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Rhodium-catalyzed synthesis of γ-butyrolactams and pyrrolidines via cycloisomerization of *N*-tethered 1,6-enynes

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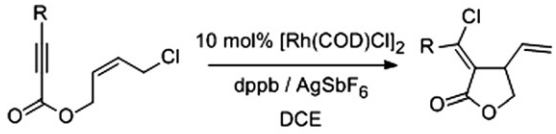
ABSTRACT

A rhodium-catalyzed cycloisomerization reaction of *N*-tethered 1,6-enynes with an intramolecular halogen shift has been developed, providing a useful process for the synthesis of stereo defined γ-butyrolactam and pyrrolidine derivatives in good to excellent yields. Effects of both electronic feature and steric structure of the substrates on the outcome of the reaction were investigated.

1. Introduction

γ-Butyrolactam and pyrrolidine structures are important building blocks in the syntheses of many natural products and pharmaceuticals.[1] Because of their important biological activities, such as cytotoxicity, antitumor, and *anti*-inflammation activities, the development of new methodologies to access these five-membered heterocyclic rings in regio- and stereo-controlled fashion appears to be highly desirable.[2] Recently, the use of transition metal catalysts in the carbon–carbon bond formation and the cyclization of enynes have been reported, which offer the unique means to construct various carbo- and heterocycles with high efficiency. Many transition metals, such as Pd,[3] Ru,[4] and Pt,[5] have been applied to catalyze these kinds of reactions. Zhang et al. firstly reported the cycloisomerization of 1,6-enyne catalyzed by Rh(I), which offers a potential methodology to the synthesis of γ-butyrolactam and pyrrolidine structures.[6a] The substrates with a functional group (OH, OAc, OBz, alkyl) at the allylic position can be cycloisomerized via a metallacyclopentane intermediate in excellent yields, regio- and enantioselectivity.[6b–e,7] Our group have developed a rhodium-catalyzed cycloisomerization of 1,6-enynes with a halogen atom at the allylic position to form stereo defined α-halomethylene-γ-butyrolactones, accompanying with a formal halogen shift (Scheme 1).[8] This sort of reactions proceeds through a π-allyl or enyl (σ+π)[9] rhodium intermediate rather than a metallacyclopentane intermediate.[6] In particular, deriving from the vinyl-chlorine structure activated by the carbonyl group, many further reactions could be easily achieved from the cyclization products (e.g., Suzuki coupling reaction, Stille coupling reaction). With the given success of the cycloisomerization of *O*-tethered and a few *N*-tethered enyne substrates, we became interested in the cyclization of broader *N*-tethered 1,6-enynes using the same rhodium catalytic system. Herein we wish to report the construction of α-chloroalkylidene-γ-butyrolactams and pyrrolidines from cationic rhodium-catalyzed intramolecular cyclization of *N*-tethered 1,6-enynes with a chloromethyl group at the alkene moiety.



R = Me, Ph, *n*-Bu, $MeOCH_2$, H up to 92% yield

Scheme 1. Cyclization of *O*-tethered enynes catalyzed by rhodium catalyst.

2. Results and discussion

Initial attempts at cycloisomerization with cationic rhodium catalysis focused on the reaction of (*Z*)-*N*-benzyl-*N*-(4-chlorobut-2-enyl)-but-2-ynamide (**1a**) as a model substrate. Employing of $[Rh(COD)Cl]_2$ as a precatalyst and common bisphosphine and monophosphine ligands, moderate to good yields of cyclization products (Table 1, entries 1–6) were obtained. The exocyclic C–C double bond in **2a** was believed to be in the *E*-configuration as compared the chemical shifts of the methyl protons adjacent to the exocyclic C–C double bond with its analogues.[8] When the reaction was carried out in 1,2-dichloroethane (DCE) with dppb as ligand, the highest yield could be achieved (Table 1, entry 4). The reaction was also evaluated with respect to solvents. Poor yields were observed when the reaction was performed in other noncoordinating solvents such as toluene and dichloromethane (Table 1, entries 7

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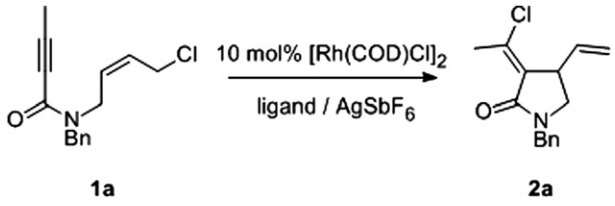
and 8). Because coordinating solvents have been reported competing the coordination with substrate to catalyst, resulting sluggish reaction,[6,8] we did not perform the reaction in polar solvents.

Table 1
Optimization for cycloisomerization of amide enyne catalyzed by $[Rh(COD)Cl]_2$[a]



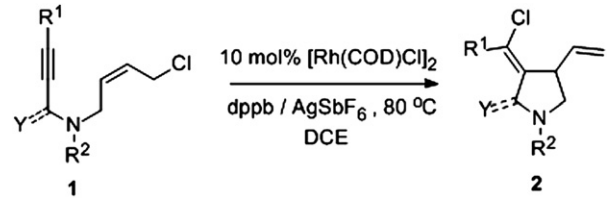
1a **2a**

Entry	Solvent	Ligand	Time (h)	Yield[c] (%)
1	DCE	PPh_3[b]	24	64
2	DCE	dppe	24	77
3	DCE	dppp	24	78
4	DCE	dppb	24	82
5	DCE	dppf	48	46
6	DCE	*rac*-binap	48	37
7	Toluene	dppb	48	Trace
8	DCM[d]	dppb	48	29

[a] All of the reactions were carried out with **1a** (0.2 mmol), $[Rh(COD)Cl]_2$ (9.9 mg, 0.02 mmol), bisphosphine (0.044 mmol), and $AgSbF_6$ (13.7 mg, 0.04 mmol) in DCE (3 mL) at 80 °C.
[b] PPh_3 (0.084 mmol) was used.
[c] Isolated yields.
[d] The reaction was performed at 50 °C.

With the experimental conditions optimized, the scope of the reaction was explored. At the onset, we assessed the reactivity of the electron-poor substrates (**1a**–**f**) by the reaction of (*Z*)-*N*-R^2-*N*-(4-chlorobut-2-enyl)-3-R^1-propiolamides (R^1, R^2=substituted groups, Table 2) in the presence of the cationic rhodium catalyst. The reactions were carried out in 1,2-dichloroethane (DCE) at 80 °C and were monitored by TLC. Most of the reactions proceeded smoothly to afford the γ-butyrolactams with an intramolecular chloride shift in high yields (Table 2, entries 1–6). Change of the substituents on the nitrogen atom and variation of groups at the alkyne moiety have little influence on the reactivity, which proves that this kind of reaction has a wide substrates tolerance. In addition, despite the NMR spectra revealed that the substrates of **1a**, **1b**, and **1c** were trans/cis-mixtures (the trans-isomers of these enyne amides have been reported unfavorable for the cycloisomerization,[6e] Scheme 2), good to excellent yields were obtained under the reaction conditions. These results revealed that this cationic Rh-catalytic system was greatly efficient to the cycloisomerization of enyne amides with a chloromethyl group at the alkene moiety as we expected.

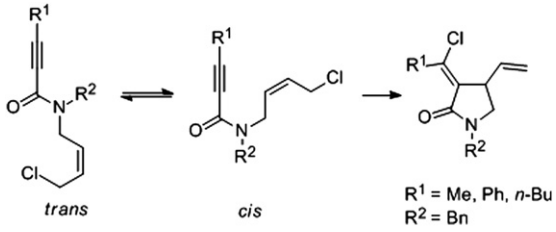
Table 2
Cycloisomerization of *N*-tethered 1,6-enynes catalyzed by $[Rh(COD)Cl]_2$/dppb/$AgSbF_6$[a]



1 **2**

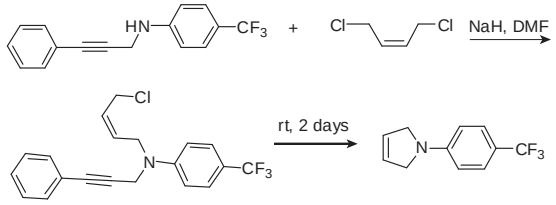
Entry	**1**	R^1	R^2	Y	**2**	Time (h)	Yield[c] (%)
1	**1a**[b]	Me	Bn	O	**2a**	18	82
2	**1b**[b]	Ph	Bn	O	**2b**	24	94
3	**1c**[b]	*n*-Bu	Bn	O	**2c**	10	76
4	**1d**	Me	Ts	O	**2d**	10	87
5	**1e**	Ph	Ts	O	**2e**	24	80
6	**1f**	*n*-Bu	Ts	O	**2f**	10	82
7	**1g**	Me	Ts	H_2	**2g**	24	82
8	**1h**	Ph	Ts	H_2	**2h**	24	50
9	**1i**	*n*-Bu	Ts	H_2	**2i**	24	77
10	**1j**	Me	Bn	H_2	—	24	Chaos[d]
11	**1k**	*n*-Bu	4-OMe–Ph	H_2	—	24	Chaos[d]

[a] All of the reactions were carried out with **1** (0.2 mmol), $[Rh(COD)Cl]_2$ (9.9 mg, 0.02 mmol), dppb (18.8 mg, 0.044 mmol), and $AgSbF_6$ (13.7 mg, 0.04 mmol) in DCE (3 mL) at 80 °C.
[b] trans/cis-Mixtures.
[c] All exocyclic double bonds of **2** were in the *E*-form as compared the chemical shifts of the protons in the group adjacent to the exocyclic C–C double bond with their analogues, see Ref. 8 and 10.
[d] The products were complicated and the target molecule was not detected.



Scheme 2. Rh-catalyzed cyclization reaction of trans/cis-isomers of amide.

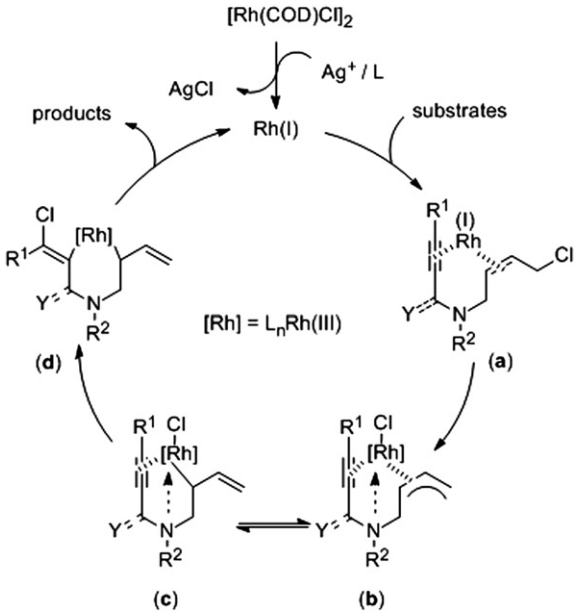
When we changed the substrates to electron-rich enynes (**1g**–**k**), to our surprise, the reaction results were highly dependent on the structures of substrates, which were quite different from the electron-poor substrates (Table 2, entries 7–11). Moderate yields could be achieved when the amines with an electron-withdrawing group (tosyl group) on the nitrogen atom were used as substrates, while no cyclization product was obtained when those substrates with electron-donating substituents (benzyl and 4-methoxyphenyl) were used (Table 1, entries 7 vs 10, 9 vs 11). We failed in making stable substrates with other electron-withdrawing groups, such as 4-nitrophenyl or 4-trifluoromethylphenyl. Luckily, when we started from *N*-(3-phenylprop-2-yn-1-yl)-4-(trifluoromethyl) aniline and (*Z*)-1,4-dichloro-2-butene to make the enyne substrate, we did isolated the desired product, but it cyclized in the absence of any catalyst at 10–15 °C in 2 days to give 1-(4-(trifluoromethyl) phenyl)-2,5-dihydro-1*H*-pyrrole; under the catalytic conditions, the substrates reacted much faster albeit to give the same product as when no catalyst was used (Scheme 3).



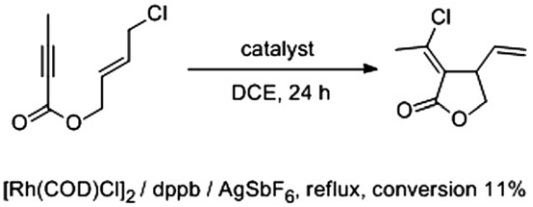
Scheme 3. Synthesis and reaction of 4-trifluoromethylphenyl substituted enyne substrate.

Lu et al. have reported that the nitrogen atom of the *N*-allylic alkynamides might coordinate with palladium to stabilize the carbon–palladium bond in the palladium(II)-catalyzed asymmetric synthesis of (*Z*)-α-alkylidene-γ-butyrolactams.[11] Based on the supposition and the mechanism of this cycloisomerization as we mentioned in our previous work, we reasoned that the nitrogen atom may also play the role of a ligand in the catalytic cycle. In the way of the conceivable mechanism (Scheme 4), the π-allyl intermediate (**b**) formed by the reaction of enyne-coordinated Rh species (**a**) with an allylic chloride is in equilibrium with the complex (**c**) via η^3–η^1 isomerization. In this process, the electronic effect of the substrates might influence

the coordinating ability of the nitrogen atom. Therefore, there might be a competition between the alkyne moiety and the nitrogen atom in the coordination with the rhodium species. For the electron-poor substrates, the weak coordinating ability of the nitrogen atom made it easier for the alkyne moiety to coordinate with the rhodium and undergo addition of the rhodium chloride bond to the alkyne. Therefore, high yields could be achieved with amide substrates. For the electron-rich substrates, the nitrogen atom of the amines, to some extent, had stronger coordinating ability; in this case, the reaction result became sensitive to the substituents on the nitrogen atom. The electron-donating substituents further increased the coordinating ability of the amino group, which might block the alkyne to coordinate with the rhodium species. Therefore, no cyclization product was isolated with these substrates. In our initial work, we have found that the cationic Rh species was poor catalyst for the cyclization of (*E*)-isomers of *O*-tethered enyne substrates (Scheme 5).[8] However, when we subjected (*E*)-isomers of amide substrates to the optimized reaction condition, good yields could be obtained. The results are shown in Table 3. The different results between *O*-tethered and *N*-tethered enynes could also be speculated based on the explanation above (Scheme 6). For the amide substrate, the nitrogen atom serves as a ligand for the cationic Rh species, which makes it easier for species (**e**) to transform to species (**f**). Therefore, it imparts significantly higher reactivity in comparison to *O*-tethered enynes.

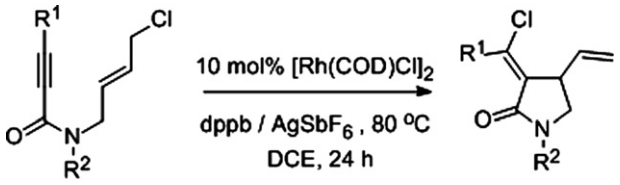


Scheme 4. A proposed mechanism involving a π-allyl rhodium species.



Scheme 5. Cyclization of (*E*)-isomer of *O*-tethered enyne.

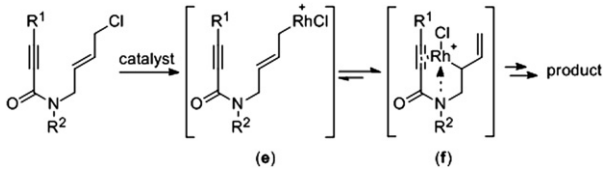
Table 3
Cycloisomerization of (*E*)-isomers of amide enynes catalyzed by $[Rh(COD)Cl]_2$/dppb/$AgSbF_6$[a]



1 **2**

Entry	**1**	R^1	R^2	**2**	Yield (%)[b]
1	**1l**[c]	Me	Bn	**2a**	80
2	**1m**[c]	Ph	Bn	**2b**	87
3	**1n**[c]	*n*-Bu	Bn	**2c**	86
4	**1o**	Ph	Ts	**2e**	88
5	**1p**	*n*-Bu	Ts	**2f**	80

[a] All of the reactions were carried out with **1** (0.2 mmol), $[Rh(COD)Cl]_2$ (9.9 mg, 0.02 mmol), dppb (18.8 mg, 0.044 mmol), and $AgSbF_6$ (13.7 mg, 0.04 mmol) in DCE (3 mL) at 80 °C.
[b] Isolated yields.
[c] trans-/cis- Mixtures.



Scheme 6. A plausible mechanism for cyclization of (*E*)-isomer of amide enyne substrates.

3. Conclusions

In conclusion, we have developed a cationic rhodium species catalyzed cyclization of *N*-tethered 1,6-enynes with a chloromethyl group at the alkene moiety. The amide substrates showed high reactivity and wide substrates tolerance, however, the cyclization of amine substrates was highly dependent on the substituents on the nitrogen atom: the amines with electron-withdrawing group on the nitrogen atom gave content results, while those with electron-donating group gave no cyclization product. The (*E*)-isomers of the amide enynes could also cyclize in content yields with the cationic Rh species in contrast to the *O*-tethered substrates. The reaction represents a useful process for the synthesis of α-chloroalkylidene-γ-butyrolactams and pyrrolidines. Further studies on the asymmetric reaction are in progress.

4. Experimental section

4.1. General procedure for the electron-poor enyne substrates; representative preparation of (*Z*)-*N*-benzyl-*N*-(4-chlorobut-2-enyl)but-2-ynamide (1a)

To a solution of but-2-ynoic acid (2.9 g, 35.0 mmol) and phenylmethanamine (3.2 g, 29.2 mmol) in CH_2Cl_2 (30 mL) was added dropwise a solution of DCC (7.2 g, 35.0 mmol) and DMAP (850 mg, 7.0 mmol) in CH_2Cl_2 (30 mL) at 0 °C. After being stirred at room temperature for 4 h, the reaction mixture was filtered to remove any precipitate and the filtrate was concentrated and purified by column chromatography (300–400 mesh silica gel, petroleum ether/ethyl acetate) to give *N*-benzylbut-2-ynamide; yield: 4.9 g (97%).

To a solution of NaH (0.9 g, 50 wt %, 18.7 mmol) in DMF (20 mL) was added dropwise a solution of *N*-benzylbut-2-ynamide (2.5 g, 14.4 mmol) in DMF (15 mL) at 0 °C. After being stirred at room

temperature for 30 min, (*Z*)-1,4-dichlorobut-2-ene (2.7 g, 21.6 mmol) was added in one portion. After further stirred at 60 °C for 20 h, the mixture was cooled to 0 °C and water (20 mL) was added carefully. The mixture was extracted with diethyl ether (3×25 mL) and the combined organic phase was washed with brine (20 mL), dried over Na_2SO_4, concentrated under reduced pressure and purified by the flash chromatography to afford the title compound; yield: 1.02 g (27%). ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 2.01 (s, 1.8H), 2.03 (s, 1.2H), 3.95–3.99 (m, 3.2H), 4.17 (dd, *J*=1.6, 6.8 Hz, 0.8H), 4.59 (s, 0.8H), 4.76 (s, 1.2H), 5.48–5.60 (m, 1H), 5.76–5.86 (m, 1H), 7.24–7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 4.04, 4.07, 38.31, 38.56, 39.60, 44.35, 46.80, 51.92, 73.12, 89.65, 90.07, 127.56, 127.69, 127.99, 128.06, 128.22, 128.69, 128.84, 128.98, 129.14, 129.38, 136.04, 136.18, 154.67, 154.69.

*4.1.1. (Z)-N-Benzyl-N-(4-chlorobut-2-enyl)-3-phenylpropiolamide (**1b**).* ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 3.96–4.07 (m, 3.2H), 4.27 (dd, *J*=1.6, 7.2 Hz, 0.8H), 4.66 (s, 0.8H), 4.85 (s, 1.2H), 5.53–5.90 (m, 2H), 7.29–7.56 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 38.28, 38.57, 39.88, 44.48, 46.93, 52.14, 81.28, 81.39, 90.67, 91.08, 120.17, 120.19, 127.65, 127.77, 127.98, 128.10, 128.31, 128.49, 128.53, 128.76, 128.92, 129.09, 129.28, 129.53, 130.15, 130.19, 132.37, 132.42, 135.93, 136.10, 154.56, 154.60.

*4.1.2. (Z)-N-Benzyl-N-(4-chlorobut-2-enyl)hept-2-ynamide (**1c**).* ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 0.87 (t, *J*=7.2 Hz, 1.8H), 0.92 (t, *J*=7.2 Hz, 1.2H), 1.35–1.46 (m, 2H), 1.51–1.59 (m, 2H), 2.33–2.40 (m, 2H), 3.94–3.99 (m, 3H), 4.17 (dd, *J*=1.6, 7.2 Hz, 1H), 4.59 (s, 0.8H), 4.75 (s, 1.2H), 5.49–5.61 (m, 1H), 5.76–5.87 (m, 1H), 7.25–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 13.37, 13.42, 18.56, 18.61, 21.86, 21.96, 29.65, 29.71, 38.30, 38.57, 39.66, 44.35, 46.72, 51.96, 73.75, 73.85, 93.73, 94.16, 127.53, 127.65, 127.94, 128.14, 128.24, 128.66, 128.79, 128.98, 129.21, 129.31, 136.11, 136.26, 154.72. HRMS calcd for $C_{18}H_{22}ClNO$: 303.1390. Found: 303.1430.

*4.1.3. (Z)-N-(4-Chlorobut-2-enyl)-N-tosylbut-2-ynamide (**1d**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3H), 2.44 (s, 3H), 4.26 (dd, *J*=1.2, 7.8 Hz, 2H), 4.69 (dd, *J*=1.2, 7.0 Hz, 2H), 5.65–5.72 (m, 1H), 5.84–5.90(m, 1H), 7.32 (dd, *J*=0.9, 8.4 Hz, 2H), 7.85 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.29, 21.65, 38.62, 43.49, 73.27, 93.58, 128.43, 128.57, 129.41, 129.44, 135.77, 145.19, 152.16.

*4.1.4. (Z)-N-(4-Chlorobut-2-enyl)-3-phenyl-N-tosylpropiolamide (**1e**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 4.28 (d, *J*=7.9 Hz, 2H), 4.75 (d, *J*=7.0 Hz, 2H), 5.72–5.77 (m, 1H), 5.86–5.91 (m, 1H), 7.30–7.56 (m, 7H), 7.88–7.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.67, 38.65, 43.49, 81.37, 93.84, 119.22, 128.24, 128.52, 128.72, 129.59, 129.73, 131.12, 132.76, 135.77, 145.32, 152.28. HRMS calcd for $C_{20}H_{18}ClNO_3S$+H: 388.0774. Found: [M^++H]: 388.0786.

*4.1.5. (Z)-N-(4-Chlorobut-2-enyl)-N-tosylhept-2-ynamide (**1f**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J*=7.5 Hz, 3H), 1.36–1.42 (m, 2H), 1.49–1.55 (m, 2H), 2.35 (t, *J*=7.1 Hz, 2H), 2.44 (s, 3H), 4.26 (dd, *J*=0.7, 7.8 Hz, 2H), 4.69 (dd, *J*=1.1, 7.0 Hz, 2H), 5.65–5.72 (m, 1H), 5.84–5.90 (m, 1H), 7.32 (d, *J*=7.6 Hz, 2H), 7.85 (d, *J*=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.40, 18.76, 21.63, 21.94, 29.26, 38.63, 43.55, 73.90, 97.74, 128.41, 128.56, 129.43, 135.81, 145.14, 152.25. HRMS calcd for $C_{18}H_{22}ClNO_3S$+H: 368.1087. Found: [M^++H]: 368.1090.

4.2. General procedure for the electron-rich enyne substrates; representative preparation of (*Z*)-*N*-(but-2-ynyl)-*N*-(4-chlorobut-2-enyl)-4-methylbenzenesulfonamide (1g)

To a solution of NaH (0.92 g, 50 wt %, 19.2 mmol) in DMF (20 mL) was added dropwise a solution of *tert*-butyl tosylcarbamate (4.8 g, 17.6 mmol) in DMF (10 mL) at 0 °C. After being stirred at room temperature for 30 min, a solution of 1-bromobut-2-yne (2.1 g, 16.0 mmol) in DMF (5 mL) was added dropwise, and then the reaction mixture was stirred for an additional 4 h at 60 °C. After the mixture was cooled to room temperature, water (20 mL) was added and the solution was extracted with diethyl ether (3×20 mL). The organic phase was combined, dried over Na_2SO_4, concentrated under reduced pressure, and purified by chromatography to give *tert*-butyl but-2-ynyl(tosyl)carbamate; yield: 3.9 g (75%).

To a solution of *tert*-butyl but-2-ynyl(tosyl)carbamate (3.9 g, 12.1 mmol) in CH_2Cl_2 (20 mL) was added dropwise TFA (4.1 g, 36.0 mmol). After stirring for 4 h at room temperature, saturated $NaHCO_3$ solution (40 mL) was added carefully and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined extracts were dried over Na_2SO_4, concentrated under reduced pressure, and purified by the flash chromatography to afford *N*-(but-2-ynyl)-4-methylbenzenesulfonamide; yield: 2.4 g (90%).

To a solution of NaH (0.26 g, 50 wt %, 5.4 mmol) in DMF (20 mL) was added dropwise a solution of *N*-(but-2-ynyl)-4-methylbenzenesulfonamide (1.0 g, 4.5 mmol) in DMF (10 mL) at 0 °C. After being stirred at room temperature for 30 min, (*Z*)-1,4-dichlorobut-2-ene (0.85 g, 6.8 mmol) was added in one portion, and then the reaction mixture was stirred for an additional 4 h at 60 °C. After the mixture was cooled to room temperature, water (20 mL) was added and the solution was extracted with diethyl ether (3×20 mL). The organic phase was combined, dried over Na_2SO_4, concentrated under reduced pressure, and purified by chromatography to give the title compound; yield: 732.3 mg (52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55 (t, *J*=2.4 Hz, 3H), 2.43 (s, 3H), 3.88 (dd, *J*=1.2, 7.6 Hz, 2H), 4.01 (q, *J*=2.0 Hz, 2H), 4.11 (dd, *J*=0.8, 7.6 Hz, 2H), 5.54–5.60 (m, 1H), 5.82–5.89 (m, 1H), 7.31 (d, *J*=8.0 Hz, 2H), 7.73 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.20, 21.49, 36.55, 38.42, 42.38, 71.30, 81.96, 127.86, 127.88, 129.33, 130.64, 135.60, 143.49. HRMS calcd for $C_{15}H_{18}ClNO_2S$: 311.0747. Found: 311.0758.

*4.2.1. (Z)-N-(4-Chlorobut-2-enyl)-4-methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide (**1h**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 3.98 (dd, *J*=0.8, 7.6 Hz, 2H), 4.13 (dd, *J*=0.8, 7.6 Hz, 2H), 4.30 (s, 2H), 5.62–5.68 (m, 1H), 5.89–5.95 (m, 1H), 7.08 (d, *J*=6.8 Hz, 2H), 7.23–7.30 (m, 5H), 7.78 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.34, 36.79, 38.33, 42.54, 81.19, 85.83, 121.79, 127.56, 127.73, 128.09, 128.48, 129.56, 131.01, 131.41, 135.40, 143.69.

*4.2.2. (Z)-N-(4-Chlorobut-2-enyl)-N-(hept-2-ynyl)-4-methylbenzenesulfonamide (**1i**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82–0.86 (m, 3H), 1.19–1.24 (m, 4H), 1.89–1.94 (m, 2H), 2.43 (s, 3H), 3.89 (dd, *J*=1.2, 7.2 Hz, 2H), 4.05 (t, *J*=2.0 Hz, 2H), 4.11 (dd, *J*=1.2, 7.6 Hz, 2H), 5.55–5.62 (m, 1H), 5.83–5.90 (m, 1H), 7.30 (d, *J*=8.4 Hz, 2H), 7.73 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.40, 17.96, 21.39, 21.73, 30.20, 36.41, 38.31, 42.21, 71.85, 86.51, 127.71, 127.78, 129.31, 130.62, 135.59, 143.36.

*4.2.3. (Z)-N-Benzyl-N-(but-2-ynyl)-4-chlorobut-2-en-1-amine (**1j**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.81 (t, *J*=2.0 Hz, 3H), 3.91–4.02 (m, 2H), 4.13–4.17 (m, 2H), 4.58 (s, 2H), 4.76 (d, *J*=6.0 Hz, 2H), 5.76–5.87 (m, 2H), 7.25–7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.47, 36.07, 38.74, 48.96, 60.62, 73.81, 127.44, 127.55, 128.14, 128.51, 129.47, 136.97, 155.63.

*4.2.4. (Z)-N-(4-Chlorobut-2-enyl)-N-(hept-2-ynyl)-4-methoxyaniline (**1k**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J*=7.2 Hz, 3H), 1.33–1.39 (m, 2H), 1.41–1.48 (m, 2H), 2.16 (tt, *J*=2.0, 7.2 Hz, 2H), 3.77 (s, 3H), 3.87–3.90 (m, 4H), 4.06–4.07 (m, 2H), 5.84–5.86 (m, 2H), 6.836–6.838 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.56, 18.36, 21.86, 30.83, 41.25, 44.56, 53.01, 55.61, 75.49, 84.81, 114.40,

117.14, 128.09, 131.59, 143.11, 152.89. HRMS calcd for $C_{18}H_{24}ClNO$: 305.1546. Found: 305.1537.

*4.2.5. (E)-N-Benzyl-N-(4-chlorobut-2-enyl)but-2-ynamide (**1l**).* ^1H NMR (400 MHz, $CDCl_3$) two isomers: δ 2.01 (s, 1.6H), 2.02 (s, 1.4H), 3.91 (d, J=4.0 Hz, 1H), 4.00–4.01 (m, 1H), 4.04 (d, J=5.6 Hz, 1H), 4.08 (d, J=4.4 Hz, 1H), 4.59 (s, 1H), 4.76 (s, 1H), 5.65–5.67 (m, 1H), 5.70–5.74 (m, 1H), 7.22–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 3.96, 43.76, 43.96, 44.25, 46.64, 48.88, 51.74, 73.02, 73.13, 89.49, 89.61, 127.50, 127.82, 128.19, 128.42, 128.54, 128.70, 129.14, 129.37, 129.57, 136.03, 136.22, 154.55, 154.70. HRMS calcd for $C_{15}H_{16}ClNO$: 261.0920. Found: 261.0923.

*4.2.6. (E)-N-Benzyl-N-(4-chlorobut-2-enyl)-3-phenylpropiolamide (**1m**).* ^1H NMR (400 MHz, $CDCl_3$) two isomers: δ 3.99–4.06 (m, 3H), 4.18 (d, J=4.4 Hz, 1H), 4.66 (s, 1H), 4.85 (s, 1H), 5.71–5.73 (m, 1H), 5.77–5.81 (m, 1H), 7.27–7.43 (m, 8H), 7.50–7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 43.72, 43.95, 44.53, 46.90, 49.03, 51.92, 81.22, 81.39, 90.51, 90.60, 120.10, 120.15, 127.57, 127.60, 127.91, 128.26, 128.29, 128.41, 128.44, 128.60, 128.78, 128.90, 129.58, 129.78, 130.08, 132.26, 132.33, 135.91, 136.11, 154.45, 154.62. HRMS calcd for $C_{20}H_{18}ClNO$: 323.1077. Found: 323.1077.

*4.2.7. (E)-N-Benzyl-N-(4-chlorobut-2-enyl)hept-2-ynamide (**1n**).* ^1H NMR (400 MHz, $CDCl_3$) two isomers: δ 0.87 (t, J=7.2 Hz, 1.6H), 0.92 (t, J=7.2 Hz, 1.4H), 1.35–1.46 (m, 2H), 1.49–1.59 (m, 2H), 2.34–2.39 (m, 2H), 3.92 (d, J=3.6 Hz, 1H), 4.01–4.02 (m, 1H), 4.05 (d, J=5.2 Hz, 1H), 4.09 (d, J=4.0 Hz, 1H), 4.59 (s, 1H), 7.46 (s, 1H), 5.66–5.68 (m, 1H), 5.71–5.75 (m, 1H), 7.23–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 13.32, 13.36, 18.49, 18.50, 21.80, 21.86, 29.57, 29.61, 43.75, 43.98, 44.32, 46.68, 48.88, 51.74, 73.68, 73.82, 93.60, 93.69, 127.46, 127.76, 128.21, 128.49, 128.52, 128.66, 129.07, 129.34, 129.46, 136.08, 136.27, 154.63, 154.78. HRMS calcd for $C_{18}H_{22}ClNO-Cl$: 268.1701. Found: $[M^+-Cl]$: 268.1725.

*4.2.8. (E)-N-(4-Chlorobut-2-enyl)-3-phenyl-N-tosylpropiolamide (**1o**).* ^1H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 4.08 (d, J=6.4 Hz, 2H), 4.69 (d, J=5.6 Hz, 2H), 5.89–6.03 (m, 2H), 7.31 (d, J=7.6 Hz, 2H), 7.38–7.42(m, 2H), 7.47–7.50 (m, 1H), 7.53–7.55 (m, 2H), 7.91 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.57, 43.77, 47.73, 81.28, 93.29, 119.10, 128.60, 128.64, 129.43, 130.40, 131.03, 132.61, 135.53, 145.23, 152.29. HRMS calcd for $C_{20}H_{18}ClNO_3S$: 387.0696. Found: 387.0671.

*4.2.9. (E)-N-(4-Chlorobut-2-enyl)-N-tosylhept-2-ynamide (**1p**).* ^1H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, J=7.2 Hz, 3H), 1.35–1.44 (m, 2H), 1.50–1.57 (m, 2H), 2.35 (t, J=6.8 Hz, 2H), 2.44 (s, 3H), 4.07 (d, J=6.4 Hz, 2H), 4.63 (d, J=5.6 Hz, 2H), 5.83–5.98 (m, 2H), 7.31 (d, J=8.8 Hz, 2H), 7.87 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.35, 18.64, 21.57, 21.87, 29.20, 43.77, 47.75, 73.89, 97.20, 128.72, 128.85, 129.32, 130.20, 135.65, 145.06, 152.29. HRMS calcd for $C_{18}H_{22}ClNO_3S$: 367.1009. Found: 367.1013.

4.3. General procedure for the cycloisomerization of *N*-tethered enynes with the cationic Rh-catalytic system

Under nitrogen atmosphere, a 25 mL Schlenk tube was charged with enyne substrate (0.2 mmol, 100 mol %), $[Rh(COD)Cl]_2$ (9.9 mg, 0.02 mmol, 10 mol %), ligands (0.044 mmol, 22 mol %), and DCE (2 mL). After being stirred for 2 min, silver salt (0.04 mmol, 20 mol %) in DCE (1 mL) was added to the system. The reaction was carried out at the indicated temperature and monitored by TLC. After the reaction was completed, the reaction mixture was evaporated and directly subjected to column chromatography using petroleum ether/ethyl acetate as eluent to give the cyclization product.

*4.3.1. (E)-1-Benzyl-3-(1-chloroethylidene)-4-vinylpyrrolidin-2-one (**2a**).* In accordance with the general procedure above, a solution of substrate **1a** (52.4 mg, 0.2 mmol, 100 mol %), $[Rh(COD)Cl]_2$ (9.9 mg, 0.02 mmol, 10 mol %), and dppb (18.8 mg, 0.044 mmol, 22 mol %) in DCE (2 mL) was stirred for 2 min, and then $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %) in DCE (1 mL) was added to the system. The reaction was performed at 80 °C and monitored by TLC. Purification by flash column chromatography (silica gel, ethyl acetate/hexane=1:20) provides the title compound; yield: 43.0 mg (82%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.71 (d, J=1.2 Hz, 3H), 2.98 (dd, J=1.6, 10.1 Hz, 1H), 3.45 (dd, J=7.6, 9.6 Hz, 1H), 3.65–3.66 (m, 1H), 4.42 (d, J=14.5 Hz, 1H), 4.58 (d, J=15.1 Hz, 1H), 5.06–5.10 (m, 2H), 5.66–5.75 (m, 1H), 7.22–7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.24, 41.10, 46.93, 48.97, 115.66, 127.63, 128.08, 128.68, 129.55, 135.90, 136.01, 142.17, 165.73.

*4.3.2. (E)-1-Benzyl-3-(chloro(phenyl)methylene)-4-vinylpyrrolidin-2-one (**2b**).* ^1H NMR (400 MHz, $CDCl_3$) δ 3.04 (dd, J=1.7, 10.4 Hz, 1H), 3.54 (dd, J=7.4, 9.6 Hz, 1H), 3.81–3.85 (m, 1H), 4.34 (d, J=14.4 Hz, 1H), 4.58 (d, J=15.2 Hz, 1H), 5.15–5.22 (m, 2H), 5.76–5.85 (m, 1H), 7.20–7.50 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.92, 47.03, 48.87, 116.12, 127.59, 127.68, 128.23, 128.68, 129.18, 129.37, 131.08, 135.53, 135.96, 136.49, 141.07, 164.09.

*4.3.3. (E)-1-Benzyl-3-(1-chloropentylidene)-4-vinylpyrrolidin-2-one (**2c**).* ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J=7.0 Hz, 3H), 1.35–1.45 (m, 2H), 1.58–1.69 (m, 2H), 2.97 (dd, J=1.6, 9.5 Hz, 1H), 3.07–3.14 (m, 1H), 3.25–3.32 (m, 1H), 3.44 (dd, J=7.4, 10.0 Hz, 1H), 3.63–3.67 (m, 1H), 4.43 (d, J=15.1 Hz, 1H), 4.57 (d, J=15.6 Hz, 1H), 5.06–5.10 (m, 2H), 5.67 (m, 1H), 7.21–7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.99, 13.90, 21.97, 30.24, 33.96, 41.14, 46.96, 49.03, 115.56, 127.64, 128.11, 128.70, 129.46, 136.04, 136.10, 147.46, 165.57. HRMS calcd for $C_{18}H_{22}ClNO$: 303.1390. Found: 303.1397.

*4.3.4. (E)-3-(1-Chloroethylidene)-1-tosyl-4-vinylpyrrolidin-2-one (**2d**).* ^1H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 2.57 (d, J=1.2 Hz, 3H), 3.69–3.74 (m, 1H), 3.78 (dd, J=1.6, 10.2 Hz, 1H), 3.90 (dd, J=7.6, 10.0 Hz, 1H), 5.09–5.16 (m, 2H), 5.68–5.77 (m, 1H), 7.35 (d, J=8.8 Hz, 2H), 7.93 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.70, 22.87, 40.88, 48.92, 116.77, 127.91, 128.18, 129.69, 134.54, 134.92, 145.29, 148.26, 163.73.

*4.3.5. (E)-3-(Chloro(phenyl)methylene)-1-tosyl-4-vinylpyrrolidin-2-one (**2e**).* ^1H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.84 (dd, J=1.5, 9.8 Hz, 1H), 3.87–3.91 (m, 1H), 3.99 (dd, J=7.5, 9.8 Hz, 1H), 5.19–5.24 (m, 2H), 5.78–5.87 (m, 1H), 7.26–7.39 (m, 7H), 7.86 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.58, 41.76, 48.82, 116.99, 127.76, 128.04, 128.82, 128.98, 129.58, 130.10, 134.23, 134.81, 135.30, 145.10, 146.60, 161.81. HRMS calcd for $C_{20}H_{18}ClNO_3S$: 387.0696. Found: 387.0692.

*4.3.6. (E)-3-(1-Chloropentylidene)-1-tosyl-4-vinylpyrrolidin-2-one (**2f**).* ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, J=7.3 Hz, 3H), 1.24–1.34 (m, 2H), 1.49–1.57 (m, 2H), 2.45 (s, 3H), 2.85–2.92 (m, 1H), 3.06–3.14 (m, 1H), 3.69–3.72 (m, 1H), 3.78 (dd, J=1.5, 9.5 Hz, 1H), 3.88 (dd, J=7.5, 9.9 Hz, 1H), 5.08–5.16 (m, 2H), 5.69–5.78 (m, 1H), 7.34 (d, J=8.0 Hz, 2H), 7.92 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.81, 21.70, 21.90, 30.09, 34.54, 40.90, 48.98, 116.67, 127.73, 128.14, 129.68, 134.63, 134.97, 145.21, 153.58, 163.46. HRMS calcd for $C_{18}H_{22}ClNO_3S$: 367.1009. Found: 367.1007.

*4.3.7. (E)-3-(1-Chloroethylidene)-1-tosyl-4-vinylpyrrolidine (**2g**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.98 (d, J=1.2 Hz, 3H), 2.44 (s, 3H), 3.14 (dd, J=6.4, 9.6 Hz, 1H), 3.40 (dd, J=1.6, 9.2 Hz, 1H), 3.45–3.48 (m, 1H), 3.60–3.63 (m, 1H), 3.94–3.98 (m, 1H), 5.04–5.11 (m, 1H), 5.64–5.72 (m, 1H), 7.34 (d, J=8.0 Hz, 2H), 7.70 (d, J=8.4 Hz, 2H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 21.55, 23.31, 46.24, 50.19, 53.14, 115.90, 124.32, 127.86, 129.74, 132.05, 132.74, 135.04, 143.94. HRMS calcd for $C_{15}H_{18}ClNO_2S-Cl$: 276.1058. Found: $[M^+-Cl]$ 276.1064.

*4.3.8. (E)-3-(Chloro(phenyl)methylene)-1-tosyl-4-vinylpyrrolidine (**2h**).* ^1H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.33–3.40 (m, 2H), 3.65–3.68 (m, 1H), 3.71 (d, J=14.4 Hz, 1H), 4.06 (dd, J=1.6, 14.4 Hz, 1H), 5.11–5.21 (m, 2H), 5.70–5.79 (m, 1H), 7.27–7.39 (m, 7H), 7.63 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.48, 47.03, 50.97, 52.50, 116.36, 126.91, 127.68, 127.81, 128.42, 128.93, 129.69, 132.44, 134.72, 135.27, 137.39, 143.85.

*4.3.9. (E)-3-(1-Chloropentylidene)-1-tosyl-4-vinylpyrrolidine (**2i**).* ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J=6.8 Hz, 3H), 1.24–1.27 (m, 2H), 1.47–1.51 (m, 2H), 2.19 (dt, J=3.2, 7.2 Hz, 2H), 2.45 (s, 3H), 3.13 (dd, J=7.2, 10.0 Hz, 1H), 3.40 (dd, J=1.6, 9.2 Hz, 1H), 3.47–3.51 (m, 1H), 3.65 (d, J=13.6 Hz, 1H), 3.98 (dd, J=1.2, 13.6 Hz, 1H), 5.04–5.11 (m, 2H), 5.65–5.73 (m, 1H), 7.35 (d, J=8.4 Hz, 2H), 7.70 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.87, 21.52, 21.79, 29.11, 36.23, 46.15, 49.94, 52.96, 115.80, 127.83, 129.51, 129.69, 132.02, 132.53, 135.09, 143.88.

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References and notes

1. For selected examples, see: (a) Obst, U.; Betschmann, P.; Lerner, C.; Seiler, P.; Diederich, F. *Helv. Chim. Acta* **2000**, *83*, 855–909; (b) Alvarez-Ibarra, C.; Csákÿ, A. G.; Lóópez, I.; Quiroga, M. L. *J. Org. Chem.* **1997**, *62*, 479–484; (c) Waid, P. P.; Flynn, G. A.; Huber, E. W.; Sabol, J. S. *Tetrahedron Lett.* **1996**, *37*, 4091–4094; (d) Bianco, A.; Maggini, M.; Scorrano, G.; Toniolo, C.; Marconi, G.; Villani, C.; Prato, M. *J. Am. Chem. Soc.* **1996**, *118*, 4072–4082; (e) Kolodziej, S. A.; Nikiforovich, G. V.; Skeean, R.; Lignon, M. F.; Martinez, J.; Marshall, G. R. *J. Med. Chem.* **1995**, *38*, 137–149; (f) Sebahar, P. R.; Williams, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 5666–5667; (g) Denhart, D. J.; Griffith, D. A.; Heathcock, C. H. *J. Org. Chem.* **1998**, *63*, 9616–9617; (h) Overman, L. E.; Tellew, J. E. *J. Org. Chem.* **1996**, *61*, 8338–8340; (i) Sisko, J.; Henry, J. R.; Weinreb, S. M. *J. Org. Chem.* **1993**, *58*, 4945–4951; (j) Murphy, M. M.; Schullek, J. R.; Gordon, E. M.; Gallop, M. A. *J. Am. Chem. Soc.* **1995**, *117*, 7029–7030; (k) Puschl, A.; Tedeschi, T.; Nielsen, P. E. *Org. Lett.* **2000**, *2*, 4161–4163.
2. (a) von Wangelin, A. J.; Neumann, H.; Gordes, D.; Spannenberg, A.; Beller, M. *Org. Lett.* **2001**, *3*, 2895–2898; (b) Stevens, R. V.; Chang, J. H.; Lapalme, R.; Schow, S.; Schlageter, M. G.; Shapiro, R.; Weller, H. N. *J. Am. Chem. Soc.* **1983**, *105*, 7719–7729; (c) Stolowich, N. J.; Wang, J.; Spencer, J. B.; Santander, P. J.; Roessner, C. A.; Scott, A. I. *J. Am. Chem. Soc.* **1996**, *118*, 1657–1662; (d) Neya, S.; Funasaki, N. *Tetrahedron Lett.* **2002**, *43*, 1057–1058; (e) Naik, R.; Joshi, P.; Kaiwar, S. P.; Deshpande, R. K. *Tetrahedron* **2003**, *59*, 2207–2213; (f) Cammidge, A. N.; Ozturk, O. *J. Org. Chem.* **2002**, *67*, 7457–7464.
3. (a) Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34–42 and references therein; (b) Gómez-Bengoa, E.; Cuerva, J. M.; Echavarren, A. M.; Martorell, G. *Angew. Chem., Int. Ed.* **1997**, *36*, 767–769; (c) Ji, J.; Wang, Z.; Lu, X. *Organometallics* **1996**, *15*, 2821–2828; (d) Zhang, Z.; Lu, X.; Xu, Z.; Zhang, Q.; Han, X. *Organometallics* **2001**, *20*, 3724–3728; (e) Zhao, L.; Lu, X.; Xu, W. *J. Org. Chem.* **2005**, *70*, 4059–4063; (f) Yang, S.; Jiang, H.; Li, Y.; Chen, H.; Luo, W.; Xu, Y. *Tetrahedron* **2008**, *64*, 2930–2937; (g) Balraju, V.; Dev, R. V.; Reddy, D. S.; Iqbal, J. *Tetrahedron Lett.* **2006**, *47*, 3569–3571; (h) Harada, K.; Tonoi, Y.; Kato, H.; Fukuyama, Y. *Tetrahedron Lett.* **2002**, *43*, 3829–3832; (i) Hatano, M.; Terada, M.; Mikami, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 249–253.
4. (a) Fuerstner, A.; Schlecker, A.; Lehmann, C. W. *Chem. Commun.* **2007**, 4277–4279; (b) Faller, J. W.; Fontaine, P. P. *J. Organomet. Chem.* **2006**, *691*, 1912–1918; (c) Tanaka, D.; Sato, Y.; Mori, M. *Organometallics* **2006**, *25*, 799–801; (d) Trost, B. M.; Surivet, J.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 15592–15602; (e) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 714–715; (f) Nishida, M.; Adachi, N.; Onozuka, K.; Matsumura, H.; Mori, M. *J. Org. Chem.* **1998**, *63*, 9158–9159.
5. (a) Zhang, L.; Sun, J.; Kozmin, S. A. *Adv. Synth. Catal.* **2006**, *348*, 2271–2296; (b) Nevado, C.; Ferrer, C.; Echavarren, A. M. *Org. Lett.* **2004**, *6*, 3191–3194; (c) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901–903; (d) Meng, Q.; Li, M.; Zhang, J.; Shen, W. *Int. J. Quantum Chem.* **2006**, *106*, 1569–1579; (e) Blaszykowski, C.; Harrak, Y.; Goncalves, M.; Cloarec, J.; Dhimane, A.; Fensterbank, L.; Malacria, M. *Org. Lett.* **2004**, *6*, 3771–3774; (f) Mendez, M.; Munoz, M. P.; Nevado, C.; Cardenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 10511–10520.
6. (a) Cao, P.; Wang, B.; Zhang, X. *J. Am. Chem. Soc.* **2000**, *122*, 6490–6491; (b) Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 8198–8199; (c) Cao, P.; Zang, X. *Angew. Chem., Int. Ed.* **2000**, *39*, 4104–4106; (d) Lei, A.; He, M.; Wu, S.; Zhang, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 3457–3460; (e) Lei, A.; Waldkirch, J. P.; He, M.; Zhang, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 4526–4529.
7. For a recent review on co-operative effect of Lewis acid with transition metal for organic synthesis, see: Wang, C.; Xi, Z. *Chem. Soc. Rev.* **2007**, *36*, 1395–1406.
8. (a) Tong, X.; Li, D.; Zhang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2004**, *126*, 7601–7607; (b) Tong, X.; Zhang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2003**, *125*, 6370–6371.
9. For rhodium-catalyzed allylic substitution reactions through an enyl ($\sigma+\pi$) organorhodium intermediate, see: (a) Evans, P. A.; Nelson, J. D. *J. Am. Chem. Soc.* **1998**, *120*, 5581–5582; (b) Evans, P. A.; Robinson, J. E.; Nelson, J. D. *J. Am. Chem. Soc.* **1999**, *121*, 6761–6762; (c) Evans, P. A.; Leahy, D. K. *J. Am. Chem. Soc.* **2000**, *122*, 5012–5013; (d) Evans, P. A.; Kennedy, L. J. *J. Am. Chem. Soc.* **2001**, *123*, 1234–1235; (e) Evans, P. A.; Leahy, D. K. *J. Am. Chem. Soc.* **2002**, *124*, 7882–7883; (f) Evans, P. A.; Uraguchi, D. *J. Am. Chem. Soc.* **2003**, *125*, 7158–7159; (g) Evans, P. A.; Leahy, D. K. *J. Am. Chem. Soc.* **2003**, *125*, 8974–8975; (h) Evans, P. A.; Lawler, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 8642–8643; (i) Evans, P. A.; Leahy, D. K.; Andrews, W. J.; Uraguchi, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 4788–4791; (j) Evans, P. A.; Robinson, J. E.; Moffett, K. K. *Org. Lett.* **2001**, *3*, 3269–3271; (k) Evans, P. A.; Kennedy, L. J. *Org. Lett.* **2000**, *2*, 2213–2215; (l) Evans, P. A.; Leahy, D. K.; Slieker, L. M. *Tetrahedron: Asymmetry* **2003**, *14*, 3613–3618; (m) Evans, P. A.; Nelson, J. D. *Tetrahedron Lett.* **1998**, *39*, 1725–1728.
10. Zhu, G.; Zhang, Z. *J. Org. Chem.* **2005**, *70*, 3339–3341.
11. (a) Xu, W.; Kong, A.; Lu, X. J. *Org. Chem.* **2006**, *71*, 3854–3858; (b) Zhang, Q.; Lu, X.; Han, X. *J. Org. Chem.* **2001**, *66*, 7676–7684; (c) Lu, X.; Zhang, Q. *Pure Appl. Chem.* **2001**, *73*, 247–250.