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Synthesis of Functionalized Molecular Motors

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Abstract: Synthetic routes to two molecular motors are reported. The sterically hindered central olefinic bond connecting the two halves of these C_2 -symmetric molecules was prepared by a McMurry reaction. In this way, a motor with two five-membered rings and a motor with two six-membered rings were prepared, both with two versatile methoxy substituents at positions not interfering with the rotary behavior.

Key words: alkenes, arenes, nanostructures, McMurry reactions

Today's silicon-based computer technology is the result of six decades of miniaturization of electrical components following a 'top-down' approach. However, since limitations can be foreseen in the near future,¹ considerable attention is being paid to construct functional devices starting from the smallest components possible, i.e. atoms and molecules. This is commonly referred to as the 'bottom-up' approach in nanotechnology. In recent years numerous devices have been designed and created at the molecular scale,² e.g. molecular motors,³ muscles,⁴ elevators,⁵ scissors,⁶ and a processive artificial enzyme.⁷ In our efforts to create functioning molecular machinery, we have designed molecular motors based on overcrowded alkenes. Actually, molecule **1** was the first example of a unidirectional rotary motor molecule capable of a repetitive 360° rotation upon irradiation.⁸ The rotation around the central double bond, functioning as an axis, is governed by the absolute configuration at the stereogenic centers. The rotation takes place in four consecutive steps using light as the source of energy. Each photochemical step, fueling the rotary motion, is followed by a thermally induced helix inversion. The direction of rotation is governed by the methyl substituent attached to the stereogenic centre adjacent to the central double bond.

We have subsequently shown that the direction of rotation can be governed by a single stereocentre,⁹ present in the second generation motors **2** and that the rate determining thermal helix inversion is considerably increased by using two five-membered rings instead of two six-membered rings as presented in **3** (Figure 1).¹⁰

A main objective is to construct functional mechanical nanodevices based on the application of our molecular motors. Recently, examples of other devices attached to surfaces or ordered in larger assemblies have been reported

Figure 1 The first-generation molecular motor **1**, the second generation molecular motor **2**, and the five-membered ring containing molecular motor **3**.

ed in the literature.¹¹ In order to attach these motors onto, for example, a gold surface or to incorporate them into a device, they will have to be functionalized in such a way that their rotary motion is not restricted. Therefore, we chose to synthesize molecular motors **4** and **5** with a five- and six-membered ring functionalized on the naphthalene moiety (Figure 2). Since it has been shown that introduction of a methyl group at the 7- and 7'-positions of the six-membered ring containing molecular motors does not interfere with the rotary behavior of the molecule, it was decided to introduce other substituents at this position.¹² For the five-membered ring motors the same position for functionalization was chosen. A major synthetic problem is the choice of substituents, since a number of reaction conditions used in the synthesis of a motor molecule are rather harsh and the substituent has to be sufficiently robust to withstand both Friedel-Crafts and McMurry reactions. Therefore the introduction of methoxy substituents into both motors **4** and **5** was envisioned.

Figure 2 Functionalized molecular motors **4** and **5**.

For the molecular motor containing a six-membered ring, the most convenient way of introducing a methoxy substituent would be a direct Friedel-Crafts reaction of 2-methoxynaphthalene with succinic anhydride in a solvent like nitrobenzene or nitromethane (Scheme 1). This reaction has been described several times. However, under similar reaction conditions different isomers were reported

ed to be the dominant product.¹³ Ghosal¹⁴ reported that the major product of the reaction is the desired isomer **8**, in which substitution has taken place at the 6-position of the naphthalene and not product **7** substituted at the 1-position, but our results are more in agreement with those of Short et al.^{13a} Indeed, when this reaction was performed, most of the product proved to be the result of the substitution at the 1-position (**7**). The desired product **8**, substituted at the 6-position, was obtained only in low yield by recrystallization from ethanol. Since this reaction gave only a poor yield of the desired keto acid, an alternative route was investigated. Conversion of 2-bromo-6-methoxy-naphthalene **9** by reaction with magnesium powder into the Grignard reagent followed by reaction with succinic anhydride gave the keto acid **8** in moderate yield. This keto acid **8** can then be converted to the acid **10** using classical Huang–Minlon conditions in the Wolff–Kishner reduction. Care must be taken not to raise the temperature too high, otherwise the methoxy substituent will be cleaved.

The acid **10** was then converted to ketone **11** by a ring closure reaction in polyphosphoric acid (PPA). Methylation of the resulting ketone **11** was performed by deprotonation at low temperature with LDA followed by quenching with methyl iodide to provide **12**. The ketone could then be coupled by a McMurry reaction using TiCl_4 and Zn powder as reagents. This gave alkene **4** in 29% yield, exclusively as the *trans* isomer. The formation of *cis*-**4** was not observed. Although the enantiomers of methoxy motor *trans*-**4** could be separated by analytical chiral HPLC

using an AD-column, it was preferred not to perform an enantioresolution at this stage. A number of synthetic steps still had to be performed and the preparative HPLC separation of material is time consuming and quite costly. Deprotection of the ether moieties with BBr_3 could be performed quite readily with good yields. The bisphenol **13** is a useful platform for the attachment of various substituents. To demonstrate its potential, bisphenol **13** was allowed to react with 1-pyrenecarbonyl chloride (**14**), prepared from 1-pyrenecarboxylic acid by treatment with thionyl chloride, to provide the functionalized motor **15**, which was obtained in moderate yield. The reason for the introduction of two pyrene moieties is that their fluorescence can be used to monitor the rotational behavior.¹⁵ Especially when **15** has a *cis*-geometry, the perpendicular orientation, indicated by molecular mechanics calculations, of the two pyrene moieties might result in the formation of exciplexes, which can easily be detected. In the UV/Vis spectrum of **15** the absorptions at 356 and 388 nm can be attributed to the two pyrene moieties.

Although several synthetic routes towards a functionalized molecular motor containing two five-membered rings proved to be effective, a route featuring a Wittig–Horner reaction was found to be most efficient. The Wittig–Horner reagent **16** was readily prepared by an Arbuzov reaction between 2-bromopropionic acid methyl ester and triethylphosphite in high yields.¹⁶ The Wittig–Horner reagent **16** was treated with NaH in anhydrous DME and the aldehyde **17**¹⁷ was added, providing the alkene **18** in 87% yield. Subsequent hydrogenation using Pd/C in a

Scheme 1 Synthesis of the functionalized racemic molecular motor **4** containing two six-membered rings and of the bispyrene functionalized molecular motor **15**.

mixture of ethanol and ethyl acetate provided ester **19** in near quantitative yield. Hydrolysis to the acid **20** was achieved using LiOH in a mixture of water and methanol at room temperature. Acid **20** was subsequently converted to ketone **21** using standard Friedel–Crafts reaction conditions in excellent yield. Two of these ketones were then reductively coupled following a McMurry protocol with TiCl_4 and Zn powder to provide the alkene **5** as a *cis-trans* mixture in a ratio of approximately 1:1. Contrary to the motor **4**, comprising two six-membered rings, both *cis*-**5** and *trans*-**5** were obtained. Unlike their unsubstituted counterparts, the methoxy-substituted *cis*- and *trans*-isomers of **5** could be separated readily by column chromatography and were obtained in 16% (*cis*-**5**) and 18% (*trans*-**5**) yield, respectively. However, various attempts to cleave the two ether functionalities resulted in either decomposition or recovery of the motor molecule. Since it proved not to be feasible to deprotect the methoxy functionality at this stage, it was decided to introduce another functionality that can be cleaved off under milder reaction conditions.

Although the use of various protecting groups was investigated, major attention was focused on the deprotection of the methoxy group in **21**. For the deprotection of aromatic methyl ethers, reagents like BBr_3 and HBr are normally used. However, previously performed reactions with similar molecules resulted in poor yields or difficult workup procedures were needed. Using simple ionic liquid methodology, recently reported in the literature,¹⁸

good results were obtained and the methyl moiety could be cleaved to provide naphthol **22** in 77% yield. The ionic liquid used was prepared easily by mixing AlCl_3 and $\text{Me}_3\text{N}\cdot\text{HCl}$ in CH_2Cl_2 followed by evaporation of the solvent after stirring for two hours at room temperature. Although cleavage could be performed according to the described conditions, the reaction was relatively slow and was therefore performed at 80 °C overnight. The resulting naphthol **22** was then efficiently protected as the TBDMS ether using DMAP in CH_2Cl_2 to yield **23**. Coupling of the ketones using the McMurry protocol resulted in a *cis-trans* mixture of the protected molecular motor **24** in a ratio of approximately 2:1 in a total yield of 90%. By recrystallization from ethanol, pure *cis*-**24** could be obtained. TBDMS-protected molecular motor **24** was prepared, starting from 6-bromo-2-naphthol in a combined yield of 30% over nine consecutive steps. Reaction with TBAF in THF at room temperature gave complete conversion to the bisphenol **25** within ten minutes. This bisphenol **25** can be used as a scaffold for the introduction of various substituents such as two fluorescent pyrene-moieties as used for the six-membered ring containing motor **15** depicted in Scheme 3. It might also be possible to resolve the phenol by attaching chiral auxiliaries to allow the separation of the two isomers.

In conclusion, in the present paper we have described general synthetic routes to molecular motors with appropriate functionalities to construct more elaborate systems without interfering with the motor function.

Scheme 2 Synthesis of molecular motor **5** containing in each half of the molecule a five-membered ring.

Scheme 3 Synthesis of molecular motor **25** ready for further functionalization.

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. ^{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); DMSO (^1H NMR: δ 2.49; ^{13}C NMR: δ 39.5 ppm), benzene (^1H NMR: δ 7.15 ppm; ^{13}C NMR: δ 128.0 ppm) and toluene (^1H NMR: δ 2.08 ppm) or relative to an external standard for ^{31}P NMR (NPCl_2)₃ at δ 19.91 ppm in CDCl_3 . Melting points were taken on a Mettler FP-2 melting point apparatus, equipped with a Mettler FP-21 microscope. Optical rotations were measured with a Perkin Elmer 241 Polarimeter. UV/Vis measurements were performed on a Hewlett-Packard HP 8453 FT spectrophotometer using Uvasol grade solvents (Merck). 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. Column chromatography was performed on silica gel (Aldrich 60, 230–400 mesh). HPLC analyses were performed on Shimadzu HPLC system equipped with two LC-10ADvp solvent delivery systems, a DGU-14A degasser, a SIL-10ADvp autosampler, a SPD-M10A UV/Vis photodiode array detector, a CTO-10Avp column oven and a SCL-10Avp controller unit using Chiralcel OD (Daicel), Chiralcel AD (Daicel), (*R,R*)-Whelk 01 (Regis) and Chiralcel OB-H (Daicel) columns. Chemicals were used as received from Acros, Aldrich, Fluka, or Merck.

(3*R,3'*R*')-(*P**,*P*')-*trans*-7,7'-Dimethoxy-3,3'-dimethyl-1,1',2,2',3,3',4,4'-tetrahydrobiphenanthrenylidene (4)**

A mixture of Zn powder (0.706 g, 10.8 mmol) and TiCl_4 (0.605 mL, 1.04 g, 5.48 mmol) in THF (3 mL) was refluxed for 90 min. To this black mixture was added ketone **12** (640 mg, 2.67 mmol) in THF (2 mL). Subsequently, the reaction mixture was refluxed for 44 h. Quenching with a sat. aq soln of NH_4Cl (100 mL) and extraction with EtOAc (3×100 mL) gave after drying (MgSO_4) and removal of the organic solvents a brown oil, which was purified by column chromatography (SiO_2 , heptane–EtOAc, 16:1, R_f 0.55). The desired compound **4** was obtained as a slightly colored oil, which under high vacuum turned to a colorless, fluffy solid (176 mg, 0.393 mmol, 29%).

^1H NMR (300 MHz, CDCl_3): δ = 0.78 (d, J = 6.6 Hz, 6 H), 1.23–1.28 (m, 2 H), 1.82–1.91 (m, 2 H), 2.64–2.73 (m, 6 H), 3.97 (s, 6 H), 7.21–7.30 (m, 6 H), 7.65 (d, J = 8.1 Hz, 2 H), 8.33 (d, J = 9.2 Hz, 2 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 18.6 (q), 27.1 (t), 31.2 (t), 33.7 (d), 55.2 (q), 106.2 (d), 118.2 (d), 125.2 (d), 127.1 (d), 127.4 (d), 127.8 (s), 133.3 (s), 134.2 (s), 134.8 (s), 136.4 (s), 156.8 (s);

MS (EI): m/z (%) = 449 (M^+ , 12), 448 (M^+ , 100).

HRMS (EI): m/z calcd for $\text{C}_{32}\text{H}_{32}\text{O}_2$: 448.2402; found: 448.2400.

UV/Vis (*n*-hexane): λ (ϵ) = 234 (72800), 304 (12900), 327 (9300), 336 (9700), 342 (11800).

The enantiomers of *trans*-**4** were resolved by chiral HPLC using a Daicel Chiralcel AD column as the stationary phase and a mixture of heptane–*i*-PrOH (95:5) as the eluent at a rate of 1 mL min^{−1} giving two fractions (first fraction: t_R 3.84 min; second fraction t_R 5.61 min).

7,7'-Dimethoxy-2,2'-dimethyl-2,2',3,3'-tetrahydro-1,1'-bicyclopenta[*a*]naphthalenyldiene (5)

To a stirred suspension of Zn powder (1.01 g, 15.4 mmol) in THF (8 mL), TiCl_4 (0.849 mL, 1.46 g, 7.70 mmol) was added carefully at 0 °C. The dark mixture was then refluxed for 90 min and ketone **21** (0.800 g, 3.54 mmol), was added in a small amount of THF (2 mL). The mixture was subsequently heated at reflux for 18 h and then poured into a sat. aq soln of NH_4Cl (100 mL) and extracted with EtOAc (3×100 mL). Drying of the combined organic layers and evaporation of all volatiles gave a yellow oil containing a small amount of starting material and the *cis* and *trans* isomers of the olefin **5**. The reaction mixture was purified by column chromatography (heptane–EtOAc, 50: 1) giving both the *trans* olefin **5** (130 mg, 0.310 mmol, 18%) and *cis* olefin (120 mg, 0.286 mmol, 16%) as yellow solids.

***trans*-5**

R_f 0.26.

^1H NMR (300 MHz, CDCl_3): δ = 1.29 (d, J = 6.2 Hz, 6 H), 2.31 (d, J = 14.6 Hz, 2 H), 2.93 (dd, J = 14.6, 5.5 Hz, 2 H), 3.00–3.08 (m, 2 H), 3.97 (s, 6 H), 7.19–7.22 (m, 4 H), 7.36 (d, J = 8.1 Hz, 2 H), 7.65 (d, J = 8.1 Hz, 2 H), 8.16 (d, J = 9.9 Hz, 2 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 19.4 (q), 41.0 (t), 43.0 (d), 55.2 (q), 106.4 (d), 117.7 (d), 124.6 (d), 125.8 (s), 126.5 (d), 128.2 (d), 134.1 (s), 138.6 (s), 139.4 (s), 141.5 (s), 156.7 (s).

***cis*-5**

Yellow solid; 190.9–191.8 °C; R_f 0.17.

^1H NMR (400 MHz, CDCl_3): δ = 1.19 (d, J = 6.6 Hz, 6 H), 2.64 (d, J = 14.3 Hz, 2 H), 3.51–3.59 (m, 4 H), 3.74 (s, 6 H), 6.10 (dd, J = 9.2, 2.6 Hz, 2 H), 6.54 (d, J = 9.2 Hz, 2 H), 6.99 (d, J = 2.6 Hz, 2 H), 7.44 (d, J = 8.1 Hz, 2 H), 7.59 (d, J = 8.1 Hz, 2 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 20.7 (q), 40.4 (t), 42.2 (d), 55.0 (q), 106.1 (d), 116.6 (d), 124.0 (d), 125.3 (s), 127.3 (d), 128.0 (d), 133.4 (s), 136.9 (s), 140.0 (s), 141.8 (s), 156.1 (s).

MS (EI): m/z (%) = 420 (M^+ , 100).

HRMS (EI): m/z calcd for $\text{C}_{30}\text{H}_{28}\text{O}_2$: 420.2089; found: 420.2108.

4-(6-Methoxynaphthalen-2-yl)-4-oxobutyric Acid (8) and 4-(2-Methoxynaphthalen-1-yl)-4-oxobutyric Acid (7)

A mixture of these compounds was obtained following the literature procedure.^{13a} Alternatively, 6-bromo-2-methoxynaphthalene (**9**; 20.0 g, 84.4 mmol) was converted to the Grignard reagent. Naphthyl compound **9** (1 g) was added to THF (5 mL) and this was added to a suspension of Mg powder (2.65 g, 109 mmol) in THF (15 mL) containing a small crystal of iodine. This mixture was heated gently for 5 min until the Grignard reaction had started. The remaining **9** (19 g) was added in THF (150 mL). After the addition was complete, the mixture was heated at reflux for 2 h. The reaction mixture was cooled to 0 °C, then succinic anhydride (12.0 g, 120 mmol) was added and the resulting solution was stirred overnight. Acidification with an aq soln of HCl (1 N; 500 mL), extraction with Et₂O (3×500 mL), and drying (MgSO_4) gave a brown oil. To this oil was added a small quantity of Et₂O (50 mL) from which the desired product **8** precipitated as a white solid (7.84 g, 30.4 mmol, 36%). The 1,2-isomer **7** was obtained by the Friedel–Crafts reaction.

1,2-Isomer 7

White solid; mp 133.5–136.5 °C (lit.^{13a} 136.5–137.5 °C).

^1H NMR (300 MHz, CDCl_3): δ = 2.88 (t, J = 6.6 Hz, 2 H), 3.29 (t, J = 6.6 Hz, 2 H), 3.96 (s, 3 H), 7.28 (d, 9.0 Hz, 1 H), 7.33–7.37 (m, 1 H), 7.44–7.49 (m, 1 H), 7.73 (d, J = 8.4 Hz, 1 H), 7.79 (d, J = 8.1 Hz, 1 H), 7.90 (d, J = 9.0 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 28.1 (t), 39.3 (t), 56.4 (q), 112.6 (d), 123.6 (d), 124.1 (d), 127.7 (d), 128.0 (d), 128.8 (2 s), 130.5 (s), 131.6 (d), 153.7 (s), 178.9 (s), 205.1 (s).

MS (EI): m/z (%) = 258 (M^+ , 25), 185 (100).

HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{14}\text{O}_4$: 258.0892, found: 258.0895.

2,6-Isomer 8

White solid; mp 147.4–148.5 °C (lit.^{13a} 148.5–149 °C).

^1H NMR (300 MHz, CDCl_3): δ = 2.80 (t, J = 6.6 Hz, 2 H), 3.37 (t, J = 6.6 Hz, 2 H), 3.89 (s, 3 H), 7.10 (s, 1 H), 7.14 (dd, J = 8.8, 2.6 Hz, 1 H), 7.72 (d, J = 8.8 Hz, 1 H), 7.80 (d, J = 8.8 Hz, 1 H), 7.96 (d, J = 8.4 Hz, 1 H), 8.38 (s, 1 H).

^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ = 2.62 (t, J = 6.0 Hz, 2 H), 3.34 (t, J = 6.0 Hz, 2 H), 3.89 (s, 3 H), 7.24 (dd, J = 8.8, 1.8 Hz, 1 H), 7.39 (d, J = 1.5 Hz, 1 H), 7.91 (m, 2 H), 8.03 (d, J = 8.8 Hz, 1 H), 8.60 (s, 1 H).

^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): δ = 28.1 (t), 33.0 (t), 55.5 (q), 106.1 (d), 119.6 (d), 124.2 (d), 127.1 (d), 127.5 (s), 129.8 (d), 131.4 (d), 131.8 (s), 137.0 (s), 159.4 (s), 174.1 (s), 198.1 (s).

MS (EI): m/z (%) = 258 (M^+ , 38), 185 (100).

HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{14}\text{O}_4$: 258.0892; found: 258.0892.

2-Bromo-6-methoxynaphthalene (9)

A suspension of 6-bromo-2-naphthol²⁰ (18.4 g, 82.5 mmol), K_2CO_3 (20.0 g, 145 mmol), and MeI (10.0 mL, 22.8 g, 160 mmol) was stirred overnight in DMF (100 mL). Addition of Et_2O (300 mL), thorough washing with H_2O (8 $\times$ 200 mL), drying over MgSO_4 , and subsequent removal of the organic volatiles gave **9** as a white solid (18.7 g, 78.9 mmol, 96%).

Mp 111.6–111.8 °C (lit.²¹ 108 °C).

^1H NMR (300 MHz, CDCl_3): δ = 3.92 (s, 3 H), 7.10 (d, J = 2.2 Hz, 1 H), 7.16 (dd, J = 8.8, 2.6 Hz, 1 H), 7.52 (d, J = 8.1 Hz, 1 H), 7.63 (m, 2 H), 7.92 (d, J = 1.5 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 55.3 (q), 105.7 (d), 117.0 (s), 119.7 (d), 128.3 (d), 128.4 (d), 129.55 (d), 129.6 (d), 130.0 (s), 133.0 (s), 157.8 (s).

MS (EI): m/z (%) = 238 (M^+ , 100), 236 (M^+ , 100), 195 (45), 193 (47).

HRMS (EI): m/z calcd for $\text{C}_{11}\text{H}_9^{81}\text{BrO}$: 235.9836; found: 235.9847.

4-(6-Methoxynaphthalen-2-yl)butyric Acid (10)

The keto acid **8** (7.40 g, 287 mmol) was mixed with KOH (8.00 g, 143 mmol), hydrazine monohydrate (5.00 mL, 5.10 g, 102 mmol), and H_2O (4.5 mL) in diethylene glycol (60 mL). The mixture was heated initially for 3 h at 120 °C and then for a further 3 h at 190 °C. The dark brown mixture was then cooled to r.t. and acidified with an aq soln of HCl (10%; 100 mL). H_2O (200 mL) was added and the mixture was extracted with Et_2O (3 $\times$ 200 mL). The combined organic layers were washed with H_2O (4 $\times$ 200 mL), dried (MgSO_4), and then all volatiles were removed in vacuo giving **10** as a slightly brown oil, that crystallized upon standing (4.29 g, 17.6 mmol, 61%).

Mp 161.5–164.8 °C (lit.¹⁹ 166–168 °C).

^1H NMR (300 MHz, CDCl_3): δ = 1.99–2.09 (m, 2 H), 2.41 (t, J = 7.5 Hz, 2 H), 2.81 (t, J = 7.5 Hz, 2 H), 3.91 (s, 3 H), 7.11–7.24 (m, 2 H), 7.30 (dd, J = 8.4, 1.5 Hz, 1 H), 7.55 (s, 1 H), 7.68 (d, J = 8.8 Hz, 2 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 26.1 (t), 33.2 (t), 34.8 (t), 55.1 (q), 105.5 (d), 118.6 (d), 126.3 (d), 126.7 (d), 127.6 (d), 128.8 (d), 128.9 (s), 128.9 (s), 133.0 (s), 136.2 (s), 157.1 (s), 179.7 (s).

MS (EI): m/z (%) = 244 (M^+ , 34), 171 (100), 128 (89).

HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$: 244.1100; found: 244.1093.

7-Methoxy-2,3-dihydro-4(1H)-phenanthrenone (11)

PPA (50 mL) was heated to 60 °C and the acid **10** (2.49 g, 10.2 mmol) was added. Stirring was continued for 3 h at 110 °C. The reaction mixture was then poured into ice-water (200 mL) and after hydrolysis overnight the mixture was extracted with Et_2O (3 $\times$ 100 mL). Drying of the combined organic layers (MgSO_4) and removal of the volatiles under reduced pressure gave a brown oil which was purified by column chromatography (SiO_2 ; hexane– EtOAc , 16:1; R_f 0.37) resulting in a slightly yellow oil (1.10 g, 4.87 mmol, 48%).

^1H NMR (300 MHz, CDCl_3): δ = 2.13–2.21 (m, 2 H), 2.76 (t, J = 6.6 Hz, 2 H), 3.07 (t, J = 6.0 Hz, 2 H), 3.91 (s, 3 H), 7.11 (d, J = 2.6 Hz, 1 H), 7.25–7.29 (m, 2 H), 7.81 (d, J = 8.4 Hz, 1 H), 9.34 (d, J = 9.5 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 22.8 (t), 30.9 (t), 40.8 (t), 54.8 (q), 106.4 (d), 120.2 (d), 126.3 (s), 126.8 (s), 127.2 (d), 128.0 (d), 132.8 (d), 134.0 (s), 144.1 (s), 156.8 (s), 200.3 (s).

MS (EI): m/z (%) = 226 (M^+ , 100), 198 (30), 170 (43).

HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2$: 226.0994; found: 226.0995.

7-Methoxy-3-methyl-2,3-dihydro-4(1H)-phenanthrenone (12)

To a solution of LDA (3.20 mmol) in THF (10 mL) was added ketone **11** (0.651 g, 2.88 mmol) at –60 °C. The solution turned red rapidly after addition of the ketone. After stirring for 1 h at –60 °C, MeI (0.500 mL, 1.14 g, 8.03 mmol) was added and the reaction mixture turned brownish. The temperature of the reaction mixture was allowed to reach r.t. overnight, the reaction mixture was quenched with a sat. aq soln of NH_4Cl (50 mL), extracted with Et_2O (3 $\times$ 50 mL), and dried over MgSO_4 . After removal of the organic volatiles under reduced pressure, the impure compound **12** was obtained as a brown oil, which was purified by column chromatography (SiO_2 ; heptane– EtOAc , 16:1, R_f 0.36) yielding a colorless oil (0.679 g, 2.83 mmol, 98%).

^1H NMR (300 MHz, CDCl_3): δ = 1.29 (d, J = 6.6 Hz, 3 H), 1.88–2.05 (m, 1 H), 2.19–2.28 (m, 1 H), 2.67–2.77 (m, 1 H), 3.03–3.23 (m, 2 H), 3.90 (s, 3 H), 7.10 (d, J = 2.9 Hz, 1 H), 7.23–7.35 (m, 2 H), 7.79 (d, J = 8.4 Hz, 1 H), 9.27 (d, J = 9.5 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 15.8 (q), 29.9 (t), 31.2 (t), 43.7 (d), 55.0 (q), 106.6 (d), 120.2 (d), 126.5 (s), 127.1 (s), 127.3 (d), 128.0 (d), 132.6 (d), 134.1 (s), 143.4 (s), 157.0 (s), 203.4 (s).

MS (EI): m/z (%) = 240 (M^+ , 100), 198 (59), 170 (73).

HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$: 240.1150; found: 240.1160.

(3*R**,3*R**)-(*P**,*P**)-trans-(±)-1,1',2,2',3,3',4,4'-Octahydro-7,7'-dihydroxy-3,3'-dimethyl-4,4'-biphenanthrylidene (13)

Motor **4** (55.0 mg, 0.123 mmol) was dissolved in CH_2Cl_2 (5 mL). After cooling to 0 °C, BBr_3 (0.100 mL, 0.377 g, 0.151 mmol) was added and the temperature of the reaction mixture was allowed to reach r.t. overnight. Additional CH_2Cl_2 (50 mL) was added and the organic layer was washed with brine (3 $\times$ 50 mL). Drying (MgSO_4) and evaporation of the solvent gave the bisphenol **13** as a slightly yellow solid (50.0 mg, 0.119 mmol, 97%).

^1H NMR (300 MHz, CDCl_3): δ = 0.78 (d, J = 6.6 Hz, 6 H), 1.23–1.28 (m, 2 H), 1.82–1.91 (m, 2 H), 2.66–2.73 (m, 6 H), 7.16–7.29 (m, 6 H), 7.59 (d, J = 8.1 Hz, 2 H), 8.33 (d, J = 8.8 Hz, 2 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 18.5 (q), 27.1 (t), 31.2 (t), 33.8 (d), 109.9 (d), 117.3 (d), 124.8 (d), 127.3 (d), 127.7 (s), 127.8 (d), 133.3 (s), 134.2 (s), 134.8 (s), 136.5 (s), 152.5 (s).

MS (EI): m/z (%) = 420 (M^+ , 100).

HRMS (EI): m/z calcd for $\text{C}_{30}\text{H}_{28}\text{O}_2$: 420.2089; found: 420.2100.

Pyrene-1-carbonyl Chloride (14)

A suspension of 1-pyrenecarboxylic acid (100 mg, 0.407 mmol) was refluxed for 1 h in CH_2Cl_2 (20 mL) in the presence of SOCl_2 (0.500 mL, 0.815 g, 6.85 mmol) and a drop of DMF. The organic volatiles were then removed under reduced pressure yielding a yellow solid which was used directly in subsequent reactions.

^1H NMR (300 MHz, CDCl_3): δ = 8.06–8.32 (m, 7 H), 8.91 (d, J = 8.1 Hz, 1 H), 9.04 (d, J = 9.5 Hz, 1 H).

(3*R*,3'*R*)-(P*,P*)-trans-(±)-1,1',2,2',3,3',4,4'-Octahydro-7,7'-[(1-pyrenylcarbonyl)oxy]-3,3'-dimethyl-4,4'-biphenanthrylidene (15)

The acid chloride **14** (100 mg, 0.407 mmol) was added to a solution of bisphenol **13** (50.0 mg, 0.119 mmol) in CH_2Cl_2 (10 mL) in the presence of Et_3N (0.500 mL, 0.360 g, 3.56 mmol). After stirring for 1 h at 0 °C and then at r.t. for 90 min the reaction mixture was quenched with a sat. soln of NH_4Cl (100 mL) and extracted with CH_2Cl_2 (50 mL). The organic layer was then washed with an aq soln of HCl (1 N; 2 × 50 mL), NaOH (1 N; 50 mL), and brine (2 × 50 mL). After drying (MgSO_4), the volatiles were removed in vacuo and the residue was purified by column chromatography (SiO_2 , heptane–EtOAc, 4:1; R_f 0.22) and obtained as a slightly yellow solid (77.0 mg, 880 μmol , 73%).

Mp >200 °C.

^1H NMR (500 MHz, CDCl_3): δ = 0.89 (d, J = 6.8 Hz, 6 H), 1.36–1.39 (m, 2 H), 1.94–2.00 (m, 2 H), 2.81–2.84 (m, 6 H), 7.40 (d, J = 8.1 Hz, 2 H), 7.61 (dd, J = 9.1, 2.2 Hz, 2 H), 7.81 (d, J = 8.8 Hz, 2 H), 7.90 (d, J = 2.0 Hz, 2 H), 8.08–8.13 (m, 2 H), 8.16 (d, J = 8.8 Hz, 2 H), 8.25 (d, J = 9.3 Hz, 2 H), 8.29–8.38 (m, 8 H), 8.59 (d, J = 9.3 Hz, 2 H), 9.00 (d, J = 8.3 Hz, 2 H), 9.47 (d, J = 9.8 Hz, 2 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 18.5 (q), 27.3 (t), 31.2 (t), 33.9 (d), 119.3 (d), 121.1 (d), 122.3 (s), 124.2 (s), 124.3 (d), 124.9 (d), 125.0 (s), 126.3 (d), 126.4 (d), 126.5 (d), 126.6 (d), 127.2 (d), 127.5 (d), 129.1 (d), 130.0 (d), 130.1 (d), 130.39 (s), 130.42 (s), 131.0 (s), 132.0 (s), 132.9 (s), 134.8 (s), 135.0 (s), 136.4 (s), 136.7 (s), 148.1 (s), 166.6 (s); one (d) was not observed.

MS (DI): m/z (%) = 876 (M^+ , 5), 648 (2), 420 (4), 229 (100), 201 (46).

It was impossible to acquire an exact mass of this compound. We attempted to separate the enantiomers of this compound, but neither of the chiral HPLC (OD, AD, AS, OJ, Whelk) columns tried gave any resolution.

UV/Vis: (CH_2Cl_2): λ_{max} (ϵ) = 275 (18800), 285 (24900), 356 (22400), 388 (9900).

2-(Diethoxyphosphoryl)propionic Acid Methyl Ester (16)

This compound was prepared according to a procedure reported in the literature¹⁶ and was obtained as a colorless liquid.

^1H NMR (300 MHz, CDCl_3): δ = 1.31–1.35 (m, 6 H), 1.44 (dd, J = 18.0, 7.0 Hz, 3 H), 2.99–3.09 (m, 1 H), 3.75 (s, 3 H), 4.10–4.20 (m, 4 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 11.1 (dq, $^2J_{\text{PC}}$ = 6.1 Hz), 15.7 (dd, $^3J_{\text{PC}}$ = 2.5 Hz), 15.8 (dd, $^3J_{\text{PC}}$ = 2.5 Hz), 38.1 (dd, $^1J_{\text{PC}}$ = 133 Hz), 51.8 (q), 61.1 (dt, $^2J_{\text{PC}}$ = 7.3 Hz), 169.5 (d, $^2J_{\text{PC}}$ = 4.9 Hz).

^{31}P NMR (81 MHz, CDCl_3): δ = 22.89.

MS (EI): m/z (%) = 224 (M^+ , 83), 165 (100).

HRMS (EI): m/z calcd for $\text{C}_8\text{H}_{17}\text{O}_5\text{P}$: 224.0813; found: 224.0820.

3-(6-Methoxynaphthalen-2-yl)-2-methylacrylic Acid Methyl Ester (18)

Wittig–Horner reagent **16** (380 mg, 1.70 mmol) was added at 0 °C to a suspension of NaH (100 mg, 4.17 mmol) in DME (10 mL) with the evolution of hydrogen gas. After stirring this mixture for 1 h at

r.t., a solution of aldehyde **17** (300 mg, 1.61 mmol) in DME (5 mL) was added. Immediately, the suspension became a clear solution while a sticky material precipitated. Stirring was continued for 1 h at r.t. To the reaction mixture was then added a sat. aq soln of NH_4Cl (50 mL), followed by extraction with Et_2O (3 × 40 mL). Drying (Na_2SO_4) and evaporation of all volatiles gave a yellow solid, which was purified by flash column chromatography (SiO_2 ; heptane–EtOAc, 4:1) giving a white solid (360 mg, 1.41 mmol, 87%). Alternatively, the product can be recrystallized from a mixture of EtOAc–EtOH giving white crystals.

Mp 109.0–110.4 °C.

^1H NMR (300 MHz, CDCl_3): δ = 2.22 (s, 3 H), 3.84 (s, 3 H), 3.94 (s, 3 H), 7.14–7.19 (m, 2 H), 7.50 (d, J = 8.4 Hz, 1 H), 7.73–7.82 (m, 4H).

^{13}C NMR (75 MHz, CDCl_3): δ = 14.1 (q), 51.9 (q), 55.1 (q), 105.5 (d), 119.1 (d), 126.6 (d), 127.3 (s), 127.5 (d), 128.4 (s), 129.3 (d), 129.7 (d), 131.0 (s), 134.1 (s), 139.0 (d), 158.3 (s), 169.1 (s).

MS (EI): m/z (%) = 256 (M^+ , 100).

HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3$: 256.1099; found: 256.1102.

Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3$: C, 75.0; H, 6.29. Found: C, 74.5; H, 6.26.

3-(6-Methoxynaphthalen-2-yl)-2-methylpropionic Acid Methyl Ester (19)

Unsaturated ester **18** (1.95 g, 7.62 mmol) was dissolved in a mixture of EtOH (50 mL) and EtOAc (50 mL) and stirred overnight under hydrogen at atmospheric pressure at r.t. in the presence of Pd/C (100 mg, 10%). After filtration, the organic volatiles were removed giving the desired saturated ester **19** as a colorless oil (2.95 g, 7.56 mmol, 99%) which solidified upon standing.

Mp 54.6–56.8 °C.

^1H NMR (300 MHz, CDCl_3): δ = 1.18 (d, J = 6.6 Hz, 3 H), 2.75–2.86 (m, 2 H), 3.12–3.19 (m, 1 H), 3.64 (s, 3 H), 3.91 (s, 3 H), 7.11–7.15 (m, 2 H), 7.27 (dd, J = 8.4, 2.6 Hz, 1 H), 7.54 (s, 1 H), 7.65–7.69 (m, 2 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 16.5 (q), 39.4 (t), 41.1 (d), 51.2 (q), 54.8 (q), 105.3 (d), 118.5 (d), 126.6 (d), 126.9 (d), 127.6 (d), 128.7 (d), 133.0 (s), 134.2 (s), 157.1 (s), 176.2 (s), one (s) was not observed.

MS (EI): m/z (%) = 258 (M^+ , 36), 171 (100).

HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3$: 258.1256; found: 258.1251.

Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3$: C, 74.4; H, 7.0. Found: C, 74.5; H, 7.0.

3-(6-Methoxynaphthalen-2-yl)-2-methylpropionic Acid (20)

Ester **19** (0.910 g, 3.53 mmol) was stirred overnight in a mixture of LiOH (1.00 g, 41.7 mmol), methanol (5 mL) and H_2O (15 mL). After acidification with an aq soln of HCl (10%), the mixture was extracted with Et_2O (2 × 50 mL). The ether layers were washed with brine (2 × 50 mL), dried over MgSO_4 , and then all the volatiles were removed to give acid **20** as a white solid (0.781 g, 3.20 mmol, 91%).

Mp 137.9–139.4 °C.

^1H NMR (300 MHz, CDCl_3): δ = 1.21 (d, J = 6.6 Hz, 3 H), 2.77–2.88 (m, 2 H), 3.17–3.22 (m, 1 H), 3.91 (s, 3 H), 7.11–7.14 (m, 2 H), 7.26–7.30 (m, 1 H), 7.56 (s, 1 H), 7.66–7.69 (m, 2 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 16.5 (q), 39.2 (t), 41.2 (d), 55.2 (q), 105.6 (d), 118.8 (d), 126.9 (d), 127.3 (d), 127.8 (d), 128.9 (s), 129.0 (d), 133.2 (s), 134.1 (s), 157.3 (s), 182.6 (s).

MS (EI): m/z (%) = 244 (M^+ , 27), 171 (100).

HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$: 244.1099; found: 244.1096.

Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$: C, 73.8; H, 6.6. Found: C, 73.9; H, 6.8.

7-Methoxy-2-methyl-2,3-dihydro-1H-cyclopenta[*a*]naphthalen-1-one (21)

Acid **20** (0.771 g, 3.16 mmol) dissolved in CH_2Cl_2 (50 mL) was heated at reflux with SOCl_2 (2.00 mL, 3.26 g, 27.4 mmol) and a catalytic amount of DMF. After 1 h the reaction mixture was allowed to cool to r.t. and all volatiles were removed under reduced pressure giving a yellow oil. This oil was dissolved in toluene and cooled to 0 °C whereupon AlCl_3 (0.534 g, 4.00 mmol) was added in one portion. The greenish reaction mixture was stirred for 1 h at 0 °C after which it was acidified with an aq soln of HCl (10%). Extraction with EtOAc (3×100 mL), drying of the organic layers (MgSO_4), and subsequent removal of the volatiles gave a brown oil. Purification using column chromatography (SiO_2 ; heptane–EtOAc, 8:1; R_f 0.38) gave the desired ketone **21** as a colorless oil (0.650 g, 2.88 mmol, 91%).

^1H NMR (300 MHz, CDCl_3): δ = 1.37 (d, J = 7.3 Hz, 3 H), 2.76–2.83 (m, 2 H), 3.45 (dd, J = 17.9, 8.1 Hz, 1 H), 3.93 (s, 3 H), 7.21 (d, J = 2.9 Hz, 1 H), 7.32 (dd, J = 9.2, 2.9 Hz, 1 H), 7.47 (d, J = 8.4 Hz, 1 H), 7.95 (d, J = 8.4 Hz, 1 H), 9.06 (d, J = 9.2 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 16.5 (q), 35.1 (t), 42.3 (d), 55.1 (q), 106.7 (d), 120.5 (d), 124.3 (d), 124.5 (s), 125.2 (d), 130.0 (s), 134.0 (s), 134.4 (d), 153.9 (s), 157.7 (s), 209.8 (s).

MS (EI): m/z (%) = 226 (M^+ , 100), 211 (67).

HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2$: 226.0994, found: 226.0999.

7-Hydroxy-2-methyl-2,3-dihydrocyclopenta[*a*]naphthalen-1-one (22)

To an ice-cooled suspension of AlCl_3 (8.00 g, 60.0 mmol) in CH_2Cl_2 (25 mL), $\text{Me}_3\text{N}\cdot\text{HCl}$ (2.87 g, 30 mmol) was added carefully. The mixture was stirred at r.t. for 2 h, a brown solution was obtained. To this solution was added **21** (0.800 g, 3.54 mmol) dissolved in a small amount of CH_2Cl_2 whereupon the reaction mixture turned dark brown. The organic volatiles were removed and the reaction mixture was stirred at 80 °C overnight. The dark brown reaction mixture was poured carefully into H_2O (200 mL) followed by acidification with an aq soln of HCl (10%; 100 mL), and extraction with CH_2Cl_2 (3×100 mL). The combined organic layers were dried (Na_2SO_4) and evaporated under reduced pressure giving a brown solid, which was purified by column chromatography (SiO_2 , heptane–EtOAc, 4:1, R_f 0.39) giving a white solid (0.581 g, 2.74 mmol, 77%).

Mp 150.9–153.7 °C.

^1H NMR (400 MHz, CDCl_3): δ = 1.32 (d, J = 7.3 Hz, 3 H), 2.72–2.78 (m, 2 H), 3.40 (dd, J = 17.5, 7.5 Hz, 1 H), 5.21 (s, 1 H), 7.19–7.24 (m, 2 H), 7.41 (d, J = 8.4 Hz, 1 H), 7.85 (d, J = 8.4 Hz, 1 H), 9.02 (d, J = 8.8 Hz, 1 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 16.7 (q), 35.2 (t), 42.5 (d), 110.4 (d), 120.2 (d), 124.5 (s), 124.6 (d), 125.8 (d), 130.2 (s), 134.3 (s), 134.5 (d), 154.2 (s), 154.5 (s), 210.7 (s).

MS (EI): m/z (%) = 212 (M^+ , 100), 197 (87).

HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2$: 212.0837; found: 212.0852.

7-(*tert*-Butyldimethylsilyloxy)-2-methyl-2,3-dihydrocyclopenta[*a*]naphthalen-1-one (23)

A mixture of the phenol **22** (0.530 g, 2.50 mmol), TBDMSiCl (0.768 g, 5.00 mmol) and DMAP (0.610 g, 5.00 mmol) was stirred overnight in CH_2Cl_2 (50 mL). The mixture was then washed with HCl (1 N; 2×100 mL) and brine (100 mL), dried (Na_2SO_4) and then all volatiles were removed under reduced pressure. The crude product was purified by column chromatography (SiO_2 ; heptane–EtOAc; R_f 0.5) and was obtained as slightly yellow solid (0.64 g, 1.96 mmol, 79%).

Mp 103.5–105.5 °C.

^1H NMR (400 MHz, CDCl_3): δ = 0.25 (s, 6 H), 1.03 (s, 9 H), 1.37 (d, J = 7.3 Hz, 3 H), 2.77–2.84 (m, 2 H), 3.46 (dd, J = 18.0, 8.1 Hz, 1 H), 7.24–7.27 (m, 2 H), 7.46 (d, J = 8.4 Hz, 1 H), 7.91 (d, J = 8.4 Hz, 1 H), 9.05 (d, J = 9.9 Hz, 1 H).

^{13}C NMR (100 MHz, CDCl_3): δ = –4.5 (q), 16.4 (q), 18.0 (s), 25.5 (q), 34.8 (t), 42.1 (d), 115.5 (d), 124.02 (d), 124.05 (d), 124.7 (s), 125.2 (d), 129.8 (d), 134.0 (s), 134.2 (d), 153.7 (s), 154.2 (s), 209.5 (s).

MS (EI): m/z (%) = 326 (M^+ , 100).

HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2\text{Si}$: 326.1702, found: 326.1703.

7,7'-Bis(*tert*-butyldimethylsilyloxy)-2,2'-dimethyl-2,3,2',3'-tetrahydro[1,1'-bi[cyclopenta-*a*]naphthalenyldiene] (24)

Using similar reaction conditions as were used for the synthesis of **5**, ketone **23** (0.619 g, 1.90 mmol) was refluxed in a mixture of the McMurry reagent prepared from TiCl_4 (0.420 mL, 0.722 g, 3.82 mmol) and Zn powder (0.497, 7.60 mmol) in THF (15 mL). After standard workup, the crude product was purified by column chromatography and was obtained as a yellow oil (0.530 g, 0.855 mmol, 90%), which solidified upon standing. The *cis* isomer was obtained pure by recrystallization from EtOH as yellow needles. Unfortunately, the *trans* isomer was not obtained in pure form; the data for *trans*-**24** were derived from a mixture of *cis* and *trans*.

***cis*-24**

Mp 169.3–170.7 °C.

^1H NMR (400 MHz, CDCl_3): δ = 0.04 (s, 6 H), 0.06 (s, 6 H), 0.90 (s, 18 H), 1.21 (d, J = 6.6 Hz, 6 H), 2.63 (d, J = 14.4 Hz, 2 H), 3.50–3.61 (m, 4 H), 6.00 (dd, J = 9.2, 2.6 Hz, 2 H), 6.48 (d, J = 9.2 Hz, 2 H), 7.01 (d, J = 2.6 Hz, 2 H), 7.42 (d, J = 8.1 Hz, 2 H), 7.55 (d, J = 8.1 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = –4.6 (q), –4.5 (q), 18.1 (s), 20.8 (q), 25.7 (q), 40.5 (t), 42.2 (d), 115.1 (d), 120.3 (d), 123.7 (d), 125.7 (s), 127.2 (d), 128.0 (d), 133.6 (s), 136.8 (s), 140.0 (s), 142.0 (s), 151.9 (s).

***trans*-24**

^1H NMR (400 MHz, CDCl_3): δ = 0.28 (s, 6 H), 0.29 (s, 6 H), 1.05 (s, 18 H), 1.28 (d, J = 6.6 Hz, 6 H), 2.30 (d, J = 14.7 Hz, 2 H), 2.92 (dd, J = 14.7, 5.5 Hz, 2 H), 3.00–3.07 (m, 2 H), 7.13 (dd, J = 9.2, 2.6 Hz, 2 H), 7.26 (d, J = 2.6 Hz, 2 H), 7.33 (d, J = 8.1 Hz, 2 H), 7.60 (d, J = 8.1 Hz, 2 H), 8.12 (d, J = 9.2 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = –4.2 (q), 18.3 (s), 19.4 (q), 25.8 (q), 41.1 (t), 43.0 (d), 115.3 (d), 121.1 (d), 124.4 (d), 126.1 (s), 126.5 (d), 128.2 (d), 134.2 (s), 138.6 (s), 139.6 (s), 141.5 (s), 152.5 (s).

MS (EI): m/z (%) = 620 (M^+ , 100).

HRMS (EI): m/z calcd for $\text{C}_{40}\text{H}_{52}\text{O}_2\text{Si}_2$: 620.3506; found: 620.3525.

2,2'-Dimethyl-2,3,2',3'-tetrahydro[1,1'-bi[cyclopenta[*a*]naphthalenyldiene]-7,7'-diol (25)

To a solution of *cis*-**24** (110 mg, 177 μmol) dissolved in THF (10 mL) was added TBAF (excess). The color of the reaction mixture turned rapidly from slightly green to orange. After stirring for 10 min, the reaction mixture was poured into a sat. soln of NH_4Cl (50 mL) and acidified to pH 2 with an aq soln of HCl (30%). The reaction mixture was extracted with Et_2O (2×50 mL) and then washed with brine (2×50 mL). After drying (Na_2SO_4) and evaporation, a yellow oil was obtained which was purified by flash column chromatography (SiO_2 , heptane–EtOAc, 1:1; R_f 0.8) and the product was finally obtained as a white solid (65.9 mg, 168 μmol , 95%). This solid, however, was not very stable, since it rapidly colored green after 30 min and went black overnight. The reaction has also been performed with a mixture of *cis*-**24** and *trans*-**24** giving a similar yield.

cis-25

Mp >250 °C.

¹H NMR (300 MHz, CDCl₃): δ = 1.20 (d, *J* = 6.6 Hz, 6 H), 2.64 (d, *J* = 14.3 Hz, 2 H), 3.46–3.61 (m, 4 H), 4.76 (s, 2 H), 6.04 (dd, *J* = 9.2, 2.6 Hz, 2 H), 6.52 (d, *J* = 9.2 Hz, 2 H), 7.00 (d, *J* = 2.6 Hz, 2 H), 7.43 (d, *J* = 8.1 Hz, 2 H), 7.54 (d, *J* = 8.1 Hz, 2 H).

trans-25

Spectral data obtained from a mixture containing *cis*-25.

¹H NMR (300 MHz, CDCl₃): δ = 1.27 (d, *J* = 6.6 Hz, 6 H), 2.30 (d, *J* = 14.3 Hz, 2 H), 2.92 (dd, *J* = 14.3, 5.5 Hz, 2 H), 3.00–3.05 (m, 2 H), 5.20 (s, 2 H), 7.16 (dd, *J* = 9.2, 2.6 Hz, 2 H), 7.23 (d, *J* = 2.6 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.59 (d, *J* = 8.1 Hz, 2 H), 8.15 (d, *J* = 9.2 Hz, 2 H).

Due to the instability and low solubility of the compound, no ¹³C NMR spectrum could be obtained.

MS (EI): *m/z* (%) = 392 (M⁺, 100).

HRMS (EI): *m/z* calcd for C₂₈H₂₄O₂: 392.1776; found: 392.1797.

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