Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Unusual Structural Changes as a Result of Weathering Benzofuran-Based Diarylethenes

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Materials and Methods

General. All chemicals and solvents were purchased from Sigma Aldrich unless otherwise stated. The starting material, 3,4-dimethoxyphenol was purchased from TCI Chemicals, Inc., (4-*tert*-butylphenyl)boronic acid was purchased from Combi-Blocks Inc., tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3) and bis(2-diphenylphosphino-phenyl)ether were purchased from Strem Chemicals, Inc., and octafluorocyclopenetene was purchased from SynQuest Labs, Inc. The solvent Rhodiasolv® IRIS was purchased from Solvay Inc. and was distilled prior to use. Column chromatography was done on a Teledyne ISCO CombiFlash Purification System. Liquid chromatography was done on an Agilent Technologies 1260 Infinity HPLC system. The LC-MS experiment was done on an Agilent 1260 Infinity LC coupled with an Agilent 6100 MS system. All NMR spectroscopy acquisition was done on a Bruker 400 MHz or 600 MHz NMR instrument. The operating temperature is at 298K unless otherwise stated. All chemical shifts are referenced to residual solvent signals, which were previously referenced to tetramethylsilane and splitting patterns are designated as s (singlet), d (doublet), dd (doublet of doubles), t (triplet) and m (multiplet).

HPLC characterization conditions. All HPLC characterizations were carried out using a mixture of 96:4 (v/v) *n*-hexane/isopropyl alcohol as the mobile phase, and a ZORBAX RX-SIL column (5 μm, 4.6 mm × 250 mm) as the stationary phase, with a 1 mL per minute flow rate, operating at 25°C. The UV absorbance signal for the different fractions was recorded at 254 nm against elution time.

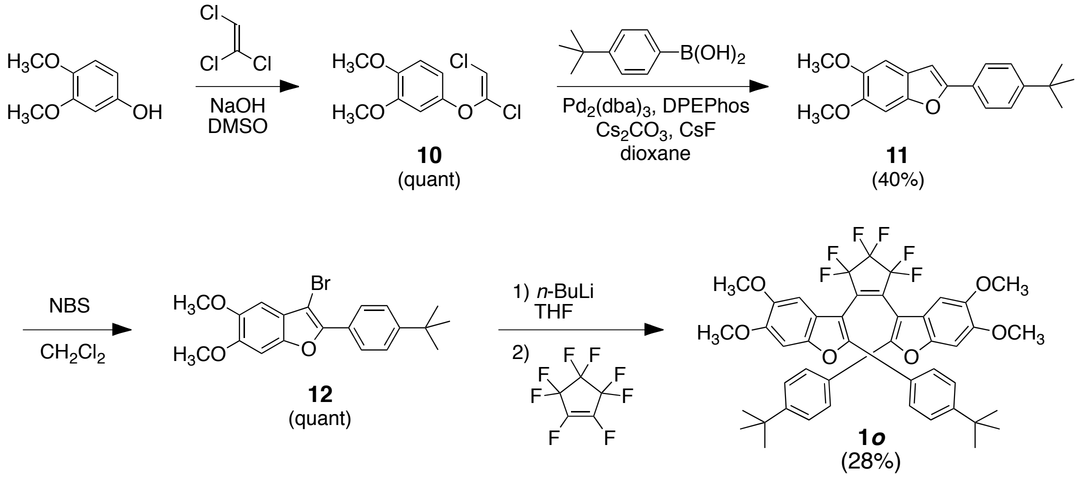
LC-MS characterization conditions. All LC-MS characterizations were carried out using a mixture of 84:13:3 (v/v) acetonitrile/water/methanol as the mobile phase, and a ZORBAX SB-C18 column (1.8 μm, 2.1 mm × 50 mm) as the stationary phase, with a 0.3 mL per minute flow rate, operating at 40 °C. The monitored signals are 254 nm UV absorption from a diode array detector, and a total ion count intensity (scanning mass/ion ratio from 400 to 1000) from a mass spec detector.

Fabrication of glass weathering cells. Two small holes (0.8 mm diameter) were drilled at opposite corners (1 cm in from each side) of a piece of 300 mm × 300 mm × 3 mm float glass, using a diamond drill bit (PreHCP Diamond burs FG BR-49) and a rotary tool (Dremmel

4200 series). The drilled glass and a matching piece of undrilled glass were cleaned using hot soapy water, rinsed with deionized water and acetone then dried with compressed air. A 5 mm wide frame and spacer dots (5 mm diameter) were cut from a sheet of EVAL EF-F (ethylene vinyl alcohol polymer film, purchased from Kuraray) using a laser engraver (GCC LaserPro Spirit) then placed carefully around the perimeter of one sheet of glass. EVAL EF-F spacer dots were spaced in a 7 cm grid pattern on the inside of the frame then sandwiched by the second sheet of glass. Binder clips (3/4 inch per each) were placed side by side around the exterior of the cell and the entire assembly was placed in a preheated oven for 15 min at 170 °C. Once the EVAL frame had melted and bonded the two sheets of glass together, the cell was removed from the oven and placed in a nitrogen glovebox to cool. The binder clips were removed from the cooled cell and it was laid flat with the fill/exit ports facing up.

Optical spectroscopy sample preparation and measurements. Samples were prepared by removing an aliquot amount (0.1 mL) from each weathering cells using a syringe and autopipette tip, and diluting it to 100 mL with *n*-hexane in a 100 mL volumetric flask. For samples prepared from diarylethene solids, the corresponding diarylethene (**1*o*** or **2*o***) was weighed and dissolved in a 50 mL volumetric flask using *n*-hexane as solvent, and then the solution was diluted to the 50 mL using *n*-hexane. Samples were irradiated using the light source from a lamp used for visualizing TLC plates at 365 nm (Spectroline E-series, 0.12 W/cm^2). Samples were faded using a 150 W tungsten source filtered with a 520 nm cutoff filter. The changes of UV-Vis spectra were recorded using Varian Cary 300 spectrometer.

Synthetic Scheme



Synthesis of (*E*)-4-((1,2-dichlorovinyl)oxy)-1,2-dimethoxybenzene (10). A solution of 3,4-dimethoxyphenol (25 g, 162 mmol) in DMSO (350 mL) was treated with NaOH (52 g, 1.3 mol). The mixture was stirred for 15 min until most of solids had dissolved, at which time it was treated drop wise over 15 min with a solution of 1,1,2-trichloroethene (15.7 mL, 175 mmol) in 15 mL DMSO. During the addition, the solution temperature increased to 90 °C and then eventually returned to ambient temperature. The reaction was monitored by TLC (99:1 v/v EtOAc:hexanes). When determined to be complete, the reaction was quenched by pouring the mixture into 500 mL ice water. The mixture was transferred to a separatory funnel and washed with hexanes (3 × 100 mL). The organic layers were combined, dried over anhydrous $MgSO_4$ and filtered through a plug of silica gel. The filter cake was washed with hexanes (2 × 50 mL). The hexanes was removed under reduced pressure to afford 40.4 g (quant) of (*E*)-4-((1,2-dichlorovinyl)oxy)-1,2-dimethoxybenzene (**10**) as a colorless oil that solidified into

white crystals upon drying on a vacuum Schlenk line. The compound was used without further purification.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (d, *J* = 8.1 Hz, 1H), 6.65 (d, *J* = 3.9 Hz, 1H), 6.61 (dd, *J1* = 7.9 Hz, *J2* = 4.0 Hz, 1H), 5.90 (s, 1H), 3.88 (s, 3H), 3.86 (s, 3H).

Synthesis of 2-(4-(tert-butyl)phenyl)-5,6-dimethoxybenzofuran (11). A mixture of (4-*tert*-butylphenyl)boronic acid (9.43 g, 53.00 mmol), $Pd_2(dba)_3$ (573 mg, 0.63 mmol), oxy-bis(2,1-phenylene)bis(diphenylphosphine) (649 mg, 1.20 mmol), cesium fluoride (15.37 g, 101 mmol) and cesium carbonate (33.0 g, 101 mmol) were placed into a 500-mL three-neck round bottom flask, equipped with a magnetic stirrer and a condenser. The flask was purged with argon for 30 min, at which time a solution of (*E*)-4-((1,2-dichlorovinyl)oxy)-1,2-dimethoxybenzene (**10**) (12.0 g, 48.2 mmol) in dioxane (300 mL) was added. The reaction mixture was vigorously stirred and heated to reflux where it was kept overnight. The reaction was allowed to cool to room temperature, the inorganic solids were filtered off through a silica plug, and the filter cake was washed with dichloromethane (200 mL). All organic extracts were combined and the solvents were removed under reduced pressure to afford the crude product as brown solid. MeOH (150 mL) was added to the brown solid and the mixture was stirred vigorously until a fine powder was obtained. The fine powder was collected by filtration and further suspended in 100 mL MeOH with vigorous stirring, then filtered through a fritted funnel to provide 6.0 g (40% yield) of 2-(4-*tert*-butylphenyl)-5,6-dimethoxybenzofuran (**11**) as white solid which was used without further purification.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.11 (s, 1H), 7.02 (s, 1H), 6.88 (s, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 1.36 (s, 9H).

Synthesis of 3-bromo-2-(4-*tert*-butylphenyl)-5,6-dimethoxybenzofuran (12). A solution of 2-(4-*tert*-butylphenyl)-5,6-dimethoxybenzofuran (**11**) (6.0 g, 19.3 mmol) in anhydrous CH_2Cl_2 (150 mL) in a 250-mL one-neck round bottom flask was treated with *N*-bromosuccinimide (3.44 g, 19.33 mmol) in portions at room temperature. The reaction mixture was stirred at room temperature until complete consumption of the starting material as indicated by TLC (1:10 v/v EtOAc:hexanes). The reaction mixture was poured into a separation funnel containing an aqueous solution of NaOH and extracted with CH_2Cl_2 (100 mL). The combined organic phases were washed with water (3 × 100 mL), filtered through a silica gel plug to remove the brown impurity and concentrated under reduced pressure to afford 7.5 g (quant) of 3-bromo-2-(4-*tert*-butylphenyl)-5,6-dimethoxybenzofuran (**12**) as a white solid, which was used without further purification.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.07 (s, 1H), 6.94 (s, 1H), 3.98 (s, 3H), 3.95 (s, 3H), 1.37 (s, 9H).

Synthesis of 3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(2-(4-*tert*-butylphenyl)-5,6-dimethoxybenzofuran) (1*o*). A solution of 3-bromo-2-(4-*tert*-butylphenyl)-5,6-dimethoxybenzofuran (**12**) (7.5 g, 19.3 mmol) in anhydrous Et_2O (50 mL) and THF (50 mL) in a 250-mL three neck round bottom flask was slowly treated with *n*-BuLi (2.5M n-hexane solution, 8.1 mL, 20.2 mmol) at –78 °C. After stirring at –78 °C for 5 min, the reaction was treated by octafluorocyclopentene (1.29 ml, 9.63 mmol) in one portion. The reaction mixture was stirred for 1 h while the temperature was allowed to increase gradually. The reaction was quenched by addition of water, and the mixture was transferred to a separatory funnel. The organic layer was extracted with Et_2O (3 × 50 mL), evaporated and the solid residue was deposited on silica gel. Purification by chromatography column using silica gel (EtOAc:hexanes gradient: 0%, 5% and 10%) afforded a yellow solid, which was further purified by sonicating it in MeOH. Filtration through a fritted funnel and vacuum drying afforded 2.1 g (28%) of **1*o*** as yellow solid. The ^{1}H and ^{13}C NMR spectra are shown in Figure S1 and Figure S2, respectively.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13-7.05 (m, 8H), 6.81 (s, 2H), 6.75 (s, 2H), 3.86 (s, 6H), 3.76 (s, 6H), 1.12 (m, 18H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 155.3, 152.5, 149.2, 148.4, 146.7, 126.8, 126.5, 125.4, 118.6, 110.2, 104.3, 102.3 (J = 6 Hz),[1] 94.8, 56.2, 56.1, 34.6, 31.0.

HRMS (M$^+$) expected: 792.2886; found: 792.2880.

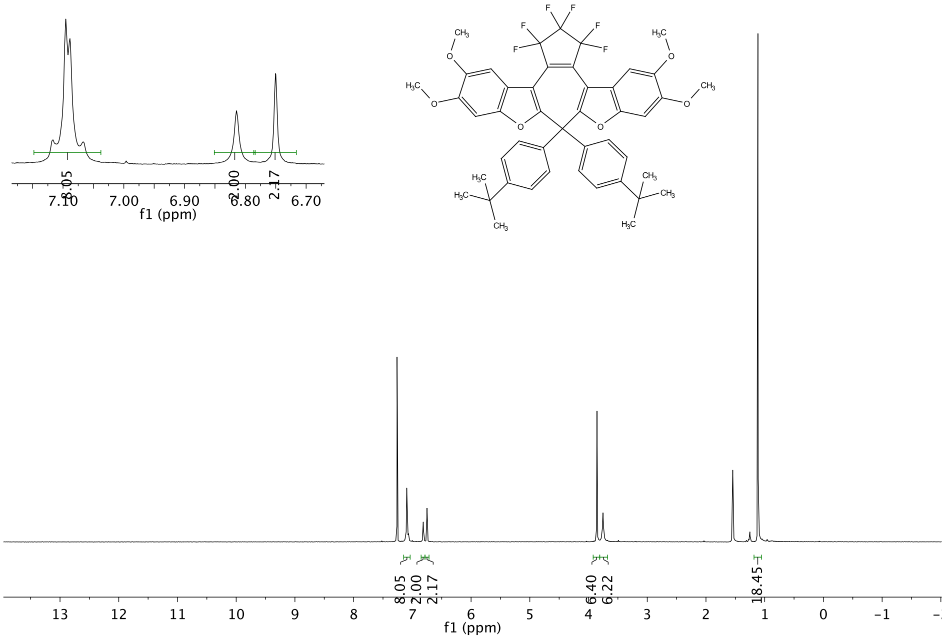


Figure S1. ^{1}H NMR (400 MHz, CDCl$_3$) of compound **1*o***.

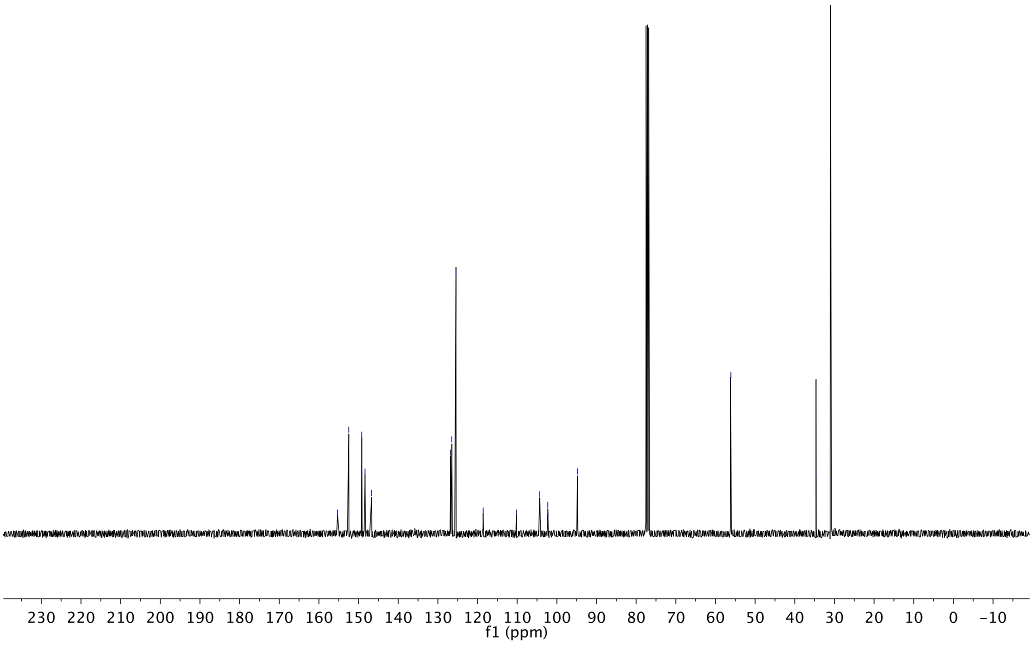


Figure S2. ^{13}C NMR (100 MHz, CDCl$_3$) of compound **1*o***.

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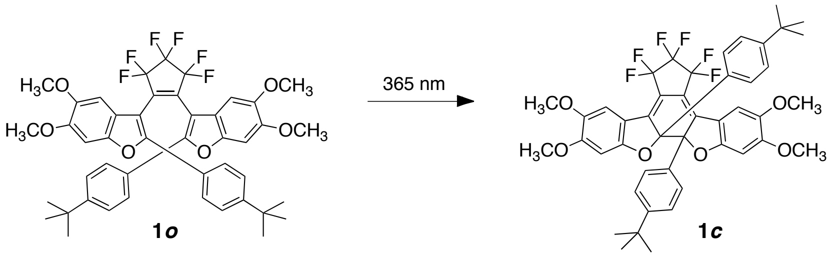
[1] There are two types of carbons coupled to fluorine in **1*o***, therefore theoretically the ^{13}C NMR spectrum should contain two signals as triplet. However, based on our experiment condition, only one triplet was observed.



Photoconversion of 1*o* to 1*c*. A solution of **1*o*** (5 mg) in *n*-hexane (20 mL) in a 50 mL round bottom flask equipped with a magnetic stir bar was bubbled with nitrogen for 20 minutes, and then irradiated with 365 nm UV light (0.12 W/cm^2)[2] for 1 h. The solvent was removed by rotary evaporator and the remaining **1*o*/1*c*** mixture was analyzed by ^{1}H NMR spectroscopy. The corresponding aromatic protons shown in Figure S3 were used to calculate the photostationary state.

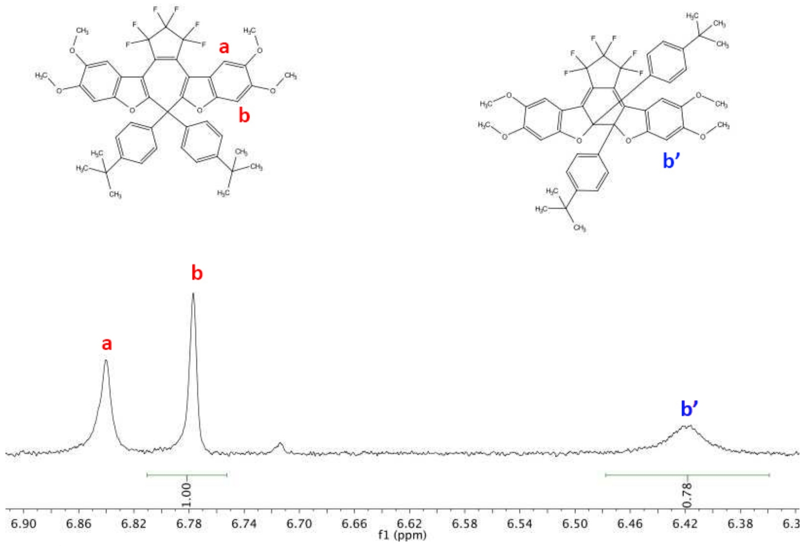


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of the photostationary state of **1*o*/1*c***.

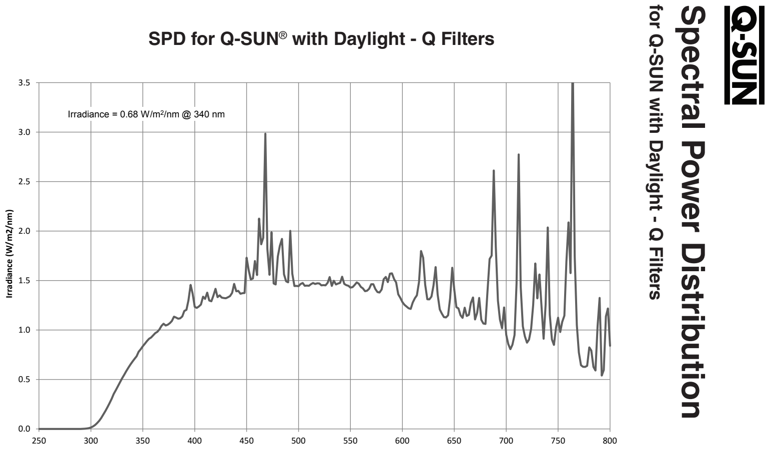


Figure S4. Emission spectrum of Q-Labs Q-SUN xenon arc lamp used for all solar

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[2] Samples were irradiated using the light source from a lamp used for visualizing TLC plates at 365 nm (Spectroline E-series, 0.12 W/cm^2).

weathering experiments.

Weathering of 1*o*. A Rhodiasolv® IRIS solution of compound **1*o*** (7.5 mM, 10 mL) was injected into a glass weathering cell using a syringe fitted with a polypropylene dispensing tip (Nordson EFD 7018391) through one of the two fill ports. Care was taken to ensure that a leak-free seal was maintained between the fill port and the dispensing tip and that constant pressure was used to deliver the solution to the cell. Once filled, the fill/exit ports were plugged with a PTFE (polytetrafluoroethylene) sphere (purchased from McMaster-Carr), covered with a Kalrez disc (purchased from McMaster-Carr) and clamped in place using custom machined clamps. The cell was placed in a Q-Labs QSUN Xe-3-HS xenon arc weatherometer at 82 °C with an irradiance of 0.68 W/m^2 at 340 nm for 69 hours, at which time a significant colour change was observed (Figure S5). The solution was removed from the cell using a syringe and an auto-pipette tip and was mixed with 10 g of silica gel (300 mesh), and the solvent in this mixture was removed by rotary evaporator. Purification using the Teledyne ISCO CombiFlash Purification System (15% EtOAc:hexanes) afforded **2*o*** as orange crystals and **3** as yellow crystals.

Figure S5. Photos showing the glass weathering cell filled with a solution of **1*o*** in Rhodiasolv® Iris (a) before weathering, (b) after being exposed to stimulated sunlight (emitted from the Q-Labs QSUN Xe-3-HS xenon arc lamp) for 30 min, and (c) after weathering for 69 hours.

Comparative weathering of compounds 1*o*, 12 and 13. Rhodiasolv® IRIS solutions of compound **1*o***, **12** and **13** (7.5 mM, 0.5 mL each) were injected into small glass weathering cells[3] using a syringe fitted with a polypropylene dispensing tip (Nordson EFD 7018391) through one of the two fill ports. Care was taken to ensure that a leak-free seal was maintained between the fill port and the dispensing tip and that constant pressure was used to deliver the solution to the cells. Once filled, the fill/exit ports were plugged with a PTFE (polytetrafluoroethylene) sphere (purchased from McMaster-Carr), covered with a Kalrez disc (purchased from McMaster-Carr) and clamped in place using custom machined clamps. The cells were placed in a Q-Labs QSUN Xe-3-HS xenon arc weatherometer at 82 °C with an irradiance of 0.68 W/m^2 at 340 nm for 10 hours, at which time an aliquot (10 μL) of weathered solutions were removed from each cell through the filling port and diluted in 1 mL LC-MS grade acetonitrile. The diluted samples were transferred to a Agilent LC-MS vial and submitted for LC-MS examination.

Compound 2*o*. ^{1}H NMR (600 MHz, DMSO-d_6, 373K[4]) δ 7.31 (m, 4H), 7.15 (m, 5H), 6.99 (d, J = 7.9 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 3.80 (s, 3H), 3.21 (s, 3H), 1.25 (s, 3H), 0.98 (s,

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[3] The small glass cell were fabricated using the same procedure as for the large ones, except the size of the small cell is 75 mm × 50 mm × 3 mm.

[4] The ^{1}H NMR spectrum was acquired at 100 °C because the proton signals were broad and not well resolved at ambient temperature in all common solvents.

3H).
^{13}C NMR (150 MHz, CD_2Cl_2) δ 152.3, 151.9, 149.2, 148.7, 148.2, 147.9, 147.4, 145.8, 139.0, 126.5, 126.2, 126.1, 126.0, 125.2, 124.6, 117.6, 117.2, 117.0 (t, $J_{C,F}$ = 22.5 Hz), 115.2 (t, $J_{C,F}$ = 22.5 Hz), 113.5 (t, $J_{C,F}$ = 22.5 and 24 Hz)[5], 109.0 (t, $J_{C,F}$ = 22.5, 24.0 Hz)[4], 107.2 (t, $J_{C,F}$ = 24 Hz) 105.4 (t, $J_{C,F}$ = 22.5, 24.0 Hz)[4], 102.0, 100.5, 94.9, 94.4, 55.8, 55.7, 55.5, 54.4, 34.1, 33.8, 30.3, 29.8, 29.2.
HRMS ($M+Na^+$) expected: 793.2764; found: 793.2734.

Compound 3. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.40 (dd, J = 8.7, 0.7 Hz, 1H), 8.33 (s, 1H), 7.86 (dd, J = 8.8, 1.7 Hz, 1H), 7.61 (s, 1H), 7.40 (s, 1H), 7.38 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 6.82 (s, 1H), 4.05 (s, 3H), 4.03 (s, 3H), 4.00 (s, 3H), 3.92 (s, 3H), 1.54 (s, 9H), 1.18 (s, 9H).
^{13}C NMR (150 MHz, CD_2Cl_2) δ 158.1, 155.6, 154.6, 153.6, 151.7, 150.7, 150.6, 144.9, 144.6, 144.4, 141.3, 133.1 (t, $J_{C,F}$ = 7.5 Hz), 127.4, 125.6, 124.8, 124.6, 123.4, 120.6, 119.4, 118.8, 118.2, 118.0, 116.1, 116.0, 113.0, 112.7, 111.8, 107.2 (t, $J_{C,F}$ = 7.5 Hz, 9.0 Hz)[4], 96.0, 94.0, 61.3, 55.9, 55.8, 55.7, 34.7, 33.7, 30.4, 30.3, 29.2.
HRMS ($M+H^+$) expected: 753.2839; found: 753.2826.

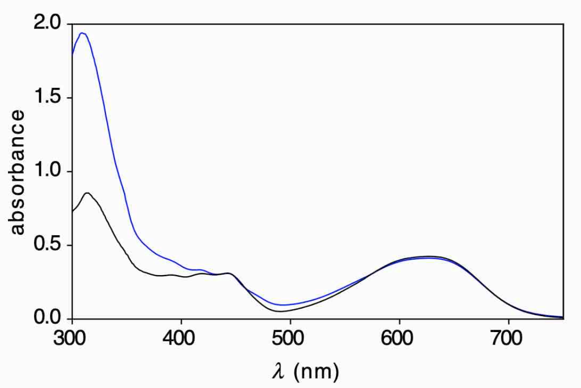

Figure S6. The UV-vis absorption spectrum that results when an aliquot solution of **1*o*** in Rhodiasolv® IRIS (trade name for dimethyl 2-methylglutarate) in a thin glass weathering cell is irradiated with simulated sunlight for 69 hours (blue line). The spectrum was acquired by diluting an aliquot amount of the solution with *n*-hexane. The sum of the UV-vis absorption spectra of isolated **2*o*** (2.85×10^{-5} M multiplied by 1.5) and isolated **3** (6.42×10^{-5} M divided by 5.6) is shown as the black line.

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[5] The splitting of this signal was expected to be a perfect triplet. However, the spectrum showed a slightly distorted triplet, from which the two coupling constants were calculated.

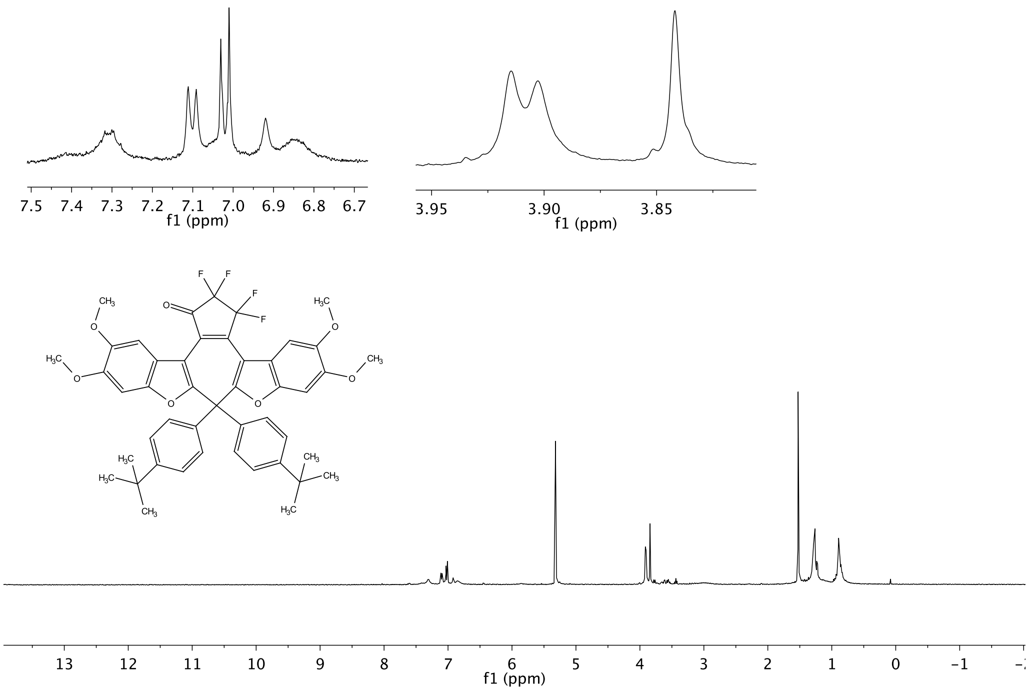


Figure S7. ^{1}H NMR of compound **2*o*** in CD_2Cl_2 at 298 K.

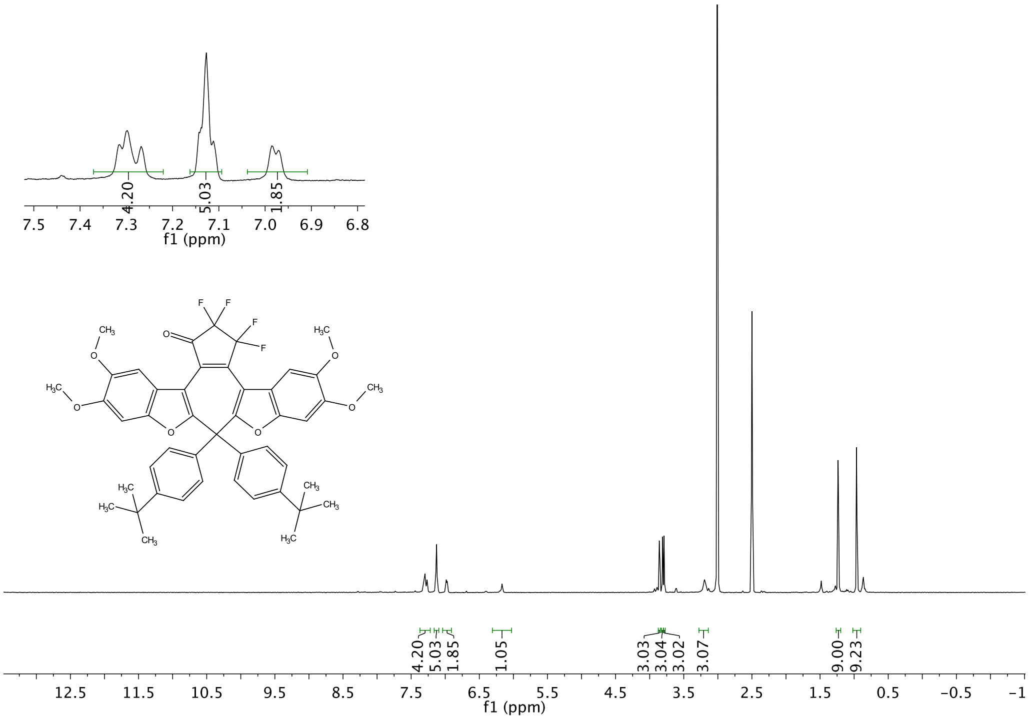


Figure S8. ^{1}H NMR of compound **2*o*** in DMSO-d_6 at 373 K.

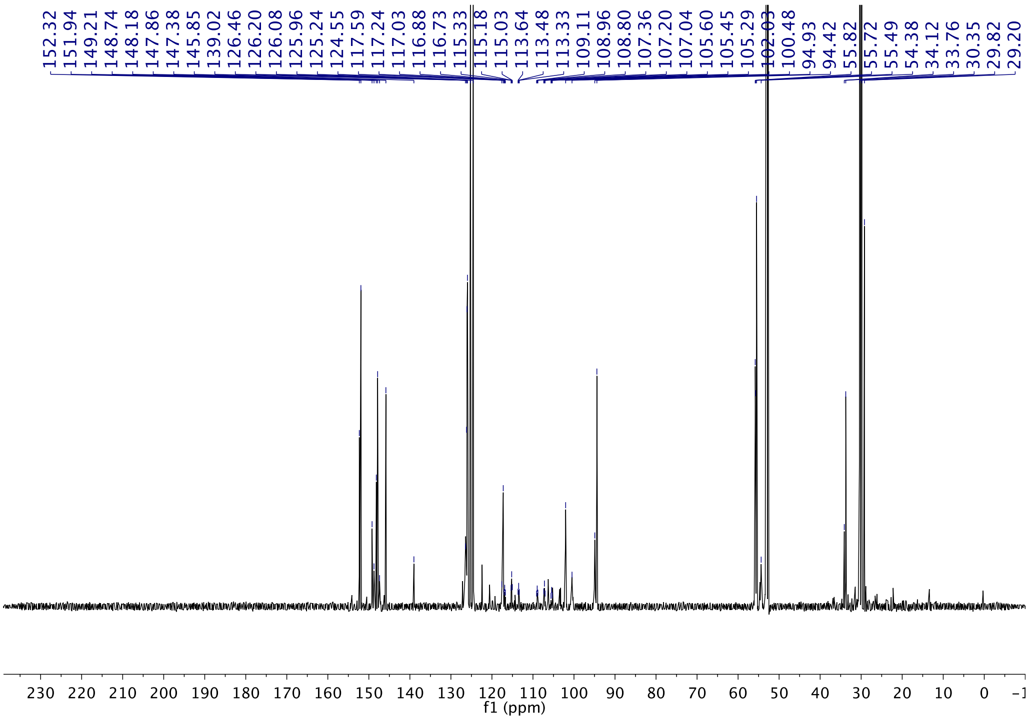


Figure S9. ^{13}C NMR of compound **2*o*** in CD_2Cl_2 at 298 K.

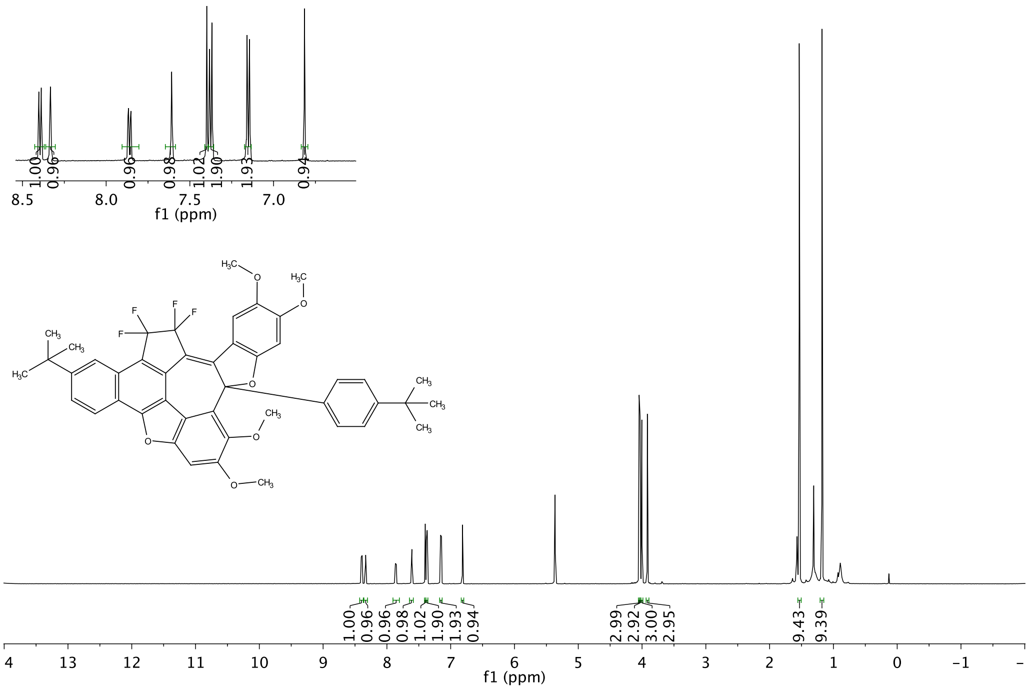


Figure S10. ^{1}H NMR of compound **3** in CD_2Cl_2 at 298 K.

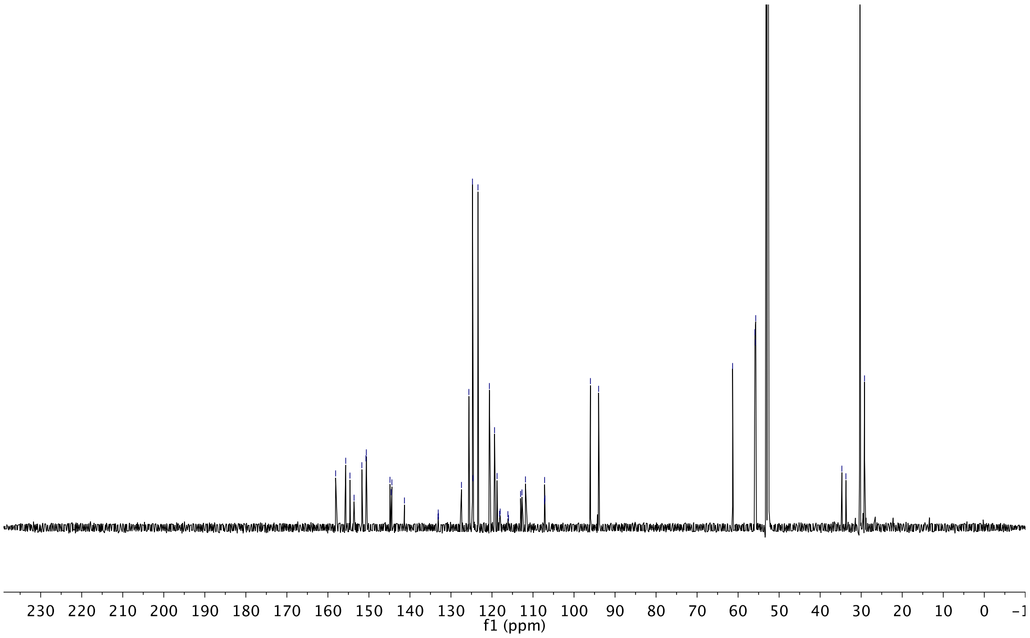


Figure S11. ^{13}C NMR of compound **3** in CD_2Cl_2 at 298 K.

Single crystal X-ray diffraction of compounds 2*o* and 3. Single crystals of appropriate quality for XRD analysis were grown by gently adding MeOH (5 mL) on top of solutions of **2*o*** or **3** (10 mg) in $CHCl_3$ (3 mL) in 20 mL scintillation vials. The vials containing these two-layer solvent systems were inserted into a sand bath to minimize environmental disturbance and were stored in a fume hood in the dark for 24 h. Single crystals of **2*o*** or **3** were observed on the bottom of the vials. The solvent was decanted and the crystals were gently washed with MeOH (3 mL) and dried in a Schlenk line. Suitable crystals were mounted on a 150 μm MiTeGen Dual-Thickness MicroMount using paraffin oil and data collected at 150 K for **2*o*** and 296 K for **3** under nitrogen atmosphere. The data was collected using a Bruker SMART APEX II Duo CCD diffractometer with TRIUMPH graphite- monochromated MoKα radiation (λ = 0.71073 Å). The data for each XRD experiment are shown in Table S1, and the structures in Figure S12.

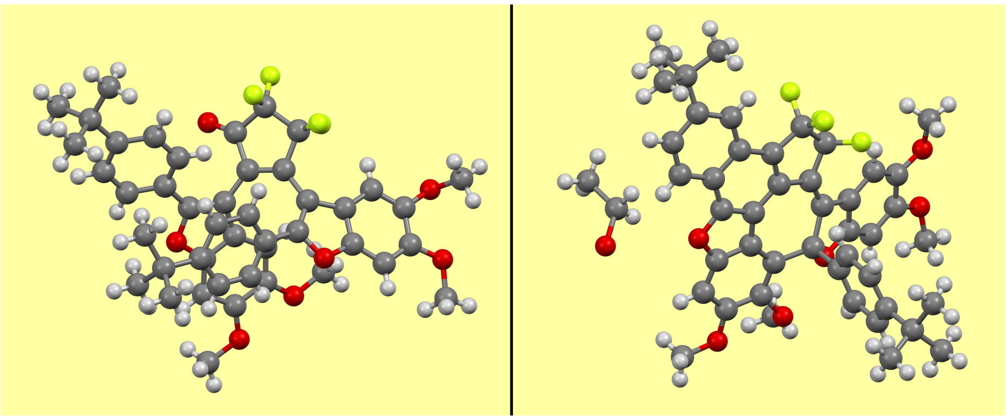
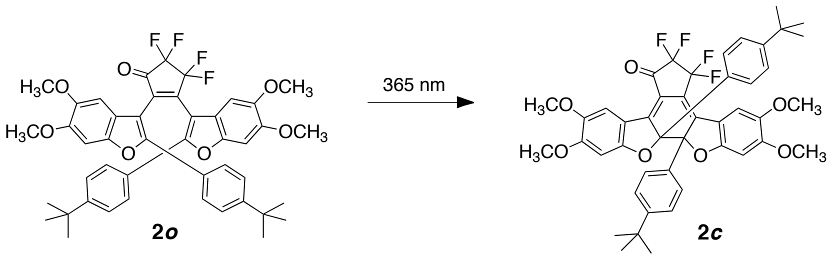


Figure S12. Structures obtained from the single crystal XRD analysis of **2*o*** (left) and **3** (right).

Table S1. Crystallographic Information (SCXRD):

	2o	**3**
empirical formula	$C_{45}H_{42}F_4O_7$	$C_{45}H_{40}F_4O_6$
formula weight (g mol^{-1})	770.78	752.80
crystal dimensions (mm)	0.142, 0.244, 0.316	0.163, 0.205, 0.406
crystal system	monoclinic	Triclinic
space group	C2/c	P-1
a (Å)	15.1446(14)	11.4709(17)
b (Å)	24.455(2)	13.897(2)
c (Å)	20.982(3)	14.895(2)
α (deg)	90	107.986(4)
β (deg)	93.450(3)	112.427(4)
γ (deg)	90	96.387(5)
V (Å^3)	7756.9(15)	2015.4(5)
Z	8	2
T (K)	150(2)	296(2)
ρ_{calcd} (g cm^{-3})	1.320	1.315
μ (mm)	0.101	0.099
$2\theta_{\text{max}}$ (deg.)	25.383	28.283
total/unique reflections	7123/5517	10011/ 5865
obsd reflns [$I_0 \geq 2\sigma(I_0)$]	5517	5865
R_1, wR_2 [$I_0 \geq 2\sigma(I_0)$]^a	0.0493, 0.1290	0.0777, 0.2288
GOF	1.041	1.082
largest difference peak/hole (e$^-$/ Å^3)	0.547/-0.488	0.734/-0.502
CCDC Number	1903676	1903677



Photoconversion of 2*o* to 2*c* and isolation of 2*c*. A solution of **2*o*** (10 mg) in *n*-hexane (20 mL) in a 50 mL round bottom flask equipped with a magnetic stir bar was bubbled with nitrogen for 20 minutes, and then irradiated with 365 nm UV light (0.12 W/cm^2) for 1 h. The solvent was removed by rotary evaporator and the remaining **2*o*/2*c*** mixture was dissolved in 5 mL dichloromethane and mixed with 1 g of silica gel (300 mesh). After removal of solvent with rotary evaporator, the mixture was purified by column chromatography (1:10 v/v

EtOAc:hexanes) to afford 5.3 mg (53%) of **2*c*** as dark blue coloured solid.[6]

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.03 (s, 1H), 7.61 (dd, *J* = 8.5, 6.0 Hz, 4H), 7.30 (dd, *J* = 8.7, 7.0 Hz, 4H), 7.09 (s, 1H), 6.44 (d, *J* = 6.7 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 1.24 (s, 9H), 1.22 (s, 9H).

HRMS (M+Na$^+$) expected: 793.2764; found: 793.2717.

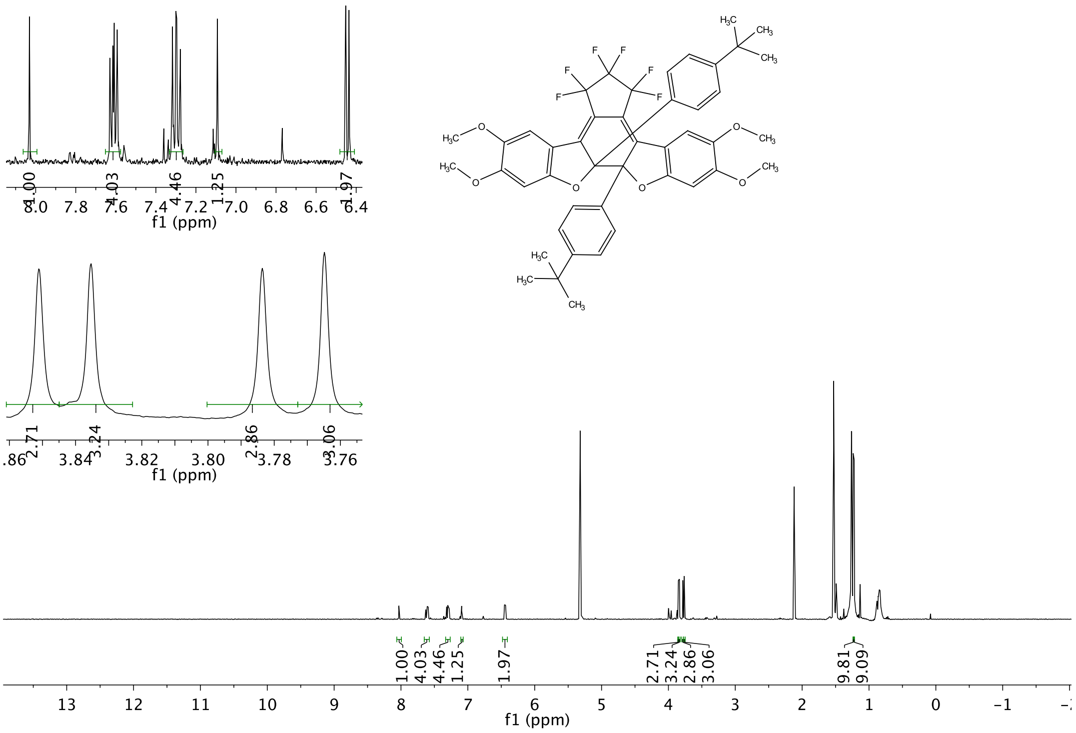


Figure S13. ^{1}H NMR of **2c** in CD_2Cl_2 at 298 K.

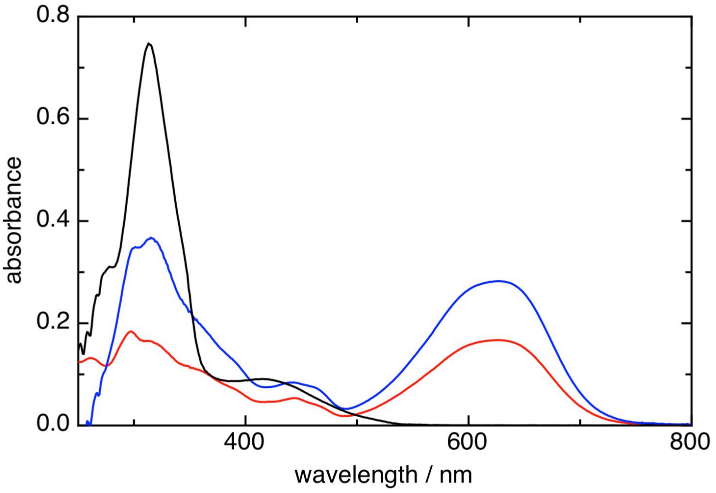


Figure S14. UV-vis absorption spectra of **2*o*** (2.85 × 10^{-5} M, black trace) in *n*-hexane), the photostationary state (blue trace) containing both **2*o*** and **2*c*** generated by irradiating **2*o*** with 365 nm UV light, and isolated **2*c*** (4.28 × 10^{-5} M, red trace) in *n*-hexane.

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[6] Only the middle fractions of the **2*c*** during column chromatography was collected, therefore the isolation yield does not reflect the **2*c*** percent at the photostationary state. The **2*c*** percent at the photostationary state was calculated based on UV-Vis spectra.

Estimation of the photostationary state (PSS) of 2*o*/2*c*. The estimation of the amount of **2*c*** in at the PSS was calculated according to Figure S12 and Beer's law as shown in Table S2. The PSS is defined as [**2c**]/([**2o**]+[**2c**]).

Table S2. Estimation of the photostationary state (PSS) of 2o/2c.

absorption of **2o** at 313 nm $A_{2o@313}$	= 0.74762	
concentration of **2o** (M)	= 2.85×10^{-5}	
$\varepsilon_{2o@313}$ ($cm^{-1}mol^{-1}$)	= $0.74762 / (2.85 \times 10^{-5} \times 1)$	= 26232
absorption of **2c** at 313 nm $A_{2o@313}$	= 0.16554	
concentration of **2c** (M)	= 4.28×10^{-5}	
$\varepsilon_{2c@313}$ ($cm^{-1}mol^{-1}$)	= $0.16554 / (4.28 \times 10^{-5} \times 0.5)$	= 7736
at the PSS		
absorption of **2o** and **2c** at PSS at 313 nm $A_{PSS@313}$	= 0.36463	
following Beer's law	$A_{PSS@313} = \varepsilon_{2o@313} \times 1 \times C_{2o} + \varepsilon_{2c@313} \times l \times C_{2c}$	
where	$C_{2o} + C_{2c}$	= 2.85×10^{-5}M
solution to the equation		
C_{2o}	= 0.82×10^{-5}M	
C_{2c}	= 2.85×10^{-5}M - 0.82×10^{-5}M	= 2.03×10^{-5}M
PSS	= 2.03×10^{-5}M / 2.85×10^{-5}M	= 71.2%

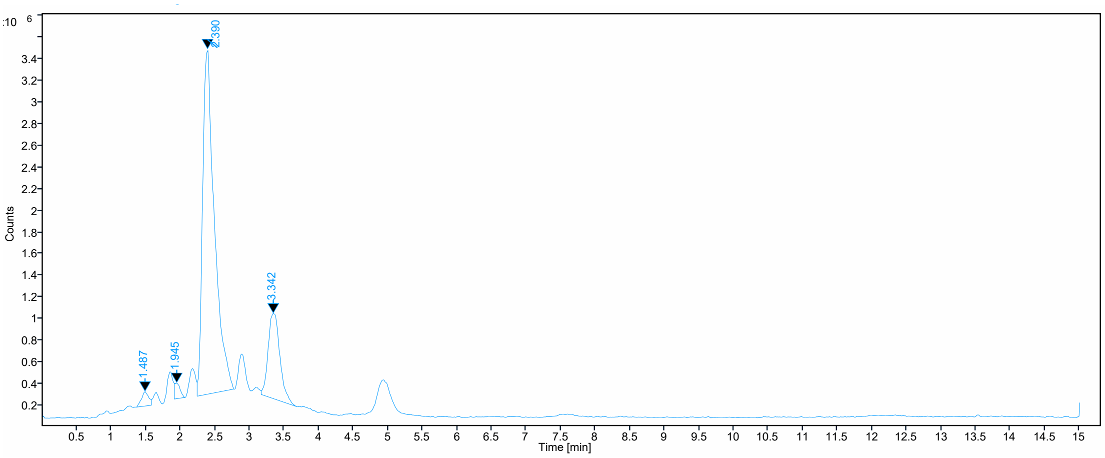
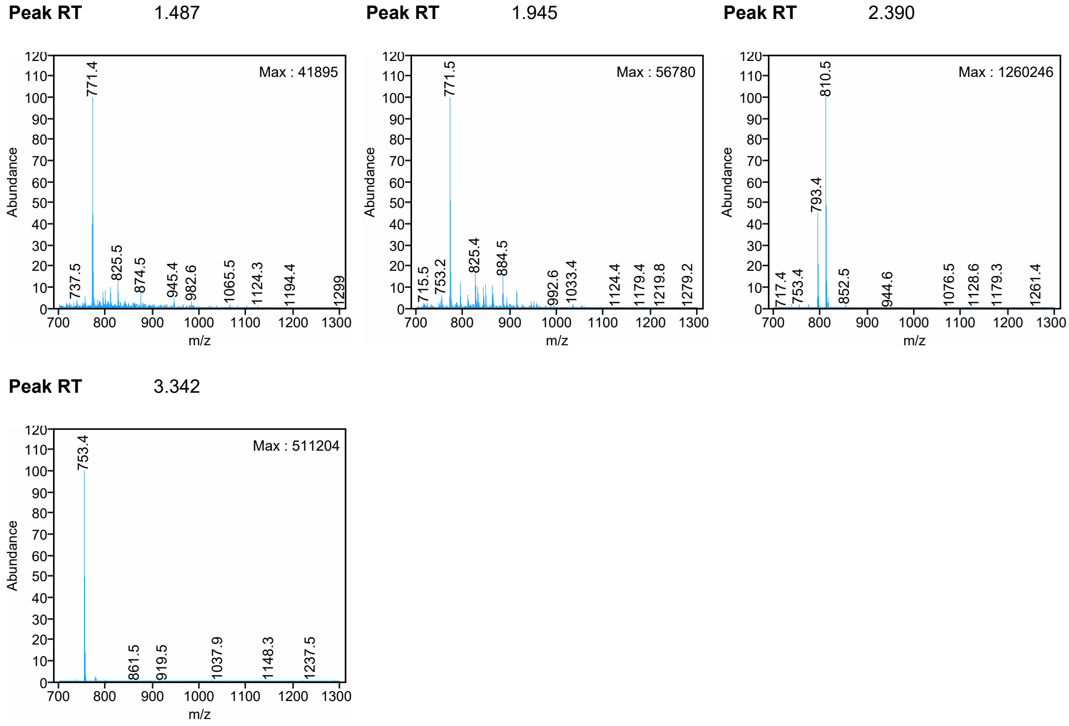


Figure S15. LC-MS chromatogram (MS channel) showing the results of weathering **1*o*** (at 2.390 min) in a small weathering cell. The ketone product appears at 1.467 min for **2*o*** and 1.945 min for **2*c***. The seven-membered ring product **3** appears at 3.342 min.



Signal: MS1 +TIC SCAN ESI Frag=135V

RT [min]	Name	Area	Area%	Max Peak%	Height	Type	Width (50%)
1.487		955936.8360	1.9564	2.530	133109.188	BV	
1.945		801254.0905	1.6398	2.120	144737.144	MB m	
2.390		37786471.8303	77.3336	100.000	3184743.575	VM m	
3.342		9317980.0702	19.0701	24.660	785938.810	VB	
	Sum	48861642.8269					

Figure S16. The corresponding mass measurements for LC-MS chromatogram (MS channel) showing the results of weathering **1*o***.

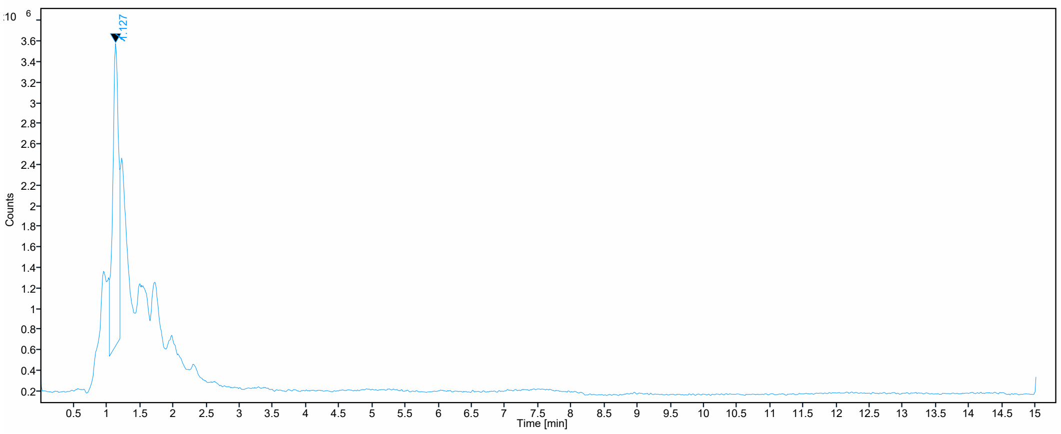
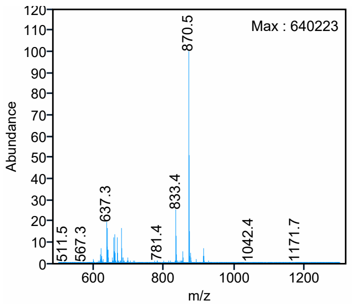


Figure S17. LC-MS chromatogram (MS channel) showing the results of weathering **11** in a small weathering cell. The ketone product appears at 1.127 minute (both isomers).

Peak RT 1.127



Signal: MS1 +TIC SCAN ESI Frag=135V

RT [min]	Name	Area	Area%	Max Peak%	Height	Type	Width (50%)
1.127		18113338.7349	100.0000	100.000	2941222.174	VV	
	Sum	18113338.7349					

Figure S18. The corresponding mass measurement for LC-MS chromatogram (MS channel) showing the results of weathering **11**.

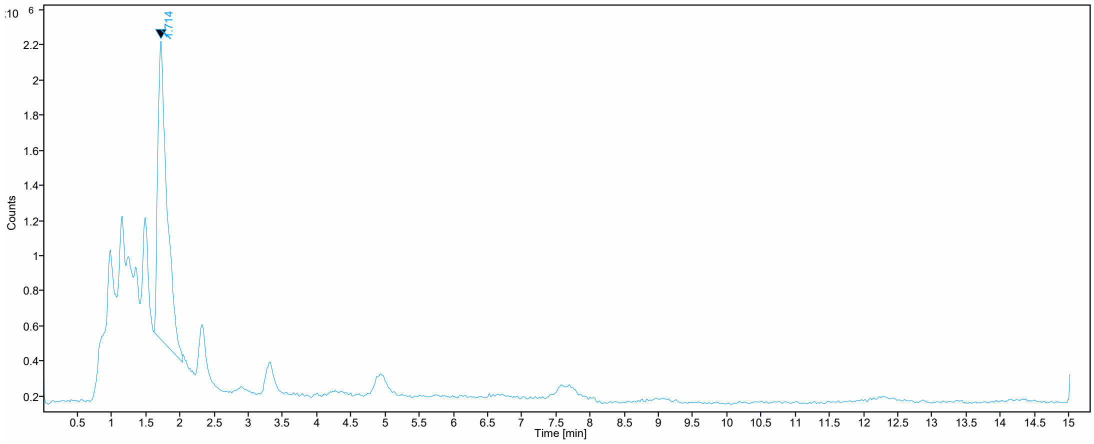
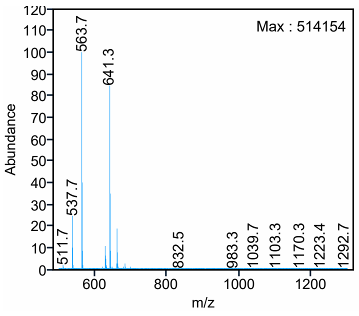


Figure S19. LC-MS chromatogram (MS channel) showing the results of weathering **10** in a small weathering cell. The seven-membered ring product of **10** appears at 1.714 min.

Signal MS1 +TIC SCAN ESI Frag=135V

Peak RT 1.714



Signal: MS1 +TIC SCAN ESI Frag=135V

RT [min]	Name	Area	Area%	Max Peak%	Height	Type	Width (50%)
1.714		16071549.8354	100.0000	100.000	1708558.267	BV	
	Sum	16071549.8354					

Figure S20. The corresponding mass measurement for LC-MS chromatogram (MS channel) showing the results of weathering **10**.