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Highly Stereoselective Synthesis of (1*E*)-2-Methyl-1,3-dienes via Pd-Catalyzed *trans*-Selective Cross-Coupling of 1,1-Dibromo-1-alkenes with Alkenylzincs and Methylation with Methylzincs Catalyzed by Pd Complexes Containing *t*Bu_3P or NHC**

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Supplementary Data

General. All experiments were conducted under argon atmosphere. THF and diethyl ether were dried and distilled by the standard methods. $ZnBr_2$ was flame-dried under vacuum prior to use. $Pd(PPh_3)_4$ was prepared according to the literature procedure.[a] Me_2Zn, Et_2Zn, *n*-BuLi and PhMgBr were purchased from Aldrich and used as received. 1,1-Dibromo-1-alkenes were prepared from their corresponding aldehydes by the method of Corey and Fuchs.[b] The preparation and identification of **5a-5c**, **5e-5j**, **5l**, **5n**, and **5p** were previously reported.[c]

Flash chromatographic separations were carried out on 230 – 400 mesh silica gel 60. Gas chromatography was performed on an HP 6890 Gas Chromatography using a HP-5 capillary column (30 m X 0.32 mm, 0.5 μm film) with appropriate hydrocarbons as internal standards. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Inova-300 spectrometer. IR spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. LRMS and HRMS were obtained on Hewlett Packed 5995 GC-MS and Finnigan MATL95 mass spectrometers, respectively. Microanalyses were performed on a Perkin-Elmer 2400 Series II CHNS/O Analyzer. Optical rotations were measured on an Autopol III automatic polarimeter.

Palladium-Catalyzed *trans*-Selective Alkenylation of 1,1-Dibromo-1-alkenes with Alkenylzincs. Representative Procedure A. Preparation of (1*E*,3*Z*)-3-Bromo-1-phenyl-1,3-decadiene (5k). To (*E*)-1-iodo-2-phenylethylene (3.45 g, 15 mmol) in ether (20 mL) cooled to -78 °C was added *t*-

BuLi (17.6 mL, 1.7 M in pentane, 30 mmol). The resultant yellow solution was stirred for 30 min. at -78 ^{o}C. To this was added *via* cannula a solution of dry $ZnBr_2$ (3.38 g, 15 mmol) in THF (20 mL). The mixture thus obtained was stirred for 5 min. at -78 ^{o}C and then warmed to 23 ^{o}C over 25 min, and added *via* cannula to a mixture of 1,1-dibromo-1-octene (2.70 g, 10 mmol) and $Pd(PPh_3)_4$ (578 mg, 0.5 mmol) in THF (20 mL) at 23 ^{o}C. The resultant yellow mixture was stirred at 23 ^{o}C and monitored by GLC analysis. After 16 h, GLC analysis indicated that the starting material had been completely consumed, and the title compound was formed in >95% yield. The reaction mixture was quenched with aqueous NH_4Cl, extracted with ether, washed with aqueous $NaHCO_3$, dried over $MgSO_4$, filtered and concentrated. Flash chromatography (silica gel, 99/1 hexanes/ethyl acetate) afforded the title compound (2.24 g, 76%, stereoisomeric purity $\geq$98%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, *J* = 6.9 Hz, 3 H), 1.3-1.6 (m, 8 H), 2.44 (q, *J* = 7.2 Hz, 2 H), 6.15 (t, *J* = 7.2 Hz, 1 H), 6.80 (d, *J* = 15.0 Hz, 1 H), 6.98 (d, *J* = 15.0 Hz, 1 H), 7.31 (t, *J* = 7.2 Hz, 1 H), 7.35-7.45 (m, 2 H), 7.45-7.55 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.07, 22.59, 28.44, 28.96, 31.65, 31.81, 125.25, 126.75 (2 C), 127.75, 127.93, 128.62 (2 C), 132.11, 135.34, 136.60; IR (neat) 1629, 1597, 1493, 1449, 949, 748, 691 cm^{-1}; Anal. Calcd. for $C_{16}H_{21}Br$: C, 65.53; H, 7.22; Br, 27.25; Found: C, 65.44; H, 7.16; Br, 27.07.

(1*Z*,3*E*)-1-Phenyl-2-bromo-1,3-decadiene (5d). The title compound was prepared according to Representative Procedure A except that 1,1-dibromo-2-phenylethylene (524 mg, 2 mmol) and 1-iodo-1-octene (619 mg, 2.6 mmol) were used. Yield: 369.6 mg (63%); Stereoisomeric purity: >98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.8-1.0 (m, 3 H), 1.2-1.6 (m, 8 H), 2.15-2.3 (m, 2 H), 6.15-6.3 (m, 2 H), 6.85 (s, 1 H), 7.2-7.4 (m, 3 H), 7.6-7.7 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ14.10, 22.61, 28.94, 29.21, 31.71, 32.33, 123.64, 127.78, 128.03 (2 C), 129.41 (2 C), 129.51, 130.37, 136.01, 137.10; IR (neat) 1493, 1446, 1378, 1272, 1141, 950, 751 cm$^{-1.}$

(*3Z*,*5R*)-3-Bromo-2,5-dimethyl-6-(*tert*-butyldimethylsilyloxy)-1,3-hexadiene (5m). The title compound was prepared according to Representative Procedure A except that (*3R*)-1,1-dibromo-3-methyl-4-(*tert*-butyldimethylsilyloxy)-1-butene and 2-bromopropene (1.3 eq) were used. Yield: 71%; Stereoisomeric purity: ≥98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 6 H), 0.88 (s, 9 H), 1.05 (d, *J* = 6.6 Hz, 3 H), 1.97 (s, 3 H) 2.8-3.0 (m, 1 H), 3.49 (dd, *J* = 9.6 and 6.3 Hz, 1 H), 3.58 (dd, *J* = 9.6 and 5.3 Hz, 1 H), 5.08 (s, 1 H), 5.46 (s, 1 H), 5.86 (d, *J* = 8.7 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.38, -5.35, 16.14, 18.27, 21.00, 25.87 (3 C), 39.93, 66.57, 117.88, 127.24, 133.75, 140.84.

(*2R*,*3Z*,*5E*)-1-(*tert*-Butyldimethylsilyloxy)-2,6-dimethyl-4-bromo-3,5-decadiene (5o): The title compound was prepared according to Representative Procedure A except that (*E*)-1-iodo-2-methyl-1-hexen and (3*R*)-1,1-dibromo-3-methyl-4-(*t*-butyldimethyl- silyloxy)-butene were used. Yield: 71%, stereoisomeric purity: ≥98%; $[\alpha]_D^{23}$ = -43.6˚ (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 6 H), 0.9-1.1 (m, 15 H), 1.25-1.5 (m, 4 H), 1.80 (s, 3 H), 2.09 (t, *J* = 7.0 Hz, 2 H), 2.8-2.9 (m, 1 H), 3.54 (dd, *J* = 6.3 Hz, *J* = 9.7 Hz, 1 H), 3.62 (dd, *J* = 5.7 Hz, *J* = 9.7 Hz, 1 H), 5.54 (d, *J* = 8.7 Hz, 1 H), 5.81 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ -5.38, -5.36, 13.96, 16.16, 17.65, 18.29, 22.30, 25.89 (3 C), 29.84, 39.05, 39.64, 66.74, 121.72, 125.53, 134.31, 141.31; IR (neat) 2951, 1630, 1095, 836, 774, 666 cm^{-1}; HRMS calculated for $C_{18}H_{35}BrOSi$ $[M+H]^+$: 375.1719; found: 375.1920.

(*2R*,*3Z*,*5Z*)-1-(*tert*-Butyldimethylsilyloxy)-2,6-dimethyl-4-bromo-3,5-decadiene (5q): The title compound was prepared according to Representative Procedure A except that (*Z*)-1-iodo-2-methyl-1-hexen[d] and (3*R*)-1,1-dibromo-3-methyl-4-(*t*-butyldimethyl- silyloxy)-butene were used. Yield: 67%; stereoisomeric purity: ≥98%; $[\alpha]_D^{23}$ = -34.8˚ (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 6 H), 0.9-1.15 (m, 15 H), 1.3-1.5 (m, 4 H), 1.77 (s, 3 H), 2.15-2.3 (m, 2 H), 2.8-2.9 (m, 1 H), 3.49 (dd, *J* = 6.2 Hz, *J* = 9.7 Hz, 1 H), 3.60 (dd, *J* = 5.4 Hz, *J* = 9.7 Hz, 1 H), 5.54 (d, *J* = 8.8 Hz, 1 H), 5.79 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -5.38 (2 C), 13.98, 16.18, 18.29, 22.70, 22.90, 25.90 (3 C), 30.33, 32.20, 39.61, 66.64, 121.43, 126.04, 133.58, 141.71; IR (neat) 2957, 1634, 1464, 1100, 836, 775, 667 cm^{-1}; HRMS calculated for $C_{18}H_{35}BrOSi$ $[M+H]^+$: 375.1719; found 375.1923.

Highly Stereoselective Synthesis of (1*E*)-2-Methyl-1,3-dienes and Related Conjugated Dienes Catalyzed by Pd Complexes Containing ^{t}Bu$_3$P or NHC. Representative Procedure B. (2*R*,3*E*,5*E*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-3,5-decadiene (7a): To a mixture of (2*R*,3*Z*,5*E*)-1-(*tert*-butyldimethylsilyloxy)-2-methyl-4-bromo-3,5-decadiene (**5a**) (181 mg, 0.5 mmol) and Pd(tBu$_3$P)$_2$ (5 mg, 0.01 mmol) in THF (4 mL) was added Me_2Zn (0.25 mL, 2.0 M in toluene, 0.5 mmol) at 23 ˚C. The resultant mixture was stirred at 23 ˚C and monitored by GLC analysis. After 1 h, GLC analysis indicated that the starting material had been completely consumed and the title compound was formed in quantitative yield. The reaction mixture was quenched with aqueous NH_4Cl, extracted with ether, washed with aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, hexane) afforded

the title compound (138 mg, 93%, stereoisomeric purity ≥98%) as oil: $[\alpha]_D^{23}$ = -10.2° (c 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.03 (s, 6 H), 0.8-1.1 (m, 15 H), 1.25-1.4 (m, 4 H), 1.74 (s, 3 H), 2.05-2.15 (m, 2 H), 2.6-2.7 (m, 1 H), 3.35 (dd, *J* = 7.4 Hz, *J* = 9.5 Hz, 1 H), 3.48 (dd, *J* = 5.9 Hz, *J* = 9.5 Hz, 1 H), 5.13 (d, *J* = 9.4 Hz, 1 H), 5.58 (dt, *J* = 6.9 Hz, *J* = 15.5 Hz, 1 H), 6.05 (d, *J* = 15.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -5.37, -5.30, 12.84, 13.96, 17.35, 18.35, 22.28, 25.94 (3 C), 31.87, 32.55, 35.59, 67.87, 128.11, 132.93, 133.79, 134.77; IR (neat) 2957, 1625, 1087, 963, 836, 776, 667 cm^{-1}; HRMS calculated for $C_{18}H_{36}OSi$ $[M+H]^+$: 297.2614; found: 297.2605.

(**2*R*,3*E*,5*E*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-3,5-dodecadiene (7b)**. The title compound was prepared according to Representative Procedure B except that (2*R*,3*Z*,5*E*)-1-(*tert*-butyldimethylsilyloxy)-2-methyl-4-bromo-3,5-dodecadiene (**5b**) was used in place of **5a**. Yield: 62%; Stereoisomeric purity: ≥98%; $[\alpha]_D^{23}$ -7.1° (c 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.02 (s, 3 H), 0.03 (s, 3 H), 0.88 (s, 12 H), 0.97 (d, *J* = 6.6 Hz, 3 H), 1.2-1.45 (m, 8 H), 1.74 (s, 3 H), 2.0-2.15 (m, 2 H), 2.55-2.75 (m, 1 H), 3.35 (dd, *J* = 9.6 and 7.6 Hz, 1 H), 3.47 (dd, *J* = 9.6 and 5.9 Hz, 1 H), 5.12 (d, *J* = 9.3 Hz, 1 H), 5.56 (dt, *J* = 15.6 and 6.9 Hz, 1 H), 6.02 (d, *J* = 15.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.38, -5.31, 12.83, 14.09, 17.35, 18.34, 22.64, 25.93 (3 C), 28.95, 29.68, 31.80, 32.91, 35.60, 67.86, 128.13, 132.92, 133.78, 134.77; IR (neat) 1474, 1256, 1087, 963, 836, 775 cm^{-1}; Anal. Calcd. For $C_{20}H_{40}OSi$: C, 74.00; H, 12.42; found: C, 73.62; H, 12.24.

(2*R*,3*E,5E*)-1-(*t*-Butyldimethylsilyloxy)-4-ethyl-2-methyl-3,5-dodecadiene (7b', R^5 = Et). The title compound was prepared according to Representative Procedure B except that (2*R*,3*Z,5E*)-4-bromo-1-(*t*-butyldimethylsilyloxy)-2-methyl-3,5-dodecadiene (**5b**) was used in place of **5a,** Et_2Zn was used in place of Me_2Zn and a catalyst generated in situ from 5% $Pd(dba)_2$, 5% NHC and 10% Cs_2CO_3 was used in place of $Pd(tBu_3P)_2$. Yield: 89%; Stereoisomeric purity: ≥98%; $[\alpha]_D^{23}$ -8.7° (c 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.02 (s, 3 H), 0.03 (s, 3 H), 0.88 (s, 12 H), 0.97 (d, *J* = 6.6 Hz, 3 H), 1.01 (t, *J* = 7.5 Hz, 3 H), 1.2-1.45 (m, 8 H), 2.07 (q, *J* = 6.9 Hz, 2 H), 2.15-2.3 (m, 2 H), 2.55-2.65 (m, 1 H), 3.34 (dd, *J* = 9.6 and 7.5 Hz, 1 H), 3.48 (dd, *J* = 9.6 and 5.7 Hz, 1 H), 5.04 (d, *J* = 9.9 Hz, 1 H), 5.59 (dt, *J* = 15.6 and 6.9 Hz, 1 H), 5.89 (d, *J* = 15.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.36, -5.29, 14.10, 14.34, 17.59, 18.39, 20.35, 22.64,

25.96 (3 C), 28.93, 29.65, 31.79, 32.98, 35.48, 68.06, 127.91, 132.19, 132.98, 140.07; IR (neat) 1471, 1256, 1087, 837, 775 cm^{-1}; Anal. Calcd. For $C_{21}H_{42}OSi$: C, 74.48; H, 12.50; Found: C, 74.62; H, 12.45.

(2*R*,3*E*,5*E*)-1-(*t*-Butyldimethylsilyloxy)-4-butyl-2-methyl-3,5-dodecadiene (7b", R^5 = *n*Bu). The title compound was prepared according to Representative Procedure B except that (2*R*,3*Z*,5*E*)-4-bromo-1-(*t*-butyldimethylsilyloxy)-2-methyl-3,5-dodecadiene (**5b**) was used in place of **5a,** *n*BuZnBr (1.3 eq) generated from n-butyllithium (1.3 eq, 2.5 M in hexanes) and $ZnBr_2$ (1.3 eq) was used in place of Me_2Zn, and a catalyst generated in situ from 5% $Pd(dba)_2$, 5% NHC and 10% Cs_2CO_3 was used in place of $Pd(tBu_3P)_2$. Yield: 94%; Stereoisomeric purity: ≥98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 6 H), 0.85-0.95 (m, 15 H), 0.97 (d, *J* = 6.6 Hz, 3 H), 1.2-1.45 (m, 12 H), 2.07 (q, *J* = 6.9 Hz, 2 H), 2.1-2.3 (m, 2 H), 2.5-2.7 (m, 1 H), 3.34 (dd, *J* = 9.6 and 7.8 Hz, 1 H), 3.48 (dd, *J* = 9.6 and 5.7 Hz, 1 H), 5.06 (d, *J* = 9.9 Hz, 1 H), 5.58 (dt, *J* = 15.9 and 6.9 Hz, 1 H), 5.90 (d, *J* = 15.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.34, -5.29, 14.06, 14.09, 17.56, 18.39, 22.64, 23.14, 25.97 (3 C), 27.17, 28.92, 29.64, 31.79, 31.88, 32.98, 35.57, 68.05, 127.90, 132.64, 133.48, 138.57.

1-Trimethylsilyl-4-methyl-3,5-decadien-1-yne (7c): The title compound was prepared according to Representative Procedure B except that 1-trimethylsilyl-4-bromo-3,5-decadien-1-yne (**5c**) was used in place of **5a**. Yield: 95%; Stereoisomeric purity: ≥99%; ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 0.88 (t, *J* = 6.9 Hz, 3 H), 1.2-1.45 (m, 4 H), 1.97 (s, 3 H), 2.14 (dt, *J* = 7.2 Hz, *J* = 14.0 Hz, 2 H), 5.36 (s, 1 H), 5.82 (dt, *J* = 6.9 Hz, *J* = 15.5 Hz 1 H), 6.09 (d, *J* = 15.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.05 (3 C), 13.89, 15.30, 22.24, 31.43, 32.64, 100.54, 103.91, 107.79, 132.54, 133.64, 148.47; IR (neat) 3015, 2129, 1635, 1090, 962, 842, 760 cm^{-1}; Anal. Calcd. for $C_{14}H_{24}Si$: C, 76.28; H, 10.98; Found: C, 75.91; H, 10.62.

(1*E*,3*E*)-1-Phenyl-2-methyl-1,3-decadiene (7d).[e] The title compound was prepared according to Representative Procedure B except that (1*Z*,3*E*)-1-Phenyl-2-bromo-1,3-decadiene (**5d**) (205 mg, 0.7 mmol) was used in place of **5a**. Yield: 151 mg (94%); Stereoisomeric purity: >98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.6 Hz, 3 H), 1.2-1.5 (m, 8 H), 1.97 (s, 3 H), 2.1-2.2 (m, 2 H), 5.77 (dt, *J* =15.6 and 6.9 Hz, 1 H), 6.23 (d, *J* = 15.6 Hz, 1 H), 6.41 (s, 1 H), 7.1-7.35 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.90, 14.09, 22.63, 28.97, 29.59, 31.77, 32.02, 126.14, 127.98 (2 C), 129.11 (2 C), 130.39, 135.12, 135.81, 138.14; IR (neat) 1598, 1494, 1456, 1378, 1078, 962, 746 cm^{-1}.

(2*E*,4*E*)-4-Methyl-1-*tert*-butyldimethylsilyloxy-2,4-undecadiene (7e). The title compound was prepared according to Representative Procedure B except that (2*E*,4*Z*)-4-Bromo-1-*tert*-butyldimethylsilyloxy-2,4-undecadiene (**5e**) was used in place of **5a**. Yield: 86%; Stereoisomeric purity: ≥98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 6 H), 0.87 (t, *J* = 6.9 Hz; 3 H), 0.91 (s, 9 H), 1.2-1.4 (m, 8 H), 1.72 (s, 3 H), 2.10 (q, *J* = 7.2 Hz; 2 H), 4.22 (d, *J* = 5.4 Hz, 2 H), 5.44 (t, *J* = 7.2 Hz, 1 H), 5.61 (dt, *J* = 15.6 and 5.4 Hz, 1 H), 6.21 (d, *J* = 15.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.14 (2 C), 12.39, 14.08, 18.42, 22.64, 25.98 (3 C), 28.23, 29.03, 29.55, 31.78, 64.21, 125.51, 132.78, 132.88, 135.07; IR (neat) 1463, 1377, 1255, 1129, 963, 837, 776 cm^{-1}; HRMS calcd. for $C_{18}H_{36}OSi$ $[M]^+$ 296.2535, found 296.2535.

(3*E*,5*E*)-5-Methyl-1-trimethylsilyl-3,5-dodecadien-1-yne (7f). The title compound was prepared according to Representative Procedure B except that (3*E*,5*Z*)-5-bromo-1-trimethylsilyl-3,5-dodecadien-1-yne (**5f**) was used in place of **5a**. Yield: 68%; Stereoisomeric purity: ≥98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 0.86 (t, *J* = 6.9 Hz, 3 H), 1.2-1.4 (m, 8 H), 1.67 (s, 3 H), 2.11 (q, *J* = 6.9 Hz, 2 H), 5.48 (d, *J* = 16.2 Hz, 1 H), 5.56 (t, *J* = 7.5 Hz, 1 H), 6.65 (d, *J* = 16.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.01 (3 C), 11.67, 14.04, 22.60, 28.49, 28.97, 29.28, 31.71, 95.07, 104.58, 105.28, 133.25, 136.76, 147.68; IR (neat) 2127, 1626, 1467, 1250, 954, 843, 760 cm^{-1}; Anal. Calcd. for $C_{16}H_{28}Si$: C, 77.34; H, 11.36; Found: C, 77.28; H, 11.39.

(3*E*,5*E*,7*R*)-8-(*t*-butyldimethylsilyloxy)-5,7-dimethyl-1-trimethylsilyl-3,5-octadien-1-yne (7g, R^5 = Me). The title compound was prepared according to Representative Procedure B except that (3*E*,5*Z*,7*R*)-5-bromo-8-(*t*-butyldimethylsilyloxy)-7-methyl-1-trimethylsilyl-3,5-octadien-1-yne (**5g**) was used in place of **5a.** Yield: 90%; Stereoisomeric purity: ≥98%; $[\alpha]_D^{23}$ = +17.1° (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ -0.01 (s, 3 H), 0.00 (s, 3 H), 0.16 (s, 9 H), 0.85 (s, 9 H), 0.94 (d, *J* = 6.9 Hz, 3 H), 1.70 (d, *J* = 0.9 Hz, 3 H), 2.55-2.7 (m, 1 H), 3.38 (dd, *J* = 9.8 and 6.5 Hz, 1 H), 3.43 (dd, *J* = 9.8 and 6.5 Hz, 1 H), 5.35 (d, *J* = 9.6 Hz, 1 H), 5.50 (d, *J* = 16.2 Hz, 1 H), 6.63 (d, *J* = 16.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.41, -5.34, 0.01 (3 C), 12.13, 16.95, 18.28, 25.89 (3 C), 35.92, 67.54, 95.32, 105.17, 105.22, 133.43, 139.09, 147.57; IR (neat) 2130, 1626, 1472, 1390, 1251, 1123, 954, 847, 776 cm^{-1}; Anal. Calcd. for $C_{19}H_{36}OSi_2$: C, 67.78; H, 10.78; Found: C, 67.39; H, 10.53.

(3*E*,5*E*,7*R*)-8-(*t*-Butyldimethylsilyloxy)-5-ethyl-7-methyl-1-trimethylsilyl-3,5-octadien-1-yne (7g', R^5 = Et). The title compound was prepared according to Representative Procedure B except that (3*E*,5*Z*,7*R*)-5-bromo-8-(*t*-butyldimethylsilyloxy)-7-methyl-1-trimethylsilyl-3,5-octadien-1-yne (**5g**) was used in place of **5a** and Et_2Zn was used in place of Me_2Zn. Yield: 86%; Stereoisomeric purity: ≥98%; $[\alpha]_D^{23}$ +26.0° (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ -0.01 (s, 3 H), 0.00 (s, 3 H), 0.16 (s, 9 H), 0.85 (s, 9 H), 0.94 (d, *J* = 6.3 Hz, 3 H), 0.98 (t, *J* = 7.5 Hz, 3 H), 2.1-2.3 (m, 2 H), 2.5-2.7 (m, 1 H), 3.3-3.45 (m, 2 H), 5.27 (d, *J* = 9.6 Hz, 1 H), 5.54 (d, *J* = 16.4 Hz, 1 H), 6.52 (d, *J* = 16.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.41, -5.33, 0.02 (3 C), 13.96, 17.20, 18.31, 19.66, 25.91 (3 C), 35.80, 67.69, 95.38, 104.98, 105.24, 138.55, 139.64, 146.29; IR (neat) 2124, 1472, 1251, 1100, 956, 843, 776 cm^{-1}; Anal. Calcd. for $C_{20}H_{38}OSi_2$: C, 68.50; H, 10.92; Found: C, 68.56; H, 10.76.

(3*E*,5*E*,7*R*)-8-(*t*-Butyldimethylsilyloxy)-7-methyl-5-phenyl-1-trimethylsilyl-3,5-octadien-1-yne (7g", R^5 = Ph). The title compound was prepared according to Representative Procedure B except that (3*E*,5*Z*,7*R*)-5-bromo-8-(*t*-butyldimethylsilyloxy)-7-methyl-1-trimethylsilyl-3,5-octadien-1-yne (**5g**) was used in place of **5a,** PhMgBr (1.0 M in THF, 1.3 eq) and $ZnBr_2$ (1.3 eq) were used in place of Me_2Zn. Yield: 91%; Stereoisomeric purity: ≥98%; $[\alpha]_D^{23}$ -0.66° (c 3.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 3 H), 0.07 (s, 3 H), 0.24 (s, 9 H), 0.95 (s, 9 H), 0.99 (d, *J* = 6.9 Hz, 3 H), 2.3-2.45 (m, 1 H), 3.45-3.55 (m, 2 H), 5.16 (d, *J* = 16.1 Hz, 1 H), 5.71 (d, *J* = 10.2 Hz, 1 H), 6.93 (d, *J* = 16.1 Hz, 1 H), 7.15-7.2 (m, 2 H), 7.3-7.45 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.43, -5.40, -0.05 (3 C), 17.12, 18.31, 25.92 (3 C), 36.51, 67.54, 96.88, 104.84, 109.03, 127.14, 128.22 (2 C), 129.42 (2 C), 136.91, 139.62 (2 C), 140.91, 146.64; IR (neat) 2123, 1599, 1472, 1387, 1251, 1089, 954, 840, 775 cm^{-1}; Anal. Calcd. for $C_{24}H_{38}OSi_2$: C, 72.29; H, 9.61; Found: C, 72.07; H, 9.59.

(3*E*,5*E*,7*R*)-8-(*t*-Butyldiphenylsilyloxy)-5,7-dimethyl-1-trimethylsilyl-3,5-octadien-1-yne (7h). The title compound was prepared according to Representative Procedure B except that (3*E*,5*Z*,7*R*)-5-Bromo-8-(*t*-butyldiphenylsilyloxy)-7-methyl-1-trimethylsilyl-3,5-octadien-1-yne (**5h**) was used in place of **5a**. Yield: 95%; Stereoisomeric purity: ≥98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 9 H), 1.06 (d, *J* = 6.6 Hz, 3 H), 1.11 (s, 9 H), 1.72 (s, 3 H), 2.7-2.85 (m, 1 H), 3.57 (d, *J* = 6.3 Hz, 2 H), 5.44 (d, *J* = 9.3 Hz, 1 H), 5.58 (d, *J* = 16.2 Hz, 1 H), 6.71 (d, *J* = 16.2 Hz, 1 H), 7.35-7.5 (m, 6 H), 7.65-7.8 (m, 4 H); ^{13}C NMR (75

MHz, $CDCl_3$) δ 0.03 (3 C), 12.06, 17.01, 19.22, 26.83 (3 C), 35.82, 68.15, 95.37, 105.22, 105.26, 127.61 (4 C), 129.55, 129.58, 133.45, 133.73, 133.77, 135.57 (2 C), 135.62 (2 C), 139.08, 147.56; HRMS calcd. for $C_{29}H_{40}OSi_2$ $[M+H]^+$ 461.2696, found 461.2686.

(3*E*,5*E*)-5-Methyl-6-phenyl-1-trimethylsilyl-3,5-hexadien-1-yne (7i). The title compound was prepared according to Representative Procedure B except that (3*E*,5*Z*)-5-bromo-6-phenyl-1-trimethylsilyl-3,5-hexadien-1-yne **(5i)** was used in place of **5a**. Yield: 94%; Stereoisomeric purity: ≥98%; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.21 (s, 9 H), 1.96 (d, *J* = 0.9 Hz, 3 H), 5.71 (d, *J* = 16.1 Hz, 1 H), 6.57 (s, 1 H), 6.84 (d, *J* = 16.1 Hz, 1 H), 7.2-7.35 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ -0.03 (3 C), 13.24, 96.82, 104.96, 107.13, 127.05, 128.18 (2 C), 129.31 (2 C), 133.96, 134.99, 137.17, 147.67; IR (neat) 2128, 1599, 1492, 1442, 1250, 1086, 958, 840 cm^{-1}; Anal. Calcd. for $C_{16}H_{20}Si$: C, 79.93; H, 8.38; Found: C, 80.23; H, 8.26.

(*1E,3E,5E*)-1-(1-Cyclohexenyl)-3-methyl-8-trimethylsilyl-1,3,5-octatrien-7-yne (7j). The title compound was prepared according to Representative Procedure B except that (*1E,3Z,5E*)-1-cyclohexenyl-3-bromo-8-trimethylsilyl-1,3,5-octatrien-7-yne (**5j**) was used in place of **5a**. Yield: 121 mg (61%); Stereoisomeric purity: ≥98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9 H), 1.5-1.75 (m, 4 H), 1.91 (s, 3 H), 2.1-2.25 (m. 4 H), 5.58 (d, *J* = 15.5 Hz, 1 H), 5.8-5.9 (m, 1 H), 6.09 (d, *J* = 11.7 Hz, 1 H), 6.16 (d, *J* = 15.9 Hz, 1 H), 6.33 (d, *J* = 15.9 Hz, 1 H), 7.00 (dd, *J* = 15.5 and 11.7 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.05 (3 C), 12.79, 22.45 (2 C), 24.49, 26.20, 97.72, 105.56, 109.70, 129.07, 129.38, 131.35, 133.48, 135.98, 138.88, 139.29; IR (neat) 2121, 1583, 1447, 1248, 957, 842, 759 cm^{-1}.

(1*E*,3*E*)-3-Methyl-1-phenyl-1,3-decadiene (7k).[f] The title compound was prepared according to Representative Procedure B except that (1*E*,3*Z*)-3-Bromo-1-phenyl-1,3-decadiene **(5k)**. was used in place of **5a.** Yield: 95%; Stereoisomeric purity: ≥98%; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.89 (t, *J* = 6.9 Hz, 3 H), 1.25-1.45 (m, 8 H), 1.84 (s, 3 H), 2.17 (q, *J* = 7.2 Hz, 2 H), 5.62 (t, *J* = 7.2 Hz, 1 H), 6.43 (d, *J* = 16.2 Hz, 1 H), 6.80 (d, *J* = 16.2 Hz, 1 H), 7.16 (t, *J* = 7.2 Hz, 1 H), 7.27 (t, *J* = 7.2 Hz, 2 H), 7.38 (d, *J* = 7.2 Hz, 2 H),; ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 12.35, 14.10, 22.66, 28.50, 29.07, 29.58, 31.80, 125.43, 126.12 (2 C), 126.76, 128.49 (2 C), 133.64, 134.08, 134.50, 138.04; IR (neat) 1630, 1598, 1493, 1448, 958, 746, 691 cm^{-1}.

(1*E*,*3E*,*5S*)-1-Phenyl-3,5-dimethyl-1,3-heptadiene (7l). The title compound was prepared according to Representative Procedure B except that (*1E,3Z,5S*)-1-Phenyl-3-bromo-5-methyl-1,3-heptadiene (**5l**) was used in place of **5a**. Yield: 92%; Stereoisomeric purity: ≥98%; $[\alpha]_D^{23}$ +60.7° (c 0.67, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.86 (t, *J* = 7.5 Hz, 3 H), 0.99 (d, *J* = 6.6 Hz, 3 H), 1.2-1.5 (m, 2 H), 1.86 (s, 3 H), 2.35-2.5 (m, 1 H), 5.40 (d, *J* = 9.6 Hz, 1 H), 6.43 (d, *J* = 15.9 Hz, 1 H), 6.79 (d, *J* = 15.9 Hz, 1 H), 7.16 (t, *J* = 7.5 Hz, 1 H), 7.28 (t, *J* = 7.5 Hz, 2 H), 7.39 (d, *J* = 7.5 Hz, 2 H),; ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 11.98, 12.69, 20.66, 30.40, 34.51, 125.54, 126.11 (2 C), 126.76, 128.50 (2 C), 132.48, 134.30, 138.03, 140.73; IR (neat) 1630, 1598, 1493, 1449, 959, 746, 691 cm^{-1}.

(*3E,5R*)-2,3,5-Trimethyl-6-(*tert*-butyldimethylsilyloxy)-1,3-hexadiene (7m). The title compound was prepared according to Representative Procedure B except that (*3Z,5R*)-3-bromo-2,5-methyl-6-(*tert*-butyldimethylsilyloxy)-1,3-hexadiene (**5m**) was used in place of **5a**. Yield: 134 mg (69%); Stereoisomeric purity: ≥98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.02 (s, 6 H), 0.88 (s, 9 H), 0.98 (d, *J* = 6.6 Hz, 3 H), 1.82 (s, 3 H), 0.89 (s, 3 H), 2.55-2.75 (m, 1 H), 3.39 (dd, *J* = 9.6 and 7.2 Hz, 1 H), 3.48 (dd, *J* = 9.6 and 6.0 Hz, 1 H), 4.88 (s, 1 H), 4.98 (s, 1 H), 5.36 (d, *J* = 9.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.39, -5.32, 14.04, 17.34, 18.33, 20.89, 25.91 (3 C), 35.99, 67.87, 111.22, 130.84, 134.89, 144.63; IR (neat) 1472, 1256, 1088, 903, 837, 775 cm^{-1}.

(2*R*,3*E*,5*E*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-5-ethyl-3,5-octadiene (7n): The title compound was prepared according to Representative Procedure B except that (2*R*,3*Z*,5*E*)-1-(*tert*-butyldimethylsilyloxy)-2-methyl-5-ethyl-4-bromo-3,5-octadiene (**5n**) was used in place of **5a**. Yield: 87%; stereoisomeric purity ≥98%; $[\alpha]_D^{23}$ = -8.8° (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 6 H), 0.8-1.05 (m, 18 H), 1.77 (s, 3 H), 2.0-2.15 (m, 4 H), 2.25 (q, *J* = 7.5 Hz, 2 H), 2.6-2.7 (m, 1H), 3.39 (dd, *J* = 7.5 Hz, *J* = 9.7 Hz, 1 H), 3.52 (dd, *J* = 5.8 Hz, *J* = 9.7 Hz, 1 H), 5.26 (d, *J* = 9.0 Hz, 1 H), 5.38 (t, *J* = 7.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -5.38, -5.31, 14.01, 14.56, 14.77, 17.50, 18.34, 20.78, 21.44, 25.94 (3 C), 35.94, 67.98, 127.15, 128.43, 134.98, 142.68; IR (neat) 2960, 1650, 1620, 1472, 1082, 939, 836, 775, 667 cm^{-1}; HRMS calculated for $C_{18}H_{36}OSi$ $[M+H]^+$: 297.2614; found: 297.2614.

(*2R*,*3E*,*5E*)-1-(*tert*-Butyldimethylsilyloxy)-2,4,6-trimethyl-3,5-decadiene (7o): The title compound was prepared according to Representative Procedure B except that (2*R*,3*Z*,5*E*)-1-(*tert*-

butyldimethylsilyloxy)-2,6-dimethyl-4-bromo-3,5-decadiene (**5o**) was used in place of **5a**. Yield: 89%; Stereoisomeric purity ≥98%; $[\alpha]_D^{23}$ = -12.2° (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 6 H), 0.8-1.0 (m, 15 H), 1.2-1.45 (m, 4 H), 1.62 (s, 3 H), 1.73 (d, *J* = 1.1 Hz, 3 H), 1.95-2.05 (m, 2 H), 2.5-2.65 (m, 1 H), 3.35 (dd, *J* = 7.5 Hz, *J* = 9.5 Hz, 1 H), 3.48 (dd, *J* = 6.0 Hz, *J* = 9.5 Hz, 1 H), 5.00 (d, *J* = 9.5 Hz, 1 H), 5.59 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ -5.37, -5.31, 14.04, 17.38, 17.42, 17.69, 18.34, 22.39, 25.95 (3 C), 30.29, 35.74, 40.33, 67.97, 128.59, 131.70, 133.05, 135.98; IR (neat) 2930, 1662, 1471, 1084, 836, 775, 667 cm^{-1}; HRMS calculated for $C_{19}H_{38}OSi$: 310.2692; found: 310.2696 .

(**2*R*,3*E*,5*Z*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-3,5-decadiene (7p):** The title compound was prepared according to Representative Procedure B except that (2*R*,3*Z*,5*Z*)-1-(*tert*-butyldimethylsilyloxy)-2-methyl-4-bromo-3,5-decadiene (**5p**) was used in place of **5a** and ether was used in place of THF. Yield: 84%; Stereoisomeric purity: 95%; $[\alpha]_D^{23}$ = -6.6° (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ -0.03 (s, 6 H), 0.8-1.0 (m, 15 H), 1.2-1.35 (m, 4 H), 1.71 (s, 3 H), 2.1-2.2 (t, *J* = 6.9 Hz, 2 H), 2.5-2.6 (m, 1 H), 3.33 (dd, *J* = 7.6 Hz, *J* = 9.2 Hz, 1 H), 3.44 (dd, *J* = 6.3 Hz, *J* = 9.2 Hz, 1 H), 5.05 (d, *J* = 9.2 Hz, 1 H), 5.23 (dt, *J* = 7.5 Hz, *J* = 11.7 Hz, 1 H), 5.73 (d, *J* = 11.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -5.38, -5.32, 13.96, 17.07, 17.28, 18.34, 22.37, 25.93 (3 C), 28.34, 32.50, 35.61, 67.85, 130.02, 132.76, 132.81, 133.03; IR (neat) 2998, 1639, 1471, 1087, 836, 775, 666 cm^{-1}; HRMS calculated for $C_{18}H_{36}OSi$ $[M+H]^+$: 297.2614; found: 297.2613.

(*2R*,*3E*,*5Z*)-1-(*tert*-Butyldimethylsilyloxy)-2,4,6-trimethyl-3,5-decadiene (7q): The title compound was prepared according to Representative Procedure B except that (2*R*,3*Z*,5*Z*)-1-(*tert*-butyldimethylsilyloxy)-2,6-dimethyl-4-bromo-3,5-decadiene (**5q**) was used in place of **5a** and ether was used in place of THF. Yield: 85%; Stereoisomeric purity ≥98%; $[\alpha]_D^{23}$ = -9.0° (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 6 H), 0.8-1.05 (m, 15 H), 1.2-1.5 (m, 4 H), 1.69 (s, 3 H), 1.70(d, *J* = 0.9 Hz, 3 H), 2.14 (t, *J* = 7.2 Hz, 2 H), 2.5-2.6 (m, 1 H), 3.34 (dd, *J* = 7.5 Hz, *J* = 9.4 Hz, 1 H), 3.47 (dd, *J* = 6.9 Hz, *J* = 9.4 Hz, 1 H), 4.98 (d, *J* = 9.4 Hz, 1 H), 5.60 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -5.37, -5.32, 14.01, 17.35, 17.39, 18.35, 22.81, 23.90, 25.94 (3 C), 30.84, 32.38, 35.72, 67.93, 129.22, 130.92, 132.95, 136.55; IR (neat) 2959, 1645, 1471, 1084, 837, 776, 651 cm^{-1}; HRMS calculated for $C_{19}H_{38}OSi$: 310.2692; found: 310.2682.

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