Impact of Connectivity on the Electronic Structure of 3D Carbazole-Bridged Conjugated Systems

Appendix. Supplementary Data

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Materials and Instruments

All chemicals and solvents were reagent grade and used as received from the supplier (Adamas, SunaTech Inc., Energy-chemical and Derthon) without any further purification unless otherwise stated. The dry solvent is collected from PURESULV Solvent Purification systems PS-MD-5ON7 (Innovative Technology). Column chromatography was performed on silica gel 60 (particle size = 300 -400 mesh) and TLC was performed on an aluminum substrate coated with silica gel 60F224 (Merck, layer thickness = 0.2 mm). Nuclear Magnetic Resonance (NMR) spectra were obtained

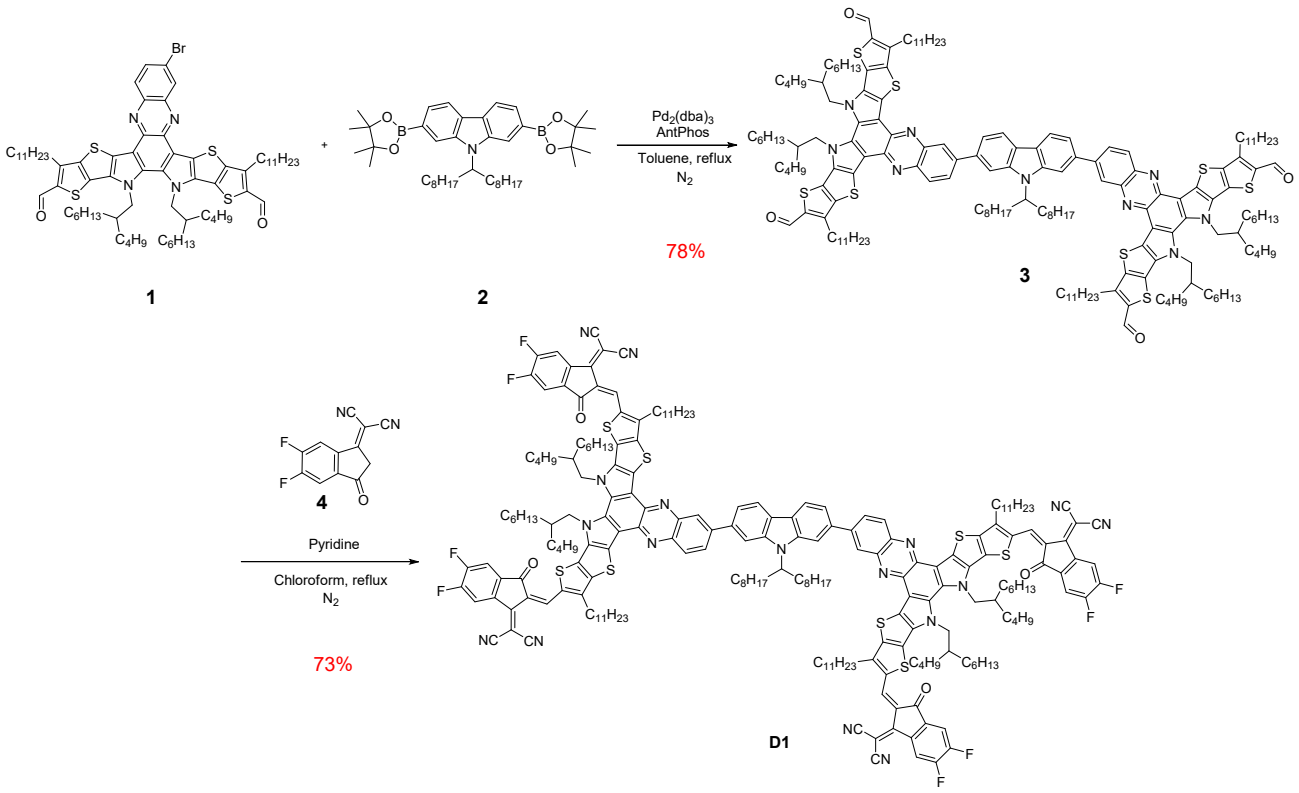
using TMS as an internal reference in Bruker Ascend ™ 400 Hz or 600 Hz in deuterated chloroform ($CDCl_3$), and spectras were referenced to the deuterated solvent peak at 7.26 and 77.16 ppm for proton and carbon NMR, respectively; all peaks were labeled and integrated accordingly. MALDI-TOF-MS spectra were obtained using Bruker Auto Bending Speed LRF using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyl]malononitrile (DCTB) as a matrix substrate. Absorption spectra were recorded at room temperature using Agilent technologies Cary series UV-Vis spectrophotometer. The film on quartz were prepared by spin-coating with chloroform solution with a concentration of 10 mg/mL. The photoluminescence spectrum was recorded on FluroMax-4 fluorescence spectrometer, with the concentration of solution 1×10^{-5} mol/L. Cyclic voltammetry experiments were performed with a LK98B II Microcomputer-based Electrochemical Analysis. All measurements were conducted at room temperature with a three electrodes configuration, including a platinum pole electrode as the working electrode, a silver chloride electrode as the reference electrode, and a platinum wire as the counter electrode. Tetrabutyl ammonium phosphorus hexafluoride in acetonitrile was employed as the supporting electrolyte, and ferrocene was employed as an internal reference. Among them, the experimental HOMO and LUMO energy levels can be determined from the $E_{HOMO} = -(5.10 + E_{ox})$ eV and $E_{LUMO} = -(5.10 + E_{red})$ eV, where E_{ox} represents the onset potential of the oxidized peak, and E_{red} represents the onset potential of the reduced peak. The information of NLO measurement: A Q-switched Nd:YAG laser (GKPPL-1064-1-10, Beijing Guoke Laser Technology Co., Ltd) operating at 532 nm was employed as the light source, with a pulse width of 4 ns and a beam waist radius of approximately 56 μm at the focal point. Device fabrication: Conventional devices were fabricated with a structure of ITO/PEDOT:PSS/PM6:Acceptor/PDINN/Ag. Pre-cleaned ITO substrates were treated with UV-ozone for 15 min. A PEDOT:PSS layer was spin-coated at 4000 rpm and annealed at 150°C for 15 min. Inside a N_2 glovebox, the PM6:Acceptor (1:1.2, 16 mg/mL in chloroform) active layer with 0.5% DIB solid additive was spin-coated (approx. 100 nm) and annealed at 80°C for 5 min. Subsequently, PDINN (2 mg/mL in MeOH) was

deposited at 3000 rpm as the electron transfer layer. Finally, 100 nm layer of Ag was thermally evaporated under vacuum (< $5*10^{-5}$ Pa) through a shadow mask, defining an active area of 0.04 cm^2.

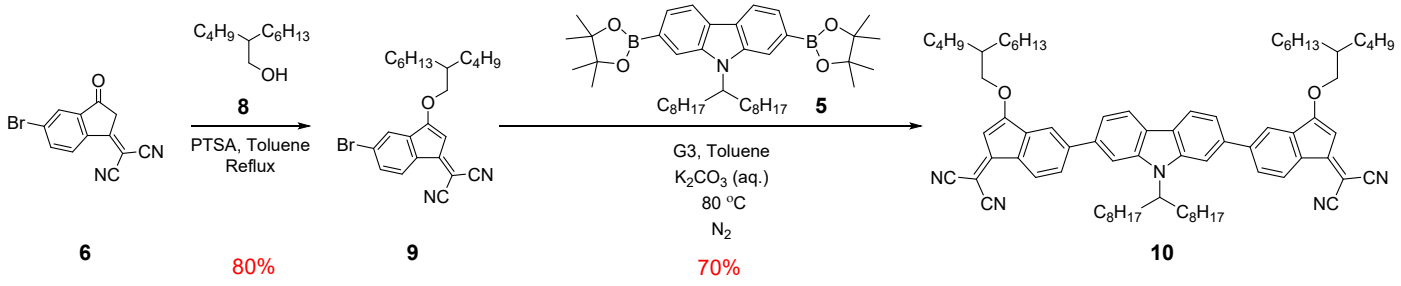
Computational Methods

All density functional theory (DFT) and time-dependent DFT (TDDFT) calculations were carried out using the Gaussian 16A suite of programs.[34] Geometry optimizations and the corresponding TD-DFT calculations were utilizing the B3LYP/6-31g(d) level of theory. Solvation effects were all taken into account using chloroform based on the polarizable continuum model (PCM).

Synthesis Procedures

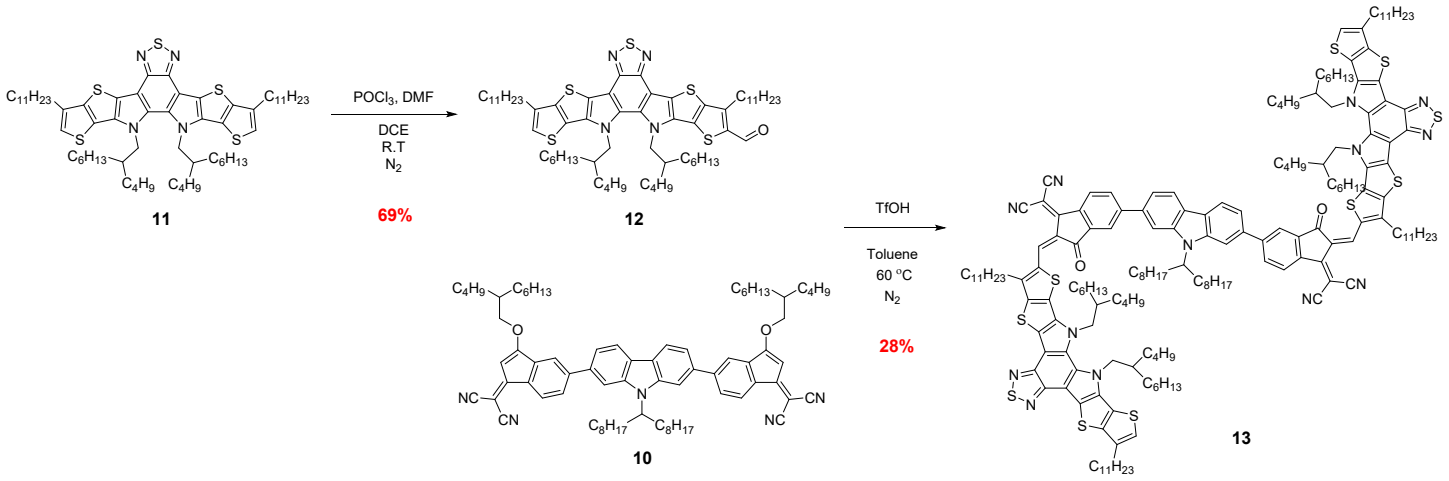


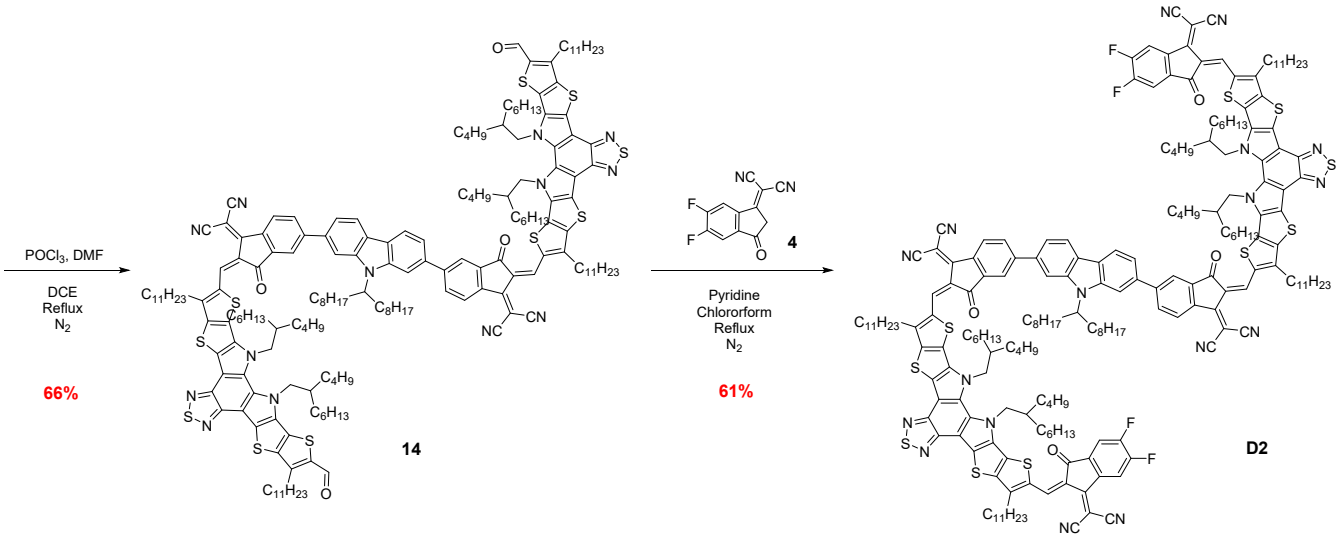
Scheme S1 Synthetic route for D1.

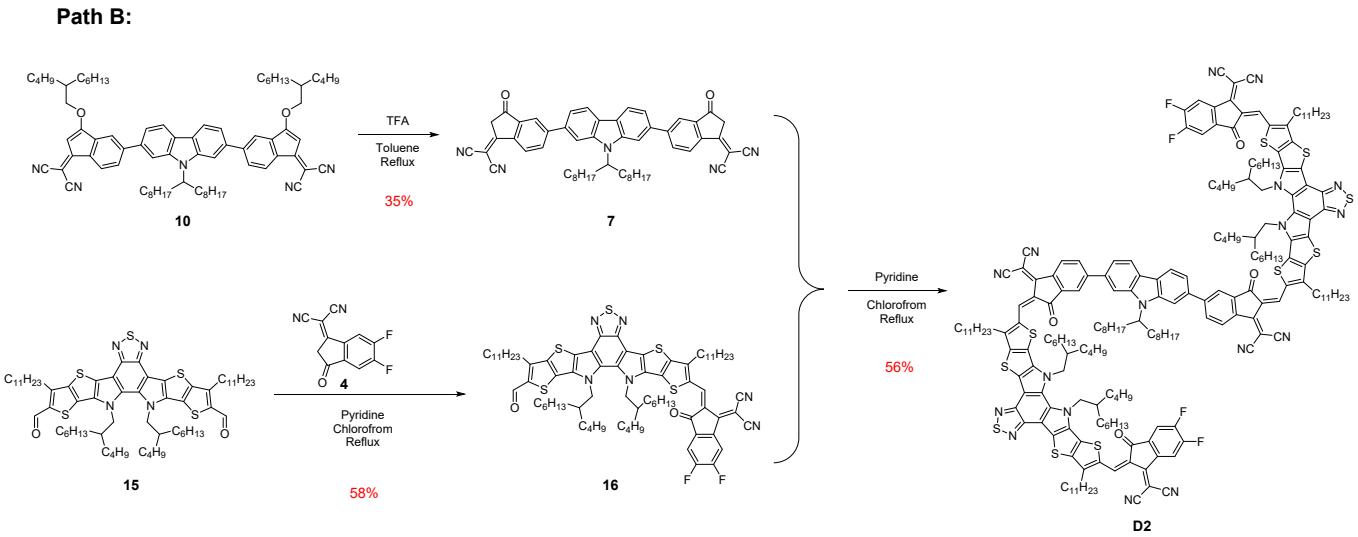


Scheme S2 Synthetic route for enol-protected substrate 10.

Path A:

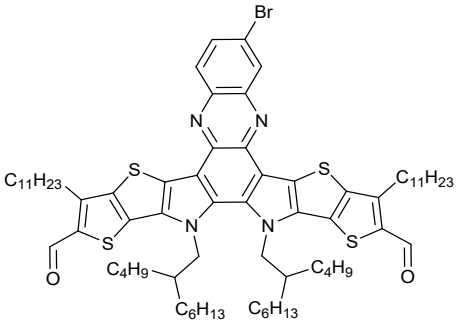






Scheme S3. Tow synthetic approaches for D2

Synthesis of Compound 1



Phosphorus oxychloride (0.2 mL) was added dropwise to a solution of 12,13-bis(2-butyloctyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole (300 mg, 1 equivalent) and N, N-Dimethylformamide (DMF, 0.2 mL) in 1, 2-dichloroethane (10 mL). The mixture was stirred and heated to reflux for overnight, then was cooled to 0 ℃. The resulting mixture was slowly added to the saturated solution of sodium carbonate, then mixture was extracted with dichloromethane and the organic layer was dried over anhydrous Na_2SO_4. After removal of solvent, the crude product was then purified by column

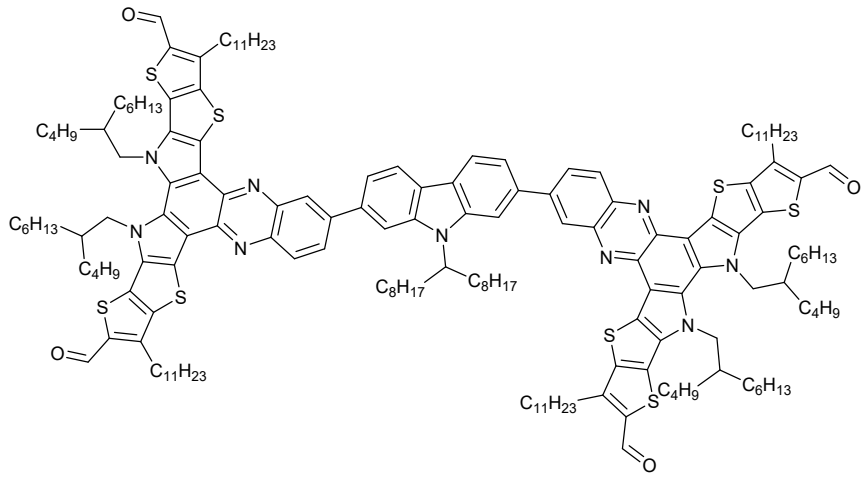
chromatography on silica gel with DCM/PCE as the gradient to afford compound **1** as a red solid in 76% yield.

MS (MALDI−TOF): calcd. for $C_{72}H_{101}BrN_4O_2S_4$ m/z = 1260.60 $[M + H]^+$, found: m/z = 1260.82 $[M + H]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 4H), 8.61 (s, 2H), 8.29 (d, *J* = 9.0 Hz, 2H), 7.90 (d, *J* = 8.9 Hz, 2H), 4.68 (d, *J* = 7.5 Hz, 8H), 3.23 (t, 8H), 2.14 (s, 4H), 1.95 (s, 10H), 1.49 (d, *J* = 6.2 Hz, 10H), 1.40 (s, 11H), 1.27 (s, 55H), 1.20 – 0.79 (m, 89H), 0.64 (dd, *J* = 13.4, 6.9 Hz, 24H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 181.83, 147.02, 146.98, 144.22, 144.19, 142.00, 140.29, 138.60, 138.34, 136.86, 136.77, 132.93, 132.76, 132.39, 131.40, 130.60, 129.58, 129.53, 128.13, 128.00, 122.93, 117.83, 117.72, 55.35, 38.95, 31.92, 31.53, 30.52, 30.29, 30.23, 30.19, 29.68, 29.64, 29.57, 29.44, 29.36, 28.20, 27.91, 27.80, 25.35, 25.22, 22.74, 22.70, 22.43, 14.14, 13.93, 13.73.

Synthesis of Compound 3



A mixture of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (200 mg, 1 equivalent), 7-bromo-15,16-bis(2-butyloctyl)-3,12-diundecyl-15,16-dihydrothieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2-*a*]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[2,3-

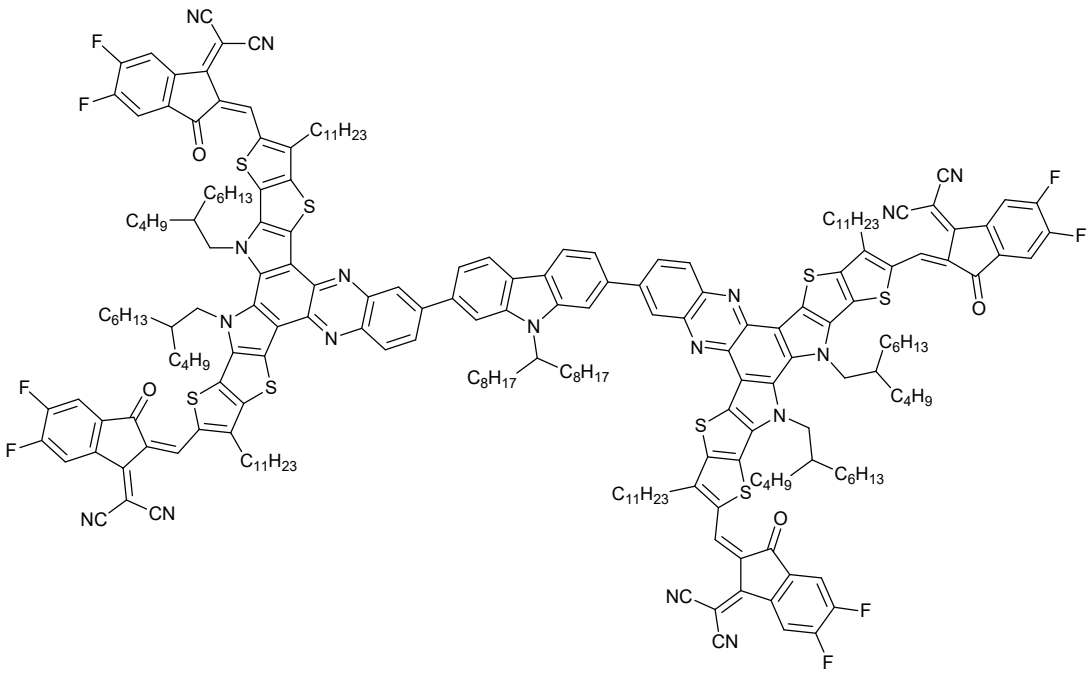
c]phenazine-2,13-dicarbaldehyde (3 equivalents), Antophos (0.2 equivalents), and Sodium tert-butoxide (7.5 equivalents) was stirred in toluene (4 ml) at room temperature and was purged with N_2 for 20 minutes. $Pd_2(dba)_3$ (0.1 equiv.) was quickly added in one portion. After stirring and purging N_2 for additional 10 minutes, the red suspension was brought to reflux for two days. Then the mixture was washed with water for several times, dried over magnesium sulphate, filtered, and the solvent was removed under reduced pressure. The crude product was chromatographically purified on a silica gel column eluting with DCM/PE as the gradient as the eluent to afford target compound **3** as red powders in 78 % yield.

MS (MALDI−TOF): calcd. for $C_{173}H_{243}BrN_9O_4S_8$ m/z = 2766.69 $[M + H]^+$, found: m/z = 2767.05 $[M + H]^+$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.17 (d, *J* = 2.3 Hz, 4H), 8.80 (d, *J* = 14.8 Hz, 2H), 8.59 (d, *J* = 8.6 Hz, 2H), 8.39 – 8.29 (m, 4H), 8.12 (s, 1H), 7.97 (s, 1H), 7.86 (d, *J* = 6.9 Hz, 2H), 4.94 – 4.87 (m, 1H), 4.71 (d, *J* = 7.7 Hz, 8H), 3.27 (d, *J* = 7.7 Hz, 8H), 2.61 – 2.53 (m, 2H), 2.15 (d, *J* = 5.2 Hz, 6H), 2.04 – 1.94 (m, 9H), 1.51 (dd, *J* = 15.2, 7.8 Hz, 8H), 1.45 – 1.37 (m, 15H), 1.37 – 0.81 (m, 176H), 0.75 (t, *J* = 6.9 Hz, 8H), 0.64 (ddd, *J* = 14.9, 11.8, 7.1 Hz, 26H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 181.81, 147.04, 146.99, 144.20, 144.13, 143.54, 143.45, 142.86, 142.08, 141.24, 140.12, 140.00, 138.73, 138.11, 136.78, 132.88, 132.68, 129.69, 128.84, 128.10, 126.90, 122.08, 121.15, 120.84, 119.27, 118.19, 118.03, 110.75, 108.15, 56.77, 55.34, 38.96, 33.98, 31.93, 31.90, 31.79, 31.54, 30.55, 30.32, 30.24, 29.69, 29.64, 29.59, 29.58, 29.53, 29.48, 29.45, 29.36, 29.34, 29.22, 28.23, 27.89, 27.81, 26.93, 25.38, 25.26, 22.75, 22.73, 22.70, 22.68, 22.59, 22.44, 14.13, 14.10, 14.02, 13.93, 13.71.

Synthesis of Compound D1

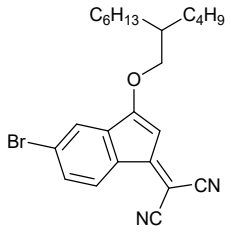


Under N_2 protection, compound **3** (100 mg, 1.0 equivalent), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1Hinden-1-ylidene)malononitrile (10 equivalents) and 10 mL dry chloroform were added to 50 mL two-necked round bottom flask. Then a few drops of pyridine was dropped into the mixture. The reaction mixture was stirred at 70 ℃ for 24 h. After cooling to room temperature, the reaction mixture was precipitated in methanol. Then the solid was purified by column chromatography on silica gel with DCM/PE as the gradient to give black target compound **D1** in 73% yield.

MS (MALDI−TOF): calcd. for $C_{221}H_{251}F_8N_{17}O_4S_8$ m/z = 3614.76 $[M + H]^+$, found: m/z = 3615.28 $[M + H]^+$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.17 (s, 4H), 8.74 (s, 2H), 8.56 (d, *J* = 8.6 Hz, 6H), 8.33 (s, 4H), 8.12 (s, 1H), 7.97 (s, 1H), 7.81 (s, 2H), 7.71 (t, *J* = 7.3 Hz, 4H), 4.86 (s, 9H), 3.30 (s, 8H), 2.57 (s, 2H), 2.30 – 2.10 (m, 9H), 2.01 (d, *J* = 5.6 Hz, 3H), 1.93 (s, 9H), 1.56 (d, *J* = 9.6 Hz, 18H), 1.47 – 0.95 (m, 243H), 0.90 – 0.78 (m, 50H), 0.77 – 0.63 (m, 37H).

Synthesis of Compound 9

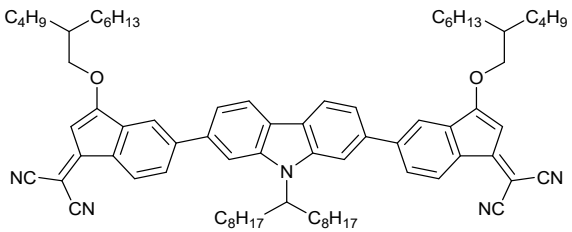


To a suspension of 2-(5-bromo-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (1.0 g, 1 equiv.) with *p*-toluenesulfonic acid (1 equiv.) in toluene (25 ml) was added 2-butyloctan-1-ol (5 equiv.) dropwise. Then the mixture was heated to reflux for overnight before cooled down to room temperature. The orange solution was diluted with DCM, washed with water for several times, dried with Na_2SO_4 and was concentrated via rotary evaporator. The residue was purified via column chromatography eluting with EtOAc/PE in 1:9 to give title product **7** as the red powder in 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.51 (dd, 1H), 7.43 (d, *J* = 1.6 Hz, 1H), 5.74 (s, 1H), 4.12 (d, *J* = 5.6 Hz, 2H), 1.93 – 1.80 (m, 1H), 1.42 (s, 4H), 1.32 (d, *J* = 7.7 Hz, 12H), 1.02 – 0.79 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.17, 164.89, 139.57, 132.80, 130.93, 126.95, 125.52, 123.69, 113.48, 97.70, 76.71, 75.82, 37.56, 31.79, 31.10, 30.79, 29.54, 28.94, 26.72, 22.94, 22.66, 14.12, 14.05.

Synthesis of Compound 10



A mixture of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H* carbazole (200 mg, 1 equiv.), 2-(5-bromo-3-((2-butyloctyl)oxy)-1*H*-inden-1-ylidene)malononitrile (3 equiv.)

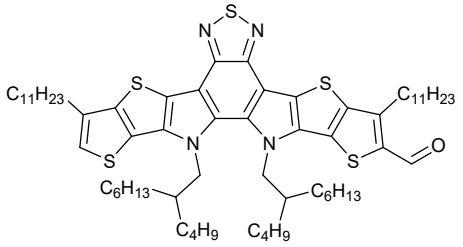
stirred in toluene (3 ml) at room temperature and 1 ml of potassium carbonate solution (2M) was added dropwise. Then the suspension was purged with N_2 for 20 minutes before quickly adding the palladium G3 regent. (0.1 equiv.) in one portion. After stirring and purging N_2 for additional 10 minutes, the red suspension was bought to reflux for two days. Then the mixture was washed with water for several times, dried over anhydrous magnesium sulphate, filtered, and the solvent was removed under reduced pressure. The crude product was chromatographically purified on a silica gel column eluting with DCM/PE in 1:4 as the eluent to afford target compound **8** as red oil in 70 % yield.

MS (MALDI−TOF): calcd. for $C_{77}H_{99}N_5O_2$ m/z = 1125.78 $[M + H]^+$, found: m/z = 1125.49 $[M + H]^+$

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.18 (m, *J* = 9.5 Hz, 4H), 7.76 (s, 1H), 7.74 – 7.57 (m, *J* = 25.0, 11.6, 5.7 Hz, 6H), 7.60 – 7.45 (m, *J* = 14.3, 8.0 Hz, 3H), 5.78 (s, 2H), 4.77 – 4.61 (m, 1H), 4.18 (d, *J* = 5.6 Hz, 4H), 2.41 – 2.30 (m, 2H), 2.07 – 1.98 (m, 2H), 1.96 – 1.90 (m, 2H), 1.47 (d, *J* = 3.4 Hz, 8H), 1.39 – 1.33 (m, 14H), 1.30 (s, 10H), 1.26 (s, 6H), 1.18 – 1.04 (m, 20H), 0.94 (t, *J* = 6.8 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 6H), 0.78 (t, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.23, 165.94, 146.66, 143.14, 139.80, 138.77, 137.88, 137.42, 130.93, 130.81, 128.85, 125.00, 123.72, 122.37, 121.15, 120.89, 119.60, 118.51, 113.91, 113.83, 110.22, 107.58, 97.40, 76.73, 75.72, 75.62, 71.90, 65.59, 56.72, 37.61, 33.85, 31.82, 31.74, 31.22, 30.91, 30.59, 29.73, 29.62, 29.39, 29.30, 29.12, 28.96, 26.82, 26.76, 22.98, 22.68, 22.58, 19.21, 14.11, 14.08, 14.03, 13.75.

Synthesis of Compound 12



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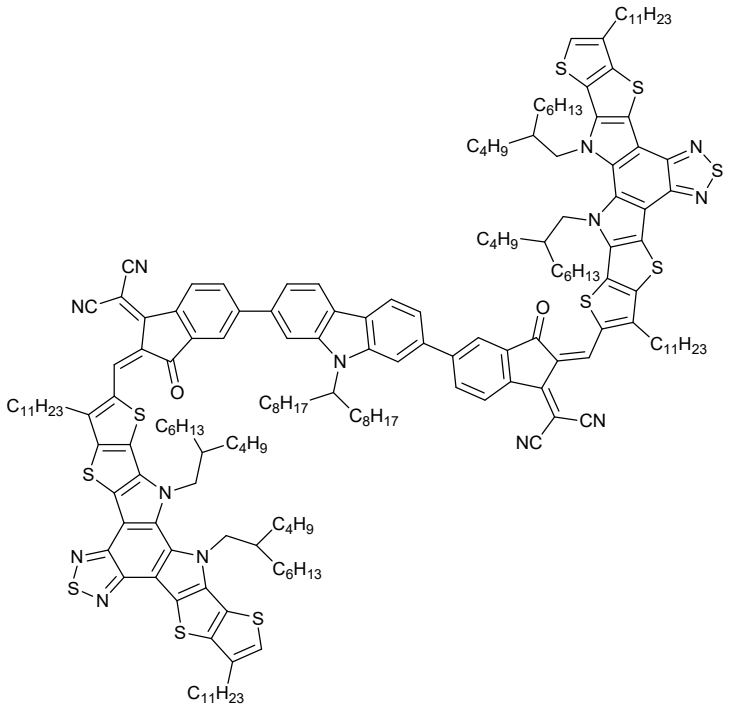
Phosphorus oxychloride (0.3 mL) was added dropwise to a solution of 12,13-bis(2-butyloctyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole (700 mg, 1 equiv.) and N, N-Dimethylformamide (DMF, 0.3 mL) in 1, 2-dichloroethane (10 mL). The mixture was stirred at room temperature for overnight. The resulting mixture was slowly added to the saturated solution of sodium carbonate, then mixture was extracted with dichloromethane and the organic layer was dried over anhydrous magnesium sulphate. After removal of solvent, the crude product was then purified by column chromatography on silica gel with PE/DCM as the gradient to afford target compound **10** as the orange oil in 69% yield.

MS (MALDI−TOF): calcd. for $C_{65}H_{98}N_4OS_5$ m/z = 1110.63 $[M + H]^+$, found: m/z = 1110.39 $[M + H]^+$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.04 (s, 1H), 4.60 (t, *J* = 16.6 Hz, 4H), 3.19 (t, *J* = 7.6 Hz, 2H), 2.83 (t, 2H), 2.08 – 2.00 (m, 2H), 1.92 (dt, *J* = 15.0, 7.6 Hz, 2H), 1.85 (dt, *J* = 14.0, 7.1 Hz, 2H), 1.49 – 1.43 (m, 4H), 1.43 – 1.35 (m, 6H), 1.25 (d, *J* = 19.9 Hz, 30H), 1.13 – 0.91 (m, 18H), 0.82 (m, 18H), 0.68 – 0.59 (m, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 180.66, 146.67, 146.43, 145.96, 141.83, 141.50, 136.85, 135.85, 135.40, 135.03, 133.00, 129.63, 128.94, 126.75, 126.71, 123.74, 122.45, 121.77, 121.74, 118.99, 111.94, 109.99, 54.14, 54.02, 37.77, 37.67, 33.27, 30.90, 30.88, 30.52, 30.48, 29.34, 29.29, 29.21, 29.14, 29.01, 28.66, 28.61, 28.58, 28.49, 28.46, 28.43, 28.36, 28.33, 28.30, 28.27, 27.80, 27.14, 27.00, 26.86, 26.80, 26.68, 24.19, 24.00, 21.71, 21.67, 21.41, 21.39, 13.09, 12.90, 12.72, 12.67, 12.63.

Synthesis of Compound 13



Under N_2 protection, 2,2'-((9-(heptadecan-9-yl)-9*H*-carbazole-2,7-diyl)bis(3-((2-butyloctyl)oxy)-1*H*-indene-5-yl-1-ylidene))dimalononitrile (150 mg, 1.0 equivalent), 12,13-bis(2-butyloctyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole-2-carbaldehyde (3 equivalents) and 10 mL toluene were added to 25 mL two-necked round bottom flask. Then a few drops of trifluoromethanesulfonic acid was dropped into the mixture. The reaction mixture was stirred at 70 ℃ for overnight. After cooling to room temperature, the dark green mixture was precipitated in methanol. Then the solid was purified by column chromatography on silica gel with petroleum ether/ DCM as the gradient to give black target compound **11** in 28% yield.

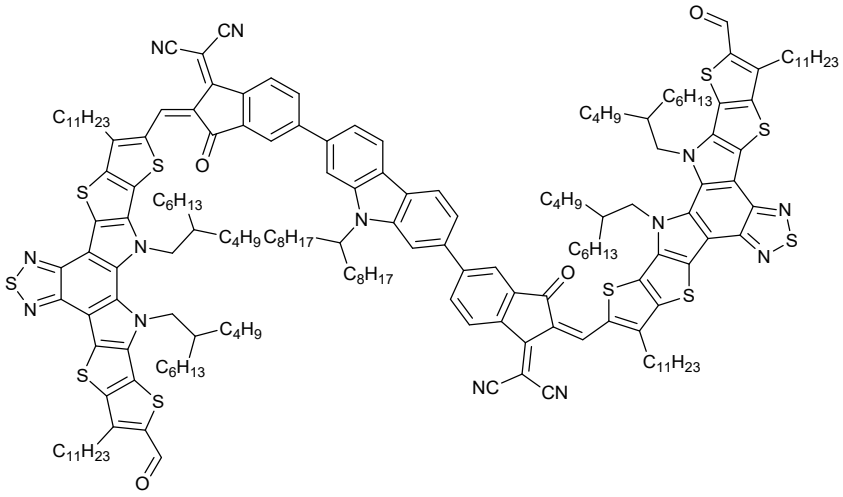
MS (MALDI−TOF): calcd. for $C_{183}H_{243}N_{13}O_2S_{10}$ m/z = 2974.65 $[M + H]^+$, found: m/z = 2974.20 $[M + H]^+$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.19 (s, 2H), 8.82 (t, *J* = 7.5 Hz, 2H), 8.32 – 8.26 (m, 4H), 8.12 (dd, *J* =

11.9, 8.6 Hz, 2H), 7.93 (s, 1H), 7.78 (s, 1H), 7.65 – 7.60 (m, 2H), 7.09 (d, *J* = 10.5 Hz, 2H), 4.73 (d, *J* = 12.2 Hz, 5H), 4.63 (d, *J* = 24.7 Hz, 4H), 3.26 (t, *J* = 7.3 Hz, 4H), 2.84 (t, *J* = 7.7 Hz, 4H), 2.42 (dt, *J* = 14.1, 9.7 Hz, 2H), 2.16 – 2.08 (m, 6H), 1.91 (dt, *J* = 11.6, 5.9 Hz, 4H), 1.86 (dd, *J* = 14.8, 7.2 Hz, 4H), 1.55 – 1.51 (m, 4H), 1.46 – 1.43 (m, 4H), 1.38 (s, 9H), 1.29 (dd, *J* = 28.9, 20.0 Hz, 87H), 1.19 (dd, *J* = 20.3, 13.5 Hz, 31H), 1.11 – 1.04 (m, 15H), 1.01 (dd, *J* = 13.7, 6.8 Hz, 16H), 0.97 – 0.92 (m, 12H), 0.91 – 0.85 (m, 28H), 0.80 (t, *J* = 7.1 Hz, 10H), 0.72 – 0.62 (m, 30H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 187.00, 186.11, 160.01, 159.07, 153.90, 153.66, 147.51, 145.15, 138.54, 138.34, 137.67, 136.04, 135.84, 135.61, 135.31, 134.14, 133.48, 133.27, 130.75, 129.47, 126.73, 126.43, 120.23, 119.86, 115.28, 114.90, 114.35, 113.57, 113.49, 112.26, 68.38, 68.33, 55.70, 39.19, 31.91, 31.62, 31.61, 31.58, 31.21, 30.47, 30.35, 29.83, 29.65, 29.62, 29.51, 29.46, 29.34, 27.92, 25.59, 22.82, 22.69, 22.50, 22.48, 14.12, 14.05, 14.03, 13.77.

Synthesis of Compound 14



Phosphorus oxychloride (0.1 mL) was added dropwise to a solution of PREVIOUS RXN. PRODUCT (150 mg, 1 equiv.) and N, N-Dimethylformamide (DMF, 0.1 mL) in 1, 2-dichloroethane (5 mL). The mixture was stirred reflux for overnight. After cooling down to room temperature, the dark green

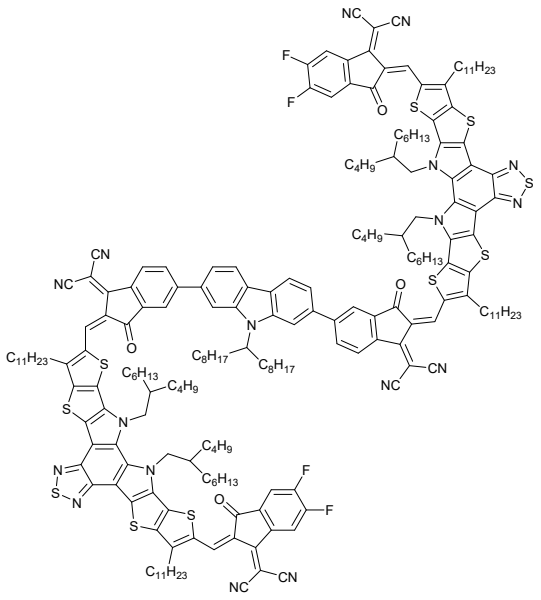
resulting mixture was slowly added to the saturated solution of sodium carbonate, then mixture was extracted with dichloromethane and the organic layer was dried over anhydrous magnesium sulphate. After removal of solvent, the crude product was then purified by column chromatography on silica gel with PE/DCM as the gradient to afford target compound **12** as a black solid in 66% yield.

MS (MALDI−TOF): calcd. for $C_{185}H_{243}N_{13}O_4S_{10}$ m/z = 3030.64 $[M + H]^+$, found: m/z = 3030.51 $[M + H]^+$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.19 (s, 2H), 8.82 (t, *J* = 7.5 Hz, 2H), 8.32 – 8.26 (m, 4H), 8.12 (dd, *J* = 11.9, 8.6 Hz, 2H), 7.93 (s, 1H), 7.78 (s, 1H), 7.65 – 7.60 (m, 2H), 7.09 (d, *J* = 10.5 Hz, 2H), 4.73 (d, *J* = 12.2 Hz, 5H), 4.63 (d, *J* = 24.7 Hz, 4H), 3.26 (t, *J* = 7.3 Hz, 4H), 2.84 (t, *J* = 7.7 Hz, 4H), 2.42 (dt, *J* = 14.1, 9.7 Hz, 2H), 2.16 – 2.08 (m, 6H), 1.91 (dt, *J* = 11.6, 5.9 Hz, 4H), 1.86 (dd, *J* = 14.8, 7.2 Hz, 4H), 1.55 – 1.51 (m, 4H), 1.46 – 1.43 (m, 4H), 1.38 (s, 9H), 1.29 (dd, *J* = 28.9, 20.0 Hz, 87H), 1.19 (dd, *J* = 20.3, 13.5 Hz, 31H), 1.11 – 1.04 (m, 15H), 1.01 (dd, *J* = 13.7, 6.8 Hz, 16H), 0.97 – 0.92 (m, 12H), 0.91 – 0.85 (m, 28H), 0.80 (t, *J* = 7.1 Hz, 10H), 0.72 – 0.62 (m, 30H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 188.21, 181.61, 161.04, 153.21, 147.50, 147.07, 144.83, 143.64, 138.37, 137.39, 135.33, 134.88, 132.19, 129.30, 125.97, 121.36, 120.91, 115.79, 115.11, 113.56, 112.96, 67.94, 67.73, 31.93, 31.91, 31.74, 31.52, 31.22, 30.35, 29.86, 29.68, 29.64, 29.60, 29.55, 29.52, 29.45, 29.38, 29.36, 29.14, 26.99, 22.80, 22.75, 22.70, 22.59, 22.49, 22.41, 14.12, 14.07, 13.97, 13.71, 13.67.

Synthesis of Compound D2



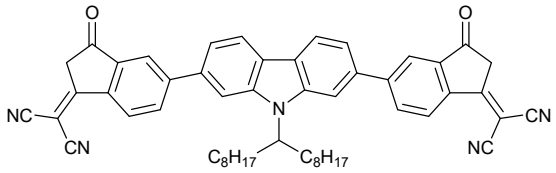
Path A:

Under N_2 protection, compound **12** (20 mg, 1.0 equivalent), 2-(5,6-difluoro-3-oxo-2,3- dihydro-1Hinden-1-ylidene)malononitrile (5 equivalents) and 5 mL chloroform were added to 15 mL two-necked round bottom flask. Then a few drops of pyridine was added into the mixture. The black reaction mixture was stirred at reflux for 12 hrs. After cooling to room temperature, the reaction mixture was precipitated in methanol. Then the solid was purified by column chromatography on silica gel with petroleum ether/ DCM as the gradient to give black target compound **D2** in 61% yield.

MS (MALDI−TOF): calcd. for $C_{209}H_{247}F_4N_{17}O_4S_{10}$ m/z = 3454.68 $[M + H]^+$, found: m/z = 3454.78 $[M + H]^+$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.23 (s, 2H), 9.14 (s, 2H), 8.92 – 8.80 (m, 2H), 8.59 – 8.49 (m, 2H), 8.41 – 8.22 (m, 4H), 8.17 (dd, *J* = 12.5, 8.5 Hz, 2H), 7.95 (s, 1H), 7.80 (s, 1H), 7.65 (dd, *J* = 16.1, 8.5 Hz, 4H), 4.78 (d, *J* = 6.1 Hz, 9H), 3.38 – 3.09 (m, 8H), 2.45 (d, *J* = 9.7 Hz, 2H), 2.20 – 2.06 (m, 6H), 1.89 (ddd, *J* = 22.6, 14.9, 7.7 Hz, 8H), 1.42 – 1.05 (m, 150H), 1.02 (d, *J* = 7.6 Hz, 20H), 0.91 – 0.80 (m, 34H), 0.78 – 0.62 (m, 28H).

Synthesis of Compound 7



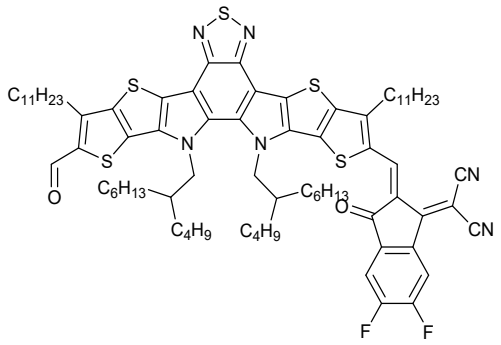
The mixture of 2,2'-((9-(heptadecan-9-yl)-9*H*-carbazole-2,7-diyl)bis(3-((2-butyloctyl)oxy)-1*H*-indene-5-yl-1-ylidene))dimalononitrile (150 mg, 1.0 equivalent)(100 mg, 1 equiv.) and *p*-toluenesulfonic acid (5 equiv.) in toluene/water (5 ml/1 ml)) was stirred at reflux. The reaction was monitored by TLC. After stopping heating, the orange suspension was washed with water, and the organic layer was dried over anhydrous magnesium sulphate. After removal of solvent, the crude product was then purified by column chromatography on silica gel with PE/DCM in 1:4 to afford target compound **13** as the orange solid in 35% yield.

MS (MALDI−TOF): calcd. for $C_{53}H_{51}N_5O_2$ m/z = 789.40 $[M + H]^+$, found: m/z = 789.29 $[M + H]^+$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 8.0, 5.0 Hz, 2H), 8.33 – 8.21 (m, 6H), 7.86 (s, 1H), 7.71 (s, 1H), 7.62 – 7.57 (m, 2H), 4.71 (dq, *J* = 15.1, 5.0 Hz, 1H), 3.81 (s, 4H), 2.40 – 2.31 (m, 2H), 2.04 (ddd, *J* = 15.2, 10.3, 5.1 Hz, 2H), 1.31 – 1.20 (m, 8H), 1.18 – 1.07 (m, 18H), 0.77 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.26, 165.65, 149.74, 141.34, 140.95, 135.28, 135.01, 126.56, 122.76, 121.79, 121.46, 118.84, 112.45, 112.28, 110.71, 107.95, 78.28, 57.00, 43.66, 33.86, 31.69, 29.37, 29.28, 29.10, 26.87, 22.54, 14.01.

Synthesis of Compound 16



12,13-bis(2-butyloctyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-dicarbaldehyde (500 mg, 1 equiv.), 2-(5,6-difluoro-3-oxo-2,3- dihydro-1Hinden-1-ylidene)malononitrile (1 equivalent) and 20 mL chloroform were added to 50 mL two-necked round bottom flask. Then a few drops of pyridine was added into the mixture. The black reaction mixture was stirred at reflux and monitored by TLC. After stopping heating, the dark green mixture was then precipitated in methanol. Then the solid was purified by column chromatography on silica gel with petroleum ether/ DCM in 4:1 to give black target compound **14** in 58% yield.

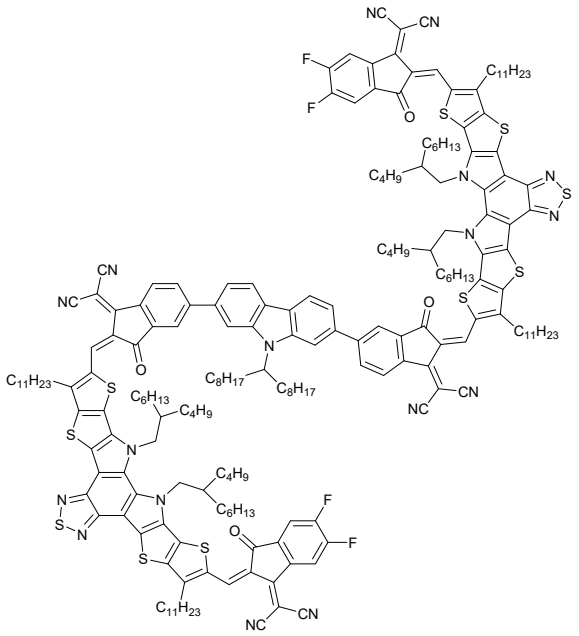
MS (MALDI−TOF): calcd. for $C_{78}H_{100}F_2N_6O_2S_5$ m/z = 1350.65 $[M + H]^+$, found: m/z = 1350.83 $[M + H]^+$.

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.16 (s, 1H), 9.17 (d, *J* = 5.6 Hz, 1H), 8.66 – 8.45 (m, 1H), 7.69 (q, *J* = 7.7 Hz, 1H), 4.75 (ddd, *J* = 23.7, 15.8, 10.1 Hz, 2H), 4.68 – 4.55 (m, 2H), 3.22 (dt, *J* = 15.6, 7.8 Hz, 4H), 2.07 (d, *J* = 6.7 Hz, 2H), 1.90 (dtd, *J* = 23.3, 15.4, 7.9 Hz, 4H), 1.48 (ddd, *J* = 22.8, 15.2, 7.8 Hz, 4H), 1.42 – 1.35 (m, 4H), 1.34 – 1.14 (m, 52H), 1.14 – 0.80 (m, 42H), 0.65 (dt, *J* = 15.7, 7.1 Hz, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 186.30, 181.85, 159.02, 154.08, 154.08, 147.59, 147.41, 147.41, 146.81, 144.61, 143.76, 137.50, 136.41, 135.39, 134.87, 132.98, 132.34, 131.09, 130.11, 129.43, 119.58, 115.04, 114.44, 113.78, 113.56, 113.18, 112.75, 112.29, 68.61, 55.76, 55.08, 38.89, 31.91, 31.55, 31.52,

31.25, 30.34, 30.13, 29.83, 29.71, 29.65, 29.62, 29.60, 29.51, 29.45, 29.37, 29.32, 28.16, 22.77, 22.72, 22.69, 22.47, 22.45, 22.43, 22.41, 14.12, 13.96, 13.77, 13.73, 13.70, 13.67.

Synthesis of Compound D2



Path B:

Under N_2 protection, 2,2'-((9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(3-oxo-2,3-dihydro-1H-indene-5-yl-1-ylidene))dimalononitrile (30 mg, 1 equiv.), (Z)-2-(2-((12,13-bis(2-butyloctyl)-10-formyl-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-*e*]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indol-2-yl)methylene)-5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (4 equiv.) and 8 ml of chloroform were added to 25 mL two-necked round bottom flask. Then a few drops of pyridine were added into the mixture. The black reaction mixture was stirred at reflux for overnight. After cooling to room temperature, the reaction mixture was precipitated in methanol. Then the crude product was purified by column chromatography on silica gel with petroleum ether/ DCM as the gradient to give black target

compound **D2** in 56% yield.

^{1}H and ^{13}C NMR Spectra

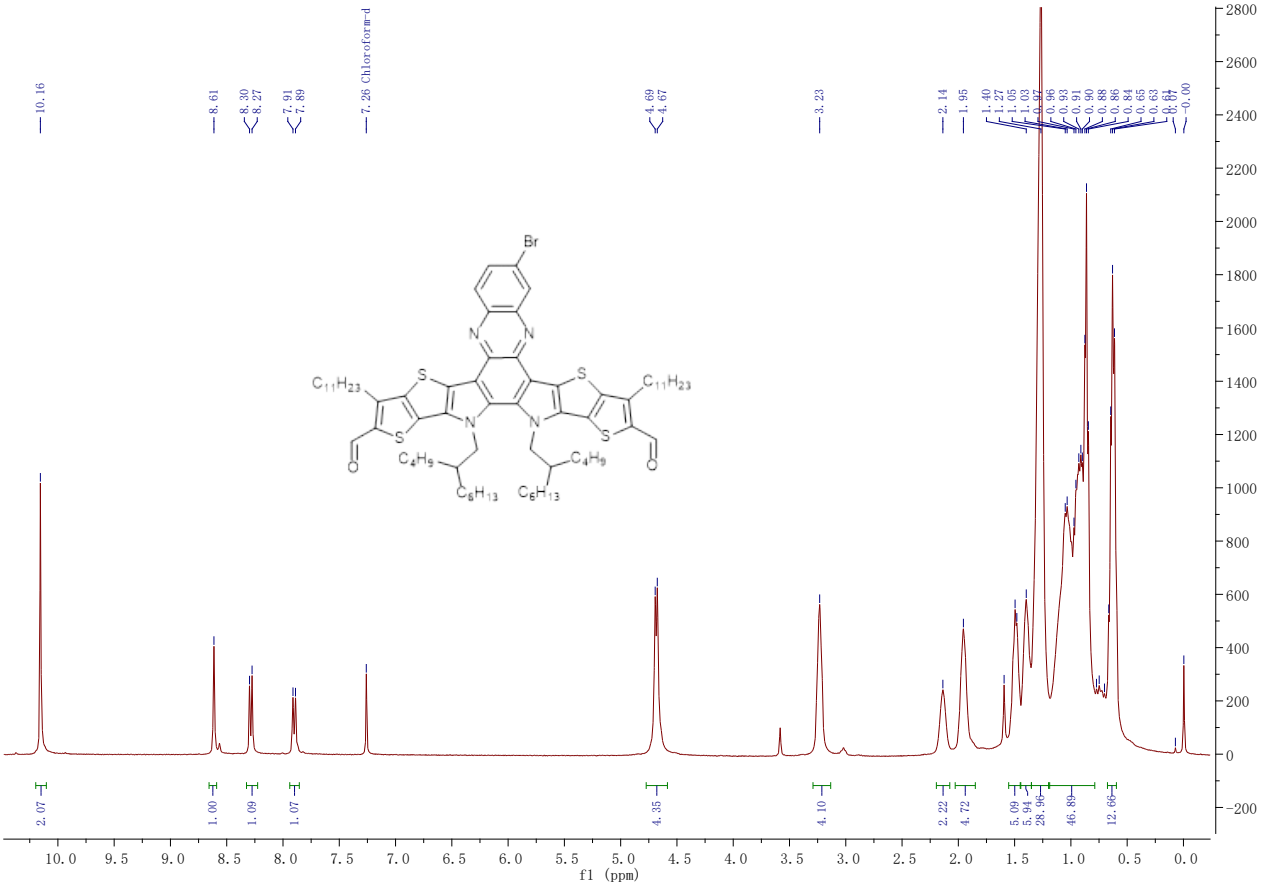


Figure S1 ^{1}H-NMR (400 MHz) of compound 1 in $CDCl_3$, 298 K.

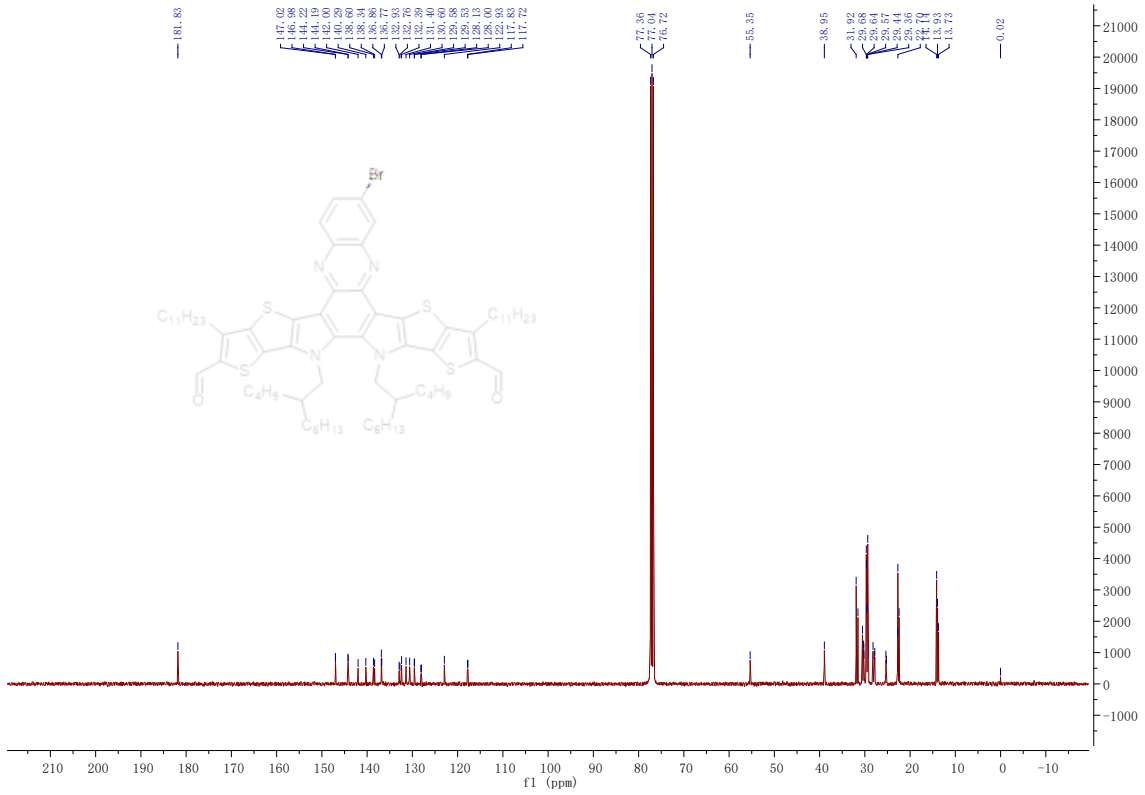


Figure S2 ^{13}C-NMR (101 MHz) of compound 1 in $CDCl_3$, 298 K.

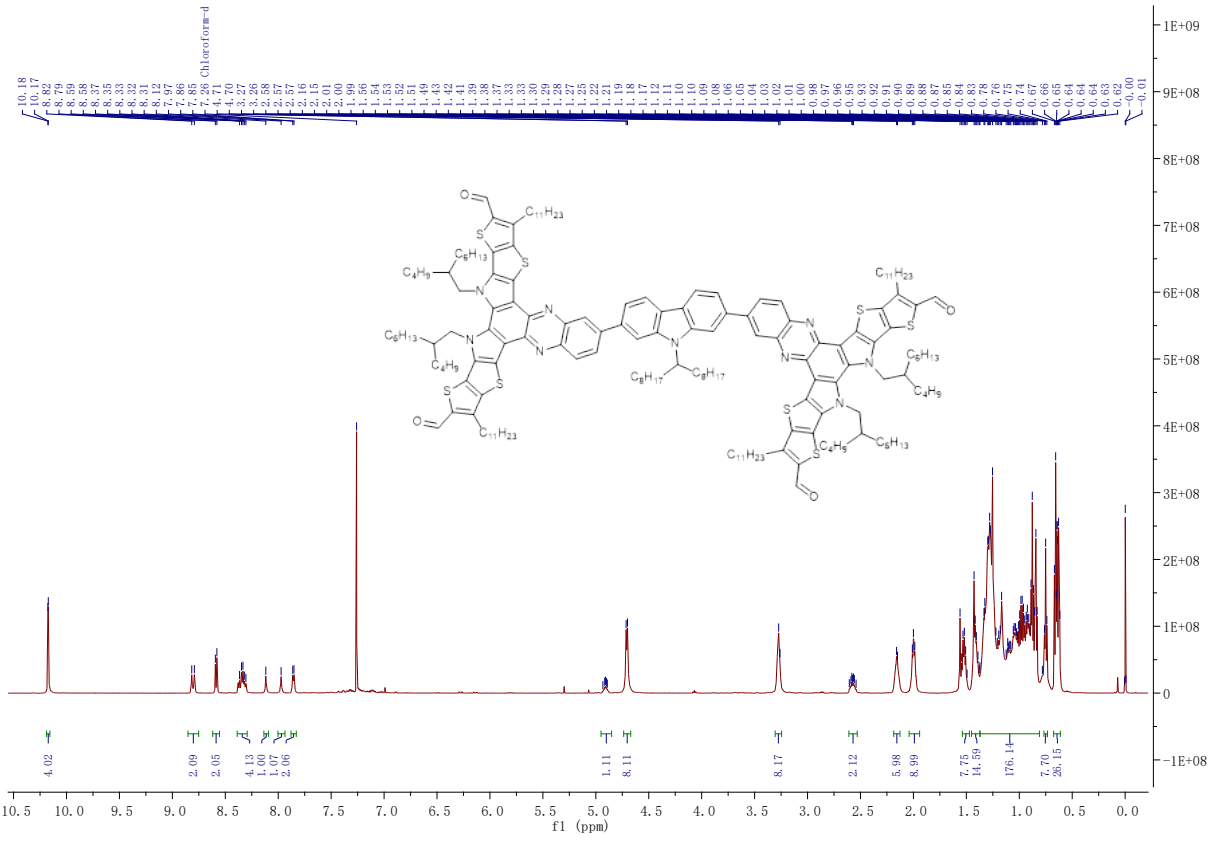


Figure S3 ^{1}H-NMR (600 MHz) of compound 3 in $CDCl_3$, 298 K.

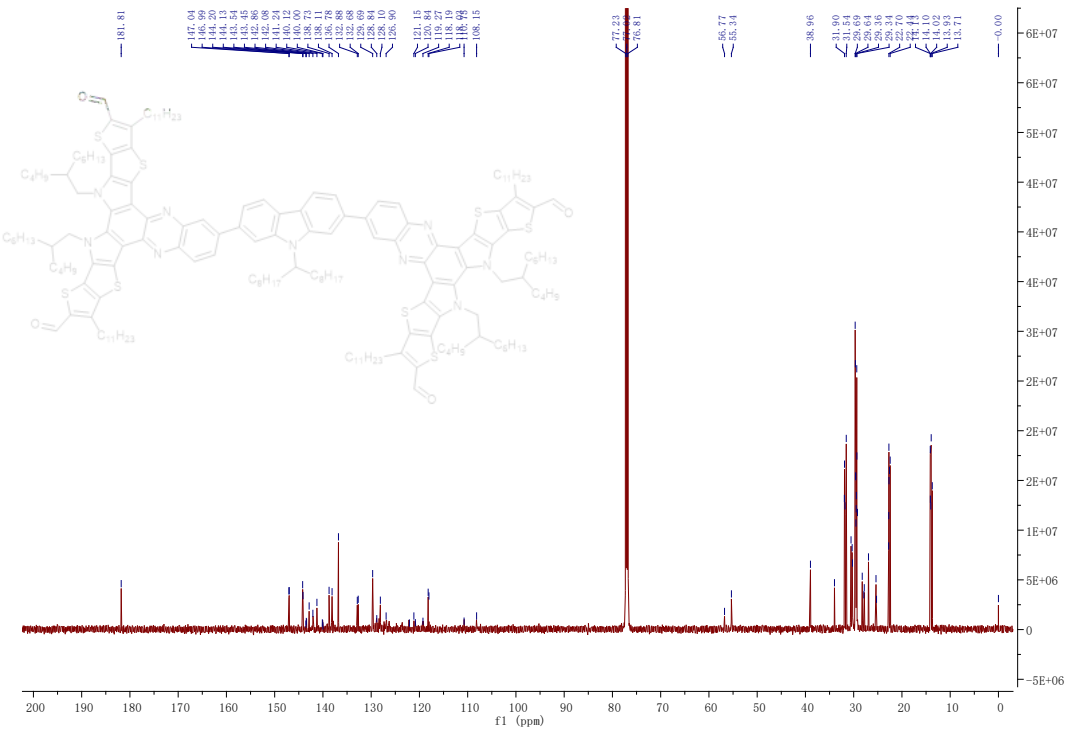


Figure S4 ^{13}C-NMR (151 MHz) of compound 3 in $CDCl_3$, 298 K.

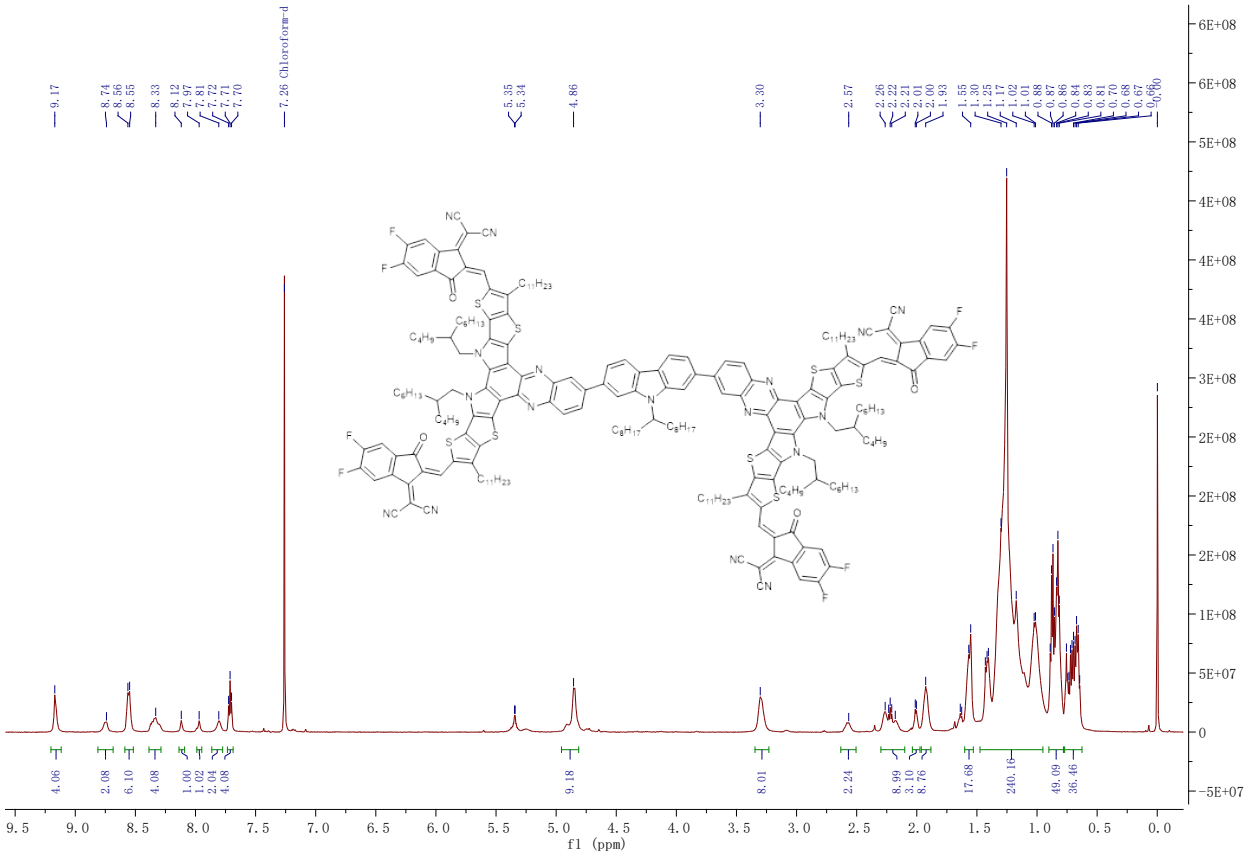


Figure S5 ^{1}H-NMR (600 MHz) of compound D1 in $CDCl_3$, 298 K.

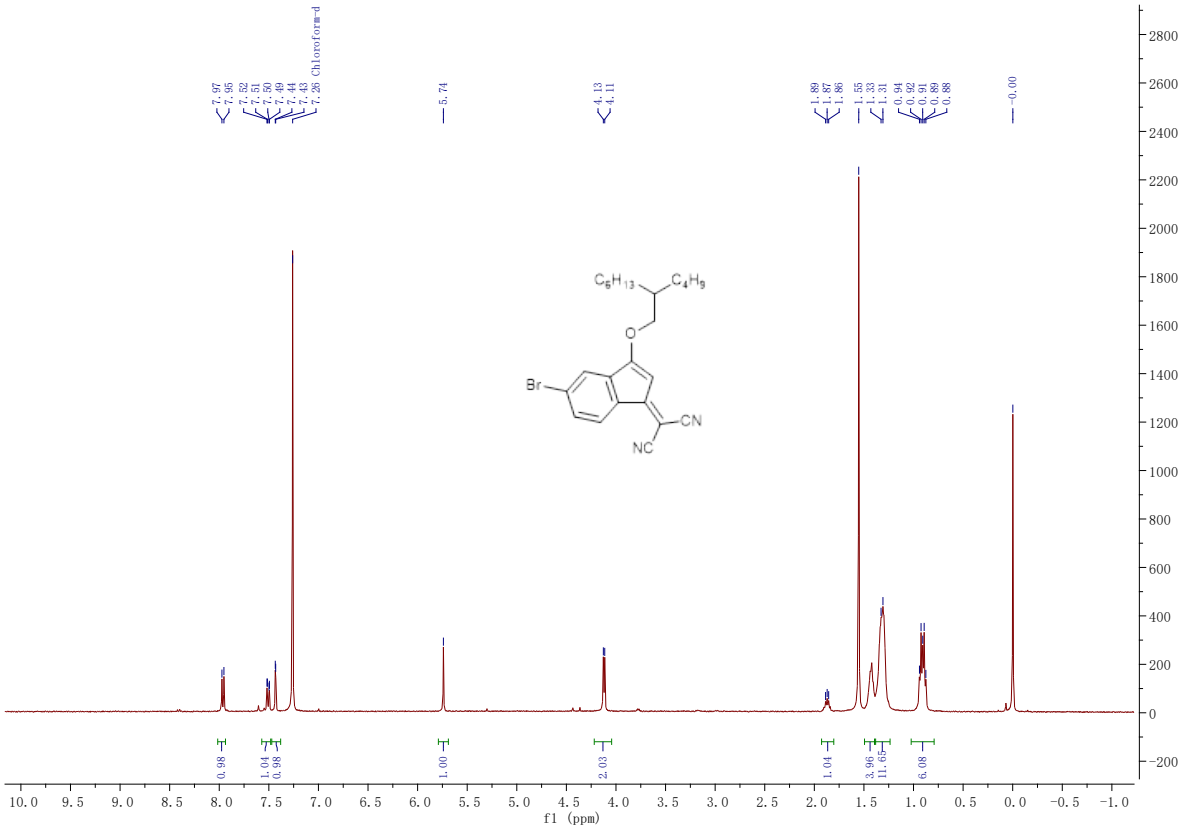


Figure S6 ^{1}H-NMR (400 MHz) of compound 9 in $CDCl_3$, 298 K.

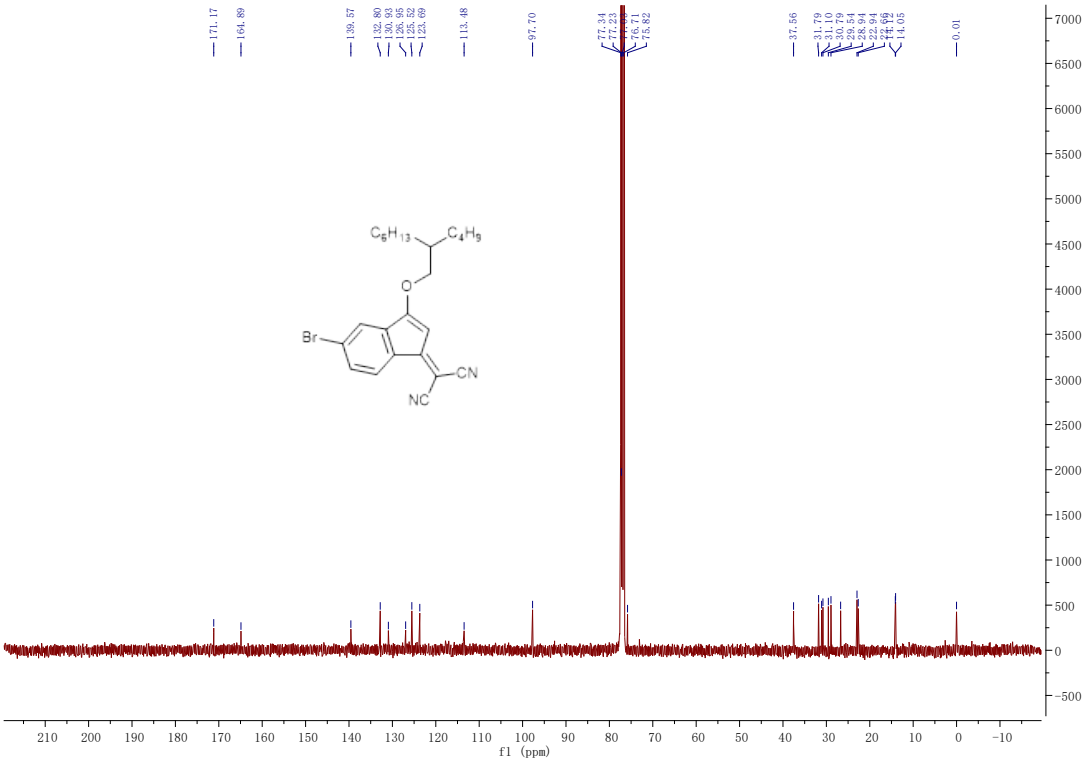


Figure S7 ^{13}C-NMR (101 MHz) of compound 9 in $CDCl_3$, 298 K.

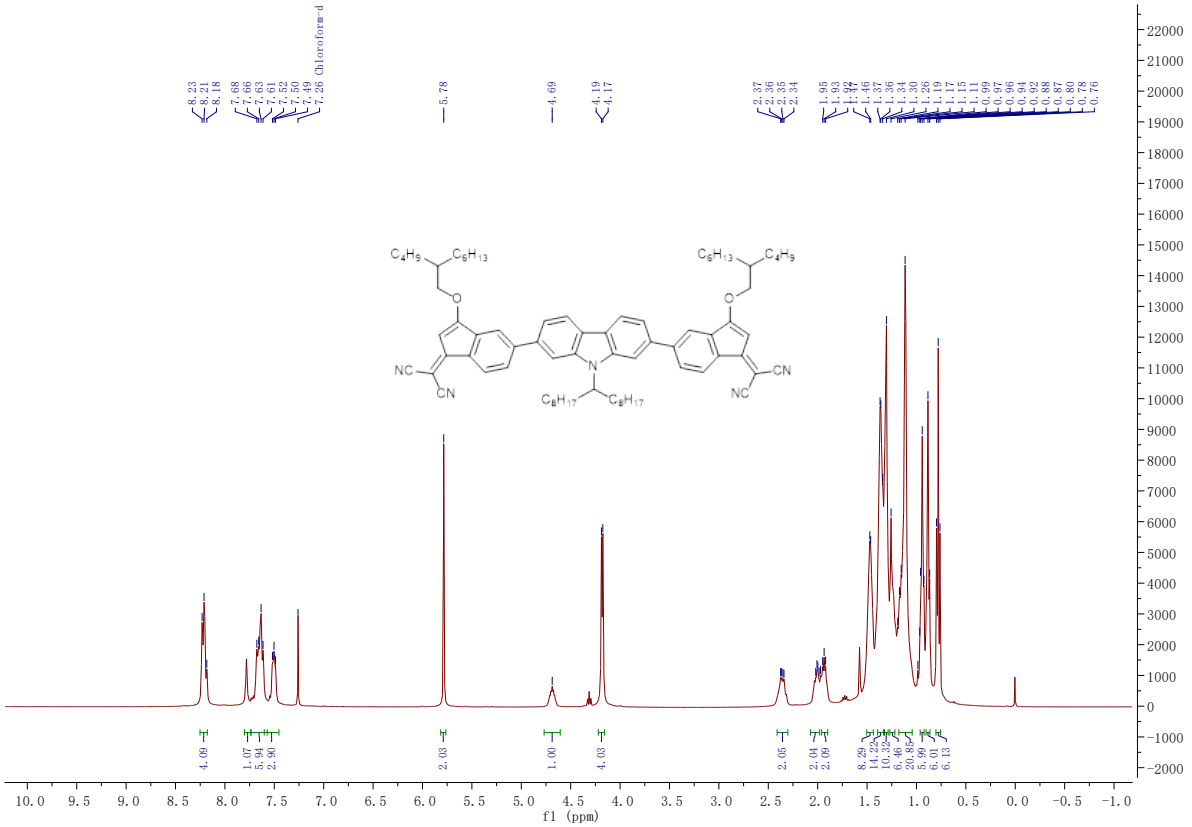


Figure S8 ^{1}H-NMR (400 MHz) of compound 10 in $CDCl_3$, 298 K.

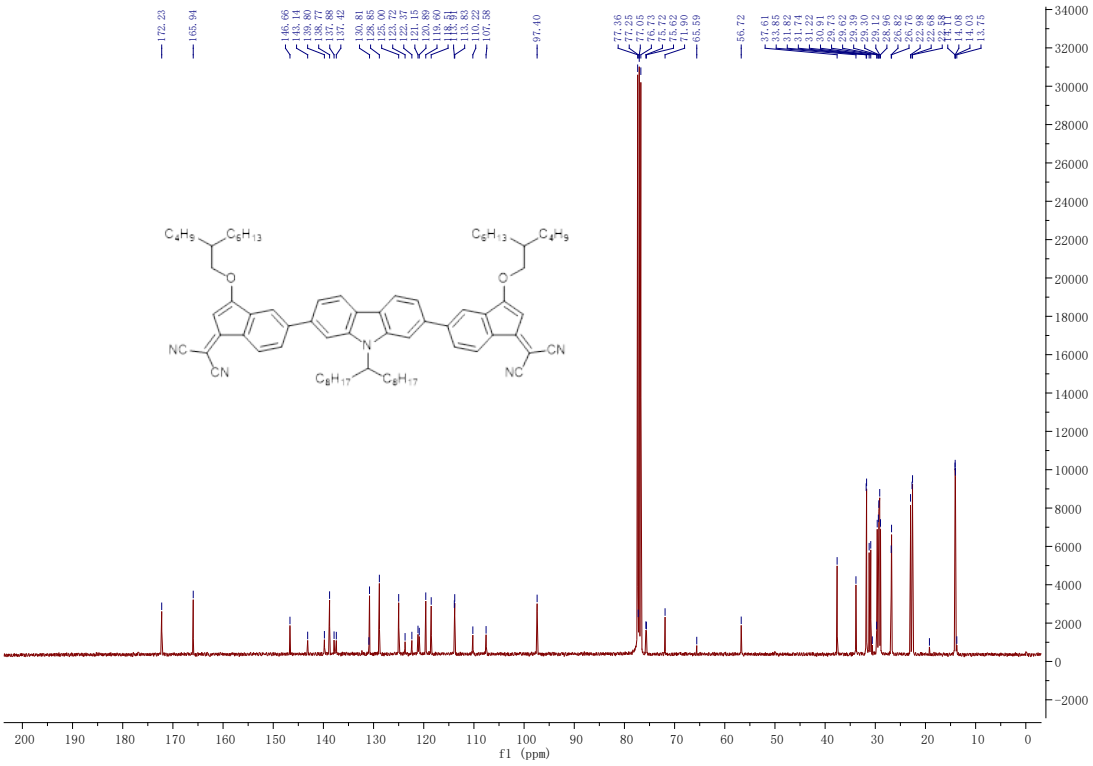


Figure S9 ^{13}C-NMR (101 MHz) of compound 10 in $CDCl_3$, 298 K

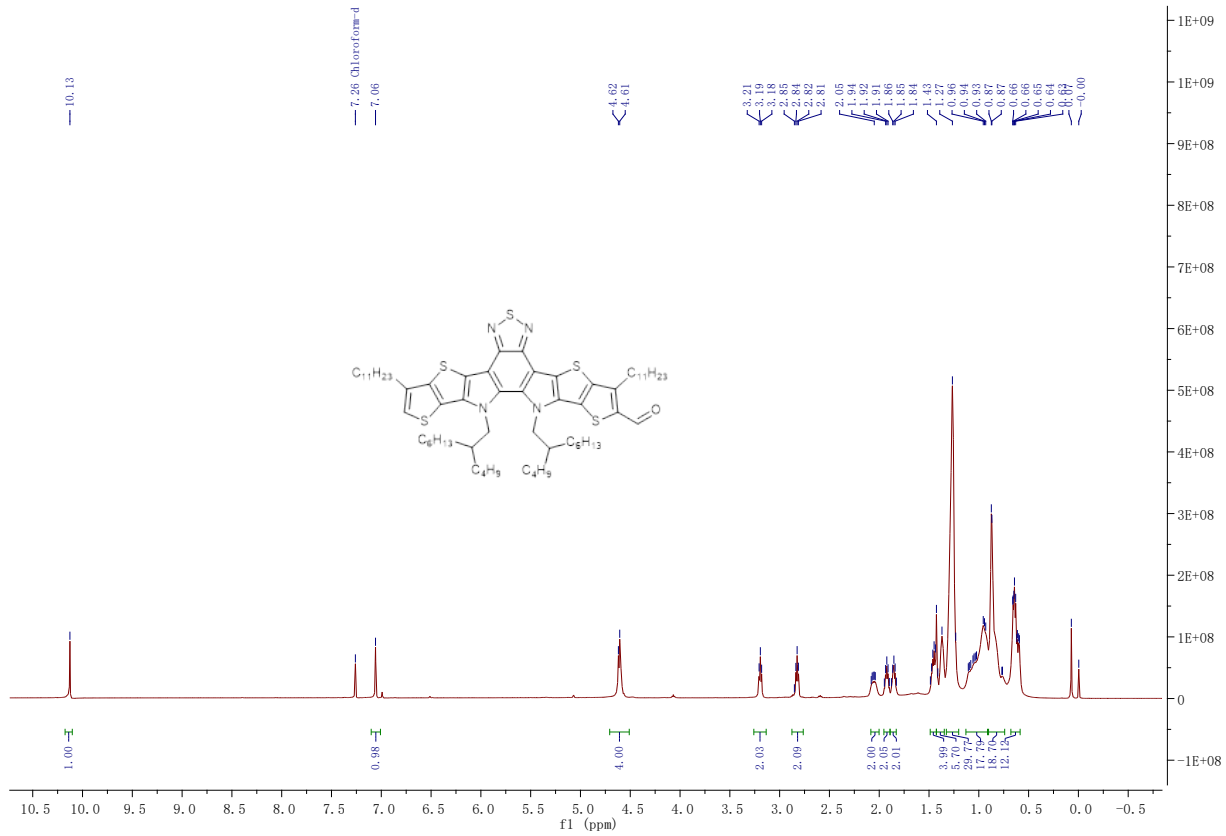


Figure S10 ^{1}H-NMR (600 MHz) of compound 12 in $CDCl_3$, 298 K.

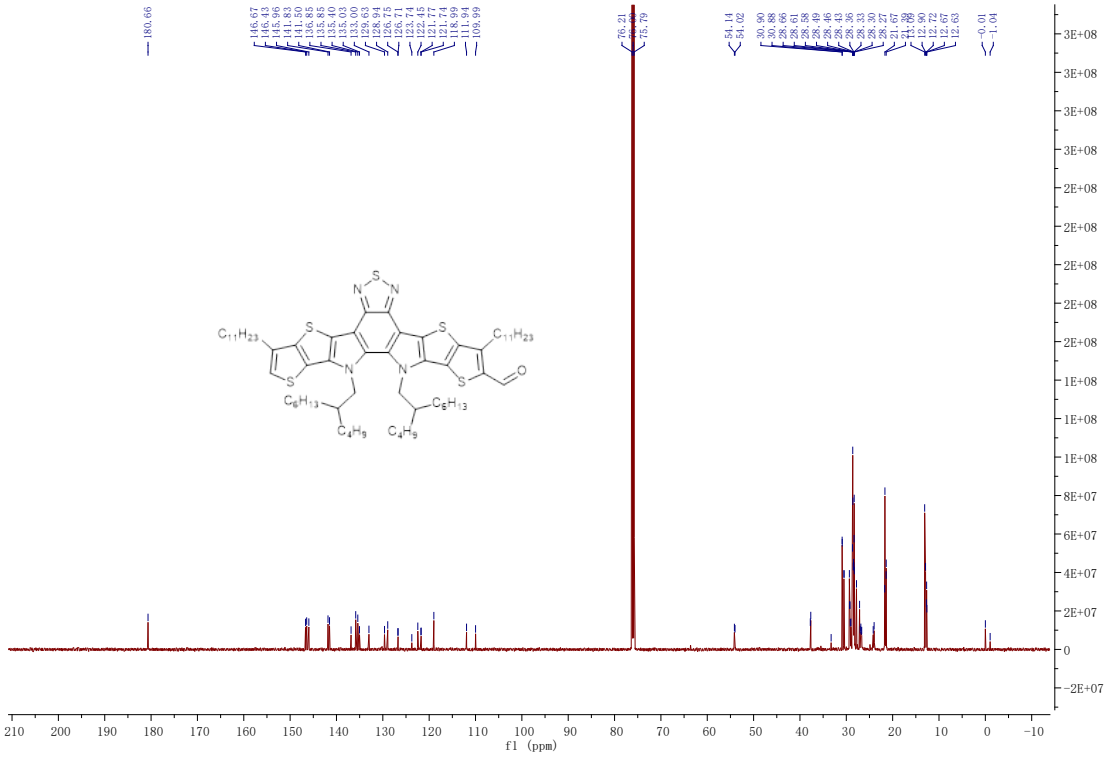


Figure S11 ^{13}C-NMR (151 MHz) of compound 12 in $CDCl_3$, 298 K.

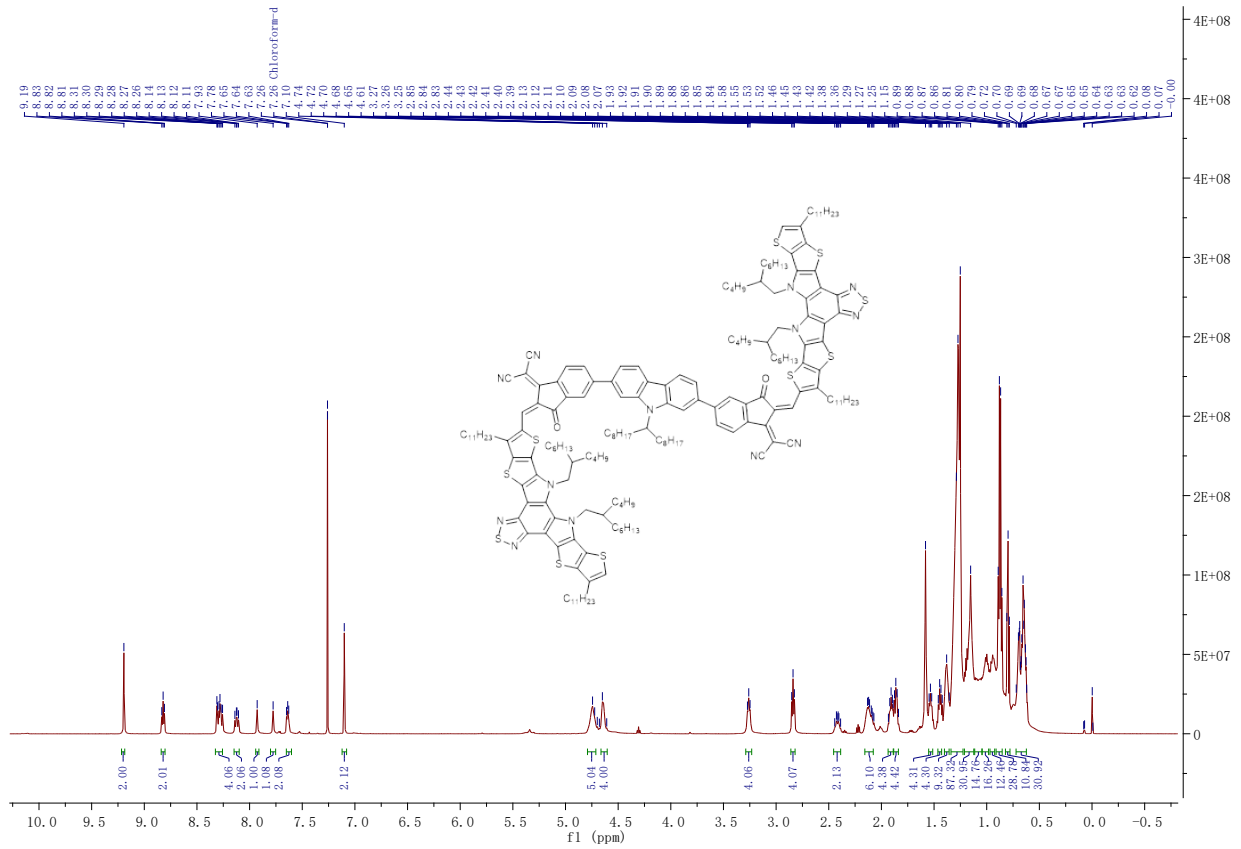


Figure S12 ^{1}H-NMR (600 MHz) of compound 13 in $CDCl_3$, 298 K.

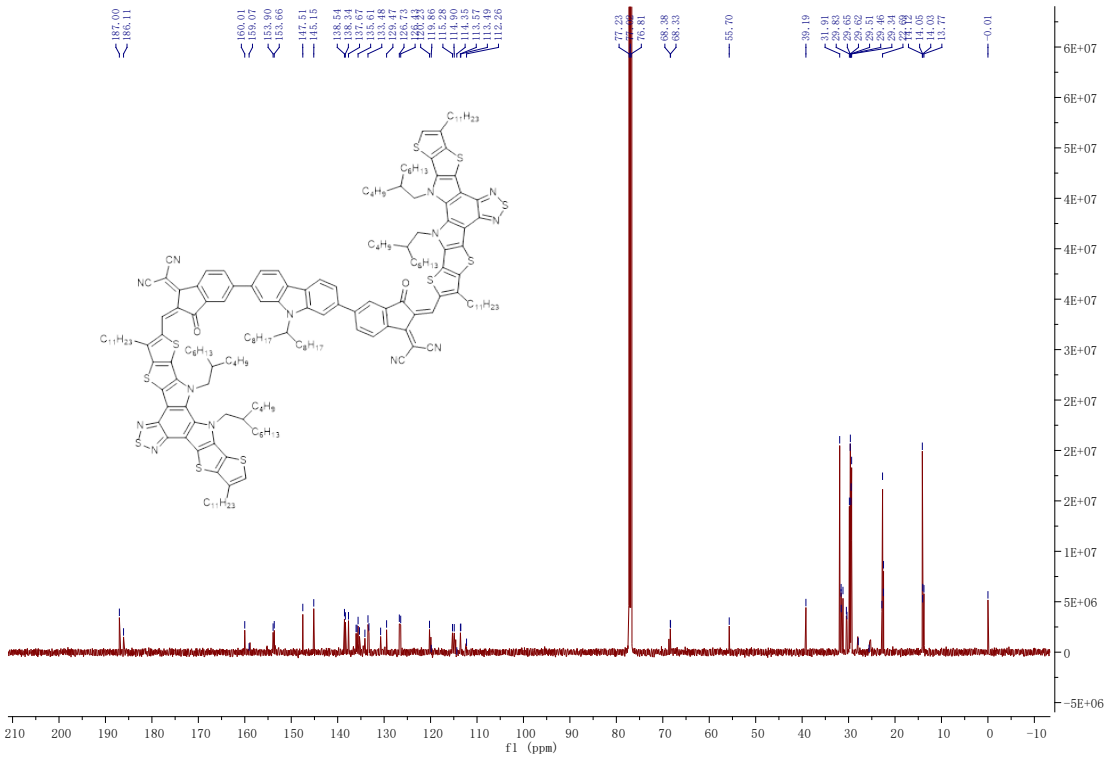


Figure S13 ^{13}C-NMR (151 MHz) of compound 13 in $CDCl_3$, 298 K.

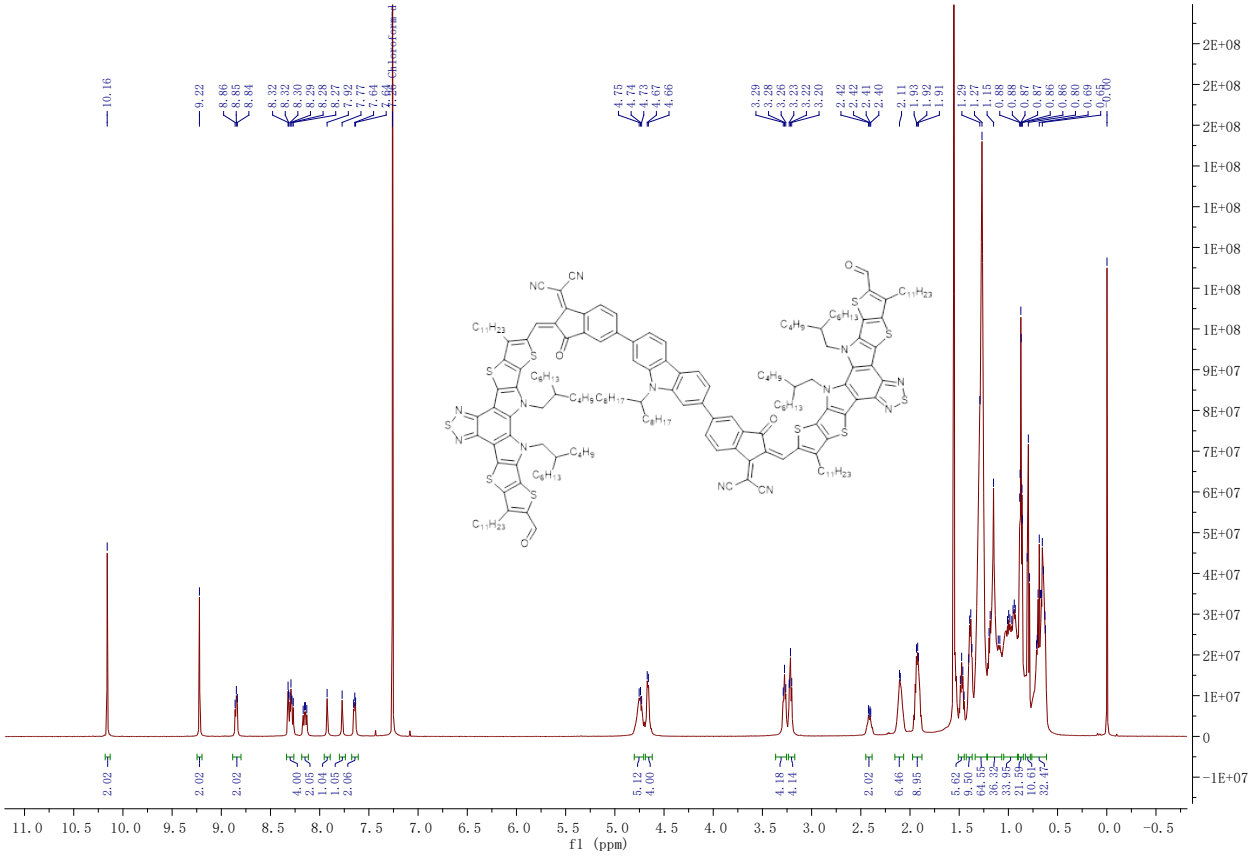


Figure S14 ^{1}H-NMR (600 MHz) of compound 14 in $CDCl_3$, 298 K.

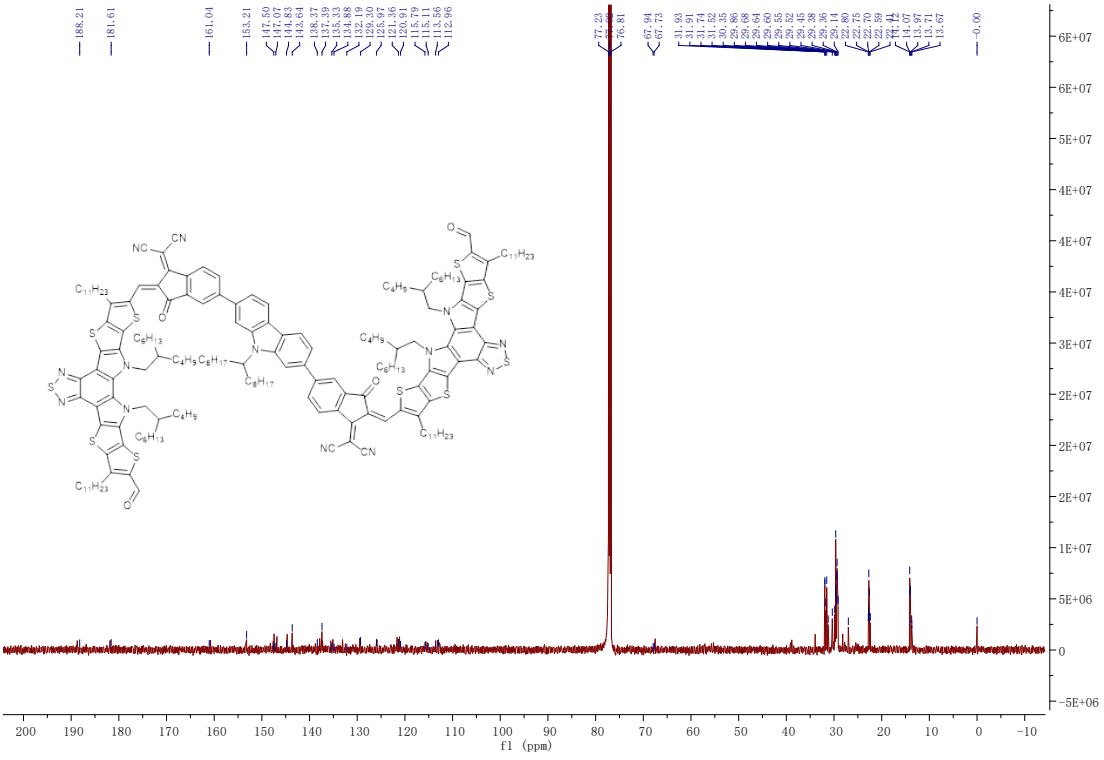


Figure S15 ^{13}C-NMR (151 MHz) of compound 14 in $CDCl_3$, 298 K.

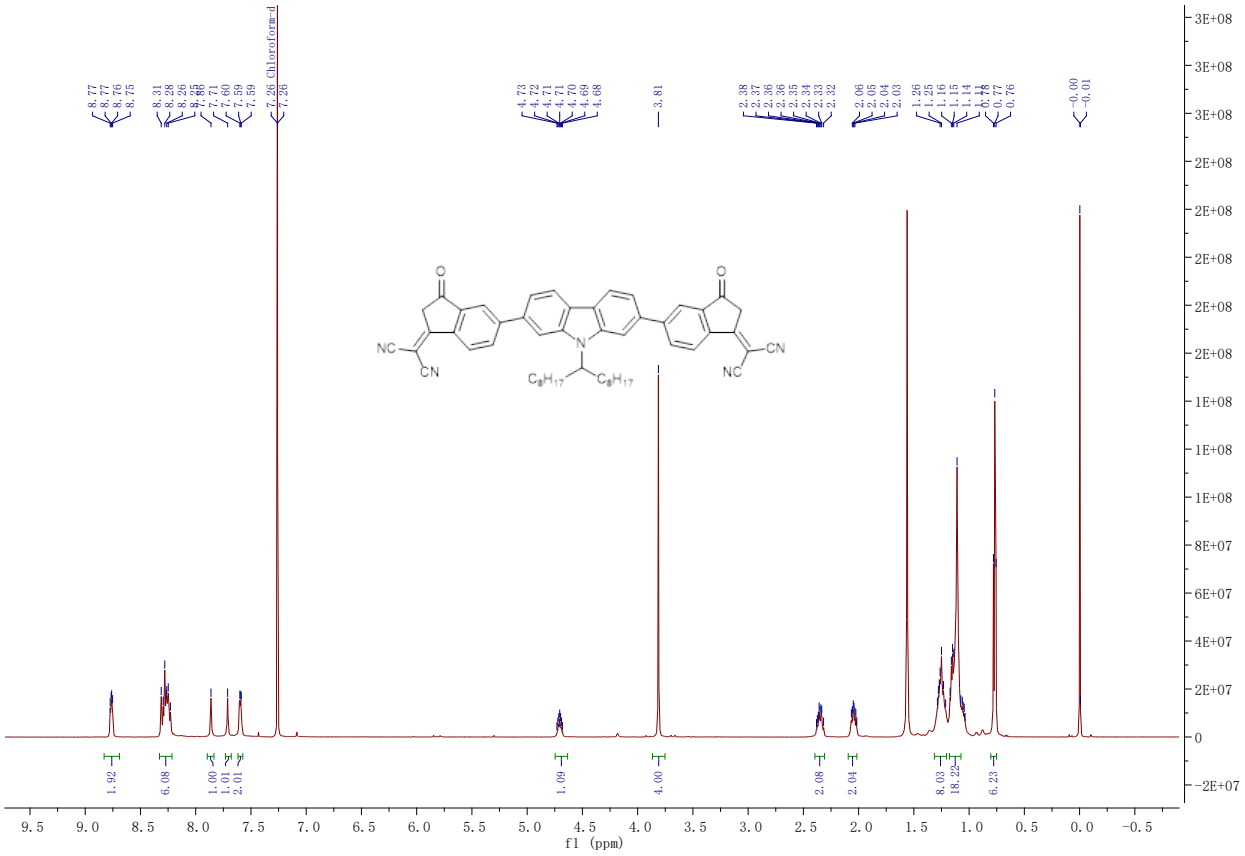


Figure 16 ^{1}H-NMR (600 MHz) of compound 7 in $CDCl_3$, 298 K.

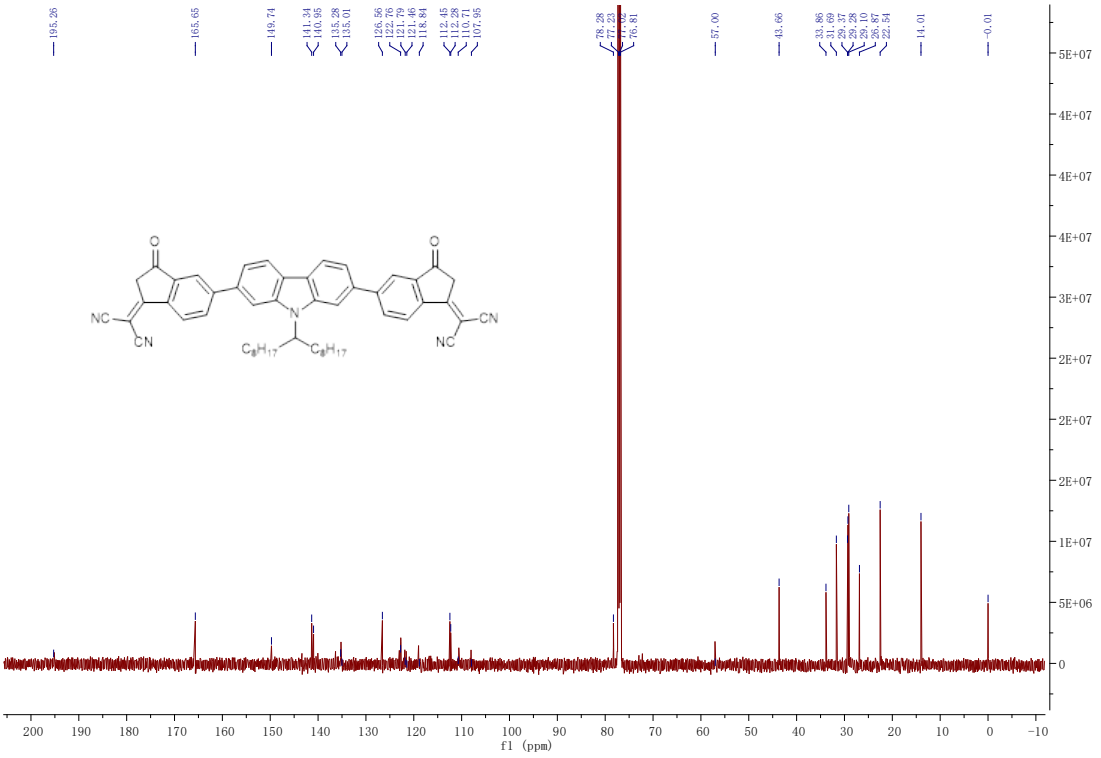


Figure 17 ^{13}C-NMR (151 MHz) of compound 7 in $CDCl_3$, 298 K.

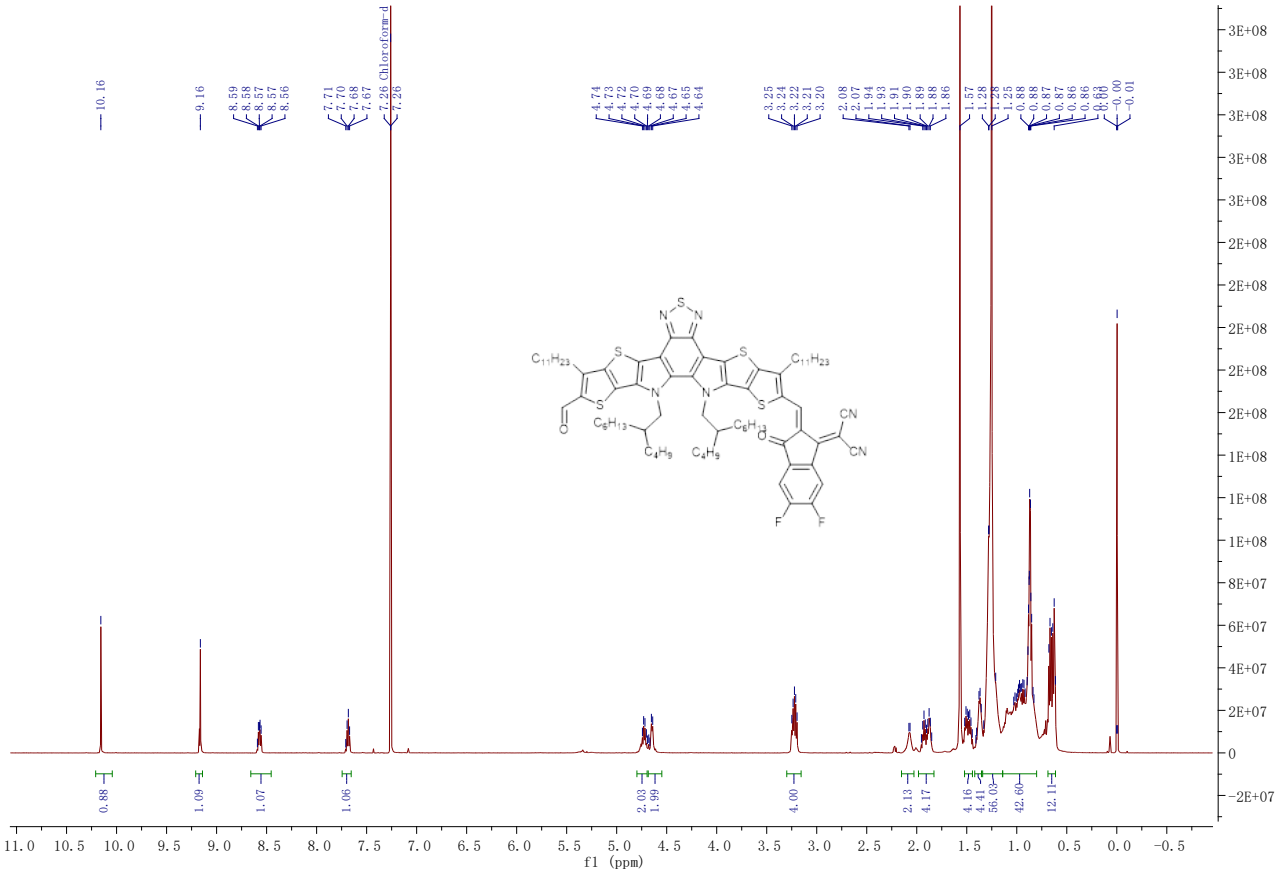


Figure S18 ^{1}H-NMR (600 MHz) of compound 16 in $CDCl_3$, 298 K

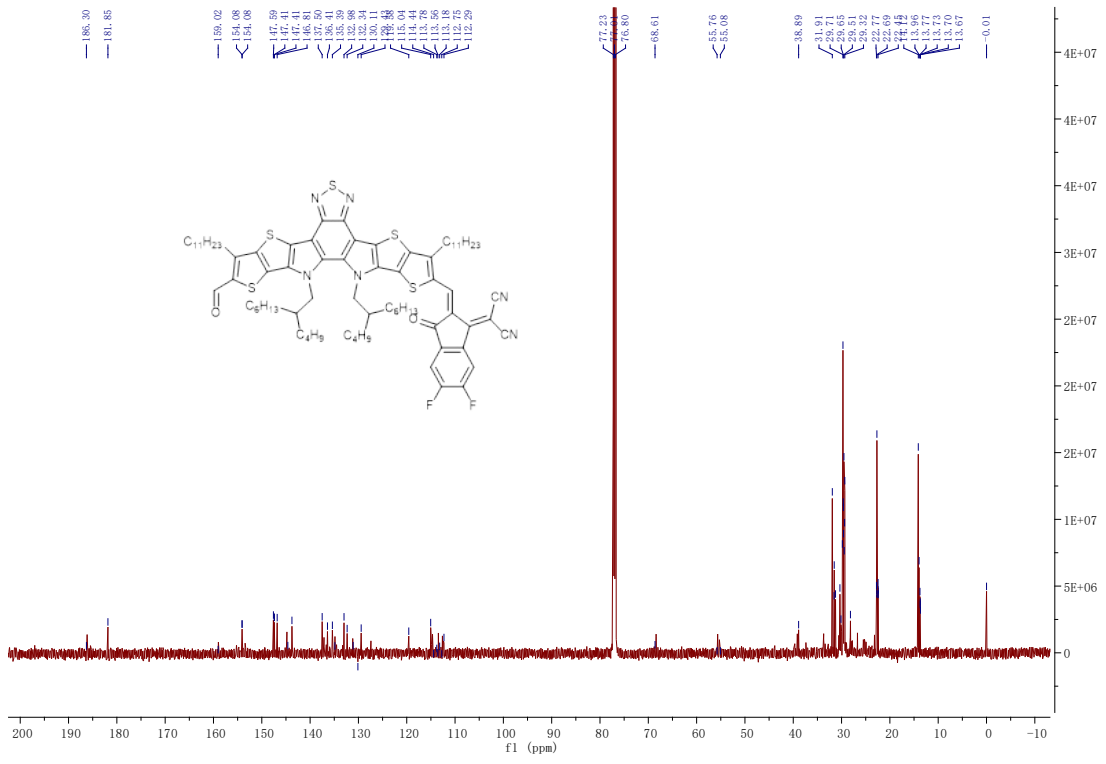


Figure S19 ^{13}C-NMR (151 MHz) of compound 16 in $CDCl_3$, 298 K.

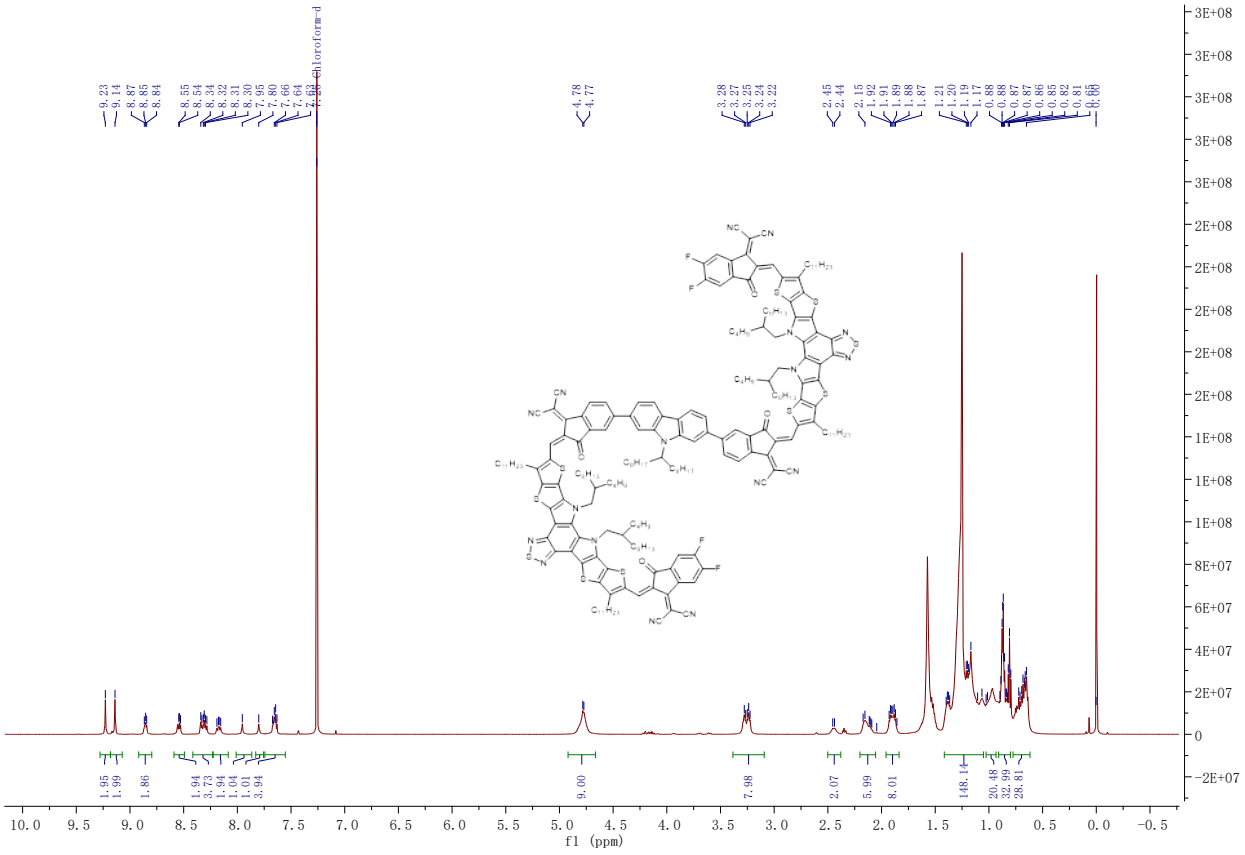


Figure S20 ^{1}H-NMR (600 MHz) of compound D2 in $CDCl_3$, 298 K

Mass Spectra

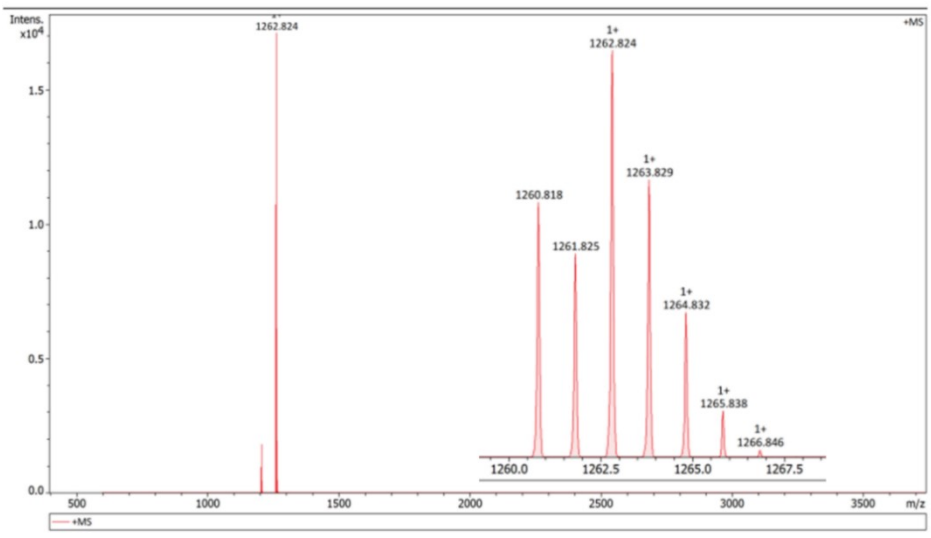


Figure S21 General mass spectrumof compound 1.

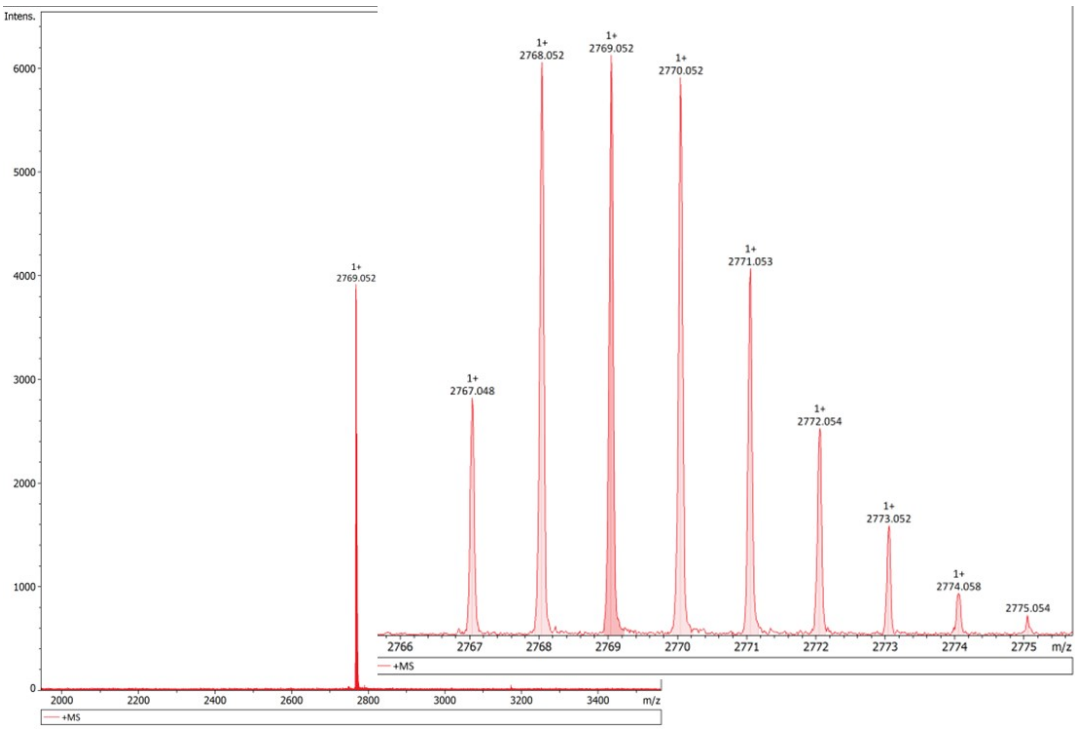


Figure S22 General mass spectrum of compound 3.

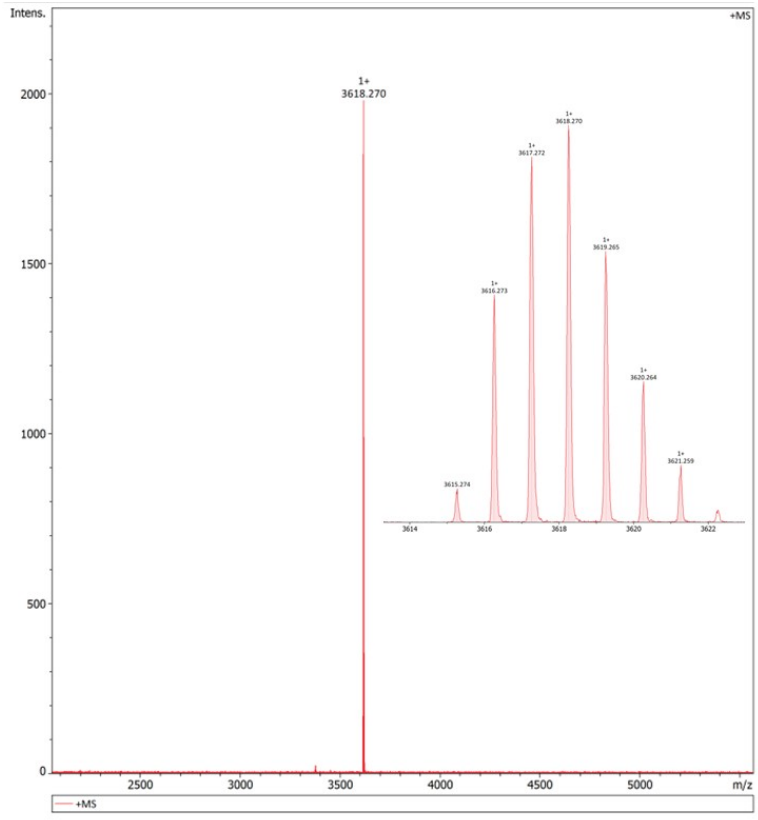


Figure S23 General mass spectrum of compound **D1**.

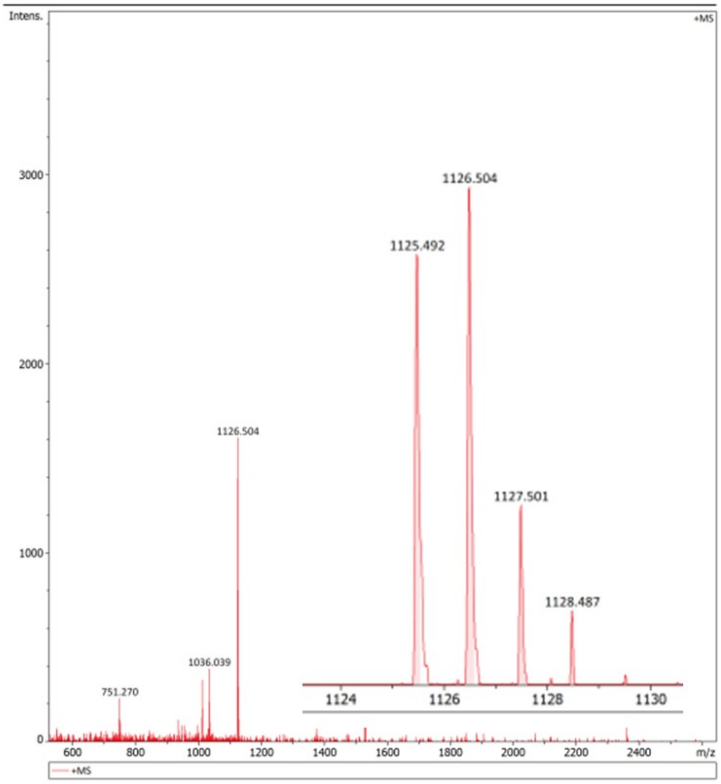


Figure S24 General mass spectrum of compound 10.

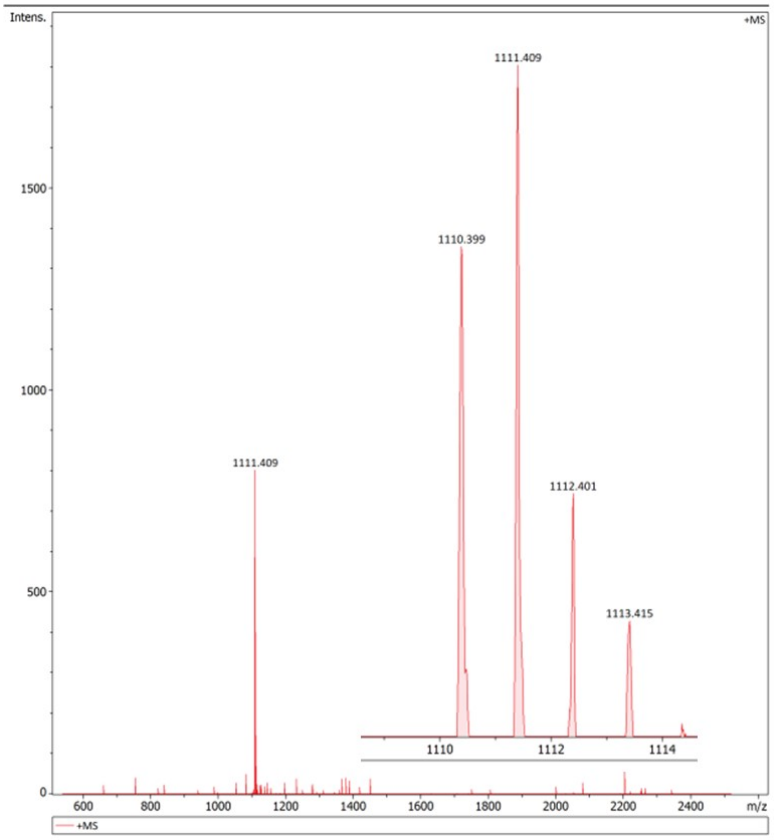


Figure S25 General mass spectrum of compound 12.

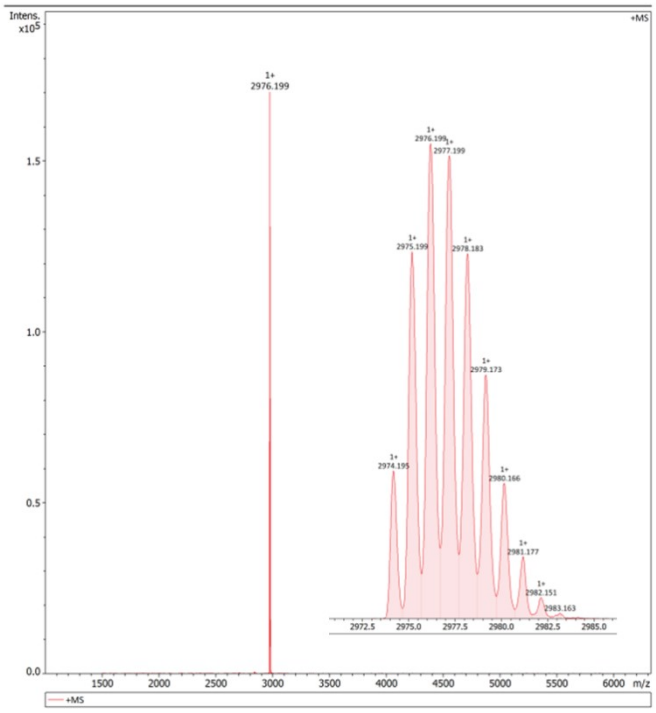


Figure S26 General mass spectrum of compound 13.

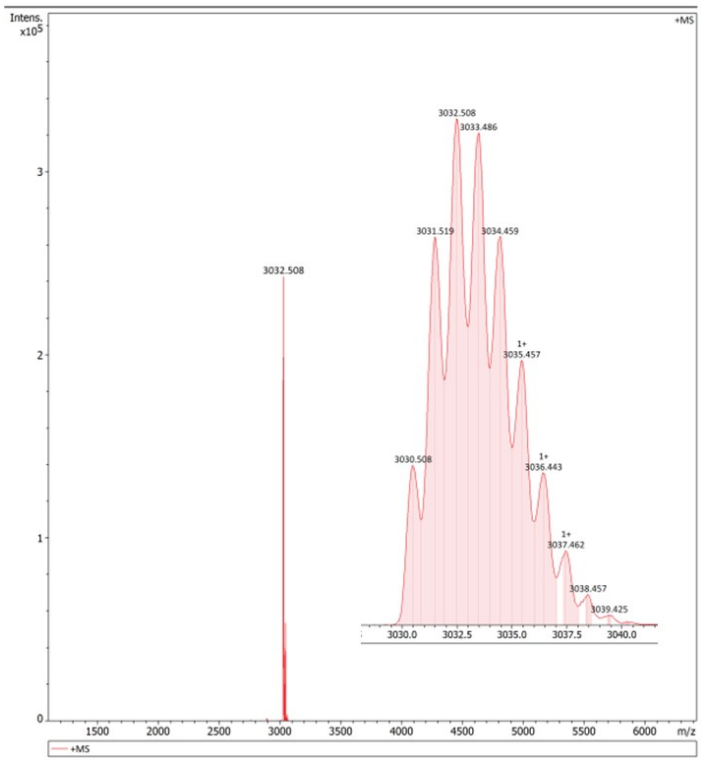


Figure S27 General mass spectrum of compound 14.

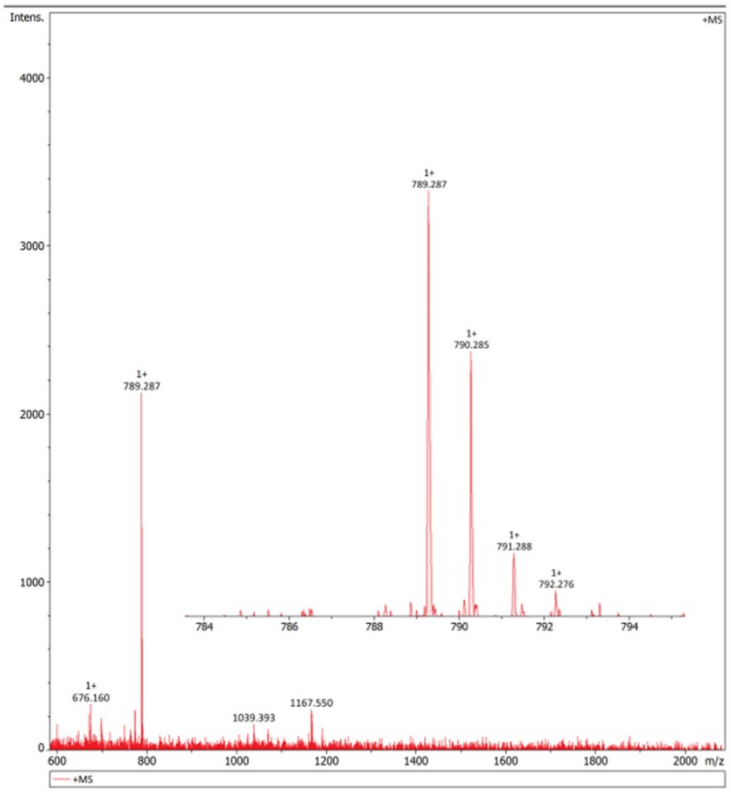


Figure S28 General mass spectrum of compound 7.

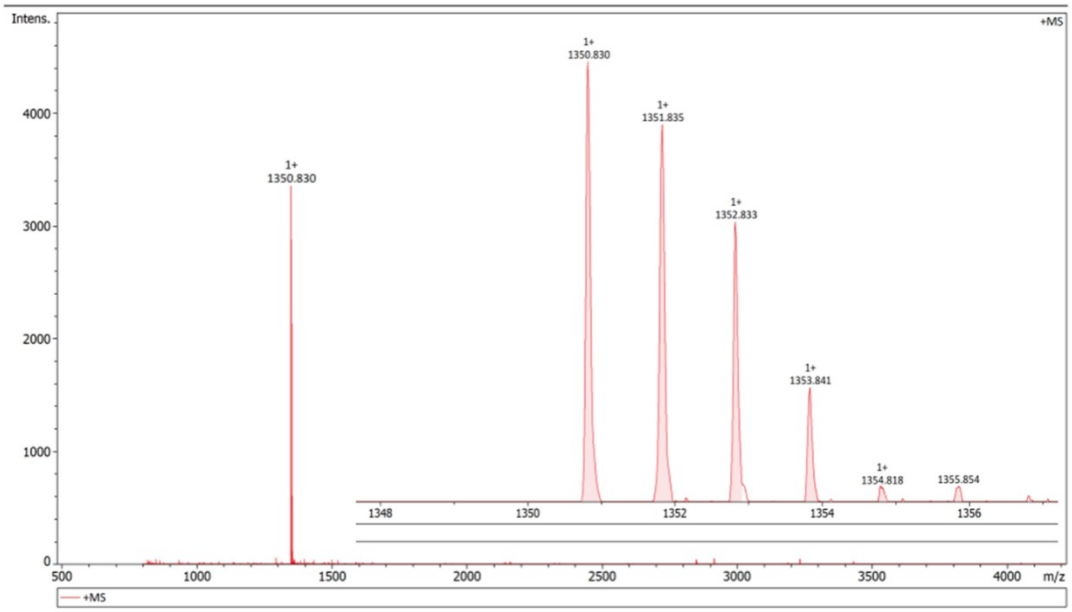


Figure S29 General mass spectrum of compound 16.

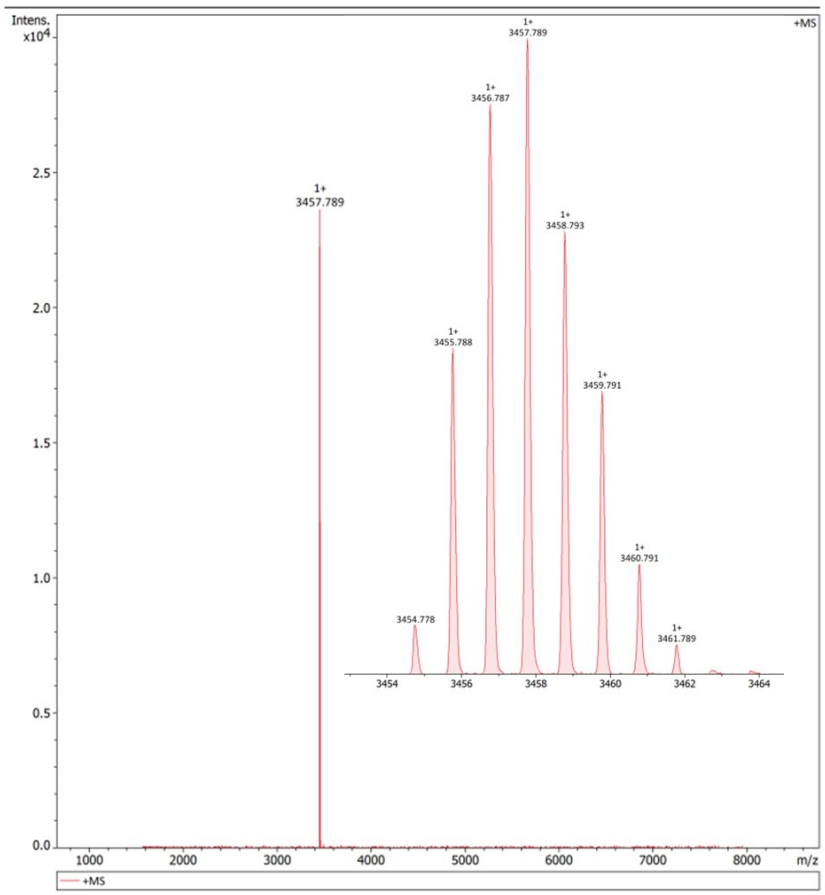


Figure S30 General mass spectrum of compound D2.

Computational Results

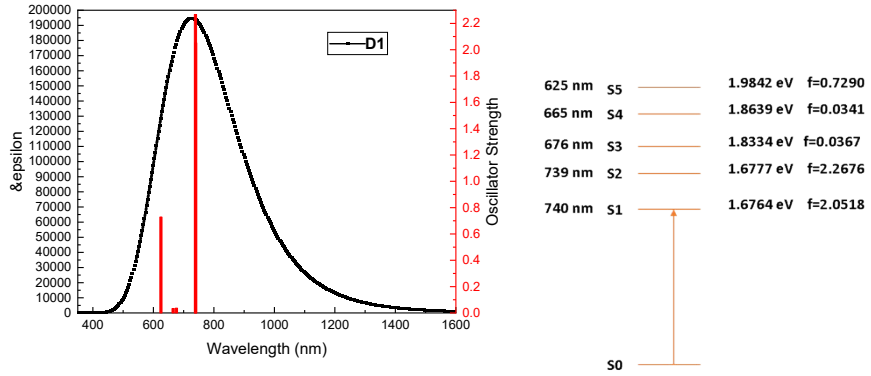


Figure S31 The calculated absorption spectrum and energy levels with oscillator strength (*f*) of D1.

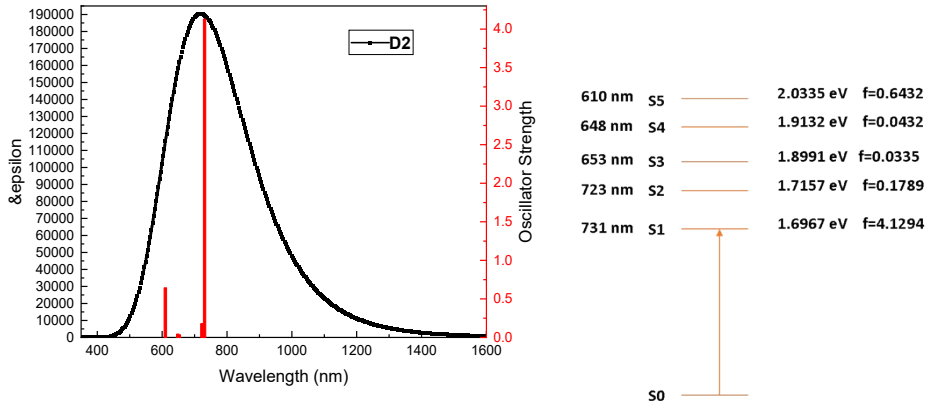


Figure S32 The calculated absorption spectrum and energy levels with oscillator strength (*f*) of D2.

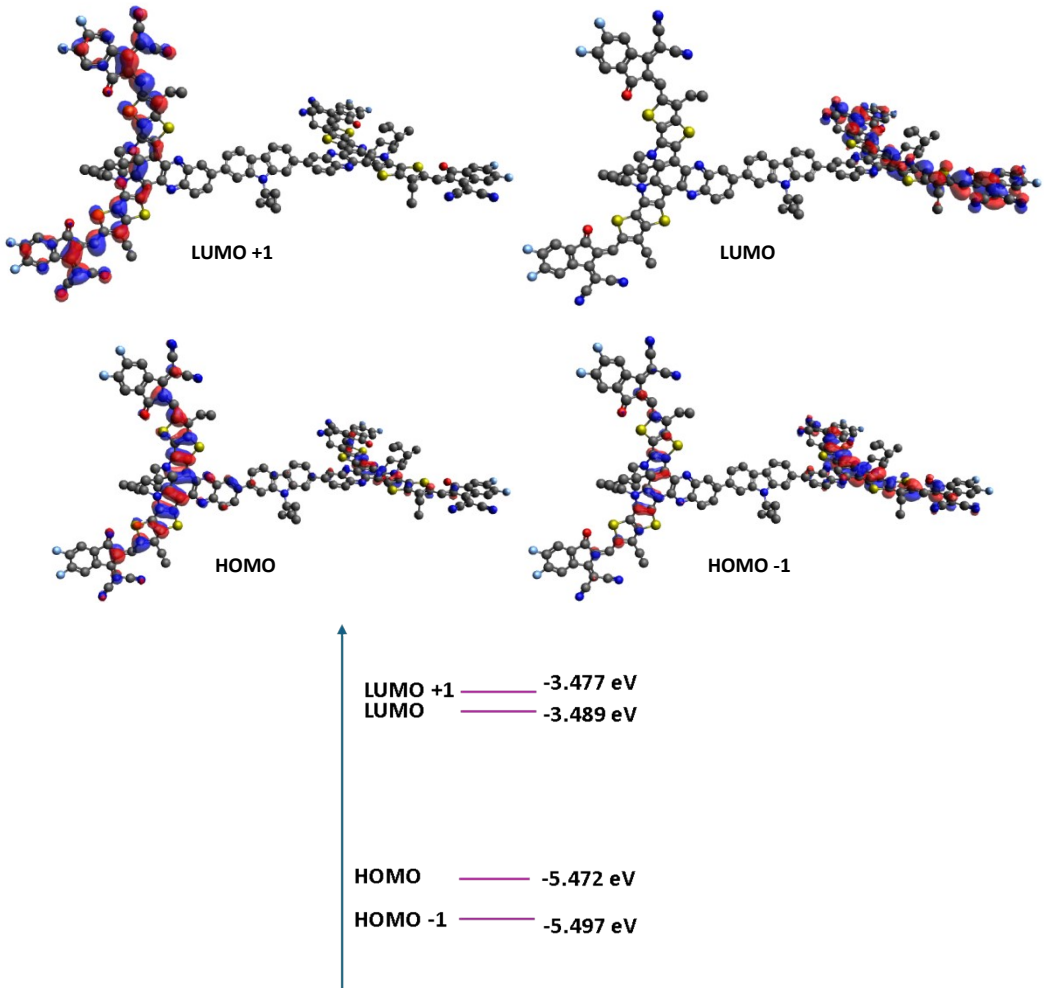


Figure S33 Calculated results of frontier molecular orbitals and correspongding orbital energy levels for D1.

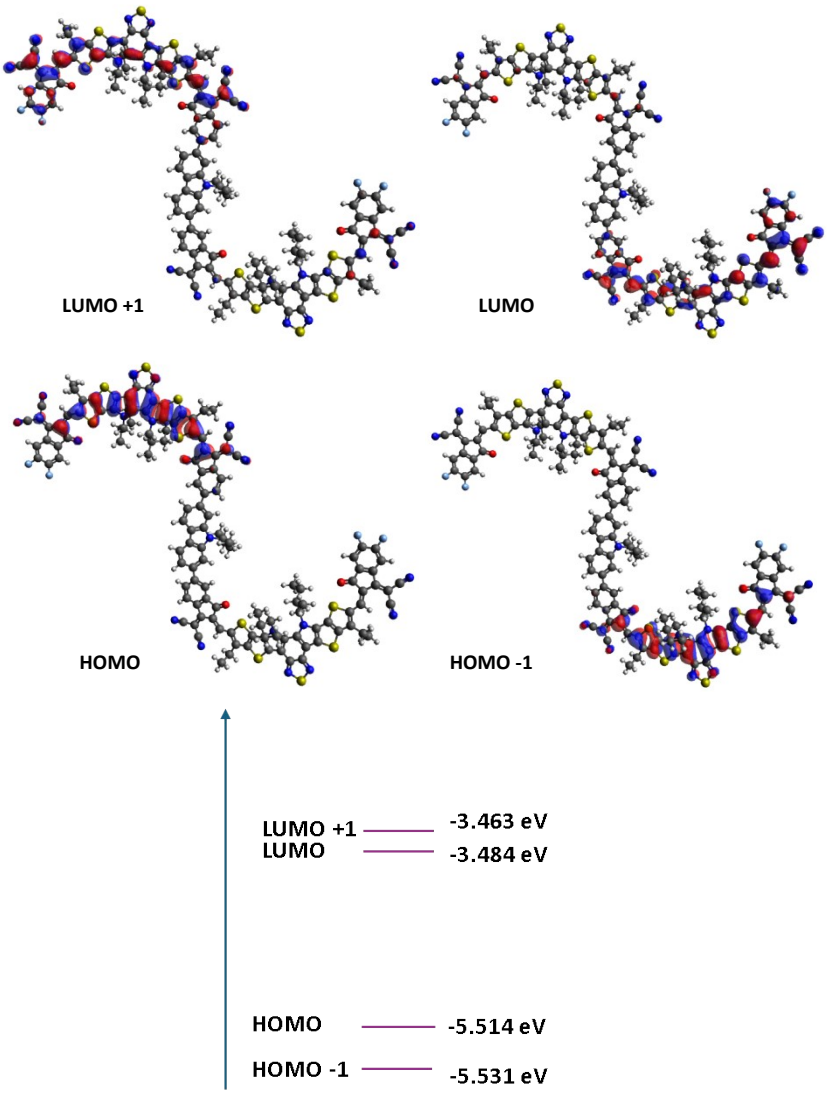


Figure S34 Calculated results of frontier molecular orbitals and correspongding energy levels for D2.

Thermogravimetric Analysis

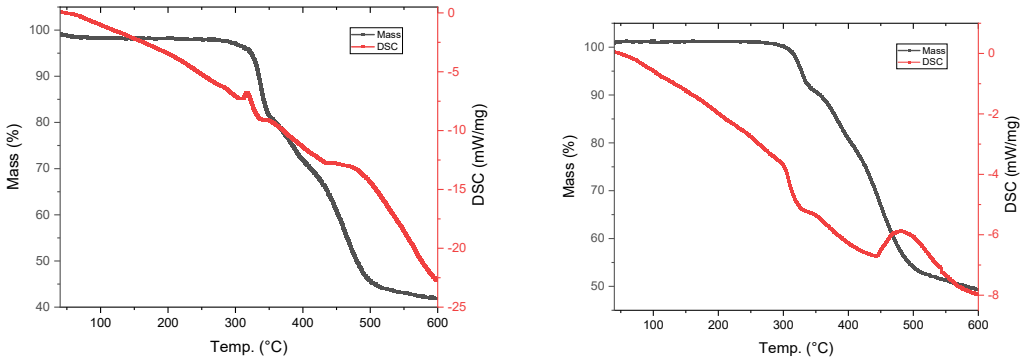


Figure S35 TGA results of D1 (left) and D2 (right).

Nonlinear Optical Absorption Analysis

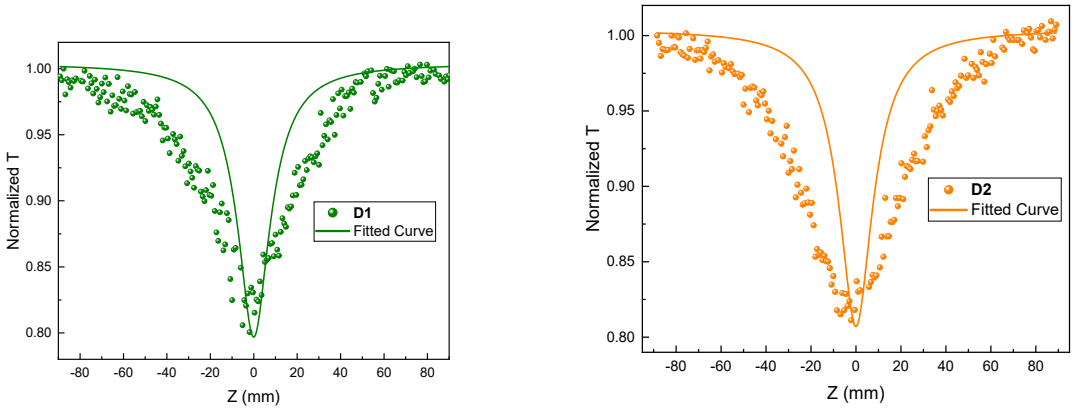


Figure S36 Nonlinear optical characterization of D1 (left) and D2 (right) in chloroform. Open-aperture Z-scan measured at an excitation wavelength of 532 nm, 75 μJ. The curve is the theoretical fit derived from the nonlinear propagation equation, incorporating an effective length L_{eff} of 0.162 cm for D1, and 0.168 cm for D2, to extract the nonlinear absorption coefficient, respectively.

Table S1 Optimization of Suzuki–Miyaura Coupling Conditions for Intermediate 3. All entries were heated up to reflux for ~36 hrs.

Entry	Solvent	Base	Catalyst/Ligand	Results
1	Toluene	Cs_2CO_3	$Pd_2(dba)_3$/ Xphos	Failed
2	Toluene	Cs_2CO_3	$Pd_2(dba)_3$/ Ruphos	Failed
3	Toluene	Cs_2CO_3	$Pd_2(dba)_3$/ Antphos	46 %
4	Toluene	Potassium acetate	$Pd_2(dba)_3$/ Antphos	Failed
5	Toluene	K_2CO_3	$Pd_2(dba)_3$/ Antphos	21 %
6	Toluene	Sodium tert-butoxide	$Pd_2(dba)_3$/ Antphos	78 %
7	Dioxane	Sodium tert-butoxide	$Pd_2(dba)_3$/ Antphos	52 %
8	THF	Sodium tert-butoxide	$Pd_2(dba)_3$/ Antphos	Trace

Optimized geometry data of compound D1

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	**3.37326**	**-0.73358**	**0.30118**
C	**2.40386**	**-1.73995**	**0.17678**
C	**1.06414**	**-1.37841**	**-0.00216**
C	**0.68132**	**-0.00851**	**-0.04945**
C	**1.65559**	**0.98889**	**0.08075**
C	**2.98402**	**0.62688**	**0.25233**
N	**-0.06934**	**-2.17555**	**-0.16036**
C	**-1.17363**	**-1.33545**	**-0.29874**
C	**-0.74702**	**0.01847**	**-0.23415**
C	**-2.52298**	**-1.65768**	**-0.46992**
C	**-3.46232**	**-0.62158**	**-0.57864**
C	**-3.03037**	**0.72618**	**-0.51858**
C	**-1.69101**	**1.04683**	**-0.34854**
C	**-0.13057**	**-3.64846**	**-0.17452**
C	**0.64038**	**-4.25149**	**-1.3665**
C	**0.25736**	**-4.23476**	**1.20077**
C	**9.74151**	**-1.43695**	**0.50079**
C	**9.39697**	**-0.27389**	**-0.28212**

C	11.13366	-1.71135	0.71862
C	12.17195	-0.90322	0.17267
C	11.8271	0.11043	-0.76983
C	10.46597	0.44979	-0.91424
C	11.76987	-2.66532	1.53542
C	13.1461	-2.39767	1.51543
N	13.39267	-1.30035	0.70188
N	12.63007	0.87962	-1.63778
C	11.73853	1.78159	-2.26426
C	10.43172	1.52234	-1.82982
S	11.33427	-4.02876	2.53276
C	13.05041	-4.24725	2.9261
C	13.88756	-3.29781	2.30921
C	13.71692	-5.18403	3.72175
C	15.12102	-4.95835	3.71934
S	15.55685	-3.55733	2.69451
C	11.78472	2.91167	-3.12027
C	10.49953	3.45729	-3.32837
S	9.22168	2.59683	-2.46148
S	12.9986	3.86666	-3.9188
C	11.75538	4.97385	-4.56425
C	10.45488	4.59613	-4.13704
C	13.00163	-6.30855	4.43
C	9.17372	5.33434	-4.43948
C	14.61123	-0.48113	0.82376
C	13.63288	0.1126	-2.45355
C	14.84874	0.1746	2.205
C	14.63265	0.94099	-3.27032
C	16.25654	0.79661	2.18521
C	13.78668	1.23424	2.58858
C	15.56556	1.84361	-2.42843
C	15.40067	-0.00903	-4.20656
N	8.13546	0.09674	-0.475
C	7.17702	-0.6746	0.09539
C	7.52233	-1.84333	0.86156
N	8.81019	-2.20734	1.0569
C	5.81185	-0.33085	-0.07647
C	4.80098	-1.09587	0.47993
C	5.16389	-2.2561	1.24012
C	6.47326	-2.61956	1.42561
C	11.96221	6.08208	-5.41424
C	16.0007	-5.77066	4.46719
C	-9.46718	0.02501	0.02944
C	-9.84914	-1.12616	-0.75029

C	**-10.51069**	**0.78136**	**0.66642**
C	**-11.89566**	**0.47812**	**0.53175**
C	**-12.27053**	**-0.5225**	**-0.42243**
C	**-11.24995**	**-1.3599**	**-0.95955**
C	**-10.42094**	**1.83338**	**1.59552**
C	**-11.71553**	**2.11544**	**2.04561**
N	**-12.62969**	**1.2806**	**1.41119**
N	**-13.49995**	**-0.91103**	**-0.94556**
C	**-13.27374**	**-2.0305**	**-1.73588**
C	**-11.903**	**-2.31755**	**-1.75712**
S	**-9.18385**	**2.81307**	**2.33777**
C	**-10.44627**	**3.62723**	**3.28135**
C	**-11.74108**	**3.14132**	**3.01496**
C	**-10.39107**	**4.66292**	**4.21879**
C	**-11.68691**	**4.99276**	**4.70261**
S	**-12.94639**	**3.97271**	**3.94323**
C	**-14.03258**	**-2.94129**	**-2.50086**
C	**-13.21143**	**-3.91666**	**-3.09952**
S	**-11.48995**	**-3.70949**	**-2.72359**
S	**-15.70848**	**-3.19573**	**-2.86187**
C	**-15.29667**	**-4.6269**	**-3.85473**
C	**-13.89463**	**-4.86645**	**-3.8643**
C	**-9.0927**	**5.28531**	**4.67119**
C	**-13.1976**	**-6.01623**	**-4.5499**
C	**-13.91488**	**0.9562**	**2.07348**
C	**-14.71377**	**-0.08932**	**-1.09143**
C	**-13.95266**	**-0.43**	**2.74875**
C	**-14.98305**	**0.49652**	**-2.49778**
C	**-12.81646**	**-0.59787**	**3.76789**
C	**-15.32379**	**-0.65758**	**3.42302**
C	**-13.93927**	**1.54172**	**-2.95816**
C	**-16.39247**	**1.11522**	**-2.46527**
N	**-8.94597**	**-1.92624**	**-1.30927**
C	**-7.64576**	**-1.60161**	**-1.12081**
C	**-7.26209**	**-0.44417**	**-0.35708**
N	**-8.19463**	**0.35699**	**0.21733**
C	**-6.6241**	**-2.40896**	**-1.6903**
C	**-5.30301**	**-2.08568**	**-1.51149**
C	**-4.90156**	**-0.93844**	**-0.75192**
C	**-5.88655**	**-0.14295**	**-0.19075**
C	**-16.19107**	**-5.44757**	**-4.5745**
C	**-11.88288**	**6.0209**	**5.64915**
C	**13.07743**	**6.69399**	**-5.96821**
C	**13.06836**	**7.84622**	**-6.86807**

C	14.48479	8.20228	-7.14807
C	15.31895	7.29324	-6.47594
C	14.48747	6.32272	-5.72969
C	15.06207	9.21929	-7.91746
C	16.44886	9.27807	-7.97878
C	17.26454	8.36058	-7.30379
C	16.70515	7.34886	-6.53749
C	11.97964	8.5121	-7.41328
O	14.92116	5.40002	-5.04582
F	17.04319	10.2369	-8.70226
F	18.59321	8.48532	-7.41572
C	17.37543	-5.81351	4.64869
C	18.10313	-6.75291	5.5009
C	19.5533	-6.4636	5.34279
C	19.70337	-5.38418	4.456
C	18.36963	-4.93603	3.99808
C	20.69399	-7.05465	5.89875
C	21.93248	-6.5362	5.54148
C	22.06215	-5.45719	4.65728
C	20.94011	-4.86312	4.09891
C	17.59624	-7.73867	6.33576
O	18.16439	-4.00872	3.22
F	23.05041	-7.07318	6.04911
F	23.29239	-5.0163	4.36517
C	-17.56836	-5.4818	-4.74116
C	-18.31274	-6.43196	-5.56588
C	-19.75902	-6.12978	-5.39543
C	-19.89062	-5.03195	-4.52857
C	-18.54799	-4.58397	-4.09677
C	-20.91052	-6.72385	-5.92514
C	-22.14099	-6.19008	-5.56252
C	-22.25226	-5.09309	-4.69831
C	-21.11924	-4.4956	-4.16625
C	-17.82296	-7.43631	-6.389
O	-18.3268	-3.64228	-3.34049
F	-23.26881	-6.72948	-6.04526
F	-23.47581	-4.63822	-4.39915
C	-12.98708	6.55612	6.29731
C	-12.97215	7.6624	7.25296
C	-14.37107	7.8705	7.71307
C	-15.20244	6.94551	7.05958
C	-14.38586	6.10325	6.15767
C	-14.93568	8.77428	8.62073
C	-16.30744	8.70956	8.83188

C	-17.12063	7.78024	8.17025
C	-16.57373	6.8795	7.26842
C	-11.89437	8.42406	7.68226
O	-14.82199	5.20488	5.44321
F	-16.88899	9.55566	9.69322
F	-18.43447	7.78336	8.42967
C	8.89627	6.48342	-3.44927
C	-13.1369	-7.28518	-3.67589
C	12.93216	-7.59757	3.58651
C	-8.50102	4.59569	5.9169
C	-0.09157	-5.71928	1.36032
C	0.18563	-3.72136	-2.7298
C	-16.52524	-0.75452	2.47464
C	-12.69046	0.98251	-3.65137
C	16.79268	1.15638	-1.81312
C	12.56156	0.7047	3.34451
C	16.20801	-8.01592	6.5164
N	15.08977	-8.28734	6.70476
C	12.09906	9.62951	-8.29391
N	12.14066	10.54431	-9.015
C	10.61513	8.16492	-7.18029
N	9.4836	7.9282	-7.02788
C	18.41514	-8.59661	7.13066
N	19.03685	-9.32207	7.79826
C	-18.6575	-8.30359	-7.15693
N	-19.29254	-9.03735	-7.8026
C	-16.43894	-7.72505	-6.58313
N	-15.3249	-8.00654	-6.78149
C	-12.0083	9.49139	8.62373
N	-12.04559	10.37059	9.38803
C	-10.54862	8.24925	7.24082
N	-9.43233	8.15365	6.91763
H	2.70666	-2.77907	0.1923
H	1.37417	2.03823	0.05795
H	3.73581	1.39872	0.3821
H	-2.85669	-2.68918	-0.48755
H	-3.75882	1.52183	-0.63692
H	-1.37886	2.08712	-0.31376
H	-1.18768	-3.88399	-0.33131
H	0.49675	-5.33763	-1.33447
H	1.71675	-4.08351	-1.24532
H	-0.27112	-3.65512	1.96737
H	1.32793	-4.08856	1.38618
H	11.98362	-5.97442	4.66247

H	**13.47281**	**-6.52922**	**5.39241**
H	**8.34538**	**4.61713**	**-4.40122**
H	**9.18213**	**5.72874**	**-5.46018**
H	**14.55131**	**0.30575**	**0.07265**
H	**15.46251**	**-1.12178**	**0.56857**
H	**14.16069**	**-0.55196**	**-1.76806**
H	**13.06367**	**-0.5286**	**-3.13895**
H	**14.84627**	**-0.61495**	**2.96818**
H	**14.04786**	**1.5942**	**-3.92475**
H	**16.50716**	**1.19655**	**3.17302**
H	**17.02361**	**0.06125**	**1.91659**
H	**16.31475**	**1.62418**	**1.46717**
H	**13.46836**	**1.7754**	**1.68619**
H	**14.27562**	**1.98311**	**3.22456**
H	**15.91671**	**2.65881**	**-3.07353**
H	**14.97549**	**2.32455**	**-1.63672**
H	**16.12201**	**0.55176**	**-4.81055**
H	**14.71653**	**-0.52064**	**-4.89274**
H	**15.95319**	**-0.77534**	**-3.65118**
H	**5.59003**	**0.54099**	**-0.68325**
H	**4.37842**	**-2.84488**	**1.70347**
H	**6.74194**	**-3.49205**	**2.01314**
H	**11.01856**	**6.54301**	**-5.676**
H	**15.45045**	**-6.52708**	**5.01166**
H	**-8.37408**	**5.21721**	**3.84595**
H	**-9.21892**	**6.35316**	**4.87296**
H	**-12.17753**	**-5.69987**	**-4.79766**
H	**-13.67848**	**-6.2545**	**-5.50333**
H	**-14.73505**	**1.06871**	**1.36692**
H	**-14.06296**	**1.72907**	**2.83211**
H	**-15.56637**	**-0.70037**	**-0.77594**
H	**-14.62984**	**0.74082**	**-0.39524**
H	**-13.83277**	**-1.19284**	**1.96637**
H	**-14.9978**	**-0.32577**	**-3.22481**
H	**-12.85825**	**-1.59488**	**4.21963**
H	**-11.82935**	**-0.48518**	**3.30825**
H	**-12.90035**	**0.13878**	**4.57677**
H	**-15.25516**	**-1.59012**	**3.99737**
H	**-15.49661**	**0.13874**	**4.16123**
H	**-14.43793**	**2.22054**	**-3.6618**
H	**-13.64708**	**2.16622**	**-2.1015**
H	**-16.66921**	**1.48314**	**-3.45839**
H	**-17.14942**	**0.38606**	**-2.15448**
H	**-16.43613**	**1.96506**	**-1.77205**

H	**-6.92216**	**-3.27248**	**-2.27697**
H	**-4.53822**	**-2.69719**	**-1.97982**
H	**-5.63564**	**0.72125**	**0.41565**
H	**-15.65354**	**-6.22159**	**-5.10685**
H	**-10.93918**	**6.48106**	**5.91179**
H	**14.49628**	**9.96119**	**-8.46364**
H	**17.33024**	**6.63554**	**-6.01128**
H	**20.67036**	**-7.8889**	**6.58598**
H	**21.03261**	**-4.02803**	**3.4129**
H	**-20.90111**	**-7.57166**	**-6.59593**
H	**-21.19753**	**-3.6465**	**-3.49586**
H	**-14.37097**	**9.51705**	**9.16681**
H	**-17.19681**	**6.15724**	**6.75214**
H	**7.94093**	**6.96052**	**-3.68963**
H	**9.67995**	**7.24616**	**-3.4988**
H	**8.84652**	**6.11441**	**-2.41958**
H	**-12.58852**	**-8.07368**	**-4.20087**
H	**-14.14086**	**-7.65993**	**-3.45218**
H	**-12.62896**	**-7.08682**	**-2.7264**
H	**12.37095**	**-8.36666**	**4.12648**
H	**13.93323**	**-7.98918**	**3.37941**
H	**12.43325**	**-7.41649**	**2.62881**
H	**-7.54307**	**5.05608**	**6.17822**
H	**-9.17044**	**4.69175**	**6.77771**
H	**-8.33183**	**3.52933**	**5.73495**
H	**0.11387**	**-6.04994**	**2.38407**
H	**0.49081**	**-6.35676**	**0.68681**
H	**-1.15464**	**-5.90156**	**1.15977**
H	**0.73376**	**-4.21744**	**-3.53799**
H	**0.35884**	**-2.64399**	**-2.82026**
H	**-0.88382**	**-3.90382**	**-2.89106**
H	**-17.43342**	**-1.0073**	**3.03263**
H	**-16.72358**	**0.1856**	**1.94762**
H	**-16.37194**	**-1.53725**	**1.72143**
H	**-12.04915**	**1.8004**	**-3.99907**
H	**-12.08654**	**0.35121**	**-2.99366**
H	**-12.96689**	**0.38368**	**-4.52753**
H	**17.32683**	**1.85151**	**-1.15609**
H	**16.52955**	**0.2775**	**-1.215**
H	**17.49663**	**0.8273**	**-2.58441**
H	**11.89487**	**1.53017**	**3.61882**
H	**12.86419**	**0.20187**	**4.27098**
H	**11.97571**	**-0.00734**	**2.7563**

Optimized geometry data of compound D2

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	**2.24418**	**4.97206**	**0.22546**
C	**2.41341**	**3.60618**	**0.49843**
C	**1.37817**	**2.7174**	**0.1904**
C	**0.16935**	**3.18691**	**-0.3973**
C	**0.01158**	**4.55154**	**-0.6685**
C	**1.03782**	**5.43144**	**-0.35658**
N	**1.29325**	**1.33745**	**0.37212**
C	**0.05067**	**0.91545**	**-0.09901**
C	**-0.67662**	**2.03688**	**-0.58304**
C	**-0.50138**	**-0.3678**	**-0.13285**
C	**-1.79236**	**-0.53892**	**-0.65464**
C	**-2.51262**	**0.58245**	**-1.1354**
C	**-1.96415**	**1.85632**	**-1.10388**
C	**2.32431**	**0.44825**	**0.93842**
C	**3.60227**	**0.40759**	**0.07581**
C	**2.6123**	**0.75233**	**2.4229**
C	**-5.77235**	**-5.22312**	**-0.52057**
C	**-4.40619**	**-5.6862**	**-0.77882**
C	**-3.52908**	**-4.4914**	**-0.79244**
C	**-4.31374**	**-3.34634**	**-0.56489**
C	**-5.72615**	**-3.75098**	**-0.38857**
C	**-2.15198**	**-4.32406**	**-0.98115**
C	**-1.6159**	**-3.03686**	**-0.9358**
C	**-2.40222**	**-1.88833**	**-0.70173**
C	**-3.78653**	**-2.06805**	**-0.51571**
C	**-3.9594**	**-6.98513**	**-0.9848**
C	**7.73983**	**7.60186**	**1.05618**
C	**6.6481**	**8.51463**	**1.40734**
C	**5.3747**	**7.79365**	**1.17024**
C	**5.66433**	**6.49206**	**0.72252**
C	**7.1315**	**6.32102**	**0.63684**
C	**4.03143**	**8.16466**	**1.30492**
C	**3.03918**	**7.23443**	**0.99342**
C	**3.33011**	**5.92812**	**0.54514**
C	**4.68421**	**5.56638**	**0.41142**
C	**6.73133**	**9.81464**	**1.88876**
N	**18.93283**	**3.5136**	**-0.73728**
C	**17.62512**	**3.30812**	**-0.64006**

C	**16.87241**	**4.48006**	**-0.25472**
N	**17.61611**	**5.56266**	**-0.063**
S	**19.1869**	**5.11158**	**-0.36058**
C	**16.94346**	**2.05611**	**-0.78102**
C	**15.5285**	**1.95726**	**-0.63228**
C	**14.77015**	**3.16863**	**-0.46442**
C	**15.4472**	**4.38793**	**-0.16906**
C	**17.43551**	**0.74492**	**-0.85713**
C	**16.352**	**-0.12977**	**-0.70157**
N	**15.17397**	**0.60388**	**-0.5872**
N	**13.39557**	**3.39997**	**-0.44624**
C	**13.20597**	**4.72073**	**-0.05852**
C	**14.45012**	**5.34061**	**0.11181**
S	**18.98883**	**-0.04452**	**-0.92839**
C	**18.16874**	**-1.59502**	**-0.68593**
C	**16.76899**	**-1.4766**	**-0.57444**
C	**18.66607**	**-2.8957**	**-0.5639**
C	**17.61979**	**-3.82602**	**-0.32288**
S	**16.02778**	**-3.01643**	**-0.268**
C	**12.1248**	**5.58432**	**0.22708**
C	**12.5739**	**6.86138**	**0.60832**
S	**14.34067**	**7.00888**	**0.61588**
S	**10.39563**	**5.46879**	**0.27292**
C	**10.27609**	**7.17125**	**0.80892**
C	**11.55844**	**7.76688**	**0.93785**
C	**20.13988**	**-3.21574**	**-0.62224**
C	**11.83719**	**9.1988**	**1.32497**
C	**13.95426**	**-0.01134**	**-0.01398**
C	**12.41216**	**2.67919**	**-1.27533**
C	**12.96274**	**-0.72615**	**-0.98645**
C	**11.93327**	**3.45374**	**-2.52374**
C	**13.58626**	**-1.19695**	**-2.30804**
C	**12.25985**	**-1.88876**	**-0.25176**
C	**13.07643**	**3.87365**	**-3.47424**
C	**10.84628**	**2.62389**	**-3.22635**
C	**9.09324**	**7.89204**	**1.09632**
N	**-15.5739**	**-7.10667**	**0.0701**
C	**-15.38693**	**-5.79423**	**0.14884**
C	**-16.56785**	**-5.0148**	**-0.10166**
N	**-17.65068**	**-5.73506**	**-0.37031**
S	**-17.17872**	**-7.32678**	**-0.30065**
C	**-14.14794**	**-5.11685**	**0.37074**
C	**-14.04645**	**-3.68884**	**0.44312**
C	**-15.26834**	**-2.90961**	**0.32733**

C	-16.47985	-3.5911	-0.02838
C	-12.84609	-5.63352	0.36232
C	-11.96129	-4.55334	0.39411
N	-12.68103	-3.3696	0.47924
N	-15.55369	-1.53873	0.36098
C	-16.87184	-1.36844	-0.03302
C	-17.45788	-2.61397	-0.26464
S	-12.0743	-7.18662	0.1701
C	-10.51257	-6.35428	0.08451
C	-10.61368	-4.9568	0.21434
C	-9.21673	-6.83771	-0.13054
C	-8.27456	-5.77842	-0.1866
S	-9.06297	-4.19198	0.04844
C	-17.75798	-0.29515	-0.2761
C	-19.02065	-0.75912	-0.69136
S	-19.12404	-2.5277	-0.77919
S	-17.68871	1.43644	-0.23712
C	-19.38855	1.53732	-0.78613
C	-19.94917	0.24529	-0.98067
C	-8.90484	-8.31024	-0.24144
C	-21.36991	-0.05101	-1.39449
C	-11.9716	-2.08199	0.50851
C	-14.87415	-0.43119	1.04934
C	-11.59427	-1.49205	1.89296
C	-15.48242	-0.00923	2.40916
C	-10.83201	-2.4359	2.8518
C	-10.78144	-0.21262	1.62217
C	-15.48411	-1.12584	3.48261
C	-14.70677	1.22882	2.89395
C	-6.89965	-6.02032	-0.41596
O	7.70915	5.29637	0.28219
O	-6.66458	-2.98732	-0.17606
C	17.87554	-5.20666	-0.17322
C	-20.13505	2.71055	-1.02964
C	17.09235	-6.3232	0.07909
C	17.56541	-7.70368	0.1765
C	16.38885	-8.55401	0.49881
C	15.24954	-7.73562	0.57884
C	15.63479	-6.33107	0.31892
C	16.25741	-9.93097	0.71392
C	14.9905	-10.42457	0.99952
C	13.86551	-9.59275	1.07403
C	13.98208	-8.22696	0.86294
C	18.85098	-8.19431	-0.00132

O	**14.86373**	**-5.37544**	**0.31556**
F	**12.67935**	**-10.14758**	**1.35384**
F	**14.81989**	**-11.73628**	**1.21371**
C	**-19.87873**	**4.07027**	**-0.9312**
C	**-20.81267**	**5.14905**	**-1.25165**
C	**-20.12025**	**6.43413**	**-0.9674**
C	**-18.82164**	**6.15475**	**-0.50952**
C	**-18.61859**	**4.68967**	**-0.47342**
C	**-20.53298**	**7.76702**	**-1.07993**
C	**-19.62556**	**8.75863**	**-0.72837**
C	**-18.33401**	**8.46053**	**-0.27456**
C	**-17.9126**	**7.14426**	**-0.15872**
C	**-22.10759**	**5.05851**	**-1.7419**
O	**-17.58455**	**4.12783**	**-0.12299**
F	**-17.51983**	**9.47496**	**0.04376**
F	**-19.97959**	**10.04779**	**-0.81996**
C	**11.83049**	**10.15683**	**0.11692**
C	**20.81195**	**-3.20201**	**0.76557**
C	**11.43725**	**-1.46676**	**0.97233**
C	**13.83838**	**2.73976**	**-4.17266**
C	**1.37555**	**0.68802**	**3.32345**
C	**3.36081**	**-0.01165**	**-1.37705**
C	**-8.54939**	**-8.95023**	**1.11561**
C	**-11.70674**	**-3.39462**	**3.67116**
C	**-16.7418**	**-2.00358**	**3.51785**
C	**-22.34001**	**-0.11899**	**-0.19789**
C	**-2.59336**	**-7.31915**	**-1.23143**
N	**-1.49476**	**-7.65149**	**-1.43509**
C	**-4.79277**	**-8.14321**	**-0.98064**
N	**-5.4233**	**-9.12437**	**-0.98894**
C	**5.5906**	**10.61318**	**2.20449**
N	**4.69813**	**11.31123**	**2.47832**
C	**7.94982**	**10.51378**	**2.13829**
N	**8.9122**	**11.13359**	**2.36166**
C	**-22.92637**	**6.19454**	**-2.02051**
N	**-23.63564**	**7.08695**	**-2.26344**
C	**-22.78167**	**3.83523**	**-2.03484**
N	**-23.38136**	**2.86891**	**-2.29222**
C	**19.98737**	**-7.39516**	**-0.32813**
N	**20.94991**	**-6.79349**	**-0.59475**
C	**19.19098**	**-9.57602**	**0.1169**
N	**19.52208**	**-10.69026**	**0.20221**
H	**3.32562**	**3.26577**	**0.97109**
H	**-0.90283**	**4.91908**	**-1.126**

H	**0.92725**	**6.48491**	**-0.59271**
H	**0.03426**	**-1.222**	**0.26543**
H	**-3.49859**	**0.43729**	**-1.56479**
H	**-2.52667**	**2.70301**	**-1.48751**
H	**1.88356**	**-0.55255**	**0.89934**
H	**4.28837**	**-0.30219**	**0.55507**
H	**4.1067**	**1.38043**	**0.10056**
H	**3.35293**	**0.01656**	**2.761**
H	**3.0919**	**1.73286**	**2.52322**
H	**-1.48992**	**-5.15747**	**-1.17202**
H	**-0.55194**	**-2.91763**	**-1.11424**
H	**-4.44144**	**-1.22722**	**-0.3107**
H	**3.73535**	**9.14596**	**1.64946**
H	**2.002**	**7.52529**	**1.12605**
H	**4.97186**	**4.58654**	**0.04356**
H	**20.62716**	**-2.47445**	**-1.2665**
H	**20.31052**	**-4.1859**	**-1.09845**
H	**12.81959**	**9.23766**	**1.81072**
H	**11.11863**	**9.55065**	**2.07105**
H	**14.31706**	**-0.7361**	**0.72292**
H	**13.44**	**0.76581**	**0.55461**
H	**11.55396**	**2.40966**	**-0.64938**
H	**12.89042**	**1.75769**	**-1.59335**
H	**12.17321**	**-0.01286**	**-1.24626**
H	**11.45677**	**4.37932**	**-2.17932**
H	**12.80149**	**-1.6047**	**-2.95438**
H	**14.06855**	**-0.37562**	**-2.84785**
H	**14.32935**	**-1.98651**	**-2.16172**
H	**13.00533**	**-2.64026**	**0.04249**
H	**11.59616**	**-2.3848**	**-0.97146**
H	**13.7883**	**4.50103**	**-2.92265**
H	**12.6373**	**4.52675**	**-4.23968**
H	**10.48019**	**3.15022**	**-4.11453**
H	**9.9903**	**2.45228**	**-2.56383**
H	**11.22022**	**1.64566**	**-3.54997**
H	**9.33065**	**8.89855**	**1.4154**
H	**-8.08981**	**-8.48672**	**-0.94948**
H	**-9.78269**	**-8.81647**	**-0.6604**
H	**-21.37996**	**-1.01221**	**-1.92203**
H	**-21.73176**	**0.69027**	**-2.11312**
H	**-11.0523**	**-2.23613**	**-0.06536**
H	**-12.55228**	**-1.36125**	**-0.07094**
H	**-13.83978**	**-0.70671**	**1.19656**
H	**-14.88114**	**0.42401**	**0.36419**

H	-12.51318	-1.20105	2.41531
H	-16.52109	0.30132	2.23869
H	-10.2804	-1.80037	3.55649
H	-10.06523	-2.99474	2.30387
H	-10.58992	0.32374	2.55695
H	-11.30614	0.47134	0.94432
H	-9.81156	-0.45317	1.16977
H	-14.59418	-1.75927	3.36513
H	-15.37751	-0.64782	4.46466
H	-15.16306	1.62906	3.805
H	-14.70482	2.02636	2.14201
H	-13.66315	0.98214	3.12696
H	-6.71614	-7.0804	-0.533
H	18.93216	-5.41226	-0.28547
H	-21.13222	2.46297	-1.36955
H	17.07957	-10.63181	0.67293
H	13.11584	-7.57666	0.91915
H	-21.51243	8.07121	-1.42193
H	-16.91429	6.90586	0.19206
H	12.5654	9.85016	-0.63469
H	12.07671	11.17181	0.44433
H	10.84604	10.18311	-0.3611
H	21.88318	-3.40139	0.66246
H	20.38456	-3.96866	1.41967
H	20.68889	-2.23028	1.25495
H	10.91969	-2.32946	1.40557
H	10.67644	-0.72429	0.70067
H	12.0605	-1.03209	1.76253
H	14.61103	3.15446	-4.82925
H	13.17813	2.12332	-4.79218
H	14.34494	2.07774	-3.46097
H	1.65056	0.86558	4.36867
H	0.63347	1.4421	3.0407
H	0.89306	-0.29523	3.2672
H	4.30768	-0.06542	-1.925
H	2.71356	0.70136	-1.89854
H	2.88621	-0.99881	-1.4329
H	-8.37268	-10.0227	0.98706
H	-9.36061	-8.8198	1.83943
H	-7.64262	-8.50477	1.53696
H	-11.0865	-3.9879	4.35246
H	-12.27029	-4.09432	3.04718
H	-12.42707	-2.83783	4.28306
H	-16.68238	-2.7254	4.34033

H	**-17.63797**	**-1.39198**	**3.67761**
H	**-16.88604**	**-2.57066**	**2.5937**
H	**-23.3449**	**-0.37589**	**-0.54732**
H	**-22.39625**	**0.84327**	**0.32095**
H	**-22.02294**	**-0.87753**	**0.52533**