ChemPubSoc Europe

DOI: 10.1002/ejoc.201801289

EurJOC European Journal of Organic Chemistry

Full Paper

C–H Activation

Domino C–H Activation Reactions through Proximity Effects

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Abstract: Proximity effects permit C–H activation reactions without directing groups. Here competitive reactions of selected substrates were investigated which allow a domino-carbopalladation/Mizoroki–Heck reaction and a domino-carbopalladation/C–H activation reaction. In the Pd-catalyzed transformation of the enantio- and diastereopure alkyne **8a** the tetra-substituted alkenes **10** and **11** were formed almost exclusively through a domino carbopalladation/Mizoroki–Heck reaction. In contrast, the diastereomer **8c** only led to the acenaphthylenes **12c** and **13c** through a domino carbopalladation/C–H activation reaction. Moreover, in the reaction of **20**, **24** and **27** containing a naphthyl moiety only the tetra-substituted alkenes **23**, **25**/**26** and **28**/**29**, respectively were obtained, whereas in the reaction of **34**, containing a phenanthrene moiety, compound **37** was the only product, formed via a C–H activation reaction.

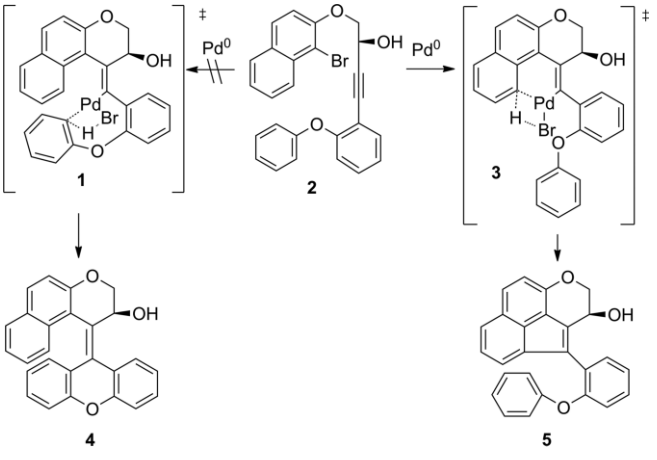
Introduction

The development of highly efficient synthetic procedures is one of the major goals in organic chemistry. These methods should permit the preparation of complex molecules starting from simple substrates in a green fashion reducing the amount of waste, being careful with our environment, and moreover have also economical advantages. Domino reactions, as a novel synthetic concept, fulfill all these demands.[1] Especially useful are catalytic domino reactions as Pd-catalyzed transformations.[2] Another important issue in synthetic chemistry is the avoidance of prefunctionalization, which can be accomplished using C–H activation reaction.[3] However, an often encountered draw back in this concept is the need of directing groups, which have to be removed or functionalized afterwards.[4] A possibility to avoid this problem is the use of proximity effects.[5]

Some time ago we have shown that the Pd-catalyzed reaction of **2** leads to the acenaphthylene **5** via a proposed transition structure **3** and not to the tetra-substituted alkene **4** via **1** (Scheme 1).[6] The preference in the formation of **5** can be explained by a proximity effect.

Here we describe competitive reactions of selected substrates which allow a domino-carbopalladation/Mizoroki–Heck reaction and a domino-carbopalladation/C–H activation reaction through proximity effects. The reactions lead either to helical tetra-substituted alkenes which might be useable as molecular switches[7] or acenaphthylenes.

As substrates compounds containing a bromonaphthyl, iodonaphthyl or a bromophenanthryl moiety with different donor groups including aromatic systems, double bonds and allylsilanes to allow a differentiation between domino-carbopalladation/Mizoroki–Heck and domino-carbopalladation/C–H activation reactions were used.



Scheme 1. Formation of an acenaphthylene through a domino-carbopalladation/C–H activation reaction. The ligands at Pd are omitted for clarity.

Results and Discussion

At first we investigated the Pd-catalyzed reaction of compound **8** as a mixture racemic diastereomers which contains a naphthyl moiety allowing a domino-carbopalladation/C–H activation reaction and a cyclohexenyl ether moiety permitting a domino-carbopalladation/Mizoroki–Heck reaction. Compound **8** can easily be prepared by reaction of the aldehyde **6** with the alkyne **7** using *n*BuLi for deprotonation of the alkyne with 91 % yield. Treatment of **8** as racemic mixture of the two diastereomers with the Herrmann–Beller catalyst **14**[8] in CH_3CN/DMF/H_2O (5:5:1) at 140 °C in a microwave oven for 45 min in the

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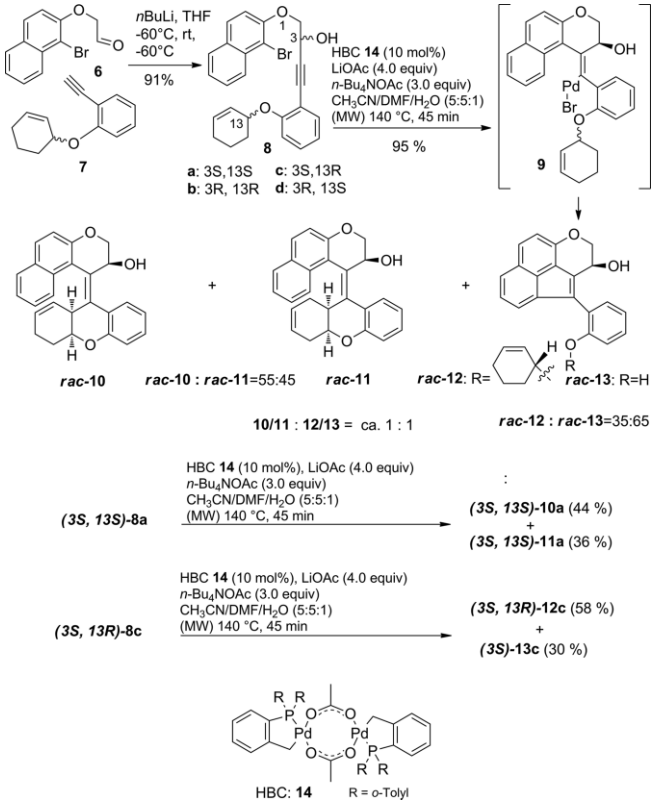
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejoc.201801289.

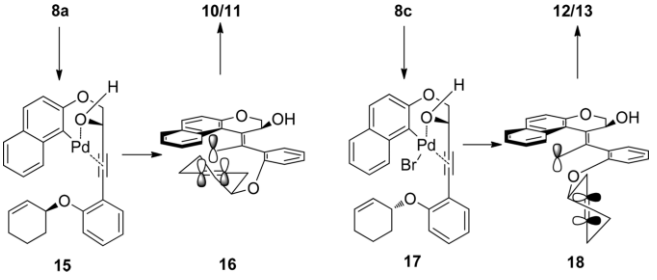
presence of LiOAc and nBu$_4$NOAC gave the two tetra-substituted alkenes **10** and **11** and the acenaphthylenes **12** and **13** as an almost 1:1 mixture (Scheme 2). The ratio of **10**/**11** is about 55:45 and the ratio of **12**/**13** is about 35:65. In the formation of **10** and **11**, it can be supposed that **10** is the primarily formed product, from which **11** is obtained by re-addition of PdHL$_3$ and elimination. In the case of the acenaphthelenes, we assume that **12** is formed first, which is then partly transformed into **13** by cleavage of the cyclohexenyl ether moiety. However, it cannot be excluded that at least to some extent the cyclohexenyl ether moiety in **8** is cleaved first which then would lead to **13** directly. The ratio of **12** and **13** varies considerably, depending on the reaction conditions. Noteworthy, in the formation of **10** and **11** only the *cis*-fused compounds are obtained as single diastereomers.



Scheme 2. Formation of tetra-substituted alkenes **10/11** through a domino-carbopalladation/Mizoroki–Heck reaction and acenaphthylenes **12/13** through a domino-carbopalladation/C–H activation reaction. The ligands at Pd are omitted for clarity.

For clarifying the selectivity in the product formation, the four stereoisomers of **8** were separated by preparative chromatography on a stationary IB-Phase. Separate reactions of the stereoisomers allowed an unambiguous identification of the mode of action and moreover a precise explanation of the formation of the two different types of products.

Reaction of alkyne **8a** with the Herrmann–Beller catalyst **14** led to the almost exclusive formation of the enantio- and diastereopure helical tetrasubstituted alkenes **10a** and **11a** in 44 % and 36 % yield, respectively (Scheme 2 and Scheme 3).



Scheme 3. Intermediates in the formation of **10/11** and **12/13**. The ligands at Pd are omitted for clarity.

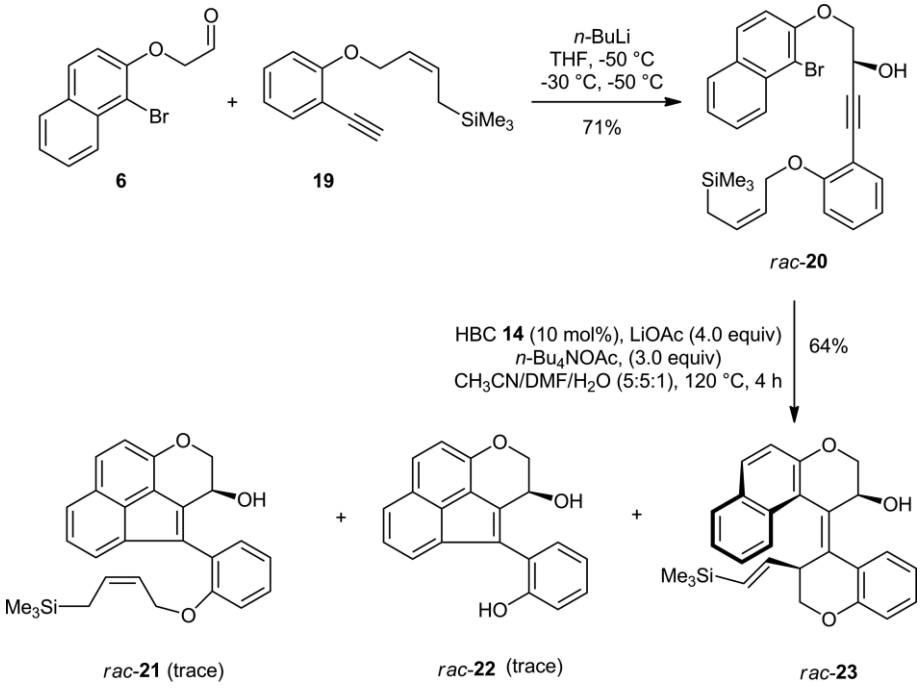
It can be anticipated that as the primary step a coordination of the Pd-atom with the hydroxyl group takes place to form a Pd complex **15** which leads to the vinyl-Pd intermediate **16**.

This could then yield the acenaphthylene **12**, but also by overlap of the Pd-atom with the π-system of the double bond the helical tetra-substituted alkene **10**. Since only **10a** and **11a** are formed from **8a** in a domino-carbopalladation/Mizoroki–Heck reaction, it can be assumed that the double bond in the cyclohexene moiety is more reactive than the naphthyl group. On the other hand, reaction of the diastereomeric alkyne **8c** with the Herrmann–Beller catalyst **14** led almost exclusively to the acenathylenes **12c** and **13c** in a domino-carbopalladation/C–H activation reaction in 58 % and 30 % yield, respectively. As intermediates the Pd complex **17** and the vinyl-Pd **18** can be supposed, in which an overlap of the Pd-atom with the double bond of the cyclohexene moiety is not possible. Therefore, only the acenaphthylenes **12c** and **13c** were obtained as products (Scheme 3).

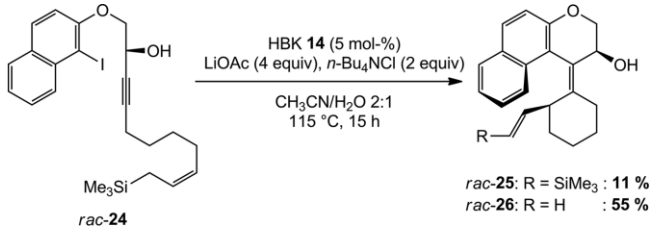
To get further information on the importance of the stereochemistry of the substrates in the cyclisation reactions, we prepared the alkyne *rac*-**20** with only one stereogenic center containing an allylsilane moiety as donor (Scheme 4). For the synthesis of *rac*-**20**, which was obtained in 71 %, the aldehyde **6** was treated with the alkyne **19** using *n*BuLi for the deprotonation. For the Pd-catalyzed reaction again the Hermann–Beller catalyst **14** (10 mol-%) in the presence of LiOAc and nBu$_4$NOAc in a solvent mixture of CH$_3$CN/DMF/H$_2$O (5:5:1) at 120 °C for 4 h was used (Scheme 4). As the major product the tetra-substituted alkene *rac*-**23** was obtained in 64 % yield via a domino-carbopalladation/Mizoroki–Heck reaction. The also expected two acenaphthylenes *rac*-**21** and *rac*-**22** were found only in traces (< 5 %).

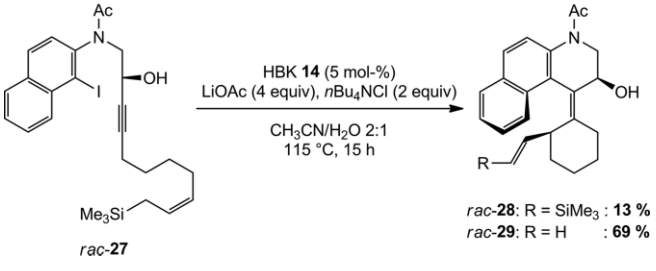
In a similar way, also compound **24** containing a long chain aliphatic allylsilane can be treated with the Herman–Beller catalyst **14** to give exclusively the tetra-substituted alkenes **25** and **26** in an overall yield of 66 % in a ratio of 1:5.3 (Scheme 5). In this case due to the employed iodide also a desilylated product **26** was formed. We then replaced the oxygene in the chain in **24** by a *N*Ac group using **27** as substrate. Again tetra-substituted alkenes **28** and **29** were obtained exclusively in a Pd-catalyzed domino-carbopalladation/Mizoroki–Heck-reaction in an overall yield of 82 % with a ratio of 1:5.3.

Also in these two transformations only one diastereomer is found, though two new stereogenic elements are created. Moreover, in the elimination step of a Pd-H species from the



Scheme 4. Synthesis and Pd-catalyzed reaction of *rac*-**20**.





Scheme 5. Synthesis and Pd-catalyzed reaction of *rac*-**24** and *rac*-**27**.

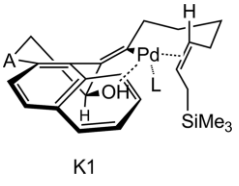


Figure 1. Proposed intermediate Pd complex **K1**.

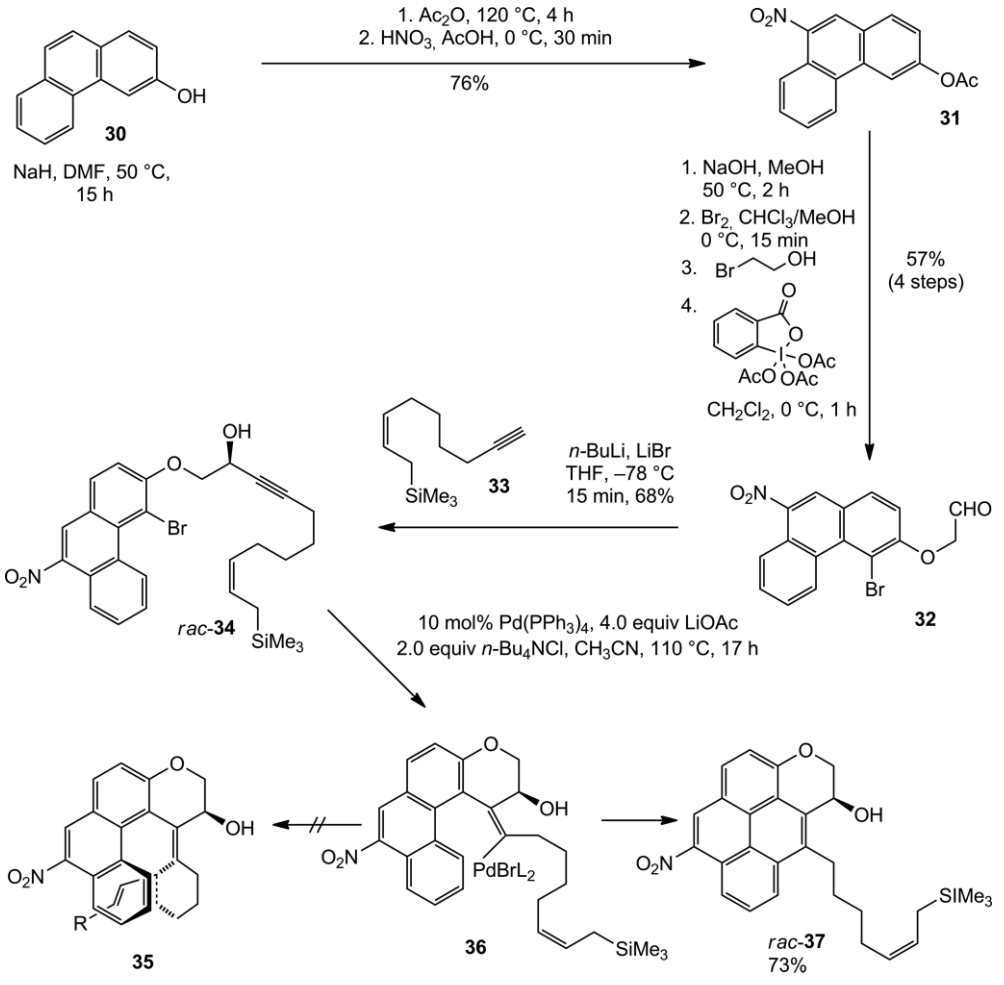
intermediately formed Pd complex only the products with a vinyl or a vinylsilane moiety are obtained. This phenomenon has been described by us earlier.[9, 2u]

The high diastereoselectivity in the formation of the new stereogenic center and the helical double bond can be explained by assuming an intermediate Pd complex **K-1** of which the formation is governed by the hydroxyl group in the starting material (Figure 1).

In the so far performed transformations the Mizoroki–Heck-reactions was favored although a C–H activation was always principally possible. Merely in the case of **8c** a C–H activation reaction was observed, but only due to the fact that the Mizoroki Heck-reaction was not feasible because of stereoelectronic reasons. Obviously, the question arises, whether a C–H activation reaction is always discriminated when an intermediate vinyl-Pd complex could react with a double bond system. To get further insight in this aspect, we designed a molecule, where proximity of the aromatic system is increased.

Thus, we prepared compound **34** where the naphthyl moiety in **24** has been replaced by a phenanthrene group (Scheme 6). The synthesis is rather simple. The commercially available phenanthrene derivative **30** with a hydroxyl group was acetylated and then nitrated to give **31** allowing a selective bromination after hydrolysis of the acetate. It followed an alkylation with 2-bromethanol and oxidation with Dess–Martin-Periodinane to give the corresponding aldehyde **32**.

In the next step the alkyne **33** containing an allylsilane moiety was introduced using *n*BuLi for deprotonation followed by addition to the aldehyde **32** to give the substrate **34** for the domino reaction in 68 % yield. Compound *rac*-**34** contains a phenanthrene moiety, where a C–H activation reaction could take place and an allylsilane suitable for a Mizoroki–Heck reaction (Scheme 6). Treatment of **34** with 10 mol-% $Pd(PPh_3)_4$ in the presence of LiOAc and nBu_4NCl in CH_3CN at 110 °C for 17 h gave exclusively compound **37** in 73 % yield via a domino-carbopalladation/C–H activation reaction. It can be assumed that the Pd-intermediate **36** or the corresponding complex with



Scheme 6. Synthesis and Pd-catalyzed reaction of *rac*-**34**.

the hydroxyl group is an intermediate. The tetra-substituted alkene **35** was not found. The formation of **37** is clearly due to a proximity effect.

The determination of the structures of the new compounds is mainly based on ^{1}H- and ^{13}C-NMR spectra and mass spectrometry. For further confirmation a crystal structure determination of *rac*-**10** was performed, which could be obtained in crystalline form.[10] For the determination of the absolute configuration of **10a**/**11a** obtained from **8a**, a CD-spectra of the mixture was measured and compared with a calculated spectra[11,12] of *(S,S,S)*-**10** showing good identity.

Conclusions

In summary, proximity effects can be used to allow C–H activation reactions without the need of directing groups. In the described experiments we have designed molecules where a competition between a domino-carbopalladation/Mizoroki–Heck reaction and a domino-carbopalladation/C–H activation reaction exists with the result that a double bond or an allylsilane to allow a Mizoroki–Heck reaction is a better donor than a naphthyl moiety. However, in the cases where the Mizoroki–Heck reaction is less appropriate due to stereo electronic reasons or the donor is a phenanthrene moiety the C–H activation reaction wins.

Experimental Section

***rac*-(2*S*,1‴*R*)- and *rac*-(2*S*,1‴*S*)-1-(1-Bromonaphthalin-2-yloxy)-4-[2-(cyclohex-2-enylmethyl)-phenyl]-but-3-yne-2-ol (*rac*-8a) and (*rac*-8c):** To a solution of *rac*-1-cyclohex-2-enyloxy-2-ethinylbenzyne 7 in anhydrous THF (24 mL) was slowly given with stirring at –60 °C *n*BuLi (2.5 M, 3.02 mL, 7.54 mmol, 2.00 equiv.). Stirring was continued at –60 °C for 1 h, then at –20 °C for 1.5 h and then the mixture was cooled down again to –60 °C. The mixture was transferred via a big transfer cannula dropwise to a solution of (1-bromonaphthalin-2-yloxy)acetaldehyde 6 (1.00 g, 3.77 mmol, 1.00 equiv.) in anhydrous THF (12 mL) at –60 °C. Stirring was continued at this temperature for 1 h and then the mixture was warmed up to room temp. within 1 h. Concentrated aqueous ammonium chloride solution (50 mL) was added and the mixture extracted with dichloromethane (3 × 50 mL). After drying over $MgSO_4$ and removal of the solvent in vacuo, the remaining residue was purified by chromatography (pentane/Et_2O, 4:1) on silica gel to give the desired compound **8** (1.42 g, 3.08 mmol, 82 %) as a colorless oil. R_f = 0.41 (pentane/Et_2O = 2:1). IR (Film): $\tilde{\nu}$ = 2926 (C–H), 1596, 1503, 1350, 1271 (Ar–O), 1077 (CH_2–O), 801, 758 cm^{-1}. UV (CH_3CN): λ_{max} (ε) = 231.5 nm (4.865), 252.5 (4.275), 272.5 (3.715), 282.0 (3.802), 294.5

(3.675), 322.5 (3.271), 334.5 (3.316). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21–1.36 (m, 1 H, 6‴-H_a), 1.48 (m_c, 1 H, 5‴-H_b), 1.61–1.77 (m, 2 H, 5‴-H_a, 6‴-H_b), 1.95 (m_c, 2 H, 4‴-H_2), 2.50 (m_c, 1 H, 1‴-H), 2.71 (ddd, *J* = 13.1, 8.1, 2.1 Hz, 1 H, 1⁗-H_b), 2.82 (ddd, *J* = 13.1, 6.9, 3.7 Hz, 1 H, 1⁗-H_a), 2.96 (d, *J* = 5.3 Hz, 1 H, OH), 4.36 (ddd, *J* = 9.5, 7.0, 0.7 Hz, 1 H, 1-H_a), 4.45 (dd, *J* = 9.5, 3.4 Hz, 1 H, 1-H_b), 5.10 (m_c, 1 H, 2-H), 5.57 (dq, *J* = 10.2, 2.1 Hz, 1 H, 3‴-H), 5.62–5.70 (m, 1 H, 2‴-H), 7.15 (dt, *J* = 7.3, 1.6 Hz, 1 H, 5″-H), 7.18 (m_c, 1 H, 3″-H), 7.26 (m_c, 1 H, 4″-H), 7.29 (d, *J* = 8.9 Hz, 1 H, 3′-H), 7.41–7.47 (m, 1 H, 6′-H, 6″-H), 7.59 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1 H, 7′-H), 7.80 (dt, *J* = 8.1, 0.6 Hz, 1 H, 5′-H), 7.82 (d, *J* = 8.9 Hz, 1 H, 4′-H), 8.23 (dq, *J* = 8.5, 0.9 Hz, 1 H, 8′-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.20 (C-5‴), 25.33 (C-4‴), 28.75 (C-6‴), 36.42 (C-1‴), 41.01 (C-1⁗), 62.08 (C-2), 74.20 (C-1), 85.27 (C-4), 89.25 (C-3), 110.5 (C-1′), 115.8 (C-3′), 121.8 (C-1″), 124.9 (C-6′), 125.8 (C-5″), 126.3 (C-8′), 127.3 (C-2‴), 127.8 (C-7′), 128.1 (C-5′), 128.5 (C-4″), 129.1 (C-4′), 129.7 (C-3″), 130.4 (C-4′a), 131.3 (C-3‴), 132.5 (C-6″), 133.0 (C-8′a), 143.4 (C-2″), 152.6 (C-2′) ppm. MS (70 eV, EI): *m/z* (%) = 462.2 (1) $[M]^+$, 381.2 (39) $[M - Br]^+$, 363.2 (84) $[M - H_2O - Br]^+$, 281.1 (28) $[M - C_6H_9 - H_2O - Br]^+$, 222.0 (50) $[C_{17}H_{18}]^+$, 81.1 (100) $[C_6H_9]^+$. $C_{27}H_{25}BrO_2$ (461.4): calcd. C 70.29, H 5.46; found C 70.66, H 5.72. HR-MS: Calculated: *m/z* = 460.1038 $[M + H]^+$; found *m/z* = 460.1038.

Pd-Catalyzed Reaction of 8: A mixture of **8** (200 mg, 0.43 mmol, 1.0 equiv.), the palladacycle **14** (10 mol-%), lithium acetate (4 equiv.) and tetrabutyl ammonium acetate (3 equiv.) in the solvent acetonitrile/DMF/water (10 mL, 5:5:1) under argon was irradiated in a microwave oven for 8 h at 120 °C (DC-control). The reaction mixture was treated with 50 mL of brine and extracted with diethyl ether (3 × 25 mL). After drying over sodium sulfate and removal of the solvent in vacuo column chromatography on silica gel (DCM/pentane = 5:1) provided the products **10**/**11** (66.0 mg, 0.173 mmol, 40 %) as colourless oil and **12** (47.9 mg, 0.125 mmol, 29 %) as orange solid. **10** and **11** were separated by preparative HPLC. In identical reactions **8a** and **8c** were treated with the Pd complex **14**. **8a** led to the enantiopure compounds **10a** and **11a**, whereas **8c** gave the enantiopure compounds **12c** and **13c**.

***rac*-(*P*)-(2*S*,4′a*S*,9′a*S*)-(*Z*)-1-(3,4,4a,9a-Tetrahydroxanthen-9-yliden)-2,3-dihydro-1*H*-benzo[*f*]chromen-2-ol (10):** R_f = 0.24 (DCM/pentane, 5:1). IR (KBr): $\tilde{\nu}$ = 1594 (C=C), 1454 (CH_2), 1231 (Ar–O), 1075 (CH_2–O), 759 (H–C=C–H *cis*) cm^{-1}. UV (CH_3CN): λ_{max} (lg ε) = 212.5 nm (4.568), 242.5 (4.360), 318.5 (3.974), 350.5 (4.022). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.57–1.63 (m, 1 H, 4′-H_a), 1.87–1.94 (m, 1 H, 3′-H_a), 1.99 (d, *J* = 7.6 Hz, 1 H, OH), 1.98–2.06 (m, 1 H, 4′-H_b), 2.22–2.31 (m, 1 H, 3′-H_b), 3.03 (s_{br}, 1 H, 9′a-H), 4.26 (dd, *J* = 12.1, 2.4 Hz, 1 H, 3-H_b), 4.32 (m_c, 1 H, 4′a-H), 4.44 (dd, *J* = 12.1, 1.8 Hz, 1 H, 3-H_a), 5.35 (dt, *J* = 7.4, 1.8 Hz, 1 H, 2-H), 5.68–5.75 (m, 2 H, 1′-H, 2′-H), 6.84 (dd, *J* = 8.3, 1.0 Hz, 1 H, 5′-H), 6.94 (ddd, *J* = 7.6, 7.6, 1.1 Hz, 1 H, 7′-H), 7.11 (d, *J* = 8.8 Hz, 1 H, 5-H), 7.24 (ddd, *J* = 8.5, 7.3, 1.6 Hz, 1 H, 6′-H), 7.36 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1 H, 8-H), 7.46 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1 H, 9-H), 7.54 (dd, *J* = 7.6, 1.6 Hz, 1 H, 8′-H), 7.74 (d, *J* = 8.8 Hz, 1 H, 6-H), 7.79 (d, *J* = 8.0 Hz, 1 H, 7-H), 7.99 (d, *J* = 8.5 Hz, 1 H, 10-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.10 (C-3′), 26.36 (C-4′), 38.88 (C-9′a), 66.30 (C-2), 73.05 (C-3), 73.91 (C-4′a), 112.4 (C-10b), 116.0 (C-5′), 118.2 (C-5), 119.8 (C-7′), 120.0 (C-8′a*), 123.1 (C-1′), 123.7 (C-8), 124.4 (C-10), 125.7 (C-1*), 126.5 (C-9), 128.3 (C-7), 129.3 (C-8′), 129.4 (C-6a*), 129.9 (C-6′), 130.0 (C-6), 130.1 (C-2′), 132.4 (C-10a), 135.1 (C-9′), 152.7 (C-4a), 156.0 (C-4′c) ppm. MS (70 eV, EI): *m/z* (%) = 382.2 (100) $[M]^+$, 364.1 (24) $[M - H_2O]^+$. HPLC (prep. RP-column G): wave length: 233 nm, flow rate 12 mL/min, eluent: acetonitrile/water, 57:43, t_R = 58.17 min, portion: 55 %. HR-MS: $C_{26}H_{22}O_3$ (382.5). Calculated: *m/z* = 382.1569 $[M]^+$; found *m/z* = 382.1563.

***rac*-(*P*)-(2*S*,4′a*S*,9′a*S*)-(*Z*)-1-(1,4,4a,9a-Tetrahydroxanthen-9-yliden)-2,3-dihydro-1*H*-benzo[*f*]chromen-2-ol (11):** R_f = 0.24 (DCM/pentane, 5:1). IR (KBr): $\tilde{\nu}$ = 2931 (C–H), 1594, 1454 (CH_2), 1344 (CH), 1232 (Ar–O), 1084 (CH_2–O), 817, 655 cm^{-1}. UV (CH_3CN): λ_{max} (lg ε) = 213.5 nm (4.652), 243.0 (4.458), 318.5 (4.068), 351.5 (4.114). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.95 (d_{br}, *J* = 6.2 Hz, 1 H, OH), 2.03–2.16 (m, 2 H, 1′-H_b, 4′-H_b), 2.25–2.31 (m, 1 H, 4′-H_a), 2.47 (ddd, *J* = 10.9, 6.1, 1.5 Hz, 1 H, 9′a-H), 2.58 (dt, *J* = 17.6, 5.5 Hz, 1 H, 1′-H_a), 4.28 (dd, *J* = 11.9, 2.5 Hz, 1 H, 3-H_b), 4.30 (m_c, 1 H, 4′a-H), 4.45 (dd, *J* = 11.9, 1.8 Hz, 1 H, 3-H_a), 5.41 (m_c, 1 H, 2-H), 5.43 (m_c, 1 H, 3′-H), 5.61 (m_c, 1 H, 2′-H), 6.89 (dd, *J* = 8.3, 0.9 Hz, 1 H, 5′-H), 6.98 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H, 7′-H), 7.11 (d, *J* = 8.8 Hz, 1 H, 5-H), 7.26 (ddd, *J* = 8.7, 7.4, 1.6 Hz, 1 H, 6′-H), 7.36 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1 H, 8-H), 7.44 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1 H, 9-H), 7.59 (dd, *J* = 7.7, 1.5 Hz, 1 H, 8′-H), 7.73 (d, *J* = 8.9 Hz, 1 H, 6-H), 7.79 (d, *J* = 8.1 Hz, 1 H, 7-H), 8.00 (d, *J* = 8.5 Hz, 1 H, 10-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.80 (C-1′), 30.77 (C-4′), 36.01 (C-9′a), 66.67 (C-2), 72.86 (C-3), 74.76 (C-4′a), 112.6 (C-10b), 116.5 (C-5′), 118.1 (C-5), 119.7 (C-1*), 120.2 (C-7′), 121.4 (C-3′), 123.8 (C-8), 124.4 (C-10), 124.8 (C-8′a*), 126.0 (C-2′), 126.3 (C-9), 128.3 (C-7), 129.4 (C-6a*), 129.8 (C-8′), 129.9 (C-6), 129.9 (C-6′), 132.8 (C-10a*), 137.6 (C-9′), 152.5 (C-4a), 154.8 (C-4′c) ppm. MS (70 eV, EI): *m/z* (%) = 382.2 (100) $[M]^+$, 364.2 (8) $[M - H_2O]^+$, 328.2 (38) $[M - C_4H_6]^+$, 311.1 (9) $[M - C_4H_7O]^+$. HPLC (prep. RP-column G): Wave length: 233 nm, flow rate 12 mL/min, eluent acetonitrile/water = 57:43, t_R = 54.49 min, portion: 45 %. $C_{26}H_{22}O_3$ (382.5). Calculated: *m/z* = 382.1569 $[M]^+$; found *m/z* = 382.1563.

(1*S*,1″*S*)-4-[2-(Cyclohex-2-enyloxy)-phenyl]-2,3-dihydro-1-oxacyclopenta[*def*]phenanthren-3-ol (12): R_f = 0.35 (DCM/pentane, 5:1). IR (Film): $\tilde{\nu}$ = 2928 (C–H), 1667, 1484 (CH_2), 1442, 1231 (Ar–O), 1113 (CH–O), 1006 (CH_2–O) cm^{-1}. UV (CH_3CN): λ_{max} (lg ε) = 243.5 nm (4.308), 309.0 (3.779), 322.5 (3.856), 362.0 (3.840), 377.5 (3.915). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.19–1.44 (m, 2 H, 5″-H_2), 1.56–1.66 (m, 2 H, 6″-H_2), 1.80–1.98 (m, 2 H, 4″-H_2), 4.16 (s_{br}, 1 H, OH), 4.40 (ddd, *J* = 11.8, 2.6, 1.4 Hz, 1 H, 2-H_b), 4.65 (dd, *J* = 11.8, 4.0 Hz, 1 H, 2-H_a), 4.79 (m_c, 1 H, 1″-H), 5.08 (m_c, 1 H, 3-H), 5.91–5.95 (m, 1 H, 3″-H), 5.96–6.00 (m, 1 H, 2″-H), 7.16 (d, *J* = 8.8 Hz, 1 H, 9-H), 7.18 (dt, *J* = 7.5, 0.8 Hz, 1 H, 5′-H*), 7.21 (d, *J* = 8.1 Hz, 3′-H*), 7.38 (ddd, *J* = 8.1, 7.5, 1.8 Hz, 1 H, 4′-H*), 7.51 (dd, *J* = 8.0, 6.7 Hz, 1 H, 6-H), 7.60 (dd, *J* = 7.5, 1.9 Hz, 1 H, 6′-H*), 7.75 (d, *J* = 6.7 Hz, 1 H, 7-H*), 7.79 (d, *J* = 8.8 Hz, 1 H, 8-H), 7.81 (d, *J* = 8.0 Hz, 1 H, 5-H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.07 (C-5″), 24.88 (C-4″), 27.59 (C-6″), 64.60 (C-3), 74.71 (C-1″), 75.89 (C-2), 117.5 (C-3′), 118.2 (C-9), 121.3 (C-9b), 122.2 (C-5′*), 124.1 (C-4a), 125.2 (C-3″), 125.4 (C-7*), 126.2 (C-5*), 126.3 (C-6), 126.9, 127.4, 127.6 (C-7a*, C-9c*, C-1′*), 128.6 (C-4′*), 130.1 (C-8), 130.9 (C-4*), 132.0 (C-6′*), 134.0 (C-2″), 140.0 (C-3a), 153.4 (C-9a), 154.8 (C-2′) ppm. MS (70 eV, EI): *m/z* (%) = 382.3 (13) $[M]^+$, 301.2 (11), $[M - C_6H_9]^+$, 283.1 (55) $[M - C_6H_9 - H_2O]^+$, 255.1 (100) $[M - C_6H_9 - H_2O - CH_2O]^+$, 81.1 (12) $[C_6H_9]^+$. $C_{26}H_{22}O_3$ (382.5). HR-MS: Calculated: *m/z* = 405.1462 $[M + Na]^+$; found *m/z* = 405.1461.

Pd-Catalyzed Reaction of *rac*-20

***rac*-(*P*)-(2*S*,3′*S*)-(*Z*)-(1″*E*)-1-[3-(2-Trimethylsilanyl-vinyl)-chroman-4-yliden]-2,3-dihydro-1*H*-benzo[*f*]chromen-2-ol (23):** A mixture of ***rac*-20** (700 mg, 1.37 mmol, 1.00 equiv.), the Pd complex **14** (10 mol-%), lithium acetate (4 equiv.) and tetrabutyl ammonium acetate (3 equiv.) in the solvent acetonitrile/DMF/water (10 mL, 5:5:1) under argon was irradiated in a microwave oven for 4 h at 120 °C (DC-control). The reaction mixture was treated with 50 mL of brine and extracted with diethyl ether (3 × 25 mL). After drying over sodium sulfate and removal of the solvent in vacuo, column chromatography on silica gel (DCM/pentane = 5:1) provided the product ***rac*-23** (378 mg, 0.881 mmol, 64 %) as colorless solid. The

compounds ***rac*-21** and ***rac*-22** were obtained in traces only. R_f = 0.33 (DCM/pentane = 4:1). IR (KBr): $\tilde{\nu}$ = 2925 (C–H), 1592, 1464 (CH_2), 1231 (Ar–O), 995 (C=C), 815, 764 (C=C_{cis}) cm^{-1}. UV (CH_3CN): λ_{max} (lg ε) = 212.0 nm (4.598), 242.0 (4.367), 319.0 (3.998), 351.0 (4.044). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.01 (s, 9 H, $SiMe_3$), 2.05 (s_{br}, 1 H, OH), 3.04 (m_c, 1 H, 3′-H), 4.04 (dd, *J* = 10.7, 2.3 Hz, 1 H, 2′-H_b), 4.19 (dd, *J* = 10.7, 1.8 Hz, 1 H, 2′-H_a), 4.26 (dd, *J* = 12.2, 2.2 Hz, 1 H, 3-H_b), 4.44 (dd, *J* = 12.2, 1.5 Hz, 1 H, 3-H_a), 5.44 (m_c, 1 H, 2-H), 5.57 (d_{br}, *J* = 19.0 Hz, 1 H, 2′′-H), 5.97 (dd, *J* = 19.0, 5.9 Hz, 1 H, 1′′-H), 6.84 (d, *J* = 8.3 Hz, 1 H, 8′-H), 6.99 (t, *J* = 7.5 Hz, 1 H, 6′-H), 7.10 (d, *J* = 8.9 Hz, 1 H, 5-H), 7.23–7.27 (m, 1 H, 7′-H), 7.29 (m_c, 1 H, 9-H), 7.33 (dd, *J* = 8.0, 6.9 Hz, 1 H, 8-H), 7.61 (m_c, 1 H, 5′-H), 7.73 (d, *J* = 8.9 Hz, 1 H, 6-H), 7.76 (d, *J* = 8.0 Hz, 1 H, 7-H), 7.86 (d, *J* = 8.4 Hz, 1 H, 10-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –1.37 ($SiMe_3$), 44.46 (C-3′), 66.15 (C-2), 72.55 (C-2′), 72.60 (C-3), 112.2 (C-10b), 116.3 (C-8′), 118.1 (C-5), 120.2 (C-6′), 120.9 (C-4′a), 123.6 (C-8), 125.5 (C-1), 126.1 (C-10), 126.4 (C-9), 128.0 (C-7), 129.2 (C-6a), 129.7 (C-5′), 129.8 (C-7′), 130.0 (C-6), 132.3 (C-10a), 133.8 (C-4′), 134.4 (C-2′′), 141.4 (C-1′′), 152.6 (C-4a), 154.7 (C-8′a) ppm. MS (70 eV, EI): *m/z* (%) = 428.2 (100) $[M]^+$, 410.2 (4) $[M - H_2O]^+$, 356.3 (6) $[C_{24}H_{20}O_3]^+$, 302.2 (14), 255.1 (21), 73.0 (33). $C_{27}H_{28}O_3Si$ (428.6). HR-MS: Calculated: *m/z* = 429.18805 $[M + H]^+$; found *m/z* = 429.18817.

Pd-Catalyzed Reaction of *rac*-24 and *rac*-27: A mixture of ***rac*-24** (100 mg, 0.197 mmol) the palladacycle **14** (5 mol-%), lithium acetate (80 mg, 7.88 mmol, 4.0 equiv.) and tetrabutyl ammonium chloride (90 mg, 39.4 mmol, 2.0 equiv.) in the solvent acetonitrile/water (8 mL, 3:1) under argon was heated for 16 h at 110 °C (DC-control). The reaction mixture was treated with 50 mL of brine and extracted with diethyl ether (3 × 25 mL). After drying over sodium sulfate and removal of the solvent in vacuo column chromatography on silica gel (pentane/ethyl acetate = 10:1 to 7:1) provided the products ***rac*-25** (8.6 mg, 12 %) and ***rac*-26** (36.4 mg, 60 %) as colorless oils together with starting material **24** (12.0 mg, 12 %).

***rac*-(1*E*,1′′*E*)-1-[2-(2-Trimethylsilyl-vinyl)-cyclohexyliden]-2,3-dihydro-1*H*-benzo[*f*]chromen-2-ol (25):** R_f = 0.28 (pentane/ethyl acetate = 5:1). IR (Film): $\tilde{\nu}$ = 3374, 3055, 2951, 2921, 1595, 1512, 1467, 1246, 1067, 838 cm^{-1}. UV (CH_3CN): λ_{max} (lg ε) = 200.5 nm (4.536), 238.5 (4.498), 290.0 (3.730), 301.5 (3.709), 333.0 (3.602), 345.0 (3.613). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.14 (s, 9 H, $SiMe_3$), 1.24–1.39 (m, 2 H, 3′-H_a, 4′-H_a), 1.40–1.49 (m, 1 H, 5′-H_a), 1.49–1.68 (m, 2 H, 3′-H_b, 4′-H_b), 1.92 (br. d, *J* = 11.4 Hz, 1 H, 5′-H_b), 2.46 (ddd, *J* = 13.6, 13.6, 3.5 Hz, 1 H, 6′-H_a), 2.81 (br. d, *J* = 13.6 Hz, 1 H, 6′-H_b), 3.03 (br. s, 1 H, 2′-H), 4.32 (dd, *J* = 11.6, 2.6 Hz, 1 H, 3-H_a), 4.55 (dd, *J* = 11.6, 1.2 Hz, 1 H, 3-H_b), 5.29 (br. s, 1 H, 2-H), 5.71 (dd, *J* = 19.3, 2.0 Hz, 1 H, 2′′-H), 6.18 (dd, *J* = 19.3, 4.5 Hz, 1 H, 1′′-H), 7.08 (d, *J* = 9.0 Hz, 1 H, 5-H), 7.25–7.34 (m, 2 H, 8-H, 9-H), 7.66 (d, *J* = 9.0 Hz, 1 H, 6-H), 7.70–7.75 (m, 2 H, 7-H, 10-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –1.1 ($SiMe_3$), 22.0, 27.4, 29.3 (C-3′, C-4′, C-5′), 35.1 (C-6′), 46.8 (C-2′), 65.0 (C-2), 74.7 (C-3), 114.2 (C-10b), 118.1 (C-5), 123.3, 125.8, 125.9, 127.8 (C-7, C-8, C-9, C-10), 123.6 (C-6a), 129.1 (C-6), 129.0 (C-10a), 132.1 (C-2′′), 132.5 (C-1), 140.8 (C-1′), 146.7 (C-1′′), 152.7 (C-4a) ppm. MS (70 eV, EI): *m/z* (%) = 378.3 (100) $[M]^+$, 306.2 (15) $[M - C_3H_8Si]^+$, 287.2 (36) $[M - SiMe_3 - H_2O]^+$, 261.2 (19) $[M - SiMe_3 - H_2O - C_2H_2]^+$, 207.1 (32), 181.1 (59) $[M - SiMe_3 - H_2O - C_8H_{10}]^+$, 144.1 (44) $[C_{10}H_8O]^+$. HR-MS: $C_{24}H_{30}O_2Si$ (378.6) Calculated: *m/z* = 378.2015; found *m/z* = 378.2015.

***rac*-(*E*)-1-(2-Vinyl-cyclohexyliden)-2,3-dihydro-1*H*-benzo[*f*]-chromen-2-ol (26):** R_f = 0.20 (pentane/ethyl acetate = 5:1). IR (KBr): $\tilde{\nu}$ = 3357, 3073, 3053, 2927, 2850, 1593, 1511, 1341, 1234, 1078, 997, 908 cm^{-1}. UV (CH_3CN): λ_{max} (lg ε) = 201.0 nm (4.540), 241.0 (4.653), 290.0 (3.824), 301.0 (3.812), 334.5 (3.695), 344.5 (3.727). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.24–1.41 (m, 2 H, 3′-H_a, 4′-H_a), 1.47 (br. d, *J* = 14.0 Hz, 1 H, 5′-H_a), 1.57–1.69 (m, 2 H, 3′-H_b, 4′-H_b), 1.95 (br. d, *J* = 14.0 Hz, 1 H, 5′-H_b), 2.48 (ddd, *J* = 13.6, 13.6, 4.0 Hz, 1 H, 6′-H_a), 2.83 (br. d, *J* = 13.6 Hz, 1 H, 6′-H_b), 3.04 (br. s, 1 H, 2′-H), 4.33 (dd, *J* = 11.5, 2.8 Hz, 1 H, 3-H_a), 4.57 (dd, *J* = 11.5, 1.2 Hz, 1 H, 3-H_b), 5.00 (ddd, *J* = 17.5, 1.7, 1.7 Hz, 1 H, 2′′-H_a), 5.26 (br. s, 1 H, 2-H), 5.28 (ddd, *J* = 10.6, 1.7, 1.7 Hz, 1 H, 2′′-H_b), 6.08 (ddd, *J* = 17.5, 10.5, 5.7 Hz, 1 H, 1′′-H), 7.10 (d, *J* = 8.9 Hz, 1 H, 5-H), 7.27–7.38 (m, 2 H, 8-H, 9-H), 7.69 (d, *J* = 8.9 Hz, 1 H, 6-H), 7.72–7.78 (m, 2 H, 7-H, 10-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.7, 27.2, 29.3 (C-3′, C-4′, C-5′), 35.4 (C-6′), 44.7 (C-2′), 65.0 (C-2), 74.8 (C-3), 114.1, 116.7 (C-10b, C-2′′), 118.1 (C-5), 123.2 (C-6a), 123.4, 125.9, 127.9 (C-7, C-8, C-9, C-10), 129.1 (C-6), 129.1 (C-10a), 132.4 (C-1), 138.4 (C-1′′), 140.7 (C-1′), 152.7 (C-4a) ppm. MS (70 eV, EI): *m/z* (%) = 306.1 (100) $[M]^+$, 288.1 (16) $[M - H_2O]^+$, 181.0 (14) $[M - H_2O - C_8H_{11}]^+$. HR-MS: $C_{21}H_{22}O_2$ (306.4): Calculated: *m/z* = 306.1620, *m/z* = found: 306.1620.

Pd-Catalyzed Reaction of 27: A mixture of ***rac*-27** (160 mg, 0.292 mmol), the palladacycle **14** (10.7 mg, 4 mol-%), lithium acetate (119 mg, 1.17 mmol, 4.0 equiv.) and tetrabutyl ammonium chloride (67 mg, 0.29 mmol, 1.0 equiv.) in the solvent acetonitrile/water (12 mL, 4:1) under argon was heated for 14 h at 120 °C (DC-control). The reaction mixture was treated with 50 mL of brine and extracted with ethyl acetate (3 × 25 mL). After drying over sodium sulfate and removal of the solvent in vacuo column chromatography on silica gel (pentane/ethyl acetate = 2:1 to 1:1) provided the products ***rac*-28** (16 mg, 13 %) and ***rac*-29** (70 mg, 69 %) as colorless oils.

(1*E*,1′′*E*)-*N*-Acetyl-1-[2-(2-trimethylsilyl-vinyl)-cyclohexyliden]-1,2,3,4-tetrahydro-benzo[*f*]chinolin-2-ol (28): R_f = 0.32 (pentane/ethyl acetate = 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.11 (s, 9 H, $SiMe_3$), 1.09–1.32 (m, 2 H, 3′-H_a, 4′-H_a), 1.40–1.66 (m, 4 H, 3′-H_b, 4′-H_b, 5′-H_a, δOH), 1.95 (br. d, *J* = 13.1 Hz, 1 H, 5′-H_b), 2.17 (s, 3 H, CH_3), 2.42 (ddd, *J* = 13.4, 13.4, 4.2 Hz, 1 H, 6′-H_a), 2.79 (br. d, *J* = 13.4 Hz, 1 H, 6′-H_b), 2.91 (br. s, 1 H, 2′-H), 3.14 (br. d, *J* = 13.4 Hz, 1 H, 3-H_a), 4.91 (br. dd, *J* = 13.4, 7.4 Hz, 1 H, 3-H_b), 5.55 (dd, *J* = 7.4, 1.4 Hz, 1 H, 2-H), 5.63 (dd, *J* = 19.0, 2.0 Hz, 1 H, 2′′-H), 6.17 (dd, *J* = 19.0, 5.2 Hz, 1 H, 1′′-H), 7.35 (m, 2 H, 5-H, 8-H), 7.45 (dd, *J* = 7.8, 7.8 Hz, 1 H, 9-H), 7.78–7.90 (m, 3 H, 6-H, 7-H, 10-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –1.1 ($SiMe_3$), 21.7, 27.1, 30.1, 35.3 (C-3′, C-4′, C-5′, C-6′), 22.5 (CH_3), 47.1 (C-2′), 52.9 (C-3), 69.5 (C-2), 123.6, 126.0, 126.6, 126.8, 127.9, 128.1 (C-5, C-6, C-7, C-8, C-9, C-10), 125.8 (C-10b), 129.8, 131.7, 132.0 (C-1, C-6a, C-10a), 132.2 (C-2′′), 137.2 (C-1′), 143.9 (C-4a), 146.4 (C-1′′), 169.7 (C=O) ppm. MS (200 eV, DCI): *m/z* (%) = 437.4 (67) $[M + NH_4]^+$, 420.3 (100) $[M + H]^+$, 365.3 (22) $[M - C_3H_8Si + NH_4]^+$, 348.3 (27) $[M - C_3H_8Si + H]^+$. $C_{26}H_{23}NO_2Si$ (419.6). HR-MS: Calculated: *m/z* = 419.2281; found *m/z* = 419.2281.

(*E*)-*N*-Acetyl-1-(2-vinyl-cyclohexyliden)-1,2,3,4-tetrahydro-benzo[*f*]chinolin-2-ol (29): R_f = 0.25 (pentane/ethyl acetate = 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.09–1.35 (m, 2 H, 3′-H_a, 4′-H_a), 1.43–1.71 (m, 4 H, 3′-H_b, 4′-H_b, 5′-H_a, OH), 1.98 (br. d, *J* = 12.6 Hz, 1 H, 5′-H_b), 2.20 (s, 3 H, CH_3), 2.42 (ddd, *J* = 13.6, 13.6, 4.1 Hz, 1 H, 6′-H_a), 2.81 (br. d, *J* = 13.6 Hz, 1 H, 6′-H_b), 2.93 (br. s, 1 H, 2′-H), 3.16 (br. d, *J* = 13.6 Hz, 1 H, 3-H_a), 4.90 (br. d, *J* = 13.6 Hz, 1 H, 3-H_b), 4.93 (ddd, *J* = 17.5, 1.7, 1.7 Hz, 1 H, 2′′-H_a), 5.21 (ddd, *J* = 10.6, 1.7, 1.7 Hz, 1 H, 2′′-H_b), 5.55 (dd, *J* = 7.3, 2.0 Hz, 1 H, 2-H), 6.08 (ddd, *J* = 17.5, 10.6, 6.2 Hz, 1 H, 1′′-H) 7.37 (d, *J* = 8.9 Hz, 1 H, 5-H), 7.42–7.51 (m, 2 H, 8-H, 9-H), 7.78–7.93 (m, 3 H, 6-H, 7-H, 10-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.4, 26.8, 30.1, 35.3 (C-3′, C-4′, C-5′, C-6′), 27.4 (CH_3), 44.8 (C-2′), 52.8 (C-3), 69.2 (C-2), 114.2, 116.5 (C-10b, C-2′′), 123.4, 125.9, 126.5, 126.8, 127.8, 128.0 (C-5, C-6, C-7, C-8, C-9, C-10), 125.3, 131.6, 131.8 (C-1, C-6a, C-10a), 137.0 (C-1′), 138.3 (C-1′′), 143.6 (C-4a), 169.6 (C=O) ppm. MS (200 eV, DCI): *m/z* (%) =

365.3 (50) $[M + NH_4]^+$, 348.3 (100) $[M + H]^+$. HR-MS: $C_{23}H_{25}NO_2$ (347.5): Calculated: *m/z* = 347.1885; found *m/z* = 347.1885.

Synthesis and Pd-Catalyzed Reaction of *rac*-34

***rac*-(*Z*)-1-(4-Brom-9-nitro-3-phenanthryloxy)-11-trimethylsilyl-9-undecen-3-yne-2-ol (34):** To a solution of the 2-ethyne **33** (378 mg, 1.94 mmol, 1.50 equiv.) in anhydrous THF (6 mL) was slowly given with stirring at –50 °C *n*BuLi (2.45 mL, 6.14 mmol, 2.0 equiv., 2.5 M in hexane). Stirring was continued at –50 °C for 1 h, then at –20 °C for 1.5 h and then the mixture was cooled down again to –50 °C. The mixture was transferred via a big transfer cannula dropwise to a solution of phenanthrene aldehyde **32** (467 mg, 1.30 mmol, 1.0 equiv.) in anhydrous THF (5 mL) at –50 °C. Stirring was continued at this temperature for 30 min and then the mixture was warmed up to room temp. within 2 h. Concentrated aqueous ammonium chloride solution (50 mL) was added and the mixture extracted with dichloromethane (3 × 50 mL). After drying over Na_2SO_4 and removal of the solvent in vacuo, the remaining residue was purified by chromatography (pentane/ethyl acetate = 5:1) on silica gel to give the desired compound ***rac*-34** (492 mg, 68 %) as yellowish oil. R_f = 0.23 (pentane/ethyl acetate = 5:1). IR (KBr): $\tilde{\nu}$ = 3520, 3085, 3005, 2936, 2231, 1596, 1526, 1446, 1280, 1084, 856 cm^{-1}. UV (CH_3CN): λ_{max} (lg ε) = 256.5 nm (4.525), 364.0 (3.919). ^1H NMR (300 MHz, $CDCl_3$): δ = –0.02 (s, 9 H, $SiMe_3$), 1.42–1.58 (m, 6 H, 6-H_2, 7-H_2, 11-H_2), 1.95 (dt, *J* = 7.0, 7.0 Hz, 2 H, 8-H_2), 2.25 (dt, *J* = 7.0, 1.9 Hz, 2 H, 5-H_2), 2.68 (br. s, 1 H, OH), 4.27 (dd, *J* = 9.2, 7.6 Hz, 1 H, 1-H_a), 4.38 (dd, *J* = 9.2, 3.6 Hz, 1 H, 1-H_b), 4.90 (m_c, 1 H, 2-H), 5.18–5.26 (m, 1 H, 9-H), 5.34–5.43 (m, 1 H, 10-H), 7.38 (d, *J* = 8.7 Hz, 1 H, 2′-H), 7.68–7.80 (m, 2 H, 6′-H, 7′-H), 7.94 (d, *J* = 8.7 Hz, 1 H, 1′-H), 8.34 (s, 1 H, 10′-H), 8.45 (dd, *J* = 8.1, 1.6 Hz, 1 H, 8′-H), 9.94 (dd, *J* = 8.3, 1.6 Hz, 1 H, 5′-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –1.8 ($SiMe_3$), 18.4, 18.6 (C-5, C-11), 26.4 (C-8), 28.1, 28.9 (C-6, C-7), 61.5 (C-2), 74.1, 76.6 (C-3, C-4), 87.7 (C-1), 109.4 (C-4′), 114.5 (C-2′), 123.1 (C-10), 124.7, 125.8 (C-8′a, C-10′a), 125.1, 125.8, 126.0, 126.9, 127.8, 128.8 (C-1′, C-5′, C-6′, C-7′, C-8′, C-10′), 130.5, 132.4 (C-4′a, C-4′b), 131.4 (C-9), 144.6 (C-9′), 157.0 (C-3′) ppm. MS (70 eV, EI): *m/z* (%) = 553.2 (6) $[M]^+$, 474.3 (30) $[M – Br]^+$, 374.1 (21) $[M – 179]^+$, 317.1 (16) $[M – C_{14}H_{25}OSi]^+$, 163.2 (16) $[C_{13}H_7]^+$, 73.0 (100) $[SiMe_3]^+$. HR-MS: $C_{28}H_{32}NO_4Si$ (554.6): Calculated: *m/z* = 553.1284; found *m/z* = 553.1284.

(*Z*)-10-Nitro-6-(7-trimethylsilyl-5-heptenyl)-4,5-dihydro-3-oxa-benzo[*cd*]pyren-5-ol (37): A mixture of ***rac*-34** (50 mg, 0.09 mmol, 1.00 equiv.), tetrakis(triphenylphosphane)palladium (10.4 mg, 10 mol-%), lithium acetate (37 mg, 0.36 mmol, 4.0 equiv.) and tetrabutylammonium chloride (37 mg, 0.36 mmol, 4.0 equiv.) in acetonitrile (4 mL) was heated for 17 h at 110 °C under an argon atmosphere in a pressure-resistant flask with stirring (TLC). The reaction mixture was diluted with 50 mL of diethyl ether (50 mL), washed with water and brine. After drying over sodium sulfate and removal of the solvent in vacuo, column chromatography on silica gel (pentane/ethyl acetate = 7:1) provided the product ***rac*-37** (31 mg, 73 %) as colorless oil. Reaction of ***rac*-34** with the Pd complex14 under similar conditions gave ***rac*-37** with 20 %. R_f = 0.31 (pentane/ethyl acetate = 5:1). IR (Film): $\tilde{\nu}$ = 3516, 3077, 3003, 2952, 2923, 1604, 1517, 1249, 1076, 981, 855 cm^{-1}. UV (CH_3CN): λ_{max} (lg ε) = 235.5 nm (4.675), 274.0 (4.243), 287.5 (4.102), 302.0 (4.106), 335.5 (4.092), 343.0 (4.097), 368.0 (4.019), 416.5 (3.860). ^1H NMR (300 MHz, $CDCl_3$): δ = –0.02 (s, 9 H, $SiMe_3$), 1.48 (d, *J* = 8.4 Hz, 2 H, 7′-H_2), 1.57 (br. s, 1 H, OH), 1.67 (tt, *J* = 7.0, 7.0 Hz, 2 H, 3′-H_2), 1.75–1.95 (m, 2 H, 2′-H_2), 2.12 (dt, *J* = 7.0, 7.0 Hz, 2 H, 4′-H_2), 3.29–3.48 (m, 2 H, 1′-H_2), 4.38 (dd, *J* = 12.0, 1.4 Hz, 1 H, 4-H_a), 4.84 (dd, *J* = 12.0, 2.0 Hz, 1 H, 4-H_b), 5.26–5.34 (m, 1 H, 5′-H), 5.40–5.49 (m, 2 H, 5-H, 6′-H), 7.60 (d, *J* = 8.4 Hz, 1 H, 2-H), 8.09 (dd, *J* = 8.2, 8.2 Hz, 1 H, 8-H), 8.07 (d, *J* = 8.4 Hz, 1 H, 1-H), 8.37 (d, *J* = 8.2 Hz, 1 H, 7-H), 8.67 (s, 1 H, 11-H), 8.83 (d, *J* = 8.2 Hz, 1 H, 9-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –1.8 ($SiMe_3$), 18.6 (C-7′), 26.8 (C-4′), 28.1, 30.3, 30.7 (C-1′, C-2′, C-3′), 63.9 (C-5), 72.1 (C-4), 114.9 (C-2a[1]), 115.9 (C-2), 121.4, 123.1 (C-1, C-11), 121.8, 123.3, 125.6, 125.9 (C-6a, C-6a[1], C-9a, C-11a), 126.1, 126.9 (C-5′, C-6′), 127.1, 127.6, 128.9 (C-7, C-8, C-9), 130.9 (C-6), 134.9 (C-5a, C-11a[1]), 143.8 (C-10), 154.0 (C-2a) ppm. MS (70 eV, EI): *m/z* (%) = 473.2 (100) $[M]^+$, 443.2 (15) $[M – CH_2O]^+$, 384.1 (13) $[M – C_2HNO_2]$, 300.0 (14) $[M – CHO – C_2HNO_2 – SiMe_3]^+$, 254.0 (20) $[M – C_2HNO_2 – C_2H_4O_2 – C_4H_{11}Si – H]^+$, 73.0 (50) $[SiMe_3]^+$. HR-MS: $C_{28}H_{31}NO_4Si$ (473.6). Calculated: *m/z* = 473.2022; found *m/z* = 473.2022.

Conflict of interest

The authors declare no conflict of interest

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (DFG), the State of Lower Saxony, the Volkswagen Foundation for their generous support. M. K. and S. S. thank the Georg-August-University Göttingen for a post-doctoral fellowship.

Keywords: Carbopalladation · C–H Activation · Domino reactions · Cross-coupling · Synthetic methods

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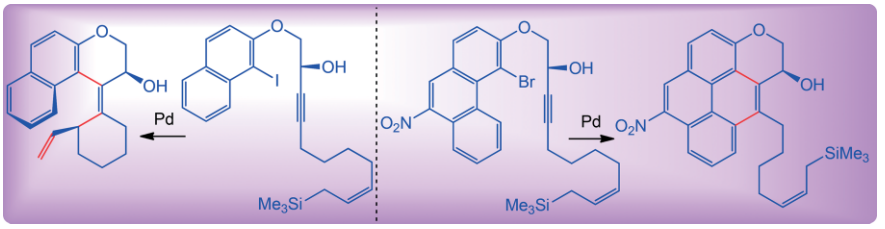
Received: August 17, 2018



Proximity effects allow C–H-activation reactions without directing groups in competition with domino-carbopalladation or Mizoroki–Heck reactions. Vinly–Pd species can be assumed as intermediates, which either react with a double bond or a naphthyl or phenanthryl moiety.

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DOI: 10.1002/ejoc.201801289