

Supplementary Information

Rhodium-Catalysed Synthesis of Multi-Substituted Silylindenanes 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. [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.¹

NMR spectra were recorded on JEOL ECX500 (500 MHz for ¹H NMR and 125 MHz for ¹³C NMR) and JEOL ECS400 (400 MHz for ¹H NMR, 100 MHz for ¹³C NMR, 376 MHz for ¹⁹F NMR, and 78 MHz for ²⁹Si NMR) spectrometers. Proton chemical shifts are reported relative to Me₄Si (CDCl₃) at δ 0.00 ppm or residual solvent peak (CDCl₃ at δ 7.26 ppm). Carbon chemical shifts are reported relative to CDCl₃ at δ 77.00 ppm. Fluorine chemical shifts are reported relative to TFA (CDCl₃) at δ -76.55 ppm as an external standard. Silicon chemical shifts are reported relative to Me₄Si (CDCl₃) at δ 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, CHCl₃).

Table 1. Investigation of several transition metal complexes and ligands^a

Entry	Catalyst	Ligand	Yield (%) ^b
1	MnBr(CO) ₅	none	0
2	Mn ₂ (CO) ₁₀	none	0
3	ReBr(CO) ₅	none	0
4	[ReBr(CO) ₃ (thf)] ₂	none	0
5	Re ₂ (CO) ₁₀	none	0
6	Fe(CO) ₅	none	0
7	Fe ₂ (CO) ₉	none	0
8	Fe ₃ (CO) ₁₂	none	0
9	[CpFe(CO) ₂] ₂	none	0
10	Ru ₃ (CO) ₁₂	none	0
11	[RhCl ₂ (<i>p</i> -cymene)] ₂	none	0
12	Co ₂ (CO) ₈	none	0
13	CoCl(PPh ₃) ₃	none	0
14	Rh ₄ (CO) ₁₂	none	0
15	RhCl(PPh ₃) ₃	none	46
16	[RhCl(cod)] ₂	PPh ₃	50 (47) ^c
17	[RhCl(cod)] ₂	PPh ₃	40 ^d
18	[RhCl(cod)] ₂	PPh ₃	39 ^e
19	[RhCl(cod)] ₂	PPh ₃	44 ^f
20	[RhCl(cod)] ₂	PPh ₃	42 ^g
21	[RhCl(cod)] ₂	PCy ₃	21
22	[RhCl(cod)] ₂	PM ₃	11
23	[RhCl(cod)] ₂	P(4-OMeC ₆ H ₄) ₃	30
24	[RhCl(cod)] ₂	P(4-CF ₃ C ₆ H ₄) ₃	49
25	[RhCl(cod)] ₂	DPPE	0
26	[RhCl(cod)] ₂	DPPF	0
27	[RhCl(cod)] ₂	(<i>R</i>)-BINAP	0
28	[RhCl(cod)] ₂	PPh ₃	47
29	[RhCl(ethylene)] ₂	PPh ₃	48
30	[RhCl(nbd)] ₂	PPh ₃	44
31	[Rh(OH)(cod)] ₂	PPh ₃	47
32	RhH(PPh ₃) ₄	PPh ₃	45
33	[Rh(cod)] ₂ OTf	PPh ₃	37
34	[Cp*RhCl ₂] ₂	none	0
35	Ir ₄ (CO) ₁₂	none	0
36	[IrCl(cod)] ₂	PPh ₃	0
37	[Ir(OMe)(cod)] ₂	DTBPY	0

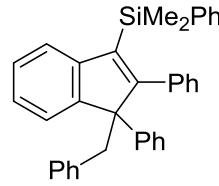
^a **1a** (2.0 equiv). ^b ¹H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard. ^c Isolated yield. ^d With MS 3A (40 mg/mmol). ^e With MS 4A (40 mg/mmol).

^f With MS 5A (40 mg/mmol). ^g With MS 13X (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 μ mol), triphenylphosphine (9.9 mg, 38 μ mol), 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-1*H*-inden-3-yl)trimethylsilane (**3a**, 57.6 mg, 47% yield).

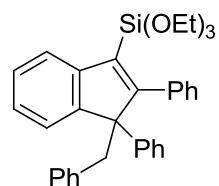
(1-Benzyl-1,2-diphenyl-1*H*-inden-3-yl)dimethyl(phenyl)silane (3a**).**

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.



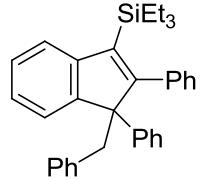
(1-Benzyl-1,2-diphenyl-1*H*-inden-3-yl)triethoxysilane (3b**).**

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 C₃₄H₃₇O₃Si [M+H]⁺ 521.2512, Found 521.2524.



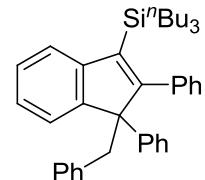
(1-Benzyl-1,2-diphenyl-1*H*-inden-3-yl)triethylsilane (3c).

Yellow oil (47.8 mg, 40%); ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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) δ -0.06; IR (neat, ν / cm^{-1}) 2952, 1456, 1264, 1002, 699; HRMS (DART+) Calcd for $\text{C}_{34}\text{H}_{37}\text{Si} [\text{M}+\text{H}]^+$ 473.2665, Found 473.2671.



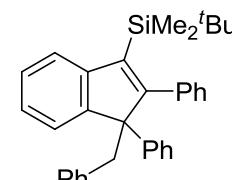
(1-Benzyl-1,2-diphenyl-1*H*-inden-3-yl)tributylsilane (3d).

Yellow oil (63.6 mg, 46%); ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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) δ -4.40; IR (neat, ν / cm^{-1}) 2955, 2923, 1456, 757, 699; HRMS (DART+) Calcd for $\text{C}_{40}\text{H}_{49}\text{Si} [\text{M}+\text{H}]^+$ 557.3604, Found 557.3593.



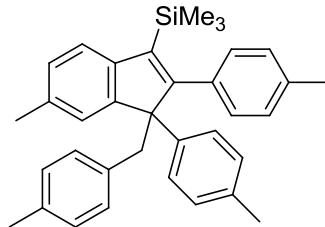
(1-Benzyl-1,2-diphenyl-1*H*-inden-3-yl)(*tert*-butyl)dimethylsilane (3e).

Yellow oil (39.1 mg, 33%); ^1H NMR (400 MHz, CDCl_3) δ -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) δ -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) δ -0.38; IR (neat, ν / cm^{-1}) 2954, 2927, 2855, 1462, 824, 701; HRMS (DART+) Calcd for $\text{C}_{34}\text{H}_{37}\text{Si} [\text{M}+\text{H}]^+$ 473.2665, Found 473.2677.



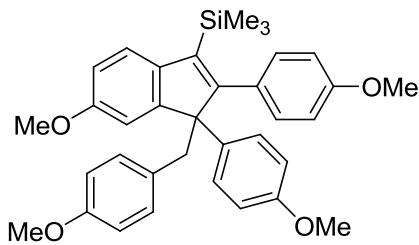
Trimethyl(6-methyl-1-(4-methylbenzyl)-1,2-di-p-tolyl-1*H*-inden-3-yl)silane (3f).

Yellow oil (36.4 mg, 30%); ^1H 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, ν / cm^{-1}) 2921, 1507, 1249, 839; HRMS (DART+) Calcd for $\text{C}_{35}\text{H}_{39}\text{Si} [\text{M}+\text{H}]^+$ 487.2821, Found 487.2814.



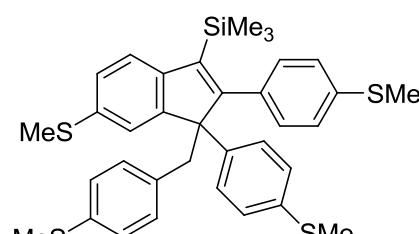
(6-Methoxy-1-(4-methoxybenzyl)-1,2-bis(4-methoxyphenyl)-1*H*-inden-3-yl)trimethylsilane (3g).

Yellow oil (60.1 mg, 44%); ^1H 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, ν / cm^{-1}) 2953, 2835, 1609, 1510, 1248, 1178, 1036, 836, 738; HRMS (DART+) Calcd for $\text{C}_{35}\text{H}_{39}\text{O}_4\text{Si} [\text{M}+\text{H}]^+$ 551.2618, Found 551.2637.



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

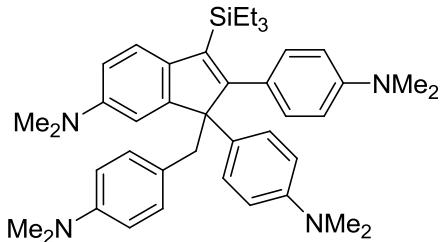
Gray solid (78.3 mg, 51%); mp 154-157 °C; ^1H NMR (400 MHz, CDCl_3) δ -0.03 (s, 9H), 2.36 (s, 3H), 2.38 (s, 3H), 2.47 (s x 2, 6H), 3.14 (d, $J = 13.3$ Hz, 1H), 3.67 (d, $J = 13.3$ Hz, 1H), 6.52 (d, $J = 6.5$ Hz, 2H), 6.58 (d, $J = 6.5$ Hz, 2H), 6.80 (s, 1H), 6.90 (d, $J = 5.8$ Hz, 2H), 7.00 (d, $J = 5.8$ Hz, 2H), 6.58 (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); ^{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, ν / cm^{-1}) 2953, 2835, 1609, 1510, 1248, 1178, 1036, 836, 738; HRMS (DART+) Calcd for $\text{C}_{35}\text{H}_{39}\text{S}_2\text{Si} [\text{M}+\text{H}]^+$ 571.2800, Found 571.2790.



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); ^{13}C NMR (100 MHz, CDCl_3) 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; ^{29}Si NMR (78 MHz, CDCl_3) δ -8.96; IR (neat, ν / cm^{-1}) 2916, 1558, 1489, 1457, 830; HRMS (DART+) Calcd for $\text{C}_{35}\text{H}_{39}\text{S}_4\text{Si}$ [M+H] $^+$ 615.1704, Found 615.1709.

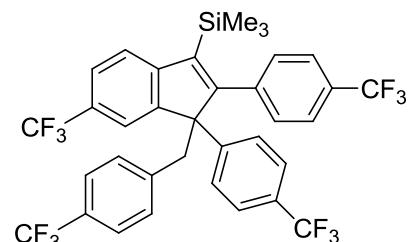
4,4'-(6-(Dimethylamino)-1-(4-(dimethylamino)benzyl)-3-(triethylsilyl)-1*H*-indene-1,2-diyl)bis(*N,N*-dimethylaniline) (3i).

Brownish yellow oil (20.3 mg, 25%); ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (100 MHz, CDCl_3) δ 4.20, 7.59, 39.7, 40.6, 40.8, 41.2, 41.4, 65.1, 110.08, 110.11, 110.9, 111.1, 112.4, 112.5, 122.1, 126.8, 127.05, 127.07, 128.2, 130.7, 131.1, 134.2, 148.1, 148.8, 149.1, 149.5, 154.4, 164.8; ^{29}Si NMR (78 MHz, CDCl_3) δ -0.52; IR (neat, ν / cm^{-1}) 2950, 2871, 1611, 1519, 1349, 948, 821, 730; HRMS (DART+) Calcd for $\text{C}_{42}\text{H}_{57}\text{N}_4\text{Si}$ [M+H] $^+$ 645.4352, Found 645.4374.



Trimethyl(6-(trifluoromethyl)-1-(4-(trifluoromethyl)benzyl)-1,2-bis(4-(trifluoromethyl)phenyl)-1*H*-inden-3-yl)silane (3j).

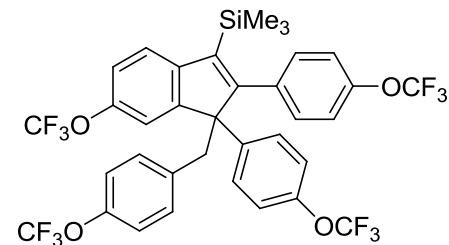
Yellow oil (63.5 mg, 36%); ^1H NMR (400 MHz, CDCl_3) δ -0.01 (s, 9H), 3.39 (d, J = 13.7 Hz, 1H), 3.85 (d, J = 13.7 Hz, 1H), 6.67 (d, J = 7.6 Hz, 2H), 6.77 (d, J = 7.6 Hz, 2H), 7.15 (s, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.52-7.63 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) 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



(q, $J = 1.4$ Hz), 151.20, 150.29 (q, $J = 1.4$ Hz), 164.4; ^{19}F NMR (376 MHz, CDCl_3) δ -63.6 (2 x CF_3), -63.4, -62.7; ^{29}Si NMR (78 MHz, CDCl_3) δ -8.14; IR (neat, ν / cm^{-1}) 2957, 1617, 1409, 1323, 1166, 1121, 1069, 1017, 841, 741; HRMS (DART+) Calcd for $\text{C}_{35}\text{H}_{27}\text{F}_{12}\text{Si} [\text{M}+\text{H}]^+$ 703.1690, Found 703.1681.

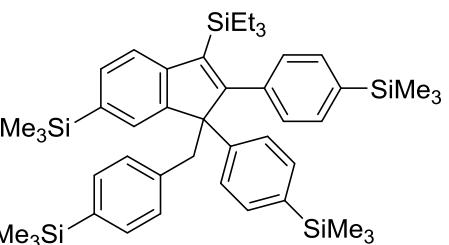
Trimethyl(6-(trifluoromethoxy)-1-(4-(trifluoromethoxy)benzyl)-1*H*-inden-3-yl)silane (3k**).**

Pale yellow oil (99.3 mg, 52%); ^1H NMR (400 MHz, CDCl_3) δ -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), 6.81-6.94 (m, 3H), 7.03-7.20 (m, 7H), 7.40 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -0.05, 39.4, 65.6, 117.7, 119.85, 119.92, 120.3, 120.40 (q, $J = 257$ Hz), 120.43 (q, $J = 257$ Hz), 120.5 (q, $J = 257$ Hz), 120.6 (q, $J = 257$ Hz), 120.9, 123.5, 128.6, 131.0, 131.2, 134.8, 135.6, 138.9, 140.6, 146.5, 147.0 (q, $J = 1.9$ Hz), 148.0 (q, $J = 1.9$ Hz), 148.4 (q, $J = 1.9$ Hz), 149.1 (q, $J = 1.9$ Hz), 152.7, 163.3; ^{19}F NMR (376 MHz, CDCl_3) δ -58.8, -58.9 (2 x CF_3), -59.0; ^{29}Si NMR (78 MHz, CDCl_3) δ -8.46; IR (neat, ν / cm^{-1}) 2957, 1508, 1471, 1258, 1218, 1166, 1019, 842; HRMS (DART+) Calcd for $\text{C}_{35}\text{H}_{27}\text{F}_{12}\text{O}_4\text{Si} [\text{M}+\text{H}]^+$ 767.1487, Found 767.1470.



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

Yellow oil (36.7 mg, 39%); ^1H NMR (400 MHz, CDCl_3) δ 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) δ -1.14, -1.07, -1.02, -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) δ -4.14, -0.46, -0.11 (3 x Si); IR (neat, ν / cm^{-1})

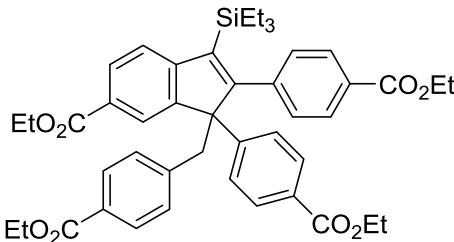


2954, 1596, 1457, 1248, 1111, 838, 735; HRMS (DART+) Calcd for $C_{46}H_{69}Si_5$ [M+H]⁺ 761.4246, Found 761.4214.

Diethyl

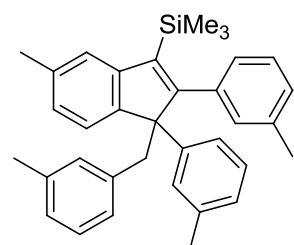
4,4'-(6-(ethoxycarbonyl)-1-(4-(ethoxycarbonyl)benzyl)-3-(triethylsilyl)-1*H*-indene-1,2-diyl)dibenzoate (3m).

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), 7.94 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.1 Hz, 1H); 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 0.57; IR (neat, ν / cm⁻¹) 2955, 1715, 1607, 1274, 1105, 1021, 733; HRMS (DART+) Calcd for C₄₆H₅₃O₈Si [M+H]⁺ 761.3510, Found 761.3509.



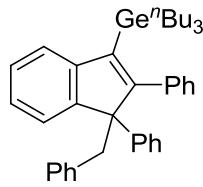
Trimethyl(5-methyl-1-(3-methylbenzyl)-1,2-di-*m*-tolyl-1*H*-inden-3-yl)silane (3n).

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-1*H*-inden-3-yl)tributylgermane (3o**).**

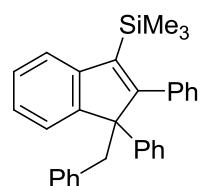
Yellow oil (32.0 mg, 21%); ^1H NMR (400 MHz, CDCl_3) δ 0.53-0.69 (m, 6H), 0.75 (t, $J = 7.2$ Hz, 9H), 0.97-1.19 (m, 12H), 3.32 (d, $J = 13.3$ Hz, 1H), 3.77 (d, $J = 13.3$ Hz, 1H), 6.50 (d, $J = 6.7$ Hz, 2H), 6.58 (d, $J = 7.6$ Hz, 2H), 6.92 (dd, $J = 7.6, 7.6$ Hz, 2H), 7.01 (t, $J = 7.6$ Hz, 1H), 7.05-7.13 (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) δ 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, ν / cm^{-1}) 3061, 3029, 2955, 2925, 1600, 1456, 1079, 1030, 757, 699; HRMS (DART+) Calcd for $\text{C}_{40}\text{H}_{49}\text{Ge} [\text{M}+\text{H}]^+$ 603.3046, Found 603.3034.



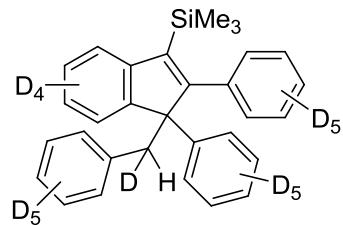
Procedure for trimethylsilylation of silyindene **3b.** A mixture of diphenylacetylene (**1a**, 89.1 mg, 0.500 mmol), triethoxysilane (**2b**, 41.1 mg, 0.250 mmol), $[\text{RhCl}(\text{cod})]_2$ (3.1 mg, 6.3 μmol), triphenylphosphine (9.9 mg, 38 μmol), and toluene (1.0 mL) was stirred at 150 °C for 24 h in a sealed tube. Then, the reaction mixture was cooled to ambient temperature, followed by addition of MeLi (1.13 M in Et_2O , 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_2SO_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-1*H*-inden-3-yl)trimethylsilane (**3p**, 77.5 mg, 72% yield).

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

Yellow oil (77.5 mg, 72%); ^1H NMR (500 MHz, CDCl_3) δ 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) δ 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) δ -9.02; IR (neat, ν / cm^{-1}) 3060, 2952, 1496, 1455, 1250, 837, 698; HRMS (DART+) Calcd for $\text{C}_{31}\text{H}_{31}\text{Si} [\text{M}+\text{H}]^+$ 431.2195, Found 431.2181.

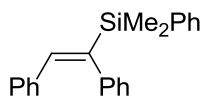


3p-D₂₀. Yellow oil (79.4 mg, 70%); ¹H NMR (400 MHz, CDCl₃) δ -0.02 (s, 9H), 3.35 (s, 0.11H), 3.78 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 0.18, 39.5 (t, *J* = 19.1 Hz), 65.5, 122.0 (t, *J* = 23.5 Hz), 124.0 (t, *J* = 23.2 Hz), 124.2 (t, *J* = 23.0 Hz), 125.5 (t, *J* = 24.0 Hz), 125.74 (t, *J* = 22.3 Hz), 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; ²⁹Si NMR (78 MHz, CDCl₃) δ -9.02; IR (neat, ν / cm⁻¹) 2953, 2898, 2277, 1377, 1250, 838; HRMS (DART+) Calcd for C₃₁H₁₁D₂₀Si [M+H]⁺ 451.3450, Found 451.3467.



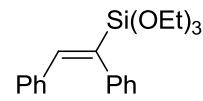
(E)-(1,2-Diphenylvinyl)dimethyl(phenyl)silane (**4a**).

Pale yellow oil (14.6 mg, 19%); ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (100 MHz, CDCl₃) δ -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, ν / cm⁻¹) 3066, 2956, 1490, 1248, 1113, 954, 832, 700; HRMS (FAB+) Calcd for Formula: C₂₂H₂₂Si [M]⁺ 314.1491, Found 314.1489.



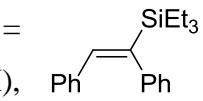
(E)-(1,2-Diphenylvinyl)triethoxysilane (**4b**).²

Yellow oil (6.6 mg, 8%); ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (100 MHz, CDCl₃) δ 18.1, 58.8, 126.1, 127.5, 127.8, 128.3, 128.5, 129.9, 136.9 (2C), 140.7, 142.4.



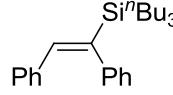
(E)-(1,2-Diphenylvinyl)triethylsilane (**4c**).³

Yellow oil (28.0 mg, 38%); ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (100 MHz, CDCl₃) δ 2.75, 7.30, 125.5, 126.9, 127.3, 127.9, 128.6, 129.5, 137.4, 138.7, 143.2, 144.1.



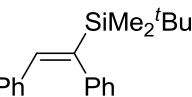
(E)-Tributyl(1,2-diphenylvinyl)silane (4d**).**

Transparent oil (47.8 mg, 50%); ^1H 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), 7.06-7.16 (m, 3H), 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: $\text{C}_{26}\text{H}_{38}\text{Si} [\text{M}]^+$ 378.2743, Found 378.2759.



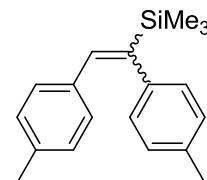
(E)-*tert*-Butyl(1,2-diphenylvinyl)dimethylsilane (4e**).**

Transparent oil (21.9 mg, 30%); ^1H NMR (400 MHz, CDCl_3) δ 0.16 (s, 6H), 0.87 (s, 9H), 6.85 (s, 1H), 6.88-6.96 (m, 2H), 7.02-7.11 (m, 5H), 7.18 (t, $J = 7.2$ Hz, 1H), 7.23-7.30 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -5.24, 17.9, 27.1, 125.6, 126.9, 127.8, 127.9, 128.5, 129.5, 137.4, 139.8, 143.4, 145.0; IR (neat, ν / cm^{-1}) 2954, 2926, 2855, 1491, 1470, 1250, 824; HRMS (FAB+) Calcd for Formula: $\text{C}_{20}\text{H}_{27}\text{Si} [\text{M}]^+$ 295.1882, Found 295.1887.



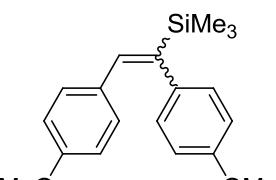
(1,2-Di-*p*-tolylvinyl)trimethylsilane (4f**).**

White solid (17.0 mg, 24%); mp 69-74 °C; (major-**4f**:minor-**4f** = 2.3:1), ^1H NMR (400 MHz, CDCl_3) δ 0.08-0.14 (m, 9H, 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 (2 x C), 21.23, 127.1, 127.2, 128.49, 128.52, 128.59 (2 x C), 128.63, 129.30 (2 x C), 129.34 (2 x 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: $\text{C}_{19}\text{H}_{25}\text{Si} [\text{M}+\text{H}]^+$ 281.1726, Found 281.1713.



(1,2-Bis(4-methoxyphenyl)vinyl)trimethylsilane (4g**).**

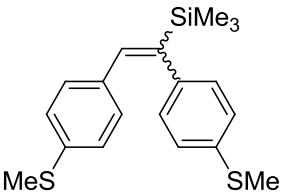
Yellow oil (20.0 mg, 26%); (major-**4g**:minor-**4g** = 1.9:1), ^1H NMR (400 MHz, CDCl_3) δ 0.12 (s, 9H, major&minor-**4g**), 3.73 (s, 3H, major-**4g**), 3.82 (s, 3H, minor-**4g**), 3.83 (s, 3H for major-**4g**, 3H for minor-**4g**), 6.64 (d, $J = 8.5$ Hz, 2H, major-**4g**), 6.72 (s, 1H, major-**4g**),



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: $\text{C}_{19}\text{H}_{24}\text{O}_2\text{Si} [\text{M}]^+$ 312.1546, Found 312.1538.

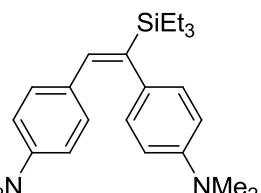
(1,2-Bis(4-(methylthio)phenyl)vinyl)trimethylsilane (**4h**).

White solid (21.9 mg, 25%); mp 65-77 °C; (major-**4h**:minor-**4h** = 2.3:1); ^1H 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**), 6.88-7.32 (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: $\text{C}_{19}\text{H}_{24}\text{S}_2\text{Si} [\text{M}]^+$ 344.1089, Found 344.1101.



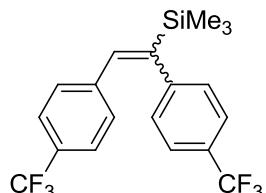
(E)-4,4'-(1-(Triethylsilyl)ethene-1,2-diyl)bis(N,N-dimethylaniline) (**4i**).

Yellow oil (45.1 mg, 47%); ^1H 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**).

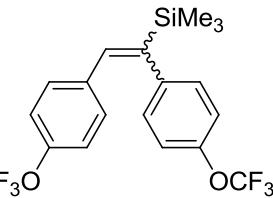
Transparent oil (17.4 mg, 18%); (major-**4j**:minor-**4j** = 2.6:1); ^1H NMR (400 MHz, CDCl_3) δ 0.21 (s, 9H, major&minor-**4j**), 6.87 (s, 1H, major-**4j**), 7.02 (d, J = 8.5 Hz, 2H, major-**4j**), 7.09 (d, J = 8.1 Hz, 2H, major-**4j**), 7.25 (s, 1H, minor-**4j**), 7.29 (d, J = 8.1 Hz, 2H, minor-**4j**), 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, J = 7.6 Hz, 2H, minor-**4j**).



Hz, 2H, minor-**4j**); ^{13}C NMR (100 MHz, CDCl_3) δ -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) δ -63.5, -63.3, -63.1 (2 x CF_3); IR (neat, ν / cm^{-1}) 2925, 2854, 1541, 1507, 1323, 1128, 1067, 842.

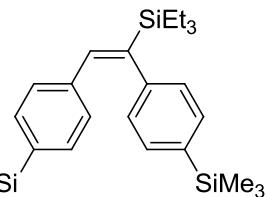
(1,2-Bis(4-(trifluoromethoxy)phenyl)vinyl)trimethylsilane (**4k**).

Transparent oil (27.9 mg, 27%); (major-**4k**:minor-**4k** = 2.3:1), ^1H NMR (400 MHz, CDCl_3) δ 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) δ -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) δ -58.8 (2 x CF_3), -58.7 (2 x CF_3); IR (neat, ν / cm^{-1}) 2958, 1506, 1259, 1221, 1165, 840; HRMS (FAB+) Calcd for Formula: $\text{C}_{19}\text{H}_{18}\text{F}_6\text{O}_2\text{Si}$ [M] $^+$ 420.0980, Found 420.0981.



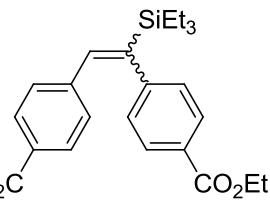
(E)-(1,2-Bis(4-(trimethylsilyl)phenyl)vinyl)triethylsilane (**4l**).

Transparent oil (25.2 mg, 23%); ^1H NMR (400 MHz, CDCl_3) δ 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) δ -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, ν / cm^{-1}) 2954, 1595, 1248, 1107, 839, 719; HRMS (FAB+) Calcd for Formula: $\text{C}_{26}\text{H}_{43}\text{Si}_3$ [M] $^+$ 439.2673, Found 439.2687.



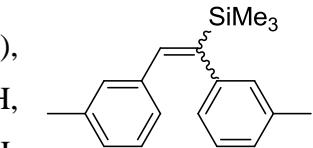
Diethyl 4,4'-(1-(triethylsilyl)ethene-1,2-diyl)dibenzoate (4m).

Transparent oil (41.4 mg, 38%); (major-**4m**:minor-**4m** = 2.9:1), major-**4m**: ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (100 MHz, CDCl_3) 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, 12.2, 166.2, 166.6; IR (neat, ν / cm^{-1}) 2954, 1716, 1605, 1272, 1175, 1102, 1020, 734, 708; HRMS (FAB+) Calcd for Formula: $\text{C}_{26}\text{H}_{35}\text{O}_4\text{Si} [\text{M}]^+$ 439.2305, Found 420.0981.



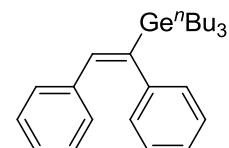
(1,2-Di-*m*-tolylvinyl)trimethylsilane (4n).

Transparent oil (16.5 mg, 24%); (major-**4n**:minor-**4n**=3.1:1), ^1H NMR (400 MHz, CDCl_3) 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**); ^{13}C NMR (100 MHz, CDCl_3) 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, 1601, 1457, 1247, 837; HRMS (FAB+) Calcd for Formula: $\text{C}_{19}\text{H}_{24}\text{Si} [\text{M}]^+$ 280.1647, Found 280.1641



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

Transparent oil (43.0 mg, 41%); ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (100 MHz, CDCl_3) 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,

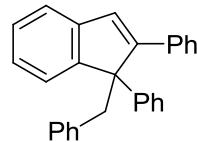


1490, 1457, 1376, 1079, 754, 695; HRMS (FAB+) Calcd for Formula: C₂₆H₃₉Ge [M+H]⁺ 425.2264, Found 425.2281.

Procedure for desilylation of silylindene 3b.⁴ 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 Schleck 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-1*H*-indene (**5a**, 61.5 mg, 69% yield).

1-Benzyl-1,2-diphenyl-1*H*-indene (**5a**).

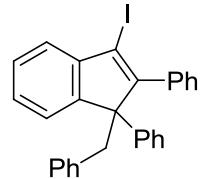
White solid (61.5 mg, 69%); mp 139-147 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.68 (d, *J* = 12.8 Hz, 1H), 3.96 (d, *J* = 12.8 Hz, 1H), 6.27 (d, *J* = 7.2 Hz, 2H), 6.80 (dd, *J* = 7.6, 7.6 Hz, 2H), 6.93 (d, *J* = 7.2 Hz, 1H), 7.04 (s, 1H), 7.11-7.17 (m, 3H), 7.20-7.31 (m, 9H), 7.36 (d, *J* = 7.6 Hz, 2H); ¹³C 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.⁵ 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-1*H*-indene (**5b**, 62.3 mg, 51% yield).

1-Benzyl-3-iodo-1,2-diphenyl-1*H*-indene (5b**).**

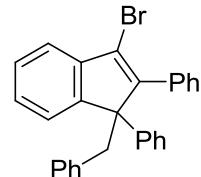
White solid (62.3 mg, 51%); mp 134-137 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.41 (d, *J* = 13.3 Hz, 1H), 3.86 (d, *J* = 13.3 Hz, 1H), 6.44 (d, *J* = 7.2 Hz, 2H), 6.84-7.09 (m, 6H), 7.15-7.37 (m, 11H); ¹³C NMR (100 MHz, CDCl₃) δ 40.0, 64.9, 96.5, 123.3, 123.4, 126.3, 126.77, 126.79, 127.0, 127.1, 127.3, 127.6, 128.1, 128.7, 129.5, 129.7, 135.7, 135.9, 141.3, 145.2, 150.4, 155.9; IR (neat, ν / cm⁻¹) 3649, 3061, 1716, 1698, 1684, 1558, 1541, 1507, 1489, 1457, 757, 697; HRMS (DART+) Calcd for C₂₈H₂₂I [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-1*H*-indene (**5c**, 26.3 mg, 48% yield).

1-Benzyl-3-bromo-1,2-diphenyl-1*H*-indene (5c**).**

Yellow solid (26.3 mg, 48%); mp 121-124 °C; ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (100 MHz, CDCl₃) δ 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, ν / cm⁻¹) 3061, 3030, 1600, 1495, 1456, 1443, 908, 757, 733, 697; HRMS (DART+) Calcd for Formula: C₂₈H₂₂Br [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.

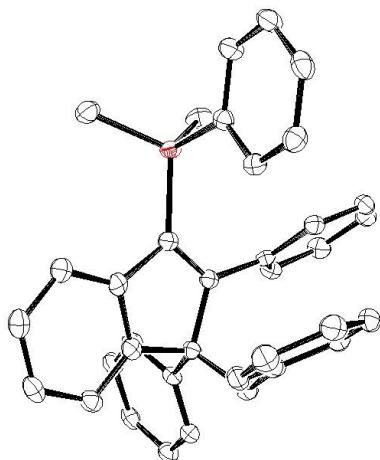


Fig. S1. X-ray crystal structure of **3a**. Thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

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 silylindene using **1a** or **1a-D₁₀** (vide infra). The resulting mixtures were evaporated in vacuo. The yields of **3c** and **3c-D₂₀** were calculated from ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

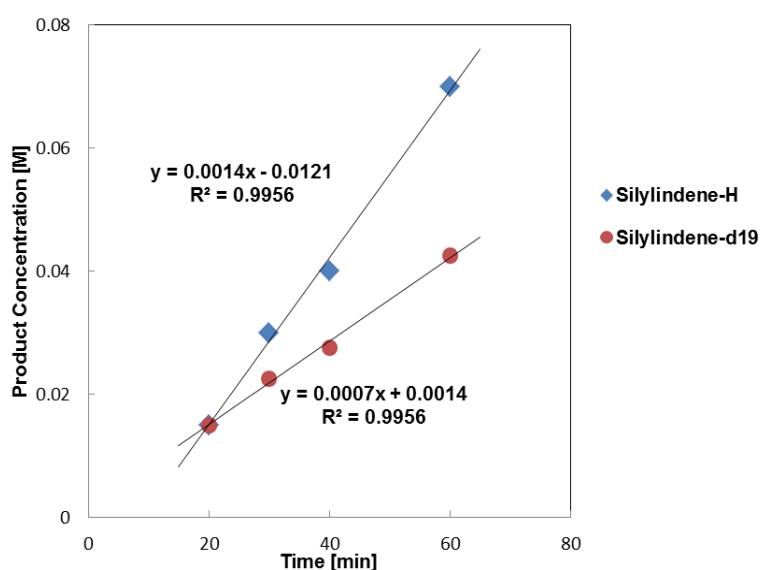
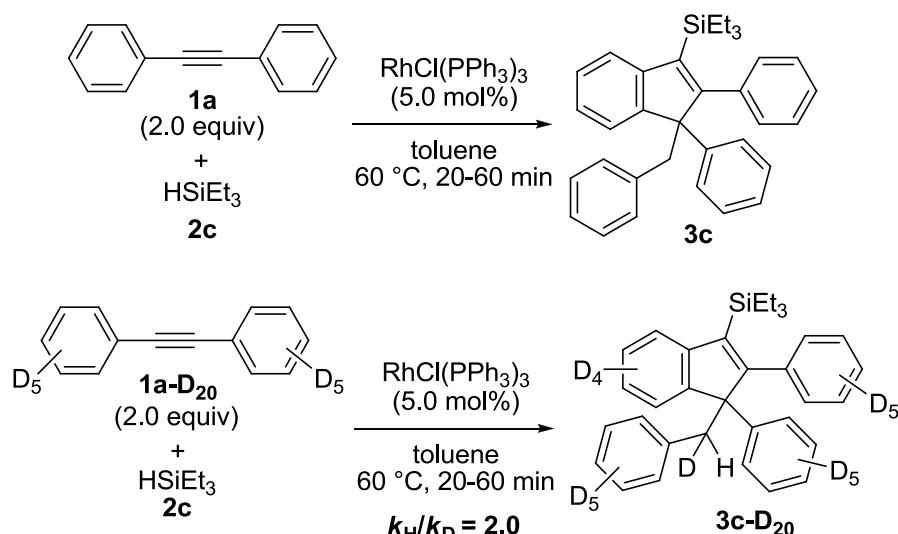


Fig. S2. Rate comparison for the rhodium-catalysed synthesis of silylindenes using **1a** (blue) and **1a-D₁₀** (red).

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