Two Novel Carbazole Dyes for Dye-sensitized Solar Cells with Open-circuit Voltages up to 1 V Based on Br^-/Br_3^- Electrolytes

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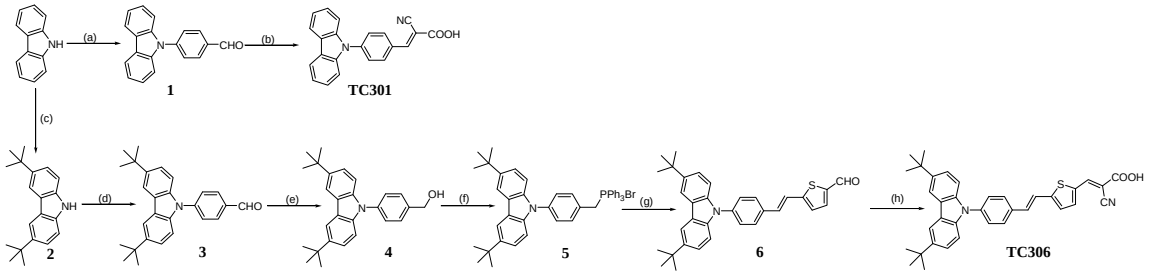
General

The synthetic routes of the dyes **TC301** and **TC306** were shown in **Scheme 1**. Carbazole was commercial available and used as received. TBP, LiI, I_2, LiBr and Br_2 were purchased from Acros and used after purification. All solvents and other chemicals were reagent grade and used without further purification. ^{1}H-NMR spectra were measured with VARIAN INOVA400 MHz (USA) with the chemical shifts against TMS. MS data were measured with GC-TOF MS (UK). Absorption and emission spectra were recorded with HP8453 (USA) and PTI700 (USA), respectively. Electrochemistry was measured with BAS100W (USA). The photovoltaic performances were obtained with an electrochemistry workstation (LK9805, China) and employed an AM 1.5 solar simulator (16S-002, Solar Light Co. Ltd., USA) as the light source. The measurement of the incident photon-to-current conversion efficiency (IPCE) was performed by a Hypermonolight (SM-25, Jasco Co. Ltd., Japan). Electrochemical impedance spectroscopy (EIS) for DSSC under dark with bias -0.7 V was measured with an impedance/gain-phase analyzer (PARSTAT 2273, USA). The spectra were scanned in a frequency range of 10^{-1}-10^5 Hz at room temperature. The alternate current (AC) amplitude was set at 10 mV.

1. Synthetic routes of the dyes TC301 and TC306:

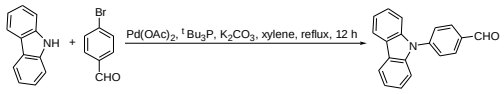


(a) 4-bromobenzaldehyde, $Pd(OAc)_2$, $^tBu_3P$, K_2CO_3, xylene, reflux, 12 h; (b) cynaoacetic acid, piperidine, CH_3CN, reflux, 2 h; (c) **1a**,

^{t}BuCl, Rt, 24 h; (d) 4-bromobenzaldehyde, $Pd(OAc)_2$, $^{t}Bu_3P$, K_2CO_3, xylene, reflux, 12 h; (e) $NaBH_4$, CH_2Cl_2, C_2H_5OH, Rt, 2 h; (f) PPh_3HBr, $CHCl_3$, reflux, 2 h; (g) (1) thiophene-2,5-dicarbaldehyde, 18-crown-6, K_2CO_3, DMF, Rt, 2 h; (2) I_2, THF, reflux, 8 h; (h) cynaoacetic acid, piperidine, CH_3CN, reflux, 2 h.

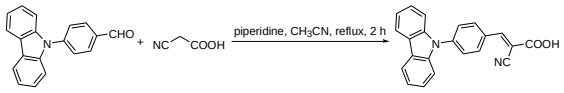
Scheme 1. Synthetic routes of **TC301** and **TC306**

4-Carbazol-9-yl-benzaldehyde (1):



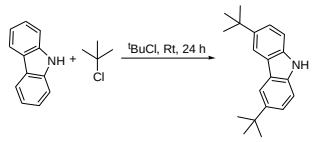
A two-necked flask containing 4-bromobenzaldehyde (201 mg, 1.1 mmol), carbazole (167 mg,1 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), K_2CO_3 (414 mg,3 mmol), $^{t}Bu_3P$ (6.1 mg, 0.03 mmol) and xylene (10 mL) equipped with a magnetic stirrer, a N_2 purge, and a reflux condenser was heated at 120 °C for 12 h. The reaction mixture was then poured into water and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography with CH_2Cl_2 : petroleum ether (v : v, 1 : 1) as eluent affording compound **1** as a pale yellow solid (120 mg, yield 44%). ^{1}H-NMR (400 MHz, acetone-d6, ppm): δ 7.179 (t, J = 8.0 Hz, 2H), 7.310 (t, J = 8.4 Hz, 2H), 7.409 (d, J = 8.4 Hz, 2H), 7.774 (d, J = 8.4 Hz, 2H), 8.097-8.129 (m, 4H), 10.049 (s, 1H). GC/TOF HRMS-EI (m/z): $[M]^+$ calcd. for $C_{19}H_{13}NO$, 271.0997; found, 271.0998.

3-(4-Carbazol-9-yl-phenyl)-2-cyano-acrylic acid (TC301):



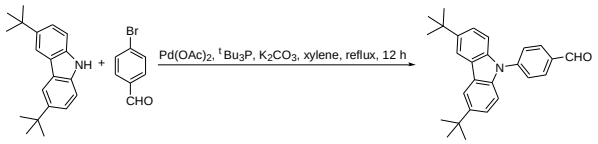
A CH_3CN (10 mL) solution of compound **1** (136 mg, 0.5 mmol), cyanoacetic acid (85 mg, 1.0 mmol), and a few drops of piperidine was charged sequentially in a three-necked flask and heated to reflux for 2 h.. After cooling to room temperature, solvents were removed by rotary evaporation, and the residue was purified by silica gel column chromatography with CH_2Cl_2 : CH_3OH (v : v, 10 : 1) as eluent to afford the dye **TC301** as a orange solid (127 mg, 75%). Mp. 204-205 ^{o}C. ^{1}H-NMR (400 MHz, DMSO, ppm): δ 7.302 (t, J = 8.0 Hz, 2H), 7.438-7.516 (m, 4H), 7.793 (d, J = 8.4 Hz, 2H), 8.106 (s, 1H), 8.190 (d, J = 8.4 Hz, 2H), 8.257 (d, J = 7.6 Hz, 2H). ^{13}C-NMR (400 MHz, DMSO, ppm): δ 140.076, 139.335, 138.481, 131.587, 130.385, 126.105, 125.779, 123.009, 120.825, 120.175, 119.862, 116.777, 109.316, 107.321. GC/TOF HRMS-EI (m/z): $[M-CO_2]^+$ calcd. for $C_{21}H_{14}N_2$, 294.1157; found, 294.1165.

3, 6-Di-tert-butyl-9H-carbazole (2):



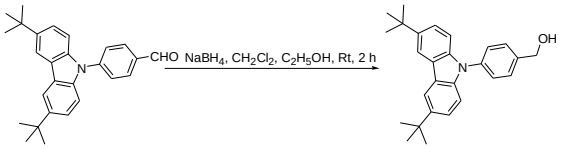
Carbazole (5.0 g, 0.03 mol) and anhydrous $AlCl_3$ (4.0 g, 0.03 mol) were dissolved in CH_2Cl_2 (100 mL). When the mixture was cooled to 0 ^oC, a solution of ^tBuCl (6.6 mL, 0.06 mol) in CH_2Cl_2 (20 mL) was added slowly. After that, the ice-bath was removed and the resulting mixture was stirred for 24 h at room temperature. Then, the mixture was poured into water, extracted with CH_2Cl_2 (3 × 50 mL), and dried with anhydrous $MgSO_4$. Solvent was evaporated to afford the crude products, which were recrystallized from petroleum ether twice to give compound **2** as a white solid (4.5 g, yield 54%). ^{1}H-NMR (400 MHz, acetone, ppm): δ 1.389 (s, 18H), 7.347 (d, J = 8.4 Hz, 2H), 7.414 (d, J = 8.4 Hz, 2H), 8.149 (s, 2H). GC/TOF HRMS-EI (m/z): $[M]^+$ calcd for $C_{20}H_{25}N$, 279.1987; found, 279.1989.

4-(3, 6-Di-tert-butyl-carbazol-9-yl)-benzaldehyde (3):



A procedure similar to that for compound **1** but with compound **2** (200 mg, 0.72 mmol) instead of carbazole. Giving compound **3** as pale yellow solid (122 mg, yield 44%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 1.399 (s, 18H), 7.397-7.412 (m, 4H), 7.709 (d, J = 8.4 Hz, 2H), 8.033 (d, J = 8.4 Hz, 2H), 8.066 (s, 2H), 10.033 (s, 1H). GC/TOF HRMS-EI (m/z): $[M]^+$ calcd. for $C_{27}H_{29}NO$, 383.2249; found, 383.2256.

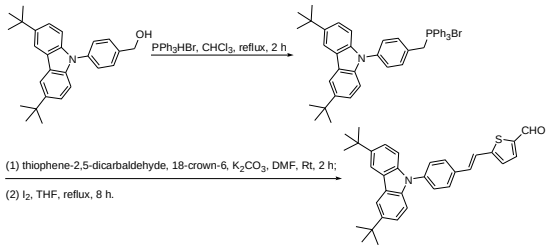
[4-(3, 6-Di-tert-butyl-carbazol-9-yl)-phenyl]-methanol (4):



To a solution of $NaBH_4$ (160 mg, 4.2 mmol) in dried CH_2Cl_2 (30 mL) and anhydrous ethanol (10 mL), compound **3** (1.15 g, 4.2 mmol) was added rapidly and the bath was stirred at room temperature for 2 h. The solution was poured into water (50 mL) with vigorously stirring and extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was dried with anhydrous sodium sulfate and then rotary evaporated to remove the solvent, gave compound **4** as white solid (1.11 g, yield 96%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 1.310 (s, 18H), 4.651 (s, 2H), 7.181 (d, J = 8.8, 2H), 7.357(d, J = 1.6 Hz, 2H), 7,378 (d, J = 2.0 Hz, 2H), 7.427 (d, J

= 8.4 Hz, 2H), 7.519 (d, J = 8.0 Hz, 2H), 8.161 (d, J= 2.0 Hz, 2H). GC/TOF HRMS-EI (m/z): $[M]^+$ calcd. for $C_{27}H_{31}NO$, 385.2406; found, 385.2424.

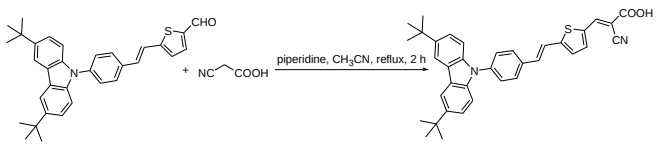
5-{2-[4-(3, 6-Di-tert-butyl-carbazol-9-yl)-phenyl]-vinyl}-thiophene-2-carbaldehyde (6):



Compound **4** (1.46 g, 3.8 mmol) and PPh_3HBr (1.37 g, 4 mmol) was dissolved in $CHCl_3$ (20 mL) and refluxed for 2 h. After removing the solvent, the residue was solidified with ether and filtrated to obtain compound **5** as white solid (yield 99%).

To a solution of thiophene-2, 5-dicarbaldehyde (140 mg, 1 mmol), 18-crown-6 ether (15 mg) and anhydrous K_2CO_3 (278 mg, 2 mmol) in DMF (20 mL), another solution of compound **5** (624 mg, 1.02 mmol) in DMF (25 mL) was added slowly with vigorously stirring at room temperature. The reaction was completed within 2 h. The reaction mixture was poured into water and filtered to collect the orange solid (a mixture of E and Z isomers), which was then dried in vacuo. Then the dried solid was dissolved in THF (30 mL) to reflux in the presence of catalysis amount iodine for 6 h. Then the mixture was added diluted solution NaOH to remove iodine, then extracted with CH_2Cl_2 (3 × 50 mL). Organic layer was dried with anhydrous Na_2SO_4 and removed the solvent, and was purified by column chromatography using silica gel and CH_2Cl_2 solvent as the eluent to give the pure compound **6** as yellow solid (301 mg, yield 62%). ^{1}H-NMR (400 MHz, acetone-d6, ppm): δ 1.452 (s, 18H), 7.41-7.70 (m, 9H), 7.93-7.98 (m, 3H), 8.31 (d, J = 1.6 Hz, 1H), 9.947 (s, 1H). GC/TOF HRMS-EI (m/z): $[M]^+$ calcd. for $C_{33}H_{33}NOS$, 491.2283; found, 491.2288.

2-Cyano-3-(5-{2-[4-(3,6-di-tert-butyl-carbazol-9-yl)-phenyl]-vinyl}-thiophen-2-yl)-acrylic acid (TC306):



A procedure similar to that for the dye **TC301** but with compound **6** (245 mg, 0.5 mmol) instead of

compound **1**. Giving the dye **TC306** as dark red solid (218 mg, yield 78%). Mp. 309-310 ^{o}C. ^{1}H-NMR (400 MHz, acetone-d6, ppm): δ 1.451 (s, 18H), 7.415-7.540 (m, 6H), 7.684 (d, J = 7.6 Hz, 3H), 7.941-8.013 (m, 3H), 8.31 (s, 2H), 8.45 (s, 1H). ^{13}C-NMR (400 MHz, DMSO, ppm): δ 163.671, 151.302, 145.332, 142.528, 141.718, 138.482, 138.086, 137.637, 134.018, 133.854, 131.287, 127.743, 126.791, 125.902, 123,176, 122.774, 120.657, 115.995, 115.587, 108.726, 34.089, 31.400. GC/TOF HRMS-EI (m/z): $[M-CO_2]^+$ calcd. for $C_{35}H_{34}N_2S$, 514.2443; found, 514.2439.

2. Spectra Data.

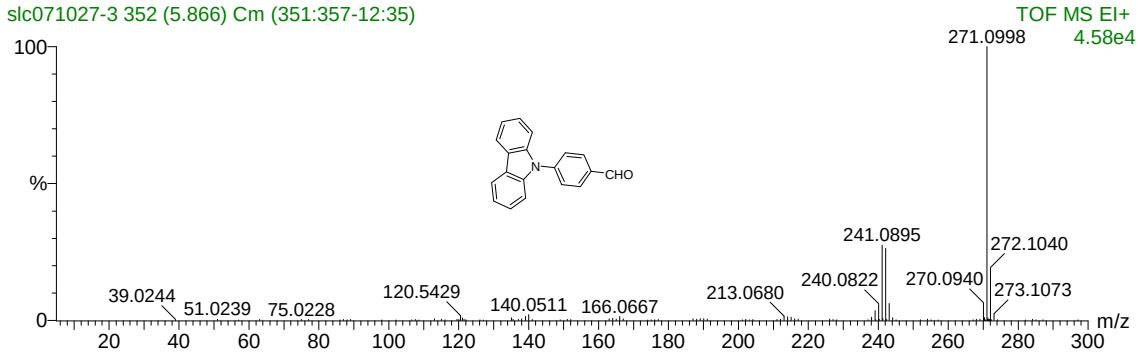


Figure 1 MS spectrum of compound **1**

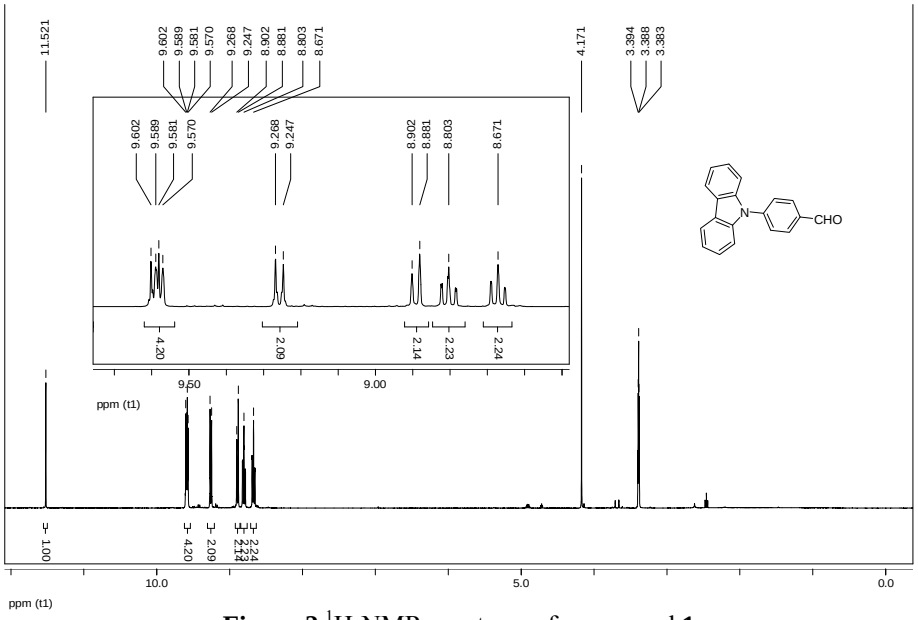


Figure 2 ^{1}H-NMR spectrum of compound **1**

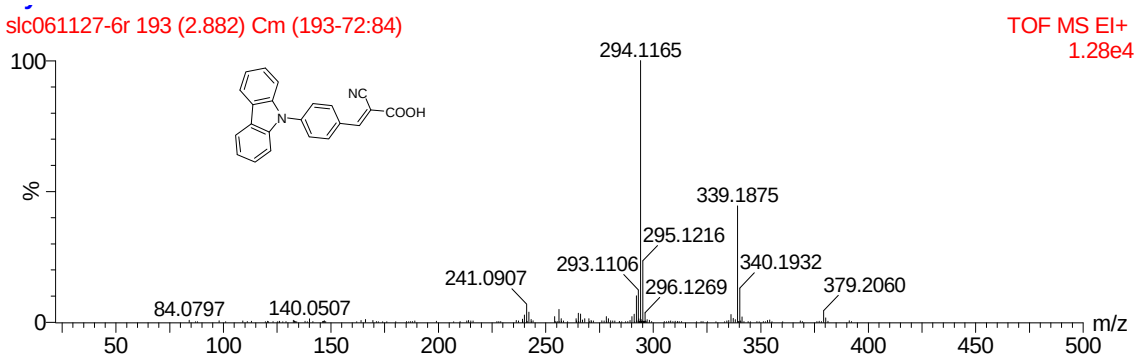


Figure 3 MS spectrum of the dye **TC301**

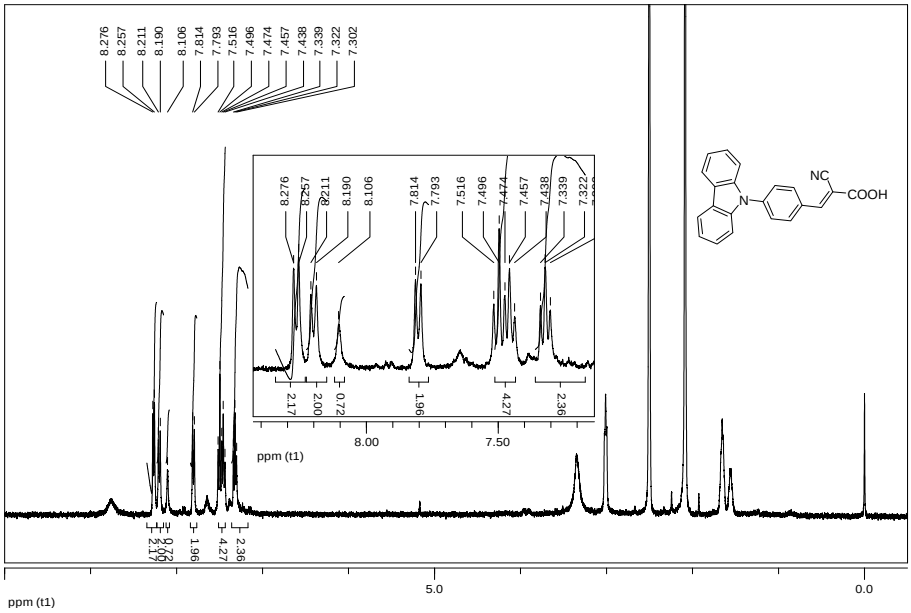


Figure 4 ^{1}H-NMR spectrum of the dye **TC301**

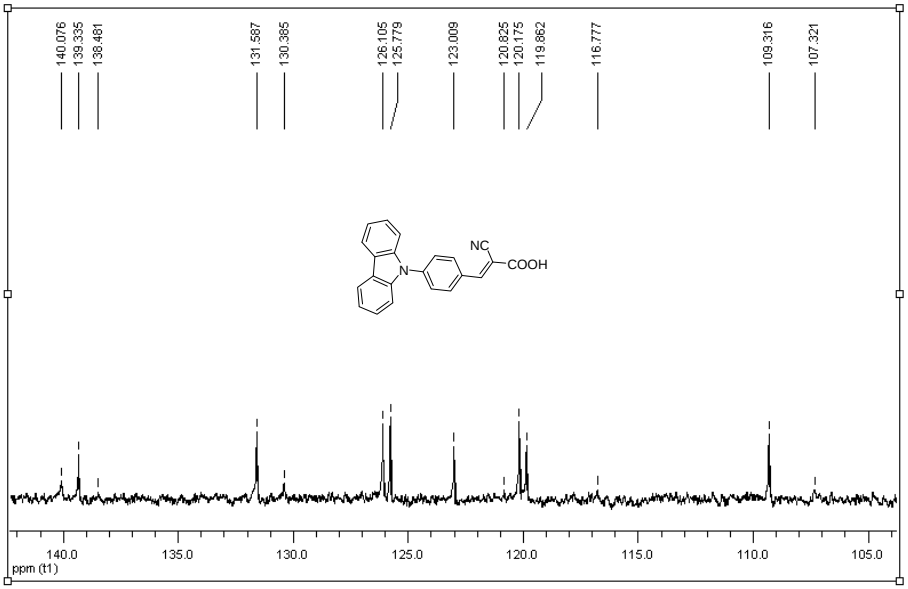


Figure 5 ^{13}C-NMR spectrum of the dye **TC301**

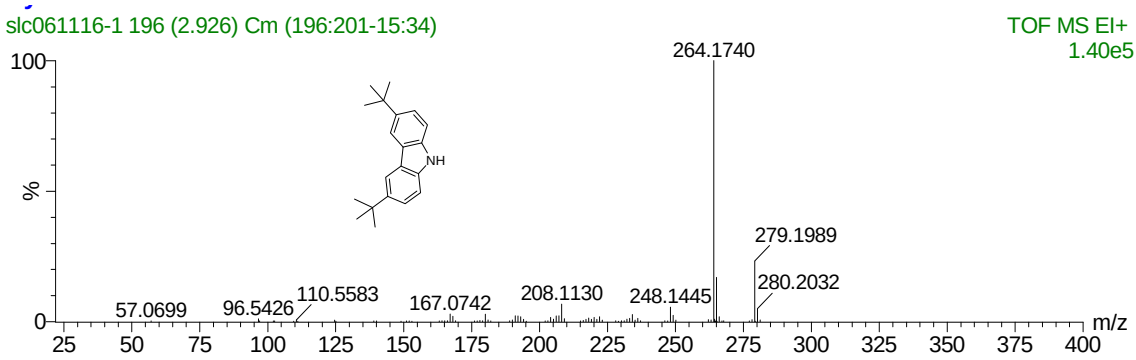


Figure 6 MS spectrum of compound **2**

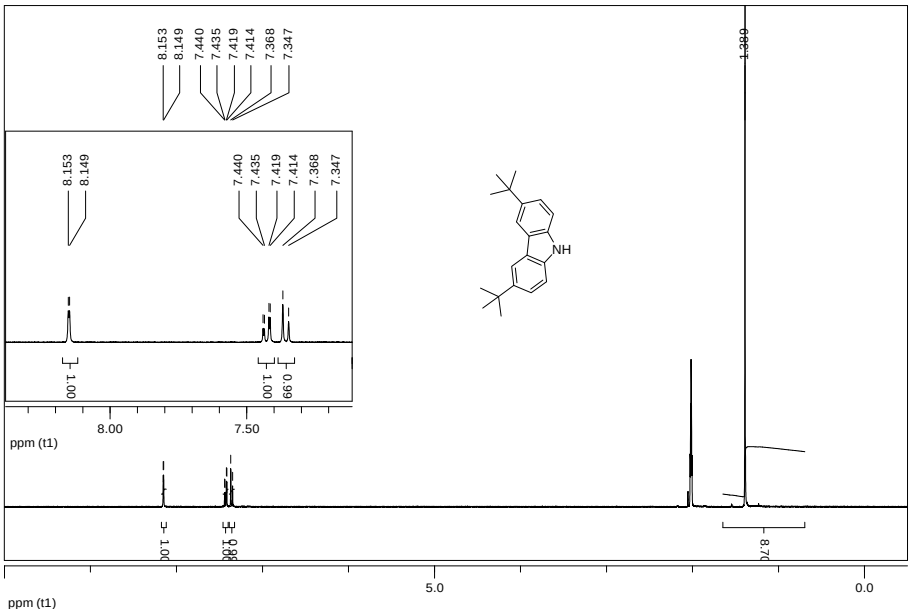


Figure 7 ^{1}H-NMR spectrum of compound **2**

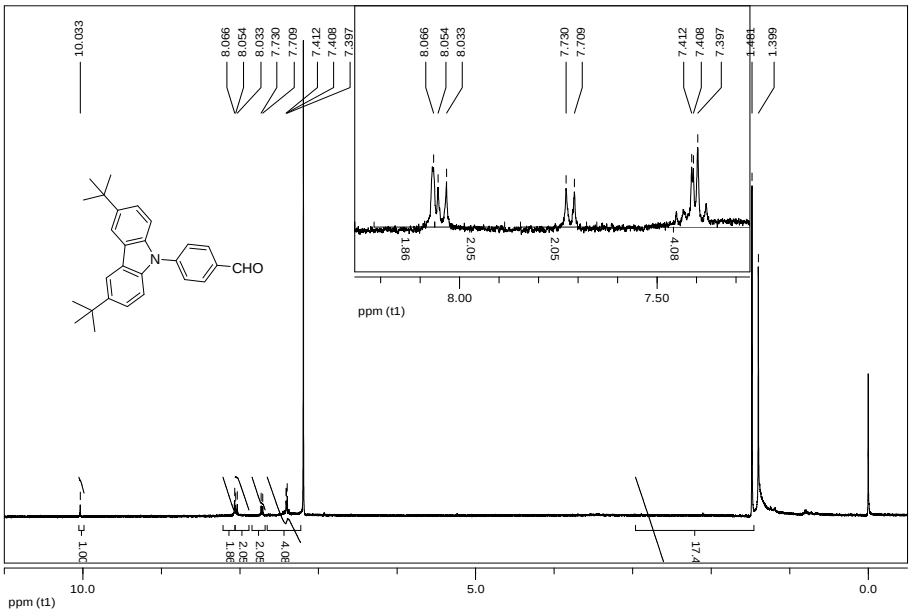


Figure 8 ^{1}H-NMR spectrum of compound **3**

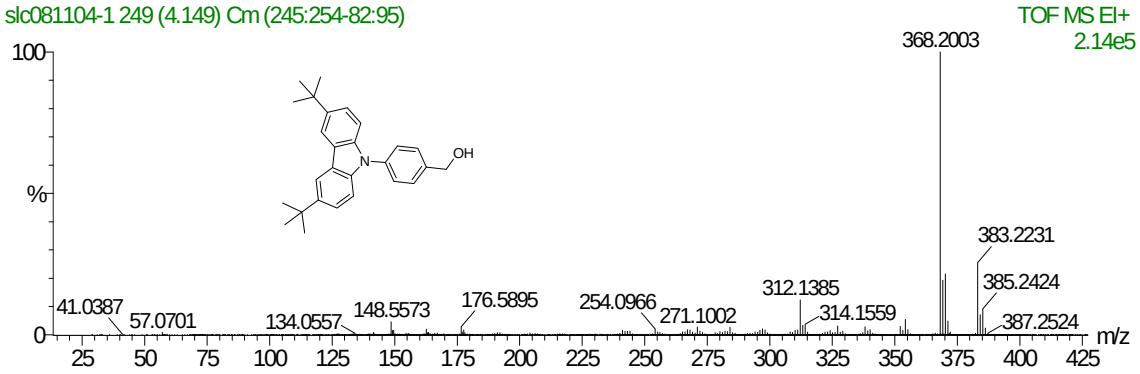


Figure 9 MS spectrum of compound **4**

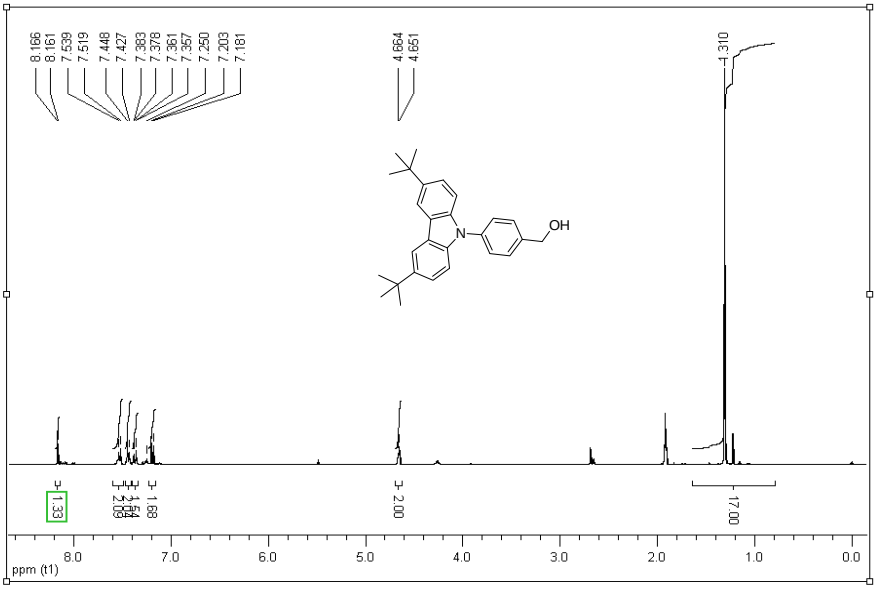


Figure 10 ^{1}H-NMR spectrum of compound **4**

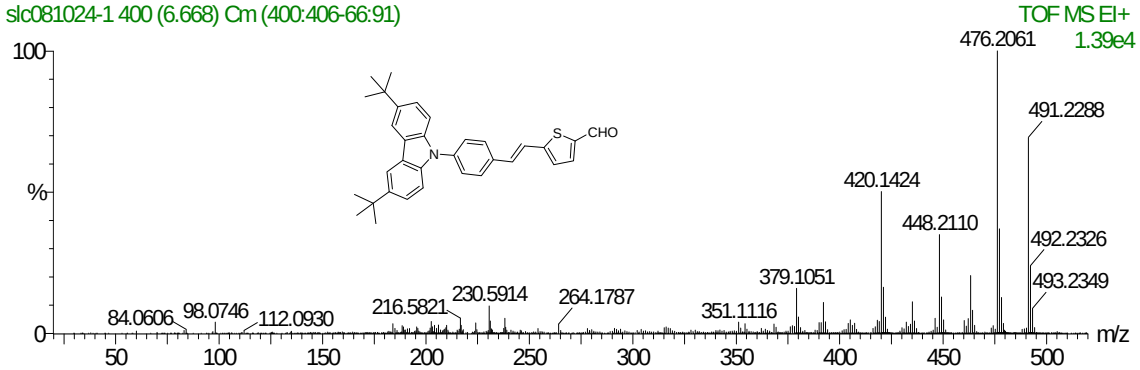


Figure 11 MS spectrum of compound **6**

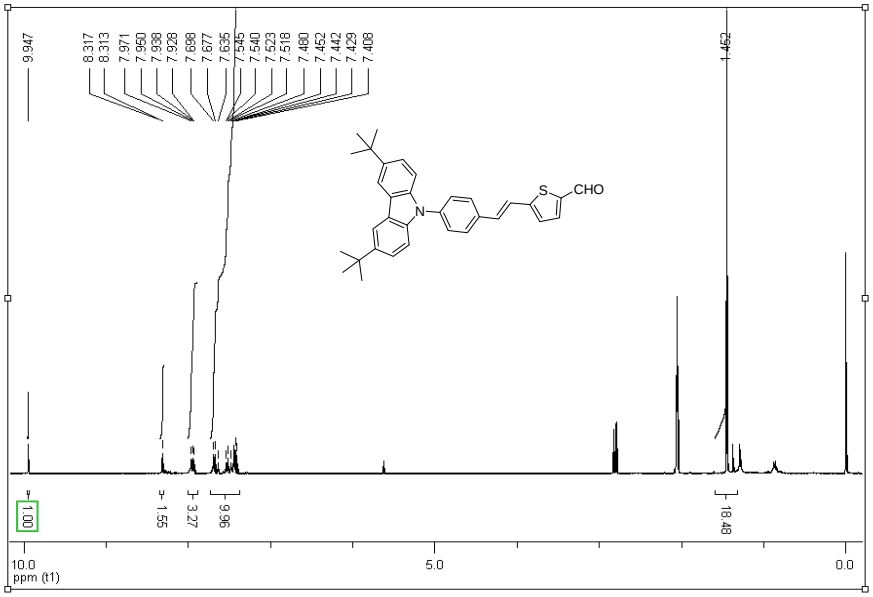


Figure 12 [1]H-NMR spectrum of compound **6**

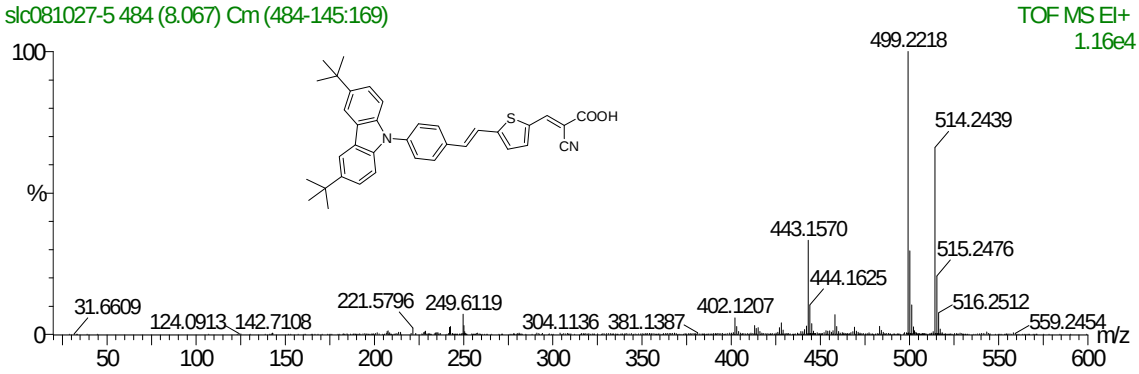


Figure 13 MS spectrum of the dye **TC306**

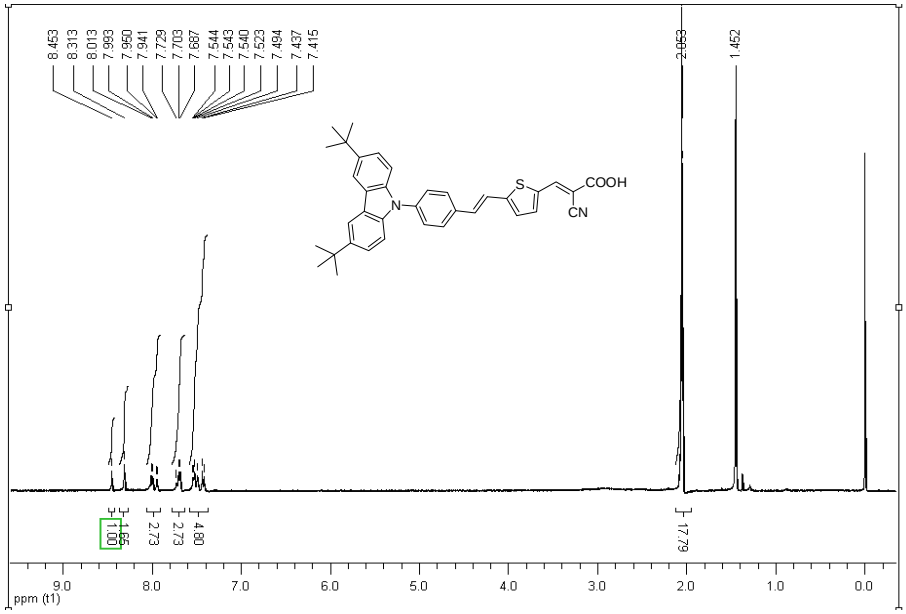


Figure 14 [1]H-NMR spectrum of the dye **TC306**

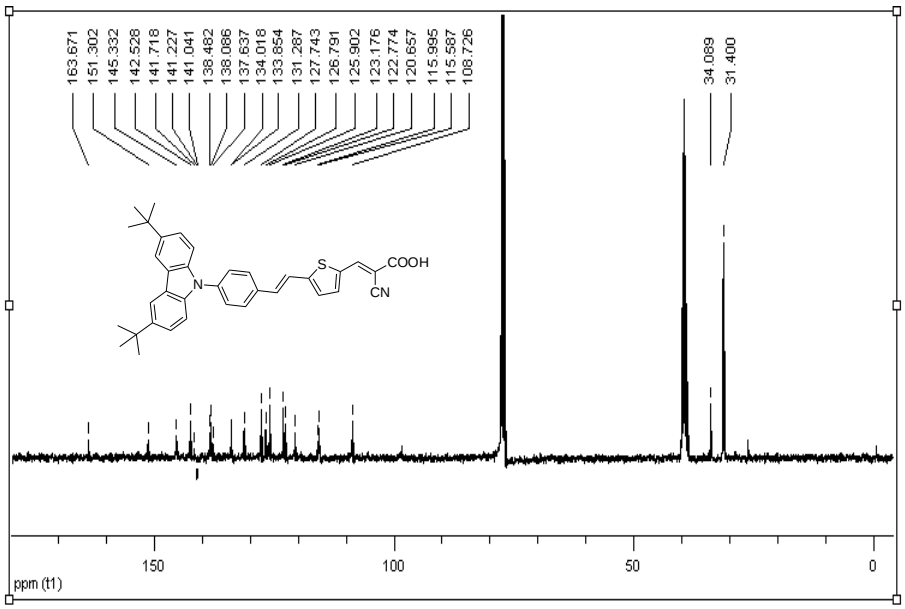


Figure 15 ^{13}C-NMR spectrum of the dye **TC306**

3. Fabrication of the Nanocrystalline TiO_2 Solar Cells.

A layer of 20 nm (DHS-TPP3, Heptachroma, China) titania paste (ca. 2 μm) was coated on the F-doped tin oxide conducting glass (TEC15, 15 Ω/square, Pilkington, USA) by screen printing and then dried for 6 min at 125 ^{o}C. This procedure was repeated for 6 times (ca. 12 μm) and coated by a layer of 300 nm (DHS-SLP1, Heptachroma, China) titania paste (ca. 4 μm) as scattering layer. The double-layer TiO_2 electrodes (area: 6×6 mm) were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The sintered film was further treated with 40 mM $TiCl_4$ aqueous solution at 70 ºC for 30 min, then washed with ethanol and water, and annealed at 500 ºC for 30 min. After the film was cooled to 40 °C, it was immersed into a 2×10^{-4} M the dye **TC301** or **TC306** solution in CH_2Cl_2 with saturated CDCA and maintained under dark for 8 h. The sensitized TiO_2 electrode was then rinsed with the solvent of dye-bath and dried. The hermetically sealed cells were fabricated by assembling the dye-loaded film as the working electrode and Pt-coated conducting glass as the counter electrode separated with a hot-melt Surlyn 1702 film (25 μm, Dupont). The electrolytes were introduced into the cell via vacuum backfilling from a hole in the back of the counter electrode. Finally, the hole was also sealed using Surlyn 1702 film and cover glass.