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Synthesis and Use of New Substituted 1,3,5-Hexatrienes in Studying Thermally Induced 6π-Electrocyclizations

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Dedicated to Professor Miguel Yus on the occasion of his 60th birthday

Keywords: Pericyclic Reactions / Regioselectivity / Palladium catalysis / Cross coupling / Oligocyclic systems

An acyclic, two heterocyclic, and two bicyclic alkenylstannanes, **3**, **4a**, **4b**, **8** and **11**, respectively, were synthesized in yields ranging from 43 to 97%, and each was subjected to a sequence of Stille and Heck couplings with 2-bromocyclohexenyl triflate (**13**) and alkyl (*tert*-butyl and methyl) acrylate to furnish seven new 1,3,5-hexatrienes **19**, **20**, **21**, **22**-*t*Bu, **22**-Me, **23** and **43**, respectively, in 58–84% yields. For the alkenylstannanes **4a**,**b**, **8** and **11**, customized combinations of catalysts had to be used. The Stille–Heck sequence involving **13**, **3** and *tert*-butyl acrylate could be performed in a one-pot mode and proceeded in 75% yield. The hexatrienes were heated in decalin solutions so as to effect 6π-electrocyclization. Temperatures and reaction times were optimized individually. The hexatrienes **29**, **31** and **36** gave the bi- and tricyclic cyclohexadienes **28**, **30** and **34**, incorporating allylic alcohol and allyl ether termini, by 6π-electrocyclization and subsequent [1,5]-hydrogen shift, as single products in good yields (85–93%). In contrast, the hexatrienes **19**, **20**, **21** and **39** furnished mixtures of the initial electrocyclization products **26**, **32**, **37** and **40** as well as the products of a subsequent [1,5]-hydrogen shift **27**, **33**, **38** and **41**, respectively. The tricyclic hexatrienes **22**-*t*Bu, **22**-Me and **23** bearing alkyl (*tert*-butyl, methyl) acrylate termini also selectively gave the tetracyclic dienes **48**-*t*Bu, **48**-Me and **50** in 71–77% yields by electrocyclizations and subsequent hydrogen shifts.

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Introduction

Although the Diels–Alder reaction remains unsurpassed in its scope and versatility as a method for accessing six-membered carbocycles,[1] the more recently developed thermal 6π-electrocyclizations of 1,3,5-hexatrienes[2] have come to complement such [4+2] cycloadditions in terms of functionality in and substitution patterns on the rings.[3] Especially since modern metal-catalyzed cross-coupling methodology[4] has made variously substituted 1,3,5-hexatrienes readily accessible,[3,5] their thermal 6π-electrocyclizations have become a feasible stereoselective approach to oligosubstituted cyclohexa-1,3-dienes.[3,6] However, when ring-annelated cyclohexadienes are formed, the initial products were frequently found to undergo subsequent [1,5]-hydrogen shifts so that mixtures of products were obtained. In order to establish whether this sigmatropic process can be retarded or accelerated and the selectivity thus enhanced by a proper choice of substituents, we set out to prepare variously unsymmetrically substituted 1,3,5-hexatrienes using previously established[6b,7] Stille–Heck cross-coupling sequences, then undertake various functional group transformations, and study the outcome of the thermal rearrangements of the compounds so formed.

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Results and Discussion

Preparation of Substrates

For the preparation of a set of diverse 1,3,5-hexatrienes by Stille–Heck cross-coupling sequences, a variety of alkenylstannanes had to be synthesized. The new acyclic (trialkylsilylethenyl)stannane **3** was prepared by a rhodium-catalyzed hydrostannylation[8] of (*tert*-butyldimethylsilyl)acetylene (**2**).[9] It is noteworthy that at 22 °C this hydrostannylation led to a 1:1 mixture of **3** and its (*Z*) isomer as well as a trace of the 1,1-disubstituted isomer. However, when this reaction was carried out at 60 °C, the desired alkene **3** was the main product (57%) and accompanied by only traces of the isomers just mentioned (Scheme 1).

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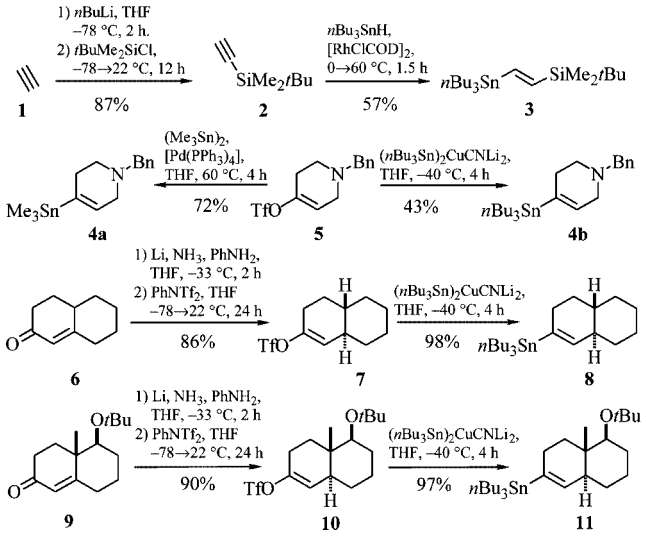


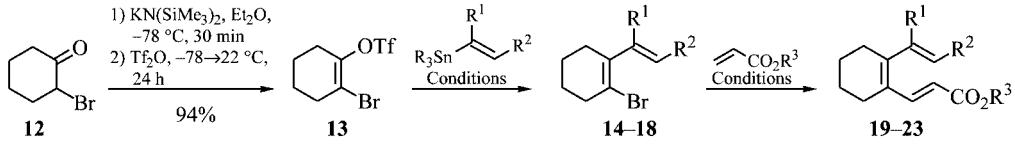
Scheme 1. Synthesis of various alkenylstannanes to be applied in Stille–Heck coupling sequences.

The 4-azacyclohexenylstannanes **4a**,**b** were synthesized from *N*-benzylpiperidinone via the enol triflate **5** which was prepared according to a standard protocol.[10] The tributylstannane **4b** was obtained from **5** and dilithium cyanobis(tributylstannyl)cuprate in 43% yield,[11] whereas the corresponding trimethyl(alkenyl)stannane **4a** was prepared by a palladium-catalyzed transfer of a trimethyltin group from hexamethylditin to **5**, and this conversion proceeded with a significantly higher yield of 72%. Because decalin-2-ones preferably form the undesired enolate regioisomers, the targeted bicyclo[4.4.0]decenylstannanes **8** and **11** had to be prepared from the α,β-unsaturated bicyclo[4.4.0]dec-1-en-3-ones **6** and **9**. Reductive enolate formation using lithium dissolved in liquid ammonia, and trapping with *N*,*N*-bis(trifluoromethylsulfonyl)aniline furnished the *trans*-annelated bicyclo[4.4.0]dec-2-enol triflates **7** and **10** with complete diastereoselectivity.[12] The latter could be transformed into the corresponding (bicyclodecenyl)tributylstannanes **8** and **11** in 98 and 97% yields, respectively, by treatment with dilithium cyanobis(tributylstannyl)cuprate. It is noteworthy that the reductive enolization of the corresponding indenone derivatives yielded lithium enolates with the same high diastereoselectivities, but furnished the *cis*-annelated bicycles (Scheme 1).[7a]

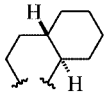
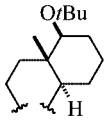
2-Tris(*n*-butylstannyl)-1,4-dioxine (**25**) was prepared from dioxine and tributyltin chloride according to a literature procedure.[13]

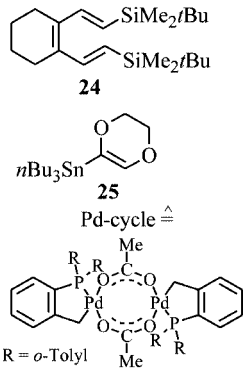
The yield associated with the conversion of 2-bromocyclohexanone (**12**) into 2-bromocyclohexenyl triflate (**13**) as described previously,[6b] was significantly improved by employing potassium bis(trimethylsilyl)amide (KHMDS) and trapping the regioselectively formed potassium enolate with trifluoromethanesulfonic anhydride. By such means the target compound **13** was obtained as the sole product in 94% yield (Scheme 2).

The Stille coupling[14] of compound **13** with the relevant acyclic (trialkylsilylethenyl)stannane **3** was effected using $[Pd(PPh_3)_4]$ as catalyst and occurred with a high degree of chemoselectivity for the triflate leaving group to give the intermediate bromodiene **14** in 80% yield (Scheme 2). With $[Pd_2(dba)_3]$ in the presence of LiCl[15] in DMF, the twofold



12 13 14–18 19–23

Stannane (R_3Sn)	R^1	R^2	Condit.[a]	Prod.	Yield (%)	R^3	Condit.[b]	Prod.	Yield (%)
3 (*n*Bu$_3$Sn)	H	SiMe$_2$*t*Bu	**A**	**14**	80	*t*Bu	**D**	**19**	78
25 (*n*Bu$_3$Sn)			**A**	**15**	82	*t*Bu	**E**	**20**	65
4b (*n*Bu$_3$Sn)			**B**	**16**	84	*t*Bu	**E**	**21**	71
8 (*n*Bu$_3$Sn)			**C**	**17**	89	*t*Bu Me	**E** **E**	**22**-*t*Bu **22**-Me	58 84
11 (*n*Bu$_3$Sn)			**C**	**18**	94	*t*Bu	**E**	**23**	60



[a] **A**: $[Pd(PPh_3)_4]$, LiCl, DMF, 90 °C, 10 h; **B**: $Pd_2(dba)_3$, CuI, LiCl, NMP, 65 °C, 5 h; **C**: $Pd_2(dba)_3$, CuI, $AsPh_3$, LiCl; NMP, 65 °C, 5 h. [b] **D**: $Pd(OAc)_2$, PPh_3, DMF, 90 °C, 10 h; **E**: Pd-cycle, $(nBu)_4NOAc$, DMF, H_2O, 105 °C, 8 h.

Scheme 2. Stille–Heck coupling sequences used to access unsymmetrically 1,6-disubstituted 1,3,5-hexatrienes.

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coupling product **24** was obtained along with the desired bromodiene **14** in a ratio of 1:1. With CuI and $AsPh_3$ as additives, the catalytic activity towards the reaction with the bromine leaving group was further increased, and the ratio of **24/14** increased to 4:3.

The subsequent Heck reaction of diene **14** with *tert*-butyl acrylate was brought about under conventional conditions using $Pd(OAc)_2$ and PPh_3 and so provided the unsymmetrically 1,5-disubstituted 1,2-dialkenylcyclohexene **19** in 78% yield. This Stille–Heck sequence could also be performed in a one-pot procedure to give product **19** in an overall yield of 75% from **13** which constitutes a real increase in efficiency. Clearly, the rather simple catalytic system derived from $Pd(OAc)_2$ and PPh_3 is not retarded by the presence of $[Pd(PPh_3)_4]$ and vice versa. As proved by an X-ray structure analysis, the 1,3,5-hexatriene system in **19** adopts an *s-trans,s-trans* conformation.[16]

The dioxinylstannane **25** was also smoothly coupled with the bromocyclohexenyl triflate **13** using $[Pd(PPh_3)_4]$ as a catalyst and so gave the bicyclic bromodiene **15** in 82% yield. An attempted Heck coupling with *tert*-butyl acrylate employing $Pd(OAc)_2$ and PPh_3 as a precatalyst gave only low yields (<20%) of the bicyclic hexatriene **20**. In bromodienes of type **15**, the alkenyl bromide moiety is sterically more encumbered than that associated with compounds of type **14**. In order to compensate for the resulting lower reactivity, the palladacycle prepared by heating palladium acetate with tris(*o*-tolyl)phosphane,[17] and a higher temperature were employed for the Heck reaction of **15** with *tert*-butyl acrylate. Through such modifications, the 1,3,5-hexatriene **20** was obtained in 65% yield although full consumption of substrate **15** required addition of the palladacycle in two portions (Scheme 2).[18]

The 4-azacyclohexenylstannane **4b** was not readily coupled with the cyclohexenyl triflate **13** when $[Pd(PPh_3)_4]$ was used as catalyst. A much better yield (84%) of the bromodiene **16** was achieved with $[Pd_2(dba)_3]$ and CuI.[19] It is noteworthy that the addition of $AsPh_3$ to the catalyst cocktail had no significant influence on the yield. The attempted coupling of the same substrate with the trimethylstannyl derivative **4a** led to low yields regardless of the catalyst. The Heck coupling of compound **16** with *tert*-butyl acrylate gave product **21** in 71% yield although, once again, the palladacycle had to be added in two portions.

Stille coupling of the bicyclodecenylstannane **8** with the bromoenol triflate **13** was achieved with the precatalyst system consisting of $[Pd_2(dba)_3]$, $AsPh_3$ and CuI in DMF and so furnished the tricyclic bromodiene **17** in 76% yield. Employing NMP instead of DMF, provided **17** in 89% yield, while product **18** was obtained from substrate **13** and the bicyclodecenylstannane **11** in an even higher yield of 94%.

Heck coupling of the bromodiene **17** with *tert*-butyl acrylate required two portions of 4 mol-% each of the palladacycle to furnish the tricyclic hexatriene **22**-*t*Bu in 58% yield. To achieve reasonable yields, a solvent mixture consisting of MeCN, DMF and water as well as the additive tetrabutylammonium acetate serving as a base proved essential. Under the same conditions, but with two portions of 8 mol-% each of the precatalyst, methyl acrylate was coupled with **17** to provide **22**-Me in 84% yield.[20]

The functionalized tricyclic bromobutadiene **23**, upon Heck reaction with *tert*-butyl acrylate and with addition of two portions of 4 mol-% each of the precatalyst, gave the tricyclic hexatriene **23** in 60% yield (Scheme 2).[18]

Attempts to combine the Stille and Heck coupling reactions so as to prepare the hexatrienes **22**-*t*Bu and **22**-Me directly could not be realized in a one pot procedure, because the Heck reaction under catalysis of the palladacycle did not proceed at all in the presence of NMP.

Studies of the 6π-Electrocyclization Reactions

The thermally induced 6π-electrocyclization reactions were conveniently carried out in the high-boiling, chemically inert solvent decalin. After completion of the reaction, the decalin could easily be removed at ambient temperature under reduced pressure.

For the cyclization of the hexatriene **19** incorporating an electron-withdrawing *tert*-butoxycarbonyl substituent, different temperatures were investigated. For example, heating the substrate at 150 °C for 11 h, afforded a mixture of the two isomeric bicyclo[4.4.0]decadienes **26** and **27**, the latter apparently arising from **26** by a [1,5]-hydrogen shift. However, the major component of the reaction mixture was the starting material **19**. At 170 and 190 °C, the transformations were also incomplete, but at 205 °C, the triene **19** was completely consumed within 1 h and so provided a 1:1.9 mixture of the dienes **26** and **27** in a combined yield of 79%. Extended heating of the mixture did not change this ratio significantly. The impossibility readily separating regioisomers **26** and **27** detracts from this approach to hexahydronaphthalenes.

In order to be able to extend this investigation to thermal 6π-electrocyclizations of 1,3,5-hexatrienes with significantly different steric and electronic properties, the *tert*-butoxycarbonyl moiety in compound **19** was reduced using diisobutylaluminum hydride (DIBALH) in toluene and thus yielded triene **29** incorporating an allylic alcohol residue that could be protected by its transformation into the tetrahydropyranyl ether **31**.[21]

Attempts to prepare the allyl ether **31** directly by Heck cross coupling of the bromodiene **14** with the relevant partners in the presence of silver acetate or carbonate[22] only provided impure samples of the product and only in low yield (0–30%). Under Heck conditions without an added silver salt, a minor amount of the non-conjugated 1,3,6-hexatriene was also formed.

Heating triene **31** in decalin at 205 °C for 45 min cleanly furnished, in 93% yield, the bicyclic diene **30** resulting from 6π-electrocyclization and a subsequent [1,5]-hydrogen shift (Scheme 3).

After 30 min at 205 °C, only a mixture of the starting material **31** and the diene **30** was observed. Since none of the primary cyclization product analogous to **26** could be detected, the [1,5]-hydrogen shift obviously proceeds more

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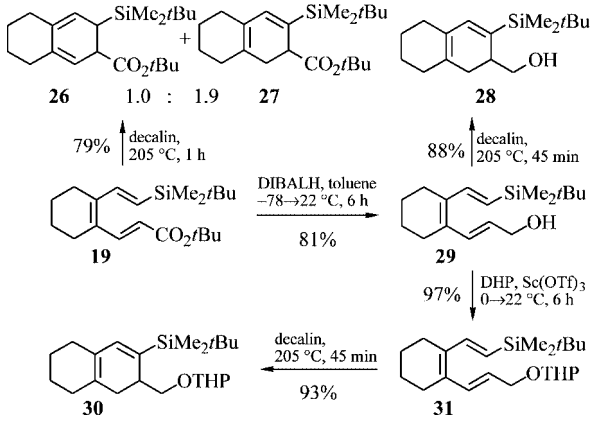
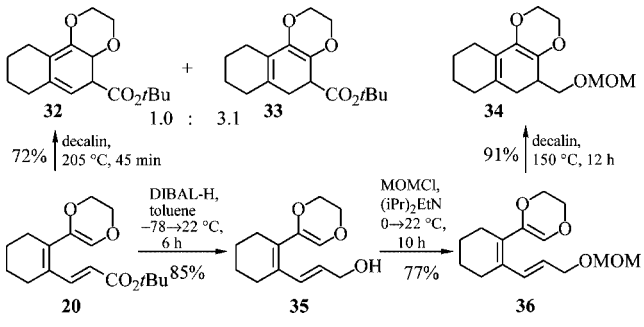


Scheme 3. Thermal 6π-electrocyclizations of the 1,2-dialkenylcyclohexene derivatives **19**, **29** and **31**.

rapidly than the 6π-electrocyclization, a situation that contrasts with the one involving substrate **19**. After 12 h at 150 °C, no consumption of **31** was observed. The free allylic alcohol **29** could also be cleanly cyclized to give the diene **28** as a single product in 88% yield. Thus, this reaction proceeds without decomposition, even at 205 °C.

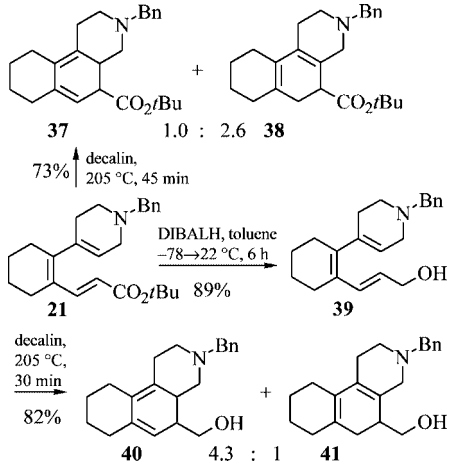
As observed for the cyclization of the hexatriene **19**, upon heating the *tert*-butoxycarbonyl-substituted hexatriene **20** at 205 °C for 45 min, a 1:3.1 mixture of the 6π-electrocyclization product **32** and isomer **33** arising from a subsequent [1,5]-hydrogen shift was obtained. In contrast, triene **36** incorporating an allyl ether moiety, which was obtained from compound **20** by reduction with DIBAL-H (85% yield) and subsequent etherification with MOMCl (77%), yielded only the tricyclic diene **34** in 86% yield upon heating at 205 °C for 1 h. Just as observed for congeners **29** and **31**, the 6π-electrocyclization of compound **36** is followed by a rapid [1,5]-hydrogen shift (Scheme 4). Interestingly, the hexatriene **36** could also be transformed into isomer **34** by heating the former at the significantly lower temperature of 150 °C for 12 h. Indeed, under such conditions the yield of the reaction could even be raised to 91%. The facility with which both the electrocyclization of compound **36** and the subsequent hydrogen migration take place, must arise from the relative electron richness of the substrate although, according to literature precedents,[2a] hexatrienes like **19** and **20** carrying electron-withdrawing substituents should cyclize more readily. As with congeners **19** and **20**,



Scheme 4. Thermal 6π-electrocylizations of the heterobicyclic hexatrienes **20** and **36**.

the heterobicyclic hexatriene **21** having a *tert*-butoxycarbonyl substituent required heating at 205 °C for 45 min to furnish, in 73% yield, a 1:2.6 mixture of the dienes **37** and **38**. Extended heating did not lead to a significant change in favor of the [1,5]-hydrogen-shifted product **38**.

In contrast, the hexatriene **39** incorporating an allylic alcohol terminus and obtained from precursor **21** in 89% yield by reduction with DIBALH, upon heating at 205 °C for 30 min furnished a mixture of the two regioisomeric **40** and **41** in a ratio of 4.3:1 in a total yield of 82%. After 2.5 h at the same temperature, the ratio of the two regioisomers was 1:2.5, although the isomerization of compound **40** to congener **41** could not be completed through extended heating, because both products decomposed under such conditions (Scheme 5).



Scheme 5. Thermal 6π-cyclizations of the heterobicyclic hexatrienes **21** and **39**.

The tricyclic 1,3,5-hexatriene **43** bearing an allylic alcohol group was prepared from **42**,[7a] as a potential precursor to the steroid framework. Upon heating compound **43** at 205 °C for 45 min, it reacted to give the regioisomeric tetracyclic compounds **44** and **45** in yields of 20 and 26%, respectively. In contrast, the oxohexatriene **46** underwent smooth cyclization and a subsequent (formal) [1,3]-hydrogen shift to yield, exclusively and in 75% yield, the conjugated steroidal dienone **47** (Scheme 6).[6c]

The tricyclic hexatrienes **22**-*t*Bu, **22**-Me and particularly **23** may be considered as precursors to Baccharan-type triterpenes.[23] In decalin solution, **22**-*t*Bu at 205 °C smoothly rearranged within 45 min to give **48**-*t*Bu as the sole reaction product and as a single diastereomer in 77% yield (Scheme 7). Apparently, the initial 6π-electrocyclization occurred with a high degree of outward-directed disrotational selectivity.[24] Under the same conditions, the tricyclic hexatriene **23** also gave the tetracycle **50** as a single product in 71% yield. By employing the enantiomerically pure and readily available form of bicyclodecenylstannane **11**[25] in the initial Stille cross coupling, the tetracyclic compound **50** would also be accessible in enantiomerically pure form.

Interestingly, upon heating the 1-methoxycarbonyl-substituted hexatriene **22**-Me at 205 °C for 30 min, a 7:1 mix-

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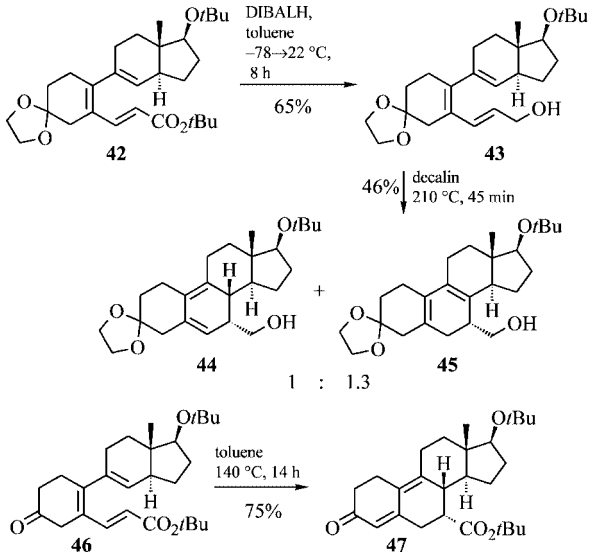
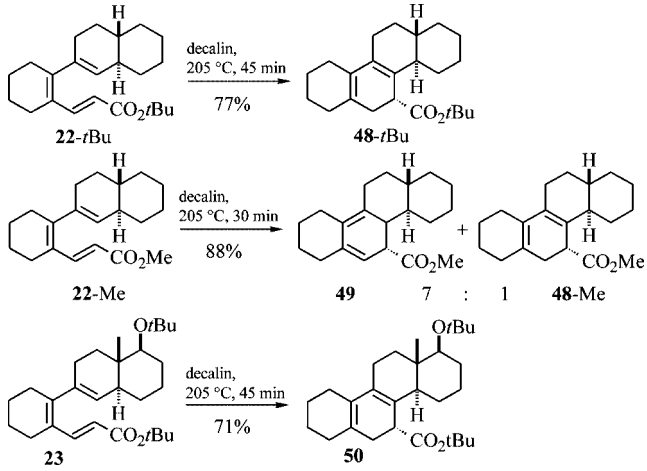


Scheme 6. Tricyclic 1,3,5-hexatrienes as precursors to steroidal compounds.



Scheme 7. Thermal rearrangement of the tricyclic hexatrienes **22**-*t*Bu, **22**-Me and **23** to tetracycles **48**, **49** and **50**.

ture of the initial 6π-electrocyclization product **49** and the [1,5]-hydrogen-shifted product **48**-Me was obtained. In contrast, heating the same reaction mixture for a total of 60 min provided compound **48**-Me exclusively and in a yield of 69%.

Conclusions

The bicyclo[4.4.0]decadienes **28** and **30** can be prepared in an efficient manner through a sequence of Stille–Heck cross couplings and subsequent thermally induced cyclization of the resulting 1,3,5-hexatrienes. They represent interesting intermediates for organic synthesis because they can be employed for the construction of various complex carbon skeletons.[26]

The Stille–Heck cross-coupling sequence also provides easy access to various unsymmetrically 1,6-disubstituted 1,3,5-hexatrienes, and further examples could be prepared through straightforward functional-group manipulations. All of those trienes underwent 6π-electrocyclizations and the primary products of such processes engaged in subsequent [1,5]-hydrogen shift reactions, and so provided mixtures of products. However, when the hexatrienes incorporate an allylic alcohol or allyl ether at their terminus, the electrocyclization/[1,5]-hydrogen shift sequences went to completion. Such transformations may find applications in the construction of multifunctional bi- and tricyclic skeletons that can participate in [4+2] cycloaddition reactions and thus resulting in further increase in molecular complexity.[26]

Experimental Section

General Remarks: ^{1}H NMR: Varian VXR-300 (300 MHz), Bruker AM 250 (250 MHz). Chemical shifts in $CDCl_3$ are reported as δ values relative to chloroform (δ = 7.26 ppm) or benzene (δ = 7.20 ppm) as internal references. ^{13}C NMR: Varian VXR-300 (75.5 MHz), Bruker AW 250 (62.9 MHz). Chemical shifts in $CDCl_3$ are reported as δ values relative to chloroform (δ = 77.0 ppm) or benzene (δ = 128 ppm); the multiplicities of the signals were determined by the DEPT (APT) (62.9 MHz) technique and quoted as (+) for CH_3 and CH groups, (–) for CH_2 groups and (C_{quat}) for quaternary carbon atoms. IR: Bruker IFS 66. Low-resolution EI mass spectra: Finnigan MAT 95, ionizing voltage 70 eV. High-resolution mass spectra: Finnigan MAT 95; preselected ion peak matching at *R* ca. 10000 to be within ±2 ppm of the exact masses. Elemental analyses: Mikroanalytisches Labor des Instituts für Organische und Biomolekulare Chemie der Universität Göttingen, Germany. Melting points are uncorrected. Solvents for extraction and chromatography were of technical grade and distilled before use. Flash chromatography (FC) was performed using Merck Kieselgel 60 (200–400 mesh). Aluminum oxide (ICN Alumina N, Super I) was obtained from ICN Biomedicals. Unless otherwise specified, aluminum oxide was deactivated with 5% water. TLC analyses were performed using Macherey–Nagel precoated plates, 0.25 mm, Alugram Sil G/UV$_{254}$ (I) and Merck precoated silica gel 60 F_{254} aluminum sheets (II). All reactions were carried out under dry nitrogen or argon in oven- and/or flame-dried glassware. Unless otherwise specified, solutions of NH_4Cl, NaCl, Na_2SO_3 and $NaHCO_3$ were saturated aqueous solutions. Benzene, decalin, toluene, THF and diethyl ether were distilled from sodium/benzophenone. Dichloromethane was distilled from CaH_2. 1-Benzyl-4-trifluoromethylsulfonyloxy-1,2,3,6-tetrahydropyridine (**5**),[10] $\Delta^{1,9}$-octalone-2 (**6**),[27] 5-*tert*-butoxy-4a-methyl-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (**9**),[25] tributyl(5,6-dihydro[1,4]dioxin-2-yl)-stannane (**25**),[13] *N*,*N*-bis(trifluoromethylsulfonyl)aniline[28] were prepared according to published procedures.

General Procedure for the Preparation of the Bicycloalkenylstannanes (GP 1): *n*-Butyllithium (2.60 equiv. of a 2.36 M solution in hexane) was added at –78 °C to a solution of diisopropylamine (2.60 equiv.) in THF and the resulting mixture was stirred for 30 min. The resulting solution was treated with tributyltin hydride (2.20 equiv.), and stirring was continued for 30 min before copper(I) cyanide (1.10 equiv.) was added in one portion. The reaction mixture was then warmed to –50 °C, and after a yellow solution had formed, this was treated with the respective enol triflate (1.00 equiv.) in THF. The resulting solution was warmed to –25 °C, then stirred continuously at this temperature for 2 h, before being poured into pentane and washed with NH_3 solution (10%), water

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and brine. After drying with $MgSO_4$ and removal of the solvents under reduced pressure, the residue was dissolved in ethyl acetate, and the ensuing solution treated with silver(I) acetate (3.00 equiv.) for 2 h at ambient temperature, using an unsealed vessel. The reaction mixture was then filtered through Celite, the filtrate washed with water, brine and dried with $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by chromatography on neutral aluminum oxide (deactivated with 5% water).

General Procedure for Stille Couplings of the 2-Bromocyclohex-1-enyl Triflate 13 (GP 2): A Pyrex bottle containing a magnetic stirring bar was charged with the specified solvent, the bromoenol triflate **13** and the specified alkenylstannane. The bottle was sealed with a septum and the solution purged, using inlet and outlet needles, with argon in an ultrasonic bath for 5 min. The specified catalyst mixture was then added, and the resulting suspension was purged with argon for another 5 min. After removal of the septum, the bottle was sealed with a screw cap and then heated with vigorous stirring at the specified temperature for the specified time. The reaction mixture was then poured into diethyl ether and aqueous NH_3 solution (5%). The organic layer was washed with water, and the combined aqueous layers were extracted with diethyl ether. The combined organic layers were then treated with satd. KF solution, dried with $MgSO_4$, concentrated under reduced pressure, and the residue was purified by chromatography on silica gel.

General Procedure for Heck Reactions of Bromobutadienes with Acrylates (GP 3): A Pyrex bottle containing a magnetic stirring bar was charged with the specified solvent, the bromobutadiene and the acrylate. The bottle was sealed with a septum, and the solution purged, using inlet and outlet needles, with argon in an ultrasonic bath for 5 min. The specified catalyst mixture was then added, and the resulting suspension was purged with argon for another 5 min. After removal of the septum, the bottle was sealed with a screw cap and then heated with vigorous stirring at the specified temperature for the stated time. The reaction mixture was then poured into diethyl ether and water. The organic layer was repeatedly washed with water, and the combined aqueous layers were extracted with diethyl ether. The combined organic layers were then dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue thus obtained was purified by FC on silica gel.

General Procedure for the Reduction of the *tert*-Butoxycarbonyl-Substituted Hexatrienes to Allylic Alcohols (GP 4): A magnetically stirred solution of the respective α,β-unsaturated carboxylic ester in toluene at –78 °C was treated dropwise with diisobutylaluminum hydride (DIBALH) (4.00–8.00 equiv., 1.00 M in toluene), and the ensuing mixture was stirred at –78 °C for 1 h. After warming to ambient temperature, it was stirred for an additional 4 h, then poured into diethyl ether and the mixture washed with 1.00 M $KHSO_4$ solution and water. After extraction of the combined aqueous phases with diethyl ether, washing of the combined organic layers with satd. $NaHCO_3$ solution, water and drying with $MgSO_4$, the volatile components were removed under reduced pressure, and the residue so obtained was subjected to FC.

General Procedure for the Thermally Induced 6π-Electrocyclization of 1,3,5-Hexatrienes in Solution (GP 5): A thick-walled Pyrex test tube, containing a magnetic stirring bar, was charged with a solution of the respective hexatriene (1.00 equiv.) in the specified solvent. The test tube was sealed with a septum and, using inlet and outlet needles, the solution was purged with argon in an ultrasonic bath for 10 min. The septum was then replaced by a screw cap, and the solution was heated in a prewarmed oil bath at the specified temperature for the stated time. The cooled reaction mixture was concentrated at 25 °C and 5 mbar, and the residue so obtained subjected to FC.

(*tert*-Butyldimethylsilyl)acetylene (2): A saturated solution of acetylene in THF (300 mL) was treated carefully and at –78 °C over 30 min with *n*BuLi (66.0 mL of a 2.38 M solution in hexane, 156 mmol). After stirring the ensuing mixture for 1 h, *tert*-butylchlorodimethylsilane (18.1 g, 120 mmol) was added over 30 min. The reaction mixture was then warmed to ambient temperature and stirred for a total of 24 h. After washing with water (50 mL), drying with $MgSO_4$, the volatile components were removed by distillation through a 25 cm Vigreux column. Further distillation of the residue without the column yielded the product **2** (14.6 g, 87%) as a clear, colorless oil. The analytical data obtained on this material are consistent with those reported previously.[29]

(*E*)-*tert*-Butyldimethyl(2-tributylstannylvinyl)silane (3): Tributyltin hydride (4.17 g, 14.3 mmol) was treated with chlorido(1,5-cyclooctadiene)rhodium(I) dimer (50.0 mg, 0.101 mmol) at 0 °C for 5 min. The resulting mixture was treated with (*tert*-butyldimethylsilyl)-acetylene (**2**) (2.69 g, 10.0 mmol), stirred at 60 °C for 1.5 h, then cooled and subjected directly to FC (70 g of silica gel, pentane) to yield, after concentration of the relevant fractions (R_f = 0.8), the alkenylstannane **3** (2.43 g, 57%) as a clear, colorless oil. IR (film): $\tilde{\nu}$ = 2956 cm^{-1}, 2927, 2872, 2856, 1524, 1463, 1418, 1376, 1361, 1340, 1291, 1247, 1197, 1181, 1156, 1110, 1071, 1047, 1008, 958, 938, 873, 862, 825, 773, 748. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.16 (s, 6 H, $SiCH_3$), 0.80–0.97 (m, 14 H, *n*Bu CH_3, *n*Bu CH_2), 0.99 [s, 9 H, $C(CH_3)_3$], 1.20–1.41 (m, 8 H, *n*Bu CH_2), 1.42–1.59 (m, 5 H, *n*Bu CH_2), 6.58 (d, ^3J = 21.6 Hz, 1 H, 2-H), 6.99 (d, ^3J = 21.6 Hz, 1 H, 1-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = –6.5 [+, 2 C, CH_3, $Si(CH_3)_2$], 8.8 [–, C_{quat}, $C(CH_3)_3$], 9.5 (–, 3 C, *n*Bu CH_2), 10.0 [+, 3 C, $C(CH_3)_3$], 13.7 (+, 3 C, *n*Bu CH_3), 27.4 (–, 3 C, *n*Bu CH_2), 29.3 (–, 3 C, *n*Bu CH_2), 151.9 (+, CH), 152.5 (+, CH) ppm.

1-Benzyl-4-trimethylstannyl-1,2,3,6-tetrahydropyridine (4a): A thick-walled Pyrex bottle, containing a magnetic stirring bar, was charged with a solution of the heterocyclic enol triflate **5** (0.840 g, 2.74 mmol) in THF (10 mL), hexamethylditin (1.00 g, 3.05 mmol) and lithium chloride (0.777 g, 6.12 mmol). This mixture was purged with argon in an ultrasonic bath for 5 min, before tetrakis(triphenylphosphane)palladium(0) (71.0 mg, 61.2 μmol) was added. The bottle was sealed with a screw cap and heated at 60 °C for 5 h. After cooling to ambient temperature, the reaction mixture was poured into diethyl ether (100 mL), the mixture washed with water (2 × 25 mL), then dried with $MgSO_4$. The volatile components were removed under reduced pressure, and the residue subjected to FC (65 g of neutral aluminum oxide, 5:1 v/v pentane/diethyl ether elution) to yield, after concentration of the relevant fractions (R_f = 0.4), **4a** (645 mg, 72%) as a clear, colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.09 (s, 9 H, $SnCH_3$), 2.24–2.40 (m, 2 H, 5-H), 2.56 (t, ^3J = 5.4 Hz, 2 H, 6-H), 3.02 (m_C, 2 H, 2-H), 3.58 (s, 2 H, $PhCH_2N$), 5.80 (m_C, 1 H, 3-H), 7.16–7.47 (m, 5 H, Ar-H) ppm.

1-Benzyl-4-tributylstannyl-1,2,3,6-tetrahydropyridine (4b): According to GP 1, a solution of diisopropylamine (1.71 g, 16.9 mmol) in THF (80 mL), *n*BuLi (10.6 mL of a 1.60 M solution in hexane, 16.9 mmol), tributyltin hydride (4.17 g, 14.3 mmol), CuCN (641 mg, 7.16 mmol), the heterocyclic enol triflate **5** (2.00 g, 6.51 mmol) in THF (10 mL), after workup with diethyl ether (100 mL), NH_3 solution (2 × 35 mL), water (2 × 25 mL), brine (30 mL), purification with AgOAc (6.50 g, 39.0 mmol) in ethyl acetate (100 mL), water (2 × 30 mL), brine (25 mL) and FC (100 g on neutral aluminum oxide, 5:1 v/v pentane/diethyl ether elution), gave

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4b (1.29 g, 43%) as a clear, colorless oil. R_f = 0.56. IR (film): $\tilde{\nu}$ = 3027 cm^{-1}, 2957, 2842, 1604, 1462, 1369, 1336, 1283, 1250, 1142, 1111, 1013, 945, 900, 870. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.79–1.01 (m, 14 H, *n*Bu CH_3, *n*Bu CH_2), 1.19–1.39 (m, 8 H, *n*Bu CH_2), 1.40–1.60 (m, 5 H, *n*Bu CH_2), 2.31 (m_C, 2 H, 5-H), 2.52 (t, ^3J = 5.5 Hz, 2 H, 6-H), 3.00–3.09 (m, 2 H, 2-H), 3.56 (s, 2 H, PhCH_2N), 5.76 (m_C, 1 H, 3-H), 7.24–7.40 (m, 5 H, Ar-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, additional APT): δ = 8.9 (–, 3 C, *n*Bu CH_2), 13.7 (+, 3 C, *n*Bu CH_3), 27.4 (–, 3 C, *n*Bu CH_2), 29.2 (–, 3 C, *n*Bu CH_2), 32.7 (–, CH_2), 50.2 (–, CH_2), 54.77 (–, CH_2), 63.1 (–, CH_2, PhCH_2), 126.9 (+, CH, Ph), 128.1 (+, 2 C, CH, Ph), 129.3 (+, 2 C, CH, Ph), 134.8 (+, CH, C-3), 138.3 (–, C_{quat}), 138.5 (–, C_{quat}) ppm. MS (70 eV): *m/z* (%) = 465/464/463/462/461 (1/1/5/1/4), 460/459/458/457/456/455/454 (2/2/9/2/8/2/4), 408/407/406/405/404/403/402 (6/8/32/12/26/11/15), 343 (52), 271/270/269/268/267/266/265 (6/3/20/5/12/4/6), 251 (6), 224 (28), 174 (9), 172 (84), 134 (6), 91 (100) 65 (6). HRMS: calcd. for $C_{24}H_{41}NSn$ 456.1839 (correct HRMS).

2-(*trans*-3,4,4a,5,6,7,8,8a-Octahydronaphthyl) Trifluoromethanesulfonate (7): Under argon, a mixture of liquid ammonia (400 mL) and diethyl ether (200 mL) at −78 °C was treated with lithium metal (322 mg, 46.4 mmol). To the resulting blue solution was added dropwise $\Delta^{1,9}$-octalone-2 (**6**) (3.00 g, 20.0 mmol) and aniline (133 μL, 1.46 mmol) in diethyl ether (50 mL). The reaction mixture was warmed to −33 °C and stirred for 2 h. Excess lithium was oxidized with isoprene, then the mixture was warmed to 22 °C, and the remaining volatile components were removed in vacuo. The residue was dissolved in THF (250 mL), the solution cooled to −78 °C, and *N*,*N*-bis(trifluoromethanesulfonyl)aniline (19.1 g, 53.4 mmol) in THF (100 mL) was added dropwise. The reaction mixture was warmed to 22 °C overnight and stirred for a total of 24 h, it was then directly absorbed on silica gel and subjected to FC (400 g of silica, pentane) to yield, after concentration of the relevant fractions (R_f = 0.56), the product **7** (4.87 g, 86%) as a clear colorless oil. IR (film): $\tilde{\nu}$ = 2926, 2857, 1684, 1448, 1418, 1369, 1248, 1208, 1145, 1081, 1060, 1048, 1024, 998, 963, 886, 854, 615 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.95−1.60 (m, 6 H), 1.79 (m_c, 6 H), 2.20−2.36 (dd, ^3J = 6.2 Hz, ^3J = 12.0 Hz, 1 H), 2.37−2.53 (m, 1 H), 5.51 (s, 1 H, 1-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 26.3 (–, CH_2), 26.9 (−, CH_2), 28.0 (–, CH_2), 29.7 (–, CH_2), 32.3 (–, CH_2), 32.5 (−, CH_2), 39.7 (+, CH), 40.9 (+, CH), 117.0 (q, C_{quat}, ^1J = 340 Hz, CF_3), 123.1 (+, C-1), 149.0 (C_{quat}, C-2) ppm. MS (70 eV): *m/z* (%) = 284 (33) [M^+], 283 (17) [M^+ − H], 151 (100), 133 (47), 119 (5), 95 (18), 91 (31), 69 (44) [CF_3^+], 55 (37), 41 (40). $C_{11}H_{15}F_3O_3S$ (284.3): calcd. C 46.47, H 5.32; found C 46.27, H 5.38.

Tributyl(*trans*-3,4,4a,5,6,7,8,8a-octahydronaphth-2-yl)stannane (8): According to GP 1, a solution of diisopropylamine (2.92 mL, 20.8 mmol) in THF (140 mL), *n*BuLi (8.80 mL of a 2.36 M solution in hexane, 20.8 mmol), tributyltin hydride (4.75 mL, 17.6 mmol), CuCN (789 mg, 8.80 mmol) and the bicyclic enol triflate **7** (2.27 g, 7.95 mmol), after workup with pentane (100 mL) aqueous NH_3 solution purification with AgOAc (4.00 g, 24.0 mmol) in ethyl acetate (140 mL), water (2 × 45 mL) and FC (93 g on silica gel deactivated with 10% NEt_3, petroleum ether), gave compound **8** (3.31 g, 98%) as a clear, colorless oil. R_f = 0.7. IR (film): $\tilde{\nu}$ = 2957 cm^{-1}, 2919, 2842, 1604, 1464, 1418, 1376, 1357, 1340, 1286, 1250, 1228, 1193, 1148, 1110, 1071, 1023, 960, 910, 875, 869, 846, 688, 663, 595. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.91–1.02 (m, 15 H, *n*Bu H), 1.03–1.37 (m, 4 H), 1.38–1.51 (m, 6 H, *n*Bu H), 1.52–1.83 (m, 12 H), 2.30–2.42 (m, 2 H, 3-H), 5.77 (m_c, 1 H, 1-H.) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 9.2 (–, CH_2), 13.9 (+, CH_3), 26.9 (–, CH_2), 27.1 (–, CH_2) 27.3 (–, CH_2), 27.8 (–, CH_2), 29.7 (–, CH_2), 31.4 (–, CH_2), 33.4 (–, CH_2), 33.6 (–, CH_2), 34.1 (–, CH_2), 41.2 (+, CH), 44.8 (+, CH), 139.5 (C_{quat}, C-2), 143.2 (+, C-1) ppm. MS (70 eV): *m/z* (%) = 424 (2) [M^+], 371/370/369/368/367/366/365 (15/19/100/40/79/31/45) [$M^+ - C_4H_9$], 315/314/313/312/311/310/309 (2/2/18/6/14/6/7) [$M^+ - C_4H_9 - C_4H_8$], 292/291/290/289/288 (0.5/1/0.5/1/0.5) [$SnBu_3^+$], 259/258/257/256/255/254/253 (4/2/30/8/25/7/17) [$M^+ - C_4H_9 - 2\times C_4H_8$], 179/178/177/176/175 (2/1/4/1/2) [$SnBu^+$], 135 (10) [$M^+ - SnBu_3$], 122/120/119/118/117/116 (1/5/2/4/2/3) [Sn^+], 91 (9), 67 (4), 41 (3). $C_{22}H_{42}Sn$ (424.9): calcd. C 62.13, H 9.96; found C 62.05, H 10.07.

2-(*trans*-5-*tert*-Butoxy-4a-methyl-3,4,4a,5,6,7,8,8a-octahydronaphthyl) Trifluoromethanesulfonate (10): Under argon, a mixture of liquid ammonia (200 mL) and THF (150 mL) at −78 °C was treated with lithium metal (233 mg, 31.2 mmol). To the resulting blue solution was added dropwise the α,β-unsaturated ketone **9** (3.20 g, 13.6 mmol) and aniline (100 μL, 1.10 mmol) in THF (75 mL). The reaction mixture was warmed to −33 °C and stirred for 2 h. Excess lithium was oxidized with isoprene, then the mixture was warmed to 22 °C, and the remaining volatile components were removed en vacuo. The residue was dissolved in THF (150 mL), the solution cooled to −78 °C, and *N*,*N*-bis(trifluoromethanesulfonyl)aniline (12.1 g, 32.5 mmol) in THF (100 mL) was added dropwise. The reaction mixture was warmed to 22 °C overnight and stirred for a total of 24 h, it was then directly absorbed on silica gel and subjected to FC (80 g of silica, 20:1 v/v pentane/diethylether elution) to yield, after concentration of the relevant fractions (R_f = 0.43), the product **10** (4.54 g, 90%) as a clear colorless oil. IR (film): $\tilde{\nu}$ = 2976, 2933, 2867, 1685, 1489, 1417, 1363, 1319, 1247, 1208, 1143, 1091, 1078, 1042, 1008, 991, 958, 929, 871, 816, 764 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.73 (s, 3 H, CH_3), 0.80−0.95 (m, 3 H), 1.02 [s, 9 H, $C(CH_3)_3$], 1.33−1.63 (m, 5 H), 1.77 (dd, ^3J = 5.0 Hz, ^3J = 11.3 Hz, 1 H, 8a-H) 1.91−2.23 (m, 2 H), 2.69 (dd, ^3J = 5.9 Hz, ^3J = 8.8 Hz, 1 H, 5-H), 5.18 (s, 1 H, 1 H). ^{13}C NMR (62.9 MHz, C_6D_6, add. DEPT): δ = 10.2 (+, CH_3), 24.6 (–, CH_2), 25.2 (–, CH_2), 26.4 (–, CH_2), 28.9 [+, 3 C, $C(CH_3)_3$], 30.3 (–, CH_2), 34.1 (–, CH_2), 37.5 (C_{quat}, C-4a), 43.2 (+, C-8a), 73.0 (+, C-5), 77.2 [C_{quat}, $C(CH_3)_3$], 121.3 (+, CH, C-1), 122.9 (q, C_{quat}, ^1J = 315 Hz, CF_3), 148.4 (C_{quat}, C-2). MS (70 eV): *m/z* (%) = 370 (2) [M^+], 313 (40) [$M^+ - C_4H_9$], 295 (21), 269 (4), 229 (3), 181 (100), 163 (22), 121 (8), 111 (3), 57 (67) [$C_4H_9^+$]. $C_{16}H_{25}F_3O_4S$ (370.4): calcd. C 51.88, H 6.80; found C 51.61, H 6.57.

(5-*tert*-Butoxy-4a-methyl-3,4,5,6,7,8,8a-heptahydronaphthyl)tributylstannane (11): According to GP 1, a solution of diisopropylamine (3.66 mL, 26.0 mmol) in THF (150 mL), *n*BuLi (11.0 mL, 26.0 mmol, 2.36 M), tributyltin hydride (5.93 mL, 22.1 mmol), CuCN (986 mg, 11.0 mmol) and the triflate **10** (3.70 g, 10.0 mmol), after workup with pentane (150 mL), aqueous NH_3 solution (3 × 40 mL), purification with AgOAc (4.99 g, 30.0 mmol) in ethyl acetate (150 mL), water (2 × 50 mL) and FC (134 g on silica gel deactivated with 10% NEt_3, light petroleum), gave compound **11** (4.96 g, 97%) as a clear, colorless oil. (R_f = 0.5, 20:1 v/v light petroleum/diethyl ether). IR (film): $\tilde{\nu}$ = 2956 cm^{-1}, 2926, 1685, 1464, 1427, 1418, 1376, 1361, 1272, 1248, 1192, 1048, 1020, 1002, 880, 877, 844, 768. ^1H NMR (250 MHz, C_6D_6): δ = 0.78–1.05 (m, 15 H, *n*Bu CH_3, *n*Bu CH_2), 1.08 (s, 3 H, CH_3), 1.11 [s, 9 H, C-$(CH_3)_3$], 1.20–1.79 (m, 19 H), 1.83–1.97 (m, 1 H), 2.00–2.12 (m, 1 H) 2.30–2.42 (m, 2 H, 3-H), 2.95 (dd, ^3J = 7.0, ^3J = 8.4 Hz, 1 H, 5-H), 5.87 (d, ^3J = 0.7 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, add. DEPT): δ = 9.2 (-, *n*Bu CH_2), 10.8 (+, CH_3), 14.0 (+, *n*Bu CH_3), 25.1 (–, CH_2), 27.3 (–, CH_2), 27.8 (–, *n*Bu CH_2), 29.2 [+, 3 C, $C(CH_3)_3$], 29.7 (–, *n*Bu CH_2), 30.7 (–, CH_2), 31.0 (–, CH_2), 35.5 (–, CH_2), 37.8 (C_{quat}, C-4a), 46.1 (+, C-8a), 72.5 [C_{quat}, $C(CH_3)$], 77.6 (+, C-5), 139.3 (C_{quat}, C-2), 141.2 (+, C-1) ppm. MS (70 eV): *m/z* (%) = 512 (1) [M^+], 457/456/455/454/453/452/451 (16/

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24/100/44/83/33/46) [$M^+ - C_4H_9$], 401/400/399/398/397/396/395 (1/1/10/4/8/4/5) [$M^+ - C_4H_9 - C_4H_8$], 345/344/343/342/341/340/339 (1/2/13/3/10/3/4) [$M^+ - C_4H_9 - 2\times C_4H_8$], 293/292/291/290/289/288/287 (1/1/6/3/5/2/3) [$SnBu_3^+$], 237/236/235/234/233/232/231 (1/1/4/2/3/2/1) [$SnBu_2H^+$], 179/178/177/176/175 (2/1/4/1/2) [$SnBu^+$], 147 (6), 105 (5), 57 (18) [Bu^+], 41 (2). $C_{27}H_{52}OSn$ (511.4): calcd. C 63.41, H 10.25; found C 63.44, H 9.98.

[(*E*)-2-(2-Bromocyclohex-1-enyl)vinyl]*tert*-butyldimethylsilane (14): According to GP 2, a solution of bromoenol triflate **13** (309 mg, 1.00 mmol) in DMF (10 mL) with the alkenylstannane **3** (431 mg, 1.00 mmol), after treatment with tetrakis(triphenylphosphane)palladium (57.8 mg, 50.0 μmol), LiCl (127 mg, 3.00 mmol) at 90 °C for 12 h, workup with diethyl ether (50 mL), water (2 × 20 mL), extraction with diethyl ether (2 × 20 mL), and FC (55 g of silica gel, pentane), gave compound **14** (240 mg, 80%) as a colorless oil. R_f = 0.6. IR (film): $\tilde{\nu}$ = 2951 cm^{-1}, 2929, 2857, 2882, 1614, 1575, 1470, 1462, 1448, 1435, 1409, 1389, 1361, 1334, 1247, 1193, 1137, 1089, 1007, 987, 973, 938, 874, 832, 811, 791. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.09 [s, 6 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $C(CH_3)_3$], 1.72 [m_c, 4 H, 4′(5′)-H], 2.29 (m_C, 2 H, 6′-H), 2.64 (m, 2 H, 3′-H), 5.92 (d, ^3J = 19.2 Hz, 1 H, 1-H), 7.10 (d, ^3J = 19.2 Hz, 1 H, 2-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$ additional APT): δ = –5.8 [+, 2 C, $Si(CH_3)_2$], 16.9 [–, C_{quat}, $C(CH_3)_3$], 22.4 (–, CH_2), 24.9 (–, CH_2), 26.8 [+, 3 C, $C(CH_3)_3$] 27.4 (–, CH_2), 38.1 (–, CH_2), 126.0 (–, C_{quat}), 127.8 (+, CH, C-1), 133.2 (–, C_{quat}), 145.2 (+, CH, C-2) ppm. MS (70 eV): *m*/*z* (%) = 302/300 (18/18) [M^+], 246/244 (38/38), 245/243 (100/97), 223 (21), 221 (10), 201 (4), 189 (7), 175 (10), 167 (13), 165 (17), 163 (30), 149 (12), 147 (27), 139/137 (74/76), 135 (8), 123 (13), 121 (17), 105 (54), 95 (13), 93 (19), 91 (24), 83 (14), 79 (27), 73 (45), 67 (12), 59 (49), 57 (46). HRMS: calcd. for $C_{14}H_{25}BrSi$ 300.0909 (correct HRMS).

5-(2-Bromocyclohex-1-en-1-yl)-2,3-dihydro-1,4-dioxine (15): According to GP 2, the bromoenol triflate **13** (309 mg, 1.00 mmol) in DMF (10 mL) and the alkenylstannane **25** (450 mg, 1.20 mmol), after treatment with tetrakis(triphenylphosphane)palladium (116 mg, 100 μmol), LiCl (127 mg, 3.00 mmol) at 90 °C for 14 h and workup with diethyl ether (50 mL), water (2 × 20 mL), extraction with diethyl ether (2 × 25 mL) and FC (45 g of silica gel, 10:1 v/v pentane/diethyl ether elution), gave compound **15** (201 mg, 82%) as a clear, colorless oil. R_f = 0.5. IR (film): $\tilde{\nu}$ = 2931 cm^{-1}, 2870, 1666, 1642, 1554, 1435, 1368, 1333, 1308, 1283, 1257, 1229, 1155, 1114, 1091, 1027, 982, 944, 920, 878, 829, 795, 750. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.56–1.85 [mc, 4 H, 4′(5′)-H], 2.23 (m_c, 2 H, 6′-H), 2.54 (m, 2 H, 3′-H), 4.09 [m_c, 4 H, 2(3)-H], 6.16 (s, 1 H, 6-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = 22.1 (–, CH_2), 24.42 (–, CH_2), 30.7 (–, CH_2), 37.1 (–, CH_2), 64.2 (–, CH_2, -OCH_2-), 64.4 (–, CH_2, -OCH_2-), 122.3 (–, C_{quat}), 126.6 (+, CH, C-6), 139.5 (–, C_{quat}), 136.7 (–, C_{quat}) ppm. MS (70 eV): *m*/*z* (%) = 246/244 (95/95) [M^+], 235 (8), 189/187 (99/100), 179/177 (8/8), 165 (40), 137 (10), 121 (10), 108 (10), 105 (7), 93 (14), 91 (26), 81 (12), 79 (85), 77 (55), 65 (20), 57 (7). HRMS: calcd. for $C_{10}H_{13}BrO_2$ 244.0100 (correct HRMS).

1-Benzyl-4-(2-bromocyclohex-1-enyl)-1,2,3,6-tetrahydropyridine (16): According to GP 2, the bromoenol triflate **13** (309 mg, 1.00 mmol) in NMP (5.00 mL) and the alkenylstannane **4b** (505 mg, 1.09 mmol), after treatment with [$Pd_2(dba)_3$] (46.0 mg, 50.2 μmol), LiCl (127 mg, 3.00 mmol) at 65 °C for 5 h, workup with diethyl ether (50 mL), water (2 × 20 mL), extraction with diethyl ether (2 × 20 mL) and FC (30 g on silica gel, 1:1 v/v pentane/diethyl ether elution), gave compound **16** (279 mg, 84%) as a clear, yellow oil. R_f = 0.4. IR (film): $\tilde{\nu}$ = 3027 cm^{-1}, 2927, 2858, 2798, 1622, 1595, 1494, 1453, 1367, 1327, 1158, 1126, 1074, 1028, 977, 877, 776, 729. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.62–1.79 [m_c, 4 H, 4′(5′)-H], 2.10–2.30 (m, 3 H), 2.48–2.59 (m, 3 H), 2.64 (t, ^3J = 5.5 Hz, 2 H), 3.08 (m_c, 2 H), 3.64 (s, 2 H, PhCH_2), 5.46 (m_c, 1 H, 3-H), 7.24–7.42 (m, 5 H, Ph-*H*) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$ add. APT): δ = 22.9 (–, CH_2), 24.6 (–, CH_2), 27.9 (–, CH_2), 31.3 (–, CH_2), 36.7 (–, CH_2), 49.8 (–, CH_2), 52.5 (–, CH_2), 62.7 (–, CH_2, PhCH_2), 118.4 (–, C_{quat}), 122.7 (+, CH, C-3), 127.3 (+, CH, Ar), 128.5 (+, 2 C, CH, Ar), 129.5 (+, 3 C), 138.5 (–, C_{quat}), 138.9 (–, C_{quat}) ppm. MS (70 eV): *m*/*z* (%) = 333/331 (33/33) [M^+], 252 (88) [M^+ – Br], 234 (13), 233 (10), 172 (33), 158 (17), 133 (20), 117 (11), 105 (17), 91 (100) [Bn^+], 77 (18), 65 (21). HRMS: calcd. for $C_{18}H_{22}BrN$ 331.0937 (correct HRMS).

***trans*-2-(2′-Bromocyclohex-1′-enyl)-3,4,4a,5,6,7,8,8a-octahydronaphthalene (17):** According to GP 2, the bromoenol triflate **13** (403 mg, 1.30 mmol) with the bicycloalkenylstannane **8** (424 mg, 1.00 mmol) in DMF (8 mL), after treatment with $[Pd_2(dba)_3]\cdot CHCl_3$ (104 mg, 100 μmol), $AsPh_3$ (24 mg, 78.0 μmol), LiCl (128 mg, 3 mmol), CuI (10 mg, 52 μmol), at 65 °C for 5 h, workup with diethyl ether (50 mL), water (2 × 20 mL), extraction with diethyl ether (2 × 35 mL) and FC (40 g of silica gel, light petroleum), gave compound **17** (261 mg, 89%) as a colorless wax. R_f = 0.7. IR (film): $\tilde{\nu}$ = 2918 cm^{-1}, 2851, 2824, 1640, 1446, 1326, 978. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.80–1.19 (m, 3 H), 1.20–1.53 (m, 3 H), 1.55–1.86 (m, 10 H), 1.96–2.35 [$m_{coalesced}$, 4 H, 3(3′)-H], 2.47–2.59 (m, 2 H, 6′-H), 5.20 (s, 1 H, 1-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 22.6 (–, CH_2), 24.7 (–, CH_2), 26.8 (–, CH_2), 26.9 (–, CH_2), 27.3 (–, CH_2), 30.1 (–, CH_2), 31.9 (–, CH_2), 33.0 (–, CH_2), 33.4 (–, CH_2), 36.3 (–, CH_2), 40.4 (+, CH), 42.1 (+, CH), 117.7 (C_{quat}, C-2), 129.4 (+, C-H, C-1), 139.5 (C_{quat}, C-1′), 139.6 (C_{quat}, C-2′) ppm. MS (70 eV): *m*/*z* (%) = 296/294 (13/13) [M^+], 215 (100) [M^+ – Br], 187 (7), 133 (10), 95 (6), 91 (6), 67 (4), 41 (3). HRMS: calcd. for $C_{16}H_{23}Br$ 294.0984 (correct HRMS).

2-(2′-Bromocyclohex-1′-enyl)-5-*tert*-butoxy-4a-methyl-1,2,3,3,4,4a,5,6,8a-octahydronaphthalene (18): According to GP 2, the bromoenol triflate **13** (0.713 g, 2.30 mmol) with the bicycloalkenylstannane **11** (1.02 g, 2.00 mmol) in NMP (20 mL), after treatment with $[Pd_2(dba)_3]\cdot CHCl_3$ (104 mg, 100 μmol), $AsPh_3$ (24.0 mg, 78.0 μmol), LiCl (384 mg, 9.05 mmol), CuI (10.0 mg, 52.0 μmol) at 65 °C for 5 h and after workup with diethyl ether (75 mL), water (2 × 25 mL), extraction with diethyl ether (2 × 20 mL) and FC (90 g of silica gel, 20:1 v/v light petroleum/diethyl ether elution), gave compound **18** (716 mg, 94%) as a colorless wax. R_f = 0.5. IR (film): $\tilde{\nu}$ = 2927 cm^{-1}, 2858, 1643, 1456, 1446, 1387, 1378, 1362, 1265, 1248, 1137, 1124, 1075, 1050, 1019, 1000, 959, 848, 740. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.84 (s, 3 H, CH_3), 1.18 [s, 9 H, $C(CH_3)_3$], 1.21–1.40 (m, 4 H), 1.43–1.81 (m, 7 H), 1.85–2.09 (m, 2 H), 2.10–2.28 (m, 4 H), 2.41–2.55 (m, 2 H), 3.08 (dd, ^3J = 6.8, ^3J = 11.0 Hz, 1 H, 5-H), 5.28–5.31 (d, ^3J = 1.3 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 10.5 (+, CH_3), 22.5 (–, CH_2), 24.4 (–, CH_2), 24.7 (–, CH_2), 24.8 (–, CH_2), 26.7 (–, CH_2), 29.1 [+, 3 C, $C(CH_3)_3$], 30.7 (–, CH_2), 32.0 (–, CH_2), 34.1 (–, CH_2), 36.3 (–, CH_2), 37.4 (C_{quat}, C-4a), 43.7 (+, CH, C-8a), 72.7 [C_{quat}, $C(CH_3)_3$], 77.4 (+, CH, C-5), 117.8 (C_{quat}, C-2), 127.5 (+, C-1), 139.0 (C_{quat}, C-2′), 139.4 (C_{quat}, C-1′) ppm. MS (70 eV): *m*/*z* (%) = 382/380 (59/58) [M^+], 326/324 (44/52) [$M^+ - C_4H_8$], 307/305 (62/52), 279 (8), 251 (10), 245 (52) [$M^+ - Br - C_4H_8$], 243 (79), 227 (98) [$M^+ - C_4H_8 - H_2O - Br$], 225 (52), 199 (13), 159 (9), 152 (10), 145 (27), 93 (38), 81/79 (21/20), 57 (100) [$C_4H_9^+$], 41 (25). HRMS: calcd. for $C_{21}H_{33}BrO$ 380.1717 (correct HRMS).

***tert*-Butyl (*E*)-3-{2′-[(*E*)-2′′-(*tert*-Butyldimethylsilyl)vinyl]cyclohex-1′-enyl}acrylate (19):** According to GP 3, the bromobutadiene **14** (230 mg, 0.764 mmol) in DMF (10.0 mL) after treatment with

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$Pd(OAc)_2$ (17.1 mg, 0.0760 mmol), PPh_3 (60.1 mg, 0.229 mmol), NEt_3 (232 mg, 2.29 mmol), *tert*-butyl acrylate (490 mg, 3.82 mmol) at 90 °C for 14 h, workup with diethyl ether (50 mL), water (20 mL), extraction with diethyl ether (25 mL) and FC (30 g on silica gel, 20:1 v/v pentane/diethyl ether elution), gave the 1,3,5-hexatriene **19** as a colorless solid (208 mg, 78%), m.p. 155–157 °C. Good-quality crystals for X-ray diffraction were grown from pentane/diethyl ether (20:1) at 23 °C by slow evaporation of the solvents. R_f = 0.3. IR (film): $\tilde{\nu}$ = 2951 cm^{-1}, 2930, 2883, 2857, 1708, 1621, 1470, 1462, 1391, 1366, 1340, 1305, 1278, 1248, 1202, 1147, 1070, 1038, 1007, 981, 938, 828, 813, 792, 751, 728. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.09 [s, 6 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $SiC(CH_3)_3$], 1.15 [s, 9 H, $CO_2C(CH_3)_3$], 1.59–1.76 [m, 4 H, 4′(5′)-H], 2.28 (m_c, 2 H, 3′-H), 2.36 (m, 2 H, 6′-H), 5.81 (d, ^3J = 15.4 Hz, 1 H, 3-H), 6.05 (d, ^3J = 18.7 Hz, 1 H, 1′′-H), 7.33 (d, ^3J = 18.9 Hz, 1 H, 2′′-H), 8.06 (d, ^3J = 15.7 Hz, 1 H, 2-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = –5.8 [+, 2 C, CH_3, $Si(CH_3)_2$], 16.9 [–, C_{quat}, $C(CH_3)_3$], 22.4 (–, CH_2), 22.5 (–, CH_2), 26.5 (–, CH_2), 26.8 [+, 3 C, CH_3, $C(CH_3)_3$], 26.9 (–, CH_2), 28.4 [+, 3 C, $CO_2C(CH_3)_3$], 80.2 [–, C_{quat}, CH_3, $C(CH_3)_3$], 118.6 (–, C_{quat}), 129.0 (+, CH, C-1′′), 131.6 (–, C_{quat}), 140.5 (+, CH, C-2′′), 141.2 (+, CH, C-3), 141.3 (+, CH, C-2), 175.6 (–, C_{quat}, C=O) ppm. MS (70 eV): *m*/*z* (%) = 348 (7) [M^+], 292 (9) [$M^+ - C_4H_8$], 247 (11), 235 (100), 207 (9), 191 (7), 189 (20), 161 (14), 159 (6), 132 (6), 131 (18), 116 (6), 115 (32) 103 (7), 91 (10), 75 (68), 57 (21) [$C_4H_9^+$]. HRMS: calcd. for $C_{21}H_{36}O_2Si$ 348.2477 (correct HRMS).

***tert*-Butyl (*E*)-3-{2′-[(*E*)-2′′-(Trimethylsilyl)vinyl]cyclohex-1′-enyl}acrylate (19-SiMe$_3$):** According to GP 3, the bromobutadiene **14**-$SiMe_3$ (200 mg, 0.775 mmol) in DMF (5.00 mL), after treatment with $Pd(OAc)_2$ (17.4 mg, 0.0780 mmol), PPh_3 (61.0 mg, 0.233 mmol), NEt_3 (235 mg, 2.33 mmol), *tert*-butyl acrylate (497 mg, 3.88 mmol) at 90 °C for 14 h, workup with diethyl ether (50 mL), water (20 mL) extraction with diethyl ether (25 mL) and FC (24 g of silica gel, 20:1 v/v pentane/diethyl ether elution), gave **19**-$SiMe_3$ (211 mg, 89%) as a colorless wax. The analytical data obtained on this material are identical with those reported previously.[7b]

***tert*-Butyl (*E*)-3-[2′-(5′′,6′′-Dihydro-1′′,4′′-dioxin-2′′-yl)cyclohex-1′-enyl]acrylate (20):** According to GP 3, the bromobutadiene **15** (230 mg, 0.764 mmol) in DMF/water (10:1) (1.10 mL), after treatment with the palladacycle (7.6 mg, 8.2 μmol), NaOAc (40.2 mg, 0.490 mmol), nBu_4NBr (52.5 mg, 0.163 mmol), *tert-b*utyl acrylate (105 mg, 0.816 mmol) at 105 °C for 12 h, workup with diethyl ether (30 mL), water (2 × 10 mL) extraction with diethyl ether (10 mL) and FC (18 g of silica gel, 5:1 v/v pentane/diethyl ether elution), gave compound **20** (31.1 mg, 65%) as a colorless wax. R_f = 0.4. IR (film): $\tilde{\nu}$ = 2974 cm^{-1}, 2930, 2871, 1703, 1640, 1608, 1458, 1391, 1366, 1311, 1278, 1258, 1150, 1091, 1028, 985, 922, 882, 855, 796. ^1H NMR (300 MHz, C_6D_6): δ = 1.49 [s, 9 H, $CO_2C(CH_3)_3$], 1.57–1.71 [m, 4 H, 4′(5′)-H], 2.16–2.24 (m, 2 H, 6′-H), 2.26–2.35 (m, 2 H, 3′-H), 4.11 [m_c, 4 H, 5′′(6′′)-H], 5.74 (d, ^3J = 15.9 Hz, 1 H, 3-H), 5.96 (m_c, 1 H, 3′′-H), 7.88 (d, ^3J = 15.9 Hz, 1 H, 2-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = 22.09 (–, CH_2), 22.14 (–, CH_2), 25.87 (–, CH_2), 28.20 [+, 3 C, $CO_2C(CH_3)_3$], 28.88 (–, CH_2), 64.20 (–, CH_2, -OCH_2-), 64.34 (–, CH_2, -OCH_2-), 79.74 [–, C_{quat}, $CO_2C(CH_3)_3$], 117.16 (+, CH, C-3), 128.06 (+, CH, C-3′′), 131.18 (–, C_{quat}), 135.71 (–, C_{quat}), 138.34 (–, C_{quat}), 143.42 (+, CH, C-2), 167.25 (–, C_{quat}, C=O) ppm. MS (70 eV): *m*/*z* (%) = 292 (7) [M^+], 236 (31) [$M^+ - C_4H_8$], 235 (34) [$M^+ - C_4H_9$], 219 (12), 217 (7), 191 (100), 162 (6), 149 (67), 134 (6), 105 (7), 91 (15), 77 (8), 57 (26) [$C_4H_9^+$]. HRMS: calcd. for $C_{17}H_{24}O_4$ 292.1676 (correct HRMS).

***tert*-Butyl (*E*)-3-[2′-(1′′-Benzyl-1′′,2′′,3′′,6′′-tetrahydropyridin-4′′-yl)cyclohex-1′-enyl]acrylate (21):** According to GP 3, the bromobutadiene **16** (110 mg, 0.331 mmol) in DMF/water (10:1) (2.2 mL) was treated with the palladacycle (16.0 mg, 16.6 μmol), NaOAc (82.0 mg, 0.993 mmol), nBu_4NBr (70.0 mg, 0.331 mmol), *tert*-butyl acrylate (1.00 mL) at 105 °C for 4 h. For complete consumption of the bromobutadiene **16**, a second portion of the palladacycle (16.0 mg, 16.6 μmol) was added and the mixture again heated at 105 °C for 4 h. Workup with diethyl ether (45 mL), water (15 mL), extraction with diethyl ether (15 mL) and FC (22 g of silica gel, 10:1 v/v diethyl ether/methanol elution) gave compound **21** (89.2 mg, 71%) as a colorless wax. R_f = 0.5. IR (film): $\tilde{\nu}$ = 3024 cm^{-1}, 2974, 2930, 2862, 1761, 1703, 1614, 1476, 1452, 1390, 1366, 1310, 1275, 1257, 1149, 1049, 985, 884, 855, 733. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.38 [m, 4 H, 4′(5′)-H], 1.47 [s, 9 H, $CO_2C(CH_3)_3$], 1.91–2.01 (m, 4 H), 2.02–2.11 (m, 2 H), 2.44 (t, ^3J = 5.5 Hz, 2 H), 2.87 (m_c, 2 H), 3.38 (s, 2 H, $PhCH_2$), 5.33 (m_c, 1 H, 3′′-H), 6.01 (d, ^3J = 15.7 Hz, 1 H, 3-H), 7.09–7.22 (m, 3 H, Ph-*H*), 7.35–7.45 (m, 2 H, Ph-*H*), 8.19 (d, ^3J = 15.8 Hz, 1 H, 2-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = 22.5 (–, CH_2), 22.6 (–, CH_2), 24.9 (–, CH_2), 25.4 (–, CH_2), 28.5 [+, 3 C, $CO_2C(CH_3)_3$], 30.5 (–, CH_2), 49.7 (–, CH_2), 52.9 (–, CH_2), 62.9 (–, CH_2, $PhCH_2$), 79.9 [C_{quat}, $CO_2C(CH_3)_3$], 116.7 (+, CH, C-3′′), 124.7 (+, CH), 127.3 (+, CH, Ph), 128.0 (–, C_{quat}), 128.5 (+, 2 C, CH, Ph), 129.4 (+, 2 C, CH, Ph), 136.9 (–, C_{quat}), 138.5 (–, C_{quat}, Ph), 144.2 (+, CH, C-2), 149.2 (–, C_{quat}), 167.7 (–, C_{quat}, C=O) ppm. MS (70 eV): *m*/*z* (%) = 379 (6) [M^+], 333 (7), 323 (7) [$M^+ - C_4H_8$], 322 (22) [$M^+ - C_4H_9$], 278 (6), 252 (33), 220 (5), 205 (17), 172 (7), 149 (7), 135 (9), 122 (24), 105 (37), 91 (100) [Bn^+], 77 (32), 65 (11), 57 (22) [$C_4H_9^+$]. HRMS: calcd. for $C_{25}H_{33}NO_2$ 379.2513 (correct HRMS).

***tert*-Butyl (*E*)-3-[2′-(*trans*-3′′,4′′,4a′′,5′′,6′′,7′′,8′′,8a′′-Octahydronaphth-2′′-enyl)cyclohex-1′-enyl]acrylate (22-*t*Bu):** According to GP 3, the bromobutadiene **17** (340 mg, 1.15 mmol) in DMF/MeCN/H_2O (10:5:1) (6 mL) was treated with the palladacycle (41.0 mg, 46.0 μmol), nBu_4NOAc (722 mg, 2.39 mmol), *tert*-butyl acrylate (2.5 mL) at 105 °C for 4 h. For complete consumption of the bromobutadiene **17**, a second portion of the palladacycle (41.0 mg, 46.0 μmol) was added and the mixture again heated at 105 °C for 4 h. Workup with diethyl ether (50 mL), water (2 × 30 mL), extraction with diethyl ether (50 mL) and FC (31 g of silica gel, 20:1 v/v light petroleum/diethyl ether elution) gave compound **22**-*t*Bu (228 mg, 58%) as a colorless wax. R_f = 0.2. IR (film): $\tilde{\nu}$ = 2976 cm^{-1}, 2922, 2852, 1704, 1613, 1449, 1391, 1367, 1311, 1296, 1273, 1255, 1207, 1149, 1068, 1036, 986, 911, 885, 854, 825, 734, 648. ^1H NMR (250 MHz, C_6D_6): δ = 0.83–1.13 (m, 4 H), 1.14–1.23 (m, 7 H), 1.28 [s, 9 H, $C(CH_3)_3$], 1.29–1.76 (m, 5 H), 1.95–2.13 (m, 6 H), 5.14 (s, 1 H, 1′′-H), 5.98 (d, ^3J = 15.8 Hz, 1 H, 2-H), 8.12 (d, ^3J = 15.8 Hz, 1 H, 3-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, add. DEPT): δ = 22.6 (–, CH_2), 22.7 (–, CH_2), 25.3 (–, CH_2), 27.0 (–, CH_2), 27.2 (–, CH_2), 28.3 [+, 3 C, $C(CH_3)_3$], 29.2 (–, CH_2), 30.4 (–, CH_2), 30.8 (–, CH_2), 33.5 (–, CH_2), 33.6 (–, CH_2), 40.8 (+, CH), 42.5 (+, CH), 79.2 [C_{quat}, $CO_2C(CH_3)_3$], 117.0 (+, C-2), 128.0 (C_{quat}), 132.0 (+, C-1′′), 138.2 (C_{quat}), 144.4 (+, C-3), 149.7 (C_{quat}), 167.8 (C_{quat}, C=O) ppm. MS (70 eV): *m*/*z* (%) = 342 (1) [M^+], 286 (21) [$M^+ - C_4H_8$], 241 (12), 226 (10), 218 (2), 192 (11), 190 (10), 162 (4), 146 (14), 145 (100), 105 (14), 91 (22), 84 (48), 69 (17), 57 (66) [$C_4H_9^+$], 56 (65) [$C_4H_8^+$], 41 (56). HRMS: calcd. for $C_{23}H_{34}O_2$ 342.2561 (correct HRMS).

Methyl (E)-3-[2′-*trans*-(3′′,4′′,4a′′,5′′,6′′,7′′,8′′,8a′′-Octahydronaphth-2′′-enyl)cyclohex-1′-enyl]acrylate (22-Me): According to GP 3, bromobutadiene **17** (205 mg, 0.695 mmol) in DMF/MeCN/H_2O (10:5:1) (6 mL) was treated with the palladacycle (49.0 mg, 55.0 μmol), nBu_4NOAc (418 mg, 1.39 mmol) and methyl acrylate

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(298 mg, 3.48 mmol) at 105 °C for 4 h. For complete consumption of **17**, a second portion of the palladacycle (49.0 mg, 55.0 μmol) was added, and the mixture again heated at 105 °C for 4 h. Workup with diethyl ether (50 mL), water (2 × 30 mL), extraction with diethyl ether (50 mL) and FC (27 g of silica gel, 20:1 v/v light petroleum/diethyl ether elution) gave compound **22**-Me (176 mg, 84%) as a colorless wax. R_f = 0.3. IR (film): $\tilde{\nu}$ = 2921 cm^{-1}, 2851, 1721, 1615, 1433, 1296, 1273, 1164, 1134, 1068, 1037, 1018, 923, 880, 852, 752, 665. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.90–1.11 (m, 3 H), 1.13–1.47 (m, 3 H), 1.52–1.80 (m, 10 H), 1.94–2.28 (m, 6 H), 3.72 (s, 3 H, CH_3), 5.14 (s, 1 H, 1′′-H), 5.71 (d, ^3J = 15.1 Hz, 1 H, 2-H), 7.78 (d, ^3J = 15.1 Hz, 1 H, 3-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 22.2 (–, CH_2), 22.4 (–, CH_2), 25.1 (–, CH_2), 26.7 (–, CH_2), 26.8 (–, CH_2), 28.8 (–, CH_2), 30.0 (–, CH_2), 30.5 (–, CH_2), 33.1 (–, CH_2), 33.3 (–, CH_2), 40.5 (+, CH), 42.3 (+, CH), 51.2 (+, CH_3), 113.4 (+, C-2), 127.4 (C_{quat}), 132.1 (+, C-1′′), 137.6 (C_{quat}), 145.6 (+, C-3), 151.6 (C_{quat}), 168.5 (C_{quat}, C=O) ppm. MS (70 eV): *m*/*z* (%) = 300 (39) [M^+], 294 (2), 269 (2) [$M^+ - OCH_3$], 257 (1), 241 (32) [$M^+ - CO_2CH_3$], 226 (8), 192 (2), 159 (3), 145 (100), 131 (7), 117 (7), 91 (10), 67 (5), 55 (4), 41 (6). HRMS: calcd. for $C_{20}H_{28}O_2$ 300.2091 (correct HRMS).

***tert*-Butyl (*E*)-3-[2′-(5′′-*tert*-Butoxy-4a′′-methyl-1′′,2′′,3′′,4′′,5′′,6′′,8a′′-heptahydronaphth-2′′-enyl)cyclohex-1′-enyl]acrylate (23):** According to GP 3, the bromobutadiene **18** (270 mg, 700 μmol) in DMF/MeCN/H_2O (10:5:1) (5 mL) was treated with the palladacycle (52.5 mg, 56 μmol), nBu$_4$NOAc (527 mg, 1.75 mmol) *tert*-butyl acrylate (2.00 mL) at 105 °C for 4 h. For complete consumption of the bromobutadiene **18**, a second portion of the palladacycle (52.5 mg, 56 μmol) was added and the mixture again heated at 105 °C for 4 h. Workup with diethyl ether (40 mL), water (2 × 30 mL), extraction with diethyl ether (40 mL) and FC (34 g on silica gel, 20:1 v/v light petroleum/diethyl ether elution) gave compound **23** (180 mg, 60%) as a colorless wax. R_f = 0.2. IR (film): $\tilde{\nu}$ = 2975 cm^{-1}, 2928, 2857, 1704, 1614, 1450, 1389, 1365, 1309, 1293, 1274, 1247, 1192, 1148, 1076, 1050, 1019, 999, 984, 899, 881, 851. ^1H NMR (250 MHz, C_6D_6): δ = 0.72–0.93 (m, 2 H), 1.07 (s, 3 H, CH_3), 1.17 [s, 9 H, $C(CH_3)_3$], 1.18–1.31 (m, 4 H), 1.43 [s, 9 H, $CO_2C(CH_3)_3$], 1.51–1.88 (m, 7 H), 1.90–2.19 (m, 6 H), 2.93 (t, ^3J = 5.8, ^3J = 6.0 Hz, 1 H, 5′′-H), 5.14 (d, ^3J = 0.6 Hz 1 H, 1′′-H), 5.98 (d, ^3J = 16.7 Hz, 1 H, 2-H) 8.11 (d, ^3J = 16.7 Hz, 1 H, 3-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, add. DEPT): δ = 11.0 (+, CH_3), 22.6 (–, CH_2), 22.8 (–, CH_2), 24.9 (–, CH_2), 25.4 (–, CH_2), 26.4 (–, CH_2), 27.1 (–, CH_2), 28.2 [+, 3 C, $C(CH_3)_3$], 29.2 [+, 3 C, $CO_2C(CH_3)$], 30.8 (–, CH_2), 31.0 (–, CH_2), 34.5 (–, CH_2), 37.7 (C_{quat}, C-4a′′), 44.1 (+, C-8a′′), 72.6 [C_{quat}, $C(CH_3)_3$], 77.5 (+, C-5′′), 79.2 [C_{quat}, $CO_2C(CH_3)_3$], 117.1 (+, C-2), 128.2 (C_{quat}), 130.2 (+, C-7′′), 137.7 (C_{quat}), 144.3 (+, C-3), 149.6 (C_{quat}), 167.0 (C_{quat}, C=O) ppm. MS (70 eV): *m*/*z* (%) = 428 (10) [M^+], 372 (51) [$M^+ - C_4H_8$], 355 (6), 316 (18) [$M^+ - 2 \times C_4H_8$], 315 (32) [$M^+ - C_4H_9 - C_4H_8$], 297 (36) [$M^+ - C_4H_9 - C_4H_8 - H_2O$], 269 (12), 253 (28), 231 (3), 205 (8), 185 (13), 171 (9), 145 (28), 105 (4), 95 (6), 84 (15), 57 (100) [$C_4H_9^+$], 41 (20). HRMS: calcd. for $C_{28}H_{44}O_3$ 428.3293 (correct HRMS).

(*E*)-1,2-Bis[2-(*tert*-butyldimethylsilyl)vinyl]cyclohexene (24): ^1H NMR (300 MHz, $CDCl_3$): δ = –0.03 [s, 12 H, $Si(CH_3)_2$], 0.83 [s, 18 H, $C(CH_3)_3$], 1.60 [m_C, 4 H, 4′(5′)-H], 2.27 [m_c, 4 H, 6′(3′)-H], 5.83 (d, ^3J = 18.9 Hz, 2 H, 1-H), 7.29 (d, ^3J = 18.9 Hz, 2 H, 2-H) ppm. MS (ESI, MeOH): *m*/*z* (%) = 599 (10), 569 (12), 455 (10), 363 (40) [M + H^+], 2291 (22), 289 (15), 235 (23), 231 (10), 179 (16), 146 (9), 115 (20), 102 (100), 74 (14).

***tert*-Butyl 3-(*tert*-Butyldimethylsilyl)-2,3,5,6,7,8-hexahydronaphthalene-2-carboxylate (26), *tert*-Butyl 3-(*tert*-Butyldimethylsilyl)-1,2,5,6,7,8-hexahydronaphthalene-2-carboxylate (27):** According to GP 5, the hexatriene **19** (70.0 mg, 0.201 mmol) in decalin (2.00 mL) was heated at 205 °C for 45 min. FC (25 g of silica gel, 20:1 v/v pentane/diethyl ether elution) yielded a mixture of diene **26** and diene **27** in a ratio of 1:1.9 (according to ^1H NMR) as a colorless wax (55.3 mg, 79%). R_f = 0.3. ^1H NMR (300 MHz, $CDCl_3$, signals which can be assigned to the minor product **26** are marked with #): δ = 0.05 [s, 6 H, $Si(CH_3)_2$], 0.08 [s, 6 H, $Si(CH_3)_2$]#, 0.85 [s, 9 H, $SiC(CH_3)_3$], 0.90 [s, 9 H, $SiC(CH_3)_3$]#, 1.18 [s, 9 H, $CO_2C(CH_3)_3$], 1.38 [s, 9 H, $CO_2C(CH_3)_3$]#, 1.77–1.89 (m, 4 H), 1.92–2.17 (m, 4 H), 2.22–2.37 (m, 2 H), 2.48 (m_c, 1 H), 2.72–2.83 (m, 3 H), 2.98 (m_c, 1 H), 6.08 (s, 1 H), 6.62 (s, 1 H)# ppm.

[3-(*tert*-Butyldimethylsilyl)-1,2,5,6,7,8-hexahydronaphthalen-2-yl]-methanol (28): According to GP 5, the hexatriene **29** (60.0 mg, 0.215 mmol) in decalin (0.60 mL) was heated at 205 °C for 1.75 h. FC (15 g of silica gel, 2:1 v/v pentane/diethyl ether elution) yielded compound **28** (52.7 mg, 88%) as a colorless wax. R_f = 0.4. IR (film): $\tilde{\nu}$ = 3306 cm^{-1}, 2951, 2927, 2856, 1655, 1566, 1470, 1462, 1437, 1360, 1315, 1247, 1187, 1147, 1050, 1024, 937, 864, 825, 809, 767. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.05 [s, 3 H, $Si(CH_3)_2$], 0.07 [s, 3 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $C(CH_3)_3$], 1.24–1.40 (m, 1 H), 1.49–1.74 [m, 4 H, 4′(5′)-H], 1.88–2.20 (m, 6 H), 2.22–2.48 (m, 1 H, 2-H), 3.37 (d, ^3J = 6.3 Hz, 2 H, CH_2O), 6.02 (s, 1 H, 4-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = –6.5 [+, CH_3, $Si(CH_3)_2$], –6.2 [+, CH_3, $Si(CH_3)_2$], 17.2 [–, C_{quat}, $C(CH_3)_3$], 22.7 (–, CH_2), 23.2 (–, CH_2), 26.9 [+, 3 C, CH_3, $C(CH_3)_3$], 27.8 (–, CH_2), 30.0 (–, CH_2), 30.6 (–, CH_2), 38.0 (+, CH, C-2), 62.4 (–, CH_2, CH_2OH), 126.7 (–, C_{quat}), 130.3 (–, C_{quat}), 132.1 (–, C_{quat}), 140.2 (+, CH) ppm. MS (70 eV): *m*/*z* (%) = 278 (3) [M^+], 221 (27) [$M^+ - C_4H_9$], 203 (20), 189 (6), 161 (4), 145 (68), 131 (17), 118 (11), 104 (8), 91 (17), 75 (100), 73 (43), 61 (8), 59 (19). HRMS: calcd. for $C_{17}H_{30}OSi$ 278.2068 (correct HRMS).

[3-(Trimethylsilyl)-1,2,5,6,7,8-hexahydronaphthalene-2-yl]methanol (28-SiMe$_3$): According to GP 5, the hexatriene **29**-$SiMe_3$ (15 mg, 0.063 mmol) in decalin (1.0 mL) was heated at 205 °C for 1.75 h. FC (10 g of silica, 2:1 v/v pentane/diethyl ether elution) yielded **28**-$SiMe_3$ (5.0 mg, 33%) as a colorless wax. R_f = 0.4. IR (film): $\tilde{\nu}$ = 3356 cm^{-1}, 2929, 2858, 1673, 1570, 1447, 1438, 1309, 1247, 1150, 1024, 998, 929, 866, 836, 752. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.19 [s, 9 H, $Si(CH_3)_3$], 1.28–1.72 (m, 1 H), 1.89–2.15 (m, 3 H), 2.23–2.39 (m, 6 H), 2.40–2.50 (m, 1 H, 2-H), 3.36–3.53 (m, 2 H, CH_2O), 6.19 (s, 1 H, 4-H) ppm. MS (70 eV): *m*/*z* (%) = 236 (26) [M^+], 219 (8) [$M^+ - OH$], 205 (8) [$M^+ - CH_2OH$], 204 (6) [$M^+ - CH_3OH$], 189 (14), 146 (17), 145 (22), 132 (15), 131 (36), 129 (11), 118 (24), 117 (13), 105 (16), 104 (18), 103 (7), 91 (31), 75 (42), 73 (100) [$Si(CH_3)^+$], 61 (6), 59 (12). HRMS: calcd. for $C_{14}H_{24}OSi$ 236.1598 (correct HRMS).

(*E*)-3-{2′-[(*E*)-2′′-(*tert*-Butyldimethylsilyl)vinyl]cyclohex-1′-enyl}prop-2-en-1-ol (29): According to GP 4, the hexatriene **19** (100 mg, 0.287 mmol) in toluene (5.00 mL), DIBALH (2.30 mL, 2.30 mmol), workup with diethyl ether (50 mL), $KHSO_4$ solution (20 mL), extraction with diethyl ether (20 mL), $NaHCO_3$ solution (20 mL), water (20 mL) and FC (20 g of silica gel, 2:1 v/v pentane/diethyl ether elution) gave compound **29** (64.7 mg, 81%) as a colorless oil. R_f = 0.4. IR (film): $\tilde{\nu}$ = 3398 cm^{-1}, 2928, 2883, 2856, 1665, 1499, 1463, 1445, 1409, 1389, 1361, 1252, 1154, 1048, 1007, 987, 938, 834, 832, 810, 777. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.07 [s, 6 H, $Si(CH_3)_2$], 0.88 [s, 9 H, $C(CH_3)_3$], 1.61–1.70 [m, 4 H, 4′(5′)-H], 2.22–2.37 [m, 4 H, 3′(6′)-H], 4.26 (dd, $^3J_1$ = 6.0, $^3J_2$ = 0.8 Hz, 2 H, 1-H), 4.87 (dt, $^3J_1$ = 15.5, $^3J_2$ = 6.0 Hz, 1 H, 2-H), 5.91 (d, ^3J = 19.0 Hz, 1 H, 1′′-H), 7.00 (d, ^3J = 15.4 Hz, 1 H, 3-H), 7.24 (d, ^3J = 19.0 Hz, 1 H, 2′′-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add.

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APT): δ = –6.01 [+, 2 C, CH_3, $Si(CH_3)_2$], 16.63 [–, C_{quat}, $C(CH_3)_3$], 22.44 (–, CH_2), 22.47 (–, CH_2), 26.14 (–, CH_2), 26.50 [+, 3 C, CH_3, $C(CH_3)_3$], 26.67 (–, CH_2), 64.40 (–, CH_2, C-1), 125.59 (+, CH), 127.20 (+, CH), 129.02 (+, CH), 132.25 (–, C_{quat}), 134.43 (–, C_{quat}), 141.64 (+, CH) ppm. MS (70 eV): *m/z* (%) = 278 (3) [M^+], 203 (6), 145 (17), 131 (7), 115 (13), 105 (3), 91 (8), 75 (100), 59 (13), 43 (7). HRMS: calcd. for $C_{17}H_{30}OSi$ 278.2068 (correct HRMS).

***tert*-Butyldimethyl[3-(tetrahydropyran-2-yloxymethyl)-3,4,5,6,7,8-hexahydronaphthalen-2-yl]silane (30):** According to GP 5, the hexatriene **31** (81.0 mg, 0.223 mmol) in decalin (3.00 mL) was heated at 205 °C for 2 h. FC (13 g of silica gel, 10:1 v/v pentane/diethyl ether elution) yielded compound **30** (75.2 mg, 93%) as a colorless wax. The diastereomeric ratio was found to be 1:1. R_f = 0.5. IR (film): $\tilde{\nu}$ = 2926 cm^{-1}, 2856, 2737, 1655, 1566, 1463, 1440, 1410, 1387, 1360, 1351, 1322, 1257, 1200, 1189, 1120, 1077, 1056, 1030, 975, 936, 907, 868, 825. ^{1}H NMR (300 MHz, $CDCl_3$ distinguishable signals of the diastereomers are marked with #): δ = 0.07 [s, 3 H, $Si(CH_3)_2$], 0.09 [s, 3 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $C(CH_3)_3$], 1.21–1.40 (m, 1 H), 1.41–1.91 (m, 11 H), 1.92–2.34 (m, 4 H), 2.48–2.61 (m, 1 H, 3-H), 3.03–3.19 (m, 1 H), 3.36–3.58 (m, 1 H), 3.70–3.95 (m, 1 H, OCHO), 4.45 (m_c, 1 H, 3-CH_2O), 4.59 (m_c, 1 H, 3-CH_2O), 5.99 (d, ^3J = 2.5 Hz, 1 H, 1-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = –6.5 [+, CH_3, $Si(CH_3)_2$], –6.4 [+, CH_3, $Si(CH_3)_2$], 17.3 [–, C_{quat}, $C(CH_3)_3$], 19.5 (–, CH_2), 20.0 (–, CH_2), 23.1 (–, CH_2), 23.4 (–, CH_2)#, 25.7 (–, CH_2), 25.8 (–, CH_2)#, 27.1 [+, 3 C, CH_3, $C(CH_3)_3$], 28.1 (–, CH_2), 28.1 (–, CH_2)#, 30.1 (–, CH_2), 30.2 (–, CH_2)#, 30.8 (–, CH_2), 30.9 (–, CH_2), 35.4 (+, CH, C-3), 36.2 (+, CH, C-3)#, 61.7 (–, CH_2), 62.6 (–, CH_2)#, 65.4 (–, CH_2), 66.9 (–, CH_2)#, 97.8 (+, CH), 100.3 (+, CH)#, 126.9 (–, C_{quat}), 130.1 (–, C_{quat}), 130.3 (–, C_{quat})#, 132.5 (–, C_{quat}), 132.8 (–, C_{quat})#, 140.2 (+, CH), 140.3 (+, CH)# ppm. MS (70 eV): *m/z* (%) = 362 (3) [M^+], 305 (12) [$M^+ - C_4H_9$], 262 (10), 221 (31), 219 (7), 205 (20), 203 (27), 189 (23), 159 (6), 146 (18), 145 (37), 131 (15), 118 (7), 115 (18), 103 (9), 89 (5), 85 (100), 73 (60), 67 (17), 57 (22) [$C_4H_9^+$]. HRMS: calcd. for $C_{22}H_{38}O_2Si$ 362.2643 (correct HRMS).

(*E*)-*tert*-Butyldimethyl(2-{(*E*)-2′-[3′′-(tetrahydropyran-2-yloxy)propenyl]cyclohex-1′-enyl}vinyl)silane (31): To a solution of the hexatriene **29** (140 mg, 0.485 mmol) and 3,4-dihydro-2*H*-pyran (81.6 mg, 0.970 mmol) in ethyl acetate (3.00 mL) was added at ambient temperature scandium(III) trifluoromethanesulfonate (3.0 mg, 0.0060 mmol), and the mixture was stirred for 1 h. It was poured into diethyl ether (50 mL), and the mixture washed with satd. $NaHCO_3$ solution (20 mL). After extraction of the combined aqueous phases with diethyl ether (2 × 20 mL), the combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. FC (24 g of silica gel, 10:1 v/v pentane/diethyl ether elution) yielded compound **31** (171 mg, 97%) as a colorless oil. R_f = 0.3. IR (film): $\tilde{\nu}$ = 2926 cm^{-1}, 2854, 1591, 1557, 1462, 1445, 1360, 1247, 1200, 1182, 1130, 1077, 1023, 980, 905, 867, 827. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.06 [s, 6 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $C(CH_3)_3$], 1.20–1.39 (m, 4 H), 1.47–1.92 (m, 6 H), 2.21–2.36 (m, 4 H), 3.45–3.62 (m, 1 H), 3.82–3.98 (m, 1 H), 4.00–4.18 (m, 1 H), 4.23–4.43 (m, 1 H), 4.63–4.76 (m, 1 H), 5.82 (dt, $^3J_1$ = 15.1, $^3J_2$ = 5.5 Hz, 1 H, 2′′-H), 5.89 (dt, ^3J = 18.7 Hz, 1 H, 1-H), 7.05 (d, ^3J = 16.5 Hz, 1 H, 3′′-H), 7.27 (d, ^3J = 18.9 Hz, 1 H, 2-H) ppm. ^{13}C NMR (75.6 MHz, C_6D_6, add. APT): δ = –5.9 [+, 2 C, CH_3, $Si(CH_3)_2$], 16.9 [–, C_{quat}, $C(CH_3)_3$], 19.4 (–, CH_2), 22.7 (–, CH_2), 22.7 (–, CH_2), 25.8 (–, CH_2), 26.3 (–, CH_2), 26.6 [+, 3 C, CH_3, $C(CH_3)_3$], 26.8 (–, CH_2), 30.9 (–, CH_2), 61.3 (–, CH_2, C-1′′), 67.8 (–, CH_2), 97.5 (+, CH, OCHO), 124.6 (+, CH), 126.0 (+, CH), 128.8 (+, CH), 133.2 (–, C_{quat}), 133.7 (–, C_{quat}), 142.8 (+, CH) ppm. MS (70 eV): *m/z* (%) = 362 (10) [M^+], 278 (2), 261 (14), 247 (6), 221 (3), 205 (14), 203 (17), 177 (7), 159 (69), 141 (27), 117 (17), 101 (12), 91 (15), 85 (91), 75 (100), 59 (41), 55 (16). HRMS: calcd. for $C_{22}H_{38}O_2Si$ 362.2643 (correct HRMS).

***tert*-Butyl 2,3,4a,5,7,8,9,10-Octahydronaphtho[1,2-*b*][1,4]dioxine-5-carboxylate (32) and *tert*-Butyl 2,3,5,6,7,8,9,10-Octahydronaphtho[1,2-*b*][1,4]dioxine-5-carboxylate (33):** According to GP 5, the hexatriene **20** (32.0 mg, 0.109 mmol) in decalin (0.50 mL) was heated at 205 °C for 45 min. After FC (20 g of silica gel, 5:1 v/v pentane/diethyl ether elution), a mixture of compounds **32** and **33** in a ratio of 1:3.1 (according to ^{1}H NMR) was obtained as a colorless wax (23.0 mg, 72%). R_f = 0.4. IR (film): $\tilde{\nu}$ = 2976 cm^{-1}, 2933, 2877, 1723, 1638, 1612, 1578, 1481, 1457, 1437, 1392, 1368, 1327, 1308, 1245, 1156, 1091, 1067, 988, 966, 919, 848. ^{1}H NMR (300 MHz, $CDCl_3$, signals which can be assigned to the minor product **32** are marked with #): δ = 1.42 [s, 9 H, $CO_2C(CH_3)_3$], 1.44 [s, 9 H, $CO_2C(CH_3)_3$]#, 1.51–1.73 (m, 4 H), 1.75–1.78 (m, 4 H)#, 1.91–2.23 (m, 6 H), 2.25–2.55 (m, 2 H), 3.04 (dd, $^3J_1$ = 8.5, $^3J_2$ = 5.8 Hz, 1 H), 3.31 (dd, $^3J_1$ = 11.3, $^3J_2$ = 5.2 Hz, 1 H)#, 3.93–4.24 (m_c, 4 H), 5.74 (m_c, 1 H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = 22.0 (–, CH_2), 22.1 (–, CH_2), 22.3 (–, CH_2), 22.6 (–, CH_2), 22.6 (–, CH_2), 22.8 (–, CH_2), 25.4 (–, CH_2), 28.2 [+, 3 C, $CO_2C(CH_3)_3$], 28.3 [+, 3 C, $CO_2C(CH_3)_3$]#, 64.4 (–, CH_2), 64.8 (–, CH_2), 65.0 (–, CH_2), 66.1 (–, CH_2), 67.4 (–, CH_2), 80.7 [C_{quat}, $CO_2C(CH_3)_3$], 80.9 [C_{quat}, $CO_2C(CH_3)_3$], 116.6 (+, CH), 123.8 (–, C_{quat}), 124.3 (–, C_{quat}), 128.1 (–, C_{quat}), 128.1 (–, C_{quat}), 131.3 (–, C_{quat}), 131.3 (–, C_{quat}), 131.9 (–, C_{quat}), 132.6 (–, C_{quat}), 172.7 (–, C_{quat}, C=O), 173.1 (–, C_{quat}, C=O)# ppm. MS (70 eV): *m/z* (%) = 292 (50) [M^+], 290 (22), 236 (65) [$M^+ - C_4H_8$], 234 (58), 217 (18), 206 (10), 191 (100), 190 (53), 162 (23), 149 (49), 134 (11), 122 (47), 107 (11), 94 (14), 91 (25), 86 (69), 84 (87), 79 (28), 77 (19), 73 (17), 65 (7), 57 (52) [$C_4H_9^+$], 55 (17). HRMS: calcd. for $C_{17}H_{24}O_4$ 292.1676 (correct HRMS).

5-Methoxymethoxymethyl-2,3,5,6,7,8,9,10-octahydronaphtho[1,2-*b*]-[1,4]dioxine (34): According to GP 5, the hexatriene **36** (36.3 mg, 0.136 mmol) in decalin (1.0 mL) was heated at 150 °C for 12 h. FC (10 g of silica gel, 2:1 v/v pentane/diethyl ether elution) yielded compound **34** (33.1 mg, 91%) as a colorless wax. R_f = 0.6. IR (film): $\tilde{\nu}$ = 2928 cm^{-1}, 2882 (C-H), 1681, 1632, 1491, 1441, 1381, 1333, 1292, 1277, 1242, 1201, 1175, 1150, 1109, 1075, 1041, 944, 918, 799 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.47–1.68 [m, 4 H, 8(9)-H], 1.92–2.00 (m, 2 H, 7-H), 2.01–2.07 (m, 2 H, 10-H), 2.08–2.17 (m, 1 H, 6-H), 2.28–2.41 (m, 1 H, 6-H), 2.53 (h, ^3J = 4.4 Hz, 1 H, 5-H), 3.35 (s, 3 H, OCH_3), 3.40 (dd, $^3J_1$ = 18.4, $^3J_2$ = 9.1 Hz, 1 H, CH_2O), 3.52 (dd, $^3J_1$ = 9.2, $^3J_2$ = 4.7 Hz, 1 H, CH_2O), 3.95–4.12 [m, 4 H, 2(3)-H], 4.60 (d, ^3J = 6.6 Hz, 1 H, OCH_2O), 4.63 (d, ^3J = 6.6 Hz, 1 H, OCH_2O) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = 22.6 (–, CH_2), 22.7 (–, CH_2), 22.9 (–, CH_2), 30.2 (–, CH_2), 32.0 (–, CH_2), 36.7 (+, CH, C-5), 55.3 (+, CH_3, OCH_3), 64.7 (–, CH_2, OCH_2CH_2O), 65.0 (–, CH_2, OCH_2CH_2O), 67.2 (–, CH_2, CH_2O), 96.8 (–, CH_2, OCH_2O), 123.6 (–, C_{quat}), 123.9 (–, C_{quat}), 129.9 (–, C_{quat}), 131.9 (–, C_{quat}) ppm. MS (70 eV): *m/z* (%) = 266 (48) [M^+], 264 (5), 235 (5) [$M^+ - CH_2OH$], 205 (14), 204 (24), 191 (100), 179 (6), 176 (7), 163 (10), 162 (8), 149 (68), 133 (5), 120 (8), 117 (6), 105 (10), 91 (28), 77 (18), 67 (5), 65 (9), 55 (12). HRMS: calcd. for $C_{15}H_{22}O_4$ 266.1519 (correct HRMS).

(*E*)-3-[2′-(5′′,6′′-Dihydro[1′′,4′′]dioxin-2′′-yl)cyclohex-1′-enyl]prop-2-en-1-ol (35): According to GP 4, the hexatriene **20** (274 mg, 0.937 mmol) in toluene (10.0 mL), DIBALH (4.69 mL, 4.69 mmol), workup with diethyl ether (75 mL), $KHSO_4$ solution (20 mL), extraction with diethyl ether (25 mL), $NaHCO_3$ solution (20 mL), water (20 mL) and FC (24 g of silica gel, 1:1 v/v pentane/diethyl ether elution) yielded compound **35** (177 mg, 85%) as a colorless

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oil. R_f = 0.3. IR (Film): $\tilde{\nu}$ = 3405 cm^{-1}, 2928, 2870, 2837, 1651, 1499, 1450, 1434, 1366, 1306, 1284, 1258, 1235, 1209, 1149, 1091, 1026, 1010, 970, 921, 902, 879. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.49–1.74 [m, 4 H, 4′(5′)-H], 2.14–2.35 [m, 4 H, 3′(6′)-H], 4.05–4.15 [m, 4 H, 5′′(6′′)-H], 4.20 (dt, $^3J_1$ = 6.3, $^3J_2$ = 1.1 Hz, 2 H, 1-H), 5.78 (dt, $^3J_1$ = 15.9, $^3J_2$ = 6.0 Hz, 1 H, 1-H), 5.92 (s, 1 H, 3′′-H), 6.86 (d, ^3J = 15.9 Hz, 1 H, 3-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = 22.3 (–, CH_2), 22.5 (–, CH_2), 25.9 (–, CH_2), 29.0 (–, CH_2), 64.2 [–, CH_2, 2 C, C-5′′(6′′)], 64.3 (–, CH_2, C-1), 125.7 (+, CH), 126.5 (+, CH), 131.3 (–, C_{quat}), 131.8 (+, CH), 132.3 (–, C_{quat}), 136.0 (–, C_{quat}) ppm. MS (70 eV): *m/z* (%) = 222 (46) [M^+], 204 (7) [$M^+ - H_2O$], 191 (98), 189 (7), 176 (8), 164 (6), 161 (11) 149 (100), 147 (100), 136 (6), 135 (8), 131 (9), 121 (8), 119 (17), 107 (20), 105 (15), 93 (13), 91 (50), 81 (9), 79 (29), 77 (32), 73 (12), 65 (16), 57 (6), 55 (23). HRMS: calcd. for $C_{13}H_{18}O_3$ 222.1257 (correct HRMS).

5-{2′-[(*E*)-3′′-Methoxymethylenoxyprop-1-enyl]cyclohex-1′-enyl}-2,3-dihydro[1,4]dioxine (36): A solution of the allylic alcohol **35** (180 mg, 0.810 mmol), ethyldiisopropylamine (523 mg, 4.05 mmol) and 4-(dimethylamino)pyridine (39.9 mg, 0.323 mmol) in dichloromethane (2.00 mL) was treated with methoxymethyl chloride (130 mg, 1.62 mmol) at 0 °C and stirred for 1 h. After warming to ambient temperature, stirring was continued for 1 h. The reaction mixture was then poured into diethyl ether (75 mL) and washed with 1 M $KHSO_4$ solution (2 × 15 mL). After extraction of the combined aqueous phases with diethyl ether (2 × 25 mL), the combined organic layers were washed with satd. $NaHCO_3$ (15 mL), water (15 mL) and dried with $MgSO_4$. Concentration under reduced pressure and FC (20 g of silica, 2:1 v/v pentane/diethyl ether elution) yielded compound **36** (166 mg, 77%) as a colorless oil. R_f = 0.5. IR (film): $\tilde{\nu}$ = 2928 cm^{-1}, 2877, 1651, 1458, 1450, 1367, 1305, 1285, 1212, 1149, 1093, 1042, 1027, 970, 953, 921, 880, 839, 787, 734, 694. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.53–1.75 [m, 4 H, 4′(5′)-H], 2.13–2.34 [m, 4 H, 3′(6′)-H], 3.38 (s, 3 H, OCH_3), 4.01–4.22 [m, 6 H, 5(6)-H, 1′′-H], 4.65 (s, 2 H, O-CH_2-O), 5.70 (dt, $^3J_1$ = 15.7, $^3J_2$ = 6.6 Hz, 1 H, 2′′-H), 5.92 (s, 1 H, 6-H), 6.87 (d, ^3J = 15.7 Hz, 1 H, 3′′-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = 22.3 (–, CH_2), 22.5 (–, CH_2), 25.9 (–, CH_2), 28.9 (–, CH_2), 55.2 (+, CH_3, OCH_3), 64.2 (–, CH_2, O-CH_2CH_2O), 64.3 (–, CH_2, O-CH_2CH_2O), 68.6 (–, CH_2, C-1′′), 95.6 (–, CH_2, O-CH_2-O), 122.7 (+, CH), 126.6 (+, CH), 131.3 (–, C_{quat}), 132.3 (–, C_{quat}), 133.2 (+, CH), 135.9 (–, C_{quat}) ppm. MS (70 eV): *m/z* (%) = 266 (29) [M^+], 234 (14) [$M^+ - CH_3OH$], 221 (13) [$M^+ - CH_3OCH_2O$], 205 (34), 204 (22), 191 (100), 176 (10), 163 (14), 149 (82), 133 (12), 120 (14), 107 (13), 105 (15), 91 (45), 81 (6), 79 (21), 65 (10), 55 (12). HRMS: calcd. for $C_{15}H_{22}O_4$ 266.1519 (correct HRMS).

***tert*-Butyl 3-Benzyl-1,2,3,4,4a,5,7,8,9,10-decahydrobenzo[*f*]isoquinoline-5-carboxylate (37) and *tert*-Butyl 3-Benzyl-1,2,3,4,5,6,7,8,9,10-decahydrobenzo[*f*]isoquinoline-5-carboxylate (38):** According to GP 5, the hexatriene **21** (40.0 mg, 0.105 mmol) in decalin (1.00 mL) was heated at 205 °C for 1.5 h. After FC (20 g of silica gel, 1:1 v/v pentane/diethyl ether elution), a mixture of compounds **37** and **38** in a ratio of 1:2.6 (according to ^1H NMR) was obtained as a colorless wax (29.1 mg, 73%). R_f = 0.4. IR (film): $\tilde{\nu}$ = 3086 cm^{-1}, 3028, 2927, 2858, 2833, 1726, 1703, 1684, 1494, 1453, 1391, 1366, 1350, 1283, 1253, 1211, 1149, 1085, 1076, 1064, 1000, 970, 934, 910, 849. ^1H NMR (300 MHz, $CDCl_3$ signals which can be assigned to the minor product **37** are marked with #): δ = 1.29 [s, 9 H, $CO_2C(CH_3)_3$], 1.43–1.64 (m, 6 H), 1.81–2.00 (m, 3 H), 2.01–2.20 (m, 5 H), 2.22–2.48 (m, 2 H), 2.46–2.60 (m, 3 H), 2.63–2.74 (m, 2 H), 2.89–3.08 (m, 3 H), 3.31–3.63 (m, 4 H), 5.39–5.53 (m, 1 H)#, 7.05–7.31 (m, 3 H, Ph), 7.33–7.52 (m, 2 H, Ph) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = 22.8 (–, CH_2), 23.2 (–, CH_2), 23.4 (–, CH_2), 23.5 (–, CH_2), 24.8 (–, CH_2), 25.8 (–, CH_2), 25.9 (–, CH_2), 28.1 [+, 3 C, $CO_2C(CH_3)_3$], 28.3 [+, 3 C, $CO_2C(CH_3)_3$]#, 29.9 (–, CH_2), 30.3 (–, CH_2), 30.5 (+, CH), 30.7 (–, CH_2), 40.0 (+, CH), 43.1 (+, CH), 55.9 (–, CH_2), 56.4 (–, CH_2), 63.2 (–, CH_2), 80.4 [C_{quat}, $CO_2C(CH_3)_3$], 123.2 (+, CH)#, 126.1 (–, C_{quat}), 127.2 (+, CH), 127.7 (+, CH), 128.1 (–, C_{quat}), 128.5 (+, CH), 129.3 (+, CH), 129.4 (+, CH), 129.5 (+, CH), 132.3 (–, C_{quat}), 133.6 (–, C_{quat}), 137.0 (–, C_{quat}), 138.8 (–, C_{quat}), 173.7 (–, C_{quat}, C=O) ppm. MS (70 eV): *m/z* (%) = 379 (77) [M^+], 324 (22), 323 (55) [$M^+ - C_4H_8$], 322 (65) [$M^+ - C_4H_9$], 306 (34), 278 (52), 276 (22), 232 (31), 204 (39), 186 (13), 159 (30), 146 (20), 134 (66), 120 (89), 117 (23), 115 (15), 105 (13), 91 (100), 77 (8), 65 (15), 57 (42) [$C_4H_9^+$]. HRMS: calcd. for $C_{25}H_{33}NO_2$ 379.2513 (correct HRMS).

(*E*)-3-[2′-(1′′-Benzyl-1′′,2′′,3′′,6′′-tetrahydropyridin-4′′-yl)cyclohex-1′-enyl]prop-2-en-1-ol (39): According to GP 4, the hexatriene **21** (90.0 mg, 0.237 mmol) in toluene (3.00 mL) was treated with DIBALH (1.90 mL, 1.90 mmol). The reaction mixture was poured into diethyl ether (75 mL), the solution washed with satd. NH_4Cl solution (2.0 mL) and treated with 1 N NaOH solution (20.0 mL). The resulting precipitate was filtered through Celite. After extraction of the combined aqueous phases with diethyl ether (2 × 30 mL), the combined organic layers were dried with $MgSO_4$. Concentration in vacuo and FC of the residue (20 g of silica gel, 10:1 v/v diethyl ether/methanol elution) yielded compound **39** (65.1 mg, 89%) as a yellow oil. R_f = 0.7. IR (film): $\tilde{\nu}$ = 3395 cm^{-1}, 3028, 2929, 2798, 1613, 1494, 1452, 1391, 1366, 1310, 1148, 1029, 983, 856, 807, 753. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.50–1.71 (m, 3 H), 2.05–2.20 (m, 4 H), 2.51–2.75 (m, 5 H), 3.00–3.07 (m, 2 H, 2′′-H), 3.60 (s, 2 H, $PhCH_2$), 4.15 (d, ^3J = 5.2 Hz, 2 H, 1-H), 5.28–5.34 (m, 1 H, 3′′-H), 5.68 (dt, $^3J_1$ = 15.9, $^3J_2$ = 5.8 Hz, 1 H, 2-H), (d, ^3J = 15.9 Hz, 1 H, 3-H), 7.23–7.39 (m, 5 H, Ph-H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = 22.5 (–, CH_2), 25.1 (–, CH_2), 28.5 (–, CH_2), 29.9 (–, CH_2), 49.7 (–, CH_2), 50.4 (–, CH_2), 52.5 (–, CH_2), 62.7 (–, CH_2, PhCH_2), 63.6 (–, CH_2, C-1), 121.7 (+, CH, C-3′′), 124.8 (+, CH), 127.2 (+, CH, Ph), 128.0 (–, C_{quat}), 128.2 (+, 2 C, CH, Ph), 129.5 (+, 2 C, CH, Ph), 131.0 (+, CH), 137.0 (–, C_{quat}), 137.7 (–, C_{quat}, Ph), 140.0 (–, C_{quat}) ppm. MS (70 eV): *m/z* (%) = 309 (42) [M^+], 308 (44), 305 (43), 292 (23), 278 (39), 264 (80), 252 (30), 218 (7) 200 (4), 172 (15), 159 (22), 146 (25), 134 (14), 105 (14), 91 (100) [Bn^+], 77 (11), 65 (16), 63 (3). HRMS: calcd. for $C_{21}H_{27}NO$ 309.2094 (correct HRMS).

(3-Benzyl-1,2,3,4,5,6,7,8,9,10-decahydrobenzo[*f*]isoquinolin-5-yl)-methanol (40) and (3-Benzyl-1,2,3,4,4a,5,7,8,9,10-decahydrobenzo-[*f*]isoquinolin-5-yl)methanol (41): According to GP 5, the hexatriene **39** (20.0 mg, 0.0650 mmol) in decalin (0.50 mL) was heated at 205 °C for 0.5 h. FC (10 g of silica gel, 20:1 v/v diethyl ether/methanol elution) gave a mixture of compounds **40** and **41** with a ratio of 4.3:1 (according to ^1H NMR) as a colorless wax (16.4 mg, 82%). R_f = 0.6. ^1H NMR (300 MHz, $CDCl_3$, signals which can be assigned to the minor component **41** are marked with #): δ = 1.05–1.29 (m, 6 H), 1.31–1.72 (m, 6 H), 1.98–2.40 (m, 3 H), 2.58–2.68 (m, 2 H, PhCH_2)#, 2.60 (m_c, 2 H, PhCH_2), 2.90 (m_c, 1 H)#, 3.12 (m_c, 1 H)#, 3.26–3.74 (m, 2 H), 3.09–3.21 (m, 2 H), 3.30–3.54 (m, 4 H), 5.34–5.38 (m, 1 H), 6.99–7.31 (m, 3 H, Ar), 7.32–7.56 (m, 2 H, Ar) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = 23.0 (–, CH_2)#, 23.5 (–, CH_2)#, 24.4 (–, CH_2), 24.5 (–, CH_2), 24.8 (–, CH_2)#, 25.1 (–, CH_2)#, 26.0 (–, CH_2), 27.0 (–, CH_2), 30.9 (–, CH_2)#, 31.0 (–, CH_2)#, 32.0 (–, CH_2), 39.1 (+, CH)#, 39.3 (+, CH), 40.0 (+, CH), 50.4 (–, CH_2)#, 52.2 (–, CH_2), 55.8 (–, CH_2), 56.4 (–, CH_2)#, 61.2 (–, CH_2), 62.3 (–, CH_2)#, 62.8 (–, CH_2)#, 63.3 (–, CH_2), 120.9 (+, CH), 125.6 (–, C_{quat})#, 125.4 (–, C_{quat}), 126.9 (–, C_{quat})#, 127.2 (–, C_{quat})#, 127.3 (+, CH, Ar), 127.3 (+, CH, Ar)#, 128.4 (+, 2 C, CH, Ar)#, 128.5 (+, 2 C, CH, Ar), 129.1 (+, 2 C,

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CH, Ar)#, 129.1 (–, C_{quat}), 129.4 (+, 2 C, CH, Ar), 136.3 (–, C_{quat}), 138.6 (–, C_{quat})#, 138.8 (–, C_{quat}, Ar), 139.4 (–, C_{quat})# ppm. MS (70 eV): *m*/*z* (%) = 309 (63) [M^+], 278 (52), 276 (6), 252 (43), 250 (6), 218 (15), 172 (14), 159 (17), 146 (15), 134 (28), 120 (16), 117 (14), 91 (100), 77 (10), 65 (14). HRMS: calcd. for $C_{21}H_{27}NO$ 309.2094 (correct HRMS).

(*E*)-(1′′*S*,3a′′*S*,7a′′*S*)-3-[8′-(1′′-*tert*-Butoxy-7a′′-methyl-2′′,3′′,3a′′,6′′,7′′,7a′′-hexahydro-1′′*H*-inden-5′′-yl)-1′,4′-dioxaspiro[4′.5′]dec-7′-en-7′-yl]prop-2-en-1-ol (43): According to GP 4, the hexatriene **42** (180 mg, 0.381 mmol) in toluene (3.00 mL), DIBALH (3.05 mL, 3.05 mmol), workup with diethyl ether (35 mL), $KHSO_4$ solution (10 mL), extraction with diethyl ether (2 × 25 mL), $NaHCO_3$ solution (20 mL), water (20 mL) and FC (24 g of silica gel, 3:2 v/v diethyl ether/pentane elution) yielded compound **43** (100 mg, 65%) as a colorless oil. R_f = 0.4. ^{1}H NMR (250 MHz, C_6D_6): δ = 1.05 (s, 3 H, CH_3), 1.15 [s, 9 H, $C(CH_3)_3$], 1.23–1.40 (m, 2 H), 1.42–1.78 (m, 4 H), 1.80–2.40 (m, 8 H), 2.56–2.75 (m, 1 H), 2.98 (br. s, 1 H, OH), 3.36 (t, ^3J = 8.3 Hz, 1 H, 1′′-H), 3.43 (m_c, 4 H, 2′-H, 3′-H), 3.71 (m_c, 2 H, 1-H), 5.44 (s, 1 H, 4′′-H), 5.83 (m_c, 1 H, 2-H), 6.90 (d, ^3J = 16.7 Hz, 1 H, 3-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 11.6 (+, CH_3), 25.0 (–, CH_2), 27.3 (–, CH_2), 28.9 [+, 3 C, $C(CH_3)_3$], 29.1 (–, CH_2), 32.1 (–, CH_2), 32.3 (–, CH_2), 34.4 (–, CH_2), 42.2 (C_{quat}, C-7a′′), 43.8 (+, CH, C-3a′′), 62.1 (–, OCH_2CH_2O), 64.1 (–, OCH_2CH_2O), 69.9 (–, CH_2, C-1), 72.2 [C_{quat}, $C(CH_3)_3$], 75.2 (+, CH, C-1′′), 79.6 [C_{quat}, $CO_2C(CH_3)_3$], 110.7 (C_{quat}, C-5′), 126.0 (+, CH), 126.43 (+, CH), 126.6 (+, CH), 130.9 (C_{quat}), 139.0 (C_{quat}), 140.5 (C_{quat}) ppm.

(13*S*,14*S*,17*S*)-(17-*tert*-Butoxy-13-methyl-1′,3′-spiro[2′,3]dioxolan-2,3,4,7,8,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[*a*]phenanthren-7-yl)methanol (44) and (13*S*,14*S*,17*S*)-(17-*tert*-Butoxy-13-methyl-1′,3′-spiro[2′,3]dioxolan-2,3,4,6,7,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[*a*]phenanthren-7-yl)methanol (45): According to GP 5, the hexatriene **43** (80 mg, 0.20 mmol) in decalin (1.0 mL) was heated at 205 °C for 0.75 h. FC (15 g of silica gel, 3:2 v/v diethyl ether/pentane) gave a mixture of compounds **44** and **45** with a ratio of 1:1.3 (according to ^{1}H NMR) as a colorless wax (37 mg, 46%). R_f = 0.4. IR (film): $\tilde{\nu}$ = 3396 cm^{-1}, 2973, 2933, 2872, 1669, 1653, 1617, 1559, 1540, 1490, 1472, 1457, 1437, 1419, 1388, 1362, 1253, 1193, 1108, 1062, 948, 895, 812, 736, 703, 668. ^{1}H NMR (300 MHz, $CDCl_3$, signals which can be assigned to the minor component **44** are marked with #): δ = 0.83 (s, 3 H, CH_3)#, 0.93 (s, 3 H, CH_3), 1.17 [s, 9 H, $C(CH_3)_3$]#, 1.18 [s, 9 H, $C(CH_3)_3$], 1.21–1.50 (m, 7 H), 1.54–2.00 (m, 8 H), 2.03–2.52 (m, 12 H), 3.20–3.38 (m, 4 H, CH_2OH), 3.41–3.74 (m, 9 H), 5.59–5.67 (m, 1 H, 6-H)# ppm. MS (70 eV): *m*/*z* (%) = 402 (5) [M^+], 358 (4), 342 (24), 311 (100), 285 (31), 255 (35), 237 (18), 209 (9), 197 (18), 181 (10), 155 (11), 143 (29), 105 (5), 91 (8), 81 (5), 57 (64) [$C_4H_9^+$], 41 (16).

***tert*-Butyl *trans*-1,2,3,4,4a,5,6,7,8,9,10,11,12,12a-Tetradecahydrochrysene-5-carboxylate (48-*t*Bu):** According to GP 5, the hexatriene **22**-*t*Bu (33.2 mg, 0.110 mmol) in decalin (0.50 mL) was heated at 205 °C for 45 min. FC (32 g of silica gel, 20:1 v/v light petroleum/diethyl ether elution) yielded compound **48**-*t*Bu (23.1 mg, 77%) as a colorless oil. R_f = 0.3. IR (film): $\tilde{\nu}$ = 2924 cm^{-1}, 2853, 1711, 1448, 1392, 1368, 1347, 1303, 1257, 1214, 1152, 1086, 1029, 846, 736. ^{1}H NMR (250 MHz, C_6D_6): δ = 1.01–1.85 (m, 18 H), 1.18 [s, 9 H, $C(CH_3)_3$], 1.87–2.08 (m, 2 H), 2.08–2.38 (m, 2 H), 2.42–2.56 (m, 2 H, 6-H), 3.20 (dd, ^3J = 6.1, ^3J = 6.3 Hz, 1 H, 7-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, add. DEPT): δ = 22.9 (–, CH_2), 23.8 (–, CH_2), 25.7 (–, CH_2), 26.4 (–, CH_2), 26.9 (–, CH_2), 27.6 (–, CH_2), 28.1 [+, 3 C, $C(CH_3)_3$], 30.8 (–, CH_2), 30.9 (–, CH_2), 31.5 (–, CH_2), 32.8 (–, CH_2), 34.5 (–, CH_2), 40.7 (+, CH), 41.4 (+, CH), 44.6 (+, CH, C-5), 79.2 [C_{quat}, $CO_2C(CH_3)_3$], 128.2 (C_{quat}), 129.1 (C_{quat}), 131.1 (C_{quat}), 173.6 (C_{quat}, C=O) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 22.5 (–, CH_2), 23.2 (–, CH_2), 25.3 (–, CH_2), 25.9 (–, CH_2), 26.9 (–, CH_2), 27.1 (–, CH_2), 28.0 [+, $C(CH_3)_3$], 29.7 (–, CH_2), 30.3 (–, CH_2), 30.8 (–, CH_2), 32.4 (–, CH_2), 34.1 (–, CH_2), 40.2 (+, CH), 41.1 (+, CH), 44.2 (+, C-7), 79.2 [C_{quat}, $CO_2C(CH_3)_3$], 127.8 (C_{quat}), 127.9 (C_{quat}), 128.9 (C_{quat}), 130.8 (C_{quat}), 174.3 (C_{quat}, C=O) ppm. MS (70 eV): *m*/*z* (%) = 342 (12) [M^+], 286 (82) [$M^+ - C_4H_8$], 267 (2), 241 (26), 208 (3), 189 (7), 165 (4), 151 (7), 145 (100), 105 (6), 91 (11),67 (6), 57 (16) [$C_4H_9^+$], 41 (10). HRMS: calcd. for $C_{23}H_{34}O_2$ 342.2561 (correct HRMS).

Methyl *trans*-1,2,3,4,4a,4b,5,6,7,8,9,10,11,12,12a-Tetradecahydrochrysene-5-carboxylate (49): According to GP 5, the hexatriene **22**-Me (40.2 mg, 0.134 mmol) in decalin (0.50 mL) was heated at 205 °C for 30 min. FC (30 g of neutral aluminum oxide, 20:1 v/v light petroleum/diethyl ether elution) gave compound **49** (30.8 mg, 77%) and tetracycle **48**-Me (4.4 mg, 11%), as a colorless oil. R_f = 0.3. IR (film): $\tilde{\nu}$ = 2922 cm^{-1}, 2853, 1739, 1616, 1446, 1433, 1330, 1272, 1259, 1232, 1190, 1165, 1112, 1095, 1070, 1023, 990, 942, 892, 863, 851, 843, 812, 765. ^{1}H NMR (250 MHz, C_6D_6): δ = 0.69–1.49 (m, 7 H), 1.50–1.84 (m, 7 H), 1.90–2.26 (m, 9 H), 3.02 (dd, ^3J = 4.5, ^3J = 6.1 Hz, 1 H, 5-H), 3.31 (s, 3 H, CH_3), 5.73 (m_c, 1 H, 6-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, add. DEPT): δ = 23.0 (–, CH_2), 23.5 (–, CH_2), 25.2 (–, CH_2), 26.7 (–, CH_2), 26.8 (–, CH_2), 31.2 (–, CH_2), 31.6 (–, CH_2), 34.0 (–, CH_2), 34.3 (–, CH_2), 35.3 (–, CH_2), 38.5 (+, CH), 39.3 (+, CH), 41.3 (+, CH), 45.1 (+, C-5), 51.2 (+, CH_3), 118.5 (+, C-6), 127.8 (C_{quat}), 128.8 (C_{quat}), 135.3 (C_{quat}), 173.9 (C_{quat}, C=O) ppm. MS (70 eV): *m*/*z* (%) = 300 (100) [M^+], 296 (7), 266 (21) [$M^+ - CO_2CH_3$], 240 (69), 238 (18), 212 (10), 197 (12), 183 (7), 171 (9), 145 (73), 141 (12), 91 (6), 79 (4), 44 (76), 41 (3). HRMS: calcd. for $C_{20}H_{28}O_2$ 300.2091 (correct HRMS).

Methyl *trans*-1,2,3,4,4a,5,6,7,8,9,10,11,12,12a-Tetradecahydrochrysene-5-carboxylate (48-Me): According to GP 5, the hexatriene **22**-Me (280 mg, 0.933 mmol) in decalin (5.00 mL) was heated at 205 °C for 45 min. FC (28 g of silica gel, 20:1 v/v light petroleum/diethyl ether elution) gave compound **48**-Me (193 mg, 69%) as a colorless wax. R_f = 0.3. IR (film): $\tilde{\nu}$ = 2925 cm^{-1}, 2853, 1728, 1595, 1447, 1331, 1275, 1195, 1072, 1021, 1001, 969, 911, 859, 735. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.82–1.89 (m, 16 H), 1.91–2.18 (m, 6 H), 2.20–2.43 (m, 2 H), 3.21 (dd, ^3J = 7.6, ^3J = 9.1 Hz, 1 H, 5-H), 3.62 (s, 3 H, CH_3) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 22.4 (–, CH_2), 22.6 (–, CH_2), 23.1 (–, CH_2), 25.3 (–, CH_2), 25.9 (–, CH_2), 26.4 (–, CH_2), 30.2 (–, CH_2), 30.4 (–, CH_2), 31.2 (–, CH_2), 32.0 (–, CH_2), 33.3 (–, CH_2), 38.7 (+, CH), 40.9 (+, CH), 43.8 (+, CH, C-5), 53.0 (+, CH_3), 127.8 (C_{quat}), 127.8 (C_{quat}), 128.0 (C_{quat}), 131.3 (C_{quat}), 175.3 (C_{quat}, C=O) ppm. MS (70 eV): *m*/*z* (%) = 300 (52) [M^+], 266 (2) [$M^+ - CO_2CH_3$], 241 (12), 226 (10), 218 (2), 192 (11), 190 (10), 162 (4), 146 (14), 145 (100), 105 (14), 239 (5), 197 (9), 171 (8), 145 (100), 129 (8), 117 (5), 91 (6), 79 (3), 67 (4), 41 (4). HRMS: calcd. for $C_{20}H_{28}O_2$ 300.2091 (correct HRMS).

***tert*-Butyl 13-*tert*-Butoxy-12a-methyl-1,2,3,4,4a,4b,5,6,7,8,9,10,11,12, 12a-tetradecahydrochrysene-5-carboxylate (50):** According to GP 5, the hexatriene **23** (100 mg, 0.234 mmol) in decalin (3.00 mL) was heated at 205 °C for 45 min. FC (33 g of silica gel, 20:1 v/v light petroleum/diethyl ether elution) gave compound **50** (71.4 mg, 71%) as a colorless wax. R_f = 0.3. IR (film): $\tilde{\nu}$ = 2974 cm^{-1}, 2927, 2854, 1725, 1595, 1450, 1388, 1378, 1368, 1332, 1284, 1270, 1249, 1227, 1192, 1154, 1067, 1023, 1000, 970, 957, 945, 903, 884, 852, 820, 759, 703. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.78 (s, 3 H, CH_3), 1.18 [s, 9 H, $C(CH_3)_3$], 1.39 [s, 9 H, $CO_2C(CH_3)_3$], 1.43–1.62 (m, 6 H), 1.64–1.85 (m, 7 H), 1.86–2.10

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(m, 5 H), 2.13–2.36 (m, 3 H), 2.91–3.00 (m, 1 H, 5-H), 3.09 (dd, ^3J = 5.6, ^3J = 11.4 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, add. DEPT): δ = 11.3 (+, CH_3), 22.9 (–, CH_2), 23.0 (–, CH_2), 23.8 (–, CH_2), 24.9 (–, CH_2), 25.1 (–, CH_2), 28.1 [+, 3 C, C(CH_3)$_3$], 29.3 [+, 3 C, $CO_2C(CH_3)_3$], 30.5 (–, CH_2), 31.0 (–, CH_2), 32.2 (–, CH_2), 34.8 (–, CH_2), 38.0 (+, CH, C-4a), 40.0 (C_{quat}, C-12a), 46.1 (+, C-5), 72.6 [C_{quat}, $C(CH_3)_3$], 78.3 (+, C-1), 79.1 [C_{quat}, $CO_2C(CH_3)_3$], 127.2 (C_{quat}), 127.8 (C_{quat}), 128.1 (C_{quat}), 130.1 (C_{quat}), 172.7 (C_{quat}, C=O) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ = 11.3 (+, CH_3), 22.8 (–, CH_2), 23.9 (–, CH_2), 24.8 (–, CH_2), 25.1 (–, CH_2), 28.2 [+, 3 C, C(CH_3)$_3$], 29.4 [+, 3 C, $CO_2C(CH_3)_3$], 30.5 (–, CH_2), 31.1 (–, CH_2), 32.3 (–, CH_2), 34.6 (–, CH_2), 37.8 (+, C-4a), 39.9 (C_{quat}, C-12a), 46.0 (+, C-5), 72.7 [C_{quat}, $C(CH_3)_3$], 78.5 (+, C-1), 126.2 (C_{quat}), 128.1 (C_{quat}), 128.2 (C_{quat}), 130.0 (C_{quat}), 173.9 (C_{quat}, C=O) ppm. MS (70 eV): *m/z* (%) = 428 (9) [M^+], 402 (11), 386 (19), 346 (18), 329 (34), 313 (52), 295 (100), 267 (29), 229 (43), 215 (14), 197 (9), 145 (7), 95 (4), 84 (10), 57 (84) [$C_4H_9^+$], 41 (18). HRMS: calcd. for $C_{28}H_{44}O_3$ 428.3293 (correct HRMS).

Supporting Information (see also the footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra of the described compounds.

Acknowledgments

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