## Supporting Information

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

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## Contents

1. General information ..... 2
2. Materials ..... 2
3. A general procedure for Table 1 ..... 3
4. Procedures for Scheme 2 ..... 3
5. A general procedure for Table 2 ..... 4
6. Procedures for Scheme 3 ..... 4
7. Procedures for Scheme 4 ..... 5
8. Characterization of the products .....  5
9. References ..... 10
10. NMR spectra of products ..... 11

## 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 ${ }^{1} \mathrm{H}, 101 \mathrm{MHz}$ for ${ }^{13} \mathrm{C}$ ) or Bruker AVANCE AV-300 spectrometer ( 300 MHz for ${ }^{1} \mathrm{H}, 75 \mathrm{MHz}$ for ${ }^{13} \mathrm{C}$ ). Chemical shifts were reported in $\delta(\mathrm{ppm})$ referenced to the residual solvent peak of $\mathrm{CDCl}_{3}(\delta 7.26)$ for ${ }^{1} \mathrm{H}$ NMR and $\mathrm{CDCl}_{3}(\delta 77.0)$ for ${ }^{13} \mathrm{C}$ NMR, the residual solvent peak of DMSO- $d_{6}(\delta 2.50)$ for ${ }^{1} \mathrm{H}$ NMR and DMSO- $d_{6}(\delta 40.0)$ for ${ }^{13} \mathrm{C}$ 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 $\mathrm{KMnO}_{4}$ followed by heating. Column chromatography separations were performed on silica gel (300400 mesh). Unless otherwise noted, all commercialized reagents were used as received without further purification.

## 2. Materials

Toluene, 1,4-dioxane, THF, EtOAc, $t \mathrm{BuOH}$ and EtOH were purchased from commercial supplier and degassed with $\mathrm{N}_{2}$ before use. Purified water was deoxygenated by bubbling with argon before use. $[\mathrm{Rh}(\mathrm{OH})(\operatorname{cod})]_{2}$ was prepared according to the reported procedures ${ }^{[1]}$. 2,3Dihydrofuran 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 $\boldsymbol{E}$-3a and Z-3a: Rhodium catalyst ( $5.0 \mu \mathrm{~mol}, 5 \mathrm{~mol} \% \mathrm{Rh}$ ), 1a (14.0 $\mathrm{mg}, 0.20 \mathrm{mmol})$ and $\mathbf{2 a}(0.30 \mathrm{mmol})$ were placed in an oven-dried Schlenk tube under nitrogen. Solvent ( 1.0 mL ) was added and the resulting mixture was stirred at $60^{\circ} \mathrm{C}$ for 12 h . Upon completion, the reaction mixture was diluted with $\operatorname{EtOAc}(5 \mathrm{~mL})$ and water ( 3 mL ). The layers were separated and the aqueous layer was extracted again with EtOAc for two more times ( $5 \mathrm{~mL} \times 2$ ). 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 $\boldsymbol{E}-\mathbf{3 a}$ and $\mathbf{Z - 3 a}$.

## 4. Procedures for Scheme 2



The synthesis of Z-3: $[\mathrm{Rh}(\mathrm{OH})(\operatorname{cod})]_{2}(2.3 \mathrm{mg}, 5.0 \mu \mathrm{~mol}, 5 \mathrm{~mol} \% \mathrm{Rh}), \mathbf{1 a}(14.0 \mathrm{mg}$, 0.20 mmol ) and $2(0.10 \mathrm{mmol})$ 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 $60^{\circ} \mathrm{C}$ for 12 h . Upon completion, the reaction mixture was diluted with EtOAc $(5 \mathrm{~mL})$ and water ( 3 mL ). The layers were separated and the aqueous layer was extracted again with EtOAc for two more times ( $5 \mathrm{~mL} \times 2$ ). 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 ( $5.0 \mu \mathrm{~mol}, 5 \mathrm{~mol} \% \mathrm{Rh}$ ), $\mathbf{4 a}(23.6 \mathrm{mg}, 0.20$ $\mathrm{mmol})$ and $\mathbf{P h}-\mathbf{M}(0.40 \mathrm{mmol})$ were placed in an oven-dried Schlenk tube under nitrogen. THF ( 1.0 mL ) was added and the resulting mixture was stirred at $60^{\circ} \mathrm{C}$ 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 $(5 \mathrm{~mL} \times 2)$. 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: $[\mathrm{RhCl}(\operatorname{cod})]_{2}(2.5 \mathrm{mg}, 5.0 \mu \mathrm{~mol}, 5 \mathrm{~mol} \% \mathrm{Rh}), 4(0.20 \mathrm{mmol})$ and $\mathbf{R M g B r}$ ( 0.40 mmol ) were placed in an oven-dried Schlenk tube under nitrogen. THF $(1.0 \mathrm{~mL})$ was added and the resulting mixture was stirred at $60^{\circ} \mathrm{C}$ 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 $(5 \mathrm{~mL} \times 2)$. 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



The isomerization from Z-3a to $\boldsymbol{E}-\mathbf{3 a}$ : $[\mathrm{Rh}(\mathrm{OH})(\mathrm{cod})]_{2}(2.3 \mathrm{mg}, 5.0 \mu \mathrm{~mol}, 5 \mathrm{~mol} \%$ Rh), 1a ( $14.0 \mathrm{mg}, 0.20 \mathrm{mmol}$ ), 2a ( $36.6 \mathrm{mg}, 0.30 \mathrm{mmol}$ ) and $\mathbf{Z - 3 a}(14.8 \mathrm{mg}, 0.10 \mathrm{mmol})$ were placed in an oven-dried Schlenk tube ( 25 mL ) under nitrogen. PhMe ( 1.0 mL ) and $\mathrm{H}_{2} \mathrm{O}\left(6 \mathrm{mmol}, 30\right.$ equiv) were added and the resulting mixture was stirred at $60^{\circ} \mathrm{C}$ 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 ( $5 \mathrm{~mL} \times 2$ ). 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 $\boldsymbol{E}$-3a.

## 8. Characterization of the products

## (Z)-4-phenylbut-3-en-1-ol ( $\boldsymbol{Z}$-3a)



Colorless oil, 25.5 mg at 0.20 mmol scale, $86 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.39-7.23(\mathrm{~m}, 5 \mathrm{H}), 6.62(\mathrm{dt}, J=11.7,1.9$ $\mathrm{Hz}, 1 \mathrm{H}), 5.72(\mathrm{dt}, J=11.7,7.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.78(\mathrm{t}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H})$, $2.65(\mathrm{qd}, J=6.5,1.8 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 137.3,131.8,128.9,128.4$, 126.9, 62.6, 32.1. HRMS-ESI (m/z): calcd for $\mathrm{C}_{10} \mathrm{H}_{13} \mathrm{O}^{+}[\mathrm{M}+\mathrm{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. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.21(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.15 (d, $J=8.0$ $\mathrm{Hz}, 2 \mathrm{H}), 6.55$ (dt, $J=11.6,1.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.64(\mathrm{dt}, J=11.6,7.3$ $\mathrm{Hz}, 1 \mathrm{H}), 3.75(\mathrm{t}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}), 2.62(\mathrm{qd}, J=6.6,1.8 \mathrm{~Hz}, 2 \mathrm{H})$, $2.35(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 136.7,134.4,131.7,129.1,128.8,127.6$, 62.7, 32.2, 21.3. HRMS-ESI (m/z): calcd for $\mathrm{C}_{11} \mathrm{H}_{15} \mathrm{O}^{+}[\mathrm{M}+\mathrm{H}]^{+}$163.1117, found 163.1136.


Yellowish oil, 41.8 mg at 0.20 mmol scale, $92 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.46-7.43(\mathrm{~m}, 2 \mathrm{H}), 7.18-7.16(\mathrm{~m}, 2 \mathrm{H})$, $6.50(\mathrm{dt}, J=11.7,1.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.73(\mathrm{dt}, J=11.7,7.4 \mathrm{~Hz}, 1 \mathrm{H})$, $3.75(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.57(\mathrm{qd}, J=6.5,1.9 \mathrm{~Hz}, 2 \mathrm{H}){ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 136.2, 131. 5, 130.6, 130.5, 129.3, 120.8, 62.5, 32.0. HRMS-ESI (m/z): calcd for $\mathrm{C}_{10} \mathrm{H}_{12}{ }^{79} \mathrm{BrO}^{+}[\mathrm{M}+\mathrm{H}]^{+}$227.0066, found 227.0080.

## (Z)-4-(4-hydroxybut-1-en-1-yl)phenyl acetate ( $\boldsymbol{Z}-\mathbf{3 d}$ )



Yellowish oil, 33.8 mg at 0.20 mmol scale, $82 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( 400 MHz, Chloroform-d) $\delta 8.00(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.37 (d, $J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.60(\mathrm{dt}, J=11.7,1.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.81$ (dt, $J=11.7,7.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.92(\mathrm{~s}, 3 \mathrm{H}), 3.81-3.74(\mathrm{~m}, 2 \mathrm{H}), 2.62(\mathrm{qd}, J=6.5,1.8 \mathrm{~Hz}$, $2 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 167.1,142.0,130.9,130.7,129.7,128.8,128.5$, 62.5, 52.2, 32.2. HRMS-ESI (m/z): calcd for $\mathrm{C}_{12} \mathrm{H}_{15} \mathrm{O}_{3}{ }^{+}[\mathrm{M}+\mathrm{H}]^{+}$207.1016, found 207.1021.

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

 $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.31-7.27(\mathrm{~m}, 2 \mathrm{H}), 7.24-7.18(\mathrm{~m}, 2 \mathrm{H}), 7.09$ (d, $J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.54(\mathrm{dt}, J=11.7,1.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.77(\mathrm{dt}, J=$ $11.7,7.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.78(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.61(\mathrm{qd}, J=6.5,1.8 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 139.1,134.2,130.4,129.9,129.6,128.8,127.0,62.5,32.1$. HRMS-ESI ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{10} \mathrm{H}_{11} \mathrm{ClOK}^{+}[\mathrm{M}+\mathrm{K}]^{+}$221.0130, found 221.0111.

## (Z)-4-(3-methoxyphenyl)but-3-en-1-ol ( $\boldsymbol{Z}$-3f)



Colorless oil, 30.6 mg at 0.20 mmol scale, $86 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.28-7.23(\mathrm{~m}, 1 \mathrm{H}), 6.91-6.77(\mathrm{~m}, 3 \mathrm{H}), 6.57$ (d, $J=11.7 \mathrm{~Hz}, 1 \mathrm{H}), 5.70(\mathrm{dt}, J=11.7,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.82(\mathrm{~s}, 3 \mathrm{H})$, $3.76(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.63(\mathrm{qd}, J=6.6,1.8 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 159.6, 138.7, 131.7, 129.3, 128.7, 121.4, 114.5, 112.4, 62.6, 55.4, 32.2. HRMS-ESI $(\mathrm{m} / \mathrm{z})$ : calcd for $\mathrm{C}_{11} \mathrm{H}_{15} \mathrm{O}_{2}{ }^{+}[\mathrm{M}+\mathrm{H}]^{+}$179.1067, found 179.1069.


Colorless oil, 30.1 mg at 0.20 mmol scale, $93 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.22-7.15(\mathrm{~m}, 4 \mathrm{H}), 6.61(\mathrm{dt}, J=11.4,1.8$ $\mathrm{Hz}, 1 \mathrm{H}), 5.75(\mathrm{dt}, J=11.4,7.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.69(\mathrm{t}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H})$, $2.45(\mathrm{qd}, J=6.6,1.7 \mathrm{~Hz}, 2 \mathrm{H}), 2.26(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 136.4,136.4$, 131.1, 130.0, 129.1, 128.2, 127.2, 125.5, 62.6, 32.0, 20.0. HRMS-ESI (m/z): calcd for $\mathrm{C}_{11} \mathrm{H}_{14} \mathrm{ONa}^{+}[\mathrm{M}+\mathrm{Na}]^{+}$185.0937, found 185.0931.

## (Z)-4-(naphthalen-1-yl)but-3-en-1-ol ( $\boldsymbol{Z}$-3h)



Yellowish oil, 36.8 mg at 0.20 mmol scale, $93 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.00-7.97(\mathrm{~m}, 1 \mathrm{H}), 7.87-7.76$ (m, 2H), $7.51-7.36(\mathrm{~m}, 4 \mathrm{H}), 7.06(\mathrm{~d}, J=11.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.98$ (dt, $J=11.4,7.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.69(\mathrm{t}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}), 2.44(\mathrm{qd}, J=6.6,1.7 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 134.4,133.6,132.0,130.1,130.1,128.5,127.6,126.5,126.1$, 125.9, 125.4, 125.0, 62.6, 32.3. HRMS-ESI (m/z): calcd for $\mathrm{C}_{14} \mathrm{H}_{15} \mathrm{O}^{+}[\mathrm{M}+\mathrm{H}]^{+}$ 199.1117, found 199.1128.

## ( $Z$ )-4-(cyclohex-1-en-1-yl)but-3-en-1-ol ( $\boldsymbol{Z}$-3i)



Yellowish oil, 25.3 mg at 0.20 mmol scale, $83 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 5.92-5.88(\mathrm{~m}, 1 \mathrm{H}), 5.66-5.65(\mathrm{~m}, 1 \mathrm{H}), 5.26$ (dt, $J=11.8,7.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.66(\mathrm{t}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}), 2.53(\mathrm{qd}, J=$ $6.6,1.7 \mathrm{~Hz}, 2 \mathrm{H}), 2.16-2.07(\mathrm{~m}, 4 \mathrm{H}), 1.65-1.54(\mathrm{~m}, 5 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 135.3,134.9,128.2,124.5,62.9,32.5,29.1,25.7,23.0,22.2$. HRMS-ESI (m/z): calcd for $\mathrm{C}_{10} \mathrm{H}_{17} \mathrm{O}^{+}[\mathrm{M}+\mathrm{H}]^{+}$153.1274, found 153.1287 .

## (E)-2-styrylphenol (5a)



Pale yellow solid, 33.4 mg at 0.20 mmol scale, $85 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.56-7.54(\mathrm{~m}, 3 \mathrm{H}), 7.41-7.36(\mathrm{~m}, 3 \mathrm{H}), 7.30$ - $7.27(\mathrm{~m}, 1 \mathrm{H}), 7.19-7.12(\mathrm{~m}, 2 \mathrm{H}), 7.00-6.95(\mathrm{~m}, 1 \mathrm{H}), 6.83-$ $6.81(\mathrm{~m}, 1 \mathrm{H}), 5.10(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 153.1,137.7,130.3,128.8$, 127.7, 127.4, 126.7, 124.8, 123.1, 121.3, 116.1. HRMS-ESI (m/z): calcd for $\mathrm{C}_{14} \mathrm{H}_{12} \mathrm{ONa}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 219.0780$, found 219.0796.

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



Yellow brown solid, 39.8 mg at 0.20 mmol scale, $88 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.52-7.46(\mathrm{~m}, 3 \mathrm{H}), 7.20-6.79(\mathrm{~m}$, $7 \mathrm{H}), 5.03(\mathrm{~s}, 1 \mathrm{H}), 3.84(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $159.4,152.9,130.5,129.9,128.4,127.9,127.2,125.1,121.3,120.9,116.0,114.2,55.5$. HRMS-ESI (m/z): calcd for $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{O}_{2}^{+}[\mathrm{M}+\mathrm{H}]^{+}$227.1067, found 227.1077.

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



White solid, 35.1 mg at 0.20 mmol scale, $82 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.47-7.41(\mathrm{~m}, 3 \mathrm{H}), 7.21-7.20(\mathrm{~m}, 1 \mathrm{H})$, $7.12-6.87(\mathrm{~m}, 5 \mathrm{H}), 6.76-6.73(\mathrm{~m}, 1 \mathrm{H}), 4.97(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 162.4(\mathrm{~d}, J=245.6 \mathrm{~Hz}), 153.1,133.9(\mathrm{~d}, J=3.3 \mathrm{~Hz}), 129.0,128.8$, 128.1 (d, $J=7.9 \mathrm{~Hz}), 127.3,124.7,122.9(\mathrm{~d}, J=2.4 \mathrm{~Hz}), 121.3,116.0(\mathrm{~d}, J=14.2 \mathrm{~Hz})$, 115.6. ${ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-114.33$. HRMS-ESI (m/z): calcd for $\mathrm{C}_{14} \mathrm{H}_{12} \mathrm{FO}^{+}$ $[\mathrm{M}+\mathrm{H}]^{+} 215.0867$, found 215.0885 .

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



Pale yellow solid, 40.0 mg at 0.20 mmol scale, $95 \%$ yield. ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.58-7.54(\mathrm{~m}, 1 \mathrm{H}), 7.42-7.37(\mathrm{~m}, 3 \mathrm{H})$, $7.31-7.28(\mathrm{~m}, 1 \mathrm{H}), 7.21-7.10(\mathrm{~m}, 3 \mathrm{H}), 7.01-6.96(\mathrm{~m}, 1 \mathrm{H}), 6.85$ - $6.82(\mathrm{~m}, 1 \mathrm{H}), 5.11(\mathrm{~s}, 1 \mathrm{H}), 2.41(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 75 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 153.0,138.3,137.6,130.4,128.7,128.7,128.6,127.3,124.9,123.9,122.8$, 121.3, 116.0, 21.6. HRMS-ESI (m/z): calcd for $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{O}^{+}[\mathrm{M}+\mathrm{H}]^{+}$211.1117, found 211.1128.

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

 Yellow brown solid, 37.0 mg at 0.20 mmol scale, $88 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.65-7.62(\mathrm{~m}, 1 \mathrm{H}), 7.55-7.52(\mathrm{~m}$, $1 \mathrm{H}), 7.38-7.33(\mathrm{~m}, 1 \mathrm{H}), 7.27-7.14(\mathrm{~m}, 5 \mathrm{H}), 7.00-6.95(\mathrm{~m}, 1 \mathrm{H})$, $6.84-6.81(\mathrm{~m}, 1 \mathrm{H}), 4.98(\mathrm{~s}, 1 \mathrm{H}), 2.43(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 153.1$, 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 $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{O}^{+}[\mathrm{M}+\mathrm{H}]^{+}$211.1117, found 211.1126.

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



Yellowish oil, 24.4 mg at 0.20 mmol scale, $91 \%$ yield. ${ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{DMSO}-d_{6}\right) \delta 9.45(\mathrm{~s}, 1 \mathrm{H}), 7.33-7.30(\mathrm{~m}, 1 \mathrm{H}), 7.01-6.97(\mathrm{~m}$, $1 \mathrm{H}), 6.79-6.70(\mathrm{~m}, 2 \mathrm{H}), 6.61-6.57(\mathrm{~m}, 1 \mathrm{H}), 6.24-6.15(\mathrm{~m}, 1 \mathrm{H})$, $1.84-1.82(\mathrm{~m}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, DMSO- $d_{6}$ ) $\delta 154.0,127.6,126.1,126.0$, 124.6, $124.2,119.0,115.5$, 18.7. HRMS-ESI $(\mathrm{m} / \mathrm{z})$ : calcd for $\mathrm{C}_{9} \mathrm{H}_{11} \mathrm{O}^{+}[\mathrm{M}+\mathrm{H}]^{+}$ 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. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.28-7.26(\mathrm{~m}, 1 \mathrm{H}), 7.08(\mathrm{td}, J=7.8 \mathrm{~Hz}, 1.6$ $\mathrm{Hz}, 1 \mathrm{H}), 6.90-6.78(\mathrm{~m}, 2 \mathrm{H}), 6.40-6.36(\mathrm{~m}, 1 \mathrm{H}), 6.24-6.16$ $(\mathrm{m}, 1 \mathrm{H}), 4.94(\mathrm{~s}, 1 \mathrm{H}), 1.71(\mathrm{dd}, J=8.2 \mathrm{~Hz}, 1.2 \mathrm{~Hz}, 2 \mathrm{H}),-0.06(\mathrm{~s}, 9 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (75 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 152.4,130.7,127.6,127.2,125.8,122.4,121.0,115.7,24.5,-1.7$. HRMS-ESI (m/z): calcd for $\mathrm{C}_{12} \mathrm{H}_{19} \mathrm{OSi}^{+}[\mathrm{M}+\mathrm{H}]^{+}$207.1200, found 207.1186.

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



Brown oil, 27.9 mg at 0.20 mmol scale, $87 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 7.31-7.28(\mathrm{~m}, 1 \mathrm{H}), 7.10(\mathrm{td}, J=7.7 \mathrm{~Hz}, 1.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.92$ $-6.87(\mathrm{~m}, 1 \mathrm{H}), 6.82-6.79(\mathrm{~m}, 1 \mathrm{H}), 6.66(\mathrm{~d}, J=15.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.72$ $(\mathrm{dd}, J=15.8 \mathrm{~Hz}, 9.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.94(\mathrm{~s}, 1 \mathrm{H}), 1.69-1.57(\mathrm{~m}, 1 \mathrm{H}), 0.89-0.83(\mathrm{~m}, 2 \mathrm{H})$, $0.57-0.52(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 152.3,137.7,127.9,127.2,125.1$, $121.5,121.0,115.8,15.1,7.5$. HRMS-ESI $(\mathrm{m} / \mathrm{z})$ : calcd for $\mathrm{C}_{11} \mathrm{H}_{13} \mathrm{O}^{+}[\mathrm{M}+\mathrm{H}]^{+} 161.0961$, found 161.0976 .

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



Yellowish oil, 17.6 mg at 0.20 mmol scale, $50 \%$ yield. ${ }^{1} \mathrm{H}$ NMR (300 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.32(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.10(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.89$ $(\mathrm{d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.79(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.49(\mathrm{~d}, J=16.2 \mathrm{~Hz}, 1 \mathrm{H})$, $6.22(\mathrm{~d}, J=16.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.94(\mathrm{~s}, 1 \mathrm{H}), 1.14(\mathrm{~s}, 9 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $152.6,144.5,128.1,127.4,125.2,121.0,118.8,115.8,33.9,29.7$. HRMS-ESI (m/z): calcd for $\mathrm{C}_{12} \mathrm{H}_{16} \mathrm{ONa}^{+}[\mathrm{M}+\mathrm{Na}]^{+}$199.1093, found 199.1107.

## (E)-2-bromo-4-methyl-6-styrylphenol (5i)



White solid, 49.2 mg at 0.20 mmol scale, $85 \%$ yield. ${ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.54(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.41-7.25(\mathrm{~m}, 5 \mathrm{H}), 7.20$ $-7.13(\mathrm{~m}, 2 \mathrm{H}), 5.62(\mathrm{~s}, 1 \mathrm{H}), 2.30(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 101 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 147.5,137.6,131.2,130.4,128.8,127.8,126.84,126.78,125.4,123.1,111.0$, 20.5. HRMS-ESI (m/z): calcd for $\mathrm{C}_{15} \mathrm{H}_{14}{ }^{79} \mathrm{BrO}^{+}[\mathrm{M}+\mathrm{H}]^{+}$289.0223, found 289.0235 .

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


(s, 1H). ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 152.2,137.2,131.3,131.2,129.7,128.8,128.1$, 127.0, 126.8, 121.7, 117.7, 113.4. HRMS-ESI (m/z): calcd for $\mathrm{C}_{14} \mathrm{H}_{11}{ }^{79} \mathrm{BrONa}^{+}$ $[\mathrm{M}+\mathrm{Na}]^{+} 296.9885$, found 296.9906.

## (E)-2-(1-phenylprop-1-en-2-yl)phenol (51)



Yellowish solid, 40.4 mg at 0.20 mmol scale, $96 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( 400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 9.43(\mathrm{~s}, 1 \mathrm{H}), 7.39-7.38(\mathrm{~m}, 4 \mathrm{H}), 7.26-7.22(\mathrm{~m}, 1 \mathrm{H})$, $7.18-7.09(\mathrm{~m}, 2 \mathrm{H}), 6.86-6.77(\mathrm{~m}, 2 \mathrm{H}), 6.50(\mathrm{~s}, 1 \mathrm{H}), 2.19(\mathrm{~d}, J=1.3$ $\mathrm{Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 154.4,137.8,137.6,132.3,129.2,128.9,128.4$, 128.22, 128.16, 126.4, 119.0, 115.6, 18.8. HRMS-ESI (m/z): calcd for $\mathrm{C}_{15} \mathrm{H}_{14} \mathrm{OK}^{+}$ $[\mathrm{M}+\mathrm{K}]^{+}$249.0676, found 249.0678.

## 9. References

[1] R. Uson, L. A. Oro and J. A. Cabeza, Inorganic Syntheses. 1985, 23, 126.
10. NMR spectra of products



${ }^{1} \mathrm{H}$ NMR, $\mathrm{CDCl}_{3}, 400 \mathrm{MHz}$



[^0]

131.4541
-130.5931
130.4803
129.2710
120.8315
$-77.1600 \mathrm{CDCl} 3$
$-62.4533$
£ $\angle$ ZO Z ® $_{-}$
${ }^{13} \mathrm{C}$ NMR， $\mathrm{CDCl}_{3}, 75 \mathrm{MHz}$





${ }^{1} \mathrm{H}$ NMR, $\mathrm{CDCl}_{3}, 300 \mathrm{MHz}$




Z-3i
${ }^{1} \mathrm{H} \mathrm{NMR}, \mathrm{CDCl}_{3}, 400 \mathrm{MHz}$




${ }^{1} \mathrm{H} \mathrm{NMR}, \mathrm{CDCl}_{3}, 300 \mathrm{MHz}$

$\left\{_{77.5831}^{77.7364} \mathrm{CDCl} 3\right.$
-55.4783

${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}, 75 \mathrm{MHz}$




${ }^{19} \mathrm{~F}$ NMR, $\mathrm{CDCl}_{3}, 282 \mathrm{MHz}$


5d
${ }^{1} \mathrm{H}$ NMR, $\mathrm{CDCl}_{3}, 300 \mathrm{MHz}$

-153.0457
$\int_{138.3362}^{137.5882}$
130.3937
128.7205
128.6816
128.5928
127.3232
124.8648
123.8978
122.8011
121.2742
116.0422


5d
${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}, 75 \mathrm{MHz}$



$5 f$
${ }^{1} \mathrm{H}$ NMR, DMSO- $d_{6}, 400 \mathrm{MHz}$


$5 f$
${ }^{13} \mathrm{C}$ NMR, DMSO-d $\mathrm{d}_{6}, 101 \mathrm{MHz}$


|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 00 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | $\begin{gathered} 90 \\ \mathrm{f} 1(\mathrm{ppa}) \end{gathered}$ | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 | -10 |



$5 i$
${ }^{1} \mathrm{H} \mathrm{NMR}, \mathrm{CDCl}_{3}, 300 \mathrm{MHz}$




$5 i$
${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}, 75 \mathrm{MHz}$





${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}, 101 \mathrm{MHz}$



[^0]:    

