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Fine Tuning of the Rotary Motion by Structural Modification in Light Driven Unidirectional Molecular Motors.

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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 \(^{1}\text{H}\) nucleus or at 100.57 and 125.70 MHz respectively for the \(^{13}\text{C}\) nucleus. Chemical shifts are reported in \(\delta\) units (ppm) relative to the residual deuterated solvent signals of CHCl\(_3\) (\(^{1}\text{H}\) NMR: \(\delta\) 7.26 ppm; \(^{13}\text{C}\) NMR: \(\delta\) 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 with a Foss-Heraeus CHN-O-Rapid or a EuroVector Euro EA Elemental Analyzer. CD spectra were recorded on a JASCO J-715 spectropolarimeter 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. Density functional theory (DFT) calculations were carried out with the GAUSSIAN 03W (rev. C.02) program package.1 All the calculations were performed on systems in the gas phase using the Becke’s three-parameter hybrid functional2 with the LYP correlation functional3 (B3LYP). The geometry optimization was followed by the frequency calculation to prove that the energy minimum or the transition state was found. For compounds with more conformations, the conformation with the lowest energy was chosen. Methyl (2-methyl-2,3-dihydro-cyclopenta[a]naphthalen-1-ylidene)-hydrazine,4 (dimethylphosphoryl)-phenylacetate,5 9-diazafluorene,6 2-methoxy-9-diazafluorene,7 and 2-methyl-2,3-dihydro-cyclopenta[a]naphthalen-1-one8 were synthesized following literature procedures.

1 See reference 28 in the main text.
Methyl 3-naphthalen-2-yl-2-phenyl-acrylate. NaH was added in portions to a solution (diethoxyphosphoryl)-phenyl-acetic acid methyl ester (15.73 g, 55 mmol) in DME (150 mL) at 0 °C. When the evolution of H₂ ceased, the reaction was stirred at room temperature for 30 min and neat 2-naphthaldehyde (7.80 g, 50 mmol) was added. The solution was stirred at room temperature for 3 h and a saturated aq. solution of NH₄Cl was then added. The resulting mixture was extracted with CH₂Cl₂ (2 x 200 mL), dried over MgSO₄ and concentrated under vacuum. The crude residue was purified by column chromatography (SiO₂, pentane:ether = 5:1), affording 11.10 g (77 %) of a mixture of alkenes Z/E (25:75) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 3.75 (s, 3H, CH₃ Z), 3.77 (s, 3H, CH₃ E), 6.93 (dd, ³J_HH = 6.9 Hz, ¹J_HH = 1.6 Hz, 1H, E), 7.16 (s, 1H, Z), 7.21 – 7.24 (m, 1H E and 1H Z), 7.33 – 7.50 (m, 3H E and 3H Z), 7.59 – 7.62 (m, 2H Z), 7.66 (d, ³J_HH = 6.9 Hz, 1H, Z), 7.76 – 7.81 (m, 2H E), 7.98 (s, 1H, E). ¹³C NMR (75 MHz, CDCl₃) δ 52.1 (CH₃, Z), 52.3 (CH₃, E), 125.3 (CH Z), 126.2 (CH E), 126.3 (CH, E), 126.4 (CH Z), 126.7 (CH Z), 126.9 (CH E), 127.3 (CH E), 127.4 (CH Z), 127.5 (CH, Z), 127.8 (CH, E), 127.9 (CH E), 128.0 (CH Z), 128.1 (CH Z), 128.3 (CH Z), 128.4 (CH E), 128.5 (2CH E), 128.6 (2CH Z), 129.8 (2CH E and 2CH Z), 131.4 (C E), 131.5 (C Z), 132.1 (C E), 132.4 (C Z), 132.8 (C Z), 132.9 (C E), 133.0 (C Z), 133.1 (C E), 134.9 (C E), 135.8 (C Z), 140.5 (CH E), 168.2 (C=O, E), 170.1 (C=O, Z). ¹³C NMR (75 MHz, CDCl₃) ð. m/z (EI, %) = 288 (M⁺, 100), 229 (78), 131 (37). HRMS (EI): calcd. for C₂₀H₁₆O₂: 288.116, found 288.115. % Elem. anal: calcd. C, 83.31; H, 5.59; O, 11.10, found C, 83.37; H, 5.62; O, 11.08.

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**Methyl 3-naphthalen-2-yl-2-phenyl-propionate.** A solution of methyl 3-naphthalen-2-yl-2-phenyl-acrylate (10.94 g, 38 mmol) in MeOH (120 mL) was stirred overnight with 10 % Pd on carbon (0.200 g) under H₂ atmosphere. The reaction mixture was then filtered through celite and the solution was concentrated under vacuum. The crude residue was purified by crystallization from EtOH, affording 10.01 g (91 %) of the hydrogenated compound as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 3.14 (dd, ³J_HH = 6.6 Hz, ²J_HH = 13.6 Hz, 1H, CH₂), 3.54 (dd, ³J_HH = 8.8 Hz, ²J_HH = 13.6 Hz, 1H, CH₂), 3.55 (s, 3H, OCH₃), 3.92 (dd, ³J_HH = 6.6 Hz, ³J_HH = 8.8 Hz, 1H, CH), 7.20 – 7.31 (m, 6H), 7.35 – 7.42 (m, 2H), 7.53 (s, 1H), 7.67 – 7.75 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 39.9 (CH₂), 52.0 (OCH₃), 53.5 (CH), 125.3 (CH), 125.8 (CH), 127.3 (CH), 127.4 (CH), 127.5 (2CH), 127.6 (CH), 127.8 (CH), 127.9 (2CH), 128.6 (2CH), 132.1 (C), 133.4 (C), 136.5 (C), 138.5 (C), 173.7 (C=O). m/z (EI, %) = 290 (M⁺, 26), 141 (100). HRMS (EI): calcd. for C₂₀H₁₈O₂: 290.131, found 290.131. % Elem. anal: calcd. C, 82.73; H, 6.25; O, 11.02; found C, 82.67; H, 6.22; O, 10.98.

**3-Naphthalen-2-yl-2-phenyl-propionic acid (12a).** A solution of methyl 3-naphthalen-2-yl-2-phenyl-propionate (9.66 g, 35 mmol) and KOH (4.49 g, 80 mmol) in H₂O/EtOH 1:1 (100 mL) was stirred overnight under reflux. The reaction mixture was then acidified with HCl to pH = 1 and EtOH was removed under vacuum. The resulting aqueous mixture was extracted with CH₂Cl₂ (2 x 200 ml) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The resulting solid was crystallized from Et₂O, affording 8.59 g (89 %) of the acid 12a as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 3.12 (dd, ³J_HH = 7.3 Hz, ²J_HH = 13.6 Hz, 1H, CH₂), 3.50 (dd, ³J_HH = 8.1 Hz, ²J_HH = 13.6 Hz, 1H, CH₂), 3.90 (dd, ³J_HH = 8.1 Hz, ³J_HH = 7.3 Hz, 1H, CH), 7.15 – 7.31 (m, 6H), 7.34 – 7.38 (m, 2H), 7.49 (s, 1H), 7.62 – 7.66 (m, 2H), 7.70 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 38.9 (CH₂), 53.6 (CH), 125.1 (CH), 125.6 (CH), 127.0 (CH), 127.1 (CH), 127.2 (2CH), 127.3 (CH), 127.6 (CH), 127.8 (2CH), 128.4 (2CH), 131.8 (C), 133.1 (C), 135.8 (C), 137.5 (C), 179.1 (C=O). m/z (EI, %) = 276 (M⁺,
24), 141 (100). HRMS (EI): calcd. for C₁₉H₁₆O₂: 276.115, found 276.116. % Elem. anal: calcd. C, 82.58; H, 5.84; O, 11.58; found C, 82.63; H, 5.81; O, 11.61.

2-Phenyl-2,3-dihydro-cyclopenta[a]naphthalen-1-one (10a). A solution of 3-naphthalen-2-yl-2-phenyl-propionic acid 12a (8.28 g, 30 mmol), SOCl₂ (20 mL) and DMF (2 drops) in CH₂Cl₂ (90 mL) was refluxed for 1h. All volatiles were removed under reduced pressure, giving the crude acid chloride, which was dissolved in ClCH₂CH₂Cl and cooled to 0 ºC. To the solution AlCl₃ (7.98 g, 60 mmol) was added quickly and the reaction mixture was stirred at 0 ºC for 30 min. The reaction was quenched with a saturated aqueous solution of NaHCO₃ (300 mL) and extracted with CH₂Cl₂, which was dried over MgSO₄ and concentrated under low pressure. The crude residue was purified by column chromatography (SiO₂, pentane:ether = 5:1), affording 5.65 g (73 %) of the ketone 10a as a white solid. ¹H NMR (400 MHz, CDCl₃) $\delta$ 3.37 (dd, $^3$JHH = 3.3 Hz, $^2$JHH = 18.0 Hz, 1H, CH₂), 3.78 (dd, $^3$JHH = 7.7 Hz, $^2$JHH = 18.0 Hz, 1H, CH₂), 4.01 (dd, $^3$JHH = 7.7 Hz, $^3$JHH = 3.3 Hz, 1H, CH), 7.24 – 7.30 (m, 3H), 7.34 – 7.37 (m, 2H), 7.58 – 7.61 (m, 2H), 7.69 (m, 1H), 7.94 (d, $^3$JHH = 8.1 Hz, 1H), 8.12 (d, $^3$JHH = 7.3 Hz, 1H), 9.17 (d, $^3$JHH = 7.3 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) $\delta$ 35.7 (CH₂), 53.5 (CH), 123.5 (CH), 123.7 (CH), 126.4 (CH), 126.6 (CH), 127.6 (2CH), 127.9 (CH), 128.5 (2CH), 128.7 (CH), 129.3 (C), 129.7 (C), 132.5 (C), 135.8 (CH), 139.7 (C), 156.8 (C), 206.0 (C=O). m/z (EI, %) = 258 (M⁺, 100), 229 (21). HRMS (EI): calcd. for C₁₀H₁₄O: 258.105, found 258.104.

2-Phenyl-2,3-dihydro-cyclopenta[a]naphthalen-1-ylidene-hydrazine (13a). A solution of 2-phenyl-2,3-dihydro-cyclopenta[a]naphthalen-1-one 10a (5.16 g, 20 mmol) in a mixture EtOH / hydrazine monohydrate 1:1 (60 ml) for 4d. The reaction mixture was then poured in water (100 ml) and extracted with AcOEt (2x 100ml). The combined organic layers were washed with brine (100 ml), dried over MgSO₄ and concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO₂, pentane:AcOEt = 1:1), affording 4.23 g (78 %) of the hydrazine 13a as a white solid ¹H NMR
(400 MHz, CDCl₃) δ 3.01 (dd, ³J_HH = 2.5 Hz, ²J_HH = 17.6 Hz, 1H, CH₂), 3.80 (dd, ³J_HH = 8.8 Hz, ²J_HH = 17.6 Hz, 1H, CH₂), 4.45 (dd, ³J_HH = 8.8 Hz, ³J_HH = 2.5 Hz, 1H, CH), 5.06 (broad s, 2H, NH₂), 7.22 – 7.33 (m, 5H), 7.36 (d, ³J_HH = 8.4 Hz, 1H), 7.52 (m, 1H), 7.61 (m, 1H), 7.80 (d, ³J_HH = 8.4 Hz, 1H), 7.88 (d, ³J_HH = 8.1 Hz, 1H), 9.31 (d, ³J_HH = 8.1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 40.9 (CH₂), 44.8 (CH), 123.2 (CH), 125.5 (CH), 125.6 (CH), 126.7 (2CH), 126.9 (CH), 127.2 (CH), 128.1 (CH), 128.7 (C), 129.1 (CH), 130.0 (CH), 132.5 (C), 133.1 (C), 141.8 (C), 145.0 (C), 159.3 (C=N). m/z (EI, %) = 272 (M⁺, 100), 254 (25). HRMS (EI): calcd. for C₁₉H₁₆N₂: 272.132, found 272.131.

**(E)-2-Isopropyl-3-naphthalen-2-yl-acrylic acid.** A 2.5 M solution of n-BuLi in hexane (37.06 mL, 92.6 mmol) was added to a solution of diisopropylamine (13.95 mL, 99.3 mmol) in THF (60 ml) at -20 ºC. This mixture was stirred for 30 min at -20 ºC and a solution of ethylisovalerate (10.97 mL, 72.8 mmol) in THF (40 mL) was then added. The mixture was stirred for 1 h. Next, a solution of 2-naphthaldehyde (10.34 g, 66.2 mmol) in THF (40 mL) was added at -20 ºC. The resulting mixture was stirred for 2 h and the reaction was quenched with a saturated aq. solution of NH₄Cl at -20 ºC. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 200 ml). The combined organic layers were dried on MgSO₄, filtered and concentrated to yield the alcohol ≥ 90%. The crude product was used without purification in the next step. A solution of the alcohol (78.1 mmol) and DMAP (0.478 g, 3.90 mmol) in THF (125 mL) was cooled to 0 ºC. Acetic acid anhydride (7.4 mL, 78.1 mmol) was added dropwise and the reaction was stirred for 1 h. A solution of potassium t-butyrate (26.32 g, 234.2 mmol) in THF (170 mL) was added drop by drop over a period of 30 min at 0 ºC and the resulting mixture stirred for 2 h at this temperature. After the addition of 80 ml of water and distilling of the THF, ethanol (250 mL) and a 2M aq. solution of KOH (35 mL) were added to the aqueous residue and the resulting mixture was stirred for 20 hours under reflux. After the reaction mixture was cooled and concentrated t-butyl methyl ether (270 mL) and a 2M aq. solution of HCl (120 mL) added to the residue. The organic layer was separated and the aqueous layer was extracted again with t-butyl methyl ether. The combined organic layers were
washed consecutively with water and brine, dried over MgSO₄, filtered and concentrated. The product was recrystallized from diisopropyl ether, affording 10.31 g (65%) of the acrylic acid as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 1.28 (d, 3JHH = 7.0 Hz, 6H, CH₃), 3.26 (m, 1H, CH), 7.39 – 7.50 (m, 3H), 7.76 – 7.90 (m, 5 H). ¹³C NMR (75 MHz, CDCl₃) δ 21.0 (CH₃), 29.5 (CH), 125.8 (CH), 126.1 (CH), 126.4 (CH), 126.5 (CH), 126.6 (CH), 127.8 (C), 127.9 (CH), 128.4 (CH), 128.5 (C), 133.1 (C), 140.3 (CH), 173.1 (C=O). m/z (EI, %) = 240 (M⁺, 100), 195 (62), 179 (60), 128 (40). HRMS (EI): calcd. for C₁₆H₁₆O₂: 240.115, found 240.117. % Elem. anal: calcd. C, 79.97; H, 6.71; O, 13.32; found C, 80.01; H, 6.71; O, 13.30.

3-Methyl-2-naphthalen-2-ylmethyl-butyric acid (12b). A solution of (E)-2-methyl-3-naphthalen-2-yl-acrylic acid (9.60 g, 40 mmol) was stirred overnight with Pd-C (5%) under H₂ (1 atm). The mixture was filtered through celite and the solution was concentrated under vacuum. The crude residue was purified by column chromatography (SiO₂, pentane:AcOEt = 9:1), affording 8.81 g (91%) of the acid 12b as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 1.03 (d, 3JHH = 6.6 Hz, 3H, CH₃), 1.06 (d, 3JHH = 6.6 Hz, 3H, CH₃), 2.00 (m, 1H, CH), 2.60 (m, 1H, CH), 2.98 – 3.04 (m, 2H, CH₂), 7.30 (dd, 4JHH = 1.8 Hz, 3JHH = 6.6 Hz, 1H), 7.40 – 7.45 (m, 2H), 7.62 (s, 1H), 7.71 – 7.79 (m, 3 H). ¹³C NMR (75 MHz, CDCl₃) δ 19.9 (CH₃), 20.3 (CH₃), 30.5 (CH₂), 35.4 (CH), 54.1 (CH), 125.3 (CH), 125.9 (CH), 127.1 (CH), 127.3 (CH), 127.5 (CH), 127.6 (CH), 128.0 (CH), 132.1 (C), 133.5 (C), 137.1 (C), 180.8 (C=O). m/z (EI, %) = 242 (M⁺, 42), 141 (100). HRMS (EI): calcd. for C₁₄H₁₄O₂: 242.131, found 242.130. % Elem. anal: calcd. C, 79.31; H, 7.49; O, 13.21; found C, 79.35; H, 7.51; O, 13.18.

2-Isopropyl-2,3-dihydro-cyclopenta[a]naphthalen-1-one (10b). A solution of 3-methyl-2-naphthalen-2-ylmethyl-butyric acid 12b (8.47 g, 35 mmol), SOCl₂ (20 mL) and DMF (2 drops) in CH₂Cl₂ (90 mL) was refluxed for 1h. All volatiles were removed under reduced pressure, giving the crude acid chloride, which was dissolved in ClCH₂CH₂Cl and cooled to 0 °C. To the solution AlCl₃ (8.78 g, 70 mmol) was added
quickly and the reaction mixture was stirred at 0 °C for 30 min. The reaction was quenched with a saturated aqueous solution of NaHCO₃ (300 mL) and extracted with CH₂Cl₂, which was dried over MgSO₄ and concentrated under low pressure. The crude residue was purified by column chromatography (SiO₂, pentane:ether = 9:1), affording 5.10 g (67 %) of the ketone 10b as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 0.81 (d, 3JHH = 6.6 Hz, 3H, CH₃), 1.10 (d, 3JHH = 6.6 Hz, 3H, CH₃), 2.50 (m, 1H, CH), 2.77 (m, 1H, CH), 2.98 (d, 2JHH = 17.4 Hz 1H, CH₂), 3.21 (dd, 3JHH = 7.3 Hz, 2JHH = 17.4 Hz, 1H, CH₂), 7.50 – 7.57 (m, 2H), 7.66 (t, 3JHH = 7.3 Hz, 1H), 7.88 (d, 3JHH = 7.8 Hz, 1H), 8.02 (d, 3JHH = 8.1 Hz, 1H), 9.18 (d, 3JHH = 8.1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 17.1 (CH₃), 18.3 (CH₃), 20.8 (CH₂), 29.0 (CH), 53.4 (CH), 123.8 (CH), 123.9 (CH), 126.3 (CH), 127.9 (CH), 128.7 (CH), 129.2 (C), 131.3 (C), 132.5 (C), 135.4 (CH), 157.3 (C), 208.1 (C=O). m/z (EI, %) = 224 (M⁺, 21), 182 (100). HRMS (EI): calcd. for C₁₆H₁₆O: 224.120, found 224.121.

2-Isopropyl-2,3-dihydro-cyclopenta[a]naphthalen-1-one (15a). A solution of 2-Isopropyl-2,3-dihydro-cyclopenta[a]naphthalen-1-one 10b (2.24 g, 10 mmol), was stirred with P₂S₅ (6.66 g, 15 mmol) in toluene for 3 h. The reaction mixture was cooled down and filtered and the resulting solution was concentrated under low pressure. The crude residue was purified by column chromatography (SiO₂, pentane:ether = 9:1), affording 5.10 g (78 %) of the thioketone 15a as a dark blue solid. ¹H NMR (400 MHz, CDCl₃) δ 0.60 (d, 3JHH = 6.9 Hz, 3H, CH₃), 1.15 (d, 3JHH = 6.9 Hz, 3H, CH₃), 2.79 (m, 1H, CH), 3.08 (d, 2JHH = 18.3 Hz, 1H, CH₂), 3.15 (m, 1H, CH), 3.22 (dd, 3JHH = 6.6 Hz, 2JHH = 18.3 Hz, 1H, CH₂), 7.54 – 7.58 (m, 2H), 7.73 (t, 3JHH = 7.3 Hz, 1H), 7.91 (d, 3JHH = 8.1 Hz, 1H), 8.06 (d, 3JHH = 8.4 Hz, 1H), 10.15 (d, 3JHH = 8.4 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 14.9 (CH₃), 21.4 (CH₃), 32.2 (CH₂), 33.2 (CH), 66.1 (CH), 123.5 (CH), 124.4 (CH), 126.6 (CH), 128.5 (CH), 129.9 (C), 130.2 (CH), 133.1 (C), 136.5 (CH), 139.9 (C), 159.9 (C), >220.0 (C=S). m/z (EI, %) = 240 (M⁺, 36), 182 (100). HRMS (EI): calcd. for C₁₆H₁₆S: 240.097, found 240.094.
**Methyl 2-tert-butyl-3-naphthalen-2-yl-acrylate.** To a solution of LDA (100 mmol) in THF (200 mL) at -80 °C was added dropwise a solution of methyl 3,3-dimethylbutanoate (13.0 g, 100 mmol) in THF (50 mL). The reaction mixture was stirred 1 h. at -80 °C and a solution of 2-bromomethylnaphthalene (17.7 g, 80 mmol) in THF (80 mL) was added dropwise at the same temperature. The resulting solution was warmed to r.t. overnight and quenched with a sat. aq. solution of NH₄Cl. The solution was extracted with EtOAc which was washed with H₂O, dried over MgSO₄ and concentrated under vacuum. The crude residue was purified by column chromatography (SiO₂, pentane:ether = 9:1), affording 17.9 g (83 %) of the ester as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 1.13 (s, 9H, CH₃), 1.62 (dd, ³JHH = 5.0 Hz, ²JHH = 15.6 Hz, 1H, CH₂), 2.95 – 3.13 (m, 2H, CH₂+CH), 3.46 (s, 3H, OCH₃), 7.30 (dd, ³JHH = 2.0 Hz, ³JHH = 11.2 Hz, 1H), 7.41 – 7.50 (m, 2H), 7.62 (s, 1H), 7.72 – 7.80 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 27.7 (CH₃), 33.1 (CH₂), 34.1 (C), 50.6 (OCH₃), 58.6 (CH), 125.3 (CH), 125.9 (CH), 126.9 (CH), 127.3 (CH), 127.5 (CH), 127.7 (CH), 127.9 (CH), 132.2 (C), 133.6 (C), 137.7 (C), 174.9 (C=O). m/z (EI, %) = 270 (M⁺, 68), 181 (73), 141 (100). HRMS (EI): calcd. for C₁₈H₂₂O₂: 270.162, found 270.161. % Elem. anal: calcd. C, 79.96; H, 8.20; O, 11.84; found C, 79.90; H, 8.17; O, 11.82.

**2-tert-Butyl-3-naphthalen-2-yl-acrylic acid (12c).** A solution of methyl 2-tert-butyl-3-naphthalen-2-yl-acrylate. (16.2 g, 60 mmol) and Ba(OH)₂ (25.6 g, 150 mmol) in H₂O /EtOH 1:1 (100 mL) was stirred 5 d under reflux. The reaction mixture was then acidified with a 37 % aq. solution of HCl to pH = 1 and EtOH was removed under vacuum. The resulting aqueous mixture was extracted with CH₂Cl₂ (2 x 200 ml) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The resulting solid was crystallized from Et₂O, affording 12.7 g (83 %) of the acid 12c as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 1.10 (s, 9H, CH₃), 2.58 (dd, ³JHH = 5.0 Hz, ³JHH = 7.1 Hz, 1H, CH), 2.99 – 3.05 (m, 2H, CH₂), 7.28 – 7.45 (m, 3H), 7.62 (s, 1H), 7.72 – 7.76 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 27.8 (CH₃), 33.0 (CH₂), 40.1 (C), 58.5 (CH), 125.3 (CH), 125.9 (CH), 127.1 (CH), 127.4 (CH), 127.7 (CH), 127.8 (CH), 128.0 (CH),
132.2 (C), 133.7 (C), 137.6 (C), 179.9 (C=O). m/z (EI, %) = 256 (M⁺, 47), 141 (100). HRMS (EI): calcd. for C₁₇H₂₀O₂: 256.146, found 256.147. % Elem. anal: calcd. C, 79.65; H, 7.86; O, 12.48; found C, C, 79.69; H, 7.88; O, 12.50.

2-tert-Butyl-2,3-dihydro-cyclopenta[a]naphthalen-1-one (10c). A solution of 2-tert-Butyl-3-naphthalen-2-yl-acrylic acid 12c (10.7 g, 45 mmol), SOCl₂ (30 mL) and DMF (2 drops) in CH₂Cl₂ (100 mL) was heated at reflux for 1h. All volatiles were removed under reduced pressure, giving the crude acid chloride, which was dissolved in ClCH₂CH₂Cl and cooled to 0 ºC. To the solution AlCl₃ (10.0 g, 90 mmol) was added quickly and the reaction mixture was stirred at 0 ºC for 30 min. The reaction was quenched with a saturated aqueous solution of NaHCO₃ (300 mL) and subsequently extracted with CH₂Cl₂, dried over MgSO₄ and concentrated under low pressure. The crude residue was purified by column chromatography (SiO₂, pentane:ether = 9:1), affording 7.50 g (75 %) of the ketone 10c as a white solid.

1H NMR (400 MHz, CDCl₃) 1.05 (s, 9H, CH₃), 2.55 (dd, 3JHH = 3.7 Hz, 3JHH = 7.7 Hz, 1H, CH), 3.01 (dd, 3JHH = 3.7 Hz, 2JHH = 18 Hz, 1H, CH₂), 3.20 (dd, 3JHH = 7.7 Hz, 2JHH = 18.0 Hz, 1H, CH₂), 7.45 (d, 3JHH = 8.4 Hz, 1H), 7.49 (t, 3JHH = 8.4 Hz, 1H), 7.59 (t, 3JHH = 8.4 Hz, 1H), 7.83 (d, 3JHH = 8.4 Hz, 1H), 7.13 (d, 3JHH = 8.4 Hz, 1H). 13C NMR (75 MHz, CDCl₃) 27.5 (CH₃), 30.3 (CH₂), 33.8 (C), 56.9 (CH), 123.8 (CH), 123.9 (CH), 126.3 (CH), 128.2 (CH), 128.8 (CH), 129.3 (C), 131.5 (C), 132.5 (C), 135.3 (CH), 156.6 (C), 208.3 (C=O). m/z (EI, %) = 238 (M⁺, 20), 182 (100). HRMS (EI): calcd. for C₁₇H₁₈O: 238.136, found 238.137.

2-tert-Butyl-2,3-dihydro-cyclopenta[a]naphthalen-1-thione (15b). A solution of 2-tert-butyl-2,3-dihydro-cyclopenta[a]naphthalen-1-one 10c (2.38 g, 10 mmol), was stirred with P₂S₅ (6.66 g, 15 mmol) in toluene for 2 d. The reaction mixture was cooled down and filtered and the resulting solution was concentrated under low pressure. The crude residue was purified by column chromatography (SiO₂, pentane:ether = 9:1), affording 1.83 g (72 %) of the thioketone 15b as a dark blue solid. 1H NMR (400 MHz, CDCl₃) 1.05
(s, 9H, CH$_3$), 3.21 (dd, $^3J_{HH} = 2.4$ Hz, $^3J_{HH} = 5.9$ Hz, 1H, CH), 3.29 – 3.31 (m, 2H, CH$_2$), 7.54 (d, $^3J_{HH} = 8.3$ Hz, 1H), 7.58 (t, $^3J_{HH} = 7.8$ Hz, 1H), 7.75 (t, $^3J_{HH} = 7.8$ Hz, 1H), 7.93 (d, $^3J_{HH} = 7.8$ Hz, 1H), 8.06 (d, $^3J_{HH} = 8.3$ Hz, 1H), 9.95 (d, $^3J_{HH} = 7.8$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 27.8 (CH$_3$), 35.0 (CH$_2$), 35.2 (C), 71.8 (CH), 123.1 (CH), 124.6 (CH), 126.4 (CH), 128.5 (CH), 129.4 (C), 129.7 (CH), 133.2 (C), 135.8 (CH), 141.0 (C), 156.7 (C), >220.0 (C=S). m/z (EI, %) = 578 (M$^+$, 100). HRMS (EI): calcd. for C$_{35}$H$_{30}$S$_2$O: 578.15855, found 578.15901.

2-Methyl-2,3-dihydro-cyclopenta[a]naphthalene-1-thione (15c). A solution of 2-methyl-2,3-dihydro-cyclopenta[a]naphthalen-1-one (1.96 g, 10 mmol), was stirred with P$_2$S$_5$ (6.66 g, 15 mmol) in toluene for 3 h. The reaction mixture was cooled down and filtered and the resulting solution was concentrated under low pressure. The crude residue was purified by column chromatography (SiO$_2$, pentane:ether = 19:1), affording 1.42 g (67 %) of the thioketone 15c as a dark blue solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.51 (d, $^3J_{HH} = 6.9$ Hz, 3H, CH$_3$), 2.90 (d, $^2J_{HH} = 18.3$ Hz, 1H, CH$_2$), 3.14 (m, 1H, CH), 3.48 (dd, $^3J_{HH} = 6.6$ Hz, $^2J_{HH} = 18.3$ Hz, 1H, CH$_2$), 7.51 (d, $^3J_{HH} = 8.4$ Hz, 1H), 7.57 (t, $^3J_{HH} = 8.1$ Hz, 1H), 7.74 (t, $^3J_{HH} = 8.1$ Hz, 1H), 7.89 (d, $^3J_{HH} = 8.1$ Hz, 1H), 8.03 (d, $^3J_{HH} = 8.1$ Hz, 1H), 10.13 (d, $^3J_{HH} = 8.4$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 21.7 (CH$_3$), 39.8 (CH$_2$), 55.5 (CH), 129.7 (CH), 124.2 (CH), 124.6 (C), 126.6 (CH), 128.6 (CH), 130.1 (C), 130.2 (CH), 133.2 (C), 136.5 (CH), 158.5 (C), >220.0 (C=S). m/z (EI, %) = 212 (M$^+$, 21), 181 (100). HRMS (EI): calcd. for C$_{14}$H$_{12}$S: 212.066, found 212.069.