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Tungsten(0)- and Rhenium(I)-Catalyzed Tandem Cyclization of Acetylenic Dienol Silyl Ethers Based on Geminal Carbo-Functionalization of Alkynes

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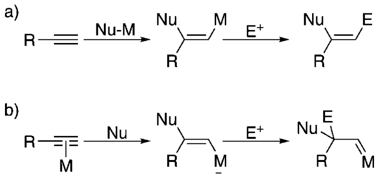
Abstract: Tungsten(0)- and rhenium(I)-catalyzed reactions of acetylenic dienol silyl ethers based on the concept of geminal carbo-functionalization of alkynes are reported. Treatment of 3-siloxy-1,3-diene-7-ynes with catalytic amounts of $[W(CO)_6]$ or $[ReCl(CO)_5]$ under photoirradiation conditions gives synthetically useful bicyclo[3.3.0]octane derivatives in good yields. Extremely high catalytic activity is noted for the rhenium(I) complex. The reaction has been extended to substrates containing a nitrogen atom in their tethers. In this case, two kinds of synthetically useful heterocyclic compounds—the 2-azabicyclo[3.3.0]octane derivatives **9** and the monocyclic dihydropyrroles **10**, with allenyl substituents—are obtained, and selective preparation of either product can be achieved through the use of an appropriate combination of the nitrogen substituent and the type of the rhenium(I) catalyst. The 2-azabicyclo[3.3.0]octane derivatives **9** are obtained selectively by carrying out treatment of N−Ns derivatives in the presence of $[ReCl(CO)_4(PPh_3)]$, whereas the dihydropyrrole derivatives **10** are obtained by treatment of N−Mbs derivatives with $[ReCl(CO)_5]/AgSbF_6$. Finally, we have applied this geminal carbo-functionalization to one-carbon-elongated substrates containing N−Ts moieties in their tethers. Selective 5-*exo* cyclization is achieved in the presence of gold(I) or rhenium(I) catalysts, whereas 6-*endo* cyclization is observed on use of $[W(CO)_6]$.

Keywords: alkynes · cyclization · nitrogen heterocycles · rhenium · tungsten

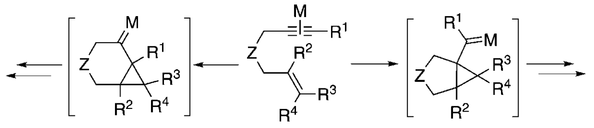
Introduction

1,2-Vicinal carbo-functionalization of alkynes can easily be carried out by their carbometalation in the presence of various kinds of organometallic reagents such as Cu, Al, Zr, and so forth, followed by treatment of the resulting alkenyl metallic species with carbon electrophiles (Scheme 1a).[1] This reaction provides a powerful method for the synthesis of polysubstituted olefins in a one-pot operation.[1] On the other hand, geminal carbo-functionalization of alkynes—addition of carbon nucleophiles and carbon electrophiles sequentially to the same alkyne carbon to afford 1,1-disubstituted products (Scheme 1b)—has remained unexplored in spite of its high potential as a useful synthetic method.[2]



Scheme 1. Vicinal (a) or geminal (b) functionalization of alkynes.

Recently, transition-metal-catalyzed electrophilic activation of alkynes has been extensively studied for the construction of carbo- and heterocyclic compounds. In particular, gold(I) and platinum(II) complexes have emerged as powerful catalysts for reactions of this type, and a very rich enyne chemistry has made it possible to prepare a variety of synthetically useful cyclic compounds atom-economically (Scheme 2).[2,3] With these alkynophilic transition-metal catalysts a kind of geminal carbo-functionalization reaction—cyclopropanation to generate cyclopropyl carbene complex intermediates—was achieved,[3,4] and almost all the reactions so far reported belong to this reaction type.



Scheme 2. Geminal carbo-functionalization: generation of cyclopropyl carbenes from enynes.

We have previously reported that $[W(CO)_5(L)]$ can activate terminal alkynes effectively and catalytically for the intramolecular nucleophilic attack of enol silyl ethers to give various kinds of carbocycles.[5] In these reactions, the produced alkenyltungsten moieties were protonated by the

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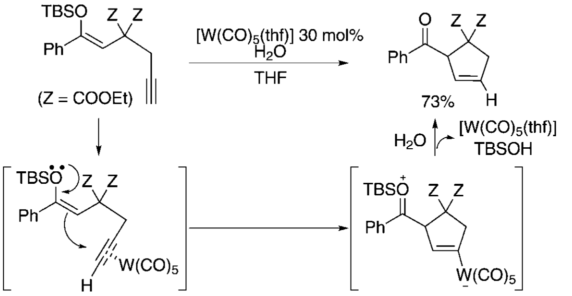
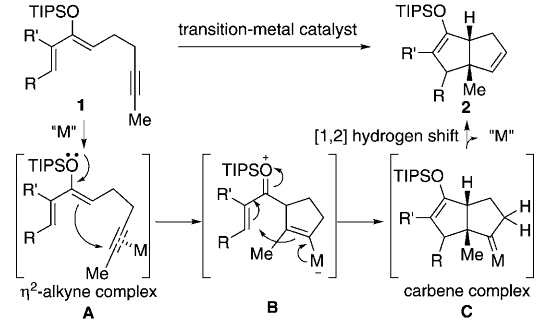


Scheme 3. $[W(CO)_5(L)]$-catalyzed 5-*endo*-dig cyclization of 6-siloxy-5-en-1-ynes.

added water to give cyclic ketones with regeneration of the catalysts (Scheme 3).

During these studies, we thought of utilizing the alkenyltungsten intermediates for further carbon–carbon bond formation, because these intermediates could be regarded as α anions of tungsten–carbene complexes.[6] We expected that synthetically useful reactions based on the geminal carbofunctionalization strategy might be achieved through appropriate design of the starting materials. We then considered the reaction behavior of the acetylenic dienol silyl ethers **1** (Scheme 4) as substrates. Treatment of the acetylenic dienol silyl ethers **1** with appropriate electrophilic transition-metal complexes should give zwitterionic intermediates of type **B** through 5-*endo* nucleophilic cyclization of the enol silyl ether systems to the electrophilically activated η^2-alkyne complexes **A**, and the resulting alkenyl metallic moieties should then attack the α,β-unsaturated silyloxonium moieties intramolecularly at the position β to the metal to generate bicyclic unstabilized carbene complexes of type **C**. Finally, the unstabilized carbene complexes should undergo a typical carbene reaction, such as [1,2] hydrogen migration,[7] to give the bicyclo[3.3.0]octane derivatives **2** with regeneration of the reactive catalytic species. These reactions would afford an efficient method for the synthesis of synthetically useful bicyclo[3.3.0]octane derivatives, which constitute basic carbon skeletons of many natural products,[8] from easily available acyclic substrates.



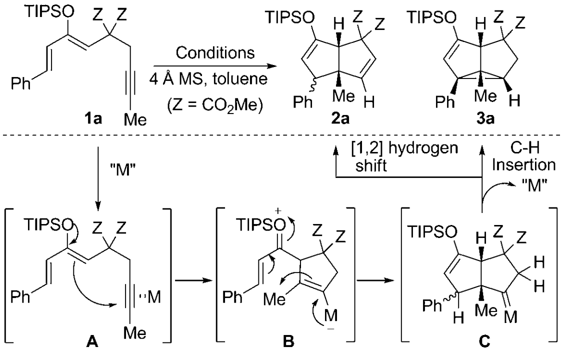
Scheme 4. Tandem cyclization of dienol silyl ethers.

In this article we report a full account of this work, including reaction scope, synthetic application, and further application to the synthesis of heterocyclic compounds.[9]

Results and Discussion

Development of tungsten(0)- and rhenium(I)-catalyzed geminal carbo-functionalization: We first examined the reaction behavior of the ω-acetylenic dienol silyl ether **1a** (Table 1) in toluene in the presence of an equimolar amount of preformed $[W(CO)_5(\text{toluene})]$[10] and molecular sieves (4 Å). The reaction proceeded as expected and the desired bicyclo[3.3.0]octane derivative **2a** was obtained in moderate yield as a mixture of diastereomers (mainly α-Ph product) accompanied by a small amount of the tricyclic compound **3a** (Table 1, entry 1). The formation of the tricyclic compound **3a** explicitly implicates the presence of the carbene complex intermediate **C**, in which the carbene moiety inserts into the neighboring benzylic C–H bond. When carried out under photoirradiation conditions, the reaction proceeded to completion even in the presence of only 10 mol% of

Table 1. Reaction behavior of the dienol silyl ether **1a**.



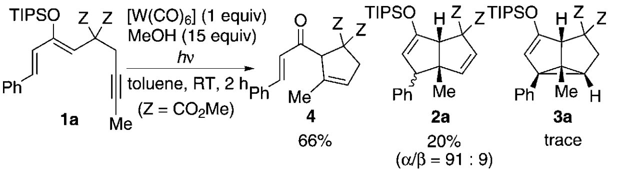
Entry	Conditions (mol %)	T, t	Yield [%]	**2a** (α/β)	**3a**
1	$[W(CO)_5(\text{toluene})]$ (100)	RT, 3.5 d	52	87 (90:10)	13
2	$[W(CO)_6]$, *hν* (10)	RT, 4 h	88	86 (90:10)	14
3	$PtCl_2$ (10)	70 °C, 48 h	67	59 (57:43)	41
4	$AuBr_3$ (10)	RT, 24 h	79	65 (89:11)	35
5[a]	$[AuCl(PPh_3)]/AgSbF_6$ (10)	RT, 24 h	<5	–	–
6	$[ReBr(CO)_5]$ (10)	110 °C, 3 h	69	84 (78:22)	16
7	$[ReBr(CO)_5]$, *hν* (10)	RT, 3 h	95	86 (88:12)	14
8	$[ReCl(CO)_5]$, *hν* (10)	RT, 3 h	98	91 (93:7)	9
9	$[Cp^*Re(CO)_3]$, *hν* (10)	RT, 23 h	68	84 (71:29)	16
10	$[W(CO)_6]$, *hν* (0.5)	RT, 16 h	<5	–	–
11	$[ReCl(CO)_5]$, *hν* (0.5)	RT, 16 h	92	86 (81:19)	14

[a] CH_2Cl_2 was used as a solvent.

$[W(CO)_6]$ (Table 1, entry 2). Because the expected geminal carbo-functionalization had been found to proceed catalytically in the presence of $[W(CO)_5(L)]$, we further examined the possibility of carrying out the reaction more efficiently through the use of other transition-metal complexes. $PtCl_2$[2,3] (67% yield, Table 1, entry 3) and $AuBr_3$[2,3] (79% yield, entry 4) also showed high catalytic activity for this transformation, and the proportion of the tricyclic compound **3a** formed was larger in these cases than in the tungsten-catalyzed reaction. Surprisingly, a cationic gold(I) complex, often used as a powerful catalyst for the electrophilic activation of alkynes,[2,3] was not suitable for this reaction, probably due to the poor nucleophilicity of the alkenylgold(I) intermediate (Table 1, entry 5).

Next, several rhenium(I) carbonyl complexes were examined.[11] $[ReBr(CO)_5]$ showed moderate activity under heating conditions, but under photoirradiation conditions a very high catalytic activity was achieved (Table 1, entries 6 and 7). Furthermore, $[ReCl(CO)_5]$ was found to have an extremely high activity: the reaction even took place in the presence of only 0.5 mol% $[ReCl(CO)_5]$ to give the cyclized products **2a** and **3a** in 92% yield and in a ratio of 86:14 upon carrying out the reaction in toluene under photoirradiation conditions (Table 1, entry 11).

When the $[W(CO)_5(L)]$-promoted reaction was carried out in the presence of a protonating agent (MeOH), the monocyclic cyclopentene derivative **4** (Scheme 5), the protonated product of the zwitterionic intermediate **B**, was mainly obtained. This bicyclization reaction is thus likely to proceed in a stepwise manner.

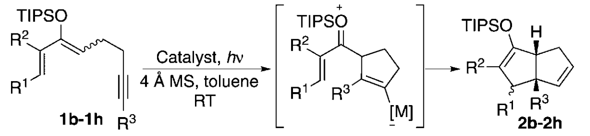


Scheme 5. Cyclization in the presence of a proton source.

Having established that $[W(CO)_6]$ and $[ReCl(CO)_5]$ catalyzed the geminal carbo-functionalization reaction very efficiently, the generality of the reaction was examined, and the results are summarized in Table 2.[12] The trisubstituted dienes **1b**–**1d**, with a methyl, primary, or secondary alkyl group at their β positions (R^1), were cyclized to afford the corresponding bicyclic enol silyl ethers (R^1-α product major) in good yields (Table 2, entries 1–3). The Ph-substituted diene (**1e**) also gave a good result, but no stereoselectivity with regard to the Ph substituent was observed (Table 2, entry 4).

It should be noted that no tricyclic enol silyl ether of type **3** was obtained when a substrate without a *gem*-diester moiety was employed. Even the tetrasubstituted dienes (**1f**, **1g**) reacted to afford the corresponding substituted bicyclic enol silyl ethers in good yields. In these cases, the stereoselectivity of the products was different from that of the corresponding trisubstituted diene (Table 2, entry 1 vs. 5). Furthermore, a substrate possessing a terminal alkyne moiety (**1h**) could also be employed for this reaction (Table 2, entry 7). The $[ReCl(CO)_5]$-catalyzed reaction gave results superior in most cases to those of the $[W(CO)_5(L)]$-catalyzed reaction: that is, the reactions of **1a**–**1g** gave the bicyclic enol silyl ethers in good yields (67–81%) in the presence of 5–20 mol% $[W(CO)_6]$ under photoirradiation conditions in toluene, whereas the $[ReCl(CO)_4(L)]$-catalyzed reaction required much smaller amounts of $[ReCl(CO)_5]$ (only 0.5–3 mol%).

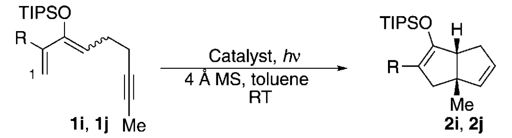
Table 2. Rhenium- and tungsten-catalyzed reaction behavior of dienol silyl ethers.



Entry	R^1, R^2, R^3	$[ReCl(CO)_5]$ (mol%)	Yield [%] (α/β)	$[W(CO)_6]$ (mol%)	Yield [%] (α/β)
1	Me, H, Me (**1b**)	0.5	92 (67:33)	5	72 (73:27)
2	Et, H, Me (**1c**)	0.5	92 (70:30)	10	79 (67: 33)
3	*i*Pr, H, Me (**1d**)	1	86 (70:30)	20	78 (70: 30)
4	Ph, H, Me (**1e**)	1	73 (50:50)	5	81 (41:59)
5	Me, Me, Me (**1f**)	3	68 (22:78)	20	67 (20:80)
6	Ph, Me, Me (**1g**)	1	76 (32:68)	10	79 (27:73)
7	Ph, Me, H (**1h**)	3	74 (85:15)	5	77 (75:25)

In particular, the rhenium-catalyzed reactions of the dienol silyl ethers **1i** and **1j** (Table 3), with no substituents at their β positions (1-positions), afforded the desired bicyclic enol silyl ethers in moderate to good yields in the presence only of 1 mol% $[ReCl(CO)_5]$, whereas the corresponding tungsten-catalyzed reactions proceeded in very low yields even with stoichiometric amounts of $[W(CO)_5(L)]$.

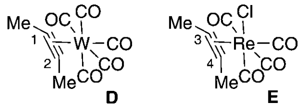
Table 3. Rhenium- and tungsten-catalyzed reaction behavior of 1-unsubstituted dienol silyl ethers.



R	$[ReCl(CO)_5]$ [mol%]	Yield [%]	$[W(CO)_6]$ [mol%]	Yield [%]
Me (**1i**)	1	81	100	17
H (**1j**)	1	51	100	0

Next, to gain an insight into the higher reactivity of the rhenium carbonyl complex, the charge distributions in the rhenium[13]– and tungsten–alkyne π complexes were evaluat-

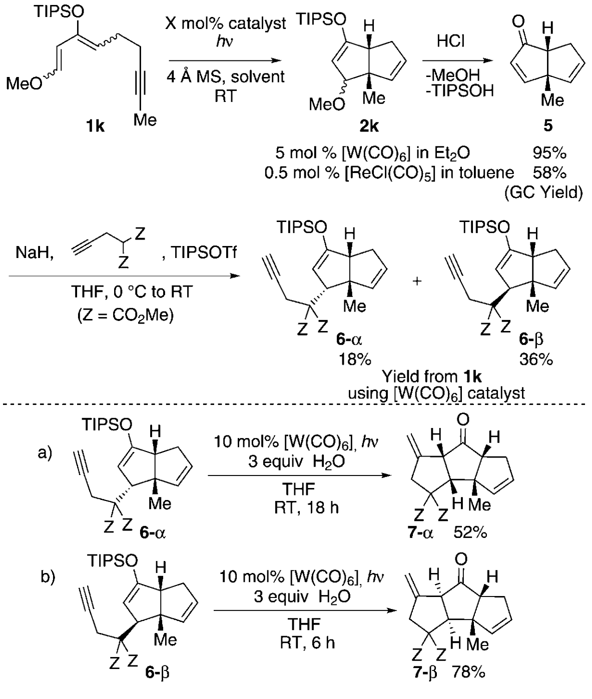
Table 4. Charge distributions in the π-alkyne complexes **D** and **E**.



	D		**E**	
	C^1	C^2	C^3	C^4
Mulliken	0.120	0.120	0.180	0.119
NBO	0.026	0.026	0.070	0.018

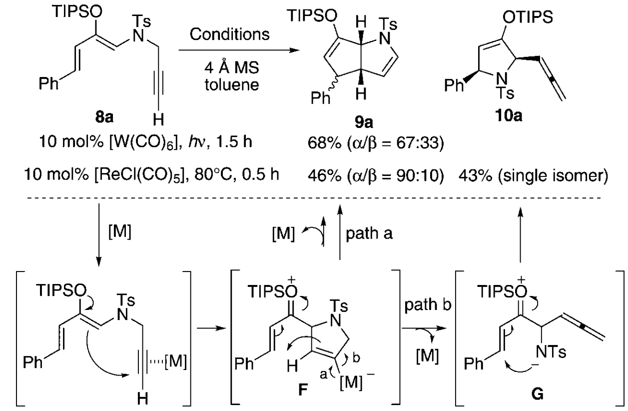
ed by DFT calculations[14] with but-2-yne as a model substrate. As shown in Table 4, one of the alkyne carbon atoms in the rhenium complex **E** has more positive charge than the alkyne carbon atoms in the tungsten complex **D**, which suggests that the rhenium–alkyne π complex is more electrophilically activated than the corresponding tungsten complex. This calculation is in good agreement with the higher reactivity of the rhenium-catalyzed reaction.

Synthetic application of tandem cyclization—synthesis of triquinane skeletons: This tandem cyclization protocol provides a facile method for the preparation of bicyclo[3.3.0]octane derivatives, which constitute the basic carbon skeletons of many natural products,[8] in a single-step fashion from easily available acyclic substrates. This protocol was therefore applied to a concise synthesis of the basic carbon skeleton of triquinanes.[15] Treatment of the dienol silyl ether **1k** (Scheme 6), containing a methoxy group at the diene terminus, either with $[W(CO)_6]$ (5 mol %) in diethyl ether or with $[ReCl(CO)_5]$ (0.5 mol %) in toluene under photoirradiation conditions gave the bicyclic dienone **2k** in 95 or 58 % yields, respectively, after acid treatment.[16] Conjugate addition of dimethyl propargylmalonate sodium salt to **5** in the presence of TIPS triflate gave the ω-acetylenic enol silyl ethers **6-α** and **6-β** in yields of 18 and 36 %, respectively.[5b] Furthermore, treatment of the two isomers **6-α** and **6-β** again with catalytic amounts of $[W(CO)_6]$ and with water (3 molequiv) under photoirradiation conditions in THF gave the tricyclic ketones **7-α** and **7-β**, each containing a triquinane skeleton, in yields of 52 and 78 %, respectively (Scheme 6a and b). The basic carbon skeleton of triquinanes can thus easily be constructed with the aid of Re- and W-catalyzed cyclizations.



Scheme 6. Synthesis of triquinane skeletons.

Rhenium-catalyzed selective preparation of nitrogen-containing cyclic compounds: We next applied these reactions to the synthesis of azabicyclo[3.3.0]octane derivatives. When the dienol silyl ether **8a** (Scheme 7), containing an N–Ts component in the tether, was treated with $[W(CO)_6]$ (10 mol %) under photoirradiation conditions, the expected bicyclic silyl enol ether **9a** was obtained in 68 % yield as a mixture of diastereoisomers. However, when the same reaction was carried out with $[ReCl(CO)_5]$ (10 mol %) under heating conditions in toluene in the presence of molecular sieves (4 Å),[17] the unexpected monocyclic dihydropyrrole **10a**, containing an allenyl substituent, was obtained in 43 % yield, along with 46 % yield of the bicyclic silyl enol ether **9a**.[2c,18] At that point, it was thought that the expected 2-azabicyclo[3.3.0]octane derivative **9a** was obtained in a similar geminal carbo-functionalization, whereas the dihydropyrrole derivative **10a** was obtained through a ring-opening reaction of the zwitterionic intermediate **F**. The ring-open reaction was thought to be caused by electron donation from the alkenylmetallic moiety to the sulfonamide group to give the acyclic intermediate **G**, containing an allenyl substituent, followed by 1,4-addition of the anion of the sulfonamide to the α,β-unsaturated silyloxonium moiety (Scheme 7, path b). Because two kinds of synthetically useful heterocyclic compounds were found to be obtained on treatment with

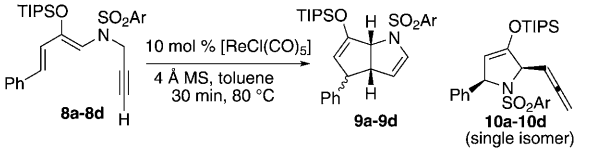


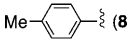
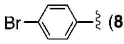
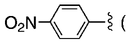
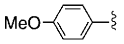
Scheme 7. Reaction behavior of the dienol silyl ether **8a**, containing an N–Ts component in the tether.

[ReCl(CO)$_5$], we decided to examine this reaction in more detail to allow the selective preparation of these two types of products.

Firstly, the reaction behavior of substrates with a variety of sulfonyl groups on the nitrogen atom was examined with the goal of achieving selective preparation of either **9** or **10**, in the expectation that arylsulfonamide units containing electron-withdrawing groups would favor the formation of dihydropyrroles **10**, because of their better ability as eliminating groups, whereas those with electron-donating groups would favor the formation of the 2-azabicyclo[3.3.0]octane derivatives **9** (Table 5). However, it was a surprise to find that the 2-azabicyclo[3.3.0]octane derivative **9c** was obtained as a major product when the substrate containing a *p*-nitrobenezenesulfonyl (Ns) group was used (Table 5, entry 3), whereas the presence of a *p*-methoxybenezenesulfonyl (Mbs) group increased the formation of the dihydropyrrole **10d** (Table 5, entry 4).

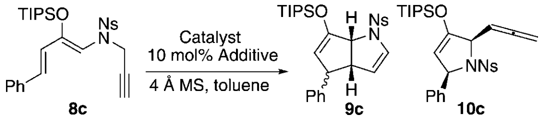
Table 5. Examination of the effects of a variety of sulfonyl groups on the nitrogen atom.



Entry	Ar	Yield [%]	
		9 (α/β)	**10**
1	 **(8a)**	46 (90:10)	43
2	 **(8b)**	49 (90:10)	34
3	 **(8c)**	76 (90:10)	17
4	 **(8d)**	28 (92:8)	55

The use of other rhenium catalysts was also examined, both to achieve selective preparation of the two types of products and to provide further information on the mechanisms of these reactions. As summarized in Table 6 and Table 7, examination of several rhenium catalysts with N–Ns and N–Mbs substrates revealed the tendency for neutral [ReCl(CO)$_4$(PPh$_3$)][19] to favor the formation of the 2-azabicyclo[3.3.0]octane derivatives **9**, whereas the cationic rhenium catalyst prepared in situ from [ReCl(CO)$_5$] and AgSbF$_6$[20] favored the formation of the dihydropyrrole derivatives **10**. The best conditions for the selective preparation of the 2-azabicyclo[3.3.0]octane derivatives **9** and of the dihydropyrrole derivatives **10** are as follows. A 2-azabicyclo[3.3.0]octane derivative **9** is obtained selectively by carrying out the treatment of the N–Ns derivative with [ReCl(CO)$_4$(PPh$_3$)] (5 mol%) in toluene at 80°C, whereas a dihydropyrrole derivative **10** is obtained with good selectivity by treatment of the N–Mbs derivative with [ReCl(CO)$_5$] (1 mol%) and AgSbF$_6$ (10 mol%) in dichloroethane at 80°C.[21]

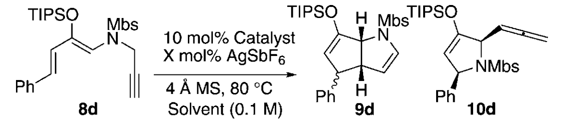
Table 6. Catalyst screening for the selective preparation of the bicyclic compound **9c**.



Entry	Catalyst (mol%)/additive	T [°C], t [h]	Yield [%]	
			9c (α/β)	**10c**
1	[ReCl(CO)$_5$] (10)	80, 0.5	76 (90:10)	17
2[a]	[ReCl(CO)$_5$] (10)/AgSbF$_6$	80, 0.5	61 (85:15)	21
3	[ReCl(CO)$_4$(PPh$_3$)] (10)	80, 1 reflux, 0.5	79 (70:30)	5
4	[ReCl(CO)$_4$(PPh$_3$)] (5)	80, 12.5	81 (60:40)	4

[a] 1,2-Dichloroethane was used as solvent.

Table 7. Catalyst screening for the selective preparation of the dihydropyrrole **10d**.

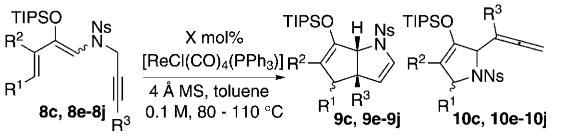


Entry	Catalyst	X	t [h]	Yield [%]	
				9d (α/β)	**10d** (*cis*/*trans*)
1	[ReCl(CO)$_5$]	0	0.5	28 (92:8)	55 (100:0)
2	[ReCl(CO)$_4$(PPh$_3$)]	0	4	47 (85:15)	33 (70:30)
3	[ReCl(CO)$_5$]	10	0.5	31 (70:30)	51 (100:0)
4[a]	[ReCl(CO)$_5$]	10	0.5	18 (90:10)	58 (100:0)
5[a,b]	[ReCl(CO)$_5$]	10	5	11 (90:10)	75 (70:30)

[a] 1,2-Dichloroethane was used as solvent. [b] 1 mol% of [ReCl(CO)$_5$] was used.

Rhenium(I)-catalyzed selective preparation of two types of nitrogen-containing cyclic compounds from 5-aza-3-siloxy-1,3-diene-7-ynes had been achieved, so the generality of these reactions was examined with several substrates.[22] Firstly, the generality of the preparation of the bicyclic compounds **9** was examined with use of N–Ns derivatives and [ReCl(CO)$_4$(PPh$_3$)] as catalyst (Table 8). The aryl-substituted dienes (R = Ph, 1-naphthyl) were cyclized to afford the corresponding 2-azabicyclo[3.3.0]octanes **9c** and **9e** as a mixture of diastereomers in good yields and with high selec-

Table 8. Generality of 2-azabicyclo[3.3.0]octane synthesis.



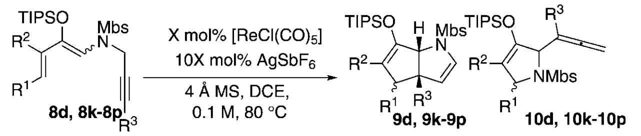
Entry	R^1, R^2, R^3	X	t [h]	Yield [%]	
				9 (α/β)	**10**
1	Ph, H, H (**8c**)	5	12.5	81 (60:40)	4
2	1-naphthyl, H, H (**8e**)	10	0.5	92 (85:15)	trace
3[a,b]	*i*Pr, H, H (**8f**)	10	1	37 (16:84)	trace
4	Ph, H, Me (**8g**)	5	4.5	87 (20:80)	0
5	1-naphthyl, H, Me (**8h**)	10	4.5	91 (30:70)	0
6[c]	Ph, Me, Me (**8i**)	5	1.5	78 (60:40)	trace
7[d]	*i*Pr, H, Me (**8j**)	10	0.5	33 (50:50)	17[e]

[a] Concentration was 0.01 M. [b] Molecular sieves (5 Å) were used instead of molecular sieves (4 Å). [c] TBS enol ether was employed. [d] Concentration was 0.05 M. [e] *cis*/*trans* = 14:86.

tivity (Table 8, entries 1 and 2). The alkyl-substituted diene could also be employed to give the corresponding 2-azabicyclo[3.3.0]octane **9f** selectively, albeit in low yield (Table 8, entry 3). Next, the reaction behavior of internal alkynes with a methyl group at the alkyne terminus was examined. The phenyl- and 1-naphthyl-substituted dienes afforded the corresponding 2-azabicyclo[3.3.0]octanes **9g** and **9h** with methyl substituents at their C^5 positions in good yields without the formation of the dihydropyrrole derivatives **10g** or **10h** (Table 8, entries 4 and 5). In these cases, the R^1-β isomers of the 2-azabicyclo[3.3.0]octanes **9g** and **9h** were each obtained as the major diastereomer. The reaction of a tetrasubstituted diene also proceeded to give the corresponding bicyclic enol silyl ether **9i** selectively and in good yield (Table 8, entry 6). However, the reaction of the alkyl-substituted diene **8j** proceeded only in moderate yield and with moderate selectivity (Table 8, entry 7).[23]

Next, the generality of selective preparation of dihydropyrrole derivatives of type **10** was examined under cationic rhenium(I) conditions (Table 9). The aryl-substituted dienes could be successfully converted into the corresponding dihydropyrroles **10**, each with an allenic substituent, with high selectivity as mixtures of diastereomers even with 1 mol% of the cationic rhenium catalyst (Table 9, entries 1–3). The alkyl-substituted dienes also gave good results for the selective preparation of dihydropyrroles **10m** and **10p** irrespective of the presence or absence of alkyne substituents (Table 9, entries 4 and 7), whereas the aryl-substituted dienes **8n** and **8o**, with internal alkyne moieties, gave two types of products with concomitant formation of the dihydropyrroles **10n** and **10o** (Table 9, entries 5 and 6).

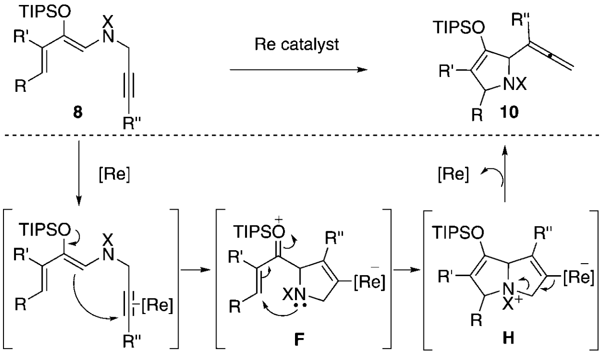
Table 9. Generality of dihydropyrrole synthesis.



Entry	R^1, R^2, R^3	X	*t* [h]	Yield [%] **9** (α/β)	**10** (*cis*/*trans*)
1	Ph, H, H (**8d**)	1	5	11 (90:10)	75 (70:30)
2	1-naphthyl, H, H (**8k**)	1	4	14 (76:24)	70 (90:10)
3	Ph, Me, H (**8l**)	1	2	9 (90:10)	86 (30:70)
4[a]	*i*Pr, H, H (**8m**)	5	0.5	11 (60:40)	69 (40:60)
5	Ph, H, Me (**8n**)	10	0.1	52 (50:50)	31 (94:6)
6	Ph, Me, Me (**8o**)	10	0.5	41 (60:40)	58 (20:80)
7[a]	*i*Pr, H, Me (**8p**)	5	0.5	14 (60:40)	72 (20:80)

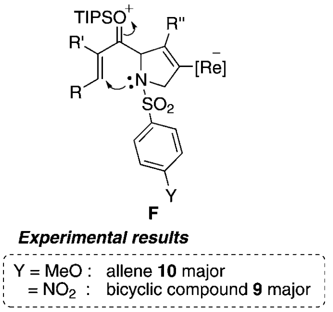
[a] Concentration was 0.01 M.

Here we would like to discuss the mechanism of the reaction, in particular with regard to the formation of the dihydropyrroles with allenic substituents. As already mentioned, the effect of the substituent on the arylsulfonyl group was not compatible with the initially proposed elimination mechanism (see Scheme 7). From the data obtained so far, we believe at present that nucleophilic addition of the sulfonamide nitrogen to the α,β-unsaturated silyloxonium moiety occurs first in the zwitterionic intermediate **F** to give the azabicyclic ammonium intermediate **H** (Scheme 8),[24] which then undergoes elimination of the dihydropyrrole derivative **10** with an allenic substituent along with the rhenium catalyst.



Scheme 8. A possible mechanism for the formation of allenes of type **10**.

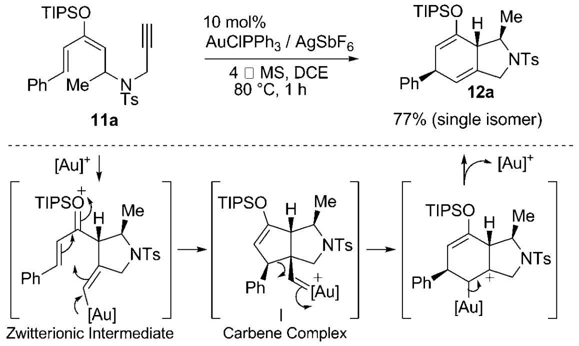
The observations that the N−Ns derivatives mainly gave the 2-azabicyclo[3.3.0]octane derivatives **9**, whereas the N−Mbs derivatives preferentially gave the dihydropyrrole derivatives **10** could be explained on the basis of this mechanism because the nucleophilicity of the nitrogen atom in the N−Mbs system is higher than that in the N−Ns system (Scheme 9). Thus, in the zwitterionic intermediate of type **F**, instead of the alkenylrhenium moiety, the nitrogen atoms of the N−Mbs derivatives preferentially underwent addition to the α,β-unsaturated silyloxonium moieties to give the bicyclic ammonium salts **H**, which gave the dihydropyrroles with regeneration of the catalyst as shown in Scheme 8. Use of the cationic rhenium catalyst should also retard the nucleophilic attack of the alkenylrhenium moieties in the zwitterionic intermediates **F**, resulting in the favorable nitrogen attack onto the α,β-unsaturated silyloxonium moieties. These reactions were thus able to provide two synthetically useful nitrogen-containing cyclic compounds selectively through variation of the substituent on the nitrogen and the kind of rhenium catalyst.



Scheme 9.

Tungsten-catalyzed tandem cyclization through 6-*endo*-dig cyclization: Finally, we applied this geminal carbo-functionalization to one-carbon-elongated substrates containing N−

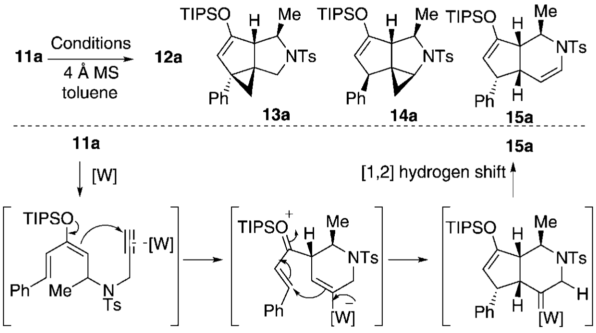
Ts components in their tethers. We had already reported that on use of the cationic gold(I) catalyst, the dienol silyl ethers **11a** diastereoselectively gave the bicyclo[4.3.0]nonane derivatives **12a** (Scheme 10), with different stereochemistry from the thermal Diels–Alder products.[25] In these reactions, geminal carbo-functionalization through initial 5-*exo* cyclization gave a bicyclic carbene complex such as **I**, which underwent 1,2-alkyl migration of the benzylic carbon to give the product with regeneration of the catalyst.[26]



Scheme 10. Gold-catalyzed geminal carbo-functionalization of **11a** through 5-*exo*-dig cyclization.

During these studies, we thought of the possibility—based on previous experimental results[27]—of geminal carbo-functionalization through initial 6-*endo* cyclization in the presence of tungsten catalyst. Surprisingly, treatment of **11a** with $[ReCl(CO)_5]$ (10 mol%) gave a 78% yield of the tricyclic compounds **13a** and **14a** (Table 10), produced by insertion of the carbene complex moiety into the neighboring C–H bonds in the carbene complex intermediate generated by 5-*exo* cyclization.[25] No other cyclized products were obtained. This high insertion ability of the carbene complex intermediate is a remarkable characteristic of the rhenium(I) catalyst. On the other hand, when **11a** was treated with an equimolar amount of $[W(CO)_6]$ under photoirradiation conditions, the desired geminal carbo-functionalization through 6-*endo*-dig cyclization occurred to give the 3-azabicyclo[4.3.0]nonane derivative **15a** as a single diastereoisomer[28] in 40% yield. In this case, no 5-*exo*-dig products **12a**, **13a**, or **14a** were observed.[29] Further examination to improve the yield of the product and to reduce the amount of the catalyst did not give satisfactory results.

Table 10. Catalyst screening for geminal carbo-functionalization through 6-*endo*-dig cyclization.

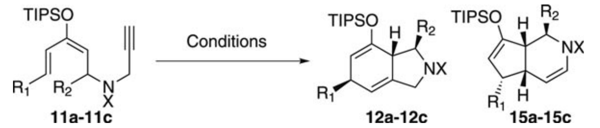


Entry	Catalyst (mol%)	*T*, *t*	Yield [%]		
			12a	**13a**+**14a** (**13a**/**14a**)	**15a**
1[a]	$[AuCl(PPh_3)]/AgSbF_6$ (10 mol%)	80°C, 1 h	77	0	0
2	$[ReCl(CO)_5]$ (10 mol%)	80°C, 20 min	0	78 (50:50)	0
3	$[W(CO)_6]$, *hν* (100 mol%)	RT, 10 min	0	0	40

[a] 1,2-Dichloroethane was used as solvent.

We next examined the generality of this tungsten-catalyzed geminal carbo-functionalization through 6-*endo*-dig cyclization (Table 11). With the three substrates **11a–11c**, use of the gold catalyst selectively gave the 8-azabicyclo[4.3.0]nonane derivatives **12**, whereas use of stoichiometric amounts of $[W(CO)_6]$ gave the 3-azabicyclo[4.3.0]nonane derivatives **15**, the 6-*endo* cyclized products, diastereoselectively and in moderate yields. We have thus succeeded in complementary construction of two types of azabicyclo[4.3.0]nonane derivatives, core skeletons of several biologically active natural products,[30] through appropriate choice of transition-metal complexes.

Table 11. Generality of tungsten-catalyzed geminal carbo-functionalization through 6-*endo*-dig cyclization.



Entry	Conditions[a]	(R^1, R^2, X)	Yield [%]	
			12	**15**
1	A	Ph, Me, Ts (**11a**)	77	–
2	B		–	40
3	A	Me, Me, Ts (**11b**)	68	–
4	B		–	37
5	A	Ph, Ph, Ms (**11c**)	72	–
6[b]	B		–	52

[a] Conditions A: $[AuCl(PPh_3)]/AgSbF_6$ (10 mol%), molecular sieves (4 Å), 1,2-dichloroethane, 80°C, 1 h. Conditions B: $[W(CO)_6]$ (100 mol%), molecular sieves (4 Å), toluene, *hν*, 5–10 min. [b] An 18% yield of the tricyclic compounds **13c** and **14c** was obtained.

Conclusion

We have developed tungsten(0)- and rhenium(I)-catalyzed geminal carbo-functionalization reactions of 3-siloxy-1,3-diene-7-ynes to give synthetically useful bicyclo[3.3.0]octane derivatives. Exceptionally high activity of $[ReCl(CO)_5]$ for these reactions is noted. The reactions were applied to the construction of the basic carbon skeletons of triquinanes. Selective preparation of two kinds of nitrogen-containing cyclic compounds from 5-aza-3-siloxy-1,3-diene-7-ynes was also achieved through appropriate choice of the catalyst and the protecting group on nitrogen. Furthermore, control of the 5-*exo* and 6-*endo* cyclizations of one-carbon-elongated substrates was achieved by use of gold and tungsten catalysts, respectively. These reactions demonstrate the high synthetic utility of geminal carbo-functionalization of alkynes and also show new potential for the use of tungsten and rhenium complexes in organic synthesis.

Experimental Section

Cyclizations of the dienol silyl ethers 1: A typical procedure for the cyclizations of **1a–1j** is described for the reaction with **1a** as substrate. Compound **1a** (292 mg, 0.60 mmol) in degassed toluene (1.0 mL) was added to a mixture of [ReCl(CO)$_5$] (1.1 mg, 0.0030 mmol, 0.5 mol %) and activated molecular sieves (4 Å, 100 mg), and the resulting mixture was stirred under photoirradiation conditions (250 W super high-pressure Hg lamp) until TLC showed the complete disappearance of **1a**. The reaction mixture was then filtered through a short pad of silica gel and the filtrate was concentrated under reduced pressure. The residue was purified by PTLC (hexane/EtOAc 9:1) to give a mixture of **2a** and **3a** (**2a**-α/**2a**-β/**3a** 69:17:14, 269 mg, 0.55 mmol) in 92 % yield.

Cyclization and hydrolysis of the dienol silyl ether 1k: Compound **1k** (215 mg, 0.67 mmol) in degassed diethyl ether (1.0 mL) was added to a mixture of [W(CO)$_6$] (13 mg, 0.037 mmol, 0.05 equiv) and activated molecular sieves (4 Å). After the mixture had been photoirradiated (250 W super high-pressure Hg lamp) for 7.5 h, hydrochloric acid (1 M, ca. 2 mL) was added and the mixture was further stirred for 30 min. The organic layer was extracted with ether, washed with sat. $NaHCO_3$ solution and brine, and dried over $MgSO_4$. The bicyclic ketone **5** was so volatile that the solvent was not removed completely. The crude ketone was purified by PTLC (diethyl ether/hexane 20 %), and the eluent (diethyl ether) was then removed under atmospheric pressure. The ketone was used for the next reaction without complete removal of the eluent (GC yield: 95 %).

Conjugate addition of dimethyl propargylmalonate sodium salt to 5: A diethyl ether solution (3.0 mL) of dimethyl (prop-2-ynyl)malonate (161 mg, 0.95 mmol) was added dropwise at 0 °C over 2 min to NaH (46 mg, 1.92 mmol). After the mixture had been stirred for 50 min, the solvent was removed under reduced pressure to afford a yellowish solid, and then CH_2Cl_2 (2.0 mL) was added to the mixture. A CH_2Cl_2 solution (3.0 mL) of the above ketone **5** was added at 0 °C to the dimethyl propargylmalonate Na salt, and TIPSOTf (0.22 mL, 0.82 mmol) was then added successively at the same temperature. After the mixture had been stirred overnight, the reaction was quenched with phosphate buffer (pH 7). The mixture was extracted three times with ethyl acetate, and the combined organic layer was washed with brine and dried over $MgSO_4$. Evaporation under reduced pressure gave a crude product, which was purified by silica gel column chromatography (ethyl acetate/hexane 5 %) to give the silyl enol ether **6** (158 mg, 54 %) as a mixture of diastereomers (**6**-α/**6**-β = 1:2). The enol silyl ethers **6**-α and **6**-β were separable by PTLC (ethyl acetate/hexane 10 %).

Synthesis of a triquinane skeleton: A typical procedure for the preparation of the tricyclic ketones (**7**-α, **7**-β) is described for the reaction with **6**-β as substrate. A THF solution (1.0 mL) of **6**-β (41.0 mg, 0.089 mmol) was added to a mixture of [W(CO)$_6$] (3.0 mg, 0.0085 mmol, 0.10 equiv) and H_2O (5.0 μL, 0.28 mmol). After the mixture had been photoirradiated (200 W high-pressure Hg lamp) for 6 h, the solvent was removed under reduced pressure to give the crude product, which was purified by PTLC (ethyl acetate in hexane 10 %) to give **7**-β (21.0 mg, 78 %).

[ReCl(CO)$_5$]-catalyzed reactions of the dienol silyl ethers 8a–8d: A typical procedure for the cyclizations of **8a–8d** is described for the reaction with **8c** as substrate. Compound **8c** (52.9 mg, 0.10 mmol) in degassed toluene (1 mL) was added to a mixture of [ReCl(CO)$_5$] (3.6 mg, 0.01 mmol) and activated molecular sieves (4 Å, 100 mg), and the resulting mixture was stirred at 80 °C until TLC showed the complete disappearance of **8c**. The reaction mixture was then filtered through a short pad of Celite, and the filtrate was concentrated under reduced pressure. Water was then poured onto the residue and organic materials were extracted twice with ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The filtrate was concentrated and the resulting crude product was purified by PTLC (toluene/EtOAc 9:1) to give a mixture of **9c** (40.3 mg, 76 %) as a mixture of diastereomers (α/β 90:10) and **10c** (9.2 mg, 17 %) as a single isomer.

Preparation of the bicyclic compounds 9: A typical procedure for the cyclizations of **8c** and **8e–8j** is described for the reaction with **8g** as substrate. Compound **8g** (55.4 mg, 0.10 mmol) in degassed toluene (1 mL) was added to a mixture of [ReCl(CO)$_4$(PPh$_3$)] (3.0 mg, 0.005 mmol) and activated molecular sieves (4 Å, 100 mg), and the resulting mixture was stirred at 80 °C until TLC showed the complete disappearance of **8g**. The reaction mixture was then filtered through a short pad of Celite, and the filtrate was concentrated under reduced pressure. Water was then poured onto the residue, and organic materials were extracted twice with ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The filtrate was concentrated and the resulting crude product was purified by PTLC (hexane/EtOAc 8:2) to give **9g** (48.2 mg, 87 %) as a mixture of diastereomers (α/β 20:80).

Preparation of the dihydropyrroles 10: A typical procedure for the cyclizations of **8d** and **8k–8p** is described for the reaction with **8l** as substrate. Compound **8l** (106.7 mg, 0.20 mmol) in degassed dichloroethane (2 mL) was added to a mixture of [ReCl(CO)$_5$] (0.7 mg, 0.002 mmol) and activated molecular sieves (4 Å, 100 mg), and the resulting mixture was stirred at 80 °C until TLC showed the complete disappearance of **8l**. The reaction mixture was then filtered through a short pad of Celite, and the filtrate was concentrated under reduced pressure. Water was then poured onto the residue and organic materials were extracted twice with ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The filtrate was concentrated and the resulting crude product was purified by PTLC (toluene/EtOAc 96:4) to give a mixture of **9l** (9.3 mg, 9 %) as a mixture of diastereomers (α/β 90:10) and **10l** (92.0 mg, 86 %) as a mixture of diastereomers (*cis*/*trans* 30:70).

Gold-catalyzed reactions of the dienol silyl ethers 11: A typical procedure for the cyclizations of **11a–11c** is described for the reaction with **11a** as substrate. Compound **11a** (53.9 mg, 0.10 mmol) in degassed dichloroethane (1 mL) was added to a mixture of [AuCl(PPh$_3$)] (4.9 mg, 0.0099 mmol, 10 mol %), $AgSbF_6$ (3.4 mg, 0.0099 mmol, 10 mol %), and activated molecular sieves (4 Å, 100 mg), and the resulting mixture was stirred at room temperature until TLC showed the complete disappearance of **11a**. The reaction mixture was then filtered through a short pad of silica gel and the filtrate was concentrated under reduced pressure. The residue was purified by PTLC (hexane/EtOAc 9:1) to give **12a** (41.5 mg, 0.077 mmol) in 77 % yield as a colorless oil.

Rhenium-catalyzed reaction of the dienol silyl ether 11a: Compound **11a** (53.9 mg, 0.10 mmol) in degassed toluene (1 mL) was added to a mixture of [ReCl(CO)$_5$] (3.6 mg, 0.01 mmol) and activated molecular sieves (4 Å, 100 mg), and the resulting mixture was stirred at 80 °C until TLC showed the complete disappearance of **11a**. The reaction mixture was then filtered through a short pad of silica gel and the filtrate was concentrated under reduced pressure. The residue was purified by PTLC (hexane/EtOAc 9:1) to give a mixture of **13a** and **14a** (1:1, 42.0 mg, 0.078 mmol) in 78 % yield as a colorless oil.

Tungsten-catalyzed reactions of the dienol silyl ethers 11: A typical procedure for the cyclizations of **11a–11c** is described for the reaction with **11a** as substrate. Compound **11a** (53.9 mg, 0.10 mmol) in degassed toluene (1 mL) was added to a mixture of [W(CO)$_6$] (35.2 mg, 0.10 mmol) and activated molecular sieves (4 Å, 100 mg), and the resulting mixture was stirred under photoirradiation conditions until TLC showed the complete disappearance of **11a**. The reaction mixture was then filtered through a short pad of Celite and the filtrate was concentrated under reduced pressure. The residue was purified by PTLC (hexane/EtOAc 9:1) to give **15a** (21.6 mg, 0.040 mmol) in 40 % yield as a pale yellow oil.

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[22] We examined the reaction of **8e**–**8p** using a mixture of Z and E isomers concerning the silyl enol ether moiety. It was confirmed that there was no difference in reactivity between (Z)-**8d** and (E)-**8d**. For details, see the Supporting Information (7.3).

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