Supplementary information

Influence of N-heterocycle substituent of dithieno[3,2-b:2',3'-d]pyrrole (DTP) spacer as well as sensitizer adsorption time on the photovoltaic properties of arylamine organic dyes

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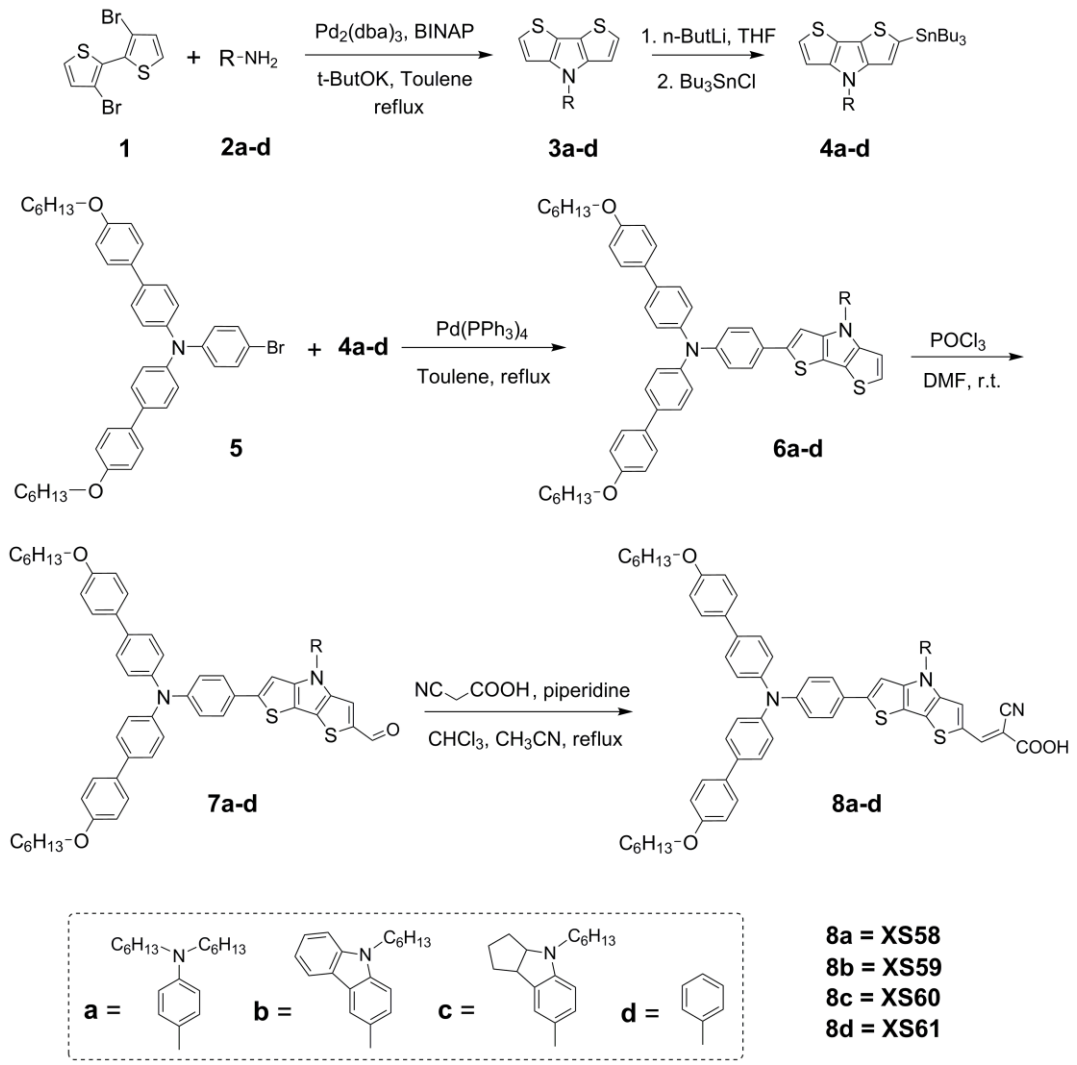
1. Experimental procedures



Scheme S1. Synthetic Routes to the XS58-61

General Procedure for the Synthesis of 3a-d

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*-ButONa (9 mmol, 864 mg) and 3,3',5,5'-tetrabromo-2,2'-bithiophene **1** (3 mmol) were then added consecutively. After five minutes, amine **2** (3.9 mmol) 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 **3**.

3a: light yellow oil (93% yield). IR (KBr): 2955, 2926, 2855, 1522, 1397, 808, 692, 655 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.9 Hz, 2H), 7.18-7.14 (m, 4H), 6.78 (d, *J* = 8.9 Hz, 2H), 3.36 (t, *J* = 7.6 Hz, 3H), 1.70- 1.65 (m, 4H), 1.44-1.40 (m, 2H), 0.98 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 146.7, 144.8, 128.1, 124.5, 122.9, 115.6, 112.3, 112.1, 51.3, 31.8, 27.3, 26.9, 22.8, 14.1. HRMS (ESI) calcd for $C_{26}H_{34}N_2S_2$ ($M+H^+$): 439.2242, found: 439.2225.

3b: light yellow oil (70% yield). IR (KBr): 2924, 2853, 1511, 1465, 1406, 1237, 805, 745, 692, 654 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 2 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 7.69 (dd, *J* = 8.4 Hz, *J* = 2 Hz, 1H), 7.60-7.50 (m, 1H), 7.34-7.30 (m, 1H), 7.24-7.21 (m, 4H), 4.38 (t, *J* = 7.2 Hz, 2H), 2.0-1.94 (m, 2H), 1.52-1.48 (m, 2H), 1.46-1.37 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.1, 141.2, 138.8, 131.7, 126.4, 123.5, 123.2, 122.5, 121.7, 120.6, 119.2, 116.1, 115.4, 112.2, 109.5, 109.1, 43.4, 31.7, 29.1, 27.1, 22.6, 14.1. HRMS (ESI) calcd for $C_{26}H_{24}N_2S_2$ ($M+H^+$): 429.1459, found: 429.1448.

3c: light yellow oil (63% yield). IR (KBr): 2954, 2926, 2855, 1499, 1399, 800, 692 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.21-7.19 (m, 2H), 7.15 (d, *J* = 5.2 Hz, 2H), 7.11 (d, *J* = 5.2 Hz, 2H), 6.36 (d, *J* = 7.8 Hz, 1H), 4.29 (m, 1H), 3.79 (t, *J* = 8.0 Hz, 1H), 3.25-3.15 (m, 2H), 2.09-1.99 (m, 1H), 1.92-1.90 (m, 1H), 1.84-1.79 (m, 1H),

1.77-1.60 (m, 5H), 1.44-1.39 (m, 6H), 0.96 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 150.9, 144.9, 134.9, 128.9, 122.9, 122.7, 119.9, 115.4, 112.3, 104.7, 69.5, 46.9, 45.7, 35.2, 33.4, 31.8, 27.3, 27.1, 24.6, 22.7, 14.1. HRMS (ESI) calcd for $C_{25}H_{28}N_2S_2$ ($M+H^+$): 421.1772, found: 421.1741.

3d: off-white crystal (91% yield). Mp: 141-143℃. IR (KBr): 3434, 3105, 1595, 1508, 1401, 1081, 771. H NMR (400 MHz, $CDCl_3$): 7.58 (d, J = 8.2 Hz, 2H), 7.53-7.49 (m, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.16 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.0, 139.9, 129.8, 126.0, 123.5, 122.6, 117.0, 112.3. HRMS (ESI) calcd for $C_{14}H_9NS_2$ ($M+H^+$): 255.0255, found: 255.0276.

Synthesis of compound of 4a-d

To a solution of compound **3** (0.6 mmol) in dry THF, n-BuLi (0.66 mmol, 2.4 M in hexane) was added dropwise at -78℃ under argon. The mixture was stirred at -78 ℃ for two hours and Tributyltin Chloride (0.66 mmol, 235 mg) was added via a syringe. The reaction was reacted 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 **6a-d** without further purification.

General Procedure for the Synthesis of 6a-d

To a 50 mL two-neck round-bottom flask, toluene (15 mL), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), compound of **5** (407 mg, 0.6 mmol) and **4** 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 **6.**

6a: light yellow oil (58% yield, two steps). IR (KBr): 2956, 2923, 2852, 1462, 1376, 1249, 1020, 817 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.48(m, 9H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.29-7.28 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 4H), 7.17-7.09 (m, 4H), 6.98 (d, *J* = 8.4 Hz, 4H), 6.76 (d, *J* = 8.6 Hz, 2), 4.02 (t, *J* = 6.4 Hz, 4H), 3.34 (t, *J* = 7.5 Hz, 4H), 1.86-1.79 (m, 4H), 1.66-1.48 (m, 8H), 1.37-1.36 (m, 20H), 0.94-0.90 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): 158.5, 146.9, 146.7, 146.1, 145.2, 144.4, 141.6, 135.5, 133.0, 130.0, 127.7, 127.4, 126.1, 124.7, 124.5, 124.1, 124.0, 122.9, 119.1, 115.9, 114.8, 114.5, 112.1, 107.5, 68.1, 51.3, 31.8, 31.6, 29.7, 29.3, 26.9, 25.8, 22.7, 22.6, 14.1, 14.0. HRMS (ESI) calcd for $C_{68}H_{79}N_3O_2S_2$ ($M+H^+$): 1034.5692, found: 1034.5697.

6b: light yellow oil (54% yield, two steps). IR (KBr): 2926, 2854, 1601, 1494, 1245, 820 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 1.8 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 7.7 (dd, *J* = 8.4Hz, *J* = 1.8 Hz, 1H), 7.57- 7.47 (m, 13H), 7.36 (s, 1H), 7.31-7.27 (m, 1H), 7.22-7.15 (m, 8H), 6.98 (d, J = 8.4 Hz, 4H), 4.39 (t, *J* = 7.2 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 4H), 1.99-1.92 (m, 2H), 1.87-1.79 (m, 4H), 154-1.49 (m, 6H), 1.44-1.36 (m, 12H), 0.94-0.90 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 158.5, 146.8, 146.1, 145.4, 144.7, 142.0, 141.2, 138.9, 135.5, 133.0, 131.6, 129.9, 127.7, 127.4, 126.4, 126.2, 124.6, 124.0, 123.5, 123.2, 122.4, 121.8, 120.7, 119.2, 116.4, 115.6, 114.9, 114.8, 112.1, 109.5, 109.1, 107.4, 68.1, 43.4, 31.6, 29.7, 29.3, 29.0, 27.0, 25.8, 22.6, 22.5, 14.1. HRMS (ESI) calcd for $C_{68}H_{69}N_3O_2S_2$ ($M+H^+$): 1024.4910, found: 1024.4967.

6c: light yellow oil (72% yield, two steps). IR (KBr): 2927, 2857, 1603, 1495, 1245, 829 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.49 (m, 10H), 7.29 (s, 1H), 7.23-7.09 (m, 10H), 6.99 (d, *J* = 8.4 Hz, 4H), 6.38 (d, *J* = 8.0 Hz, 1H), 4.32-4.29 (m, 1H), 4.02 (t, *J* = 6.5 Hz, 4H), 3.85-3.79 (m, 1H), 3.28-3.14 (m, 2H), 2.10-2.0 (m, 1H), 1.93-1.91 (m, 1H), 1.87-1.80 (m, 5H), 1.76-1.62 (m, 5H), 1.55-1.47 (m, 4H), 1.41-1.34 (m, 14H), 0.98-0.90 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): 158.5, 151.0, 146.7, 146.1, 145.3, 144.5, 141.5, 135.5, 134.9, 133.0, 130.0, 128.8, 127.7, 127.4, 126.2, 124.6,124.1, 123.1, 122.8, 120.1, 115.8, 114.8, 114.4, 112.2, 107.6, 104.7, 69.5, 68.1, 46.8, 45.7, 35.2, 33.5, 31.8, 31.7, 29.3, 27.3, 27.1, 25.8, 24.6, 22.7, 22.6, 14.2, 14.1. HRMS (ESI) calcd for $C_{67}H_{73}N_3O_2S_2$ ($M+H^+$): 1016.5222, found: 1016.5226.

6d: light yellow oil (54% yield, two steps). IR (KBr): 2924, 2858, 1601, 1496, 1224, 1174, 818. H NMR (400 MHz, $CDCl_3$): 7.65(d, *J* = 8.0 Hz, 2H), 7.60-7.49 (m, 12H), 7.40-7.37 (m, 2H), 7.23-7.16 (m, 8H), 7.0-6.97 (d, *J* = 8.6 Hz, 4H), 4.02 (t, *J* = 6.4 Hz, 4H), 1.87-1.80 (m, 4H), 1.55-1.46 (m, 4H), 1.41-1.37 (m, 8H), 0.95 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 158.5, 146.9, 146.0, 144.3, 143.5, 142.3, 139.8, 135.6, 132.9, 129.8, 129.6, 127.7, 127.4, 126.3, 126.1, 124.6, 123.9, 123.5, 122.8, 117.3, 115.7, 114.8, 112.2, 107.4, 68.1, 31.6, 29.3, 25.8, 22.6, 14.1. HRMS (ESI) calcd for $C_{56}H_{54}N_2O_2S_2$ ($M+H^+$): 851.3705, found: 851.3751.

General Procedure for the Synthesis of 7a-d

$POCl_3$ (0.5 mmol, 77 mg) was added dropwise to dry DMF (5 mL) at 0 ℃. The reaction was kept at 0 ℃ for 30 minutes and the dry DMF (5 mL) solution of compound **6** (0.2 mmol) was added via a syringe. After the addition, the mixture was

stirred for four hours 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 compounds **7**.

7a: yellow solid (64% yield). Mp: 51-53℃. IR (KBr): 2956, 2924, 2853, 1657, 1463, 1377, 821 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 9.85 (s, 1H), 7.70 (s, 1H), 7.56-7.49 (m, 10H), 7.40 (d, *J* = 9 Hz, 2H), 7.25-7.21 (m, 5H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 4H), 6.77 (d, *J* = 9.0 Hz, 2H), 4.02 (t, *J* = 6.6 Hz, 4H), 3.35 (t, *J* = 7.4 Hz, 4H), 1.87-1.80 (m, 4H), 1.67-1.64 (m, 4H), 1.54-1.47 (m, 4H), 1.39-1.36 (m, 20H), 0.96-0.92 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): 182.8, 160.1, 158.6, 154.7, 150.4, 149.6, 147.6, 147.4, 145.9, 145.8, 135.9, 135.8, 132.8, 127.7, 127.5, 126.5, 126.4, 124.9, 124.8, 123.4, 123.3, 114.8, 112.0, 107.4, 105.3, 68.1, 51.3, 31.8, 31.6, 29.7, 29.3, 26.9, 25.8, 22.7, 22.6, 14.1, 14.0. HRMS (ESI) calcd for $C_{69}H_{79}N_3O_3S_2$ ($M+H^+$): 1062.5641, found: 1062.5627.

7b: yellow solid (85% yield). Mp: 89-92℃. IR (KBr): 2955, 2924, 2853, 1654, 1601, 1494, 1244, 820 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 9.86 (s, 1H), 8.27 (d, *J* = 1.8 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 7.76 (s, 1H), 7.67 (dd, *J* = 8.4 Hz, *J* = 1.8 Hz, 1H), 7.6-7.48 (m, 13H), 7.33-7.28 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 4H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 4H), 4.41 (t, *J* = 7.2 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 4H), 2.0-1.92 (m, 2H), 1.86-1.79 (m, 4H), 1.52-1.46 (m, 6H), 1.39-1.36 (m, 12H), 0.94-0.91 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 182.8, 158.6, 149.8, 147.8, 147.7,

145.8, 144.2, 141.3, 140.1, 139.3, 135.9, 132.8, 130.9, 130.3, 128.8, 128.5, 127.7, 127.5, 126.7, 126.6, 124.9, 124.7, 123.7, 123.3, 122.2, 121.8, 120.7, 119.4, 115.9, 114.8, 109.7, 109.2, 106.7, 68.1, 43.4, 31.9, 31.6, 29.7, 29.3, 27.0, 25.8, 22.6, 22.5, 14.1, 14.0. HRMS (ESI) calcd for $C_{69}H_{69}N_3O_3S_2$ ($M+H^+$): 1052.4858, found: 1052.4884.

7c: yellow solid (71% yield). Mp: 122-124℃. IR (KBr): 2955, 2925, 2854, 1655, 1599, 1496, 1246, 820 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.67 (s, 1H), 7.55-7.49 (m, 10H), 7.23-7.15 (m, 9H), 6.98 (d, *J* = 8.6 Hz, 4H), 6.36 (d, *J* = 8.2 Hz, 1H), 4.34-4.31 (m, 1H), 4.02 (t, *J* = 6.5 Hz, 4H), 3.84-3.79 (m, 1H), 3.27-3.14 (m, 2H), 2.09-2.01 (m, 1H), 1.95-1.89 (m, 1H), 1.87-1.80 (m, 4H), 1.76-1.61 (m, 6H), 1.54-1.49 (m, 4H), 1.41-1.36 (m, 14H), 0.96-0.91 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 180.8, 158.6, 151.5, 149.7, 147.7, 147.3, 145.8, 144.1, 139.8, 135.9, 135.2, 132.9, 128.7, 127.7, 127.5, 127.3, 126.6, 124.9, 124.1, 123.5, 123.4, 120.7, 120.2, 114.8, 114.1, 106.9, 104.6, 69.4, 68.1, 46.5, 45.6, 35.3, 33.4, 31.7, 31.6, 29.3, 27.2, 27.0, 25.8, 24.5, 22.7, 22.6, 14.1, 14.0. HRMS (ESI) calcd for $C_{68}H_{73}N_3O_3S_2$ ($M+H^+$): 1044.5172, found: 1044.5199.

7d: yellow solid (83% yield). Mp: 90-93℃. IR (KBr): 2925, 2857, 1654, 1600, 1496, 1404, 1285, 1242, 819. H NMR (400 MHz, $CDCl_3$): 9.87 (s, 1H), 7.78 (s, 1H), 7.64-7.59 (m, 4H), 7.56-7.49 (m, 10H), 7.47-7.42 (m, 1H), 7.32 (s, 1H), 7.22 (d, *J* = 8.4 Hz, 4H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 4H), 4.02 (t, *J* = 6.5 Hz, 4H), 1.87-1.79 (m, 4H), 1.54- 1.45 (m, 4H), 1.40-1.37 (m, 8H), 0.94 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 182.8, 158.6, 148.5, 148.0, 147.9, 145.8, 143.0,

140.3, 138.8, 136.0, 132.8, 130.1, 128.3, 127.7, 127.5, 127.1, 126.6, 125.4, 125.0, 123.2, 123.1, 115.4, 114.8, 106.7, 68.1, 31.6, 29.3, 25.8, 22.6, 14.1. HRMS (ESI) calcd for $C_{57}H_{54}N_2O_3S_2$ ($M+H^+$): 879.3654, found: 879.3672.

General Procedure for the Synthesis of 8a-d

To a stirred solution of compound **7** (0.1 mmol) and cyanoacetic acid (0.15 mmol) in acetonitrile (6 ml) was added chloroform (3 mL) and piperidine (0.3 mmol). The reaction mixture was refluxed for 8 hours. Additional cyanocertic acid (0.1 mmol) and piperdine (0.2 mmol) were added. The mixture was refluxed continued for 8 hours and then acidified with 1 M hydrochloric acid aqueous solution (15 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 the target dyes.

8a: red power (58% yield). Mp: 152-155℃. IR (KBr): 3426, 2956, 2925, 1736, 1609, 1463, 1377, 1283, 1019, 821 cm^{-1}. H NMR (400 MHz, DMSO-d_6): δ 8.49 (s, 1H), 8.05 (s, 1H), 7.74-7.63 (m, 3H), 7.53-7.48 (m, 9H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 4H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 4H), 6.75 (d, *J* = 8.4 Hz, 2H), 3.91 (t, *J* = 8.2 Hz, 4H), 3.29 (m, 4H), 1.70-1.62 (m, 4H), 1.53-1.38 (m, 8H), 1.29-1.23 (m, 20H), 0.91-0.86 (m, 12H). ^{13}C NMR (100 MHz, Pyridine-d_5): 160.2, 151.3, 150.2, 149.1, 148.9, 147.2, 145.6, 137.3, 136.9, 136.5, 136.3, 135.9, 135.1, 133.9, 130.2, 129.1, 128.9, 128.1, 127.8, 126.4, 126.3, 126.0, 124.9, 123.9, 116.4, 115.8, 113.7, 108.8, 69.2, 55.9, 32.9, 32.7, 30.4, 28.5, 27.9, 26.9, 23.9, 23.7, 15.1, 15.0. HRMS (ESI) calcd for $C_{72}H_{80}N_4O_4S_2$ ($M+H^+$): 1129.5699, found:

1129.5662.

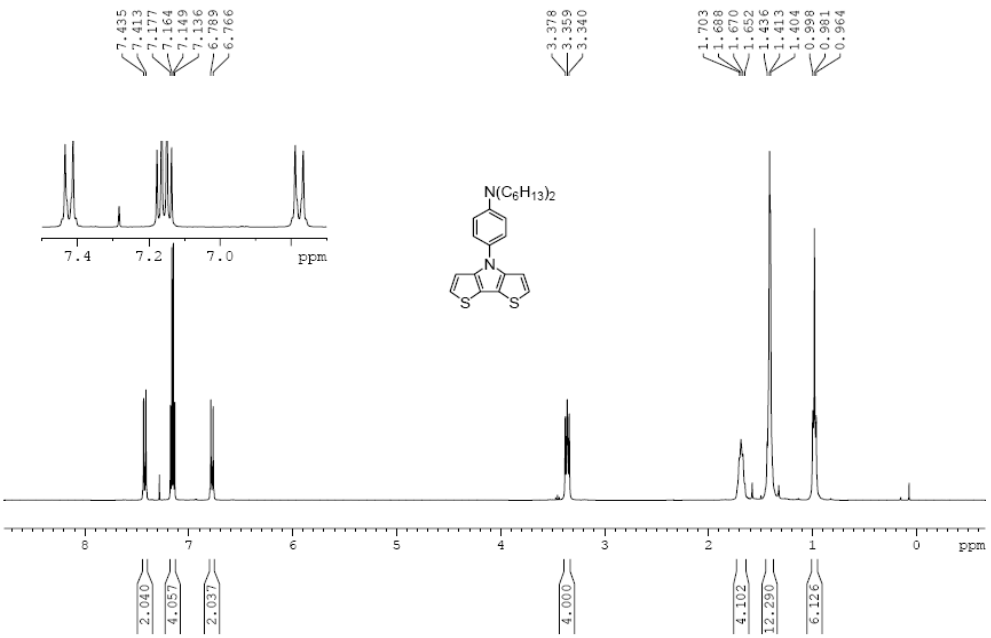
8b: red power (75% yield). Mp: 160-163℃. IR (KBr): 2956, 2924, 2850, 1675, 1603, 1462, 1377, 1022, 820 cm^{-1}. H NMR (400 MHz, DMSO-d_6): δ 8.51 (s, 1H), 8.46 (d, *J* = 1.4 Hz, 1H), 8.27 (d, *J* = 7.6 Hz, 1H), 8.16 (s, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.73-7.65 (m, 4H), 7.60 (s, 1H), 7.53-7.50 (m, 9H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 4H), 7.0 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 4H), 4.45 (t, *J* = 6.4 Hz, 2H), 3.94 (t, *J* = 6.4 Hz, 4H), 1.83-1.76 (m, 2H), 1.73-1.66 (m, 4H), 1.42-1.38 (m, 4H), 1.31-1.23 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 6H), 0.81 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, Pyridine-d_5): 159.0, 150.2, 149.1, 147.9, 146.1, 144.7, 141.5, 139.5, 136.1, 135.8, 135.4, 135.1, 134.7, 134.1, 132.8, 130.5, 129.0, 127.9, 127.7, 127.0, 126.9, 125.3, 123.8, 123.7, 123.4, 123.1, 122.7, 122.1, 121.2, 119.6, 116.2, 115.2, 115.0, 110.3, 109.7, 107.7, 68.0, 43.1, 31.5, 29.3, 29.1, 26.8, 25.8, 22.6, 22.5, 13.9, 13.8. HRMS (ESI) calcd for $C_{72}H_{70}N_4O_4S_2$ ($M+H^+$): 1119.4917, found: 1119.4961.

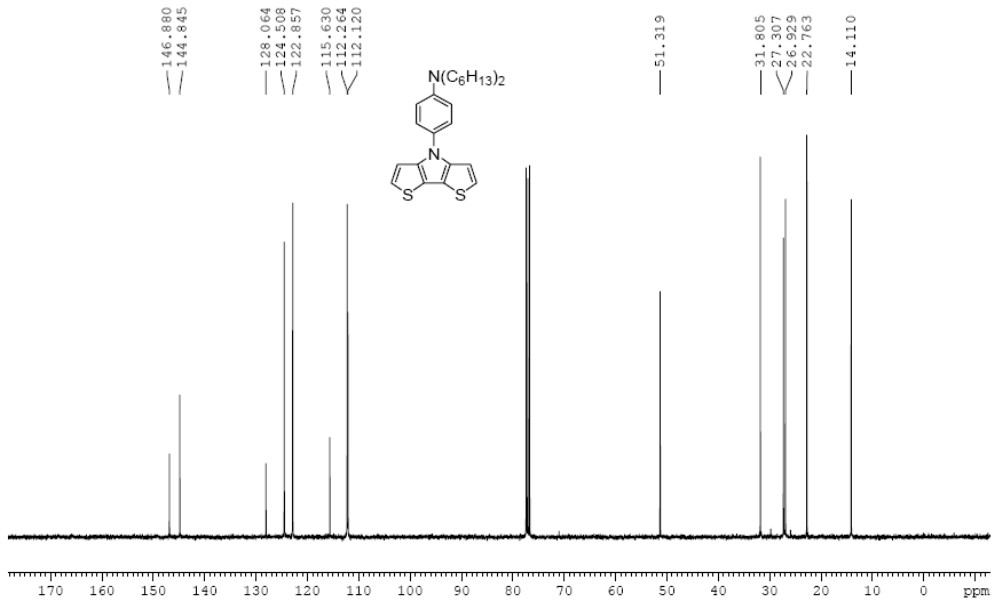
8c: red power (91% yield). Mp: 194-198℃. IR (KBr): 3423, 2928, 2856, 1676, 1571, 1495, 1246, 1137 cm^{-1}. H NMR (400 MHz, DMSO-d_6): δ 8.52 (s, 1H), 8.06 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.55-7.49 (m, 9H), 7.19-7.17 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 4H),7.01(d, *J* = 8.4 Hz, 2H), 6.93(d, *J* = 8.4 Hz, 4H), 6.40 (d, *J* = 8.8 Hz, 1H), 4.27−4.24 (m, 1H), 3.94 (t, *J* = 6.4 Hz, 4H), 3.77-3.73 (m, 1H), 3.5-3.48 (m, 1H), 3.26-3.19 (m, 2H), 3.13-3.06 (m, 1H), 2.02-1.95 (m, 1H), 1.85-1.75 (m, 2H), 1.73-1.62 (m, 5H), 1.57-1.49 (m, 2H), 1.44-1.37 (m, 4H), 1.32-1.30 (m, 14H), 0.90-0.87 (m, 9H). ^{13}C NMR (100 MHz, Pyridine-d_5): 159.0, 151.8, 150.2, 149.1, 147.9, 146.1, 144.7, 136.1, 135.8, 135.6, 135.4, 135.1, 134.7, 133.9, 132.8, 129.1,

127.9, 127.7, 127.6, 126.9, 125.3, 123.7, 123.4, 123.1, 122.712.4, 115.3, 114.5, 107.8, 105.0, 69.4, 68.0, 46.4, 45.7, 35.5, 33.4, 31.7, 31.5, 29.3, 27.3, 26.9, 25.8, 24.6, 22.7, 22.6, 14.0, 13.9. HRMS (ESI) calcd for $C_{71}H_{74}N_4O_4S_2$ ($M+H^+$): 1111.5229, found: 1111.5166.

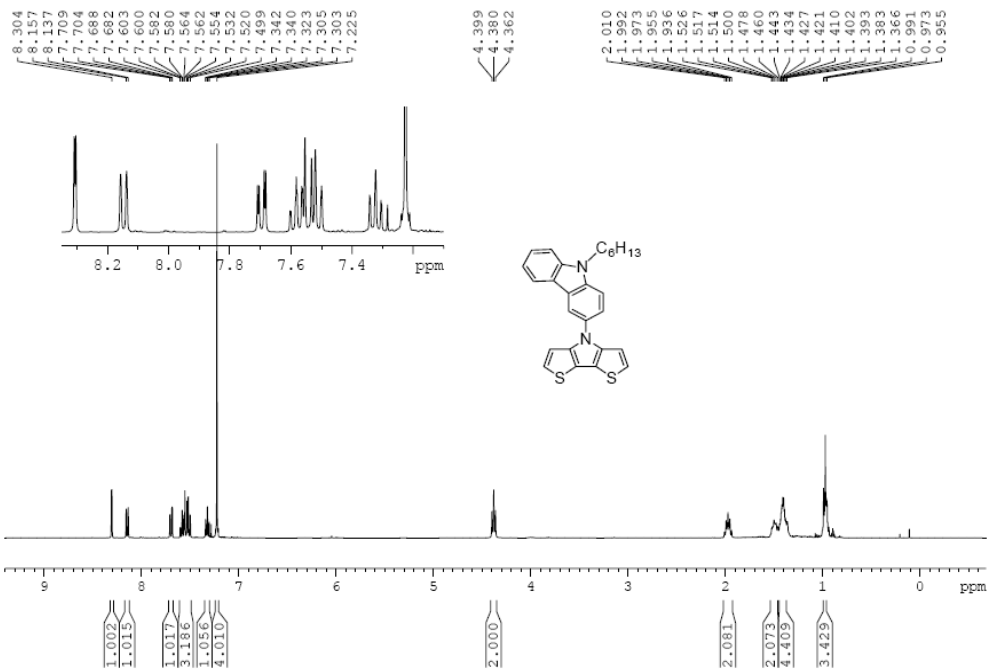
8d: red power (89% yield). Mp: 152-154℃. IR (KBr): 3441, 2924, 2856, 1678, 1570, 1495, 1400, 1249, 821. H NMR (400 MHz, DMSO-d_6): 8.46 (s, 1H), 8.17 (s, 1H), 7.75-7.71 (m, 4H), 7.68-7.62 (m, 3H), 7.58-7.53 (m, 8H), 7.48-7.44 (m, 1H), 7.11 (d, J = 8.4 Hz, 4H), 7.05 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.4 Hz, 4H), 3.95 (t, J = 6.4 Hz, 4H), 1.74-1.67 (m, 4H), 1.43-1.38 (m, 4H), 1.32-1.30 (m, 8H), 0.88 (t, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, Pyridine-d_5): 159.1, 150.2, 149.1, 148.5, 148.0, 146.9, 146.1, 143.4, 138.8, 136.2, 135.8, 135.4, 135.1, 134.7, 134.4, 132.8, 130.2, 128.9, 127.7, 127.0, 125.3, 123.7, 122.7, 115.8, 115.3, 107.7, 73.5, 31.5, 29.3, 25.8, 22.6, 13.9. HRMS (ESI) calcd for $C_{60}H_{55}N_3O_4S_2$ ($M+H^+$): 946.3712, found: 946.3798.

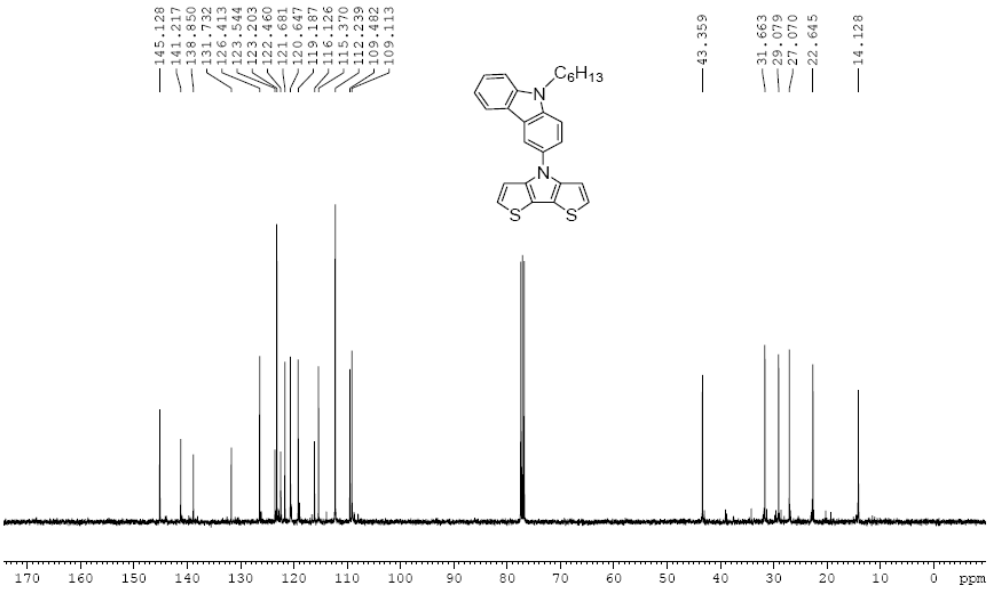
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 3a



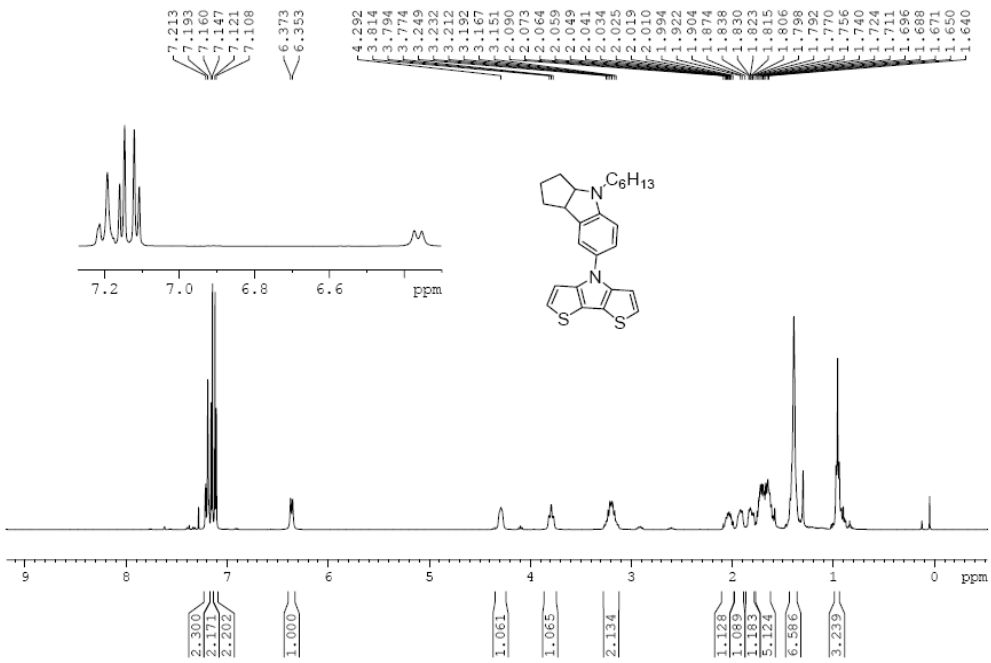


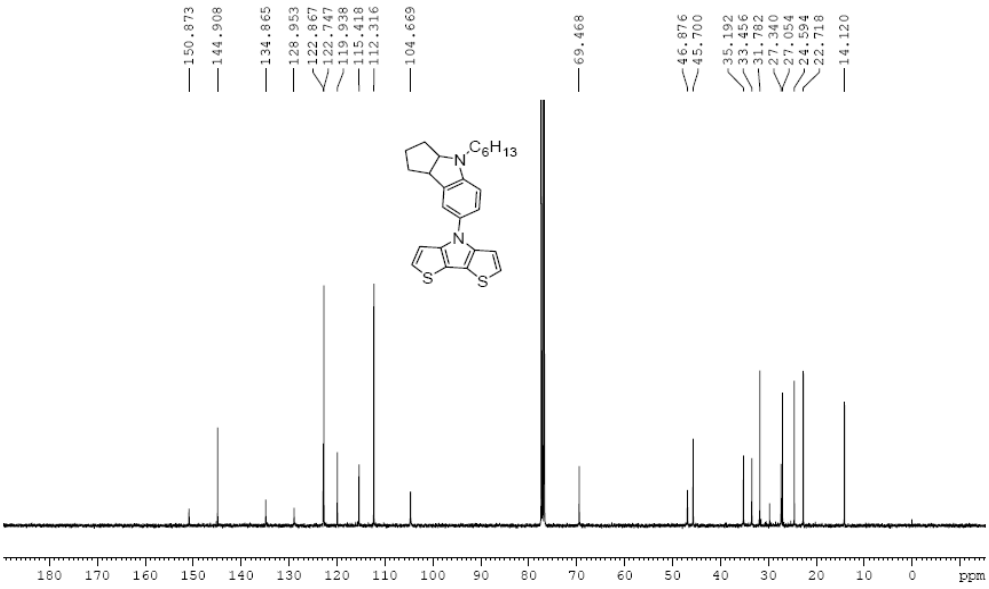
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 3b



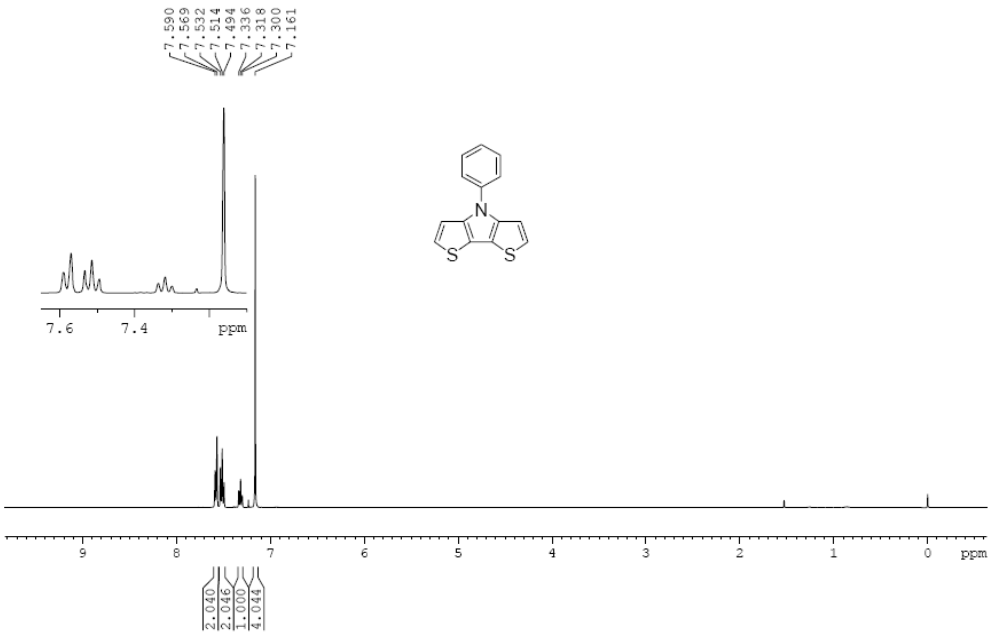


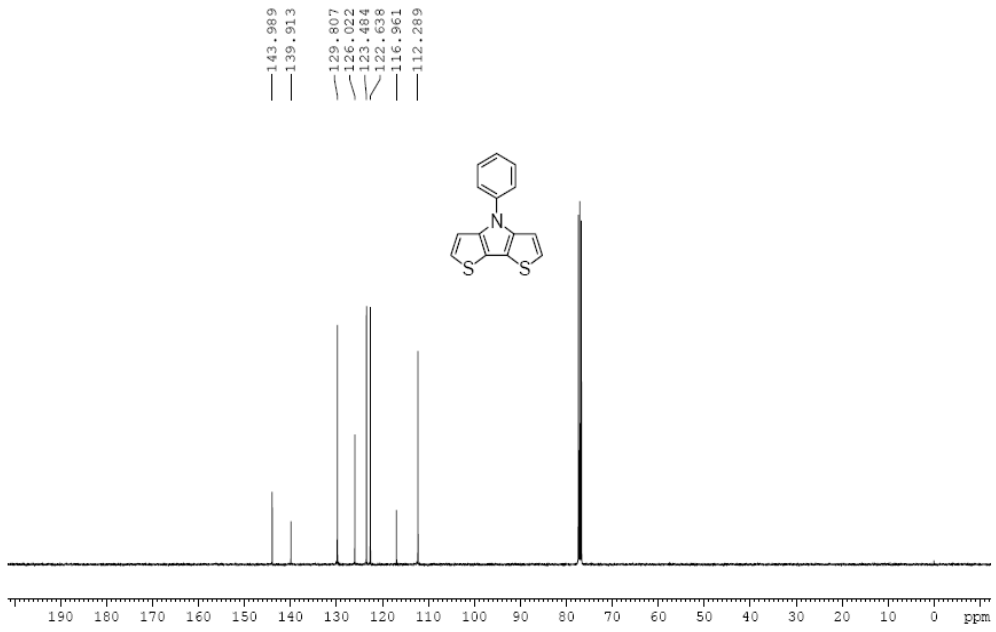
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 3c



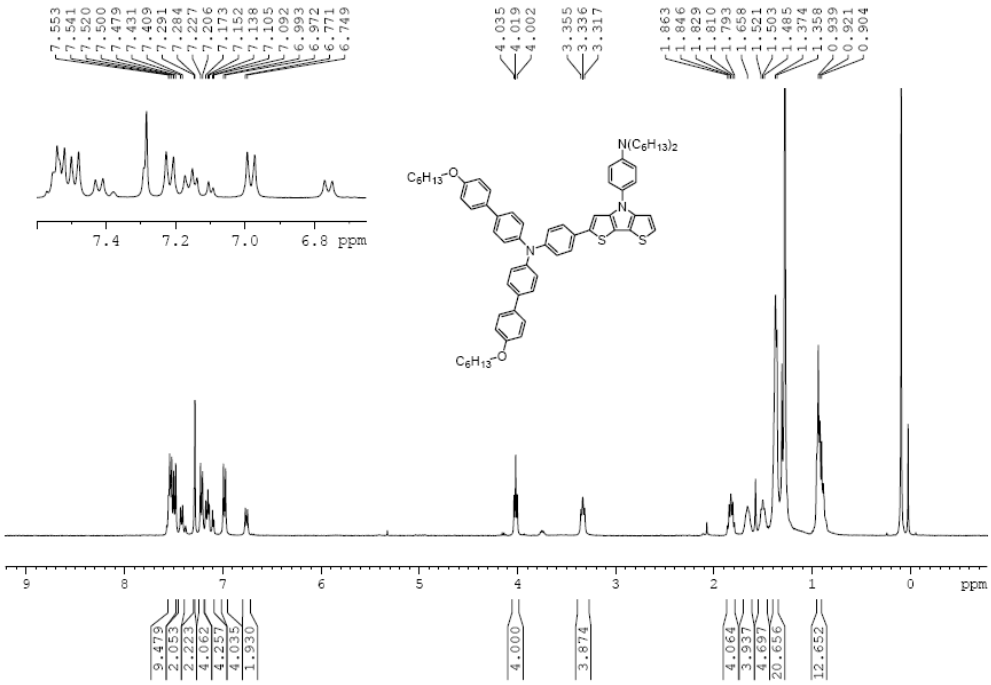


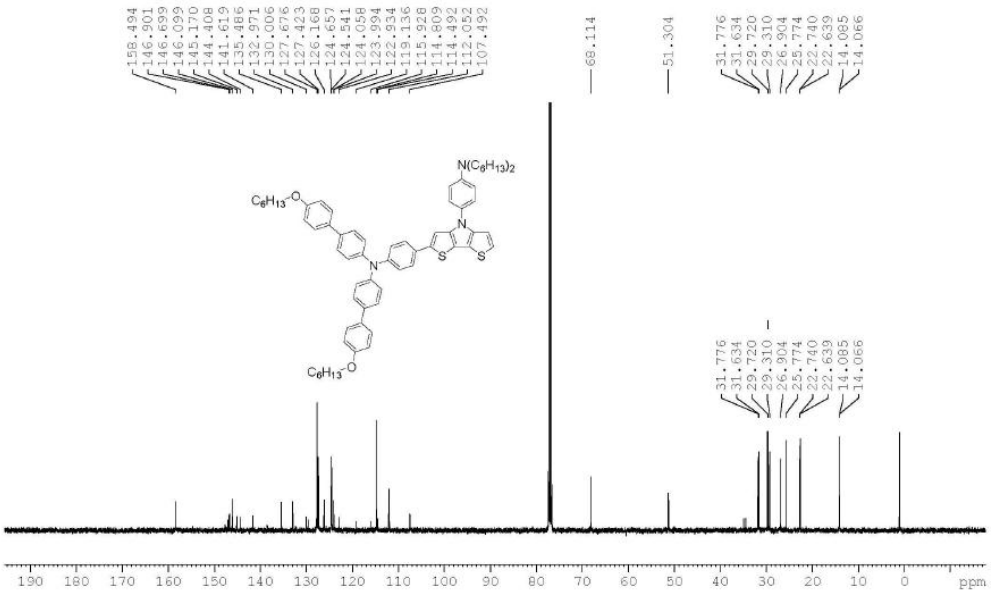
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 3d



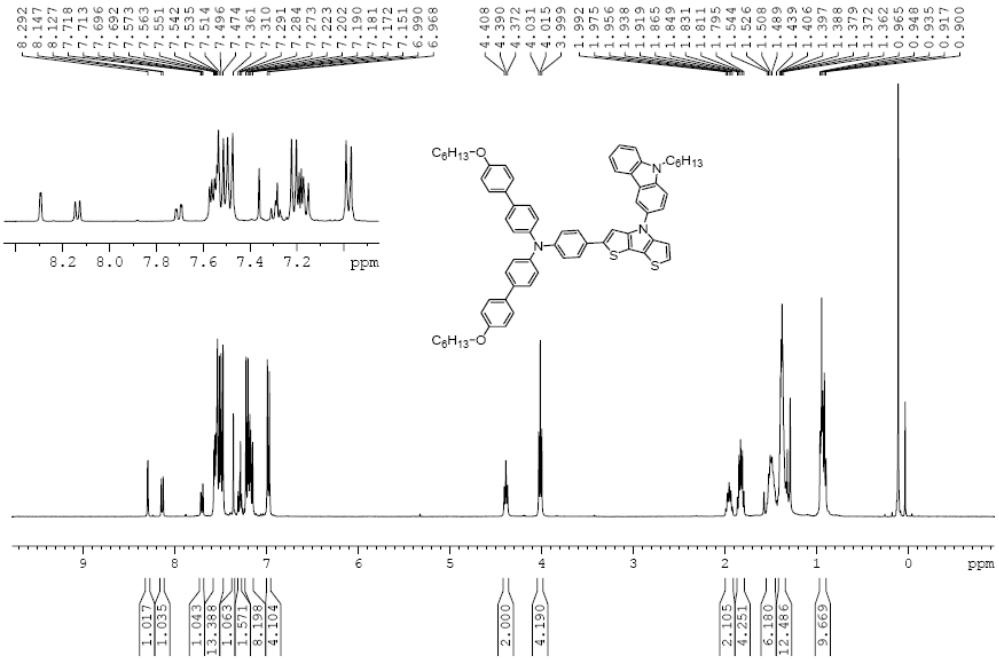


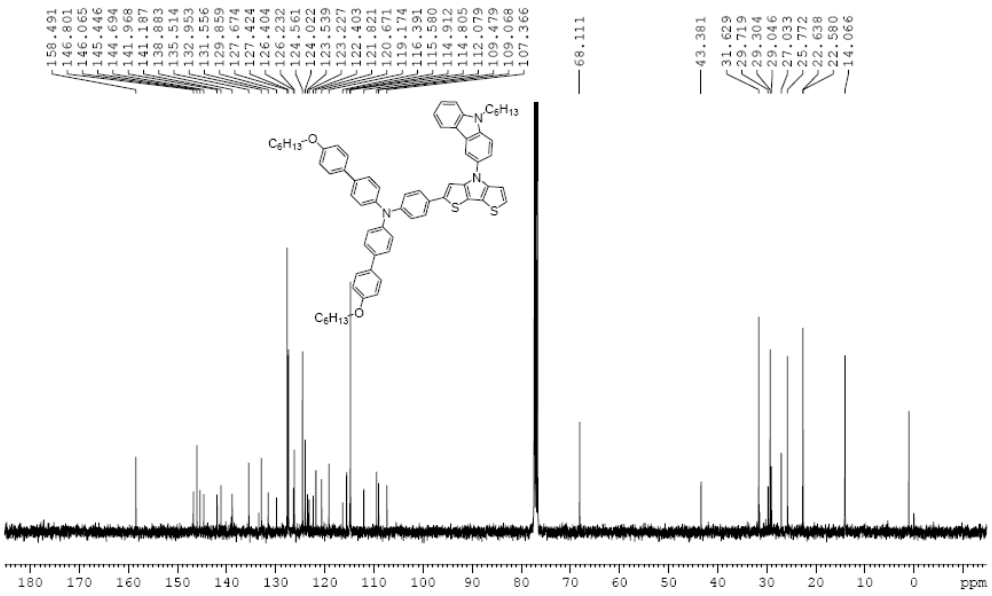
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 6a



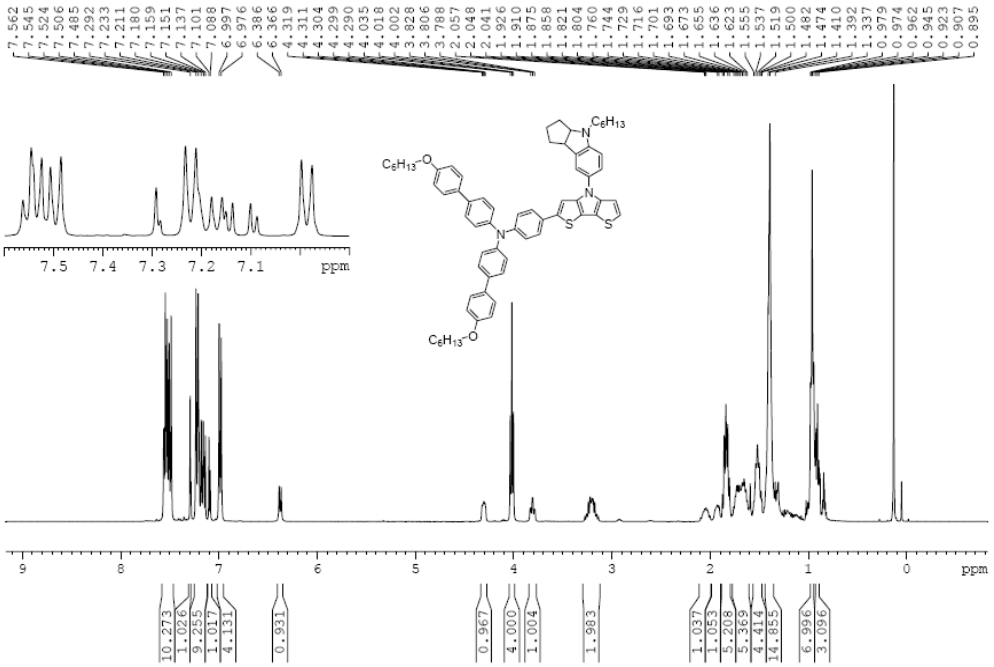


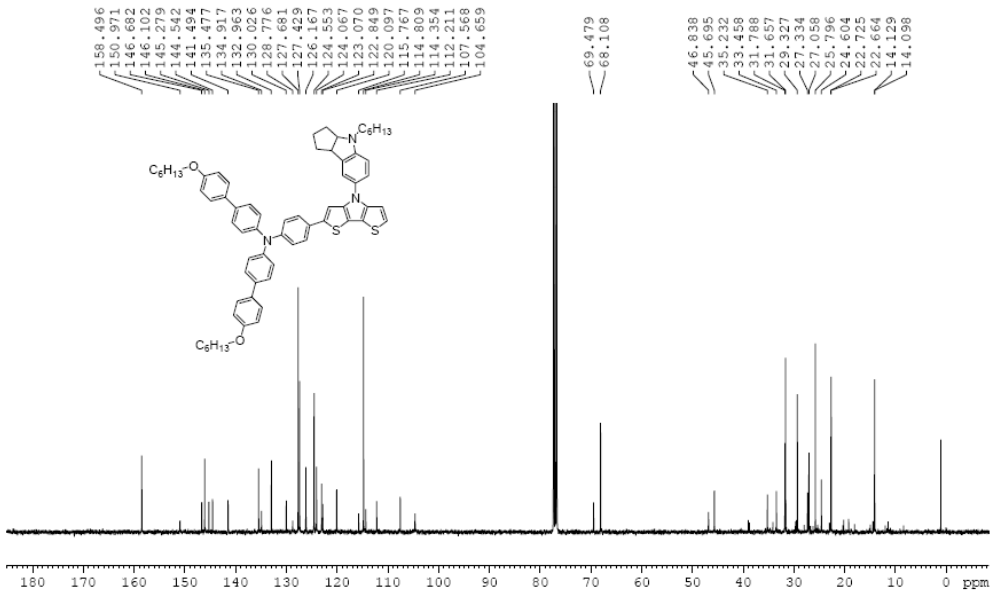
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 6b



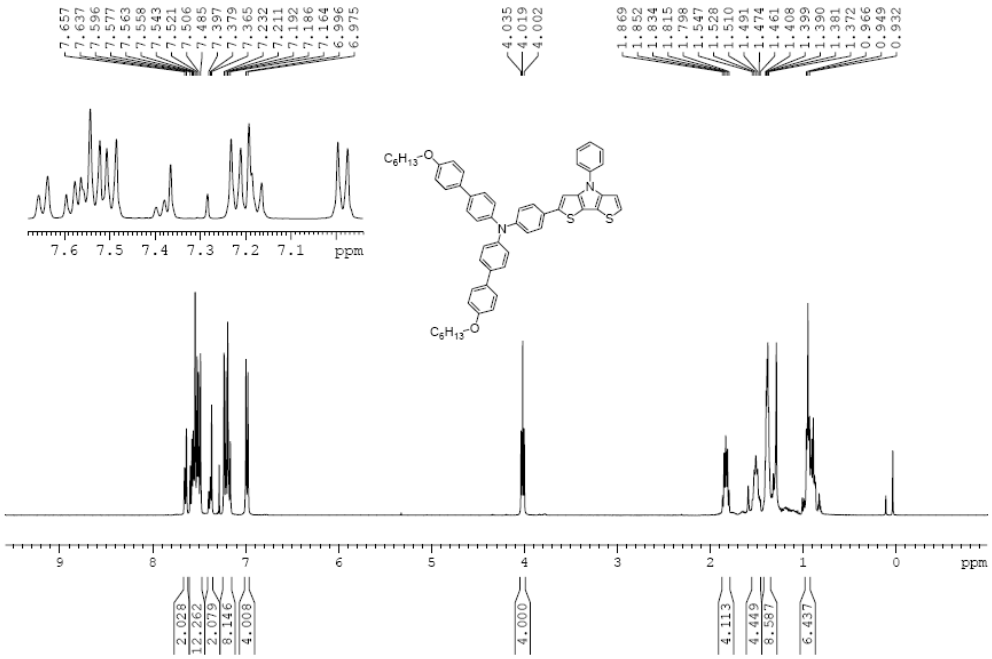


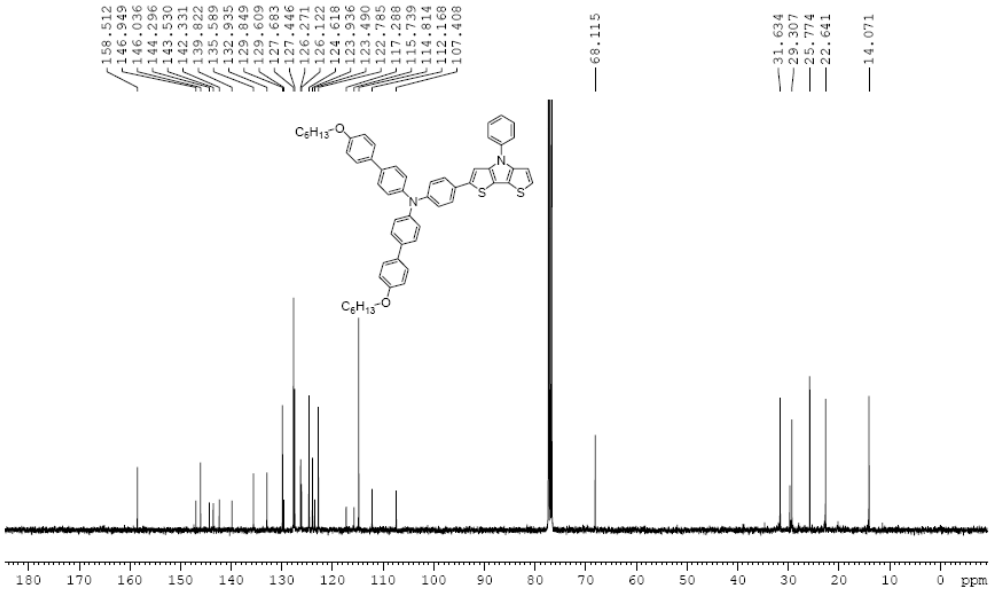
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 6c



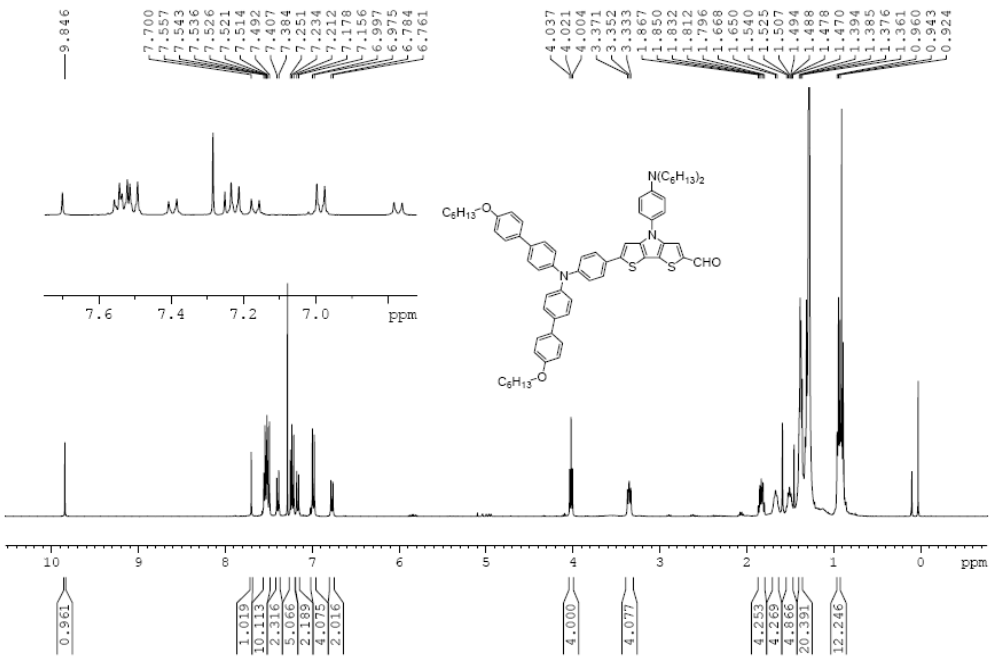


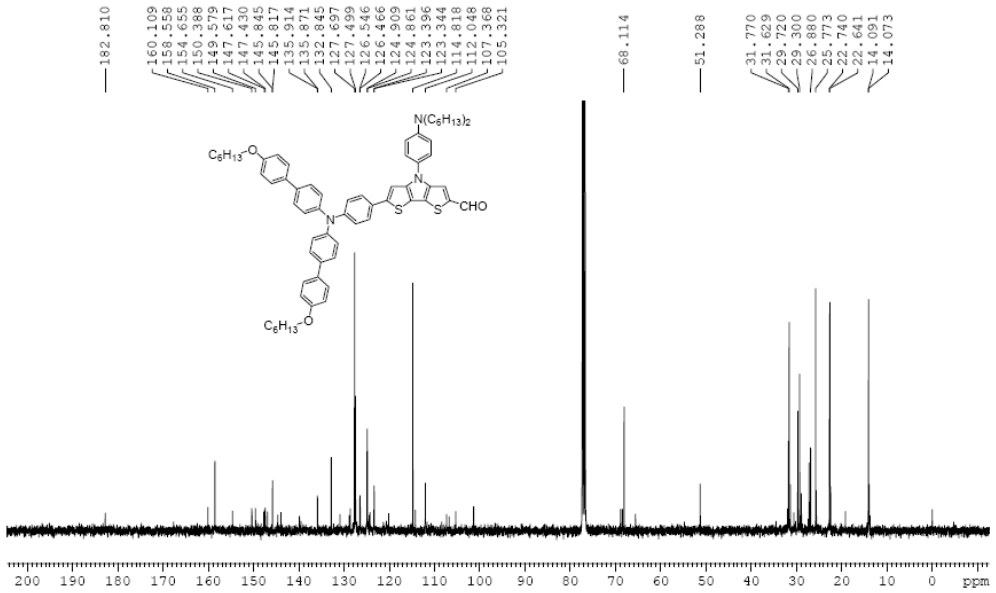
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 6d



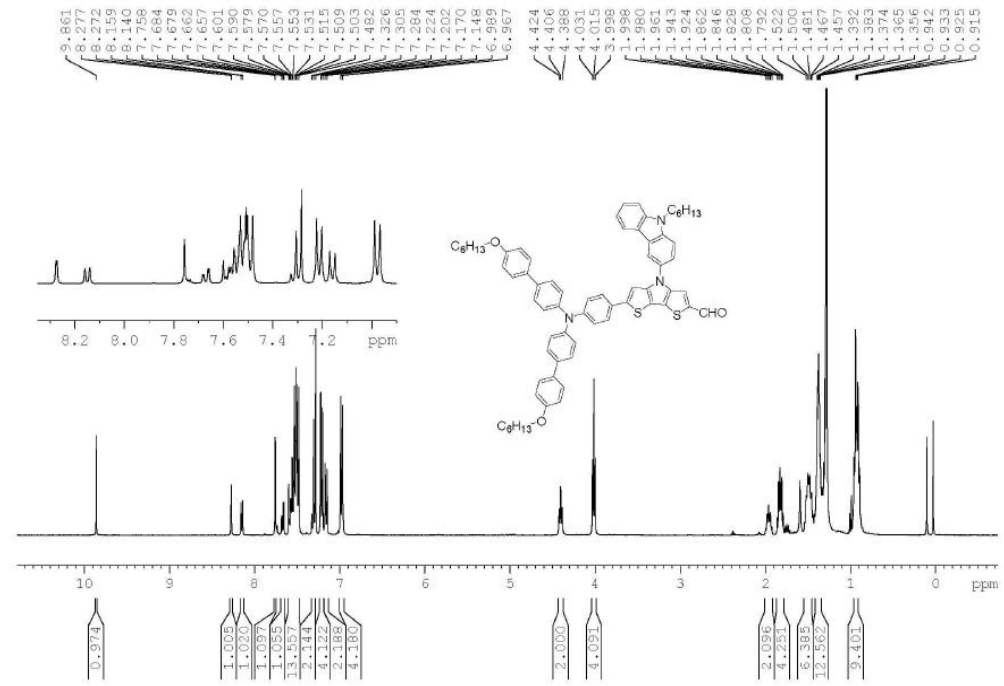


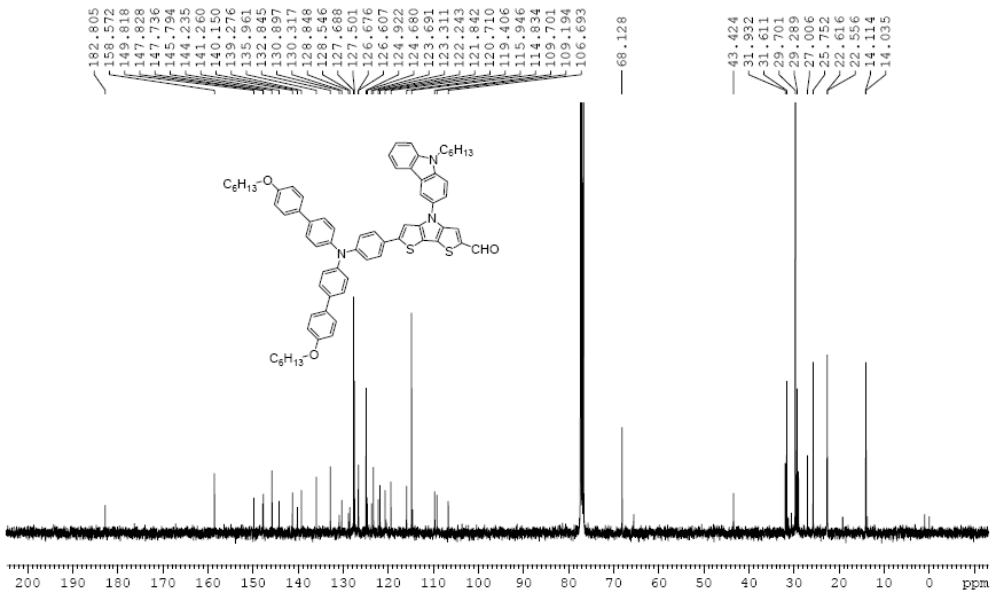
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 7a



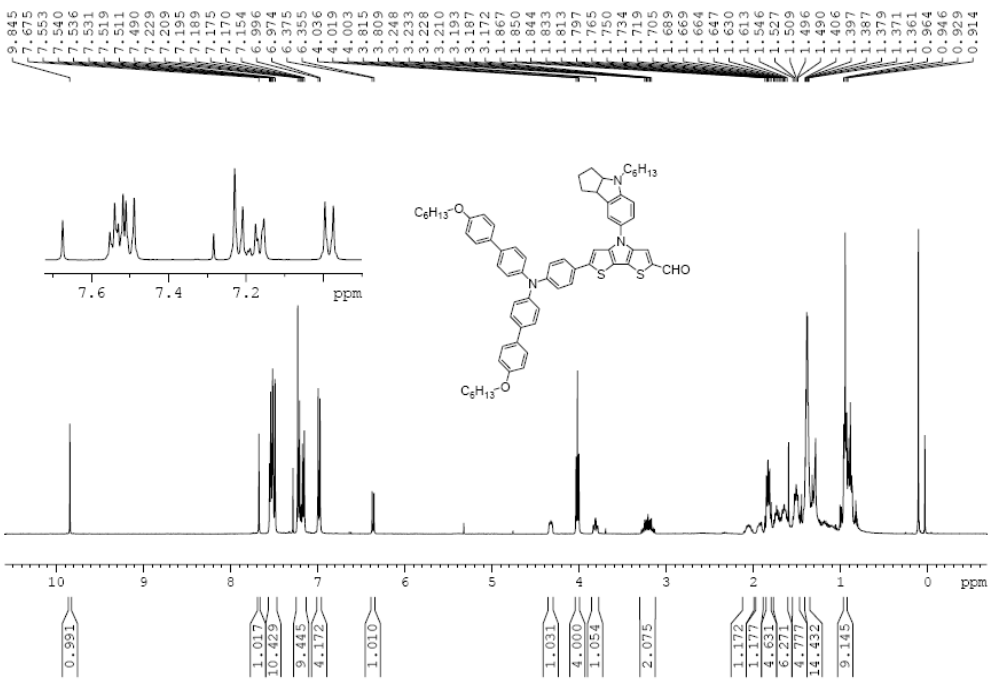


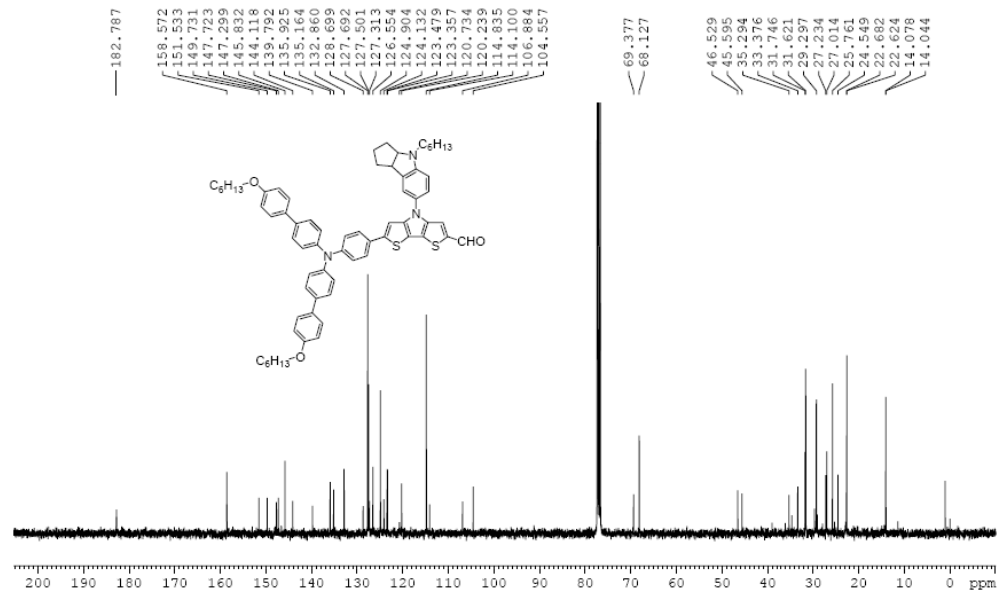
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 7b



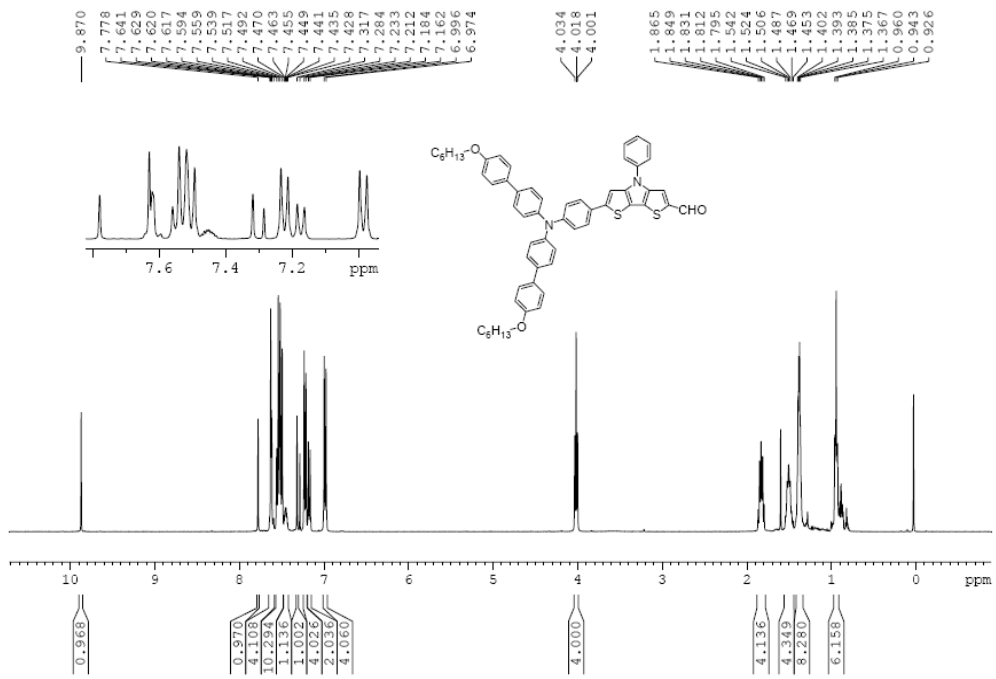


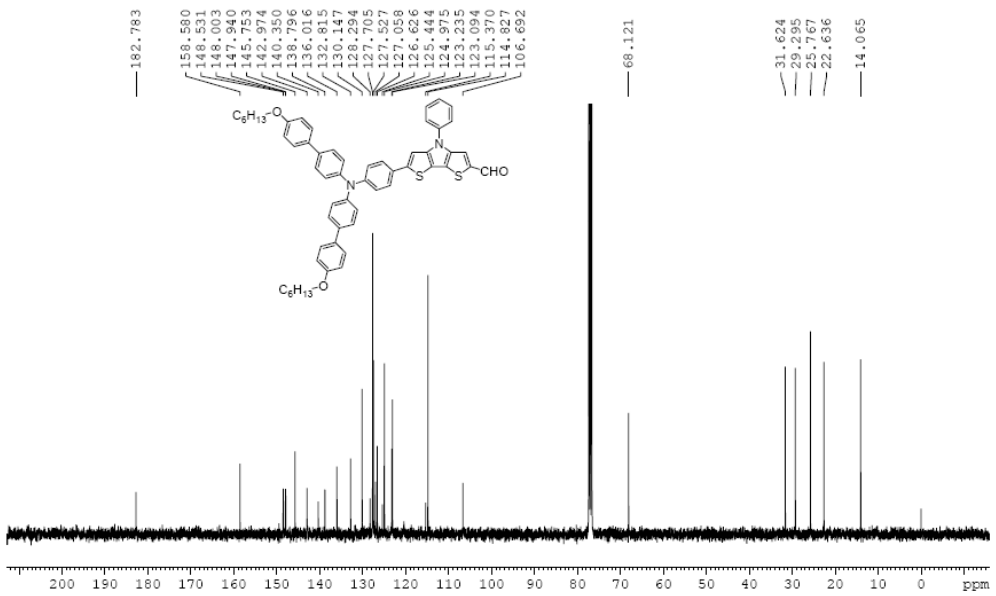
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 7c



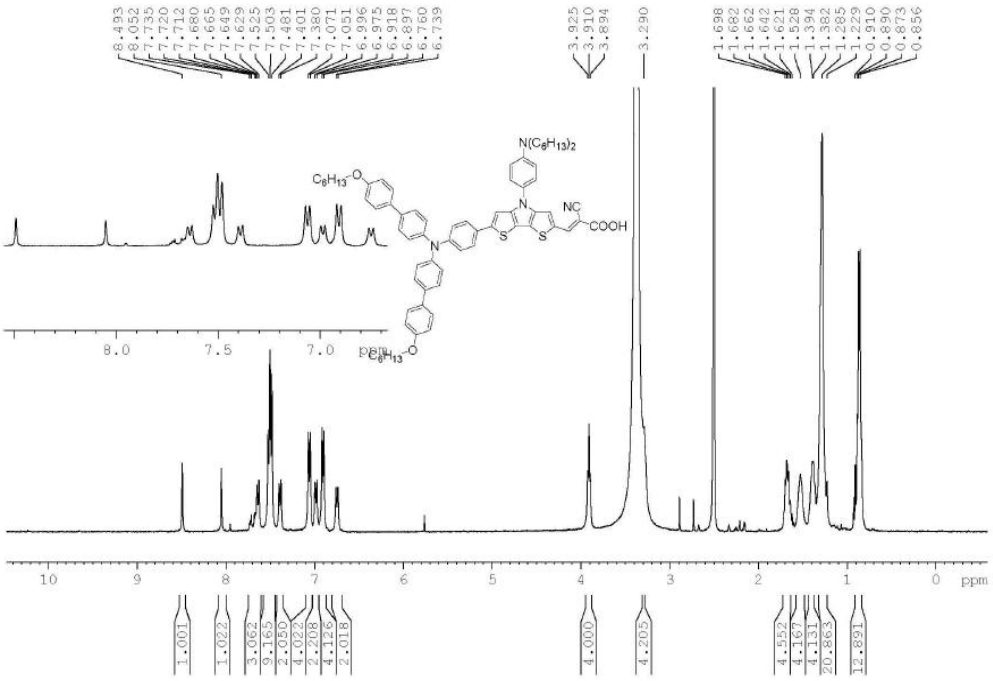


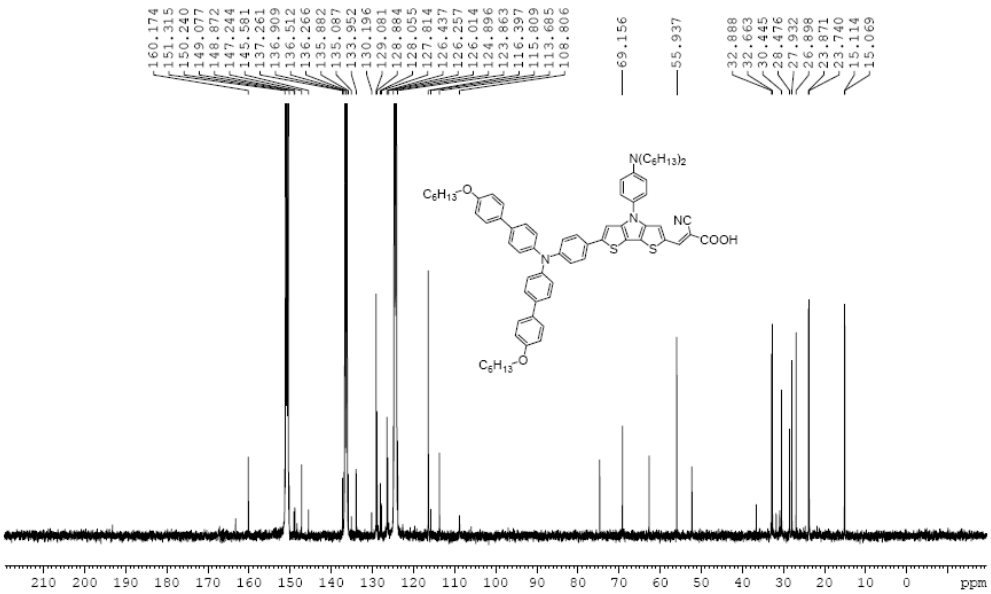
^{1}H and ^{13}C NMR ($CDCl_3$) spectra of compound 7d



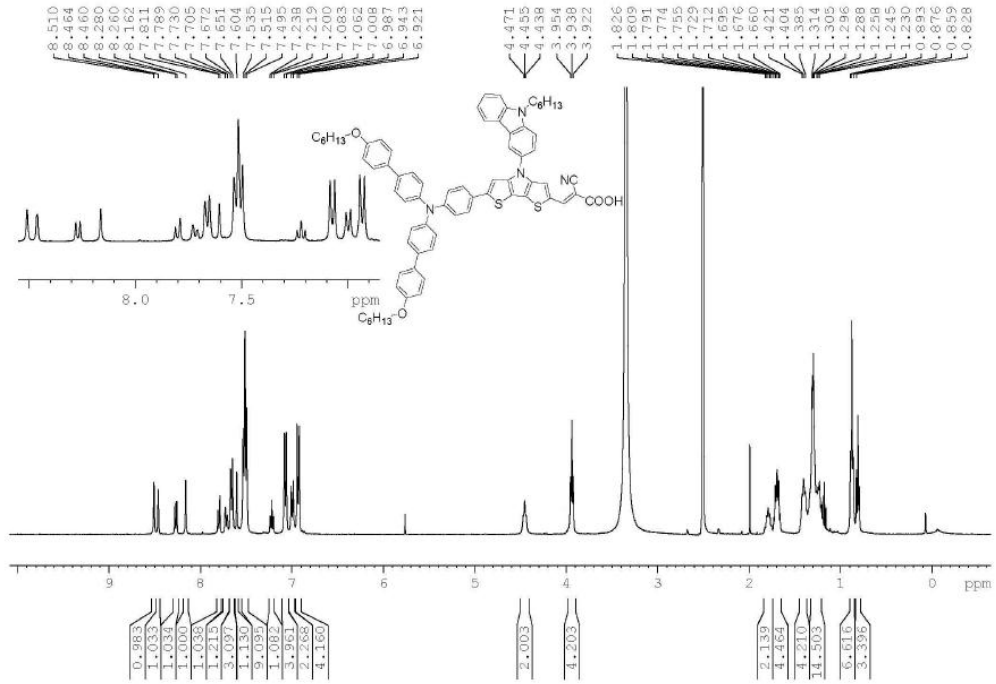


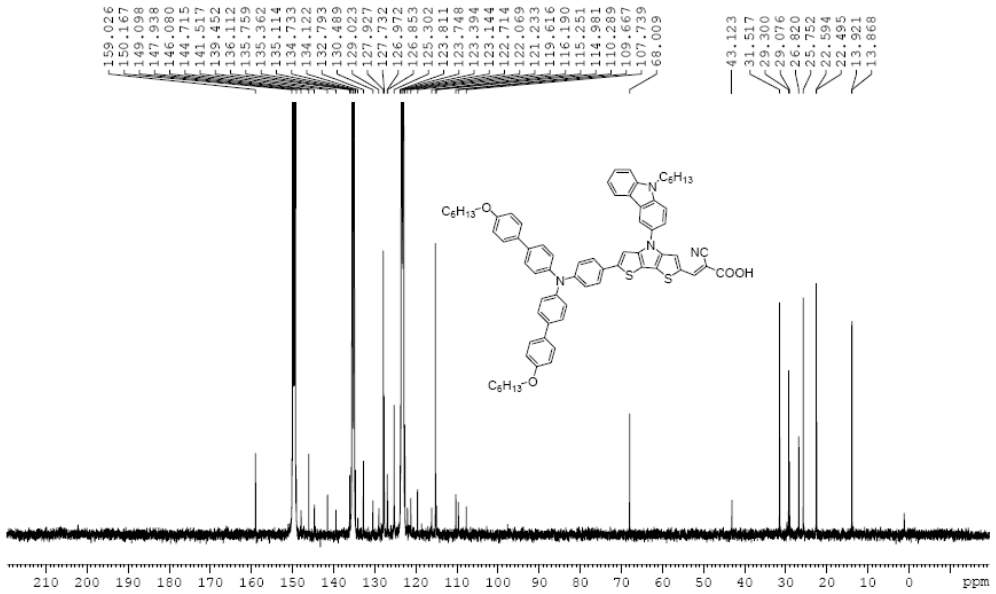
^{1}H (DMSO-d_6) and ^{13}C NMR (Pyridine-d_5) spectra of compound 8a



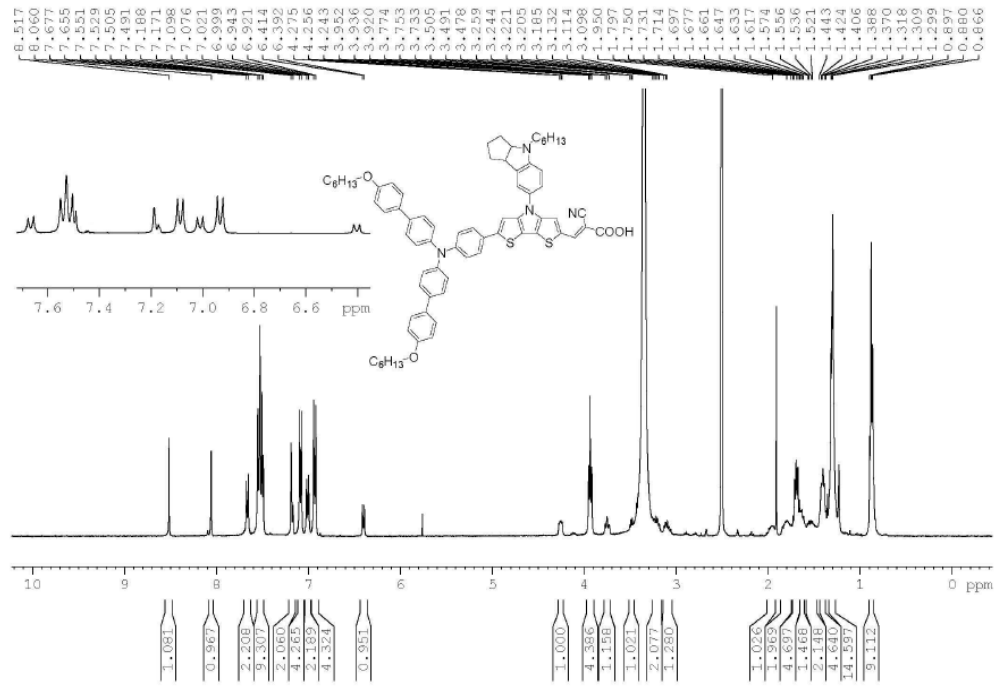


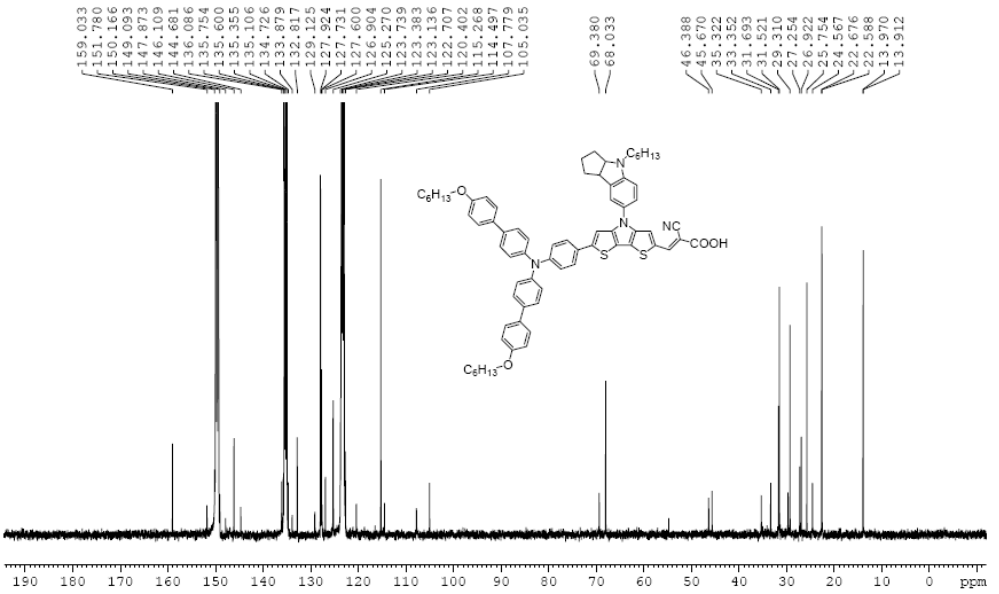
^{1}H (DMSO-d_6) and ^{13}C NMR (Pyridine-d_5) spectra of compound 8b



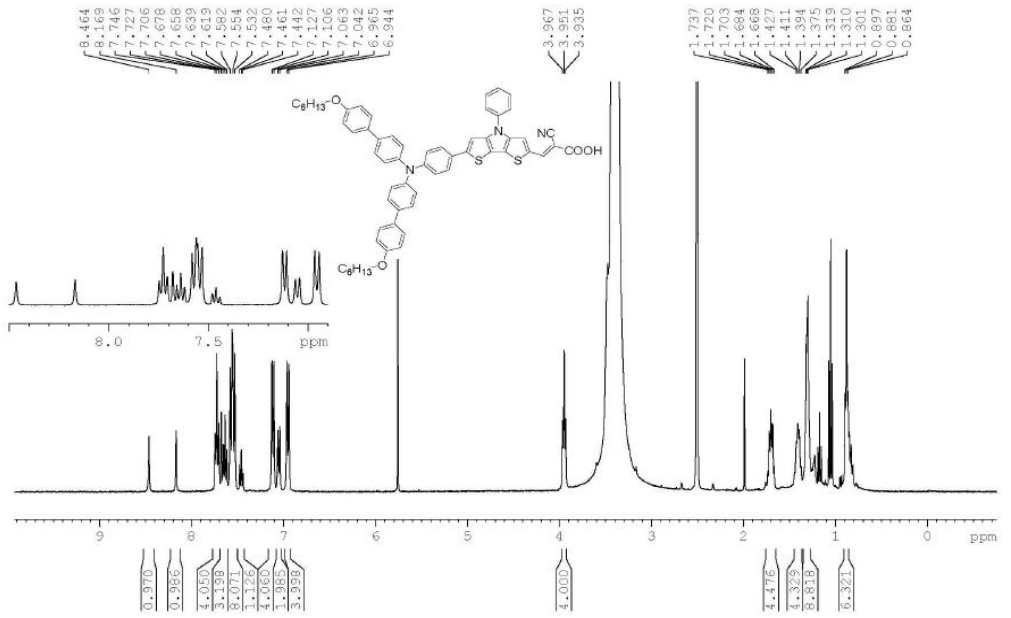


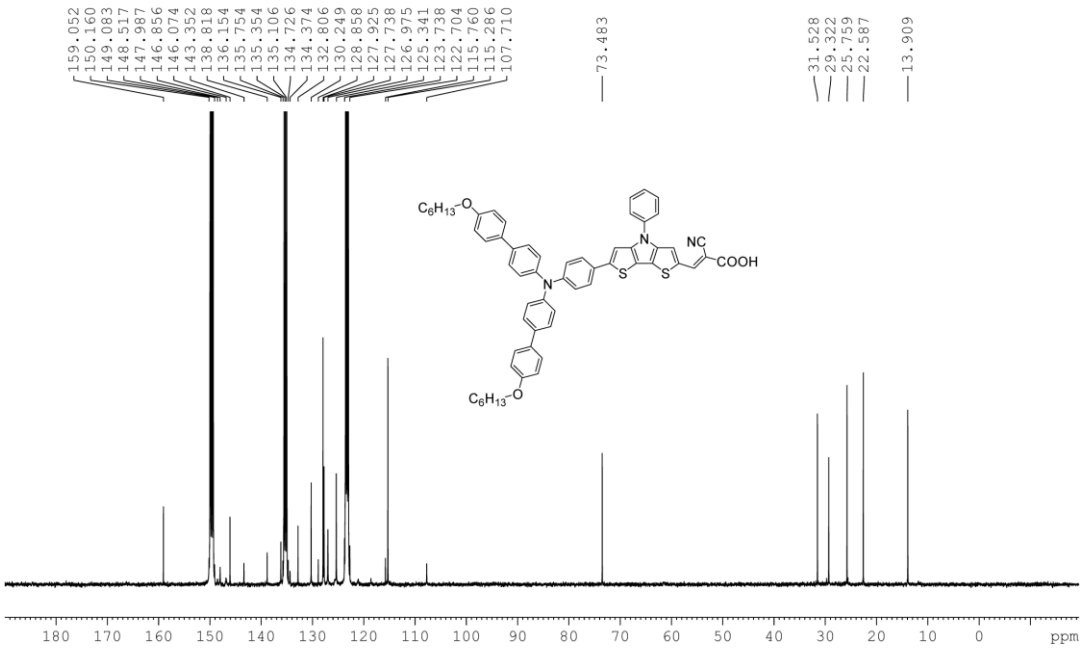
^{1}H (DMSO-d_6) and ^{13}C NMR (Pyridine-d_5) spectra of compound 8c





^{1}H (DMSO-d_6) and ^{13}C NMR (Pyridine-d_5) spectra of compound 8d





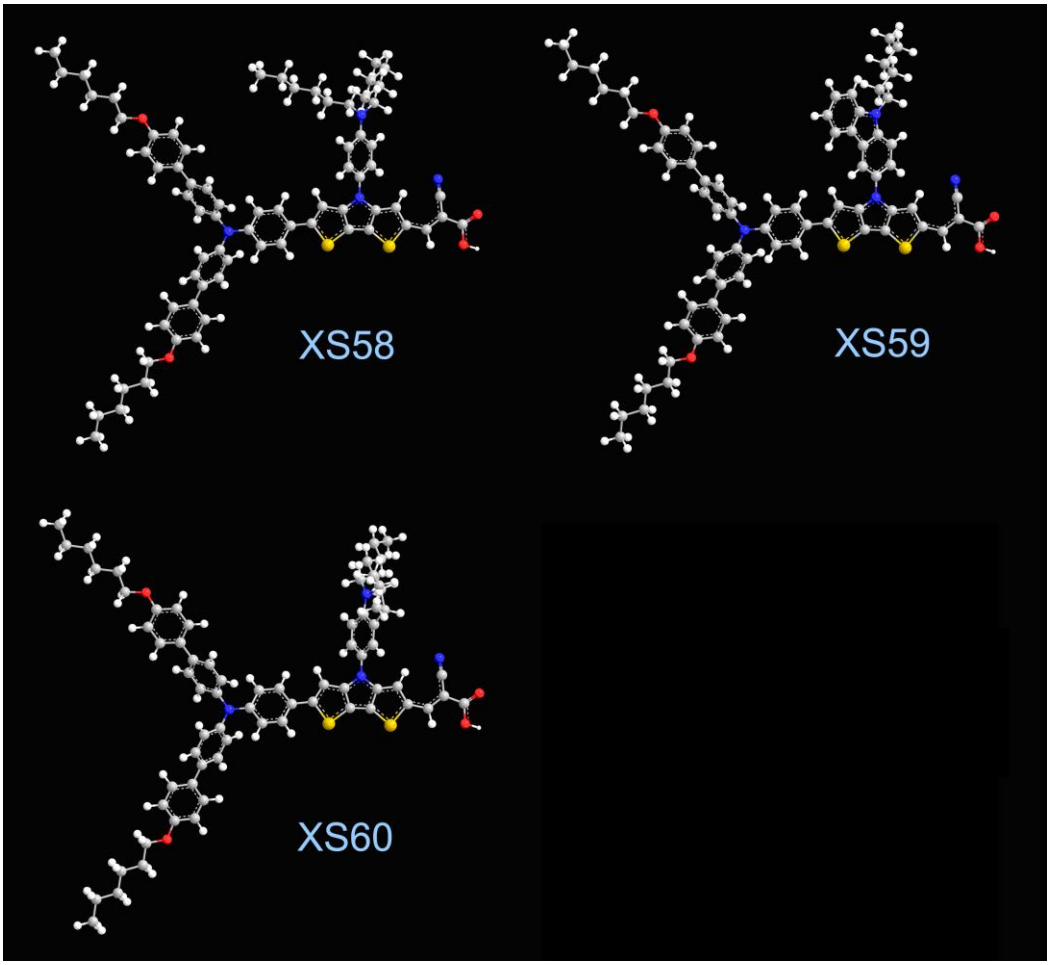


Figure S1. Optimized geometrical configuration of the dyes.