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Diastereoselective [4 + 1] Cycloaddition of Alkenyl Propargyl Acetates with CO Catalyzed by $[RhCl(CO)_2]_2$

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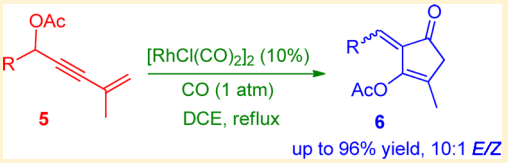
Supporting Information

ABSTRACT: A class of alkenyl propargyl acetates, RCH(OAc)C≡CC(CH_3)=CH_2 (**5**), are found to undergo [4 + 1] cycloaddition with CO (1 atm) in the presence of $[RhCl(CO)_2]_2$ in refluxing 1,2-dichloroethane to give cyclopentenones (**6**) in good yields. It has been demonstrated that, when the R group of **5** is a phenyl group bearing *o*-electron-withdrawing substituents, up to 10:1 diastereoselectivity and 96% yield can be achieved for the [4 + 1] cycloaddition. This process provides a convenient method to construct highly functionalized cyclopentenones that are useful in organic synthesis.

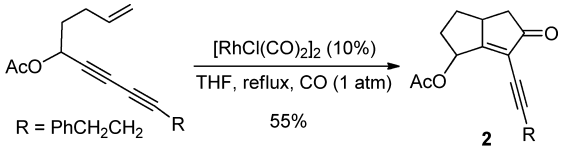


INTRODUCTION

Both chiral and achiral propargylic alcohols can be easily prepared from the reaction of deprotonated terminal alkynes with aldehydes or ketones.[1] This class of compounds is found to be versatile precursors to structurally diverse organic molecules, and their application in organic synthesis has been extensively studied.[2,3] These activities include the currently highly active field of transition-metal-catalyzed isomerizations and reactions of propargyl esters.[4−10]

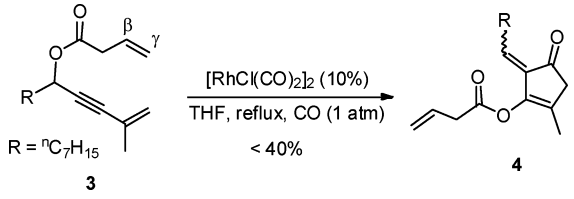
In recent years, our laboratory has also conducted research projects in the development of the synthetic application of functional propargylic alcohols.[11−14] An example of the catalytic Pauson−Khand (PK) cycloaddition of the functional propargylic alcohols investigated in our laboratory is shown in Scheme 1.[14b] In this reaction, the 1,3-diyne-based compound **1**

Scheme 1. Catalytic PK Cycloaddition of Diynoate 1



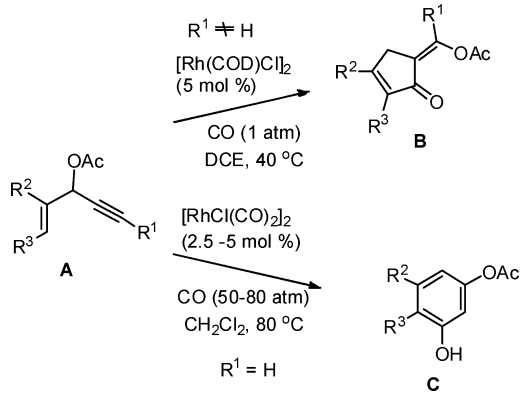
underwent the PK cycloaddition with CO catalyzed by $[RhCl(CO)_2]_2$ to generate the bicyclic cyclopentenone **2** with good diastereoselectivity. We also attempted a PK cycloaddition of an alkenyl propargyl ester **3** in the presence of $[RhCl(CO)_2]_2$ and CO (Scheme 2). This reaction, however, did not generate the expected PK cycloaddition product. Instead, an apparent [4 + 1] cycloaddition involving the enyne unit of **3** and CO took place to give a novel cyclopentenone product **4** in low yield with 1.2:1 *E*/*Z* isomers. The *β*,*γ*-double bond of the ester group did not participate in the cyclization. While this paper was in preparation, Tang and Fukuyama

Scheme 2. Attempted Catalytic Conversion of 3



reported conversions from a different enyne susbtrate **A** ($R^1 \neq H$) to **B** catalyzed by $[Rh(COD)Cl]_2$ (Scheme 3).[4e,j] Earlier,

Scheme 3. Catalytic Cycloadditions of Enynes A with CO



Brancour reported the reaction of the terminal alkyne-based substrate **A** (R^1 = H) in the presence of $[RhCl(CO)_2]_2$ and CO to give the six membered ring products **C**.[4d] To improve both the yield and the diastereoselectivity for the conversion of **3** to **4** in Scheme 2, we have explored the reactions of a number of

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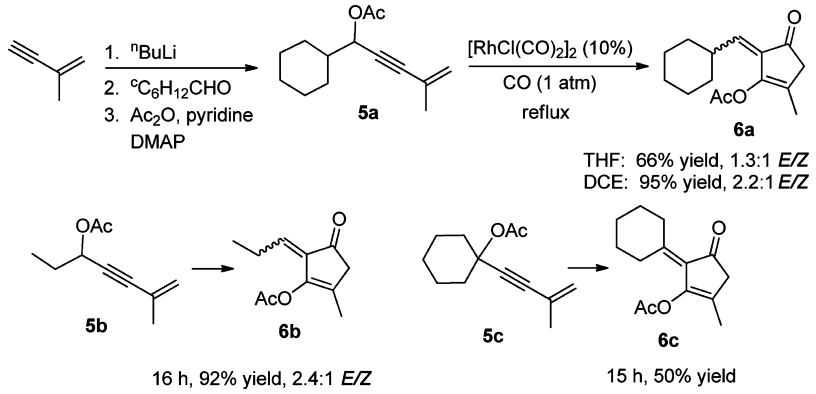
Scheme 4. Rh(I)-Catalyzed [4 + 1] Cycloaddition of the Alkyl-Substituted Propargyl Acetates



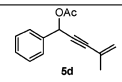
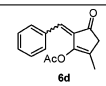
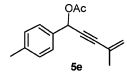
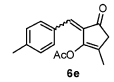
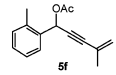
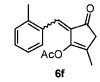
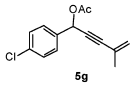
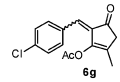
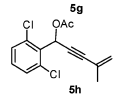
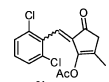
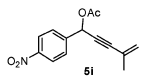
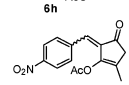
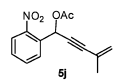
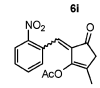
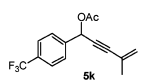
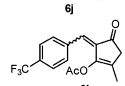
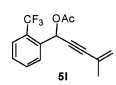
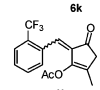
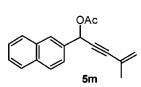
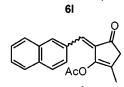
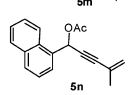
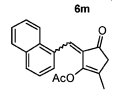
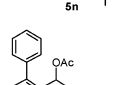
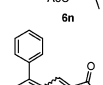
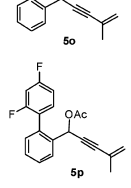
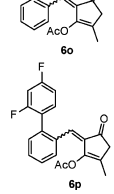
other enyne substrates by replacing the carboxylate group of **3** with acetate and its R group with various alkyl or aryl groups. We found that an excellent yield and high diastereoselectivity could be achieved for this Rh(I)-catalyzed [4 + 1] cycloaddition. Herein, these results are reported.

RESULTS AND DISCUSSION

Catalytic [4 + 1] Cycloaddition of Alkyl-Substituted Propargyl Acetates. We first prepared compound **5a**[15] by treatment of 2-methyl-but-1-en-3-yne with ^{n}BuLi, followed by addition to cyclohexanecarboaldehyde and esterification (Scheme 4). This compound was then heated with $[RhCl(CO)_2]_2$ in THF at reflux under 1 atm CO. After 24 h, the [4 + 1] cyclopentenone product **6a** was obtained in 66% yield with 1.3:1 *E*/*Z* selectivity. Further study found that, when THF was replaced with 1,2-dichloroethane (DCE) as the reaction solvent, after 15 h, **6a** was obtained in 95% yield with 2.2:1 *E*/*Z* selectivity. Thus, using DCE led to excellent yield and improved diastereoselectivity. Under the same conditions, compound **5b**[16] with a primary alkyl substituent at the propargylic position gave the [4 + 1] product **6b** in 92% yield with 2.4:1 *E*/*Z* selectivity. The reaction was also found to work for substrate **5c**[17] that has a tertiary propargylic center, which gave **6c** in 50% yield. These results show that the enyne substrates containing alkyl substituents on the propargylic carbon can undergo efficient [4 + 1] cycloaddition with CO in the presence of the Rh(I) catalyst with modest diastereoselectivity. Previously, a Pd(0)-catalyzed vicinal double carbonylation of 4-en-2-ynyl carbonates, analogues of **5**, was reported to generate cyclopentenone products that are structurally related to **6**.[8b]

Catalytic [4 + 1] Cycloaddition of Aryl-Substituted Propargyl Acetates. We then studied the reaction of the enyne substrates containing various *aryl* substituents at the propargylic position by using the same reaction conditions as described in Scheme 4 with DCE as the solvent. The results are summarized in Table 1. As shown in entry 1, compound **5d**[15] containing a phenyl substituent at the propargylic carbon gave the [4 + 1] product **6d** in 85% yield with 2.0:1 *E*/*Z* selectivity. This result is similar to those obtained with the alkyl-substituted enynes. When an electron-donating methyl group is introduced to the *p*-position of the phenyl ring of **5d**, the diastereoselectivity is reduced to 1:1.1, as shown in the conversion of **5e** to **6e** (entry 2). However, when the *p*-methyl substituent of **5e** is placed at the *o*-position in **5f**, the *E*/*Z* selectivity is significantly improved to 4.9:1, as observed in the product **6f** (entry 3). When the electron-donating *p*-methyl of

Table 1. Rh(I)-Catalyzed [4 + 1] Cycloaddition of Aryl-Substituted Propargyl Acetates with CO[a]

Entry	Substrate	Time (h)	Product	Yield (%)	*E*/*Z*
1		15		85	2.0:1
2		15		61	1:1.1
3		4		86	4.9:1
4		15		69	2.9:1
5		5		84	5.7:1
6		24		90	4.0:1
7		16		96	6.3:1
8		8		85	4.1:1
9		8		82	7.0:1
10		15		88	1.4:1
11		15		84	6.2:1
12		15		82	7.2:1
13		16		73	10.0:1

[a]Conditions: $[RhCl(CO)_2]_2$ (10%), CO (1 atm), DCE, reflux.

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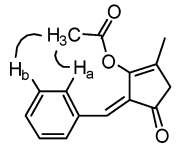
5e is replaced with an electron-withdrawing *p*-Cl in **5g**, its conversion to **6g** shows a better *E*/*Z* selectivity of 2.9:1 than both **5d** and **5e** (entry 4). When two electron-withdrawing Cl's are incorporated to the *o*-positions of the phenyl ring, as in **5h**, its conversion to **6h** gives a much improved *E*/*Z* selectivity of 5.7:1 (entry 5). When the more strongly electron-withdrawing NO_2 and CF_3 are introduced to the *p*-position of the phenyl ring, as in **5i** and **5k** (entries 6 and 8), the *E*/*Z* selectivities (4.0:1 and 4.1:1) are better than those of **5d**, **5e**, and **5g**. When these strongly electron-withdrawing groups are attached to the *o*-position of the phenyl ring, further enhancement of the *E*/*Z* selectivity to 6.3:1 and 7.0:1 is observed in the conversions of **5j** and **5l** to the products **6j** and **6l**, respectively (entries 7 and 9). These results demonstrate that the stereoselectivity of the Rh(I)-catalyzed [4 + 1] cycloaddition can be enhanced by reducing the electron density of the phenyl substituent at the propargylic carbon and also by placing *o*-substituents on the phenyl ring to increase the steric bulkiness adjacent to the propargylic center.

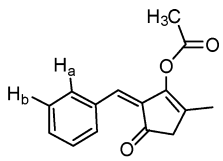
The transformations of the enyne substrates containing 1-naphthyl (**5m**) and 2-naphthyl (**5n**) on the propargylic carbon were also studied (entries 10, 11). The 2-naphthyl group of **5m** is equivalent to a phenyl group containing a *m*- and a *p*-substituent, and the conversion of **5m** to **6m** proceeded with 88% yield with 1.4:1 *E*/*Z* selectivity (entry 10). The 1-naphthyl group of **5n** is equivalent to a phenyl group containing an *o*- and a *m*-substituent, and the conversion of **5n** to **6n** proceeded with a much higher *E*/*Z* selectivity of 6.2:1 in 84% yield (entry 11). Thus, similar to those shown in entries 1−9, an *o*-substituent on the phenyl ring increases the stereoselectivity, but a *p*- or *m*-substituent is less favorable.

The reaction of compound **5o** with a biphenyl substituent *o*-linked to the propargylic carbon gave the product **6o** in 82% yield with a good 7.2:1 *E*/*Z* selectivity (entry 12). When two electron-withdrawing fluorine substituents were introduced, the resulting substrate **5p** showed a further enhanced *E*/*Z* selectivity of 10:1 (entry 13). This is consistent with the observation that an electron-withdrawing *o*-substituent on the phenyl ring at the propargylic position can lead to high *E*/*Z* selectivity for the Rh(I)-catalyzed [4 + 1] cycloaddition of the alkenyl propargylic esters.

The NOESY spectra of *E*- and *Z*-**6d** have allowed the determination of their stereochemistry (Supporting Information, page S48). NOE effects were observed for *E*-**6d** between the aromatic protons H_a and H_b at δ 7.35 and the AcO proton signal at δ 1.80. In contrast, no NOE effect between the aromatic protons and the AcO protons was observed for *Z*-**6d**. The AcO protons in *E*-**6d** are also significantly shielded by the aromatic ring to give a more upfield-shifted signal than those in *Z*-**6d**. The *E*/*Z* isomers of the other reaction products were determined by comparison of their NMR spectra with those of *E*- and *Z*-**6d**.



E-**6d**



Z-**6d**

Mechanistic Illustration of the Stereoselectivity. Transition-metal-catalyzed isomerization of propargylic esters and the subsequent inter- or intramolecular conversions have been studied extensively.[4−10] On the basis of these previous reports, a mechanism for the Rh(I)-catalyzed [4 + 1] cycloaddition can be proposed in Scheme 5. Coordination of the triple bond of the substrate **6** to the Rh(I) center could generate the intermediate **7**. 1,3-Acetate migration of **7** could generate the allene intermediate **8a** and **8b**.[4] It is expected that the *o*-substituted phenyl ring of **8a** should have increased the steric interaction with the ligands on the Rh, which makes **8b** more favorable than **8a**. Previously, Murakami had reported a Rh catalyzed reaction of isolated vinyl allenes with CO that gave similar [4 + 1] cycloaddition products.[18] According to their mechanistic study, the η^4 complexes **8a** and **8b** could undergo oxidative coupling to generate the metallacyclopentene intermediates **9a** and **9b**, respectively. In **9b**, an electron-deficient benzene ring could have a favorable $\pi-\pi$ attraction with the π electrons of the acetate group. This $\pi-\pi$ interaction is supported by the significantly shielded AcO proton signal of *E*-**6d** in its ^{1}H NMR spectrum. Therefore, an *o*-electron-withdrawing substituent on the phenyl ring would favor the formation of the intermediate **9b**. Complexes **9a** and **9b** can then undergo CO insertion and reductive elimination to generate the *Z* and *E* products **6**, respectively. Thus, the *o*-electron-withdrawing group on the phenyl ring of the substrate would lead to the formation of *E*-**6** as the major product via the formation of the sterically and electronically more favorable intermediates **8b** and **9b**.

Catalytic [4 + 1] Cycloaddition of the Substrates Containing a Vinyl Group on the Propargylic Carbon. We also investigated the Rh(I)-catalyzed [4 + 1] cycloaddition of the constitutional isomers of the enyne substrates **5**, such as **10a** and **10b**, similar to **A** (R ≠ H) in Scheme 3, in which the vinyl groups are on the propargylic carbon rather than on the alkyne carbon (Scheme 6). It was found that both **10a** and **10b** were converted to the cyclopentenone products **11a** and **11b** with good *Z*/*E* selectivities of 7.0:1 and 5.7:1, respectively, in the presence of $[RhCl(CO)_2]_2$ and CO. The stereochemistry of *Z*-**11a** was determined by observing the NOE effect between its aromatic protons and the vinyl proton on the cyclopentenone ring in its 2D NOESY spectrum (see the Supporting Information, page S49). Unlike those in products **6**, the acetate groups in **11a** and **11b** are not on the cyclopentenone ring. The mechanism proposed for the conversion of **5** to **6** in Scheme 5 could also be applied to illustrate the conversion of **10** to **11**. That is, the Rh(I)-promoted 1,3-migration of the acetate group of the Rh(I)−alkyne complex **12**, followed by cyclization, should give an intermediate like **13**. The coordination of the acetate group to the Rh(I) center in **13** and the subsequent CO insertion and reductive elimination can explain the stereoselective formation of the products *Z*-**11**. These results resemble those reported by Tang and Fukuyama.[4e,j]

Summary. In summary, we have discovered a Rh(I)-catalyzed [4 + 1] cycloaddition of vinyl propargyl acetates with CO to generate cyclopentenone products. In this reaction, it has been demonstrated that good diastereoselectivity can be achieved for the enyne substrates bearing an aromatic ring at the propargylic carbon with electron-withdrawing or *o*-substituents. The stereoelectronic effects of the substrates on the diastereoselectivity can be rationalized by a mechanism involving the Rh(I)-promoted 1,3-acetate migration, followed by the [4 + 1] cycloaddition of the Rh(I)-coordinated vinyl allene intermediates with CO. Because of the easily available starting material and the mild reaction conditions, this work

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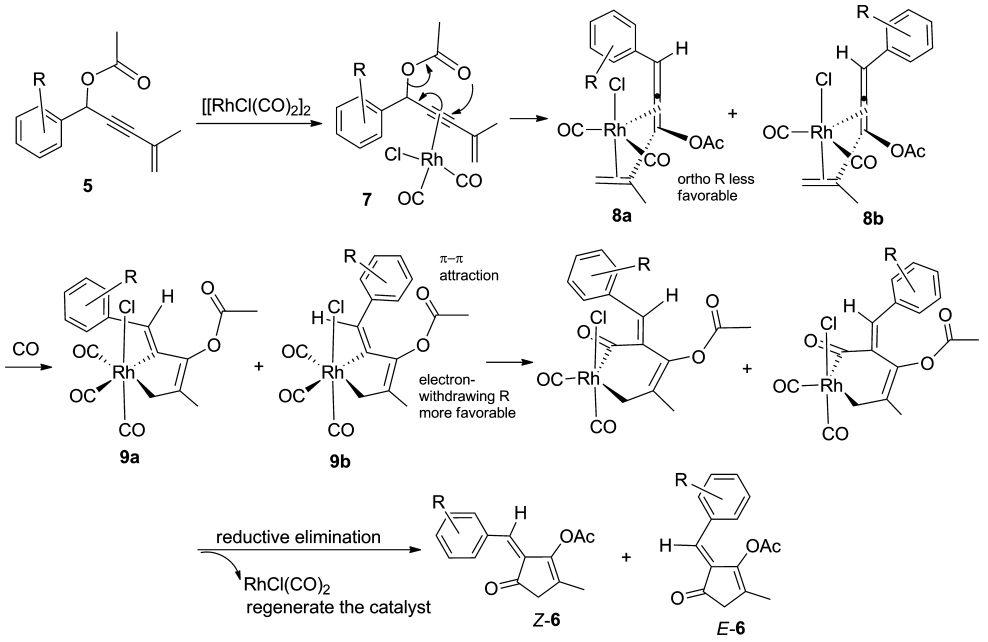
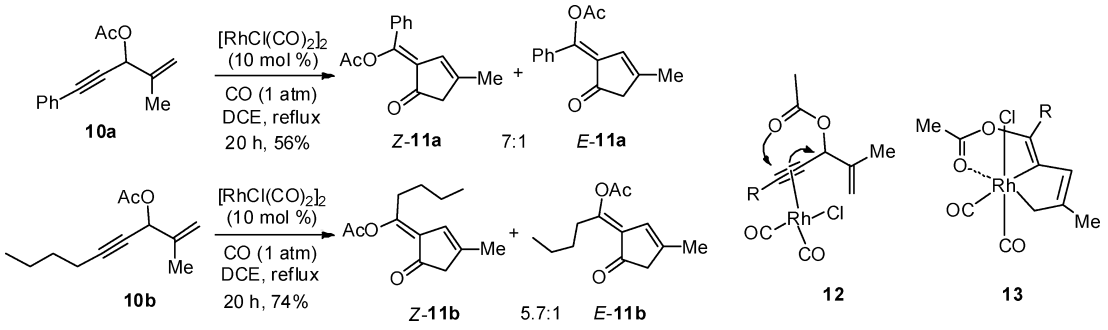
Scheme 5. Proposed Mechanism for the Rh(I)-Catalyzed [4 + 1] Cycloaddition



Scheme 6. Rh(I)-Catalyzed [4 + 1] Cycloaddition of Compounds 10



provides a convenient method to construct functional cyclopentenones that are useful in organic synthesis.

EXPERIMENTAL SECTION

General Procedure for the Preparation of Alkenyl Propargylic Esters 3, 5, and 10. Under nitrogen, an alkyne (1.6 equiv) was dissolved in THF (5.0 mL) and cooled to −78 °C. ^{n}BuLi (1.4 equiv) was added, and the mixture was stirred for 30 min. An aldehyde (1.0 mmol) was then added. After 1 h, the reaction was quenched with saturated aqueous ammonium chloride and extracted three times with CH_2Cl_2. The organic layer was dried with sodium sulfate and concentrated by rotary evaporation. The resultant oil was purified by flash column chromatography on silica gel eluted with hexanes/ethyl acetate to afford the product in 50−95% yield. The product was then dissolved in CH_2Cl_2 (0.5 M), and Ac_2O (2 equiv), pyridine (4 equiv) [*4-pentenoic acid (2 equiv) and DCC (2 equiv) were added instead to prepare ester* **3**], and DMAP (0.1 equiv) were added. After the reaction was determined to be complete by TLC, it was quenched with saturated aqueous ammonium chloride and extracted three times with CH_2Cl_2. The organic layer was dried with sodium sulfate and concentrated by rotary evaporation. The resultant oil was purified by flash column chromatography on silica gel eluted with hexanes/ethyl acetate to afford the product in 90−99% yield.

Characterizations of Alkenyl Propargylic Esters 3, 5, and 10. *2-Methyldodec-1-en-3-yn-5-yl But-3-enoate,* ***3:*** 147 mg, 56% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.90 (m, 1H), 5.48 (t, 1H, J = 6.8 Hz), 5.27 (s, 1H), 5.21 (m, 1H), 5.18 (m, 1H), 5.13 (t, 1H, J = 1.4 Hz), 3.10 (t, 1H, J = 1.4 Hz), 3.08 (t, 1H, J = 1.4 Hz), 1.84 (s, 3H), 1.74 (m, 2H), 1.38 (m, 2H), 1.26 (m, 8H), 0.85 (t, 3H, J = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 130.2, 126.2, 122.8, 118.8, 86.6, 85.7, 64.9, 39.3, 35.0, 31.9, 29.3, 29.2, 25.2, 23.5, 22.8, 14.3. Colorless oil. HRMS (EI) for $C_{17}H_{26}O_2$ (M) Calcd: 262.1933. Found: 262.1931.

Cyclohexyl-4-methylpent-4-en-2-yn-1-yl Acetate, ***5a:***[15] 161 mg, 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.28 (m, 2H), 5.20 (m, 1H), 2.04 (s, 3H), 1.84 (m, 3H), 1.71 (m, 6H), 1.13 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 126.3, 122.7, 87.2, 84.8, 68.8, 42.1, 28.8, 28.3, 26.4, 26.0, 25.9, 23.5, 21.2.

6-Methylhept-6-en-4-yn-3-yl Acetate, ***5b:***[16] 136 mg, 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.43 (t, 1H, J = 6.6 Hz), 5.30 (s, 1H), 5.23 (m, 1H), 2.08 (s, 3H), 1.87 (s, 3H), 1.79 (m, 2H), 1.00 (t, 3H, J = 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 126.3, 122.9, 86.7, 85.5, 65.8, 28.4, 23.5, 21.3, 9.6.

1-(3-Methylbut-3-en-1-yn-1-yl)cyclohexyl Acetate, ***5c:***[17] 93 mg, 45% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.26 (s, 1H), 5.18 (m, 1H), 2.10 (m, 2H), 2.01 (s, 3H), 1.86 (s, 3H), 1.80 (m, 2H), 1.60 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3, 126.6, 122.0, 88.4, 87.6, 76.0, 37.3, 25.4, 23.6, 22.9, 22.2.

4-Methyl-1-phenylpent-4-en-2-yn-1-yl Acetate, ***5d:***[15] 152 mg, 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (m, 2H), 7.38 (m, 3H), 6.60 (s, 1H), 5.38 (s, 1H), 5.29 (m, 1H), 2.11 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.0, 137.4, 129.1, 128.9, 128.0, 126.1, 123.5, 88.4, 84.7, 66.2, 23.4, 21.4.

4-Methyl-1-(p-tolyl)pent-4-en-2-yn-1-yl Acetate, ***5e:*** 171 mg, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, 2H, J = 8.1 Hz), 7.21 (d, 2H, J = 7.8 Hz), 6.59 (s, 1H), 5.39 (s, 1H), 5.30 (m, 1H), 2.38 (s,

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3H), 2.10 (s, 3H), 1.93 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.0, 139.1, 134.6, 129.6, 128.0, 126.2, 123.3, 88.2, 85.0, 66.1, 23.4, 21.5, 21.4. Colorless liquid. HRMS (EI) for $C_{15}H_{16}O_2$ (M) Calcd: 228.1150. Found: 228.1154.

4-Methyl-1-(o-tolyl)pent-4-en-2-yn-1-yl Acetate, ***5f:*** 157 mg, 69% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (m, 1H), 7.27 (m, 2H), 7.20 (m, 1H), 6.71 (s, 1H), 5.37 (s, 1H), 5.30 (m, 1H), 2.45 (s, 3H), 2.12 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 136.5, 135.5, 131.0, 129.1, 128.3, 126.5, 126.2, 123.3, 88.2, 84.7, 64.3, 23.4, 21.2, 19.3. Colorless liquid. HRMS (EI) for $C_{15}H_{16}O_2$ (M) Calcd: 228.1150. Found: 228.1152.

1-(4-Chlorophenyl)-4-methylpent-4-en-2-yn-1-yl Acetate, ***5g:*** 144 mg, 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, 2H, *J* = 8.1 Hz), 7.33 (d, 2H, *J* = 8.1 Hz), 6.55 (s, 1H), 5.37 (s, 1H), 5.30 (m, 1H), 2.09 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 136.0, 135.0, 129.4, 129.0, 126.0, 123.7, 88.7, 84.3, 65.4, 23.3, 21.2. Colorless liquid. HRMS (EI) for $C_{14}H_{13}ClO_2$ (M) Calcd: 248.0604. Found: 248.0601.

1-(2,6-Dichlorophenyl)-4-methylpent-4-en-2-yn-1-yl Acetate, ***5h:*** 181 mg, 64% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35−7.13 (m, 4H), 5.32 (s, 1H), 5.24 (m, 1H), 2.07 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 135.7, 132.6, 130.4, 129.4, 126.2, 123.8, 88.1, 82.6, 62.3, 23.2, 20.9. Colorless liquid. HRMS (EI) for $C_{14}H_{12}Cl_2O_2$ (M) Calcd: 282.0214. Found: 282.0211.

4-Methyl-1-(4-nitrophenyl)pent-4-en-2-yn-1-yl Acetate, ***5i:*** 181 mg, 70% yield.^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (m, 2H), 7.69 (m, 2H), 6.63 (s, 1H), 5.39 (s, 1H), 5.32 (m, 1H), 2.14 (d, 3H, *J* = 1.8 Hz), 1.90 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 148.3, 144.2, 128.7, 125.7, 124.2, 124.1, 89.5, 83.3, 65.0, 23.2, 21.2. Light brown liquid. HRMS (EI) for $C_{14}H_{13}NO_4$ (M) Calcd: 259.0845. Found: 259.0844.

4-Methyl-1-(2-nitrophenyl)pent-4-en-2-yn-1-yl Acetate, ***5j:*** 176 mg, 68% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, 1H, *J* = 8.1 Hz), 7.90 (d, 1H, *J* = 8.1 Hz), 7.68 (t, 1H, *J* = 7.8 Hz), 7.52 (t, 1H, *J* = 7.8 Hz), 7.13 (s, 1H), 5.36 (s, 1H), 5.30 (m, 1H), 2.10 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.4, 148.1, 133.7, 132.3, 129.8, 129.6, 125.8, 125.0, 124.0, 89.0, 83.1, 62.3, 23.3, 20.9. Brown oil. HRMS (EI) for $C_{14}H_{13}NO_4$ (M) Calcd: 259.0845. Found: 259.0842.

4-Methyl-1-(4-(trifluoromethyl)phenyl)pent-4-en-2-yn-1-yl Acetate, ***5k:*** 211 mg, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (m, 4H), 6.62 (s, 1H), 5.38 (s, 1H), 5.31 (m, 1H), 2.12 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.6, 141.1, 130.9 (q, *J* = 32.3 Hz), 125.64, 125.61, 125.60, 123.9 (q, *J* = 270.8 Hz), 123.6, 88.8, 83.6, 65.2, 23.0, 20.9. Light brown oil. HRMS (EI) for $C_{15}H_{13}F_3O_2$ (M) Calcd: 282.0868. Found: 282.0872.

4-Methyl-1-(2-(trifluoromethyl)phenyl)pent-4-en-2-yn-1-yl Acetate, ***5l:*** 194 mg, 69% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, 1H, *J* = 7.8 Hz), 7.64 (m, 2H), 7.47 (t, 1H, *J* = 7.8 Hz), 6.86 (s, 1H), 5.35 (s, 1H), 5.28 (s, 1H), 2.10 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.1, 135.5, 132.3, 129.9, 128.9, 127.6 (q, *J* = 30.9 Hz), 126.0 (q, *J* = 5.5 Hz), 125.7, 123.8 (q, *J* = 272.6 Hz), 123.3, 88.5, 84.0, 62.1, 22.9, 20.7. Light brown oil. HRMS (EI) for $C_{15}H_{13}F_3O_2$ (M) Calcd: 282.0868. Found: 282.0869.

4-Methyl-1-(naphthalen-2-yl)pent-4-en-2-yn-1-yl Acetate, ***5m:*** 174 mg, 66% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.84 (m, 3H), 7.67 (m, 1H), 7.51 (m, 2H), 6.81 (s, 1H), 5.44 (s, 1H), 5.33 (m, 1H), 2.15 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ170.0, 134.8, 133.7, 133.3, 128.9, 128.5, 128.0, 127.4, 126.9, 126.7, 126.2, 125.4, 123.6, 88.7, 84.9, 66.4, 23.5, 21.4. Light brown oil. HRMS (EI) for $C_{18}H_{16}O_2$ (M) Calcd: 264.1150. Found: 264.1151.

4-Methyl-1-(naphthalen-1-yl)pent-4-en-2-yn-1-yl Acetate, ***5n:*** 166 mg, 63% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, 1H, *J* = 8.4 Hz), 7.80 (m, 3H), 7.53 (m, 3H), 7.26 (s, 1H), 5.40 (s, 1H), 5.30 (m, 1H), 2.14 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1, 134.2, 132.7, 130.8, 130.2, 129.1, 126.9, 126.2, 125.5, 124.0, 123.5, 89.0, 84.8, 64.6, 23.4, 21.3. Light brown oil. HRMS (EI) for $C_{18}H_{16}O_2$ (M) Calcd: 264.1150. Found: 264.1152.

1-([1,1′-Biphenyl]-2-yl)-4-methylpent-4-en-2-yn-1-yl Acetate, ***5o:*** 148 mg, 51% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (m, 1H), 7.50−7.29 (m, 8H), 6.52 (s, 1H), 5.36 (s, 1H), 5.28 (m, 1H), 2.01 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.4, 141.8, 140.2, 135.2, 130.4, 129.4, 128.9, 128.5, 128.4, 128.1, 127.8, 126.3, 123.2, 88.5, 85.5, 64.1, 23.4, 21.1. Brown oil. HRMS (EI) for $C_{20}H_{18}O_2$ (M) Calcd: 290.1307. Found: 290.1301.

1-(2′,4′-Difluoro-[1,1′-biphenyl]-2-yl)-4-methylpent-4-en-2-yn-1-yl Acetate, ***5p:*** 157 mg, 48% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (dd, 1H, *J* = 7.6, 1.5 Hz), 7.52−7.40 (m, 2H), 7.30−7.22 (m, 2H), 6.98−6.88 (m, 2H), 6.39 (s, 1H), 5.33 (s, 1H), 5.27 (m, 1H), 2.00 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 163.1 (dd, *J* = 228.0, 11.6 Hz), 159.9 (dd, *J* = 228.0, 11.6 Hz), 136.2, 134.4, 132.6, 131.0, 129.0, 128.7, 126.2, 123.3, 111.6 (dd, *J* = 21.1, 3.0 Hz,), 111.3, 104.3 (t, *J* = 25.7 Hz), 88.5, 84.7, 64.1, 63.8, 23.3, 21.0. Brown oil. HRMS (EI) for $C_{20}H_{16}F_2O_2$ (M) Calcd: 326.1118. Found: 326.1109.

2-Methyl-5-phenylpent-1-en-4-yn-3-yl Acetate, ***10a:*** 174 mg, 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (m, 2H), 7.31 (m, 3H), 6.07 (s, 1H), 5.29 (s, 1H), 5.05 (s, 1H), 2.01 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 140.6, 132.1, 129.0, 128.5, 122.4, 115.2, 86.5, 85.0, 57.8, 21.3, 18.6. Colorless liquid. HRMS (EI) for $C_{14}H_{14}O_2$ (M) Calcd: 214.0994. Found: 214.0999.

2-Methylnon-1-en-4-yn-3-yl Acetate, ***10b:*** 159 mg, 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.80 (s, 1H), 5.18 (s, 1H), 4.96 (s, 1H), 2.22 (td, 2H, *J* = 6.9, 1.8 Hz), 2.09 (s, 3H), 1.82 (s, 3H), 1.49 (m, 2H), 1.38 (m, 2H), 0.89 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.0, 141.1, 114.5, 87.6, 76.1, 67.8, 30.7, 22.1, 21.3, 18.6, 18.5, 13.8. Colorless liquid. HRMS (M) for $C_{12}H_{18}O_2$ Calcd: 194.1307. Found: 194.1311.

General Procedure for $[RhCl(CO)_2]_2$-Catalyzed [4 + 1] Cycloaddition of the Alkenyl Propargylic Acetates with CO. Under nitrogen, an alkenyl propargyl acetate **5** or **10** (0.20 mmol) and $[RhCl(CO)_2]_2$ (7.8 mg, 0.10 equiv) were weighed into a tared two-neck round-bottom flask and dissolved with DCE (5 mL). The flask was fitted with a reflux condenser fit with a septum, and the side arm of the flask was also fitted with a septum. The solution was bubbled with CO gas for 2 min through the side arm and a vent needle in the septum of the reflux condenser. The solution was then placed under a CO atmosphere by using a balloon. The reaction mixture was heated at reflux until the reaction was determined to be complete by TLC (4−24 h). The resulting solution was cooled to room temperature, and the CO was released cautiously in the hood. The reaction mixture was concentrated, and the *E*/*Z* ratio of the products was determined by ^{1}H NMR analysis before the crude product was purified by flash column chromatography eluted with hexanes/ethyl acetate.

Characterizations of the [4 + 1] Cycloaddition Products 4, 6, and 11. *E-2-Methyl-5-octylidene-4-oxocyclopent-1-en-1-yl But-3-enoate,* ***4:*** <20 mg, < 40% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.18 (t, 1H, *J* = 8.1 Hz), 6.01 (m, 1H), 5.29 (m,1H), 5.25 (m, 1H), 3.31 (dt, 2H, *J* = 7.2, 1.2 Hz), 2.97 (d, 2H, *J* = 0.9 Hz), 2.24 (q, 2H, *J* = 7.5 Hz), 1.77 (s, 3H), 1.40 (m, 2H), 1.26 (m, 8H), 0.87 (t, 3H, *J* = 6.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.9, 168.6, 145.4, 132.5, 131.6, 129.3, 127.8, 120.0, 44.5, 39.1, 32.0, 29.6, 29.4, 29.3, 27.2, 22.9, 14.3, 12.8. Brown oil. HRMS (EI) for $C_{18}H_{26}O_3$ (M) Calcd: 290.1882. Found: 290.1879.

5-(Cyclohexylmethylene)-2-methyl-4-oxocyclopent-1-en-1-yl Acetate, ***6a:*** 47 mg, 95% yield. *E*-**6a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.03 (d, 1H, *J* = 10.5 Hz), 2.96 (s, 2H), 2.42 (m, 1H) 2.29 (s, 3H), 1.78 (s, 3H), 1.65 (m, 4H), 1.19 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.5, 168.0, 145.3, 136.1, 130.8, 127.9, 44.5, 36.6, 32.9, 26.0, 25.9, 20.8, 12.8. White solid, mp 98−100 °C. HRMS (EI) for $C_{15}H_{20}O_3$ (M) Calcd: 248.1412. Found: 248.1410.

2-Methyl-4-oxo-5-propylidenecyclopent-1-en-1-yl Acetate, ***6b:*** 36 mg, 92% yield. *E*-**6b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.16 (t, 1H, *J* = 8.1 Hz), 2.96 (s, 2H), 2.27 (m, 5H) 1.78 (s, 3H), 1.05 (t, 3H, *J* = 7.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.9, 168.1, 145.5, 132.6, 132.1, 127.8, 44.5, 20.8, 20.5, 13.9., 12.7. Colorless oil. HRMS (EI) for $C_{11}H_{14}O_3$ (M) Calcd: 194.0943. Found: 194.0934. *Z*-**6b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.62 (t, 1H, *J* = 8.0 Hz), 2.93 (s, 2H), 2.70 (m, 5H), 2.29 (s, 3H), 1.77 (s, 3H), 1.03 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.3, 167.9, 145.3, 135.1, 131.5, 124.1, 45.3, 20.7,

dx.doi.org/10.1021/jo3009403 | J. Org. Chem. XXXX, XXX, XXX−XXX

20.6, 13.9., 12.7. Colorless oil. HRMS (EI) for $C_{11}H_{14}O_3$ (M) Calcd: 194.0943. Found: 194.0948.

5-Cyclohexylidene-2-methyl-4-oxocyclopent-1-en-1-yl Acetate, ***6c:*** 23 mg, 50% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.96 (t, 2H, J = 5.6 Hz), 2.90 (s, 2H), 2.41 (t, 2H, J = 5.9 Hz), 2.24 (s, 3H), 1.72 (s, 3H), 1.61 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.1, 168.1, 152.1, 145.9, 124.8, 123.9, 45.5, 30.8, 29.7, 28.9, 28.8, 26.5, 21.0, 12.5. Colorless oil. HRMS (EI) for $C_{14}H_{18}O_3$ (M) Calcd: 234.1256. Found: 234.1261.

5-Benzylidene-2-methyl-4-oxocyclopent-1-en-1-yl Acetate, ***6d:*** 41 mg, 85% yield. *E*-**6d**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 (d, 2H, J = 7.2 Hz), 7.34 (t, 2H, J = 7.2 Hz), 7.31 (t, 1H, J = 6.9 Hz), 7.13 (s, 1H), 3.08 (d, 2H, J = 1.2 Hz), 1.87 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.9, 167.5, 145.6, 134.4, 131.7, 130.7, 129.9, 128.7, 128.2, 127.5, 44.4, 20.3, 13.0. Colorless oil. HRMS (EI) for $C_{15}H_{14}O_3$(M) Calcd: 242.0943. Found: 242.0950. *Z*-**6d**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (m, 2H), 7.38−7.32 (m, 3H), 6.34 (s, 1H), 3.04 (s, 2H), 2.37(s, 3H), 1.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.8, 167.5, 146.2, 134.0, 131.3, 130.8, 129.6, 129.0, 128.1, 125.8, 45.0, 20.5, 12.9. Colorless oil. HRMS (EI) for $C_{15}H_{14}O_3$ (M) Calcd: 242.0943. Found: 242.0938.

2-Methyl-5-(4-methylbenzylidene)-4-oxocyclopent-1-en-1-yl Acetate, ***6e:*** 31 mg, 61% yield. *E*-**6e**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (d, 2H, J = 8.4 Hz), 7.14 (d, 2H, J = 7.8 Hz), 7.10 (s, 1H), 3.07 (d, 2H, J = 1.2 Hz), 2.36 (s, 3H), 1.88 (s, 3H), 1.86 (d, 3H, J = 0.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.9, 167.3, 145.4, 138.8, 131.3, 130.8, 129.94, 129.9, 128.8, 127.6, 44.2, 21.4, 20.2, 12.7. White solid, mp 138−139 °C. HRMS (EI) for $C_{16}H_{16}O_3$(M) Calcd: 256.1099. Found: 256.1104. *Z*-**6e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, 2H, J = 8.4 Hz), 7.17 (d, 2H, J = 7.8 Hz), 6.31 (s, 1H), 3.03 (s, 2H), 2.37 (s, 6H), 1.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.1, 167.8, 146.5, 140.3, 131.6, 131.2, 130.7, 129.4, 129.1, 125.2, 45.3, 21.8, 20.7, 13.1. Yellow solid, mp 85−86 °C. HRMS (EI) for $C_{16}H_{16}O_3$ (M) Calcd: 256.1099. Found: 256.1101.

2-Methyl-5-(2-methylbenzylidene)-4-oxocyclopent-1-en-1-yl Acetate, ***6f:*** 44 mg, 86% yield. *E*-**6f**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16 (m, 5H), 3.08 (d, 2H, J = 0.9 Hz), 2.25 (s, 3H), 1.84 (s, 3H), 1.52 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.9, 167.6, 145.6, 137.9, 133.7, 132.2, 130.3, 129.9, 129.6, 128.6, 126.6, 125.2, 44.4, 20.3, 19.7, 12.8. Colorless oil. HRMS (EI) for $C_{16}H_{16}O_3$ (M) Calcd: 256.1099. Found: 256.1091.

5-(4-Chlorobenzylidene)-2-methyl-4-oxocyclopent-1-en-1-yl Acetate, ***6g:***[19] 38 mg, 69% yield. *E*-**6g**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (m, 4H), 7.04 (s, 1H), 3.09 (s, 2H), 1.88 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.2, 167.0, 145.1, 134.4, 132.6, 132.1, 131.8, 130.1, 128.1, 125.5, 44.0, 20.0, 12.7. Brown oil. HRMS (EI) for $C_{15}H_{13}ClO_3$ (M) Calcd: 276.0553. Found: 276.0558. *Z*-**6g**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, 2H, J = 8.4 Hz), 7.33 (m, 2H), 6.27 (s, 1H), 3.04 (s, 2H), 2.37 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.7, 167.4, 146.1, 135.3, 132.5, 131.6, 131.3, 128.2, 127.2, 126.4, 44.9, 20.3, 12.9. Brown oil. HRMS (EI) for $C_{15}H_{13}ClO_3$ (M) Calcd: 276.0553. Found: 276.0558.

5-(2,6-Dichlorobenzylidene)-2-methyl-4-oxocyclopent-1-en-1-yl Acetate, ***6h:*** 52 mg, 84% yield. *E*-**6h**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, 2H, J = 7.8 Hz), 7.19 (t, 1H, J = 8.1 Hz), 6.85 (s, 1H), 3.10 (s, 2H), 1.84 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.7, 167.3, 145.3, 135.5, 133.0, 132.5, 129.5, 127.8, 119.9, 44.5, 19.4, 13.1. White solid, mp 150−151 °C. HRMS (ESI) for $C_{15}H_{13}Cl_2O_3$ (MH+) Calcd: 311.0242. Found: 311.0239. *Z*-**6h**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 (d, 2H, J = 7.8 Hz), 7.16 (t, 1H, J = 7.8 Hz), 6.23 (s, 1H), 2.99 (d, 2H, J = 1.2 Hz), 2.36 (s, 3H), 1.88 (d, 3H, J = 1.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 197.5, 167.3, 145.24, 134.7, 134.6, 132.7, 129.8, 129.1, 127.6, 119.5, 44.6, 20.4, 13.1. Yellow solid, mp 85−87 °C. HRMS (ESI) for $C_{15}H_{13}Cl_2O_3$ (MH+) Calcd: 311.0242. Found: 311.0239.

2-Methyl-5-(4-nitrobenzylidene)-4-oxocyclopent-1-en-1-yl Acetate, ***6i:***[19] 52 mg, 90% yield. *E*-**6i**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, 2H, J = 8.7 Hz), 7.55 (d, 2H, J = 8.4 Hz), 7.06 (s, 1H), 3.13 (s, 2H), 1.90 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.8, 167.1, 147.5, 145.4, 141.3, 134.2, 131.5, 130.7, 124.0, 123.4, 44.3, 20.3, 13.4. Yellow solid. HRMS (EI) for $C_{15}H_{13}NO_5$ (M) Calcd: 287.0794. Found: 287.0786. *Z*-**6i**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, 2H, J = 7.5 Hz), 8.03 (d, 2H, J = 8.7 Hz), 6.34 (s, 1H), 3.08 (s, 2H), 2.38 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.5, 167.6, 148.0, 145.4, 140.3, 134.0, 131.5, 130.7, 125.5, 123.5, 45.1, 20.7, 13.5. Yellow solid. HRMS (EI) for $C_{15}H_{13}NO_5$ (M) Calcd: 287.0794. Found: 287.0786.

2-Methyl-5-(2-nitrobenzylidene)-4-oxocyclopent-1-en-1-yl Acetate, ***6j:*** 55 mg, 96% yield. *E*-**6j**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, 1H, J = 7.5 Hz), 7.61 (t, 1H, J = 7.8 Hz), 7.51 (t, 1H, J = 7.2 Hz), 7.34 (m, 2H), 3.09 (s, 2H), 1.81 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.8, 167.3, 148.0, 144.9, 133.0, 132.8, 132.4, 132.1, 130.9, 129.1, 125.0, 122.8, 44.4, 19.8, 13.1. Yellow solid, mp 65−67 °C. HRMS (EI) for $C_{15}H_{13}NO_5$ (M) Calcd: 287.0794. Found: 287.0801. *Z*-**6j**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, 1H, J = 8.4 Hz), 7.09 (d, 1H, J = 7.5 Hz), 7.59 (t, 1H, J = 7.5 Hz), 7.48 (t, 1H, J = 7.8 Hz), 6.73 (s, 1H), 3.02 (s, 2H), 2.35 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.5, 167.8, 147.8, 146.0, 132.9, 132.7, 132.6, 130.0, 129.5, 129.0, 124.8, 123.3, 45.2, 20.7, 13.3. Brown oil. HRMS (EI) for $C_{15}H_{13}NO_5$ (M) Calcd: 287.0794. Found: 287.0790.

2-Methyl-4-oxo-5-(4-(trifluoromethyl)benzylidene)cyclopent-1-en-1-yl Acetate, ***6k:***[19] 53 mg, 85% yield. *E*-**6k**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, 2H, J = 8.1 Hz), 7.48 (d, 2H, J = 8.1 Hz), 7.09 (s, 1H), 3.10 (s, 2H), 1.88 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.0, 166.9, 145.1, 138.0, 133.0, 132.4, 130.7, 129.8 (m), 124.8 (m), 124.0 (q, J = 258.6 Hz), 44.0, 19.8, 12.8. Yellow solid. HRMS (ESI) for $C_{16}H_{14}F_3O_3$ (MH+) Calcd: 311.0895. Found: 311.0889. *Z*-**6k**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, 2H, J = 7.8 Hz), 7.60 (d, 2H, J = 7.8 Hz), 6.33 (s, 1H), 3.06 (s, 2H), 2.37 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.4, 167.4, 146.1, 137.2, 133.1, 130.2, 130.0, 128.0, 126.5, 124.8 (m), 124.1 (q, J = 258.6 Hz), 44.8, 20.3, 13.0. Yellow solid. HRMS (ESI) for $C_{16}H_{14}F_3O_3$ (MH +) Calcd: 311.0895. Found: 311.0891.

2-Methyl-4-oxo-5-(2-(trifluoromethyl)benzylidene)cyclopent-1-en-1-yl Acetate, ***6l:*** 51 mg, 82% yield. *E*-**6l**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, 1H, J = 7.5 Hz), 7.51 (t, 1H, J = 7.4 Hz), 7.43 (t, 1H, J = 7.5 Hz), 7.31 (d, 1H, J = 7.5 Hz), 7.26 (s, 1H), 3.10 (s, 2H), 1.83 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.9, 166.9, 144.9, 133.5, 133.0, 132.2, 131.1, 130.7, 129.1 (q, J = 29.9 Hz), 128.0, 125.7 (q, J = 4.9 Hz), 123.7 (q, J = 272.2 Hz), 122.7, 44.0, 19.5, 12.8. Yellow solid, mp 92−93 °C. HRMS (ESI) for $C_{16}H_{14}F_3O_3$(MH +) Calcd: 311.0895. Found: 311.0894. *Z*-**6l**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, 1H, J = 7.8 Hz), 7.65 (d, 1H, J = 7.8 Hz), 7.51 (t, 1H, J = 7.8 Hz), 7.41 (t, 1H, J = 7.8 Hz), 6.64 (s, 1H), 3.03 (s, 2H), 2.35 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.1, 167.5, 146.0, 132.8, 132.1, 131.7, 131.0, 128.6, 128.4, 128.2, 125.6 (q, J = 5.2 Hz), 124.2 (q, J = 271.9 Hz), 123.2, 45.0, 20.3, 12.9. Brown oil. HRMS (ESI) for $C_{16}H_{14}F_3O_3$ (MH+) Calcd: 311.0895. Found: 311.0898.

2-Methyl-5-(naphthalen-2-ylmethylene)-4-oxocyclopent-1-en-1-yl Acetate, ***6m:*** 51 mg, 88% yield. *E*-**6m**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.81 (m, 3H, J = 8.7 Hz), 7.50 (m, 3H), 7.28 (s, 1H), 3.12 (s, 2H), 1.89 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.9, 167.4, 145.7, 133.3, 133.1, 131.9, 131.8, 131.0, 129.7, 128.4, 127.9, 127.8, 127.6, 127.5, 127.0, 126.8, 44.5, 20.3, 13.1. Yellow solid, mp 49−51 °C. HRMS (EI) for $C_{19}H_{16}O_3$ (M) Calcd: 292.1099. Found: 292.1105. *Z*-**6m**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.11 (dd, 1H, J = 8.7, 1.8 Hz), 7.86 (m, 1H), 7.80 (m, 2H), 7.47 (m, 2H), 6.51 (s, 1H), 3.08 (s, 2H), 2.40 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.1, 167.8, 146.6, 134.0, 133.3, 132.0, 131.7, 131.5, 129.2, 129.0, 128.1, 127.8, 127.2, 126.4, 126.1, 45.3, 20.8, 13.2. Yellow solid, mp 90−91 °C. HRMS (EI) for $C_{19}H_{16}O_3$ (M) Calcd: 292.1099. Found: 292.1107.

2-Methyl-5-(naphthalen-1-ylmethylene)-4-oxocyclopent-1-en-1-yl Acetate, ***6n:*** 49 mg, 84% yield. *E*-**6n**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (m, 3H), 7.63 (s, 1H), 7.45 (m, 4H), 3.14 (s, 2H), 1.85 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.8, 167.4, 145.6, 133.4, 132.1, 131.7, 131.0, 129.8, 129.1, 128.5, 127.4, 126.9, 126.5, 125.5, 125.2, 124.9, 44.5, 19.7, 13.0. Brown oil. HRMS (EI) for $C_{19}H_{16}O_3$ (M) Calcd: 292.1099. Found: 292.1108.

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5-([1,1′-Biphenyl]-2-ylmethylene)-2-methyl-4-oxocyclopent-1-en-1-yl Acetate, ***6o:*** 52 mg, 82% yield. *E*-**6o**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40−7.32 (m, 9H), 6.93 (s, 1H), 3.07 (s, 2H), 1.90 (s, 3H), 1.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.7, 167.9, 142.7, 140.3, 132.5, 132.0, 130.8, 130.0, 129.9, 129.0, 128.4, 128.3, 127.8, 126.4, 44.5, 20.1, 12.8. Light yellow solid, mp 110−112 °C. HRMS (EI) for $C_{21}H_{18}O_3$ (M) Calcd: 318.1256. Found: 318.1249.

5-((2′,4′-Difluoro-[1,1′-biphenyl]-2-yl)methylene)-2-methyl-4-oxocyclopent-1-en-1-yl Acetate, ***6p:*** 52 mg, 73% yield. *E*-**6p**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (m, 4H), 7.16 (m, 1H), 6.87 (m, 3H), 3.04 (s, 2H), 1.87 (s, 3H), 1.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.5, 167.8, 163.0 (dd, J = 238.4, 12.0 Hz), 159.5 (dd, J = 238.9, 12.0 Hz), 145.5, 135.5, 133.6, 133.5, 133.4, 132.5, 130.8, 130.7, 130.6, 128.6, 127.3, 126.7, 111.4 (dd, J = 20.9, 11.3 Hz), 104.3 (t, J = 25.6 Hz) 44.4, 20.0, 12.9. Light yellow solid, mp 172−173 °C. HRMS (ESI) for $C_{21}H_{17}F_2O_3$ (MH+) Calcd: 355.1146. Found: 355.1148.

(3-Methyl-5-oxocyclopent-2-en-1-ylidene)(phenyl)methyl Acetate, ***11a:*** 27 mg, 56% yield. *Z*-**11a**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (m, 2H), 7.41 (m, 3H), 6.22 (m, 1H), 2.92 (s, 2H), 2.35 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.2, 169.1, 144.1, 143.1, 134.7, 129.8, 128.5, 128.1, 127.2, 126.1, 46.7, 20.9, 18.0. Brown oil. HRMS (EI) for $C_{15}H_{14}O_3$ (M) Calcd: 242.0943. Found: 242.0948.

1-(3-Methyl-5-oxocyclopent-2-en-1-ylidene)pentyl Acetate, ***11b:*** 33 mg, 74% yield. *Z*-**11b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.29 (m, 1H), 2.83 (m, 2H), 2.33 (t, 2H, J = 7.4 Hz), 2.26 (s, 3H), 1.95 (s, 3H), 1.52 (m, 2H), 1.37 (m, 2H), 0.91 (t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.9, 169.1, 149.0, 140.5, 127.2, 125.2, 47.1, 32.8, 28.5, 22.6, 21.1, 18.1, 14.0. Brown oil. HRMS (EI) for $C_{13}H_{18}O_3$ (M) Calcd: 222.1256. Found: 222.1261.

■ ASSOCIATED CONTENT

Supporting Information

Detailed synthesis and characterization of the compounds are provided. 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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■ REFERENCES

(1) (a) Frantz, D. E.; Fässler, R.; Tomooka, C. S.; Carreira, E. M. *Acc. Chem. Res.* **2000**, *33*, 373−381. (b) Pu, L. *Tetrahedron* **2003**, *59*, 9873−9886. (c) Cozzi, P. G.; Hilgraf, R.; Zimmermann, N. *Eur. J. Org. Chem.* **2004**, 4095−4105. (d) Lu, G.; Li, Y.-M.; Li, X.-S.; Chan, A. S. C. *Coord. Chem. Rev.* **2005**, *249*, 1736−1744. (e) Trost, B. M.; Weiss, A. H. *Adv. Synth. Catal.* **2009**, *351*, 963−983. (f) Gao, G.; Pu, L. *Sci. China: Chem.* **2010**, *53*, 21−35.

(2) (a) Tejedor, D.; López-Tosco, S.; Cruz-Acosta, F.; Méndez-Abt, G.; García-Tellado, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 2090−2098. (b) Guillarme, S.; Plé, K.; Banchet, A.; Liard, A.; Haudrechy, A. *Chem. Rev.* **2006**, *106*, 2355−2403. (c) Detz, R. J.; Henk Hiemstra, H.; van Maarseveen, J. H. *Eur. J. Org. Chem.* **2009**, 6263−6276.

(3) Selected applications of chiral propargylic alcohols in synthesis: (a) Trost, B. M.; Müller, T. J. J. *J. Am. Chem. Soc.* **1994**, *116*, 4985−4986. (b) Arcadi, A.; Cacchi, S.; Fabrizi, G.; Marinelli, F.; Pace, P. *Eur. J. Org. Chem.* **1999**, 3305−3313. (c) Marshall, J. A.; Chobanian, H. R.; Yanik, M. M. *Org. Lett.* **2001**, *3*, 3369−3372. (d) Alfonsi, M.; Arcadi, A.; Chiarini, M.; Marinelli, F. *J. Org. Chem.* **2007**, *72*, 9510−9517. (e) Crimmins, M. T.; Jung, D. K.; Gray, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 3146−3155. (f) Roethle, P. A.; Trauner, D. *Org. Lett.* **2006**, *8*, 345. (g) Trost, B. M.; Weiss, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 7664−7666. (h) Imagawa, H.; Saijo, H.; Kurisaki, T.; Yamamoto, M. K.; Fukuyama, Y.; Nishizawa, M. *Org. Lett.* **2009**, *11*, 1253−1255.

(4) Using Rh: (a) Li, X.; Zhang, M.; Shu, D.; Robichaux, P. J.; Huang, S.; Tang, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 10421−10424. (b) Shu, D.; Li, X.; Zhang, M.; Robichaux, P. J.; Tang, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 1346−1349. (c) Shibata, Y.; Noguchi, K.; Tanaka, K. *J. Am. Chem. Soc.* **2010**, *132*, 7896−7898. (d) Brancour, C.; Fukuyama, T.; Ohta, Y.; Ryu, I.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. *Chem. Commun.* **2010**, *46*, 5470−5472. (e) Li, X.; Huang, S.; Schienebeck, C. M.; Shu, D.; Tang, W. *Org. Lett.* **2012**, *14*, 1584−1587. (f) Shu, X. Z.; Huang, S. Y.; Shu, D. X.; Guzei, I. A.; Tang, W. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 8153−8156. (g) Zhang, D.-H.; Shi, M. *Tetrahedron Lett.* **2012**, *53*, 487−490. (h) Shibata, Y.; Noguchi, K.; Tanaka, K. *Org. Lett.* **2010**, *12*, 5596−5599. (i) Shibata, Y.; Noguchi, K.; Tanaka, K. *J. Am. Chem. Soc.* **2010**, *132*, 7896−7898. (j) Fukuyama, T.; Ohta, Y.; Brancour, C.; Miyagawa, K.; Ryu, I.; Dhimane, A.; Fensterbank, L.; Malacria, M. *Chem.—Eur. J.* **2012**, *18*, 7243−7247.

(5) Using Au: (a) Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 18002−18003. (b) Gorin, D. J.; Dube, P.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 14480−14481. (c) Gorin, D. J.; Watson, I. D. G.; Toste, F. D. *J. Am. Chem. Soc.* **2008**, *130*, 3736−3737. (d) Li, G.; Zhang, G.; Zhang, L. *J. Am. Chem. Soc.* **2008**, *130*, 3740−3741. (e) Marion, N.; de Frèmont, P.; Lemière, G.; Stevens, E. D.; Fensterbank, L.; Malacria, M.; Nolan, S. P. *Chem. Commun.* **2006**, 2048−2050. (f) Zhang, L. *J. Am. Chem. Soc.* **2005**, *127*, 16804−16805. (g) Marion, N.; Díez-Gonzàlez, S.; de Frèmont, P.; Noble, A. R.; Nolan, S. P. *Angew.Chem., Int. Ed.* **2006**, *45*, 3647−3650. (h) Mamane, V.; Gress, T.; Krause, A.; Fürstner, A. *J. Am. Chem. Soc.* **2004**, *126*, 8654−8655. (i) Zhang, D.-H.; Yao, L.-F.; Wei, Y.; Shi, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 2583−2587.

(6) Using Pt: (a) Mainetti, E.; Mouries, V.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2132−2135. (b) Harrak, Y.; Blaszykowski, C.; Bernard, M.; Cariou, K.; Mainetti, E.; Mouriès, V.; Dhimane, A. -L.; Fensterbank, L.; Malacria, M. *J. Am. Chem. Soc.* **2004**, *126*, 8656−8657. (c) Prasad, B. A. B.; Yoshimoto, F. K.; Sarpong, R. *J. Am. Chem. Soc.* **2005**, *127*, 12468−12469. (d) Pujanauski, B. G.; Prasad, B. A. B.; Sarpong, R. *J. Am. Chem. Soc.* **2006**, *128*, 6786. (e) Ji, K.-G.; Shu, X.-Z.; Chen, J.; Zhao, S.-C.; Zheng, Z.-J.; Lu, L.; Liu, X.-Y.; Liang, Y. M. *Org. Lett.* **2008**, *10*, 3919−3922. (f) Cho, E. J.; Kim, M.; Lee, D. *Org. Lett.* **2006**, *8*, 5413−5416. (g) Zheng, H.; Xie, X. G.; Yang, J.; Zhao, C. G.; Jing, P.; Fang, B. W.; She, X. G. *Org. Biomol. Chem.* **2011**, *9*, 7755−7762.

(7) Using Ru: (a) Miki, K.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2003**, *68*, 8505−8513. (b) Tenaglia, A.; Marc, S. *J. Org. Chem.* **2006**, *71*, 3569−3575. (c) Kikuchi, H.; Uno, M.; Takahashi, S. *Chem. Lett.* **1997**, 1273−1274. (d) Villeneuve, K.; Tam, W. *Organometallics* **2006**, *25*, 843−848.

(8) Using Pd: (a) Rautenstrauch, V. *J. Org. Chem.* **1984**, *49*, 950−952. (b) Mandai, T.; Tsuji, J.; Tsujiguchi, Y.; Saito, S. *J. Am. Chem. Soc.* **1993**, *115*, 5865−5866. (c) Kato, K.; Nouchi, H.; Ishikura, K.; Takaishi, S.; Motodate, S.; Tanaka, H.; Okudaira, K.; Mochida, T.; Nishigaki, R.; Shigenobu, K.; Akita, H. *Tetrahedron* **2006**, *62*, 2545−2554. (d) Using Pd(II) and Hg(II): Caruana, P. A.; Frontier, A. J. *Tetrahedron* **2007**, *63*, 10646−10656. (e) Kato, K.; Teraguchi, R.; Yamamura, S.; Mochida, T.; Akita, H.; Peganova, T. A.; Vologdin, N. V.; Gusev, O. V. *Synlett* **2007**, 638−642. (f) Kato, K.; Teraguchi, R.; Motodate, S.; Uchida, A.; Mochida, T.; Peganova, T. A.; Vologdin, N. V.; Akita, H. *Chem. Commun.* **2008**, 3687−3689.

(9) (a) Using Re and W: Saito, K.; Onizawa, Y.; Kusama, H.; Iwasawa, N. *Chem.—Eur. J.* **2010**, *16*, 4716−4720. (b) Using Cu, Ag, and Au: Schwier, T.; Sromek, A. W.; Yap, D. M. L.; Chernyak, D.; Gevorgyan, V. *J. Am. Chem. Soc.* **2007**, *129*, 9868−9878. (c) Using Pt and Cu: Barluenga, J.; Riesgo, L.; Vicente, R.; López, L. A.; Tomás, M. *J. Am. Chem. Soc.* **2007**, *129*, 7772−7773. (d) Using Au and Pt: Brabander, J. K. D.; Liu, B.; Qian, M. *Org. Lett.* **2008**, *10*, 2533−2536.

(e) Using Ti: Zhang, Z.; Shi, M. *Tetrahedron Lett.* **2011**, *52*, 6541−6544.
(10) Reviews: (a) Marco-Contelles, J.; Soriano, E. *Chem.—Eur. J.* **2007**, *13*, 1350−1357. (b) Marion, N.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2750−2752.
(11) (a) Rajaram, A. R.; Pu, L. *Org. Lett.* **2006**, *8*, 2019−2021. (b) Zhou, L.-H.; Yu, X.-Q.; Pu, L. *J. Org. Chem.* **2009**, *74*, 2013−2017. (c) Yang, Y.; Turlington, M.; Yu, X.-Q.; Pu, L. *Chem.—Eur. J.* **2009**, *15*, 5104−5107.
(12) Yang, Y.; Turlington, M.; Yu, X.-Q.; Pu, L. *J. Org. Chem.* **2009**, *74*, 8681−8689.
(13) Turlington, M.; Yue, Y.; Yu, X.-Q.; Pu, L. *J. Org. Chem.* **2010**, *75*, 6941−6952.
(14) (a) Turlington, M.; Du, Y.-H.; Ostrum, S. G.; Santosh, V.; Wren, K.; Lin, T.; Sabat, M.; Pu, L. *J. Am. Chem. Soc.* **2011**, *133*, 11780−11794. (b) Turlington, M.; Pu, L. *Org. Lett.* **2011**, *13*, 4332−4335.
(15) Zhang, L.; Wang, S. *J. Am. Chem. Soc.* **2006**, *128*, 1442−1443.
(16) Tao, B.; Ruble, J. C.; Hoic, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 5091−5092.
(17) Cordonnier, M.-C.; Blanc, A.; Pale, P. *Org. Lett.* **2008**, *10*, 1569−1572.
(18) (a) Murakami, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2691−1694. (b) Murakami, M.; Itami, K.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 11672−11673. (c) Murakami, M.; Itami, K.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 2950−2951.
(19) The NMR spectra were obtained for the mixture of the *E* and *Z* products.

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