Palladium-Catalyzed Approach to Allenic Aromatic Ethers
and First Total Syntheses of Terricollene A

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General Information. NMR spectra were taken with a Bruker-400 spectrometer (400 MHz for $^1$H NMR; 100 MHz for $^{13}$C NMR; 376 MHz for $^{19}$F NMR) in CDCl$_3$. All $^1$H NMR experiments were measured with tetramethylsilane (0 ppm) in CDCl$_3$ as the internal reference; $^{13}$C NMR experiments were measured in relative to the signal of CDCl$_3$ (77.0 ppm); $^{19}$F NMR experiments were measured in relative to the signal of CFCl$_3$ (0 ppm) in CDCl$_3$. All reactions were carried out in flame-dried Schlenk tubes. Pd$_2$(dba)$_3$ was purchased from Alfa Aesar (China) Chemical Co. Ltd.; Xantphos was purchased from J&K Chemicals; methyl (E)-3-(4-hydroxyphenyl)acrylate was purchased from Energy Chemical; Diethyl ether (Et$_2$O), ethyl tert-butyl ether (MTBE), and 1,4-dioxane were dried over sodium wire with benzophenone as the indicator and distilled freshly before use. Petroleum ether (60 °C - 90 °C) was used for chromatography. Recoveries of substrates were determined by $^1$H NMR analysis using nitromethane as the internal standard.
Table S1. Optimization of the reaction condition

![Diagram of reaction]

| Ligand:          | Yield | Recovery |
|------------------|-------|----------|
| 1aa              | 2%    | 97%      |
| 2a'              | 2%    | 98%      |
| 3aa              | 9%    | 85%      |
| 4a               | 2%    | 87%      |
| 5aa              | 2%    | 97%      |
| 6aa              | 7%    | 84%      |
| 7aa              |       | 100%     |
| 8aa              |       | 98%      |
| 9aa              |       | 99%      |

4 Reaction condition: 1a (0.2 mmol), 2a (0.4 mmol), CuI (5 mol%), ligand (10 mol %), Cs2CO3 (2.0 equiv.), toluene (0.2 mL), 90 °C, 24 h; Yield and recovery of 1a' were determined by 1H-NMR analysis using CH2Br2 as internal standard.

Buchwald's condition 1:1

![Diagram of reaction]
Buchwald's condition:\textsuperscript{2} reported

\begin{align*}
\text{Br} & \quad \text{HO-CH=CH} \\
\text{OMe} & \quad (2.0 \text{ equiv.}) \\
\text{1a''}, \ 1 \text{ mmol} & \quad 2b' \\
\end{align*}

\begin{align*}
\text{Pd(OAc)}_2 (2 \text{ mol%}) & \quad \text{Ligand (7.5 mol%)} \\
\text{Cs}_2\text{CO}_3 (1.5 \text{ equiv.}) & \\
\text{Toluene (1.0 mL), 70 }^\circ\text{C} & \\
\text{OMe} & \quad \text{Pr} \\
\text{Pr} & \quad \text{Pr} \\
\text{3aa''}, \ 84\% \text{ yield} & \quad \text{Ligand:} \\
\end{align*}

\begin{align*}
\text{Br} & \quad \text{HO-CH=CH} \\
\text{OMe} & \quad (2.0 \text{ equiv.}) \\
\text{1a''}, \ 1 \text{ mmol} & \quad 2a' \\
\text{Pd(OAc)}_2 (2 \text{ mol%}) & \quad \text{Ligand (7.5 mol%)} \\
\text{Cs}_2\text{CO}_3 (1.5 \text{ equiv.}) & \\
\text{Toluene (1.0 mL), 70 }^\circ\text{C} & \\
\text{OMe} & \quad \text{Pr} \\
\text{Pr} & \quad \text{Pr} \\
\text{3aa, complicated} & \quad \text{Ligand:} \\
\end{align*}

Ma's condition:\textsuperscript{3} reported

\begin{align*}
\text{I} & \quad \text{OH} \\
\text{OMe} & \quad \text{Bu} \\
\text{1a'}, \ 2 \text{ mmol} & \quad 1a'' \quad (1.5 \text{ equiv.}) \\
\text{Cul (2 mol%)} & \quad \text{Ligand (7.5 mol%)} \\
\text{Cs}_2\text{CO}_3 (2.0 \text{ equiv.}) & \\
\text{Dixoane (4 mL), 90 }^\circ\text{C} & \\
\text{OMe} & \quad \text{Ligand:} \\
\text{3aa''}, \ 82\% \text{ yield} & \quad \text{HCl} \\
\end{align*}

\begin{align*}
\text{I} & \quad \text{OH} \\
\text{OMe} & \quad \text{Bu} \\
\text{1a'}, \ 1 \text{ mmol} & \quad 2a' \quad (1.5 \text{ equiv.}) \\
\text{Cul (2 mol%)} & \quad \text{Ligand (7.5 mol%)} \\
\text{Cs}_2\text{CO}_3 (2.0 \text{ equiv.}) & \\
\text{Dixoane (4 mL), 90 }^\circ\text{C} & \\
\text{OMe} & \quad \text{Ligand:} \\
\text{3aa, 2\% yield} & \\
\text{recovery of 1a' = 98\%} & \quad \text{HCl} \\
\end{align*}
Experimental details and analytical data

1. Synthesis of allenyllic carbonates

(1) Preparation of methyl 2,3-tetradecadienyl carbonate (2c) (hcf-4-139)

Typical Procedure I: To an oven-dried Schlenk tube with a reflux condenser, CuI (5.714 g, 30 mmol), 1-undecanal (19.8 mL, d = 0.825 g/mL, 16.335 g, 96 mmol), diisobutylamine (15.0 mL, d = 0.74 g/mL, 11.1 g, 84 mmol), 2-propyn-1-ol (3.50 mL, d = 0.963 g/mL, 3.3705 g, 60 mmol), and dioxane (30 mL) were sequentially added under argon atmosphere. After being stirred in an oil bath preheated at 130 °C for 12 h, the reaction was complete as monitored by TLC. After cooling to room temperature, the resulting mixture was filtrated through a short pad of celite eluted with Et2O (20 mL × 3). The filtrate was washed with an aqueous solution of hydrochloric acid (2 M, 40 mL × 3). The organic layer was washed with brine (40 mL) and dried over anhydrous Na2SO4. After filtration and evaporation, the residue was purified by chromatography on silica gel to afford tetradeca-2,3-dien-1-ol (5.7272 g) as an oil [eluent: petroleum ether/ethyl acetate = 80:1 (400 mL), 60/1 (1800 mL)], which was used in the next step without further purification.

Typical Procedure II: To a round bottom flask were added DMAP (662.9 mg, 5.4 mmol), tetradeca-2,3-dien-1-ol (5.7272 mg, 27 mmol), pyridine (4.3 mL, d = 0.983 g/mL, 4.2269 g, 54 mmol), and DCM (100 mL) sequentially. After the resulting mixture was stirred at 0 °C with an ice-water bath for 10 min, methyl chloroformate (6.3 mL, d = 1.22 g/mL, 7.686 g, 81 mmol) was added dropwise over 5 min. After the addition, the resulting mixture was removed from the cooling bath and allowed to warm up to room temperature gradually. The reaction was complete after being stirred at room temperature for 4 h as monitored by TLC. The resulting mixture was quenched with an aqueous solution of hydrochloric acid (1 M, 60 mL). The organic layer was separated and the aqueous layer was extracted with DCM (30 mL) for three
times. The combined organic layer was washed with brine (40 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration and evaporation, the residue was purified by flash chromatography on silica gel to afford 2c (4.6373 g, overall yield of two steps: 29%) as an oil [eluent: petroleum ether/DCM = 20:1 (2000 mL)]: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 5.34-5.19 (m, 2 H, 2 x =CH), 4.67-4.52 (m, 2 H, OCH$_2$), 3.78 (s, 3 H, OCH$_3$), 2.07-1.94 (m, 2 H, CH$_2$), 1.48-1.06 (m, 16 H, 8 x CH$_2$), 0.88 (t, $J = 6.6$ Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 205.7, 155.6, 93.1, 86.4, 66.4, 54.7, 31.9, 29.6, 29.4, 29.3, 29.0, 28.9, 28.2, 22.6, 14.0; MS (ESI) $m/z$ : 291 (M+Na)$^+$, 286 (M+NH$_4^+$); IR (neat): $\nu$ = 2955, 2923, 2854, 1966, 1749, 1444 cm$^{-1}$; HRMS calcld for C$_{16}$H$_{29}$O$_3$ [M+H]$^+$: 269.2111, found: 269.2111.

(2) Preparation of methyl 4-(4-methoxyphenyl)buta-2,3-dienyl carbonate (2h) (lj-4-176)$^5$

Typical Procedure III: To an oven-dried Schlenk tube with a polytetrafluoroethylene plug were added diphenylprolinol (10.1342 g, 40 mmol) and CuBr$_2$ (3.5736 g, 16 mmol, in glove box). After replacing air with argon for three times at rt under vacuum, 4-methoxybenzaldehyde (7.3 mL, $d = 1.121$ g/mL, 8.1833 g, 60 mmol), 2-propyn-1-ol (3.5 mL, $d = 0.963$ g/mL, 3.3705 g, 60 mmol), and dioxane (15.0 mL) were added sequentially. The Schlenk tube was then sealed by screwing the polytetrafluoroethylene plug tightly. After being vigorously stirred in an oil bath preheated at 70 °C for 24 h, the reaction was complete as monitored by TLC and the resulting mixture was diluted with Et$_2$O (100.0 mL) and washed with an aqueous solution of hydrochloric acid (2 M, 100.0 mL). The organic layer was separated and the aqueous layer was extracted with Et$_2$O (100.0 mL) for three times. The combined organic layer was washed with brine (100 mL) and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was purified by flash
chromatography on silica gel to afford 4-(4-methoxyphenyl)-2,3-butadien-1-ol (4.4054 g) [eluent: petroleum ether/ethyl acetate = 40:1 (820 mL), 5/1 (960 mL)] as an oil, which was used in the next step without further purification.

**Following Typical Procedure II**, the reaction of DMAP (611.2 mg, 5.0 mmol), pyridine (4.0 mL, d = 0.983 g/mL, 3.9550 g, 50 mmol), DCM (80 mL), and methyl chloroformate (5.8 mL, d = 1.223 g/mL, 7.0871 g, 75 mmol) afforded 2h (2.1803 g, overall yield of two steps: 36%) as an oil [eluent: petroleum ether/DCM = 20:1 (420 mL), 10/1 (1760 mL), 5/1 (480 mL)]: \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 7.21\) (d, \(J = 8.8\) Hz, 2 H, Ar-H), 6.85 (d, \(J = 8.8\) Hz, 2 H, Ar-H), 6.32-6.24 (m, 2 H, =CH), 5.71 (q, \(J = 6.5\) Hz, 1 H, =CH), 4.80-4.60 (m, 2 H, OCH\(_2\)), 3.86-3.70 (m, 6 H, 2 x OCH\(_3\)); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta = 206.2, 159.1, 155.5, 128.1, 125.3, 114.2, 96.1, 90.5, 65.5, 55.3, 54.8\); \(\text{IR}\) (neat): \(\nu = 3003, 2955, 2840, 1952, 1746, 1695, 1604, 1510, 1447, 1367, 1244, 1171, 1109, 1028\) cm\(^{-1}\); \(\text{MS}\) (70 eV, EI) \(m/z\) (%): 234 (M\(^+\), 58.07), 115 (100); \(\text{HRMS}\) calcd. for C\(_{13}\)H\(_{14}\)O\(_4\) [M\(^+\)]: 234.0887, found 234.0882.

(3) Preparation of methyl 4-(4-trifluoromethylphenyl)buta-2,3-dienyl carbonate (2l) (whn-2-192)

Following **Typical Procedure III**, the reaction of diphenylprolinol (10.1351 g, 40 mmol), CuBr\(_2\) (3.5644 g, 16 mmol), 4-trifluoromethylbenzaldehyde (10.6746 g, 60 mmol), 2-propyn-1-ol (3.5217 g, 45 mmol), and dioxane (120 mL) afforded 4-(4-(trifluoromethyl)phenyl)-2,3-butadien-1-ol (3.4391 g) [eluent: petroleum ether/ethyl acetate = 10:1 (440 mL), 5:1 (960 mL), 2:1 (300 mL)], as a yellow solid, which was used in the next step without further purification.

Following **Typical Procedure II**, the reaction of 4-(4-(trifluoromethyl)phenyl)buta-2,3-dien-1-ol (2.1680 g, 10 mmol), DMAP (0.2462 g, 2.0 mmol), pyridine (1.6 mL, d = 0.983 g/mL, 1.5728 g, 20 mmol), DCM (20 mL),
and methyl chloroformate (2.5 mL, d = 1.223 g/mL, 2.835 g, 30 mmol) afforded 2l (2.208 g, overall yield of two steps: 38%) as an oil [eluent: petroleum ether/ethyl acetate = 10/1 (550 mL)]: 1H NMR (400 MHz, CDCl3): δ = 7.56 (d, J = 8.0 Hz, 2 H, Ar-H), 7.39 (d, J = 8.0 Hz, 2 H, Ar-H), 6.25-6.75 (m, 1 H, =CH), 5.81 (q, J = 6.5 Hz, 1 H, =CH), 4.65-4.85 (m, 2 H, CH2), 3.78 (s, 3 H, OCH3); 13C NMR (100 MHz, CDCl3) δ = 207.2, 155.5, 137.1, 129.3 (q, J = 3.9 Hz), 127.2, 125.6 (q, J = 3.9 Hz), 141.1 (q, J = 270.2 Hz), 96.0, 91.3, 64.7, 54.9; 19F NMR (376 MHz, CDCl3) δ = -63.0; MS (70eV, EI) m/z (%): 272 (M+, 15.7), 59 (100); IR (neat): ν = 3007, 2960, 1956, 1747, 1616, 1441, 1323, 1255, 1107, 1065 cm⁻¹; HRMS calcd m/z for C13H11F3O3 [M⁺]: 272.0655, found 272.0657.

(4) Preparation of methyl 4-(4-nitrophenyl)buta-2,3-dienyl carbonate (2m) (hcf-4-135)⁵

Following Typical Procedure III, the reaction of diphenylprolinol (7.6021 g, 30 mmol), CuBr2 (2.6807 g, 12 mmol), 4-nitrobenzaldehyde (6.8032 g, 45 mmol), 2-propyn-1-ol (2.6 mL, d = 0.963 g/mL, 2.5038 g, 45 mmol), and dioxane (90 mL) afforded 4-(4-nitrophenyl)-2,3-butadien-1-ol (3.0856 g) [eluent: petroleum ether/ethyl acetate = 5:1 (1 L), 2:1 (1 L)] as an oil, which was used in the next step without further purification.

Following Typical Procedure II, the reaction of 4-(4-(nitromethyl)phenyl)buta-2,3-dien-1-ol (3.085 g, 16 mmol), DMAP (0.3929 g, 3.2 mmol), pyridine (2.6 mL, d = 0.983 g/mL, 2.5558 g, 32 mmol), DCM (20 mL), and methyl chloroformate (3.7 mL, d = 1.223 g/mL, 4.514 g, 48 mmol) afforded 2m (2.2435 g, overall yield of two steps: 30%) as a white solid [eluent: petroleum ether/ethyl acetate = 10/1 (550 mL)]: m.p. 63.9-64.3 °C (petroleum ether/DCM); 1H NMR (400 MHz, CDCl3): δ = 8.17 (d, J = 8.8 Hz, 2 H, Ar-H), 7.43 (d, J = 8.8 Hz, 2 H, Ar-H), 6.44-6.35 (m, 1 H, =CH), 5.87 (t, J = 6.5 Hz, 1 H, =CH), 4.85-4.67 (m, 2 H,
OCH₂), 3.79 (s, 3 H, OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 207.9, 155.4, 146.8, 140.4, 127.4, 124.0, 95.7, 91.7, 64.3, 54.9; MS (70 eV, EI) m/z (%): 250 (M⁺+1, 1.95), 249 (M⁺, 13.51), 115 (100); IR (neat): ν = 3077, 3011, 2960, 1950, 1741, 1593, 1508, 1446, 1248, 1105 cm⁻¹; Anal. Calcd. for C₁₂H₁₁NO₅: C 57.83, H 4.45; found C 57.93, H 4.28.

(5) Preparation of methyl 4-(4-cyanophenyl)buta-2,3-dienyl carbonate (2n) (zy-5-79)⁵

Following Typical Procedure III, the reaction of diphenylprolinol (7.7537 g, 30 mmol), CuBr₂ (2.6802 g, 12 mmol), 4-cyanobenzaldehyde (6.0217 g, 45 mmol), 2-propyn-1-ol (2.7 mL, d = 0.963 g/mL, 2.6001 g, 45 mmol), and dioxane (60 mL) afforded 4-(4-cyanophenyl)-2,3-butadien-1-ol (2.0390 g) [eluent: petroleum ether/ethyl acetate = 6:1 (980 mL), 2:1 (1.2 L)] as an oil, which was used in the next step without further purification.

Following Typical Procedure II, the reaction of 4-(4-cyanophenyl)buta-2,3-dien-1-ol (2.0289 g, 12.0 mmol), DMAP (0.2931 mg, 2.4 mmol), pyridine (1.9 mL, d = 0.983 g/mL, 1.8677 g, 24 mmol), DCM (24 mL), and methyl chloroformate (2.8 mL, d = 1.223 g/mL, 3.4244 g, 36 mmol) afforded 2n (1.4969 g, overall yield of two steps: 22%) as an oil [eluent: petroleum ether/ethyl acetate = 10/1 (2750 mL)]: ¹H NMR (400 MHz, CDCl₃): δ = 7.58 (d, J = 8.4 Hz, 2 H, Ar-H), 7.39 (d, J = 8.0 Hz, 2 H, Ar-H), 6.39-6.31 (m, 1 H, =CH), 5.71 (q, J = 6.5 Hz, 1 H, =CH), 4.83-4.67 (m, 2 H, CH₂), 3.78 (s, 3 H, OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 207.2, 155.2, 138.2, 132.2, 127.3, 118.6, 110.4, 95.8, 91.5, 64.2, 54.7; IR (neat): ν = 2958, 2358, 2225, 1952, 1745, 1604, 1504, 1446, 1366, 1253, 1175, 1110 cm⁻¹; MS (70 eV, EI) m/z (%): 229 (M⁺, 32.32), 154 (100); HRMS Calc m/z for C₁₃H₁₁NO₃ [M⁺]: 229.0733, found 229.0736.
2. Synthesis of allenic aromatic ethers

(1) Preparation of buta-2,3-dienyl 4-methoxyphenyl ether (3aa) (hcf-4-102)

Typical Procedure IV: To a flame-dried Schlenk tube were added Pd2dba3 (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1a (124.1 mg, 1.0 mmol), 2a (193.1 mg, 1.5 mmol), and Et2O (5 mL) sequentially under argon atmosphere. The resulting mixture was stirred at room temperature for 22 h. After the completion of the reaction as monitored by TLC, the resulting mixture was diluted with 3 mL of ethyl acetate, filtered through a short column of silica gel (3 cm), eluted with ethyl acetate (20 x 2 mL), and concentrated. The residue was purified by column chromatography on silica gel to afford 3aa6 (166.8 mg, 95%) as a white solid [eluent: petroleum ether/DCM = 200/1 (600 mL), 150/1 (300 mL)]: m. p. 43.8-44.4 °C (petroleum ether/DCM); \(^1\)H NMR (400 MHz, CDCl3): δ = 6.91-6.77 (m, 4 H, Ar-H), 5.37 (quint, \(J = 6.7 \text{ Hz}, 1 \text{ H}, =\text{CH})\), 4.84 (dt, \(J_1 = 6.8 \text{ Hz}, J_2 = 2.6 \text{ Hz}, 2 \text{ H}, =\text{CH}_2\)), 4.51 (dt, \(J_1 = 6.8 \text{ Hz}, J_2 = 2.6 \text{ Hz}, 2 \text{ H}, \text{CH}_2\)), 3.76 (s, 3 H, OCH3); \(^13\)C NMR (100 MHz, CDCl3): δ = 209.4, 154.0, 152.4, 116.0, 114.6, 87.2, 76.3, 66.6, 55.7; MS (70 eV, EI) \(m/z\) (%): 177 (M++1, 2.79), 176 (M+, 22.92), 109 (100); IR (neat): \(v = 2954, 2923, 1957, 1506, 1381, 1223, 1179, 1033, 1014 \text{ cm}^{-1}\).

(2) Preparation of buta-2,3-dienyl phenyl ether (3ba) (hcf-4-71)

Following Typical Procedure IV, the reaction of Pd2dba3 (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1b (94.1 mg, 1 mmol), 2a (192.9 mg, 1.5 mmol), and Et2O (5.0 mL) afforded 3ba6 (122.4 mg, 84%) as an oil [eluent: petroleum ether/DCM = 150/1 (450 mL)]: \(^1\)H NMR (400 MHz, CDCl3): δ = 7.32-7.18 (m, 2 H, Ar-H), 6.99-6.77 (m, 3 H, Ar-H), 5.39 (quint, \(J = 6.7 \text{ Hz}, 1 \text{ H}, =\text{CH})\), 4.85 (dt, \(J_1 = 6.8 \text{ Hz}, J_2 = 2.6 \text{ Hz}, 2 \text{ H}, =\text{CH}_2\)), 3.76 (s, 3 H, OCH3); \(^13\)C NMR (100 MHz, CDCl3): δ = 209.4, 154.0, 152.4, 116.0, 114.6, 87.2, 76.3, 66.6, 55.7; MS (70 eV, EI) \(m/z\) (%): 177 (M++1, 2.79), 176 (M+, 22.92), 109 (100); IR (neat): \(v = 2954, 2923, 1957, 1506, 1381, 1223, 1179, 1033, 1014 \text{ cm}^{-1}\).
= 2.4 Hz, 2 H, =CH2), 4.55 (dt, J1 = 6.8 Hz, J2 = 2.4 Hz, 2 H, CH2); 13C NMR (100 MHz, CDCl3): δ = 209.4, 158.3, 129.4, 120.9, 114.8, 87.1, 76.4, 65.7; MS (70 eV, EI) m/z (%): 147 (M++1, 1.15), 146 (M+, 11.36), 94 (100); IR (neat): ν = 3062, 3040, 2930, 2871, 1957, 1598, 1494, 1238, 1213, 1030, 1011 cm⁻¹.

(3) Preparation of buta-2,3-dienyl 4-methylphenyl ether (3ca) (hcf-4-107)

Following Typical Procedure IV, the reaction of Pd2dba3 (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1c (108.2 mg, 1 mmol), 2a (193.3 mg, 1.5 mmol), and Et2O (5.0 mL) afforded 3ca6 (150.5 mg, 94%) as an oil [eluent: petroleum ether/DCM = 200/1 (600 mL), 150/1 (150 mL)]: 1H NMR (400 MHz, CDCl3): δ = 7.07 (d, J = 8.4 Hz, 2 H, Ar-H), 6.81 (d, J = 8.4 Hz, 2 H, Ar-H), 5.38 (quint, J = 6.7 Hz, 1 H, =CH), 4.85 (dt, J1 = 6.8 Hz, J2 = 2.4 Hz, 2 H, =CH2), 4.54 (dt, J1 = 7.2 Hz, J2 = 2.6 Hz, 2 H, CH2), 2.28 (s, 3 H, CH3); 13C NMR (100 MHz, CDCl3): δ = 209.4, 156.2, 130.2, 129.9, 114.8, 87.2, 76.4, 65.9, 20.4; MS (70 eV, EI) m/z (%): 161 (M++1, 2.3), 160 (M+, 18.4), 108 (100); IR (neat): ν = 3030, 2922, 2865, 1956, 1508, 1235, 1212, 1175, 1016 cm⁻¹.

(4) Preparation of buta-2,3-dienyl 2,6-dimethylphenyl ether (3da) (xjz-3-154)

Following Typical Procedure IV, the reaction of Pd2dba3 (23.0 mg, 0.025 mmol), Xantphos (57.5 mg, 0.1 mmol), 1d (122.0 mg, 1 mmol), 2a (192.1 mg, 1.5 mmol), and Et2O (5.0 mL) afforded 3da (123.7 mg, 71%) as an oil [eluent: petroleum ether (800 mL)]: 1H NMR (400 MHz, CDCl3): δ = 6.99 (d, J = 7.6 Hz, 2 H, Ar-H), 6.91 (dd, J1 = 8.0 Hz, J2 = 6.8 Hz, 1 H, Ar-H), 5.45 (quint, J = 6.8 Hz, 1 H, =CH), 4.82 (dt, J1 = 6.8 Hz, J2 = 2.5 Hz, 2 H, =CH2), 4.33 (dt, J1 = 7.2 Hz, J2 = 2.4 Hz, 2 H, CH2), 2.28 (s, 6 H, 2 x CH3); 13C NMR (100 MHz, CDCl3): δ = 209.4, 155.7, 131.0, 128.7, 123.9,
87.7, 76.0, 70.0, 16.4; IR (neat): ν = 2921, 1956, 1474, 1369, 1263, 1192, 1091 cm⁻¹; MS (70 eV, EI) m/z (%): 174 (M⁺, 12.7), 122 (100); HRMS calcd for C₁₂H₁₄O [M⁺]: 174.1045, found: 174.1051.

(5) Preparation of buta-2,3-dienyl 2,6-diphenylphenyl ether (3ea) (cyf-3-90)

Following Typical Procedure IV, the reaction of Pd₂dba₃ (23.0 mg, 0.025 mmol), Xantphos (58.2 mg, 0.1 mmol), 1e (168.3 mg, 1 mmol), 2a (192.8 mg, 1.5 mmol), and Et₂O (5.0 mL) afforded 3ea (250.6 mg, 84%) as an oil [eluent: petroleum ether (800 mL)]: ¹H NMR (400 MHz, CDCl₃): δ = 7.64-7.58 (m, 4 H, Ar-H), 7.45-7.38 (m, 4 H, Ar-H), 7.37-7.30 (m, 4 H, Ar-H), 7.27-7.20 (m, 1 H, Ar-H), 4.69 (quint, J = 6.9 Hz, 1 H, =CH), 4.48 (dt, J₁ = 6.8 Hz, J₂ = 2.2 Hz, 2 H, =CH₂), 3.77 (dt, J₁ = 6.4 Hz, J₂ = 2.2 Hz, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 209.1, 153.3, 138.7, 136.2, 130.1, 129.5, 128.1, 127.1, 124.4, 87.0, 75.2, 70.8; MS (70 eV, EI) m/z (%): 298 (M⁺, 37.30), 246 (100); IR (neat) ν = 3056, 3027, 2931, 2866, 1954, 1737, 1598, 1573, 1496, 1460, 1440, 1416, 1367, 1313, 1275, 1199, 1157, 1119, 1072, 1029, 1012 cm⁻¹; HRMS calcd for C₂₂H₂O (M⁺): 298.1358. Found: 298.1366.

(6) Preparation of buta-2,3-dienyl 2-allylphenyl ether (3fa) (hcf-4-85)

Following Typical Procedure IV, the reaction of Pd₂dba₃ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1f (134.3 mg, 1 mmol), 2a (193.2 mg, 1.5 mmol), and Et₂O (5.0 mL) afforded 3fa (167.8 mg, 90%) as an oil [eluent: petroleum ether/dichloromethane = 200/1 (600 mL)]: ¹H NMR (400 MHz, CDCl₃): δ = 7.21-7.06 (m, 2 H, Ar-H), 6.96-6.78 (m, 2 H, Ar-H), 6.07-5.86 (m, 1 H, =CH), 5.38 (quint, J = 6.6 Hz, 1 H, C=CH), 5.12-4.94 (m, 2 H, CH₂), 4.90-4.72 (m, 2 H, =CH₂), 4.62-4.46 (m, 2 H, CH₂), 3.40 (d, J = 6.8 Hz, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 209.2,
156.0, 137.0, 129.9, 129.2, 127.2, 120.8, 115.3, 112.0, 87.4, 76.5, 65.9, 34.3; MS (70 eV, EI) m/z (%): 186 (M⁺, 5.57), 145 (100); IR (neat): ν = 3076, 2978, 2915, 1957, 1600, 1588, 1490, 1453, 1236, 1218, 1014 cm⁻¹; HRMS calcd for C₁₃H₁₄O [M⁺]: 186.1039, found: 186.1043.

(7) Preparation of buta-2,3-dienyl 2-bromophenyl ether (3ga) (hcf-4-89)

Following Typical Procedure IV, the reaction of Pd₂dba₃ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1g (173.0 mg, 1 mmol), 2a (193.1 mg, 1.5 mmol), and Et₂O (5.0 mL) afforded 3ga (197.7 mg, 86%, 98% purity) as an oil [eluent: petroleum ether/DCM = 200/1 (600 mL)]: ¹H NMR (400 MHz, CDCl₃): δ = 7.53 (dd, J₁ = 7.8 Hz, J₂ = 1.4 Hz, 1 H, Ar-H), 7.29-7.18 (m, 1 H, Ar-H), 6.96-6.88 (m, 1 H, Ar-H), 6.84 (dt, J₁ = 7.6 Hz, J₂ = 1.2 Hz, 1 H, Ar-H), 5.41 (quint, J = 6.7 Hz, 1 H, =CH), 4.87 (dt, J₁ = 6.8 Hz, J₂ = 2.4 Hz, 2 H, =CH₂), 4.65 (dt, J₁ = 6.8 Hz, J₂ = 2.6 Hz, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 209.5, 154.8, 133.5, 128.3, 122.1, 114.0, 112.5, 86.8, 76.7, 67.0; MS (70 eV, EI) m/z (%): 226 (M⁺(⁸¹Br)⁺, 3.31), 224 (M⁺(⁷⁹Br)⁺, 4.04), 53 (100); IR (neat): ν = 2988, 2883, 1956, 1587, 1572, 1474, 1281, 1215, 1009 cm⁻¹; HRMS calcd for C₁₀H₉BrO [M⁺]: 223.9831, found: 223.9830.

Gram-scale synthesis of buta-2,3-dienyl 2-bromophenyl ether (3ga) (hcf-4-127)

Following Typical Procedure IV, the reaction of Pd₂dba₃ (22.9 mg, 0.025 mmol), Xantphos (144.8 mg, 0.25 mmol), 1g (865.1 mg, 5 mmol), 2a (800.9 mg, 6.25 mmol), and Et₂O (20.0 mL) afforded 3ga (1.0465 g, 93%) as an oil [eluent: petroleum ether/DCM = 80/1 (1000 mL)]: ¹H NMR (400 MHz, CDCl₃): δ = 7.53 (d, J = 7.6 Hz, 1 H, Ar-H), 7.31-7.16 (m, 1 H, Ar-H), 6.92 (d, J = 8.0 Hz, 1 H, Ar-H), 6.84 (t, J = 7.6 Hz, 1 H, Ar-H), 5.41 (quint, J = 6.5 Hz, 1 H, =CH), 4.93-4.75 (m, 2 H, =CH₂),
4.70-4.51 (m, 2 H, CH₂); \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta = 209.5, 154.8, 133.5, 128.3, 122.1, 114.0, 112.5, 86.8, 76.7, 67.0.

(8) Preparation of buta-2,3-dienyl 3-bromophenyl ether (3ha) (hcf-4-88)

\[
\begin{align*}
\text{OH} & \quad \text{OCD₂Me} \\
\text{Br} & \quad \text{Br} \\
1h & \quad 2a, \text{1.5 equiv.} \\
\text{Et₂O, rt, Ar, 24 h} & \quad 3ha, 92\% \\
\end{align*}
\]

Following Typical Procedure IV, the reaction of Pd₂dba₃ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1h (173.1 mg, 1 mmol), 2a (193.1 mg, 1.5 mmol), and Et₂O (5.0 mL) afforded 3ha\(^6\) (206.8 mg, 90%) as an oil [eluent: petroleum ether/DCM = 200/1 (600 mL)]: \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 7.18-6.96 (m, 3 \text{ H, Ar-H}), 6.89-6.72 (m, 1 \text{ H, Ar-H}), 5.36 (\text{quint, } J = 6.7 \text{ Hz, 1 H, } =\text{CH}), 4.87 \text{ (dt, } J_1 = 6.4 \text{ Hz, } J_2 = 2.4 \text{ Hz, 2 H, } =\text{CH₂}), 4.54 \text{ (dt, } J_1 = 6.8 \text{ Hz, } J_2 = 2.4 \text{ Hz, 2 H, CH₂}); \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta = 209.6, 159.1, 130.5, 124.0, 122.7, 118.2, 113.9, 86.6, 76.7, 66.0; \text{ MS (70 eV, EI) } m/z (\%): 226 (M(⁸¹Br)⁺, 1.78), 224 (M(⁷⁹Br)⁺, 1.88), 172 (100); \text{ IR (neat): v } = 3064, 2988, 2873, 1956, 1586, 1573, 1475, 1459, 1274, 1244, 1225, 1030 \text{ cm}^{-1}.

(9) Preparation of buta-2,3-dienyl 4-bromophenyl ether (3ia) (hcf-4-81)

\[
\begin{align*}
\text{OH} & \quad \text{OCD₂Me} \\
\text{Br} & \quad \text{Br} \\
1i & \quad 2a, \text{1.5 equiv.} \\
\text{Et₂O, rt, Ar, 24 h} & \quad 3ia, 90\% \\
\end{align*}
\]

Following Typical Procedure IV, the reaction of Pd₂dba₃ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1i (173.1 mg, 1 mmol), 2a (193.1 mg, 1.5 mmol), and Et₂O (5.0 mL) afforded 3ia (202.7 mg, 90%) as an oil [eluent: petroleum ether/dichloromethane = 200/1 (600 mL)]: \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 7.41-7.28 (m, 2 \text{ H, Ar-H}), 6.83-6.66 (m, 2 \text{ H, Ar-H}), 5.36 (\text{quint, } J = 6.7 \text{ Hz, 1 H, } =\text{CH}), 4.86 \text{ (dt, } J_1 = 6.8 \text{ Hz, } J_2 = 2.6 \text{ Hz, 2 H, =CH₂}), 4.53 \text{ (dt, } J_1 = 6.4 \text{ Hz, } J_2 = 2.6 \text{ Hz, 2 H, CH₂}); \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta = 209.6, 157.4, 132.2, 116.7, 113.1, 86.8, 76.7, 66.0; \text{ MS (70 eV, EI) } m/z (\%): 226 (M(⁸¹Br)⁺, 3.5), 224 (M(⁷⁹Br)⁺, 3.75), 53 (100); \text{ IR (neat): v } = 2930, 2873, 1956, 1589, 1578, 1461, 1284, 1235, 1219, 1171, 1072 \text{ cm}^{-1}; \text{ HRMS }
calcd for C_{10}H_{9}OBr [M^+] 223.9831, found: 223.9827.

(10) Preparation of buta-2,3-dienyl 4-fluorophenyl ether (3ja) (hcf-4-111)

Following Typical Procedure IV, the reaction of Pd_{2}dba_{3} (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1j (112.1 mg, 1 mmol), 2a (193.4 mg, 1.5 mmol), and Et_{2}O (5.0 mL) afforded 3ja (154.3 mg, 94%) as an oil [eluent: petroleum ether /ethyl acetate = 200/1 (600 mL)]: ^{1}H NMR (400 MHz, CDCl_{3}): δ = 7.02-6.88 (m, 2 H, Ar-H), 6.88-6.74 (m, 2 H, Ar-H), 5.36 (quint, J = 6.7 Hz, 1 H, =CH), 4.92-4.75 (m, 2 H, =CH_{2}), 4.60-4.39 (m, 2 H, CH_{2}); ^{13}C NMR (100 MHz, CDCl_{3}): δ = 209.5, 157.4 (d, J = 237.0 Hz), 154.4 (d, J = 1.6 Hz), 116.0 (d, J = 7.9 Hz), 115.8 (d, J = 22.9 Hz), 87.0, 76.5, 66.5; ^{19}F NMR (376 MHz, CDCl_{3}): δ = -124.2; MS (70 eV, EI) m/z (%): 164 (M^{+}, 8.54), 112 (100); IR (neat): ν = 2927, 2916, 1502, 1244, 1196, 1097, 1008 cm^{-1}; HRMS calcd for C_{10}H_{9}OF [M^{+}]: 164.0632, found: 164.0634.

(11) Preparation of buta-2,3-dienyl 4-chlorophenyl ether (3ka) (hcf-4-77)

Following Typical Procedure IV, the reaction of Pd_{2}dba_{3} (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1k (128.4 mg, 1 mmol), 2a (193.2 mg, 1.5 mmol), and Et_{2}O (5.0 mL) afforded 3ka (156.9 mg, 87%) as an oil [eluent: petroleum ether /CH_{2}Cl_{2} = 150/1 (450 mL)]: ^{1}H NMR (400 MHz, CDCl_{3}): δ = 7.26-7.10 (m, 2 H, Ar-H), 6.87-6.74 (m, 2 H, Ar-H), 5.35 (quint, J = 6.7 Hz, 1 H, =CH), 4.86 (dt, J_{1} = 6.4 Hz, J_{2} = 2.6 Hz, 2 H, =CH_{2}), 4.52 (dt, J_{1} = 6.8 Hz, J_{2} = 2.4 Hz, 2 H, CH_{2}); ^{13}C NMR (100 MHz, CDCl_{3}): δ = 209.5, 156.9, 129.3, 125.8, 116.2, 86.8, 76.6, 66.1; MS (70 eV, EI) m/z (%): 182 (M^{37}Cl^{+}, 1.17), 180 (M^{35}Cl^{+}, 3.56), 128 (100); IR (neat): ν = 2930, 2874, 1956, 1596, 1488, 1237, 1218, 1170, 1091, 1008 cm^{-1}.

(12) Preparation of buta-2,3-dienyl 4-iodophenyl ether (3la) (hcf-4-116)
Following **Typical Procedure IV**, the reaction of Pd$_2$dba$_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1I (220.1 mg, 1 mmol), 2a (193.3 mg, 1.5 mmol), and MTBE (5.0 mL) at 35°C afforded 3Ia$^6$ (239.2 mg, 88%) as an oil [eluent: petroleum ether/ethyl acetate = 200/1 (600 mL)]: $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.54 (d, $J$ = 8.8 Hz, 2 H, Ar-H), 6.69 (d, $J$ = 8.8 Hz, 2 H, Ar-H), 5.35 (quint, $J$ = 6.7 Hz, 1 H, =CH), 4.93-4.73 (m, 2 H, =CH$_2$), 4.57-4.40 (m, 2 H, CH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 209.5, 158.2, 138.2, 117.3, 86.7, 83.0, 65.9; MS (70 eV, EI) $m/z$ (%): 272 (M$^+$, 12.18), 220 (100); IR (neat): $v$ = 3064, 2927, 2871, 1955, 1584, 1482, 1280, 1235, 1217, 1173 cm$^{-1}$.

**(13) Preparation of methyl 4-((buta-2,3-dienyl)oxy)benzoate (3ma) (hcf-5-77)**

Following **Typical Procedure IV**, the reaction of Pd(PPh$_3$)$_4$ (57.8 mg, 0.05 mmol), 1m (152.1 mg, 1 mmol), 2a (193.0 mg, 1.5 mmol), and dioxane (5.0 mL) at 35°C afforded 3ma$^7$ (167.4 mg, 82%) as a white solid [eluent: petroleum ether/ethyl acetate = 15/1 (500 mL)]: m. p. 42.1-42.7 °C (petroleum ether/ethyl acetate); $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.02-7.95 (m, 2 H, Ar-H), 6.96-6.89 (m, 2 H, Ar-H), 5.38 (quint, $J$ = 6.7 Hz, 1 H, =CH), 4.92-4.84 (m, 2 H, =CH$_2$), 4.65-4.58 (m, 2 H, CH$_2$), 3.88 (s, 3 H, OCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 209.6, 166.8, 162.1, 131.5, 122.7, 114.4, 86.6, 76.8, 65.9, 51.8; MS (70 eV, EI) $m/z$ (%): 204 (M$^+$, 4.33), 121 (100); IR (neat): $v$ = 2958, 2876, 1958, 1719, 1603, 1507, 1430, 1280, 1247, 1231, 1169, 1106, 1010 cm$^{-1}$.

**(14) Preparation of buta-2,3-dienyl 4-cyanophenyl ether (3na) (hcf-6-65)**
Following **Typical Procedure IV**, the reaction of Pd(PPh₃)₄ (57.8 mg, 0.05 mmol), 1n (119.1 mg, 1 mmol), 2a (192.3 mg, 1.5 mmol), and MTBE (5.0 mL) at 40°C afforded 3na (119.8 mg, 70%) as an oil [eluent: petroleum ether/ethyl acetate = 15/1 (500 mL)]: ¹H NMR (400 MHz, CDCl₃): δ = 7.58 (dt, J₁ = 8.8 Hz, J₂ = 2.4 Hz, 2 H, Ar-H), 6.96 (dt, J₁ = 8.8 Hz, J₂ = 2.4 Hz, 2 H, Ar-H), 5.37 (quint, J = 6.7 Hz, 1 H, =CH), 4.90 (dt, J₁ = 6.8 Hz, J₂ = 2.6 Hz, 2 H, =CH₂), 4.62 (dt, J₁ = 6.8 Hz, J₂ = 2.4 Hz, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 209.6, 161.6, 133.9, 119.1, 115.5, 104.1, 86.2, 77.0, 66.0; MS (70 eV, EI) m/z (%): 172 (M⁺+1, 1.39), 171 (M⁺, 12.52), 119 (100); IR (neat): ν = 3074, 2931, 2874, 2224, 1956, 1604, 1506, 1251, 1228, 1171 cm⁻¹; HRMS calcd for C₁₁H₉NO [M⁺]: 171.0679, found: 171.0675.

(15) Preparation of buta-2,3-dienyl 2-naphthyl ether (3oa) (hcf-4-73)

Following **Typical Procedure IV**, the reaction of Pd₂dba₃ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1o (144.2 mg, 1 mmol), 2a (193.2 mg, 1.5 mmol), and Et₂O (5.0 mL) afforded 3oa (164.7 mg, 84%) as a white solid [eluent: petroleum ether/DCM = 150/1 (450 mL)]: m. p. 60.6-61.4 °C (petroleum ether/DCM); ¹H NMR (400 MHz, CDCl₃): δ = 7.72 (q, J = 8.7 Hz, 3 H, Ar-H), 7.41 (t, J = 7.4 Hz, 1 H, Ar-H), 7.32 (t, J = 7.4 Hz, 1 H, Ar-H), 7.19-7.01 (m, 2 H, Ar-H), 5.44 (quint, J = 6.7 Hz, 1 H, =CH), 4.87 (dt, J₁ = 6.8 Hz, J₂ = 2.4 Hz, 2 H, =CH₂), 4.66 (dt, J₁ = 6.8 Hz, J₂ = 2.4 Hz, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 209.6, 156.2, 134.4, 129.4, 129.0, 127.6, 126.8, 126.3, 123.7, 119.0, 107.3, 87.0, 76.5, 65.8; MS (70 eV, EI) m/z (%): 197 (M⁺+1, 6.06), 196 (M⁺, 38.8), 144 (100); IR (neat): ν = 3055, 2931, 1955, 1626, 1597, 1382, 1255, 1212, 1177 cm⁻¹; Anal. Caled. for C₁₄H₁₂O: C 85.68, H 6.16; found C 85.67, H 6.06.
(16) Preparation of buta-2,3-dienyl 1-naphthyl ether (3pa) (hcf-4-92)

\[
\begin{array}{c}
\text{1p} \quad \text{2a, 1.5 equiv.} \quad \text{Pd} \text{2dba} \text{3 (2.5 mol%) Xantphos (10 mol%)} \quad \text{Et} \text{2O, rt, Ar, 12 h} \\
\text{3pa, 95%}
\end{array}
\]

Following **Typical Procedure IV**, the reaction of Pd2dba3 (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1p (144.2 mg, 1 mmol), 2a (193.4 mg, 1.5 mmol), and Et2O (5.0 mL) afforded 3pa (187.4 mg, 95%) as an oil [eluent: petroleum ether/dichloromethane = 200/1 (400 mL)]: \(^1\)H NMR (400 MHz, CDCl3): \(\delta = 8.34-8.17 \text{ (m, 1 H, Ar-H)}, 7.82-7.70 \text{ (m, 1 H, Ar-H)}, 7.52-7.26 \text{ (m, 4 H, Ar-H)}, 6.80 \text{ (d, } J = 7.6 \text{ Hz, 1 H, Ar-H)}, 5.50 \text{ (quint, } J = 6.6 \text{ Hz, 1 H, } \text{CH}), 4.89 \text{ (dt, } J_1 = 6.4 \text{ Hz, } J_2 = 2.8 \text{ Hz, 2 H, } \text{CH}_2), 4.73 \text{ (dt, } J_1 = 6.8 \text{ Hz, } J_2 = 2.6 \text{ Hz, 2 H, } \text{CH}_2); \(^{13}\)C NMR (100 MHz, CDCl3): \(\delta = 209.4, 154.1, 134.5, 127.4, 126.4, 125.8, 125.7, 125.2, 122.1, 120.5, 105.2, 87.2, 76.6, 66.0; \) MS (70 eV, El) \(m/z\) (%): 197 (M++1, 5.65), 196 (M+, 24.78), 115 (100); IR (neat): \(\nu = 3052, 2930, 2870, 1956, 1578, 1507, 1399, 1371, 1265, 1238, 1095 \text{ cm}^{-1}; \) HRMS calcd for C14H12O \([M^+]\): 196.0883, found: 196.0881.

(17) Preparation of di(buta-2,3-dienyl) 1,4-phenylene ether (3qa) (hcf-4-93)

\[
\begin{array}{c}
\text{1q} \quad \text{2a, 2.5 equiv.} \quad \text{Pd} \text{2dba} \text{3 (2.5 mol%) Xantphos (10 mol%)} \quad \text{Et} \text{2O, rt, Ar, 24 h} \\
\text{3qa, 91%}
\end{array}
\]

Following **Typical Procedure IV**, the reaction of Pd2dba3 (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1q (110.2 mg, 1 mmol), 2a (320.9 mg, 2.5 mmol), and Et2O (5.0 mL) afforded 3qa (195.7 mg, 91%) as a white solid [eluent: petroleum ether/DCM = 200/1 (400 mL), 150/1 (150 mL)]: m. p. 72.0-72.8 °C (petroleum ether/DCM); \(^1\)H NMR (400 MHz, CDCl3): \(\delta = 6.84 \text{ (s, 4 H, Ar-H)}, 5.37 \text{ (quint, } J = 6.7 \text{ Hz, 2 H, } \text{CH}), 4.84 \text{ (dt, } J_1 = 6.8 \text{ Hz, } J_2 = 2.4 \text{ Hz, 4 H, } \text{CH}, 4.52 \text{ (dt, } J_1 = 6.8 \text{ Hz, } J_2 = 2.6 \text{ Hz, 4 H, } \text{CH}_2); \(^{13}\)C NMR (100 MHz, CDCl3): \(\delta = 209.4, 152.7, 115.9, 87.2, 76.4, 66.5; \) MS (70 eV, El) \(m/z\) (%): 215 (M++1, 1.48), 214 (M+, 8.77), 53 (100); IR (neat): \(\nu = 2923, 2871, 1956, 1505, 1462, 1382, 1219, 1016, 1002 \text{ cm}^{-1}; \) Anal.
Calcd. for C\textsubscript{14}H\textsubscript{12}O\textsubscript{2}: C 78.48, H 6.59; found C 78.25, H 6.36.

(18) Preparation of di(buta-2,3-dienyl) 1,3-phenylene ether (3ra) (hcf-4-117)

Following Typical Procedure IV, the reaction of Pd\textsubscript{2}dba\textsubscript{3} (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1r (110.1 mg, 1 mmol), 2a (320.9 mg, 2.5 mmol), and MTBE (5.0 mL) at 35\degree C afforded 3ra (201.2 mg, 94\%) as an oil [eluent: petroleum ether/ethyl acetate = 150/1 (600 mL)]: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.15 (t, J = 8.0 Hz, 1 H, Ar-H), 6.62-6.37 (m, 3 H, Ar-H), 5.38 (quint, J = 6.6 Hz, 2 H, 2 x =CH), 4.98-4.75 (m, 4 H, 2 x =CH\textsubscript{2}), 4.62-4.37 (m, 4 H, 2 x CH\textsubscript{2}); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 209.4, 159.5, 129.8, 107.4, 102.2, 87.0, 76.4, 65.8; MS (70 eV, EI) m/z (%): 214 (M\textsuperscript{+}, 9.93), 110 (100); IR (neat): ν = 2939, 2874, 1956, 1589, 1489, 1175, 1144, 1033 cm\textsuperscript{-1}; HRMS calcd for C\textsubscript{14}H\textsubscript{14}O\textsubscript{2} [M\textsuperscript{+}]: 214.0988, found: 214.0987.

(19) Preparation of di(buta-2,3-dienyl) 1,2-phenylene ether (3sa) (hcf-4-96)

Following Typical Procedure IV, the reaction of Pd\textsubscript{2}dba\textsubscript{3} (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1s (110.1 mg, 1 mmol), 2a (320.5 mg, 2.5 mmol), and Et\textsubscript{2}O (5.0 mL) afforded 3sa\textsuperscript{8} (202.8 mg, 95\%) as an oil [eluent: petroleum ether/DCM = 150/1 (600 mL)]: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 6.99-6.80 (m, 4 H, Ar-H), 5.42 (quint, J = 6.7 Hz, 2 H, 2 x =CH), 4.83 (dt, J\textsubscript{1} = 6.4 Hz, J\textsubscript{2} = 2.4 Hz, 4 H, 2 x =CH\textsubscript{2}), 4.64 (dt, J\textsubscript{1} = 6.8 Hz, J\textsubscript{2} = 2.6 Hz, 4 H, 2 x CH\textsubscript{2}); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 209.5, 148.3, 121.4, 114.6, 87.3, 76.3, 66.9; MS (70 eV, EI) m/z (%): 214 (M\textsuperscript{+}, 4.7), 110 (100); IR (neat): ν = 3064, 2933, 2868, 1956, 1592, 1498, 1246, 1203, 1122, 1006 cm\textsuperscript{-1}.

(20) Preparation of di(buta-2,3-dienyl) 2,2'-(1,1'-binaphthalene)diyl ether (3ta) (hcf-4-110)
Following **Typical Procedure IV**, the reaction of Pd$_2$dba$_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1t (286.3 mg, 1 mmol), 2a (320.9 mg, 2.5 mmol), and Et$_2$O (5.0 mL) afforded 3ta ($90\%$) as an oil [eluent: petroleum ether/ethyl acetate = 150/1 (900 mL)].

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.86$ (dd, $J_1 = 6.6$ Hz, $J_2 = 1.8$ Hz, 4 H, Ar-H), 7.52-7.01 (m, 8 H, Ar-H), 5.03 (quint, $J = 6.6$ Hz, 2 H, 2 $\times$ $\text{CH}$), 4.77-4.38 (m, 8 H, 2 $\times$ $\text{CH}_2$ and 2 $\times$ $\text{CH}_2$);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 209.0, 153.7, 134.1, 129.4, 129.1, 127.8, 126.2, 125.5, 123.7, 120.8, 116.2, 87.6, 76.1, 67.3; MS (70 eV, EI) $m/z$ (%): 391 (M$^++1$, 20.78), 390 (M$^+$, 58.54), 268 (100); IR (neat): $\nu =$ 3056, 2988, 1954, 1590, 1505, 1259, 1212, 1015 cm$^{-1}$.

(21) **Preparation of buta-2,3-dienyl 2-(hydroxymethyl)phenyl ether (3ua)**

Following **Typical Procedure IV**, the reaction of Pd$_2$dba$_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1u (124.1 mg, 1 mmol), 2a (192.9 mg, 1.5 mmol), and Et$_2$O (5.0 mL) afforded 3ua ($93\%$) as an oil [eluent: petroleum ether/DCM = 10/1 (1000 mL)].

$^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.33-7.13 (m, 2 H, Ar-H), 6.93 (t, $J = 7.4$ Hz, 1 H, Ar-H), 6.86 (d, $J = 8.0$ Hz, 1 H, Ar-H), 5.38 (quint, $J = 6.5$ Hz, 1 H, $=\text{CH}$), 4.96-4.76 (m, 2 H, $=\text{CH}_2$), 4.67 (s, 2 H, CH$_2$), 4.63-4.48 (m, 2 H, CH$_2$), 2.61 (br, 1 H, OH);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 209.1, 156.2, 129.5, 128.72, 128.69, 120.9, 111.5, 87.0, 76.7, 65.3, 62.0; MS (70 eV, EI) $m/z$ (%): 176 (M$^+$, 1.16), 78 (100); IR (neat): $\nu =$ 3372, 2929, 2874, 1956, 1602, 1589, 1489, 1454, 1232, 1217, 1005 cm$^{-1}$; HRMS calcd for C$_{11}$H$_{12}$O$_2$Na [M+Na$^+$]: 199.0730, found: 199.0732.

(22) **Preparation of buta-2,3-dienyl**
(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl ether (3va) (hcf-4-101)

Following **Typical Procedure IV**, the reaction of Pd$_2$(dba)$_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1v (270.4 mg, 1 mmol), 2a (193.4 mg, 1.5 mmol), and Et$_2$O (5.0 mL) afforded 3va (303.1 mg, 94%) as a white solid [elu ent: petroleum ether/DCM = 150/1 (450 mL), 100/1 (600 mL)]: m. p. 86.7-87.2 °C (petroleum ether/DCM); $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.19 (d, $J_1 = 8.8$ Hz, 1 H, Ar-H), 6.72 (dd, $J_1 = 8.4$ Hz, 1 H, Ar-H), 6.68-6.61 (m, 1 H, Ar-H), 5.38 (quint, $J_1 = 6.7$ Hz, 1 H, =CH), 4.90-4.79 (m, 2 H, =CH$_2$), 4.58-4.48 (m, 2 H, CH$_2$), 2.93-2.81 (m, 2 H, CH$_2$), 2.55-2.45 (m, 1 H, CH), 2.43-2.32 (m, 1 H, CH), 2.30-1.80 (m, 5 H, 2 x CH$_2$ and CH), 1.75-1.34 (m, 6 H, 3 x CH$_2$), 0.90 (s, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 220.8, 209.4, 156.3, 137.7, 132.3, 126.2, 114.9, 112.4, 87.2, 76.3, 65.8, 50.4, 47.9, 43.9, 38.3, 35.8, 31.5, 29.6, 26.5, 25.8, 21.5, 13.8; MS (70 eV, El) m/z (%): 323 (M$^+$+1, 12.01), 322 (M$^+$, 45.1), 158 (100); IR (neat): ν = 2930, 2914, 2876, 1975, 1950, 1732, 1494, 1248, 1052, 1026 cm$^{-1}$; Anal. Calcd. for C$_{22}$H$_{26}$O$_2$: C 81.95, H 8.13; found C 82.29, H 8.62.

(23) Preparation of dodeca-2,3-dienyl phenyl ether (3bb) (zyz-5-65)

Following **Typical Procedure IV**, the reaction of Pd$_2$(dba)$_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1b (94.2 mg, 1 mmol), 2b (361.3 mg, 2.5 mmol), and Et$_2$O (5.0 mL) afforded 3bb (226.7 mg, 88%) as an oil [elu ent: petroleum ether/ethyl acetate = 150/1 (900 mL)]: $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.30-7.23 (m, 2 H, Ar-H), 6.96-6.89 (m, 3 H, Ar-H), 5.38-5.20 (m, 2 H, 2 x =CH), 4.57-4.50 (m, 2 H, CH$_2$),
2.05-1.96 (m, 2 H, CH₂), 1.43-1.20 (m, 12 H, 6 x CH₂), 0.88 (t, J = 6.8 Hz, 3 H, CH₃);

¹³C NMR (100 MHz, CDCl₃): δ = 205.1, 158.4, 129.3, 120.7, 114.9, 92.9, 87.6, 66.4, 31.9, 29.4, 29.3, 29.08, 29.06, 28.4, 22.7, 14.1; MS (EI, 70 eV) m/z (%): 259 (M⁺+1, 4.42), 258 (M⁺, 21.95), 94 (100); IR (neat): 2955, 2923, 2853, 1965, 1599, 1587, 1494, 1462, 1365, 1301, 1238, 1213, 1171, 1153, 1078, 1030, 1011 cm⁻¹; HRMS (ESI) Calcd for C₁₈H₂₆O [M⁺]: 258.1984, Found: 258.1991.

(24) Preparation of tetradeca-2,3-dienyl 1-naphthyl ether (3pc) (hcf-4-140)

Following Typical Procedure IV, the reaction of Pd₂dba₃ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1p (144.2 mg, 1 mmol), 2c (402.6 mg, 1.5 mmol), and Et₂O (5.0 mL) afforded 3pc (319.7 mg, 95%) as an oil [eluent: petroleum ether/DCM = 100/1 (500 mL)]; ¹H NMR (400 MHz, CDCl₃): δ = 8.29 (d, J = 8.0 Hz, 1 H, Ar-H), 7.78 (d, J = 6.8 Hz, 1 H, Ar-H), 7.51-7.38 (m, 3 H, Ar-H), 7.35 (t, J = 7.8 Hz, 1 H, Ar-H), 6.83 (d, J = 7.2 Hz, 1 H, Ar-H), 5.51-5.40 (m, 1 H, =CH), 5.35-5.24 (m, 1 H, =CH), 4.72 (dd, J₁ = 6.6 Hz, J₂ = 1.8 Hz, 2 H, CH₂), 2.08-1.94 (m, 2 H, CH₂), 1.46-1.35 (m, 2 H, CH₂), 1.35-1.00 (m, 14 H, 7 x CH₂), 0.88 (t, J = 6.4 Hz, 3 H, CH₃);

¹³C NMR (100 MHz, CDCl₃): δ = 205.1, 154.3, 134.6, 127.4, 126.3, 125.9, 125.7, 125.1, 122.2, 120.3, 105.4, 93.0, 87.7, 66.7, 31.9, 29.6, 29.4, 29.3, 29.1, 28.4, 22.7, 14.1; MS (70 eV, EI) m/z (%): 337 (M⁺+1, 5.37), 336 (M⁺, 21.3), 144 (100); IR (neat): ν = 3053, 2922, 2852, 1965, 1581, 1400, 1266, 1066 cm⁻¹; HRMS calcd for C₂₄H₃₂O [M⁺]: 336.2448, found: 336.2448.

(25) Preparation of 5-methyl-hexa-2,3-dienyl 1-naphthyl ether (3pd) (wpl-5-101)

Following Typical Procedure IV, the reaction of Pd₂dba₃ (22.9 mg, 0.025 mmol), Xantphos (57.8 mg, 0.1 mmol), 1p (144.4 mg, 1 mmol), 2d (255.6 mg, 1.5 mmol),
and Et₂O (5.0 mL) afforded 3pd (234.5 mg, 98%) as an oil [eluent: petroleum ether/ethyl acetate = 150/1 (600 mL)]; ¹H NMR (400 MHz, CDCl₃): δ = 8.33-8.27 (m, 1 H, Ar-H), 7.82-7.75 (m, 1 H, Ar-H), 7.51-7.32 (m, 4 H, Ar-H), 6.83 (d, J = 7.6 Hz, 1 H, Ar-H), 5.55-5.48 (m, 1 H, =CH), 5.35-5.29 (m, 1 H, =CH), 4.72 (dd, J₁ = 6.4 Hz, J₂ = 2.0 Hz, 2 H, CH₂), 2.40-2.28 (m, 1 H, CH), 1.02 (dd, J₁ = 6.8 Hz, J₂ = 1.6 Hz, 6 H, 2 x CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 203.6, 154.3, 134.5, 127.4, 126.3, 125.9, 125.7, 125.1, 122.2, 120.3, 105.4, 100.4, 89.0, 66.7, 27.8, 22.5, 22.4; MS (70 eV, EI) m/z (%): 238 (M⁺, 15.16), 144 (100); IR (neat): ν = 3053, 2959, 2925, 2867, 1963, 1595, 1399, 1267, 1238, 1066 cm⁻¹; HRMS calcd for C₁₇H₁₈O [M⁺]: 238.1352, found: 238.1355.

(26) Preparation of 11-(benzyloxy)-undeca-2,3-dienyl 2-naphthyl ether (3oe) (hcf-4-109)

Following Typical Procedure IV, the reaction of Pd₂dba₃ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1o (144.3 mg, 1 mmol), 2e (499.1 mg, 1.5 mmol), and Et₂O (5.0 mL) afforded 3oe (384.8 mg, 96%) as an oil [eluent: petroleum ether/ethyl acetate = 200/1 (600 mL), 150/1 (300 mL)]; ¹H NMR (400 MHz, CDCl₃): δ = 7.80-7.60 (m, 3 H, Ar-H), 7.41 (t, J = 7.6 Hz, 1 H, Ar-H), 7.37-7.20 (m, 6 H, Ar-H), 7.19-7.04 (m, 2 H, Ar-H), 5.44-5.32 (m, 1 H, =CH), 5.32-5.22 (m, 1 H, =CH), 4.65 (dd, J₁ = 6.6 Hz, J₂ = 1.8 Hz, 2 H, CH₂), 4.48 (s, 2 H, CH₂), 3.43 (t, J = 6.6 Hz, 2 H, CH₂), 2.07-1.95 (m, 2 H, CH₂), 1.64-1.52 (m, 2 H, CH₂), 1.45-1.08 (m, 8 H, 4 x CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 205.3, 156.4, 138.7, 134.5, 129.3, 129.0, 128.3, 127.62, 127.58, 127.4, 126.7, 126.3, 123.6, 119.1, 107.4, 92.9, 87.6, 72.8, 70.5, 66.5, 29.7, 29.2, 29.00, 28.97, 28.4, 26.1; MS (70 eV, EI) m/z (%): 400 (M⁺, 9.32), 144 (100); IR (neat): ν = 3060, 3028, 2928, 2853, 1965, 1629, 1600, 1363, 1255, 1213, 1175, 1007 cm⁻¹; HRMS calcd for C₂₈H₃₂O₂ [M⁺]: 400.2397, found: 400.2399.

(27) Preparation of 4-phenyl-buta-2,3-dienyl phenyl ether (3bf) (XHB-2-130)
Following **Typical Procedure IV**, the reaction of Pd$_2$dba$_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1b (94.2 mg, 1 mmol), 2f (306.7 mg, 1.5 mmol), and Et$_2$O (5.0 mL) afforded 3bf (220.1 mg, 99%) as an oil [eluent: petroleum ether/ethyl acetate = 200:1 (200 mL), 100:1 (200 mL)]: ¹H NMR (400 MHz, CDCl$_3$) δ = 7.32-7.18 (m, 7 H, Ar-H), 6.98-6.91 (m, 3 H, Ar-H), 6.29 (dt, $J_1 = 6.4$ Hz, $J_2 = 2.6$ Hz, 1 H, =CH), 5.80 (q, $J = 6.5$ Hz, 1 H, =CH), 4.68 (dd, $J_1 = 6.8$ Hz, $J_2 = 2.4$ Hz, 2 H, CH$_2$); ¹³C NMR (100 MHz, CDCl$_3$): δ = 206.2, 158.1, 133.4, 129.4, 128.6, 127.2, 127.0, 121.0, 115.0, 96.2, 91.8, 65.7; MS (70 eV, EI) m/z (%): 222 (M$^+$, 27.33), 128 (100); IR ( neat): v = 3061, 3030, 1952, 1729, 1701, 1597, 1586, 1493, 1458, 1363, 1301, 1237, 1213, 1171, 1154, 1076, 1029 cm$^{-1}$; HRMS calcd for C$_{16}$H$_{14}$O [M$^+$]: 222.1045, Found: 222.1055.

(28) **Preparation of p-tolyl-buta-2,3-dienyl 1-naphthyl ether (3pg) (hcf-4-119)**

Following **Typical Procedure IV**, the reaction of Pd$_2$dba$_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1p (144.2 mg, 1 mmol), 2g (327.5 mg, 1.5 mmol), and Et$_2$O (5.0 mL) afforded 3pg (274.3 mg, 96%) as an oil [eluent: petroleum ether/DCM = 80:1 (600 mL)]: ¹H NMR (400 MHz, CDCl$_3$): δ = 8.30 (d, $J = 7.6$ Hz, 1 H, Ar-H), 7.78 (d, $J = 7.2$ Hz, 1 H, Ar-H), 7.54-7.39 (m, 3 H, Ar-H), 7.33 (t, $J = 8.0$ Hz, 1 H, Ar-H), 7.21-7.14 (m, 2 H, Ar-H), 7.14-7.02 (m, 2 H, Ar-H), 6.84 (d, $J = 7.6$ Hz, 1 H, Ar-H), 6.35-6.24 (m, 1 H, =CH), 5.90 (q, $J = 6.5$ Hz, 1 H, =CH), 4.84 (dd, $J_1 = 6.4$ Hz, $J_2 = 2.4$ Hz, 2 H, CH$_2$), 2.32 (s, 3 H, CH$_3$); ¹³C NMR (100 MHz, CDCl$_3$): δ = 206.1, 154.1, 137.1, 134.6, 130.5, 129.4, 127.4, 126.9, 126.4, 125.9, 125.8, 125.2, 122.1, 120.5, 105.6, 96.2, 91.8, 66.2, 21.2; MS (70 eV, EI) m/z (%): 287 (M$^{+1}$, 8.1), 286 (M$^+$, 37.44), 128 (100); IR ( neat): v = 3050, 2987, 2918, 1952, 1579, 1509, 1266,
1095 cm⁻¹; HRMS calcd for C₂₁H₁₈O [M⁺]: 286.1352, found: 286.1350.

(29) Preparation of 4-methoxyphenyl-buta-2,3-dienyl 1-naphthyl ether (3ph)

Following Typical Procedure IV, the reaction of Pd₂dba₃ (23.0 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1p (144.3 mg, 1 mmol), 2h (351.4 mg, 1.5 mmol), and Et₂O (5.0 mL) afforded 3ph (296.9 mg, 84%) as an oil [eluent: petroleum ether/ethyl acetate = 200/1 (600 mL)]: ¹H NMR (400 MHz, CDCl₃): δ = 8.30 (d, J = 7.6 Hz, 1 H, Ar-H), 7.79 (d, J = 7.2 Hz, 1 H, Ar-H), 7.53-7.37 (m, 3 H, Ar-H), 7.34 (t, J = 8.0 Hz, 1 H, Ar-H), 7.26-7.16 (m, 2 H, Ar-H), 6.91-6.79 (m, 3 H, Ar-H), 6.34-6.25 (m, 1 H, =CH), 5.90 (q, J = 6.4 Hz, 1 H, =CH₂), 4.90-4.80 (m, 2 H, CH₂), 3.80 (s, 3 H, OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 205.9, 159.0, 154.0, 134.6, 132.4, 130.0, 128.1, 127.4, 126.4, 125.9, 125.8, 125.7, 125.2, 122.1, 120.5, 114.1, 105.6, 95.8, 91.2, 66.2, 55.3; MS (70 eV, El) m/z (%): 302 (M⁺, 35.7), 115 (100); IR (neat): ν = 3054, 3002, 2945, 2837, 1950, 1581, 1508, 1453, 1396, 1359, 1239, 1169, 1097, 1027 cm⁻¹; HRMS calcd for C₂₁H₁₈O₂ [M⁺]: 302.1301, found: 302.1298.

(30) Preparation of 4-chlorophenyl-buta-2,3-dienyl 1-naphthyl ether (3pi)

Following Typical Procedure IV, the reaction of Pd₂dba₃ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1p (144.2 mg, 1 mmol), 2i (358.3 mg, 1.5 mmol), and Et₂O (5.0 mL) afforded 3pi (269.9 mg, 88%) as an oil [eluent: petroleum ether/ethyl acetate = 200/1 (800 mL)]: ¹H NMR (400 MHz, CDCl₃): δ = 8.27 (d, J = 7.6 Hz, 1 H, Ar-H), 7.79 (d, J = 7.6 Hz, 1 H, Ar-H), 7.55-7.39 (m, 3 H, Ar-H), 7.33 (t, J = 8.0 Hz, 1 H, Ar-H), 7.29-7.08 (m, 4 H, Ar-H), 6.84 (d, J = 7.6 Hz, 1 H, Ar-H), 6.35-6.18 (m, 1 H, Ar-H), 6.84 (d, J = 7.6 Hz, 1 H, Ar-H), 6.35-6.18 (m, 1 H, Ar-H), 6.29-6.08 (m, 3 H, Ar-H), 5.89 (q, J = 6.4 Hz, 1 H, =CH₂), 4.90-4.80 (m, 2 H, CH₂), 3.80 (s, 3 H, OCH₃).
H, =CH), 5.93 (q, J = 6.4 Hz, 1 H, =CH), 4.86 (dd, J1 = 6.6 Hz, J2 = 2.2 Hz, 2 H, CH2); 13C NMR (100 MHz, CDCl3): δ = 206.4, 153.9, 134.6, 132.9, 132.0, 128.8, 128.2, 127.5, 126.4, 125.9, 125.7, 125.3, 122.0, 120.7, 105.6, 95.6, 92.3, 65.8; MS (70 eV, El) m/z (%): 308 (M (37Cl)+, 13.09), 306 (M (35Cl)+, 39.44), 144 (100); IR (neat): ν = 3051, 2925, 2864, 1954, 1490, 1266, 1093, 1013 cm⁻¹; HRMS calcd for C20H15O35Cl [M⁺]: 306.0806, found: 306.0803.

(31) Preparation of 4-bromophenyl-buta-2,3-dienyl phenyl ether (3bj) (lc-1-55)

Following Typical Procedure IV, the reaction of Pd2dba3 (23.0 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1b (94.3 mg, 1 mmol), 2j (424.9 mg, 1.5 mmol), and Et2O (5.0 mL) afforded 3bj (213.9 mg, 71%) as an oil [eluent: petroleum ether/ethyl acetate = 200/1 (500 mL)]; 1H NMR (400 MHz, CDCl3) δ = 7.43-7.36 (m, 2 H, Ar-H), 7.30-7.23 (m, 2 H, Ar-H), 7.12-7.06 (m, 2 H, Ar-H), 6.99-6.89 (m, 3 H, Ar-H), 6.22 (dt, J1 = 6.4 Hz, J2 = 2.4 Hz, 1 H, =CH), 5.79 (q, J = 6.8 Hz, 1 H, =CH), 6.22 (dd, J1 = 6.8 Hz, J2 = 2.4 Hz, 2 H, CH2); 13C NMR (100 MHz, CDCl3) δ = 206.3, 158.1, 132.4, 131.7, 129.5, 128.5, 121.1, 120.9, 115.1, 95.5, 92.3, 65.4; IR (neat) ν = 3039, 2930, 1952, 1586, 1488, 1236, 1213, 1008 cm⁻¹; MS (70 eV, El) m/z (%): 300 (M(79Br)+, 2.62), 302 (M(81Br)+, 1.82), 101 (100); HRMS Calcd. for C16H13O79Br [M⁺]: 300.1044, found: 300.0143.

(32) Preparation of 4-iodophenyl-buta-2,3-dienyl 1-naphthyl ether (3pk) (wpl-5-107)

Following Typical Procedure IV, the reaction of Pd2dba3 (22.9 mg, 0.025 mmol), Xantphos (58.0 mg, 0.1 mmol), 1p (144.3 mg, 1 mmol), 2k (495.4 mg, 1.5 mmol), and Et2O (5.0 mL) afforded 3pk (366.7 mg, 92%) as an oil [eluent: petroleum
ether/ethyl acetate = 150/1 (800 mL): \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 8.38-8.26 (m, 1 H, Ar-H), 7.79-7.73 (m, 1 H, Ar-H), 7.56 (d, J = 8.4 Hz, 2 H, Ar-H), 7.48-7.38 (m, 3 H, Ar-H), 7.30 (t, J = 8.0 Hz, 1 H, Ar-H), 6.95 (d, J = 8.4 Hz, 2 H, Ar-H), 6.78 (d, J = 7.6 Hz, 1 H, Ar-H), 6.23-6.18 (m, 1 H, =CH), 5.87 (q, J = 6.4 Hz, 1 H, =CH), 4.80 (dd, J\textsubscript{1} = 6.4 Hz, J\textsubscript{2} = 2.4 Hz, 2 H, CH\textsubscript{2}); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 206.3, 153.9, 137.6, 134.5, 133.1, 128.7, 127.4, 126.4, 125.8, 125.7, 125.2, 122.0, 120.7, 105.5, 95.7, 92.3, 65.6; MS (70 eV, EI) m/z (%): 398 (M\textsuperscript{+}, 30.56), 128 (100); IR (neat): ν = 2963, 2907, 1260, 1091, 1019 cm\textsuperscript{-1}; HRMS calcd for C\textsubscript{20}H\textsubscript{15}OI [M\textsuperscript{+}]: 398.0162, found: 398.0169.

(33) Preparation of 4-(trifluoromethyl)phenyl-buta-2,3-dienyl 1-naphthyl ether (3pl) (hcf-4-122)

Following Typical Procedure IV, the reaction of Pd\textsubscript{2}dba\textsubscript{3} (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1p (144.2 mg, 1 mmol), 2l (408.5 mg, 1.5 mmol), and Et\textsubscript{2}O (5.0 mL) afforded 3pl (306.1 mg, 90%) as an oil [eluent: petroleum ether/DCM = 80/1 (600 mL)]: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 8.27 (d, J = 8.0 Hz, 1 H, Ar-H), 7.77 (d, J = 7.2 Hz, 1 H, Ar-H), 7.60-7.38 (m, 5 H, Ar-H), 7.38-7.24 (m, 3 H, Ar-H), 6.82 (d, J = 7.6 Hz, 1 H, Ar-H), 6.40-6.24 (m, 1 H, =CH), 5.96 (q, J = 6.4 Hz, 1 H, =CH), 4.85 (dd, J\textsubscript{1} = 6.4 Hz, J\textsubscript{2} = 2.4 Hz, 2 H, CH\textsubscript{2}); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 207.0, 153.9, 137.4, 134.6, 129.1 (q, J = 32.1 Hz), 127.5, 127.1, 126.5, 125.9, 125.7, 125.5 (q, J = 3.9 Hz), 125.3, 124.2 (q, J = 270.4 Hz), 122.0, 120.8, 105.6, 95.7, 92.5, 65.5; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): δ = -63.0; MS (70 eV, EI) m/z (%): 341 (M\textsuperscript{+}+1, 9.88), 340 (M\textsuperscript{+}, 45.17), 144 (100); IR (neat): ν = 3054, 2938, 2874, 1595, 1579, 1396, 1322, 1267, 1096, 1064, 1016 cm\textsuperscript{-1}; HRMS calcd for C\textsubscript{21}H\textsubscript{15}OF\textsubscript{3} [M\textsuperscript{+}]: 340.1070, found: 340.1069.

(34) Preparation of 4-nitrophenyl-buta-2,3-dienyl phenyl ether (3bm) (hcf-4-138)
Following **Typical Procedure IV**, the reaction of Pd$_2$dba$_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1b (94.1 mg, 1 mmol), 2m (373.9 mg, 1.5 mmol), and Et$_2$O (5.0 mL) afforded 3bm (213.5 mg, 80%) as an oil [eluent: petroleum ether/DCM = 5/1 (500 mL), 2/1 (600 mL)]; **$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ = 8.12 (d, $J$ = 8.0 Hz, 2 H, Ar-H), 7.41-7.18 (m, 4 H, Ar-H), 7.02-6.82 (m, 3 H, Ar-H), 6.42-6.26 (m, 1 H, =CH), 5.92 (q, $J$ = 6.3 Hz, 1 H, =CH), 4.72 (d, $J$ = 6.0 Hz, 2 H, CH$_2$); **$^{13}$C NMR** (100 MHz, CDCl$_3$): $\delta$ = 207.7, 157.9, 146.7, 140.8, 129.5, 127.4, 123.9, 121.3, 115.1, 95.4, 92.9, 64.9; **MS** (70 eV, EI) $m/z$ (%): 268 (M$^+$+1, 7.36), 267 (M+, 40.01), 94 (100); **IR** (neat): $\nu$ = 3075, 2930, 2850, 1952, 1594, 1512, 1493, 1335, 1236, 1012 cm$^{-1}$; **HRMS** calcd for C$_{16}$H$_{13}$NO$_3$ [M$^+$]: 267.0890, found: 267.0891.

**Preparation of 4-cyanophenyl-buta-2,3-dienyl 1-naphthyl ether (3pn) (hcf-4-121)**

Following **Typical Procedure IV**, the reaction of Pd$_2$dba$_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1p (144.2 mg, 1 mmol), 2n (344.1 mg, 1.5 mmol), and Et$_2$O (5.0 mL) afforded 3pn (223.3 mg, 75%) as an oil [eluent: petroleum ether/DCM = 20/1 (200 mL), 10/1 (500 mL), 50/1 (200 mL)]; **$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ = 8.25 (d, $J$ = 8.4 Hz, 1 H, Ar-H), 7.80 (d, $J$ = 8.0 Hz, 1 H, Ar-H), 7.61-7.38 (m, 5 H, Ar-H), 7.38-7.27 (m, 3 H, Ar-H), 6.84 (d, $J$ = 7.6 Hz, 1 H, Ar-H), 6.39-6.25 (m, 1 H, =CH), 6.01 (q, $J$ = 6.4 Hz, 1 H, =CH), 4.89 (dd, $J_1$ = 6.2 Hz, $J_2$ = 2.2 Hz, 2 H, CH$_2$); **$^{13}$C NMR** (100 MHz, CDCl$_3$): $\delta$ = 207.4, 153.8, 138.7, 134.6, 132.3, 127.5, 127.4, 126.5, 125.8, 125.6, 125.3, 121.9, 120.9, 118.9, 110.4, 105.6, 95.8, 92.8, 65.3; **MS** (70 eV, EI) $m/z$ (%): 298 (M$^+$+1, 12.94), 297 (M+, 60.93), 144 (100); **IR** (neat): $\nu$ = 3052, 2929, 2877, 2224, 1951, 1579, 1395, 1267, 1095 cm$^{-1}$; **HRMS** calcd for...
(36) Preparation of 3-furyl-buta-2,3-dienyl phenyl ether (3bo) (hcf-4-132)

Following Typical Procedure IV, the reaction of Pd$_2$dba$_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1b (94.2 mg, 1 mmol), 2o (291.9 mg, 1.5 mmol), and Et$_2$O (5.0 mL) afforded 3bo (195.4 mg, 92%) as an oil [eluent: petroleum ether/DCM = 80/1 (600 mL)]: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.35 (d, $J$ = 12.8 Hz, 2 H, Ar-H), 7.27 (t, $J$ = 8.0 Hz, 2 H, Ar-H), 7.01-6.81 (m, 3 H, Ar-H), 6.31 (s, 1 H, Ar-H), 6.23-6.12 (m, 1 H, =CH), 5.70 (q, $J$ = 6.5 Hz, 1 H, =CH), 4.63 (dd, $J_1$ = 6.6 Hz, $J_2$ = 2.2 Hz, 2 H, CH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 206.2, 158.2, 143.5, 139.7, 129.4, 121.0, 119.2, 115.0, 108.9, 91.0, 86.4, 65.7; MS (70 eV, EI) $m/z$ (%): 213 (M$^+$+1, 6.92), 212 (M$^+$, 43.04), 91 (100); IR (neat): $\nu$ = 3062, 3031, 2930, 2874, 1954, 1598, 1494, 1238, 1212, 1155, 1014 cm$^{-1}$; HRMS calcd for C$_{14}$H$_{12}$O$_2$ [M$^+$]: 212.0832, found: 212.0829.

(37) Preparation of 3-thienyl-buta-2,3-dienyl 1-naphthyl ether (3pp) (hcf-4-120)

Following Typical Procedure IV, the reaction of Pd$_2$dba$_3$ (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), 1p (144.2 mg, 1 mmol), 2p (315.6 mg, 1.5 mmol), and Et$_2$O (5.0 mL) afforded 3pp (250.5 mg, 90%) as an oil [eluent: petroleum ether/DCM = 80/1 (600 mL)]: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.29 (dd, $J_1$ = 6.6 Hz, $J_2$ = 2.6 Hz, 1 H, Ar-H), 7.78 (d, $J$ = 7.2 Hz, 1 H, Ar-H), 7.54-7.37 (m, 3 H, Ar-H), 7.37-7.29 (m, 1 H, Ar-H), 7.28-7.17 (m, 1 H, Ar-H), 7.13-6.95 (m, 2 H, Ar-H), 6.83 (d, $J$ = 7.6 Hz, 1 H, Ar-H), 6.45-6.26 (m, 1 H, =CH), 5.85 (q, $J$ = 6.4 Hz, 1 H, =CH), 4.83 (dd, $J_1$ = 6.6 Hz, $J_2$ = 2.2 Hz, 2 H, CH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 206.7, 154.0, 134.63, 134.56, 127.4, 126.4, 126.0, 125.9, 125.7, 125.2, 122.1, 121.4, 120.6,
105.5, 91.1, 90.9, 66.1; **MS** (70 eV, EI) *m/z* (%): 279 (M$^{+}$+1, 15.14), 278 (M$^{+}$, 59.4), 144 (100); **IR** (neat): $\nu$ = 3098, 3051, 2988, 1953, 1578, 1401, 1265, 1236, 1094 cm$^{-1}$; **HRMS** calcd for C$_{18}$H$_{14}$OS [M$^{+}$]: 278.0760, found: 278.0756.

3. Synthetic applications

(1) **Preparation of (Z)-2-bromophenyl 4-oxo-3-(phenylselanyl)but-2-enyl ether (4) (hcf-4-186)$^{10}$**

\[
\begin{align*}
\text{O} & \quad \text{Br} \\
\text{Ph} & \quad \text{N} \quad \text{F} \quad \text{OTf} \\
\text{CHO} & \quad \text{SePh} \\
\text{Br} & \quad \text{CHO}
\end{align*}
\]

To a Schlenk tube equipped with a stirring bar were added [PyF][OTf]$^{-}$ (59.3 mg, 0.24 mmol), (PhSe)$_{2}$ (62.4 mg, 0.2 mmol), and a solution of the allenic ether 3ga in MeCN/THF (1:1, v/v, 4 mL) sequentially in the glove box. Then the resulting mixture was removed from the glove box and stirred at room temperature until disappearance of the starting material as monitored by TLC and extracted with ethyl acetate (3 x 5 mL). The organic extract was washed with brine, dried over anhydrous Na$_{2}$SO$_{4}$, and concentrated under reduced pressure. Chromatography of the residue gave analytically pure compound 4 as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (600 mL)]: **1H NMR** (400 MHz, CDCl$_{3}$): $\delta$ = 9.44 (s, 1 H, CHO), 7.65-7.37 (m, 4 H, Ar-H), 7.37-7.16 (m, 4 H, Ar-H), 6.87 (t, $J$ = 7.8 Hz, 1 H, Ar-H), 6.71 (d, $J$ = 8.4 Hz, 1 H, =CH), 4.89 (d, $J$ = 4.8 Hz, 2 H, CH$_{2}$), the following signal is discernible for (E)-4:

$\delta$ = 9.92 (s, 1 H, CHO), 5.06 (d, $J$ = 5.6 Hz, 2 H, CH$_{2}$); **13C NMR** (100 MHz, CDCl$_{3}$): $\delta$ = 189.5, 154.2, 153.4, 136.4, 133.7, 129.5, 128.5, 128.0, 122.8, 113.3, 112.2, 68.2; **MS** (70 eV, EI) *m/z* (%): 398 (M($^{81}$Br)$^{+}$, 7.2), 396 (M($^{79}$Br)$^{+}$, 8.86), 133 (100); **IR** (neat): $\nu$ = 3061, 2819, 2718, 1697, 1575, 1475, 1438, 1244, 1225, 1141, 1051, 1031 cm$^{-1}$.

(2) **Preparation of 2-bromophenyl 3-bromo-2-hydroxybut-3-enyl ether (5) (hcf-4-200)$^{11}$**
To a Schlenk tube equipped with a stirring bar, NBS (42.7 mg, 0.24 mmol), a solution of the allenic ether 3ga (45.0 mg, 0.2 mmol) in 1,4-dioxane (1.5 mL), and water (1.5 mL) were added sequentially. The resulting mixture was stirred at room temperature until disappearance of the starting material as determined by TLC, quenched with 5 mL of sat. aq. Na₂S₂O₃, extracted with ethyl acetate (5 mL×3), washed with brine, and dried over anhydrous Na₂SO₄. After filtration and concentration, column chromatography of the residue afforded compound 5 as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (400 mL)]: \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 7.54 \text{ (dd, } J_1 = 8.0 \text{ Hz, } J_2 = 1.6 \text{ Hz, 1 H, Ar-H)}, 7.34-7.20 \text{ (m, 1 H, Ar-H)}, 7.01-6.80 \text{ (m, 2 H, Ar-H)}, 6.17 \text{ (dd, } J_1 = 2.0 \text{ Hz, } J_2 = 1.2 \text{ Hz, 1 H, one proton of } =\text{CH}_2\)}, 5.74 \text{ (dd, } J_1 = 2.2 \text{ Hz, } J_2 = 0.6 \text{ Hz, 1 H, one proton of } =\text{CH}_2\)}, 4.62 \text{ (q, } J = 5.1 \text{ Hz, 1 H, CH}), 4.27 \text{ (dd, } J_1 = 9.4 \text{ Hz, } J_2 = 3.8 \text{ Hz, 1 H, one proton of } O\text{CH}_2\)}, 4.13 \text{ (dd, } J_1 = 9.4 \text{ Hz, } J_2 = 2.6 \text{ Hz, 1 H, one proton of } O\text{CH}_2\)}, 3.02-2.86 \text{ (m, 1 H, OH)}; \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta = 154.5, 133.4, 130.6, 128.6, 122.8, 119.0, 114.1, 112.6, 74.0, 71.3; \) \(^{79}\)MS (70 eV, EI) \(m/z\) (%): 324 (M \(^{81}\Br \times 2\)\(^{+}\), 11.4), 322 (M \(^{81}\Br + ^{79}\Br\)\(^{+}\), 22.4), 320 (M \(^{79}\Br \times 2\)\(^{+}\), 10.65), 172 (100); IR (neat): \(\nu = 3416, 2938, 2878, 1627, 1585, 1479, 1442, 1277, 1247, 1053, 1030 \text{ cm}^{-1}; \) HRMS calcd for C₁₀H₁₀\(^{79}\Br\^{81}\BrO₂ \text{ [M]}\): 321.9022, found: 321.9025.

(3) Preparation of (E)-2-bromophenyl but-2-en-1,4-diol ether (6) (hcf-5-57)\(^1\)²

To a Schlenk tube were added IPrAuCl (6.2 mg, 0.01 mmol), AgOTf (2.6 mg, 0.01 mmol), 3ga (45.0 mg, 0.2 mmol) in 1,4-dixoane (0.6 mL), and H₂O (0.3 mL) sequentially under argon. The resulting mixture was stirred at room temperature for
24 h until disappearance of the starting material as monitored by TLC, quenched with 5 mL of H2O, and extracted with Et2O (3 x 5 mL). The combined organic layer was washed with brine (5 mL) and dried with anhydrous Na2SO4. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel to afford 6 (34.0 mg, 70%) as an oil [eluent: DCM (300 mL)]: ¹H NMR (400 MHz, CDCl₃): δ = 7.55 (dd, J₁ = 7.8 Hz, J₂ = 1.4 Hz, 1 H, Ar-H), 7.26-7.21 (m, 1 H, Ar-H), 6.95-6.80 (m, 2 H, Ar-H), 6.17-5.92 (m, 2 H, 2 x =CH), 4.68-4.58 (m, 2 H, CH2), 4.23 (d, J = 4.4 Hz, 2 H, CH2), 1.57 (br, 1 H, OH), the following signal is discernible for (Z)-6: δ = 4.70 (d, J = 4.8 Hz, 2 H, CH2), 4.31 (d, J = 6.0 Hz, 2 H, CH2); ¹³C NMR (100 MHz, CDCl₃): δ = 154.8, 133.4, 132.7, 128.4, 125.4, 122.0, 113.5, 112.2, 68.7, 62.8; MS (70 eV, EI) m/z (%): 244 (M⁺(81Br)⁺, 3.61), 242 (M⁺(79Br)⁺, 3.58), 172 (100); IR (neat): ν = 3328, 2918, 2865, 1585, 1476, 1442, 1275, 1242, 1030 cm⁻¹; HRMS calcd for C₁₀H₁₁⁷⁹BrO₂ [M⁺]: 241.9937, found: 241.9937.

(4) Preparation of (Z)-2-bromophenyl 3,4-diiodobut-2-enyl ether ((Z)-7) (hcf-5-62)¹³

![diagram]

To a flame-dried Schlenk tube were added I₂ (60.8 mg, 0.24 mmol), 3ga (45.0 mg, 0.2 mmol), and Et₂O (2 mL) sequentially under argon. The resulting mixture was stirred at room temperature for 1 h until disappearance of the starting material as monitored by TLC, quenched with 5 mL of sat. aq. Na₂S₂O₃, extracted with Et₂O (5 mL x 3), and dried over anhydrous Na₂SO₄. After filtration and concentration, column chromatography of the residue afforded compounds (Z)-7 as an oil [eluent: petroleum ether/DCM = 80/1 (500 mL)]: ¹H NMR (400 MHz, CDCl₃): δ = 7.54 (dd, J₁ = 8.0 Hz, J₂ = 1.6 Hz, 1 H, Ar-H), 7.27 (dt, J₁ = 7.8 Hz, J₂ = 1.5 Hz, 1 H, Ar-H), 6.92-6.80 (m, 2 H, Ar-H), 6.42 (t, J = 5.0 Hz, 1 H, =CH), 4.59 (d, J = 5.2 Hz, 2 H, CH₂), 4.42 (s, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 154.4, 134.7, 133.5, 128.5, 122.5, 113.7,
112.2, 104.6, 73.5, 16.5; **MS** (70 eV, EI) \( m/z \) (%): 480 (M\(^{81}\text{Br}\)^+, 2.85), 478 (M\(^{79}\text{Br}\)^+, 2.72), 53 (100); **IR** (neat): \( \nu = 3003, 2948, 2917, 2848, 1584, 1569, 1479, 1438, 1283, 1245, 1155, 1017 \text{ cm}^{-1} \); **HRMS** calcd for C\(_{10}\)H\(_{9}\)BrI\(_2\)O [M\(^+\)]: 477.7921, found: 477.7928.

(5) Synthesis of naturally occurring allenes

(5.1) Eucalyptene A (hcf-5-67)

Following **Typical Procedure IV**, the reaction of Pd(PPh\(_3\))\(_4\) (57.8 mg, 0.05 mmol), methyl (E)-3-(4-hydroxyphenyl)acrylate (178.2 mg, 1 mmol), 2a (192.2 mg, 1.5 mmol), and Et\(_2\)O (5.0 mL) afforded eucalyptene A\(^7\) (207.1 mg, 90%) as a white solid [elucent: petroleum ether/ethyl acetate = 10/1 (600 mL)]: m. p. 65.1-65.9 °C (petroleum ether/DCM); \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \( \delta = 7.64 \text{ (d, } J = 16.4 \text{ Hz, 1 H, } =\text{CH}) \), 7.46 (d, \( J = 8.4 \text{ Hz, 2 H, Ar-H} \)), 6.91 (d, \( J = 8.8 \text{ Hz, 2 H, Ar-H} \)), 6.31 (d, \( J = 16.0 \text{ Hz, 1 H, } =\text{CH} \)), 5.38 (quint, \( J = 6.7 \text{ Hz, 1 H, } =\text{CH} \)), 4.92-4.84 (dt, \( J_1 = 6.8 \text{ Hz, } J_2 = 2.7 \text{ Hz, 2 H, } =\text{CH}_2 \)), 4.67-4.53 (m, 2 H, OCH\(_2\)), 3.79 (s, 3 H, OCH\(_3\)); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \( \delta = 209.5, 167.7, 160.1, 144.4, 129.6, 127.3, 115.3, 115.1, 86.7, 76.7, 65.8, 51.5 \); **MS** (70 eV, EI) \( m/z \) (%): 231 (M\(^+\)+1, 2.43), 230 (M\(^+\), 11.69), 147 (100); **IR** (neat): \( \nu = 2956, 2932, 2874, 2842, 1958, 1720, 1509, 1283, 1167, 1010 \text{ cm}^{-1} \).

(5.2) Terricollene A

Preparation of buta-2,3-dienyl 4-(hydroxymethyl)phenyl ether (hcf-5-68)

Following **Typical Procedure IV**, the reaction of Pd\(_2\)dba\(_3\) (22.9 mg, 0.025 mmol), Xantphos (57.9 mg, 0.1 mmol), \( p \)-hydroxylmethylphenol (124.1 mg, 1 mmol), 2a
(192.1 mg, 1.5 mmol), and Et₂O (5.0 mL) afforded 10⁷ (158.4 mg, 90%) as a white solid [eluent: petroleum ether/ethyl acetate = 5/1 (600 mL)]: m.p. 46.2-46.9 °C (petroleum ether/ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ = 7.26 (d, J = 8.4 Hz, 2 H, Ar-H), 6.94-6.84 (m, 2 H, Ar-H), 5.38 (quint, J = 6.7 Hz, 1 H, =CH), 4.86 (dt, J₁ = 6.5 Hz, J₂ = 2.4 Hz, 2 H, C=CH₂), 4.63-4.50 (m, 4 H, 2 x CH₂), 1.91 (br, 1 H, OH); ¹³C NMR (100 MHz, CDCl₃) δ = 209.4, 157.9, 133.4, 128.5, 114.9, 87.0, 76.5, 65.8, 64.9; MS (70 eV, EI) m/z (%): 176 (M⁺, 4.75), 95 (100); IR (neat): ν = 3341, 3256, 2930, 2864, 1958, 1509, 1381, 1241, 1230, 1044, 1011 cm⁻¹.

70 mmol scale preparation of buta-2,3-dienyl 4-(hydroxymethyl)phenyl ether (hcf-6-75)

Following Typical Procedure IV, the reaction of Pd₂dba₃ (641.9 mg, 0.7 mmol), Xantphos (1.6213 g, 2.8 mmol), p-hydroxylmethylphenol (8.6895 g, 70 mmol), 2a (10.2517 g, 80 mmol), and Et₂O (250.0 mL) afforded 10⁷ (9.9913 g, 81%) as a white solid [eluent: petroleum ether/ethyl acetate = 5/1 (1500 mL)]: ¹H NMR (400 MHz, CDCl₃) δ = 7.25 (d, J = 8.4 Hz, 2 H, Ar-H), 6.88 (d, J = 8.4 Hz, 2 H, Ar-H), 5.38 (quint, J = 6.8 Hz, 1 H, =CH), 4.86 (dt, J₁ = 6.4 Hz, J₂ = 2.4 Hz, 2 H, C=CH₂), 4.69-4.46 (m, 4 H, 2 x CH₂), 2.07 (br, 1 H, OH); ¹³C NMR (100 MHz, CDCl₃) δ = 209.4, 157.8, 133.3, 128.5, 114.8, 86.9, 76.5, 65.8, 64.8.

4.5 Gram-scale synthesis of terricollene A
To a solution of D-glucose (4 g, 22.2 mmol) in anhydrous pyridine (40 mL) at room temperature under argon atmosphere was slowly added TMSCl (16.9 mL, 133.2 mmol). The resulting mixture was stirred overnight. CH₂Cl₂ (150 mL) was added to dilute the reaction mixture, which was then washed with ice-cold H₂O, hydrochloric acid (1 M, 30 mL×2), saturated sodium bicarbonate solution (30 mL×2), and a saturated sodium chloride solution (50 mL), respectively. The aqueous phase was extracted with CH₂Cl₂ (30 mL×2). The organic phases were combined, dried over anhydrous Na₂SO₄, and evaporated in vacuo. The residue was purified by silica gel column chromatograph (petroleum ether/ethyl acetate = 9:1) to afford compound 8 (11.1 g, 92.4% yield) as a colorless oil [eluent: petroleum ether/ethyl acetate = 9:1]:

1H NMR (400 MHz, CDCl₃) δ = [5.00 (d, J = 2.8 Hz, 0.79 H), 4.45 (d, J = 7.2 Hz, 0.21 H), 1 H, anomer CH], [3.82-3.56 (m, 3.86 H), 3.26-3.19 (m, 0.47 H), 4 H, 4 x CH], 3.47-3.30 (m, 2 H, CH₂), 0.21-0.08 (m, 45 H).

To a solution of 8 (10.96 g, 20.29 mmol) in dry CH₂Cl₂ (70 mL) at room temperature under argon atmosphere was added iodos trimethylsilane (2.92 mL, 20.29 mmol). The resulting mixture was stirred for 30 min. Then a solution of 10 (7.15 g, 40.58 mmol) and 2,6-di-tert-butylpyridine (4.9 mL, 40.6 mmol) in dry CH₂Cl₂ (48 mL) was added. After being stirred for 4 h at room temperature, MeOH (90 mL) was added to the mixture, and the stirring was continued for 15 min. Resin(OH) was added to neutralize the reaction mixture, which was then filtered. The filtrates were concentrated to give a residue, which was purified by silica gel column chromatograph to afford target compound terricollene A (4.5 g, 58% yield, α only,
96% purity) as a white solid [eluent: CH2Cl2/MeOH = 10:1]: m.p. 84.2-84.9 °C (dichloromethane/methanol); H NMR (500 MHz, CD3OD) δ = 7.33 (d, J = 9.0 Hz, 2 H, Ar-H), 6.89 (d, J = 9.0 Hz, 2 H, Ar-H), 5.37 (quint, J = 6.7 Hz, 1 H, =CH), 4.85 – 4.82 (m, 1 H, CH), 4.68 (d, J = 11.5 Hz, 1 H, CH), 4.54 (dt, J1 = 6.5 Hz, J2 = 2.4 Hz, 2 H, C=CH2), 4.48 (d, J = 12.0 Hz, 1 H, CH), 3.80 (dd, J1 = 12.0 Hz, J2 = 2.5 Hz, 1 H, CH), 3.71 – 3.59 (m, 3 H, CH2 and CH), 3.40 (dd, J1 = 9.5 Hz, J2 = 3.5 Hz, 1 H, CH), 3.36-3.28 (m, 1 H, CH); C NMR (126 MHz, CD3OD) δ = 209.3, 158.1, 129.9, 129.5, 114.0, 97.6, 86.6, 75.1, 73.7, 72.4, 72.1, 70.4, 68.5, 65.4, 61.2; MS (ESI) m/z : 361 (M+Na)+; IR (neat): v = 3346, 2924, 1958, 1611, 1511, 1234, 1034, 1005 cm⁻¹.
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SOLVENT: CDCl3
F2 = 1.00000 MHz
F1 = 376.8072 MHz
P = 19.8

1H 4.11 ppm
