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Rhodium-Catalyzed Carbonylation of Cyclopropyl Substituted Propargyl Esters: A Tandem 1,3-Acyloxy Migration [5 + 1] Cycloaddition

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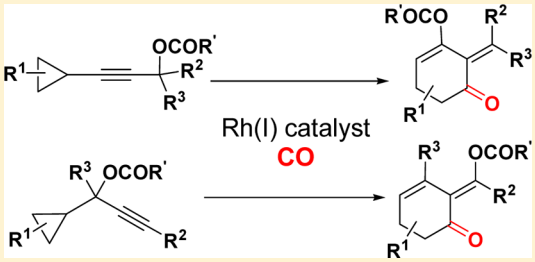
Supporting Information

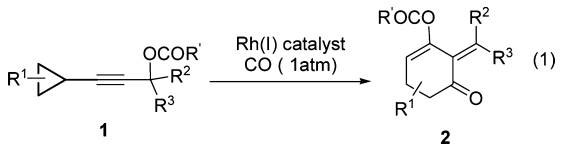
ABSTRACT: We have developed two different types of tandem reactions for the synthesis of highly functionalized cyclohexenones from cyclopropyl substituted propargyl esters. Both reactions were initiated by rhodium-catalyzed Saucy–Marbet 1,3-acyloxy migration. The resulting cyclopropyl substituted allenes derived from acyloxy migration then underwent [5 + 1] cycloaddition with CO. The acyloxy group not only eased the access to allene intermediates but also provided a handle for further selective functionalizations.



1. INTRODUCTION

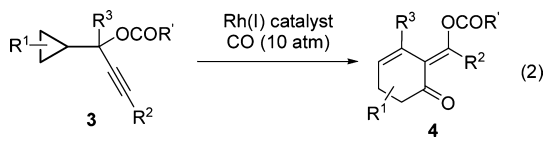
Transition metal-catalyzed cycloaddition reaction is one of the most efficient ways to access ring systems.[1] Diels–Alder cycloaddition represents the most powerful method for the synthesis of cyclohexenes and has proven to be extremely valuable in the preparation of natural products and pharmaceutical agents.[2] However, efficient syntheses of cyclohexenes with diverse substitutions, stereochemistry, and functionalities are still challenging and continue to stimulate the development of novel cycloaddition reactions.

We previously discovered a tandem 1,3-acyloxy migration [5 + 1] cycloaddition reaction for the synthesis of alkylidene cyclohexenone **2** from cyclopropyl substituted propargyl ester **1** (eq 1).[3] In this account, we presented the details for the



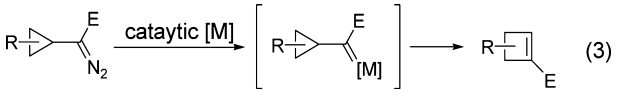
1 2 (1)

development of this tandem reaction. We also disclosed our study on a related 1,3-acyloxy migration [5 + 1] cycloaddition cascade reaction for the synthesis of alkylidene cyclohexenone **4** from cyclopropyl substituted propargyl ester **3** for the first time (eq 2).[4] These two new tandem reactions provided easy access to functionalized six- membered rings from readily available starting materials.



3 4 (2)

In 2008, we reported a synthesis of cyclobutenes from cyclopropyl metal carbenes derived from transition metal-catalyzed decomposition of diazo compounds (eq 3).[5,6] During



(3)

our search for more stable alternative cyclopropyl carbene precursors, we were attracted by the method of metal carbene formation from propargyl esters via a transition metal-catalyzed 1,2-acyloxy migration. This convenient and atom-economical[7] process was first described by Rautenstrauch in 1984[8] and has been applied in numerous cascade reactions.[9,10] We originally proposed that if cyclopropyl substituted propargyl ester **1** could undergo a Rautenstrauch 1,2-acyloxy migration via intermediate **5**, we might be able to access cyclopropyl metal carbene **6** from compound **1** (Scheme 1).

An obvious competing pathway is the 1,3-acyloxy migration of compound **1** to form allene **8** (Scheme 1).[11] The 1,3-acyloxy migration of propargyl esters was initially discovered by Saucy and Marbet in 1959 using a silver catalyst.[12] Other transition metal complexes including copper, platinum, and gold have also been found to promote the Saucy–Marbet rearrangement.[13,14] The regioselectivity for 1,2- or 1,3-acyloxy migration of propargyl ester was often dependent on the substrates and catalysts.[14]

Cyclopropyl substituted propargyl ester **1** has been employed in gold-catalyzed reactions. When R^1 was an alkyl group, 2-alkylidene 1,3-diketone **9** was formed and the cyclopropane ring was left untouched (Scheme 2).[15] When R^1 was a vinyl or phenyl group, cyclopentene **10** was obtained.[16] In the presence

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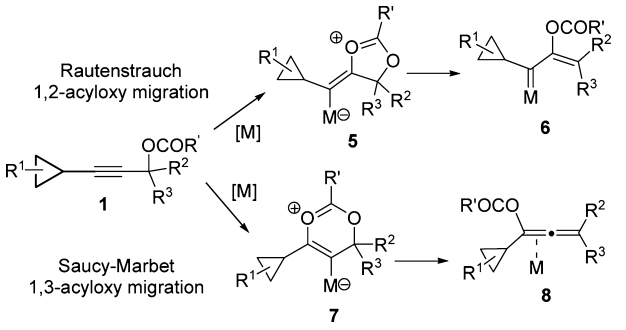
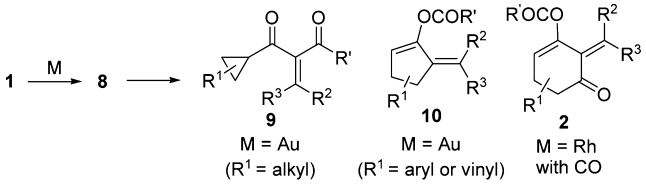
Scheme 1. Rautenstrauch 1,2-Acyloxy Migration and Saucy–Marbet 1,3-Acyloxy Migration of Cyclopropyl Propargyl Esters



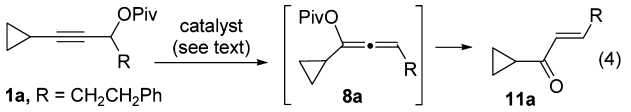
Scheme 2. Diverse Products Derived from Transition Metal-Catalyzed Saucy–Marbet 1,3-Acyloxy Migration of Cyclopropyl Substituted Propargyl Esters



of Rh(I) catalyst and CO, we isolated alkylidene cyclohexenone **2**.[3] All three products **9**, **10**, and **2** were proposed to be derived from allene intermediate **8** via a transition metal-catalyzed Saucy–Marbet 1,3-acyloxy migration.

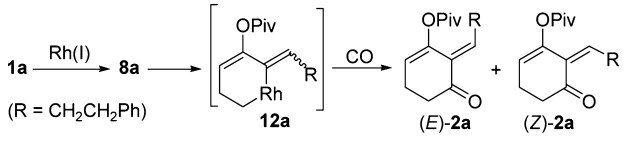
2. RESULTS AND DISCUSSION

We first prepared propargyl ester **1a** and treated it with $AuCl_3$, $(Ph_3P)AuCl$, $(Ph_3P)AuCl/AgSbF_6$, $PtCl_2$, $PtCl_4$, $AgSbF_6$, $Cu(MeCN)_4PF_6$, $PdCl_2(MeCN)_2$, $[CpRu(MeCN)_3]PF_6$, and $Rh_2(OAc)_4$ catalysts. We observed either no reaction or the formation of enone **11a**, presumably derived from hydrolysis of the corresponding allenyl ester intermediate **8a** (eq 4).



We then decided to examine transition metals that were not commonly used as catalysts for acyloxy migration of propargyl esters. We found that alkylidene cyclohexenone **2a** (Scheme 3) was formed as a mixture of *E*/*Z* isomers (ratio = 1:1) in about 30% yield when 20 mol % of $[Rh(CO)_2Cl]_2$ was employed as the catalyst in toluene at rt. Product **2a** was presumably generated by a Rh(I)-catalyzed [5 + 1] cycloaddition of allenyl ester **8a** with CO via metallacycle **12a**. While [5 + 1] cycloaddition of allenylcyclopropanes or vinylcyclopropanes with CO have been investigated by several groups, the reaction generally required stoichiometric amount of metals, and the scope was often limited.[17] A relatively general Rh-catalyzed [5 + 1] cycloaddition of vinylcyclopropanes with CO was recently reported by Yu's group.[18] Intercepting the allenyl ester intermediate derived from 1,3-acyloxy migration of propargyl ester has been realized in Ag(I), Cu(I), Pt(II), and Au(I)-catalyzed cascade reactions.[13,14] However, no cyclocarbonylation of the above allene intermediate has been reported prior to our study.[3] The combination of the novel reactivity of $[Rh(CO)_2Cl]_2$ catalyst for facilitating Saucy–Marbet 1,3-acyloxy migration and its known reactivity for catalyzing carbonylation reaction made the cascade transformation in Scheme 3 possible.[19]

Scheme 3. Proposed Mechanism for the Formation of Alkylidene Cyclohexenone 2a from Cyclopropyl Substituted Propargyl Ester 1a



The reaction condition for the synthesis of alkylidene cyclohexenone **2a** was then optimized. Simply attaching a CO balloon to the reaction flask, compound **2a** was isolated in 93% yield with an *E*/*Z* ratio of 1:1.3 at 60 °C after 5 h (Table 1). We could run the reaction at rt without decreasing the yield of **2a** when the CO pressure was lowered to 0.1–0.2 atm by diluting the balloon with nitrogen.[20] We also separated the two geometric isomers of **2a** and resubmitted each of them back to the reaction. We did not observe any change of the configuration. This suggested that the *E*/*Z* isomers did not equilibrate under the reaction conditions. When a cationic rhodium complex (e.g., $[Rh(CO)_2Cl]_2/AgOTf$ or $[Rh(COD)_2]BF_4$) was employed as the catalyst, significant amount of enone **11a** (eq 4) was observed. Addition of ligands (e.g., PPh_3, $P(OMe)_3$, $P(OPh)_3$, and pyridine) either decreased the conversion of the $[Rh(CO)_2Cl]_2$ catalyzed reaction or completely shut it down. Slightly different *E*/*Z* ratios for product **2a** were observed in other solvents, such as THF (1:1), EtOAc (1:1), or DCE (2:1). No reaction occurred in MeCN or DMF.

The scope of this tandem 1,3-acyloxy migration [5 + 1] cycloaddition was first examined with substrates **1b–1i** (Table 1), all derived from cyclopropyl acetylene. Although the reaction worked at rt with reduced CO pressure, conducting it under 1 atm of CO at 60 °C is more convenient and provided us consistent results. No reaction occurred for secondary propargyl acetate **1b**. For substrates with a tertiary ester, the tandem reaction worked well when the propargyl ester was changed from pivalate to acetate (e.g., **1h**). High *E*/*Z* selectivity could be obtained for propargyl esters with sterically demanding substituents (e.g., **1f** and **1i**). A single product was obtained for substrate **1g**. Highly functionalized product **2i** could also be prepared from substrate **1i**, which was derived from a steroid derivative. The structure and the configuration of the exocyclic olefin of product **2f** were further confirmed by X-ray analysis.[21]

The cleavage of different cyclopropane C–C σ-bonds may lead to regioisomers for unsymmetrically substituted cyclopropanes. On the basis of studies from our lab[5] and others,[22,23] the regioselectivity for the cleavage of C–C σ-bonds in cyclopropanes was dependent on the stereochemistry of the cyclopropane ring, the electronic and steric properties of the substituents, and the metal catalysts.

We prepared a series of *trans*-substituted cyclopropanes to examine the regioselectivity of the C–C σ-bond cleavage (Table 2). We found opposite regioselectivity for *trans*-**1j** and *trans*-**1k**, which had a phenyl and an alkyl substituent on the cyclopropane ring, respectively. When the free alcohol in **1k**

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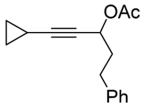
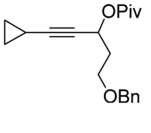
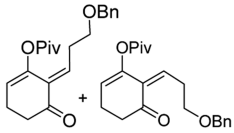
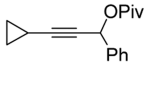
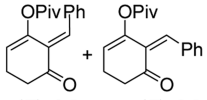
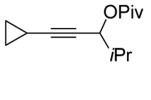
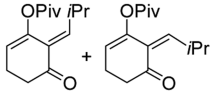
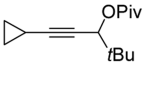
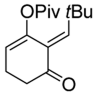
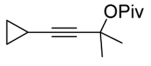
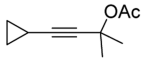
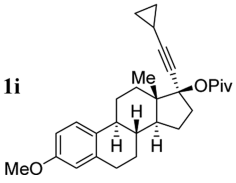
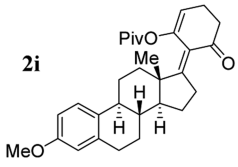
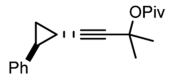
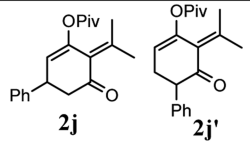
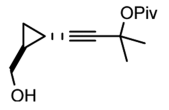
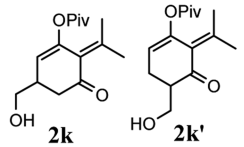
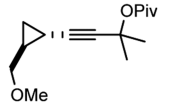
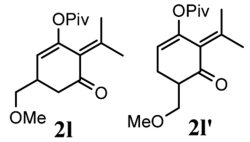
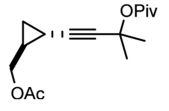
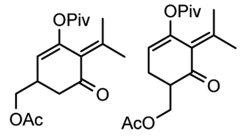
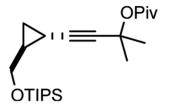
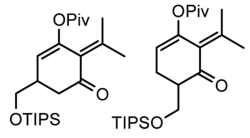
Table 1. Scope of Substrates with Nonsubstituted Cyclopropanes[a]

substrates	products	yield[b] (*E*/*Z*)
1a	(*E*)-**2a** + (*Z*)-**2a**	93% (1:1.3)
1b 	–	0%
1c 	 (*E*)-**2c** (*Z*)-**2c**	81% (1:1.3)
1d 	 (*E*)-**2d** (*Z*)-**2d**	95% (2:1)
1e 	 (*E*)-**2e** (*Z*)-**2e**	87% (1:1)
1f 	**2f** 	92% (10:1)
1g 	**2g** 	88%[c]
1h 	**2h** 	85%
1i 	**2i** 	91% (13:1)

[a]Conditions: 5 mol % $[Rh(CO)_2Cl]_2$, CO (1 atm), toluene, 60 °C, 5 h. [b]Isolated yields of both isomers. [c]2.5 mol % catalyst, 60 °C, 1 h.

Table 2. Regioselectivity for the Cleavage of C−C σ-Bond in *trans*-Disubstituted Cyclopropanes[a]

substrates	products	yield[c]
trans-**1j** 	 **2j** **2j'** (**2j** : **2j'** = 1 : 2.5)[b]	90%[d]
trans-**1k** 	 **2k** **2k'** (**2k** : **2k'** = 3.5 : 1)[b]	64%
trans-**1l** 	 **2l** **2l'** (**2l** : **2l'** = 6 : 1)[b]	68%
trans-**1m** 	 **2m** **2m'** (**2m** : **2m'** = 6 : 1)[b]	78%
trans-**1n** 	 **2n** **2n'** (**2n** : **2n'** = 10 : 1)[b]	91%

[a]Conditions: see Table 1, footnote a, unless noted otherwise. [b]Regioisomeric ratios were determined by ^1H NMR of the crude products. [c]Yields are isolated yields of the major isomer unless noted otherwise. [d]Yields are combined yields of **2j** and **2j'**.

was functionalized to methyl ether **1l**, acetate **1m**, or silyl ether **1n**, the regioselectivity was increased.

We also found opposite regioselectivity for cyclopropanes *trans*-**1j** and *cis*-**1j**, both of which had a phenyl substituent on the cyclopropane ring (Tables 2 and 3). High regioselectivity was observed for alkyl substituted *cis*-**1k** and *cis*-**1n**. The 1,3-acyloxy migration [5 + 1] cycloaddition cascade reaction worked for substrate *cis*-**1n** even at rt with 1 atm of CO. We obtained essentially one regioisomeric product at rt from this substrate, while a 16:1 ratio was observed at 60 °C. The same trend of regioselectivity was found for other substituted cyclopropanes (e.g., **1o**−**1s**). Cyclopropanes with a quaternary carbon, such as compounds **1p** and **1q**, yielded only one isomer. A 16:1 regioisomeric ratio was observed for 1,2,3-trisubstituted cyclopropane **1r**. The *trans*-aryl group and *cis*-$PMBOCH_2$ group in cyclopropane **1r** should direct the cleavage of the same C−C σ-bond preferentially on the basis of regioselectivity observed for substrates *trans*-**1j** and *cis*-**1n**. The chirality in substrate **1q** was completely transferred to the corresponding cyclohexenone product. This paved the way for enantioselective synthesis of highly substituted cyclohexenones from optical pure cyclopropanes. In contrast, the chirality on the cyclopropane ring was not completely transferred in gold-catalyzed ring-opening reactions.[16,24]

An *E*/*Z* ratio of 10:1 was observed for product **2s** when a mixture of cyclopropane **1s** (dr = 1:1) was employed. We have shown that the two *E*/*Z* isomers of alkylidene cyclohexenone product **2a** do not equilibrate under the reaction conditions. As shown in Scheme 4, if the Rh-catalyzed 1,3-acyloxy migration of the propargyl ester was stereospecific and the configuration of the resulting allenes (**8s-1** and **8s-2**) was stable under the condition, one would predict a 1:1 *E*/*Z* ratio for product **2s**. Our result indicated that either the Rh-catalyzed 1,3-acyloxy migration was not stereospecific or the two diastereomeric allenes could interconvert to each other. We propose that allenes **8s-1** and **8s-2** may interconvert to each other through ionic intermediate **8s-3** as shown in Scheme 4. Coordination of rhodium to isomer **8s-1** is favored because of steric interaction between *tert*-butyl group and the metal catalyst in isomer **8s-2**.

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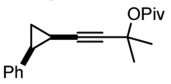
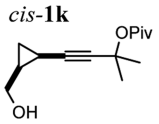
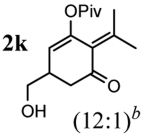
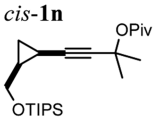
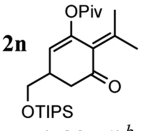
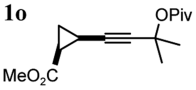
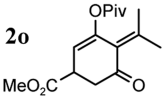
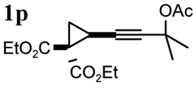
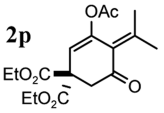
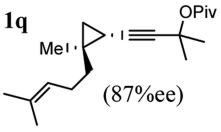
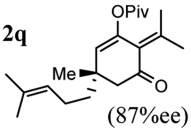
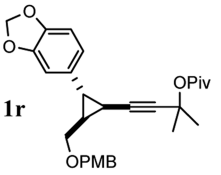
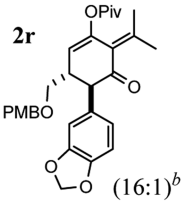
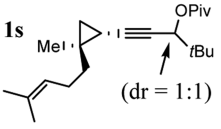
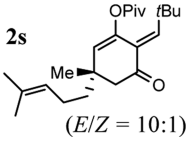
Table 3. Regioselectivity for the Cleavage of C−C σ-Bond in *cis*-Disubstituted and Trisubstituted Cyclopropanes[a]

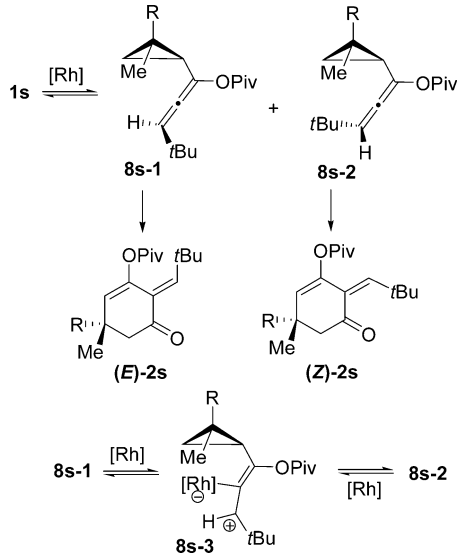
substrates	products	yield[c]
cis-**1j** 	(**2j** : **2j'** = 3.5 : 1)[b]	95%[d]
cis-**1k** 	**2k**  (12:1)[b]	79%
cis-**1n** 	**2n**  (>20 : 1)[b]	93%[e]
1o 	**2o** 	76%
1p 	**2p** 	74%
1q  (87%ee)	**2q**  (87%ee)	86%
1r 	**2r**  (16:1)[b]	80%
1s  (dr = 1:1)	**2s**  (*E*/*Z* = 10:1)	74%[f]

[a]Conditions: see Table 1, footnote a, unless noted otherwise. [b]Regioisomeric ratios were determined by ^{1}H NMR of the crude products. [c]Yields are isolated yields of the major isomer unless noted otherwise. [d]Yields are combined yields of **2j** and **2j'**. [e]The reaction was run at rt. [f]80 °C, 24 h.

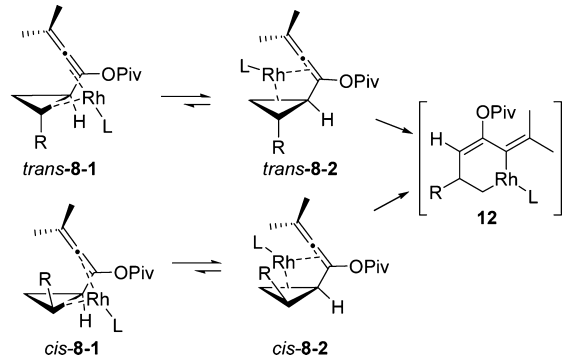
This may explain why (*E*)-**2s** is the major product. The proposed isomerization between **8s-1** and **8s-2** is consistent with results from gold-catalyzed 1,3-acyloxy migrations of chiral propargyl esters.[16] In fact, a dynamic kinetic transformation of racemic propargyl ester was recently realized using a chiral-gold complex as the catalyst.[25]

For all *trans*-substituted cyclopropanes except *trans*-**1j** in Table 2, the less hindered C−C σ-bond was selectively cleaved, presumably because of the steric interaction between the substituent R and the rhodium complex in intermediate *trans*-**8-1** (Scheme 5). Higher regioselectivity was observed for more sterically demanding substituent (e.g., *trans*-**1k** to *trans*-**1n**). The less hindered C−C σ-bond was also selectively cleaved for

Scheme 4. Proposed Mechanism for the Conversion of 1s to 2s



Scheme 5. Proposed Mechanism for Regioselective Cleavage of C−C σ-Bond of Substituted Cyclopropanes



all *cis*-disubstituted cyclopropanes in Table 3 for the same reason. Substrates with a substituent *cis* to the propargyl ester group generally had higher regioselectivity than the corresponding *trans*-substituent (e.g., *trans*-**1k** vs *cis*-**1k** and *trans*-**1n** vs *cis*-**1n**). This can be rationalized by the more significant steric interactions between the R group and rhodium complex in intermediate *cis*-**8-1** than that in *trans*-**8-1** (Scheme 5). For substrate *trans*-**1j**, the C−C σ-bond that was adjacent to aryl group was selectively cleaved, presumably because of the electronic effect of the adjacent π-system.[5,22,23] The overall low regioselectivity observed for *trans*- and *cis*-phenyl substituted cyclopropanes **1j** may be due to competing steric and electronic effects.

For bicyclic substrates **1t** and **1u**, the desired decalin derivatives **2t** and **2u** were isolated in 80 and 82% yields, respectively, with high regioselectivity (Scheme 6). In these two cases, the five-membered isomerization products **13** and **14** were also isolated in 19 and 11% yields, respectively, under the standard condition.[22] The 5−6 fused bicyclic compounds **13** and **14** could be isolated in good yields by running the reaction in the absence of external CO with a lower catalyst loading. For cyclopropane **1u**, the C−C σ-bond that was adjacent to alkene was selectively cleaved for the formation of both products **2u** and **14**. This was presumably because of the electronic effect of the adjacent π-system. It is interesting to note that no five-

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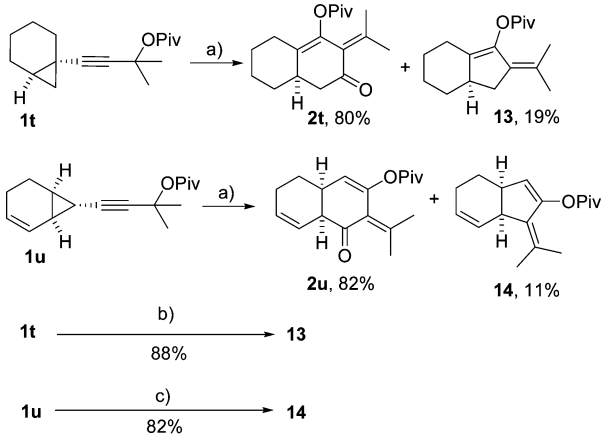
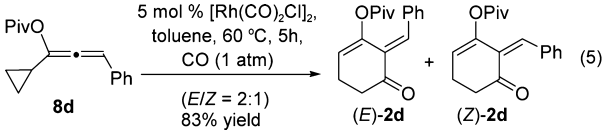
Scheme 6. Rh-Catalyzed Ring Expansion of Cyclopropanes in Bicyclic Systems



Conditions: a) 5 mol % $[Rh(CO)_2Cl]_2$, toluene, 60 °C, 5h, CO (1 atm);
b) 2 mol % $[Rh(CO)_2Cl]_2$, toluene, 60 °C, 4h;
c) 2 mol % $[Rh(CO)_2Cl]_2$, toluene, 60 °C, 5h.

membered isomerization product was observed in the monocyclic system even in the absence of a CO balloon.

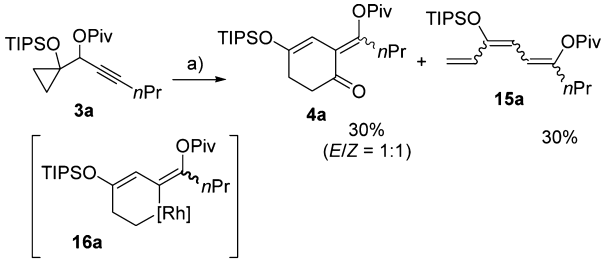
We also prepared allene **8d** from propargyl ester **1d** using a silver catalyst.[12] Under standard conditions, product **2d** was obtained in 83% yield (eq 5). The *E*/*Z* ratio of alkylidene



cyclohexenone **2d** was the same as products directly derived from **1d** using a Rh(I) catalyst (Table 1). This result further confirmed the mechanism we proposed in Scheme 3.

After the development of Rh-catalyzed 1,3-acyloxy migration [5 + 1] cycloaddition of cyclopropyl substituted propargyl esters **1** with CO to form product **2**, we envisioned the acyloxy group could also be placed between the cyclopropane and the alkyne (e.g., substrate **3a**, Scheme 7). Under previously

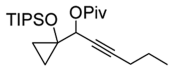
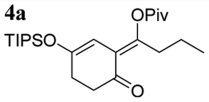
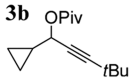
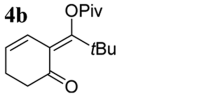
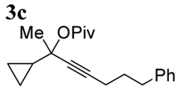
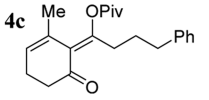
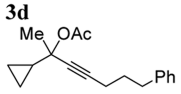
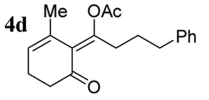
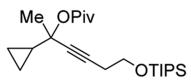
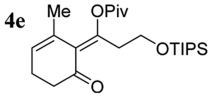
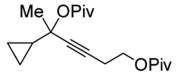
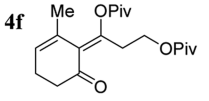
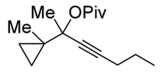
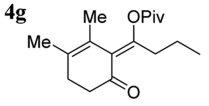
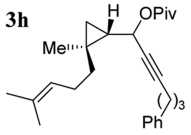
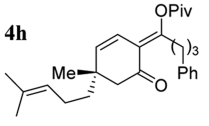
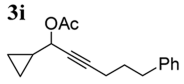
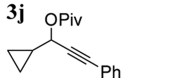
Scheme 7. Rh-Catalyzed 1,3-Acyloxy Migration [5 + 1] Cycloaddition for Substrates 3a



a) $[Rh(CO)_2Cl]_2$ (5 mol%), Toluene, CO(1 atm), 60 °C, 2h.

optimized condition for substrate **1**, we found that the reaction afforded 30% yield of the desired product **4a** and 30% yield of a mixture of inseparable trienes **15a** based on ^{1}H NMR. All of these products are presumably derived from metallacycle **16a**. For substrate **3b** (Table 4) without the siloxy substituent, we also obtained a mixture of [5 + 1] cycloaddition product and triene byproducts under the same condition.

Table 4. Scope of Rh-Catalyzed 1,3-Acyloxy Migration [5 + 1] Cycloaddition for Substrates 3a−3h[a]

substrates	products	yield (*E*/*Z*)
3a 	**4a** 	70%[b] (1:1)
3b 	**4b** 	72%[c] (2:1)[d]
3c 	**4c** 	86%[e] (1.8:1)
3d 	**4d** 	84%[e] (1:2)
3e 	**4e** 	91%[e] (2:1)
3f 	**4f** 	84%[e] (3.3:1)
3g 	**4g** 	52%[e,f] (2:1)
3h 	**4h** 	62%[e,g] (2:1)[d,h]
3i 	–	no reaction
3j 	–	complex mixture

[a]Conditions: 5 mol % $[Rh(CO)_2Cl]_2$, CO (10 atm), toluene (0.05M), overnight. All *E*/*Z* ratios were determined by ^{1}H NMR of the crude product unless noted otherwise. [b]70 °C. [c]100 °C. [d]The stereochemistry of the exocyclic olefin could not be determined by ^{1}H NMR. [e]50 °C. [f]Isolated yield of *E*-isomer. [g]1 atm CO. [h]The ratio was determined by ^{13}C NMR.

In order to suppress the formation triene byproducts, we decided to increase the amount of [5 + 1] cycloaddition product by changing the pressure of CO from 1 to 10 atm. We found that the desired cycloaddition product **4a** could be isolated in 70% yield and the triene byproduct was not formed under this condition (Table 4). The scope of this Rh-catalyzed 1,3-acyloxy migration [5 + 1] cycloaddition for the formation of product **4** from propargyl ester **3** was then investigated. For substrate **3b** with a sterically demanding *tert*-butyl group, the reaction required higher temperature. For substrates with a tertiary ester (**3c**, **3d**, **3e**, **3f**, and **3g**), lowering the temperature to 50 °C was necessary to achieve a higher yield. We also demonstrated that substituents on the cyclopropane ring could be tolerated (e.g., **3a**, **3g**, and **3h**). The tandem reaction worked well when the propargyl ester was changed from pivalate to acetate (e.g., **3d**). Functional groups such as siloxy group and

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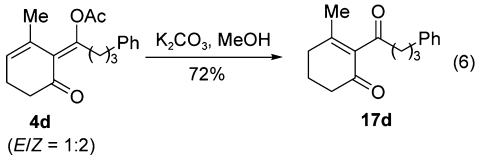
ester were tolerated (e.g., **3e** and **3f**). In the case of product **4g**, the *Z* isomer decomposed during workup and we only isolated the *E* isomer. The two diastereomers of substrate **3h** could be separated by chromatography. Each of them worked smoothly in the presence of 1 atm of CO and yielded identical result. The relative stereochemistry of the secondary ester in substrate **3h** was therefore not determined. Only one regioisomeric product (**4h**) was obtained for either diastereomer of substrate **3h**. No reaction occurred for secondary acetate **3i**, which was consistent with previous observation for substrate **1b**. A complex mixture was obtained for substrate **3j** with a phenyl substituent.

Although the *E*/*Z* stereoselectivity for the exocyclic alkene in products **4a**−**4h** is not high, it is inconsequential after hydrolysis. Diketone **17d** could be obtained in good yield from the corresponding acetate **4d** (eq 6).



4d (*E*/*Z* = 1:2) **17d** (6)

3. CONCLUSION

In summary, we have developed an efficient method for the synthesis of various highly functionalized monocyclic cyclohexenones from readily available cyclopropyl substituted propargyl esters. Several examples of bicyclic compounds were also prepared. The combination of the novel reactivity of Rh(I) catalyst for promoting 1,3-acyloxy migration of propargyl esters and its ability to facilitate carbonylation reaction made the tandem transformation possible. Regioselective cleavage of C−C σ-bonds could be achieved for various *cis*-disubstituted and trisubstituted cyclopropanes. The acyloxy group in the propargyl ester starting material not only eliminated the need for the preformation of allenes but also provided a useful handle for further selective functionalizations of the cyclohexenone products.

4. EXPERIMENTAL SECTION

All reactions were conducted under a positive pressure of dry argon in glassware that had been oven-dried prior to use. Anhydrous solutions of reaction mixtures were transferred via an oven-dried syringe or cannula. All solvents were dried prior to use unless noted otherwise. Thin layer chromatography (TLC) was performed using precoated silica gel plates. Flash column chromatography was performed with silica gel. Infrared spectra (IR) were obtained as neat oils. ^{1}H and ^{13}C nuclear magnetic resonance spectra (NMR) were recorded in ppm (δ) downfield of TMS (δ = 0) in $CDCl_3$. Signal splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (*J*) in hertz. High resolution mass spectra (HRMS) were performed on an electron spray injection (ESI) TOF mass spectrometer. Enantiomeric excess was determined by chiral HPLC analysis.

General Procedures for the Rh-Catalyzed 1,3-Acyl Migration [5 + 1] Cycloaddition. Method for substrate **1**: To an oven-dried flask attached with a CO balloon was added $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), anhydrous toluene (1 mL), and cyclopropyl propargyl ester (0.1 mmol). The oil bath was heated to 60 °C. The reaction was monitored by TLC. After the reaction was complete, the solvent was evaporated and the residue was purified by flash column chromatography on silica gel.

Method for substrate **3**: To an oven-dried vial was added $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), anhydrous toluene (2 mL), and cyclopropyl propargyl ester (0.1 mmol). The vial was placed in a high pressure reactor, which was subsequently filled with 10 atm of CO. The reaction was heated overnight. The solvent was evaporated, and the residue was purified by flash column chromatography on silica gel.

General synthetic procedures, characterization data, and copies of NMR spectra for substrates in Table 1 (**1a**, **1c**−**1i**), Table 2 (*trans*-**1j** and *trans*-**1n**), Table 3 (*cis*-**1j**, cis-**1k**, *cis*-**1n**, **1o**−**1s**), and Scheme 6 (**1t** and **1u**) were reported in the previous communication.[3]

Characterization data and copies of NMR spectra for products in Table 1 (**2a**−**2i**), Table 2 (**2j**, **2k**, and **2n**), Table 3 (**2j**−**2s**), and Scheme 6 (**2t** and **2u**) were reported in the previous communication.[3]

1-Cyclopropyl-5-phenylpent-1-yn-3-yl acetate (1b). To an oven-dried flask were added THF (50 mL) and cyclopropyl acetylene (10 mmol), and the solution was cooled to −78 °C. *n*-BuLi (6.3 mL, 10 mmol) was added, and the solution was stirred at −78 °C for 10 min. 3-Phenyl propanal (1.3 mL, 10 mmol) was added, and the solution was allowed to warm to room temperature. The reaction was quenched with water, extracted with EtOAc for three times, and dried over $MgSO_4$. The solvent was evaporated, and the crude alcohol intermediate was used for next step without further purification. To an oven-dried flask were added THF (50 mL) and the above alcohol. The solution was cooled to −78 °C. *n*-BuLi (6.3 mL, 10 mmol) was added, and the solution was stirred for 10 min. PivCl (1.2 mL, 10 mmol) was added dropwise, and the solution was allowed to warm to room temperature. The reaction was quenched with water, extracted with EtOAc for three times, and dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by chromatography (EtOAc/hexane = 1:50) to yield a colorless oil (1.92 g, 79%): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.70 (m, 2H), δ 0.76 (m, 2H), 1.28 (m, 1H), 2.04 (m, 2H), 2.05 (s, 3H), 2.74 (d, *J* = 8.0 Hz, 2H), 5.33 (td, *J* = 6.8, 2.0 Hz, 1H), 7.16 (m, 3H), 7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.4. 8.5, 21.3, 31.5, 36.8, 64.2, 72.7, 89.9, 126.2, 128.55, 128.62, 141.1, 170.2; IR (film) ν 3027, 2936, 2360, 2247, 1738, 1496, 1454, 1369, 1229, 1175, 1018, 958, 909, 813, 730, 699 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{18}O_2$ (M + Na)$^+$ 265.1199, found 265.1190.

2,2-Dimethyl-propionic Acid 3-(2-Hydroxymethyl-cyclopropyl)-1,1-dimethyl-prop-2-ynyl Ester (*trans*-1k). To a solution of *trans*-**1n**[3] (1.19 g, 3.0 mmol) in THF (45 mL) at 0 °C was added a solution of TBAF in THF (1.2 mL, 3.6 mmol, 3M). The solution was warmed to room temperature and stirred overnight. The reaction was quenched with water, extracted with EtOAc for three times, and dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by chromatography (EtOAc/hexane = 1:4) to yield a colorless oil (661 mg, 92%): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.73 (ddd, *J* = 8.8, 5.6, 4.4 Hz, 1H), 0.88 (dt, *J* = 8.8, 4.8 Hz, 1H), 1.16 (s, 9H), 1.20 (m, 1H), 1.42 (m, 1H), 1.59 (s, 6H), 1.75 (br, 1H), 3.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.3, 13.2, 24.4, 27.2, 29.32, 29.35, 39.3, 65.5, 72.2, 76.9, 86.2, 177.0 IR (film) ν 2981, 2241, 1733, 1288, 1176, 1128, 1062, 1028 cm^{-1}; HRMS (ESI) *m*/*z* calcd. For $C_{14}H_{22}O_3$ (M + Na)$^+$ 261.1461, found 261.1465.

2,2-Dimethyl-propionic Acid 3-(2-Methoxymethyl-cyclopropyl)-1,1-dimethyl-prop-2-ynyl Ester (*trans*-1l). To an oven-dried flask were added NaH (15 mg, 0.37 mmol) and THF (1.25 mL). The solution was cooled to 0 °C and *trans*-**1k** (40 mg, 0.17 mmol) was added. The solution was stirred at 0 °C for 0.5 h, raised to room temperature, and stirred for 1 h. MeI (52 uL, 0.84 mmol) was added, and the reaction was stirred for another hour. The reaction was quenched with saturated NH_4Cl, extracted with EtOAc, and dried over MgSO4. The solvent was evaporated, and the residue was purified by flash chromatography (EtOAc/hexane = 1:20) to provide 12.1 mg (29%) of product as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.71 (ddd, *J* = 8.5, 5.5, 4.5 Hz, 1H), 0.88 (dt, *J* = 8.5, 4.5 Hz, 1H), 1.16 (s, 9H), 1.17 (m, 1H), 1.38 (m, 1H), 1.59 (s, 6H), 3.25 (m, 2H), 3.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.5, 13.5, 21.7, 27.3, 29.4, 39.3, 58.7, 72.3, 75.2, 77.7, 86.1, 176.9; IR (film) ν 2984, 2244, 1734, 1115 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{24}O_3$ (M + Na)$^+$ 275.1618, found 275.1624.

2,2-Dimethyl-propionic Acid 3-(2-Acetoxymethyl-cyclopropyl)-1,1-dimethyl-prop-2-ynyl Ester (*trans*-1m). To a sol-

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ution of *trans*-**1k** (42 mg, 0.17 mmol), pyridine (0.84 mL, 10.4 mmol), DMAP (17 mg, 0.14 mmol) was added acetyl chloride (0.12 mL, 1.68 mmol) at 0 °C. The solution was allowed to reach room temperature and stirred for 2 h. The solvent was evaporated, and the residue was purified by chromatography (EtOAc/hexane = 1:20) to yield a colorless oil (46 mg, 98%): ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.80 (ddd, J = 9.0, 6.0, 5.0 Hz, 1H), 0.94 (dt, J = 9.0, 5.0 Hz, 1H), 1.20 (s, 9H), 1.27 (m, 1H), 1.48 (m, 1H), 1.62 (s, 6H), 2.10 (s, 3H), 3.91 (dd, J = 11.5, 7.0 Hz,1H), 3.99 (d, J = 11.5, 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.9, 13.8, 20.8, 21.2, 27.3, 29.4, 39.3, 67.0, 72.1, 78.0, 85.5, 171.3, 176.9; IR ν 2976, 2243, 1733, 1231, 1116 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{16}H_{24}O_4$ (M + Na)$^+$ 303.1566, found 303.1571.

2,2-Dimethyl-propionic Acid 6-Isopropylidene-3-methoxymethyl-5-oxo-cyclohex-1-enyl Ester (2l). Yield 8.0 mg, 68%; colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.27 (s, 9H), 1.98 (s, 3H), 2.15 (s, 3H), 2.40 (dd, J = 16.5, 8.5 Hz, 1H), 2.56 (dd, J = 16.0, 5.5 Hz, 1H), 2.83 (m, 1H), 3.35 (s, 3H), 3.35 (m, 2H), 5.55 (d, J = 4.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.5, 25.4, 27.5, 32.9, 39.3, 41.9, 59.2, 75.3, 118.5, 128.4, 147.3, 147.8, 176.6, 200.6; IR (film) ν 2983, 1749, 1692, 1109, 916 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{16}H_{24}O_4$ (M + Na)$^+$ 303.1567, found 303.1572.

2,2-Dimethyl-propionic Acid 3-Acetoxymethyl-6-isopropylidene-5-oxo-cyclohex-1-enyl Ester (2m). Yield 36.0 mg, 78%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.27 (s, 9H), 1.99 (s, 3H), 2.05 (s, 3H), 2.16 (s, 3H), 2.42 (dd, J = 16.4, 7.6 Hz, 1H), 2.62(dd, J = 16.4, 5.6 Hz, 1H), 2.89 (m, 1H), 4.06 (d, J = 6.4 Hz, 2H), 5.52 (d, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 24.5, 25.4, 27.4, 31.9, 39.3, 41.7, 66.1, 117.0, 128.1, 148.3, 148.4, 171.1, 176.4, 199.8; IR ν 2974, 1744, 1692, 1229, 1116 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{24}O_5$ (M + Na)$^+$ 331.1516, found 331.1525.

General Procedures for the Synthesis of Compound 3. To an oven-dried flask were added THF (0.2 M) and diisopropylamine (1.0 equiv), and the solution was cooled to 0 °C. A solution of *n*-BuLi (1.0 equiv) was added, and the resulting mixture was stirred at 0 °C for 10 min and then cooled to −78 °C. The alkyne (1.0 equiv) was added dropwise and stirred for 30 min. The aldehyde or ketone (1.0 equiv) was added, and the solution was allowed to warm to room temperature. The reaction was quenched with water, extracted with EtOAc for 3 times, and dried over $MgSO_4$. The solvent was evaporated, and the crude alcohol intermediate was used for next step without purification. To an oven-dried flask was added THF (0.2 M) and the above alcohol. The solution was cooled to −78 °C. A solution of *n*-BuLi (1.0 equiv) was added, and the solution was stirred for 10 min. PivCl or acetic anhydride (1.1 equiv) was added dropwise, and the solution was allowed to warm to room temperature. The reaction was quenched with water, extracted with EtOAc for three times, and dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by chromatography.

6-Phenyl-1-(1-((triisopropylsilyl)oxy)cyclopropyl)hex-2-yn-1-yl Pivalate (3a). Yield 174 mg, 88%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.77−0.97 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H), 1.04 (m, 21H), 1.22 (s, 9H), 1.49 (tq, J = 7.2, 7.2 Hz, 2H), 2.13 (td, J = 7.2, 2.0 Hz, 2H), 6.00 (t, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 12.8, 13.0, 13.5, 18.30, 18.32, 20.9, 22.0, 27.2, 39.0, 58.2, 69.5, 76.1, 86.0, 177.7; IR (film) ν 2964, 2868, 1723, 1462, 1279, 1216, 1145, 1044, 1015, 955, 882, 668 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{23}H_{42}O_3Si$ (M + Na)$^+$ 417.2795, found 417.2791.

1-Cyclopropyl-4,4-dimethylpent-2-yn-1-yl Pivalate (3b). Yield 484 mg, 62%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.38−0.55 (m, 4H), 1.19 (s, 9H), 1.19 (m, 1H), 1.21 (s, 9H), 5.30 (d, J = 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.9, 3.1, 14.4, 27.2, 27.5, 31.0, 38.9, 67.5, 74.1, 94.4, 177.7; IR (film) ν 2971, 2361, 1727, 1479, 1364, 1279, 1152, 1029, 954, 849, 667 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{15}H_{24}O_2$ (M + Na)$^+$ 259.1668, found 259.1662.

2-Cyclopropyl-7-phenylhept-3-yn-2-yl Pivalate (3c). Yield 986 mg, 79%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.50 (m, 3H), δ 0.72 (m, 1H), 1.18 (s, 9H), 1.34 (m, 1H), 1.73 (s, 3H), 1.78 (m, 2H), 2.19 (t, J = 8.5 Hz, 2H), 2.70 (t, J = 10.0 Hz, 2H), 7.18 (m, 3H), 7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.3, 3.0, 18.2, 20.4, 27.3, 27.6, 30.6, 34.8, 39.4, 77.5, 78.7, 85.3, 126.0, 128.5, 128.8, 141.9, 176.8; IR (film) ν 2983, 2360, 1732, 1478, 1455, 1363, 1281, 1141, 1070, 1051, 927, 743, 699 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{21}H_{28}O_2$ (M + Na)$^+$ 335.1982, found 335.1994.

2-Cyclopropyl-7-phenylhept-3-yn-2-yl Acetate (3d). Yield 165 mg, 60%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.50 (m, 3H), δ 0.72 (m, 1H), 1.37 (m, 1H), 1.75 (s, 3H), 1.78 (m, 2H), 2.02 (s, 3H), 2.19 (t, J = 7.2 Hz, 2H), 2.69 (t, J = 7.2 Hz, 2H), 7.18 (m, 3H), 7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.5, 3.3, 18.3, 20.1, 22.4, 27.7, 30.5, 34.9, 78.0, 78.7, 85.9, 126.1, 128.5, 128.7, 141.8, 169.6; IR (film) ν 2936, 1737, 1366, 1238, 1148, 1071, 1012, 910, 699 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{18}H_{22}O_2$ (M + Na)$^+$ 293.1512, found 293.1526.

2-Cyclopropyl-6-((triisopropylsilyl)oxy)hex-3-yn-2-yl Pivalate (3e). Yield 429 mg, 47%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.48 (m, 3H), δ 0.68 (m, 1H), 1.06 (m, 21H), 1.17 (s, 9H), 1.34 (m, 1H), 1.70 (s, 3H), 2.43 (t, J = 7.2 Hz, 2H), 3.75 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.3, 2.9, 12.2, 18.2, 20.3, 23.4, 27.3, 27.5, 39.4, 62.3, 77.6, 79.0, 82.7, 176.9; IR (film) ν 2958, 2867, 1736, 1462, 1366, 1283, 1143, 1109, 1071, 917, 856, 681 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{23}H_{42}O_3Si$ (M + Na)$^+$ 417.2795, found 417.2790.

5-Cyclopropylhex-3-yne-1,5-diyl Bis(2,2-dimethylpropanoate) (3f). Yield 50.7 mg, 79%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.48 (m, 3H), δ 0.68 (m, 1H), 1.17 (s, 9H), 1.21 (s, 9H), 1.34 (m, 1H), 1.70 (s, 3H), 2.52 (t, J = 6.8 Hz, 2H), 4.11 (t, J = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 2.3, 3.0, 19.4, 20.3, 27.3, 27.4, 27.5, 38.9, 39.4, 62.5, 77.5, 79.5, 81.4, 176.8, 178.5; IR (film) ν 2975, 1730, 1480, 1281, 1143, 1071, 769 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{19}H_{30}O_4$ (M + Na)$^+$ 345.2036, found 345.2032.

2-(1-Methylcyclopropyl)hept-3-yn-2-yl Pivalate (3g). Yield 52.3 mg, 72%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.25(m, 1H), δ 0.33(m, 1H), δ 0.73 (m, 1H), 0.94 (t, J = 7.2 Hz, 3H), 1.02 (m, 1H), 1.12 (s, 3H), 1.16 (s, 9H), 1.48 (m, 2H), 1.67 (s, 3H), 2.13 (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.0, 12.6, 13.5, 19.8, 20.8, 22.3, 22.9, 25.0, 27.3, 39.6, 78.6, 79.0, 85.3, 176.4; IR (film) ν 2965, 2361, 1738, 1284, 1158, 1065, 913, 873, 860, 658 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{16}H_{26}O_2$ (M + Na)$^+$ 273.1825, found 273.1824.

(*R*)-1-((1*S*,2*S*)-2-Methyl-2-(4-methylpent-3-en-1-yl)-cyclopropyl)-6-phenylhex-2-yn-1-yl Pivalate (3h). Yield 50.3 mg, 38%; colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.34 (t, J = 5.0 Hz, 1H), 0.67 (t, J = 9.0, 5.0 Hz, 1H), 1.01 (m, 1H), 1.02 (s, 3H), 1.15 (ddd, J = 10.0, 9.0, 5.0 1H), 1.23 (s, 9H), 1.40 (ddd, J = 13.5, 10.5, 7.0 Hz, 1H), 1.60 (s, 3H), 1.67 (s, 3H). 1.81 (pentet, J = 7.0 Hz, 2H), 2.03 (m, 2H), 2.21 (td, J = 7.0, 2.0 Hz, 2H), 2.71 (t, J = 7.0 Hz, 2H), 4.88 (dt, J = 10.0, 2.0 Hz, 1H), 5.10 (tt, J = 7.0, 1.5 Hz, 1H), 7.16−7.30 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.4, 17.8, 18.3, 18.7, 21.5, 25.5, 25.9, 27.3, 28.4, 30.3, 34.8, 38.8, 41.2, 66.0, 79.1, 84.5, 124.6, 126.1, 128.5, 128.8, 131.6, 141.8, 177.3; IR (film) ν 2929, 2359, 1729, 1454, 1287, 1149, 1134, 934, 745, 698 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{27}H_{38}O_2$ (M + Na)$^+$ 417.2764, found 417.2746.

1-Cyclopropyl-6-phenylhex-2-yn-1-yl Acetate (3i). Yield 526 mg, 78%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.51 (m, 4H), δ 1.26 (m, 1H), 1.81 (pentet, J = 7.2 Hz, 2H), 2.10 (s, 3H), 2.21 (td, J = 7.2, 2.0 Hz, 2H), 2.70 (t, J = 7.2 Hz, 2H), 5.28 (dt, J = 8.0, 2.0 Hz, 1H), 7.19 (m, 3H), 7.27(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.3, 3.6, 14.7, 18.3, 21.4, 30.3, 34.9, 68.1, 76.2, 86.1, 126.1, 128.6, 128.7, 141.7, 170.4; IR (film) ν 2938, 1735, 1496, 1454, 1367, 1230, 1026, 965, 894, 746, 699 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{20}O_2$ (M + Na)$^+$ 279.1355, found 279.1344.

1-Cyclopropyl-3-phenylprop-2-yn-1-yl Pivalate (3j). Yield 494 mg, 77%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.58 (m, 4H), δ 1.24 (s, 9H), 1.36 (m, 1H), 5.43(d, J = 6.8 Hz, 1H), 7.30(m, 3H), 7.42(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.4, 3.5, 14.9, 27.3, 39.0, 67.7, 85.1, 85.2, 122.6, 128.4, 128.7, 132.1, 177.8; IR (film) ν 2973, 1728, 1490, 1479, 1277, 1144, 1070, 1029, 697 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{20}O_2$ (M + Na)$^+$ 279.1355, found 279.1353.

1-(6-Oxo-3-((triisopropylsilyl)oxy)cyclohex-2-en-1-ylidene)-4-phenylbutyl Pivalate (4a, A Mixture *E* and *Z* Isomers). Yield 42.8 mg, 70%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.93

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(m, 3H), δ 0.93 (m, 3H), 1.09 (m, 21H), 1.09 (m, 21H), 1.30 (s, 9H), 1.30 (s, 9H), 1.50 (m, 2H), 1.50 (m, 2H), 2.21 (t, J = 7.6 Hz, 2H), 2.55 (m, 2H), 2.55 (m, 4H), 2.66 (m, 2H), 2.66 (m, 2H), 5.61 (s, 1H), 5.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 12.9, 14.1, 18.10, 18.11, 20.0, 21.0, 27.3, 29.6, 29.9, 33.6, 39.2, 39.4, 39.7, 40.3, 102.7, 103.2, 121.0, 122.0, 147.9, 153.0, 153.69, 153.74, 175.7, 176.6, 197.3, 199.3; IR (film) ν 2962, 2868, 1744, 1701, 1638, 1598, 1462, 1375, 1253, 1107, 998, 881, 684, 666 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{42}O_4Si$ (M + Na)$^+$ 445.2744, found 445.2734.

2,2-Dimethyl-1-(6-oxocyclohex-2-en-1-ylidene)propyl Pivalate (4b, A Mixture *E* and *Z* Isomers). Yield 70 mg, 72%; colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.17 (s, 9H), δ 1.21 (s, 9H), 1.23 (s, 9H), 1.33 (s, 9H), 2.38 (m, 4H), 2.60 (m, 4H), 5.74 (m, 1H), 5.79 (dt, J = 10.0, 4.0 Hz, 1H), 5.84 (m, 1H), 6.10 (dt, J = 10.0, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.3, 25.4, 26.9, 27.1, 27.5, 28.4, 28.8, 37.9, 39.0, 39.5, 41.5, 44.7, 122.5, 124.0, 125.1, 125.2, 125.3, 128.5, 145.8, 159.0, 175.9, 176.1, 202.4, 210.4; IR (film) ν 2970, 1746, 1694, 1478, 1122, 1096, 731, 707 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{24}O_3$ (M + Na)$^+$ 287.1617, found 287.1610.

(*E*)-1-(2-Methyl-6-oxocyclohex-2-en-1-ylidene)-4-phenylbutyl Pivalate (*E*-4c). Yield 37.3 mg, 55%; colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.23 (s, 9H), δ 1.86 (m, 2H), 1.89 (q, J = 1.5 Hz, 3H), 2.38(m, 2H), 2.49 (t, J = 7.5 Hz, 2H), 2.57 (t, J = 7.5 Hz, 2H), 2.65 (t, J = 8.0 Hz, 2H), 5.73 (tq, J = 4.5, 1.5 Hz, 1H), 7.16 (m, 3H), 7.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.5, 23.9, 27.3, 29.9, 32.8, 35.8, 38.9, 39.4, 126.0, 127.5, 128.2, 128.5, 128.6, 132.5, 142.2, 155.9, 175.9, 203.1; IR (film) ν 2972, 1744, 1696, 1603, 1454, 1269, 1104, 910, 731, 699 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{28}O_3$ (M + Na)$^+$ 363.1931, found 363.1938.

(*Z*)-1-(2-Methyl-6-oxocyclohex-2-en-1-ylidene)-4-phenylbutyl Pivalate (*Z*-4c). Yield 21.3 mg, 31%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.18 (s, 9H), δ 1.67 (d, J = 1.2 Hz, 3H), 1.92 (pentet, J = 7.6 Hz, 2H), 2.29(m, 4H), 2.55 (t, J = 7.6 Hz, 2H), 2.63 (t, J = 7.6 Hz, 2H), 5.49 (m, 1H), 7.17 (m, 3H), 7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 23.1, 25.4, 26.1, 27.1, 35.4, 39.1, 43.9, 121.3, 126.2, 128.4, 128.59, 128.63, 129.0, 141.7, 148.0, 176.2, 205.0; IR (film) ν 2935, 1748, 1697, 1453, 1364, 1276, 1252, 1229, 1107, 909, 730, 699 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{28}O_3$ (M + Na)$^+$ 363.1931, found 363.1945.

1-(2-Methyl-6-oxocyclohex-2-en-1-ylidene)-4-phenylbutyl Acetate (4d, A Mixture *E* and *Z* Isomers). Yield 36.3 mg, 84%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.68 (q, J = 1.2 Hz, 3H), δ 1.84 (m, 2H), 1.92 (s, 3H), 1.94(m, 2H), 2.03 (s, 3H), 2.15 (s, 3H), 2.27 (m, 2H), 2.36 (m, 4H), 2.48(m, 2H), 2.56 (t, J = 7.2 Hz, 2H), 2.64 (m, 6H), 5.50 (m, 1H), 5.76 (tq, J = 4.8, 1.2 Hz, 1H), 7.18(m, 3H), 7.18(m, 3H), 7.27 (m, 2H), 7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 20.9, 21.4, 22.1, 23.1, 23.7, 25.4, 26.3, 29.5, 32.7, 35.3, 35.7, 38.7, 43.7, 121.5, 126.0, 126.2, 127.2, 128.49, 128.57, 128.58, 128.65, 128.8, 129.0, 132.2, 141.7, 142.2, 148.3, 155.5, 168.1, 168.4, 202.9, 204.7; IR (film) ν 2941, 1762, 1695, 1602, 1453, 1367, 1208, 1187, 1037, 1013, 700 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{22}O_3$ (M + Na)$^+$ 321.1461, found 321.1482.

1-(2-Methyl-6-oxocyclohex-2-en-1-ylidene)-3-((triisopropylsilyl)oxy)propyl Pivalate (4e, A Mixture *E* and *Z* Isomers). Yield 39 mg, 91%; colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.10 (m, 21H), δ 1.10 (m, 21H), 1.29 (s, 9H), 1.33 (s, 9H), 1.77(s, 3H), 1.95 (q, J = 1.5 Hz, 3H), 2.33 (m, 4H), 2.42 (m, 2H), 2.53 (m, 2H), 2.84(m, 4H), 3.91 (t, J = 7.0 Hz, 2H), 4.03 (t, J = 6.5 Hz, 2H), 5.54 (m, 1H), 5.78 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.1, 12.2, 18.16, 18.19, 19.6, 22.5, 23.1, 23.8, 26.3, 27.2, 27.3, 37.4, 38.7, 39.2, 39.4, 47.9, 59.0, 62.1, 121.2, 128.3, 128.5, 129.5, 132.4, 148.7, 153.4, 176.0, 176.1, 202.8, 203.4; IR (film) ν 2942, 2866, 1747, 1698, 1462, 1382, 1271, 1096, 1027, 935, 881, 680 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{42}O_4Si$ (M + Na)$^+$ 445.2744, found 445.2735.

(*E*)-1-(2-Methyl-6-oxocyclohex-2-en-1-ylidene)propane-1,3-diyl Bis(2,2-dimethylpropanoate) (*E*-4f). Yield 41.0 mg, 84% combined yield; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.10 (s, 9H), δ 1.29 (s, 9H), 1.91 (q, J = 1.6 Hz, 3H), 2.40 (m, 2H), 2.51 (t, J = 6.8 Hz, 2H), 2.89 (t, J = 6.8 Hz, 2H), 4.22 (t, J = 7.2 Hz, 2H), 5.78 (tq, J = 4.8, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 23.7, 27.3, 27.4, 32.9, 38.6, 38.8, 39.4, 62.1, 128.9, 130.0, 132.2, 151.7, 176.0, 178.5, 202.6; IR (film) ν 2971, 1727, 1698, 1281, 1147, 1097, 1031 cm^{-1}; HRMS (ESI) *m*/*z* calcd. For $C_{20}H_{30}O_5$ (M + Na)$^+$ 373.1985, found 373.1979.

(*Z*)-1-(2-Methyl-6-oxocyclohex-2-en-1-ylidene)propane-1,3-diyl Bis(2,2-dimethylpropanoate) (*Z*-4f). Yield 41.0 mg, 84% combined yield; colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.17 (s, 9H), δ 1.25 (s, 9H), 1.72 (q, J = 1.5 Hz, 3H), 2.31 (m, 4H), 2.89 (t, J = 6.5 Hz, 2H), 4.34 (t, J = 6.5 Hz, 2H), 5.52 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.6, 23.1, 26.4, 27.2, 27.4, 38.9, 39.2, 43.3, 59.5, 121.6, 127.9, 129.1, 149.5, 176.1, 178.5, 201.4; IR (film) ν 2973, 1726, 1480, 1363, 1282, 1151, 1106, 133, 909, 729 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{30}O_5$ (M + Na)$^+$ 373.1985, found 373.1979.

(*E*)-1-(2,3-Dimethyl-6-oxocyclohex-2-en-1-ylidene)butyl Pivalate (*E*-4g). Yield 30.3 mg, 52%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.93 (t, J = 7.6 Hz, 3H), δ 1.28 (s, 9H), 1.52 (sextet, J = 7.6 Hz, 2H), 1.78 (s, 3H), 1.79 (s, 3H), 2.31 (m, 2H), 2.39 (m, 2H), 2.55 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 17.8, 19.9, 21.3, 27.4, 29.4, 33.9, 37.6, 39.3, 124.5, 129.5, 134.7, 154.2, 175.5, 204.0; IR (film) ν 2963, 1744, 1696, 1608, 1479, 1461, 1273, 1101, 1027, 914, 731 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{26}O_3$ (M + Na)$^+$ 301.1774, found 301.1771.

(*S*)-1-(4-Methyl-4-(4-methylpent-3-en-1-yl)-6-oxocyclohex-2-en-1-ylidene)-4-phenylbutyl Pivalate (4h, A Mixture *E* and *Z* Isomers). Yield 67 mg, 62%; colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.06 (s, 3H), 1.28 (s, 9H), 1.37 (m, 2H), 1.57 (s, 3H), 1.65 (s, 3H), 1.83 (m, 2H), 1.93 (m, 2H), 2.37 (m, 1H), 2.37 (d, J = 14.0 Hz, 1H), 2.56 (d, J = 14.0, 1H), 2.65 (t, J = 8.0 Hz, 2H), 2.80 (ddd, J = 8.0, 7.5, 1.5 Hz, 1H), 5.05 (m, 1H), 5.72 (d, J = 10.0 Hz, 1H), 6.21 (d, J = 10.0 Hz, 1H), 7.16−7.30 (m, 5H); the two isomers have nearly identical ^{1}H NMR; ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.8, 23.3, 25.84, 25.85, 27.27, 27.34, 29.2, 31.8, 35.4, 35.8, 39.3, 39.5, 39.9, 42.4, 53.3, 120.8, 122.3, 124.2, 126.0, 126.2, 128.5, 128.58, 128.60, 132.0, 138.2, 142.2, 157.5, 175.7, 176.0, 200.0; IR (film) ν 2967, 1712, 1454, 1361, 1220, 1123, 914, 732, 700 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{28}H_{38}O_3$ (M + Na)$^+$ 445.2613, found 445.2607.

1-Cyclopropyl-3-phenylpropa-1,2-dienyl Pivalate (8d). Yield 49 mg, 49%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.62−0.64 (m, 2H), 0.75−0.78 (m, 2H), 1.26 (s, 9H), 1.54−1.60 (m, 1H), 6.59 (d, J = 2.0 Hz, 1H), 7.24−7.26 (m, 1H), 7.31−7.35 (m, 2H), 7.41−7.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.8, 6.3, 12.3, 27.4, 39.4, 105.0, 128.1, 128.2, 128.5, 128.9, 134.2, 176.2, 196.8; HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{20}O_2$ (M + Na)$^+$ 279.1356, found 279.1360.

General Procedures for the Synthesis of Compound 13 and 14. To an oven-dried flask were added $[Rh(CO)_2Cl]_2$ (2 mol %), anhydrous toluene (0.1 M), and 1 equiv of cyclopropyl propargyl ester. The oil bath was heated to 60 °C. The reaction was monitored by TLC. After the reaction was complete, the solvent was evaporated, and the residue was purified by flash column chromatography on silica gel (EtOAc/hexane = 50:1).

2-(Propan-2-ylidene)-2,4,5,6,7,7a-hexahydro-1*H*-inden-3-yl Pivalate (13). Yield 35 mg, 89%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.03−1.12 (m, 2H), 1.19−1.28 (m, 2H), 1.31 (s, 9H), 1.64 (s, 3H), 1.70−1.82 (m, 5H), 1.91−1.98 (m, 1H), 2.06 (d, br, J = 16.0 Hz, 1H), 219−2..23 (m, 1H), 2.42−2.50 (m, 1H), 2.73 (dd, J = 16.0, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 23.2, 25.3, 26.0, 26.2, 27.7, 35.2, 35.7, 39.3, 39.4, 119.2, 131.2, 138.0, 142.5, 176.3; IR ν 2976, 2930, 2858, 2360, 2342, 1751, 1120; HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{26}O_2$ (M + 1) 263.2006, found 263.2017.

1-(Propan-2-ylidene)-3a,4,5,7a-tetrahydro-1*H*-inden-2-yl Pivalate (14). Yield 44 mg, 82%; colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.27 (s, 9H), 1.62−1.71 (m, 2H), 1.79 (s, 3H), 1.84 (s, 3H), 1.87−1.91 (m, 1H), 2.04−2.13 (m, 1H), 3.14 (s, br, 1H), 3.44 (s, br, 1H), 5.51−5.52 (m, 1H), 5.54 (s, 1H), 5.70−5.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 21.1, 23.0, 24.8, 27.4, 37.8, 39.4, 41.3, 123.4, 124.1, 127.6, 127.7, 134.8, 151.4, 176.4; IR ν 2977, 2362, 2343, 1712, 1362, 1222; HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{24}O_2$ (M + 1) 261.1849, found 261.1840.

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3-Methyl-2-(4-phenylbutanoyl)cyclohex-2-enone (17d). To a round-bottom flask were added compound **4d** (60.2 mg, 0.20 mmol), 2 mL of MeOH, and K_2CO_3 (28 mg, 0.2 mmol). The reaction was stirred for 10 min. About 5 mL of Et_2O and 5 mL of H_2O were added, and the aqueous phase was extracted with 5 mL of Et_2O for 3 times. The combined organic solution was dried over $MgSO_4$ and evaporated under a vacuum, and the residue was purified by flash column chromatography (EtOAc/hexane = 1:4) to provide a colorless oil (40.2 mg, 0.144 mmol, 72% yield): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.89 (s, 3H), 1.97 (m, 4H), 2.39 (m, 4H), 2.64 (q, J = 7.2 Hz, 4H), 7.18 (m, 3H), 7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 22.0, 25.3, 32.3, 35.4, 37.6, 43.7, 126.1, 128.5, 128.7, 139.9, 142.0, 159.6, 197.2, 207.0; IR (film) ν 2931, 2360, 1698, 1661, 1378, 1181, 907, 727, 700 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{20}O_2$ $(M + Na)^+$ 279.1356, found 279.1355.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of all new compounds and crystal data for **2f** (CIF). 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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