Cyclization of *o*-Allylstyrene via Hydrosilylation: Mechanistic Aspects of Hydrosilylation of Styrenes Catalyzed by Palladium−Phosphine Complexes

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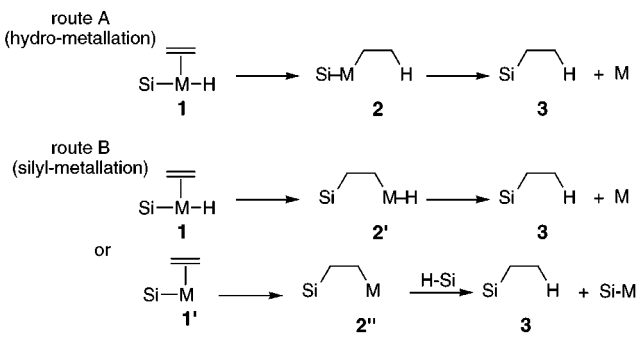
Hydrosilylation of *o*-allylstyrene with trichlorosilane in the presence of 0.3 mol % of a palladium catalyst bearing triphenylphosphine gave *trans*-1-methyl-2-(trichlorosilylmethyl)indan, 1-(2-(2-propenyl)phenyl)-1-trichlorosilylethane, and 1-(2-((*E*)-1-propenyl)phenyl)-1-trichlorosilylethane. The reaction of styrene with trichlorosilane gave a quantitative yield of 1-phenyl-1-(trichlorosilyl)ethane while allylbenzene did not give silylation products under the same reaction conditions. These results show that the hydropalladation process is operative in the hydrosilylation of styrene derivatives with trichlorosilane catalyzed by palladium−phosphine complexes.

Transition metal-catalyzed hydrosilylation is a versatile means for carbon−silicon bond formation.[1,2] The mechanism widely accepted for the hydrosilylation of olefins, the key features of which were first proposed by Chalk and Harrod,[3] involves insertion of olefin into hydrogen−metal bond of intermediate **1** (hydrometalation pathway) (Scheme 1, route A) forming alkyl(silyl)-metal **2**, and reductive elimination of the alkyl and silyl fragments from **2** generating a silicon−carbon bond.[4] Recently another pathway has been proposed which involves insertion of olefin into silicon−metal bond (silyl-metalation pathway) (Scheme 1, route B) followed by reductive elimination or silanolysis on the intermediate **2′** or **2″** giving hydrosilylation product **3**.[5] We have developed palladium-catalyzed asymmetric hydrosilylation of olefins with trichlorosilane where palladium

Scheme 1



complexes of monodentate optically active phosphine ligands exhibited high enantioselectivity.[6] A novel cyclization of *o*-allylstyrene (**4**) giving 1-methyl-2-(trichlorosilylmethyl)indan (**5**) under the palladium-catalyzed hydrosilylation conditions provides a mechanistic insight into hydrosilylation of styrenes catalyzed by palladium−phosphine complexes. We wish to report here that the hydropalladation process is operative in the hydrosilylation of styrenes with trichlorosilane catalyzed by palladium−phosphine complexes.[7]

o-Allylstyrene (**4**) was allowed to react with 1 equiv of trichlorosilane in the presence of 0.3 mol % of a palladium complex generated in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and triphenylphosphine (1.1 equiv to palladium).[8] The reaction was completed in 2 h at 50 °C, which was monitored by GC analysis. Distillation of the reaction mixture gave 90% yield of the addition product which consists of *trans*-

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(2) Recent examples of mechanistic studies on transition metal-catalyzed hydrosilylation of olefins: (a) Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151. (b) Tamao, K.; Nakagawa, Y.; Ito, Y. *Organometallics* **1993**, *12*, 2297. (c) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90. (d) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2128.

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(5) Recent mechanistic studies on catalytic hydrosilylation demonstrates that some catalytic systems operate by this silyl-metalation mechanism. (a) Takeuchi, R.; Yasue, H. *Organometallics* **1996**, *15*, 2098. (b) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366. (c) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289. Also see ref 2.

(6) (a) Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887. (b) Uozumi, Y.; Kitayama, K.; Hayashi, T.; Yanagi, K.; Fukuyo, E. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 713. (c) Uozumi, Y.; Lee, S.-Y.; Hayashi, T. *Tetrahedron Lett.* **1992**, *33*, 7185. (d) Uozumi, Y.; Hayashi, T. *Tetrahedron Lett.* **1993**, *34*, 2335. (e) Kitayama, K.; Tsuji, H.; Uozumi, Y.; Hayashi, T. *Tetrahedron Lett.* **1996**, *37*, 4169. See also refs 3c and 3d.

(7) Very recently, a mechanistic study on olefin hydrosilylation by use of a cationic palladium catalyst was reported: Lapointe, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906.

(8) We have observed that the reaction of $[PdCl(\pi\text{-}C_3H_5)]_2$ with hydrosilane $HSiEt_3$ in the presence of bisphosphine ligand dppf generates a Pd(0)(dppf) species together with $ClSiEt_3$ and C_3H_6 (Hayashi, T.; Yamane, M. Unpublished results). The reaction with $HSiCl_3$ and triphenylphosphine should also produce a Pd(0) species.

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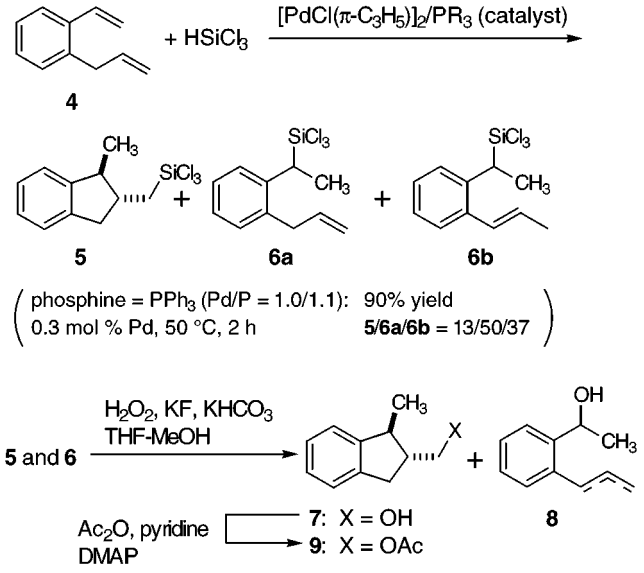
Scheme 2

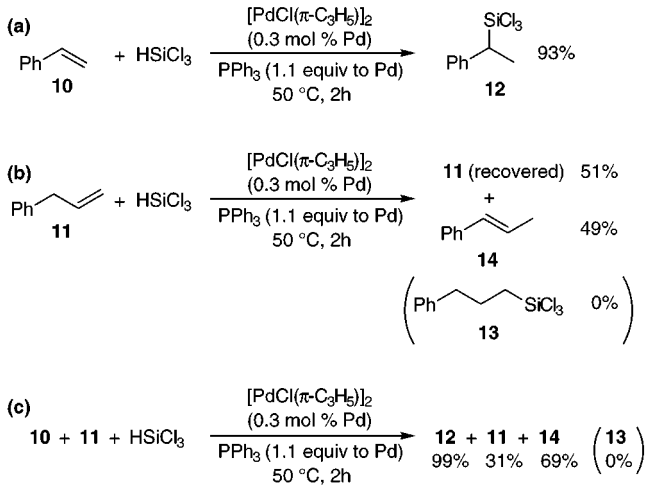


1-methyl-2-(trichlorosilylmethyl)indan (**5**), 1-(2-(2-propenyl)phenyl)-1-trichlorosilylethane (**6a**), and 1-(2-((*E*)-1-propenyl)phenyl)-1-trichlorosilylethane (**6b**) in a ratio of 13/50/37 (Scheme 2). No vinylsilanes or saturated alkanes were detected. Oxidation of **5** and **6** according to Tamao's method[9] gave the corresponding alcohols **7** and **8**, which were isolated by silica gel chromatography and fully characterized by NMR analysis. The trans stereochemistry of **5** was determined by NOE experiments on acetate **9**.

Hydrosilylation of styrene (**10**)[10] with trichlorosilane catalyzed by the triphenylphosphine−palladium complex at 50 °C gave 1-phenyl-1-(trichlorosilyl)ethane (**12**) in 93% isolated yield as a single regioisomer (**a** in Scheme 3). On the other hand, allylbenzene (**11**) showed little reactivity toward hydrosilylation. No 3-(trichlorosilyl)-propylbenzene (**13**) was formed, and 49% of allylbenzene was isomerized into *β*-methylstyrene (**14**) under the same reaction conditions (**b** in Scheme 3). Treatment of a one to one mixture of **10** and **11** with 1 equiv of trichlorosilane in the presence of the palladium catalyst resulted in the formation of a 99% yield of **12** and a 69% yield of **14** (**c** in Scheme 3). Thus, the hydrosilylation of styrene (**10**) is much faster than that of allylbenzene (**11**). Here again, no production of unsaturated silylated products was observed in the reaction of styrene or allylbenzene.

The formation of cyclized product **5** is accounted for by the hydropalladation mechanism. Hydropalladation of the double bond of vinyl group forming **16** followed by insertion of the double bond of the allyl group into the alkyl−palladium bond forms five-membered-ring intermediate **17** which undergoes reductive elimination leading to indan **5** (Scheme 4). Benzylic silanes **6** are formed

Scheme 3



by reductive elimination from **16** before the insertion. The hydropalladation route is also supported by the regiospecific formation of benzylic silanes **6**. The benzylic palladium intermediate **16** generated by the hydropalladation is stabilized by an equilibrium with its *π*-benzylic form.[11] The olefin isomerization from 2-propenyl to 1-propenyl in **6** is readily accommodated in the hydropalladation mechanism, hydropalladation followed by *β*-hydrogen elimination causing the isomerization (Scheme 5).

The cyclization product **5** could be reached via the silylpalladation route which involves (*β*-silylalkyl)palladium **19** as a key intermediate, but silyl-palladation is very unlikely because the products **20**, **21**, and/or **22** which would be derived from (*β*-silylalkyl)palladium intermediate **19** were not detected at all. The hydropalladation mechanism is also consistent with the results observed in the hydrosilylation of styrene and allylbenzene. Thus, the hydrosilylation of styrene with trichlorosilane gave benzylic silane **12** exclusively, demonstrating the intermediacy of benzyl(silyl)palladium. The formation of *β*-methylstyrene (**14**) from allylbenzene demonstrates that the hydropalladation is taking place, the resulting alkyl(silyl)palladium undergoing *β*-hydrogen elimination rather than reductive elimination (Scheme 5). Little reactivity of palladium−silicon bond where the silicon is substituted with electron-withdrawing groups toward insertion of alkenes or alkynes[12] also excludes the insertion of olefin into palladium−silicon bond.

It is noteworthy that the selectivity toward the cyclization was affected by the phosphine ligand used. The results obtained for the hydrosilylation of **4** with various phosphine ligands are summarized in Table 1. The reaction with tri(*o*-tolyl)phosphine gave cyclized product **5** as the main product, the ratio of **5**/**6** being 87/13 at 50 °C (Table 1, run 2). With tri(*p*-methoxyphenyl)phosphine, the reaction was completed in 1.5 h to give a 97% yield of silylated products where benzylic silanes **6** were obtained as main products (run 3). The present catalytic hydrosilylation was strongly inhibited by use of bisphosphines as ligands. Thus, the reaction in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) or 2,2′-bis-

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(10) For examples, see: (a) Hayashi, T.; Tamao, K.; Katsuro, Y.; Nakae, I.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 1871. (b) Okada, T.; Morimoto, T.; Achiwa, K. *Chem. Lett.* **1990**, 999. (c) Uozumi, Y.; Kitayama, K.; Hayashi, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1533. (d) Uozumi, Y.; Kitayama, K.; Hayashi, T. *Tetrahedron: Asymmetry* **1993**, *4*, 2419.

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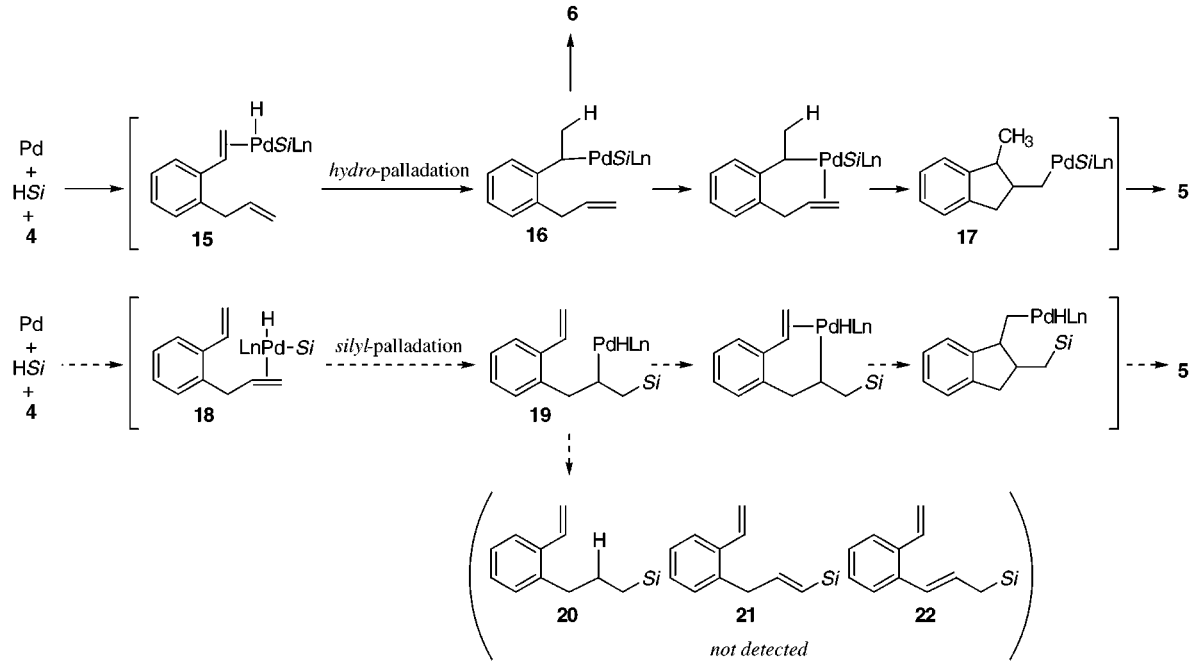
(12) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237.

Scheme 4



Scheme 5

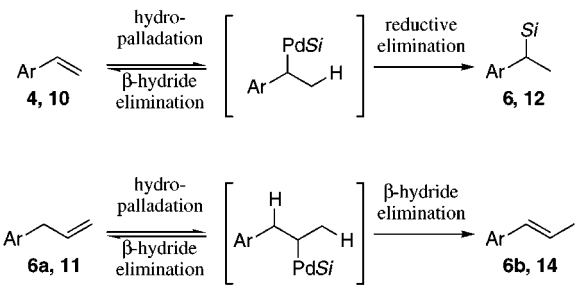


Table 1. Reaction of 4 with $HSiCl_3$ in the Presence of Palladium−Phosphine Complexes[a]

run	ligand (1.1 equiv to Pd)	temp/time (°C/h)	yield (%)[b] of **5** and **6**	ratio[c] of **5**/**6**
1	PPh_3	50/2	90	13/87
2	P(*o*-Tol)$_3$[d]	50/1	90	87/13
3	P(*p*-An)$_3$[e]	20/1.5	97	7/93
4	dppe[f]	50/24	0	
5	BINAP[g]	50/24	0	

[a] All reactions were carried out without solvent in the presence of palladium catalyst prepared in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and a phosphine ligand. The ratio of **4**/$HSiCl_3$/Pd = 1.0/1.0/0.003. [b] Isolated yield by bulb-to-bulb distillation. [c] Determined by GC and ^{1}H NMR analysis. [d] Tri(*o*-tolyl)phosphine. [e] Tri(*p*-methoxyphenyl)phosphine. [f] 1,2-Bis(diphenylphosphino)ethane. [g] 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl.

(diphenylphosphino)-1,1′-binaphthyl (BINAP) did not take place at all at 50 °C (runs 4 and 5). These results indicate that the palladium-catalyzed hydrosilylation proceeds via an intermediate possessing one monophosphine ligand, though the electronic and/or steric effects of the monophosphine ligand are still not clear in the present catalysis. The palladium−monophosphine catalyst can activate hydrosilane and olefin by oxidative addition and coordination, respectively, to form tetracoordinated palladium(II) intermediate PdH($SiCl_3$)(olefin)L (L = monophosphine) which cannot be formed with chelating bisphosphine ligands.

In conclusion, hydrosilylation of olefins with trichlorosilane catalyzed by palladium−phosphine complexes must proceed via the hydropalladation pathway which is demonstrated by the novel cyclization of *o*-allylstyrene forming 1-methyl-2-(trichlorosilylmethyl)indan.

Experimental Section

General. NMR spectra were recorded on a JEOL JNM-EX270 spectrometer (270 MHz for ^{1}H) or JEOL JNM LA500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C) in $CDCl_3$. Chemical shifts of protons are reported in δ and referenced to tetramethylsilane as an internal standard. Detailed ^{1}H NMR assignments were performed by decoupling experiments. Air- and moisture-sensitive reactions were performed under usual inert atmosphere techniques. All dry solvents were distilled under N_2. THF and Et_2O were distilled from sodium/benzophenone ketyl.

Palladium-Catalyzed Hydrosilylation of 4. Typical Procedure (Scheme 2, Table 1, Run 1). To a mixture of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.55 mg, 1.5 μmol), triphenylphosphine (0.86 mg, 1.7 μmol), and *o*-allylstyrene (**4**)[13] (144 mg, 1.0 mmol) was added trichlorosilane (135 mg, 1.0 mmol) at 0 °C, and the reaction mixture was stirred at 50 °C for 2 h. The reaction progress was monitored by GC analysis. GC and ^{1}H NMR study on the whole crude mixture indicated that the ratio of 1-methyl-2-(trichlorosilylmethyl)indan (**5**)/1-(2-(2-propenyl)-phenyl)-1-trichlorosilylethane (**6a**)/1-(2-((*E*)-1-propenyl)phenyl)-1-trichlorosilylethane (**6b**) was 13/50/37. The crude mixture was purified by bulb-to-bulb distillation under reduced pressure to give 252 mg of mixture of **5**, **6a**, and **6b** (90%). **1-Methyl-2-(trichlorosilylmethyl)indan (5):** ^{1}H NMR ($CDCl_3$) δ 1.33 (d, J = 6.6 Hz, 3H), 1.62 (dd (overlapped), 1H), 1.90 (dd, J = 3.6, 15.2 Hz, 1H), 2.16−2.29 (m, 1H), 2.68 (dd, J = 9.6, 15.5 Hz, 1H), 2.83 (dq, J = 7.3, 6.6 Hz, 1H), 3.23 (dd, J = 7.6, 15.5 Hz, 1H), 7.1−7.4 (m (overlapped), aromatic). **1-(2-(2-Propenyl)phenyl)-1-trichlorosilylethane (6a):** ^{1}H NMR ($CDCl_3$) δ 1.57 (d, J = 7.3 Hz, 3H), 3.16 (q, J = 7.3 Hz, 1H), 3.36 (ddt, J = 4.0, 16.2, 1.7 Hz, 1H), 3.53 (ddt, J = 6.3, 16.2, 1.7 Hz, 1H), 4.95 (ddt, J = 3.3, 17.2, 1.7 Hz, 1H), 5.08 (ddt, J = 3.3, 10.2, 1.7 Hz, 1H), 5.97 (dddd, J = 4.0, 6.3, 10.2, 17.2 Hz, 1H), 7.1−7.4 (m (overlapped), aromatic). **1-(2-(1-Propenyl)phenyl)-1-trichlorosilylethane (6b):** ^{1}H NMR ($CDCl_3$)

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δ 1.59 (d, J = 7.3 Hz, 3H), 1.91 (d, J = 6.4 Hz, 3H), 3.28 (q, J = 7.3 Hz, 1H), 6.03 (dq, J = 15.1, 6.4 Hz, 1H), 6.64 (d, J = 15.1 Hz, 1H), 7.1−7.4 (m (overlapped), aromatic).

Since complete separation of **5** and **6** was difficult, the silylation products were isolated and fully characterized in the corresponding alcohols **7** and **8**, and the combustion analysis was performed on trimethylsilyl derivatives (vide infra). Stereochemistry of **5** was determined by an NOE experiment on its acetate **9** (vide infra).

Hydrosilylation of Styrene. The same procedure as employed for the hydrosilylation of **4** was followed with styrene (**10**) (104 mg, 1.0 mmol), $HSiCl_3$ (135 mg, 1.0 mmol), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.55 mg, 1.5 μmol), and triphenylphosphine (0.86 mg, 1.7 μmol) to give 222 mg (93%) of 1-phenyl-1-(trichlorosilyl)ethane (**12**).[10]

Hydrosilylation of Allylbenzene. The same procedure as employed for the hydrosilylation of **4** was followed with allylbenzene (**11**) (118 mg, 1.0 mmol), $HSiCl_3$ (135 mg, 1.0 mmol), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.55 mg, 1.5 μmol), and triphenylphosphine (0.86 mg, 1.7 μmol) to give a mixture of β-methylstyrene (**14**) and recovered allylbenzene. The ratio of **11**/**14** was determined by ^{1}H NMR analysis to be 51/49.

Oxidation of 5 and 6. To a suspension of KF (500 mg, 8.61 mmol) and $KHCO_3$ (1.35 g, 13.5 mmol) in 40 mL of THF/MeOH (1/1) was added a mixture of **5** and **6** (167 mg, 0.60 mmol) which contains **5** and **6** in a ratio of 61/39. To the suspension was added 1.3 mL of 30% H_2O_2 at ambient temperature, and the reaction mixture was vigorously stirred for 12 h. To the reaction mixture was added 5.0 mL of saturated $Na_2S_2O_3$ solution, and then the entire mixture was stirred for 1 h. The mixture was filtered through Celite plug, and the filtercake was rinsed with Et_2O. The filtrate was concentrated in vacuo, and the residue was extracted with Et_2O. After drying over $MgSO_4$, organic solvent was removed in vacuo and the resulting crude mixture was chromatographed on silica gel (AcOEt/hexane = 1/5) to give 59 mg of **7** (100%) and 34 mg of **8** (89%). **1-Methyl-2-(hydroxymethyl)indan (7):** ^{1}H NMR ($CDCl_3$) δ 1.34 (d, J = 6.9 Hz, 3H), 1.41 (br s, 1H), 2.23 (dddt, J = 5.9, 7.3, 14.2, 7.9 Hz, 1H), 2.73 (dd, J = 7.9, 15.8 Hz, 1H), 2.99 (dq, J = 14.2, 6.9 Hz, 1H), 3.10 (dd, J = 7.9, 15.8 Hz, 1H), 3.72 (dd, J = 7.3, 10.6 Hz, 1H), 3.84 (dd, J = 5.9, 10.6 Hz, 1H), 7.13−7.22 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.40, 34.96, 41.67, 50.57, 65.61, 123.36, 124.44, 126.32, 126.36, 142.03, 147.69; GC-MS *m/e* 162 (M^+). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.17; H, 8.83. **1-(2-(2-Propenyl)phenyl)ethanol (8a):** ^{1}H NMR ($CDCl_3$) δ 1.48 (d, J = 6.6 Hz, 3H), 1.65 (br s, 1H), 3.46 (dd, J = 1.7, 6.3 Hz, 2H), 4.98 (dt, J = 17.2, 1.7 Hz, 1H), 5.08 (dt, J = 9.9, 1.7 Hz, 1H), 5.17 (q, J = 6.6 Hz, 1H), 6.00 (ddt, J = 9.9, 17.2, 6.3 Hz, 1H), 7.14−7.57 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.28, 24.00, 67.02, 124.48, 126.71, 127.29, 127.93, 127.95, 129.56, 134.51, 143.82; GC-MS *m/e* 162 (M^+). **1-(2-((*E*)-1-Propenyl)phenyl)-ethanol (8b):** ^{1}H NMR ($CDCl_3$) δ 1.48 (d, J = 6.3 Hz, 3H), 1.77 (br s, 1H), 1.91 (dd, J = 1.5, 6.8 Hz, 3H), 5.22 (q, J = 6.3 Hz, 1H), 6.08 (dq, J = 15.6, 6.8 Hz, 1H), 6.69 (dd, J = 1.5, 15.6 Hz, 1H), 7.14−7.57 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 18.81, 24.12, 66.69, 124.59, 126.32, 127.22, 127.32, 127.91, 128.39, 135.51, 142.20; GC-MS *m/e* 162 (M^+). Elemental analysis of a mixture of isomers **8a** and **8b**. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.17; H, 8.85.

Methylation of 5 and 6. To a solution of 311 mg of a mixture of **5** and **6** (**5**/**6** = 50/50) in Et_2O was added 3.0 mL of MeMgBr (2 M in Et_2O) at 0 °C, and the reaction mixture was refluxed for 4 h. After being cooled, the reaction was quenched with 2.0 mL of saturated NH_4Cl at 0 °C. The mixture was extracted with Et_2O, and the organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was purified by silica gel chromatography (pentane) to give 202 mg of a mixture of 1-methyl-2-(trimethylsilylmethyl)indan (**5′**) and 1-(2-(propenyl)phenyl)-1-trimethylsilylethane (**6′**) (83%).

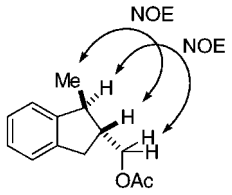

Figure 1. NOE experiments of **9**.

1-Methyl-2-(trimethylsilylmethyl)indan (5′): ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9H), 0.65 (dd, J = 11.2, 14.2 Hz, 1H), 1.05 (dd, J = 3.3, 14.2 Hz, 1H), 1.28 (d, J = 6.6 Hz, 3H), 2.08 (ddddd, J = 3.3, 7.3, 9.2, 10.2, 11.2 Hz, 1H), 2.48 (dd, J = 10.2, 15.2, 1H), 2.67 (dq, J = 9.2, 6.6 Hz, 1H), 3.02 (dd, J = 7.3, 15.2 Hz, 1H), 7.00−7.34 (m (overlapped), aromatic); ^{13}C NMR ($CDCl_3$) δ −0.81, 17.07, 21.27, 40.39, 46.10, 48.68, 122.92, 124.00, 126.08, 126.10, 143.25, 148.15; GC-MS *m/e* 162 (M^+). **1-(2-(2-Propenyl)phenyl)-1-trimethylsilylethane (6a′):** ^{1}H NMR ($CDCl_3$) δ −0.04 (s, 9H), 1.32 (d, J = 7.3 Hz, 3H), 2.40 (q, J = 7.3 Hz, 1H), 3.26 (br dd, J = 6.3, 15.8 Hz, 1H), 3.44 (br dd, J = 6.3, 15.8 Hz, 1H), 4.97 (dd, J = 1.7, 18.5 Hz, 1H), 5.05 (dd, J = 1.0, 9.9 Hz, 1H), 5.95 (ddt, J = 9.9, 18.5, 6.3 Hz, 1H), 7.00−7.34 (m (overlapped), aromatic); ^{13}C NMR ($CDCl_3$) δ −2.83, 16.11, 23.81, 37.76, 115.44, 124.25, 126.29, 126.69, 129.46, 136.31, 137.45, 144.60; GC-MS *m/e* 162 (M^+). **1-(2-((*E*)-1-Propenyl)phenyl)-1-trimethylsilylethane (6b′):** ^{1}H NMR ($CDCl_3$) δ −0.05 (s, 9H), 1.31 (d, J = 5.9 Hz, 3H), 1.88 (dd, J = 1.5, 6.3 Hz, 3H), 2.54 (q, J = 5.9 Hz, 1H), 5.98 (dq, J = 15.6, 6.3 Hz, 1H), 6.62 (br d, J = 15.6 Hz, 1H), 7.00−7.34 (m (overlapped), aromatic); ^{13}C NMR ($CDCl_3$) δ −2.88, 15.61, 18.80, 23.98, 124.17, 126.22, 126.37, 126.71, 127.06, 129.90, 136.13, 143.25; GC-MS *m/e* 162 (M^+). Elemental analysis of the mixture of the products. Anal. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.15. Found: C, 77.26; H, 10.28.

1-Methyl-2-(acetoxymethyl)indan (9). To a solution of 31 mg of **7** (0.19 mmol) were added pyridine (38 mg, 0.48 mmol), acetic anhydride (39 mg, 0.38 mmol), and a catalytic amount of DMAP at room temperature, and the reaction mixture was stirred for 18 h. The reaction mixture was concentrated in vacuo, and the crude residue was chromatographed on silica gel to give 36 mg of **9** (92%): ^{1}H NMR ($CDCl_3$) δ 1.34 (d, J = 6.6 Hz, 3H), 2.08 (s, 3H), 2.32 (dddt, J = 5.9, 6.9, 8.6, 7.9 Hz, 1H), 2.72 (dd, J = 8.6, 15.8 Hz, 1H), 2.99 (dq, J = 7.9, 6.6 Hz, 1H), 3.07 (dd, J = 7.9, 15.8 Hz, 1H), 4.18 (dd, J = 6.9, 10.9 Hz, 1H), 4.25 (dd, J = 5.9, 10.9, 1H), 7.17 (br m, 4H); ^{13}C NMR ($CDCl_3$) δ 18.93, 20.92, 35.16, 42.03, 47.25, 66.71, 123.29, 124.35, 126.45, 126.47, 141.69, 147.28, 171.18; GC-MS *m/e* 204 (M^+). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.73; H, 7.81. NOE experiments were performed by irradiation of signals at 1.34, 2.32, 2.99, 4.18, and 4.25 ppm. Pairs of signals showing NOE were indicated in Figure 1.

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Supporting Information Available: ^{1}H NMR spectrum of a mixture of **5**, **6a**, and **6b** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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