# Electronic Supplementary Information (ESI)

# Rigid triarylamine-based D-A-π-A Structural Organic Sensitizers for Solar Cells: Significant Enhancement of Open-Circuit Photovoltage with Long Alkyl Group

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1. **Fig. S1** Frontier molecular orbital contours of **DIA6-DIA10**, obtained from single point calculations at the CAM-B3LYP/SVP level of theory.
2. **Fig. S2** Cyclic voltammograms of dyes attached on 8 μm $TiO_2$ films.
3. **Fig. S3** Absorption curves of dyes **DIA6-DIA10** upon light irradiation of AM 1.5 solar light (30 min) with and without UV cutoff filter at 400 nm.
4. Synthetic procedure of intermediate **2**, **3, B1**, **B2 and D1-D4.**
5. **Fig. S4-S8** $^{1}H$ and $^{13}C$NMR spectrum of **DIA6-DIA10**.

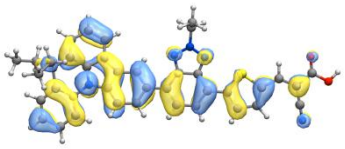
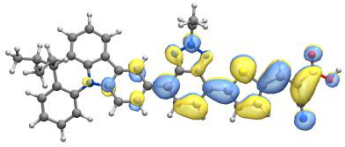
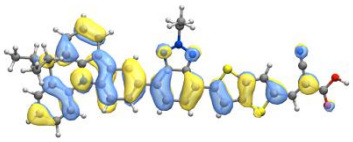
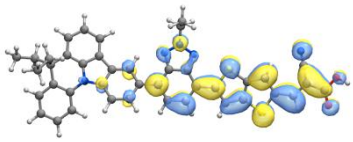
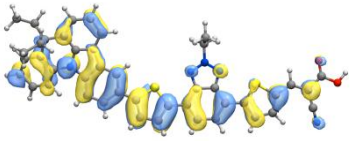
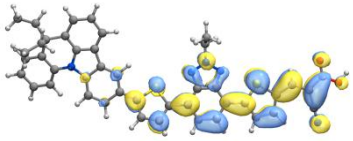
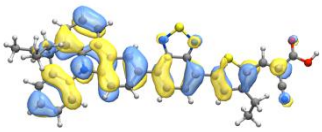
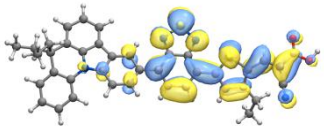
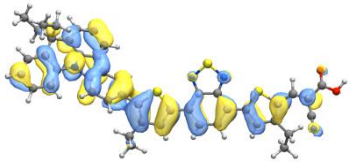
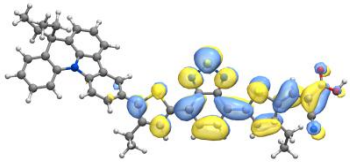
| Compound | HOMO | LUMO |
|---|---|---|
| **DIA6** |  |  |
| **DIA7** |  |  |
| **DIA8** |  |  |
| **DIA9** |  |  |
| **DIA10** |  |  |

**Fig. S1** Frontier molecular orbital contours of **M3** and **MD3**, obtained from single point calculations at the CAM-B3LYP/SVP level of theory.

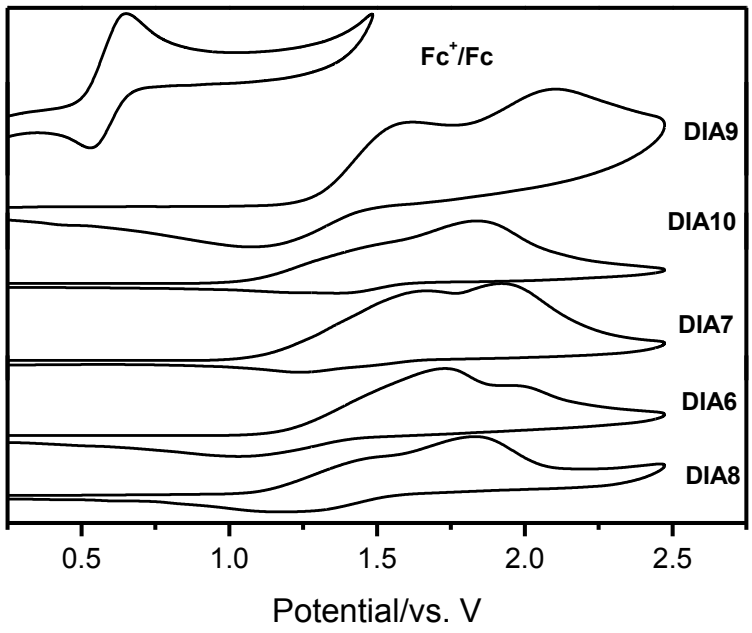
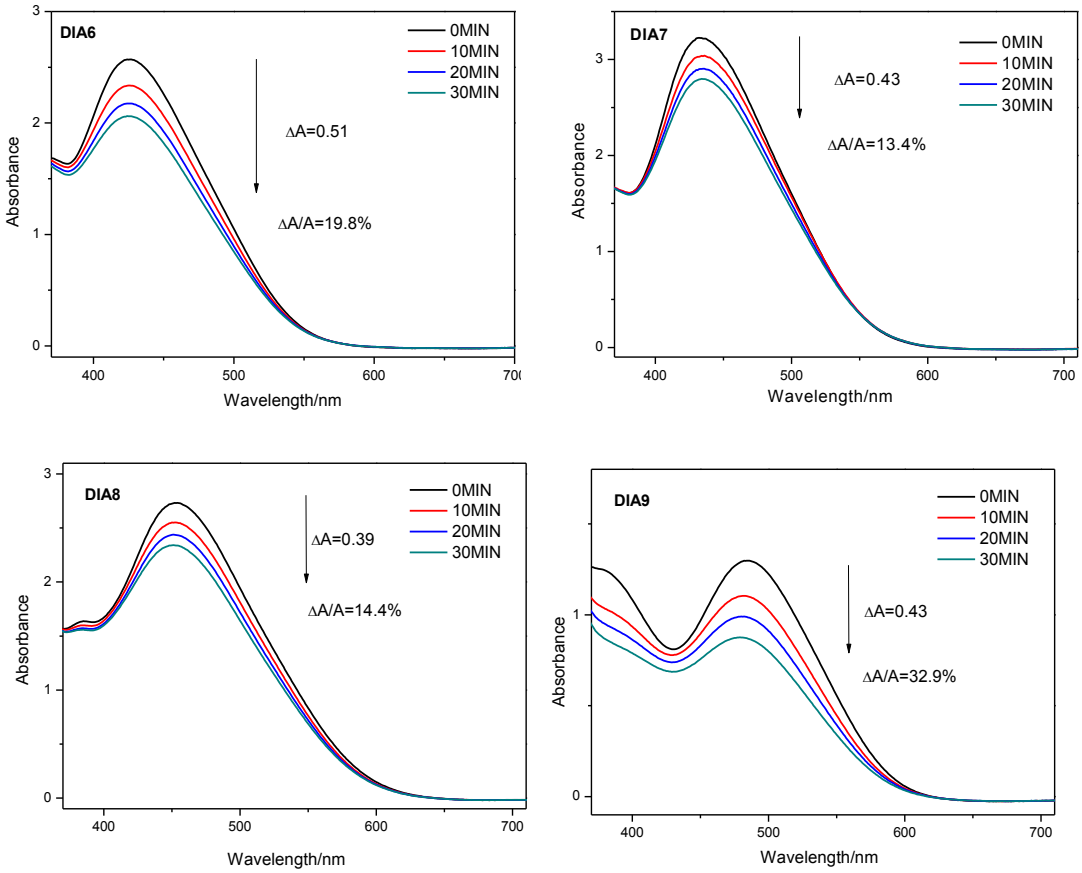



**Fig. S2** Cyclic voltammograms of dyes attached on 8 μm $TiO_2$ films.



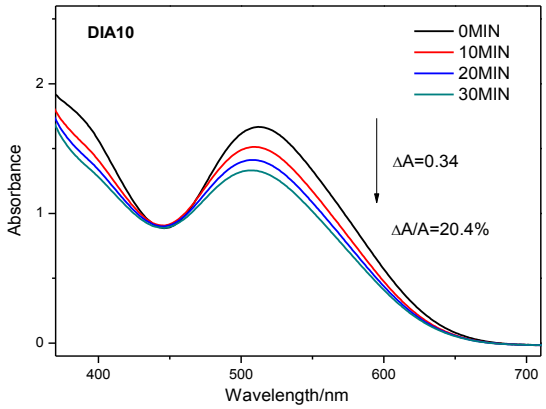
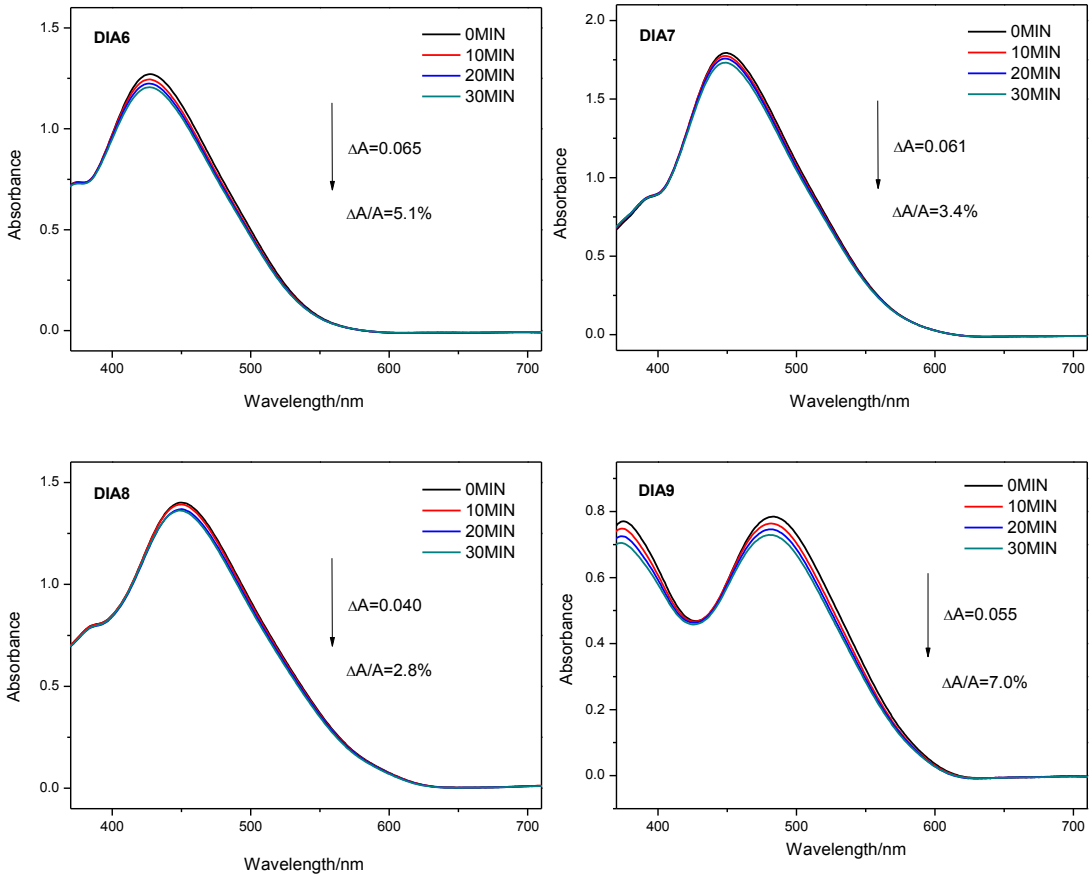



**Fig. S3 (a)** Absorption curves of dyes **DIA6-DIA10** upon light irradiation of AM 1.5 solar light (30 min) without UV cutoff filter.



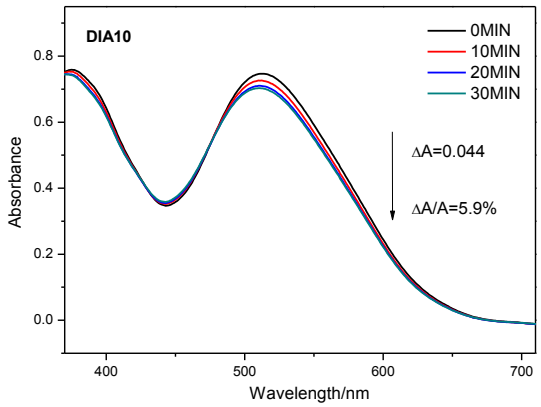



**Fig. S3 (b)** Absorption curves of dyes **DIA6-DIA10** upon light irradiation of AM 1.5 solar light (30 min) with UV cutoff filter at 400 nm.

**Synthesis:**

Synthesis of **2.** In a 100 mL three-necked round-bottom flask, 2.4 M n-BuLi in hexane (1.3 mL, 3.0 mmol) was added dropwise to a solution of compound **1** (780mg, 2.0 mmol) in THF at -78°C under a $N_2$ atmosphere. After stirring for 1.5 h at this temperature, triisopropylborate (1.2 mL, 5.0 mmol) was added dropwise and the mixture was allowed to warm to r.t. 1h later. Then 4,7-dibromo-2-octyl-2*H*-benzo[*d*][1,2,3]triazole (778 mg, 2.0 mmol), $K_2CO_3$ (1.38 g, 10 mmol), $Pd(PPh_3)_4$ (50 mg, 0.05 mmol), water (5 mL), and THF (15 mL) was added and the mixture was heated to 80-90 °C under a recharged $N_2$ atmosphere to reflux for 12 h. After cooling to room temperature, the mixture was extracted with $CH_2Cl_2$. The organic portion was combined and removed by rotary evaporation. The residue was purified by column chromatography using silica gel ($CH_2Cl_2$/petroleum ether =2:1) to give a green solid of 557 mg (Yield 45%). $^1$H NMR (400 MHz, $CDCl_3$), δ: 8.76 (d, *J* = 1.3 Hz, 1H), 8.33 (s, 1H), 8.29 (d, *J* = 8.9 Hz, 1H), 8.18 (m, 2H), 7.97 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.40 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 4.83 (t, *J* = 7.3 Hz, 2H), 2.13 (m, 6H), 1.41 (m, 4H), 1.28 (m, 6H), 0.87 (t, *J* = 6.1 Hz, 3H), 0.52 (t, *J* = 7.4 Hz, 6H).

Synthesis of **5.** In a dry flask, a solution of diisopropylamine (2.1 ml, 15 mmol) in anhydrous THF (20 ml) was stirred under a nitrogen atmosphere. The reaction mixture was cooled to -78°C, then 2.4 M BuLi in hexane (6.2 ml, 15 mmol) was injected into the mixture slowly. After stirred for 1 h, the solution of **4** in THF (10 ml) was added dropwise. DMF (2.3 ml, 30 mmol) was added slowly 1 h later. The mixture was stirred for another 1 h and then warmed to the r.t. Water was added. The mixture was extracted with $CH_2Cl_2$ and the combined organic layer was vaporized. The residue was recrystallized from hexane. A brown solid was obtained with a yield of 0.991 g, 59%. $^1$H NMR (400 MHz, $CDCl_3$), δ: 9.98 (s, 1H), 7.96 (s, 1H), 7.71 (d, *J* = 5.3 Hz, 1H), 7.35 (m, 1H).

Synthesis of **6.** A solution of NBS (1.96 g, 10 mmol) in DMF (20 ml) were added dropwise to the solution of **5** (1.68 g, 10 mmol) in DMF (30 ml) at ambient temperature and then the reaction was stirred for 2 h. The reaction mixture was poured into water and filtered off. The brown solid was obtained with a yield of 1.98 g, 80%. $^1$H NMR (400 MHz, $CDCl_3$), δ: 9.97 (d, *J* = 2.6 Hz, 1H), 7.85 (s, 1H), 7.36 (s, 1H).

Synthesis of **7.** A mixture of **6** (1.24 g, 5 mmol), $Me_3SiCl$ (3.4 ml, 25 mmol) and $CH_2Cl_2$ (50 ml) was stirred at r.t., and ethane-1, 2-diol (1.4 ml, 25 mmol) was slowly added. The reaction mixture was heated to reflux for overnight. After cooling down, the mixture was washed with water and extracted with $CH_2Cl_2$. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator. The residue was put on to the next reaction without further purification.

Synthesis of **B1.** In a 100 mL three-necked round-bottom flask, 2.4 M n-BuLi in hexane (2.0 ml, 4.6 mmol) was added dropwise to a solution of compound **7** (900mg, 3.1mmol) in THF at -78 $^o$C under a $N_2$ atmosphere. After stirring for 1.5 h at this temperature, triisopropyl borate (3.6 ml, 15.5 mmol) was added dropwise and the mixture was allowed to warm to r.t 1h later. Then 4,7-dibromo-2-octyl-benzotriazole (1.21 g, 3.1 mmol), $K_2CO_3$ (2.14 g, 15.5 mmol), $Pd(PPh_3)_4$ (20 mg, 0.02 mmol), water (7.5 mL), and THF (30mL) was added and the mixture was heated to 80−90 °C under a recharged $N_2$ atmosphere to reflux for 12 h. After cooling to room temperature, the mixture was extracted with $CH_2Cl_2$. The organic portion was combined and removed by rotary evaporation. The crude materials was purified by silica gel column chromatography using a petroleum and dichloromethane mixture as the eluent to obtain the desired product as a yellow solid. The solid was added to a mixture of THF (10 ml) and 6 M HCl (10 ml) and the reaction mixture was heated to reflux for 4h. The mixture was refluxed and extracted with $CH_2Cl_2$. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was recrystallized from EtOH to give a yellow solid with a yield of 487mg, 33%. $^1$H NMR (400 MHz, $CDCl_3$), δ: 9.99 (s, 1H), 8.42 (s, 1H), 7.96 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 4.83 (t, *J* = 7.4 Hz, 2H), 2.19 (m, 2H), 1.32 (m, 10H), 0.84 (m, 3H).

Synthesis of **9.** In a dry flask, a mixture of 4,7-dibromo-2-octyl-benzotriazole (1.56g, 4.0 mmol), $K_2CO_3$ (2.76 g, 20 mmol), $Pd(PPh_3)_4$ (70 mg, 0.07mmol), water (10 mL), and THF (20 mL) were heated to 45 $^o$C for 1 h under an argon atmosphere. Then, thiophen-2-ylboronic acid (1.54g, 12.0 mmol) dissolved in 20 mL THF was added dropwise and the reaction mixture was heated to reflux for 4 h and then allowed to cool down to r.t. The mixture was washed with water and extracted with $CH_2Cl_2$. The combined layer was dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator. The resident was purified by column chromatography on silica (petroleum ether/dichloromethane=2:1, v/v) to yield the crude product as a yellow powder (711mg, 45%). $^1$H NMR (400 MHz, $CDCl_3$), δ: 8.09 (dd, *J* = 3.7, 0.8 Hz, 2H), 7.60 (s,

2H), 7.36 (dd, *J* = 5.1, 0.9 Hz, 2H), 7.17 (dd, *J* = 5.0, 3.7 Hz, 2H), 4.79 (t, *J* = 7.3 Hz, 2H), 2.27 (m, 2H), 1.25 (m, 10H), 0.82 (m, 3H).

Synthesis of **10.** In a dry flask, 2.4 M n-BuLi in hexane (2.6 ml, 6.0 mmol) was added dropwise to a solution of compound **5** (1.6 g, 4.0 mmol) in THF at -78 $^{o}$C under a $N_2$ atmosphere. After stirring for 1.5 h at this temperature, DMF (1 ml, 12.0 mmol) was added dropwise and the mixture was allowed to warm to r.t 1h later. Then, water was added to quench the reaction. The mixture was extracted with $CH_2Cl_2$. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was recrystallized from hexane. A yellow solid was obtained with a yield of 964mg, 57%. $^1$H NMR (400 MHz, $CDCl_3$), δ: 9.95 (s, 1H), 8.16 (d, *J* = 3.8 Hz, 2H), 7.83 (d, *J* = 4.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 4.8 Hz, 1H), 7.17 (m, 1H), 4.83 (t, *J* = 7.2 Hz, 2H), 2.20 (m, 2H), 1.43 (m, 10H), 0.87 (t, *J* = 6.5 Hz, 3H).

Synthesis of **B2. C**ompound **B2** was synthesized by the same procedure as described for **6.** The yellow solid was obtained with a yield of 854mg, 81%. $^1$H NMR (400 MHz, $CDCl_3$), δ: 9.96 (s, 1H), 8.17 (d, *J* = 4.0 Hz, 1H), 7.84 (dd, *J* = 7.3, 4.0 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 4.0 Hz, 1H), 4.83 (t, *J* = 7.3 Hz, 2H), 2.20 (m, 2H), 1.30 (m, 10H), 0.87 (t, *J* = 5.8 Hz, 3H).

Synthesis of **3.** In a dry flask, a mixture of compound **2** (1.24g, 2.0 mmol), $K_2CO_3$ (1.38 g, 10 mmol), $Pd(PPh_3)_4$ (50 mg, 0.05 mmol), water (5 mL), and THF (30 mL) were heated to 45 $^{o}$C for 1 h under an argon atmosphere. Then, (5-formylthiophen-2-yl)boronic acid (414 mg, 3.0 mmol), dissolved in 20 mL THF was added dropwise and the reaction mixture was heated to reflux for 4 h. After cooling to room temperature, the mixture was extracted with $CH_2Cl_2$. The organic portion was combined and removed by rotary evaporation. The residue was purified by column chromatography using silica gel ($CH_2Cl_2$/petroleum ether =2:1) to give a deep yellow solid of 495 mg (Yield: 38%). $^1$H NMR (400 MHz, $CDCl_3$), δ: 9.98 (s, 1H), 8.86 (s, 1H), 8.30 (m, 2H), 8.22 (d, *J* = 3.9 Hz, 1H), 8.17 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 7.0 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 4.0 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.40 (m, 3H), 7.21 (t, *J* = 7.8 Hz, 1H), 4.87 (t, *J* = 7.4 Hz, 2H), 2.18 (m, 6H), 1.26 (m, 10H), 0.87 (d, *J* = 3.6 Hz, 3H), 0.52 (t, *J* = 7.3 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$), δ: 182.83, 149.89, 143.32, 142.30, 138.27, 138.05, 137.82, 137.15, 132.64, 130.28, 129.01, 127.70, 127.13, 126.99, 126.95, 126.25, 125.41, 124.50, 123.62, 123.36, 122.53, 122.24, 121.63, 121.44, 121.00, 117.27, 114.06, 113.17, 56.88, 46.31, 38.51, 31.69, 29.64, 29.06, 28.95, 26.57, 22.55, 14.01, 9.45. HRMS (*m*/*z*): $[M + H]^+$ calcd for $C_{42}H_{43}N_4OS$, 651.3158; found, 651.3161.

Synthesis of **D1.** In a dry flask, 2.4 M n-BuLi in hexane (1.3 mL, 3.0 mmol) was added dropwise to a solution of compound **1** (780mg, 2.0 mmol) in THF at -78$^{o}$C under a $N_2$ atmosphere. After stirring for 1.5 h at this temperature, triisopropylborate

(1.2 mL, 5.0 mmol) was added dropwise and the mixture was allowed to warm to r.t. 1h later. Then compound **B1** (952 mg, 2.0 mmol), $K_2CO_3$ (1.38 g, 10 mmol), $Pd(PPh_3)_4$ (50 mg, 0.05 mmol), water (5 mL), and THF (15 mL) was added and the mixture was heated to reflux under a recharged $N_2$ atmosphere to reflux for 12 h. After cooling to room temperature, the mixture was extracted with $CH_2Cl_2$. The organic portion was combined and removed by rotary evaporation. The residue was purified by column chromatography using silica gel ($CH_2Cl_2$/petroleum ether =2:1) to give an orange solid of 551 mg (Yield 39%). $^1$H NMR (400 MHz, $CDCl_3$), δ: 9.99 (s, 1H), 8.86 (s, 1H), 8.49 (s, 1H), 8.30 (m, 2H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.98 (m, 2H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.40 (m, 3H), 7.21 (t, *J* = 7.4 Hz, 1H), 4.88 (t, *J* = 7.2 Hz, 2H), 2.25 (dt, *J* = 14.6, 7.3 Hz, 2H), 2.11 (tt, *J* = 13.8, 6.9 Hz, 4H), 1.45 (m, 4H), 1.29 (t, *J* = 13.6 Hz, 6H), 0.87 (t, *J* = 6.7 Hz, 3H), 0.52 (t, *J* = 7.3 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$), δ: 182.86, 148.56, 146.84, 144.74, 143.16, 142.01, 138.26, 138.04, 137.72, 131.66, 130.24, 128.96, 127.73, 127.07, 126.83, 126.20, 125.45, 123.79, 123.41, 122.61, 122.28, 122.02, 121.72, 120.97, 119.59, 117.33, 114.09, 113.11, 56.75, 46.32, 38.52, 31.75, 29.99, 29.13, 28.99, 26.64, 22.62, 14.10, 9.58. HRMS (*m*/*z*): $[M + H]^+$ calcd for $C_{44}H_{43}N_4OS_2$, 707.2878; found, 707.2874.

Synthesis of **D2.** Compound **D2** was synthesized according to the same procedure as that of D1, as light red solid in 37% yield. $^1$H NMR (400 MHz, $CDCl_3$), δ: 9.96 (s, 1H), 8.44 (d, *J* = 1.8 Hz, 1H), 8.20 (m, 3H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.96 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.88 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.83 (d, *J* = 4.0 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 5.9 Hz, 2H), 7.39 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 4.87 (t, *J* = 7.2 Hz, 2H), 2.24 (m, 2H), 2.11 (m, 4H), 1.45 (m, 4H), 1.29 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.52 (t, *J* = 7.3 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$), δ: 183.02, 149.80, 146.07, 142.37, 142.11, 141.89, 138.26, 138.15, 137.95, 137.49, 137.37, 130.32, 129.35, 127.81, 127.27, 127.09, 126.71, 126.44, 126.05, 125.55, 124.49, 124.39, 123.72, 123.46, 122.66, 122.51, 121.93, 121.56, 121.34, 118.07, 117.34, 114.05, 113.46, 57.05, 46.37, 38.61, 31.79, 30.14, 29.16, 29.04, 26.65, 22.65, 14.12, 9.57. HRMS (*m*/*z*): $[M + H]^+$ calcd for $C_{46}H_{45}N_4OS_2$, 733.3035; found, 733.3039.

Synthesis of **D3.** Compound **D3** was synthesized according to the same procedure as that of D1, as red solid in 40% yield. $^1$H NMR (400 MHz, $CDCl_3$), δ: 10.12 (s, 1H), 8.78 (d, *J* = 1.7 Hz, 1H), 8.33 (d, *J* = 8.8 Hz, 1H), 8.19 (d, *J* = 2.0 Hz, 1H), 8.17 (d, *J* = 1.8 Hz, 1H), 8.11 (t, *J* = 3.6 Hz, 2H), 7.98 (dd, *J* = 6.9, 1.4 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.54 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.40 (m, 3H), 7.21 (t, *J* = 7.5 Hz, 1H), 3.06 (m, 2H), 2.12 (tt, *J* = 13.8, 7.0 Hz, 4H), 1.80 (m, 2H), 1.35 (m, 6H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.52 (t, *J* = 7.3 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$), δ: 182.22, 154.15, 153.57, 152.72, 147.83, 138.28, 138.15, 138.00, 137.31, 135.13, 130.52, 130.43, 129.09, 127.83, 127.54, 127.31, 127.11, 126.29, 125.54, 124.33, 123.56, 122.73, 122.46, 121.81, 121.57, 117.41, 114.16, 113.22, 46.40, 38.64, 31.64, 31.53, 29.11,

28.73, 22.62, 14.14, 9.56. HRMS (*m*/*z*): $[M + H]^+$ calcd for $C_{40}H_{38}N_3OS_2$, 640.2456; found, 640.2458.

Synthesis of **D4.** Compound **D4** was synthesized according to the same procedure as that of D1, as brilliant red solid in 37% yield. $^1$H NMR (400 MHz, $CDCl_3$), δ: 10.11 (s, 1H), 8.28 (d, *J* = 1.6 Hz, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 8.14 (d, *J* = 7.4 Hz, 2H), 8.08 (s, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 2H), 7.71 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.53 (d, *J* = 6.8 Hz, 1H), 7.38 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 3.05 (t, *J* = 7.7 Hz, 2H), 2.85 (m, 2H), 2.12 (qd, *J* = 13.8, 7.0 Hz, 4H), 1.77 (m, 4H), 1.35 (m, 12H), 0.91 (t, *J* = 7.0 Hz, 3H), 0.86 (t, *J* = 6.9 Hz, 3H), 0.52 (t, *J* = 7.3 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$), δ: 182.14, 153.53, 152.49, 152.42, 147.68, 141.30, 139.85, 138.34, 138.06, 137.33, 137.24, 136.44, 131.23, 130.35, 130.32, 127.99, 127.81, 127.51, 127.38, 127.09, 126.45, 126.15, 125.51, 124.47, 123.83, 123.45, 122.65, 122.47, 121.49, 121.33, 117.30, 114.07, 113.16, 46.39, 38.67, 31.74, 31.63, 31.51, 31.15, 29.36, 29.11, 29.06, 28.71, 22.70, 22.62, 14.14, 9.59. HRMS (*m*/*z*): $[M + H]^+$ calcd for $C_{50}H_{52}N_3OS_3$, 806.3273; found, 806.3276.

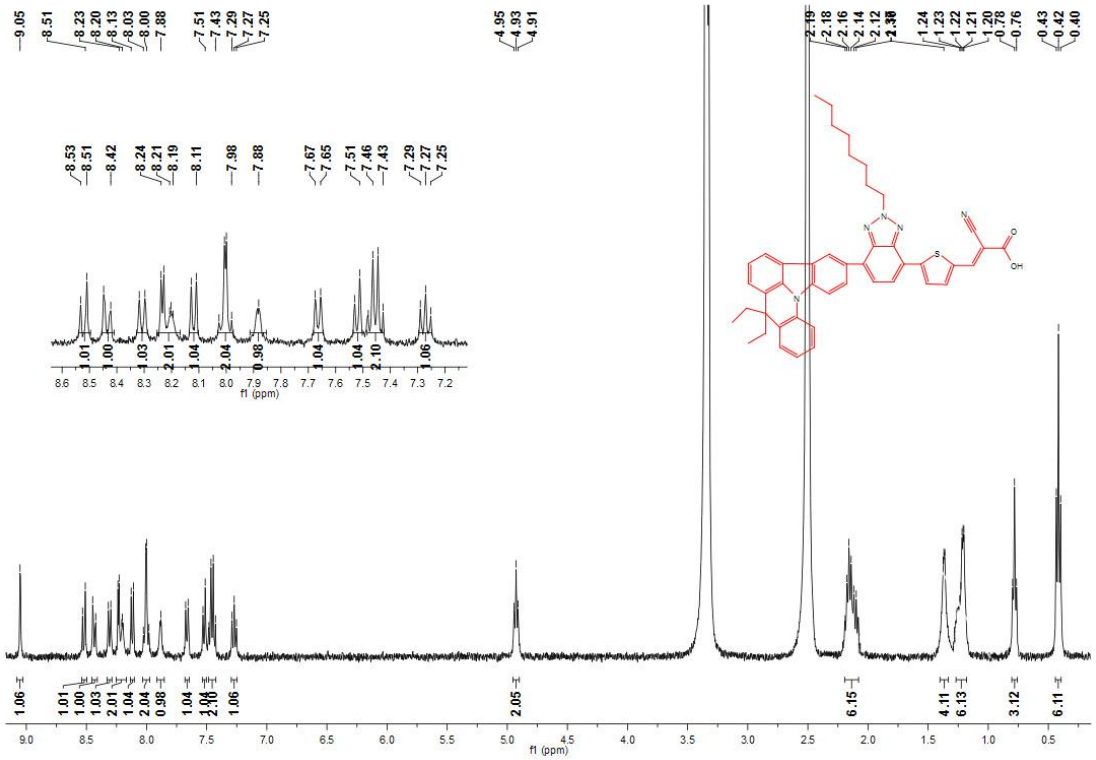


**Fig. S4 (a)** $^{1}$H NMR (DMSO-$d_6$, 400 MHz) spectrum of **DIA6**.

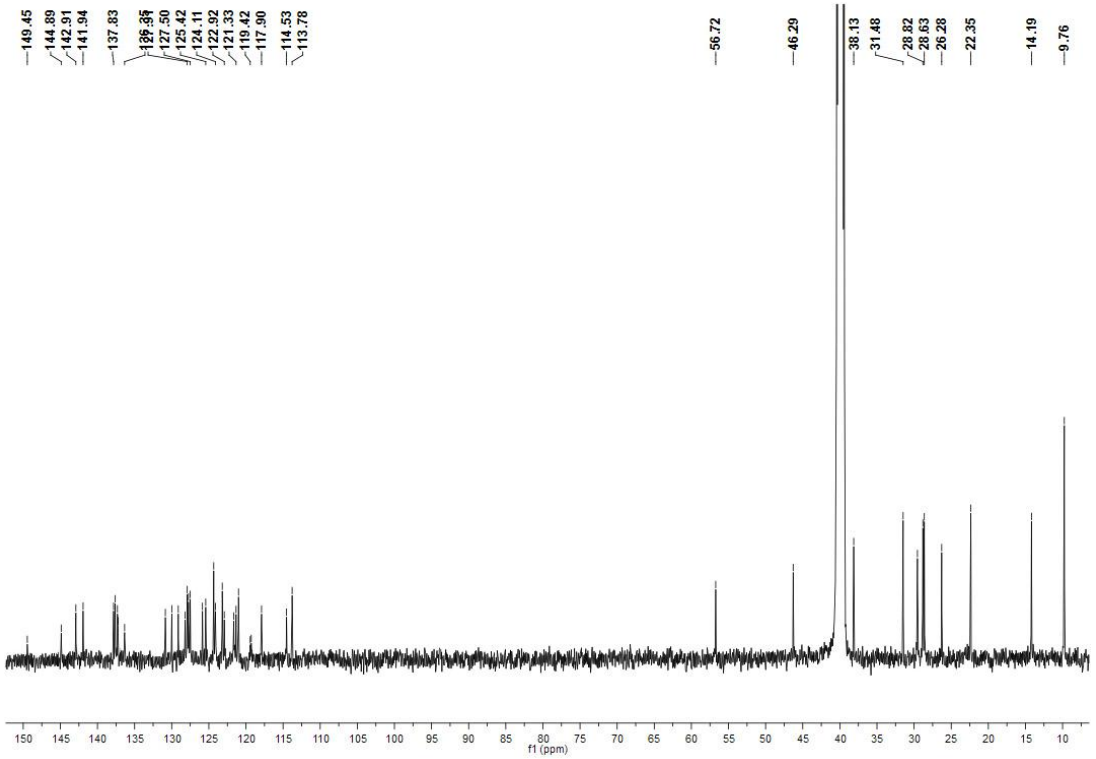


**Fig. S4 (b)** $^{13}$C NMR (THF-$d_8$, 126 MHz) spectrum of **DIA6**.

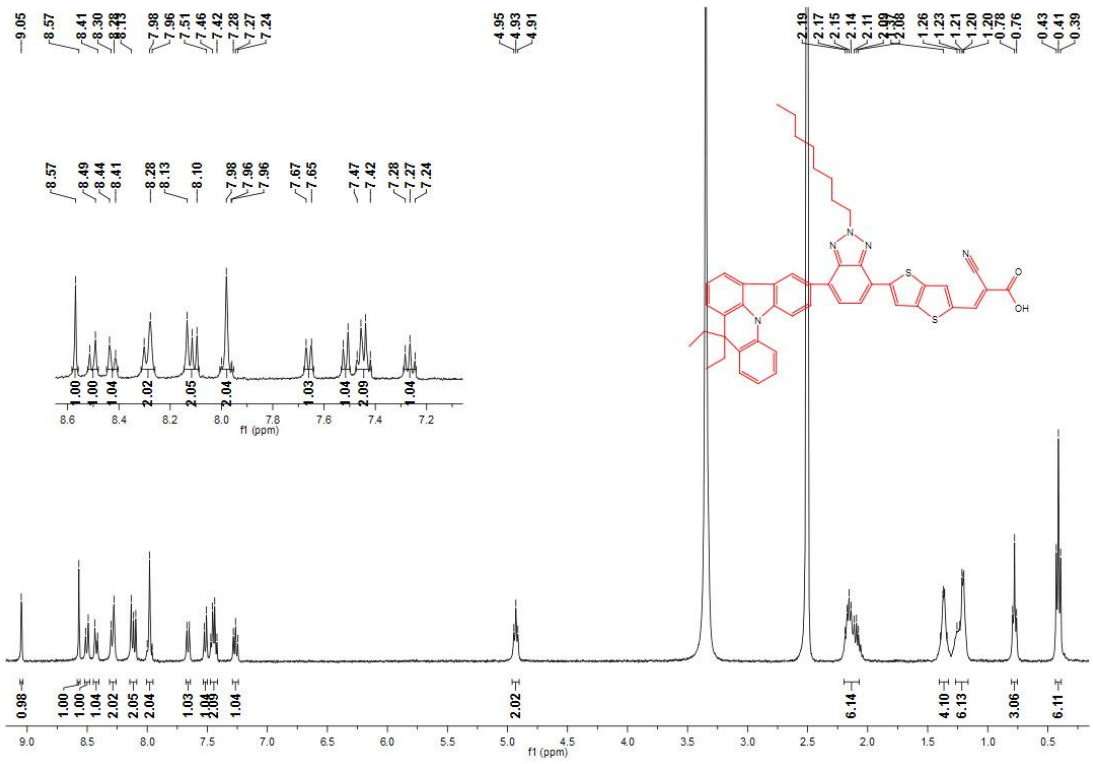


**Fig. S5 (a)** $^{1}$H NMR (DMSO-$d_6$, 400 MHz) spectrum of **DIA7**.

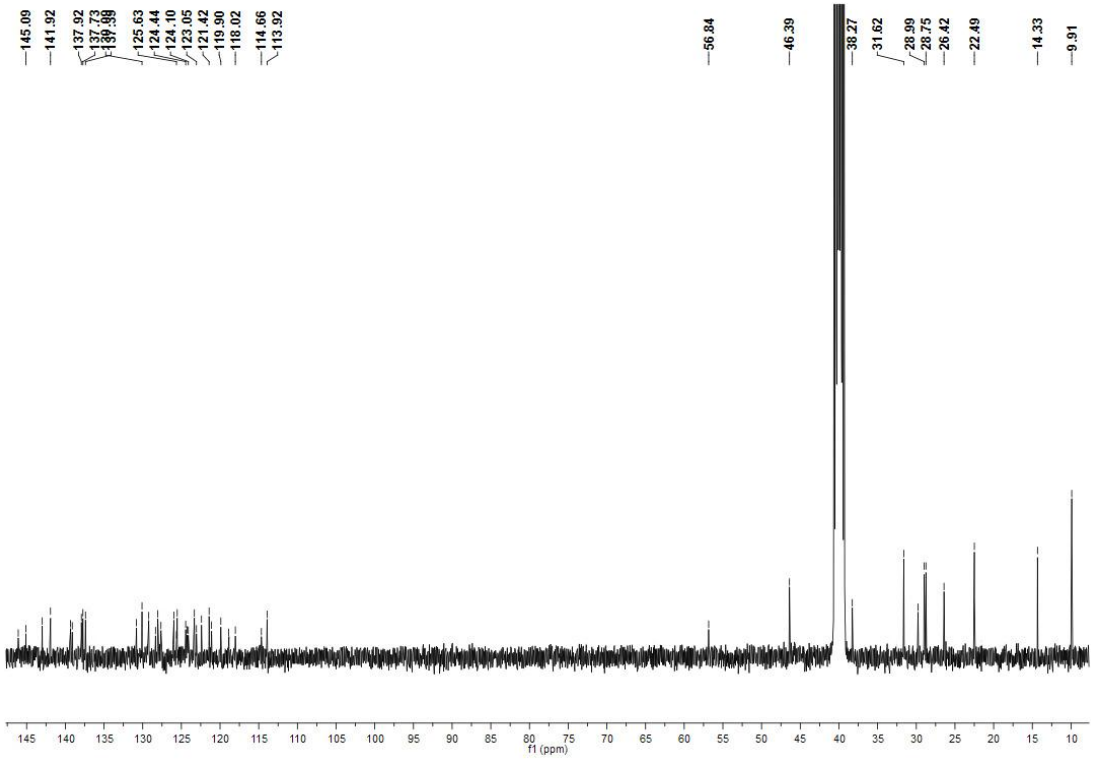


**Fig. S5 (b)** $^{13}$C NMR (THF-$d_8$, 126 MHz) spectrum of **DIA7**.

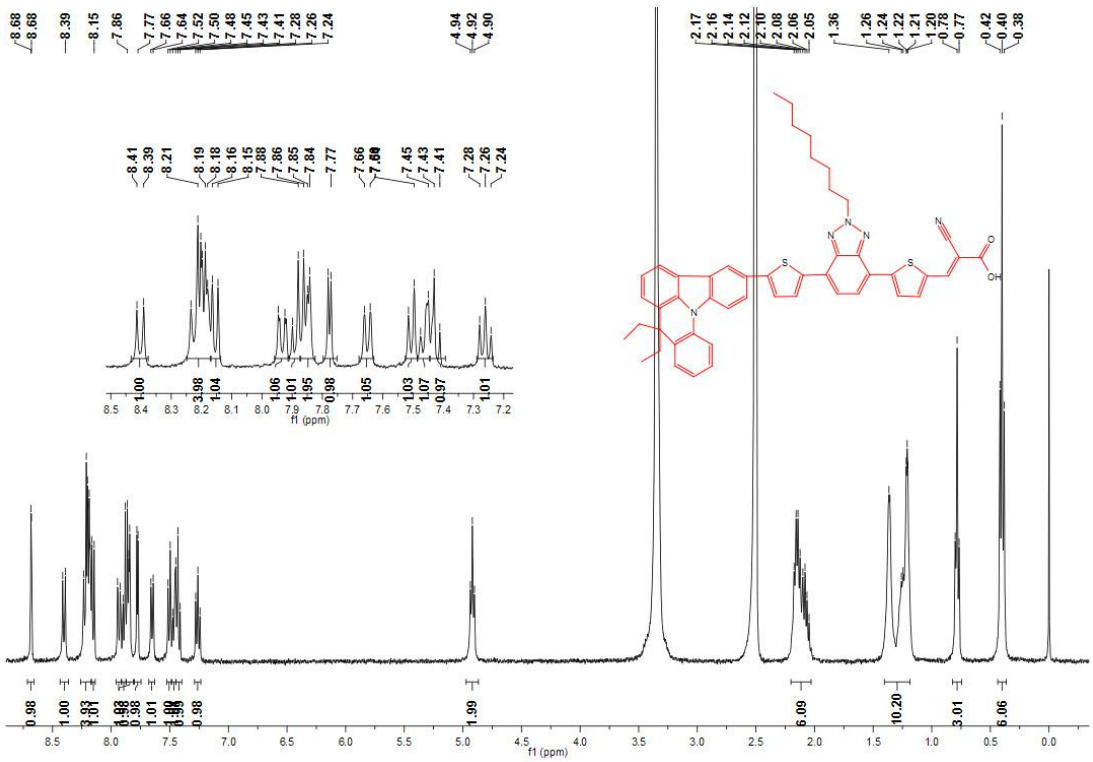


**Fig. S6 (a)** $^{1}$H NMR (DMSO-$d_6$, 400 MHz) spectrum of **DIA8**.

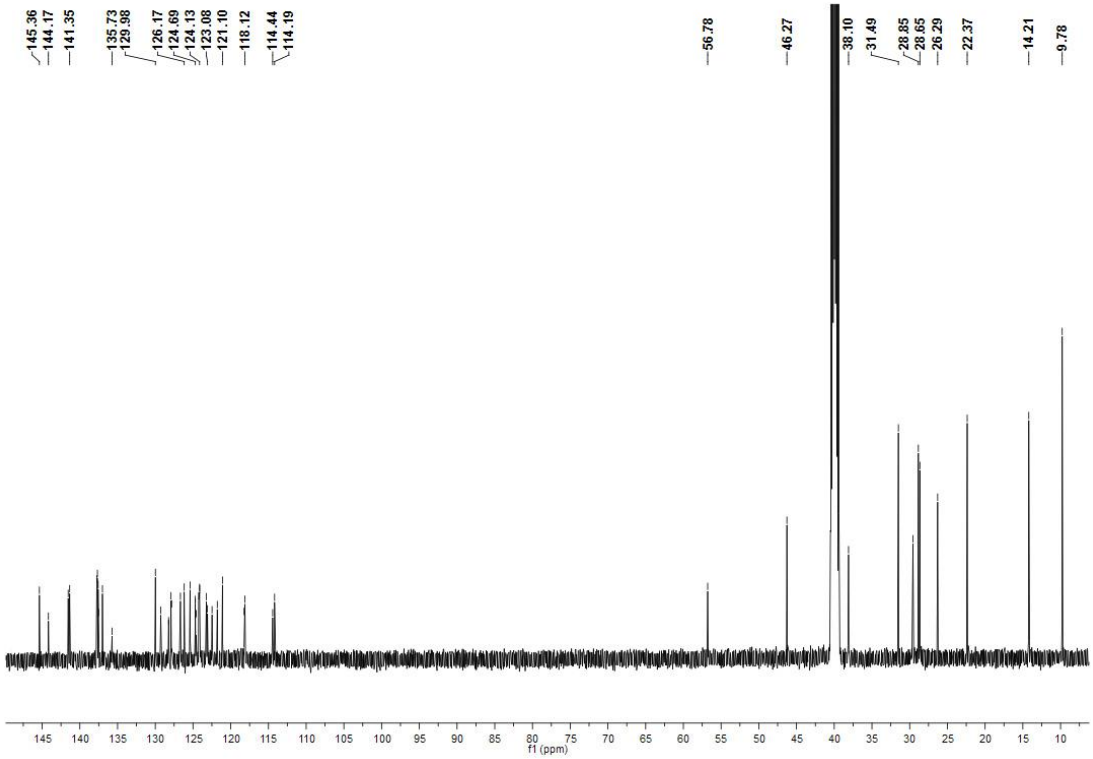


**Fig. S6 (b)** $^{13}$C NMR (THF-$d_8$, 126 MHz) spectrum of **DIA8**.

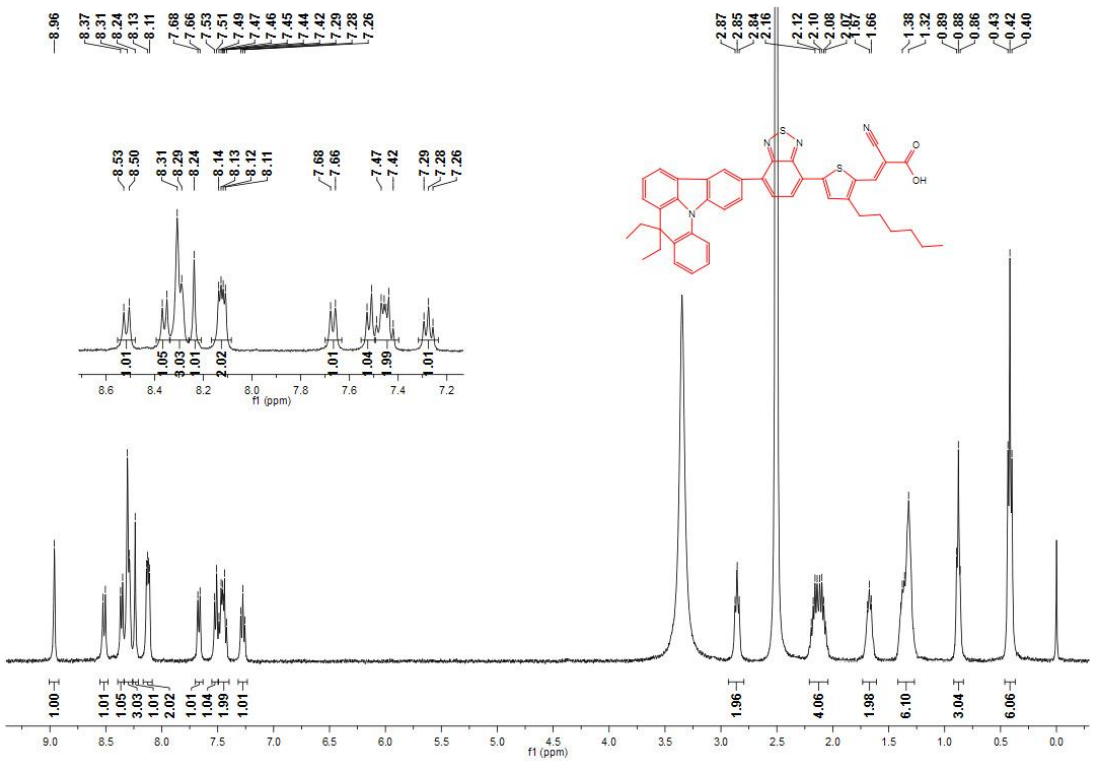


**Fig. S7 (a)** $^{1}$H NMR (DMSO-$d_6$, 400 MHz) spectrum of **DIA9**.

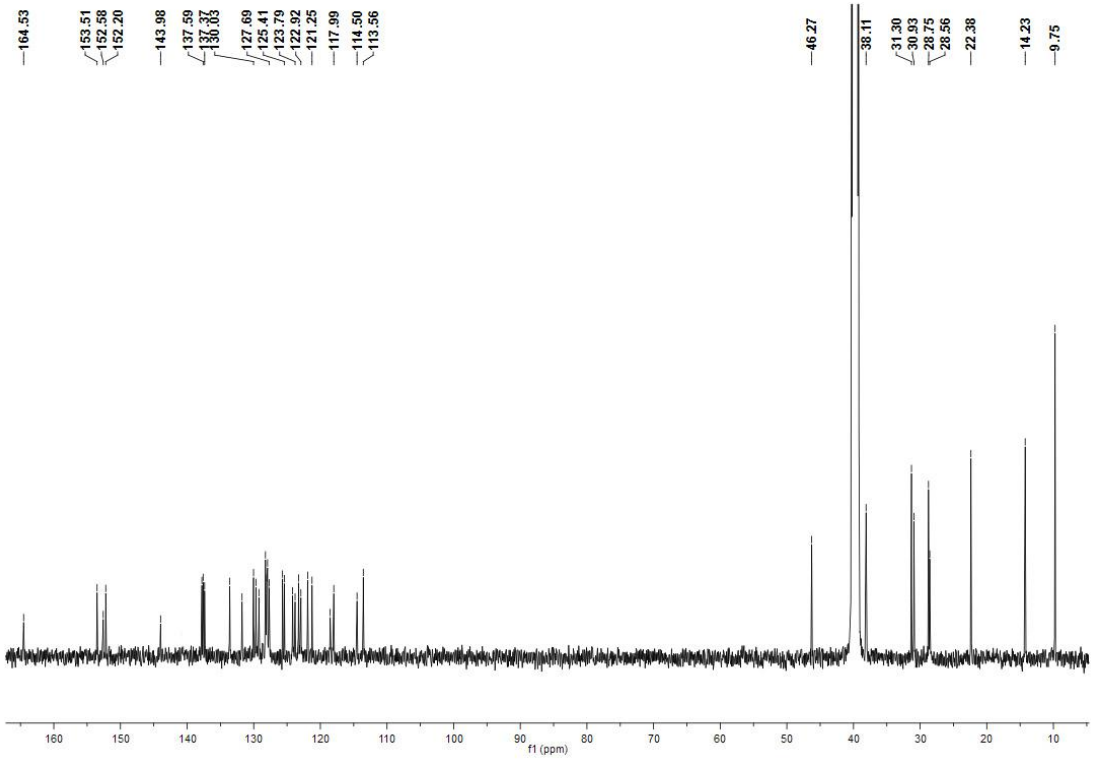


**Fig. S7 (b)** $^{13}$C NMR (THF-$d_8$, 126 MHz) spectrum of **DIA9**.

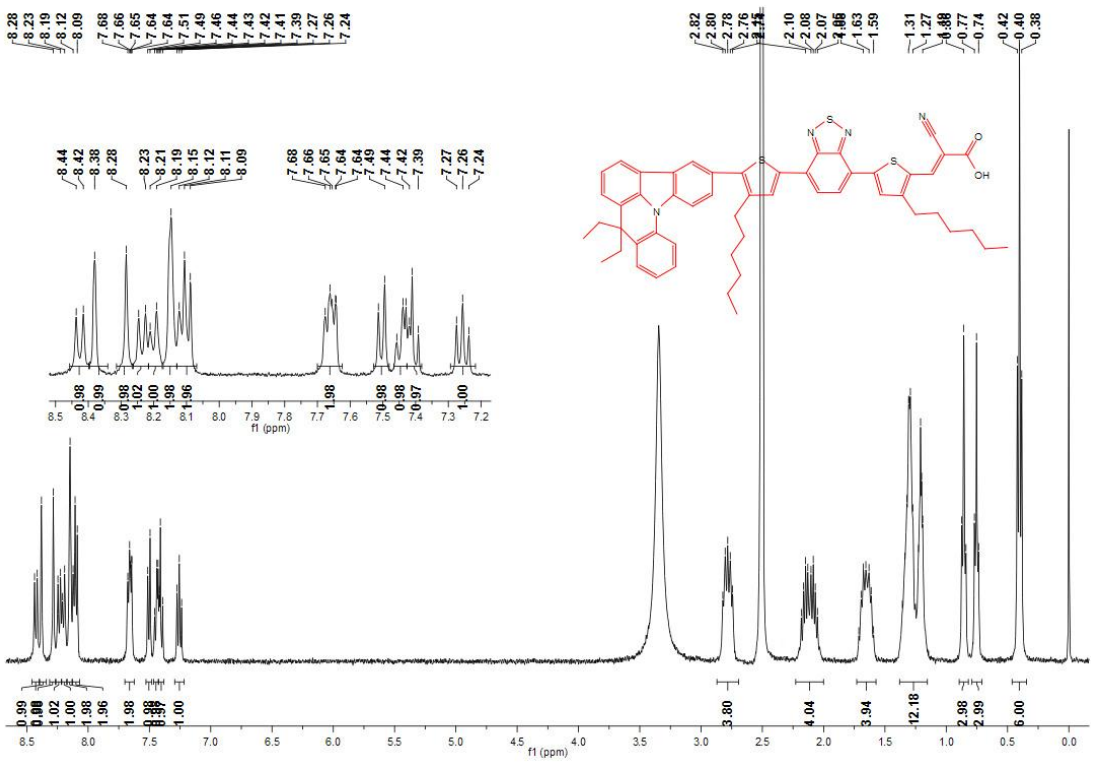



**Fig. S8 (a)** $^{1}$H NMR (DMSO-$d_6$, 400 MHz) spectrum of **DIA10**.

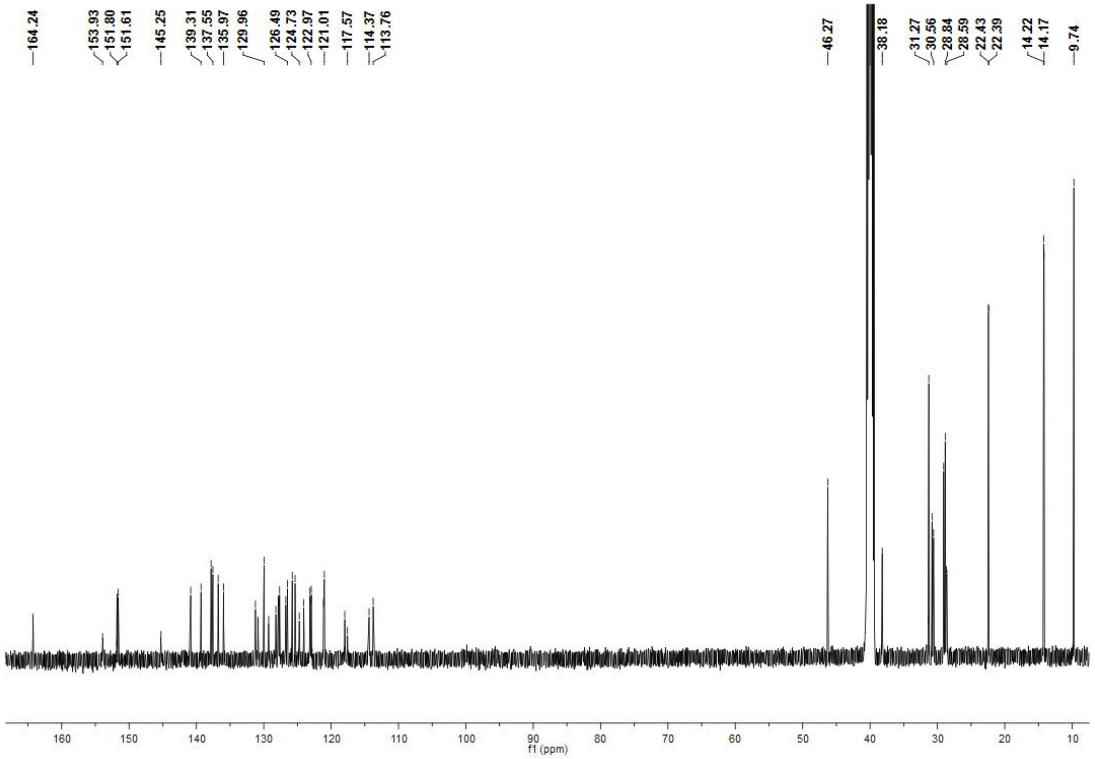



**Fig. S8 (b)** $^{13}$C NMR (THF-$d_8$, 126 MHz) spectrum of **DIA10**.