

Supporting Information

Molecular engineering of alkyl chain in planar carbazole dye toward efficient interfacial charge transfer processes

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1. Experimental details

1.1 Materials and Instruments

All the chemicals, including all solvents, were purchased from Energy Chemical Co., Ltd and used as received. The FTO conducting glass was obtained from YingKou OPV Tech New Energy Co., Ltd., China. The TiO₂ paste was purchased from Dyesol Ltd. and JGC C&C Ltd., respectively. Other materials for DSSCs fabrication were purchased from Energy Chemical Co., Ltd. and used as received.

¹H NMR and ¹³C NMR spectra of all intermediates and target sensitizers were obtained by Bruker AVIII-500 spectrometer with tetramethylsilane as an internal standard. The synthetic route, procedure, and all the characterization of the CS dyes and their intermediates were shown below.

1.2 Optical and electrochemical measurements

UV-visible spectra of CS dyes both in solution and on TiO₂ electrode were recorded by a Shimadzu UV-2501PC spectrometer. The photoluminescence was measured on Hitachi F-4600 spectrometer. The time-correlated PL signals of all three dyes both in solution and on electrode were recorded by FLS980 Spectrometer (Edinburgh Instrument). The PL decay signals were detected at 680 nm upon excitation with picosecond pulsed diode laser EPL-450 at 450 nm. The cyclic voltammograms tests were performed on a CHI660B electrochemical workstation (CH Instruments) using a glassy carbon electrode as the working electrode and a Pt wire as the counter electrode

with a SCE reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphoric was used as the supporting electrolyte.

1.3 Fabrication and measurement of solar cells

For fabrication of DSSCs based on CS dyes, 6 μm nanocrystalline TiO_2 electrodes with a 4 μm scattering layer were used as the TiO_2 electrodes. All the TiO_2 electrodes were prepared and modified according to the reported procedure.¹ The dye-loaded electrodes were prepared by immersing TiO_2 electrodes into around 0.3 mM dye solution (chloroform) overnight. The active area was controlled to be 0.25 cm^2 . In this work, a mixture of 0.5 M 1-butyl-3-methylimidazolium iodide (BMII), 0.10 M LiI, 0.05 M I_2 , and 0.5 M *tert*-butylpyridine (t-BP) in acetonitrile was used as the redox electrolyte. The dye-loaded amount was determined by desorbing the dye from the surface of dye-sensitized TiO_2 electrode (thickness: 6 μm , area: $2 \times 2 \text{ cm}^2$) into NaOH solution ($\text{H}_2\text{O}/\text{EtOH} = 1/1$, v/v) and analyzed by a UV-visible spectrometer. For dummy cell, 3 μm ZrO_2 electrode was prepared by exactly same method as described above, except using ZrO_2 paste instead, which was prepared according to the published procedure.²

J-V curves were obtained by using an AM 1.5 solar simulator equipped with a 150 W xenon lamp (OTENTO-SUN II, Bunkoukeiki Co., Ltd) as the light source. The power was calibrated to 100 mW cm^{-2} using a reference silicon cell (BS-520, Bunkoukeiki Co., Ltd). The photocurrent action spectra were measured with a monochromator (M10-

T, Bunkoukeiki Co., Ltd). The intensity of monochromic light was calibrated by a reference silicon cell (S1337-1010BQ, Bunkoukeiki Co., Ltd).

The electrochemical impedance spectroscopy (EIS) measurements were characterized with Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany), with a frequency range of 0.1 Hz–100 kHz and an alternative signal of 5 mV at a constant temperature of 25 °C in the dark conditions. The spectra were characterized using Zsimpwin software.

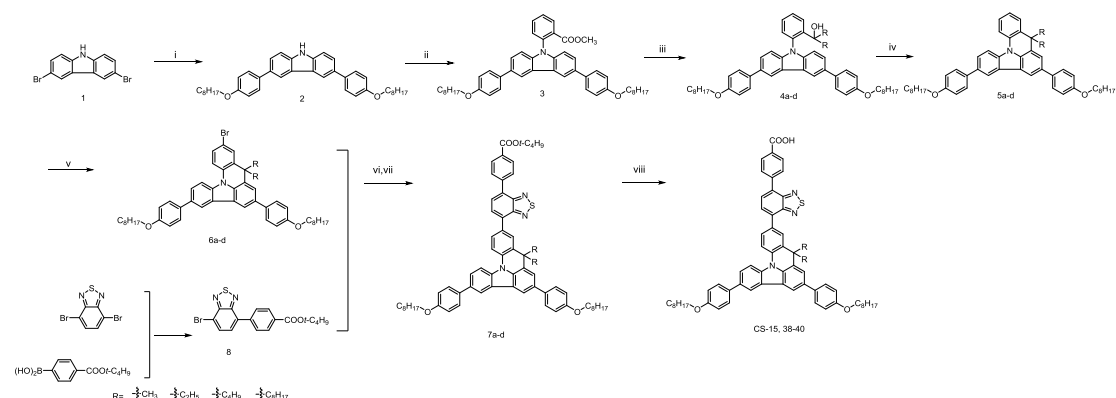
The charge lifetime and charge density in the complete DSSCs were measured by the stepped light-induced transient measurements of photocurrent and voltage (SLIM-PCV) of the photocurrent and voltage using PSL-100 (EKO Co. Ltd).³ A laser ($\lambda = 473 \text{ nm}$) was used as the light source. The transients were induced by a stepwise change in the laser intensity which was controlled by adjusting its voltage. The photocurrent and photovoltage transients were monitored using a digital oscilloscope through an amplifier. Through varying the laser intensity, the lifetime could be estimated over a range of open-circuit voltages by fitting a decay of the photovoltage transient with $\exp(-t/\tau)$.³ The electron density measurements were performed as follows: the DSSC was illuminated for 5 s while a bias voltage was applied to make the cell open-circuit, then the laser as shut down simultaneously, and the cell was switched from open to short circuit. The resulting current was measured over 25 s and then the electron density could be calculated through integrating the electric charge. All experiments were conducted

at room temperature. Ten samples were fabricated and tested for each measurement and median values were selected to be shown in this paper.

1.4 Theoretical calculations

All the theoretical calculation analysis was performed using Gaussian 09 program.⁴ The ground-state geometries of the dyes were optimized on the basis of hybrid density functional theory (B3LYP) with the 6-311G(d,p) basis set. TDDFT excited states calculation and the molecular geometries of both dyes at the first excited singlet states were performed at the MPWPW91/6-311G (d,p) level with the optimized ground-state geometry. Solvation effects (chloroform) were taken into account in the TDDFT calculations with the CPCM model implemented in Gaussian 09 program.

2. Synthesis and characterization of new compounds



Scheme S1. Synthetic route and chemical structure of dye **CS-15** and 38-40, where R represents hydrogen, methyl, ethyl, butyl and octyl of compounds a-d, respectively. Reaction conditions: (i) 4-octyloxyphenylboronic acid, 2M Na₂CO₃, Pd (PPh₃)₄, toluene; (ii) Methyl o-bromobenzoate, CuI, Cs₂CO₃, o-dichlorobenzene; (iii) Alkyl Format Reagent; (iv) Toluene, Amberlyst 15; (v) DCM, NBS, acetonitrile; (vi) Dry THF, n-butyllithium, triisopropyl borate; (vii) K₂CO₃, Pd (PPh₃)₄, toluene; (viii) CF₃COOH, DCM.

Synthesis of compound 2: Compound 1 (2.00 g, 6.15 mmol), 4-octyloxyphenylboronic acid (3.77 g, 15.08 mmol), Na₂CO₃ (5 mL) and Pd (PPh₃)₄ (0.71 g, 0.61 mmol) were dissolved in a toluene solution (70 mL). The mixture was then refluxed under nitrogen for 24 h. After cooling to normal temperature, water and the mixture were added and the mixture was extracted and separated with dichloromethane. The organic layer was then dried over anhydrous Na₂SO₄, and the organic solvent was removed by evaporation under reduced pressure. The crude product was purified through silica gel column chromatography (PE / EA = 100: 1) to obtain the product as white solid (2.66

g, 75%. m.p.: 117-118 °C).

Characterization of compound 2: ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.27 (s, 2H), 8.06 (s, 1H), 7.63 (d, $J = 8.0$ Hz, 6H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 4H), 4.02 (t, $J = 6.4$ Hz, 4H), 1.80-1.85 (m, 4H), 1.46-1.52 (m, 4H), 1.31-1.38 (m, 16H), 0.90 (t, $J = 6.4$ Hz, 6H). ν (KBr)/ cm^{-1} : 2930.08 (C-H), 2861.41 (C-H), 1719.95 (1608.92 (aromatic C=C), 1498.09 (Ar-), 1471.62 (Ar-), 1454.50 (Ar-), 1297.61 (C-O), 1249.26 (C-O-C), 1224.11 (C-O-C), 1181.44 (C-N), 826.75 (C-H), 811.30 (C-H), 758.62 (C-H).

Synthesis of compound 3: The compound 2 (1.00g, 1.74mmol), methyl o-bromobenzoate (0.98g, 3.46mmol), CuI (0.33g, 1.74mmol) and K_2CO_3 (1.13g, 3.46mmol) were dissolved in o-dichlorobenzene, and refluxed at 180 degrees for 24 hours under the protection of nitrogen. After cooling, the organic solvent was distilled off under reduced pressure, and then the mixture was extracted with water and dichloromethane. After the extraction was completed, a desiccant Na_2SO_4 was added.

The crude product was purified through silica gel column chromatography (PE / EA = 100: 1) to obtain the product as yellow oil (1.10 g, 89%. m.p.: 63-64 °C).

*Characterization of compound 3:*⁵ ^1H NMR (500 MHz, CDCl_3 , ppm): δ 8.36 (s, 2H), 8.17 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 7.5$ Hz, 1H), 7.61-7.68 (m, 8H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 8.0$ Hz, 4H), 4.06 (t, $J = 6.5$ Hz, 4H), 3.32 (s, 3H), 1.83-1.89 (m, 4H), 1.51-1.54 (m, 4H), 1.35-1.42 (m, 16H), 0.94 (t, $J = 6.5$ Hz, 6H). ν (KBr)/ cm^{-1} : 2930.08 (C-H), 2850.60 (C-H), 1719.95 (C=O), 1646.12 (aromatic C=C), 1477.27 (Ar-), 1461.28 (Ar-), 1445.12 (Ar-), 1292.50 (C-O), 1276.63 (C-O-C), 1250.31 (C-O-C),

1171.44(C-N), 822.11 (C-H), 790.13 (C-H).

General Synthesis of compound 4a: Compound 3 (3.0 g, 4.23 mmol) was added with Grignard reagent (methyl magnesium bromide) in THF (15 mL). The mixture was stirred for 12 h at 70 °C under nitrogen and then the saturated NH₄Cl (100mL) solution was slowly added to stop the reaction. The mixture was extracted with dichloromethane and the combined organic layer was dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography (PE / EA = 200: 1) on silica gel to yield the product as yellow solid.

The synthesis procedures of compounds 4b-d were exactly same as that of compound 4a except the Grignard reagent for compounds 4b-d was changed to ethyl magnesium bromide, butyl magnesium chloride, octyl magnesium bromide, respectively. The characterization of compounds 4b-d were presented as followed:

Characterization of compound 4b: 2.03g, 65%. m.p.: 76-77 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.36 (s, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 4H), 7.61 (d, *J* = 8.0 Hz, 3H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.04-7.07 (m, 7H), 4.07 (t, *J* = 6.6 Hz, 4H), 1.84-1.95 (m, 6H), 1.69-1.76 (m, 2H), 1.51-1.54 (m, 4H), 1.31-1.41 (m, 16H), 0.96 (t, *J* = 6.4 Hz, 6H), 0.88 (t, *J* = 7.2 Hz, 6H). ν (KBr)/cm⁻¹: 3445.10 (O-H), 2935.32 (C-H), 2856.21 (C-H), 1646.12 (aromatic C=C), 1487.60 (Ar-), 1465.60 (Ar-), 1445.12 (Ar-), 1276.63 (C-O-C), 1250.31 (C-O-C), 1170.67 (C-N), 815.34 (C-H), 758.62 (C-H).

Characterization of compound 4c: 2.02g, 60%. m.p.: 70-71 °C. ¹H NMR (400 MHz,

CDCl₃, ppm): δ 8.39 (s, 2H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 4H), 7.63 (d, $J = 8.0$ Hz, 3H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.06-7.11 (m, 7H), 4.09 (t, $J = 6.6$ Hz, 4H), 1.79-1.93 (m, 6H), 1.63-1.70 (m, 2H), 1.53-1.58 (m, 4H), 1.38-1.43 (m, 16H), 1.16-1.23 (m, 8H), 0.97 (t, $J = 6.5$ Hz, 6H), 0.88 (t, $J = 7.0$ Hz, 6H). ν (KBr)/cm⁻¹: 3443.10 (O-H), 2919.32 (C-H), 2856.21 (C-H), 1646.12 (aromatic C=C), 1498.60 (Ar-), 1467.82 (Ar-), 1456.12 (Ar-), 1276.40 (C-O), 1250.16 (C-O-C), 1170.62 (C-N), 811.37 (C-H), 750.82 (C-H).

Characterization of compound 4d: 2.17g, 57%. m.p.: 75-76 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.36 (s, 2H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.68 (d, $J = 8.0$ Hz, 4H), 7.60 (d, $J = 8.0$ Hz, 3H), 7.45 (t, $J = 7.4$ Hz, 1H), 7.03-7.10 (m, 7H), 4.08 (t, $J = 6.4$ Hz, 4H), 1.82-1.90 (m, 6H), 1.75-1.80 (m, 2H), 1.51-1.57 (m, 4H), 1.26-1.40 (m, 16H), 1.12-1.21 (m, 24H), 0.96 (t, $J = 6.6$ Hz, 6H), 0.88 (t, $J = 7.0$ Hz, 6H). ν (KBr)/cm⁻¹: 3558.90 (O-H), 2924.91 (C-H), 2856.61 (C-H), 1624.92 (aromatic C=C), 1487.60 (Ar-), 1469.86 (Ar-), 1453.20 (Ar-), 1270.81 (C-O-C), 1223.35 (C-O-C), 1165.40 (C-N), 806.10 (C-H), 763.80 (C-H).

Synthesis of **compound 5a**: The compounds 4a (1.16g, 1.63 mmol) and Amberlyst 15 (1.50 g) were mixed in toluene and refluxed for 12 h. After extraction with dichloromethane, the organic layer was dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography to obtain as white solid.

The synthesis procedures of compounds 5b-d were exactly same as that of compound 5a except the solvent of compound 5c-d was changed to *o*-dichlorobenzene. The

characterization of compounds 5b-d were presented as followed:

Characterization of compound 5b: 0.83g, 71%. m.p.: 73-74 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.39 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 8.13 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.70-7.73 (m, 4H), 7.57 (d, *J* = 6.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 4H), 4.09 (t, *J* = 6.6 Hz, 4H), 2.15-2.22 (m, 4H), 1.85-1.92 (m, 4H), 1.51-1.59 (m, 4H), 1.36-1.42 (m, 16H), 0.96 (t, *J* = 6.6 Hz, 6H), 0.60 (t, *J* = 7.2 Hz, 6H). ν (KBr)/cm⁻¹: 2935.31 (C-H), 2845.41 (C-H), 1614.62 (aromatic C=C), 1499.04 (Ar-), 1465.71 (Ar-), 1445.60 (Ar-), 1270.10 (C-O-C), 1245.65 (C-O-C), 1170.60 (C-N), 837.60 (C-H), 795.31 (C-H).

Characterization of compound 5c: 0.94g, 75%. m.p.: 75-76 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.42 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.16 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.60-7.63 (m, 4H), 7.61 (d, *J* = 6.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 4H), 4.11 (t, *J* = 6.6 Hz, 4H), 2.15-2.20 (m, 4H), 1.88-1.94 (m, 4H), 1.54-1.62 (m, 4H), 1.38-1.48 (m, 16H), 1.16-1.24 (m, 4H), 0.92-0.99 (m, 10H), 0.75 (t, *J* = 7.2 Hz, 6H). ν (KBr)/cm⁻¹: 2935.31 (C-H), 2850.61 (C-H), 1609.00 (aromatic C=C), 1490.30 (Ar-), 1473.70 (Ar-), 1450.08 (Ar-), 1270.80 (C-O-C), 1244.46 (C-O-C), 1175.80 (C-N), 801.50 (C-H), 742.63 (C-H).

Characterization of compound 5d: 0.96g, 67%. m.p.: 64-65 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.39 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 8.13 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.70-7.74 (m, 4H), 7.58 (d, *J* = 6.4 Hz, 2H), 7.44 (t, *J* =

7.6 Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 4H), 4.10 (t, $J = 6.6$ Hz 4H), 2.12-2.16 (m, 4H), 1.86-1.92 (m, 4H), 1.52-1.58 (m, 4H), 1.36-1.45 (m, 16H), 1.10-1.21 (m, 24H), 0.97 (t, $J = 6.6$ Hz, 6H), 0.85 (t, $J = 7.0$ Hz, 6H). ν (KBr)/ cm^{-1} : 2942.31 (C-H), 2856.20 (C-H), 1614.60 (C=C), 1485.60 (Ar-), 1458.00 (Ar-), 1430.36 (Ar-), 1276.4 (C-O-C), 1255.31.80 (C-O-C), 1175.80 (C-N), 832.50 (C-H), 790.13 (C-H).

Synthesis of compound 6a: Compound 5a (0.14g, 0.2 mmol) was dissolved in dichloromethane, NBS (0.09g, 0.5 mmol) was dissolved in acetonitrile and added dropwise to the mixture, stirred in an ice bath for 4h and then at room temperature for 1h. After the reaction, the mixture was extracted with dichloromethane and the combined organic layer was dried over Na_2SO_4 . The crude product was distilled under reduced pressure. Then the crude product was purified by column chromatography with pure petroleum ether to obtain white solid compound 6a.

The synthesis procedures of compounds 6b-d were exactly same as that of compound 6a. The characterization of compounds 6b-d were presented as followed:

Characterization of compound 6b: 0.10g, 74%. m.p.: 67-68 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.22 (s, 1H), 8.20 (d, $J = 8.0$ Hz, 1H), 8.08 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 8.0$ Hz, 2H), 7.32 d, $J = 8.0$ Hz, 1H), 7.07 (t, $J = 8.0$ Hz, 4H), 4.09 (t, $J = 6.6$ Hz, 4H), 2.07-2.13 (m, 4H), 1.85-1.90 (m, 4H), 1.51-1.57 (m, 4H), 1.35-1.40 (m, 16H), 0.96 (t, $J = 6.6$ Hz, 6H), 0.62 (t, $J = 7.4$ Hz, 6H). ν (KBr)/ cm^{-1} : 2930.91 (C-H), 2855.60 (C-H), 1609.80 (aromatic C=C), 1483.90 (Ar-), 1457.30 (Ar-), 1448.42 (Ar-),

1276.31 (C-O-C), 1250.65 (C-O-C), 1175.80 (C-N), 827.50 (C-H), 790.55 (C-H), 618.25 (C-Br).

Characterization of compound 6c: 0.11g, 73%. m.p.: 70-71 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 9.27 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.33-7.38 (m, 2H), 7.12 (t, *J* = 8.0 Hz, 4H), 4.15 (t, *J* = 6.6 Hz, 4H), 2.07-2.11 (m, 4H), 1.85-1.95 (m, 4H), 1.56-1.62 (m, 4H), 1.40-1.45 (m, 16H), 1.18-1.26 (m, 4H), 0.91-1.01 (m, 10H), 0.79 (t, *J* = 7.2 Hz, 6H). ν (KBr)/cm⁻¹: 2924.91 (C-H), 2856.20 (C-H), 1619.80 (aromatic C=C), 1499.04 (Ar-), 1465.64 (Ar-), 1445.30 (Ar-), 1274.56 (C-O-C), 1244.50 (C-O-C), 1181.40 (C-N), 832.50 (C-H), 795.31 (C-H), 621.29 (C-Br).

Characterization of compound 6d: 0.12g, 70%. m.p.: 64-65 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 9.24 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.50-7.56 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 4H), 4.09 (t, *J* = 6.6 Hz, 4H), 2.02-2.08 (m, 4H), 1.85-1.94 (m, 4H), 1.51-1.60 (m, 4H), 1.26-1.42 (m, 16H), 1.17-1.26 (m, 24H), 0.95 (t, *J* = 6.6 Hz, 6H), 0.88 (t, *J* = 7.0 Hz, 6H). ν (KBr)/cm⁻¹: 2919.30 (C-H), 2856.20 (C-H), 1609.80 ((aromatic C=C), 1482.40 (Ar-), 1458.33 (Ar-), 1448.42 (Ar-), 1281.50 (C-O-C), 1239.29 (C-O-C), 1170.60 (C-N), 832.50 (C-H), 795.32 (C-H), 615.65 (C-Br).

Synthesis of intermediate 8: The intermediate 8 was synthesized according to the

published procedure⁶.

Synthesis of compound 7a-d: The compound 6a (0.34 g, 0.46 mmol) in dry THF (25 mL) was cooled to -78 °C under nitrogen. Then the n-BuLi (3mL) was slowly dropped and the mixture was stirred for 2 h. The triisopropyl borate (0.26g, 1.38 mmol) was slowly dropped and the mixture was stirred for another 1 h at -78 °C. Then the mixture stirred for 12 h at room temperature. After the reaction was completed, the mixture was poured into water and extracted with ethyl acetate. Then 2 M K₂CO₃ (4 mL), above obtained crude compound 8 and Pd (PPh₃)₄ (0.05 g, 0.043 mmol) were dissolved in toluene (30 mL), and the mixture was refluxed for 12 h under nitrogen. After the reaction was completed, the reaction solution was poured into water and extracted with ethyl acetate. The organic layers were combined, dried over anhydrous Na₂SO₄, and the organic solvent was removed by evaporation under reduced pressure. The crude product was purified through silica gel column chromatography (PE / EA = 100: 1) to obtain the product as orange solid.

The synthesis procedures of compounds 7b-d were exactly same as that of compound 7a. The characterization of compounds 7b-d were presented as followed:

Characterization of compound 7b: 0.32g, 67%. m.p.: 134-135 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.41 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 4H), 8.10-8.16 (m, 4H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.72-7.76 (m, 4H), 7.63 (s, 1H), 7.09-7.11 (m, 4H), 4.09 (t, *J* = 6.6 Hz, 4H), 2.27-2.29 (m, 4H), 1.87-1.91 (m, 4H), 1.70 (s, 9H), 1.52-1.56 (m, 4H), 1.35-1.39 (m, 16H), 0.96 (t, *J* = 6.2 Hz, 6H), 0.71

(t, $J = 7.2$ Hz, 6H). ^{13}C NMR (125MHz, CDCl_3 , ppm): δ 165.6, 158.5, 158.4, 154.2, 154.1, 141.4, 138.6, 137.3, 137.2, 136.1, 134.7, 134.0, 133.7, 133.5, 131.8, 131.6, 130.5, 129.7, 129.0, 128.6, 128.4, 128.3, 128.2, 128.0, 127.0, 126.8, 125.5, 122.3, 121.7, 118.8, 115.6, 115.0, 114.8, 114.1, 113.5, 81.15, 68.2, 46.9, 31.9, 29.5, 29.4, 29.3, 28.3, 26.2, 22.7, 14.2, 9.8. HRMS (FAB^+ , m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{68}\text{H}_{75}\text{N}_3\text{O}_4\text{S}$, 1029.5478; found, 1029.5492. ν (KBr)/ cm^{-1} : 2930.10 (C-H), 2850.60 (C-H), 1714.80 (C=O), 1635.77 (C=N), 1609.80 (aromatic C=C), 1477.32 (Ar-), 1450.40 (Ar-), 1428.75 (Ar-), 1292.50 (C-O), 1275.48 (C-O-C), 1243.56 (C-O-C), 1175.40 (C-N), 1107.10 (N-S), 827.30 (C-H), 797.85 (C-H), 767.35 (C-H).

Characterization of compound 7c: 0.33g, 67%. m.p.: 126-127 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.40 (s, 1H), 8.34 (d, $J = 8.0$ Hz, 1H), 8.23 (d, $J = 8.0$ Hz, 4H), 8.10-8.15 (m, 4H), 7.94 (d, $J = 8.0$ Hz, 2H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.71-7.74 (m, 4H), 7.62 (s, 1H), 7.08-7.11 (m, 4H), 4.09 (t, $J = 6.6$ Hz, 4H), 2.21-2.28 (m, 4H), 1.85-1.91 (m, 4H), 1.69 (s, 9H), 1.53-1.55 (m, 4H), 1.36-1.41 (m, 16H), 1.20-1.25 (m, 4H), 0.93-0.97 (m, 10H), 0.75 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (125MHz, CDCl_3 , ppm): 165.6, 158.6, 158.5, 154.2, 154.1, 141.5, 138.3, 137.4, 137.0, 136.8, 136.1, 134.7, 134.0, 133.6, 131.8, 131.6, 131.4, 129.8, 129.1, 128.7, 128.4, 128.3, 127.9, 126.9, 126.8, 125.6, 122.3, 121.5, 118.9, 115.7, 115.4, 115.2, 115.0, 114.7, 113.9, 81.2, 68.3, 45.6, 31.9, 31.9, 30.1, 29.9, 29.5, 28.3, 26.2, 23.2, 22.8, 14.2, 14.0. HRMS (FAB^+ , m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{72}\text{H}_{83}\text{N}_3\text{O}_4\text{S}$, 1085.6104; found, 1085.6112. ν (KBr)/ cm^{-1} : 2930.10 (C-H), 2850.60 (C-H), 1714.80 (C=O), 1639.94 (C=N), 1614.60 (aromatic C=C), 1461.32 (Ar-), 1453.09 (Ar-), 1426.28 (Ar-), 1291.93 (C-O), 1274.47 (C-O-C), 1241.27 (C-O-C),

1169.20 (C-N), 1109.88 (N-S), 832.50 (C-H), 796.44 (C-H), 770.26 (C-H).

Characterization of compound 7d: 0.36g, 65%. m.p.: 113-114 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.40 (s, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 4H), 8.10-8.15 (m, 4H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.71-7.74 (m, 4H), 7.63 (s, 1H), 7.09-7.12 (m, 4H), 4.10 (t, *J* = 6.5Hz, 4H), 2.17-2.30 (m, 4H), 1.88-1.89 (m, 4H), 1.70 (s, 9H), 1.54-1.58 (m, 4H), 1.35-1.42 (m, 16H), 1.12-1.19 (m, 24H), 0.96 (t, *J* = 6.0 Hz, 6H), 0.80 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (125MHz, CDCl₃, ppm): δ 165.6, 158.5, 158.5, 154.2, 154.1 141.4, 138.1, 137.3, 136.7, 136.1, 134.8, 133.9, 133.7, 133.6, 131.7, 131.7, 131.6, 131.3, 129.8, 129.0, 128.6, 128.4, 128.3, 127.8, 126.9, 126.8, 126.5, 125.5, 122.3, 121.5, 118.9, 115.6, 114.9, 114.1, 113.5, 81.1, 68.2, 45.6, 31.9, 31.9, 30.1, 29.8, 29.5, 29.4, 29.4, 29.3, 28.3, 26.2, 25.0 22.8, 22.6, 14.2, 14.1. HRMS (FAB⁺, *m/z*): [M+H]⁺ calcd for C₈₀H₉₉N₃O₄S, 1197.7356; found, 1197.9366. ν (KBr)/cm⁻¹: 2923.10 (C-H), 2856.62 (C-H), 1720.80 (C=O), 1638.89 (C=N), 1609.60 (aromatic C=C), 1475.41 (Ar-), 1456.12 (Ar-), 1425.99 (Ar-), 1297.61 (C-O), 1275.02 (C-O-C), 1246.79 (C-O-C), 1175.80 (C-N), 1106.48 (N-S), 837.60 (C-H), 792.91 (C-H), 774.30 (C-H).

General Synthesis of target dyes: Compound 7a (or compounds 7b-d) (0.13 g, 0.13 mmol) was dissolved in CH₂Cl₂ (10 mL), then CF₃COOH (2 mL) was added, and the mixture was stirred at room temperature for 3 h. After the reaction was completed, the reaction solution was poured into water and extracted with CH₂Cl₂. Dry over anhydrous Na₂SO₄ and remove the organic solvent by evaporation under reduced pressure. The crude product was purified by column chromatography (DCM/MeOH =100:1) on silica

gel to yield the product as orange solid.

Characterization of compound CS-38: 0.11g, 84%. m.p.: 182-183 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.69 (s, 1H), 8.53 (m, 3H), 8.45 (s, 1H), 8.29 (m, 5H), 8.18 (d, *J* = 8.0 Hz, 2H), 7.94 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 5H), 7.13 (d, *J* = 7.6 Hz, 4H), 4.12 (t, *J* = 6.6 Hz, 4H), 2.40-2.43 (m, 4H), 1.86-1.88 (m, 4H), 1.55-1.58 (m, 4H), 1.33-1.37 (m, 16H), 0.93 (t, *J* = 6.0 Hz, 6H), 0.70 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (125MHz, CDCl₃, ppm): δ 165.6, 158.8, 158.5, 154.1, 154.0, 142.5, 138.5, 137.1, 137.0, 135.9, 134.8, 134.0, 133.7, 133.5, 131.5, 131.0, 130.4, 130.1, 129.4, 129.3, 129.2, 128.4, 128.2, 127.9, 126.5, 126.4, 125.3, 122.5, 121.4, 118.6, 115.8, 115.0, 114.9, 114.0, 113.1, 68.2, 46.8, 31.9, 29.6, 29.5, 29.4, 26.2, 26.2, 22.8, 14.2, 9.9. HRMS (FAB⁺, *m/z*): [M+H]⁺ calcd for C₆₄H₆₈N₃O₄S, 974.4931; found, 974.4914. ν (KBr)/cm⁻¹: 3421.6 (O-H), 2924.90 (C-H), 2850.62 (C-H), 1686.60 (C=O), 1636.73 (C=N), 1614.60 (aromatic C=C), 1484.46 (Ar-), 1456.12 (Ar-), 1355.50 (Ar-), 1298.94 (C-O), 1275.14 (C-O-C), 1246.35 (C-O-C), 1181.40 (C-N), 1116.07 (N-S), 843.60 (C-H), 791.76 (C-H), 766.39 (C-H).

Characterization of compound CS-39: 0.12g, 82%. m.p.: 199-200 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.67 (s, 1H), 8.60 (s, 1H), 8.43 (m, 3H), 8.27 (s, 5H), 8.14 (d, *J* = 8.0 Hz, 2H), 7.93 (t, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 5H), 7.11 (d, *J* = 8.0 Hz, 4H), 4.11 (t, *J* = 6.6 Hz, 4H), 2.40-2.43 (m, 4H), 1.86-1.87 (m, 4H), 1.55-1.58 (m, 4H), 1.36-1.41 (m, 16H), 1.23-1.25 (m, 4H), 0.91-0.93 (m, 10H), 0.72 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (125MHz, CDCl₃, ppm): δ 165.6, 158.6, 158.5, 154.2, 153.8, 141.9, 138.1, 137.8, 137.1, 136.5, 136.3, 135.8, 134.9, 133.8, 133.5, 133.2, 131.1, 130.4, 130.1, 129.4, 129.2, 128.5, 128.5, 128.3, 128.3, 127.9, 127.7, 126.4, 126.3, 125.0, 124.3, 122.5, 120.3, 115.0, 114.9, 68.3, 45.6, 32.0, 32.0, 29.6, 29.6, 29.6, 29.5, 26.3, 23.3, 22.9, 14.3, 14.2. HRMS (FAB⁺, *m/z*): [M+H]⁺ calcd for C₆₈H₇₆N₃O₄S, 1030.5557; found, 1030.5553. ν

(KBr)/cm⁻¹: 3421.6 (O-H), 2924.90 (C-H), 2850.62 (C-H), 1688.88 (C=O), 1639.00 (C=N), 1614.60 (aromatic C=C), 1483.06 (Ar-), 1452.23 (Ar-), 1425.92 (Ar-), 1294.44 (C-O), 1272.73 (C-O-C), 1244.56 (C-O-C), 1177.49 (C-N), 1115.39 (N-S), 843.97 (C-H), 793.33 (C-H), 771.86 (C-H).

Characterization of compound CS-40: 0.12g, 82%. m.p.: 164-165 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.66 (s, 1H), 8.61 (s, 1H), 8.44 (m, 3H), 8.26 (s, 5H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.81 (t, *J* = 8.0 Hz, 5H), 7.11 (d, *J* = 8.0 Hz, 4H), 4.11 (t, *J* = 6.6 Hz, 4H), 2.40-2.43 (m, 4H), 1.82-1.89 (m, 4H), 1.52-1.56 (m, 4H), 1.36-1.42 (m, 16H), 1.10-1.21 (m, 24H), 0.93 (t, *J* = 6.0 Hz, 6H), 0.74 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (125MHz, CDCl₃, ppm): δ 167.2, 158.5, 158.4, 154.1, 154.0, 153.7, 153.7, 148.6, 142.4, 138.0, 137.9, 136.4, 136.2, 135.6, 134.9, 133.8, 133.5, 133.3, 132.9, 131.3, 131.2, 130.9, 130.3, 129.1, 128.5, 128.4, 128.2, 126.1, 125.1, 122.5, 121.1, 118.5, 115.0, 114.9, 114.0, 68.2, 45.6, 32.0, 31.9, 30.1, 29.8, 29.6, 29.5, 29.4, 29.4, 26.3, 26.2, 25.3, 22.8, 22.7, 14.2, 14.1. HRMS (FAB⁺, *m/z*): [M+H]⁺ calcd for C₇₆H₉₂N₃O₄S, 1142.6809; found, 1142.6895. ν (KBr)/cm⁻¹: 3415.96 (O-H), 2924.90 (C-H), 2850.62 (C-H), 1688.40 (C=O), 1638.81 (C=N), 1619.60 (aromatic C=C), 1479.17 (Ar-), 1450.52 (Ar-), 1423.07 (Ar-), 1295.88 (C-O), 1275.15 (C-O-C), 1242.83 (C-O-C), 1173.74 (C-N), 1108.99 (N-S), 837.60 (C-H), 794.40 (C-H), 770.98 (C-H).

3. Figures

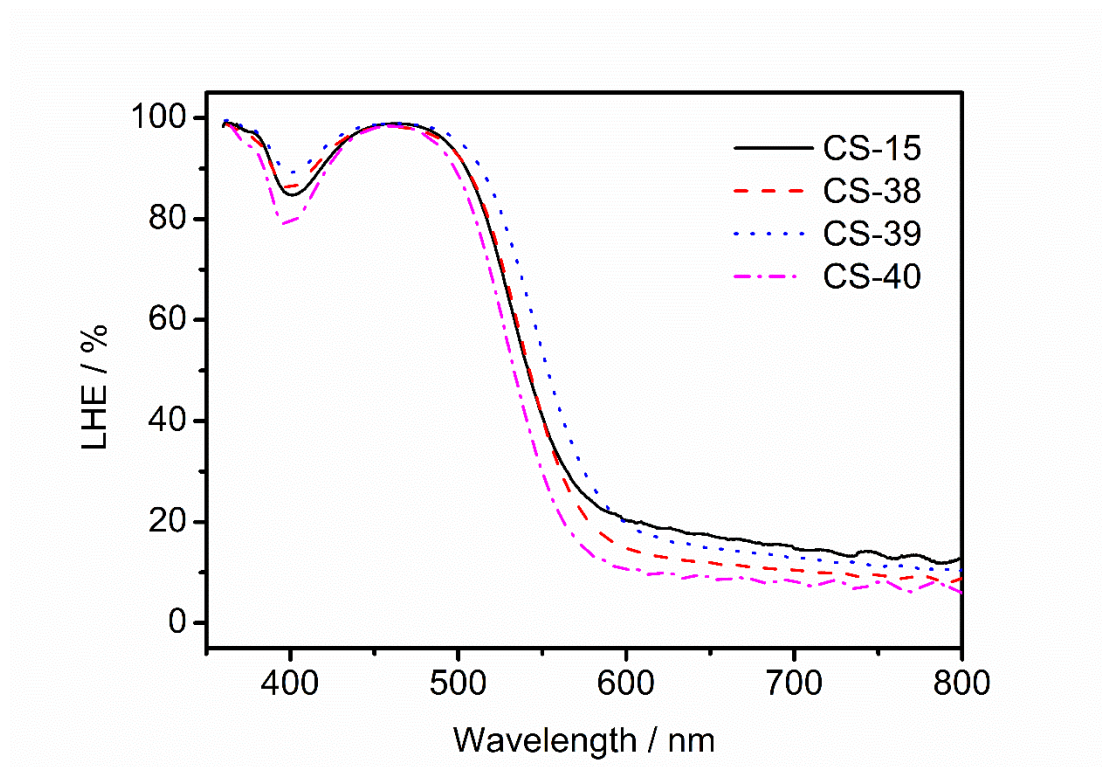


Figure S1. Light-harvesting efficiencies of CS-15, CS-38, CS-39, and CS-40 calculated from their absorption spectra of dye-loaded TiO₂ film.

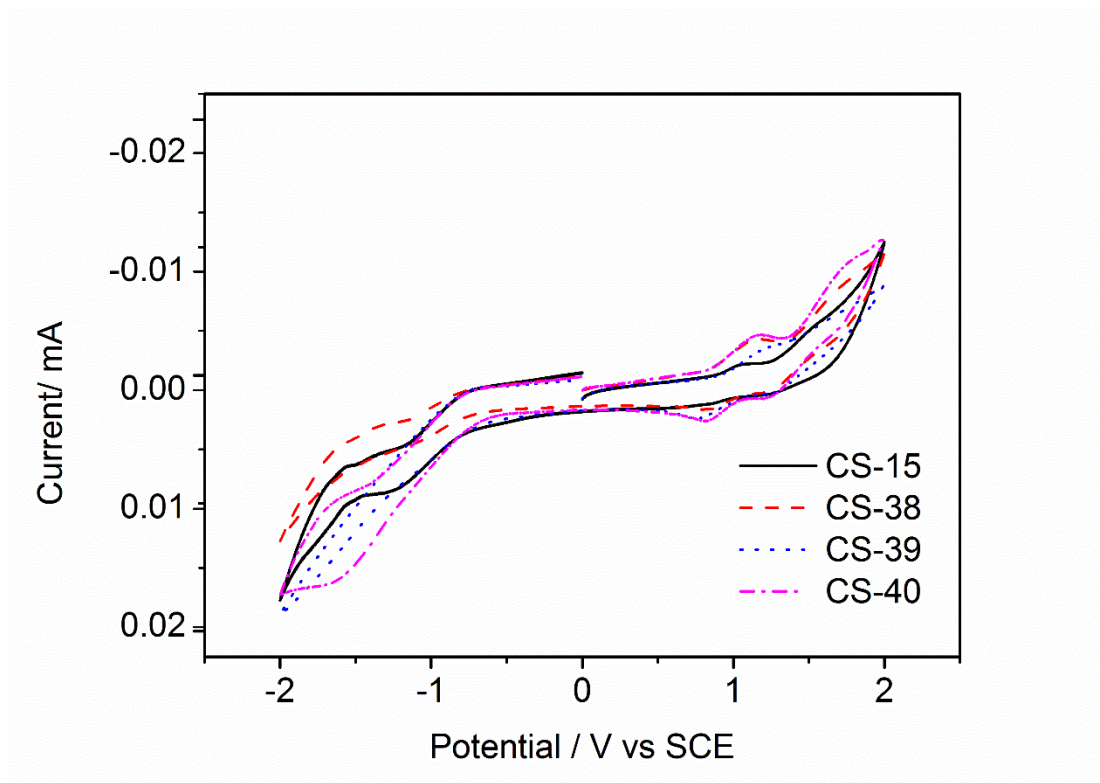


Figure S2. Cyclic voltammograms of CS-15, CS-38, CS-39 and CS-40 in CHCl_3 using 0.1 M TBAP.

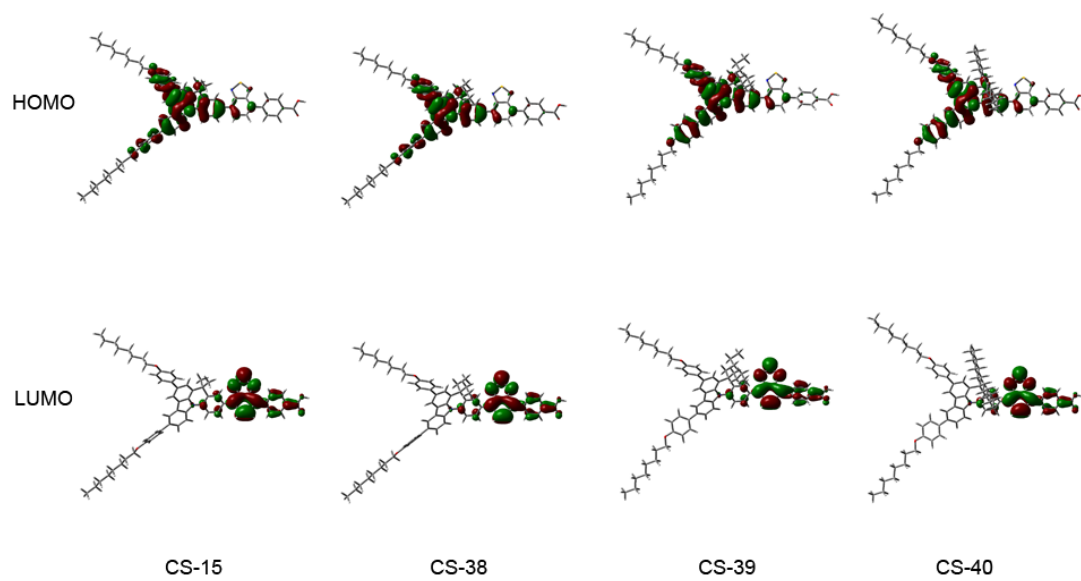


Figure S3. Frontier molecular orbit distribution of four dyes.

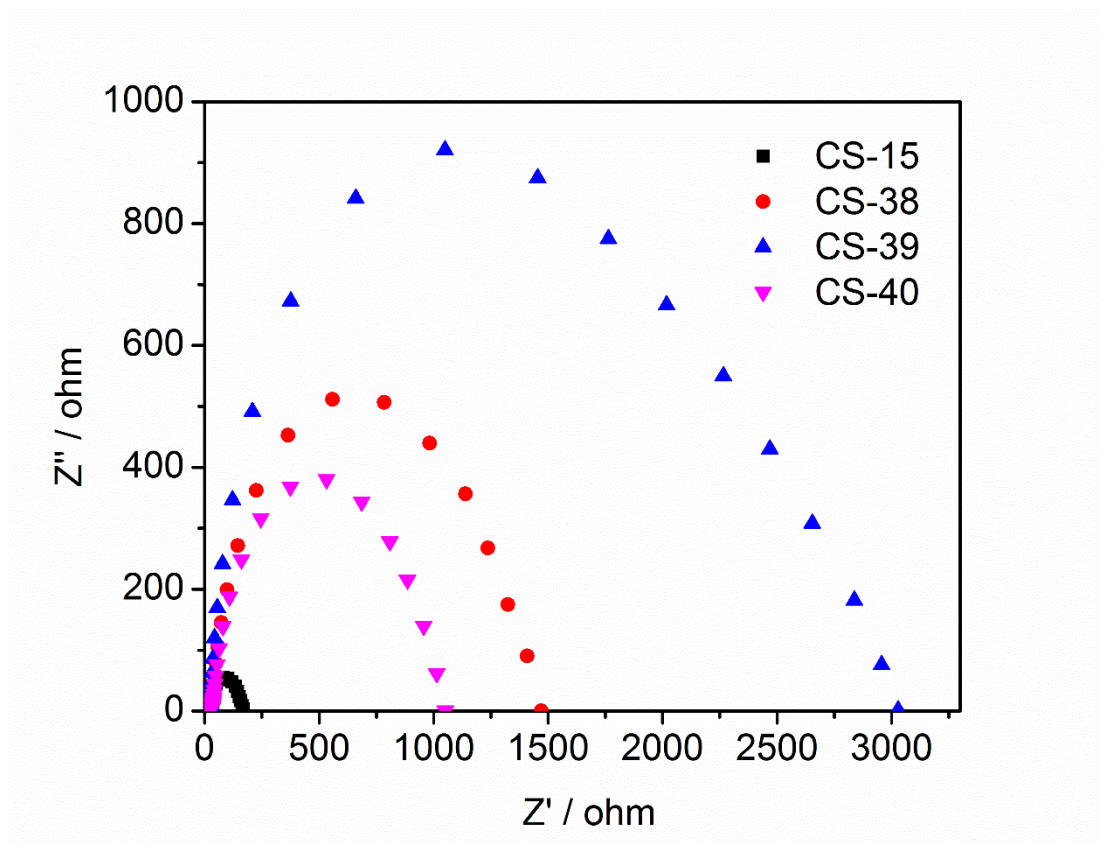


Figure S4. Nyquist plots of CS-15, CS-38, CS-39 and CS-40 based DSSCs measured under a dark condition, applying a 10 mV AC sinusoidal modulation superimposed on constant forward bias (-0.7 V) with the frequency ranging from 10^5 to 10^{-1} Hz.

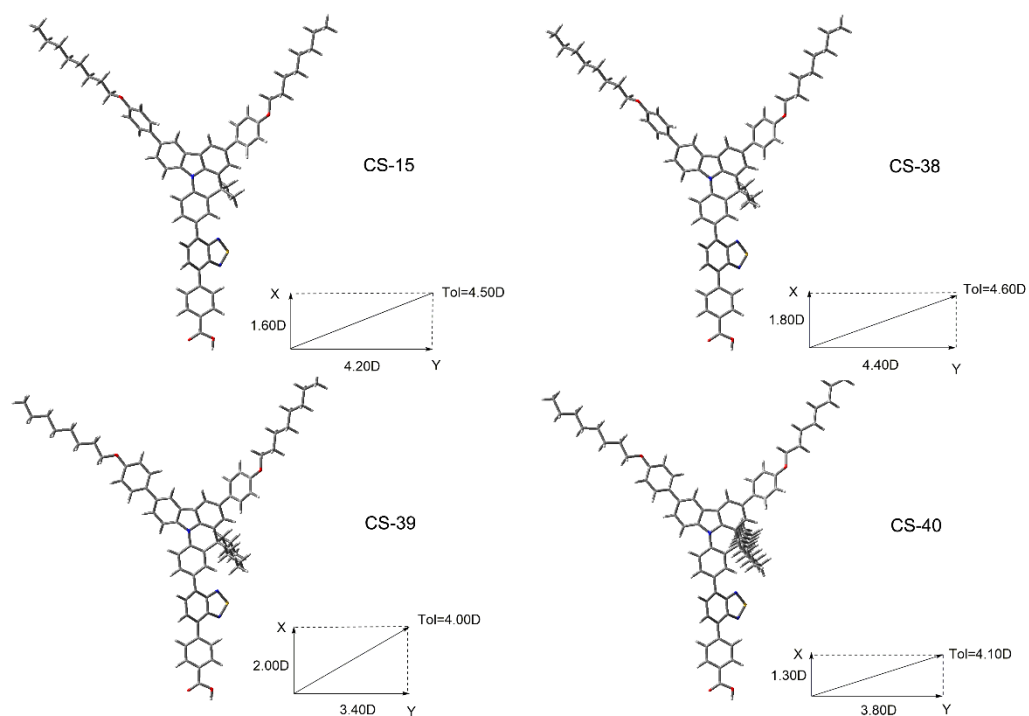


Figure S5. The vertical dipole moments of CS-15, CS-38, CS-39 and CS-40 calculated at their optimized geometries of the ground singlet states.

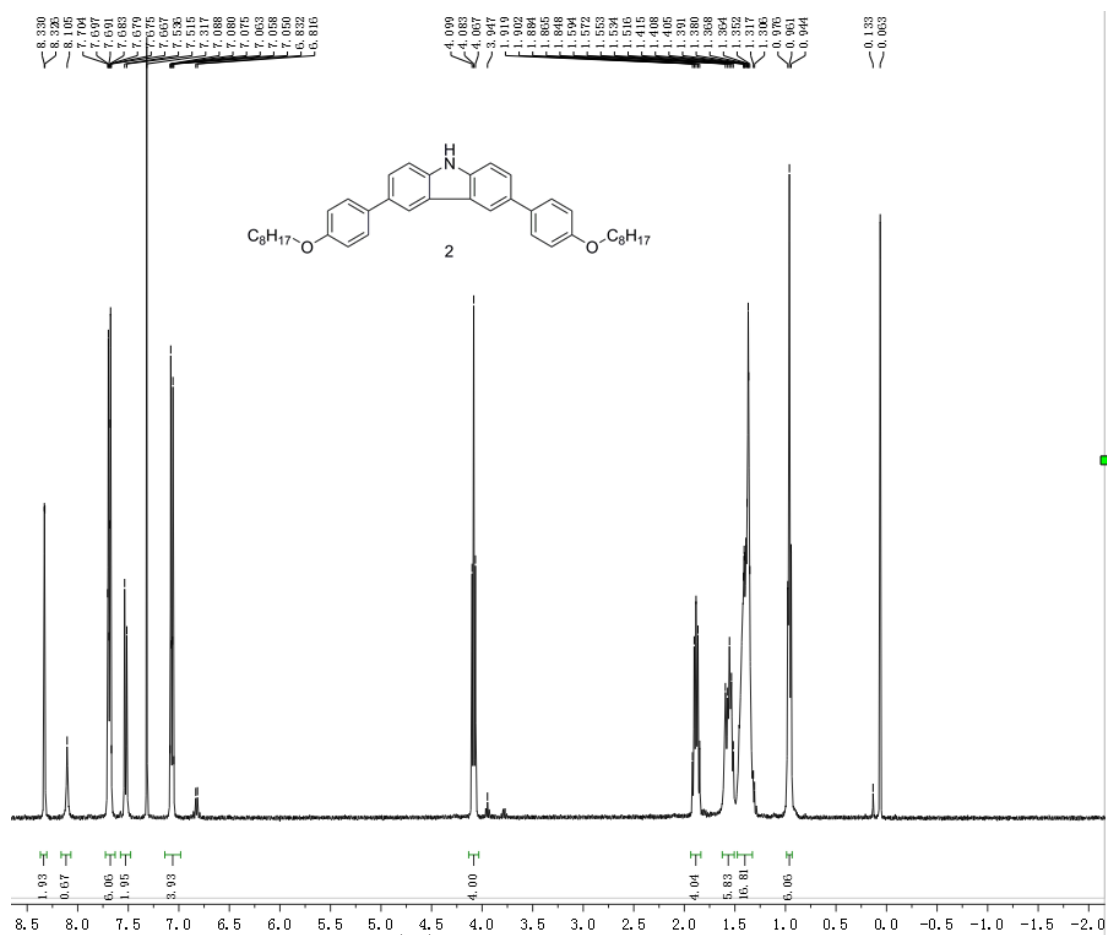


Figure S6. The ¹H NMR spectrum of compound 2 (CDCl₃).

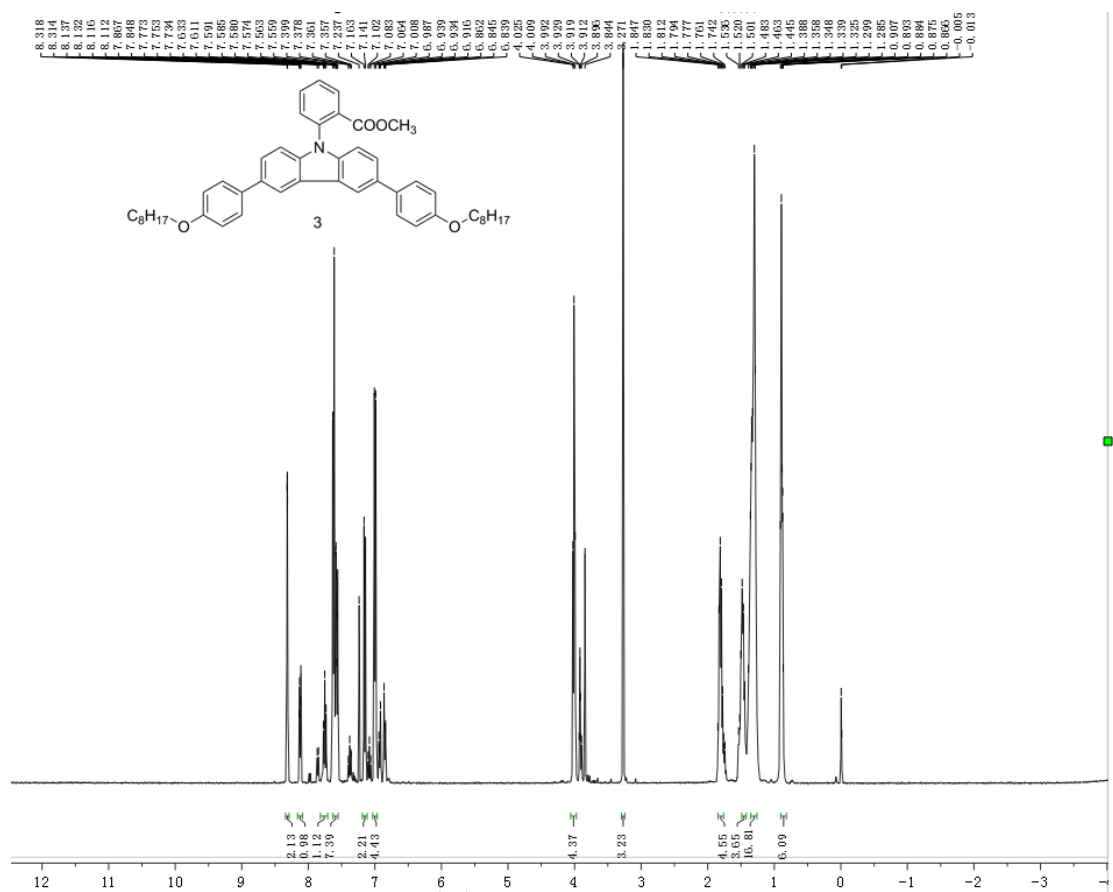


Figure S7. The ¹H NMR spectrum of compound 3 (CDCl₃).

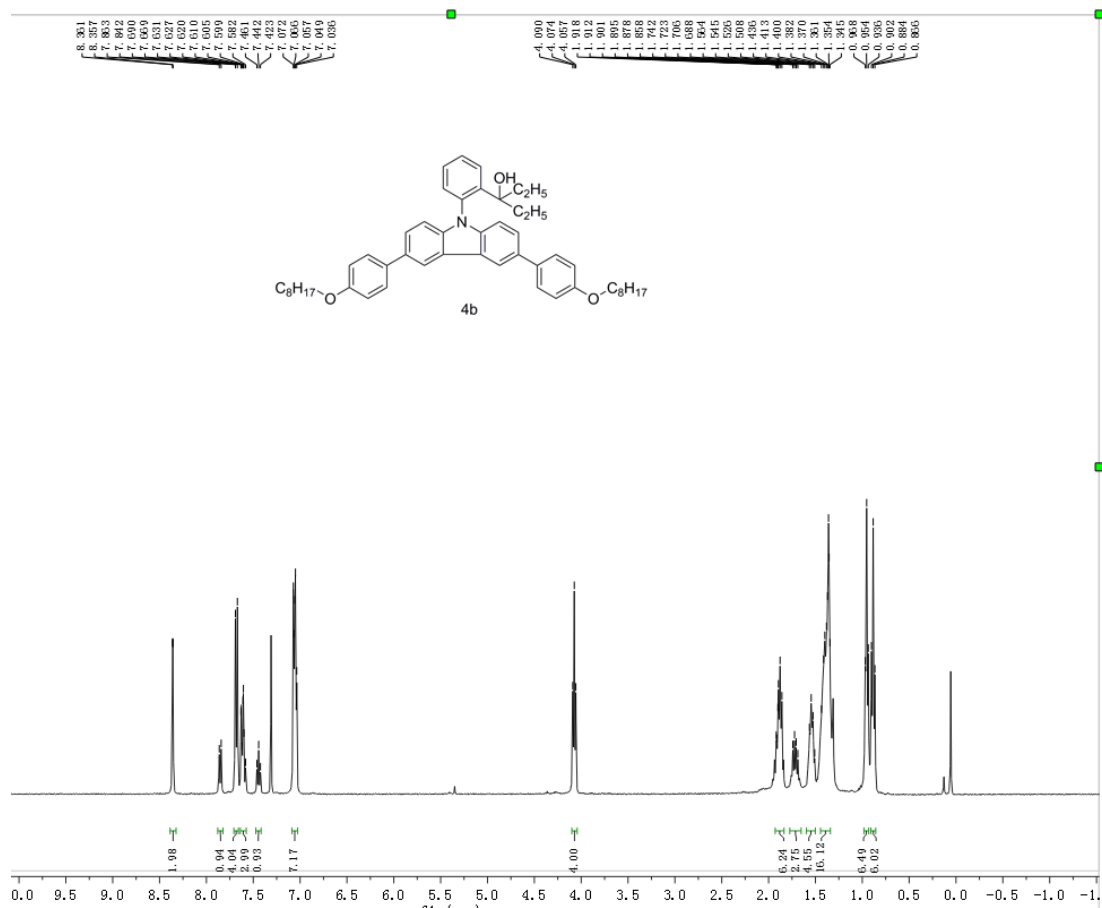


Figure S8. The ¹H NMR spectrum of compound 4b (CDCl₃).

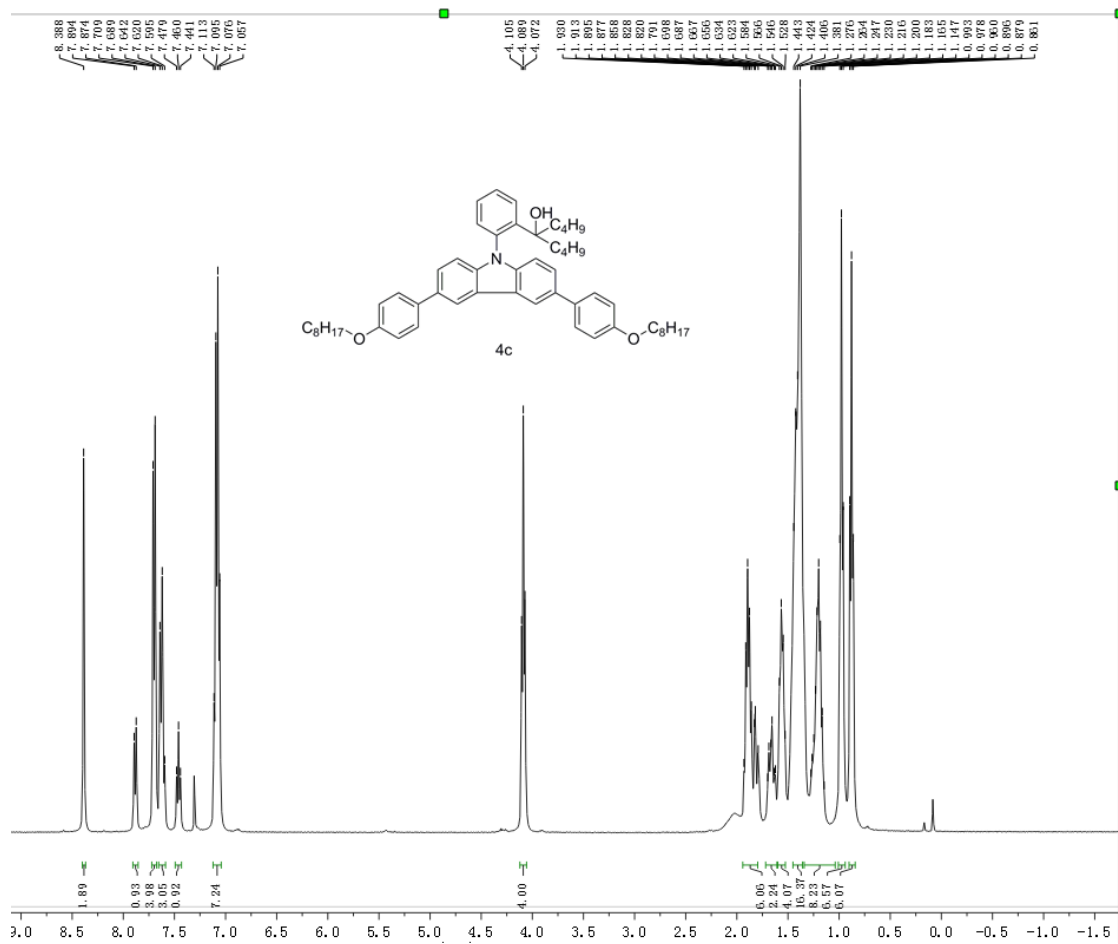


Figure S9. The ¹H NMR spectrum of compound 4c (CDCl₃).

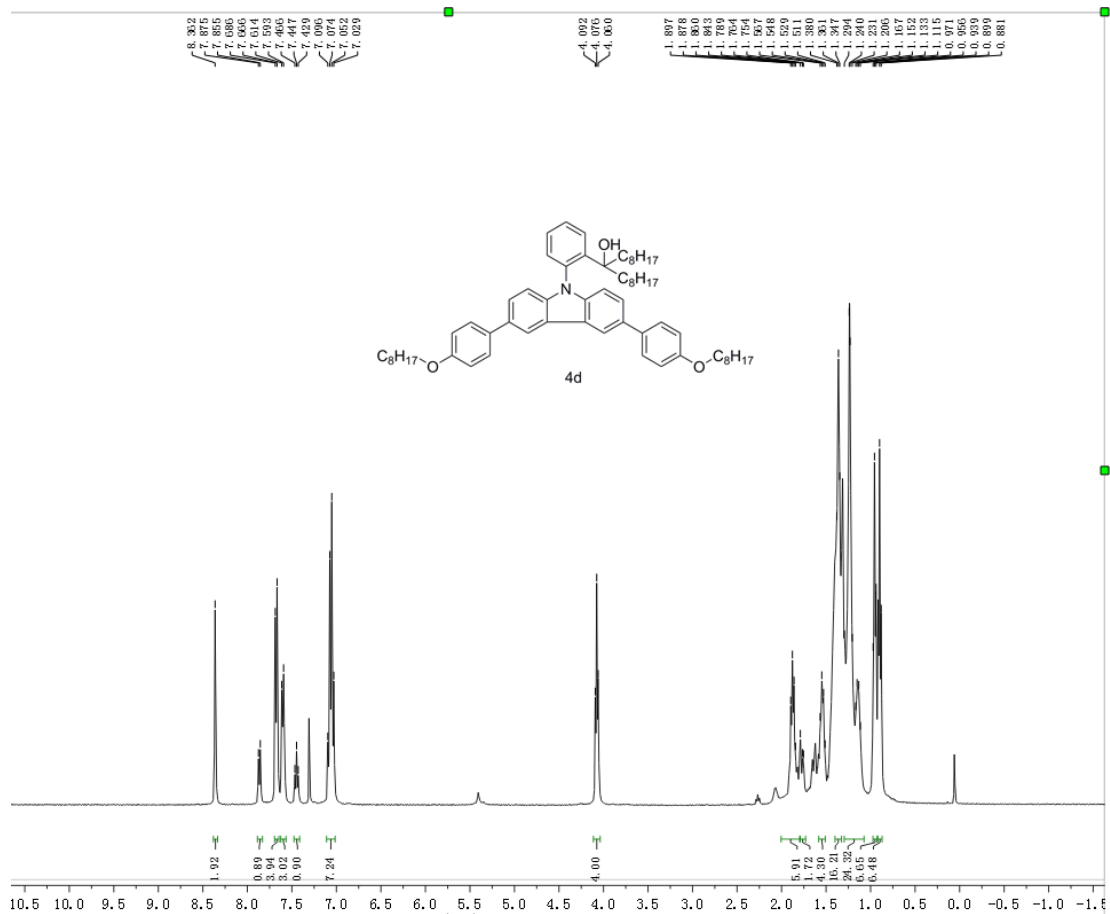


Figure S10. The ¹H NMR spectrum of compound 4d (CDCl₃).

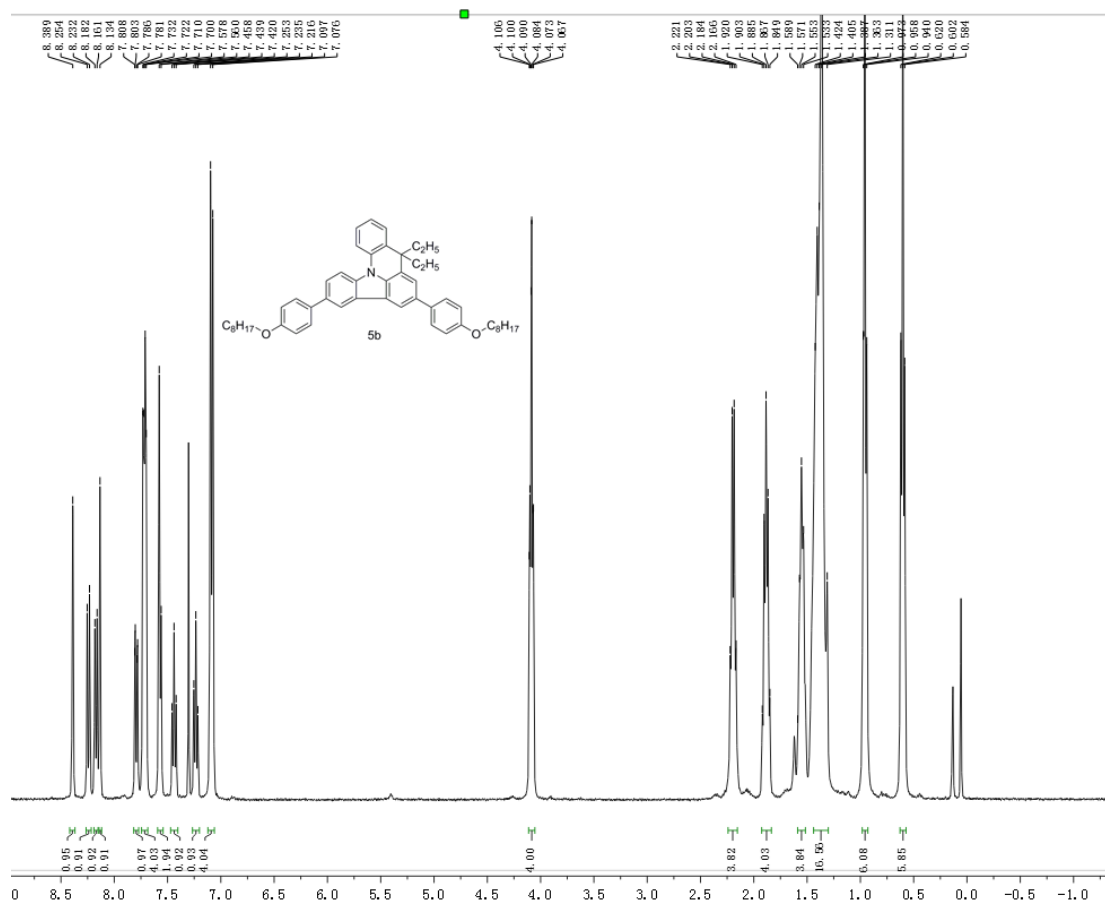


Figure S11. The ¹H NMR spectrum of compound 5b (CDCl₃).

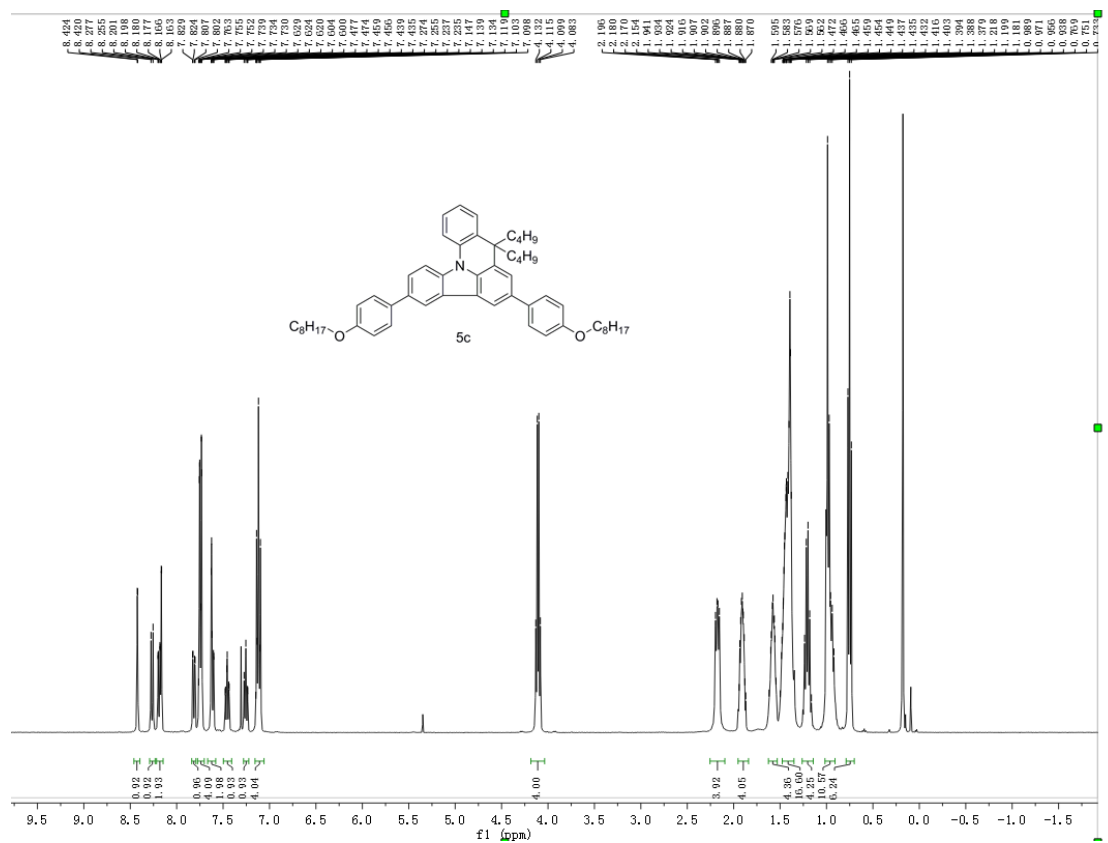


Figure S12. The ¹H NMR spectrum of compound 5c (CDCl₃).

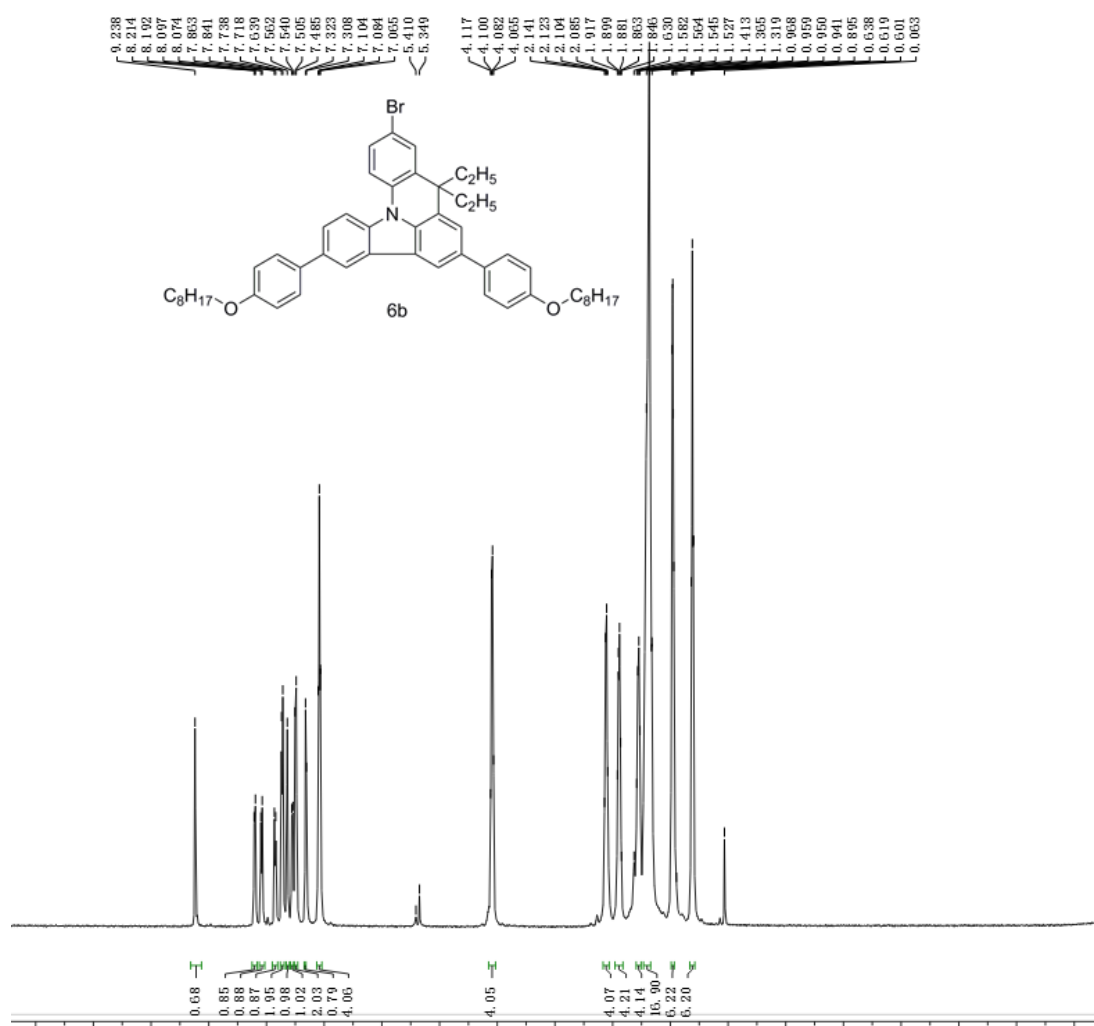


Figure S14. The ¹H NMR spectrum of compound 6b (CDCl₃).

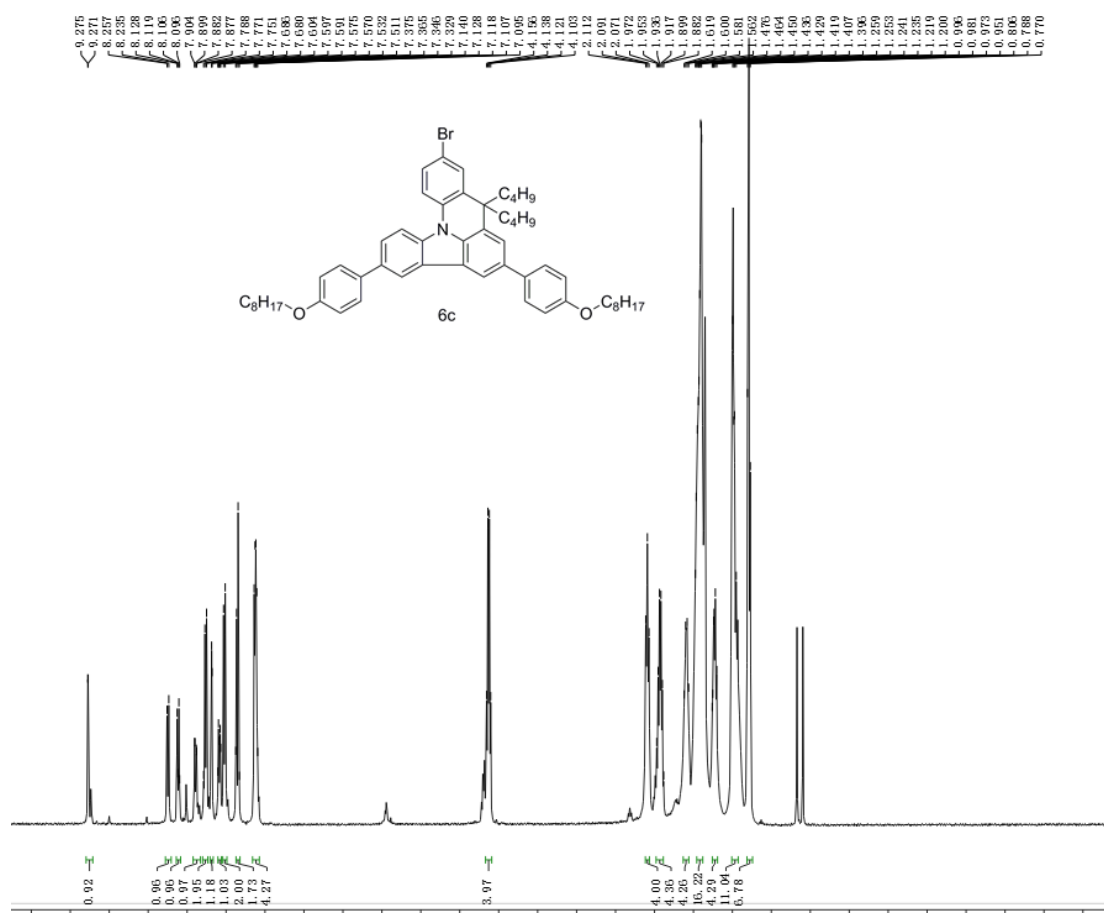
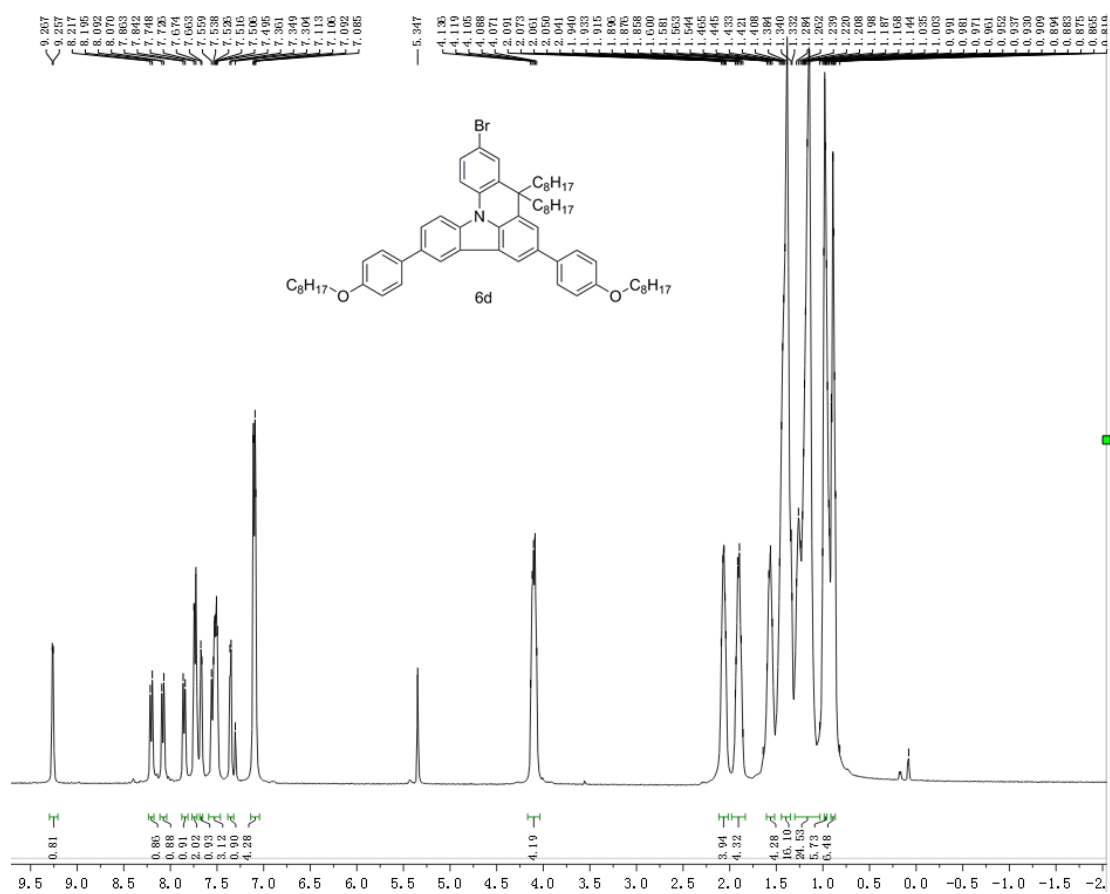


Figure S15. The ¹H NMR spectrum of compound 6c (CDCl₃).



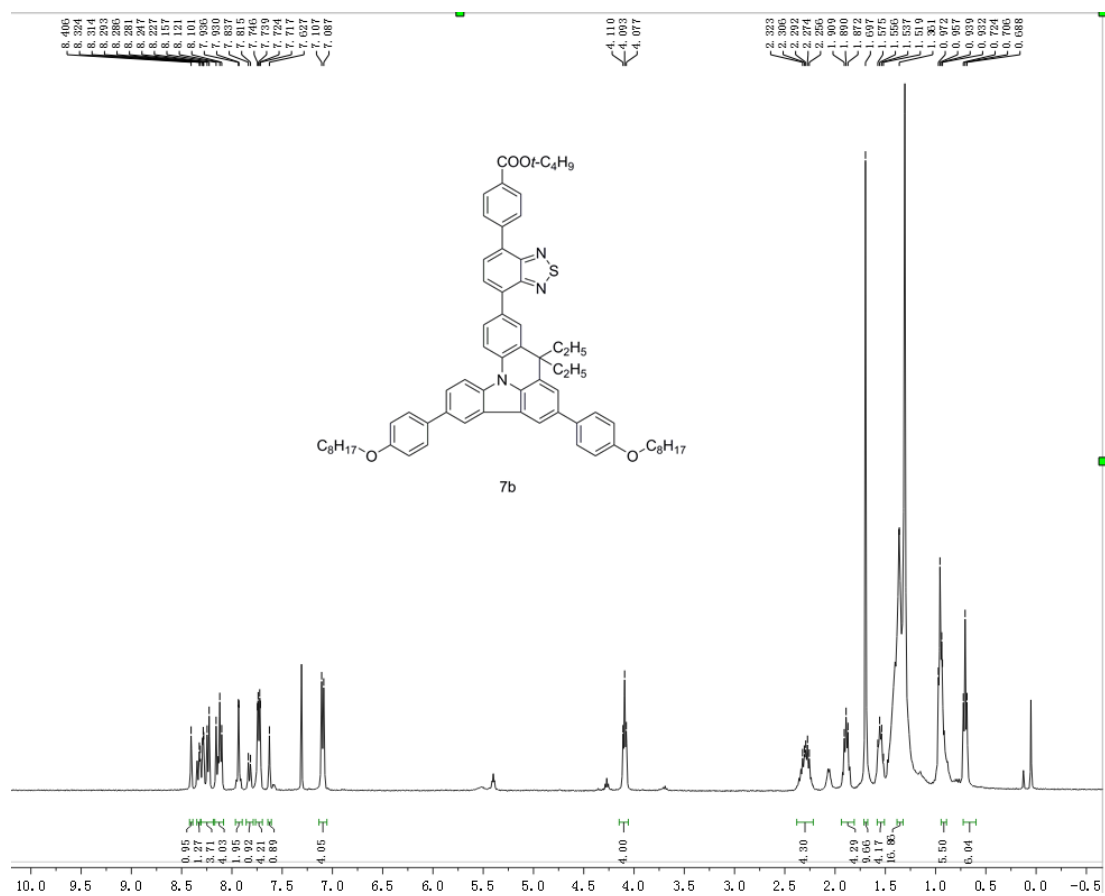


Figure S17. The ¹H NMR spectrum of compound 7b (CDCl₃).

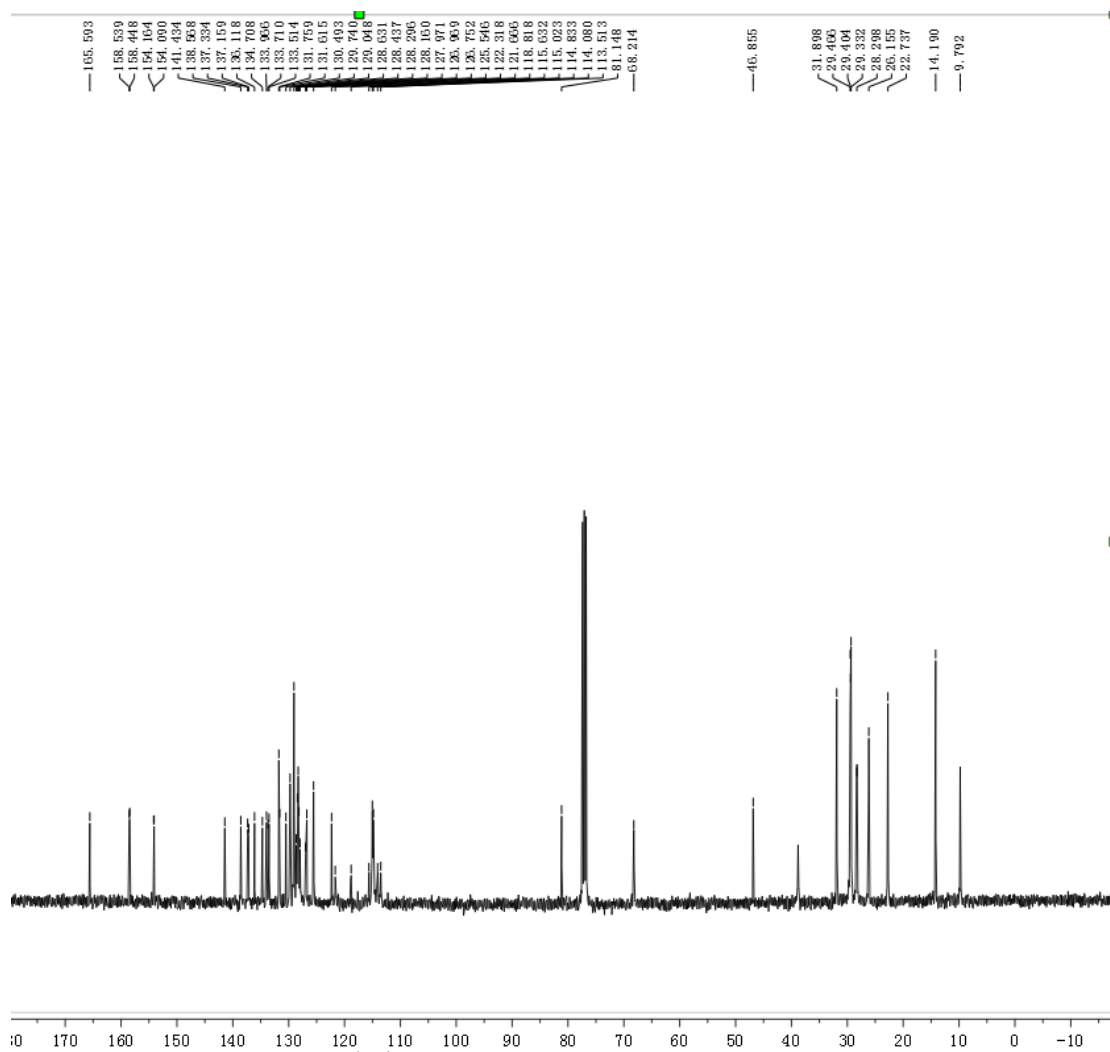


Figure S18. The ^{13}C NMR spectrum of compound 7b (CDCl_3).

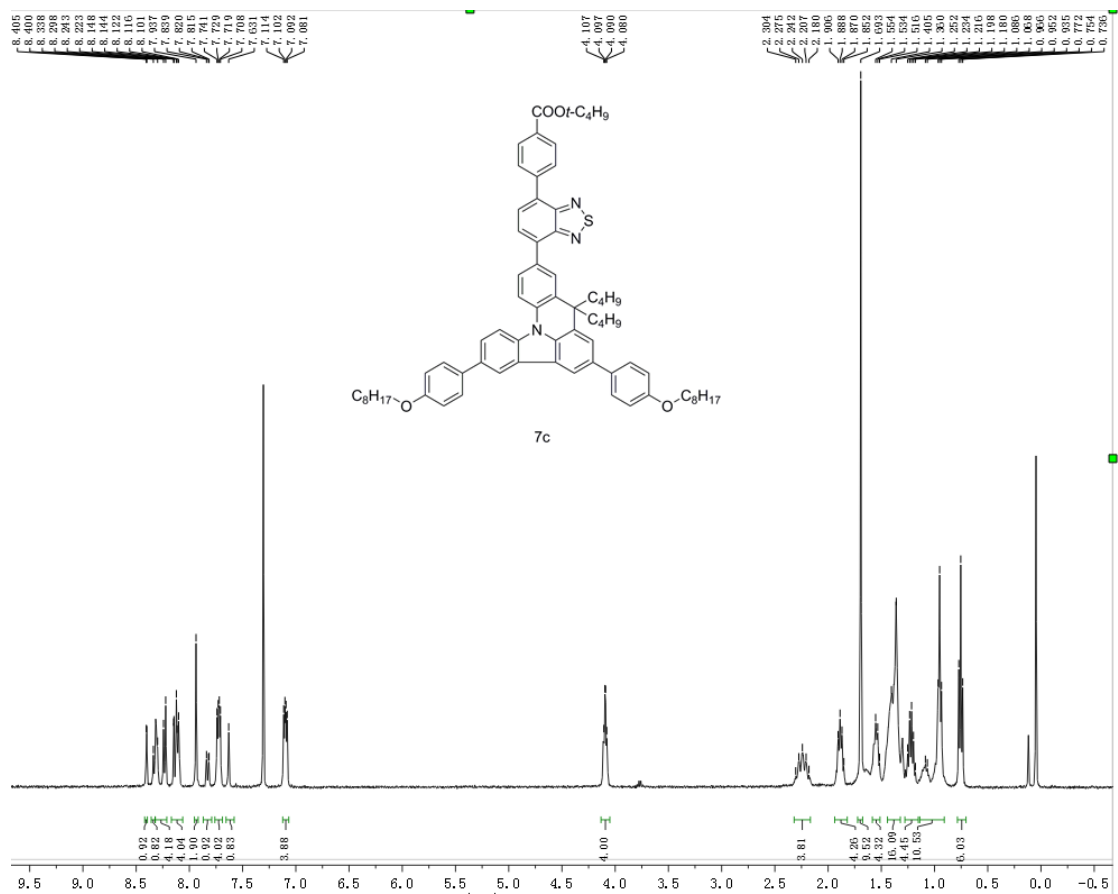


Figure S19. The ¹H NMR spectrum of compound 7c (CDCl₃).

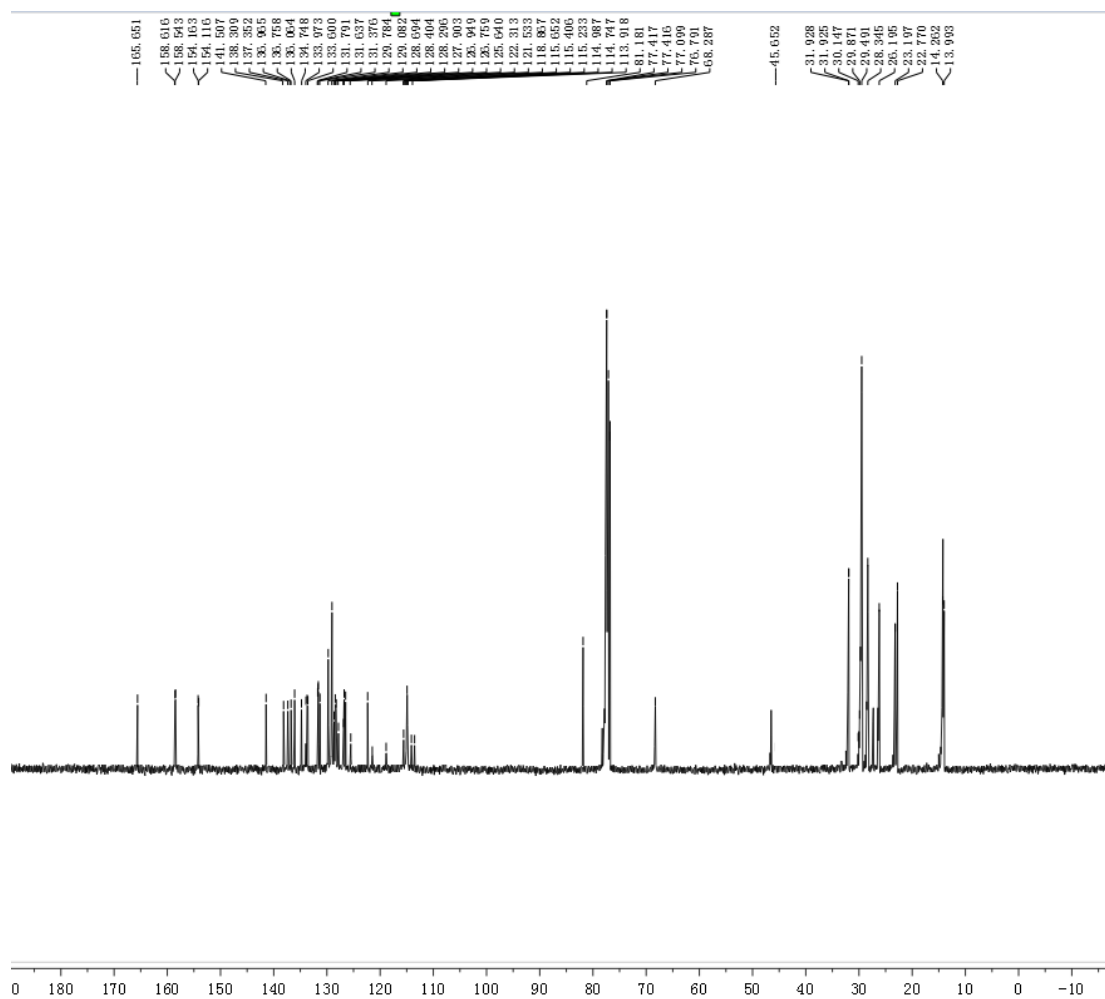


Figure S20. The ^{13}C NMR spectrum of compound 7c (CDCl_3).

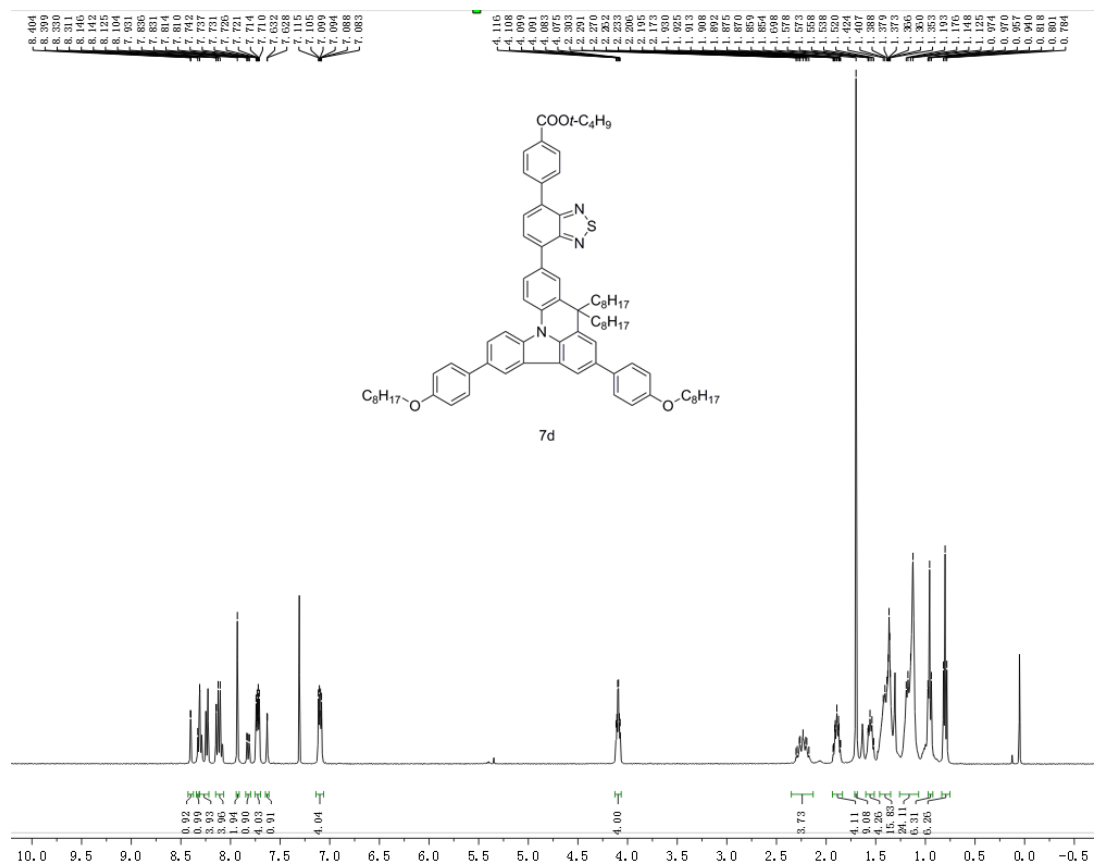


Figure S21. The ¹H NMR spectrum of compound 7d (CDCl₃).

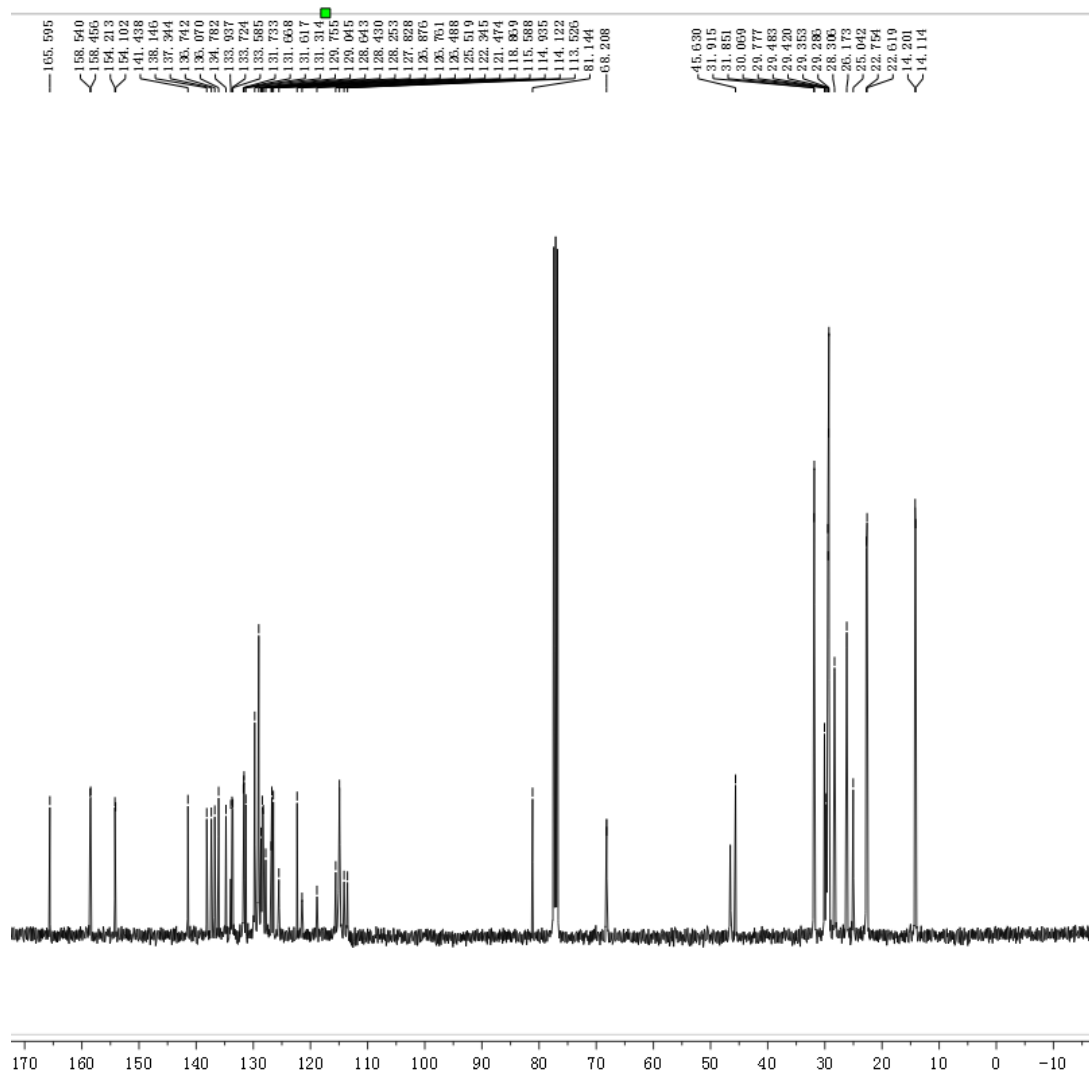


Figure S22. The ^{13}C NMR spectrum of compound 7d (CDCl_3).

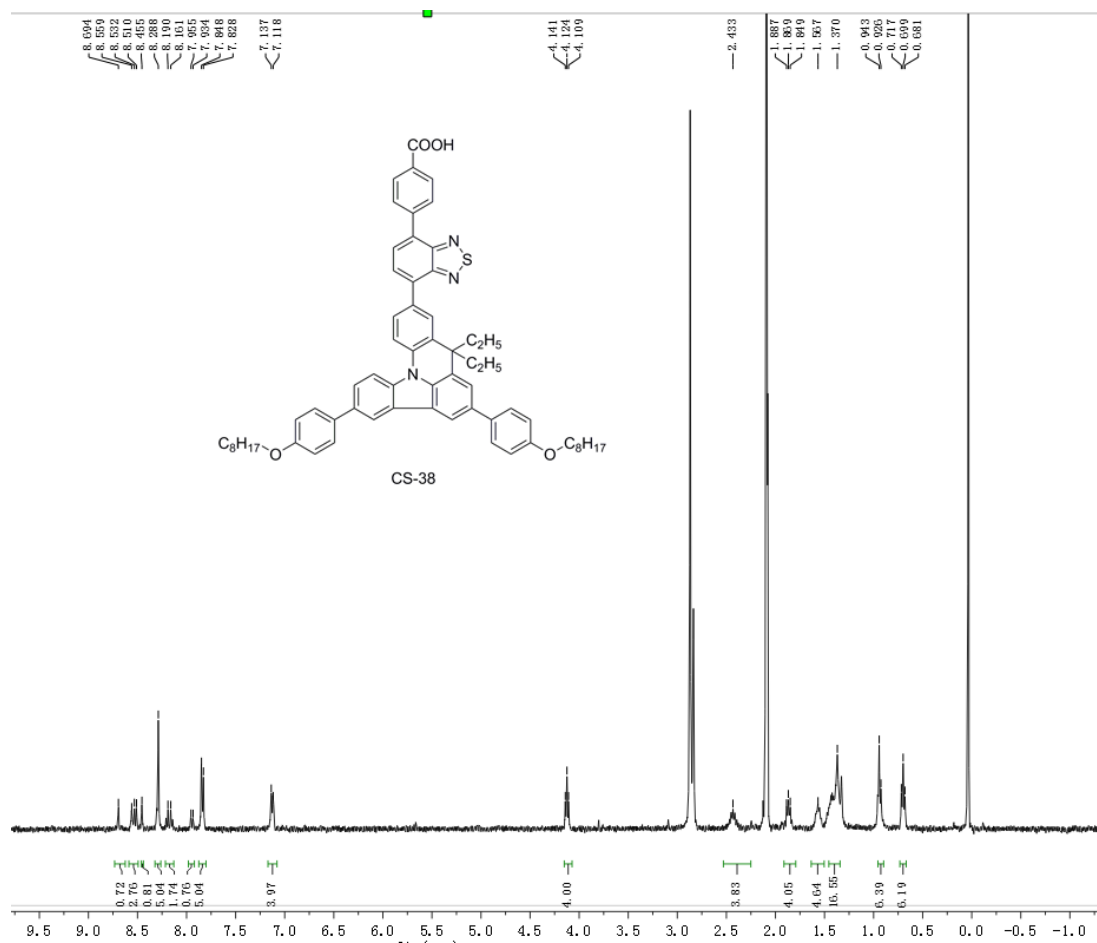


Figure S23. The ¹H NMR spectrum of compound CS-38 (Acetone).

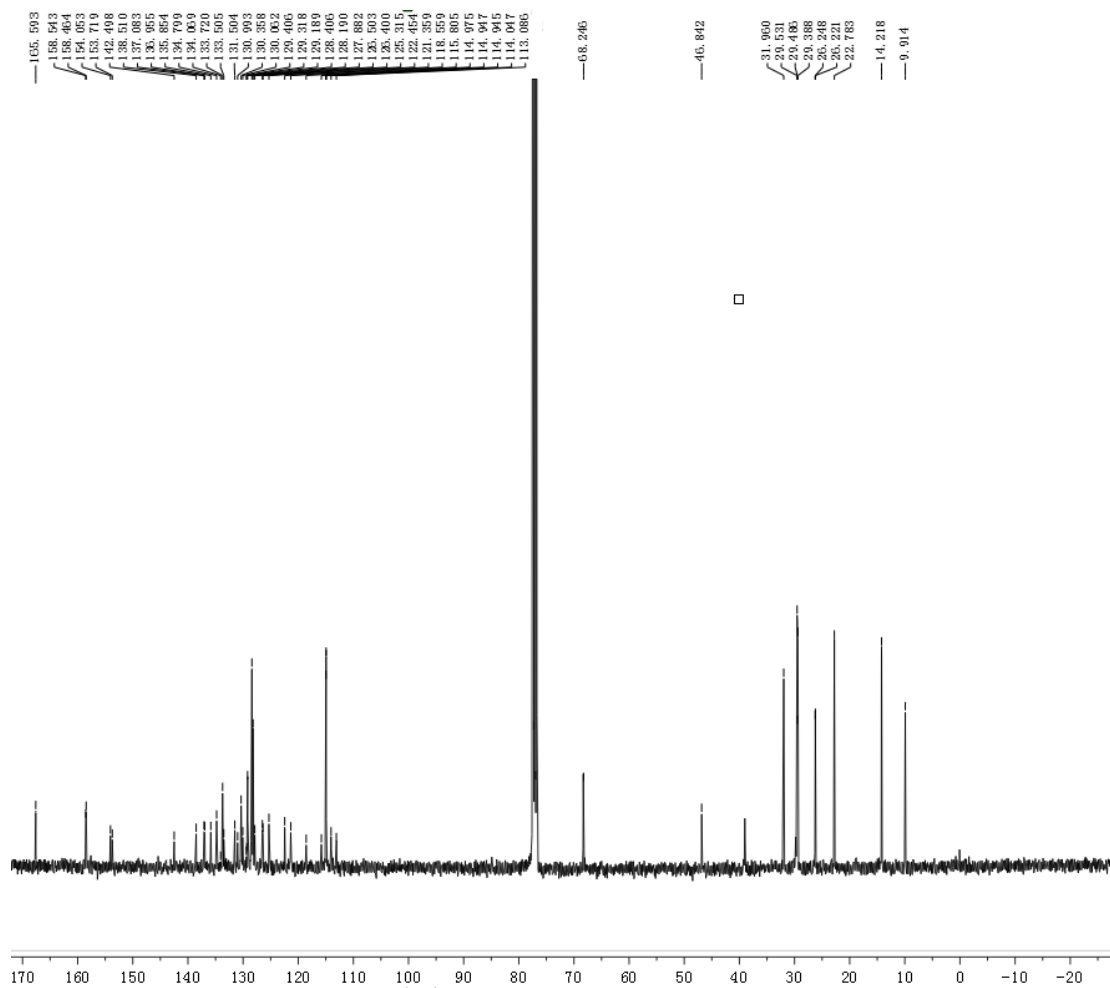


Figure S24. The ^{13}C NMR spectrum of compound CS-38 (CDCl_3).

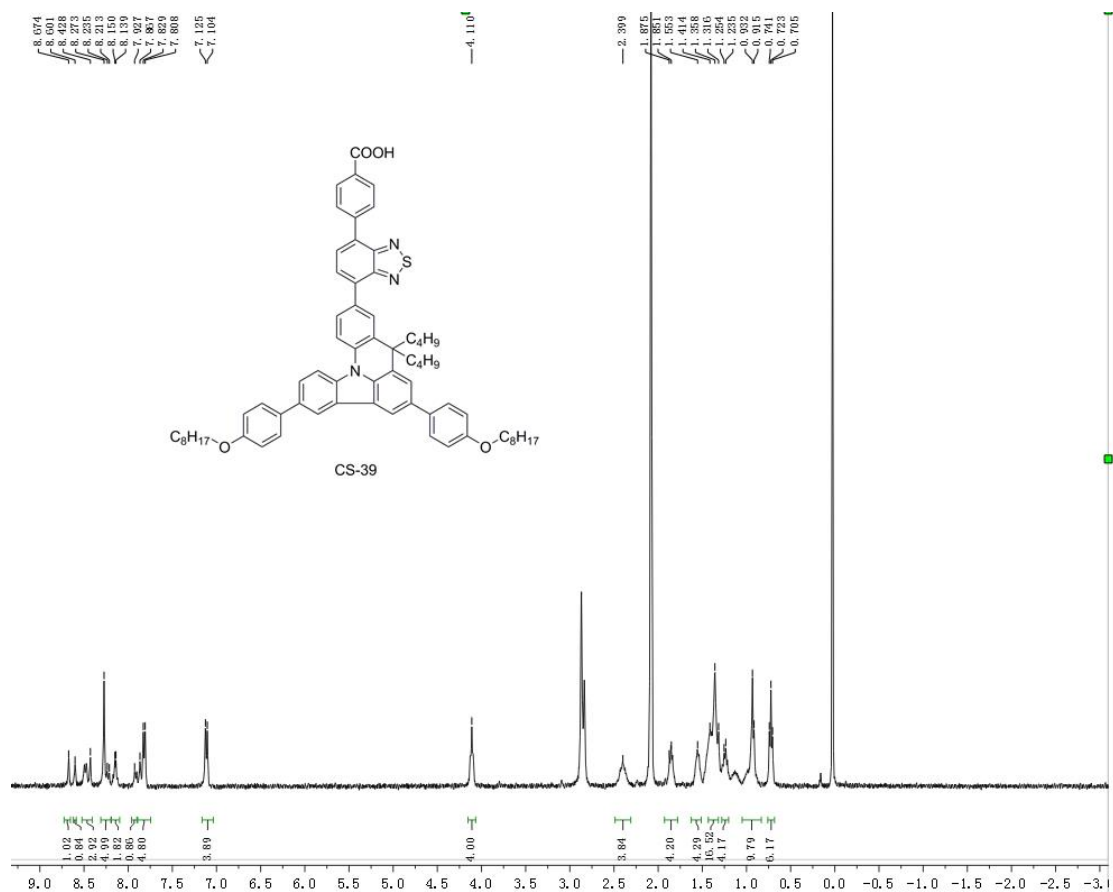


Figure S25. The ¹H NMR spectrum of compound CS-39 (Acetone).

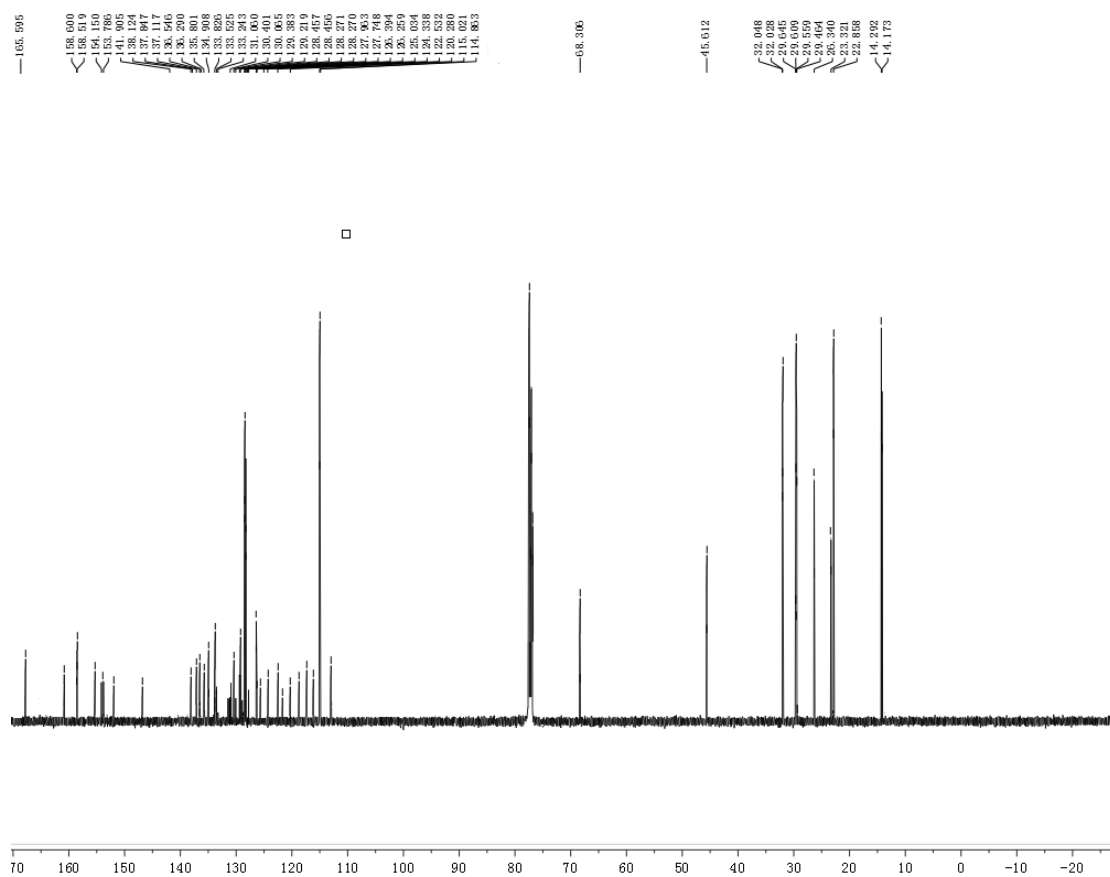


Figure S26. The ^{13}C NMR spectrum of compound CS-39 (CDCl_3).

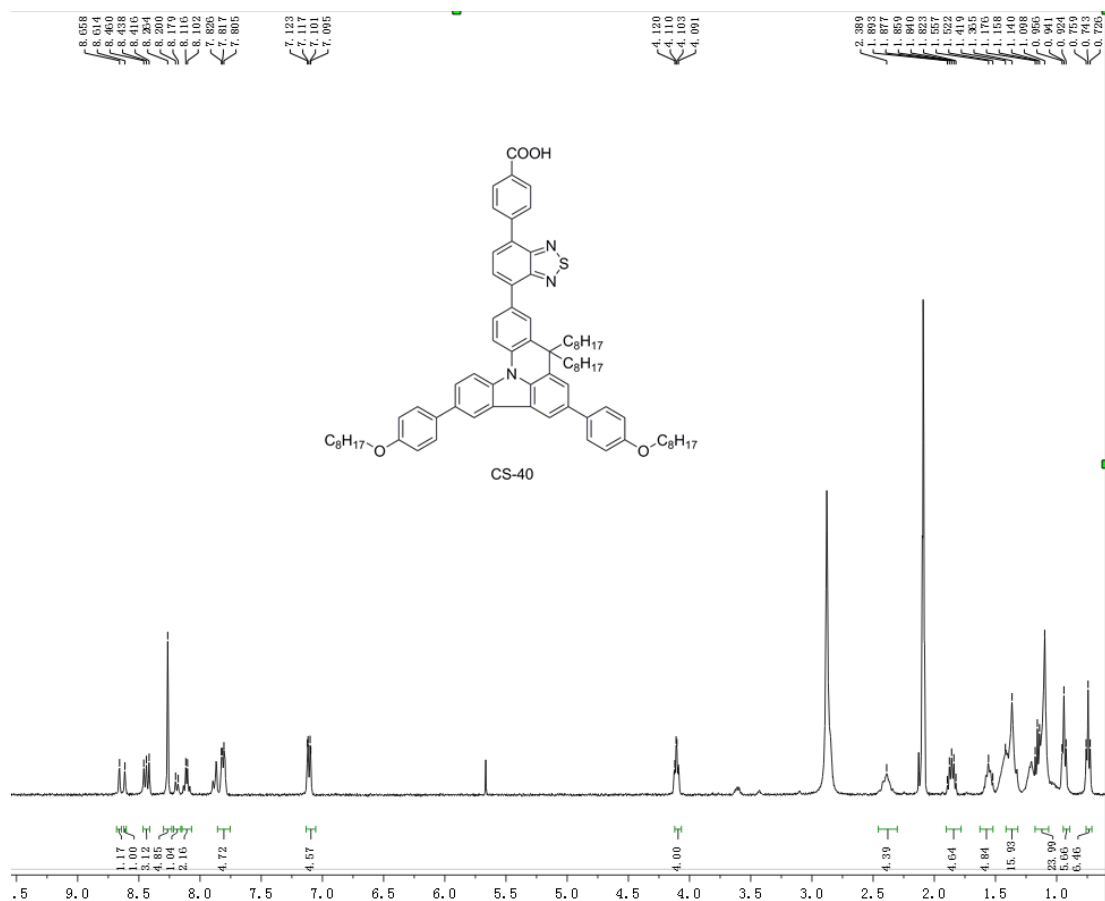


Figure S27. The ¹H NMR spectrum of compound CS-40 (Acetone).

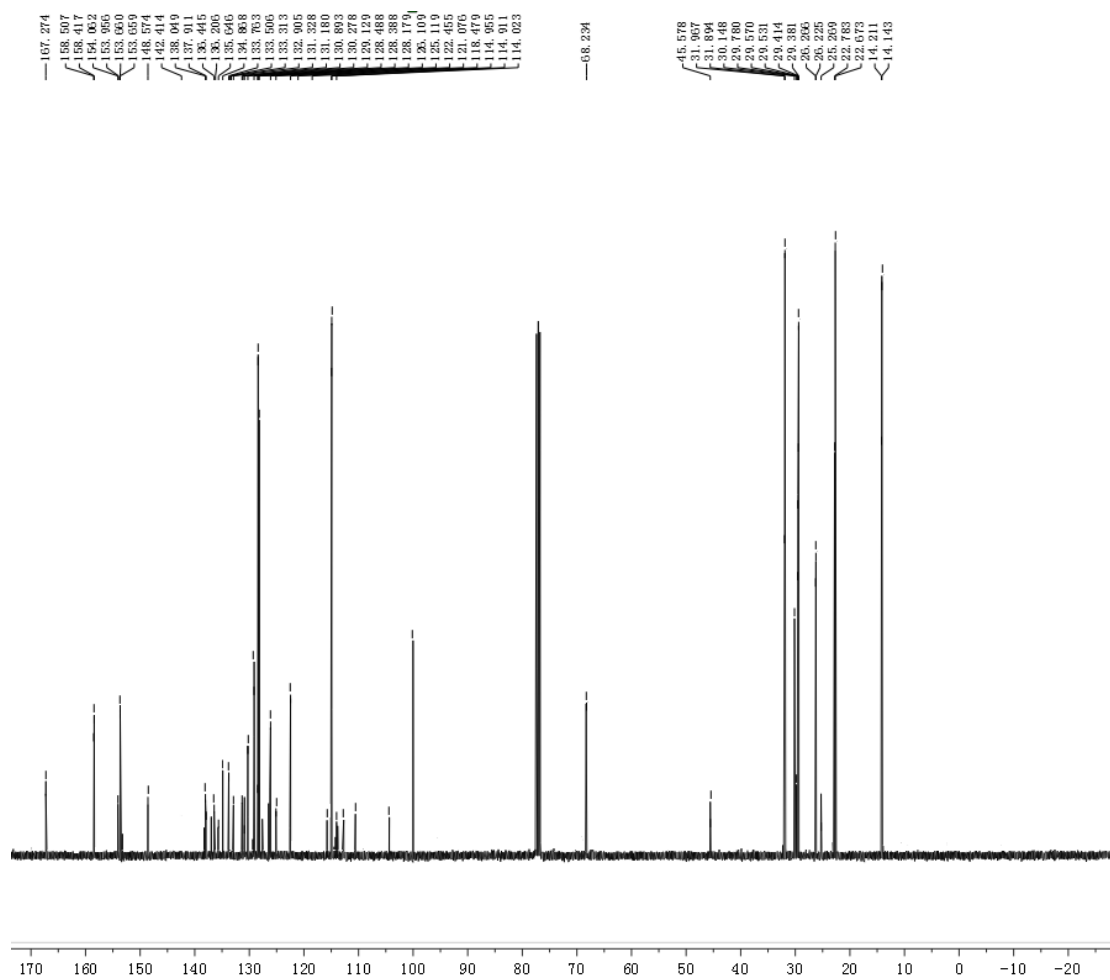


Figure S28. The ^{13}C NMR spectrum of compound CS-40 (CDCl_3).

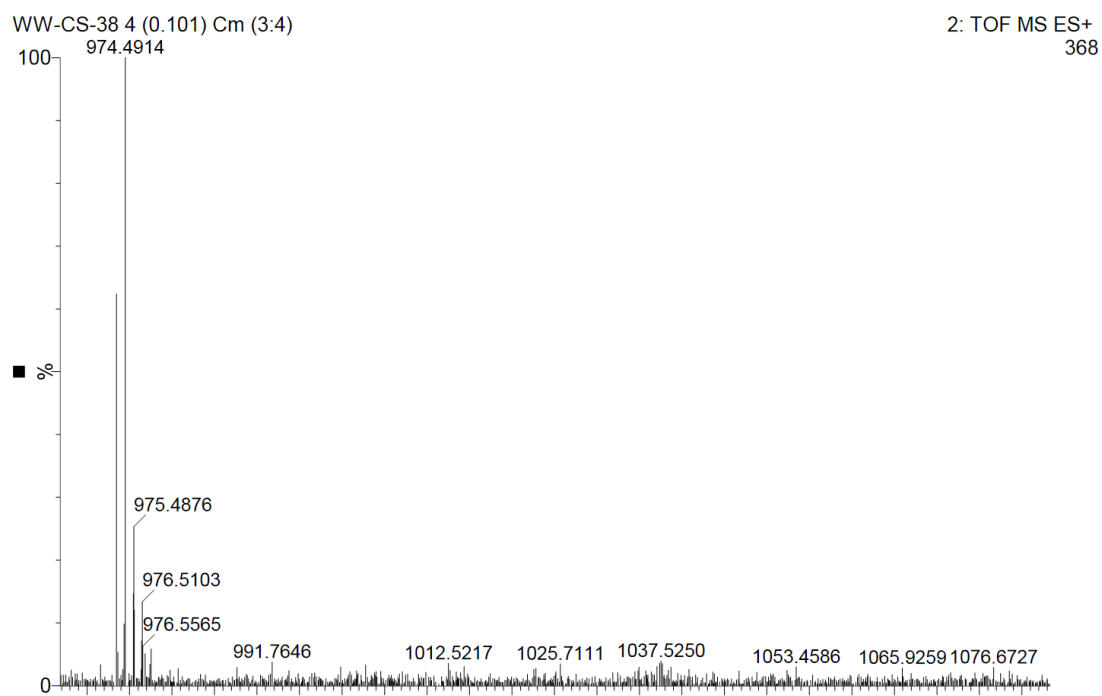


Figure S29. The HR-MS spectrum of compound **CS-38**.

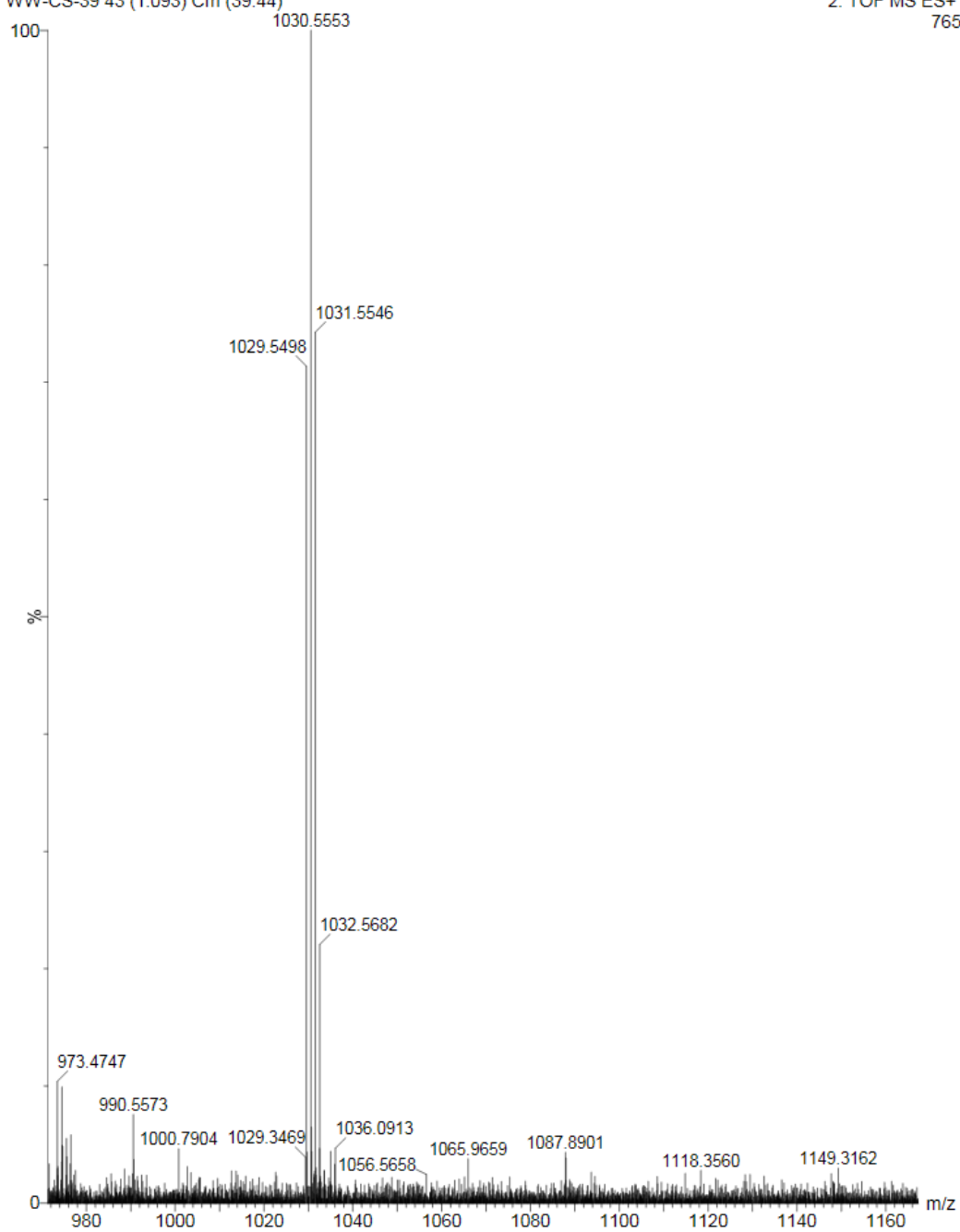


Figure S30. The HR-MS spectrum of compound **CS-39**.

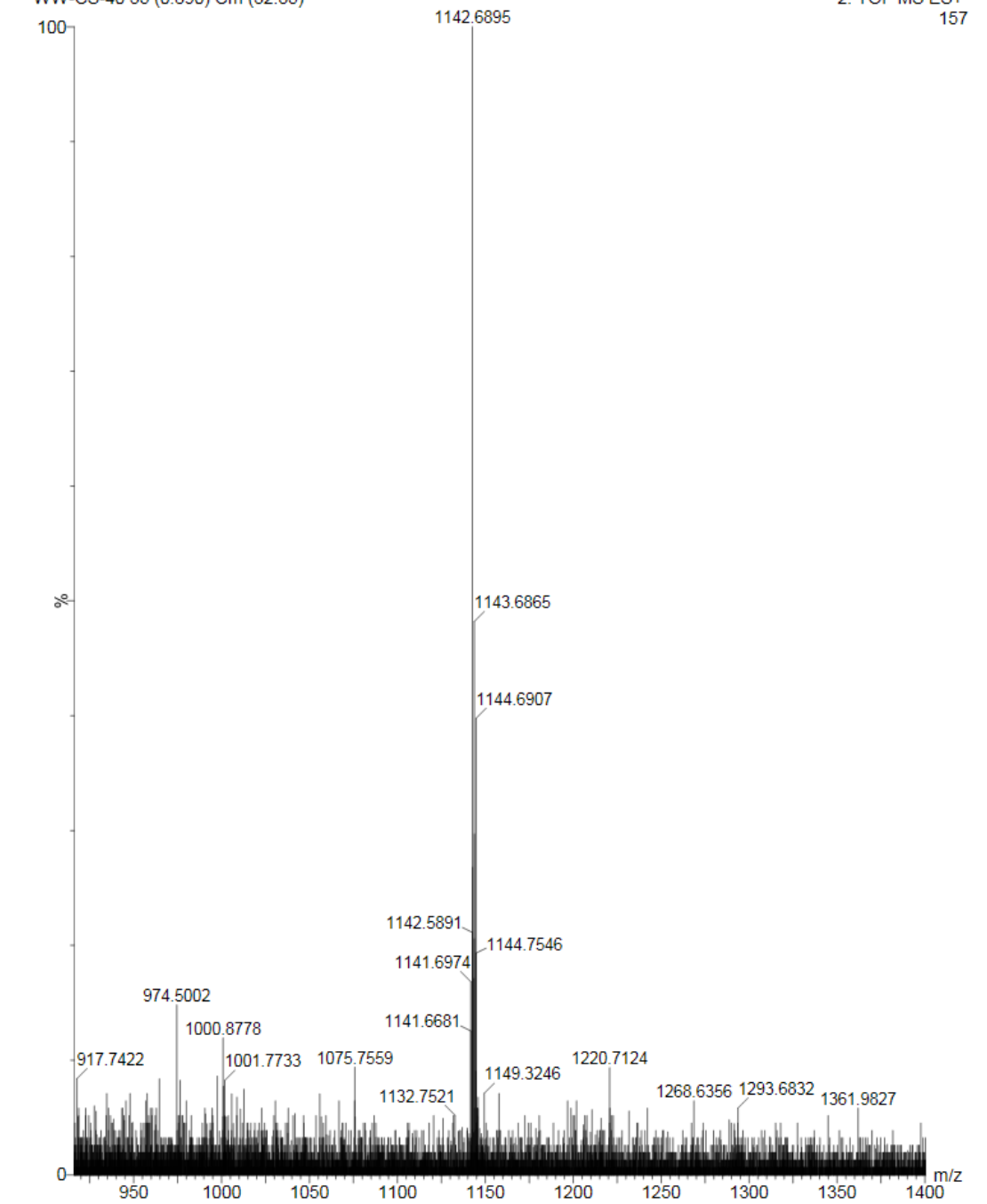


Figure S31. The HR-MS spectrum of compound CS-40.

4. Reference

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