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Regioselective and Stereospecific Dehydrogenative Annulation Utilizing Silylium Ion-Activated Alkenes

Hidekazu Arii,*[,†] Yuto Yano,[†] Kenichi Nakabayashi,[†] Syuhei Yamaguchi,[‡] Masaki Yamamura,[§] Kunio Mochida,*[,⊥] and Takayuki Kawashima*[,¶]

[†]Faculty of Education, University of Miyazaki, 1-1 Gakuen Kibanadai Nishi, Miyazaki, 889-2192 Miyazaki, Japan

[‡]Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama, 790-8577 Ehime, Japan

[§]Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, 305-8571 Ibaraki, Japan

[⊥]Department of Chemistry, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, 171-8588 Tokyo, Japan

[¶]Graduate School of Science and Technology, Gunma University, 1-5-1 Tenjin-cho, Kiryu, 376-8515 Gunma, Japan

Supporting Information

ABSTRACT: Treatment of dialkylbenzylsilanes (**1**) with trityl tetrakis(pentafluorophenyl)borate (TPFPB) afforded the corresponding silylium ions in equilibrium with their intra- or intermolecular π-complexes, which underwent dehydrogenative annulation with various alkenes to form 1,2,3,4-tetrahydro-2-silanaphthalenes (**4**) in up to 82% isolated yield. Sterically bulkier substituents on the silicon atom tended to increase the yield of cyclic products **4**. The annulation products retained the stereochemistry in cases of the reactions using internal alkenes. The use of diisopropyl(1-naphthyl)silane (**2**) instead of **1** also resulted in annulation to obtain the 2,3-dihydro-1-sila-1*H*-phenalene derivatives **6**. Electrophilic aromatic substitution at the 8-position was predominant, despite the two potentially reactive positions on the naphthyl group. The steric hindrance of the naphthyl group prevented addition of the *cis*-alkene to the silylium ion, which would considerably decrease yields of the desired products from **2** compared to those from **1**.

INTRODUCTION

The silylium ion is a strong Lewis acid and has attracted attention for organic synthesis due to its reactivity toward compounds containing multiple bonds.[1] The silyl cation center can coordinate to compounds with electron-rich π bonds, such as arenes, as well as Lewis bases.[2] The electronegativity-induced polarity of the $Si^{\delta+}-H^{\delta-}$ bond promotes the formation of silylium ions through exergonic hydride abstraction by the trityl cation.[3] The coordination of unsaturated compounds to the generated silylium ion is expected to produce a corresponding labile reactive intermediate. The silylium ion has been utilized not only in stoichiometric systems but also in catalytic systems, such as [4 + 2] cycloaddition and hydrosilylation of unsaturated compounds.[4−8] Moreover, several Lewis acids (LA) induce activation of the Si−H bond to form intermediates, such as Si−(μ-H)−LA, which are functionally equivalent to the silylium ion. The Lewis acid facilitates heterolytic cleavage of the Si−H bond, resulting in the formation of a silylium ion complex and hydride−Lewis acid species. For example, $AlCl_3$ and $B(C_6F_5)_3$ were found to catalyze the hydrosilylation of olefins, ketones, and imines.[9,10]

We developed a sila-Friedel−Crafts reaction, in which the addition of silylium ion to the aromatic moiety followed by deprotonation induces Si−C bond formation, and applied the reaction to synthesize various dibenzosiloles (Figure 1(1)).[11] Recently, we reported the dehydrogenative annulation between dialkylbenzylsilane and alkynes via a silylium ion intermediate

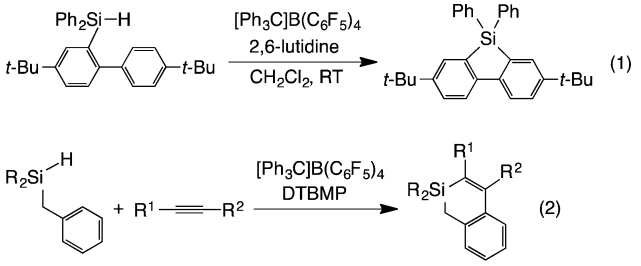

Figure 1. Syntheses of silicon-containing cyclic compounds associated with silylium ion.

(Figure 1(2)).[12] Silacyclic compounds have been reported to possess medicinal activity,[13] which indicates that it is important to explore a new approach for their synthesis. Herein we disclose reactions using dialkylbenzylsilanes R_2BnSiH (R = Me (**1a**), *i*-Pr (**1b**), *t*-Bu (**1c**)) and diisopropyl(1-naphthyl)silane *i*-$Pr_2NaphSiH$ (**2**) as substrates and terminal and internal alkenes as reactants and describe the scope and limitations of the reaction as well as its regioselectivity and stereospecificity.

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RESULTS AND DISCUSSION

A solution of trityl tetrakis(pentafluorophenyl)borate (TPFPB, 1.1 equiv) in benzene was slowly added to a benzene solution of benzyldimethylsilane (**1a**), 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 1.5 equiv), and trimethylvinylsilane (**3a**, 1.5 equiv), which was defined as method A (for details, see Experimental Section), to give 1,2,3,4-tetrahydro-2-silanaphthalene **4aa** in 30% isolated yield (Scheme 1 and Table 1, entry 1). For the

Scheme 1. Dehydrogenative Annulation Using Hydrosilanes 1 and Alkenes 3

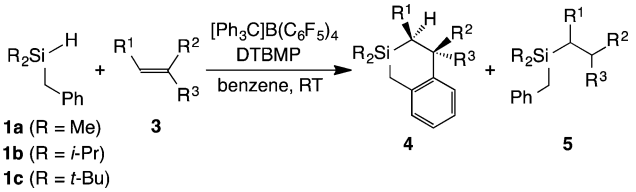


Table 1. Dehydrogenative Annulation Using Hydrosilanes 1a and Alkenes 3a–c[a]

	alkene				yield (%)[b]	
entry	3	R^1	R^2	R^3	4	5
1	**3a**	$SiMe_3$	H	H	30 (**4aa**)	–[c]
2	**3b**	H	H	Ph	–[c]	41 (**5ab**)
3	**3c**	H	H	*n*-Bu	24 (**4ac**)	44 (**5ac**)

[a]Using method A. [b]Isolated yields based on **1a**. [c]Not detected.

other alkenes (entries 2 and 3), hydrosilylation products **5** were obtained as a major product. Similar hydrosilylation of unsaturated compounds was observed in the reaction of **1a** with 1-hexyne using method A.[12] Because the reaction solution contains a greater amount of **1a** than that of the silylium ion during the dropping of TPFPB, hydride abstraction of the carbocation formed by coordination of the silylium ion to **3** from the Si–H bond of **1a** competed with intramolecular electrophilic addition to the benzene ring. To prevent this reaction, the benzene solution of **1a** was slowly added to the solution of TPFBP (1.1 equiv), DTBMP (1.5 eqiv), and alkenes **3a–c** (3 equiv), which was defined as method B (for details, see Experimental Section). Except for the reaction using **3b**, giving a complex mixture, the yields of **4** increased, with a decrease in the yields of **5** (Table 2, entries 1–3).[14] The 1,2,3,4-tetrahydro-2-silanaphthalene analogues were alternatively synthesized by $AlCl_3$-catalyzed intramolecular Friedel–Crafts alkylation and transition metal-catalyzed ring expansion of unsaturated hydrocarbons.[15]

For the scope and limitation of **1** and **3** (Table 2), the sterically bulkier substituents on the silicon atom in **1** improved the yields of **4**; that is, the yields of **4ac**, **4bc**, and **4cc** were 64%, 74%, and 82%, respectively. The hydrosilylation products **5** in entries 5–15 were isolated in yields less than 3%. The formation of **4ba** or **4ca** was accompanied by that of $R_2BnSiMe$ in 31% (R = *i*-Pr) or 58% (R = *t*-Bu) yield. Sekiguchi et al. reported methyl abstraction by a silylium ion from the saturated silicon atom, giving the more stable silylium ion.[16] The dimethylvinylsilylium ion derived from trimethylvinylsilane (**3a**) is more stable than the silylium ions derived from **1b** and **1c** due to the conjugation with the double bond, so methyl abstraction is considered to have occurred to give $R_2BnSiMe$. The yields of **4** in the reactions using 1-hexene (**3c**) and 1-

Table 2. Dehydrogenative Annulation Using Hydrosilanes 1a–c and Alkenes 3a–g[a]

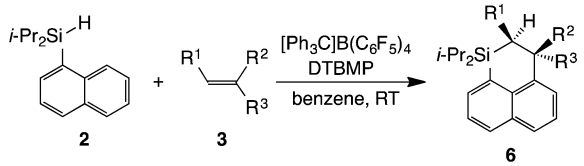
		alkene				
entry	silane **1**	3	R^1	R^2	R^3	yield of **4** (%)[b]
1	**1a**	**3a**	$SiMe_3$	H	H	52 (**4aa**)
2	**1a**	**3b**	H	H	Ph	–[c]
3	**1a**	**3c**	H	H	*n*-Bu	64 (**4ac**)
4	**1a**	**3d**	H	H	*n*-Hex	67 (**4ad**)
5	**1a**	**3e**	*n*-Pr	H	*n*-Pr	23 (**4ae**)[d]
6	**1b**	**3a**	$SiMe_3$	H	H	17 (**4ba**)
7	**1b**	**3c**	H	H	*n*-Bu	74 (**4bc**)
8	**1b**	**3d**	H	H	*n*-Hex	70 (**4bd**)
9	**1b**	**3e**	*n*-Pr	H	*n*-Pr	54 (**4be**)
10	**1b**	**3f**	*n*-Pr	*n*-Pr	H	56 (**4bf**)
11	**1b**	**3g**	$(CH_2)_4$		H	61 (**4bg**)
12	**1c**	**3a**	$SiMe_3$	H	H	14 (**4ca**)
13	**1c**	**3c**	H	H	*n*-Bu	82 (**4cc**)
14	**1c**	**3d**	H	H	*n*-Hex	80 (**4cd**)
15	**1c**	**3e**	*n*-Pr	H	*n*-Pr	19 (**4ce**)

[a]Using method B. [b]Isolated yields based on **1**. [c]Not detected. [d]Obtained as a cis/trans mixture.

octene (**3d**) also increased with increasing bulkiness of the substituent on the silicon atom. This tendency may be explained based on the Thorpe–Ingold effect.[17] However, the conversion of **1c** required a longer reaction time (24 h) and higher temperature (80 °C) than that of **1a** or **1b**. In the reactions using internal alkenes, annulation products were obtained in low to moderate yields, with retention of the alkene stereochemistry (entries 9, 10, 11, and 15 in Table 2), except for the reaction using **1a** and **3e**, giving a cis/trans mixture of **4ae**. The stereochemistry of **4be** and **4bf** was identified as trans and cis, respectively, by temperature-dependent NMR spectroscopy. The signals due to **4be** showed no temperature dependence, while those due to **4bf** showed temperature dependence, suggesting that **4be** has only one stable conformation, while **4bf** has two exchangeable conformations, which was supported by the DFT calculations (Figure S2, Supporting Information).

Reactions using **2**, containing a 1-naphthyl group, and alkenes **3c–h** were carried out using method B to give the corresponding 2,3-dihydro-1-sila-1*H*-phenalene derivatives **6** in 40–66% yields (Scheme 2 and Table 3). Although the 2-

Scheme 2. Dehydrogenatice Annulation Using Hydrosilanes 2 and Alkenes 3



position of the naphthyl group is potentially reactive in electrophilic aromatic substitution, no five-membered ring products were detected. Product **6e** was obtained as single crystals suitable for X-ray diffraction analysis. The crystal structure revealed that the C=C moiety of *trans*-4-octene bridges the silicon atom and the 8-position on the naphthyl group to form a six-membered ring and that two *n*-propyl groups are oriented in a trans configuration (Figure S3, Supporting Information). However, the reaction using *cis*-4-

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Table 3. Dehydrogenative Annulation Using Hydrosilanes 2 and Alkenes 3c–i[a]

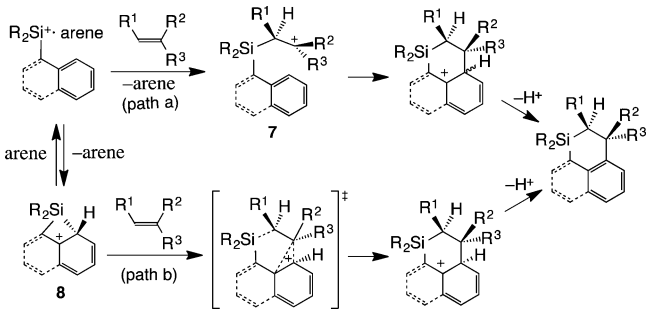
		alkene			
entry	3	R^1	R^2	R^3	yield of 6 (%)[b]
1	3c	H	H	*n*-Bu	63 (6c)
2	3d	H	H	*n*-Hex	66 (6d)
3	3e	*n*-Pr	H	*n*-Pr	43 (6e)
4	3f	*n*-Pr	*n*-Pr	H	–[c]
5	3g	$(CH_2)_4$		H	46 (6g)
6	3h	Et	H	Et	40 (6h)
7[d]	3i	Et	Et	H	5 (6i)[e]

[a]Using method B. [b]Isolated yields based on **2**. [c]Not detected. [d]Solvent is changed from benzene to toluene. [e]Cis/trans = 9/1.

octene (**3f**) did not produce the annulation product, suggesting that the isopropyl and naphthyl groups prevented access of *cis*-4-octene to the silylium ion center. When the less-hindered *cis*-3-hexene was used, **6i** was obtained in 5% yield by changing the solvent from benzene to toluene, but a cis/trans (9:1) mixture was obtained. Although the 2,3-dihydro-1-sila-1*H*-phenalenes were previously synthesized by the thermolysis of the corresponding dichloro(1-naphthyl)vinylsilane,[18] our method has the advantage that alkyl groups can be introduced at 2- and 3-positions under milder conditions.

A mechanism for the dehydrogenative annulation can be proposed based on the above results (Scheme 3). Electrophilic

Scheme 3. Plausible Mechanism of the Dehydrogenative Annulation



addition of the silylium ion to alkenes generates carbocation **7**, leading to an intramolecular Friedel–Crafts reaction (path a). The regioselectivity of the cyclic products is associated with the stability of **7**, as previously reported in reactions using terminal alkynes.[12] The 3-substituted products **4aa**, **4ba**, and **4ca** and other 4-substituted products form via carbocations that are stabilized by the β-effect of the two silyl groups and by the corresponding secondary carbocations. The intramolecular electrophilic aromatic substitution is remarkably rapid because of the retention of alkene stereochemistry and no detection of benzene- or toluene-derived sila-Friedel–Crafts products. Alternatively, the benzosilacyclobutenium ion **8** undergoes a [π2s + σ2a] reaction with the alkene to retain the stereochemistry (path b).[19] A partial positive charge appears at the β-position in the transition state of the [2 + 2] reaction, which causes the regioselectivity of cyclic products **4** and **6**, similarly to path a. The four-membered ring intermediate **9** generated from deprotonation of **8** can be ruled out because the reaction of **9** with alkenes affords 1,2,3,4-tetrahydro-1-silanaphthalene derivatives via an *o*-silaquinone methide species in the case of the reaction using **1** (Scheme S1, Supporting Information). The retention of alkene stereochemistry is an interesting behavior in the silylium ion-based annulation.

CONCLUSION

We investigated the dehydrogenative annulation of hydrosilanes bearing a benzyl or a naphthyl group to terminal, internal, and cyclic alkenes. The regioselectivity observed in the annulation for terminal alkenes depends on the stability of the cationic intermediate. Moreover, the retention of the alkene stereochemistry of internal alkenes is attributed to the rapid intramolecular Friedel–Crafts reaction via the resulting carbocation or [π2s + σ2a] reaction of the benzosilacyclobutenium ion. This procedure provides a useful method for the synthesis of silicon-containing cyclic compounds under mild and transition metal-free conditions.

EXPERIMENTAL SECTION

General Procedure. All experiments were carried out using standard vacuum line and Schlenk techniques in an Ar atmosphere or drybox. All the reagents were of the highest grade available and were used without further purification. All solvents used for the syntheses were distilled according to the general procedure. Benzyldimethylsilane (**1a**),[20] benzyldiisopropylsilane (**1b**),[12] and trityl tetrakis(pentafluorophenyl)borate[21] were synthesized according to the previously reported method. Benzyldi-*tert*-butylsilane (**1c**) was prepared by the same method as **1a** except for the use of di-*tert*-butylchlorosilane as a starting material. Diisopropyl(1-naphthyl)silane (**2**) was synthesized by the reaction of 1-naphthyllithium with chlorodiisopropylsilane in Et_2O. The NMR spectral measurements were performed on a 400 or 600 MHz spectrometer. The ^1H and ^{13}C chemical shifts are reported relative to the residual protonated solvent and the solvent, respectively, according to the literature.[22] High-resolution mass spectroscopy was performed on a double-focusing mass spectrometer with EI mode or on a TOF mass spectrometer with ESI mode and was calibrated using a suitable standard material. Elemental analysis was conducted with a correction for acetoanilide. Gel permeation liquid chromatography (GPLC) was performed using chloroform as an eluent. All calculations were performed using the SPARTAN 08 package.[23] Calculations were performed with the B3LYP functional and the basis sets 6-31G*. All structures were subject to full optimization, and the transition states were checked by numerical frequency analysis.

X-ray Crystallography. Single crystals of **6e** suitable for XRD analyses were obtained. Each crystal was mounted on a glass fiber, and the diffraction data were collected on a CCD detector using graphite monochromated Mo Kα radiation.

All the structures were solved by the combination of the direct method and Fourier techniques, and all the non-hydrogen atoms were anisotropically refined by full-matrix least-squares calculations. The atomic scattering factors and anomalous dispersion terms were obtained from the International Tables for X-ray Crystallography IV.[24] The refinement of all structures was carried out by full-matrix least-squares method of SHELXL-97.[25]

Preparation of Compounds. *Method A.* To **1a** (0.20 mmol), an alkene (0.30 mmol), and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 0.30 mmol) in benzene (3 mL) was slowly added a benzene solution (4 mL) of trityl tetrakis(pentafluorophenyl)borate (TPFPB, 203 mg, 0.22 mmol) at room temperature under Ar atmosphere, and the resulting solution was stirred for 15 min. The reaction mixture was quenched with 1 M HCl, and then the organic layer was extracted. After extraction with hexane, the organic layers were combined and dried over anhydrous sodium sulfate. After filtration, the filtrate was concentrated under reduced pressure to remove volatiles, and the residue was purified by silica gel column (eluent: hexane). Further purification was carried out by GPLC to obtain each of products.

Method B. To TPFPB (203 mg, 0.22 mmol), an alkene (0.60 mmol), and DTBMP (0.30 mmol) in benzene (4 mL) was slowly added a benzene solution (2 mL) of a hydrosilane (0.20 mmol) at

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room temperature under Ar atmosphere, and the resulting solution was stirred for 15, 30, and 90 min at room temperature for **1a**, **1b**, and **2**, respectively, and for 24 h at 80 °C for **1c**. The following workup was done according to method A. Other products such as polymeric materials, disiloxanes, and hydrosilylation products were removed by GPLC.

*2,2-Dimethyl-3-trimethylsilyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4aa**).* **4aa** (26.0 mg, 52%) was obtained as a colorless oil from the reaction using **1a** (30.4 mg, 0.202 mmol) and trimethyl(vinyl)-silane (**3a**) by method B. ^{1}H NMR data are consistent with those reported previously.[12]

*Benzyldimethyl(2-phenylethyl)silane (**5ab**).* **5ab** (26.0 mg, 52%)) was obtained as a colorless oil from the reaction using **1a** (29.6 mg, 0.197 mmol) and styrene (**3b**) by method A. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30−7.15 (m, 7H, ArH), 7.09 (t, 1H, J = 7.2 Hz, ArH), 7.03 (d, 2H, J = 7.2 Hz, ArH), 2.65−2.55 (m, 2H, CH_2CH_2Ph), 2.13 (s, 2H, $SiCH_2Ph$), 0.95−0.85 (m, 2H, CH_2CH_2Ph), 0.024 (s, 6H, $SiMe_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.0, 140.2, 128.3, 128.2, 128.1, 127.8, 125.5, 123.9, 29.9, 25.5, 16.9, −3.6. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{17}H_{22}Si$, 254.1491; found, 254.1476.

*4-Butyl-2,2-dimethyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4ac**).* **4ac** (30.1 mg, 64%) was obtained as a colorless oil from the reaction using **1a** (30.4 mg, 0.202 mmol) and 1-hexene (**3c**) by method B. ^{1}H NMR data are consistent with those reported previously.[12]

*Benzyl(hexyl)dimethylsilane (**5ac**).* **5ac** (20.5 mg, 44%) was obtained with **4ac** (11.0 mg, 24%) as a colorless oil from the reaction of **1a** (29.7 mg, 0.198 mmol) with 1-hexene (**3c**) by method A. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.21 (t, 2H, J = 7.6 Hz, ArH), 7.07 (t, 1H, J = 7.2 Hz, ArH), 7.00 (d, 2H, J = 7.2 Hz, ArH), 2.09 (s, 2H, $SiCH_2Ph$), 1.40−1.20 (m, 8H, *n*-Hex), 0.90 (t, 3H, J = 7.2 Hz, *n*-Hex), 0.55−0.45 (m, 2H, *n*-Hex), −0.038 (s, 6H, $SiMe_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.5, 128.1, 128.0, 123.8, 33.3, 31.6, 25.6, 23.7, 22.6, 14.8, 14.1, −3.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{26}Si$, 234.1804; found, 234.1814.

*4-Hexyl-2,2-dimethyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4ad**).* **4ad** (35.0 mg, 67%) was obtained as a colorless oil from the reaction using **1a** (30.0 mg, 0.200 mmol) and 1-octene (**3d**) by method B. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.15−7.05 (m, 4H, ArH), 2.80−2.70 (m, 1H, C*H*(*n*-Hex)), 2.06 (d, 1H, J = 14.4 Hz, $SiCH_2Ar$), 1.98 (d, 1H, J = 14.8 Hz, $SiCH_2Ar$), 1.90−1.80 (m, 1H, *n*-Hex), 1.65−1.50 (m, 1H, *n*-Hex), 1.50−1.20 (m, 8H, *n*-Hex), 0.99 (dd, 1H, J = 14.4 Hz, J = 4.8 Hz, $SiCH_2CH$), 0.91 (t, 3H, J = 6.8 Hz, *n*-Hex), 0.51 (dd, 1H, J = 14.4 Hz, J = 8.8 Hz, $SiCH_2CH$), 0.11 (s, 3H, $SiMe_2$), 0.004 (s, 3H, $SiMe_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.3, 138.0, 130.2, 126.3, 125.9, 124.7, 40.0, 35.3, 31.9, 29.5, 28.1, 22.7, 20.8, 18.0, 14.1, −1.2, −1.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{24}Si$, 232.1647; found, 232.1621.

*trans-2,2-Dimethyl-3,4-dipropyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4ae**).* **4ae** (12.1 mg, 23%) was obtained as a colorless oil from the reaction using **1a** (29.7 mg, 0.198 mmol) and *trans*-4-octene (**3e**) by method B. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.10−6.95 (m, 4H, ArH), 2.80 (ddd, 1H, J = 8.8 Hz, J = 6.0 Hz, J = 2.0 Hz, ArC*H*(*n*-Pr)), 2.10 (d, 1H, J = 15.2 Hz, $SiCH_2Ar$), 1.89 (d, 1H, J = 15.2 Hz, $SiCH_2Ar$), 1.70−1.40 (m, 3H, *n*-Pr), 1.35−1.05 (m, 5H, *n*-Pr), 1.05−0.95 (m, 1H, $SiCH$(*n*-Pr)), 0.86 (t, 3H, J = 7.6 Hz, *n*-Pr), 0.84 (t, 3H, J = 7.2 Hz, *n*-Pr), 0.21 (s, 3H, $SiMe_2$), −0.14 (s, 3H, $SiMe_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.5, 137.0, 130.9, 130.5, 126.2, 124.6, 49.2, 37.4, 34.1, 27.9, 22.5, 21.6, 20.4, 14.2, 14.1, 0.58, −3.9. HRMS (EI) m/z: $[M]^+$ calcd for $C_{17}H_{28}Si$, 260.1960; found, 260.1960.

*2,2-Diisopropyl-3-trimethylsilyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4ba**).* **4ba** (10.5 mg, 17%) was obtained with *i*-Pr_2BnSiMe (13.7 mg, 31%) as a colorless oil from the reaction using **1b** (41.5 mg, 0.201 mmol) and **3a**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.15−7.00 (m, 4H, ArH), 2.71 (dd, 1H, J = 14.0 Hz, J = 3.6 Hz, $CHCH_2Ar$), 2.62 (dd, 1H, J = 13.6 Hz, J = 12.0 Hz, Si_2CHCH_2Ar), 2.03 (d, 1H, J = 14.8 Hz, $SiCH_2Ar$), 1.98 (d, 1H, J = 14.8 Hz, $SiCH_2Ar$), 1.20−1.10 (m, 1H, *i*-Pr), 1.10−1.05 (m, 6H, *i*-Pr), 0.95−0.85 (m, 1H, *i*-Pr), 0.84 (d, 3H, J = 6.4 Hz, *i*-Pr), 0.79 (d, 3H, J = 6.8 Hz, *i*-Pr), 0.12 (s, 9H, $SiMe_3$), −0.05 (dd, 1H, J = 12.0 Hz, J = 3.6 Hz, $CHCH_2Ar$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.8, 138.7, 129.6, 127.2, 126.3, 124.5, 32.2, 19.3, 18.8, 18.7, 14.8, 12.7, 12.0, 9.3, −0.01. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{18}H_{32}Si_2$, 304.2043; found, 304.2039. *i*-Pr_2BnSiMe: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.20 (t, 2H, J = 7.6 Hz, ArH), 7.08−7.02 (m, 3H, ArH), 2.13 (s, 2H, $SiCH_2Ar$), 1.00−0.87 (m, 14H, *i*-Pr), −0.11 (s, 3H, SiMe). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.8, 128.3, 128.1, 123.8, 20.8, 18.04, 18.01, 11.6, −8.9. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{14}H_{24}Si$, 220.1647; found, 220.1650.

*4-Butyl-2,2-diisopropyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4bc**).* **4bc** (42.6 mg (74%) was obtained as a colorless oil from the reaction using **1b** (41.1 mg, 0.199 mmol) and **3c**. ^{1}H NMR data are consistent with those reported previously.[12]

*4-Hexyl-2,2-diisopropyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4bd**).* **4bd** (44.4 mg, 70%) was obtained as a colorless oil from the reaction using **1b** (41.2 mg, 0.200 mmol) and **3d**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.15−7.05 (m, 4H, ArH), 2.70−2.60 (m, 1H, C*H*(*n*-Hex)), 2.05 (d, 1H, J = 14.8 Hz, $SiCH_2Ar$), 2.00 (d, 1H, J = 14.4 Hz, $SiCH_2Ar$), 1.95−1.85 (m, 1H, *n*-Hex), 1.65−1.25 (m, 9H, *n*-Hex and *i*-Pr), 1.06 (dd, 1H, J = 14.4 Hz, J = 4.4 Hz, $SiCH_2CH$), 1.01 (brs, 7H, *i*-Pr), 0.91 (t, 3H, J = 7.2 Hz, *n*-Hex), 0.90−0.80 (m, 7H, *i*-Pr), 0.36 (dd, 1H, J = 14.8 Hz, J = 10.0 Hz, $SiCH_2CH$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.4, 138.6, 130.0, 125.9, 125.4, 124.6, 39.3, 35.6, 31.9, 29.6, 28.0, 22.7, 18.3, 18.14, 18.10, 17.9, 15.0, 14.1, 12.3, 11.8, 11.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{36}Si$, 316.2586; found, 316.2609.

*trans-2,2-Diisopropyl-3,4-dipropyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4be**).* **4be** (34.2 mg, 54%) was obtained as a colorless oil from the reaction using **1b** (41.0 mg, 0.199 mmol) and **3e**. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.08−7.03 (m, 2H, ArH), 7.01−6.96 (m, 2H, ArH), 2.75 (ddd, 1H, J = 9.0, 6.6, 1.5 Hz, ArC*H*(*n*-Pr)), 2.04 (d, 1H, J = 15 Hz, $SiCH_2Ar$), 1.98 (d, 1H, J = 15 Hz, $SiCH_2Ar$), 1.63−1.45 (m, 3H), 1.41−1.00 (m, 13H), 0.98−0.90 (m, 4H), 0.90 (t, 3H, J = 7.4 Hz, *n*-Pr), 0.85 (t, 3H, J = 7.4 Hz, *n*-Pr), 0.61 (d, 3H, J = 7.3 Hz, *i*-Pr). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 143.2, 137.8, 131.0, 130.4, 126.3, 124.4, 48.9, 38.6, 33.9, 25.6, 22.9, 21.6, 19.0, 18.7, 18.4, 18.3, 14.7, 14.2, 14.1, 12.7, 10.9. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{36}Si$, 316.2586; found, 316.2598.

*cis-2,2-Diisopropyl-3,4-dipropyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4bf**).* **4bf** (35.7 mg, 56%) was obtained as a colorless oil from the reaction using **1b** (41.2 mg, 0.200 mmol) and **3f**. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.08−6.97 (m, 4H, ArH), 2.88 (ddd, 1H, J = 12.0, 3.6, 3.6 Hz, ArC*H*(*n*-Pr)), 2.08 (d, 1H, J = 16 Hz, $SiCH_2Ar$), 1.95 (d, 1H, J = 16 Hz, $SiCH_2Ar$), 1.66−1.38 (m, 5H), 1.37−1.28 (m, 1H), 1.22−0.99 (m, 10H), 0.98−0.81(m, 13H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 144.0, 138.0, 130.8, 128.9, 126.2, 124.3, 46.3, 32.2, 30.4, 25.3, 22.7, 21.6, 19.2, 18.9, 18.3, 18.2, 15.3, 14.3, 14.2, 12.7, 11.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{36}Si$, 316.2586; found, 316.2602.

*cis-10,10-Diisopropyl-1,2,3,4,4a,9,10,10a-octahydro-10-silaphenanthrene (**4bg**).* **4bg** (34.8 mg, 61%) was obtained as a colorless oil from the reaction using **1b** (41.0 mg, 0.200 mmol) and **3g**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33−7.27 (m, 1H, ArH), 7.14−7.06 (m, 3H, ArH), 2.92−2.84 (m, 1H, ArCH), 2.23−2.13 (m, 1H), 2.08 (d, 1H, J = 14.4 Hz), 1.94 (d, 1H, J = 14.8 Hz), 1.95−1.72 (m, 2H), 1.70−1.25 (m, 6H), 1.07−0.86 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.7, 138.7, 130.1, 127.4, 125.8, 124.4, 40.7, 29.6, 27.5, 26.0, 23.9, 23.7, 19.0, 18.7, 18.6, 18.3, 18.2, 15.5, 11.9, 11.3. HRMS (EI) m/z: $[M]^+$ calcd for $C_{19}H_{30}Si$, 286.2117; found, 286.2137.

*2,2-Di-tert-butyl-3-trimethylsilyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4ca**).* **4ca** (9.0 mg, 14%) was obtained with *t*-Bu_2BnSiMe (28.5 mg, 58%) as a colorless oil from the reaction using **1c** (46.7 mg, 0.199 mmol) with **3a**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.12−6.98 (m, 4H, ArH), 2.07 (s, 2H, $SiCH_2Ar$), 1.90 (dd, 1H, J = 12.8 Hz, J = 3.6 Hz, $ArCH_2CH$), 1.12−1.06 (m, 1H, $ArCH_2CH$), 1.03 (s, 9H, *t*-Bu), 0.77 (s, 9H, *t*-Bu), 0.40 (dd, 1H, J = 14.4 Hz, J = 12.8 Hz, SiCH), 0.20 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.5, 141.0, 130.4, 127.8, 125.6, 124.4, 28.6, 28.5, 27.9, 20.1, 19.7, 15.6, 7.5, −1.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{36}Si_2$, 332.2356; found, 332.2365. *t*-Bu_2BnSiMe: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.20 (t, 2H, J = 7.6 Hz, ArH), 7.10 (d, 2H, J = 8.0 Hz, ArH), 7.06, (t, 1H J = 7.2 Hz, ArH), 2.22 (s, 2H, $SiCH_2Ar$), 0.98 (s, 18H, *t*-Bu), −0.05 (s, 3H, SiMe). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.5, 128.8, 128.0, 123.8, 28.6, 19.8,

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19.7, −9.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{28}Si$, 248.1960; found, 248.1960.

*4-Butyl-2,2-di-tert-butyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4cc**).* **4cc** (51.3 mg, 82%) was obtained as a colorless oil from the reaction using **1c** (46.2 mg, 0.197 mmol) and **3c**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16−7.02 (m, 4H, ArH), 2.60−2.50 (m, 1H, C*H*(*n*-Bu)), 2.12−1.93 (d, 3H), 1.65−1.30 (m, 5H), 1.17 (dd, 1H, J = 14.4 Hz, J = 3.6 Hz, SiCH_2CH), 1.06 (s, 9H, *t*-Bu), 0.95 (t, 3H, J = 6.8 Hz, *n*-Bu), 0.75 (s, 9H, *t*-Bu), 0.24 (dd, 1H, J = 14.8 Hz, J = 12.4 Hz, SiCH_2CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.1, 139.6, 130.0, 125.7, 124.6, 124.3, 38.5, 35.3, 30.1, 28.56, 28.49, 23.1, 20.0, 19.5, 15.1, 14.2, 13.0. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{21}H_{36}Si$, 316.2586; found, 316.2565.

*2,2-Di-tert-butyl-4-hexyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4cd**).* **4cd** (54.3 mg, 80%) was obtained as a colorless oil from the reaction using **1c** (45.9 mg, 0.196 mmol) and **3d**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16−7.03 (m, 4H, ArH), 2.60−2.50 (m, 1H, C*H*(*n*-Hex)), 2.12−1.94 (d, 3H), 1.66−1.55 (m, 1H), 1.44−1.28 (m, 5H), 1.16 (dd, 1H, J = 14.4 Hz, J = 3.6 Hz, SiCH_2CH), 1.06 (s, 9H, *t*-Bu), 0.94−0.86 (m, 3H, *n*-Hex), 0.75 (s, 9H, *t*-Bu), 0.23 (dd, 1H, J = 14.4 Hz, J = 12.0 Hz, SiCH_2CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.1, 139.6, 130.0, 125.7, 124.6, 124.3, 38.5, 35.6, 31.9, 29.7, 28.56, 28.50, 27.9, 22.7, 20.0, 19.5, 15.1, 14.1, 13.0. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{23}H_{40}Si$, 344.2899; found, 344.2883.

*trans-2,2-Di-tert-butyl-3,4-dipropyl-1,2,3,4-tetrahydro-2-silanaphthalene (**4ce**).* **4ce** (13.3 mg, 19%) was obtained as a colorless oil from the reaction using **1c** (46.8 mg, 0.200 mmol) and **3e**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.10−6.94 (m, 4H, ArH), 2.65 (ddd, 1H, J = 9.6, 6.4, 2.0 Hz, ArC*H*(*n*-Pr)), 2.12 (d, 1H, J = 14.4 Hz, SiCH_2Ar), 2.05 (d, 1H, J = 14.4 Hz, SiCH_2Ar), 1.74−1.16 (m, 7H), 1.14−1.06 (m, 2H), 1.06 (s, 9H, *t*-Bu), 0.96 (t, 3H, J = 6.8 Hz, *n*-Pr), 0.85 (t, 3H, J = 7.2 Hz, *n*-Pr), 0.71 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.5, 138.2, 130.4, 129.8, 126.3, 124.4, 49.3, 39.8, 35.0, 29.7, 29.0, 27.5, 23.8, 21.6, 20.6, 19.6, 15.8, 14.4, 14.2. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{23}H_{40}Si$, 344.2899; found, 344.2879.

*3-Butyl-1,1-diisopropyl-2,3-dihydro-1-sila-1H-phenalene (**6c**).* **6c** (40.5 mg, 63%) was obtained as a white solid from the reaction using **2** (48.3 mg, 0.199 mmol) and **3c**. Mp: 69−70 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (dd, 1H, J = 8.4 Hz, J = 1.6 Hz, ArH), 7.71 (dd, 1H, J = 6.8 Hz, J = 1.6 Hz, ArH), 7.69 (dd, 1H, J = 5.2 Hz, J = 1.2 Hz, ArH), 7.46 (dd, 1H, J = 8.0 Hz, J = 6.4 Hz, ArH), 7.39 (t, 1H, J = 8.0 Hz, ArH), 7.33 (d, 1H, J = 6.8 Hz, ArH), 3.35−3.25 (m, 1H, ArC*H*(*n*-Bu)), 1.80−1.60 (m, 2H), 1.50−1.10 (m, 11H), 1.09 (d, 3H, J = 7.6 Hz, *i*-Pr), 1.03 (d, 3H, J = 7.2 Hz, *i*-Pr), 0.89 (t, 3H, J = 7.2 Hz, *n*-Bu), 0.87 (d, 3H, J = 7.6 Hz, *i*-Pr). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.2, 136.7, 133.8, 132.8, 132.0, 129.9, 127.2, 125.3, 124.9, 124.3, 40.8, 38.4, 30.2, 22.8, 18.8, 18.6, 18.4, 18.3, 14.1, 13.0, 12.4, 10.3. Anal. calcd for **6c**·0.2H_2O ($C_{22}H_{32.4}O_{0.2}Si$): C, 80.52; H, 9.95. found: C, 80.56; H, 10.01.

*3-Hexyl-1,1-diisopropyl-2,3-dihydro-1-sila-1H-phenalene (**6d**).* **6d** (46.3 mg, 66%) was obtained as a colorless oil from the reaction using **2** (48.3 mg, 0.199 mmol) and **3d**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (dd, 1H, J = 8.0 Hz, J = 1.2 Hz, ArH), 7.70 (dd, 1H, J = 6.4 Hz, J = 1.6 Hz, ArH), 7.68 (dd, 1H, J = 5.2 Hz, J = 1.2 Hz, ArH), 7.46 (dd, 1H, J = 8.4 Hz, J = 6.8 Hz, ArH), 7.38 (t, 1H, J = 8.0 Hz, ArH), 7.32 (d, 1H, J = 7.2 Hz, ArH), 3.35−3.25 (m, 1H, ArC*H*(*n*-Hex)), 1.80−1.60 (m, 2H), 1.50−1.10 (m, 15H), 1.09 (d, 3H, J = 7.6 Hz, *i*-Pr), 1.02 (d, 3H, J = 7.2 Hz, *i*-Pr), 0.92−0.83 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.2, 136.7, 133.8, 132.8, 132.0, 129.9, 127.2, 125.3, 124.9, 124.3, 40.8, 38.7, 31.9, 29.4, 27.9, 22.7, 18.8, 18.7, 18.4, 18.3, 14.1, 13.0, 12.4, 10.3. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{24}H_{36}Si$, 352.2586; found, 352.2576.

*trans-1,1-Diisopropyl-2,3-dipropyl-2,3-dihydro-1-sila-1H-phenalene (**6e**).* **6e** (30.3 mg, 43%) was obtained as a colorless crystal from the reaction using **2** (48.4 mg, 0.200 mmol) and **3e**. Mp: 54−55 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (dd, 1H, J = 8.0 Hz, J = 1.2 Hz, ArH), 7.69 (dd, 1H, J = 8.0 Hz, J = 1.2 Hz, ArH), 7.67 (dd, 1H, J = 6.8 Hz, J = 1.6 Hz, ArH), 7.46 (dd, 1H, J = 8.0 Hz, J = 6.8 Hz, ArH), 7.34 (dd, 1H, J = 8.0 Hz, J = 6.8 Hz, ArH), 7.23 (dd, 1H, J = 7.2 Hz, J = 1.2 Hz, ArH), 3.23 (ddd, 1H, J = 8.8 Hz, J = 6.4 Hz, J = 2.8 Hz, ArC*H*(*n*-Pr)), 1.78−1.63 (m, 1H), 1.60−0.95 (m, 18H), 0.92 (t, 3H, J = 7.2 Hz, *n*-Pr), 0.87 (d, 3H, J = 7.6 Hz, *i*-Pr), 0.84 (d, 3H, J = 7.2 Hz, *i*-Pr), 0.77 (t, 3H, J = 7.2 Hz, *n*-Pr). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.7, 135.9, 133.7, 133.0, 131.4, 129.7, 127.8, 127.2, 124.8, 124.4, 47.6, 41.1, 32.3, 24.3, 22.0, 21.7, 19.1, 19.0, 18.7 (2C), 14.1, 13.9 (2C), 11.9. Anal. Calcd for **6e** ($C_{24}H_{36}Si$): C, 81.75; H, 10.29. Found: C, 81.59; H, 10.51.

*cis-7,7-Diisopropyl-7a,8,9,10,11,11a-hexahydro-7-sila-7H-benzo[de]anthracene (**6g**).* **6g** (29.5 mg, 46%) was obtained as a colorless oil from the reaction using **2** (48.4 mg, 0.200 mmol) and **3g**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (dd, 1H, J = 8.4 Hz, J = 1.6 Hz, ArH), 7.72 (d, 1H, J = 8.0 Hz, ArH), 7.66 (dd, 1H, J = 6.4 Hz, J = 1.2 Hz, ArH), 7.52 (d, 1H, J = 7.2 Hz, ArH), 7.46 (dd, 1H, J = 8.4 Hz, J = 6.8 Hz, ArH), 7.44 (t, 1H, J = 7.6 Hz, ArH), 3.42−3.35 (m, 1H, ArCH), 2.45−2.31 (m, 1H), 1.97−1.37 (m, 9H), 1.30−1.13 (m, 1H), 1.18 (d, 3H, J = 7.6 Hz, *i*-Pr), 1.10 (t, 6H, J = 6.8 Hz, *i*-Pr), 1.02 (d, 3H, J = 7.2 Hz, *i*-Pr). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.8, 137.2, 133.8, 133.1, 131.3, 130.1, 127.2, 126.1, 125.2, 124.3, 41.0, 33.1, 27.2, 25.5, 23.9, 23.1, 19.4, 19.1, 18.7, 18.3, 12.9, 11.3. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{22}H_{30}Si$, 322.2117; found, 322.2111.

*trans-2,3-Diethyl-1,1-diisopropyl-2,3-dihydro-1-sila-1H-phenalene (**6h**).* **6h** (25.7 mg, 40%) was obtained as a white solid from the reaction using **2** (48.2 mg, 0.199 mmol) and **3h**. Mp: 70−71 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (dd, 1H, J = 8.0 Hz, J = 1.2 Hz, ArH), 7.70 (dd, 1H, J = 8.0 Hz, J = 1.2 Hz, ArH), 7.68 (dd, 1H, J = 6.8 Hz, J = 1.6 Hz, ArH), 7.46 (dd, 1H, J = 8.0 Hz, J = 6.8 Hz, ArH), 7.35 (dd, 1H, J = 8.0 Hz, J = 6.8 Hz, ArH), 7.25 (dd, 1H, J = 6.4 Hz, J = 1.2 Hz, ArH), 3.15 (ddd, 1H, J = 9.2 Hz, J = 5.2 Hz, J = 2.8 Hz, ArC*H*(Et)), 1.75−1.50 (m, 3H), 1.48−1.36 (m, 2H), 1.35−1.22 (m, 8H), 1.10 (t, 3H, J = 6.8 Hz, Et), 0.86 (d, 3H, J = 7.2 Hz, *i*-Pr), 0.85 (d, 3H, J = 7.2 Hz, *i*-Pr), 0.69 (t, 3H, J = 7.2 Hz, Et). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.1, 135.9, 133.7, 133.1, 131.4, 129.7, 128.1, 127.3, 124.7, 124.4, 49.3, 31.5, 27.3, 22.9, 19.1, 19.0, 18.7 (2C), 14.2, 13.9, 13.4, 11.9. Anal. Calcd for **6h** ($C_{22}H_{32}Si$): C, 81.41; H, 9.94. Found: C, 81.32; H, 10.10.

*cis-2,3-Diethyl-1,1-diisopropyl-2,3-dihydro-1-sila-1H-phenalene (**6i**).* **6i** (3.4 mg, 5%) was obtained as a colorless oil from the reaction using **2** (47.8 mg, 0.197 mmol) and **3i**. ^{1}H NMR ($CDCl_3$, 400 MHz, 253 K): δ 7.86 (d, 1H, J = 8.0 Hz, ArH), 7.71 (d, 1H, J = 8.0 Hz, ArH), 7.68 (d, 1H, J = 6.8 Hz, ArH), 7.44 (dd, 1H, J = 8.4 Hz, J = 6.8 Hz, ArH), 7.35 (dd, 1H, J = 8.0 Hz, J = 6.8 Hz, ArH), 7.27−7.22 (m, 1H, ArH), 3.04 (td, 1H, J = 12.0 Hz, J = 2.8 Hz, ArC*H*(Et)), 1.95−1.70 (m, 3H), 1.55−1.45 (m, 1H), 1.53−1.42 (m, 1H), 1.28 (t, 6H, J = 6.0 Hz, *i*-Pr), 1.25−1.12 (m, 2H), 1.09 (t, 3H, J = 7.2 Hz, Et), 0.81 (d, 3H, J = 7.6 Hz, *i*-Pr), 0.69 (d, 3H, J = 7.2 Hz, *i*-Pr), 0.55 (t, 3H, J = 7.2 Hz, Et). ^{13}C NMR ($CDCl_3$, 100 MHz, 253 K): δ 142.5, 135.6, 133.7, 132.9, 132.2, 129.7, 127.22, 127.16, 124.4, 124.1, 48.1, 27.8, 25.5, 21.6, 19.7, 19.6, 18.6, 18.5, 13.9, 13.6, 13.0, 12.5. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{22}H_{32}Si$, 324.2273; found, 324.2269.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00793.

The selected NMR spectra of **4**−**6** and crystallographic data of **6e** (PDF)

CIF data for **6e** (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: hidekazu.arii@cc.miyazaki-u.ac.jp.

*E-mail: kunio.mochida@gakushuin.ac.jp.

*E-mail: kawashima.t@gunma-u.ac.jp.

Notes

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