

Pd-Catalysed Domino Arylation/CH Activation for the Synthesis of Acenaphthylenes

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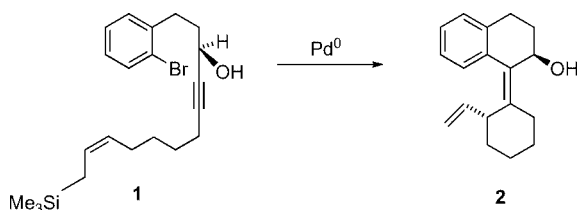
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The palladium-catalysed domino cyclisation of the aryl bromides **4**, containing an alkyne and a bromonaphthyl moiety, leads to tetracycles of type **5** in good yields. The substrates **4** are easily accessible by addition of the corresponding lithiated alkynes **7** to the aldehyde **6**.

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Introduction

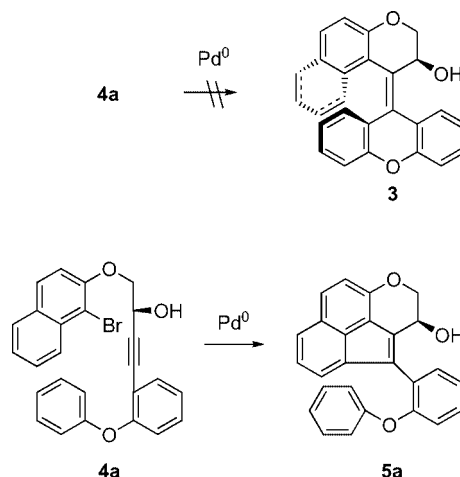
The development of highly efficient synthetic procedures towards complex molecules is an important aim in modern preparative organic chemistry. One way to improve efficiency is the use of domino reactions.^[1] Some time ago, we have developed a domino-Heck reaction for the synthesis of tetra-substituted sterically hindered alkenes such as **2** using compounds of type **1** as substrates (Scheme 1).^[2] The reactions proceed with excellent selectivity and high yields. Moreover, a multitude of ring-size analogues have been prepared. The obtained sterically hindered alkenes are of great interest as molecular switches as well as for the design of molecular motors.^[3]



Scheme 1. Palladium-catalysed domino cyclisation of **1** for the synthesis of sterically hindered alkenes.

In order to enlarge the scope of this transformation and prepare more rigid compounds it was our intention to employ an aromatic moiety instead of the allylic silane as terminating acceptor group in the domino process, where the desired final C–C bond would be formed by a CH activation.^[4]

However, by using **4a** as substrate the expected alkene **3** was not obtained but the acenaphthylene **5a** (Scheme 2).



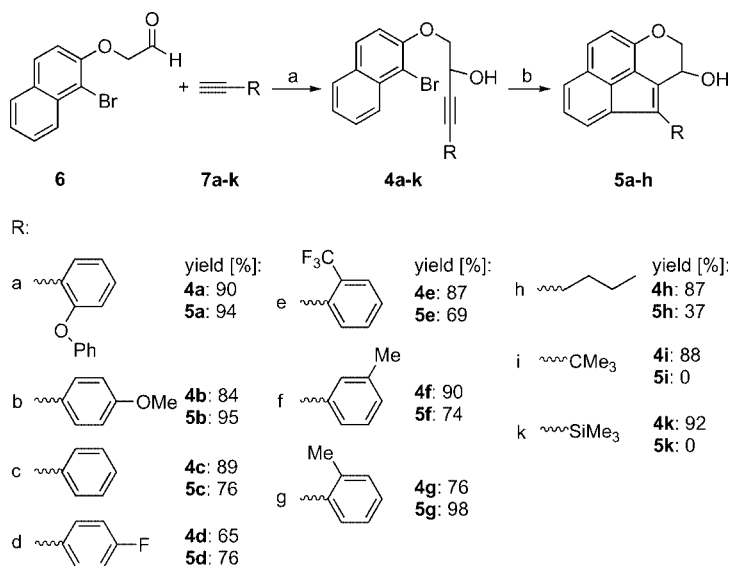
Scheme 2. Pd-catalysed transformation of **4a**.

Here we describe the scope and limitation of this new procedure using different substrates of type **4**, namely **4a–k** and their Pd-catalysed transformations to give the acenaphthylenes **5a–h**.

Results and Discussion

The substrates **4a–k** for the twofold palladium-catalysed process to give the acenaphthylenes **5a–h** were synthesised in high yields of usually over 84% by addition of the lithiated alkynes **7a–k** to the (bromonaphthyl)oxyacetaldehyde **6** at –60 °C in THF (Scheme 3). Only **7d** and **7g** had slightly lower yields (65% and 76%, respectively). It should be noted that the alkyne has usually to be employed in a two-

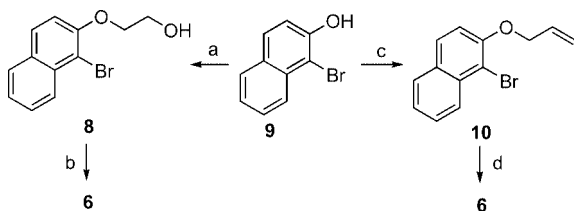
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Scheme 3. Synthesis of the substrates **4a-k** from **6** and **7a-k** as well as Pd-catalysed formation of the acenaphthylenes **5a-h**: a) *n*BuLi, THF, -60°C , room temp., -60°C ; b) LiOAc, Bu₄NOAc, CH₃CN/DMF/H₂O (5:5:1), Herrmann–Beller catalyst **14**.

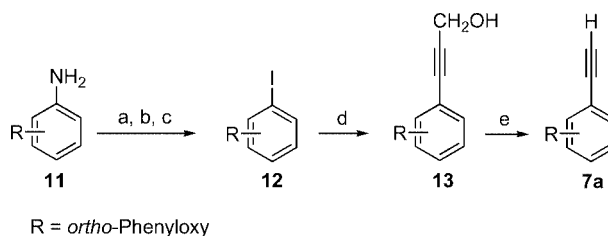
fold excess to give good results; the excess alkyne can easily be recovered by chromatography after the transformation. Thus, reaction of **6** with 1.2 equiv. of **7k** afforded **4k** in only 24% yield whereas with 2.0 equiv. of **7k** the product was obtained in 92% yield. However, in some cases as in the reaction of **6** with **7a** and **7h** 1.2 equiv. were sufficient to give high yields; in the first of the two transformations an addition of LiBr was favourable.

The (bromonaphthoxy)acetaldehyde **6** was either obtained by alkylation of the commercially available bromonaphthol **9** with 2-bromoethanol followed by an oxidation of the formed **8** with Dess–Martin periodinane^[5] or by alkylation of **9** with allyl bromide to give **10** which was transformed into **6** by ozonolysis (Scheme 4).



Scheme 4. Synthesis of the aldehyde **6** from bromonaphthol **9**: a) NaH, DMF, room temp., 15 h at 50°C , 78%; b) CH₂Cl₂, DMP, 20 h room temp., 79%; c) K₂CO₃, acetone, reflux overnight, 81%; d) O₃, CH₂Cl₂, -78°C , 9 min, Me₂S, $-78^{\circ}\text{C} \rightarrow 20^{\circ}\text{C}$, 49%.

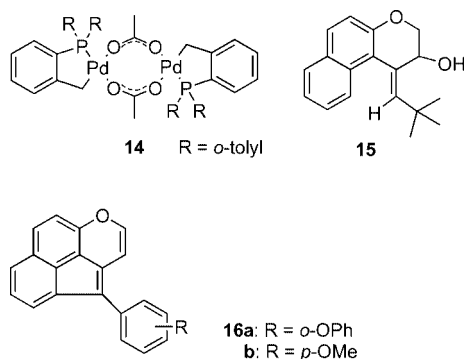
The alkynes **7b-k** are commercially available. On the other hand these alkynes can also be prepared using a procedure which we have developed for the synthesis of alkyne **7a**. This compound was obtained from the commercially available arylamine **11** by treatment with NaNO₂ and KI to form the corresponding iodo compound **12**, which was used in a Pd-catalysed coupling with propargylic alcohol under Sonogashira conditions to give the propargylic alcohol **13** followed by oxidation with MnO₂ (Scheme 5).



Scheme 5. Synthesis of the arylalkyne **7a**: a) HCl, H₂O, NaNO₂, 0°C , 40 min; b) KI, -5°C , 2 h; c) room temp. $\rightarrow 45^{\circ}\text{C} \rightarrow 80^{\circ}\text{C}$; d) *i*Pr₂NH, Pd(PPh₃)₂Cl₂, CuI, 18 h, room temp.; e) MnO₂, KOH, Et₂O, 1 h, room temp.

The domino reactions of **4a-k** were performed using catalytic amounts of the Herrmann–Beller palladacycle **14**^[6,7] (10 mol-%, Scheme 6) at $120\text{--}140^{\circ}\text{C}$ in a solvent mixture of DMF/CH₃CN/H₂O (5:5:1). The best results were obtained employing the aromatic alkynes **4a-4g**, which led to the desired acenaphthylenes **5a-g** in 69–98% yield (Scheme 3). Notably, the hydroxy group does not have to be protected in these transformations. Aliphatic alkynes can also be used; however, with much lower yield. Thus, reaction of **4h** led to **5h** in only 37% yield. On the other hand, sterically hindered aliphatic alkynes such as **4i** and the trimethylsilyl alkyne **4k** did not give any of the desired product. Using **4i** as substrate only the first Pd-catalysed C–C bond formation took place to give **15** in 33% yield (Scheme 6). In the reaction of **4k** decomposition was observed only.

In addition to the use of the palladacycle **14** several other Pd⁰ compounds like Pd(OAc)₂ and Pd₂(dba)₃ were employed in the transformation in the presence and absence of HP(*t*Bu)₃BF₄. However, in none of these reactions the desired products **5a-k** were obtained employing even harsh

Scheme 6. Palladacene **14** and the products **15** and **16**.

conditions with reaction temperatures up to 170 °C. Due to the failure with these catalysts and the unlikelihood of a Pd^{II}/Pd^{IV} process using the palladacene **14**, we assume that in the formation of **5a–h** nanoparticles of Pd are formed from **14**. However, the use of preformed nanoparticles^[8] stabilised with a tenside did not give any transformation.^[9]

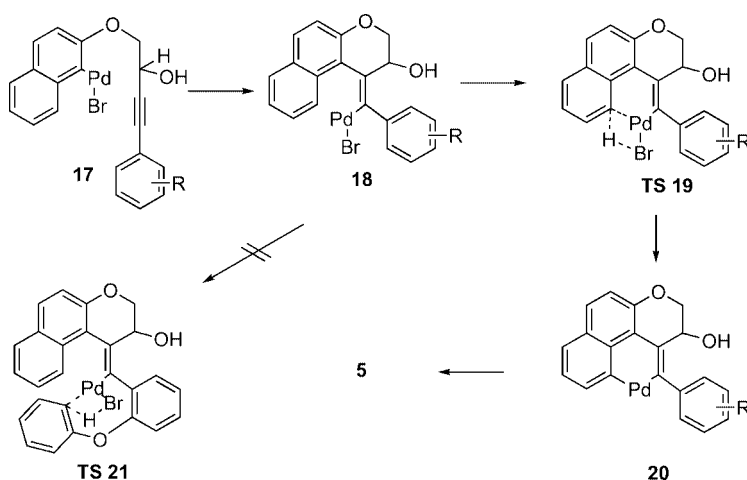
The products **5** were obtained as racemic mixtures, because the substrates **4** were used as racemic mixtures. However, one can easily perform a resolution of the substrates **4** as well as of the products **5** using HPLC on a chiral stationary phase.

The acenaphthylenes **5a–h** tend to undergo an elimination of water to form a pyran moiety, which for **5a** and **5b** already took place upon standing in CDCl₃ at room temperature for some hours to give **16a** and **16b**, respectively (Scheme 6).

The structures of the new compounds were determined by NMR and mass spectroscopy. At the beginning, the structural differentiation between **5a** and **3** was not an easy task, as both compounds have the same mass and contain one aryl–H less than the substrate **4a**. However, comparison of the spectroscopic data of the cyclisation product of **4a**

with those obtained from the product of **4c** where a formation of products such as **3** is not possible clearly indicated that both (**5a** and **5c**) have the same structural core. Thus, the UV spectra of **5a** and **5c** are nearly identical with a λ_{max} at 378.0 nm and 380.0 nm, respectively. The signals in the ¹³C NMR spectra for the oxacyclopenta[*def*]phenanthrene moiety in **5a** and **5c** are again nearly identical. Moreover, 2-H₂ and 3-H of **5a** resonate at δ = 4.62 and δ = 4.44 with J = 11.7 Hz and a centred multiplett at δ = 5.26 ppm. For the same hydrogen atoms signals are observed in the ¹H NMR spectrum of **5c** at δ = 4.72 as well as δ = 4.39 with J = 12.0 Hz and a centred multiplett at δ = 5.09 ppm.

As a mechanism for the formation of **5** from **4** we propose the following (Scheme 7). In the first step an oxidative addition of **4** to give **17** takes place which then undergoes an insertion into the triple bond to form a vinyl-Pd species **18** as an intermediate. This undergoes a CH activation via the transition state **19** to give **20**, which leads to **5** in a reductive elimination. This mechanism also allows to explain that compound **3** is not formed starting from **4a** because a transition structure as **21** would be of higher energy than **19** due to its greater flexibility. This proposal for CH activation is in agreement with recent publications.^[10] One could argue that by changing the substituent pattern at the aromatic ether system a reversed selectivity could be induced. However, as shown by Echavarren in CH activation of aromatic compounds, electron-donating and -withdrawing groups have nearly the same effect on the reaction rate. This finding is clearly incompatible with an electrophilic substitution mechanism where the electron density of the substituents would have a great influence. We therefore focus in our approach towards the synthesis of compounds of type **3** on a blocking of the position C-8 in **4a** with a methyl group or the use of a tetraline derivative, because the CH activation of an aliphatic compound should be less feasible, though it was recently shown that even that is possible.^[11]



The ligands at Pd are omitted for clarity

Scheme 7. Proposed mechanism of the Pd-catalysed domino reaction of **4** to give **5**.

Conclusions

The palladium-catalysed cyclisation of substrates of type **4** containing an alkyne and a bromonaphthyl moiety permits a highly efficient and regioselective synthesis of the acenaphthylenes **5a–h** in a domino fashion. The yields of the process and the reactivity of the substrates mainly depend on the substituent R at the triple bond in **4**, whereas the compounds containing an aryl substituent gave the best results. The products can be obtained in an enantiopure form, since the substrates and products can be easily resolved on a chiral stationary phase (HPLC).

Experimental Section

General: All reactions were performed under argon in flame-dried flasks and the reactants were introduced by syringe. All solvents were dried by standard methods. Solvents used in Pd-catalysed reactions were degassed by pump and freeze methodology. All reagents obtained from commercial sources were used without further purification. Thin-layer chromatography was performed on pre-coated silica gel plates (SIL G/UV₂₅₄, Macherey–Nagel GmbH & Co. KG). Silica gel 60 (0.032–0.064 mm) (Merck) was used for column chromatography. Ozone: Fischer Ozone generator model 502 (flow: 3 g O₃ per hour). UV/Vis spectra (CH₃CN): Mettler Lambda 2 spectrometer. IR spectra (KBr pellets or films): Bruker Vector 22 spectrometer. ¹H and ¹³C NMR spectra: Varian Mercury 200, Varian Mercury 300, Unity 300 or Inova 600 spectrometer with tetramethylsilane (TMS) as the internal standard in [D]₂chloroform or [D₆]benzene. Mass spectra (70 eV): Finnigan MAT95. Analytical HPLC: Jasco, with AS-2055 Plus Sampler, DG-1580-54 Degasser, LG-1580-04 mixing chamber, PU-2080 Plus Pump and a MD-2010 Plus Multiwave Detector. Resolution: Chiracel OD (Diacel Chemical Industries); Solvents 2-propanol and *n*-hexane (Acros).

2-(1-Bromonaphth-2-yloxy)ethanol (8): NaH (60% in paraffin, 468 mg, 11.7 mmol) was added to a stirred solution of 1-bromo-2-naphthol (**9**) (2.01 g, 9.00 mmol) in DMF (25 mL) at room temp. After the formation of gas had ceased, 2-bromoethanol (3.37 g, 1.92 mL, 27.0 mmol) was added and stirring was continued at 50 °C for 15 h. Water was added, and the mixture extracted with Et₂O. The organic phases were washed with brine, dried with MgSO₄ and the solvent removed in vacuo. Purification of the residue by flash chromatography yielded **8** as a colourless solid (1.87 g, 78%). *R*_f = 0.53 (pentane/ethyl acetate, 1:1). ¹H NMR (300 MHz, CDCl₃): δ = 8.22 (d, *J* = 8.6 Hz, 1 H, 8'-H), 7.81 (d, *J* = 8.9 Hz, 1 H, 4'-H), 7.79 (d, *J* = 8.2 Hz, 1 H, 5'-H), 7.58 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1 H, 7'-H), 7.42 (ddd, *J* = 8.3, 6.9, 1.5 Hz, 1 H, 6'-H), 7.26 (d, *J* = 8.9 Hz, 1 H, 3'-H), 4.30 (t, *J* = 4.3 Hz, 2 H, 2-H₂), 4.03 (t, *J* = 4.3 Hz, 2 H, 1-H₂), 2.37 (s, 1 H, OH) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 152.8 (C-2'), 133.0 (C-4'a), 130.2 (C-8'a), 129.0 (C-4'), 128.0 (C-5'), 127.8 (C-7'), 124.7 (C-6'), 115.6 (C-3'), 110.1 (C-1'), 71.90 (C-2), 61.40 (C-1) ppm. IR (KBr): ν̄ = 3214 (OH), 2873 (C–H), 1451 (CH₂), 1269 (Ar–O), 1058 (CH₂–O) cm^{−1}. UV (CH₃CN): λ_{max} (lg ε) = 335.0 (3.372), 323.0 (3.329), 294.5 (3.696), 282.5 (3.767), 231.0 nm (4.832). MS (ESI): *m/z* (%) = 289.1 (100) [M + Na]⁺, 291.0 (92) [M + Na]⁺. C₁₂H₁₁BrO₂ (267.12): calcd. C 53.96, H 4.15; found C 53.91, H 4.12.

1-Bromo-2-(prop-2-enyloxy)naphthalene (10): A mixture of 1-bromo-2-naphthol (**9**) (12.0 g, 53.8 mmol), allyl bromide (9.12 g, 75.4 mmol) and K₂CO₃ (11.9 g, 86.0 mmol) in dry acetone (100 mL) was refluxed under argon for 18 h. After removal of the

solvent in vacuo, water was given to the residue and the mixture extracted with Et₂O. The organic layer was washed with 5% NaOH solution, water and brine, dried (MgSO₄) and the solvent was removed in vacuo. Purification by flash chromatography gave **10** as a colourless solid (11.5 g, 81%). *R*_f = 0.55 (pentane/Et₂O, 20:1). ¹H NMR (600 MHz, CDCl₃): δ = 8.21 (d, *J* = 8.0 Hz, 1 H, 8-H), 7.74–7.79 (m, 2 H, 3-H, 5-H), 7.55 (m, 1 H, 7-H), 7.38 (m, 1 H, 6-H), 7.23 (d, *J* = 8.9 Hz, 1 H, 3-H), 6.11 (ddt, *J* = 17.4, 10.7, 5.0 Hz, 1 H, 2'-H), 5.51 (dq, *J* = 17.3, 1.5 Hz, 1 H, 3'-H_{trans}), 5.31 (dq, *J* = 10.7, 1.5 Hz, 1 H, 3'-H_{cis}), 4.75 (dt, *J* = 5.0, 1.5 Hz, 2 H, 1'-H) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 152.9 (C-2), 133.1 (C-8a), 132.8 (C-2'), 130.0 (C-4a), 128.8 (C-4), 128.0 (C-5), 127.6 (C-7), 126.2 (C-8), 124.4 (C-6), 117.9 (C-3'), 115.3 (C-3), 109.6 (C-1), 70.61 (C-1') ppm. IR (KBr): ν̄ = 3376 (OH), 2987, 2928 (CH), 1622 (C=C cm^{−1}). UV (CH₃CN): λ_{max} (lg ε) = 335 (3.3916), 322.5 (3.3333), 294.5 (3.7041), 282.5 (3.7718), 273.0 (3.6486), 232.0 nm (4.8681). MS (70 eV, EI): *m/z* (%) = 264 (46) [M]⁺, 223.0 (28) [C₁₀H₆BrO]⁺, 183.1 (36) [M – Br]⁺. C₁₃H₁₁BrO (263.13): calcd. C 59.34, H 4.21; found C 59.26, H 4.08.

2-(1-Bromonaphth-2-yloxy)acetaldehyde (6). Method A: A solution of 2-(1-bromonaphthyl-2-yloxy)ethanol (**8**) (1.00 g, 3.74 mmol) in CH₂Cl₂ (40 mL) was treated with Dess–Martin periodinane (2.38 g, 5.62 mmol) in one portion and stirred for 20 h at room temp. The reaction was quenched by addition of saturated aqueous solution of NaHCO₃ and 1 M Na₂S₂O₃, and the mixture was stirred for 1 h. After extraction with CH₂Cl₂, washing with brine and drying over MgSO₄ the solvent was evaporated in vacuo and the residue purified by flash chromatography to give **6** as colourless solid (780 mg, 2.94 mmol, 79%). **Method B:** A solution of 1-bromo-2-(prop-2-enyloxy)naphthalene (**10**) (1.00 g, 3.80 mmol) in dry CH₂Cl₂ (20 mL) was treated with O₃ (9 min, 0.05 A, O₂ stream: 50 mbar) by using a glass pipe. The reaction was finished by bubbling N₂ for 5 min through the solution and addition of SME₂ (3.8 mL). After removal of the solvent in vacuo the residue was taken up in CH₂Cl₂ (20 mL) and washed with brine and dried (MgSO₄). The solvent was removed in vacuo and the obtained crude product purified by flash chromatography to give **6** as a colourless solid (494 mg, 49%). *R*_f = 0.41 (CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ = 9.96 (t, *J* = 1.1 Hz, 1 H, 1-H), 8.24 (m, 1 H, 8'-H), 7.76–7.82 (m, 2 H, 4'-H, 5'-H), 7.58 (m, 1 H, 7'-H), 7.43 (m, 1 H, 6'-H), 7.10 (d, *J* = 9.0 Hz, 1 H, 3'-H), 4.73 (d, *J* = 1.1 Hz, 2 H, 2-H₂) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 198.9 (C-1), 152.2 (C-2'), 133.1 (C-8'a), 130.5 (C-4'a), 129.2 (C-4'), 128.0, 128.1 (C-7', C-5'), 126.4 (C-8'), 125.1 (C-6'), 115.2 (C-3'), 110.4 (C-1'), 74.80 (C-2) ppm. IR (KBr): ν̄ = 2924, 2832, 2717 (C–H), 1729 (C=O cm^{−1}). UV (CH₃CN): λ_{max} (lg ε) = 333.5 (3.342), 321.0 (3.280), 294.5 (3.701), 282.5 (3.767), 231.0 nm (4.830). MS (200 eV, DCI): *m/z* (%) = 548.1 (14) [2M + NH₄]⁺, 299.1 (100) [M + NH₃ + NH₄]⁺, 282.0 (53) [M + NH₄]⁺. C₁₂H₉BrO₂ (265.10): calcd. C 54.37, H 3.42; found: C 54.17, H 3.25.

1-Iodo-2-phenoxybenzene (12): A solution of 2-phenoxyaniline (**11**) (9.26 g, 50.0 mmol) in 50 mL water and 15 mL concd. HCl was treated with a solution of NaNO₂ (3.60 g, 52.2 mmol) in 10 mL water at 0 °C for 40 min. The reaction mixture was transferred within 2 h into a KI solution (8.60 g, 52.0 mmol) in 15 mL water at −5 °C. The formed orange suspension was stirred at room temp. (5 min), at 45 °C (15 min) and at 80 °C (15 min). After cooling down to 0 °C 25 mL of an aqueous 1 M Na₂S₂O₃ solution was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, the solvent removed in vacuo, and the crude product purified by flash chromatography to give **12** as a colourless solid (9.91 g, 67%). *R*_f = 0.49 (pentane/ethyl acetate, 100:1). ¹H NMR (300 MHz, CDCl₃): δ = 7.86 (dd, *J* = 7.8, 1.5 Hz,

1 H, 6-H), 7.25–7.39 (m, 3 H, 4-H, 3'-H, 5'-H), 7.13 (tt, $J = 7.4$, 1.3 Hz, 1 H, 4'-H), 6.97–7.02 (m, 2 H, 2'-H, 6'-H), 6.84–6.93 (m, 2 H, 5-H, 3-H) ppm. ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 156.8$ (C-1'), 156.4 (C-2), 139.8 (C-6), 129.8 (C-3', C-5'), 129.6 (C-4), 125.3 (C-5), 123.4 (C-4'), 119.4 (C-3), 118.4 (C-2', C-6'), 88.90 (C-1) ppm. IR (KBr): $\tilde{\nu} = 3051$ (C-H), 1228 (Ar-O) cm^{-1} . UV (CH_3CN): λ_{max} ($\lg \epsilon$) = 276.5 (3.318), 269.5 nm (3.322). MS (70 eV, EI): m/z (%) = 296.0 (100) $[\text{M}]^+$, 169.1 (57) $[\text{M} - \text{I}]^+$, 141.1 (32) $[\text{M} - \text{ClO}]^+$, 115.0 (16) $[\text{M} - \text{C}_3\text{H}_2\text{IO}]$. $\text{C}_{12}\text{H}_9\text{IO}$ (296.10): calcd. C 48.67, H 3.06; found C 48.79, H 2.89.

General Procedure I

Alkynylation of Aryl Iodides: Propargylic alcohol (12.0 mmol), bis(triphenylphosphane)palladium dichloride (0.08 mmol) and copper(I) iodide (0.16 mmol) were added to a magnetically stirred solution of the aryl iodide (4.0 mmol) in $i\text{Pr}_2\text{NH}$ (10 mL). The solution was carefully heated to 30–40 °C (1 min) until the yellow suspension got dark green/brown. After stirring for the stated time at room temp. the reaction mixture was poured into 40 mL of Et_2O , passed through a small layer of silica gel which was washed with Et_2O and the solvent was removed in vacuo. The crude product was dissolved in Et_2O (25 mL). Activated MnO_2 (40 mmol) and KOH (20 mmol) were added and the mixture stirred for 1 h at room temp. The reaction mixture was again filtered through a small layer of silica gel which was washed with Et_2O . The residue was purified by column chromatography after evaporation of the solvent.

1-Ethynyl-2-phenyloxybenzene (7a): Reaction of aryl iodide **12** (1.18 g, 4.00 mmol), $i\text{Pr}_2\text{NH}$ (10 mL), propargylic alcohol (675 mg, 0.710 mL, 12.0 mmol), bis(triphenylphosphane)palladium dichloride (56.2 mg, 0.080 mmol) and copper(I) iodide (30.5 mg, 0.16 mmol) [crude product $R_f = 0.10$ (pentane/ Et_2O , 3:1)] followed by treatment of activated MnO_2 (3.48 g, 40.0 mmol) and potassium hydroxide (1.12 g, 20.0 mmol) was performed according to the general procedure I. Column chromatography (pentane/ Et_2O , 10:1) afforded **7a** (544 mg, 70% over two steps) as a colourless solid. $R_f = 0.22$ (pentane). ^1H NMR (300 MHz, CDCl_3): $\delta = 7.54$ (dd, $J = 7.9$, 1.9 Hz, 1 H, 6-H), 7.24–7.37 (m, 3 H, 4-H, 3'-H, 5'-H), 7.11 (tt, $J = 7.4$, 1.3 Hz, 1 H, 4'-H), 6.99–7.07 (m, 3 H, 3-H, 2'-H, 6'-H), 6.86 (dd, $J = 8.3$, 1.1 Hz, 1 H, 5-H), 3.22 (s, 1 H, 2''-H) ppm. ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 158.4$ (C-1'), 156.9 (C-2), 134.3 (C-4), 130.2 (C-6), 129.7 (C-5', C-3'), 123.5 (C-5), 123.2 (C-4'), 118.9 (C-2', C-6'), 118.5 (C-3), 114.3 (C-1), 81.70 (C-2''), 79.30 (C-1'') ppm. IR (KBr): $\tilde{\nu} = 3283$ ($\text{C}_{\text{sp}}\text{-H}$), 3054 (Ar-H), 1477 (CH_2), 1236 (Ar-O). UV (CH_3CN): λ_{max} ($\lg \epsilon$) = 297.0 (3.233), 278.0 (3.240), 288.0 (3.313), 270.5 nm (3.181) cm^{-1} . MS (70 eV, EI): m/z (%) = 194.2 (54) $[\text{M}]^+$, 168.1 (24) $[\text{M} - \text{C}_2\text{H}_2]^+$, 165.2 (56) $[\text{M} - \text{CHO}]^+$, 77.1 (34) $[\text{C}_6\text{H}_5]^+$. $\text{C}_{14}\text{H}_{10}\text{O}$ (194.23): calcd. C 86.57, H 5.19; found C 86.80, H 4.89.

General Procedure II

Addition of Lithiated Alkynes to Aldehydes: $n\text{BuLi}$ (2.5 M in hexane, 0.80 mL, 2.0 mmol) was added to a stirred solution of the alkyne (2.0 mmol) in THF (2 mL) at –60 °C and the reaction mixture was allowed to reach room temp. within 1 h. After cooling again to –60 °C, a solution of the aldehyde (1.0 mmol) in THF (2.5 mL) was added dropwise at –60 °C with a transfer cannula, and the mixture was stirred for 30 min. Stirring was continued at –45 °C for 30 min and 1 h at room temp. An aqueous saturated NH_4Cl solution (2 mL) was added, the organic layer separated, and the aqueous phase extracted with Et_2O (4×10 mL). The combined extracts were washed with brine, dried (Na_2SO_4) and the solvents evaporated in vacuo. The crude product was purified by column chromatography to give the desired alcohols.

1-(1-Bromonaphth-2-yloxy)-4-(2-phenoxyphenyl)but-3-yn-2-ol (4a):

Reaction of aldehyde **6** (500 mg, 1.89 mmol) and alkyne **7a** (439 mg, 2.26 mmol) with LiBr (197 mg, 2.26 mmol) according to general procedure II afforded **4a** (781 mg, 90%) as a colourless solid after column chromatography. $R_f = 0.14$ (pentane/ethyl acetate, 10:1). ^1H NMR (300 MHz, CDCl_3): $\delta = 8.20$ (d, $J = 8.7$ Hz, 1 H, 8'-H), 7.78 (d, $J = 7.9$ Hz, 1 H, 4'-H), 7.76 (d, $J = 8.9$ Hz, 1 H, 5'-H), 7.56 (ddd, $J = 7.0$, 5.5, 1.5 Hz, 1 H, 7'-H), 7.48 (dd, $J = 7.6$, 1.5 Hz, 1 H, 6''-H), 7.41 (ddd, $J = 8.3$, 7.0, 1.3 Hz, 1 H, 6'-H), 7.22–7.32 (m, 3 H, 4''-H, 3'''-H, 5'''-H), 7.18 (d, $J = 9.0$ Hz, 1 H, 3'-H), 6.12–7.12 (m, 5 H, 3''-H, 5''-H, 2'''-H, 4'''-H, 6'''-H), 4.95 (ddd, $J = 7.6$, 4.9, 3.4 Hz, 1 H, 2-H), 4.18 (dd, $J = 9.8$, 3.4 Hz, 1 H, 1-H_a), 4.09 (dd, $J = 9.8$, 7.6 Hz, 1 H, 1-H_b), 3.77 (d, $J = 4.9$ Hz, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 157.4$, 157.3 (C-2'', C-1'''), 152.6 (C-2'), 133.9 (C-4'''), 133.0 (C-8'a), 130.3 (C-4'a), 130.2 (C-6'''), 129.6 (C-3''', C-5'''), 129.0 (C-4'), 128.0, 127.8 (C-5', C-7'), 126.3 (C-8'), 124.8 (C-6'), 123.6 (C-5''), 123.0 (C-4'''), 119.5 (C-3'''), 118.2 (C-2''', C-6'''), 116.0 (C-3'), 114.7 (C-1'''), 110.4 (C-1'), 90.73 (C-3), 82.03 (C-4), 73.88 (C-4), 73.88 (C-1), 61.96 (C-1) ppm. IR (KBr): $\tilde{\nu} = 3555$ (OH), 2925 (C-H), 1486, 1442 (CH_2), 1221 (O-Ar) cm^{-1} . UV (CH_3CN): λ_{max} ($\lg \epsilon$) = 335.5 (3.270), 322.0 (3.253), 292.5 (3.855), 282.5 (3.918), 271.5 (3.844), 231.0 nm (4.935). MS (70 eV, EI): m/z (%) = 458.3 (4) $[\text{M}]^+$, 379.2 (4) $[\text{M} - \text{Br}]^+$, 361.2 (100) $[\text{M} - \text{HOBu}]^+$, 222.0 (20) $[\text{C}_{16}\text{H}_{14}\text{O}]^+$. $\text{C}_{26}\text{H}_{19}\text{BrO}_3$ (459.33): calcd. C 67.99, H 4.17; found C 67.72, H 3.91.

1-(1-Bromonaphth-2-yloxy)-4-(4-methoxybenzene)but-3-yn-2-ol (4b):

Reaction of aldehyde **6** (250 mg, 0.943 mmol) and alkyne **7b** (249.3 mg, 1.89 mmol) according to general procedure II afforded **4b** (313 mg, 84%) as a light green/yellow solid after column chromatography. $R_f = 0.19$ (pentane/ Et_2O , 2:1). ^1H NMR (300 MHz, CDCl_3): $\delta = 8.20$ (d, $J = 8.6$ Hz, 1 H, 8'-H), 7.74–7.80 (m, 2 H, 4'-H, 5'-H), 7.57 (ddd, $J = 8.6$, 7.0, 1.3 Hz, 1 H, 7'-H), 7.41 (ddd, $J = 8.2$, 7.0, 1.1 Hz, 1 H, 6'-H), 7.36 (m, 2 H, 2''-H, 6''-H), 7.26 (d, $J = 9.0$ Hz, 1 H, 3'-H), 6.80 (m, 2 H, 3''-H, 5''-H), 5.45 (dd, $J = 7.3$, 3.4 Hz, 1 H, 2-H), 4.42 (dd, $J = 9.6$, 3.4 Hz, 1 H, 1-H_a), 4.31 (dd, $J = 9.6$, 7.3 Hz, 1 H, 1-H_b), 3.77 (s, 3 H, OMe), 3.05 (br. s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 159.9$ (C-4'a), 152.6 (C-2'), 133.3 (C-2'', C-6'), 133.0 (C-8'a), 130.4 (C-4'a), 129.1 (C-4'), 128.1 (C-5'), 127.8 (C-7'), 126.3 (C-8'), 124.9 (C-6'), 116.1 (C-3'), 114.1 (C-1''), 113.9 (C-3'', C-5''), 110.5 (C-1'), 86.3 (C-3), 84.2 (C-4), 74.32 (C-1), 62.07 (C-2), 55.24 (C-OMe) ppm. IR (KBr): $\tilde{\nu} = 3374$ (OH), 2929 (C-H), 1246 (O-Ar) cm^{-1} . UV (CH_3CN): λ_{max} ($\lg \epsilon$) = 334.0 (3.335), 322.0 (3.296), 293.5 (3.789), 282.0 (3.930), 252.0 (4.490), 231.0 (4.868), 204.5 nm (4.606). MS (70 eV, EI): m/z (%) = 396.1 (3) $[\text{M}]^+$, 317.2 (100) $[\text{M} - \text{Br}]^+$, 222.0 (28) $[\text{C}_{10}\text{H}_6\text{BrO}]^+$, 181.1 (77) $[\text{C}_{13}\text{H}_9\text{O}]^+$, 161.1 (52) $[\text{C}_{10}\text{H}_9\text{O}_2]^+$, 126.1 (17) $[\text{C}_{10}\text{H}_6]^+$. HRMS (EI): 396.0361. $\text{C}_{21}\text{H}_{17}\text{BrO}_3$ [M]⁺ requires 396.0361. $\text{C}_{21}\text{H}_{17}\text{BrO}_3$ (397.26): calcd. C 63.49, H 4.31; found C 63.35, H 4.06.

1-(1-Bromonaphth-2-yloxy)-4-phenylbut-3-yn-2-ol (4c):

Reaction of aldehyde **6** (200 mg, 0.754 mmol) and alkyne **7c** (154 mg, 1.51 mmol) according to general procedure II afforded **4c** (248 mg, 89%) as a colourless solid after column chromatography. $R_f = 0.24$ (pentane/ Et_2O , 4:1). ^1H NMR (300 MHz, CDCl_3): $\delta = 8.21$ (dd, $J = 8.5$, 0.6 Hz, 1 H, 8'-H), 7.79 (d, $J = 9.0$ Hz, 1 H, 4'-H), 7.78 (d, $J = 8.1$ Hz, 1 H, 5'-H), 7.53–7.61 (m, 1 H, 7'-H), 7.38–7.46 (m, 3 H, 6'-H, 2''-H, 6''-H), 7.23–7.35 (m, 4 H, 3'-H, 3''-H, 4''-H, 5''-H), 5.06 (dd, $J = 7.3$, 3.4 Hz, 1 H, 2-H), 4.44 (dd, $J = 9.6$, 3.4 Hz, 1 H, 1-H_a), 4.33 (dd, $J = 9.6$, 7.3 Hz, 1 H, 1-H_b), 2.99 (br. s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 152.6$ (C-2'), 133.0 (C-8'a), 131.8 (C-2'', C-6'), 130.4 (C-4'a), 129.1 (C-4'), 128.7 (C-4'), 128.3 (C-3'', C-5''), 128.1 (C-5'), 127.9 (C-7'), 126.3 (C-8'),

124.9 (C-6'), 122.0 (C-1''), 116.0 (C-3'), 110.6 (C-1'), 86.33 (C-3), 85.55 (C-4), 74.21 (C-1), 62.02 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3376 (OH), 3053, 2929, 2873 (CH) cm^{-1} . UV (CH₃CN): λ_{max} (lg ϵ) = 282.0 (3.790), 250 (4.371), 232 (4.882), 202 nm (4.623). MS (70 eV, EI): m/z (%) = 287.2 (100) [C₂₀H₁₅O₂]⁺, 131.1 (64) [C₉H₇O]⁺, 222.0 (95) [C₁₀H₆BrO]⁺, 115.1 (100) [C₉H₇]⁺, 77.0 (62) [C₆H₅]⁺. HRMS (EI): 366.0256. C₂₀H₁₅BrO₂ [M]⁺ requires 366.0255. C₂₀H₁₅BrO₂ (367.23): calcd. C 65.41, H 4.12; found C 62.54, H 3.94.

1-(1-Bromonaphth-2-yloxy)-4-(4-fluorophenyl)but-3-yn-2-ol (4d):

Reaction of aldehyde **6** (250 mg, 0.943 mmol) and alkyne **7d** (227 mg, 1.89 mmol) according to general procedure II afforded **4d** (236 mg, 0.613 mmol, 65%) as a colourless solid after column chromatography. R_f = 0.10 (pentane/Et₂O, 4:1). ¹H NMR (600 MHz, CDCl₃): δ = 8.20 (dd, J = 8.6, 0.7 Hz, 1 H, 8'-H), 7.78 (t, J = 8.9 Hz, 2 H, 4'-H, 5'-H), 7.55–7.59 (m, 1 H, 7'-H), 7.37–7.44 (m, 3 H, 6'-H, 2''-H, 6''-H), 7.28 (d, J = 9.1 Hz, 1 H, 3'-H) ppm. 6.94–6.99 (m, 2 H, 3''-H, 5''-H), 5.03 (ddd, J = 7.2, 5.2, 3.4 Hz, 1 H, 2-H), 4.43 (dd, J = 9.6, 3.4 Hz, 1 H, 1-H_a), 4.32 (dd, J = 9.6, 7.2 Hz, 1 H, 1-H_b), 2.99 (d, J = 5.2 Hz, 1 H, OH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 164.4, 161.0 (C-4''*), 152.6 (C-2'), 133.8, 133.7 (C-2''*, C-6''*), 133.0 (C-8'a), 130.4 (C-4'a), 129.1 (C-4'), 128.1 (C-5'), 127.9 (C-7'), 126.3 (C-8'), 125.0 (C-6'), 118.2, 118.1 (C-1''*), 116.0 (C-3'), 115.7, 115.4 (C-3''*, C-5''*), 110.6 (C-1'), 85.39 (C-3), 85.28 (C-4), 74.17 (C-1), 61.97 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3363 (OH), 3048, 2873 (C–H), 1149 (O–Ar) cm^{-1} . UV (CH₃CN): λ_{max} (lg ϵ) = 334.0 (3.332), 322.5 (3.294), 294.5 (3.698), 283.0 (3.807), 273.5 (3.734), 231.0 nm (4.882). MS (70 eV, EI): m/z (%) = 384.2 (16) [M]⁺, 305.2 (100) [M – Br]⁺, 222.1 (95) [C₆H₆BrO]⁺, 149.1 (42) [C₉H₆FO]⁺, 126.1 (50) [C₁₀H₆]⁺. C₂₀H₁₄BrFO₂ (385.23): calcd. C 62.36, H 3.66; found C 62.11, H 3.48.

1-(1-Bromonaphth-2-yloxy)-4-(2-trifluoromethylphenyl)but-3-yn-2-ol (4e):

Reaction of aldehyde **6** (250 mg, 0.943 mmol) and alkyne **7e** (320.8 mg, 1.89 mmol) according to general procedure II afforded **4e** (356.2 mg, 87%) as a colourless solid after column chromatography. R_f = 0.21 (pentane/Et₂O, 3:1). ¹H NMR (300 MHz, CDCl₃): δ = 8.20 (d, J = 8.6 Hz, 1 H, 8'-H), 7.78 (d, J = 9.0 Hz, 1 H, 4'-H), 7.77 (dt, J = 8.1, 0.6 Hz, 1 H, 5'-H), 7.53–7.66 (m, 3 H, 7'-H, 4''-H, 6''-H), 7.33–7.48 (m, 3 H, 6'-H, 3''-H, 5''-H), 7.27 (d, J = 9.0 Hz, 1 H, 3'-H), 5.10 (m, 1 H, 2-H), 4.44 (dd, J = 9.7, 3.4 Hz, 1 H, 1-H_a), 4.34 (dd, J = 9.7, 7.3 Hz, 1 H, 1-H_b), 3.07 (br. s, 1 H, OH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 152.6 (C-2'), 134.2 (C-4''), 133.0 (C-2''), 131.6 (C-8'a), 131.4 (C-5''), 131.3 (C-4'a), 129.2 (C-4'), 128.5 (C-3''), 128.1 (C-5'), 127.9 (C-7'), 126.3 (C-8'), 125.8 (C-6''), 125.2 (C–CF₃), 124.9 (C-6'), 121.6 (C-1''), 116.1 (C-3'), 110.6 (C-1'), 91.23 (C-3), 82.18 (C-4), 73.94 (C-1), 62.03 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3330 (OH), 2943, 2874 (C–H), 1451 (CH₂) cm^{-1} . UV (CH₃CN): λ_{max} (lg ϵ) = 334.0 (3.316), 322.0 (3.278), 285.5 (3.905), 280.0 (3.917), 231.0 nm (4.861). MS (70 eV, EI): m/z (%) = 434.1 (32) [M]⁺, 355.2 (60) [M – Br]⁺, 224.0 (100) [C₁₀H₆BrO]⁺, 156.1 (17) [C₁₁H₈O]⁺. C₂₁H₁₄BrF₃O₂ (435.23): calcd. C 57.95, H 3.24; found C 57.71, H 3.01.

1-(1-Bromonaphth-2-yloxy)-4-(3-methylphenyl)but-3-yn-2-ol (4f):

Reaction of aldehyde **6** (200 mg, 0.754 mmol) and alkyne **7f** (175 mg, 1.51 mmol) according to general procedure II afforded **4f** (260 mg, 90%) as a colourless solid after column chromatography. R_f = 0.16 (pentane/Et₂O, 4:1). ¹H NMR (300 MHz, CDCl₃): δ = 8.21 (d, J = 8.4 Hz, 1 H, 8'-H), 7.75–7.81 (m, 2 H, 4'-H, 5'-H), 7.57 (ddd, J = 8.4, 7.0, 1.4 Hz, 1 H, 7'-H), 7.42 (ddd, J = 8.3, 7.0, 1.3 Hz, 1 H, 6'-H), 7.27 (d, J = 8.9 Hz, 1 H, 3'-H), 7.08–7.25 (m, 4 H, 2''-H, 4''-H, 5''-H, 6''-H), 5.06 (ddd, J = 7.2, 5.0, 3.4 Hz, 1 H, 2-H), 4.43 (dd, J = 9.7, 3.4 Hz, 1 H, 1-H_a), 4.33 (dd, J = 9.7,

7.2 Hz, 1 H, 1-H_b), 3.05 (d, J = 5.0 Hz, OH), 2.28 (s, 3 H, Me) ppm. ¹³C NMR (75.6 MHz, CDCl₃): δ = 152.6 (C-2'), 137.9 (C-3''), 133.0 (C-8'a), 132.4 (C-2''), 130.4 (C-4'a), 129.6 (C-6''), 129.1 (C-4'), 128.9, 128.05 (C-4'', C-5''), 128.1 (C-5'), 127.8 (C-7'), 126.3 (C-8'), 124.9 (C-6'), 121.8 (C-1''), 116.0 (C-3'), 110.6 (C-1'), 86.50 (C-3), 85.20 (C-4), 74.23 (C-1), 62.02 (C-2), 21.16 (C-Me) ppm. IR (KBr): $\tilde{\nu}$ = 3384 (OH), 2923 (C–H), 2231 (C_{sp}C_{sp}), 1271 (O–Ar) cm^{-1} . UV (CH₃CN): λ_{max} (lg ϵ) = 334.0 (3.302), 322.5 (3.262), 294.5 (3.671), 282.0 (3.785), 251.0 (4.336), 231.5 nm (4.853). MS (70 eV, EI): m/z (%) = 380.2 (2) [M]⁺, 301.3 (34) [M – Br]⁺, 222.1 (58) [C₁₀H₆BrO]⁺, 115.1 (100) [C₉H₇]⁺, 91.1 (28) [C₇H₇]⁺. C₂₁H₁₇BrO₂ (381.26): calcd. C 66.16, H 4.49; found C 65.92, H 4.28.

1-(1-Bromonaphth-2-yloxy)-4-(2-methylphenyl)but-3-yn-2-ol (4g):

Reaction of aldehyde **6** (200 mg, 0.754 mmol) and alkyne **7g** (175.3 mg, 1.51 mmol) according to general procedure II afforded **4g** (218.5 mg, 76%) as a colourless solid after column chromatography. R_f = 0.26 (pentane/Et₂O, 3:1). ¹H NMR (300 MHz, CDCl₃): δ = 8.21 (d, J = 8.6 Hz, 1 H, 8'-H), 7.79 (d, J = 9.0 Hz, 1 H, 4'-H), 7.78 (m, 1 H, 5'-H), 7.57 (ddd, J = 8.6, 6.9, 1.3 Hz, 1 H, 7'-H), 7.38–7.45 (m, 2 H, 6'-H, 6''-H), 7.28 (d, J = 9.0 Hz, 1 H, 3'-H), 7.07–7.25 (m, 3 H, 5''-H, 4''-H, 3''-H), 5.10 (ddd, J = 7.1, 5.2, 3.4 Hz, 1 H, 2-H), 4.44 (dd, J = 9.6, 3.4 Hz, 1 H, 1-H_a), 4.35 (dd, J = 9.6, 7.1 Hz, 1 H, 1-H_b), 3.01 (d, J = 5.2 Hz, 1 H, OH), 2.42 (s, 3 H, Me) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 152.6 (C-2'), 140.4 (C-2''), 133.0 (C-8'a), 132.2 (C-6''), 130.4 (C-4'a), 129.4 (C-3''), 129.1 (C-4'), 128.7 (C-4''), 128.1 (C-5'), 127.8 (C-7'), 126.3 (C-8'), 125.5 (C-5''), 124.9 (C-6'), 121.8 (C-1''), 116.0 (C-3'), 110.5 (C-1'), 89.47 (C-3), 85.16 (C-4), 74.27 (C-1), 62.10 (C-2), 20.65 (C-Me) ppm. IR (KBr): $\tilde{\nu}$ = 3554 (OH), 3051, 2926 (C–H), 1451 (CH₂), 1267 (Ar–O), 761 (Ar–Me) cm^{-1} . UV (CH₃CN): λ_{max} (lg ϵ) = 334.0 (3.338), 322.5 (3.296), 294.5 (3.686), 282.0 (3.814), 273.0 (3.729), 251.0 (4.324), 231.0 nm (4.872). MS (70 eV, EI): m/z (%) = 382.0 (3) [M]⁺, 301.1 (58) [M – Br]⁺, 283.1 (14) [M – Br–OH]⁺, 221.9 (100) [C₁₀H₆BrO]⁺, 209.0 (53) [C₁₄H₉O₂]⁺, 126.0 (42) [C₁₀H₈]⁺, 115.0 (80) [C₉H₇]⁺, 91.0 (34) [C₇H₇]⁺. C₂₁H₁₇BrO₂ (381.26): calcd. C 66.16, H 4.49; found C 66.32, H 4.29.

1-(1-Bromonaphth-2-yloxy)oct-3-yn-2-ol (4h):

Reaction of aldehyde **6** (250 mg, 0.943 mmol) and alkyne **7h** (93.0 mg, 1.13 mmol) according to general procedure II afforded **4h** (286 mg, 87%) as a colourless oil after column chromatography. R_f = 0.18 (pentane/Et₂O, 5:1). ¹H NMR (300 MHz, CDCl₃): δ = 8.20 (m, 1 H, 8'-H), 7.78 (d, J = 8.9 Hz, 1 H, 4'-H), 7.74–7.79 (m, 1 H, 5'-H), 7.56 (ddd, J = 8.5, 7.0, 1.4 Hz, 1 H, 7'-H), 7.41 (ddd, J = 8.0, 7.0, 1.2 Hz, 1 H, 6'-H), 7.23 (d, J = 8.9 Hz, 1 H, 3'-H), 4.83 (m, 1 H, 2-H), 4.32 (dd, J = 9.8, 3.4 Hz, 1 H, 1-H_a), 4.18 (dd, J = 9.8, 7.7 Hz, 1 H, 1-H_b), 2.81 (d, J = 4.4 Hz, 1 H, OH), 2.22 (td, J = 7.0, 2.0 Hz, 2 H, 5-H), 1.31–1.53 (m, 4 H, 6-H, 7-H), 0.88 (t, J = 7.2 Hz, 3 H, 8-H) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 152.6 (C-2'), 133.0 (C-8'a), 130.3 (C-4'a), 129.0 (C-4'), 128.0 (C-5'), 127.8 (C-7'), 126.3 (C-8'), 124.8 (C-6'), 116.0 (C-3'), 110.4 (C-1'), 87.44 (C-4), 76.58 (C-3), 74.54 (C-1), 61.65 (C-2), 30.43 (C-6), 21.88 (C-7), 18.37 (C-5), 13.54 (C-8) ppm. IR (KBr): $\tilde{\nu}$ = 3396 (OH), 2932, 2871 (C–H), 2238 (C_{sp}C_{sp}), 1464 (CH₂) cm^{-1} . UV (CH₃CN): λ_{max} (lg ϵ) = 334.0 (3.352), 322.5 (3.310), 294.5 (3.713), 282.5 (3.790), 232.0 nm (4.875). MS (70 eV, EI): m/z (%) = 346.1 (18) [M]⁺, 267.2 (4) [M – Br]⁺, 224.0 (100) [C₁₆H₁₆O]⁺, 126.1 (20) [C₁₀H₆]⁺. C₁₈H₁₉BrO₂ (346.26): calcd. 346.0568; found 346.0568.

1-(1-Bromonaphth-2-yloxy)-5,5-dimethylhex-3-yn-2-ol (4i):

Reaction of aldehyde **6** (200 mg, 0.754 mmol) and alkyne **7i** (123.9 mg, 1.51 mmol) according to general procedure II afforded **4i** (229 mg, 88%) as a colourless oil after column chromatography. R_f = 0.16 (pentane/Et₂O, 6:1). ¹H NMR (600 MHz, CDCl₃): δ = 8.20 (d, J

= 8.6 Hz, 1 H, 8'-H), 7.76–7.81 (m, 2 H, 4'-H, 5'-H), 7.56 (ddd, J = 8.6, 7.0, 1.2 Hz, 1 H, 7'-H), 7.42 (ddd, J = 8.0, 7.0, 1.2 Hz, 1 H, 6'-H), 7.27 (d, J = 9.0 Hz, 1 H, 3'-H), 4.81 (dd, J = 7.8, 3.2 Hz, 1 H, 2-H), 4.31 (dd, J = 9.6, 3.2 Hz, 1 H, 1-H_a), 4.17 (dd, J = 9.6, 7.8 Hz, 1 H, 1-H_b), 2.73 (br. s, 1 H, OH), 1.19 (s, 9 H, *t*Bu) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 152.6 (C-2'), 132.9 (C-8'a), 130.3 (C-4'a), 129.0 (C-4'), 128.0 (C-5'), 127.8 (C-7'), 126.2 (C-8'), 124.8 (C-6'), 116.0 (C-3'), 110.4 (C-1'), 95.39 (C-4), 75.05 (C-3), 74.55 (C-1), 61.58 (C-2), 30.77 (3×C-Me), 27.30 (C-5) ppm. IR (KBr): $\tilde{\nu}$ = 3422 (OH), 3067 (C–H), 2236 (C_{sp}C_{sp}), 1452 (CH₂), 1274 (O–Ar) cm⁻¹. UV (CH₃CN): λ_{max} (lg ϵ) = 334.0 (3.327), 322.5 (3.293), 294.5 (3.691), 282.5 (3.773), 273.5 (3.663), 231.5 nm (4.865). MS (70 eV, EI): m/z (%) = 346.2 (24) [M]⁺, 222.0 (100) [C₁₀H₆BrO]⁺, 193.1 (5) [C₁₄H₉O]⁺, 126.1 (9) [C₈H₁₃O]⁺. C₁₈H₁₉BrO₂ (347.25): calcd. C 62.26, H 5.52; found C 61.93, H 5.49.

1-(1-Bromonaphth-2-yloxy)-4-trimethylsilylbut-3-yn-2-ol (4k): Reaction of aldehyde **6** (250 mg, 0.943 mmol) and alkyne **7k** (185.2 mg, 1.89 mmol) according to general procedure II afforded **4k** (315.9 mg, 92%) as a colourless oil after column chromatography. R_f = 0.21 (pentane/Et₂O, 6:1). ¹H NMR (600 MHz, CDCl₃): δ = 8.20 (d, J = 8.6 Hz, 1 H, 8'-H), 7.76–7.80 (m, 2 H, 4'-H, 5'-H), 7.57 (ddd, J = 8.6, 7.0, 1.2, 1 H, 7'-H), 7.42 (ddd, J = 8.0, 7.0, 1.2 Hz, 1 H, 6'-H), 7.27 (d, J = 9.0 Hz, 1 H, 3'-H), 4.82 (dd, J = 7.6, 3.5 Hz, 1 H, 2-H), 4.35 (dd, J = 9.7, 3.5 Hz, 1 H, 1-H_a), 4.22 (dd, J = 9.7, 7.6 Hz, 1 H, 1-H_b), 2.78 (br. s, 1 H, OH), 0.15 (s, 9 H, SiMe₃) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 152.6 (C-2'), 133.0 (C-8'a), 130.4 (C-4'a), 129.1 (C-4'), 128.1 (C-5'), 127.9 (C-7'), 126.3 (C-8'), 124.9 (C-6'), 116.1 (C-3'), 110.6 (C-1'), 101.9 (C-3), 91.60 (C-4), 74.19 (C-1), 61.94 (C-2), –0.20 (SiMe₃) ppm. IR (KBr): $\tilde{\nu}$ = 3532 (OH), 3067 (C–H), 2177 (C_{sp}C_{sp}), 1452 (CH₂), 1273 (O–Ar) cm⁻¹. UV (CH₃CN): λ_{max} (lg ϵ) = 334.0 (3.285), 322.0 (3.247), 294.5 (3.658), 282.5 (3.737), 273.5 (3.628), 231.5 nm (4.829). MS (70 eV, EI): m/z (%) = 364.2 (22) [M]⁺, 267.2 (3) [M – Br–OH]⁺, 222.1 (100), [C₁₀H₆BrO]⁺, 193.1 (30) [C₁₄H₉O]⁺, 73.1 (63) [SiMe₃]⁺. C₁₇H₁₉BrO₂Si (363.32): calcd. C 56.20, H 5.27; found C 55.98, H 4.98.

General Procedure III

Palladium-Catalysed Domino Cyclisation of 4: palladacycle **14** (0.1 equiv.) was added to a stirred mixture of 4.0 equiv. lithium acetate, 3.0 equiv. tetrabutylammonium acetate, 1.0 equiv. of **4** in (CH₃CN/DMF/H₂O, 5:5:1, 28 mL/mol) at 60 °C and stirring was continued with reflux at 120–140 °C. For quenching the reaction, water was added (1 mL/mmol) and the mixture was extracted with Et₂O. The organic layers were washed with brine and dried (MgSO₄). After evaporation of the solvent the residue was purified by column chromatography.

4-(2-Phenoxyphenyl)-2,3-dihydro-1-oxacyclopenta[def]phenanthren-3-ol (5a): Reaction of **4a** (90 mg, 0.196 mmol) according to general procedure III at 120 °C for 2 h yielded **5a** (70 mg, 94%) as a yellow foam. R_f = 0.27 (pentane/ethyl acetate, 7:1). ¹H NMR (600 MHz, CDCl₃): δ = 7.86 (d, J = 7.1 Hz, 1 H, 5-H*), 7.80 (d, J = 7.9 Hz, 1 H, 7-H*), 7.78 (d, J = 8.8 Hz, 1 H, 8-H), 7.75 (dd, J = 7.5, 1.7 Hz, 1 H, 4''-H), 7.52 (dd, J = 7.9, 7.1 Hz, 1 H, 6-H), 7.34 (m_c, 1 H, 5'-H), 7.29 (m_c, 1 H, 4'-H), 7.24 (m_c, 2 H, 3''-H, 5''-H), 7.12 (d, J = 8.8 Hz, 1 H, 9-H), 7.05 (dd, J = 8.0, 1.1 Hz, 1 H, 6'-H*), 7.02 (dt, J = 7.5, 0.9 Hz, 1 H, 3'-H*), 6.95 (m_c, 2 H, 2''-H, 6''-H), 5.26 (m_c, 1 H, 3-H), 4.62 (dd, J = 11.7, 4.6 Hz, 1 H, 2-H_a), 4.44 (dd, J = 11.7, 3.0 Hz, 1 H, 2-H_b), 3.05 (d, J = 4.0 Hz, 1 H, OH) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 156.6 (C-2), 154.2, 153.5 (C-1'', C-9a), 139.5 (C-1'), 132.2 (C-4''), 131.0 (C-3a), 130.5 (C-8), 129.8 (C-3'', C-5'), 128.8 (C-5*), 127.6 (C-4), 127.0 (C-9c), 126.7

(C-7a), 126.4 (C-6, C-7), 125.9 (C-5), 124.2 (C-4a), 123.9, 123.6, (C-4', C-6'), 121.1 (C-9b), 119.4 (C-3'), 118.5 (C-2'', C-6''), 118.0 (C-9), 75.83 (C-2), 65.27 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3051 (C–H), 1666 (C=C), 1481 (CH₂), 1230 (Ar–O) cm⁻¹. UV (CH₃CN): λ_{max} (lg ϵ) = 362.5 (3.744), 378.0 (3.820), 323.0 (3.753), 309.5 nm (3.656). MS (70 eV, EI): m/z (%) = 378.3 (100) [M]⁺, 361.3 (78) [M – OH]⁺, 285.2 (36) [M – C₆H₅O]⁺, 255.2 (43) [M – C₆H₅O₃]⁺, 226.2 (50) [M – C₈H₈O₃]⁺, 181.2 (14) [M – C₁₃H₈O₂]⁺, 77.1 (16) [M – C₂₀H₁₃O₃]⁺. C₂₆H₁₈O₃ (378.42): calcd. C 82.52, H 4.79; found C 80.78, H 4.73.

Resolution: HPLC: Flow: 0.8 mL/min, eluent: *n*-hexane/*i*PrOH, 95:5, $t_{R,I}$ = 47.88 min, $t_{R,II}$ = 58.51 min.

4-(4-Methoxyphenyl)-2,3-dihydro-1-oxacyclopenta[def]phenanthren-3-ol (5b): Reaction of **4b** (90.0 mg, 0.227 mmol) according to general procedure III at 125 °C for 3 h yielded **5b** (68.1 mg, 0.215 mmol, 95%) as an orange foam. R_f = 0.22 (pentane/Et₂O, 2:1). ¹H NMR (600 MHz, CDCl₃): δ = 7.99 (d, J = 7.0 Hz, 1 H, 5-H*), 7.79–7.84 (m, 3 H, 3'-H, 5'-H, 7-H*), 7.73 (d, J = 8.8 Hz, 1 H, 8-H), 7.53 (dd, J = 8.0, 7.0 Hz, 1 H, 6-H), 7.10 (d, J = 8.8 Hz, 1 H, 9-H), 7.04 (m_c, 2 H, 2'-H, 6'-H), 5.07 (m_c, 1 H, 3-H), 4.72 (dd, J = 12.0, 9.6 Hz, 1 H, 2-H_a), 4.39 (dd, J = 12.0, 9.8 Hz, 1 H, 2-H_b), 3.86 (s, 3 H, OMe), 2.24 (br. s, 1 H, OH) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 159.1 (C-4'), 152.9 (C-9a), 138.7 (C-3a), 132.6 (C-4), 130.1 (C-7), 129.9 (C-2', C-6'), 127.9 (C-1'), 127.6 (C-9c), 126.7 (C-8), 126.6, 126.5 (C-6, C-5), 126.5 (C-4a), 124.5 (C-7a), 121.3 (C-9b), 118.0 (C-9), 114.5 (C-3', C-5'), 76.93 (C-2), 64.62 (C-3), 55.34 (C–OMe) ppm. IR (KBr): $\tilde{\nu}$ = 3418 (OH), 2908 (C–H), 1665 (C=C), 1441 (CH₂) cm⁻¹. UV (CH₃CN): λ_{max} (lg ϵ) = 419.0 (3.527), 381.5 (3.936), 364.5 (3.833), 322.5 (3.906), 307.5 (3.857), 271.5 (4.168), 232.5 nm (4.422). MS (70 eV, EI): m/z (%) = 316.2 (100), [M]⁺, 299.2 (47) [M – OH]⁺, 283.2 (22) [C₂₀H₁₁O₂]⁺, 226.1 (17) [C₁₈H₉]⁺, 149.1 (5) [C₁₂H₅]⁺. C₂₁H₁₆O₃ (316.36): calcd. 316.1099; found 316.1099.

Resolution: HPLC: Flow: 0.8 mL/min, eluent: *n*-hexane/*i*PrOH, 95:5, $t_{R,I}$ = 49.21 min, $t_{R,II}$ = 84.84 min.

4-Phenyl-2,3-dihydro-1-oxacyclopenta[def]phenanthren-3-ol (5c): Reaction of **4c** (100 mg, 0.272 mmol) according to general procedure III at 130 °C for 3 h yielded **5c** (59.2 mg, 76%) as an orange foam. R_f = 0.24 (pentane/Et₂O, 4:1). ¹H NMR (600 MHz, CDCl₃): δ = 8.02 (d, J = 7.1 Hz, 1 H, 7-H*), 7.86–7.89 (m, 2 H, 2'-H, 6'-H), 7.81 (d, J = 8.0 Hz, 1 H, 5-H*), 7.76 (d, J = 8.8 Hz, 1 H, 8-H), 7.54 (dd, J = 8.0, 7.1 Hz, 1 H, 6-H), 7.50 (m_c, 2 H, 3'-H, 5'-H), 7.37 (m_c, 1 H, 4'-H), 7.11 (d, J = 8.8 Hz, 1 H, 9-H), 5.09 (m_c, 1 H, 3-H), 4.72 (dd, J = 12.0, 2.3 Hz, 1 H, 2-H_a), 4.39 (dd, J = 12.0, 2.3 Hz, 1 H, 2-H_b), 2.26 (br. s, 1 H, OH) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 153.3 (C-9a), 138.5 (C-1'), 135.3 (C-3a), 132.8 (C-4), 130.6 (C-7), 129.0 (C-2', C-6'), 128.7 (C-3', C-5'), 127.8 (C-9c, C-4a), 127.4 (C-8), 126.8, 126.7, 126.6 (C-4', C-6, C-5), 124.5 (C-7a), 121.1 (C-9b), 118.0 (C-9), 76.93 (C-2), 64.60 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3386 (OH), 3050, 2908 (C–H), 1664 (C=C), 1441 (CH₂) cm⁻¹. UV (CH₃CN): λ_{max} (lg ϵ) = 364.5 (3.901), 380.0 (4.001), 323.5 (3.920), 309.0 (3.810), 245.5 nm (4.345). MS (70 eV, EI): m/z (%) = 286.1 (100) [M]⁺, 269.1 (68) [M – OH]⁺, 239.1 (34) [M – CH₃O₂]⁺, 226.1 (32) [M – C₂H₄O₂]⁺. C₂₀H₁₄O₂ (286.32): calcd. 286.0994; found 286.0994.

Resolution: HPLC: Flow: 0.8 mL/min, eluent: *n*-hexane/*i*PrOH, 95:5, $t_{R,I}$ = 31.45 min, $t_{R,II}$ = 46.16 min.

4-(4-Fluorophenyl)-2,3-dihydro-1-oxacyclopenta[def]phenanthren-3-ol (5d): Reaction of **4d** (70 mg, 0.182 mmol) according to general procedure III at 130 °C for 4.5 h yielded **5d** (41.8 mg, 76%) as yellow foam. R_f = 0.23 (pentane/Et₂O, 4:1). ¹H NMR (300 MHz,

CDCl_3 : δ = 7.96 (d, J = 7.0 Hz, 1 H, 5-H), 7.80–7.87 (m, 2 H, 2'-H, 6'-H), 7.81 (d, J = 8.0 Hz, 1 H, 7-H), 7.75 (d, J = 8.8 Hz, 1 H, 8-H), 7.53 (dd, J = 8.0, 7.0 Hz, 1 H, 6-H), 7.19 (m_c, 2 H, 3'-H, 5'-H), 7.10 (d, J = 8.0 Hz, 1 H, 9-H), 5.03 (m_c, 1 H, 3-H), 4.71 (dd, J = 12.1, 2.4 Hz, 1 H, 2-H_a), 4.38 (dd, J = 12.1, 2.4 Hz, 1 H, 2-H_b), 2.18 (br. s, 1 H, OH) ppm. ^{13}C NMR (50.3 MHz, CDCl_3): δ = 163.9 (C-4'), 160.6 (C-9a), 153.3 (C-3a), 138.3 (C-4), 131.8 (C-1'), 131.4 (C-9c), 130.6 (C-7), 130.3 (d, J = 8.1 Hz, 2 C, C-2', C-6'), 127.5 (C-4a), 126.9 (C-8), 126.6, 126.5 (C-6, C-5), 124.5 (C-7a), 121.0 (C-9b), 118.0 (C-9), 116.0 (d, J = 21.3 Hz, 2 C, C-3', C-5'), 76.95 (C-2), 64.49 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3356 (OH), 2917 (C-H), 1665 (C=C), 1441 (CH_2) cm^{-1} . UV (CH_3CN): λ_{max} (lg ϵ) = 380.0 (3.990), 364.5 (3.889), 323.0 (3.919), 309.0 (3.805), 245.0 nm (4.353). MS (70 eV, EI): m/z (%) = 304.2 (100) $[\text{M}]^+$, 287.2 (68), $[\text{M} - \text{OH}]^+$, 262.2 (30) $[\text{C}_{18}\text{H}_{11}\text{FO}]^+$, 257.1 (36) $[\text{C}_{19}\text{H}_{10}\text{F}]^+$, 244.2 (40) $[\text{C}_{18}\text{H}_9\text{F}]^+$, 122.1 (35) $[\text{C}_8\text{H}_7\text{F}]^+$. $\text{C}_{20}\text{H}_{13}\text{FO}_2$ (304.31): calcd. C 78.94, H 4.31; found C 78.82, H 4.43.

Resolution: HPLC: Flow: 0.8 mL/min, eluent: *n*-hexane/*i*PrOH, 95:5, $t_{\text{R,I}}$ = 36.65 min, $t_{\text{R,II}}$ = 62.08 min.

4-(2-Trifluoromethylphenyl)-2,3-dihydro-1-oxacyclopenta[def]phenanthren-3-ol (5e): Reaction of **4e** (90 mg, 0.207 mmol) according to general procedure III at 140 °C for 4.5 h yielded **5e** (65.8 mg, 69%) as a yellow foam. R_f = 0.33 (pentane/ Et_2O , 2:1). ^1H NMR (300 MHz, CDCl_3): δ = 7.78–7.86 (m, 2 H, 7-H*, 5-H*), 7.81 (d, J = 8.9 Hz, 1 H, 8-H), 7.42–7.65 (m, 5 H, 6-H*, 3'-H*, 4'-H*, 5'-H*, 6'-H*), 7.14 (d, J = 8.9 Hz, 1 H, 9-H), 5.01–5.07 (m, 1 H, 3-H), 4.57 (dd, J = 11.9, 4.0 Hz, 1 H, 2-H_a), 4.45 (dd, J = 11.9, 2.8 Hz, 1 H, 2-H_b), 1.87 (br. s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 153.7 (C-9a), 140.7 (C-3a), 133.7 (C-1'), 132.7 (C-5'), 131.4 (C-4'), 131.2 (C-4*), 130.9 (C-8*), 129.3 (C-9c*), 128.2 (C-6*), 127.9 (C-3'), 127.0 (C-2'), 126.6 (C-7*), 126.4 (C-6'), 126.0 (C-4a*), 125.4 (C-5*), 124.2 (C-CF₃), 122.3 (C-7a*), 120.4 (C-9b*), 117.9 (C-9), 76.42 (C-2), 64.73 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3384 (OH), 2917 (C-H), 1668 (C=C), 1442 (CH_2), 1231 (Ar-O) cm^{-1} . UV (CH_3CN): λ_{max} (lg ϵ) = 371.5 (3.964), 357.5 (3.905), 320.5 (3.962), 306.5 (3.841), 239.0 nm (4.376). MS (70 eV, EI): m/z (%) = 354.3 (35) $[\text{M}]^+$, 337.3 (34) $[\text{M} - \text{OH}]^+$, 104.1 (86) $[\text{C}_8\text{H}_8]^+$, 77.1 (30) $[\text{C}_6\text{H}_5]^+$, 66.0 $[\text{C}_4\text{H}_2\text{O}]^+$. $\text{C}_{21}\text{H}_{13}\text{F}_3\text{O}_2$ (354.33): calcd. 354.0868; found 354.0868.

Resolution: HPLC: Flow: 0.8 mL/min, eluent: *n*-hexane/*i*PrOH, 95:5, $t_{\text{R,I}}$ = 28.39 min, $t_{\text{R,II}}$ = 29.97 min.

4-(3-Methylphenyl)-2,3-dihydro-1-oxacyclopenta[def]phenanthren-3-ol (5f): Reaction of **4f** (90 mg, 0.236 mmol) according to general procedure III at 130 °C for 4.5 h yielded **5f** (52.2 mg, 74%) as a yellow foam. R_f = 0.19 (pentane/ Et_2O , 4:1). ^1H NMR (300 MHz, CDCl_3): δ = 8.00 (d, J = 7.1 Hz, 1 H, 5-H), 7.79 (d, J = 8.0 Hz, 1 H, 7-H), 7.71 (d, J = 8.8 Hz, 1 H, 8-H), 7.63–7.69 (m, 2 H, 4'-H, 2'-H), 7.53 (dd, J = 8.0, 7.1 Hz, 1 H, 6-H), 7.39 (m_c, 1 H, 5'-H), 7.16–7.21 (m, 1 H, 6'-H), 7.08 (d, J = 8.8 Hz, 1 H, 9-H), 5.05 (m_c, 1 H, 3-H), 4.68 (dd, J = 12.1, 2.6 Hz, 1 H, 2-H_a), 4.33 (dd, J = 12.1, 2.3 Hz, 1 H, 2-H_b), 2.42 (d, J = 7.9 Hz, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 153.2 (C-9a), 138.5 (C-1', C-3'), 135.2 (C-3a), 132.8 (C-4), 130.3 (C-8), 129.2 (C-4'), 128.9 (C-5'), 128.1 (C-6'), 127.7 (C-9c), 127.6 (C-4a), 126.7 (C-5, C-7), 126.5 (C-6), 125.8 (C-2'), 124.4 (C-7a), 121.1 (C-9b), 117.9 (C-9), 76.83 (C-2), 64.51 (C-3), 21.62 (C-Me) ppm. IR (KBr): $\tilde{\nu}$ = 3389 (OH), 2919 (C-H), 736 (Ar-Me), 1666 (C=C) cm^{-1} . UV (CH_3CN): λ_{max} (lg ϵ) = 364.5 (3.828), 380.0 (3.926), 323.0 (3.850), 309.0 (3.761), 245.5 nm (4.274). MS (70 eV, EI): m/z (%) = 300.1 (100) $[\text{M}]^+$, 283.1 (94) $[\text{M} - \text{OH}]^+$, 239.1 (44) $[\text{C}_{19}\text{H}_{11}]^+$. $\text{C}_{21}\text{H}_{16}\text{O}_2$ (300.36): calcd. 300.1150; found 300.1150.

Resolution: HPLC: Flow: 0.8 mL/min, eluent: *n*-hexane/*i*PrOH, 95:5, $t_{\text{R,I}}$ = 33.23 min, $t_{\text{R,II}}$ = 46.40 min.

4-(2-Methylphenyl)-2,3-dihydro-1-oxacyclopenta[def]phenanthren-3-ol (5g): Reaction of **4g** (70 mg, 0.184 mmol) according to general procedure III at 140 °C for 2.5 h yielded **5g** (53.9 mg, 98%) as a yellow foam. R_f = 0.34 (pentane/ Et_2O , 3:1). ^1H NMR (300 MHz, CDCl_3): δ = 7.75–7.82 (m, 2 H, 5-H, 8-H), 7.61 (m_c, 1 H, 7-H), 7.44–7.51 (m, 2 H, 3'-H, 6-H), 7.22–7.37 (m, 3 H, 4'-H, 5'-H, 6'-H), 7.12 (d, J = 8.8 Hz, 1 H, 9-H), 5.02 (m_c, 1 H, 3-H), 4.52 (dd, J = 11.5, 4.5 Hz, 1 H, 2-H_a), 4.42 (dd, J = 11.7, 3.1 Hz, 1 H, 2-H_b), 2.40 (s, 3 H, Me), 2.16 (m_c, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 153.2 (C-9a), 139.9 (C-1', C-2'), 134.2 (C-3a), 132.7 (C-4), 130.5 (C-3', C-4'), 130.4 (C-8), 129.8 (C-9c), 127.8 (C-5'), 127.4 (C-4a), 126.5 (C-6), 126.4 (C-5), 126.0 (C-7), 125.7 (C-6'), 124.3 (C-7a), 121.0 (C-9b), 117.9 (C-9), 76.31 (C-2), 65.32 (C-3), 20.79 (C-Me) ppm. IR (KBr): $\tilde{\nu}$ = 3387 (OH), 2920 (C-H), 1667 (C=C), 1442 (CH_2), 1210 (Ar-O) cm^{-1} . UV (CH_3CN): λ_{max} (lg ϵ) = 374.0 (3.958), 359.5 (3.891), 320.5 (3.920), 307.0 (3.793), 240.5 nm (4.412). MS (70 eV, EI): m/z (%) = 300.1 (92) $[\text{M}]^+$, 283.1 (100) $[\text{M} - \text{OH}]^+$, 239.1 (94) $[\text{C}_{19}\text{H}_{11}]^+$, 226.1 (55) $[\text{C}_{18}\text{H}_{10}]^+$, 126.0 (37) $[\text{C}_{10}\text{H}_6]^+$, 91.0 (8) $[\text{C}_7\text{H}_7]^+$. $[\text{C}_{21}\text{H}_{16}\text{O}_2 + \text{H}]^+$ (301.36): calcd. 301.1223; found 301.1223.

Resolution: HPLC: Flow: 0.8 mL/min, eluent: *n*-hexane/*i*PrOH, 95:5, $t_{\text{R,I}}$ = 26.88 min, $t_{\text{R,II}}$ = 29.63 min.

4-Butyl-2,3-dihydro-1-oxacyclopenta[def]phenanthren-3-ol (5h): Reaction of **4h** (90 mg, 0.259 mmol) according to general procedure III at 140 °C for 22 h yielded **5h** (25.2 mg, 37%) as a yellow oil. R_f = 0.18 (pentane/ Et_2O , 5:1). ^1H NMR (300 MHz, CDCl_3): δ = 7.75, (d, J = 6.9 Hz, 1 H, 7-H), 7.74 (d, J = 8.0 Hz, 1 H, 5-H), 7.66 (d, J = 8.9 Hz, 1 H, 8-H), 7.47 (dd, J = 8.0, 6.9 Hz, 1 H, 6-H), 7.05 (d, J = 8.9 Hz, 1 H, 9-H), 5.07 (m_c, 1 H, 3-H), 4.56 (dd, J = 11.9, 3.5 Hz, 1 H, 2-H_a), 4.33 (dd, J = 11.9, 2.9 Hz, 1 H, 2-H_b), 2.88 (t, J = 7.7 Hz, 2 H, 1'-H), 1.99 (m_c, 1 H, OH), 1.79 (m_c, 2 H, 2'-H), 1.47 (m_c, 2 H, 3'-H), 0.97 (t, J = 7.3 Hz, 3 H, 4'-H) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 151.9 (C-4), 140.1 (C-9a), 134.8 (C-3a), 129.4 (C-8), 127.7, 127.5 (C-9c, C-4a), 126.3 (C-5), 126.2 (C-6), 124.5 (C-7), 124.1 (C-7a), 121.0 (C-9b), 117.9 (C-9), 76.42 (C-2), 64.84 (C-3), 32.79 (C-2'), 26.58 (C-1'), 22.91 (C-3'), 13.98 (C-4') ppm. IR (KBr): $\tilde{\nu}$ = 3339 (OH), 2928, 2857 (C-H) cm^{-1} . UV (CH_3CN): λ_{max} (lg ϵ) = 369.0 (3.820), 353.0 (3.745), 316.5 (3.845), 302.5 (3.717), 232.0 nm (4.348). MS (70 eV, EI): m/z (%) = 266.3 (100) $[\text{M}]^+$, 249.3 (18) $[\text{M} - \text{OH}]^+$, 223.2 (95) $[\text{M} - \text{OH}-\text{C}_2\text{H}_5]^+$, 195.2 (82) $[\text{M} - \text{OH}-\text{C}_4\text{H}_9]^+$, 165.2 (69) $[\text{C}_{12}\text{H}_5\text{O}]^+$. $\text{C}_{18}\text{H}_{18}\text{O}_2$ (266.34): calcd. 266.1307; found 266.1307.

Resolution: HPLC: Flow: 0.8 mL/min, eluent: *n*-hexane/*i*PrOH, 95:5, $t_{\text{R,I}}$ = 31.71 min, $t_{\text{R,II}}$ = 38.60 min.

1-(2,2-Dimethylpropylidene)-2,3-dihydro-1H-benzol[*f*]chromen-2-ol (15): Reaction of **4i** (90.0 mg, 0.26 mmol) according to general procedure III at 140 °C for 46 h yielded **15** (22.6 mg, 0.085 mmol, 33%) as a colourless oil. R_f = 0.22 (pentane/ Et_2O , 3:1). ^1H NMR (300 MHz, CDCl_3): δ = 8.29 (d, J = 8.6 Hz, 1 H, 10-H), 7.74 (dd, J = 8.0, 1.3 Hz, 1 H, 7-H), 7.62 (d, J = 8.9 Hz, 1 H, 6-H), 7.42 (ddd, J = 8.6, 6.9, 1.5 Hz, 1 H, 9-H), 7.31 (ddd, J = 8.0, 6.9, 1.2 Hz, 1 H, 8-H), 7.03 (d, J = 8.9 Hz, 1 H, 5-H), 6.11 (s, 1 H, 1'-H), 5.28 (m_c, 1 H, 2-H), 4.51 (dd, J = 11.8, 2.1 Hz, 1 H, 3-H_a), 4.28 (dd, J = 11.8, 2.0 Hz, 1 H, 3-H_b), 2.00 (d, J = 5.5 Hz, 1 H, OH), 1.32 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 151.0 (C-4a), 141.2 (C-1'), 131.9 (C-1), 130.2 (C-10a), 129.0 (C-6), 128.6 (C-6a), 128.5 (C-7), 126.3 (C-9), 123.6 (C-10), 123.2 (C-8), 117.9 (C-5), 114.4 (C-10b), 72.02 (C-3), 62.55 (C-2), 33.44 (C-2'), 31.56 (3 × C-2' Me) ppm. IR (KBr): $\tilde{\nu}$ = 3383 (OH), 2958 (C-H), 1595 (C=C), 1467 (CH_2), 1231 (Ar-O), 1075 ($\text{CH}_2\text{-O}$) cm^{-1} . UV (CH_3CN): λ_{max}

(lg ϵ) = 346.0 (3.649), 333.5 (3.599), 301.0 (3.685), 289.5 (3.746), 278.5 (3.701), 240.5 nm (4.564). MS (70 eV, EI): m/z (%) = 268.1 (56) [M]⁺, 253.1 (10) [C₁₈H₂₁O]⁺, 195.1 (32) [C₁₄H₁₁O]⁺, 181.0 (38) [C₁₃H₉O]⁺. C₁₈H₂₀O₂ (268.36): calcd. 268.1463; found 268.1463.

Synthesis of 16 by Elimination of Water from 5: A solution of **5** in CHCl₃ was kept for 10 h at room temp. Removal of the solvent in vacuo gave **16**.

4-(2-Phenoxyphenyl)-1-oxacyclopenta[def]phenanthrene (16a): ¹H NMR (600 MHz, CDCl₃): δ = 8.23 (d, J = 7.2 Hz, 1 H, 10-H), 8.11 (d, J = 8.8 Hz, 1 H, 6-H*), 7.99 (d, J = 7.9 Hz, 1 H, 7-H*), 7.87 (dd, J = 7.9, 7.3 Hz, 1 H, 9-H*), 7.57 (d, J = 8.8 Hz, 1 H, 5-H*), {7.87–7.90 (m, 1 H), 7.58 (d, J = 4.8 Hz, 1 H), 7.28–7.34 (m, 2 H), 7.12–7.19 (m, 4 H), 6.90–6.96 (m, 3 H), (2-H, 3-H, 8-H, 1'-H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H, 7'-H, 8'-H)} ppm. C₂₆H₁₆O₂ + H⁺ (361.41): calcd. 361.12231, found 361.12233.

4-(4-Methoxyphenyl)-1-oxacyclopenta[def]phenanthrene (16b): ¹H NMR (200 MHz, CDCl₃): δ = 8.23 (d, J = 7.1 Hz, 1 H, 5-H), 8.14 (d, J = 8.9 Hz, 1 H, 8-H), 8.05 (d, J = 7.9 Hz, 1 H, 7-H), 7.90 (dd, J = 7.9, 7.1 Hz, 1 H, 6-H), 7.84 (m, 2 H, 3'-H, 5'-H), 7.61 (d, J = 8.9 Hz, 1 H, 9-H), 7.58 (d, J = 6.0 Hz, 1 H, 2-H), 7.15 (d, J = 6.0, 1 H, 3-H), 7.10 (m, 2 H, 2'-H, 6'-H), 3.91 (s, 1 H, Me) ppm. C₂₁H₁₄O₂ (298.34): calcd. 298.0994, found 298.0994.

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