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Rhodium-catalyzed asymmetric 1,4-addition of alkenylsilanes generated by hydrosilylation of alkynes: a one-pot procedure where a rhodium/(*S*)-binap complex catalyzes the two successive reactions

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Abstract—A rhodium complex [Rh((*S*)-binap)$(MeCN)_2$]BF_4 (3 mol%) catalyzes successively hydrosilylation of 1-alkynes with triethoxysilane and asymmetric 1,4-addition of the resulting alkenylsilanes to cyclic α,β-unsaturated ketones. This one-pot procedure gave high yield of the corresponding 1,4-addition products with over 90% enantioselectivity.

1. Introduction

Rhodium-catalyzed asymmetric 1,4-addition of organometallic reagents provides an efficient method of introducing aryl and alkenyl groups at the β-position of electron deficient olefins with high enantioselectivity.[1] The organometallic reagents first used for the catalytic asymmetric 1,4-addition are organoboronic acids,[2,3] and then they are extended to organotitanium,[4] -silicon,[5,6] and -tin[7] reagents. We have previously reported that (alkenyl)catecholboranes generated by hydroboration of alkynes with catecholborane can be used, without isolation or purification, for the rhodium-catalyzed asymmetric 1,4-addition to α,β-unsaturated ketones giving β-alkenyl ketones with over 90% enantioselectivity.[8] The hydroboration and 1,4-addition can be carried out successively in one-pot. Herein we report another one-pot reaction system where hydrosilylation of alkynes with triethoxy(hydro)silane followed by asymmetric 1,4-addition of the resulting alkenylsilane is catalyzed by a single chiral phosphine–rhodium complex.

2. Results and discussion

Oi and Inoue reported[5] that the asymmetric 1,4-addition of (*E*)-2-phenylethenyl(triethoxy)silane **2m** to 2-cyclohexenone **1a** proceeds in dioxane/H_2O at 90 °C in the presence of a cationic binap–rhodium catalyst generated in situ from [Rh(cod)$(MeCN)_2$]BF_4 (4 mol%) and binap (6 mol%) to give 85% yield of the 1,4-addition product **3am** with 91% ee. In our hands, the use of isolated phosphine–rhodium complex [Rh((*S*)-binap)$(MeCN)_2$]BF_4 (3 mol%) gave slightly higher enantioselectivity (94% ee), although the yield of **3am** was lower (70% yield). Higher yields (89%) of **3am** with the same enantioselectivity were obtained in the reaction carried out in the presence of 1 mol% of (*S*)-binap ligand and 3 mol% of [Rh((*S*)-binap)$(MeCN)_2$]BF_4 (Scheme 1).

It was found that the cationic rhodium/(*S*)-binap system used for the 1,4-addition catalyzes the hydrosilylation of phenylacetylene **4m** with triethoxysilane.[9] The reaction with 1.5 equiv of the hydrosilane in dioxane was completed in 1 h at room temperature to give a quantitative yield of a mixture of (*E*)-2-phenylethenyl(triethoxy)-silane **2m**, its *Z* isomer and the regioisomer 1-phenylethenyl(triethoxy)silane **5m** in a ratio of 74:1:25. The use of this hydrosilylation mixture, which contains remaining triethoxysilane and the rhodium–binap catalyst, for the next 1,4-addition step by the addition of enone **1a** and water and heating the mixture at 90 °C did not give a satisfactory yield of the 1,4-addition product **3am**. It is mainly due to the reduction of enone **1a** with the hydrosilane giving cyclohexanone. This problem was solved by treatment of the hydrosilylation mixture with water for 0.5 h at room temperature before the

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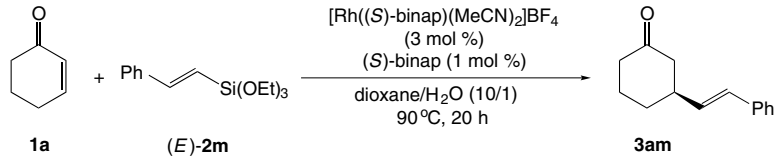
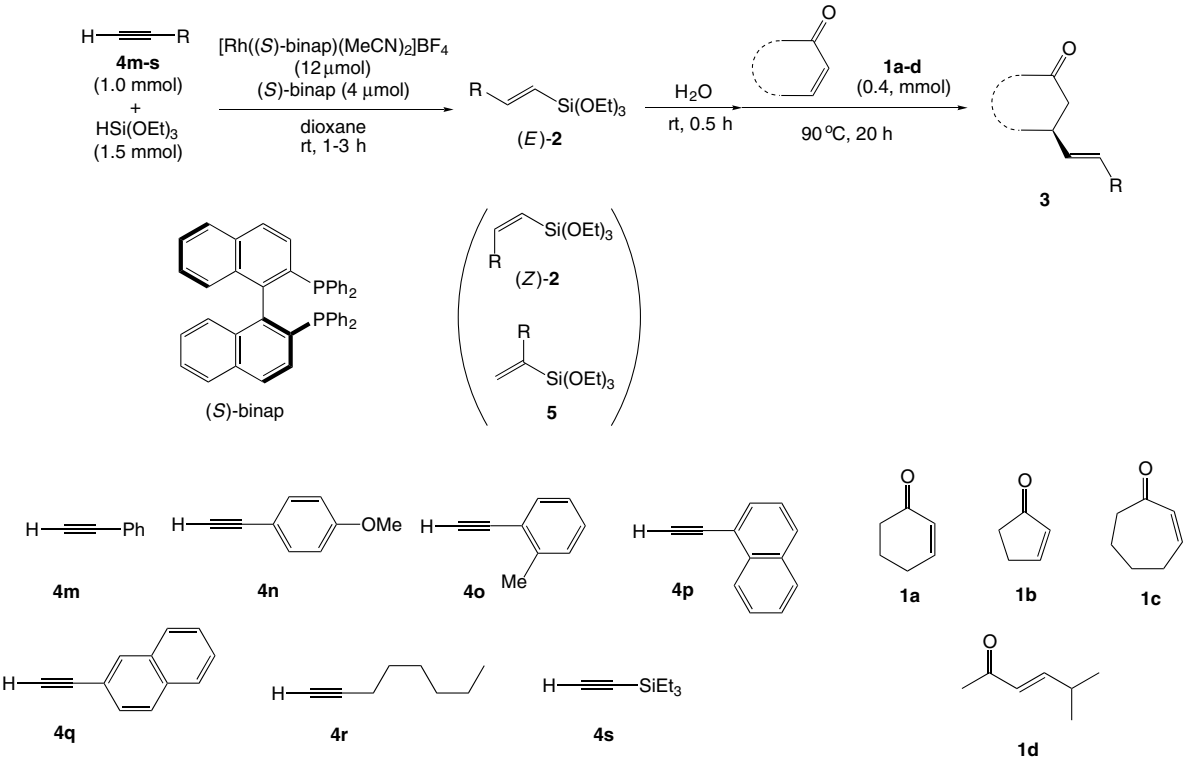


Scheme 1.

addition of enone **1a**, which probably decomposes the remaining hydrosilane by the rhodium-catalyzed hydrolysis of hydrosilane.[10] Thus, the rhodium-catalyzed hydrosilylation and 1,4-addition in one-pot was realized according to the following procedures: to a solution of $[Rh((S)\text{-binap})(MeCN)_2]BF_4$ (12 μmol) and (*S*)-binap (4 μmol) in dioxane (2 mL) was added phenylacetylene **4m** (1.0 mmol) and triethoxysilane (1.5 mmol), and the mixture was stirred at room temperature for 1 h. Water (0.2 mL) was added and the mixture was stirred at room temperature for 0.5 h. To the resulting reaction mixture was added 2-cyclohexenone **1a** (0.4 mmol) and it was heated at 90 °C for 20 h. Addition of hexane to remove precipitates followed by chromatography on silica gel gave 89% yield of the 1,4-addition product, which consists of (*S*)-3-((*E*)-2-phenylethenyl)cyclohexanone **3am** (93% ee) and its *Z* isomer in a ratio of 99:1 (entry 1 in Table 1). It is remarkable that the formation of 1,4-addition product resulting from 1-phenylethenyl(triethoxy)silane **5m** was not observed under the reaction conditions. It is probably due to the much lower reactivity of the sterically more bulky 1-phenylethenyl group. Unfortunately, the (*Z*)-alkenylsilane was as reactive as the *E* isomer towards the 1,4-addition, resulting in the formation of the 1,4-addition product with the same *E*,*Z* ratio as the alkenylsilane.

The one-pot procedure starting from phenylacetylene **4m** was successfully applied to the asymmetric 1,4-addition to cyclic enones, 2-cyclopentenone **1b** and 2-cycloheptenone **1c** giving the corresponding (*S*)-3-(*E*)-2-phenylethenylcycloalkanes **3bm** and **3cm** with high (90–93%) enantioselectivity (entries 2 and 3). For the linear enone **1d**, the enantioselectivity was lower (entry 4). The regioselectivity in forming linear or branch alkenylsilane by the rhodium-catalyzed hydrosilylation is dependent on the substituents on the alkyne **4**. Arylacetylenes **4m**–**4q** gave the hydrosilylation products containing 12–25% of branch alkenylsilanes **5** (entries 5–8), while the linear/branch ratio for 1-octyne **4r** was about one to one (entry 9). In any cases, however, the 1,4-addition products were not contaminated with those resulting from the branch alkenylsilanes. The highest regioselectivity in forming linear alkenylsilane (*E*)-**2** was observed in the hydrosilylation of triethylsilylacetylene **4s**, whose reaction with 2-cyclohexenone **1a** gave 85% yield of the corresponding 1,4-addition product with 98% enantioselectivity (entry 10) (Scheme 2).



Scheme 2.

Table 1. Rhodium-catalyzed asymmetric 1,4-addition of alkenylsilanes **2** generated by hydrosilylation of alkynes **4**[a]

Entry	Acetylene **4**	Time (h) of hydrosilylation	Ratio[b] of (*E*)-**2**/(*Z*)-**2**/**5**	Enone **1**	Yield (%)[c] of **3**	% Ee of **3**[d] (config)[e]	Ratio[f] of (*E*)-**3**/(*Z*)-**3**
1	**4m**	1	74:1:25	**1a**	89 (**3am**)	93 (*S*)	99:1
2	**4m**	1	74:1:25	**1b**	74 (**3bm**)	90 (*S*)	99:1
3	**4m**	1	74:1:25	**1c**	79 (**3cm**)	93 (*S*)	98:2[g]
4	**4m**	1	74:1:25	**1d**	76 (**3dm**)	78 (*S*)	100:0
5	**4n**	1	85:0:15	**1a**	66 (**3an**)	92 (*S*)	100:0
6	**4o**	2	72:12:16	**1a**	65 (**3ao**)	92 (*S*)	91:9
7	**4p**	2	80:8:12	**1a**	67 (**3ap**)	90 (*S*)	99:1
8	**4q**	3	76:0:24	**1a**	70 (**3aq**)	92 (*S*)	100:0
9	**4r**	1	53:2:45	**1a**	73 (**3ar**)	98[h] (*S*)	97:3
10	**4s**	3	98:0:2	**1a**	85 (**3as**)	98[h] (*S*)	100:0

[a] A typical experimental procedure is shown in the text. The ratio of **4**/$HSi(OEt)_3$/[Rh((*S*)-binap)$(MeCN)_2$]BF_4/(*S*)-binap/**1** = 100:150:1.2:0.4:40.
[b] Determined by ^1H NMR and/or GC of the crude hydrosilylation product.
[c] Isolated yield of 1,4-addition product **3** based on enone **1**.
[d] Determined by HPLC analysis with a chiral stationary phase column (Chiralcel AS). Eluent: hexane/2-propanol = 90:10 for **3am**, **3cm**, **3an**, **3ao**, **3ap** and **3aq**. 98:2 for **3bm**. 100:1 for **3dm**.
[e] The absolute configuration of **3am** was determined by comparison of its optical rotation with that reported in Ref. 8. The others were assigned to have (*S*)-configuration by consideration of stereochemical pathway of the asymmetric 1,4-addition reactions catalyzed by a (*S*)-binap/rhodium complex (Ref. 2).
[f] Determined by ^1H NMR of the 1,4-addition product **3**.
[g] Contaminated with ca. 10% of 3-(2-phenylethylidene)cycloheptanone.
[h] Determined by ^{13}C NMR of diastereomeric cyclic ketals obtained with (2*R*,3*R*)-(−)-2,3-butanediol.

3. Conclusion

In summary, we reported a one-pot reaction procedure where a rhodium/(*S*)-binap complex catalyzes the two successive reactions, that is, hydrosilylation of 1-alkynes with triethoxysilane and the asymmetric 1,4-addition of the resulting alkenylsilanes to α,β-unsaturated ketones. Although the regioselectivity at the hydrosilylation is not always high, the linear alkenylsilanes are much more reactive than the branch isomers giving the linear 1,4-addition products with high chemoselectivity. The enantioselectivity is all high (>90% ee) for cyclic enones.

4. Experimental

4.1. General

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk technique under predried nitrogen or glovebox techniques under prepurified argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^1H, 125 MHz for ^{13}C, and 202 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^1H NMR, chloroform-*d* (δ 77.05) for ^{13}C NMR and external 85% H_3PO_4 standard for ^{31}P NMR. Optical rotations were measured on a JASCO DIP-370 polarimeter.

4.2. Materials

Dioxane was distilled from sodium benzophenone-ketyl under nitrogen. Arylacetylenes were prepared by palladium-catalyzed coupling reaction of 2-methyl-3-butyn-2-ol with aryl bromides according to the procedures reported by Sonogashira et al.,[11] followed by removal of acetone by heating with KOH in toluene.[12]

4.2.1. [Rh((*S*)-binap)$(MeCN)_2$]BF_4. A mixture of [RhCl((*S*)-binap)]$_2$[2g] (381 mg, 0.25 mmol) and $AgBF_4$ (97.3 mg, 0.50 mmol) in acetonitrile was stirred at room temperature for 1 h. Removal of the precipitates followed by recrystallization (acetonitrile/hexane/diethyl ether) gave 310 mg (69% yield) of [Rh((*S*)-binap)-$(MeCN)_2$]BF_4. ^1H NMR ($CDCl_3$, 55 °C): δ 1.76 (s, 6H), 6.54 (d, J = 8.7 Hz, 2H), 6.67 (t, J = 7.3 Hz, 4H), 6.78 (t, J = 7.4 Hz, 2H), 6.97 (t, J = 7.8 Hz, 2H), 7.28 (t, J = 7.5 Hz, 2H), 7.39 (ddd, J = 9.0, 4.7, and 4.3 Hz, 2H), 7.43–7.46 (m, 6H), 7.48 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.58–7.68 (br m, 4H), 7.76–7.82 (m, 4H). ^{31}P NMR ($CDCl_3$, 55 °C): δ 46.2 (d, J = 176 Hz).

4.3. General procedure of rhodium-catalyzed hydrosilylation of alkynes and subsequent asymmetric 1,4-addition of alkenylsilanes to α,β-unsaturated ketones

To a solution of [Rh((*S*)-binap)$(MeCN)_2$]BF_4 (10.7 mg, 12 μ mol) and (*S*)-BINAP (2.5 mg, 4.0 μmol) in dioxane (2 mL) was added a terminal alkyne **4** (1.0 mmol) and triethoxysilane (246 mg, 1.5 mmol), and the mixture was stirred at room temperature for 1–3 h. After the addition of H_2O (0.2 mL), the mixture was stirred at room temperature for 30 min. An α,β-unsaturated ketone **1** (0.40 mmol) was added at room temperature, and the mixture was stirred at 90 °C for 20 h. The reaction mixture was added to hexane and the resulting precipitates were removed by filtration. The solution was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, benzene) to give the 1,4-addition product **3**. The results are summarized in Table 1.

4.3.1. 3-((*E*)-2-Phenylethenyl)cyclohexanone 3am.[8] ^1H NMR ($CDCl_3$): δ 1.58–1.66 (m, 1H), 1.70–1.80 (m,

1H), 1.98–2.04 (m, 1H), 2.07–2.14 (m, 1H), 2.28–2.35 (m, 2H), 2.38–2.43 (m, 1H), 2.50–2.56 (m, 1H), 2.63–2.72 (m, 1H), 6.16 (dd, $J=16.0$ and 6.9 Hz, 1H), 6.39 (d, $J=16.0$ Hz, 1H), 7.22 (t, $J=7.4$ Hz, 1H), 7.30 (t, $J=7.4$ Hz, 2H), 7.35 (d, $J=7.4$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 24.96, 31.36, 41.24, 41.91, 47.32, 126.09, 127.32, 128.53, 129.06, 132.88, 137.06, 210.85. $[\alpha]_D^{20} = +5.2$ (c 1.02, $CHCl_3$) for *S* isomer of 93% ee.

4.3.2. 3-((*E*)-2-Phenylethenyl)cyclopentanone 3bm.[13] ^{1}H NMR ($CDCl_3$): δ 1.79–1.86 (m, 1H), 2.13 (ddd, $J=18.2$, 10.4 and 1.2 Hz, 1H), 2.19–2.30 (m, 2H), 2.35–2.42 (m, 1H), 2.49 (dd, $J=18.2$ and 7.5 Hz, 1H), 2.98–3.06 (m, 1H), 6.22 (dd, $J=15.9$ and 7.3 Hz, 1H), 6.46 (d, $J=15.9$ Hz, 1H), 7.23 (t, J = 7.4 Hz, 1H), 7.31 (t, $J=7.4$ Hz, 2H), 7.36 (d, $J=7.4$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 29.89, 38.21, 40.24, 44.80, 126.08, 127.38, 128.57, 129.76, 132.00, 136.93, 218.57. $[\alpha]_D^{20} = -77.7$ (c 0.78, $CHCl_3$) for *S* isomer of 90% ee.

4.3.3. 3-((*E*)-2-Phenylethenyl)cycloheptanone 3cm. ^{1}H NMR ($CDCl_3$): δ 1.45–1.58 (m, 2H), 1.62–1.71 (m, 1H), 1.88–2.05 (m, 3H), 2.50–2.70 (m, 5H), 6.15 (dd, $J=15.9$ and 7.5 Hz, 1H), 6.39 (d, $J=15.9$ Hz, 1H), 7.21 (t, $J=7.3$ Hz, 1H), 7.30 (t, $J=7.3$ Hz, 2H), 7.33 (d, $J=7.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 24.00, 28.37, 37.11, 39.45, 44.04, 49.43, 126.05, 127.18, 128.42, 128.50, 134.25, 137.21, 213.51. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.12; H, 8.44. $[\alpha]_D^{20} = -11.3$ (c 0.84, $CHCl_3$) for *S* isomer of 93% ee.

4.3.4. 5-Methyl-4-((*E*-2-phenylethenyl)hexan-2-one 3dm. ^{1}H NMR ($CDCl_3$): δ 0.90 (d, $J=6.9$ Hz, 3H), 0.93 (d, $J=6.9$ Hz, 3H), 1.69–1.75 (m, 1H), 2.12 (s, 3H), 2.50–2.62 (m, 3H), 6.03 (dd, $J=15.9$ and 8.9 Hz, 1H), 6.37 (d, $J=15.9$ Hz, 1H), 7.20 (t, $J=7,3$ Hz, 1H), 7.29 (t, $J=7.3$ Hz, 2H), 7.33 (d, $J=7.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 18.98, 20.53, 30.64, 32.00, 45.12, 46.76, 126.09, 127.09, 128.44, 130.83, 131.28, 137.33, 208.39. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.44; H, 9.53. $[\alpha]_D^{20} = -35.2$ (c 1.00, $CHCl_3$) for *S* isomer of 78% ee.

4.3.5. 3-{(*E*)-2-(4-Methoxyphenyl)ethenyl}cyclohexanone 3an. ^{1}H NMR ($CDCl_3$): δ 1.55–1.64 (m, 1H), 1.68–1.77 (m, 1H), 1.96–2.02 (m, 1H), 2.05–2.12 (m, 1H), 2.27–2.33 (m, 2H), 2.36–2.41 (m, 1H), 2.49–2.53 (m, 1H), 2.60–2.68 (m, 1H), 3.79 (s, 3H), 6.01 (dd, $J=15.9$ and 6.9 Hz, 1H), 6.33 (d, $J=15.9$ Hz, 1H), 6.84 (d, $J=8.8$ Hz, 2H), 7.28 (d, $J=8.8$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 24.92, 31.45, 41.21, 41.87, 47.43, 55.21, 113.90, 121.17, 128.36, 129.80, 130.73, 158.95, 210.92. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.13; H, 7.91. $[\alpha]_D^{20} = -4.4$ (c 0.87, $CHCl_3$) for *S* isomer of 92% ee.

4.3.6. 3-{(*E*)-2-(2-Methylphenyl)ethenyl}cyclohexanone 3ao. ^{1}H NMR ($CDCl_3$): δ 1.59–1.67 (m, 1H), 1.71–1.81 (m, 1H), 2.00–2.05 (m, 1H), 2.08–2.14 (m, 1H), 2.32 (s, 3H), 2.29–2.45 (m, 3H), 2.52–2.56 (m, 1H), 2.67–2.75 (m, 1H), 6.02 (dd, $J=15.8$ and 7.0 Hz, 1H), 6.60 (d, $J=15.8$ Hz, 1H), 7.12–7.18 (m, 3H), 7.39–7.41 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 19.75, 24.96, 31.47, 41.26, 42.22, 47.46, 125.39, 126.04, 126.99, 127.25, 130.22, 134.32, 135.21, 136.22, 210.91. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.20; H, 8.53. $[\alpha]_D^{20} = -13.0$ (c 0.88, $CHCl_3$) for *S* isomer of 92% ee.

4.3.7. 3-{(*E*)-2-(1-Naphthyl)ethenyl}cyclohexanone 3ap. ^{1}H NMR ($CDCl_3$): δ 1.64–1.72 (m, 1H), 1.74–1.83 (m, 1H), 2.05–2.15 (m, 2H), 2.30–2.45 (m, 3H), 2.59–2.63 (m, 1H), 2.75–2.83 (m, 1H), 6.15 (dd, $J=15.7$ and 6.8 Hz, 1H), 7.13 (d, $J=15.7$ Hz, 1H), 7.42 (t, $J=7.9$ Hz, 1H), 7.45–7.54 (m, 3H), 7.76 (d, $J=8.1$ Hz, 1H), 7.84 (d, $J=7.9$ Hz, 1H), 8.06 (d, $J=8.3$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 24.93, 31.37, 41.26, 42.20, 47.33, 123.61, 123.68, 125.54, 125.72, 125.96, 126.40, 127.69, 128.47, 131.07, 133.53, 134.89, 136.21, 210.84. Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.30; H, 7.25. $[\alpha]_D^{20} = -12.4$ (c 0.54, $CHCl_3$) for *S* isomer of 90% ee.

4.3.8. 3-{(*E*)-2-(2-Naphthyl)ethenyl}cyclohexanone 3aq. ^{1}H NMR ($CDCl_3$): δ 1.60–1.68 (m, 1H), 1.70–1.80 (m, 1H), 2.00–2.06 (m, 1H), 2.08–2.14 (m, 1H), 2.28–2.44 (m, 3H), 2.53–2.59 (m, 1H), 2.68–2.75 (m, 1H), 6.27 (dd, $J=15.9$ and 6.9 Hz, 1H), 6.54 (d, $J=15.9$ Hz, 1H), 7.40–7.47 (m, 2H), 7.56 (dd, $J=8.6$ and 1.6 Hz, 1H), 7.69 (s, 1H), 7.75–7.80 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 24.95, 31.37, 41.25, 41.99, 47.32, 123.35, 125.70, 125.89, 126.21, 127.59, 127.83, 128.13, 129.17, 132.80, 133.27, 133.56, 134.49, 210.83. Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.09; H, 7.26. $[\alpha]_D^{20} = +6.1$ (c 1.05, $CHCl_3$) for *S* isomer of 92% ee.

4.3.9. 3-((*E*)-2-Octenyl)cyclohexanone 3ar. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $J=7.0$ Hz, 3H), 1.23–1.36 (m, 8H), 1.44–1.52 (m, 1H), 1.63–1.73 (m, 1H), 1.87–1.92 (m, 1H), 1.95–2.07 (m, 3H), 2.15–2.30 (m, 2H), 2.32–2.49 (m, 3H), 5.36 (dd, $J=15.5$ and 6.2 Hz, 1H), 5.43 (dt, J = 15.5 and 6.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.05, 22.58, 24.94, 28.72, 29.32, 31.57, 31.65, 32.44, 41.25, 41.56, 47.70, 129.97, 132.89, 211.45. Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.45; H, 11.48. $[\alpha]_D^{20} = -17.7$ (c 1.00, $CHCl_3$) for *S* isomer of 98% ee. The enantiomeric purity of this ketone was determined by $^{13}C\{^1H\}$ NMR spectra of a mixture of diastereomeric ketals obtained with (2*R*,3*R*)-(−)-2,3-butanediol.[14] The resonances of octenyl sp^2 carbons (δ 128.31 vs 128.36, 134.86 vs 134.95) were used for the determination of % ee.

4.3.10. 3-((*E*)-2-Triethylsilylethenyl)cyclohexanone 3as. ^{1}H NMR ($CDCl_3$): δ 0.55 (q, $J=8.0$ Hz, 6H), 0.92 (t, $J=8.0$ Hz, 9H), 1.48–1.56 (m, 1H), 1.65–1.75 (m, 1H), 1.92–1.97 (m, 1H), 2.02–2.08 (m, 1H), 2.21–2.31 (m, 2H), 2.34–2.39 (m, 1H), 2.42–2.47 (m, 1H), 2.49–2.56 (m, 1H), 5.57 (dd, J = 18.9 and 1.5 Hz, 1H), 5.98 (dd, $J=18.9$ and 5.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 3.36, 7.30, 24.92, 30.91, 41.29, 44.67, 46.81, 124.87, 150.06, 211.35. Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.60; H, 11.14. $[\alpha]_D^{20} = -8.1$ (c 0.35, $CHCl_3$) for *S* isomer of 98% ee. In a similar manner to **3ar**, the ketone **3as** was converted into the diastereomeric ketals of (2*R*,3*R*)-(−)-2,3-butanediol. The

resonances of ethenyl sp^2 carbons (δ 112.02 vs 112.06, 143.30 vs 143.39) were used for the determination of % ee.

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