unreacted *Z* diene. For the reaction with phenyl vinyl sulfone, excess diene (diene/dienophile molar ratio 2:1) was employed. The adducts thus obtained gave correct analytical and NMR spectral data.

When **3a** (206 mg, 1 mmol) was allowed to react with dimethyl acetylenedicarboxylate (1 mL, 12 mmol) in benzene under reflux for 24 h, a crude mixture of **14** and **15** (1:1) resulted. Column chromatography of this mixture on silica gel (15:1 hexane–ethyl acetate) yielded pure **15** (126 mg, 40%).

Preparation of Cyclohexadienes 12 (Typical Example). Method A. To a THF solution (15 mL) of **11f** (276 mg, 1 mmol) was added 2 mL of 20% H_2SO_4 at 0 °C and the resulting solution was stirred at this temperature for 24 h. The reaction mixture was poured into benzene (50 mL) and washed with water and sodium bicarbonate solution. The organic layer was dried ($MgSO_4$) and evaporated to give an oil that was chromatographed on silica gel (5:1 hexane–ether) yielding the desired cyclohexadiene compound (216 mg, 85%): ^{1}H NMR (CCl_4) δ 2.15 (s, 3 H, CH_3CO), 2.32 (br s, 4 H, CH_2CH_2), 3.48 (s, 2 H, CH_2S), 5.65 (d, 1 H, CH=C, J = 5 Hz), 6.52 (d, 1 H, CH=CCO, J = 5 Hz), and 7.10 (br s, 5 H, Ph).

Method B. To a methanol solution (10 mL) of MeONa (1.08 mmol) was added **11c** (150 mg, 0.54 mmol) at 0 °C and the mixture was stirred for 1 h at room temperature. Then the reaction mixture was diluted with benzene and washed with water and sodium bicarbonate solution. Drying ($MgSO_4$) and evaporation yielded an oil that was chromatographed on a silica gel column to give the desired cyclohexadiene compound (74 mg, 67%) and unreacted *exo*-**11c** (45 mg, 30%).

Acknowledgment. This work was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan (No. 58740239).

Registry No. (*E*)-**2a**, 91228-15-8; (*Z*)-**2a**, 91228-16-9; (*E*)-**2b**, 91237-76-2; (*Z*)-**2b**, 91237-77-3; (*E*)-**2c**, 91228-17-0; (*E*)-**2d**, 91228-18-1; (*E*)-**3a**, 86531-05-7; (*Z*)-**3a**, 86531-33-1; (*E*)-**3b**, 86531-06-8; (*Z*)-**3b**, 86531-34-2; (*E*)-**3c**, 86531-07-9; (*Z*)-**3c**, 86531-35-3; (*E*)-**3d**, 86531-08-0; (*Z*)-**3d**, 86531-36-4; **4** (R_1 = C_5H_{11}), 4125-23-9; **4** (R_1 = Me), 78-85-3; **5** (R_2 = Me), 20763-19-3; **5** (R_2 = ME), 91228-19-2; **6** (R_3 = ME), 628-82-0; **6** (R_3 = $PhSCH_2CH_2$), 91228-20-5; **6** (R_3 = $PhSeCH_2CH_2$), 91228-21-6; **7**, 29219-35-0; **8a**, 57432-86-7; **8b**, 19157-14-3; **9a**, 86531-03-5; **9b**, 86531-04-6; **10a**, 5535-48-8; **10b**, 78-94-4; **10c**, 96-33-3; **10d**, 24903-94-4; *endo*-**11a**, 91228-22-7; *exo*-**11a**, 91228-23-8; *endo*-**11b**, 91228-24-9; *exo*-**11b**, 91228-25-0; *endo*-**11c**, 91228-26-1; *exo*-**11c**, 91228-27-2; *endo*-**11d**, 91228-28-3; *exo*-**11d**, 91228-29-4; *endo*-**11e**, 91228-30-7; *exo*-**11e**, 91228-31-8; *endo*-**11f**, 86531-09-1; *exo*-**11f**, 86531-10-4; *endo*-**11g**, 86531-11-5; *exo*-**11g**, 86531-12-6; *endo*-**11h**, 91228-32-9; *exo*-**11h**, 91228-33-0; *endo*-**11i**, 86531-15-9; *exo*-**11i**, 86531-16-0; *endo*-**11j**, 86531-17-1; *exo*-**11j**, 86531-18-2; *endo*-**11k**, 86531-19-3; *exo*-**11k**, 86531-20-6; *endo*-**11l**, 86531-21-7; *exo*-**11l**, 86531-22-8; *endo*-**11m**, 86531-27-3; *exo*-**11m**, 86531-28-4; *endo*-**11n**, 86531-29-5; *exo*-**11n**, 86544-08-3; *endo*-**11p**, 91228-34-1; *exo*-**11p**, 91228-35-2; **12** (X = SPh, Y = Ac), 86531-30-8; **12** (X = OH, Y = Ac), 86531-31-9; **12** (X = H, Y = Ac), 24243-12-7; **12** (X = H, Y = $COCH_2CH_2CH$=$C(CH_3)_2$), 64504-55-8; **12** (X = OH, Y = CO_2Me), 86531-32-0; **12** (X = OH, Y = SO_2Ph), 91228-36-3; **14**, 91228-37-4; **15**, 91228-38-5; MeOCOC≡CCOOMe, 762-42-5.

Supplementary Material Available: Full NMR and analytical data for **11a–o** (2 pages). Ordering information is given on any current masthead page.

The sp^3-Carbon-Attached Trimethylsilyl Group as Removable Asymmetry-Inducing Auxiliary. 1. Aromatic Resin Acid Ring Systems

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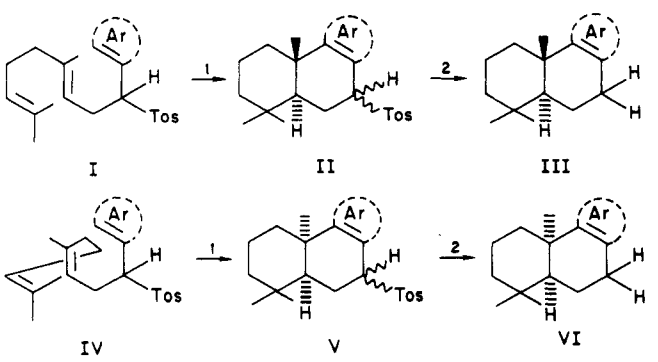
The use of the trimethylsilyl (Me_3Si) unit as detachable diastereoselectivity-inducing auxiliary during cationic polycyclization reactions has been examined. Model studies show **2a,b** to be easily cyclized to **3a–c** in CF_3COOH-containing CH_2Cl_2. Polycyclization of **5a**, on treatment with $SnCl_4$ in CH_2Cl_2, gives a 85:15 ratio of **6a**/**7a**. The same conditions transform **5b** into 5% of 100% diastereoselectively ortho-cyclized **6b** and 46% of para-cyclized **6c**/**7c**, occurring as a 77:23 epimeric mixture. Desilylation of the cyclized materials, using KO-*t*-Bu/Me_2SO, provides **4a–c** and **8a,c**.

Recent work from our laboratories demonstrated a biomimetically modeled entry into aromatic resin acid frameworks III and VI, involving cationic polycyclization of I and IV and Dibal-H mediated detosylation of the obtained systems II and V (Scheme I).[1] The cyclization proceeded, like all concerted polyene cyclizations,[2] stereospecifically, giving either entirely trans- or cis-fused II and V from the preceding *trans*- or *cis*-alkenes I and IV, respectively. Each process produced hereby unequal amounts of tosyl isomers differing configurationally about the epimeric center in product ratios of 60:40 for II and 70:30 for V. The preponderance lay clearly in favor of isomers with the tosyl group occupying positions least impeded by unfavorable 1,3-interactions and reflect an early attainment of product-like transition states, avoiding the development of energetically unpromising species.

Scheme I[a]



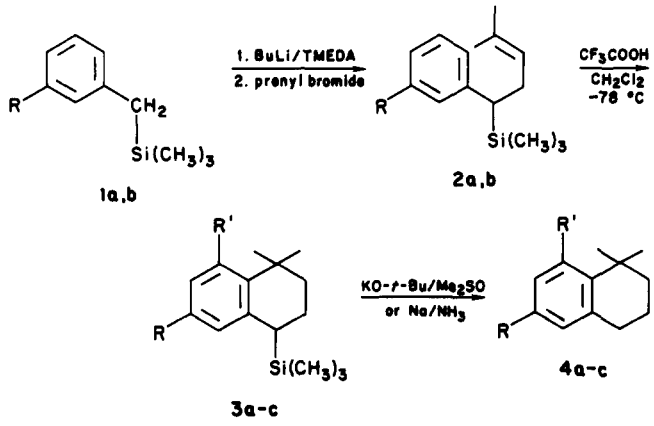
[a] 1, FSO_3H-SO_2; 2, Dibal-H.

The principles underlying asymmetric synthesis have found extensive application in steroid strategies[3] where,

(1) Janssen, C. G. M.; Godefroi, E. F. *J. Org. Chem.* **1982**, *47*, 3274.
(2) van Tamelen, E. E. *Acc. Chem. Res.* **1968**, *1*, 111; **1975**, *8*, 152.

0022-3263/84/1949-3600$01.50/0

Scheme II[a]



[a] 1 and 2: a, R = H; b, R = OMe. 3 and 4: a, R = R' = H; b, R = H, R' = OMe; c, R = OMe, R' = H.

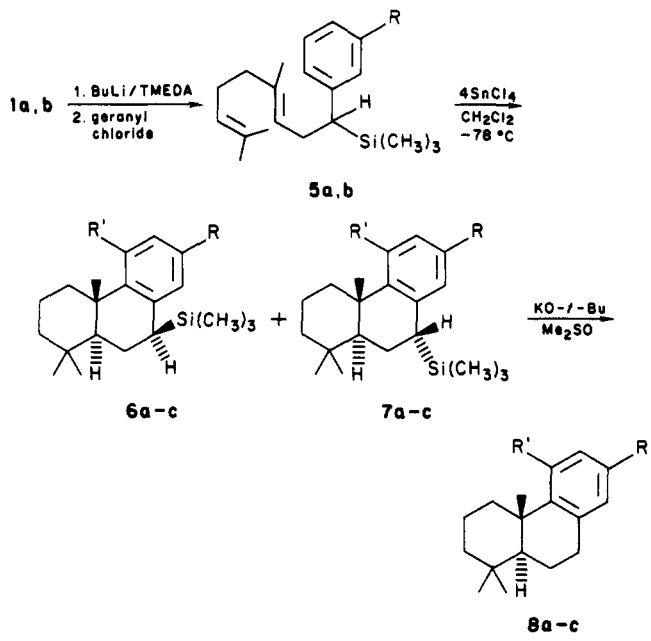
for instance, cyclization of certain 3-anisyl *pro*-C-6-methylated alkenes has featured 90% optical induction toward the 6-α-methylated estrone precursor.[4] The achieved enantioselectivity was further improved upon by cyclizing the corresponding 2-thienyl analogues, leading to 97% selectivity on ring-closing the *pro*-C-5-methylated alkene and ultimately reaching 100% by incorporating the even more sterically demanding *t*-Bu substituent as asymmetry-inducing unit at the prochiral center.[5]

Our interest in removable enantioselectivity inducing carbon substituents would preclude using the *t*-Bu fragment for this purpose, because its removal from carbon appears to be limited to detachment from aromatic systems only.[6] A survey of *t*-Bu-related systems led us to consider the trimethylsilyl (Me_3Si) group for this purpose. Sterically it resembles the *t*-Bu group, differing only in the longer Si–C bonds, while featuring prior art for its removability from vinylic, allylic, and benzylic substrates.[7] To our knowledge there is no precedent for Me_3Si units ever having served as enantioselectivity-inducing auxiliaries. The present paper describes the feasibility of this tactic as exemplified by model studies leading to simple bicyclic systems **4a–c** (Scheme II) and its extension to include a potentially enantioselective synthesis of aromatic resin acid frameworks **8a,c** (Scheme III).

Results and Discussion

Model Studies Leading to 4a–c. Realization of the concept presupposed easy access to **2a,b**, necessitating, in turn, large-scale availability of **1a,b**. (Benzyltrimethyl)silane (**1a**) was prepared in 83% yield by treatment of benzylmagnesium chloride, generated according to Benkeser,[8] with Me_3SiCl. Similar transformations on *m*-methoxybenzyl chloride provided **1b** (77%). These systems were then prenylated via their anions. Base-catalyzed alkylation of α-silylated carbanions seems to have drawn surprisingly little attention short of the reaction of [(phenylseleno)trimethylsilyl]lithium with primary alkyl bromides or iodides.[9] The deprotonation of **1a** using BuLi in hexamethylphosphoramide had been reported;[10] we

Scheme III[a]



[a] 5a, R = H, b, R = MeO. 6–8: a, R = H; b, R = H, R' = MeO; c, R = MeO, R' = H.

chose to perform the proton abstraction from **1a,b** by treatment with 2 equiv of BuLi in the presence of tetramethylethylenediamine (TMEDA) at room temperature. Subsequent addition of prenyl bromide then gave, after 18 h, 42–46% of **2a,b**.

Conditions for cyclizing **2a,b** were derived from those generally encountered in cationic polycyclizations.[3] Treatment of **2a** with an excess of trifluoroacetic acid at room temperature for 30 min produced ca. 80% of distilled GLC-pure **3a**. The conditions also brought about cyclization of **1b** to give, after chromatographic separation, 26% of ortho-cyclized **3b** and 39% of the para-cyclized **3c**. Identification was based on the NMR aromatic signals showing for **3b** a complex pattern of three vicinal protons and for **3c** only two vicinal protons appearing as simpler peaks.

Although nucleophilic or electrophilic desilylation of allylic or vinylic substrates constitutes a widely used tactic in synthesis,[7] cleavage of (benzyltrimethyl)silanes has hitherto been restricted to the use of nucleophilic agents such as sodium or potassium amide in liquid ammonia and sodium ethoxide or potassium hydroxide in refluxing ethanol.[11] In the present studies **3a** gave desilylated **4a** quantitatively on treatment with ammoniacal sodium amide, the material being identical with product already obtained during previous detosylation studies.[12] As the method is not amenable to infinite upscaling, a more practical desilylation tactic was sought. This led us to the use of potassium *tert*-butoxide in dry Me_2SO,[13] a system causing 81% conversion of **3a** to distilled **4c** after 15 min at room temperature. These conditions also produced crude GLC-pure **4b,c** in essentially quantitative yields (Scheme II).

Aromatic Resin Acid Related Frameworks 8a,c via Desilylation of Polyene Cyclization Derived 7a–c.

(3) Johnson, W. S. *Bioorg. Chem.* **1976**, *5*, 51.
(4) Groen, M. B.; Zeelen, F. J. *J. Org. Chem.* **1978**, *43*, 1961.
(5) Macco, A. A.; de Brouwer, R. J.; Buck, H. M. *J. Org. Chem.* **1977**, *42*, 3196.
(6) Tashiro, M. *Synthesis* **1979**, 761.
(7) Colvin, E. "Silicon in Organic Synthesis" Butterworths: London, 1981.
(8) Benkeser, R. A.; deTalvo, E. *J. Am. Chem. Soc.* **1967**, *89*, 2141.
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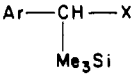
(10) Chan, T. H.; Chang, E. *J. Org. Chem.* **1974**, *39*, 3264.
(11) Hauser, C. R.; Hance, C. R. *J. Am. Chem. Soc.* **1951**, *73*, 5846.
(12) Janssen, C. G. M.; Hendriks, A. H. M.; Godefroi, E. F. *Recl. Trav. Chim Pays-Bas*, accepted for publication.
(13) We thank Dr. I. Fleming, University Chemical Laboratories, Cambridge, England, for the timely suggestion to examine the cited conditions.

Table I. Trimethylsilylated Cyclization Precursors:



compd	Ar	X	yield,[a] %	bp, °C (mm)	^{1}H NMR (CCl_4), δ
2a	phenyl	prenyl	46	103–105 (3.5)	0.00 (s, 9, $Si(CH_3)_3$), 1.64 (s, 6, 2 CH_3), 1.83–2.33 (m, 2, CH_2), 2.47 (t, 1, CH), 4.99 (t, 1, olefinic H), 6.78–7.33 (m, 5, Ar H)
2b	*m*-anisyl	prenyl	42	112–115 (0.1)	0.00 (s, 9, $Si(CH_3)_3$), 1.63 (s, 6, 2 CH_3), 1.79–2.27 (m, 2, CH_2), 2.44 (t, 1, CH), 3.72 (s, 3, OCH_3), 4.78–5.20 (m, 1, olefinic H), 6.33–7.24 (m, 4, Ar H)
5a	phenyl	geranyl	62	167–169 (3.0)	0.00 (s, 9, $Si(CH_3)_3$), 1.54 and 1.57 (2 s, 3 and 6, 3 CH_3), 1.66–2.71 (m, 6, 3 CH_2), 2.42 (t, 1, CH), 4.64–5.16 (m, 2, olefinic H), 6.66–7.30 (m, 5, Ar H)
5b	*m*-anisyl	geranyl	40	160–164 (0.03)	0.00 (s, 9, $Si(CH_3)_3$), 1.47–2.70 (m, 7, aliph H), 1.57 and 1.64 (3 s, 9, 3 CH_3), 3.73 (s, 3, OCH_3), 4.67–5.27 (m, 2, olefinic H), 6.36–7.29 (m, 4, Ar H)

[a] Yields based on 98 % GLC-pure materials.

The above strategy was applied next to the construction of aromatic resin acid models for purposes of probing the diastereoselectivity-inducing potential of Me_3Si units. Deprotonated **1a** was therefore treated with geranyl chloride[14] to give 62% of distilled **5a**. Similarly 40% of **5b** was obtained from *m*-methoxy analogue **1a**. Trifluoracetic acid, having been previously successful in generating **3a–c**, failed to bring about the polycyclization of **5a,b**. $SnCl_4$, on the other hand, did induce these systems to ring-close with best results being obtained on allowing **5a,b** to react with 4 equiv of the agent in CH_2Cl_2 for 2 h at −78 °C. For **5a** these conditions produced 51% of an oily GLC-determined 85:15 epimeric mixture of **6a/7a**. Its major component was designated as having the Me_3Si fragment in the β-configuration **6a** by analogy with the previously reported tosylated versions.[1] Methanol trituration afforded 29% of crystalline β-isomer **6a** melting sharply at 83–84 °C.

Comparable $SnCl_4$-induced cyclization of **5b** yielded both ortho- and para-ring-closed materials. These were separated chromatographically to give 5% of GLC-pure **6b** and 46% of a GLC-binary 77/23 mixture of **6c/7c**. Compound **6b** solidified on standing to melt sharply at 108–109 °C on trituration with methanol. The experiments demonstrate the Me_3Si fragment to induce high (77–100%) diastereoselectivity in three examined cases of aromatic resin acid directed polycyclization strategies. The optical inductions stem undoubtedly from unfavorable H–Me_3Si 1,3-interactions counteracting production of the sterically more impeded epimers. In addition, though, the measure of asymmetric induction appears to be related to the cyclizing agent used. For instance, when **6a** was cyclized in the system FSO_3H–SO_2, a 25% yield of **6a/7a** was produced featuring a 68:32 ratio toward **6a**, which compared unfavorably with the 85:15 ratio attained earlier on using $SnCl_4$ as cyclizing initiating agent.

Desilylation of **6a/7a** and **6c/7c**, using the KO-*t*-Bu/Me_2SO reagent gave, upon filtration of the crude product through silica, GLC-pure **8a,c** in ca. 80% yield. Product identification rested on their CH_3 NMR signals corresponding to those of related transannelated detosylated systems, previously reported by us[1] and by Wenkert et al.[15]

Concluding Remarks

The Me_3Si fragment has been made to function as a removable diastereoselectivity-inducing unit in a biomimetically modeled polycyclization tactic into aromatic resin acid-derived ring systems. The concept parallels our earlier reported tosyl-mediated strategy in providing easy access to product racemates.[1] Its merit stems inter alia from the ease of performing ring-closures in CF_3COOH- or $SnCl_4$-containing CH_2Cl_2 rather than in the FSO_3H/SO_2 medium required for cyclizing the tosylated congeners, plus the facile way of benzylic Me_3Si removal on treatment with KO-*t*-Bu in Me_2SO; this complements our previous reductive Dibal-H methodology for cleaving tosylated benzylic substrates.[12] The method's prime strength, though, would appear to lie in the Me_3Si-proven ability for bringing about a high degree of optical induction during cited polycyclizations, thus offering clear perspectives for preparing enantiomerically pure aromatic resin acid type systems. Its application in steroid synthesis will be reported shortly.[16]

Experimental Section

General Methods. Microanalytical data were supplied by P. van den Bosch and H. Eding. ^{1}H NMR spectra were obtained on a Varian EM 360 spectrometer. Melting points (recorded on a Fischer-Johns block) are uncorrected. Chromatography was carried out over a 20-fold weight of silica gel. GLC analyses were carried out by G. Bezemer, using a Carbowax column (fused silica; CP Wax 51) of 25 m and 0.23-mm diameter at 220-235 °C.

Phenyl(trimethylsilyl)methane (1a). Benzylmagnesium chloride was prepared according to Benkeser[8] as follows. A three-necked, round-bottomed flask containing 39 g (1.6 mol) of nitrogen-covered magnesium was thoroughly flame-dried. To it was added 90 mL of dry ether after which 50.6 g (0.4 mol) of benzyl chloride in 135 mL of dry ether was introduced dropwise and with stirring while maintainig a gentle reflux. After stirring for an additional hour, 43.4 g (0.4 mol) of freshly distilled chlorotrimethyl silane was added. The mixture was stirred overnight and was then poured onto 200 mL of ice–water. It was then filtered through Hy-Flow (Celite 545) and the organic phase was washed with water, 0.1 N HCl, $NaHCO_3$ solution, and water until neutral. Drying of the organic layer and ether evaporation left 61.4 g of crude product which was fractionated to give 54 g (83%) of **2a**; bp 88–90 °C (18 mm); ^{1}H NMR (CCl_4) δ 0.00 (s, 9, $Si(CH_3)_3$, 2.03 (s, 2, CH_2), 6.70–7.33 (m, 5, Ar H).

***m*-Anisyl(trimethylsilyl)methane (1b)** was prepared analogously to **1a**: yield 77%; bp 92–93 °C (9 mm); ^{1}H NMR (CCl_4) δ 0.00 (s, 9, $Si(CH_3)_3$), 1.95 (s, 2, CH_2), 3.62 (s, 3, OCH_3), 6.23–7.10 (m, 4, Ar H).

Compounds **2a,b** and **5a,b** were prepared from **1a,b** via prenylation and geranylation (see Table I). The procedure is exemplified by directions for **2a**.

1-Phenyl-1-(trimethylsilyl)-4-methylpent-3-ene (2a). To 0.2 mol of freshly prepared BuLi in ether was added at 0–10 °C 23.2 g (0.2 mol) of TMEDA. After stirring for 0.5 h at 0 °C, 16.4 g (0.1 mol) of **1a** was added and anion formation was allowed to proceed for 5 h at room temperature. Dropwise introduction of 16.4 g (0.11 mol) of 90% pure prenyl bromide to the yellow reaction mixture caused a highly exothermic reaction. The mixture was stirred for an additional 18 h, whereupon it was poured onto water. Separation of the organic layer and washing with respectively water, 0.1 N HCl, saturated $NaHCO_3$ solution,

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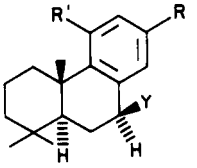
(15) Wenkert, E.; Afonso, A.; Beak, P.; Carney, R. W. J.; Jeffs, P. W.; McChesney, J. D. *J. Org. Chem.* **1965**, *30*, 713.
(16) Janssen, C. G. M.; Godefroi, E. F., manuscript in preparation.

Table II. Aromatic Resin Acid Related Frameworks:



compd	R	R'	Y	yield,[a] %	mp, °C	^{1}H NMR (CCl_4), δ
6a	H	H	Me_3Si	29	83–84	0.00 (s, 9, $Si(CH_3)_3$), 0.87, 0.95 and 1.07 (3 s, 9, 3 CH_3), 1.07–2.75 (m, 10, aliph H), 6.61–7.25 (m, 4, Ar H)
6b	H	MeO	Me_3Si	5.2	108–109	0.25 (s, 9, $Si(CH_3)_3$), 1.13, 1.21 and 1.43 (3 s, 9, 3 CH_3), 0.91–2.79 (m, 10, aliph H), 3.95 (s, 3, OCH_3), 6.50–7.40 (m, 3 *vic*-H, 3, Ar H)
8a	H	H	H	80	*b*	0.71–2.53 (m, 9, aliph H), 0.93, 0.93 and 1.18 (3 s, 9, 3 CH_3), 2.63–3.07 (m, 2, Ar CH_2), 6.72–7.27 (m, 4, Ar H)
8c	MeO	H	H	79	*b*	0.74–3.07 (m, 11, aliph H), 0.96, 0.96 and 1.18 (3 s, 9, 3 CH_3), 3.68 (s, 3, OCH_3), 6.29–7.24 (m, 2 *vic*-H, 3, Ar H)

[a] Isolated yields. [b] 98% GLC-pure compounds.

and water gave, on drying and solvent evaporation, 27.0 g of crude product. The low boiling, foaming components were removed by distillation below 100 °C (35 mm) after which the residue (14.0 g) was fractionated to give 10.7 g (46%) of product, bp 103–105 °C (3.5 mm); ^{1}H NMR (CCl_4) δ 0.00 (s, 9, $Si(CH_3)_3$), 1.64 (s, 6, 2 CH_3), 1.83–2.33 (m, 2, CH_2), 2.47 (t, 1, CH), 4.99 (t, 1, olefinic H), 6.78–7.33 (m, 5, Ar H).

1-(Trimethylsilyl)-4,4-dimethyl-1,2,3,4-tetrahydronaphthalene (3a). To 11.5 g (0.05 mol) of **2a** in 25 mL of CH_2Cl_2 was added dropwise 37 g (0.325 mol) of trifluoroacetc acid in 75 mL of CH_2Cl_2. After being stirred for 0.5 h, the mixture was poured onto water. The organic layer was washed with a saturated sodium bicarbonate solution and water until neutral, dried, and evaporated to leave 11.5 g of crude material. Fractionation gave 9.2 g (80%) of pure product: bp 96–99 °C (2.1 mm); ^{1}H NMR (CCl_4) δ 0.00 (s, 9, $Si(CH_3)_3$), 1.13–2.18 (m, 4, 2 CH_2), 1.18 and 1.27 (2 s, 6, 2 CH_3), 2.30 (t, 1, CHSi), 6.62–7.31 (m, 4, Ar H).

Treatment of **2b** with CF_3COOH in CH_2Cl_2 as above produced a mixture of **3b,c**. This was subsequently chromatographed through silica by using as eluent hexane–1% acetone to yield **3b** and **3c** in 26% and 39% yield: R_f in hexane-1% acetone 0.56 and 0.21, respectively. **3b**: ^{1}H NMR (CCl_4) δ 0.14 (s, 9, $Si(CH_3)_3$), 1.26–2.75 (m, 5, aliphatic H), 1.46 and 1.54 (2 s, 6, 2 CH_3), 3.84 (s, 3, OCH_3), 6.39–7.14 (m, 3 *vic*-H, 3, Ar H). **3c**: ^{1}H NMR (CCl_4) δ 0.14 (s, 9, $Si(CH_3)_3$), 1.10–2.66 (m, 5, aliphatic H), 1.33 and 1.42 (2 s, 6, 2 CH_3), 3.76 (s, 3, OCH_3), 6.33–7.33 (m, 2 *vic*-H, 3, Ar H).

Compounds **6a,b** (Table II) were derived via the $SnCl_4$-induced cyclization of **5a,b**. The procedure for **6a** serves as illustration.

***d,l*-1,2,3,4,4a,9,10,10a-Octahydro-1,1,4a-trimethyl-9-(trimethylsilyl)phenanthrene (6a).** To a solution of 3.6 g (0.0125 mol) of **5a** in 50 mL of CH_2Cl_2 was added, at −78 °C, 6.25 mL (0.05 mol) of freshly distilled $SnCl_4$ in 25 mL of CH_2Cl_2. The mixture was stirred for 2 h at −78 °C whereupon 31.2 mL of 8% (w/v) NaOH in methanol was introduced dropwise while maintaining the temperature below −70 °C. The mixture was then allowed to come to room temperature and 20 mL of water was added. The organic phase was separated, dried over K_2CO_3, and evaporated. Chromatography over silica using hexane as eluent (R_f 0.53) yielded 1.83 g (51%) of an 85:15 mixture of GLC-pure **6a/7a**. Trituration with methanol afforded 1.05 g (29%) of solid **6a**, mp 83–84 °C. Analytical material was obtained on recrystallization from methanol: mp 86–87 °C; ^{1}H NMR (CCl_4) δ 0.00 (s, 9, $Si(CH_3)_3$), 0.87, 0.95 and 1.07 (3 s, 9, 3 CH_3), 1.07–2.75 (m, 10, aliphatic H), 6.61–7.25 (m, 4, Ar H).

Anal. Calcd for $C_{20}H_{32}Si$: C, 79.92; H, 10.73. Found: C, 79.91; H, 10.93.

Comparable cyclization of **5b** produced an ortho/para-cyclized mixture of **6b** and **6c/7c**. They were separated via chromatography using hexane–1% acetone to give 5.2% of GLC-pure **6b**. Change of eluent to hexane–2% acetone afforded 26.2% of a GLC-pure mixture of **6c/7c** in a 77:23 ratio in favor of **6c**. Compound **6b** solidified on standing, having after trituration with methanol, mp 108–109 °C. Analytical material obtained from methanol had mp 108–109 °C; R_f of **6b** in hexane-1% acetone 0.47. **6b**: ^{1}H NMR (CCl_4) δ 0.25 (s, 9, $Si(CH_3)_3$), 1.13, 1.21 and 1.43 (3 s, 9, 3 CH_3), 0.91–2.79 (m, 10, aliphatic H), 3.95 (s, 3, OCH_3), 6.50–7.40 (m, 3 *vic*-H, 3, Ar H). **6c**: ^{1}H NMR (CCl_4) δ 0.23 (s, 9, $Si(CH_3)_3$), 0.97–2.80 (m, 10, aliphatic H), 1.09, 1.19 and 1.27 (3 s, 9, 3 CH_3), 3.83 (s, 3, OCH_3), 6.40–7.37 (m, 2 *vic*-H, 3, Ar H).

Desilylation of **3a–c**, **6a/7a**, and **6c/7c** to **4a–c** and **8a,c** (Table II), respectively, are typified by the production of **4a**.

1,1-Dimethyl-1,2,3,4-tetrahydronaphthalene (4a). To a stirred mixture of 2.5 g (0.022 mol) of potassium *tert*-butoxide in 5 mL of dry Me_2SO was added 4.6 g (0.02 mol) of **3a**. A slightly exothermic reaction ensued. After 15 min, 50 mL of ether were added and the mixture was scrubbed with water and dried. Evaporation of the ether left 3.55 g of crude, completely desilylated material, which was fractionated to afford 2.6 g (81%) of pure product, bp 99–101 °C (17 mm). It was identical with material obtained via detosylation of 1-(*p*-tolylsulfonyl)-4,4-dimethyl-1,2,3,4-tetrahydronaphthalene:[12] ^{1}H NMR (CCl_4) δ 1.27 (s, 6, 2 CH_3), 1.60–1.65 (m, 2, CH_2), 1.70 (t, 2, CH_2), 2.70 (t, 2, Ar CH_2), 7.00 (m, 4, Ar H). **4b**: yield 95%; ^{1}H NMR (CCl_4) δ 1.22–1.47 (m, 4, CH_2CH_2), 1.22 (s, 6, 2 CH_3), 2.30–2.80 (m, 2, Ar CH_2), 3.63 (s, 3, OCH_3), 6.24–6.95 (m, 3 *vic*-H, 3, Ar H). **4c**: yield 95%; ^{1}H NMR (CCl_4) δ 1.10 (s, 6, 2 CH_3), 1.31–1.96 (m, 4, CH_2CH_2), 2.32–2.76 (m, 2, Ar CH_2), 3.53 (s, 3, OCH_3), 6.17–7.08 (m, 2 *vic*-H, 3, Ar H).

Registry No. **1a**, 770-09-2; **1b**, 51755-56-7; (±)-**2a**, 91425-01-3; (±)-**2b**, 91425-02-4; (±)-**3a**, 91425-03-5; (±)-**3b**, 91425-04-6; (±)-**3c**, 91425-05-7; **4a**, 1985-59-7; **4b**, 91425-13-7; **4c**, 33214-69-6; (±)-**5a**, 91425-06-8; (±)-**5b**, 91425-07-9; (±)-**6a**, 91425-08-0; (±)-**6b**, 91425-09-1; (±)-**6c**, 91425-11-5; (±)-**7a**, 91425-10-4; (±)-**7c**, 91425-12-6; (±)-**8a**, 38301-74-5; (±)-**8c**, 91465-64-4; *m*-methoxybenzylmagnesium chloride, 26905-40-8; benzylmagnesium chloride, 6921-34-2; benzyl chloride, 100-44-7; chlorotrimethylsilane, 75-77-4; prenyl bromide, 870-63-3; geranyl chloride, 5389-87-7.