

Cyclization/Hydrosilylation of Functionalized 1,7-Dienes to Form Substituted Six-Membered Carbocycles.

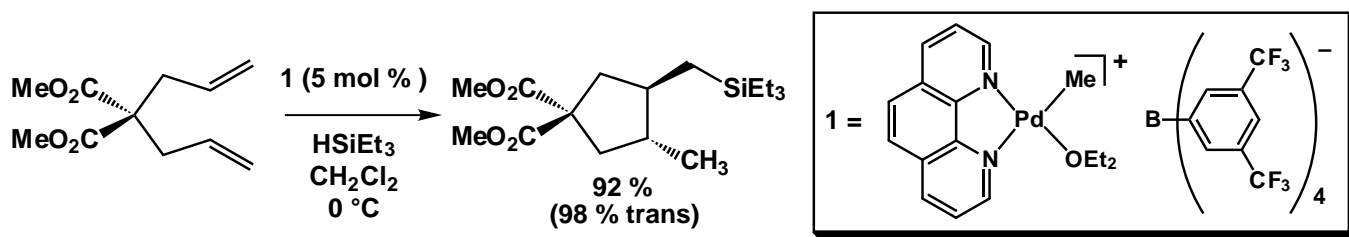
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Abstract: The cationic palladium complex (phen)Pd(Me)(OEt)₂⁺ BAr₄⁻ [phen = 1,10-phenanthroline; Ar = 3,5-C₆H₃(CF₃)₂] catalyzed the cyclization/hydrosilylation of functionalized 1,7-dienes to form silylated cyclohexanes in good yield and with moderate to good trans-selectivity.

Keywords: catalysis, cyclization, dienes, palladium

We recently reported that the cationic Pd(II) complex (phen)PdMe(OEt)₂⁺ BAr₄⁻ [phen = 1,10-phenanthroline; Ar = 3,5-C₆H₃(CF₃)₂] (**1**) in CH₂Cl₂ serves as an effective catalyst for the cyclization/hydrosilylation of 1,6-dienes to form silylated cyclopentane derivatives (Scheme 1).¹⁻³ The potential of this protocol stems from its high reactivity, good functional group compatibility, low air- and moisture-sensitivity, and high trans-selectivity of ring closure. Because six-membered carbocycles represent the most common ring size found in naturally occurring compounds, we hoped to apply our cyclization/hydrosilylation protocol to the synthesis of silylated cyclohexane derivatives. Unfortunately, our initial attempts to cyclize 1,7-dienes employing **1** met with limited success. However, our recent discovery that 1,2-dichloroethane (DCE) is a superior solvent to methylene chloride for both the Pd-catalyzed cyclization/hydrosilylation of 1,6-dienes⁴ and cyclization of alkenylsilanes⁵ has led to the development of an effective protocol for the cyclization of 1,7-dienes to form silylated cyclohexanes. Here we report our initial results in this area.



Scheme 1

We began our study employing dimethyl-4,4-dicarboxy-1,7-octadiene (**2**). Treatment of **2** with triethylsilane and **1** (5 mol %) led to rapid and complete consumption of starting material, but formed an intractable mixture of mono-silylated products in 71 % combined yield (Table 1, entry 1). We reasoned that the lack of selectivity arose, at least in part, from indiscriminate attack of the Pd–Si intermediate on either olefin of the diene.¹ In an effort to circumvent this problem, we employed the symmetric tetracarboxylate derivative **3**. Reaction of **3** with triethylsilane and **1** (5 mol %) was complete within 5 min at room temperature with formation of a 22:1 mixture of *trans*:*cis* silylated cyclohexanes **4** (entry 2). Evaporation of solvent and flash chromatography of the residue gave *trans*-**4** in 93% and *cis*-**4** in 3% yield.⁶ Diene **3** also reacted with dimethyl-*t*-butylsilane to give carbocycle **5** in good yield and with good diastereoselectivity (entry 3). However, reaction of **3** with dimethylbenzylsilane led to formation of both carbocycle **6** and disilylated-uncyclized product **7** (entry 4), while reaction of **3** with dimethylphenylsilane led to exclusive formation of the disilylated product **8** (entry 5).

The cyclization/hydrosilylation protocol tolerated substitution at the terminal olefinic carbon atom. For example, reaction of triethylsilane with substituted tetracarboxylate derivative **9** in the presence of **1** (10 %) formed carbocycle **10** in 51 % yield as a single isomer by NMR spectroscopy (entry 6). The substituted dicarboxylate derivative **11** also reacted with triethylsilane in the presence of **1** (5 %) to form carbocycle **12** in 68 % yield as a 1.6:1 mixture of *trans*:*cis* isomers (entry 7). We have also applied this protocol to the formation of fused bicyclic compounds employing acylated 2,3-diallyl-4,5-dimethylhydroquinone derivative **13**. For example, treatment of **13** with triethylsilane in the presence of **1** (5 mol %) led to the isolation of the corresponding fused bicycle **14** in 64 % yield as a 6:1 mixture of *trans*:*cis* diastereomers (entry 8). Higher catalyst loading (10 %) led to dramatic improvement in the yield (99 %) as well as slight improvement in diastereoselectivity (8:1) (entry 9). Diene **13** also reacted with dimethylphenylsilane, dimethylbenzylsilane, and dimethyl-*t*-butylsilane to form bicycles **15** - **17**, respectively, in fair to good yield and with good *trans* selectivity (entries 10-12).

In summary, we have shown that **1** in DCE solvent serves as an effective catalyst system for the cyclization/hydrosilylation of selected 1,7-dienes to form silylated cyclohexanes. However, formation of six-membered rings employing **1** is clearly less favorable than is the formation of five-membered carbocycles. For example, cyclization of 1,7-dienes was typically slower, required higher catalyst loading, and gave lower *trans*-selectivity than did the cyclization of 1,6-dienes. In addition, cyclization of 1,7-dienes with sterically hindered silanes or cyclization of substituted dienes tended to form silylated-uncyclized products in addition to the desired carbocycles. This behavior is not surprising as palladium complexes are typically more effective for the formation of five-membered rings than for the corresponding six-membered rings.⁷ We are currently working towards the development of more active catalysts for the cyclization/hydrosilylation of 1,7-dienes.

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Table 1. Cyclization/hydrosilylation of 1,7-dienes catalyzed by **1** in 1,2-dichloroethane at 25 °C.

Entry	Diene	Silane	Silylated product(s) (% isolated yield) ^a	% Pd	Time	trans:cis ratio ^b
1	 2 (E = CO ₂ Me)	HSiEt ₃	mono-silylated products (71)	5	30 min	—
2	 3 (E = CO ₂ Et)	HSiEt ₃	 <i>trans</i> -4 (93) + <i>cis</i> -4 (3)	5	15 min	22:1
3		HSiMe ₂ <i>t</i> -Bu	 5 (94)	5	3 h	>25:1 ^c
4		HSiMe ₂ Bn	 6 (35) + 7 (8)	5	45 min	>25:1 ^c
5		HSiMe ₂ Ph	 8 (62)	5	2 h	—
6	 9 (E = CO ₂ Et) ^d	HSiEt ₃	 10 (51)	10	90 min	>25:1 ^c
7	 11 (E = CO ₂ Me) ^d		 12 (68)	5	2 h	1.6:1
8	 13	HSiEt ₃	 14 (64)	5	30 min	6:1
9			14 (99)	10	20 min	8:1
10		HSiMe ₂ Ph	15 (93)	10	1 h	12:1
11		HSiMe ₂ Bn	16 (40)	10	15 min	20:1
12		HSiMe ₂ <i>t</i> -Bu	17 (35)	10	2 h	20:1

^aYields refer to material of >95 % purity as determined by ¹H NMR and GC analysis. All new compounds characterized by ¹H and ¹³C NMR spectroscopy, IR spectroscopy, combustion analysis, and/or HRMS. ^bcis-trans Ratio of the carbocyclic product determined by capillary GC or HPLC analysis of the crude reaction mixture. ^cDetermined by ¹H and ¹³C NMR analysis. ^d4:1 Mixture of trans:cis isomers.

References and Notes

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- 6) Synthesis and NMR data for *cis-4* and *trans-4*: Diene **3** (100 mg, 0.25 mmol) and triethylsilane (350 mg, 3.01 mmol) were added sequentially via syringe to a solution of **1** (0.013 mmol) [generated in situ from (phen)PdMe₂ (4 mg, 0.013 mmol) and HBAr₄⁻·(Et₂O)₂ (13 mg, 0.013 mmol)]⁸ in DCE (10 mL) at 0° C and then stirred for 10 minutes at room temperature. The resulting brown solution was concentrated under vacuum and the residue was chromatographed (SiO₂, 9:1 hexane:EtOAc) to give *trans-4* (120 mg, 93%) and *cis-4* (4 mg, 3 %) as colorless oils. *trans-4*: ¹H NMR: δ 4.23-4.10 (m, 8 H), 2.26 (dd, *J* = 4.1, 14.2 Hz, 1 H), 2.15 (dd, *J* = 4.1, 14.3 Hz, 1 H), 2.07 (dd, *J* = 12.1, 14.0 Hz, 1 H), 1.97 (dd, *J* = 12.1, 14.2 Hz, 1 H), 1.22 (t, *J* = 6.2 Hz, 12 H), 0.898 (t, *J* = 7.9 Hz, 9 H), 0.896 (d, *J* = 6.27 Hz, 3 H), 0.50 (q, *J* = 7.9 Hz, 6 H), 0.22 (dd, *J* = 10.5, 14.96 Hz, 1 H), 1.50-1.35 (m, 2 H), one SiCH₂CH₃ proton obscured. ¹³C {¹H} NMR: δ 170.8, 169.5, 169.4, 65.8, 61.5, 61.4, 61.2, 61.1, 59.5, 58.7, 37.4, 37.2, 35.2, 34.9, 19.8, 15.7, 15.2, 13.8, 13.73, 13.72, 7.3, 3.9. *cis-4*: ¹H NMR: 4.22-4.09 (m, 8 H), 2.08-1.93 (m, 4 H), 1.50-1.35 (m, 2 H), 1.24 (t, *J* = 7.2 Hz, 12 H), 0.90 (d, *J* = 6.3 Hz, 3 H), 0.89 (t, *J* = 8.0 Hz, 9 H), 0.46 (q, *J* = 8.0 Hz, 6 H), SiCH₂CH₃ protons obscured.
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Cyclization/Hydrosilylation of Functionalized 1,7-Dienes to Form Substituted Six-Membered Carbocycles.

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Analytical and spectroscopic data for new compounds.

Tetraethyl-5-methyl-4-[(triethylsilyl) methyl] cyclohexane-1,1,2,2-tetracarboxylate (4).

trans-4: ^1H NMR: δ 4.23-4.10 (m, 8 H), 2.26 (dd, $J = 4.1, 14.2$ Hz, 1 H), 2.15 (dd, $J = 4.1, 14.3$ Hz, 1 H), 2.07 (dd, $J = 12.1, 14.0$ Hz, 1 H), 1.97 (dd, $J = 12.1, 14.2$ Hz, 1 H), 1.50-1.35 (m, 2 H), 1.22 (t, $J = 6.2$ Hz, 12 H), 0.90 (t, $J = 7.9$ Hz, 9 H), 0.89 (d, $J = 6.3$ Hz, 3 H), 0.50 (q, $J = 7.9$ Hz, 6 H), 0.22 (dd, $J = 10.5, 15.0$ Hz, 1 H). ^{13}C { ^1H } NMR: δ 170.8, 169.5, 169.4, 65.8, 61.5, 61.4, 61.2, 61.1, 59.5, 58.7, 37.4, 37.2, 35.2, 34.9, 19.8, 15.7, 15.2, 13.8, 13.73, 13.72, 7.3, 3.9. IR (neat, cm^{-1}): 2953, 2874, 2391, 2349, 1729, 1556, 1365, 1299, 1151, 1101, 1035, 971, 864, 759, 729, 622. HRMS (CI) calcd for $\text{C}_{26}\text{H}_{47}\text{O}_8\text{Si}$ (MH^+): 515.3040; found, 515.3074. Anal. calcd (found) for $\text{C}_{26}\text{H}_{46}\text{O}_8\text{Si}$: H, 9.01 (8.76); C, 60.67 (60.46).

cis-4: ^1H NMR: 4.22-4.09 (m, 8 H), 2.08-1.93 (m, 4 H), 1.50-1.35 (m, 2H), 1.24 (t, $J = 7.2$ Hz, 12 H), 0.90 (d, $J = 6.3$ Hz, 3 H), 0.89 (t, $J = 8.0$ Hz, 9 H), 0.46 (q, $J = 8.0$ Hz, 6 H). SiCH_2CH_3 protons obscured.

Tetraethyl-*trans*-5-methyl-[(dimethyl *tert*-butylsilyl)methyl] cyclohexane-1,1,2,2-tetracarboxylate (5). ^1H NMR: δ 4.28-4.08 (m, 8 H), 2.27 (dd, $J = 4.0, 14.0$ Hz, 1 H), 2.15 (dd, $J = 4.4, 14.8$ Hz, 1 H), 2.03 (dd, $J = 12.4, 30.4$ Hz, 1 H), 1.99 (dd, $J = 12.4, 23.6$ Hz, 1 H), 1.26 (q, $J = 6.8$ Hz, 12 H), 1.22-1.20 (m, 3 H), 0.89 (d, $J = 6.4$ Hz, 3 H), 0.82 (s, 9 H), 0.18 (dd, $J = 10.4, 16.4$ Hz, 1 H), -0.03 (s, 3 H), -0.07 (s, 3 H). ^{13}C { ^1H } NMR: δ 171.2, 170.4, 169.9, 169.8, 61.9, 61.8, 61.7, 61.6, 59.9, 59.1, 37.8, 37.7, 35.6, 35.2, 26.8, 20.2, 16.9, 16.7, 14.3, 14.2, 14.15, 14.13, -4.2, -5.7. IR (neat, cm^{-1}): 2979, 2932, 2857, 2392, 2349, 1730, 1650, 1556, 1538, 1504, 1469, 1445, 1390, 1365, 1300, 1264, 1187, 1151, 1100, 1036, 864, 828, 809, 622. HRMS (CI) calcd for $\text{C}_{26}\text{H}_{47}\text{O}_8\text{Si}$ (MH^+): 515.3040; found, 515.3063. Anal. calcd (found) for $\text{C}_{26}\text{H}_{46}\text{SiO}_8$: H, 9.01 (9.07); C, 60.67 (60.55).

Tetraethyl-*trans*-5-methyl-[(dimethylbenzylsilyl)methyl] cyclohexane-1,1,2,2-tetracarboxylate (6). ^1H NMR: δ 7.20-7.16 (m, 2 H), 7.04 (t, $J = 7.6$ Hz, 1 H), 6.96 (d, $J = 7.2$ Hz, 2 H), 4.28-4.10 (m, 8 H), 2.27 (dd, $J = 4.0, 10.0$ Hz, 1 H), 2.16 (dd, $J = 4.0, 10.0$ Hz, 1 H), 2.08 (dd, $J = 1.6, 12.4$ Hz, 1 H), 2.06 (s, 2 H), 1.94 (dd, $J = 12.0, 14.0$ Hz, 1 H), 1.29-1.20 (m, 14 H), 0.91 (dd, $J = 2.4, 14.8$ Hz, 1 H), 0.86 (d, $J = 6.4$ Hz, 3 H), 0.26 (dd, $J = 10.4, 15.2$ Hz, 1 H), -0.023 (s, 3 H), -0.033 (s, 3 H). ^{13}C { ^1H } NMR: δ 171.2, 171.1, 169.9, 169.8, 140.4, 128.44, 128.42, 124.3, 62.0, 61.8, 61.7, 61.5, 60.0, 59.0, 37.7, 37.6, 35.8, 34.9, 26.6, 20.1, 19.7, 19.6, 14.3, 14.2, 14.1, -1.95, -2.41. IR (neat, cm^{-1}): 2981, 2397, 2350, 1730, 1650, 1600, 1556, 1537, 1503, 1494,

1367, 1034, 837, 701. HRMS (CI) calcd for C₂₉H₄₅SiO₈ (MH⁺): 549.2884; found 549.2870. Anal. calcd (found) for C₂₉H₄₄O₈Si: H, 8.08 (7.99); C, 63.47 (63.82).

Tetraethyl-1,8-di(dimethylbenzylsilyl)octane-4,4,5,5-tetracarboxylate (7). ¹H NMR: δ 7.19-7.15 (m, 4 H), 7.03 (t, *J* = 7.2 Hz, 2 H), 6.95 (d, *J* = 7.2 Hz, 4 H), 4.23-4.08 (m, 8 H), 2.04-1.99 (m, 4 H), 2.03 (s, 4 H), 1.43-1.34 (m, 4 H), 1.23 (t, *J* = 6.8 Hz, 12 H), 0.52-0.46 (m, 4 H), -0.09 (s, 12 H). HRMS (CI) calcd for C₃₈H₅₉O₈Si₂ (MH⁺), 699.3749; found, 699.3738.

Tetraethyl-1,8-di(dimethylphenylsilyl)octane-4,4,5,5-tetracarboxylate (8). ¹H NMR: δ 7.48-7.44 (m, 4 H), 7.31-7.28 (m, 6 H), 4.15-2.06 (m, 8 H), 2.01-1.92 (m, 4 H), 1.61 (*J* = 7.6 Hz, 12 H), 0.78-0.71 (m, 4 H), 0.22 (s, 12 H). ¹³C{¹H} NMR: δ 170.1, 139.7, 133.8, 129.1, 128.0, 63.2, 61.5, 35.4, 20.6, 16.9, 14.2, -2.7. IR (neat, cm⁻¹): 2980, 2954, 2391, 1731, 1555, 1427, 1366, 1249, 1151, 1112, 1035, 836, 731, 702. HRMS (CI) calcd for C₃₆H₅₄O₈Si₂ (MH⁺), 671.3357; found, 671.3436.

Tetraethyl-1,7-nonadiene-4,4,5,5-tetracarboxylate (9). ¹H NMR: δ 5.93 (tdd, *J* = 7.2, 10.4, 17.2 Hz, 1 H), 5.59-5.43 (m, 2 H), 5.06 (d, *J* = 17.2 Hz, 1 H), 5.00 (d, *J* = 10 Hz, 1 H), 4.21-4.06 (m, 8 H), 2.85 (d, *J* = 7.2 Hz, 2H), 2.75 (d, *J* = 6.0 Hz, 2 H), 1.58 (d, *J* = 6.4 Hz, 3 H), 1.22 (t, *J* = 7.2 Hz, 12 H). ¹³C{¹H} NMR: δ 169.3, 169.2, 134.2, [129.6, 127.2 (9:1)], [126.4, 125.7 (9:1)], 118.7, [62.9, 62.9 (9:1)], [62.8, 62.7 (9:1)], 61.3, 61.3, [35.2, 35.8 (1:9)], [36.0, 34.9 (1:9)], [18.3, 17.9 (1:9)], 13.84, 13.81. IR (neat, cm⁻¹): 3078, 2981, 2937, 2392, 2349, 1729, 1636, 1556, 1538, 1504, 1444, 1390, 1366, 1204, 1034, 974, 919, 865, 652. Anal. calcd (found) for C₂₁H₃₂O₈: H, 7.82 (7.91); C, 61.15 (61.26).

Tetraethyl-*trans*-5-ethyl-4-[(triethylsilyl)methyl] cyclohexane-1,1,2,2-tetracarboxylate (10). ¹H NMR: δ 4.25-4.12 (m, 8 H), 2.29 (td, *J* = 4.4, 14.4 Hz, 1 H), 2.00 (ddd, *J* = 12.0, 14.4, 21.2 Hz, 2 H), 1.62 (m, 1 H), 1.294-1.219 (m, 12 H), 0.92 (t, *J* = 8.0 Hz, 9 H), 0.85 (t, *J* = 7.2 Hz, 3 H), 0.52 (q, *J* = 8.0 Hz, 6 H), 0.20 (dd, *J* = 10.8, 14.8 Hz, 1 H). One Et₃SiCH₂, and tertiary ring protons obscured. ¹³C{¹H} NMR: δ 171.4, 171.3, 169.91, 169.88, 61.9, 61.8, 61.7, 61.6, 59.41, 59.35, 41.5, 37.6, 34.3, 32.8, 25.8, 16.1, 14.2, 14.15, 14.13, 10.9, 7.8, 4.4. IR (neat, cm⁻¹): 2952, 2870, 2340, 1730, 1556, 1366, 1256, 1151, 1101, 1047, 860, 754, 624. Anal. calcd (found) for C₂₇H₄₈O₈Si: H, 9.15 (9.15); C, 61.33 (61.11).

Dimethyl-1,7-nonadiene-4,4-dicarboxylate (11). ¹H NMR: δ 5.75 (m, 1 H), 5.50 (tqd, *J* = 1.2, 6.4, 14.8 Hz, 1 H), 5.38 (qtd, *J* = 1.6, 7.2, 15.2 Hz, 1 H), 5.01 (d, *J* = 17.6 Hz, 1 H), 4.95 (*J* = 10.4 Hz, 1 H), 3.69 (s, 6 H), 2.58 (td, *J* = 1.2, 7.2 Hz, 2 H), 1.94 (t, *J* = 5.2 Hz, 2 H), 1.94 (d, *J* = 2.8, 2 H), 1.63 (dd, *J* = 1.6, 6.4 Hz, 3 H). ¹³C{¹H} NMR: δ [172.04, 171.99 (1:4)], [137.8, 137.7 (4:1)], [130.0, 128.2 (4:1)], [124.8, 123.8 (4:1)], [115.3, 115.2 (4:1)], [57.8, 57.5 (4:1)], [52.6, 52.5 (4:1)], 36.3, [31.8, 30.3 (4:1)], [28.8, 28.6 (4:1)], [18.3, 13.1 (4:1)]. IR (neat, cm⁻¹): 3077, 2952, 2857, 2391, 2349, 1737, 1642, 1556, 1504, 1434, 1270, 1205, 1137, 1040, 996, 969, 914, 821, 639. Anal. calcd (found) for C₁₃H₂₀O₄: H, 8.39 (8.55); C, 64.98 (65.26).

Dimethyl-*trans*-3-ethyl-4-[(triethylsilyl)methyl] cyclohexane-1,1-dicarboxylate (12). ¹H NMR: δ 3.689 (s, 3 H), 3.688 (s, 3 H), [2.55-2.48 (m), 1.87-1.83 (m), 1:1.5, 3 H], [1.79-1.71 (m), 1.87-1.83 (m), 1:1.5, 3 H], [1.60-1.49 (m), 1.18-1.06 (m), 1.5:1, 3 H], 0.90 (t, *J* = 8.0 Hz, 9 H), 0.89 (t, *J* = 6.4 Hz, 3 H), 0.53-0.48 (m, 2 H), 0.47 (q, *J* = 8.0 Hz, 6 H). One CH₂SiEt₃ proton obscured. ¹³C {¹H} NMR: δ [173. 8, 172.8 (1:1.5)], [58.5, 57.9 (1:1.5)], [52.9, 52.5 (1:1.5)], [48.6, 46.8 (1:1.5)], [40.6, 40.5 (1:1.5)], [32.6, 32.5 (1:1.5)], [28.5, 27.8 (1:1.5)], [26.8, 26.6 (1:1.5)], [24.5, 23.3 (1:1.5)], [14.2, 12.8 (1:1.5)], [11.6, 9.7 (1:1.5)], 7.8, 3.6. IR (neat, cm⁻¹):

2952, 2873, 2391, 1736, 1556, 1461, 1434, 1416, 1378, 1249, 1156, 1015, 758, 730. Anal. calcd (found) for C₁₉H₃₆O₂Si: H, 10.18 (10.47); C, 64.00 (64.20).

2,3-diallyl-5,6-dimethyl-1,4-hydroquinone diacetate (13). ¹H NMR: δ 5.80 (tdd, *J* = 6.0, 12.0, 16.0 Hz, 2 H), 4.99 (dd, *J* = 1.6, 8.4 Hz, 2 H), 4.95 (dd, *J* = 2.0, 17.2, 2 H), 3.49-3.11 (m, 4 H), 2.31 (s, 6 H), 2.04 (s, 6 H). ¹³C{¹H} NMR: δ 169.5, 146.3, 136.0, 129.1, 129.0, 115.9, 109.3, 31.9, 21.0, 13.8. IR (CCl₄, cm⁻¹): 2392, 2350, 1650, 1556, 1538, 1504, 1191, 1078, 910, 736. Anal. calcd (found) for C₁₈H₂₂O₄: H, 7.43 (7.58); C, 71.50 (71.44).

5,8-diacetoxy-6,7-dimethyl-*trans*-3-methyl-2-(triethylsilyl)methyl-1,4-dihydronaphthalene (14). ¹H NMR: δ 2.3-2.6 (m, 2 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 1.78 (s, 6 H), 1.22 (m, 4 H), 0.76 (d, *J* = 6.0 Hz, 3 H), 0.69 (t, *J* = 8.0 Hz, 9 H), 0.29 (q, *J* = 8.0 Hz, 6 H), 0.19-0.00 (m, 1 H). One Et₃SiCH₂ proton obscured. ¹³C{¹H} NMR: δ 169.3, 145.3, 127.9, 127.2, 35.5, 32.6, 20.9, 20.8, 20.1, 15.9, 13.2, 7.9, 7.8, 7.7, 4.5, 3.6, 3.5. IR (CCl₄, cm⁻¹): 3053, 2408, 2350, 1755, 1714, 1681, 1650, 1556, 1538, 1504, 1265, 1200, 1077, 896, 738, 705. Anal. calcd (found) for C₂₄H₃₈SiO₄: H, 9.17 (9.28); C, 69.04 (68.80).

5,8-diacetoxy-6,7-dimethyl-*trans*-3-methyl-2-(dimethylphenylsilyl)methyl-1,4-dihydronaphthalene (15). ¹H NMR: δ 7.53-7.51 (m, 2 H), 7.36-7.26 (m, 3 H), 2.80-2.60 (m, 2 H), 2.33 (s, 6 H), 2.15 (d, *J* = 3.6 Hz, 3 H), 2.02 (s, 6 H), 1.54-1.51 (m, 4 H), 0.91-0.86 (m, 1 H), 0.32 (s, 3 H), 0.30 (s, 3 H), 0.25 - 0.24 (m, 1 H). ¹³C{¹H} NMR: δ 169.0, 144.7, 139.5, 133.33, 133.27, 128.7, 127.7, 127.6, 127.5, 126.6, 57.8, 34.0, 20.3, 20.2, 20.1, 20.0, 19.5, 18.0, 13.0, 12.6, -2.3, -3.4. IR (neat, cm⁻¹): 3054, 2956, 2408, 2350, 1757, 1556, 1427, 1369, 1265, 1247, 1198, 1112, 1079, 1013, 894, 834, 738, 703. Anal. calcd (found) for C₂₆H₃₄SiO₄: H, 7.81 (8.17); C, 71.19 (71.37).

5,8-diacetoxy-6,7-dimethyl-*trans*-3-methyl-2-(dimethylbenzylsilyl)methyl-1,4-dihydronaphthalene (16). ¹H NMR: δ 7.20-6.96 (m, 5 H), 2.85-2.45 (m, 2 H), 2.31 (s, 3 H), 2.28 (s, 3 H), 2.08 (s, 2 H), 2.02 (s, 6 H), 1.62-1.39 (m, 2 H), 1.30-1.21 (m, 2 H), 0.95 (d, *J* = 6.4 Hz, 3 H), 0.40-0.30 (m, 1 H), 0.00 (s, 3 H), -0.02 (s, 3 H). One BnMe₂SiCH₂ proton partially obscured. ¹³C{¹H} NMR: δ 170.1, 170.0, 146.0, 141.3, 141.2, 129.23, 129.18, 128.5, 128.02, 127.97, 125.05, 125.04, 36.5, 35.2, 33.2, 27.4, 23.4, 21.59, 21.55, 20.7, 20.4, 15.1, 14.0, -1.0, -1.6. Anal. calcd (found) for C₂₇H₃₆SiO₄: H, 8.02 (8.29); C, 71.64 (71.89).

5,8-diacetoxy-6,7-dimethyl-*trans*-3-methyl-2-(dimethyl *tert*-butylsilyl)methyl-1,4-dihydronaphthalene (17). ¹H NMR: δ 2.90-2.50 (m, 2 H), 2.34 (s, 3 H), 2.33 (s, 3 H), 2.04 (s, 6 H), 1.53-1.45 (m, 2 H), 1.02 (d, *J* = 6.0 Hz, 3 H), 0.87 (s, 9 H), 0.33-0.25 (m, 1 H), 0.03 (s, 3 H), -0.02 (s, 3 H). One (CH₃)₃SiMe₂CH₂ proton obscured, both tertiary ring protons obscured. ¹³C{¹H} NMR: δ 169.4, 145.3, 127.8, 127.2, 36.0, 32.5, 26.9, 20.9, 20.8, 20.1, 17.0, 16.8, 13.2, -3.9, -5.4. Anal. calcd (found) for C₂₄H₃₈SiO₄: H, 9.15 (9.31); C, 68.86 (69.12).