

Supporting Information

Derivatization of Sumanenetrione through Lewis acid-mediated Suzuki-Miyaura coupling and an unprecedented ring opening

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Content

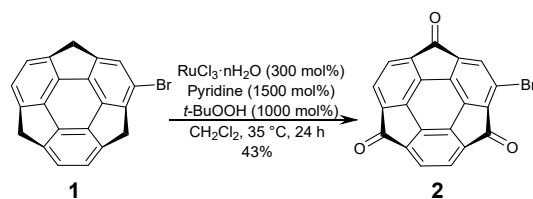
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1) General Methods

All the chemical reagents and solvents were commercially purchased and purified according to the standard methods, if necessary. Air- and moisture-sensitive reactions were carried out using commercially available anhydrous solvents under inert atmosphere of nitrogen. Unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 and Bruker AVANCE III 600 spectrometers. Chemical shift (δ) are expressed relative to the resonances of the residual non-deuterated solvent for ^1H (CDCl_3 : $^1\text{H}(\delta) = 7.26$ ppm, $\text{THF-}d_8$: $^1\text{H}(\delta) = 3.58, 1.72$ ppm, $\text{DMSO-}d_6$: $^1\text{H}(\delta) = 2.50$ ppm) and for ^{13}C (CDCl_3 : $^{13}\text{C}(\delta) = 77.0$ ppm, $\text{THF-}d_8$: $^{13}\text{C}(\delta) = 67.21, 25.31$ ppm). High resolution mass spectra (HRMS) were measured using electron impact (EI) methods on JEOL JMS-777V spectrometer. Recycling preparative high-performance liquid chromatography (HPLC) was performed by a LC-908W (Japan Analytical Industry Co., Ltd.) with high-resolution gel permeation chromatography (GPC) column (Japan Analytical Industry Co., Ltd., JAIGEL-1H and 2H) with CHCl_3 as an eluent. The preparative TLC (PTLC) purification was conducted using Wako gel B-5F PTLC plates. Flash column chromatography was prepared using Kanto Silica gel 60N (neutral, spherical, 40-50 μm) and performed with a Yamazen preparative medium pressure liquid chromatography system. UV-vis spectra were recorded on a JASCO V-670 spectrophotometer. Steady-state emission spectra were recorded on a JASCO FP-6500DS spectrometer. Melting points were determined on an Optimelt MPA100 automated melting point apparatus (Stanford Research Systems, Inc.), and expressed without correction. Infrared (IR) absorption spectra were measured by attenuated total reflection (ATR) method on a JASCO FT/IR-4100 Fourier transform IR spectrometer equipped with a JASCO ATR PRO ONE single reflection ATR optical attachment and a diamond crystal plate.

2) Synthesis and NMR spectra

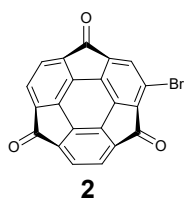
a) Synthesis of Bromosumanenetrione (2)



Scheme S1. Synthetic route to 2.

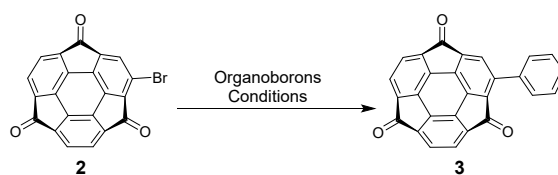
2-bromo-1H-tricyclopenta[def,jkl,pqr]triphenylene-1,4,7-trione (2)

To a CH_2Cl_2 (11 mL) solution of bromosumanene^{S1} (34.4 mg, 0.10 mmol) in 30 mL round-bottomed flask was added pyridine (1.2 mL, 15.25 mmol), $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (85 mg, 0.33 mmol), and a 70% aqueous solution of *t*-BuOOH (1.0 mL, 7.78 mmol) at room temperature. The reaction mixture was warmed to 35 °C. After being stirred for 24 h. The reaction mixture was diluted by CH_2Cl_2 at rt, filtered through silica pad, and evaporated. The residue was purified by PTLC (CH_2Cl_2) to give bromosumanenetrione 2 (16.6 mg, 43% yield) as an orange solid.



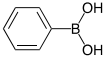
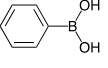
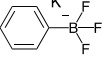
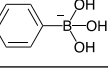
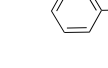
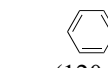
2: mp: 267 °C (dec.); TLC: $R_f = 0.45$ (CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.52 (s, 1H), 7.49 (d, $J = 7.4$ Hz, 1H), 7.47 (d, $J = 7.4$ Hz, 1H), 7.46 (d, $J = 7.4$ Hz, 1H), 7.43 (d, $J = 7.3$ Hz, 1H); ^{13}C NMR (100 MHz, Chloroform- d) δ (ppm) 187.95, 186.95, 185.65, 150.30, 149.82, 149.67, 149.38, 147.83, 147.04, 144.73, 143.87, 143.55, 143.40, 143.37, 140.32, 131.21, 127.21, 127.15, 127.01, 126.78, 121.35. IR (ATR): ν 2974, 2952, 1720, 1636, 1562, 1390, 1366, 1329, 1293, 1266, 1195, 1178, 1073, 947, 857, 842, 774, 734, 723, 697 cm^{-1} ; HRMS (EI) m/z Calcd. for $[\text{C}_{21}\text{H}_5\text{BrO}_3]$ (M^+): 383.9422, found 383.9410.

b) Optimization of the reaction conditions in Suzuki-Miyaura cross coupling



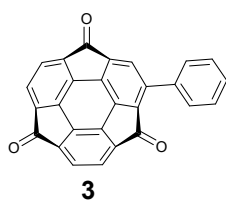
Scheme S2. Synthetic approach to **3**.

Table S1 Optimization of the reaction conditions in Suzuki-Miyaura cross coupling.

Entry	Organoborons	Conditions ^a	Yield
1	 (120 mol%)	$\text{Pd}(\text{PPh}_3)_4$ (10 mol%) K_2CO_3 (100 mol%) THF/ H_2O , 80 °C, 1 h	0
2	 (120 mol%)	$\text{Pd}(\text{PPh}_3)_4$ (10 mol%) CsF (100 mol%) toluene/ H_2O , 80 °C, 1 h	0
3	 (120 mol%)	$\text{Pd}(\text{OAc})_2$ (10 mol%) ChOH/ H_2O , 100 °C, 1 h	0
4	 (100 mol%)	$\text{PdCl}_2(\text{dppf})$ (10 mol%) toluene, reflux, 1 h	0
5	 (100 mol%)	$\text{Pd}(\text{OAc})_2$ (10 mol%) DMF, 80 °C, 1 h	0
6	 (120 mol%)	$\text{PdCl}_2(\text{amphos})_2$ (2 mol%) $((\text{tmeda})\text{Zn}(\text{OH})(\text{OTf}))_3$ (150 mol%) THF, 80 °C, 1 h	89%

^a **2** (0.050 mmol), solvent (2mL). ^b ChOH: choline hydroxide

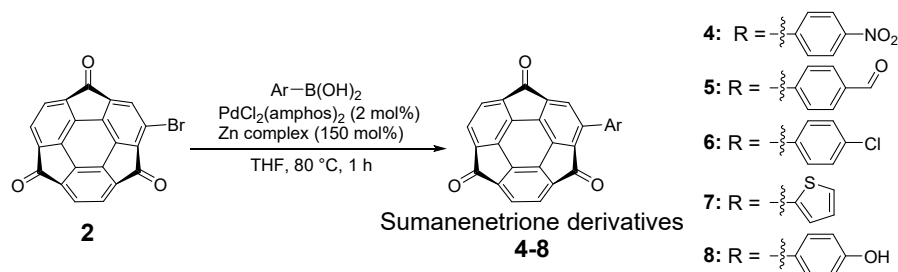
2-phenyl-1H-tricyclopenta[def,jkl,pqr]triphenylene-1,4,7-trione (3)



3: mp: 312 °C (dec.); TLC: $R_f = 0.65$ (CH_2Cl_2); ^1H NMR (600 MHz, Chloroform- d) δ (ppm) 7.63 (s, 1H), 7.63 (m, 2H), 7.49 (m, 3H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 7.4$ Hz, 1H), 7.40 (d, $J = 7.4$ Hz, 1H), 7.35 (d, $J = 7.3$ Hz, 1H); ^{13}C NMR (100 MHz, Chloroform- d) δ (ppm) 188.54, 188.38, 186.91, 150.32, 150.15, 149.92, 149.27, 149.18, 147.42, 144.58, 144.29, 143.97, 143.91, 143.71, 143.44, 138.36,

135.69, 130.06, 129.98, 128.62, 127.18, 126.77, 126.62, 126.48, 126.37. IR (ATR): ν 3057, 2961, 2923, 2852, 1717, 1633, 1562, 1450, 1397, 1343, 1262, 1176, 1071, 1027, 950, 908, 853, 742, 729, 693 cm^{-1} ; HRMS (EI) m/z Calcd. for $[\text{C}_{27}\text{H}_{10}\text{O}_3]$ (M^+): 382.0630, found 382.0622.

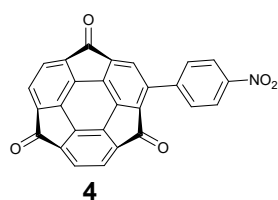
c) Synthesis of sumanenetrione derivatives 4-8



Scheme S3. Synthetic route to the sumanenetrione derivatives 4-8.

To a test tube equipped with a magnetic stir bar was added **2** (0.050 mmol, 1 equiv), organo boronic acid (0.060 mmol, 1.2 equiv), $\text{PdCl}_2(\text{amphos})_2$ (0.7 mg, 0.5 μmol , 0.02 equiv), $((\text{tmeda})\text{Zn}(\text{OH})(\text{OTf}))_3$ (0.075 mmol/ Zn , 1.5 equiv/ Zn)^{S2}, and THF (2.0 mL). The reaction mixture was stirred for 1 h at 80 °C and then cooled to room temperature. The mixture was extracted with DCM (ca. 20 mL \times 3). The combined organic extract was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by PTLC (CH_2Cl_2) to give the corresponding products. Further purification was conducted with GPC by using CHCl_3 as an eluent.

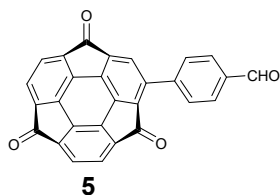
2-(4-nitrophenyl)-1H-tricyclopenta[def,jkl,pqr]triphenylene-1,4,7-trione (4)



4: mp: 344 °C (dec.); TLC: R_f = 0.65 (CH_2Cl_2); ^1H NMR (600 MHz, Chloroform- d) δ (ppm) 8.35 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.62 (s, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform- d) δ (ppm) 188.08, 187.87, 186.74, 150.05, 149.98, 149.68, 149.50, 149.20, 148.59, 148.50, 143.95, 143.90,

143.88, 143.78, 143.73, 143.64, 141.81, 141.28, 139.05, 130.84, 127.02, 126.99, 126.84, 126.73, 123.84. IR (ATR): ν 2959, 2923, 2851, 1718, 1518, 1346, 1259, 1087, 1015, 947, 855, 795, 742, 731, 693 cm^{-1} ; HRMS (EI) m/z Calcd. for $[\text{C}_{27}\text{H}_9\text{NO}_5]$ (M^+): 427.0481, found 427.0475.

4-(1,4,7-trioxo-4,7-dihydro-1H-tricyclopenta[def,jkl,pqr]triphenylene-2-yl)benzaldehyde (5)

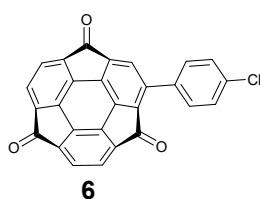


5: mp: 323 °C (dec.). TLC: R_f = 0.20 (CH_2Cl_2). ^1H NMR (600 MHz, Chloroform- d) δ 10.10 (s, 1H), 8.01 (d, J = 7.8 Hz, 2H), 7.80 (d, J = 7.8 Hz, 2H), 7.65 (s, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 7.3 Hz, 1H), 7.38 (d, 7.3 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 191.81, 188.24, 188.05, 186.80, 150.13, 149.96, 149.83, 149.44, 149.21, 148.19, 144.01, 143.90,

143.84, 143.79, 143.58, 142.60, 141.41, 138.90, 136.97, 130.63, 129.86, 127.02, 126.94, 126.87, 126.80, 126.72. IR (ATR): ν 2955, 2922, 2853, 1717, 1632, 1640, 1567, 1460, 1447,

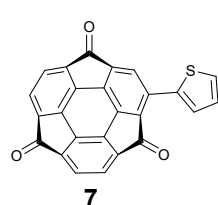
1396, 1369, 1342, 1285, 1260, 1226, 1196, 1177, 1110, 1053, 1018, 950, 845, 743, 727 cm⁻¹. HRMS (EI) m/z Calcd. for [C₂₈H₁₀O₄⁺] (M⁺): 410.0579, found 410.0583.

2-(4-chlorophenyl)-1H-tricyclopenta[def,jkl,pqr]triphenylene-1,4,7-trione (6)



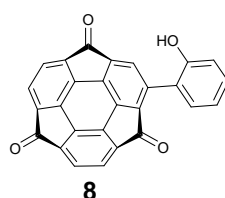
6: mp: 333 °C (dec.). TLC: R_f = 0.55 (CH₂Cl₂). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ (ppm) 188.39, 188.19, 186.86, 150.28, 150.04, 149.93, 149.30, 149.13, 147.61, 144.17, 143.91, 143.87, 143.83, 143.50, 143.07, 138.32, 136.37, 134.05, 131.21, 128.93, 126.84, 126.79, 126.72, 126.60, 126.51. IR (ATR): ν 2956, 2922, 2853, 1716, 1625, 1591, 1485, 1377, 1260, 1177, 1091, 1041, 1013, 947, 854, 831, 745, 731, 696 cm⁻¹. HRMS (EI) m/z Calcd. for [C₂₇H₉ClO₃⁺] (M⁺): 416.0240, found 416.0248.

2-(thiophen-2-yl)-1H-tricyclopenta[def,jkl,pqr]triphenylene-1,4,7-trione (7)

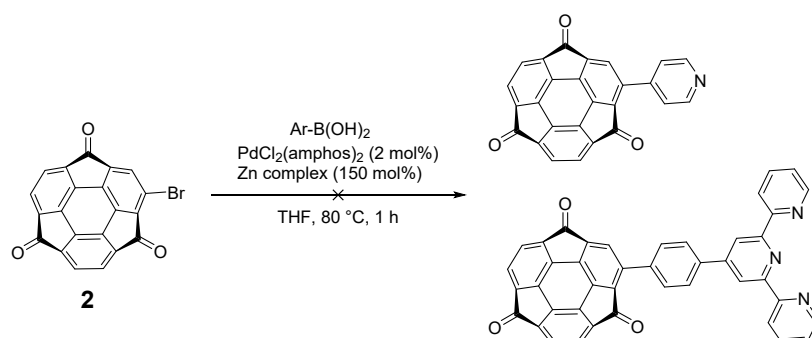


7: mp: 345 °C (dec.). TLC: R_f = 0.45 (CH₂Cl₂). ¹H NMR (600 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 3.7 Hz, 1H), 7.70 (s, 1H), 7.50 (d, *J* = 4.9 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.23 (dd, *J* = 4.9, 3.7 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ (ppm) 188.54, 188.06, 186.70, 151.09, 150.28, 150.12, 149.78, 148.98, 148.74, 148.52, 146.08, 143.98, 143.86, 143.33, 138.85, 137.01, 136.13, 132.57, 129.07, 128.70, 126.86, 126.75, 126.52, 126.48, 126.15. IR (ATR): ν 2953, 2923, 2852, 1717, 1558, 1420, 1283, 1261, 1196, 1177, 1126, 1049, 949, 844, 791, 744, 725, 693 cm⁻¹. HRMS (EI) m/z Calcd. for [C₂₅H₈O₃S⁺] (M⁺): 388.0194, found 388.0189.

2-(2-hydroxyphenyl)-1H-tricyclopenta[def,jkl,pqr]triphenylene-1,4,7-trione (8)



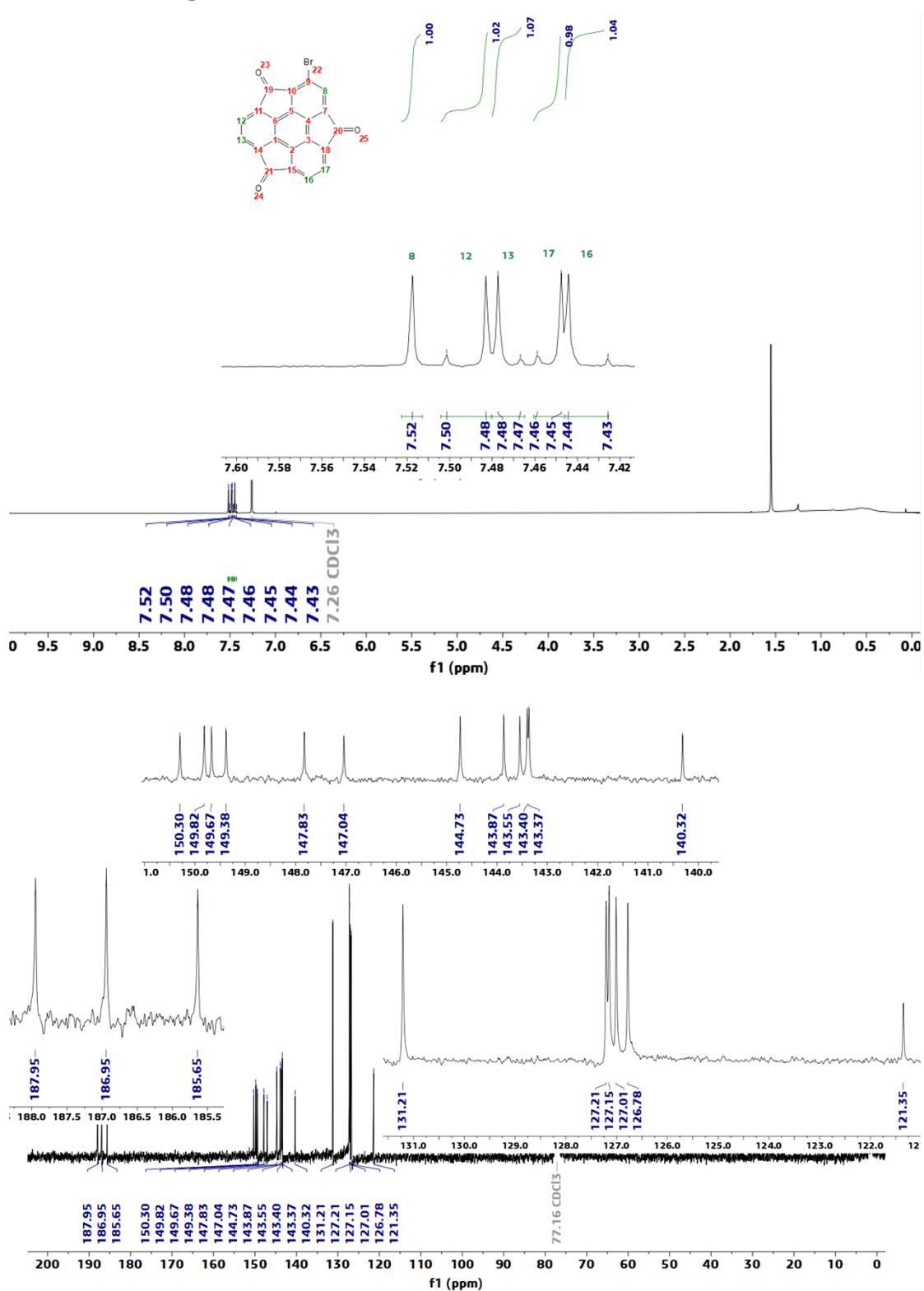
8: TLC: R_f = 0.15 (CH₂Cl₂). ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm) 9.84 (s, 1H), 7.60 (s, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.27 (ddd, *J* = 7.6, 7.6, 1.8 Hz, 1H), 6.95 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.87 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H). IR (ATR): ν 2959, 2920, 2853, 1719, 1456, 1274, 1187, 1123, 1070, 1037, 938, 854, 827, 798, 742 cm⁻¹. HRMS (EI) m/z Calcd. for [C₂₇H₁₀O₄⁺] (M⁺): 398.0579, found 398.0561.



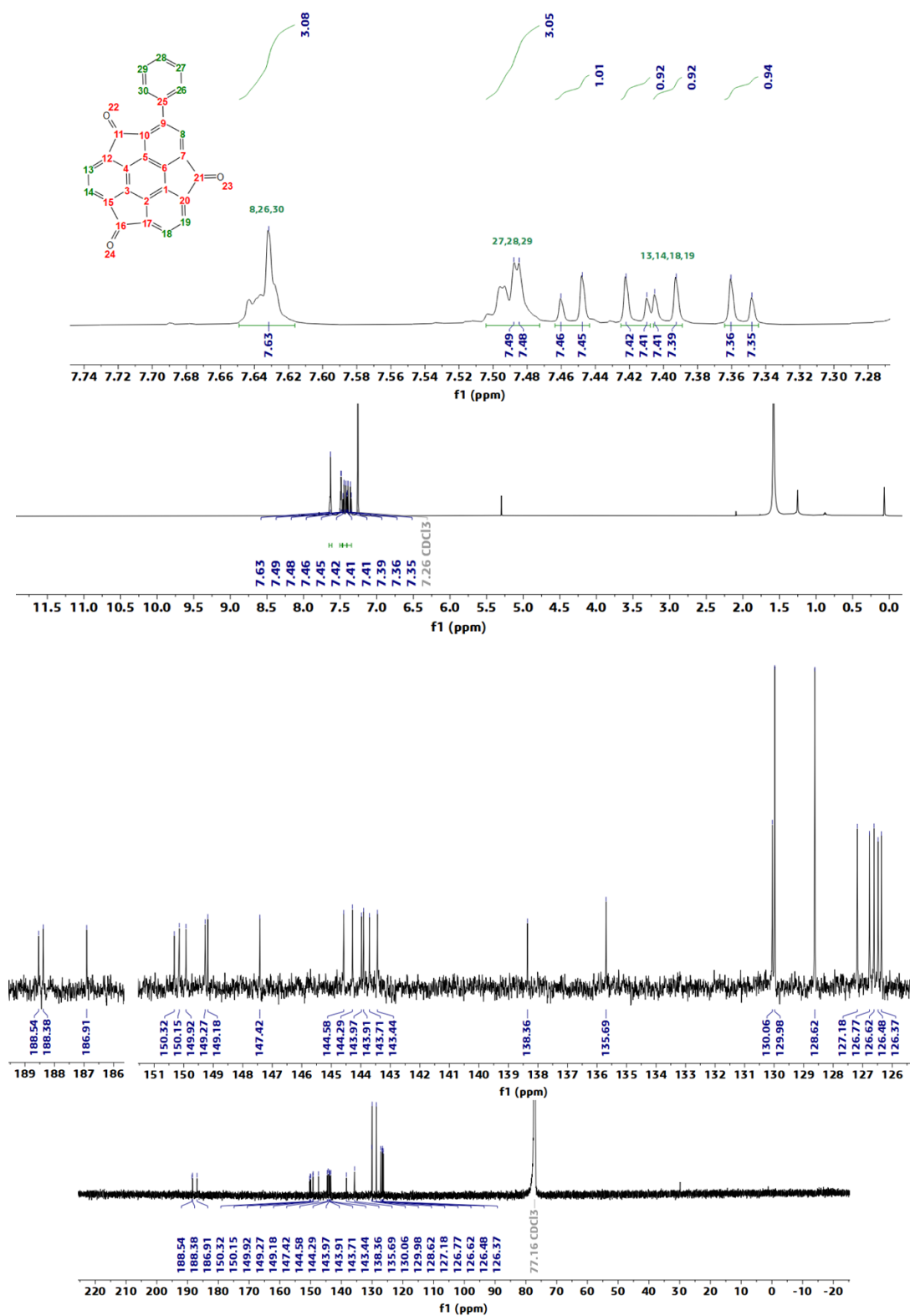
Scheme S4. Failed synthesis of pyridine-sumanenetrione derivatives. It is noteworthy that the reaction using pyridylboronic acid or terpyridylphenylboronic under standard conditions gave

recovery of **2** instead of affording the desired products.

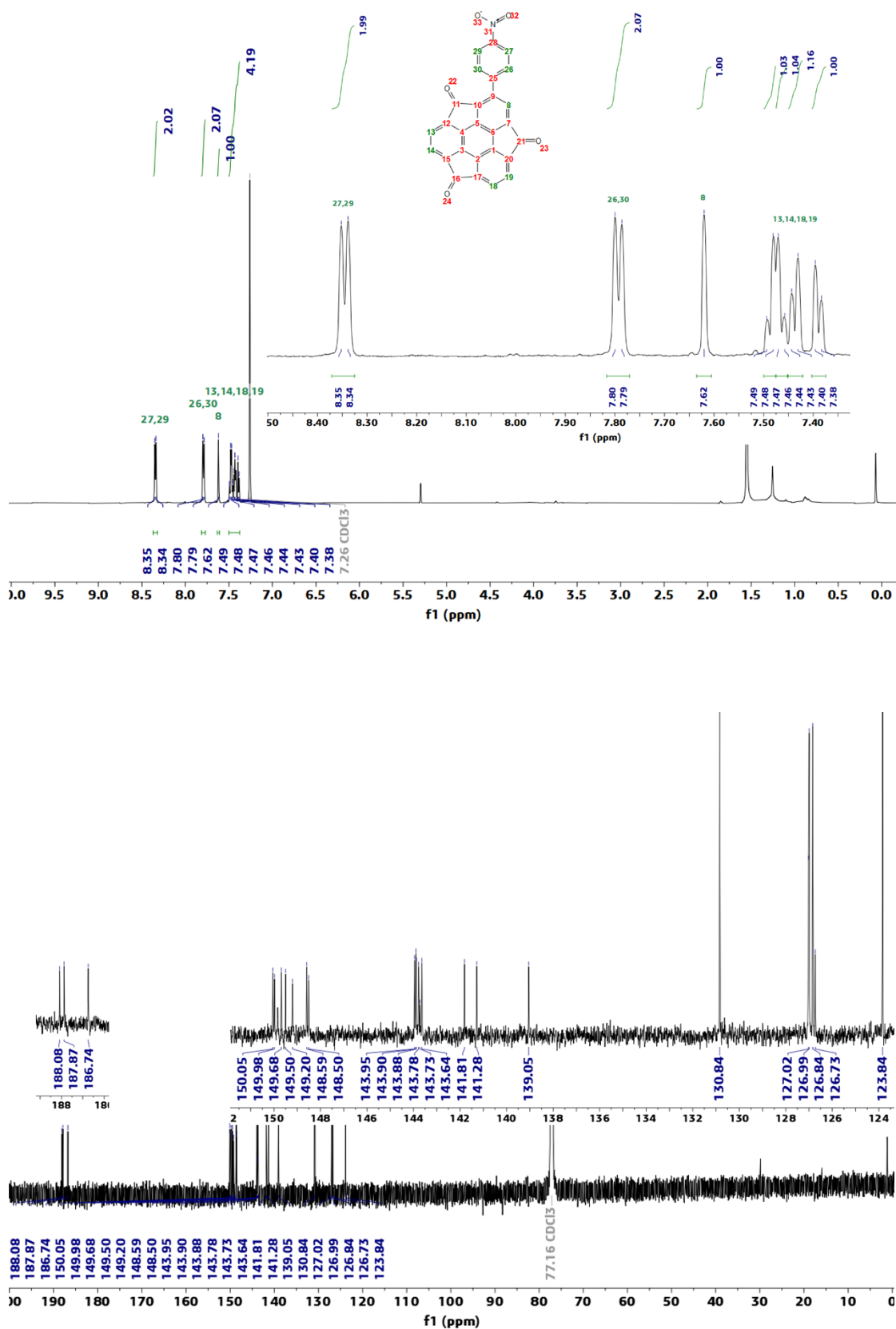
^1H and ^{13}C NMR spectra of **2**



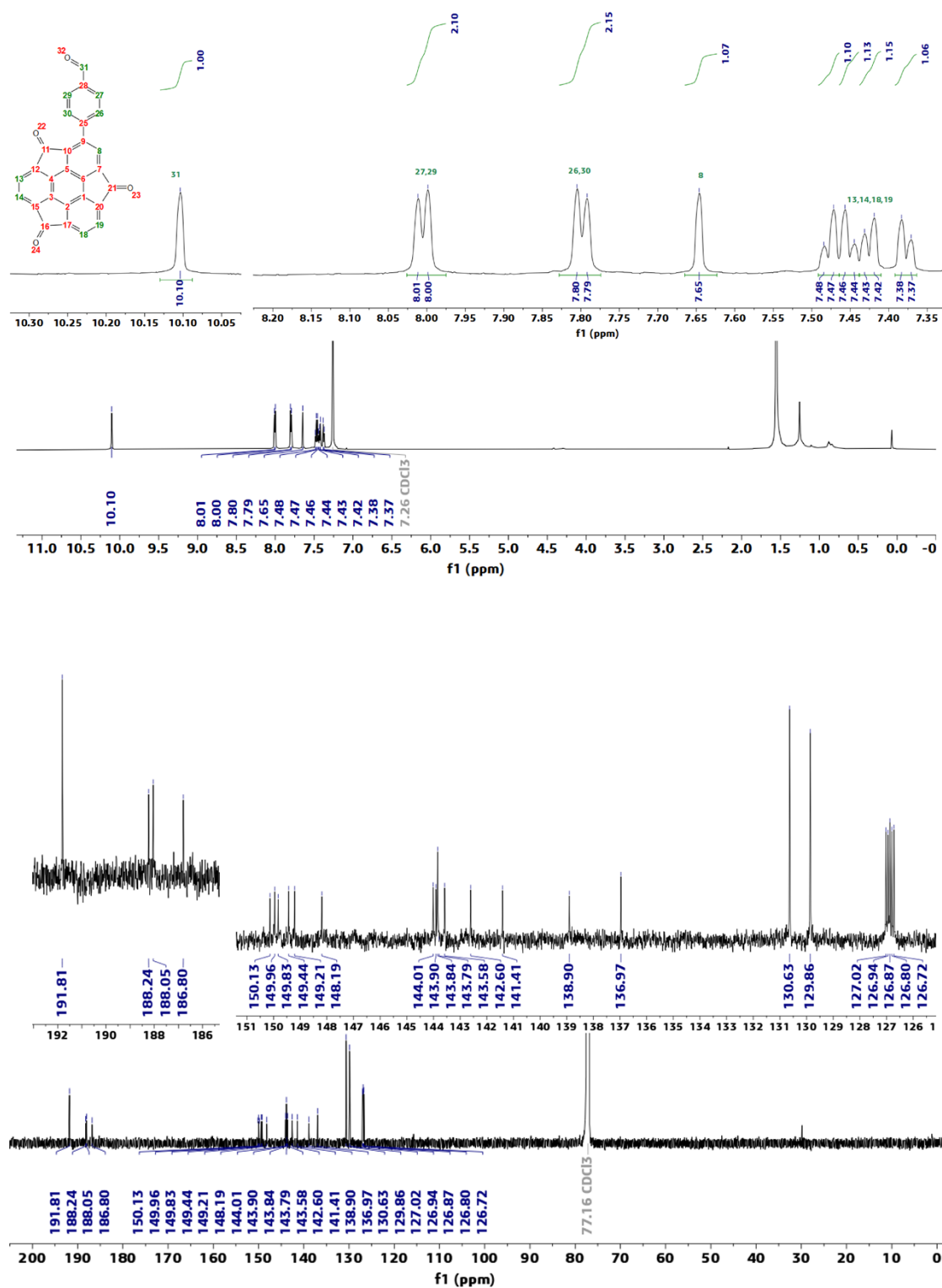
^1H and ^{13}C NMR spectra of **3**



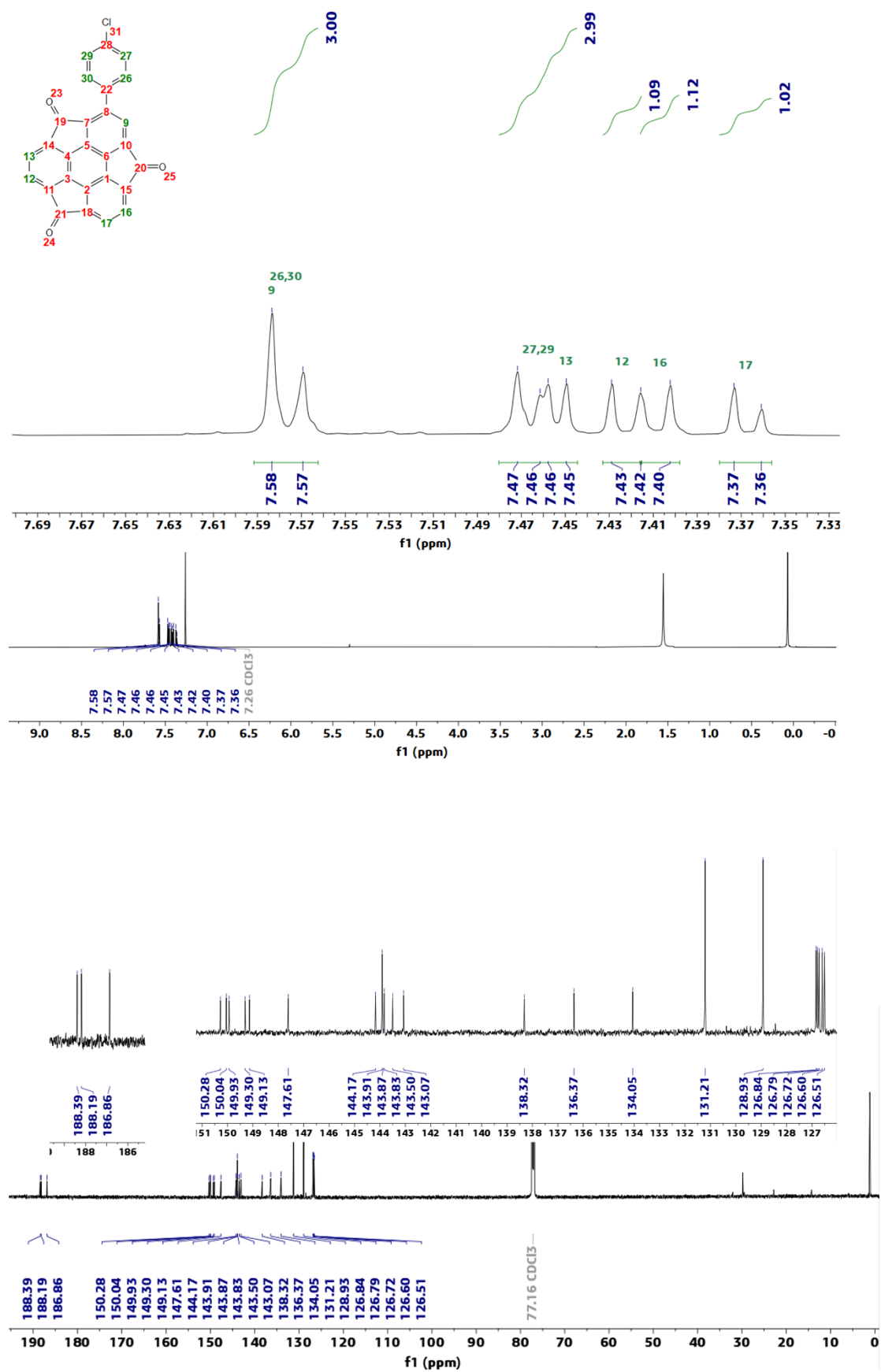
^1H and ^{13}C NMR spectra of **4**



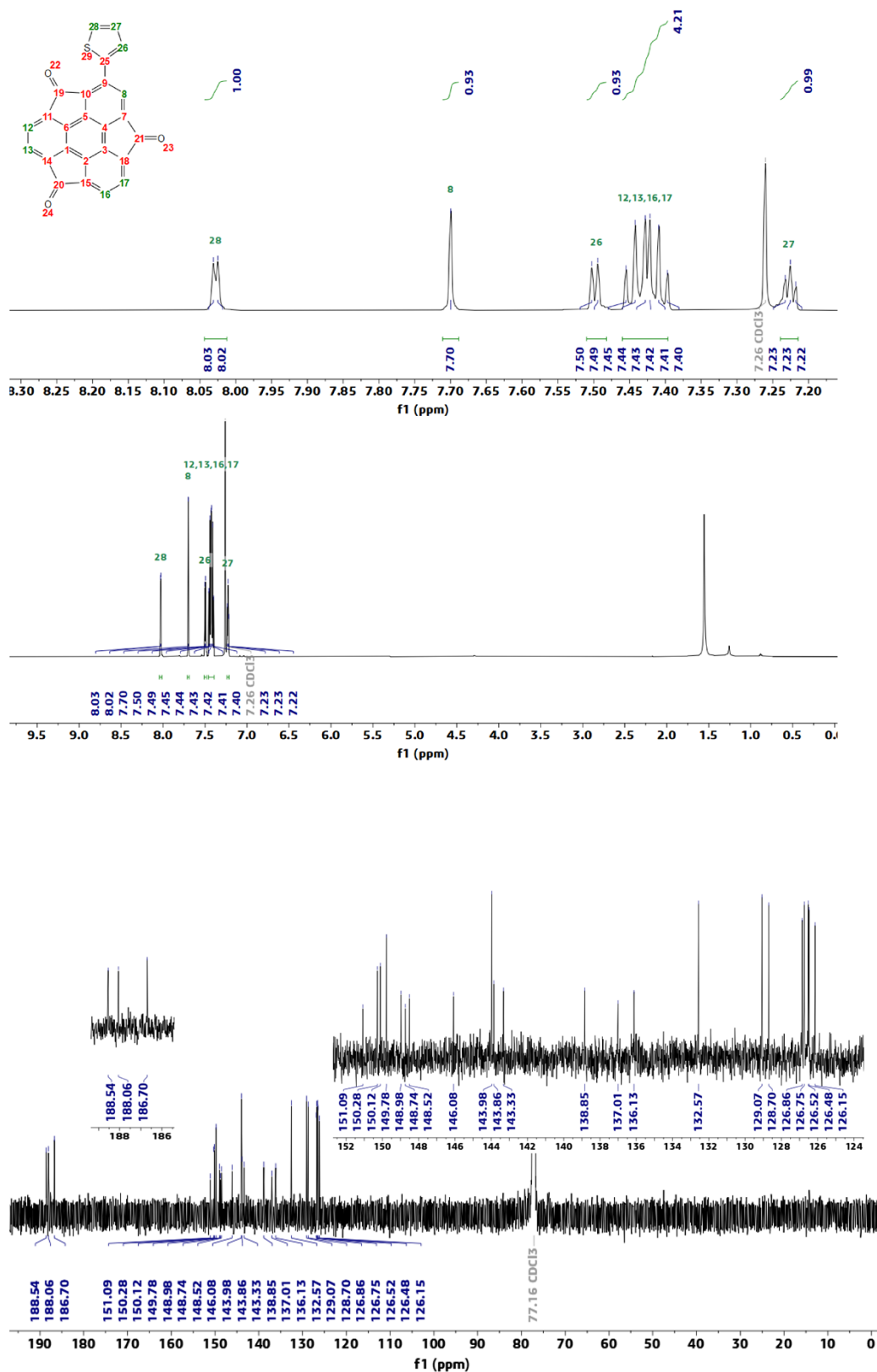
^1H and ^{13}C spectra of **5**



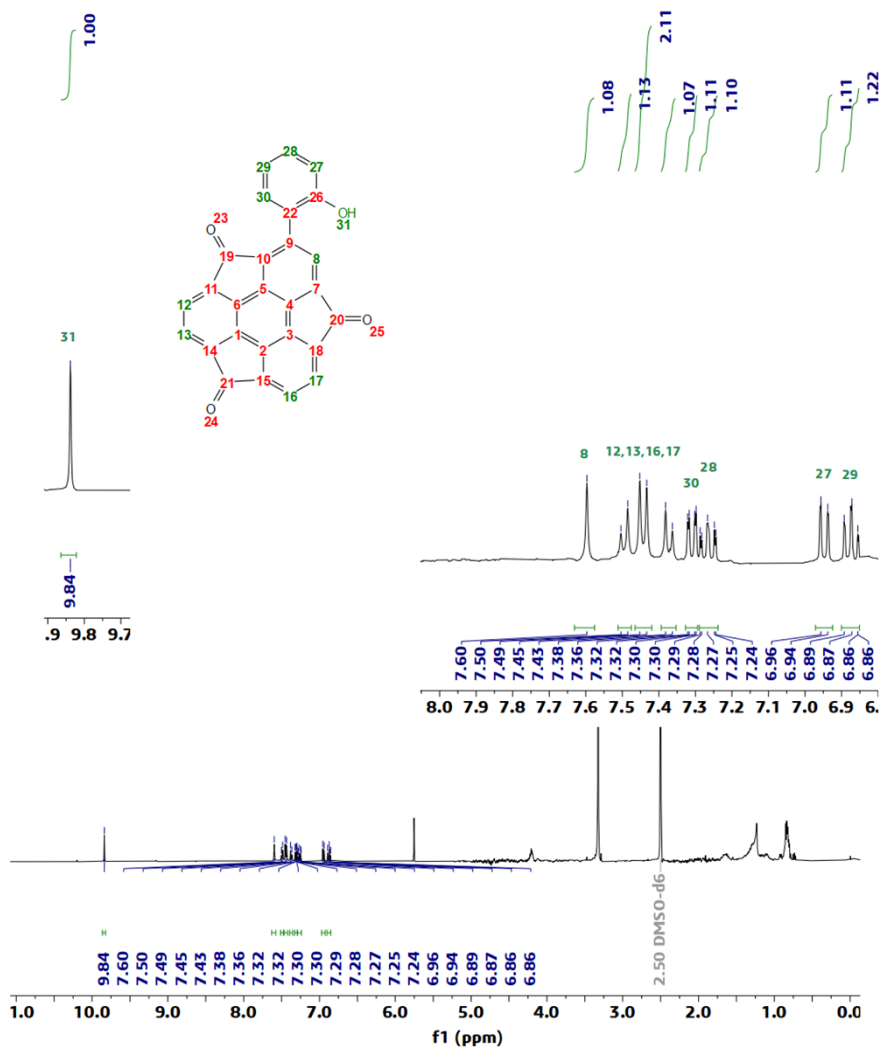
^1H and ^{13}C NMR spectra of **6**



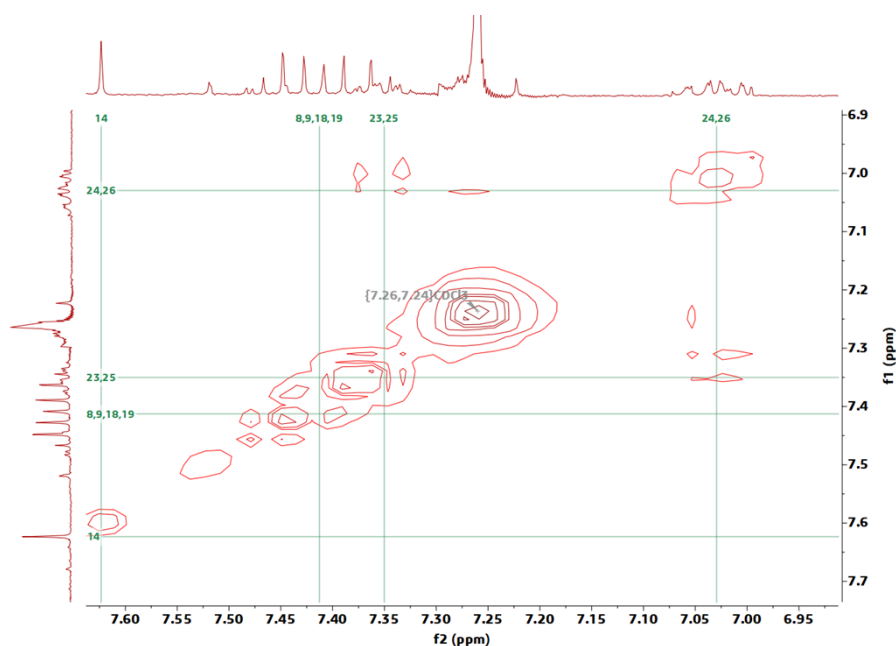
^1H and ^{13}C NMR spectra of 7



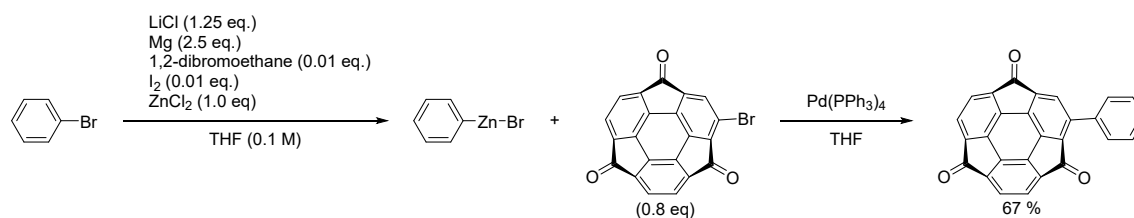
^1H and ^{13}C NMR spectra of **8**



COSY NMR spectrum of **8**



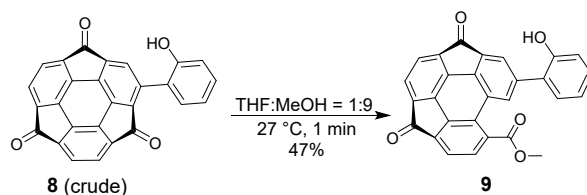
*d) Synthesis of phenylsumanenetrione **3** by Negishi coupling reaction conditions*



A flask was charged with LiCl (1.25 eq.), and the flask was flame-dried under a vacuum. Upon cooling the flask was backfilled with argon, and Mg turnings (2.5 eq.) were added. THF (0.1M relative to aryl bromide) was added, and the mixture was vigorously stirred. A small amount of 1,2-dibromoethane (ca 0.01 eq.) was added, and the mixture was stirred until effervescence ensued. At this time, a small piece of I₂ (ca 0.01 eq.) was added, and a small amount of PhBr (ca 0.1 eq.) was added. The mixture was stirred until the solution was discolored. The remaining portion of PhBr was added dropwise, and the mixture was stirred for 1 hour prior to titration with I₂. Concentrations were 0.081M for PhMgBr.

A flask was charged with ZnCl₂, and the flask was flame-dried under a vacuum. The solution of PhMgBr was then added, and the mixture was stirred for at least 30 minutes. This step was assumed to occur in quantitative yield, and the resulting organozinc reagent was not titrated prior to use in the Negishi coupling reaction. Mixed bromosumanenetrione (0.8 eq.) with Pd(PPh₃)₄ (ca. 0.01eq) in a test tube filled with N₂. The organozinc reagent (1 eq.) was added, and the temperature was raised to 80 °C. After 15 mins of stirring. The reaction mixture was washed with water before being extracted with CH₂Cl₂, filtered through a silica pad, and evaporated. The residue was purified by PTLC (CH₂Cl₂) to give the products phenylsumanenetrione **3** (6.7 mg, 67%).

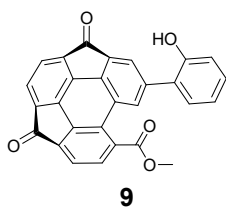
e) Preparation of ring-opened compound **9**



Scheme S5. Synthetic route to the **9**.

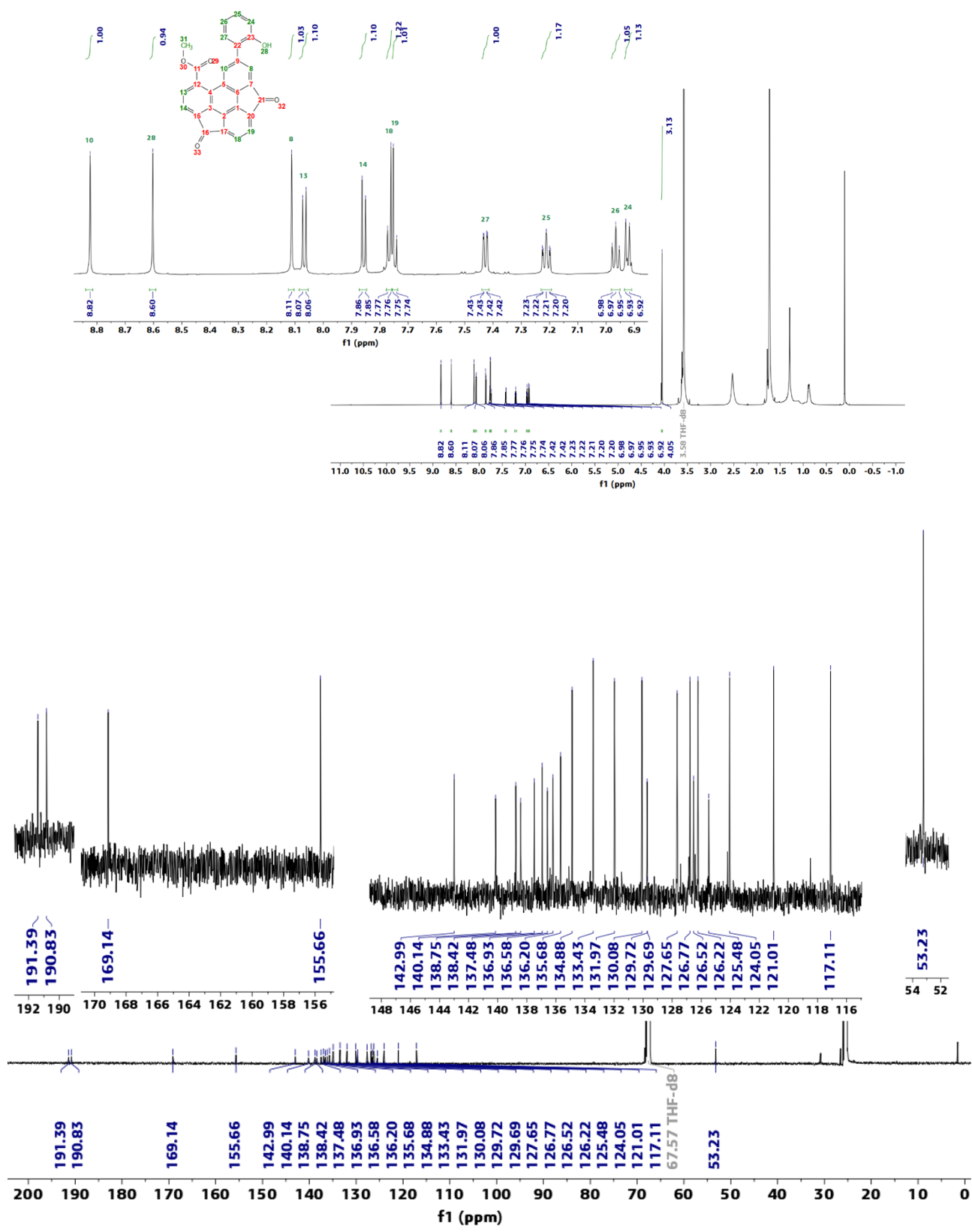
To a test tube equipped with a magnetic stir bar was added crude **8** (10.0 mg, 0.025 mmol) in a 10 mL mixture of THF/MeOH (1:9) solution at 27 °C. After 1 minute of stirring, the reaction mixture color changed from red to yellow. After the removal of solvent under the reduced pressure, the residue was washed with chloroform and then was purified by PTLC (THF:CH₂Cl₂=1:19) to give **9** (5.1 mg, 47% yield) as an orange solid.

Methyl-6-(2-hydroxyphenyl)-1,8-dioxo-1,8-dihydrodicyclopenta[def,jkl]triphen-ylene-4-carboxylate
(9)



9: mp: 223 °C (dec.). TLC: R_f = 0.45 (THF:CH₂Cl₂=1:19). ¹H NMR (600 MHz, THF-*d*₈) δ 8.82 (s, 1H), 8.60 (s, 1H), 8.11 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 7.3 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 7.0 Hz, 1H), 7.43 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.21 (td, *J* = 7.5, 1.8 Hz, 1H), 6.97 (td, *J* = 7.4, 0.9 Hz, 1H), 6.92 (dd, *J* = 8.1, 0.8 Hz, 1H), 4.05 (s, 3H). ¹³C NMR (151 MHz, THF-*d*₈) δ 191.39, 190.83, 169.14, 155.66, 142.99, 140.14, 138.75, 138.42, 137.48, 136.93, 136.58, 136.20, 135.68, 134.88, 133.43, 131.97, 130.08, 129.72, 129.69, 127.65, 126.77, 126.52, 126.22, 125.48, 124.05, 121.01, 117.11, 53.23. IR (ATR): ν 3423, 2953, 2928, 2856, 1714, 1632, 1601, 1453, 1369, 1337, 1267, 1185, 1101, 1036, 907, 857, 808, 755, 727 cm⁻¹. HRMS (EI) *m/z* Calcd. for [C₂₈H₁₄O₅⁺] (M⁺): 430.0841, found 430.0855.

^1H and ^{13}C NMR spectrum of **9**



Lippert Mataga plot

The Stokes shift was determined as the difference in wavenumber between the lowest energy absorption and the highest energy fluorescence band. Estimates of these values obtained experimentally using the Lippert-Mataga equation.^{S3}

$$\Delta\nu = [2(\mu_e - \mu_g)^2/hca^3]\Delta f + \nu^0$$

$$\Delta f = [(\varepsilon - 1)/(2\varepsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$$

Where $\Delta\nu$ is Stokes shift, the superscript “0” indicates the absence of solvent, μ_g and μ_e are dipole moments in the ground state and the excited state, respectively. h is the Planck constant, c represents the light speed in vacuum, a is Onsager cavity radius, here the value gets from gaussian calculation. ε and n are solvent dielectric constant and refractive index respectively.

Table S2. The parameter used to calculate dipole moment change ($\Delta\mu = \mu_e - \mu_g$).

Onsager cavity radius (Å)	Solvents	$\Delta\nu$	Δf
5.98	MeCN	2893	0.305
	CH ₂ Cl ₂	2650	0.217
	CHCl ₃	2620	0.148
	Toluene/CH ₂ Cl ₂ (1:1)	1965	0.080
	Toluene	1341	0.013
	Hexane	1139	0.001

Single crystal X-ray analysis of **9**

Slow evaporation using THF solution of **9** at 20 °C afforded single crystals of **9** as red platelets.

The diffraction data for **9** was recorded on a XtaLAB Synergy with a Cu-target ($\lambda = 1.54184$ Å) equipped with a Rigaku HyPix-6000HE as the detector at 150 K in house. The diffraction images were processed by using CrysAlisPro^{S4}. Initial structure was obtained by direct methods (SHELXT-2018/2)^{S5} and refined by full-matrix least squares calculations on F^2 (SHELXL-2018/3)^{S4b} using the Olex2^{S6} program package.

2: 2(C₂₈H₁₄O₅)2(C₄H₈O), monoclinic, space group $P2_1/n$ (No. 14), $a = 6.97530(10)$ Å, $b = 30.7394(6)$ Å, $c = 22.7853(5)$ Å, $\beta = 97.729(2)^\circ$, $V = 4841.16(16)$ Å³, $\rho_{\text{calcd}} = 1.379$ g/cm³, $Z = 4$, 8614 unique reflections out of 9783 with $I > 2\sigma(I)$, 689 parameters, $3.479^\circ < \theta < 74.375^\circ$, $R_1 = 0.1308$, $wR_2 = 0.4001$, GOF = 1.799. CCDC 2232816.

3) Supporting Figures

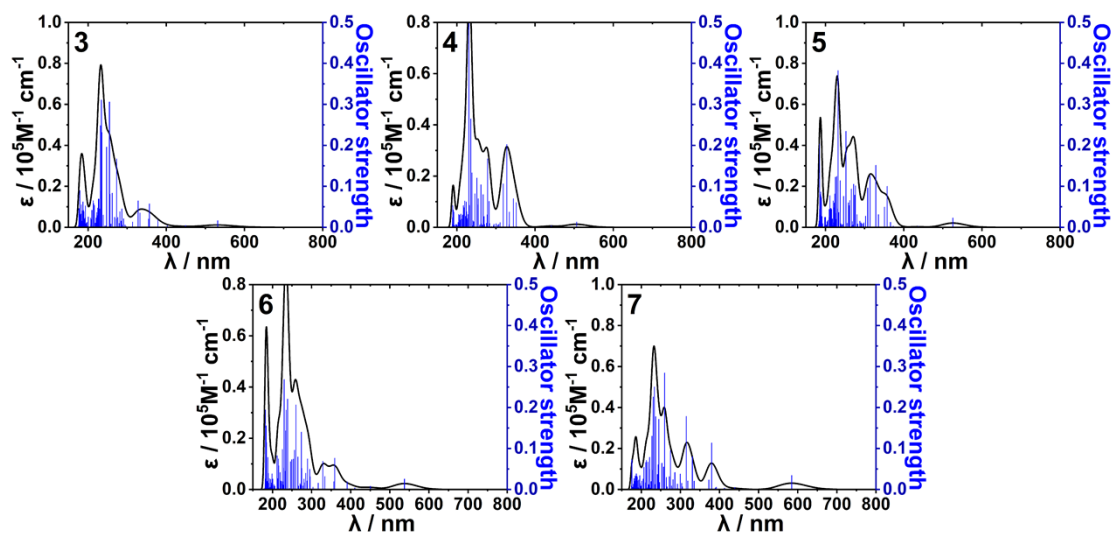


Figure S1. Simulated UV-vis spectrum of 3-8.

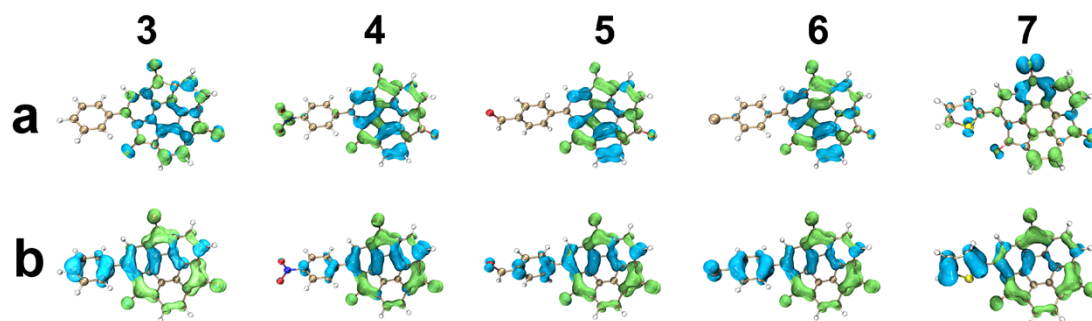
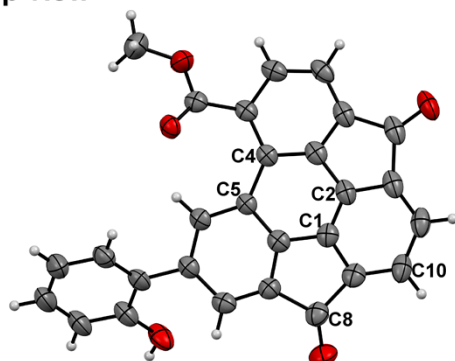


Figure S2. The distribution of hole (blue) and electron (green) of 3-7 at absorption around a) 380 nm and b) 550 nm.

Top view



Side view

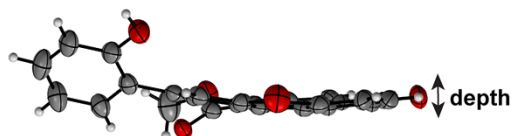


Figure S3. Thermal displacement ellipsoid plot of 9 in a crystal structure with 50% probability. The bond length of C1 to C2 is 1.340 Å and C4 to C5 is 1.512 Å, the depths of 9 at C10 and C8 are 0.331 and 0.232 Å, respectively.

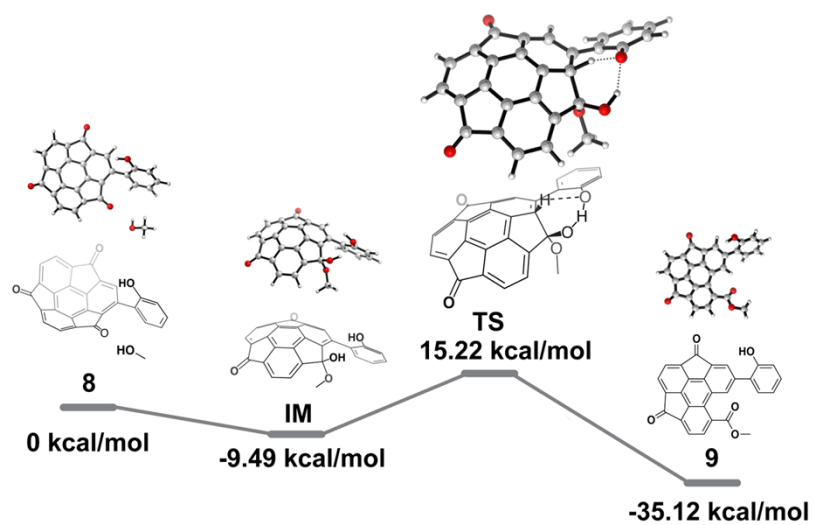


Figure S4. Computed free energy profile for the ring opening reaction of **8** to **9** at B3LYP/def2-TZVP level in SMD (methanol) solvent model.

4) Computational Experiments

All density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were performed with Gaussian 16 software package.^{S7}

In the free energy profile calculation for the ring opening reaction, all the geometry optimization and transition state (TS) calculations were carried out at the B3LYP level of theory with the def2-TZVP basis set for all atoms with using the SMD model^{S8} with methanol as the solvent. Harmonic frequency calculations were conducted at the same level of theory on the optimized geometries to check all the stationary points as minima points. Intrinsic reaction coordinate (IRC) calculations^{S9} were carried out at the B3LYP/def2-TZVP level of theory to confirm the transition states connecting the correct reactants and products on the potential energy surface. Vibrational frequencies were computed to evaluate its zero-point vibrational energy (ZPVE) and thermal energy corrections at 298 K and to check whether each optimized structure is an energy minimum or a transition state.

For TDDFT calculation, the geometry optimization was carried out at the B3LYP level of theory with the 6-311G(d,p) basis set for all atoms. Multiwfn 3.8 was used to analyze the wave functions.^{S10} The 3D diagrams of computed species were generated using CYLView.^{S11}

Optimized cartesian coordinates of **3**

C	2.779182	0.349505	-0.686728	C	4.306322	-1.001723	0.491196
C	1.863728	1.372012	-0.796214	C	-3.563599	0.136696	0.060743
C	0.475536	1.075838	-1.028639	C	-3.962522	-0.900707	0.914292
C	0.047132	-0.228678	-1.111313	C	-5.300787	-1.054573	1.261524
C	1.009148	-1.294001	-1.021157	C	-5.885257	0.844349	-0.097377
C	2.340682	-1.014678	-0.806575	C	-4.546218	1.008183	-0.436285
C	3.157705	-1.874543	-0.067204	O	-1.943685	-2.960005	-0.121701
C	2.616909	-3.095929	0.335769	O	0.287079	4.218118	0.54815
C	1.240144	-3.392165	0.096936	O	5.23752	-1.359691	1.162471
C	0.418279	-2.45843	-0.534499	H	3.196611	-3.776671	0.94923
C	-1.093483	-2.17046	-0.441707	H	0.817011	-4.290787	0.531865
C	-1.227433	-0.639158	-0.695072	H	-2.325327	2.4544	0.243786
C	-2.144341	0.369547	-0.321211	H	3.319613	3.624853	1.264313
C	-1.661711	1.727557	-0.20998	H	4.955002	1.787881	1.465962
C	-0.346915	2.069535	-0.49487	H	-3.230773	-1.591848	1.305212
C	0.595885	3.175026	0.035853	H	-5.588393	-1.859143	1.92869
C	2.011328	2.566263	-0.084124	H	-6.628673	1.520982	-0.503238
C	3.180699	2.736853	0.657699	H	-4.259827	1.805656	-1.112679
C	4.127768	1.673503	0.774361	C	-6.26718	-0.187009	0.757079
C	3.896835	0.449339	0.145837	H	-7.309583	-0.315607	1.025503

Optimized cartesian coordinates of **4**

C	-3.640547	0.309949	0.584561	C	2.731969	0.256206	0.222903
C	-2.763245	1.361452	0.725035	C	3.199444	-0.780311	-0.597864
C	-1.383634	1.109841	1.044601	C	4.554916	-0.917898	-0.86489
C	-0.926678	-0.180522	1.187745	C	5.449134	-0.016529	-0.299903
C	-1.850967	-1.275832	1.064117	C	5.023027	1.01922	0.522065
C	-3.173587	-1.038347	0.762869	C	3.66453	1.151258	0.774228
C	-3.921191	-1.937084	-0.003068	N	6.894364	-0.163659	-0.57918
C	-3.324775	-3.151446	-0.343676	O	1.19717	-2.86768	0.370941
C	-1.957125	-3.403302	-0.017514	O	-1.186295	4.22222	-0.58702
C	-1.20022	-2.433	0.639857	O	-5.937993	-1.508752	-1.364058
C	0.303888	-2.103554	0.627896	O	7.654407	0.647414	-0.067504
C	0.379909	-0.562389	0.857162	O	7.239367	-1.085931	-1.304885
C	1.286941	0.464613	0.514386	H	-3.848405	-3.862215	-0.973181
C	0.781468	1.805851	0.344653	H	-1.485001	-4.299062	-0.405123
C	-0.558317	2.11502	0.539744	H	1.452596	2.543595	-0.080089
C	-1.498643	3.182775	-0.070987	H	-4.156183	3.527459	-1.467587
C	-2.900807	2.535722	-0.021257	H	-5.724142	1.639489	-1.723354
C	-4.028136	2.656645	-0.834396	H	2.507118	-1.488073	-1.027492
C	-4.936167	1.563445	-0.98243	H	4.926876	-1.708777	-1.500865
C	-4.709048	0.359809	-0.314254	H	5.749681	1.695856	0.94914
C	-5.058665	-1.109646	-0.648513	H	3.322838	1.947491	1.424601

Optimized cartesian coordinates of 5

C	-3.366638	0.19386	0.587664	C	-0.34786	2.087869	0.762441
C	-2.52982	1.257281	0.844729	C	-1.309137	3.176974	0.231038
C	-1.150429	1.022844	1.179219	C	-2.689727	2.486895	0.197152
C	-0.653867	-0.259851	1.240389	C	-3.799575	2.644325	-0.632835
C	-1.532404	-1.369001	0.971868	C	-4.664972	1.540156	-0.901267
C	-2.854586	-1.149393	0.652478	C	-4.411806	0.290752	-0.335399
C	-3.545684	-1.993047	-0.222384	C	-4.697257	-1.15042	-0.816495
C	-2.8934	-3.141993	-0.669455	C	2.968794	0.28984	0.2764
C	-1.524312	-3.37188	-0.335213	C	3.72766	-0.661598	0.973159
C	-0.824559	-2.447814	0.44006	C	5.069734	-0.851287	0.672185
C	0.666669	-2.066464	0.511715	C	5.682413	-0.101426	-0.334561
C	0.674214	-0.566645	0.917375	C	4.93076	0.844276	-1.042906
C	1.544225	0.50405	0.621764	C	3.594158	1.038024	-0.739823
C	0.999896	1.836985	0.543681	C	7.114365	-0.310685	-0.652165

O	7.723687	0.290562	-1.506082	H	-3.939881	3.563068	-1.191332
O	1.600234	-2.762688	0.209651	H	-5.435464	1.654352	-1.655589
O	-1.020102	4.265267	-0.19024	H	3.263029	-1.244516	1.757014
O	-5.543853	-1.509998	-1.590709	H	5.64809	-1.587061	1.221914
H	-3.372704	-3.800962	-1.38481	H	5.415883	1.408807	-1.830227
H	-1.00419	-4.1993	-0.804745	H	3.018314	1.754425	-1.313335
H	1.650661	2.635802	0.207971	H	7.615402	-1.085511	-0.032697

Optimized cartesian coordinates of **6**

C	-3.422157	0.314553	0.610759	C	-4.869737	-1.071466	-0.625667
C	-2.53228	1.354924	0.755852	C	2.954601	0.224036	0.171939
C	-1.150933	1.08602	1.052865	C	3.431121	-0.829862	-0.619402
C	-0.70208	-0.209786	1.162705	C	4.786644	-0.959304	-0.898917
C	-1.638953	-1.293577	1.03534	C	5.685643	-0.036368	-0.375856
C	-2.964194	-1.040348	0.758913	C	5.246621	1.015365	0.419953
C	-3.73097	-1.919548	-0.01076	C	3.8875	1.140881	0.682386
C	-3.150106	-3.132846	-0.381122	Cl	7.4005	-0.204414	-0.720594
C	-1.780147	-3.401653	-0.079347	O	1.3797	-2.90531	0.267093
C	-1.005236	-2.449056	0.582783	O	-0.948525	4.222842	-0.53247
C	0.501998	-2.132522	0.55363	O	-5.76314	-1.450786	-1.335053
C	0.597823	-0.598213	0.8089	H	-3.68911	-3.828109	-1.015009
C	1.5128	0.427377	0.475542	H	-1.321225	-4.294457	-0.489133
C	1.009124	1.774552	0.331035	H	1.677501	2.512654	-0.096865
C	-0.323789	2.092167	0.551446	H	-3.935275	3.569443	-1.381435
C	-1.262129	3.177311	-0.028643	H	-5.525135	1.700847	-1.645795
C	-2.669627	2.542623	0.030876	H	2.74725	-1.563325	-1.018666
C	-3.807165	2.687249	-0.764122	H	5.142479	-1.773201	-1.517095
C	-4.727763	1.605451	-0.917247	H	5.956051	1.721816	0.83078
C	-4.502571	0.388981	-0.271896	H	3.550452	1.953741	1.315081

Optimized cartesian coordinates of **7**

C	2.258372	-1.143311	0.754288	C	0.011934	-0.235016	1.093656
C	2.785373	0.195411	0.735152	C	0.907192	-1.350866	0.929829
C	1.931264	1.265227	0.888608	C	-0.22157	2.110029	0.565558
C	0.523543	1.042291	1.076667	C	-1.541918	1.871442	0.220441

C	-2.109844	0.541398	0.259368	O	5.172137	-1.541669	-1.181263
C	-1.278618	-0.537952	0.636311	C	-3.489747	0.38273	-0.201637
C	0.253067	-2.427129	0.329427	C	-4.159814	1.135351	-1.145118
C	1.025164	-3.361429	-0.360065	C	-5.516649	0.764392	-1.306524
C	2.424356	-3.145366	-0.543377	C	-5.882404	-0.260267	-0.475063
C	3.034013	-1.998903	-0.033686	S	-4.567944	-0.800077	0.49836
C	3.925412	0.277288	-0.069224	H	-2.152702	2.671051	-0.181451
C	4.247938	1.519893	-0.614922	H	0.551413	-4.186431	-0.880301
C	3.365178	2.630878	-0.453029	H	2.973313	-3.812476	-1.198673
C	2.169566	2.487824	0.251254	H	5.096849	1.622427	-1.281638
C	-1.233676	-2.033372	0.229387	H	3.571898	3.543616	-1.000765
C	4.249374	-1.169932	-0.505484	H	-3.682101	1.914106	-1.724482
C	0.799196	3.186503	0.12946	H	-6.191941	1.232069	-2.010184
O	-2.124547	-2.722135	-0.195023	H	-6.845933	-0.738339	-0.386337
O	0.565673	4.272869	-0.330912				

Optimized cartesian coordinates of **8**

C	-2.937357	0.185781	-0.718097	C	-4.370184	-1.075224	0.66194
C	-2.060946	1.219433	-0.966781	C	3.383876	0.120195	-0.115958
C	-0.67254	0.94248	-1.221213	C	4.127407	-0.819819	-0.844625
C	-0.20615	-0.35157	-1.209769	C	5.456225	-1.097444	-0.552219
C	-1.123676	-1.430079	-0.948105	C	6.07607	-0.435072	0.503481
C	-2.455778	-1.170373	-0.708306	C	5.363452	0.493525	1.253749
C	-3.211518	-1.964827	0.159267	C	4.029886	0.773236	0.9549
C	-2.610582	-3.10908	0.683918	O	1.929814	-2.856579	0.046018
C	-1.231459	-3.380086	0.432592	O	-0.535216	4.227975	0.04408
C	-0.470184	-2.502057	-0.337908	O	-5.264208	-1.386717	1.4041
C	1.03258	-2.153472	-0.340002	O	3.311273	1.664107	1.70226
C	1.095072	-0.674484	-0.800751	H	-3.142089	-3.728953	1.397414
C	1.975998	0.383728	-0.495644	H	-0.755633	-4.198665	0.961118
C	1.460187	1.732114	-0.488904	H	2.102041	2.517334	-0.11463
C	0.134388	2.003195	-0.796409	H	-3.514383	3.62736	0.915011
C	-0.824389	3.13015	-0.354018	H	-5.080167	1.771857	1.365131
C	-2.223046	2.474166	-0.369593	H	3.642791	-1.329933	-1.667354
C	-3.369895	2.686779	0.395085	H	6.000587	-1.824991	-1.141324
C	-4.275822	1.613814	0.655305	H	7.112302	-0.638378	0.747866
C	-4.025604	0.339853	0.14562	H	5.83912	1.005346	2.085606

H 3.866064 1.999558 2.414189

Optimized cartesian coordinates of **9**

C	0.519816	13.174656	13.735952	C	0.773236	17.478651	8.907027
C	0.701149	12.376367	12.579307	C	0.797898	14.401007	11.163164
C	0.909612	10.503375	10.696063	C	1.872541	17.348418	8.046374
H	0.999898	9.760528	9.915802	H	2.648998	16.63651	8.302989
C	0.868064	12.898224	11.279697	C	0.475094	14.512304	13.629045
C	0.023749	13.303763	16.039057	C	0.167423	16.757649	14.029313
H	-0.173126	12.862867	17.009591	C	-0.024387	14.736403	15.920546
O	0.862562	11.126389	8.061659	H	-0.256391	15.316014	16.806817
O	1.936601	13.058202	8.44888	C	0.718411	10.065373	12.020577
C	0.291047	12.500654	14.925632	H	0.65302	9.008061	12.248598
C	0.36018	11.019494	14.517885	C	1.992889	18.12105	6.897662
C	0.601097	15.115692	12.359465	H	2.858801	18.008526	6.256397
O	-0.032812	17.824355	14.547936	C	0.678919	16.649781	10.142608
O	0.228682	10.040318	15.204425	C	-0.231246	18.404416	8.56408
C	0.829599	15.254544	10.032645	C	1.193793	11.260359	6.665857
H	0.985425	14.846562	9.047167	H	2.275874	11.283089	6.530978
C	0.616729	11.04148	12.988793	H	0.763655	12.176778	6.260056
C	1.315816	12.108372	8.865924	H	0.762379	10.386965	6.182797
O	-1.361355	18.585327	9.311022	C	-0.112714	19.182189	7.41124
H	-1.406852	17.907239	9.995225	H	-0.908728	19.879664	7.180174
C	0.99714	11.85154	10.306027	C	0.995799	19.045012	6.586093
C	0.469833	17.287774	11.39931	H	1.077572	19.657467	5.695233
C	0.196283	15.360056	14.689063	H	0.373123	18.366351	11.457033
C	0.42458	16.490994	12.525726				

Optimized cartesian coordinates of **IM**

O	1.964114	2.469421	-0.609109	C	0.756632	5.699366	-3.397788
O	1.987003	8.634479	-4.043435	C	0.683201	4.382647	-2.858011
O	8.171101	5.299393	-1.534752	C	1.797404	3.547354	-2.85891
C	2.259836	2.333601	-1.971853	C	3.830453	2.44523	-2.061072
C	2.554137	7.574813	-4.072075	C	4.850767	2.126231	-1.152842
C	7.191769	5.078874	-2.195539	C	6.10031	2.8274	-1.232282
C	1.937782	6.170675	-3.960473	C	6.318163	3.80915	-2.188321

C	6.4329	6.065437	-3.106726	O	1.733197	1.163221	-2.527603
C	6.32945	7.451881	-3.105542	H	4.318525	-0.027459	-2.151552
C	5.146096	8.089138	-3.584892	C	0.596742	2.38212	-0.219601
C	4.080156	7.33203	-4.057114	H	-0.083871	6.365274	-3.247216
C	5.327517	4.006229	-3.149762	H	-0.226459	4.100879	-2.347948
C	5.395116	5.335326	-3.693212	H	6.826738	2.652549	-0.448574
C	4.254813	5.948868	-4.150864	H	7.081486	8.056248	-2.614179
C	2.991419	5.265142	-4.080602	H	5.038181	9.15708	-3.442997
C	2.924433	3.995022	-3.550027	H	5.290135	2.568433	1.479447
C	4.11792	3.348254	-3.082045	H	4.845358	1.048086	3.370003
C	4.620098	1.200111	-0.021434	H	3.885339	-1.201643	2.94092
C	4.898323	1.576702	1.29413	H	3.431673	-1.920814	0.60343
C	4.636745	0.727023	2.358293	H	0.595763	2.041848	0.814283
C	4.095431	-0.531404	2.11756	H	0.115383	3.361457	-0.270916
C	3.831798	-0.938815	0.817517	H	0.053104	1.666368	-0.836953
C	4.095084	-0.079183	-0.238938	H	2.195743	0.404137	-2.130913
O	3.804256	-0.536473	-1.508392				

Optimized cartesian coordinates of TS

O	2.12633	2.916969	-0.46996	C	5.442273	3.892158	-2.823184
O	2.182325	8.270086	-4.731197	C	5.558441	5.16842	-3.47213
O	7.896109	5.530984	-0.872608	C	4.499593	5.683479	-4.182655
C	2.288628	2.378678	-1.765361	C	3.256064	4.967278	-4.190737
C	2.771763	7.24078	-4.538147	C	3.149645	3.76274	-3.515249
C	7.063236	5.197106	-1.673023	C	4.282399	3.164688	-2.885012
C	2.180121	5.844211	-4.317464	C	4.683774	1.057453	0.198943
C	0.946898	5.423254	-3.832336	C	5.238227	1.08315	1.498006
C	0.836313	4.202775	-3.113127	C	5.303932	-0.044535	2.274785
C	1.958741	3.41499	-2.874102	C	4.876145	-1.275234	1.741574
C	3.909144	2.198097	-1.881982	C	4.367406	-1.357003	0.469249
C	4.813939	2.140642	-0.723006	C	4.174178	-0.194019	-0.316763
C	5.932946	3.03189	-0.633418	O	3.613086	-0.28904	-1.482098
C	6.240935	3.8899	-1.658983	O	1.543919	1.238502	-1.976293
C	6.460136	6.013679	-2.811336	H	3.921024	0.977767	-2.098283
C	6.334005	7.385844	-2.999759	C	0.791332	3.128471	-0.021362
C	5.239482	7.913186	-3.742163	H	0.087864	6.081286	-3.875074
C	4.284559	7.060642	-4.28316	H	-0.113568	3.966628	-2.655361

H	6.526235	3.033307	0.271304	H	4.034505	-2.297644	0.052033
H	6.980713	8.070744	-2.466272	H	0.839713	3.16294	1.065624
H	5.082962	8.984472	-3.749334	H	0.399648	4.080449	-0.389561
H	5.576275	2.028788	1.900954	H	0.138008	2.311227	-0.328552
H	5.68736	0.007151	3.284541	H	2.07397	0.466841	-1.682876
H	4.941871	-2.171063	2.347075				

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