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Rhodium-Catalyzed Cycloisomerization of 1,6-Enynes with an Intramolecular Halogen Shift: Reaction Scope and Mechanism

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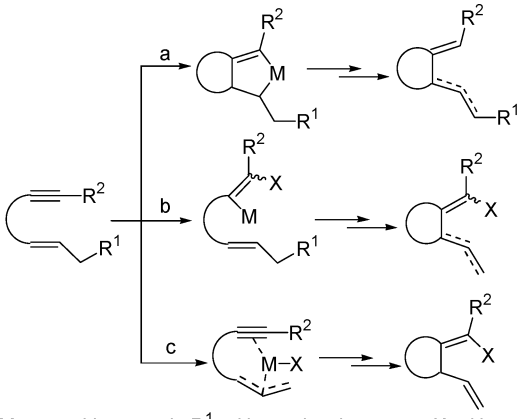
Abstract: The rhodium(I)-species-catalyzed cycloisomerization reaction of a wide spectrum of 1,6-enynes with an unusual intramolecular halogen shift was investigated. This Rh-catalyzed enyne cyclization reaction represents a new process for the synthesis of stereodefined α-halomethylene-γ-butyrolactones, lactams, tetrahydrofurans, pyrrolidines, and cyclopentanes. Coordinatively unsaturated rhodium species ($[Rh(COD)Cl]_2$ + dppb + $AgSbF_6$) only catalyzes the reaction with enyne substrates bearing a *Z*-form double bond, while neutral rhodium species ($RhCl(PPh_3)_3$) could catalyze enyne substrates bearing a *Z*- or *E*-form double bond to form the desired products and has a wider substrate scopes. The mechanism of the reaction was studied by the employment of control experiments with different enyne isomers, and a π-allyl rhodium intermediate was suggested to explain the formation of the cyclic products with an intramolecular halogen shift.

Introduction

The development of new methodologies for carbon−carbon bond formation is important in modern synthetic organic chemistry. Intramolecular carbon−carbon bond formation is a key strategy for the construction of cyclic compounds. Cyclization of 1,6-enynes has been reported as one of the most efficient methods for the synthesis of various types of cyclic compounds.[1] These cyclizations atom-economically[2] generate functionalized 1,3- or 1,4-diene cyclic compounds. Several transition metals catalyze these cyclizations under mild reaction conditions.[3,4]

Three possible mechanistic rationales have been proposed for transition metal-catalyzed cyclization reactions (Scheme 1).[1e,3k] One process involves simultaneously oxidative cyclization of the two unsaturated bonds to form a metallocycle, followed by β-H elimination and reductive elimination to complete the catalytic cycle (path a).[3] Another process includes activation of an alkyne to form a corresponding vinylmetal species, followed by insertion of an alkene and then β-X elimination (X = H, halogen, OAc) (path b).[4] In addition to these two fundamental processes, it is conceivable that the presence of an activated group in the allylic position allows the formation of a metal π-allyl complex which could be the possible

Scheme 1. Possible Mechanisms of the Cyclization of 1,6-Enynes



M = transition matel; R^1 = H or a leaving group; X = H or nucleophile

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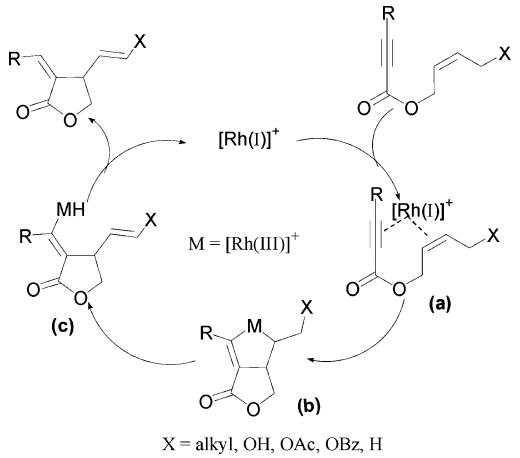
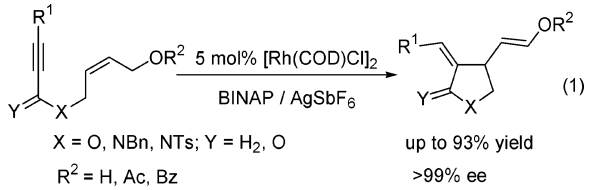
(1) For reviews: (a) Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34. (b) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635. (c) Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1. (d) Trost, B. M.; Toste, F. D.; Pinkerson, A. B. *Chem. Rev.* **2001**, *101*, 2067. (e) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813.
(2) (a) Trost, B. M. *Science* **1991**, *254*, 1471. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259.
(3) Cyclization via metallacyclopentene intermediate; for Pd: (a) Trost, B. M.; Lautens, M.; Chan, C.; Jebaratnam, D. J.; Mueller, T. *J. Am. Chem. Soc.* **1991**, *113*, 636. (b) Trost, B. M.; Romero, D. L.; Rise, F. *J. Am. Chem. Soc.* **1994**, *116*, 4268. (c) Hatano, M.; Terada, M.; Mikami, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 249. For Ru: (d) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 714. (e) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049. For Ti: (f) Sturla, S.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 1976. For Pt: (g) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901. For Ni: (h) Tamao, K.; Kobayashi, K.; Ito, Y. *Synlett* **1992**, 539. (i) Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5268. For Co: (j) Krafft, M. E.; Wilson, A. M.; Dasse, O. A.; Bonaga, L. V. R.; Cheung, Y. Y.; Fu, Z.; Shao, B.; Scott, I. L. *Tetrahedron Lett.* **1998**, *39*, 5911. (k) Buisine, O.; Aubert, C.; Malacria, M. *Chem.-Eur. J.* **2001**, *7*, 3517.
(4) Cyclization via vinylmetal intermediate; for Pd: (a) Trost, B. M.; Lee, D. C.; Rise, F. *Tetrahedron Lett.* **1989**, *30*, 651. (b) Trost, B. M.; Li, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6625. (c) Ma, S.; Lu, X. *J. Chem. Soc., Chem. Commun.* **1990**, 733. (d) Ma, S.; Lu, X. *J. Org. Chem.* **1991**, *56*, 5120. For Ru: (e) Nishida, M.; Adachi, N.; Onozuka, K.; Matsumura, H.; Mori, M. *J. Org. Chem.* **1998**, *63*, 9158.

Scheme 2



intermediate for the enyne cyclization (path c). However, this type of enyne cyclization is relatively unexplored.[5]

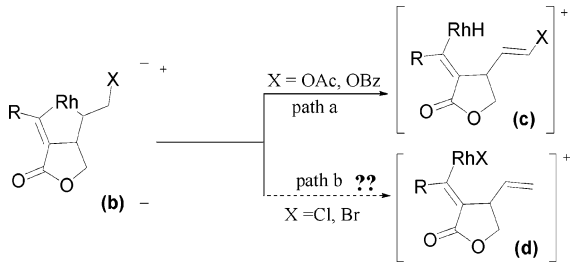


Recently, Zhang et al. reported the cycloisomerization of 1,6-enyne catalyzed by Rh(I).[6] In this reaction, a variety of 1,6-enyne substrates with a functional group (OH, OAc, OBz, alkyl) in the allylic position can be cycloisomerized in excellent yields, regio-, and enantioselectivity (eq 1).[7] The generally accepted mechanism for this transformation was outlined in Scheme 2. The coordinated intermediate (**a**) is formed by the coordination of enynes with a cationic Rh(I) species generated in situ. Oxidative cyclization of enynes affords the metallacyclopentane (**b**). Subsequently, β-H elimination of (**b**) yields the Rh−H species (**c**). Finally, the reductive elimination of this Rh−H species (**c**) produces the product.

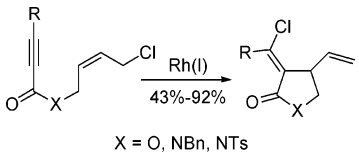
From the reaction product, we envision that a β-H elimination is much faster than β-oxygen elimination for the intermediate (**b**). However, it was reported that the β-halide was preferentially eliminated to a β-H in palladium-catalyzed intermolecular enyne coupling reactions and 1,6-enyne cyclization reactions.[8] Thus, for 1,6-enyne substrates with a halogen atom in the allylic position, β-halide elimination may also occur preferentially to a β-H elimination under the reported reaction conditions (Scheme 3).

In fact, we found that halogen behaves like an H-atom in the Alder-ene reaction and 1,4-dienes with halo-alkene moieties are formed in this transformation (Scheme 4).[9] Further investigation shows that this transformation represents a novel process with

Scheme 3



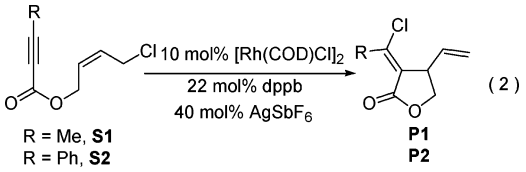
Scheme 4



a π-allyl rhodium as the key intermediate. In this paper, we will discuss the scope and mechanism of this reaction in detail.

Results and Discussion

Cationic Rh(I)-Catalytic System and Neutral Rh(I)-Catalytic System. Treatment of **S1** with $[Rh(COD)Cl]_2$, dppb, and $AgSbF_6$ (eq 2) produced α-chloromethylene-γ-butyrolactone **P1** in 43% yield.



The *E*-configuration of the exo double bond was confirmed by NOESY data from compound **P1**. X-ray crystallographic analysis of compound **P2** (Figure 1) further confirmed the exo double bond of the product is in *E*-form.

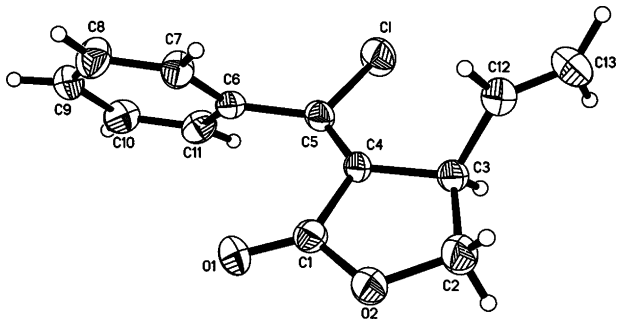


Figure 1. The ORTEP drawings of compound **P2**.

Through extensive screening of the reaction conditions, we found that the amount of the added $AgSbF_6$ is crucial for this transformation. If the ratio of $AgSbF_6$ to $[Rh(COD)Cl]_2$ exceeds 2:1, the reaction failed to go to completion and yields were low even with longer reaction times (Table 1, entries 1,2), while the reaction does not occur without $AgSbF_6$ (Table 1, entry 11). Ligands and solvents were also important factors influencing the reaction, and the results are summarized in Table 1.

When the reaction was carried out in DCE with dppb or racemic BINAP as the ligand, high yields could be achieved. Other common bisphosphine and monophosphine ligands are

(5) (a) Oppolzer, W.; Keller, T. H. *Tetrahedron Lett.* **1989**, *30*, 5883. (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 38.
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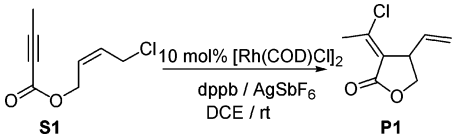
(7) (a) Cao, P.; Zhang, X. *Angew. Chem., Int. Ed.* **2000**, *39*, 410. (b) Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 8198. (c) Lei, A.; He, M.; Wu, S.; Zhang, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 3457. (d) Lei, A.; Waldkirch, J. P.; He, M.; Zhang, X. *Angew. Chem, Int. Ed.* **2002**, *41*, 4526.
(8) (a) Kaneda, K.; Uchiyama, T.; Fujiwara, Y.; Imanaka, T.; Teranishi, S. *J. Org. Chem.* **1979**, *44*, 55. (b) Lu, X.; Zhu, G.; Wang, Z. *Synlett* **1998**, 115. (c) Lu, X.; Ma, S.; Ji, J.; Zhu, G.; Jiang, H. *Pure Appl. Chem.* **1994**, *66*, 1501. (d) Zhang, Z.; Lu, X.; Xu, Z.; Zhang, Q.; Han, X. *Organometallics* **2001**, *20*, 3724.
(9) Tong, X.; Zhang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2003**, *125*, 6370.

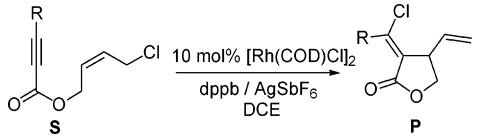
Table 1. Cycloisomerization of **S1** Catalyzed by $[Rh(COD)Cl]_2$[a]



entry	$AgSbF_6$ (equiv)[b]	solvent	ligand	time (h)	yield (%)
1	4	DCE	dppb	24	43
2	3	DCE	dppb	10	62
3	2	DCE	dppb	3	87
4	2	DCE	PPh_3[c]	24	0
5	2	DCE	dppe	120	trace
6	2	DCE	dppp	120	trace
7	2	DCE	dppf	24	0
8	2	DCE	binap	4	84
9	2	toluene	dppb	16	20[d]
10	2	DCM	dppb	16	4[d]
11	0	DCE	dppb	24	0

[a] All of the reactions were carried out with **S1** (34.6 mg, 0.2 mmol), $[Rh(COD)Cl]_2$ (10.0 mg, 0.02 mmol), and bisphosphine (0.044 mmol) with an indicated amount of $AgSbF_6$ in 3 mL of specified solvent. [b] Ratio relative to $[Rh(COD)Cl]_2$. [c] $[Rh]:PPh_3 = 1:2.1$. [d] Yield determined by ^1H NMR.

Table 2. Cycloisomerization Catalyzed by $[Rh(COD)Cl]_2$ and $AgSbF_6$[a]



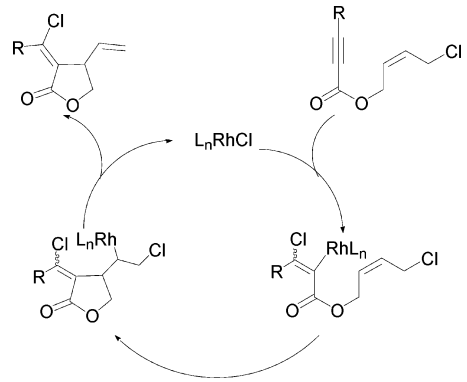
entry	S	R	temp	time (h)	P	yield (%)[b]
1	S1	Me	rt	3	P1	87
2	S2	Ph	65 °C	6	P2	78
3	S3	*n*-Bu	rt	9	P3	92
4	S4	MeOC H_2	65 °C	8	P4	68
5	S5	H	reflux	10	P5	43

[a] All of the reactions were carried out with enyne substrate (0.2 mmol), $[Rh(COD)Cl]_2$ (10.0 mg, 0.02 mmol), dppb (19.0 mg, 0.044 mmol), and $AgSbF_6$ (14.0 mg, 0.04 mmol) in 3 mL of DCE at the indicated temperature. [b] Isolated yield.

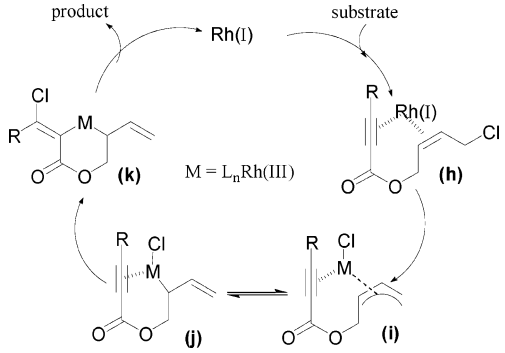
either totally inert or very inefficient under the reaction conditions (Table 1, entries 4−7). The reaction is also very sensitive to solvents. With other noncoordinating solvents such as toluene and dichloromethane, poor yields were observed (Table 1, entries 9,10). Because coordinating solvents were poor solvents for this reaction, we did not attempt to run the reaction in such solvents.[6,7] Under the reaction conditions in Table 1 (Table 1, entry 3), a variety of enyne substrates were investigated, and the results are summarized in Table 2.

There are at least three reasonable mechanistic pathways for this process (Scheme 1). Oxidative cyclometalation (Scheme 2) was first considered, because it is precedented in other systems and accounts for the formation of the product with the correct olefin geometry.[10] However, this would require β-chloro elimination (path b, Scheme 3) (a favored process) followed by reductive elimination of RhCl from intermediate (**d**) (Scheme 3).[11] Because the latter process is not favored,[12] this pathway was considered unlikely.

Scheme 5. A Reaction Mechanism via Chlororhodation



Scheme 6. A Proposed Mechanism Involving a π-Allyl Rhodium Species



A mechanism involving chlororhodation followed by alkene insertion and β-Cl elimination (Scheme 5) is another proposed mechanism to account for the formation of the product. However, further analysis indicated that it is impossible under the reaction conditions, because there is no free chloride ion in the reaction system to initiate chlororhodation in the presence of an excess halide scavenger, $AgSbF_6$ (Table 1, entries 1,2). More detailed control experiments to exclude this possibility are discussed in the following sections.

The third mechanism involving a π-allyl rhodium complex as the reaction intermediate was then proposed (Scheme 6). If the oxidative addition of an allylic chloride is a faster step than the oxidative cyclometalation, then an enyne-coordinated Rh(I) species (**h**) will react with the allylic chloride to form a π-allyl rhodium complex (**i**). The π-allyl intermediate (**i**) could convert to the species (**j**) via $\eta^3-\eta^1$ isomerization. Addition of the rhodium chloride bond of intermediate (**j**) to the alkyne forms another intermediate (**k**). Reductive elimination of (**k**) gives the product and regenerates the catalytic Rh(I) species.[13]

Wilkinson et al. reported that the oxidative addition of an allyl chloride to $RhCl(PPh_3)_3$ would generate a $Rh(PPh_3)Cl_2(\pi\text{-}C_3H_5)$ species.[14] On the basis of this result and the proposed mechanism in Scheme 6, we speculated that Wilkinson's catalyst might also catalyze this transformation. Treatment of **S1** with

(10) (a) Jolly, R. S.; Luedtke, G.; Sheehan, D.; Livinghouse, T. *J. Am. Chem. Soc.* **1990**, *112*, 4965. (b) Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, *117*, 4720. (c) Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 1940. (d) Evans, P. A.; Robinson, J. E.; Baum, E. W.; Fazal, A. N. *J. Am. Chem. Soc.* **2002**, *124*, 8782. (e) Gilbertson, S. R.; DeBoef, B. *J. Am. Chem. Soc.* **2002**, *124*, 8784.

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(12) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry;* University Science Books: Mill Valley, CA, 1987. (b) Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99. (c) Blum, J.; Scharf, G. *J. Org. Chem.* **1970**, *35*, 1895. (d) Kampmeier, J. A.; Harris, S. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 1478.

(13) Sato, Y.; Oonishi, Y.; Mori, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1218.

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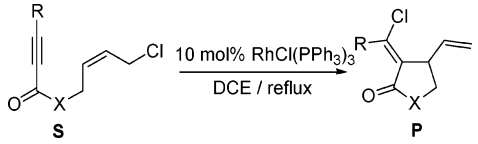
Table 3. Cycloisomerization Catalyzed by $RhCl(PPh_3)_3$[a]

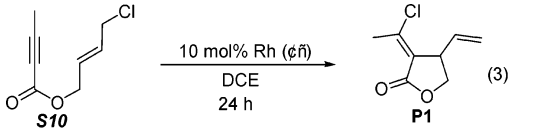


entry	S	R	X	time (h)	P	yield (%)[b]
1	S1	Me	O	1	P1	92
2	S10	Me	O	1	P1	90
3	S2	Ph	O	2	P2	87
4	S3	*n*-Bu	O	2	P3	90
5	S4	$MeOCH_2$	O	2	P4	72[c]
6	S5	H	O	24	P5	ND[d]
7	S6	$BnOCH_2$	O	3	P6	71[c]
8	S7	Me	NBn	3	P7	89
9	S8	Ph	NBn	6	P8	85
10	S9	Me	NTs	4	P9	83

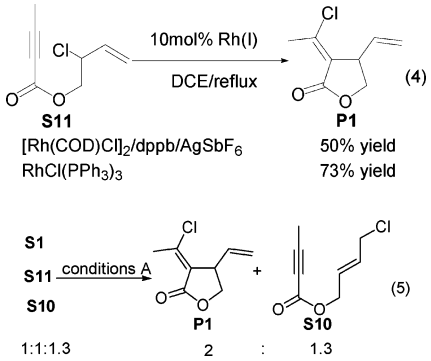
[a] All of the reactions were carried out with enyne substrate (0.2 mmol) and $RhCl(PPh_3)_3$ (18.5 mg, 0.02 mmol) in 3 mL of DCE under reflux. [b] Isolated yield. [c] With an unidentified product. [d] ND = no detected product.

Wilkinson's catalyst in DCE under reflux produced **P1** in 92% yield. In comparison with the former standard condition, the procedure for the $RhCl(PPh_3)_3$-catalyzed reaction is simpler: a substrate was directly subjected to the solution of $RhCl(PPh_3)_3$ in DCE without activation of the catalyst. Further investigation showed that a wide spectrum of enynes could be employed as substrates when $RhCl(PPh_3)_3$ was applied as the catalyst. These results are summarized in Table 3.

Further Investigation of the Mechanistic Details. Although both the cationic catalytic system $[Rh(COD)Cl]_2$/dppb/$AgSbF_6$ (conditions A) and the neutral system $RhCl(PPh_3)_3$ (conditions B) can catalyze the transformation, there are some differences between the two systems: (a) The terminal alkyne **S5** can be easily cycloisomerized to the product under conditions A (Table 2, entry 5), while no product was obtained under conditions B. When **S5** was used as substrate, $RhCl_2(PPh_3)_2$[15] was isolated in 90% yield based on $RhCl(PPh_3)_3$. (b) **S10** (the *trans*-isomer of **S1**) shows a quite different reactivity toward the two catalytic systems (eq 3). It should be noted that the *trans*-substrate was inert to the previously reported Rh(I)-catalyzed enyne cycloisomerization reaction (eq 1).

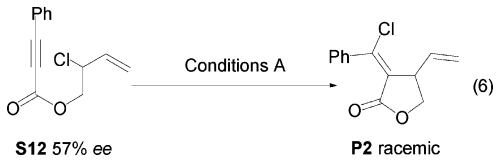


Further evidence to support the mechanistic pathway involving a π-allyl rhodium species outlined in Scheme 6 was given by two control experiments. The first one employed **S11**, the regioisomer of **S1** and **S10**, as the substrate (eq 4). Under either reaction conditions A or reaction conditions B, **S11** could be transformed into the same compound **P1** as the sole product in good yields. The second control experiment was carried out by utilization of a mixture of **S1**, **S11**, and **S10** (1:1:1.3 in mol) under reaction conditions A at room temperature (eq 5). The reaction was monitored by GC (see Supporting Information).

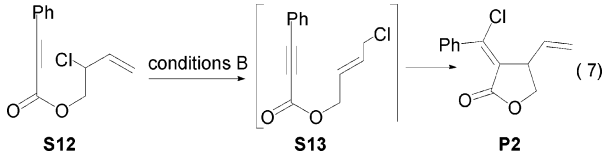


The results show that **S1** and **S11** can be readily transformed to the product **P1,** while **S10** does not convert during the course of the reaction. On the basis of these results, we exclude the possibility that substrate **S11** first isomerized to **S1** and/or **S10** before it transformed to the product. These two control experiments showed that formation of the common intermediate for both substrates **S1** and **S11** is possible in the catalytic reaction. The common intermediate for **S1** and **S11** is most likely a π-allyl rhodium chloride. Therefore, the reaction pathway outlined in Scheme 6 through intermediates (**i**) and (**j**) is the proposed pathway.

Further information about the oxidative addition step in this proposed mechanism is available from the study of the reactivity of chiral substrate **S12** under conditions A and conditions B. Under reaction conditions A, chiral substrate **S12** was transformed to the racemic product **P2** (eq 6). During the course of the experiment, we have not detected the isomers *cis*-**S2** or *trans*-**S2** (**S13**). Therefore, we speculate that oxidative addition of 3-substituted allylic halides to rhodium(I) that is possible either by a S_N2' type reaction or by a direct S_N2 type reaction,[16] followed by isomerization of the resulting π-allylrhodium(III), leads to the racemic product **P2**.[17]



To our surprise, when **S12** was used as the substrate under conditions B, we did detect the **S13** isomer and could isolate it during the course of the reaction (eq 7). Compound **S13** can be cycloisomerized to product **P2** with prolonged reaction time.

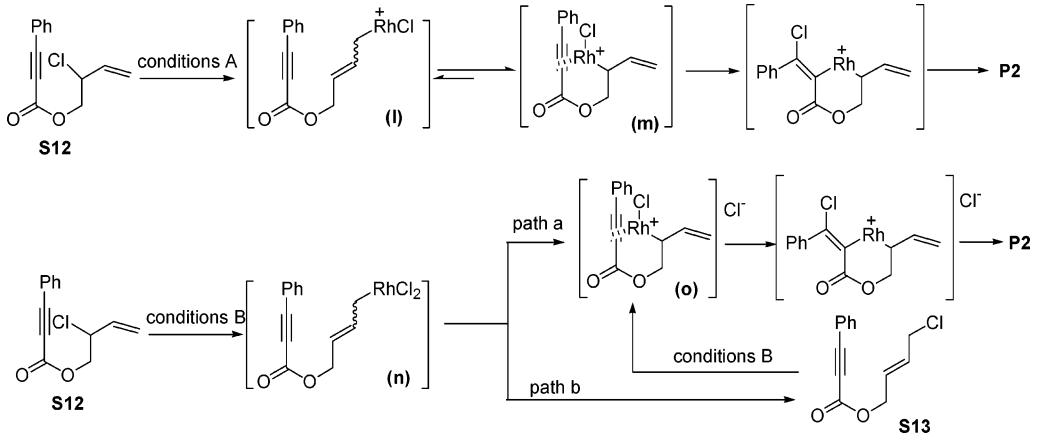


(15) The compound $RhCl_2(PPh)_2$ is characterized by X-ray crystallographic analysis. (a) Osborn, J. A.; Jardine, F. H.; Yong, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711. (b) Ogle, C. A.; Masterman, T. C.; Hubbard, J. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1733.

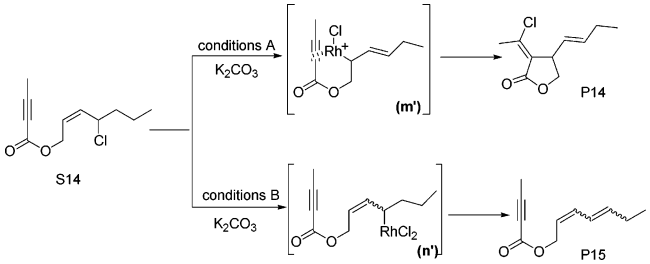
(16) (a) Payne, M. J.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, 3167. (b) Empsall, H. D.; Hyde, E. M.; Jones, C. E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 1980. (c) Griffin, T. R.; Cook, D. B.; Haynes, A.; Pearson, J. M.; Monti, D.; Morris, G. E. *J. Am. Chem. Soc.* **1996**, *118*, 3029.

(17) Rh-catalyzed nucleophilic substitution of allylic carbonate with chirality retention: (a) Evans, P. A.; Nelson, J. D. *Tetrahedron Lett.* **1998**, *39*, 1725. (b) Evans, P. A.; Nelson, J. D. *J. Am. Chem. Soc.* **1998**, *120*, 5581.

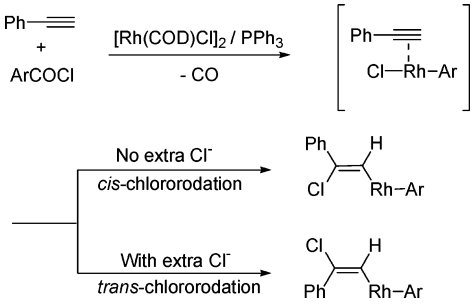
Scheme 7



Scheme 8



Scheme 9

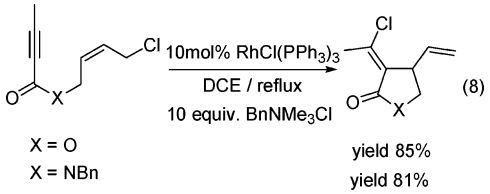


We speculate the reason for the difference of the two catalytic systems is the different coordinative ability between the cationic Rh-species generated in situ and the neutral Rh-species $RhCl(PPh_3)_3$ (Scheme 7).[18] For the highly coordinatively unsaturated environment of the cationic Rh-species, the triple bond of the substrate serves as a ligand for the cationic Rh-species. Therefore, the balance between species (**l**) and (**m**) favors the formation of species (**m**). Species (**m**) undergoes further transformations to afford **P2**. In contrast to conditions A, the neutral Rh-species is coordinatively saturated, and species (**n**) may be the more favorable species. The fate of species (**n**) accounts for the detection of **S13**: if species (**n**) can isomerize easily to species (**o**) (path a), then the formation of **S13** is impossible; if species (**n**) is stable enough, reductive elimination may occur to produce **S13**, and because the cycloisomerization reaction rate for **S13** is slow, the isolation of it becomes possible.

On the basis of these conclusions, we envision that for the species (**n**), with a β-H, β-H elimination might occur under reaction conditions B and a base. We synthesized the compound **S14** and subjected it to reaction conditions A and B, respectively, with K_2CO_3 as the base. We found that the cyclic compound **P14** was isolated in 51% yield under conditions A with K_2CO_3 as a base and no β-H elimination product was detected. Under reaction conditions B in the presence of K_2CO_3, the conjugated diene **P15** was obtained in 43% yield (Scheme 8).[19] It is noteworthy that without K_2CO_3, **P14** can be obtained in 63% and 8% yields under conditions A and conditions B, respectively.

Another remaining problem is how the intermediate (**j**) in Scheme 6 was transformed to (**k**). We proposed that insertion of the alkyne into the rhodium−chloride bond of intermediate (**j**) is more likely than chlororhodation. Chlororhodation of alkynes is not common, and the stereochemistry of chlororhodation of alkynes is dependent on the chloride ion concentration: (a) without extra chloride ion, *cis*-chlororhodation is the exclusive product, (b) with the addition of chloride ion, the ratio of *trans*-chlororhodation is increased (Scheme 9).[20] Similar results for other late transition metals were also reported.[21]

Under catalysis by $RhCl(PPh_3)_3$, we did not detect any product with an exo double bond in *Z*-form, which is the *trans*-chlororhodation product, even when 10 equiv of $BnNMe_3Cl$ was added (eq 8). On the basis of these results, we believe that the conversion of intermediate (**j**) to (**k**) may not involve the halorhodation pathway as outlined in Scheme 6 (otherwise, *trans*-chlororhodation will probably occur under high concentration of chloride); instead, direct insertion of the triple bond to the Rh−Cl bond is most likely. The insertion step gives the product with right stereochemistry and can be used to explain that why **P1** was isolated as the sole product with a stereodefined double bond even in the presence of a large amount of chloride ion.



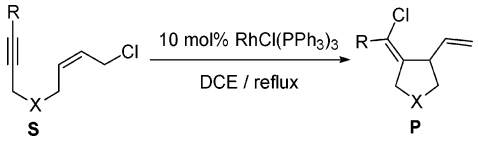
Scope and Limitation. When we subjected electron-rich 1,6-enynes to reaction conditions A, only poor yields were obtained.

(18) (a) Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331. (b) Fairlie, D.; Bosnich, B. *Organometallics* 1**988**, *7*, 936. (c) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(19) **P15** is characterized by ^{1}H NMR, GC-MS (see Supporting Information).

(20) (a) Kokubo, K.; Matsumasa, K.; Miura, M.; Nomura, M. *J. Org. Chem.* **1996**, *61*, 6941. (b) Hua, R.; Shimada, S.; Tanaka, M. *J. Am. Chem. Soc.* **1998**, *120*, 12365.

Table 4. Cycloisomerization of Electron-Rich 1,6-Enyne Catalyzed by $RhCl(PPh_3)_3$[a]

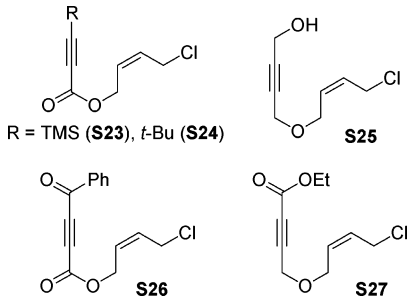


entry	S	R	X	time (h)	P	yield (%)[b]
1	S16	Me	O	6	P16	81
2	S17	Ph	O	8	P17	86
3	S18	Ph	NTs	9	P18	76
4	S19	*n*-Bu	NTs	8	P19	81
5	S20	Me	$C(CO_2Et)_2$	3	P20	93
6	S21	Ph	$C(CO_2Et)_2$	3	P21	89
7	S22	*n*-Bu	$C(CO_2Et)_2$	3	P22	93

[a] All of the reactions were carried out with enyne substrate (0.2 mmol) and $RhCl(PPh_3)_3$ (18.5 mg, 0.02 mmol) in 3 mL of DCE under reflux. [b] Isolated yield.

However, these substrates could be cycloisomerized to give good to excellent yields under reaction conditions B. The results are shown in Table 4.

This reaction has a wide substrate tolerance (Tables 2−4); however, substrates containing a bulky substituent at the triple bond (**S23**, **S24**), or substrates with an unprotected hydroxy, α,β propargylic ketone, or ester group (**S25**−**27**) produced no cyclic compounds.



Conclusion

We have found a Rh(I)-catalyzed enyne cycloisomerization reaction with an intramolecular halogen shift proceeding through a π-allyl rhodium intermediate. This reaction represents a useful process for the synthesis of stereodefined α-halomethylene-γ-butyrolactones and lactams. Furthermore, this method can also afford multifunctional tetrahydrofurans, pyrrolidine, and cyclopentanes.

Experimental Section

A. General. All reactions and manipulations were conducted in an argon-filled glovebox or using standard Schlenk techniques. Column chromatography was performed using Silica gel (300−400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts were reported in ppm with the solvent resonance as the internal standard. MS, IR, and microanalysis were conducted by the state authorized analytical center in the Shanghai Institute of Organic Chemistry.

B. General Method for Cycloisomerization of Enyne with $RhCl(PPh_3)_3$. Under argon atmosphere, a 25 mL Schlenk tube was charged with 0.2 mmol of enyne substrate, 10 mol % of $RhCl(PPh_3)_3$, and 3 mL of $ClCH_2CH_2Cl$ (DCE). The mixture was stirred under reflux, and the reaction was monitored by TLC. After the reaction was complete, the reaction mixture was directly subjected to column chromatography using hexanes−EtOAc (20:1−10:1) as eluent.

P1 (Table 3, entry 1). Yield: 92%. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.67 (d, J = 1.4 Hz, 3H), 3.83−3.91 (m, 1H), 4.15 (dd, J = 2.3, 9.0 Hz, 1H), 4.39 (dd, J = 7.5, 9.0 Hz, 1H), 5.17−5.24 (m, 2H), 5.75−5.87 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.9, 44.7, 69.5, 117.0, 124.4, 134.3, 149.2, 167.6. IR (cm^{-1}): 1755, 1658. MS (*m*/*z*): 172 (M^+, ^{35}Cl). Anal. Calcd for $C_8H_9ClO_2$: C, 55.67; H, 5.26. Found: C, 55.90; H, 5.46.

P2 (Table 3, entry 3). Yield: 87%. mp 66−68 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 4.03−4.09 (m, 1H), 4.22 (dd, J = 2.1, 9.0 Hz, 1H), 4.50 (dd, J = 7.2, 9.0 Hz, 1H), 5.30−5.36 (m, 2H), 5.88−6.00 (m, 1H), 7.37−7.50 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 45.8, 69.3, 117.4, 125.3, 128.0, 128.9, 130.3, 134.0, 135.3, 147.9, 196.0. IR (cm^{-1}): 1757, 1642. MS (*m*/*z*): 234 (M^+, ^{35}Cl). Anal. Calcd for $C_{13}H_{11}ClO_2$: C, 66.53; H, 4.72. Found: C, 66.53; H, 4.90.

P3 (Table 3, entry 4). Yield: 90%. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.86 (t, J = 7.2 Hz, 3H), 1.24−1.37 (m, 2H), 1.47−1.60 (m, 2H), 2.97−3.20 (m, 2H), 3.76−3.83 (m, 1H), 4.07 (dd, J = 2.4, 9.0 Hz, 1H), 4.32 (dd, J = 6.9, 9.0 Hz, 1H), 5.08−5.16 (m, 2H), 5.76−5.88 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.7, 21.8, 30.0, 34.5, 44.8, 69.5, 116.9, 124.2, 134.4, 154.5, 167.4. IR (cm^{-1}): 1757, 1652. MS (*m*/*z*): 214 (M^+, ^{35}Cl). Anal. Calcd for $C_{11}H_{15}ClO_2$: C, 61.54; H, 7.04. Found: C, 61.47; H, 7.21.

P4 (Table 3, entry 5). Yield: 72%. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.40 (s, 3H), 3.91−3.96 (m, 1H), 4.22 (dd, J = 2.1, 9.0 Hz, 1H), 4.46 (dd, J = 7.5, 9.0 Hz, 1H), 4.70 (d, J = 13.2 Hz, 1H), 4.82 (d, J = 13.2 Hz, 1H), 5.21−5.28 (m, 2H), 5.77−5.89 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 44.7, 58.1, 69.0, 69.9, 117.6, 128.2, 133.5, 148.4, 166.8. IR (cm^{-1}): 1756, 1655. MS (*m*/*z*): 202 (M^+, ^{35}Cl). Anal. Calcd for $C_9H_{10}ClO_2$: C, 53.37; H, 5.43. Found: C, 53.59; H, 5.42.

P5 (Table 2, entry 5).[22] Yield: 43%. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.81−3.88 (m, 1H), 4.13 (dd, J = 3.6, 9.3 Hz, 1H), 4.44 (dd, J = 8.4, 9.3 Hz, 1H), 5.15−5.22 (m, 2H), 5.68−5.80 (m, 1H), 7.34 (d, J = 2.4 Hz, 1H).

P6 (Table 3, entry 7). Yield: 71%. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.84−3.90 (m, 1H), 4.17 (dd, J = 2.4, 9.0 Hz, 1H), 4.39 (dd, J = 7.5, 9.0 Hz, 1H), 4.57 (s, 2H), 4.76 (dd, J = 1.2, 6.9 Hz, 1H), 4.97 (dd, J = 6.9, 12.9 Hz, 1H), 5.18−5.25 (m, 2H), 5.72−5.84 (m, 1H), 7.25−7.39 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 44.8, 67.3, 70.0, 72.8, 117.6, 127.9, 128.0, 128.4, 133.5, 137.5, 148.8, 166.8. IR (cm^{-1}): 1755, 1655. MS (*m*/*z*): 187 (M^+ − Bn, ^{35}Cl). HRMS calcd for $C_{15}H_{15}ClO_3$−Bn: 187.0162. Found: 187.0174.

P7 (Table 3, entry 8). Yield: 89%. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.71 (d, J = 1.2 Hz, 3H), 2.98 (dd, J = 1.2, 9.9 Hz, 1H), 3.45 (dd, J = 8.1, 9.9 Hz, 1H), 3.63−3.66 (m, 1H), 4.42 (d, J = 15.0 Hz, 1H), 4.58 (d, J = 15.0 Hz, 1H), 5.05−5.11 (m, 1H), 5.64−5.76 (m, 1H), 7.22−736 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.2, 41.1, 46.9, 49.0, 115.7, 127.6, 128.1, 128.7, 128.1, 129.5, 136.0, 142.2, 165.7. IR (cm^{-1}): 1689, 1656. MS (*m*/*z*): 261 (M^+, ^{35}Cl). Anal. Calcd for $C_{15}H_{15}ClNO$: C, 68.83; H, 6.16; N, 5.35. Found: C, 68.63; H, 6.26; N, 5.26.

P8 (Table 3, entry 9). Yield: 85%. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.03 (dd, J = 1.8, 10.2 Hz, 1H), 3.51 (dd, J = 1.5, 10.2 Hz, 1H), 3.80−3.85 (m, 1H), 4.33 (d, J = 14.4 Hz, 1H), 4.57 (d, J = 14.4 Hz, 1H), 5.14−5.22 (m, 2H), 5.73−5.86 (m, 1H), 7.18−7.50 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 41.9, 47.0, 48.8, 116.1, 127.6, 127.7, 128.2, 128.6, 129.1, 129.4, 131.0, 135.5, 135.9, 136.5, 141.0, 164.0; IR (cm^{-1}): 1637, 1694. MS (*m*/*z*): 323 (M^+, ^{35}Cl). HRMS calcd for $C_{20}H_{18}ClNO$: 323.1077. Found: 323.1078.

P9 (Table 3, entry 10). Yield: 83%. mp 94−96 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.44 (s, 3H), 2.57 (d, J = 1.2 Hz, 3H), 3.69−3.74

(21) For a chloroalkylation of alkynes using palladium and ruthenium catalysis, see: (a) Wang, Z.; Lu, X. *Chem. Commun*. **1996**, 535. (b) Wang, Z.; Lu, X. *J. Org. Chem.* **1996**, *61*, 2254. (c) Dietl, H.; Reiheimer, H.; Moffatt, J.; Maitlis, P. M. *J. Am. Chem. Soc*. **1970**, *92*, 2276. (d) Trost, B. M.; Pinkerton, A. B. *J. Am. Chem. Soc*. **1999**, *121*, 1988.

(22) (a) Ma, S.; Lu, X. *J. Org. Chem.* **1991**, *56*, 5120. (b) Zhu, G.; Ma, S.; Lu, X. *J. Chem. Res. Miniprint* **1993**, *9*, 2467.

(m, 1H), 3.78 (dd, J = 1.5, 10.0 Hz, 1H), 3.90 (dd, J = 7.8, 10.0 Hz, 1H), 5.08−5.16 (m, 2H), 5.67−5.79 (m, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.7, 22.9, 40.9, 48.9, 116.7, 128.1, 129.7, 129.7, 134.5, 134.8, 145.3, 148.2, 163.7. IR (cm^{-1}): 1713, 1651. MS (m/z): 325 (M^+, ^{35}Cl). Anal. Calcd for $C_{15}H_{16}ClNOS$: C, 55.30; H, 4.95; N, 4.30. Found: C, 55.45; H, 5.10; N, 4.19.

P16 (Table 4, entry 1). Yield 81%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.02−2.04 (m, 3H), 3.49−3.54 (m, 1H), 3.84 (dd, J = 2.7, 11.7 Hz, 1H), 3.93 (dd, J = 6.0, 8.7 Hz, 1H), 4.29 (dd, J = 0.6, 12.9 Hz, 1H), 4.42 (dt, J = 1.5, 12.9 Hz, 1H), 5.10−5.19 (m, 1H), 5.75−5.86 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 23.49, 48.31, 69.79, 73.88, 115.59, 121.67, 135.83, 136.76. MS (m/z): 158 (M^+, ^{35}Cl). HRMS calcd for $C_8H_{11}ClO$: 158.0498. Found: 158.0475.

P17 (Table 4, entry 2). Yield 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.72−3.78 (m, 1H), 3.85 (dd, J = 3.6, 8.7 Hz, 1H), 4.05 (dd, J = 6.3, 8.7 Hz, 1H), 4.27 (d, J = 13.5 Hz, 1H), 4.49 (dd, J = 13.5, 1.8 Hz, 1H), 5.18−5.30 (m, 2H), 5.83−5.97 (m, 1H), 7.24−7.36 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 49.3, 70.5, 73.3, 116.3, 124.7, 127.7, 128.3, 128.6, 135.4, 138.1, 139.7. MS (m/z): 219 (M^+, ^{35}Cl). Anal. Calcd for $C_{13}H_{13}ClO$: C, 70.75; H, 5.94. Found: C, 70.88; H, 6.18. IR (cm^{-1}): 1455, 1071, 921.

P18 (Table 4, entry 3). Yield 76%. mp 78−80 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.44 (s, 3H), 3.32−3.41 (m, 2H), 3.64−3.71 (m, 1H), 3.72 (d, J = 14.4 Hz, 1H), 4.06 (dd, J = 1.2, 14.4 Hz, 1H), 5.10−5.22 (m, 2H), 5.69−5.80 (m, 1H), 7.26−7.38 (m, 7H), 7.63 (d, J = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.5, 47.0, 51.0, 52.5, 116.4, 126.9, 127.7, 127.8, 128.4, 128.9, 129.7, 132.4, 134.7, 135.2, 137.4, 143.9. MS (m/z): 374 (M^+, ^{35}Cl). HRMS calcd for $C_{20}H_{20}ClNO_2S$: 373.0903. Found: 373.0935. IR (cm^{-1}): 1349, 1163, 1093.

P19 (Table 4, entry 4). Yield: 81%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, J = 7.5 Hz, 3H), 1.19−1.32 (m, 2H), 1.43−1.60 (m, 2H), 2.19 (t, J = 6.9 Hz, 2H), 2.45 (s, 3H), 3.14 (dd, J = 6.9, 9.3 Hz, 1H), 3.40 (dd, J = 1.8, 9.3 Hz, 1H), 3.46−3.52 (m, 1H), 3.66 (d, J = 13.8 Hz, 1H), 3.98 (d, J = 13.8 Hz, 1H), 5.01−5.12 (m, 2H), 5.63−5.75 (m, 1H), 7.35 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 7.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.9, 21.7, 21.8, 29.2, 36.3, 46.3, 50.0, 53.0, 115.8, 127.9, 129.5, 129.7, 132.2, 132.6, 135.1, 143.9. MS (m/z): 353 (M^+, ^{35}Cl). Anal. Calcd for $C_{18}H_{24}ClNO_2S$: C, 61.09; H, 6.84; N, 3.96. Found: C, 61.33; H, 6.94; N, 3.91. IR (cm^{-1}): 2959, 1350, 1166.

P20 (Table 4, entry 5). Yield 93%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.25 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H), 2.09−2.11 (m, 3H), 2.19 (dd, J = 6.0, 13.5 Hz, 1H), 2.65 (ddd, J = 0.9, 8.7, 9.3 Hz, 1H), 2.91 (dt, J = 1.2, 16.2 Hz, 1H), 3.04 (dt, J = 1.8, 16.2 Hz, 1H), 3.46−3.56 (m, 1H), 4.14−4.23 (m, 4H), 5.00−5.07 (m, 2H), 5.64−5.76 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.96, 13.99, 23.6, 38.7, 39.5, 46.2, 59.6, 61.7, 114.8, 124.0, 136.0, 137.9, 171.1, 171.2. MS (m/z): 300 (M^+, ^{35}Cl). HRMS calcd for $C_{15}H_{21}ClO_4$: 300.1128. Found: 300.1122.

P21 (Table 4, entry 6). Yield: 89%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.15 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.5 Hz, 3H), 2.16 (dd, J = 7.2, 13.5 Hz, 1H), 2.77 (ddd, J = 1.5, 8.4, 13.5 Hz, 1H), 2.92 (dd, J = 1.5, 16.2 Hz, 1H), 3.11 (dd, J = 2.1, 16.2 Hz, 1H), 3.67−3.76 (m, 1H), 4.142 (q, J = 7.5 Hz, 2H), 4.144 (q, J = 7.2 Hz, 2H), 5.10−5.21 (m, 2H), 5.78−5.90 (m, 1H), 7.26−7.42 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.89, 13.94, 39.1, 40.2, 46.7, 59.7, 61.6, 61.7, 115.1, 126.6, 128.1, 128.3, 128.5, 137.6, 138.6, 139.0, 170.84, 170.87. MS (m/z): 363 (M^+, ^{35}Cl). HRMS calcd for $C_{20}H_{23}ClO_4$: 362.1285. Found: 362.1306. IR (cm^{-1}): 1733, 1247.

P22 (Table 4, entry 7). Yield: 93%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.92 (t, J = 7.5 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.5 Hz, 3H), 1.20−1.29 (m, 2H), 1.43−1.53 (m, 2H), 2.14 (dd, J = 5.4, 13.2 Hz, 1H), 2.34 (t, J = 6.9 Hz, 2H), 2.67 (ddd, J = 1.2, 8.7, 13.6 Hz, 1H), 2.92 (d, J = 16.5 Hz, 1H), 3.03 (d, J = 15.0 Hz, 1H), 3.48−3.55 (m, 1H), 4.12−4.24 (m, 4H), 5.00−5.06 (m, 2H), 5.64−5.76 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.9, 21.8, 29.5, 36.4, 38.6, 39.4, 46.1, 59.5, 61.6, 114.6, 129.3, 135.8, 138.0, 171.1, 171.1. MS (m/z): 342 (M^+, ^{35}Cl). Anal. Calcd for $C_{18}H_{27}O_4Cl$: C, 63.06; H, 7.94. Found: C, 62.65; H, 7.94. IR (cm^{-1}): 1735, 1257.

P14. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.89 (t, J = 6.9 Hz, 3H), 1.33−1.46 (m, 2H), 1.98−2.05 (m, 2H), 2.65 (d, J = 1.5 Hz, 3H), 3.78−3.84 (m, 1H), 4.10 (dd, J = 1.8, 8.7 Hz, 1H), 4.37 (dd, J = 7.5, 8.7 Hz, 1H), 5.35−5.43 (m, 1H), 5.54−5.64 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.5, 22.2, 23.0, 34.3, 44.1, 70.3, 125.2, 126.3, 133.5, 148.8, 168.0. IR (cm^{-1}): 1758, 1658. MS (m/z): 214 (M^+, ^{35}Cl). Anal. Calcd for $C_{11}H_{13}ClO_2$: C, 61.54; H, 7.04. Found: C, 61.70; H, 7.11.

C. Procedure for the Syntheses of Compounds S11 and S12. In a three-necked flask, the substituted propynoic acid (5 mmol) and 2-chloro-3-butene-1-ol (0.53 g, 5 mmol) in CH_2Cl_2 (10 mL) were stirred at −20 °C under argon. To this mixture was added dropwise a solution of DCC (1.03 g, 5 mmol) and DMAP (6 mg, 0.05 mmol) in CH_2Cl_2 (10 mL). After 6 h, the reaction mixture was filtrated, and the residue was washed with Et_2O. After the solvent evaporated, the residue was subjected to column chromatography to obtain the desired product.

S11. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.01 (s, 3H), 4.32−4.35 (m, 2H), 4.54−4.57 (m, 1H), 4.30 (dd, J = 1.0, 10.2 Hz, 1H), 5.43 (dd, J = 1.0, 16.8 Hz, 1H), 5.82−5.88 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 3.8, 58.0, 67.4, 71.7, 86.8, 119.6, 133.9, 152.9. IR (cm^{-1}): 2246, 1716, 1252, 1069. MS (m/z): 137 ($M^+ - {}^{35}$Cl). HRMS calcd for $C_8H_9O_2Cl-Cl$: 137.0590. Found: [$M^+ - Cl$] 137.0587.

S12. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.40−4.43 (m, 2H), 4.57−4.63 (m, 1H), 5.33 (d, J = 10.2 Hz, 1H), 5.46 (d, J = 16.8 Hz, 1H), 5.85−6.00 (m, 1H), 7.26−7.62 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 58.1, 67.8, 80.0, 87.5, 119.3, 128.6, 130.9, 133.1, 134.0, 153.4. MS (m/z): 199 ($M^+ - {}^{35}$Cl). Anal. Calcd for $C_{13}H_{11}ClO_2$: C, 66.53; H, 4.72. Found: C, 66.92; H, 4.71.

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Supporting Information Available: Experimental details and ^{1}H NMR and ^{13}C NMR spectra for **P1**−**P22**, **S11**, **S12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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