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Supporting Information

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Gold(I)-Catalyzed Synthesis of Funtionalized Cyclopentadienes

*Jun Hee Lee and F. Dean Toste**

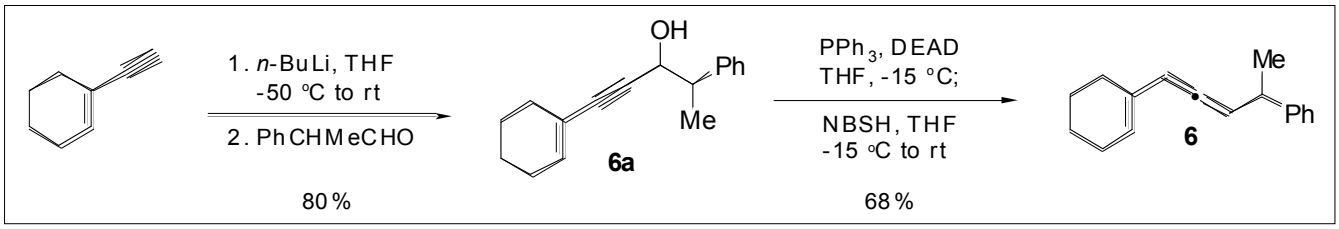
Department of Chemistry, University of California, Berkeley, CA 94720

General Information: Unless otherwise noted all commercial materials were used without purification. Dichloromethane were purchased from EMD and used as is unless otherwise mentioned. THF was distilled from sodium/benzophenone ketyl under a positive pressure of nitrogen prior to use. Silver hexafluoroantimonate ($AgSbF_6$) was obtained from Aldrich Chemical Company and stored in a drybox. Chloro(triphenylphosphine)gold(I) chloride (Ph_3PAuCl) and Chloro(tri-*tert*-butylphosphine)gold(I) chloride (*tert*-Bu_3PAuCl) were prepared according to the literature procedures.[1] Vinylallene **4** was prepared according to the procedure of Palenzuela *et al*[2] and *d*-**4** was also prepared similarly using deurobenzaldehyde.[3] Experiments involving moisture- and/or air-sensitive compounds were performed in oven- or flame-dried glassware with rubber septa under a positive pressure of nitrogen. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as a visualizing agent and phosphomolybdic acid/cerium sulfate in ethanol and sulfuric acid, and heat as developing agent. Flash chromatography was carried out on Merck 60 silica gel (32-63 mm) according to the procedure of Still *et al*.[4] ^{1}H and ^{13}C NMR spectra were recorded with Bruker AVB-400 (400 MHz and 100 MHz, respectively), AVQ-400 (400 MHz and 100 MHz, respectively) and DRX-500 (500 MHz and 125 MHz, respectively) spectrometers. ^{1}H NMR spectra were referenced to residual $CHCl_3$ (7.26 ppm) and are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.0 ppm). 1H and 13C NMR spectra of the *N*-Boc derivatives were obtained at 50 °C to minimize peak broadening. Mass spectral data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley. Optical rotations were determined using a Perkin-Elmer polarimeter and are reported as follows: $[\alpha]_D^{23}$ (concentration *c* = g/100 mL, solvent). HPLC separations were performed on a Shimadzu VP series chiral HPLC using a CHIRALCEL OD and a CHIRALCEL OJ-H column purchased from Daicel Chemical Industries.

General Procedure for the Gold(I)-Catalyzed Cycloisomerization of vinylallene (Table 1, entry 3): A typical procedure is given for the reaction of vinylallene **4**. In a drybox, a 25 mL one-necked round-bottomed flask equipped with a stir bar was charged with silver hexafluoroantimonate (2.1 mg, 6.0 μmol), sealed with a rubber

septum, and removed from the drybox. Chloro(triphenylphosphine)gold(I) chloride (3.0 mg, 6.0 μmol) was added followed by dichloromethane (1.0 mL) and the resulting mixture was stirred at room temperature for 5 min. The mixture was then cooled at 0 °C (ice-water bath) and vinylallene **4** (63 mg, 0.30 mmol) in CH_2Cl_2 (6 mL) was added dropwise via cannula. After stirring at 0 °C for 1 min, the reaction mixture was filtered on a small plug of silica gel and concentrated using a rotatory evaporator. The crude mixture was loaded directly on a short silica gel column and eluted with 5% CH_2Cl_2 in *n*-hexane to give the desired cyclopentadiene **5** (60.5 mg, 96%) as a pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.65 (s, 1H), 2.75 (m, 1H), 3.09 (dd, *J* = 12.4, 5.2 Hz, 1H), 2.39-2.36 (m, 1H), 2.20-2.08 (m, 1H), 1.99 (d, *J* = 10.4 Hz, 1H), 1.93 (s, 3H), 1.81 (d, *J* = 12.8 Hz, 1H), 1.54-1.49 (m, 1H), 1.19 (dt, *J* = 12.8, 4.0 Hz, 1H), 0.88-0.78 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.94, 144.74, 135.73, 130.90, 135.15, 125.88, 122.41, 51.96, 33.47, 31.58, 29.17, 28.72, 26.18, 25.82. HRMS (EI^+) calc'd for $[C_{16}H_{18}]^+$: *m/z* 210.1409, found 210.1411.

Preparation of (4-Cyclohex-1-enyl-1-methylbuta-2,3-dienyl)benzene (6) (Table 2, entry 1).

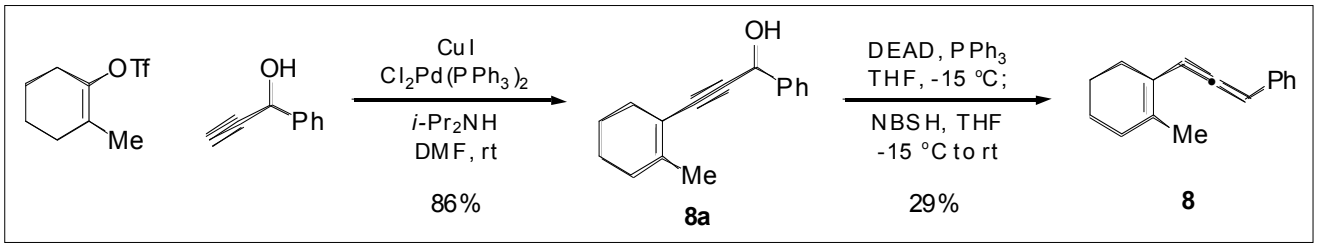


General Procedure for the Preparation of Vinylallene Using Myers' Method: A typical procedure is given for the preparation of vinylallene **6**.[5] DEAD (40 w% in toluene, 3.27 mL, 7.50 mmol, 1.5 equiv) was added to a solution of Ph_3P (1.97 g, 7.50 mmol, 1.5 equiv) in THF (25 mL) at –15 °C. After 10 min, a solution of propargylic alcohol **6a** (1.20 g, 5.00 mmol, 1 equiv) in THF (13 mL) was added to the yellow reaction mixture, followed 10 min later by a solution of NBSH (1.63 g, 7.50 mmol, 1.5 equiv) in THF (16 mL). The resulting suspension was held at –15 °C for 1 h, after which time TLC analysis indicated complete consumption of the starting alcohol. The reaction mixture was slowly warmed to 23 °C and allowed to stand overnight (8-12 h). The reaction mixture was diluted with *n*-hexane (50 mL), washed with an ice cold water (50 mL × 3) and brine (50 mL), and dried over anhydrous $MgSO_4$. Concentration of the reaction mixture and purification of the residue by chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 19:1) afforded two diastereomers of vinylallene **6** as a colorless oil (762 mg, 68%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35-7.26 (m, 4H), 7.24-7.22 (m, 1H), 5.98 (dd, *J* = 6.0, 3.0 Hz, 1H), 5.70 (s, 1H), 5.62-5.60

(m, 1H), 3.53-3.49 (m, 1H), 2.14-2.13 (m, 4H), 1.76-1.68 (m, 2H), 1.66-1.61 (m, 2H), 1.37 (d, *J* = 7.0 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) (major isomer) δ 203.39, 146.19, 132.25, 128.39, 127.11, 126.21, 125.95, 99.66, 99.62, 39.61, 25.84, 25.8, 22.60, 22.47, 21.61. HRMS (EI^+) calc'd for $[C_{17}H_{20}]^+$: *m/z* 224.1565, found 224.1559.

3-(1-Phenylethyl)-4,5,6,7-tetrahydro-3a*H*-indene (7) (Table 2, entry 1): The general procedure was followed with $AgSbF_6$ (23.3 mg, 67.9 μmol), Ph_3PAuCl (33.6 mg, 67.9 μmol), and vinylallene **6** (762 mg, 3.40 mmol) in dichloromethane (40 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 19:1) to afford two diastereomers (d.r. = 1:1.4) of cyclopentadiene **7** as a colorless oil (746 mg, 98%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.31-7.16 (m, 5H), 6.24 (s, 1H, minor), 5.95 (s, 1H, minor), 5.89 (s, 1H, major), 5.85 (s, 1H, major), 3.78-3.71 (m, 1H), 2.63-2.58 (m, 2H), 2.28-2.08 (m, 2H), 1.91-1.88 (m, 1H), 1.72-1.69 (m, 1H), 1.48 (d, *J* = 7.0 Hz, 3H, major), 1.47 (d, *J* = 7.0 Hz, 3H, minor), 1.39-1.23 (m, 1H), 1.18-1.08 (m, 1H), 0.80-0.73 (m, 1H, minor), 0.65-0.56 (m, 1H, major). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 155.46, 155.11, 151.51, 150.73, 147.54, 145.85, 128.35, 128.06, 127.70, 127.31, 125.87, 125.83, 125.57, 124.45, 121.08, 120.82, 53.37, 52.01, 40.29, 39.33, 32.23, 31.85, 29.30, 28.94, 28.88, 25.56, 25.34, 22.51, 21.56. HRMS (EI^+) calc'd for $[C_{17}H_{20}]^+$: *m/z* 224.1565, found 224.1566.

Preparation of [3-(2-Methylcyclohex-1-enyl)propa-1,2-dienyl]benzene (8) (Table 2, entry 2).

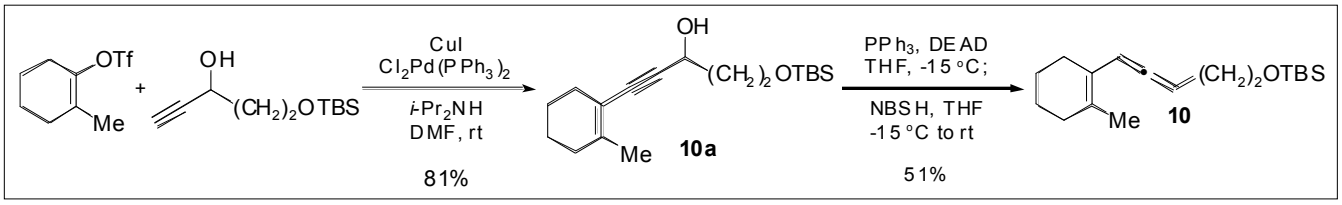


The general procedure was followed with DEAD (40 w% in toluene, 2.61 mL, 6.00 mmol, 3.0 equiv), Ph_3P (1.57 g, 6.00 mmol, 3.0 eq), NBSH (1.30 g, 6.00 mmol, 3.0 equiv), and propargyl alcohol **8a** (453 mg, 2.00 mmol, 1.0 equiv) in THF (39 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 19:1) to afford the desired vinylallene **8** as a pale yellow oil (122 mg, 29%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.30 (m, 4H), 7.21-7.19 (m, 1H), 6.69 (d, *J* = 6.4 Hz, 1H), 6.40 (d, *J* = 6.4 Hz, 1H), 2.15-2.00 (m, 4H), 1.81 (s, 3H), 1.62-1.61 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 207.66, 134.94, 132.12, 128.58, 126.74,

126.61, 123.43, 97.22, 97.17, 32.81, 26.87, 23.02, 22.83, 19.41. HRMS (EI^+) calc'd for $[C_{16}H_{18}]^+$: *m/z* 210.1409, found 210.1411.

3a-Methyl-3-phenyl-4,5,6,7-tetrahydro-3a*H*-indene (9) (Table 2, entry 2): The general procedure was followed with $AgSbF_6$ (1.0 mg, 2.8 μmol), Ph_3PAuCl (1.4 mg, 2.8 μmol), and vinylallene **8** (60 mg, 0.28 mmol) in dichloromethane (5.0 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5:1) to afford the desired cyclopentadiene **9**[6] as a pale yellow oil (55 mg, 92%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 1.5 Hz, 1H), 6.04 (s, 1H), 2.68-2.65 (m, 1H), 2.45 (d, *J* = 13 Hz, 1H), 2.33-2.28 (m, 1H), 2.01-1.99 (m, 1H), 1.67-1.63 (m, 2H), 1.22 (s, 3H), 1.20-1.14 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 159.02, 155.07, 136.31, 128.29, 126.22, 125.99, 125.83, 120.06, 53.30, 38.08, 29.49, 27.09, 21.70, 19.25. HRMS (EI^+) calc'd for $[C_{16}H_{18}]^+$: *m/z* 210.1409, found 210.1405.

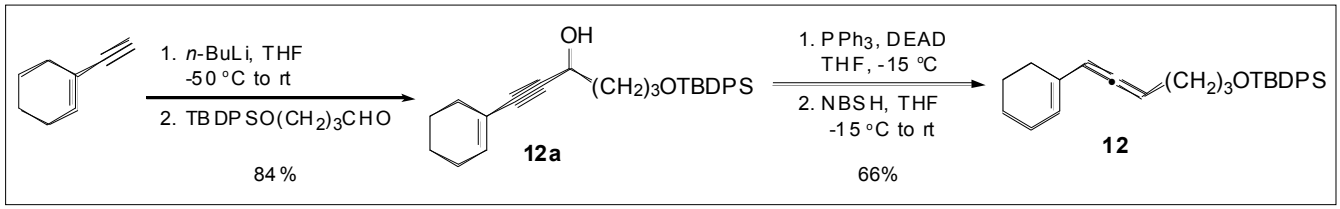
Preparation of *tert*-Butyldimethyl[5-(2-methylcyclohex-1-enyl)penta-3,4-dienyloxy]silane (10) (Table 2, entry 3).



The general procedure was followed with DEAD (40 w% in toluene, 1.74 mL, 4.00 mmol, 2.0 equiv), Ph_3P (1.05 g, 4.00 mmol, 2.0 equiv), NBSH (869 mg, 4.00 mmol, 2.0 equiv), and propargyl alcohol **10a** (617 mg, 2.00 mmol, 1.0 equiv) in THF (30 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5:1) to afford the desired vinylallene **10** as a colorless oil (301 mg, 51%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.78 (s, 1H), 5.636 (s, 1H), 5.36 (d, *J* = 6.0 Hz, 1H), 3.68 (t, *J* = 6.5 Hz, 2H), 2.24 (d, *J* = 4.5 Hz, 2H), 2.09 (s, 2H), 2.01 (s, 2H), 1.64 (d, *J* = 5.5 Hz, 2H), 1.59 (d, *J* = 5.5 Hz, 2H), 0.90 (s, 9H), 0.057 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 204.79, 132.25, 125.55, 97.64, 90.66, 62.94, 32.90, 25.93, 25.82, 25.71, 22.54, 22.49, 18.34, –5.28. HRMS (EI^+) calc'd for $[C_{18}H_{32}OSi]^+$: *m/z* 278.2066, found 278.2065.

***tert*-Butyldimethyl[2-(7a-methyl-5,6,7,7a-tetrahydro-4*H*-inden-1-yl)ethoxy]silane (11) (Table 2, entry 3)**: The general procedure was followed with $AgSbF_6$ (2.1 mg, 6.0 μmol), Ph_3PAuCl (3.0 mg, 6.0 μmol), and vinylallene **10** (88 mg, 0.30 mmol) in dichloromethane (6 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 4:1) to afford the desired cyclopentadiene **11** as a pale yellow oil (55 mg, 62%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.95 (d, *J* = 1.5 Hz, 1H), 5.83 (s, 1H), 3.80 (t, *J* = 7.5 Hz, 2H), 2.56-2.53 (m, 1H), 2.47-2.42 (m, 2H), 2.16-2.12 (m, 1H), 1.90-1.88 (m, 2H), 1.59-1.49 (m, 2H), 1.08-1.00 (m, 1H), 0.97 (s, 3H), 0.91 (s, 9H), 0.79 (td, *J* = 12.5, 4.5 Hz, 1H), 0.077 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 155.27, 154.55, 123.07, 119.38, 62.71, 52.94, 36.76, 30.48, 29.71, 26.81, 25.99, 21.59, 18.37, 18.21, –5.22. HRMS (EI^+) calc'd for $[C_{18}H_{32}OSi]^+$: *m/z* 292.2222, found 292.2229.

Preparation of *tert*-Butyl(6-cyclohex-1-enylhexa-4,5-dienyloxy)diphenylsilane (12) (Table 2, entry 4).

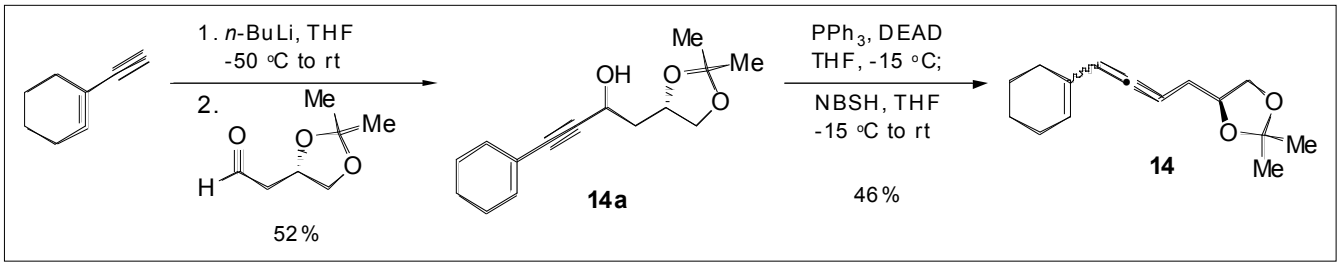


The general procedure was followed with DEAD (0.46 mL, 3.00 mmol, 2.0 equiv), Ph_3P (789 mg, 3.00 mmol, 2.0 equiv), NBSH (652 mg, 3.00 mmol, 2.0 equiv), and propargyl alcohol **12a** (649 mg, 1.50 mmol, 1.0 equiv) in THF (23 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 4:1) to afford the desired vinylallene **12** as a colorless oil (412 mg, 66%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.69-7.66 (m, 4H), 7.44-7.36 (m, 6H), 5.81-5.78 (m, 1H), 5.63 (s, 1H), 5.38-5.34 (m, 1H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.17-2.09 (m, 4H), 2.00-1.98 (m, 2H), 1.73-1.66 (m, 2H), 1.63-1.58 (m, 2H), 1.06 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.14, 135.04, 134.04, 132.43, 129.49, 127.57, 125.42, 98.04, 93.68, 63.31, 31.97, 26.85, 25.80, 25.69, 25.45, 22.54, 22.48, 19.22. HRMS (FAB^+) calc'd for [$C_{24}H_{27}OSi$ = M – *t*-Bu]$^+$: *m/z* 359.1831, found 359.1830.

***tert*-Butyldiphenyl[3-(5,6,7,7a-tetrahydro-4*H*-inden-1-yl)propoxy]silane (13) (Table 2, entry 4):** The general procedure was followed with $AgSbF_6$ (1.0 mg, 3.0 μmol), Ph_3PAuCl (1.5 mg, 3.0 μmol), and vinylallene **12** (125 mg, 0.30 mmol) in dichloromethane (6 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 4:1) to afford the desired cyclopentadiene **13** as a colorless oil (107 mg, 86%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.69-7.67 (m, 4H), 7.44-7.37 (m, 6H), 5.95 (s, 1H), 5.88 (s, 1H), 3.71 (t, *J* = 6.4 Hz, 2H),

2.62-2.60 (m, 1H), 2.46-2.19 (m, 5H), 1.95-1.92 (m, 1H), 1.87-1.70 (m, 3H), 1.46-1.36 (m, 1H), 1.22-1.10 (m, 1H), 1.06 (s, 9H), 0.72 (qd, *J* = 12.4, 3.2 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 151.18, 150.34, 135.58, 134.11, 129.49, 127.57, 124.67, 121.20, 63.71, 53.06, 32.24, 31.76, 29.23, 28.88, 26.87, 25.54, 25.02, 19.22. HRMS (EI^+) calc'd for [$C_{24}H_{27}OSi$ = M – *t*-Bu]$^+$: *m/z* 359.1831, found 359.1833.

Preparation of (4*S*)-4-(3-Cyclohex-1-enylpropa-1,2-dienyl)-2,2-dimethyl[1,3]dioxolane (14) (Table 2, entry 5).

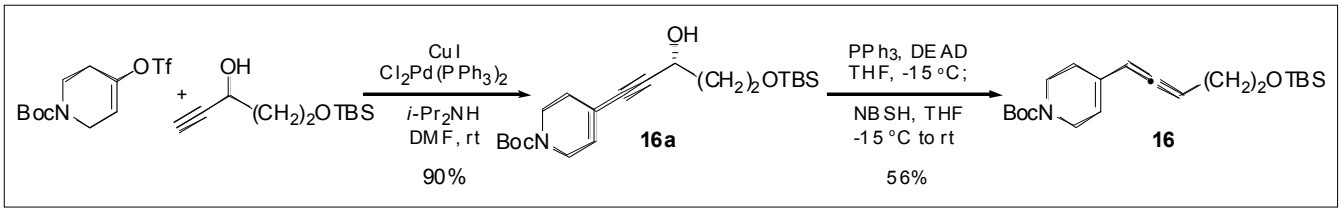


The general procedure was followed with DEAD (0.61 mL, 4.00 mmol, 2.0 equiv), Ph_3P (1.05 g, 4.00 mmol, 2.0 equiv), NBSH (869 mg, 4.00 mmol, 2.0 equiv), and propargyl alcohol **14a** (501 mg, 2.00 mmol, 1.0 equiv) in THF (30 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 15:1) to afford two diastereomeris (d.r. = 1:1) of vinylallene **14** as a yellow oil (218 mg, 46%). $[\alpha]_D^{23}$ = +1.04° (*c* = 1.00, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.82 (t, *J* = 3.2 Hz, 1H), 5.64 (s, 1H), 5.35 (d, *J* = 6.4 Hz, 1H), 4.20-4.14 (m, 1H), 4.08-4.03 (m, 1H), 3.63-3.58 (m, 1H), 2.41-2.35 (m, 1H), 2.28-2.21 (m, 1H), 2.08 (s, 2H), 2.00 (d, *J* = 6.0 Hz, 2H), 1.64-1.56 (m, 4H), 1.41 (s, 3H), 1.34 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 205.08, 205.01, 131.88, 131.81, 126.15, 126.13, 108.82, 108.79, 98.21, 98.15, 89.32, 89.20, 75.29, 75.27, 69.06, 68.97, 33.60, 33.57, 26.83, 26.81, 25.77, 25.68, 25.58, 22.48, 22.38. HRMS (EI^+) calc'd for [$C_{15}H_{22}O_2$]$^+$: *m/z* 234.1620, found 234.1618.

(4*S*)-2,2-Dimethyl-4-(5,6,7,7a-tetrahydro-4*H*-inden-1-ylmethyl)[1,3]dioxolane (15) (Table 2, entry 5): The general procedure was followed with $AgSbF_6$ (2.1 mg, 6.0 μmol), *tert*-Bu_3PAuCl (2.6 mg, 6.0 μmol), and vinylallene **14** (70 mg, 0.30 mmol) in dichloromethane (6 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 12:1) to afford two diastereomers (d.r. = 1:1) of cyclopentadiene **15** as a yellow oil (55 mg, 78%). $[\alpha]_D^{23}$ = +0.30° (*c* = 0.93, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.04 (s, 1H), 5.88 (s, 1H), 4.30-4.22 (m, 1H), 4.07-4.00 (m, 1H), 3.60-3.54 (m, 1H), 2.69 (td, *J* = 16.5, 5.5 Hz, 1H), 2.60 (d, *J* = 10.0

Hz, 1H), 2.51-2.44 (m, 2H), 1.93 (d, *J* = 11.5 Hz, 1H), 1.79 (d, *J* = 13 Hz, 1H), 1.43 (s, 3H), 1.43-1.39 (m, 1H), 1.36 (s, 3H), 1.18-1.10 (m, 1H), 0.76-0.67 (m, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 151.42, 151.07, 146.31, 145.96, 127.17, 126.80, 121.28, 121.18, 108.86, 108.71, 75.63, 75.32, 69.64, 69.35, 53.80, 53.19, 33.47, 33.04, 31.74, 31.63, 30.27, 29.16, 29.00, 28.82, 28.79, 26.98, 26.91, 25.62, 25.60, 25.43, 25.41. HRMS (EI^+) calc'd for $[C_{15}H_{22}O_2]^+$: *m/z* 234.1620, found 234.1618.

Preparation of 4-[5-(*tert*-Butyldimethylsilanyloxy)penta-1,2-dienyl]-3,6-dihydro-2*H*-pyridine-1-carboxylic acid *tert*-butyl ester (16) (Table 2, entry 6).

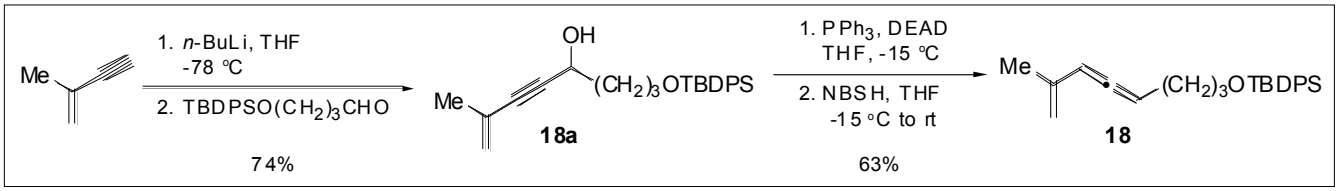


The general procedure was followed with DEAD (40 w% in toluene, 2.38 mL, 5.46 mmol, 2.0 equiv), Ph_3P (1.43 g, 5.46 mmol, 2.0 equiv), NBSH (1.19 g, 5.46 mmol, 2.0 equiv), and propargyl alcohol **16a** (1.08 g, 2.73 mmol, 1.0 equiv) in THF (40 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/EtoOAc = 10:1) to afford the desired vinylallene **16** as a yellow oil (585 mg, 56%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.80 (t, *J* = 3.2 Hz, 1H), 5.52 (s, 1H), 5.40 (d, *J* = 6.8 Hz, 1H), 3.93 (s, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 3.49 (m, 2H), 2.22 (ddd, *J* = 13.2, 6.4, 2.8 Hz, 2H), 2.12 (s, 2H), 1.44 (s, 9H), 0.88 (s, 9H), 0.031 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 205.33, 154.81, 131.30, 121.00, 96.31, 91.54, 79.40, 62.71, 43.66, 40.26, 32.73, 28.45, 28.13, 25.87, 18.25, –5.33. HRMS (EI^+) calc'd for $[C_{17}H_{28}NO_3Si$ = M – *t*-Bu$]^+$: *m/z* 322.1836, found 322.1836.

7-[2-(*tert*-Butyldimethylsilanyloxy)ethyl]-1,3,4,7a-tetrahydro-[2]pyrindine-2-carboxylic acid *tert*-butyl ester (17) (Table 2, entry 6): The general procedure was followed with $AgSbF_6$ (2.1 mg, 6.0 μmol), *tert*-Bu_3PAuCl (2.6 mg, 6.0 μmol), and vinylallene **14** (70 mg, 0.30 mmol) in dichloromethane (6 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 12:1) to afford the desired cyclopentadiene **17** as a pale yellow oil (60 mg, 53%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.13 (s, 1H), 6.01 (s, 1H), 4.65 (s, 1H), 4.30 (s, 1H), 3.74 (td, *J* = 7.2, 2.0 Hz, 2H), 2.75 (dd, *J* = 11.2, 6.8 Hz, 1H), 2.55-2.46 (m, 5H), 1.98 (t, *J* = 12 Hz, 1H), 1.50 (s, 9H), 0.89 (s, 9H), 0.048 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.87, 147.03, 144.95,

128.28, 123.43, 79.70, 63.01, 52.94, 49.21, 46.30, 32.68, 28.96, 28.45, 25.92, 18.25, –5.32. HRMS (EI^+) calc'd for $[C_{17}H_{29}NO_2Si]^+$: *m/z* 323.1917, found 323.1917.

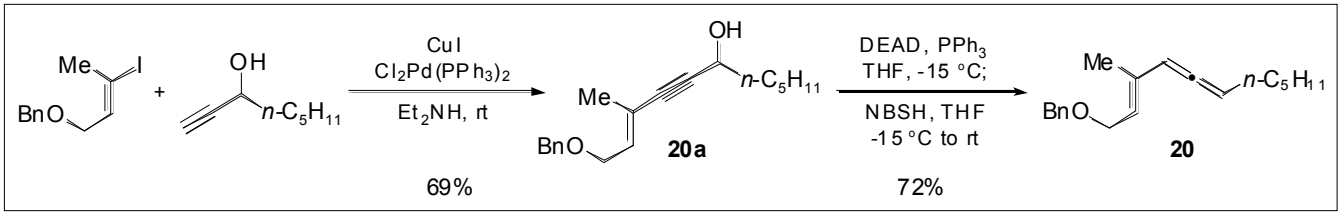
Preparation of *tert*-Butyl(6-cyclohex-1-enylhexa-4,5-dienyloxy)diphenylsilane (18) (Table 2, entry 7).



The general procedure was followed with DEAD (0.61 mL, 4.00 mmol, 2.0 equiv), Ph_3P (1.05 g, 4.00 mmol, 2.0 equiv), NBSH (869 mg, 4.00 mmol, 2.0 equiv), and propargyl alcohol **18a** (783 mg, 2.00 mmol, 1.0 equiv) in THF (30 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 4:1) to afford the desired vinylallene **18** as a colorless oil (473 mg, 63%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.69-7.67 (m, 4H), 7.45-7.40 (m, 6H), 5.90-5.87 (m, 1H), 5.40 (q, *J* = 6.4 Hz, 1H), 4.89 (s, 1H), 4.81 (d, *J* = 1.6 Hz, 1H), 3.72 (t, *J* = 6.4 Hz, 2H), 2.20-2.14 (m, 2H), 1.75 (s, 3H), 1.73-1.68 (m, 2H), 1.07 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 205.74, 139.54, 135.56, 134.00, 129.53, 127.60, 112.89, 97.95, 93.56, 63.26, 31.94, 26.86, 25.20, 19.61, 19.23. HRMS (EI^+) calc'd for [$C_{21}H_{23}OSi$ = M – *t*-Bu]$^+$: *m/z* 319.1518, found 319.1514.

***tert*-Butyl[3-(4-methylcyclopenta-1,3-dienyl)propoxy]diphenylsilane (19) (Table 2, entry 7):** The general procedure was followed with $AgSbF_6$ (2.1 mg, 6.0 μmol), Ph_3PAuCl (3.0 mg, 6.0 μmol), and vinylallene **18** (113 mg, 0.30 mmol) in dichloromethane (6 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 3:1) to afford the desired cyclopentadiene **19** as a colorless oil (81 mg, 72%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (m, 4H), 7.46-7.37 (m, 6H), 5.98 (s, 1H), 5.97 (s, 1H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.74 (s, 2H), 2.44 (t, *J* = 7.6 Hz, 2H), 2.02 (s, 3H), 1.82-1.75 (m, 2H), 1.07 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.57, 142.07, 135.57, 134.07, 129.50, 127.58, 127.05, 126.41, 63.58, 46.51, 32.51, 27.00, 26.86, 19.22, 16.13. HRMS (FAB^+) calc'd for [$C_{21}H_{23}OSi$ = M – *t*-Bu]$^+$: *m/z* 319.1518, found 319.1519.

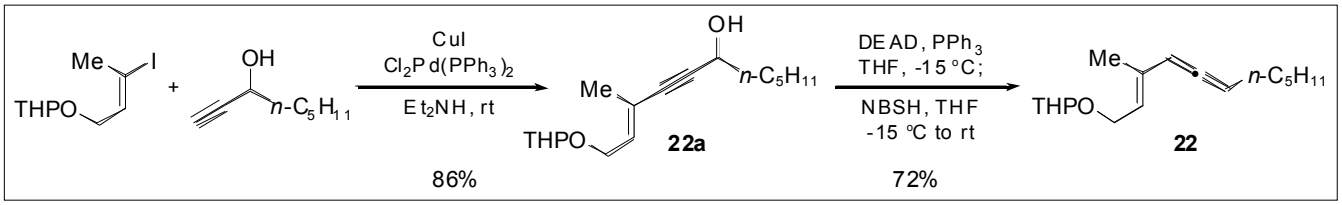
Preparation of (3-Methylundeca-2,4,5-trienyloxymethyl)benzene (20) (Table 2, entry 8).



The general procedure was followed with DEAD (0.61 mL, 4.00 mmol, 2.0 equiv), Ph_3P (1.05 g, 4.00 mmol, 2.0 equiv), NBSH (869 mg, 4.00 mmol, 2.0 equiv), and propargyl alcohol **20a** (573 mg, 2.00 mmol, 1.0 equiv) in THF (30 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/Et_2O = 20:1) to afford the desired vinylallene **20** as a yellow oil (388 mg, 72%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 5.90-5.86 (m, 1H), 5.59 (t, *J* = 6.8 Hz, 1H), 5.42 (q, *J* = 6.4 Hz, 1H), 4.53 (s, 2H), 4.14 (d, *J* = 6.8 Hz, 1H), 2.05-2.01 (m, 2H), 1.72 (s, 3H), 1.46-1.40 (m, 2H), 1.37-1.32 (m, 4H), 0.92-0.89 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 205.50, 138.40, 134.64, 128.33, 127.78, 127.54, 128.31, 72.07, 66.63, 66.06, 31.34, 28.89, 28.77, 22.43, 14.03, 13.85. HRMS (EI^+) calc'd for $[C_{19}H_{26}O]^+$: *m/z* 270.1984, found 270.1987.

(2-Methyl-5-pentylcyclopenta-2,4-dienylmethoxymethyl)benzene (21) (Table 2, entry 8): The general procedure was followed with $AgSbF_6$ (2.7 mg, 7.8 μmol), *tert*-Bu_3PAuCl (3.4 mg, 7.8 μmol), and vinylallene **20** (105 mg, 0.39 mmol) in dichloromethane (8 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/Et_2O = 35:1) to afford the desired cyclopentadiene **21** as a yellow oil (82 mg, 78%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 5H), 6.01-6.00 (m, 2H), 4.53 (s, 2H), 3.65-3.58 (m, 2H), 2.93 (t, *J* = 5.6 Hz, 1H), 2.36-2.22 (m, 2H), 1.99 (s, 3H), 1.56-1.44 (m, 2H), 1.34-1.28 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 205.50, 138.40, 134.64, 128.33, 127.78, 127.54, 128.31, 72.07, 66.63, 66.06, 31.34, 28.89, 28.77, 22.43, 14.03, 13.85. HRMS (EI^+) calc'd for $[C_{19}H_{26}O]^+$: *m/z* 270.1984, found 270.1982.

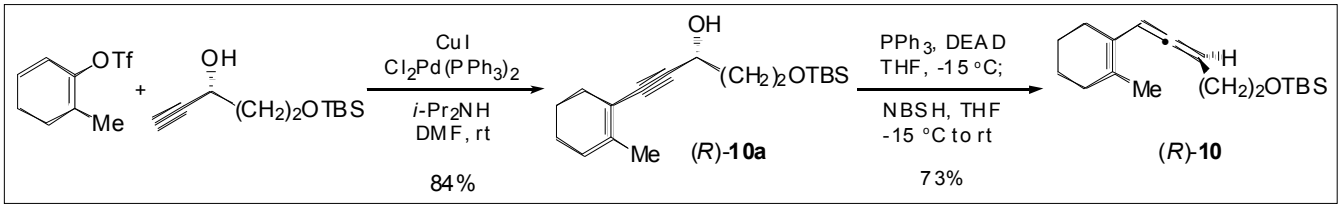
Preparation of 2-(3-Methylundeca-2,4,5-trienyloxy)tetrahydropyran (22) (Table 2, entry 9).



The general procedure was followed with DEAD (0.67 mL, 4.40 mmol, 2.0 equiv), Ph_3P (1.15 g, 4.40 mmol, 2.0 equiv), NBSH (956 mg, 4.40 mmol, 2.0 equiv), and propargyl alcohol **22a** (618 mg, 2.20 mmol, 1.0 equiv) in THF (32 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 9:1) to afford the desired vinylallene **22** as a yellow oil (429 mg, 72%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.85 (t, *J* = 3.0 Hz, 1H), 5.52 (t, *J* = 7.0 Hz, 1H), 5.39 (t, *J* = 6.5 Hz, 1H), 4.64 (d, *J* = 3.0 Hz, 1H), 4.31 (dd, *J* = 12.5, 6.5 Hz, 1H), 4.13-4.09 (m, 1H), 3.90-3.86 (m, 1H), 3.52-3.50 (m, 1H), 2.03-2.02 (m, 2H), 1.84-1.81 (m, 1H), 1.73 (s, 3H), 1.58-1.53 (m, 4H), 1.41 (t, *J* = 7.0 Hz, 2H), 1.30 (d, *J* = 3.5 Hz, 4H), 0.88 (m, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 205.48, 134.53, 123.60, 98.94, 97.83, 94.40, 63.67, 62.23, 62.19, 31.34, 30.65, 28.90, 28.79, 28.77, 25.46, 22.44, 19.52, 19.49, 14.03, 13.76. HRMS (EI^+) calc'd for $[C_{17}H_{28}O_2]^+$: *m/z* 264.2089, found 264.2087.

2-(2-Methyl-5-pentylcyclopenta-2,4-dienylmethoxy)tetrahydropyran (23) (Table 2, entry 9): The general procedure was followed with $AgSbF_6$ (2.1 mg, 6.0 μmol), *tert*-Bu_3PAuCl (2.6 mg, 6.0 μmol), and vinylallene **22** (79 mg, 0.30 mmol) in dichloromethane (6 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 3:2) to afford two diastereomers (d.r. = 1:1) of cyclopentadiene **23** as a yellow oil (69 mg, 87%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.97-5.96 (m, 2H), 4.62-4.60 (m, 1H), 3.89-3.83 (m, 2H), 3.54-3.49 (m, 1H), 3.48-3.42 (m, 1H), 2.97-2.94 (m, 1H), 2.34-2.27 (m, 2H), 2.00 &1.99 (s, 3H), 1.85-1.82 (m, 1H), 1.79-1.67 (m, 1H), 1.62-1.44 (m, 6H), 1.34-1.25 (m, 4H), 0.90-0.87 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.82, 149.55, 144.57, 144.33, 127.03, 126.98, 125.86, 125.85, 98.99, 97.77, 67.52, 67.44, 62.08, 62.05, 55.60, 55.50, 31.80, 31.78, 30.59, 29.84, 29.77, 29.14, 25.51, 22.57, 19.43, 19.40, 15.51, 14.06. HRMS (EI^+) calc'd for $[C_{17}H_{28}O_2]^+$: *m/z* 264.2089, found 264.2095.

Preparation of (*R*)-*tert*-Butyl(6-cyclohex-1-enylhexa-4,5-dienyloxy)diphenylsilane ((*R*)-10) (Eq. 2).



Preparation of (*R*)-5-(*tert*-Butyldimethylsilanyloxy)-1-(2-methylcyclohex-1-enyl)pent-1-yn-3-ol ((*R*)-10a): To a stirred mixture of CuI (33 mg, 172 μmol) and $Cl_2Pd(PPh_3)_2$ (79 mg, 68 μmol) in DMF (3 mL) was added a

solution of 2-methyl-cyclohex-1-enyl trifluoromethanesulfonate (1.12 g, 4.60 mmol) in diisopropylamine (6 mL) via cannula at room temperature. The reaction mixture was stirred for 5 min and then a solution of enantioenriched (*R*)-5-(*tert*-butyldimethylsilanyloxy)pent-1-yn-3-ol (858 mg, 4.00 mmol) in diisopropylamine (6 mL) was added dropwise via cannula at room temperature. After stirring for 90 min, the reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with ether. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated using a rotatory evaporator. The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 9:1) to afford the desired carbinol **(*R*)-10a** as a yellow oil (1.03 g, 84%). Enantiomeric excess was determined to be 94.9% by HPLC analysis using a chiral stationary column [Daicel CHIRALCEL OD column; eluent: *n*-hexane/2-propanol = 99:1; flow rate = 1.0 mL/min; retention time: 6.83 min (major), 9.18 min (minor)]. $[\alpha]_D^{23}$ = +6.7° (*c* = 0.475, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.76 (dd, *J* = 10.5, 6.0 Hz, 1H), 4.07-4.03 (m, 1H), 3.85-3.81 (m, 1H), 3.34 (d, *J* = 6.0 Hz, 1H), 2.11 (s, 2H), 2.04-1.98 (m, 3H), 1.92-1.87 (m, 1H), 1.85 (s, 3H), 1.58-1.57 (m, 4H), 0.89 (s, 9H), 0.077 (s, 3H), 0.071 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.75, 113.70, 91.26, 85.61, 62.35, 61.13, 39.12, 31.16, 29.80, 25.83, 22.47, 22.14, 18.13, –5.55. HRMS (EI$^+$) calc'd for [$C_{17}H_{29}O_2Si$ = M – CH_3]$^+$: *m/z* 293.1937, found 293.1934.

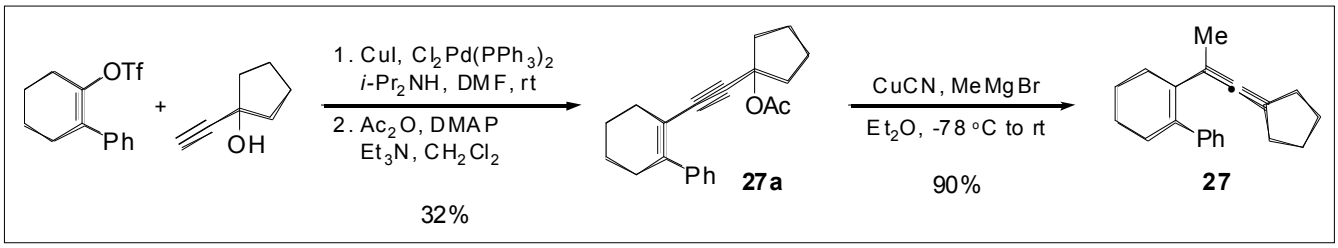
Preparation of (*R*)-*tert*-Butyldimethyl[5-(2-methylcyclohex-1-enyl)penta-3,4-dienyloxy]silane ((*R*)-10): The general procedure was followed with DEAD (40 w% in toluene, 1.74 mL, 4.00 mmol, 2.0 equiv), Ph_3P (1.05 g, 4.00 mmol, 2.0 equiv), NBSH (869 mg, 4.00 mmol, 2.0 equiv), and propargyl alcohol (*R*)-**10a** (617 mg, 2.00 mmol, 1.0 equiv) in THF (30 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5:1) to afford the desired chiral vinylallene (*R*)-**10** as a colorless oil (428 mg, 73%). Enantiomeric excess was determined to be 81.8% by HPLC analysis using a chiral stationary column [Daicel CHIRALCEL OJ-H column; eluent: *n*-hexane/2-propanol = 99.9:0.1; flow rate = 0.6 mL/min; retention time: 38.26 min (major), 41.31 min (minor)] after desilylation with TBAF. $[\alpha]_D^{23}$ = –21.9° (*c* = 0.475, $CHCl_3$).

Chirality Transfer Experiment Using Vinylallene (*R*)-10: In a drybox, a 25 mL one-necked round-bottomed flask equipped with a stir bar was charged with $AgSbF_6$ (2.1 mg, 6.0 μmol), sealed with a rubber septum, and removed from the drybox. Ph_3PAuCl (3.0 mg, 6.0 μmol) was added followed by dichloromethane (1.0 mL) and the resulting mixture was stirred at room temperature for 5 min. The mixture was cooled at –20 °C and enantioenriched vinylallene **(*R*)-10** (88 mg, 0.30 mmol) in CH_2Cl_2 (6 mL) was added dropwise via cannula. After stirring at –20 °C for 20 h, the reaction was quenched with a drop of Et_3N. The reaction mixture was filtered on a small plug of silica gel and concentrated using a rotatory evaporator. The crude mixture was purified by flash

column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5:1) to afford an inseparable mixture of cyclopentadiene **11** and the starting material **10** (64 mg, 72%) as a pale yellow oil. The ratio of **10** and **11** was determined to be 1.0 to 3.1 by 1H NMR. The enatiomeric excesses of both **10** and **11** were determined to zero by HPLC analysis using a chiral stationary column (Daicel CHIRALCEL OJ-H column; eluent: *n*-hexane/2-propanol = 99.9:0.1; flow rate = 0.6 mL/min) after desilylation with TBAF.

Deuterium Labeling Crossover Experiment Using Vinylallenes *d*-4 and 12 (Eq. 3): In a drybox, a 25 mL one-necked round-bottomed flask equipped with a stir bar was charged with $AgSbF_6$ (2.0 mg, 5.8 μmol), sealed with a rubber septum, and removed from the drybox. Ph_3PAuCl (2.9 mg, 5.8 μmol) was added followed by dichloromethane (1.0 mL) and the resulting mixture was stirred at room temperature for 5 min. The reaction flask was then cooled at 0 °C (ice-water bath) and a mixture of *d*-**4** (32 mg, 0.15 mmol) and vinylallene **12** (64 mg, 0.15 mmol) in CH_2Cl_2 (3 mL) was added dropwise via cannula. After stirring at 0 °C for 5 min, the reaction mixture was filtered on a small plug of silica gel and concentrated using a rotatory evaporator. The crude mixture was loaded directly on a short silica gel column and eluted with 20% CH_2Cl_2 in *n*-hexane to afford the mixture of two cyclopentadienes *d*-**5** and **13** (79 mg, 82%) as a pale yellow oil. Complete deuterium incorporation and no crossover was observed in 1H NMR analysis.

Preparation of [2-(2-Cyclopentylidene-1-methylvinyl)cyclohex-1-enyl]benzene (27) (Eq. 4)

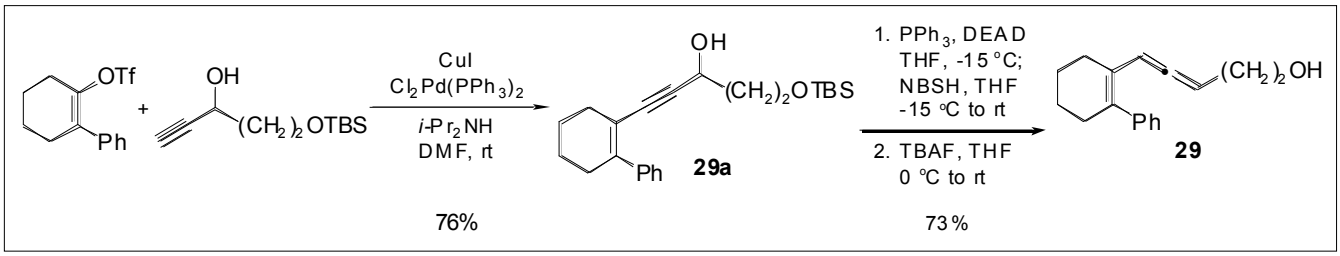


In a drybox, a 250 mL one-necked round-bottomed flask equipped with a stir bar was charged with CuCN (1.00 g, 11.2 mmol, 6.0 equiv), sealed with a rubber septum, and removed from the drybox. The flask was filled with dry ether (28 mL) under nitrogen atmosphere and the resulting mixture was cooled to –30 °C. A solution of methylmagnesium bromide (3.0 M in Et_2O, 7.50 mL, 22.4 mmol, 12.0 equiv) was added dropwise via syringe and the resulting slurry was stirred for 15 min at –30 °C. The mixture was then cooled to –78 °C and a solution of acetate **27a** (576 mg, 1.87 mmol, 1.0 equiv) in ether (15 mL) was added dropwise via cannula. The reaction was

allowed to slowly warm to 0 °C over 3 h and quenched with a saturated aqueous solution of NH_4Cl. The mixture was extracted with ether and the combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. After evaporating the solvent, the crude mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 19:1) to afford the desired vinylallene **27** as a colorless oil (442 mg, 90%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.28-7.25 (m, 2H), 7.20-7.16 (m, 3H), 2.32 (s, 2H), 2.24 (s, 2H), 2.10-2.07 (m, 2H), 1.96-1.92 (m, 2H), 1.73-1.72 (m, 4H), 1.56-1.53 (m, 4H), 1.50 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 197.54, 145.10, 133.35, 133.18, 128.25, 127.71, 125.77, 101.94, 101.86, 32.38, 30.48, 29.77, 26.86, 23.24, 23.05, 19.52. HRMS (EI^+) calc'd for $[C_{20}H_{24}]^+$: *m/z* 264.1878, found 264.1877.

9-Methyl-4a-phenyl-2,3,4,4a,5,6,7,8-octahydro-1*H*-fluorene (28) (Eq. 4): The general procedure was followed with $AgSbF_6$ (2.1 mg, 6.0 μmol), Ph_3PAuCl (3.0 mg, 6.0 μmol), and vinylallene **27** (92.3 mg, 0.349 mmol) in dichloromethane (7 mL). The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 19:1) to afford the ring-enlarged cyclopentadiene **28** as a colorless oil (92.0 mg, 99%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.0 Hz, 2H), 7.15 (t, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 2.74-2.67 (m, 2H), 2.22 (s, 2H), 2.10 (d, *J* = 17.5 Hz, 1H), 1.94-1.81 (m, 2H), 1.89 (s, 3H), 1.70-1.54 (m, 4H), 1.40-1.30 (m, 2H), 1.21-1.13 (m, 1H), 1.02-0.96 (m, 1H), 0.93-0.87 (m, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 148.63, 145.71, 135.77, 131.54, 128.33, 126.76, 125.40, 60.36, 34.43, 29.42, 24.38, 23.13, 23.10, 22.85, 22.36, 21.51, 10.15. HRMS (EI^+) calc'd for $[C_{20}H_{24}]^+$: *m/z* 264.1878, found 264.1875.

Preparation of 5-(2-Phenylcyclohex-1-enyl)penta-3,4-dien-1-ol (27) (Eq. 5)

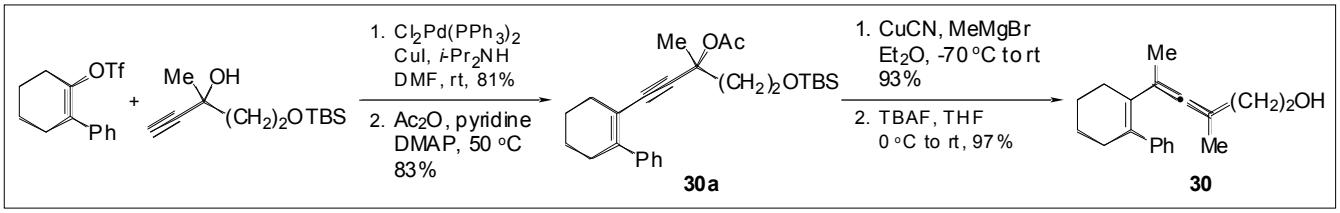


DEAD (40 w% in toluene, 1.48 mL, 3.40 mmol, 1.7 equiv) was added to a solution of Ph_3P (892 mg, 3.40 mmol, 1.7 equiv) in THF (12 mL) at –15 °C. After 10 min, a solution of propargylic alcohol **29a** (741 mg, 2.00 mmol, 1 equiv) in THF (7 mL) was added to the yellow reaction mixture, followed 10 min later by a solution of NBSH (738 mg, 3.40 mmol, 1.7 equiv) in THF (9 mL). The resulting suspension was held at –15 °C for 1 h, after which time

TLC analysis indicated complete consumption of the starting alcohol. The reaction mixture was slowly warmed to 23 °C and allowed to stand overnight. The reaction mixture was diluted with *n*-hexane (50 mL), washed with an ice cold water (50 mL × 3) and brine (50 mL), and dried over anhydrous $MgSO_4$. Concentration of the reaction mixture and purification of the residue by chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5:1) afforded *tert*-butyldimethyl-[5-(2-phenylcyclohex-1-enyl)penta-3,4-dienyloxy]silane as a colorless oil (497 mg, 70%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.26-7.22 (m, 1H), 7.20-7.18 (m, 2H), 5.92-5.90 (m, 1H), 5.35-5.33 (m, 1H), 3.67 (td, *J* = 6.8, 2.0 Hz), 2.36 (s, 2H), 2.26-2.16 (m, 4H), 1.75-1.74 (m, 4H), 0.90 (s, 9H), 0.060 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 205.75, 143.24, 136.08, 128.68, 128.04, 126.91, 126.39, 94.74, 90.27, 62.97, 32.86, 32.73, 26.74, 25.93, 23.30, 22.66, 18.34, –5.27. HRMS (EI$^+$) calc'd for $[C_{23}H_{34}OSi]^+$: *m/z* 354.2379, found 354.2383.

To a stirred solution of *tert*-butyldimethyl[5-(2-phenylcyclohex-1-enyl)penta-3,4-dienyloxy]silane (313 mg, 0.883 mmol, 1.0 equiv) in THF (5 mL) was added a solution of tetra-*n*-butylammonium fluoride (1.0 M in THF, 1.32 mL, 1.32 mmol, 1.5 equiv) at 0 °C (ice-water bath). The ice bath was removed immediately and the reaction mixture was stirred at room temperature for 60 min. The solvent was evaporated and the reaction mixture was purified by chromatography on silica gel (*n*-hexane/EtOAc = 2:1) to afford the desired carbinol **29** as a pale yellow oil (203 mg, 96%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.26-7.22 (m, 1H), 7.18 (d, *J* = 7.0 Hz, 2H), 5.98-5.97 (m, 1H), 5.35 (dd, *J* = 13.0, 6.5 Hz, 1H), 3.71 (s, 2H), 2.37 (s, 2H), 2.30-2.26 (m, 2H), 2.23-2.14 (m, 2H), 1.75-1.74 (m, 4H), 1.58 (br s, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 205.80, 143.07, 136.83, 128.62, 128.07, 126.49, 126.44, 95.43, 90.02, 62.07, 32.73, 32.45, 26.73, 23.20, 22.61. HRMS (EI$^+$) calc'd for $[C_{17}H_{20}O]^+$: *m/z* 240.1514, found 240.1513.

Preparation of 3-Methyl-5-(2-phenylcyclohex-1-enyl)hexa-3,4-dien-1-ol (30) (Eq. 5)



In a drybox, a 250 mL one-necked round-bottomed flask equipped with a stir bar was charged with CuCN (1.34 g, 11.2 mmol, 6.0 equiv), sealed with a rubber septum, and removed from the drybox. The flask was filled with dry

ether (38 mL) under nitrogen atmosphere and the resulting mixture was cooled to –30 °C. A solution of methylmagnesium bromide (2.8 M in Et_2O, 10.7 mL, 30.0 mmol, 12.0 equiv) was added dropwise via syringe and the resulting slurry was stirred for 15 min at –30 °C. The mixture was then cooled to –70 °C and a solution of acetate **30a** (1.07 g, 2.50 mmol, 1.0 equiv) in ether (20 mL) was added dropwise via cannula. The reaction was allowed to slowly warm to 0 °C over 3 h and quenched with a saturated aqueous solution of NH_4Cl. The mixture was extracted with ether and the combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. After evaporating the solvent, the crude mixture was purified by flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5:1 → 4:1) to afford *tert*-butyldimethyl[3-methyl-5-(2-phenylcyclohex-1-enyl)hexa-3,4-dienyloxy]silane as a colorless oil (887 mg, 93%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.21-7.16 (m, 3H), 3.61 (t, *J* = 7.2 Hz, 2H), 2.30-2.15 (m, 2H), 2.01 (t, *J* = 7.2 Hz, 2H), 1.72-1.71 (m, 4H), 1.44 (s, 3H), 1.39 (s, 3H), 0.91 (s, 9H), 0.06 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.81, 144.95, 133.51, 132.86, 128.27, 127.75, 125.91, 101.06, 94.58, 62.17, 37.41, 32.32, 30.32, 30.01, 25.97, 23.24, 23.07, 19.54, 18.77, 18.33, –5.24. HRMS (EI$^+$) calc'd for $[C_{25}H_{38}OSi]^+$: *m/z* 382.2692, found 382.2691.

To a stirred solution of *tert*-butyldimethyl[3-methyl-5-(2-phenylcyclohex-1-enyl)hexa-3,4-dienyloxy]silane (823 mg, 2.15 mmol, 1.0 equiv) in THF (7 mL) was added a solution of tetra-*n*-butylammonium fluoride (1.0 M in THF, 3.23 mL, 3.23 mmol, 1.5 equiv) at 0 °C (ice-water bath). The ice bath was removed immediately and the reaction mixture was stirred at room temperature for 60 min. The solvent was evaporated and the reaction mixture was purified by chromatography on silica gel (*n*-hexane/EtOAc = 3:1) to afford the desired carbinol **30** as a colorless oil (560 mg, 97%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.20-7.16 (m, 3H), 3.56 (d, *J* = 4.8 Hz, 2H), 2.37-2.14 (m, 4H), 2.04-1.93 (m, 2H), 1.72-1.69 (m, 4H), 1.55 (s, 3H), 1.52 (br s, 1H), 1.28 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 201.29, 144.83, 134.31, 132.54, 128.13, 127.87, 125.94, 101.84, 94.23, 60.60, 37.05, 32.27, 29.57, 23.14, 22.96, 19.38, 18.26. HRMS (EI$^+$) calc'd for $[C_{19}H_{24}O]^+$: *m/z* 268.1827, found 268.1828.

2-(7a-Phenyl-5,6,7,7a-tetrahydro-4*H*-inden-1-yl)ethanol (31) (Eq. 5): The general procedure was followed with $AgSbF_6$ (2.1 mg, 6.0 μmol), Ph_3PAuCl (3.0 mg, 6.0 μmol), and vinylallene **29** (72 mg, 0.30 mmol) in dichloromethane (6 mL). The reaction was stirred at 23 °C for 90 min. The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/ EtOAc = 3:1) to afford the cyclopentadienyl carbinol **31** as a pale yellow oil (55 mg, 77%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.5 Hz, 2H), 7.17 ((t, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 2H), 6.10 (s, 1H), 6.03 (s, 1H), 3.54-3.40 (m, 2H), 2.83 (d, *J* = 13 Hz, 1H), 2.61 (d, *J* = 11.5 Hz, 1H), 2.41-2.36 (m, 1H), 2.19-2.13 (m, 1H), 2.01-1.96 (m, 1H), 1.86 (d, J = 11.0 Hz, 1H), 1.67-1.60 (m, 1H), 1.46-1.38

(m, 1H), 1.31 (br s, 1H), 1.24-1.19 (m, 1H), 1.03-0.98 (m, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 156.43, 155.18, 139.12, 128.77, 126.55, 126.23, 124.66, 122.60, 61.79, 61.15, 34.15, 30.56, 29.65, 27.39, 21.89. HRMS (EI^+) calc'd for $[C_{17}H_{20}O]^+$: *m/z* 240.1514, found 240.1511.

3a,8-Dimethyl-3b-phenyl-3,3a,3b,4,5,6,7,8a-octahydro-2*H*-1-oxa-cyclopenta[*a*]indene (32) (Eq. 5): The general procedure was followed with $AgSbF_6$ (1.41 mg, 4.1 μmol), Ph_3PAuCl (2.0 mg, 4.1 μmol), and vinylallene **30** (47 mg, 0.18 mmol) in nitromethane (4 mL). The reaction was stirred at 23 °C for 8 h. The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/ EtOAc = 15:1) to afford a 1:1 diastereomeric mixture of tetrahydrofuran **32** as a pale yellow oil (14 mg, 30%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.34-6.98 (m, 10H), 4.35 (s, 1H), 4.26 (s, 1H), 3.90 (dd, *J* = 9.0, 4.5 Hz, 2H), 3.71-3.66 (m, 1H), 3.63-3.59 (m, 1H), 2.58 (d, *J* = 12.0 Hz, 1H), 2.48-2.45 (m, 1H), 2.44-2.39 (m, 2H), 2.28-2.23 (m, 1H), 2.13-2.07 (m, 1H), 1.76 (s, 3H), 1.74 (s, 3H), 1.71-1.66 (m, 4H), 1.62-1.57 (m, 2H), 1.50-1.46 (m, 2H), 1.43 (s, 3H), 1.42-1.37 (m, 1H), 1.25-1.16 (m, 3H), 0.92-0.89 (m, 1H), 0.76-0.71 (m, 1H), 0.57 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.59, 143.23, 142.28, 138.68, 135.72, 132.38, 131.10, 130.87, 128.50, 128.22, 127.38, 125.77, 125.57, 125.50, 96.66, 95.69, 68.19, 67.34, 58.33, 58.16, 54.72, 53.59, 39.40, 37.63, 37.60, 30.75, 30.29, 29.68, 28.64, 26.63, 25.32, 24.18, 23.25, 22.54, 22.08, 20.59, 11.27, 10.48. HRMS (EI^+) calc'd for $[C_{19}H_{24}O]^+$: *m/z* 268.1827, found 268.1830.

References:

[1] a) M. I. Bruce, B. K. Nicholson, O, Bin Shawkataly *Inorg. Syn*. **1989**, *26*, 324; b) F. Bonati, M. Felici, B. R. Pietroni, A. Burini, *Gazz. Chim. Ital.* **1982**, *112*, 5.

[2] D. Regas, M. N. Afonso, M. L. Rodriguez, J. A. Palenzuela *J. Org. Chem*. **2003**, 68, 7845.

[3] P. L. Polavarapu, L. P. Fontana, H.E. Smith *J. Am. Chem. Soc*. **1986**, *108*, 94.

[4] W. C. Still, M. Kahn, A. Mitra *J. Org. Chem.* **1978**, *43*, 2923.

[5] A. G. Myers, B. Zheng. *J. Am. Chem. Soc*. **1996**, *118*, 4492.

[6] K. Matcheva, M. Beckmann, D. Schomburg, E. Winterfeldt *Synthesis* **1989**, 814.