RADICAL REACTION OF 1-(2-BROMOARYLMETHYL)-2-SILATETRALINS : FORMATION OF POLYCYCLIC ORGANOSILICON COMPOUNDS

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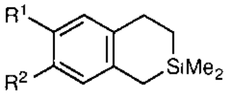
Abstract ----Radical reaction of 1-(2-bromoarylmethyl)-2-silatetralins (**4a**-**f**) with Bu_3SnH in boiling benzene containing AIBN was found to give novel tetracyclic (**5a**-**f**) and tricyclic (**6a**-**f**) organosilicon compounds, and 9-silylphenanthrenes (**7a**-**c**), respectively.

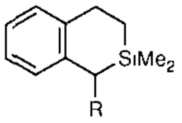
Introduction

Recently,[1] we have reported that 2-silatetralins (**1**) having oxygen functional groups are readily synthesized by intramolecular Friedel-Crafts reaction coupled with the Grignard reaction. Furthermore, alkylation[2] of 2-silatetralins (**1a**) with alkyl halides under basic conditions was found to give rise to the corresponding 1-alkyl-2-silatetralins (**2**) in fair to good yields. In connection of our studies on synthesis and reaction of organosilicon compounds, the 1-alkyl-2-silatetralins thus obtained attracted our attention on synthesis of polycyclic silicon-containing compounds from them, because they might have a promise of biologically active silicon-containing compounds.

Numerous methods for construction of polycyclic ring systems have been reported ; photochemical cyclization,[3] phenolic[4] and non-phenolic[5] oxidative coupling reaction, the Pschorr reaction,[6] the intramolecular benzyne reaction,[7] radical reaction[8] and so on. Among them, at the present time, we tried synthesis of polycyclic silicon-containing compounds by radical reaction, because the reaction is known to proceed under mild conditions.[9] The present paper deals with synthesis of polycyclic silicon-containing compounds by radical reaction.



1 : R^1=H, OMe
R^2=H, OMe



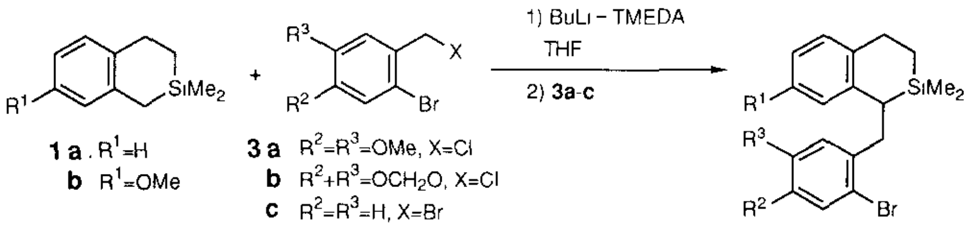
2 R=Me, CH_2Ph

RESULT AND DISCUSSION

Synthesis of 1-(2-Bromoarylmethyl)-2-silatetralins (4a-f)

Alkylation[2] of 2-silatetralin (**1a**) with alkyl halide under basic conditions readily proceeded at 1-position to give 1-alkyl-2-silatetralins (**2**) in fair to good yields. Therefore, the method was applied to synthesis of the 1-(2-bromoarylmethyl)-2-silatetralins (**4a-f**) as the starting material for radical cyclization.

Lithiation of 2-silatetralin (**1a**) with butyllithium (BuLi) (1.2 eq.) in tetrahydrofuran (THF) containing tetramethylethylenediamine (TMEDA) (1.2 eq.) at 0-5 °C for 1.5 h followed by treatment with 2-bromoveratryl chloride[10] gave in 67 % yield 1-(2-bromoveratryl)-2-silatetralin (**4a**) as colorless oil. Structure of **4a** was determined on the basis of proton nuclear magnetic resonance and mass spectra (^{1}H-nmr and ms). Analogously, 1-(2-bromoarylmethyl)-2-silatetralins (**4b-f**) were obtained in moderate yields. The results are listed in Table 1.



1 a : R^1=H
b R^1=OMe

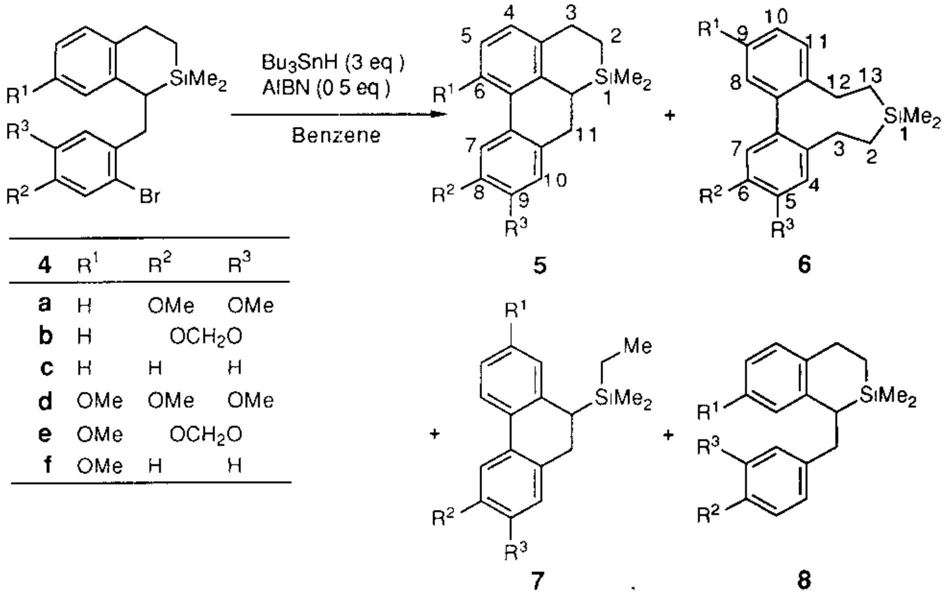
3 a R^2=R^3=OMe, X=Cl
b R^2+R^3=OCH_2O, X=Cl
c R^2=R^3=H, X=Br

4a-f

Table 1 Yields and ^{1}H-Nmr Spectra for 1-(2-Bromoarylmethyl)-2-silatetralins (**4a-f**)

	Compound **4**			Yield (%)	^{1}H-Nmr δ (*J*, Hz)				
	R^1	R^2	R^3		SiMe$_2$	3-H	1-H	OMe	OCH$_2$O
a	H	OMe	OMe	67	-0.06, 0.11 (each s)	0.84 (t, 7.1)	2.41 (dd, 7.1, 8.6)	3.59, 3.84 (each s)	—
b	H	OCH$_2$O		16	-0.02, 0.01 (each s)	0.59-0.95 (m)	2.46 (t, 7.1)	—	5.89 (s)
c	H	H	H	24	-0.05, 0.04 (each s)	0.68-0.95 (m)	2.56 (t, 8.6)	—	—
d	OMe	OMe	OMe	48	-0.06, 0.09 (each s)	0.82 (t, 7.1)	2.41 (dd, 7.1, 8.6)	3.64, 3.65, 3.84 (each s)	—
e	OMe	OCH$_2$O		36	-0.02, -0.01 (each s)	0.64-0.94 (m)	2.44 (t, 7.1)	3.69 (s)	5.89 (s)
f	OMe	H	H	36	-0.06, 0.04 (each s)	0.59-0.99 (m)	2.52 (t, 7.1)	3.64 (s)	—

Radical Reaction of 4 leading to Cyclized Products (5, 6, and 7)



4	R^1	R^2	R^3
a	H	OMe	OMe
b	H	OCH$_2$O	
c	H	H	H
d	OMe	OMe	OMe
e	OMe	OCH$_2$O	
f	OMe	H	H

5 **6** **7** **8**

The reaction of **4a** with tributyltin hydride (Bu_3SnH) (2.0 eq) in boiling benzene (0.01 M) containing azobisisobutyronitrile (AIBN ; 0.5 eq.) for 2 h did not take place completely. Therefore, the reaction was carried out with 3 eq. of Bu_3SnH in the same concentration. After usual work-up, the reaction mixture was separated by silica gel column chromatography followed by medium pressure liquid and then preparative thin layer chromatographies (mplc and prep. tlc) to give tetracyclic (**5a**) and tricyclic silicon compounds (**6a** and **7a**) together with debrominated product (**8a**) (14 %) in 32, 19, and 3 % yields, respectively. ^{1}H-Nmr spectrum of **5a** showed one proton due to aromatic proton at 7-position at δ 7.21 (s) and one proton due to aromatic proton at 6-position at δ 7.59 (dd, *J* = 1.4, 7.1 Hz) and in the ms a molecular peak (M^+) was measured at *m/z* 324. On the other hand, ms of **6a**, **7a**, and **8a** showed the same molecular peaks (M^+) at *m/z* 326. ^{1}H-Nmr spectrum of **6a** indicated a pair of two methylene protons at δ 0.60-0.89 (4H) and 2.17-2.84 (4H) as each multiplet, while that of **7a** showed peaks due to an ethyl group at δ 0.31 (q, *J* = 7.1 Hz) and 0.79 (t, *J* = 7.1 Hz). From these spectral data structures of **5a**, **6a**, and **7a** were proved to be 8,9-dimethoxydibenzo[*de,g*]-1-siladecalin, 5,6-dimethoxydibenzo[*d,f*]-1,1-dimethyl-1-silacyclononane, and 9-ethyldimethylsilyl-2,3-dimethoxy-9,10-dihydrophenanthrene, respectively. Compound (**8a**) was also determined to be 1-veratryl-2,2-dimethyl-2-silatetralin on the basis of ^{1}H-nmr. Moreover, in order to examine effect of the solvent and the concentration on yield of **5a**, the reaction of **4a** in toluene (0.01 M) or *o*-xylene (0.01 M) was carried out under conditions similar to those noted for the reaction of **4a** in benzene However, no remarkable improvement[11] in the reaction was observed. The reaction in benzene (0 01 M) using syringe pump or in low concentration (0.002 M) did not proceed completely Thus, the reaction of **4b** and **4c** was performed under the conditions similar to those noted for the reaction of **4a** in benzene to provide **5b** (23 %), **6b** (24 %), and **7b** (3 %) and **5c**,[12] **6c** (19 %), and **7c** (4 %) along with **8b** (8 %) and **8c**,[2, 12] respectively. Carbon nuclear magnetic resonance (^{13}C-nmr) spectrum for **6c** supported also the structure.

Next, radical reaction of **4d** was investigated, because the presence of a methoxyl group at 7-position might decrease formation of a phenanthrene such as **7** (see Scheme 1). Thus, the reaction of **4d** was performed under the conditions similar to those noted for **4a**. However, the reaction did not proceed completely and the starting material (**4d**) was recovered in 35 % yield.

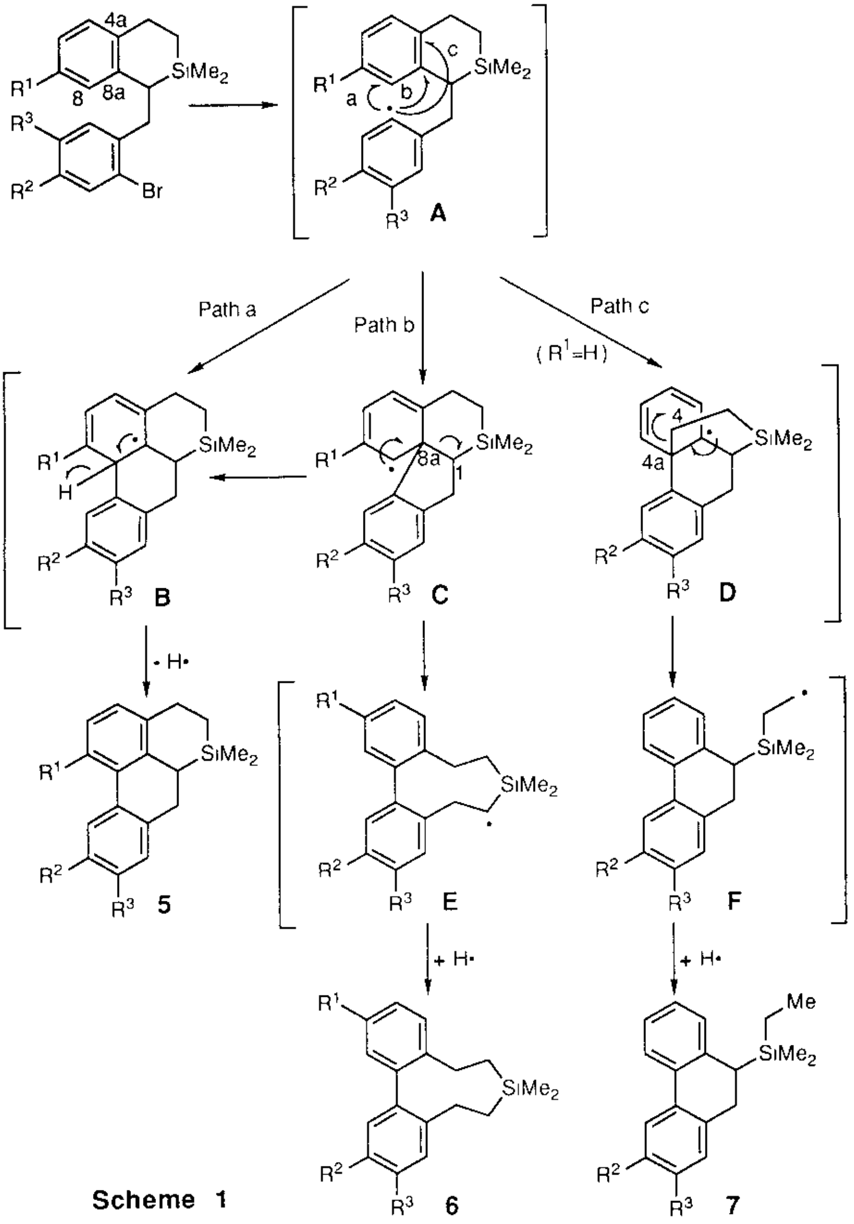
After several attempts to examine reaction conditions, 12 molar eq. of Bu_3SnH were required for disappearance of the starting material on tlc. Purification of the reaction mixture by the methods similar to those noted for **4a** gave **5d**, **6d**, and **8d** together with **3d** (4 %) in 11, 12, and 14 % yields, respectively. No phenanthrene derivative (**7d**) was detected. Structures of **5d**, **6d**, and **8d** were characterized on the spectral data. Similarly, **4e**, **f** gave **5e**, **f**, **6e**, **f**, and **8e**, **f**,[2] respectively. The results are listed in Table 2.

Table 2 Yields of Cyclized Products (**5**, **6**) and Debrominated Compounds (**8**)

Starting Materials	Bu_3SnH (eq.)	Yield (%) a)		
4 (R^1=OMe)		**5**	**6**	**8**
d : R^2=R^3=OMe	3b)	23	6	5
	12c)	11	12	14
e : R^2+R^3=OCH_2O	3	21	8	–d)
	12e)	24	14	22
f : R^2=R^3=H	3	22	7	–f)
	12	23	8	–g)

a) Isolated yield b) **4d** was recovered in 35 % yield c) **4d** was recovered in 4 % yield.
d) Product ratio (**8e** : **4e** = 2.0 : 1) was estimated by glc analysis.
e) **4e** was not isolated. f) Product ratio (**8f** : **4f** = 1.6 : 1) was estimated by glc analysis.
g) Product ratio (**8f** : **4f** = 5.1 : 1) was estimated by glc analysis.

The reaction pathway on formation of **5**, **6**, and **7** was deduced as follows. A radical intermediate (**A**) generated from **4** would be able to attack on 8- (path a), 8a- (path b), or 4a-position (path c) to produce further radical intermediate (**B**, **C** or **D**) as depicted in Scheme 1. Elimination of hydrogen radical from intermediate (**B**) provided **5**, which might be also formed from intermediate (**C**) by rearrangement and elimination of hydrogen radical (paths a and b). Compound (**6**) would be produced through intermediate (**E**) by cleavage of a carbon-carbon bond between 8a- and 1-positions in intermediate (**C**) (path b). On the other hand, intermediate (**D**) would provide radical (**F**) by ß-effect of a silicon atom to give **7**. With **4d**-**f**, however, generation of radical intermediate **D** might be prevented by a methoxyl group at 7-position, although the reason remains uncertain.



Scheme 1

In conclusion, radical reaction of 1-(2-bromoarylmethyl)-2-silatetralins was proved to give tetracyclic (**5**) and tricyclic (**6**) organosilicon compounds, and 9-silylphenanthrenes (**7a**-**c**), respectively. The present results suggested the possibility on synthesis of polycyclic organosilicon compounds Evaluation on biological activity of the polycyclic organosilicon compounds is now under way.

ACKNOWLEDGEMENT

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EXPERIMENTAL

General.—— All melting points were measured on Büchi or Yanagimoto (hot plate) melting point apparatus and are uncorrected. Ir spectra were taken with a Hitachi model 260-10 spectrophotometer in $CHCl_3$ solution, unless otherwise noted. ^{1}H-Nmr and ^{13}C-nmr spectra were recorded on a JEOL model FX-100 spectrometer in $CDCl_3$ solution using $CHCl_3$ as internal standard, unless otherwise noted. Ms were measured on a Hitachi M-80 or M-80A spectrometer. HRms were measured on a Hitachi M-80 spectrometer. Ball-to-ball distillation was carried out by means of a Sibata glass tube oven model GTO-250RS. Mplc was carried out by a Kusano kagakukikai KP-6H or KPW-20 micro pump. Prep tlc was performed with Kieselgel 60F$_{254}$ Art. 5744 (Merck) or Kieselgel 60GF$_{254}$ Art 7730 (Merck) For column chromatography, silica gel (Wako gel C-200) was used.

Materials.—— THF was distilled from sodium wire and benzophenone prior to use. Benzene, toluene or *o*-xylene was distilled from CaH_2 or $LiAlH_4$ prior to use. Bu_3SnH was purchased from Aldrich Chemical Company, Inc.

General Procedure for Preparation of 1-(2-Bromoarylmethyl)-2,2-dimethyl-2-silatetralins (4a-f) —— A solution of BuLi (BuLi-hexane) was added dropwise to an ice-cold, stirred solution of 2-silatetralin (**1a**) and TMEDA in THF under Ar stream and the whole was stirred at 0-5 °C for 1.5 h. A solution of 2-bromoarylmethyl bromide or chloride in THF was added dropwise to the mixture and stirring was continued at the same temperature for 1 h. The reaction was quenched with addition of water The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with 10 % HCl and brine, and dried ($MgSO_4$). Removal of the solvent *in vacuo* followed by ball-to-ball distillation under reduced pressure gave an oily residue, which was purified by column chromatography combined with prep. tlc.

4a : A mixture of **1a** (529 mg, 3.0 mmol), TMEDA (0 54 ml, 3.6 mmol) and 1.18 M BuLi-hexane (3.1 ml, 3.6 mmol) in THF (30 ml) was allowed to react with **3a**[10] (956 mg, 3.6 mmol) in THF (6 ml) to give a brown oil (967 mg). Column chromatography (twice) of the oil with hexane-AcOEt (30 : 1) and (40 . 1), successively, furnished **4a** (811 mg, 67 %), which was purified by ball-to-ball distillation to give **4a** [679 mg, 56 %, bp 156-187 °C / (5.0-6.0)x10^{-3} Torr.] as a colorless oil. ^{1}H-Nmr δ : -0.06, 0.11 (6H, each s, $SiMe_2$), 0.84 (2H, t, *J* = 7.1 Hz, C_3-H), 2.41 (1H, dd, *J* = 7.1, 8.6 Hz, C_1-H), 2.65-3.34 (4H, m, C_4-H, C*H*$_2$Ph), 3.59, 3.84 (6H, each s, 2xOMe), 6 28 (1H, s, Ar-H), 6.61-6.81 (1H, m, Ar-H), 6.85-7.21 (4H, m, 4xAr-H). Ir : 1260 (SiMe) cm^{-1}. Ms *m/z* (rel. int., %) : 406 (M^++2, 22), 404 (M^+, 21), 229 (100) ; HRms *m/z* calcd for $C_{20}H_{25}O_2BrSi$ (M^+) : 404.0806, found : 404.0800.

4b : A mixture of **1a** (529 mg, 3.0 mmol), TMEDA (0.54 ml, 3 6 mmol) and 1.55 M BuLi-hexane (2.3 ml, 3.6 mmol) in THF (30 ml) was allowed to react with **3b**[13] (898 mg, 3.6 mmol) in THF (7 ml) to give a brown oil (450 mg). Column chromatography of the oil with hexane and hexane-AcOEt (100 : 1) followed by that with hexane afforded **4b** (192 mg, 16 %), purification of which by ball-to-ball distillation gave a pale yellow oil (161 mg, 14 %, bp 170-185 °C / 7.8x10^{-3} Torr.). ^{1}H-Nmr δ : -0.02, 0.01 (6H, each s, $SiMe_2$), 0.59-0.95 (2H, m, C_3-H), 2.46 (1H, t, *J* = 7.1 Hz, C_1-H), 2.65-2.99 (2H, m, C_4-H), 3.12 (2H, d, *J* = 7.1 Hz, C*H*$_2$Ph), 5.89 (2H, s, OCH_2O), 6.48 (1H, s, Ar-H), 6.64-7.15 (5H, m, 5xAr-H). Ir : 1245 (SiMe) cm^{-1}. Ms *m/z* (rel int., %) : 390 (M^++2, 22), 388 (M^+, 21), 59 (100) ; HRms *m/z* calcd for $C_{19}H_{21}O_2BrSi$ (M^+) : 388 0492, found : 388.0490.

4c · A mixture of **1a** (529 mg, 3.0 mmol), TMEDA (0.54 ml, 3 6 mmol) and 1.59 M BuLi-hexane (2.3 ml, 3.6 mmol) in THF (30 ml) was allowed to react with **3c**[14] (900 mg, 3.6 mmol) in THF (6 ml) to give a brown oil (777 mg). Repeated (four times) column chromatography of the oil with hexane gave **4c** (251 mg, 24 %) as a colorless oil, which was crystallized by trituration in MeOH to give a solid. Analytical sample had mp 70-70.5 °C (MeOH). Anal. Calcd for $C_{18}H_{21}BrSi$: C, 62.60; H, 6.13 Found : C, 62.53; H, 6.12. ^{1}H-Nmr δ -0 05, 0 04 (6H, each s, $SiMe_2$), 0.68-0.95 (2H, m, C_3-

H), 2.56 (1H, t, J = 8.6 Hz, C_1-H), 2.76-3.02 (2H, m, C_4-H), 3.21 (2H, d, J = 8.6 Hz, CH_2Ph), 6.68-7.21 (7H, m, 7xAr-H), 7.44-7.64 (1H, m, Ar-H). Ir (KBr) : 1270 (SiMe) cm^{-1}, ms m/z (rel. int., %) : 346 (M^++2, 5), 344 (M^+, 6), 59 (100).

4d : A *mixture* of **1b**[1] (516 mg, 2.5 mmol), TMEDA (0.45 ml, 3.0 mmol) and 1.48 M BuLi-hexane (2.0 ml, 3.0 mmol) in THF (25 ml) was allowed to react with **3a** (730 mg, 2.75 mmol) in THF (7.5 ml) to give an orange red oil (1.03 g). Column chromatography of the oil with hexane-AcOEt (70 : 1 and 50 : 1) produced fractions A (165 mg) and B (500 mg). The fraction A was separated by prep. tlc (three developments with hexane : AcOEt = 20 : 1) to give fraction C (140 mg). Combined fractions B and C were twice chromatographed with hexane-AcOEt (70 : 1, 50 : 1) to afford **4d** (552 mg, 48 %), purification of which by ball-to-ball distillation furnished **4d** [497 mg, 46 %, bp 190-210 °C / (5.0-6.6)x10^{-3} Torr.] as a pale yellow oil. ^{1}H-Nmr δ : -0.06, 0.09 (6H, each s, $SiMe_2$), 0.82 (2H, t, J = 7.1 Hz, C_3-H), 2.41 (1H, dd, J = 7.1, 8.6 Hz, C_1-H), 2.68-3.21 (4H, m, C_4-H, CH_2Ph), 3.64, 3.65, 3.84 (9H, each s, 3xOMe), 6.36 (2H, s, C_8-H, Ar-H), 6.56 (1H, dd, J = 2.9, 8.6 Hz, C_6-H), 6.99 (1H, s, Ar-H), 7.02 (1H, d, J = 8.6 Hz, C_5-H). Ir : 1260 (SiMe) cm^{-1}. Ms m/z (rel. int., %) : 436 (M^++2, 8), 434 (M^+, 7), 231 (100) ; HRms m/z calcd for $C_{21}H_{27}O_3BrSi$ (M^+) : 434.0912, found : 434.0911.

4e : A mixture of **1b** (516 mg, 2.5 mmol), TMEDA (0.45 ml, 3.0 mmol) and 1.21 M BuLi-hexane (2.5 ml, 3.0 mmol) in THF (25 ml) was allowed to react with **3b** (748 mg, 3.0 mmol) in THF (7.5 ml) to give a brownish oily crystals (598 mg). Column chromatography with hexane : AcOEt = 150 : 1 followed by flash chromatography wiht hexane : AcOEt = 20 : 1 gave fractions A (173 mg) and B (269 mg). Prep. tlc of the fraction A (five developments with AcOEt = 40 : 1) gave fraction C (157 mg). Combined fractions B and C were crystallized by trituration to give **4e** (381 mg, 36 %, mp 84.5-91 °C) as pale yellow crystals. Colorless prisms of mp 97-99 °C (hexane) were used as analytical sample. Anal. Calcd for $C_{20}H_{23}O_3BrSi$: C, 57.28; H, 5.53. Found : C, 57.30; H, 5.63. ^{1}H-Nmr δ : -0.02, -0.01 (6H, each s, $SiMe_2$), 0.64-0.94 (2H, m, C_3-H), 2.44 (1H, t, J = 7.1 Hz, C_1-H), 2.68-2.94 (2H, m, C_4-H), 3.09 (2H, d, J = 7.1 Hz, CH_2Ph), 3.69 (3H, s, OMe), 5.89 (2H, s, OCH_2O), 6.42 (1H, d, J = 2.9 Hz, C_8-H), 6.51 (1H, s, Ar-H), 6.58 (1H, dd, J = 2.9, 8.6 Hz, C_6-H), 6.99 (1H, s, Ar-H), 7.01 (1H, d, J = 8.6 Hz, C_5-H). Ir (KBr) : 1240 (SiMe) cm^{-1}; ms m/z (rel. int., %) : 420 (M^++2, 5), 418 (M^+, 5), 59 (100).

4f : A mixture of **1b** (516 mg, 2.5 mmol), TMEDA (0.45 ml, 3.0 mmol) and 1.48 M BuLi-hexane (2.0 ml, 3.0 mmol) in THF (25 ml) was allowed to react with **3c** (687 mg, 2.75 mmol) in THF (7.5 ml) to give a brownish oil (665 mg). Twice column chromatography with hexane gave **4f** (334 mg, 36 %), purification of which by ball-to-ball distillation gave **4f** [317 mg, 34 %, bp 130-170 °C / (5.5-6.0)x 10^{-3} Torr.]. ^{1}H-Nmr δ : -0.06, 0.04 (6H, each s, $SiMe_2$), 0.59-0.99 (2H, m, C_3-H), 2.52 (1H, t, J = 7.1 Hz, C_1-H), 2.66-2.99 (2H, m, C_4-H), 3.19 (2H, d, J = 7.1 Hz, CH_2Ph), 3.64 (3H, s, OMe), 6.38 (1H, d, J = 2.9 Hz, C_8-H), 6.58 (1H, dd, J = 2.9, 7.1 Hz, C_6-H), 6.85-7.19 (4H, m, 4xAr-H), 7.44-7.61 (1H, m, Ar-H). Ir : 1250 (SiMe) cm^{-1}. Ms *m/z* (rel. int., %) : 376 (M^++2, 23), 374 (M^+, 22), 205 (100) ; HRms *m/z* calcd for $C_{19}H_{23}OBrSi$ (M^+) : 374.0700, found : 374.0697

Radical Reaction of 1-(2-Bromoarylmethyl)-2,2-dimethyl-2-silatetralins (4a-f) —— With **4a** : **4a** (203 mg, 0.5 mmol), AIBN (41 mg, 0.25 mmol), Bu_3SnH (437 mg, 1.5 mmol), and benzene (50 ml) were used. After refluxing for 2 h, a residue (684 mg) obtained on removal of the solvent was purified by column chromatography with hexane and AcOEt to give a yellow oil (234 mg). The oil was purified by further column chromatography with hexane-AcOEt (30 : 1) to furnish a pale yellow oil (207 mg), which was subjected to mplc [petroleum ether (bp 47-64 °C) : AcOEt = 400 : 1, 200 : 1, 100 : 1, and 10 : 1] to be separated into fractions A (40 mg), B (8 mg), C (27 mg), and D (66 mg), respectively. Fraction A . **6a** (31 mg, 19 %) as a colorless oil was obtained by further prep. tlc [twice developments with petroleum ether : AcOEt = 10 : 1]. **6a** : ^{1}H-Nmr (CD_3OD) δ : -0.41, -0.39 (6H, each s, $SiMe_2$), 0.60-0.89 [4H, m, $(CH_2)_2Si$], 2.17-2.84 [4H, m, $(CH_2CH_2)_2Si$], 3.73, 3.84 (6H, each s, 2xOMe), 6.56, 6.84 (2H, each s, 2xAr-H), 6.90-7.33 (4H, m, 4xAr-H). Ir : 1240 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{20}H_{26}O_2Si$ (M^+) . 326.1701, found : 326.1710; ms *m/z* (rel. int., %) : 326 (M^+, 75), 255 (100). Fraction B : **7a** (5 mg, 3 %) as a colorless oil was obtained by further prep. tlc similar to that noted for **6a**. **7a** : ^{1}H-Nmr δ -0.29, -0.28 (6H, each s, $SiMe_2$), 0.31 (2H, q, J = 7.1 Hz, $SiCH_2Me$), 0.79 (3H, t, J = 7.1 Hz, $SiCH_2Me$), 2.45 (1H, dd, J = 1.4, 7.1 Hz, CHSi), 2.76 [1H, dd, J = 1.4, 14.3 Hz, CH(H)CHSi], 3.25 [1H, dd, J = 7.1, 14.3 Hz, CH(H)CHSi], 3.91, 3.95 (6H, each s, 2xOMe), 6.69 (1H, s, Ar-H), 6.96-7.22 (4H, m, 4xAr-H), 7.52-7.71 (1H, m, Ar-H). Ir : 1265 (SiMe) cm^{-1} HRms *m/z* calcd for $C_{20}H_{26}O_2Si$ (M^+) : 326.1700, found : 326.1689; ms *m/z* (rel. int., %) : 326 (M^+, 52), 311 (100), 238 (M^+-$SiHMe_2Et$, 58). Fraction C : **8a** (22 mg, 14 %, mp 62-64 °C) was obtained by further prep. tlc similar to that noted for **6a**. Colorless prisms of mp

68-69 °C (MeOH-H_2O) was used as analytical sample **8a**. Anal. Calcd for $C_{20}H_{26}O_2Si$: C, 73.57; H, 8.03. Found : C, 73.62, H, 7.99. ^{1}H-Nmr δ : -0.15, -0.06 (6H, each s, $SiMe_2$), 0.59-0.99 (2H, m, C_3-H), 2.36 (1H, dd, *J* = 7.1, 8.6 Hz, C_1-H), 2.64-3.28 (4H, m, C_4-H, $SiCHC\mathit{H}_2$), 3.79, 3.85 (6H, each s, 2xOMe), 6.64 (1H, s, Ar-H), 6.74 (2H, s, 2xAr-H), 6.85-7.16 (4H, m, 4xAr-H). Ir (KBr) : 1255 (SiMe) cm^{-1}; ms *m/z* (rel. int., %) : 326 (M^+, 10), 151 (100). Fraction D : **5a** (52 mg, 32 %) was obtained by further prep. tlc similar to that noted for **6a** (four developments). Analytical sample had mp 106 °C (hexane) as colorless plates. **5a** : Anal. Calcd for $C_{20}H_{24}O_2Si$: C, 74.03; H, 7.45. Found : C, 73.70; H, 7.49. ^{1}H-Nmr δ : 0.04, 0.25 (6H, each s, $SiMe_2$), 0.64-1.21 (2H, m, C_2-H), 2.09 (1H, dd, *J* = 8.6, 11.4 Hz, CHSi), 2.56-3.16 (4H, m, C_3-H, C_{11}-H), 3.92, 3.95 (6H, each s, 2xOMe), 6.74 (1H, s, Ar_{10}-H), 7.02 (1H, dd, *J* = 1.4, 7.1 Hz, Ar_4-H), 7.15 (1H, t, *J* = 7.1 Hz, Ar_5-H), 7.21 (1H, s, Ar_7-H), 7.59 (1H, dd, *J* = 1.4, 7.1 Hz, Ar_6-H). Ir (KBr) : 1260 (SiMe) cm^{-1}; ms *m/z* (rel. int., %) : 324 (M^+, 100).

With **4b** : **4b** (195 mg, 0.5 mmol), AIBN (41 mg, 0.25 mmol) Bu_3SnH (437 mg, 1.5 mmol), and benzene (50 ml) were used. After refluxing for 2 h, a residue (656 mg) obtained on removal of the solvent *in vacuo* was subjected to column chromatography with hexane and hexane-AcOEt (20 : 1) to give a pale yellow oil (182 mg). The oil was purified by further column chromatography with hexane-AcOEt (40 : 1) to furnish a pale yellow oil (160 mg), mplc of which with hexane-AcOEt (400 : 1) afforded fractions A (40 mg) and B (73 mg), respectively. From fraction A, **6b** (37 mg, 24 %, colorless oil) and **7b** (5 mg, 3 %, colorless oil) were obtained by further prep. tlc (five developments with hexane : AcOEt = 50 : 1). **6b** : ^{1}H-Nmr (CD_3OD) δ : -0.41, -0.36 (6H, each s, $SiMe_2$), 0.57-0.93 [4H, m, $(CH_2)_2Si$], 2.13-2.86 [4H, m, $(C\mathit{H}_2CH_2)_2Si$], 5.90 (2H, s, OCH_2O), 6.44, 6.74 (2H, each s, 2xAr-H), 6.87-7.33 (4H, m, 4xAr-H). Ir : 1245 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{19}H_{22}O_2Si$ (M^+) : 310.1387, found : 310.1387; ms *m/z* (rel. int., %) : 310 (M^+, 68), 239 (100). **7b** : ^{1}H-Nmr δ : -0.26, -0.25 (6H, each s, $SiMe_2$), 0.34 (2H, q, *J* = 7.1 Hz, $SiC\mathit{H}_2Me$), 0.81 (3H, t, *J* = 7.1 Hz, $SiCH_2\mathit{Me}$), 2.42 (1H, dd, *J* = 1.4, 7.1 Hz, CHSi), 2.76 [1H, dd, *J* = 1.4, 14.3 Hz, C*H*(H)CHSi], 3.22 [1H, dd, *J* = 7.1, 14.3 Hz, CH(*H*)CHSi], 5.95, 5.98 (2H, each d, *J* = 1.4 Hz, OCH_2O), 6.66 (1H, s, Ar-H), 6.92-7.24 (4H, m, 4xAr-H), 7.45-7.76 (1H, m, Ar-H). Ir : 1275 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{19}H_{22}O_2Si$ (M^+) : 310.1388, found : 310.1396; ms *m/z* (rel. int., %) : 310 (M^+, 27), 222 (M^+-$SiHMe_2Et$, 59), 59 (100). Mplc of fraction B with hexane-AcOEt (400 : 1) produced an oil (67 mg), prep. tlc of which [developing solvents; hexane : AcOEt = 30 : 1 (two developments), 20 : 1 and 30 : 1 and, petroleum ether : AcOEt = 30 : 1 and 10 : 1 (two developments)] afforded fractions C (13 mg) and D (39 mg). Fraction D gave fraction E (5 mg) and **5b** (35 mg, 23 %, colorless oil) by further prep. tlc (three developments with petroleum ether : AcOEt = 10 : 1). **5b** : ^{1}H-Nmr δ : 0.04, 0.25 (6H, each s, $SiMe_2$), 0.62-1.06 (2H, m, C_2-H), 2.05 (1H, dd, *J* = 8.6, 11.4 Hz, CHSi), 2.59-3.19 (4H, m, C_3-H, C_{11}-H), 5.95 (2H, s, OCH_2O), 6.69 (1H, s, Ar_{10}-H), 7.02 (1H, dd, *J* = 1.4, 7.1 Hz, Ar_4-H), 7.14 (1H, t, *J* = 7.1 Hz, Ar_5-H), 7.18 (1H, s, Ar_7-H), 7.52 (1H, dd, *J* = 1.4, 7.1 Hz, Ar_6-H). Ir : 1245 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{19}H_{20}O_2Si$ (M^+) : 308.1231, found : 308.1231; ms *m/z* (rel. int., %) : 308 (M^+, 100). Combined fractions C and E were further separated by prep. tlc (two developments with the same developing solvent as noted for fraction D) to give **8b** (13 mg, 8 %, colorless oil). **8b** : ^{1}H-Nmr δ : -0.12, -0.09 (6H, each s, $SiMe_2$), 0.56-1.06 (2H, m, C_3-H), 2.36 (1H, dd, *J* = 7.1, 8.6 Hz, C_1-H), 2.62-3.35 (4H, m, C_4-H, $SiCHCH_2$), 5.91 (2H, s, OCH_2O), 6.68 (3H, s, 3xAr-H), 6.85-7.16 (4H, m, 4xAr-H). Ir : 1250 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{19}H_{22}O_2Si$ (M^+) : 310.1388, found : 310.1391; ms *m/z* (rel. int., %) : 310 (M^+, 18), 135 (100).

With **4c** : **4c** (207 mg, 0.6 mmol), AIBN (49 mg, 0.3 mmol), Bu_3SnH (524 mg, 1.8 mmol), and benzene (60 ml) were used. After refluxing for 2 h, removal of the solvent *in vacuo* gave a pale yellow oily solid (788 mg), which was chromatographed with hexane to give a yellow oil (534 mg). Further column chromatography of the oil with hexane gave a colorless oil (485 mg), mplc of which with cyclohexane was separated into fractions A (110 mg) and B (104 mg). Each fraction was purified by prep. tlc (twice developments with hexane). From fraction A, **6c** (31 mg, 19 %) were obtained. **6c** : ^{1}H-Nmr δ : -0.42 (6H, s, $SiMe_2$), 0.64-0.88 [4H, m, $(CH_2)_2Si$], 2.19-2.84 [4H, m, $(CH_2CH_2)_2Si$], 6.85-7.34 (8H, m, 8xAr-H). ^{13}C-Nmr δ : -1.468 (q, SiMe), 17.545 (t, CH_2Si), 27.605 (t, $ArCH_2$), 125.483, 127.472, 129.286, 129.637 (each d, Ar-C), 141.162, 142.683 (each s, Ar-C). Ir : 1250 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{18}H_{22}Si$ (M^+) : 266.1490, found : 266.1496; ms *m/z* (rel. int., %) : 266 (M^+, 16), 195 (100). The mixture (90 mg) combined with a component obtained from fractions A and B was purified by prep. tlc (three developments with the same developing solvent) to produce **7c** (6 mg, 4 %) and a mixture (71 mg), respectively. **7c** : ^{1}H-Nmr δ : -0.29 (6H, s, $SiMe_2$), 0.31 (2H, q, *J* = 7.1 Hz, $SiCH_2Me$), 0.79 (3H, t, *J* = 7.1 Hz, $SiCH_2Me$), 2.48 (1H, dd, *J* = 1.4, 7.1 Hz, CHSi), 2.88 [1H, dd, *J* = 1.4, 14.3 Hz, *CH*(H)CHSi], 3.31 [1H, dd, *J* = 7.1, 14.3 Hz,

$CH(H)CHSi]$, 6.96-7.41 (6H, m, 6xAr-H), 7.49-7.81 (2H, m, 2xAr-H). Ir 1270 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{18}H_{22}Si$ (M^+) : 266.1489, found : 266.1485; ms *m/z* (rel. int., %) : 266 (M^+, 10), 178 (M^+-$SiHMe_2Et$, 100). The mixture (71 mg) was further purified by prep. tlc (five developments with petroleum ether) to afford an inseparable mixture of **5c** and **8c** in 2.4 : 1 product ratio, which was estimated by glc analysis (column : 1 % OV-1, column temperature, 230 °C, Rt 27.5 min for **5c** ; Rt 13.5 min for **8c**). **5c** : ^{1}H-Nmr δ : 0.05, 0.26 (6H, each s, $SiMe_2$), 2.14 (1H, dd, J = 7.1, 11.4 Hz, CHSi), 7.56-7.81 (2H, m, 2xAr-H); ms *m/z* (rel. int., %) : 264 (M^+, 100). **8c**^{2} : ^{1}H-Nmr δ : -0.16, -0.06 (6H, each s, $SiMe_2$), 2.45 (1H, dd, J = 7.1, 8.6 Hz, C_1-H), ms *m/z* (rel. int., %) : 266 (M^+, 16), 59 (100)

With **4d** : **4d** (218 mg, 0.5 mmol), AIBN (41 mg, 0.25 mmol), Bu_3SnH (1.75 g, 6.0 mmol), and benzene (50 ml) were used. After refluxing for 2 h, work-up similar to noted for **4a** gave an oily solid (2.0g), which was subjected to column chromatography with hexane and hexane-AcOEt (10 : 1 and 5 : 1) to produce an oily solid (244 mg). Mplc of the oily solid with hexane-AcOEt (100 : 1, 70 : 1, 50 : 1, 30 : 1, 20 : 1, and 5 : 1) gave **6d** (21 mg, 12 %, mp 78-80 °C), **4d** (8 mg, 4 %), and fraction A (70 mg). Analytical sample for **6d** had mp 80-80.5 °C (hexane) as colorless prisms. **6d** : Anal. Calcd for $C_{21}H_{28}O_3Si$: C, 70.74; H, 7.91. Found : C, 70.82; H, 7.91. ^{1}H-Nmr δ : -0.36, -0.35 (6H, each s, $SiMe_2$), 0.62-0.91 [4H, m, $(CH_2)_2Si$], 2.19-2.79 [4H, m, $(CH_2CH_2)_2Si$], 3.79, 3.82, 3.92 (9H, each s, 3xOMe), 6.58 (1H, s, Ar_4-H), 6.62 (1H, d, J = 2.9 Hz, Ar_8-H), 6.76 (1H, s, Ar_7-H), 6.85 (1H, dd, J = 2.9, 8.6 Hz, Ar_{10}-H), 7.18 (1H, d, J = 8.6 Hz, Ar_{11}-H). *Ir (KBr) : 1260 (SiMe) cm*$^{-1}$; *ms* *m/z* (rel. int., %) : 356 (M^+, 82), 285 (100). Prep. tlc (four developments with hexane : AcOEt = 5 : 1) of fraction A gave fractions B (36 mg) and C (26 mg). Further purification of fraction B by prep. tlc (three developments with hexane : AcOEt = 5 : 1) led to fractions D (26 mg, mp 141-144.5 °C) and E (3 mg). Prep. tlc (three developments with hexane : AcOEt = 10 : 1) of combined fractions C and E *furnished* ***8d*** *(24 mg, 14 %, colorless oil).* ***8d*** : ^{1}H-Nmr δ : -0.15, -0.06 (6H, each s, $SiMe_2$), 0.51-0.99 (2H, m, C_3-H), 2.34 (1H, t, J = 8.6 Hz, C_1-H), 2.64-3.19 (4H, m, C_4-H, CH_2Ph), 3.69, 3.81, 3.85 (9H, each s, 3xOMe), 6.42-6.76 (5H, m, 5xAr-H), 7.01 (1H, d, J = 8.6 Hz, Ar_5-H). Ir : 1260 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{21}H_{28}O_3Si$ (M^+) : 356.1806, found : 356.1813; ms *m/z* (rel. int., %) : 356 (M^+, 10), 151 (100). Fraction D gave after prep. tlc (four developments with hexane : AcOEt = 5 : 1) **5d** *(20 mg, 11 %, mp 142-146 °C). Analytical sample had mp 151.5-153 °C (hexane) as colorless* prisms. **5d** : Anal. Calcd for $C_{21}H_{26}O_3Si$: C, 71.44, H, 7.39. Found : C, 71.05; H, 7.30. ^{1}H-Nmr δ : -0.04, 0.21 (6H, each s, $SiMe_2$), 0.62-1.02 (2H, m, C_2-H), 1.96 (1H, dd, J = 7.1, 11.4 Hz, CHSi), 2.42-2.99 (4H, m, C_3-H, C_{11}-H), 3.88, 3.89, 3.91 (9H, each s, 3xOMe), 6.72 (1H, s, Ar_{10}-H), 6.76 (1H, d, J = 7.1 Hz, Ar_5-H), 6.98 (1H, d, J = 7.1 Hz, Ar_4-H), 7.89 (1H, s, Ar_7-H). Ir (KBr) : 1255 (SiMe) cm^{-1}; ms m/z (rel. int., %) : 354 (M^+, 100).

With **4e** : **4e** (210 mg, 0.5 mmol), AIBN (41 mg, 0.25 mmol), Bu_3SnH (1.75 g, 6.0 mmol), and benzene (50 ml) were used. After refluxing for 2 h, a residue (2.0 g) obtained in a way similar to that noted for **4a** was subjected to column chromatography with hexane and hexane-AcOEt (20 : 1) to afford a pale yellow oil (246 mg), mplc of which with hexane-AcOEt (100 : 1 and 5 : 1) gave fractions A (67 mg), B (49 mg), and C (45 mg), respectively. Prep. tlc (three developments with hexane : AcOEt = 50 : 1 and three developments with hexane : AcOEt = 40 : 1) of fraction A gave **6e** (23 mg, 14 %, colorless oil). **6e** : ^{1}H-Nmr δ : -0.36, -0.34 (6H, each s, $SiMe_2$), 0.62-0.85 [4H, m, $(CH_2)_2Si$], 2.19-2.75 [4H, m, $(CH_2CH_2)_2Si$], 3.78 (3H, s, OMe), 5.95 (2H, s, OCH_2O), 6.56 (1H, s, Ar_4-H), 6.59 (1H, d, J = 2.9 Hz, Ar_8-H), 6.75 (1H, s, Ar_7-H), 6.84 (1H, dd, J = 2.9, 8.6 Hz, Ar_{10}-H), 7.16 (1H, d, J = 8.6 Hz, Ar_{11}-H). Ir : 1235 (SiMe) cm^{-1}. HRms m/z calcd for $C_{20}H_{24}O_3Si$ (M^+) : 340.1493, found : 340.1495; ms m/z (rel. int., %) : 340 (M^+, 69), 269 (100). Fraction B afford **5e** (40 mg, 24 %, pale yellow oil) by prep. tlc (four developments with hexane : AcOEt = 100 : 1). **5e** : ^{1}H-Nmr δ : -0.02, 0.21 (6H, each s, $SiMe_2$), 0.46-1.15 (2H, m, C_2-H), 1.92 (1H, dd, J = 7.1, 11.4 Hz, CHSi), 2.38-3.06 (4H, m, C_3-H, C_{11}-H), 3.86 (3H, s, OMe), 5.94 (2H, s, OCH_2O), 6.71 (1H, s, Ar_{10}-H), 6.75 (1H, d, J = 7.1 Hz, Ar_5-H), 6.98 (1H, d, J = 7.1 Hz, Ar_4-H), 7.76 (1H, s, Ar_7-H). Ir : 1270 (SiMe) cm^{-1}. HRms m/z calcd for $C_{20}H_{22}O_3Si$ (M^+) : 338.1336, found : 338.1333; ms m/z (rel. int., %) : 338 (M^+, 100). Prep. tlc (development with hexane and four developments with hexane : AcOEt = 100 : 1) of fraction C gave **8e** (38 mg, 22 %, mp 89-92 °C). Analytical sample had mp 93-94 °C (hexane) as colorless prisms. **8e** : Anal. Calcd for $C_{20}H_{24}O_3Si$: C, 70.55; H, 7.10. Found : C, 70.65; H, 7.12. ^{1}H-Nmr δ : -0.14, -0.11 (6H, each s, $SiMe_2$), 0.46-1.02 (2H, m, C_3-H), 2.34 (1H, t, J = 7.1 Hz, C_1-H), 2.58-3.31 (4H, m, C_4-H, CH_2Ph), 3.71 (3H, s, OMe), 5.89 (2H, s, OCH_2O), 6.48-6.78 (5H, m, 5xAr-H), 6.99 (1H, d, J = 8.6 Hz, Ar_5-H). Ir (KBr) : 1245 (SiMe) cm^{-1} , ms m/z (rel. int., %) : 340 (M^+, 19), 135 (100).

With **4f** : **4f** (225 mg, 0.6 mmol), AIBN (49 mg, 0.3 mmol), Bu_3SnH (2.1 g, 7.2 mmol), and benzene (60 ml) were used. After refluxing for 2 h, a residue (2.45 g) obtained on removal of the solvent *in vacuo* was subjected to column chromatography with hexane and hexane-AcOEt (30 : 1) to afford a pale yellow oil (283 mg), which was further separated by mplc with hexane-AcOEt (200 : 1 and 5 : 1) to produce fractions A (186 mg, colorless oil) and B (24 mg, colorless oil). Prep. tlc of fraction A (three developments with hexane : AcOEt = 100 : 1) gave fractions C (17 mg, colorless oil), D (57 mg, pale yellow solid), and E (21 mg, pale yellow oil), respectively. Fractions B [by prep. tlc (three developments with hexane : AcOEt = 50 : 1)] and C [by prep. tlc (four developments with hexane : AcOEt = 100 : 1)] gave an inseparable mixture (32 mg) of **4f** and **8f** in 1 : 5.1 of product ratio, which was estimated by glc analysis (column : 1 % OV-1, column temperature, 255 °C, Rt 23.1 min for **4f** ; Rt 13.7 min for **8f**). **8f**[2] : ^{1}H-Nmr δ : -0.18, -0.08 (6H, each s, $SiMe_2$), 0.48-0.99 (2H, m, C_3-H), 2.41 (1H, t, J = 7.1 Hz, C_1-H), 2.59-3.39 (4H, m, C_4-H, CH_2Ph), 3.69 (3H, s, OMe), 6.48-6.64 (2H, m, 2xAr-H), 6.88-7.24 (6H, m, 6xAr-H); ms *m/z* (rel. int., %) : 296 (M^+, 36), 205 (100). Prep. tlc (five developments with hexane : AcOEt = 100 : 1) of fraction D gave a solid (47 mg, mp 75-77 °C), which was further purified by prep. tlc (three developments with the same developing solvent as noted for fraction D) to produce **5f** (41 mg, 23 %, mp 74.5-77 °C). Analytical sample had mp 82-83 °C (hexane) as colorless needles. **5f** : Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53. Found : C, 77.86; H, 7.40. ^{1}H-Nmr δ : -0.04, 0.21 (6H, each s, $SiMe_2$), 0.49-1.14 (2H, m, C_2-H), 1.95 (1H, dd, J = 7.1, 11.4 Hz, CHSi), 2.46-3.06 (4H, m, C_3-H, C_{11}-H), 3.88 (3H, s, OMe), 6.75 (1H, d, J = 7.1 Hz, Ar_5-H), 6.99 (1H, d, J = 7.1 Hz, Ar_4-H), 7.02-7.22 (3H, m, 3xAr-H), 8.09-8.29 (1H, m, Ar_7-H). Ir (KBr) : 1270 (SiMe) cm^{-1}; ms *m/z* (rel. int., %) : 294 (M^+, 100). Repeated (twice) prep. tlc (three developments with hexane : AcOEt = 100 : 1) of fraction E gave **6f** (15 mg, 8 %) as a pale yellow oil. **6f** : ^{1}H-Nmr δ : -0.38, -0.35 (6H, each s, $SiMe_2$), 0.59-0.91 [4H, m, $(CH_2CH_2)_2Si$], 2.24-2.84 [4H, m, $(CH_2CH_2)_2Si$], 3.78 (3H, s, OMe), 6.62 (1H, d, J = 2.9 Hz, Ar_8-H), 6.85 (1H, dd, J = 2.9, 8.6 Hz, Ar_{10}-H), 6.99-7.35 (5H, m, 5xAr-H). Ir : 1260 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{19}H_{24}OSi$ (M^+) : 296.1594, found : 296.1586; ms *m/z* (rel. int., %) : 296 (M^+, 61), 225 (100).

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11. The product ratios were estimated to be 7 : 1 : 1.4 : 1 (toluene) or 8 : 1 : 3 : 2 (*o*-xylene) for **5a** : **6a** : **7a** : **8a** by hplc analysis. When the boiling point of the solvent became high, the product ratio for **7a** increased slightly.

12. Compounds **5c** and **8c** were inseparable. Therefore, the product ratio was estimated to be 2.4 : 1 for **5c** : **8c** by hplc analysis.

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