Supporting Information

Spiro-fused Dibenzo[*g,p*]chrysene:

Annulative π-Extension (APEX) Synthesis and Properties

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1. General information

1.1 Chemicals information

Unless otherwise specified, all other chemicals and solvents were purchased from Energy chemical, J&K, Adamas, or TCI chemicals, and were used as received without further purification.

1.2 Characterization of synthesized compounds

Newly synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectroscopy. Chemical shift values were recorded as parts per million (ppm) relative to tetramethylsilane (TMS), chloroform, or Dimethyl sulfoxide as internal standard, and coupling constants (*J*) in Hertz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on an Agilent Q-TOF 6520 system using electrospray ionization in Positive/Negative ion detection ($APCI^+$ /$APCI^-$) or (ESI^+ /ESI^-) mode. Significant fragments are reported in the following fashion: m/z (relative intensity).

1.3 Photophysical measurements

The ultraviolet−visible (UV−vis) spectra were obtained using UV-2700 220v CH and the photoluminescence (PL) spectra were recorded at room temperature on a HITACHI F-7000. UV−vis measurements were carried out using anhydrous cyclohexane solution at a sample concentration of 0.1 mM. (Transparent cuvette on four sides: 1×1×5 cm^3); PL measurements were carried out using anhydrous cyclohexane solution at the same concentration as UV measure.

1.4 Electrochemical measurements

Cyclic voltammetry experiments were carried out with electrochemical workstation PGSTAT204 Autolab, Vantone, Switzerland. A standard three-electrode system was used: Ag/AgCl (3.0 M KCl solution) electrode reference electrode; Glassy carbon electrode working electrode; A platinum wire

electrode is the opposite electrode. 0.1 M tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte, and the sweep speed of the cyclic voltammetry test was 100 mV/s. The samples were treated with N_2 before the test. Before performing electrochemical cleaning, the electrode should be sonicated in ethanol and deionized water for 1~3 mins respectively to obtain a clean electrode. There is no graininess on the electrode surface when polishing on a Microcloth polishing fleece coated with 1 μM and 0.05 μM alumina powder (both purchased from Shanghai Chenhua) and the polishing can be stopped. Specifically, the electrode is a silver wire that is coated with a thin layer of silver chloride and an insulated lead wire connects the silver wire with a measuring instrument. The electrode also consists of a porous plug on one end which will allow contact between the field environment with the silver chloride electrolyte. Saturated potassium chloride is added inside the body of the electrode to stabilize the silver chloride concentration and in this condition, the electrode's reference potential is known to be +0.197 V at 25 °C. The measurements were done in 1.0 mM DMF solution with 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6, TCI chemicals) as supporting electrolyte at a scan rate of 100 mV/s. The experiment was performed with a positive scan from 0 V to 1.6-1.8 V (determined by the nature of the compound); and a negative scan from 0 V to −2.6-−2.8 V (again, determined by the nature of the compound).

We determined the E_{Fc/Fc^+} of ferrocene in each test to calibrate the *E* values of **SFC**s. The following empirical formula was used for HOMO or LUMO determined from cyclic voltammetry (EC):

$$LUMO_{EC} = -e(4.8 + E_{re})$$

$$HOMO_{EC} = -e(4.8 + E_{ox})$$

1.5 Computational study

The Gaussian 16W running on the Linux system was used for optimization B3LYP/6-31G(d). Structures were optimized without any symmetry assumptions. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase studies. Harmonic vibration frequency calculation at the same level was performed to verify all stationary points as local minima (with no imaginary frequency) or transition states (with one imaginary frequency). Visualization of the results was performed by the use of GaussView 6.0 software[1] and Multiwfn software[2].

1.6 X-ray crystal diffraction

Crystal data were collected using a Rigaku-AFC7 eqipped with a Rigakuj Saturn CCD area-detector system. The measurements were made using monochromatic Mo Kα radiation (λ = 0.71073 Å) under a cold nitrogen stream.

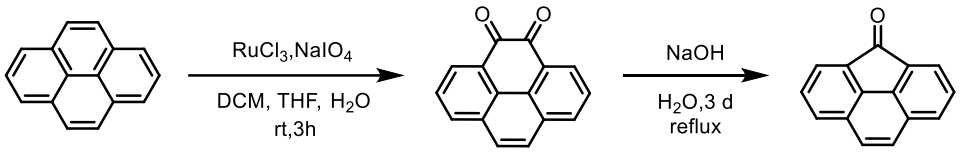
1.7 Thermal property test

The thermogravimetric analyses (TGA) were obtained using NETZSCH 449F5.

2. The experiment method

2-1. Spiro compounds **(1a**, **1b**, **1c**, **1d**, **1e)**[3] and 2-bromo-2'-ethynyl-1,1'-biphenyl[4] were prepared according to reported method.

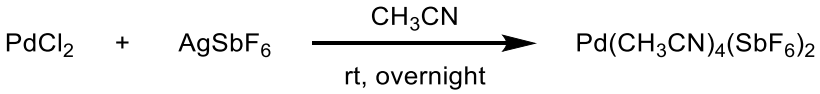
Phenanthrenone



Scheme S1: Synthesis of phenanthrenone

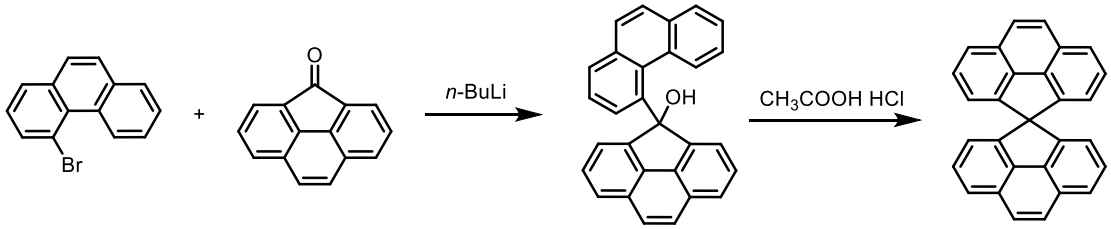
The synthesis of phenanthrenone followed the procedure of Filippov, Schneider and co-workers.[5] ^{1}H and ^{13}C NMR spectra are consistent with the previous report. ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.78 (d, *J* = 8.0Hz, 2H), 7.69 (d, *J* = 7.0Hz, 2H), 7.64 (s, 2H), 7.49 (t, *J* = 7.0Hz, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) *δ* 193.6, 138.9, 132.9, 130.7, 129.1, 127.2, 125.3, 122.4.

$Pd(CH_3CN)_4(SbF_6)_2$



To a suspension of $PdCl_2$ (88 mg, 0.50 mmol) in CH_3CN (5.0 mL) was added $AgSbF_6$ (344 mg, 1.00 mmol), and the resultant mixture was stirred at room temperature overnight. The reaction mixture was filtrated, then Et_2O was added into the filtrate to recrystallize $Pd(CH_3CN)_4(SbF_6)_2$. The complex was collected by filtration (315 mg, 85%).

4,4'-spirobi[cyclopenta[*def*]phenanthrene] (SBP)



Scheme S2: Synthesis of **SBP**

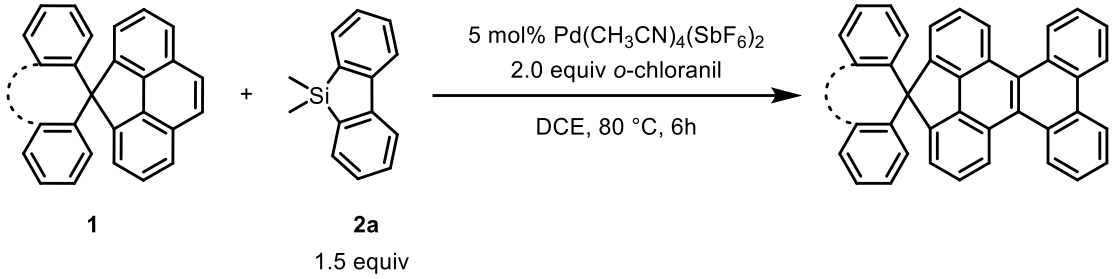
2-bromo-2'-ethynyl-1,1'-biphenyl (91 mg, 0.35 mmol, 1.1 equiv.) was dissolved in dry THF (1.0 mL) under argon atmosphere, cooled at −78°C, and stirred during 10 minutes at this temperature. *n*-BuLi solution (1.6 M in hexane, 0.3 ml, 1.3 equiv.) was then slowly injected via a syringe. The resulting yellow mixture was stirred at the same temperature for 1 hour. 4H-cyclopenta[def]phenanthren-4-one (65 mg, 0.32 mmol, 1.0 equiv.) was then added immediately, the mixture was stirred for 3 hours in room temperature.

Add 2.0 ml of methanol to the reaction solution, then concentrated the solution under reduced pressure. Without other purification, the crude was dissolved into a mixture of acetic acid/hydrochloric acid (5.0 mL/0.5 mL) and warned at 100°C during 3 hours under stirring. Then, the mixture was poured into water/ice (50.0 mL), and the solution was neutralized with solid sodium hydroxide until pH reach 7. Then, the organic layer was extracted three times with dichloromethane (3 × 50.0 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether) to afford a white solid (70 mg, 60%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 (s, 4H), 7.89 (d, J = 7.9 Hz, 4H), 7.48 (t, J = 7.5 Hz, 4H), 6.91 (td, J = 12.8, 11.2, 7.1 Hz, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.0, 138.3, 128.3, 128.3, 125.8, 123.9, 120.4, 69.5.

HRMS (ESI): Exact mass calculated for $C_{29}H_{16}$ $[M+H]^+$: 365.1325, mass found: 365.1326.

2-2. APEX Reaction of spiro compounds with Siloles

General procedure

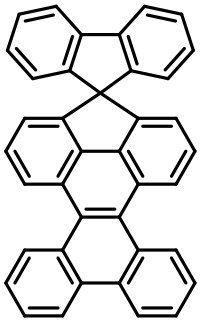


1 **2a** 1.5 equiv

Scheme S3: APEX synthesis for **SFCs**

A solution of phenanthrene derivative **1** (0.30 mmol, 1.0 equiv.), dimethyldibenzosilole **2a** (0.45 mmol, 1.5 equiv.), $Pd(CH_3CN)_4(SbF_6)_2$ (11 mg, 15 μmol, 5 mol%), and *o*-chloranil (148 mg, 0.60 mmol, 2.0 equiv.) in 1,2-Dichloroethane (3.0 mL) was stirred at 80 °C in the screw cap glass tube. After 6 hours, the reaction mixture was cooled to room temperature, and then passed through a short pad of silica gel (eluent: petroleum ether/dichloromethane). After the organic solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography to yield π-extended spiro compounds.

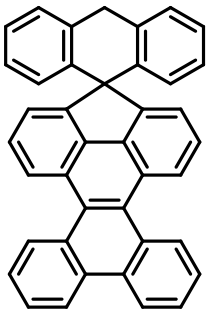
spiro[benzo[*p*]indeno[7,1,2-*ghi*] chrysene-4,9'-fluorene] (SFC)



Flash column chromatography (petroleum ether/dichloromethane = 20:1), Yield: 80 mg, 54%, white solid. ^{1}H NMR (600 MHz,) *δ* 9.16 (d, *J* = 7.9 Hz, 2H), 8.83 (d, *J* = 7.9 Hz, 2H), 8.73 (d, *J* = 7.9 Hz, 2H), 7.95 (d, *J* = 7.7 Hz, 2H), 7.80 – 7.72 (m, 4H), 7.61 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 7.1 Hz, 2H), 6.75 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) *δ* 148.1, 147.8, 142.0, 138.4, 131.0, 130.7, 128.8, 128.6, 128.3, 128.1, 128.0, 127.0, 126.1, 125.9, 124.4, 123.8, 120.6, 120.3, 67.7.

HRMS (ESI): Exact mass calculated for $C_{39}H_{22}$ $[M]^+$: 490.1716, mass found: 490.1722.

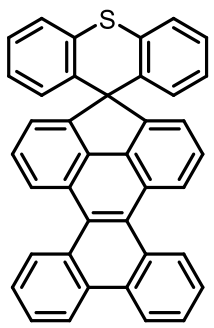
10*H*-spiro[anthracene-9, 4'-benzo[*p*]indeno[7,1,2-*ghi*] chrysene] (*C*-SFC)



Flash column chromatography (petroleum ether/dichloromethane = 20:1), Yield: 87 mg, 58%, white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 9.14 (dd, *J* = 7.8, 1.8 Hz, 2H), 8.82 (dd, *J* = 7.9, 1.7 Hz, 2H), 8.73 (dd, *J* = 8.2, 2.4 Hz, 2H), 7.79 – 7.71 (m, 4H), 7.66 (t, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.39 (dd, *J* = 7.2, 2.6 Hz, 2H), 7.23 (td, *J* = 7.4, 1.3 Hz, 2H), 6.94 – 6.89 (m, 2H), 6.53 (dd, *J* = 8.3, 4.0 Hz, 2H), 4.65 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) *δ* 153.3, 138.9, 136.8, 134.9, 130.9, 130.6, 128.8, 128.6, 128.5, 128.4, 127.3, 127.0, 126.9, 126.7, 126.1, 125.6, 123.7, 121.5, 35.7.

HRMS (ESI): Exact mass calculated for $C_{40}H_{24}$ $[M]^+$: 504.1873, mass found: 504.1869.

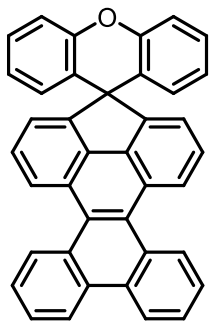
spiro[benzo[*p*]indeno[7,1,2-*ghi*] chrysene-4,9'-thioxanthene] (*S*-SFC)



Flash column chromatography (petroleum ether/dichloromethane = 15:1), Yield: 120 mg, 76%, white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 9.10 (dd, *J* = 8.0, 1.5 Hz, 2H), 8.80 (dd, *J* = 8.0, 1.6 Hz, 2H), 8.74 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 7.1 Hz, 2H), 7.78 – 7.68 (m, 6H), 7.55 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.20 (ddd, *J* = 8.0, 7.2, 1.4 Hz, 2H), 6.88 (ddd, *J* = 8.3, 7.1, 1.4 Hz, 2H), 6.69 (dd, *J* = 8.1, 1.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) *δ* 151.2, 137.1, 136.0, 131.8, 130.8, 130.6, 128.7, 128.6, 128.4, 127.8, 127.5, 127.0, 126.9, 126.6, 126.4, 126.3, 126.2, 123.7, 122.2, 63.4.

HRMS (ESI): Exact mass calculated for $C_{39}H_{22}S$ $[M]^+$: 522.1437, mass found: 522.1453.

spiro[benzo[*p*]indeno[7,1,2-*ghi*] chrysene-4,9'-xanthene] (*O*-SFC)

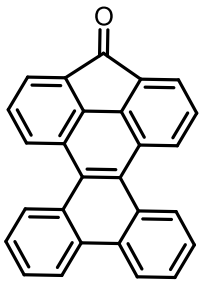


Flash column chromatography (petroleum ether/dichloromethane = 15:1), Yield: 118 mg, 78%, white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 9.13 (dd, *J* = 7.9, 1.6 Hz, 2H), 8.82 (dd, *J* = 7.9, 1.7 Hz, 2H), 8.74 (d, *J* = 8.1 Hz, 2H), 7.75 (dddd, *J* = 16.8, 8.3, 6.9, 1.5 Hz, 4H), 7.47 (d, *J* = 7.1 Hz, 2H), 7.33 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.27 – 7.22 (m, 3H), 6.77 (ddd, *J* = 8.2, 7.1, 1.3 Hz, 2H), 6.45 (dd, *J* = 7.9, 1.6 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) *δ* 153.1, 151.8, 136.3, 130.9, 130.7, 128.8, 128.7, 128.6, 128.5, 127.9, 127.1, 127.0, 126.1, 126.0, 124.6, 123.8, 123.5, 121.8, 117.1, 56.6.

HRMS (ESI): Exact mass calculated for $C_{39}H_{22}O$ $[M]^+$: 506.1665, mass found: 506.1675.

4*H*-benzo[*p*]indeno[7,1,2-*ghi*] chrysen-4-one (1f)

A solution of phenanthrene derivative 4H-cyclopenta[*def*]phenanthren-4-one (62 mg, 0.30 mmol, 1.0 equiv.), silicon-bridged aromatics **2a** (95 mg, 0.450 mmol, 1.5 equiv.), $Pd(CH_3CN)_4(SbF_6)_2$ (12 mg, 15 μmol, 5 mol%), and *o*-chloranil (148 mg, 0.60 mmol, 2.0 equiv.) in DCE (2.0 mL) was stirred at 80 °C in the screw cap glass tube. After 4 hours, the reaction mixture was cooled to room temperature, and then passed through a short pad of silica gel (eluent: petroleum ether/dichloromethane = 5:1). After the organic solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography to yield **4*H*-benzo[*p*]indeno[7,1,2-*ghi*] chrysen-4-one** (93 mg, 88%).

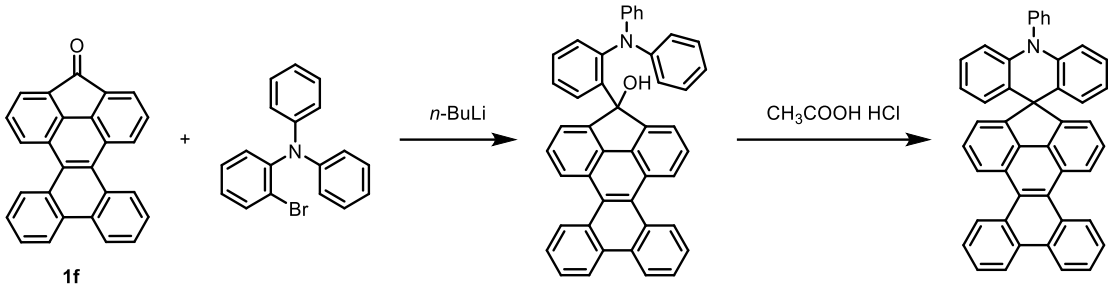


^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 8.76 (d, *J* = 8.1 Hz, 2H), 8.70 (dd, *J* = 8.2, 1.4 Hz, 2H), 8.61 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 6.8 Hz, 2H), 7.70 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 2H), 7.64 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 2H), 7.58 (ddd, *J* = 8.2, 6.8, 1.7 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) *δ* 193.8, 139.6, 132.9, 132.5, 130.5, 130.2, 129.0, 128.1, 127.7, 127.3, 127.0, 125.4, 123.7, 122.3. HRMS (ESI): Exact mass calculated for $C_{27}H_{15}O$ $[M+H]^+$: 355.1117, mass found: 355.1116.

The large scale synthesis of 1f

A solution of phenanthrene derivative 4H-cyclopenta[*def*]phenanthren-4-one (204 mg, 1.0 mmol, 1.0 equiv.), silicon-bridged aromatics **2a** (315 mg, 1.5 mmol, 1.5 equiv.), $Pd(CH_3CN)_4(SbF_6)_2$ (37 mg, 50 μmol, 5 mol%), and *o*-chloranil (491 mg, 2.0 mmol, 2.0 equiv.) in DCE (9.0 mL) was stirred at 80 °C in the screw cap glass tube. After 8 hours, the reaction mixture was cooled to room temperature, and then passed through a short pad of silica gel (eluent: petroleum ether/dichloromethane = 5:1). After the organic solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography to yield **4*H*-benzo[*p*]indeno[7,1,2-*ghi*] chrysen-4-one** (195 mg, 55%).

2-3. **10-phenyl-10*H*-spiro[acridine-9,4'-benzo[*p*]indeno[7,1,2-*ghi*]chrysene] (*N*-SFC)**



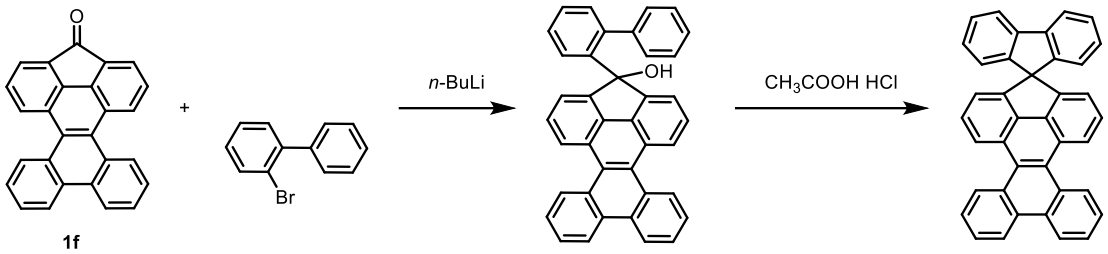
Scheme S4: Synthesis for ***N*-SFC**

2-Bromo-N,N-diphenylbenzenamine (36 mg, 0.11 mmol, 1.1 equiv.) was dissolved in dry THF (0.5 mL) under argon atmosphere, cooled at −78°C, and stirred for 10 minutes at this temperature. n-BuLi solution (1.6 M in hexane, 0.3 ml, 1.3 equiv.) was then slowly injected via a syringe. The resulting yellow mixture was stirred at the same temperature for 1 hour. 4H-cyclopenta[*def*]phenanthren-4-one (36 mg, 0.1 mmol, 1 equiv.) was then added immediately, the mixture was stirred for 3 hours in room temperature.

Add 2.0 ml of methanol to the reaction solution, then concentrated the solution under reduced pressure. Without other purification, the crude was dissolved into a mixture of acetic acid/hydrochloric acid (3.0 mL/0.3 mL) and warned at 100°C during 3 hours under stirring. Then, the mixture was poured into water/ice (40.0 mL), and the solution was neutralized with solid sodium hydroxide until pH reach 7. Then, the organic layer was extracted three times with dichloromethane (3 × 40.0 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether) to afford a white solid (35 mg, 61%).^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 9.15 (dd, *J* = 7.7, 1.7 Hz, 2H), 8.82 (dd, *J* = 7.7, 1.8 Hz, 2H), 8.74 (dd, *J* = 7.7, 1.0 Hz, 2H), 7.78 – 7.71 (m, 10H), 7.64 – 7.60 (m, 3H), 6.98 (ddd, *J* = 8.5, 7.0, 1.6 Hz, 2H), 6.57 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 2H), 6.48 (ddd, *J* = 10.0, 8.2, 1.4 Hz, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) *δ* 153.9, 141.7, 141.2, 135.8, 131.3, 131.2, 130.9, 130.6, 128.8, 128.6, 128.6, 127.6, 127.4, 126.9, 126.1, 125.7,

124.4, 123.7, 121.8, 120.8, 114.8, 59.5. HRMS (ESI): Exact mass calculated for $C_{45}H_{27}N$ $[M]^+$: 581.2138, mass found: 581.2146.

Synthesis of SFC from 1f and 2-Bromobiphenyl

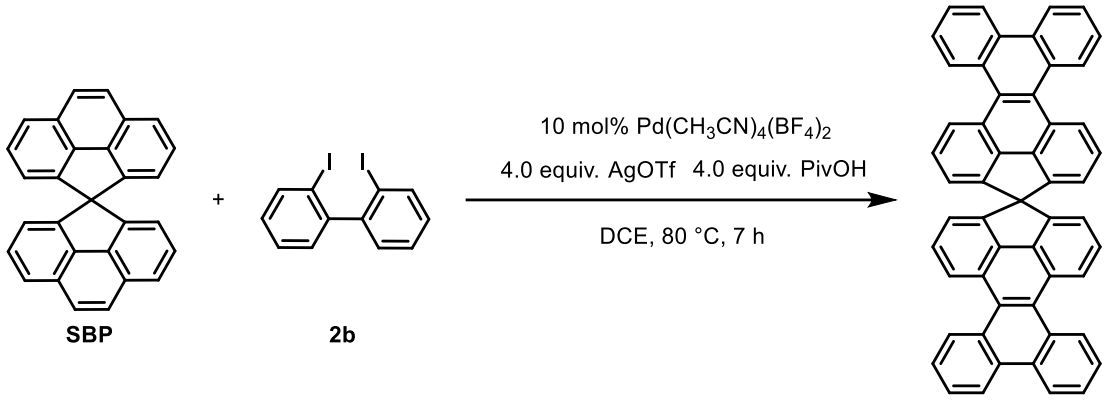


Scheme S5: Synthesis of SFC from 1f and 2-Bromobiphenyl

2-Bromobiphenyl (77 mg, 0.33 mmol, 1.1 equiv.) was dissolved in dry THF (1.5 mL) under argon atmosphere, cooled at −78°C, and stirred for 10 minutes at this temperature. n-BuLi solution (1.6 M in hexane, 2.6 ml, 1.4 equiv.) was then slowly injected via a syringe. The resulting yellow mixture was stirred at the same temperature for 1 hour. 4H-cyclopenta[*def*]phenanthren-4-one (106 mg, 0.3 mmol, 1 equiv.) was then added immediately, the mixture was stirred for 3 hours in room temperature.

Add 2.0 ml of methanol to the reaction solution, then concentrated the solution under reduced pressure. Without other purification, the crude was dissolved into a mixture of acetic acid/hydrochloric acid (5.0 mL/0.5 mL) and warned at 100°C during 3 hours under stirring. Then, the mixture was poured into water/ice (50.0 mL), and the solution was neutralized with solid sodium hydroxide until pH reach 7. Then, the organic layer was extracted three times with dichloromethane (3 × 50.0 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether) to afford a white solid (75 mg, 51%).

2:1 APEX reaction of 2,2'-diiodobiphenyl with **SBP**



Scheme S6: APEX synthesis for **SBC**

4, 4'-spirobi[benzo[*p*]indeno[7,1,2-*ghi*] chrysene] (SBC)

To a screw-capped glass tube containing a magnetic stirrer bar were added 4,4'-spirobi[cyclopenta[*def*]phenanthrene] (37 mg, 0.10 mmol, 1.0 equiv.), 2,2'-diiodobiphenyl (163 mg, 0.40 mmol, 4.0 equiv.), AgOTf (103 mg, 0.40 mmol, 4.0 equiv.), $Pd(CH_3CN)_4(BF_4)_2$ (5 mg, 10 μmol, 10 mol%), PivOH (41 mg, 0.40 mmol, 4.0 equiv.) and 1,2-dichloroethane (2.0 mL) under a stream of nitrogen. After stirring at 80 °C for 7 hours, the reaction mixture was cooled to room temperature, and then passed through a short pad of silica gel (eluent: dichloromethane). After the organic solvent was removed under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 10:1) to yield **SBC** (40 mg, 60%) as a white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.21 (dd, J = 7.7, 1.8 Hz, 4H), 8.88 – 8.84 (m, 4H), 8.80 (d, J = 8.1 Hz, 4H), 7.83 – 7.75 (m, 8H), 7.63 (dd, J = 8.1, 7.1 Hz, 4H), 7.09 (d, J = 7.1 Hz, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.9, 138.5, 131.0, 130.7, 128.7, 128.6, 128.3, 127.0, 127.0, 126.2, 126.0, 123.7, 120.8, 69.1.

HRMS (ESI): Exact mass calculated for $C_{53}H_{28}$ $[M]^+$: 664.2186, mass found: 664.2192.

3. Spectroscopic data

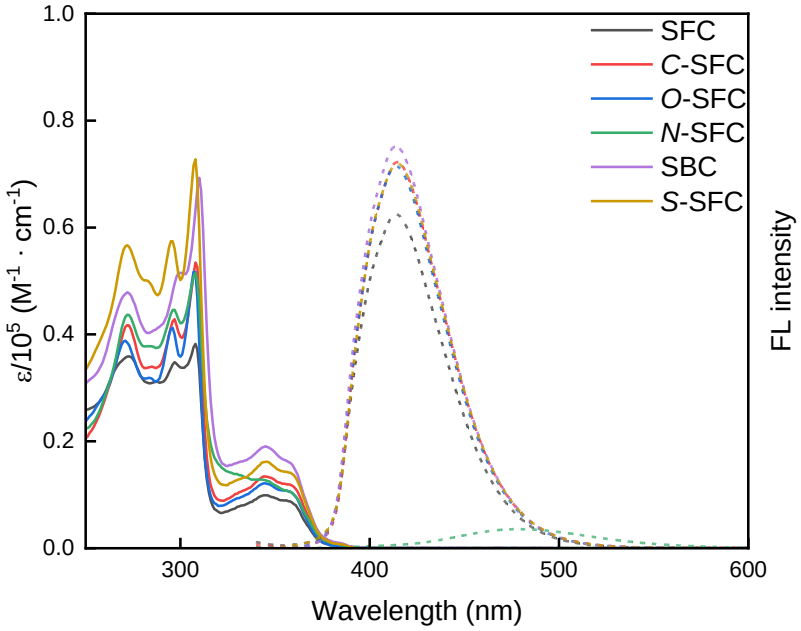


Figure S1 UV/vis absorption spectra (solid line) and fluorescence spectra (dotted line) of **SFC**s (c = 1×10^{-5} M) in dichloromethane.

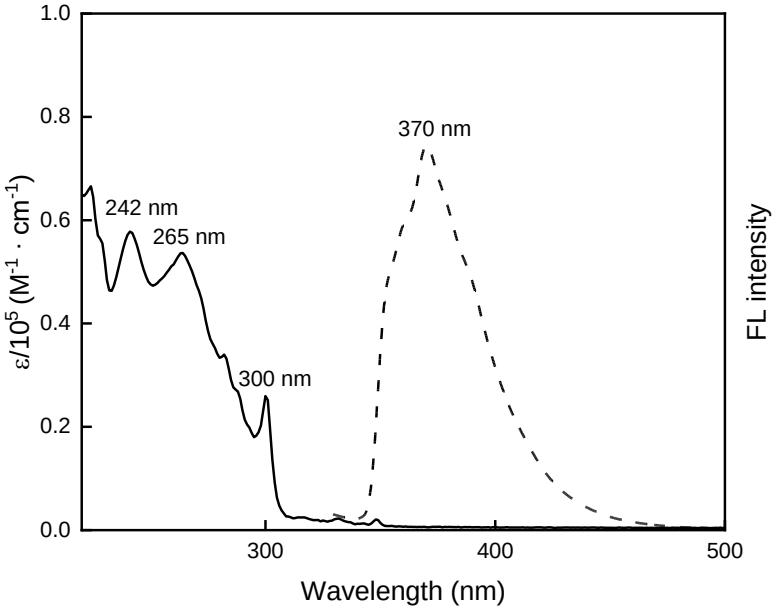


Figure S2 UV/vis absorption spectra (solid line) and fluorescence spectra (dotted line) of **SBP** (c = 1×10^{-5} M) in cyclohexane.

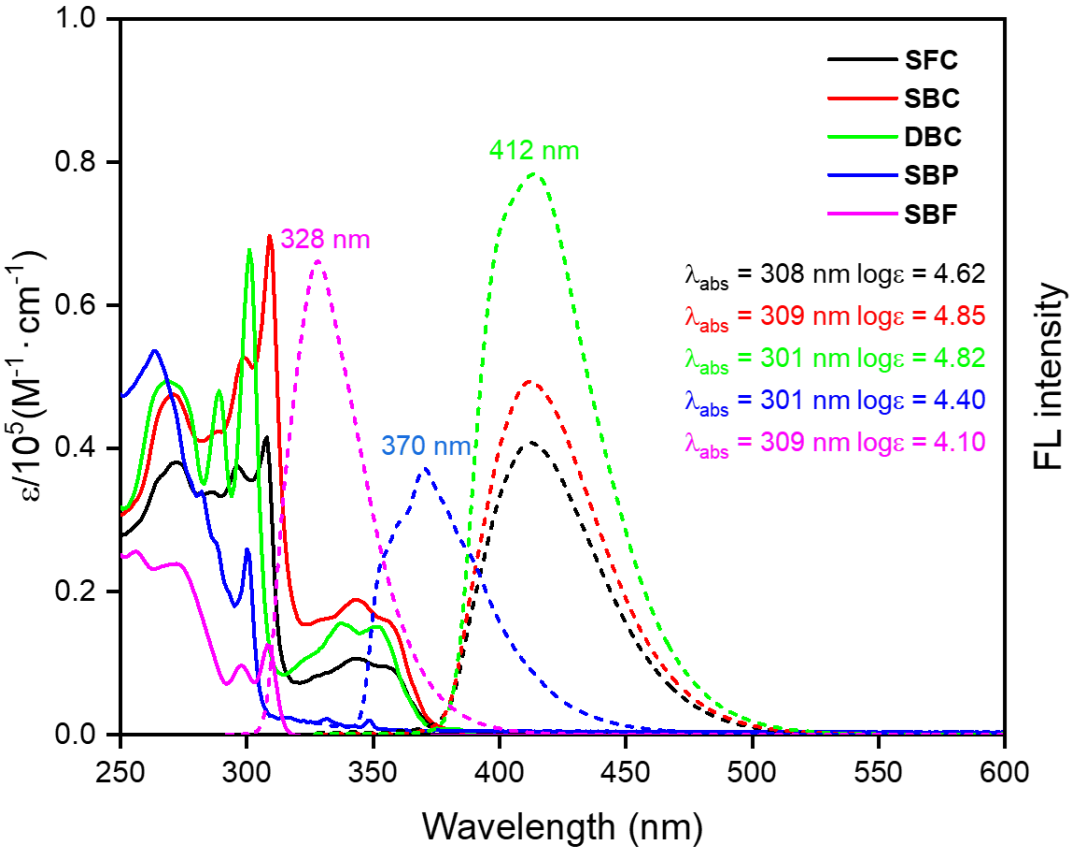


Figure S3 UV/vis absorption (solid line) and emission (dotted line) spectra of **SFC, SBC DBC, SBP** and **SBF** in cyclohexane (c = 1×10^{-5} M);

3.1 The comparison of S**FC**s with other model compounds.

Compared to spirofluorene compounds containing common heteroatoms, **SFC**s exhibit a smaller energy gap (Table S1). For instance, ***N*-SFC** and ***N*-SF**, which possess identical phenyl acridine groups, the larger conjugated system in ***N*-SFC** leads to a decrease in the energy gap. ***N*-SFC** incorporates a phenyl acridine donor unit, resulting in a distinctive frontier molecular orbital distribution characterized by HOMO-LUMO segregation. This segregation is accompanied by a reversible oxidation peak of E_{onset}^{ox} =0.56 V.

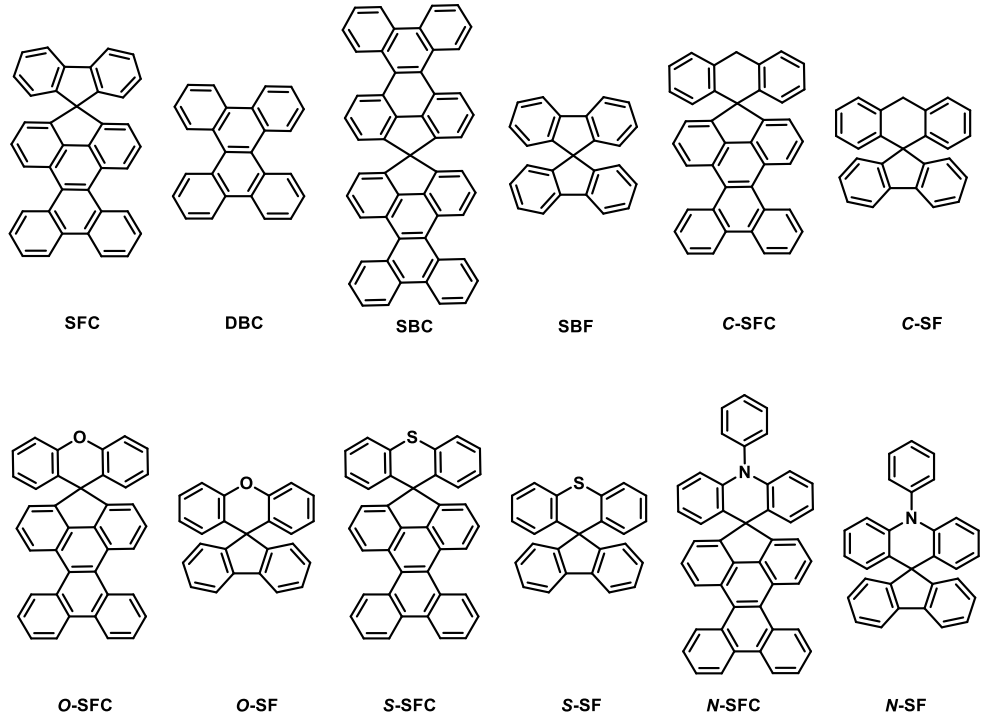


Table S1 The comparison of **SFC**s with other model compounds.

	λ_{abs} (nm)[a]	λ_{em} (nm)[a]	QY (%)[a]	τ(ns)[a]	$HOMO_{EC}$/ $_{Theo}$ (eV)[b]	$LUMO_{EC}$ /$_{Theo}$ (eV)[b]	ΔE_{EC}/ ΔE_{Theo}/ ΔE_{opt} (eV)[c]
SFC	272, 296 308,344, 356	412	7.6	5.49	-5.75/ -5.35	-2.48/ -1.50	3.27/ 3.85/ 3.30
DBC	269,289, 300,337, 352	412	13.1		-5.65[6]/ -5.30	-2.49[6]/ -1.44	3.16/ 3.86/ 3.32
SBC	271, 299 309, 344 356	412	8.0	5.65	-5.73/ -5.38	-2.51/ -1.54	3.22/ 3.84/ 3.26
SBF	257,275, 296,308	310,323	20.3	4.6[7]	-5.94[7]/ -5.99	-1.89[7]/ -1.27	4.05[7]/ 4.72/ 3.97
***C*-SFC**	271,296 307, 344 354	413	7.9	4.64	-5.76/ -5.35	-2.50/ -1.51	3.26/ 3.84/ 3.28
***C*-SF**					-/ -5.71	-/ -0.82	-/ 4.89/ -
***O*-SFC**	270,295, 306, 343 357	413	7.4	4.01	-2.51/ -1.55	-2.51/ -1.55	3.27/ 3.84/ 3.30
***O*-SF**					-/ -5.66	-/ -0.86	-/ 4.80/ -
***S*-SFC**	271,295, 307, 344 357	413	8.0	5.12	-5.73/ -5.39	-2.50/ -1.56	3.23/ 3.83/ 3.28
***S*-SF**					-/ -5.48	-/ -0.91	-/ 4.57/ -
***N*-SFC**	271, 295 307, 345 355	412	7.9	3.37	-5.36/ -5.17	-2.51/ -1.52	3.82/ 3.65/ 3.29
***N*-SF**[8]	309	429		5.6	-5.33/ -4.92	-1.94/ -0.72	3.39/ 4.20/ 3.59

[a]Absorption, fluorescence quantum yields (QY), fluorescence lifetime (τ) and emission maxima measured in cyclohexane solution at room temperature. [b] HOMO or LUMO determined from cyclic voltammetry ($_{EC}$) or theoretically calculated ($_{Theo}$). $LUMO_{EC} =$

$-e(4.8+E_{re})$, $HOMO_{EC}=-e(4.8+E_{ox})$. [c] ΔE_{EC} calculated from the HOMO and LUMO level determined through cyclic voltammetry recorded in DMF; ΔE_{Theo} calculated from the HOMO and LUMO level theoretically calculated; ΔE_{opt} calculated from the onset of the absorption spectrum recorded in cyclohexane.

Table S2 Summary of optical properties of **SFC**s

	SFC	***C*-SFC**	***O*-SFC**	***N*-SFC**	***S*-SFC**	**SBC**
Φ_{PL}[a]	0.076	0.079	0.074	0.079	0.080	0.080
τ[a] (ns)	5.49	4.64	4.01	3.37	5.12	5.65
k_f[b] (10^8 s^{-1})	0.014	0.017	0.018	0.023	0.016	0.014
k_{nr}[c] (10^8 s^{-1})	0.17	0.20	0.23	0.27	0.18	0.16

a. fluorescence quantum yields (Φ_{PL}), fluorescence lifetime (τ) and emission maxima measured in cyclohexane solution at room temperature; b. Radiative rate constant k_f is calculated as $k_f = \Phi_{PL}/\tau$; c. Nonradiative rate constant k_{nr} is calculated as $k_{nr} = (1-\Phi_{PL})/\tau$.

4. Electrochemical data

4.1 SFC

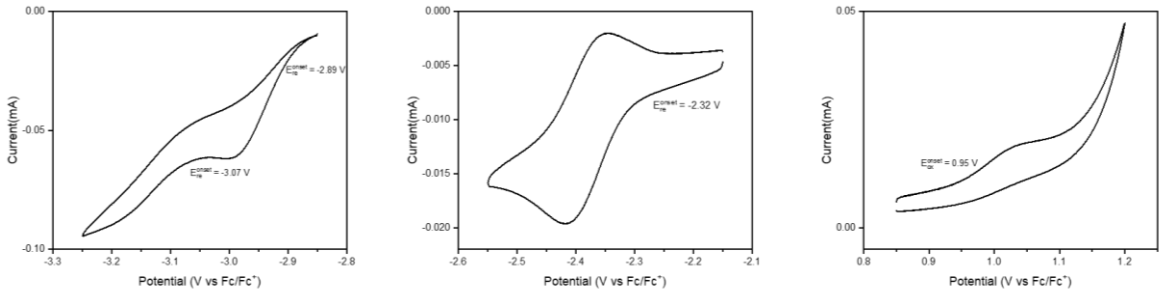


Figure S4 Cyclic voltammogram of **SFC** in DMF solution containing 0.1 M *n*-Bu_4NPF_6 at room temperature at a scan rate of 0.1 V/s.

4.2 *C*-SFC

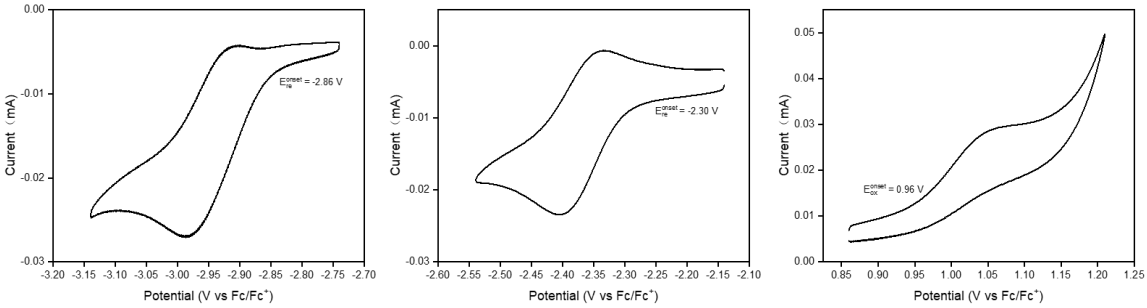


Figure S5 Cyclic voltammogram of ***C*-SFC** in DMF solution containing 0.1 M *n*-Bu_4NPF_6 at room temperature at a scan rate of 0.1 V/s.

4.3 *O*-SFC

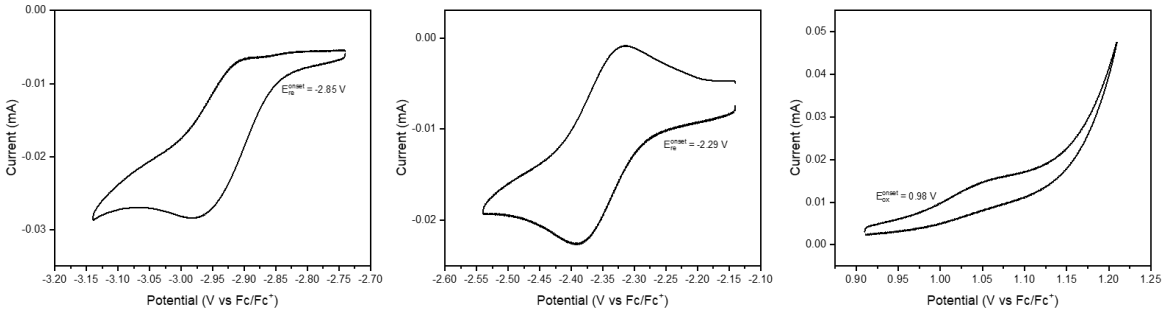


Figure S6 Cyclic voltammogram of ***O*-SFC** in DMF solution containing 0.1 M *n*-Bu_4NPF_6 at room temperature at a scan rate of 0.1 V/s.

4.4 *S*-SFC

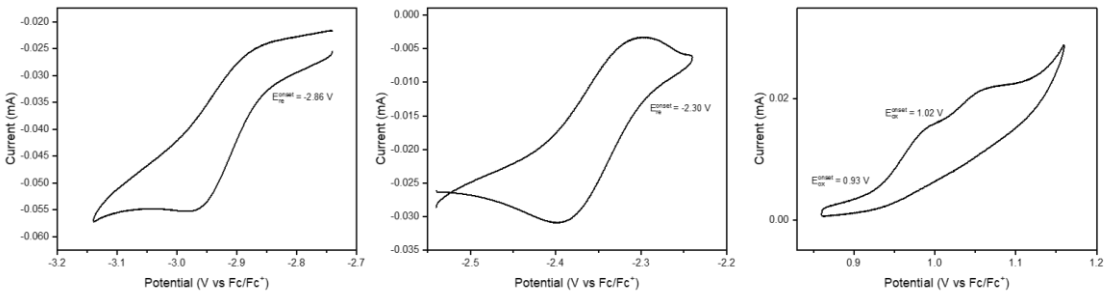


Figure S7 Cyclic voltammogram of ***S*-SFC** in DMF solution containing 0.1 M *n*-Bu_4NPF_6 at room temperature at a scan rate of 0.1 V/s.

4.5 *N*-SFC

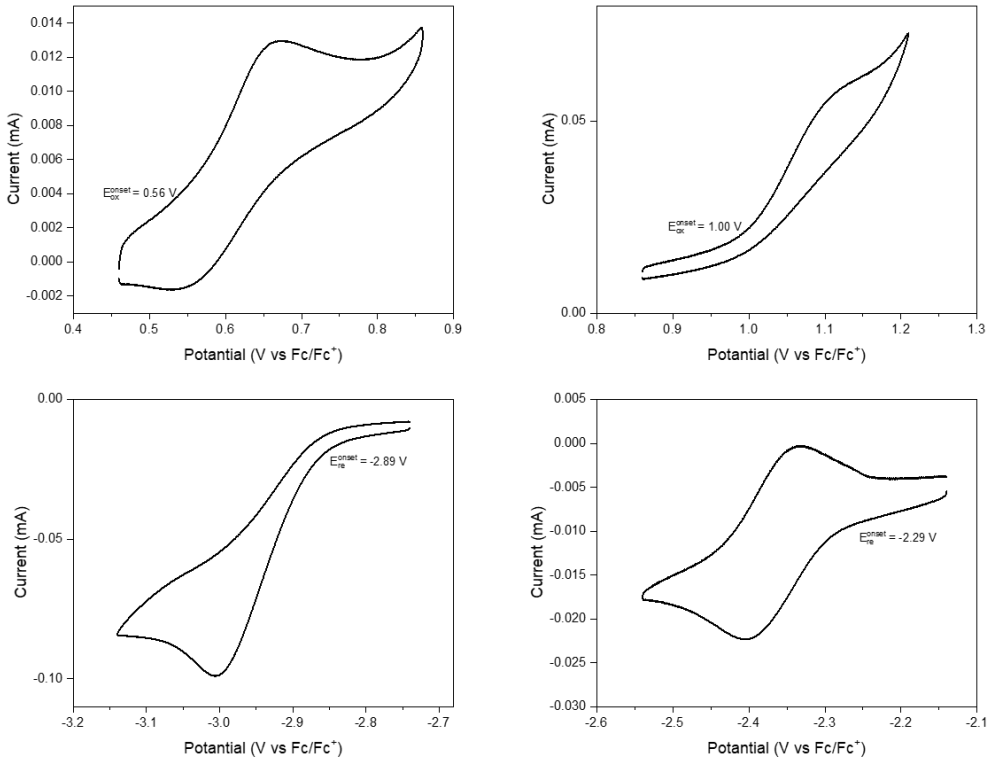


Figure S8 Cyclic voltammogram of ***N*-SFC** in DMF solution containing 0.1 M *n*-Bu_4NPF_6 at room temperature at a scan rate of 0.1 V/s.

4.6 SBC

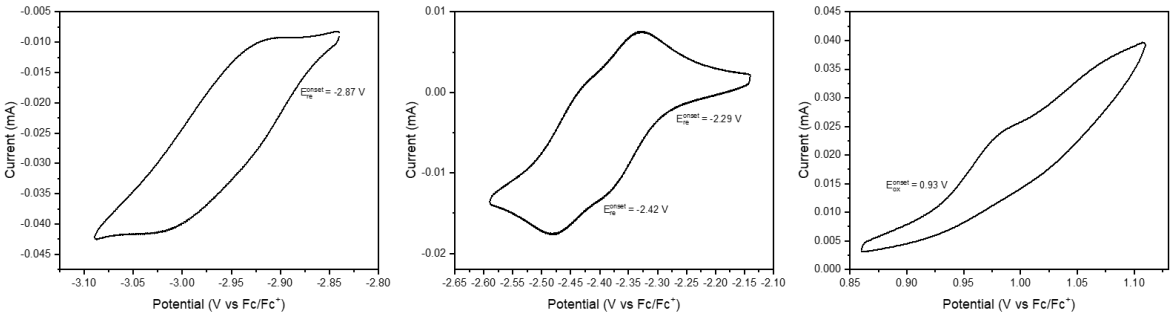


Figure S9 Cyclic voltammogram of **SBC** in DMF solution containing 0.1 M *n*-Bu_4NPF_6 at room temperature at a scan rate of 0.1 V/s.

4.7 SBP

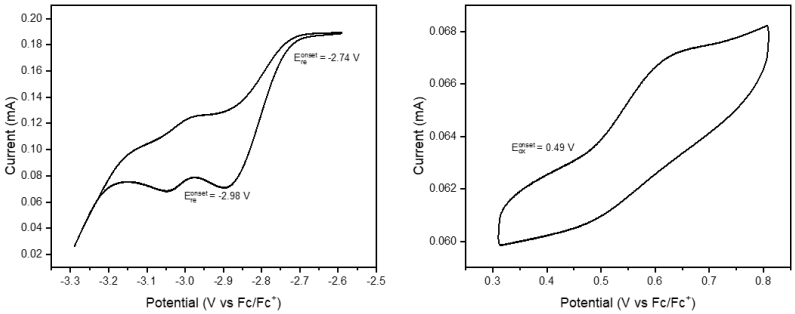


Figure S10 Cyclic voltammogram of **SBP** in DMF solution containing 0.1 M *n*-Bu_4NPF_6 at room temperature at a scan rate of 0.1 V/s.

5. Computational study

5.1 The TD-DFT calculation

Since the HOMO and LUMO is predominantly concentrated at the DBC, **SFC**s exhibits similar adsorption peaks to DBC. The dominant excitations for the respective compounds are clearly defined: for **SFC**, it is the transition from S0→S5 (HOMO→LUMO+1) occurring at λ = 308 nm with an oscillator strength of f = 0.8111; for ***C*-SFC**, it's the S0→S4 (HOMO →LUMO+1) transition at λ = 311 nm with f = 0.7730; ***O*-SFC** exhibits the S0→S5 (HOMO →LUMO+1) transition at λ = 311 nm, boasting an oscillator strength of f = 0.8148; ***S*-SFC** undergoes the S0→S5 (HOMO→LUMO+1) transition at λ = 312 nm with a notably high f value of 0.8301; **SBC** displays the unique S0→S11 (HOMO-3→LUMO+1) transition at λ = 312 nm, characterized by an exceptionally strong oscillator strength of f = 1.4379; and finally, ***N*-SFC** shows the S0→S7 (HOMO-1→LUMO+1) transition at λ = 312 nm with a robust oscillator strength of f = 0.9270. The molecular orbital transitions and corresponding absorption peaks align with the experimental spectra.

Table S3 Major electronic transitions for **SFC** by TD-DFT method using B3LYP/6-31G(d).

	Energy (eV)	**Excitation (nm)**	**Oscillator strength (*f*)**	**Description**
1	3.4367	360.77	0.20030	H -> L 92.1%
5	4.0125	308.99	0.81110	H -> L+1 49.7%, H-2 -> L 41.4%
8	4.2348	292.77	0.11810	H-1 -> L+1 79.0%, H-1 -> L+2 6.2%
12	4.5027	275.36	0.29180	H-2 -> L+1 66.1%, H-1 -> L+4 12.8%
15	4.5548	272.21	0.31160	H-4 -> L 82.8%, H -> L+4 11.1%

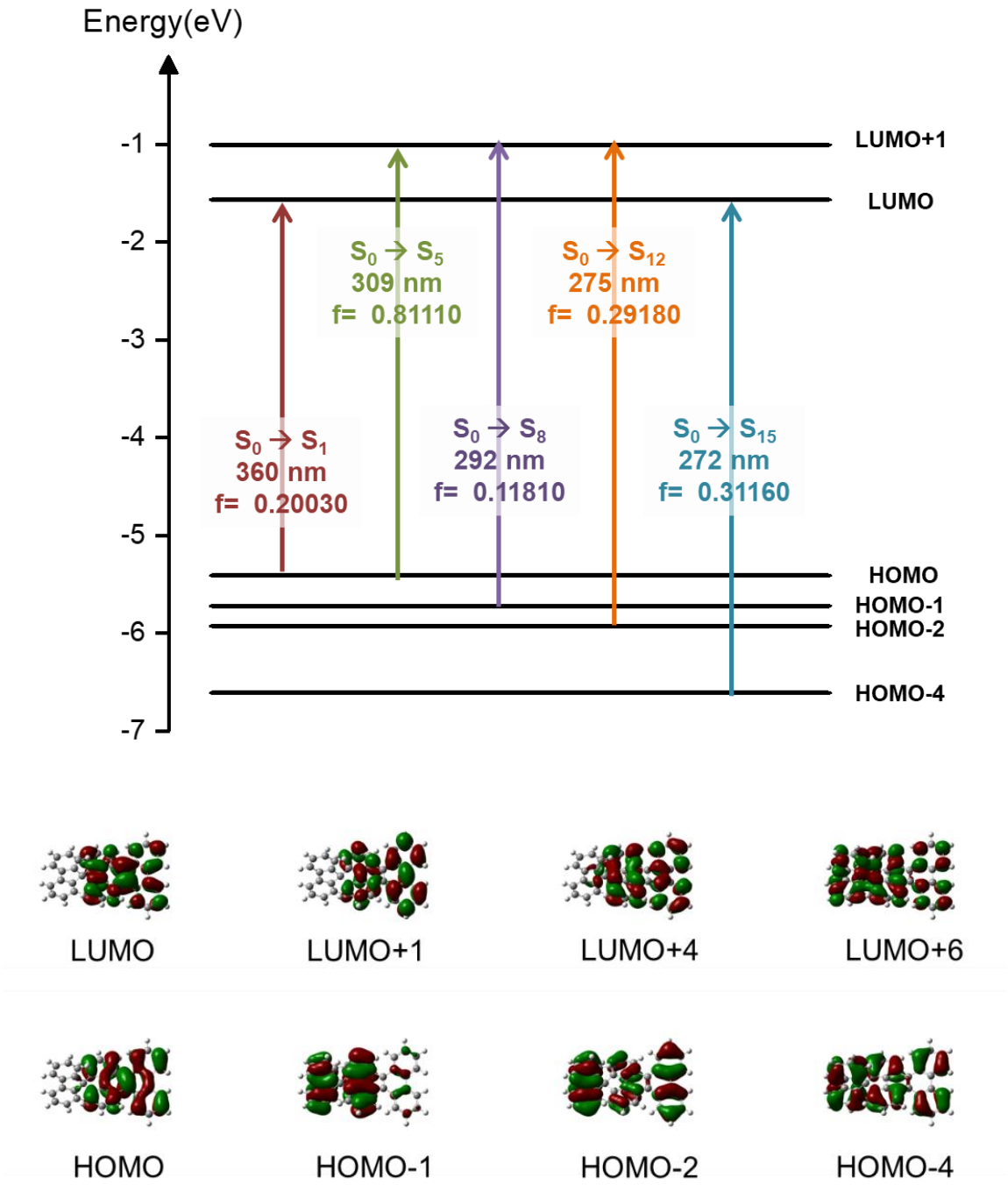


Figure S11 Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of **SFC** obtained by TD-DFT B3LYP/6-31G(d). For clarity purposes, only the major contributions (>10%) of each transition are shown.

For ***C*-SFC**, it's the S0→S4 (HOMO→LUMO+1) transition at λ = 311 nm with f = 0.7730.

Table S4 Major electronic transitions for ***C*-SFC** by TD-DFT method using B3LYP/6-31G(d).

	Energy (eV)	**Excitation (nm)**	**Oscillator strength (*f*)**	**Description**
1	3.4313	361.33	0.19450	H -> L 92.1%, H-1 -> L+1 5.5%
4	3.9780	311.67	0.77300	H -> L+1 44.6%, H-1 -> L 22.2%, H -> L+2 22.0%, H-2 -> L 6.4%
7	4.2934	288.78	0.18140	H-1 -> L+1 76.9%, H-2 -> L+1 8.3%
10	4.4591	278.05	0.28070	H-4 -> L 66.4%, H -> L+3 16.6%, H-1 -> L+2 7.8%
12	4.5184	274.40	0.13040	H-2 -> L+1 38.5%, H-5 -> L 31.1%, H-1 -> L+1 7.2%, H-7 -> L 5.7%
18	4.8467	255.81	0.10420	H-8 -> L 62.1%, H -> L+5 6.4%, H-2 -> L+2 6.2%, H-7 -> L 5.7%, H-2 -> L+1 5.5%
20	4.8708	254.55	0.15450	H-8 -> L 26.5%, H -> L+5 18.0%, H-2 -> L+1 12.6%, H-7 -> L 11.3%, H-2 -> L+2 10.5%, H-4 -> L+1 9.5%

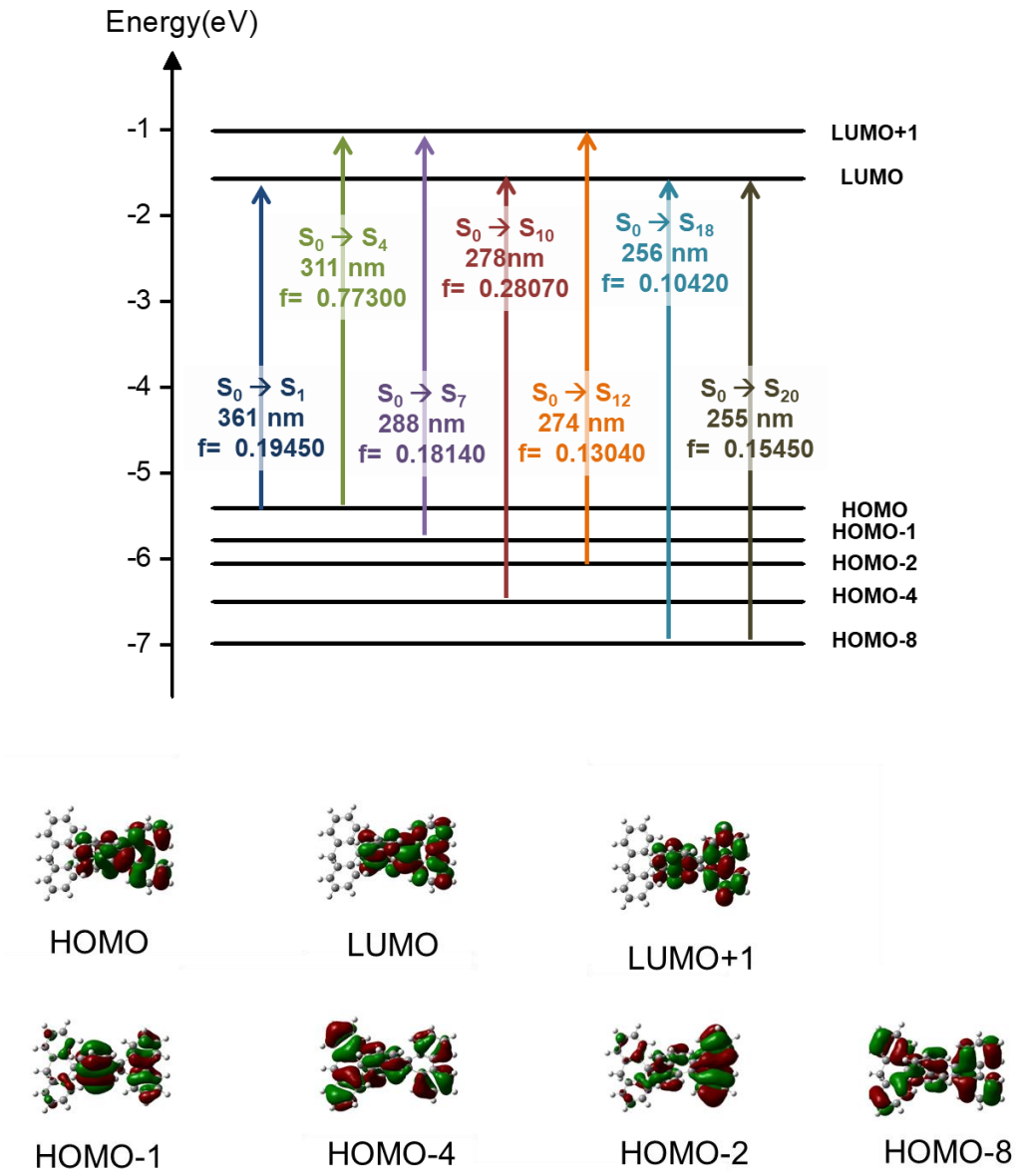


Figure S12 Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of ***C*-SFC** obtained by TD-DFT B3LYP/6-31G(d). For clarity purposes, only the major contributions (>10%) of each transition are shown.

For ***O*-SFC** exhibits the S0→S5 (HOMO→LUMO+1) transition at λ = 311 nm, boasting an oscillator strength of f = 0.8148;

Table S5 Major electronic transitions for ***O*-SFC** by TD-DFT method using B3LYP/6-31G(d).

	Energy (eV)	**Excitation (nm)**	**Oscillator strength (*f*)**	**Description**
1	3.4333	361.12	0.19830	H -> L 92.2%, H-2 -> L+1 5.5%
5	3.9847	311.15	0.81480	H -> L+1 47.8%, H-2 -> L 22.8%, H -> L+2 18.5%, H-3 -> L 6.5%
9	4.3156	287.29	0.18230	H-2 -> L+1 74.8%, H-3 -> L+1 9.7%
13	4.5062	275.14	0.29310	H-4 -> L 64.4%, H -> L+3 14.7%, H -> L+4 12.5%
14	4.5101	274.90	0.19680	H-3 -> L+1 49.7%, H -> L+5 19.8%, H-2 -> L+1 13.0%

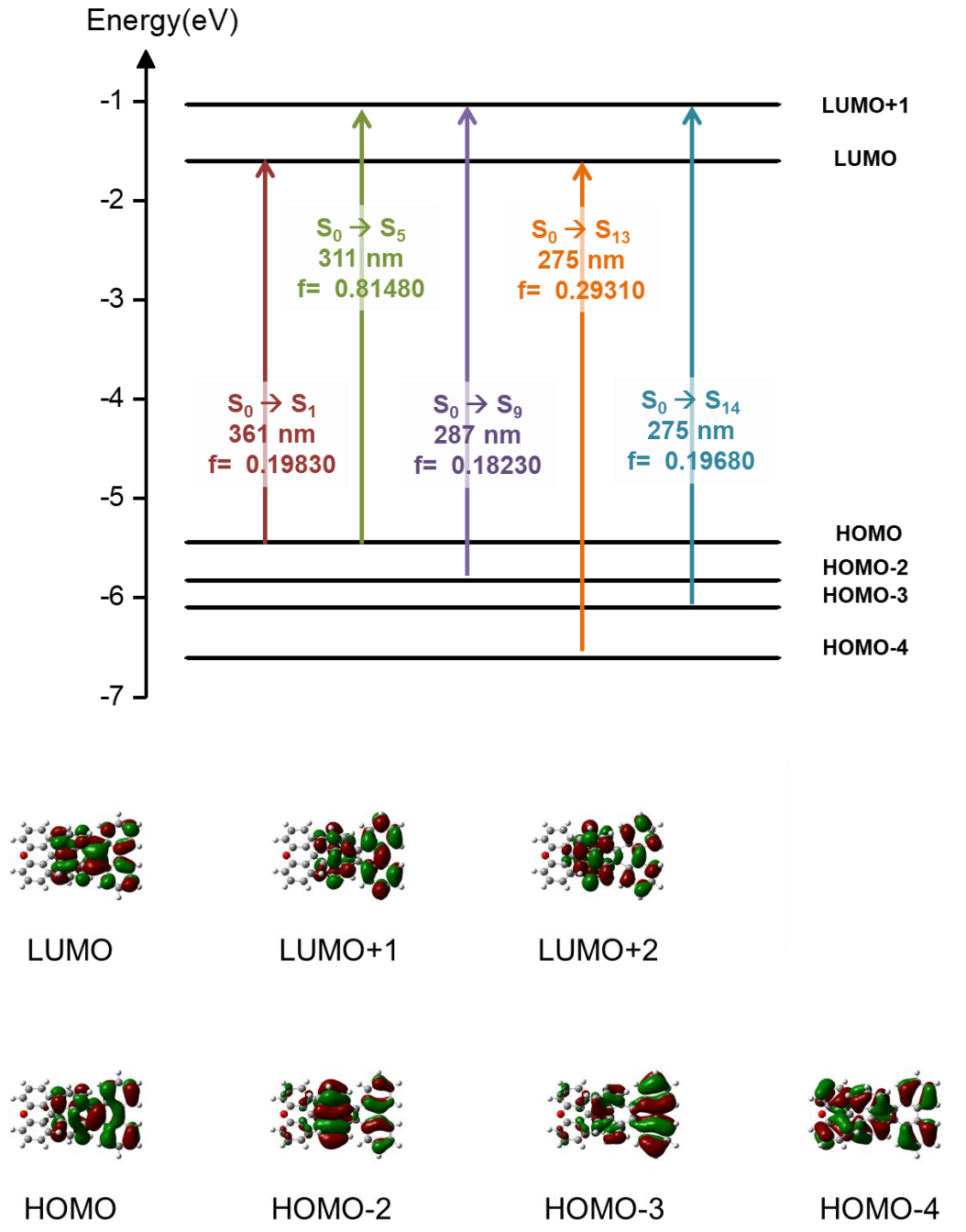


Figure S13 Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of ***O*-SFC** obtained by TD-DFT B3LYP/6-31G(d). For clarity purposes, only the major contributions (>10%) of each transition are shown.

***N*-SFC** shows the S0→S7 (HOMO-1→LUMO+1) transition at λ = 312 nm with a robust oscillator strength of f = 0.9270.

Table S6 Major electronic transitions for ***N*-SFC** by TD-DFT method using B3LYP/6-31G(d).

	Energy (eV)	**Excitation (nm)**	**Oscillator strength (*f*)**	**Description**
1	3.2351	383.25	0.00020	H -> L 99.3%
2	3.4301	361.46	0.18680	H-1 -> L 92.1%, H-2 -> L+1 5.7%
7	3.9674	312.51	0.92700	H-1 -> L+1 49.2%, H-2 -> L 26.8%, H-1 -> L+2 14.4%
11	4.1758	296.91	0.17950	H -> L+5 57.5%, H -> L+4 23.8%, H -> L+3 7.4%
13	4.3316	286.23	0.19110	H-2 -> L+1 70.5%, H-3 -> L+1 10.2%, H-2 -> L+2 8.4%
16	4.4835	276.53	0.25730	H-4 -> L 61.2%, H-3 -> L+1 11.5%, H-1 -> L+3 10.4%
18	4.5262	273.93	0.15070	H-3 -> L+1 49.9%, H-4 -> L 13.6%, H-2 -> L+1 6.6%, H-8 -> L 5.6%

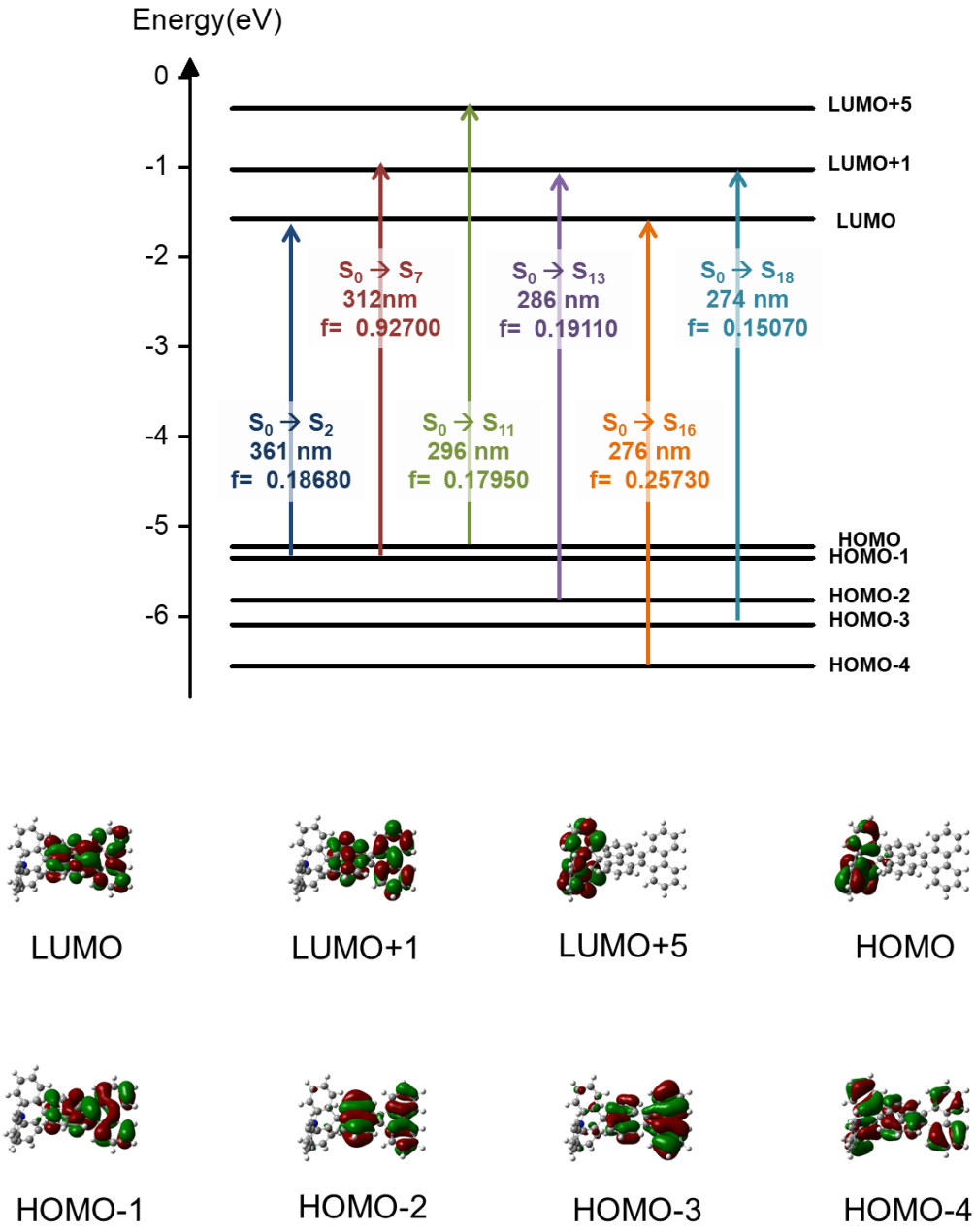
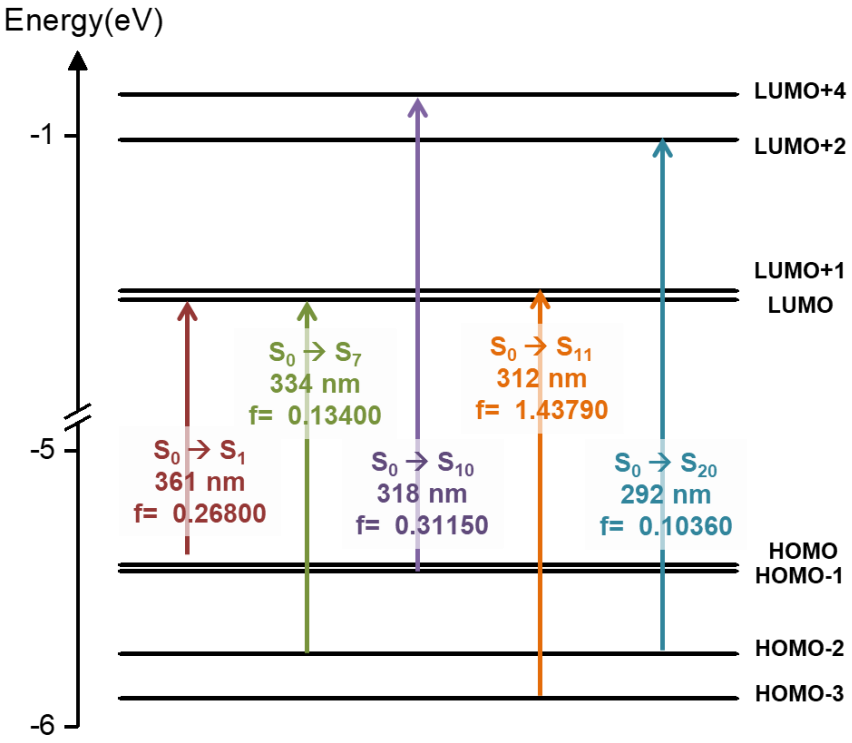


Figure S14 Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of ***N*-SFC** obtained by TD-DFT B3LYP/6-31G(d). For clarity purposes, only the major contributions (>10%) of each transition are shown.

SBC displays the unique S0→S11 (HOMO-3→LUMO+1) transition at λ = 312 nm, characterized by an exceptionally strong oscillator strength of f = 1.4379;

Table S7 Major electronic transitions for **SBC** by TD-DFT method using B3LYP/6-31G(d).

	Energy (eV)	Excitation (nm)	Oscillator strength (*f*)	Description
1	3.4316	361.30	0.26800	H -> L 76.7%, H-1 -> L+1 16.2%
7	3.7095	334.23	0.13400	H-2 -> L 27.4%, H-4 -> L 22.2%, H -> L+3 14.0%, H-3 -> L+1 11.1%, H-1 -> L+2 8.6%, H-1 -> L+4 6.6%
10	3.8924 eV	318.53	0.31150	H-1 -> L+4 23.3%, H-2 -> L 17.4%, H -> L+5 17.0%, H-5 -> L+1 14.8%, H-4 -> L 8.7%, H-1 -> L+2 8.4%, H-3 -> L+1 7.2%
11	3.9740	311.99	1.43790	H-3 -> L+1 55.5%, H-1 -> L+2 22.3%, H -> L+3 17.6%
20	4.2420	292.28	0.10360	H-2 -> L+2 79.5%, H-2 -> L+4 7.9%



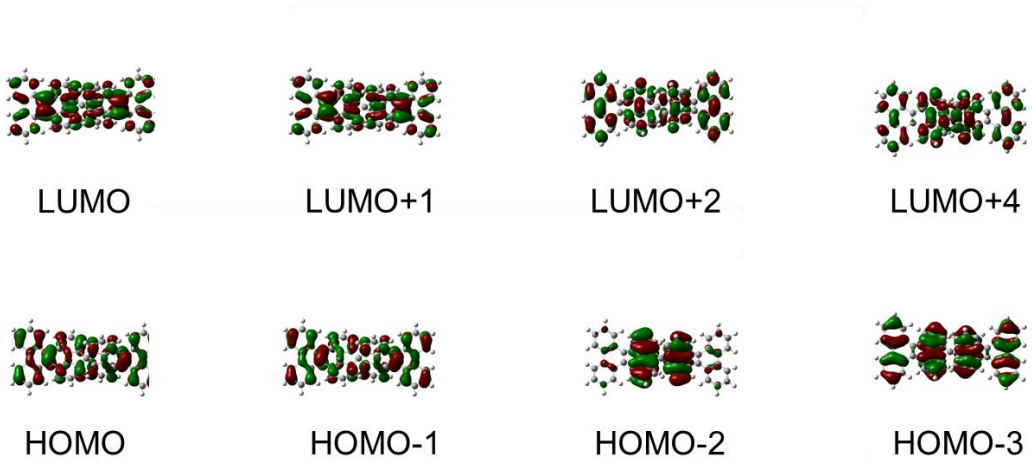


Figure S15 Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of **SBC** obtained by TD-DFT B3LYP/6-31G(d). For clarity purposes, only the major contributions (>10%) of each transition are shown.

***S*-SFC** undergoes the S0→S5 (HOMO→LUMO+1) transition at λ = 312 nm with a notably high f value of 0.8301.

Table S8 Major electronic transitions for ***S*-SFC** by TD-DFT method using B3LYP/6-31G(d).

	Energy (eV)	**Excitation (nm)**	**Oscillator strength (*f*)**	**Description**
1	3.4254	361.96	0.18850	H -> L 92.0%, H-2 -> L+1 5.7%
5	3.9648	312.71	0.83010	H -> L+1 52.8%, H-2 -> L 28.7%, H -> L+2 13.0%
10	4.3309	286.28	0.17160	H-2 -> L+1 64.8%, H-2 -> L+2 11.9%, H-3 -> L+1 11.5%
11	4.4152	280.81	0.10170	H-2 -> L+2 67.8%, H-2 -> L+1 10.9%, H -> L+5 6.0%
14	4.4808	276.70	0.19090	H-4 -> L 25.6%, H-3 -> L+1 22.9%, H-2 -> L+1 9.5%, H-1 -> L+3 9.2%, H -> L+5 7.3%, H -> L+3 5.9%
15	4.5245	274.03	0.18760	H-4 -> L 42.8%, H-3 -> L+1 22.7%, H -> L+5 14.8%

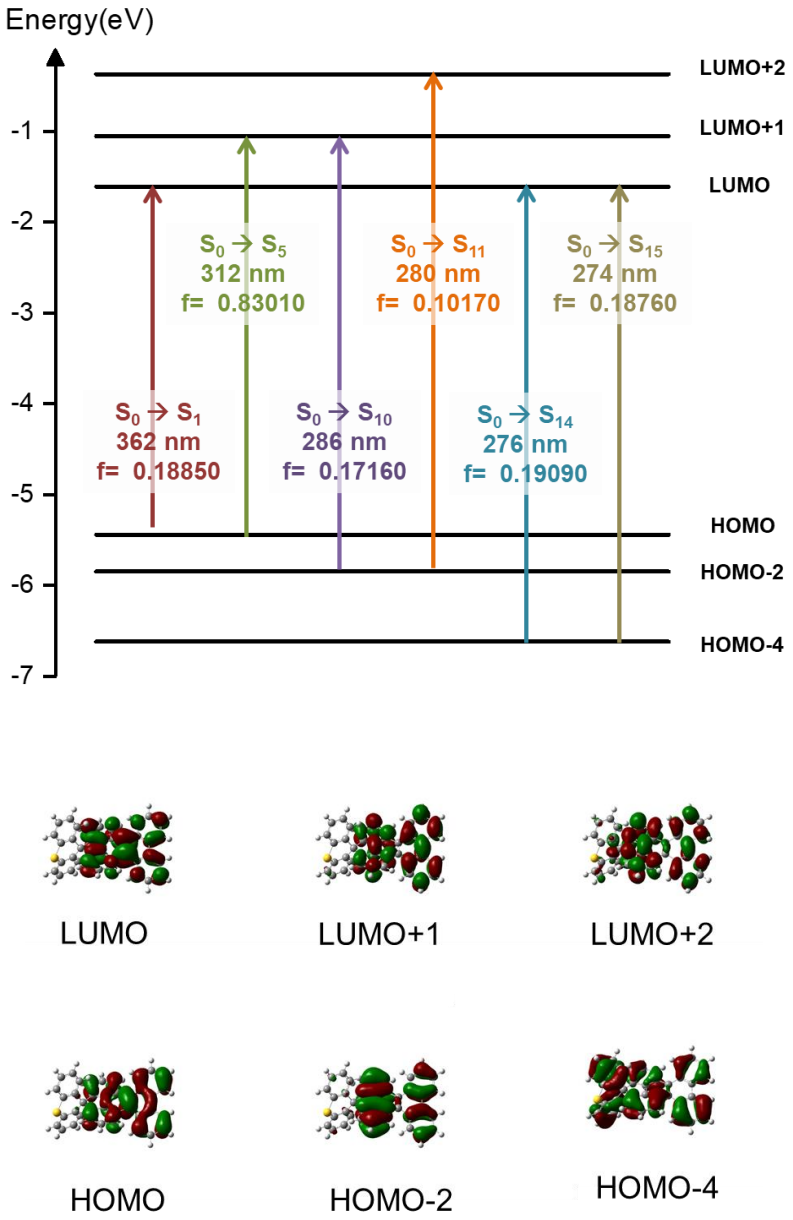


Figure S16 Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of ***S*-SFC** obtained by TD-DFT B3LYP/6-31G(d). For clarity purposes, only the major contributions (>10%) of each transition are shown.

Table S9 Major electronic transitions for **SBP** by TD-DFT method using B3LYP/6-31G(d).

	Energy (eV)	**Excitation (nm)**	**Oscillator strength (*f*)**	**Description**
9	4.4853	276.42	0.11150	H -> L+3 80.5%, H-3 -> L+3 7.4%
10	4.4853	276.42	0.11140	H -> L+2 80.5%, H-3 -> L+2 7.4%
13	4.6534	266.44	0.45260	H-3 -> L+1 45.5%, H-1 -> L+3 21.8%, H-2 -> L+2 21.8%
15	4.8412	256.10	0.11210	H-3 -> L+3 61.8%, H -> L+5 25.9%, H-3 -> L+5 5.4%
16	4.8412	256.10	0.11200	H-3 -> L+2 61.8%, H -> L+4 25.9%, H-3 -> L+4 5.4%
19	5.0887	243.65	0.35450	H -> L+5 47.3%, H-3 -> L+3 23.3%, H-4 -> L+3 14.5%
20	5.0887	243.65	0.35430	H -> L+4 47.3%, H-3 -> L+2 23.3%, H-4 -> L+2 14.5%

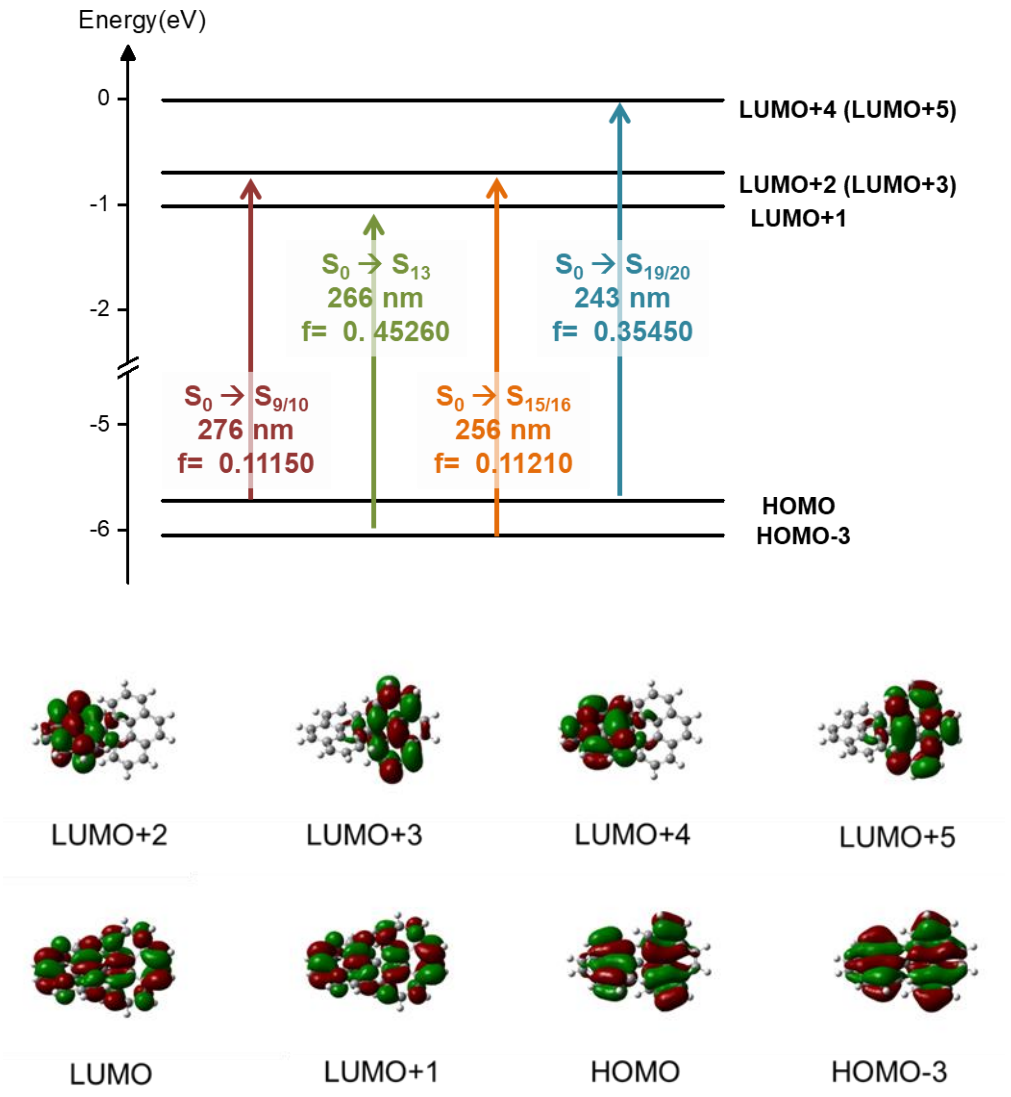


Figure S17 Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of **SBP** obtained by TD-DFT B3LYP/6-31G(d). For clarity purposes, only the major contributions (>10%) of each transition are shown.

5.2 Cartesian coordinates of optimized structures

Table S10 Cartesian coordinates of optimized structures calculated by B3LYP/6-31G(d) (**SFC, *C*-SFC, *O*-SFC, *S*-SFC, *N*-SFC, SBC, SBP**).

SFC

C	1.68735900	2.15621400	1.39510300	C	-3.51083700	-2.82732900	-0.19434700
C	1.50788500	1.01069800	0.64348000	C	-4.69068300	-3.54124500	-0.08258100
C	0.19534200	0.60706700	0.36029700	C	-5.91099100	-2.86186700	0.03684600
C	-0.97848900	1.28543900	0.69886600	C	-5.91801700	-1.47941100	0.07682100
C	-0.76454400	2.42742300	1.51738600	C	-5.91801100	1.47941700	-0.07681600
C	0.52863600	2.83115200	1.84565100	C	-5.91098000	2.86187300	-0.03684600
C	0.19534200	-0.60709000	-0.36026200	C	-4.69066900	3.54124700	0.08257900
C	-0.97849000	-1.28545300	-0.69884800	C	-3.51082500	2.82732600	0.19434700
C	-2.23158400	-0.66687700	-0.24076300	H	2.67411400	2.52707300	1.65781100
C	-2.23158200	0.66686900	0.24077300	H	-1.59747300	2.97773600	1.93780600
C	1.50788500	-1.01072300	-0.64344200	H	0.64993400	3.70448000	2.48125600
C	1.68735900	-2.15623400	-1.39507300	H	2.67411400	-2.52709500	-1.65777800
C	0.52863600	-2.83116300	-1.84563400	H	0.64993500	-3.70448800	-2.48124300
C	-0.76454500	-2.42743000	-1.51737700	H	-1.59747300	-2.97773400	-1.93780900
C	2.48724800	-0.00001000	0.00001500	H	6.87733600	0.70837600	-1.10494500
C	3.45725400	-0.64091400	0.99673000	H	6.36040100	2.02093300	-3.14874100
C	4.79124400	-0.39708300	0.61807600	H	4.01111700	2.44588500	-3.80860100
C	4.79122100	0.39710400	-0.61811200	H	2.13644100	1.56300600	-2.43169000
C	3.45721700	0.64091400	-0.99673100	H	2.13653100	-1.56302700	2.43172500
C	5.84447800	0.89203500	-1.38987300	H	4.01125900	-2.44587500	3.80858700
C	5.55048100	1.62981300	-2.53871200	H	6.36051800	-2.02088500	3.14866400
C	4.22340600	1.87011800	-2.91184000	H	6.87737700	-0.70832200	1.10485300
C	3.16640800	1.37525900	-2.14005500	H	-2.57653100	-3.37161100	-0.20529900
C	3.16648800	-1.37526300	2.14006300	H	-4.66271900	-4.62725000	-0.05859900
C	4.22351500	-1.87010500	2.91182000	H	-6.84186400	-3.41383100	0.13336800
C	5.55057500	-1.62977900	2.53865700	H	-6.86112700	-0.96791800	0.23384200
C	5.84453000	-0.89199700	1.38980900	H	-6.86112300	0.96792700	-0.23383400
C	-3.49099300	-1.41006800	-0.20925100	H	-6.84185000	3.41384000	-0.13336800
C	-4.72845000	-0.72709700	-0.03531900	H	-4.66270000	4.62725100	0.05859200
C	-4.72844700	0.72709800	0.03532600	H	-2.57651700	3.37160300	0.20529900
C	-3.49098900	1.41006400	0.20925600				

C-SFC

C	-1.56196700	2.05800100	1.69696100	C	3.46106000	-2.84050600	-0.55979200
C	-1.43004000	1.00334400	0.81254600	C	4.62091600	-3.59478000	-0.55234200
C	-0.13483000	0.60193400	0.45878900	C	5.86221200	-2.96781900	-0.37646300
C	1.06423500	1.20499200	0.85139300	C	5.91060900	-1.60013400	-0.17645500
C	0.89742400	2.24778800	1.80212900	C	5.99527000	1.35552700	0.01468200
C	-0.37799900	2.64474700	2.20120500	C	6.02934100	2.72353800	0.21547100
C	-0.18122900	-0.51751500	-0.40018000	C	4.83135300	3.41747600	0.43462500
C	0.96863100	-1.18050400	-0.83782200	C	3.63282000	2.72795900	0.48340700
C	2.24552000	-0.65494000	-0.33270000	H	-2.53351400	2.42138200	2.01999500
C	2.29185300	0.61240800	0.30108200	H	1.75313600	2.72233100	2.26689500
C	-1.50887100	-0.84949900	-0.70483800	H	-0.46366000	3.44032600	2.93685400
C	-1.72706100	-1.89210600	-1.58513100	H	-2.72469800	-2.20748100	-1.87707200
C	-0.59436700	-2.53802000	-2.13394600	H	-0.74970500	-3.32497400	-2.86749700
C	0.71358200	-2.21075600	-1.78275600	H	1.52552300	-2.72731600	-2.27999500
C	-2.45954900	0.10777500	0.07924800	H	-6.40451300	-2.08026300	1.43316400
C	-3.31970100	0.92811900	-0.89886800	H	-5.41817200	-2.81852500	3.58437100
C	-4.63844900	0.55095000	-1.19189000	H	-3.05759200	-2.20632200	4.12681800
C	-4.63390600	-1.06256600	0.76086400	H	-1.74480500	-0.85711200	2.53884200
C	-3.31517700	-0.70043500	1.07167600	H	-1.75414000	2.34272900	-1.33670400
C	-5.37722000	-1.81803500	1.67820000	H	-3.07540300	3.64317400	-2.95746200
C	-4.82541300	-2.23439300	2.88547600	H	-5.43596800	2.98890100	-3.44831900
C	-3.50695800	-1.88958700	3.18945200	H	-6.41344900	1.01353700	-2.31344500
C	-2.76574200	-1.12855700	2.29034600	H	-5.16454500	-1.52205600	-1.26032300
C	-2.77526200	2.04511100	-1.55196100	H	-6.33412500	-0.52391400	-0.43305600
C	-3.52123000	2.78187000	-2.46725200	H	2.51089500	-3.35354200	-0.61727200
C	-4.83957800	2.41487000	-2.74416900	H	4.56133000	-4.67502200	-0.65385300
C	-5.38639100	1.30667400	-2.10521200	H	6.77776100	-3.55269800	-0.36114400
C	-5.25491300	-0.67491700	-0.56027100	H	6.87049600	-1.13658700	0.02235400
C	3.48288000	-1.43115100	-0.41002000	H	6.92056400	0.84015300	-0.21765500
C	4.74222500	-0.80739200	-0.17962000	H	6.97454300	3.25722700	0.16754700
C	4.78595600	0.62813200	0.05959100	H	4.83481600	4.49922900	0.53758300
C	3.57165800	1.31975100	0.33380100	H	2.71507300	3.29270400	0.57383400

O-SFC

C	-1.63249200	1.95211100	1.66937800	C	3.54520900	1.37035000	0.39324600
C	-1.45326700	0.91657600	0.77255400	C	3.56507000	-2.77709900	-0.56513500
C	-0.14157300	0.55413800	0.43772700	C	4.74492900	-3.49950400	-0.54796900
C	1.03288600	1.18164800	0.86260300	C	5.96513700	-2.84176000	-0.33969300
C	0.81917700	2.20491200	1.82546500	C	5.97220600	-1.47658700	-0.11803300
C	-0.47389000	2.56150600	2.20526000	C	5.97210800	1.47683700	0.11821200
C	-0.14152200	-0.55427600	-0.43781500	C	5.96494200	2.84200800	0.33987800
C	1.03299600	-1.18170000	-0.86266800	C	4.74468300	3.49967500	0.54809600
C	2.28598500	-0.62932400	-0.32653800	C	3.56486800	2.77719600	0.56519700
C	2.28593000	0.62934700	0.32652800	H	-2.61935700	2.28477800	1.97924400
C	-1.45318200	-0.91677300	-0.77271300	H	1.65239200	2.69484600	2.31445900
C	-1.63229500	-1.95229100	-1.66958200	H	-0.59467800	3.34270300	2.95126800
C	-0.47363600	-2.56160000	-2.20543600	H	-2.61912600	-2.28499800	-1.97951500
C	0.81939400	-2.20493800	-1.82557700	H	-0.59434500	-3.34277400	-2.95148000
C	-2.44290000	-0.00014100	-0.00010900	H	1.65266000	-2.69480100	-2.31455500
C	-3.31424900	0.81492300	-0.95814000	H	-6.58180500	-1.43990800	1.69550300
C	-4.70983700	0.76823400	-0.90302000	H	-5.51517100	-2.90340600	3.41880200
C	-4.70981400	-0.76807900	0.90322700	H	-3.02211700	-3.01900000	3.55514600
C	-3.31422500	-0.81519400	0.95795500	H	-1.64734500	-1.69088900	1.98984300
C	-5.50247600	-1.51479500	1.78300300	H	-1.64739400	1.68998700	-1.99060300
C	-4.89937600	-2.32429700	2.73633300	H	-3.02220100	3.01842400	-3.55559800
C	-3.50338000	-2.38920800	2.81273200	H	-5.51525100	2.90373000	-3.41843200
C	-2.73102200	-1.64130800	1.93128000	H	-6.58184600	1.44065600	-1.69475100
C	-2.73106900	1.64077000	-1.93170600	H	2.63080200	-3.31526300	-0.64789400
C	-3.50344600	2.38886400	-2.81297700	H	4.71701900	-4.57919800	-0.66720800
C	-4.89944000	2.32443600	-2.73613500	H	6.89597200	-3.40166000	-0.31640600
C	-5.50251900	1.51518400	-1.78257800	H	6.91521000	-0.99018700	0.10535200
O	-5.40306900	0.00015500	0.00017800	H	6.91515400	0.99049600	-0.10512700
C	3.54531300	-1.37025200	-0.39319300	H	6.89574400	3.40196700	0.31664300
C	4.78266000	-0.71606600	-0.13057100	H	4.71670000	4.57936700	0.66734200
C	4.78261000	0.71624100	0.13068500	H	2.63056100	3.31530100	0.64791200

S-SFC

C	1.34386900	2.15535100	1.72514700	C	-3.74742500	1.28390300	0.29002800
C	1.25059900	1.08539900	0.85311900	C	-3.52800700	-2.88534900	-0.54056100
C	-0.02764000	0.64948900	0.48298900	C	-4.67037900	-3.66583500	-0.53957500
C	-1.24634500	1.23140700	0.84738500	C	-5.92822700	-3.06489000	-0.39230200
C	-1.11958700	2.28975000	1.78660400	C	-6.01096600	-1.69592500	-0.21345800
C	0.13907800	2.72195300	2.20181900	C	-6.16592900	1.25923000	-0.06616800
C	0.05870700	-0.47966200	-0.35977300	C	-6.23438300	2.62876300	0.11440600
C	-1.07052500	-1.17214700	-0.80590000	C	-5.05604500	3.35323000	0.34146100
C	-2.36659200	-0.66922400	-0.32756500	C	-3.84296400	2.69228500	0.41821000
C	-2.45191700	0.60520200	0.28666400	H	2.30145500	2.54527800	2.05886800
C	1.39768200	-0.78754300	-0.64082300	H	-1.99396600	2.75033400	2.23002800
C	1.65062000	-1.83688600	-1.50554100	H	0.19445600	3.52916000	2.92750300
C	0.53817000	-2.51141100	-2.06174100	H	2.65841200	-2.13364600	-1.77678500
C	-0.78108900	-2.20779200	-1.73418200	H	0.72124200	-3.30363100	-2.78305600
C	2.31381400	0.20475200	0.14937300	H	-1.57524700	-2.74668700	-2.23639500
C	3.15939900	-0.57656100	1.17759300	H	6.12562500	1.01554700	-2.53591200
C	4.41913600	-1.10995200	0.85876400	H	5.17748300	3.10262200	-3.48428600
C	4.42187800	0.61495100	-1.28212800	H	2.93123400	3.88736800	-2.71681100
C	3.16160400	1.04197200	-0.83158700	H	1.68578000	2.59210500	-1.04397700
C	5.14309900	1.36035800	-2.22537400	H	1.68091900	-0.44954600	2.73422300
C	4.61248500	2.53303500	-2.75164800	H	2.92074200	-1.81030700	4.35931000
C	3.36134100	2.97248600	-2.31923800	H	5.16641200	-2.73172400	3.76046700
C	2.65699700	2.23695000	-1.36887400	H	6.11985300	-2.25209900	1.52100300
C	2.65171800	-0.84539700	2.45860600	H	-2.56563700	-3.37719600	-0.57593000
C	3.35286300	-1.61813900	3.38135400	H	-4.58475700	-4.74575500	-0.62395200
C	4.60377700	-2.13660200	3.04653900	H	-6.83032300	-3.67037100	-0.38233400
C	5.13738000	-1.87359800	1.78964700	H	-6.98421300	-1.25180900	-0.03659600
S	5.16906400	-0.90501000	-0.74033800	H	-7.07552500	0.71947000	-0.30488200
C	-3.58446700	-1.47485400	-0.41233300	H	-7.19062100	3.13980000	0.04443400
C	-4.86098500	-0.87674300	-0.21030200	H	-5.08587500	4.43594700	0.42852200
C	-4.94115500	0.56065900	0.00741500	H	-2.93998600	3.27960100	0.51367800

N-SFC

C	-0.09320600	-3.09893200	1.04935700	C	4.63048700	-0.92476900	-0.25213600
C	-0.25299500	-1.80153400	0.59591800	C	3.71131000	3.17716900	0.41740200
C	0.90001700	-1.05088300	0.33490800	C	4.71965600	4.10035900	0.62998700
C	2.22298000	-1.49800800	0.41461400	C	6.06077500	3.71469400	0.49748900
C	2.35510000	-2.81268700	0.93662700	C	6.36300900	2.40081400	0.18873700
C	1.22599800	-3.57147500	1.24025500	C	6.96643000	-0.36026400	-0.70123000
C	0.55772300	0.25974400	-0.06195500	C	7.25489900	-1.67785500	-1.00736700
C	1.51911200	1.24647800	-0.29891800	C	6.22754800	-2.63116100	-0.98359900
C	2.91866600	0.84875500	-0.08872500	C	4.94572600	-2.25629500	-0.62192000
C	3.25626500	-0.52113600	0.04410300	H	-0.94150900	-3.73880300	1.27576100
C	-0.83498700	0.40405700	-0.15260300	H	3.33036600	-3.23326300	1.14958900
C	-1.32839600	1.61891600	-0.59112500	H	1.36819700	-4.57006400	1.64513600
C	-0.39237100	2.62242000	-0.93648400	H	-2.38923600	1.81740200	-0.69770600
C	0.98404100	2.46354300	-0.79921300	H	-0.76714100	3.56292900	-1.33188200
C	-1.50029900	-0.93860600	0.29401700	H	1.63247300	3.26791600	-1.12463500
C	-2.38633500	-0.74580400	1.53723600	H	-5.62224300	-1.55937300	-1.83584700
C	-3.73943800	-0.40651400	1.35870600	H	-4.71245600	-3.18961800	-3.46915700
C	-3.72287600	-1.18179000	-0.90155300	H	-2.28478600	-3.76926200	-3.41198900
C	-2.36881100	-1.55321200	-0.81725800	H	-0.82728700	-2.77078300	-1.68802700
C	-4.56439700	-1.80056200	-1.83584300	H	-0.86115900	-1.16775700	2.99061600
C	-4.05111100	-2.72228400	-2.74472800	H	-2.34451400	-0.90417600	4.94644400
C	-2.69665500	-3.05420200	-2.70550400	H	-4.76999600	-0.42075700	4.60529900
C	-1.87231500	-2.48459500	-1.73632900	H	-5.65207000	-0.13890700	2.30405200
C	-1.90535500	-0.91564400	2.84042200	H	-4.89531600	0.48818800	-2.49867800
C	-2.74422400	-0.77427900	3.94473500	H	-5.98415200	2.54438400	-3.20138000
C	-4.09758700	-0.49343500	3.75490800	H	-6.58971800	4.31018400	-1.54046300
C	-4.59543900	-0.32533800	2.46535900	H	-6.00546500	3.93924600	0.86053300
N	-4.23725700	-0.23336500	0.03259800	H	-4.91597800	1.88888500	1.57933900
C	-4.86747600	0.97186200	-0.38496700	H	2.68873900	3.47640900	0.60217800
C	-5.16161600	1.21438500	-1.74299900	H	4.46720000	5.11445800	0.92764100
C	-5.77427200	2.40007300	-2.14445800	H	6.85962100	4.43058200	0.67035900
C	-6.10651400	3.39122200	-1.22233900	H	7.40434400	2.10069900	0.15264200
C	-5.78621200	3.17668300	0.11730300	H	7.75550000	0.37867000	-0.78565300
C	-5.17351000	1.99666100	0.53463900	H	8.26279000	-1.96095700	-1.29806600
C	3.98837400	1.83700500	0.04815100	H	6.42569700	-3.65867300	-1.27643300
C	5.35334600	1.43911800	-0.03311400	H	4.15470100	-2.99069700	-0.68835700
C	5.66730200	0.04842200	-0.32875700				

SBC

C	2.29019800	0.51659600	0.48096400	C	-0.79770100	1.81053200	-1.82138600
C	3.46384200	1.10734300	0.95619800	C	-1.95650600	2.37382700	-2.40554200
C	4.71705400	0.60034300	0.37711800	C	-3.24964800	2.04889400	-1.99903600
C	4.71705400	-0.60034300	-0.37711800	C	-8.40341500	-1.46178400	0.24049300
C	3.46384200	-1.10734300	-0.95619800	C	-8.39630600	-2.80401500	0.57397500
C	2.29019800	-0.51659600	-0.48096400	C	-7.17594500	-3.44250900	0.83490300
C	5.97640600	1.33323500	0.50469100	C	-5.99610500	-2.72120400	0.79177900
C	7.21381000	0.70288300	0.18944400	C	-5.99610500	2.72120400	-0.79177900
C	7.21381000	-0.70288300	-0.18944400	C	-7.17594500	3.44250900	-0.83490300
C	5.97640600	-1.33323500	-0.50469100	C	-8.39630600	2.80401500	-0.57397500
C	5.99610500	2.72120400	0.79177900	C	-8.40341500	1.46178400	-0.24049300
C	7.17594500	3.44250900	0.83490300	C	0.00000000	0.00000000	0.00000000
C	8.39630600	2.80401500	0.57397500	H	5.06182600	3.25080800	0.91802700
C	8.40341500	1.46178400	0.24049300	H	7.14802600	4.50873800	1.04251900
C	8.40341500	-1.46178400	-0.24049300	H	9.32717100	3.36385000	0.59755300
C	8.39630600	-2.80401500	-0.57397500	H	9.34663200	0.99549000	-0.02143500
C	7.17594500	-3.44250900	-0.83490300	H	9.34663200	-0.99549000	0.02143500
C	5.99610500	-2.72120400	-0.79177900	H	9.32717100	-3.36385000	-0.59755300
C	0.97773400	0.85119300	0.84333900	H	7.14802600	-4.50873800	-1.04251900
C	0.79770100	1.81053200	1.82138600	H	5.06182600	-3.25080800	-0.91802700
C	1.95650600	2.37382700	2.40554200	H	-0.18893500	2.11737800	2.15698400
C	3.24964800	2.04889400	1.99903600	H	1.83508100	3.09178800	3.21244700
C	3.24964800	-2.04889400	-1.99903600	H	4.08253100	2.49708200	2.52702300
C	1.95650600	-2.37382700	-2.40554200	H	4.08253100	-2.49708200	-2.52702300
C	0.79770100	-1.81053200	-1.82138600	H	1.83508100	-3.09178800	-3.21244700
C	0.97773400	-0.85119300	-0.84333900	H	-0.18893500	-2.11737800	-2.15698400
C	-7.21381000	-0.70288300	0.18944400	H	-4.08253100	-2.49708200	2.52702300
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C	-7.21381000	0.70288300	-0.18944400	H	-4.08253100	2.49708200	-2.52702300
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C	-0.79770100	-1.81053200	1.82138600	H	-9.32717100	3.36385000	-0.59755300
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C	-0.97773400	0.85119300	-0.84333900				

SBP

C	-3.38624200	0.00000000	1.98784800	C	0.00000000	0.68873300	-4.69103600
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C	0.00000000	-0.70422500	-2.28906800	H	0.00000000	-4.46607100	-1.86317600
C	0.00000000	-1.45921200	-3.46722800	H	0.00000000	-3.53509400	-4.13363100
C	0.00000000	-0.68873300	-4.69103600				

6. X–ray data

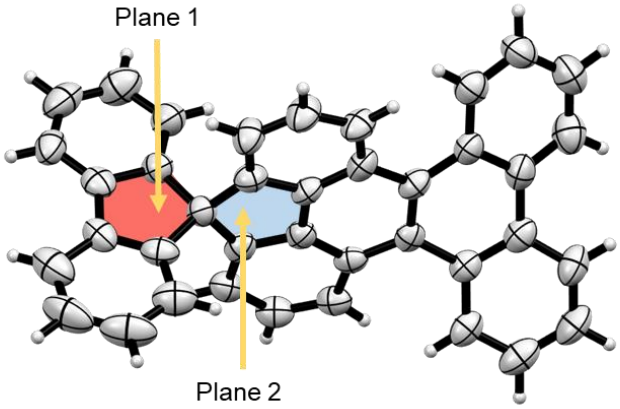

Figure S18 Plane selection for dihedral angles of the spiral part: represented by **SFC**

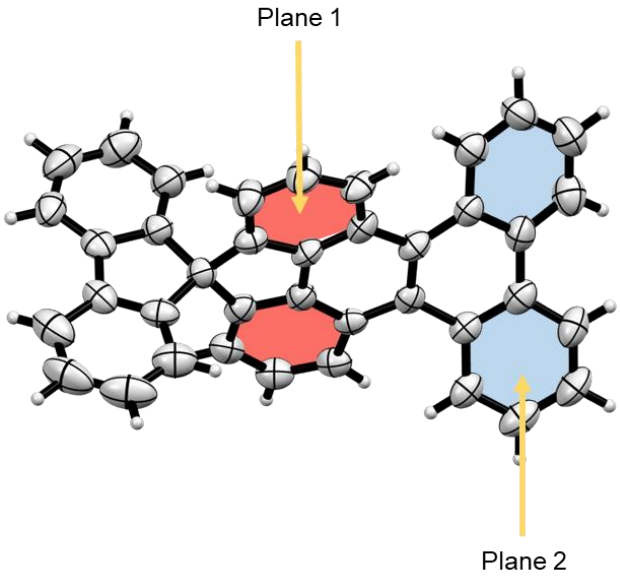

Figure S19 Plane selection for DBC partial dihedral angles: represented by **SFC**

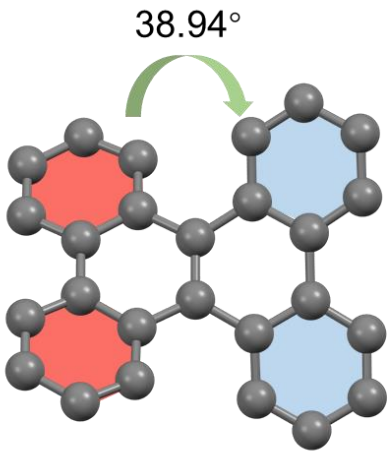

Figure S20 Dihedral angle of the **DBC** (See CCDC: 860843)

Table S11 Crystallographic data and structure refinement details for **SFC**.

2376775 (CCDC)	**SFC**
Empirical formula	$C_{39}H_{22}$
Formula weight	490.56
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.705(2)
b/Å	12.2325(19)
c/Å	10.991(2)
α/°	90
β/°	107.73(2)
γ/°	90
Volume/Å^3	1242.8(5)
Z	2
ρ_{calc}g/cm^3	1.311
μ/mm^{-1}	0.074
F(000)	512
Crystal size/mm^3	0.02 × 0.01 × 0.01
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.406 to 50.052
Index ranges	-11 ≤ h ≤ 10, -14 ≤ k ≤ 11, -11 ≤ l ≤ 13
Reflections collected	7932
Independent reflections	3628 [R_{int} = 0.0821, R_{sigma} = 0.1237]
Data/restraints/parameters	3628/1/353
Goodness-of-fit on F^2	0.982
Final R indexes [I>=2σ (I)]	R_1 = 0.0666, wR_2 = 0.1636
Final R indexes [all data]	R_1 = 0.1110, wR_2 = 0.1934
Largest diff. peak/hole / e Å^{-3}	0.27/-0.23
Flack parameter	10.0(10)

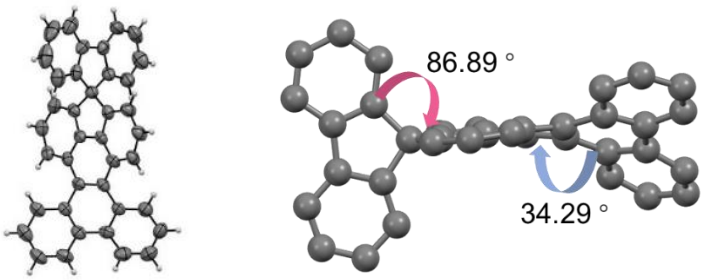

Figure S21 The thermal ellipsoid plot (left, at 50% probability) and dihedral angle (right) for **SFC**. Solvent: $CH_3OH/CHCl_3$.

Table S12 Crystallographic data and structure refinement details for ***C*-SFC**.

2376798 (CCDC)	***C*-SFC**
Empirical formula	$C_{40}H_{24}$
Formula weight	504.59
Temperature/K	100.00(12)
Crystal system	triclinic
Space group	P-1
a/Å	12.1966(2)
b/Å	15.0518(2)
c/Å	15.8144(2)
α/°	74.5940(10)
β/°	67.6580(10)
γ/°	88.5750(10)
Volume/Å^3	2579.34(7)
Z	4
ρ_{calc}g/cm^3	1.299
μ/mm^{-1}	0.356
F(000)	1056
Crystal size/mm^3	0.05 × 0.05 × 0.03
Radiation	Ga Kα (λ = 1.3405)
2Θ range for data collection/°	5.314 to 120.482
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 19, -20 ≤ l ≤ 20
Reflections collected	32363
Independent reflections	11475 [R_{int} = 0.0314, R_{sigma} = 0.0361]
Data/restraints/parameters	11475/0/729
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0407, wR_2 = 0.1025
Final R indexes [all data]	R_1 = 0.0473, wR_2 = 0.1063
Largest diff. peak/hole / e Å^{-3}	0.32/-0.22

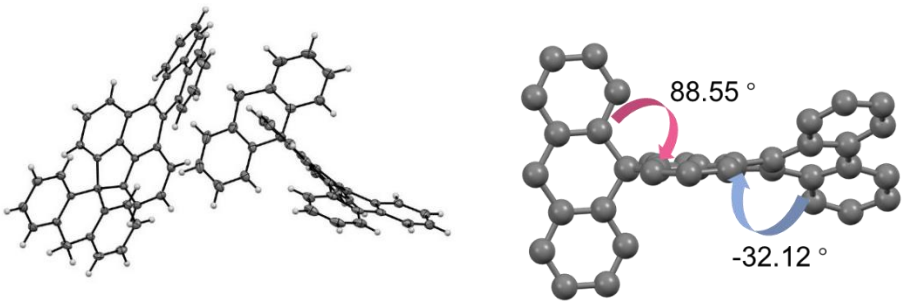

Figure S22 The thermal ellipsoid plot (left, at 50% probability) and dihedral angle (right) for ***C*-SFC**. Solvent: EtOAc/CH_2Cl_2.

Table S13 Crystallographic data and structure refinement details for ***O*-SFC**.

2376799 (CCDC)	***O*-SFC**
Empirical formula	$C_{39}H_{22}O$
Formula weight	506.56
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.6353(8)
b/Å	12.3817(8)
c/Å	10.9952(9)
α/°	90
β/°	105.922(8)
γ/°	90
Volume/Å^3	1261.42(17)
Z	2
ρ_{calc}g/cm^3	1.334
μ/mm^{-1}	0.078
F(000)	528
Crystal size/mm^3	0.05 × 0.04 × 0.02
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.976 to 58.766
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 15, -12 ≤ l ≤ 15
Reflections collected	9958
Independent reflections	4976 [R_{int} = 0.0469, R_{sigma} = 0.0665]
Data/restraints/parameters	4976/1/362
Goodness-of-fit on F^2	1
Final R indexes [I>=2σ (I)]	R_1 = 0.0469, wR_2 = 0.1044
Final R indexes [all data]	R_1 = 0.0712, wR_2 = 0.1143
Largest diff. peak/hole / e Å^{-3}	0.13/-0.15
Flack parameter	-2.4(10)

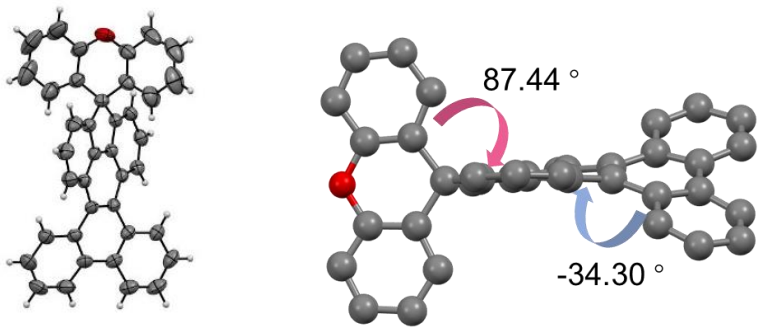

Figure S23 The thermal ellipsoid plot (left, at 50% probability) and dihedral angle (right) for ***O*-SFC**. Solvent: CH_3OH/CH_2Cl_2.

Table S14 Crystallographic data and structure refinement details for **SBC**.

2376797 (CCDC)	**SBC**
Empirical formula	$C_{53}H_{28}$
Formula weight	664.75
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.63(2)
b/Å	13.920(17)
c/Å	17.22(2)
α/°	90
β/°	114.31(3)
γ/°	90
Volume/Å^3	3415(7)
Z	4
ρ_{calc}g/cm^3	1.293
μ/mm^{-1}	0.073
F(000)	1384
Crystal size/mm^3	0.05 × 0.04 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.09 to 49.872
Index ranges	-18 ≤ h ≤ 18, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20
Reflections collected	22223
Independent reflections	5747 [R_{int} = 0.1266, R_{sigma} = 0.2411]
Data/restraints/parameters	5747/0/478
Goodness-of-fit on F^2	0.957
Final R indexes [I>=2σ (I)]	R_1 = 0.0650, wR_2 = 0.1091
Final R indexes [all data]	R_1 = 0.2694, wR_2 = 0.1728
Largest diff. peak/hole / e Å^{-3}	0.19/-0.21

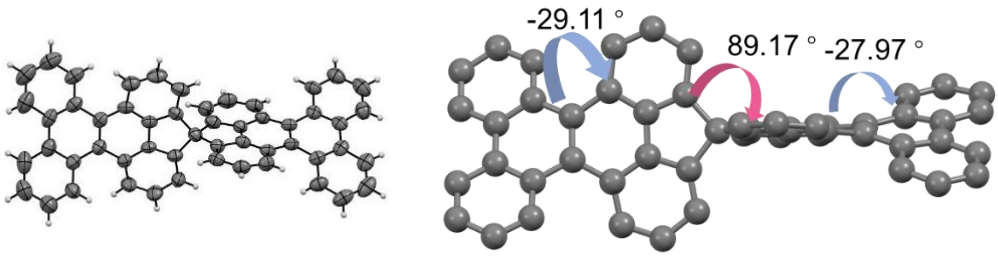

Figure S24 The thermal ellipsoid plot (left, at 50% probability) and dihedral angle (right) for **SBC**. Solvent: CH_3OH/CH_2Cl_2.

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NMR Spectrogram

spiro[benzo[*p*]indeno[7,1,2-*ghi*] chrysene-4,9'-fluorene] (SFC)

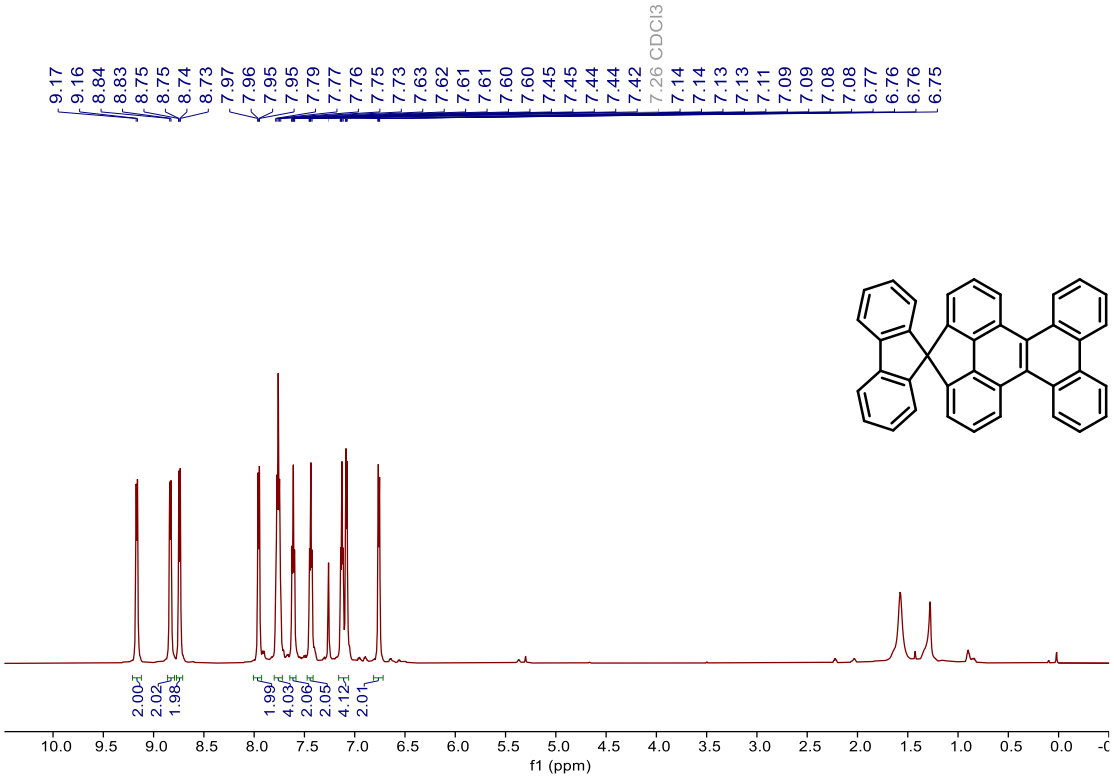

Figure S25 ^{1}H NMR spectrum (600 MHz, Chloroform-*d*) of **SFC**

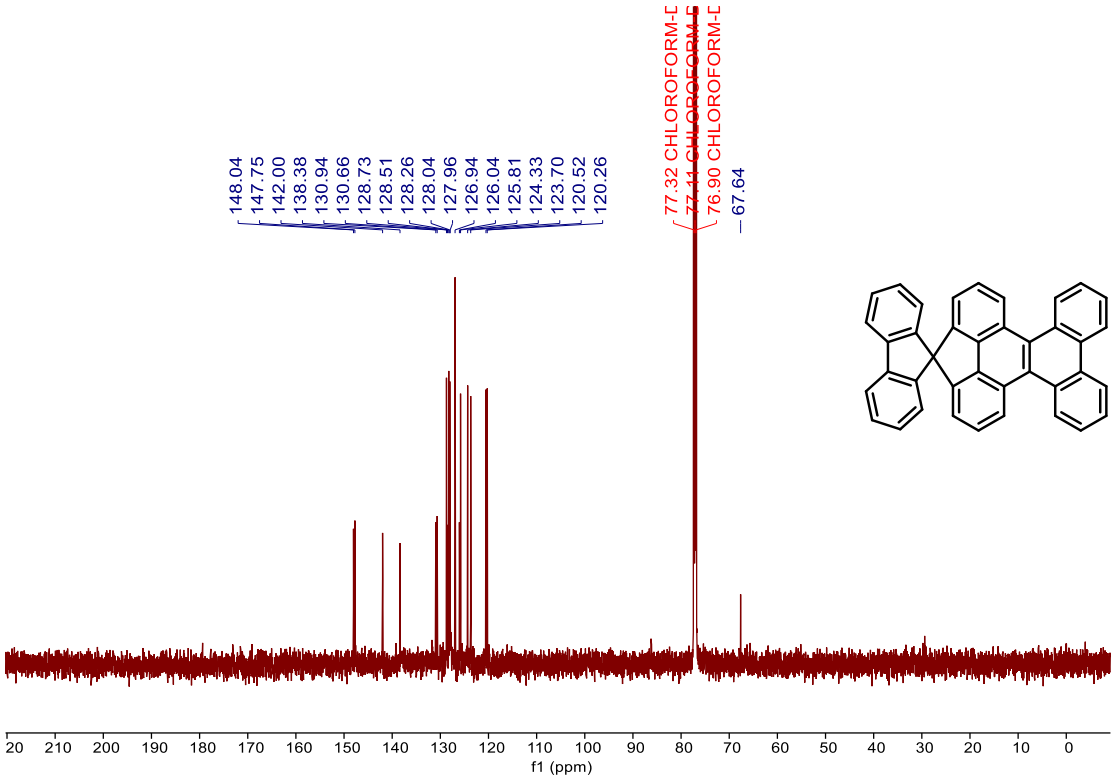

Figure S26 ^{13}C NMR spectrum (151 MHz, Chloroform-*d*) of **SFC**

10*H*-spiro[anthracene-9, 4'-benzo[*p*]indeno[7,1,2-*ghi*] chrysene] (*C*-SFC)

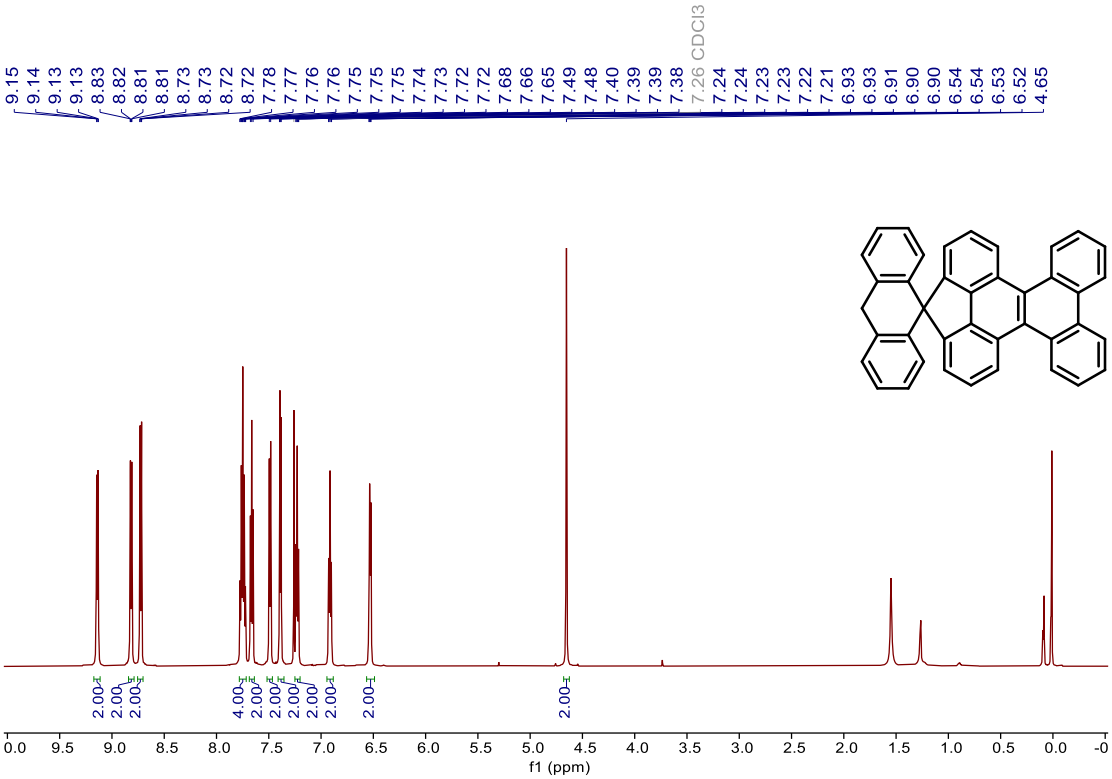

Figure S27 ^{1}H NMR spectrum (600 MHz, Chloroform-*d*) of ***C*-SFC**

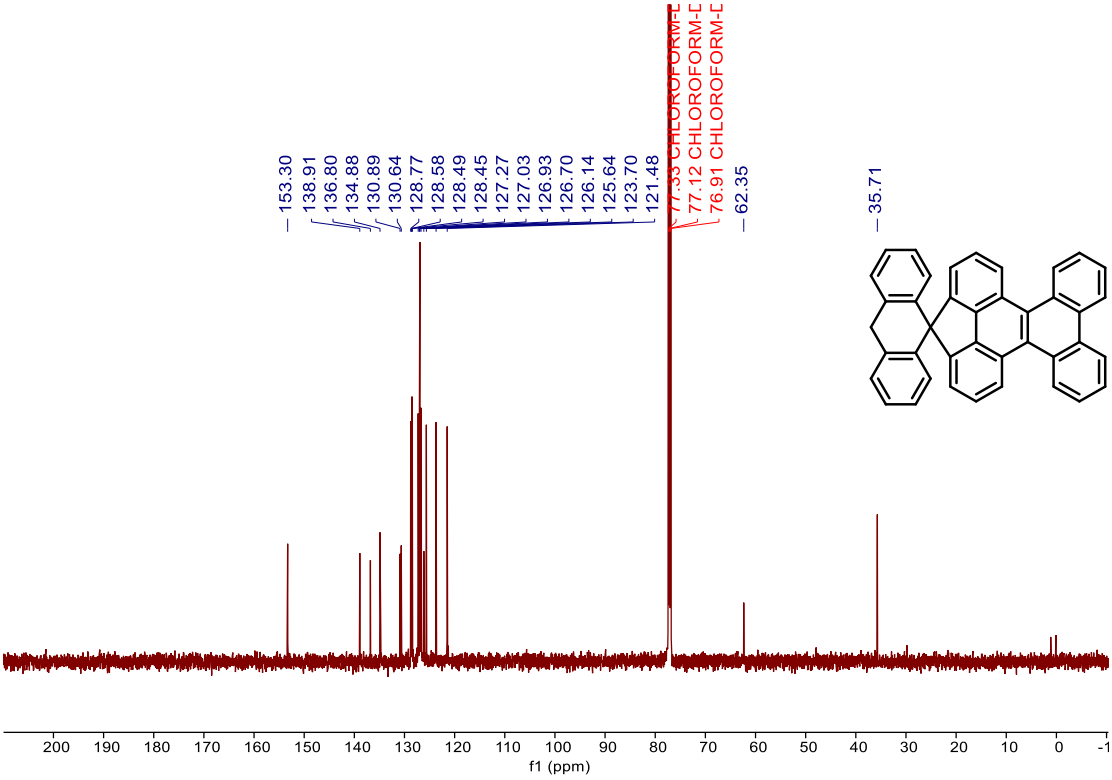

Figure S28 ^{13}C NMR spectrum (151 MHz, Chloroform-*d*) of ***C*-SFC**

spiro[benzo[*p*]indeno[7,1,2-*ghi*] chrysene-4,9'-xanthene] (O-SFC)

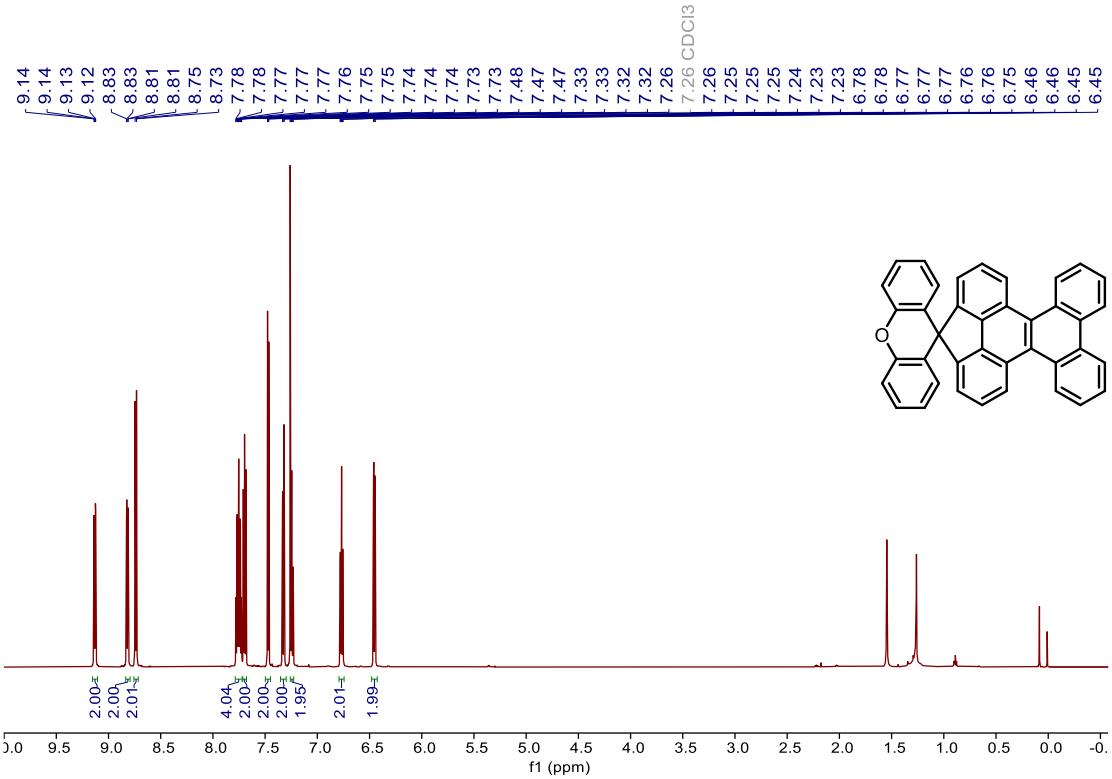

Figure S29 ^{1}H NMR spectrum (600 MHz, Chloroform-*d*) of ***O*-SFC**

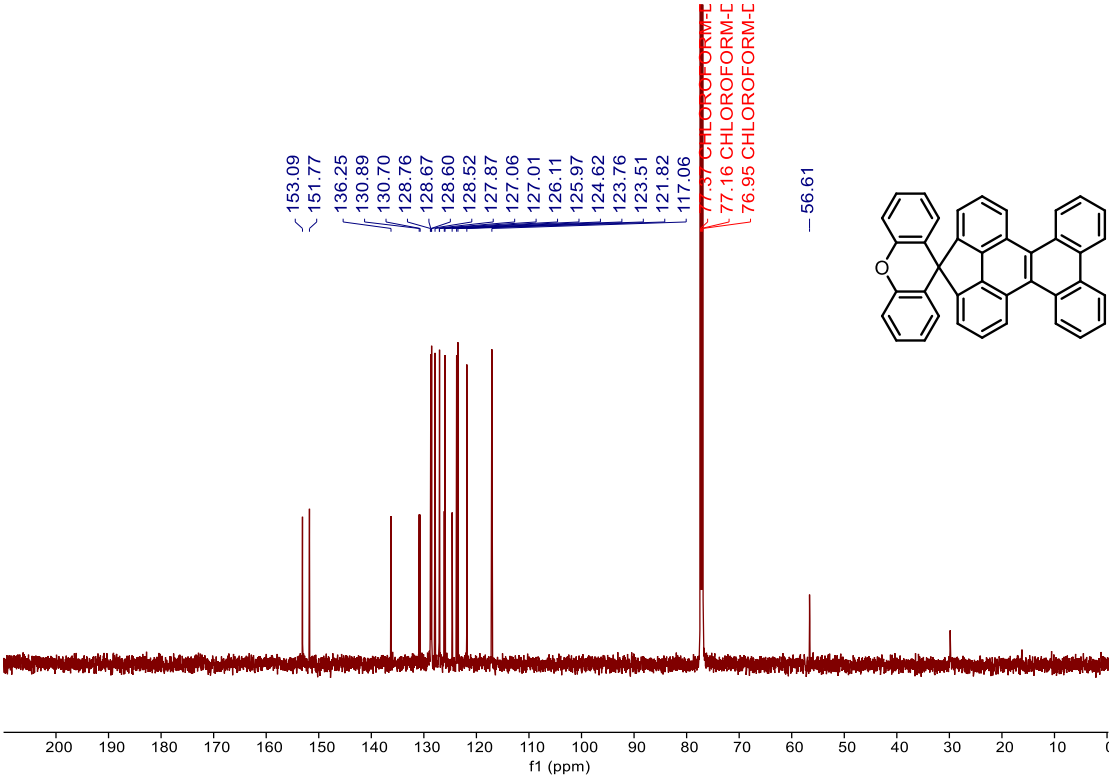

Figure S30 ^{13}C NMR spectrum (151 MHz, Chloroform-*d*) of ***O*-SFC**

spiro[benzo[*p*]indeno[7,1,2-*ghi*] chrysene-4,9'-thioxanthene] (*S*-SFC)

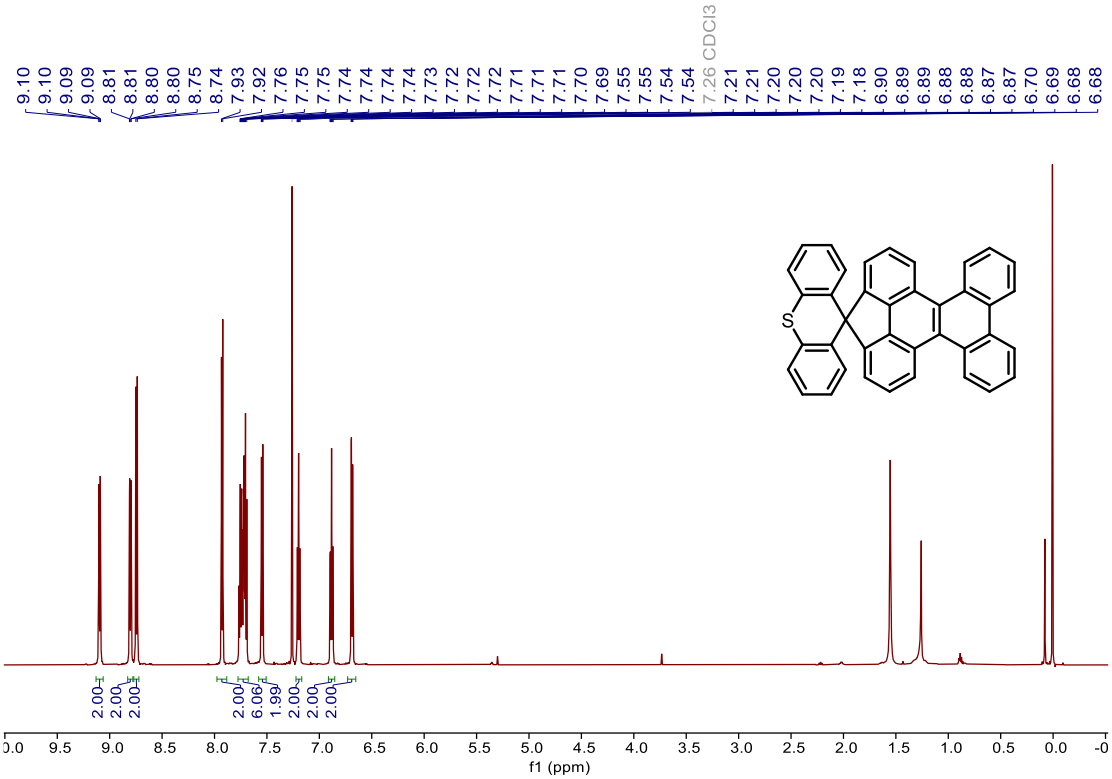

Figure S31 ^{1}H NMR spectrum (600 MHz, Chloroform-*d*) of ***S*-SFC**

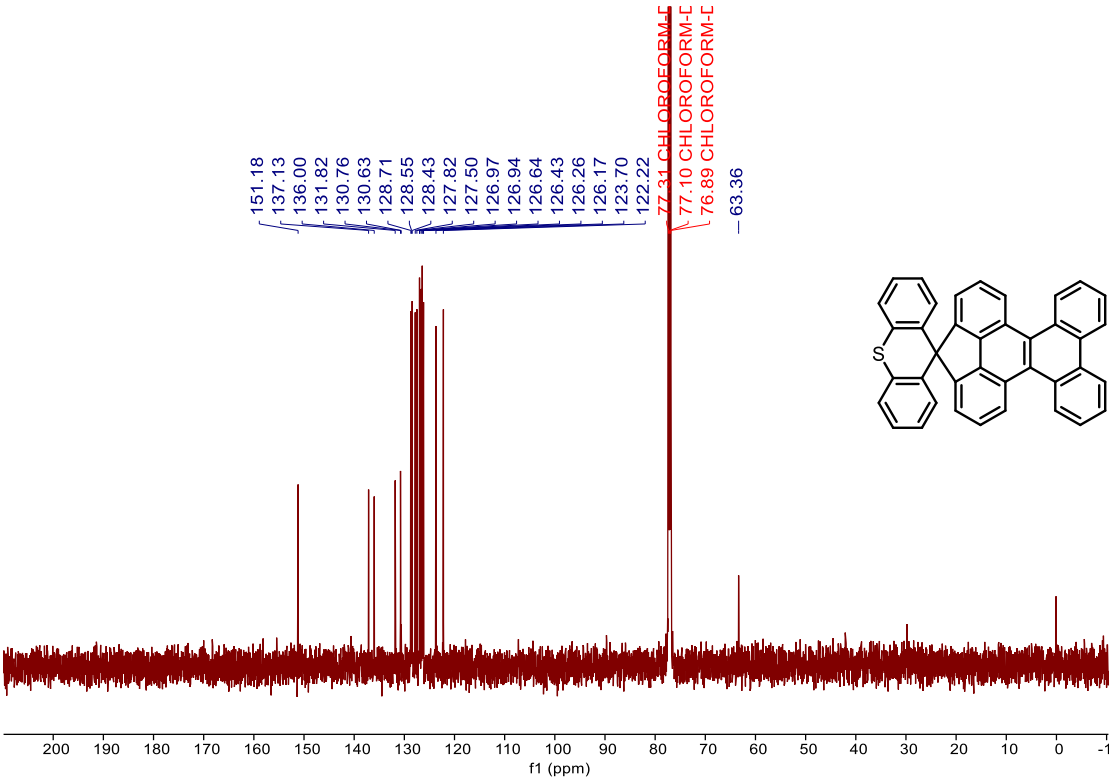

Figure S32 ^{13}C NMR spectrum (151 MHz, Chloroform-*d*) of ***S*-SFC**

10-phenyl-10*H*-spiro[acridine-9,4'-benzo[*p*]indeno[7,1,2-*ghi*]chrysene] (*N*-SFC)

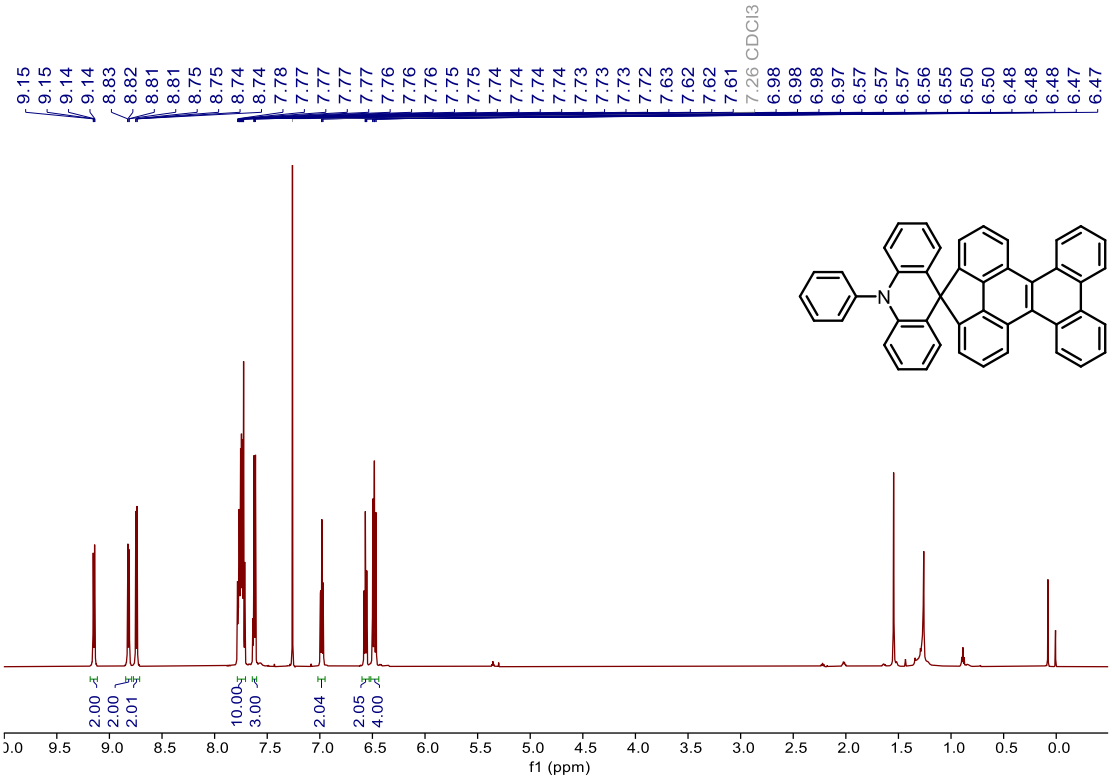

Figure S33 ^{1}H NMR spectrum (600 MHz, Chloroform-*d*) of ***N*-SFC**

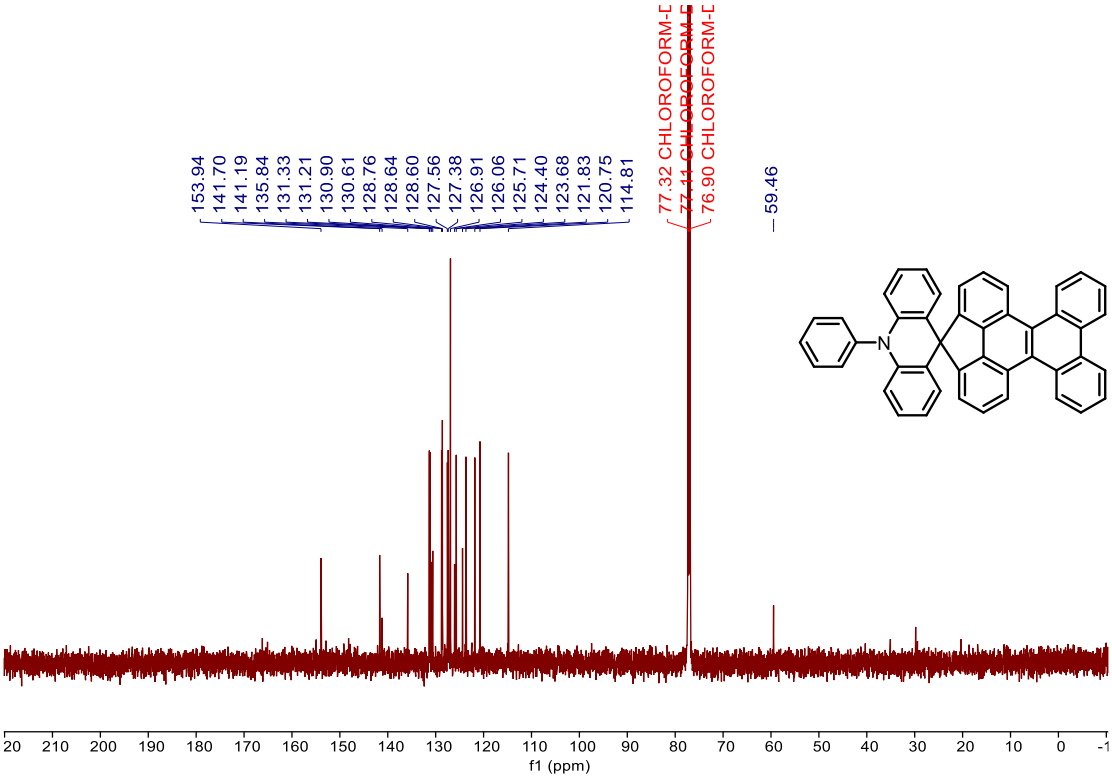

Figure S34 ^{13}C NMR spectrum (151 MHz, Chloroform-*d*) of ***N*-SFC**

4, 4'-spirobi[benzo[*p*]indeno[7,1,2-*ghi*]chrysene] (SBC)

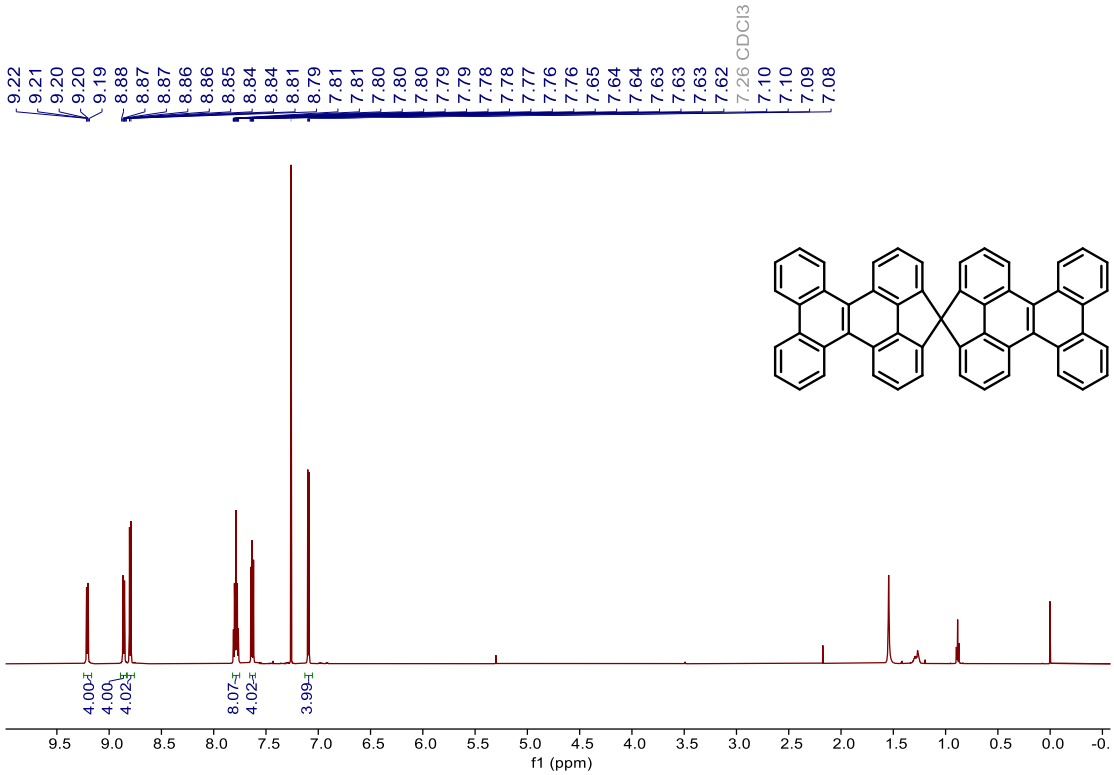

Figure S35 ^{1}H NMR spectrum (600 MHz, Chloroform-*d*) of **SBC**

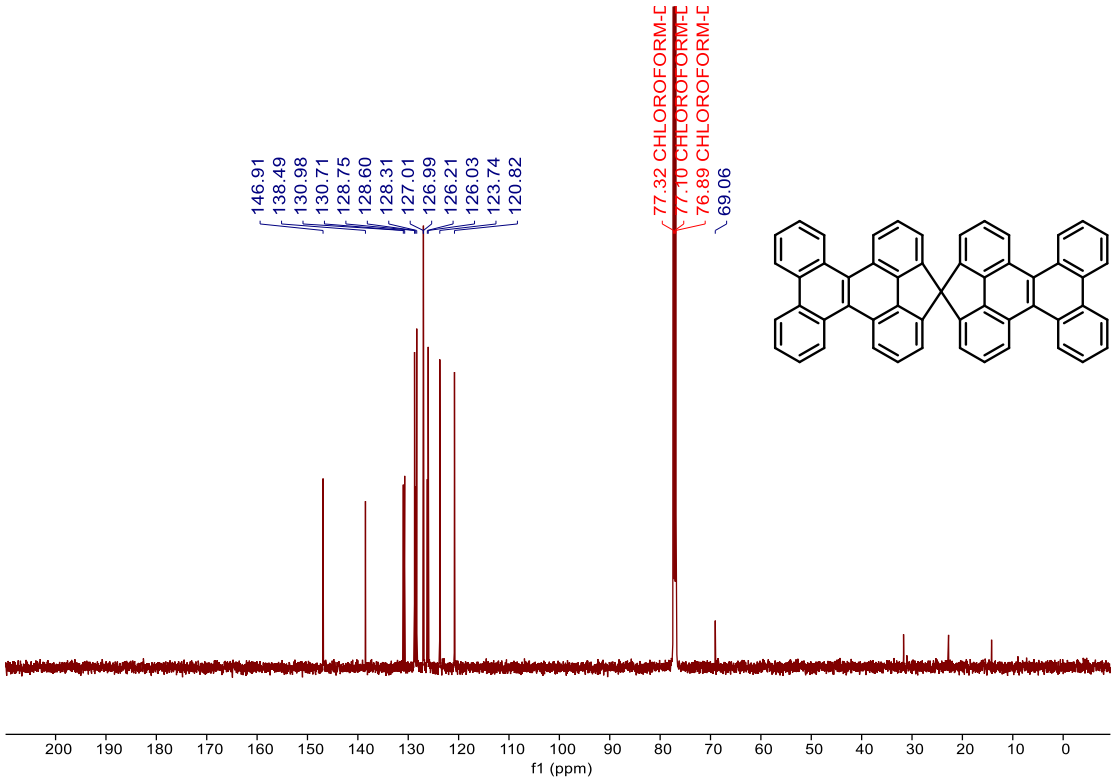

Figure S36 ^{13}C NMR spectrum (151 MHz, Chloroform-*d*) of **SBC**

4,4'-spirobi[cyclopenta[*def*]phenanthrene] (SBP)

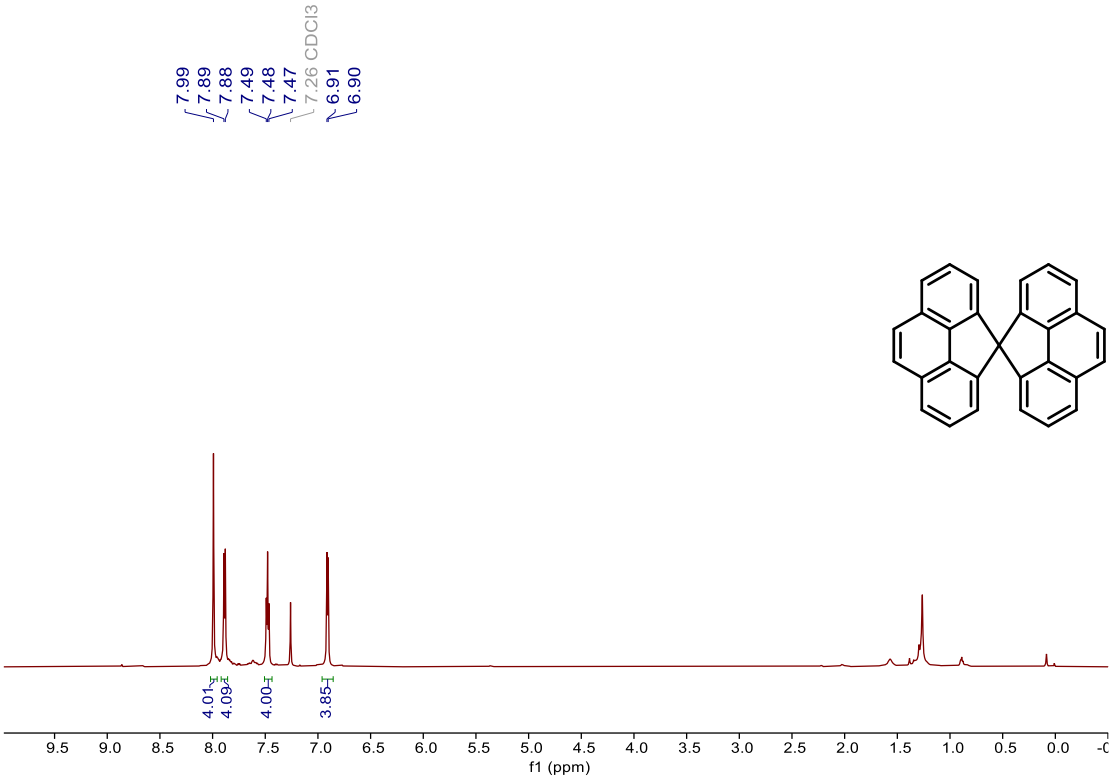

Figure S37 ^{1}H NMR spectrum (600 MHz, Chloroform-*d*) of **SBP**

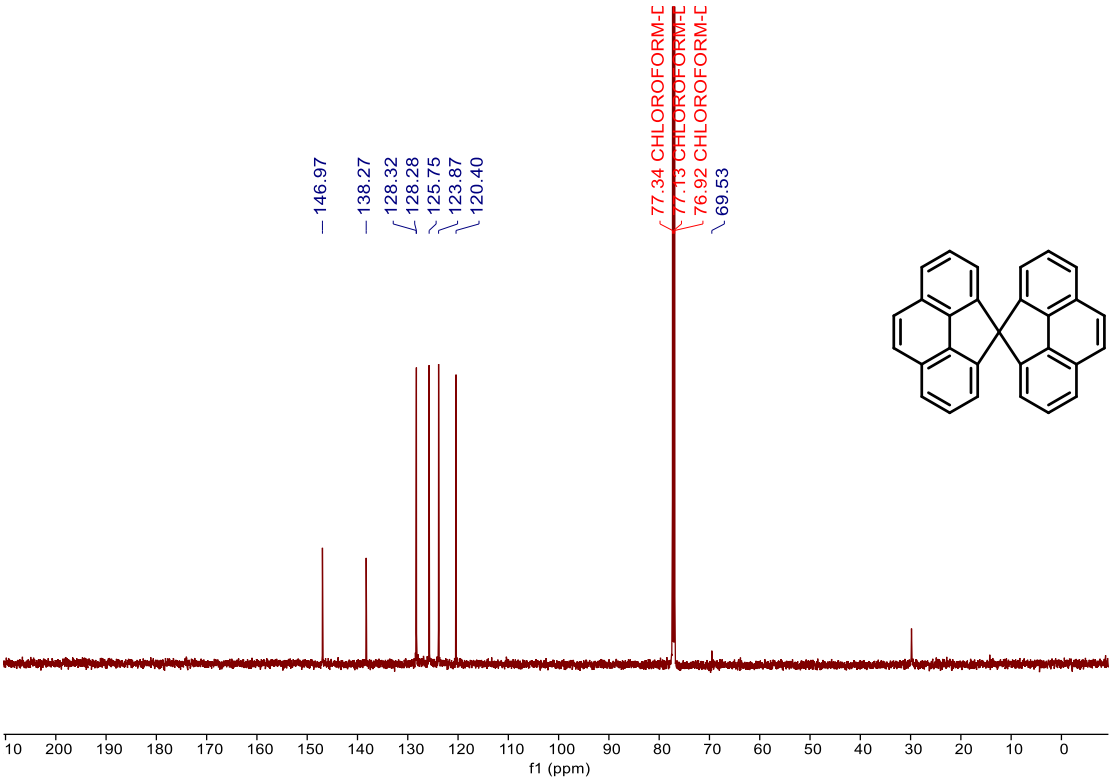

Figure S38 ^{13}C NMR spectrum (151 MHz, Chloroform-*d*) of **SBP**

4H-benzo[p]indeno[7,1,2-ghi] chrysen-4-one (1f)

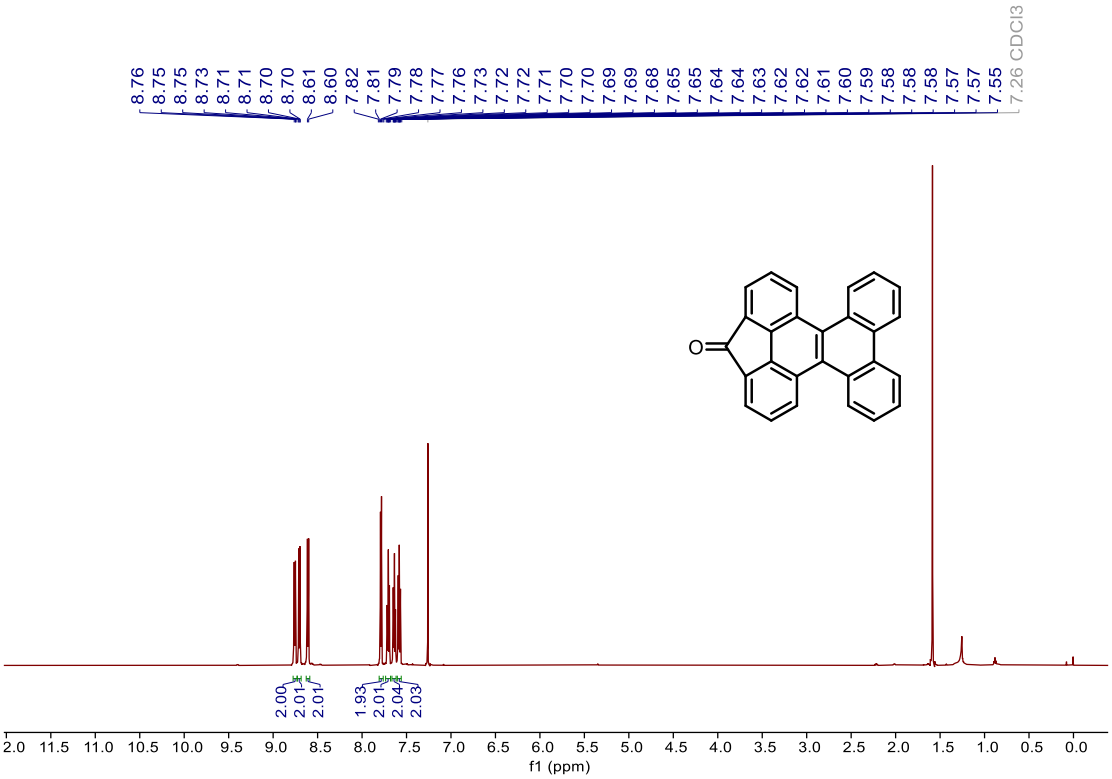

Figure S39 ^{1}H NMR spectrum (600 MHz, Chloroform-*d*) of **4*H*-benzo[*p*]indeno[7,1,2-*ghi*] chrysen-4-one**

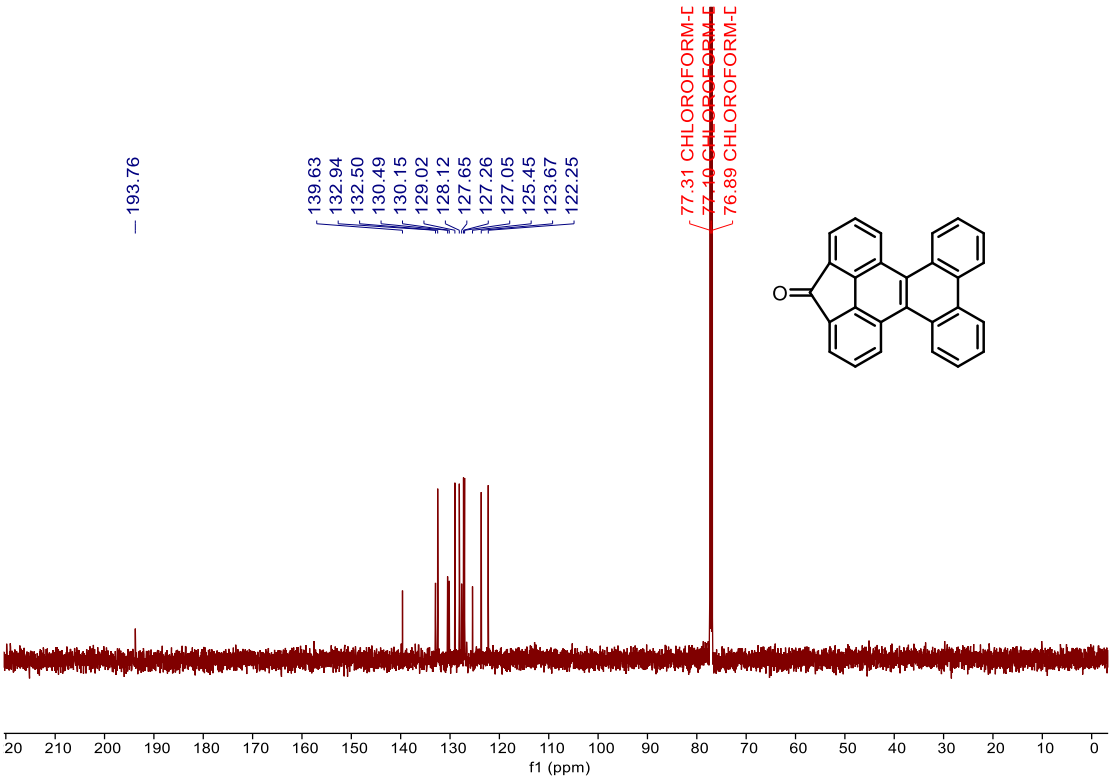

Figure S40 ^{13}C NMR spectrum (151 MHz, Chloroform-*d*) of **4*H*-benzo[*p*]indeno[7,1,2-*ghi*] chrysen-4-one**