Cascade Cyclization: an Easy Access to Highly Unsaturated Polycyclic Ring Systems through a Tandem Stille/[4+2] Reaction under Mild Conditions

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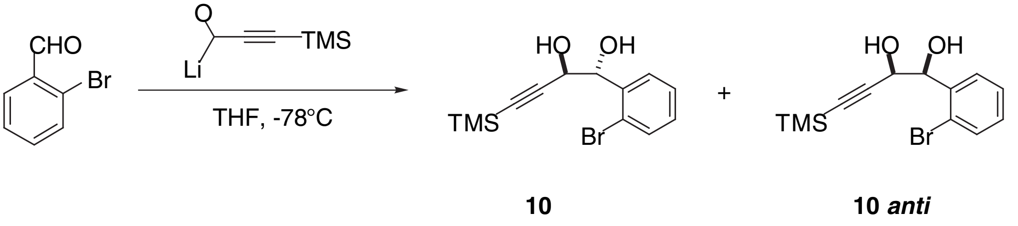
Supporting Information

General Methods. Reactions were run under an atmosphere of argon in oven-dried glassware using a standard syringe, cannula, and septa apparatus. Et_2O and THF were distilled from sodium benzophenone. Benzene, CH_2Cl_2 and DMF were distilled from CaH_2. Et_3N and *i*-Pr_2NH were distilled from KOH. Crude products were purified by flash column chromatography on Merck 230-400 mesh silica gel. For some compounds, 2 % Et_3N treated silica gel was used to avoid decomposition. Analytical TLC was carried out on Merck (Kieselgel 60F-254) silica gel plates. ^1H and ^{13}C NMR spectra were recorded at 200, 300 or 500 MHz using the residual solvent signal as internal reference ($CDCl_3$, 7.27 and 77 ppm ; C_6D_6, 7.16). Chemical shifts are quoted in ppm, coupling constants (*J*) are given in Hz. The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad). Melting points were determined with a glass capillary apparatus and are uncorrected. Mass spectra (MS) by Electronical Impact (EI) were obtained from the Service de spectrométrie de Masse of the Chemistry Institut of Strasbourg (France) and Mass Spectral Analysis by Electro-Spray were performed using a Mariner ESI-Tof instrument from Applied Bio-System /Perking Elmer. Combustion analyses were carried out by the Service de Microanalyse of the Chemistry Institut of Strasbourg (France). Infrared data were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer. *n*-BuLi and *t*-BuLi were titrated using *N*-pivaloyl *o*-toluidine following the Suffert's procedure[1].

(1*R**,2*R**)-1-(2-bromophenyl)-4-(trimethylsilyl)but-3-yne-1,2-diol (10) and (1*S**,2*R**)-1-(2-bromophenyl)-4-(trimethylsilyl)but-3-yne-1,2-diol (10 *anti*)



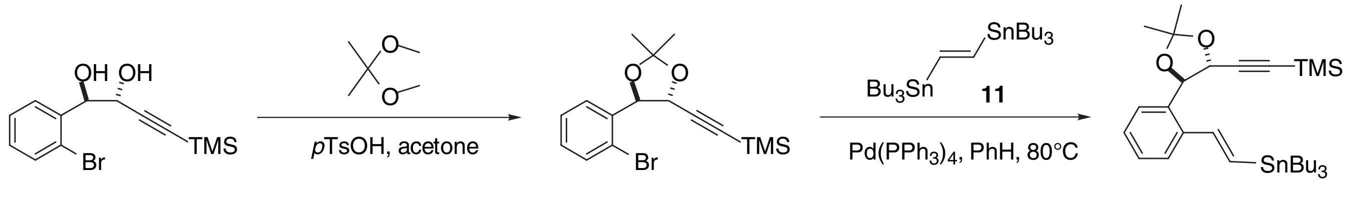
10 **10 *anti***

A solution of *n*-butyllithium (8.6 mL, 13.2 mmol, 1.1 equiv, 1.54 M in hexane) was added to a dried round-bottom flask containing 3-(1-methoxy-1-methyl-ethoxy)-prop-1-ynyl]-trimethylsilyl (2.64 g, 13.2 mmol, 1.1 equiv) in freshly distilled THF (10 mL) at -78 °C. The reaction was stirred 30 min at this temperature and then cannulated to a solution of 2-bromobenzaldehyde (2.22 g, 12 mmol, 1 equiv) in THF (20 mL) at -78 °C. The mixture was stirred for 2 h at -78 °C and then quenched by addition of saturated aqueous $NaHCO_3$ (10 mL) and water (30 mL). After extraction with Et_2O, the combined organic layers were washed with water, brine, dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel flash column chromatography (ether/hexane 5/95) to give the protected alcohols as an oil. The alcohols were deprotected by disolving this oil in methanol (30 mL) containing PPTS (0.30 g, 1.2 mmol, 0.1 equiv). The solution was stirred for 30 min at r.t. and quenched with the addition of brine (40 mL). The mixture was extracted with Et_2O and the combined extracts were washed with water, brine and dried over Na_2SO_4. Silica gel flash column chromatography (ether/hexane 5/95) afforded compound **10** (1.8 g, 5.7 mmol) and **10** ***anti*** (1.8 g, 5.7 mmol) as white solids for a global yield of 96 %.

Data for **10**:
TLC: R_f 0.23 (ether/hexane 4/6). **mp**: 78-80 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ -0.14 (s, 9H), 2.71 (s br, 2H, OH), 4.55 (d, 1H, *J* = 5.3), 5.22 (d, 1H, *J* = 5.3), 7.18 (td, 1H, *J* = 7.5, 1.9), 7.35 (td, 1H, *J* = 7.5, 1.9), 7.54 (s, 1H), 7.56 (s, 1H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ -0.38, 66.43, 75.34, 91.75, 102.58, 123.05, 127.44, 128.69, 129.46, 132.57, 138.29. **IR** (CCl_4): ν 3401 (br, OH), 2962, 2177 (C≡C), 1654, 1570, 1473, 1440, 1250, 1122, 1055, 846, 785. **MS** (EI, 70 eV): *m/z* (%) 296 (1) $[M-OH]^+$, 258 (13), 233 (1) $[M-Br]^+$, 184 (20), 127 (56).

Data for **10** ***anti***:
TLC: R_f 0.32 (ether/hexane 4/6). **mp** 107-109 °C. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 0.11 (s, 9H), 3.39 (s br, 2H, OH), 4.71 (d, 1H, *J* = 3.2), 5.27 (d, 1H, *J* = 3.1), 7.16 (td, 1H, *J* = 7.6, 1.8), 7.33 (td, 1H, *J* = 7.6, 1.2), 7.51 (dd, 1H, *J* = 7.9, 1.2), 7.67 (dd, 1H, *J* = 7.9, 1.8). **^{13}C NMR** (50 MHz, $CDCl_3$): δ - 0.36, 65.86, 74.60, 92.69, 101.62, 122.12, 127.09, 129.07, 129.40, 132.20, 137.86.

[((4*R**,5*R**)-2,2-dimethyl-5-{2-[(*E*)-2-(tributylstannyl)ethenyl]phenyl}-1,3-dioxolan-4-yl)ethynyl](trimethyl)silane (12) via {[(4*R**,5*R**)-5-(2-bromophenyl)-2,2-dimethyl-1,3-dioxolan-4-yl]ethynyl}(trimethyl)silane (A)



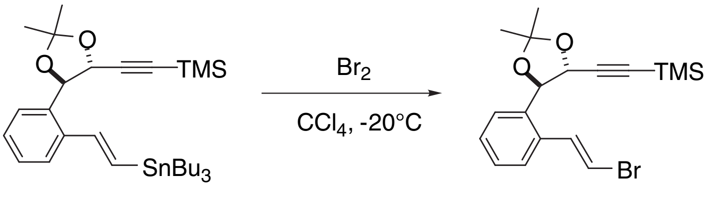
A solution of compound **10** (0.589 g, 1.88 mmol, 1 equiv), 2,2-dimethoxypropane (1.15 mL, *d* = 0.847, 9.4 mmol, 5 equiv) and *p*-TsOH (0.036 g, 0.19 mmol, 0.1 equiv) in acetone (10 mL) was stirred at r.t. for one hour. The mixture was when added to brine (20 mL) and extracted with $\mathrm{Et_2O}$. The combined organic extract was washed with water, brine and dried over $\mathrm{Na_2SO_4}$. After evaporation of the solvents in vacuo, the residue was purified by silica gel flash column chromatography (ether/hexane 5/95) to give the protected diol **A** as a yellowish oil (0.66 g, 1.87 mmol, 99 %).

TLC: R_f 0.33 (ether/hexane 5/95). **^{1}H NMR** (200 MHz, $\mathrm{CDCl_3}$): δ 0.18 (s, 9H), 1.61 (s, 3H), 1.64 (s, 3H), 4.43 (d, 1H, J = 7.1), 5.54 (d, 1H, J = 7.1), 7.19 (td, 1H, J = 7.6, 1.7), 7.36 (td, 1H, J = 7.6, 1.7), 7.56 (m, 2H). **^{13}C NMR** (50 MHz, $\mathrm{CDCl_3}$): δ -0.41, 26.33, 26.89, 73.00, 81.46, 92.72, 101.40, 110.92, 123.05, 127.65, 127.97, 129.67, 132.94, 136.83. **IR** (film): ν 3069, 2987, 2960, 2899, 2177 (C≡C), 1570, 1472, 1440, 1374, 1343, 1250, 1210, 1163, 1121, 1061, 843, 758. **MS** (EI, 70 eV): *m/z* (%) 338 (2) $[\mathrm{M\text{-}CH_3}]^+$, 336 (2) $[\mathrm{M\text{-}OH}]^+$, 280 (1) $[\mathrm{M\text{-}TMS}]^+$, 274 (1) $[\mathrm{M\text{-}Br}]^+$, 167 (100), 152 (39). **Anal.** Calcd for $\mathrm{C_{16}H_{21}BrO_2Si}$: C, 54.39; H, 5.99. Found: C, 54.47; H, 6.10.

A solution of the protected diol **A** (5.3 g, 15 mmol, 1 equiv), *trans*-1,2-bis(tributylstannyl)ethylene **11** (11.2 g, 19.5 mmol, 1.3 equiv) and $\mathrm{Pd(PPh_3)_4}$ (0.87 g, 0.7 mmol, 0.05 equiv) in dry degassed benzene (100 mL) was heated at reflux, under argon, for several hours until the reaction was completed (monitored by TLC). The solvent was then evaporated under reduced pressure and the crude residue was purified by flash column chromatography (ether/hexane 1/99) using $\mathrm{Et_3N}$ pretreated (2 %) silica gel. The title compound **12** was isolated as a yellowish oil (6.72 g, 11.4 mmol, 76 %).

TLC: R_f 0.45 (ether/hexane 5/95). **^{1}H NMR** (300 MHz, $\mathrm{CDCl_3}$): δ 0.16 (s, 9H), 0.93 (m, 15H), 1.36 (m, 6H), 1.56 (m, 6H), 1.59 (s, 3H), 1.60 (s, 3H), 4.61 (d, 1H, J = 7.8), 5.35 (d, 1H, J = 7.8), 6.75 (d, 1H, J = 19.5), 7.28-7.36 (m, 2H), 7.39 (d, 1H, J= 19.5), 7.42-7.52 (m, 2H). **^{13}C NMR** (50 MHz, $\mathrm{CDCl_3}$): δ -0.30, 9.71 ($^1J_{\mathrm{C\text{-}Sn}}$= 336), 13.71, 26.18, 26.99, 27.28 ($^2J_{\mathrm{C\text{-}Sn}}$ = 52), 29.14 ($^3J_{\mathrm{C\text{-}Sn}}$ = 21), 71.67, 72.56, 80.14, 92.42, 101.44, 110.37, 126.72, 127.54, 128.53, 132.60, 134.54, 139.80, 143.63. **IR** ($\mathrm{CHCl_3}$): ν 3065, 2958, 2927, 2854, 2176 (C≡C), 1602, 1561, 1456, 1379, 1250, 1213, 1118, 1053, 845, 757. **Anal.** Calcd for $\mathrm{C_{30}H_{50}O_2SiSn}$: C, 61.12; H, 8.55. Found: C, 61.05; H, 8.32.

[((4R*,5R*)-5-{2-[(*E*)-2-bromoethenyl]phenyl}-2,2-dimethyl-1,3-dioxolan-4-yl)ethynyl](trimethyl)silane (13)

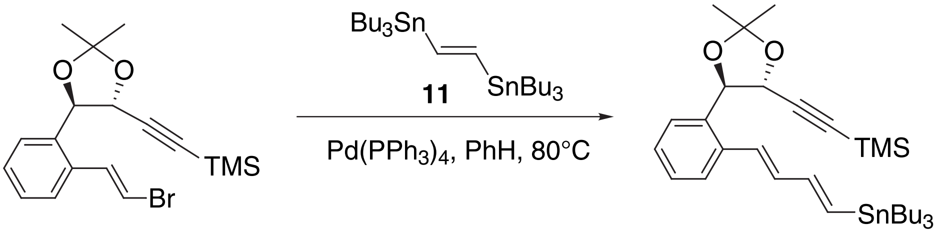


12 **13**

To a cold (-20 °C) stirred solution of vinylstannane **12** (4.90 g, 8.31 mmol, 1 equiv) in CCl_4 (50 mL) was added dropwise (slowly) a solution of bromine (1M in CCl_4, 8.31 mL, 8.31 mmol, 1 equiv). The mixture was stirred for 5 min, the solvent was then evaporated under reduced pressure and the crude product purified by silica gel flash column chromatography (ether/hexane 1/99 to 3/97) to afford the vinyl bromide **13** as a yellowish oil (3.14 g, 8.29 mmol, 100 %).

TLC: R_f 0.35 (ether/hexane 5/95). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 0.20 (s, 9H), 1.60 (s, 3H) 1.61 (s, 3H), 4.40 (d, 1H, J = 7.6), 5.28 (d, 1H, J = 7.6), 6.65 (d, 1H, J = 13.7), 7.26-7.36 (m, 3H), 7.54 (d br, 1H, J = 7.8), 7.68 (d, 1H, J = 13.7). **^{13}C NMR** (50 MHz, $CDCl_3$): δ -0.29, 26.30, 26.79, 73.00, 79.93, 93.35, 100.92, 108.65, 110.65, 126.66, 126.80, 128.63, 128.65, 133.87, 134.98, 135.22. **IR** ($CHCl_3$): ν 2977, 2934, 2870, 2805, 2243 (C≡C), 1608, 1490, 1446, 1383, 1252, 1114, 910, 845, 734. **MS** (EI, 70 eV) (intensity): calc'd for ($C_{18}H_{23}BrO_2Si^+$) 379; found: 379 (1) $[M]^+$, 363 (1) $[M-CH_3]^+$, 306 (1) $[M-OH]^+$, 240 (3), 167 (100), 152 (35). **Anal.** Calcd for $C_{18}H_{23}BrO_2Si$: C, 56.99; H, 6.11. Found: C, 57.12; H, 6.17

[((4*R**,5*R**)-2,2-dimethyl-5-{2-[(1*E*,3*E*)-4-(tributylstannyl)buta-1,3-dienyl]phenyl}-1,3-dioxolan-4-yl)ethynyl](trimethyl)silane (14)



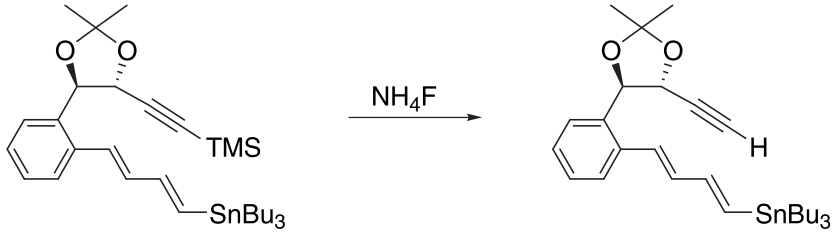
13 **14**

A solution of compound **13** (0.328 g, 0.865 mmol, 1 equiv), *trans*-1,2-bis(tributylstannyl)ethylene **11** (0.681 g, 1.12 mmol, 1.3 equiv) and $Pd(PPh_3)_4$ (50 mg, 0.04 mmol, 0.05 equiv) in dry degassed benzene (15 mL) was heated at reflux, under argon, for several hours until the reaction was completed (monitored by TLC). The solvent was then evaporated under reduced pressure and the crude residue was purified by flash column chromatography (ether/hexane 1/99) using Et_3N pretreated (2 %) silica gel. The title compound **14** was isolated as a yellowish oil (0.287 g, 0.466 mmol, 54 %).

TLC: R_f 0.40 (ether/hexane 5/95). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.19 (s, 9H), 0.94 (m, 15H), 1.35 (m, 6H), 1.55 (m, 6H), 1.62 (s, 3H), 1.63 (s, 3H), 4.44 (d, 1H, J = 7.8), 5.42 (d, 1H, J = 7.8), 6.44 (d, 1H, J = 17.3), 6.69 (dd, 1H, J = 13.9, 10), 6.74 (dd, 1H, J = 17.3, 10), 7.06 (d, 1H, J = 13.9), 7.27-7.31 (m, 2H), 7.52-7.56 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ -0,25, 9.53 ($^1J_{C\text{-}Sn}$ = 330), 13.70, 26.41, 26.86, 27.30 ($^2J_{C\text{-}Sn}$ = 55), 29.11 ($^3J_{C\text{-}Sn}$ = 20), 73.11, 79.69, 92.89, 101.18, 110.41, 125.99, 126.39, 127.72, 127.89, 128.32, 134.07, 134.73, 136.29, 136.56, 146.94. **IR** ($CHCl_3$): ν 2958, 2927, 2871, 2253 (C≡C), 1556, 1464, 1382, 1250, 1142, 1049, 908, 846, 734. **MS** (EI, 70 eV) (intensity): calc'd for ($C_{32}H_{52}O_2SiSn^+$)

615; found: 615 (1) $[M]^+$, 557 (10) $[(M-OC(CH_3)_2]^+$, 265 (20), 250 (56), 167 (100), 109 (19). **Anal.** Calcd for $C_{32}H_{52}O_2SiSn$: C, 62.44; H, 8.51. Found: C, 62.27; H, 8.42.

tributyl((1*E*,3*E*)-4-{2-[(4*R**,5*R**)-5-ethynyl-2,2-dimethyl-1,3-dioxolan-4-yl]phenyl}buta-1,3-dienyl)stannane (15)

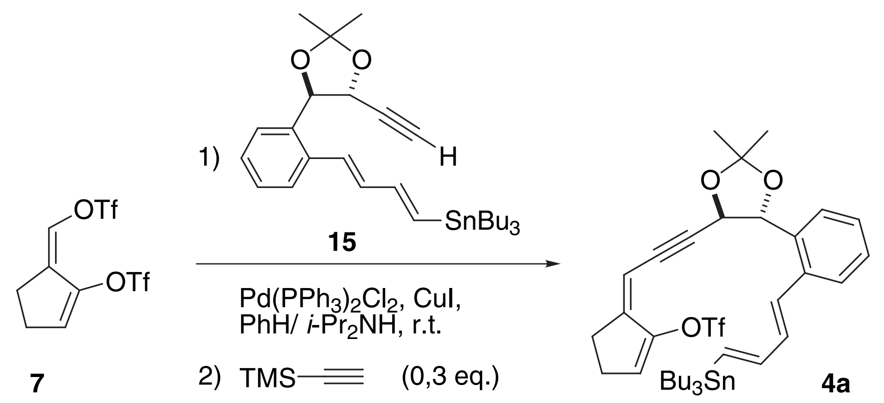


14 **15**

To a solution of the protected alcyne **14** (1.8 g, 2.9 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (9 mL) was added a solution of NH_4F in water (6 mL, 45 %) and *n*-Bu_4NHSO_4 (0.2 g, 0.58 mmol, 0.2 equiv). The mixture was stirred at r.t. and monitored by TLC until starting material disappearance (a few min). The mixture was then poured in water (10 mL) and extracted with CH_2Cl_2 (2 x 10 mL) and Et_2O (10 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (ether/hexane 1/99) using Et_3N pretreated (2 %) silica gel and gave the deprotected compound **15** as a yellowish oil (1.46 g, 2.69 mmol, 93 %).

TLC: R_f 0.36 (ether/hexane 5/95). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.96 (m, 15H), 1.37 (m, 6H), 1.56 (m, 6H), 1.64 (s, 3H), 1.65 (s, 3H), 2.58 (d, 1H, J = 2.2), 4.50 (dd, 1H, J = 7.5, 2.2), 5.46 (d, 1H, J = 7.5), 6.44 (d, 1H, J = 18.1), 6.69 (dd, 1H, J = 14.5, 9.7), 6.74 (dd, 1H, J = 18.1, 9.7), 7.04 (d, 1H, J = 14.5), 7.29-7.32 (m, 2H), 7.52-7.57 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 9.54 ($^1J_{C\text{-}Sn}$ = 337), 13.68, 26.11, 26,80, 27.24 ($^2J_{C\text{-}Sn}$ = 55), 29.09 ($^3J_{C\text{-}Sn}$ = 22), 72.05, 75.46, 80.23, 80.58, 110.74, 126.01, 126.49, 127.66, 128.03, 128.43, 133.90, 134.52, 136.10, 136.46, 146.92. **IR** ($CHCl_3$): ν 3307, 2958, 2927, 2872, 1574, 1456, 1383, 1215, 1162, 1055, 1001, 908, 734. **MS** (EI, 70 eV): m/z (%) 485 (82) $[M-OC(CH_3)_2]^+$, 429 (10), 178 (30). **Anal.** Calcd for $C_{29}H_{44}O_2Sn$: C, 64.10; H, 8.16. Found: C, 63.95; H, 8.05.

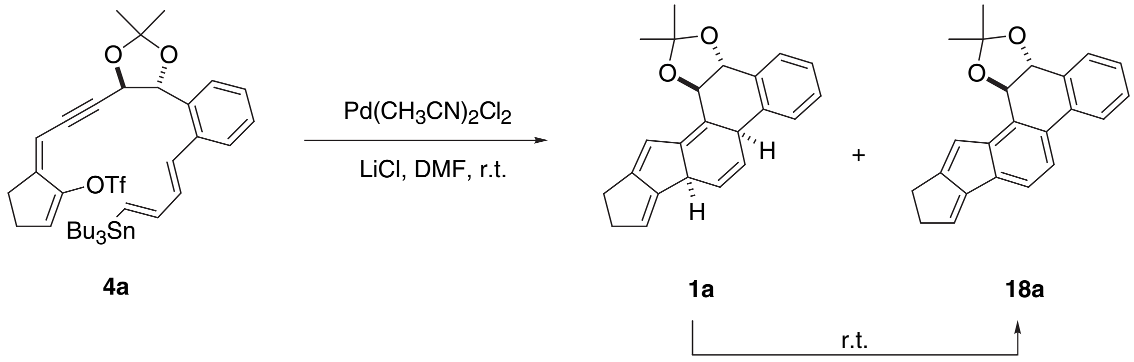
(5*Z*)-5-[3-((4*R**,5*R**)-2,2-dimethyl-5-{2-[(1*E*,3*E*)-4-(tributylstannyl)buta-1,3-dienyl]phenyl}-1,3-dioxolan-4-yl)prop-2-ynylidene]cyclopent-1-en-1-yl trifluoromethanesulfonate (4a)



To a solution of the deprotected alkyne **15** (1.46 g, 2.69 mmol, 1.1 equiv) and the bis-enoltriflate **7** (0.919 g, 2.44 mmol, 1 equiv) in dry benzene (30 mL) was added the catalyst $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.1 mmol, 0.04 equiv), CuI (0.0457 g, 0.24 mmol, 0.1 equiv) and anhydrous *i*-Pr_2NH (10 mL). The mixture was then carefully degassed and placed under argon. Reaction at r.t., was monitored by TLC until the disappearance of the bis-enoltriflate **7** (around 2 h). To elimitate the minor *endo*-enoltriflate product **16** (versus the *exo* **4a**), TMS-acetylene was added (0.1 mL, *d* = 0.695, 0.73 mmol, 0.3 equiv) in a kinetic differentiation reaction[2]. Thus the reaction mixture was stirred for an additional 2 h, then quenched by addition of saturated aqueous NH_4Cl (10 mL) and extracted with Et_2O. The extract was washed with water, brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography (ether/hexane 3/97) using Et_3N pretreated (2 %) silica gel and gave the title product **4a** as a yellow oil (1.48 g, 1.92 mmol, 79 %).

TLC: R_f 0.34 (ether/hexane 1/9). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.89-0.96 (m, 15H), 1.27-1.40 (m, 6H), 1.49-1.56 (m, 6H), 1.61 (s, 6H), 2.52 (m, 2H), 2.43 (d, 1H, *J* = 7.7), 4.67 (dd, 1H, *J* = 7.7, 2.2), 5.43 (d, 1H, *J* = 7.7), 5.46 (s br, 1H), 6.20 (s br, 1H), 6.37 (d, 1H, *J* = 18.6), 6.66 (dd, 1H, *J* = 13.8, 9.8), 6.71 (dd, 1H, *J* = 18.6, 9.8), 7.04 (d, 1H, *J* = 13.8), 7.26-7.29 (m, 2H), 7.51-7.54 (m, 2H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 9.51 ($^1J_{C\text{-}Sn}$= 337), 13.68, 26.26, 26.32, 26.93, 27.28 ($^2J_{C\text{-}Sn}$ = 54), 28.79, 29.09 ($^3J_{C\text{-}Sn}$ = 20), 73.02, 79.78, 82.99, 91.21, 98.41, 110.24, 118.49 ($J_{C\text{-}F}$ = 322), 125.93, 126.65, 127.61, 128.23, 128.42, 129.34, 134.03, 134.25, 134.99, 135.22 ($^2J_{C\text{-}Sn}$= 370), 136.60, 147.26 ($^3J_{C\text{-}Sn}$ = 288), 148.94. **IR** ($CHCl_3$): ν 2957, 2929, 2871, 2250 (C≡C), 1575, 1427, 1382, 1214, 1142, 1050, 1002, 909, 866, 734. **MS** (EI, 70 eV) (intensity): calc'd for ($C_{36}H_{49}F_3O_5SSn^+$) 769; found: (%) 769 (1) $[M]^+$, 711 (66) $[(M\text{-}OC(CH_3)_2)]^+$, 695 (1) $[(M\text{-}O_2C(CH_3)_2)]^+$, 636 (2) $[(M\text{-}SO_2CF_3)]^+$, 479 (2) $[(M\text{-}Bu_3Sn)]^+$, 322 (100), 251 (60), 195 (49).

(3aR*,7bR*,9aS*,13cR*)-2,2-dimethyl-3a,7b,9a,11,12,13c-hexahydropentaleno[1',2':7,8]phenanthro[9,10-d][1,3]dioxole (1a) and (3aR*,13cR*)-2,2-dimethyl-3a,11,12,13c-tetrahydropentaleno[1',2':7,8]phenanthro[9,10-d][1,3]dioxole (18a)

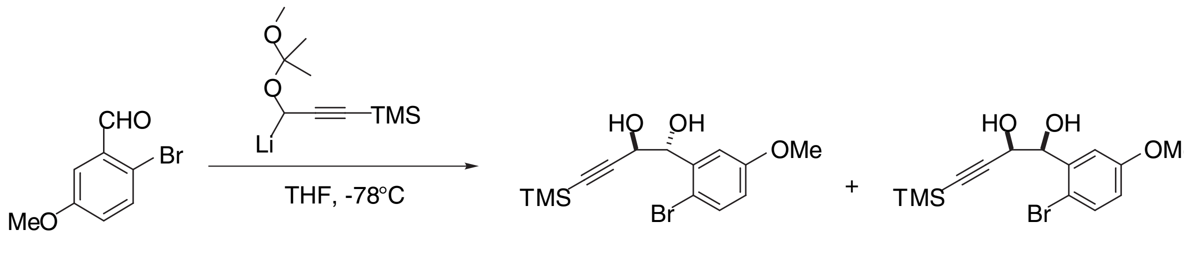


A solution of the enoltriflate **4a** (0.309 g, 0.4 mmol, 1 equiv), $Pd(CH_3CN)_2Cl_2$ (0.0052 g, 0.02 mmol, 0.05 equiv) and LiCl (0.034 g, 0.8 mmol, 2 equiv) in anhydrous DMF (12 mL) was carefully degassed and placed under argon. The mixture was stirred at r.t. for 2 h 30 (monitored by TLC) and, as the reaction was completed, the DMF was reduced in vacuo. The crude was directly purified by flash column chromatography (ether/hexane 5/95) using Et_3N pretreated (2 %) silica gel without any aqueous work-up. The cyclized products **1a** and **18a** were obtained as a yellow oil (0.0637 g, 0.193 mmol, 48 %). We noted that compound **1a** smoothly aromatized in **18a**.

Data for **1a**:
TLC: R_f 0.43 (ether/hexane 1/9). **^{1}H NMR** (500 MHz, C_6D_6): δ 1.47 (s, 3H), 1.58 (s, 3H), 2.27-2.31 (m, 2H), 2.54-2.60 (m, 2H), 3.66 (m, 1H), 3.89 (d br, 1H, *J* = 10.7), 4.16 (d, 1H, *J* = 9.6), 4.78 (d, 1H, *J* = 9.6), 5.42 (dt, 1H, *J* = 4.6, 2.1), 6.26 (dddd, 1H, *J* = 9.2, 3.2, 1.9, 0.5), 6.51 (dddd, 1H, *J* = 9.2, 3.2, 1.9, 0.5), 6.64 (s br, 1H), 7.13-7.20 (2t overlapped with **18a**, 2H), 7.35 (dd, 1H, *J* = 7.3, 2.6), 7.74 (ddd, 1H, *J* = 7.3, 2.6, 1.2). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 27.34, 27.53, 37.11, 40.84, 77.21, 78.03, 112.89, 115.20, 117.18, 120.29, 121.97, 124.28, 126.27, 126.86, 127.08, 128.67, 132.58, 134.22, 135.11, 136.54, 146.54, 153.79, 162.80. **MS** (EI, 70 eV) (intensity): calc'd for ($C_{23}H_{22}O_2^+$) 330; found 330 (96) $[M]^+$, 272 (100) $[(M-OC(CH_3)_2)]^+$, 256 (28) $[(M-O_2C(CH_3)_2)]^+$, 244 (92), 215 (85).

Data for **18a**:
TLC: R_f 0.35 (ether/hexane 1/9). **^{1}H NMR** (500 MHz, C_6D_6): δ 1.52 (s, 3H), 1.53 (s, 3H), 2.41-2.45 (m, 2H), 2.62 (td, 2H, *J* = 4.4, 2.8), 4.93 (syst AB, 2H, J_{AB} = 11, Δν = 25 Hz), 6.34 (td, 1H, *J* = 2.8, 1.8), 7.14 (td, 1H, *J* = 7.4, 1.3), 7.17 (dd, 1H, *J* = 1.6, 0.7), 7.22 (d, 1H, *J* = 1.0 Hz), 7.52 (syst AB, 2H, J_{AB} = 7.8, Δν = 52 Hz), 7.63 (dd, 1H, *J* = 7.5, 1.5), 7.69 (ddd, 1H, *J* = 7.2, 1.2, 1.2). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 23.31, 27.33, 27.38, 39.46, 79.52, 80.19, 113.49, 115.03, 119.75, 121.26, 122.54, 124.84, 125.79, 127.66, 127.68, 130.13, 132.56, 133.69, 134.21, 134.96, 146.36, 149.37, 155.48. **IR** ($CHCl_3$): ν 2927, 2857, 1774, 1702, 1458, 1377, 1235, 1213, 1054, 840, 774. **MS** (EI, 70 eV) (intensity): calc'd for ($C_{23}H_{20}O_2^+$) 328; found 328 (40) $[M]^+$, 270 (96) $[(M-OC(CH_3)_2]^+$, 242 (100).

(1*R,2*R**)-1-(2-bromo-5-methoxyphenyl)-4-(trimethylsilyl)but-3-yne-1,2-diol (10b) and (1*S**,2*R**)-1-(2-bromo-5-methoxyphenyl)-4-(trimethylsilyl)but-3-yne-1,2-diol (10b *anti*)**



10b **10b *anti***

A solution of *n*-butyllithium (3.92 mL, 6.045 mmol, 1.3 equiv, 1.54 M in hexane) was added to a dried round-bottom flask containing 3-(1-methoxy-1-methyl-ethoxy)-prop-1-ynyl]-trimethylsilyl (1.211 g, 6.045 mmol, 1.3 equiv) in freshly distilled THF (10 mL) at -78 °C. The reaction was stirred 30 min at this temperature and then cannulated to a solution of 2-bromo-5-methoxy-benzaldehyde[3] (1.00 g, 4.650 mmol, 1 equiv) in THF (20 mL) kept at -78 °C. The mixture was stirred for 1 h at -78 °C and then quenched by addition of saturated aqueous $NaHCO_3$ (10 mL) and water (30 mL). After extraction with Et_2O, the combined organic layers were washed with water, brine, dried over $MgSO_4$ and concentrated in vacuo. The crude product was dissolved in methanol (30 mL) containing PPTS (0.301 g, 1.2 mmol, 0.1 equiv). The solution was stirred for 30 min at r.t. and quenched with the addition of brine (40 mL). The mixture was extracted with Et_2O and the combined extracts were washed with water, brine and dried over $MgSO_4$. Silica gel column chromatography (ether/hexane 5/95) afforded compound **10b** (0.758 g, 2.209 mmol) as a yellowish oil and **10b *anti*** (0.758 g, 2.209 mmol) as a white solid for a global yield of 95 %.

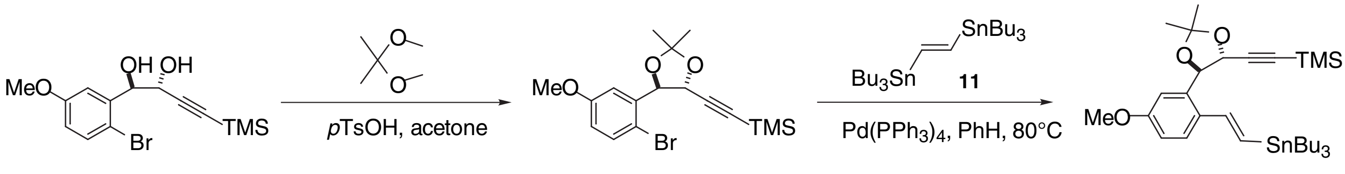
Data for **10b**:

TLC: R_f 0.18 (ether/hexane 5/5). **^{1}H NMR** (200 MHz, CDCl3): δ 0.16(s, 9H), 2.42 (s br, 1H, OH), 3.13 (s br, 1H, OH), 3.81 (s, 3H), 4.56 (t br, 1H, *J* = 4.6), 5.17 (d br, 1H, *J* = 4.6), 6.75 (dd, 1H, *J* = 8.5, 3.2), 7.12 (d, 1H, *J* = 3.2), 7.43 (d, 1H, *J* = 8.5). **^{13}C NMR** (75 MHz, $CDCl_3$): δ -0.35, 55.45, 66.35, 75.30, 91.79, 102.63, 113.18, 114.11, 115.61, 133.15, 139.18, 158.95. **IR** (neat): ν 3284 (br, OH), 2956, 2839, 2176 (C≡C), 1603, 1577, 1460, 1419, 1250, 1161, 1137, 1040, 1011, 940, 849, 760. **MS** (ESI, positive ion 150 eV) (intensity): calc'd for ($C_{14}H_{19}BrO_3SiNa^+$) 365.02; found: 367.03 (100) $[M^{81}+Na]^+$, 365.03 (95) $[M^{79}+Na]^+$. **Anal.** Calcd for $C_{14}H_{19}BrO_3Si$: C, 48.98; H, 5.58. Found: C, 49.05; H, 5.44.

Data for **10b *anti***:

TLC: R_f 0.28 (ether/hexane 5/5). **mp** 120-122 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.13 (s, 9H), 2.60 (d, 1H, *J* = 6.8, OH), 2.81 (d, 1H, *J* = 4.4, OH), 3.82 (s, 3H), 4.71 (dd, 1H, *J* = 6.8, 4.4), 5.21 (t, 1H, *J* = 4.4), 6.75 (dd, 1H, *J* = 8.7, 3.1), 7.23 (d, 1H, *J* = 3.1), 7.40 (d, 1H, *J* = 8.7). **^{13}C NMR** (75 MHz, $CDCl_3$): δ -0.35, 55.39, 65.93, 74.65, 92.79, 101.69, 112.33, 114.43, 115.45, 132.82, 138.93, 158.88.

[((4*R,5*R**)-5-{5-methoxy-2-[(*E*)-2-(tributylstannyl)ethenyl]phenyl}-2,2-dimethyl-1,3-dioxolan-4-yl)ethynyl](trimethyl)silane (12b) via {[(4*R**,5*R**)-5-(2-bromo-5-methoxyphenyl)-2,2-dimethyl-1,3-dioxolan-4-yl]ethynyl}(trimethyl)silane (D)**



10b **D** **12b**

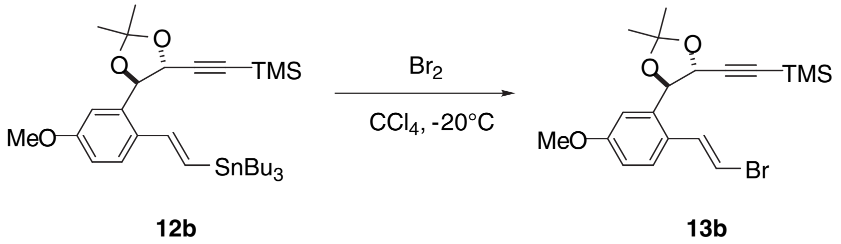
A solution of compound **10b** (7.269 g, 21.175 mmol, 1 equiv), 2,2-dimethoxypropane (13 mL, *d* = 0.847, 105.873 mmol, 5 equiv) and *p*-TsOH (0.403 g, 2.117 mmol, 0.1 equiv) in acetone (100 mL) was stirred at r.t. for 30 min. The mixture was when added to brine (50 mL) and extracted with Et_2O. The combined organic extract was washed with water, brine and dried over $MgSO_4$. After evaporation of the solvents in vacuo, the residue was purified by silica gel flash column chromatography (ether/hexane 10/90) to give the protected diol **D** as a yellowish oil (8.117 g, 21.174 mmol, 100 %).

TLC: R_f 0.25 (ether/hexane 5/95). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.18 (s, 9H), 1.61 (s, 3H), 1.64 (s, 3H), 3.80 (s, 3H), 4.43 (d, 1H, *J* = 6.8), 5.49 (d, 1H, *J* = 6.8), 6.75 (dd, 1H, *J* = 9.0, 3.0), 7.09 (d, 1H, *J* = 3.0), 7.45 (d, 1H, *J* = 9.0). **^{13}C NMR** (75 MHz, $CDCl_3$): δ -0.35, 26.39, 27.00, 55.44, 73.13, 81.60, 92.80, 101.63, 111.13, 113.25, 113.49, 115.56, 133.64, 138.08, 159.23. **IR** (neat): ν 3078, 2958, 2850, 2836, 2177 (C≡C), 1580, 1470, 1380, 1250, 1165, 1055, 840, 761. **MS** (ESI, positive ion 180 eV) (intensity): calc'd for ($C_{17}H_{23}BrO_3SiNa^+$) 405.05; found: 407.08 (100) $[M^{81}+Na]^+$, 405.08 (93) $[M^{79}+Na]^+$. **Anal.** Calcd for $C_{17}H_{23}BrO_3Si$: C, 53.26; H, 6.05. Found: C, 53.06; H, 6.24.

A solution of the protected diol **D** (3.601 g, 9.393 mmol, 1 equiv), *trans*-1,2-bis(tributylstannyl)ethylene **11** (7.402 g, 12.211 mmol, 1.3 equiv) and $Pd(PPh_3)_4$ (0.543 g, 0.470 mmol, 0.05 equiv) in dry degassed benzene (50 mL) was heated at reflux, under argon, for several hours until the reaction was completed (monitored by TLC). The solvent was then evaporated under reduced pressure and the crude residue was purified by flash column chromatography (hexane) using Et_3N pretreated (2 %) silica gel. The title compound **12b** was isolated as a yellowish oil (3.841 g, 6.2 mmol, 66 %).

TLC: R_f 0.33 (ether/hexane 5/95). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 0.20 (s, 9H), 0.89-0.99 (m, 15H), 1.28-1.48 (m, 6H), 1.53-1.65 (m, 6H), 1.63 (s, 6H), 3.86 (s, 3H), 4.62 (d, 1H, *J* = 7.3), 5.37 (d, 1H, *J* = 7.3), 6.65 (d, 1H, *J* = 19.2), 6.89 (dd, 1H, *J* = 8.6, 2.6), 7.08 (d, 1H, *J* = 2.6), 7.32 (d, 1H, *J* = 19.2), 7.49 (d, 1H, *J* = 8.6). **^{13}C NMR** (50 MHz, $CDCl_3$): δ -0.28, 9.6 ($^1J_{C\text{-}Sn}$ = 336), 13.72, 26.24, 27.02, 27.29 ($^2J_{C\text{-}Sn}$ = 55), 29.14 ($^3J_{C\text{-}Sn}$ = 20), 55.26, 72.69, 80.01, 92.56, 101.46, 110.55, 111.80, 114.19, 127.93, 131.94, 132.50, 134.23, 142.90, 159.12. **IR** (neat): ν 2953, 2925, 2861, 2842, 2172 (C≡C), 1608, 1590, 1493, 1466, 1378, 1291, 1250, 1162, 1052, 988. **MS** (ESI, positive ion 135 eV) (intensity): calc'd for ($C_{31}H_{52}O_3SiSnNa^+$) 641.3; found: 641.3 (100) $[M+Na]^+$.

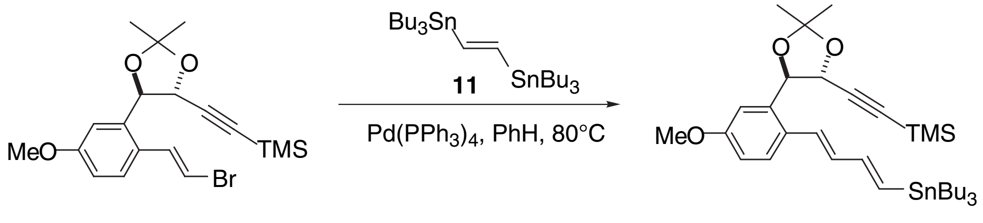
[((4*R**,5*R**)-5-{2-[(*E*)-2-bromoethenyl]-5-methoxyphenyl}-2,2-dimethyl-1,3-dioxolan-4-yl)ethynyl](triethyl)silane (13b)



To a cold (-20 °C) stirred solution of vinylstannane **12b** (3.150 g, 5.084 mmol, 1 equiv) in CCl_4 (30 mL) was added dropwise (slowly) a solution of bromine (1M in CCl_4, 5.09 mL, 5.09 mmol, 1 equiv). The mixture was stirred for 5 min, the solvent was then evaporated under reduced pressure and the crude product purified by silica gel flash column chromatography (ether/hexane 5/95) to afford the vinyl bromine **13b** as a yellowish oil (1.909 g, 4.663 mmol, 92 %).

TLC: R_f 0.19 (ether/hexane 5/95). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 0.21 (s, 9H), 1.61 (s, 3H) 1.62 (s, 3H), 3.82 (s, 3H), 4.39 (d, 1H, *J* = 7.6), 5.27 (d, 1H, *J* = 7.6), 6.55 (d, 1H, *J* = 13.7), 6.84 (dd, 1H, *J* = 8.5, 2.7), 7.07 (d, 1H, *J* = 2.7), 7.29 (d, 1H, *J* = 8.5), 7.6 (d, 1H, *J* = 13.7). **^{13}C NMR** (50 MHz, $CDCl_3$): δ -0.30, 26.26, 26.77, 55.24, 73.02, 79.79, 93.38, 100.95, 106.66, 110.68, 111.72, 114.13, 127.76, 128.02, 134.39, 135.62, 159.91. **IR** ($CHCl_3$): ν 2959, 2172 (C≡C), 1608, 1500, 1434, 1381, 1299, 1251, 1164, 1056, 845, 761. **MS** (ESI, positive ion 135 eV) (intensity): calc'd for ($C_{19}H_{25}BrO_3SiNa^+$) 431.06; found: 433.08 (100) $[M^{81}+Na]^+$, 431.05 (95) $[M^{79}+Na]^+$.

[((4*R,5*R**)-5-{5-methoxy-2-[(1*E*,3*E*)-4-(tributylstannyl)buta-1,3-dienyl]phenyl}-2,2-dimethyl-1,3-dioxolan-4-yl)ethynyl](trimethyl)silane (14b)**



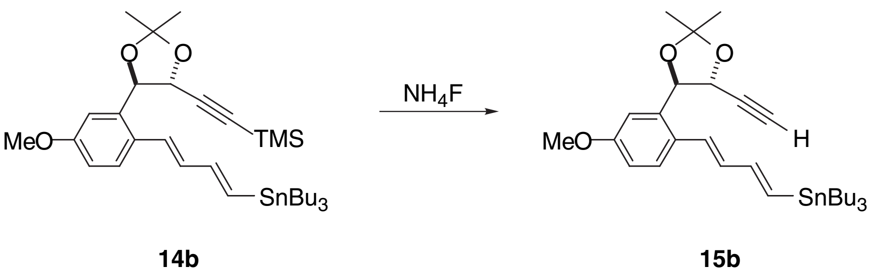
13b **14b**

A solution of compound **13b** (0.873 g, 2.132 mmol, 1 equiv), *trans*-1,2-bis(tributylstannyl)ethylene **11** (1.68 g, 2.772 mmol, 1.3 equiv) and $Pd(PPh_3)_4$ (123 mg, 0.107 mmol, 0.05 equiv) in dry degassed benzene (60 mL) was heated at reflux, under argon, for several hours until the reaction was completed (monitored by TLC). The solvent was then evaporated under reduced pressure and the crude residue was purified by flash column chromatography (hexane) using Et_3N pretreated (2 %) silica gel. The title compound **14b** was isolated as a yellowish oil (0.418 g, 0.647 mmol, 47 %).

TLC: R_f 0.23 (ether/hexane 5/95). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 0.18 (s, 9H), 0.88-0.98 (m, 15H), 1.25-1.42 (m, 6H), 1.49-1.58 (m, 6H), 1.62 (s, 3H), 1.63 (s, 3H), 3.83 (s, 3H), 4.42 (d, 1H, *J* = 7.6), 5.40

(d, 1H, J = 7.6), 6.36 (d, 1H, J = 18), 6.61 (dd, 1H, J = 14.4, 9.2), 6.70 (dd, 1H, J = 18, 9.2), 6.85 (dd, 1H, J = 8.8, 2.9), 6.97 (d, 1H, J = 14.4), 7.07 (d, 1H, J = 2.9), 7.50 (d, 1H, J = 8.8). **^{13}C NMR** (50 MHz, $CDCl_3$): δ -0,24, 9.52 ($^1J_{C\text{-}Sn}$ = 330), 13.70, 26.40, 26.85, 27.30 ($^2J_{C\text{-}Sn}$ = 54), 29.12 ($^3J_{C\text{-}Sn}$ = 20), 55.24, 73.16, 79.53, 92.98, 101.18, 110.51, 111.32, 114.16, 127.29, 127.52, 129.11, 133.00, 134.81, 135.76, 147.15, 159.36. **IR** (neat): ν 2956, 2926, 2860, 2176 (C≡C), 1606, 1556, 1494, 1464, 1379, 1250, 1055, 841, 761. **MS** (ESI, positive ion 135 eV)) (intensity): calc'd for ($C_{33}H_{54}O_3SiSn^+$) 643.94; found: 643.95 (100) [M]$^+$.

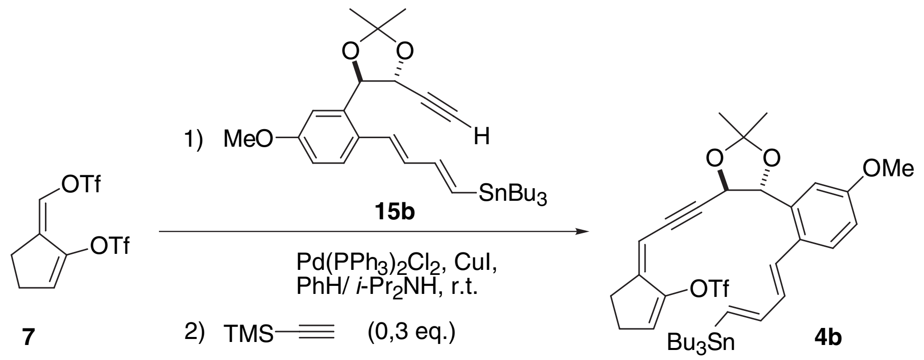
tributyl((1*E*,3*E*)-4-{2-[(4*R**,5*R**)-5-ethynyl-2,2-dimethyl-1,3-dioxolan-4-yl]-4-methoxyphenyl}buta-1,3-dienyl)stannane (15b)



To a solution of the protected alcyne **14b** (0.459 g, 0.711 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (5 mL) was added a solution of NH_4F in water (0.9 mL, 45 %) and n-Bu_4NHSO_4 (0.048 g, 0.142 mmol, 0.2 equiv). The mixture was stirred at r.t. for one hour. The mixture was then poured in water (5 mL) and extracted with CH_2Cl_2 (2 x 10 mL) and Et_2O (10 mL). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (hexane) using Et_3N pretreated (2 %) silica gel and gave the deprotected compound **15b** as a yellowish oil (0.407 g, 0.711 mmol, 100 %).

TLC: R_f 0.52 (ether/hexane 1/9). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 0.88-0.99 (m, 15H), 1.25-1.40 (m, 6H), 1.43-1.60 (m, 6H), 1.63 (s, 3H), 1.64 (s, 3H), 2.58 (d, 1H, J = 2.0), 3.83 (s, 3H), 4.46 (dd, 1H, J = 7.3, 2.0), 5.44 (d, 1H, J = 7.3), 6.35 (d, 1H, J = 18.1), 6.60 (dd, 1H, J = 14.7, 9.5), 6.69 (dd, 1H, J = 18.1, 9.5), 6.86 (dd, 1H, J = 8.7, 2.7), 6.94 (d, 1H, J = 14.7), 7.08 (d, 1H, J = 2.7), 7.50 (d, 1H, J = 8.7). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 9.58 ($^1J_{C\text{-}Sn}$ = 339), 13.70, 26.13, 26.84, 27.28 ($^2J_{C\text{-}Sn}$ = 54), 28.91 ($^3J_{C\text{-}Sn}$ = 21), 55.26, 72.19, 75.55, 80.03, 80.68, 110.86, 111.57, 114.12, 127.33, 127.73, 128.94, 132.75, 134.61 ($^1J_{C\text{-}Sn}$ = 370), 135.73, 147.17 ($^2J_{C\text{-}Sn}$ = 47), 159.33. **IR** (neat): ν 3307, 2956, 2925, 1606, 1558, 1493, 1377, 1252, 1053, 1000, 874, 660. **MS** (ESI, positive ion 135 eV) (intensity): calc'd for ($C_{30}H_{46}O_3SnNa^+$) 597.33; found: 597.88(100) [M+Na]$^+$. **Anal.** Calcd for $C_{30}H_{46}O_3Sn$: C, 62.84; H, 8.09. Found: C, 63.18; H, 8.45.

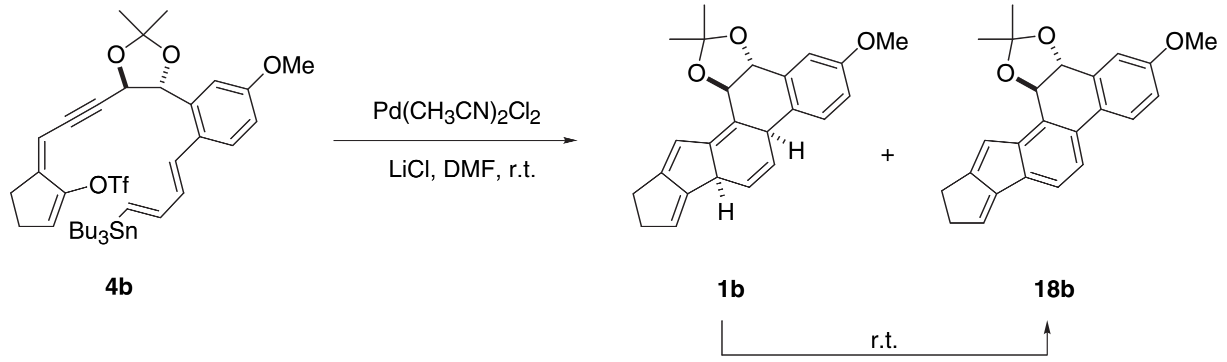
(5*Z*)-5-[3-((4*R**,5*R**)-5-{5-methoxy-2-[(1*E*,3*E*)-4-(tributylstannyl)buta-1,3-dienyl]phenyl}-2,2-dimethyl-1,3-dioxolan-4-yl)prop-2-ynylidene]cyclopent-1-en-1-yl trifluoromethanesulfonate (4b)



To a solution of the deprotected alkyne **15b** (0.543 g, 0.947 mmol, 1.1 equiv) and the bis-enoltriflate **7** (0.324 g, 0.861 mmol, 1 equiv) in dry benzene (7.5 mL) was added the catalyst $Pd(PPh_3)_2Cl_2$ (0.024 g, 0.0344 mmol, 0.04 equiv), CuI (0.024 g, 0.129 mmol, 0.15 equiv) and anhydrous *i*-Pr_2NH (2.5 mL). The mixture was then carefully degassed and placed under argon. Reaction at r.t., was monitored by TLC until the disappearance of the bis-enoltriflate **7** (2 h). To elimitate the minor *endo*-enoltriflate product **16b** (versus the *exo* **4b**), TMS-acetylene was added (0.04 mL, *d* = 0.695, 0.258 mmol, 0.3 equiv) in a kinetic differentiation reaction[2]. Thus the reaction mixture was stirred for an additional 2 h, then quenched by addition of saturated aqueous NH_4Cl (7 mL) and extracted with Et_2O. The extract was washed with water, brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (ether/hexane 0/100 to 5/95) using Et_3N pretreated (2 %) silica gel and gave the title product **4b** as a yellow oil (0.536 g, 0.670 mmol, 78 %).

TLC: R_f 0.18 (ether/hexane 1/9). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.89-0.95 (m, 15H), 1.27-1.40 (m, 6H), 1.47-1.61 (m, 6H), 1.61 (s br, 6H), 2.51-2.55 (m, 2H), 2.72-2.73 (m, 2H), 3.83 (s, 3H), 4.64 (dd, 1H, *J* = 7.5, 2.2), 5.36 (d, 1H, *J* = 7.5), 5.48 (s br, 1H), 6.21 (s br, 1H), 6.30 (d, 1H, *J* = 18.3), 6.56 (dd, 1H, *J* = 14.9, 9.8), 6.70 (dd, 1H, *J* = 18.3, 9.8), 6.83 (dd, 1H, *J* = 8.6, 3), 6.96 (d, 1H, *J* = 14.9), 7.08 (d, 1H, *J* = 3), 7.47 (d, 1H, *J* = 8.6). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 9.52 ($^1J_{C\text{-}Sn}$= 336), 13.69, 26.27, 26.34, 26.95, 27.29 ($^2J_{C\text{-}Sn}$ = 53), 28.81, 29.12 ($^3J_{C\text{-}Sn}$ = 20), 55.25, 73.14, 79.67, 83.08, 91.34, 98.45, 110.36, 111.54, 114.21, 118.53 ($^1J_{C\text{-}F}$ = 322), 127.24, 128.12, 129.12, 129.34, 132.48, 133.70, 135.79, 147.30, 147.50, 148.97, 159.29. **IR** (neat): ν 2957, 2926, 2853, 2253 (C≡C), 1605, 1557, 1492, 1426, 1380, 1289, 1215, 1142, 1044, 1003, 910, 814, 736. **MS** (ESI, positive ion 135 eV) (intensity): calc'd for ($C_{37}H_{51}F_3O_6SSnNa^+$) 823.32; found: 823.27 (82) $[M+Na]^+$, 743.22 (100).

(3a*R**,7b*R**,9a*S**,13c*R**)-5-methoxy-2,2-dimethyl-3a,7b,9a,11,12,13c-hexahydropentaleno[1',2':7,8]phenanthro[9,10-*d*][1,3]dioxole (1b)
and
(3a*R**,13c*R**)-5-methoxy-2,2-dimethyl-3a,11,12,13c-tetrahydropentaleno[1',2':7,8]phenanthro[9,10-*d*][1,3]dioxole (18b)

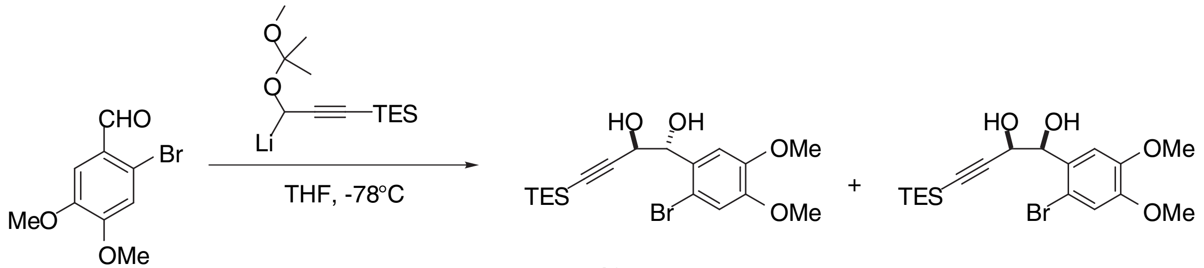


A solution of the enoltriflate **4b** (0.247 g, 0.309 mmol, 1 equiv), $Pd(CH_3CN)_2Cl_2$ (0.004 g, 0.0154 mmol, 0.05 equiv) and LiCl (0.026 g, 0.6178 mmol, 2 equiv) in anhydrous DMF (15 mL) was carefully degassed and placed under argon. The mixture was stirred at r.t. for 2 h (monitored by TLC) and, as the reaction was completed, the DMF was reduced in vacuo. The crude was directly purified by flash column chromatography (hexane) using Et_3N pretreated (2 %) silica gel without any aqueous work-up. The cyclized products **1b** and **18b** were obtained as a yellow oil (0.068 g, 0.190 mmol, 61 %). We noted that compound **1b** smoothly aromatized in **18b**.

Data for **1b**:
TLC: R_f 0.43 (ether/hexane 25/75). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.64 (s br, 6H), 2.59 (m, 2H), 2.87 (m, 2H), 3.74 (m, 1H), 4.02 (m, 1H), 4.14 (m, 1H), 4.74 (d, 1H, J = 9.3), 5.66 (tt, 1H, J = 1.7, 0.48), 6.29 (d br, 1H, J = 9.8), 6.31 (s br, 1H), 6.59 (d br, 1H, J = 9.8), 6.82 (m overlapped with **18b**, 1H), 7.40 (dd, 1H, J = 8.3, 3.4), 7.60 (d, 1H, J = 8.3). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 27.36, 29.70, 29.70, 30.16, 37.12, 39.44, 55.44, 79.54, 80.24, 108.39, 125.51, 126.63, 126.84, 126.95, 128.34, 131.32, 134.22, 136.44, 138.26, 138.35, 144.58, 147.17, 154.12, 155.85. **MS** (EI, 70 eV) (intensity): calc'd for $(C_{24}H_{24}O_3^+)$ 360.2; found: 360.2 (45) $[M]^+$, 358.1 (100) [**18b**]$^+$, 300.1 (78), 272.1 (60), 149.0 (70), 113.2 (29), 69.1 (23), 57.2 (31).

Data for **18b**:
TLC: R_f 0.38 (ether/hexane 25/75). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.64 (s br, 6H), 2.79 (dddd, 2H, J = 2.5, 2.2, 1.9, 1.8), 3.14 (dd, 2H, J = 2.5, 1.9), 3.90 (s, 3H), 4.84 (syst AB, 2H, J_{AB} = 10.9, $\Delta\nu$ = 15.3 Hz), 6.78 (q, 1H, J = 2.5), 6.83 (s br, 1H), 6.91 (dd, 1H, J = 8.4, 2.8), 7.06 (d br, 1H, J = 2.8), 7.51 (syst AB, 2H, J_{AB} = 7.8, $\Delta\nu$ = 35.6 Hz), 7.68 (d, 1H, J = 8.4). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 23.36, 27.41, 27.41, 39.47, 55.42, 79.62, 80.29, 107.81, 113.60, 113.60, 115.04, 119.09, 121.29, 124.94, 126.38, 129.30, 132.57, 133.72, 136.57, 140.21, 146.39, 149.42, 155.49, 159.48. **IR** ($CHCl_3$): ν 3019, 2929, 2854, 1685, 1605, 1566, 1490, 1414, 1376, 1299, 1216, 1175, 1085, 1059, 1027, 763. **MS** (EI, 70 eV) (intensity): calc'd for $(C_{24}H_{22}O_3^+)$ 358.1; found: 358.1 (100) $[M]^+$, 300.1 (94) $[M-OC(CH_3)_2)]^+$, 272.1 (74), 257.1 (51), 227.1 (35), 113.1 (29), 69.2 (26), 57.2 (46).

(1*R**,2*R**)-1-(2-bromo-4,5-dimethoxyphenyl)-4-(triethylsilyl)but-3-yne-1,2-diol (10c) and (1*S**,2*R**)-1-(2-bromo-4,5-dimethoxyphenyl)-4-(triethylsilyl)but-3-yne-1,2-diol (10c *anti*) (named "5,6-dimethoxy" for convenience in the communication)



10c **10c *anti***

A solution of *n*-butyllithium (35.5 mL, 53.046 mmol, 1.3 equiv, 1.494 M in hexane) was added to a dried round-bottom flask containing 3-(1-methoxy-1-methyl-ethoxy)-prop-1-ynyl]-trimethylsilyl (12.86 g, 53.046 mmol, 1.3 equiv) in freshly distilled THF (45 mL) at -78 °C. The reaction was stirred 30 min at this temperature and then cannulated to a solution of 2-bromoveratraldehyde (10 g, 40.805 mmol, 1 equiv) suspended in a THF/ether solution (45/45 mL) kept at -5 °C. The mixture was stirred for 10 min at this temperature and then poured into saturated aqueous $NaHCO_3$ (50 mL). After washing with water (30 mL) and extraction with Et_2O, the combined organic layers were washed with water, brine, dried over $MgSO_4$ and concentrated in vacuo. The crude product, containing the protected alcohols as an oil, was dissolved in methanol (120 mL) containing PPTS (1.025 g, 4.08 mmol, 0.1 equiv). The solution was stirred for 30 min at r.t. and quenched with the addition of brine (50 mL). The mixture was extracted with Et_2O and the combined extracts were washed with water, brine and dried over Na_2SO_4. Silica gel column chromatography (ether/hexane 3/7) afforded compound **10c** (7.882 g, 18.975 mmol) as a yellowish oil and **10c** ***anti*** (7.882 g, 18.975 mmol) as a white solid for a global yield of 93 %.

Data for **10c**:

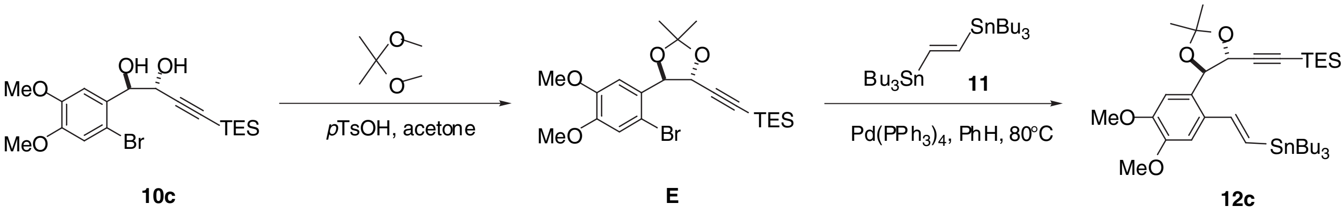
TLC: R_f 0.08 (ether/hexane 3/7). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.57 (q, 6H,J = 7.9), 0.93 (t, 9H, J = 7.9), 2.51 (s br, 1H, OH), 2.95 (s br, 1H, OH), 3.86 (s, 3H), 3.88 (s, 3H), 4.54 (d br, 1H, J = 5.6), 5.13 (d br, 1H, J = 5.6), 6.99 (s, 1H), 7.04 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 4.10, 7.33, 56.02, 56.15, 66.72, 75.49, 89.45, 103.70, 111.01, 113.20, 115.31, 130.23, 148.53, 149.30. **IR** (CCl_4): ν 3466 (br, OH), 3003, 2956, 2875, 2176 (C≡C), 1604, 1503, 1450, 1260, 1160, 1053, 787, 782. **MS** (ESI, positive ion 135 eV) (intensity): calc'd for ($C_{18}H_{27}BrO_4SiNa^+$) 437.08; found: 439.95 (95) $[M^{81}+Na]^+$, 437.08 (100) $[M^{79}+Na]^+$.

.

Data for **10c** ***anti***:

TLC: R_f 0.16 (ether/hexane 3/7). **mp** 128-130 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.56 (q, 6H, J = 7.9), 0.93 (t, 9H, J = 7.9), 2.52 (s br, 1H, OH), 2.80 (s br, 1H, OH), 3.87 (s, 3H), 3.90 (s, 3H), 4.73 (d br, 1H, *J* = 3.9), 5.15 (d br, 1H, *J* = 3.9), 6.99 (s, 1H), 7.21 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 4.15, 7.33, 55.96, 56.16, 66.35, 74.53, 90.40, 103.11, 111.19, 112.19, 115.07, 130.10, 148.44, 149.21.

[((4*R**,5*R**)-5-{4,5-dimethoxy-2-[(*E*)-2-(tributylstannyl)ethenyl]phenyl}-2,2-dimethyl-1,3-dioxolan-4-yl)ethynyl](triethyl)silane (12c) via {[(4*R**,5*R**)-5-(2-bromo-4,5-dimethoxyphenyl)-2,2-dimethyl-1,3-dioxolan-4-yl]ethynyl}(triethyl)silane (E) (named "5,6-dimethoxy" for convenience in the communication)



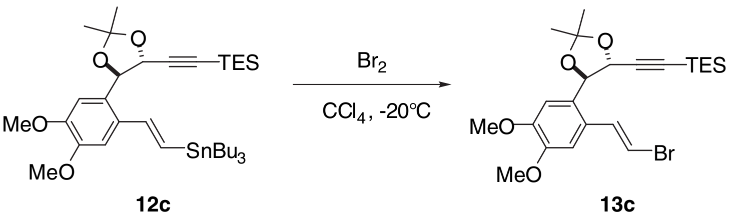
A solution of compound **10c** (4.286 g, 10.318 mmol, 1 equiv), 2,2-dimethoxypropane (6.34 mL, *d* = 0.847, 51.589 mmol, 5 equiv) and *p*-TsOH (0.196 g, 1.032 mmol, 0.1 equiv) in acetone (80 mL) was stirred at r.t. for 30 min. The mixture was when added to brine (50 mL) and extracted with Et_2O. The combined organic extract was washed with water, brine and dried over $MgSO_4$. After evaporation of the solvents in vacuo, the residue was purified by silica gel flash column chromatography (ether/hexane 5/95) to give the protected diol **E** as a yellowish oil (4.700 g, 10.318 mmol, 100 %).

TLC: R_f 0.24 (ether/hexane 7/93). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 0.62 (q, 6H, *J* = 7.8), 0.99 (t, 9H, *J* = 7.8), 1.61 (s, 3H), 1.64 (s, 3H), 3.88 (s, 6H), 4.46 (d, 1H, *J* = 6.9), 5. 49 (d, 1H, *J* = 6.9), 7.00 (s, 1H), 7.01 (s, 1H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 4.15, 7.38, 26.11, 27.02, 55.92, 56.16, 73.05, 81.89, 90.05, 103.23, 110.21, 111.00, 113.15, 115.47, 129.02, 148.76, 149.48. **IR** (neat): ν 3088, 2956, 2875, 2841, 2175 (C≡C), 1603, 1514, 1440, 1256, 1058, 860, 725. **MS** (ESI, positive ion 135 eV) (intensity): calc'd for ($C_{21}H_{31}BrO_4SiNa^+$) 477.11; found: 479.62 (100) $[M^{81}+Na]^+$, 477.62 (75) $[M^{79}+Na]^+$. **Anal.** Calcd for $C_{21}H_{31}BrO_4Si$: C, 55.38; H, 6.86. Found: C, 55.88; H, 7.24.

A solution of the protected diol **E** (4.323 g, 9.491 mmol, 1 equiv), *trans*-1,2-bis(tributylstannyl)ethylene **11** (7.479 g, 12.339 mmol, 1.3 equiv) and $Pd(PPh_3)_4$ (0.548 g, 0.474 mmol, 0.05 equiv) in dry degassed benzene (65 mL) was heated at reflux, under argon, for several hours until the reaction was completed (monitored by TLC). The solvent was then evaporated under reduced pressure and the crude residue was purified by flash column chromatography (ether/hexane 0/100 to 1/99) using Et_3N pretreated (2 %) silica gel. The title compound **12c** was isolated as a yellowish oil (4.119 g, 5.955 mmol, 63 %).

TLC: R_f 0.28 (ether/hexane 2/8). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.59 (q, 6H, *J* = 7.9), 0.89-1.02 (t, 9H, *J* = 7.9 overlapped with m, 15H), 1.29-1.44 (m, 6H), 1.52-1.62 (m, 6H), 1.59 (s, 3H), 1.60 (s, 3H), 3.89 (s, 3H), 3.93 (s, 3H), 4.63 (d, 1H, *J* = 7.5), 5.32 (d, 1H, *J* = 7.5), 6.63 (d, 1H, *J* = 19.2), 6.89 (s, 1H), 7.02 (s, 1H), 7.30 (d, 1H, J = 19.2). **^{13}C NMR** (50 MHz, CDCl$_3$): δ 4.15, 7.36, 9.67 ($^1J_{\text{C-Sn}}$= 336), 13.69, 25.95, 27.05, 27.29 ($^2J_{\text{C-Sn}}$ = 55), 29.14 ($^3J_{\text{C-Sn}}$ = 20), 55.84, 55.87, 72.41, 80.62, 89.74, 103.08, 109.20, 109.94, 110.37, 124.99, 131.87 ($^1J_{\text{C-Sn}}$ = 337), 132.69 ($^2J_{\text{C-Sn}}$ = 64), 142.79, 148.64, 149.14. **IR** (neat): ν 2956, 2873, 2173 (C≡C), 1607, 1509, 1464, 1378, 1212, 1050, 865, 739, 727. **MS** (ESI, positive ion 150 eV) (intensity): calc'd for ($C_{35}H_{60}O_4SiSnNa^+$) 715.42; found: *m/z* (%) 715.58 (100) [M+Na]$^+$.

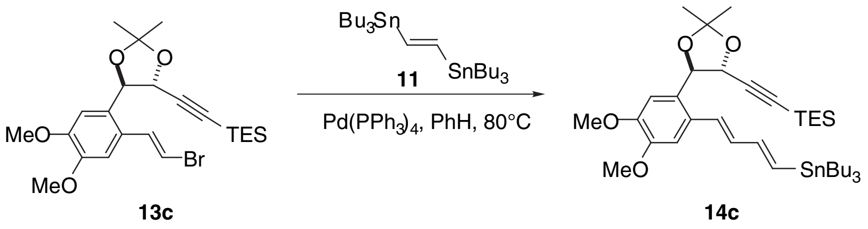
[((4R*,5R*)-5-{2-[(E)-2-bromoethenyl]-4,5-dimethoxyphenyl}-2,2-dimethyl-1,3-dioxolan-4-yl)ethynyl](triethyl)silane (13c) (named "5,6-dimethoxy" for convenience in the communication)



To a cold (-20 °C) stirred solution of vinylstannane **12c** (4.024 g, 5.818 mmol, 1 equiv) in CCl$_4$ (50 mL) was added dropwise (slowly) a solution of bromine (1M in CCl$_4$, 5.82 mL, 5.82 mmol, 1 equiv). The mixture was stirred for 5 min, the solvent was then evaporated under reduced pressure and the crude product purified by silica gel flash column chromatography (ether/hexane 1/99 to 3/97) to afford the vinyl bromine **13c** as a yellowish oil (2.800 g, 5.817 mmol, 100 %).

TLC: R_f 0.18 (ether/hexane 2/8). **^{1}H NMR** (300 MHz, CDCl$_3$): δ 0.64 (q, 6H, J = 7.9), 0.99 (t, 9H, J = 7.9), 1.61 (s br, 6H), 3.89 (s, 3H), 3.90 (s, 3H), 4.43 (d, 1H, J = 7.5), 5. 26 (d, 1H, J = 7.5), 6.59 (d, 1H, J = 13.7), 6.81 (s, 1H), 6.98 (s, 1H), 7.58 (d, 1H, J = 13.7). **^{13}C NMR** (50 MHz, CDCl$_3$): δ 4.14, 7.44, 26.07, 26.86, 55.77, 55.80, 73.03, 80.21, 90.59, 102.58, 107.02, 109.23, 109.32, 110.63, 126.55, 127.88, 134.38, 148.99, 149.41. **IR** (CHCl$_3$): ν 2955, 2772, 2167 (C≡C), 1610, 1550, 1465, 1380, 1272, 1220, 1108, 1055, 913, 742. **MS** (ESI, positive ion 135 eV) (intensity): calc'd for ($C_{23}H_{33}BrO_4SiNa^+$) 503.12; found: 505.56 (10) [M^{81}+Na]$^+$, 503.54 (14) [M^{79}+Na]$^+$, 425 (100), 423 (82), 395 (21), 393 (13).

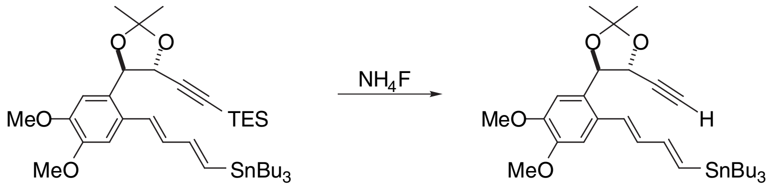
[((4R*,5R*)-5-{4,5-dimethoxy-2-[(1E,3E)-4-(tributylstannyl)buta-1,3-dienyl]phenyl}-2,2-dimethyl-1,3-dioxolan-4-yl)ethynyl](triethyl)silane (14c) (named "5,6-dimethoxy" for convenience in the communication)



A solution of compound **13c** (2.365 g, 4.912 mmol, 1 equiv), *trans*-1,2-bis(tributylstannyl)ethylene **11** (3.87 g, 6.385 mmol, 1.3 equiv) and $Pd(PPh_3)_4$ (284 mg, 0.245 mmol, 0.05 equiv) in dry degassed benzene (35 mL) was heated at reflux, under argon, for 4 hours (monitored by TLC). The solvent was then evaporated under reduced pressure and the crude residue was purified by flash column chromatography (hexane) using Et_3N pretreated (2 %) silica gel. The title compound **14c** was isolated as a yellowish oil (2.643 g, 3.683 mmol, 75 %).

TLC: R_f 0.29 (ether/hexane 2/8). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.63 (q, 6H, *J* = 7.8), 0.89-1.00 (t, 9H, *J* = 7.8 overlapped with m, 15H), 1.25-1.41 (m, 6H), 1.48-1.60 (m, 6H), 1.62 (s, 3H), 1.63 (s, 3H), 3.90 (s, 3H), 3.93 (s, 3H), 4.45 (d, 1H, *J* = 7.5), 5.39 (d, 1H, *J* = 7.5), 6.39 (d, 1H, *J* = 18.2), 6.61 (dd, 1H, *J* = 15, 9.7), 6.70 (dd, 1H, *J* = 18.2, 9.7), 6.98 (d, 1H, *J* = 15), 6.99 (s, 1H), 7.02 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 4.15, 7.39, 9.50 ($^1J_{C\text{-}Sn}$ = 336), 13.66, 26.15, 26.90, 27.29 ($^2J_{C\text{-}Sn}$ = 53), 29.11 ($^3J_{C\text{-}Sn}$ = 20), 55.74, 55.85, 73.15, 79.95, 90.08, 102.88, 108.36, 109.17, 110.42, 126.90, 127.51, 129.31, 133.09, 135.15 ($^1J_{C\text{-}Sn}$ = 376), 146.92, 148.90, 148.90. **IR** (neat): ν 3086, 2952, 2860, 2174 (C≡C), 1602, 1556, 1510, 1463, 1238, 1052, 868, 739. **MS** (ESI, positive ion 135 eV) (intensity): calc'd for ($C_{37}H_{62}O_4SiSnNa^+$) 741.43; found: 741.42 (100) $[M+Na]^+$.

tributyl((1*E*,3*E*)-4-{2-[(4*R**,5*R**)-5-ethynyl-2,2-dimethyl-1,3-dioxolan-4-yl]-4,5-dimethoxy phenyl}buta-1,3-dienyl)stannane (15c) (named "5,6-dimethoxy" for convenience in the communication)

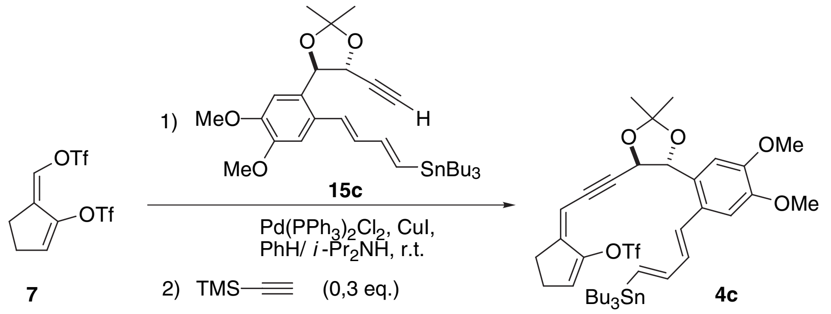


14c **15c**

To a solution of the protected alcyne **14c** (0.983 g, 1.37 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (7 mL) was added a solution of NH_4F in water (1.7 mL, 45 %) and *n*-Bu_4NHSO_4 (0.093 g, 0.274 mmol, 0.2 equiv). The mixture was stirred at r.t. and monitored by TLC until starting material disappearance (1 h). The mixture was then poured in water (5 mL) and extracted with CH_2Cl_2 (2 x 10 mL) and Et_2O (10 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (hexane) using Et_3N pretreated (2 %) silica gel and gave the deprotected compound **15c** as a yellowish oil (0.826 g, 1.37 mmol, 100 %).

TLC: R_f 0.11 (ether/hexane 1/9). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 0.87-0.98 (m, 15H), 1.27-1.39 (m, 6H), 1.46-1.58 (m, 6H), 1.63 (s, 6H), 2.56 (d, 1H, *J* = 1.5), 3.90 (s, 3H), 3.92 (s, 3H), 4.42 (dd, 1H, *J* = 7.6, 1.5), 5.42 (d, 1H, *J* = 7.6), 6.38 (d, 1H, *J* = 18.9), 6.61 (dd, 1H, *J* = 15.6, 9.9), 6.69 (dd, 1H, *J* = 18.9, 9.9), 6.96 (d, 1H, *J* = 15.6), 7.01 (s, 1H), 7.02 (s, 1H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 9.57 ($^1J_{C\text{-}Sn}$ = 336), 13.70, 26.12, 26,86, 27.81 ($^2J_{C\text{-}Sn}$ = 55), 29.11 ($^3J_{C\text{-}Sn}$ = 20), 55.81, 55.86, 72.21, 75.55, 79.79, 80.49, 108.34, 108.99, 110.61, 126.66, 127.73, 129.11, 132.74, 135.89, 147.00, 148.89, 148.92. **IR** ($CHCl_3$): ν 3307, 2958, 2860, 1601, 1554, 1456, 1378, 1273, 1212, 1114, 1049, 1002, 908, 737. **MS** (ESI, positive ion 135 eV) (intensity): calc'd for ($C_{31}H_{48}O_4SnNa^+$) 627.34; found: 627.25 (100) $[M+Na]^+$.

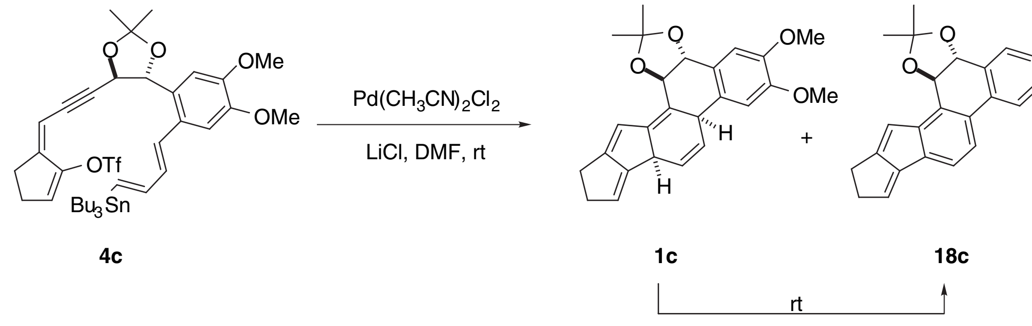
(5*Z*)-5-[3-((4*R,5*R**)-5-{4,5-dimethoxy-2-[(1*E*,3*E*)-4-(tributylstannyl)buta-1,3-dienyl]phenyl}-2,2-dimethyl-1,3-dioxolan-4-yl)prop-2-ynylidene]cyclopent-1-en-1-yl trifluoromethanesulfonate (4c) (named "5,6-dimethoxy" for convenience in the communication)**



To a solution of the deprotected alkyne **15c** (0.687 g, 1.138 mmol, 1.1 equiv) and the bis-enoltriflate **7** (0.389 g, 1.035 mmol, 1 equiv) in dry benzene (9 mL) was added the catalyst $Pd(PPh_3)_2Cl_2$ (0.029 g, 0.0414 mmol, 0.04 equiv), CuI (0.029 g, 0.155 mmol, 0.15 equiv) and anhydrous *i*-Pr_2NH (3 mL). The mixture was then carefully degassed and placed under argon. Reaction at r.t., was monitored by TLC until the disappearance of the bis-enoltriflate **7** (around 2 h). To elimitate the minor *endo*-enoltriflate product **16c** (versus the *exo* **4c**), TMS-acetylene was added (0.040 mL, *d* = 0.695, 0.310 mmol, 0.3 equiv) in a kinetic differentiation reaction[2]. Thus the reaction mixture was stirred for an additional 2 h, then quenched by addition of saturated aqueous NH_4Cl (5 mL) and extracted with Et_2O. The extract was washed with water, brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (ether/hexane 0/100 to 10/90) using Et_3N pretreated (2 %) silica gel and gave the title product **4c** as a yellow oil (0.774 g, 0.933 mmol, 90 %).

TLC: R_f 0.37 (ether/hexane 3/7). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 0.88-0.97 (m, 15H), 1.22-1.39 (m, 6H), 1.49-1.59 (m, 6H), 1.61 (s, 6H), 2.50-2.56 (m, 2H), 2.69-2.75 (m, 2H), 3.90 (s, 3H), 3.92 (s, 3H), 4.64 (dd, 1H, *J* = 7.7, 2.4), 5.41 (d, 1H, *J* = 7.7), 5.47 (s br, 1H), 6.21 (s br, 1H), 6.34 (d, 1H, *J* = 18.1), 6.59 (dd, 1H, *J* = 13.8, 9.8), 6.70 (dd, 1H, *J* = 18.1, 9.8), 6.98 (d, 1H, *J* = 13.8), 7.02 (s, 1H), 7.03 (s, 1H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 9.53 ($^1J_{C\text{-}Sn}$= 337), 13.69, 26.26, 26.99, 26.99, 27.28 ($^2J_{C\text{-}Sn}$ = 55), 28.91, 29.11 ($^3J_{C\text{-}Sn}$ = 21), 55.78, 55.86, 73.05, 79.54, 83.03, 91.25, 98.45, 108.43, 109.40, 110.13, 118.53 ($J_{C\text{-}F}$ = 321), 126.84, 128.17, 129.31, 129.45, 132.47, 134.15, 147.33, 147.34, 148.80, 148.85, 148.99. **IR** (neat): ν 2958, 2927, 2871, 2854, 2254 (C≡C),1604, 1511, 1427, 1380, 1213, 1142, 1050, 1002, 910, 867, 735. **MS** (ESI, positive ion 135 eV) (intensity): calc'd for ($C_{38}H_{53}F_3O_7SSnNa^+$) 853.3; found: 853.3 (100) $[M+Na]^+$.

(3a*R**,7b*R**,9a*S**,13c*R**)-5,6-dimethoxy-2,2-dimethyl-3a,7b,9a,11,12,13c-hexahydropentaleno[1',2':7,8]phenanthro[9,10-*d*][1,3]dioxole (1c) and (3a*R**,13c*R**)-5,6-dimethoxy-2,2-dimethyl-3a,11,12,13c-tetrahydropentaleno[1',2':7,8]phenanthro[9,10-*d*][1,3]dioxole (18c)



A solution of the enoltriflate **4c** (0.751 g, 0.9052 mmol, 1 equiv), $Pd(CH_3CN)_2Cl_2$ (0.012 g, 0.0452 mmol, 0.05 equiv) and LiCl (0.077 g, 1.810 mmol, 2 equiv) in anhydrous DMF (90 mL) was carefully degassed and placed under argon. The mixture was stirred at r.t. for 3 h (monitored by TLC) and, as the reaction was completed, the DMF was reduced in vacuo. The crude was directly purified by flash column chromatography (ether/hexane 5/95) using Et_3N pretreated (2 %) silica gel without any aqueous work-up. The cyclized products **1c** and **18c** were obtained as a yellow oil (0.247 g, 0.632 mmol, 70 %). We noted that compound **1c** smoothly aromatized in **18c**.

Data for **1c**:

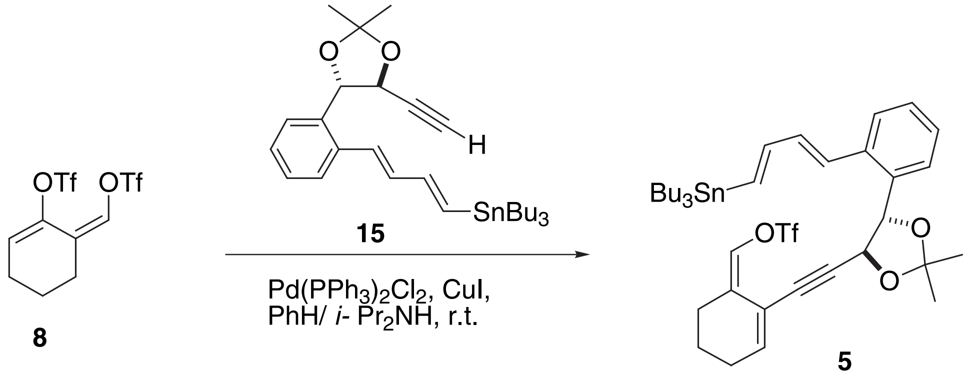
TLC: R_f 0.42 (ether/hexane 5/5). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.62 (s, 6H), 2.56 (m, 2H), 2.85 (m, 2H), 3.66-3.71 (m, 1H), 3.89 (s, 3H), 3.92 (s, 3H), 4.04-4.12 (d, 1H, *J* = 9.3 overlapped with m, 1H), 4.68 (d, 1H, *J* = 9.3), 5.64 (s br, 1H), 6.30 (d, 1H, *J* = 1.7 overlapped with m, 1H), 6.54 (dt, 1H, *J* = 9.4, 2), 6.99 (s, 1H), 7.03 (s, 1H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 23.61, 23.61, 27.40, 27,40, 39.22, 40.94, 56.11, 56.35, 77.77, 80.53, 106.05, 109.27, 112.86, 115.58, 117.16, 118.43, 120.31, 126.87, 127.38, 128.92, 146.53, 147.79, 150.23, 153.79, 162.80. **MS** (EI, 70 eV) (intensity): calc'd for ($C_{25}H_{26}O_4^+$) 390.1; found: 390.1 (68) $[M]^+$, 332.2 (100) $[M-(CH_3)_2CO]^+$, 330.1 (52), 315.1 (43), 304.2 (45), 301.1 (37), 113.1 (16).

Data for **18c**:

TLC: R_f 0.36 (ether/hexane 1/9). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.62 (s, 3H), 1.64 (s, 3H), 2.78 (m, 2H), 3.12 (m, 2H), 3.96 (s, 3H), 3.96 (s, 3H), 4.78 (syst AB, 2H, J_{AB} = 11.0, Δν = 17.1 Hz), 6.77 (t, 1H, *J* = 2.3), 6.81 (sbr, 1H), 7.01 (s br, 1H), 7.47 (syst AB, 2H, J_{AB} = 7.8, Δν = 39.7 Hz), 7.99 (s, 1H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 23.26, 27.30, 27.34, 39.40, 56.08, 56.17, 79.21, 80.56, 106.03, 108.73, 113.39, 114.92, 118.92, 121.14, 125.26, 125.91, 128.07, 129.33, 132.60, 133.81, 146.40, 148.30, 148.90, 149.29, 155.48. **IR** ($CHCl_3$): ν 3013, 2944, 2853, 1669, 1606, 1504, 1458, 1401, 1373, 1213, 1151, 1082, 997, 769. **MS** (EI, 70 eV) (intensity): calc'd for ($C_{25}H_{24}O_4^+$) 388.1; found: 388.1 (65) $[M]^+$, 341.3

(1) [M-CH$_3$OCH$_2$]$^+$, 330.1 (56) [M-OC(CH$_3$)$_2$]$^+$, 322.1 (25) [M-(CH$_3$)$_2$-H$_2$O]$^+$, 269.0 (100) [M+H-OC(CH$_3$)$_2$-2OCH$_3$]$^+$, 265.0 (54), 264.1 (55), 194.9 (49), 57.2 (34).

(*Z*)-{2-[((4*R**,5*R**)-2,2-dimethyl-5-{2-[(1*E*,3*E*)-4-(tributylstannyl)buta-1,3-dienyl}phenyl-1,3-dioxolan-4-yl)ethynyl]cyclohex-2-en-1-ylidene}methyl trifluoromethanesulfonate (5)



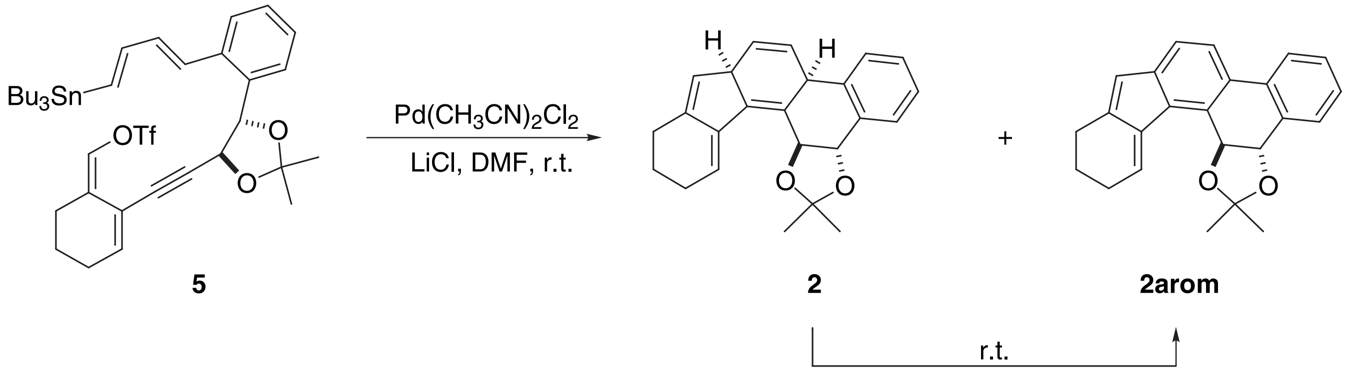
To a solution of the deprotected alkyne **15** (0.598 g, 1.1 mmol, 1.1 equiv) and the bis-enoltriflate **8** (0.390 g, 1 mmol, 1 equiv) in dry benzene (15 mL) was added the catalyst Pd(PPh$_3$)$_2$Cl$_2$ (0.0281 g, 0.04 mmol, 0.04 equiv), CuI (0.019 g, 0.1 mmol, 0.1 equiv) and anhydrous diisopropylamine (5 mL). The mixture was then carefully degassed and placed under argon. Reaction at r.t., was monitored by TLC until the disappearance of the bis-enoltriflate **8** (around 2 h). The reaction mixture was then quenched by addition of saturated aqueous NH$_4$Cl (10 mL) and extracted with Et$_2$O. The extract was washed with water, brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (ether/hexane 5/95) using Et$_3$N pretreated (2 %) silica gel and gave the title product **5** as a yellow oil (0.564 g, 0.72 mmol, 72 %).

TLC: R_f 0.49 (ether/hexane 2/8). **^{1}H NMR** (300 MHz, CDCl$_3$): δ 0.89-0.97 (m, 15H), 1.28-1.40 (m, 6H), 1.48-1.59 (m, 6H), 1.61 (s, 6H), 1.71-1.79 (m, 2H), 2.18-2.22 (m, 2H), 2.25-2.30 (m, 2H), 4.65 (d, 1H, J = 7.8), 5.41 (d, 1H, J = 7.8), 6.39 (d, 1H, J = 17.5), 6.39 (s br, 1H), 6.40 (s br, 1H), 6.68 (dd, 1H, J = 14.7, 10), 6.70 (dd, 1H, J = 17.5, 10), 7.05 (d, 1H, J = 14.7), 7.26-7.30 (m, 2H), 7.51-7.55 (m, 2H). **^{13}C NMR** (50 MHz, CDCl$_3$): δ 9.52 ($^1J_{\text{C-Sn}}$= 335), 13.68, 21.68, 26.29, 26.58, 26.94, 27.29 ($^2J_{\text{C-Sn}}$= 54), 27.33, 29.12 ($^3J_{\text{C-Sn}}$= 21), 72.82, 79.81, 84.94, 85.00, 110.29, 115.39, 118.59 (q, $J_{\text{C-F}}$ = 319), 123.70, 126.00, 126.82, 127.67, 128.24, 128.29, 129.22, 133.94, 134.32, 135.54, 136.64, 144.62, 147.09. **IR** (CHCl$_3$): ν 2957, 2929, 2872, 2854, 2253 (C≡C), 1794, 1653, 1556, 1424, 1382, 1246, 1218, 1140, 1056, 1025, 1002, 908, 843, 734. **MS** (EI, 70 eV): *m/z* (%) 783 (1) [M]$^+$, 650 (7) [(M-SO$_2$CF$_3$)]$^+$, 471 (80), 494 (2) [(M-Bu$_3$Sn)]$^+$, 336 (100).

(3a*R**,7b*R**,9a*S**,14d*R**)-2,2-dimethyl-7b,9a,11,12,13,14d-hexahydro-3a*H*-indeno[1',2':1,2]phenanthro[9,10-*d*][1,3]dioxole (2)

and

(3a*R,14d*R**)-2,2-dimethyl-11,12,13,14d-tetrahydro-3a*H*-indeno[1',2':1,2]phenanthro[9,10-*d*][1,3]dioxole (2arom)**



A solution of the enoltriflate **5** (0.500 g, 0.64 mmol, 1 equiv), $Pd(CH_3CN)_2Cl_2$ (0.0083 g, 0.032 mmol, 0.05 equiv) and LiCl (0.054 g, 1.28 mmol, 2 equiv) in anhydrous DMF (15 mL) was carefully degassed and placed under argon. The mixture was stirred at r.t. until the disapearance of the starting material (monitored by TLC, 4 h). Then the reaction was quenched with a saturated aqueous solution of NH_4Cl (5 mL) and extracted with Et_2O (3 x 10mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (ether/hexane 5/95) using Et_3N pretreated (2 %) silica gel. The cyclized products **2** and **2arom** were obtained as yellow oils (0.448 mg, 1.300 mmol, 51 % global yield).

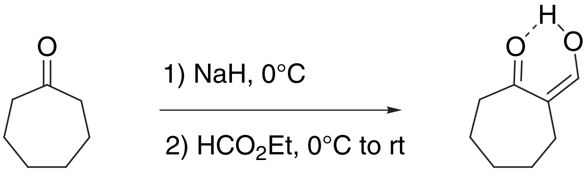
Data for **2**:

TLC: R_f 0.56 (ether/hexane 2/8). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.49-1.59 (m, 2H), 1.64 (s, 3H), 1.69 (s, 3H), 1.81-1.97 (m, 2H), 2.34-2.66 (m, 2H), 3.86 (td, 1H, J = 10.9, 2.8), 4.09 (d br, 1H, J = 9.4), 4.18 (d br, 1H, J = 10.9), 4.94 (dd, 1H, J = 9.1, 0.8), 5.73 (s br, 1H), 6.24 (dt, 1H, J = 9.7, 2.7), 6.50 (dt, 1H, J = 9.7, 2.7), 6.74 (t br, 1H, J = 4.7), 7.30-7.32 (m, 1H), 7.41-7.47 (m, 1H), 7.54-7.57 (m, 1H), 7.73-7.76 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 21.95, 25.92, 26.10, 30.31, 30.31, 39.72, 47.19, 77.58, 79.00, 112.14, 121.24, 123.39, 124.32, 125.50, 126.43, 128.79, 129.22, 130.85, 132.33, 135.57, 135.78, 136.10, 138.31, 141.81. **MS** (EI, 70 eV) (intensity): calc'd for ($C_{24}H_{24}O_2^+$) 344.1; found 344.1 (1) $[M]^+$, 270.1 (100) $[M-(CH_3)_2CO_2]^+$.

Data for **2arom**:

TLC: R_f 0.56 (ether/hexane 2/8). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.66 (s, 3H), 1.68 (s, 3H), 1.83-1.97 (m, 2H), 2.51-2.61 (m, 2H), 2.75 (td, 2H, J = 6.2, 1.4), 4.90 (syst AB, 2H, J_{AB} = 10.6, $\Delta\nu$ = 31.3 Hz), 6.46 (d, 1H, J = 1.3), 7.24 (d, 1H, J = 7.8), 7.36 (tt, 2H, J = 8.7, 1.6), 7.51 (td br, 1H, J = 6.8, 1.2), 7.63 (d, 1H, J = 7.8), 7.68 (d br, 1H, J = 7.5), 7.90 (td, 1H, J = 4.7, 1.6 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 23.98, 25.68, 27.23, 27.37, 27.37, 79.36, 80.12, 112.41, 119.19, 122.10, 122.64, 124.45, 124.73, 127.02, 127.67, 128.42, 129.74, 130.65, 134.06, 134.33, 138.69, 139.09, 141.04, 144.88. **IR** ($CHCl_3$): ν 3019, 2990, 2850, 1604, 1522, 1478, 1415, 1376, 1215, 1161, 1120, 758. **MS** (EI, 70 eV) (intensity): calc'd for ($C_{24}H_{22}O_2^+$) 344.1; found 344.1 (1) $[M]^+$, 270.1 (100) $[M-(CH_3)_2CO_2]^+$.

(2*Z*)-2-(hydroxymethylene)cycloheptanone (B)

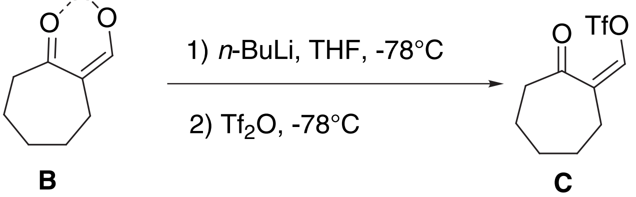


B

To a stirred solution of sodium hydride (60 % NaH in oil, 13.907 g, 347.68 mmol, 1.3 equiv) in dry THF (250 mL) at 0°C and under argon was first slowly added cycloheptanone (31.54 mL, *d* = 0.951, 267.5 mmol, 1 equiv) and then a solution of ethyl formate (32.7 mL, *d* = 0.917, 401.2 mmol, 1.5 equiv) in dry THF (30 mL). The mixture was stirred for 3 h, while the temperature was allowed to warm up to r.t.. The obtained mudy reaction mixture is poured carefully into ice/water (400 g/400 mL). The aqueous layer was extracted with ether (1 x 50 mL) and then neutralised with solid sodium dihydrogen phosphate ($NaH_2PO_4.H_2O$, 150 g) and acidified with concentrated hydrochloric acid (20 mL, 36 %). The solution was extracted with ether (6 x 300 mL) and the combined organic extract was washed with brine and dried over $MgSO_4$. After evaporation of the solvents in vacuo, the residue was purified by silica gel flash column chromatography (ether/hexane 3/97) to give the title compound **B** as a pinkish oil (33.20 g, 237 mmol, 89 %).

TLC: R_f 0.13 (ether/hexane 3/97). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.57-1.62 (m, 2H), 1.67-1.75 (m, 4H), 2.24 (t, 2H, *J* = 5.6), 2.52 (t, 2H, *J* = 5.1), 7.62 (d, 1H, *J* = 8.7), 14.67 (d, 1H, *J* = 8.7). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 24.47, 28.41, 29.66, 31.52, 41.83, 114.45, 170.70, 204.02. **IR** ($CHCl_3$): ν 2977, 2929, 2858, 2243, 1638, 1582, 1450, 1383, 1264, 1222, 1112, 909, 734. **MS** (ESI, positive ion 130 eV) (intensity): calc'd for ($C_8H_{12}O_2Na^+$) 163.0735; found 163.0751 (50) $[M+Na]^+$, 153 (70), 141.1482 (100) $[M+H]^+$.

(*Z*)-(2-oxocycloheptylidene)methyl trifluoromethanesulfonate (C)

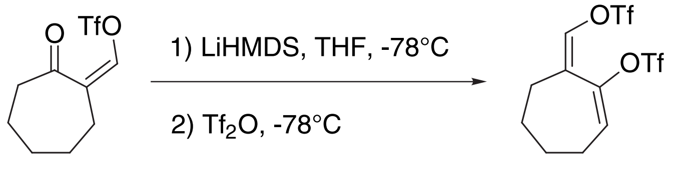


B **C**

A refrigerated solution (-78°C) of *t*-butyllithium (1.54 M in pentane, 92.7 mL, 143 mmol, 1 equiv) was added in a dried round-bottom flask under argon containing compound **B** (20 g, 143 mmol, 1 equiv) in freshly distilled THF (560 mL) at -78 °C. The reaction was stirred 15 min at this temperature and a refrigerated solution (-78°C) of trifluoromethansulfonic anhydride (28.94 mL, *d* = 1.677, 172 mmol, 1.2 equiv) was added dropwise. The reaction was stirred for 15 min at this temperature and then quenched by addition of a saturated solution of $NaHCO_3$ (40 mL) and brine (80 mL). The organic medium was washed with water (200 mL) and the mixture was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by Et_3N pretreated silica gel flash column chromatography (hexane) to afford the title compound **C** as a yellowish oil (20.42 g, 75 mmol, 53 %).

TLC: R_f 0.11 (ether/hexane 1/9). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.75 (s br, 6H), 2.34 (m, 2H), 2.59 (m, 2H), 6.60 (s br, 1H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 24.41, 29.11, 30.29, 30.51, 43.81, 118.42 (q, $J_{C\text{-}F}$ = 320.80), 132.29, 135.18, 201.08. **IR** ($CHCl_3$): ν 3093, 2935, 2860, 2359, 1702, 1626, 1426, 1248, 1212, 1142, 1004, 942, 895, 838, 618. **MS** (ESI, positive ion 130 eV) (intensity): calc'd for ($C_9H_{11}F_3O_4SNa^+$) 295.0228; found 295.0327 (100) $[M+Na]^+$, 244.1832 (3), 203.1480 (2) $[M-CF_3]^+$, 162.0645 (1) $[M-SO_2CF_3+Na]^+$, 153 (5).

(Z)-(2-{[(trifluoromethyl)sulfonyl]oxy}cyclohept-2-en-1-ylidene)methyl trifluoromethanesulfonate (9)

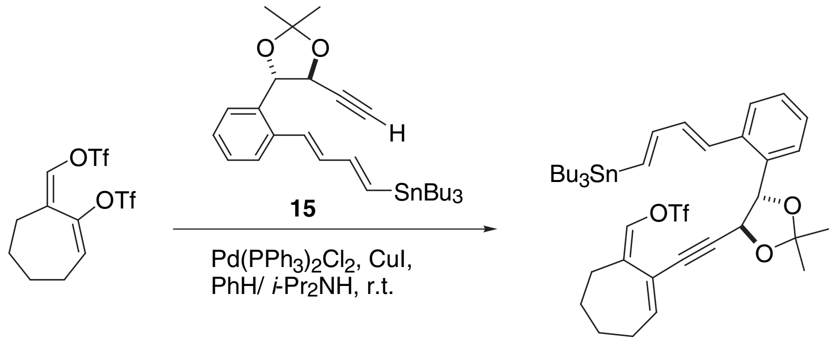


C **9**

A refrigerated solution (-78°C) of *n*-butyllithium (1.46 M in hexane, 5.53 mL, 8.081 mmol, 1.1 equiv) was added to a dried round-bottom flask under argon containing hexamethyldisilylazane (1.86 mL, *d* = 0.765, 8.816 mmol, 1.2 equiv) in freshly distilled THF (30 mL) at -78 °C. The reaction was stirred 15 min at this temperature and a refrigerated solution (-78°C) of compound **C** (2 g, 7.346 mmol, 1 equiv) in freshly distilled THF (10 mL) was added. The reaction was stirred 15 min at this temperature and a refrigerated solution (-78°C) of trifluoromethansulfonic anhydride (1.23 mL, *d* = 1.677, 7.346 mmol, 1 equiv) was added dropwise. The reaction was then quenched by addition of a saturated solution of $NaHCO_3$ (15 mL) and brine (30 mL). After extraction with Et_2O, the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel flash column chromatography (ether/hexane 3/97) to afford the title compound **9** as a colorless oil (1.13 g, 2.795 mmol, 38 %).

TLC: R_f 0.20 (ether/hexane 10/90). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.65-1.88 (m, 4H), 2.23-2.38 (m, 4H), 6.14 (t, 1H, *J* = 6.23), 6.65 (s br, 1H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 24.90, 25.51, 29.45, 29.53, 118.49 (2q, $J_{C\text{-}F}$ = 320.8), 124.84, 128.56, 133.73, 143.14. **IR** ($CHCl_3$): ν 3102, 2940, 2864, 1688, 1633, 1431, 1249, 1214, 1141, 1068, 1031, 993, 882, 840, 612. **MS** (ESI, positive ion 130 eV): *m/z* (%) 385 (50) $[M-F]^+$, 271 (3) $[M+H-SO_2CF_3]^+$.

(*Z*)-{2-[((4*R**,5*R**)-2,2-dimethyl-5-{2-[(1*E*,3*E*)-4-(tributylstannyl)buta-1,3-dienyl]penyl}-1,3-dioxolan-4-yl)ethynyl]cyclohept-2-en-1-ylidene}methyl trifluoromethanesulfonate (6)



9 **6**

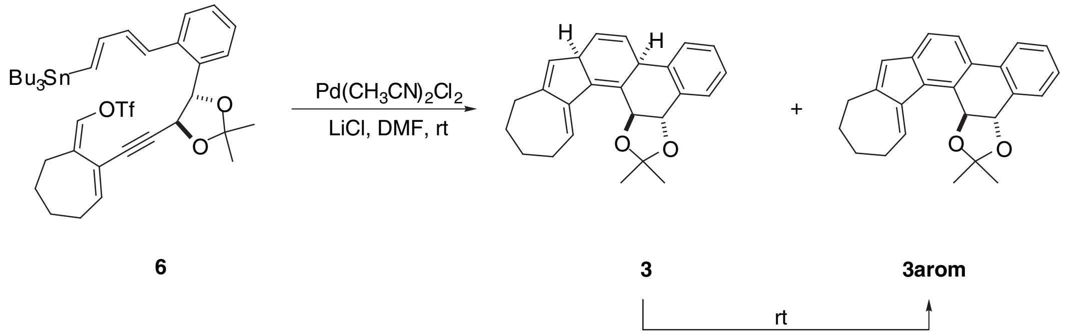
To a solution of the deprotected alkyne **15** (1.00 g, 1.84 mmol, 1.1 equiv) and the bis-enoltriflate **9** (0.676 g, 1.67 mmol, 1 equiv) in dry benzene (23 mL) was added the catalyst $Pd(PPh_3)_2Cl_2$ (0.047 g, 0.067 mmol, 0.04 equiv), CuI (0.032 g, 0.167 mmol, 0.1 equiv) and anhydrous diisopropylamine (6.7 mL). The mixture was then carefully degassed and placed under argon. Reaction at r.t., was monitored by TLC until the disappearance of the bis-enoltriflate **9** (around 45 min.). The reaction mixture was then quenched by addition of a saturated solution of NH_4Cl (7 mL) and extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by Et_3N pretreated silica gel flash column chromatography (ether/hexane 5/95) to afford the title compound **6** as a yellow oil (0.88 g, 0.11 mmol, 66 %).

TLC: R_f 0.19 (ether/hexane 5/95). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 0.88-0.99 (m, 15H), 1.26-1.40 (m, 6H), 1.47-1.61 (m, 6H), 1.61 (s, 6H), 1.58-1.83 (m, 4H), 2.19-2.29 (m, 4H), 4.61 (d, 1H, *J* = 7.7), 5.38 (d, 1H, *J* = 7.7), 6.40 (d, 1H, *J* = 17.8), 6.41 (s br, 1H), 6.44 (s br, 1H), 6.69 (dd, 1H, *J* = 14.8, 9.3), 6.71 (dd, 1H, *J* = 17.8, 9.3), 7.04 (d, 1H, *J* = 14.8), 7.26-7.30 (m, 2H), 7.49-7.56 (m, 2H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 9.51 ($^1J_{C\text{-}Sn}$ = 336), 13.66, 24.88, 26.24, 26.89, 27.28 ($^2J_{C\text{-}Sn}$ = 55), 29.08 ($^3J_{C\text{-}Sn}$ = 18), 29.29, 30.38, 30.72, 72.91, 80.13, 83.55, 85.91, 110.32, 118.52 (q, $J_{C\text{-}F}$ = 319), 119.50, 126.04, 126.89, 127.69, 128.13, 128.33, 130.02, 131.65, 133.81, 134.42, 135.68, 136.63, 144.80, 147.08. **IR** ($CHCl_3$): 2978, 2933, 2871, 2810, 2243 (C≡C), 1654, 1560, 1446, 1383, 1351, 1246, 1150, 1113, 909, 844, 734. **MS** (ESI, positive ion 130 eV) (intensity): calc'd for ($C_{38}H_{53}F_3O_5SSnNa^+$) 821.34; found: 821.33 (25) $[M+Na]^+$, 804.56 $[M+Na-CH_3]^+$, 663.33 (18), 531.15 (13) $[M+H-SnBu_3]^+$.

(3a*R**,7b*R**,9a*S**,15d*R**)-2,2-dimethyl-3a,7b,9a,11,12,13,14,15d-octahydroazuleno[1',2':1,2]phenanthro[9,10-*d*][1,3]dioxole(1:1) (3)

and

(3a*R**,15d*R**)-2,2-dimethyl-3a,11,12,13,14,15d-hexahydroazuleno[1',2':1,2]phenanthro[9,10-*d*][1,3]dioxole (3arom)



A solution of the enoltriflate **6** (0.500 g, 0.627 mmol, 1 equiv), Pd(CH_3CN)$_2$$Cl_2$ (0.008 g, 0.031 mmol, 0.05 equiv) and LiCl (0.053 g, 1.254 mmol, 2 equiv) in anhydrous DMF (15 mL) was carefully degassed and placed under argon. The mixture was stirred at r.t. until the disapearance of the starting material (monitored by TLC, 1 h). Then the reaction was quenched with water (5 mL) and extracted with Et_2O (3 x 10mL). The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by Et_3N pretreated silica gel flash column chromatography (hexane) to afford the cyclized and inseparable products **3** and **3arom**. (which resulted from the aromatisation of **3**) as a yellow oil for a global yield around 50 %. We noticed that after 5 days the isolated mixture only contained **3arom**.

Data for **3**:
TLC: R_f 0.54 (ether/hexane 2/8). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.70 (s, 3H), 1.71 (s, 3H), 1.59-1.75 (m, 2H), 1.87-1.91 (m, 2H), 2.58-2.66 (m, 2H), 2.75-2.95 (m, 2H), 3.90 (d br, 1H, *J* = 10.6), 4.06 (d br, 1H, *J* = 9), 4.20 (d br, 1H, *J* = 11.2), 4.97 (d, 1H, *J* = 8.7), 5.82 (s br, 1H), 6.20 (d br, 1H, *J* = 10), 6.44 (d br, 1H, *J* = 10), 6.89 (t br, 1H, *J* = 5.9), 7.40 (s br, 1H), 7.52 (m, 2H), 7.66 (d, 1H, *J* = 7.5). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 25.97, 26.91, 28.24, 28.28, 30.25, 30.48, 39.31, 46.30, 77.48, 78.56, 111.70, 119.00, 120.88, 124.20, 127.32, 128.55, 129.66, 130.20, 135.19, 135.67, 136.90, 139.00, 139.71, 142.07, 146.42. **MS** (EI, 70 eV) (intensity): calc'd for ($C_{25}H_{26}O_2^+$) 358.2; found: 358.5 (5) $[M]^+$, 300.5 (5) $[M-(CH_3)_2CO]^+$, 284.4 (3) $[M-(CH_3)_2CO_2]^+$, 272.4 (2), 254.3 (13), 241.3 (28).

Data for **3arom.**:
TLC: R_f 0.54 (ether/hexane 2/8). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.60-1.78 (m, 2H), 1.62 (s, 3H), 1.66 (s, 3H), 1.87-1.95 (m, 2H), 1.90-1.99 (m, 2H), 2.50-2.67 (m, 2H), 4.88 (syst AB, 2H, J_{AB} = 10.5, Δν = 32.6 Hz), 6.57 (s br, 1H), 7.22 (d, 1H, *J* = 7.8), 7.36 (td, 2H, *J* = 6.7, 1.8), 7.49 (m, 1H), 7.59 (d, 1H, *J* = 7.8), 7.64 (dd, 1H, *J* = 7.6, 1.7), 7.76 (td, 1H, *J* = 5.9, *J* = 1.5). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 25.71, 27.33, 27.33, 27.74, 29.70, 30.65, 79.29, 79.69, 112.11, 119.06, 121.93, 124.08, 124.88, 126.97, 127.12, 127.40, 127.68, 130.26, 133.77, 134.10, 134.49, 141.19, 141.63, 143.53, 145.67. **MS** (EI, 70 eV): *m/z* (%) 357 [M+H], (11), 356 [M], (57), 298 [(M-$(CH_3)_2CO$]. **IR** ($CHCl_3$): ν 3019, 2929, 2855, 1718, 1632, 1522, 1480, 1418, 1376, 1262, 1216, 1088, 1059, 1028, 758. **MS** (EI, 70 eV) (intensity): calc'd for

($C_{25}H_{24}O_2^+$) 356.2; found: 356.3 (56) $[M]^+$, 297.8 (100) $[M-(CH_3)_2CO]^+$, 282.4 (8) $[M-(CH_3)_2CO_2]^+$, 270.4 (21), 252.2 (36), 239.2 (58).

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