Electronic Supplementary Information (ESI) for

Highly Efficient and Regiospecifical Photocyclization of

2,2'-Diacylbixanthenylidenes

Mao Mao, Qing-Qing Wu, Ming-Guang Ren, Qin-Hua Song*

Department of Chemistry, Joint Laboratory of Green Synthetic Chemistry, University of Science and Technology of China, Hefei 230026, China

<u>qhsong@ustc.edu.cn</u> (Q.-H. Song)

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I. Synthesis and Characterization Data of New Compounds

2-Fluoroxanthone (4b): *p*-Fluorophenol (1.29 g, 11.5 mmol), *o*-chlorobenzoic acid (1.80 g, 11.5 mmol), K₂CO₃ (2.29 g, 16.6 mmol), Cu powder (200 mg) and CuI (200 mg) were added into anisole (20 mL), and stirred at reflux temperature for 5h under nitrogen protection. After cooling, the solvent was removed in vacuo, and concentrated H₂SO₄ (10 mL, 98%) was added, and then the mixture was stirred for 1h at room temperature. The reaction was terminated by pouring the mixture into cold water (~100 mL). The crude product was extracted with chloroform (3×50 mL) and the insoluble was removed by filtering. The combined organic layers were dried with MgSO₄, and concentrated in vacuo. The resulting residue was then purified by chromatography on silica gel with CH₂Cl₂ as the eluent to give **4b** as white solid (1.75 g, 71%). $R_f = 0.40$ (petroleum ether/ethyl acetate 15:1); m.p. 286-287°C; ¹H NMR (300 MHz, CDCl₃): δ 8.34 (dd, J = 8.0, 1.7 Hz, 1H; H_{Ar}), 7.98 (dd, J = 8.2, 2.9 Hz, 1H; H_{Ar}), 7.78-7.72 (m, 1H; H_{Ar}), 7.54-7.38 (m, 4H; H_{Ar}); ¹³C NMR (75 MH_z, CDCl₃): δ 160.3, 157.0, 156.0, 135.0, 126.6, 124.1, 123.0, 122.7, 120.0, 119.9, 117.9, 111.5, 111.2; IR (KBr, cm⁻¹): 1664 (s), 1612 (m), 1319 (s), 1261 (m), 1136 (m), 868 (m), 825 (m), 757 (m); TOFMS (EI): calcd for (M⁺) C₁₃H₇FO₂: 214.0430, found = 214.0433.

2-Methoxyxanthone (4d): Synthesis from *p*-methoxyphenol (1.43 g, 11.5 mmol) by the same procedure, purification of **4d** was performed with chromatography on silica gel with petroleum ether/ethyl acetate (6:1) as the eluent to give **4d** as white solid (1.69 g, 65%). $R_f = 0.29$ (petroleum ether/ethyl acetate 15:1); m.p. 129-130°C; ¹H NMR (300 MHz, CDCl₃): δ 8.36 (dd, J = 7.8, 0.9 Hz, 1H; H_{Ar}), 7.74-7.69 (m, 2H; H_{Ar}), 7.51-7.31 (m, 4H; H_{Ar}), 3.93 (s, 3H; CH₃); ¹³C NMR (75 MH_Z, CDCl₃): δ 156.0, 134.5, 126.7, 124.8, 123.7, 121.3, 119.4, 118.0, 105.9, 55.9 (CH₃); IR (KBr, cm⁻¹): 1650 (s), 1617 (s), 1490 (s), 1467 (s), 1318 (s), 1212 (m), 1143 (m), 1025 (m), 777 (m); TOFMS (EI) calcd for (M⁺) C₁₄H₁₀O₃: 226.0630, found = 226.0625.

2-Ethylxanthone (**4e**): Synthesis from *p*-ethylphenol (1.40 g, 11.5 mmol) by the same procedure, the residue was subjected to chromatography on silica gel with petroleum ether/ethyl acetate (10:1)

as the eluent to yield **4e** as white solid (1.60 g, 62%). $R_f = 0.43$ (petroleum ether/ethyl acetate 15:1); m.p. 72-73°C; ¹H NMR (300 MHz, CDCl₃): δ 8.35 (dd, J = 7.9, 1.5 Hz, 1H; H_{Ar}), 8.16 (d, J = 1.8 Hz, 1H; H_{Ar}), 7.75-7070 (m, 1H; H_{Ar}), 7.58 (dd, J = 8.6, 2.3 Hz, 1H; H_{Ar}), 7.51-7.35 (m, 3H; H_{Ar}), 2.78 (q, J = 7.5 Hz, 2H; CH₂), 1.31 (t, J = 7.5 Hz, 3H; CH₃); ¹³C NMR (75 MH_z, CDCl₃): δ 176.9 (C=O), 155.7, 154.1, 139.6, 134.7, 134.2, 126.3, 124.4, 123.3, 121.4, 121.1, 117.6, 117.5, 27.9 (CH₂), 15.2 (CH₃); IR (KBr, cm⁻¹): 2963 (w), 1661 (s), 1609 (s), 1492 (s), 1466 (s), 1322 (s), 1219 (s), 1145 (m), 1121 (m), 756 (s); TOFMS (EI) calcd for (M⁺) C₁₅H₁₂O₂: 224.0837, found = 224.0834.

Xanthone-2-carbonitrile (4f): Under nitrogen protecting, 2-bromoxanthone (0.27 g, 1.0 mmol), CuCN (0.36 g, 4mmol) were refluxed for 8 h in DMF (5 mL). After cooling, the mixture was poured to CH₂Cl₂ (50 mL) and 1,2-ethylenediamine (5 mL). The organic layers was washed by water and dried (MgSO₄), and concentrated in vacuo. The residue was subjected to chromatography on silica gel with CH₂Cl₂ as the eluent to yield **4f** as white solid (0.20 g, 90%). $R_f = 0.33$ (petroleum ether/CH₂Cl₂ 1:2); m.p. 217-219°C; ¹H NMR (300 MHz, CDCl₃): δ 8.67 (d, J = 1.8 Hz, 1H; H_{Ar}), 8.34 (dd, J = 8.0, 1.7 Hz, 1H; H_{Ar}), 7.94 (dd, J = 8.7, 2.1 Hz, 1H; H_{Ar}), 7.83-7.77 (m, 1H; H_{Ar}), 7.61 (d, J = 8.7 Hz, 1H; H_{Ar}), 7.54 (d, J = 8.4 Hz, 1H; H_{Ar}), 7.49-7.44 (m, 1H; H_{Ar}); ¹³C NMR (100 MHz, CDCl₃): $\delta = 175.4$ (C=O), 158.0, 155.9, 136.9, 135.8, 132.3, 126.9, 125.1, 122.2, 121.6, 119.7, 118.2, 117.7, 108.1; IR (KBr, cm⁻¹): 2231 (s), 1669 (s), 1609 (s), 1489 (s), 1463 (s), 1318 (s), 1238 (m), 755 (s); TOFMS (EI) calcd for (M⁺) C₁₄H₇NO₂: 221.0469, found = 221.0477.

2-Acetylxanthone (4g): To a solution of 2-(1-hydroxyethyl)-xanthone (0.48 g, 2.0 mmol) in CH₂Cl₂ (20 mL) under a nitrogen atmosphere was added manganese dioxide (1.74 g, 20.0 mmol) in portions. After the suspension was refluxed for 2 days, the black solid was removed by filtration. The filtrate was evaporated under reduced pressure, and the crude product was purified by chromatography on silica gel (CH₂Cl₂) to afford **4g** as a white solid (0.43 g, 90%). $R_f = 0.12$ (petroleum ether/CH₂Cl₂ 1:4); m.p. 204-205°C; ¹H NMR (300 MHz, CDCl₃): δ 8.89 (d, J = 2.4 Hz, 1H; H_{Ar}), 8.38-8.34 (m, 2H; H_{Ar}), 7.79-7.73 (m, 1H, H_{Ar}), 7.57-7.51 (m, 2H; H_{Ar}), 7.45-7.40 (m, 1H;

 H_{Ar}), 2.71 (s, 3H; COCH₃); ¹³C NMR (75 MH_Z, CDCl₃): δ = 196.3 (COCH₃), 176.6 (C=O), 158.8, 155.9, 135.3, 133.8, 132.9, 128.3, 126.8, 124.6, 121.7, 121.2, 118.8, 118.1, 26.6 (CH₃); IR (KBr, cm⁻¹): 1678 (s), 1670 (s), 1604 (s), 1466 (s), 1427 (m), 1367 (m), 1256 (s), 761 (m); TOFMS (EI) calcd for (M⁺) C₁₅H₁₀O₃: 238.0630, found = 238.0621.

Xanthone-2-carboxylic acid (4h): 2-(4-Ethylphenoxy)benzoic acid (3.00 g, 12.4 mmol) was stirred with 180 ml of water and KMnO₄ (9.00 g) was added in portions, and refluxed for 8h. After treatment with dilute potassium hydroxide solution and extraction with ether, organic phase was acidified by introducing sulfur dioxide. The product was separated as white fluffy crystals **3h** (2.88 g, 90%). **3h** (1.29 g, 5.0 mmol) are heated with 21 g polyphosphoric acid to 180°C. After reacting for 4 h, 50 mL ice-water was added into the mixture when it cooled down to room temp. After stirring overnight the precipitate was collected, washed with water and crystallized from ethanol. **4h** (1.02 g, 85%) was obtained as a white powder. $R_f = 0.29$ (CH₂Cl₂/THF 5:1); m.p. 298-300°C; ¹H NMR (300 MHz, [D₆]DMSO): δ 13.32 (s, 1H; COOH), 8.75 (d, J = 1.8 Hz, 1H; H_{Ar}), 8.37 (dd, J = 8.7, 1.8 Hz, 1H; H_{Ar}), 8.23 (d, J = 7.8Hz, 1H; H_{Ar}), 7.96-7.90 (m, 1H; H_{Ar}), 7.79-7.71 (m, 2H; H_{Ar}), 7.53 (m, 1H; H_{Ar}); ¹³C NMR (75 MHZ, [D₆]DMSO): δ 175.9 (C=O), 166.5 (CO₂H), 158.3, 155.8, 136.2, 135.8, 128.2, 127.1, 126.4, 125.2, 121.4, 121.1, 119.1, 118.6; IR (KBr, cm⁻¹): 3072 (br), 1703 (s), 1669 (s), 1613 (s), 1467(s), 1425 (s), 1301 (s), 1132 (m), 754 (m); TOFMS (EI) calcd for (M⁺) C₁₄H₈O₄: 240.0423, found = 240.0431.

Xanthone-2-carboxylic acid methyl ester (4i): **4h** (0.24 g, 1.0 mmol) were suspended in 10 mL CH₃OH and cooled to 0°C. Thionyl chloride was added portionwise through a septum, and stirred for 20 min at room temperature, then refluxed about 2 h. After cooling, the solvent was removed in vacuo. Separation of flash column chromatography (CH₂Cl₂) afforded **4i** (0.24 g, 95%). $R_f = 0.16$ (petroleum ether/CH₂Cl₂ 2:3); m.p. 216-217°C; ¹H NMR (300 MHz, CDCl₃): δ 9.02 (d, J = 2.1 Hz, 1H; H_{Ar}), 8.40-8.33 (m, 2H; H_{Ar}), 7.76-7.69 (m, 1H; H_{Ar}), 7.57-7.51 (m, 2H, H_{Ar}), 7.45-7.42 (m, 1H; H_{Ar}), 3.97 (s, 3H; CH₃); ¹³C NMR (75 MH_z, CDCl₃): $\delta = 158.6$, 155.8, 135.2, 135.1, 129.2, 126.7, 125.9, 124.4, 121.7, 121.4, 118.3, 117.9, 52.2 (CH₃); IR (KBr, cm⁻¹): 1718 (s), 1663 (s), 1612 (s),

1467 (m), 1443 (m), 1283 (m), 1257 (s), 752 (m); TOFMS (EI) calcd for $(M^+) C_{15}H_{10}O_4$: 254.0579, found = 254.0577.

Xanthone-2-carboxylic acid diethylamide (4j): 4h (0.24 g, 1.0 mmol) are refluxed for 30 min with 5 mL thionyl chloride. After cooling, the excess of SOCl₂ was removed under reduced pressure and the residue was dissolved in freshly distilled CHCl₃ (5 mL). A solution of diethylamine (1mL) was added and the mixture was refluxed for 2 h. After cooling, the solution was concentrated in vacuo and the residue was extracted with ethyl ether, and filtered and concentrated in vacuo and the residue was dissolved and recrystallized in CH₃OH, giving **4j** as white solid (0.28 g, 96%). ¹H NMR (300 MHz, CDCl₃): δ 8.36-8.33 (m, 2H; H_{Ar}), 7.83-7.73 (m, 2 H; H_{Ar}), 7.57-7.51 (m, 2H; H_{Ar}), 7.44-7.39(m, 1H; H_{Ar}), 3.56-3.36 (br, 4H, CH₂), 1.22 (br, 6H; CH₃); ¹³C NMR (75 MH_z, CDCl₃): δ 176.6 (C=O), 169.7 (CON), 156.3, 156.0, 135.1, 133.5, 132.9, 126.6, 124.6, 124.2, 121.7, 121.2, 118.6, 118.0, 43.6 (CH₂), 39.5 (CH₂), 14.2 (CH₃), 12.9 (CH₃); IR (KBr, cm⁻¹): 2987 (w), 1654 (s), 1640 (s), 1465 (s), 1428 (s), 1267 (m), 1126 (m), 764 (s); TOFMS (EI) calcd for (M⁺) C₁₈H₁₇NO₃: 295.1208, found = 295.1204.

2,2'-Disubstituted bixanthenylidenes: synthesis procedures are method A for **1a–e**, and method B for **1f–1j**, respectively. Method A: xanthone (8.8 mmol) was refluxed overnight in oxalyl dichloride (10 mL). The excess of oxalyl dichloride was removed, and the residue was dissolved in freshly distilled *p*-xylene (30 mL). Activated Cu powder (3.81 g, 60.0 mmol) was added and refluxed for 7h with occasional shaking. The reaction solution was filtered, and the filter was concentrated and crystallized to give the target product. Method B: Under nitrogen, xanthone (10.0 mmol) in glacial AcOH (20 mL) was heated to 135–140°C, and zinc powder (1.20 g, 18.3 mmol) was added. The mixture was refluxed for 1h. A few drops of concentrated HCl were introduced from time to time (total amount, 2 mL). After the reaction mixture cooling, methanol (10 mL) was added, and the precipitating product was filtered and dried.

2,2'-Difluorobixanthenylidene (1b): Yield: 68%; $R_f = 0.67$ (petroleum ether/ethyl acetate 15:1); m.p. >250°C; UV/Vis (THF): λ_{max} (log ε) 370(4.2), 282(3.9), 253(4.1) nm; ¹H NMR (300 MHz, CDCl₃): δ 7.29-7.10 (m, 8H; H_{Ar}), 6.98-6.75 (m, 6H; H_{Ar}); ¹³C NMR (75 MH_Z, CDCl₃): δ 155.4, 129.1, 128.8, 128.0, 127.8, 122.8, 122.6, 121.4, 118.3, 117.3, 117.2, 115.7, 115.4, 114.2, 114.0, 113.9; IR (KBr, cm⁻¹): 1620 (m), 1589 (m), 1491 (s), 1470 (s), 1446 (s), 1428 (m), 1290 (m), 1239 (m), 1195 (s), 745 (m); TOFMS (EI) calcd for (M⁺) C₂₆H₁₄O₂F₂: 396.0962, found = 396.0966.

2,2'-Dimethoxybixanthenylidene (1d): Yield: 70%; $R_f = 0.57$ (petroleum ether/ethyl acetate 5:2); m.p. 266-268°C; UV/Vis (THF) $\lambda_{max}(\log \varepsilon)$: 380(4.3), 283(4.0), 235(4.5) nm; ¹H NMR (300 MHz, CDCl₃): δ 7.27-7.11 (m, 8H; H_{Ar}), 6.95-6.61 (m, 6H; H_{Ar}), 3.51 and 3.46 (2s, 6H; CH₃(*E*,*Z*)); ¹³C NMR (75 MH_Z, CDCl₃): δ 155.8, 155.6, 154.6, 154.5, 149.8, 149.6, 128.5, 128.3, 128.1, 125.2, 125.0, 124.6, 124.5, 122.3, 122.2, 121.4, 117.9, 117.1, 117.0, 116.3, 116.2, 111.5, 111.1, 55.4 (CH₃), 55.3 (CH₃); IR (KBr, cm⁻¹): 1619 (m), 1584 (m), 1567 (m), 1494 (s), 1471 (s), 1448 (s), 1206 (s), 1161 (s), 1043 (s), 766 (s); TOFMS (EI) calcd for (M⁺) C₂₈H₂₀O₄: 420.1362, found = 420.1356.

2,2'-Diethylbixanthenylidene (1e): Yield: 75%; $R_f = 0.76$ (petroleum ether/ethyl acetate 15:1); m.p. 260-262°C; UV/Vis (THF) $\lambda_{max}(\log \varepsilon)$: 369(4.2), 282(4.0), 253(4.1), 235(4.3) nm; ¹H NMR (300 MHz, CDCl₃): δ 7.27-7.13 (m, 8H; H_{Ar}), 7.06-6.85 (m, 6H; H_{Ar}), 2.42-2.36 (m, 4H; CH₂), 1.06–0.99 (m, 6H; CH₃); ¹³C NMR (75 MH_z, CDCl₃): δ 149.9, 147.9, 147.8, 132.4, 132.3, 122.4, 122.3, 122.2, 122.1, 121.5, 121.4, 119.3, 119.1, 118.9, 116.5, 115.6, 111.3, 111.0, 22.5 (CH₂), 22.4 (CH₂), 9.7 (CH₃), 9.5 (CH₃); IR (KBr, cm⁻¹): 1585 (m), 1493 (m), 1470 (s), 1445 (s), 1252 (s), 1237 (s), 1209 (s), 1126 (m), 772 (s); TOFMS (EI) calcd for (M⁺) C₃₀H₂₄O₂: 416.1776, found = 416.1769.

Bixanthenylidene 2,2'-dicarbonitrile (1f): Yield: 89%; $R_f = 0.42$ (petroleum ether/CH₂Cl₂ 1:2); m.p. >250°C; UV/Vis (THF) $\lambda_{max}(\log \varepsilon)$: 368(4.2), 293(4.0) nm; ¹H NMR (300 MHz, CDCl₃): δ 7.58-7.54 (m, 2H; H_{Ar}), 7.45-7.31(m, 7H; H_{Ar}), 7.26-6.99 (m, 5H; H_{Ar}); ¹³C NMR (75 MH_Z, CDCl₃): δ 158.4, 158.3, 154.7, 132.6, 132.5, 132.3, 131.9, 130.0, 129.5, 127.7, 127.2, 125.1, 124.9, 123.7, 123.5, 123.1, 122.7, 121.0, 120.9, 119.0, 118.7, 118.2, 117.8, 117.5, 106.7, 106.4; IR (KBr, cm⁻¹): 2230 (s), 1597 (m), 1470 s), 1446 (s), 1259 (s), 1240 (m), 837 (sm), 747 (m); TOFMS (EI) calcd for (M⁺) C₂₈H₁₄N₂O₂: 410.1055, found = 410.1056. **2**, **2'-Diacetylbixanthenylidene** (**1g**): Yield: 70%; $R_f = 0.16$ (petroleum ether/CH₂Cl₂ 1:4); m.p. 240-241°C; UV/Vis (THF): λ_{max} (log ε) 369 (4.2), 239 (4.7) nm; ¹H NMR (300 MHz, CDCl₃): δ 7.95-7.89 (m, 2H; H_{Ar}), 7.77-7.69 (m, 2H; H_{Ar}), 7.38-7.29 (m, 6H; H_{Ar}), 7.20-7.10 (m, 2H; H_{Ar}), 6.97-6.89 (m, 2H; H_{Ar}), 2.24 and 2.19 (2s, 6H; CH₃(*E*,*Z*)); ¹³C NMR (100 MH_z, CDCl₃): δ 195.4 (C=O), 195.0 (C=O), 157.9, 157.8, 154.0, 153.8, 130.8, 130.7, 128.6, 128.1, 128.0, 127.9, 127.6, 127.5, 126.8, 126.4, 122.9, 122.8, 122.6, 122.2, 122.1, 120.2, 120.2, 116.9, 116.8, 116.7, 116.3, 25.2 (CH₃), 25.0 (CH₃); IR (KBr, cm⁻¹): 1674 (s), 1596 (s), 1480 (s), 1452 (s), 1301 (m), 1282 (m), 1264 (s), 1204 (m), 1134 (m), 751 (s); TOFMS (EI) calcd for (M⁺) C₃₀H₂₀O₄: 444.1362, found = 444.1369.

Bixanthenylidene 2,2'-dicarboxylic acid (1h): Method B. Product **1h** (1.82 g, 81 %) was obtained from **4h** (2.38 g, 10.0 mmol). $R_f = 0.18$ (CH₂Cl₂/THF 5:1); m.p. >250 °C; UV/Vis (THF): $\lambda_{max}(\log \varepsilon)$ 368(4.1), 237(4.8) nm; ¹H NMR (300 MHz, [D₆]DMSO): δ 12.57 (br, 2H, COOH), 7.91-7.87 (m, 2H; H_{Ar}), 7.69-7.66 (m, 2H; H_{Ar}), 7.49-7.38 (m, 6H; H_{Ar}), 7.10-6.95 (m, 4H; H_{Ar}); ¹³C NMR (100 MH_z, [D₆]DMSO): δ 172.0 (C=O), 166.2 (C=O), 166.0, 157.8, 157.6, 154.3, 154.2, 130.1, 129.4, 129.2, 128.8, 127.5, 127.1, 125.4, 125.3, 123.7, 123.4, 123.3, 123.2, 123.1, 120.7, 120.6, 117.5, 117.3, 117.2; IR (KBr, cm⁻¹): 3075 (br), 1686 (s), 1599 (m), 1567 (m), 1300 (m), 1259 (s), 1152 (s), 1126 (s), 776 (m); TOFMS (EI) calcd for (M⁺) C₂₈H₁₆O₆: 448.0947, found = 448.0941.

Bixanthenylidene 2,2'-dicarboxylic acid methyl ester (1i): Yield: 85%; $R_f = 0.24$ (petroleum ether/CH₂Cl₂ 2:3); m.p. 272-274°C; UV/Vis (THF) $\lambda_{max}(\log \varepsilon)$: 369(4.2), 239(4.7) nm; ¹H NMR (300 MHz, CDCl₃): δ 7.97-7.92 (m, 2H; H_{Ar}), 7.86-7.80 (m, 2H; H_{Ar}), 7.34-7.25 (m, 6H; H_{Ar}), 7.15-7.06 (m, 2H; H_{Ar}), 6.94-6.85 (m, 2H; H_{Ar}), 3.78, 3.72 (2s, 6H; CH₃(*E*,*Z*)); ¹³C NMR (75 MH_{*Z*}, CDCl₃): δ 166.2 (C=O), 158.7, 155.1, 130.3, 130.1, 130.0, 129.8, 129.0, 128.2, 127.5, 124.7, 124.2, 123.7, 123.3, 123.2, 117.6, 117.5, 117.4, 52.1 (CH₃), 51.9 (CH₃); IR (KBr, cm⁻¹): 1722 (s), 1713 (s), 1600 (m), 1472 (m), 1447 (m), 1433 (m), 1296 (m), 1261 (s), 1222 (m), 773 (s); TOFMS (EI) calcd for (M⁺) C₃₀H₂₀O₆: 476.1260, found = 476.1262.

Bixanthenylidene 2, 2'-dicarboxylic acid diethylamide (1j): Yield: 62%; $R_f = 0.49$ (CH₂Cl₂/ethyl acetate 5:1); m.p. >250°C; UV/Vis (THF): λ_{max} (log ε) 367 (4.2), 236 (4.6) nm; ¹H NMR (300 MHz, CDCl₃): δ 7.34-7.16 (m, 12H; H_{Ar}), 6.96-6.88 (m, 2H; H_{Ar}), 3.29 (m, 8 H; CH₂), 1.06 (m, 12 H; CH₃); ¹³C NMR (75 MH_Z, CDCl₃): δ 170.2 (C=O), 156.0, 155.3, 131.7, 128.9, 128.0, 127.8, 127.2, 126.5, 124.6, 124.2, 123.1, 122.8, 121.4, 117.3, 43.1 (br, CH₂), 39.8 (br, CH₂), 13.5 (br, CH₃); IR (KBr, cm⁻¹): 2986 (w), 1624 (s), 1446 (s), 1379 (m), 1314 (m), 1292 (m), 1255 (s), 1207 (s), 1105 (m), 773 (m); TOFMS (EI) calcd for (M⁺) C₃₆H₃₄N₂O₄: 558.2519, found = 558.2516.

3,10-Difluoro-7,16-dioxa-dibenzo[a,o]perylene (**2b**(*E*)): $R_f = 0.68$ (petroleum ether/ethyl acetate 15:1); m.p. >250°C; UV/Vis (THF): λ_{max} (log ε) 447 (4.2), 425 (4.2), 453 (3.9), 337 (3.9), 298 (4.2), 251 (4.5) nm; ¹H NMR (300 MHz, CDCl₃): δ 8.48 (d, J = 8.4 Hz, 1H; H_{Ar}), 7.84 (d, J = 8.1 Hz, 1H; H_{Ar}), 7.55-7.50 (m, 2H; H_{Ar}), 7.31-7.14 (m, 6H; H_{Ar}), 7.00-6.96 (m, 2H; H_{Ar}); IR (KBr, cm⁻¹): 1743 (m), 1621 (m), 1496 (m), 1461 (s), 1378 (m), 1309 (m), 1261 (s), 1097 (s), 751 (m); TOFMS (EI) calcd for (M⁺) C₂₆H₁₂O₂F₂: 394.0805, found = 394.0804.

10,13-Difluoro-7,16-dioxa-dibenzo[a,o]perylene (**2b**(**Z**)): $R_f = 0.49$ (petroleum ether/ethyl acetate 15:1); m.p. >250°C; UV/Vis (THF): λ_{max} (log ε) 447 (4.2), 425 (4.2), 453 (4.0), 337 (3.9), 296 (4.2), 273 (4.3), 244 (4.5) nm; ¹H NMR (300 MHz, CDCl₃): δ 8.06 (d, J = 8.1 Hz, 2H; H_{Ar}), 7.61-7.57 (m, 2H; H_{Ar}), 7.53 (t, J = 8.0 Hz, 2H; H_{Ar}), 7.26-7.16(m, 4H; H_{Ar}), 7.05-6.98 (m, 2H; H_{Ar}); IR (KBr, cm⁻¹): 1739 (m), 1622 (s), 1593 (m), 1497 (m), 1478 (s), 1454 (s), 1260 (s), 1193 (m), 770 (m); TOFMS (EI) calcd for (M⁺) C₂₆H₁₂O₂F₂: 394.0805, found = 394.0810.

3,10-Dimethyl-7,16-dioxa-dibenzo[a,o]perylene (**2**c(*E*)): $R_f = 0.70$ (petroleum ether/ethyl acetate 15:1); m.p.>250°C; UV/Vis (THF): λ_{max} (log ε) 447 (4.2), 422 (4.2), 352 (4.0), 336 (3.9), 298 (4.2), 254 (4.5) nm; ¹H NMR (300 MHz, CDCl₃): δ 8.07 (d, J = 8.4 Hz, 1H; H_{Ar}), 7.84 (d, J = 7.8 Hz, 1H; H_{Ar}), 7.60 (s, 1H; H_{Ar}), 7.42 (t, J = 8.1 Hz, 1H; H_{Ar}), 7.32 (d, J = 8.1 Hz, 1H; H_{Ar}), 7.25-7.22 (m, 1H), 7.18-7.12 (m, 3H), 7.04 (m, 2H; H_{Ar}), 6.85 (td, J = 7.5, 0.8 Hz, 1H; H_{Ar}), 2.89(s, 3H; CH₃), 2.14 (s, 3H; CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 152.7, 150.6, 150.1, 148.5, 131.7, 131.1, 130.6, 130.4, 129.7, 129.1, 128.5, 127.6, 126.4, 125.7, 122.9, 122.7, 122.1, 121.6, 121.3,

118.2, 118.0, 117.0, 116.9, 112.1, 111.9, 25.2 (CH₃), 20.7 (CH₃); IR (KBr, cm⁻¹): 2957 (w), 1589 (s), 1564 (m), 1482 (s), 1453 (s), 1356 (m), 1267 (s), 752 (m); TOFMS (EI) calcd for (M⁺) $C_{28}H_{18}O_2$: 386.1307, found = 386.1277.

10,13-Dimethoxy-7,16-dioxa-dibenzo[a,o]perylene (**2c**(**Z**)): UV/Vis (THF): λ_{max} (log ε) 442 (4.2), 420 (4.2), 352 (4.0), 336 (3.9), 296 (4.2), 274 (4.7), 245 (4.5) nm; TOFMS (EI) calcd for (M⁺) C₂₈H₁₈O₂: 386.1307, found = 386.1313.

3,10-Dimethoxy-7,16-dioxa-dibenzo[a,o]perylene (**2d**(*E*)): $R_f = 0.45$ (petroleum ether/ethyl acetate 15:1); m.p. 227-229°C; UV/Vis (THF): λ_{max} (log ε) 455 (4.2), 433 (4.1), 366 (3.9), 350 (3.8), 310 (4.0), 232 (4.6) nm; ¹H NMR (300 MHz, CDCl₃): δ 8.94 (d, *J*= 8.1 Hz, 1H; H_{Ar}), 7.83 (d, *J* = 7.8 Hz, 1H; H_{Ar}), 7.45 (m, 1H; H_{Ar}), 7.30 (d, *J* = 2.7 Hz, 1H; H_{Ar}), 7.20-7.03 (m, 6H; H_{Ar}), 6.94-6.85 (m, 2H; H_{Ar}), 4.03 (s, 3H; CH₃), 3.53 (s, 3H; CH₃); ¹³C NMR (75 MH_z, CDCl₃): δ 154.7, 153.5, 153.2, 150.1, 147.4, 144.6, 129.8, 129.3, 128.4, 126.8, 122.1, 122.0, 119.4, 118.3, 118.1,117.2, 112.2, 112.0, 110.4, 109.7, 56.4 (CH₃), 55.6 (CH₃); IR (KBr, cm⁻¹): 2924 (w), 1615 (m), 1590 (m), 1483 (s), 1450 (s), 1421 (s), 1316 (s), 1252 (s), 1102 (m), 749 (m); TOFMS (EI) calcd for (M⁺) C₂₈H₁₈O₄: 418.1205, found = 418.1198.

10,13-Dimethoxy-7,16-dioxa-dibenzo[a,o]perylene (**2d**(**Z**)): UV/Vis (THF): λ (log ε) 454 (4.2), 432 (4.2), 366 (3.9), 350 (3.8), 300 (4.1), 276 (4.2), 249 (4.62) nm; TOFMS (EI) calcd for (M⁺) C₂₈H₁₈O₄: 418.1205, found = 418.1202.

3,10-Diethyl-7,16-dioxa-dibenzo[a,o]perylene (2e(*E*)): $R_f = 0.72$ (petroleum ether/ethyl acetate 15:1); m.p.>250°C; UV/Vis (THF): λ_{max} (log ε) 446 (4.2), 427 (4.1), 352 (4.0), 336 (3.8), 297 (4.0), 252 (4.6) nm; ¹H NMR (300 MHz, CDCl₃): δ 7.97 (d, *J* = 8.1 Hz, 1H; H_{Ar}), 7.88 (d, *J* = 7.8 Hz, 1H; H_{Ar}), 7.64 (s, 1H; H_{Ar}), 7.45-7.40 (m, 2H, H_{Ar}), 7.25-7.07 (m, 6H, H_{Ar}), 6.85 (t, *J* = 7.5 Hz, 1H; H_{Ar}), 3.36-3.26 (q, *J* = 7.2 Hz, 1H; CH₂), 3.26-3.17 (q, *J* = 7.2 Hz, 1H; CH₂), 2.44(q, *J* = 7.4 Hz, 2H; CH₂), 1.45(t, *J* = 7.4 Hz, 3H; CH₃), 1.07 (t, *J* = 7.7 Hz, 3H; CH₃); ¹³C NMR (100 MH_z, CDCl₃): δ 152.6, 150.7, 150.1, 148.2, 138.3, 134.7, 129.7, 129.6, 129.5, 129.2, 128.7, 127.6, 126.4, 125.9, 122.7, 122.5, 122.1, 121.6, 121.4, 121.2, 118.0, 117.9, 117.0, 116.9, 112.4, 111.9, 28.8 (CH₂), 28.3

(CH₂), 15.9 (CH₃), 15.7 (CH₃); IR (KBr, cm⁻¹): 2958 (w), 1588 (s), 1564 (m), 1480 (s), 1451 (s), 1421 (s), 1357 (m), 1313 (s), 1266 (s), 752 (m); TOFMS (EI) calcd for (M⁺) $C_{30}H_{22}O_2$: 414.162, found = 414.1585.

10,13-Diethyl-7,16-dioxa-dibenzo[a,o]perylene (**2e**(**Z**)): UV/Vis (THF): λ_{max} (log ε) 441 (4.2), 419 (4.2), 350 (4.0), 334 (3.8), 295 (4.1), 274 (4.3), 246 (4.6) nm; TOFMS (EI) calcd for (M⁺) C₃₀H₂₂O₂: 414.1620, found = 414.1523.

7,16-Dioxa-dibenzo[a,o]perylene-3,10-dicarbonitrile (**2f**(*E*)): $R_{\rm f} = 0.51$ (petroleum ether/CH₂Cl₂ 1:2); m.p. >250°C; UV/Vis (THF): $\lambda_{\rm max}$ (log ε) 442 (4.2), 422 (4.2), 352 (4.0), 336 (4.0), 302 (4.2), 294 (4.2), 245 (4.7) nm; ¹H NMR (300 MHz, CDCl₃): δ 9.06 (d, J = 8.4 Hz, 1H; H_{Ar}), 8.19 (s, 1H; H_{Ar}), 7.96 (d, J = 8.1 Hz, 1H; H_{Ar}), 7.82 (d, J = 7.6 Hz, 1H; H_{Ar}), 7.65 (t, J = 8.0 Hz, 1H; H_{Ar}), 7.56 (d, J = 8.3 Hz, 1H; H_{Ar}), 7.43-7.30 (m, 5H), 7.03 (t, J = 7.5 Hz, 1H; H_{Ar}); IR (KBr, cm⁻¹): 2225(s), 1581 (s), 1482 (s), 1460 (s), 1318 (s), 1271 (s), 750 (m); TOFMS (EI) calcd for (M⁺) C₂₈H₁₂N₂O₂: 408.0899, found = 408.0898.

1-(10-Acetyl-7,16-dioxa-dibenzo[a,o]perylen-3-yl)-ethanone (**2**g(*E*)): $R_{\rm f} = 0.28$ (petroleum ether/CH₂Cl₂ 1:4); m.p. >250°C; UV/Vis (THF): $\lambda_{\rm max}$ (log ε) 443 (4.2), 424 (4.2), 349 (4.1), 337 (4.1), 297 (4.3), 259 (4.7) nm; ¹H NMR (300 MHz, CDCl₃): δ 8.54 (s, 1H; H_{Ar}), 7.94 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.62-7.44 (m, 3H; H_{Ar}), 7.36-7.24 (m, 5H; H_{Ar}), 6.93 (t, 1H; *J* = 7.4 Hz, H_{Ar}), 2.39 (s, 3H; CH₃), 3.32 (s, 3H; CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 205.5 (C=O), 196.5 (C=O), 156.5, 152.6, 151.8, 150.1, 134.5, 131.7, 130.1 128.0, 126.6, 123.0, 121.9, 121.3, 120.3, 118.1 118.0, 117.9, 113.1, 112.5, 31.1 (CH₃), 26.5 (CH₃); IR (KBr, cm⁻¹): 2923 (w), 1672 (s), 1594 (s), 1585 (s), 1484 (m), 1461 (s), 1451 (s), 1319 (s), 1266 (s), 752 (s); TOFMS (EI) calcd for (M⁺) C₃₀H₁₈O₄: 442.1205, found = 442.1197.

7,16-Dioxa-dibenzo[a,o]perylene-3,10-dicarboxylic acid (**2h**(*E*)): $R_f = 0.26$ (CH₂Cl₂/THF 5:1); m.p. >250°C; UV/Vis (THF): λ_{max} (log ε) 441 (4.1), 420 (4.1), 347 (3.9), 334 (3.8), 297 (4.1), 245 (4.7) nm; ¹H NMR (400 MHz, [D₆]DMSO): δ 13.33 (s, 1H; COOH), 12.83 (s, 1H; COOH), 8.47 (s, 1H; H_{Ar}), 7.93 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 7.88 (d, *J* = 8.0 Hz, 1H; H_{Ar}), 7.82 (d, *J* = 8.0 Hz, 1H; H_{Ar}), 7.77 (d, J = 8.4 Hz, 1H; H_{Ar}), 7.58 (t, J = 8.0 Hz, 1H; H_{Ar}), 7.44-7.34 (m, 5H; H_{Ar}), 7.02 (t, J = 7.4 Hz, 1H; H_{Ar}); IR (KBr, cm⁻¹): 3440 (br), 1618 (s), 1594 (m), 1493 (s), 1462 (m), 1292 (s), 766 (s); TOFMS (EI) calcd for (M⁺) C₂₈H₁₄O₆: 446.0790, found = 446.0781.

7,16-Dioxa-dibenzo[a,o]perylene-3,10-dicarboxylic acid dimethyl ester (2i(*E*)): $R_{\rm f} = 0.37$ (petroleum ether/CH₂Cl₂ 2:3); m.p. 292-294°C; UV/Vis (THF): $\lambda_{\rm max}$ (log ε) 440 (4.2), 420 (4.2), 348 (4.0), 334 (3.9), 297 (4.2), 239 (4.7) nm; ¹H NMR (300 MHz, CDCl₃): δ 8.59 (s, 1H; H_{Ar}), 7.96-7.88 (m, 2 H; H_{Ar}), 7.76 (d, *J* = 8.1 Hz, 1H; H_{Ar}), 7.55 (d, *J* = 8.1, 1H; H_{Ar}), 7.45-7.40 (m, 1H; H_{Ar}), 7.31 (m, 1H; H_{Ar}), 7.26-7.20 (m, 4 H; H_{Ar}), 6.90 (t, *J* = 7.5 Hz, 1H; H_{Ar}), 3.90 (s, 3 H; CH₃), 3.80 (s, 3 H; CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 171.5 (C=O), 156.2, 152.2, 149.8, 131.3, 131.0, 130.6, 130.1, 129.4, 128.9, 127.9, 126.6, 126.5, 124.7, 124.0, 123.1, 121.4, 120.3, 118.0, 117.7, 117.6, 112.6, 112.0, 52.5 (CH₃), 52.1 (CH₃); IR (KBr, cm⁻¹): 2926 (m), 1722 (s), 1651 (w), 1595 (m), 1461 (m), 1285 (s), 1266 (s), 1211 (s), 1126 (s), 757 (m); TOFMS (EI) calcd for (M⁺) C₂₈H₁₈O₄: 474.1103, found = 474.1097.

7,16-Dioxa-dibenzo[a,o]perylene-3,10-dicarboxylic acid bis-diethylamide(2j(*E***)): R_f = 0.67 (CH₂Cl₂/ethyl acetate 5:1); m.p. >250°C; UV/Vis (THF): \lambda_{max} (log \varepsilon) 443 (4.2), 421 (4.2), 350 (3.9), 335 (3.9), 297 (4.2), 246 (4.7) nm; ¹H NMR (300 MHz, CDCl₃): \delta 8.10 (d, J = 8.4 Hz, 1H; H_{Ar}), 7.93-7.90 (m, 2H; H_{Ar}), 7.46-7.40 (m, 2H; H_{Ar}), 7.31-7.19 (m, 6H; H_{Ar}), 7.28(m, 1H; H_{Ar}), 7.24-7.19(m, 4H; H_{Ar}), 6.90 (t, J = 7.6 Hz, 1H; H_{Ar}), 3.93-3.86 (m, 2H; CH₂), 3.44-3.32 (m, 4H; CH₂), 2.72-2.60 (m, 2H; CH₂), 1.10 (m, 12H; CH₃); ¹³C NMR (100 MHz, CDCl₃): 171.1 (C=O), 169.1 (C=O), 152.5, 151.5, 149.4, 148.9, 130.7, 129.4, 127.5, 127.4, 126.2, 124.9, 124.8, 124.5, 121.9, 121.0, 120.8, 120.7, 119.9, 119.7, 117.3, 116.6, 116.5, 118.8, 111.6, 41.6 (CH₂), 38.2 (CH₂), 28.7 (CH₂), 12.3 (CH₃), 11.2 (CH₃); IR (KBr, cm⁻¹): 2964 (m), 1722 (m), 1629 (s), 1564 (m), 1454 (s), 1412 (s), 1348 (m), 1311 (s), 1264 (s), 757 (m); TOFMS (EI) calcd for (M⁺) C₃₆H₃₂N₂O₄: 556.2362, found = 556.2357.**

II. Sequential HPLC analysis of the photolysis of **1f**



Fig. S1 HPLC chromatograms of the crude products in the photolysis of **1f** in aerated THF/methanol (v/v 1:9) solution irradiated for (a) 0 min, (b) 1.5 min, (c) 3.0 min, (d) 4.5 min, (e) 6.0 min, (f) 7.5 min upon 365 nm light; (g) pure **2f**(E).

III. Photoconversion of 1 to 2 Monitored by UV/Vis Spectrometer



Figure S2a. UV/vis absorption spectra of **1a** in THF recorded after irradiation for different times $(0\rightarrow 12 \text{ min})$ irradiated under 365nm light from a handheld UV lamp.



Figure S2b. UV/vis absorption spectra of **1b** in THF recorded after irradiation for different times $(0\rightarrow 60 \text{ min})$ irradiated under 365nm light from a handheld UV lamp.



Figure S2c. UV/vis absorption spectra of **1c** in THF recorded after irradiation for different times $(0\rightarrow78 \text{ min})$ irradiated under 365nm light from a handheld UV lamp.



Figure S2d. UV/vis absorption spectra of **1d** in THF recorded after irradiation for different times $(0\rightarrow 150 \text{ min})$ irradiated under 365nm light from a handheld UV lamp.



Figure S2e. UV/vis absorption spectra of **1e** in THF recorded after irradiation for different times $(0\rightarrow 85 \text{ min})$ irradiated under 365nm light from a handheld UV lamp.



Figure S2f. UV/vis absorption spectra of **1f** in THF recorded after irradiation for different times $(0\rightarrow 18 \text{ min})$ irradiated under 365nm light from a handheld UV lamp.



Figure S2g. UV/vis absorption spectra of **1g** in THF recorded after irradiation for different times $(0\rightarrow 1 \text{ min})$ irradiated under 365nm light from a handheld UV lamp.



Figure S2h. UV/vis absorption spectra of **1h** in THF recorded after irradiation for different times $(0\rightarrow 1.3 \text{ min})$ irradiated under 365nm light from a handheld UV lamp.



Figure S2i. UV/vis absorption spectra of **1i** in THF recorded after irradiation for different times $(0\rightarrow 4 \text{ min})$ irradiated under 365nm light from a handheld UV lamp.



Figure S2j. UV/vis absorption spectra of **1j** in THF recorded after irradiation for different times $(0\rightarrow 1.4 \text{ min})$ irradiated under 365nm light from a handheld UV lamp.

IV. HPLC Chromatograms for Photolysis crude products of 1 in aerated CH₃CN/THF (v/v, 9:1) solutions



1. HPLC chromatograms of compounds $\mathbf{1b}$ (R = F), $\mathbf{2b}(E)$ and $\mathbf{2b}(Z)$

Condition:

Flow phase: methanol/water = 95:5. Flow rate: 1 mL/min, Column temperature: 20° C Retention times: 5.7 min, 15.5 min and 21.7 min for **1b**, **2b**(*Z*) and **2b**(*E*), respectively.



2. HPLC chromatograms of compounds 1c (R = CH₃), 2c(E) and 2c(Z)

Condition:

Flow phase: methanol/water = 87:13, Flow rate: 1 mL/min, Column temperature: 20° C Retention times: 84.5 min, 178.1 min and 182.9 for **1**, 2c(Z) and 2c(E), respectively.



3. HPLC chromatograms of compounds 1d ($R = OCH_3$), 2d(E) and 2d(Z)

Flow phase: methanol/water = 90:10, Flow rate: 1 mL/min, Column temperature: 20° C, Retention times: 11.2 min, 31.8 min and 33.5 min for **1d**, **2d**(*E*) and **2d**(*Z*), respectively.

4. HPLC chromatograms of compounds **1e** (R=Et), **2e**(*Z*) and **2e**(*E*)



Condition:

Flow phase: methanol/water = 96:4, Flow rate: 1 mL/min, Column temperature: 20° C Retention times: 14.0 min, 37.3 min and 39.0 min for **1e**, **2e**(*Z*) and **2e**(*E*), respectively.



5. HPLC chromatograms of compounds 1f(R = CN) and 2f(E)

Flow phase: methanol/water = 92:8, Flow rate: 1 mL/min, Column temperature: 20° C Retention times: 3.1 min and 7.3 min for **1f** and **2f**(*E*), respectively.

6. HPLC chromatograms of compounds 1g (R = COCH₃) and 2g(E)



Condition:

Flow phase: methanol/water = 90:10, Flow rate: 1 mL/min, Column temperature: 20° C Retention times: 4.9 min, 8.6 min for **1g** and **2g** (*E*), respectively.

8. HPLC chromatograms of compounds **1h** (R = COOH) and **2h**(E)



Flow phase: *n*-hexane/ethanol = 85:15, Flow rate: 1 mL/min, Column temperature: 20° C Retention times: 1.7 min, 2.4 min for **1h** and **2h**(*E*), respectively.



7. HPLC chromatograms of compounds $1i (R = COOCH_3)$ and 2i(E)

Condition:

Flow phase: methanol/water = 94:6, Flow rate: 1 mL/min, Column temperature: 20° C Retention times: 5.4 min, 7.5 min for **1i** and **2i**(*E*), respectively.





Flow phase: methanol/water = 80:20, Flow rate: 1 mL/min, Column temperature: 20° C Retention times: 8.2 min, 10.8 min for **1j** and **2j**(*E*), respectively.

V. Copies of ¹H NMR and ¹³C NMR Spectra

¹H NMR spectrum of compound **4b**



10 ppm

¹H NMR spectrum of compound **4d**

130 120



10 ppm

¹H NMR spectrum of compound **4e**



¹³C NMR spectrum of compound **4e**



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¹H NMR spectrum of compound **4f**



¹³C NMR spectrum of compound **4f**



¹H NMR spectrum of compound **4g**



1 H NMR spectrum of compound **4h**



^{13}C NMR spectrum of compound **4h**

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¹H NMR spectrum of compound **4i**



¹³C NMR spectrum of compound **4i**



¹H NMR spectrum of compound **4**j





10 ppm

¹H NMR spectrum of compound **1b**



¹H NMR spectrum of compound **1d**



¹³C NMR spectrum of compound 1d



¹H NMR spectrum of compound **1e**



¹H NMR spectrum of compound **1f**



¹³C NMR spectrum of compound **1f**



¹H NMR spectrum of compound **1g**



^{13}C NMR spectrum of compound 1g



¹H NMR spectrum of compound **1h**



¹³H NMR spectrum of compound **1h**



¹H NMR spectrum of compound **1i**



10 ppm

¹H NMR spectrum of compound **1**j



¹³C NMR spectrum of compound **1**j



¹H NMR spectrum of compound $2\mathbf{b}(E)$



¹H NMR spectrum of compound $2\mathbf{b}(Z)$



¹H NMR spectrum of compound 2c(E)



¹H NMR spectrum of compound 2d(E)



¹³C NMR spectrum of compound 2d(E)



¹H NMR spectrum of compound 2e(E)



¹³C NMR spectrum of compound 2e(E)



¹H NMR spectrum of compound 2f(E)



¹H NMR spectrum of compound 2g(E)



¹³C NMR spectrum of compound 2g(E)



¹H NMR spectrum of compound 2h(E)



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¹H NMR spectrum of compound 2i(E)



¹³C NMR spectrum of compound 2i(E)



¹H NMR spectrum of compound 2j(E)



¹³H NMR spectrum of compound 2j(E)

