# *Notes*

## Development of a New Building Block for the Synthesis of Silicon-Based Drugs and Odorants: Alternative Synthesis of the Retinoid Agonist Disila-bexarotene

Matthias W. Büttner, Jennifer B. Nätscher, Christian Burschka, and Reinhold Tacke*

*Universität Würzburg, Institut für Anorganische Chemie, Am Hubland, D-97074 Würzburg, Germany*

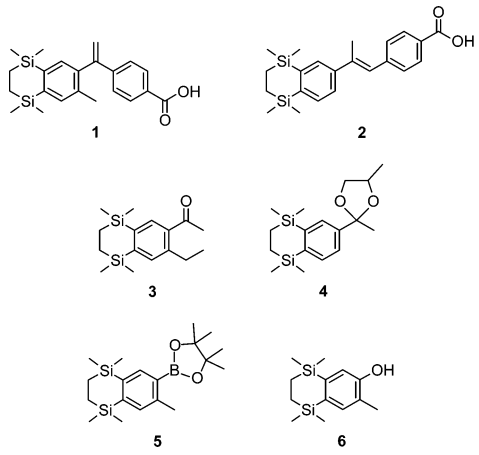
*Received June 12, 2007*

*Summary: With 4,4,5,5-tetramethyl-2-(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)-1,3,2-dioxaborolane (**5**) a new building block for the synthesis of biologically active 5,8-disila-5,6,7,8-tetrahydronaphthalene derivatives has been made available. The high synthetic potential of **5** has been demonstrated by the development of a new synthesis of the retinoid agonist disila-bexarotene (**1**).*

### Introduction

Disila-substitution of the 5,6,7,8-tetrahydronaphthalene skeleton (→5,8-disila-5,6,7,8-tetrahydronaphthalene) has been demonstrated to be a very useful approach for the development of novel silicon-based drugs and odorants.[1] The retinoid agonists disila-bexarotene[1d] (**1**) and disila-TTNPB[1h] (**2**), the musky odorant disila-versalide[1f] (**3**), and the ambergris odorant disila-okoumal[1g] (**4**) are examples of this principle.

The synthesis of such compounds is not trivial. The 5,8-disila-5,6,7,8-tetrahydronaphthalene skeleton can be built up by using [2+2+2] cycloadditions of the silicon-containing diyne 1,2-bis(ethynyldimethylsilyl)ethane and appropriately functionalized monoynes in the presence of $CpCo(CO)_2$ or $Co_2(CO)_8$. However, in all cases studied so far the yields were very poor, and the workup and product isolation were difficult and tedious.[1] Recently, we have reported on a new catalytic system ($CoI_2$/Zn in acetonitrile) for such [2+2+2] cycloadditions that can overcome these problems.[2] Using this particular method, we have succeeded in preparing a novel and versatile building block, the 2-(5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)-1,3,2-dioxaborolane **5**, that can be used for the synthesis of various biologically active 5,8-disila-5,6,7,8-tetrahydronaphthalene derivatives. This approach has been applied to an alternative synthesis of disila-bexarotene (**1**) and to the synthesis of the 5,8-disila-5,6,7,8-tetrahydronaphth-2-ol **6**, which can also serve as a precursor in the synthesis of related biologically active silicon compounds. We report here on the syntheses and crystal structure analyses of **5** and **6** and a new synthesis of disila-bexarotene (**1**).




### Results and Discussion

Compounds **1**, **5**, and **6** were synthesized according to Scheme 1. Disila-bexarotene (**1**) was prepared in a multistep synthesis, starting from the 1,3,2-dioxaborolane **7**. Thus, treatment of **7** with propyn-1-yllithium provided the 2-alkynyl-1,3,2-dioxaborolane **8** (89% yield),[3] which was allowed to react with the silicon-containing diyne **9** in the presence of $CoI_2$/Zn to afford the 2-(5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)-1,3,2-dioxaborolane **5** in 48% yield (in this context, see also ref 4). Compound **5** was then treated with the triflate **10**,[5] in the presence of $(PPh_3)_2PdCl_2$,[6] to provide the disila-bexarotene precursor **11** (86% yield), which upon treatment with potassium hydroxide in methanol/water and subsequent acidification with hydrochlo-

* To whom correspondence should be addressed. Phone: +49-931-888-5250. Fax: +49-931-888-4609. E-mail: r.tacke@mail.uni-wuerzburg.de.

(1) (a) Montana, J. G.; Fleming, I.; Tacke, R.; Daiss, J. (Inventors) (Amedis Pharmaceuticals Ltd.) PCT Int. Pat. Appl. WO 2004/045625 A1, June 3, 2004. (b) Montana, J. G.; Showell, G. A.; Fleming, I.; Tacke, R.; Daiss, J. (Inventors) (Amedis Pharmaceuticals Ltd.) PCT Int. Pat. Appl. WO 2004/048390 A1, June 10, 2004. (c) Montana, J. G.; Showell, G. A.; Tacke, R. (Inventors) (Amedis Pharmaceuticals Ltd.) PCT Int. Pat. Appl. WO 2004/048391 A1, June 10, 2004. (d) Daiss, J. O.; Burschka, C.; Mills, J. S.; Montana, J. G.; Showell, G. A.; Fleming, I.; Gaudon, C.; Ivanova, D.; Gronemeyer, H.; Tacke, R. *Organometallics* **2005**, *24*, 3192−3199. (e) Miller, D. J.; Showell, G. A.; Conroy, R.; Daiss, J.; Tacke, R.; Tebbe, D. (Inventors) (Amedis Pharmaceuticals Ltd.) PCT Int. Pat. Appl. WO 2005/005443 A1, January 20, 2005. (f) Büttner, M. W.; Penka, M.; Doszczak, L.; Kraft, P.; Tacke, R. *Organometallics* **2007**, *26*, 1295−1298. (g) Büttner, M. W.; Burschka, C.; Junold, K.; Kraft, P.; Tacke, R. *ChemBioChem* **2007**, in press. (h) Büttner, M. W.; Burschka, C.; Daiss, J. O.; Ivanova, D.; Rochel, N.; Kammerer, S.; Peluso-Iltis, C.; Bindler, A.; Gaudon, C.; Germain, P.; Moras, D.; Gronemeyer, H.; Tacke, R. *ChemBioChem* **2007**, in press.

(2) Doszczak, L.; Fey, P.; Tacke, R. *Synlett* **2007**, *5*, 753−756.

(3) Compound **8** has already been reported in the literature, but to the best of our knowledge, a detailed procedure for its synthesis is missing. Concerning the NMR and physical data of **8**, see also: Hansen, E. C.; Lee, D. *J. Am. Chem. Soc.* **2005**, *127*, 3252−3253 (Supporting Information).

(4) Gandon, V.; Leca, D.; Aechtner T.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *Org. Lett.* **2004**, *6*, 3405−3407.

(5) Qing, F.-L.; Fan, J.; Sun, H.-B.; Yue, X.-J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3053−3057.

(6) (a) Chemler, S. R.; Trauner, D.; Danishefsky, S. J. *Angew. Chem.* **2001**, *113*, 4676−4701; *Angew. Chem., Int. Ed.* **2001**, *40*, 4544−4568. (b) Occhiato, E. G.; Trabocchi, A.; Guarna, A. *J. Org. Chem.* **2001**, *66*, 2459−2465.

10.1021/om700570f CCC: $37.00 
Publication on Web 08/16/2007

**Scheme 1**

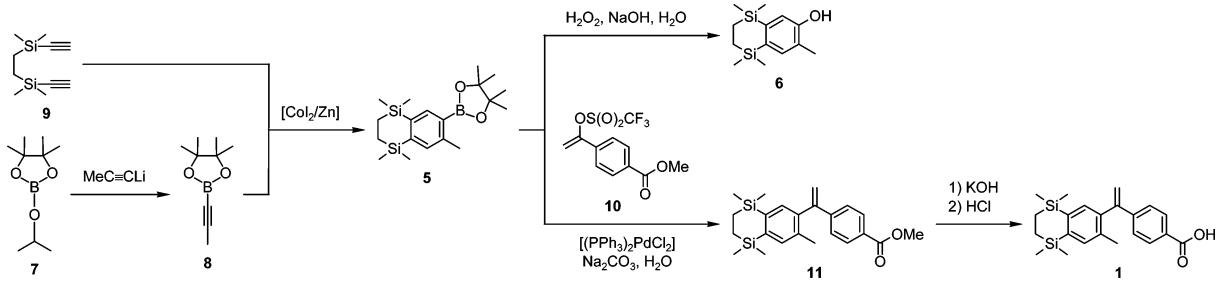



**Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 5 and 6**

| | **5** | **6** |
|---|---|---|
| empirical formula | $C_{19}H_{33}BO_2Si_2$ | $C_{13}H_{22}OSi_2$ |
| formula mass, g mol$^{-1}$ | 360.44 | 250.49 |
| collection *T*, K | 193(2) | 173(2) |
| $\lambda$(Mo K$\alpha$), Å | 0.71073 | 0.71073 |
| cryst syst | monoclinic | triclinic |
| space group (No.) | $P2_1/c$ (14) | $P\bar{1}$ (2) |
| *a*, Å | 15.5982(19) | 9.2211(18) |
| *b*, Å | 13.2100(15) | 10.489(2) |
| *c*, Å | 11.1157(12) | 16.445(3) |
| $\alpha$, deg | 90 | 92.22(3) |
| $\beta$, deg | 108.847(12) | 102.27(3) |
| $\gamma$, deg | 90 | 100.55(3) |
| *V*, Å$^3$ | 2167.6(4) | 1522.9(5) |
| *Z* | 4 | 4 |
| *D*(calcd), g cm$^{-3}$ | 1.104 | 1.093 |
| $\mu$, mm$^{-1}$ | 0.172 | 0.214 |
| *F*(000) | 784 | 544 |
| cryst dimens, mm | 0.5 × 0.5 × 0.4 | 0.3 × 0.3 × 0.1 |
| 2$\theta$ range, deg | 6.16−55.90 | 4.54−56.00 |
| index ranges | $-20 \le h \le 20$, $-17 \le k \le 17$, $-14 \le l \le 14$ | $-12 \le h \le 12$, $-13 \le k \le 13$, $-21 \le l \le 21$ |
| no. of collected reflns | 24 408 | 22 192 |
| no. of indep reflns | 5141 | 6771 |
| $R_{int}$ | 0.0695 | 0.0400 |
| no. of reflns used | 5141 | 6771 |
| no. of params | 226 | 301 |
| *S*[a] | 1.038 | 1.027 |
| weight params *a*/*b*[b] | 0.0510/0.7449 | 0.0564/0.5354 |
| $R_1$[c] [$I > 2\sigma(I)$] | 0.0498 | 0.0413 |
| $wR_2$[d] (all data) | 0.1072 | 0.1132 |
| max./min. residual electron density, e Å$^{-3}$ | +0.344/−0.195 | +0.546/−0.587 |

[a] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; $n$ = no. of reflections; $p$ = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

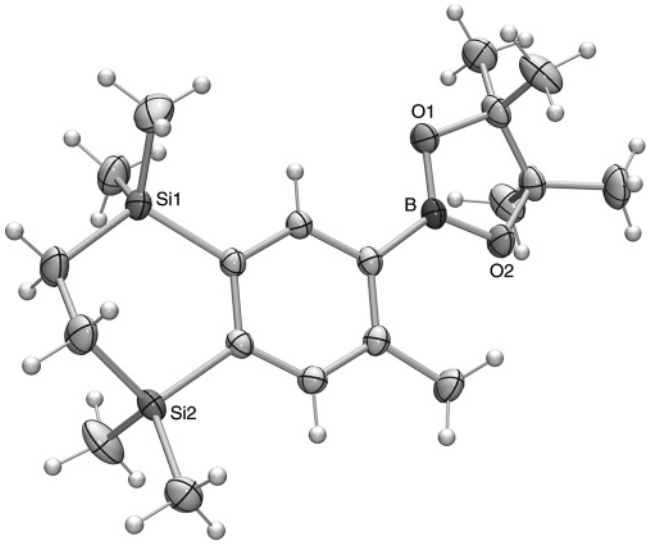



**Figure 1.** Molecular structure of **5** in the crystal (probability level of displacement ellipsoids 50%).

ric acid afforded disila-bexarotene (**1**) in 96% yield. Compound **6** was prepared in 62% yield by treatment of **5** with hydrogen peroxide in the presence of sodium hydroxide and water.

Compounds **1**, **5**, **6**, and **11** were isolated as colorless crystalline solids, whereas **8** was obtained as a colorless liquid. The identities of these compounds were established by elemental analyses (C, H) and NMR studies ($^1$H, $^{11}$B, $^{13}$C, $^{29}$Si), and **5** and **6** were additionally characterized by crystal structure analyses. The crystal data and experimental parameters used for these studies are given in Table 1. The molecular structures of **5** and **6** are depicted in Figures 1 and 2 (for further details concerning the crystal structure analyses, see the Supporting Information).

In summary, with compound **5** a new building block for the synthesis of biologically active 5,8-disila-5,6,7,8-tetrahydronaphthalene derivatives has been made available. The high synthetic potential of **5** has been demonstrated by the development of a new synthesis of the retinoid agonist disila-bexarotene (**1**), which is much more advantageous compared to the original synthesis

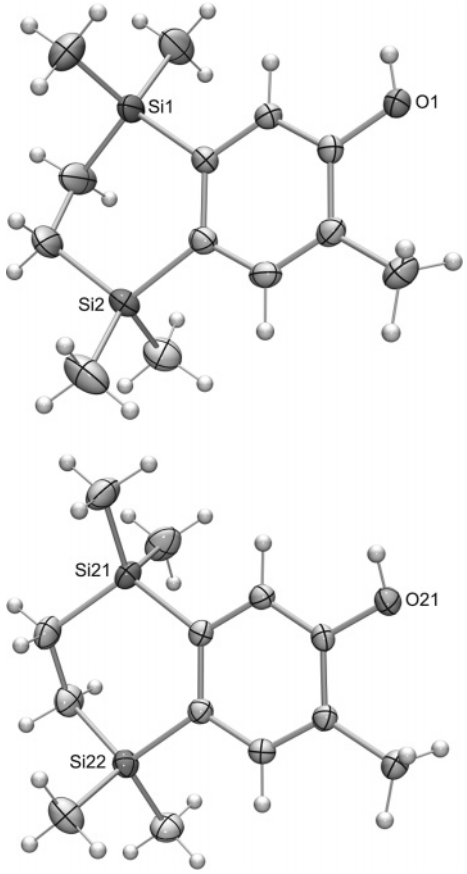



**Figure 2.** Molecular structures of the two crystallographically independent molecules in the crystal of **6** (probability level of displacement ellipsoids 50%).

reported in the literature.[1d] As shown with the synthesis of **6**, compound **5** may additionally serve as a building block for the synthesis of biologically active 5,8-disila-5,6,7,8-tetrahydronaphthalene derivatives with OR (R = organyl) substituents at the carbon atom C-2.

## Experimental Section

**General Procedures.** All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under dry nitrogen. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed glass capillaries. The $^{1}$H, $^{11}$B, $^{13}$C, and $^{29}$Si NMR spectra were recorded at 23 °C on a Bruker DRX-300 NMR spectrometer ($^{1}$H, 300.1 MHz; $^{11}$B, 96.3 MHz; $^{13}$C, 75.5 MHz; $^{29}$Si, 59.6 MHz). $C_6D_6$ or $CD_2Cl_2$ was used as the solvent. Chemical shifts were determined relative to internal $C_6HD_5$ ($^{1}$H, $\delta$ 7.28; $C_6D_6$), internal $C_6D_6$ ($^{13}$C, $\delta$ 128.0; $C_6D_6$), internal $CHDCl_2$ ($^{1}$H, $\delta$ 5.32; $CD_2Cl_2$), internal $CD_2Cl_2$ ($^{13}$C, $\delta$ 53.8; $CD_2Cl_2$), external TMS ($^{29}$Si, $\delta$ 0; $C_6D_6$, $CD_2Cl_2$), or external $BF_3 \cdot OEt_2$ ($^{11}$B, $\delta$ 0; $C_6D_6$). Assignment of the $^{1}$H NMR data was supported by $^{1}$H,$^{1}$H gradient-selected COSY, $^{13}$C,$^{1}$H gradient-selected HMQC and gradient-selected HMBC, and $^{29}$Si,$^{1}$H gradient-selected HMQC experiments (optimized for $^{2}J_{SiH}$ = 7 Hz). Assignment of the $^{13}$C NMR data was supported by DEPT 135 and the aforementioned $^{13}$C,$^{1}$H correlation experiments. The $^{2}J_{HH}$ coupling constant reported for the C=$CH_2$ group of **11** represents an absolute value.

**Preparation of 4-[1-(3,5,5,8,8-Pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)ethenyl]benzoic Acid (Disila-bexarotene, 1).** This compound was synthesized from **11** according to ref 1d (96% yield).

**Preparation of 4,4,5,5-Tetramethyl-2-(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)-1,3,2-dioxaborolane (5).** Iodine (17.0 mg, 134 $\mu$mol) was added to a stirred suspension of zinc (40.0 mg, 612 $\mu$mol) in acetonitrile (10 mL), and the mixture was heated for 1 min until the yellow color disappeared. Compound **8** (1.66 g, 10.0 mmol) and a 0.1 M solution of cobalt(II) iodide in acetonitrile (1.25 mL, 125 $\mu$mol of $CoI_2$) were added sequentially, each in a single portion, and after warming of the resulting mixture to 50 °C, compound **9** (972 mg, 5.00 mmol) was added within 5 min. The reaction mixture was stirred for 15 min at 50 °C and then for 30 min at 20 °C. After addition of sodium carbonate (100 mg, 943 $\mu$mol), the resulting mixture was applied to the top of a pad of silica gel in a glass frit (frit dimensions, 5 × 6 cm; silica gel (63−200 $\mu$m, 60 g), and the product was washed out of the residue with diethyl ether/*n*-hexane (4:1 (v/v), 100 mL). The wash solutions were combined, the solvent was removed under reduced pressure, triethylamine (1 mL) was added to the residue, and the resulting mixture was purified by column chromatography on silica gel (column dimensions, 35 × 3 cm; silica gel (32−63 $\mu$m), 180 g; eluent, *n*-hexane/ethyl acetate (96:4 (v/v))). The relevant fractions (GC control) were combined, activated carbon (150 mg) was added, and the suspension was heated under reflux for 30 min. The hot mixture was applied to the top of a pad of silica gel in a glass frit (frit dimensions, 5 × 6 cm; silica gel (63−200 $\mu$m), 60 g), and the product was washed out of the residue with *n*-hexane/ethyl acetate (96:4 (v/v), 150 mL). The total volume of the solution was reduced in vacuo to 2 mL, and the product crystallized from this mixture (crystallization at 20 °C over a period of 2 h). The product was then recrystallized from *n*-pentane (5 mL; crystallization at 20 °C over a period of 24 h) to afford **5** in 48% yield as a colorless crystalline solid (865 mg, 2.40 mmol); mp 133−134 °C. $^{1}$H NMR ($C_6D_6$): $\delta$ 0.36 (s, 6 H, SiC$H_3$), 0.38 (s, 6 H, SiC$H_3$), 1.13 (s, 4 H, SiC$H_2$C), 1.23 (s, 12 H, C(C$H_3$)$_2$), 2.87−2.89 (m, 3 H, CC$H_3$), 7.57−7.61 (m, 1 H, *H*-4, Naph (Naph = 5,5,8,8-tetramethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)), 8.58 (s, 1 H, *H*-1, Naph). $^{13}$C NMR ($C_6D_6$): $\delta$ −1.5 (2 C, SiC$H_3$), −1.3 (2 C, SiC$H_3$), 8.0 (SiC$H_2$C), 8.2 (SiC$H_2$C), 22.8 (CC$H_3$), 24.9 (4 C, C(C$H_3$)$_2$), 83.3 (2 C, *C*(CH$_3$)$_2$), 135.3 (*C*-1, Naph), 141.2 (*C*-3, Naph), 142.0 (*C*-4, Naph), 144.8 (*C*-4a, Naph), 149.2 (*C*-8a, Naph), B*C* not detected. $^{29}$Si NMR ($C_6D_6$): $\delta$ −7.1, −7.4. $^{11}$B NMR ($C_6D_6$): $\delta$ 31.3. Anal. Calcd for $C_{19}H_{33}BO_2Si_2$: C, 63.31; H, 9.23. Found: C, 63.2; H, 9.1.

**Preparation of 3,5,5,8,8-Pentamethyl-5,8-disila-5,6,7,8-tetrahydronaphth-2-ol (6).** A 30% solution of hydrogen peroxide in water (*D*, 1.11 g cm$^{-1}$; 1.14 mL, 11.2 mmol of $H_2O_2$) was added dropwise over a period of 3 min to a stirred mixture of **5** (400 mg, 1.11 mmol), sodium hydroxide (1.25 g, 31.3 mmol), water (13 mL), and THF (16 mL). The reaction mixture was stirred for 15 min at 20 °C, and diethyl ether (24 mL) and water (24 mL) were added. The organic layer was separated, the aqueous layer was extracted with diethyl ether (4 × 25 mL), and the organic extracts were combined and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was dried in vacuo (0.001 mbar, 20 °C, 2 h) to give a yellow oil, which was crystallized from *n*-hexane (3 mL; crystallization at −20 °C over a period of 8 days), followed by recrystallization from *n*-hexane, to afford **6** in 62% yield as a colorless crystalline solid (173 mg, 691 $\mu$mol); mp 138−139 °C. $^{1}$H NMR ($CD_2Cl_2$): $\delta$ 0.186 (s, 6 H, SiC$H_3$), 0.190 (s, 6 H, SiC$H_3$), 0.96 (s, 4 H, SiC$H_2$C), 2.22−2.25 (m, 3 H, CC$H_3$), 4.6 (br s, 1 H, O*H*), 6.86−6.89 (m, 1 H, *H*-1, Naph), 7.22−7.24 (m, 1 H, *H*-4, Naph). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ −1.5 (2 C, SiC$H_3$), −1.3 (2 C, SiC$H_3$), 7.5 (SiC$H_2$C), 7.7 (SiC$H_2$C), 15.6 (CC$H_3$), 119.6 (*C*-1, Naph), 124.1 (*C*-3, Naph), 136.7 (*C*-4, Naph), 136.9 (*C*-4a, Naph), 145.2 (*C*-8a, Naph), 154.0 (*C*-2, Naph). $^{29}$Si NMR ($CD_2Cl_2$): $\delta$ −6.9, −7.5. Anal. Calcd for $C_{13}H_{22}OSi_2$: C, 62.34; H, 8.85. Found: C, 62.2; H, 8.6.

**Preparation of 4,4,5,5-Tetramethyl-2-propyloxy-1,3,2-dioxaborolane (7).** This compound was synthesized according to ref 7.

**Preparation of 4,4,5,5-Tetramethyl-2-prop-1-ynyl-1,3,2-dioxaborolane (8).** A 2.5 M solution of *n*-butyllithium in hexanes (80 mL, 200 mmol of *n*-BuLi) was added dropwise at −75 °C within 30 min to a stirred solution of propyne (9.05 g, 226 mmol) in diethyl ether (250 mL), and the resulting suspension was stirred for 1.5 h at −75 °C. A solution of **7** (37.2 g, 200 mmol) in diethyl ether (150 mL) was added dropwise to the reaction mixture within 1 h, and the suspension was then allowed to warm to 20 °C within 4 h and was stirred for 16 h. A 2.0 M solution of hydrogen chloride in diethyl ether (100 mL, 200 mmol of HCl) was added dropwise to the stirred reaction mixture at 0 °C within 45 min, and the resulting mixture was then stirred for 30 min at 0 °C and for a further 1.5 h at 20 °C. The precipitate was filtered off and washed with *n*-hexane (2 × 50 mL), the organic solutions were combined, and the solvent was removed under reduced pressure. The resulting residue was purified by fractional distillation to give **8** in 89% yield as a colorless liquid (29.6 g, 178 mmol); bp 66−68 °C/5 mbar. $^{1}$H NMR ($C_6D_6$): $\delta$ 1.12 (s, 12 H, C(C$H_3$)$_2$), 1.51 (s, 3 H, CC$H_3$). $^{13}$C NMR ($C_6D_6$): $\delta$ 4.0 (*C*CH$_3$), 24.6 (C(*C*H$_3$)$_2$), 82.5 (*C*(CH$_3$)$_2$), B*C* not detected. $^{11}$B NMR ($C_6D_6$): $\delta$ 23.5. Anal. Calcd for $C_9H_{15}BO_2$: C, 65.11; H, 9.11. Found: C, 64.8; H, 9.3.

**Preparation of 1,2-Bis(ethynyldimethylsilyl)ethane (9).** This compound was synthesized according to ref 1d.

**Preparation of Methyl 4-[1-(Trifluoromethylsulfonyloxy)-ethenyl]benzoate (10).** This compound was synthesized according to ref 5.

**Preparation of Methyl 4-[1-(3,5,5,8,8-Pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)ethenyl]benzoate (11).** $(Ph_3P)_2PdCl_2$ (48.6 mg, 69.2 $\mu$mol), **5** (600 mg, 1.66 mmol), and a 2 M solution of sodium carbonate in water (4.80 mL, 9.60 mmol of $Na_2CO_3$) were added one after another to a stirred solution of **10** (430 mg, 1.39 mmol) in THF (16 mL). The mixture was stirred for 2 h at 20 °C, while its color changed from colorless to red. Additional **10**

(200 mg, 645 $\mu$mol) was added, and the reaction mixture was stirred for 3 h at 20 °C. Water (20 mL) was added, the aqueous layer was separated and extracted with diethyl ether (3 × 20 mL), and the combined organic solutions were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was dried in vacuo (0.001 mbar, 20 °C, 1 h) and then purified by column chromatography on silica gel (column dimensions, 70 × 5 cm; silica gel (32−63 $\mu$m), 400 g; eluent, *n*-hexane/ethyl acetate (97:3 (v/v))). The relevant fractions (GC control) were combined, and the solvent was removed under reduced pressure. The residue was redissolved in boiling *n*-hexane (2 mL), and the product was crystallized (slow cooling to 0 °C and crystallization at this temperature over a period of 2 h) to afford **11** in 86% yield as a colorless crystalline solid (560 mg, 1.42 mmol); mp 129−130 °C. $^1$H NMR ($CD_2Cl_2$): $\delta$ 0.22 (s, 6 H, SiC$H_3$), 0.25 (s, 6 H, SiC$H_3$), 1.04 (s, 4 H, SiC$H_2$C), 1.98−2.00 (m, 3 H, CC$H_3$), 3.88 (s, 3 H, C(O)OC$H_3$), 5.31 (d, $^2J_{HH}$ = 1.2 Hz, 1 H, C=C$H_A$H$_X$), 5.87 (d, $^2J_{HH}$ = 1.2 Hz, 1 H, C=CH$_A$$H_X$), 7.30−7.38 (m, 4 H, *H*-3/*H*-5, Phe (Phe = 1-(methoxycarbonyl)phenyl), *H*-1/*H*-4, Naph), 7.92−7.97 (m, 2 H, *H*-2/*H*-6, Phe). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ −1.42 (2 C, Si*C*H$_3$), −1.40 (2 C, Si*C*H$_3$), 7.86 (Si*C*H$_2$C), 7.89 (Si*C*H$_2$C), 20.2 (C*C*H$_3$), 52.3 (C(O)O*C*H$_3$), 117.2 (C=*C*H$_2$), 126.8 (*C*-3/*C*-5, Phe), 129.6 (*C*-1, Phe), 129.9 (*C*-2/*C*-6, Phe), 135.1 (*C*-1, Naph), 135.7 (*C*-4, Naph), 136.0 (*C*-3, Naph), 141.1 (*C*-2, Naph), 143.3 (*C*-4a, Naph), 145.4 (*C*-4, Phe), 145.7 (*C*-8a, Naph), 149.4 (*C*=CH$_2$), 167.0 (*C*(O)OCH$_3$). $^{29}$Si NMR ($CD_2Cl_2$): $\delta$ −7.1, −7.0. Anal. Calcd for $C_{23}H_{30}O_2Si_2$: C, 70.00; H, 7.66. Found: C, 70.0; H, 7.5.

**Crystal Structure Analyses.** The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS; graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å)). The structures were solved by direct methods.[8] All non-hydrogen atoms were refined anisotropically.[9] A riding model was employed in the refinement of the C*H* hydrogen atoms. The O*H* hydrogen atoms were localized in difference Fourier syntheses and refined freely.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Centre as supplementary publication nos. CCDC-653122 (**5**) and CCDC-653123 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223/336033; e-mail: depositqccdc.cam.ac.uk).

**Supporting Information Available:** Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles for **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700570F

(7) Andersen, M. W.; Hildebrandt, B.; Köster, G.; Hoffman, R. W. *Chem. Ber.* **1989**, *122*, 1777−1782.

(8) (a) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

(9) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.