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

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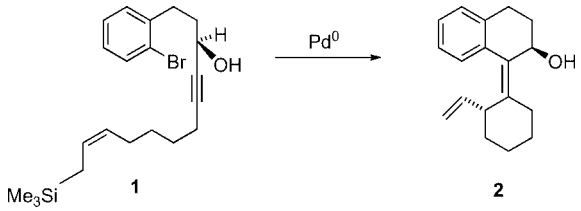
**Keywords:** Acenaphthylenes / Alkynes / CH activation / Domino reactions / Oxacyclopentaphenanthrenes / Palladium catalysis / Pyrans

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**.



## 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]

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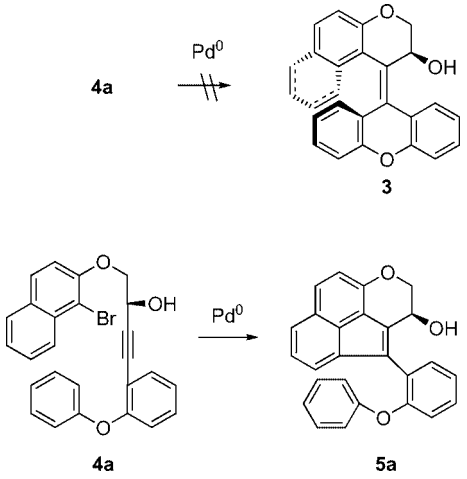
However, by using **4a** as substrate the expected alkene **3** was not obtained but the acenaphthylene **5a** (Scheme 2).



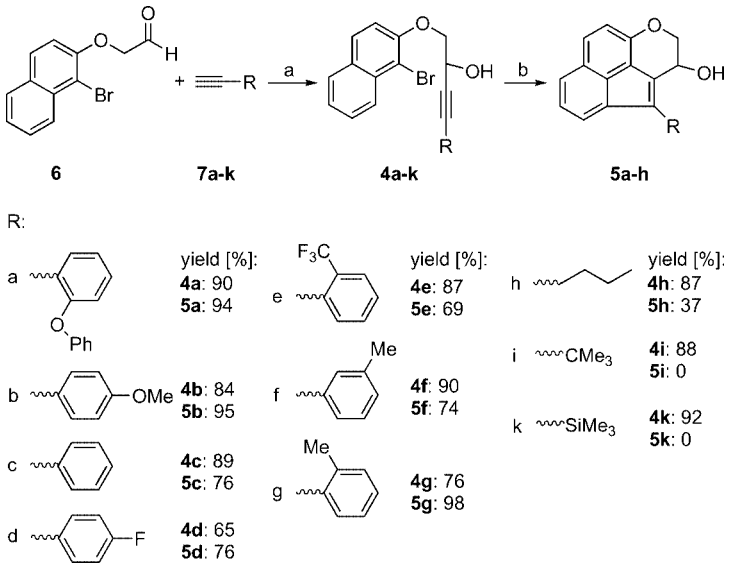

Scheme 2. Pd-catalysed transformation of **4a**.

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 (bromonaphthyloxy)acetaldehyde **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-

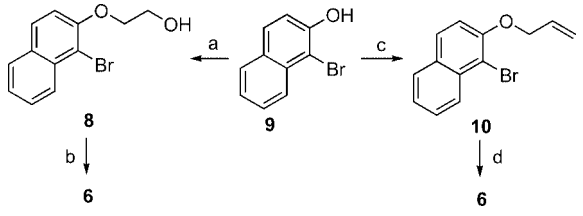
  




Scheme 3. Synthesis of the substrates **4a**–**k** from **6** and **7a**–**k** as well as Pd-catalysed formation of the acenaphthylenes **5a**–**h**: a) *n*BuLi, THF, –60 °C, room temp., –60 °C; b) LiOAc, $Bu_4NOAc$, $CH_3CN/DMF/H_2O$ (5:5:1), Herrmann–Beller catalyst **14**.

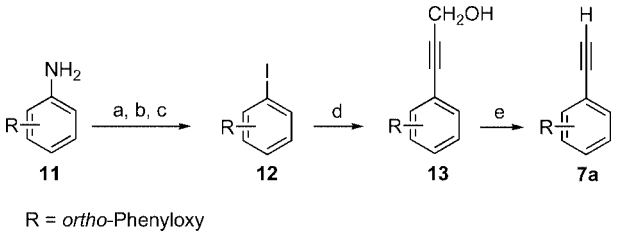
fold excess to give good results; the excess alkyne can easily be recovered by chromatography after the transformation. Thus, reaction of **6** with 1.2 equiv. of **7k** afforded **4k** in only 24% yield whereas with 2.0 equiv. of **7k** the product was obtained in 92% yield. However, in some cases as 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 (bromonaphthyloxy)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) $CH_2Cl_2$, DMP, 20 h room temp., 79%; c) $K_2CO_3$, acetone, reflux overnight, 81%; d) $O_3$, $CH_2Cl_2$, –78 °C, 9 min, $Me_2S$, –78 °C→20 °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 $NaNO_2$ 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 $MnO_2$ (Scheme 5).

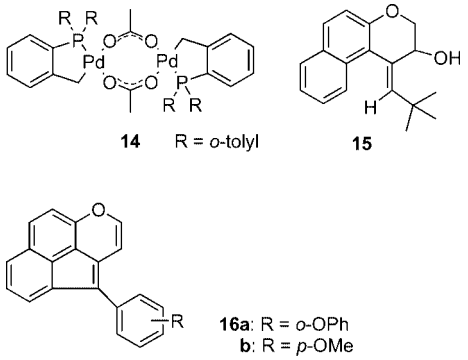



Scheme 5. Synthesis of the arylalkyne **7a**: a) HCl, $H_2O$, $NaNO_2$, 0 °C, 40 min; b) KI, –5 °C, 2 h; c) room temp.→45 °C→80 °C; d) $iPr_2NH$, $Pd(PPh_3)_2Cl_2$, CuI, 18 h, room temp.; e) $MnO_2$, KOH, $Et_2O$, 1 h, room temp.

The domino reactions of **4a**–**k** were performed using catalytic amounts of the Herrmann–Beller palladacycle **14**[6,7] (10 mol-%, Scheme 6) at 120–140 °C in a solvent mixture of $DMF/CH_3CN/H_2O$ (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 palladacene **14** several other $Pd^0$ compounds like $Pd(OAc)_2$ and $Pd_2(dba)_3$ were employed in the transformation in the presence and absence of $HP(tBu)_3BF_4$. 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**.

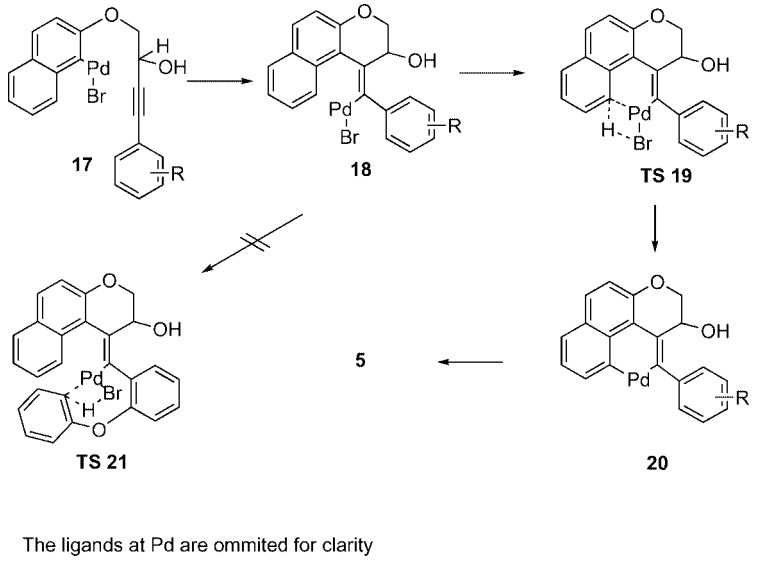
conditions with reaction temperatures up to 170 °C. Due to the failure with these catalysts and the unlikeliness of a $Pd^{II}/Pd^{IV}$ process using the palladacene **14**, we assume that in the formation of **5a**–**h** nanoparticles of Pd are formed from **14**. However, the use of preformed nanoparticles[8] 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 $CDCl_3$ 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 $\lambda_{max}$ at 378.0 nm and 380.0 nm, respectively. The signals in the $^{13}C$ NMR spectra for the oxacyclopenta[*def*]phenanthrene moiety in **5a** and **5c** are again nearly identical. Moreover, 2-$H_2$ and 3-H of **5a** resonate at $\delta$ = 4.62 and $\delta$ = 4.44 with $J$ = 11.7 Hz and a centred multiplett at $\delta$ = 5.26 ppm. For the same hydrogen atoms signals are observed in the $^1H$ NMR spectrum of **5c** at $\delta$ = 4.72 as well as $\delta$ = 4.39 with $J$ = 12.0 Hz and a centred multiplett at $\delta$ = 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]




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 precoated silica gel plates (SIL G/UV$_{254}$, 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 $O_3$ per hour). UV/Vis spectra ($CH_3CN$): Mettler Lambda 2 spectrometer. IR spectra (KBr pellets or films): Bruker Vector 22 spectrometer. $^1H$ and $^{13}C$ NMR spectra: Varian Mercury 200, Varian Mercury 300, Unity 300 or Inova 600 spectrometer with tetramethylsilane (TMS) as the internal standard in [D]chloroform or [$D_6$]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 $Et_2O$. The organic phases were washed with brine, dried with $MgSO_4$ 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, $CDCl_3$): $\delta$ = 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-$H_2$), 4.03 (t, $J$ = 4.3 Hz, 2 H, 1-$H_2$), 2.37 (s, 1 H, OH) ppm. $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$ = 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): $\tilde{\nu}$ = 3214 (OH), 2873 (C–H), 1451 ($CH_2$),1269 (Ar–O), 1058 ($CH_2$–O) cm$^{-1}$. UV ($CH_3CN$): $\lambda_{max}$ (lg$\varepsilon$) = 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]$^+$. $C_{12}H_{11}BrO_2$ (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 $K_2CO_3$ (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 $Et_2O$. The organic layer was washed with 5% NaOH solution, water and brine, dried ($MgSO_4$) 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/$Et_2O$, 20:1). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 8.21 (d, $J$ = 8.0 Hz, 1 H, 8-H), 7.74–7.79 (m, 2 H, 3-H, 5-H), 7.55 ($m_c$, 1 H, 7-H), 7.38 ($m_c$, 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. $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$ = 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): $\tilde{\nu}$ = 3376 (OH), 2987, 2928 (CH), 1622 (C=C cm$^{-1}$). UV ($CH_3CN$): $\lambda_{max}$ (lg$\varepsilon$) = 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) [$C_{10}H_6BrO$]$^+$, 183.1 (36) [M – Br]$^+$. $C_{13}H_{11}BrO$ (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 $CH_2Cl_2$ (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 $NaHCO_3$ and 1 M $Na_2S_2O_3$, and the mixture was stirred for 1 h. After extraction with $CH_2Cl_2$, washing with brine and drying over $MgSO_4$ 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 $CH_2Cl_2$ (20 mL) was treated with $O_3$ (9 min, 0.05 A, $O_2$ stream: 50 mbar) by using a glass pipe. The reaction was finished by bubbling $N_2$ for 5 min through the solution and addition of $SMe_2$ (3.8 mL). After removal of the solvent in vacuo the residue was taken up in $CH_2Cl_2$ (20 mL) and washed with brine and dried ($MgSO_4$). 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 ($CH_2Cl_2$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 9.96 (t, $J$ = 1.1 Hz, 1 H, 1-H), 8.24 ($m_c$, 1 H, 8′-H), 7.76–7.82 (m, 2 H, 4′-H, 5′-H), 7.58 ($m_c$, 1 H, 7′-H), 7.43 ($m_c$, 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-$H_2$) ppm. $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$ = 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): $\tilde{\nu}$ = 2924, 2832, 2717 (C–H), 1729 (C=O cm$^{-1}$). UV ($CH_3CN$): $\lambda_{max}$ (lg$\varepsilon$) = 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 + $NH_4$]$^+$, 299.1 (100) [M + $NH_3$ + $NH_4$]$^+$, 282.0 (53) [M + $NH_4$]$^+$. $C_{12}H_9BrO_2$ (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 $NaNO_2$ (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 $Na_2S_2O_3$ 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, $CDCl_3$): $\delta$ = 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 ($CH_3CN$): $\lambda_{max}$ (lg$\varepsilon$) = 276.5 (3.318), 269.5 nm (3.322). MS (70 eV, EI): $m/z$ (%) = 296.0 (100) $[M]^+$, 169.1 (57) $[M - I]^+$, 141.1 (32) $[M - CIO]^+$, 115.0 (16) $[M - C_3H_2IO]$. $C_{12}H_9IO$ (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 $i$Pr$_2$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-Ethinyl-2-phenyloxybenzene (7a):** Reaction of aryl iodide **12** (1.18 g, 4.00 mmol), $i$Pr$_2$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). $^1$H 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 ($C_{sp}$–H), 3054 (Ar–H), 1477 ($CH_2$), 1236 (Ar–O). UV ($CH_3CN$): $\lambda_{max}$ (lg$\varepsilon$) = 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) $[M]^+$, 168.1 (24) $[M - C_2H_2]^+$, 165.2 (56) $[M - CHO]^+$, 77.1 (34) $[C_6H_5]^+$. $C_{14}H_{10}O$ (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:** $n$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). $^1$H 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 ($CH_3CN$): $\lambda_{max}$ (lg$\varepsilon$) = 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) $[M]^+$, 379.2 (4) $[M - Br]^+$, 361.2 (100) $[M - HOBr]^+$, 222.0 (20) $[C_{16}H_{14}O]^+$. $C_{26}H_{19}BrO_3$ (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). $^1$H 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$_c$, 2 H, 2′′-H, 6′′-H), 7.26 (d, $J$ = 9.0 Hz, 1 H, 3′-H), 6.80 (m$_c$, 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′′), 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 ($CH_3CN$): $\lambda_{max}$ (lg$\varepsilon$) = 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) $[M]^+$, 317.2 (100) $[M - Br]^+$, 222.0 (28) $[C_{10}H_6BrO]^+$, 181.1 (77) $[C_{13}H_9O]^+$, 161.1 (52) $[C_{10}H_9O_2]^+$, 126.1 (17) $[C_{10}H_6]^+$. HRMS (EI): 396.0361. $C_{21}H_{17}BrO_3$ $[M]^+$ requires 396.0361. $C_{21}H_{17}BrO_3$ (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). $^1$H 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 ($CH_3CN$): $\lambda_{max}$ ($lg\varepsilon$) = 282.0 (3.790), 250 (4.371), 232 (4.882), 202 nm (4.623). MS (70 eV, EI): *m/z* (%) = 287.2 (100) $[C_{20}H_{15}O_2]^+$, 131.1 (64) $[C_9H_7O]^+$, 222.0 (95) $[C_{10}H_6BrO]^+$, 115.1 (100) $[C_9H_7]^+$, 77.0 (62) $[C_6H_5]^+$. HRMS (EI): 366.0256. $C_{20}H_{15}BrO_2$ $[M]^+$ requires 366.0255. $C_{20}H_{15}BrO_2$ (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/$Et_2O$, 4:1). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 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. $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$ = 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 ($CH_3CN$): $\lambda_{max}$ ($lg\varepsilon$) = 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) $[C_6H_6BrO]^+$, 149.1 (42) $[C_9H_6FO]^+$, 126.1 (50) $[C_{10}H_6]^+$. $C_{20}H_{14}BrFO_2$ (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 colourless solid after column chromatography. $R_f$ = 0.21 (pentane/$Et_2O$, 3:1). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 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 ($m_c$, 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. $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$ = 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–$CF_3$), 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 ($CH_2$) $cm^{-1}$. UV ($CH_3CN$): $\lambda_{max}$ ($lg\varepsilon$) = 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) $[C_{10}H_6BrO]^+$, 156.1 (17) $[C_{11}H_8O]^+$. $C_{21}H_{14}BrF_3O_2$ (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/$Et_2O$, 4:1). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 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. $^{13}C$ NMR (75.6 MHz, $CDCl_3$): $\delta$ = 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 ($CH_3CN$): $\lambda_{max}$ ($lg\varepsilon$) = 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) $[C_{10}H_6BrO]^+$, 115.1 (100) $[C_9H_7]^+$, 91.1 (28) $[C_7H_7]^+$. $C_{21}H_{17}BrO_2$ (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/$Et_2O$, 3:1). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 8.21 (d, *J* = 8.6 Hz, 1 H, 8′-H), 7.79 (d, *J* = 9.0 Hz, 1 H, 4′-H), 7.78 ($m_c$, 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. $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$ = 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 ($CH_2$), 1267 (Ar–O), 761 (Ar–Me) $cm^{-1}$. UV ($CH_3CN$): $\lambda_{max}$ ($lg\varepsilon$) = 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) $[M - Br\text{-}OH]^+$, 221.9 (100) $[C_{10}H_6BrO]^+$, 209.0 (53) $[C_{14}H_9O_2]^+$, 126.0 (42) $[C_{10}H_8]^+$, 115.0 (80) $[C_9H_7]^+$, 91.0 (34) $[C_7H_7]^+$. $C_{21}H_{17}BrO_2$ (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/$Et_2O$, 5:1). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 8.20 ($m_c$, 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 ($m_c$, 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. $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$ = 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 ($CH_2$) $cm^{-1}$. UV ($CH_3CN$): $\lambda_{max}$ ($lg\varepsilon$) = 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) $[C_{16}H_{16}O]^+$, 126.1 (20) $[C_{10}H_6]^+$. $C_{18}H_{19}BrO_2$ (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/$Et_2O$, 6:1). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 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. $^{13}$C NMR (75.5 MHz, $CDCl_3$): 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): ṽ = 3422 (OH), 3067 (C–H), 2236 ($C_{sp}C_{sp}$), 1452 ($CH_2$), 1274 (O–Ar) cm$^{-1}$. UV ($CH_3CN$): $\lambda_{max}$ (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) $[C_{10}H_6BrO]^+$, 193.1 (5) $[C_{14}H_9O]^+$, 126.1 (9) $[C_8H_{13}O]^+$. $C_{18}H_{19}BrO_2$ (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/$Et_2O$, 6:1). $^1$H NMR (600 MHz, $CDCl_3$): 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, $SiMe_3$) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): 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 ($SiMe_3$) ppm. IR (KBr): ṽ = 3532 (OH), 3067 (C–H), 2177 ($C_{sp}C_{sp}$), 1452 ($CH_2$), 1273 (O–Ar) cm$^{-1}$. UV ($CH_3CN$): $\lambda_{max}$ (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), $[C_{10}H_6BrO]^+$, 193.1 (30) $[C_{14}H_9O]^+$, 73.1 (63) $[SiMe_3]^+$. $C_{17}H_{19}BrO_2Si$ (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 ($CH_3CN$/DMF/$H_2O$, 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 $Et_2O$. The organic layers were washed with brine and dried ($MgSO_4$). 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). $^1$H NMR (600 MHz, $CDCl_3$): 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. $^{13}$C NMR (50.3 MHz, $CDCl_3$): 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): ṽ = 3051 (C–H), 1666 (C=C), 1481 ($CH_2$), 1230 (Ar–O) cm$^{-1}$. UV ($CH_3CN$): $\lambda_{max}$ (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 – $C_6H_5O$]$^+$, 255.2 (43) [M – $C_6H_3O_3$]$^+$, 226.2 (50) [M – $C_8H_8O_3$]$^+$, 181.2 (14) [M – $C_{13}H_8O_2$]$^+$, 77.1 (16) [M – $C_{20}H_{13}O_3$]$^+$. $C_{26}H_{18}O_3$ (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/$Et_2O$, 2:1). $^1$H NMR (600 MHz, $CDCl_3$): 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. $^{13}$C NMR (50.3 MHz, $CDCl_3$): 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): ṽ = 3418 (OH), 2908 (C–H), 1665 (C=C), 1441 ($CH_2$) cm$^{-1}$. UV ($CH_3CN$): $\lambda_{max}$ (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) $[C_{20}H_{11}O_2]^+$, 226.1 (17) $[C_{18}H_9]^+$, 149.1 (5) $[C_{12}H_5]^+$. $C_{21}H_{16}O_3$ (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/$Et_2O$, 4:1). $^1$H NMR (600 MHz, $CDCl_3$): 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. $^{13}$C NMR (50.3 MHz, $CDCl_3$): 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): ṽ = 3386 (OH), 3050, 2908 (C–H), 1664 (C=C), 1441 ($CH_2$) cm$^{-1}$. UV ($CH_3CN$): $\lambda_{max}$ (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 – $CH_3O_2$]$^+$, 226.1 (32) [M – $C_2H_4O_2$]$^+$. $C_{20}H_{14}O_2$ (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/$Et_2O$, 4:1). $^1$H NMR (300 MHz,

$CDCl_3$): $\delta$ = 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, $CDCl_3$): $\delta$ = 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 ($CH_3CN$): $\lambda_{max}$ (lg$\varepsilon$) = 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) $[M]^+$, 287.2 (68), $[M - OH]^+$, 262.2 (30) $[C_{18}H_{11}FO]^+$, 257.1 (36) $[C_{19}H_{10}F]^+$, 244.2 (40) $[C_{18}H_9F]^+$, 122.1 (35) $[C_8H_7F]^+$. $C_{20}H_{13}FO_2$ (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, $t_{R,I}$ = 36.65 min, $t_{R,II}$ = 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). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 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, $CDCl_3$): $\delta$ = 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–$CF_3$*), 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 ($CH_3CN$): $\lambda_{max}$ (lg$\varepsilon$) = 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) $[M]^+$, 337.3 (34) $[M - OH]^+$, 104.1 (86) $[C_8H_8]^+$, 77.1 (30) $[C_6H_5]^+$, 66.0 $[C_4H_2O]^+$. $C_{21}H_{13}F_3O_2$ (354.33): calcd. 354.0868; found 354.0868.

Resolution: HPLC: Flow: 0.8 mL/min, eluent: *n*-hexane/*i*PrOH, 95:5, $t_{R,I}$ = 28.39 min, $t_{R,II}$ = 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). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 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, $CDCl_3$): $\delta$ = 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 ($CH_3CN$): $\lambda_{max}$ (lg$\varepsilon$) = 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) $[M]^+$, 283.1 (94) $[M - OH]^+$, 239.1 (44) $[C_{19}H_{11}]^+$. $C_{21}H_{16}O_2$ (300.36): calcd. 300.1150; found 300.1150.

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

**4-(2-Methylphenyl)-2,3-dihydro-1-oxacyclopenta[*def*]phenanthrene-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). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 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, $CDCl_3$): $\delta$ = 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 ($CH_3CN$): $\lambda_{max}$ (lg$\varepsilon$) = 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) $[M]^+$, 283.1 (100) $[M - OH]^+$, 239.1 (94) $[C_{19}H_{11}]^+$, 226.1 (55) $[C_{18}H_{10}]^+$, 126.0 (37) $[C_{10}H_6]^+$, 91.0 (8) $[C_7H_7]^+$. $[C_{21}H_{16}O_2 + H]^+$ (301.36): calcd. 301.1223; found 301.1223.

Resolution: HPLC: Flow: 0.8 mL/min, eluent: *n*-hexane/*i*PrOH, 95:5, $t_{R,I}$ = 26.88 min, $t_{R,II}$ = 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). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 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, $CDCl_3$): $\delta$ = 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 ($CH_3CN$): $\lambda_{max}$ (lg$\varepsilon$) = 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) $[M]^+$, 249.3 (18) $[M - OH]^+$, 223.2 (95) $[M - OH\text{-}C_2H_5]^+$, 195.2 (82) $[M - OH\text{-}C_4H_9]^+$, 165.2 (69) $[C_{12}H_5O]^+$. $C_{18}H_{18}O_2$ (266.34): calcd. 266.1307; found 266.1307.

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

**1-(2,2-Dimethylpropylidene)-2,3-dihydro-1*H*-benzo[*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). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 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, $CDCl_3$): $\delta$ = 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 ($CH_2$–O) $cm^{-1}$. UV ($CH_3CN$): $\lambda_{max}$

($\lg\varepsilon$) = 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) $[C_{18}H_{21}O]^+$, 195.1 (32) $[C_{14}H_{11}O]^+$, 181.0 (38) $[C_{13}H_9O]^+$. $C_{18}H_{20}O_2$ (268.36): calcd. 268.1463; found 268.1463.

**Synthesis of 16 by Elimination of Water from 5:** A solution of **5** in $CHCl_3$ was kept for 10 h at room temp. Removal of the solvent in vacuo gave **16**.

**4-(2-Phenoxyphenyl)-1-oxacyclopenta[*def*]phenanthrene (16a):** $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 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. $C_{26}H_{16}O_2$ + $H^+$ (361.41): calcd. 361.12231, found 361.12233.

**4-(4-Methoxyphenyl)-1-oxacyclopenta[*def*]phenanthrene (16b):** $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 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 ($m_c$, 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 ($m_c$, 2 H, 2′-H, 6′-H), 3.91 (s, 1 H, Me) ppm. $C_{21}H_{14}O_2$ (298.34): calcd. 298.0994, found 298.0994.

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