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Doing it Twice: Asymmetric Deprotonation/Alkylation of Weiss Diketone Derivatives as Key Steps in the Functionalization of Bicyclo[3.3.0]octanes

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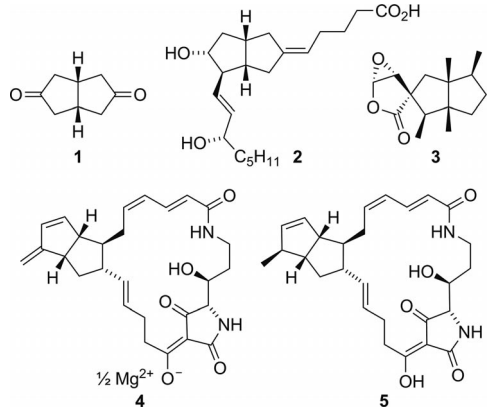
Dedicated to Professor Larry E. Overman on the occasion of his 70th birthday

Keywords: Alkylation / Asymmetric synthesis / Bicyclic compounds / Stereoselectivity / Natural products

The silyl-protected allylhydropentalenone derivative **9**, derived from the Weiss diketone, was functionalized by enantioselective deprotonation in the presence of lithium bis(1-phenylethyl)amide/LiCl as the chiral base, which was generated in situ from bis(1-phenylethyl)ammonium chloride [(*R*,*R*)- or (*S*,*S*)-**14**] and BuLi, and trapping of the resulting enolate with alkyl halide electrophiles to give pseudo-C_2 or -C_s-symmetrical bicyclo[3.3.0]octanones **10** and **11**. The influence of the chiral base and electrophiles on the regioselectivity and double stereodifferentiation was investigated. Taking the double stereocontrol into account, a matched selectivity for the pseudo-C_2 pair (1*R*,4*R*)-**10**/(1*S*,4*R*)-**10** and a mismatched selectivity for the pseudo-C_s pair (1*S*,6*R*)-**11**/(1*R*,6*R*)-**11** were observed in the presence of (*R*,*R*)-**14**. The use of (*S*,*S*)-**14**, however, produced a mismatched selectivity for (1*R*,4*R*)-**10**/(1*S*,4*R*)-**10** and a matched selectivity for (1*S*,6*R*)-**11**/(1*R*,6*R*)-**11** with complementary diastereoselectivity depending on the electrophile. Furthermore, the hydropentalenone derivative **10a** provided an alternative route to the bicyclo[3.3.0]octene core of the macrocyclic tetramic acid lactam, cylindramide (**5**).

Introduction

The enantioselective desymmetrization of *meso* ketones by asymmetric deprotonation with chiral bases and subsequent electrophilic trapping was pioneered by Koga,[1,2] Simpkins[3] and Leonard[4] and their co-workers and later extended by other groups[5] because this strategy provides efficient access to enantiomerically pure α-substituted ketones. Bicyclo[3.3.0]octane derivatives of the Weiss diketone **1** (Scheme 1), which is readily available even on a multigram scale,[6] are particularly attractive for this purpose. Functionalized bicyclo[3.3.0]octanes are important key building blocks of a variety of natural products and biologically or medicinally important compounds. Prominent examples include carbacycline (**2**),[7] ptychenolide (**3**)[8] and complex tetramic acid lactams[9] such as the geodin A magnesium salt (**4**)[9b,10] and cylindramide (**5**;[11] Scheme 1).



Scheme 1. Weiss diketone **1** and selected examples of prominent biologically important bicyclo[3.3.0]octane-containing compounds.

Although several routes to functionalized bicyclo[3.3.0]-octanes are known,[12] some methods suffer from harsh reaction conditions, toxic reagents, poor regio- or stereoselectivity or the use of complex starting materials requiring multistep syntheses. In contrast, Weiss diketone derivatives allow a bottom-up functionalization through enantioselective desymmetrization, as was shown for the deprotonation/electrophilic trapping by Koga,[2c] Leonard[4] and Gais,[13,14] for cuprate addition by Gais[15] and for enzymatic demethoxycarbonylation by Petzoldt[16] and Mulzer.[17] In particular, stereogenic centres can be introduced at a later stage on demand. Recently, we reported on the application of reactive electrophiles like methyl iodide or benzyl, prenyl or allyl halides for the desymmetrization of Weiss diketone derivatives such as **6**, which gave products **8** with high diastereo-

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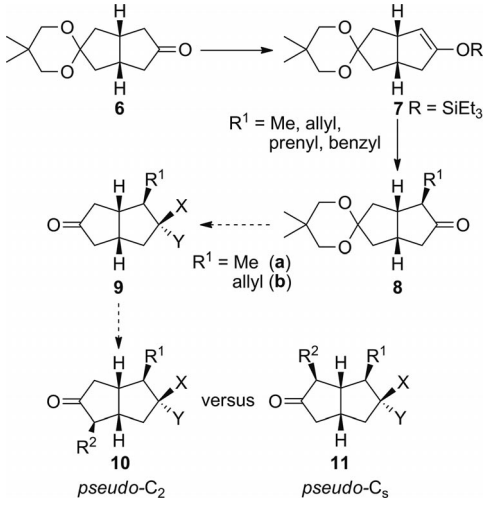
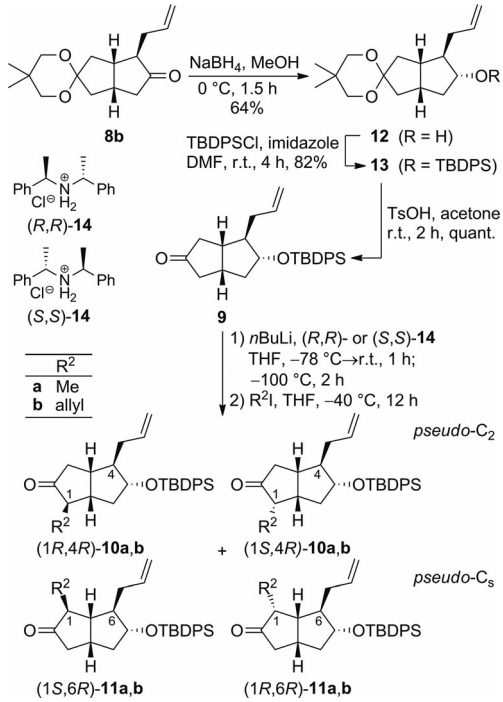
selectivity via silyl enol ether **7** as intermediate (Scheme 2).[18] Based on these results, we surmised that the conversion of hydropentalenone derivative **8** into ketone **9** should open up the possibility of a second deprotonation/alkylation sequence to give either pseudo-C_2- or -C_s-symmetrical bicyclo[3.3.0]octanones **10** and **11**.



Scheme 2. First deprotonation/alkylation via intermediate silyl enol ether **7**[18] and envisioned follow-up reaction of hydropentalenone derivatives **8**.



Scheme 3. TBDPS = *tert*-butyldiphenylsilane, TsOH = *p*-toluenesulfonic acid.

The second deprotonation/alkylation sequence is not only of more general interest with regard to regioselectivity and double stereodifferentiation in such highly congested substrates, but would also provide a convenient access to the core units of macrocyclic tetramic acid lactams such as geodin A (**4**) or cylindramide (**5**). The results are described below.

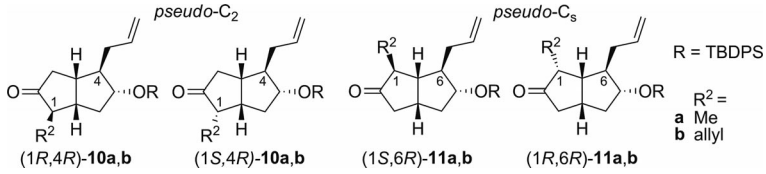
Results and Discussion

For the current investigations, acetals **8**[18] were chosen because enantioselectivities of the α-substituted ketones could be determined by capillary GC without further functionalization. As the allyl substituent provides many more opportunities for further derivatization than the methyl group, the α-allylated precursor **9** was considered to be synthetically more valuable. As shown in Scheme 3, the preparation of **9** commenced with the reduction of bicyclo[3.3.0]-octanone **8b** with $NaBH_4$ to give alcohol **12** in 64% yield, which was protected with TBDPSCl and imidazole. Subsequent deprotection of the acetal moiety in **13** with *p*-toluenesulfonic acid yielded ketone **9** quantitatively.

With ketone **9** in hand, first the effect of the chiral base on the regio- and diastereoselectivity of the deprotonation/alkylation step was studied (Scheme 3, Table 1). Lithium bis(1-phenylethyl)amide/LiCl as the chiral base was generated in situ from (*R*,*R*)-**14** or (*S*,*S*)-**14** and *n*BuLi in THF at –78 °C.[13,18,19b] Then derivative **9** was deprotonated with 1.2 equiv. of the base in THF at –100 °C for 2 h, followed by addition of methyl or allyl iodide at –40 °C. After 12 h, the mixture was submitted to aqueous work-up. Table 1 shows the regioselectivity to be in favour of the pseudo-C_2-symmetrical regioisomers (1*R*,4*R*)-**10a**,**b**/(1*S*,4*R*)-**10a**,**b** in the presence of (*R*,*R*)-**14**/*n*BuLi independently of the electrophile (entries 1 and 2). Derivatives (1*R*,4*R*)-**10a**,**b** were found to be the major diastereomers, whereas low diastereomeric ratios were observed for the pseudo-C_s-symmetrical pairs (1*S*,6*R*)-**11a**,**b**/(1*R*,6*R*)-**11a**,**b** (*dr* = 65:35 and 52:48). In the presence of the enantiomeric (*S*,*S*)-**14** and *n*BuLi, both the pseudo-C_2/pseudo-C_s regioselectivity and the diastereoselectivity of (1*R*,4*R*)-**10**/(1*S*,4*R*)-**10** were reversed, irrespective of the electrophile (methyl or allyl), preferring the pseudo-C_s regioisomers (1*S*,6*R*)-**11a**,**b**/(1*R*,6*R*)-**11a**,**b** and diastereomers (1*S*,4*R*)-**10a**,**b** (entries 3 and 4). The electrophile, however, strongly influenced the pseudo-C_s pairs (1*S*,6*R*)-**11a**,**b**/(1*R*,6*R*)-**11a**,**b**, leading to a complementary diastereoselectivity. Enolate trapping with methyl iodide gave exclusively (1*S*,6*R*)-**11a** (entry 3), whereas ketone (1*R*,6*R*)-**11b** was the major diastereomer in the allylation (entry 4). With regard the double stereocontrol, the base (*R*,*R*)-**14** produced a matched selectivity for the pseudo-C_2 pair (1*R*,4*R*)-**10**/(1*S*,4*R*)-**10**, favouring (1*R*,4*R*)-**10**, and a mismatched selectivity for the pseudo-C_s pair (1*S*,6*R*)-**11**/(1*R*,6*R*)-**11**. In contrast, the base (*S*,*S*)-**14** produced a mismatched selectivity for the pseudo-C_2 (1*R*,4*R*)-**10**/(1*S*,4*R*)-**10**, favouring (1*S*,4*R*)-**10**, and a matched selectivity for the pseudo-C_s pair (1*S*,6*R*)-**11**/(1*R*,6*R*)-**11**, with complementary diastereoselectivity depending on the substituents.

The observed double stereodifferentiation and regiochemical control is not determined by the presence of the base, but rather by the enolate, as was proven by performing the two-step reaction via a silyl enol ether (Scheme 4). Fol-

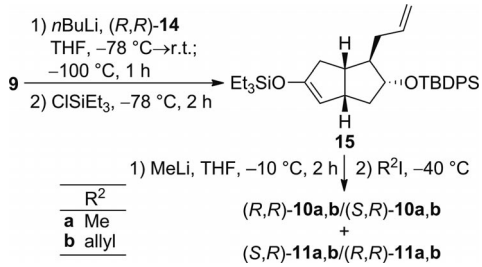
Table 1. Asymmetric deprotonation/alkylation of ketone **9** with lithium bis(1-phenylethyl)amide/LiCl derived from (*R*,*R*)- or (*S*,*S*)-**14**/*n*BuLi.[a]



Entry	Base	**10**,**11**	Regioisomeric ratio (1*R*,4*R*)-**10**/(1*S*,4*R*)-**10**/(1*S*,6*R*)-**11**/(1*R*,6*R*)-**11**	Yield of **10** [%][b]	Yield of **11** [%][c]	*dr* (*R*,*R*)-**10**/(*S*,*R*)-**10**	*dr* (*S*,*R*)-**11**/(*R*,*R*)-**11**	Pseudo-C_2	Pseudo-C_s
1	(*R*,*R*)-**14**	**a**	79:21	58	15	99.5:0.5	65:35	matched	mismatched
2	(*R*,*R*)-**14**	**b**	76:24	28	9	98:2	52:48	matched	mismatched
3	(*S*,*S*)-**14**	**a**	21:79	16	60	13:87	100:0	mismatched	matched
4	(*S*,*S*)-**14**	**b**	20:80	17	68	29:71	1:99	mismatched	matched
5	(*R*,*R*)-**14**	**a**[d]	84:16	43	9	99.5:0.5	65:35		
6	(*R*,*R*)-**14**	**b**[d]	76:24	28	9	98:2	52:48		

[a] Reaction conditions as in Scheme 3. [b] Yield of (1*R*,4*R*)-**10** + (1*S*,4*R*)-**10**. [c] Yield of (1*S*,6*R*)-**11** + (1*R*,6*R*)-**11**. [d] Alkylation via silyl enol ether **15**, as outlined in Scheme 4.

lowing a previously described method,[13,18] ketone **9** was deprotonated with (*R*,*R*)-**14**/*n*BuLi and the resulting enolate was trapped as silyl enol ether **15** by addition of chlorotriethylsilane.

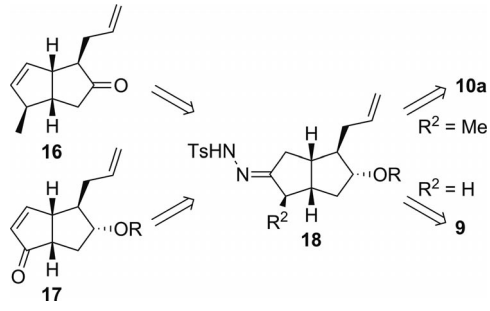


Scheme 4.

Subsequent treatment of **15** with MeLi regenerated the lithium enolate prior to alkylation with methyl or allyl iodide. As shown in Table 1, the regioisomers (1*R*,4*R*)-**10a**,**b**/(1*S*,4*R*)-**10a**,**b** and (1*S*,6*R*)-**11a**,**b**/(1*R*,6*R*)-**11a**,**b** were isolated in ratios and diastereoselectivities (entries 5 and 6) similar to those obtained in the in situ deprotonation.

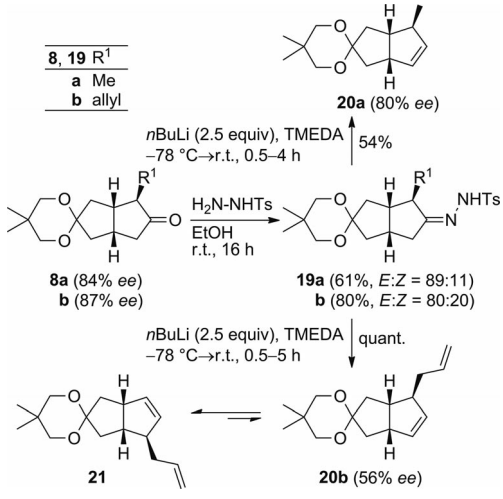
Applying the in situ deprotonation/alkylation route to the α-methyl-substituted analogue of **9** resulted in poor regioselectivities and yields. Replacing the *tert*-butyl(diphenyl)silyl protecting group in **9** by TBS did not change the stereoselection. In the presence of the chiral base (*R*,*R*)-**14**/*n*BuLi, the TBS-protected analogue of **9** provided comparable results to those obtained with **9** (see the Supporting Information).

To use the functionalized ketones **9** and **10** in the synthesis of the bicyclo[3.3.0]octene core precursors **16** and **17** of cylindramide (**5**) and geodin A (**4**), respectively, we planned to introduce the required double bond through a Shapiro reaction (Scheme 5).[20]



Scheme 5.

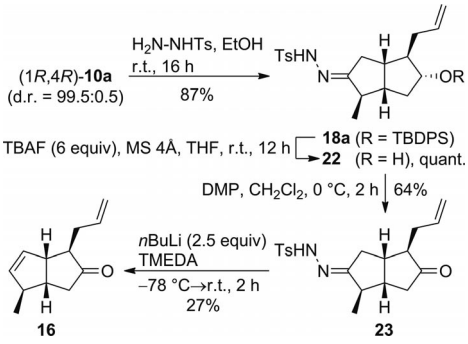
Although Shapiro reactions are reported to form preferentially the less substituted double bond,[21] we were initially concerned that a strong base might induce elimination of the tosylhydrazone to yield the undesired regioisomer, a more substituted C=C double bond. Therefore we started with model reactions using acetals **8** as the starting materials (Scheme 6). α-Allylated ketone **8b** (87% *ee*) was treated



Scheme 6. TMEDA = tetramethylethylenediamine.

with tosylhydrazine in EtOH[22] to give the corresponding tosylhydrazone **19b** in 80% yield with an *E*/*Z* ratio of 80:20. Derivative **19b** was treated with 2.5 equiv. of *n*BuLi and TMEDA in THF at –78 °C for 30 min. The reaction mixture was then warmed to room temperature over 5 h and, after aqueous work-up, the desired alkene **20b** was obtained quantitatively, albeit with a considerable loss of enantiomeric purity (56% *ee*). In this case, racemization may occur during a [3,3]sigmatropic Cope rearrangement between **20b** and **21**. Indeed, in a control experiment, tosylhydrazone **19a** derived from α-methyl-substituted ketone **8a** (84% *ee*) gave, under the Shapiro conditions, the desired alkene **20a**, which could be isolated in 54% yield with similar optical purity (80% *ee*) as starting **8a** (84% *ee*).

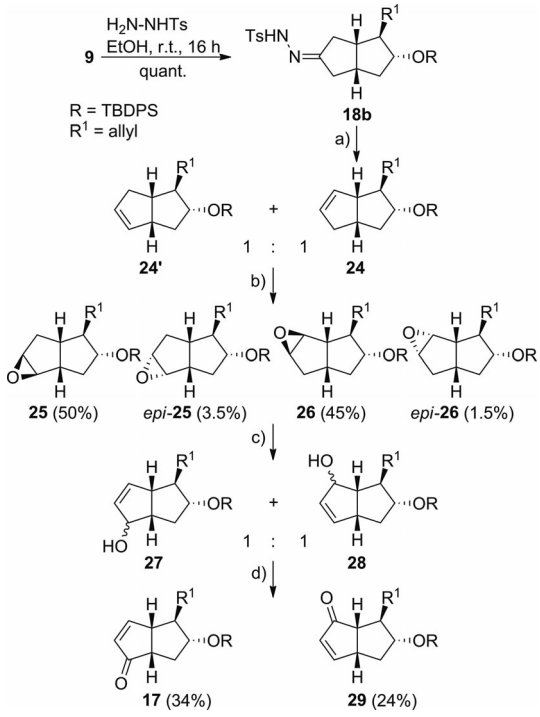
The Shapiro route was then applied to the starting ketone **10a** (99% *de*) for the synthesis of the hydropentalene core **16** of cylindramide (Scheme 7). This strategy obviates the kilogram amounts of toxic lead tetraacetate that were necessary in the first-generation synthesis of **5** starting from cycloocta-1,5-diene.[23] The conversion of (1*R*,4*R*)-**10a** into tosylhydrazone **18a** proceeded in 87% yield under the usual conditions. Hydrazone **18a** was then deprotected at the TBDPS ether with 6 equiv. of TBAF to give alcohol **22** quantitatively. The latter was oxidized with Dess–Martin periodinane[24] to yield ketone **23** in 64% yield. Finally, Shapiro reaction of **23** provided tetrahydropentalenone **16** in 27% yield.



Scheme 7. Application of the Shapiro reaction to ketone **10a**. TBAF = tetrabutylammonium fluoride, DMP = Dess–Martin periodinane.

The monofunctionalized bicyclo[3.3.0]octanone **9** should provide access to geodin A core precursor **17** (Scheme 8). The conversion of **9** into tosylhydrazone **18b** followed by the Shapiro reaction resulted in an inseparable 1:1 mixture of regioisomeric alkenes **24** and **24′** in a 70% combined yield. Their treatment with MCPBA gave a 48% yield of a mixture of four regio- and diastereomeric epoxides **25**, *epi*-**25**, **26** and *epi*-**26** in a ratio of 50:3.5:45:1.5, as determined by GC.

Analysis of the NMR spectra identified *exo*-epoxide **25** as the major product. Under the assumption that the attack of MCPBA on alkene **24** and **24′** occurs preferentially from the sterically less hindered *exo* face, the regioisomeric epoxide **26** was expected to be the other major product.[25] The epoxide mixture was submitted to base-induced epoxide



Scheme 8. Synthesis of the geodin A core unit **17**. Reagents and conditions: a) *n*BuLi (2.5 equiv.), TMEDA, –78 °C→r.t., 4 h, 70%; b) $NaHCO_3$ (5 equiv.), MCPBA (2 equiv.), abs. CH_2Cl_2, r.t., 1 h, 48%; c) TMEDA (5 equiv.), LDA (2.5 equiv.), Et_2O, r.t., 6 h, 59%; d) DMP (1.3 equiv.), abs. CH_2Cl_2, 0 °C, 2 h. MCPBA = *meta*-chloroperoxybenzoic acid.

opening[26] with LDA to yield a 1:1 mixture of the allylic alcohols **27** and **28** in 59% yield, followed by oxidation with Dess–Martin periodinane. Chromatographic purification afforded the desired enone **17** and its regioisomer **29** in yields of 34 and 24%, respectively.

Conclusions

The secondary functionalization of the α-allylated hydropentalenone derivative **9** has been investigated with regard to stereoselectivity of the resulting alkylated bicyclo[3.3.0]-octanes **10** and **11** and possible follow-up reactions. The enolate formed in the direct asymmetric deprotonation/alkylation sequence was found to determine both the stereodifferentiation and the regiochemical control. Although the reactions in the presence of the base (*R*,*R*)-**14**/*n*BuLi were independent of the incoming electrophile, complementary diastereoselectivity was observed when (*S*,*S*)-**14** was used.

The synthetic strategy presented herein offers an approach to hydropentalene precursors, as has been demonstrated for derivative **10a**. The latter was submitted to a Shapiro reaction and subsequent oxidation gave the bicyclo[3.3.0]octene core of cylindramide (**5**). Shapiro reaction followed by epoxidation of the resulting alkene, epoxide opening and oxidation converted derivative **9** into the potential geodin A precursor **17**.

Experimental Section

General Methods: NMR spectra were recorded with a Bruker Avance 500 spectrometer in $CDCl_3$ with TMS (δ = 0.00 ppm) as an internal standard. IR spectra were recorded with a Bruker FTIR Vektor 22 spectrometer equipped with an MKII golden gate single reflection Diamant ATR system. Mass spectra were recorded with a Finnigan MAT 95 spectrometer (CI, APCI) with ammonia as carrier gas, a Varian MAT 711 (EI, 70 eV) and a Bruker Daltonics micrOTOF_Q (ESI) with nitrogen as carrier gas. Optical rotations were measured with a Perkin–Elmer 241 polarimeter at 20 °C. The reactions and purity of the products were monitored by GC using a Hewlett–Packard HP 6890 instrument with a HP-5 column (30 m × 0.32 mm), hydrogen as carrier gas and different temperature programs. Enantioselectivities were determined by GC on chiral stationary phases Amidex C (Amidex-pob-12-un-5.0-Et-133) or Bondex un-β-5.5 (pure β-cyclodextrin phase) using different temperature programs. Flash chromatography was performed on silica gel (grain size 40–63 μm, Fluka).

All reactions were performed under nitrogen in oven-dried glassware. All reagents were used as purchased unless otherwise noted. Alkyl halides were distilled prior to use. THF was distilled from sodium/benzophenone, CH_2Cl_2 and toluene from CaH_2, and MeOH from magnesium. The reactions were monitored by TLC (Merck 60 F_{254} plates) and visualized with an ethanolic solution of *p*-anisaldehyde and sulfuric acid.

General Procedure for the Enantioselective Deprotonation/Alkylation of 9 (GP1): A 1.6 M solution of *n*BuLi in hexane (1.95 equiv.) was added dropwise to a solution of **14** (1 equiv.) in THF (20 mL) at –78 °C . The mixture was warmed to room temperature until it became a clear yellow solution (1 h). It was recooled to –100 °C, a solution of **9** (0.8 equiv.) in THF (5 mL) was added dropwise and the reaction mixture stirred at –100 °C for a further 2 h. After deprotonation, the reaction mixture was treated with the corresponding electrophile (1.7–3.3 equiv.), warmed to –40 °C and stirred for 12 h. A saturated solution of $NaHCO_3/H_2O$ (2–10 mL) was added, the mixture was warmed to room temperature and the organic solvent was removed. The aqueous layer was extracted three times with CH_2Cl_2. The combined extracts were dried ($MgSO_4$), concentrated and the residue purified by chromatography on SiO_2 with hexanes/EtOAc.

General Procedure for the Alkylation of 9 via Silyl Enol Ether 15 (GP2): A 1.6 M solution of MeLi in Et_2O (1.1 equiv.) was added dropwise to a solution of **15** (1 equiv.; see below for the preparation of **15**) in THF (5 mL) at –10 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. Then it was cooled to –40 °C and treated with the corresponding electrophile R^2I (2 equiv.). After stirring the mixture for 22 h at –40 °C, a saturated solution of $NaHCO_3/H_2O$ (2–10 mL) was added, the mixture was warmed to room temperature and the organic solvent was removed. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$), concentrated and the residue purified by chromatography on SiO_2 with hexanes/EtOAc.

[((3a*S*,5*R*,6*R*,6a*S*)-6-Allyl-5-{[*tert*-butyl(diphenyl)silyl]oxy}-1,3a,4,5,6,6a-hexahydropentalen-2-yl)oxy](triethyl)silane (15): Deprotonation according to GP1, from (*R*,*R*)-**14** (579 mg, 2.21 mmol) in THF (25 mL), *n*BuLi (2.69 mL, 1.6 M in hexane, 4.31 mmol) and **9** (212 mg, 1.70 mmol). After stirring for 1 h at –100 °C, the mixture was warmed to –78 °C, treated with $ClSiEt_3$ (570 μL, 512 mg, 3.40 mmol) and stirred for a further 2 h. A saturated solution of $NaHCO_3/H_2O$ (5 mL) was added, the reaction mixture was warmed to room temperature and the layers were separated. The organic layer was dried ($MgSO_4$) and concentrated. The regenerated **14** was precipitated by the addition of *n*-pentane and filtered off. The filtrate was concentrated and the residue purified by chromatography on SiO_2 with hexanes/EtOAc/NEt_3 (50:1:1) to give **15** (849 mg, 1.59 mmol, 94%, 80% purity by GC) as a colourless oil. R_f = 0.89 (hexanes/EtOAc = 5:1). $[a]_D^{20}$ = –12.6 (*c* = 1.0, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.67 [q, *J* = 8.0 Hz, 6 H, $Si(CH_2CH_3)_3$], 0.97 [t, *J* = 8.0 Hz, 9 H, $Si(CH_2CH_3)_3$], 1.04 [s, 9 H, $SiC(CH_3)_3$], 1.53 (dt, *J* = 12.9, 6.5 Hz, 1 H, 4-H_a), 1.75–1.89 (m, 2 H, 1′-H_a, 6-H), 1.96–2.03 (m, 2 H, 4-H_b, 6a-H), 2.23–2.35 (m, 1 H, 1-H_a), 2.40–2.50 (m, 3 H, 1-H_b, 1′-H_b, 3a-H), 3.60–3.67 (m, 1 H, 5-H), 4.55–4.65 (m, 1 H, 3-H), 4.89–4.97 (m, 2 H, 3′-H), 5.71 (ddt, *J* = 17.0, 10.1, 6.9 Hz, 1 H, 2′-H), 7.34–7.43 (m, 6 H, *m*-H, *m*′-H, *p*-H, *p*′-H), 7.63–7.69 (m, 4 H, *o*-H, *o*′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.8 [$Si(CH_2CH_3)_3$], 6.7 [$Si(CH_2CH_3)_3$], 19.3 [$SiC(CH_3)_3$], 27.0 [$SiC(CH_3)_3$], 40.1 (C-6a), 40.5 (C-1′), 41.7 (C-4), 45.2 (C-1), 49.0 (C-3a), 55.1 (C-6), 78.4 (C-5), 107.2 (C-3), 115.7 (C-3′), 127.56, 127.60 (C-*m*, C-*m*′), 129.6, 129.71 (C-*p*, C-*p*′), 134.3, 134.7 (C-*i*, C-*i*′), 135.9 (C-*o*, C-*o*′), 137.8 (C-2′), 152.6 (C-2) ppm.

General Procedure for Desilylation with TBAF (GP3): $TBAF{\cdot}3H_2O$ (2.5 or 6 equiv.) was dried with 4 Å molecular sieves (15–20 pellets) under high vacuum at 40 °C for 1 h and then dissolved in THF (5 mL). The corresponding silyl ether (1 equiv.) was dried with 4 Å molecular sieves (5–10 pellets) under high vacuum, dissolved in abs. THF (3 mL) and cooled to 0 °C. The TBAF solution was added dropwise through a syringe and the reaction mixture stirred for 30 min. Then the mixture was warmed to room temperature and stirred for a further 12 h. A saturated solution of $NaHCO_3/H_2O$ (5 mL) was added and the organic solvent removed. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$), concentrated and the residue purified by chromatography on SiO_2 with hexanes/EtOAc.

General Procedure for the Preparation of *p*-Tosylhydrazones (GP4): *p*-Tosylhydrazine (1 equiv.) was added to a solution of the corresponding ketone (1 equiv.) in absolute ethanol (2 mL) and dissolved by careful warming. The reaction mixture was then stirred at room temperature for 16 h. Precipitated tosylhydrazone was filtered off and dried under high vacuum. Otherwise the solvent was removed and the residue purified by chromatography on SiO_2 with hexanes/EtOAc.

(3a′*S*,4′*R*,5′*R*,6a′*R*)-4′-Allyl-5,5-dimethylhexahydro-1′*H*-spiro-[1,3-dioxane-2,2′-pentalen]-5′-ol (12): Finely powered $NaBH_4$ (321 mg, 8.49 mmol) was added portionwise to a solution of **8b** (749 mg, 2.83 mmol) in abs. methanol (20 mL) at 0 °C and the reaction mixture was stirred for 1.5 h. After addition of H_2O (5 mL), the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were washed with brine (5 mL), dried ($MgSO_4$) and concentrated. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc = 10:1) to give **12** (483 mg, 1.81 mmol, 64%, 97% purity by GC) as a colourless oil. R_f = 0.16 (hexanes/EtOAc = 5:1), $[a]_D^{20}$ = –9.2 (*c* = 1.0, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.95 [s, 3 H, $C(CH_3)_2$], 0.97 [s, 3 H, $C(CH_3)_2$], 1.44–1.51 (m, 1 H, 6′-H_a), 1.64–1.71 (m, 1 H, 4′-H), 1.76–1.83 (m, 2 H, 1′-H_a, 3′-H_a), 1.88 (br. s, 1 H, O*H*), 2.06–2.29 (m, 6 H, 1′-H_b, 3′-H_b, 3a′-H, 1′′-H_a, 1′′-H_b, 6′-H_b), 2.37–2.46 (m, 1 H, 6a′-H), 3.46 (s, 2 H, OCH_2), 3.49 (s, 2 H, OCH_2), 3.71–3.79 (m, 1 H, 5′-H), 5.00–5.12 (m, 2 H, 3′′-H_a, 3′′-H_b), 5.87 (dddd, *J* = 14.5, 10.1, 7.6, 6.9 Hz, 1 H, 2′′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.5 [$C(CH_3)_2$], 22.6 [$C(CH_3)_2$], 30.1 (C-5), 35.9 (C-6a′), 37.8 (C-1′′), 40.1 (C-1′), 40.3 (C-3′), 41.3 (C-6′), 43.9 (C-3a′), 53.8 (C-4′), 72.0 (OCH_2), 72.2

(OCH_2), 79.2 (C-5′), 110.4 (C-2′), 116.1 (C-3′′), 137.5 (C-2′′) ppm. FTIR (ATR): $\tilde{\nu}$ = 3402 (br), 3075 (w), 2953 (m), 2933 (m), 2863 (m), 2374 (w), 2184 (w), 11974 (br), 1640 (w), 1456 (w), 1327 (w), 1313 (w), 1105 (s), 1039 (w), 1014 (w), 908 (s), 870 (w), 735 (s) 599 (w) cm^{-1}. MS (APCI): *m*/*z* (%) = 267.2 (37) $[M + H]^+$, 249.2 (18) $[M - H_2O]^+$, 229.2 (9), 181.1 (14) $[C_{11}H_{17}O_2]^+$, 163.1 (100) $[M - C_5H_{13}O_2]^+$, 145.1 (37), 135.1 (50), 121.1 (20), 105.1 (20) $[C_5H_{13}O_2]^+$, 93.1 (4). HRMS (APCI): calcd. for $C_{16}H_{27}O_3^+$ $[M + H]^+$ 267.1995; found 267.1953.

{[(3a′*S*,4′*R*,5′*R*,6a′*R*)-4′-Allyl-5,5-dimethylhexahydro-1′*H*-spiro-[1,3-dioxane-2,2′-pentalen]-5′-yl]oxy}(*tert*-butyl)diphenylsilane (13): Imidazole (395 mg, 5.80 mmol) was added to a solution of **12** (617 mg, 2.32 mmol) in abs. DMF (5 mL) at 0 °C followed by the dropwise addition of TBDPSCl (0.72 mL, 764 mg, 2.78 mmol) over 10 min. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for a further 4 h. The reaction was quenched with H_2O (3 mL) and the resulting slurry extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc = 10:1) to give **13** (960 mg, 1.90 mmol, 82%, >99% purity by GC) as a colourless oil. R_f = 0.75 (hexanes/EtOAc = 5:1). $[\alpha]_D^{20}$ = –14.8 (*c* = 1.3, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.94 [s, 3 H, $C(CH_3)_2$], 0.96 [s, 3 H, $C(CH_3)_2$], 1.05 [s, 9 H, $SiC(CH_3)_3$], 1.45 (dt, *J* = 12.3, 7.7 Hz, 1 H, 6′-H_a), 1.68–1.82 (m, 3 H, 1′′-H_a, 4′-H, 6′-H_b), 1.94–1.99 (m, 1 H, 3a′-H), 2.19–2.26 (m, 4 H, 1′′-H_b, 3′-H_a, 3′-H_b, 6a′-H), 2.43 (dd, *J* = 10.1, 1.9 Hz, 1 H, 1′-H_a), 2.47 (dd, *J* = 8.8, 1.9 Hz, 1 H, 1′-H_b), 3.44 (s, 2 H, OCH_2), 3.47 (s, 2 H, OCH_2), 3.77 (dt, *J* = 6.0, 7.7 Hz, 1 H, 5′-H), 4.86–4.93 (m, 2 H, 3′′-H), 6.62 (dddd, *J* = 17.0, 13.8, 10.1, 6.9 Hz, 1 H, 2′′-H), 7.34–7.39 (m, 4 H, *m*-H), 7.40–7.45 (m, 2 H, *p*-H), 7.63–7.68 (m, 4 H, *o*-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.2 [$C(CH_3)_2$], 22.8 [$C(CH_3)_2$], 26.9 [$SiC(CH_3)_3$], 30.1 [$SiC(CH_3)_3$], 36.3 (C-6a′), 37.4 (C-1′′), 40.9 (C-6′), 42.8 (C-3a′), 45.2 (C-1′), 54.1 (C-4′), 71.0 (OCH_2), 72.6 (OCH_2), 80.2 (C-5′), 110.3 (C-2′), 115.5 (C-3′′), 127.4, 127.5 (C-*m*), 129.47, 129.53 (C-*p*), 134.2, 134.6 (C-*i*), 136.0 (C-*o*), 137.3 (C-2′′) ppm. FTIR (ATR): $\tilde{\nu}$ = 3072 (w), 2953 (m), 2857 (m), 2185 (w), 1961 (br), 1640 (w), 1472 (m), 1428 (m), 1393 (w), 1362 (w), 1330 (w), 1261 (m), 1109 (vs), 1047 (m), 996 (w), 909 (m), 822 (m), 740 (m), 702 (s), 612 (m) cm^{-1}. MS (ESI): *m*/*z* = 505.3 $[M + H]^+$, 341.2, 249.2 $[M - HSitBuPh_2]^+$, 163.1. HRMS (ESI): calcd. for $C_{32}H_{44}O_3SiNa^+$ $[M + Na]^+$ 527.2952; found 527.2960.

(3a*S*,4*R*,5*R*,6a*R*)-4-Allyl-5-{[*tert*-butyl(diphenyl)silyl]oxy}-hexahydropentalen-2(1*H*)-one (9): A catalytic amount of *p*TsOH (2 mol-%) was added to a solution of **13** (926 mg, 1.83 mmol) in abs. acetone (10 mL). After stirring at room temperature for 3 h, the reaction was quenched by the addition of Et_3N (3 drops). The solvent was removed and the residue purified by chromatography on SiO_2 (hexanes/EtOAC = 15:1) to give **9** (766 mg, 1.83 mmol, quant., >99% purity by GC) as a colourless oil. R_f = 0.59 (hexanes/EtOAc = 5:1). $[\alpha]_D^{20}$ = –6.0 (*c* = 0.5, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.04 [s, 9 H, $SiC(CH_3)_3$], 1.50–1.56 (m, 1 H, 6-H_a), 1.78–1.87 (m, 2 H, 1′-H_a, 4-H), 2.00 (ddd, *J* = 13.4, 8.2, 6.2 Hz, 1 H, 6-H_b), 2.06–2.11 (m, 1 H, 1′-H_b), 2.23–2.36 (m, 3 H, 1-H_a, 3-H_a, 3a-H), 2.41–2.51 (m, 2 H, 1-H_b, 3-H_b), 2.54–2.62 (m, 1 H, 6a-H), 3.92 (dt, *J* = 6.0, 5.1 Hz, 1 H, 5-H), 4.85–4.91 (m, 2 H, 3′-H), 5.50–5.59 (m, 1 H, 2′-H), 7.35–7.39 (m, 4 H, *m*-H), 7.41–7.45 (m, 2 H, *p*-H), 7.63–7.67 (m, 4 H, *o*-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.1 [$SiC(CH_3)_3$], 27.0 [$SiC(CH_3)_3$], 36.5 (C-6a), 37.1 (C-1′), 41.7 (C-6), 42.6 (C-3a), 44.8, 45.2 (C-1, C-3), 55.1 (C-4), 80.0 (C-5), 116.2 (C-3′), 127.58, 127.61 (C-*m*), 129.65, 129.70 (C-*p*), 133.9, 134.1 (C-*i*), 135.9, 136.0 (C-*o*), 136.5 (C-2′), 220.7 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3055 (m), 2987 (m), 2307 (w), 1422 (m), 1265 (s), 896 (w), 731 (vs), 703 (s), 565 (w) cm^{-1}. MS (APCI): *m*/*z* = 419.3 $[M + H]^+$, 341.2 $[M + H - C_6H_6]^+$, 295.2, 263.2 $[M + H - 2C_6H_6]^+$, 177.1 $[M + H - HSitBuPh_2]^+$, 145.1. HRMS (ESI): calcd. for $C_{27}H_{34}O_2SiNa^+$ $[M + Na]^+$ 441.2220; found 441.2217.

(1*R*,3a*S*,4*R*,5*R*,6a*S*)-4-Allyl-5-{[*tert*-butyl(diphenyl)silyl]oxy}-1-methylhexahydropentalen-2(1*H*)-one [(1*R*,4*R*)- and (1*S*,4*R*)-10a] and (1*S*,3a*R*,5*R*,6*R*,6a*S*)-6-Allyl-5-{[*tert*-butyl(diphenyl)silyl]oxy}-1-methylhexahydropentalen-2(1*H*)-one [(1*S*,6*R*)- and (1*R*,6*R*)-11a]: a) According to GP1, from (*R*,*R*)-**14** (1.26 g, 4.82 mmol), *n*BuLi (5.88 mL, 9.40 mmol), **9** (1.68 g, 4.02 mmol) and MeI (0.50 mL, 1.14 g, 8.04 mmol), flash chromatography on SiO_2 [hexanes/EtOAc = 50:1, (*R*,*R*)- and (*S*,*R*)-**10a**: R_f = 0.75; (*S*,*R*)- and (*R*,*R*)-**11a**: R_f = 0.70 (hexanes/EtOAc = 10:1)] gave (*R*,*R*)- and (*S*,*R*)-**10a** [1.01 g, 2.33 mmol, 58%, >99% purity by ^1H NMR; *dr* = 99.5:0.5 (99% *de*, ODH); $[\alpha]_D^{20}$ = –12.0 (*c* = 1.0, CH_2Cl_2)] and (*S*,*R*)- and (*R*,*R*)-**11a** [251 mg, 0.58 mmol, 15%, >99% purity by ^1H NMR; *dr* = 65:35 (30% *de*, ODH); $[\alpha]_D^{20}$ = –8.6 (*c* = 0.8, CH_2Cl_2)] as colourless oils. In a first fraction, the two-fold methylated ketone was isolated as a byproduct (137 mg, 0.31 mmol, 8%). The diastereomeric mixtures were separated by preparative HPLC on a Kromasil 100 Sil 5 µm column [hexanes/EtOAc = 100:1, flow 2.5 mL/min, t_R(*R*,*R*-**10a**) = 10.91 min, t_R(*S*,*R*-**10a**) = 9.62 min; t_R(*S*,*R*-**11a**) = 16.09 min, t_R(*R*,*R*-**11a**) = 10.48 min].

b) According to GP1, from (*S*,*S*)-**14** (251 mg, 0.96 mmol), *n*BuLi (1.17 mL, 1.87 mmol), **9** (335 mg, 0.80 mmol) and MeI (100 µL, 227 mg, 1.60 mmol), flash chromatography on SiO_2 (hexanes/EtOAc = 30:1) and subsequent separation by preparative HPLC gave (*R*,*R*)- and (*S*,*R*)-**10a** [54.0 mg, 125 µmol, 16%, 88% purity by GC; *dr* = 13:87 (74% *de*, ODH); $[\alpha]_D^{20}$ = –4.2 (*c* = 0.8, CH_2Cl_2)] and (*S*,*R*)- and (*R*,*R*)-**11a** [208 mg, 481 µmol, 60%, 82% purity by GC; *dr* = 100:0 (>99% *de*, ODH); $[\alpha]_D^{20}$ = –2.2 (*c* = 1.0, CH_2Cl_2)] as colourless oils.

c) According to GP2, from **15** (42.6 mg, 80.0 µmol), MeLi (0.55 mL, 88.0 µmol) and MeI (10.0 µL, 22.7 mg, 160 µmol), the isomers (*R*,*R*)- and (*S*,*R*)-**10a** (15.0 mg, 34.7 µmol, 43%, 96% purity by GC, *dr* = 99.5:0.5) and (*S*,*R*)- and (*R*,*R*)-**11a** (3.00 mg, 6.93 µmol, 9%, 88% purity by GC, *dr* = 65:35) were obtained as colourless oils.

(*R*,*R*)- and (*S*,*R*)-10a: ^1H NMR (500 MHz, $CDCl_3$): δ = 1.04 (d, *J* = 6.9 Hz, 3 H, 1′-H), 1.04 [s, 9 H, $SiC(CH_3)_3$], 1.62 (dt, *J* = 13.2, 4.6 Hz, 1 H, 6-H_a), 1.79–1.88 (m, 2 H, 1′′-H_a, 4-H), 2.01 (ddd, *J* = 13.2, 8.0, 6.4 Hz, 1 H, 6-H_b), 2.07 (dq, *J* = 8.4, 4.2 Hz, 1 H, 6a-H), 2.09–2.19 (m, 2 H, 1′′-H_b, 3a-H), 2.32–2.39 (m, 2 H, 1-H, 3-H_a), 2.43 (dd, *J* = 19.1, 9.1 Hz, 1 H, 3-H_b), 3.96 (dt, *J* = 6.5, 5.3 Hz, 1 H, 5-H), 4.85–4.90 (m, 2 H, 3′′-H), 5.55 (ddt, *J* = 14.9, 12.3, 6.9 Hz, 1 H, 2′′-H), 7.35–7.40 (m, 4 H, *m*-H, *m*′-H), 7.41–7.45 (m, 2 H, *p*-H, *p*′-H), 7.63–7.67 (m, 4 H, *o*-H, *o*′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2 (C-1′), 19.1 [$SiC(CH_3)_3$], 27.0 [$SiC(CH_3)_3$], 37.1 (C-1′′), 40.2 (C-6), 40.5 (C-3a), 43.4 (C-3), 45.9 (C-6a), 50.2 (C-1), 54.9 (C-4), 80.2 (C-5), 116.3 (C-3′′), 127.58, 127.61 (C-*m*, C-*m*′), 129.65, 129.71 (C-*p*, C-*p*′), 133.9, 134.1 (C-*i*, C-*i*′), 135.90, 135.93 (C-*o*, C-*o*′), 136.4 (C-2′′), 221.8 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3071 (w), 2929 (m), 2857 (m), 1737 (vs), 1640 (w), 1589 (w), 1471 (w), 1427 (m), 1375 (w), 1107 (vs), 1042 (s), 998 (m), 910 (m), 821 (m), 741 (m), 702 (vs), 611 (m) cm^{-1}. MS (ESI): *m*/*z* = 455.2 $[M + Na]^+$, 356.2 $[M + H - C_6H_6]^+$, 254.1, 159.1. HRMS (ESI): calcd. for $C_{28}H_{36}O_2SiNa^+$ $[M + Na]^+$ 455.2377; found 455.2350.

(*S*,*R*)- and (*R*,*R*)-11a: ^1H NMR (500 MHz, $CDCl_3$): δ = 1.04 [s, 9 H, $SiC(CH_3)_3$], 1.06 (d, *J* = 7.3 Hz, 3 H, 1′-H), 1.55 (dt, *J* = 13.5, 6.7 Hz, 1 H, 6-H_a), 1.79 (dddt, *J* = 13.6, 8.8, 7.6, 1.2 Hz, 1 H, 1′′-H_a), 1.84 (dt, *J* = 4.3, 8.3 Hz, 1 H, 3a-H), 1.94 (ddt, *J* = 9.1, 4.5,

4.5 Hz, 1 H, 4-H), 2.01–2.03 (m, 1 H, 1′′-Hb), 2.05 (ddd, J = 13.5, 8.2, 6.3 Hz, 1 H, 6-H_b), 2.32 (ddd, J = 18.7, 4.8, 1.8 Hz, 1 H, 1-H_a), 2.37–2.42 (m, 1 H, 3-H), 2.42 (dd, J = 18.7, 9.1 Hz, 1 H, 1-H_b), 2.45–2.53 (m, 1 H, 6a-H), 3.97 (dt, J = 4.7, 6.1 Hz, 1 H, 5-H), 4.86–4.91 (m, 2 H, 3′′-H), 5.54 (dddd, J = 17.4, 9.7, 7.1, 6.6 Hz, 1 H, 2′′-H), 7.36–7.40 (m, 4 H, *m*-H, *m*′-H), 7.41–7.45 (m, 2 H, *p*-H, *p*′-H), 7.63–7.67 (m, 4 H, *o*-H, *o*′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.5 (C-1′), 19.1 [Si*C*$(CH_3)_3$], 27.0 [SiC(*C*$H_3)_3$], 34.3 (C-6a), 37.5 (C-1′′), 41.8 (C-6), 43.8 (C-1), 49.3 (C-3), 51.5 (C-3a), 54.1 (C-4), 80.6 (C-5), 116.2 (C-3′′), 127.6 (C-*m*, C-*m*′), 129.66, 129.72 (C-*p*, C-*p*′), 133.9, 134.1 (C-*i*, C-*i*′), 135.86, 135.91 (C-*o*, C-*o*′), 136.7 (C-2′′), 222.0 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3072 (w), 2929 (m), 2857 (m), 1737 (vs), 1640 (w), 1472 (w), 1427 (m), 1373 (w), 1264 (m), 1107 (vs), 1041 (s), 997 (s), 912 (s), 822 (m), 739 (s), 700 (vs), 611 (s), 505 (s) cm^{-1}. MS (ESI): m/z = 455.2 [M + Na]$^+$, 356.2 [M + H – C_6H_6]$^+$, 282.2, 203.7, 159.1. HRMS (ESI): calcd. for $C_{28}H_{36}O_2SiNa^+$ [M + Na]$^+$ 455.2377; found 455.2370.

(1*R*,3a*S*,4*R*,5*R*,6a*S*)-1,4-Diallyl-5-{[*tert*-butyl(diphenyl)silyl]oxy}-hexahydropentalen-2(1*H*)-one [(1*R*,4*R*)- and (1*S*,4*R*)-10b] and (1*S*,3a*R*,5*R*,6*R*,6a*S*)-1,6-Diallyl-5-{[*tert*-butyl(diphenyl)silyl]oxy}-hexahydropentalen-2(1*H*)-one [(1*S*,6*R*)- and (1*R*,6*R*)-11b]: a) According to GP1, from (*R*,*R*)-**14** (314 mg, 120 mmol), *n*BuLi (1.46 mL, 2.34 mmol), **9** (419 mg, 1.00 mmol) and allyl iodide (180 μL, 336 mg, 2.00 mmol), flash chromatography on SiO_2 [hexanes/EtOAc = 30:1, (*R*,*R*)- and (*S*,*R*)-**10b**: R_f = 0.34; (*S*,*R*)- and (*R*,*R*)-**11b**: R_f = 0.30] gave (*R*,*R*)- and (*S*,*R*)-**10b** [128 mg, 0.28 mmol, 28%, 98% purity by GC, *dr* = 98:2; $[\alpha]_D^{20}$ = –16.0 (*c* = 0.7, CH_2Cl_2)] and (*S*,*R*)- and (*R*,*R*)-**11b** [40.0 mg, 90.0 μmol, 9%, 92% purity by GC, *dr* = 52:48; $[\alpha]_D^{20}$ = +1.6 (*c* = 0.5, CH_2Cl_2)] as colourless oils. The diastereoisomers were separated by preparative HPLC on a Kromasil 100 Sil 5 μm column (hexanes/EtOAc = 100:1, flow 2.5 mL/min, detection wavelength 254 nm).

b) According to GP1, from (*S*,*S*)-**14** (251 mg, 0.96 mmol), *n*BuLi (1.17 mL, 1.87 mmol), **9** (335 mg, 0.80 mmol) and allyl iodide (150 μL, 269 mg, 1.60 mmol), flash chromatography on SiO_2 (hexanes/EtOAc = 30:1) and subsequent separation by preparative HPLC gave (*R*,*R*)- and (*S*,*R*)-**10b** [62.0 mg, 135 μmol, 17%, 81% purity by GC; $[\alpha]_D^{20}$ = –11.4 (*c* = 1.0, CH_2Cl_2)] and (*S*,*R*)- and (*R*,*R*)-**11b** [251 mg, 547 μmol, 68%, 92% purity by GC; $[\alpha]_D^{20}$ = –6.4 (*c* = 0.8, CH_2Cl_2)] as colourless oils.

c) According to GP2, from **15** (528 mg, 0.99 mmol), MeLi (0.66 mL, 1.09 mmol) and allyl iodide (0.18 mL, 333 mg, 1.98 mmol), (*R*,*R*)- and (*S*,*R*)-**10b** (128 mg, 0.28 mmol, 28%, 96% purity by GC, *dr* = 98:2) and (*S*,*R*)- and (*R*,*R*)-**11b** (40.0 mg, 0.09 mmol, 9%, 96% purity by GC, *dr* = 52:48) were obtained as colourless oils.

(*R*,*R*)- and (*S*,*R*)-10b: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04 [s, 9 H, SiC$(CH_3)_3$], 1.61 (dt, J = 13.6, 5.1 Hz, 1 H, 6-H_a), 1.76–1.86 (m, 2 H, 1′′-H_a, 4-H), 1.99 (ddd, J = 13.6, 7.9, 6.1 Hz, 1 H, 6-H_b), 2.03–2.12 (m, 2 H, 1′-H_a, 1′′-H_b), 2.14–2.21 (m, 1 H, 3a-H), 2.22–2.29 (m, 1 H, 6a-H), 2.35–2.47 (m, 4 H, 1′-H_b, 1-H, 3-H_a, 3-H_b), 3.94 (dt, J = 5.1, 5.6 Hz, 1 H, 5-H), 4.84–4.94 (m, 2 H, 3′′-H), 4.97–5.04 (m, 2 H, 3′-H), 5.48–5.57 (m, 1 H, 2′′-H), 5.65–5.75 (m, 1 H, 2′-H), 7.35–7.40 (m, 4 H, *m*-H, *m*′-H), 7.41–7.45 (m, 2 H, *p*-H, *p*′-H), 7.63–7.67 (m, 4 H, *o*-H, *o*′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.1 [Si*C*$(CH_3)_3$], 27.0 [SiC(*C*$H_3)_3$], 34.8 (C-1′), 37.1 (C-1′′), 40.6 (C-3a), 41.1 (C-6), 43.0 (C-6a), 44.3 (C-3), 55.0 (C-1), 55.1 (C-4), 80.2 (C-5), 116.2 (C-3′′), 116.7 (C-3′), 127.57, 127.61 (C-*m*, C-*m*′), 129.65, 129.70 (C-*p*, C-*p*′), 133.9, 134.1 (C-*i*, C-*i*′), 135.7 (C-2′), 135.91, 135.94 (C-*o*, C-*o*′), 136.4 (C-2′′), 221.0 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3073 (w), 2930 (m), 2857 (m), 1736 (vs), 1640 (w), 1589 (w), 1472 (w), 1427 (m), 1390 (w), 1362 (w), 1259 (w), 1108 (vs), 997 (m), 912 (s), 822 (m), 740 (m), 701 (vs), 612 (s) cm^{-1}. MS (ESI): m/z = 481.3 [M + Na]$^+$, 381.2, 261.1, 203.1, 185.1. HRMS (ESI): calcd. for $C_{30}H_{38}O_2SiNa^+$ [M + Na]$^+$ 481.2553; found 481.2520.

(*S*,*R*)- and (*R*,*R*)-11b: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.03 [s, 9 H, SiC$(CH_3)_3$], 1.54 (dt, J = 13.4, 5.7 Hz, 1 H, 4-H_a), 1.78–1.87 (m, 1 H, 1′′-H_a), 1.90–1.99 (m, 2 H, 1′′-H_b, 6-H), 2.00–2.09 (m, 2 H, 4-H_b, 6a-H), 2.15–2.22 (m, 1 H, 1′-H_a), 2.32–2.42 (m, 2 H, 1′-H_b, 3-H_a), 2.43 (dd, J = 18.8, 9.2 Hz, 1 H, 3-H_b), 2.48–2.57 (m, 2 H, 1-H, 3a-H), 3.98 (dt, J = 5.7, 4.7 Hz, 1 H, 5-H), 4.83–4.89 (m, 2 H, 3′′-H), 5.00–5.07 (m, 2 H, 3′-H), 5.45–5.54 (m, 1 H, 2′′-H), 5.71 (ddt, J = 17.1, 10.0, 7.1 Hz, 1 H, 2′-H), 7.35–7.39 (m, 4 H, *m*-H, *m*′-H), 7.41–7.45 (m, 2 H, *p*-H, *p*′-H), 7.62–7.66 (m, 4 H, *o*-H, *o*′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.0 [Si*C*$(CH_3)_3$], 27.0 [SiC(*C*$H_3)_3$], 34.8 (C-3a), 34.9 (C-1′), 37.2 (C-1′′), 41.7 (C-4), 44.9 (C-3), 48.7 (C-6a), 54.0 (C-1), 54.2 (C-6), 80.4 (C-5), 116.4 (C-3′′), 117.1 (C-3′), 127.58, 127.61 (C-*m*, C-*m*′), 129.6, 129.7 (C-*p*, C-*p*′), 133.9, 134.0 (C-*i*, C-*i*′), 135.6 (C-2′′), 135.87, 135.94 (C-*o*, C-*o*′), 136.5 (C-2′), 221.3 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3072 (w), 2930 (m), 2858 (m), 1736 (vs), 1640 (w), 1590 (w), 1472 (w), 1428 (m), 1390 (w), 1259 (w), 1111 (vs), 1063 (w), 998 (m), 912 (s), 852 (w), 822 (m), 741 (m), 703 (vs), 612 (m) cm^{-1}. MS (ESI): m/z = 481.3 [M + Na]$^+$, 381.2, 261.1, 203.1, 185.1. HRMS (ESI): calcd. for $C_{30}H_{38}O_2SiNa^+$ [M + Na]$^+$ 481.2553; found 481.2527.

4-Methyl-*N*′-[(3a′*S*,4′*R*,5′*E*/*Z*,6a′*R*)-4′,5,5-trimethyltetrahydro-1′*H*-spiro[1,3-dioxane-2,2′-pentalen]-5′(3′*H*)-ylidene]benzenesulfonohydrazide (19a): According to GP4, from **8a** (102 mg, 0.45 mmol) and *p*-tosylhydrazine (84.0 mg, 0.45 mmol), the precipitate was filtered off and dried under high vacuum; yield 112 mg (0.28 mmol, 61%, >95% purity by ^{1}H NMR, *E*/*Z* = 89:11), colourless resin. $[\alpha]_D^{20}$ = –11.8 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 [s, 3 H, C$(CH_3)_2$], 0.94 [s, 3 H, C$(CH_3)_2$], 1.03 (d, J = 6.8 Hz, 3 H, 1′′-H), 1.58 (dd, J = 13.6, 8.1 Hz, 1 H, 1′-H_a), 1.79 (dd, J = 13.9, 4.3 Hz, 1 H, 3′-H_a), 2.04–2.12 (m, 2 H, 3a′-H, 6′-H_a), 2.18 (ddd, J = 13.9, 8.4, 1.1 Hz, 1 H, 3′-H_b), 2.28 (ddd, J = 13.6, 8.4, 0.9 Hz, 1 H, 1′-H_b), 2.40 (dd, J = 9.0, 1.7 Hz, 1 H, 6′-H_b), 2.43 (s, 3 H, *p*-CH_3), 2.43–2.49 (m, 1 H, 4′-H), 2.60–2.69 (m, 1 H, 6a′-H), 3.36 (d, J = 3.9 Hz, 2 H, OCH_2), 3.44 (s, 2 H, OCH_2), 4.89–4.94 (m, 2 H, 3′′-H), 5.59 (dddd, J = 14.2, 10.3, 7.6, 6.7 Hz, 1 H, 2′′-H), 7.05 (br. s, 1 H, NH), 7.30 (d, J = 8.2 Hz, 2 H, *m*-H), 7.84 (d, J = 8.2 Hz, 2 H, *o*-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.7 (C-1′′), 21.6 (*p*-CH_3), 22.3, 22.4 [C(*C*$H_3)_2$], 30.0 [*C*$(CH_3)_2$], 32.6 (C-6′), 36.3 (C-6a′), 38.7 (C-3′), 41.2 (C-1′), 44.8 (C-4′), 47.9 (C-3a′), 71.8 (OCH_2), 72.3 (OCH_2), 110.0 (C-2′), 128.1 (C-*o*), 129.4 (C-*m*), 135.4 (C-*p*), 143.9 (C-*i*), 170.0 (C-5′) ppm (signals of the *Z* isomer were not assigned due to overlapping). FTIR (ATR): $\tilde{\nu}$ = 3415 (br, w), 2989 (m), 2933 (m), 1603 (w), 1456 (m), 1434 (w), 1396 (w), 1380 (m), 1243 (m), 1217 (s), 1164 (s), 1063 (vs), 991 (m), 909 (w), 876 (w), 860 (w), 782 (w), 753 (w), 729 (m), 100 (s) cm^{-1}. MS (ESI): m/z = 429.2 [M + Na]$^+$, 407.2 [M + H]$^+$, 321.1 [M + H – $C_5H_{10}O$]$^+$, 305.1, 263.1, 251.2, 236.2 [M + H – $C_7H_8NO_2S$]$^+$, 165.1, 150.1, 132.1, 108.1. HRMS (ESI): calcd. for $C_{21}H_{31}N_2O_4S^+$ [M + H]$^+$ 407.1999; found 407.2003.

***N*′-[(3a′*S*,4′*R*,5′*E*/*Z*,6a′*R*)-4′-Allyl-5,5-dimethyltetrahydro-1′*H*-spiro[1,3-dioxane-2,2′-pentalen]-5′(3′*H*)-ylidene]-4-methylbenzenesulfonohydrazide (19b):** According to GP4, from **8b** (493 mg, 2.00 mmol) and *p*-tosylhydrazine (373 mg, 2.00 mmol), the precipitate was filtered off and dried under high vacuum; yield 686 mg (1.58 mmol, 80%, >99% purity by GC, *E*/*Z* = 80:20), colourless resin. $[\alpha]_D^{20}$ = –21.2 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 [s, 3 H, C$(CH_3)_2$], 0.93 [s, 3 H, C$(CH_3)_2$], 1.58 (dd, J = 13.6, 7.4 Hz, 1 H, 1′-H_a), 1.72 (dd, J = 13.9, 5.4 Hz, 1 H, 3′-H_a),

2.00–2.08 (m, 1 H, 1′′-H_a), 2.12 (dd, J = 18.3, 4.3 Hz, 1 H, 6′-H_a), 2.17 (ddd, J = 13.9, 8.4, 1.3 Hz, 1 H, 3′-H_b), 2.25 (ddd, J = 13.6, 8.4, 1.3 Hz, 1 H, 1′-H_b), 2.25–2.35 (m, 2 H, 3a-H, 1′′-H_b), 2.41 (ddd, J = 18.3, 9.3, 1.7 Hz, 1 H, 6′-H_b), 2.43 (s, 3 H, p-CH_3), 2.48–2.55 (m, 1 H, 4′-H), 2.59–2.68 (m, 1 H, 6a′-H), 3.35 (d, J = 3.5 Hz, 2 H, OCH_2), 3.43 (s, 2 H, OCH_2), 4.89–4.94 (m, 2 H, 3′′-H), 5.59 (dddd, J = 14.2, 10.3, 7.6, 6.7 Hz, 1 H, 2′′-H), 7.28 (br. s, 1 H, NH), 7.30 (d, J = 8.2 Hz, 2 H, m-H), 7.83 (d, J = 8.2 Hz, 2 H, o-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6 (p-CH_3), 22.40, 22.42 [C(CH_3)$_2$], 30.0 [C(CH_3)$_2$], 33.3 (C-6′), 37.0 (C-1′′), 37.7 (C-6a′), 40.3 (C-3′), 41.3 (C-1′), 44.7 (C-3a′), 49.8 (C-4′), 71.8 (OCH_2), 72.3 (OCH_2), 109.7 (C-2′), 116.6 (C-3′′), 128.1 (C-o), 129.5 (C-m), 135.4 (C-p), 135.8 (C-2′′), 144.0 (C-i), 168.9 (C-5′) ppm (signals of the Z isomer were not assigned due to low intensity and overlapping). FTIR (ATR): $\tilde{\nu}$ = 3214 (br), 2950 (m), 2863 (m), 1967 (br), 1643 (w), 1598 (w), 1398 (m), 1335 (s), 1217 (w), 1164 (s), 1112 (m), 1012 (m), 916 (m), 814 (m), 671 (m), 549 (m), 499 (w) cm^{-1}. MS (EI): m/z (%) = 432.2 (12) [M]$^+$, 277.2 (100) [M – $C_7H_7O_2S$]$^+$, 262.2 (7) [M – $C_7H_7NO_2S$]$^+$, 191.1 (40), 163.1 (10), 133.1 (5), 105.1 (6), 91.0 (11) [C_7H_7]$^+$, 79.0 (7), 69.0 (14), 55.0 (3), 40.9 (10). HRMS (ESI): calcd. for $C_{23}H_{33}N_2O_4S^+$ [M + H]$^+$ 433.2156; found 433.2165.

(3a′*R*,4′*S*,6a′*S*)-4′-Allyl-5,5-dimethyl-3′,3a′,4′,6a′-tetrahydro-1′*H*-spiro[1,3-dioxane-2,2′-pentalene] (20b): A 1.6 M solution of *n*BuLi in hexane (0.73 mL, 1.16 mmol) was added dropwise to a solution of **19b** (216 mg, 0.50 mmol) in abs. THF (7 mL) and TMEDA (1 mL) at –78 °C in a Schlenk flask, and the reaction mixture was warmed to room temperature with a colour change from orange to brown. After stirring for a further 5 h, a saturated solution of $NaHCO_3$/H_2O (3 mL) was added and the organic solvent removed. The remaining aqueous layer was extracted with $CHCl_3$ (3 × 30 mL), and the combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc = 5:1) to give **20b** (123 mg, 0.5 mmol, quant., >95% purity by ^{1}H NMR) as a colourless viscous resin. R_f = 0.88. $[a]_D^{20}$ = –8.2 (c = 1.0, CH_2Cl_2); *e.r.* = 78:22 (56% *ee*, GC: Amidex C, temperature program: 100 °C isothermal, 1 °C/min gradient to 200 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 [s, 6 H, C(CH_3)$_2$], 1.52–1.60 (m, 2 H, 1′-H_a, 3′-H_a), 2.01–2.07 (m, 1 H, 1′′-H_a), 2.10–2.16 (m, 1 H, 1′′-H_b), 2.28–2.38 (m, 3 H, 1′-H_b, 3a′-H, 3′-H_b), 2.47–2.52 (m, 1 H, 4′-H), 3.13–3.20 (m, 1 H, 6a′-H), 3.44 (s, 2 H, OCH_2), 3.50 (s, 2 H, OCH_2), 4.79–5.04 (m, 2 H, 3′′-H), 5.55 (dt, J = 5.2, 2.3 Hz, 1 H, 6′-H), 5.63 (dt, J = 5.2, 2.3 Hz, 1 H, 5′-H), 5.78 (tt, J = 9.1, 6.9 Hz, 1 H, 2′′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.4, 22.5 [C(CH_3)$_2$], 30.0 [C(CH_3)$_2$], 38.4 (C-1′), 40.1 (C-3′), 40.2 (C-1′′), 43.9 (C-3a′), 46.6 (C-6a′), 52.1 (C-4′), 71.5 (OCH_2), 72.7 (OCH_2), 109.0 (C-2′), 115.6 (C-3′′), 132.7 (C-6′), 134.4 (C-5′), 137.1 (C-2′′) ppm. FTIR (ATR): $\tilde{\nu}$ = 3044 (w), 2952 (s), 2859 (s), 1968 (br), 1730 (w), 1640 (w), 1468 (m), 1394 (w), 1315 (m), 1217 (m), 1110 (vs), 1056 (w), 999 (m), 909 (m), 798 (w), 742 (m) cm^{-1}. MS (EI): m/z (%) = 248.2 (66) [M]$^+$, 207.2 (91) [M – C_3H_5]$^+$, 162.2 (17) [M – $C_5H_{10}O$]$^+$, 128.1 (100), 121.1 (33), 104.1 (13), 93.1 (23), 79.1 (43), 57.1 (11), 41.0 (17). HRMS (EI): calcd. for $C_{16}H_{24}O_2^+$ [M]$^+$ 248.1776; found 248.1776.

(3a′*R*,4′*S*,6a′*S*)-4′,5,5-Trimethyl-3′,3a′,4′,6a′-tetrahydro-1′*H*-spiro[1,3-dioxane-2,2′-pentalene] (20a): As described above for the synthesis of **20b**, from **19a** (83.0 mg, 0.20 mmol) in abs. THF (5 mL) and TMEDA (1 mL), *n*BuLi (0.29 mL, 0.47 mmol), 4 h at room temperature, extraction with CH_2Cl_2 and flash chromatography on SiO_2 (hexanes/EtOAc = 10:1); yield 25.0 mg (0.11 mmol, 54%, >95% purity by ^{1}H NMR), colourless viscous resin. R_f = 0.76 (hexanes/EtOAc = 5:1). $[a]_D^{20}$ = –1.4 (c = 0.5, CH_2Cl_2); *e.r.* = 90:10 (80% *ee*, GC: Amidex C, temperature program: 40 °C isothermal, 10 °C/min gradient to 140 °C, then 1 °C/min gradient to 200 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 [s, 6 H, C(CH_3)$_2$], 1.00 (d, J = 7.1 Hz, 3 H, 1′′-H), 1.54–1.61 (m, 2 H, 1′-H_a, 3′-H_a), 2.24 (dq, J = 8.4, 2.4 Hz, 1 H, 3a′-H), 2.28–2.35 (m, 2 H, 1′-H_b, 3′-H_b), 2.45–2.52 (m, 1 H, 4′-H), 3.18–3.24 (m, 1 H, 6a′-H), 3.45 (d, J = 1.9 Hz, 2 H, OCH_2), 3.50 (d, J = 3.2 Hz, 2 H, OCH_2), 5.53 (dt, J = 5.6, 2.0 Hz, 1 H, 6′-H), 5.57 (dt, J = 5.6, 2.0 Hz, 1 H, 5′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.4 (C-1′′), 22.5, 22.6 [C(CH_3)$_2$], 30.1 [C(CH_3)$_2$], 38.6 (C-1′), 39.8 (C-3′), 46.5 (C-4), 46.77 (C-3a′), 46.80 (C-6a′), 71.6 (OCH_2), 72.7 (OCH_2), 109.2 (C-2′), 133.3 (C-6′), 135.0 (C-5′) ppm. FTIR (ATR): $\tilde{\nu}$ = 3044 (w), 2952 (s), 2859 (s), 1968 (br), 1730 (w), 1640 (w), 1468 (m), 1394 (w), 1315 (m), 1217 (m), 1110 (vs), 1056 (w), 999 (m), 909 (m), 798 (w), 742 (m) cm^{-1}. MS (EI): m/z (%) = 222.2 (76) [M]$^+$, 207.1 (18) [M – Me]$^+$, 152.1 (12), 136.1 (37) [M – $C_5H_{10}O$]$^+$, 128.1 (100), 121.1 (11) [M – Me – $C_5H_{10}O$]$^+$, 107.1 (22), 93.1 (42), 79.1 (15), 69.1 (35), 57.1 (11), 43.0 (15). HRMS (EI): calcd. for $C_{14}H_{22}O_2^+$ [M]$^+$ 222.1620; found 222.1617.

***N*′-[(1*R*,2*E*,3a*S*,4*R*,5*R*,6a*S*)-4-Allyl-5-{[*tert*-butyl(diphenyl)silyl]-oxy}-1-methylhexahydropentalen-2(1*H*)-ylidene]-4-methylbenzenesulfonohydrazide (18a):** According to GP4, from **10a** (130 mg, 0.30 mmol) and *p*-tosylhydrazine (56.0 mg, 0.30 mmol), chromatography on SiO_2 (hexanes/EtOAc = 10:1); yield 157 mg (0.26 mmol, 87%, >99% purity by GC), colourless fluffy resin. R_f = 0.53 (hexanes/EtOAc = 5:1). $[a]_D^{20}$ = –26.4 (c = 1.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99 (d, J = 6.9 Hz, 3 H, 1′-H), 1.01 [s, 9 H, SiC(CH_3)$_3$], 1.46 (dt, J = 13.1, 5.5 Hz, 1 H, 6-H_a), 1.67–1.78 (m, 2 H, 4-H, 1′′-H_a), 1.82 (dq, J = 5.0, 8.0 Hz, 1 H, 6a-H), 1.88 (dt, J = 13.1, 7.4 Hz, 1 H, 6-H_b), 2.05 (dq, J = 3.9, 8.0 Hz, 1 H, 3a-H), 2.10–2.16 (m, 1 H, 1′′-H_b), 2.15 (dd, J = 18.1, 3.9 Hz, 1 H, 3-H_a), 2.37 (ddd, J = 18.1, 3.9, 1.5 Hz, 1 H, 3-H_b), 2.42 (s, 3 H, p′′-CH_3), 2.56 (dq, J = 8.0, 6.9 Hz, 1 H, 1-H), 3.83 (q, J = 6.4 Hz, 1 H, 5-H), 4.82–4.90 (m, 2 H, 3′′-H), 5.54 (dddd, J = 17.0, 13.9, 10.3, 6.7 Hz, 1 H, 2′′-H), 6.90 (br. s, 1 H, NH), 7.28–7.31 (m, 2 H, m′′-H), 7.34–7.38 (m, 4 H, m-H, m′-H), 7.40–7.44 (m, 2 H, p-H, p′-H), 7.60–7.64 (m, 4 H, o-H, o′-H), 7.83–7.87 (m, 2 H, o′′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.7 (C-1′), 19.1 [SiC(CH_3)$_3$], 21.6 (p′′-CH_3), 27.0 [SiC(CH_3)$_3$], 32.8 (C-3), 36.9 (C-1′′), 39.5 (C-6), 43.2 (C-3a), 46.0 (C-1), 47.5 (C-6a), 54.2 (C-4), 78.0 (C-5), 116.3 (C-3′′), 127.5, 127.6 (C-m, C-m′), 128.1 (C-o′′), 129.4 (C-m′′), 129.6, 129.7 (C-p, C-p′), 133.9, 134.2 (C-i, C-i′), 135.5 (C-p′′), 136.5 (C-o, C-o′), 136.5 (C-2′′), 143.9 (C-i′′), 170.3 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3055 (m), 2988 (m), 2539 (w), 1422 (w), 1264 (s), 896 (w), 731 (s), 703 (s), 544 (w) cm^{-1}. MS (ESI): m/z = 601.3 [M + H]$^+$, 363.0, 345.2 [M + H – TBDPSOH]$^+$, 257.1, 189.1 [M + H – TBDPSOH – $C_7H_8O_2S$]$^+$, 174.1 [M + H – TBDPSOH – $C_7H_8O_2S$ – CH_3]$^+$, 133.1. HRMS (ESI): calcd. for $C_{35}H_{45}N_2O_3SSi^+$ [M + H]$^+$ 601.2915; found 601.2929.

***N*′-[(1*R*,2*E*,3a*S*,4*R*,5*R*,6a*S*)-4-Allyl-5-hydroxy-1-methylhexahydropentalen-2(1*H*)-ylidene]-4-methylbenzenesulfonohydrazide (22):** According to GP3, from **18a** (61.0 mg, 100 μmol) and TBAF (189 mg, 600 μmol), chromatography on SiO_2 (hexanes/EtOAc = 2:1); yield 38.0 mg (100 μmol, quant., >95% purity by ^{1}H NMR), colourless sticky resin. R_f = 0.50 (hexanes/EtOAc = 1:1). $[a]_D^{20}$ = –38.4 (c = 1.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.06 (d, J = 6.9 Hz, 3 H, 1′-H), 1.25 (br. s, 1 H, OH), 1.42 (ddd, J = 13.6, 7.5, 5.2 Hz, 1 H, 6-H_a), 1.53–1.59 (m, 1 H, 4-H), 1.96 (ddd, J = 16.4, 8.2, 5.2 Hz, 1 H, 3a-H), 2.13–2.21 (m, 4 H, 6a-H, 1′′-H_a, 1′′-H_b, 3-H_a), 2.29 (dt, J = 13.6, 7.5 Hz, 1 H, 6-H_b), 2.40–2.51 (m, 2 H, 3-H_b, 1-H), 2.43 (s, 3 H, p-CH_3), 3.91 (q, J = 7.5 Hz, 1 H, 5-H), 5.01–5.12 (m, 2 H, 3′′-H), 5.82 (dddd, J = 17.4, 14.7, 10.3, 7.2 Hz, 1 H, 2′′-H), 7.02 (br. s, 1 H, NH), 7.30 (d, J = 8.8 Hz, 2 H, m-H), 7.84 (d, J = 8.8 Hz, 2 H, o-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6

(*p*-CH_3), 26.6 (C-1′), 32.3 (C-3), 37.1 (C-1′′), 39.2 (C-6), 44.0 (C-6a), 46.6 (C-1), 46.8 (C-3a), 53.1 (C-4), 79.1 (C-5), 116.8 (C-3′′), 128.1 (C-*o*), 129.5 (C-*m*), 136.8 (C-2′′, C-*p*), 144.1 (C-*i*), 170.0 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3069 (br), 2958 (m), 2927 (m), 2872 (m), 2859 (m), 2254 (w), 1732 (s), 1455 (w), 1359 (w), 1165 (s), 1087 (w), 1008 (w), 904 (vs), 814 (m), 725 (vs), 683 (m), 650 (m), 554 (m) cm^{-1}. MS (ESI): *m*/*z* = 385.2 $[M + Na]^+$, 363.2 $[M + H]^+$, 345.2 $[M + H - H_2O]^+$, 226.2 $[M + H - H_2O - C_7H_8 - C_2H_4]^+$, 192.1 $[M + H - C_7H_9NO_2S]^+$, 105.1. HRMS (ESI): calcd. for $C_{19}H_{27}N_2O_3S^+$ $[M + H]^+$ 363.1737; found 363.1739.

***N*′-[(1*R*,2*E*,3a*S*,4*R*,6a*S*)-4-Allyl-1-methyl-5-oxohexahydropentalen-2(1*H*)-ylidene]-4-methylbenzenesulfonohydrazide (23):** DMP (105 mg, 250 μmol) was added to a solution of **22** (50.0 mg, 140 μmol) in abs. CH_2Cl_2 (5 mL) at 0 °C in a Schlenk flask and the reaction mixture was stirred for 2 h. A saturated solution of $NaHCO_3/H_2O$ (3 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2× 20 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc = 2:1) to give **23** (33.0 mg, 90.0 μmol, 64%, >90% purity by ^{13}C NMR) as a colourless sticky resin. R_f = 0.42. $[\alpha]_D^{20}$ = –11.2 (*c* = 1.0, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 6.1 Hz, 3 H, 1′-H), 1.83–1.91 (m, 1 H, 4-H), 2.15 (dt, *J* = 15.1, 7.6 Hz, 1 H, 1′′-H_a), 2.19–2.25 (m, 2 H, 1-H, 6a-H), 2.20–2.39 (m, 3 H, 3-H_a, 6-H_a, 6-H_b), 2.44 (s, 3 H, *p*-CH_3), 2.45–2.57 (m, 3 H, 1′′-H_b, 3a-H, 3-H_b), 5.00–5.08 (m, 2 H, 3′′-H), 5.68 (ddt, *J* = 17.1, 9.9, 7.2 Hz, 1 H, 2′′-H), 7.32 (d, *J* = 8.2 Hz, 2 H, *m*-H), 7.48 (br. s, 1 H, NH), 7.85 (d, *J* = 8.2 Hz, 2 H, *o*-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.3 (C-1′), 21.6 (*p*-CH_3), 33.1 (C-6), 33.8 (C-1′′), 42.2 (C-3), 42.4 (C-3a), 44.4, 44.7 (C-1, C-6a), 52.8 (C-4), 117.7 (C-3′′), 128.1 (C-*o*), 129.5 (C-*m*), 134.8 (C-2′′), 135.2 (C-*p*), 144.1 (C-*i*), 167.0 (C-2), 218.5 (C-5) ppm. FTIR (ATR): $\tilde{\nu}$ = 3213 (br, w), 3074 (w), 2964 (w), 2928 (m), 2872 (w), 2254 (w), 1733 (s), 1641 (w), 1598 (w), 1404 (m), 1337 (m), 1164 (s), 1093 (m), 1019 (m), 906 (vs), 614 (m), 729 (vs), 669 (m), 649 (m), 550 (m) cm^{-1}. MS (ESI): *m*/*z* = 361.2 $[M + H]^+$, 263.1, 205.2 $[M + H - C_7H_8O_2S]^+$, 190.1 $[M + H - C_7H_8NO_2S]^+$, 148.1, 139.0, 123.1, 108.1. HRMS (ESI): calcd. for $C_{19}H_{25}N_2O_3S^+$ $[M + H]^+$ 361.1580; found 361.1586.

(1*R*,3a*R*,4*S*,6a*S*)-1-Allyl-4-methyl-3,3a,4,6a-tetrahydropentalen-2(1*H*)-one (16): As described above for **20b**, from **23** (81.0 mg, 0.23 mmol) in abs. THF (3 mL) and TMEDA (0.5 mL), *n*BuLi (0.33 mL, 0.56 mmol), 2 h at room temperature, extraction with $CHCl_3$ (3× 50 mL), flash chromatography on SiO_2 (hexanes/EtOAc = 70:1); yield 11.0 mg (60.0 μmol, 27%, >90% purity by ^{13}C NMR) containing up to 10% starting material, yellowish oil. R_f = 0.27 (hexanes/EtOAc = 20:1). $[\alpha]_D^{20}$ = –4.2 (*c* = 1.0, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.05 (d, *J* = 7.1 Hz, 3 H, 1′′-H), 1.93 (dd, *J* = 19.1, 6.6 Hz, 1 H, 1-H_a), 2.03 (ddt, *J* = 14.9, 7.6, 1.1 Hz, 1 H, 1′-H_a), 2.43–2.50 (m, 2 H, 3-H, 6a-H), 2.50–2.56 (m, 1 H, 6-H), 2.57–2.63 (m, 1 H, 1′-H_b), 2.64 (ddd, *J* = 19.1, 10.2, 1.8 Hz, 1 H, 1-H_b), 3.60–3.65 (m, 1 H, 3a-H), 5.05 (dq, *J* = 10.2, 1.4 Hz, 1 H, 3′-H_a), 5.13 (dq, *J* = 13.6, 1.4 Hz, 1 H, 3′-H_b), 5.61 (dt, *J* = 5.7, 1.5 Hz, 1 H, 4-H), 5.77 (dt, *J* = 5.7, 2.5 Hz, 1 H, 5-H), 5.89 (dddd, *J* = 13.6, 10.2, 7.7, 5.9 Hz, 1 H, 2′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.8 (C-1′′), 30.3 (C-1′), 41.5 (C-3), 42.8 (C-1), 47.0 (C-6), 48.0 (C-3a), 50.2 (C-6a), 114.9 (C-3′), 127.0 (C-4), 135.5 (C-2′), 137.1 (C-5), 217.9 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3429 (br, vs), 2251 (m), 2128 (w), 1660 (br, s), 1051 (s), 1023 (vs), 1003 (vs), 1373 (w), 822 (s), 759 (s), 731 (m), 624 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 176.1 (72) $[M]^+$, 161.1 (37) $[M - Me]^+$, 147.1 (11) $[M - H_2O - Me]^+$, 134.1 (51), 119.1 (41) $[M - Me - C_3H_6]^+$, 105.1 (25), 96.1 (76), 91.0 (69), 79.0 (100), 65.0 (12), 55.0 (17), 38.9 (20). HRMS (ESI): calcd. for $C_{12}H_{17}O^+$ $[M + H]^+$ 177.1274; found 177.1269.

***N*′-[(2*E*/*Z*,3a*S*,4*R*,5*R*,6a*S*)-4-Allyl-5-{[*tert*-butyl(diphenyl)silyl]-oxy}hexahydropentalen-2(1*H*)-ylidene]-4-methylbenzenesulfonohydrazide (18b):** According to GP4, from **9** (50.0 mg, 120 μmol) and *p*-tosylhydrazine (22.3 mg, 120 μmol), repeated freezing with liquid N_2 under high vacuum gave **18b** (70.0 mg, 120 μmol, quant., >99% purity by GC, *E*/*Z* = 1:1 by ^{13}C NMR) as a colourless viscous resin. R_f = 0.28 (hexanes/EtOAc = 5:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.00 [s, 9 H, $SiC(CH_3)_3$], 1.40 (dq, *J* = 12.5, 6.3 Hz, 1 H, 6-H_a), 1.67–1.80 (m, 2 H, 4-H, 1′-H_a), 1.85–1.93 (m, 1 H, 6-H_b), 2.02–2.08 (m, 1 H, 1′-H_b), 2.08–2.24 (m, 2 H, 3a-H, 3-H_a), 2.27–2.36 (m, 1 H, 6a-H), 2.37–2.46 (m, 2 H, 3-H_b, 1-H_a), 2.42 (s, 3 H, *p*′-CH_3), 2.61 (ddt, *J* = 10.5, 8.9, 1.4 Hz, 1 H, 1-H_b), 3.82 (dt, *J* = 12.5, 6.3 Hz, 1 H, 5-H), 4.82–4.91 (m, 2 H, 3′-H), 5.52 (dddd, *J* = 16.7, 13.4, 10.2, 6.7 Hz, 1 H, 2′-H), 7.06 (br. s, 1 H, NH), 7.31 (d, *J* = 8.4 Hz, 2 H, *m*′-H), 7.33–7.38 (m, 4 H, *m*-H), 7.40–7.44 (m, 2 H, *p*-H), 7.59–7.63 (m, 4 H, *o*-H), 7.84 (d, *J* = 8.4 Hz, 2 H, *o*′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.4 [Si*C*$(CH_3)_3$*], 19.0 [Si*C*$(CH_3)_3$], 21.6 (*p*′-CH_3, *p*′-CH_3*), 27.0 [SiC(*C*$H_3)_3$, SiC-(*C*$H_3)_3$*], 34.1 (C-3), 34.5 (C-3*), 36.9 (C-1′*), 37.0 (C-1′), 37.9 (C-6a), 39.0 (C-6a*), 39.2 (C-1*), 39.7 (C-1), 40.9 (C-6), 41.4 (C-6*), 44.2 (C-3a), 44.8 (C-3a*), 53.8 (C-4*), 54.6 (C-4), 79.8 (C-5), 79.9 (C-5*), 116.1 (C-3′*), 116.3 (C-3′), 127.5 (C-*m**), 127.6 (C-*m*), 128.0 (C-*o*′, C-*o*′*), 129.6 (C-*m*′, C-*m*′*), 129.7 (C-*p*, C-*p**), 133.9 (C-*i*, C-*i**), 134.1 (C-*p*′, C-*p*′*), 135.6 (C-*i*′, C-*i*′*), 135.9 (C-*o*, C-*o**), 136.5 (C-2′*), 136.6 (C-2′), 144.0 (C-2, C-2*) ppm (* denotes signals of the *Z* isomer).

{[(1*R*,2*R*,3a*S*,6a*R*)-1-Allyl-1,2,3,3a,4,6a-hexahydropentalen-2-yl]oxy}(*tert*-butyl)diphenylsilane (24) and {[(2*R*,3*R*,3a*S*,6a*R*)-3-Allyl-1,2,3,3a,4,6a-hexahydropentalen-2-yl]oxy}(*tert*-butyl)diphenylsilane (24′): As described above for the synthesis of **20b**, from **18b** (1.11 g, 1.90 mmol), TMEDA (1.50 mL, 9.91 mmol) in abs. THF (12 mL) and *n*BuLi (3.32 mL, 5.31 mmol), 4 h at room temperature, extraction with $CHCl_3$ (3× 150 mL), flash chromatography on SiO_2 (hexanes/EtOAc = 20:1); yield 535 mg (1.33 mmol, 70%, 95% purity by GC, 1 signal) of a 1:1 mixture of **24** and **24′** (by NMR). R_f = 0.95 (hexanes/EtOAc = 5:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.04 [s, 9 H, $SiC(CH_3)_3$], 1.23–1.35 (m, 1 H, 3-H_a), 1.31 (tt, *J* = 13.2, 9.1 Hz, 1 H, 3-H_a*), 1.64 (dq, *J* = 8.5, 4.2 Hz, 1 H, 1-H), 1.79 (dt, *J* = 13.6, 8.7 Hz, 1 H, 1′-H_a), 1.82–1.92 (m, 1 H, 3-H_b), 1.84–1.90 (m, 2 H, 1′-H_a*, 3-H_b*), 2.04–2.12 (m, 2 H, 4-H_a, 6a-H), 2.05–2.10 (m, 1 H, 6a-H*), 2.14–2.20 (m, 1 H, 6-H_a*), 2.35–2.41 (m, 1 H, 1′-H_b), 2.44–2.58 (m, 2 H, 3a-H, 4-H_b), 2.44–2.52 (m, 1 H, 6-H_b*), 2.74–2.81 (m, 1 H, 3a-H*), 3.68 (dq, *J* = 8.9, 6.1 Hz, 1 H, 2-H), 4.88–4.98 (m, 2 H, 3′-H), 5.51–5.54 (m, 1 H, 6-H, 4-H*), 5.57–5.60 (m, 1 H, 5-H*), 5.62–5.65 (m, 1 H, 5-H), 5.66–6.76 (m, 1 H, 2′-H), 7.34–7.39 (m, 4 H, *m*-H, *m*′-H), 7.40–7.45 (m, 2 H, *p*-H, *p*′-H), 7.64–7.70 (m, 4 H, *o*-H, *o*′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.2 [Si*C*$(CH_3)_3$], 27.0 [SiC(*C*$H_3)_3$], 36.8 (C-1′*), 37.6 (C-1′), 39.6 (C-6*), 39.7 (C-4), 40.1 (C-3), 42.3 (C-6a,6a*), 42.3 (C-3*), 53.1 (C-1), 53.4 (C-3a), 54.6 (C-1*), 78.3 (C-2), 78.7 (C-2*), 115.4 (C-3′), 127.4, 127.5 (C-*m*, C-*m*′), 127.8 (C-6), 127.9 (C-4*), 129.4, 129.5 (C-*p*, C-*p*′), 134.2, 134.3 (C-*i*, C-*i*′), 134.5 (C-5), 134.6 (C-5*), 135.9, 136.0 (C-*o*, C-*o*′), 137.4 (C-2′), 137.7 (C-2′*) ppm (* denotes signals of **24′**).

{[(1a*R*,1b*S*,3*R*,4*R*,4a*S*,5a*S*)-4-Allyloctahydropentaleno[1,2-*b*]oxiren-3-yl]oxy}(*tert*-butyl)diphenylsilane (25 and *epi*-25) and {[(1a*S*,1b*S*,2*R*,3*R*,4a*S*,5a*R*)-2-Allyloctahydropentaleno[1,2-*b*]oxiren-3-yl]oxy}(*tert*-butyl)diphenylsilane (26 and *epi*-26): MCPBA (129 mg, 0.75 mmol) was added to a suspension of **24**, **24′** (150 mg, 0.37 mmol) and $NaHCO_3$ (156 mg, 1.86 mmol) in abs. CH_2Cl_2

(5 mL) in a Schlenk flask and the reaction mixture was stirred for 1 h at room temperature. The reaction was quenched with a saturated solution of $Na_2S_2O_5$ (10 mL) and the layers were separated. The organic layer was washed with a saturated solution of $NaHCO_3/H_2O$ (10 mL), dried ($MgSO_4$) and concentrated. The residue was purified by chromatography on SiO_2 (hexanes/EtOAC = 20:1) to give a mixture of epoxides **25**, *epi*-**25**, **26** and *epi*-**26** in a ratio of 50:3.5:45:1.5 (by GC; 73.0 mg, 0.17 mmol, 48%, 87% purity by GC) as a colourless oil. R_f = 0.52 (hexanes/EtOAc = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05 [s, 9 H, $SiC(CH_3)_3$], 1.42 (ddd, J = 8.4, 4.8, 2.1 Hz, 1 H, 6-H_a), 1.47 (ddd, J = 13.2, 5.0, 2.3 Hz, 1 H, 3-H_a), 1.65–1.90 (m, 5 H, 1-H, 1′-H_a, 3-H_b, 6-H_b, 3a-H), 2.01–2.10 (m, 1 H, 1′-H_b), 2.48 (dt, J = 8.5, 8.5 Hz, 1 H, 6a-H), 3.36 (d, J = 2.8 Hz, 1 H, 4-H), 3.53–3.55 (m, 1 H, 5-H), 3.85–3.89 (m, 1 H, 2-H), 4.84–4.94 (m, 2 H, 3′-H), 5.54 (dddd, J = 14.5, 11.1, 7.3, 4.6 Hz, 1 H, 2′-H), 7.35–7.40 (m, 4 H, *m*-H, *m*′-H), 7.40–7.45 (m, 2 H, *p*-H, *p*′-H), 7.63–7.67 (m, 4 H, *o*-H, *o*′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.3 [Si*C*$(CH_3)_3$], 27.1 [SiC(*C*$H_3)_3$], 36.1 (C-6), 37.7 (C-1′), 41.0 (C-3), 43.0 (C-6a), 50.0 (C-3a), 55.4 (C-1), 60.0 (C-5), 62.1 (C-4), 80.8 (C-2), 116.4 (C-3′), 127.96, 127.73 (C-*m*, C-*m*′), 129.77, 129.84 (C-*p*, C-*p*′), 134.3, 134.4 (C-*i*, C-*i*′), 136.0, 136.1 (C-*o*, C-*o*′), 136.7 (C-2′) ppm. FTIR (ATR): $\tilde{\nu}$ = 2931 (w), 2858 (w), 2253 (w), 1428 (w), 1110 (m), 904 (vs), 726 (vs), 649 (s), 613 (w) cm^{-1}. MS (CI): *m*/*z* (%) = 419.3 (11) [M + H]$^+$, 401.3 (22), 361.2 (100) [M – C_4H_9]$^+$, 341.2 (38) [M – C_6H_5]$^+$, 283.1 (25), 199.1 (21), 163.1 (5) [M – $C_{16}H_{19}OSi$]$^+$, 145.1 (37). HRMS (CI): calcd. for $C_{27}H_{35}O_2Si^+$ [M + H]$^+$ 419.2400; found 419.2405.

(3a*S*,4*R*,5*R*,6a*S*)-4-Allyl-5-{[*tert*-butyl(diphenyl)silyl]oxy}-1,3a,4,5,6,6a-hexahydropentalen-1-ol (27) and (3a*R*,5*R*,6*R*,6a*S*)-6-Allyl-5-{[*tert*-butyl(diphenyl)silyl]oxy}-1,3a,4,5,6,6a-hexahydropentalen-1-ol (28): A solution of the epoxide mixture **25**,*epi*-**25**, **26**, *epi*-**26** (62.0 mg, 0.15 mmol) and TMEDA (111 μL, 0.74 mmol) in Et_2O (2 mL) was slowly added to a solution of LDA [prepared in situ by the dropwise addition of *n*BuLi (230 μL, 0.37 mmol, 1.6 M in *n*-hexane) to a solution of diisopropylamine (53.0 μL, 0.37 mmol) in Et_2O (1 mL) at –20 °C and then warming to room temperature] and the reaction mixture was stirred at room temperature for 6 h. The reaction was quenched by the addition of a saturated solution of NH_4Cl/H_2O (3 mL), the layers were separated and the aqueous layer was extracted with $CHCl_3$ (3 × 25 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography on SiO_2 [hexanes/EtOAc = 5:1, R_f = 0.29 (**27**), R_f = 0.27 (**28**)] to give a 1:1 mixture (by GC and NMR) of **27** and **28** (37.0 mg, 88.0 μmol, 59%, >90% purity by ^{13}C NMR) as a colourless oil. FTIR (ATR): $\tilde{\nu}$ = 3073 (w), 2930 (m), 2858 (w), 2362 (m), 2253 (w), 2178 (w), 2014 (w), 1716 (w), 1472 (w), 1428 (m), 1377 (m), 1261 (w), 1111 (s), 1007 (w), 903 (vs), 821 (w), 725 (vs), 650 (s) cm^{-1}. MS (ESI): *m*/*z* = 441.2 [M + Na]$^+$, 401.2 [M + Na – C_3H_6]$^+$, 341.2, 329.2, 301.1, 223.2, 203.1, 145.1, 119.1. HRMS (ESI): calcd. for $C_{27}H_{34}O_2SiNa^+$ [M + Na]$^+$ 441.2220; found 441.2209. **27**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.03 [s, 9 H, $SiC(CH_3)_3$], 1.22–1.29 (m, 1 H, 6-H_a), 1.54 (br. s, 1 H, OH), 1.73–1.78 (m, 1 H, 4-H), 1.83 (dt, J = 3.2, 6.3 Hz, 1 H, 6-H_b), 1.83–1.90 (m, 1 H, 1′-H_a), 1.92–1.97 (m, 1 H, 3a-H), 2.35–2.42 (m, 1 H, 1′-H_b), 2.99–3.06 (m, 1 H, 6a-H), 3.77 (dt, J = 5.4, 7.4 Hz, 1 H, 5-H), 4.66–4.68 (m, 1 H, 1-H), 4.95–5.03 (m, 2 H, 3′-H), 5.64–5.68 (m, 1 H, 2-H), 5.78 (dddd, J = 17.0, 14.6, 10.1, 7.6 Hz, 1 H, 2′-H), 5.89 (dd, J = 5.7, 2.5 Hz, 1 H, 3-H), 7.34–7.39 (m, 4 H, *m*-H, *m*′-H), 7.40–7.45 (m, 2 H, *p*-H, *p*′-H), 7.62–7.67 (m, 4 H, *o*-H, *o*′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.5 [Si*C*$(CH_3)_3$], 27.3 [SiC(*C*$H_3)_3$], 37.8 (C-1′), 37.9 (C-1′*), 39.1 (C-4*), 39.2 (C-6), 46.0 (C-6a), 48.6 (C-3a*), 51.9 (C-6*), 52.2 (C-4), 53.0 (C-6a*), 54.9 (C-3a), 79.4 (C-5*), 79.5 (C-5), 84.6 (C-1), 85.0 (C-1*), 116.2 (C-3′*), 116.3 (C-3′), 127.81, 127.84 (C-*m*, C-*m*′), 127.88, 127.89 (C-*m**, C-*m*′*), 129.90, 129.91 (C-*p*, C-*p*′), 129.9, 130.0 (C-*p**, C-*p*′*), 130.6 (C-2*), 130.7 (C-2), 134.36, 134.42 (C-*i*, C-*i*′), 136.27, 136.29 (C-*o*, C-*o*′), 137.4 (C-2′*), 138.0 (C-2′), 140.3 (C-3), 140.4 (C-3*) ppm (* denotes signals of **28**). **28**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.03 [s, 9 H, $SiC(CH_3)_3$], 1.43 (dt, J = 13.2, 7.6 Hz, 1 H, 4-H_a), 1.54 (br. s, 1 H, OH), 1.58–1.64 (m, 1 H, 6-H), 1.76–1.79 (m, 1 H, 1′-H_a), 1.94–1.99 (m, 1 H, 4-H_b), 2.20 (ddt, J = 16.4, 8.2, 1.9 Hz, 1 H, 3a-H), 2.22–2.28 (m, 1 H, 1′-H_b), 2.77–2.82 (m, 1 H, 6a-H), 3.77 (dt, J = 5.4, 7.4 Hz, 1 H, 5-H), 4.58–4.60 (m, 1 H, 1-H), 4.90–4.97 (m, 2 H, 3′-H), 5.63 (dddd, J = 17.1, 14.3, 10.0, 6.9 Hz, 1 H, 2′-H), 5.64–5.68 (m, 1 H, 2-H), 5.94 (dd, J = 5.7, 2.5 Hz, 1 H, 3-H), 7.34–7.39 (m, 4 H, *m*-H, *m*′-H), 7.40–7.45 (m, 2 H, *p*-H, *p*′-H), 7.62–7.67 (m, 4 H, *o*-H, *o*′-H) ppm.

(3a*R*,4*R*,5*R*,6a*S*)-4-Allyl-5-{[*tert*-butyl(diphenyl)silyl]oxy}-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (17) and (3a*R*,5*R*,6*R*,6a*S*)-6-Allyl-5-{[*tert*-butyl(diphenyl)silyl]oxy}-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (29): DMP (38.0 mg, 90.0 μmol) was added to a mixture of **27** and **28** (31.0 mg, 70.0 μmol) in abs. CH_2Cl_2 (3 mL) at 0 °C and the suspension was stirred for 2 h. Then a saturated solution of $NaHCO_3/H_2O$ (3 mL) was added and the layers were separated. The aqueous layer was extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography on SiO_2 (hexanes/EtOAc = 10:1) to give in the first fraction **29** (7.00 mg, 16.8 μmol, 24%, >95% purity by ^{1}H NMR) as a colourless oil, in the second fraction a mixture of **17** and **29** (5.00 mg, 12.0 μmol, 17%) and in the third fraction **17** and **29** in a GC ratio of 95:5 (10.0 mg, 24.0 μmol, 34%, 95% purity by GC) as a colourless oil. Ketone **17**: R_f = 0.44 (hexanes/EtOAc = 5:1). $[\alpha]_D^{20}$ = –9.2 (c = 1.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 [s, 9 H, $SiC(CH_3)_3$], 1.79 (dd, J = 13.5, 7.7 Hz, 1 H, 1′-H_a), 1.86 (ddd, J = 12.1, 6.1, 3.1 Hz, 1 H, 6a-H), 1.95–2.03 (m, 3 H, 1′-H_b, 6-H_a, 6-H_b), 2.69 (tt, J = 5.0, 4.9 Hz, 1 H, 4-H), 2.95–2.99 (m, 1 H, 3a-H), 3.92 (q, J = 7.7 Hz, 1 H, 5-H), 4.89–4.94 (m, 2 H, 3′-H), 5.43–5.53 (m, 1 H, 2′-H), 6.08 (dd, J = 5.5, 2.0 Hz, 1 H, 2-H), 7.35–7.39 (m, 4 H, *m*-H, *m*′-H), 7.40–7.44 (m, 2 H, *p*-H, *p*′-H), 7.58–7.62 (m, 4 H, *o*-H, *o*′-H), 7.65 (dd, J = 5.5, 2.9 Hz, 1 H, 3-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.9 [Si*C*$(CH_3)_3$], 26.8 [SiC(*C*$H_3)_3$], 36.7 (C-6), 37.6 (C-1′), 47.7 (C-4), 50.5 (C-6a), 51.4 (C-3a), 80.2 (C-5), 116.6 (C-3′), 127.57, 127.59 (C-*m*, C-*m*′), 129.7 (C-*p*, C-*p*′), 132.1 (C-2), 133.6, 133.8 (C-*i*, C-*i*′), 135.9 (C-*o*, C-*o*′), 136.1 (C-2′), 167.3 (C-3), 213.1 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 2932 (m), 2858 (w), 2364 (w), 1702 (s), 1588 (w), 1428 (w), 1110 (s), 1063 (m) cm^{-1}. MS (ESI): *m*/*z* = 439.2 [M + Na]$^+$, 339.2 [M + H – C_6H_6]$^+$. HRMS (ESI): calcd. for $C_{27}H_{32}O_2SiNa^+$ [M + Na]$^+$ 439.2064; found 439.2072. Ketone **29**: R_f = 0.51 (hexanes/EtOAc = 5:1). $[\alpha]_D^{20}$ = –8.7 (c = 1.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 [s, 9 H, $SiC(CH_3)_3$], 1.68 (d, J = 13.7 Hz, 1 H, 4-H_a), 1.84–1.93 (m, 3 H, 4-H_b, 1′-H), 2.33–2.39 (m, 1 H, 6-H), 2.49 (dd, J = 6.1, 2.1 Hz, 1 H, 6a-H), 3.29–3.34 (m, 1 H, 3a-H), 3.97 (dt, J = 4.0, 2.0 Hz, 1 H, 5-H), 4.86–4.91 (m, 2 H, 3′-H), 5.48 (dddd, J = 16.4, 13.7, 9.6, 6.8 Hz, 1 H, 2′-H), 6.12 (dd, J = 5.5, 2.0 Hz, 1 H, 2-H), 7.34–7.38 (m, 4 H, *m*-H, *m*′-H), 7.40–7.44 (m, 2 H, *p*-H, *p*′-H), 7.57–7.61 (m, 4 H, *o*-H, *o*′-H), 7.68 (dd, J = 5.5, 2.9 Hz, 1 H, 3-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.9 [Si*C*$(CH_3)_3$], 26.7 [SiC(*C*$H_3)_3$], 36.2 (C-4), 37.5 (C-1′), 45.4 (C-3a), 51.4 (C-6), 53.8 (C-6a), 79.9 (C-5), 116.6 (C-3′), 127.5, 127.6 (C-*m*, C-*m*′), 129.6, 129.7 (C-*p*, C-*p*′), 132.7 (C-2), 133.4, 134.0 (C-*i*, C-*i*′), 135.8, 136.0 (C-*o*, C-*o*′), 136.9 (C-2′), 167.8 (C-3), 212.4 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 3072 (m), 2857 (m), 2253 (w), 1703 (s), 1588 (w), 1427 (w), 1109 (s), 1070 (s) cm^{-1}. MS (ESI): *m*/*z* = 434.2 [M + NH_4]$^+$, 339.2 [M + H –

$C_6H_6]^+$. HRMS (ESI): calcd. for $C_{27}H_{32}O_2SiNH_4^+$ $[M + NH_4]^+$ 434.2510; found 434.2515.

Supporting Information (see footnote on the first page of this article): Further experimental results, NOESY spectra for spectral assignments and NMR spectra of all new compounds.

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