Supplementary Material (ESI) for Chemical Communications

Gold-Catalysed Intramolecular *trans*-Allylsilylation of Alkynes Forming 3-Allyl-1-silaindenes

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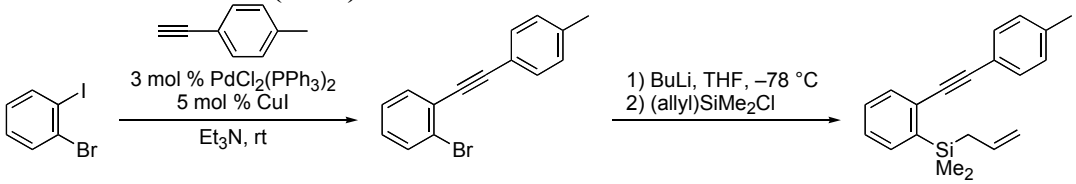
General. All manipulations were carried out in a nitrogen-filled gloved box and with standard Schlenk techniques under an argon atmosphere. Column chromatography was performed with silica gel 60N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF_{254} (Merck). Gel permeation chromatography was carried out on a JAI LC-908. NMR spectra were recorded on a Varian Gemini 2000 (^{1}H at 300.77 MHz and ^{13}C NMR at 75.46 MHz), a JEOL JNM-A400 (^{11}B at 128.15 MHz and ^{29}Si at 79.30 Hz), or a JEOL JNM-ECA600 (^{13}C NMR at 150.92 MHz). Proton chemical shifts were referenced to the residual proton signals in $CDCl_3$ (δ 7.26 ppm) and C_6D_6 (δ 7.16 ppm). Carbon chemical shifts were referenced to the carbon signals in $CDCl_3$ (δ 77.00 ppm) and C_6D_6 (δ 128.00 ppm). Boron and silicon chemical shifts were referenced to external standards $BF_3{\cdot}OEt_2$ (δ 0.0 ppm) and $SiMe_4$ (δ 0.0 ppm), respectively. High resolution mass spectra were recorded on a JEOL JMS-SX102A. UV-vis spectra were recorded on a JASCO V-550. Fluorescence spectra were recorded on a JASCO FP-777. Thermal data were obtained using an SII EXSTAR6000 DSC6220 at a heating rate 10 °C/min.

Materials. (*Z*)-chloro(crotyl)dimethylsilane,[1] chloro(cyclohex-2-enyl)dimethylsilane,[1] 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane,[2] (bromoethynyl)triisopropylsilane,[3] (triphenylphosphine)gold(I) bis(trifluoromethanesulfonyl)imide,[4] chloro(2-di-*tert*-butylphosphinobiphenyl)gold(I),[4] and (2-di-*tert*-butylphosphinobiphenyl)gold(I) bis(trifluoromethanesulfonyl)imide (**3**)[4] were prepared according to the literature methods. All other commercially available chemical resources were used as received without further purification.

Preparation of Silaenynes

General Procedure I (GP-I)

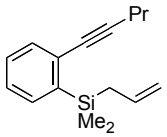


Allyldimethyl{2-[(4-methylphenyl)ethynyl]phenyl}silane (1f). To a mixture of

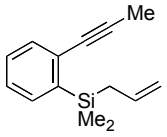
(1) Fürstner, A.; Voigtländer, *Synthesis* **2000**, 959.
(2) Perttu, E. K.; Arnold, M.; Iovine, P. M. *Tetrahedron Lett.* **2005**, *46*, 8753.
(3) Jiang, M. X.-W.; Rawat, M.; Wulff, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 5970.
(4) Mézailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133.

$PdCl_2(PPh_3)_2$ (906 mg, 1.29 mmol), CuI (410 mg, 2.15 mmol), 1-bromo-2-iodobenzene (12.2 g, 43.2 mmol) in Et_3N (210 mL) was added dropwise 1-ethynyl-4-methylbenzene (5.01 g, 43.1 mmol) in Et_3N (70 mL) at room temperature. After stirring for 1.5 h, saturated NH_4Cl aqueous solution was added to the reaction mixture. The mixture was extracted with Et_2O, washed with brine and water, dried over Na_2SO_4, and evaporated. The residue was filtered through a plug of Florisil® (hexane:Et_2O = 9:1) and concentrated. Recrystallization from EtOH afforded 1-bromo-2-[(4-methylphenyl)ethynyl]benzene (9.95 g, 85%).

To a solution of 1-bromo-2-[(4-methylphenyl)ethynyl]benzene (3.71 g, 13.7 mmol) in THF (30 mL) was added dropwise *n*-BuLi (1.55 M in hexane, 11.6 mL, 18.0 mmol) at –78 °C. After stirring at –78 °C for 1 h, allylchlorodimethylsilane (3.03 g, 22.5 mmol) was added dropwise to the mixture. The reaction mixture was stirred at –78 °C for 1 h, and then allowed to warm to room temperature. The volatile materials was removed in vacuo, and the residue was subjected to column chromatography on silica gel (hexane:AcOEt = 100:1, 50:1) to give **1#** (3.74 g, 94%). ^{1}H NMR ($CDCl_3$) δ0.49 (s, 6H), 2.09 (dd, J = 7.9, 1.1 Hz, 2H), 2.42 (s, 3H), 4.87-4.98 (m, 2H), 5.88 (ddt, J = 17.0, 10.1, 7.9 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.32-7.42 (m, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.55-7.64 (m, 2H); ^{13}C NMR ($CDCl_3$) δ–3.2, 21.5, 23.0, 90.4, 92.3, 113.3, 120.3, 127.2, 128.6, 128.9, 129.2, 131.1, 132.5, 134.3, 134.9, 138.4, 140.5. HRMS (EI) calcd for $C_{20}H_{22}Si$ (M^+) 290.1491, found 290.1490.

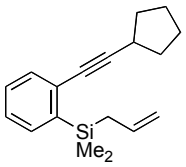


Allyldimethyl[2-(pent-1-ynyl)phenyl]silane (1a). The title compound was prepared according to the GP-I using 1-bromo-2-iodobenzene, pent-1-yne, and allylchlorodimethylsilane. ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 6H), 1.06 (t, J = 7.3 Hz, 3H), 1.67 (sext, J = 7.3 Hz, 2H), 1.96 (dt, J = 8.0, 1.1 Hz, 2H), 2.43 (t, J = 7.3 Hz, 2H), 4.80-4.91 (m, 2H), 5.79 (ddt, J = 17.1, 10.2, 8.0 Hz, 1H), 7.21-7.32 (m, 2H), 7.39-7.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ–3.2, 13.8, 21.7, 22.1, 23.0, 82.2, 93.2, 113.1, 126.6, 128.8, 129.4, 132.5, 134.1, 135.0, 140.1; HRMS (EI) calcd for $C_{16}H_{22}Si$ (M^+) 242.1491, found 242.1489. Anal. Calcd for $C_{16}H_{22}Si$: C, 79.29; H, 9.15. Found: C, 79.24; H, 9.23.

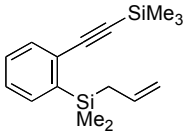


Allyldimethyl[2-(prop-1-ynyl)phenyl]silane (1b). The title compound was prepared according to the GP-I using 1-bromo-2-(prop-1-ynyl)benzene, which was prepared by Colvin rearrangement of 2-bromobenzaldehyde with $Me_3Si(Li)CN_2$, [5] and allylchlorodimethylsilane. ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6H), 1.99 (dd, J = 8.3, 0.9 Hz, 2H), 2.11 (s, 3H), 4.86-4.96 (m, 2H), 5.85 (ddt, J = 16.8, 10.2, 8.3 Hz, 1H), 7.28-7.34 (m, 2H), 7.45-7.50 (m, 2H); ^{13}C NMR ($CDCl_3$) δ–3.3, 4.3, 23.0, 81.4, 88.8, 113.1, 126.7, 128.8, 129.3, 132.2, 134.1, 135.0, 140.3; HRMS (EI) calcd for $C_{14}H_{18}Si$ (M^+) 214.1178, found 214.1178.

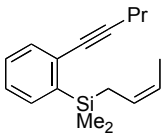
(5) Miwa, K.; Aoyama, T.; Shioiri, T. *Synlett* **1994**, 107.



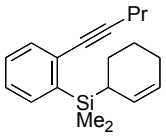
Allyl[2-(cyclopentylethynyl)phenyl]dimethylsilane (1c). The title compound was prepared according to the GP-I using 1-bromo-2-iodobenzene, ethynylcyclopentane, and allylchlorodimethylsilane. ^{1}H NMR ($CDCl_3$) δ0.36 (s, 6H), 1.57-1.80 (m, 6H), 1.94-2.03 (m, 2H), 1.95 (dd, J = 7.9, 0.9 Hz, 2H), 2.86 (quint, J = 7.9 Hz, 1H), 4.80-4.90 (m, 2H), 5.79 (ddt, J = 16.7, 9.8, 7.9 Hz, 1H), 7.20-7.30 (m, 2H), 7.37-7.44 (m, 2H); ^{13}C NMR ($CDCl_3$) δ–3.3, 22.9, 25.0, 31.0, 33.5, 81.8, 97.2, 113.1, 126.6, 128.8, 129.4, 132.5, 134.1, 135.0, 139.9; HRMS (EI) calcd for $C_{18}H_{24}Si$ (M^+) 268.1647, found 268.1647.



Allyldimethyl{2-[(trimethylsilyl)ethynyl]phenyl}silane (A). The title compound was prepared according to the GP-I using 1-bromo-2-iodobenzene, ethynyltrimethylsilane, and allylchlorodimethylsilane. ^{1}H NMR ($CDCl_3$) δ0.26 (s, 9H), 0.37 (s, 6H), 1.97 (dd, J = 8.0, 0.9 Hz, 2H), 4.80-4.91 (m, 2H), 5.78 (ddt, J = 17.7, 9.8, 8.0 Hz, 1H), 7.25-7.32 (m, 2H), 7.43-7.51 (m, 2H); ^{13}C NMR ($CDCl_3$) δ–3.4, –0.2, 22.8, 97.2, 106.7, 113.2, 127.6, 128.3, 128.8, 132.9, 134.2, 134.9, 140.9; HRMS (EI) calcd for $C_{16}H_{24}Si_2$ (M^+) 272.1417, found 272.1415.

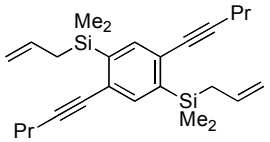


(*Z*)-Crotyldimethyl[2-(pent-1-ynyl)phenyl]silane (1p). The title compound was prepared according to the GP-I using 1-bromo-2-iodobenzene, pent-1-yne, and (*Z*)-chloro(crotyl)dimethylsilane. ^{1}H NMR ($CDCl_3$) δ0.36 (s, 6H), 1.05 (t, J = 7.3 Hz, 3H), 1.54 (d, J = 6.6 Hz, 3H), 1.66 (sext, J = 7.3 Hz, 2H), 1.92 (d, J = 7.8 Hz, 2H), 2.42 (t, J = 7.3 Hz, 2H), 5.30-5.50 (m, 2H), 7.20-7.30 (m, 2H), 7.39-7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ–3.0, 12.7, 13.8, 16.3, 21.7, 22.1, 82.3, 93.2, 121.8, 126.2, 126.6, 128.7, 129.4, 132.5, 134.1, 140.5; HRMS (EI) calcd for $C_{17}H_{24}Si$ (M^+) 256.1647, found 256.1650.



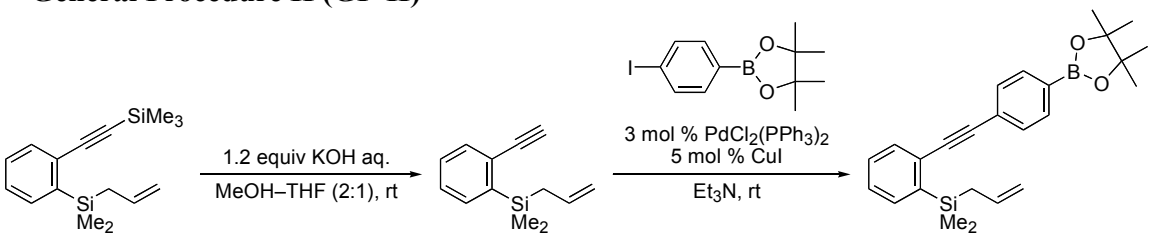
Cyclohex-2-enyldimethyl[2-(pent-1-ynyl)phenyl]silane (1q). The title compound was prepared according to the GP-I using 1-bromo-2-iodobenzene, pent-1-yne, and chloro(cyclohex-2-enyl)dimethylsilane. ^{1}H NMR ($CDCl_3$) δ0.32 (s, 3H), 0.33 (s, 3H), 1.03

(t, J = 7.5 Hz, 3H), 1.39-1.78 (m, 6H), 1.84-2.05 (br s, 2H), 2.16-2.27 (br s, 1H), 2.38 (t, J = 7.2 Hz, 2H), 5.53-5.66 (m, 2H), 7.17-7.28 (m, 2H), 7.36-7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –4.5, –4.3, 13.8, 21.7, 22.1, 22.8, 23.9, 24.3, 25.1, 82.3, 93.0, 125.4, 126.6, 128.0, 128.7, 129.4, 132.6, 134.5, 139.8.



[2,5-Di(pent-1-ynyl)-1,4-phenylene]bis(allyldimethylsilane) (4b). The title compound was prepared according to the GP-I using 1,4-dibromo-2,5-diiodobenzene, pent-1-yne, and allylchlorodimethylsilane. ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 12H), 1.05 (t, J = 5.5 Hz, 6H), 1.66 (sext, J = 5.5 Hz, 4H), 1.93 (dd, J = 7.9, 0.9 Hz, 4H), 2.42 (t, J = 5.5 Hz, 4H), 4.81-4.90 (m, 4H), 5.78 (ddt, J = 17.0, 10.1, 7.9 Hz, 2H), 7.46 (s, 2H); ^{13}C NMR ($CDCl_3$) δ –3.4, 13.8, 21.8, 22.1, 22.8, 82.4, 94.6, 113.2, 127.4, 134.8, 138.1, 140.7; HRMS (EI) calcd for $C_{26}H_{38}Si_2$ (M^+) 406.2512, found 406.2521.

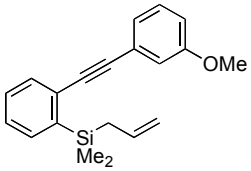
General Procedure II (GP-II)



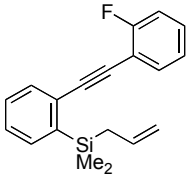
Allyl(2-ethynylphenyl)dimethylsilane (B). To a solution of allyldimethyl{2-[(trimethylsilyl)ethynyl]phenyl}silane (**A**, 3.43 g, 12.6 mmol) in MeOH–THF (2:1, 210 mL) was added KOH aqueous solution (0.8 M, 19 mL) at room temperature. After 30 min., the reaction mixture was concentrated under reduced pressure. To the residue was added saturated NH_4Cl aqueous solution, and it was extracted with hexane, washed with water, dried over Na_2SO_4, and evaporated. The crude product was purified by column chromatography on silica gel (hexane) to give **B** (1.89 g, 75%). ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 6H), 1.95 (dd, J = 7.9, 0.9 Hz, 2H), 3.23 (s, 1H), 4.79-4.89 (m, 2H), 5.76 (ddt, J = 17.0, 10.1, 7.9 Hz, 1H), 7.26-7.33 (m, 2H), 7.42-7.53 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –3.2, 22.9, 80.4, 85.1, 113.3, 127.3, 127.9, 128.8, 133.4, 134.3, 134.8, 141.2; HRMS (EI) calcd for $C_{13}H_{16}Si$ (M^+) 200.1021, found 200.1015.

Allyldimethyl(2-{[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethynyl}phenyl)silane (1g). To a mixture of $PdCl_2(PPh_3)_2$ (42 mg, 0.060 mmol), CuI (19 mg, 0.10 mmol), 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (661.4 g, 2.00 mmol) in Et_3N (20 mL) was added allyl(2-ethynylphenyl)dimethylsilane (464.1 mg, 2.32 mmol) at room temperature. After stirring overnight at room temperature, the volatile materials were removed in vacuo. The residue was filtered through a plug of Florisil® (hexane:AcOEt = 4:1), and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel to afford **1g**. ^{1}H NMR ($CDCl_3$) δ 0.42 (s, 6H), 1.36 (s, 12H), 2.01 (dd, J = 7.9, 0.9 Hz, 2H), 4.80-4.90 (m, 2H), 5.80 (ddt, J = 16.8, 10.2, 7.9 Hz, 1H), 7.29-7.38 (m. 2H),

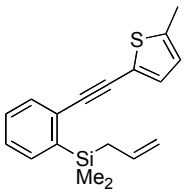
7.50-7.59 (m, 4H), 7.81 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ–3.2, 23.0, 24.9, 84.0, 92.2, 92.4, 113.4, 126.1, 127.5, 128.3, 128.9, 130.4, 132.6, 134.3, 134.7, 134.8, 140.8 [carbon attached to boron was not observed due to quadrupole broadening caused by the boron nucleus]; ^{11}B NMR ($CDCl_3$, 128.15 MHz) δ 30.6; HRMS (EI) calcd for $C_{25}H_{31}BO_2Si$ (M^+) 402.2186, found 402.2186.



Allyl{2-[(3-methoxyphenyl)ethynyl]phenyl}dimethylsilane (1h). The title compound was prepared according to the GP-II using **B** and 3-iodoanisole. ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6H), 1.99 (d, J = 7.9 Hz, 2H), 3.82 (s, 3H), 4.79-4.88 (m, 2H), 5.78 (ddt, J = 17.6, 10.0, 7.9 Hz, 1H), 6.92-6.96 (m, 1H), 7.02-7.06 (m, 1H), 7.08-7.04 (m, 1H), 7.22-7.36 (m, 3H), 7.46-7.50 (m, 1H), 7.52-7.58 (m, 1H); ^{13}C NMR ($CDCl_3$) δ–3.2, 23.0, 55.2, 90.9, 92.0, 113.4, 114.7, 116.2, 123.7, 124.3, 127.4, 128.3, 128.9, 129.5, 132.6, 134.3, 134.7, 140.6, 159.4; HRMS (EI) calcd for $C_{20}H_{22}OSi$ (M^+) 306.1440, found 306.1440.

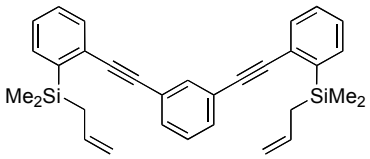


Allyl{2-[(2-fluorophenyl)ethynyl]phenyl}dimethylsilane (1i). The title compound was prepared according to the GP-II using **B** and 1-fluoro-2-iodobenzene. ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6H), 2.01 (dd, J = 8.4, 1.1 Hz, 2H), 4.79-4.89 (m, 2H), 5.81 (ddt, J = 17.1, 9.5, 8.1 Hz, 1H), 7.07-7.17 (m, 2H), 7.27-7.39 (m, 3H), 7.47-7.54 (m, 2H), 7.56-7.62 (m, 1H); ^{13}C NMR ($CDCl_3$) δ–3.3, 22.9, 85.6, 95.9 ($^3J_{C–F}$ = 2.3 Hz), 112.0 ($^2J_{C–F}$ = 16.2 Hz), 113.3, 115.6 ($^2J_{C–F}$ = 20.9 Hz), 124.0 ($^3J_{C–F}$ = 3.5 Hz), 127.7, 128.0, 128.9, 129.9 ($^3J_{C–F}$ = 6.9 Hz), 132.9, 133.1, 134.3, 134.9, 140.8, 162.6 ($^1J_{C–F}$ = 251.7 Hz); HRMS (EI) calcd for $C_{19}H_{19}FSi$ (M^+) 294.1240, found 294.1237.



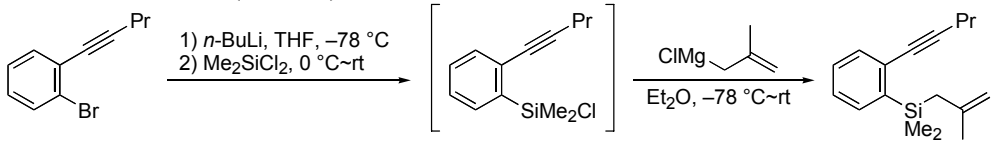
Allyldimethyl{2-[(5-methyl-2-thienyl)ethynyl]phenyl}silane (1j). The title compound was prepared according to the GP-II using **B** and 2-bromo-5-methylthiophene but in Et_3N–THF (1:1). ^{1}H NMR ($CDCl_3$) δ 0.40 (s, 6H), 1.98 (d, J = 8.1 Hz, 2H), 2.49 (s, 3H), 4.80-4.91 (m, 2H), 5.80 (ddt, J = 17.1, 10.1, 8.1 Hz, 1H), 6.66-6.68 (m, 1H), 7.07 (d, J = 3.3 Hz, 1H), 7.24-7.36 (m, 2H), 7.49 (d, J = 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ–3.2, 15.4, 23.0, 86.1, 94.0, 113.4, 120.9, 125.4, 127.3, 128.3, 128.9, 131.7, 132.0, 134.3, 134.8, 140.5, 142.2;

HRMS (EI) calcd for $C_{18}H_{20}SSi$ (M^+) 296.1055, found 296.1056.



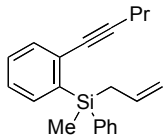
1,3-Bis{[2-(allyldimethylsilyl)phenyl]ethynyl}benzene (4a). The title compound was prepared according to the GP-II using **B** and 1,3-diiodobenzene. ^{1}H NMR ($CDCl_3$) δ0.46 (s, 12H), 2.04 (d, J = 8.4 Hz, 4H), 4.83-4.94 (m, 4H), 5.82 (ddt, J = 17.1, 9.9, 7.8 Hz, 2H), 7.31-7.42 (m, 5H), 7.51-7.55 (s, 4H), 7.59-7.62 (m, 2H), 7.70-7.71 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –3.1, 23.1, 91.2, 91.7, 113.5, 123.8, 127.6, 128.1, 128.7, 129.0, 131.0, 132.7, 133.7, 134.4, 134.7, 140.8; HRMS (EI) calcd for $C_{32}H_{34}Si_2$ (M^+) 474.2199, found 474.2184.

General Procedure III (GP-III)



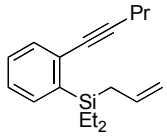
Dimethyl(methallyl)[2-(pent-1-ynyl)phenyl]silane (1o). To a solution of 1-bromo-2-(pent-1-ynyl)benzene (2.2 g, 9.9 mmol) in THF (17 mL) was added dropwise *n*-BuLi (1.55 M in hexane) at –78 °C. After stirring at –78 °C for 1 h, the reaction mixture was added dropwise to a solution of dichlorodimethylsilane (2.4 mL) in THF (17 mL) at –78 °C, and stirred for 11 h at room temperature. The reaction mixture was diluted with hexane and filtered through a glass filter. Evaporation of the filtrate gave crude chlorodimethyl[2-(pent-1-ynyl)phenyl]silane (2.58 g).

To a solution of chlorodimethyl[2-(pent-1-ynyl)phenyl]silane in THF (30 mL) was added dropwise methallylmagenisum chloride in Et_2O (excess) at –78 °C. After stirring for 15 h at room temperature, saturated NH_4Cl aqueous solution was added to the reaction mixture. The mixture was extracted with Et_2O, dried over $MgSO_4$, and concentrated. The residue was subjected to column chromatography on silica gel (hexane) to afford **1o** (1.0 g, 40%). ^{1}H NMR ($CDCl_3$) δ0.42 (s, 6H), 1.09 (t, J = 7.2 Hz, 3H), 1.66 (s, 3H), 1.70 (sext, J = 7.2 Hz, 2H), 2.03 (s, 2H), 2.45 (t, J = 7.2 Hz, 2H), 4.52 (s, 1H), 4.61-4.62 (m, 1H), 7.24-7.34 (m, 2H), 7.45-7.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ–2.7, 13.8, 21.7, 22.1, 25.1, 26.8, 82.3, 93.3, 108.6, 126.6, 128.7, 129.4, 132.5, 134.1, 140.5, 143.6; HRMS (EI) calcd for $C_{17}H_{24}Si$ (M^+) 256.1647, found 256.1650.

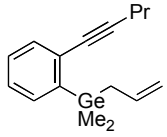


Allyl(methyl)[2-(pent-1-ynyl)phenyl](phenyl)silane (1m). The title compound was prepared according to the GP-III using 1-bromo-2-(pent-1-ynyl)benzene, dichloro(methyl)(phenyl)silane, and allylmagnesium chloride. ^{1}H NMR ($CDCl_3$) δ0.63 (s, 3H), 0.92 (t, J = 7.4 Hz, 3H), 1.47 (sext, J = 7.4 Hz, 2H), 2.15-2.35 (m, 4H), 4.82-4.94 (m,

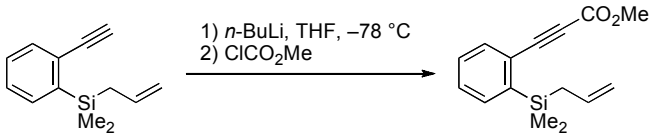
2H), 5.80 (dt, J = 17.4, 8.3 Hz, 1H), 7.19-7.44 (m, 7H), 7.52-7.55 (m, 2H); ^{13}C NMR (C_6D_6) δ –4.2, 13.7, 21.7, 22.1, 22.3, 83.0, 94.2, 114.3, 127.1, 129.2, 129.5, 130.6, 133.0, 134.8, 134.9, 135.9, 137.2, 138.7 [one aromatic carbon signal was not observed]; HRMS (EI) calcd for $C_{21}H_{24}Si$ (M^+) 304.1647, found 306.1650.



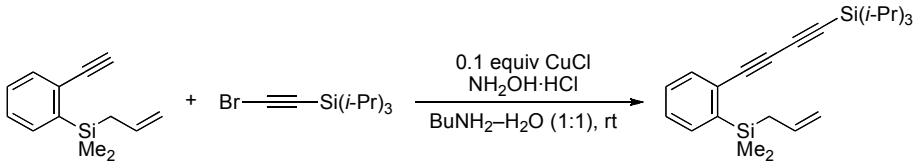
Allyldiethyl[2-(pent-1-ynyl)phenyl]silane (1n). The title compound was prepared according to the GP-III using 1-bromo-2-(pent-1-ynyl)benzene, dichlorodiethylsilane, and allylmagnesium chloride. ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 10H), 1.05 (t, J = 7.3 Hz, 3H), 1.66 (sext, J = 7.3 Hz, 2H), 2.00 (dd, J = 8.1, 0.9 Hz, 2H), 2.41 (t, J = 7.3 Hz, 2H), 4.78-4.92 (m, 2H), 5.80 (dt, J = 17.0, 8.1 Hz, 1H), 7.20-7.31 (m, 2H), 7.40-7.43 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –3.2, 7.5, 13.8, 19.5, 21.7, 22.1, 82.2, 92.7, 113.0, 126.5, 128.7, 129.6, 132.7, 134.9, 135.2, 138.2; HRMS (EI) calcd for $C_{18}H_{26}Si$ (M^+) 270.1804, found 270.1806.



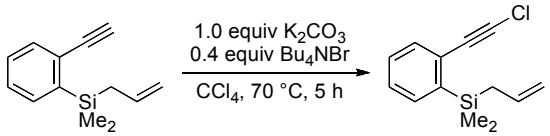
Allyldimethyl[2-(pent-1-ynyl)phenyl]germane (1r). The title compound was prepared according to the GP-III using 1-bromo-2-(pent-1-ynyl)benzene, dichlorodimethylgermane, and allylmagnesium chloride. ^{1}H NMR ($CDCl_3$) δ 0.46 (s, 6H), 1.06 (t, J = 7.4 Hz, 3H), 1.66 (sext, J = 7.4 Hz, 2H), 2.05 (dd, J = 0.6, 8.3 Hz, 2H), 2.41 (t, J = 7.4 Hz, 2H), 4.77-4.90 (m, 2H), 5.84 (ddt, J = 16.7, 9.7, 8.3 Hz, 1H), 7.22-7.28 (m, 2H), 7.37-7.43 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –3.7, 13.8, 21.6, 22.1, 23.0, 81.9, 92.4, 112.4, 126.8, 128.3, 129.2, 132.3, 133.3, 135.8, 142.7; HRMS (EI) calcd for $C_{16}H_{22}Ge$ (M^+) 288.0933, found 288.0932.



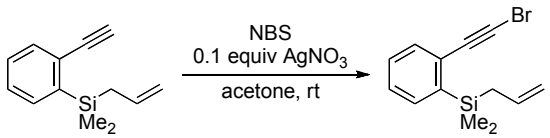
Methyl 3-[2-(allyldimethylsilyl)phenyl]prop-2-ynoate (1d). The title compound was prepared using **B**, *n*-butyllithium, and methyl chloroformate. ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6H), 1.97 (d, J = 7.8 Hz, 2H), 3.84 (s, 3H), 4.82-4.94 (m, 2H), 5.77 (ddt, J = 17.1, 9.9, 7.8 Hz, 1H), 7.32-7.43 (m, 2H), 7.53 (dd, J = 7.5, 1.5 Hz, 1H), 7.61 (dd, J = 6.9, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –3.4, 22.8, 52.6, 83.0, 87.7, 113.6, 124.4, 128.9, 129.6, 134.1, 134.2, 134.5, 143.4, 154.3; HRMS (EI) calcd for $C_{15}H_{18}O_2Si$ (M^+) 258.1076, found 258.1079.



Allyldimethyl{2-[(triisopropylsilyl)buta-1,3-diynyl]phenyl}silane (1e). The title compound was prepared according to the procedure reported by Dabdoub.[6] ^{1}H NMR ($CDCl_3$) δ0.36 (s, 6H), 1.10 (s, 21H), 1.93 (d, J = 8.1 Hz, 2H), 4.80-4.91 (m, 2H), 5.77 (dt, J = 17.1, 8.1 Hz, 1H), 7.27-7.34 (m, 2H), 7.42-7.53 (m, 2H); ^{13}C NMR (C_6D_6) δ –3.1, 11.7, 18.8, 23.3, 78.0, 78.6, 89.2, 90.6, 113.8, 126.9, 128.6, 129.2, 134.0, 134.7, 143.1 [one aromatic carbon signal was not observed because of overlap]; HRMS (EI) calcd for $C_{24}H_{36}Si_2$ (M^+) 380.2356, found 380.2350.

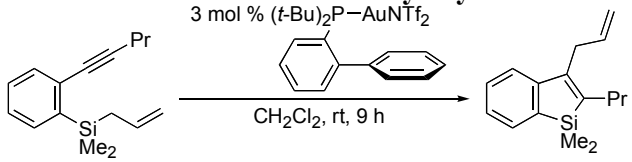


Allyl[2-(chloroethynyl)phenyl]dimethylsilane (1k). The title compound was prepared according to the procedure reported by Sasson.[7] ^{1}H NMR ($CDCl_3$) δ0.33 (s, 6H), 1.90 (dd, J = 8.1, 0.9 Hz, 2H), 4.80-4.90 (m, 2H), 5.76 (ddt, J = 17.3, 9.5, 8.1 Hz, 1H), 7.24-7.33 (m, 2H), 7.41-7.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –3.3, 23.0, 70.7, 70.9, 113.4, 127.2, 127.7, 128.9, 132.8, 134.3, 134.6, 141.4; HRMS (EI) calcd for $C_{13}H_{15}ClSi$ (M^+) 234.0632, found 234.0630.



Allyl[2-(bromoethynyl)phenyl]dimethylsilane (1l). To a solution of **B** (404.1 mg, 2.02 mmol), NBS (392 mg, 2.20 mmol) in acetone was added $AgNO_3$ (34.0 mg, 0.20 mmol). After stirring for 3 h at room temperature, the reaction mixture was diluted with hexane and filtered off the precipitate formed. The filtrate was concentrated, and the residue was subjected to column chromatography on silica gel (hexane) to afford **1l** (408.3 mg, 72%). ^{1}H NMR ($CDCl_3$) δ0.35 (s, 6H), 1.91 (dd, J = 8.3, 0.9 Hz, 2H), 4.80-4.91 (m, 2H), 5.77 (ddt, J = 17.4, 9.9, 8.3 Hz, 1H), 7.28-7.34 (m, 2H), 7.42-7.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ–3.3, 23.0, 52.7, 81.6, 100.0, 113.4, 127.8, 128.9, 132.8, 134.3, 134.7, 141.5; HRMS (EI) calcd for $C_{13}H_{15}BrSi$ (M^+) 278.0126, found 278.0120.

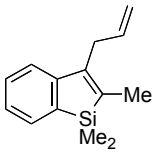
General Procedure for Intramolecular *trans*-Allylsilylation of Alkynes.



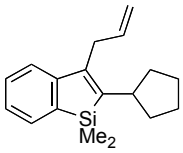
3-Allyl-1,1-dimethyl-2-propyl-1-silaindene (2a). To a Schlenk tube containing [2-PhC_6H_4P(*t*-Bu)$_2$]AuNTf$_2$ (**3**, 7.0 mg, 9.0 μmol, 3 mol %) was added a solution of allyldimethyl[2-(pent-1-ynyl)phenyl]silane (**1a**, 72.7 mg, 0.30 mmol) in dichloromethane

(6) Dabdoub, M. J.; Baroni, A. C. M.; Lenardão, E. J.; Gianeti, T. R.; Hurtado, G. R. *Tetrahedron* **2001**, *57*, 4271.
(7) Sasson, Y. US Pat. 5138107, 1992.

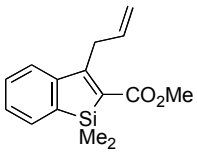
(0.37 mL) under an argon atmosphere. After stirring for 9 h at room temperature, the volatile material was removed under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane) to give **2a** (70.2 mg, 97 %). ^{1}H NMR ($CDCl_3$) δ0.34 (s, 6H), 0.99 (t, J = 7.4 Hz, 3H), 1.56 (sext, J = 7.4 Hz, 2H), 2.42 (t, J = 7.4 Hz, 2H), 3.34 (dt, J = 5.7, 1.6 Hz, 2H), 5.01-5.14 (m, 2H), 5.79 (ddt, J = 17.1, 10.1, 5.7 Hz, 1H), 7.18 (dt, J = 6.8, 1.6 Hz, 1H), 7.29-7.37 (m, 2H), 7.55 (d, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ–3.5, 14.6, 23.6, 31.1, 31.9, 115.4, 121.3, 125.7, 129.5, 131.2, 135.5, 138.1, 143.6, 148.1, 150.0; ^{29}Si NMR ($CDCl_3$, 79.30 MHz) δ1.78; HRMS (EI) calcd for $C_{16}H_{22}Si$ (M^+) 242.1491, found 242.1493.



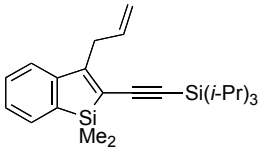
3-Allyl-1,1,2-trimethyl-1-silaindene (2b). The title compound (37.3 mg, 58%) was prepared by the reaction of **1b** (64.3 mg, 0.30 mmol) in the presence of **3** (3 mol %). ^{1}H NMR ($CDCl_3$) δ0.26 (s, 6H), 1.94 (s, 3H), 3.30 (d, J = 5.8 Hz, 2H), 4.97-5.09 (m, 2H), 5.89 (ddt, J = 17.1, 10.1, 5.8 Hz, 1H), 7.15 (t, J = 6.9 Hz, 1H), 7.25-7.34 (m, 2H), 7.49 (d, J = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ–4.7, 13.4, 30.8, 115.3, 121.0, 125.5, 129.6, 131.4, 135.0, 137.9, 138.4, 148.1, 150.2; HRMS (EI) calcd for $C_{14}H_{18}Si$ (M^+) 214.1178, found 214.1180.



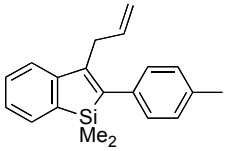
3-Allyl-2-cyclopentyl-1,1-dimethyl-1-silaindene (2c). The title compound (57.1 mg, 71%) was prepared by the reaction of **1c** (80.5 mg, 0.30 mmol) in the presence of **3** (6 mol %). ^{1}H NMR ($CDCl_3$) δ0.37 (s, 6H), 1.35-1.48 (m, 2H), 1.59-1.82 (m, 4H), 1.89-2.00 (m, 2H), 2.91-3.03 (m, 1H), 3.35 (d, J = 5.9 Hz, 2H), 5.01-5.14 (m, 2H), 5.94 (ddt, J = 15.6, 10.5, 5.9 Hz, 1H), 7.15-7.20 (m, 1H), 7.28-7.35 (m, 2H), 7.48 (d, J = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –2.3, 25.3, 31.6, 34.2, 42.1, 115.4, 121.2, 125.7, 129.5, 130.9, 135.9, 138.2, 147.3, 148.1, 149.8; HRMS (EI) calcd for $C_{18}H_{24}Si$ (M^+) 268.1647, found 268.1646.



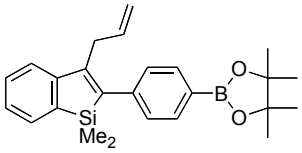
Methyl 3-allyl-1,1-dimethyl-1-silaindene-2-carboxylate (2d). The title compound (69.1 mg, 89%) was prepared by the reaction of **1d** (77.5 mg, 0.30 mmol) in the presence of **3** (3 mol %). ^{1}H NMR ($CDCl_3$) δ0.37 (s, 6H), 3.78 (s, 3H), 3.91 (d, J = 6.2 Hz, 2H), 5.04-5.18 (m, 2H), 5.97 (ddt, J = 16.8, 9.9, 6.2 Hz, 1H), 7.32-7.43 (m, 2H), 7.57 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –4.1, 32.8, 51.2, 116.3, 124.2, 129.0, 129.7, 130.4, 131.8, 134.9, 139.8, 147.8, 166.7, 168.7; HRMS (EI) calcd for $C_{15}H_{18}O_2Si$ (M^+) 258.1076, found 258.1080.



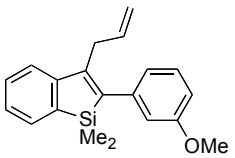
3-Allyl-1,1-dimethyl-2-[(triisopropylsilyl)ethynyl]-1-silaindene (2e). The title compound (64.2 mg, 84%) was prepared by the reaction of **1e** (76.1 mg, 0.20 mmol) in the presence of **3** (3 mol %). ^{1}H NMR ($CDCl_3$) δ0.35 (s, 6H), 1.12 (s, 21H), 3.57 (dd, J = 6.3, 1.2 Hz, 2H), 5.02-5.21 (m, 2H), 5.94 (ddt, J = 16.7, 10.1, 6.3 Hz, 1H), 7.22-7.27 (m, 1H), 7.32-7.42 (m, 2H), 7.49 (d, J = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ–4.6, 11.4, 18.8, 34.8, 101.4, 105.8, 116.2, 122.6, 124.0, 127.4, 129.8, 131.8, 134.7, 137.8, 148.3, 160.8; HRMS (EI) calcd for $C_{24}H_{36}Si_2$ (M^+) 380.2356, found 380.2353.



3-Allyl-1,1-dimethyl-2-(4-methylphenyl)-1-silaindene (2f). The title compound (65.2 mg, 75%) was prepared by the reaction of **1f** (87.1 mg, 0.30 mmol) in the presence of **3** (6 mol %). ^{1}H NMR ($CDCl_3$) δ0.37 (s, 6H), 2.38 (s, 3H), 3.33 (d, J = 5.4 Hz, 2H), 5.05-5.12 (m, 2H), 6.02 (ddt, J = 17.7, 9.8, 5.4 Hz, 1H), 7.10 (d, J = 8.1 Hz, 2H), 7.17-7.27 (m, 3H), 7.37-7.40 (m, 2H), 7.57 (d, J = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –3.9, 21.2, 32.4, 116.1, 122.6, 126.3, 127.4, 129.0, 129.7, 131.4, 135.4, 136.2, 137.6, 138.3, 144.0, 149.1, 149.6; HRMS (EI) calcd for $C_{20}H_{22}Si$ (M^+) 290.1491, found 290.1492.

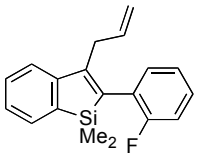


3-Allyl-1,1-dimethyl-2-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-1-sila indene (2g). The title compound (37.6 mg, 81%) was prepared by the reaction of **1g** (46.7 mg, 0.12 mmol) in the presence of **3** (6 mol %). ^{1}H NMR ($CDCl_3$) δ0.35 (s, 6H), 1.37 (s, 12H), 3.29 (d, J = 5.7 Hz, 2H), 5.04-5.09 (m, 2H), 5.98 (ddt, J = 17.4, 10.4, 5.7 Hz, 1H), 7.18-7.27 (m, 3H), 7.35-7.43 (m, 2H), 7.57 (d, J = 6.9 Hz, 1H), 7.82 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –4.0, 24.9, 32.4, 83.7, 116.1, 122.7, 126.5, 126.9, 129.7, 131.4, 134.7, 136.0, 138.4, 144.0, 144.2, 149.4, 149.7 [carbon attached to boron was not observed due to quadrupole broadening caused by the boron nucleus]; ^{11}B NMR ($CDCl_3$, 128.15 MHz) δ 30.8; HRMS (EI) calcd for $C_{25}H_{31}BO_2Si$ (M^+) 402.2186, found 402.2185.

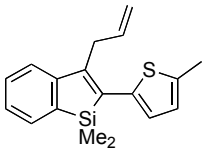


3-Allyl-2-(3-methoxyphenyl)-1,1-dimethyl-1-silaindene (2h). The title compound (43.5

mg, 71%) was prepared by the reaction of **1h** (61.3 mg, 0.20 mmol) in the presence of **3** (6 mol %). ^{1}H NMR ($CDCl_3$) δ0.37 (s, 6H), 3.33 (d, J = 5.4 Hz, 2H), 3.82 (s, 3H), 5.05-5.11 (m, 2H), 6.02 (ddt, J = 17.7, 10.2, 5.4 Hz, 1H), 6.75-6.81 (m, 3H), 7.23-7.30 (m, 2H), 7.34-7.42 (m, 2H), 7.57 (d, J = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ–3.9, 32.5, 55.1, 111.3, 113.0, 116.1, 120.1, 122.7, 126.4, 129.2, 129.7, 131.4, 136.1, 138.2, 142.2, 144.1, 149.4, 149.5, 159.5; HRMS (EI) calcd for $C_{20}H_{22}OSi$ (M^+) 306.1440, found 306.1441.

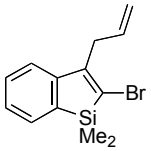


3-Allyl-2-(2-fluorophenyl)-1,1-dimethyl-1-silaindene (2i). The title compound (45.2 mg, 77%) was prepared by the reaction of **1i** (58.9 mg, 0.20 mmol) in the presence of **3** (12 mol %). ^{1}H NMR ($CDCl_3$) δ0.34 (s, 6H), 3.25 (d, J = 5.7 Hz, 2H), 5.02 (s, 1H), 5.07 (d, J = 8.7 Hz, 1H), 5.92 (ddt, J = 16.5, 11.0, 5.5 Hz, 1H), 7.06-7.15 (m, 3H), 7.19-7.28 (m, 2H), 7.36-7.46 (m, 2H), 7.59 (d, J = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –4.2, –4.1, 32.0, 115.5 ($^2J_{C–F}$ = 23.2 Hz), 116.2, 122.8, 123.8 ($^4J_{C–F}$ = 3.5 Hz), 126.6, 127.6 ($^3J_{C–F}$ = 8.1 Hz), 128.1 ($^2J_{C–F}$ = 17.4 Hz), 129.6, 129.9 ($^3J_{C–F}$ = 3.5 Hz), 131.5, 135.6, 138.0, 138.9, 148.9, 151.7, 159.3 ($^1J_{C–F}$ = 243.6 Hz); HRMS (EI) calcd for $C_{19}H_{19}FSi$ (M^+) 294.1240, found 294.1241.

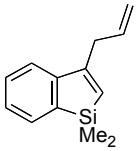


3-Allyl-1,1-dimethyl-2-(5-methyl-2-thienyl)-1-silaindene (2j). The title compound (24.9 mg, 42%) was prepared by the reaction of **1j** (59.3 mg, 0.20 mmol) in the presence of **3** (6 mol %). ^{1}H NMR ($CDCl_3$) δ0.45 (s, 6H), 2.52 (s, 3H), 3.65-3.68 (m, 2H), 5.09-5.19 (m, 2H), 6.05 (ddt, J = 17.1, 10.7, 5.6 Hz, 1H), 6.72-6.74 (m, 1H), 6.87 (d, J = 3.3 Hz, 1H), 7.18-7.26 (m, 1H), 7.34-7.40 (m, 2H), 7.55 (dd, J = 6.9. 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ–3.1, 15.4, 32.8, 116.2, 122.3, 125.4, 126.2, 126.3, 129.9, 131.3, 134.7, 135.0, 137.6, 139.7, 140.5, 146.7, 150.0; HRMS (EI) calcd for $C_{18}H_{20}SSi$ (M^+) 296.1055, found 296.1055.

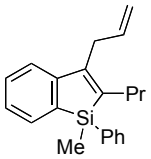
3-Allyl-2-chloro-1,1-dimethyl-1-silaindene (2k). The title compound (37.1 mg, 79%) was prepared by the reaction of **1k** (47.0 mg, 0.20 mmol) in the presence of **3** (3 mol %). ^{1}H NMR ($CDCl_3$) δ0.40 (s, 6H), 3.53 (d, J = 6.2 Hz, 2H), 5.07-5.20 (m, 2H), 5.92 (ddt, J = 16.7, 11.3, 6.2 Hz, 1H), 7.21-7.28 (m, 1H), 7.32-7.40 (m, 2H), 7.51 (d, J = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –5.0, 31.3, 116.3, 121.7, 126.6, 130.0, 131.8, 133.6, 136.1, 137.1, 147.4, 150.1; HRMS (EI) calcd for $C_{13}H_{15}ClSi$ (M^+) 234.0632, found 234.0635.



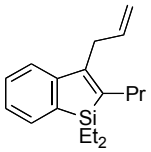
3-Allyl-2-bromo-1,1-dimethyl-1-silaindene (2l). The title compound (43.2 mg, 77%) was prepared by the reaction of **1l** (55.9 mg, 0.20 mmol) in the presence of **3** (3 mol %). ^{1}H NMR ($CDCl_3$) δ0.37 (s, 6H), 3.49 (dt, J = 6.3, 1.4 Hz, 2H), 5.07-5.21 (m, 2H), 5.91 (ddt, J = 16.2, 10.1, 6.3 Hz, 1H), 7.21-7.27 (m, 1H), 7.36 (d, J = 3.6 Hz, 2H), 7.52 (d, J = 6.8, 1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ–5.0, 33.8, 116.4, 121.9, 126.6, 128.0, 130.0, 131.9, 133.3, 137.2, 147.8, 152.5; HRMS (EI) calcd for $C_{13}H_{15}BrSi$ (M^+) 278.0126, found 278.0120.



3-Allyl-1,1-dimethyl-1-silaindene (C). The title compound was obtained (13–14%) as a byproduct from the reaction of **1k** or **1l**. ^{1}H NMR ($CDCl_3$) δ0.36 (s, 6H), 3.27 (d, J = 6.6 Hz, 2H), 5.02-5.09 (m, 2H), 5.76 (ddt, J = 16.8, 9.9, 6.7 Hz, 1H), 5.98 (s, 1H), 7.14 (d, J = 6.7 Hz, 1H), 7.26-7.36 (m, 2H), 7.64 (d, J = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ2.6, 38.2, 116.9, 117.5, 126.8, 128.6, 129.0, 133.4, 134.9, 137.6, 142.6, 145.5; HRMS (FAB) calcd for $C_{13}H_{15}Si$ (M^+ – H) 199.0934, found 199.0943.



3-Allyl-1-methyl-1-phenyl-2-propyl-1-silaindene (2m). The title compound (76.1 mg, 83%) was prepared by the reaction of **1m** (91.4 mg, 0.30 mmol) in the presence of **3** (3 mol %). ^{1}H NMR ($CDCl_3$) δ 0.65 (s, 3H), 0.86 (t, J = 7.4 Hz, 3H), 1.33-1.49 (m, 2H), 2.23-2.47 (m, 2H), 3.37 (d, J = 5.7 Hz, 2H), 5.02-5.14 (m, 2H), 5.94 (ddt, J = 16.5, 10.7, 5.7 Hz, 1H), 7.12-7.17 (m, 1H), 7.29-7.39 (m, 5H), 7.44-7.52 (m, 3H); ^{13}C NMR ($CDCl_3$) δ–5.6, 14.5, 23.6, 31.2, 31.9, 115.5, 121.5, 126.0, 127.9, 129.6, 129.8, 131.9, 134.4, 134.8, 135.3, 136.8, 142.4, 149.7, 150.6; HRMS (EI) calcd for $C_{21}H_{24}Si$ (M^+) 304.1647, found 304.1649.

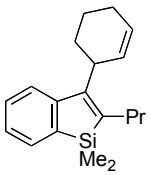


3-Allyl-1,1-diethyl-2-propyl-1-silaindene (2n). The title compound (42.7 mg, 53%) was prepared by the reaction of **1n** (81.1 mg, 0.30 mmol) in the presence of **3** (6 mol %). ^{1}H NMR ($CDCl_3$) δ0.77-1.01 (m, 13H), 1.52 (sext, J = 7.7 Hz, 2H), 2.37 (t, J = 7.7 Hz, 2H), 3.34 (d, J = 5.7 Hz, 2H), 4.99-5.10 (m, 2H), 5.92 (ddt, J = 17.1, 9.9, 5.8 Hz, 1H), 7.13-7.18 (m, 1H), 7.26-7.36 (m, 2H), 7.50 (d, J = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ3.9, 7.6, 14.7, 23.5, 31.1,

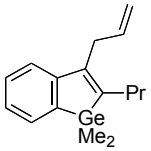
32.3, 115.3, 121.3, 125.4, 129.4, 131.8, 135.5, 136.1, 141.9, 149.3, 150.8; HRMS (EI) calcd for $C_{18}H_{26}Si$ (M^+) 270.1804, found 270.1803.

1,1-Dimethyl-3-methallyl-2-propyl-1-silaindene (2o). The title compound (64.2 mg, 83%) was prepared by the reaction of **1o** (76.9 mg, 0.30 mmol) in the presence of **3** (3 mol %). ^{1}H NMR ($CDCl_3$) δ0.31 (s, 6H), 0.96 (t, J = 7.6 Hz, 3H), 1.52 (sext, J = 7.6 Hz, 2H), 1.80 (s, 3H), 2,36 (t, J = 7.6 Hz, 2H), 3.23 (s, 2H), 4.64 (s, 1H), 4.74 (s, 1H), 7.14 (dt, J = 6.9, 1.2 Hz, 1H), 7.21-7.32 (m, 2H), 7.47 (d, J = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ–3.4, 14.6, 23.1, 23.5, 32.1, 34.9, 110.8, 121.5, 125.6, 129.5, 131.0, 137.9, 142.6, 144.2, 148.2, 150.3; HRMS (EI) calcd for $C_{17}H_{24}Si$ (M^+) 256.1647, found 256.1647.

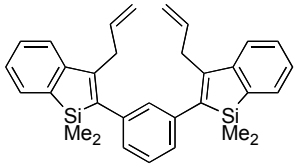
3-(But-3-en-2-yl)-1,1-dimethyl-2-propyl-1-silaindene (2p). The title compound (35.4 mg, 69%) was prepared by the reaction of **1p** (51.3 mg, 0.20 mmol) in the presence of **3** (3 mol %). ^{1}H NMR ($CDCl_3$) δ0.32 (s, 6H), 0.99 (dt, J = 7.5, 1.5 Hz, 3H), 1.45 (dd, J = 7.5, 1.7 Hz, 3H), 1.53 (sext, J = 8.7 Hz, 2H), 2,43 (dt, J = 8.1, 1.5 Hz, 2H), 3.86-3.95 (m, 1H), 5.09-5.17 (m, 2H), 6.12-6.23 (m, 1H), 7.12-7.18 (m, 1H), 7.25-7.31 (m, 1H), 7.45-7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ–3.5, –3.4, 14.6, 17.5, 23.7, 31.8, 35.7, 113.4, 123.4, 125.3, 129.0, 131.3, 138.7, 142.2, 142.7, 149.1, 153.2; HRMS (EI) calcd for $C_{17}H_{24}Si$ (M^+) 256.1647, found 256.1646.



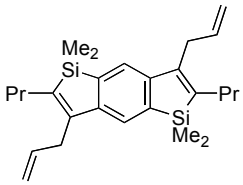
3-(Cyclohex-2-enyl)-1,1-dimethyl-2-propyl-1-silaindene (2q). The title compound (26.1 mg, 46%) was prepared by the reaction of **1q** (56.5 mg, 0.20 mmol) in the presence of **3** (3 mol %). ^{1}H NMR ($CDCl_3$) δ0.29 (s, 6H), 0.95 (t, J = 7.5 Hz, 3H), 1.49 (sext, J = 7.5 Hz, 2H), 1.60-1.84 (m, 2H), 1.85-2.00 (m, 2H), 2.21-2.35 (m, 2H), 2.40-2.45 (m, 2H), 3.70-3.82 (m, 1H), 5.69-5.85 (m, 2H), 7.12 (t, J = 7.1 Hz, 1H), 7.22-7.27 (m, 1H), 7.47 (d, J = 6.6 Hz, 1H), 7.53-7.64 (m, 1H); ^{13}C NMR ($CDCl_3$) δ–3.4, 14.5, 23.1, 23.8, 25.0, 27.8 (br), 31.7, 36.5, 123.4 (br), 125.2, 126.6 (br), 129.1, 131.2, 131.6, 138.8, 153.4 [two sp^2 carbons are missing due to overlap]; HRMS (EI) calcd for $C_{19}H_{26}Si$ (M^+) 282.1804, found 282.1806.



3-Allyl-1,1-dimethyl-2-propyl-1-germaindene (2r). The title compound (72.8 mg, 85%) was prepared by the reaction of **1r** (86.1 mg, 0.30 mmol) in the presence of **3** (3 mol %). ^{1}H NMR ($CDCl_3$) δ0.49 (s, 6H), 0.96 (t, J = 7.5 Hz, 3H), 1.54 (sext, J = 7.5 Hz, 2H), 2.46 (t, J = 7.4 Hz, 2H), 3.33 (d, J = 5.7 Hz, 2H), 4.98-5.10 (m, 2H), 5.91 (ddt, J = 17.1, 10.5, 5.7 Hz, 1H), 7.15-7.20 (m, 1H), 7.30-7.31 (m, 2H), 7.50 (d, J = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –2.8, 14.4, 23.9, 31.2, 33.1, 115.3, 122.0, 125.8, 128.8, 131.3, 135.7, 140.3, 144.2, 146.2, 148.6; HRMS (EI) calcd for $C_{16}H_{22}Ge$ (M^+) 288.0933, found 288.0934.



1,3-Bis(3-allyl-1,1-dimethyl-1-silainden-2-yl)benzene (5a). The title compound (68.1 mg, 72%) was prepared by the reaction of **4a** (95.0 mg, 0.20 mmol) in the presence of **3** (12 mol %). ^{1}H NMR ($CDCl_3$) δ0.35 (s, 12H), 3.33 (d, J = 5.6 Hz, 4H), 5.01-5.11 (m, 4H), 5.97 (ddt, J = 17.1, 11.3, 5.6 Hz, 2H), 6.94-6.98 (m, 1H), 7.05 (dd, J = 13.2, 2.0 Hz, 2H), 7.21-7.28 (m, 1H), 7.31-7.42 (m, 6H), 7.57 (d, J = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ–3.9, 32.4, 116.1, 122.7, 125.0, 126.37, 126.41, 128.2, 129.7, 131.4, 136.0, 138.6, 140.7, 144.4, 149.4, 149.5; HRMS (EI) calcd for $C_{32}H_{34}Si_2$ (M^+) 474.2199, found 474.2202.



3,7-Diallyl-1,1,5,5-tetramethyl-2,6-dipropyl-1,5-disila-*s*-indacene (5b). The title compound (52.1 mg, 60%) was prepared by the reaction of **4b** (87.5 mg, 0.22 mmol) in the presence of **3** (6 mol %). ^{1}H NMR ($CDCl_3$) δ0.30 (s, 12H), 0.95 (t, J = 7.2 Hz, 6H), 1.51 (sext, J = 7.2 Hz, 4H), 2.37 (t, J = 7.2 Hz, 4H), 3.34 (d, J = 5.7 Hz, 4H), 4.98-5.11 (m, 4H), 5.91 (ddt, J = 16.2, 10.2, 5.7 Hz, 2H), 7.42 (s, 2H); ^{13}C NMR ($CDCl_3$) δ–3.4, 14.6, 23.6, 31.2, 31.9, 115.3, 124.1, 135.6, 139.8, 142.6, 147.6, 148.3; HRMS (EI) calcd for $C_{26}H_{38}Si_2$ (M^+) 406.2512, found 406.2515.