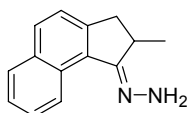


Supplementary Information

General Remarks

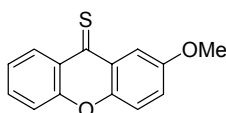
The high-resolution one- and two-dimensional ^1H NMR spectra were obtained using a Varian Gemini-200, Varian VXR-300, Varian Mercury Plus and a Varian Unity Plus Varian-500 operating at 199.97, 299.97, 399.93 and 499.86 MHz, respectively, for the ^1H nucleus. ^{13}C NMR spectra were recorded on a Varian Gemini-200, Varian VXR-300, Varian Mercury Plus and a Varian Unity Plus Varian-500 operating at 50.29, 75.43, 100.57 and 125.70 MHz, respectively. Chemical shifts are reported in δ units (ppm) relative to the residual deuterated solvent signals of CHCl_3 (^1H NMR: δ 7.26 ppm; ^{13}C NMR: δ 77.0 ppm). The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). One-dimensional ^1H NMR spectra were recorded using the acquisition parameters: $\pi/2$ pulse width, 6.5 μs ; spectral width, 6.000 Hz; data size, 16 K; recycling delay, 1 s; number of transients, 32; temperature 298 K. Melting points were taken on a Mettler FP-2 melting point apparatus, equipped with a Mettler FP-21 microscope. MS (EI) and HRMS (EI) spectra were obtained with a Jeol JMS-600 spectrometer. Elemental analyses were performed in the microanalytical department with a Foss-Heraeus CHN-O-Rapid or a EuroVector Euro EA Elemental Analyzer. The average value of duplo measurements are reported. Chemicals were used as received from Acros, Aldrich, Fluka or Merck. Ketones **3**¹ and **11**² and thioketones **7a**³, **7b**⁴, **7c**⁵, **7d**⁶, **7e**⁵ and **7g**⁵ were prepared according to published procedures.

(2-Methyl-2,3-dihydro-cyclopenta[*a*]naphthalen-1-ylidene)-hydrazine (**4**)



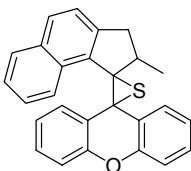
A mixture of ketone **3** (0.90 g, 4.6 mmol) was heated under reflux in pure hydrazine monohydrate (20 ml) for 3d. The reaction mixture was then poured in water (100 ml) and extracted with ether (2x 100ml). The combined ether layers were washed with brine (100 ml), dried (Na_2SO_4) and all volatiles were removed under reduced pressure giving the hydrazone **4** as a brown oil (0.80 g, 3.8 mmol, 83%); ^1H (300 MHz, CDCl_3) δ 1.31-1.33 (d, J = 7.0 Hz, 3H), 2.68-2.73 (d, J = 15.4 Hz, 1H), 3.35-3.48 (m, 2H), 5.38 (br s, 2H), 7.35-7.38 (d, J = 8.4 Hz, 1H), 7.45-7.59 (m, 2H), 7.75-7.78 (d, J = 8.1 Hz, 1H), 7.83-7.86 (d, J = 8.1 Hz, 1H), 9.19-9.22 (d, J = 8.4 Hz, 1H); ^{13}C (75 MHz, CDCl_3) δ 17.0 (q), 32.4 (d), 38.5 (t), 123.5 (d), 125.4 (d), 125.5 (d), 127.0 (d), 128.1 (d), 129.1 (s), 129.8 (d), 131.3 (s), 133.0 (s), 144.7 (s), 162.2 (s); m/z (EI, %) = 210 (M^+ , 100); HRMS (EI): calcd. for $\text{C}_{14}\text{H}_{14}\text{N}_2$: 210.1157, found 210.1151.

2-Methoxy-9*H*-xanthene-9-thione (**7f**)



A mixture of ketone **11** (1.0 g, 4.4 mmol) was heated at reflux overnight in toluene (40 ml) in presence of P_4S_{10} (2.1 g, 4.7 mmol). The hot reaction mixture was filtered and the residue was washed with a small amount of CH_2Cl_2 . The solid obtained after removal of the volatiles was purified using column chromatography (SiO_2 , heptane:ethyl acetate=16:1, R_f =0.37) and the thioketone **7f** was obtained as a light green solid (0.70 g, 2.9 mmol, 66%); m.p. 158.7-159.0°C; ^1H (300 MHz, CDCl_3) δ 3.95 (s, 3H), 7.35-7.51 (m, 4H), 7.72-7.74 (m, 1H), 8.14-8.15 (d, J = 2.9 Hz, 1H), 8.75-8.77 (d, J = 8.1 Hz, 1H); ^{13}C (100 MHz, CDCl_3) δ 55.8 (q), 108.6 (d), 118.2 (d), 119.6 (d), 124.5 (d), 125.4 (d), 128.5 (s), 129.8 (d), 134.5 (d), 145.3 (s), 150.3 (s), 156.6 (s), 203.4 (s); m/z (EI, %) = 242 (M^+ , 100); HRMS (EI): calcd. for $\text{C}_{14}\text{H}_{10}\text{O}_2\text{S}$: 242.0399, found 242.0401.

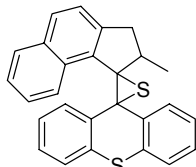
Dispiro[2,3-dihydro-2-methyl-1*H*-cyclopenta[*a*]naphthalene-1,2'-thiirane-3',9''-(9''*H*-xanthene)] (**8a**)



A solution of hydrazone **4** (200 mg, 0.95 mmol) in DMF (10 ml) was cooled to -50°C and [bis(trifluoroacetoxy)iodo]benzene **5** (400 mg, 0.93 mmol) was added. After stirring for approximately 5s, thioketone **7a** (120 mg, 0.57 mmol) was added and the cooling bath was removed. The reaction mixture was allowed to reach room temperature gradually. Additional ethyl acetate (100 ml) was added and the reaction mixture was extracted with water (5x 100ml). Drying of the organic layers (Na_2SO_4) and removal of the organic volatiles under reduced pressure gave a greenish oil which was purified by column chromatography (SiO_2 , heptane:ethyl acetate= 50:1, R_f = 0.55) giving a mixture of thioketone **7a** and the episulfide **8a**. The episulfide **8a** (140 mg, 0.36 mmol, 63%) was recrystallized from ethanol and obtained as a colorless solid consisting of a single diastereomer according to ^1H NMR; m.p. 220.4-220.6°C. Crystal suitable for X-ray crystallographic analysis were grown by slow diffusion of acetonitrile into a solution of chloroform; ^1H (400 MHz, CDCl_3) δ 1.07-1.09 (d, J = 7.0 Hz, 3H), 1.85-1.92 (m, 1H), 2.23-2.27 (d, J = 15.4 Hz, 1H), 2.89-2.94 (dd, J = 15.4, 5.9 Hz, 1H), 6.48-6.53 (m, 1H), 6.73-6.81 (m, 2H), 7.12-7.21 (m, 3H), 7.25-7.34 (m, 2H), 7.37-7.41 (m, 1H), 7.48-7.50 (d, J = 8.1 Hz, 1H), 7.56-7.58 (d, J = 8.1 Hz, 1H), 7.60-7.64 (m, 2H), 9.26-9.28 (d, J = 8.8 Hz, 1H); ^{13}C (75 MHz, CDCl_3) δ 19.8 (q), 36.9 (t), 41.7 (d), 53.7 (s), 70.4 (s), 115.0 (d), 116.0 (d), 122.0 (d), 123.0 (d), 123.3 (d), 124.4 (d), 126.7 (s), 127.8 (d), 127.9 (d), 128.2 (d), 128.3 (d), 129.0 (d), 129.4 (d), 131.7 (s), 132.0 (s), 132.8 (s), 141.3 (s), 155.1 (s), 156.0

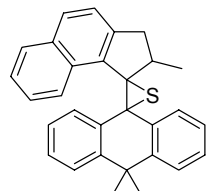
(s), two (d) and one (s) were not observed; m/z (EI, %) = 392 (M^+ , 100); HRMS (EI): calcd. for $C_{27}H_{20}OS$: 392.1219, found 392.1235; Ele. anal., calc. (%): C, 82.6; H, 5.1; found (%): C, 82.6; H, 5.2.

Dispiro[2,3-dihydro-2-methyl-1H-cyclopenta[a]naphthalene-1,2'-thiirane-3',9''-(9''H-thioxanthene)] (8b)



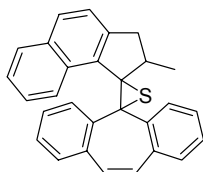
Following the procedure used for the preparation of episulfide **8a**, hydrazone **4** (190 mg, 0.90 mmol) was allowed to react with [bis(trifluoroacetoxy)iodo]benzene **4.65** (400 mg, 0.93 mmol) and thioketone **7b** (200 mg, 0.88 mmol) in DMF (10 ml). After the standard work-up procedure, the episulfide **8b** was obtained as a slightly yellow solid (210 mg, 0.51 mmol, 58%) after purification by column chromatography (SiO_2 , heptane:ethyl acetate= 50:1, R_f = 0.65); m.p. 221.4-222.1°C; 1H NMR (400 MHz, $CDCl_3$) δ 1.07-1.09 (d, J = 7.0 Hz, 3H), 2.38-2.42 (d, J = 15.4 Hz, 1H), 3.46-3.52 (dd, J = 15.4, 6.6 Hz, 1H), 6.73-6.77 (m, 1H), 6.88-6.93 (m, 1H), 6.96-6.98 (dd, J = 7.7, 0.7 Hz, 1H), 7.15-7.26 (m, 4H), 7.29-7.33 (m, 1H), 7.44-7.45 (d, J = 7.7 Hz, 1H), 7.51-7.55 (m, 2H), 7.70-7.72 (dd, J = 7.7, 1.1 Hz, 1H), 7.90-7.92 (d, J = 7.7 Hz, 1H), 8.98-9.00 (d, J = 7.3 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 21.7 (q), 38.1 (t), 40.6 (d), 62.4 (s), 72.0 (s), 123.5 (d), 124.1 (d), 124.2 (d), 124.8 (d), 125.7 (d), 126.42 (d), 126.44 (d), 126.48 (d), 126.78 (d), 126.81 (d), 127.6 (d), 128.8 (d), 129.3 (d), 130.8 (d), 131.1 (s), 131.5 (s), 132.6 (s), 134.8 (s), 135.7 (s), 136.6 (s), 139.4 (s), 142.5 (s); m/z (EI, %) = 408 (M^+ , 100); HRMS (EI): calcd. for $C_{27}H_{20}S_2$: 408.1006, found 408.1010.

Dispiro[2,3-dihydro-2-methyl-1H-cyclopenta[a]naphthalene-1,2'-thiirane-3',9''-(10'',10''-dimethyl-9''(10''H)-anthracene)] (8c)



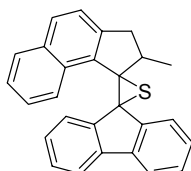
Following the procedure used for the preparation of episulfide **8a**, hydrazone **4** (200 mg, 0.95 mmol) was allowed to react with [bis(trifluoroacetoxy)iodo]benzene **5** (400 mg, 0.93 mmol) and thioketone **7c** (130 mg, 0.55 mmol) in DMF (10 ml). After the standard work-up procedure, the episulfide **8c** was obtained as a white solid (180 mg, 0.43 mmol, 79%) after purification by column chromatography (SiO_2 , heptane:ethyl acetate= 50:1, R_f = 0.60). An analytically pure sample was obtained by recrystallization from a mixture of ethanol and ethyl acetate; m.p. 202.1-204.1°C; 1H (300 MHz, $CDCl_3$) δ 1.10 (s, 3H), 1.20-1.22 (d, J = 7.3 Hz, 3H), 1.75 (s, 3H), 2.03-2.08 (m, 1H), 2.30-2.36 (d, J = 16.5 Hz, 1H), 2.96-3.04 (dd, J = 16.5 Hz, 7.3 Hz, 1H), 6.84-6.95 (m, 2H), 7.09-7.12 (d, J = 8.1 Hz, 1H), 7.16-7.18 (d, J = 7.3 Hz, 1H), 7.24-7.39 (m, 4H), 7.54-7.60 (m, 3H), 7.85-7.87 (d, J = 7.0 Hz, 1H), 8.21-8.23 (d, J = 7.7 Hz, 1H), 9.47-9.50 (d, J = 8.4 Hz, 1H); ^{13}C (75 MHz, $CDCl_3$) δ 22.9 (q), 26.8 (q), 33.3 (q), 37.5 (t), 38.8 (d), 39.3 (s), 62.4 (s), 74.1 (s), 122.8 (d), 123.1 (d), 124.0 (d), 124.1 (d), 124.6 (d), 124.8 (d), 125.0 (d), 125.1 (d), 127.1 (d), 127.7 (d), 128.1 (d), 129.8 (d), 131.8 (s), 131.9 (d), 132.4 (s), 133.2 (s), 133.9 (s), 138.1 (s), 142.2 (s), 147.3 (s), 147.5 (s); m/z (EI, %) = 418 (M^+ , 100); HRMS (EI): calcd. for $C_{30}H_{26}S$: 418.1755, found 418.1745.

Dispiro[2,3-dihydro-2-methyl-1H-cyclopenta[a]naphthalene-1,2'-thiirane-3',5''-(5''H)-dibenzo[a,d]cycloheptene)] (8d)



Following the procedure used for the preparation of episulfide **8a**, hydrazone **4** (280 mg, 1.33 mmol) was allowed to react with [bis(trifluoroacetoxy)iodo]benzene **5** (400 mg, 0.93 mmol) and thioketone **7d** (100 mg, 0.45 mmol) in DMF (10 ml). After the standard work-up procedure, the episulfide **8d** was obtained as a white solid (80 mg, 0.20 mmol, 44%) after purification by column chromatography (SiO_2 , heptane:ethyl acetate= 50:1, R_f = 0.80); 1H NMR (300 MHz, $CDCl_3$) δ 1.05-1.07 (d, J = 7.0 Hz, 3H), 1.38-1.47 (m, 1H), 2.47-2.52 (d, J = 15.4 Hz, 1H), 3.29-3.37 (dd, J = 15.4, 6.6 Hz, 1H), 6.06-6.10 (d, J = 11.7 Hz, 1H), 6.55-6.58 (d, J = 7.7 Hz, 1H), 6.79-6.94 (m, 3H), 7.07-7.42 (m, 4H), 7.52-7.55 (d, J = 8.4 Hz, 1H), 7.58-7.61 (d, J = 8.4 Hz, 1H), 7.72-7.75 (d, J = 7.7 Hz, 1H), 7.91-7.94 (d, J = 7.7 Hz, 1H), 8.32-8.35 (d, J = 8.4 Hz, 1H); ^{13}C (75 MHz, $CDCl_3$) δ 23.1 (q), 38.2 (t), 39.6 (t), 123.5 (d), 123.9(d), 124.3 (2xd), 126.0 (d), 126.3 (d), 126.7 (d), 127.3 (d), 127.5 (d), 127.9 (d), 128.5 (d), 128.9 (d), 129.3 (d), 130.0 (d), 130.2 (d), 130.4 (d), 131.1 (s), 132.4 (s), 134.2 (s), 134.7 (s), 136.6 (s), 140.8 (s), 141.8 (s), one (s) was not observed; m/z (EI, %) = 402 (M^+ , 100), 189 (53); HRMS (EI): calcd. for $C_{29}H_{22}S$: 402.1442, found 402.1432.

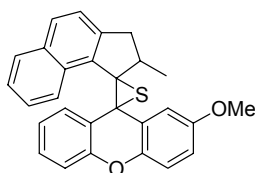
Dispiro[9H-fluorene-9,2'thiirane-3',1''-(2''-methyl-2'',3''-dihydro-1H-cyclopenta[a]naphthalene)] (8e)



To a stirred solution of fluorenone (0.540 g, 3 mmol) in toluene (9 mL) was added Lawesson's reagent (0.909 g, 2.25 mmol). The mixture was heated at 80 °C until a dark green colour was observed (approx. 1.5 h) and was then cooled under an atmosphere of nitrogen and poured onto

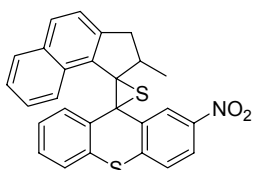
a SiO₂ column. After rapid chromatography, using a mixture hexane / CH₂Cl₂ 9:1 as the eluent, the green fluid from the column was directly added to a stirred solution of diazo compound prepared by addition of bis(trifluoroacetoxy)iodobenzene **5** (1.290 g, 3 mmol) to a solution of hydrazone **4** (0.630 g, 3 mmol) in DMF (6 mL) at -30 °C. The reaction was allowed to warm to room temperature and the solvents were removed under reduced pressure. The resulting oil was washed with a sat. sol. of NH₄Cl (25 mL) and extracted with ether, which was washed with H₂O, dried over MgSO₄ and concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO₂, pentane:ether=9:1) affording 0.542 g (48%) of **8e** as a white solid; ¹H NMR (300 MHz, CDCl₃) δ 1.25-1.28 (d, *J*= 7.0 Hz, 3H), 2.33-2.28 (d, *J*= 15.4 Hz, 1H), 2.72-2.79 (dd, *J*= 15.4, 5.5 Hz, 1H), 3.15-3.19 (m, 1H), 6.59-6.64 (m, 1H), 7.05-7.72 (m, 11H), 7.83-7.86 (d, *J*= 8.1 Hz, 1H), 9.74-9.77 (d, *J*= 8.8 Hz, 1H); ¹³C (75 MHz, CDCl₃) δ 19.5 (q), 37.5 (t), 43.1 (d), 56.9 (s), 67.0 (s), 119.4 (d), 119.7 (d), 123.8 (d), 124.1 (d), 124.5 (d), 125.4 (d), 125.7 (2xd), 126.1 (d), 126.2 (d), 127.4 (d), 127.9 (d), 129.0 (d), 129.6 (d), 129.6 (d), 132.7 (s), 133.0 (s), 133.6 (s), 140.9 (s), 142.6 (s), 143.6 (s), 145.4 (s), one (s) was not observed; *m/z* (EI, %) = 376 (*M*⁺, 98), 344 (86), 329 (100), 165 (75); HRMS (EI): calcd. for C₂₇H₂₀S: 376.1286, found 376.1289.

Dispiro[2,3-dihydro-2-methyl-1H-cyclopenta[*a*]naphthalene-1,2'-thiirane-3',9''-(2''-methoxy-9''H-xanthene)] (8f)



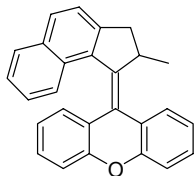
Following the procedure used for the preparation of episulfide **8a**, hydrazone **4** (550 mg, 2.6 mmol) was allowed to react with [bis(trifluoroacetoxy)iodo]benzene **5** (1.1 g, 2.55 mmol) and thioketone **7f** (380 mg, 1.57 mmol) in DMF (15 ml). After the standard work-up procedure, the episulfides **8f** were obtained as a mixture of two isomers as a slightly yellow solid (590 mg, 1.40 mmol, 89%) after purification by column chromatography (SiO₂, heptane:ethyl acetate= 50:1, *R*_f= 0.35). The isomers of **8f** were not separated but directly used in the subsequent reaction. Spectral data are given for the mixture of isomers; ¹H NMR (400 MHz, CDCl₃) δ 1.17-1.19 (d, *J*= 7.0 Hz, 3H), 1.19-1.20 (d, *J*= 7.0 Hz, 3H), 1.94-1.99 (m, 1H), 2.08-2.13 (m, 1H), 2.34-2.38 (d, *J*= 15.4 Hz, 1H), 2.36-2.40 (d, *J*= 15.4 Hz, 1H), 3.01-3.09 (m, 2H), 3.66 (s, 3H), 3.97 (s, 3H), 6.43-6.46 (dd, *J*= 8.8, 2.9 Hz, 1H), 6.58-6.62 (m, 1H), 6.78-6.90 (m, 3H), 6.95-6.98 (dd, *J*= 8.8, 3.3 Hz, 1H), 7.18-7.73 (m, 18H), 9.35-9.37 (d, *J*= 8.4 Hz, 1H), 9.41-9.43 (d, *J*= 8.8 Hz, 1H); ¹³C (100 MHz, CDCl₃) δ 19.6 (q), 19.7 (q), 36.84 (t), 36.85 (t), 41.6 (d), 41.8 (d), 53.9 (s), 54.0 (s), 55.4 (q), 55.6 (q), 70.3 (s), 70.4 (s), 112.9 (d), 113.6 (d), 113.7 (d), 114.2 (d), 115.0 (d), 115.8 (d), 116.0 (d), 116.8 (d), 121.8 (d), 122.7 (s), 122.8 (d), 123.4 (d), 124.0 (d), 124.1 (s), 124.2 (d), 124.26 (d), 124.27 (d), 124.20 (d), 124.6 (d), 126.4 (s), 127.75 (d), 127.78 (s), 127.9 (d), 128.16 (d), 128.20 (d), 129.00 (d), 129.05 (d), 129.3 (d), 131.47 (s), 131.51 (s), 131.94 (s), 131.97 (s), 132.70 (s), 132.75 (s), 141.28 (s), 141.33 (s), 149.3 (s), 150.1 (s), 154.4 (s), 155.4 (s), 156.3 (s); *m/z* (EI, %) = 422 (*M*⁺, 100), 390 (45); HRMS (EI): calcd. for C₂₈H₂₂O₂S: 422.1340, found 422.1338.

Dispiro[2,3-dihydro-2-methyl-1H-cyclopenta[*a*]naphthalene-1,2'-thiirane-3',9''-(2''-nitro-9''H-thioxanthene)] (8g)



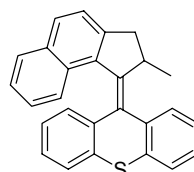
Following the procedure used for the preparation of episulfide **8a**, hydrazone **4** (200 mg, 0.95 mmol) was allowed to react with [bis(trifluoroacetoxy)iodo]benzene **5** (400 mg, 0.93 mmol) and thioketone **7g** (120 mg, 0.44 mmol) in DMF (10 ml). After the standard work-up procedure, the episulfide **8g** was obtained as a mixture of two isomers as a fluffy yellow solid (130 mg, 0.29 mmol, 65%) after purification by column chromatography (SiO₂, heptane:ethyl acetate= 50:1, *R*_f= 0.22). The isomers of **8g** were not separated but directly used in the subsequent reaction. Spectral data are given for the mixture of isomers; ¹H NMR (300 MHz, CDCl₃) δ 1.11-1.15 (m, 6H), 1.43-1.54 (m, 1H), 1.55-1.61 (m, 1H), 2.44-2.49 (d, *J*= 15.4 Hz, 2H), 3.41-3.48 (m, 2H), 6.77-6.81 (m, 1H), 6.93-7.57 (m, 18H), 7.74-7.77 (d, *J*= 7.7 Hz, 1H), 7.94-7.96 (d, *J*= 7.7 Hz, 1H), 8.08-8.12 (m, 1H), 8.57-8.58 (d, *J*= 2.2 Hz, 1H), 8.77-8.78 (d, *J*= 2.2 Hz, 1H), 8.96-9.00 (m, 2H); ¹³C (50 MHz, CDCl₃) δ 21.5 (q), 21.7 (q), 37.9 (t), 38.1 (t), 40.2 (d), 40.8 (d), 60.8 (s), 61.2 (s), 71.9 (s), 72.2 (s), 121.1 (d), 121.9 (d), 123.5 (d), 123.6 (d), 123.8 (d), 124.2 (d), 124.4 (d), 124.5 (d), 124.6 (d), 126.2 (d), 126.4 (d), 126.5 (d), 126.6 (d), 126.7 (d), 127.1 (d), 127.3 (d), 127.4 (d), 127.6 (d), 127.7 (d), 127.9 (d), 129.2 (d), 129.7 (d), 130.5 (s), 130.7 (s), 130.8 (s), 131.5 (d), 132.6 (s), 132.7 (s), 133.3 (s), 133.8 (s), 134.4 (s), 135.8 (s), 137.4 (s), 140.9 (s), 142.2 (s), 142.4 (s), 144.1 (s), 145.1 (s), 145.4 (s), 146.6 (s), three (d) and one (s) were not observed individually; *m/z* (EI, %) = 453 (*M*⁺, 100); HRMS (EI): calcd. for C₂₇H₁₉NO₂S₂: 453.0857, found 453.0837.

9-(2'-Methyl-2',3'-dihydro-1'H-cyclopenta[a]naphthalen-1'-ylidene)-9H-xanthene (2a)



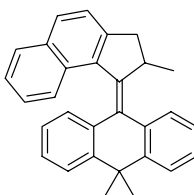
Following the procedure described for **2b**, episulfide **8a** (100 mg, 2.55 mmol) was reacted with triphenylphosphine. After removal of the triphenylphosphine by reaction with methyl iodide, the alkene **2a** was obtained pure by column chromatography (SiO₂, heptane:ethyl acetate= 50:1, *R*_f= 0.48) as a green solid (80 mg, 2.22 mmol, 87%); m.p. 227.4-227.5°C; ¹H NMR (300 MHz, CDCl₃) δ 0.93-0.95 (d, *J*= 7.0 Hz, 3H), 2.66-2.71 (d, *J*= 15.7 Hz, 1H), 3.67-3.74 (dd, *J*= 15.7, 6.6 Hz, 1H), 4.39-4.48 (m, 1H), 6.38-6.43 (m, 1H), 6.70-6.73 (d, *J*= 7.7 Hz, 1H), 6.84-6.90 (m, 1H), 7.00-7.05 (m, 1H), 7.10-7.13 (d, *J*= 8.4 Hz, 1H), 7.16-7.29 (m, 5H), 7.43-7.45 (d, *J*= 8.0 Hz, 1H), 7.70-7.73 (d, *J*= 8.1 Hz, 2H), 8.07-8.10 (d, *J*= 7.7 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 17.9 (q), 39.7 (d), 41.1 (t), 116.5 (d), 117.1 (d), 120.1 (s), 122.8 (d), 123.4 (d), 123.7 (d), 124.2 (d), 124.8 (d), 125.4 (d), 126.5 (d), 126.7 (s), 127.3 (d), 127.8 (s), 127.9 (d), 128.0 (d), 128.5 (s), 128.7 (d), 129.7 (d), 133.0 (s), 136.7 (s), 143.9 (s), 145.9 (s), 153.8 (s), 154.0 (s); *m/z* (EI, %) = 360 (*M*⁺, 100), 345 (54); HRMS (EI): calcd. for C₂₇H₂₀O: 360.1514, found 360.1513.

9-(2'-Methyl-2',3'-dihydro-1'H-cyclopenta[a]naphthalen-1'-ylidene)-9H-thioxanthene (2b)



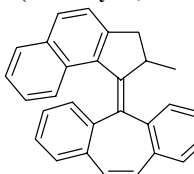
A solution of episulfide **8b** (66 mg, 162 μmol) was heated at reflux overnight in *p*-xylene (15 ml) in presence of excess of triphenylphosphine (300 mg, 1.1 mmol). The *p*-xylene was removed under reduced pressure and the fractions containing the desired alkene and triphenylphosphine were collected after column chromatography (SiO₂, heptane: ethyl acetate, *R*_f= 0.48). The mixture containing the alkene **2b** and triphenylphosphine was stirred overnight in a mixture of methyl iodide (1.0 ml) and DMF (10 ml). The reaction mixture was poured into water (200 ml) and ethyl acetate (100 ml) was added. The organic layer was then washed with water (5x 100 ml) and brine (100 ml) and dried (Na₂SO₄). After removal of all volatiles, the alkene **2b** could be obtained after column chromatography (SiO₂, heptane: ethyl acetate, *R*_f= 0.48) as a slightly yellow solid (53 mg, 141 μmol, 87%); m.p. 200.9-201.9°C; ¹H NMR (400 MHz, CDCl₃) δ 0.78-0.79 (d, *J*= 6.6 Hz, 3H), 2.61-2.65 (d, *J*= 15.4 Hz, 1H), 3.63-3.68 (dd, *J*= 15.4, 6.2 Hz, 1H), 4.28-4.34 (m, 1H), 6.61-6.65 (m, 1H), 6.73-6.81 (m, 2H), 6.86-6.89 (d, *J*= 8.8 Hz, 1H), 6.99-7.03 (m, 1H), 7.15-7.26 (m, 2H), 7.32-7.36 (m, 1H), 7.42-7.44 (d, *J*= 8.4 Hz, 1H), 7.57-7.60 (dd, *J*= 7.7, 1.1 Hz, 1H), 7.61-7.63 (dd, *J*= 7.7, 1.1 Hz, 1H), 7.68-7.70 (d, *J*= 7.7 Hz, 1H), 7.72-7.74 (d, *J*= 8.1 Hz, 1H), 7.80-7.82 (dd, *J*= 7.7, 1.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 19.4 (q), 37.8 (d), 39.7 (t), 123.7 (d), 124.1 (d), 124.7 (d), 125.9 (d), 126.16 (d), 126.18 (d), 126.22 (d), 126.28 (d), 127.4 (d), 127.68 (d), 127.70 (d), 127.72 (d), 128.5 (s), 128.6 (d), 128.9 (s), 130.0 (d), 132.9 (s), 135.2 (s), 135.4 (s), 135.7 (s), 137.9 (s), 140.2 (s), 145.8 (s), 145.9 (s); *m/z* (EI, %) = 376 (*M*⁺, 100), 235 (87); HRMS (EI): calcd. for C₂₇H₂₀S: 376.1286, found 376.1267.

9,9-Dimethyl-10-(2-methyl-2,3-dihydro-cyclopenta[a]naphthalen-1-ylidene)-9,10-dihydro-anthracene (2c)



Following the procedure described for **2b**, episulfide **8c** (120 mg, 290 μmol) was reacted with triphenylphosphine. After removal of the triphenylphosphine by reaction with methyl iodide, the alkene was obtained pure by column chromatography (SiO₂, heptane:ethyl acetate= 50:1, *R*_f= 0.75) as a white solid (100 mg, 260 μmol, 90%); m.p. 228.5-228.9°C; ¹H NMR (300 MHz, CDCl₃) δ 0.84-0.86 (d, *J*= 7.0 Hz, 3H), 1.81 (s, 3H), 1.97 (s, 3H), 2.61-2.66 (d, *J*= 15.8 Hz, 1H), 3.64-3.71 (dd, *J*= 15.8, 6.2 Hz, 1H), 4.51-4.56 (m, 1H), 6.58-6.63 (m, 1H), 6.75-6.82 (m, 2H), 6.99-7.02 (d, *J*= 8.4 Hz, 1H), 7.05-7.10 (m, 1H), 7.17-7.28 (m, 3H), 7.45-7.48 (d, *J*= 8.4 Hz, 1H), 7.53-7.58 (m, 1H), 7.72-7.75 (m, 2H), 7.85-7.88 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 18.7 (q), 24.7 (q), 29.4 (q), 37.7 (d), 39.6 (t), 40.5 (s), 123.1 (d), 123.2 (d), 124.01 (d), 124.05 (d), 124.2 (d), 125.2 (d), 125.3 (d), 126.0 (d), 126.3 (d), 126.99 (d), 127.02 (d), 127.5 (d), 127.9 (d), 129.1 (s), 129.5 (s), 129.8 (d), 133.2 (s), 135.9 (s), 139.8 (s), 140.4 (s), 143.4 (s), 145.5 (s), 146.0 (s), 147.2 (s); *m/z* (EI, %) = 386 (*M*⁺, 100), 371 (57); HRMS (EI): calcd. for C₃₀H₂₆: 386.2035, found 386.2048.

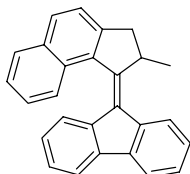
5-(2-Methyl-2,3-dihydro-cyclopenta[a]naphthalen-1-ylidene)-5H-dibenzo[a,d]cycloheptene (2d)



Following the procedure described for **2b**, episulfide **8d** (40 mg, 100 μmol) was reacted with triphenylphosphine. After removal of the triphenylphosphine by reaction with methyl iodide, the alkene was obtained pure by column chromatography (SiO₂, heptane:ethyl acetate= 50:1, *R*_f= 0.70) as a white solid (30 mg, 81 μmol, 81%); ¹H NMR (300 MHz, CDCl₃) δ 0.69-0.71 (d, *J*= 7.0 Hz, 3H), 2.50-2.55 (d, *J*= 15.7 Hz, 1H), 3.50-3.57 (dd, *J*= 15.7, 6.6 Hz, 1H), 3.73-3.78 (m, 1H), 6.73-6.83 (m, 3H), 7.08-7.50 (m, 11H), 7.66-7.72 (m, 2H); ¹³C NMR (75 MHz,

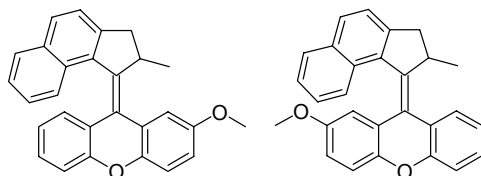
CDCl_3) δ 19.8 (q), 38.1 (d), 39.1 (t), 123.85 (d), 123.90 (d), 124.4 (d), 126.0 (d), 126.2 (d), 126.5 (d), 127.6 (d), 127.9 (d), 128.2 (d), 128.7 (d), 129.1 (s), 129.5 (s), 131.2 (d), 131.6 (d), 132.4 (s), 132.9 (s), 134.6 (s), 135.1 (s), 135.3 (s), 139.2 (s), 142.2 (s), 144.9 (s), 146.8 (s), one (s) was not observed; m/z (EI, %) = 370 (M^+ , 100), 229 (47); HRMS (EI): calcd. for $\text{C}_{27}\text{H}_{20}\text{S}_2$: 370.1722, found 370.1704.

9-(2-Methyl-2,3-dihydro-cyclopenta[*a*]naphthalen-1-ylidene)-9*H*-fluorene (2e)



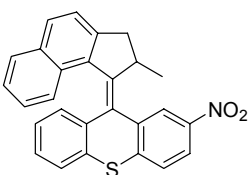
A solution of **8e** (0.190 g, 0.5 mmol) and triphenylphosphine (0.393 g, 1.50 mmol) in xylene (5 mL) was stirred under reflux for 3 h. The reaction was then cooled to room temperature and methyl iodide (0.093 mL, 3 mmol) was added. After 30 min the volatiles were removed under reduced pressure and the crude residue was purified by column chromatography (SiO_2 , pentane:ether=9.1) affording 0.141 g, (81 %) of **2e** as a yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 1.24-1.26 (d, J = 6.6 Hz, 3H), 2.60-2.65 (d, J = 15.0 Hz, 1H), 3.41-3.48 (dd, J = 15.0, 5.5 Hz, 1H), 4.18-4.26 (m, 1H), 6.58-6.70 (m, 2H), 7.05-7.35 (m, 5H), 7.43-7.45 (d, J = 8.1 Hz, 1H), 7.61-7.86 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 19.3 (q), 41.9 (t), 45.5 (d), 118.9 (d), 119.6 (d), 124.0 (d), 124.1 (d), 125.3 (d), 125.8 (d), 125.9 (d), 126.5 (d), 126.8 (d), 126.9 (d), 127.5 (d), 128.6 (d), 129.8 (d), 130.4 (s), 130.8 (s), 132.6 (d), 136.3 (s), 137.1 (s), 139.5 (s), 139.8 (s), 140.1 (s), 147.4 (s), 151.1 (s); m/z (EI, %) = 344 (M^+ , 81), 329 (100); HRMS (EI): calcd. for $\text{C}_{27}\text{H}_{20}$: 344.1565, found 344.1571.

2-Methoxy-9-(2'-methyl-2',3'-dihydro-1'H-cyclopenta[*a*]naphthalen-1'-ylidene)-9*H*-xanthene (2f)



Following the procedure described for **2b**, episulfide **8f** (570 mg, 1.35 mmol) was reacted with triphenylphosphine. After removal of the solvent, the alkene **2f** was obtained pure after column chromatography (SiO_2 , heptane:ethyl acetate = 50:1, R_f = 0.37) as a slightly green solid as a mixture of *cis*-**2f** and *trans*-**2f** (430 mg, 1.11 mmol, 82%); *cis*-**2f**: ^1H NMR (300 MHz, CDCl_3) δ 0.94-0.96 (d, J = 6.6 Hz, 3H), 2.66-2.71 (d, J = 15.7 Hz, 1H), 2.78 (s, 3H), 3.66-3.73 (dd, J = 15.7, 6.6 Hz, 1H), 4.38-4.49 (m, 1H), 6.18-6.19 (d, J = 2.9 Hz, 1H), 6.57-6.61 (dd, J = 8.8, 2.9 Hz, 1H), 6.89-6.94 (m, 1H), 7.11-7.28 (m, 6H), 7.42-7.45 (d, J = 8.4 Hz, 1H), 7.69-7.73 (m, 2H), 8.05-8.08 (d, J = 8.1 Hz, 1H); m.p. 221.2-223.7°C; *trans*-**2f**: ^1H NMR (300 MHz, CDCl_3 , spectrum derived from a sample containing *cis*-**2f**) δ 0.98-1.00 (d, J = 7.0 Hz, 3H), 2.66-2.71 (d, J = 15.7 Hz, 1H), 3.66-3.73 (dd, J = 15.7, 6.6 Hz, 1H), 3.88 (s, 3H), 4.38-4.48 (m, 1H), 6.35-6.40 (m, 1H), 6.69-6.71 (d, J = 6.2 Hz, 1H), 6.84-6.87 (m, 1H), 6.98-7.03 (m, 1H), 7.62-7.63 (d, J = 2.9 Hz, 1H); due to overlap 8 proton signals could not be assigned individually; ^{13}C NMR (50 MHz, CDCl_3 , data are given for a mixture containing both *cis*-**2f** and *trans*-**2f**) δ 17.9 (q), 18.1 (q), 39.3 (d), 39.9 (d), 40.9 (t), 41.1 (t), 55.3 (q), 55.9 (q), 110.6 (d), 112.1 (d), 112.9 (d), 116.1 (d), 116.5 (d), 117.0 (d), 117.3 (d), 117.4 (d), 120.2 (s), 120.3 (s), 122.5 (d), 123.1 (d), 123.6 (d), 123.7 (d), 124.2 (d), 124.3 (d), 124.8 (d), 125.5 (s), 126.1 (d), 126.4 (d), 126.8 (d), 127.2 (d), 127.4 (d), 127.7 (d), 127.9 (d), 128.0 (d), 128.5 (s), 128.7 (d), 128.8 (s), 129.6 (s), 129.7 (d), 132.9 133.0 136.5 136.7 143.7 145.8 145.9 148.1 148.3 153.9 154.3 155.1 155.5 (s); two (s) and two (d) were not observed individually; m/z (EI, %) = 390 (M^+ , 100), 375 (64); HRMS (EI): calcd. for $\text{C}_{28}\text{H}_{22}\text{O}_2$: 390.1620, found 390.1613.

9-(2-Methyl-2,3-dihydro-cyclopenta[*a*]naphthalen-1-ylidene)-2-nitro-9*H*-thioxanthene (2g)



Following the general procedure described for **2b**, episulfide **8g** (130 mg, 0.29 mmol) was reacted with triphenylphosphine. After workup, the desired alkenes were separated into two fractions using column chromatography (SiO_2 , heptane, ethyl acetate=50:1, R_f = 0.52, R_f 0.44) each containing an isomer of **2g** (isomer 1, 50 mg, 0.12 mmol, isomer 2, 55 mg, 0.13 mmol, combined yield 87%); isomer 1: yellow solid; m.p. 221.5-222.8°C; ^1H NMR (300 MHz, CDCl_3) δ 0.78-0.81 (d, J = 7.0 Hz, 3H), 2.66-2.71 (d, J = 15.7 Hz, 1H), 3.70-3.38 (dd, J = 15.7, 5.9 Hz, 1H), 4.19-4.31 (m, 1H), 6.68-6.86 (m, 4H), 7.05-7.21 (m, 2H), 7.45-7.47 (d, J = 8.1 Hz, 1H), 7.58-7.60 (d, J = 7.7 Hz, 1H), 7.63-7.87 (m, 3H), 8.08-8.12 (m, 1H), 8.69 (s, 1H); ^{13}C (50 MHz, CDCl_3) δ 19.4 (q), 37.9 (d), 39.8 (t), 120.8 (d), 122.6 (d), 123.8 (d), 124.3 (d), 124.9 (d), 125.8 (d), 126.4 (s), 126.9 (d), 127.1 (d), 127.5 (d), 127.9 (d), 128.1 (d), 128.7 (s), 129.0 (d), 130.8 (d), 133.0 (s), 133.8 (s), 134.3 (s), 138.6 (s), 139.1 (s), 144.9 (s), 146.6 (2xs), 148.3 (s); isomer 2: yellow solid; 218.6-219.8°C; ^1H NMR (300 MHz, CDCl_3) δ 0.82-0.84 (d, J = 6.6 Hz, 3H), 2.65-2.71 (d, J = 15.8 Hz, 1H), 3.66-3.73 (dd, J = 15.8, 6.2 Hz, 1H), 4.22-4.37 (m, 1H), 6.70-6.82 (m, 2H), 7.10-7.18 (m, 1H), 7.26-7.31 (m, 1H), 7.3-7.87 (m, 9H); ^{13}C (75 MHz, CDCl_3) δ 19.4 (q), 37.8 (d), 39.7 (t), 120.9 (d), 123.6 (d), 123.9 (d), 124.3 (d), 124.8 (d), 125.2 (d), 126.0 (s), 126.7 (d), 127.2 (d), 127.75 (d), 127.79 (d), 128.0 (d), 128.2 (s), 128.4 (d), 130.9 (d), 133.1 (s), 133.9 (s), 134.0 (s), 136.5 (s), 140.9 (s), 144.2 (s), 146.2 (s), 146.4 (s), 148.6 (s); m/z (EI, %) = 421 (M^+ , 100), 280 (68); HRMS (EI): calcd. for $\text{C}_{27}\text{H}_{19}\text{NO}_2\text{S}_2$: 421.1136, found 421.1140.

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