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Experimental and Theoretical Investigation of Hydrogenative Cyclization of Allenynes

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Keywords: Cumulenes / Allenes / Alkynes / Platinum / Hydrogenation / Reductive cyclization / Density functional calculations

Upon platinum-catalyzed hydrogenation, allenynes underwent reductive cyclization to provide hetero- and carbocycles with completely controlled regio- and stereoselectivity. By employing hydrogen as a reductant, the use of stoichiometric amounts of toxic organometallic reductants was avoided, leading to clean and cost-effective synthesis. A possible catalytic cycle is proposed on the basis of a deuterium-labeling study and theoretical calculations.

Introduction

The transition-metal-catalyzed reductive cyclization of π-unsaturated compounds has been studied extensively as a convenient route for producing synthetically useful carbo- and heterocycles.[1–3] Among the π-unsaturated compounds used for reductive cyclization, alkynes have often been employed because they are subjected to facile hydrometalation at the onset of the catalytic cycle. On the other hand, allenes are less preferred for reductive cyclization because of their poor selectivity and reactivity. Accordingly, studies on reductive cyclization of allenynes that aim to assess the product distribution and the related reaction mechanism are of interest.[3–6] We expect that our experimental results and theoretical calculations on reductive cyclization of allenynes will contribute to a better understanding of the reactivity and selectivity of allenyne cyclization under hydrogenative conditions.

Recently, our research group studied platinum-catalyzed, hydrogen-mediated, reductive cyclization by using a wide range of π-functional groups: bis(enones), enone–aldehydes, alkyne–alkenes, alkyne–α,β-unsaturated carbonyl compounds, alkyne–dienes, alkyne–aldehydes, and allene–hydrazones.[7] As part of an ongoing effort to extend the scope of platinum-catalyzed hydrogenative cyclization and to gain mechanistic insights, investigations on the reductive cyclization of allenynes and related theoretical calculations were carried out. A remarkable achievement pertaining to the reductive cyclization of allenynes was that complete control of the regiochemistry and alkene stereochemistry of the product was realized. In addition, the use of a large excess of organometallic reductants was avoided, and the amounts of byproducts were reduced by using hydrogen, leading to an atom-economical and clean process. As reaction mechanisms, the hydrometalation of the alkyne or the allene and the metallacycle formation are considered. On the basis of theoretical calculations, a catalytic cycle initiated with hydrometalation of the alkyne is proposed, implying that the alkyne shows higher reactivity toward the platinum–hydride complex than the allene. The mechanism involving a metallacyclic intermediate appears to be an energetically difficult route.

Results and Discussion

Table 1 lists the optimization results of the hydrogenative cyclization of allenyne **1a**. Initially, compound **1a** was subjected to reaction conditions involving [$PtCl_2$(cod)] (5 mol-%), P[2,4,6-$(OMe)_3C_6H_2]_3$ (5 mol-%), and $SnCl_2$ (25 mol-%) in dichloroethane (DCE) under 1 atm of H_2 at 80 °C to afford the five-membered ring product **1b** in 47% yield (Table 1, entry 1). The indicated alkene geometry was confirmed by a NOESY experiment. The yield was increased significantly by increasing the stoichiometry of the phosphane ligand to 10 mol-% (Table 1, entry 2). The electronic effect of the phosphane ligands was then evaluated: electron-rich phosphanes tended to form the desired reductive cyclization products (Table 1, entries 2–5). Interestingly, the NHC carbene ligand, which is a strong σ donor, showed a yield that was lower than the yield of the reaction involving P[2,4,6-$(OMe)_3C_6H_2]_3$ (Table 1, entry 6). The reaction did not occur in the presence of 10 mol-% NHC ligand. The Pt complex without the COD ligand produced a reductive cyclization product with a yield (69%) similar to that of the [$PtCl_2$]-catalyzed reaction (Table 1, entry 7).

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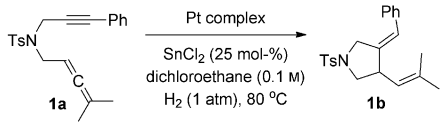
Table 1. Optimization of reductive cyclization of allenyne **1a**.

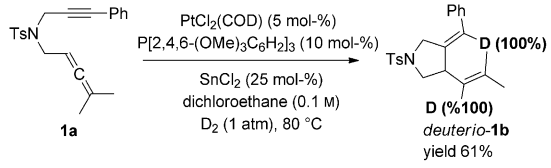


Entry	Pt complex[a] (5 mol-%)	Ligand	Yield [%]
1	$[PtCl_2(cod)]$	$P[2,4,6\text{-}(OMe)_3C_6H_2]_3$ (5 mol-%)	47
2	$[PtCl_2(cod)]$	$P[2,4,6\text{-}(OMe)_3C_6H_2]_3$ (10 mol-%)	71
3	$[PtCl_2(cod)]$	$P(p\text{-}OMeC_6H_4)_3$ (10 mol-%)	44
4	$[PtCl_2(cod)]$	$P(p\text{-}CF_3C_6H_4)_3$ (10 mol-%)	n.r.[b]
5	$[PtCl_2(cod)]$	$P(2\text{-furyl})_3$ (10 mol-%)	10
6	$[PtCl_2(cod)]$	NHC (5 mol-%)[c]	45
7	$[PtCl_2]$	$P[2,4,6\text{-}(OMe)_3C_6H_2]_3$ (10 mol-%)	69

[a] COD = 1,5-cyclooctadiene. [b] n.r. = no reaction. [c] NHC = 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene.

A range of allenynes were evaluated under the indicated conditions (Table 2). From the results for compounds **1b**, **2b**, and **3b**, the allenyne possessing additional methyl groups at the allene terminal was found to provide a higher yield (Table 2, entries 1–3).[8] Next, the effect of the substituent at the alkyne was assessed. Allenynes with 2-naphthyl, 2-anisol, and 3-anisol groups underwent cyclization and provided the corresponding products in 73, 65, and 72% yield, respectively (Table 2, entries 4–6). The cyclization of TMS-substituted compound **7a** gave a lower yield (33%) compared with the aromatic substituted substrates (Table 2, entry 7). In the case of compound **8b**, the *gem*-dimethyl group proximal to the alkyne affected the yield of the cyclization, resulting in a slightly decreased yield (56%; Table 2, entry 8). In addition to the reductive cyclization of nitrogen-tethered compounds, the reductive cyclization of carbon-tethered compound **9a** was attempted, and it was found to provide the product **9b** in 57% yield (Table 2, entry 9).

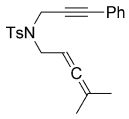
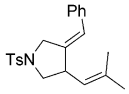
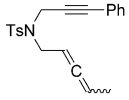
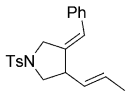
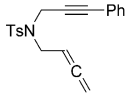
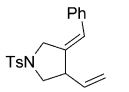
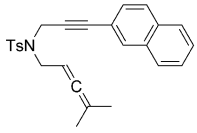
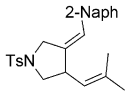
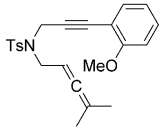
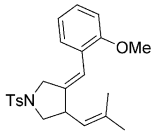
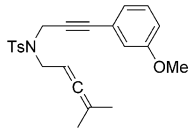
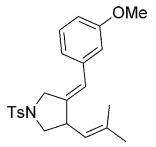
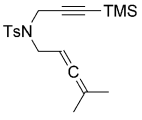
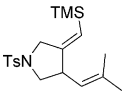
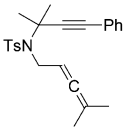
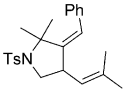
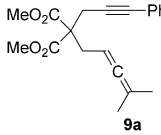
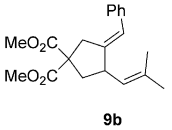
A deuterium-labeling experiment was carried out by using allenyne **1a** to gain some insights into the reaction mechanism (Scheme 1). Under 1 atm of D_2, the reaction afforded **1b**, in which 100% deuteration occurred at both alkenes. It is apparent that hydrogen gas is the source of protons at the two vinyl positions and that the hydrogenation process is indeed occurring through Pt catalysts, which in turn implies that the reaction pathway is most probably by hydrometalation or oxidative cyclization of Pt catalysts.[7,9]



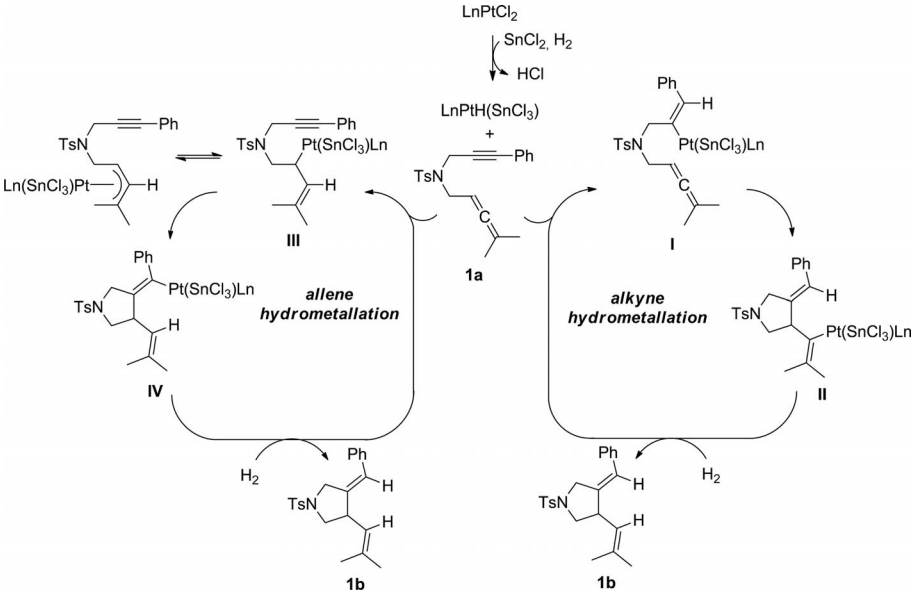
Scheme 1. A deuterium-labeling study.

To delineate the reaction mechanism further, we performed DFT calculations.[10,11] On the basis of previously reported studies, as well as the deuterium-labeling experiment shown above, we focused on two major reaction pathways that included hydrometalation and oxidative cycliza-

Table 2. Cycloreduction of allenynes.[a]

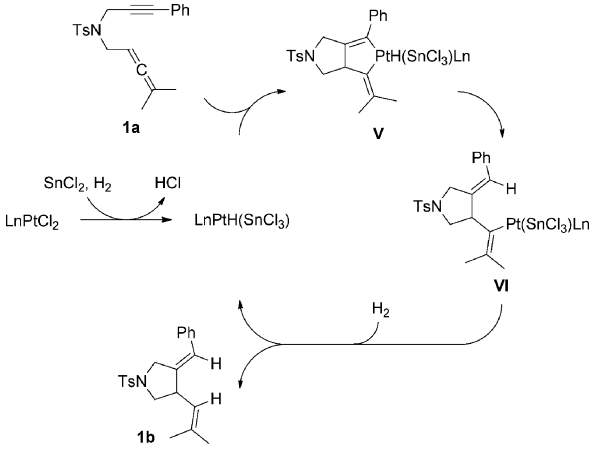
Entry	Reactant	Product	Yield
1	 **1a**	 **1b**	71 %[b]
2	 **2a**	 **2b**	40 %[b] 60 %[c]
3	 **3a**	 **3b**	0 %[b] 16 %[d]
4	 **4a**	 **4b**	31 %[b] 73 %[e]
5	 **5a**	 **5b**	51 %[b] 65 %[e]
6	 **6a**	 **6b**	49 %[b] 72 %[e]
7	 **7a**	 **7b**	24 %[b] 33 %[f]
8	 **8a**	 **8b**	56 %[b]
9	 **9a**	 **9b**	57 %[b]

[a] Reagents and conditions: starting materials (0.25 mmol), Pt complex (5 mol-%), ligand (indicated mol-%), $SnCl_2$ (25 mol-%), DCE (0.1 M), H_2 (1 atm), 80°C; Ts = tosyl, TMS = trimethylsilyl. [b] $[PtCl_2(cod)]$, $P[2,4,6\text{-}(OMe)_3C_6H_2]_3$ (10 mol-%). [c] $[PtCl_2(cod)]$, $P(2\text{-furyl})_3$ (5 mol-%). [d] $[PtCl_2]$, $P[2,4,6\text{-}(OMe)_3C_6H_2]_3$ (5 mol-%). [e] $PtCl_2$, $P[2,4,6\text{-}(OMe)_3C_6H_2]_3$ (10 mol-%). [f] $[PtCl_2(cod)]$, $P[2,4,6\text{-}(OMe)_3C_6H_2]_3$ (5 mol-%).



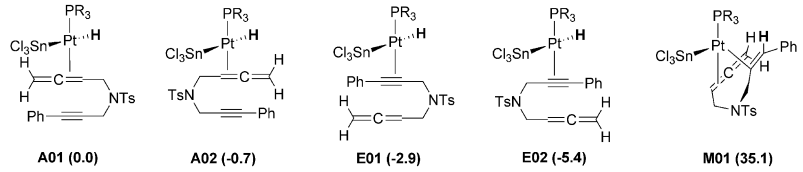
Scheme 2. Proposed mechanism involving hydrometalation.

tion, as schematically shown in Schemes 2 and 3, respectively. Other possible routes involving cycloisomerization of allene–enes and enynes, which can be formed by partial reduction of allenynes, are excluded, based on the control experiments.[12,13] Separately prepared allene–ene and enyne compounds were not converted to 1,4-diene products under platinum-catalyzed hydrogenation conditions.[14]



Scheme 3. Proposed mechanism involving oxidative cyclization.

Before pursuing the catalytic pathway, we needed to define the active catalyst species first. On the basis of many past studies, including our previous work, we presumed that $[PtH(PR_3)_2(SnCl_3)]$ [R = 2,4,6-$(OMe)_3C_6H_2$] was formed when a $[PtCl_2(cod)]$ or $[PtCl_2]$ catalyst precursor was treated with phosphane ligands and $SnCl_2$ under an H_2 atmosphere.[7,15] The optimized geometry of the compound's structure is square planar with two phosphane ligands in the *trans* position. Owing to the sterically congested nature of tris(2,4,6-trimethoxyphenyl)phosphane, the axial position of the Pt ion is barely accessible, inhibiting the approach of additional ligands. Consequently, the optimization process starts by forcefully positioning alkyne or allene groups at the axial position of the Pt ion in a square pyramidal geometry, which leads to the detachment of one of the phosphane ligands. Therefore, we adopted $[PtH(PR_3)(SnCl_3)]$ as the real catalyst species. We then considered the conformation of a catalyst–substrate adduct. Compound **3a** was chosen as the substrate for its structural simplicity. Since it was not clear which unsaturated π bond (alkyne or allene) was more favorable for binding with the Pt ion, we built four different conformational representations, as illustrated in Scheme 4. The calculation results indicated that while the alkyne-bound adduct (**E02**) had the most stable conformation, its stabilization energy was only



Scheme 4. Five different conformational representations of possible reactant states. Numbers in parentheses are relative zero-point energy (ZPE)-corrected free energies in units of kcal mol^{-1}, obtained by frequency calculations for the gas phase. R denotes the 2,4,6-trimethoxy-1-phenyl group.

5.4 kcal mol^{-1}; this implied that the thermal energy at the experimental reaction temperature (80 °C) could easily exceed the stabilization energy. Thus, we decided to consider the reaction pathways starting from both the alkyne-bound geometry (**E02**) and allene-bound one (**A02**). When both alkyne and allene groups were coordinated to the [PtH(PR_3)($SnCl_3$)] catalyst species, the optimized geometry turned out to be **M01**. The five-coordinate stationary state could not be located. Moreover, the free energy of **M01** was higher than that of **E02** by 40.5 kcal mol^{-1}. Therefore, it was thought to be reasonable to remove the five-coordinate stationary state from the list of suitable reactant states.

Once two reactant states were defined with the full geometry, for further calculations and to save computational cost, we used simplified models in which the PR_3 (R = 2,4,6-trimethoxy-1-phenyl) ligand was replaced by PH_3 and the tosyl group at the nitrogen atom was replaced with H. The simplified models are labeled **A2** and **E2** and are shown in Figure 1. The thermodynamic free energies of these two reactant states are coincidently isoenergetic.

We examined the pathway starting from **E2**. The reaction pathways could be further partitioned to (1) 5-*exo* cyclization (occurring first) and hydrometalation, or (2) vice versa. The **E2-IE0-IE01** pathway corresponds to 5-*exo* cyclization followed by hydrometalation, whereas the **E2-IE1-IE12** pathway corresponds to hydrometalation followed by cyclization. The reaction barrier for the 5-*exo* cyclization from the **E2** state was 20.7 kcal mol^{-1} and that for the hydrometalation was only 8.8 kcal mol^{-1}. The latter is more favorable. The hydrometallated intermediate **IE1** proceeds to **IE12** via **TS_IE1_IE12** with a reaction barrier of 14 kcal mol^{-1}. Although this barrier is only 1 kcal mol^{-1} lower than that for the reverse reaction, the forward reaction toward **IE12** is highly exothermic, and thus, the overall process from **E2** to **IE12** appears to be very smooth. On the other hand, the cyclized intermediate **IE0** needs to overcome an activation barrier of 29 kcal mol^{-1} to proceed to **IE01**. This activation barrier is quite large and cannot be overcome by the conventional thermal reaction carried out at 80 °C. Moreover, the activation barrier for the forward reaction at the **IE0** state rather higher than that for the reverse reaction by 6.6 kcal mol^{-1}, which would retard the reaction. For these reasons, the pathway via **IE0** is less favorable than that via **IE1**. After the oxidative addition of a hydrogenation molecule to the Pt ion (**IE121**), reductive elimination leads to the product state **PE3**.

Besides the mechanism involving hydrometalation, we examined the route involving metallacycle **IE2**. The geometry of the transition state that leads **E2** to **IE2** is a five-coordinate square pyramid in which the alkyne and the allene groups occupy two coordination sites in *cis* conformation and the hydride is at the pyramidal vertex. The energy of this state is extremely high (47.9 kcal mol^{-1}) and thus the reaction through this transition state is practically unfavorable.

The allene-bound reactant state, **A2**, showed a different reaction pattern. Importantly, despite our extensive search, the pathway involving hydrometalation from **A2** could not be found due to the lack of appropriate transition states. However, the metallacyclic intermediate **IA2** and the transition state leading to it were successfully located. The reaction from **A2** to **IA2** is exothermic by 13.5 kcal mol^{-1}. **IA2** can evolve to **IA01**, which is geometrically and energetically similar to **IE12**. The reaction barrier for this process is only 5.1 kcal mol^{-1}. Upon oxidative addition of a hydrogen molecule to the Pt ion of **IA01**, hydrometalation to the vinyl group occurs, leading to the product state **PA2**. However, it should be noted that the activation barrier of the first step (**A2**→**IA2**) is 34.6 kcal mol^{-1}, which is 25.8 kcal mol^{-1} higher than that of the **E2**→**IE1** counterpart. Therefore,

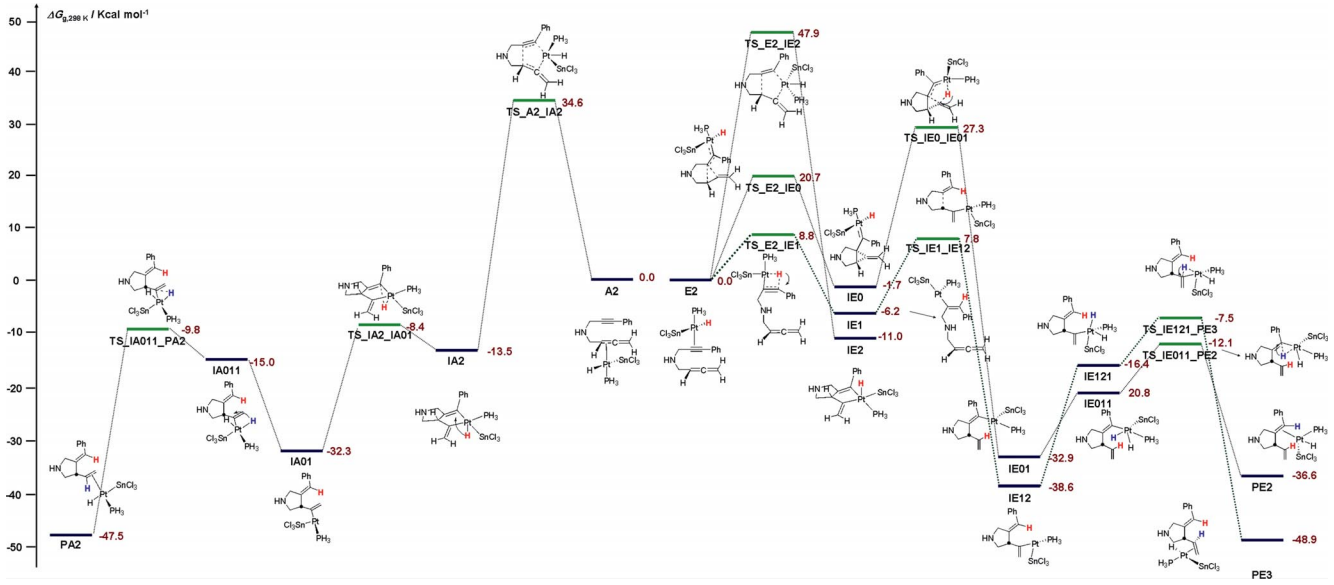


Figure 1. Free energy reaction profile of platinum-catalyzed reductive cyclization reactions of 1,6-allenyne. Numbers in red denote ZPE-corrected free energies in kcal mol^{-1} calculated by DFT at the B3LYP/6-31G(d) and LANL2DZ levels. Green dotted lines signify most probable reaction pathways. For details of structures of all compounds listed in this diagram, see the Supporting Information.

the working mechanism would most likely consist of i. catalyst binding to the alkyne group of 1,6-allenyne (**E2**), ii. hydrometalation (**E2**→**TS_E2_IE1**→**IE1**), iii. 5-*exo* cyclization (**IE1**→**TS_IE1_IE12**→**IE12**), iv. oxidative addition of a hydrogen molecule (**IE12**→**IE121**), and v. reductive elimination (**IE121**→**TS_IE121_PE3**→**PE3**). It is important to note that the model calculation indicates the conformation required for the hydrometalation of the alkyne and the stereochemical outcome of the exomethylene alkene as a Z type (**TS_E2_IE1**), which accounts for the experimental results .

Conclusions

We have found that allenynes participate in reductive cyclization to afford cyclic compounds with good stereoselectivity and reasonable yield under hydrogenation conditions. Depending on the substitution pattern of the substrates, the yields are variable. Allenynes with an aromatic group at the alkyne and a dimethyl group at the allene show good yield. On the basis of a deuterium-labeling study and theoretical calculations, a tentative mechanism beginning with hydrometalation of the alkyne by a [PtHLn] complex has been proposed.

Experimental Section

General: All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred by an oven-dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. DCE was distilled from calcium hydride. Product **2b**[7c] exhibited spectral properties consistent with previous literature reports.

Representative Experimental Procedure for the Cyclization of 1a: The starting material was added to a premixed solution of Pt^{II} (5 mol-%), phosphane (indicated mol-% in Table 2), and $SnCl_2$ (25 mol-%) under H_2 (1 atm) in DCE (0.1 M) at room temperature. The resulting mixture was allowed to react at 80 °C under H_2 (1 atm) until the starting material was completely consumed.

(Z)-3-Benzylidene-4-(2-methylprop-1-enyl)-1-tosylpyrrolidine (1b): The representative experimental procedure was applied to compound **1a** (91 mg, 0.25 mmol) to yield product **1b** (65.4 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.0 Hz, 2 H, aromatic H), 7.31 (m, 4 H, aromatic H), 7.21 (m, 1 H, aromatic H), 7.12 (d, J = 7.6 Hz, 2 H, aromatic H), 6.07 (s, 1 H, =CHPh), 4.87 (d, J = 8.4 Hz, 1 H, =CH), 4.39 (d, J = 15.1 Hz, 1 H, CH_2-NTs), 3.91 (d, J = 15.0 Hz, 1 H, CH_2-NTs), 3.65 (m, 2 H, CH_2-NTs), 2.60 (t, J = 8.8 Hz, 1 H, allylic H), 2.40 (s, 3 H, CH_3Ts), 1.76 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 140.0, 136.6, 136.5, 132.8, 129.8, 128.6, 128.1, 127.8, 127.0, 123.1, 122.0, 52.6, 51.0, 44.2, 26.1, 21.8, 18.5 ppm. HRMS: calcd. for $C_{22}H_{25}NO_2S$ [M^+] 367.1606; found 367.1602. IR (KBr): $\tilde{\nu}$ = 3055, 2925, 2853, 1598, 1447, 1376, 1348, 1165, 1094, 815, 754, 697, 664 cm^{-1}.

Deuterio-(*Z*)-3-Benzylidene-4-(2-methylprop-1-enyl)-1-tosylpyrrolidine (deuterio-1b): The representative experimental procedure was applied to compound **1a** (91 mg, 0.25 mmol) to yield product deuterio-**1b** (56 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.4 Hz, 2 H, aromatic H), 7.3 (m, 4 H, aromatic H), 7.21 (m, 1 H, aromatic H), 7.12 (d, J = 7.2 Hz, 2 H, aromatic H), 4.39 (d, J = 14.8 Hz, 1 H, CH_2-NTs), 3.91 (d, J = 15.2 Hz, 1 H, CH_2-NTs), 3.65 (m, 2 H, CH_2-NTs), 2.60 (t, J = 8.0 Hz, 1 H, allylic H), 2.40 (s, 3 H, CH_3Ts), 1.76 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3) ppm.

(*Z*)-3-Benzylidene-1-tosyl-4-vinylpyrrolidine (3b): The representative experimental procedure was applied to compound **3a** (84 mg, 0.25 mmol) to yield product **1b** (13.6 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (m, 2 H, aromatic H), 7.27 (m, 5 H, aromatic H), 7.08 (m, 2 H, aromatic H), 6.18 (s, 1 H, =CHPh), 5.57 (m, 1 H, CH=CH_2), 5.18 (m, 2 H, CH=CH_2), 4.30 (d, J = 14.8 Hz, 1 H, CH_2-NTs), 3.98 (d, J = 15.2 Hz, 1 H, CH_2-NTs), 3.63 (m, 1 H, CH_2-NTs), 3.43 (d, J = 7.6 Hz, 1 H, CH_2-NTs), 2.84 (m, 1 H, allylic H), 2.42 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 139.0, 136.4, 136.0, 129.9, 128.7, 128.6, 128.2, 127.9, 127.3, 124.3, 118.7, 52.3, 51.0, 49.6, 21.9 ppm. HRMS: calcd. for $C_{20}H_{21}NO_2S$ [M + H]$^+$ 340.1371; found 340.1366. IR (KBr): $\tilde{\nu}$ = 2955, 2924, 2853, 1598, 1493, 1447, 1347, 1163, 1093, 1041 cm^{-1}.

(*Z*)-3-(2-Methylprop-1-enyl)-4-(naphthalen-2-ylmethylene)-1-tosylpyrrolidine (4b): The representative experimental procedure was applied to compound **4a** (51 mg, 0.12 mmol) to yield product **4b** (37.7 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (m, 5 H, aromatic H), 7.57 (s, 1 H, aromatic H), 7.47 (m, 2 H, aromatic H), 7.29 (m, 3 H, aromatic H), 6.25 (s, 1 H, =CHNaph), 4.93 (d, J = 7.4 Hz, 1 H, =CH), 4.53 (d, J = 15.2 Hz, 1 H, CH_2-NTs), 4.01 (d, J = 14.8 Hz, 1 H, CH_2-NTs), 3.70 (m, 2 H, CH_2-NTs), 2.64 (m, 1 H, allylic H), 2.39 (s, 3 H, CH_3Ts), 1.79 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 140.5, 136.8, 134.2, 133.5, 132.8, 132.3, 129.9, 128.3, 128.2, 127.9, 127.7, 127.2, 126.5, 126.3, 126.2, 123.2, 122.0, 52.7, 51.2, 44.4, 26.3, 21.9, 18.6 ppm. HRMS: calcd. for $C_{26}H_{27}NO_2S$ [M^+] 417.1763; found 417.1764. IR (KBr): $\tilde{\nu}$ = 2971, 2920, 2851, 1597, 1347, 1165, 1093, 1037 cm^{-1}.

(*Z*)-3-(2-Methoxybenzylidene)-4-(2-methylprop-1-enyl)-1-tosylpyrrolidine (5b): The representative experimental procedure was applied to compound **5a** (99 mg, 0.25 mmol) to yield product **5b** (65 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.4 Hz, 2 H, aromatic H), 7.25 (m, 3 H, aromatic H), 7.05 (d, J = 6.8 Hz, 1 H, aromatic H), 6.93 (m, 1 H, aromatic H), 6.84 (d, J = 8.4 Hz, 1 H, aromatic H), 6.36 (s, 1 H, =CHanisol), 4.94 (d, J = 8.4 Hz, 1 H, =CH), 4.30 (d, J = 14.8 Hz, 1 H, CH_2-NTs), 3.88 (d, J = 16.0 Hz, 1 H, CH_2-NTs), 3.79 (s, 3 H, OCH_3), 3.65 (m, 2 H, CH_2-NTs), 2.66 (m, 1 H, allylic H), 2.41 (s, 3 H, CH_3Ts), 1.75 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5, 143.6, 140.0, 136.2, 132.9, 129.7, 128.6, 128.5, 127.8, 125.6, 122.2, 120.5, 117.8, 110.6, 55.7, 52.8, 50.9, 44.1, 26.1, 21.8, 18.6 ppm. HRMS: calcd. for $C_{23}H_{27}NO_3S$ [M^+] 397.1712; found 397.1716. IR (KBr): $\tilde{\nu}$ = 2962, 2927, 2853, 1598, 1489, 1463, 1347, 1289, 1246, 1164, 1106, 1093, 1028 cm^{-1}.

(*Z*)-3-(3-Methoxybenzylidene)-4-(2-methylprop-1-enyl)-1-tosylpyrrolidine (6b): The representative experimental procedure was applied to compound **6a** (99 mg, 0.25 mmol) to yield product **6b** (72 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.0 Hz, 2 H, aromatic H), 7.27 (m, 3 H, aromatic H), 6.76 (m, 2 H, aromatic H), 6.66 (s, 1 H, aromatic H), 6.06 (s, 1 H, =CHanisol), 4.88 (d, J = 8.6 Hz, 1 H, =CH), 4.38 (d, J = 15.2 Hz, 1 H, CH_2-NTs), 3.91 (d, J = 16.0 Hz, 1 H, CH_2-NTs), 3.80 (s, 3 H, OCH_3), 3.65 (m, 2 H, CH_2-NTs), 2.61 (m, 1 H, allylic H), 2.41 (s, 3 H, CH_3Ts), 1.77 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 143.7, 140.4, 137.9, 136.6, 132.7, 129.8, 129.5, 127.8, 123.0, 121.9, 120.5, 114.0, 112.4, 55.4, 52.6, 51.0, 44.1, 26.1, 21.8, 18.5 ppm. HRMS: calcd. for $C_{23}H_{27}NO_3S$

[M+] 397.1712; found 397.1714. IR (KBr): ṽ = 2965, 2926, 2852, 1598, 1578, 1492, 1453, 1377, 1347, 1292, 1272, 1165, 1094, 1040 cm^{-1}.

(*Z*)-3-(2-Methylprop-1-enyl)-1-tosyl-4-[(trimethylsilyl)methylene]-pyrrolidine (7b): The representative experimental procedure was applied to compound **7a** (90 mg, 0.25 mmol) to yield product **7b** (31 mg, 33%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, J = 8 Hz, 2 H, aromatic H), 7.34 (d, J = 7.2 Hz, 2 H, aromatic H), 5.23 (s, 1 H, =CHTMS), 4.75 (d, J = 5.6 Hz, 1 H, =CH), 4.07 (d, J = 15.2 Hz, 1 H, CH_2-NTs), 3.63 (m, 2 H, CH_2-NTs), 3.43 (m, 1 H, CH_2-NTs), 2.54 (t, J = 9.8 Hz, 1 H, allylic H), 2.45 (s, 3 H, CH_3Ts), 1.72 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 146.7, 136.5, 132.5, 129.7, 127.8, 122.0, 120.9, 53.0, 51.6, 45.3, 29.9, 26.0, 21.8, 18.5 ppm. HRMS: calcd. for $C_{19}H_{29}NO_2SSi$ [M+] 363.1688; found 363.1685. IR (KBr): ṽ = 2955, 2926, 2855, 1933, 1633, 1598, 1452, 1377, 1351, 1249, 1165, 1092, 1031, 872, 840 cm^{-1}.

(*Z*)-3-Benzylidene-2,2-dimethyl-4-(2-methylprop-1-enyl)-1-tosylpyrrolidine (8b): The representative experimental procedure was applied to compound **8a** (98 mg, 0.25 mmol) to yield product **8b** (56 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.4 Hz, 2 H, aromatic H), 7.23 (m, 5 H, aromatic H), 7.09 (d, J = 7.2 Hz, 2 H, aromatic H), 6.20 (s, 1 H, =CHPh), 4.94 (d, J = 8.8 Hz, 1 H, =CH), 3.66 (m, 2 H, CH_2-NTs), 2.85 (m, 1 H, allylic H), 2.40 (s, 3 H, CH_3Ts), 1.72 (m, 9 H, *gem*-dimethyl and CH_3), 1.28 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6, 142.8, 138.1, 137.4, 136.6, 129.4, 128.8, 128.0, 127.4, 126.6, 122.7, 122.5, 68.2, 52.2, 42.4, 30.5, 26.2, 26.0, 21.8, 18.5 ppm. HRMS: calcd. for $C_{24}H_{29}NO_2S$ [M+] 395.1919; found 395.1920. IR (KBr): ṽ = 2974, 2928, 2856, 1599, 1442, 1363, 1338, 1159, 1093, 1026, 815, 739, 704, 670, 582, 550 cm^{-1}.

Dimethyl (*E*)-3-Benzylidene-4-(2-methylprop-1-enyl)cyclopentane-1,1-dicarboxylate (9b): The representative experimental procedure was applied to compound **9a** (81 mg, 0.25 mmol) to yield product **9b** (47 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (m, 5 H, aromatic H), 6.09 (d, J = 2.4 Hz, 1 H, =CHPh), 5.03 (d, J = 8.8 Hz, 1 H, =CH), 3.74 (s, 3 H, CO_2CH_3), 3.72 (s, 3 H, CO_2CH_3), 3.54 (m, 1 H), 3.40 (d, J = 16.8 Hz, 1 H), 3.20 (dt, J = 2.8, 17.6 Hz, 1 H), 2.57 (dd, J = 7.2, 12.4 Hz, 1 H), 1.85 (t, J = 12.4 Hz, 1 H),1.79 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.3, 172.1, 144.3, 137.9, 134.3, 128.4, 126.3, 125.8, 122.9, 59.4, 53.5, 53.1, 44.5, 40.4, 39.0, 26.1, 18.6 ppm. HRMS: calcd. for $C_{20}H_{24}O_4$ [M+] 328.1675; found 328.1675. IR (KBr): ṽ = 3057, 2955, 2928, 1735, 1436, 1268, 1203, 1164, 1064, 738, 699 cm^{-1}.

Supporting Information (see footnote on the first page of this article): 2D-NOESY data for compound **1b** and computational results.

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[1] For reviews of reductive cyclization of diynes and allenynes, see: a) H.-Y. Jang, M. J. Krische, *Acc. Chem. Res.* **2004**, *37*, 653–661; b) M. J. Krische, H.-Y. Jang, *Comprehensive Organometallic Chemistry III*, Elsevier, Oxford, **2006**, vol. 10, p. 511.

[2] For selected articles for reductive cyclization of diynes, see: a) J. W. Madine, X. Wang, R. A. Widenhoefer, *Org. Lett.* **2001**, *3*, 385–388; b) H.-Y. Jang, M. J. Krische, *J. Am. Chem. Soc.* **2004**, *126*, 7875–7880; c) I. G. Jung, J. Seo, S. Y. Choi, Y. K. Chung, *Organometallics* **2006**, *25*, 4240–4242; d) K. T. Sylvester, P. J. Chirik, *J. Am. Chem. Soc.* **2009**, *131*, 8772–8774.

[3] For selected articles for reductive cyclization of allenynes, see: a) C. H. Oh, S. H. Jung, D. I. Park, J. H. Choi, *Tetrahedron Lett.* **2004**, *45*, 2499–2502; b) C. H. Oh, S. H. Jung, C. Y. Rhim, *Tetrahedron Lett.* **2001**, *42*, 8669–8671.

[4] For selected articles for Pd-catalyzed cyclization of allenynes, see: a) S. Shin, T. V. RajanBabu, *J. Am. Chem. Soc.* **2001**, *123*, 8416–8417; b) R. Kumareswaran, S. Shin, I. Gallou, T. V. RajanBabu, *J. Org. Chem.* **2004**, *69*, 7157–7170; c) A. K. Gupta, C. Y. Rhim, C. H. Oh, *Tetrahedron Lett.* **2005**, *46*, 2247–2250; d) C. H. Oh, A. K. Gupta, D. I. Park, N. Kim, *Chem. Commun.* **2005**, 5670–5672; e) V. Pardo-Rodríquez, J. Marco-Martínez, E. Bunuel, D. J. Cárdenas, *Org. Lett.* **2009**, *11*, 4548–4551.

[5] For selected articles for Au-catalyzed cyclization of allenynes, see: a) G. Lemière, V. Gandon, N. Agenet, J.-P. Goddard, A. D. Kozak, C. Aubert, L. Fensterbank, M. Malacria, *Angew. Chem. Int. Ed.* **2006**, *45*, 7596–7599; b) R. Zriba, V. Gandon, C. Aubert, L. Fensterbank, M. Malacria, *Chem. Eur. J.* **2008**, *14*, 1482–1491; c) C.-Y. Yang, G.-Y. Lin, H.-Y. Liao, S. Datta, R.-S. Liu, *J. Org. Chem.* **2008**, *73*, 4907–4914; d) P. H.-Y. Cheong, P. Morganelli, M. R. Luzung, K. N. Houk, F. D. Toste, *J. Am. Chem. Soc.* **2008**, *130*, 4517–4526; e) Á. González-Gómez, G. Domínguez, J. Pérez-Castells, *Eur. J. Org. Chem.* **2009**, 5057–5062.

[6] For Pt-catalyzed reactions of allenynes, see: a) N. Cadran, K. Cariou, G. Hervé, C. Aubert, L. Fensterbank, M. Malacria, J. Marco-Contelles, *J. Am. Chem. Soc.* **2004**, *126*, 3408–3409; b) T. Matsuda, S. Kadowaki, M. Murakami, *Helv. Chim. Acta* **2006**, *89*, 1672–1680; for Rh-catalyzed reactions of allenynes, see: c) K. M. Brummond, H. Chen, P. Sill, L. You, *J. Am. Chem. Soc.* **2002**, *124*, 15186–15187; for Ru-catalyzed reactions of allenynes, see: d) N. Saito, Y. Tanaka, Y. Sato, *Organometallics* **2009**, *28*, 669–671; for Co-catalyzed reactions of allenynes, see: e) D. Lierena, C. Aubert, M. Malacria, *Tetrahedron Lett.* **1996**, *37*, 7027–7030; for Mo-catalyzed reactions of allenynes, see: f) Q. Shen, G. B. Hammond, *J. Am. Chem. Soc.* **2002**, *124*, 6534–6535; for Hg-catalyzed reactions of allenynes, see: g) S. H. Sim, S. I. Lee, J. Seo, Y. K. Chung, *J. Org. Chem.* **2007**, *72*, 9818–9821; for Ga-catalyzed reactions of allenynes, see: h) S. I. Lee, S. H. Sim, S. M. Kim, K. Kim, Y. K. Chung, *J. Org. Chem.* **2006**, *71*, 7120–7123; for Ir-catalyzed reactions of allenynes, see: i) T. Shibata, S. Kadowaki, M. Hirase, K. Takagi, *Synlett* **2003**, 573–575; for thermal reactions of allenynes, see: j) H. Ohno, T. Mizutani, Y. Kadoh, A. Aso, K. Miyamura, N. Fujii, T. Tanaka, *J. Org. Chem.* **2007**, *72*, 4378–4389.

[7] a) H. Lee, M.-S. Jang, J.-T. Hong, H.-Y. Jang, *Tetrahedron Lett.* **2008**, *49*, 5785–5788; b) H. Lee, M.-S. Jang, Y.-J. Song, H.-Y. Jang, *Bull. Korean Chem. Soc.* **2009**, *30*, 327–333; c) M. P. Shinde, X. Wang, E. J. Kang, H.-Y. Jang, *Eur. J. Org. Chem.* **2009**, 6091–6094; d) M.-S. Jang, X. Wang, W.-Y. Jang, H.-Y. Jang, *Organometallics* **2009**, *28*, 4841–4844; e) J.-T. Hong, M.-J. Kang, H.-Y. Jang, *Bull. Korean Chem. Soc.* **2010**, *31*, 2085–2087; f) J.-T. Hong, X. Wang, J.-H. Kim, K. Kim, H. Yun, H.-Y. Jang, *Adv. Synth. Catal.* **2010**, *352*, 2949–2954.

[8] a) K. M. Brummond, H. Chen, B. Mitasev, A. D. Casarez, *Org. Lett.* **2004**, *6*, 2161–2163; b) G. Zhu, Z. Zhang, *Org. Lett.* **2004**, *6*, 4041–4044.

[9] For selected articles proposing metallacyclic platinum complexes, see: a) J. Cámpora, P. Palma, E. Carmona, *Coord. Chem. Rev.* **1999**, *193–195*, 207–281; b) R.-X. He, M. Li, X.-Y. Li, *THEOCHEM* **2005**, *717*, 21–32.

[10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y.

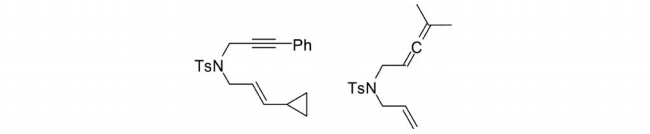
Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, rev. C.02, Gaussian, Inc., Wallingford CT, **2004**.

[11] a) S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117–129; b) S. Miertus, J. Tomasi, *Chem. Phys.* **1982**, *65*, 239–245; c) M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* **1996**, *255*, 327–335; d) B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *106*, 5151–5158; e) B. Mennucci, E. Cances, J. Tomasi, *J. Phys. Chem. B* **1997**, *101*, 10506–10517; f) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995–2001; g) J. Tomasi, B. Mennucci, E. Cances, *THEOCHEM* **1999**, *464*, 211–226; h) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669–681.

[12] For selected articles for cycloisomerization of enynes, see: a) S. J. Sturla, N. M. Kablaoui, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 1976–1977; b) B. M. Trost, C. D. Haffner, D. J. Jebaratnam, M. J. Krische, A. P. Thomas, *J. Am. Chem. Soc.* **1999**, *121*, 6183–6192; c) B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **1999**, *121*, 9728–9729; d) B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **2000**, *122*, 714–715; e) P. Cao, B. Wang, X. Zhang, *J. Am. Chem. Soc.* **2000**, *122*, 6490–6491; f) X. Tong, Z. Zhang, X. Zhang, *J. Am. Chem. Soc.* **2003**, *125*, 6370–6371; g) B. M. Trost, J.-P. Surivet, F. D. Toste, *J. Am. Chem. Soc.* **2004**, *126*, 15592–15602; h) K. C. Nicolaou, A. Li, S. P. Ellery, D. J. Edmonds, *Angew. Chem. Int. Ed.* **2009**, *48*, 6293–6295.

[13] For selected articles for cycloisomerization of allene-enes, see: a) S. K. Kang, B. S. Ko, D. M. Lee, *Tetrahedron Lett.* **2002**, *43*, 6693–6696; b) T. Makino, K. Itoh, *Tetrahedron Lett.* **2003**, *44*, 6335–6338.

[14] Compounds used for the control experiments:



[15] H. J. Ruegg, P. S. Pregosin, *J. Organomet. Chem.* **1986**, *316*, 233–241.

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