1156 © 1994 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 67, 1156—1160(1994) [Vol. 67, No. 4

Regioselective Alkylation of (η^6-Triisopropylsilylbenzene)chromium(0) Complex with Organolithium Compounds

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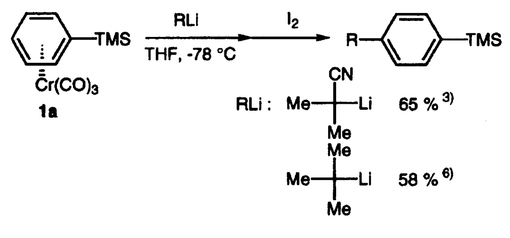
(Received October 26, 1993)

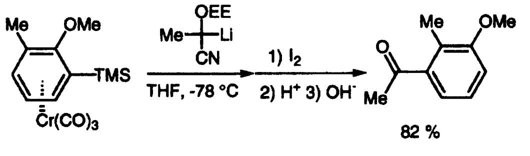
Reactions of tricarbonyl(η^6-triisopropylsilyl(TIPS)benzene)chromium(0) complex **1b** with various alkyllithiums proceed regioselectively, giving *para*-substituted TIPSbenzenes in high yield after oxidation with iodine. Vinyllithiums also react with the TIPSbenzenechromium complex to give *para*-TIPSstyrenes in good yield. In the reaction with phenyllithium, although the *para*-substituted product is obtained as a main product, deprotonation of the aryl group of the chromium complex also occurs competitively to afford bisTIPSbiphenyls as a by-product. Alkynyllithium, however, attacks the TIPS group to yield alkynylsilane and TIPSbiphenyl.

Arene chromium(0) complexes have often been used in the preparation of substituted arene compounds, because the chromium complexes tend to suffer a nucleophilic attack on the aryl group in contrast to the original arene compounds.[1] Especially, the introduction of a strong π-donor group, such as an alkoxyl, amino, or fluoro group, on the aryl group can generally realize *meta*-selective substitution in high regioselectivity.[1a,2]

According to this substituent effect of the π-donor groups, the introduction of a trialkylsilyl group on the aryl group would be expected to control a nucleophilic attack on the *ortho* and *para* positions because of its π-acceptor character.[3,4] Arylsilane is wellknown as a unique intermediate for the preparation of various kinds of substituted arene compounds, such as phenol and aryl halide, through electrophilic substitution at the *ipso* position.[5] Accordingly, an efficient method for a regioselective preparation of *para*-substituted benzene derivatives could be developed by controlling the nucleophilic attack on the tricarbonyl(η^6-trialkylsilylbenzene)chromium(0) complex. To carry out regioselective alkylation, possible side reactions should be suppressed, such as a nucleophilic attack on the silyl and carbonyl groups and/or deprotonation of the aryl group. Two examples have been reported concerning a nucleophilic attack of alkyllithiums to a (η^6-trimethylsilylbenzene)chromium(0) complex **1a**, which yielded *para*-substituted silylbenzenes in moderate yield (Eq. 1).[3,6] However, the reactions were examined with only specific nucleophiles, such as 2-lithioisobutanenitrile[3] and *t*-butyllithium.[6] In addition, the desilylation pathway was often observed in such a reaction (Eq. 2),[3] which made it difficult to develop a general method for the regioselective preparation of *para*-substituted silylbenzenes by alkylation of the silylbenzenechromium complex.



(1)

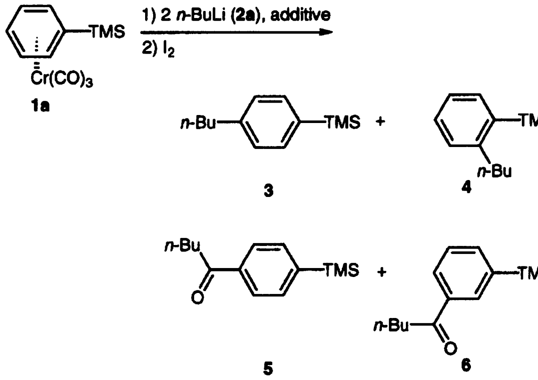


(2)

In this paper we report on details concerning the reactions of silylbenzenechromium(0) complexes **1** with various alkyllithiums for the synthesis of *para* substituted silylbenzenes.

Results and Discussion

First, we examined the reaction of the tricarbonyl(η^6-trimethylsilyl(TMS)benzene)chromium(0) complex **1a** with butyllithium. Generally, a deprotonation reaction takes place when a benzenechromium complex is treated with butyllithium, because the acidity of the benzene protons is extremely increased by the strong electron-withdrawing effect of the $Cr(CO)_3$ group.[7—9] On the contrary, the introduction of a TMS group greatly influenced the reaction course. The TMSbenzenechromium complex **1a** was found to suffer a nucleophilic attack with butyllithium quite easily in THF, giving *ortho*- and *para*-butylTMSbenzenes **3** and **4** and 1-pentanoylTMSbenzenes **5** and **6** in 44 and 12% yield, respectively, after oxidation with iodine (Eq. 3). Furthermore, the *para*-substituted TMSbenzene **3** could be obtained selectively in 64% yield by the addition of hexamethylphosphoric triamide (HMPA), as depicted in Table 1.



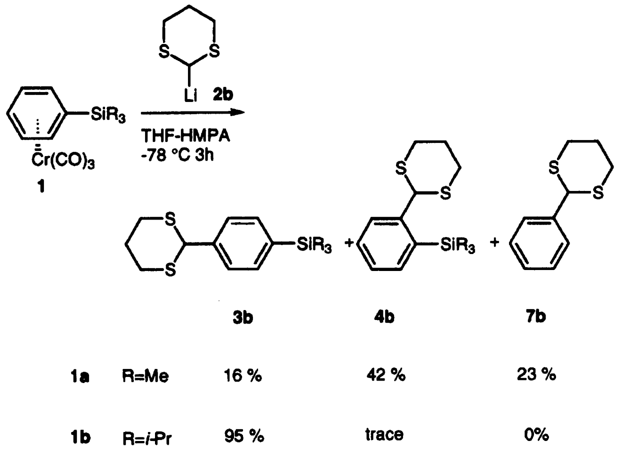
(3)

Under these reaction conditions, however, 2-lithio-

Table 1. Examination on the Effect of Additives in the **1a**/*n*-BuLi System

Additive (equiv)	Products (yield/%)			
	3	**4**	**5**	**6**
None	33	11	6	6
$BF_3 \cdot Et_2O$ (2)	32	32	2	2
TMSOTf (2)	30	30	Trace	Trace
PPh_3 (2)	25	25	10	10
Me_2S (2)	39	Trace	11	11
HMPA (5)	64	0	0	0

1,3-dithiane **2b** reacted with the TMSbenzenechromium complex **1a** to give mainly *ortho*-substituted product **4b** accompanied by a *para*-substituted product **3b** and a desilylated product **7b** (Eq. 4).



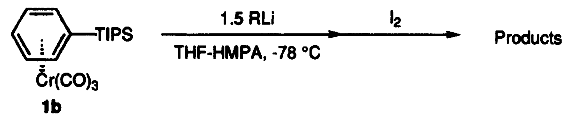
(4)

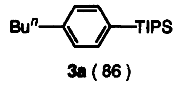
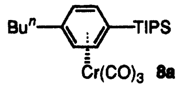
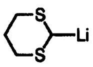
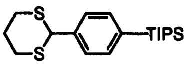
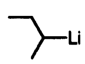
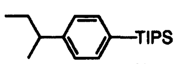
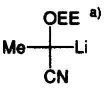
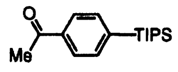
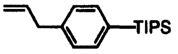
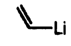
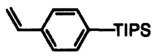
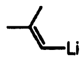
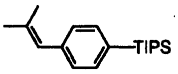
To prevent these side reactions, the alkyl group on the silyl group was changed to a bulkier one, expecting that the desilylation and *ortho* substitution may be suppressed by a steric effect. Thus, the tricarbonyl(η^6-triisopropylsilyl(TIPS)benzene)chromium(0) complex **1b** was prepared according to the conventional method,[10] and was found to be rather stable and easy to handle in the air, as compared with **1a**.

When the TIPSbenzenechromium complex **1b** was treated with **2b** (Eq. 4), side reactions were completely suppressed and only a *para*-substituted product was obtained in 95% yield. Some sp^3 hybridized carbanions and vinyllithiums also reacted with the TIPSbenzenechromium complex **1b** in high regioselectivity, giving *para*-substituted TIPSbenzenes in good yield (73—95%). These results are listed in Table 2.

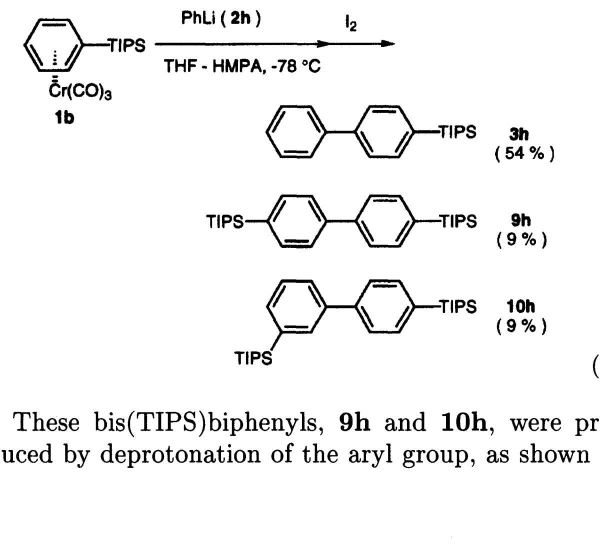
In the reaction with phenyllithium, although the desired biphenyl derivative **3h** was produced in 54% yield, bis(TIPS)biphenyls **9h** and **10h** were also detected (Eq. 5).

Table 2. Reactions of **1b** with Various Kinds of Nucleophiles



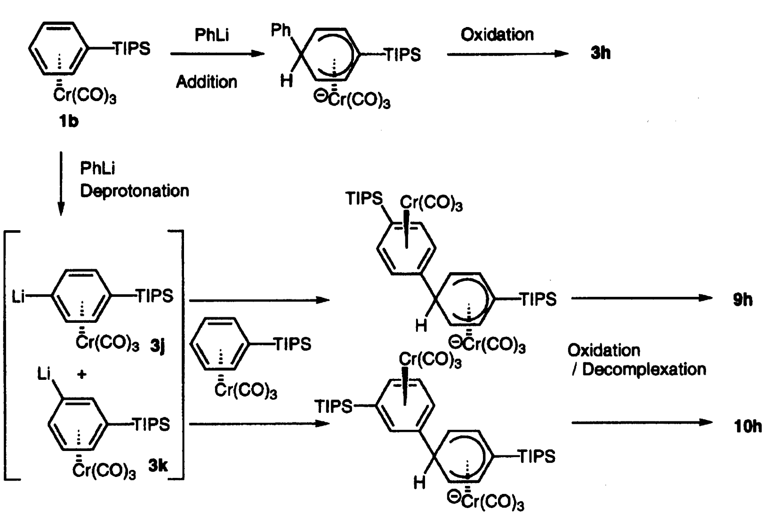
RLi	Products (yield/%)	
n-BuLi **2a**	 **3a** (86)	 **8a** (8)
 **2b**	 **3b** (95)	
 **2c**	 **3c** (83) b)	
 **2d**	 **3d** (82) c)	
 **2e**	 **3e** (88)	
 **2f**	 **3f** (81)	
 **2g**	 **3g** (73)	

a) EE=1-ethoxyethyl. b) The reaction was performed without HMPA. Addition of HMPA decreased the yield. c) The yield was determined as an acyl product resulting from hydrolysis of the cyanohydrin acetal unit.

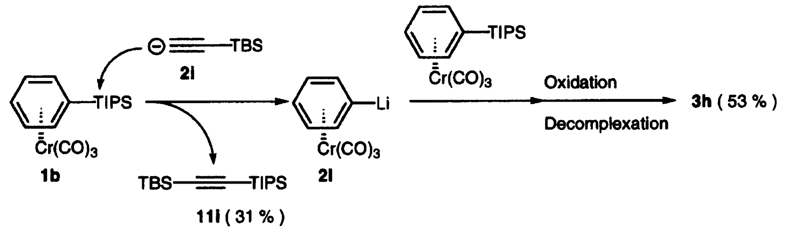


(5)

These bis(TIPS)biphenyls, **9h** and **10h**, were produced by deprotonation of the aryl group, as shown in



Scheme 1.



Scheme 2.

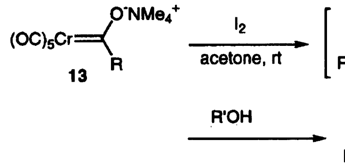
Scheme 1. The generation of **9h** and **10h** indicated that the chromium complex **1b** suffered a nucleophilic attack, even with the lithiated benzenechromium complex, **3j** and **3k**.

On the other hand, alkynyllithium **2i** reacted with **1b** in a different reaction pathway. Neither substitution on the arene ring nor deprotonation took place, and the alkynylsilane **11i** and the biphenyl compound **3h** were isolated in 31 and 53% yield, respectively. These compounds were produced by the nucleophilic attack of **2i** on the TIPS group and a successive reaction of the lithiated benzenechromium complex **2l** with **1b**, as shown in Scheme 2.

As described above, using tricarbonyl(η^6-triisopropylsilylbenzene)chromium(0) complex **1b**, *para*-substituted silylbenzenes were synthesized in high regioselectivity, especially when alkyl- or alkenyllithiums were used. The reactivity of nucleophiles in the addition reaction to the benzenechromium complex has been well-documented by Semmelhack and co-workers. That is, rather stable carbanions generated from the acidic compounds with $\mathrm{p}K_a > 20$ are successfully introduced in the aryl groups.[1a,11] On the other hand, butyllithium usually causes deprotonation of the aryl group, since the acidity of the proton is substancially increased by the $\mathrm{Cr(CO)_3}$ group.[7] The TIPS group is considered to prevent deprotonation, thus allowing a nucleophilic attack of butyllithium on only the aryl group.

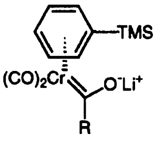
As shown in Table 1, the carbonyl-insertion products **5** and **6** were obtained in the reaction of the TMSbenzenechromium complex **1a** with butyllithium in the absence of HMPA. The generation of **5** and **6** strongly suggested the existence of the (η^6-benzene)dicarbonyl(1-oxidoalkylidene)chromium(0) complex **12** as a possible intermediate (Chart 1).[12]

Two mechanisms are considered to produce carbonyl-insertion compounds **5** and **6** from **12**. One possibility is that the acyl anion species is generated from **12** and attacks the benzene ring nucleophilically. The other possibility is that acylation proceeds at the oxidation step by iodine. Recently, Söderberg and Bouden reported that acyl iodide were generated by a treatment of pentacarbonyl(1-oxidoalkylidene)chromium(0) complex **13** with iodine (Eq. 6).[13] According to the literature, acyl iodide was also generated from **12** treated with iodine and a successive Friedel–Crafts type reaction onto the arene ring carried out, to give **5** and **6**.



(6)

Particularly noteworthy is that the lithiated benzenechromium complex attacks the original benzenechromium complex nucleophilically to give biphenyl compounds, as shown in Schemes 1 and 2. This lithi-



12

Chart 1.

ated benzenechromium complex is known to be less nucleophilic, which indicated that the silyl substituted chromium complex **1b** is quite susceptible to a nucleophilic attack of alkyllithiums.

Experimental

General. All melting points are uncorrected. The IR spectra were measured with a Horiba FT-300S spectrometer. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded on a Bruker AM500 spectrometer with $\mathrm{CHCl_3}$ (δ=7.24 and 77) or $\mathrm{C_6H_6}$ (δ=7.15 and 128) as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operating at 70 eV. Flash column chromatography was carried out on silica gel (Merck Silica gel 60) and preparative TLC was carried out using Wakogel B-5F. Tetrahydrofuran (THF) was freshly distilled from sodium diphenylketyl. Hexamethylphosphoric triamide (HMPA) was distilled under reduced pressure and stored over MS 4A. Dibutyl ether was distilled from $\mathrm{CaH_2}$ and stored over MS 4A. The solvents were degassed before use, and all of the operations were performed under an argon atmosphere. Hexacarbonylchromium(0) was purchased (Soekawa Chemicals). Tricarbonyl(η^6-trimethylsilylbenzene)chromium(0) (**1a**)[14] and triisopropylphenylsilane[15] were prepared according to methods from the literature.

Preparation of Organolithiums: Butyllithium (**2a**) in hexane, *s*-butyllithium (**2c**) in cyclohexane, and phenyllithium (**2h**) in cyclohexane–ether were commercially available (Aldrich) and were titrated according to methods described in the literature.[16] 2-Lithio-1,3-dithiane (**2b**),[17] 2-(1-ethoxyethoxy)-2-lithiopropanenitrile (**2d**),[18] and 2-(*t*-butyldimethylsilyl)ethynyllithium (**2i**)[19] were generated as THF solutions according to literature methods. Allyllithium (**2e**) was prepared as a petroleum ether solution by the method of Eisch.[20] Vinyllithium (**2f**) was prepared by the method of Seyferth and Weiner,[21] and was used as a THF solution. 2-Methyl-1-propenyllithium (**2g**) was prepared as an ether solution according to a literature method.[22]

Preparation of Tricarbonyl(η^6-triisopropylsilylbenzene)chromium(0) (1b): This reaction was conducted according to the conventional method.[10] A mixture of triisopropylsilylbenzene 2.34 g (10 mmol) and hexacarbonylchromium(0) 2.65 g (12 mmol) in 150 ml dibutyl ether and 12 ml of THF was heated at 130—150 °C for 72 h. The reaction mixture was cooled and the unreacted $\mathrm{Cr(CO)_6}$ was filtered off. The filtrate was evaporated under reduced pressure. The residual yellow solid was purified by flash column chromatography (hexane/AcOEt=10/1), and was then recrystallized from petroleum ether to afford yellow crystals. Yield 3.26 g (88 %). mp 73.5—74.5 °C; IR (KBr) 1959, 1892 cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$) δ=0.95—1.14 (21H, m), 4.27 (2H, t, J=6.0 Hz), 4.69 (1H, t, J=6.0 Hz), 4.94 (2H, d, J=6.0 Hz); ^{13}C NMR ($\mathrm{C_6D_6}$) δ=11.1, 18.5, 89.3, 95.3, 96.0, 100.2, 215.4. Found: C, 58.49; H, 6.98%. Calcd for $\mathrm{C_{18}H_{26}CrO_3Si}$: C, 58.36; H, 7.07%.

General Procedure for The Reaction of Tricarbonyl(η^6-triisopropylsilylbenzene)chromium(0) (1b) with Various Organolithiums: To a THF solution (4 ml) of organolithium (**2**) (1.5 mmol) and HMPA (1.5 ml) was added **1b** (370.5 mg, 1 mmol) in THF (4 ml) at −78°C; the mixture was stirred overnight. Iodine (1000 mg, 3.9 mmol) in THF (3 ml) was added at −78°C. After stirring at room temperature for 1 h, saturated aq $\mathrm{NaHSO_3}$ and ether were added and the mixture was stirred for 30 min. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic extracts were washed with water and brine, dried over $\mathrm{Na_2SO_4}$, and evaporated. PTLC gave the addition/oxidation products as follows.

4-Butylphenyltriisopropylsilane (3a): Colorless crystals (from petroleum ether); mp 45—46 °C; IR (KBr) 1465, 883, 679, 669 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.93 (3H, t, J=7.4 Hz), 1.07 (18H, d, J=7.5 Hz), 1.32—1.41 (5H, m), 1.56—1.64 (2H, m), 2.60 (2H, t, J=7.8 Hz), 7.16 (2H, d, J=7.6 Hz), 7.39 (2H, d, J=7.6 Hz); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=10.8, 14.0, 18.6, 22.5, 33.4, 35.7, 127.6, 131.2, 135.2, 143.1. Found: C, 78.25, H, 11.60%. Calcd for $\mathrm{C_{19}H_{34}Si}$: C, 78.54; H, 11.79%.

(η^6-4-Butylphenyltriisopropylsilane)tricarbonylchromium(0) (8a): Yellow crystals (from petroleum ether); mp 73—74.5 °C; IR (KBr) 1961, 1890, 1871 cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$) δ=0.80 (3H, t, J=7.2 Hz), 1.05—1.29 (23H, m), 1.35—1.43 (2H, m), 2.12 (2H, t, J=7.7 Hz), 4.42 (2H, d, J=6.5 Hz), 5.19 (2H, d, J=6.5 Hz); ^{13}C NMR ($\mathrm{C_6D_6}$) δ=11.5, 13.9, 18.8, 22.5, 32.9, 34.8, 90.3, 94.1, 101.1, 115.7, 215.2. Found: m/z 426.1698. Calcd for $\mathrm{C_{22}H_{34}CrO_3Si}$: M, 426.1673.

2-(4-Triisopropylsilylphenyl)-1,3-dithiane (3b): Colorless crystals (from petroleum ether/ether); mp 105—106 °C; IR (KBr) 1460, 883, 681, 675 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.04 (18H, d, J=7.5 Hz), 1.36 (3H, hept, J=7.5 Hz), 1.88—1.98 (1H, m), 2.12—2.19 (1H, m), 2.87—2.93 (2H, m), 3.02—3.10 (2H, m), 5.15 (1H, s), 7.40 (2H, d, J=8.0 Hz), 7.43 (2H, d, J=8.0 Hz); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=10.8, 18.5, 25.2, 32.1, 51.6, 126.7, 135.4, 135.6, 139.0. Found: C, 64.45, H, 9.02, S, 18.27%. Calcd for $\mathrm{C_{19}H_{32}S_2Si}$: C, 64.71; H, 9.15, S, 18.18%.

Triisopropyl[4-(1-methylpropyl)phenyl]silane (3c): Colorless oil; IR (neat) 1464, 883, 679, 669 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.81 (3H, t, J=7.4 Hz), 1.05 (18H, d, J=7.5 Hz), 1.23 (3H, d, J=7.0 Hz), 1.36 (3H, hept, J=7.5 Hz), 1.51—1.62 (2H, m), 2.56 (1H, tq, J=7.0 and 7.0 Hz), 7.13 (2H, d, J=8.0 Hz), 7.37 (2H, d, J=8.0 Hz); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=10.8, 12.3, 18.6, 21.4, 31.2, 41.5, 126.2, 131.4, 135.2, 147.9. Found: C, 78.64, H, 11.65%. Calcd for $\mathrm{C_{19}H_{34}Si}$: C, 78.54, 11.79%.

4-(Triisopropylsilyl)acetophenone (3d): Colorless crystals (from petroleum ether/ether); mp 52—53 °C; IR (KBr) 1683, 883, 681, cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.05 (18H, d, J=7.5 Hz), 1.41 (3H, hept, J=7.5 Hz), 2.58 (3H, s), 7.58 (2H, d, J=8.2 Hz), 7.89 (2H, d, J=8.2 Hz); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=10.7, 18.4, 26.6, 126.9, 135.4, 137.0, 142.2, 198.6. Found: C, 73.57, H, 10.21%. Calcd for $\mathrm{C_{17}H_{28}OSi}$: C, 73.85, H, 10.21%.

Triisopropyl[4-(2-propenyl)phenyl]silane (3e): Colorless oil; IR (neat) 1639, 1463, 995, 916, 883, 679, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.07 (18H, d, J=7.5 Hz), 1.39 (3H, hept, J=7.5 Hz), 3.39 (2H, d, J=6.7 Hz), 5.06—5.12 (2H, m), 5.95—6.05 (1H, m), 7.18 (2H, d, J=7.7 Hz), 7.42 (2H, d, J=7.7 Hz); ^{13}C NMR ($CDCl_3$) δ=10.8, 18.6, 40.3, 115.8, 127.7, 132.0, 135.4, 137.3, 140.3. Found: C, 78.77, H, 10.85%. Calcd for $C_{18}H_{30}Si$: C, 78.75, H, 11.01%.

4-(Triisopropylsilyl)styrene (3f): Colorless oil; IR (neat) 1464, 989, 906, 883, 679, 656, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.08 (18H, d, J=7.5 Hz), 1.40 (3H, hept, J=7.5 Hz), 5.25 (1H, dd, J=10.9 and 0.8 Hz), 5.79 (1H, dd, J=17.6 and 0.8 Hz), 6.72 (1H, dd, J=17.6 and 10.9 Hz), 7.40 (2H, d, J=8.0 Hz), 7.46 (2H, d, J=8.0 Hz); ^{13}C NMR ($CDCl_3$) δ=10.8, 18.5, 113.9, 125.3, 134.7, 135.5, 137.0, 137.6. Found: C, 78.08, H, 10.72%. Calcd for $C_{17}H_{28}Si$: C, 78.38, H, 10.83%.

Triisopropyl[4-(2-methyl-1-propenyl)phenyl]silane (3g): Colorless oil; IR (neat) 1462, 883, 682 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.06 (18H, d, J=7.5 Hz), 1.38 (3H, hept, J=7.5 Hz), 1.88 (3H, d, J=1.1 Hz), 1.89 (3H, d, J=1.2 Hz), 6.24 (1H, m), 7.19 (2H, d, J=7.9 Hz), 7.41 (2H, d, J=7.9 Hz); ^{13}C NMR ($CDCl_3$) δ=10.8, 18.6, 19.6, 27.0, 125.2, 127.7, 131.9, 135.0, 135.6, 138.7. Found: C, 79.13, H, 10.97%. Calcd for $C_{19}H_{32}Si$: C, 79.09, H, 11.18%.

4-(Triisopropylsilyl)biphenyl (3h): Colorless crystals (from petroleum ether); mp 81.5—82.5 °C; IR (KBr) 1460, 885, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.09 (18H, d, J=7.5 Hz), 1.42 (3H, hept, J=7.5 Hz), 7.30—7.35 (1H, m), 7.42 (2H, t, J=7.7 Hz), 7.55 (2H, d, J=8.3 Hz), 7.57 (2H, d, J=8.3 Hz), 7.59—7.63 (2H, m); ^{13}C NMR ($CDCl_3$) δ=10.8, 18.6, 126.1, 127.1, 127.2, 128.7, 133.7, 135.7, 141.0, 141.1. Found: C, 81.28, H, 9.72%. Calcd for $C_{21}H_{30}Si$: C, 81.22, H, 9.74%.

4,4′-Bis(triisopropylsilyl)biphenyl (9h): IR (KBr) 1462, 883, 694, 681, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.08 (36H, d, J=7.5 Hz), 1.41 (6H, hept, J=7.5 Hz), 7.54 (4H, d, J=8.0 Hz), 7.59 (4H, d, J=8.0 Hz); ^{13}C NMR ($CDCl_3$) δ= 10.8, 18.6, 126.0, 133.7, 135.7, 140.9. Found: m/z 466.3452. Calcd for $C_{30}H_{50}Si_2$: M, 466.3438.

3,4′-Bis(triisopropylsilyl)biphenyl (10h): IR ($CHCl_3$ solution) 1464, 883, 787, 708, 679, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.09 (36H, d, J=7.5 Hz), 1.39—1.48 (6H, m), 7.39—7.42 (1H, m), 7.43—7.47 (1H, m), 7.52—7.59 (5H, m), 7.71 (1H, s); ^{13}C NMR δ=10.8, 18.6, 126.2, 127.4, 127.8, 133.4, 133.8, 134.3, 135.3, 135.7, 140.0, 141.6. Found: m/z 466.3475. Calcd for $C_{30}H_{50}Si_2$: M, 466.3438.

1-(*t*-Butyldimethylsilyl)-2-(triisopropylsilyl)acetylene (11i): Colorless oil; IR (neat) 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.09 (6H, s), 0.93 (9H, s) 1.03—1.09 (21H, m); ^{13}C NMR ($CDCl_3$) δ=−4.6, 11.1, 16.5, 18.6, 26.0, 110.7, 114.2. Found: m/z 296.2357. Calcd for $C_{17}H_{36}Si_2$: M, 296.2346.

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