# Palladium-Catalyzed Cascade Oligocyclizations Involving Competing Elementary Steps Such as Thermal [1,5]-Acyl Shifts

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Palladium(Pd)-catalyzed oligocyclizations of 2-bromotetradec-1-ene-7,13-diynes with an unsubstituted terminal acetylene moiety like **3** and **5** and 15-bromohexadec-15-ene-3,9-diyn-2-ones like **4** and **6** afforded fulvene derivatives **20** and **21** (*Scheme 7*) and bis(cyclohexane)-annulated methylenecyclopentene systems **16** and **18** (*Schemes 5* and *6*), respectively. These transformations constitute cascades of cyclizing carbopalladation steps with ensuing [1,5]-sigmatropic H-atom and acyl shifts, respectively (*Scheme 8*). In contrast, analogous substrates with one three-atom and one four-atom tether between the unsaturated C,C-bonds, such as **1** and **2**, behave differently in that the Pd-substituted hexa-1,3,5-triene intermediates **12** undergo a 6$\pi$-electrocyclization instead of a 5-*exo-trig* carbopalladation followed by $\beta$-hydride elimination to furnish tricyclic bis-annulated benzene derivatives **13** and **14** (*Scheme 4*).

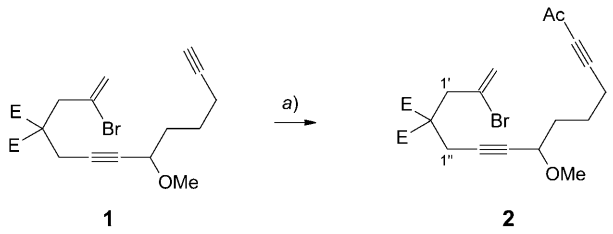
**Introduction.** – Thermal [1,5]-sigmatropic H-atom migrations are well documented in the literature as concerted processes. However, thermal [1] and photochemical (see, *e.g.*, [2]) [1,5]-acyl migrations have rarely been described. In a study involving appropriately substituted indenes, the thermal [1,5]-migratory aptitude of different groups was found to decrease in the following order: HCO > Bz ≈ Ac > H > vinyl > CONHMe > $CO_2$Ph > $CO_2$Me > CN ≈ C≡C > alkyl [3]. Accordingly, an H-atom or an Ac group are considered to have a relatively good tendency towards migration in a thermal [1,5]-sigmatropic rearrangement.

As we previously reported [4], the results of the Pd-catalyzed intramolecular oligocyclization of various 2-bromoalk-1-ene-7,13-diyne substrates initially leading to the formation of two six-membered rings, are highly affected by the lengths of the tethers between each two multiple bonds and the nature of the substituent at the acetylene terminus. As some of these oligocyclizations are followed by the formation of a bis-annulated cyclopentadiene system, [1,5]-sigmatropic rearrangements might become feasible subsequent processes for substrates bearing a terminal group with a high migratory aptitude such as an Ac group or an H-atom. Such bromoalkenediynes would, therefore, lead to yet another type of product, and we here report on the results of a corresponding investigation.

**Results and Discussion.** – The substrates used in this study were prepared following the same synthetic routes described earlier for the synthesis of 2-bromotridec-1-ene-

6,12-diynes and 2-bromotetradec-1-ene-7,13-diyne derivatives [4]. Thus, a substrate with one three-atom and one four-atom tether between the 2-bromoene and the central C≡C bond and between the latter and the terminal C≡C bond, respectively, was obtained from **1** [4] by installing the Ac group at the acetylene terminus by deprotonation with BuLi at −78° and treatment of the resulting lithium acetylide with $Ac_2O$ to furnish diethyl 2-(2-bromoprop-2-en-1-yl)-2-(4-methoxy-10-oxoundeca-2,8-diyn-1-yl)propanedioate (**2**) in 68% yield (*Scheme 1*).

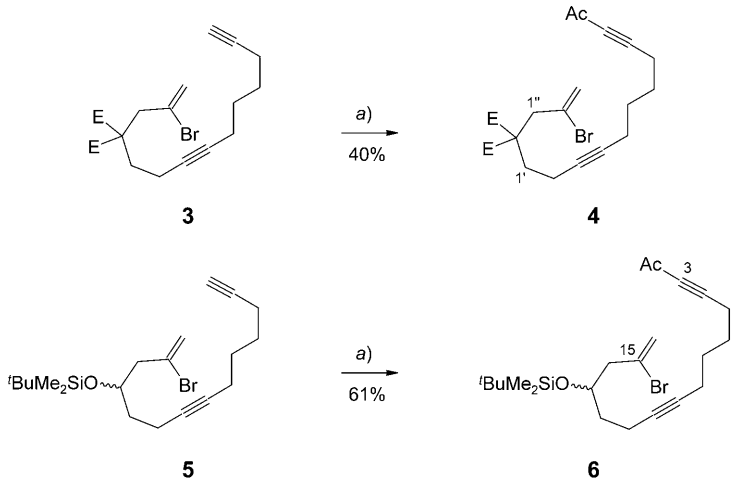
Scheme 1. *Synthesis of Diethyl 2-(2-Bromoprop-2-en-1-yl)-2-(4-methoxy-10-oxoundeca-2,8-diyn-1-yl)-propanedioate* (**2**) *with a Three- and a Four-Atom Tether between the Three C,C-Multiple Bonds.* E = $CO_2Et$.




*a*) BuLi, −78°, THF, $Ac_2O$; 68%.

The synthesis of substrates analogous to **1** and **2**, but with two four-atom tethers, was accomplished as shown in *Scheme 2*. The Ac group was installed at the acetylene terminus of dimethyl 2-(2-bromoprop-2-en-1-yl)-2-(deca-3,9-diyn-1-yl)propanedioate (**3**) by deprotonation with lithium diisopropylamide (LDA) at −78° and treatment of the resulting acetylide with $Ac_2O$ to furnish the desired substrate **4** in 40% yield. Analogously, installation of the Ac group at the terminal acetylene moiety of **5** [4] as described for **4** gave the desired substrate **6** in 61% yield.

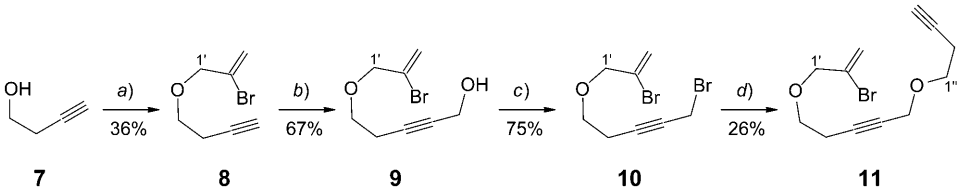
Scheme 2. *Synthesis of 15-Bromohexadec-15-ene-3,9-diyn-2-one Derivatives* **4** *and* **6**. E = $CO_2Me$.




*a*) LDA, $Ac_2O$, THF, −78°, 1 h, r.t., 2 h.

A further substrate analogous to **3** and **5** with two four-atom tethers each containing an O-atom was prepared by deprotonating the OH group of but-3-yn-1-ol (**7**) in $CH_2Cl_2$ with NaOH in the presence of cetyltrimethylammonium bromide (CETAB) [5] and allylating the resulting sodium but-3-yn-1-olate with 2,3-dibromoprop-1-ene to furnish 4-[(2-bromoprop-2-en-1-yl)oxy]but-1-yne (**8**) in 36% yield. The acetylene terminus of **8** was deprotonated at $-78°$ with BuLi, and the resulting lithium acetylide was treated with paraformaldehyde to yield (67%) 5-[(2-bromoprop-2-en-1-yl)oxy]pent-2-yn-1-ol (**9**). The formal propargyl alcohol **9** was converted in 78% yield into the corresponding propargyl bromide **10** by treatment in $CH_2Cl_2$ at 0° with $Ph_3P/Br_2$ in the presence of pyridine. A further *Williamson* etherification conducted by treating **10** with sodium but-3-yn-1-olate, generated by deprotonating but-3-yn-1-ol with NaH, afforded the desired 5-[(2-bromoprop-2-en-1-yl)oxy]-1-(but-3-yn-1-yloxy)pent-2-yne (**11**) in 26% yield (*Scheme 3*).

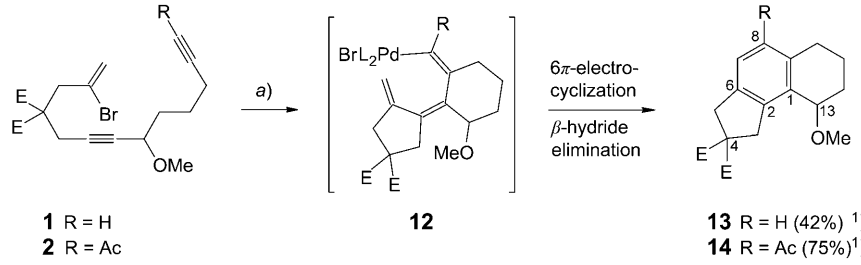
Scheme 3. *Synthesis of 5-[(2-Bromoprop-2-en-1-yl)oxy]-1-(but-3-yn-1-yloxy)pent-2-yne* (**11**) *with Two Four-Atom Tethers each Containing an O-Atom*




*a*) NaOH (50%), CETAB (5 mol-%), $CH_2Cl_2$, 2,3-dibromoprop-1-ene, r.t., 3 h. *b*) 1) BuLi, $-78°$, THF, 30 min; 2) paraformaldehyde, $-78° \rightarrow$ r.t., 12 h. *c*) $Ph_3P$, $Br_2$, pyridine, $CH_2Cl_2$, $-10 \rightarrow 0°$, 2 h. *d*) 1) NaH, **7**, THF, r.t., 1 h; 2) **10**, r.t., 1 d.

Treatment of **1** and **2** in MeCN at 120° with $[Pd(AcO)_2]$ (5 mol-%), $Ph_3P$ (20 mol-%), and $K_2CO_3$ (2 equiv.) afforded the tricyclic systems **13**[1]) and **14**[1]), each with a bis-fused benzene ring in 42 and 75% yield, respectively (for a preliminary communication of these results, see [6]) (*Scheme 4*).

Scheme 4. *Pd-Catalyzed Tricyclization of 2-(2-Bromoprop-2-en-1-yl)-2-(4-methoxynona-2,8-diyn-1-yl)-propanedioate* **1** *and 2-(2-Bromoprop-2-en-1-yl)-2-(4-methoxy-10-oxoundeca-2,8-diyn-1-yl)propane-dioate* **2** *Containing one Three- and one Four-Atom Tether.* E = $CO_2Et$.

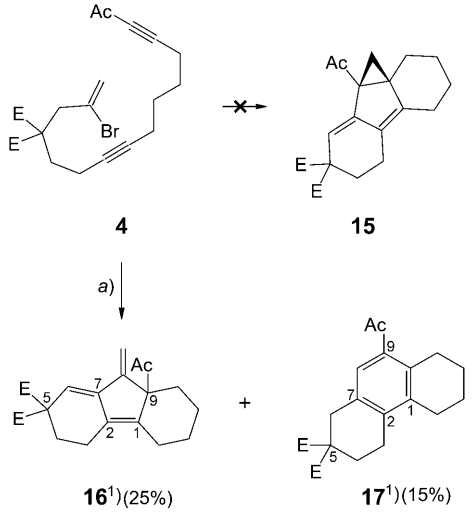



*a*) $[Pd(AcO)_2]$ (5 mol-%), $Ph_3P$ (20 mol-%), $K_2CO_3$ (2 equiv.), MeCN, 120°, 2 h.

[1]) Trivial atom numbering; for systematic names, see *Exper. Part.*

As was previously reported [4], the Pd-catalyzed oligocyclizations of 2-bromotetradec-1-ene-7,13-diynes like **4** with two four-atom tethers between each pair of multiple bonds, but bearing an electron-withdrawing COOMe group at the acetylene terminus, led to tetracyclic systems of type **15**. In contrast, the bromoalkenediyne **4** with a terminal Ac group, upon treatment with a Pd precatalyst typically employed for *Heck* reactions, unexpectedly, furnished the tricyclic compounds **16** and **17** in 25 and 15% yield, respectively, and none of the tetracycle **15**, despite the electron-withdrawing nature of the Ac group (*Scheme 5*).

Scheme 5. *Pd-Catalyzed Oligocyclization of a 2-Bromotetradec-1-ene-7,13-diyne Derivative Bearing an Ac Group at the Acetylene Terminus.* E = $CO_2$Me.




*a*) [Pd(AcO)$_2$] (10 mol-%), $Ph_3P$ (25 mol-%), $K_2CO_3$ (3 equiv.), MeCN, 60°, 12 h.

The structure of **16** was unequivocally established by 1D- and 2D-NMR measurements. An $^1$H,$^1$H-NOESY plot confirmed the position of the C=C bond in one of the two six-membered rings of **16** (*Figure*, *a*), while the position of the newly formed quaternary center was corroborated by the strong coupling between this C-atom and the H-atoms of the exocyclic methylene group as well as the Ac group in the HMBC spectrum (*Figure*, *b*).

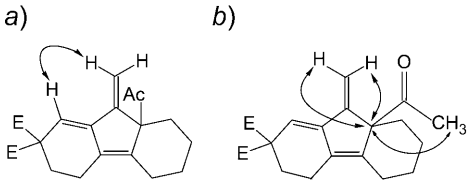
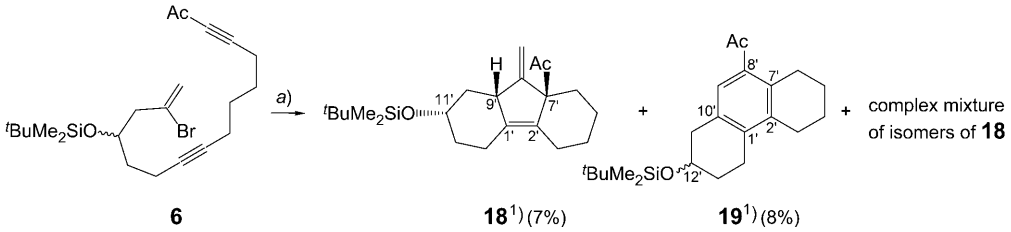



Figure. a) *Key $^1$H,$^1$H-NOESY correlation and* b) *Key HMBCs of compound* **16**

The terminally Ac-substituted 2-bromotetradec-1-ene-7,13-diyne **6** with a [(*tert*-butyl)dimethylsilyl]oxy group instead of the *geminal* bis(methoxycarbonyl) substitu-

tion in the first tether gave, upon treatment with a Pd precatalyst mixture containing $HCO_2Na$, the bis(cyclohexane)-annulated 4-methylenecyclopentene derivative **18** resulting from a tricyclization with [1,5]-Ac migration and eventual hydride capture [7], in poor yield (7%). In addition to **18**, the bis(cyclohexane)-annulated benzene derivative **19** (8% yield) and a complex mixture of inseparable products was obtained (*Scheme 6*).

Scheme 6. *Pd-Catalyzed Oligocyclization of a 14-Acetyl-2-bromotetradec-1-ene-7,13-diyne Derivative without an Incorporated Propanedioate Moiety*



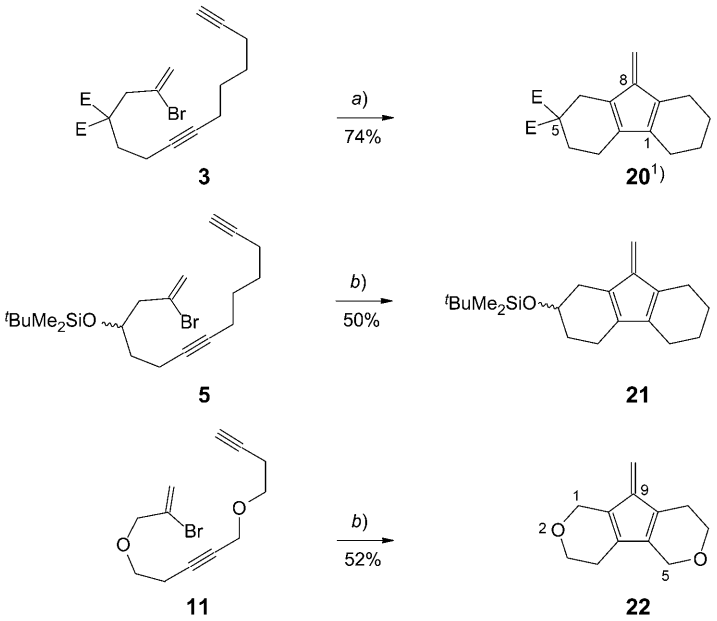

**6** **18**[1] (7%) **19**[1] (8%)

*a*) [Pd(AcO)$_2$] (10 mol-%), $Ph_3P$ (25 mol-%), $HCO_2Na$ (1.5 equiv.), DMF, 80°, 5 h.

As was previously reported in a preliminary communication [8], the 2-bromotetradec-1-ene-7,13-diyne derivative **3** with an unsubstituted terminal C≡C bond underwent, under typical *Heck* reaction conditions, tricyclization to yield the bis(cyclohexane)-annulated fulvene **20** (74%). The analogous bromoalkenediynes **5** and **11** with a [(*tert*-butyl)dimethylsilyl]oxy group at one of the all-C-atom tethers and an O-atom in each of the four-atom tethers, respectively, instead of the geminal bis(methoxycarbonyl) substitution, also gave, upon treatment with a Pd precatalyst system containing $HCO_2Na$, the corresponding bis-annulated fulvenes **21** and **22** in 50 and 52% yield, respectively (*Scheme 7*).

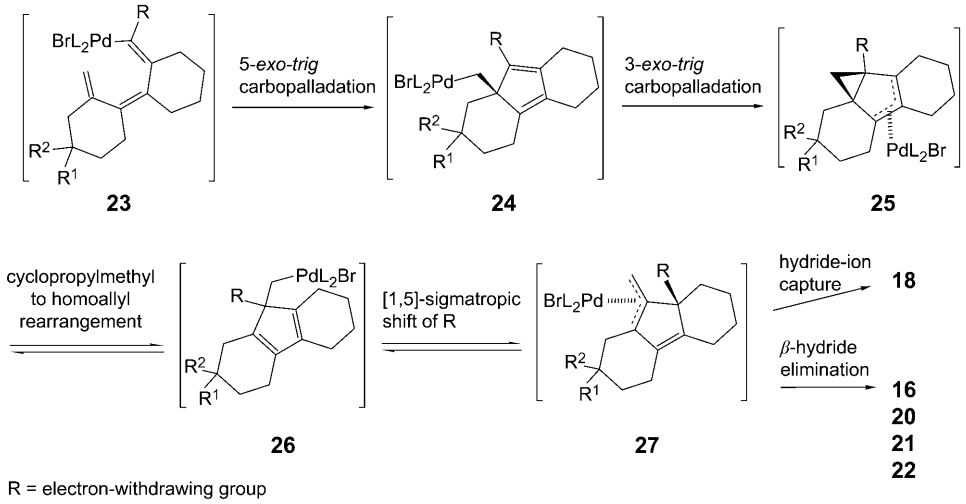
As was previously reported [4], 2-bromoalkenediyne substrates containing at least one three-atom tether leading to a five-membered ring will undergo, after the oxidative addition step, two consecutive 5-*exo-dig* and *n*-*exo-dig* carbopalladations followed by 6$\pi$-electrocyclization and $\beta$-hydride elimination to furnish tricyclic bis-annulated benzene derivatives such as **13** and **14** (*Scheme 4*). On the other hand, substrates having tethers longer than three atoms will undergo Pd-catalyzed oligocyclization cascades in which 5-*exo-trig* carbopalladations instead of 6$\pi$-electrocyclizations take part as the fourth step. Accordingly, all these transformations leading to **16**, **18**, **20**, **21**, and **22** can be rationalized assuming a [1,5]-sigmatropic shift as the last but one step in the cascade reactions (*Scheme 8*). Thus, the 2-bromotetradec-1-ene-7,13-diynes with two four-atom tethers between the multiple bonds undergo two 6-*exo-dig Heck*-type carbopalladations (→**23**) followed by a 5-*exo-trig* carbopalladation to produce the 'neopentyl'-type $\sigma$-alkylpalladium intermediate **24**. The succeeding sequence of events is determined by the nature of the substituent at the terminal C≡C bond. Initially, **24** undergoes another cyclization by 3-*exo-trig* carbopalladation to give **25** and ensuing cyclopropylmethyl- to homoallylpalladium rearrangement to yield the (cyclopentadienylmethyl)palladium intermediate **26** isomeric to **24**. At this stage, the high propensity of an Ac group and a H-atom to undergo a [1,5]-sigmatropic shift to furnish **27** apparently overcomes the possibility for a further *3-exo-trig* carbopalladation and the immediately ensuing $\beta$-

Scheme 7. *Pd-Catalyzed Oligocyclizations of 2-Bromotetradec-1-ene-7,13-diyne Derivatives with an Unsubstituted Acetylene Terminus.* E = $CO_2Me$.




*a*) [$Pd(AcO)_2$] (10 mol-%), $Ph_3P$ (25 mol-%), $K_2CO_3$ (3 equiv.), MeCN, 60°, 1 h. *b*) [$Pd(AcO)_2$] (10 mol-%), $Ph_3P$ (25 mol-%), $HCO_2Na$ (1.5 equiv.), DMF, 80°, 5 h.

Scheme 8. *Mechanistic Rationalization of the Formation of Compounds* **16**, **20**, **21**, **22**, *and* **18**. R = H, Ac.




hydride elimination, respectively. After the [1,5]-sigmatropic shift, the resulting intermediates from **4**, **3**, **5**, and **11** furnish **16**, **20**, **21**, and **22**, respectively, by $\beta$-hydride

elimination, whereas hydride-ion capture of the intermediate of type **27** arising from **6** yields the dihydrofulvene **18**.

The bis-cyclohexane-annulated benzene derivatives **17** and **19** are formed by cyclopropylmethyl- to homoallylpalladium rearrangement with cleavage of the inner cyclopropyl bond in the intermediates of type **25** and subsequent $\beta$-dehydropalladation [4].

**Conclusions.** – The newly discovered oligocyclization mode of 2-bromotetradec-1-ene-7,13-diynes involving a [1,5]-sigmatropic rearrangement that can be provoked by a terminal substituent with a good migratory aptitude enhances the versatility of such cascade transformations leading to various tri-, tetra-, and even higher oligocyclic systems in single-pot operations (for reviews, see [9]).

Mechanistically, the formation of bis-annulated fulvenes described here proceeds differently from the previously reported Pd-catalyzed inter-intramolecular cocyclization of a 1,6-diyne with $\beta$-bromostyrene [10] and all-intermolecular cocyclization of (*Z*)-$\beta$-bromostyrene with two molecules of diphenylacetylene [11].

This work was supported by the Land Niedersachsen, the *Fonds der Chemischen Industrie* as well as *Chemetall GmbH* (chemicals). The authors are grateful to *Daniel Frank*, Göttingen, for technical assistance in preparing the final version of this manuscript.

## Experimental Part

*General.* All operations were performed under $N_2$ or Ar. Solvents were purified and dried according to conventional methods; DMF = dimethylformamide; petroleum ether of boiling range 40–50°. Prep. TLC: 20 × 20 cm glass plates coated with *Merck* silica gel ($SiO_2$) *$PF_{254}$* containing $CaSO_4$. TLC: *Macherey-Nagel Alugram G/$UV_{254}$* 0.25 mm aluminum foil coated with $SiO_2$ containing a fluorescent indicator; developer: 10% molybdenumphosphoric acid soln. in EtOH. Column chromatography (CC): *Merck* $SiO_2$ *60* (0.063–0.200 mm). IR Spectra: *Bruker-FT-IR* spectrometer *IFS 66*; $\tilde{\nu}$ in $cm^{-1}$. $^1$H- and $^{13}$C-NMR Spectra: *Bruker-AM-250* (250 and 62.5 MHz, resp.), *Varian-Inova-500* (500 and 125.7 MHz, resp.), and *Varian-Inova-600* (600 and 150.8 MHz, resp.) instruments at r.t. in $CDCl_3$ or $C_6D_6$; $\delta$ in ppm rel. to $Me_4Si$ ($^1$H) or $CDCl_3$ ($^{13}$C) as internal standard ($\delta(CDCl_3)$ 77.0), *J* in Hz; ambiguous assignments are marked with an asterisk (*); multiplicities of $^{13}$C-NMR signals by either DEPT (distortionless enhancement by polarization transfer) or APT (attached-proton test) and are designated as follows: Me or CH, (+) (DEPT and APT); $CH_2$, (−) (DEPT and APT); quaternary C, (−) (APT) or ($C_q$) (DEPT). MS: *Finnigan MAT CH 7*, *MAT 731* with electron-impact ionization (ET) at 70 eV or direct chemical ionization (DCI) with $NH_3$ as reactant gas; in *m/z* (rel. %). HR-MS: *Finnigan MAT 311*, *INCOS 50* with *Varian 34000* (GC/MS) by using preselected ion-peak matching at $R \approx 10000$ to be within ±2 ppm.

*Diethyl 2-(2-Bromoprop-2-en-1-yl)-2-(4-methoxy-10-oxoundeca-2,8-diyn-1-yl)propanedioate* (**2**). To a soln. of **1** [4] (1.00 g, 2.3 mmol) in THF (20 ml), kept at −78°, was added dropwise 2.4M BuLi in hexane (1.1 ml, 2.6 mmol), and stirring was continued for 30 min. After adding $Ac_2O$ (1.1 g, 10.9 mmol), the mixture was allowed to warm to r.t. After stirring for an additional 2 h, the mixture was added to $H_2O$ (50 ml) and extracted with $Et_2O$ (3 × 50 ml). The combined org. layers were washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by CC (flash $SiO_2$ (40 g), column 2.5 × 20 cm, petroleum ether/$Et_2O$ 8:1); 0.75 g (68%) of **2**. Colorless oil. $R_f$ (petroleum ether/$Et_2O$ 2:1) 0.30. IR (film): 2950, 2220 (C≡C), 1750 (C=O), 1680 (C=C), 1440, 1365, 1295, 1230, 1200, 1110, 910, 860. $^1$H-NMR (250 MHz, $CDCl_3$): 1.13 (*t*, *J* = 7.2, 2 *Me*$CH_2$O); 1.47–1.76 (*m*, 2 H–C(5″), 2 H–C(6″)); 2.17 (*s*, Me(11″)); 2.26 (*t*, *J* = 6.2, 2 H–C(7″)); 2.82 (*d*, *J* = 1.5, 2 H–C(1″)); 3.12 (*s*, 2 H–C(1′)); 3.20 (*s*, MeO); 3.80 (br. *s*, H–C(4″)); 4.04–4.12 (*m*, 2 MeC*$H_2$*O); 5.47 (*d*, *J* = 1.3, 1 H–C(3′)); 5.65 (br. *s*, 1 H–C(3′)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$, DEPT): 13.6 (+, *Me*$CH_2$O); 18.3 (−, C(7″)); 22.2 (−, C(1″));

23.2 (–, C(6″)); 32.3 (+, C(11″)); 34.4 (–, C(5″)); 42.5 (–, C(1′)); 55.9 ($C_q$, C(2)); 56.0 (+, MeO); 61.6 (–, Me*C*$H_2$O); 70.2 (+, C(4″)); 80.7 ($C_q$, C(2″)); 81.3 ($C_q$, C(3″)); 82.0 ($C_q$, C(9″)); 92.7 ($C_q$, C(8″)); 122.0 (–, C(3′)); 126.3 ($C_q$, C(2′)); 168.6 ($C_q$, *C*$O_2$Et); C(10″) could not be detected. EI-MS (70 eV): 469 (2), 95 (2), 88 (14), 82 (4), 59 (10).

*Dimethyl 2-(2-Bromoprop-2-en-1-yl)-2-(11-oxododeca-3,9-diyn-1-yl)propanedioate* (**4**). A soln. of LDA (16.8 mmol) in anh. THF (30 ml) (prepared by dropwise addition, at –78°, of $^i$Pr$_2$NH (1.7 g, 16.8 mmol) to a soln. of 2.30M BuLi in hexane (7.8 ml, 17.9 mmol) in THF (30 ml) and stirring for 30 min) was added dropwise, at –78°, to a soln. of dimethyl 2-(2-bromoprop-2-en-1-yl)-2-(deca-3,9-diyn-1-yl)propanedioate (**3**) [4] (6.0 g, 15.7 mmol) in THF (30 ml). After stirring for 30 min, *N*,*N*,*N*′,*N*′,*N*″,*N*″-hexamethylphosphoric triamide (HMPA; 2.74 ml, 15.1 mmol) and $Ac_2O$ (14.8 ml, 157 mmol) were added, and stirring was continued at –78° for 1 h, and at r.t. for 2 h. The reaction was then quenched by addition of a sat. $NH_4Cl$ soln. (50 ml), and the mixture was extracted with $Et_2O$ (4 × 50 ml). The combined org. layers were dried ($MgSO_4$) and concentrated. The residue was purified by CC ($SiO_2$ (100 g), column 2.5 × 80 cm, pentane/$Et_2O$ 8:1 until the starting materials were removed, then pentane/$Et_2O$ 6:1 and finally pentane/$Et_2O$ 4:1): 2.6 g (40%) of **4**. Colorless oil. $R_f$ (pentane/$Et_2O$ 4:1) 0.36. IR (film): 3003, 2953, 2841, 2211, 1725, 1677, 1625, 1434, 1360, 1276, 1247, 1178, 1152, 1082, 902, 738, 559. $^1$H-NMR (250 MHz, $CDCl_3$): 1.54–1.69 (*m*, 2 H–C(6′), 2 H–C(7′)); 2.08–2.25 (*m*, 2 H–C(2′), 2 H–C(5′), 2 H–C(8′)); 2.31 (*s*, MeCO); 2.37 (*t*, *J* = 6.82, 2 H–C(1′)); 3.16 (*d*, *J* = 0.70, 2 H–C(1″)); 3.73 (*s*, $CO_2$Me), 5.58 (*d*, *J* = 1.80, 1 H–C(3″)); 5.67 (*d*, *J* = 1.73, 1 H–C(3″)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$, DEPT): 14.3 (–, C(8′)); 18.2 (–, C(2′)*); 18.5 (–, C(5′)*); 26.7 (–, C(6′)); 27.8 (–, C(7′)); 31.1 (–, C(1′)); 32.8 (+, *Me*CO); 43.2 (–, C(1″)); 52.6 (+, $CO_2$*Me*); 56.5 ($C_q$, C(2)); 78.9 ($C_q$, C(10′)); 80.1 ($C_q$, C(3′)); 81.5 ($C_q$, C(4′)); 93.5 ($C_q$, C(9′)); 122.1 (–, C(3″)); 126.8 ($C_q$, C(2″)); 170.5 ($C_q$, *C*$O_2$Me); 184.9 ($C_q$, Me*C*O). DCI-MS ($NH_3$): 868 (0.1, $[2M + NH_4]^+$), 442 and 444 (93 and 100, $[M - H + NH_4]^+$), 364 (52, $[M - Br + NH_4]^+$), 324 (36, $[M - 2CO_2Me + NH_4]^+$), 282 (12).

*15-Bromo-13-{[(1,1-dimethylethyl)dimethylsilyl]oxy}hexadec-15-ene-3,9-diyn-2-one* (**6**). As described for **4**, with LDA (7.0 mmol) in anh. THF (20 ml) (from $^i$Pr$_2$NH (0.7 g, 7.0 mmol) and 2.0M BuLi in hexane (3.5 ml, 7.0 mmol) in THF (20 ml)), 2-bromo-4-{[(1,1-dimethylethyl)dimethylsilyl]-oxy}tetradec-1-ene-7,13-diyne (**5**) [4] (2.5 g, 6.3 mmol) in THF (20 ml), HMPA (1.1 ml, 6.0 mmol), and $Ac_2O$ (6.0 ml, 63 mmol). CC ($SiO_2$ (100 g), column 2.5 × 80 cm, pentane/$Et_2O$ 20:1) afforded 1.7 (61%) of **6**. Colorless oil. $R_f$ (pentane/$Et_2O$ 20:1) 0.20. IR (film): 3336, 2956, 2856, 2211, 1678, 1631, 1471, 1433, 1358, 1227, 1077, 1004, 837, 776, 661. $^1$H-NMR (250 MHz, $CDCl_3$): 0.086 (*s*, 3 H of $Me_2$Si); 0.87 (*s*, $Me_3$C); 0.091 (*s*, 3 H of $Me_2$Si); 1.52–1.75 (*m*, 2 H–C(6), 2 H–C(7), 2 H–C(12)); 2.18–2.24 (*m*, 2 H–C(8), 2 H–C(11)); 2.31 (*s*, MeCO); 2.37 (*t*, *J* = 6.80, 2 H–C(5)); 2.51 (*d*, *J* = 6.90, 1 H–C(14)); 2.55 (*d*, *J* = 6.90, 1 H–C(14)); 4.02–4.12 (*m*, 1 H–C(13)); 5.43 (*d*, *J* = 1.50, 1 H–C(16)); 5.60 (br. *s*, 1 H–C(16)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$, DEPT): –4.6 (+, $Me_2$Si); –4.4 (+, $Me_2$Si); 14.7 (–, C(5)); 18.0 ($C_q$, $Me_3$*C*); 18.2 (–, C(11)*); 18.5 (–, C(8)*); 25.8 (+, *Me*$_3$C); 26.7 (–, C(7)**); 28.0 (–, C(6)**); 32.7 (+, *Me*CO); 35.7 (–, C(12)); 49.3 (–, C(14)); 68.8 (+, C(13)); 79.6 ($C_q$, C(4)); 80.2 ($C_q$, C(10)); 81.5 ($C_q$, C(9)); 93.5 ($C_q$, C(3)); 119.2 (–, C(16)); 130.8 ($C_q$, C(15)); 210.1 ($C_q$, Me*C*O). DCI-MS ($NH_3$): 896 (0.1, $[2M + NH_4]^+$), 458 and 456 (100 and 96, $[M - H + NH_4]^+$), 441 and 439 (20 and 19, $M^+$), 378 (35, $[M - Br + NH_4]^+$), 319 (15).

*4-[(2-Bromoprop-2-en-1-yl)oxy]but-1-yne* (**8**). But-3-yn-1-ol (**7**; 0.70 g, 10.0 mmol), cetyltrimethylammonium bromide (CETAB; 182 mg, 0.5 mmol), and 2,3-dibromoprop-1-ene (1.90 g, 9.50 mmol) were dissolved at r.t. in a mixture of $CH_2Cl_2$ (12 ml) and 50% aq. NaOH soln. (12 ml). After stirring for 3 h, $H_2O$ (20 ml) was added to the mixture, and it was extracted with $Et_2O$ (2 × 30 ml). The combined org. layer was concentrated and the residue purified by CC ($SiO_2$ (40 g), column 5 × 10 cm, pentane/$Et_2O$ 10:1): 0.65 g (36%) of **8**. Colorless liquid. $R_f$ (pentane/$Et_2O$ 10:1) 0.70. IR (film): 3289 (C≡C–H), 2871, 1640, 1106, 901, 668. $^1$H-NMR (250 MHz, $CDCl_3$): 2.00 (*t*, *J* = 2.6, 1 H–C(1)); 2.50 (*dt*, *J* = 6.8, 2.6, 2 H–C(3)); 3.61 (*t*, *J* = 6.8, 2 H–C(4)); 4.19 (*s*, 2 H–C(1′)); 5.62 (*s*, 1 H–C(3′)); 5.97 (*s*, 1 H–C(3′)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$, DEPT): 19.8 (–, C(3)); 68.3 (–, $CH_2O$)); 69.5 ($C_q$, C(2)); 74.9 (–, $CH_2O$)); 80.9 (+, C(1)); 117.6 (–, C(3′)); 129.1 ($C_q$, C(2′)). DCI-MS ($NH_3$): 208 and 206 (100 and 100, $[M + NH_4]^+$).

*5-[(2-Bromoprop-2-en-1-yl)oxy]pent-2-yn-1-ol* (**9**). To a soln. of **8** (1.89 g, 10 mmol) in anh. THF (50 ml) was added dropwise, at –78°, 2.36M BuLi in hexane (4.9 ml, 11.6 mmol). After stirring at –78°

for 30 min, paraformaldehyde (0.63 g, 21.0 mmol) was added to the resulting soln. The mixture was allowed to warm to r.t., and stirring was continued for an additional 12 h. The mixture was then diluted with $H_2O$ (50 ml) and extracted with $Et_2O$ (3 × 40 ml). The combined org. layer was dried ($MgSO_4$) and concentrated and the residue purified by CC ($SiO_2$ (40 g), column 5 × 10 cm, pentane/$Et_2O$ 3:1): 1.47 g (67%) of **9**. Colorless liquid. $R_f$ (pentane/$Et_2O$ 3:1) 0.15. IR (film): 3388 (OH, C≡C–H), 2915, 2868, 1640, 1419, 1102, 1018. $^1$H-NMR (250 MHz, $CDCl_3$): 1.77 (br. *s*, OH); 2.50–2.57 (*m*, 2 H–C(4)); 3.59 (*t*, *J* = 6.7, 2 H–C(5)); 4.13 (*s*, 1 $CH_2O$)); 4.25 (br. *s*, 1 $CH_2O$)); 5.63 (*s*, 1 H–C(3′)); 5.94 (*s*, 1 H–C(3′)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$, DEPT): 20.1 (–, C(4)); 51.3 (–, $CH_2O$); 68.3 (–, $CH_2O$); 74.9 (–, $CH_2O$); 79.6 ($C_q$, C(2)*); 82.8 ($C_q$, C(3)*); 117.8 (–, C(3′)); 129.2 ($C_q$, C(2′)). DCI-MS ($NH_3$): 458, 456, and 454 (5, 7, and 5, $[2M + NH_4]^+$), 238 and 236 (96 and 100, $[M + NH_4]^+$).

*1-Bromo-5-[(2-bromoprop-2-en-1-yl)oxy]pent-2-yne* (**10**). To a soln. of $Ph_3P$ (1.26 g, 4.8 mmol) in $CH_2Cl_2$ (30 ml) was added dropwise, at −10°, $Br_2$ (0.25 ml, 4.9 mmol). After stirring at −10° for 40 min, **9** (1.01 g, 4.6 mmol) and pyridine (0.38 ml, 4.7 mmol) were added to the colorless suspension of the $Ph_3P \cdot Br_2$ complex, and stirring was continued at 0° for 2 h. $CH_2Cl_2$ was then evaporated and the resulting residue purified by CC ($SiO_2$ (45 g), column 3 × 15 cm, petroleum ether/$Et_2O$ 10:1): 0.97 g (75%) of **10**. Colorless liquid. $R_f$ (petroleum ether/$Et_2O$ 10:1) 0.71. IR (film): 2869, 2237 (C≡C), 1640, 1425, 1411, 1104, 902. $^1$H-NMR (250 MHz, $CDCl_3$): 2.56 (*tt*, *J* = 6.8, 2.3, 2 H–C(4)); 3.59 (*t*, *J* = 6.8, 2 H–C(5)); 3.91 (*t*, *J* = 2.3, 2 H–C(1)); 4.13 (*s*, 2 H–C(1′)); 5.61–5.63 (*m*, 1 H–C(3′)); 5.94–5.96 (*m*, 1 H–C(3′)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$, DEPT): 15.2 (–, C(1)); 20.4 (–, C(4)); 68.1 (–, $CH_2O$); 74.9 (–, $CH_2O$); 76.5 ($C_q$, C(2)*); 84.3 ($C_q$, C(3)*); 117.7 (–, C(3′)); 129.1 ($C_q$, C(2′)). DCI-MS ($NH_3$): 586, 584, 582, 580, and 578 (5, 18, 24, 18, and 5, $[2M + NH_4]^+$), 302, 300, and 298 (43, 100, and 46, $[M + NH_4]^+$).

*5-[(2-Bromoprop-2-en-1-yl)oxy]-1-(but-3-yn-1-yloxy)pent-2-yne* (**11**). But-3-yn-1-ol (0.23 g, 3.3 mmol) was added dropwise at r.t. to a 55% suspension of NaH in mineral oil (0.14 g, 3.2 mmol) in THF (15 ml). After stirring at r.t. for 1 h, **10** (0.88 g, 3.12 mmol) was added, and stirring was continued at r.t. for 1 d. The mixture was then diluted with $H_2O$ (50 ml) and extracted with $Et_2O$ (3 × 30 ml). The combined org. phase was dried ($MgSO_4$) and concentrated and the residue purified by CC ($SiO_2$ (15 g), column 2 × 10 cm, pentane/$Et_2O$ 10:1): 0.22 g (26%) of **11**. Colorless liquid. $R_f$ (pentane/$Et_2O$ 10:1) 0.35. IR (film): 3293 (C≡C–H), 2866, 2236 (C≡C), 2120 (C≡CH), 1640, 1359, 1104, 907, 669. $^1$H-NMR (250 MHz, $CDCl_3$): 1.99 (*t*, *J* = 2.7, H–C(4″)); 2.49 (*dt*, *J* = 2.7, 6.8, 2 H–C(2″)); 2.54 (*tt*, *J* = 2.1, 6.8, 2 H–C(4)); 3.59 (*t*, *J* = 6.8, 2 H–C(1″)*); 3.63 (*t*, *J* = 6.8, 2 H–C(5)*); 4.12 (*s*, 2 H–C(1′)); 4.17 (*t*, *J* = 2.1, 2 H–C(1)); 5.61 (*s*, 1 H–C(3′)); 5.94 (*s*, 1 H–C(3′)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$, DEPT): 19.7 (–, $CH_2$); 20.1 (–, $CH_2$); 58.6 (–, $CH_2O$); 67.7 (–, $CH_2O$); 68.4 (–, $CH_2O$); 69.4 ($C_q$, C(2)*); 74.9 (–, $CH_2O$); 76.9 ($C_q$, C(3)*); 81.6 ($C_q$, C(3″)); 83.5 (+, C(4″)); 117.7 (–, C(3′)); 129.2 ($C_q$, C(2′)). DCI-MS ($NH_3$): 290 and 288 (91 and 87, $[M + NH_4]^+$).

*Pd-Catalyzed Oligocyclizations of 2-Bromoalkenediynes: General Procedure* (*GP*). *Method A:* [$Pd(AcO)_2$] (0.1 equiv.) was added at 60° to a degassed mixture of $Ph_3P$ (0.25 equiv.), $K_2CO_3$ (2.5 equiv.), and the respective 2-bromoalkenediyne (1 equiv.) in MeCN (80 ml) in a *Pyrex*® bottle with a screw cap. After having been stirred at 60° for 1 to 12 h, the mixture was allowed to cool to r.t., filtered over a layer of *Celite*® and charcoal each, and then concentrated. The residue was purified by either CC or TLC.

*Method B:* [$Pd(AcO)_2$] (0.1 equiv.) was added at 80° to a degassed mixture of $Ph_3P$ (0.25 equiv.), $HCO_2Na$ (1.2 equiv.), and the respective 2-bromotetradec-1-enediyne (1 equiv.) in DMF (10 ml) in a *Pyrex*® bottle with a screw cap. After having been stirred at 80° for 1 to 12 h, the mixture was poured into $H_2O$ (30 ml) and extracted with $Et_2O$ (3 × 20 ml). The combined $Et_2O$ layer was dried ($MgSO_4$) and concentrated and the residue purified by either CC or TLC.

*Diethyl 13-Methoxytricyclo[7.4.0.0$^{2,6}$]trideca-1,6,8-triene-4,4-dicarboxylate* (= *Diethyl 1,3,6,7,8,9-Hexahydro-9-methoxy-2*H*-cyclopenta[*a*]naphthalene-2,2-dicarboxylate*; **13**). Following the *GP*, *Method A*, with **1** (400 mg, 0.94 mmol), [$Pd(AcO)_2$] (12 mg, 0.056 mmol, 6 mol-%), $Ph_3P$ (50 mg, 0.20 mmol, 21 mol-%), and $K_2CO_3$ (259 mg, 1.86 mmol, 2 equiv.) in MeCN (10 ml). The mixture was heated at 120° for 2 h, and after workup, the resulting residue was purified by CC (flash $SiO_2$ (8 g), column 1 × 15 cm, petroleum ether/$Et_2O$ 8:1): 136 mg of **13** (42%). Colorless oil. $R_f$ (petroleum ether/$Et_2O$ 2:1) 0.40. IR (film): 2970, 2920, 2850, 1720 (C=O), 1595 (C=C), 1435, 1365, 1250, 1180, 1020, 860. $^1$H-NMR (250 MHz, $CDCl_3$)[1]): 1.24 (*t*, *J* = 7.1, 1 *Me*$CH_2O$); 1.26 (*t*, *J* = 7.1, 1 *Me*$CH_2O$); 1.60–1.95 (*m*, 2 H–C(11),

1 H–C(12)); 2.15–2.25 (*m*, 1 H–C(12)); 2.62 (*ddd*, *J* = 16.4, 10.3, 5.2, 1 H–C(10)); 2.77 (*dt*, *J* = 4.4, 16.5, 1 H–C(10)); 3.44 (*s*, MeO); 3.54–3.60 (*m*, 2 H–C(3), 2 H–C(5)); 4.13–4.25 (*m*, 2 MeC*H*$_2$O); 4.29 (*t*, *J* = 3.7, H–C(13)); 6.91 (*d*, *J* = 7.8, H–C(7)); 7.02 (*d*, *J* = 7.7, H–C(8)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$, DEPT[1]): 13.9 (+, *Me*CH$_2$O)); 18.1 (–, C(11)); 26.4 (–, C(12)); 29.3 (–, C(10)); 38.9 (–, C(3)); 40.2 (–, C(5)); 55.8 (+, MeO)); 60.2 (C$_q$, C(4)); 61.4 (–, Me*C*H$_2$O)); 74.1 (+, C(13)); 123.1 (+, C(7)); 127.9 (+, C(8)); 132.0 (C$_q$, C(2)); 136.0 (C$_q$, C(9)); 137.6 (C$_q$, C(1)); 140.3 (C$_q$, C(6)); 171.4 (C$_q$, *C*O$_2$Et)); 171.8 (C$_q$, *C*O$_2$Et). EI-MS (70 eV): 346 (2, $M^+$), 314 (84), 242 (44), 241 (100), 240 (35), 213 (15), 143 (45), 86 (35), 84 (58), 69 (15). HR-MS: 346.1779 ($M^+$, $C_{20}H_{26}O_5^+$; calc. 346.1780).

*Diethyl 8-Acetyl-13-methoxytricyclo[7.4.0.0$^{2,6}$]trideca-1,6,8-triene-4,4-dicarboxylate* (= *Diethyl 5-Acetyl-1,3,6,7,8,9-hexahydro-9-methoxy-2*H-*cyclopenta[*a*]naphthalene-2,2-dicarboxylate*; **14**). Following the *GP*, *Method A*, with **2** (500 mg, 1.07 mmol) [Pd(AcO)$_2$] (13 mg, 0.060 mmol, 5 mol-%), Ph$_3$P (56 mg, 0.22 mmol, 20 mol-%), and $K_2CO_3$ (294 mg, 2.11 mmol, 2 equiv.) in MeCN (10 ml). The mixture was heated at 120° for 2 h, and after workup, the resulting residue was purified by CC (flash $SiO_2$ (4 g), column 1 × 15 cm, petroleum ether/Et$_2$O 2 :1): 310 mg (75%) of **14**. Colorless oil. $R_f$ (petroleum ether/Et$_2$O 2 :1) 0.16. IR (film): 294, 1750 (C=O), 1690 (C=C), 1450, 1250, 1190, 1095, 910. $^1$H-NMR (250 MHz, $CDCl_3$)[1]): 1.20–1.30 (*m*, 2 *Me*CH$_2$O); 1.60–1.80 (*m*, 2 H–C(11), 1 H–C(12)); 2.10–2.22 (*m*, 1 H–C(12)); 2.46 (*s*, MeCO); 2.75–2.95 (*m*, 1 H–C(10)); 3.40 (*s*, MeO); 3.60–3.70 (*m*, 2 H–C(3), 2 H–C(5)); 4.10–4.30 (*m*, 2 MeC*H*$_2$O); 4.27 (*t*, *J* = 3.4, 1 H–C(13)); 7.38 (br. *s*, 1 H–C(7)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$, DEPT)[1]): 13.8 (+, *Me*CH$_2$O); 17.7 (–, C(11)); 25.5 (–, C(12)); 27.9 (–, C(10)); 29.3 (–, C(3)); 29.8 (+, *Me*CO)); 40.0 (–, C(5)); 55.8 (+, MeO); 60.1 (C$_q$, C(4)); 61.5 (–, Me*C*H$_2$O); 74.2 (+, C(13)); 123.9 (+, C(7)); 133.5 (C$_q$, C(1)); 136.2 (C$_q$, C(6)); 137.4 (C$_q$, C(9)); 144.5 (C$_q$, C(2)); 171.0 (C$_q$, *C*O$_2$Et); 171.4 (C$_q$, *C*O$_2$Et); 201.8 (C$_q$, Me*C*O). EI-MS (70 eV): 388 (13, $M^+$), 357 (14), 356 (54), 310 (5), 283 (73), 241 (18), 213 (13), 195 (10), 167 (17), 121 (13), 86 (88), 84 (100), 43 (45). HR-MS: 388.1887 ($M^+$, $C_{22}H_{28}O_6^+$; calc. 388.1886).

*Oligocyclization of* **4**. Following the *GP*, *Method A*, with **4** (2.3 g, 5.42 mmol), [Pd(AcO)$_2$] (120 mg, 0.55 mmol), Ph$_3$P (350 mg, 1.35 mmol), and $K_2CO_3$ (2.24 g, 16.2 mmol) in MeCN (80 ml). After 12 h, workup and purification by CC ($SiO_2$ (50 g), column 2 × 35 cm, pentane/Et$_2$O 2 :1) gave three fractions, the second of which weighed 430 mg (23%) and consisted of *dimethyl 9-acetyl-8-methylenetricyclo[7.4.0.0$^{2,7}$]trideca-1,6-diene-5,5-dicarboxylate* (= *dimethyl 8a-acetyl-3,4,5,6,7,8,8a,9-octahydro-9-methylene-2*H-*fluorene-2,2-dicarboxylate*; **16**). Gummy, yellowish material. $R_f$ (pentane/Et$_2$O 5 :1) 0.14. IR (film): 2937, 1729, 1703, 1434, 1357, 1263, 1068, 906, 835. $^1$H-NMR (500 MHz, $CDCl_3$)[1]): 1.08 (*dt*, *J* = 13.5, 4, 1 H–C(10)); 1.14 (*dt*, *J* = 13.5, 4, 1 H–C(12)); 1.37 (*tq*, *J* = 13.5, 3, 1 H–C(11)); 1.60–1.65 (*m*, 1 H–C(11)); 1.70–1.80 (*m*, 1 H–C(12), 1 H–C(13)); 1.87 (*s*, MeCO); 2.01–2.11 (*m*, 1 H–C(4)); 2.23–2.29 (*m*, 1 H–C(4)); 2.51–2.60 (*m*, 2 H–C(3), 1 H–C(10), 1 H–C(13)); 3.74 (*s*, 1 CO$_2$Me); 3.75 (*s*, 1 CO$_2$Me); 4.90 (*s*, 1 H of =CH$_2$); 5.50 (*s*, 1 H of =CH$_2$); 6.00 (*s*, H–C(6)). $^{13}$C-NMR (125.707 MHz, $CDCl_3$, APT)[1]): 19.5 (–, C(3)); 23.6 (–, C(11)); 25.7 (–, C(13)); 25.8 (+, *Me*CO); 26.6 (–, C(12)); 28.6 (–, C(4)); 33.5 (–, C(10)); 52.8 (+, CO$_2$*Me*); 52.9 (+, CO$_2$*Me*); 55.1 (–, C(5)); 67.3 (–, C(9)); 107.2 (–, =CH$_2$)); 110.3 (+, C(6)); 132.6 (–, C(2)); 143.2 (–, C(7)*); 143.3 (–, C(1)*); 148.5 (–, C(8)); 171.1 (–, *C*O$_2$Me); 171.4 (–, *C*O$_2$Me); 207.0 (–, Me*C*O). EI-MS (70 eV): 344 (12, $M^+$), 301 (100, [$M$ – MeCO]$^+$), 242 (8, [$M$ – CO$_2$Me – MeCO]$^+$), 241 (32, [$M$ – H – CO$_2$Me – MeCO]$^+$), 209 (6), 183 (4), 155 (6), 43 (0.7, $C_2H_3O^+$). HR-MS: 344.1624 ($M^+$, $C_{20}H_{24}O_5^+$; calc. 344.1624).

The third fraction weighed 213 mg (11%) and consisted of *dimethyl 9-acetyltricyclo[8.4.0.0$^{2,7}$]tetradeca-1,7,9-triene-5,5-dicarboxylate* (= *dimethyl 9-acetyl-3,4,5,6,7,8-hexahydrophenanthrene-2,2(1*H*)-dicarboxylate*; **17**) as a colorless solid. M.p. 152°. $R_f$ (pentane/Et$_2$O, 5 :1) 0.08. IR (KBr): 2956, 1752, 1731, 1677, 1433, 1278, 1079. $^1$H-NMR (500 MHz, $CDCl_3$)[1]): 1.56–1.69 (*m*, 2 H–C(12)); 1.71–1.82 (*m*, 2 H–C(13)); 2.34 (*t*, *J* = 6, 2 H–C(4)); 2.53 (*s*, MeCO); 2.56 (*t*, *J* = 6.2, 2 H–C(14)); 2.60 (*t*, *J* = 6.5, 2 H–C(3)); 2.95 (*t*, *J* = 6, 2 H–C(11)); 3.28 (*s*, 2 H–C(6)); 3.72 (*s*, 6 H, 2 CO$_2$Me); 7.24 (*s*, 1 H–C(8)). $^{13}$C-NMR (125.707 MHz, $CDCl_3$, DEPT; 62.9 MHz)[1]): 22.5 (–, C(13)*); 22.5 (–, C(12)*); 23.8 (–, C(3)); 26.9 (–, C(14)); 28.1 (–, C(4)); 28.3 (–, C(11)); 30.1 (+, *Me*CO); 35.0 (–, C(6)); 52.7 (+, CO$_2$*Me*); 52.8 (+, CO$_2$*Me*); 52.9 (C$_q$, C(5)); 126.0 (+, C(8)); 130.0 (C$_q$, arom. C); 134.7 (C$_q$, arom. C); 136.5 (C$_q$, arom. C); 136.6 (C$_q$, arom. C); 136.8 (C$_q$, arom. C); 171.6 (C$_q$, *C*O$_2$Me)); 202.7 (C$_q$, Me*C*O). EI-MS (70 eV): 344 (100, $M^+$), 329 (17, [$M$ – Me]$^+$), 301 (3, [$M$ – MeCO]$^+$), 285 (23, [$M$ – CO$_2$Me]$^+$), 284 (58, [$M$ – H – CO$_2$Me]$^+$), 269 (19, [$M$ – H – CO$_2$Me – Me]$^+$), 241 (11, [$M$ – H – CO$_2$Me –

MeCO]$^+$), 225 (13, [$M$ – H – 2 $CO_2$Me]$^+$), 209 (6), 181 (15), 43 (18, $C_2H_3O^+$). HR-MS: 344.1625 ($M^+$, $C_{20}H_{24}O_5^+$; calc. 344.1624).

*Oligocyclization of* **6**) Following the *GP*, *Method B*, with **6** (300 mg, 0.68 mmol) [Pd(AcO)$_2$] (15.3 mg, 0.068 mmol), $Ph_3P$ (44.7 mg, 0.17 mmol), and $HCO_2Na$ (70 mg, 1 mmol) in DMF (8 ml). After 3 h, workup and threefold TLC (pentane/$Et_2O$ 20:1), gave a complex mixture of diastereoisomeric products. The *Fractions IV* and *VI* were isolated and identified. *Fr. IV:* 20 mg (8%) of rel-*1-{(7*R,*9*S,*11*S*)-8-methylene-11-{[(*tert-*butyl)dimethylsilyl]oxy}tricyclo[7.4.0.0$^{2,7}$]tridec-1-en-7-yl}ethanone* (= rel-*1-{(2*R,*8a*S,*9a*R*)-2-{[(1,1-Dimethylethyl)dimethylsilyl]oxy}-1,2,3,4,5,6,7,8,9,9a-decahydro-9-methylene-8a*H-*fluoren-8a-yl}ethanone*; **18**). Colorless oil. $R_f$ (pentane/$Et_2O$ 20:1) 0.60. IR (film): 2956, 2930, 2857, 1707, 1470, 1443, 1353, 1254, 1100, 1068, 836, 775. $^1$H-NMR (600 MHz, $CDCl_3$)[1]): 0.077 (*s*, $Me_2Si$); 0.87 (*s*, $Me_3C$); 1.04 (*dt*, *J* = 13.5, 4, 1 H–C(6′)); 1.07–1.09 (*m*, 1 H–C(4′)); 1.14 (*q*, *J* = 12, 1 H–C(10′)); 1.20–1.30 (*m*, 1 H–C(12′)); 1.35 (*tq*, *J* = 14, 3.5, 1 H–C(5′)); 1.56–1.64 (*m*, 1 H–C(3′), 1 H–C(5′)); 1.70–1.74 (*m*, 1 H–C(4′)); 1.84–1.92 (*m*, 1 H–C(13′)); 1.95 (*s*, MeCO); 1.93–1.98 (*m*, 1 H–C(12′)); 2.18–2.20 (*m*, 1 H–C(10′)); 2.46–2.50 (*m*, 1 H–C(3′)); 2.52–2.60 (*m*, 2 H, 1 H–C(6′), 1 H–C(13′)); 3.16–3.19 (*m*, H–C(9′)); 3.76 (*tt*, *J* = 12, 4, H–C(11′)); 4.85 (*d*, *J* = 2, 1 H of =$CH_2$); 4.96 (*d*, *J* = 1.5, 1 H of =$CH_2$). $^{13}$C-NMR (150.82 MHz, $CDCl_3$, APT)[1]): –4.6 (+, $Me_2Si$); 18.2 (–, $Me_3C$); 22.9 (–, C(13′)); 23.9 (–, C(4′)*); 25.2 (–, C(3′)); 25.9 (+, 3 *Me*$_3$C); 25.9 (+, *Me*CO); 27.2 (–, C(5′)*); 35.6 (–, C(6′)); 35.9 (–, C(12′)); 43.6 (–, C(10′)); 48.4 (+, C(9′)); 68.9 (–, C(7′)); 70.8 (+, C(11′)); 108.1 (–, =$CH_2$); 134.4 (–, C(2′)); 135.6 (–, C(1′)); 156.4 (–, C(8′)); 208.4 (–, Me*C*O). EI-MS (70 eV): 360 (2, $M^+$), 317 (32, [$M$ – MeCO]$^+$), 303 (4, [$M$ – $Me_3C$]$^+$), 228 (4), 211 (3), 185 (100), 159 (4), 143 (7), 129 (5), 73 (6), 43 (3, $C_2H_3O^+$). HR-MS: 360.2484 ($M^+$, $C_{22}H_{36}O_2Si^+$; calc. 360.2485).

*Fr. VI:* 20 mg (8%) of *1-{12-{[(*tert-*butyl)dimethylsilyl]oxy}tricyclo[8.4.0.0$^{2,7}$]tetradeca-1,7,9-trien-8-yl}ethanone* (=*1-{2-{[(1,1-dimethylethyl)dimethylsilyl]oxy}-1,2,3,4,5,6,7,8-octahydrophenanthren-9-yl}ethanone*; **19**). Colorless oil. $R_f$ (pentane/$Et_2O$ 20:1) 0.35. IR (film): 2958, 2927, 2855, 1709, 1681, 1564, 1467, 1431, 1355, 1275, 1252, 1100, 884, 836, 776, 627. $^1$H-NMR (600 MHz, $CDCl_3$)[1]): 0.060 (*s*, 3 H, $Me_2Si$); 0.069 (*s*, 3 H, $Me_2Si$); 0.88 (*s*, $Me_3C$); 1.64–1.70 (*m*, 1 H–C(4′), 1 H–C(5′)); 1.72–1.82 (*m*, 1 H–C(4′), 1 H–C(5′), 1 H–C(13′)); 1.95–2.02 (*m*, 1 H–C(13′)); 2.51 (*s*, MeCO); 2.52–2.62 (*m*, 2 H–C(3′), 1 H–C(14′)); 2.71–2.80 (*m*, 1 H–C(11′), 1 H–C(14′)); 2.87–2.95 (*m*, 2 H–C(6′), 1 H–C(11′)); 4.00–4.06 (*m*, H–C(12′)); 7.17 (*s*, H–C(9′)). $^{13}$C-NMR (150.82 MHz, $CDCl_3$, APT)[1]): –4.7 (+, $Me_2Si$); –4.6 (+, $Me_2Si$); 18.2 (–, $Me_3C$); 22.7 (–, C(4′)); 22.7 (–, C(5′)); 25.3 (–, C(14′)); 25.9 (+, (*Me*$_3$C); 27.11 (–, C(3′)); 28.3 (–, C(6′)); 30.1 (+, *Me*CO)); 32.0 (–, C(13′)); 39.4 (–, C(11′)); 67.4 (–, C(12′)); 127.5 (+, C(9′)); 131.9 (–, arom. C); 134.2 (–, arom. C); 136.3 (–, arom. C*); 136.4 (–, C(8′)*); 138.4 (–, arom. C); 202.7 (–, Me*C*O). EI-MS (70 eV): 358 (1, $M^+$), 301 (100, [$M$ – $Me_3C$]$^+$), 285 (7), 227 (7), 185 (15), 75 (13), 43 (8, $C_2H_3O^+$). HR-MS: 358.2328 ($M^+$, $C_{22}H_{34}O_2Si^+$; calc. 358.2328).

*Dimethyl 8-Methylenetricyclo[7.4.0.0$^{2,7}$]trideca-1(9),2(7)-diene-5,5-dicarboxylate* (=*Dimethyl 1,3,4,5,6,7,8,9-Octahydro-9-methylene-2*H-*fluorene-2,2-dicarboxylate*; **20**). Following the *GP*, *Method A*, with **3** (192 mg, 0.50 mmol), [Pd(AcO)$_2$] (11 mg, 0.05 mmol), $Ph_3P$ (33 mg, 0.13 mmol), and $K_2CO_3$ (207 mg, 1.5 mmol) in MeCN (5 ml). After 1 h, workup, and CC (flash $SiO_2$ (20 g), column 1 × 25 cm, hexane/$Et_2O$ 10:1) afforded 112 mg (74%) of **20**. Fluorescent liquid. $R_f$ (pentane/$Et_2O$ 5:1) 0.28. IR (film): 3050, 2983, 1731 (C=O), 1422, 1266, 897, 738, 707. $^1$H-NMR (250 MHz, $C_6D_6$)[1]): 1.46–1.60 (*m*, 2 H–C(11), 2 H–C(12)); 1.95–2.05 (*m*, 2 H–C(13)); 2.19–2.27 (*m*, 2 H–C(10)); 2.30–2.34 (*m*, 2 H–C(3)); 2.35–2.42 (*m*, 2 H–C(4)); 3.21 (*s*, 2 H–C(6)); 3.34 (*s*, 2 $CO_2$Me); 5.30 (*d*, *J* = 0.5, 1 H of =$CH_2$); 5.35 (*d*, *J* = 0.5, 1 H of =$CH_2$). $^{13}$C-NMR (62.9 MHz, $C_6D_6$, DEPT)[1]): 20.3 (–, C(3)); 21.4 (–, C(10)); 22.5 (–, C(13)); 23.1 (–, C(11)*); 23.1 (–, C(12)*); 28.1 (–, C(6)); 28.9 (–, C(4)); 52.2 (+, 2 $CO_2$*Me*); 54.2 ($C_q$, C(5)); 110.4 (–, =$CH_2$)); 124.7 ($C_q$); 128.7 ($C_q$); 140.0 ($C_q$); 140.4 ($C_q$); 152.2 ($C_q$); 171.8 ($C_q$, 2 C=O). EI-MS (70 eV): 302 (20, $M^+$), 251 (10), 243 (14, [$M$ – $C_2H_3O_2$]$^+$), 242 (24), 183 (12), 131 (12), 105 (10), 91 (10), 73 (12), 61 (100), 45 (40), 43 (57). HR-MS: 302.1519 ($M^+$, $C_{18}H_{22}O_4^+$; calc. 302.1518).

*5-{[(*tert-*Butyl)dimethylsilyl]oxy}-8-methylenetricyclo[7.4.0.0$^{2,7}$]trideca-1(9),2(7)-diene* (=*2-{[(1,1-Dimethylethyl)dimethylsilyl]oxy}-2,3,4,5,6,7,8,9-octahydro-9-methylene-1*H-*fluorene*; **21**). Following the *GP*, *Method B*, with **5** (300 mg, 0.72 mmol), [Pd(AcO)$_2$] (16.82 mg, 0.072 mmol), $Ph_3P$ (49.6 mg, 0.18 mmol), and $HCO_2Na$ (60 mg, 0.90 mmol) in DMF (10 ml). After 2 h, workup, and purification by CC (flash $SiO_2$ (25 g), column 1 × 20 cm, pentane/$Et_2O$ 100:2) afforded 127 mg (53%) of **21**. Orange oil.

$R_f$ (pentane/$Et_2O$ 100:2) 0.60. IR (film): 3079, 2928, 1635, 1472, 1251, 1096, 904, 835, 774, 669. $^1$H-NMR (600 MHz, $CDCl_3$)[1]): 0.09 (*s*, 2 $Me_2Si$); 0.90 (*s*, $Me_3C$); 1.64–1.72 (*m*, 1 H–C(4), 2 H–C(11), 2 H–C(12)); 1.86–1.92 (*m*, 1 H–C(4)); 2.15–2.21 (*m*, 2 H–C(10)); 2.22–2.24 (*m*, 1 H–C(6)); 2.25–2.28 (*m*, 1 H–C(3)); 2.29–2.38 (*m*, 3 H, 1 H–C(3), 2 H–C(13)); 2.61 (*dd*, $J$ = 6, 18, 1 H–C(6)); 3.92–3.94 (*m*, 1 H–C(5)); 5.44 (*d*, $J$ = 0.5, 1 H of $=CH_2$); 5.45 (*d*, $J$ = 0.5, 1 H of $=CH_2$). $^{13}$C-NMR (150.82 MHz, $CDCl_3$, DEPT, 62.9 MHz)[1]): −4.7 (+, $Me_2Si$); −4.6 (+, $Me_2Si$); 18.3 ($C_q$, $Me_3C$); 21.2 (−, C(3)); 21.5 (−, C(13)); 22.5 (−, C(10)); 22.7 (−, C(11)*); 22.9 (−, C(12)*); 25.9 (+, 3 $Me_3C$); 31.4 (−, C(6)); 32.4 (−, C(4)); 69.3 (+, C(5)); 111.1 (−, $=CH_2$)); 125.5 ($C_q$, C(9)); 128.3 ($C_q$, C(7)); 140.7 ($C_q$, C(1)**); 140.8 ($C_q$, C(2)**); 151.5 ($C_q$, C(8)). EI-MS (70 eV): 316 (20, $M^+$), 259 (13, $[M - Me_3C]^+$), 186 (8, $[M - {}^t BuMe_2SiO]^+$), 185 (10, $[M - H - {}^t BuMe_2SiO]^+$), 158 (100, $[M - H - {}^t BuMe_2SiO - C_2H_4]^+$), 143 (4). HR-MS: 316.2221 ($M^+$, $C_{20}H_{32}OSi^+$; calc. 316.2222).

*3,4,5,7,8,9-Hexahydro-9-methylene-1*H*-2,6-dioxafluorene* (= *3,4,5,7,8,9-Hexahydro-9-methylene-1*H-*cyclopenta[1,2-*c:*3,4-*c′*]dipyran*; **22**). Following the *GP*, *Method B*, with **11** (136 mg, 0.50 mmol), [$Pd(AcO)_2$] (8.0 mg, 0.04 mmol), $Ph_3P$ (21.0 mg, 0.08 mmol), and $HCO_2Na$ (68 mg, 1.0 mmol) in DMF (5 ml). After 2 h, workup and purification by CC (flash $SiO_2$ (5.0 g), column 1 × 5.0 cm, pentane/$Et_2O$ 5:1) afforded 49 mg (52%) of **22**. Yellow liquid. $R_f$ (pentane/$Et_2O$ 5:1) 0.46. IR (film): 3444, 2923, 2849, 1621, 1434, 1290, 1101, 1034, 736. $^1$H-NMR (500 MHz, $CDCl_3$): 2.28 (*t*, $J$ = 3.0, 2 H, $CH_2$); 2.40–2.45 (*m*, 2 H, $CH_2$); 3.82 (*t*, $J$ = 5.4, 2 H, $CH_2O$); 3.84 (*t*, $J$ = 5.4, 2 H, $CH_2O$); 4.39 (*t*, $J$ = 3.0, 2 H, $CH_2O$); 4.53 (*t*, $J$ = 3.0, 2 H, $CH_2O$); 5.40 (*d*, $J$ = 0.6, 1 H of $=CH_2$); 5.52 (*d*, $J$ = 0.6, 1 H of $=CH_2$). $^{13}$C-NMR (62.9 MHz, $CDCl_3$, DEPT): 22.0 ($CH_2$); 23.3 ($CH_2$); 63.9 (−, $CH_2O$); 64.0 (−, $CH_2O$); 64.1 (−, $CH_2O$); 64.5 (−, $CH_2O$); 113.0 (−, $=CH_2$); 125.7 ($C_q$); 126.4 ($C_q$); 136.4 ($C_q$); 138.7 ($C_q$); 148.6 ($C_q$). EI-MS (70 eV): 190 (100, $M^+$), 175 (22), 160 (62, $[M - CH_2O]^+$), 130 (23), 115 (24). HR-MS: 190.0995 ($M^+$, $C_{12}H_{14}O_2^+$; calc. 190.0994).

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*Received February 27, 2009*