Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

The Synthesis, Properties, and Application of Phenanthrenone: An Undeveloped Building Block and Photocatalyst

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1. General information

1.1 Chemicals information

Methyl methacrylate (MMA) was purchased from TCI chemicals. MMA was first degassed and dried over CaH_2 overnight, followed by vacuum distillation; then MMA was further purified by titration with neat tri(noctyl)aluminum (Aldrich Chemical) to a yellow endpoint and distillation under reduced pressure. The monomer was deoxygenized by freeze–pump–thaw cycle three times, stored under a nitrogen atmosphere, and sealed up. Subsequently, all of the purified monomers were stored under an inert atmosphere at –20 °C. HPLC-grade dichloromethane (DCM) was first purged with argon and then dried by CaH_2 overnight, followed by vacuum distillation, deoxygenized by freeze–pump–thaw cycle three times, and sealed up after adding activated 4 Å molecular sieves. *N*,*N*-dimethylacetamide (DMA, 99.8%, Superdry, J&K Seal) was purchased from J&K and used as received. Other solvents were purified by vacuum distillation followed by three freeze-pump-thaw cycles and stored under an argon atmosphere before use. The storage life of all the monomers and solvents shall not exceed four weeks. Diethyl 2-bromo-2-methylmalonate (DBMM) was purchased from Alfa Aesar Chemicals and used as received. The initiator was stored in a brown bottle inside a freezer below 5 °C. 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. ^{1}H NMR, and ^{13}C NMR spectra were recorded using AVANCE NEO 600 spectrometer. Chemical shift values were recorded as parts per million (ppm) relative to tetramethylsilane (TMS), chloroform, or dichloromethane 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 ($APCI^{+}$ /$APCI^{-}$) mode. Significant fragments are reported in the following fashion: m/z (relative intensity).

Newly synthesized polymers were characterized by ^{1}H NMR and gel permeation chromatography (GPC). The number-average molecular weight ($M_{n,\ GPC}$) and molecular weight distribution (M_w/M_n) values of the obtained polymers were determined by a Waters 1515 gel permeation chromatography (GPC) equipped with a Waters 2414 refractive index detector, using a Styragel HR 3 THF (7.8 × 300 mm) Column and a Styragel HR 4 THF (7.8 × 300 mm) column with measurable molecular weights ranging from 102 to 106 $g \cdot mol^{-1}$. THF was used as an eluent at a flow rate of 1.0 mL/min at 35 °C. GPC samples were injected manually and PSS poly(methyl methacrylate) standards were used for calibration.

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 DCM 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 DCM solution at a sample concentration of 0.1 mM. Steady-state emission spectra were acquired using Edinburgh Instruments, FLS980 spectrometer. Transient-state emission spectra were acquired using Edinburgh Instruments, FLS980 spectrometer with EPL-405 laser radiation, and the number of points for transient-state emission test was 3000.

1.4 Electrochemical measurements

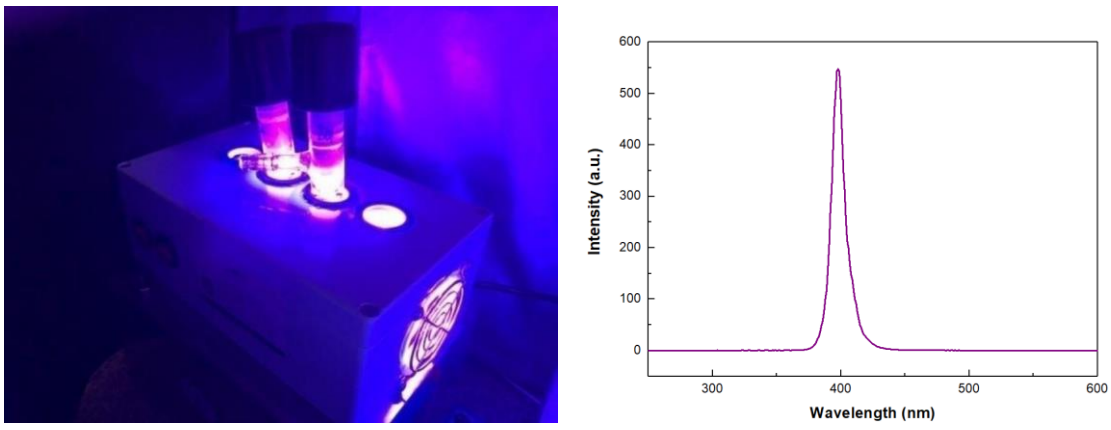
Cyclic voltammetry experiments were carried out with electrochemical workstation PGSTAT204 Autolab, Vantone, Switzerland. A standard three-electrode system was used: Ag/AgCl (3.0 mol/L KCl solution) electrode reference electrode; Glassy carbon electrode working electrode; A platinum wire electrode is the opposite electrode. 0.1 mol/L tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte, and the sweep speed of the cyclic voltammetry test was 50 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 MeCN: DCM (7:3, v/v) solution with 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6, TCI chemicals) as supporting electrolyte at a scan rate of 50 mV/s.

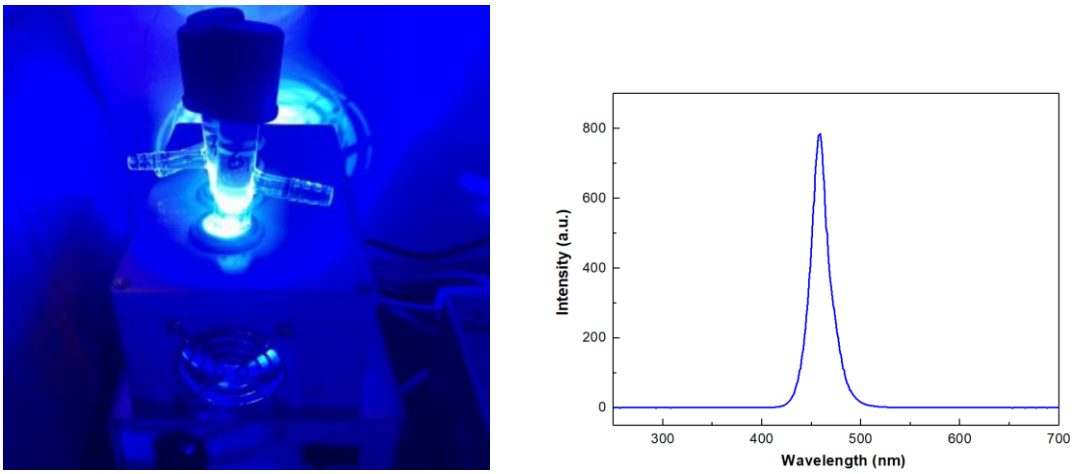
1.5 Computational study

The Gaussian 16W running on the Linux system was used for optimization (B3LYP/6-31G(d); CAM-B3LYP/6-31G(d); ωB97XD/6-311G(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 Mutilwfn software[2].

1.6 The photoreactor



Purple photoreactor and light intensity data



Blue photoreactor and light intensity data

6 W purple LEDs (λ_{max} = 400 nm) and 6 W blue LEDs (λ_{max} = 460 nm) reactors were purchased from GeAo Chemical (see: www.geaochem.com/). All reactions were conducted in a 6 W LEDs reactor placed 1 cm from light. At this distance, we estimate the light intensity of 6 W purple LEDs and 6 W blue LEDs to be ~25 mW/cm^2 and ~30 mW/cm^2 respectively. Light intensity data was tested by spectroradiometer (SpectriLight^{TM}, ILT950).

1.7 X-ray test

Crystal data were collected using a Rigaku-AFC7 equipped 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.

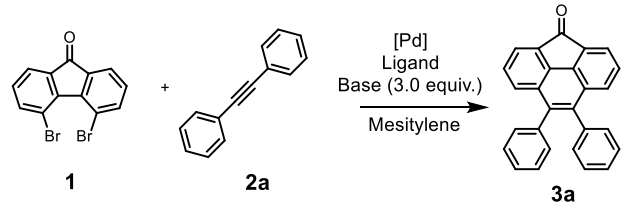
2. The experiment method

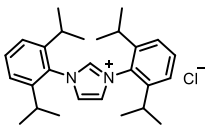
2.1 The preparation of reaction material

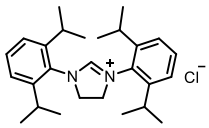
The synthesis of **1** followed the procedure of Nozaki and co-workers.[3] Alkynes **2a**-**2h** were synthesized from their iodine precursors and CaC_2.[4] ^{1}H and ^{13}C NMR spectra are consistent with the previous report.[5] And alkyne **2i** was supplied by Shinuo Xu. ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.77 – 7.70 (m, 4H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-d) *δ* 172.6, 144.7, 139.0, 132.7, 132.4, 127.6, 127.2, 123.5, 111.0, 90.4.

2.2 The optimization of the annulation reaction

Table S1. The Synthetic condition screening of Phenanthrenone




IPr·HCl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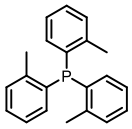
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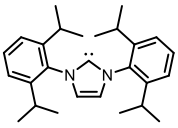
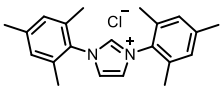
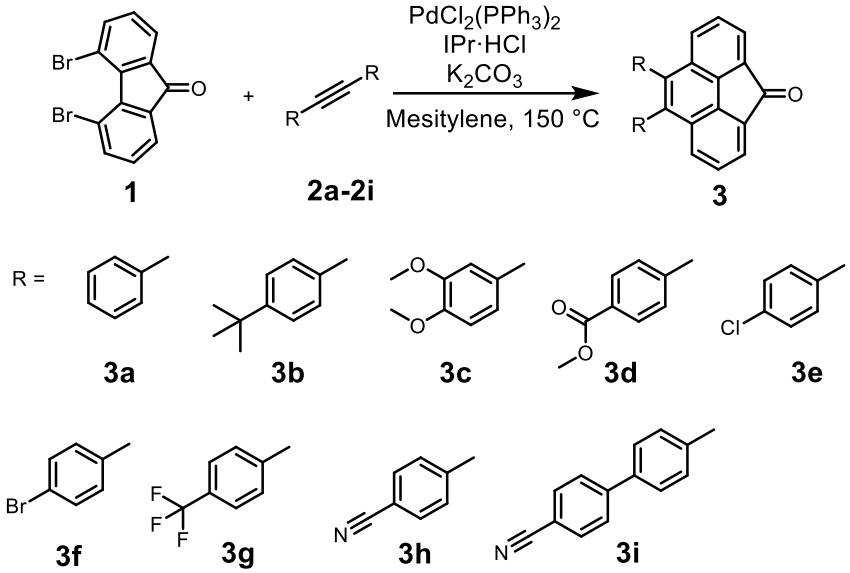

NHC1


NHC2

Entry	Cat. (mol%)	Ligand (mol%)	Base	t [h]	T [°C]	Yield
1	$PdCl_2(PPh_3)_2$ (10)	IPr·HCl (11)	K_2CO_3	24	150	67
2	$Pd(OAc)_2$ (10)	IPr·HCl (11)	K_2CO_3	24	150	53
3	$Pd(PPh_3)_4$ (10)	IPr·HCl (11)	K_2CO_3	24	150	9
4	$PdCl_2$ (10)	IPr·HCl (11)	K_2CO_3	24	150	20
5	$Pd_2(dba)_3$ (10)	IPr·HCl (11)	K_2CO_3	24	150	38
6	$PdCl_2(PPh_3)_2$ (10)	PPh_3 (11)	K_2CO_3	24	150	50
7	$PdCl_2(PPh_3)_2$ (10)	$P(Cy)_3$ (11)	K_2CO_3	24	150	41
8	$PdCl_2(PPh_3)_2$ (10)	X-Phos (11)	K_2CO_3	24	150	42
9	$PdCl_2(PPh_3)_2$ (10)	S-Phos (11)	K_2CO_3	24	150	28
10	$PdCl_2(PPh_3)_2$ (10)	*tri*-o-tolylphosphine (11)	K_2CO_3	24	150	34
11	$PdCl_2(PPh_3)_2$ (10)	DPPB (11)	K_2CO_3	24	150	45
12	$PdCl_2(PPh_3)_2$ (10)	Xantphos (11)	K_2CO_3	24	150	46
13	$PdCl_2(PPh_3)_2$ (10)	NHC1 (11)	K_2CO_3	24	150	33
14	$PdCl_2(PPh_3)_2$ (10)	SIPr·HCl (11)	K_2CO_3	24	150	37
15	$PdCl_2(PPh_3)_2$ (10)	NHC2 (11)	K_2CO_3	24	150	40
16	$PdCl_2(PPh_3)_2$ (10)	—	K_2CO_3	24	150	none
17	$PdCl_2(PPh_3)_2$ (8)	IPr·HCl (8.8)	K_2CO_3	24	150	56
18	$PdCl_2(PPh_3)_2$ (12)	IPr·HCl (13.2)	K_2CO_3	24	150	30
19	$PdCl_2(PPh_3)_2$ (5)	IPr·HCl (11)	K_2CO_3	24	150	20
20	$PdCl_2(PPh_3)_2$ (10)	IPr·HCl (22)	K_2CO_3	24	150	13
21	$PdCl_2(PPh_3)_2$ (10)	IPr·HCl (11)	Na_2CO_3	24	150	0
22	$PdCl_2(PPh_3)_2$ (10)	IPr·HCl (11)	Cs_2CO_3	24	150	42
23	$PdCl_2(PPh_3)_2$ (10)	IPr·HCl (11)	K_2CO_3	16	150	43
24	$PdCl_2(PPh_3)_2$ (10)	IPr·HCl (11)	K_2CO_3	32	150	27
25	$PdCl_2(PPh_3)_2$ (10)	IPr·HCl (11)	K_2CO_3	24	130	44
26	$PdCl_2(PPh_3)_2$ (10)	IPr·HCl (11)	K_2CO_3	24	170	56

2.3 The general synthesis route of phenanthrenone



Scheme S1. The general synthetic route of phenanthrenone

To a dry Schlenk tube containing a magnetic stirring bar were added **1** (0.1 mmol), alkyne (1.1 equiv.), $PdCl_2(PPh_3)_2$ (0.1 equiv.), IPr·HCl (0.11 equiv.), and K_2CO_3 (3.0 equiv.) under argon atmosphere. Then to this flask was added 1.6 mL mesitylene as solvent. After stirring at 150 °C for 24 h, the reaction mixture was then purified by silica gel column chromatography with gradient elution of PE/DCM to give target product **3**.

8,9-diphenyl-4H-cyclopenta[def]phenanthren-4-one (3a):

Purification by silica gel chromatography (PE/DCM = 2/1) gave **3a** (24 mg, 0.066 mmol, 66%) as a yellow solid. R_f (PE/DCM = 2/1): 0.3; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.80 (d, J = 7.0 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.30–7.27 (m, 4H), 7.26–7.23 (m, 2H), 7.22–7.19 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-d) δ 194.0, 138.7, 137.8, 136.7, 132.8, 131.0, 130.8, 129.4, 128.0, 128.0, 127.1, 122.4. HRMS (APCI): Exact mass calculated for $C_{27}H_{17}O$ ($[M+H]^+$): 357.1274, mass found: 357.1271.

8,9-bis(4-(tert-butyl)phenyl)-4H-cyclopenta[def]phenanthren-4-one (3b):

Purification by silica gel chromatography (PE/DCM = 3/1) gave **3b** (25 mg, 0.053 mmol, 53%) as a yellow solid. R_f (PE/DCM = 3/1): 0.4; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.79 (d, J = 6.7 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H), 7.50 (dd, J = 8.2, 6.9 Hz, 2H), 7.25 (d, J = 7.9 Hz, 4H), 7.08 (d, J = 8.4 Hz, 4H), 1.30 (s, 18H). ^{13}C NMR (151 MHz, Chloroform-d) δ 194.2, 149.8, 138.7, 136.9, 134.9, 132.8, 131.0, 130.7, 129.2, 128.1, 124.6, 122.2, 34.6, 30.8. HRMS (APCI): Exact mass calculated for $C_{35}H_{33}O$ ($[M+H]^+$): 469.2526, mass found: 469.2520.

8,9-bis(3,4-dimethoxyphenyl)-4H-cyclopenta[def]phenanthren-4-one (3c):

Purification by silica gel chromatography (PE/DCM = 1/1) gave **3c** (21 mg, 0.044 mmol, 44%) as a yellow solid. R_f (PE/DCM = 1/1): 0.3; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.80 (d, J = 6.9 Hz, 2H), 7.74–7.70 (m, 2H), 7.52 (dd, J = 8.2, 6.9 Hz, 2H), 6.91–6.76 (m, 5H), 6.62 (d, J = 1.9 Hz, 1H), 3.90 (s, 6H), 3.68 (d, J = 45.6 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-d) δ 194.0, 148.7, 148.5, 148.1, 138.7, 136.5, 136.4, 132.8, 130.8, 130.6, 130.5, 129.4, 128.2, 128.1, 123.6, 123.2, 122.4, 114.6, 114.3, 110.9, 110.6, 56.1, 56.0, 55.95, 55.87. HRMS (APCI): Exact mass calculated for $C_{31}H_{25}O_5$ ($[M+H]^+$): 477.1697, mass found: 477.1690.

dimethyl 4,4'-(4-oxo-4H-cyclopenta[def]phenanthrene-8,9-diyl)dibenzoate (3d):

Purification by silica gel chromatography (PE/DCM = 1/2) gave **3d** (29 mg, 0.062 mmol, 62%) as a yellow solid. R_f (PE/DCM = 1/2): 0.3; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.97 (d, J = 8.5 Hz, 4H), 7.82 (dd, J = 6.4, 1.1 Hz, 2H), 7.57–7.50 (m, 4H), 7.28 (d, J = 8.5 Hz, 4H), 3.91(s, 6H). ^{13}C NMR (151 MHz, Chloroform-d) δ 193.4, 166.9, 142.4, 138.8, 135.9, 132.8, 131.0, 130.4, 129.8, 129.5, 129.2, 127.2, 122.9, 52.3. HRMS (APCI): Exact mass calculated for $C_{31}H_{21}O_5$ ($[M+H]^+$): 473.1384, mass found: 473.1379.

8,9-bis(4-chlorophenyl)-4H-cyclopenta[def]phenanthren-4-one (3e):

Purification by silica gel chromatography (PE/DCM = 2/1) gave **3e** (20 mg, 0.048 mmol, 48%) as a yellow solid. R_f (PE/DCM = 2/1): 0.4; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.81 (dd, J = 6.8, 0.7 Hz, 2H), 7.56 (dd, J = 8.2, 0.7 Hz, 2H), 7.52 (dd, J = 8.2, 6.7 Hz, 2H), 7.30 (d, J = 8.4 Hz, 4H), 7.13 (d, J = 8.4 Hz, 4H). ^{13}C NMR (151 MHz, Chloroform-d) δ 193.6, 138.7, 136.0, 135.7, 133.4, 132.8, 132.2, 130.4, 129.7, 128.6, 127.6, 122.8. HRMS (APCI): Exact mass calculated for $C_{27}H_{15}Cl_2O$ ([M+H]$^+$): 425.0494, mass found: 425.0474.

8,9-bis(4-bromophenyl)-4H-cyclopenta[def]phenanthren-4-one (3f):

Purification by silica gel chromatography (PE/DCM = 2/1) gave **3f** (22 mg, 0.042 mmol, 42%) as a yellow solid. R_f (PE/DCM = 2/1): 0.4; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.81 (dd, J = 6.7, 0.8 Hz, 2H), 7.56 (dd, J = 8.2, 0.8 Hz, 2H), 7.52 (dd, J = 8.2, 6.7 Hz, 2H), 7.46 (d, J = 8.4 Hz, 4H), 7.07 (d, J = 8.4 Hz, 4H). ^{13}C NMR (151 MHz, Chloroform-d) δ 193.5, 138.7, 136.5, 135.6, 132.8, 132.6, 131.5, 130.4, 129.7, 127.5, 122.8, 121.7. HRMS (APCI): Exact mass calculated for $C_{27}H_{15}Br_2O$ ([M+H]$^+$): 514.9464, mass found: 514.9447.

8,9-bis(4-(trifluoromethyl)phenyl)-4H-cyclopenta[def]phenanthren-4-one (3g):

Purification by silica gel chromatography (PE/DCM = 1/1) gave **3g** (14 mg, 0.029 mmol, 29%) as a yellow solid. R_f (PE/DCM = 1/1): 0.3; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.86 (dd, J = 6.5, 1.0 Hz, 2H), 7.59 (d, J = 7.7 Hz, 4H), 7.58–7.52 (m, 4H), 7.34 (d, J = 7.8 Hz, 4H). ^{13}C NMR (151 MHz, Chloroform-d) δ 195.8, 141.2, 138.8, 135.6, 132.9, 131.3, 130.3, 129.9, 129.9, 129.7, 127.3, 126.8, 125.4, 125.3, 125.3, 125.3, 125.0, 123.2, 123.1, 121.4. ^{19}F NMR (471 MHz, Chloroform-d) δ –62.5. HRMS (APCI): Exact mass calculated for $C_{29}H_{15}F_6O$ ([M+H]$^+$): 493.1022, mass found: 493.1018.

4,4'-(4-oxo-4H-cyclopenta[def]phenanthrene-8,9-diyl)dibenzonitrile (3h):

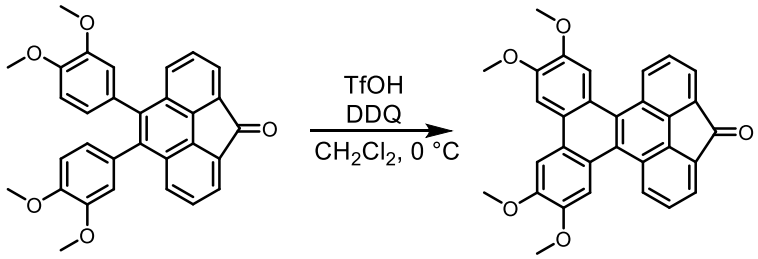
Purification by silica gel chromatography (PE/DCM = 1/2) gave **3h** (11 mg, 0.027 mmol, 27%) as a yellow solid. R_f (PE/DCM = 1/2): 0.3; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.87 (d, J = 6.8 Hz, 1H), 7.64 (d, J = 8.3 Hz, 1H), 7.58 (dd, J = 8.2, 6.9 Hz, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 193.0, 142.3, 138.9, 135.2, 132.9, 132.2, 131.7, 130.2, 130.0, 126.7, 123.5, 118.5, 111.8. HRMS (APCI): Exact mass calculated for $C_{29}H_{15}N_2O$ ($[M+H]^+$): 407.1179, mass found: 407.1137.

4',4'''-(4-oxo-4H-cyclopenta[def]phenanthrene-8,9-diyl)bis(([1,1'-biphenyl]-4-carbonitrile)) (3i):

Purification by silica gel chromatography (PE/DCM = 1/2) gave **3i** (12 mg, 0.021 mmol, 21%) as a yellow solid. R_f (PE/DCM = 1/2): 0.3; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.84 (d, J = 6.8 Hz, 2H), 7.74–7.69 (m, 8H), 7.66 (d, J = 8.2 Hz, 2H), 7.59–7.53 (m, 6H), 7.37 (d, J = 8.4 Hz, 4H). ^{13}C NMR (151 MHz, Chloroform-d) δ 193.6, 145.0, 138.8, 138.3, 137.8, 136.0, 132.9, 132.8, 131.8, 130.6, 129.6, 127.69, 127.67, 127.0, 122.8, 119.0, 111.2. HRMS (APCI): Exact mass calculated for $C_{41}H_{23}N_2O$ ($[M+H]^+$): 559.1805, mass found: 559.1765.

2.4 The derivatization reactions of phenanthrenone

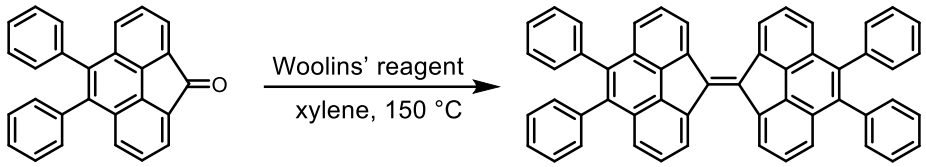
The synthesis route of 9,10,13,14-tetramethoxy-4H-benzo[p]indeno[7,1,2-ghi]chrysen-4-one (4):



3c **4**

A dry reaction tube was charged with **3c** (0.1 mmol) and 2,3-dicyano-5,6-dichlorobenzoquinone (0.1 mmol, 1.0 equiv.) under argon atmosphere, then dissolved by 9.0 mL CH_2Cl_2. Cooled the mixture to 0 °C, and added Trifluoromethanesulfonic acid (12.5 mmol, 125.0 equiv.) dropwise. After stirring 2 h under 0 °C, the resulting reaction mixture was quenched by pouring it onto saturated aqueous $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with dichloromethane three times. Combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The crude residue was purified by recrystallizing from *n*-Hexane. The pure product is a yellow solid (28 mg, 0.060 mmol, 60%). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.75 (d, J = 8.3 Hz, 2H), 8.33 (s, 2H), 7.91 (s, 2H), 7.82 (d, J = 6.8 Hz, 2H), 7.65 (dd, J = 8.3, 6.9 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-d) δ 194.0, 149.6, 148.9, 139.4, 133.1, 131.6, 129.1, 126.3, 126.0, 125.1, 124.5, 121.9, 109.4, 104.2, 56.29, 56.28. HRMS (APCI): Exact mass calculated for $C_{31}H_{23}O_5$ ($[M+H]^+$): 475.1540, mass found: 475.1537.

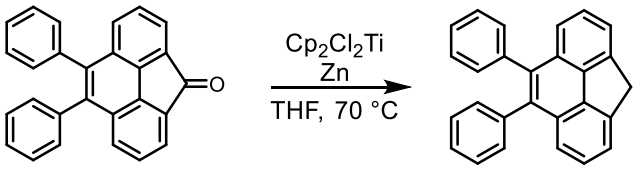
The synthesis route of 8,8',9,9'-tetraphenyl-4,4'-bi(cyclopenta[def]phenanthrenylidene) (5):



3a **5**

A dry reaction tube was charged with **3a** (0.1 mmol, 2.2 equiv.), Woolins' reagent (1.0 equiv.) and 1.0 mL anhydrous xylene as solvent under argon atmosphere. Heat solution to 150 °C for 48 h, and then was cooled to room temperature. After removed the solvent, the crude residue was purified by silica gel chromatography (PE) to get **5** (4 mg, 0.058 mmol, 33%) as a pink solid. R_f (PE): 0.5; ^{1}H NMR (600 MHz, Chloroform-d/CS_2) δ 8.78 (d, J = 7.2 Hz, 4H), 7.62 (t, J = 7.6 Hz, 4H), 7.57 (d, J = 8.0 Hz, 4H), 7.33–7.28 (m, 20H). ^{13}C NMR (151 MHz, Chloroform-d/CS_2) δ 143.1, 138.6, 136.9, 136.7, 136.4, 131.3, 128.5, 128.1, 127.9, 126.8, 125.9, 123.9. HRMS (APCI): Exact mass calculated for $C_{54}H_{33}$ ([M+H]$^+$): 681.2577, mass found: 681.2574.

The synthesis route of 8,9-diphenyl-4H-cyclopenta[def]phenanthrene (6):

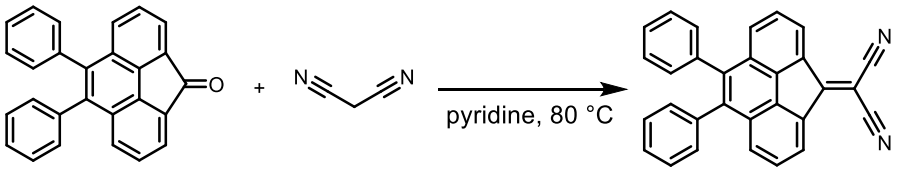


3a **6**

A dry 30 mL reaction tube charged with zinc powder (1.01 mmol, 14.0 equiv.), THF (4.8 mL), and Cp_2TiCl_2 (0.50 mmol, 7.0 equiv.) at room temperature under an atmosphere of argon. The mixture was stirred at 70 °C for 2 h. A dry THF solution (1.0 mL) of **3a** (0.072 mmol) was added to the mixture. After stirring at 70 °C for 6 h, the reaction mixture was cooled to room temperature. The crude residue was purified by silica gel chromatography (PE) to get **6** (12 mg, 0.036 mmol, 50%) as a white solid. R_f (PE): 0.6; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.74 (d, J = 7.8 Hz, 2H), 7.60 (dd, J = 8.1, 6.9 Hz, 2H),

7.55 (d, *J* = 8.1 Hz, 2H), 7.32–7.22 (m, 10H), 4.44 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-d) *δ* 141.6, 139.0, 137.9, 136.7, 131.3, 128.5, 127.8, 127.5, 126.7, 122.7, 121.4, 37.7.

The synthesis route of 2-(8,9-diphenyl-4H-cyclopenta[def]phenanthrene-4-ylidene)malononitrile (7):



3a **7**

A dry reaction tube was charged with **3a** (0.1mmol), malononitrile (10.0 equiv.), and 1.0 mL anhydrous pyridine as solvent under an argon atmosphere. The solution was heated to 80 °C for 1 h, and then 2.0 mL EtOH was added to the mixture. The mixture was allowed to cool to −20 °C for 2 h. Filter the formed crystals. The formed crystals were washed with chilled EtOH three times and recrystallized the product from $CHCl_3$. The pure product is orange solid (0.087 mmol, 35 mg, 87%); ^{1}H NMR (600 MHz, Chloroform-d/CS_2) *δ* 8.37 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.54 (dd, *J* = 8.2, 7.2 Hz, 2H), 7.31–7.25 (m, 6H), 7.20–7.17 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-d/CS_2) *δ* 163.2, 137.4, 137.1, 136.7, 133.1, 131.2, 131.0, 129.4, 128.7, 128.1, 127.3, 125.8, 113.0, 78.8. HRMS (ESI): Exact mass calculated for $C_{30}H_{17}N_2$ ($[M+H]^+$): 405.1386, mass found: 405.1357.

3. Spectroscopic data

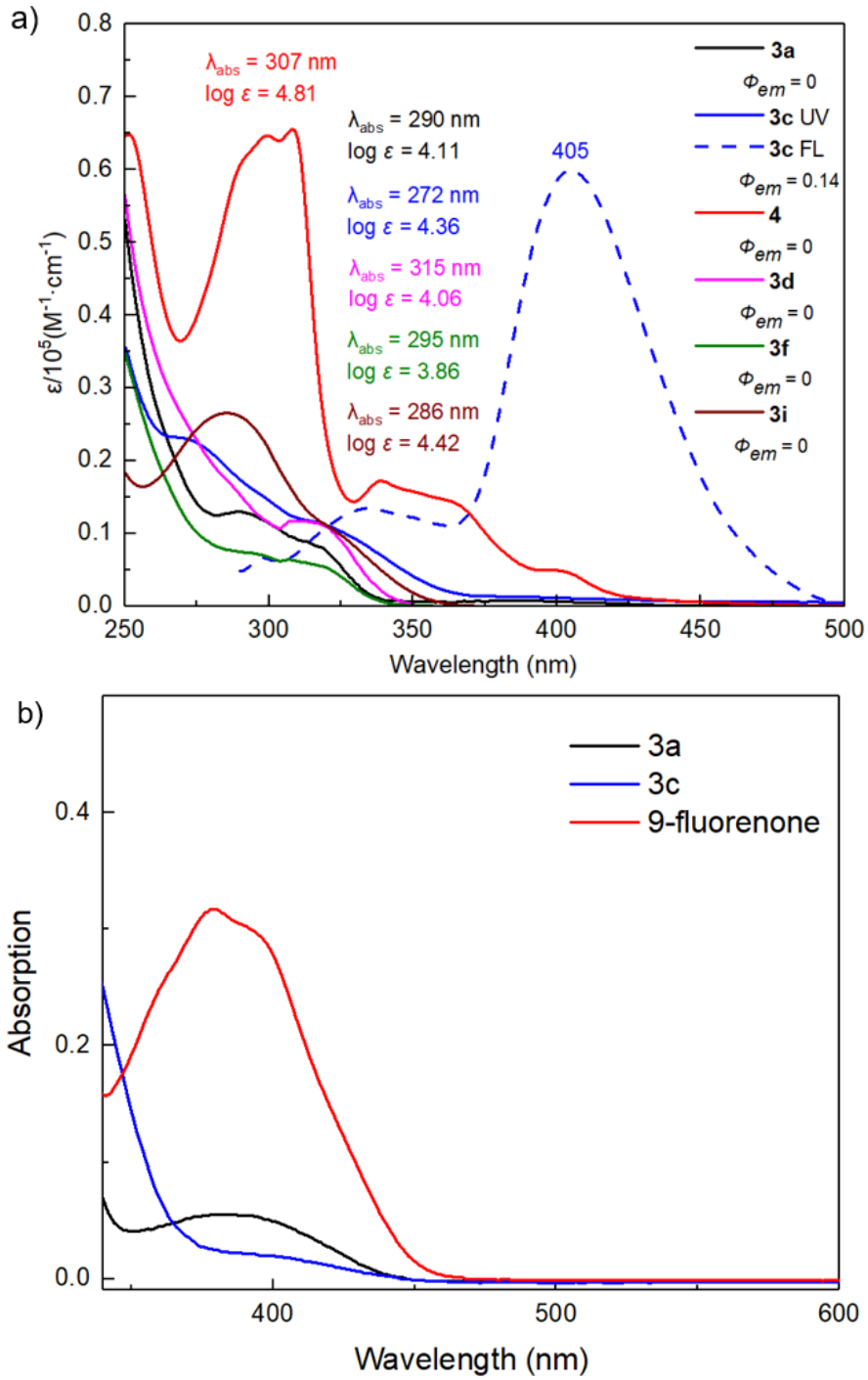


Figure S1. a) UV/vis absorption (in CH_2Cl_2; solid line) of **3a**, **3c**, **4, 3d, 3f, 3i** and fluorescence spectra (in CH_2Cl_2; broken line) of **3c** (λ_{ex} = 270 nm); b) The enlarged view of absorption at 400nm of **3a**, **3c** and 9-fluorenone.

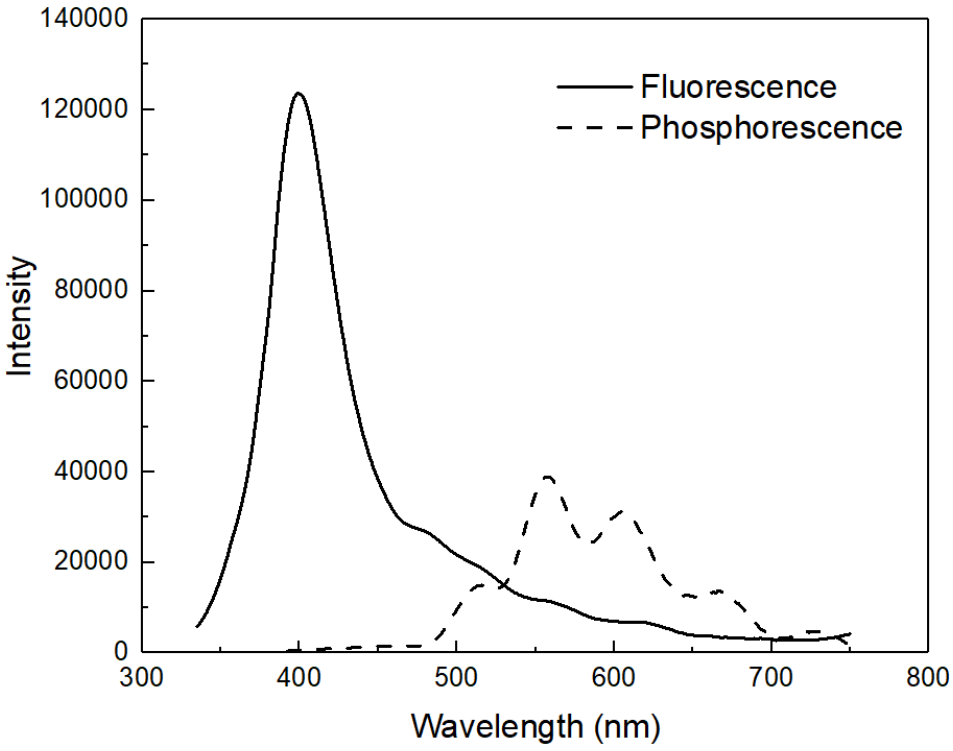


Figure S2. Fluorescence and phosphorescence spectra (in 2-methyltetrahydrofuran) of **3a** at 77 K (λ_{ex} = 315 nm)

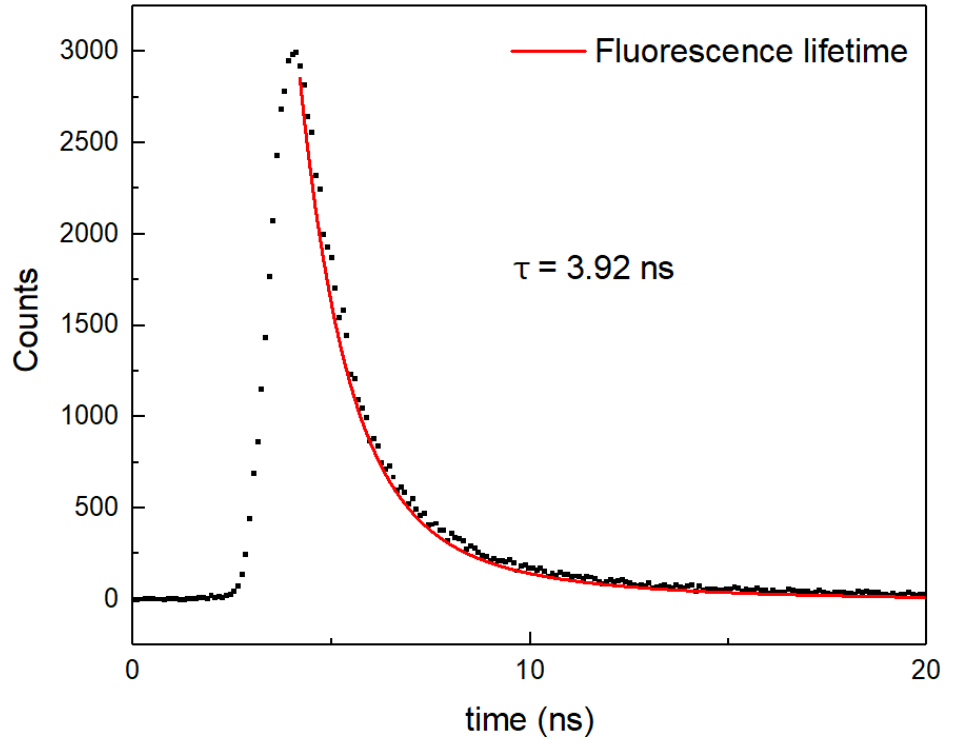


Figure S3. Fluorescence lifetime curve (in 2-methyltetrahydrofuran, single exponential fits) of **3a** at 77 K (λ_{ex} = 405 nm)

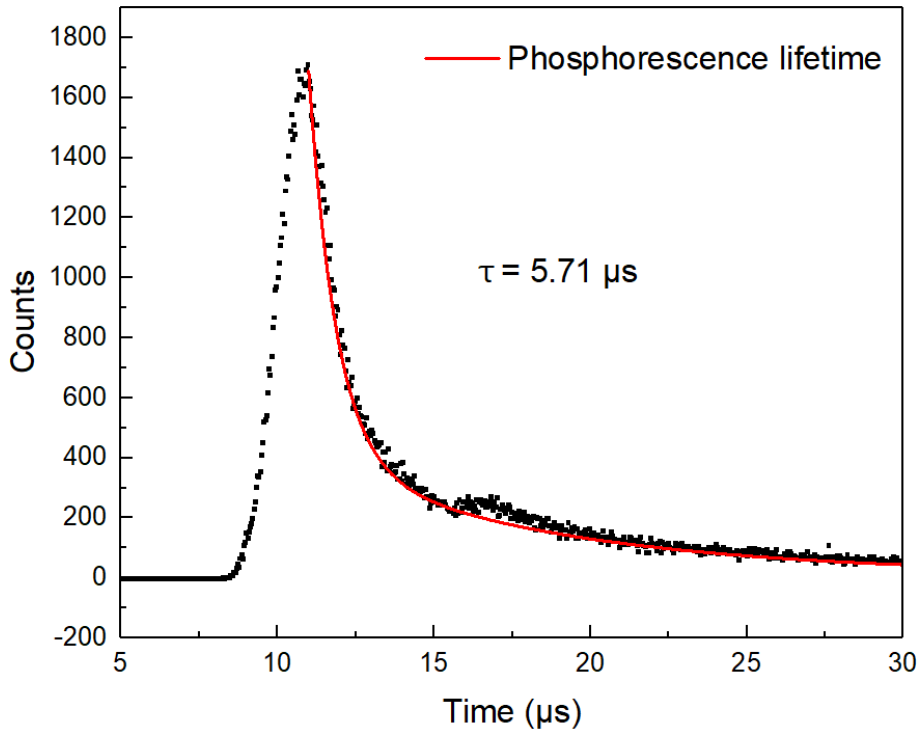


Figure S4. Phosphorescence lifetime curve (in 2-methyltetrahydrofuran, single exponential fits) of **3a** at 77 K (λ_{ex} = 405 nm)

4. Computational study

4.1 Frontier molecular orbitals

Table S2. The HOMO LUMO data of selected compounds.

	9-fluorenone	phenanthrenone	**3a**	**3c**	**3g**	**3h**	**4**	**5**	**6**	**7**
LUMO	–2.24	–2.26	–2.21	–2.10	–2.48	–2.64	–2.12	–2.44	–1.13	–3.17
HOMO	–6.23	–6.20	–5.88	–5.49	–6.30	–6.48	–5.32	–5.16	–5.49	–6.09
Gap	3.99	3.94	3.67	3.39	3.82	3.84	3.20	2.72	4.36	2.92

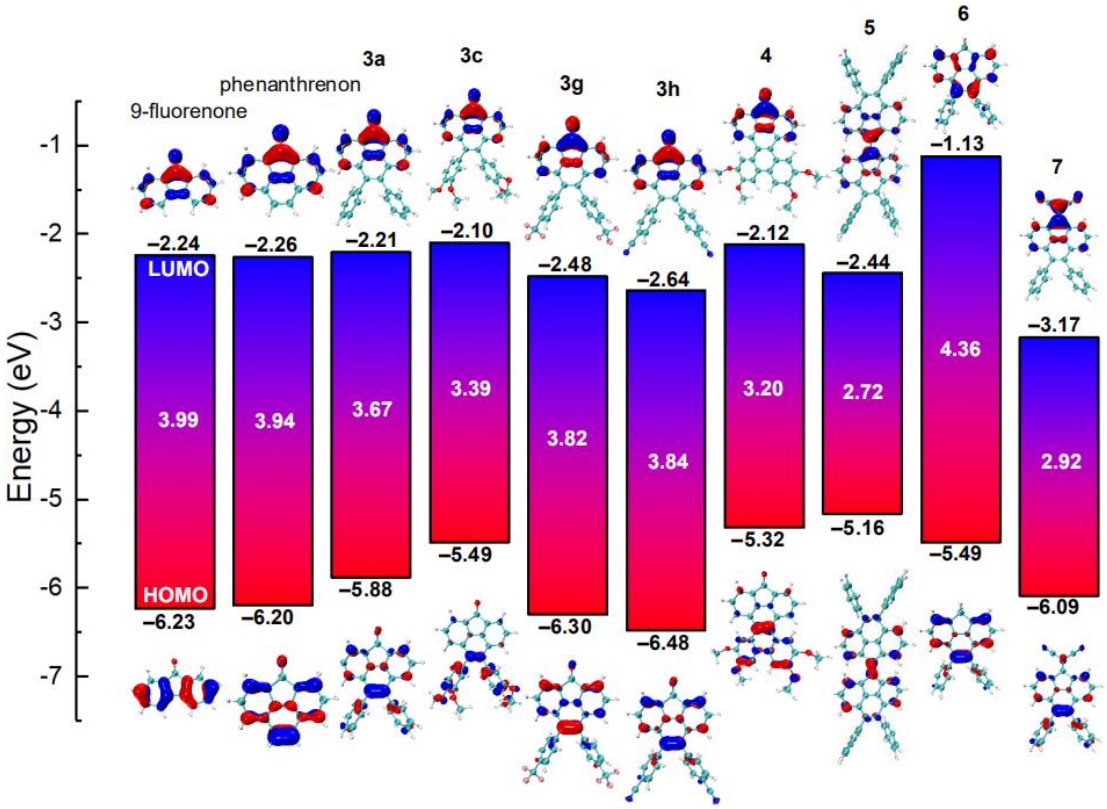
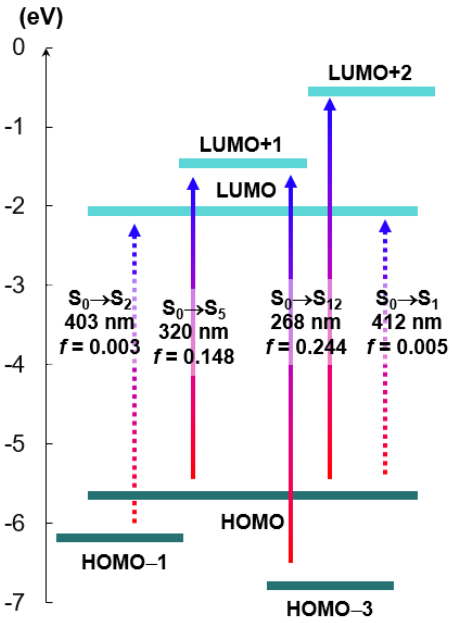


Figure S5. Energy diagrams and frontier molecular orbitals of 9-fluorenone, phenanthrenone, **3a**, **3c**, **3g**, **3h**, **4**, **5**, **6**, and **7** (from left to right) calculated at the B3LYP/6-31G(d) level of theory (unit: eV)

4.2 The TD-DFT calculation

Table S3. Major electronic transitions for **3a** by TD-DFT method using B3LYP/6-31G(d).

3a	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	3.0123	411.59	0.0047	H→L (96.4%)
S2	3.0799	402.56	0.0032	H–1→L (98.9%)
S3	3.2736	378.75	0.0003	H–6→L (79.3%); H-4→L (12.9%); H–2→L (5.0%);
S5	3.8753	319.93	0.1482	H→L+1 (82.3%);H–5→L (8.8%) H–7→L (5.6%)
S8	4.1601	298.03	0.0992	H–5→L (84.4%); H→L+1 (8.7%)
S12	4.6280	267.90	0.2438	H→L+2 (49.2%); H–3→L+1 (31.8%); H–1→L+1 (10.6%)



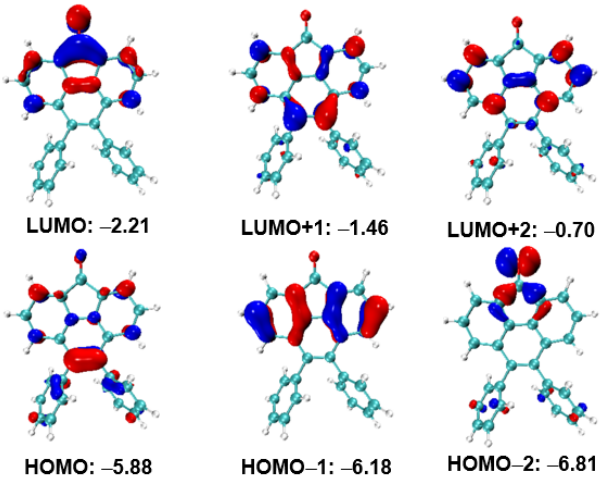


Table S4. Major electronic transitions for **3a** by TD-DFT method using CAM-B3LYP/6-31G(d).

3a	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	3.5762	346.69	0.0000	H–6→L (88.2%); H–6→L+8 (3.9%); H–4→L (1.7%)
S2	3.6086	343.58	0.0039	H–1→L (96.1%)
S3	3.7747	328.46	0.0081	H→L (81.5%); H-1→L+1 (7.0 %); H–2→L (4.8%);
S4	4.4285	279.97	0.3738	H→L+1 (93.0%);H–1→L+2 (3.6%)
S5	4.5973	269.69	0.0808	H–1→L+1 (65.5%); H→L+2 (15.3%); H→L (11.8%)
S6	4.9260	251.70	0.0366	H–7→L (51.6%); H–5→L (21.6%); H–1→L+2 (16.9%)

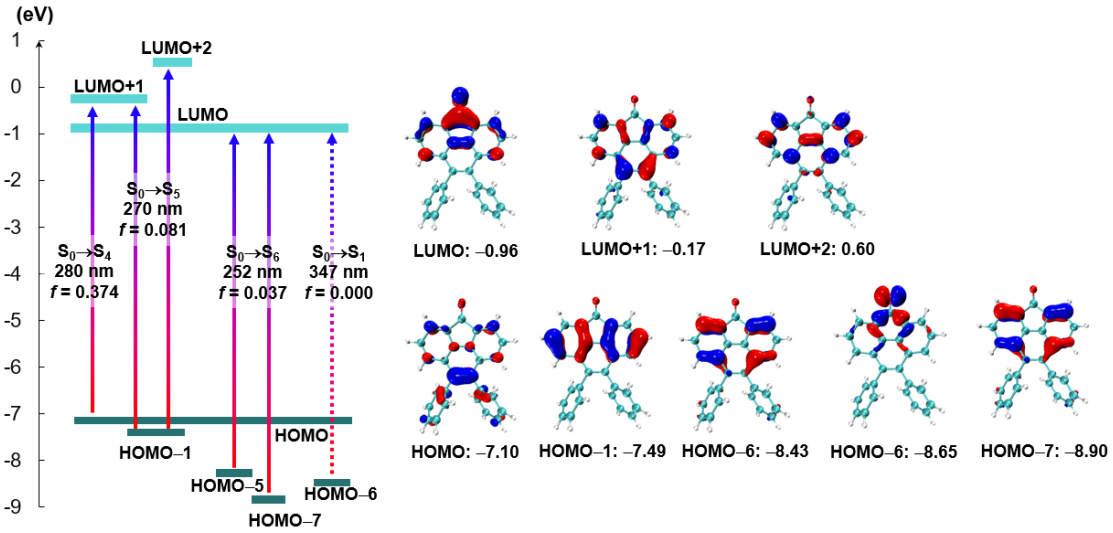


Table S5. Major electronic transitions for **3a** by TD-DFT with the Tamm–Dancoff approximation (TDA) method using CAM-B3LYP/6-31G(d).

3a	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	3.6045	343.97	0.0000	H–6→L (88.2%); H–6→L+8 (3.8%); H–4→L (1.7%)
S2	3.6933	335.70	0.0072	H–1→L (95.3%)
S3	3.8547	321.65	0.0081	H→L (78.5%); H-1→L+1 (9.9 %); H–2→L (3.7%);
S4	4.5617	271.80	0.3777	H→L+1 (89.7%);H–1→L+2 (4.2%)
S5	4.7017	263.70	0.0652	H–1→L+1 (56.0%); H→L+2 (19.5%); H→L (15.0%)
S6	4.9902	248.46	0.0485	H–7→L (48.5%); H–5→L (20.9%); H–1→L+2 (20.8%)

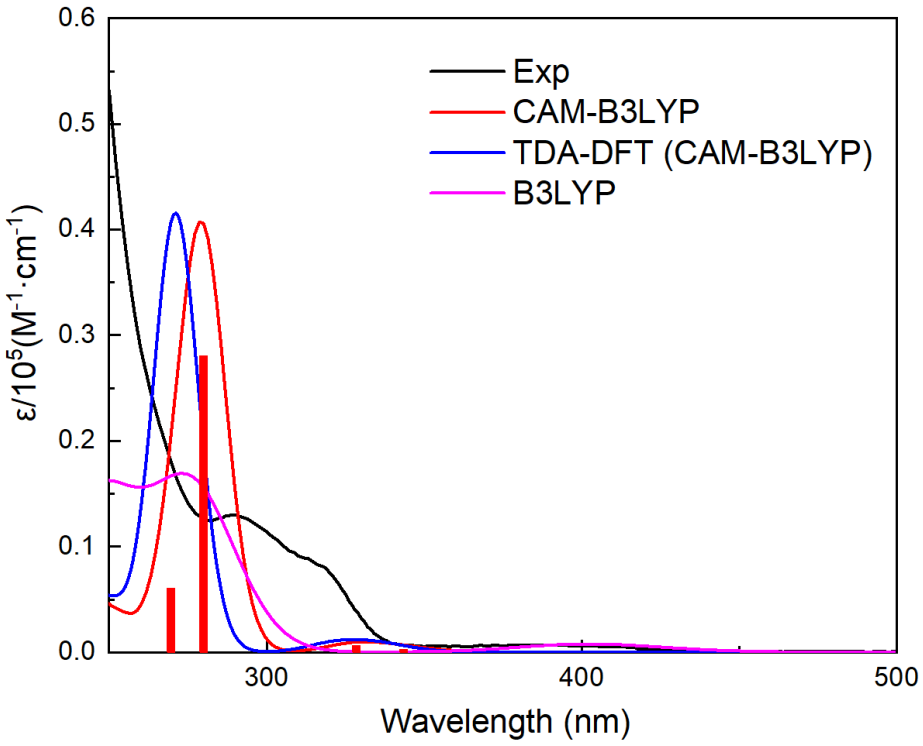
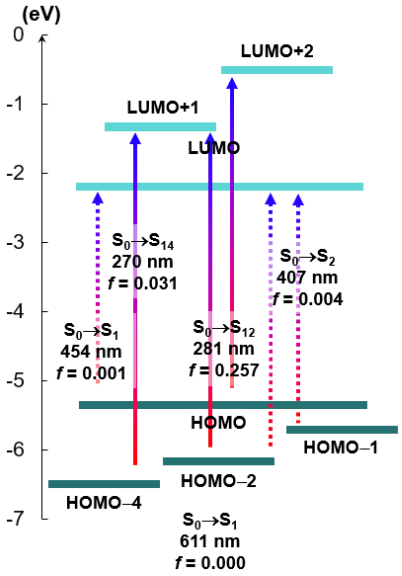


Figure S6. Experimental and calculated UV/vis spectra by TDDFT (B3LYP/6-31G(d) and CAM-B3LYP/6-31G(d)) and TDDFT with the Tamm–Dancoff approximation method using CAM-B3LYP/6-31G(d) of **3a.**

Major electronic transitions for **3c** by TD-DFT method using B3LYP/6-31G(d).

3c	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	2.7281	454.47	0.0007	H→L (98.2%)
S2	3.0461	407.03	0.0042	H–2→L (50.9); H–1→L (44.8%);
S3	3.2743	378.66	0.0006	H–6→L (91.1%)
S7	3.8942	318.38	0.0122	H–4→L (77.3%); H–1→L+1 (9.7%); H–5→L (5.2%)
S12	4.4061	281.39	0.2573	H→L+2 (59.6%); H–2→L+1 (26.4%)
S14	4.5915	270.03	0.0314	H–4→L+1 (77.2%); H–5→L+1 (5.5%); H→L+4 (5.3%)



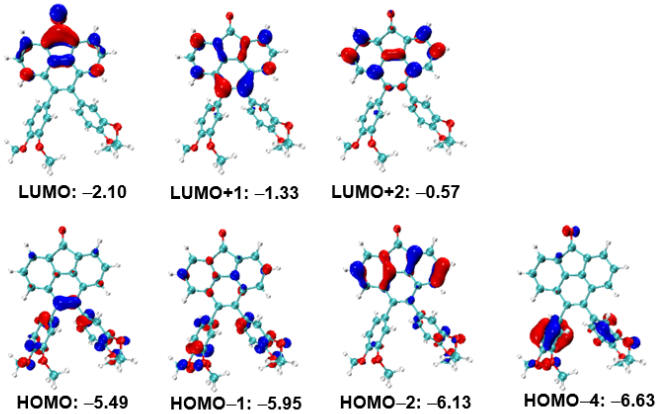


Table S6. Major electronic transitions for **3c** by TD-DFT method using CAM-B3LYP/6-31G(d).

3c	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	3.5719	347.11	0.0002	H–6→L (86.3%); H→L (4.7%); H–6→L+8 (3.6%)
S2	3.6008	344.32	0.0041	H–2→L (42.8%); H–1→L (28.7%); H–3→L (23.5%)
S3	3.7004	335.06	0.0070	H→L (59.4%); H-2→L (17.4 %); H–3→L (9.4%);
S4	4.2599	291.05	0.3305	H→L+1 (88.6%); H–3→L+1 (3.0%)
S5	4.5160	274.54	0.0501	H–1→L+1 (25.2%); H–2→L+1 (22.8%); H→L (20.2%)
S6	4.7964	258.49	0.0248	H–2→L (27.6%); H–1→L (18.9%); H–3→L (12.3%)
S7	4.8579	255.22	0.0610	H–7→L (34.0%); H–3→L (21.3%); H–1→L (14.1%)
S8	4.9875	248.59	0.0646	H–2→L+1 (31.4%); H–1→L+1 (22.1%); H→L+3 (10.5%)

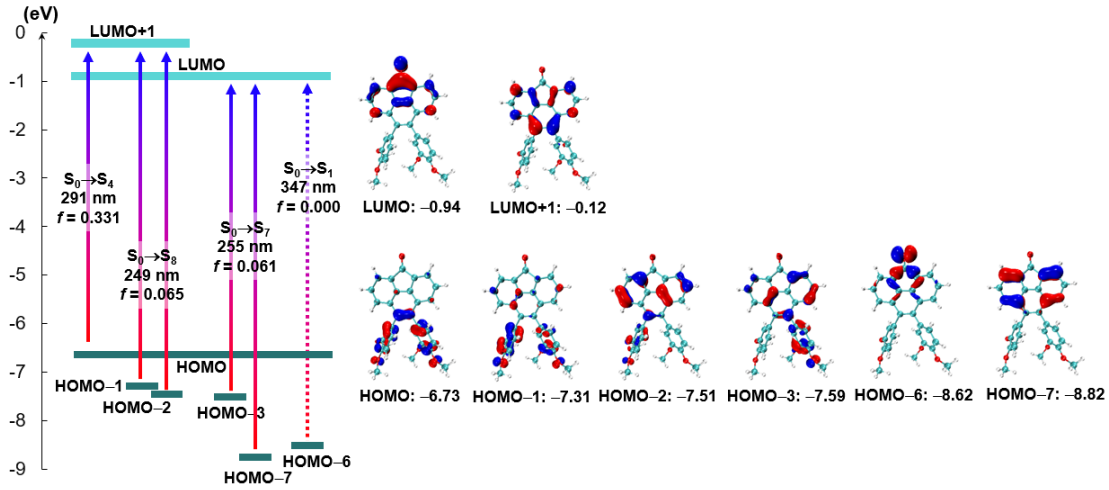


Table S7. Major electronic transitions for **3c** by TD-DFT with the Tamm–Dancoff approximation (TDA) method using CAM-B3LYP/6-31G(d).

3c	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	3.6010	344.31	0.0001	H–6→L (87.8%); H–6→L+8 (3.7%); H→L (3.3%)
S2	3.6847	336.49	0.0077	H–2→L (41.3%); H–1→L (29.0%); H–3→L (23.5%)
S3	3.7738	328.54	0.0073	H→L (61.0%); H-2→L (16.5 %); H–3→L (7.1%);
S4	4.3646	284.07	0.3311	H→L+1 (89.3%); H–3→L+1 (1.4%)
S5	4.5678	271.43	0.0299	H→L (25.0%); H–1→L+1 (22.0%); H–2→L+1 (16.5%)
S6	4.8646	254.87	0.0399	H–1→L (28.0%); H–2→L (25.3%); H→L+2 (13.3%)
S7	4.9238	251.81	0.0526	H–3→L (30.9%); H–7→L (24.5%); H–1→L (10.7%)
S8	5.0437	245.82	0.0811	H–2→L+1 (34.9%); H–1→L+1 (28.9%); H–3→L+1 (8.7%)

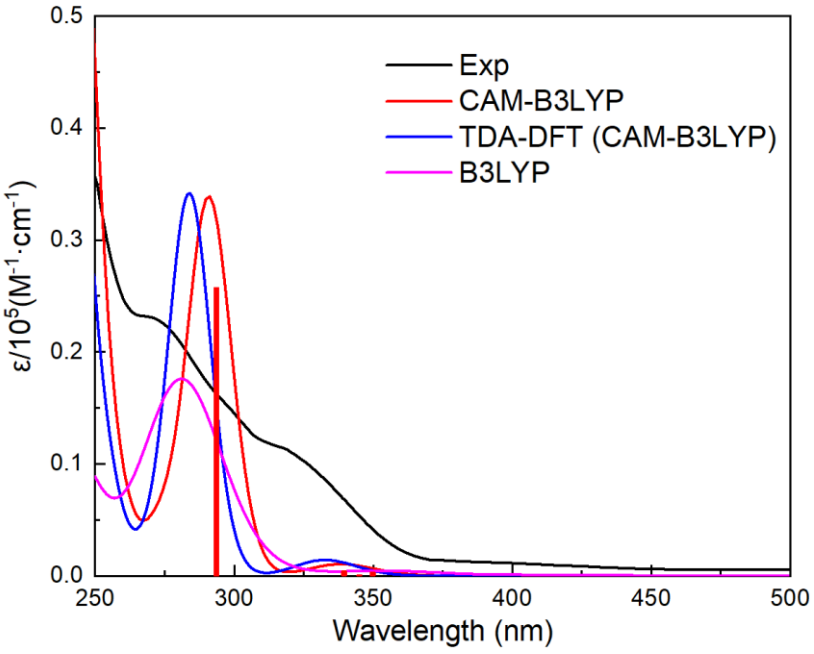
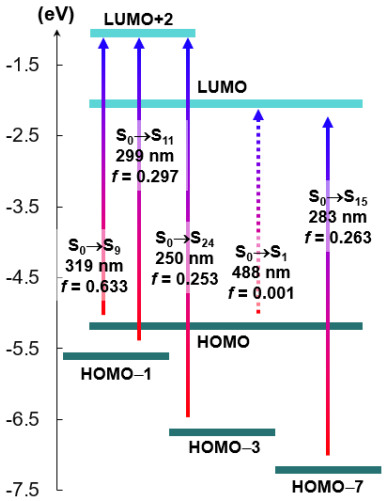


Figure S7. Experimental and calculated UV/vis spectra by TDDFT (B3LYP/6-31G(d) and CAM-B3LYP/6-31G(d)) and TDDFT with the Tamm–Dancoff approximation method using CAM-B3LYP/6-31G(d) of **3c.**

Major electronic transitions for **4** by TD-DFT method using B3LYP/6-31G(d).

4	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	2.5388	488.36	0.0005	H→L (98.9%)
S2	2.8028	442.36	0.0064	H–1→L (88.9%); H–2→L (10.1%)
S3	3.1696	391.17	0.0059	H-2→L (83.6%); H–1→L (10.1%)
S9	3.8866	319.01	0.6332	H→L+2 (60.4%); H–1→L+1 (17.2%); H–4→L (10.9%); H–2→L+1 (5.3%)
S11	4.1511	298.68	0.2673	H–1→L+2 (79.0%); H–7→L (6.8%); H–1→L+3 (6.0%)
S15	4.3820	282.94	0.2633	H–7→L (53.7%); H–2→L+2 (10.2%); H–1→L+3 (9.1%); H–1→L+2 (8.6%)
S24	4.9568	250.13	0.2534	H–3→L+2 (72.6%); H–1→L+3 (7.0%); H→L+4 (6.0%); H–1→L+5 (5.9%)



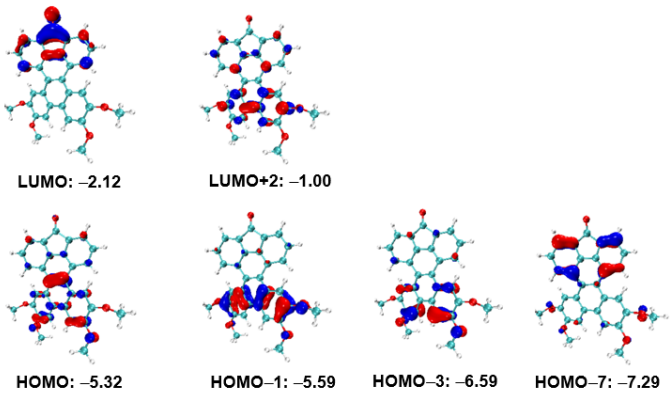


Table S8. Major electronic transitions for **4** by TD-DFT method using CAM-B3LYP/6-31G(d).

4	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	3.4851	355.75	0.0017	H→L (74.7%); H–6→L (10.4%); H–4→L (6.9%)
S2	3.5124	352.99	0.0075	H–2→L (62.6%); H–1→L (30.4%); H–3→L (4.5%)
S3	3.5981	344.58	0.0001	H–6→L (80.3%); H→L (10.9 %); H–6→L+8 (3.0%);
S4	3.8049	325.85	0.2824	H→L+1 (90.2%); H–1→L+2 (5.6%)
S7	4.4650	277.68	1.1783	H→L+2 (56.1%); H–1→L+1 (28.2%); H→L+3 (6.3%)
S8	4.4770	276.94	0.2077	H–2→L+1 (46.4%); H→L+3 (27.6%); H→L+2 (5.3%)
S9	4.7817	259.29	0.9107	H–1→L+2 (58.3%); H–1→L+3 (25.7%); H→L+1 (4.4%)
S12	5.0549	245.27	0.0770	H–1→L+3 (19.2%); H–1→L+2 (14.3%); H–2→L+2 (11.5%)

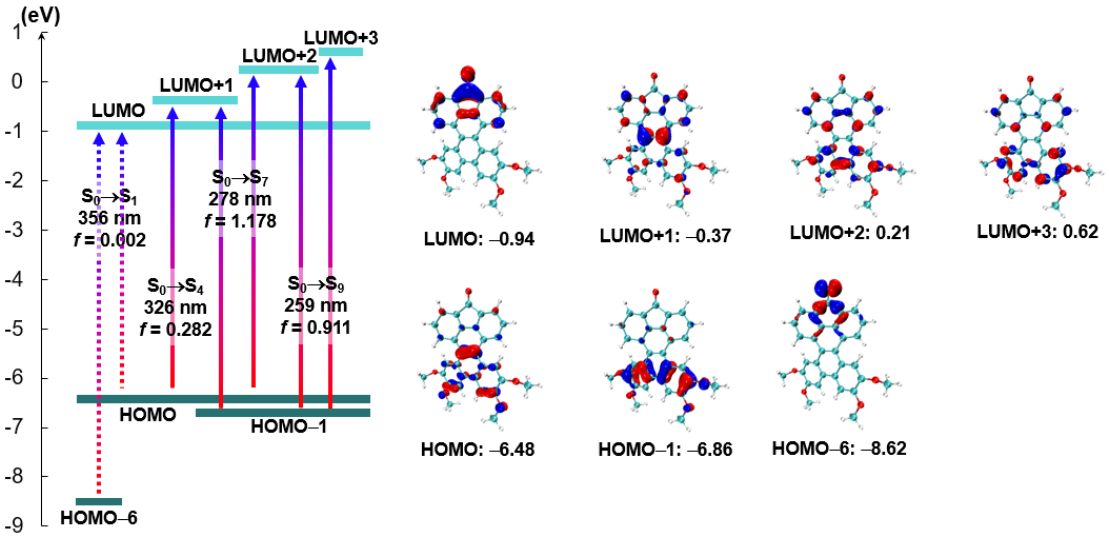


Table S9. Major electronic transitions for **4** by TD-DFT with the Tamm–Dancoff approximation (TDA) method using CAM-B3LYP/6-31G(d).

4	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	3.5401	350.23	0.0017	H→L (65.9%); H–6→L (19.2%); H–4→L (5.5%)
S2	3.5920	345.17	0.0134	H–2→L (60.2%); H–1→L (32.2%); H–3→L (4.1%)
S3	3.6328	341.29	0.0002	H–6→L (71.3%); H→L (19.1 %); H–6→L+8 (2.7%);
S4	3.9459	314.21	0.3006	H→L+1 (86.3%); H–1→L+2 (8.1%)
S7	4.5294	273.73	0.0308	H–2→L+1 (43.0%); H→L+3 (35.4%); H→L (4.5%)
S8	4.6154	268.63	1.6933	H→L+2 (54.8%); H–1→L+1 (32.1%); H–2→L+1 (4.3%)
S9	4.9300	251.49	0.6246	H–1→L+2 (42.9%); H–7→L (12.7%); H–1→L+3 (11.5%)
S10	4.9785	249.04	0.2518	H–1→L+3 (37.2%); H–7→L (17.3%); H–2→L+2 (10.3%)

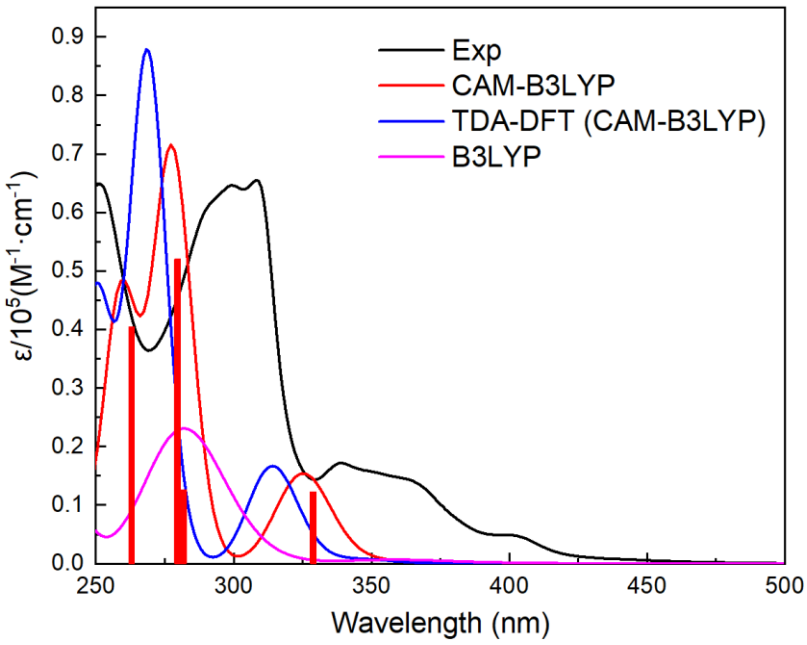


Figure S8. Experimental and calculated UV/vis spectra by TDDFT (B3LYP/6-31G(d) and CAM-B3LYP/6-31G(d)) and TDDFT with the Tamm–Dancoff approximation method using CAM-B3LYP/6-31G(d) of **4.**

Table S10. Major electronic transitions for **5** by TD-DFT method using CAM-B3LYP/6-31G(d).

5	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	2.8255	438.81	0.7935	H→L (96.4%); H–4→L (1.7%)
S2	3.4063	363.98	0.0004	H–2→L (95.2%); H–10→L (0.7%)
S3	3.4246	362.04	0.0001	H–3→L (94.9%); H–11→L (0.9 %);
S5	4.1209	300.87	0.4229	H–4→L (36.2%); H–3→L+1 (14.5%); H–12→L (13.9%)
S6	4.1722	297.16	0.0639	H→L+1 (77.0%); H–1→L+2 (16.7%); H–3→L+4 (1.4%)
S7	4.2512	291.64	0.5020	H→L+2 (72.3%); H–1→L+1 (18.4%); H–3→L+3 (2.2%)
S11	4.7834	259.20	0.1209	H–13→L (43.2%); H–10→L (26.1%); H–2→L+4 (6.5%)
S14	5.0142	247.27	1.7353	H→L+4 (59.8%); H–3→L+1 (13.1%); H–2→L+2 (12.6%)

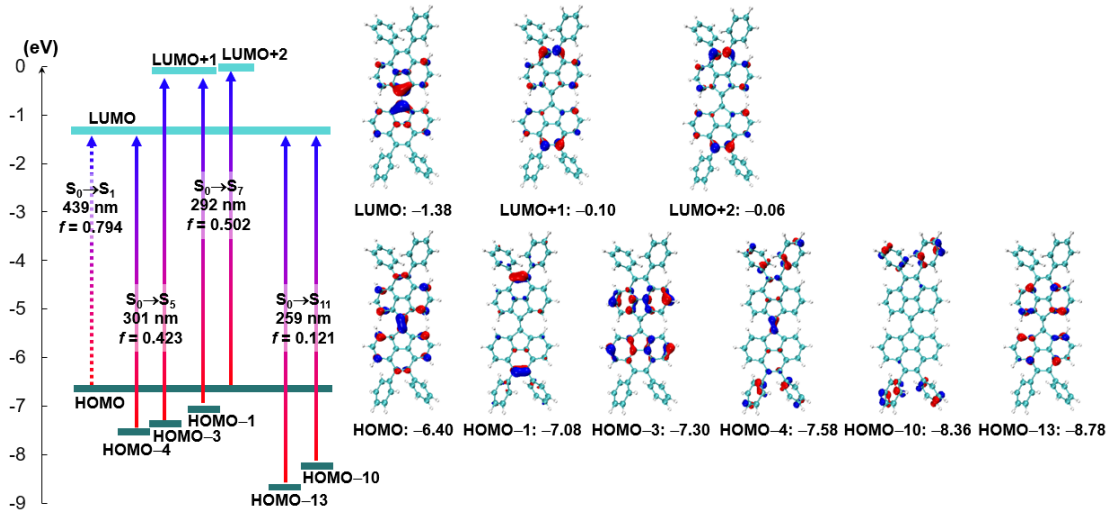


Table S11. Major electronic transitions for **5** by TD-DFT with the Tamm–Dancoff approximation (TDA) method using CAM-B3LYP/6-31G(d).

5	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	2.9548	419.61	0.9260	H→L (96.0%); H–4→L (0.9%)
S2	3.4635	357.97	0.0013	H–2→L (95.1%)
S3	3.4790	356.38	0.0002	H–3→L (95.0%); H–11→L (0.8%)
S5	4.1925	295.73	0.5583	H–4→L (36.2%); H–3→L+1 (15.3%); H–2→L+2 (14.1%)
S6	4.2870	289.21	0.0658	H→L+1 (79.1%); H–1→L+2 (12.8%); H–2→L+3 (1.9%)
S7	4.3582	284.49	0.4735	H→L+2 (73.3%); H–1→L+1 (13.1%); H–13→L (3.5%)
S11	4.8412	256.10	0.1812	H–13→L (39.0%); H–10→L (24.2%); H–2→L+4 (8.7%)
S13	4.9354	251.21	0.0450	H–1→L+1 (40.5%); H–4→L+2 (29.7%); H→L+2 (12.0%)

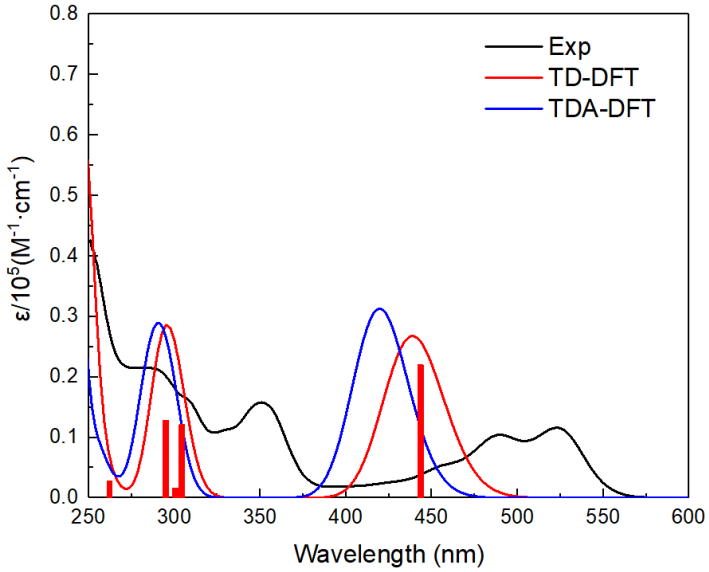


Figure S9. Experimental and calculated UV/vis spectra by TDDFT and TDDFT with the Tamm–Dancoff approximation method using CAM-B3LYP/6-31G(d) of **5.**

Table S12. Major electronic transitions for **6** by TD-DFT method using CAM-B3LYP/6-31G(d).

6	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	4.3106	287.63	0.0068	H–1→L (56.9%); H→L+1 (34.7%)
S2	4.3611	284.30	0.3627	H→L (89.2%); H–1→L+1 (8.1%)

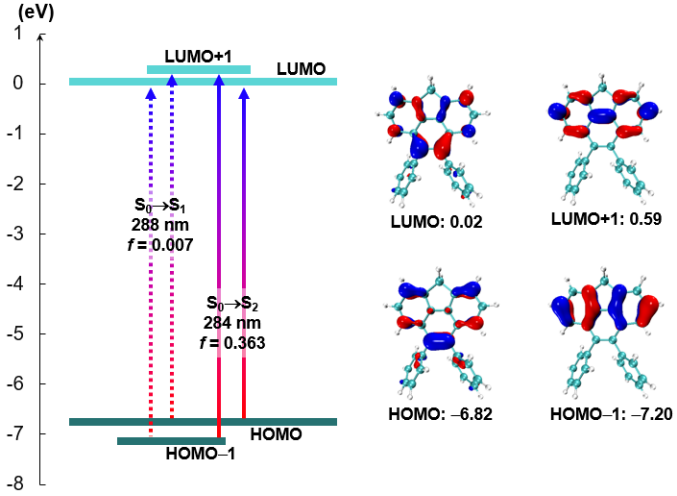


Table S13. Major electronic transitions for **6** by TD-DFT with the Tamm–Dancoff approximation (TDA) method using CAM-B3LYP/6-31G(d).

6	energy (eV)	Excitation (nm)	Oscillator strength (f)	Description
S1	4.3633	284.15	0.0046	H–1→L (53.7%); H→L+1 (37.8%)
S2	4.5078	275.05	0.3974	H→L (85.6%); H–1→L+1 (10.6%)

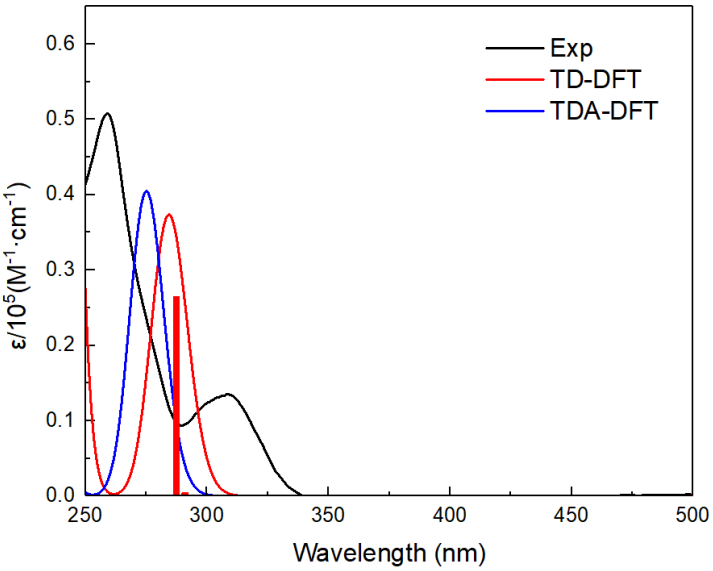


Figure S10. Experimental and calculated UV/vis spectra by TDDFT and TDDFT with the Tamm–Dancoff approximation method using CAM-B3LYP/6-31G(d) of **6.**

4.3 Jablonski diagram of 3a

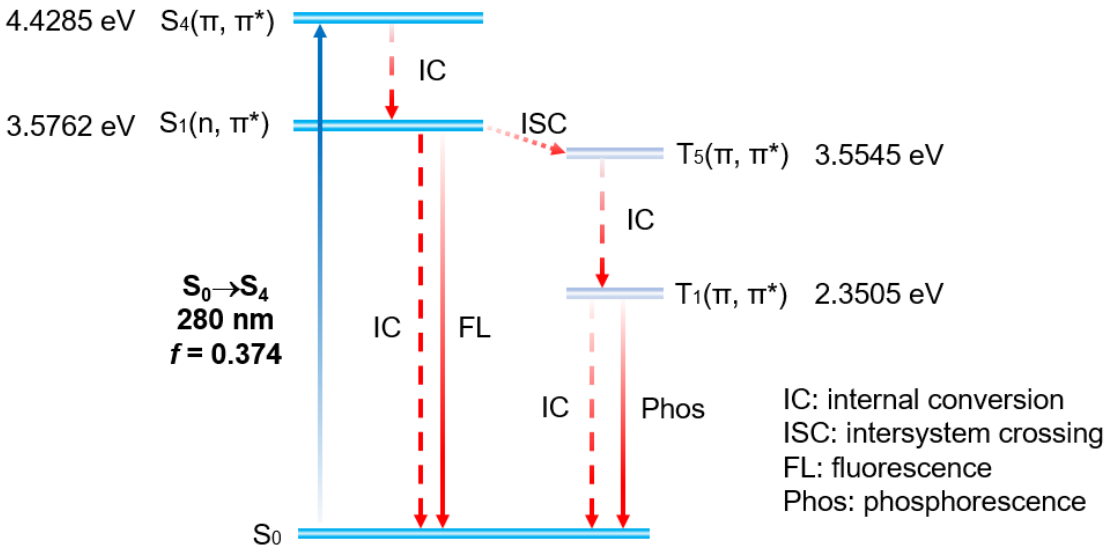


Figure S11. Jablonski diagram of **3a** excited states at room temperature. The excited state energy data was calculated by CAM-B3LYP/6-31G*.

4.4 Cartesian coordinates of optimized structures

Table S14. Cartesian coordinates of optimized structures calculated by B3LYP/6-31G(d) 9-Fluorenone, Phenanthrenone, **3a**, **3c**, **3g**, **3h**, **4**, **5**, **6**, and **7**).

9-Fluorenone

C	0.00000000	1.18946100	0.66562200	C	0.00000000	3.03147700	–1.39309500
C	0.00000000	0.74206000	–0.67141200	C	0.00000000	1.66455900	–1.71091700
C	0.00000000	–0.74206000	–0.67141200	O	0.00000000	0.00000000	2.79645100
C	0.00000000	–1.18946100	0.66562200	H	0.00000000	–1.34566800	–2.74991500
C	0.00000000	0.00000000	1.57802200	H	0.00000000	–3.76367300	–2.19630600
C	0.00000000	–1.66455900	–1.71091700	H	0.00000000	–4.53254400	0.15159600
C	0.00000000	–3.03147700	–1.39309500	H	0.00000000	–2.85474900	2.02329700
C	0.00000000	–3.46808400	–0.06531700	H	0.00000000	2.85474900	2.02329700
C	0.00000000	–2.53894300	0.98369500	H	0.00000000	4.53254400	0.15159600
C	0.00000000	2.53894300	0.98369500	H	0.00000000	3.76367300	–2.19630600
C	0.00000000	3.46808400	–0.06531700	H	0.00000000	1.34566800	–2.74991500

Phenanthrenone

C	0.00000000	2.57945200	1.29940000	C	0.00000000	–2.57945200	1.29940000
C	0.00000000	3.39132800	0.13147400	C	0.00000000	–1.20887400	1.13015400
C	0.00000000	2.86472200	–1.15755000	C	0.00000000	0.00000000	2.05967300
C	0.00000000	1.45673900	–1.35459800	O	0.00000000	0.00000000	3.27417200
C	0.00000000	0.70752200	–0.17975500	H	0.00000000	3.03491500	2.28568000
C	0.00000000	1.20887400	1.13015400	H	0.00000000	4.47126800	0.25246400
C	0.00000000	0.68883400	–2.58095300	H	0.00000000	3.53811300	–2.01149000
C	0.00000000	–0.68883400	–2.58095300	H	0.00000000	1.21724400	–3.53138700
C	0.00000000	–1.45673900	–1.35459800	H	0.00000000	–1.21724400	–3.53138700
C	0.00000000	–0.70752200	–0.17975500	H	0.00000000	–3.53811300	–2.01149000
C	0.00000000	–2.86472200	–1.15755000	H	0.00000000	–4.47126800	0.25246400
C	0.00000000	–3.39132800	0.13147400	H	0.00000000	–3.03491500	2.28568000

3a

C	0.00277800	3.38717100	2.35886200	C	–0.03184100	3.00242300	–4.03046200
C	0.00576400	2.86186000	1.06914100	C	1.06585300	3.06569600	–3.17067200
C	0.02000900	1.45252200	0.86433800	C	1.11426700	–2.18227200	–3.70667700
C	0.00902800	0.70651600	2.03905800	C	0.03184100	–3.00242300	–4.03046200
C	0.00754600	1.20705700	3.34977800	C	–1.06585300	–3.06569600	–3.17067200
C	0.00752000	2.57623300	3.52536500	C	–1.07910700	–2.31423000	–1.99487900
C	0.01200800	0.69802400	–0.38688300	H	–0.00735300	4.46731000	2.47755500
C	–0.01200800	–0.69802400	–0.38688300	H	–0.00595800	3.53763900	0.22007100
C	–0.02000900	–1.45252200	0.86433800	H	0.00578400	3.02747500	4.51350600
C	–0.00902800	–0.70651600	2.03905800	H	0.00595800	–3.53763900	0.22007100
C	–0.00576400	–2.86186000	1.06914100	H	0.00735300	–4.46731000	2.47755500
C	–0.00277800	–3.38717100	2.35886200	H	–0.00578400	–3.02747500	4.51350600
C	–0.00752000	–2.57623300	3.52536500	H	1.93817200	2.36438600	–1.33066300
C	–0.00754600	–1.20705700	3.34977800	H	1.94328100	–0.79221400	–2.28699400
C	0.00000000	0.00000000	4.27841700	H	–1.94328100	0.79221400	–2.28699400

O	0.00000000	0.00000000	5.49334600	H	–1.97502100	2.12933700	–4.36808800
C	0.00000000	1.47928100	–1.66231500	H	–0.04414800	3.58848500	–4.94548800
C	1.07910700	2.31423000	–1.99487900	H	1.91471300	3.69925200	–3.41445200
C	1.09855900	–1.42833600	–2.53366800	H	1.97502100	–2.12933700	–4.36808800
C	0.00000000	–1.47928100	–1.66231500	H	0.04414800	–3.58848500	–4.94548800
C	–1.09855900	1.42833600	–2.53366800	H	–1.91471300	–3.69925200	–3.41445200
C	–1.11426700	2.18227200	–3.70667700	H	–1.93817200	–2.36438600	–1.33066300

3c

C	–3.52151100	–3.44234600	0.25837700	O	3.24471700	2.14661800	–1.94495700
C	–2.26193000	–2.84954600	0.29671300	C	4.49838600	1.54584900	–1.61506500
C	–2.12597800	–1.43630000	0.18323300	O	3.71125300	3.98184200	0.01673100
C	–3.33387400	–0.75674500	0.05870300	C	3.93434200	4.99605800	0.98353500
C	–4.61561200	–1.32595300	0.01623700	C	–5.60027600	–0.17436100	–0.13305200
C	–4.72336900	–2.69873800	0.11425600	O	–6.81127100	–0.23973800	–0.20982500
C	–0.91646700	–0.61729800	0.21322200	H	–3.58712200	–4.52354600	0.34560600
C	–0.98558000	0.77526300	0.12102300	H	–1.38359400	–3.47569400	0.41562600
C	–2.27049200	1.45840200	–0.01360400	H	–5.68595000	–3.20158700	0.08800300
C	–3.40412500	0.65144100	–0.03750200	H	–1.72913200	3.56579600	–0.17756600
C	–2.54334500	2.84857300	–0.16039800	H	–4.02423300	4.36889500	–0.40000000
C	–3.85399600	3.30123300	–0.28971700	H	–5.98375600	2.82629200	–0.39381700
C	–4.97706700	2.43129100	–0.29056700	H	0.25975700	–2.40667000	–1.50126500
C	–4.73470200	1.07818800	–0.16469600	H	2.98311100	–1.65405100	2.56186800
C	0.39072100	–1.32346800	0.37641400	H	0.86648300	–0.44464600	2.28238000
C	0.24916000	1.61724400	0.12568900	H	1.09064000	0.76993500	–1.68498400
C	0.84246200	–2.22495100	–0.60295100	H	1.74712800	4.10390700	1.91548500
C	2.04499600	–2.91070600	–0.46694500	H	–0.26112900	2.69308700	1.92159200
C	2.83644900	–2.71506400	0.68750100	H	5.62958300	–3.99936200	1.78526000
C	2.39633200	–1.81828500	1.66510400	H	5.16200100	–2.29641900	2.05294300
C	1.18846700	–1.13419800	1.50850800	H	4.23111300	–3.61419600	2.82693800
C	1.21796300	1.49037200	–0.88391200	H	3.64509500	–4.27543600	–2.96268300
C	2.36235300	2.27731100	–0.89878900	H	3.40179200	–2.52139600	–2.72807200
C	2.56894500	3.24030400	0.11515300	H	4.45168400	–3.44135000	–1.60411300
C	1.61235100	3.37504100	1.12419600	H	5.05604300	1.47580500	–2.55207900
C	0.46617400	2.57371500	1.12319900	H	5.06028200	2.15639900	–0.90064400
O	3.98811500	–3.44580900	0.76040900	H	4.35131400	0.53836400	–1.20247600
C	4.78656100	–3.32070900	1.92677900	H	4.87555400	5.47289700	0.70418100
O	2.39800700	–3.81935400	–1.43506700	H	3.13110800	5.74425800	0.97321700
C	3.54610600	–3.48304800	–2.21716400	H	4.02499400	4.57882500	1.99539400

3g

C	2.53438900	2.86646300	0.03240100	C	–1.07290500	1.43200800	1.12508700
C	2.32290700	1.45840300	0.00065100	C	–3.85783500	3.78703200	0.07976300
C	3.49290000	0.70488200	–0.00095900	C	–3.83871700	–3.80600800	–0.08975000
C	4.80614700	1.19886100	0.00373500	F	–3.75908000	4.93641100	–0.62532800
C	4.98870100	2.56680300	0.02064100	F	–4.86522300	3.07287800	–0.47491600
C	3.82677300	3.38436200	0.03866700	F	–4.24981600	4.11018100	1.33204800
C	1.06966200	0.70819300	0.00155100	F	–4.81375400	–3.23204000	–0.82782800
C	1.06278200	–0.68767600	0.00814800	F	–3.59541800	–5.02071800	–0.63722200
C	2.30854000	–1.45022000	0.00278200	F	–4.33965800	–4.02823400	1.14602500
C	3.48591200	–0.70833700	–0.00169200	C	5.72905200	–0.01286500	–0.00690100
C	2.50575700	–2.86032600	–0.02969300	O	6.94331300	–0.01883600	–0.00989600
C	3.79289000	–3.39103000	–0.04236800	H	1.69025100	3.54815400	0.05593900
C	4.96296100	–2.58504600	–0.03041400	H	5.97910100	3.01282700	0.02567300
C	4.79414800	–1.21533600	–0.01287900	H	3.95157300	4.46343800	0.06224900
C	–0.20360300	1.49206600	0.02530700	H	1.65471600	–3.53351800	–0.04872600
C	–0.21774600	–1.45980200	–0.00864500	H	3.90683900	–4.47129300	–0.06634500
C	–1.09415500	–1.38964000	–1.10205800	H	5.94883300	–3.04091600	–0.04033400
C	–2.27280900	–2.13075400	–1.12269800	H	–0.84933300	–0.74708900	–1.94184600
C	–2.59575400	–2.95929800	–0.04541700	H	–2.94436300	–2.06195400	–1.97213000
C	–1.73271900	–3.04381000	1.04970800	H	–1.98744200	–3.67916800	1.89171800
C	–0.55332300	–2.30282300	1.06335100	H	0.11065000	–2.36703100	1.92092000
C	–0.53574000	2.34114800	–1.04287000	H	0.12749000	2.40514500	–1.90101400
C	–1.70736200	3.09433700	–1.02157000	H	–1.95252100	3.74515100	–1.85453100
C	–2.56495200	3.01737000	0.07829000	H	–2.90297700	2.13454900	2.01360800
C	–2.24376100	2.18500200	1.15326600	H	–0.82562200	0.79234300	1.96637600

3h

C	–0.04744300	2.86402300	1.73632000	C	–0.07957000	2.99074500	–3.36658200
C	–0.00628700	1.45515000	1.53181200	C	–1.15086100	2.14106100	–3.04514900
C	–0.00396300	0.70663500	2.70513100	C	–1.11820200	1.39592100	–1.87157400
C	–0.01483200	1.20708800	4.01583600	C	–0.10707000	3.76304500	–4.57424600
C	–0.04006800	2.57566700	4.19184400	C	0.10707000	–3.76304500	–4.57424600
C	–0.06006000	3.38779400	3.02617000	C	0.00000000	0.00000000	4.94503700
C	0.00000000	0.69814500	0.28281600	O	0.00000000	0.00000000	6.15891100
C	0.00000000	–0.69814500	0.28281600	N	–0.12825300	4.39165600	–5.55288200
C	0.00628700	–1.45515000	1.53181200	N	0.12825300	–4.39165600	–5.55288200
C	0.00396300	–0.70663500	2.70513100	H	–0.07395600	3.54244600	0.88966700
C	0.04744300	–2.86402300	1.73632000	H	–0.05028100	3.02622100	5.18009600
C	0.06006000	–3.38779400	3.02617000	H	–0.09074300	4.46719500	3.14579000
C	0.04006800	–2.57566700	4.19184400	H	0.07395600	–3.54244600	0.88966700
C	0.01483200	–1.20708800	4.01583600	H	0.09074300	–4.46719500	3.14579000
C	–0.02502200	1.47502900	–0.99391200	H	0.05028100	–3.02622100	5.18009600
C	0.02502200	–1.47502900	–0.99391200	H	1.95197000	–0.74541500	–1.62768300
C	1.11820200	–1.39592100	–1.87157400	H	2.00191800	–2.07349500	–3.71505400
C	1.15086100	–2.14106100	–3.04514900	H	–1.84740400	–3.73761300	–2.74340600
C	0.07957000	–2.99074500	–3.36658200	H	–1.89022800	–2.40938400	–0.65463500
C	–1.01803400	–3.08312300	–2.49523800	H	1.89022800	2.40938400	–0.65463500
C	–1.03668600	–2.33522700	–1.32245200	H	1.84740400	3.73761300	–2.74340600
C	1.03668600	2.33522700	–1.32245200	H	–2.00191800	2.07349500	–3.71505400
C	1.01803400	3.08312300	–2.49523800	H	–1.95197000	0.74541500	–1.62768300

4

C	–1.58577100	2.98998400	3.53855800	C	–0.69782000	5.70053500	–2.18835600
C	–1.29680100	2.55391100	2.24656100	O	–0.34882100	–4.90144000	–1.63192300
C	–0.57904200	1.34165000	2.02061900	C	0.69782000	–5.70053500	–2.18835600
C	–0.30579200	0.64019700	3.19102100	O	–0.44749000	–3.61565600	–4.04105700
C	–0.55372500	1.06909500	4.50340900	C	–0.61989400	–2.96471100	–5.28995000
C	–1.19551400	2.27585200	4.69724800	C	0.00000000	0.00000000	5.42940500
C	–0.18173600	0.68679000	0.76423000	O	0.00000000	0.00000000	6.64490200
C	0.18173600	–0.68679000	0.76423000	H	–2.14112900	3.91658500	3.65611000
C	0.57904200	–1.34165000	2.02061900	H	–1.67233600	3.13941800	1.41629800
C	0.30579200	–0.64019700	3.19102100	H	–1.41515300	2.65628300	5.69057700
C	1.29680100	–2.55391100	2.24656100	H	1.67233600	–3.13941800	1.41629800
C	1.58577100	–2.98998400	3.53855800	H	2.14112900	–3.91658500	3.65611000
C	1.19551400	–2.27585200	4.69724800	H	1.41515300	–2.65628300	5.69057700
C	0.55372500	–1.06909500	4.50340900	H	0.03432500	3.40938800	0.38520600
C	–0.10237300	1.41858600	–0.49454300	H	0.33214400	0.92771900	–3.85434000
C	0.10237300	–1.41858600	–0.49454300	H	–0.03432500	–3.40938800	0.38520600
C	0.00000000	2.83285300	–0.52834900	H	–0.33214400	–0.92771900	–3.85434000
C	0.16305100	3.54282700	–1.69909900	H	0.76183100	3.75988800	–6.02381400
C	0.25435200	2.84541800	–2.93249700	H	1.50390600	2.31392300	–5.28365600
C	0.19220200	1.46247800	–2.92477700	H	–0.26399300	2.37209500	–5.56129400
C	0.02066800	0.72604100	–1.72901700	H	–0.40771600	6.73923300	–2.01460500
C	0.00000000	–2.83285300	–0.52834900	H	–0.80952200	5.52593400	–3.26284200
C	–0.16305100	–3.54282700	–1.69909900	H	–1.65202200	5.50095300	–1.68197200
C	–0.25435200	–2.84541800	–2.93249700	H	0.40771600	–6.73923300	–2.01460500
C	–0.19220200	–1.46247800	–2.92477700	H	0.80952200	–5.52593400	–3.26284200
C	–0.02066800	–0.72604100	–1.72901700	H	1.65202200	–5.50095300	–1.68197200
O	0.44749000	3.61565600	–4.04105700	H	–0.76183100	–3.75988800	–6.02381400
C	0.61989400	2.96471100	–5.28995000	H	–1.50390600	–2.31392300	–5.28365600
O	0.34882100	4.90144000	–1.63192300	H	0.26399300	–2.37209500	–5.56129400

5

C	–0.83495900	2.73193600	–3.90712400	C	–0.63102700	1.69498900	7.49282300
C	–0.42581900	1.38642300	–4.09713800	C	–0.42134700	2.41582700	8.66815200
C	–0.18385000	0.67699600	–2.92020700	C	0.85738900	2.86983400	8.99634700
C	–0.29029300	1.15543100	–1.59470100	C	1.92496900	2.59995700	8.13860200
C	–0.75928500	2.45740300	–1.45066200	C	1.71348800	1.88175300	6.96096200
C	–1.00871200	3.22265400	–2.61591900	C	–1.71348800	–1.88175300	6.96096200
C	–0.21256200	0.66398100	–5.34732100	C	–1.92496900	–2.59995700	8.13860200
C	0.21256200	–0.66398100	–5.34732100	C	–0.85738900	–2.86983400	8.99634700
C	0.42581900	–1.38642300	–4.09713800	C	0.42134700	–2.41582700	8.66815200
C	0.18385000	–0.67699600	–2.92020700	C	0.63102700	–1.69498900	7.49282300
C	0.83495900	–2.73193600	–3.90712400	C	0.00000000	0.00000000	0.68770300
C	1.00871200	–3.22265400	–2.61591900	H	–1.02623100	3.37713000	–4.75813600
C	0.75928500	–2.45740300	–1.45066200	H	–0.94887500	2.90083500	–0.48035200
C	0.29029300	–1.15543100	–1.59470100	H	–1.34977600	4.24712300	–2.49112800
C	–0.43355600	1.41273300	–6.62365100	H	1.02623100	–3.37713000	–4.75813600
C	0.43355600	–1.41273300	–6.62365100	H	1.34977600	–4.24712300	–2.49112800
C	–0.63102700	–1.69498900	–7.49282300	H	0.94887500	–2.90083500	–0.48035200
C	–0.42134700	–2.41582700	–8.66815200	H	–1.62775000	–1.34403200	–7.24274700

C	0.85738900	−2.86983400	−8.99634700	H	−1.25962400	−2.62391500	−9.32795600
C	1.92496900	−2.59995700	−8.13860200	H	1.02045400	−3.43032900	−9.91303500
C	1.71348800	−1.88175300	−6.96096200	H	2.92501100	−2.94715100	−8.38547500
C	−1.71348800	1.88175300	−6.96096200	H	2.54861500	−1.67204700	−6.29751000
C	−1.92496900	2.59995700	−8.13860200	H	−2.54861500	1.67204700	−6.29751000
C	−0.85738900	2.86983400	−8.99634700	H	−2.92501100	2.94715100	−8.38547500
C	0.42134700	2.41582700	−8.66815200	H	−1.02045400	3.43032900	−9.91303500
C	0.63102700	1.69498900	−7.49282300	H	1.25962400	2.62391500	−9.32795600
C	0.00000000	0.00000000	−0.68770300	H	1.62775000	1.34403200	−7.24274700
C	−0.83495900	−2.73193600	3.90712400	H	−1.02623100	−3.37713000	4.75813600
C	−0.42581900	−1.38642300	4.09713800	H	−0.94887500	−2.90083500	0.48035200
C	−0.18385000	−0.67699600	2.92020700	H	−1.34977600	−4.24712300	2.49112800
C	−0.29029300	−1.15543100	1.59470100	H	1.02623100	3.37713000	4.75813600
C	−0.75928500	−2.45740300	1.45066200	H	1.34977600	4.24712300	2.49112800
C	−1.00871200	−3.22265400	2.61591900	H	0.94887500	2.90083500	0.48035200
C	−0.21256200	−0.66398100	5.34732100	H	−1.62775000	1.34403200	7.24274700
C	0.21256200	0.66398100	5.34732100	H	−1.25962400	2.62391500	9.32795600
C	0.42581900	1.38642300	4.09713800	H	1.02045400	3.43032900	9.91303500
C	0.18385000	0.67699600	2.92020700	H	2.92501100	2.94715100	8.38547500
C	0.83495900	2.73193600	3.90712400	H	2.54861500	1.67204700	6.29751000
C	1.00871200	3.22265400	2.61591900	H	−2.54861500	−1.67204700	6.29751000
C	0.75928500	2.45740300	1.45066200	H	−2.92501100	−2.94715100	8.38547500
C	0.29029300	1.15543100	1.59470100	H	−1.02045400	−3.43032900	9.91303500
C	−0.43355600	−1.41273300	6.62365100	H	1.25962400	−2.62391500	9.32795600
C	0.43355600	1.41273300	6.62365100	H	1.62775000	−1.34403200	7.24274700

6

C	−0.04164300	2.85992800	1.24924900	C	−0.08190100	2.99185300	−3.84533300
C	−0.00500200	1.45519100	1.05475400	C	−1.15269800	2.15864500	−3.51644200
C	−0.00312700	0.70356200	2.23296800	C	−1.12458300	1.40908300	−2.34074000
C	−0.01273700	1.20074300	3.54703700	C	0.00000000	0.00000000	4.50222700
C	−0.03521400	2.57384200	3.70627400	H	−0.06419700	3.53391900	0.39920000
C	−0.05312000	3.38244300	2.54004300	H	−0.04458400	3.04387900	4.68664900
C	0.00000000	0.69782200	−0.19398800	H	−0.08030100	4.46238600	2.66161700
C	0.00000000	−0.69782200	−0.19398800	H	0.06419700	−3.53391900	0.39920000
C	0.00500200	−1.45519100	1.05475400	H	0.08030100	−4.46238600	2.66161700
C	0.00312700	−0.70356200	2.23296800	H	0.04458400	−3.04387900	4.68664900
C	0.04164300	−2.85992800	1.24924900	H	1.96022600	−0.76247900	−2.09032300
C	0.05312000	−3.38244300	2.54004300	H	2.01404800	−2.09203400	−4.17601500
C	0.03521400	−2.57384200	3.70627400	H	0.10351000	−3.57459700	−4.76242800
C	0.01273700	−1.20074300	3.54703700	H	−1.85618800	−3.71644000	−3.23473800
C	−0.02539700	1.47648600	−1.47129900	H	−1.89977700	−2.38969500	−1.14555500
C	0.02539700	−1.47648600	−1.47129900	H	1.89977700	2.38969500	−1.14555500
C	1.12458300	−1.40908300	−2.34074000	H	1.85618800	3.71644000	−3.23473800
C	1.15269800	−2.15864500	−3.51644200	H	−0.10351000	3.57459700	−4.76242800
C	0.08190100	−2.99185300	−3.84533300	H	−2.01404800	2.09203400	−4.17601500
C	−1.01622800	−3.07226700	−2.98746000	H	−1.96022600	0.76247900	−2.09032300
C	−1.04144800	−2.32485100	−1.80928800	H	−0.87924600	−0.00960800	5.16024800
C	1.04144800	2.32485100	−1.80928800	H	0.87924600	0.00960800	5.16024800
C	1.01622800	3.07226700	−2.98746000				

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C	–0.03389200	2.85777800	0.28236900	C	0.06931200	–3.00425200	–4.81123300
C	0.00000000	1.44928200	0.08114200	C	–1.02901400	–3.07827700	–3.95315900
C	–0.00081800	0.70259700	1.25468700	C	–1.05166300	–2.32619400	–2.77788900
C	–0.00895000	1.19607100	2.57660800	C	0.00000000	0.00000000	4.84045500
C	–0.02775900	2.57458600	2.74084000	C	–0.00921600	1.20957000	5.60314100
C	–0.04376200	3.37921400	1.57230300	C	0.00921600	–1.20957000	5.60314100
C	0.00264300	0.69783500	–1.17067400	N	–0.01668200	2.19387400	6.22481700
C	–0.00264300	–0.69783500	–1.17067400	N	0.01668200	–2.19387400	6.22481700
C	0.00000000	–1.44928200	0.08114200	H	–0.05507700	3.53261400	–0.56697000
C	0.00081800	–0.70259700	1.25468700	H	–0.03559400	3.04829400	3.71569300
C	0.03389200	–2.85777800	0.28236900	H	–0.06851200	4.45806300	1.69631800
C	0.04376200	–3.37921400	1.57230300	H	0.05507700	–3.53261400	–0.56697000
C	0.02775900	–2.57458600	2.74084000	H	0.06851200	–4.45806300	1.69631800
C	0.00895000	–1.19607100	2.57660800	H	0.03559400	–3.04829400	3.71569300
C	0.00000000	0.00000000	3.46808100	H	1.91154000	2.38423900	–2.11530600
C	–0.01878000	1.48040800	–2.44504800	H	1.87092100	3.72059600	–4.19774100
C	1.05166300	2.32619400	–2.77788900	H	–0.08891400	3.59086500	–5.72569700
C	1.02901400	3.07827700	–3.95315900	H	–2.00384400	2.11162900	–5.14728800
C	–0.06931200	3.00425200	–4.81123300	H	–1.95586300	0.77301600	–3.06748700
C	–1.14293000	2.17278500	–4.48692400	H	1.95586300	–0.77301600	–3.06748700
C	–1.11805600	1.41803700	–3.31463600	H	2.00384400	–2.11162900	–5.14728800
C	0.01878000	–1.48040800	–2.44504800	H	0.08891400	–3.59086500	–5.72569700
C	1.11805600	–1.41803700	–3.31463600	H	–1.87092100	–3.72059600	–4.19774100
C	1.14293000	–2.17278500	–4.48692400	H	–1.91154000	–2.38423900	–2.11530600

5. Cyclic voltammetry

The three compounds showed different peak situations between 1.0 and 1.8 V. Compounds **3c** and **4** can be detected anode peaks in this section while **3a** is detected no peak. The different peak numbers could be attributed to the presence and quantity of methoxyl groups[6].

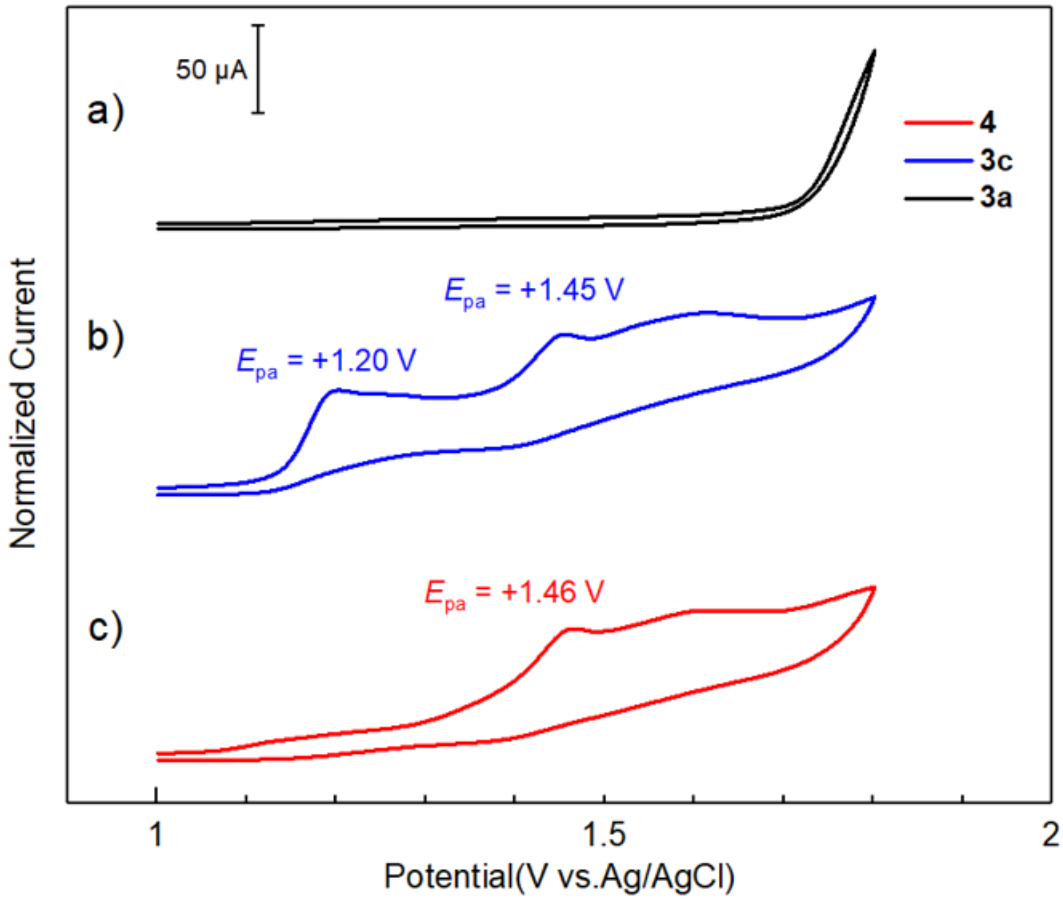


Figure S12. Cyclic voltammogram of **3a**, **3c**, and **4** in CH_3CN/CH_2Cl_2 (7:3, v/v) solution containing 0.1 M n-Bu_4NPF_6 at room temperature at a scan rate of 0.05 V/s.

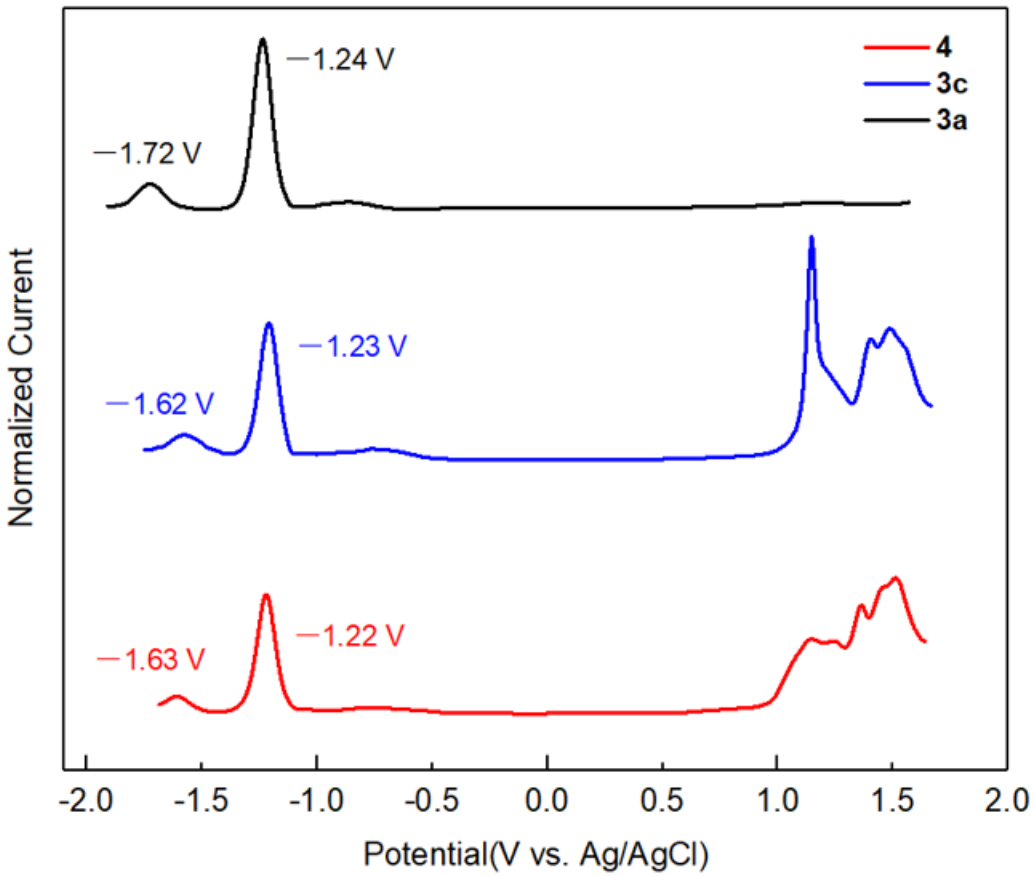
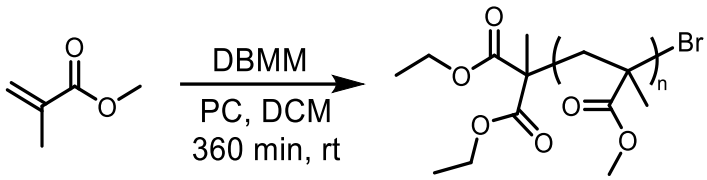


Figure S13. Differential pulse voltammetry of **3a**, **3c**, and **4** in CH_3CN/CH_2Cl_2 (7:3, v/v) solution containing 0.1 M n-Bu_4NPF_6 at room temperature at a scan rate of 0.05 V/s.

6. Polymerization

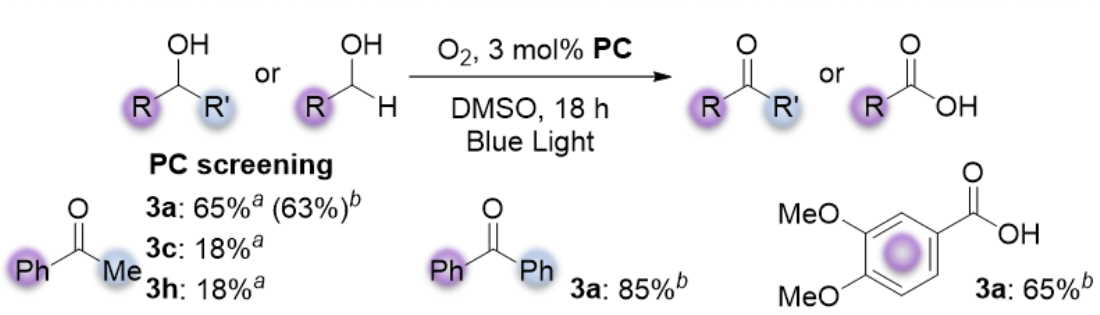


A dry Schlenk tube was charged with methyl methacrylate, DBMM, PC, and anhydrous DMA as solvent (0.5 mL), inside the glove box. Subsequently, the polymerization was carried out for a certain period under purple LED irradiation at room temperature. The tube was opened under argon and 20.0 μL of mixture were syringed out and quenched into $CDCl_3$ to determine the monomer conversion by ^1H NMR. To isolate the polymers, the reaction mixture was dropped into a beaker containing methanol (50.0 mL) which caused the polymer to precipitate. Subsequent stirring for 0.5 h, followed by vacuum filtration resulted in dried polymers.

Table S15. Polymerization results of MMA in various conditions.

Entry	Ratio	PC	Solvent	Conv	$M_{n,exp}$ (kDa)	Đ
1	100:1	—	DMA	19	198.2	1.51
2	100:1:0.05	**4a**	DMA	40	66.6	1.52
3	100:1:0.05	**4c**	DMA	53	47.6	1.61
4	100:1:0.05	**6**	DMA	67	15.8	1.44
5	100:1:0.05	**6**	DCM	62	6.3	1.76
6	100:1:0.05	**6**	THF	24	7.2	1.93
7	200:1:0.1	**6**	DMA	55	10.6	2.07
8	100:1:0.01	**6**	DMA	53	34.5	1.34
9	100:1:0.05	phenanthrene	DMA	28	139.9	1.66
10	100:1:0.05	9-fluorenone	DMA	36	40.4	2.21

7. Photocatalytic reaction



[a]Yields were determined by ^{1}H NMR spectroscopy
[b]isolated yields.

A dry Schlenk tube was charged with alcohol, PC (3% mmol), and anhydrous DMSO as solvent (1.0 mL). Subsequently, the reaction tube was carried out for a certain period under blue LED irradiation at room temperature. The reaction reacted in the atmosphere of oxygen. After 18 h, the mixture was poured into 200.0 mL water and extracted three times with DCM. After being concentrated under vacuum, the crude residue was purified by silica gel chromatography to get a pure product.

8. X–ray data

Table S16. Crystallographic data and structure refinement details for **3a**.

2236009 (CCDC)	**3a**
formula	$C_{27}H_{16}O$
fw	356.40
T (K)	293(2)
λ (Å)	0.71073
Crystal system	triclinic
Space group	P-1
a/Å	9.6312(6)
b/Å	9.8993(8)
c/Å	10.4806(6)
α (deg)	91.871(6)
β (deg)	112.284(6)
γ (deg)	101.558(6)
V (Å^3)	899.34(11)
Z	2
*D*calc (g/cm^3)	1.316
μ (mm^{-1})	0.078
F(000)	372.0
cryst size (mm)	0.05 × 0.02 × 0.01
2θ range (deg)	5.552 to 50.054
reflns collected	11227
indep reflns/*R*int	3166/0.0377
params	253
GOF on F^2	1.050
*R*1, *wR*2 [*I*>2σ(*I*)]	0.0449, 0.1164
*R*1, *wR*2 (all data)	0.0673, 0.1289

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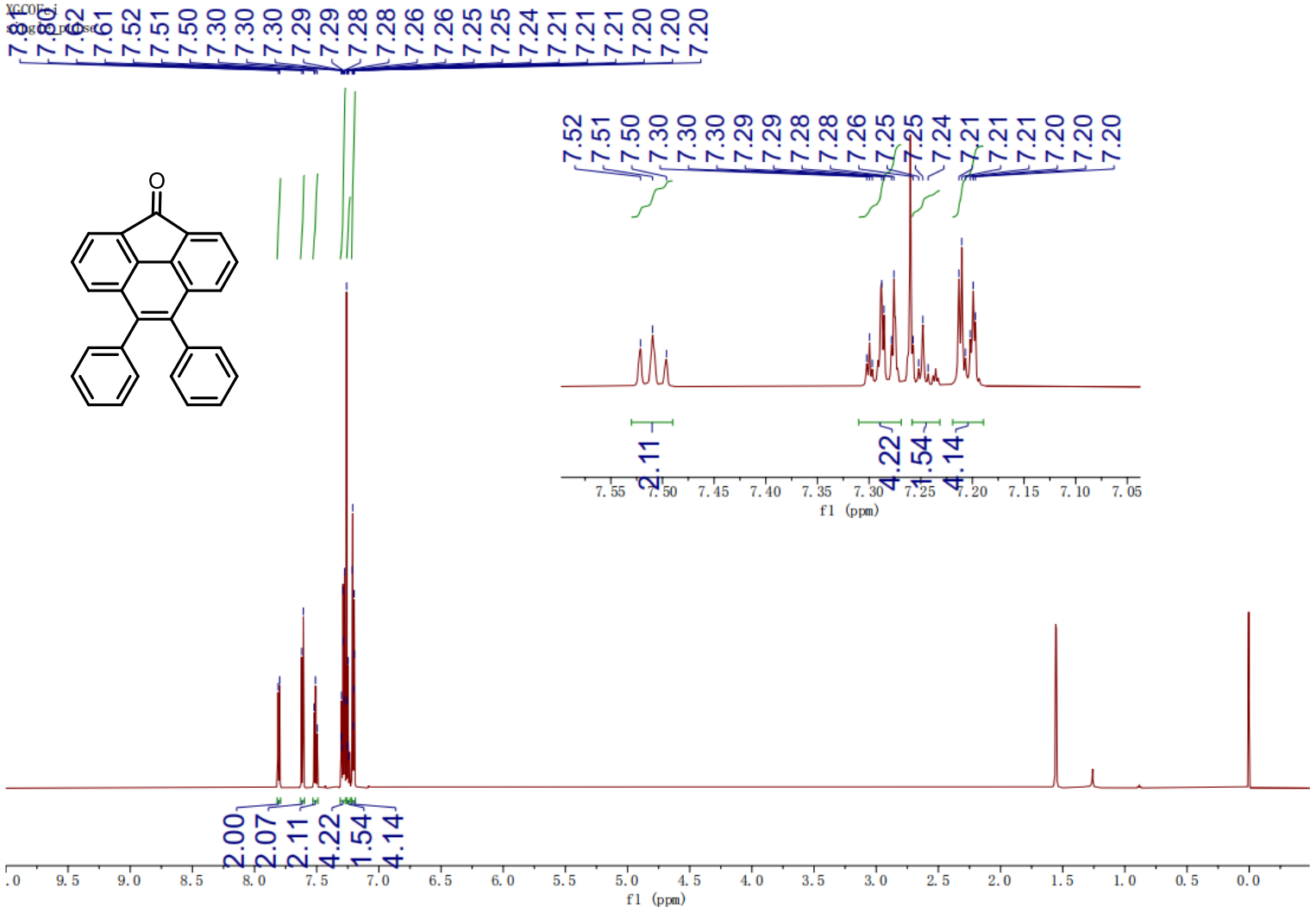
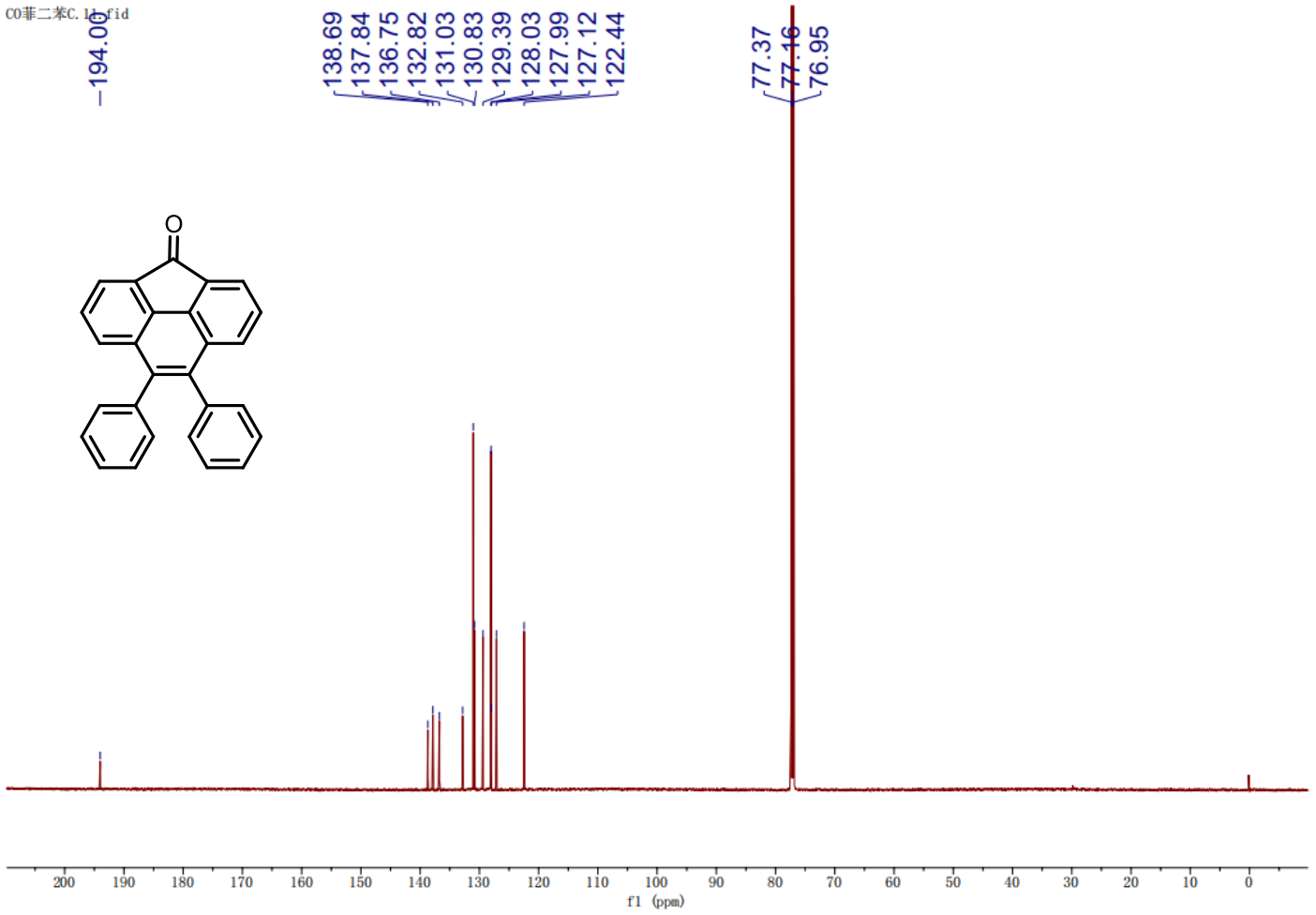
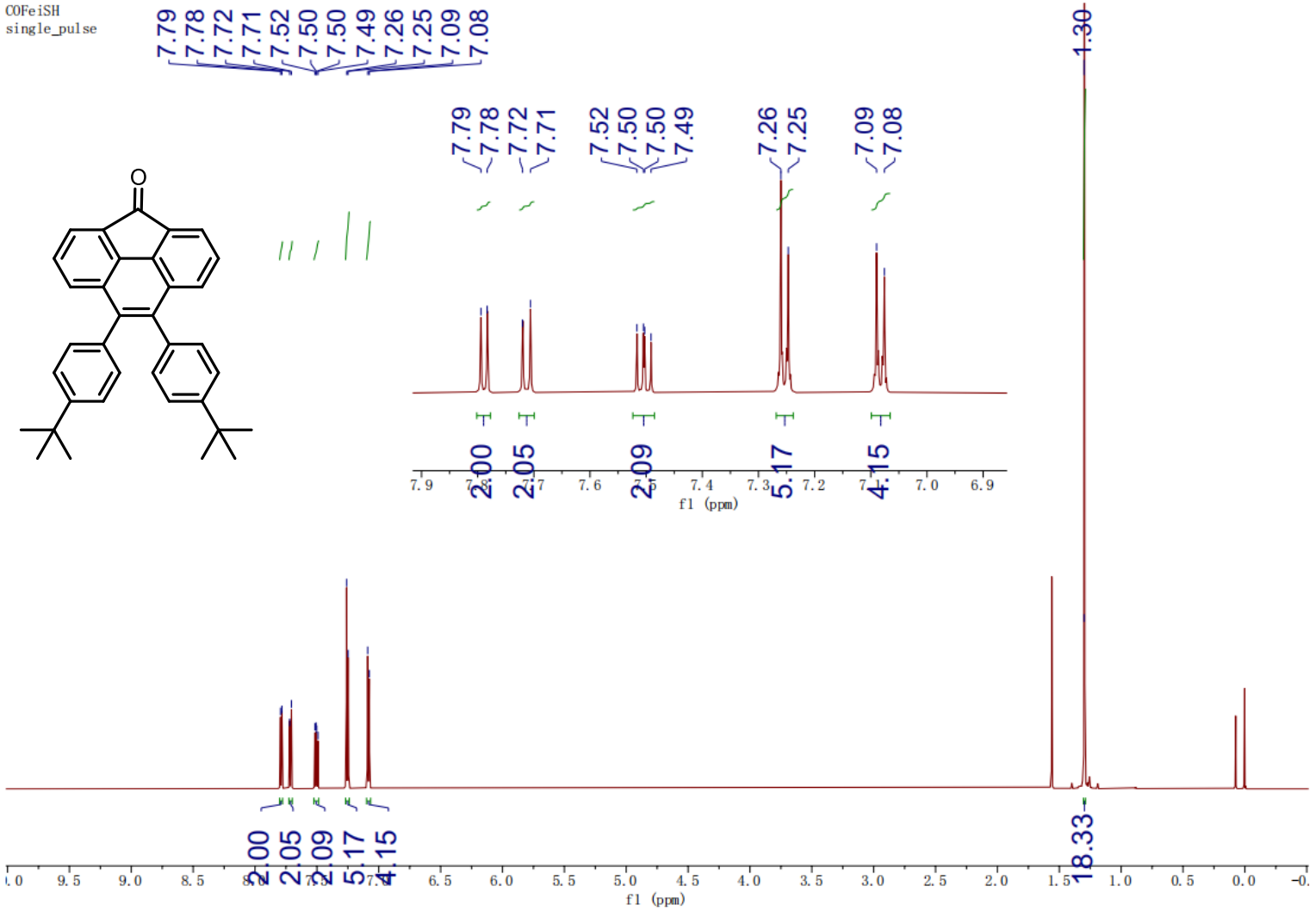
NMR Spectrogram

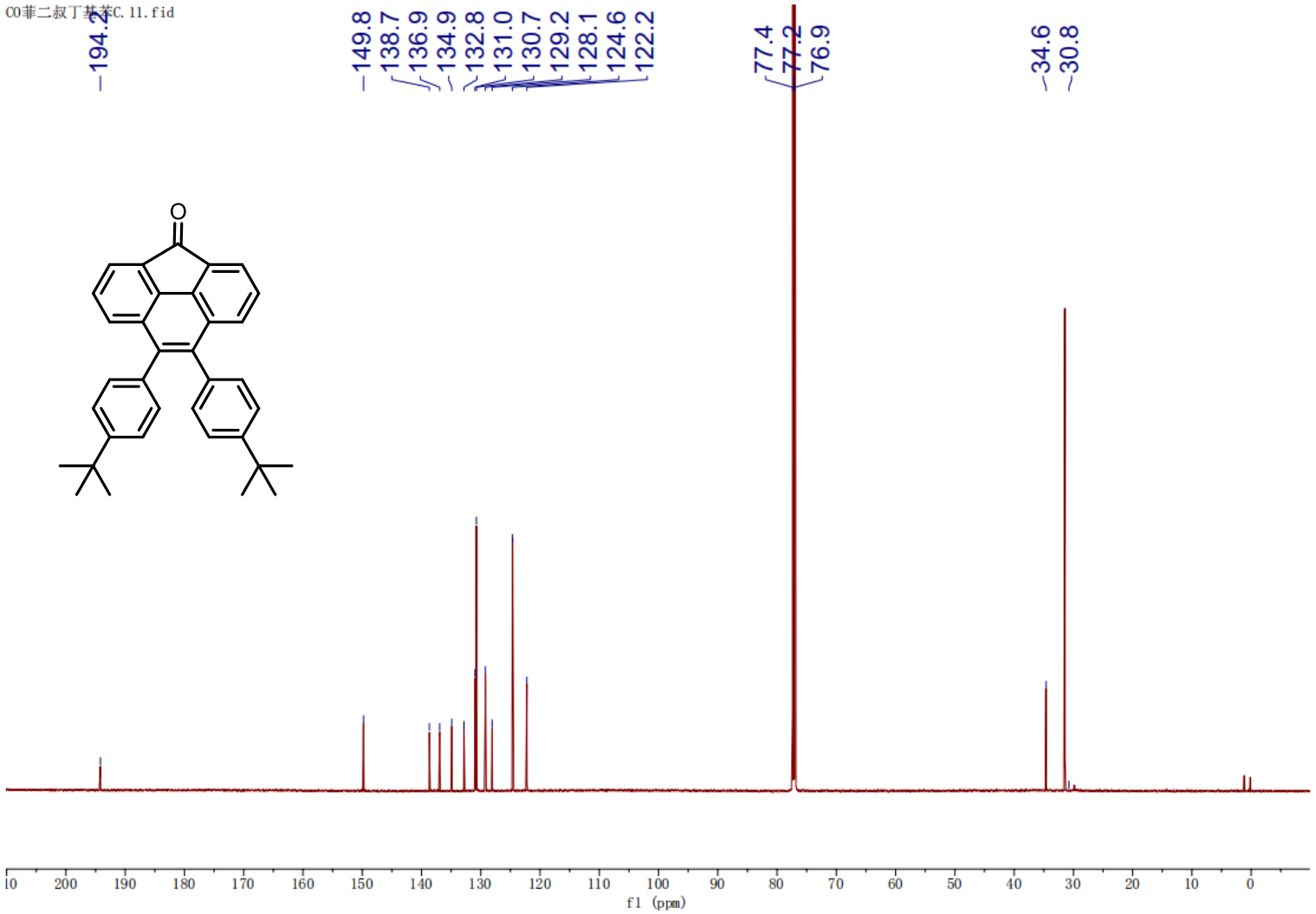
8,9–diphenyl–4H–cyclopenta[def]phenanthren–4–one (3a):



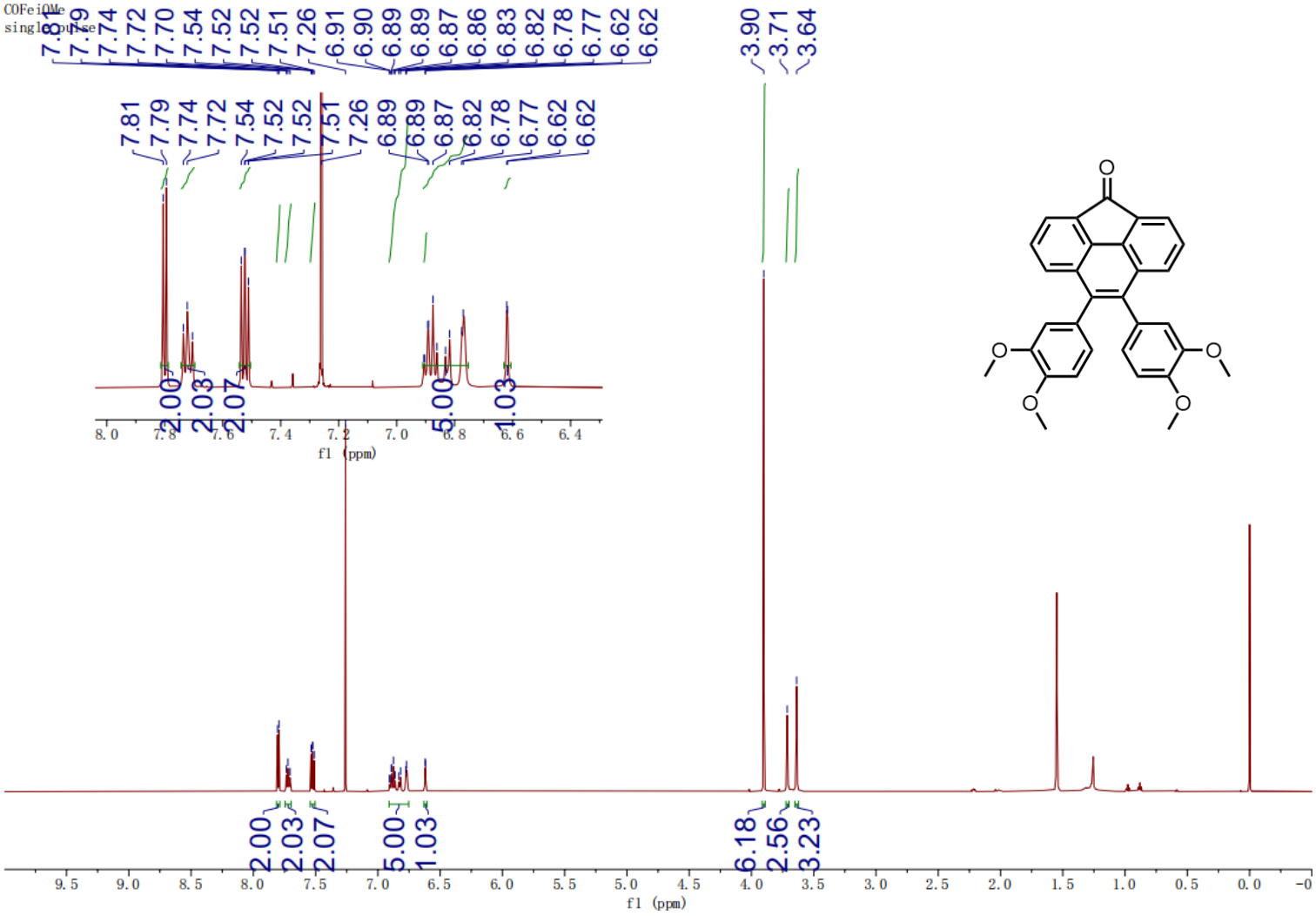

C0菲二苯C.1.fid
194.06
138.69
137.84
136.75
132.82
131.03
130.83
129.39
128.03
127.99
127.12
122.44
77.37
77.16
76.95
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

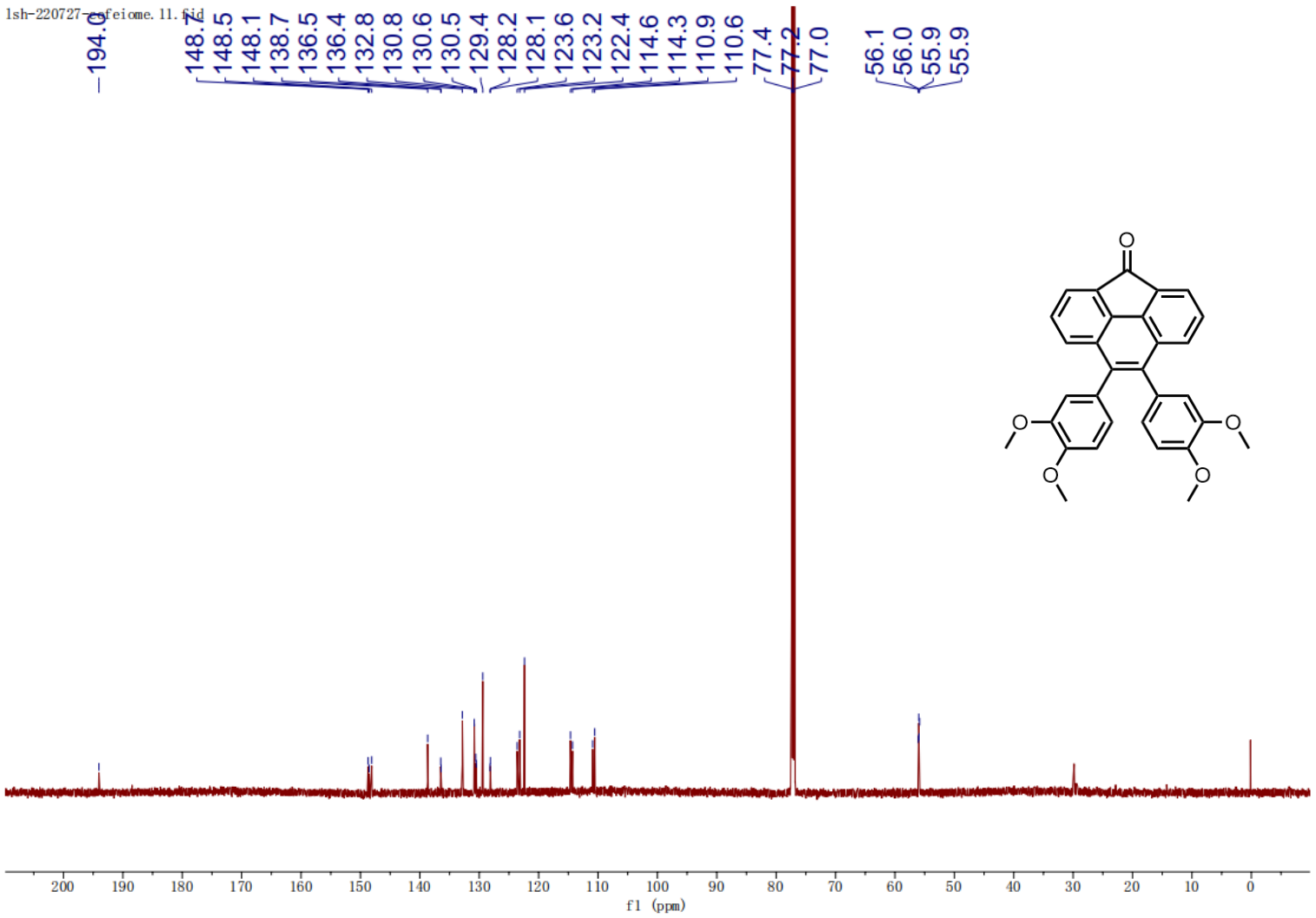
8,9–bis(4–(tert–butyl)phenyl)–4H–cyclopenta[def]phenanthren–4–one (3b):



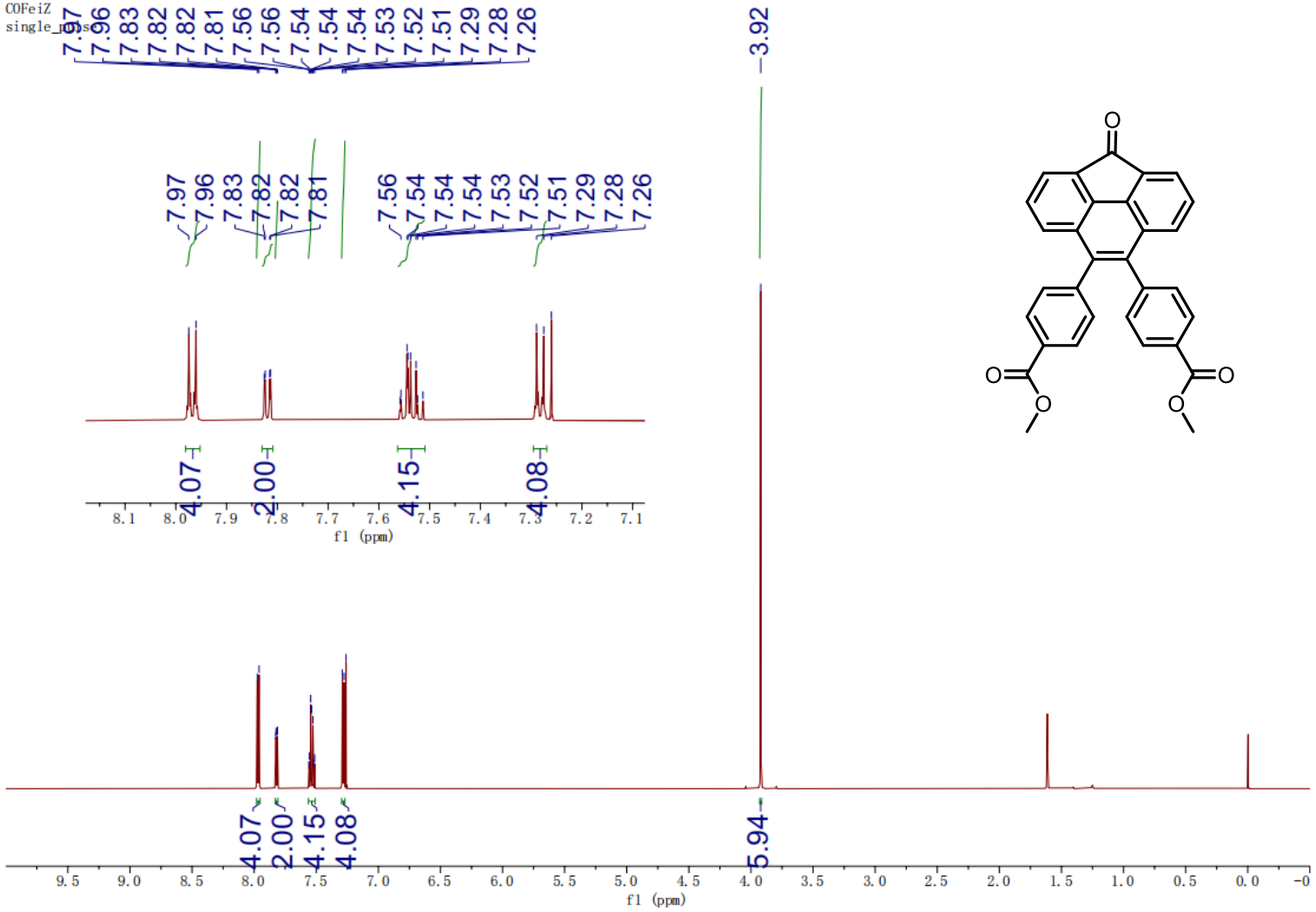

C0菲二叔丁基苯C.11.fid
194.4
149.8
138.7
136.9
134.9
132.8
131.0
130.7
129.2
128.1
124.6
122.2
77.4
77.2
76.9
34.6
30.8
O
f1 (ppm)

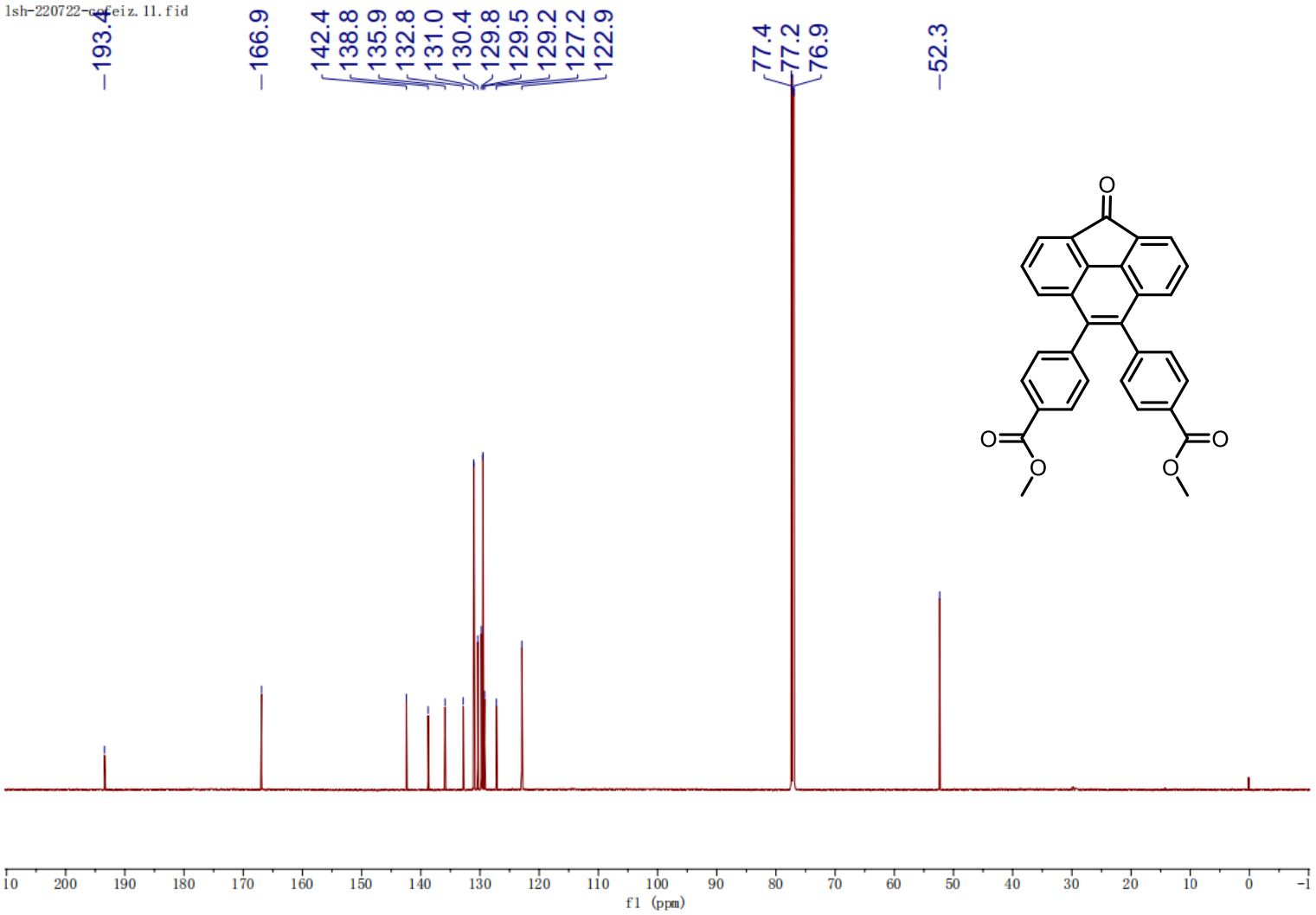
8,9–bis(3,4–dimethoxyphenyl)–4H–cyclopenta[def]phenanthren–4–one (3c):



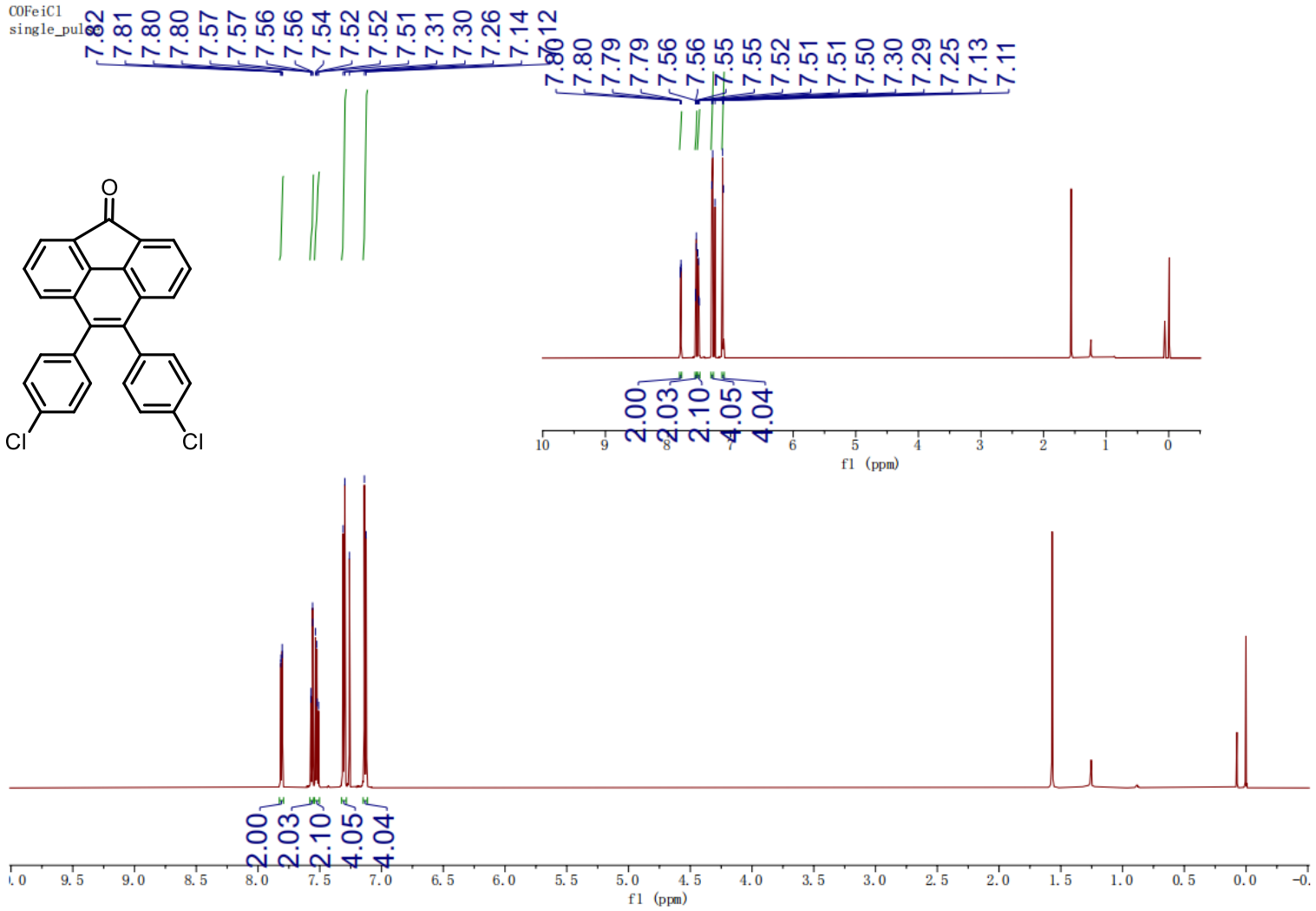

lsh-220727-caffeiome.11.fid
194.0
148.7
148.5
148.1
138.7
136.5
136.4
132.8
130.8
130.6
130.5
129.4
128.2
128.1
123.6
123.2
122.4
114.6
114.3
110.9
110.6
77.4
77.2
77.0
56.1
56.0
55.9
55.9
O
O
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

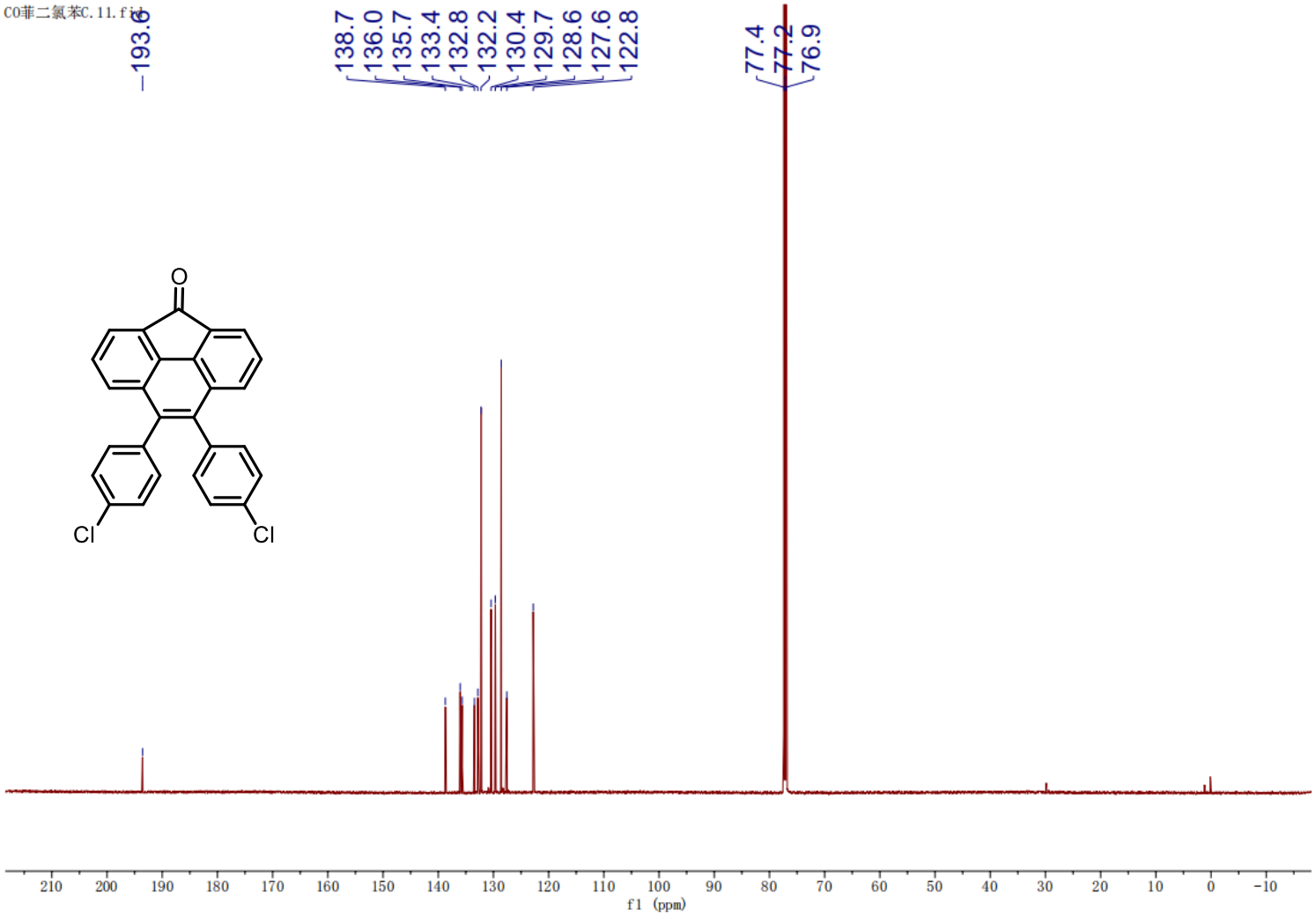
dimethyl 4,4'–(4–oxo–4H–cyclopenta[def]phenanthrene–8,9–diyl)dibenzoate (3d):



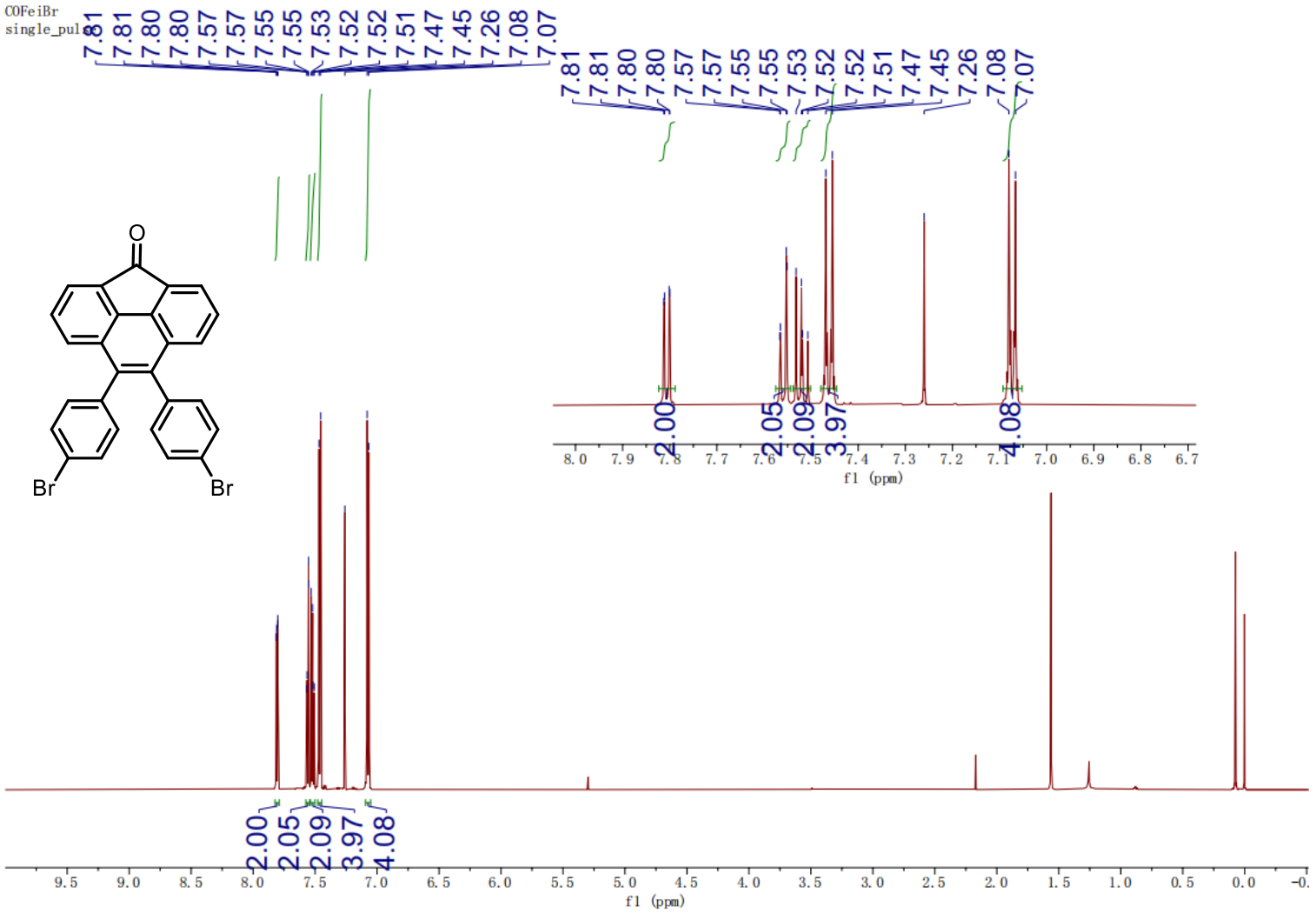

lsh-220722-cefeiz.11.fid
193.4
166.9
142.4
138.8
135.9
132.8
131.0
130.4
129.8
129.5
129.2
127.2
122.9
77.4
77.2
76.9
52.3
O
O
O
O
O
f1 (ppm)

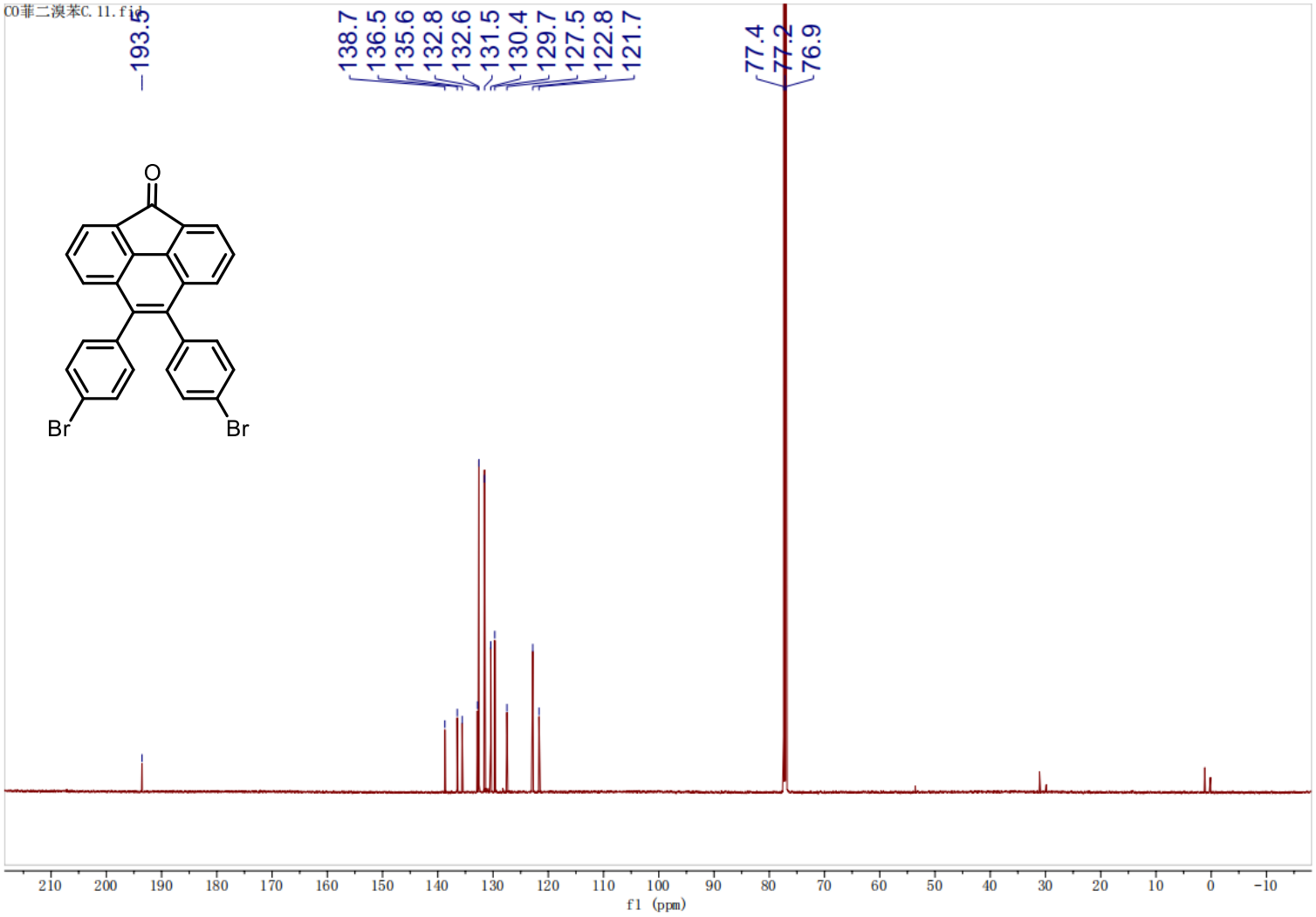
8,9–bis(4–chlorophenyl)–4H–cyclopenta[def]phenanthren–4–one (3e):



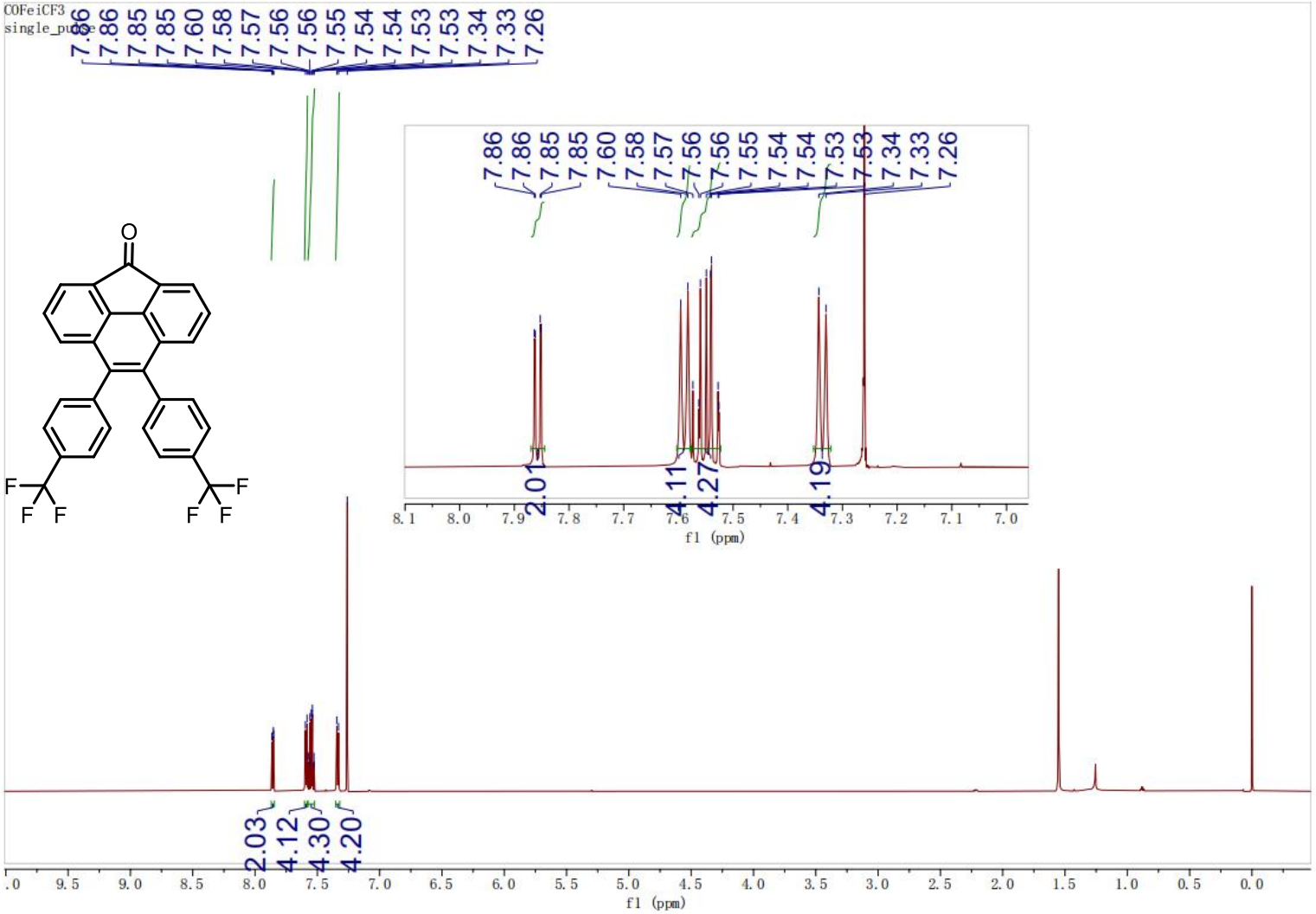

CO菲二氯苯C.11.fid
193.6
138.7
136.0
135.7
133.4
132.8
132.2
130.4
129.7
128.6
127.6
122.8
77.4
77.2
76.9
O
Cl
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

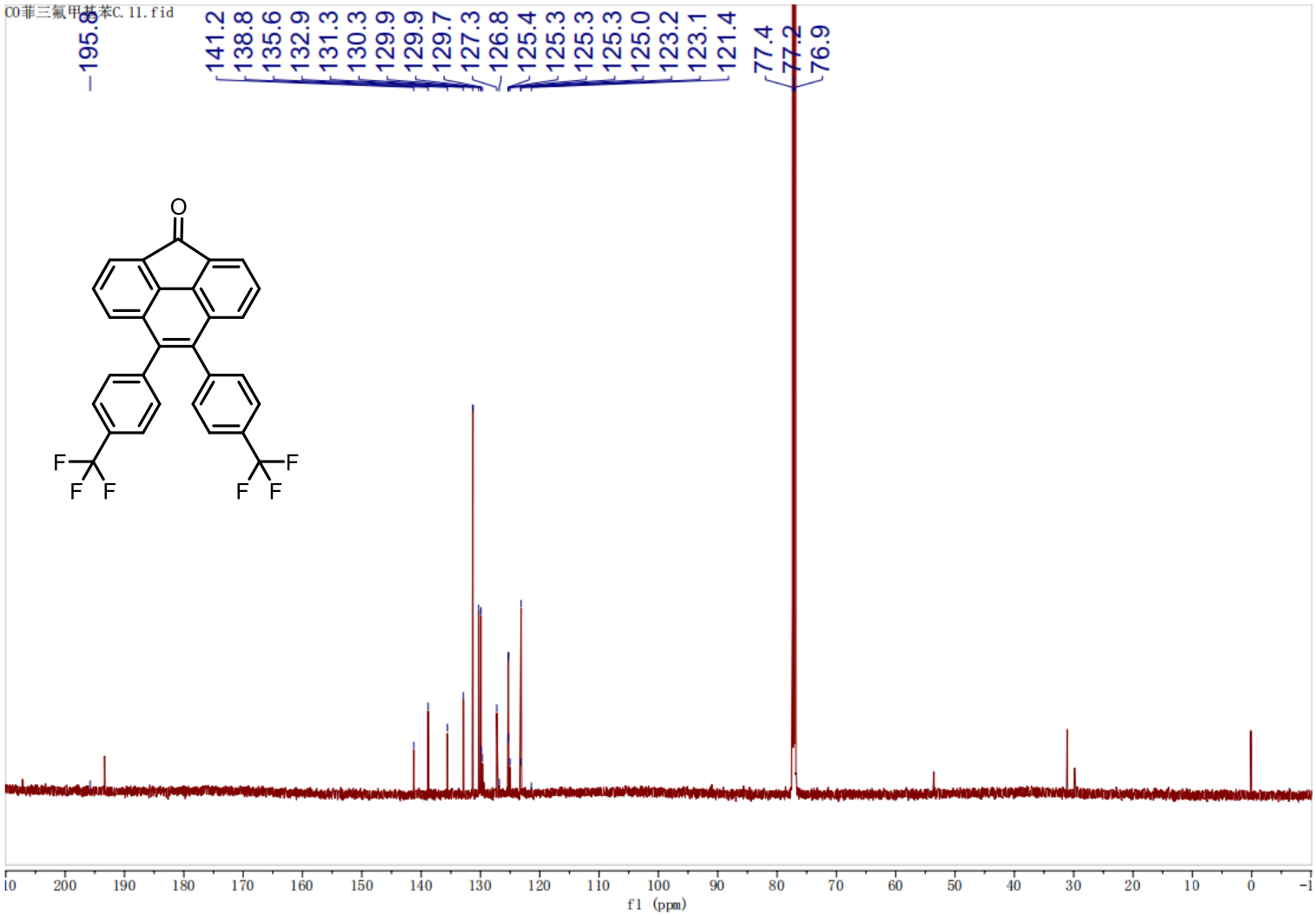
8,9–bis(4–bromophenyl)–4H–cyclopenta[def]phenanthren–4–one (3f):

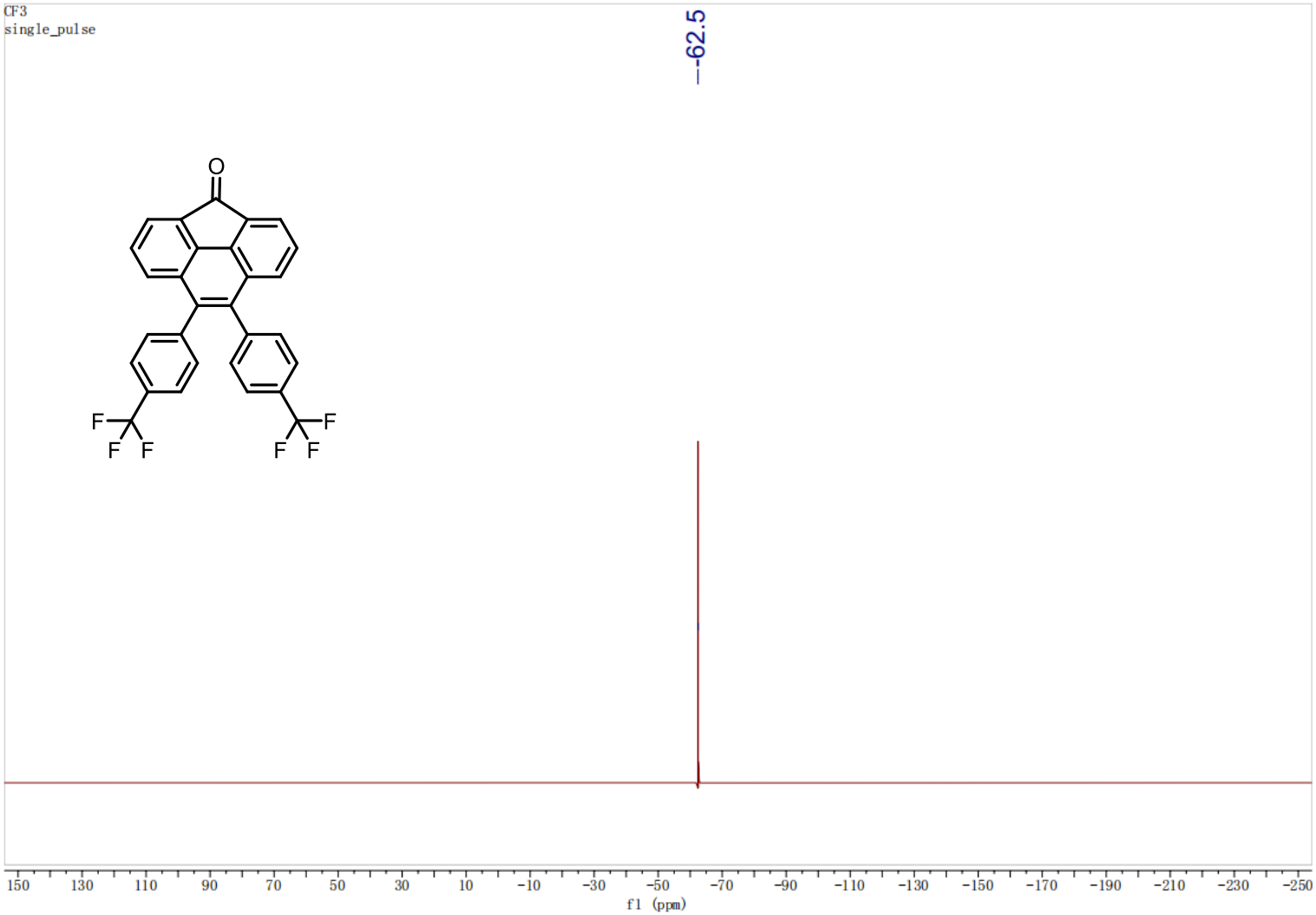



C0菲二溴苯C. 11. fid
193.5
138.7
136.5
135.6
132.8
132.6
131.5
130.4
129.7
127.5
122.8
121.7
77.4
77.2
76.9
O
Br
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

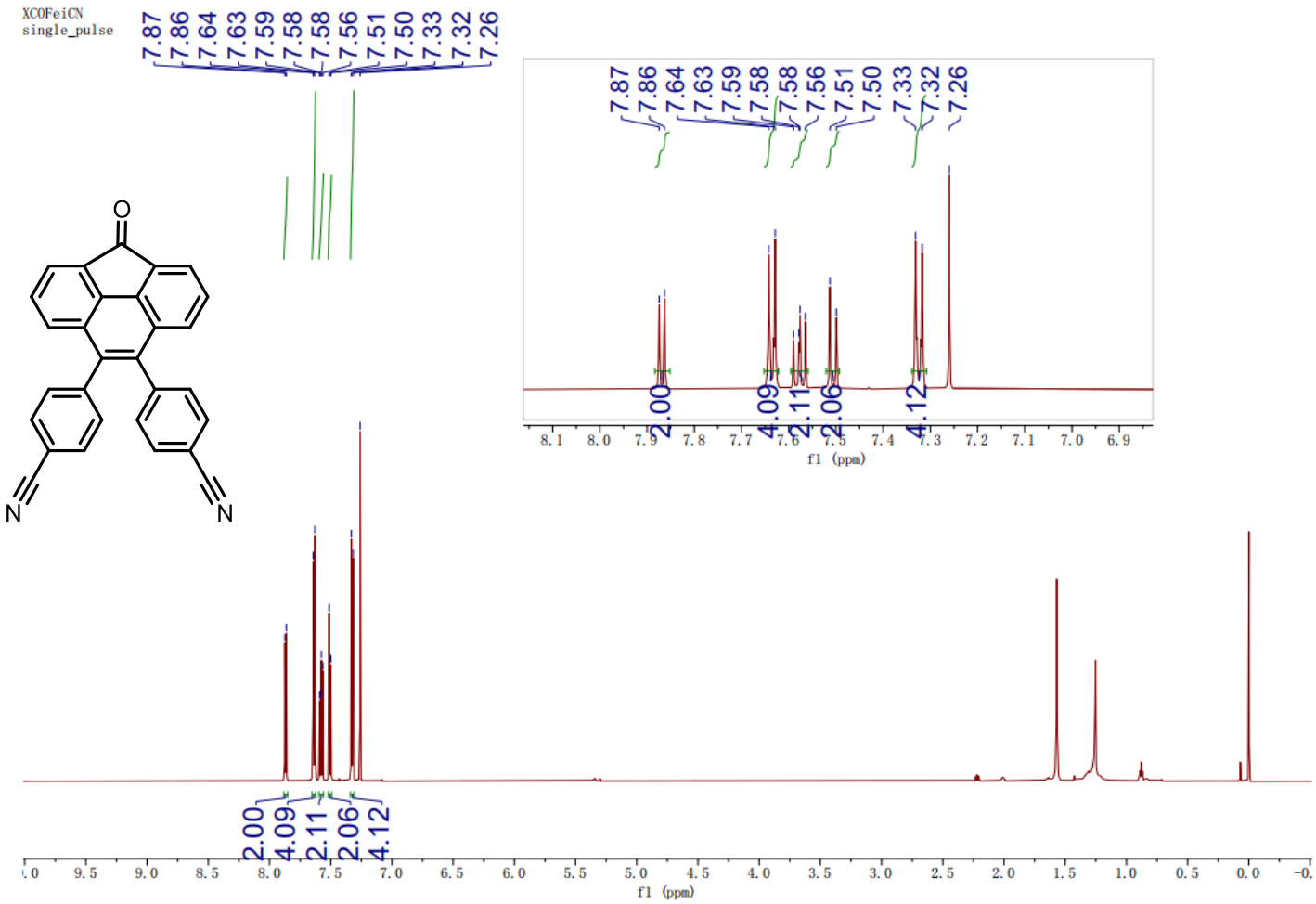
8,9–bis(4–(trifluoromethyl)phenyl)–4H–cyclopenta[def]phenanthren–4–one (3g):

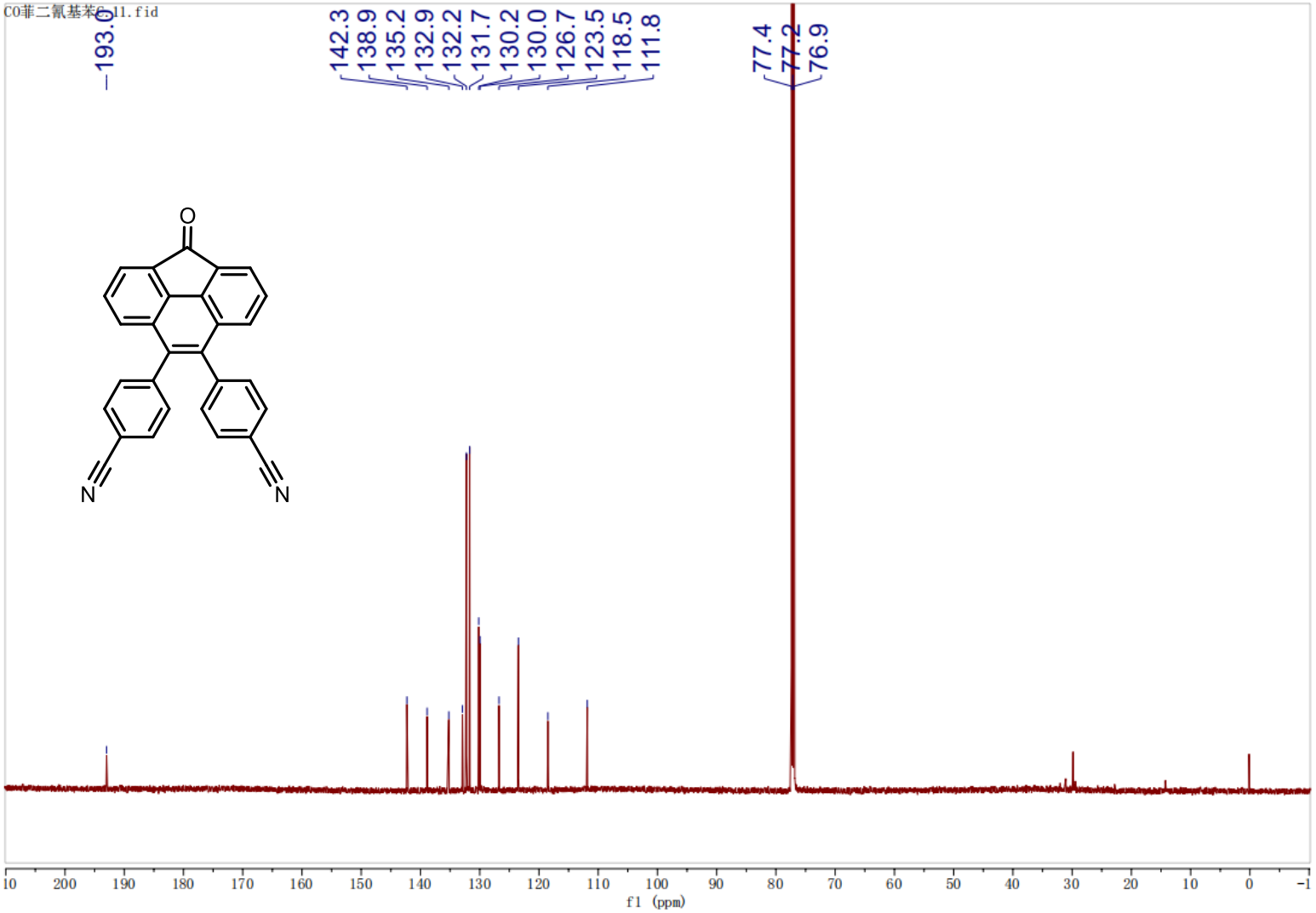



CO菲三氟甲基苯C.11.fid
195.8
141.2
138.8
135.6
132.9
131.3
130.3
129.9
129.9
129.7
127.3
126.8
125.4
125.3
125.3
125.3
125.0
123.2
123.1
121.4
77.4
77.2
76.9
O
F
F
F
F
F
f1 (ppm)

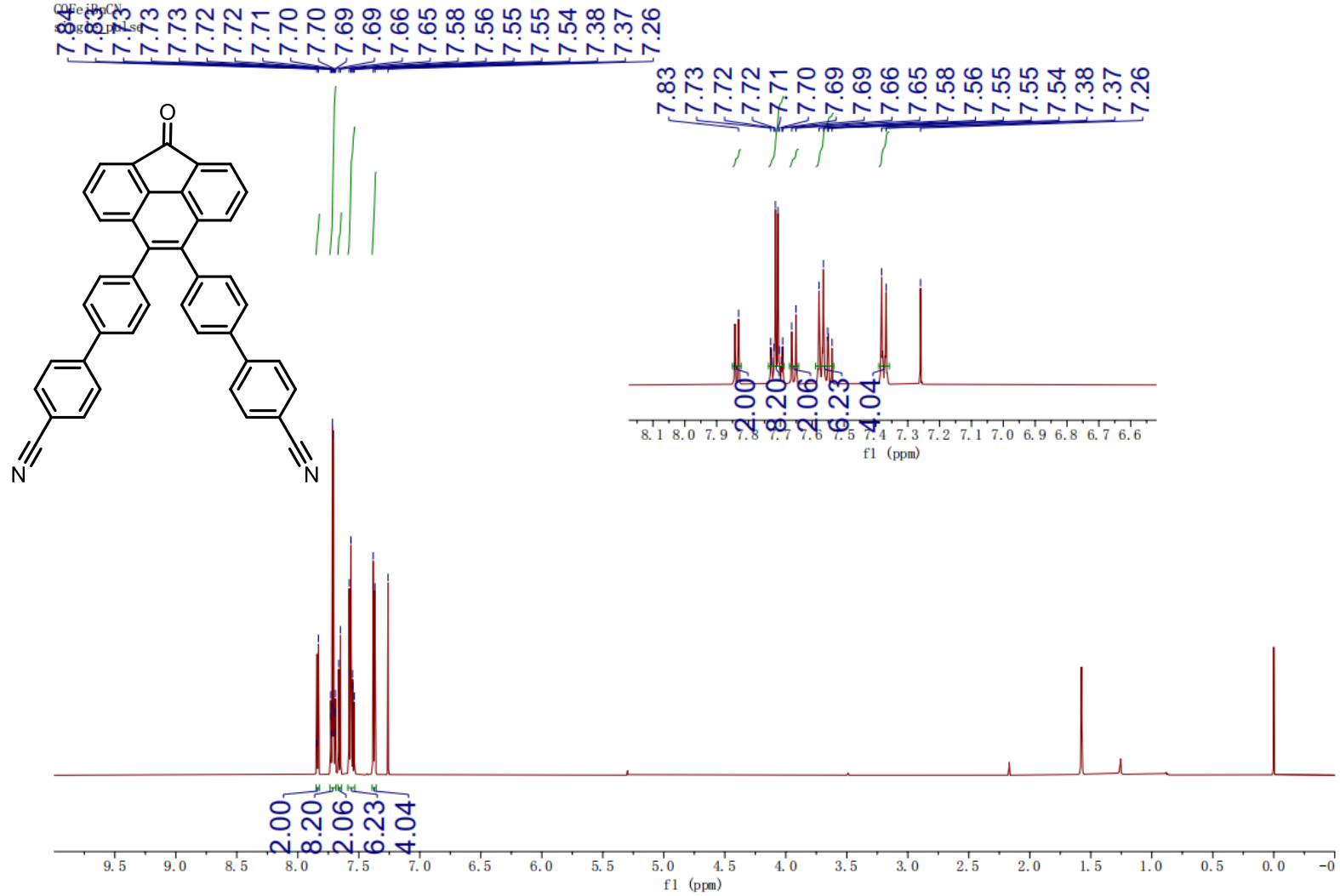

CF3
single_pulse
-62.5
O
F
F
F
F
F
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)

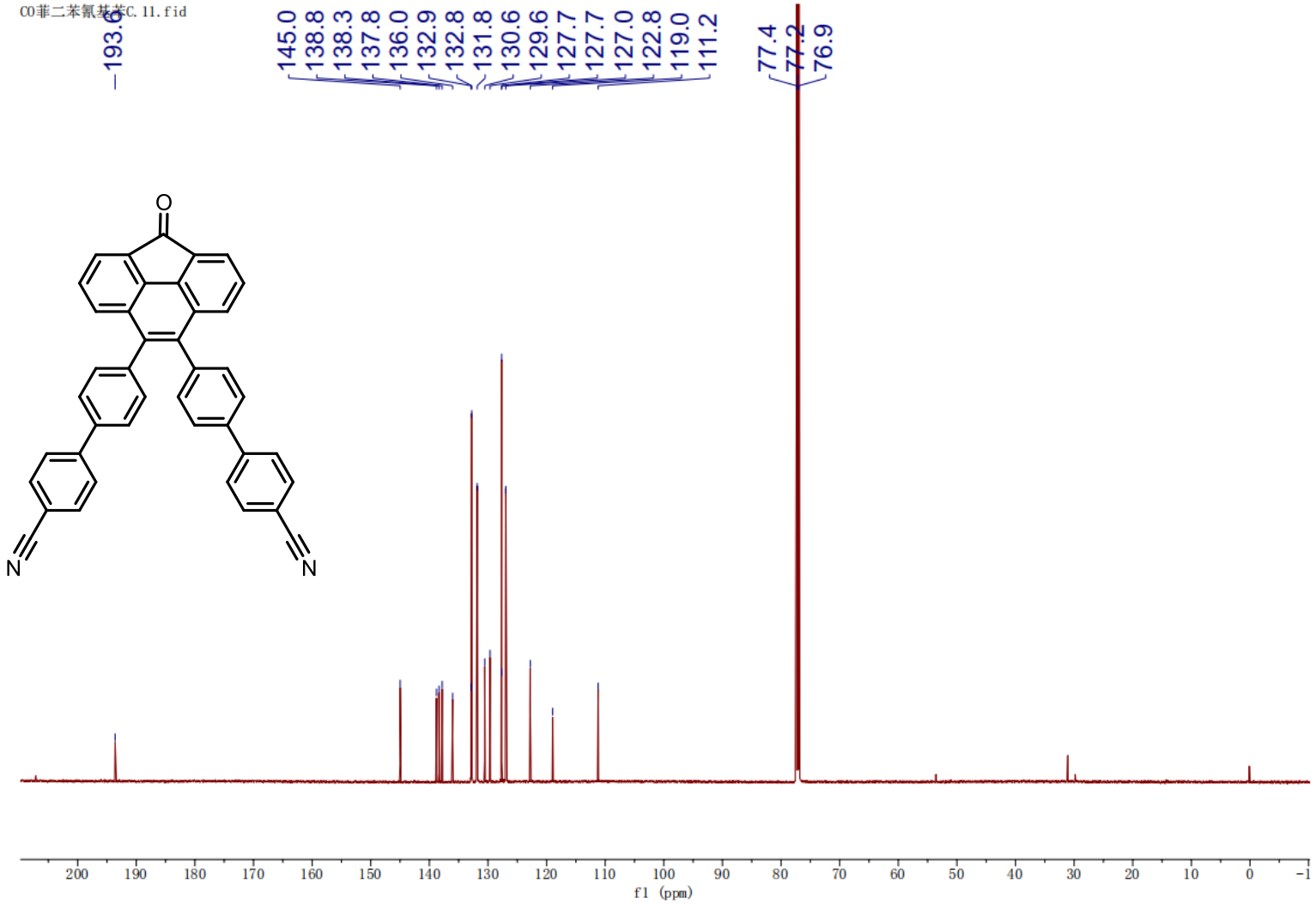
4,4'–(4–oxo–4H–cyclopenta[def]phenanthrene–8,9–diyl)dibenzonitrile (3h):



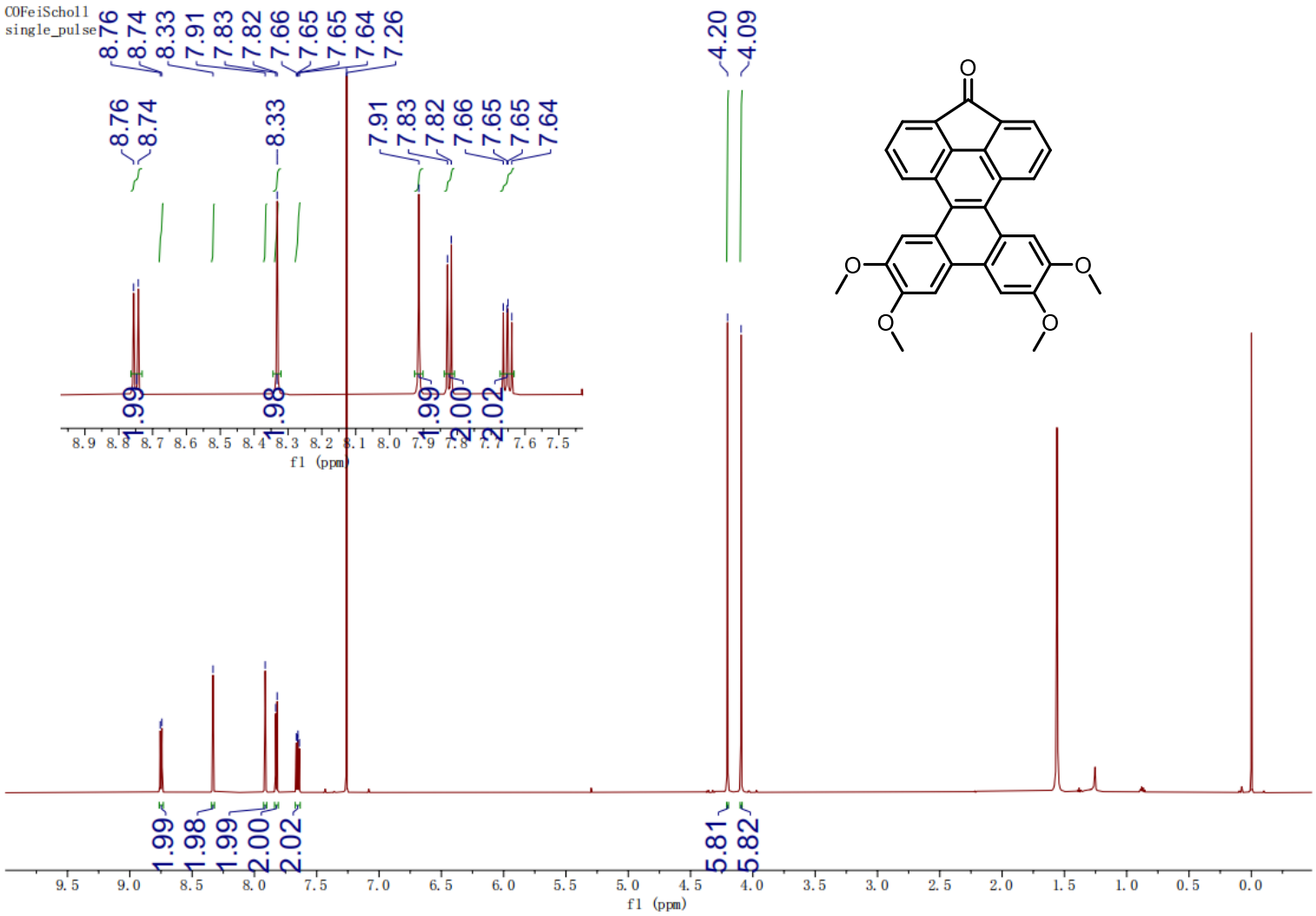

CO菲二氰基苯c_11.fid
193.0
142.3
138.9
135.2
132.9
132.2
131.7
130.2
130.0
126.7
123.5
118.5
111.8
77.4
77.2
76.9
O
N
N
f1 (ppm)

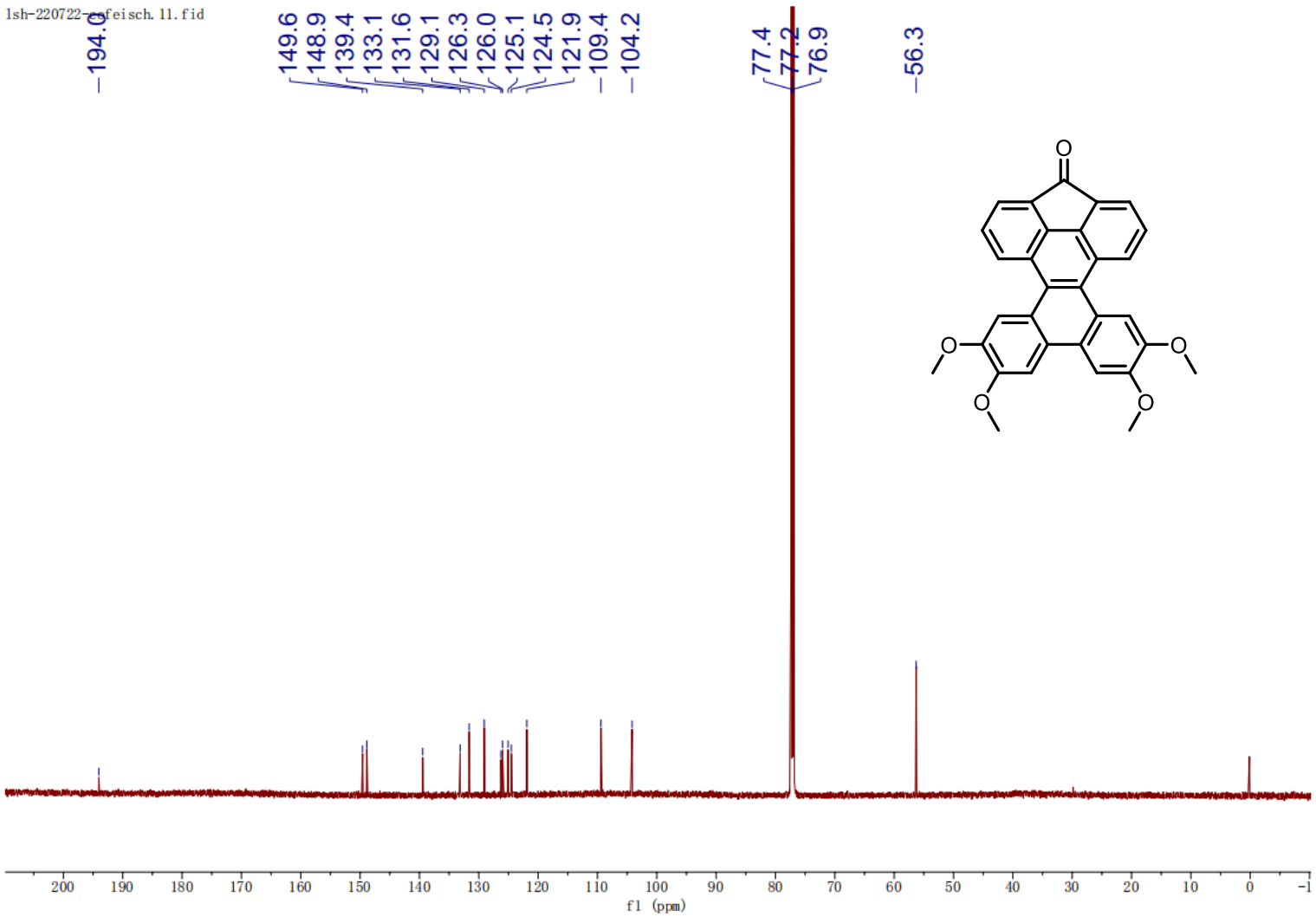
4',4'''–(4–oxo–4H–cyclopenta[def]phenanthrene–8,9–diyl)bis(([1,1'–biphenyl]–4–carbonitrile)) (3i):



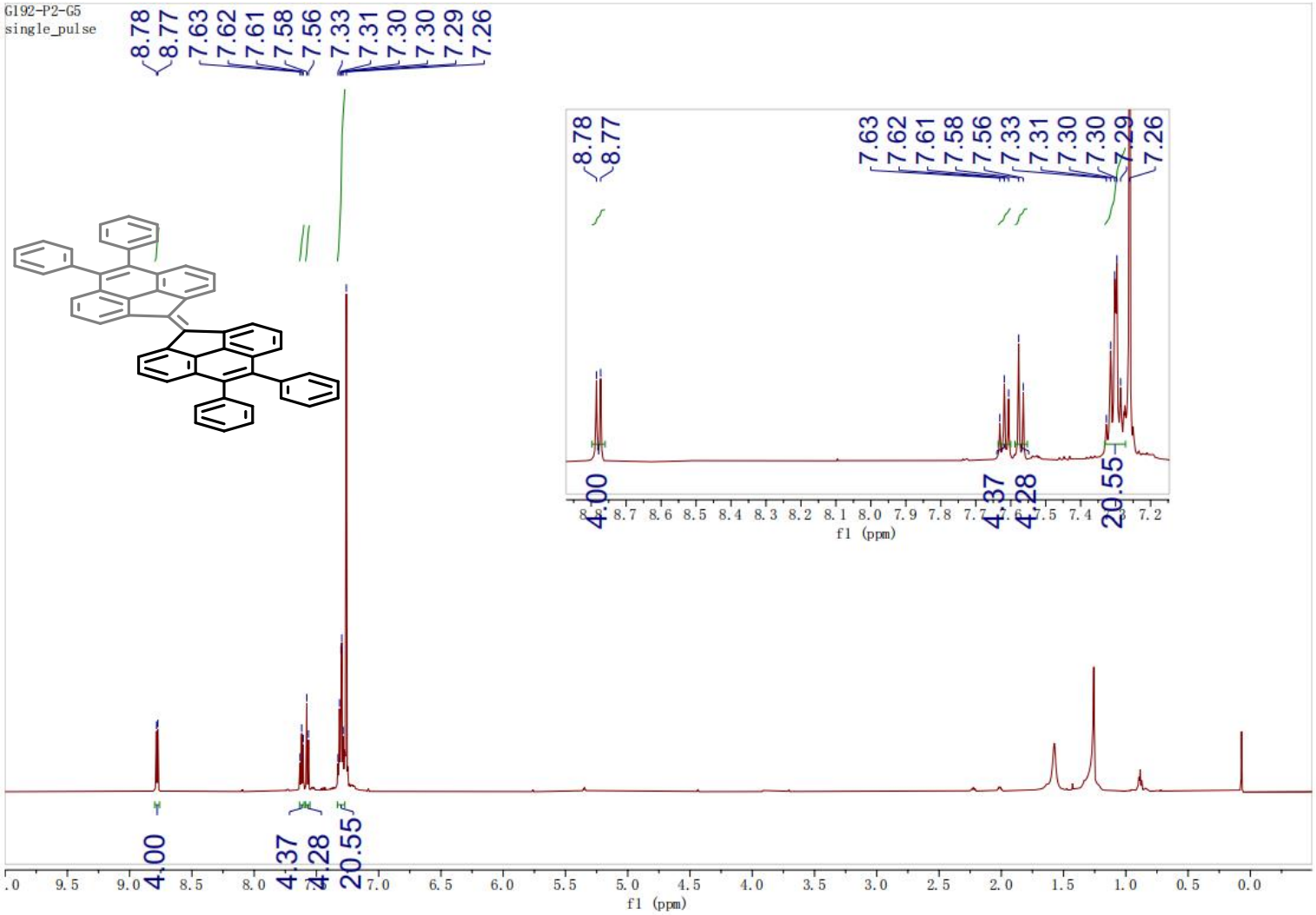

CO菲二苯氰基苯C.11.fid
193.6
145.0
138.8
138.3
137.8
136.0
132.9
132.8
131.8
130.6
129.6
127.7
127.7
127.0
122.8
119.0
111.2
77.4
77.2
76.9
O
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

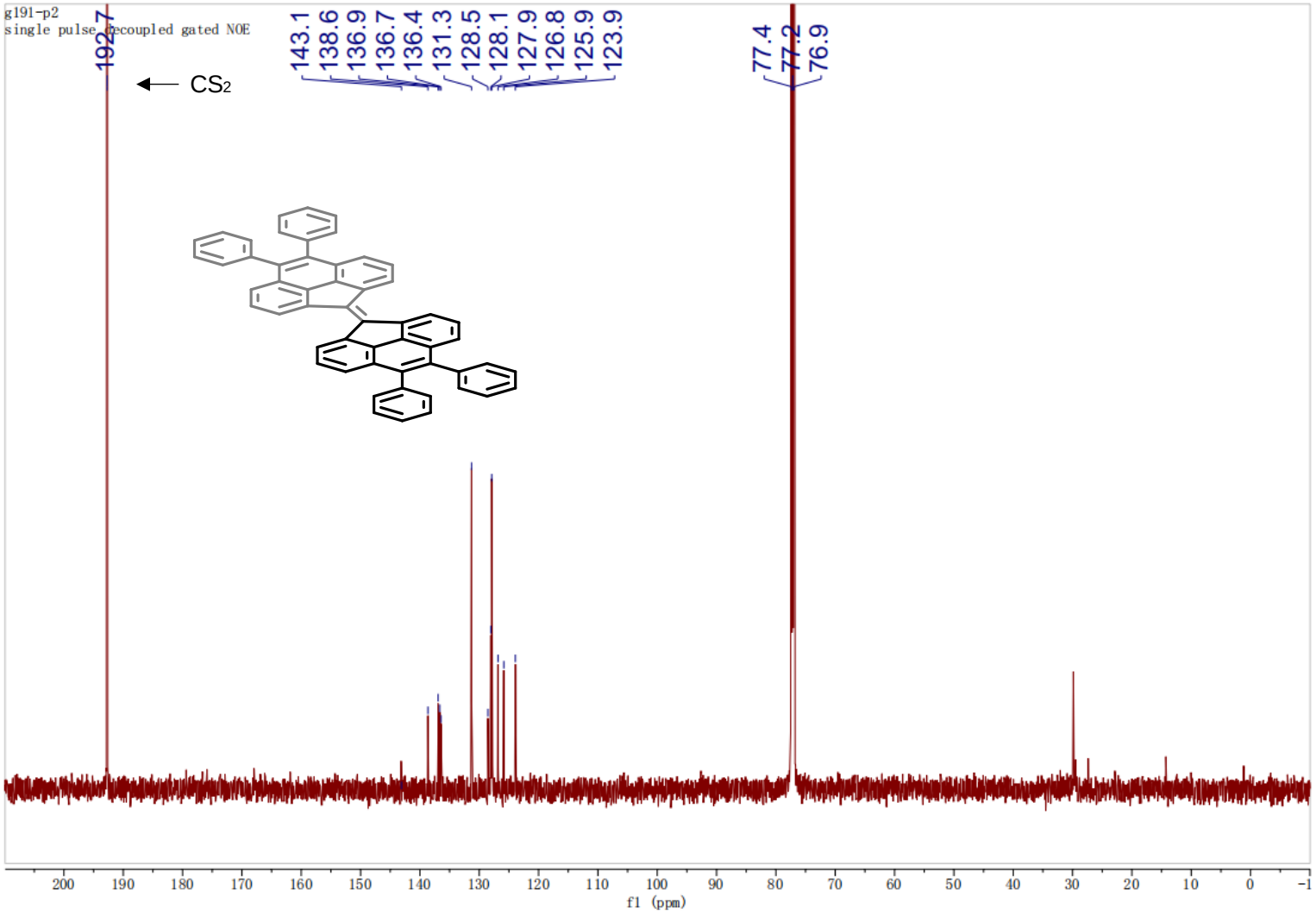
9,10,13,14–tetramethoxy–4H–benzo[p]indeno[7,1,2–ghi]chrysen–4–one (4):



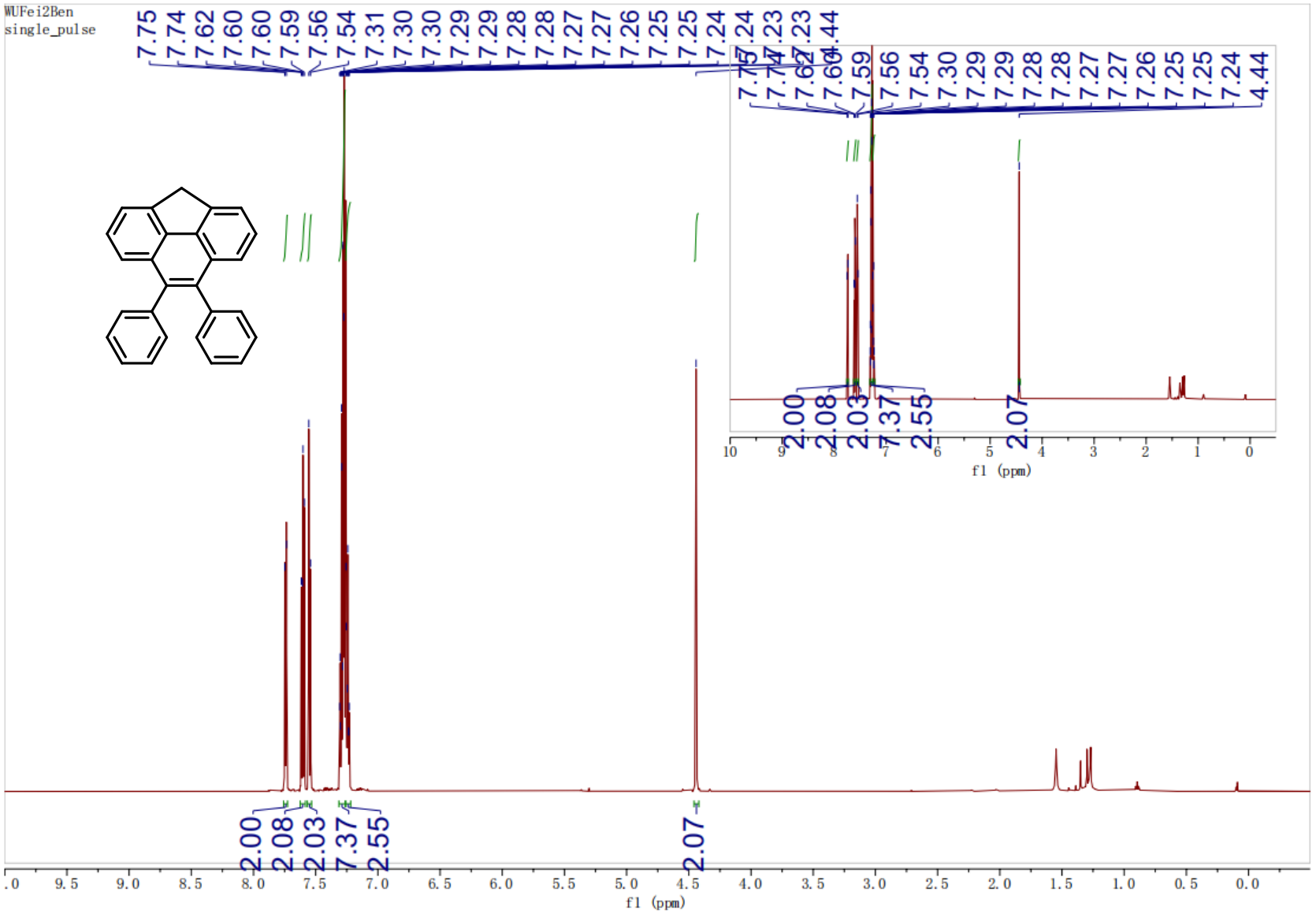

lsh-220722-zefeisch.11.fid
194.0
149.6
148.9
139.4
133.1
131.6
129.1
126.3
126.0
125.1
124.5
121.9
109.4
104.2
77.4
77.2
76.9
56.3
O
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

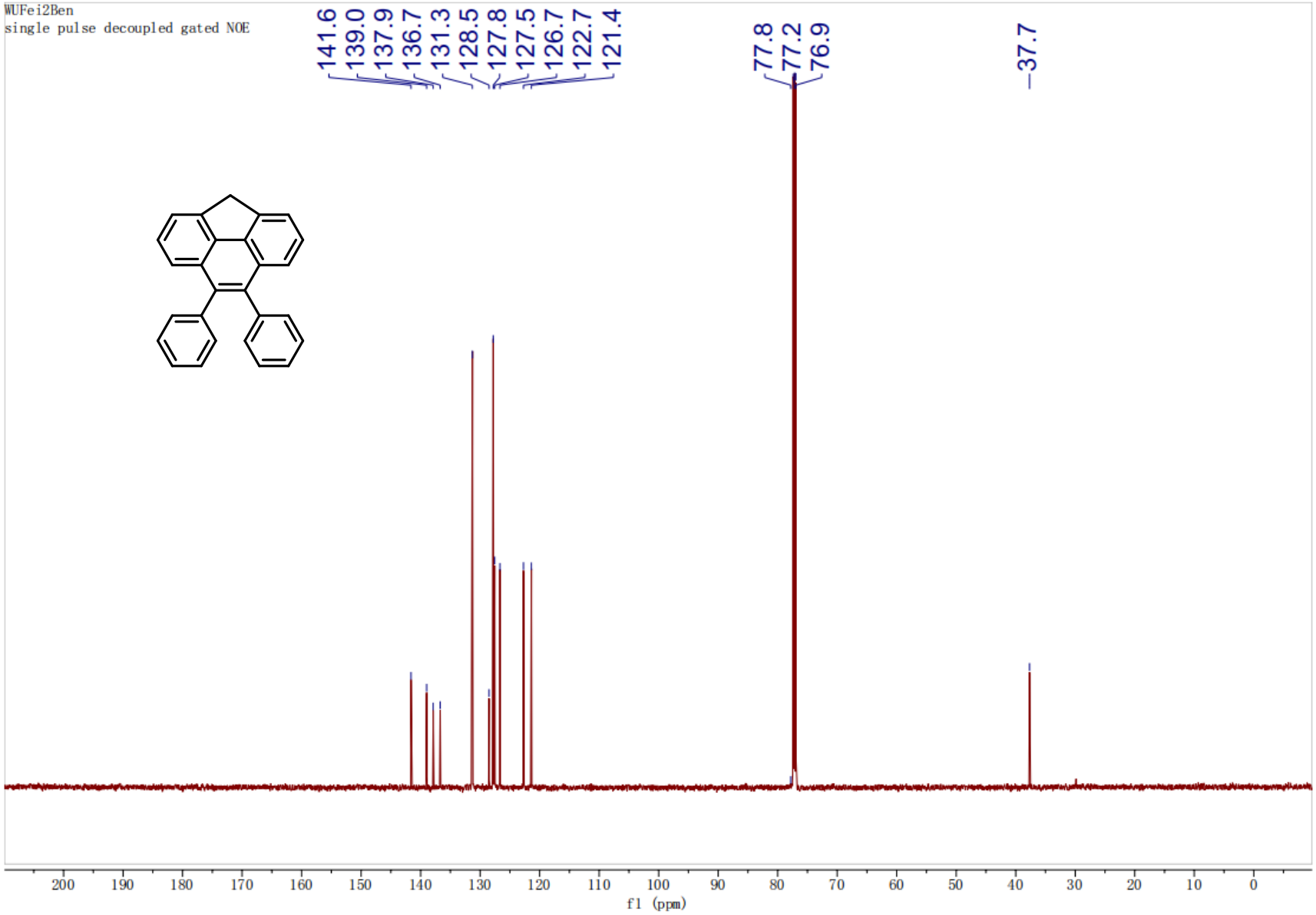
8,8',9,9'–tetraphenyl–4,4'–bi(cyclopenta[def]phenanthrenylidene) (5):



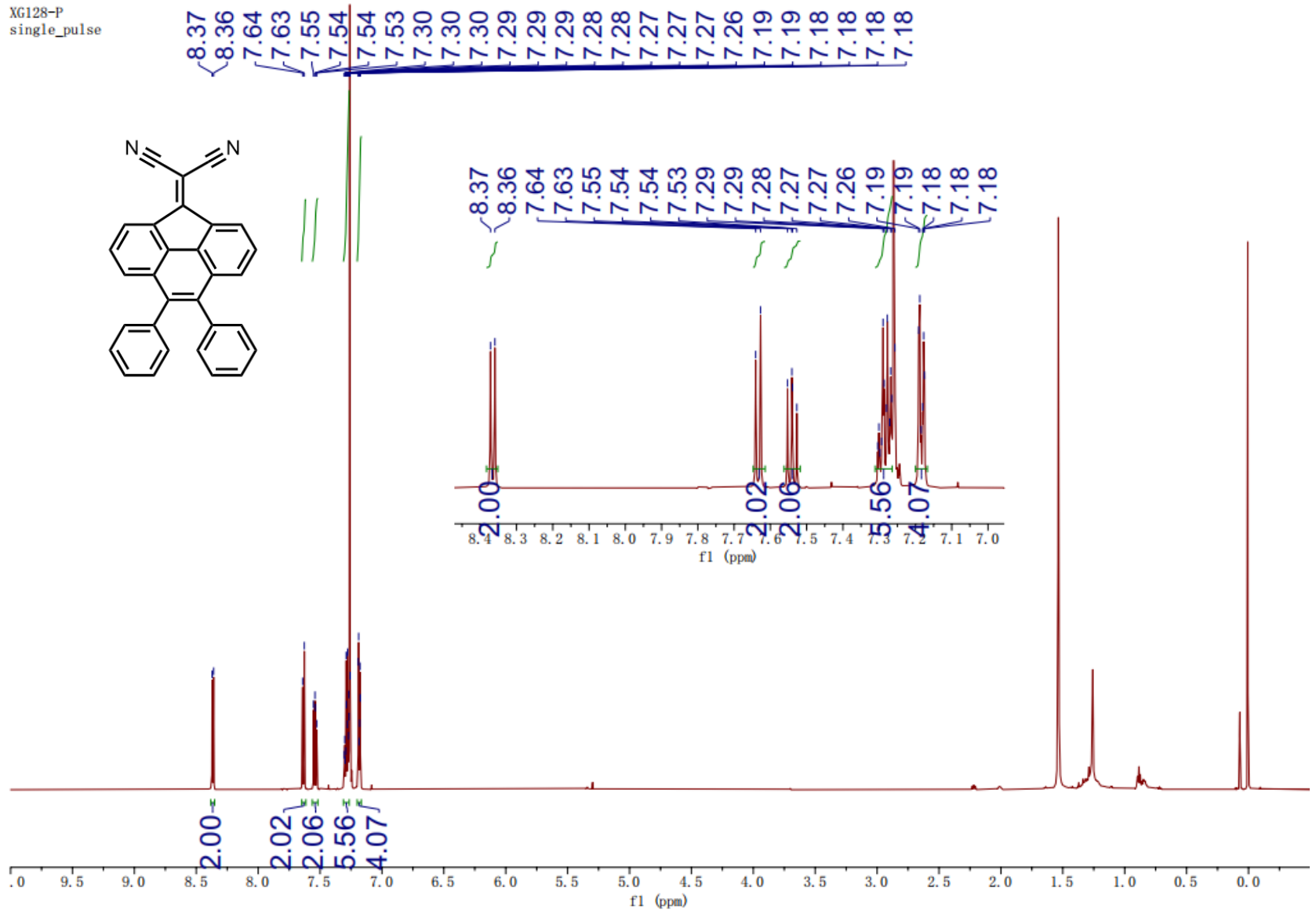

g191-p2
single pulse decoupled gated NOE
192.7
CS2
143.1
138.6
136.9
136.7
136.4
131.3
128.5
128.1
127.9
126.8
125.9
123.9
77.4
77.2
76.9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

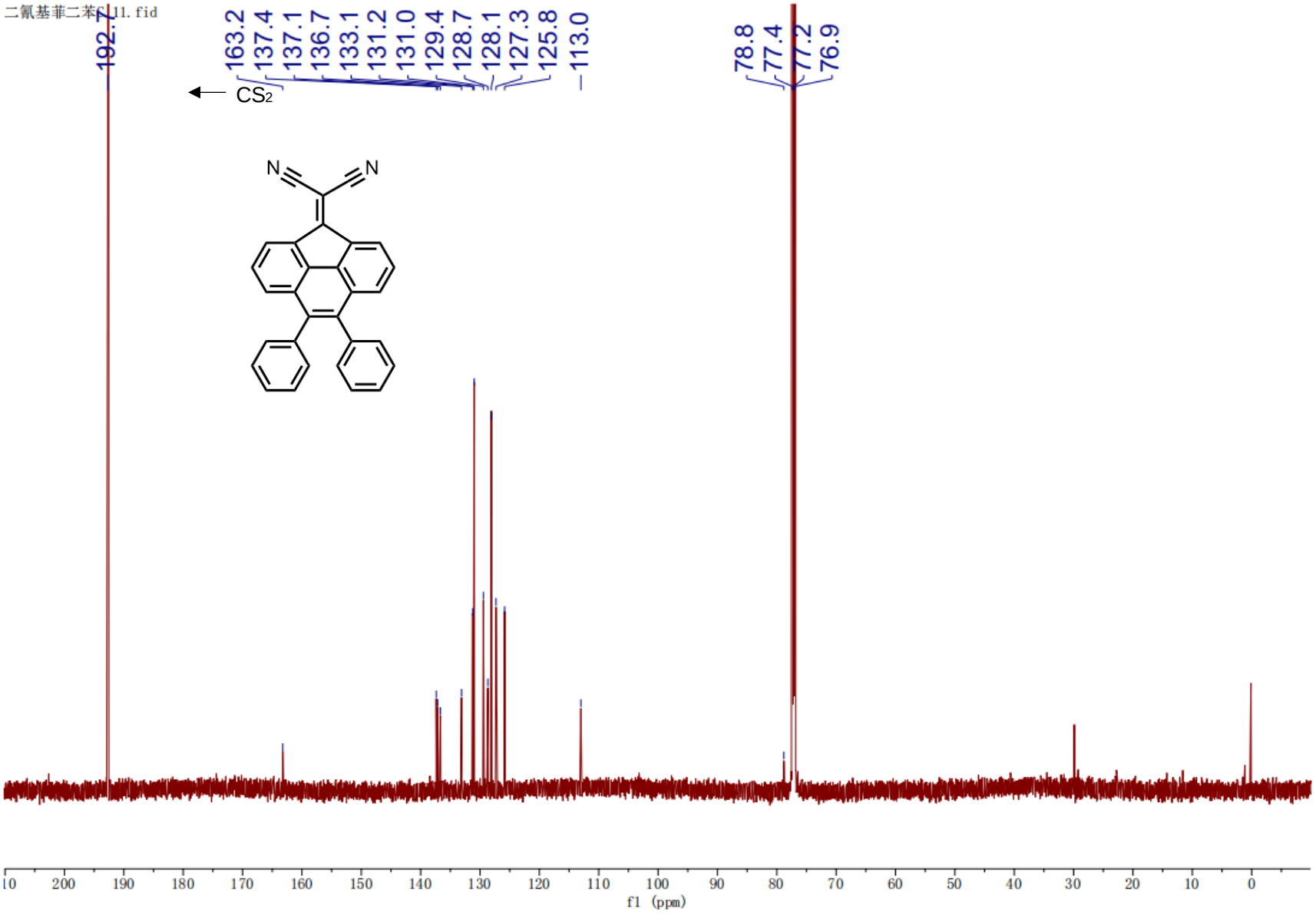
8,9–diphenyl–4H–cyclopenta[def]phenanthrene (6):




WUFei2Ben
single pulse decoupled gated NOE
141.6
139.0
137.9
136.7
131.3
128.5
127.8
127.5
126.7
122.7
121.4
77.8
77.2
76.9
37.7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2–(8,9–diphenyl–4H–cyclopenta[def]phenanthren–4–ylidene)malononitrile (7):




二氰基菲二苯C_11.fid
192.7
163.2
137.4
137.1
136.7
133.1
131.2
131.0
129.4
128.7
128.1
127.3
125.8
113.0
CS2
78.8
77.4
77.2
76.9
N
N
f1 (ppm)