Supplementary Information

Rhodium-Catalysed Synthesis of Multi-Substituted Silylindenenes from Aryl Alkynes and Hydrosilanes via C-H Bond Activation

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General. All reactions were carried out in a dry solvent under an argon atmosphere. Toluene was purchased from Wako Pure Chemical Industries and was dried and degassed before use. \([\text{RhCl(cod)}]_2\) was purchased from Tokyo Kasei Kogyo Co.. Diphenylacetylene (1a) and all organosilanes 2a-2e and tributylgermane (2f) were purchased from Aldrich Co., Kanto Kagaku Reagent Division, Tokyo Kasei Kogyo Co., and Wako Pure Chemical Industries. Substituted diarylalkynes 1b-1j were prepared according to the literature methods.\textsuperscript{1}

NMR spectra were recorded on JEOL ECX500 (500 MHz for \(^1\)H NMR and 125 MHz for \(^{13}\)C NMR) and JEOL ECS400 (400 MHz for \(^1\)H NMR, 100 MHz for \(^{13}\)C NMR, 376 MHz for \(^{19}\)F NMR, and 78 MHz for \(^{29}\)Si NMR) spectrometers. Proton chemical shifts are reported relative to Me\(_4\)Si (CDCl\(_3\)) at \(\delta 0.00\) ppm or residual solvent peak (CDCl\(_3\) at \(\delta 7.26\) ppm). Carbon chemical shifts are reported relative to CDCl\(_3\) at \(\delta 77.00\) ppm. Fluorine chemical shifts are reported relative to TFA (CDCl\(_3\)) at \(\delta -76.55\) ppm as an external standard. Silicon chemical shifts are reported relative to Me\(_4\)Si (CDCl\(_3\)) at \(\delta 0.00\) ppm as an external standard. Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. DART-mass spectra were measured on a JEOL JMS-T100LC AccuTOF spectrometer for HRMS. FAB-mass spectra were measured on a JEOL JMS-700T spectrometer for HRMS. Indene 5b and 5c were purified by recycling preparative HPLC (LC-9210NEXT; column, JAIGEL-1H and JAIGEL-2H; solvent, CHCl\(_3\)).
Table 1. Investigation of several transition metal complexes and ligands

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^a 1a (2.0 equiv). ^b 1H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard. ^c Isolated yield. ^d With MS 3A (40 mg/mmol). ^e With MS 4A (40 mg/mmol). ^f With MS 5A (40 mg/mmol).
Typical procedure for Rhodium-Catalyzed Synthesis of Multi-Substituted Silylindenes by C-H Bond Activation. A mixture of dimethylphenylsilane (1a, 34.1 mg, 0.250 mmol), diphenylacetylene (2a, 89.1 mg, 0.500 mmol), [RhCl(cod)]₂ (3.1 mg, 6.3 µmol), triphenylphosphine (9.9 mg, 38 µmol), and toluene (1.0 mL) was stirred at 150 °C for 24 h in a sealed tube. Then the solvent was removed in vacuo. The product was isolated by column chromatography on silica gel (hexane) to give (1-benzyl-1,2-diphenyl-1H-inden-3-yl)trimethylsilane (3a, 57.6 mg, 47% yield).

(1-Benzyl-1,2-diphenyl-1H-inden-3-yl)dimethyl(phenyl)silane (3a).
White solid (57.6 mg, 47%); mp 133-135 °C; ¹H NMR (500 MHz, CDCl₃) δ -0.12 (s, 3H), 0.28 (s, 3H), 3.39 (d, J = 12.9 Hz, 1H), 3.80 (d, J = 12.9 Hz, 1H), 6.54 (d, J = 7.4 Hz, 2H), 6.63 (d, J = 6.9 Hz, 2H), 6.98 (dd, J = 7.7, 7.7 Hz, 2H), 7.06 (dd, J = 7.7, 7.7 Hz, 2H), 7.08-7.13 (m, 4H), 7.14-7.34 (m, 12H); ¹³C NMR (125 MHz, CDCl₃) δ -0.86, -0.29, 40.0, 65.7, 123.2, 124.0, 124.9, 126.1, 126.6, 127.0, 127.1, 127.2 (2C), 127.6, 127.7, 128.4, 128.7, 130.05, 130.08, 133.9, 136.8, 137.4, 137.9, 139.2, 141.9, 148.2, 152.5, 166.4; ²⁹Si NMR (78 MHz, CDCl₃) δ -12.3; IR (neat, ν / cm⁻¹) 3063, 2959, 1456, 1261, 1109, 822, 699; HRMS (DART+) Calcd for C₃₆H₃₃Si [M+H]⁺ 493.2352, Found 493.2364.

(1-Benzyl-1,2-diphenyl-1H-inden-3-yl)triethoxysilane (3b).
Yellow oil (62.0 mg, 48%); ¹H NMR (400 MHz, CDCl₃) δ 0.98 (t, J = 7.2 Hz, 9H), 3.35 (d, J = 13.0 Hz, 1H), 3.45 (q, J = 7.2 Hz, 6H), 3.81 (d, J = 13.0 Hz, 1H), 6.35 (d, J = 6.7 Hz, 2H), 6.78-6.91 (m, 4H), 6.91-7.01 (m, 1H), 7.09-7.20 (m, 4H), 7.20-7.30 (m, 7H), 7.75 (d, J = 6.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 17.9, 40.0, 58.0, 65.4, 123.5, 123.6, 125.3, 126.1, 126.7, 126.8, 126.88, 126.94, 127.0, 127.9, 128.6, 129.6, 129.9, 132.7, 136.3, 136.7, 142.2, 147.3, 152.9, 167.7; ²⁹Si NMR (78 MHz, CDCl₃) δ -58.1; IR (neat, ν / cm⁻¹) 3062, 2969, 2920, 2890, 1491, 1443, 1163, 1065, 963, 813, 795, 758, 700; HRMS (DART+) Calcd for C₃₆H₃₇O₃Si [M+H]⁺ 521.2512, Found 521.2524.
(1-Benzyl-1,2-diphenyl-1H-inden-3-yl)triethylsilane (3c).

Yellow oil (47.8 mg, 40%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.35-0.56 (m, 6H), 0.69 (t, \(J = 8.1\) Hz, 9H), 3.30 (d, \(J = 13.5\) Hz, 1H), 3.75 (d, \(J = 13.5\) Hz, 1H), 6.57 (dd, \(J = 6.7, 7.2\) Hz, 4H), 6.94 (t, \(J = 7.2\) Hz, 2H), 6.99-7.05 (m, 2H), 7.07-7.17 (m, 5H), 7.19-7.31 (m, 5H), 7.47 (d, \(J = 7.6\) Hz, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 3.95, 7.42, 39.7, 65.7, 122.5, 124.2, 124.8, 126.1, 126.5, 126.7, 126.9, 127.2, 127.3, 127.5, 128.2, 129.9, 130.0, 137.1, 137.4, 137.8, 142.1, 149.0, 152.3, 166.5; \(^{29}\)Si NMR (78 MHz, CDCl\(_3\)) \(\delta\) -0.06; IR (neat, \(\nu / \text{cm}^{-1}\)) 2952, 1456, 1264, 1002, 699; HRMS (DART +) Calcd for C\(_{34}\)H\(_{37}\)Si [M+H]\(^+\) 473.2665, Found 473.2671.

(1-Benzyl-1,2-diphenyl-1H-inden-3-yl)tributylsilane (3d).

Yellow oil (63.6 mg, 46%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.35-0.53 (m, 6H), 0.74 (t, \(J = 7.2\) Hz, 9H), 0.89-1.17 (m, 12H), 3.30 (d, \(J = 14.2\) Hz, 1H), 3.75 (d, \(J = 14.2\) Hz, 1H), 6.55 (d, \(J = 7.6\) Hz, 4H), 6.94 (dd, \(J = 7.6, 7.6\) Hz, 2H), 6.99-7.15 (m, 7H), 7.16-7.28 (m, 5H), 7.46 (d, \(J = 7.6\) Hz, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 12.8, 13.6, 25.9, 26.5, 39.6, 65.6, 122.6, 124.1, 124.8, 126.1, 126.5, 126.7, 126.8, 127.1, 127.3, 127.4, 128.2, 129.9, 130.0, 137.1, 137.9, 138.1, 142.2, 149.1, 152.4, 165.9; \(^{29}\)Si NMR (78 MHz, CDCl\(_3\)) \(\delta\) -4.40; IR (neat, \(\nu / \text{cm}^{-1}\)) 2955, 2923, 1456, 757, 699; HRMS (DART +) Calcd for C\(_{40}\)H\(_{49}\)Si [M+H]\(^+\) 557.3604, Found 557.3593.

(1-Benzyl-1,2-diphenyl-1H-inden-3-yl)(tert-butyl)dimethylsilane (3e).

Yellow oil (39.1 mg, 33%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) -0.43 (s, 3H), 0.00 (s, 3H), 0.81 (s, 9H), 3.31 (d, \(J = 14.2\) Hz, 1H), 3.75 (d, \(J = 14.2\) Hz, 1H), 6.60 (d, \(J = 7.2\) Hz, 2H), 6.71 (d, \(J = 7.2\) Hz, 2H), 6.93-7.04 (m, 5H), 7.05-7.15 (m, 4H), 7.15-7.25 (m, 5H), 7.51 (d, \(J = 7.6\) Hz, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) -4.02, -2.99, 18.0, 27.8, 39.7, 68.2, 124.0, 124.5, 124.7, 126.2, 126.4, 126.5, 126.7, 127.2, 127.3, 127.6, 128.0, 129.9, 130.3, 137.4, 137.5, 137.7, 141.7, 149.1, 151.7, 166.8; \(^{29}\)Si NMR (78 MHz, CDCl\(_3\)) \(\delta\) -0.38; IR (neat, \(\nu / \text{cm}^{-1}\)) 2954, 2927, 2855, 1462, 824, 701; HRMS (DART +) Calcd for C\(_{34}\)H\(_{37}\)Si [M+H]\(^+\) 473.2665, Found 473.2677.
Trimethyl(6-methyl-1-(4-methylbenzyl)-1,2-di-p-tolyl-1H-inden-3-yl)silane (3f).

Yellow oil (36.4 mg, 30%); $^1$H NMR (400 MHz, CDCl$_3$) δ -0.05 (s, 9H), 2.21 (s, 3H), 2.29 (s, 3H), 2.32 (s, 3H), 2.33 (s, 3H), 3.24 (d, $J$ = 13.5 Hz, 1H), 3.68 (d, $J$ = 13.5 Hz, 1H), 6.49 (d, $J$ = 8.1 Hz, 2H), 6.54 (d, $J$ = 8.1 Hz, 2H), 6.75-6.81 (m, 3H), 6.94 (d, $J$ = 8.1 Hz, 2H), 6.97-7.06 (m, 5H), 7.29 (d, $J$ = 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 0.27, 20.9, 21.0, 21.2, 21.4, 39.6, 65.1, 121.9, 125.1, 127.1, 127.3, 127.63, 127.64, 128.8, 129.8, 130.0, 134.0, 134.4, 135.1, 135.2, 135.7, 136.8, 138.9, 139.1, 145.9, 152.6, 164.4; $^{29}$Si NMR (78 MHz, CDCl$_3$) δ -9.23; IR (neat, v / cm$^{-1}$) 2921, 1507, 1249, 839; HRMS (DART+) Calcd for C$_{35}$H$_{39}$Si [M+H]$^+$ 487.2821, Found 487.2814.

(6-Methoxy-1-(4-methoxybenzyl)-1,2-bis(4-methoxyphenyl)-1H-inden-3-yl)trimethylsilane (3g).

Yellow oil (60.1 mg, 44%); $^1$H NMR (400 MHz, CDCl$_3$) δ -0.03 (s, 9H), 3.16 (d, $J$ = 13.7 Hz, 1H), 3.63 (d, $J$ = 13.7 Hz, 1H), 3.70 (s, 3H), 3.71 (s, 3H), 3.79 (s, 3H), 3.80 (s, 3H), 6.49-6.58 (m, 7H), 6.69 (d, $J$ = 9.0 Hz, 2H), 6.74-6.81 (m, 3H), 7.02 (d, $J$ = 8.5 Hz, 2H), 7.30 (d, $J$ = 8.1 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 0.32, 39.6, 55.07, 55.11, 55.14, 55.4, 65.0, 110.3, 112.2, 112.35, 112.44, 113.4, 122.7, 128.4, 129.5, 130.5, 130.9, 131.3, 133.9, 138.2, 141.5, 154.0, 157.3, 157.8, 158.0, 158.8, 163.3; $^{29}$Si NMR (78 MHz, CDCl$_3$) δ -9.30; IR (neat, v / cm$^{-1}$) 2953, 2835, 1609, 1510, 1248, 1178, 1036, 836, 738; HRMS (DART+) Calcd for C$_{35}$H$_{39}$O$_4$Si [M+H]$^+$ 551.2618, Found 551.2637.

Trimethyl(6-(methylthio)-1-(4-(methylthio)benzyl)-1,2-bis(4-(methylthio)phenyl)-1H-inden-3-yl)silane (3h).

Gray solid (78.3 mg, 51%); mp 154-157 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ -0.03 (s, 9H), 2.36 (s, 3H), 2.38 (s, 3H), 2.47 (s x 2, 6H), 3.14 (d, $J$ = 13.3 Hz, 1H), 3.67 (d, $J$ = 13.3 Hz, 1H), 6.52 (d, $J$ = 6.5 Hz, 2H), 6.58 (d, $J$ = 6.5 Hz, 2H), 6.80 (s, 1H), 6.90 (d, $J$ = 5.8 Hz, 2H), 7.00 (d, $J$ = 5.8 Hz, 2H), 6.90 (d, $J$ = 5.8 Hz, 2H), 6.80 (s, 1H), 6.90 (d, $J$ = 5.8 Hz, 2H), 7.00 (d, $J$ = 5.8 Hz, 2H), 6.90 (d, $J$ = 5.8 Hz, 2H), 6.80 (s, 1H), 6.90 (d, $J$ = 5.8 Hz, 2H), 7.00 (d, $J$ = 5.8 Hz, 2H).
Hz, 2H), 7.04 (d, J = 5.8 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 7.16 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 0.30, 15.5, 15.7, 16.2, 16.5, 39.7, 65.2, 122.8, 123.2, 124.9, 125.7, 125.8, 126.3, 127.9, 130.4 (2C), 134.1, 134.2, 134.3, 135.8, 136.5, 137.8, 137.9, 139.3, 145.9, 152.4, 163.5; 29Si NMR (78 MHz, CDCl3) δ -8.96; IR (neat, v / cm⁻¹) 2916, 1558, 1489, 1457, 830; HRMS (DART+) Calcd for C₃₅H₃₉S₄Si [M+H]+ 615.1704, Found 615.1709.

4,4’-(6-(Dimethylamino)-1-(4-(dimethylamino)benzyl)-3-(triethylsilyl)-1H-indene-1,2-diyl)bis(N,N-dimethylaniline) (3i).
Brownish yellow oil (20.3 mg, 25%); 1H NMR (400 MHz, CDCl3) δ 0.36-0.55 (m, 6H), 0.70 (t, J = 8.1 Hz, 9H), 2.79 (s, 6H), 2.85 (s, 6H), 2.92 (s, 6H), 2.93 (s, 6H), 3.07 (d, J = 13.5 Hz, 1H), 3.57 (d, J = 13.5 Hz, 1H), 6.35-6.53 (m, 9H), 6.58-6.68 (m, 3H), 7.02 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.1 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 4.20, 7.59, 39.7, 40.6, 40.8, 41.2, 41.4, 65.1, 110.08, 110.09, 111.1, 112.4, 122.1, 126.8, 127.0, 127.07, 128.2, 130.7, 131.1, 134.2, 148.1, 148.8, 149.1, 149.5, 154.4, 164.8; 29Si NMR (78 MHz, CDCl3) δ -0.52; IR (neat, v / cm⁻¹) 2950, 2871, 1611, 1519, 1349, 948, 821, 730; HRMS (DART+) Calcd for C₄₂H₅₇N₄Si [M+H]+ 645.4374, Found 645.4352.

Trimethyl(6-(trifluoromethyl)-1-(4-(trifluoromethyl)benzyl)-1,2-bis(4-(trifluoromethyl)phenyl)-1H-inden-3-yl)silane (3j).
Yellow oil (63.5 mg, 36%); 1H NMR (400 MHz, CDCl3) δ -0.01 (s, 9H), 3.39 (d, J = 13.7 Hz, 1H), 3.85 (d, J = 13.7 Hz, 1H), 6.67 (d, J = 7.6 Hz, 2H), 6.77 (d, J = 7.6 Hz, 2H), 7.15 (s, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.52-7.63 (m, 4H); 13C NMR (100 MHz, CDCl3) δ 0.00, 39.7, 65.8, 121.20 (q, J = 3.8 Hz), 123.24, 123.4 (q, J = 272 Hz), 123.9 (q, J = 272 Hz), 124.0 (q, J = 272 Hz), 124.4 (q, J = 3.8 Hz), 124.6 (q, J = 3.8 Hz), 125.0 (q, J = 3.8 Hz), 121.2 (q, J = 3.8 Hz), 125.70 (q, J = 272 Hz), 125.74 (q, J = 3.8 Hz), 127.7 (q, J = 32 Hz), 129.2 (q, J = 32 Hz), 129.8 (q, J = 32 Hz), 129.98, 130.03, 130.5 (q, J = 32 Hz), 139.9 (q, J = 1.4 Hz), 140.4 (q, J = 1.4 Hz), 141.9, 143.9
Trimethyl(6-(trifluoromethoxy)-1-(4-(trifluoromethoxy)benzyl)-1,2-bis(4-(trifluoromethoxy)phenyl)-1H-inden-3-yl)silane (3k).

Pale yellow oil (99.3 mg, 52%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ -0.02 (s, 9H), 3.33 (d, $J = 13.7$ Hz, 1H), 3.68 (d, $J = 13.7$ Hz, 1H), 6.64 (d, $J = 8.5$ Hz, 2H), 6.68 (d, $J = 8.5$ Hz, 2H), 6.81-7.20 (m, 7H), 7.03-7.70 (m, 7H), 7.40 (d, $J = 8.5$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ -1.14, -1.07, -0.87, 3.95, 7.44, 40.1, 66.0, 121.8, 126.9, 129.3, 129.4 129.5 (2C), 131.65, 131.73, 132.2, 133.1, 135.9, 136.8, 137.5, 138.1, 138.2, 139.3, 142.2, 149.8, 151.0, 167.1; $^{29}$Si NMR (78 MHz, CDCl$_3$) $\delta$ -4.14, -0.46, -0.11 (3 x Si); IR (neat, $\nu /$ cm$^{-1}$) 2957, 1617, 1409, 1323, 1166, 1121, 1069, 1017, 841, 741; HRMS (DART+) Calcd for C$_{35}$H$_{27}$F$_{12}$O$_4$Si $[M+H]^+$ 767.1487, Found 767.1470.

(4,4'-((Triethylsilyl)-6-(trimethylsilyl)-1-(4-(trimethylsilyl)benzyl)-1H-indene-1,2-diyl)bis(4,1-phenylene))bis(trimethylsilane) (3l).

Yellow oil (36.7 mg, 39%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.16 (s, 9H), 0.19 (s, 9H), 0.25 (s, 9H), 0.26 (s, 9H), 0.35-0.52 (m, 6H), 0.65 (t, $J = 7.9$ Hz, 9H), 3.15 (d, $J = 13.7$ Hz, 1H), 3.79 (d, $J = 13.7$ Hz, 1H), 6.51 (d, $J = 7.6$ Hz, 2H), 6.53 (d, $J = 7.6$ Hz, 2H), 7.02-7.12 (m, 5H), 7.21-7.26 (m, 2H), 7.35 (d, $J = 7.6$ Hz, 2H), 7.40 (d, $J = 7.2$ Hz, 1H), 7.44 (d, $J = 8.1$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ -1.14, -1.07, -0.87, 3.95, 7.44, 40.1, 66.0, 121.8, 126.9, 129.3, 129.4 129.5 (2C), 131.65, 131.73, 132.2, 133.1, 135.9, 136.8, 137.5, 138.1, 138.2, 139.3, 142.2, 149.8, 151.0, 167.1; $^{29}$Si NMR (78 MHz, CDCl$_3$) $\delta$ -4.14, -0.46, -0.11 (3 x Si); IR (neat, $\nu /$ cm$^{-1}$)
Diethyl 4,4’-(6-(ethoxycarbonyl)-1-(4-(ethoxycarbonyl)benzyl)-3-(triethylsilyl)-1H-indene-1,2-diyl)dibenzoate (3m).
Yellow oil (33.6 mg, 36%); ¹H NMR (400 MHz, CDCl₃) δ 0.34-0.56 (m, 6H), 0.67 (t, J = 8.1 Hz, 9H), 1.34 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.41 (t, J = 7.2 Hz, 3H), 3.37 (d, J = 13.3 Hz, 1H), 3.89 (d, J = 13.3 Hz, 1H), 4.25-4.44 (m, 8H), 6.57 (d, J = 8.1 Hz, 2H), 6.65 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 8.5 Hz, 2H), 7.70 (s, 1H), 7.84 (d, J = 8.5 Hz, 2H), 13C NMR (100 MHz, CDCl₃) δ 3.93, 7.32, 14.26, 14.29, 14.30, 14.31, 39.4, 60.8, 60.9, 61.0, 61.1, 65.8, 122.7, 124.8, 127.0, 127.5, 128.5, 128.6, 128.8, 129.3, 129.4, 129.6, 129.7, 129.9, 130.1, 139.7, 141.3, 141.6, 145.9, 151.6, 153.3, 166.2, 166.3, 166.4, 166.6, 167.2; ²⁹Si NMR (78 MHz, CDCl₃) δ -9.21; IR (neat, ν/cm⁻¹) 2955, 1715, 1607, 1274, 1105, 1021, 733; HRMS (DART+) Calcd for C₄₆H₅₉Si₅ [M+H]^+ 761.4214, Found 761.4214.

Trimethyl(5-methyl-1-(3-methylbenzyl)-1,2-di-m-tolyl-1H-inden-3-yl)silane (3n).
Yellow oil (72.3 mg, 59%); ¹H NMR (400 MHz, CDCl₃) δ -0.01 (s, 9H), 2.13 (s, 3H), 2.23 (s, 3H), 2.29 (s, 3H), 2.43 (s, 3H), 3.24 (d, J = 13.0 Hz, 1H), 3.72 (d, J = 13.0 Hz, 1H), 6.39 (d, J = 8.1 Hz, 3H), 6.44 (d, J = 7.4 Hz, 1H), 6.85-6.90 (m, 2H), 6.90-6.98 (m, 4H), 6.99-7.08 (m, 3H), 7.12 (t, J = 7.4 Hz, 1H), 7.24 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 0.34, 21.2, 21.3, 21.7, 21.8, 40.2, 65.1, 123.1, 123.9, 124.5, 125.4, 126.5, 126.7, 126.8 (2C), 126.9, 127.0, 127.9 (2C), 128.0, 131.0, 131.5, 135.9, 136.0, 136.1, 137.28, 138.33, 137.9, 139.2, 142.0, 148.7, 149.5, 165.3; ²⁹Si NMR (78 MHz, CDCl₃) δ -9.21; IR (neat, ν/cm⁻¹) 3032, 2921, 2860, 1604, 1488, 1472, 866, 837, 702; HRMS (DART+) Calcd for C₃₅H₃₉Si [M+H]^+ 487.2821, Found 487.2828.
(1-Benzyl-1,2-diphenyl-1H-inden-3-yl)tributylgermane (3o).

Yellow oil (32.0 mg, 21%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.53-0.69 (m, 6H), 0.75 (t, $J = 7.2$ Hz, 9H), 0.97-1.19 (m, 12H), 3.32 (d, $J = 13.3$ Hz, 1H), 3.77 (d, $J = 13.3$ Hz, 1H), 6.50 (d, $J = 6.7$ Hz, 2H), 6.58 (d, $J = 7.6$ Hz, 2H), 6.92 (dd, $J = 7.6$, 7.6 Hz, 2H), 7.01 (t, $J = 7.6$ Hz, 1H), 7.05-7.13 (m, 4H), 7.13-7.18 (m, 2H), 7.19-7.27 (m, 5H), 7.37 (d, $J = 8.1$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.6, 13.9, 28.3, 27.2, 39.7, 65.3, 122.3, 123.9, 124.8, 126.1, 126.4, 126.7, 127.0 (2C), 127.2, 127.4, 128.3, 129.86, 129.89, 137.0, 137.8, 140.2, 142.4, 149.1, 152.5, 163.4; IR (neat, $\nu$ / cm$^{-1}$) 3061, 3029, 2955, 2925, 1600, 1456, 1079, 1030, 757, 699; HRyMS (DART+) Calcd for C$_{40}$H$_{49}$Ge [M+H]$^+$ 603.3046, Found 603.3034.

Procedure for trimethylsilylation of silylinden 3b. A mixture of diphenylacetylene (1a, 89.1 mg, 0.500 mmol), triethoxysilane (2b, 41.1 mg, 0.250 mmol), [RhCl(cod)]$_2$ (3.1 mg, 6.3 $\mu$mol), triphenylphosphine (9.9 mg, 38 $\mu$mol), and toluene (1.0 mL) was stirred at 150 °C for 24 h in a sealed tube. Then, the reaction mixture was cooled to ambient temperature, followed by addition of MeLi (1.13 M in Et$_2$O, 0.66 mL, 0.75 mmol) under argon atmosphere. The mixture was stirred at 25 °C for 24 h, was quenched with diluted aq. HCl, and was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was dried over Na$_2$SO$_4$, was filtrated, and the solvent was removed in vacuo. The product was isolated by column chromatography on silica gel (hexane) to give (1-benzyl-1,2-diphenyl-1H-inden-3-yl)trimethylsilane (3p, 77.5 mg, 72% yield).

(1-Benzyl-1,2-diphenyl-1H-inden-3-yl)trimethylsilane (3p).

Yellow oil (77.5 mg, 72%); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.05 (s, 9H), 3.33 (d, $J = 13.2$ Hz, 1H), 3.76 (d, $J = 13.2$ Hz, 1H), 6.55-6.69 (m, 4H), 6.90-7.05 (m, 4H), 7.06-7.16 (m, 5H), 7.17-7.29 (m, 5H), 7.40 (d, $J = 7.4$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 0.20, 40.0, 65.7, 122.5, 124.4, 124.7, 126.1, 126.5, 126.6, 127.1 (2C), 127.39, 127.41, 128.1, 129.9, 130.1, 137.2, 137.9, 139.8, 141.8, 148.5, 152.0, 164.9; $^{29}$Si NMR (78 MHz, CDCl$_3$) $\delta$ -9.02; IR (neat, $\nu$ / cm$^{-1}$) 3060, 2952, 1496, 1455, 1250, 837, 698; HRMS (DART+) Calcd for C$_{31}$H$_{31}$Si [M+H]$^+$ 431.2195, Found 431.2181.
3p-D_{20}. Yellow oil (79.4 mg, 70%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ -0.02 (s, 9H), 3.35 (s, 0.11H), 3.78 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 0.18, 39.5 (t, $J = 19.1$ Hz), 65.5, 122.0 (t, $J = 23.5$ Hz), 124.0 (t, $J = 23.2$ Hz), 124.2 (t, $J = 23.0$ Hz), 125.5 (t, $J = 24.0$ Hz), 125.74 (t, $J = 22.3$ Hz), 126.1 (t, $J = 25.8$ Hz), 126.5 (t, $J = 24.2$ Hz, 2C), 126.9 (t, $J = 23.5$ Hz), 127.2, 127.6 (t, $J = 24.4$ Hz), 129.4 (t, $J = 23.5$ Hz), 129.6 (t, $J = 24.4$ Hz), 137.0, 137.7, 139.6, 141.6, 148.3, 152.0, 164.8; $^{29}$Si NMR (78 MHz, CDCl$_3$) $\delta$ -9.02; IR (neat, $\nu$ / cm$^{-1}$) 2953, 2898, 2277, 1377, 1250, 838; HRMS (DART+) Calcd for C$_{31}$H$_{11}$D$_{20}$Si [M+H]$^+$ 451.3450, Found 451.3467.

(E)-(1,2-Diphenylvinyl)dimethyl(phenyl)silane (4a).
Pale yellow oil (14.6 mg, 19%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.39 (s, 6H), 6.82 (s, 1H), 6.89 (d, $J = 8.1$ Hz, 2H), 6.91-6.96 (m, 2H), 7.02-7.10 (m, 3H), 7.14-7.27 (m, 3H), 7.29-7.39 (m, 3H), 7.51-7.57 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ -3.11, 125.7, 127.1, 127.6, 127.7, 127.9, 128.5, 129.1, 129.5, 134.3, 137.2, 137.7, 139.1, 142.3, 145.0; IR (neat, $\nu$ / cm$^{-1}$) 3066, 2956, 1490, 1248, 1113, 954, 832, 700; HRMS (FAB+) Calcd for Formula: C$_{22}$H$_{22}$Si [M]$^+$ 314.1491, Found 314.1489.

(E)-(1,2-Diphenylvinyl)triethoxysilane (4b).$^2$
Yellow oil (6.6 mg, 8%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.21 (t, $J = 7.2$ Hz, 9H), 3.84 (q, $J = 7.2$ Hz, 6H), 7.01-7.08 (m, 2H), 7.08-7.13 (m, 3H), 7.15-7.24 (m, 4H), 7.26-7.32 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 18.1, 58.8, 126.1, 127.5, 127.8, 128.3, 128.5, 129.9, 136.9 (2C), 140.7, 142.4.

(E)-(1,2-Diphenylvinyl)triethylsilane (4c).$^3$
Yellow oil (28.0 mg, 38%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.66 (q, $J = 8.1$ Hz, 6H), 3.84 (t, $J = 8.1$ Hz, 9H), 6.78 (s, 1H), 6.93-6.99 (m, 2H), 7.01 (d, $J = 7.2$ Hz, 2H), 7.06-7.13 (m, 3H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.27-7.34 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 2.75, 7.30, 125.5, 126.9, 127.3, 127.9, 128.6, 129.5, 137.4, 138.7, 143.2, 144.1.
(E)-Tributyl(1,2-diphenylvinyl)silane (4d).
Transparent oil (47.8 mg, 50%); $^1$H NMR (400 MHz, CDCl$_3$)  δ 0.50-0.77 (m, 6H), 0.90 (t, $J = 7.2$ Hz, 9H), 1.23-1.47 (m, 12H), 6.79 (s, 1H), 6.93-7.05 (m, 4H), 7.21 (t, $J = 7.9$ Hz, 1H), 7.31 (dd, $J = 7.9$, 7.9 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 11.4, 13.8, 25.9, 26.7, 125.5, 126.9, 127.3, 127.9, 128.6, 129.5, 137.5, 138.5, 143.2, 144.8; IR (neat, ν/cm$^{-1}$) 2955, 2922, 700; HRMS (FAB+) Calcd for Formula: C$_{26}$H$_{38}$Si [M]$^+$ 378.2743, Found 378.2759.

(2,2-Di-p-tolylvinyl)trimethylsilane (4f).
White solid (17.0 mg, 24%); mp 69-74 °C; (major-4f:minor-4f = 2.3:1), $^1$H NMR (400 MHz, CDCl$_3$) δ 0.08-0.14 (m, 9 H, major&minor-4f), 2.24 (s, 3H, major-4f), 2.36 (s, 3H for major-4f, 3H for minor-4f), 2.37 (s, 3H, minor-4f), 6.75 (s, 1H, major-4f), 6.82-7.25 (m, 8H for major-4f, 9H for minor-4f); $^{13}$C NMR (100 MHz, CDCl$_3$) δ -1.16, 0.83, 21.12, 21.18 (2x C), 21.23, 127.1, 127.2, 128.49, 128.52, 128.59 (2x C), 128.63, 129.30 (2x C), 129.34 (2x C), 134.7, 134.9, 136.7, 137.1 (2C), 139.7 (2C), 144.8, 145.9; IR (neat, ν/cm$^{-1}$) 2955, 2923, 1508, 1246, 840; HRMS (FAB+) Calcd for Formula: C$_{19}$H$_{25}$Si [M+H]$^+$ 281.1713, Found 281.1713.

(1,2-Bis(4-methoxyphenyl)vinyl)trimethylsilane (4g).
Yellow oil (20.0 mg, 26%); (major-4g:minor-4g = 1.9:1), $^1$H NMR (400 MHz, CDCl$_3$) δ 0.12 (s, 9H, major&minor-4g), 3.73 (s, 3H, major-4g), 3.82 (s, 3H, minor-4g), 3.83 (s, 3H for major-4g, 3H for minor-4g), 6.64 (d, $J = 8.5$ Hz, 2H, major-4g), 6.72 (s, 1H, major-4g),
6.81-7.25 (m, 6H for major-4g, 9H for minor-4g), $^{13}$C NMR (100 MHz, CDCl$_3$) δ -1.62, 0.87, 55.10, 55.14, 55.2 (2 x C), 113.21, 113.29 (2 x C), 113.34, 114.2, 128.2, 128.5 (2 x C), 129.8, 130.3, 130.7 (2 x C), 135.0, 136.9, 144.0, 144.3, 157.6, 157.7, 158.4, 158.8; IR (neat, ν / cm$^{-1}$) 2956, 1603, 1508, 1254, 1029, 833; HRMS (FAB+) Calcd for Formula: C$_{19}$H$_{24}$O$_2$Si [M] $^+$ 312.1546, Found 312.1538.

(1,2-Bis(4-(methylthio)phenyl)vinyl)trimethylsilane (4h).
White solid (21.9 mg, 25%); mp 65-77 °C; (major-4h:minor-4h = 2.3:1), $^1$H NMR (400 MHz, CDCl$_3$) δ 0.12-0.21 (m, 9H, major&minor-4h), 2.44 (s, 3H, major-4h), 2.51-2.59 (m, 3H for major-4h, 6H for minor-4h), 6.76 (s, 1H, major-4h), 6.8-7.32 (m, 8H for major-4g, 9H for minor-4g); $^{13}$C NMR (100 MHz, CDCl$_3$) δ -1.87, 0.85, 15.4, 15.8, 15.9, 16.1, 125.7, 125.9, 126.5, 126.9, 127.6, 127.9, 129.0, 129.8, 134.0, 135.2, 135.3, 136.6, 136.9, 137.3, 137.4, 139.6, 144.3, 144.4, 145.8, 146.4; IR (neat, ν / cm$^{-1}$) 2956, 2918, 1489, 1436, 1245, 1091, 839; HRMS (FAB+) Calcd for Formula: C$_{19}$H$_{24}$S$_2$Si [M] $^+$ 344.1089, Found 344.1101.

(E)-4,4′-(1-(Triethylsilyl)ethene-1,2-diyl)bis(N,N-dimethylaniline) (4i).
Yellow oil (45.1 mg, 47%); $^1$H NMR (400 MHz, CDCl$_3$) δ 0.64 (q, $J = 8.1$ Hz, 6H), 0.97 (t, $J = 8.1$ Hz, 9H), 2.89 (s, 6H), 2.97 (s, 6H), 6.49 (d, $J = 8.3$ Hz, 2H), 6.64 (s, 1H), 6.76 (d, $J = 8.3$ Hz, 2H), 8.92 (d, $J = 8.8$ Hz, 2H), 8.93 (d, $J = 8.8$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 2.87, 7.41, 40.3, 40.9, 111.8, 113.3, 126.5, 128.2 (2C), 130.6 (2C), 138.6, 138.7, 149.2; IR (neat, ν / cm$^{-1}$) 1521, 1507, 1222, 815.

(1,2-Bis(4-(trifluoromethyl)phenyl)vinyl)trimethylsilane (4j).
Transparent oil (17.4 mg, 18%); (major-4j:minor-4j = 2.6:1), $^1$H NMR (400 MHz, CDCl$_3$) δ 0.21 (s, 9H, major&minor-4j), 6.87 (s, 1H, major-4j), 7.02 (d, $J = 8.5$ Hz, 2H, major-4j), 7.09 (d, $J = 8.1$ Hz, 2H, major-4j), 7.25 (s, 1H, minor-4j), 7.29 (d, $J = 8.1$ Hz, 2H, minor-4j), 7.36 (d, $J = 8.5$ Hz, 2H, major-4j), 7.43 (d, $J = 8.1$ Hz, 2H, minor-4j), 7.58 (d, $J = 7.6$ Hz, 2H, major-4j), 7.59 (d, $J = 7.6$ Hz, 2H, minor-4j), 7.59 (d, $I = 7.6$  

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Hz, 2H, minor-4j); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ -1.76, 0.60, 124.0 (q, $J = 272$ Hz), 124.1 (q, $J = 272$ Hz), 124.3 (q, $J = 272$ Hz), 125.0 (q, $J = 3.6$ Hz), 125.1 (q, $J = 3.6$ Hz), 125.8 (q, $J = 3.6$ Hz), 126.5 (q, $J = 271$ Hz), 127.3, 127.6 (2 x C), 128.30 (q, $J = 32.4$ Hz), 128.33 (q, $J = 32.4$ Hz), 128.8, 129.04 (q, $J = 32.4$ Hz), 129.07 (q, $J = 32.4$ Hz), 129.5 (2 x C), 136.7, 140.2, 143.1, 144.1, 146.3, 148.6, 149.0; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.5, -63.3, -63.1 (2 x CF$_3$); IR (neat, $\nu$ / cm$^{-1}$) 2925, 2854, 1541, 1507, 1323, 1128, 1067, 842.

(1,2-Bis(4-(trifluoromethoxy)phenyl)vinyl)trimethylsilane (4k).
Transparent oil (27.9 mg, 27%); (major-4k:minor-4k = 2.3:1), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.14 (s, 9H, major&minor-4k), 6.80 (s, 1H, major-4k), 6.90-6.95 (m, 4H, major&minor-4k), 6.99 (d, $J = 8.5$ Hz, 2H, major-4k), 7.13-7.22 (m, 2H for major-4k, 3H for minor-4k), 7.32 (d, $J = 8.1$ Hz, 2H, minor-4k); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ -1.77, 0.59, 120.3, 120.39 (q, $J = 257$ Hz), 120.49 (q, $J = 257$ Hz), 120.50, 120.54 (q, $J = 256$ Hz), 120.6, 121.4 (2 x C), 128.4, 128.6 (2 x C), 129.9, 130.7, 135.6, 136.6, 138.3, 141.0, 143.9, 145.5, 146.9, 147.4, 147.6 (q, $J = 1.9$ Hz), 148.0 (q, $J = 1.4$ Hz), 148.6 (q, $J = 1.4$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -58.8 (2 x CF$_3$), -58.7 (2 x CF$_3$); IR (neat, $\nu$ / cm$^{-1}$) 2958, 1506, 1259, 1211, 1165, 840; HRMS (FAB+) Calcd for Formula: C$_{19}$H$_{18}$F$_6$O$_2$Si $[M]^+$ 420.0980, Found 420.0981.

(E)-(1,2-Bis(4-(trimethylsilyl)phenyl)vinyl)triethylsilane (4l).
Transparent oil (25.2 mg, 23%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.18 (s, 9H), 0.28 (s, 9H), 0.63 (q, $J = 7.9$ Hz, 6H), 0.95 (t, $J = 7.9$ Hz, 9H), 6.72 (s, 1H), 6.93 (d, $J = 7.6$ Hz, 2H), 6.98 (d, $J = 7.4$ Hz, 2H), 7.25 (d, $J = 7.6$ Hz, 2H), 7.44 (d, $J = 7.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ -1.20, -0.96, 2.69, 7.29, 126.3, 128.8, 133.0, 133.6, 136.9, 137.7, 138.5, 139.3, 143.7, 144.5; IR (neat, $\nu$ / cm$^{-1}$) 2954, 1595, 1248, 1107, 839, 719; HRMS (FAB+) Calcd for Formula: C$_{26}$H$_{42}$Si$_3$ $[M]^+$ 439.2673, Found 439.2687.
Diethyl 4,4’-(1-(triethylsilyl)ethene-1,2-diyl)dibenzoate (4m).

Transparent oil (41.4 mg, 38%); (major-4m:minor-4m = 2.9:1), major-4m: ¹H NMR (400 MHz, CDCl₃) δ major-4m:
0.65 (q, J = 8.1 Hz, 6H), 0.95 (t, J = 8.1 Hz, 9H), 1.34 (t, J = 7.2 Hz, 3H), 1.40 (t, J = 7.2 Hz, 3H), 4.30 (q, J = 7.2 Hz, 2H), 4.39 (q, J = 7.2 Hz, 2H), 6.84 (s, 1H), 6.98 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H); minor-4m: 0.41 (q, J = 8.1 Hz, 6H), 0.80 (t, J = 8.1 Hz, 9H), 1.34 (t, J = 7.2 Hz, 3H), 1.42 (t, J = 7.2 Hz, 3H), 4.39 (q, J = 7.2 Hz, 4H), 7.24 (d, J = 8.4 Hz, 2H), 7.30 (s, 1H), 7.39 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 7.9 Hz, 2H), 8.03 (d, J = 7.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 2.70, 4.59, 7.23, 7.43, 14.25, 14.32 (3 x C), 60.8 (2 x C), 60.9, 61.0, 127.2 (2 x C), 128.0, 128.3, 128.8, 129.18 (2 x C), 129.22, 129.3, 130.0, 138.3, 141.3, 144.1, 145.5, 146.5, 146.6, 148.1, 148.4, 130.5, 137.1, 137.3, 137.5, 137.7, 137.9, 138.0, 142.7, 144.9, 147.0; IR (neat, ν / cm⁻¹) 2954, 1716, 1605, 1272, 1175, 1102, 1020, 734, 708; HRMS (FAB+) Calcd for Formula: C₂₆H₃₅O₄Si [M]⁺ 439.2305, Found 420.0981.

(1,2-Di-m-tolylvinyl)trimethylsilane (4n).

Transparent oil (16.5 mg, 24%); (major-4n:minor-4n=3:1), ¹H NMR (400 MHz, CDCl₃) δ 0.14-0.25 (m, 9H, major&minor-4n), 2.22 (s, 3H, major-4n), 2.37 (s, 3H, major-4n), 2.43 (s, 6H, minor-4n), 6.74-7.34 (m, 9H, major&minor-4n); ¹³C NMR (100 MHz, CDCl₃) δ -1.67, 0.80, 21.3, 21.4, 21.5 (2 x C), 124.3, 124.4, 125.6, 126.2 (2 x C), 126.3 (2 x C), 126.36, 126.49, 127.1 (2 x C), 127.73, 127.77, 127.79, 127.8, 127.9, 128.4, 129.4, 130.5, 137.1, 137.3, 137.5, 137.7, 137.9, 138.0, 142.7, 144.9, 147.0; IR (neat, ν / cm⁻¹) 2925, 1716, 1605, 1272, 1175, 1102, 1020, 734, 708; HRMS (FAB+) Calcd for Formula: C₁₉H₂₄Si [M]⁺ 280.1647, Found 280.1641

(E)-Tributyl(1,2-diphenylvinyl)germane (4o).

Transparent oil (43.0 mg, 41%); ¹H NMR (400 MHz, CDCl₃) δ 0.73-0.97 (m, 15H), 1.21-1.40 (m, 12H), 6.64 (s, 1H), 6.92-7.01 (m, 4H), 7.03-7.12 (m, 3H), 7.15 (t, J = 7.2 Hz, 1H), 7.23-7.31 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 12.3, 13.7, 26.5, 27.2, 125.4, 126.7, 126.9, 127.9, 128.5, 129.3, 136.3, 137.4, 143.7, 147.0; IR (neat, ν / cm⁻¹) 3056, 3022, 2955, 2925,
Procedure for desilylation of silylindene 3b. A mixture of diphenylacetylene (1a, 89.1 mg, 0.500 mmol), triethoxysilane (2b, 41.1 mg, 0.250 mmol), [RhCl(cod)]2 (3.1 mg, 6.3 µmol), triphenylphosphine (9.9 mg, 38 µmol), and toluene (1.0 mL) was stirred at 150 °C for 24 h in a sealed tube. Then the solvent was removed in vacuo and the crude mixture was dissolved in dry DMF (1.0 mL). To the solution was added TBAF·3H2O (158 mg, 0.500 mmol) and the mixture was stirred at 100 °C for 17 h in a Schlecker tube. The reaction mixture was cooled to ambient temperature, dissolved in CH2Cl2 (10 mL), and was washed with phosphate buffered saline solution (3 x 10 mL). The combined organic layer was dried over Na2SO4, was filtered, and was evaporated in vacuo. The product was isolated by column chromatography on silica gel (hexane/EtOAc= 10/1) to give 1-benzyl-1,2-diphenyl-1H-indene (5a, 61.5 mg, 69% yield).

1-Benzyl-1,2-diphenyl-1H-indene (5a).
White solid (61.5 mg, 69%); mp 139-147 °C; 1H NMR (400 MHz, CDCl3) δ 3.68 (d, J = 12.8 Hz, 1H), 3.96 (d, J = 12.8 Hz, 1H), 6.27 (d, J = 7.2 Hz, 2H), 6.80 (dd, J = 7.6, 7.6 Hz, 2H), 6.93 (d, J = 7.2 Hz, 1H), 7.04 (s, 1H), 7.11-7.17 (m, 3H), 7.20-7.31 (m, 9H), 7.36 (d, J = 7.6 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 40.6, 62.1, 121.1, 123.1, 125.5, 125.9 (2C), 126.6, 126.7, 126.80, 126.81, 127.3, 128.4, 128.93, 128.97, 129.5, 135.1, 136.2, 142.7, 143.1, 151.4, 153.5; IR (neat, ν / cm⁻¹) 3061, 3030, 1600, 1495, 1456, 1443, 908, 757, 733, 697; HRMS (DART+) Calcd for C28H23 [M+H]+ 359.1800, Found 359.1803.

Procedure for deprotection and iodination of silylindene 3p. A mixture of silylindene (3p, 108 mg, 0.25 mmol) and MeOH (1.8 mL) was cooled to 0 °C. Then AgBF4 (97.0 mg, 0.500 mmol) was added, and the resulting mixture was stirred at 0 °C for 5 min in a sealed tube. Then I2 (127 mg, 0.500 mmol) was added and the mixture was stirred at 25 °C for 17 h. The reaction mixture was diluted with ether (10 mL) and was washed with aq. Na2S2O3 (3 x 10 mL). The combined organic layer was dried over Na2SO4 was filtered, and was evaporated in vacuo. The product was isolated by column chromatography on silica gel (hexane/Et2O= 99/1) and GPC purification to give 1-benzyl-3-iodo-1,2-diphenyl-1H-indene (5b, 62.3 mg, 51% yield).
1-Benzyl-3-iodo-1,2-diphenyl-1H-indene (5b).
White solid (62.3 mg, 51%); mp 134-137 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.41 (d, \(J = 13.3\) Hz, 1H), 3.86 (d, \(J = 13.3\) Hz, 1H), 6.44 (d, \(J = 7.2\) Hz, 2H), 6.84-7.09 (m, 6H), 7.15-7.37 (m, 11H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 40.0, 64.9, 96.5, 123.3, 123.4, 126.3, 126.77, 126.79, 127.0, 127.1, 127.3, 127.6, 128.1, 128.7, 129.5, 129.7, 135.7, 135.9, 141.3, 145.2, 150.4, 155.9; IR (neat, \(\nu / \text{cm}^{-1}\) ) 3061, 1716, 1698, 1684, 1558, 1541, 1507, 1489, 1457, 757, 697; HRMS (DART+) Calcd for C\(_{28}\)H\(_{22}\)I [M+H]\(^+\) 485.0766, Found 485.0758.

Procedure for deprotection and bromination of silylindene 3p.\(^6\) A mixture of silylindene (3p, 54.0 mg, 0.125 mmol), NBS (28.9 mg, 0.163 mmol), and NaBr (16.7 mg, 0.163 mmol) in MeOH (1.0 mL) was stirred at 25 °C for 24 h. Then the reaction mixture was evaporated in vacuo. The product was isolated by column chromatography on silica gel (hexane/EtOAc = 30/1) and GPC purification to give 1-benzyl-3-bromo-1,2-diphenyl-1H-indene (5c, 26.3 mg, 48% yield).

1-Benzyl-3-bromo-1,2-diphenyl-1H-indene (5c).
Yellow solid (26.3 mg, 48%); mp 121-124 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.47 (d, \(J = 12.6\) Hz, 1H), 3.90 (d, \(J = 12.6\) Hz, 1H), 6.37 (d, \(J = 7.2\) Hz, 2H), 6.89 (dd, \(J = 7.9, 7.9\) Hz, 2H), 7.01 (t, \(J = 7.4\) Hz, 1H), 7.04-7.17 (m, 3H), 7.21-7.35 (m, 11H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 39.9, 63.7, 119.7, 121.0, 123.2, 126.3, 126.5, 126.9, 127.0 (2C), 127.3, 127.8, 128.0, 128.9, 129.3, 129.7, 134.2, 135.7, 141.8, 142.7, 148.2, 150.4; IR (neat, \(\nu / \text{cm}^{-1}\) ) 3061, 3030, 1600, 1495, 1456, 1443, 908, 757, 733, 697; HRMS (DART+) Calcd for Formula: C\(_{28}\)H\(_{22}\)Br [M+H]\(^+\) 437.0905, Found 437.0890.
**Preparation of single crystal of 3a.** Single crystal of 3a was obtained as a transparent block by recrystallization from ethyl acetate/hexane.

![Fig. S1. X-ray crystal structure of 3a. Thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.](image)
KIE experiments.

Side-by-side reactions were performed (20, 30, 40, and 60 min) according to the typical procedure for a rhodium-catalysed synthesis of multi-substituted silylindenene using 1a or 1a-D_{10} (vide infra). The resulting mixtures were evaporated in vacuo. The yields of 3c and 3c-D_{20} were calculated from $^1$H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

**Fig. S2.** Rate comparison for the rhodium-catalysed synthesis of silylidenes using 1a (blue) and 1a-D_{10} (red).
References


