Supporting Information
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Gold-Catalyzed Stereoselective Synthesis of Di- or Trisubstituted Olefins Possessing a 1,4-Diene Framework via Intramolecular Allylation of Alkynes

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I. General Information
Unless otherwise noted, all reagents were obtained commercially and used without further purification. Solvents were distilled according to the usual procedures.¹ TLC analysis of reaction mixture was performed on Merck silica gel 60 F₂₅₄ TLC plates. Flash chromatography was carried out using KANTO silica gel 60N (63-210 µm). Nuclear magnetic resonance spectra were taken on a JEOL α-GX 400 spectrometer using residual chloroform (¹H) or CDCl₃ (¹³C) as an internal standard. High resolution mass spectra were taken with a JEOL MStation JMS-700.

II. Materials
Diphenyl(N,N-diethylamino)chlorosilane and Methylphenyl(N,N-diethylamino)chlorosilane were prepared according to the literature procedures.² Chloro(triphenylphosphine)gold(I)³, Chloro(tri-tert-butylphosphine)gold(I)⁴, Chloro[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]gold(I)⁵ were prepared according to the literature methods. Silver salts were obtained form Aldrich Chemical Company.

Preparation of allylchlorosilanes
General Procedure I

Allyl(N,N-diethylamino)diphenylsilane (A). To a solution of Ph₂Si(NEt₂)Cl² (26.2 g, 115 mmol) in

dry Et2O (50 mL) was added allylmagnesium bromide (1 M Et2O solution, 120 mmol) dropwise over 10 min at 0 °C. After addition was complete, the resulting mixture was allowed to warm to ambient temperature and stirred overnight. The reaction mixture was filtered through Celite, and the filtrate was concentrated in vacuo. To the residue was added dry hexane (100 mL) followed by filtration through Celite. This was repeated additionally twice. The crude product was used for next reaction without further purification.

**Allyl(chloro)diphenylsilane (B).** Dry HCl gas prepared from NaCl and conc. H2SO4 was blown into a suspension of A (34.0 g, 115.0 mmol) in dry Et2O (300 mL) at 0 °C for 0.5 h and stirred for 1 h at ambient temperature. The reaction mixture was changed quickly to a white suspension. To the reaction mixture was added dry hexane (100 mL) and white precipitate was quickly removed by filtration. The filtrate was concentrated in vacuo. To the residue was added another dry hexane (100 mL) and the mixture was filtrated. After removal of solvent in vacuo, the residue was distilled under reduced pressure to give 21.8 g (84.2 mmol, 73% yield for two steps, bp 106 ºC/3 mmHg) of Ph2Si(allyl)Cl as a colorless oil. The spectral data were identical to those reported in literature.6

**Allyl[(N,N-diethylamino)methyl(phenyl)silane (C).** The title compound was prepared according to the General Procedure I using Me(Ph)Si(allyl)NEt2 and Dry HCl gas prepared from NaCl and conc. H2SO4. The crude product was used for next reaction without further purification.

**Allyl(chloro)methyl(phenyl)silane (D).** Colorless oil. (63% for two steps, bp 74 °C/3 mmHg). The title compound was prepared according to the General Procedure I using Me(Ph)Si(allyl)Cl and allylmagnesium bromide. The spectral data were identical to those reported in literature.6

**Preparation of 1-alkynyl-2-allylsilylbenzenes (1)**

**General Procedure II**

1-(1-Hexynyl)-2-(allyldimethylsilyl)benzene (1a). A typical procedure for the synthesis of 1-alkynyl-2-allylsilylbenzenes is described by Murakami7.

To a solution of Pd(PPh3)4 (866.7 mg, 0.75 mmol), CuI (238.1 mg, 1.25 mmol), 1-bromo-2-iodobenzene (7.07 g, 250 mmol) in Et3N (100 mL) was added dropwise 1-hexyne (3.7, 32.5 mmol) in Et3N (20 mL) at ambient temperature. After stirring for 3 h, saturated NH4Cl aqueous solution was added to the reaction mixture. The mixture was extracted with Et2O, washed with brine and water, dried over MgSO4, and evaporated. The residue was purified by column chromatography on silica gel (hexanes) to afforded 1-bromo-2-(1-hexynyl)benzene (5.86 g, 99%) as a yellow oil. The

To a solution of 1-bromo-2-(1-hexynyl)benzene (1.19 g, 5.0 mmol) in THF (30 mL) was added dropwise n-BuLi (2.6 M in hexane, 2.1 mL, 5.5 mmol) at −78 °C. After stirring at −78 °C for 1 h, allylchlorodimethylsilane (0.8 mL, 5.5 mmol) was added dropwise to the mixture. The reaction mixture was stirred at −78 °C for 1 h, and then allowed to warm to ambient temperature. Upon completion, the volatile materials were removed in vacuo, and the residue was subjected to column chromatography on silica gel (hexane: EtOAc = 50:1) to give 1a (1.22 g, 95%). 1H NMR (CDCl 3, 400 MHz) δ 0.35 (s, 6H), 0.95 (t, J = 7.6 Hz, 3H), 1.44-1.65 (m, 4H), 1.95 (d, J = 8.0 Hz, 2H), 2.44 (t, J = 7.6 Hz, 2H), 4.82 (dm, J = 10.0 Hz, 1H), 4.87 (dm, J = 17.2 Hz, 1H), 5.78 (ddt, J = 10.0, 17.2, 8.0 Hz, 1H), 7.24 (dt, J = 1.6, 7.6 Hz, 1H), 7.29 (dd, J = 1.6, 7.6 Hz, 1H), 7.40-7.44 (m, 2H); 13C NMR (CDCl 3, 100 MHz) δ -3.4, 13.6, 19.3, 22.2, 22.9, 30.6, 82.1, 93.3, 113.1, 126.6, 128.8, 129.4, 132.5, 134.1, 135.0, 140.1; HRMS (EI) calcd for C17H24Si (M+) 256.1647; Found m/z 256.1652.

1-[Allyl(methyl)phenylsilyl]-2-(1-hexynyl)benzene (1b). Yellow oil, purified by column chromatography on silica gel (hexane: EtOAc = 50:1) (81%). 1H NMR (CDCl 3, 400 MHz) δ 0.67 (s, 3H), 0.91 (t, J = 7.2 Hz, 3H), 1.32-1.48 (m, 4H), 2.28 (t, J = 7.2 Hz, 2H), 2.29 (dm, J = 7.6 Hz, 2H), 4.87 (dm, J = 9.6 Hz, 1H), 4.96 (dm, J = 17.6 Hz, 1H), 5.84 (ddt, J = 9.6, 17.6, 7.6 Hz, 1H), 7.25 (dt, J = 0.8, 7.6 Hz, 1H), 7.31 (m, 6H), 7.56-7.59 (m, 2H); 13C NMR (CDCl 3, 100 MHz) δ -4.6, 13.6, 19.3, 22.2, 22.9, 30.6, 82.1, 94.1, 113.9, 126.7, 127.6, 128.9, 129.1, 130.0, 132.6, 134.5, 134.6, 135.4, 136.8, 138.3; HRMS (EI) calcd for C22H26Si (M+) 318.1804; Found m/z 318.1805.

1-(Allyldiphenylsilyl)-2-(1-hexynyl)benzene (1c). Yellow oil, purified by column chromatography on silica gel (hexane: EtOAc = 49:1) (88%). 1H NMR (CDCl 3, 400 MHz) δ 0.87 (t, J = 7.2 Hz, 3H), 1.13-1.19 (m, 4H), 2.04 (t, J = 7.2 Hz, 1H), 2.58 (d, J = 8.0 Hz, 2H), 4.87 (dm, J = 10.0 Hz, 1H), 4.99 (dm, J = 17.2 Hz, 1H), 5.91 (ddt, J = 10.0, 17.2, 8.0 Hz, 1H), 7.20 (dt, J = 1.2, 7.6 Hz, 1H), 7.27 (tm, J = 7.6 Hz, 1H), 7.32-7.42 (m, 7H), 7.46 (d, J = 7.6 H, 1H), 7.54 (dd, J = 1.6, 8.0 Hz, 4H); 13C NMR (CDCl 3, 100 MHz) δ 13.6, 19.0, 21.3, 21.9, 30.1, 82.2, 94.9, 114.6, 126.7, 127.6, 129.2, 129.4, 130.5, 132.5, 134.6, 134.9, 135.7, 136.6, 137.0; HRMS (EI) calcd for C 27H28Si (M +) 380.1960; Found m/z 380.1960.

1-(Allyldiphenylsilyl)-2-(trimethylsilylethynyl)benzene (E). Yellow oil, purified by column chromatography on silica gel (hexane: EtOAc = 49:1) (87%). 1H NMR (CDCl 3, 400 MHz) δ 0.06 (s, 9H), 2.73 (d, J = 7.6 Hz, 2H), 4.97 (dm, J = 10.0 Hz, 1H), 5.11 (dm, J = 17.2 Hz, 1H), 6.02 (ddt, J = 10.0, 17.2, 7.6 Hz, 1H), 7.29 (dt, J = 1.2, 7.2 Hz, 1H), 7.35 (dm, J = 7.2 Hz, 1H), 7.39-7.49 (m, 7H), 7.62-7.65 (m, 5H); 13C


S3
NMR (CDCl₃, 100 MHz) δ -0.7, 21.1, 98.4, 106.3, 114.7, 127.63, 127.65, 129.3, 129.3(6), 129.4, 133.2, 134.5, 134.7, 135.8, 137.1, 137.2; HRMS (EI) calcd for C₂₆H₂₈Si₂ [M⁺] 396.1730; Found m/z 396.1733.

General Procedure III

![Reaction Diagram]

1-(Allyldiphenylsilyl)-2-(ethynyl)benzene (1d). To a solution of E (3.97 g, 10.0 mmol) in MeOH–THF (2:1, 170 mL) was added KOH aqueous solution (0.8 M, 15 mL) at ambient temperature. After 0.5 h, the reaction mixture was concentrated under reduced pressure. To the residue was added saturated NH₄Cl aqueous solution, and it was extracted with hexane, washed with water, dried over MgSO₄, and evaporated. The crude product was purified by column chromatography on silica gel (hexane:EtOAc = 49:1) to give 1d (2.89 g, 89%) as a yellow solid. Mp 66.4-67.4 °C; ¹H NMR (CDCl₃, 400 MHz) δ 2.71 (dt, J = 8.0, 1.2 Hz, 2H), 3.01 (s, 1H), 4.96 (dm, J = 10.0 Hz, 1H), 5.08 (dm, J = 17.2 Hz, 1H), 6.00 (ddt, J = 10.0, 17.2, 8.0 Hz, 1H), 7.32-7.51 (m, 9H), 7.60-7.66 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.2, 81.3, 84.7, 114.9, 127.7, 127.9, 128.4, 129.3(7), 129.4(4), 133.6, 134.4, 134.6, 135.8, 137.1, 137.5; HRMS (EI) calcd for C₂₃H₂₀Si [M⁺] 324.1334; Found m/z 324.1334.

1-(Allyldiphenylsilyl)-2-(1-propynyl)benzene (1e). To a mixture of 1d (162.1 mg, 0.5 mmol) was added n-BuLi (2.6 M in hexane, 231 μL, 0.6 mmol) at -78 °C under N₂. The mixture was stirred for 1 h at ambient temperature before addition of iodomethane (94 μL, 1.5 mmol) at -78 °C. The mixture was warmed up to ambient temperature and further stirred for overnight. Upon completion, the mixture was quenched with saturated NH₄Cl solution and extracted with ether twice. The combined organic layers were washed with brine and dried over MgSO₄. The filtrate was concentrated in vacuo to give crude product, which was purified by column chromatography on silica gel (hexanes) to give 160.7 mg of 1e as a colorless oil (95%) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 1.64 (s, 3H), 2.60 (d, J = 8.0 Hz, 2H), 4.90 (dd, J = 1.2, 9.6 Hz, 1H), 5.02 (dd, J = 1.2, 17.2 Hz, 1H), 5.94 (ddt, J = 9.6, 17.2, 8.0 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.31 (m, 9H), 7.59 (d, J = 7.2 Hz, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 4.0, 21.2, 81.6, 90.5, 114.6, 126.7, 127.6, 129.2, 129.4, 130.4, 132.1, 134.5, 134.9, 135.6, 136.8, 136.9; HRMS (EI) calcd for C₂₄H₂₂Si [M⁺] 338.1491; Found m/z 338.1491.
Preparation of 1-(allyldiphenylsilyl)-2-(5-hexene-1-yl)benzene (1g). To a stirred solution of 1d (324.5 mg, 1.0 mmol) in dry DMF (10 mL) under N₂ were added sequentially K₂CO₃ (230 mg, 1.66 mmol), tetrabutylammonium bromide (129.0 mg, 0.4 mmol) and copper(I) iodine (38.2 mg, 0.2 mmol) at ambient temperature. After 10 min, allyl bromide (0.13 mL, 1.53 mmol) was added. The reaction mixture was stirred for 24 h at 50 °C. Upon completion, the mixture was quenched with saturated NH₄Cl solution and extracted with ether twice. The combined organic phases were washed with brine, dried over MgSO₄ and concentrated. The crude obtained was purified by column chromatography on silica gel (hexane:EtOAc = 49:1), yielding title compound 1g (421.6 mg, 98%) as a yellow oil. 

\[ ^1H \text{NMR (CDCl}_3, 400 \text{ MHz)} \delta 2.57 \text{ (dm, } J = 8.0 \text{ Hz, 2H), 2.79 \text{ (dm, } J = 5.6 \text{ Hz, 2H), 4.85-5.05 \text{ (m, 4H), 5.00 \text{ (dm, } J = 17.6 \text{ Hz, 1H), 5.43-5.53 \text{ (m, 1H), 5.84-5.96 \text{ (m, 1H), 7.22 \text{ (s, } J = 7.2 \text{ Hz, 1H), 7.30-7.42 \text{ (m, 8H), 7.29 \text{ (tm, } J = 7.6 \text{ Hz, 1H), 7.54 \text{ (dm, } J = 7.2 \text{ Hz, 4H);}}^{13}C \text{NMR (CDCl}_3, 100 \text{ MHz)} \delta 21.2, 23.7, 84.2, 91.1, 114.1, 116.2, 127.0, 127.6, 129.2, 129.4, 130.1, 131.8, 132.5, 134.5, 134.8, 135.6, 136.8, 136.9;} \]

HRMS (EI) calcd for C₂₆H₂₄Si [M⁺] 364.1647; Found m/z 364.1647.

1-Bromo-2-(5-hydroxy-1-pentyl)benzene (F). The title compound was prepared according to the General Procedure II using 1-bromo-2-iodobenzene and 1-hydroxy-4-pentyne. Yellow oil, purified by column chromatography on silica gel (hexane:EtOAc = 8:2) (98%). 

\[ ^1H \text{NMR (CDCl}_3, 400 \text{ MHz)} \delta 1.90 \text{ (quint, } J = 6.8 \text{ Hz, 2H), 2.60 \text{ (t, } J = 6.8 \text{ Hz, 2H), 3.87 \text{ (t, } J = 6.8 \text{ Hz, 2H), 7.12 \text{ (dt, } J = 1.6, 8.0 \text{ Hz, 1H), 7.23 \text{ (dt, } J = 1.6, 8.0 \text{ Hz, 1H), 7.42 \text{ (dd, } J = 1.6, 8.0 \text{ Hz, 1H), 7.55 \text{ (dd, } J = 1.6, 8.0 \text{ Hz, 1H);}}^{13}C \text{NMR (CDCl}_3, 100 \text{ MHz)} \delta 16.0, 31.0, 61.4, 79.7, 94.4, 125.3, 125.6, 126.8, 128.7, 132.5, 134.8, 135.6, 136.8, 136.9;} \]

HRMS (EI) calcd for C₁₁H₁₅BrO [M⁺] 242.0306; Found m/z 242.0310.

5-(2-Bromophenyl)pent-4-ynal. To a solution of F (1.20 g, 5 mmol) in CH₂Cl₂ (20 mL) was added Dess-Martin Periodinane (3.2 g, 7.5 mmol) in one portion at ambient temperature. The mixture was stirred for 3 h. Upon completion, the reaction mixture was poured into saturated NH₄Cl aqueous solution, and extracted with ethyl acetate twice. The combined organic phases were washed with brine, dried over MgSO₄ and concentrated. The crude obtained was purified by chromatography on silica gel (hexane:EtOAc = 9:1) to give 1.14 g of 5-(2-bromophenyl)pent-4-ynal as a colorless oil (96%). 

\[ ^1H \text{NMR (CDCl}_3, 400 \text{ MHz)} \delta 2.77 \text{ (tm, } J = 7.2 \text{ Hz, 2H), 2.81 \text{ (tm, } J = 7.2 \text{ Hz, 2H), 7.12 \text{ (dt, } J = 1.6, 8.0 \text{ Hz, 1H, 7.22 \text{ (dt, } J = 1.6, 8.0 \text{ Hz, 1H);}}^{13}C \text{NMR (CDCl}_3, 100 \text{ MHz)} \delta 21.2, 23.7, 84.2, 91.1, 114.1, 116.2, 127.0, 127.6, 129.2, 129.4, 130.1, 131.8, 132.5, 134.5, 134.8, 135.6, 136.8, 136.9;} \]

HRMS (EI) calcd for C₁₆H₁₄BrO [M⁺] 262.0665; Found m/z 262.0667.

Preparation of 1-(allyldiphenylsilyl)-2-(5-hexene-1-yl)benzene (1g).
9.87 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 12.7, 42.2, 80.0, 92.7, 125.2, 125.3, 126.8, 128.9, 132.1, 133.1, 200.2; HRMS (EI) caled for C$_{11}$H$_9$Br [M$^+$] 235.9837; Found m/z 235.9830.

1-Bromo-2-(5-hexen-1-ynyl)benzene (G). To a suspension of methyl triphenylphosphonium bromide (2.86 g, 8 mmol) in THF (50 mL) was added n-BuLi (2.6 M in hexane, 3.0 mL, 8.0 mmol) at 0 °C. The mixture was allowed to warm to ambient temperature and stirred for 0.5 h. To the resulting solution was added 5-(2-bromophenyl)pent-4-ynal (4 mmol) in THF (5 mL) via cannula at 0 °C, and stirred for 2 h at ambient temperature. Upon completion, the mixture was poured into saturated NH$_4$Cl aqueous solution, and extracted with ethyl acetate twice. The combined organic layer was washed with saturated NaHCO$_3$ aqueous solution, and then the organic phase was dried over MgSO$_4$ and concentrated in vacuo to give a yellow oil, which was purified by chromatography on silica gel (hexane:EtOAc = 19:1) to give 705.3 mg of 1-bromo-2-(5-hexen-1-ynyl)benzene G as a colorless oil (75%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.41 (dt, $J$ = 6.8, 7.2 Hz, 2H), 2.56 (t, $J$ = 7.2 Hz, 2H), 5.08 (dm, $J$ = 10.0 Hz, 1H), 5.16 (dm, $J$ = 16.8 Hz, 1H), 5.97 (dtt, $J$ = 10.0, 16.8, 6.8 Hz, 1H), 7.11 (dt, $J$ = 1.6, 8.0 Hz, 1H), 7.22 (dt, $J$ = 1.6, 8.0 Hz, 1H), 7.43 (dd, $J$ = 1.6, 8.0 Hz, 1H), 7.56 (dd, $J$ = 1.6, 8.0 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 19.4, 32.7, 79.7, 94.6, 115.8, 125.4, 125.8, 126.8, 128.7, 133.2, 133.3, 136.7; HRMS (EI) caled for C$_{12}$H$_{11}$Br [M$^+$] 234.0044; Found m/z 234.0047.

1-(Allyldiphenylsilyl)-2-(5-hexen-1-ynyl)benzene (1g). The title compound was prepared according to the General Procedure II using 1-bromo-2-(5-hexen-1-ynyl)benzene and allyl(chloro)diphenylsilane. Colourless oil, purified by column chromatography on silica gel (hexane:EtOAc = 8:2) (50%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.93 (dt, $J$ = 7.2, 6.8 Hz, 2H), 2.12 (t, $J$ = 7.2 Hz, 2H), 2.59 (d, $J$ = 8.0 Hz, 2H), 4.87-5.02 (m, 4H), 5.64 (ddt, $J$ = 10.4, 17.2, 6.8 Hz, 1H), 5.92 (ddt, $J$ = 8.0, 17.2, 8.0 Hz, 1H), 7.22 (t, $J$ = 7.6 Hz, 1H), 7.30-7.43 (m, 8H), 7.47 (d, $J$ = 7.6 Hz, 1H), 7.56 (d, $J$ = 6.4 Hz, 4H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 19.2, 21.3, 32.1, 77.3, 82.6, 94.0, 114.6, 115.3, 126.8, 127.6, 129.2, 129.4, 130.3, 132.5, 134.6, 134.9, 135.7, 136.6, 136.9(6), 137.0; HRMS (EI) caled for C$_{27}$H$_{26}$Si [M$^+$] 378.1804; Found m/z 378.1805.

Ethyl 3-[2-(allyldiphenylsilyl)phenyl]propynoate (1h). To a mixture of 1d (324.5, 1.0 mmol) in THF (5 mL) was added n-BuLi (2.6 M hexane, 461 $\mu$L, 1.2 mmol) at -78 °C under N$_2$. The mixture was stirred for 1 h at ambient temperature before addition of ethyl chloroformate (144 $\mu$L, 1.5 mmol) at -78 °C. The mixture was warmed to ambient temperature and further stirred for 2 h. Upon completion, the mixture was quenched with saturated NH$_4$Cl aqueous solution and extracted with diethyl ether twice. The combined organic layers were washed with brine and dried over MgSO$_4$. The filtrate was concentrated in vacuo to give crude product, which was purified by column chromatography on silica gel (hexane:EtOAc = 9:1) to give 285.7 mg of 1h as a white solid (72%). Mp 92.9-93.9 °C; $^1$H
NMR (CDCl₃, 400 MHz) δ 1.26 (t, J = 7.2 Hz, 3H), 2.66 (dd, J = 0.8, 7.6 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 4.88 (dm, J = 10.0 Hz, 1H), 5.02 (dm, J = 16.8 Hz, 1H), 5.88 (ddt, J = 10.0, 16.8, 7.6 Hz, 1H), 7.34-7.44 (m, 9H), 7.55 (dd, J = 0.8, 6.4 Hz, 2H), 7.64 (d, J = 6.8 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 14.0, 20.8, 61.7, 84.1, 87.0, 115.1, 125.7, 127.7, 127.8, 129.5(1), 129.5(8), 133.9, 134.0, 134.4, 135.7, 137.2, 139.9, 153.6; HRMS (EI) calcd for C₂₆H₂₄O₂Si [M⁺] 396.1546; Found m/z 396.1543.

1-(Allyldiphenylsilyl)-2-(phenylethynyl)benzene (1i). The title compound was prepared according to the General Procedure I using 1d and iodobenzene. Yellow solid, purified by column chromatography on silica gel (hexane:EtOAc = 49:1) (86%). Mp 101.1-102.1 °C; ¹H NMR (CDCl₃, 400 MHz) δ 2.67 (dt, J = 8.0, 1.2 Hz, 2H), 4.91 (dm, J = 10.0 Hz, 1H), 5.01 (dm, J = 16.8 Hz, 1H), 5.97 (ddt, J = 10.0, 16.8, 8.0 Hz, 1H), 6.98 (dd, J = 2.0, 7.6 Hz, 1H), 7.20-7.33 (m, 5H), 7.38-7.47 (m, 8H), 7.63-7.67 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.3, 91.1, 93.4, 114.8, 127.5, 127.7, 128.0, 128.1, 129.4, 129.5(6), 129.5(8), 131.2, 132.6, 134.4, 134.7(two carbons), 135.8, 137.0; HRMS (EI) calcd for C₂₉H₂₄Si [M⁺] 400.1647; Found m/z 400.1641.

4-[2-(Allyldiphenylsilyl)phenylethynyl]benzoic acid methyl ester (1j). The title compound was prepared according to the General Procedure II using 1d and methyl 4-iodobenzoate. White solid, purified by column chromatography on silica gel (hexane:EtOAc = 49:1) (91%). Mp 92.5-93.5 °C; ¹H NMR (CDCl₃, 400 MHz) δ 2.57 (d, J = 7.6 Hz, 2H), 3.90 (s, 3H), 4.84 (dm, J = 10.0 Hz, 1H), 4.94 (dm, J = 17.2 Hz, 1H), 5.88 (ddt, J = 10.0, 17.6, 7.6 Hz, 1H), 6.90 (d, J = 8.4 Hz, 2H), 7.27-7.45 (m, 9H), 7.57 (dd, J = 1.6, 8.4 Hz, 4H), 7.62 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.3, 52.0, 92.6, 94.0, 114.9, 127.5, 127.7, 128.0, 128.1, 129.4, 129.5(6), 129.5(8), 131.2, 132.6, 134.4, 134.7(two carbons), 135.8, 137.0; HRMS (EI) calcd for C₃₁H₂₆O₂Si [M⁺] 458.1702; Found m/z 458.1701.

1-(Allyldiphenylsilyl)-2-(4-bromophenylethynyl)benzene (1k). The title compound was prepared according to the General Procedure II using 1d and 1-bromo-4-iodobenzene. Yellow oil, purified by column chromatography on silica gel (hexane:EtOAc = 19:1) (87%). Mp 19:1 (87%). ¹H NMR (CDCl₃, 400 MHz) δ 2.57 (d, J = 8.0 Hz, 2H), 4.85 (dm, J = 10.0 Hz, 1H), 4.94 (dm, J = 17.6 Hz, 1H), 5.89 (ddt, J = 10.0, 17.6, 8.0 Hz, 1H), 6.71 (d, J = 8.0 Hz, 2H), 7.27 (m, 12H), 7.57 (dm, J = 7.2 Hz, 3H), 7.60 (dm, J = 8.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.3, 92.3, 92.4, 114.9, 121.9, 122.4, 127.7, 128.4, 128.5, 128.7, 129.2, 129.4, 129.6, 131.1, 132.5, 132.6, 133.6, 133.8, 134.2, 134.5, 135.8, 137.1, 137.2; HRMS (EI) calcd for C₂₉H₂₃BrSi [M⁺] 478.0752; Found m/z 478.0750.
1-(Allyldiphenylsilyl)-2-(2-bromophenylethynyl)benzene (1l). The title compound was prepared according to the General Procedure II using 1d and 1-bromo-2-iodobenzene. Yellow oil, purified by column chromatography on silica gel (hexane:EtOAc = 19:1) (98%). \(^1H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.69 (dt, \(J = 8.0, 1.2\) Hz, 2H), 4.92 (dm, \(J = 10.4\) Hz, 1H), 5.04 (dm, \(J = 16.8\) Hz, 1H), 5.99 (ddt, \(J = 10.4, 16.8, 8.0\) Hz, 1H), 6.67 (dt, \(J = 6.8, 2.4\) Hz, 1H), 7.11 (m, 2H), 7.33 (t, \(J = 7.6\) Hz, 1H), 7.37-7.44 (m, 8H), 7.53-7.56 (m, 1H), 7.65 (dm, \(J = 6.8\) Hz, 4H), 7.76 (d, \(J = 7.6\) Hz, 1H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 21.4, 91.9, 95.4, 114.9, 125.0, 125.1, 126.6, 127.7, 127.8, 129.1, 129.6, 131.3, 133.0, 134.3, 134.6, 135.8, 136.9, 137.2; HRMS (EI) calcd for C\(_{29}\)H\(_{23}\)BrSi [M\(^+\)] 478.0752; Found m/z 478.0747.

1-(Allyldiphenylsilyl)-2-(2-methoxyphenylethynyl)benzene (1m). The title compound was prepared according to the General Procedure II using 1d and ethyl 2-iodoamisole. White solid, purified by chromatography on silica gel (hexane:EtOAc = 19:1) (81%). Mp 89.9-90.9 \(^o\)C; \(^1H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.70 (d, \(J = 8.0\) Hz, 2H), 3.77 (s, 3H), 4.87 (dm, \(J = 10.0\) Hz, 1H), 4.99 (dd, \(J = 1.6, 17.2\) Hz, 1H), 5.97 (ddt, \(J = 10.0, 17.2, 8.0\) Hz, 1H), 6.70 (dd, \(J = 1.6, 7.6\) Hz, 1H), 6.77 (dt, \(J = 0.8, 7.6\) Hz, 1H), 6.81 (d, \(J = 7.6\) Hz, 1H), 7.20-7.47 (m, 2H), 7.31-7.43 (m, 8H), 7.61 (dd, \(J = 1.6, 7.6\) Hz, 4H), 7.68 (d, \(J = 7.6\) Hz, 1H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 21.2, 55.5, 89.9, 95.0, 110.5, 112.4, 114.6, 120.1, 127.3, 127.6, 129.2, 129.4, 129.5, 129.9, 132.9, 133.2, 134.7, 134.8, 135.9, 136.8, 137.2, 159.8; HRMS (EI) calcd for C\(_{30}\)H\(_{26}\)OSi [M\(^+\)] 430.1753; Found m/z 430.1753.

1-(Allyldiphenylsilyl)-2-(bromoethynyl)benzene (1n). Yellow solid, purified by column chromatography on silica gel (hexane:EtOAc = 49:1) (80%). Mp 40.0-41.0 \(^o\)C; \(^1H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.56 (dd, \(J = 1.2, 8.0\) Hz, 2H), 4.90 (dm, \(J = 9.6\) Hz, 1H), 5.00 (dm, \(J = 17.6\) Hz, 1H), 5.89 (ddt, \(J = 9.6, 17.6, 8.0\) Hz, 1H), 7.29 (tm, \(J = 7.6\) Hz, 1H), 7.35-7.44 (m, 8H), 7.50 (dm, \(J = 6.8\) Hz, 1H), 7.56 (dm, \(J = 7.2\) Hz, 4H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 21.1, 54.4, 81.5, 114.9, 127.7, 127.8, 129.0, 129.4, 129.5, 133.0, 134.2, 134.3, 135.6, 136.9, 138.0; HRMS (EI) calcd for C\(_{23}\)H\(_{19}\)BrSi [M\(^+\)] 402.0439; Found m/z 402.0439.

Preparation of 1-[Allyl(methyl)phenylsilyl]-2-ethynylcycloalkenes (1o) and (1p)

2-Bromo-1-cyclopenten-1-carbaldehyde (H). \(^9\) To a mixture of dry DMF (11.5 mL, 135 mmol) and dry CHCl\(_3\) (80 mL) was added PBr\(_3\) (13.6 mL, 150 mmol) in CHCl\(_3\) (20 mL) dropwise at 0 \(^o\)C.

After stirring for 1 h at ambient temperature, cyclopentanone (4.4 mL, 50 mmol) in dry CHCl₃ (10 mL) was added at 0 °C and the resulting solution was stirred at ambient temperature for overnight (12 h). The reaction mixture was poured into 300 mL of ice water, neutralized with solid NaHCO₃, and extracted with dichloromethylene. The extract was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by elution through a short silica gel column to afford compound H (5.50 g, 31.1 mmol, 62 %) as a yellow oil. The spectral data were identical to those reported in literature.¹⁰

1-Bromo-2-(2,2-dibromoethenyl)cyclopentene (I).¹¹ To a solution of triphenylphosphine (24.4 g, 93.0 mmol) in CH₂Cl₂ (100 mL) under N₂ was added a solution of carbon tetrabromide (20.6 g, 62.2 mmol) in CH₂Cl₂ (50 mL) at ambient temperature. After the reaction mixture was allowed to stir at ambient temperature for 2 h, a solution of H (5.40 g, 31.0 mmol) in CH₂Cl₂ (20 mL) was added at ambient temperature and stirred at ambient temperature for an additional 16 h before addition of hexane (200 mL). The precipitate was removed by filtration and the solvent was removed in vacuo. Another 100 mL of hexane was added followed by filtration through Celite to remove the additional residue. The residue was purified by column chromatography on silica gel to give title compound I (8.12 g, 24.8 mmol, 81% yield) as a brown oil. The spectral data were identical to those reported in literature.¹¹

1-Bromo-2-(trimethylsilylethynyl)cyclopentene (J). To a solution of I (3.31 g, 10.0 mmol) in THF (30 mL) was added n-BuLi (13.8 mL of 1.6 M hexane solution, 22.0 mmol) at -78 °C. The reaction mixture was allowed to stir at -78 °C for 1 h and at ambient temperature for 2 h, and then trimethylsilyl chloride (1.55 mL, 12.2 mmol) was added. The mixture was stirred at ambient temperature for overnight (14 h). The reaction mixture was poured into 50 mL of ice water, and extracted with diethyl ether twice. The combined organic phases were dried over MgSO₄ and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel to give title compound J (1.97 g, 8.1 mmol, 81% yield) as a brown oil. The spectral data were identical to those reported in literature.¹¹

1-(Allyldiphenylsilyl)-2-(trimethylsilylethynyl)cyclopentene (K). To a solution of J (1.95 g, 8.0 mmol) in THF (20 mL) was added n-BuLi (2.6 M hexane solution, 3.4 mL, 8.8 mmol) at -78 °C. The mixture was allowed to warm to ambient temperature and stirred for 1 h, and then allylchloro(methyl)phenylsilane (1.89 g, 9.6 mmol) in THF (10 mL) was added via cannula at -78 °C. The reaction mixture was allowed to stir at -78 °C for 1 h and at ambient temperature for overnight. Upon completion, the reaction mixture was poured into saturated NH₄Cl aqueous solution, and extracted with ethyl acetate twice. The combined organic layer was washed with saturated NaHCO₃

aqueous solution, and then the organic phase was dried over MgSO₄ and concentrated in vacuo to give yellow oil, which was purified by chromatography on silica gel (hexane:EtOAc = 97:3) to give title compound K (2.03 g, 6.3 mmol, 78% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 0.15 (s, 9H), 0.48 (s, 3H), 1.82 (quint, J = 7.6 Hz, 2H), 2.07 (dm, J = 8.0 Hz, 2H), 2.44-2.50 (m, 2H), 2.57 (tt, J = 2.4, 7.6 Hz, 2H), 4.85 (dm, J = 10.0 Hz, 1H), 4.91 (dm, J = 17.6 Hz, 1H), 5.82 (ddt, J = 10.0, 17.6, 8.0 Hz, 1H), 7.33-7.37 (m, 3H), 7.54-7.56 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ -5.2, -0.2, 21.7, 24.1, 38.9, 40.2, 98.6, 104.1, 113.8, 127.6, 129.0, 134.2, 134.5, 135.3, 136.8, 149.2; HRMS (EI) calcd for C₂₀H₂₈Si₂ [M⁺] 324.1730; Found m/z 324.1731.

1-[Allyl(methyl)phenylsilyl]-2-ethynylcyclopentene (1o). To a solution of K (3.43 g, 12.6 mmol) in MeOH–THF (2:1, 120 mL) was added KOH aqueous solution (0.8 M, 19 mL) at ambient temperature. After 0.5 h, the reaction mixture was concentrated under reduced pressure. To the residue was added saturated NH₄Cl aqueous solution, and it was extracted with hexane, washed with water, dried over MgSO₄, and evaporated. The crude product was purified by column chromatography on silica gel (hexane:EtOAc = 49:1) to give 1o (2.96 g, 93%) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 0.49 (s, 3H), 1.84 (quint, J = 7.6 Hz, 2H), 2.07 (dm, J = 8.0 Hz, 2H), 2.46-2.51 (m, 2H), 2.57-2.62 (m, 2H), 3.10 (s, 1H), 4.86 (dm, J = 10.4 Hz, 1H), 4.92 (dm, J = 17.6 Hz, 1H), 5.82 (ddt, J = 10.4, 17.6, 8.0 Hz, 1H), 7.32-7.38 (m, 3H), 7.53-7.56 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ -5.2, 21.7, 23.9, 38.8, 40.3, 81.6, 82.4, 113.9, 127.6(6), 127.6(9), 129.1, 134.1, 134.3, 136.5, 149.2; HRMS (EI) calcd for C₁₇H₂₀Si [M⁺] 252.1334; Found m/z 252.1330.

2-Bromo-1-cyclohexen-1-carbaldehyde. The title compound was prepared according to the procedure described above using phosphorus tribromide (6.00 g, 22.2 mmol), DMF (2.05 g, 28.1 mmol), and cyclohexanone (0.931 g, 9.50 mmol). Light yellow oil. (718.4 mg, 40%). The spectral data were identical to those reported in literature.¹²

1-Bromo-2-(2,2-dibromoethenyl)cyclohexene. The title compound was prepared according to the similar method described above. Yellow oil, purified by column chromatography on silica gel (hexane:EtOAc = 99:1) (51%). ¹H NMR (CDCl₃, 400 MHz) δ 0.21 (s, 9H), 1.54-1.72 (m, 4H), 2.24-2.28 (m, 2H), 2.52-2.56 (m, 2H).

1-(Allyldiphenylsilyl)-2-(trimethylsilylethynyl)cyclohexene. The title compound was prepared according to the similar method described above, and used for next reaction without further

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puriﬁcation.

I-[Allyl(methyl)phenylsilyl]-2-ethynylcyclohexene (1p). The title compound was prepared according to the similar method described above. Yellow oil, puriﬁed by column chromatography on silica gel (hexane:EtOAc = 8:2) (78%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 0.47 (s, 3H), 1.51-1.56 (m, 2H), 1.59-1.65 (m, 2H), 2.06-2.10 (m, 2H), 2.10 (dm, $J$ = 8.0 Hz, 2H), 2.23-2.27 (m, 2H), 2.93 (s, 1H), 4.85 (dm, $J$ = 10.0 Hz, 1H), 4.91 (dm, $J$ = 17.6 Hz, 1H), 5.82 (ddt, $J$ = 10.0, 17.6, 8.0 Hz, 1H), 7.32-7.36 (m, 3H), 7.53-7.56 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ -4.6, 21.8, 22.0(9), 22.1(4), 30.0, 32.4, 79.5, 86.3, 113.8, 127.5, 128.9, 130.0, 134.3, 134.7, 137.0, 144.0; HRMS (EI) calcd for C$_{18}$H$_{22}$Si [M$^+$] 266.1491; Found m/z 266.1490.

I-[Z-crotyldiphenylsilyl]-2-(ethynyl)benzene (1q). To a solution of 1-bromo-2-(trimethylsilyl-ethynyl)benzene (506.4 mg, 2.0 mmol) in THF (10 mL) was added dropwise n-BuLi (2.6 M in hexane, 850 µL, 2.2 mmol) at –78 $^\circ$C. After stirring at –78 $^\circ$C for 1 h, (Z)-crotylbromodiphenylsilane$^{13}$ (952 µL, 3 mmol) was added dropwise to the mixture. The reaction mixture was stirred at –78 $^\circ$C for 1 h, and then allowed to warm to ambient temperature. The volatile materials were removed in vacuo, and the residue was subjected to next reaction without further puriﬁcation. The removal of trimethylsilyl group was carried out using the same method of general procedure III. Colorless oil, puriﬁed by column chromatography on silica gel (hexane:EtOAc = 9:1) (48% for two steps). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.50 (dt, $J$ = 6.8, 0.8 Hz, 3H), 2.60 (d, $J$ = 8.4 Hz, 2H), 2.97 (s, 1H), 5.42 (m, 1H), 5.60 (m, 1H), 7.27-7.45 (m, 8H), 7.56-7.61 (m, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 12.8, 14.6, 81.3, 84.8, 123.4, 125.5, 127.6, 127.9, 128.4, 129.3, 129.4, 133.6, 134.7, 135.8, 137.0, 137.6; HRMS (EI) calcd for C$_{24}$H$_{22}$Si [M$^+$] 338.1491; Found m/z 338.1490.

General Procedure for Gold-Catalyzed Intramolecular Allylation to Alkynes.

The cationic gold catalyst was generated in a 1 dram vial with a threaded cap by addition of AgNTf$_2$ (0.01 equiv.), (Ph$_3$P)AuCl (0.01 equiv.) and nitromethane (0.4 M based on starting material). After allowing the catalyst mixture to sit for 10 minutes, the appropriate starting material (1 equiv.) and water (2 equiv.) in nitromethane (0.4 M) were added. The resulting mixture (0.2 M) was monitored by TLC until all starting material was consumed. Upon completion, the reaction mixture was concentrated and loaded directly onto a silica column resulted in isolation of analytically pure products.

Table 1. Solvent effects for the gold-catalyzed intramolecular alkylation of 1c

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**[2-(1-Allyl-(E)-1-hexenyl)phenyl]dimethylsilanol (2a).** Colorless oil, purified by column chromatography (hexane:EtOAc = 9:1); ¹H NMR (CDCl₃, 400 MHz) δ 0.38 (s, 6H), 0.93 (t, J = 7.6 Hz, 3H), 1.35-1.47 (m, 4H), 1.95 (brs, 1H), 2.20 (dt, J = 7.2 Hz, 2H), 3.18 (d, J = 6.4 Hz, 2H), 5.01 (dm, J = 10.0 Hz, 1H), 5.05 (dm, J = 16.8 Hz, 1H), 5.44 (t, J = 7.6 Hz, 1H), 5.78 (ddt, J = 10.0, 16.8, 6.4 Hz, 1H), 7.14 (dd, J = 1.2, 7.2 Hz, 1H), 7.25 (dt, J = 1.2, 7.2 Hz, 1H), 7.29 (dt, J = 1.2, 7.2 Hz, 1H), 7.58 (dd, J = 1.2, 7.2 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 2.1, 13.9, 22.6, 28.0, 31.7, 37.8, 115.9, 125.9, 128.4, 128.8, 131.6, 134.4, 135.6, 136.8, 140.3, 150.3; HRMS (EI) calcd for C₁₇H₂₆OSi [M⁺] 274.1753; Found m/z 274.1750.

**Di[[2-(1-Allyl-(E)-1-hexenyl)phenyl]dimethylsilyl] ether (3).** ¹H NMR (CDCl₃, 400 MHz) δ 0.31 (s, 12H), 0.90 (t, J = 7.2 Hz, 6H), 1.33-1.38 (m, 8H), 2.13 (dm, J = 7.6 Hz, 4H), 3.10 (d, J = 6.4 Hz, 4H), 4.96 (dm, J = 10.0 Hz, 2H), 5.01 (dm, J = 16.8 Hz, 2H), 5.36 (t, J = 7.6 Hz, 2H), 5.76 (ddt, J = 10.0, 16.8, 6.4 Hz, 2H), 7.12 (dd, J = 1.2, 7.2 Hz, 2H), 7.20 (dt, J = 1.2, 7.2 Hz, 2H), 7.27 (dt, J = 1.2, 7.2 Hz, 2H), 7.66 (dd, J = 1.2, 7.2 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 3.0, 14.0, 22.7, 28.1, 31.5, 37.9, 115.4, 125.6, 128.4, 128.5, 131.6, 134.4, 135.9, 137.2, 139.3, 150.6; HRMS (EI) calcd for C₃₄H₅₀OSi₂ [M⁺] 530.3400; Found m/z 530.3400.

**[2-(1-Allyl-(E)-1-hexenyl)phenyl]methyl(phenyl)silanol (2b).** Colorless oil, purified by column chromatography (hexane:EtOAc = 9:1); ¹H NMR (CDCl₃, 400 MHz) δ 0.63 (s, 3H), 0.86 (t, J = 6.8 Hz, 3H), 1.20-1.28 (m, 4H), 2.05 (dm, J = 6.8 Hz, 2H), 2.30 (brs, 1H), 2.96 (m, 2H), 4.96 (dm, J = 10.4 Hz, 1H), 4.97 (dm, J = 17.6 Hz, 1H), 5.26 (t, J = 6.8 Hz, 1H), 5.71 (ddt, J = 10.4, 17.6, 6.8 Hz, 1H), 7.12 (dd, J = 1.2, 7.2 Hz, 1H), 7.27 (dt, J = 1.6, 7.2 Hz, 1H), 7.31-7.37 (m, 4H), 7.53 (dd, J = 1.6, 7.6 Hz, 2H), 7.64 (dd, J = 1.2, 7.6 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 0.4, 13.9, 22.5, 27.9, 31.4, 37.3, 115.9, 125.8, 127.7, 128.5, 129.2, 129.4, 132.2, 133.6, 134.7, 135.4, 135.7, 139.2, 140.1, 150.8; HRMS (EI) calcd for C₂₅H₂₆OSi [M⁺] 336.1909; Found m/z 336.1910.
[2-(1-Allyl-(E)-1-hexenyl)phenyl]diphenylsilanol (2c). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); $^1$H NMR (CDCl$_3$, 400 MHz) δ 0.86 (t, $J = 6.8$ Hz, 3H), 1.14-1.26 (m, 4H), 2.03 (dt, $J = 6.8$, 7.2 Hz, 2H), 2.74 (brs, 1H), 2.99 (d, $J = 6.8$ Hz, 2H), 5.01 (dm, $J = 16.4$ Hz, 1H), 5.02 (dm, $J = 9.6$ Hz, 1H), 5.31 (t, $J = 7.2$ Hz, 1H), 5.76 (ddt, $J = 9.6$, 16.4, 6.8 Hz, 1H), 7.22 (m, 2H), 7.36-7.45 (m, 8H), 7.60 (dm, $J = 7.6$ Hz, 4H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 3.9, 22.4, 27.8, 31.3, 37.3, 116.1, 125.7, 127.7, 128.6, 129.4, 129.7, 132.5, 133.1, 134.9, 135.6, 136.8, 136.9, 140.3, 151.1; HRMS (EI) calcd for C$_{27}$H$_{30}$OSi [M$^+$] 398.2066; Found m/z 398.2073.

[2-(1-Allyl- (E)-2-deuterio-1-hexenyl)phenyl]diphenylsilanol ((E)-2c-d). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); $^1$H NMR (CDCl$_3$, 400 MHz) δ 0.86 (m, 3H), 1.14-1.26 (m, 4H), 2.03 (m, 2H), 2.74 (brs, 1H), 2.99 (d, $J = 6.8$ Hz, 2H), 5.01 (dm, $J = 16.4$ Hz, 1H), 5.02 (m, $J = 9.6$ Hz, 1H), 5.31 (tm, $J = 7.2$ Hz, 0.3H), 5.76 (ddt, $J = 9.6$, 16.4, 6.8 Hz, 1H), 7.22 (m, 2H), 7.36-7.45 (m, 8H), 7.60 (dm, $J = 7.6$ Hz, 4H).

[2-(1-Methylene-3-butenyl)phenyl]diphenylsilanol (2d). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.56 (brs, 1H), 2.92 (dd, $J = 1.2$, 7.2 Hz, 2H), 4.91-4.98 (m, 2 H), 5.03-5.09 (m, 2H), 5.72 (dddt, $J = 1.6$, 10.4, 17.6, 7.2 Hz, 1H), 7.21 (d, $J = 7.6$ Hz, 1H), 7.24 (tt, $J = 1.2$, 7.6 Hz, 1H), 7.35-7.46 (m, 8H), 7.59 (dm, $J = 8.0$ Hz, 4H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 42.6, 115.1, 117.3, 126.1, 127.8, 127.9, 129.6, 129.8, 132.8, 134.9, 135.0, 136.4, 136.8, 150.0, 151.9; HRMS (EI) calcd for C$_{23}$H$_{22}$OSi [M$^+$] 342.1440; Found m/z 342.1437.

[2-(1-Methylene-3-butenyl)phenyl]diphenylsilanol (2e). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); $^1$H NMR (CDCl$_3$, 400 MHz) δ 1.57 (d, $J = 6.8$ Hz, 3 H), 2.76 (brs, 1H), 2.93 (d, $J = 7.2$ Hz, 2H), 5.00 (dm, $J = 10.8$ Hz, 1H), 5.01 (dm, $J = 16.8$ Hz, 1H), 5.72 (ddm, $J = 10.8$, 16.8 Hz, 1H), 7.21 (t, $J = 7.6$ Hz, 2H), 7.35-7.46 (m, 8H), 7.59-7.61 (m, 4H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 13.5, 36.9, 116.0, 125.7, 126.5, 127.7, 128.4, 129.5, 129.7, 133.2, 134.8, 135.3, 136.7, 136.8, 141.1, 151.3; HRMS (EI) calcd for C$_{24}$H$_{24}$OSi [M$^+$] 356.1596; Found m/z 356.1600.

[2-(1-Allyl-(E)-1,4-pentadienyl)phenyl]diphenylsilanol (2f). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.75 (t, $J = 7.2$ Hz, 2H), 2.49 (d, $J = 7.2$ Hz, 2H), 2.59 (brs, 1H), 4.95-5.01 (m, 4H), 5.32 (t, $J = 7.2$ Hz, 1H), 5.63 (ddt, $J = 16.8$, 10.0, 6.8 Hz, 1H), 5.73 (ddt, $J = 9.2$, 21.2, 6.8 Hz, 1H), 7.19-7.22 (m, 2H), 7.34-7.44 (m, 8H), 7.57 (dd, $J = 1.2$, 7.6 Hz, 4H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 32.6, 37.2, 115.6, 116.2, 125.8, 127.7, 128.5, 129.1, 129.5, 129.7, 133.2, 134.9, 135.3, 136.0, 136.7, 136.9, 141.3, 151.0; HRMS (EI) calcd for C$_{26}$H$_{26}$OSi [M$^+$] 382.1753; Found m/z 382.1759.
[2-(1-Allyl-(E)-1,5-hexadienyl)phenyl]diphenylsilanol (2g). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.94 (q, $J = 6.8$ Hz, 2H), 2.11 (q, $J = 6.8$ Hz, 2H), 2.77 (brs, 1H), 2.95 (d, $J = 6.8$ Hz, 2H), 4.92-5.01 (m, 4H), 5.28 (t, $J = 6.8$ Hz, 1H), 5.66-5.78 (m, 2H), 7.18-7.22 (m, 2H), 7.34-7.44 (m, 8H), 7.56-7.59 (m, 4H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 27.4, 33.0, 37.4, 115.1, 116.1, 125.7, 127.7, 128.6, 129.4, 129.7, 131.3, 133.0, 134.9, 135.5, 136.8, 136.9, 138.1, 140.9, 151.1; HRMS (EI) calcd for C$_{27}$H$_{28}$OSi [M$^+$] 396.1909; Found m/z 396.1909.

(E)-3-[2-(Hydroxydiphenylsilyl)phenyl]-2,5-hexadienoic acid ethyl ester (2h). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.24 (t, $J = 7.2$ Hz, 3H), 2.59 (brs, 1H), 3.46 (d, $J = 7.2$ Hz, 2H), 4.11 (q, $J = 7.2$ Hz, 2H), 4.99 (dm, $J = 10.4$ Hz, 1H), 5.00 (dm, $J = 17.2$ Hz, 1H), 5.62 (s, 1H), 5.74 (ddt, $J = 10.4$, 17.2, 7.2 Hz, 1H), 7.11 (d, $J = 3.6$ Hz, 1H), 7.28 (dt, $J = 1.2$, 7.6 Hz, 1H), 7.34-7.45 (m, 7H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.58 (dd, $J = 1.2$, 8.0 Hz, 4H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 14.2, 38.8, 59.9, 117.1, 120.8, 126.8, 127.7, 127.8, 129.6, 129.9, 132.9, 134.7, 134.8, 136.1, 137.0, 149.2, 159.6, 165.8; HRMS (EI) calcd for C$_{26}$H$_{26}$O$_3$Si [M$^+$] 414.1651; Found m/z 414.1654.

[2-[(E)-1-benzylidene-3-butenyl]phenyl]diphenylsilanol (2i). Yellow oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.73 (brs, 1H), 3.23 (dm, $J = 6.8$ Hz, 2H), 5.02 (dm, $J = 16.8$ Hz, 1H), 5.03 (dm, $J = 16.8$ Hz, 1H), 5.66 (ddt, $J = 10.4$, 16.8, 6.8 Hz, 1H), 6.36 Hz (s, 1H), 7.12 (dm, $J = 8.4$ Hz, 1H), 7.23-7.45 (m, 12H), 7.52 (dm, $J = 7.6$ Hz, 1H), 7.60 (dm, $J = 7.6$ Hz, 4H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 37.8, 116.8, 124.3, 126.1, 126.9, 127.8, 128.2, 128.6, 128.7, 129.5, 129.8, 131.3, 133.2, 135.0, 135.3, 136.6, 136.7, 137.1, 142.7, 150.9; HRMS (EI) calcd for C$_{29}$H$_{26}$OSi [M$^+$] 418.1753; Found m/z 418.1753.

[2-[(E)-1-(4-methoxycarbonylbenzylidene)-3-butenyl]phenyl]diphenylsilanol (2j). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 8:2); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.76 (brs, 1H), 3.16 (d, $J = 6.4$ Hz, 2H), 3.91 (s, 3H), 5.02 (dm, $J = 16.8$ Hz, 1H), 5.04 (dm, $J = 10.0$ Hz, 1H), 7.01 (d, $J = 7.6$ Hz, 2H), 7.27-7.46 (m, 9H), 7.55-7.58 (d, $J = 8.0$ Hz, 5H), 7.93 (d, $J = 7.6$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 37.9, 52.0, 117.0, 126.3, 127.8, 128.2, 128.4, 128.6, 129.4, 129.6, 129.8, 130.6, 133.2, 134.8(9), 134.9(4), 136.4, 137.2, 141.5, 144.5, 150.8, 166.9; HRMS (EI) calcd for C$_{32}$H$_{30}$O$_3$Si [M$^+$] 476.1808; Found m/z 476.1810.
[2-[(E)-1-(4-bromobenzylidene)-3-butenyl]phenyl]diphenylsilanol (2k). Yellow oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\) 2.62 (s, 1H), 3.14 (d, \(J = 6.4\) Hz, 2H), 5.02 (dd, \(J = 1.6, 16.8\) Hz, 1H), 5.05 (dd, \(J = 1.6, 10.4\) Hz, 1H), 5.75 (ddt, \(J = 10.4, 16.8, 6.4\) Hz, 1H), 6.23 Hz (s, 1H), 6.82 (d, \(J = 8.8\) Hz, 2H), 7.28-7.45 (m, 10H), 7.54 (d, \(J = 8.0\) Hz, 2H), 7.57 (dm, \(J = 8.0\) Hz, 1H), \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\) 37.7, 117.0, 120.8, 126.2, 127.8, 128.4, 129.6, 129.8, 130.2, 130.3, 131.3, 133.1, 134.9, 135.0, 135.6, 136.5, 137.2, 143.2, 150.8; HRMS (EI) calcd for C\textsubscript{29}H\textsubscript{25}BrOSi [M\textsuperscript{+}] 496.0858; Found \textit{m/z} 496.0850.

[2-[(E)-1-(2-bromobenzylidene)-3-butenyl]phenyl]diphenylsilanol (2l). Yellow oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\) 2.95 (brs, 1H), 3.11 (d, \(J = 6.8\) Hz, 2H), 4.84 (dd, \(J = 1.2, 17.2\) Hz, 1H), 4.92 (dd, \(J = 1.2, 17.2\) Hz, 1H), 5.66 (ddt, \(J = 10.4, 17.2, 6.8\) Hz, 1H), 6.39 (s, 1H), 7.12 (dt, \(J = 1.6, 8.4\) Hz, 1H), 7.19 (dd, \(J = 1.6, 7.6\) Hz, 1H), 7.27 (t, \(J = 7.6\) Hz, 1H), 7.33-7.48 (m, 10H), 7.55 (d, \(J = 8.0\) Hz, 1H), 7.60 (dm, \(J = 8.0\) Hz, 1H), \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\) 38.0, 116.7, 124.3, 126.3, 127.0, 127.8, 128.6, 129.2, 129.6, 129.9, 130.1, 130.5, 132.5, 132.9, 134.9, 135.1, 136.4, 137.1, 137.3, 144.9, 149.8; HRMS (EI) calcd for C\textsubscript{29}H\textsubscript{25}BrOSi [M\textsuperscript{+}] 496.0858; Found \textit{m/z} 496.0850.

[2-[(E)-1-(2-Methoxybenzylidene)-3-butenyl]phenyl]diphenylsilanol (2m). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\) 2.96 (d, \(J = 6.8\) Hz, 2H), 3.91 (s, 3H), 4.84 (dm, \(J = 17.2\) Hz, 1H), 4.91 (dm, \(J = 10.0\) Hz, 1H), 5.02 (d, \(J = 1.2\) Hz, 1H), 5.73 (ddt, \(J = 10.0, 17.2, 6.8\) Hz, 1H), 6.92-6.98 (m, 2H), 7.12 (d, \(J = 6.8\) Hz, 1H), 7.20-7.41 (m, 11H), 7.60 (dm, \(J = 8.0\) Hz, 1H), \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\) 38.1, 55.3, 107.8, 116.4, 120.8, 125.8, 125.9, 126.0, 127.7, 128.4, 128.5, 129.0, 129.6, 130.3, 134.9, 135.1, 136.4, 137.1, 137.3, 144.9, 149.8; HRMS (EI) calcd for C\textsubscript{30}H\textsubscript{28}O\textsubscript{2}Si [M\textsuperscript{+}] 448.1859; Found \textit{m/z} 448.1856.

[2-(1-Bromomethylene-3-butenyl)phenyl]methoxydiphenylsilane (2n). Yellow oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\) 2.71 (d, \(J = 6.8\) Hz, 2H), 3.54 (s, 3H), 4.88 (dm, \(J = 17.2\) Hz, 1H), 4.91 (dm, \(J = 10.0\) Hz, 1H), 5.53 (ddt, \(J = 10.0, 17.2, 6.8\) Hz, 1H), 5.90 (s, 1H), 7.12 (d, \(J = 7.6\) Hz, 1H), 7.30-7.46 (m, 8H), 7.60 (d, \(J = 7.6\) Hz, 4H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\) 39.8, 51.7, 107.8, 116.6, 126.6, 127.8, 128.9, 129.6, 129.9, 132.7, 133.6, 134.2, 135.5, 135.6, 136.9, 145.4.; HRMS (EI) calcd for C\textsubscript{24}H\textsubscript{23}BrOSi [M\textsuperscript{+}] 434.0702; Found \textit{m/z} 434.0705.
General Procedure for Tamao-Fleming Oxidation.

Upon completion of gold-catalyzed reaction (0.2 mmol scale), the reaction mixture was filtered through neutral silica gel pad, and the filtrate was concentrated in vacuo. The crude product was used for the Tamao-Fleming oxidation without further purification. To a suspension of KF (47 mg, 0.8 mmol) and KHCO₃ (163 mg, 1.6 mmol) in MeOH (3 mL) was added a solution of crude product 2o (0.20 mmol) in THF (3 mL) at ambient temperature. Aqueous H₂O₂ (30-35%, 0.5 mL, 0.4 mmol) was sequentially added dropwise. After being stirring for 36 h at room temperature, the resulting mixture was poured into aqueous sodium thiosulfate and extracted with Et₂O (3 x 5 mL). The extracts were concentrated followed by chromatography on silica gel to afford 16.8 mg (0.112 mmol, 56% for two steps) of (Z)-4a as a colorless oil.

2-[(Z)-1-Methyl-3-butenylidene]cyclopentanone ((Z)-4a). Colorless oil, purified by column chromatography on silica gel (pentane:Et₂O = 8:2) (56%); ¹H NMR (CDCl₃, 400 MHz) δ 1.81 (t, J = 1.2 Hz, 3H), 1.87 (quint, J = 7.6 Hz, 2H), 2.33 (t, J = 1.2 Hz, 2H), 2.60 (tm, J = 7.6 Hz, 2H), 3.49 (dt, J = 6.4, 1.6 Hz, 2H), 5.01 (dm, J = 10.0 Hz, 1H), 5.07 (dm, J = 10.0 Hz, 1H), 5.76 (ddt, J = 10.0, 16.8, 6.8 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 19.3, 21.8, 29.5, 37.6, 40.6, 116.0, 131.3, 135.4, 148.0, 207.3; HRMS (EI) calcd for C₁₀H₁₄O [M⁺] 150.1045; Found m/z 150.1043.

NOE experiments

2-[(Z)-1-Methyl-3-butenylidene]cyclohexanone ((Z)-4b). The title compound was prepared according to the procedure described above using 1-[allyl(methyl)phenylsilyl]-2-ethynylecyclohexene 1p. Colorless oil, purified by column chromatography on silica gel (pentane:Et₂O = 8:2) (62% for two steps); ¹H NMR (CDCl₃, 400 MHz) δ 1.67-1.76 (m, 2H), 1.83-1.89 (m, 2H), 1.92 (t, J = 1.6 Hz, 3H), 2.41 (t, J = 6.4 Hz, 2H), 2.49 (tm, J = 6.4 Hz, 2H), 2.84 (dt, J = 6.4, 1.6 Hz, 2H), 5.04 (dm, J = 9.6 Hz, 1H), 5.05 (dm, J = 17.6 Hz, 1H), 5.65 (ddt, J = 9.6, 17.6, 1.6 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.1, 24.8, 25.0, 29.7, 39.6, 42.9, 115.8, 134.1, 134.4, 140.7, 202.4; HRMS (EI) calcd for C₁₁H₁₆O [M⁺] 164.1201; Found m/z 164.1202.
NOE experiments

[2-(1-Methylene-2-methyl-3-butenyl)phenyl]diphenylsilanol (2q). Yellow oil, purified by column chromatography on silica gel (hexane:EtOAc = 8:2); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.11 (d, $J = 7.2$ Hz, 3H), 3.12 (quint, $J = 7.2$ Hz, 1H), 4.93 (dm, $J = 16.8$ Hz, 1H), 4.94 (s, 1H), 5.00 (dm, $J = 10.0$ Hz, 1H), 5.14 (t, $J = 1.2$ Hz, 1H), 5.81 (ddd, $J = 7.2$, 10.0, 16.8 Hz, 1H), 7.19-7.25 (m, 3H), 7.34-7.44 (m, 7H), 7.55-7.58 (m, 4H); $^{13}$C NMR (CD$_2$D$_6$, 100 MHz) $\delta$ 19.3, 45.5, 114.7, 115.1, 127.1, 128.8, 129.7, 130.2, 130.7(1), 130.7(2), 134.3, 136.1, 136.2, 138.0, 142.6, 157.6; HRMS (EI) calcd for C$_{24}$H$_{24}$OSi [M+] 356.1596; Found m/z 356.1593.

9-Hexylidene-7-methoxy-5,5-diphenyl-6,7,8,9-tetrahydro-5-sila-benzocycloheptene (8). The gold-catalyzed reaction was carried out according to the similar method described in general procedure. This condition provided the compound 8 selectively (see table 1 shown below). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 24:1) (86%); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 0.71(t, $J = 7.2$ Hz, 3H), 1.02 (m, 4H), 1.43 (dd, $J = 11.6$, 12.8 Hz, 1H), 1.81-2.01 (m, 3H), 2.15 (dd, $J = 10.0$, 13.2 Hz, 1H), 2.90 (d, $J = 13.2$ Hz, 1H), 3.32 (s, 3H), 3.45 (m, 1H), 5.23 (t, $J = 7.2$ Hz, 1H), 7.06-7.08 (m, 2H), 7.11 (d, $J = 7.2$ Hz, 1H), 7.19-7.36 (m, 11H); $^{13}$C NMR (CD$_2$D$_6$, 100 MHz) $\delta$ 14.0, 20.5, 22.3, 28.1, 31.3, 38.3, 55.5, 79.2, 125.7, 127.7, 127.8, 128.0, 129.3, 129.4, 130.0, 132.0, 134.5, 135.0, 135.3, 135.4, 135.5, 136.2, 137.1, 153.8; HRMS (EI) calcd for C$_{28}$H$_{32}$OSi [M+] 412.2222; Found m/z 412.2228.

[2-(1-Allyl-(E))-1-hexenyl)phenyl]dimethylsilyl methyl ether (9). To a solution of compound 8 (0.15 mmol) in dry CH$_2$Cl$_2$ (1 mL) was added Tf$_2$NH (2.1 mg, 5 mol%). The reaction mixture was stirred for 0.5 h at ambient temperature, and saturated aqueous NaHCO$_3$ (2 mL) was added and extracted with dichloromethane. The extracts were concentrated in vacuo, and purified by chromatography on silica gel to afford 55.7 mg (0.135 mmol, 90%) of 9 as colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 0.81 (t, $J = 7.2$ Hz, 3H), 1.06-1.20 (m, 4H), 1.78 (q, $J = 6.8$ Hz, 2H), 2.52 (d, $J = 6.4$ Hz, 2H), 3.52 (s, 3H), 4.83 (dm, $J = 16.8$ Hz, 1H), 4.84 (dm, $J = 10.4$ Hz, 1H), 5.16 (t, $J =$...
6.8 Hz, 1H), 5.54 (ddt, J = 10.4, 16.8, 6.4 Hz, 1H), 7.15(d, J = 7.6 Hz, 1H), 7.26 (dt, J = 1.2, 7.2 Hz, 1H), 7.33-7.42 (m, 7H), 7.58 (dd, J =1.2, 7.6 Hz, 4H), 7.72 (dd, J =1.6, 8.0 Hz, 1H); 

$^{13}$C NMR (CDCl$_3$, 100 MHz) δ 14.0, 22.4, 17.7, 31.1, 37.0, 51.5, 115.0, 125.4, 127.6, 128.9, 129.4(7), 129.5(5), 131.7, 132.5, 135.2, 135.4, 136.1, 137.0, 138.9, 152.5. HRMS (EI) calcd for C$_{28}$H$_{32}$OSi [M$^+$] 412.2222; Found m/z 412.2219.

Table 2. Solvent effects for the gold-catalyzed reaction of 1c with methanol

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<th>time (h)</th>
<th>8 (%)</th>
<th>9 (%)</th>
<th>2c (%)</th>
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<td>71</td>
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<td>24</td>
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<td>79</td>
<td>20</td>
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Mechanistic Study on Au(I)-Catalyzed Intramolecular Allylation of Alkynes.

Table 3. Synthesis of 3-allyl-1-silaindenes 10

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<th>R$^2$</th>
<th>time (h)</th>
<th>10 (%)</th>
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<td>Me</td>
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<td>10a (62)</td>
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<tr>
<td>2</td>
<td>1b</td>
<td>Ph</td>
<td>Me</td>
<td>9</td>
<td>10b (73)</td>
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<tr>
<td>3</td>
<td>1c</td>
<td>Ph</td>
<td>Ph</td>
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<td>complex mixture</td>
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Table 4. Hydrolysis of 3-allyl-1-silaindenes 10

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<th>R$^2$</th>
<th>cat.</th>
<th>time (h)</th>
<th>product</th>
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<td>3-$d$ (71%$d$, 77%)</td>
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<td>2</td>
<td>10b</td>
<td>Ph</td>
<td>Me</td>
<td>(PPh$_3$)AuNT$_2$</td>
<td>7</td>
<td>2b-$d$ (65%$d$, 76%)</td>
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<tr>
<td>3</td>
<td>10b</td>
<td>Ph</td>
<td>Me</td>
<td>TF$_2$NH</td>
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<td>2b-$d$ (66%$d$, 60%)</td>
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Another possible alternative mechanism for the formation of 2 involves initial formation of
3-allyl-1-silaindenes 10 and subsequent hydrolysis of 3-allyl-1-silaindenes 10. Although we have observed the formation of 3-d and 2b-d respectively from isolated 3-allyl-1-silaindenes 10a and 10b (table 4), both formation of 3-allyl-1-silaindenes 10 and their hydrolysis to produce desired product 2 are quite slow. Furthermore, 3-allyl-2-(n-butyl)-1,1-diphenyl-1-silaindene 10c was not produced from 1c. Therefore, this hypothesis might be ruled out.

3-Allyl-2-(n-butyl)-1,1-dimethyl-1-silaindene (10a). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 19:1); 1H NMR (CDCl3, 400 MHz) δ 0.32 (s, 6H), 0.94 (t, J = 7.4 Hz, 3H), 1.37 (sext, J = 7.4 Hz, 2H), 1.44-1.52 (m, 2H), 2.41 (t, J = 7.4 Hz, 2H), 3.32 (dt, J = 6.0, 1.6 Hz, 2H), 5.02 (dm, J = 10.0 Hz, 1H), 5.08 (dm, J = 16.9 Hz, 1H), 5.90 (ddt, J = 16.9, 10.0, 6.0 Hz, 1H), 7.16 (dt, J = 1.6, 7.0 Hz, 1H), 7.27-7.34 (m, 2H), 7.49 (dm, J = 7.0 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ -3.5, 14.0, 23.1, 29.4, 31.1, 32.5, 115.4, 121.3, 125.7, 129.5, 131.2, 135.5, 138.2, 143.8, 147.9, 150.0; HRMS (EI) calcd for C17H24Si [M+] 256.1647; Found m/z 256.1648.

3-Allyl-2-(n-butyl)-1-methyl-1-phenyl-1-silaindene (10b). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 19:1); 1H NMR (CDCl3, 400 MHz) δ 0.66 (s, 3H), 0.83 (t, J = 7.2 Hz, 3H), 1.24-1.43 (m, 4H), 2.30-2.50 (m, 4H), 3.38 (dm, J = 6.0 Hz, 2H), 5.05 (dm, J = 10.0 Hz, 1H), 5.12 (dm, J = 17.2 Hz, 1H), 7.16 (dt, J = 2.0, 6.8 Hz, 1H), 7.30-7.38 (m, 5H), 7.47-7.53 (m, 3H); 13C NMR (CDCl3, 100 MHz) δ -5.6, 13.9, 23.0, 29.4, 31.2, 32.4, 115.6, 121.5, 126.0, 128.0, 129.6, 129.9, 131.8, 134.4, 134.9, 135.4, 136.8, 142.6, 149.6, 150.7; HRMS (EI) calcd for C22H26Si [M+] 318.1804; Found m/z 318.1806.

[2-(1-Allyl-(E)-2-deuterio-1-hexenyl)phenyl]dimethylsilanol ((E)-3-d). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); 1H NMR (CDCl3, 400 MHz) δ 0.38 (s, 6H), 0.93 (t, J = 7.6 Hz, 3H), 1.35-1.43 (m, 4H), 1.95 (brs, 1H), 2.20 (dt, J = 7.2 Hz, 2H), 3.18 (d, J = 6.4 Hz, 2H), 5.01 (dm, J = 10.0 Hz, 1H), 5.05 (dm, J = 16.8 Hz, 1H), 5.44 (t, J = 7.6 Hz, 0.29H), 5.78 (ddt, J = 10.4, 17.6, 6.4 Hz, 1H), 7.14 (dd, J = 1.2, 7.2 Hz, 1H), 7.25 (dt, J = 1.2, 7.2 Hz, 1H), 7.29 (dt, J = 1.2, 7.2 Hz, 1H), 7.58 (dd, J = 1.2, 7.2 Hz, 1H).

[2-(1-Allyl-(E)-2-deuterio-1-hexenyl)phenyl]methyl(phenyl)silanol ((E)-2b-d). Colorless oil, purified by column chromatography on silica gel (hexane:EtOAc = 9:1); 1H NMR (CDCl3, 400 MHz) δ 0.63 (s, 3H), 0.86 (t, J = 6.8 Hz, 3H), 1.20-1.28 (m, 4H), 2.05 (dm, J = 6.8 Hz, 2H), 2.30 (brs, 1H), 2.96 (m, 2H), 4.96 (dm, J = 10.4 Hz, 1H), 4.97 (dm, J = 17.6 Hz, 1H), 5.26 (t, J = 6.8 Hz, 0.34H), 5.71 (ddt, J = 10.4, 17.6, 6.8 Hz, 1H), 7.12 (dd, J = 1.2, 7.2 Hz, 1H), 7.27 (dt, J = 1.6, 7.2 Hz, 1H), 7.31-7.37 (m, 4H), 7.53 (dd, J = 1.6, 7.6 Hz, 2H), 7.64 (dd, J = 1.2, 7.6 Hz, 1H).