A New Synthetic Approach to Phenol Derivatives: Use of Ring-Closing Olefin Metathesis

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Supporting Data

General. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under prepurified argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^1H , 76.5 MHz for ^2H , and 125 MHz for ^{13}C) and LA-400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR, chloroform-*d* (δ 7.26) for ^2H NMR, and chloroform-*d* (δ 77.05) for ^{13}C NMR.

Materials. Anhydrous THF was purchased and used as received. Dichloromethane was distilled from CaH_2 under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. Toluene was distilled from sodium benzophenone-ketyl under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. Ruthenium complexes, $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{C}(\text{H})\text{Ph}$ (**10**)¹ and $(\text{PCy}_3)(\text{Imes})\text{Cl}_2\text{Ru}=\text{C}(\text{H})\text{Ph}$ (**11**)², were prepared according to the reported procedures. Bromodienes **5** were prepared by bromoallylation of alkynes according to the reported procedures.³ (*E*)-Hex-4-en-1-yn-3-ol⁴, MnO_2 ⁵, 2-ethyl-propenal⁶, and (*Z*)-4-chloro-2,7-dimethyl-5-phenyl-octa-1,5,7-trien-3-one (**15j**)⁷ were prepared according to the reported procedures. Acrolein, methacrolein, 2-ethylacrolein, *N,N*-diisopropylethylamine, acetyl chloride, imidazole, TBDMSCl, crotonaldehyde, and Lindlar catalyst (5 wt%) were used as received.

Scheme S-1

Preparation of trienol 4. *t*-BuLi (1.47 M solution in pentane, 10.0 mmol) was added to a solution of bromodiene **5** (5.00 mmol) in THF (12.5 mL) at -78°C . After 5 min, aldehyde (15.0 mmol) was added and the mixture was stirred for 30 min at the same temperature. The reaction mixture was then quenched by addition of water and extracted with EtOAc twice. The organic phases were dried with MgSO_4 and concentrated under vacuum. The residue was purified by silica gel column chromatography to give trienol **4**.

(Z)-4,5-Dipropyl-octa-1,4,7-trien-3-ol (4a): purified by silica gel column chromatography (hexane/EtOAc = 4/1) (70% yield); ^1H NMR (CDCl_3) δ 0.91 (t, $J = 7.3$ Hz, 3H), 0.92 (t, $J = 7.4$ Hz, 3H), 1.35-1.60 (m, 5H), 1.95-2.07 (m, 4H), 2.84 (dd, $J = 15.6, 6.1$ Hz, 1H), 2.91 (dd, $J = 15.6, 6.1$ Hz, 1H), 4.99 (dd, $J = 11.0, 1.8$ Hz, 1H), 5.02 (dd, $J = 17.1, 1.9$ Hz, 1H), 5.07 (br d, $J = 6.4$ Hz, 1H), 5.11 (dd, $J = 10.7, 1.5$ Hz, 1H), 5.27 (dd, $J = 17.1, 1.5$ Hz, 1H), 5.80 (ddt, $J = 16.8, 10.1, 6.1$ Hz, 1H), 5.89 (ddd, $J = 16.8, 10.4, 4.6$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 14.45, 14.75, 21.79, 24.35, 30.16, 34.90, 35.57, 72.44, 113.95, 114.97, 135.24, 135.81, 137.19, 139.52. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{22}$ ($\text{M}^+ - \text{H}_2\text{O}$) 190.1722, found 190.1735.

4a

(Z)-4-Phenyl-octa-1,4,7-trien-3-ol (4b): purified by silica gel column chromatography (hexane/EtOAc = 5/1) (69% yield); ^1H NMR (CDCl_3) δ 1.74 (d, $J = 5.2$ Hz, 1H), 3.00-3.11 (m, 2H), 5.06 (dq, $J = 10.1, 1.5$ Hz, 1H), 5.13 (dq, $J = 17.1, 1.9$ Hz, 1H), 5.17-5.20 (m, 1H), 5.30-5.35 (m, 2H), 5.72 (t, $J = 7.7$ Hz, 1H), 5.90 (ddt, $J = 16.5, 10.4, 6.1$ Hz, 1H), 6.02 (ddd, $J = 17.7, 10.7, 4.3$ Hz, 1H), 7.24-7.32 (m, 3H), 7.36-7.39 (m, 2H). ^{13}C NMR (CDCl_3) δ 32.25, 71.41, 115.04, 115.54, 127.20, 128.11, 129.33, 136.32, 139.33, 140.39, 141.98. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}$ ($\text{M}^+ - \text{H}_2\text{O}$) 182.1096, found 182.1107.

4b

(Z)-5-Deuterio-4-phenyl-octa-1,4,7-trien-3-ol (4c): purified by silica gel column chromatography (hexane/EtOAc = 5/1) (45% yield); ^2H NMR (CHCl_3) δ 5.74.

4c

(Z)-2-Methyl-4,5-dipropyl-octa-1,4,7-trien-3-ol (4d): purified by silica gel column chromatography (hexane/EtOAc = 20/1) (54% yield); ^1H NMR (CDCl_3) δ 0.89 (t, $J = 7.3$ Hz, 3H), 0.92 (t, $J = 7.3$ Hz, 3H), 1.28-1.49 (m, 4H), 1.61 (br s, 1H), 1.62 (s, 3H), 1.87-2.10 (m, 4H), 2.88 (ddt, $J = 15.6, 6.1, 1.9$ Hz, 1H), 2.94 (ddt, $J = 15.6, 6.1, 1.9$ Hz, 1H), 4.89-4.91 (m, 1H), 4.93 (s, 1H), 5.00 (dq, $J = 10.1, 1.5$ Hz, 1H), 5.05 (dq, $J = 17.1, 1.9$ Hz, 1H), 5.12-5.14 (m, 1H), 5.81 (ddt, $J = 16.5, 10.1, 6.4$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 14.37, 14.82, 20.14, 21.69, 24.32, 29.98, 34.78, 35.54,

73.96, 109.43, 115.04, 135.13, 136.39, 137.28, 146.05. HRMS (EI) calcd for $C_{15}H_{26}O$ (M^+) 222.1985, found 222.1994.

(E)-2-Ethyl-4-trimethylsilyl-octa-1,4,7-trien-3-ol (4e): purified by silica gel column chromatography (hexane/EtOAc = 20/1) (50% yield); 1H NMR ($CDCl_3$) δ 0.11 (s, 9H), 1.06 (t, J = 7.3 Hz, 3H), 1.59 (br s, 1H), 1.92-2.07 (m, 2H), 2.84-2.99 (m, 2H), 4.91 (quint, J = 1.5 Hz, 1H), 5.01 (dq, J = 10.1, 1.5 Hz, 1H), 5.04 (dq, J = 17.1, 1.6 Hz, 1H), 5.10 (br s, 1H), 5.12 (quint, J = 1.2 Hz, 1H), 5.82 (ddt, J = 16.5, 10.1, 6.2 Hz, 1H), 5.91 (td, J = 7.0, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 0.45, 12.15, 25.25, 33.64, 74.24, 108.25, 115.36, 136.44, 139.72, 143.81, 151.95. HRMS (EI) calcd for $C_{12}H_{21}OSi$ ($M^+ - CH_3$) 209.1362, found 209.1360.

(Z)-3-Methylene-5-phenyl-nona-5,8-diene-1,4-diol (4f): purified by silica gel column chromatography (hexane/EtOAc = 2/3) (39% yield); mp = 72-74 °C; 1H NMR ($CDCl_3$) δ 2.23 (dt, J = 14.7, 5.8 Hz, 1H), 2.33 (dt, J = 14.7, 6.1 Hz, 1H), 2.35 (br s, 1H), 2.78 (br s, 1H), 3.00-3.11 (m, 2H), 3.69 (t, J = 6.4 Hz, 2H), 5.00-5.01 (m, 1H), 5.05 (dq, J = 10.1, 1.6 Hz, 1H), 5.12 (dq, J = 17.1, 1.6 Hz, 1H), 5.22-5.23 (m, 1H), 5.26 (s, 1H), 5.81 (t, J = 7.7 Hz, 1H), 5.89 (ddt, J = 16.5, 10.4, 6.4 Hz, 1H), 7.21-7.28 (m, 3H), 7.36 (dd, J = 8.2, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 32.50, 36.15, 61.58, 72.49, 112.90, 115.51, 127.05, 127.93, 127.97, 130.80, 136.36, 140.63, 141.10, 146.38. HRMS (FAB) calcd for $C_{16}H_{19}O$ ($M^+ - OH$) 227.1436, found 227.1435.

(Z)-2,7-Dimethyl-4-phenyl-octa-1,4,7-trien-3-ol (4h): purified by silica gel column chromatography (hexane/EtOAc/ $CHCl_3$ = 5/2/5) (36% yield); 1H NMR ($CDCl_3$) δ 1.69 (t, J = 0.6 Hz, 3H), 1.81 (s, 3H), 1.87 (d, J = 5.2 Hz, 1H), 2.97-3.06 (m, 2H), 4.80-4.81 (m, 2H), 4.92-4.94 (m, 1H), 5.10-5.12 (m, 1H), 5.21 (br d, J = 5.2 Hz, 1H), 5.85 (t, J = 7.6 Hz, 1H), 7.23-7.30 (m, 3H), 7.37-7.39 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 19.85, 22.91, 36.33, 72.98, 110.68, 111.01, 127.11, 127.95, 128.01, 130.88, 140.56, 141.49, 144.52, 145.44. HRMS (EI) calcd for $C_{16}H_{20}O$ (M^+) 228.1515, found 228.1513.

4h

Preparation of trienone 3. To a solution of trienol **4** (0.500 mmol) in hexane (3.2 mL) or CH_2Cl_2 (3.2 mL) was added MnO_2 (869 mg, 10.0 mmol) in one portion under air and stirred for 30 min at room temperature. The mixture was passed through celite and concentrated under reduced pressure. Purification by column chromatography gave trienone **3**.

(Z)-4,5-Dipropyl-octa-1,4,7-trien-3-one (3a): purified by silica gel column chromatography (hexane/EtOAc = 8/1) (84% yield); ^1H NMR (CDCl_3) δ 0.89 (t, $J = 7.3$ Hz, 3H), 0.95 (t, $J = 7.3$ Hz, 3H), 1.31-1.39 (m, 2H), 1.42-1.49 (m, 2H), 2.08-2.11 (m, 2H), 2.22-2.25 (m, 2H), 2.73 (dt, $J = 6.8, 1.5$ Hz, 2H), 4.98-5.03 (m, 2H), 5.69 (ddt, $J = 17.4, 9.5, 6.4$ Hz, 1H), 5.93 (dd, $J = 10.4, 1.3$ Hz, 1H), 6.17 (dd, $J = 17.4, 1.5$ Hz, 1H), 6.43 (dd, $J = 17.7, 10.4$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 14.09, 14.31, 21.56, 22.10, 32.26, 32.75, 37.93, 116.34, 130.21, 136.04, 136.66, 137.44, 138.59, 201.38. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{22}\text{O}$ (M^+) 206.1671, found 206.1671.

3a

(Z)-4-Phenyl-octa-1,4,7-trien-3-one (3b): purified by florisil column chromatography (hexane/EtOAc = 10/1) (54% yield); ^1H NMR (CDCl_3) δ 2.97 (ddt, $J = 7.9, 6.4, 1.5$ Hz, 2H), 5.06 (dq, $J = 10.1, 1.6$ Hz, 1H), 5.11 (dq, $J = 17.1, 1.5$ Hz, 1H), 5.86 (ddt, $J = 16.5, 10.1, 6.1$ Hz, 1H), 5.96 (dd, $J = 10.4, 1.3$ Hz, 1H), 6.15 (t, $J = 7.6$ Hz, 1H), 6.24 (dd, $J = 17.7$ Hz, 1.3 Hz, 1H), 6.44 (dd, $J = 17.4, 10.4$ Hz, 1H), 7.26-7.34 (m, 5H). ^{13}C NMR (CDCl_3) δ 33.92, 116.20, 126.54, 127.92, 128.73, 131.35, 131.84, 135.46, 136.99, 137.30, 141.48, 197.87. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}\text{O}$ (M^+) 198.1045, found 198.1034. This material proved to be unstable. The half-life period is about 1 day in CDCl_3 at room temperature.

3b

(Z)-5-Deuterio-4-phenyl-octa-1,4,7-trien-3-one (3c): purified by florisil column chromatography (hexane/EtOAc = 10/1) (52% yield); ^2H NMR (CHCl_3) δ 6.15.

3c

(Z)-2-Methyl-4,5-dipropyl-octa-1,4,7-trien-3-one (3d): purified by silica gel column chromatography (hexane/EtOAc = 8/1) (82% yield); ^1H NMR (CDCl_3) δ 0.89 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H), 1.30-1.37 (m, 2H), 1.42-1.49 (m, 2H), 1.90 (s, 3H), 2.06-2.09 (m, 2H), 2.18-2.21 (m, 2H), 2.63 (d, J = 6.7 Hz, 2H), 4.96-5.00 (m, 2H), 5.61-5.69 (ddt, J = 16.2, 11.0, 6.7 Hz, 1H), 5.86-5.90 (m, 2H). ^{13}C NMR (CDCl_3) δ 14.16, 14.31, 16.71, 21.46, 22.04, 32.35, 32.89, 38.16, 116.26, 127.94, 136.13, 136.45, 136.78, 144.89, 203.45. HRMS (EI) calcd for $\text{C}_{15}\text{H}_{24}\text{O}$ (M^+) 220.1827, found 220.1840.

3d

(E)-2-Ethyl-4-trimethylsilyl-octa-1,4,7-trien-3-one (3e): purified by silica gel column chromatography (hexane/EtOAc = 10/1) (59% yield); ^1H NMR (CDCl_3) δ 0.11 (s, 9H), 1.07 (t, J = 7.3 Hz, 3H), 2.35 (qt, J = 7.3, 1.2 Hz, 2H), 2.74 (tt, J = 6.5, 1.5 Hz, 2H), 4.98-5.03 (m, 2H), 5.75 (ddt, J = 17.7, 9.8, 6.4 Hz, 1H), 5.86 (q, J = 1.5 Hz, 1H), 5.91-5.94 (m, 2H). ^{13}C NMR (CDCl_3) δ -1.34, 12.82, 22.95, 36.14, 115.97, 127.27, 135.53, 139.64, 147.03, 150.97, 203.23. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{22}\text{OSi}$ (M^+) 222.1440, found 222.1432.

3e

(Z)-2-(2-Hydroxy-ethyl)-4-phenyl-octa-1,4,7-trien-3-one (3f): purified by silica gel column chromatography (hexane/EtOAc = 2/1) (83% yield); ^1H NMR (CDCl_3) δ 1.93 (br s, 1H), 2.65 (t, J = 6.1 Hz, 2H), 2.85 (ddt, J = 7.6, 6.4, 1.6 Hz, 2H), 3.78 (br t, J = 5.8 Hz, 2H), 5.06 (dq, J = 10.1, 1.5 Hz, 1H), 5.09 (dq, J = 17.1, 1.5 Hz, 1H), 5.82 (ddt, J = 16.5, 10.1, 6.4 Hz, 1H), 6.03 (d, J = 0.6 Hz, 1H), 6.13 (t, J = 7.8 Hz, 1H), 6.13 (d, J = 0.6 Hz, 1H), 7.24-7.33 (m, 5H). ^{13}C NMR (CDCl_3) δ 33.83, 33.92, 61.82, 116.23, 125.81, 127.87, 128.77, 128.91, 132.18, 135.23, 137.37, 141.25, 145.72, 200.87. HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2$ ($\text{M}^+ + \text{H}$) 243.1386, found 243.1370.

3f

(Z)-2,7-Dimethyl-4-phenyl-octa-1,4,7-trien-3-one (3h): purified by silica gel column chromatography (hexane/EtOAc = 4/1) (73% yield); ^1H NMR (CDCl_3) δ 1.75 (s, 3H), 1.97 (dd, J = 1.5, 0.9 Hz, 3H), 2.78 (d, J = 7.9 Hz, 2H), 4.76 (s, 1H), 4.79 (s, 1H), 5.92 (dq, J = 2.8, 1.3 Hz, 1H), 6.00 (dq, J = 2.8, 0.9 Hz, 1H), 6.15 (t, J = 7.7 Hz, 1H), 7.24-7.33 (m, 5H). ^{13}C NMR (CDCl_3) δ 16.58, 22.77, 37.94, 111.43, 125.84, 127.74, 128.70, 128.77, 130.14, 137.60, 141.88, 143.62, 144.52, 200.49. HRMS (EI) calcd for $\text{C}_{16}\text{H}_{18}\text{O}$ (M^+) 226.1358, found 226.1370.

(Z)-Acetic acid 3-methylene-4-oxo-5-phenyl-nona-5,8-dienyl ester (3g): To a solution of **3f** (20.0 mg, 0.0825 mmol) in CH_2Cl_2 (1.7 mL) at -78°C under N_2 were added *N,N*-diisopropylethylamine (57 μL , 0.330 mmol) and acetyl chloride (12 μL , 0.165 mmol). The reaction mixture was stirred for 5 min, then warmed to room temperature and stirred for additional 15 min. After quenching with sat. NH_4Cl (aq) and extracting with CH_2Cl_2 (3 times), the combined extracts were dried over MgSO_4 , filtered, and concentrated *in vacuo*. Purification by silica gel column chromatography (hexane/EtOAc = 3/1) gave the desired product **3g** (96% yield); ^1H NMR (CDCl_3) δ 2.01 (s, 3H), 2.73 (t, J = 6.7 Hz, 2H), 2.84 (ddt, J = 8.0, 6.4, 1.6 Hz, 2H), 4.25 (t, J = 6.8 Hz, 2H), 5.06 (dq, J = 10.1, 1.6 Hz, 1H), 5.09 (dq, J = 17.1, 1.9 Hz, 1H), 5.81 (ddt, J = 16.8, 10.4, 6.4 Hz, 1H), 6.00 (s, 1H), 6.13 (t, J = 7.7 Hz, 1H), 6.14 (s, 1H), 7.24–7.33 (m, 5H). ^{13}C NMR (CDCl_3) δ 20.92, 29.40, 33.88, 62.73, 116.22, 125.82, 127.84, 128.72, 128.77, 131.98, 135.24, 137.33, 141.13, 144.69, 170.92, 199.61. HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{17}\text{O}$ ($\text{M}^+ - \text{OAc}$) 225.1280, found 225.1262.

Preparation of (E)-3-tert-butyldimethylsilyloxy-hex-4-en-1-yne (9i). To a solution of (*E*)-hex-4-en-1-yn-3-ol (865 mg, 9.00 mmol) in CH_2Cl_2 (50 mL) were added imidazole (695 mg, 14.4 mmol) and TBDMSCl (1.63g, 10.8 mmol) under air. The mixture was stirred for 5 h at room temperature and then passed through celite. Solvent concentration *in vacuo* followed by column chromatography of the crude oil (hexane) yielded compound **9i** (1.89 g, 99% yield).; ^1H NMR (CDCl_3) δ 0.13 (d, J = 5.2 Hz, 6H), 0.92 (s, 9H), 1.72 (dt, J = 7.0, 1.3 Hz, 3H), 2.48 (d, J = 2.1 Hz, 1H), 4.83–4.85 (m, 1H), 5.55 (ddq, J = 15.3, 5.8, 1.5 Hz, 1H), 5.82 (dq, J = 15.3, 6.4, 1.5 Hz, 1H). ^{13}C NMR (CDCl_3) δ -4.78, -4.57, 17.43, 18.34, 25.83, 63.31, 72.99, 84.17, 127.07, 130.70. HRMS (EI) calcd for $\text{C}_{12}\text{H}_{22}\text{OSi}$ (M^+) 210.1440, found 210.1435.

Preparation of (2E, 8E)-7-tert-butyldimethylsilyloxy-deca-2,8-dien-5-yn-4-ol (8i). *n*-BuLi (1.60 M solution in hexane, 3.30 mmol) was added to a solution of **9i** (631 mg, 3.00 mmol) in THF (5 mL) at -78°C . After 5 min, crotonaldehyde (3.60 mmol) was added and the mixture was stirred for 20 min at the same temperature. The reaction mixture was then quenched by addition of saturated aqueous NH_4Cl and extracted with Et_2O twice. The organic phases were dried with MgSO_4 and concentrated under vacuum. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10/1) to give **8i**. (773 mg, 92% yield).; ^1H NMR (CDCl_3) δ 0.12 (s, 3H), 0.13 (s, 3H), 0.91 (s, 9H), 1.70–1.74 (m, 6H), 1.85 (br s, 1H), 4.84–4.87 (m, 1H), 4.88–4.91 (m, 1H), 5.54 (ddq, J

= 15.3, 5.5, 1.5 Hz, 1H), 5.61 (ddq, J = 15.3, 6.4, 1.9 Hz, 1H), 5.79 (dq, J = 14.7, 6.7, 1.3 Hz, 1H), 5.89 (dq, J = 15.3, 6.4, 1.2 Hz, 1H). ^{13}C NMR (CDCl_3) δ -4.70, -4.48, 17.43, 17.45, 18.36, 25.85, 63.01, 63.52, 84.38, 86.25, 126.86, 128.85, 130.11, 130.80. HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{27}\text{O}_2\text{Si}$ (M^+-H) 279.1781, found 279.1782.

8i

Preparation of (2E, 8E)-7-tert-butyldimethylsilyloxy-deca-2,8-dien-5-yn-4-one (7i). To a solution of **8i** (112 mg, 0.399 mmol) in hexane (2.6 mL) was added MnO_2 (695 mg, 7.99 mmol) in one portion under air and stirred for 30 min at room temperature. The mixture was passed through celite and concentrated under reduced pressure. The resulting residue was purified by column chromatography (hexane/EtOAc = 10/1) to give **7i** (86.3 mg, 78% yield).; ^1H NMR (CDCl_3) δ 0.13 (s, 3H), 0.15 (s, 3H), 0.92 (s, 9H), 1.73 (dt, J = 6.4, 1.6 Hz, 3H), 1.98 (dd, J = 7.1, 1.5 Hz, 3H), 5.00-5.02 (d quint, J = 5.8, 1.2 Hz, 1H), 5.56 (ddq, J = 15.3, 5.8, 1.5 Hz, 1H), 5.84 (dq, J = 15.3, 6.4, 1.6 Hz, 1H), 6.17 (dq, J = 15.6, 1.6 Hz, 1H), 7.19 (dq, J = 15.6, 7.0 Hz, 1H). ^{13}C NMR (CDCl_3) δ -4.79, -4.65, 17.48, 18.28, 18.42, 25.73, 63.47, 81.91, 91.97, 128.20, 129.29, 133.76, 149.89, 178.11. HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{25}\text{O}_2\text{Si}$ (M^+-H) 277.1625, found 277.1626.

7i

Preparation of (2E, 5Z, 8E)-7-tert-butyldimethylsilyloxy-deca-2,5,8-trien-4-one (3i). To a solution of **7i** (36.9 mg, 0.133 mmol) in 1-hexene/EtOAc (1:1, 4 mL) was added Lindlar catalyst (11.0 mg, 5 wt%) and the mixture was stirred under hydrogen atmosphere for 10 min at room temperature. The mixture was passed through celite and concentrated under reduced pressure. The resulting residue was purified by column chromatography (hexane/EtOAc = 10/1) to give trienone **3i** (28.8 mg, 77% yield).; ^1H NMR (CDCl_3) δ 0.01 (s, 3H), 0.02 (s, 3H), 0.87 (s, 9H), 1.67 (dt, J = 6.4, 1.6 Hz, 3H), 1.91 (dd, J = 7.0, 1.8 Hz, 3H), 5.49 (ddq, J = 15.3, 4.9, 1.8 Hz, 1H), 5.66 (ddq, J = 7.7, 4.9, 1.5 Hz, 1H), 5.79 (dq, J = 15.3, 6.7, 1.5 Hz, 1H), 6.01 (dd, J = 11.6, 7.7 Hz, 1H), 6.19 (dq, J = 15.6, 1.9 Hz, 1H), 6.23 (dd, J = 11.6, 1.2 Hz, 1H), 6.87 (dq, J = 15.6, 6.8 Hz, 1H). ^{13}C NMR (CDCl_3) δ -4.74, -4.69, 17.77, 18.29, 18.39, 25.89, 69.60, 122.60, 125.77, 131.01, 132.95, 143.49, 150.26, 190.37. HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{27}\text{O}_2\text{Si}$ (M^+-H) 279.1781, found 279.1794.

3i

General procedure of the ring-closing olefin metathesis for phenol derivatives. A solution of trienone **3** (0.200 mmol) in CH_2Cl_2 (20mL, 0.01 M) was treated with 7.5 mol% catalyst **11** (12.7 mg, 0.015 mmol) in one portion under nitrogen and stirred for 2 h at room temperature. The

mixture was concentrated under reduced pressure and purified by silica gel column chromatography or PTLC on silica gel to phenol **1**.

2,3-Dipropylphenol (1a): purified by silica gel column chromatography (hexane/EtOAc = 20/1) (93% yield); ^1H NMR (CDCl_3) δ 0.98 (t, $J = 7.4$ Hz, 3H), 1.01 (t, $J = 7.4$ Hz, 3H), 1.52-1.63 (m, 4H), 2.55-2.62 (m, 4H), 4.78 (br s, 1H), 6.59 (d, $J = 8.0$ Hz, 1H), 6.75 (d, $J = 7.7$ Hz, 1H), 6.97 (dd, $J = 8.0, 7.7$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 14.26, 14.50, 23.16, 24.55, 28.11, 35.03, 112.81, 121.90, 126.25, 127.00, 142.42, 153.69. HRMS (EI) calcd for $\text{C}_{12}\text{H}_{18}\text{O}$ (M^+) 178.1358, found 178.1370.

1a

2-Phenylphenol (1b): purified by PTLC (hexane/EtOAc = 4/1) (90% yield); ^1H NMR (CDCl_3) δ 5.21 (s, 1H), 6.96-7.00 (m, 2H), 7.23-7.27 (m, 2H), 7.37-7.41 (m, 1H), 7.44-7.50 (m, 4H). ^{13}C NMR (CDCl_3) δ 115.86, 120.88, 127.90, 128.17, 129.13, 129.18, 129.31, 130.27, 137.13, 152.46. This product was characterized by comparison of the spectroscopic data with those reported previously.⁸

1b

3-Deuterio-2-phenylphenol (1c): purified by PTLC (hexane/EtOAc = 4/1) (92% yield); ^2H NMR (CHCl_3) δ 7.28.

1c

6-Methyl-2,3-dipropylphenol (1d): purified by silica gel column chromatography (hexane/EtOAc = 20/1) (92% yield); mp = 30-31 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 0.97 (t, $J = 7.3$ Hz, 3H), 1.02 (t,

$J = 7.3$ Hz, 3H), 1.52-1.62 (m, 4H), 2.20 (s, 3H), 2.52-2.61 (m, 4H), 4.57 (s, 1H), 6.67 (d, $J = 7.6$ Hz, 1H), 6.89 (d, $J = 7.7$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 14.28, 14.58, 15.84, 23.16, 24.66, 28.37, 35.04, 120.22, 121.29, 126.33, 127.76, 139.87, 151.98. HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{19}\text{O}$ ($\text{M}^+ - \text{H}$) 191.1436, found 191.1446.

1d

2-Ethyl-6-trimethylsilylphenol (1e): purified by PTLC (hexane/ $\text{CH}_2\text{Cl}_2 = 1/1$) (97% yield); ^1H NMR (CDCl_3) δ 0.31 (s, 9H), 1.27 (t, $J = 7.7$ Hz, 3H), 2.59 (q, $J = 7.7$ Hz, 2H), 4.81 (s, 1H), 6.90 (t, $J = 7.4$ Hz, 1H), 7.15 (dd, $J = 7.3, 1.9$ Hz, 1H), 7.23 (dd, $J = 7.3, 1.9$ Hz, 1H). ^{13}C NMR (CDCl_3) δ -0.73, 13.72, 22.75, 120.69, 125.06, 127.64, 130.19, 133.01, 158.24. HRMS (EI) calcd for $\text{C}_{11}\text{H}_{18}\text{OSi}$ (M^+) 194.1127, found 194.1112.

1e

6-(2-Hydroxy-ethyl)-2-phenylphenol (1f): purified by silica gel column chromatography (hexane/EtOAc = 2/1) (93% yield); ^1H NMR (CDCl_3) δ 2.34 (br s, 1H), 2.94 (t, $J = 5.8$ Hz, 2H), 3.92 (t, $J = 5.5$ Hz, 2H), 6.92 (t, $J = 7.7$ Hz, 1H), 7.09 (dd, $J = 7.3, 1.9$ Hz, 1H), 7.15 (br s, 1H), 7.17 (dd, $J = 7.7, 1.9$ Hz, 1H), 7.34 (tt, $J = 7.3, 1.2$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.50 (dd, $J = 8.3$ Hz, 1.3 Hz, 2H). ^{13}C NMR (CDCl_3) δ 34.59, 64.10, 120.47, 126.74, 127.35, 128.65, 129.27, 129.37, 129.44, 130.47, 138.14, 151.79. HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$ (M^+) 214.0994, found 214.0991.

1f

6-(2-Acetoxy-ethyl)-2-phenylphenol (1g): purified by silica gel column chromatography (hexane/EtOAc = 4/1) (98% yield); ^1H NMR (CDCl_3) δ 2.06 (s, 3H), 3.03 (t, $J = 7.0$ Hz, 2H), 4.33 (t, $J = 7.0$ Hz, 2H), 5.55 (s, 1H), 6.93 (t, $J = 7.6$ Hz, 1H), 7.12-7.15 (m, 2H), 7.40 (tt, $J = 9.2, 1.9$ Hz, 1H), 7.44-7.51 (m, 4H). ^{13}C NMR (CDCl_3) δ 21.08, 30.15, 64.00, 120.39, 124.28, 127.94, 128.28, 128.89, 129.19, 129.33, 130.44, 137.17, 150.82, 171.27. HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3$ (M^+) 256.1100, found 256.1088.

1g

2,3-Dimethyl-6-phenylphenol (1h): purified by PTLC (hexane/CH₂Cl₂ = 1/1) (92% yield); ¹H NMR (CDCl₃) δ 2.23 (s, 3H), 2.31 (s, 3H), 5.26 (s, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 7.38 (tt, *J* = 7.3, 1.6 Hz, 1H), 7.42-7.44 (m, 2H), 7.46-7.49 (m, 2H). ¹³C NMR (CDCl₃) δ 11.94, 20.16, 121.86, 123.11, 125.47, 126.68, 127.75, 129.21, 129.41, 137.69, 137.91, 150.31. HRMS (FAB) calcd for C₁₄H₁₄O (M⁺) 198.1045, found 198.1062.

1h

2-Chloro-5,6-dimethyl-3-phenylphenol (1j): purified by PTLC (hexane/CH₂Cl₂ = 1/1) (84% yield); mp = 40-41 °C; ¹H NMR (CDCl₃) δ 2.25 (s, 3H), 2.27 (s, 3H), 5.81 (s, 1H), 6.75 (s, 1H), 7.34-7.38 (m, 1H), 7.40-7.42 (m, 4H). ¹³C NMR (CDCl₃) δ 12.50, 19.79, 115.85, 123.09, 123.85, 127.51, 128.07, 129.34, 136.44, 137.45, 139.43, 149.44. HRMS (FAB) calcd for C₁₄H₁₃ClO (M⁺) 232.0656, found 232.0663.

1j

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