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Molecular Switches Flipped by Oxygen

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Experimental procedures:

General methods: All reagents were purchased from Aldrich and used without further purifications. Solvents were dried according to standard procedures. Column chromatography was performed using Merck silica gel 60. TLC was performed on silica gel coated aluminum foils (0.25 mm thick, 60 F_{254}, Merck, Germany). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer at 300 MHz and 75 MHz, respectively. Deuterochloroform was used as internal standard (δ = 7.26 and 77.0 ppm, respectively). ^{19}F NMR spectra were recorded on a Bruker AC 300 spectrometer at 282.4 MHz using trichlorofluoromethane as internal standard. Melting points were determined on a Barnstaed/ Electrothermal 9100. IR spectra were recorded on a Perkin Elmer 16 PC FT-IR. UV-vis spectra were measured on a Unicam UV3 instrument. X-ray structures were obtained from a STOE Imaging Plate Diffraction System (IPDS II) at 210 K using graphite-monochromated Mo-Kα radiation (λ=0.71073 Å)

General procedure for the synthesis of anthracenes. In a 100 mL three necked round bottom flask, the boronic acid (2.5 eq, 7.35 mmol), 9,10-dibromoanthracene (990 mg, 1 eq, 2.94 mmol) and K_2CO_3 (3.28 g, 23 mmol) were dissolved in toluene (40 mL), ethanol (8 mL) and water (16 mL). Argon was bubbled vigorously through the solution for 5 min followed by the addition of tetrakis-(triphenylphosphine)-palladium (254 mg, 0.2 mmol), after which argon was bubbled again through the solution for another 5 min. The solution was then refluxed for 24 hours. For all anthracenes, except **1f**, a solid has formed after cooling, which was separated by filtration and recrystallized from chloroform. The structure of the solid was assigned to the *trans*-isomer for all anthracenes, based on distinct NMR data and X-ray crystal structures. The filtrate (a mixture of both isomers and mono-coupling products) was washed with brine, dried over sodium sulfate and the solvent was removed under reduced pressure. The residue was subjected to column chromatography affording the *cis*-isomer. In the case of compound **1f**, the crude reaction solution was treated analogously. The quantitative separation of the isomers oft **1f** was not possible. The yields of all couplings are given in Figure 2.

***cis*-9,10-Bis(2-methylphenyl)-anthracene (*cis*-1b).** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.95 (s, 6 H, 21-H), 7.4-7.5 (m, 6 H, 2-H, 3-H, 6-H, 7-H, 17-H), 7.32-7.3 (m, 6 H, 18-H, 19-H, 20-H), 7.56-7.61 (m, 4 H, 1-H, 4-H, 5-H, 8-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.7 (q, C-21), 125.1 (d, C-2, C-3, C-6, C-7), 125.8 (s, C-18), 126.7 (d, C-1, C-4, C-5, C-8), 127.8 (s, C-11, C-12, C-13, C-14), 129.7, 130.0, 131.3 (3 d, C-17, C-19, C-20), 136.2, 137.8, 138.4 (3 s, C-9, C-10, C-15, C-16). mp=330 °C. IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 3012, 2918, 1489, 1438, 1382, 941, 771, 753.

***trans*-9,10-Bis(2-methylphenyl)-anthracene (*trans*-1b).** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93 (s, 6 H, 21-H), 7.30-7.35 (m, 6 H, 2-H, 3-H, 6-H, 7-H, 17-H), 7.38-7.48 (m, 6 H, 18-H, 19-H, 20-H), 7.52-7.59 (m, 4 H, 1-H, 4-H, 5-H, 8-H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 19.8 (q, C-21), 125.1 (d, C-2, C-3, C-6, C-7), 125.8 (s, C-18), 126.7 (d, C-1, C-4, C-5, C-8), 127.8 (s, C-11, C-12, C-13, C-14), 129.7, 130.0, 131.4 (3 d, C-17, C-19, C-20), 136.3, 137.9, 138.4 (3 s, C-9, C-10, C-15, C-16). mp=330 °C.

IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1}, 3012, 2919, 1491, 1438, 1381, 942, 768, 750. Elemental analysis calcd (%) for $C_{28}H_{22}$ (358.3): C 93.81, H 6.19; found: C 93.61, H 6.27.

***cis*-9,10-Bis(2-ethylphenyl)-anthracene (*cis*-1c).** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.5Hz, 6 H, 22-H), 2.25 (q, *J* = 7.5Hz, 4 H, 21-H), 7.28-7.33 (m, 6 H, 2-H, 3-H, 6-H, 7-H), 7.38-7.45 (m, 2 H, 18-H), 7.52-7.58 (m, 8 H, 1-H, 4-H, 5-H, 8-H, 17-H, 19-H, 20-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7 (q, C-22), 26.3 (t, C-21), 124.9 (d, C-2, C-3, C-6, C-7), 125.8 (d, C-18), 126.9 (d, C-1, C-4, C-6, C-8), 128.0, 128.2 (2 d, C-17, C-19), 129.9 (s, C-11, C-12, C-13, C-14), 131.5 (d, C-20), 136.2, 137.2, 143.8 (3 s, C-9, C-10, C-15, C-16). IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1}, 2965, 2931, 2870, 1488, 1438, 1386, 942, 752, 667.

***trans*-9,10-Bis(2-ethylphenyl)-anthracene (*trans*-1c).** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.5Hz, 6 H, 22-H), 2.24 (q, *J* = 7.5Hz, 4 H, 21-H), 7.28-7.33 (m, 6 H, 2-H, 3-H, 6-H, 7-H), 7.38-7.45 (m, 2 H, 18-H), 7.52-7.58 (m, 8 H, 1-H, 4-H, 5-H, 8-H, 17-H, 19-H, 20-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9 (q, C-22), 26.2 (t, C-21), 125.0 (d, C-2, C-3, C-6, C-7), 125.7 (d, C-18), 126.9 (d, C-1, C-4, C-5, C-8), 128.0, 128.2 (2 d, C-17, C-19), 130.0 (s, C-11, C-12, C13, C-14), 131.5 (d, C-20), 136.2, 137.9, 143.8 (3 s, C-9, C-10, C-15, C-16). IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1}, 2964, 2930, 2868,1486, 1439, 1387, 942, 771, 757, 668. Elemental analysis calcd (%) for $C_{30}H_{26}$ (386.3): C 93.22, H 6.78; found: C 92.98, H 6.90.

***cis*-9,10-Bis(2-isopropylphenyl)-anthracene (*cis*-1d).** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (d, *J* = 6.8 Hz, 12 H, 22-H, 22'-H), 2.51 (sept, *J* = 6.8 Hz, 2 H, 21-H), 7.24 (dd, *J* = 7.5, 1.1 Hz, 2 H), 7.29-7.32 (m, 6 H, 2-H, 3-H, 6-H, 7-H, 17-H), 7.38 (dt, *J* = 7.5, 1.6 Hz, 2 H, 18-H), 7.56-7.61 (m, 8 H, 1-H, 4-H, 5-H, 8-H, 19-H, 20-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.2 (q, C-22, C-22'), 30.5 (d, C-21, C-21'), 124.9 (d, C-2, C-3, C-6, C-7), 125.6 (d, C-17, C-18), 127.1 (d, C-1, C-4, C-5, C-8), 128.3 (d, C-19), 130.2 (s, C-11, C-12, C-13, C14), 131.4 (d, C-20), 136.2, 137.3, 148.6 (3 s, C-9, C-10, C-15, C-16). IR (KBr): $\tilde{\nu}$ = 3059 cm^{-1}, 2960, 2926, 2866, 1488, 1439, 1386, 1082, 1025, 944, 771, 668.

***trans*-9,10-Bis(2-isopropylphenyl)-anthracene (*trans*-1d).** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (d, *J* = 6.8 Hz, 12 H, 22-H, 22'-H), 2.44 (sept, *J* = 6.9 Hz, 2 H, 21-H), 7.17 (d, *J* = 7.5, 2 H), 7.29-7.32 (m, 6 H, 2-H, 3-H, 6-H, 7-H, 17-H), 7.38 (dt, *J* = 7.5, 1.8 Hz, 2 H, 18-H), 7.55-7.59 (m, 8 H, 1-H, 4-H, 5-H, 8-H, 19-H, 20-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.2 (q, C-22, C-22'), 30.4 (d, C-21, C-21'), 124.9 (d, C-2, C-3, C-6, C-7), 125.6, 125.7 (d, C-17, C-18), 127.1 (d, C-1, C-4, C-5, C-8), 128.3 (d, C-19), 130.1 (s, C-11, C-12, C-13, C14), 131.4 (d, C-20), 136.2, 137.2, 148.8 (3 s, C-9, C-10, C-15, C-16). IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1}, 2961, 2926, 2865,1488, 1440, 1385, 1079, 1027, 944, 761, 667. Elemental analysis calcd (%) for $C_{32}H_{30}$ (414.3): C 92.71, H 7.29; found: C 92.66, H 7.33.

***cis*-9,10-Bis-(2-methoxyphenyl)-anthracene (*cis*-1e).** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 6 H, 21-H), 7.18-7.24 (m, 4 H), 7.32-7.36 (m, 6 H, 2-H, 3-H, 6-H, 7-H), 7.57 (dt, *J* = 7.4, 1.8 Hz, 2 H), 7.67-7.70 (m, 4 H, 1-H, 4-H, 5-H, 8-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.6 (q, C-21), 111.3 (d, C-17), 120.6 (d, C-18), 124.7 (d, C-2, C-3, C-6, C-7), 126.9 (d, C-1, C-4, C-5, C-8), 127.7 (s, C-11, C-12, C-13, C-14), 129.2, 130.1 (2 d, C-19, C-20), 133.0, 133.7 (2 s, C-9, C-10, C-15), 158.1 (s, C-16). mp=308 °C. IR (KBr): $\tilde{\nu}$ = 3059, 2933, 2833, 1597, 1577, 1494, 1459, 1432, 1274, 1243, 1106, 1046, 1022, 942, 752, 665.

***trans*-9,10-Bis-(2-methoxyphenyl)-anthracene (*trans*-1e).** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 6 H, 21-H), 7.18-7.24 (m, 4 H), 7.32-7.36 (m, 6 H, 2-H, 3-H, 6-H, 7-H), 7.57 (dt, J = 7.4, 1.8 Hz, 2 H), 7.67-7.70 (m, 4 H, 1-H, 4-H, 5-H, 8-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.6 (q, C-21), 111.3 (d, C-17), 120.6 (d, C-18), 124.7 (d, C-2, C-3, C-6, C-7), 126.9 (d, C-1, C-4, C-5, C-8), 127.7 (s, C-11, C-12, C-13, C-14), 129.2, 130.1 (2 d, C-19, C-20), 133.0, 133.7 (2 s, C-9, C-10, C-15), 158.1 (s, C-16). mp=318 °C. IR (KBr): $\tilde{\nu}$ = 3024, 2931, 2834, 1596, 1576, 1491, 1459, 1431, 1291, 1277, 1240, 1104, 1046, 1019, 942, 752, 665. Elemental analysis calcd (%) for $C_{28}H_{22}O_2$ (390.2): C 86.13, H 5.68; found: C 85.73, H 5.51.

***cis*-9,10-Bis-(2-fluorophenyl)-anthracene (*cis*-1f) and *trans*-9,10-Bis-(2-fluorophenyl)-anthracene (*trans*-1f).** The isolation of the isomers of the fluorophenylanthracenes was not possible. However, the *cis* and *trans* isomers were distinguishable by the characteristic resonances in the ^{13}C and ^{19}F NMR spectra.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33-7.42 (m, 8 H, 2-H, 3-H, 6-H, 7-H), 7.44-7.51 (m, 2 H), 7.54-7.62 (m, 2 H), 7.66-7.70 (m, 4 H, 1-H, 4-H, 5-H, 8-H).

(*cis*-1f)

^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.9 (d, $J_{C,F}$ = 22.2 Hz, C-17), 124.2 (d, $J_{C,F}$ = 3.8 Hz, C-19), 125.5 (d, C-2, C-3, C-6, C-7), 126.1 (s, $J_{C,F}$ = 17.5 Hz, C-15), 126.5 (d, C-1, C-4, C-5, C-8), 129.9 (d, $J_{C,F}$ = 7.6 Hz, C-18), 130.1 (s, C-11, C-12, C-13, C-14), 131.1 (s, C-9, C-10), 131.2 (s, C-9, C-10), 133.4 (d, $J_{C,F}$ = 3.5 Hz, C-20), 160.8 (s, $J_{C,F}$ = 246 Hz, C-16).

^{19}F NMR (282.4 MHz, $CDCl_3$+$CFCl_3$) = -113.15 (m, 1 F).

***trans*-1f**

^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.8 (d, $J_{C,F}$ = 22.2 Hz, C-17), 124.3 (d, $J_{C,F}$ = 3.8 Hz, C-19), 125.5 (d, C-2, C-3, C-6, C-7), 126.1 (s, $J_{C,F}$ = 17.5 Hz, C-15), 126.5 (d, C-1, C-4, C-5, C-8), 129.9 (d, $J_{C,F}$ = 7.6 Hz, C-18), 130.1 (s, C-11, C-12, C-13, C-14), 131.1 (s, C-9, C-10), 131.2 (s, C-9, C-10), 133.5 (d, $J_{C,F}$ = 3.5 Hz, C-20), 160.8 (s, $J_{C,F}$ = 246 Hz, C-16).

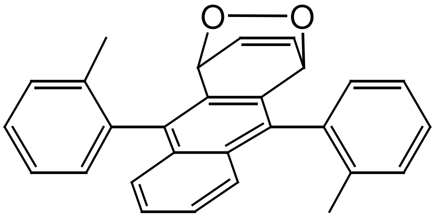
^{19}F NMR (282.4 MHz, $CDCl_3$+$CFCl_3$) = -114.1 (m, 1 F).

mp=266 °C. IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1}, 1490, 1447, 1387, 1262, 1223, 1094, 1028, 944, 817, 756. Elemental analysis calcd (%) for $C_{26}H_{16}F_2$ (366.7): C 85.29, H 4.37; found: C 85.78, H 3.88.

Sensitized Photooxidation of the anthracenes. The photooxidations were carried out in 20 mL glass tubes, where the anthracene (1 mmol) and a catalytic amount of methylene blue were dissolved in $CDCl_3$ (6 mL). The tube was sealed with a rubber stopper and cooled to -20 ºC. A slow constant stream of oxygen was bubbled into the solution via a needle, while the cooled tube was irradiated with two sodium lamps (200 W). The course of the photooxidation was monitored by TLC and stopped after complete conversion. The solvent was removed under vacuum at room temperature and the crude product was purified by column chromatography. The yields are given in Figure 2.

9,10-Bis-(2-methylphenyl)-9,10-dihydro-9,10-epidioxidoanthracene (2b). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 6 H, 21-H), 7.08-7.05 (m, 4 H, 2-H, 3-H, 6-H, 7-H), 7.22-7.25 (m, 4 H, 1-H, 4-H, 5-H, 8-H), 7.38-7.52 (m, 6 H, 17-H, 18-H, 19-H), 7.73 (d, J = 7.2 Hz, 2 H, 20-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.9 (q, C-21), 84.0 (s, C-9, C-10), 124.2 (d, C-2, C-3, C-6, C-7), 126.3, 126.7 (2 d, C-17, C-18), 127.8 (d, C-1, C-4, C-5, C-8), 128.3, 131.3 (2 d, C-19, C-20), 133.0, 135.6, 137.7 (3 s, C-11, C-12, C-13, C-14, C-15, C-16). IR (KBr): $\tilde{\nu}$ = 3059 cm^{-1}, 2920, 1491, 1458, 1437, 1383, 1246, 1024, 942, 767, 751, 666. Elemental analysis calcd (%) for $C_{28}H_{22}O_2$ (390.2): C 86.13, H 5.68; found: C 85.81, H 5.82.

9,10-Bis-(2-methylphenyl)-1,4-dihydro-1,4-epidioxidoanthracene.

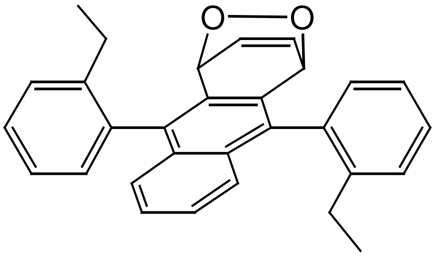


The 1,4-endoperoxide was obtained after photooxidation of **1b** as byproduct with 10% yield. The compound was not isolated.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.98 (s, 3 H, 21-H), 2.11 (s, 3 H, 22-H), 5.34 (ddd, *J* = 4.5, 3.0, 0.7 Hz, 1 H, 1-H), 5.40 (ddd, *J* = 4.6, 2.9, 0.7 Hz, 1 H, 4-H), 6.91-6.96 (m, 2 H, 2-H, 3-H), 7.19 (d, *J* = 7.1 Hz, 1 H), 7.31-7.51 (m, 11 H).

9,10-Bis-(2-ethylphenyl)-9,10-dihydro-9,10-epidioxidoanthracene (2c). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.31 (t, *J* = 7.5 Hz, 6 H, 22-H), 2.53 (q, *J* = 7.5 Hz, 4 H, 21-H), 7.07-7.10 (m, 4 H, 2-H, 3-H, 6-H, 7-H), 7.24-7.27 (m, 4 H, 1-H, 4-H, 5-H, 8-H), 7.43 (t, *J* = 8.4 Hz, 2 H, 18-H), 7.55 (dt, *J* = 7.5, 1.3 Hz, 2 H, 19-H), 7.69 (d, *J* = 7.3 Hz, 2 H, 17-H), 7.73 (dd, *J* = 7.9, 1.1 Hz, 2 H, 20-H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 14.1 (q, C-22), 27.3 (t, C-21), 84.1 (s, C-9, C-10), 124.1 (d, C-2, C-3, C-6, C-7), 125.9, 126.7 (2 d, C-17, C-18), 127.7 (d, C-1, C-4, C-5, C-8), 128.4, 128.5 (2 d, C-19, C-20), 132.3, 137.9, 141.3 (3 s, C-11, C-12, C-13, C-14, C-15, C-16).

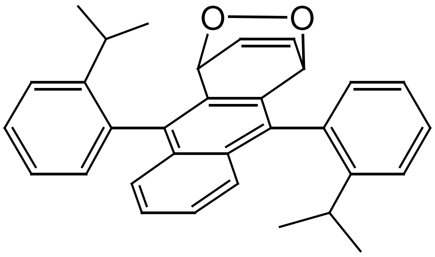
9,10-Bis-(2-ethylphenyl)-1,4-dihydro-1,4-epidioxidoanthracene.



Photooxidation of **1c** afforded the 1,4-endoperoxide as byproduct, which could be isolated with 27% yield.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.97 (t, *J* = 7.5 Hz, 3 H, 22-H), 1.05 (t, *J* = 7.5Hz, 3 H, 24-H), 2.29 (q, *J* = 7.5 Hz, 1 H, 21-H), 2.31 (q, *J* = 7.5 Hz, 1 H, 21-H), 2.44 (q, *J* = 7.5 Hz, 2 H, 23-H), 5.36 (ddd, *J* = 5.0, 2.5, 1.0 Hz, 1 H, 1-H), 5.41 (ddd, *J* = 5.1, 2.4, 0.9 Hz, 1 H, 4-H), 6.89-6.95 (m, 2 H, 3-H, 4-H), 7.18 (d, *J* = 7.3 Hz, 1 H,), 7.31-7.48 (m, 11 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 14.9, 15.4 (2 q, C-24), 26.3 (t, C-21, C-23), 73.7, 73.9 (2 s, C-1, C-4), 125.6, 126.0, 126.2, 126.8, 126.9 (5 d), 128.3, 128.4, 128.4, 128.5 (4 d), 130.9, 131.0 (2 d), 131.5, 131.6, 132.4, 132.7, 132.8 (5 s), 135.1, 135.2, 135.3, 135.5 (4 d, C-2, C-3), 143.5, 143.8 (2 s, C-16).

9,10-Bis-(2-isopropylphenyl)-1,4-dihydro-1,4-epidioxidoanthracene.



Photooxidation of **1d** afforded the 1,4-endoperoxide as byproduct, which could be isolated with 16% yield.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.54 (sept, J = 6.8 Hz, 1 H), 2.75 (sept, J = 6.7 Hz, 1 H), 5.36 (ddd, J = 5.5, 1.7, 1.0 Hz, 1 H), 5.41 (ddd, J = 5.3, 1.7, 0.9 Hz, 1 H), 6.91 (ddd, J = 7.9, 5.5, 1.7 Hz, 2 H), 7.16 (dd, J = 7.4, 0.8 Hz, 1 H), 7.29-7.59 (m, 11 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 23.8, 24.2 (2 q, C-22, C-27), 30.0, 30.2 (2 d, C-21, C-26), 73.7, 73.9 (2 d, C-1, C-4), 124.8, 125.5, 125.5, 125.9, 125.9, 126.2, 126.9, 127.0 (8 d), 128.6, 128.7 (2 d), 130.8, 130.8, 131.7 (3 d), 131.8, 132.6, 132.7, 132.8, 134.5 (5 s), 135.2, 135.4 (2 d, C-2, C-3), 148.3, 148.7 (2 s, C-16).

9,10-Bis-(2-methoxyphenyl)-9,10-dihydro-9,10-epidioxidoanthracene (2e). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.75 (s, 6 H, 21-H), 6.96-6.99 (m, 4 H, 2-H, 3-H, 6-H, 7-H), 7.15-7.18 (m, 4 H, 1-H, 4-H, 5-H, 8-H), 7.21 (d, J = 7.6 Hz, 4 H), 7.55 (dt, J = 7.5, 1.7 Hz, 2 H), 7.73 (dd, J = 7.4, 1.1 Hz, 2 H, 20-H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 55.0 (q, C-21), 83.4 (s, C-9, C-10), 111.0 (d, C-17), 121.5 (d), 122.9 (s, C-15), 123.6 (d, C-2, C-3, C-6, C-7), 126.8 (d, C-1, C-4, C-5, C-8), 127.4 (d), 129.7 (d), 137.7 (s, C-11, C-12, C-13, C-14), 156.2 (s, C-16). IR (KBr): $\tilde{\nu}$ = 3071 cm^{-1}, 2936, 2835, 1602, 1583, 1493, 1461, 1435, 1266, 1245, 1025, 910, 754, 662, 639. Elemental analysis calcd (%) for $C_{28}H_{22}O_4$ (422.3): C 79.62, H 5.21; found: C 79.61, H 5.34.

9,10-Bis-(2-fluorophenyl)-9,10-dihydro-9,10-epidioxidoanthracene (2f). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.09-7.14 (m, 4 H), 7.26- 7.29 (m, 4 H), 7.39-7.45 (m, 4 H), 7.57-7.65 (m, 2 H), 7.75-7.81 (m, 2 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 82.8 (s, $J_{C,F}$ = 1.9 Hz, C-9, C-10), 115.9 (d, $J_{C,F}$ = 21.1 Hz, C-17), 121.6 (s, $J_{C,F}$ = 13.7 Hz, C-15), 123.1 (d, $J_{C,F}$ = 3.0 Hz, C-2, C-3, C-6, C-7), 125.3 (d, $J_{C,F}$ = 3.0 Hz, C-19), 127.6 (d, $J_{C,F}$ = 3.0 Hz, C-20), 127.9 (d, C-1, C-4, C-5, C-8), 130.6 (d, $J_{C,F}$ = 7.9 Hz, C-18), 137.5 (s, C-11, C-12, C-13, C-14), 158.8 (s, $J_{C,F}$ = 248 Hz, C-16). ^{19}F NMR (282.4 MHz, CDCl$_3$) = -105.27 (m, 2 F). IR (KBr): $\tilde{\nu}$ = 3071 cm^{-1}, 3070, 3038, 1618, 1579, 1493, 1457, 1322, 1218, 912, 758, 638. Elemental analysis calcd (%) for $C_{26}H_{16}F_2O_2$ (398.6): C 78.43, H 4.02; found: C 78.24, H 3.46.

X-Ray crystal structures:

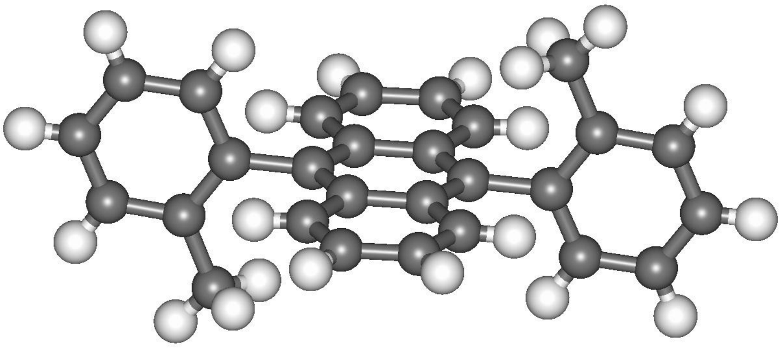


Figure S1. Crystal structure of *trans*-**1b**

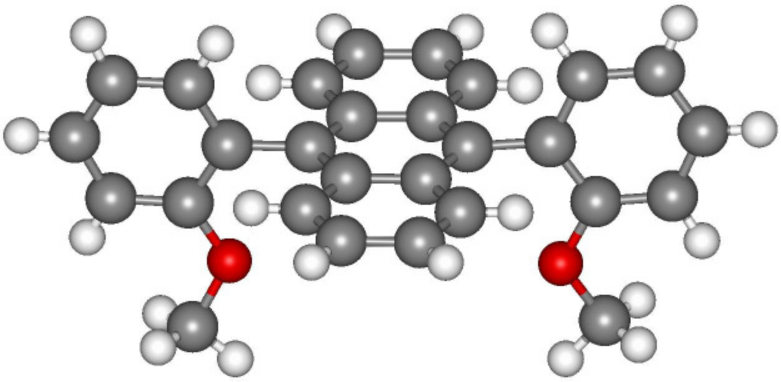


Figure S2. Crystal structure of *cis*-**1e**

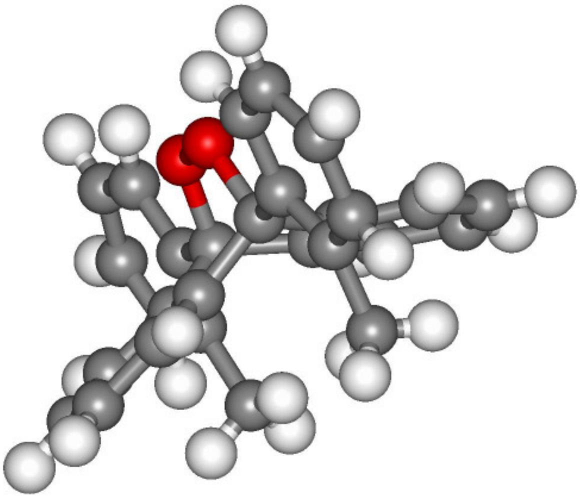


Figure S3. Crystal structure of **2b**

Thermolysis of the endoperoxides 2b – 5f:

The endoperoxide (0.5 mmol) was dissolved in toluene (40 mL) and heated at reflux under argon for 6 hrs. The course of the reaction was monitored by TLC. After complete conversion, the solvent was removed. NMR spectroscopy confirmed the quantitative formation of the parent anthracene and no byproduct or endoperoxide. Endoperoxides **2b, 2c, 2d** and **2e** afforded the corresponding parent anthracene in the *cis* form, exclusively. The thermolysis of the fluoroanthracene resulted in a mixture of both the *cis* and the *trans* form.

Thermal isomerization of the anthracnes:

Anthracene *cis*-**1e** (0.1 mmol, 40 mg) was heated in order to enforce the thermal rotation around the biaryl axis. Heating was carried out in solid state in an oven at increasing temperatures. After 20 min of heating at a constant temperature, the cooled crude material was dissolved in $CDCl_3$ and analyzed by NMR spectroscopy. The appearance of the *trans* isomer was observed at temperatures exceeding 320 °C. At this temperature, melting had already occurred. After 5 min heating, the ratio *trans*:*cis* reached already 90:10, as determined by NMR.

Figure S4. ^{1}H NMR spectra of anthracene **1b**, its corresponding endoperoxide and the product of thermolysis.

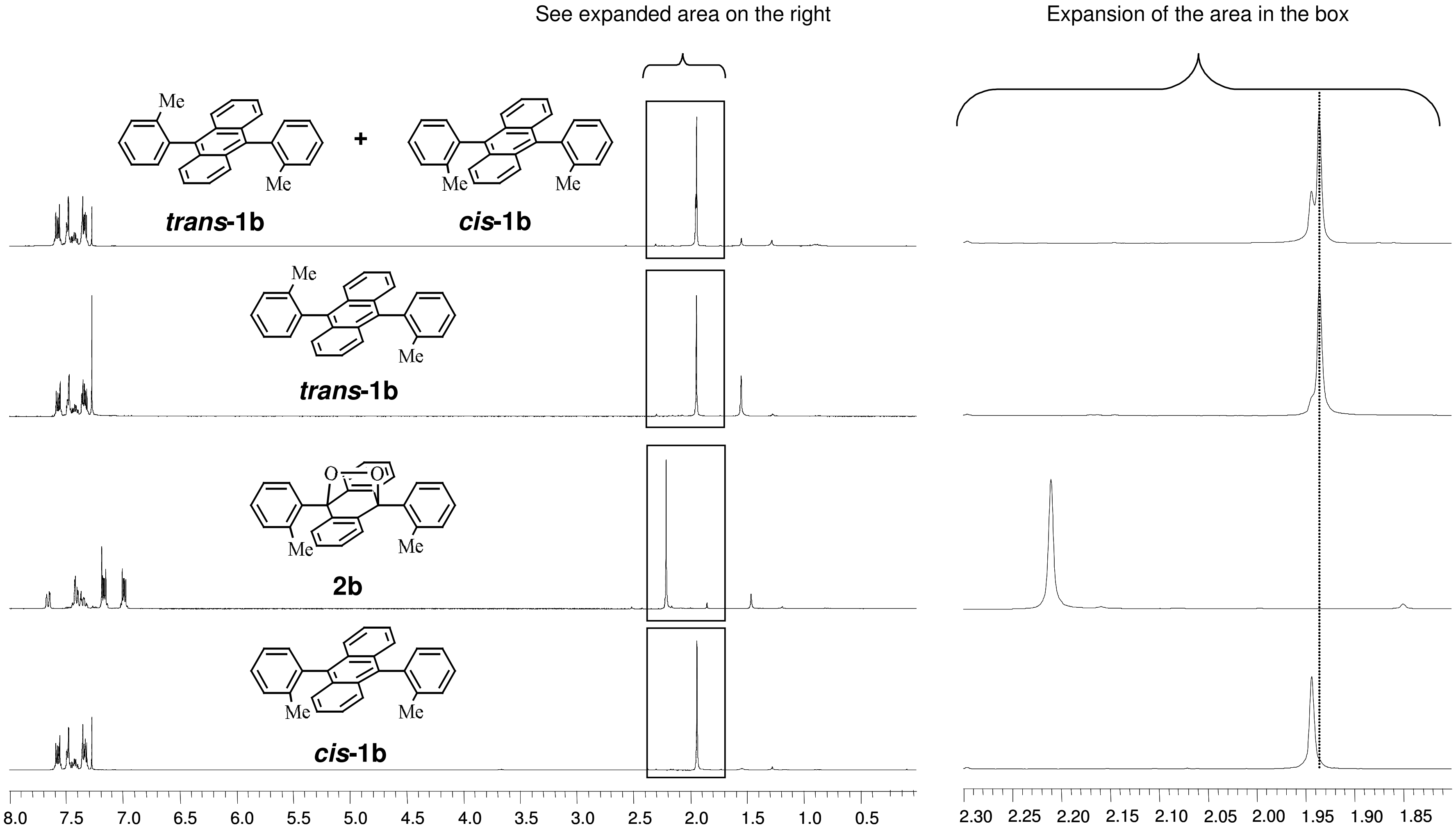


Figure S5. ^{1}H NMR spectra of anthracene **1e**, its corresponding endoperoxide and the product of thermolysis.

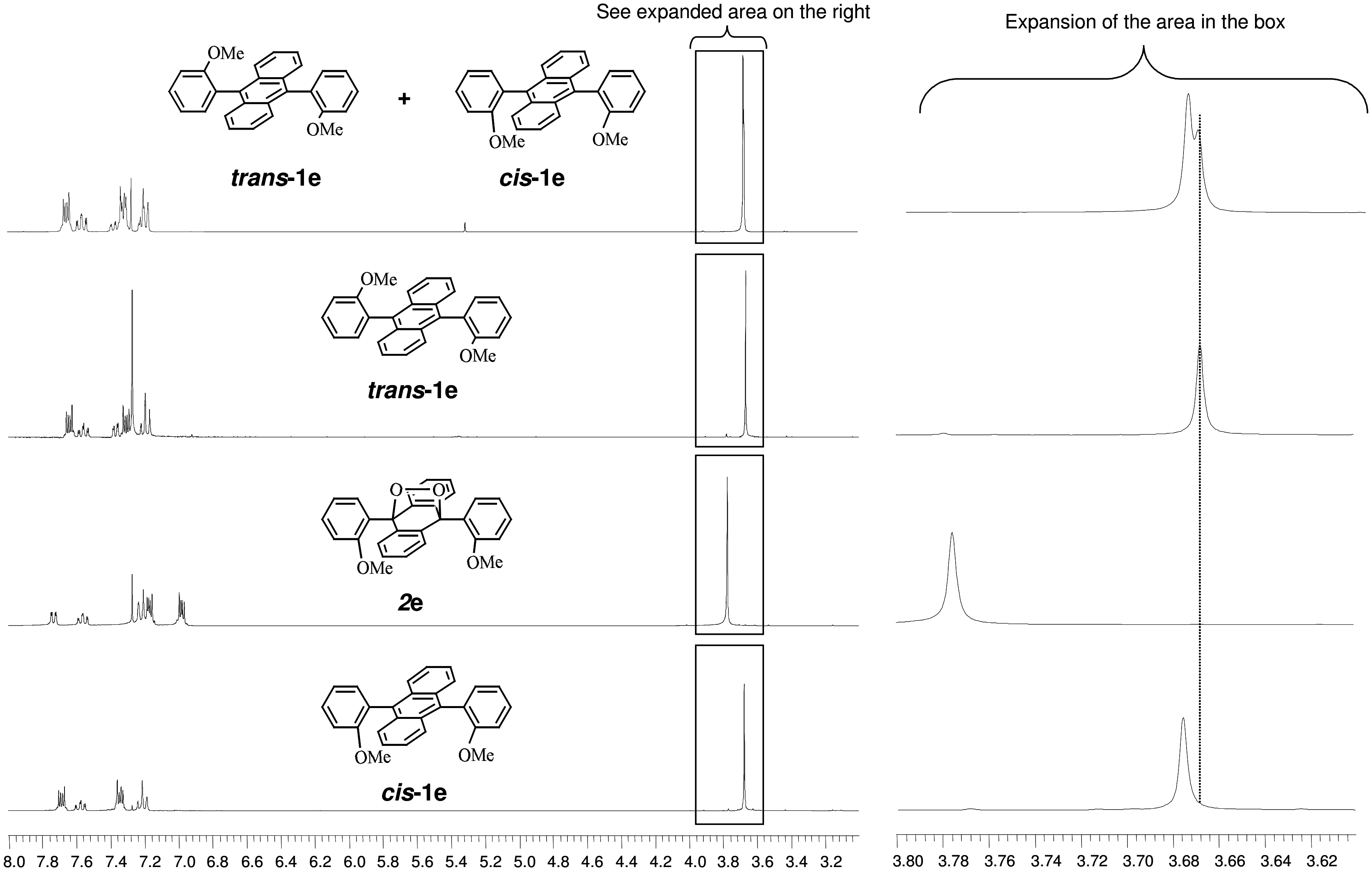
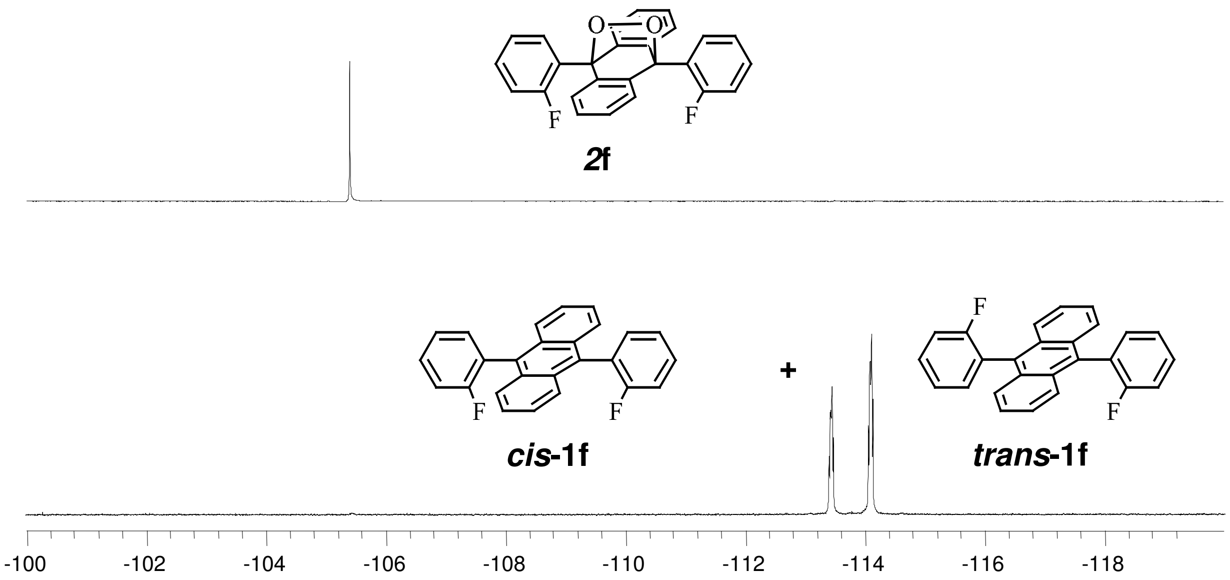


Figure S6. ^{19}F NMR spectra of the endoperoxide **2f** and the product of thermolysis.



Endoperoxide thermolysis and isomerization of the fluoroanthracene 1f:

A 10 mg sample of the endoperoxide **2f** dissolved in 1,1,2,2-tetrachloroethane-*d*2 was heated in an NMR tube at 100 °C. ^{19}F NMR spectra were recorded in intervals of 5 min.

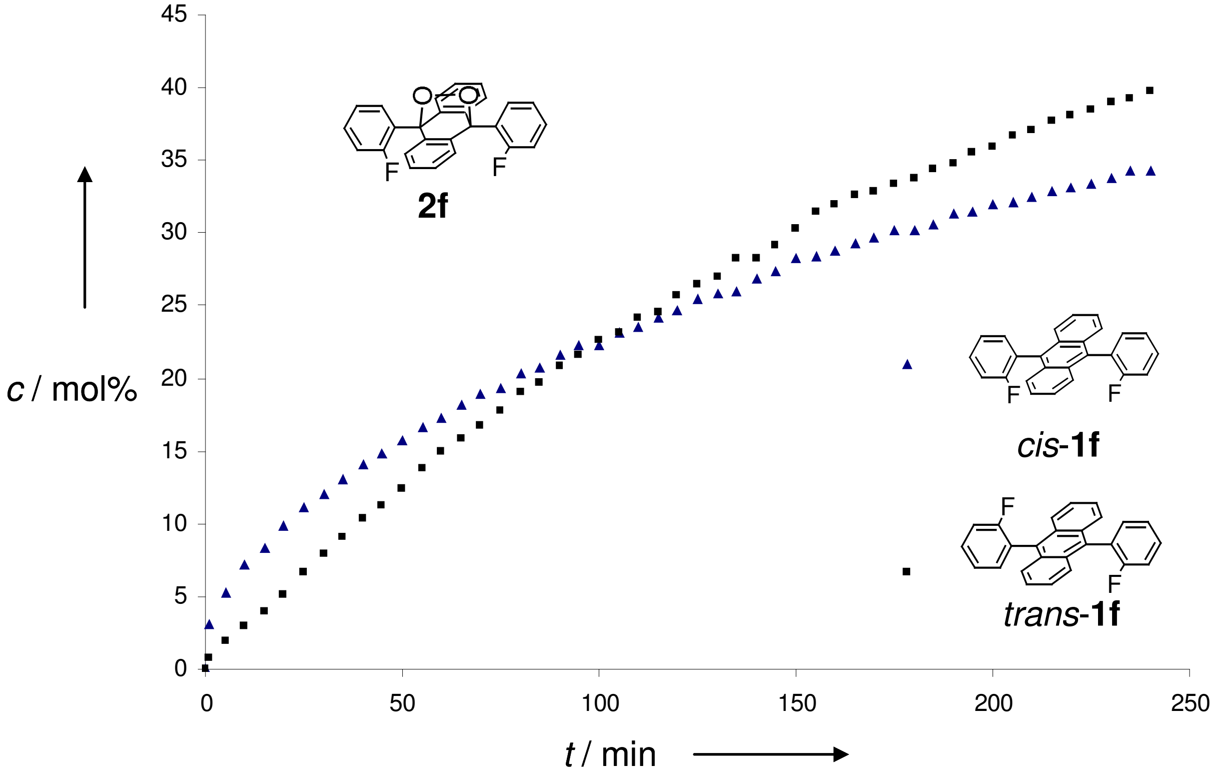


Figure S7. Evolution of *cis*-**1f** and *trans*-**1f** from the endoperoxide **2f** upon heating at 100 °C.

UV-vis spectra and optical images of 2f and 1f in chloroform:

The optical images were taken by using a consumer digital camera (Canon) from solutions of **2f** and **1f** in chloroform (10^{-4} M) in a glass vial. The samples were illuminated with UV-lamp at 366 nm. The UV-vis spectra were measured from solutions of **2f** and **1f** in chloroform at 10^{-6} M.

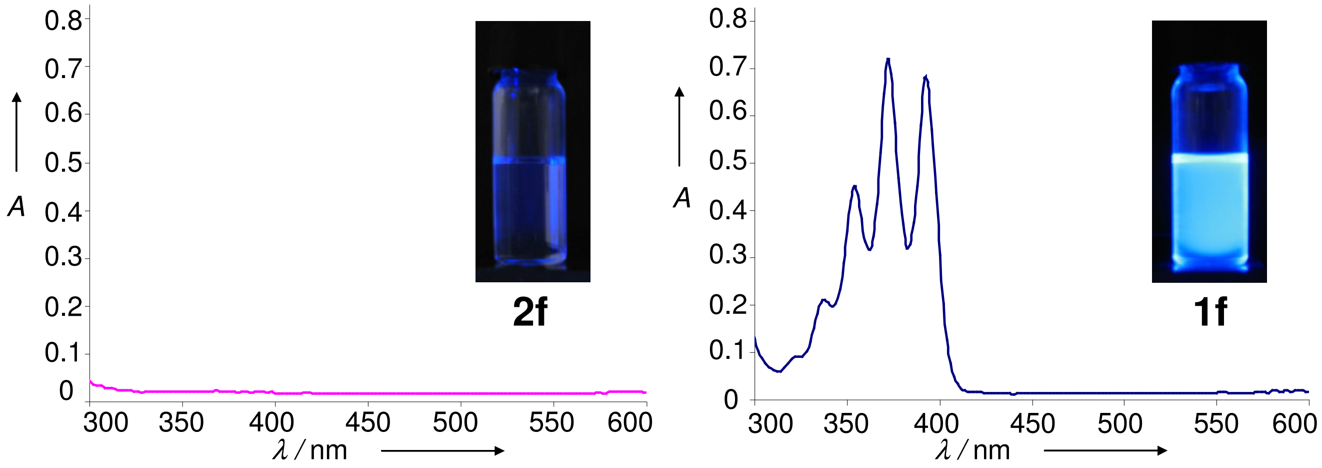


Figure S8. UV-vis spectra and photographical images (insets) of endoperoxide **2f** and anthracene **1f** in chloroform.