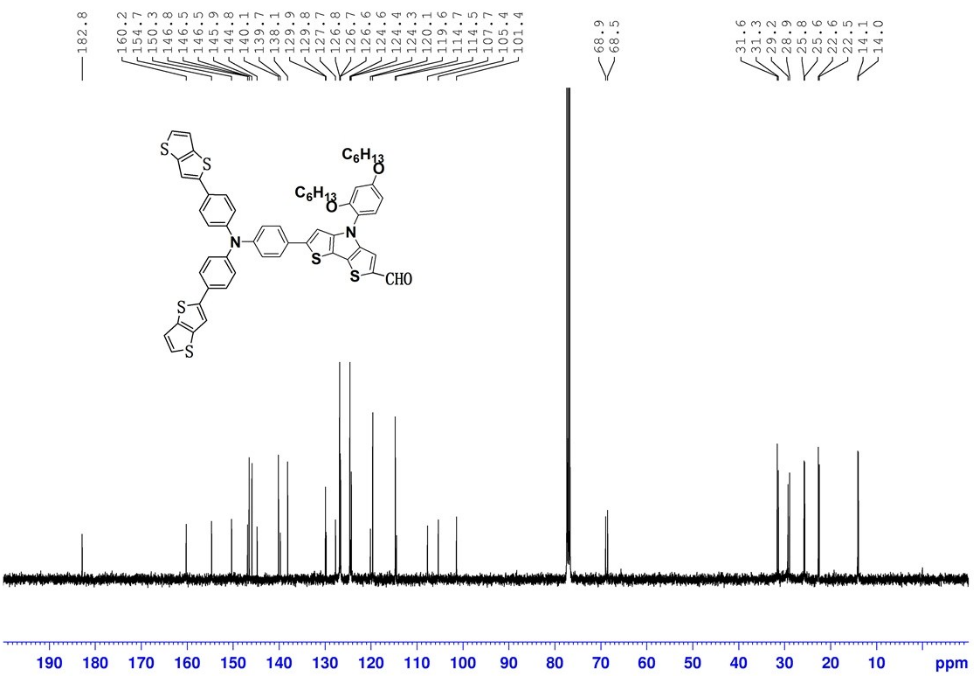
^{13}C NMR ($CDCl_3$) spectra of compound 3b



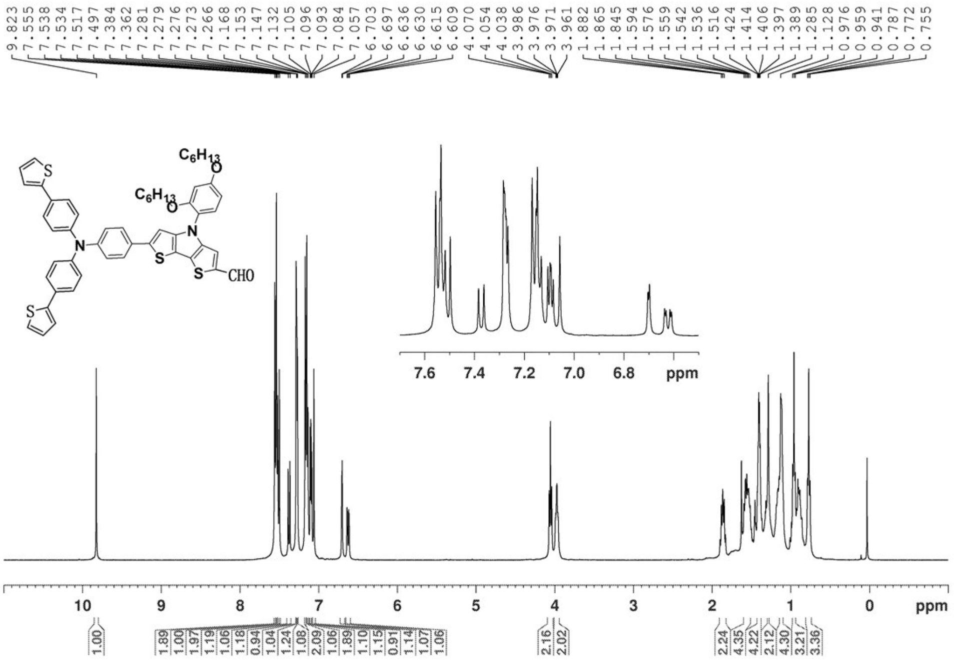
^{1}H NMR ($CDCl_3$) spectra of compound 3c



^{13}C NMR ($CDCl_3$) spectra of compound 3c



^{1}H NMR (CDCl$_3$) spectra of compound 3d



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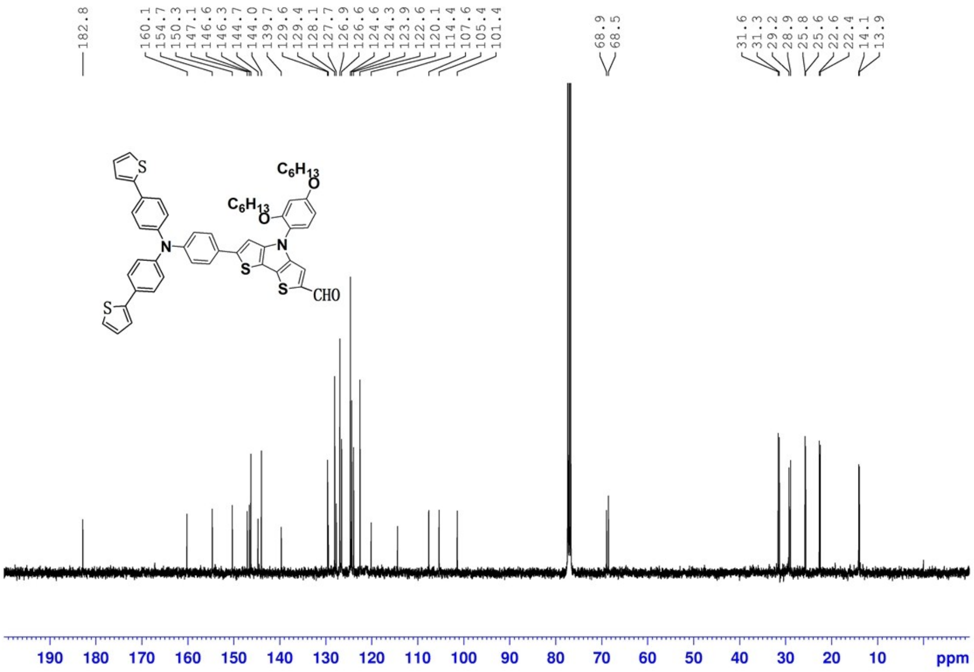

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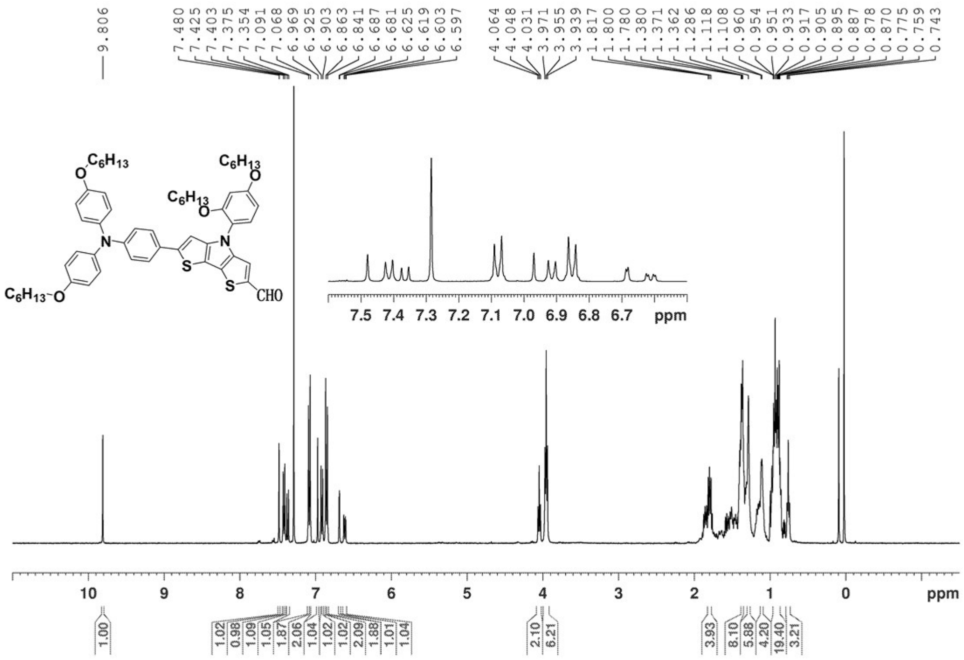

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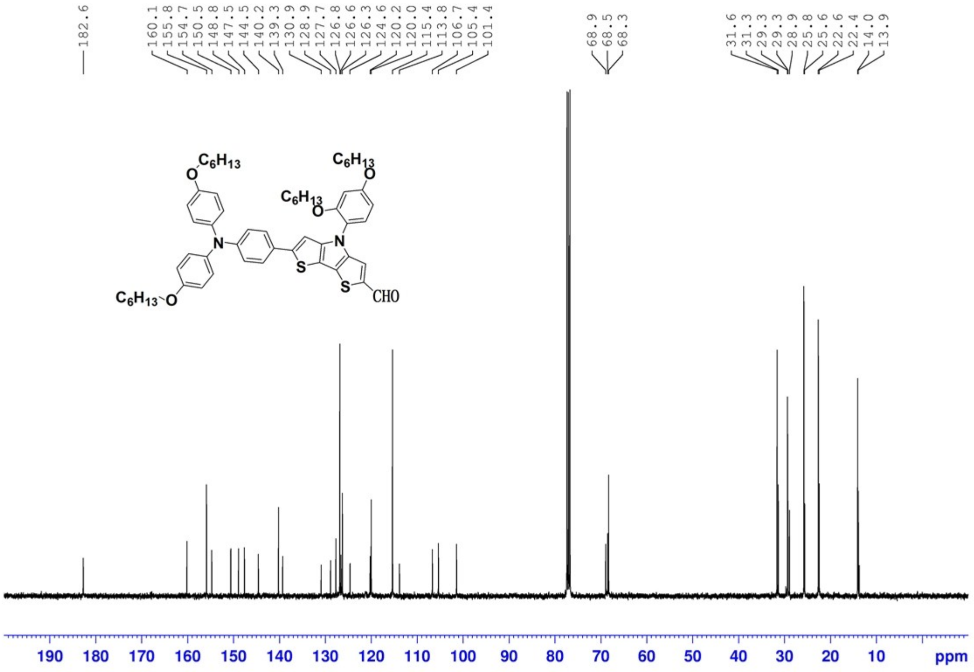

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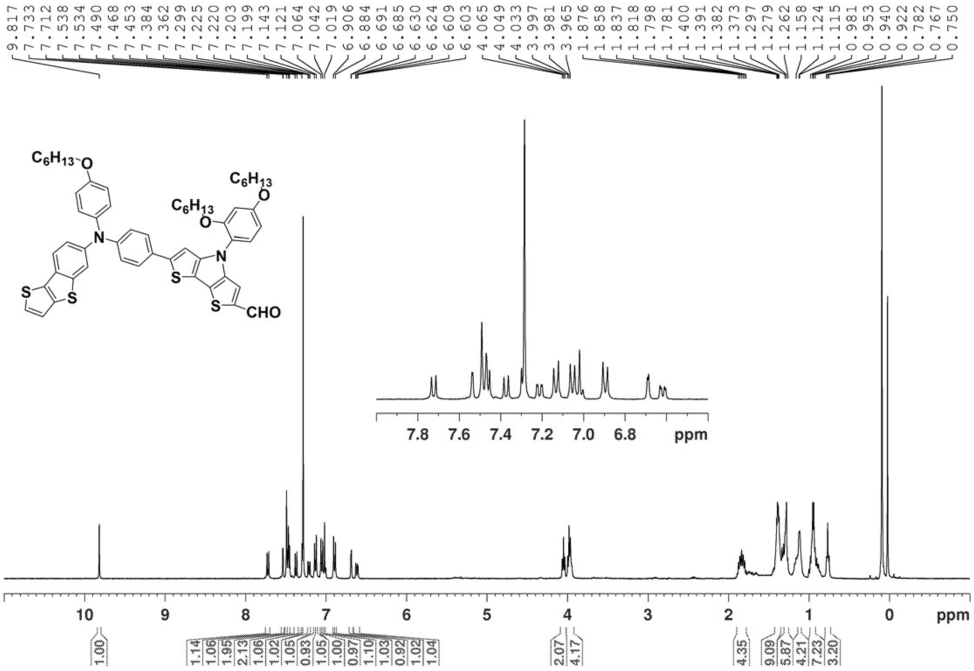
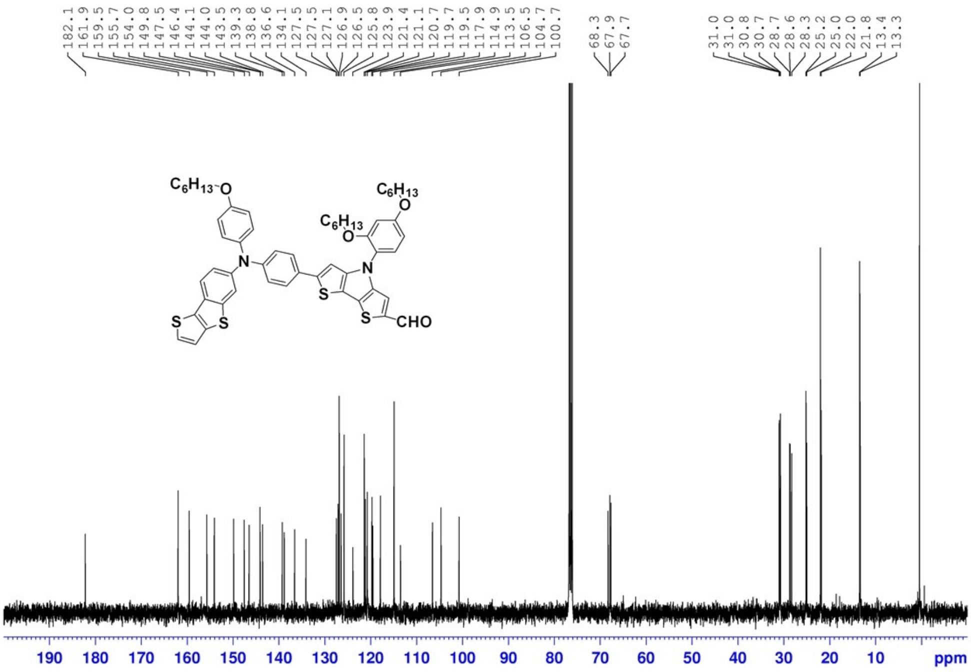
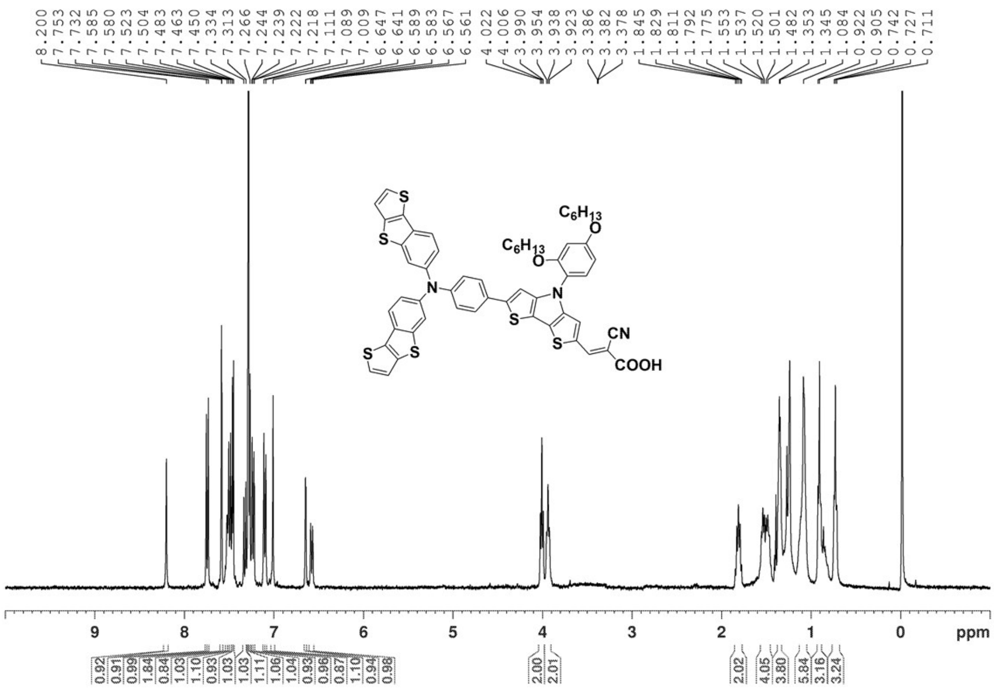


^{13}C NMR ($CDCl_3$) spectra of compound 3f



^{1}H NMR ($CDCl_3$+MeOD-d_4) spectra of compound M52



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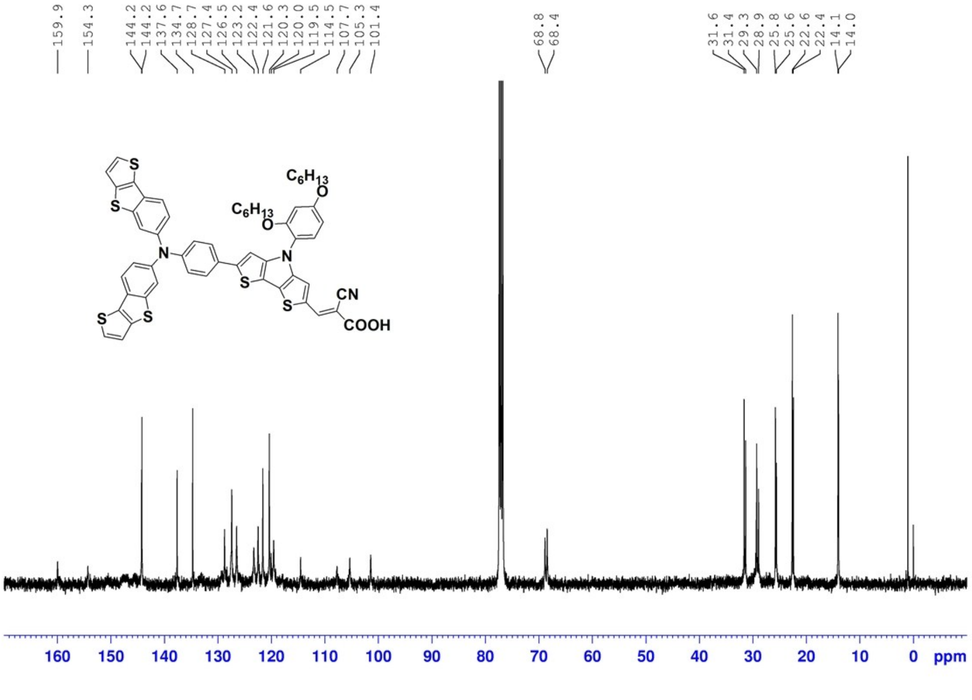

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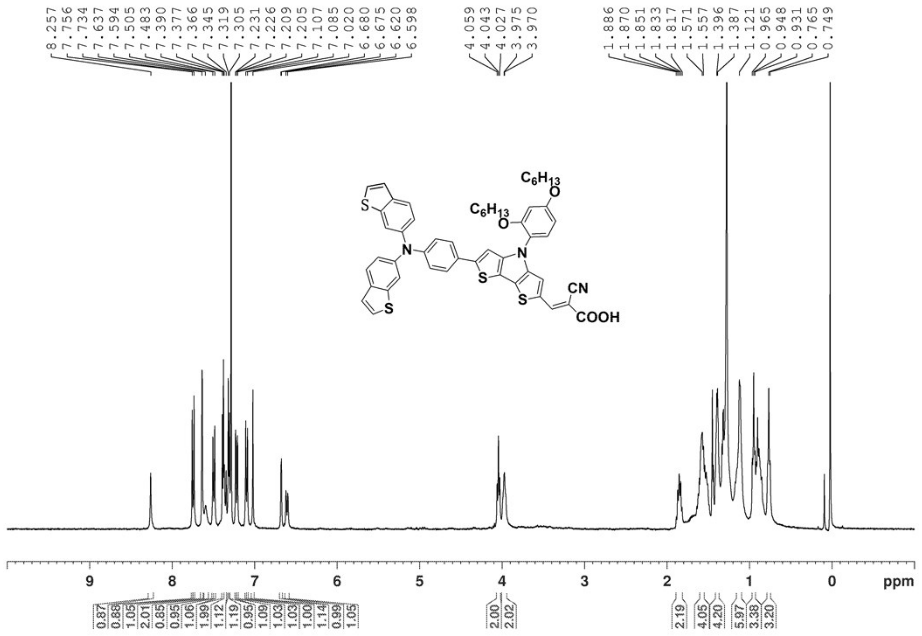
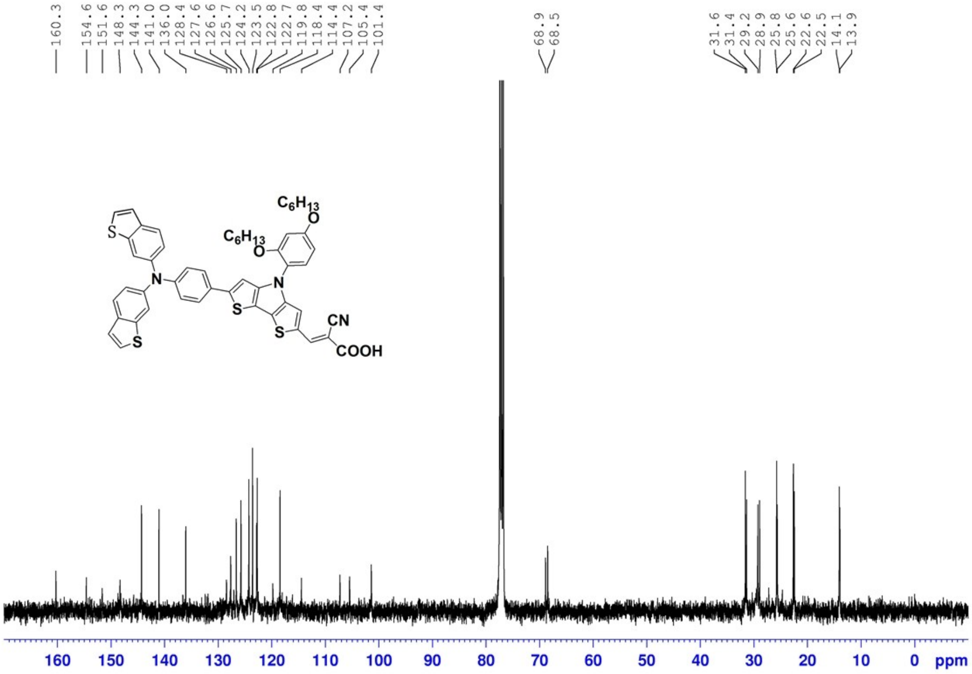
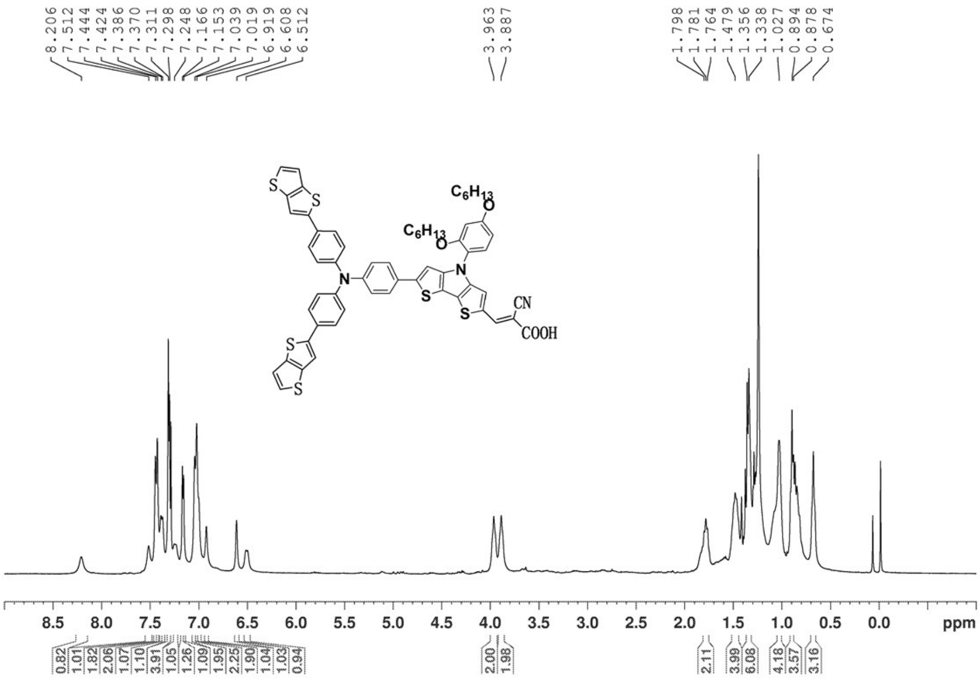


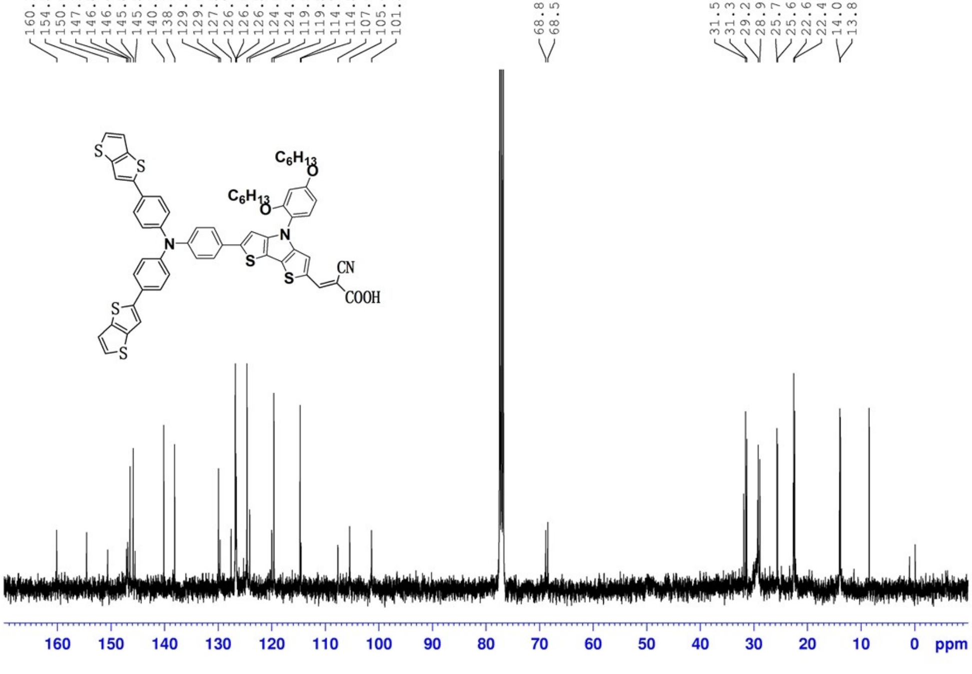
^{13}C NMR ($CDCl_3$) spectra of compound M53



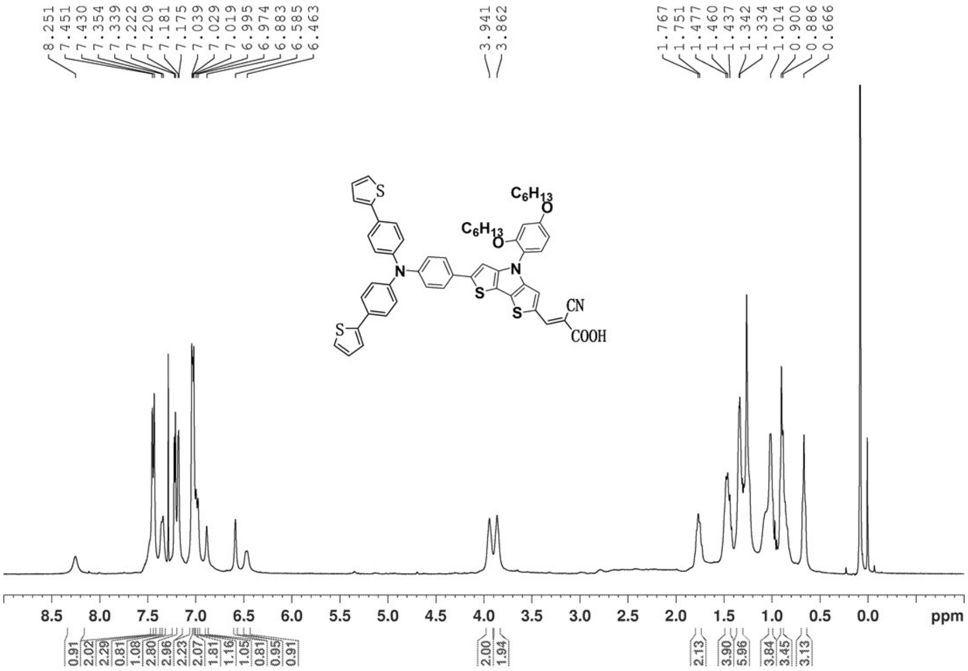
^{1}H NMR (CDCl$_3$+MeOD-d_4) spectra of compound M56



^{13}C NMR (CDCl$_3$) spectra of compound M56



^{1}H NMR ($CDCl_3$+MeOD-d_4) spectra of compound M57



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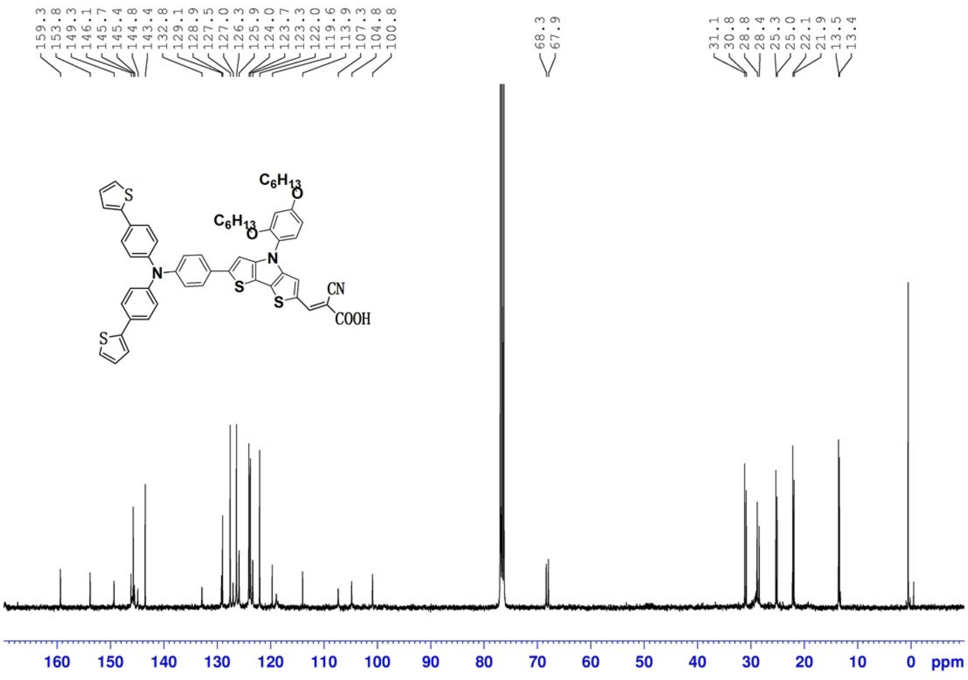
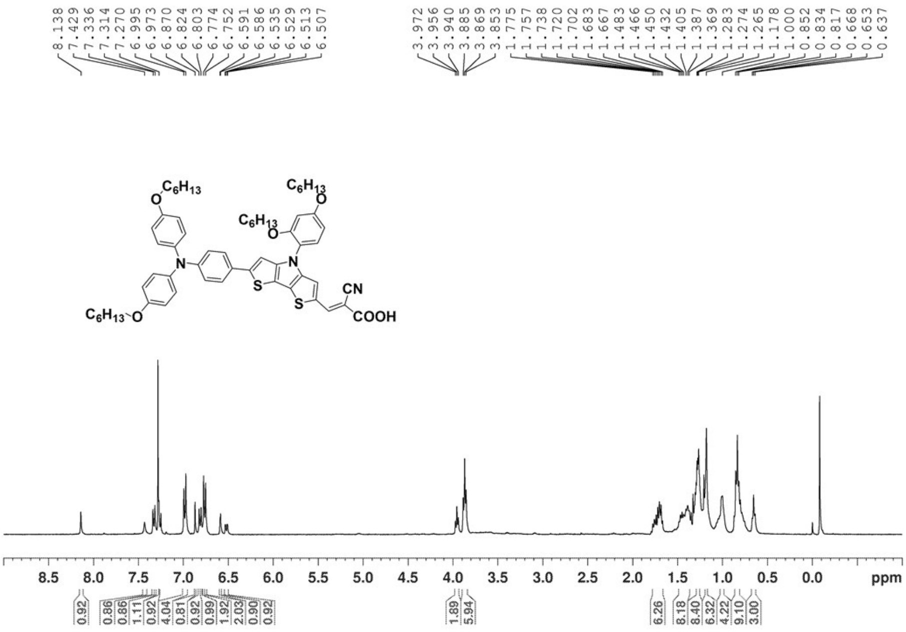


^{1}H NMR (CDCl$_3$+MeOD-d_4) spectra of compound M55



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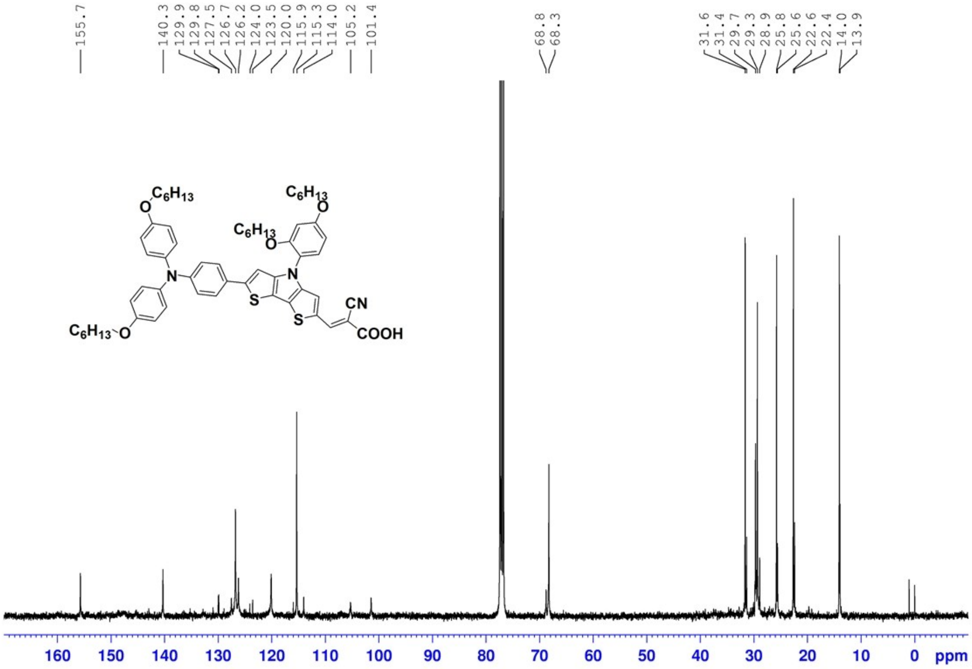
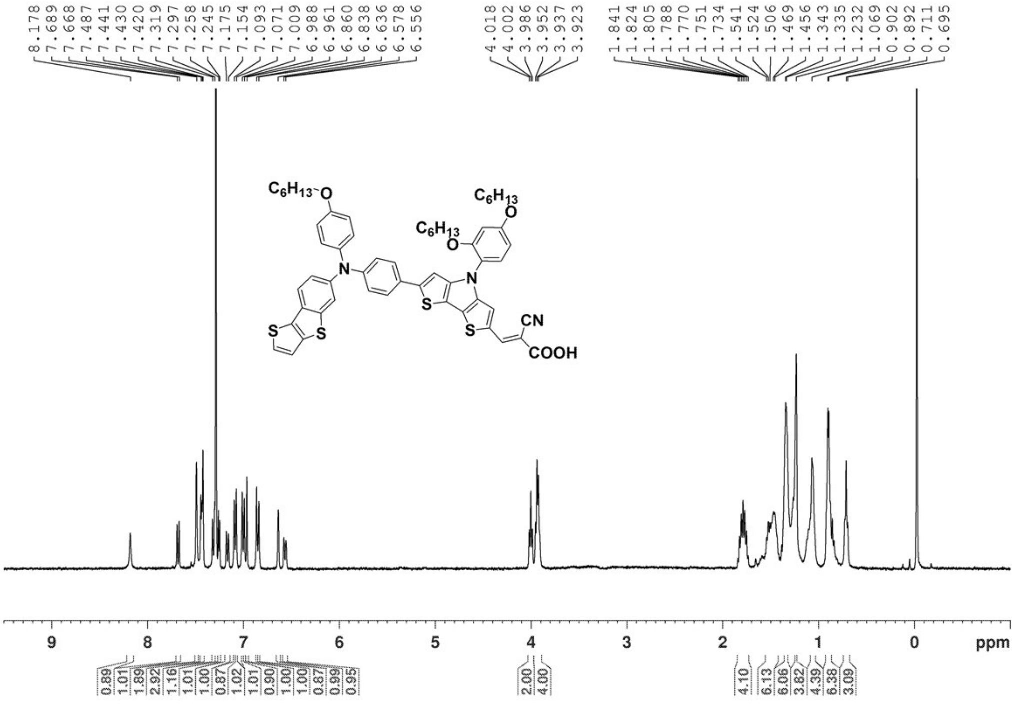
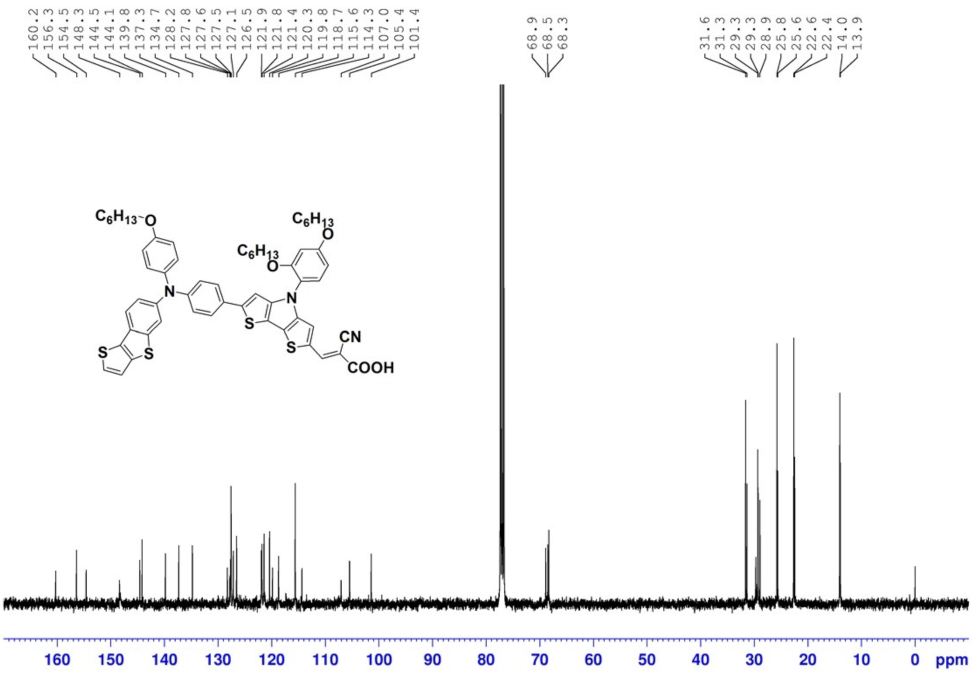


^{1}H NMR ($CDCl_3$+MeOD-d_4) spectra of compound M52A



^{13}C NMR ($CDCl_3$) spectra of compound M52A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