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Zn(II)- or Rh(I)-Catalyzed Rearrangement of Silylated [1,1′-Bi(cyclopropan)]-2′-en-1-ols

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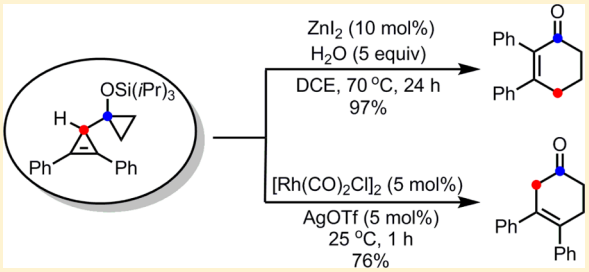
Supporting Information

ABSTRACT: The rearrangement reactions of silylated alcohols bearing the highly strained structures of cyclopropene and cyclopropanol connected in adjacent positions have been studied under ZnI_2- and Rh(I)-catalyzed conditions. The results show intriguing carbon skeletal reorganizations of such system under these conditions. The ZnI_2-catalyzed reaction proceeds with C−O cleavage and the rearrangement of the resultant carbon cation, leading to the breaking of the C−C single bond that connects two three-memebered rings. In contrast, the Rh(I)-catalyzed reaction involves σ-bond oxidative addition of the cyclopropene moiety, followed by β-carbon elimination of the cyclopropane moiety.



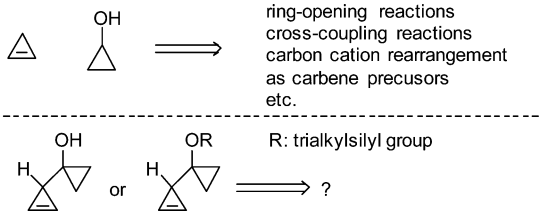
INTRODUCTION

Cyclopropene and cyclopropane are the two representatives of highly strained small ring molecules that possess unique chemical properties. Cyclopropene has strain energy of 228 kJ/mol, which is 110 kJ/mol more than that of cyclopropane. In recent years, transition-metal-catalyzed reaction of cyclopropenes has attracted significant attentions.[1] As recent examples, Yamamoto, Gevorgyan, and Rubin have studied the Pd-catalyzed coupling reactions with cyclopropenes.[2] Shi and Lee have investigated the gold-catalyzed reaction of cyclopropenes.[3] Meyer, Cossy, and co-workers have demonstrated that Rh(II) carbene generated from cyclopropene undergoes highly efficient stereoselective intramolecular C(sp^3)-H insertions.[4] Cyclopropenes are also well-known as carbene precursors in olefin metathesis.[5] We have recently reported a Au(I)-catalyzed cycloisomerization of enynes bearing a cyclopropene moiety.[6] These selected examples have demonstrated the diverse reaction modes of cyclopropenes.[7]

On the other hand, the reaction of cyclopropanols has also been studied extensively.[8] Cyclopropanols undergo a series of ring-opening reactions involving O−H bond breaking under various conditions,[9] while the C−O bond break that leads to ring opening through a carbocation process has also been well-documented.[10] Moreover, cyclopropanols and their derivatives are useful three-carbon units in transition-metal-catalyzed cyclizations.[11]

Since both cyclopropene and cyclopropanol have unique reactivities due to their high strain, it would be interesting to study the reaction of compounds that bear both cyclopropene and cyclopropane moieties in adjacent positions (Scheme 1). It is expected that both cyclopropene and cyclopropane moieties may undergo ring opening to afford products with extra-ordinary carbon skeletal reorganization. Herein we report the results of study along this line. We have found with ZnI_2 or Rh(I) complex as the catalysts the trialkylsilylated [1,1′-bi(cyclopropan)]-2′-en-1-ols rearrange to cyclohexenone derivatives through different reaction pathways.

Scheme 1. Merging the High Reactivities of Cyclopropenes and Cyclopropanols



RESULTS AND DISCUSSION

First, we have synthesized a series of substituted [1,1′-bi(cyclopropan)]-2′-en-1-ols **1a−h** from the corresponding substituted ethyl cycloprop-2-ene-1-carboxylates by Kulinkovich cyclopropanation (Scheme 2).[12,13] The starting material ethyl cycloprop-2-ene-1-carboxylates could be easily prepared by Rh(II)-catalyzed cyclopropanation of alkyne with ethyl diazoacetate.[6,14] The cyclopropanols **1a−h** were then converted to the corresponding silyl ethers **3** (*vide infra*). The overall yields for two steps ranged from 27% to 65%.

At the outset, we studied the rearrangement reaction of **1a** under Lewis acid catalyzed conditions. However, the reaction

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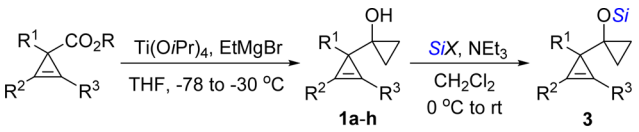
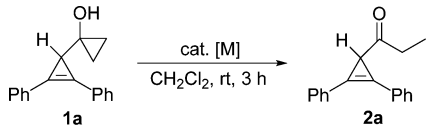
Scheme 2. Preparation of [1,1′-Bi(cyclopropan)]-2′-en-1-ols 1a–h and Their Silylated Counterparts



1a, R^1 = H, R^2 = R^3 = Ph
1b, R^1 = R^2 = R^3 = Ph
1c, R^1 = H, R^2 = R^3 = *n*-Bu
1d, R^1 = H, R^2 = R^3 = cyclohexanyl (Cy)
1e, R^1 = H, R^2 = Ph, R^3 = Me
1f, R^1 = H, R^2 = Ph, R^3 = *n*-Bu
1g, R^1 = H, R^2 = Ph, R_3 = CH_2Ph
1h, R^1 = H, R^2 = *n*-Bu, R_3 = Me

SiX = TIPSOTf, TESOTf, TMSCl
yields for two steps: 27-65%

under various conditions afforded only cyclopropane ring-opening product **2a** as the major product (eq 1). Notably, the



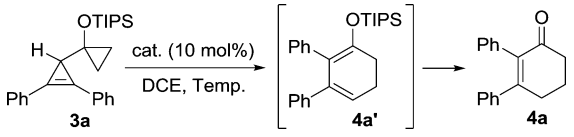
(1)

[M] = $Rh_2(O_2CCF_3)_4$, $PtCl_2$, CuCl, $FeCl_3$

cyclopropene moiety remains intact in these reactions. The ring opening of cyclopropanols to afford the corresponding carbonyl compounds has been well-documented in the literature.[8−10]

We then conceived the protection of the hydroxyl group with trialkylsilyl (TIPS) group in order to avoid the direct cyclopropane ring opening. Thus, the silylated [1,1′-bi-(cyclopropan)]-2′-en-1-ol substrate **3a** was submitted to Lewis acid catalyzed conditions (Table 1). To our delight, with $Cu(CH_3CN)_4PF_6$ or $Cu(OTf)_2$ as the catalyst, we could isolate cyclohexenone **4a**, albeit in low yields (entries 1 and 2). Then we examined other Lewis acid catalysts. MgI_2, AuCl-(PPh_3), and $AlCl_3$ could afford only trace amount of the cyclohexenone product (entries 3−5). On the contrary, Zn(II) halides under the same conditions gave **4a** in good yields,

Table 1. Lewis Acid Catalyzed Reaction of 3a[a]

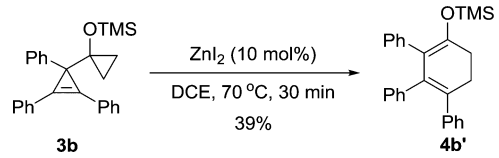


entry	catalyst (10 mol %)	*T* (°C)	*t* (h)	yield (%)[b]
1	$Cu(CH_3CN)_4PF_6$	70	4	17
2	$Cu(OTf)_2$	70	4	13
3	MgI_2	70	12	trace[c]
4	AuCl(PPh_3)	70	12	trace[c]
5	$AlCl_3$	25	0.5	trace[d]
6	$ZnCl_2$	70	12	34
7	$ZnBr_2$	70	12	64
8	ZnI_2	70	12	71
9	ZnF_2	70	12	trace[c]
10	$Zn(OTf)_2$	70	12	8
11	ZnI_2	70	24	97[e]

[a]Reaction conditions: **3a** (81 mg, 0.02 mmol) in DCE (4 mL). [b]GC yield. [c]**3a** was recovered unchanged. [d]**3a** decomposed. [e]H_2O (5 equiv) was added upon the completion of the reaction after 24 h. Stirring was continued for another 2 h.

except ZnF_2 (entries 6−9), while $Zn(OTf)_2$ was found not effective (entry 10). Since silyl enolate **4a′** is considered as the primary rearrangement product, hydrolysis upon the completion of the rearrangement is thus carried out in order to improve the reaction. Indeed, we found that with ZnI_2 as the catalyst the reaction afforded clean cyclohexenone product when the reaction was treated with 5 equiv of water for 2 h upon the completion of the rearrangement (24 h) (entry 11).

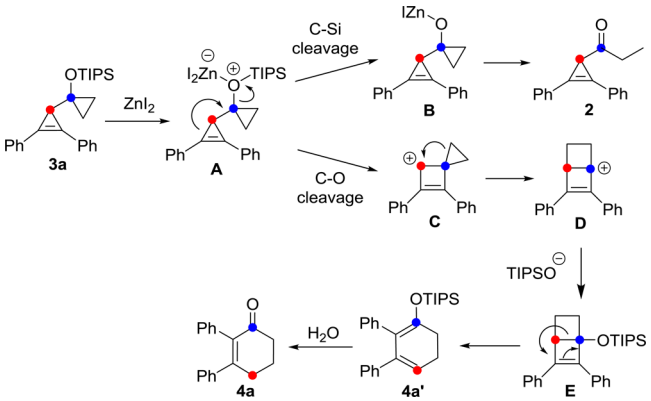
To confim that the silyl enolate is the primary rearrangement product, we have attempted the isolation of **4a′**. However, this was proved unsuccessful due to the instability of **4a′**. The reaction of **3b** was then carried out under the above optimized reaction conditions. The expected silyl enolate **4b′** was isolated in 39% yield when the reaction was terminated after 30 min (eq 2).



(2)

Possible mechanism for this ZnI_2-catalyzed rearrangement is proposed in Scheme 3. First, the ZnI_2 coordinates to the

Scheme 3. Proposed Mechanism for Zn(II)-Catalyzed Rearrangement



oxygen of **3a** to form complex **A**. From **A**, both C−O and O−Si bond cleavage are possible. If O−Si bond is cleaved, intermediate **B** is formed, and ketone **2a** would be the product. In the optimization experiments, ketone **2a** has been identified as the byproduct in most cases. Alternatively, C−O bond cleavage generates the cyclopropyl carbocation **C**, from which cyclopropyl ring opening occurs to give cation **D**. This cation can be captured by the $TIPSO^-$ to form intermediate **E**, from which the ring-opening process occurs to afford silyl enolate **4a′**. Finally, hydrolysis of the silyl enolate affords the cyclohexenone product **4a**.

It is noteworthy that O−Si bond cleavage is generally more facile than the corresponding C−O bond cleavage since the former is weaker than the latter. Indeed, when Lewis acid is employed as the catalyst, significant amounts of ketone and other related byproducts were observed. The preferential C−O bond cleavage in the ZnI_2-catalyzed reaction may be rationalized by the simultaneous release of the strain of cyclopropene ring as a driving force.

The generality of this rearrangement reaction was then examined under the optimized conditions with a series of

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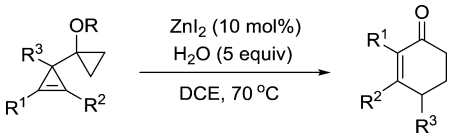
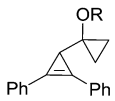
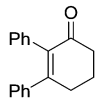
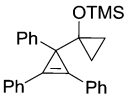
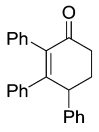
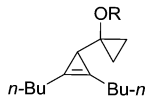
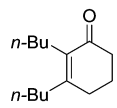
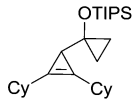
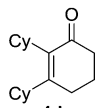
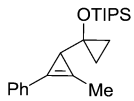
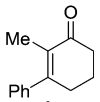
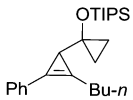
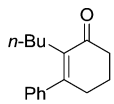
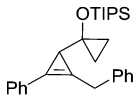
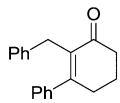
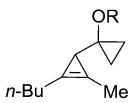
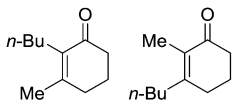
silylated [1,1′-bi(cyclopropan)]-2′-en-1-ol substrates. As summarized in Table 2, when R^1 was equal to R^2 most of the reaction could give the corresponding cyclohexenone products in good yields (entries 1−8). However, as the silyl protecting group became small and unstable, the yields were slightly diminished (entries 1−3 and 5−7). For the reaction with **3ab**, we could observe the byproduct of ketone **2a**, which is formed through desilylation and subsequent ring opening as shown in eq 1.

When the two substituents R^1 and R^2 are not the same, the reaction could afford two isomeric products. We have observed that if one of the two substituents is alkyl and the other one is phenyl, only one product is isolated in each case (entries 9−11). However, when the two substituents are different alkyl groups, the reaction gives two isomeric products with low selectivities (entries 12−14).

We have previously reported Rh(I)-catalyzed [3 + 2 + 1] carbonylative carbocyclization reactions of ene- and yne-cyclopropene systems, which demonstrates that the highly strained cyclopropene structure can be used as a three-carbon component in transition-metal-catalyzed carbocyclizations.[15] Encouraged by this reaction and other related transition-metal-catalyzed reactions of cyclopropenes,[4,5,16] we further proceeded to carry out the investigation on the Rh(I)-catalyzed reaction of silylated [1,1′-bi(cyclopropan)]-2′-en-1-ols. The substrate **3a** was also employed as model compound to examine a series of Rh(I) catalysts. As shown in Table 3, all of the Rh(I) catalysts employed in this study were effective in catalyzing the reaction of **3a**. However, four products were observed depending on the reaction conditions. In the absence of Ag(I) co-catalyst, **5a** was isolated in good yields, but the reactions require high temperature (entries 1−3). The combination of $[Rh(CO)_2Cl]_2$ with Ag(I) salts afforded cyclohexenone **7a** in moderate yields at room temperature with short reaction times (entries 4−6). The combination of $[Rh(COD)_2Cl]_2$ with AgOTf resulted in a complex mixture, while the $Rh(PPh_3)_3Cl$ + AgOTf catalyst system gave **6a** in 77% yield (entires 8, 9). It was confirmed that the product **5a** could be converted to **8a** when AgO_2CCF_3 (0.1 equiv) was added and the mixture was stirred under open air for 3 h (entry 10). Also, **5a** could be converted to **6a** by the treatment with H_2O (5 equiv) at 110 °C for 12 h.

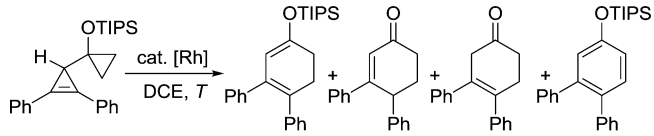
Table 2. Zn(II)-Catalyzed Rearrangement of Silylated [1,1′-Bi(cyclopropan)]-2′-en-1-ol Substrates



entry	substrate (reaction time)	product	yield (%)[a]
1	 **3a**: R = TIPS (24 h)	 **4a**	95
2	**3aa**: R = TES (18 h)		85
3	**3ab**: R = TMS (12 h)		79
4	 **3b** (12 h)	 **4b**	83
5	 **3c**: R = TIPS (1 h)	 **4c**	94
6	**3ca**: R = TES (1 h)		89
7	**3cb**: R = TMS (1 h)		64
8	 **3d** (1 h)	 **4d**	85[b]
9	 **3e** (12 h)	 **4e**	61[c]
10	 **3f** (12 h)	 **4f**	82[c]
11	 **3g** (12 h)	 **4g**	91[c]
12	 **3h**, R = TIPS (1 h)	 **4ha** : **4hb** = 1 : 0.98	92
13	**3ha**, R = TES (1 h)	1 : 1.5	86
14	**3hb**, R = TMS (1 h)	1 : 2.2	60

[a]Isolated yield. [b]Cy = cyclohexanyl. [c]The corresponding isomer was not observed by NMR or GC−MS.

Table 3. Rh(I)-Catalyzed Rearrangement of 3a[a]



3a **5a** **6a** **7a** **8a**

entry	Rh(I) (5 mol %)	conditions	yields (%)[b]
1	$[Rh(CO)_2Cl]_2$	70 °C, 3 h	**5a**, 83
2	$[Rh(COD)Cl]_2$	110 °C, 24 h	**5a**, 95
3	$Rh(PPh_3)_3Cl$	70 °C, 24 h	**5a**, 50
4	$[Rh(CO)_2Cl]_2$ + AgOTf	25 °C, 1 h	**7a**, 76
5	$[Rh(CO)_2Cl]_2$ + $AgSbF_6$	25 °C, 1 h	**7a**, 54
6	$[Rh(CO)_2Cl]_2$ + $AgPF_6$	25 °C, 1 h	**7a**, 67
7	$[Rh(COD)Cl]_2$ +AgOTf	25 °C, 1 h	complex mixture
8	$Rh(PPh_3)_3Cl$ + AgOTf	70 °C, 6 h	**6a**, 77
9	$[Rh(CO)_2Cl]_2$	70 °C, 3 h[c]	**8a**, 71
10	$[Rh(COD)Cl]_2$	110 °C, 24 h[c]	**8a**, 92
11	$[Rh(CO)_2Cl]_2$	70 °C, 3 h[d]	**6a**, 81

[a]Reaction conditions: **3a** (81 mg, 0.02 mmol) in DCE (4 mL); 5 mol % Ag(I) salt was used in the cases of entries 4−8. [b]Isolated yield. [c]After the reaction finished, AgO_2CCF_3 (0.1 equiv) was added, and the mixture was stirred at room temperature for 3 h under air. [d]Upon completion of the reaction, H_2O (5 equiv) was added, and the mixture was stirred at 110 °C for 12 h.

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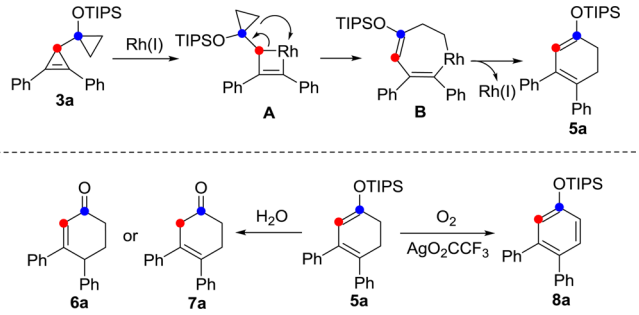
We have proposed a possible reaction mechanism to account for the above results (Scheme 4). First, the rhodacyclobutene

Scheme 4. Proposed Mechanism for Rh(I)-Catalyzed Rearrangement



intermediate **A** is formed though σ-bond oxidative addition.[15] This is followed by a β-carbon elimination process to afford rhodacycloheptdiene **B**,[11g,i] from which reductive elimination occurs to afford product **5a**. From the primary product **5a**, cyclohexenones **6a** and **7a** could be formed through the reaction with H_2O, while product **8a** is formed through oxidation.

Under the reaction conditions described in Table 3, several silylated [1,1′-bi(cyclopropan)]-2′-en-1-ols were studied. As summarized in Table 4, the reactions proceeded smoothly, but the products varied according to the reaction conditions and also to the stability of the silyl group. For the reactions shown in entries 6–8, oxidative conditions were employed in order to achieve clean conversion to the phenol products. Notably, a silyl group was lost in the case of reaction with **3b** (entry 6), this is attributed to the relative instability of the TMS ether product.

CONCLUSION

In summary, we have reported herein the ZnI_2- and Rh(I)-catalyzed reaction of silylated [1,1′-bi(cyclopropan)]-2′-en-1-ols. Both cyclopropene and cyclopropane moieties undergo ring opening to afford products with intriguing carbon skeletal reorganization. The results demonstrate the unique reactivity of the system in which highly strained structure of cyclopropene and cyclopropanol are connected in adjacent positions.

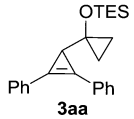
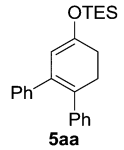
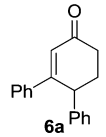
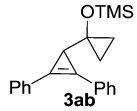
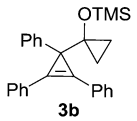
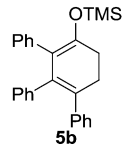
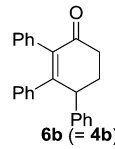
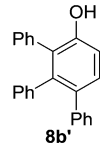
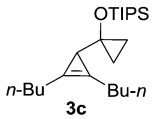
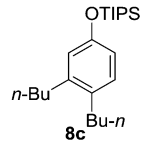
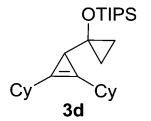
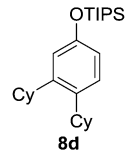
EXPERIMENTAL SECTION

General. Air- and moisture-sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under nitrogen atmosphere. THF and Et_2O were distilled from sodium with benzophenone as indicator. DCE was distilled over calcium hydride. ZnI_2, $[Rh(CO)_2Cl]_2$, $[Rh(COD)Cl]_2$, AgOTf, and other metal salts were commercially available. Purification of products was accomplished by flash chromatography on silica gel (200–300 mesh). Chemical shifts for ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra are reported relative to the chemical shift of tetramethylsilane (TMS). IR spectra are reported in wave numbers, cm^{-1}. For HRMS measurements, the mass analyzer is FT-ICR.

The Preparation of Silylated [1,1′-Bi(cyclopropan)]-2′-en-1-ols. Preparation of Cyclopropene Esters. The corresponding cyclopropene esters for the preparation of **1a**, **1b**, **1c**, **1e**, **1f**, **1g**, and **1h** were known and were prepared via literature procedures.[6,14] The cyclopropene ester for preparing **1d** is synthesized by the following procedure.

Ethyl 2,3-Dicyclohexylcycloprop-2-enecarboxylate. A 50 mL two-neck round-bottom flask was charged with 1,2-dicyclohexylethyne (prepared via literature procedures,[17] 3.8 g, 20 mmol, 1.0 equiv), $Rh_2(OAc)_4$ (44 mg, 0.1 mmol, 0.005 equiv), and DCM (10 mL). A solution of ethyl diazoacetate (EDA) (4.6 g, 40 mmol, 2 equiv) in DCM (5 mL) was added via syringe pump over 10 h. The solvent was removed, and the residue was purified with flash column chromatography (petroleum ether/EtOAc = 30:1) to afford a colorless oil product (5.3 g, 96%). FTIR (film) 2927 (s), 2852 (m), 1721 (s), 1448 (m), 1366 (w), 1336 (w), 1241 (w), 1173 (s), 1028 (w), 996 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.09 (q, J = 7.1 Hz, 2H), 2.45 (m, 2H), 2.04 (s, 1H), 1.83–1.89 (m, 4H), 1.68–1.71 (m, 4H), 1.59–1.62 (m, 2H), 1.21–1.37 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 108.4, 59.6, 34.1, 30.8, 26.0, 25.4, 21.2, 14.4; MS (EI, 70 eV) m/z (%) = 276 (10), 247 (6), 233 (8), 203 (100), 165 (10), 147 (12), 119 (24), 91 (23), 79 (26), 67 (22), 55 (28), 29 (30); HRMS (ESI) m/e calcd for $C_{18}H_{29}O_2$ $[M + H]^+$ 277.2162, found 277.2163.

Table 4. Scope of Rh(I)-Catalyzed Rearrangement

entry	substrate	conditions	product	yield (%)[a]
1	 **3aa**	$[Rh(COD)Cl]_2$ 110 °C, 12 h	 **5aa**	89
2	**3aa**	$[Rh(CO)_2Cl]_2$ 70 °C, 3 h	 **6a**	82
3	 **3ab**	$[Rh(CO)_2Cl]_2$ 70 °C, 3 h	**6a**	73
4	 **3b**	$[Rh(CO)_2Cl]_2$ 70 °C, 3 h	 **5b**	95
5	**3b**	$[Rh(CO)_2Cl]_2$ 70 °C, 3 h[b]	 **6b (= 4b)**	87
6	**3b**	$[Rh(CO)_2Cl]_2$ 70 °C, 3 h[c]	 **8b'**	77
7	 **3c**	$[Rh(COD)Cl]_2$ 110 °C, 3 h[c]	 **8c**	79
8	 **3d**	$[Rh(CO)_2Cl]_2$ 70 °C, 9 h[c]	 **8d**	68

[a]Isolated yield. [b]Upon completion of the reaction, H_2O (5 equiv) was added, and the mixture was stirred at 110 °C for 12 h. [c]Upon completion of the reaction, AgO_2CCF_3 (0.1 equiv) was added, and the mixture was stirred at room temperature for 3 h under air.

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Preparation of Silylated [1,1′-Bi(cyclopropan)]-2′-en-1-ols. To a well-stirred solution of ester (10 mmol, 1 equiv) and $Ti(OiPr)_4$ (10 mmol, 1 equiv) in THF (40 mL) was added n solution of EtMgBr (30 mmol, 3 equiv) dropwise over 2 h at −78 °C. After addition, the mixture was stirred for an additional 10 h at −30 °C. Then the mixture was carefully quenched with 30 mL of 10% aqueous HCl. The solution was then extracted with Et_2O, and the combined organic layers were washed with a saturated $NaHCO_3$ solution and saturated brine and dried over Na_2SO_4. Removal of the solvent gave a crude residue that was purified with flash column chromatography to afford [1,1′-bi(cyclopropan)]-2′-en-1-ol products **1a−h**.

The [1,1′-bi(cyclopropan)]-2′-en-1-ol product **1a−h** was dissolved in CH_2Cl_2 (0.16 M). To the solution were added NEt_3 (3 equiv) and TMSCl (or TESOTf, TIPSOTf, 1.5 equiv) at 0 °C. The resultant mixture was stirred at room temperature for 30 min before saturated aqueous $NaHCO_3$ was added. The reaction mixture was stirred at room temperature for another 10 min. The mixture was then extracted with CH_2Cl_2, and the organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified with flash column chromatography (eluted with petroleum ether) to afford the silylated product **3**.

*((2′,3′-Diphenyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)-triisopropylsilane (**3a**).* A colorless oil (the yield for two steps: 2.6 g, 65%); FTIR (film) 2942 (w), 2865 (w), 1599 (w), 1495 (w), 1446 (w), 1463 (w), 1383 (w), 1341 (w), 1288 (w), 1220 (m), 1173 (w), 1039 (m), 1017 (m), 940 (w), 910 (w), 882 (m), 803 (w), 754 (s), 687 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.6 Hz, 4H), 7.43 (t, J = 7.6 Hz, 4H), 7.32 (t, J = 7.6 Hz, 2H), 2.72 (s, 1H), 1.12 (m, 21H), 0.70 (dd, J = 5.2 Hz, J = 6.8 Hz, 2H), 0.46 (dd, J = 5.2 Hz, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.7, 129.7, 128.6, 128.4, 115.0, 61.0, 26.8, 18.4, 13.3, 13.2; MS (EI, 70 eV) m/z (%) = 404 (100), 361 (27), 331 (16), 303 (39), 287 (36), 231 (14), 215 (27), 191 (59), 165 (11), 115 (27), 75 (23), 59 (48); HRMS (ESI) m/e calcd for $C_{27}H_{37}OSi$ $[M + H]^+$ 405.2608, found 405.2610.

*((2′,3′-Diphenyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)-triethylsilane (**3aa**).* A colorless oil (the yield for two steps: 2.3 g, 63%); FTIR (film) 2954 (w), 2910 (w), 2875 (w), 1495 (w), 1446 (w), 1413 (w), 1220 (m), 1016 (s), 1003 (m), 941 (w), 812 (w), 754 (s), 740 (s), 688 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.3 Hz, 4H), 7.44 (t, J = 7.4 Hz, 4H), 7.33 (t, J = 7.3 Hz, 2H), 2.65 (s, 1H), 0.99 (t, J = 7.8 Hz, 9H), 0.70 (m, 8H), 0.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.7, 129.6, 128.7, 128.4, 114.9, 61.1, 26.7, 13.0, 7.0, 6.0; MS (EI, 70 eV) m/z (%) = 362 (55), 333 (7), 305(6), 271 (11), 245 (3), 231 (10), 215 (13), 191 (34), 165 (8), 115 (38), 87 (100), 59 (62); HRMS (ESI) m/e calcd for $C_{24}H_{31}OSi$ $[M + H]^+$ 363.2139, found 363.2144.

*((2′,3′-Diphenyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)-trimethylsilane (**3ab**).* A colorless oil (the yield for two steps: 1.5 g, 48%); FTIR (film) 3080 (w), 2956 (w), 1672 (w), 1598 (w), 1495 (w), 1446 (w), 1250 (m), 1222 (m), 1017 (m), 860 (m), 841 (s), 755 (s), 688 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.4 Hz, 4H), 7.44 (t, J = 7.3 Hz, 4H),7.33 (t, J = 7.2 Hz, 2H), 2.66 (s, 1H), 0.73 (m, 2H), 0.53 (m, 2H), 0.19 (s, 9H); ^{13}C NMR (100 MHz,$CDCl_3$) δ 129.7, 129.6, 128.7, 128.4, 114.8, 61.6, 26.6, 12.8, 1.6; MS (EI, 70 eV) m/z (%) = 320 (21), 292 (9), 243 (5), 229 (22), 215 (6), 203 (4), 191 (18), 178 (7), 165 (6), 115 (4), 73 (100), 59 (3); HRMS (EI) m/e calcd for $C_{21}H_{24}OSi$ $[M]^+$ 320.1596, found 320.1602.

*Trimethyl((1′,2′,3′-triphenyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)-oxy)silane (**3b**).* A white solid (the yield for two steps: 1.7 g, 42%); mp 90−92 °C; FTIR (film) 3080 (w), 2956 (w), 1599 (w), 1494 (m), 1446 (m), 1246 (s), 1155 (w), 1029 (m), 1005 (m), 872 (m), 840 (s), 755 (s), 688 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.4 Hz, 4H), 7.62 (d, J = 7.7 Hz, 2H), 7.42 (t, J = 7.5 Hz, 4H), 7.34 (t, J = 7.4 Hz, 2H), 7.26 (t, J = 7.6 Hz, 2H),7.16 (t, J = 7.3 Hz, 1H), 1.01 (t, J = 6.3 Hz, 2H), 0.77 (t, J = 6.3 Hz, 2H), 0 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 129.8, 128.7, 128.6, 128.2, 127.7, 127.4, 125.1, 115.5, 63.8, 38.5, 14.5, 1.5; MS (EI, 70 eV) m/z (%) = 396 (80), 368 (6), 320 (9), 305 (40), 289 (8), 267 (18), 215 (12), 189 (5), 165 (4), 103 (6), 73 (100); HRMS (ESI) m/e calcd for $C_{27}H_{29}OSi$ $[M + H]^+$ 397.1982, found 397.1994.

*((2′,3′-Dibutyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)-triisopropylsilane (**3c**).* A colorless oil (the yield for two steps: 1.4 g, 39%); FTIR (film) 2958 (m), 2930 (m), 2866 (m), 1464 (m), 1380 (w), 1347 (w), 1223 (s), 1038 (s), 1010 (m), 958 (w), 935 (w), 882 (s), 805 (w), 755 (w), 679 (s), 665 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.24−2.38 (m, 4H), 1.94 (s, 1H), 1.47−1.54 (m, 4H), 1.29−1.38 (m, 4H), 1.08 (m, 21H), 0.90 (t, J = 7.2 Hz, 6H), 0.57 (dd, J = 4.8, 6.8 Hz, 2H), 0.26 (dd, J = 4.8, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.4, 62.1, 29.7, 26.4, 25.1, 22.6, 18.3, 13.8, 13.0, 12.9; MS (EI, 70 eV) m/z (%) = 364 (6), 335 (4), 321 (100), 307 (31), 266 (15), 151 (12), 129 (8), 115 (50), 101 (12), 87 (23), 73 (23), 59 (31); HRMS (ESI) m/e calcd for $C_{23}H_{45}OSi$ $[M + H]^+$ 365.3234, found 365.3241.

*((2′,3′-Dibutyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)triethylsilane (**3ca**).* A colorless oil (the yield for two steps: 1.2 g, 38%); FTIR (film) 2956 (s), 2931 (s), 2875 (m), 1460 (m), 1220 (s), 1028 (s), 1010 (s), 808 (w), 741 (s), 725 (s), 668 (w), 657 (m), 651 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.28−2.36 (m, 4H), 1.87 (s, 1H), 1.47−1.58 (m, 4H), 1.31−1.36 (m, 4H), 0.96 (t, J = 7.7 Hz, 9H), 0.91 (t, J = 7.2 Hz, 6H), 0.64 (q, J = 7.6 Hz, 6H), 0.56 (m, 2H), 0.27 (m, 2H); ^{13}C NMR (100 MHz,$CDCl_3$) δ 113.3, 62.1, 29.7, 26.3, 25.1, 22.5, 13.8, 12.5, 6.9, 5.8; MS (EI, 70 eV) m/z (%) = 322 (3), 307 (3), 293 (5), 279 (81), 265 (19), 224 (8), 209 (3), 151 (8), 115 (38), 103 (9), 87 (100), 75 (14), 59 (41); HRMS (ESI) m/e calcd for $C_{20}H_{39}OSi$ $[M + H]^+$ 323.2765, found 323.2771.

*((2′,3′-Dibutyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)-trimetylsilane (**3cb**).* A colorless oil (the yield for two steps: 0.84 g, 30%); FTIR (film) 2958 (m), 2931 (m), 2873 (w), 1701 (w), 1459 (w), 1379 (w), 1250 (m), 1222 (m), 1029 (m), 1010 (m), 938 (w), 842 (s), 752 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.24−2.40 (m, 4H), 1.86 (s, 1H), 1.49−1.53 (m, 4H), 1.31−1.37 (m, 4H), 0.91 (t, J = 7.1 Hz, 6H), 0.56 (m, 2H), 0.28 (m, 2H), 0.15(s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.2, 62.3, 29.7, 26.3, 25.0, 22.5, 13.8, 12.2, 1.5; MS (EI, 70 eV) m/z (%) = 280 (1), 265 (1), 251 (1), 237 (48), 223 (10), 209 (3), 195 (6), 182 (7), 167 (3), 151 (4), 105 (4), 91 (5), 73 (100); HRMS (EI) m/e calcd for $C_{17}H_{32}OSi$ $[M]^+$ 280.2222, found 280.2227.

*((2′,3′-Dicyclohexyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)-triisopropylsilane (**3d**).* A colorless oil (the yield for two steps: 2.3 g, 55%); FTIR (film) 2926 (s), 2853 (m), 1458 (m), 1448 (m), 1220 (m), 1038 (m), 1010 (m), 936 (w), 882 (m), 804 (w), 711 (w), 670 (m), 663 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.28−2.33 (m, 2H), 1.97 (s, 1H), 1.82−1.88 (m, 4H), 1.60−1.71 (m, 6H), 1.17−1.32 (m, 10H), 1.08 (m, 21H), 0.55 (dd, J = 4.8, 6.8 Hz, 2H), 0.26 (dd, J = 4.8, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.2, 62.3, 34.7, 31.8, 31.2, 26.3, 25.8, 25.5, 18.3, 12.9; MS (EI, 70 eV) m/z (%) = 416 (82), 373 (49), 333 (100), 317 (3), 291 (16), 251 (11), 223 (8), 203 (13), 179 (5), 157 (21), 131 (30), 115 (68), 87 (50), 59 (89); HRMS (ESI) m/e calcd for $C_{27}H_{49}OSi$ $[M + H]^+$ 417.3547, found 417.3553.

*Triisopropyl((2′-methyl-3′-phenyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)silane (**3e**).* A colorless oil (the yield for two steps: 0.92 g, 27%); FTIR (film) 2943 (m), 2866 (m), 1848 (w), 1708 (w), 1598 (w), 1489 (m), 1464 (m), 1446 (m), 1383 (w), 1344 (w), 1223 (s), 1031 (s), 1000 (m), 919 (w), 882 (s), 808 (m), 760 (m), 691 (s), 680 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.25 (t, J = 6.4 Hz, 1H), 2.35 (s, 1H), 2.28 (s, 3H), 1.10 (m, 21H), 0.66−0.72 (m, 1H), 0.58−0.64 (m, 1H), 0.43−0.48 (m, 1H), 0.27−0.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.8, 128.7, 128.4, 127.5, 114.4, 112.7, 61.9, 27.2, 18.3, 13.8, 13.0, 12.6, 11.5; MS (EI, 70 eV) m/z (%) = 342 (94), 299 (47), 269 (44), 241 (100), 225 (53), 129 (44), 115 (53), 87 (38), 73 (49), 59 (69); HRMS (ESI) m/e calcd for $C_{22}H_{35}OSi$ $[M + H]^+$ 343.2452, found 343.2458.

*((2′-Butyl-3′-phenyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)-triisopropylsilane (**3f**).* A colorless oil (the yield for two steps: 1.4 g, 37%); FTIR (film) 2928 (m), 2865 (m), 1464 (m), 1221 (s), 1032 (s), 1020 (s), 1002 (m), 938 (w), 882 (m), 805 (w), 757 (m), 690 (s), 681 (s), 668 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H),7.25 (t, J = 6.9 Hz, 1H), 2.54−2.70

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(m, 2H), 2.36 (s, 1H), 1.68−1.75 (m, 2H), 1.38−1.46 (m, 2H), 1.02 (m, 21H), 0.95 (t, J = 7.4 Hz, 3H), 0.66−0.72 (m, 1H), 0.56−0.62 (m, 1H), 0.42−0.47 (m, 1H), 0.26−0.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.8, 128.8, 128.4, 127.5, 118.7, 111.9, 61.7, 30.0, 26.8, 26.2, 22.7, 18.3, 13.8, 13.0, 12.5; MS (EI, 70 eV) m/z (%) = 384 (34), 369 (2), 355(9), 341 (100), 327 (11), 299 (21), 283 (9), 227 (8), 211 (9), 171 (10), 157 (9), 129 (17), 115 (67), 101 (18), 87 (36); HRMS (ESI) m/e calcd for $C_{25}H_{41}OSi$ $[M + H]^+$ 385.2921, found 385.2929.

*((2′-Benzyl-3′-phenyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)-triisopropylsilane (**3g**).* A colorless oil (the yield for two steps: 1.7 g, 41%); FTIR (film) 2925 (m), 2865 (m), 1463 (m), 1222 (s), 1031 (s), 1020 (m), 1002 (w), 938 (w), 918 (w), 882 (m), 806 (w), 758 (m), 734 (m), 692 (m), 682 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18−7.35 (m, 8H), 7.08−7.10 (m, 2H), 3.93 (dd, J = 17.8, 52.6 Hz, 2H), 2.48 (s, 1H), 1.10 (m, 21H), 0.68−0.73 (m, 1H), 0.60−0.65 (m, 1H), 0.45−0.50 (m, 1H), 0.27−0.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 129.2, 129.1, 128.9, 128.6, 128.3, 127.7, 126.5, 117.3, 113.2, 61.5, 33.2, 27.5, 18.3, 13.7, 12.9, 12.6; MS (EI, 70 eV) m/z (%) = 418 (100), 375 (29), 347(2), 327 (13), 285 (8), 245 (5), 228 (6), 207 (8), 154 (25), 131 (10), 115 (33); HRMS (ESI) m/e calcd for $C_{28}H_{39}OSi$ $[M + H]^+$ 419.2765, found 419.2769.

*((2′-Butyl-3′-methyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)-triisopropylsilane (**3h**).* A colorless oil (the yield for two steps: 1.4 g, 42%); FTIR (film) 2928 (m), 2866 (m), 1464 (m), 1380 (w), 1346 (w), 1223 (s), 1040 (s), 1000 (m), 955 (w), 933 (w), 882 (s), 804 (w), 679 (s), 665 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27−2.34 (m, 2H), 1.96 (t, J = 1.5 Hz, 3H), 1.92 (s, 1H), 1.48−1.53 (m, 2H), 1.32−1.38 (m, 2H), 1.08 (m, 21H), 0.91 (t, J = 7.3 Hz, 3H), 0.57−0.59 (m, 2H), 0.24−0.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.1, 109.1, 62.1, 29.6, 26.6, 25.1, 22.5, 18.3, 13.9, 12.9, 12.8, 10.4 MS (EI, 70 eV) m/z (%) = 322 (5), 307 (4), 293(3), 279 (79), 265 (11), 249 (10), 237 (42), 221 (39), 207 (20), 193 (13), 179 (8), 165 (24), 151 (18), 129 (11), 115 (79), 103 (26), 87 (65), 73 (82), 59(100); HRMS (ESI) m/e calcd for $C_{20}H_{39}OSi$ $[M + H]^+$ 323.2765, found 323.2766.

*((2′-Butyl-3′-methyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)-triethylsilane (**3ha**).* A colorless oil (the yield for two steps: 1.1 g, 39%); FTIR (film) 2956 (m), 2933 (m), 2875 (m), 1649 (w), 1618 (w), 1458 (m), 1429 (w), 1357 (w), 1221 (m), 1018 (m), 759 (m), 738 (m), 727 (m), 701 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27−2.34 (m, 2H), 1.96 (s, 3H), 1.85 (s, 1H), 1.50−1.54 (m, 2H), 1.32−1.38 (m, 2H), 0.96 (t, J = 7.9 Hz, 9H), 0.91 (t, J = 7.3 Hz, 3H), 0.64 (q, J = 8.0 Hz, 6H), 0.56 (dd, J = 5.2, 6.8 Hz, 2H), 0.26 (dd, J = 5.2, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.9, 109.1, 62.1, 29.6, 26.6, 25.0, 22.5, 13.8, 12.4, 10.4, 6.9, 5.7; MS (EI, 70 eV) m/z (%) = 280 (2), 265 (4), 251(5), 237 (35), 223 (6), 209 (11), 195 (3), 181 (3), 165 (3), 115 (40), 103 (13), 87 (100); HRMS (ESI) m/e calcd for $C_{17}H_{33}OSi$ $[M + H]^+$ 281.2295, found 281.2298.

*((2′-Butyl-3′-methyl-[1,1′-bi(cyclopropan)]-2′-en-1-yl)oxy)-trimethylsilane (**3hb**).* A colorless oil (the yield for two steps: 0.74 g, 31%); FTIR (film) 2959 (m), 2929 (m), 2873 (w), 1738 (w), 1712 (w), 1665 (w), 1460 (w), 1377 (w), 1250 (m), 1221 (w), 1103 (w), 1032 (m), 843 (m), 798 (w), 765 (w), 699 (m), 661 (m), 651 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27−2.36 (m, 2H), 1.98 (t, J = 1.5 Hz, 3H), 1.84 (s, 1H), 1.48−1.57 (m, 2H), 1.32−1.40 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H), 0.57 (dd, J = 5.2, 6.8 Hz, 2H), 0.28 (dd, J = 5.2, 6.8 Hz, 2H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.9, 109.0, 62.2, 29.6, 26.5, 25.0, 22.5, 13.8, 12.1, 10.4, 1.4; MS (EI, 70 eV) m/z (%) = 238 (2), 223 (3), 209 (2), 195 (24), 181 (10), 165 (7), 151 (3), 127 (3), 109 (4), 91 (5), 73 (100); HRMS (ESI) m/e calcd for $C_{14}H_{27}OSi$ $[M + H]^+$ 239.1826, found 239.1823.

General Procedure for the Zn(II)-Catalyzed Rearrangement. A 10 mL oven-dried Schlenk flask was charged with ZnI_2 (6.4 mg, 0.02 mmol, 10 mol %) under argon. Then a solution of silylated [1,1′-bi(cyclopropan)]-2′-en-1-ol substrate (0.2 mmol) in DCE (4 mL) was added, and the mixture was stirred at 70 °C under argon. Upon completion of the reaction, H_2O (18 μL, 5 equiv) was added, and the mixture was stirred at 70 or 110 °C under argon for additional 2 h. The solvent was then removed in vacuum, and the residue was purified with flash column chromatography (petroleum ether/ethyl acetate = 30:1) to afford the corresponding α,β-unsaturated cyclohexenone product.

*2,3-Diphenyl-2-cyclohexenone (**4a**).*[18] When R = TIPS, yield = 95% (47 mg); when R = TES, yield = 85% (42 mg); when R = TMS, yield =79% (39 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10−7.16 (m, 6H), 7.00−7.02 (m, 2H), 6.91−6.93 (m, 2H), 2.84 (t, J = 6.1 Hz, 2H), 2.66 (t, J = 6.1 Hz, 2H), 2.19−2.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 157.8, 140.8, 137.7, 135.5, 130.9, 128.0, 127.8, 127.7, 127.5, 126.7, 38.2, 32.9, 22.6.

*2,3,4-Triphenyl-2-cyclohexenone (**4b**).* A colorless oil (83%, 54 mg); FTIR 2924 (w), 1668 (m), 1592 (w), 1492 (w), 1443 (w), 1346 (w), 1297 (w), 1203 (w), 1162 (w), 1075 (w), 1032 (w), 983 (w), 910 (w), 863 (w), 821 (w), 758 (m), 731 (s), 696 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.35 (m, 4H), 7.14−7.19 (m, 4H), 7.00−7.05 (m, 5H), 6.91−6.94 (m, 2H), 3.27 (dd, J = 3.5, 4.4 Hz, 1H), 2.70−2.78 (m, 1H), 2.60−2.69 (m, 1H), 2.49−2.55 (m, 1H), 2.18−2.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 157.7, 140.1, 139.6, 135.5, 131.0, 128.7, 128.5, 128.4, 127.6, 127.6, 127.6, 126.9, 126.9, 47.2, 33.4, 31.2; MS (EI, 70 eV) m/z (%) = 324 (100), 309 (2), 296 (17), 282 (35), 267 (24), 252 (14), 239 (7), 219 (21), 205 (20), 191 (79), 178 (34), 165 (14), 152 (10), 139 (4); HRMS (ESI) m/e calcd for $C_{24}H_{21}O$ $[M + H]^+$ 325.1587, found 325.1592.

*2,3-Dibutyl-2-cyclohexenone (**4c**).*[19] When R = TIPS, yield = 94% (39 mg); when R = TES, yield = 89% (37 mg); when R = TMS, yield = 64% (27 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30−2.38 (m, 4H), 2.22−2.27 (m, 4H), 1.88−1.94 (m, 2H), 1.25−1.47 (m, 8H), 0.88−0.97 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 158.9, 135.7, 38.2, 34.7, 32.0, 30.7, 30.2, 24.9, 23.0, 22.6, 14.0, 13.9.

*2,3-Dicyclohexyl-2-cyclohexenone (**4d**).* A colorless oil (85%, 44 mg); IR (FTIR) 2925 (s), 2852 (m), 1665 (s), 1450 (m), 1345 (m), 1297 (w), 996 (w), 891 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70−2.73 (m, 1H), 2.57−2.64 (m, 1H), 2.30 (t, J = 6.0 Hz, 2H), 2.25 (t, J = 6.0 Hz, 2H), 1.88−1.92 (m, 2H), 1.78−1.85 (m, 4H), 1.73−1.76 (m, 4H), 1.36−1.39 (m, 6H), 1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 162.9, 138.5, 42.2, 39.2, 37.9, 30.7, 30.4, 27.5, 26.8, 26.3, 26.1, 26.0, 22.5; MS (EI, 70 eV) m/z (%) = 260 (72), 242 (6), 231 (2), 217 (5), 203 (9), 189 (8), 177 (100), 159 (9), 147 (8), 135 (12); HRMS (ESI) m/e calcd for $C_{18}H_{29}O$ $[M + H]^+$ 261.2213, found 261.2217.

*2-Methyl-3-phenyl-2-cyclohexenone (**4e**).*[20] Yield = 61% (23 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, J = 7.2 Hz, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.20 (d, J = 7.2 Hz, 2H), 2.63 (t, J = 5.6 Hz, 2H), 2.53 (t, J = 6.8 Hz, 2H), 2.07−2.13 (m, 2H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 156.5, 141.4, 131.9, 128.4, 127.8, 127.1, 37.8, 33.0, 22.8, 12.8.

*2-Butyl-3-phenyl-2-cyclohexenone (**4f**).*[21] Yield = 82% (37 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.41 (m, 2H), 7.32−7.34 (m, 1H), 7.16−7.18 (m, 2H), 2.60 (t, J = 6.0 Hz, 2H), 2.50 (t, J = 6.0 Hz, 2H), 2.04−2.14 (m, 4H), 1.22−1.28 (m, 2H), 1.11−1.19 (m, 2H), 0.74 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 156.8, 141.6, 136.7, 128.3, 127.6, 126.7, 38.2, 33.5, 31.8, 26.3, 22.8, 22.7, 13.7.

*2-Benzyl-3-phenyl-2-cyclohexenone (**4g**).*[22] Yield = 91% (48 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.36 (m, 3H), 7.09−7.18 (m, 5H), 6.95−6.97 (m, 2H), 3.57 (s, 2H), 2.68 (t, J = 6.0 Hz, 2H), 2.54 (t, J = 6.0 Hz, 2H), 2.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 158.4, 141.1, 140.9, 135.1, 128.4, 128.2, 128.0, 127.9, 126.7, 125.5, 38.0, 33.5, 31.9, 22.7.

*2-Butyl-3-methyl-2-cyclohexenone (**4ha**).*[21] When R = TIPS, yield (**4ha** + **4hb**) = 92% (31 mg); when R = TES, yield (**4ha** + **4hb**) = 86% (29 mg); when R = TMS, yield (**4ha** + 4hb) = 60% (20 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25−2.38 (m, 6H), 1.90−1.93 (m, 5H), 1.24−1.32 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 154.9, 135.9, 37.9, 32.8, 31.3, 24.9, 22.9, 22.3, 21.1, 14.0.

*3-Butyl-2-methyl-2-cyclohexenone (**4hb**).*[23] When R = TIPS, yield (**4ha** + **4hb**) = 92% (31 mg); when R = TES, yield (**4ha** + **4hb**) = 86% (29 mg); when R = TMS, yield (**4ha** + **4hb**) = 60% (20 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32−2.40 (m, 4H), 2.24 (m, 2H), 1.91−1.93 (m, 2H), 1.77 (s, 3H), 1.33−1.47 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 159.3, 130.8, 37.8, 35.1, 30.9, 29.6, 22.9, 22.6, 13.9, 10.6.

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General Procedure for the Rh(I)-Catalyzed Rearrangement. A 10 mL oven-dried Schlenk flask was charged with Rh(I) catalyst (0.01 mmol, 5 mol %) under argon. Then a solution of silylated [1,1′-bi(cyclopropan)]-2′-en-1-ol substrate (0.2 mmol) in DCE (4 mL) was added, and the mixture was stirred at 70 or 110 °C under argon. After the reaction finished, the solvent was removed in vacuum, and the residue was purified with flash column chromatography (petroleum ether or 30:1 petroleum ether/ethyl acetate) to obtain the final product.

*(3,4-Diphenyl-cyclohexa-1,3-dienol)triisopropylsilane (**5a**).* A colorless oil (95%, 77 mg); FTIR (film) 2944 (m), 2867 (m), 1639 (m), 1599 (w), 1580 (w), 1463 (w), 1444 (w), 1373 (m), 1272 (w), 1222 (w), 1196 (m), 1158 (w), 1015 (w), 970 (w), 883 (s), 761 (s), 699 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.07−7.15 (m, 5H), 6.98−7.04 (m, 5H), 5.40 (s, 1H), 2.81 (t, J = 9.3 Hz, 2H), 2.46 (t, J = 9.3 Hz, 2H), 1.12 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 142.7, 142.2, 133.6, 129.3, 128.9, 127.8, 127.6, 126.1, 125.5, 125.4, 107.3, 31.9, 29.5, 17.9, 12.7; MS (EI, 70 eV) m/z (%) = 404 (100), 359 (8), 331 (9), 303 (15), 287 (21), 271 (2), 247 (4), 228 (10), 215 (17), 202 (12), 189 (8), 178 (5), 165 (5), 152 (7), 141 (5), 129 (4); HRMS (ESI) m/e calcd for $C_{27}H_{37}OSi$ $[M + H]^+$ 405.2608, found 405.2618.

*3,4-Diphenyl-2-cyclohexenone (**6a**).*[24] Yield = 81% (40 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44−7.46 (m, 2H), 7.23−7.30 (m, 8H), 6.70 (s, 1H), 4.31 (m, 1H), 2.52−2.61 (m, 1H), 2.36−2.39 (m, 2H), 2.17−2.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 159.4, 140.2, 137.9, 129.8, 128.8, 128.7, 128.0, 127.0, 126.8, 43.2, 32.8, 32.0.

*3,4-Diphenyl-3-cyclohexenone (**7a**).* A colorless oil (76%, 38 mg); FTIR (film) 2955 (m), 2924 (s), 2853 (m), 1717 (m), 1671 (w), 1493 (w), 1461 (m), 1377 (m), 1261 (w), 1193 (w), 1068 (w), 1031 (w), 910 (w), 840 (w), 800 (w), 761 (m), 699 (s), 671 (m), 658 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.12−7.15 (m, 6H), 6.98−7.02 (m, 4H), 3.34 (s, 2H), 2.94 (t, J = 6.8 Hz, 2H), 2.71 (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 141.7, 141.0, 135.5, 131.9, 128.8, 128.8, 128.0, 127.9, 126.6, 126.5, 45.7, 38.6, 31.9; MS (EI, 70 eV) m/z (%) = 248 (100), 205 (72), 191 (33), 178 (12), 165 (12), 128 (19), 115 (17), 103 (10), 91 (38); HRMS (ESI) m/e calcd for $C_{18}H_{17}O$ $[M + H]^+$ 249.1274, found 249.1277.

*(3,4-Diphenylphenoxy)triisopropylsilane (**8a**).* A colorless oil (92%, 74 mg); FTIR (film) 2944 (m), 2867 (m), 1601 (m), 1476 (s), 1446 (w), 1428 (w), 1401 (w), 1383 (w), 1307 (m), 1255 (w), 1213 (m), 1174 (m), 1127 (m), 941 (m), 883 (m), 796 (m), 765 (m), 700 (s), 679 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.08−7.21 (m, 10H), 6.91−6.95 (m, 2H), 1.13−1.15 (m, 21H); ^{13}C NMR (100 MHz,$CDCl_3$) δ 155.4, 141.6, 141.5, 141.4, 133.4, 131.6, 129.9, 129.8, 127.8, 127.7, 126.4, 125.9, 121.8, 118.7, 17.9, 12.7; MS (EI, 70 eV) m/z (%) = 402 (91), 359 (88), 331 (55), 317 (17), 303 (73), 287 (100), 273 (11), 257 (7), 242 (6), 228 (30), 217 (15), 207 (20), 189 (9), 176 (7), 165 (9); HRMS (ESI) m/e calcd for $C_{27}H_{35}OSi$ $[M + H]^+$ 403.2452, found 403.2458.

*(3,4-Diphenyl-cyclohexa-1,3-dienol)triethylsilane (**5aa**).* A colorless oil (89%, 64 mg); FTIR (film) 2955 (m), 2876 (m), 1640 (m), 1599 (w), 1580 (w), 1374 (m), 1271 (w), 1255 (w), 1195 (m), 1158 (w), 1006 (w), 963 (w), 881 (w), 811 (w), 762 (m), 747 (m), 698 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.97−7.15 (m, 10H), 5.39 (s, 1H), 2.80 (t, J = 9.4 Hz, 2H), 2.43 (t, J = 9.4 Hz, 2H), 1.02 (t, J = 7.9 Hz, 9H), 0.75 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz,$CDCl_3$) δ 154.4, 142.6, 142.1, 133.5, 129.3, 128.9, 127.8, 127.6, 126.1, 125.8, 125.5, 107.4, 31.9, 29.4, 6.7, 5.0; MS (EI, 70 eV) m/z (%) = 362 (100), 347 (1), 333 (5), 319 (1), 301 (6), 285 (4), 271 (11), 255 (2), 243 (3), 229 (4), 215 (5), 202 (4), 189 (2), 178 (1), 167 (2), 152 (3); HRMS (ESI) m/e calcd for $C_{24}H_{31}OSi$ $[M + H]^+$ 363.2139, found 363.2145.

*(2,3,4-Triphenyl-cyclohexa-1,3-dienol)trimethylsilane (**5b**).* A colorless oil (95%, 75 mg); FTIR (film) 2956 (w), 1632 (w), 1599 (w), 1578 (w), 1492 (w), 1443 (w), 1366 (w), 1338 (w), 1252 (m), 1205 (m), 1141 (w), 1076 (w), 1031 (w), 976 (w), 902 (m), 844 (s), 802 (w), 758 (s), 697 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.09−7.13 (m, 2H), 7.03−7.06 (m, 3H), 6.96−7.00 (m, 5H), 6.88−6.90 (m, 3H), 6.75−6.77 (m, 2H), 2.90 (t, J = 8.8 Hz, 2H), 2.57 (t, J = 8.8 Hz, 2H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 143.2, 140.1, 137.8, 136.6, 131.1, 131.0, 129.8, 128.6, 127.4, 126.9, 126.8, 125.3, 125.3, 125.1, 120.9, 31.5, 29.9, 0.4; MS (EI, 70 eV) m/z (%) = 396 (100), 381 (3), 363 (3), 319 (8), 305 (24), 289 (4), 276 (3), 265 (3), 252 (3), 229 (3), 215 (6), 202 (4), 179 (3), 165 (3), 115 (3); HRMS (EI) m/e calcd for $C_{27}H_{28}OSi$ (M) 396.1909, found 396.1914.

*2,3,4-Triphenylphenol (**8b′**).*[25] Yield = 77% (50 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.38 (m, 1H), 7.28−7.29 (m, 1H), 7.21−7.23 (m, 1H), 7.04−7.12 (m, 9H), 6.92−6.93 (m, 3H), 6.78−6.80 (m, 2H), 5.00 (s, 1H); ^{13}C NMR (100 MHz,$CDCl_3$) δ 152.2, 141.7, 140.5, 139.4, 135.1, 134.1, 131.2, 130.9, 130.9, 130.0, 128.8, 127.8, 127.6, 127.5, 127.0, 125.8, 125.8, 114.4.

*(3,4-Dibutylphenoxy)triisopropylsilane (**8c**).* A colorless oil (79%, 57 mg); IR (FTIR) 2956 (s), 2929 (s), 2866 (s), 1606 (m), 1574 (w), 1495 (m), 1464 (m), 1380 (w), 1284 (m), 1261 (m), 1189 (w), 1161 (w), 1121 (w), 1070 (w), 988 (m), 920 (w), 890 (s), 845 (m), 683 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, J = 8.2 Hz, 1H), 6.66 (d, J = 2.6 Hz, 1H), 6.62 (dd, J = 2.6, 8.2 Hz, 1H), 1.49−1.54 (m, 4H), 1.34−1.41 (m, 4H), 1.19−1.28 (m, 4H), 1.08−1.10 (m, 21H), 0.91−0.96 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 141.5, 132.9, 129.7, 120.4, 116.9, 33.6, 33.3, 32.4, 31.7, 22.7, 22.7, 17.9, 14.0, 14.0, 12.7; MS (EI, 70 eV) m/z (%) = 362 (42), 346 (2), 331 (3), 319 (100), 291 (32), 277 (11), 263 (42), 249 (21), 233 (7), 219 (10), 207 (14), 191 (9), 177 (8), 163 (10); HRMS (ESI) m/e calcd for $C_{23}H_{43}OSi$ $[M + H]^+$ 363.3078, found 363.3083.

*(3,4-Dicyclohexylphenoxy)triisopropylsilane (**8d**).* A colorless oil (68%, 56 mg); FTIR 2924 (s), 2865 (m), 2851 (m), 1495 (m), 1463 (w), 1448 (w), 1274 (m), 1255 (m), 947 (w), 913 (m), 883 (m), 813 (w), 709 (w), 684 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, J = 2.1 Hz, 1H), 6.83 (dd, J = 2.1, 8.2 Hz, 1H), 6.67 (d, J = 8.2 Hz, 1H), 2.96−3.02 (m, 1H), 2.37−2.43 (m, 1H), 1.71−1.84 (m, 10H), 1.26−1.38 (m, 13H), 1.10−1.12 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 140.1, 137.1, 125.1, 123.8, 117.4, 43.9, 37.1, 34.7, 33.3, 27.2, 27.0, 26.5, 26.2, 18.2, 13.1; MS (EI, 70 eV) m/z (%) = 414 (60), 371 (100), 343 (4), 327 (5), 304 (5), 289 (20), 259 (7), 231 (8), 207 (7), 191 (6), 175 (9), 151 (10), 115 (10); HRMS (ESI) m/e calcd for $C_{27}H_{47}OSi$ $[M + H]^+$ 415.3391, found 415.3389.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H and ^{13}C spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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