JOC The Journal of Organic Chemistry

Brief Communication

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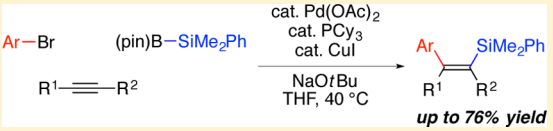
# Intermolecular Three-Component Arylsilylation of Alkynes under Palladium/Copper Cooperative Catalysis

Ryo Shintani,* Hiroki Kurata, and Kyoko Nozaki*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Supporting Information

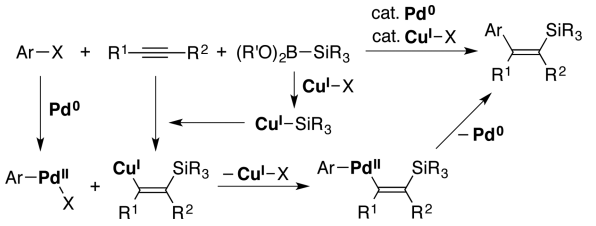
**ABSTRACT:** An intermolecular three-component arylsilylation of alkynes has been developed under mild palladium/copper cooperative catalysis. The reaction proceeds through *syn*-addition of an aryl group and a silyl group across the carbon−carbon triple bond of an alkyne. This represents the first transition-metal-catalyzed fully intermolecular arylsilylation of alkynes, and transformations of the resulting products have also been demonstrated.




Carbosilylation of alkynes can provide highly substituted alkenylsilanes efficiently from relatively simple substrates. In particular, a catalytic and fully intermolecular three-component reaction composed of a carbon donor, a silicon donor, and an alkyne is attractive in view of the convergence and efficiency of the process. The most well-known reaction of this type is silylformylation of alkynes using hydrosilanes and carbon monoxide catalyzed by rhodium complexes.[1] A related silylimination reaction with isocyanides in place of carbon monoxide has also been reported.[2] Other catalytic intermolecular processes are currently limited to a palladium-catalyzed alkynylsilylation of terminal alkynes,[3] a copper-catalyzed silacarboxylation of internal alkynes,[4] and a palladium/copper-catalyzed allylsilylation of alkynoates.[5] In contrast, no intermolecular three-component arylsilylation of alkynes has been reported to date under transition-metal catalysis as far as we are aware, although Baba and co-workers recently reported a montmorillonite-catalyzed arylsilylation of ethynylbenzenes using nucleophilic aromatic solvents (mesitylene and anisole) as the carbon donor.[6,7] In this context, herein we describe the development of an intermolecular three-component arylsilylation of internal alkynes under palladium/copper cooperative catalysis,[8] which allows for a facile access to 1,2-disubstituted 2-arylethenylsilanes compared to the existing methods.[9]

To realize such an arylsilylation reaction, we decided to employ a nucleophilic silicon donor in combination with an aryl electrophile. Specifically, we envisioned that the use of a silylboronate[10] under copper catalysis would provide a silylcopper(I) species,[4,5,11,12] which undergoes silylcupration of an alkyne to give an alkenylcopper(I) species,[4,5,12,13] and that the use of an aryl halide under palladium catalysis would provide an arylpalladium(II) species, which undergoes a coupling with the alkenylcopper(I) through transmetalation (Scheme 1).[8a,b,14] Based on this strategy, we initially employed 3-bomoanisole (**1a**), diphenylacetylene (**2a**), and dimethylphenylsilylboronic acid pinacol ester[15] as a model substrate combination and conducted a reaction in the presence of $Pd(OAc)_2$ (4 mol %), $PPh_3$ (8 mol %), and CuI (20 mol %) as the catalysts with stoichiometric NaO*t*Bu as the base in THF at

**Scheme 1. Arylsilylation of Alkynes with Aryl Halides and Silylboronates under Palladium/Copper Cooperative Catalysis**




40 °C (Table 1, entry 1). Under these conditions, desired arylsilylation product **3aa** was successfully obtained in 35% yield. The yield of **3aa** was significantly improved by changing the ligand to $PCy_3$ (entry 2), but bulkier $P(tBu)_3$ was found to be less effective (entry 3), and the use of an *N*-heterocyclic carbene ligand, IPr (1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene), resulted in a low yield of **3aa** (entry 4). The yield of **3aa** was also low in the absence of any ligand (entry 5). In the presence of $PCy_3$ as the ligand, the amount of CuI could be reduced to 10 mol %, although the yield of **3aa** became somewhat lower (entry 5). It is worth noting that both palladium and copper catalysts were found to be necessary to promote this reaction as shown in entries 6 and 7. In addition, we confirmed that the arylsilylation took place in a *syn*-fashion by X-ray crystallographic analysis of compound **3aa**.[16]

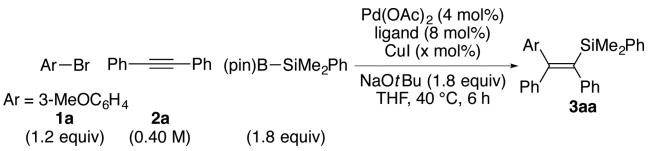
Under the conditions in Table 1, entry 2, several electronically different aryl bromides can be used for the present catalysis to give the corresponding arylsilylation products **3** in 60−76% yield (Table 2, entries 1−5). In addition, other (hetero)aryl bromides such as 2-naphthyl, 1-methyl-5-indolyl, and 2-pyridyl bromides are also applicable in moderate to good yields (51−74% yield; entries 6−8). Furthermore, not only arylsilylation but also alkylsilylation[17] can be achieved by using

**Received:** March 18, 2016
**Published:** April 4, 2016




DOI: 10.1021/acs.joc.6b00587
J. Org. Chem. 2016, 81, 3065−3069

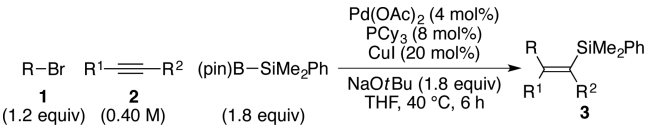
**Table 1. Palladium/Copper-Catalyzed Arylsilylation of Diphenylacetylene: Catalyst and Ligand Effect**




| entry | ligand | $x$ | yield (%)[a] |
|---|---|---|---|
| 1 | $PPh_3$ | 20 | 35 |
| **2** | **$PCy_3$** | **20** | **82 (75)**[b] |
| 3 | $P(tBu)_3$[c] | 20 | 60 |
| 4 | IPr[d] | 20 | 8 |
| 5 | none | 20 | 7 |
| 6 | $PCy_3$ | 10 | 66 |
| 7 | $PCy_3$ | 0 | 0[e] |
| 8[f] | $PCy_3$ | 20 | <1[g] |

[a]Determined by $^1H$ NMR against internal standard ($MeNO_2$). [b]Isolated yield in parentheses. [c]$P(tBu)_3{\cdot}HBF_4$/NaO*t*Bu was used. [d]IPr·HCl/NaO*t*Bu was used. [e]Major product was 3-$MeOC_6H_4B$(pin) (34% based on the amount of 3-$MeOC_6H_4Br$ employed). [f]In the absence of $Pd(OAc)_2$. [g]Major products were 3-$MeOC_6H_4B$(pin) (31% based on the amount of 3-$MeOC_6H_4Br$ employed) and (*E*)-(1,2-diphenylethenyl)dimethylphenylsilane (17%).

**Table 2. Scope of Carbosilylation of Alkynes**



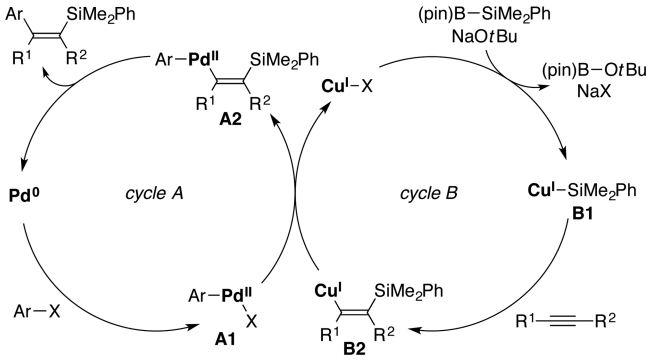

| entry | **1** (R) | **2** ($R^1$, $R^2$) | **3** | yield[a] (%) |
|---|---|---|---|---|
| 1 | **1a** (3-$MeOC_6H_4$) | **2a** (Ph, Ph) | **3aa** | 75 |
| 2 | **1b** (2-$MeOC_6H_4$) | **2a** | **3ba** | 60[b] |
| 3 | **1c** (4-$MeOC_6H_4$) | **2a** | **3ca** | 71 |
| 4 | **1d** (4-$FC_6H_4$) | **2a** | **3da** | 62[c] |
| 5 | **1e** (4-$tBuO_2CC_6H_4$) | **2a** | **3ea** | 76 |
| 6 | **1f** (2-naphthyl) | **2a** | **3fa** | 74 |
| 7[d] | **1g** (1-Me-5-indolyl) | **2a** | **3ga** | 51 |
| 8 | **1h** (2-pyridyl) | **2a** | **3ha** | 53 |
| 9 | **1i** ($(CH_2)_4OMe$) | **2a** | **3ia** | 26 |
| 10[e] | **1a** | **2b** (4-$MeC_6H_4$, 4-$MeC_6H_4$) | **3ab** | 68[f] |
| 11[e] | **1a** | **2c** (4-$FC_6H_4$, 4-$FC_6H_4$) | **3ac** | 64[f] |
| 12[d] | **1a** | **2d** (Et, Et) | **3ad** | 45[g] |
| 13 | **1a** | **2e** (Ph, Me) | **3ae** | 59[h] |

[a]Isolated yield (*Z*-isomer (*E*-isomer for entry 9) was obtained exclusively unless otherwise noted). [b]*Z*/*E* = 97/3. [c]Containing an inseparable impurity (ca. 5%). [d]The reaction was conducted with 8 mol % of $Pd(OAc)_2$ and 16 mol % of $PCy_3$. [e]The reaction was conducted with 2.2 equiv of (pin)B-$SiMe_2Ph$ and NaO*t*Bu. [f]*Z*/*E* = 99/1. [g]*Z*/*E* = 98/2. [h]Regioselectivity = 76/24 along with 7% of inseparable side product (3-$MeOC_6H_4$)$SiMe_2Ph$.

an alkyl bromide, although the yield becomes lower under the present reaction conditions (26% yield; entry 9). With regard to the alkyne component, substituted diarylacetylenes as well as dialkyl- and alkyl(aryl)acetylenes undergo arylsilylation with moderate efficiency (45–68% yield; entries 10–13).

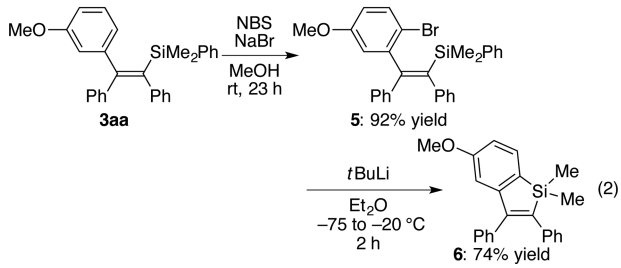
On the basis of the literature precedents for related palladium/copper cooperative catalysis,[5,8d−f] a proposed reaction pathway of the present arylsilylation of alkynes is illustrated in Scheme 2. Thus, oxidative addition of an aryl bromide to palladium(0) generated in situ gives arylpalladium-

**Scheme 2. Proposed Catalytic Cycles for the Arylsilylation of Alkynes under Palladium/Copper Cooperative Catalysis**




(II) **A1** as shown in cycle A. At the same time, a silylboronate undergoes transmetalation to copper(I) halide with the aid of NaO*t*Bu to give silylcopper(I) **B1**,[4,5,11,12] which then reacts with an alkyne to give alkenylcopper(I) **B2** as shown in cycle B.[4,5,12,13] Subsequent transmetalation of **B2** with **A1** leads to the formation of alkenyl(aryl)palladium(II) **A2** along with regeneration of copper(I) halide. Reductive elimination of **A2** gives the arylsilylation product and the palladium(0) species to close the catalytic cycles.

We have also briefly investigated synthetic transformations using the present arylsilylation products. For example, desilylative bromination of compound **3fa** proceeded smoothly to give the corresponding alkenyl bromide **4** in 85% yield while retaining the alkene geometry (eq 1).[16,18] In contrast,


bromination of **3aa** possessing a methoxy group selectively occurred at its *para*-position without cleavage of the carbon–silicon bonds to give aryl bromide **5**,[19] which could be further transformed into benzosilole **6** through a lithiation–cyclization process (eq 2).[20,21]

In summary, we have developed an intermolecular three-component arylsilylation of alkynes under mild palladium/copper cooperative catalysis. The reaction proceeds through *syn*-addition of an aryl group and a silyl group across the carbon–carbon triple bond of an alkyne. This represents the first transition-metal-catalyzed fully intermolecular arylsilylation of alkynes, and transformations of the resulting products have



DOI: 10.1021/acs.joc.6b00587
J. Org. Chem. 2016, 81, 3065−3069

also been demonstrated. Future studies will be directed toward the improvement and expansion of the present catalysis as well as the development of other processes under bimetallic cooperative catalysis.

## EXPERIMENTAL SECTION

**General Procedure for Table 2.** Aryl bromide **1** (0.24 mmol) and dimethylphenylsilylboronic acid pinacol ester (99 μL, 0.36 mmol) were added with the aid of THF (0.20 mL) to a mixture of alkyne **2** (0.20 mmol), $Pd(OAc)_2$ (1.8 mg, 8.0 μmol), $PCy_3$ (4.5 mg, 16 μmol), CuI (7.7 mg, 40 μmol), and NaO*t*Bu (35 mg, 0.36 mmol) in THF (0.30 mL) at 0 °C. The resulting mixture was stirred for 6 h at 40 °C and then diluted with $Et_2O$. This was passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC to afford compound **3**.

*Entry 1 ((Z)-(2-(3-Methoxyphenyl)-1,2-diphenylethenyl)-dimethylphenylsilane (**3aa**)).* EtOAc/hexane = 1/15 → 1/30 was used for preparative TLC. White solid. 75% yield (63.3 mg). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.38−7.32 (m, 2H), 7.32−7.22 (m, 3H), 7.12 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.09 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.04−6.88 (m, 8H), 6.80−6.72 (m, 2H), 6.66 (s 1H), 3.60 (s, 3H), 0.01 (s, 6H). $^{13}$C NMR ($CDCl_3$, 126 MHz): δ 159.2, 155.2, 145.3, 143.9, 143.1, 142.3, 140.4, 134.0, 129.9, 129.6, 129.0, 128.6, 127.6, 127.5, 127.4, 126.2, 125.2, 122.3, 115.0, 113.3, 55.1, −0.6. Mp: 88−90 °C. HRMS (ESI-TOF): calcd for $C_{29}H_{28}OSiNa$ (M + $Na^+$) 443.1802, found 443.1781.

*Entry 2 ((Z)-(2-(2-Methoxyphenyl)-1,2-diphenylethenyl)-dimethylphenylsilane (**3ba**)).* EtOAc/hexane = 1/30 → 1/10 was used for preparative TLC. White solid. 60% yield (50.7 mg; *Z*/*E* = 97/3). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.35−7.10 (m, 7H), 7.07 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.03−6.87 (m, 8H), 6.83 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.67 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 3.62 (s, 3H), 0.04 (s, 3H), −0.07 (s, 3H). $^{13}$C NMR ($CDCl_3$, 126 MHz): δ 157.0, 151.8, 143.9, 143.1, 142.9, 139.8, 134.0, 133.0, 131.3, 129.9, 129.4, 128.9, 128.4, 127.41, 127.36, 127.0, 125.9, 125.0, 119.9, 110.7, 55.1, −0.5, −1.6. Mp: 60−63 °C. HRMS (ESI-TOF): calcd for $C_{29}H_{28}OSiNa$ (M + $Na^+$) 443.1802, found 443.1817.

*Entry 3 ((Z)-(2-(4-Methoxyphenyl)-1,2-diphenylethenyl)-dimethylphenylsilane (**3ca**)).* EtOAc/hexane = 1/10 → 1/30 was used for preparative TLC. White solid. 71% yield (59.6 mg). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.37−7.23 (m, 5H), 7.12−6.87 (m, 12H), 6.71 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.79 (s, 3H), 0.02 (s, 6H). $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 158.9, 155.0, 144.1, 143.6, 142.3, 140.5, 136.7, 133.9, 130.9, 129.9, 129.7, 128.5, 127.5, 127.4, 127.3, 126.1, 125.1, 113.3, 55.4, −0.5. Mp: 75−77 °C. HRMS (ESI-TOF): calcd for $C_{29}H_{28}OSiNa$ (M + $Na^+$) 443.1802, found 443.1803.

*Entry 4 ((Z)-(2-(4-Fluorophenyl)-1,2-diphenylethenyl)-dimethylphenylsilane (**3da**)).* EtOAc/hexane = 1/10 → 1/30 → 1/50 was used for preparative TLC. Pale yellow oil. 62% yield (50.7 mg; containing ca. 5% inseparable impurity). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.35−7.23 (m, 5H), 7.13−6.91 (m, 10H), 6.91−6.81 (m, 4H), 0.03 (s, 6H). $^{13}$C NMR ($CDCl_3$, 126 MHz): δ 162.2 (d, $^1J_{CF}$ = 246 Hz), 154.2, 143.8, 143.3, 143.2, 140.1, 139.9 (d, $^4J_{CF}$ = 3.6 Hz), 133.8, 131.4 (d, $^3J_{CF}$ = 8.2 Hz), 129.8, 129.6, 128.7, 127.7, 127.6, 127.4, 126.3, 125.3, 114.8 (d, $^2J_{CF}$ = 21.8 Hz), −0.6. HRMS (ESI-TOF): calcd for $C_{28}H_{25}FSiCs$ (M + $Cs^+$) 541.0759, found 541.0768.

*Entry 5 ((Z)-(2-(4-tert-Butoxycarbonylphenyl)-1,2-diphenylethenyl)dimethylphenylsilane (**3ea**)).* EtOAc/hexane = 1/30 → 1/10 was used for preparative TLC. Pale yellow oil. 76% yield (74.3 mg). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.35−7.28 (m, 3H), 7.27−7.22 (m, 2H), 7.19 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.10 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.05−6.84 (m, 8H), 1.60 (s, 9H), 0.02 (s, 6H). $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 165.7, 154.2, 148.2, 143.6, 143.3, 142.7, 139.7, 133.9, 130.7, 129.7, 129.6, 129.5, 129.1, 128.7, 127.64, 127.55, 127.4, 126.4, 125.3, 81.0, 28.4, −0.6. HRMS (ESI-TOF): calcd for $C_{33}H_{34}O_2SiNa$ (M + $Na^+$) 513.2220, found 513.2207.

*Entry 6 ((Z)-(2-(2-Naphthyl)-1,2-diphenylethenyl)-dimethylphenylsilane (**3fa**)).* EtOAc/hexane = 1/30 was used for preparative TLC, and the solid thus obtained was washed with hexane. White solid. 74% yield (65.1 mg). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.82−7.74 (m, 1H), 7.64 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 7.62−7.55 (m, 2H), 7.50−7.43 (m, 2H), 7.32−7.18 (m, 5H), 7.18−7.10 (m, 3H), 7.08−6.90 (m, 8H), −0.04 (s, 6H). $^{13}$C NMR ($CDCl_3$, 126 MHz): δ 155.2, 144.1, 143.1, 143.0, 141.5, 140.6, 133.9, 132.8, 132.6, 130.0, 129.9, 128.7, 128.6, 128.3, 127.9, 127.8, 127.63, 127.59, 127.4, 126.3, 126.2, 126.0, 125.3, −0.6. Mp: 159−161 °C dec. HRMS (ESI-TOF): calcd for $C_{32}H_{28}SiCs$ (M + $Cs^+$) 573.1009, found 573.0997.

*Entry 7 ((Z)-(2-(1-Methyl-5-indolyl)-1,2-diphenylethenyl)-dimethylphenylsilane (**3ga**)).* EtOAc/hexane = 1/30 → 1/20 was used for preparative TLC. The reaction was conducted with 8 mol % of $Pd(OAc)_2$ and 16 mol % of $PCy_3$. Pale yellow solid. 51% yield (45.5 mg). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.39 (s, 1H), 7.35−7.22 (m, 5H), 7.17−7.06 (m, 3H), 7.06−6.87 (m, 10H), 6.36 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 3.78 (s, 3H), −0.07 (s, 6H). $^{13}$C NMR ($CDCl_3$, 126 MHz): δ 156.5, 144.5, 144.2, 141.8, 141.1, 136.1, 135.6, 134.0, 130.2, 129.9, 129.2, 128.4, 127.9, 127.43, 127.41, 127.2, 125.9, 125.0, 123.8, 122.6, 108.7, 101.4, 33.0, −0.7. Mp: 108−109 °C. HRMS (ESI-TOF): calcd for $C_{31}H_{29}NSiNa$ (M + $Na^+$) 466.1961, found 466.1940.

*Entry 8 ((Z)-(2-(2-Pyridyl)-1,2-diphenylethenyl)-dimethylphenylsilane (**3ha**)).* EtOAc/hexane = 1/10 → 1/30 was used for preparative TLC. Pale yellow solid. 53% yield (41.8 mg). $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.41 (d, $^3J_{HH}$ = 4.7 Hz, 1H), 7.48−7.37 (m, 3H), 7.26−7.18 (m, 3H), 7.12−6.89 (m, 12H), 0.10 (s, 6H). $^{13}$C NMR ($CDCl_3$, 126 MHz): δ 159.8, 152.8, 148.3, 145.6, 144.1, 141.5, 140.9, 136.0, 133.4, 129.9, 129.3, 128.1, 127.6, 127.5, 127.4, 126.5, 125.1, 124.3, 122.2, 0.3. Mp 65−67 °C. HRMS (ESI-TOF): calcd for $C_{27}H_{25}NSiNa$ (M + $Na^+$) 414.1648, found 414.1632.

*Entry 9 ((E)-(6-Methoxy-1,2-diphenyl-1-hexen-1-yl)-dimethylphenylsilane (**3ia**)).* EtOAc/hexane = 1/30 → 1/50 was used for preparative TLC. White solid. 26% yield (20.6 mg). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.73−7.64 (m, 2H), 7.43−7.35 (m, 3H), 7.08−7.00 (m, 4H), 7.00−6.87 (m, 4H), 6.84−6.76 (m, 2H), 3.20 (s, 3H), 3.06 (t, $^3J_{HH}$ = 6.8 Hz, 2H), 2.44 (t, $^3J_{HH}$ = 8.0 Hz, 2H), 1.30−1.20 (m, 2H), 1.15−1.05 (m, 2H), 0.27 (s, 6H). $^{13}$C NMR ($CDCl_3$, 126 MHz): δ 155.7, 144.5, 142.9, 140.3, 138.7, 133.9, 129.3, 129.0, 128.8, 128.0, 127.44, 127.37, 125.9, 124.6, 72.7, 58.5, 38.5, 29.5, 25.0, −0.1. Mp: 59−60 °C. HRMS (ESI-TOF) calcd for $C_{27}H_{32}OSiNa$ (M + $Na^+$) 423.2115, found 423.2105.

*Entry 10 ((Z)-(2-(3-Methoxyphenyl)-1,2-di(4-methylphenyl)-ethenyl)dimethylphenylsilane (**3ab**)).* EtOAc/hexane = 1/30 → 1/100 was used for preparative TLC. The reaction was conducted with 2.2 equiv of (pin)B−$SiMe_2$Ph and NaO*t*Bu. White solid. 68% yield (60.7 mg; *Z*/*E* = 99/1). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.39−7.32 (m, 2H), 7.32−7.22 (m, 3H), 7.10 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.92 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 6.84 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 6.81 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 6.78 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.76−6.70 (m, 2H), 6.62 (t, $^4J_{HH}$ = 2.0 Hz, 1H), 3.58 (s, 3H), 2.25 (s, 3H), 2.15 (s, 3H), −0.02 (s, 6H). $^{13}$C NMR ($CDCl_3$, 126 MHz): δ 159.1, 154.8, 145.7, 141.5, 141.0, 140.7, 140.2, 135.7, 134.4, 133.9, 129.7, 129.6, 128.9, 128.5, 128.3, 128.1, 127.6, 122.4, 115.0, 113.2, 55.1, 21.23, 21.20, −0.5. Mp 109−110 °C. HRMS (ESI-TOF): calcd for $C_{31}H_{32}OSiNa$ (M + $Na^+$) 471.2115, found 471.2105.

*Entry 11 ((Z)-(2-(3-Methoxyphenyl)-1,2-di(4-fluorophenyl)-ethenyl)dimethylphenylsilane (**3ac**)).* EtOAc/hexane = 1/50 → 1/100 was used for preparative TLC. The reaction was conducted with 2.2 equiv of (pin)B−$SiMe_2$Ph and NaO*t*Bu. Pale yellow solid. 64% yield (58.0 mg; *Z*/*E* = 99/1). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.35−7.23 (m, 5H), 7.15 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 6.90−6.72 (m, 8H), 6.72−6.60 (m, 3H), 3.63 (s, 3H), 0.01 (s, 6H). $^{13}$C NMR ($CDCl_3$, 126 MHz): δ 161.2 (d, $^1J_{CF}$ = 246 Hz), 160.9 (d, $^1J_{CF}$ = 243 Hz), 159.3, 154.6, 144.9, 141.8, 139.9, 139.5 (d, $^3J_{CF}$ = 3.6 Hz), 138.9 (d, $^3J_{CF}$ = 3.6 Hz), 133.9, 131.24, 131.18, 129.2, 128.8, 127.7, 122.2, 115.1, 114.6 (d, $^2J_{CF}$ = 20.9 Hz), 114.5 (d, $^2J_{CF}$ = 21.8 Hz), 113.3, 55.2, −0.8. Mp 86−88 °C. HRMS (ESI-TOF): calcd for $C_{29}H_{26}F_2OSiCs$ (M + $Cs^+$) 589.0770, found 589.0742.

*Entry 12 ((Z)-(4-(3-Methoxyphenyl)-3-hexen-3-yl)-dimethylphenylsilane (**3ad**)).* EtOAc/hexane = 1/30 → 1/80 was used for preparative TLC. The reaction was conducted with 8 mol % of $Pd(OAc)_2$ and 16 mol % of $PCy_3$. Pale yellow oil. 45% yield (28.4 mg; *Z*/*E* = 98/2). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.41−7.33 (m,



DOI: 10.1021/acs.joc.6b00587
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2H), 7.32−7.22 (m, 3H), 7.08 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 6.70 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 2.6 Hz, 1H), 6.59 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 6.45 (d, $^4J_{HH}$ = 1.5 Hz, 1H), 3.58 (s, 3H), 2.43 (q, $^3J_{HH}$ = 7.5 Hz, 2H), 2.28 (q, $^3J_{HH}$ = 7.5 Hz, 2H), 0.99 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 0.90 (t, $^3J_{HH}$ = 7.5 Hz, 3H), −0.03 (s, 6H). $^{13}$C NMR ($CDCl_3$, 126 MHz): δ 158.9, 155.9, 146.2, 141.3, 135.6, 133.9, 128.6, 128.3, 127.5, 121.9, 114.7, 112.5, 55.1, 28.3, 25.1, 15.6, 13.2, −0.7. HRMS (ESI-TOF): calcd for $C_{21}H_{28}OSiNa$ (M + $Na^+$) 347.1802, found 347.1786.

*Entry 13 ((Z)-(1-(3-Methoxyphenyl)-1-phenyl-1-propen-2-yl)-dimethylphenylsilane/(Z)-(2-(3-Methoxyphenyl)-1-phenyl-1-propen-1-yl)dimethylphenylsilane (**3ae**)*. EtOAc/hexane = 1/20 → 1/50 was used for preparative TLC. Pale yellow oil. **3ae**. 59% yield (46.2 mg; regioselectivity = 76/24, along with (3-$MeOC_6H_4$)$SiMe_2Ph$ (7% yield based on 3-bromoanisole)). The structures of the regioisomers were deduced by NOE experiments. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.52−7.45 (m, 1.52H), 7.38−7.04 (m, 9H), 7.02 (d, $^3J_{HH}$ = 7.3 Hz, 0.48H), 6.78−6.64 (m, 2H), 6.63−6.57 (m, 1H), 3.62 (s, 0.72H), 3.55 (s, 2.28H), 1.85 (s, 2.28H), 1.81 (s, 0.72H), 0.06 (s, 4.56H), −0.11 (s, 1.44H). Major isomer: $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 159.1, 154.0, 146.9, 143.3, 140.5, 133.8, 133.6, 129.3, 128.9, 128.7, 128.0, 127.8, 126.7, 122.4, 115.1, 113.0, 55.0, 21.6, −1.3. Minor isomer: $^{13}$C NMR ($CDCl_3$): δ 159.2, 151.3, 146.4, 144.8, 140.3, 139.7, 133.9, 129.0, 128.5, 128.4, 128.1, 127.5, 125.4, 120.7, 113.4, 113.0, 55.1, 24.8, −0.8. HRMS (ESI-TOF): calcd for $C_{24}H_{26}OSiNa$ (M + $Na^+$) 381.1645, found 381.1629.

**Procedure for Equation 1.** $Br_2$ (11.5 μL, 0.224 mmol) and NaOMe (0.38 mL, 0.38 mmol; 1.0 M in MeOH) were added to a solution of compound **3fa** (66.1 mg, 0.150 mmol) in $CH_2Cl_2$ (1.5 mL) at −78 °C, and the mixture was stirred for 30 min at −78 °C. The reaction was quenched with $H_2O$ and then warmed to room temperature. This was extracted with $Et_2O$, and the organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with toluene/hexane = 1/3, and the solid thus obtained was washed with hexane to afford (*Z*)-2-(2-bromo-1,2-diphenylethenyl)naphthalene (**4**) as a white solid (49.2 mg, 0.128 mmol; 85% yield). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.91−7.80 (m, 4H), 7.54−7.45 (m, 3H), 7.40−7.33 (m, 2H), 7.24−7.15 (m, 3H), 7.13−7.04 (m, 3H), 7.04−6.97 (m, 2H). $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 143.6, 141.3, 141.21, 141.18, 133.3, 132.8, 130.6, 130.5, 128.8, 128.3, 128.1, 128.0, 127.88, 127.86, 127.7, 127.2, 126.4, 126.3, 122.6. Mp: 168−169 °C dec. HRMS (ESI-TOF): calcd for $C_{24}H_{17}BrCs$ (M + $Cs^+$) 516.9563, found 516.9582.

**Procedure for Equation 2.** NaBr (41.1 mg, 0.399 mmol) and *N*-bromosuccinimide (71.2 mg, 0.400 mmol) were added with the aid of MeOH (1.4 mL) to a solution of compound **3aa** (84.2 mg, 0.200 mmol) in MeOH (0.6 mL), and the mixture was stirred for 23 h at room temperature. The solvent was removed under vacuum, and the residue was extracted with $Et_2O$−$H_2O$. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. This residue was purified by silica gel preparative TLC with EtOAc/hexane = 1/12 → $CH_2Cl_2$, and the solid thus obtained was washed with hexane to afford (*Z*)-(2-(2-bromo-5-methoxyphenyl)-1,2-diphenylethenyl)dimethylphenylsilane (**5**) as a white solid (91.5 mg, 0.183 mmol; 92% yield, ca. 97% purity). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.41−7.32 (m, 3H), 7.32−7.23 (m, 3H), 7.15−7.07 (m, 2H), 7.07−6.91 (m, 8H), 6.76 (d, $^4J_{HH}$ = 3.1 Hz, 1H), 6.66 (dd, $^3J_{HH}$ = 8.8 Hz and $^4J_{HH}$ = 3.1 Hz, 1H), 3.61 (s, 3H), 0.06 (s, 3H), 0.02 (s, 3H). $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 158.5, 152.5, 144.5, 143.7, 143.3, 140.9, 139.7, 134.0, 133.5, 130.2, 129.7, 128.7, 127.6, 127.1, 126.4, 125.4, 117.2, 115.23, 115.19, 55.4, −0.6, −2.1. Mp: 152−154 °C. HRMS (ESI-TOF): calcd for $C_{29}H_{27}BrOSiCs$ (M + $Cs^+$) 631.0064, found 631.0035.

*t*BuLi (244 μL, 0.403 mmol; 1.65 M solution in pentane) was slowly added to a suspension of compound **5** (91.5 mg, 0.183 mmol) in $Et_2O$ (10 mL) at −72 °C, and the mixture was stirred for 2 h while gradually the temperature was gradually raised to −20 °C. The reaction was quenched with $H_2O$, and this was extracted with $Et_2O$. The organic layer was washed with saturated NaCl aq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane = 1/20, and the solid thus obtained was washed with cold hexane to afford 5-methoxy-1,1-dimethyl-2,3-diphenyl-1*H*-benzo[*b*]silole (**6**) as a white solid (46.4 mg, 0.135 mmol; 74% yield). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.36−7.25 (m, 3H), 7.22−7.16 (m, 2H), 7.12 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.05 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.00−6.94 (m, 2H), 6.79 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 2.3 Hz, 1H), 6.65 (d, $^4J_{HH}$ = 2.3 Hz, 1H), 3.73 (s, 3H), 0.45 (s, 6H). $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 161.7, 153.0, 152.7, 144.6, 140.1, 138.1, 132.8, 129.8, 128.8, 128.7, 128.5, 128.0, 127.2, 125.8, 111.6, 111.2, 55.3, −3.0. Mp: 132−134 °C. HRMS (ESI-TOF) calcd for $C_{23}H_{22}OSiNa$ (M + $Na^+$) 365.1332, found 365.1322.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00587.

NMR spectra of new compounds (PDF)
X-ray data for compound **3aa** (CIF)
X-ray data for compound **4** (CIF)

## ■ AUTHOR INFORMATION


### Corresponding Authors

*E-mail: shintani@chembio.t.u-tokyo.ac.jp.
*E-mail: nozaki@chembio.t.u-tokyo.ac.jp.


### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS


Support has been provided in part by Challenging Exploratory Research, the Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank Mr. Ryo Takano for help with the X-ray crystallographic analyses.


## ■ REFERENCES


(1) (a) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332. (b) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1993**, *12*, 11. (c) Donskaya, N. A.; Yur'eva, N. M.; Sigeev, A. S.; Voevodskaya, T. I.; Beletskaya, I. P.; Tretyakov, V. F. *Mendeleev Commun.* **1995**, *5*, 220. (d) Matsuda, I.; Fukuta, Y.; Tsuchihashi, T.; Nagashima, H.; Itoh, K. *Organometallics* **1997**, *16*, 4327. (e) Biffis, A.; Conte, L.; Tubaro, C.; Basato, M.; Aronica, L. A.; Cuzzola, A.; Caporusso, A. M. *J. Organomet. Chem.* **2010**, *695*, 792.

(2) Fukumoto, Y.; Hagihara, M.; Kinashi, F.; Chatani, N. *J. Am. Chem. Soc.* **2011**, *133*, 10014.

(3) Chatani, N.; Amishiro, N.; Murai, S. *J. Am. Chem. Soc.* **1991**, *113*, 7778.

(4) Fujihara, T.; Tani, Y.; Semba, K.; Terao, J.; Tsuji, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 11487.

(5) Vercruysse, S.; Cornelissen, L.; Nahra, F.; Collard, L.; Riant, O. *Chem. - Eur. J.* **2014**, *20*, 1834.

(6) Motokura, K.; Matsunaga, S.; Miyaji, A.; Yashima, T.; Baba, T. *Tetrahedron Lett.* **2011**, *52*, 6687.

(7) For catalytic two-component arylsilylation reactions, see: (a) Luo, F.-T.; Wang, R.-T. *Tetrahedron Lett.* **1991**, *32*, 7703. (b) Asao, N.; Shimada, T.; Shimada, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2001**, *123*, 10899. (c) Tobisu, M.; Onoe, M.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2009**, *131*, 7506. (d) Shirakawa, E.; Masui, S.; Narui, R.; Watabe, R.; Ikeda, D.; Hayashi, T. *Chem. Commun.* **2011**, *47*, 9714. (e) Liang, Y.; Geng, W.; Wei, J.; Xi, Z. *Angew. Chem., Int. Ed.* **2012**, *51*, 1934. (f) Arii, H.; Kurihara, T.; Mochida, K.; Kawashima, T. *Chem. Commun.* **2014**, *50*, 6649.

(8) For pioneering examples of palladium/copper cooperative catalysis, see: (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467. (b) Liebeskind, L. S.; Fengl, R. W. *J. Org. Chem.* **1990**, *55*, 5359. For selected recent examples, see: (c) Nahra, F.;




DOI: 10.1021/acs.joc.6b00587
*J. Org. Chem.* 2016, 81, 3065−3069

Macé, Y.; Lambin, D.; Riant, O. *Angew. Chem., Int. Ed.* **2013**, *52*, 3208. (d) Semba, K.; Nakao, Y. *J. Am. Chem. Soc.* **2014**, *136*, 7567. (e) Smith, K. B.; Logan, K. M.; You, W.; Brown, M. K. *Chem. - Eur. J.* **2014**, *20*, 12032. (f) Jia, T.; Cao, P.; Wang, B.; Lou, Y.; Yin, X.; Wang, M.; Liao, J. *J. Am. Chem. Soc.* **2015**, *137*, 13760.

(9) For selected examples, see: (a) Jiao, J.; Hyodo, K.; Hu, H.; Nakajima, K.; Nishihara, Y. *J. Org. Chem.* **2014**, *79*, 285. (b) Nishihara, Y.; Saito, D.; Tanemura, K.; Noyori, S.; Takagi, K. *Org. Lett.* **2009**, *11*, 3546. (c) Zhou, C.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 3184.

(10) For reviews on the transition-metal-catalyzed reactions using silylboronates, see: (a) Ohmura, T.; Suginome, M. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 29. (b) Oestreich, M.; Hartmann, E.; Mewald, M. *Chem. Rev.* **2013**, *113*, 402. (c) Shintani, R. *Synthesis* **2016**, *48*, 1087.

(11) (a) Lee, K.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 2898. (b) Vyas, D. J.; Oestreich, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 8513. (c) Kleeberg, C.; Feldmann, E.; Hartmann, E.; Vyas, D. J.; Oestreich, M. *Chem. - Eur. J.* **2011**, *17*, 13538.

(12) (a) Wang, P.; Yeo, X.-L.; Loh, T.-P. *J. Am. Chem. Soc.* **2011**, *133*, 1254. (b) Meng, F.; Jang, H.; Hoveyda, A. H. *Chem. - Eur. J.* **2013**, *19*, 3204. (c) Calderone, J. A.; Santos, W. L. *Angew. Chem., Int. Ed.* **2014**, *53*, 4154. (d) Linstadt, R. T. H.; Peterson, C. A.; Lippincott, D. J.; Jette, C. I.; Lipshutz, B. H. *Angew. Chem., Int. Ed.* **2014**, *53*, 4159. (e) Hazra, C. K.; Fopp, C.; Oestreich, M. *Chem. - Asian J.* **2014**, *9*, 3005. (f) García-Rubia, A.; Romero-Revilla, J. A.; Mauleón, P.; Arrayás, R. G.; Carretero, J. C. *J. Am. Chem. Soc.* **2015**, *137*, 6857.

(13) For examples of carbosilylation of alkynes via stoichiometric silylcupration followed by the reaction with carbon electrophiles, see: (a) Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527. (b) Cuadrado, P.; González-Nogal, A. M.; Sánchez, A. *J. Org. Chem.* **2001**, *66*, 1961. (c) Liepins, V.; Karlström, A. S. E.; Bäckvall, J.-E. *J. Org. Chem.* **2002**, *67*, 2136.

(14) Song, C.; Sun, Y.; Wang, J.; Chen, H.; Yao, J.; Tung, C.-H.; Xu, Z. *Org. Chem. Front.* **2015**, *2*, 1366.

(15) For pioneering work on the preparation and use of this silylboronate, see: (a) Suginome, M.; Nakamura, H.; Ito, Y. *Chem. Commun.* **1996**, 2777. (b) Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 4647.

(16) CCDC-1468754 and CCDC-1468755 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See also the Supporting Information for details.

(17) For selected examples of catalytic two-component alkylsilylation reactions, see: (a) Sakurai, H.; Imai, T. *Chem. Lett.* **1975**, 891. (b) Nevárez, Z.; Woerpel, K. A. *Org. Lett.* **2007**, *9*, 3773. (c) Shintani, R.; Moriya, K.; Hayashi, T. *J. Am. Chem. Soc.* **2011**, *133*, 16440.

(18) (a) Kubota, K.; Iwamoto, H.; Yamamoto, E.; Ito, H. *Org. Lett.* **2015**, *17*, 620. (b) Nagao, K.; Ohmiya, H.; Sawamura, M. *Org. Lett.* **2015**, *17*, 1304.

(19) Miller, R. B.; Tsang, T. *Tetrahedron Lett.* **1988**, *29*, 6715.

(20) Wang, Z.; Fang, H.; Xi, Z. *Tetrahedron Lett.* **2005**, *46*, 499.

(21) For examples of direct synthesis of benzosiloles by catalytic two-component arylsilylation reactions, see ref 7c–f.



DOI: 10.1021/acs.joc.6b00587
*J. Org. Chem.* 2016, 81, 3065−3069