Supporting Information for:

Site-selective Iodine-Magnesium Exchange Reaction of 1,4-Diiodo-1,3-alkadienes by Organomagnesium Ate Complex, and Its Application to Synthesis of Polysubstituted Styrenes and Phenols.

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General. ^1H and ^{13}C NMR spectra were taken on a Varian Gemini-300 spectrometer at 300 and 75 MHz, respectively. CDCl_3 was used as the solvent. Chemical shifts are reported in parts per million shift (δ value) from Me_4Si (δ 0 ppm for ^1H) or based on the middle peak of the solvent (CDCl_3) (δ 77.00 ppm for ^{13}C NMR) as an internal standard. Signal patterns are indicated as br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (J) are given in hertz. Infrared (IR) spectra were recorded on a JASCO A-230 FT/IR spectrometer and are reported in wave numbers (cm^{-1}). Elemental analyses were performed on an Elementar Vario-EL. All reactions were carried out under an argon atmosphere, using flame-dried glassware and were monitored by TLC (Merck, Kieselgel 60 F254); visualization was done with UV light (254 nm) / KMnO_4 .

Material. Isopropylmagnesium bromide was prepared in THF as 0.7-1.0 M solution from isopropyl bromide and magnesium turnings by the usual procedure, titrated and stored under an argon atmosphere. Dry solvents (THF, ethyl ether, CH_2Cl_2 , toluene) and butyllithium in hexane as 1.56-1.60 M solution were purchased from Kanto Chemicals Co. (Japan). Chemicals were purified or dried in a standard manner, if necessary.

Preparation of Lithium dibutylisopropylmagnesate reagent ($i\text{PrBu}_2\text{MgLi}$).¹ To a solution of isopropylmagnesium bromide (1.16 ml, 0.860 M solution in THF, 1.00 mmol) in THF (1.06 ml) was added butyllithium (1.28 ml, 1.56 M solution in hexane,

2.00 mmol) at 0 °C, and the mixture was stirred for 10 min. This reagent was used for the next reaction immediately.

Typical Procedure for the Site-selective Iodine-Magnesium Exchange Reaction of 1, 4-Diiodo-1, 3-alkadienes 1. (1Z, 3E)-2-Hexyl-1-iodo-1-(trimethylsilyl)-1, 3-decadiene (2a).

To a solution of **1a** (0.109 g, 0.200 mmol) in THF (1.00 mL) was added a *i*PrBu₂MgLi (0.700 mL, 0.285 M solution, 0.200 mmol) at –78 °C, and the mixture was stirred for 1 hr at the same temperature. Then the reaction was terminated by the addition of saturated aqueous NH₄Cl and resulting mixture was extracted with ether. The extracts were washed with brine and dried over MgSO₄. Evaporation *in vacuo* afforded a crude oil, which was purified by silica gel column chromatography (hexane) to afford the title compounds **2a** (0.0698 g) in 83 % yield. ¹H NMR δ 0.32 (s, 9H, -Si(CH₃)₃), 0.85-0.92 (m, 6H, -(CH₂)₅CH₃), 1.20-1.50 (m, 16H, alkyl-H), 2.17 (dt, *J* = 6.9, 7.2 Hz, 2H, allylic-H), 2.42-2.49 (m, 2H, allylic-H), 5.86 (dt, *J* = 15.6, 6.9 Hz, 1H, -CH=CH-Hex), 6.54 (d, *J* = 15.6 Hz, 1H, -CH=CH-Hex); ¹³C NMR δ 2.09, 13.90, 13.94, 22.49, 22.51, 28.79, 29.02, 29.30, 30.45, 31.55, 31.63, 32.81, 33.38, 111.09, 135.88, 137.52, 153.82; IR (neat) 2926, 2855, 1629, 1534, 1466, 1378, 1249, 964, 841 cm⁻¹. Anal. Calcd for C₁₉H₃₇ISI: C, 54.27 ; H, 8.87. Found : C, 54.40 ; H, 8.85.

(1Z, 3E)-1, 4-Bis(trimethylsilyl)-2-hexyl-1-iodo-1, 3-butadiene (2b).

¹H NMR δ 0.14 (s, 9H, -Si(CH₃)₃), 0.33 (s, 9H, -Si(CH₃)₃), 0.84-0.94 (m, 3H, -CH₃), 1.20-1.44 (m, 8H, alkyl-H), 2.44-2.52 (m, 2H, allylic-H), 5.99 (d, *J* = 18.9 Hz, 1H, -CH=CHTMS), 6.97 (d, *J* = 18.9 Hz, 1H, -CH=CHTMS); ¹³C NMR δ 2.00, 2.22, 14.14, 22.66, 29.46, 30.44, 31.66, 33.05, 114.62, 133.98, 150.65, 153.96; IR (neat) 2955, 2862,

1529, 1466, 1405, 1378, 1248, 1195, 985, 839, 759, 693 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{33}\text{ISi}_2$: C, 47.04 ; H, 8.14. Found : C, 46.85 ; H, 8.03.

(1Z, 3E)-4-Cyclohexyl-2-hexyl-1-iodo-1-(trimethylsilyl)-1, 3-butadiene (2c).

^1H NMR δ 0.31 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 0.89 (t, $J = 6.9$ Hz, 3H, $-\text{CH}_3$), 1.10-1.80 (m, 18H, alkyl-H), 2.05-2.20 (m, 1H, $=\text{CHCH}_2$), 2.41-2.48 (m, 2H, allylic-H), 5.78 (dd, $J = 7.2$, 15.9 Hz, 1H, $-\text{CH}=\text{CH}-c\text{-Hex}$), 6.50 (dd, $J = 1.2$, 15.9 Hz, 1H, $-\text{CH}=\text{CH}-c\text{-Hex}$); ^{13}C NMR δ 2.08, 13.90, 22.46, 22.51, 25.83, 25.94, 26.03, 29.27, 30.40, 31.52, 32.63, 33.26, 41.03, 111.49, 135.22, 141.31, 153.92; IR (neat) 2926, 2854, 1628, 1534, 1448, 1249, 965, 840, 759, 686 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{35}\text{ISi}$: C, 54.53; H, 8.43. Found: C, 54.30; H, 8.25.

(E)-1-Benzoyloxy-8-chloro-5-[(Z)-iodo(trimethylsilyl)methylene]-3-octene (2d).

^1H NMR δ 0.34 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 1.84-1.95 (m, 2H, $-\text{CH}_2\text{CH}_2\text{Cl}$), 2.45-2.54 (m, 2H, $-\text{CH}=\text{CHCH}_2$), 2.61-2.68 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 3.53 (t, $J = 6.6$ Hz, 2H, $-\text{CH}_2\text{Cl}$), 3.59 (t, $J = 6.6$ Hz, 2H, $-\text{CH}_2\text{OBn}$), 4.54 (s, 2H, $-\text{OCH}_2\text{Ph}$), 5.95 (dt, $J = 15.9$, 6.9 Hz, 1H, $-\text{CH}=\text{CHCH}_2$), 6.64 (d, $J = 15.9$ Hz, 1H, $-\text{CH}=\text{CHCH}_2$), 7.20-7.38 (m, 5H, Ph); ^{13}C NMR δ 2.06, 30.45, 32.64, 33.21, 44.50, 69.44, 72.95, 113.04, 127.64, 127.75, 128.43, 132.27, 138.39, 138.81, 151.63; IR (neat) 3425, 2953, 2854, 1630, 1534, 1454, 1362, 1249, 1115, 967, 841, 736, 697 cm^{-1} . Anal. Calcd. for $\text{C}_{19}\text{H}_{28}\text{ClIOSi}$: C, 49.30 ; H, 6.10. Found: C, 49.64 ; H, 5.73.

(4Z, 6E)-4-Iodo-5-propyl-4, 6-decadiene (2e).

^1H NMR δ 0.89-0.96 (m, 6H, $-\text{CH}_3 \times 2$), 0.93 (t, $J = 7.2$ Hz, 3H, $-\text{CH}_3$), 1.35-1.49 (m, 4H, $-\text{CH}_2\text{CH}_3 \times 2$), 1.52-1.66 (m, 2H, $-\text{CH}_2\text{CH}_3$), 2.13 (ddt, $J = 1.5, 6.9, 6.9$ Hz, 2H, allylic-H), 2.28-2.36 (m, 2H, allylic-H), 2.62 (t, $J = 7.5$ Hz, 2H, allylic-H), 5.74 (dt, $J = 15.6, 6.9$ Hz, 1H, $-\text{CH}=\text{CHC}_3\text{H}_7$), 6.34 (dt, $J = 15.6, 1.5$ Hz, 1H, $-\text{CH}=\text{CHC}_3\text{H}_7$); ^{13}C NMR δ 13.01, 13.62, 14.04, 22.42, 22.52, 23.06, 31.15, 35.03, 43.80, 108.50, 133.50, 136.51, 140.20; IR (neat) 2959, 2870, 1636, 1577, 1463, 1378, 1102, 962, 889, 746 cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_{23}\text{I}$: C, 50.99 ; H, 7.57. Found: C, 50.89 ; H, 7.44.

(Z)-2-[(E)-2-Cyclohexylethenyl]-1-iodo-1-cyclododecene (2f)

^1H NMR δ 1.06-1.85 (m, 26H, alkyl-H), 2.02-2.15 (m, 1H, $=\text{CH}-\text{CH}_2$), 2.45 (t, $J = 7.2$ Hz, 2H, allyl-H), 2.68 (t, $J = 7.2$ Hz, 2H, allyl-H), 5.69 (dd, $J = 6.6, 15.9$ Hz, 1H, $-\text{CH}=\text{CH}(\text{c-Hex})$), 6.32 (d, $J = 15.9$ Hz, 1H, $-\text{CH}=\text{CH}(\text{c-Hex})$); ^{13}C NMR δ 22.95, 24.63, 25.28, 25.35, 25.73, 26.06 ($\times 2$), 26.23, 26.61, 27.13, 28.01, 32.97 ($\times 3$), 38.68, 41.29, 110.57, 133.99, 139.64, 140.03; IR (neat) 2923, 2848, 1636, 1570, 1468, 1348, 1247, 1091, 1028, 963, 907, 734 cm^{-1} . Anal. Calcd. for $\text{C}_{20}\text{H}_{33}\text{I}$: C, 60.00 ; H, 8.31. Found: C, 59.86 ; H, 8.31.

Typical Procedure for the Site-selective Iodine-Magnesium Exchange of 1, 4-Diiodo-1, 3-alkadienes 1 and the Following Reaction with Allyl bromide. (1Z, 3Z)-2-Hexyl-1-iodo-4-(2-propenyl)-1-(trimethylsilyl)-1, 3-decadiene (4a).

To a solution of **1a** (0.109 g, 0.200 mmol) in THF (1.00 mL) was added a *i*PrBu₂MgLi (0.700 mL, 0.285 M solution, 0.200 mmol) at -78°C . After the reaction mixture was stirred for 1 hr at the same temperature, CuCN•2LiCl² (0.120 mL, 0.500 M solution in THF, 0.0600 mmol) and allyl bromide (0.0610 mL, 0.700 mmol) were sequentially added, and warmed up to -20°C . After the resulting mixture was stirred for 14 hr at -20°C , the reaction was terminated by the addition of saturated aqueous NH₄Cl and the resulting mixture was extracted with ether. The extracts were washed with brine and dried over MgSO₄. Evaporation *in vacuo* afforded a crude oil, which was purified by silica gel column chromatography (hexane) to afford the title compounds **4a** (0.0765 g) in 83 % yield. ¹H NMR δ 0.31 (s, 9H, -Si(CH₃)₃), 0.84-0.94 (m, 6H, -CH₃), 1.20-1.53 (m, 16H, alkyl-H), 2.07 (t, *J* = 7.8 Hz, 2H, allylic-H), 2.29-2.37 (m, 2H, allylic-H), 2.72 (d, *J* = 6.6 Hz, 2H, bis-allylic-H), 4.99-5.08 (m, 2H, -CH=CH₂), 5.63 (s, 1H, -CH=C(allyl)-), 5.78 (ddt, *J* = 10.1, 17.0, 6.6 Hz, 1H, -CH=CH₂); ¹³C NMR δ 1.92, 13.90, 14.01, 22.46, 22.59, 27.53, 29.04, 29.19, 29.22, 31.58, 31.71, 35.11, 36.11, 37.78, 109.07, 116.13, 133.27, 136.17, 138.14, 158.90; IR (neat) 2928, 2862, 1636, 1570, 1466, 1249, 993, 840, 759, 687 cm⁻¹. Anal. Calcd. for C₂₂H₄₁ISi: C, 57.37 ; H, 8.97. Found: C, 57.65 ; H, 8.80.

Typical Procedure for the Site-selective Iodine-Magnesium Exchange of 1, 4-Diiodo-1, 3-alkadienes 1 and the Following Reaction with Aldehydes. (Z)-2-Hexyl-4-[(Z)-iodo(trimethylsilyl)methylene]-1-phenyl-2-decen-1-ol (5a).

To a solution **1a** (0.109 g, 0.200 mmol) in THF (1.00 mL) was dropwise added a *i*PrBu₂MgLi (0.700 mL, 0.285 M solution in THF/hexane, 0.200 mmol) at -78°C . After the mixture was stirred for 1 hr at the same temperature, benzaldehyde (0.0710 mL, 0.700 mmol) was sequentially added, and warmed up to -20°C . After the mixture was

stirred for 14 hr at $-20\text{ }^{\circ}\text{C}$, the reaction was terminated by the addition of saturated aqueous NH_4Cl and the resulting mixture was extracted with ether. The extracts were washed with brine and dried over MgSO_4 . Evaporation *in vacuo* afforded a crude oil, which was purified by silica gel column chromatography (hexane- Et_2O) to afford the title compounds **5a** (0.0716 g) in 68 % yield. ^1H NMR δ 0.33 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 0.84 (t, $J = 6.9$ Hz, 3H, $-\text{CH}_3$), 0.89 (t, $J = 6.9$ Hz, 3H, $-\text{CH}_3$), 1.15-1.60 (m, 16H, alkyl-H), 1.76-1.88 (m, 1H, allylic-H), 2.00-2.12 (m, 1H, allylic-H), 2.16 (br, 1H, $-\text{OH}$), 2.36-2.47 (m, 1H, allylic-H), 2.50-2.61 (m, 1H, allylic-H), 5.51 (s, 1H, $-\text{CH}(\text{OH})\text{Ph}$), 5.85 (s, 1H, $-\text{CH}=\text{C}(\text{C}_6\text{H}_{13})-$), 7.24-7.40 (m, 5H, Ph); ^{13}C NMR δ 1.87, 13.91, 13.96, 22.50, 22.52, 28.31, 29.16, 29.20, 29.23, 29.26, 31.54, 31.65, 38.86, 72.43, 110.18, 126.00, 127.02, 128.18, 135.55, 140.57, 141.81, 158.75; IR (neat) 3461, 2927, 2862, 1735, 1653, 1560, 1449, 1377, 1249, 1185, 1024, 841, 735, 700 cm^{-1} . Anal. Calcd. for $\text{C}_{26}\text{H}_{43}\text{IOSi}$: C, 59.30 ; H, 8.23. Found: C, 59.28 ; H, 8.14.

(2E, 5Z)-5-Hexyl-7-[(Z)-iodo(trimethylsilyl)methylene]-2, 5-tridecadien-4-ol (6a).

^1H NMR δ 0.30 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 0.82-0.96 (m, 6H, $-\text{CH}_3$ x2), 1.20-1.42 (m, 14H, alkyl-H), 1.46-1.60 (m, 2H, alkyl-H), 1.71 (d, $J = 6.3$ Hz, 3H, $-\text{CH}=\text{CHCH}_3$), 1.80 (s, 1H, $-\text{OH}$), 1.99-2.24 (m, 2H, allylic-H), 2.34 (t, $J = 7.8$ Hz, 2H, allylic-H), 4.79 (br, 1H, $-\text{CH}(\text{OH})-$), 5.48-5.57 (m, 1H, $-\text{CH}=\text{CHCH}_3$), 5.59-5.75 (m, 1H, $-\text{CH}=\text{CHCH}_3$), 5.64 (s, 1H, $-\text{CH}=\text{C}(\text{C}_6\text{H}_{13})-$); ^{13}C NMR δ 1.84, 13.90, 14.00, 17.69, 22.43, 22.58, 28.62, 29.10, 29.16, 29.25, 29.30, 31.54, 31.74, 38.26, 72.01, 109.25, 127.04, 130.87, 133.94, 140.58, 158.86; IR (neat) 3448, 2928, 2862, 1636, 1560, 1458, 1249, 1071, 967, 841, 759 cm^{-1} . Anal. Calcd. for $\text{C}_{23}\text{H}_{43}\text{IOSi}$: C, 56.31 ; H, 8.83. Found: C, 56.28 ; H, 8.91.

(2E, 5Z)-5-[2-(Benzyloxy)ethyl]-10-chloro-7-[(Z)-iodo(trimethylsilyl)methylene]-2, 5-decadien-4-ol (6d).

^1H NMR δ 0.33 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 1.64-1.76 (br, 1H, $-\text{OH}$), 1.70 (d, $J = 6.6$ Hz, 3H, $-\text{CH}=\text{CHCH}_3$), 1.80-1.91 (m, 2H, $-\text{CH}_2\text{CH}_2\text{Cl}$), 2.28-2.37 (m, 1H, $-\text{CH}_2\text{CH}_2\text{OBn}$), 2.42-2.60 (m, 1H, $-\text{CH}_2\text{CH}_2\text{OBn}$), 2.56 (t, $J = 7.8$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 3.45 (t, $J = 6.3$ Hz, 2H, $-\text{CH}_2\text{Cl}$), 3.57-3.66 (m, 1H, $-\text{CH}_2\text{OBn}$), 3.70-3.78 (m, 1H, $-\text{CH}_2\text{OBn}$), 4.55 (s, 2H, $-\text{OCH}_2\text{Ph}$), 4.71 (br, 1H, $=\text{CHCH}(\text{OH})\text{CH}=\text{}$), 5.45-5.54 (m, 1H, $-\text{CH}=\text{CHCH}_3$), 5.60-5.80 (m, 1H, $-\text{CH}=\text{CHCH}_3$), 5.72 (s, 1H, $-\text{CH}=\text{C}(\text{CH}_2\text{CH}_2\text{OBn})-$), 7.21-7.42 (m, 5H, Ph); ^{13}C NMR δ 2.03, 17.86, 30.83, 31.72, 35.38, 44.44, 70.58, 71.08, 73.26, 111.31, 126.55, 127.66, 127.68, 128.30, 131.09, 135.54, 137.40, 138.93, 155.30; IR (neat) 3430, 2954, 2857, 1635, 1570, 1453, 1362, 1250, 1096, 969, 911, 842, 735, 698 cm^{-1} . Anal. Calcd. for $\text{C}_{23}\text{H}_{34}\text{ClIO}_2\text{Si}$: C, 51.83 ; H, 6.43. Found: C, 52.10 ; H, 6.50.

(2E, 5Z, 7Z)-5, 7-Dipropyl-8-iodo-2, 5, 7-undecatrien-4-ol (6e).

^1H NMR δ 0.89 (t, $J = 7.5$ Hz, 3H, $-\text{CH}_3$), 0.93 (t, $J = 7.2$ Hz, 3H, $-\text{CH}_3$), 0.97 (t, $J = 7.2$ Hz, 3H, $-\text{CH}_3$), 1.35-1.62 (m, 6H, alkyl-H), 1.71 (ddd, $J = 1.3, 1.5, 6.3$ Hz, 3H, $-\text{CH}=\text{CHCH}_3$), 1.77 (d, $J = 2.7$ Hz, 1H, $-\text{OH}$), 1.96-2.20 (m, 2H, allylic-H), 2.24 (dt, $J = 2.3, 7.7$ Hz, 2H, allylic-H), 2.54 (dt, $J = 1.2, 7.5$ Hz, 2H, allylic-H), 4.82-4.85 (m, 1H, $-\text{CH}(\text{OH})-$), 5.54 (ddq, $J = 5.7, 15.3, 1.5$ Hz, 1H, $-\text{CH}=\text{CHCH}_3$), 5.65 (s, 1H, $-\text{CH}=\text{CH}(\text{C}_3)-$), 5.60-5.74 (m, 1H, $-\text{CH}=\text{CHCH}_3$); ^{13}C NMR δ 12.87, 13.87, 14.11, 17.69, 21.52, 21.82, 22.85, 31.49, 36.19, 42.26, 71.89, 106.88, 126.83, 130.94, 132.48, 141.61, 143.25; IR (neat) 3446, 2959, 2870, 1653, 1456, 1377, 1238, 1101, 968 cm^{-1} . Anal. Calcd. for $\text{C}_{17}\text{H}_{29}\text{IO}$: C, 54.62 ; H, 7.77. Found: C, 54.32 ; H, 7.44.

(Z)-4-Hexyl-6-[(Z)-iodo(trimethylsilyl)methylene]-1, 4-dodecadien-3-ol (9a).

^1H NMR δ 0.30 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 0.83-0.91 (m, 6H, $-\text{CH}_3$ x2), 1.20-1.43 (m, 14H, alkyl-H), 1.46-1.60 (m, 2H, alkyl-H), 1.91 (br, 1H, $-\text{OH}$), 1.97-2.26 (m, 2H, allylic-H), 2.34 (t, $J = 7.8$ Hz, 2H, allylic-H), 4.86 (br, 1H, $\text{CH}_2=\text{CHCH}(\text{OH})-$), 5.17 (d, $J = 10.8$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 5.31 (d, $J = 17.4$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 5.69 (s, 1H, $-\text{CH}=\text{C}(\text{C}_6\text{H}_{13})-$), 5.87 (ddd, $J = 4.8, 10.8, 17.4$ Hz, 1H, $-\text{CH}=\text{CH}_2$); ^{13}C NMR δ 1.82, 13.88, 13.98, 22.43, 22.57, 28.55, 29.04(x2), 29.15, 29.27, 31.52, 31.71, 38.36, 71.88, 109.51, 114.84, 134.51, 138.17, 139.96, 158.65; IR (neat) 3461, 2927, 2862, 1653, 1560, 1466, 1249, 1116, 988, 841, 759 cm^{-1} . Anal. Calcd. for $\text{C}_{20}\text{H}_{41}\text{IOSi}$: C, 55.45 ; H, 8.67. Found: C, 55.66 ; H, 8.28.

Typical Procedure for Intramolecular Heck Reaction of 6. 4, 6-Dihexyl-3-(trimethylsilyl)-2-ethenyl-3, 5-cyclohexadien-1-ol (7a).

To a mixture of K_2CO_3 (86.3 mg, 0.625 mmol), $\text{Pd}(\text{OAc})_2$ (3.40 mg, 0.0150 mmol), PPh_3 (15.7 mg, 0.0600 mmol) in DMF (0.750 mL) was added compound **6a** (73.6 mg, 0.150 mmol) in DMF (0.45 mL), and the solution was heated to 70~80 $^\circ\text{C}$ and stirred for 10 hr. After the mixture was cooled down to room temperature, diethyl ether was added and the precipitate filtered off. The organic solution was treated with water and the resulting mixture was extracted with ether. The extracts were washed with brine and dried over MgSO_4 . Evaporation *in vacuo* afforded a crude oil, which was purified by silica-gel column chromatography (hexane- Et_2O) to afford the title compounds **7a** (41.9 mg) in 77 % yield. ^1H NMR δ 0.14 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 0.85-0.93 (m, 6H, $-\text{CH}_3$ x2), 1.20-1.54 (m, 16H, alkyl-H), 1.51 (d, $J = 10.2$ Hz, 1H, $-\text{OH}$), 2.09-2.26 (m, 4H, allylic-H), 3.26 (m, 1H, $-\text{CH}(\text{CH}=\text{CH}_2)-$), 3.64 (dd, $J = 1.8, 10.2$ Hz, 1H, $-\text{CH}(\text{OH})-$), 4.92-4.98 (m, 1H, $-\text{CH}=\text{CH}_2$), 5.01-5.09 (m, 1H, $-\text{CH}=\text{CH}_2$), 5.40 (ddd, $J = 7.7, 10.0, 17.5$ Hz, 1H,

-CH=CH₂), 5.66 (s, 1H, -CH=C(C₆H₁₃)-); ¹³C NMR δ 0.25, 13.93, 13.96, 22.50(x2), 27.40, 28.88, 29.51, 30.04, 31.58, 31.74, 34.88, 36.19, 50.32, 70.66, 115.91, 124.14, 127.23, 137.72, 140.92, 145.31; IR (neat) 3431, 2927, 2854, 2177, 1635, 1560, 1466, 1248, 1009, 838, 759 cm⁻¹. Anal. Calcd. for C₂₃H₄₂IOSi: C, 76.17 ; H, 11.67. Found: C, 76.37 ; H, 11.67.

Typical Procedure for the Conversion of 7 to Styrene Derivatives 8. 3, 5-Dihexyl-2-(trimethylsilyl)styrene (8a).

To a mixture of compound **7a** (41.9 mg, 0.115 mmol) in MeOH (1.00 mL) was added *p*-toluenesulfonic acid monohydrate (4.40 mg, 0.0230 mmol) and the solution was stirred for 20 min at room temperature. After addition of water, the solution was extracted with ether. The extracts were washed with brine and dried over MgSO₄. Evaporation *in vacuo* afforded a crude oil, which was purified by silica gel column chromatography (hexane) to afford the title derivative **8a** (34.0 mg) in 86 % yield. ¹H NMR δ 0.38 (s, 9H, -Si(CH₃)₃), 0.85-0.93 (m, 6H, -CH₃ x2), 1.24-1.42 (m, 12H, alkyl-H), 1.44-1.67 (m, 4H, alkyl-H), 2.55 (t, *J* = 7.8 Hz, 2H, ArCH₂-), 2.68 (t, *J* = 8.1 Hz, 2H, ArCH₂-), 5.19 (dd, *J* = 1.5, 10.8 Hz, 1H, -CH=CH₂), 5.46 (dd, *J* = 1.5, 17.1 Hz, 1H, -CH=CH₂), 6.92 (s, 1H, Ar-H), 7.09 (s, 1H, Ar-H), 7.13 (dd, *J* = 10.8, 17.1 Hz, 1H, -CH=CH₂); ¹³C NMR δ 3.71, 13.97(x2), 22.54(x2), 29.13, 29.41, 31.10, 31.67, 31.80, 33.59, 35.64, 36.79, 114.67, 124.97, 129.18, 132.60, 140.89, 143.69, 145.83, 149.57; IR (neat) 3082, 2926, 1597, 1466, 1250, 1062, 993, 841, 691 cm⁻¹. Anal. Calcd. for C₂₃H₄₀Si: C, 80.15 ; H, 11.70. Found: C, 80.00 ; H, 11.66.

6-[2-(Benzyloxy)ethyl]-4-(3-chloropropyl)-2-ethenyl-3-(trimethylsilyl)-3, 5-cyclohexadien-1-ol (7d)

^1H NMR δ 0.16 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 1.84-1.95 (m, 2H, $-\text{CH}_2\text{CH}_2\text{Cl}$), 2.33-2.41 (m, 2H, $-\text{CH}_2\text{CH}_2\text{OBn}$), 2.41-2.52 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 2.55 (d, $J = 6.2$ Hz, 1H, $-\text{OH}$), 3.28 (d, $J = 7.8$ Hz, 1H, $-\text{CH}(\text{CH}=\text{CH}_2)-$), 3.56 (t, $J = 6.6$ Hz, 2H, $-\text{CH}_2\text{Cl}$), 3.58-3.72 (m, 2H, $-\text{CH}_2\text{OBn}$), 3.73 (d, $J = 6.2$ Hz, 1H, $-\text{CH}(\text{OH})-$), 4.52 (s, 2H, $-\text{OCH}_2\text{Ph}$), 4.92-4.98 (m, 1H, $-\text{CH}=\text{CH}_2$), 4.99-5.08 (m, 1H, $-\text{CH}=\text{CH}_2$), 5.41 (ddd, $J = 7.8, 9.6, 17.4$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 5.77 (s, 1H, $-\text{CH}=\text{C}(\text{CH}_2\text{CH}_2\text{OBn})-$), 7.26-7.38 (m, 5H, Ph); ^{13}C NMR δ 0.52, 32.89, 33.41, 36.23, 44.93, 49.66, 69.48, 70.43, 73.04, 115.86, 125.79, 127.60(x2), 128.30, 130.03, 137.28, 137.40, 137.65, 142.18; IR(neat) 3431, 2954, 2854, 1632, 1569, 1454, 1363, 1248, 1099, 1013, 918, 837, 753, 698 cm^{-1} . Anal. Calcd. for $\text{C}_{23}\text{H}_{33}\text{ClO}_2\text{Si}$: C, 68.20 ; H, 8.21. Found: C, 68.12 ; H, 8.34.

5-[2-(Benzyloxy)ethyl]-3-(3-chloropropyl)-2-(trimethylsilyl)styrene (8d)

^1H NMR δ 0.41 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 1.98-2.09 (m, 2H, $-\text{CH}_2\text{CH}_2\text{Cl}$), 2.82-2.95 (m, 4H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ and $-\text{CH}_2\text{CH}_2\text{OBn}$), 3.57 (t, $J = 6.6$ Hz, 2H, $-\text{CH}_2\text{Cl}$), 3.72 (t, $J = 7.2$ Hz, 2H, $-\text{CH}_2\text{OBn}$), 4.55 (s, 2H, $-\text{OCH}_2\text{Ph}$), 5.23 (dd, $J = 1.5, 10.8$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 5.48 (dd, $J = 1.5, 17.1$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 6.99 (d, $J = 1.5$ Hz, 1H, Ar-H), 7.13 (dd, $J = 10.8, 17.1$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 7.18 (d, $J = 1.5$ Hz, 1H, Ar-H), 7.26-7.38 (m, 5H, Ph); ^{13}C NMR δ 3.93, 33.75, 35.79, 36.02, 44.59, 70.88, 72.97, 115.06, 125.67, 127.44, 127.53, 128.25, 129.45, 133.53, 138.22, 139.74, 140.18, 145.91, 147.19; IR(neat) 2952, 2853, 1598, 1544, 1454, 1361, 1251, 1102, 909, 842, 742, 697 cm^{-1} . Anal. Calcd. for $\text{C}_{23}\text{H}_{31}\text{ClO}_2\text{Si}$: C, 71.38 ; H, 8.07. Found: C, 71.14 ; H, 7.97.

3, 4, 6-Tripropyl-2-ethenyl-3,5-cyclohexadien-1-ol (7e).

^1H NMR δ 0.86-0.94 (m, 9H, $-\text{CH}_3$ x3), 1.30-1.58 (m, 6H, alkyl-H), 1.75-1.87 (m, 1H, allylic-H), 2.00-2.32 (m, 6H, allylic-H and $-\text{OH}$), 2.93 (d, $J = 8.4$ Hz, 1H, $-\text{CH}(\text{CH}=\text{CH}_2)-$), 3.65 (m, 1H, $-\text{CH}(\text{OH})-$), 4.97 (dd, $J = 1.8, 9.9$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 5.04-5.12 (m, 1H, $-\text{CH}=\text{CH}_2$), 5.40 (ddd, $J = 8.4, 9.9, 17.1$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 5.64 (s, 1H, $-\text{CH}=\text{C}(\text{C}_3\text{H}_7)-$); ^{13}C NMR δ 13.88, 14.09, 14.35, 21.22, 22.02, 22.64, 32.85, 33.20, 36.88, 51.84, 71.17, 115.74, 124.59, 128.66, 130.16, 136.62, 136.71; IR (neat) 3391, 3075, 2927, 1633, 1465, 1377, 1256, 1075, 995, 911, 741 cm^{-1} . Anal. Calcd. for $\text{C}_{17}\text{H}_{28}\text{O}$: C, 82.20 ; H, 11.36. Found: C, 82.34 ; H, 11.45.

2, 3, 5-Tripropylstyrene (8e).

^1H NMR δ 0.95 (t, $J = 7.5$ Hz, 3H, $-\text{CH}_3$), 0.99 (t, $J = 7.5$ Hz, 3H, $-\text{CH}_3$), 1.01 (t, $J = 7.5$ Hz, 3H, $-\text{CH}_3$), 1.43-1.70 (m, 6H, alkyl-H), 2.49-2.64 (m, 6H, ArCH_2- x3), 5.24 (dd, $J = 1.8, 10.8$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 5.59 (dd, $J = 1.8, 17.4$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 6.91 (d, $J = 1.8$ Hz, 1H, Ar-H), 7.01 (dd, $J = 10.8, 17.4$ Hz, 1H, $-\text{CH}=\text{CH}_2$), 7.15 (d, $J = 1.8$ Hz, 1H, Ar-H); ^{13}C NMR δ 14.11, 14.47, 14.75, 24.37, 24.67, 24.84, 30.79, 35.41, 37.84, 114.88, 123.76, 129.20, 135.33, 135.78, 136.74, 139.69, 140.32; IR (neat) 3084, 2957, 1625, 1604, 1570, 1465, 1377, 1263, 1090, 989, 907 cm^{-1} . Anal. Calcd. for $\text{C}_{17}\text{H}_{26}$ (230.39): C, 88.63 ; H, 11.37. Found: C, 88.59 ; H, 11.23.

Typical Procedure of Synthesis of 2-Methyl-3, 4, 6-Trisubstituted Phenols by Intramolecular Heck Reaction. 4, 6-Dihexyl-2-methyl-3-(trimethylsilyl)phenol (10a).

To a mixture of Et₃N (0.278 mL, 2.00 mmol) and Pd₂(dba)₃•CHCl₃ (3.40 mg, 0.0200 mmol) in dry toluene (0.500 mL) was added compound **9a** (73.6 mg, 0.200 mmol) in dry toluene (0.500 mL), and the solution was heated to 100 °C and stirred for 36 hr. After the mixture was cooled down to room temperature, the reaction was terminated by the addition of saturated aqueous NH₄Cl and the resulting mixture was extracted with ether. The extracts were washed with brine and dried over MgSO₄. Evaporation *in vacuo* afforded a crude oil, which was purified by silica gel column chromatography (hexane-Et₂O) to afford the phenol derivative **10a** (41.9 mg) in 77 % yield. ¹H NMR δ 0.39 (s, 9H, -Si(CH₃)₃), 0.85-0.92 (m, 6H, -CH₃ x2), 1.20-1.65 (m, 16H, alkyl-H), 2.34 (s, 3H, ArMe), 2.54 (t, *J* = 7.8 Hz, 2H, ArCH₂-), 2.61 (t, *J* = 8.0 Hz, 2H, ArCH₂-), 4.48 (s, 1H, -OH), 6.79 (s, 1H, Ar-H); ¹³C NMR δ 3.65, 13.97(x2), 16.82, 22.53(x2), 29.28, 29.32, 29.46, 30.16, 31.64, 31.81, 34.16, 36.27, 128.57, 129.02, 129.18, 135.12, 141.32, 149.81; IR (neat) 3481, 2927, 2862, 1636, 1467, 1251, 1170, 1015, 841, 763 cm⁻¹. Anal. Calcd. for C₂₂H₄₀IOSi: C, 75.79 ; H, 11.56. Found: C, 75.85 ; H, 11.54

Reaction of 1, 4-Diiodo-1, 3-Alkadienes **1** with *t*BuLi.

As shown above, the iodine exchange reaction of **1** with *t*BuLi proceeded with similar site-selectivity to afford 1-iodo-1, 3-alkadiene compounds **2** after hydrolysis. However,

in comparison with the reaction of **1** with *i*PrBu₂MgLi, dilithiated compound **3** was obtained in considerable amount. Meanwhile, the reaction of **1** with isopropylmagnesium bromide³ did not proceed and resulted in the recovery of the starting substrate.

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