Supporting Information

Rh-Catalyzed Ring-Opening Coupling of Cyclic Vinyl Ethers with Organometallic Reagents

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1. General information

All air-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or argon. NMR spectra were recorded on Bruker AVANCE AV-400 spectrometer (400 MHz for ¹H, 101 MHz for ¹³C) or Bruker AVANCE AV-300 spectrometer (300 MHz for ¹H, 75 MHz for ¹³C). Chemical shifts were reported in δ (ppm) referenced to the residual solvent peak of CDCl₃ (δ 7.26) for ¹H NMR and CDCl₃ (δ 77.0) for ¹³C NMR, the residual solvent peak of DMSO-*d*₆ (δ 2.50) for ¹H NMR and DMSO-*d*₆ (δ 40.0) for ¹³C NMR. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Coupling constants were reported in Hertz (Hz). High resolution mass spectra (HRMS) were obtained on Waters XEVO G2-S TOF (ESI). For thin layer chromatography (TLC), Yantai pre-coated TLC plates (HSGF 254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with KMnO4 followed by heating. Column chromatography separations were performed on silica gel (300–400 mesh). Unless otherwise noted, all commercialized reagents were used as received without further purification.

2. Materials

Toluene, 1,4-dioxane, THF, EtOAc, *t*BuOH and EtOH were purchased from commercial supplier and degassed with N₂ before use. Purified water was deoxygenated by bubbling with argon before use. $[Rh(OH)(cod)]_2$ was prepared according to the reported procedures^[1]. 2,3-Dihydrofuran and benzofuran were purchased from Energy Chemical. All the organoboronic acids and Grignard reagents were purchased from commercial suppliers.

3. A general procedure for Table 1



The synthesis of *E*-3a and *Z*-3a: Rhodium catalyst (5.0 μ mol, 5 mol% Rh), 1a (14.0 mg, 0.20 mmol) and 2a (0.30 mmol) were placed in an oven-dried Schlenk tube under nitrogen. Solvent (1.0 mL) was added and the resulting mixture was stirred at 60 °C for 12 h. Upon completion, the reaction mixture was diluted with EtOAc (5 mL) and water (3 mL). The layers were separated and the aqueous layer was extracted again with EtOAc for two more times (5 mL × 2). The combined organic layers were then concentrated in vacuo, and the residue was purified by silica gel chromatography eluting with petroleum ether/EtOAc to give *E*-3a and *Z*-3a.

4. Procedures for Scheme 2



The synthesis of Z-3: $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μ mol, 5 mol% Rh), 1a (14.0 mg, 0.20 mmol) and 2 (0.10 mmol) were placed in an oven-dried Schlenk tube (25 mL) under nitrogen. Anhydrous toluene (1.0 mL) was added and the resulting mixture was stirred at 60 °C for 12 h. Upon completion, the reaction mixture was diluted with EtOAc (5 mL) and water (3 mL). The layers were separated and the aqueous layer was extracted again with EtOAc for two more times (5 mL × 2). The combined organic layers were then concentrated in vacuo, and the residue was purified by silica gel chromatography eluting with petroleum ether/EtOAc to give Z-3.

5. A general procedure for Table 2



The synthesis of 5a: Rhodium catalysts (5.0 μ mol, 5 mol% Rh), 4a (23.6 mg, 0.20 mmol) and Ph-M (0.40 mmol) were placed in an oven-dried Schlenk tube under nitrogen. THF (1.0 mL) was added and the resulting mixture was stirred at 60 °C for 12 h. Upon completion, the reaction mixture was diluted with EtOAc (5 mL) and water (3 mL). The layers were separated and the aqueous layer was extracted again with EtOAc for two more times (5 mL × 2). The combined organic layers was then concentrated in vacuo, and the residue was purified by silica gel chromatography eluting with petroleum ether/EtOAc to give 5a.

6. Procedures for Scheme 3



The synthesis of 5: [RhCl(cod)]₂ (2.5 mg, 5.0 μ mol, 5 mol% Rh), 4 (0.20 mmol) and **RMgBr** (0.40 mmol) were placed in an oven-dried Schlenk tube under nitrogen. THF (1.0 mL) was added and the resulting mixture was stirred at 60 °C for 12 h. Upon completion, the reaction mixture was diluted with EtOAc (5 mL) and water (3 mL). The layers were separated and the aqueous layer was extracted again with EtOAc for two more times (5 mL × 2). The combined organic layers was then concentrated in vacuo, and the residue was purified by silica gel chromatography eluting with petroleum ether/EtOAc to give **5**.

7. Procedures for Scheme 4

$$\begin{array}{c} \overbrace{}^{O} \\ 1a \end{array} + PhB(OH)_{2} + Z-3a \\ 1a \qquad 2a \end{array} \xrightarrow{cat. [Rh(OH)(cod)]_{2}} E-3a \\ \hline toluene/H_{2}O, 60 \ ^{\circ}C \end{array}$$

The isomerization from Z-3a to E-3a: $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μ mol, 5 mol% Rh), 1a (14.0 mg, 0.20 mmol), 2a (36.6 mg, 0.30 mmol) and Z-3a (14.8 mg, 0.10 mmol) were placed in an oven-dried Schlenk tube (25 mL) under nitrogen. PhMe (1.0 mL) and H₂O (6 mmol, 30 equiv) were added and the resulting mixture was stirred at 60 °C for 12 h. Upon completion, the reaction mixture was diluted with EtOAc (5 mL) and water (3 mL). The layers were separated and the aqueous layer was extracted again with EtOAc for two more times (5 mL × 2). The combined organic layers were then concentrated in vacuo, and the residue was purified by silica gel chromatography eluting with petroleum ether/EtOAc to give *E*-3a.

8. Characterization of the products

(Z)-4-phenylbut-3-en-1-ol (Z-3a)

OH



Colorless oil, 25.5 mg at 0.20 mmol scale, 86% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.39 – 7.23 (m, 5H), 6.62 (dt, J = 11.7, 1.9 Hz, 1H), 5.72 (dt, J = 11.7, 7.4 Hz, 1H), 3.78 (t, J = 6.5 Hz, 2H),

2.65 (qd, J = 6.5, 1.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 137.3, 131.8, 128.9, 128.4, 126.9, 62.6, 32.1. HRMS-ESI (m/z): calcd for C₁₀H₁₃O⁺ [M+H]⁺ 149.0961, found 149.0965.

(Z)-4-(p-tolyl)but-3-en-1-ol (Z-3b)



Colorless oil, 29.5 mg at 0.20 mmol scale, 91% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.55 (dt, J = 11.6, 1.9 Hz, 1H), 5.64 (dt, J = 11.6, 7.3 Hz, 1H), 3.75 (t, J = 6.5 Hz, 2H), 2.62 (qd, J = 6.6, 1.8 Hz, 2H),

2.35 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 136.7, 134.4, 131.7, 129.1, 128.8, 127.6, 62.7, 32.2, 21.3. HRMS-ESI (m/z): calcd for C₁₁H₁₅O⁺ [M+H]⁺ 163.1117, found 163.1136.

(Z)-4-(4-bromophenyl)but-3-en-1-ol (Z-3c)

ОН



Yellowish oil, 41.8 mg at 0.20 mmol scale, 92% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.43 (m, 2H), 7.18 – 7.16 (m, 2H), 6.50 (dt, *J* = 11.7, 1.9 Hz, 1H), 5.73 (dt, *J* = 11.7, 7.4 Hz, 1H),

3.75 (t, J = 6.4 Hz, 2H), 2.57 (qd, J = 6.5, 1.9 Hz, 2H).¹³C NMR (75 MHz, CDCl₃) δ 136.2, 131. 5, 130.6, 130.5, 129.3, 120.8, 62.5, 32.0. HRMS-ESI (m/z): calcd for $C_{10}H_{12}^{79}BrO^{+}[M+H]^{+}$ 227.0066, found 227.0080.

(Z)-4-(4-hydroxybut-1-en-1-yl)phenyl acetate (Z-3d)



OH Yellowish oil, 33.8 mg at 0.20 mmol scale, 82% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 6.60 (dt, J = 11.7, 1.9 Hz, 1H), 5.81

(dt, J = 11.7, 7.4 Hz, 1H), 3.92 (s, 3H), 3.81 – 3.74 (m, 2H), 2.62 (qd, J = 6.5, 1.8 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 142.0, 130.9, 130.7, 129.7, 128.8, 128.5, 62.5, 52.2, 32.2. HRMS-ESI (m/z): calcd for C₁₂H₁₅O₃⁺ [M+H]⁺ 207.1016, found 207.1021.

(Z)-4-(3-chlorophenyl)but-3-en-1-ol (Z-3e)

OH Yellowish oil, 28.1 mg at 0.20 mmol scale, 77% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.31 – 7.27 (m, 2H), 7.24 – 7.18 (m, 2H), 7.09 (d, J = 8.0 Hz, 1H), 6.54 (dt, J = 11.7, 1.9 Hz, 1H), 5.77 (dt, J = 11.7, 7.4 Hz, 1H), 3.78 (t, J = 6.4 Hz, 2H), 2.61 (qd, J = 6.5, 1.8 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 139.1, 134.2, 130.4, 129.9, 129.6, 128.8, 127.0, 62.5, 32.1. HRMS-ESI (m/z): calcd for C₁₀H₁₁ClOK⁺ [M+K]⁺ 221.0130, found 221.0111.

(Z)-4-(3-methoxyphenyl)but-3-en-1-ol (Z-3f)

OH Colorless oil, 30.6 mg at 0.20 mmol scale, 86% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.28 – 7.23 (m, 1H), 6.91 – 6.77 (m, 3H), 6.57 (d, J = 11.7 Hz, 1H), 5.70 (dt, J = 11.7, 7.3 Hz, 1H), 3.82 (s, 3H), 3.76 (t, J = 6.4 Hz, 2H), 2.63 (qd, J = 6.6, 1.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 159.6, 138.7, 131.7, 129.3, 128.7, 121.4, 114.5, 112.4, 62.6, 55.4, 32.2. HRMS-ESI (m/z): calcd for C₁₁H₁₅O₂⁺ [M+H]⁺ 179.1067, found 179.1069.

<u>(Z)-4-(o-tolyl)but-3-en-1-ol (Z-3g)</u>



2.45 (qd, J = 6.6, 1.7 Hz, 2H), 2.26 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 136.4, 136.4, 131.1, 130.0, 129.1, 128.2, 127.2, 125.5, 62.6, 32.0, 20.0. HRMS-ESI (m/z): calcd for C₁₁H₁₄ONa⁺ [M+Na]⁺ 185.0937, found 185.0931.

(Z)-4-(naphthalen-1-yl)but-3-en-1-ol (Z-3h)



OH Yellowish oil, 36.8 mg at 0.20 mmol scale, 93% yield. ¹H
 NMR (300 MHz, CDCl₃) δ 8.00 - 7.97 (m, 1H), 7.87 - 7.76 (m, 2H), 7.51 - 7.36 (m, 4H), 7.06 (d, J = 11.4 Hz, 1H), 5.98

(dt, J = 11.4, 7.4 Hz, 1H), 3.69 (t, J = 6.5 Hz, 2H), 2.44 (qd, J = 6.6, 1.7 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 134.4, 133.6, 132.0, 130.1, 130.1, 128.5, 127.6, 126.5, 126.1, 125.9, 125.4, 125.0, 62.6, 32.3. HRMS-ESI (m/z): calcd for C₁₄H₁₅O⁺ [M+H]⁺ 199.1117, found 199.1128.

(Z)-4-(cyclohex-1-en-1-yl)but-3-en-1-ol (Z-3i)

OH Yellowish oil, 25.3 mg at 0.20 mmol scale, 83% yield. ¹H NMR (400 MHz, CDCl₃) δ 5.92 – 5.88 (m, 1H), 5.66 – 5.65 (m, 1H), 5.26 (dt, J = 11.8, 7.5 Hz, 1H), 3.66 (t, J = 6.5 Hz, 2H), 2.53 (qd, J = 6.6, 1.7 Hz, 2H), 2.16 – 2.07 (m, 4H), 1.65 – 1.54 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 135.3, 134.9, 128.2, 124.5, 62.9, 32.5, 29.1, 25.7, 23.0, 22.2. HRMS-ESI (m/z): calcd for C₁₀H₁₇O⁺[M+H]⁺ 153.1274, found 153.1287.

(E)-2-styrylphenol (5a)

OH

Pale yellow solid, 33.4 mg at 0.20 mmol scale, 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.54 (m, 3H), 7.41 – 7.36 (m, 3H), 7.30 – 7.27 (m, 1H), 7.19 – 7.12 (m, 2H), 7.00 – 6.95 (m, 1H), 6.83 –

6.81 (m, 1H), 5.10 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 153.1, 137.7, 130.3, 128.8, 127.7, 127.4, 126.7, 124.8, 123.1, 121.3, 116.1. HRMS-ESI (m/z): calcd for C₁₄H₁₂ONa⁺[M+Na]⁺219.0780, found 219.0796.

(E)-2-(4-methoxystyryl)phenol (5b)



Yellow brown solid, 39.8 mg at 0.20 mmol scale, 88% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.52 – 7.46 (m, 3H), 7.20 – 6.79 (m, 7H), 5.03 (s, 1H), 3.84 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ

159.4, 152.9, 130.5, 129.9, 128.4, 127.9, 127.2, 125.1, 121.3, 120.9, 116.0, 114.2, 55.5. HRMS-ESI (m/z): calcd for $C_{15}H_{15}O_2^+$ [M+H]⁺227.1067, found 227.1077.

(E)-2-(4-fluorostyryl)phenol (5c)



White solid, 35.1mg at 0.20 mmol scale, 82% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.47 – 7.41 (m, 3H), 7.21 – 7.20 (m, 1H), 7.12 – 6.87 (m, 5H), 6.76 – 6.73 (m, 1H), 4.97 (s, 1H). ¹³C NMR

(75 MHz, CDCl₃) δ 162.4 (d, J = 245.6 Hz), 153.1, 133.9 (d, J = 3.3 Hz), 129.0, 128.8, 128.1 (d, J = 7.9 Hz), 127.3, 124.7, 122.9 (d, J = 2.4 Hz), 121.3, 116.0 (d, J = 14.2 Hz), 115.6. ¹⁹F NMR (282 MHz, CDCl₃) δ -114.33. HRMS-ESI (m/z): calcd for C₁₄H₁₂FO⁺ [M+H]⁺ 215.0867, found 215.0885.

(E)-2-(3-methylstyryl)phenol (5d)



Pale yellow solid, 40.0 mg at 0.20 mmol scale, 95% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.58 – 7.54 (m, 1H), 7.42 – 7.37 (m, 3H), 7.31 – 7.28 (m, 1H), 7.21 – 7.10 (m, 3H), 7.01 – 6.96 (m, 1H), 6.85 – 6.82 (m, 1H), 5.11 (s, 1H), 2.41 (s, 3H). ¹³C NMR (75 MHz,

CDCl₃) δ 153.0, 138.3, 137.6, 130.4, 128.7, 128.7, 128.6, 127.3, 124.9, 123.9, 122.8, 121.3, 116.0, 21.6. HRMS-ESI (m/z): calcd for C₁₅H₁₅O⁺ [M+H]⁺ 211.1117, found 211.1128.

(E)-2-(2-methylstyryl)phenol (5e)

 Me
 Yellow brown solid, 37.0 mg at 0.20 mmol scale, 88% yield. ¹H

 NMR (300 MHz, CDCl₃) δ 7.65 – 7.62 (m, 1H), 7.55 – 7.52 (m, 1H), 7.38 – 7.33 (m, 1H), 7.27 – 7.14 (m, 5H), 7.00 – 6.95 (m, 1H),

6.84 – 6.81 (m, 1H), 4.98 (s, 1H), 2.43 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 153.1, 136.7, 135.9, 130.5, 128.8, 128.4, 127.7, 127.6, 126.3, 125.6, 125.1, 124.4, 121.3, 116.1, 20.1. HRMS-ESI (m/z): calcd for C₁₅H₁₅O⁺ [M+H]⁺ 211.1117, found 211.1126.

(E)-2-(prop-1-en-1-yl)phenol (5f)

OH Yellowish oil, 24.4 mg at 0.20 mmol scale, 91% yield. ¹H NMR (400 MHz, DMSO-d₆) δ 9.45 (s, 1H), 7.33 – 7.30 (m, 1H), 7.01 – 6.97 (m, 1H), 6.79 – 6.70 (m, 2H), 6.61 – 6.57 (m, 1H), 6.24 – 6.15 (m, 1H),
1.84 – 1.82 (m, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 154.0, 127.6, 126.1, 126.0,
124.6, 124.2, 119.0, 115.5, 18.7. HRMS-ESI (m/z): calcd for C₉H₁₁O⁺ [M+H]⁺
135.0804, found 135.0805.

(E)-2-(3-(trimethylsilyl)prop-1-en-1-yl)phenol (5g)

Yellowish oil, 34.2 mg at 0.20 mmol scale, 84% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.26 (m, 1H), 7.08 (td, J = 7.8 Hz, 1.6 Hz, 1H), 6.90 – 6.78 (m, 2H), 6.40 – 6.36 (m, 1H), 6.24 – 6.16 (m, 1H), 4.94 (s, 1H), 1.71 (dd, J = 8.2 Hz, 1.2 Hz, 2H), -0.06 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 152.4, 130.7, 127.6, 127.2, 125.8, 122.4, 121.0, 115.7, 24.5, -1.7. HRMS-ESI (m/z): calcd for C₁₂H₁₉OSi⁺ [M+H]⁺ 207.1200, found 207.1186.

(E)-2-(2-cyclopropylvinyl)phenol (5h)

Brown oil, 27.9 mg at 0.20 mmol scale, 87% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.31 – 7.28 (m, 1H), 7.10 (td, J = 7.7 Hz, 1.7 Hz, 1H), 6.92 – 6.87 (m, 1H), 6.82 – 6.79 (m, 1H), 6.66 (d, J = 15.8 Hz, 1H), 5.72 (dd, J = 15.8 Hz, 9.0 Hz, 1H), 4.94 (s, 1H), 1.69 – 1.57 (m, 1H), 0.89 – 0.83 (m, 2H), 0.57 – 0.52 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 152.3, 137.7, 127.9, 127.2, 125.1, 121.5, 121.0, 115.8, 15.1, 7.5. HRMS-ESI (m/z): calcd for C₁₁H₁₃O⁺ [M+H]⁺ 161.0961, found 161.0976.

(E)-2-(3,3-dimethylbut-1-en-1-yl)phenol (5i)

OH (Bu (d, J = 7.7 Hz, 1H), 6.79 (d, J = 8.1 Hz, 1H), 6.49 (d, J = 16.2 Hz, 1H),

6.22 (d, J = 16.3 Hz, 1H), 4.94 (s, 1H), 1.14 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 152.6, 144.5, 128.1, 127.4, 125.2, 121.0, 118.8, 115.8, 33.9, 29.7. HRMS-ESI (m/z): calcd for C₁₂H₁₆ONa⁺ [M+Na]⁺ 199.1093, found 199.1107.

(E)-2-bromo-4-methyl-6-styrylphenol (5j)



(E)-4-bromo-2-styrylphenol (5k)

Orange yellow solid, 51.7 mg at 0.20 mmol scale, 94% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.65 (d, J = 2.4 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.40 – 7.21 (m, 5H), 7.10 (d, J = 16.4 Hz, 1H), 6.69 (d, J = 8.6 Hz, 1H), 5.19 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 152.2, 137.2, 131.3, 131.2, 129.7, 128.8, 128.1, 127.0, 126.8, 121.7, 117.7, 113.4. HRMS-ESI (m/z): calcd for C₁₄H₁₁⁷⁹BrONa⁺ [M+Na]⁺ 296.9885, found 296.9906.

(E)-2-(1-phenylprop-1-en-2-yl)phenol (5l)

Yellowish solid, 40.4 mg at 0.20 mmol scale, 96% yield. ¹H NMR (400 MHz, CDCl₃) δ 9.43 (s, 1H), 7.39 – 7.38 (m, 4H), 7.26 – 7.22 (m, 1H), 7.18 – 7.09 (m, 2H), 6.86 – 6.77 (m, 2H), 6.50 (s, *I*H), 2.19 (d, *J* = 1.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 154.4, 137.8, 137.6, 132.3, 129.2, 128.9, 128.4, 128.22, 128.16, 126.4, 119.0, 115.6, 18.8. HRMS-ESI (m/z): calcd for C₁₅H₁₄OK⁺ [M+K]⁺ 249.0676, found 249.0678.

9. References

[1] R. Uson, L. A. Oro and J. A. Cabeza, *Inorganic Syntheses*. 1985, 23, 126.









S14











140 130





30 20

-10

90 80 fl (ppm)





100 90 fl (ppm) -10









10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)



S24















00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

