



Published in final edited form as:

Org Lett. 2015 October 16; 17(20): 5128–5131. doi:10.1021/acs.orglett.5b02665.

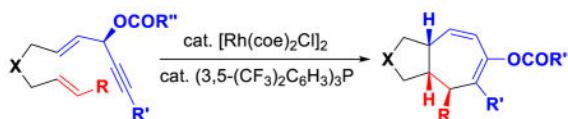
## Rhodium-Catalyzed Stereoselective Intramolecular [5 + 2] Cycloaddition of 3-Acyloxy-1,4-enyne and Alkene

Xing-zhong Shu<sup>†</sup>, Casi M. Schienebeck<sup>†</sup>, Xiaoxun Li<sup>†</sup>, Xin Zhou<sup>†</sup>, Wangze Song<sup>†</sup>, Lianqing Chen<sup>†</sup>, Ilia A. Guzei<sup>‡</sup>, and Weiping Tang<sup>\*,†,‡</sup>

<sup>†</sup>School of Pharmacy, University of Wisconsin-Madison, Madison, 53705, United States

<sup>‡</sup>Department of Chemistry, University of Wisconsin-Madison, Madison, 53706, United States

### Abstract



The first rhodium-catalyzed intramolecular [5 + 2] cycloaddition of 3-acyloxy-1,4-enyne and alkene was developed. The cycloaddition is highly diastereoselective in most cases. Various *cis*-fused bicyclo[5.3.0]decadienes were prepared stereoselectively. The chirality in the propargylic ester starting materials could be transferred to the bicyclic products with high efficiency. Electron-deficient phosphine ligand greatly facilitated the cycloaddition. Up to three new stereogenic centers could be generated. The resulting diene in the products could be hydrolyzed to enones, which allowed the introduction of more functional groups to the seven-membered ring.

The importance of seven-membered ring in organic synthesis<sup>1</sup> continues to stimulate the development of novel and efficient stereoselective methods.<sup>2</sup> Cycloaddition is one of the most efficient means to achieve high atom- and step-economic efficiency.<sup>3</sup> An important breakthrough in this area is the [5+2] cycloaddition of vinylcyclopropane (VCP) with alkyne, which can be catalyzed by Rh,<sup>4</sup> Ru,<sup>5</sup> Ni,<sup>6</sup> or Fe<sup>7</sup> for the formation of cycloheptadienes.<sup>8,9</sup> The [5+2] cycloaddition of VCP with less reactive alkene may generate multiple new stereogenic centers. However, it proved to be a much more challenging process and has only been realized by research groups of Wender<sup>10</sup> and Yu<sup>11</sup> using Rh catalysts.<sup>12</sup> We recently found that 3-acyloxy-1,4-enyne (ACE) could also serve as a 5-carbon component for Rh-catalyzed [5+2] cycloaddition with alkynes for the synthesis of cycloheptatrienes (Scheme 1).<sup>13</sup> A 1,2-acyloxy migration was accompanied with this [5+2] cycloaddition.<sup>14</sup> We herein report the first Rh-catalyzed highly stereoselective intramolecular [5+2] cycloaddition of ACEs and alkene for the synthesis of bicyclo[5.3.0]decane carbon skeletons, which are present in numerous bioactive

Corresponding Author: weiping.tang@wisc.edu.

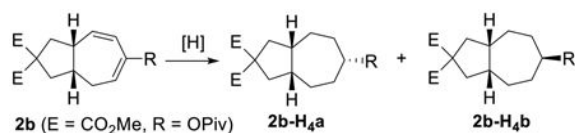
Supporting Information

Detailed experimental procedures, characterization data, and spectra (<sup>1</sup>H, <sup>13</sup>C NMR, IR, HRMS and X-ray). This material is available free of charge via the Internet at <http://pubs.acs.org>.

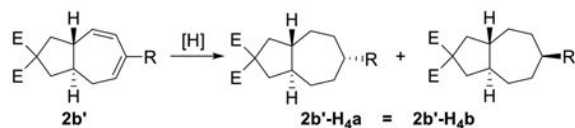
sesquiterpenes and diterpenes (Scheme 1).<sup>1</sup> This new reaction complements existing methods for the preparation of highly functionalized seven-membered rings.

No desired cycloaddition product was observed when substrate **1a** was treated with cationic rhodium catalyst (entry 1, Table 1). The addition of various ligands did not result in any cycloaddition product. Gratifyingly, a 63% yield of [5+2] cycloaddition product **2a** was obtained in the presence of Wilkinson's catalyst at 80 °C (entry 2). Other neutral Rh(I) complexes such as [Rh(cod)Cl]<sub>2</sub> or [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> provided either no product or lower yield in the absence of any phosphine ligand (entries 3 and 4). We then examined the effect of phosphine ligands. While the addition of the (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>P ligand shut down the reaction (entry 5), the (*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P ligand was beneficial (entry 6). Finally, the combination of [Rh(cod)Cl]<sub>2</sub> and [3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>3</sub>P ligand afforded the desired cycloaddition product in 80% isolated yield (entry 7). Lower yields were obtained in other solvents or by running the reaction at lower temperatures (entries 8 and 9). Switching the metal complex to [Rh(coe)<sub>2</sub>Cl]<sub>2</sub> slightly improved the yield (entry 10).

Having the optimized conditions in hand, we next investigated the scope of this [5+2] cycloaddition with alkenes (Table 2). Cycloaddition product **2b** with an all carbon linker was isolated in a 82% yield. The diene moiety in product **2b** could be completely reduced to afford a mixture of two diastereomeric isomers in a 1:1 ratio as shown in eq. 1. For *trans*-fused cycloaddition product **2b'**, only one stereoisomer would be expected after hydrogenation as shown in eq. 2. The relative stereochemistry of bicyclic compound **2b** was therefore assigned as the *cis*-configuration.<sup>10</sup>



(1)



(2)

The yield of cycloaddition product was slightly increased when the pivalate in **1c** was changed to *para*-dimethylamino-benzoate in **1d** (entry 3).<sup>15</sup> Similarly, the yield of product **2f** was slightly higher than that of product **2e** (entries 4 and 5) but lower than **2b**, presumably due to the Thorpe-Ingold effect.<sup>16</sup> The yield of cycloaddition for acetate substrate **1g** with a sulfonamide tether (entry 6) was as good as the corresponding pivalate substrate **1a** in Table 1. Substrate **1h** with a bis-nitrile tether also worked well (entry 7).

Propargylic esters with an internal alkyne generally prefer to undergo 1,3-acyloxy migration to form allene intermediates in the presence of rhodium(I) catalysts.<sup>17</sup> An electron-withdrawing group such as ester, ketone or halogen on the alkyne may switch the regioselectivity back to 1,2-acyloxy migration. This was demonstrated by the successful Rh-catalyzed [5+2] cycloadditions of this type of electron-deficient ACEs and alkynes.<sup>13</sup> We were pleased to find that ACEs in substrates **1i**, **1j**, and **1k** also underwent [5+2] cycloadditions with the tethered alkenes (entries 8–10). A small amount of isomeric diene products was observed in these cases. We also found that a free hydroxyl group could be tolerated in the tether region (entry 11).

Catalytic asymmetric [5+2] cycloaddition of vinylcyclopropanes with alkenes or alkynes is a very challenging reaction.<sup>18</sup> Highly enantioselective processes only appeared recently using chiral phosphine ligands.<sup>10b,19</sup> Inspired by Toste's work on Au-catalyzed Rautenstrauch rearrangement<sup>20</sup> of enantio-enriched ACEs to cyclopentenones<sup>21</sup> through a center-to-helix-to-center chirality transfer mechanism,<sup>22</sup> we demonstrated that it was also possible to transfer the chirality from ACEs to bicyclic products in Rh-catalyzed intramolecular [5+2] cycloaddition of ACEs and alkynes.<sup>13c</sup> If a similar process can be realized for the cycloaddition between ACE and alkene, we will then be able to access highly valuable enantio-enriched 5–7 bicyclic products with multiple stereogenic centers from readily available starting materials. Substrates **1b**, **1m**, and **1n** were easily prepared with high optical purity from the corresponding propargylic alcohols (Scheme 2). The chirality in these substrates could be transferred to the cycloaddition products efficiently. The *ees* of bicyclic products **2b**, **2m**, and **2n** ranged from 86% to 90%. Only one diastereomer was observed in all three cases. The absolute and relative stereochemistry of product **2n** was confirmed by X-ray analysis (CCDC977964).

It has been shown that Rh-catalyzed [5+2] cycloaddition of VCPs and alkenes works with substrates bearing a 1,1-disubstituted olefin but not a 1,2-disubstituted olefin as the 2-carbon component.<sup>10a,18</sup> In our case, no reaction occurred for substrate **3a**, while a complex mixture was observed for substrate **3b** (Scheme 3). Interestingly, substrates with a styrene moiety participated in the cycloaddition.<sup>23</sup> Bicyclic compounds with three new stereogenic centers were prepared diastereoselectively in all three cases (*dr* > 20:1). The relative stereochemistry of the three stereogenic centers was assigned based on nOe analysis.

Although only styrene-type disubstituted alkenes participated in the cycloaddition reaction, the diene moiety in all products is essentially a masked enone, which may allow for the introduction of diverse functional groups and substituents to the seven-membered ring. Indeed, the pivalate group in cycloaddition product **2b** was hydrolyzed to afford enone **5**, which could undergo diastereoselective conjugate addition with carbon or sulfur nucleophiles to yield substituted bicyclo[5.3.0]decanes **6** and **7**, respectively (Scheme 4).

We also found that no cross-over product **2b'** or **2g'** was formed under standard conditions when a mixture of compounds **1b** and **1g** was employed as the substrate in a ratio of 1:1. This suggests that the acyloxy group does not completely dissociate from the enyne substrate.

The mechanism for the Rh-catalyzed [5+2] cycloaddition of ACEs with alkenes is proposed in Scheme 6. Recent DFT calculations suggested that coordination of the Rh catalyst anti to the acyloxy group on the ACE was preferred as shown in complex **8**.<sup>24</sup> The Rh catalyst can then promote 1,2-acyloxy migration and oxidative cyclization to form metallacyclohexadiene intermediate **9**. Insertion of the tethered alkene to this metallacycle may afford intermediate **10**. Reductive elimination of metallacyclooctadiene **10** can then produce cycloheptadiene product **11**. This mechanism is consistent with the observed absolute stereochemistry of propargylic ester **1n** and product **2n**, which was confirmed by X-ray structure.

In summary, we have demonstrated for the first time that ACEs can serve as the 5-carbon synthon in Rh-catalyzed intra-molecular [5+2] cycloadditions with less reactive alkenes. The chirality transfer from readily available optically pure propargylic esters to cycloaddition products was also shown to be feasible for this new [5+2] cycloaddition. The 2-carbon alkene component could be either a terminal or a 1,2-disubstituted alkene with an aryl substituent, which produced products with three new stereogenic centers.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

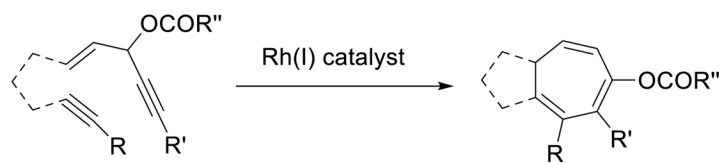
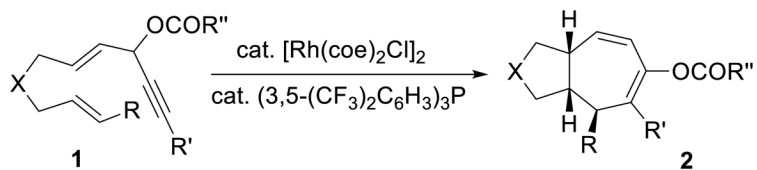
## Acknowledgments

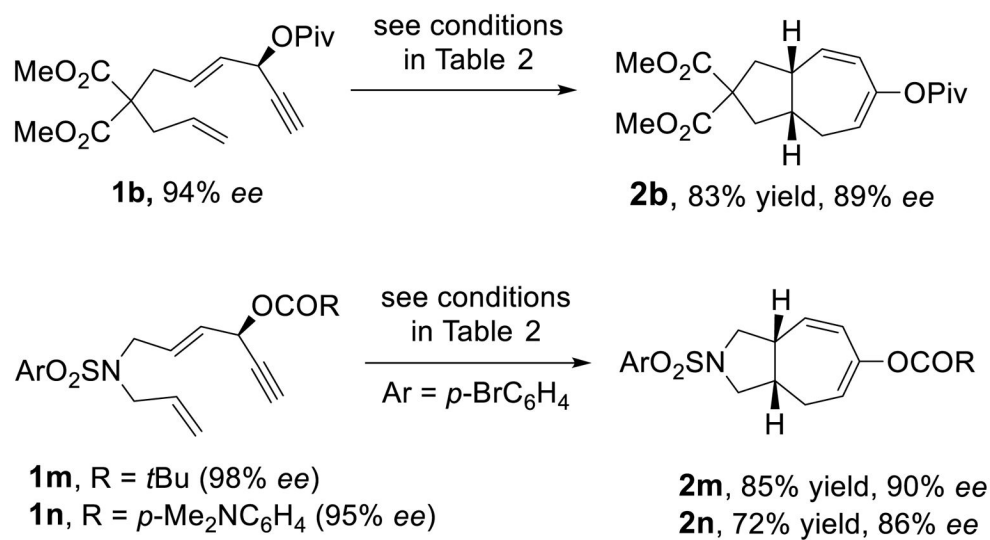
We thank the NIH (R01GM088285), NSF (CHE-1464754) and the University of Wisconsin for funding. L. C. thanks the Chinese Scholarship Council for financial support.

## References

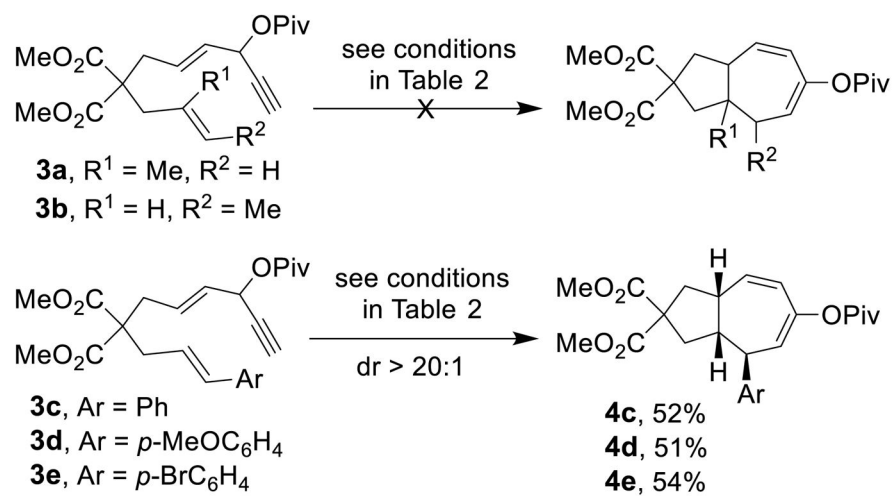
1. a) Battiste MA, Pelphrey PM, Wright DL. *Chem Eur J.* 2006; 12:3438. [PubMed: 16402402] b) Butenschön H. *Angew Chem Int Ed.* 2008; 47:5287.c) Foley DA, Maguire AR. *Tetrahedron.* 2010; 66:1131.
2. a) Harmata M. *Chem Commun.* 2010; 46:8886.b) Harmata M. *Chem Commun.* 2010; 46:8904.c) Lohse AG, Hsung RP. *Chem Eur J.* 2011; 17:3812. [PubMed: 21384451] d) Pellissier H. *Adv Synth Catal.* 2011; 353:189.e) Ylijoki KEO, Stryker JM. *Chem Rev.* 2013; 113:2244. [PubMed: 23153111]
3. a) Trost BM. *Science.* 1991; 254:1471. [PubMed: 1962206] b) Trost BM. *Angew Chem Int Ed.* 1995; 34:259.c) Wender PA, Verma VA, Paxton TJ, Pillow TH. *Acc Chem Res.* 2008; 41:40. [PubMed: 18159936] d) Wender PA, Miller BL. *Nature.* 2009; 460:197. [PubMed: 19587760]
4. a) Wender PA, Takahashi H, Witulski B. *J Am Chem Soc.* 1995; 117:4720.b) Wender PA, Rieck H, Fuji M. *J Am Chem Soc.* 1998; 120:10976.c) Wender PA, Barzilay CM, Dyckman AJ. *J Am Chem Soc.* 2001; 123:179. [PubMed: 11273617]
5. a) Trost BM, Toste FD, Shen H. *J Am Chem Soc.* 2000; 122:2379.b) Trost BM, Shen HC. *Angew Chem Int Ed.* 2001; 40:2313.c) Trost BM, Shen HC, Horne DB, Toste FD, Steinmetz BG, Koradin C. *Chem Eur J.* 2005; 11:2577. [PubMed: 15736147]
6. Zuo G, Louie J. *J Am Chem Soc.* 2005; 127:5798. [PubMed: 15839672]
7. Fürstner A, Majima K, Martin R, Krause H, Kattinig E, Goddard R, Lehmann CW. *J Am Chem Soc.* 2008; 130:1992. [PubMed: 18197669]
8. For computational studies on [5+2] cycloadditions involving VCPs, see: Yu ZX, Wender PA, Houk KN. *J Am Chem Soc.* 2004; 126:9154. [PubMed: 15281784] Yu ZX, Cheong PHY, Liu P, Legault CY, Wender PA, Houk KN. *J Am Chem Soc.* 2008; 130:2378. [PubMed: 18251468] Liu P, Cheong PHY, Yu ZX, Wender PA, Houk KN. *Angew Chem Int Ed.* 2008; 47:3939.Liu P, Sirois LE,

- Cheong PHY, Yu ZX, Hartung IV, Rieck H, Wender PA, Houk KN. *J Am Chem Soc.* 2010; 132:10127. [PubMed: 20586494] Xu X, Liu P, Lesser A, Sirois LE, Wender PA, Houk KN. *J Am Chem Soc.* 2012; 134:11012. [PubMed: 22668243] Hong X, Liu P, Houk KN. *J Am Chem Soc.* 2013; 135:1456. [PubMed: 23273283] Hong X, Trost BM, Houk KN. *J Am Chem Soc.* 2013; 135:6588. [PubMed: 23611430]
9. For selected synthetic applications of Rh-catalyzed [5+2] cycloadditions, see: Wender PA, Fuji M, Husfeld CO, Love JA. *Org Lett.* 1999; 1:137. Wender PA, Zhang L. *Org Lett.* 2000; 2:2323. [PubMed: 10930274] Wender PA, Bi FC, Brodney MA, Gosselin F. *Org Lett.* 2001; 3:2105. [PubMed: 11418060] Wender PA, Gamber GG, Scanio MJC. *Angew Chem Int Ed.* 2001; 40:3895. Ashfeld BL, Martin SF. *Org Lett.* 2005; 7:4535. [PubMed: 16178577] Ashfeld BL, Martin SF. *Tetrahedron.* 2006; 62:10497. Trost BM, Hu Y, Horne DB. *J Am Chem Soc.* 2007; 129:11781. [PubMed: 17760442] Trost BM, Waser J, Meyer A. *J Am Chem Soc.* 2007; 129:14556. [PubMed: 17985906] Trost BM, Waser J, Meyer A. *J Am Chem Soc.* 2008; 130:16424. [PubMed: 18998641] Jiao L, Yuan C, Yu ZX. *J Am Chem Soc.* 2008; 130:4421. [PubMed: 18335933] Wender PA, Stemmler RT, Sirois LE. *J Am Chem Soc.* 2010; 132:2532. [PubMed: 20141136] Trost BM, Nguyen HM, Koradin C. *Tetrahedron Lett.* 2010; 51:6232. [PubMed: 21076637] For Rh-catalyzed intramolecular [5+2] cycloaddition of allenyl cyclopropanes with alkynes, see: Inagaki F, Sugikubo K, Miyashita Y, Mukai C. *Angew Chem Int Ed.* 2010; 49:2206. For related Rh-catalyzed hetero-[5+2] cycloadditions, see: Wender PA, Pedersen TM, Scanio MJC. *J Am Chem Soc.* 2002; 124:15154. [PubMed: 12487573] Feng JJ, Zhang J. *J Am Chem Soc.* 2011; 133:7304. [PubMed: 21524076] Feng JJ, Lin TY, Wu HH, Zhang J. *J Am Chem Soc.* 2015; 137:3787. [PubMed: 25763476]
10. a) Wender PA, Husfeld CO, Langkopf E, Love JA. *J Am Chem Soc.* 1998; 120:1940. b) Wender PA, Haustedt LO, Lim J, Love JA, Williams TJ, Yoon JY. *J Am Chem Soc.* 2006; 128:6302. [PubMed: 16683779]
11. Jiao L, Ye S, Yu ZX. *J Am Chem Soc.* 2008; 130:7178. [PubMed: 18479103]
12. For Rh-catalyzed [5+2] cycloaddition of VCPs with allenes, see: Wender PA, Glorius F, Husfeld CO, Langkopf E, Love JA. *J Am Chem Soc.* 1999; 121:5348. Wegner HA, de Meijere A, Wender PA. *J Am Chem Soc.* 2005; 127:6530. [PubMed: 15869263]
13. a) Shu XZ, Huang S, Shu D, Guzei IA, Tang W. *Angew Chem Int Ed.* 2011; 50:8153. b) Shu XZ, Li X, Shu D, Huang S, Schienebeck CM, Zhou X, Robichaux PJ, Tang W. *J Am Chem Soc.* 2012; 134:5211. [PubMed: 22364320] c) Shu XZ, Schienebeck CM, Song W, Guzei IA, Tang W. *Angew Chem Int Ed.* 2013; 52:13601.
14. Shu XZ, Shu D, Schienebeck CM, Tang W. *Chem Soc Rev.* 2012; 41:7698. [PubMed: 22895533]
15. a) Schienebeck CM, Robichaux PJ, Li X, Chen L, Tang W. *Chem Commun.* 2013; 49:2616. b) Schienebeck CM, Song W, Smits AM, Tang W. *Synthesis.* 2015; 47:1076.
16. Ingold CK, Thorpe JF. *J Chem Soc Trans.* 1915; 107:1080.
17. a) Li X, Zhang M, Shu D, Robichaux PJ, Huang S, Tang W. *Angew Chem Int Ed.* 2011; 50:10421. b) Shu D, Li X, Zhang M, Robichaux PJ, Tang W. *Angew Chem Int Ed.* 2011; 50:1346. c) Shu D, Li X, Zhang M, Robichaux PJ, Guzei IA, Tang W. *J Org Chem.* 2012; 77:6463. [PubMed: 22793991] d) Li X, Huang S, Schienebeck CM, Shu D, Tang W. *Org Lett.* 2012; 14:1584. [PubMed: 22381143] e) Huang S, Li X, Lin CL, Guzei IA, Tang W. *Chem Commun.* 2012; 48:2204. f) Fukuyama T, Ohta Y, Brancour C, Miyagawa K, Ryu I, Dhimane AL, Fensterbank L, Malacria M. *Chem Eur J.* 2012; 18:7243. [PubMed: 22505021]
18. Wender PA, Husfeld CO, Langkopf E, Love JA, Pleuss N. *Tetrahedron.* 1998; 54:7203.
19. Shintani R, Nakatsu H, Takatsu K, Hayashi T. *Chem Eur J.* 2009; 15:8692. [PubMed: 19637169]
20. Rautenstrauch V. *J Org Chem.* 1984; 49:950.
21. Shi X, Gorin DJ, Toste FD. *J Am Chem Soc.* 2005; 127:5802. [PubMed: 15839674]
22. Faza ON, Lopez CS, Alvarez R, de Lera AR. *J Am Chem Soc.* 2006; 128:2434. [PubMed: 16478199]
23. For discussions on the effect of conjugation in Rh-catalyzed cycloadditions, see: Croatt MP, Wender PA. *Eur J Org Chem.* 2010; 19
24. Xu X, Liu P, Shu XZ, Tang W, Houk KN. *J Am Chem Soc.* 2013; 135:9271. [PubMed: 23725341]

**Previous Work:****This Work:****Scheme 1. Rh-Catalyzed [5+2] Cycloadditions of ACE**

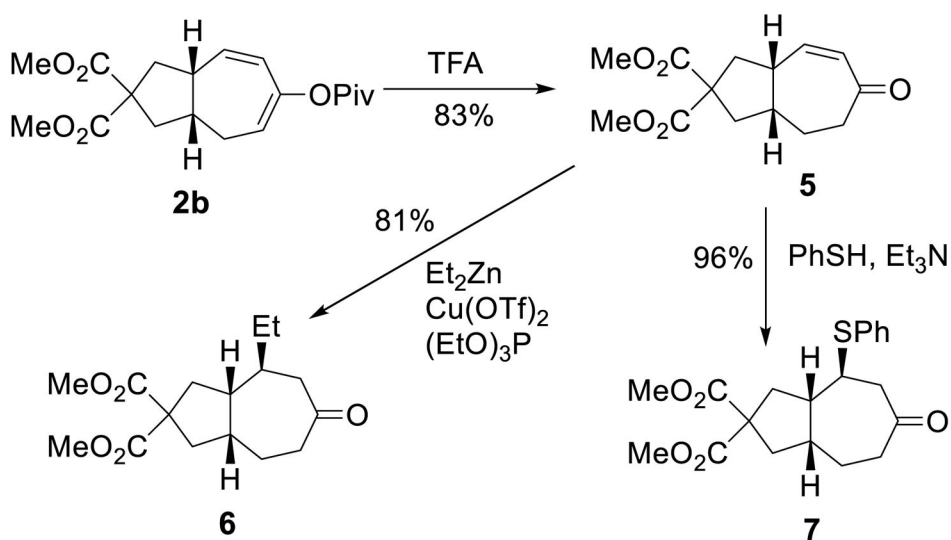


Scheme 2. Transfer of Chirality

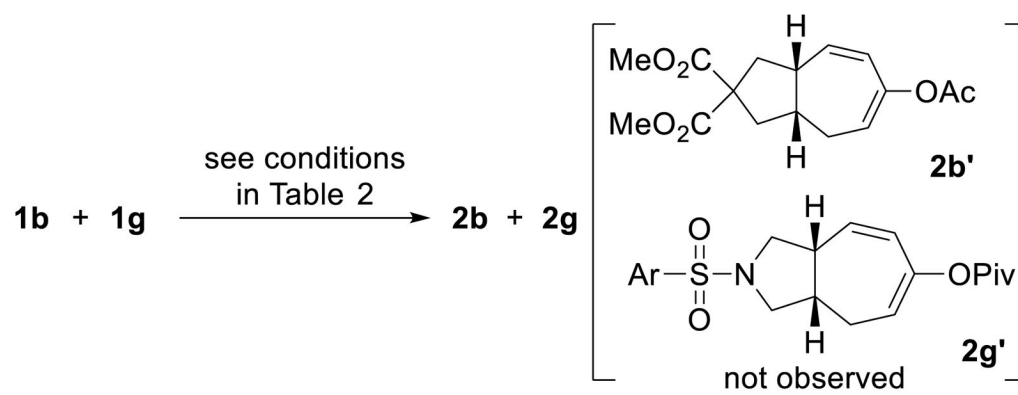


Scheme 3. Cycloaddition of ACE with Substituted Alkene

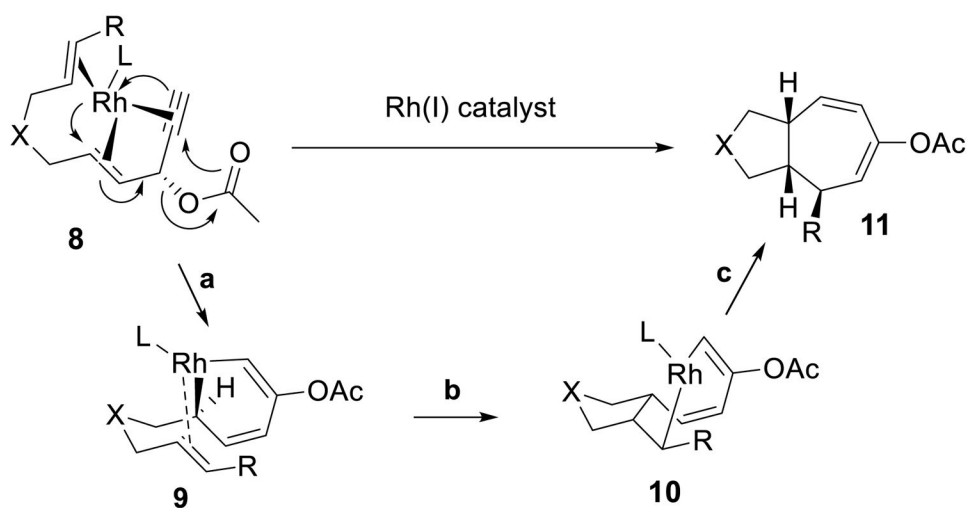




Scheme 4. Functionalization of Cycloaddition Product



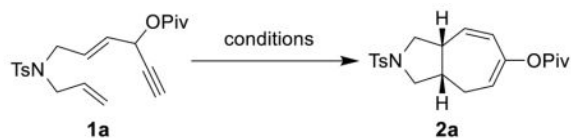
Scheme 5. Cross-over Experiment



**Scheme 6. Proposed Mechanism**

Table 1

Screening of Catalysts and Conditions for 1a



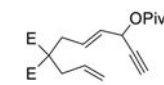
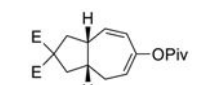
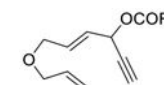
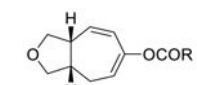
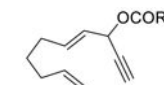
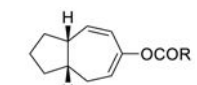
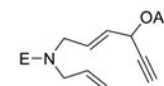
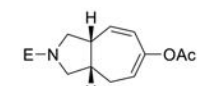
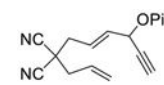
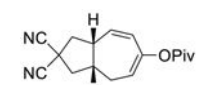
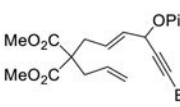
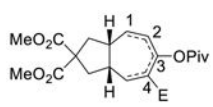
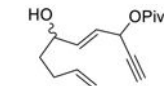
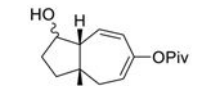
entry	catalyst and ligands	conditions	yield <sup>a</sup>
1	[Rh(cod) <sub>2</sub> ]BF <sub>4</sub> (10 mol %)	DCE, 8 h, rt or 80 °C	0
2	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl (10 mol %)	DCE, 10 h 80 °C,	63%
3	[Rh(cod)Cl] <sub>2</sub> (5 mol %)	DCE, 8 h, 80 °C,	0
4	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (5 mol %)	DCE, 8 h, 80 °C	32%
5	[Rh(cod)Cl] <sub>2</sub> (5 mol %), (C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> P (30 mol%)	DCE, 20 h, 80 °C	0
6	[Rh(cod)Cl] <sub>2</sub> (5 mol %), ( <i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P (30 mol%)	DCE, 20 h, 80 °C	50%
7	[Rh(cod)Cl] <sub>2</sub> (5 mol %), [3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sub>3</sub> P (30 mol%)	DCE, 20 h, 80 °C	91% (80%) <sup>b</sup>
8	[Rh(cod)Cl] <sub>2</sub> (5 mol %), [3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sub>3</sub> P (30 mol%)	CHCl <sub>3</sub> , 20 h, 50 °C	34%
9	[Rh(cod)Cl] <sub>2</sub> (5 mol %), [3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sub>3</sub> P (30 mol%)	CH <sub>2</sub> Cl <sub>2</sub> , 20 h, 50 °C	31%
10	[Rh(coe) <sub>2</sub> Cl] <sub>2</sub> (5 mol %), [3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sub>3</sub> P (30 mol%)	DCE, 20 h, 80 °C	(82%) <sup>b</sup>

<sup>a</sup>Yields were calculated based on <sup>1</sup>H NMR using internal standard.

<sup>b</sup>Isolated yield.

Table 2

Scope of Rh(I)-Catalyzed [5+2] Cycloaddition of ACE with Mono-substituted Alkene<sup>a</sup>

entry	substrate	product	yield <sup>b</sup>
1	 <b>1b</b> (E = CO <sub>2</sub> Me)	 <b>2b</b>	82%
2	 <b>1c</b> (R = <i>t</i> Bu)	 <b>2c</b>	62%
3	<b>1d</b> (R = <i>p</i> -Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> )	<b>2d</b>	67%
4	 <b>1e</b> (R = <i>t</i> Bu)	 <b>2e</b>	56%
5	<b>1f</b> (R = <i>p</i> -Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> )	<b>2f</b>	61%
6	 <b>1g</b> (E = <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> )	 <b>2g</b>	84%
7	 <b>1h</b>	 <b>2h</b>	83%
8	 <b>1i</b> (E = CO <sub>2</sub> Et)	 <b>2i</b> (14:1) <sup>c</sup>	76%
9	<b>1j</b> (E = C(O) <i>n</i> C <sub>4</sub> H <sub>9</sub> )	<b>2j</b> (5:1) <sup>c</sup>	73%
10 <sup>d</sup>	<b>1k</b> (E = Br)	<b>2k</b> (13:1) <sup>c</sup>	53%
11	 <b>1l</b> (dr = 1:1)	 <b>2l</b> (dr = 1.5:1)	71%

<sup>a</sup>Condition: [Rh(coe)<sub>2</sub>Cl]<sub>2</sub> (5 mol %), [3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>3</sub>P (30 mol%), DCE, 80 °C, 20 h.<sup>b</sup>All yields were isolated yields. Dr > 20:1 unless noted otherwise.

<sup>c</sup>The ratio of 1,3-diene and 2,4-diene.

<sup>d</sup>[Rh(cod)<sub>2</sub>Cl]<sub>2</sub> was employed as the catalyst.

Author Manuscript

Author Manuscript

Author Manuscript

Author Manuscript