Gold(I)-Catalyzed Synthesis of Functionalized Cyclopentadienes

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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 (AgSbF₆) was obtained from Aldrich Chemical Company and stored in a drybox. Chloro(triphenylphosphine)gold(I) chloride (Ph₃PAuCl) and Chloro(tri-tert-butylphosphine)gold(I) chloride (tert-Bu₃PAuCl) 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] ¹H and ¹³C 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. ¹H NMR spectra were referenced to residual CHCl₃ (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 ¹³C NMR spectra were measured relative to CDCl₃ (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: [α]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 \( \mu \)mol) 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 \( \text{CH}_2\text{Cl}_2 \) (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% \( \text{CH}_2\text{Cl}_2 \) in \( \text{n-hexane} \) to give the desired cyclopentadiene 5 (60.5 mg, 96%) as a pale yellow oil.

\[ \begin{align*}
{^1}^\text{H-NMR} &\quad (400 \text{ MHz, CDCl}_3) \delta 7.42 (d, J = 7.2 \text{ Hz}, 2\text{H}), 7.32 (t, J = 7.6 \text{ Hz}, 2\text{H}), 7.17 (t, J = 7.2 \text{ Hz}, 1\text{H}), 6.65 (s, 1\text{H}), 2.75 (m, 1\text{H}), 3.09 (dd, J = 12.4, 5.2 \text{ Hz}, 1\text{H}), 2.39-2.36 (m, 1\text{H}), 2.20-2.08 (m, 1\text{H}), 1.99 (d, J = 10.4 \text{ Hz}, 1\text{H}), 1.93 (s, 3\text{H}), 1.81 (d, J = 12.8 \text{ Hz}, 1\text{H}), 1.54-1.49 (m, 1\text{H}), 1.19 (dt, J = 12.8, 4.0 \text{ Hz}, 1\text{H}), 0.88-0.78 (m, 1\text{H}).
\end{align*} \]

13C-NMR (100 MHz, CDCl3) \( \delta \) 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 [\( \text{C}_{16}\text{H}_{18}\)]⁺: \( m/z \) 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. DEAD (40 w% in toluene, 3.27 mL, 7.50 mmol, 1.5 equiv) was added to a solution of Ph₃P (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 \( \text{n-hexane} \) (50 mL), washed with an ice cold water (50 mL × 3) and brine (50 mL), and dried over anhydrous MgSO₄. Concentration of the reaction mixture and purification of the residue by chromatography on silica gel (\( \text{n-hexane/CH}_2\text{Cl}_2 = 19:1 \)) afforded two diastereomers of vinylallene 6 as a colorless oil (762 mg, 68%). 

\[ \begin{align*}
{^1}^\text{H-NMR} &\quad (500 \text{ MHz, CDCl}_3) \delta 7.35-7.26 (m, 4\text{H}), 7.24-7.22 (m, 1\text{H}), 5.98 (dd, J = 6.0, 3.0 \text{ Hz}, 1\text{H}), 5.70 (s, 1\text{H}), 5.62-5.60
\end{align*} \]
3-(1-Phenylethyl)-4,5,6,7-tetrahydro-3aH-indene (7) (Table 2, entry 1): The general procedure was followed with AgSbF₆ (23.3 mg, 67.9 µmol), Ph₃PAuCl (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/CH₂Cl₂ = 19:1) to afford two diastereomers (d.r. = 1:1.4) of cyclopentadiene 7 as a colorless oil (746 mg, 98%). ¹H-NMR (500 MHz, CDCl₃) 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). ¹³C-NMR (125 MHz, CDCl₃) δ 155.46, 155.11, 151.51, 150.73, 147.54, 145.85, 128.35, 128.06, 127.70, 127.31, 125.87, 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 [C₁₇H₂₀]⁺: m/z 224.1565, found 224.1559.

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), Ph₃P (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/CH₂Cl₂ = 19:1) to afford the desired vinylallene 8 as a pale yellow oil (122 mg, 29%). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) δ 207.66, 134.94, 132.12, 128.58, 126.74,
3a-Methyl-3-phenyl-4,5,6,7-tetrahydro-3aH-indene (9) (Table 2, entry 2): The general procedure was followed with AgSbF₆ (1.0 mg, 2.8 μmol), Ph₃PAuCl (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/CH₂Cl₂ = 5:1) to afford the desired cyclopentadiene 9 as a pale yellow oil (55 mg, 92%). ¹H-NMR (500 MHz, CDCl₃) 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). ¹³C-NMR (125 MHz, CDCl₃) δ 159.02, 155.07, 136.31, 128.29, 126.22, 125.99, 125.83, 125.99, 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 [C₁₆H₁₈]⁺: m/z 210.1409, found 210.1411.

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), Ph₃P (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/CH₂Cl₂ = 5:1) to afford the desired vinylallene 10 as a colorless oil (301 mg, 51%). ¹H-NMR (500 MHz, CDCl₃) 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). ¹³C-NMR (125 MHz, CDCl₃) δ 204.79, 132.25, 125.55, 97.64, 90.66, 62.94, 32.90, 25.93, 25.71, 25.71, 22.54, 22.49, 18.34, -5.28. HRMS (EI⁺) calc’d for [C₁₈H₃₂OSi]⁺: m/z 278.2066, found 278.2065.
**tert-Butyldimethyl[2-(7a-methyl-5,6,7a-tetrahydro-4H-inden-1-yl)ethoxy]silane (11) (Table 2, entry 3):** The general procedure was followed with AgSbF₆ (2.1 mg, 6.0 µmol), Ph₃PAuCl (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/CH₂Cl₂ = 4:1) to afford the desired cyclopentadiene 11 as a pale yellow oil (55 mg, 62%). ¹H-NMR (500 MHz, CDCl₃) 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), 2.42–2.41 (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), 0.90 (td, J = 12.5, 4.5 Hz, 1H), 0.077 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃) 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 [C₁₈H₃₂OSi]⁺: m/z 292.2222, found 292.2229.

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

![Diagram](image)

The general procedure was followed with DEAD (0.46 mL, 3.00 mmol, 2.0 equiv), Ph₃P (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/CH₂Cl₂ = 4:1) to afford the desired vinylallene 12 as a colorless oil (412 mg, 66%). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 [C₂₄H₂₉OSi = M – t-Bu]⁺: m/z 359.1831, found 359.1830.

**tert-Butyldiphenyl[3-(5,6,7a-tetrahydro-4H-inden-1-yl)propoxy]silane (13) (Table 2, entry 4):** The general procedure was followed with AgSbF₆ (1.0 mg, 3.0 µmol), Ph₃PAuCl (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/CH₂Cl₂ = 4:1) to afford the desired cyclopentadiene 13 as a colorless oil (107 mg, 86%). ¹H-NMR (400 MHz, CDCl₃) 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). $^1$$^3$C-NMR (100 MHz, CDCl$_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 (4S)-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$_3$P (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 diastereomers (d.r. = 1:1) of vinylallene 14 as a yellow oil (218 mg, 46%). $[^1$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, 98.32, 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.

(4S)-2,2-Dimethyl-4-(5,6,7,7a-tetrahydro-4H-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$_3$PAuCl (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%). $[^1$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). $^1$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-Butyldimethylsilyloxy)penta-1,2-dienyl]-3,6-dihydro-2H-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$_3$P (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/EtOAc = 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). $^1$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$_3$Si = M – t-Bu$^+$]: m/z 322.1836, found 322.1836.

7-[2-(tert-Butyldimethylsilyloxy)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-But$_3$PAuCl (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). $^1$C-NMR (100 MHz, CDCl$_3$) δ 154.87, 147.03, 144.95,
HRMS (El⁺) calc’d for [C₁₇H₂₉NO₂Si]⁺: 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), Ph₃P (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/CH₂Cl₂ = 4:1) to afford the desired vinylallene 18 as a colorless oil (473 mg, 63%). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 (El⁺) calc’d for [C₂₁H₂₃OSi = 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 AgSbF₆ (2.1 mg, 6.0 µmol), Ph₃PAuCl (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/CH₂Cl₂ = 3:1) to afford the desired cyclopentadiene 19 as a colorless oil (81 mg, 72%). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 [C₂₁H₂₃OSi = M–t-Bu]⁺: m/z 319.1518, found 319.1519.
Preparation of (3-Methylundeca-2,4,5-trienyloxy)methyl)benzene (20) (Table 2, entry 8).

![Chemical diagram](attachment:image.png)

The general procedure was followed with DEAD (0.61 mL, 4.00 mmol, 2.0 equiv), Ph₃P (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/Et₂O = 20:1) to afford the desired vinylallene 20 as a yellow oil (388 mg, 72%).¹H-NMR (400 MHz, CDCl₃) 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).¹³C-NMR (100 MHz, CDCl₃) 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 [C₁₉H₂₈O]⁺: m/z 270.1984, found 270.1987.

(2-Methyl-5-pentylcyclopenta-2,4-dienyloxy)methyl]benzene (21) (Table 2, entry 8): The general procedure was followed with AgSbF₆ (2.7 mg, 7.8 µmol), tert-Bu₃PAuCl (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/Et₂O = 35:1) to afford the desired cyclopentadiene 21 as a yellow oil (82 mg, 78%).¹H-NMR (400 MHz, CDCl₃) 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).¹³C-NMR (100 MHz, CDCl₃) 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 [C₁₉H₂₆O]⁺: m/z 270.1984, found 270.1982.

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

![Chemical diagram](attachment:image.png)
The general procedure was followed with DEAD (0.67 mL, 4.40 mmol, 2.0 equiv), Ph₃P (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%). ¹H-NMR (500 MHz, CDCl₃) 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). ¹³C-NMR (125 MHz, CDCl₃) 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 (El⁺) calc’d for [C₁₁H₂₈O₂]⁺: 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 AgSbF₆ (2.1 mg, 6.0 µmol), tert-But₂PAuCl (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/CH₂Cl₂ = 3:2) to afford two diastereomers (d.r. = 1:1) of cyclopentadiene 23 as a yellow oil (69 mg, 87%). ¹H-NMR (400 MHz, CDCl₃) δ 5.97-5.96 (m, 2H), 4.62 (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). ¹³C-NMR (100 MHz, CDCl₃) 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 (El⁺) calc’d for [C₁₁H₂₈O₂]⁺: m/z 264.2089, found 264.2095.

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

![Chemical Reaction Diagram](attachment:image.png)

Preparation of (R)-5-(tert-Butyldimethylsilanyloxy)-1-(2-methylcyclohex-1-enyl)pent-1-yn-3-ol ((R)-10a): To a stirred mixture of Cul (33 mg, 172 µmol) and Cl₂Pd(PP₃)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-butyldimethylsilyloxy)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 NH₄Cl and extracted with ether. The combined organic layers were washed with brine, dried over anhydrous MgSO₄, 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)]. [α]D²³ = +6.7° (c = 0.475, CHCl₃). ¹H-NMR (500 MHz, CDCl₃) 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). ¹³C-NMR (125 MHz, CDCl₃) 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 [C₁₇H₂₉O₂Si = M – CH₃]⁺: 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), Ph₃P (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/CH₂Cl₂ = 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. [α]D²³ = −21.9° (c = 0.475, CHCl₃).

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 AgSbF₆ (2.1 mg, 6.0 μmol), sealed with a rubber septum, and removed from the drybox. Ph₃PAuCl (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 CH₂Cl₂ (6 mL) was added dropwise via cannula. After stirring at −20 °C for 20 h, the reaction was quenched with a drop of Et₃N. 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/CH₂Cl₂ = 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 enantiomeric 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 AgSbF₆ (2.0 mg, 5.8 µmol), sealed with a rubber septum, and removed from the drybox. Ph₃PAuCl (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 CH₂Cl₂ (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% CH₂Cl₂ 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-eny]benzene (27) (Eq. 4)

![Reactions](image)

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 Et₂O, 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 NH₄Cl. The mixture was extracted with ether and the combined organic layers were washed with brine and dried over anhydrous MgSO₄. After evaporating the solvent, the crude mixture was purified by flash column chromatography on silica gel (n-hexane/CH₂Cl₂ = 19:1) to afford the desired vinylallene 27 as a colorless oil (442 mg, 90%). ¹H-NMR (500 MHz, CDCl₃) 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). ¹³C-NMR (125 MHz, CDCl₃) 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 [C₂₀H₂₄]⁺: m/z 264.1878, found 264.1877.

9-Methyl-4a-phenyl-2,3,4,4a,5,6,7,8-octahydro-1H-fluorene (28) (Eq. 4): The general procedure was followed with AgSbF₆ (2.1 mg, 6.0 μmol), Ph₃PAuCl (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/CH₂Cl₂ = 19:1) to afford the ring-enlarged cyclopentadiene 28 as a colorless oil (92.0 mg, 99%). ¹H-NMR (500 MHz, CDCl₃) δ 7.28 (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). ¹³C-NMR (125 MHz, CDCl₃) 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 [C₂₀H₂₄]⁺: m/z 264.1878, found 264.1875.

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

![Chemical Reaction Diagram]

DEAD (40 w% in toluene, 1.48 mL, 3.40 mmol, 1.7 equiv) was added to a solution of Ph₃P (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 MgSO4. Concentration of the reaction mixture and purification of the residue by chromatography on silica gel (n-hexane/CH2Cl2 = 5:1) afforded tert-butyl(dimethyl)[5-(2-phenylcyclohex-1-enyl)penta-3,4-dienyloxy]silane as a colorless oil (497 mg, 70%). 1H-NMR (500 MHz, CDCl3) 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). 13C-NMR (125 MHz, CDCl3) 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 [C23H34OSi]+: m/z 354.2379, found 354.2383.

To a stirred solution of tert-butyl(dimethyl)[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%). 1H-NMR (500 MHz, CDCl3) 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). 13C-NMR (125 MHz, CDCl3) 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 [C17H20O]+: 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 Et₂O, 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 NH₄Cl. The mixture was extracted with ether and the combined organic layers were washed with brine and dried over anhydrous MgSO₄. After evaporating the solvent, the crude mixture was purified by flash column chromatography on silica gel (n-hexane/CH₂Cl₂ = 5:1 → 4:1) to afford tert-butylidimethyl[3-methyl-5-(2-phenylcyclohex-1-enyl)hexa-3,4-dienyloxy]silane as a colorless oil (887 mg, 93%). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 [C₂₃H₃₅OSi]+: m/z 382.2692, found 382.2691.

To a stirred solution of tert-butylidimethyl[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%). ¹H-NMR (500 MHz, CDCl₃) 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). ¹³C-NMR (125 MHz, CDCl₃) 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 [C₁₉H₂₄O⁺]: m/z 268.1827, found 268.1828.

2-(7a-Phenyl-5,6,7,7a-tetrahydro-4H-inden-1-yl)ethanol (31) (Eq. 5): The general procedure was followed with AgSbF₆ (2.1 mg, 6.0 µmol), Ph₃PAuCl (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%). ¹H-NMR (500 MHz, CDCl₃) δ 7.26 (t, J = 7.5 Hz, 2H), 7.17 (tt, 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-2H-1-oxa-cyclopenta[a]indene (32) (Eq. 5): The general procedure was followed with AgSbF$_6$ (1.41 mg, 4.1 µmol), Ph$_3$PAuCl (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), 3.59 (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:


