Supplementary Material (ESI) for Chemical Communications

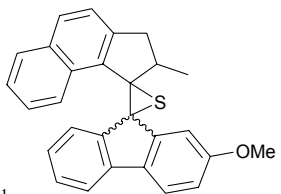
Supporting information.

General:

Chemicals were purchased from Acros, Aldrich, Fluka or Merck. Solvents for extraction and chromatography were technical grade. All solvents used in reactions were freshly distilled from appropriate drying agents before use. All other reagents were recrystallized or distilled as necessary Analytical TLC was performed with Merck silica gel 60 F_{254} plates and visualization was accomplished by UV light. Flash chromatography was carried out using Merck silica gel 60 (230-400 mesh ASTM). NMR spectra were obtained using a Varian Mercury Plus and a Varian Unity Plus Varian-500, operating at 399.93 and 499.86 MHz respectively for the ^{1}H nucleus or at 100.57 and 125.70 MHz respectively for the ^{13}C nucleus. Chemical shifts are reported in δ units (ppm) relative to the residual deuterated solvent signals of $CHCl_3$ (^{1}H 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). MS (EI) spectra were obtained with a Jeol JMS-600 spectrometer. Elemental analyses were performed in with a Foss-Heraeus CHN-O-Rapid or a EuroVector Euro EA Elemental Analyzer. UV measurments were performed on a Hewlet-Packard HP 8543 FT spectrophothometer and CD spectra were recorded on a JASCO J-715 spectropolarimeter and a JASCO PFD-350S/350L Peltier-type FDCD attachment with a temperature control, using Uvasol-grade solvents (Merck). Preparative HPLC was performed on a Gilson HPLC system consisting of a 231XL sampling injector, a 306 (10SC) pump, an 811C dynamic mixer, a 805 manometric module, with a 119 UV-vis detector, and a 202 fraction collector, using the Chiralcel OD (Daicel) column. Elution speed was 1 mL/min. Solvents were distilled and dried before use by standard methodology. Irradiation experiments were performed with a 180 W Oriel Hg-lamp. Photostationary states were ensured by monitoring composition changes in time by taking UV spectra at distinct intervals until no changes were observed. Thermal helix inversions were monitored by CD spectroscopy using the apparatus described above and a JASCO PFD-350S/350L Peltier-type FDCD attachment with a temperature control. 2-Methoxy-fluoren-9-one,[1], (2-methyl-2,3-dihydro-cyclopenta[a]naphthalen-1-ylidene)-hydrazine and (2-Methyl-2,3-dihydro-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene[2] and (3-Methyl-2,3-dihydro-1H-phenanthren-4-ylidene)-hydrazine[3] were synthesized following literature procedures

General procedure for the synthesis of episulfides. To a stirred solution of the corresponding fluorenone in toluene (9 mL) was added Lawesson's reagent (0.909 g, 2.25 mmol). The mixture was heated at 80 ºC until a dark green colour was observed (aprox. 2 h) and then cooled under an atmosphere of nitrogen and poured onto a SiO_2 column. After rapid chromatography, using a mixture hexane / CH_2Cl_2 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(trifluoroacethoxy)iodobenzene (1.290 g, 3 mmol) to a solution of hydrazone (3 mmol) in DMF (6 mL) at -30 ºC. The reaction mixture 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 NH_4Cl (25 mL) and extracted with ether, which was washed with H_2O, dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by column chromatograpy (SiO_2, pentane:ether = 9:1).

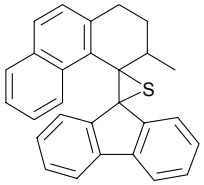
Dispiro[2-methoxy-9H-fluorene-9,2'thiirane-3',1''-(2''-methyl-2'',3''-dihydro-1H-cyclopenta[a]naphthalene)]. The general procedure was followed, using 2-methoxy-fluoren-9-one (0.588 g, 3 mmol) and (2-methyl-2,3-dihydro-cyclopenta[a]naphthalen-1-ylidene)-hydrazine (0.630 g, 3 mmol), affording 0.670 g (55%) of the mixture of episulfides *Z*/*E* (4:1) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3 *E*), 1.22 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3 *Z*), 2.34 (d, $^2J_{HH}$ = 15.4 Hz, 1H, CH_2 *Z* and 1H, CH_2 *E*), 2.71-2.80 (m, 1H, CH_2 *Z* and



[1] S. Dei, E. Teodori, A. Garnier-Suillerot, F. Gualtieri, S. Scapecchi, R. Budriesi, A. Chiarmi, *Biol. & Med. Chem.*, **2001**, *9*, 2673.
[2] M. K. ter Wiel, J. Vicario, S. G. Davey, A. Meetsma and B.L. Feringa, *Org. Biomol. Chem.*, **2005**, *3*, 28.
[3] N. Koumura E. M Geertsema, M. B. van Gelder, A. Meetsma and B. L. Feringa, *J. Am. Chem. Soc.*, **2002**, *124*, 5037.

1H, CH_2 *E*), 2.75 (s, 3H, OCH_3 *Z*), 3.09-3.19 (m, 1H, CH *Z* and 1H, CH *E*), 3.83 (s, OCH_3, *E*), 6.57 (dd, $^3J_{HH}$ = 11.2 Hz, $^4J_{HH}$ = 3.2 Hz, 1H, *Z*), 6.67 (d, $^4J_{HH}$ = 3.2 Hz, 1H, *Z*), 6.89 (dd, $^3J_{HH}$ = 11.2 Hz, $^4J_{HH}$ = 3.6 Hz, 1H, *E*), 6.95 (d, $^4J_{HH}$ = 3.6 Hz, 1H, *E*), 6.98 (t, $^3J_{HH}$ = 9.6 Hz, 1H, *Z* and 1H, *E*), 7.08 (d, $^3J_{HH}$ = 10.8 Hz, 1H, *E*), 7.15 (d, $^3J_{HH}$ = 10.8 Hz, 1H, *Z*), 7.21 (t, $^3J_{HH}$ = 10.8 Hz, 1H, *Z* and 1H, *E*), 7.31 (t, $^3J_{HH}$ = 9.6 Hz, 1H, *Z* and 1H, *E*), 7.38 (d, $^3J_{HH}$ = 11.2 Hz, 1H, *Z* and 1H, *E*), 7.40 (t, $^3J_{HH}$ = 10.8 Hz, 1H, *Z* and 1H, *E*), 7.53 (d, $^3J_{HH}$ = 10.8 Hz, 1H, *Z* and 1H, *E*), 7.55 (d, $^3J_{HH}$ = 9.6 Hz, 1H, *Z* and 1H, *E*), 7.58 (d, $^3J_{HH}$ = 10.8 Hz, 1H, *E*), 7.63 (d, $^3J_{HH}$ = 10.8 Hz, 1H, *Z*), 7.78 (d, $^3J_{HH}$ = 10.8 Hz, 1H, *Z*), 7.86 (d, $^3J_{HH}$ = 10.8 Hz, 1H, *E*), 9.68 (d, $^3J_{HH}$ = 9.6 Hz, 1H, *E*), 9.76 (d, $^3J_{HH}$ = 9.6 Hz, 1H, *Z*). ^{13}C NMR(75 MHz, $CDCl_3$) δ 19.3 (CH_3, *E*,) 19.4 (CH_3, *Z*), 37.6 (CH_2, *Z* and *E*), 42.8 (CH, *E*), 43.0 (CH, *Z*), 54.2 (CHS, *E*), 54.6 (OCH_3, *Z*), 55.6 (CHS, *Z*), 56.7 (CHS, *Z*), 56.9 (CHS, *E*), 67.0 (CHS, *E*), 109.3 (CH, Z), 112.1 (CH, E), 113.4 (CH, *E*), 116.2 (CH, *Z*), 118.6 (CH, *E*), 118.9 (CH, *Z*), 120.2 (CH, *Z*), 120.5 (CH, *E*), 123.7 (CH, *E*), 123.8 (CH, *Z*), 124.0 (CH *Z* and *E*), 124.2 (CH, *Z*), 124.5 (CH, *E*), 124.9 (CH, *Z*), 125.1 (CH, *Z*), 125.3 (CH, *E*), 125.5 (CH, *Z*), 125.7 (CH, *E*), 126.0 (CH *Z*), 127.4 (CH, *E*), 127.9 (CH, *Z*), 129.0 (CH, *E*), 129.2 (CH, *Z*), 129.7 (CH, *Z* and *E*), 132.0 (C, *E*), 132.5 (C, *Z*), 133.0 (C, *Z* and *E*), 133.5 (C, *Z*), 133.6 (C, *E*), 133.9 (C, *Z* and *E*), 140.9 (C, *E*), 141.0 (C, *Z*), 142.6 (C, *E*), 142.9 (C, *E*), 143.2 (C, *E*), 144.9 (C, *Z*), 145.3 (C, *Z*), 147.5 (C, *E*), 158.6 (C, *E*), 158.7 (C, *Z*). *m/z* (EI, %) = 406 (M^+, 4), 374 (100), 359 (77), 327 (26). HRMS (EI): calcd. for $C_{28}H_{22}OS$: 406.139, found 406.138.

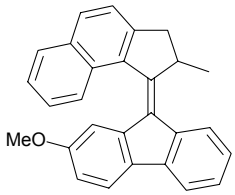
Dispiro [9H-fluorene-9,2'thiirane-3',1''-(2''-methyl-2'',3''-dihydro-1H- phenanthren-4-ylidene)].



The general procedure was followed, using (3-Methyl-2,3-dihydro-1H-phenanthren-4-ylidene)- hydrazine (0.672 g, 3 mmol), affording 0.762 g (65%) of the episulfide as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (m, 1H, CH_2)1.07 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3), 2.58 (m, 1H, CH_2), 2.85 (m, 1H, CH_2), 2.15 (dd, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 3.5 Hz, 1H, CH_2), 3.12 (m, 1H, CH), 5.83 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 6.50 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 6.94 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 7.08 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.35 (t, $^3J_{HH}$ =7.3 Hz, 1H), 7.42 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.44 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.49 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.59 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.62 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 7.71 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.77 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 7.89 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 9.14 (t, $^3J_{HH}$ = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7, (CH_3), 29.4 (CH_2), 29.7 (CH_2), 38.1 (CH), 56.5 (CHS), 59.4 (CHS), 119.1 (CH), 120.3 (CH), 123.2 (CH), 123.9 (CH), 124.4 (CH), 125.2 (CH), 125.4 (CH), 125.5 (CH); 126.0 (CH), 126.7 (CH), 127.4(CH), 127.7 (CH), 128.0 (CH), 128.8 (CH), 131.7 (C), 132.4 (C), 133.5 (C), 140.0 (C), 140.2 (C), 141.6 (C), 143.5 (C), 144.9 (C). m/z (EI, %) = 390 (M^+, 94), 358 (100), 343 (50). HRMS (EI): calcd. for $C_{28}H_{22}S$: 390.144, found 390.143.

General procedure for the synthesis of akenes from episulfides. A solution of episulfide (0.5 mmol) and triphenylphosphine (0.393 g, 1.50 mmol) in xylene (5 mL) was stirred under reflux for 3 h. The reaction mixture was then cooled to room temperature and an excess of 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).

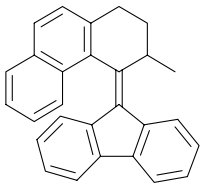
(*Z*)-9-(2-methyl-2,3-dihydro-cyclopenta[a]naphthalen-1-ylidene)-2-methoxy-9H-fluorene.



The general procedure was followed, using dispiro[2-methoxy-9H-fluorene 9,2'thiirane-3',1''-(2''-methyl-2'',3''-dihydro-1H-cyclopenta[a]naphthalene)] (0.203 g, 0.5 mmol), affording 0.159 g (85 %) of a *Z*/*E* mixture (4:1). 67 mg (36 %) Of pure *Z* alkene were isolated by means of three crystallizations from heptane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3), 2.77 (d, $^2J_{HH}$ = 15.0 Hz, 1H, CH_2), 2.96 (s, 3H, CH_3), 3.58 (dd, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, CH_2), 4.35 (m, 1H, CH), 6.29 (d, $^4J_{HH}$ = 2.2 Hz, 1H), 6.79 (dd, $^4J_{HH}$ = 2.2 Hz, $^3J_{HH}$ = 8.4 Hz, 1H), 7.29 – 740 (m, 3H), 7.46 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.58 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.61 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.73 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.79 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 7.90 – 7.95 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3 (CH_3), 41.9 (CH_2), 45.2 (CH), 54.3 (OCH_3), 109.8 (CH), 115.1 (CH), 118.9 (CH), 119.6 (CH), 123.9 (CH), 124.1 (CH), 125.2 (CH), 125.8 (CH), 126.7 (CH), 127.0 (CH), 127.8 (CH), 128.7 (CH), 129.7 (C), 130.8 (CH), 130.9 (C), 132.5 (C), 132.8 (C), 136.2 (C), 138.4 (C), 139.5 (C),

140.2 (C), 147.4 (C), 151.0 (C), 158.3 (C). m/z (EI, %) = 374 (M^+, 100), 359 (80). HRMS (EI): calcd. for $C_{28}H_{22}O$: 374.167, found 374.167.

4-Fluoren-9-ylidene-3-methyl-1,2,3,4-tetrahydro-phenanthrene. The general procedure was followed, using dispiro[2-methoxy-9H-fluorene-9,2'thiirane-3',1''-(2''-methyl-2'',3''-dihydro-1H- phenanthren-4-ylidene)] (0.195 g, 0.5 mmol), affording 0.147 (82 %) of the alkene as a pale yellow solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (m, 1H, CH_2), 1.40 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3), 2.42 (m, 1H, CH_2), 2.55 (m, 1H, CH_2), 2.72 (m, 1H, CH_2), 4.31 (m, 1H, CH), 5.98 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 6.58 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.08 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.23 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.39 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.44 (d, $^3J_{HH}$ = 5.5 Hz, 1H), 7.45 (d, $^3J_{HH}$ = 5.5 Hz, 1H), 7.48 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.66 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.84 (dd, $^3J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 5.5 Hz, 1H), 7.89 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.91 (d, $^3J_{HH}$ = 8.1 Hz, 1H) 7.94 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 8.13 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 5.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9 (CH_3), 29.7 (CH_2), 30.9 (CH_2), 34.7 (CH), 124.7 (CH), 124.9 (CH), 125.0 (CH), 125.2 (CH), 125.8 (CH), 126.5 (CH), 126.7 (2C), 126.9 (CH), 127.4 (CH), 128.2 (CH), 128.6 (CH), 132.1 (C), 132.2 (C), 133.4 (C), 133.5 (C), 137.9 (C), 138.0 (C), 139.4 (C), 139.8 (C), 140.9 (C), 144.4 (C). m/z (EI, %) = 358 (M^+, 100), 343 (51). HRMS (EI): calcd. for $C_{28}H_{22}$: 358.172, found 358.170.