Stereocontrolled Synthesis of Functionalized Bicyclic α-Methylene Butyrolactones via Tungsten-Mediated Intramolecular Allylation of Aldehydes

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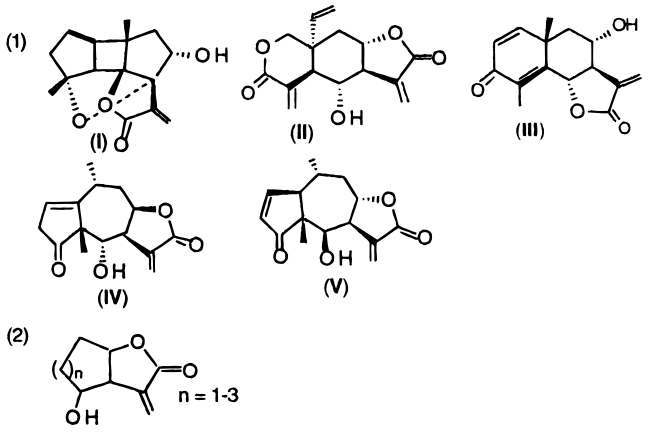
Received June 2, 1999

The syntheses of a series of $CpW(CO)_2(\pi$-γ-lactonyl) complexes bearing a tethered aldehyde are described. These π-allyl complexes are prepared as either *syn*- or *anti*-stereoisomers. Treatment of these dicarbonyl complexes with $NOBF_4$ and NaI in CH_3CN effects an intramolecular allylation of the tethered aldehyde, yielding bicyclic α-methylene butyrolactones comprising a homoallylic alcohol. Both *syn*- and *anti*-isomers of tungsten-π-allyl compounds produce the same α-methylene butyrolactones. The cyclizations proceed with high diastereoselectivities to give only the cis-fused bicyclic γ-lactones. The preference for *cis*-fused stereoselection can be rationalized based on a tricyclic transition state mechanism.

Introduction

The synthesis of α-methylene butyrolactones has received considerable attention because of their wide occurrence in bioactive natural products.[1] These structural units are also useful building blocks for natural products such as alkaloids, macrocyclic antibiotics, and pheromones.[2] Many naturally occurring compounds not only have an α-methylene butyrolactone unit but often bear an additional hydroxyl group, particularly in the family of sesquiterpenes.[1f,3] α-Methylene butyrolactones bearing a homoallylic alcohol are the most frequently encountered. Scheme 1 shows several natural compounds **I**−**V** of which the homoallylic alcohols have been shown to be closely related to their biological activities.[4] Stereocontrolled syntheses of the core structure (Scheme 1, eq 2) of these bioactive natural compounds are easily accessible, and a few synthetic methods were reported previously.[5−8]

Scheme 1



Recently, we reported that propargyltungsten compounds undergo acid-catalyzed alkoxycarbonylation to give tungsten-π-2-alkoxycarbonylallyl compounds as shown in Scheme 2 (eq 1).[9] Further ligand substitution of these dicarbonyl complexes with $NOBF_4$ and NaI generated their CpW(NO)I derivatives that reacted with aldehydes to yield *trans*-α-methylene butyrolactones via a chairlike transition state structure.[9,10] The reaction was extended to intramolecular alkoxycarbonylation as shown in eq 2. Both *syn*- and *anti*-π-allyl complexes yielded the same diastereomeric *trans*-α-methylene butyrolactones bearing an *anti*-homoallylic alcohol. In principle, selection of suitable R and R″ substituents of these γ-lactones could lead to *trans*-fused γ-lactones bearing a homoallylic alcohol. *Cis*-fused and *trans*-fused α-methylene butyrolactones occur equally in natural sources.[1f,3] In this paper,

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† To whom the theoretic work should be addressed.

(1) For review papers, see (a) Grieco, P. A. *Synthesis* **1975**, 67. (b) Hoffman, H. M. R.; Rabe, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 94. (c) Petragnani, N.; Ferraz, H. M. C.; Silva, G. V. J. *Synthesis* **1986**, 157.

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(6) Ziegler, F. E.; Marino, A. F.; Petroff, O. A. C.; Stadt, W. L. *Tetrahedron Lett.* **1974**, 2035.

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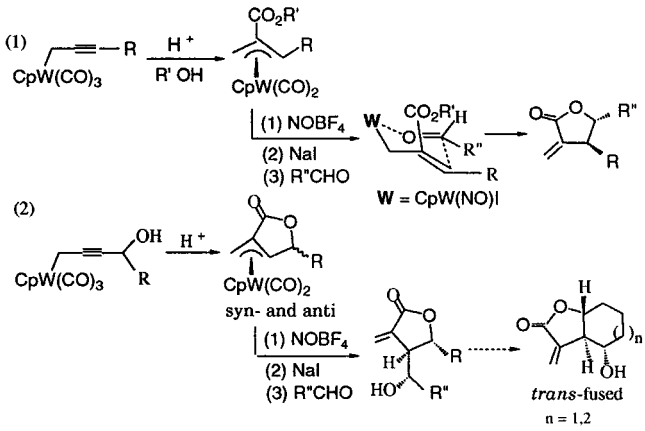
(9) (a) Lin, S.-H.; Vong, W.-J.: Liu, R.-S. *Organometallics* **1995**, *14*, 1619. (b) Chen, C.-H.; Fan, J.-S.; Lee, G.-H.; Shieh, S.-J.; Wang, S.-L.; Peng S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 9279. (c) Shiu, L. H.; Wang, S.-L.; Wu, M.-J.; Liu, R. S. *J. Chem. Soc. Chem. Commun.* **1997**, 2055.

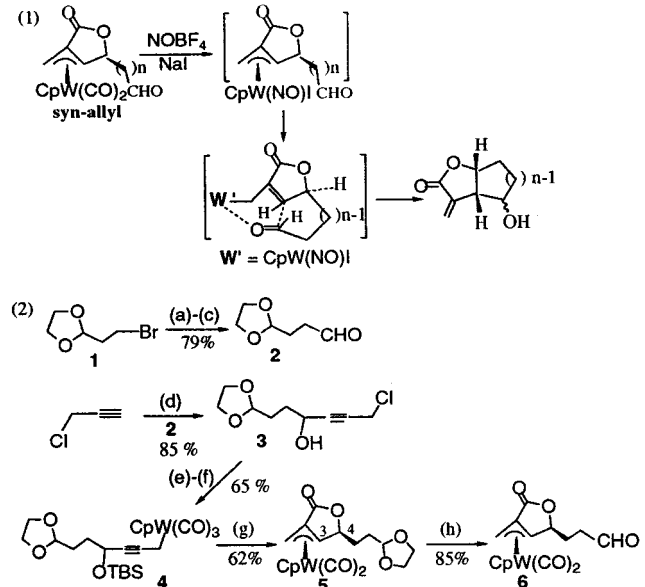
(10) (a) Faller, J. W.; Linebarrier D. L. *J. Am. Chem. Soc.* **1989**, *111*, 1937. (b) Faller, J. W.; John, J. A.; Mazzier, M. R. *Tetrahedron Lett.* **1989**, *31*, 1769.

10.1021/jo9909002 CCC: $18.00
Published on Web 09/11/1999

Scheme 2



Scheme 3

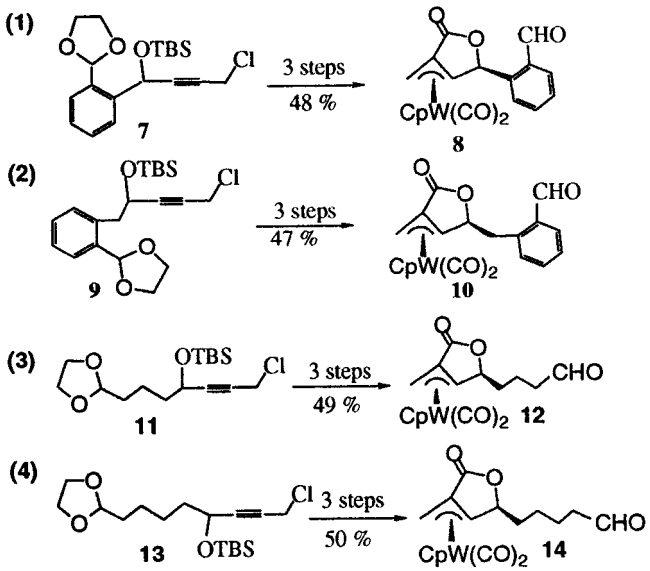


we describe a new tungsten-mediated synthesis of *cis*-fused bicyclic γ-lactones; the reaction protocol is shown in Scheme 3 (eq 1).

Results

Synthesis of Organic Substrates and Tungsten-π-allyl Compounds. The strategy toward the synthesis of *cis*-fused α-methylene butyrolactones is designed based on intramolecular allylation of the tethered aldehydes of tungsten-*syn*-π-γ-lactonyl compounds. As shown in Scheme 3, we envision that the tethered aldehyde of the CpW(NO)I(π-allyl) compound may approach the highly acidic tungsten center to form a tricyclic transition state. The two hydrogens on the γ-lactone ring are likely to have a *cis*-configuration due to its planar *syn*-γ-lactone structure. This cyclic transition state is expected to give the *cis*-fused bicyclic lactone bearing a *syn*- or *anti*-homoallylic alcohol. Eq 2 represents a typical case for the synthesis of propargyl substrate **3**, further preceding to the desired π-γ-lactonyl complex **5**. The chloropropargyl derivative **3** is readily prepared from 2-(2-bromoethyl)-[1,3]-dioxolane **1** in a four-step syntheses; the overall yield was 70%. Further treatment of the dimethyl(*tert*-butyl)siloxyl

Scheme 4. *Syn*-π-allyl Compound



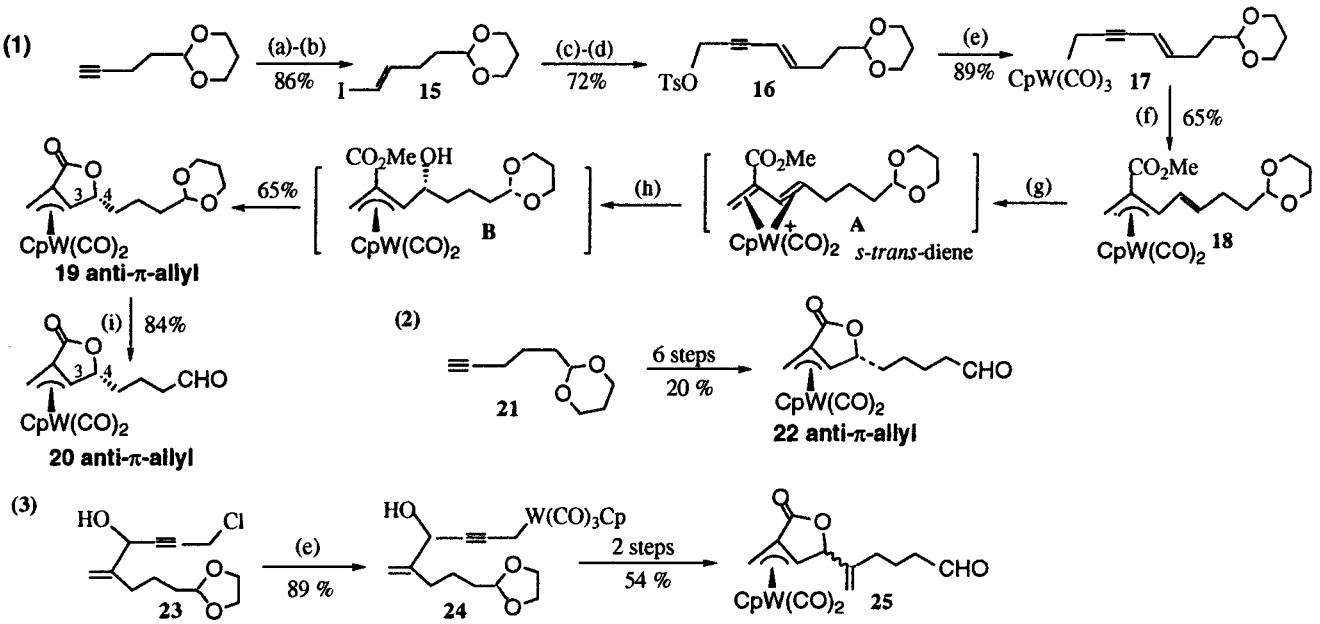
derivative of compound **3** with $CpW(CO)_3Na$ (1.2 equiv) in THF (23 °C, 8 h) smoothly afforded its propargyltungsten derivative **4**. Subsequent treatment of **4** with CF_3SO_3H catalyst (0.25 equiv) in cold CH_2Cl_2 (−40 °C) delivered the *syn*-π-allyl compound **5** in 62% yield. The tethered substituent of π-allyl complex **5** and tungsten center are on the same side as indicated by the hydrogen coupling constant $J_{3,4}$ =3.7 Hz.[9b] The effect of dimethyl(*tert*-butyl)siloxyl group on the *syn*-selectivity of compound **5** has been elucidated in our previous study.[9b] Heating compound **5** with *p*-TSA catalyst (0.10 equiv) in EtCHO/acetone (0.03/1.0 volume ratio) provided the aldehyde **6** in 85% yield.

Scheme 4 (eqs 1−4) shows additional examples for the syntheses of tungsten π-allyl compounds **8**, **10**, **12**, and **14** having *syn*-configuration in their tethered aldehyde substituents. These π-allyl complexes were easily prepared from the corresponding (*tert*-butyl)dimethylsiloxyl derivatives **7**, **9**, **11**, and **13** according to the same procedure for synthesis of π-allyl compound **6** (Scheme 3, eq 2). The detailed procedures for the syntheses of organic substrates **7**, **9**, **11**, **13** and transformation of these substrates into tungsten-syn-π-allyl complexes **8**, **10**, **12**, and **14** are described in the Supporting Information.

We also prepared tungsten-π-allyl compounds **19** and **20** having *anti*-aldehyde substituents according to the procedures shown in Scheme 5 (eq 1). These *anti*-π-allyl complexes were prepared in order to compare their stereochemical outcome with those of their *syn*-π-allyl diastereomers. In this synthetic sequence, 2-but-3-ynyl-[1,3]-dioxane was treated with Bu_3SnH, followed by I_2-oxidation[11] to give iodovinyl derivative **15** in overall 86% yield. A Pd-catalyzed coupling reaction[12] of **15** with propargyl alcohol proceeded smoothly, and the product was subsequently converted to its tosylate derivative **16** in a combined 72% yield. Metalation of **16** with $CpW(CO)_3Na$ produced its tungsten-propargyl derivative **17** (89%) that was subsequently treated with *p*-toluenesulfonic acid catalyst in MeOH, inducing alkoxycarbo-

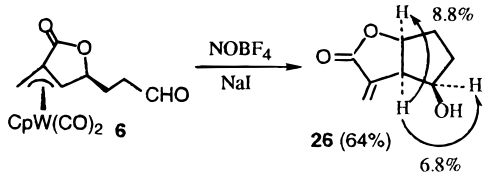
(11) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138.
(12) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

Scheme 5. *Anti*-π-allyl Isomer and *Syn*−Anti Mixtures



Conditions (a) BuSnH, AIBN, 130^{0}C, 2 h (b) I_2 , 0 ^{0}C (c) CuI (2 mol%), $PdCl_2(PPh_3)_2$, (1 mol%) Et_2NH, propargyl alcohol (d) p-TsCl, KOH, acetone (e) $NaCpW(CO)_3$ (f) CF_3SO_3H, -78 ^{0}C, MeOH (g) CF_3SO_3H (h) NaOH (aq) (i) p-TSA, EtCHO/acetone = 0.03/1.00

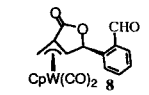
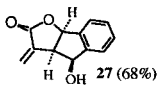
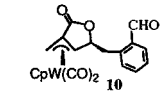
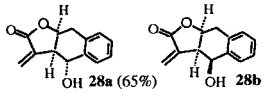
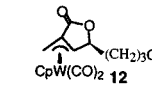
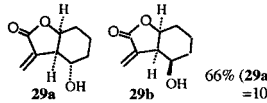
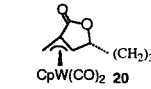
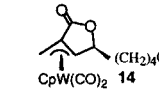
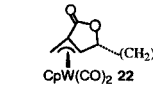
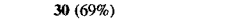
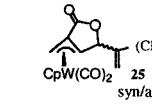
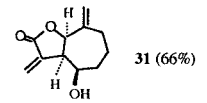
Scheme 6



nylation reaction to give tungsten-π-pentadienyl derivative **18** in 65% yield. Protonation of **18** with CF_3SO_3H (1.0 equiv) in cold diethyl ether (−78 °C) generated a reactive *s-trans*-diene cation[13] **A** that was subsequently treated with an aqueous NaOH solution to give an α-hydroxyallyl species **B**, finally forming a γ-lactone **19** (65% yield) under basic medium.[9c] Compound **19** and its aldehyde derivative **20** have an *anti*-configuration according to the magnitude of coupling constant $J_{3,4} = 0$ Hz.[9b,13] We also prepared the *anti*-π-allyl complex **22** derived from 2-pent-4-ynyl-[1,3]-dioxane **21** following the same synthetic procedure (See Supporting Information). Finally, we prepared tungsten-π-allyl compound **25** via treatment of propargyltungsten compounds with CF_3SO_3H (0.25 equiv) in cold CH_2Cl_2 (−78 °C), yielding a mixture of *syn*- and *anti*-isomers (*syn*/*anti* = 1/2.2). The alcohol of compound **24** cannot direct stereoselection in this intramolecular alkoxycarbonylation according to our previous studies.[9b]

Intramolecular Allylation of Tethered Aldehydes. The preceding tungsten-π-allyl complexes can be transformed into bicyclic α-methylene lactones in a single operation. As shown in Scheme 6, the *syn*-π-allyl complex **6** was sequentially treated with $NOBF_4$ (1.0 equiv) and NaI (1.0 equiv) in CH_3CN to effect an intramolecular cyclization,[9,10,14] yielding *cis*-fused α-methylene butyrolactone **26** in 64% yield after workup. The stereochemistry of **26** was determined by ^{1}H-NOE NMR spectra to have a *cis*-fusion and a *syn*-hydroxyl group; its spectral data were identical to those of authentic sample.[7]

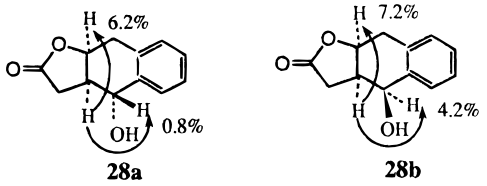
Table 1. Intramolecular Allylation of Tethered Aldehydes

Entry	π-allyl complexes	Products and Yields
1		
2		
3		
4		
5		
6		
7		

(13) Cheng, M.-H.; Ho, Y.-H.; Lee, G.-H.; Peng, S.-M.; Chu, S.-Y.; Liu, R.-S. *Organometallics* **1994**, *13*, 4082.

(14) Shieh, S.-J.; Cheng, C.-C.; Liu, R.-S. *J. Org. Chem.* **1997**, *62*, 1986.

Scheme 7

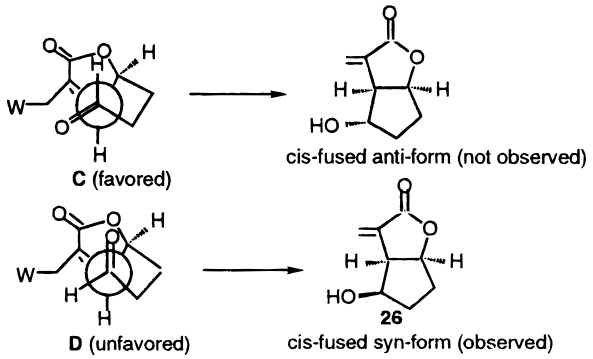


tethered aldehyde. In each case, 1 equiv of $NOBF_4$ and NaI was sequentially added to the π-allyl complexes in CH_3CN at 23 °C to effect intramolecular cyclizations.[9b,10,14] The yields of products **27**−**31** were calculated after purification from silica TLC-plates. The stereochemistries of these γ-lactones were determined by proton-NOE spectra. Entry 1 shows the outcome for *syn*-π-allyl complex **8** to yield a *cis*-fused γ-lactone **27** having a *syn*-alcohol (68%). We extended this cyclization to another *syn*-π-allyl complex **10** (entry 2) to yield *cis*-fused six-membered carbocycles **28a** and **28b**; the yields of **28a** and **28b** were 65% and 7%, respectively, after separation from silica TLC-plate. According to proton NOE experiment shown in Scheme 7, the major diastereomer **28a** has an *anti*-alcohol and the minor diastereomer **28b** has a *syn*-alcohol configuration. In the cyclization of *syn*-π-allyl compound **12** (entry 3), two diastereomers **29a** and **29b** were obtained in a combined 66% yield with a ratio of **29a**/**29b** = 10.1. Similar to the six-member carbocyclics **28a**,**b**, the major diastereomer **29a** is elucidated to have a *cis*-fused geometry bearing an *anti*-alcohol whereas the minor isomer **29b** has a *cis*-fused γ-lactone having a *syn*-alcohol configuration. ^{1}H NMR spectral data of **29b** were also consistent with those of an authentic sample.[7] The reaction of *anti*-π-allyl species **20** was performed to compare its stereochemical outcome with that of its *syn*-π-allyl isomer **12**. Following the same operation, compound **20** afforded the same compositions of bicyclic lactones **29a** and **29b** (68%, **29a**/**29b** = 9.9). This information suggests that both *syn*- and *anti*-isomers **11** and **20** have the same transition state in the cyclizations. The same phenomenon is also observed for the *syn*- and *anti*-π-allyl complexes **14** and **22** (entries 5 and 6) that also afford the same *cis*-fused product **30** bearing a *syn*-alcohol in good yields. To gain an additional insight for this phenomenon, we prepared a mixture of *syn*- and *anti*-isomers of tungsten-π-allyl complex **25** (*syn*/*anti* = 1/2.2). This isomeric mixture produced a single bicyclic lactone **31** in 66% yield. Compound **31** is shown to have a *cis*-fused geometry bearing a *syn*-alcohol configurations according to proton NOE analysis.

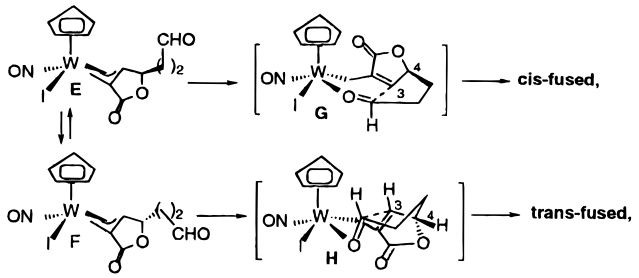
Discussion

Condensation of metal-allyl complexes with aldehydes can proceed in either an open or a closed transition state.[15] Scheme 8 shows two open transition states **C** and **D** that have synclinic conformation in the intramolecular allylation reaction. State **C** is obviously more favorable than **D** because the carbonyl group of **D** is placed in a more congested environment. Nevertheless, the expected *cis*-fused, *anti*-alcohol product is not the preferable product according to our study whereas the *syn*-alcohol **26** is formed exclusively. It is difficult to rationalize our outcome based on open transition state.

Scheme 8



Scheme 9



Two important features are noticeable in the results shown in Scheme 6 and Table 1: (1) *syn*- and *anti*-π-allyl isomers such as **12** and **20**, **14** and **22** afford the same diastereomeric products. (2) The *cis*-fused bicyclic lactones are formed exclusively. Shown in Scheme 9 is a mechanism to rationalize these observations. Previous work by Faller[16] and us[9] have shown that the *syn*- and *anti*-π-allyl complexes **E** and **F** can undergo mutual exchange via a π-σ-π allyl rearrangement mechanism. We envision that these two isomers will yield the same product if the isomerization rates between **E** and **F** are much more rapid than their respective rates in the allylation reaction. For both **E** and **F**, the π-allyl carbon opposite the nitrosyl group is prone to dissociation to give a vacant site to coordinate a tethered aldehyde. In state **G**, the tethered aldehyde and the vacant site are on the same side, thus forming a tricyclic transition state more feasibly. In contrast, the tethered aldehyde of **H** and the vacant site are on the opposite sides, and coordination of this aldehyde requires a significant distortion of the γ-lactone ring to achieve a tricyclic transition state. The planar nature of the γ-lactone ring and the allylic C(3)-proton in state **H** will keep the aldehyde chain away from the vacant site and further prohibit the generation of *trans*-fused bicyclic lactones. A subsequent calculation shows that the two tricyclic transitions states associated with **H** are unlikely to participate in the cyclizations because of their high energies (see Supporting Information).

Four possible tricyclic transition states are conceivable to produce the *cis*-fused and *trans*-fused γ-lactones bearing a *syn*- or *anti*-alcohol. We performed semiemperical calculations with the pm3(tm) using the program suit SPARTAN 5.0.[17] The α-methylene butyrolactones fused

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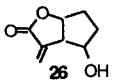
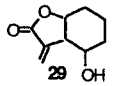
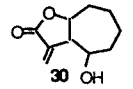
(16) Adams, R. D.; Chodosh, D. F.; Faller. J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2570.

(17) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. J. P. *J. Comput. Chem.* **1991**, *12*, 320. (c) SPARTAN 5.1.1, Wave function Inc., Irvine, CA.

Table 2. Product Selectivities and Relative Energies of Transition States

Product	Selectivity	Calcd. Energy (kcal/mol)
 **26**	**cis-syn**[a] (100%)[b]	**5cs** (10.183[c])
	cis-anti	**5ca** (17.032)
	trans-syn	**5ts** (58.313)
	trans-anti	**5ta** (74.717)
 **29**	***cis-syn*** (9%)	**6cs** (28.507)
	cis-anti (91%)	**6ca** (27.458)
	trans-syn	**6ts** (49.668)
	trans-anti	**6ta** (49.804)
 **30**	***cis-syn*** (100%)	**7cs** (40.807)
	cis-anti	**7ca** (39.805)
	trans-syn	**7ts** (60.338)
	trans-anti	**7ta** (52.769

[a] *cis* = *cis*-fused, *syn* = *syn*-alcohol, *trans* = *trans*-fused, *anti* = *anti*-alcohol. [b] Observed selectivity. [c] These values were expressed as relative energies.

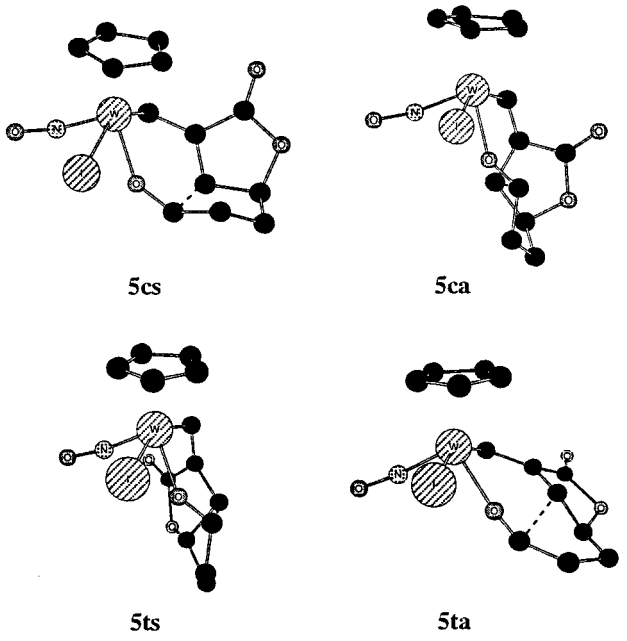


Figure 1. Four possible transition state structures for [3.3.0]-α-methylene butyrolactones.

with five-, six-, and seven-membered carbocyclic compounds **26**, **29**, and **30** were chosen for study. Reliability of this calculation depends on the magnitute of the energy differences among the four transition states derived from **G** and **H** since calculations on tungsten are not precise. The nitrosyl group around the tungsten center is trans to the aldehyde in accordance with Faller's model.[16] Shown in Table 2 are the relative energies of the four transition states and their corresponding bicyclic lactone products. Figure 1 shows the four transition state structures for [3.3.0]-bicyclic γ-lactones. The remaining transition state structures are provided in the Supporting Information. For [3.3.0]-bicyclic lactone **26**, state **5cs** is considerably more stable than its counterpart **5ca** by 6.9 kcal/mol, consistent with our observation that *cis*-fused, *syn*-alcohol is the sole product.

For six- and seven-membered fused γ-lactones **29** and **30**, the energy differences between the most stable two pairs **6cs**−**6ca** and **7cs**−**7ca** are small, being 1.1 and 1.0 kcal/mol, respectively, in favor of *anti*-alcohol products. We obtain mainly the *cis*-fused, *anti*-alcohol for compound **29** and the *cis*-fused, *syn*-alcohol for compound **30**, respectively. It is less meaningful to rationalize the outcome for compounds **29** and **30** as the small energy difference 1.0 kcal/mol is considered within the limit of error for heavy tungsten atom. We also estimate the energies of the six transition states **5ts**, **5ta**, **6ts**, **6ta**, **7ts**, and **7ta** corresponding to the *trans*-fused products of **26**, **29**, and **30**. These transition states are much higher (>15 kcal/mol) in energy than those of the preferable transition states **5cs**, **6ca**, and **7cs**, indicating that *trans*-fused bicyclic lactones are unlikely to form.

In summary, we have developed a new stereocontrolled synthesis of bicyclic α-methylene butyrolactones bearing a homoallylic alcohol. The kep step involves intramolecular allylation of the tethered aldehydes of tungsten-p-lactonyl compound. The resulting products have the *cis*-fused geometry containing a *syn*- or *anti*-homoallylic alcohol depending on the sizes of carbocyclic rings. A semiemperical calculation using Spartan program shows that the *cis*-fused stereoselection is the preferable pathway in a tricyclic state mechanism. The *trans*-fused products are unlikely to form because of their higher energies in transition states.

Experimental Section

General procedures and spectroscopic methods are described elsewhere.[9b] $NaCpW(CO)_3$ was prepared by stirring of $[CpW(CO)_3]_2$ with sodium amalgam in THF for 8 h, and it was used in situ. Syntheses of organic substrates **7**, **9**, **11**, **13**, **23** and tungsten-π-allyl complexes **8**, **10**, **12**, **14**, **22**, and **25** are provided in the Supporting Information. Spectral data of compounds **7**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **22**, **23**, and **25** are also given in the Supporting Information.

3-[1,3]-Dioxolan-2-ylpropanal (2). To a THF solution (10.0 mL) containing Mg (0.54 g, 22.1 mmol) was added 2(2-bromoethyl)-[1,3]-dioxolane **1** (2.00 g, 11.5 mmol), and the mixture was stirred for 2 h at 23 °C. The solutiom was cooled to −78 °C and treated with paraformaldehyde (2.00 g, 66.6 mmol). The solution was stirred for 1.5 h at −78 °C and warmed to 23 °C and stirred for 4 h. To this solution was added an aqueous NH_4Cl solution (5.0 mL), and the organic layer was concentrated to yield a colorless oil (ca. 1.19 g, 9.10 mmol, 79%). To a CH_2Cl_2 (15 mL) solution of this oil (3.00 g, 22.1 mmol) was added PCC (7.33 g, 34.1 mmol) at 23 °C, and the mixture was stirred for 3 h. The solution was filtered through a short silica column and concentrated. Elution of the residues through a silica column gave a colorless oil of **2** (2.51 g, 19.3 mmol, 87%). IR (neat, cm^{-1}): ν (CO) 3030 (w), 1725 (s); ^1H NMR (300 MHz, $CDCl_3$): δ 9.81 (1H, s), 4.80 (1H, t, J = 4.5 Hz), 3.79−3.90 (4H, m), 2.57 (2H, t, J = 4.6 Hz), 1.67−1.69 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 104.3, 65.7, 37.9, 30.8; MS (EI, 75 eV, *m/e*) 130 (M^+). HRMS calcd for $C_6H_{10}O_3$: 130.1448; found: 130.1445.

6-Chloro-1-[1,3]-dioxolan-2-ylhex-4-yn-3-ol (3). To a diethyl solution (20 mL) of propargyl chloride (1.38 g, 18.4 mmol) was added BuLi (1.60 M in hexane, 11.5 mL) at − 78 °C, and the mixture was stirred for 2 h. To this solution was added the aldehyde **2** (2.00 g, 15.4 mmol) at −78 °C, and the mixture was stirred for 2 h before it was brought to 28 °C. To this solution was added an aqueous NH_4Cl solution, and the organic layer was extracted with diethyl ether. The extract was concentrated and eluted through a silica column to yield an oil of alkynol **3** (2.67 g, 13.1 mmol, 85%). IR (neat, cm^{-1}): ν (OH) 3350 (br s), ν (C≡C) 2262 (w); ^1H NMR (300 MHz, $CDCl_3$): δ 4.81 (1H, t, J = 4.5 Hz), 4.35 (1H, br t, J = 7.1 Hz), 4.14 (1H, d, J = 3.2 Hz), 3.79−3.90 (4H, m), 1.58−1.43 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 104.3, 87.5, 78.9, 64.8, 64.7, 62.3, 33.7, 30.4, 30.3; MS (75 eV): 204 (M^+); HRMS Calcd for $C_9H_{13}ClO_3$: 204.6551; found: 204.6549.

$CpW(CO)_3$(η^1-4-*tert*-butyldimethylsiloxy-6-[1,3]-dioxolan-2-ylhe-xyn-1-yl) (4). Dimethyl(*tert*-butyl)silyl chloride

(1.77 g, 11.7 mmol) and imidazole (1.66 g, 24.5 mmol) were dissolved in DMF (6.0 mL), and to this solution was added alkynol **3** (2.00 g, 9.80 mmol) at 23 °C. The solution was warmed to 40 °C and stirred for 12 h. To the mixture was added diethyl ether (15 mL) and water (5 mL), and the organic layer was extracted with diethyl ether. The extract was dried over $MgSO_4$, concentrated, and eluted through a silica column to yield a colorless oil of its siloxy derivative (2.81 g, 8.80 mmol). To a THF solution (20 mL) of this chloroproargylsiloxy derivative was added $NaCpW(CO)_3$ (ca. 1.89 mmol) at 23 °C, and the mixture was stirred for 14 h before it was filtered through a short silica bed. The filtrate was chromatographed through a silica column to afford a yellow oil of propargyltungsten compound (0.85 g, 1,38 mmol, 87%). IR (neat, cm^{-1}): ν (CO) 2040 (s), 1945(s); ^1H NMR (300 MHz, $CDCl_3$): δ 5.31 (5H, s), 4.81 (1H, t, J = 4.3 Hz), 4.33 (1H, br t, J = 7.2 Hz), 3.77−3.92 (4H, m), 2.21 (2H, s), 1.59−1.63 (4H, m), 0.85 (9H, s), 0.08 (3H, s), 0.06 (3H, s); ^{13}C NMR (75 MHz, *m/e*): 616 (M^+). Anal. Calcd. for $C_{23}H_{32}WSiO_6$: C, 44.81; H, 5.23. Found: C, 44.79; H, 5.20.

Tungsten-π-*syn*-γ-lactonyl Compound (5). To a CH_2Cl_2 solution of propargyltungsten complex (0.50 g, 0.80 mmol) was added CF_3SO_3H (15 mL, 0.15 mmol) at − 40 °C, and the mixture was stirred for 6 h before addition of a saturated $NaHCO_3$ solution (5 mL). The solution was concentrated and eluted through a silica column to yield a yellow viscous solid of tungsten-π-allyl complex **5** (240 mg, 0.50 mmol, 62%). IR (neat, cm^{-1}): ν (CO) 1960 (s), 1885(s), 1748 (s); ^1H NMR (300 MHz, $CDCl_3$); δ 5.36 (5H, s), 5.08 (1H, m), 4.95 (1H, t, J = 4.1 Hz), 3.67−3.97 (4H, m), 3.66 (1H, d, J = 3.7 Hz), 3.08 (1H, J = 3.7 Hz), 1.90−1.93 (4H, m), 1.47 (1H, d, J = 3.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 212.2, 210.6, 170.7, 102.2, 92.9, 80.4, 70.1, 65.6, 65.5, 35.3, 32.5, 22.8; MS (75 eV, *m/e*): 502 (M^+). Anal. Calcd for $C_{17}H_{18}WO_6$: C, 40.66; H, 3.61. Found: C, 40.63; H, 3.58.

Tungsten-π-*syn*-γ-lactonyl Compound (6). To an acetone (5 mL) solution of tungsten-π-allyl compound **5** (250 mg, 0.55 mmol) was added *p*-TSA (10 mg, 0.050 mmol), water (5 mL), and EtCHO (0.15 mL). The solution was heated under reflux for 5 h, and a saturated $NaHCO_3$ solution (5.0 mL) was added. The organic layer was extracted with diethyl ether, dried with $MgSO_4$, and eluted through a silica column (diethyl/ether = 1/1) to yield a yellow viscous oil of **6** (205 mg, 0.45 mmol, 85%). IR (neat, cm^{-1}): ν (CO) 1960 (s), 1885 (s), 1748(s), 1725 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 9.81 (1H, s), 5.41 (5H, s), 5.03 (1H, m), 3.63 (1H, d, J = 3.1 Hz), 3.04 (1H, d, J = 3.7 Hz), 2.10−2.15 (2H, m), 1.64−1.69 (2H, m), 1.47 (1H, d, J = 3.7 Hz); ^{13}C NMR (100 MHz): δ 224.6, 219.2, 200.2, 175.6, 93.7, 79.7, 70.1, 69.0, 40.1, 30.8, 19.8. MS (75 eV, *m/e*): 458 (M^+). Anal. Calcd for $C_{15}H_{14}WO_5$: C, 39.33; H, 3.08. Found: C, 39.30; H, 3.06.

2-(4-Iodo-but-3-enyl)-[1,3]-dioxane (15). To 2-but-3-ynyl-[1,3]-dioxane (3.43 g, 24.5 mmol) were added Bu_3SnH (7.1 mL, 26.9 mmol) and AIBN (48 mg, 0.29 mmol), and the mixture was heated at 130 °C for 2 h. The solution was cooled at 0 °C before an addition of Et_2O (20 mL), and the mixture was treated with I_2 (6.85 g, 26.9 mmol). The solution was stirred for 2 h and then quenched with an aqueous solution (2 mL) of $Na_2S_2O_3$ (0.50 g). The organic layer was extracted with diethyl ether, concentrated, and eluted through a silica column (diethyl ether/hexane = 1/1) to yield a colorless oil of compound **15** (5.60 g, 21.1 mmol, 86%). IR (neat, cm^{-1}): ν (C=C) 1660 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 6.43 (1H, m), 5.92 (1H, d, J = 13.4 Hz), 4.43 (1H, t J = 4.8 Hz), 3.97−4.03 (2H, m), 3.62−3.71 (2H, m), 1.91−2.14 (2H, m), 1.56−1.64 (2H, m), 1.23 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 140.4, 100.8, 66.6, 66.5, 34.4, 33.0, 25.6; MS (75 ev, *m/e*): 268 (M^+); MS (75 eV, *m/e*): 268 (M^+). HRMS calcd. for $C_8H_{13}IO_2$: 268.0961, found: 268.0957.

Toluene-4-sulfonic Acid 7-[1,3]Dioxan-2-ylhept-4-en-2-ynyl Ester (16). To a diethylamine solution (40 mL) of $PdCl_2(PPh_3)_2$ (120 mg, 0.17 mmol) and CuI (58 mg, 0.34 mmol) were added iodovinyl compound **15** (4.55 g, 17.1 mmol) and propargyl alcohol (1.0 mL, 17.1 mmol), and the mixture was stirred for 8 h. The solution was concentrated, an aqueous NH_4Cl solution (10 mL) was added, and the organic layer was extracted with diethyl ether (2 × 30 mL). The ether extract was dried with $MgSO_4$ and eluted through a silica column (diethyl ether/hexane = 1.1/1) to yield a colorless oil of propargyl alcohol (2.74 g, 14.00 mmol, 82%). To an acetone solution of this alcohol (3.18 g, 16.2 mmol) and TsCl (3.12 g, 16.2 mmol) was slowly added KOH (1.36 g, 24.3 mmol) at 0 °C, and the mixture was stirred for 8 h. The solution was concentrated and added with an aqueous NH_4Cl (20 mL) solution. The organic layer was extracted with diethyl ether, dried over $MgSO_4$, and eluted through a silica column (diethyl ether/hexane = 1.2) to yield a colorless oil of compound **16** (4.99 g, 14.3 mmol, 88%). IR (neat, cm^{-1}): ν (C≡C) 2262 (w), ν (C=C) 1621 (w), 1590 (w). ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (1H, d, J = 8.6 Hz), 7.26 (1H, d, J = 8.6 Hz), 6.00 (1H, d, J = 14.2 Hz), 5.27 (1H, d, J = 14.2 Hz), 4.80 (2H, s), 4.44 (1H, t, J = 4.8 Hz), 3.99−4.05 (2H, m), 3.64−3.72 (2H, m), 2.38 (3H, s), 1.95−2.23 (4H, m), 1.55−1.65 (4H, m), 1.14 (1H, m); ^{13}C NMR (100 M Hz): δ 146.5, 144.2, 133.3, 129.7, 128.1, 101.2, 87.7, 79.2, 66.9, 66.8, 58.7, 33.8, 27.4, 25.7, 24.9, 21.5; MS (75 ev, *m/e*): 300 (M^+); HRMS calcd for $C_{19}H_{24}O_3$: 300.4013; found: 300.4010.

$CpW(CO)_3\{\eta^1$-7-[1,3]-dioxan-2-ylhept-4-en-2-yn-1-yl$\}$ (17). To a THF solution (20 mL) of the tosylate **16** (0.20 g, 0.57 mmol) was added $NaCpW(CO)_3$ (ca. 1.14 mmol) at 0 °C, and the mixture was stirred for 6 h. The solution was concentrated and eluted through a silica column (diethyl ether/hexane = 1/1) to give a yellow viscous oil of propargyltungsten compound **17** (0.26 g, 0.51 mmol, 89%). IR (neat, cm^{-1}): ν (C≡C) 2262 (w), ν (CO) 2020 (s), 1930 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 5.85 (1H, m), 5.65 (1H, m), 5.44 (5H, s), 4.45 (1H, t, J = 4.8 Hz), 3.99−4.05 (2H, m), 3.66−3.73 (2H, m), 1.93−2.37 (6H, m), 1.57−1.66 (2H, m), 1.25 (1H, m); ^{13}C NMR (100 M Hz): δ 229.5, 216.3, 216.2, 139.9, 110.1, 104.3, 101.4, 92.5, 79.7, 66.7, 66.5, 34.3, 25.6, 24.6, −31.2; MS (75 ev, *m/e*): 512 (M^+). Anal. Calcd. Calcd for $C_{19}H_{20}WO_5$: C, 44.55; H, 3.94. Found: C, 44.52; H, 3.90.

$CpW(CO)_2\{\eta^3$-7-[1,3]-dioxan-2-yl(methoxycarbonyl)-hepta-2,4-dien-1-yl$\}$ (18). To a diethyl ether solution (10 mL) of alkynyltungsten compound **17** (0.11 g, 0.22 mmol) was added CF_3SO_3H (23 uL, 0.26 mmol) at − 60 °C, and the solution was stirred for 2 h to yield a deep red precipitate. To this cold solution was added MeOH (10 mL), and the solution was kept at −60 °C and stirred for 1 h before treatment with an aqueous Na_2CO_3 solution (5.0 mL). The organic layer was extracted with diethyl ether, dried over $MgSO_4$, and eluted through a silica column to give a yellow viscous oil of **18** (76 mg, 0.14 mmol, 65%). ν (CO) 1945 (s), 1875 (s), 1750 (s); ^1H NMR (300 MHz, $CDCl_3$): *endo* conformer, δ 6.73 (1H, dd, J = 14.1, 2.8 Hz), 5.45 (1H, m), 5.25 (5H, s), 4.51 (1H, t, J = 4.8 Hz), 4.06−4.52 (4H, m), 3.73−3.74 (2H, m), 3.70 (3H, s), 2.93 (1H, d, J = 2.8 Hz), 2.73 (1H, d, J = 1.5 Hz), 2.01−2.09 (2H, m), 1.33−1.55 (4H, m), 1.20 (1H, J = 1.5 Hz); *exo* conformer, δ, 6.12 (1H, dd, J = 14.1, 2.5 Hz), 5.61 (1H, m), 5.32 (5H, s), 4.06 (1H, t, J = 4.8 Hz), 3.76 (2H, m), 2.96 (1H, d, J = 2.5 Hz), 2.10 (1H, d, J = 2.5 Hz), 0.71 (1H, d, J = 2.5 Hz), ^{13}C NMR (100 M Hz): δ 223.5, 223.4, 174.0, 130.5, 129.5, 101.8, 93.1, 88.1, 86.8, 75.3, 52.0, 51.8, 34.1, 32.2, 25.5, 23.1. Anal. Calcd for $C_{21}H_{26}WO_6$: C, 44.14; H, 4.44. Found: C, 44.10; H, 4.40.

$CpW(CO)_2\{\eta^3$-π-*anti*-allyl) Complex (19). To a diethyl ether solution (10 mL) of tungsten π-allyl complex **18** (127 mg, 0.23 mmol) was added triflic acid (21 uL, 0.24 mmol) at − 60 °C, and the mixture was stirred for 1 h to yield a red precipitate. The solution was treated with an aqueous NaOH solution (3.0 M, 10 mL), and the mixture was brought to 23 °C and kept stirring for 48 h. The solution was concentrated and extracted with diethyl ether. The diethyl ether extract was dried over $MgSO_4$ and eluted through a silica column (diethyl ether/hexane = 1/1) to give a yellow solid of **19** (79 mg, 0.15 mmol, 65%). IR (neat, cm^{-1}): ν (CO) 1945 (s), 1875 (s), 1750 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 5.32 (5H, s), 4.58 (1H, t, J = 4.8 Hz), 4.49 (1H, m), 4.04−4.09 (2H, m), 3.70−3.76 (2H, m), 3.38 (1H, s), 3.09 (1H, d, J = 3.5 Hz), 2.01 (1H, m), 1.77−1.81 (2H, m), 1.28−1.58 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 225.6, 219.3, 175.9, 112.7, 110.1, 102.1, 93.9, 88.7, 83.9, 68.6,

67.0, 66.8, 38.1, 34.9, 34.8, 25.8, 24.6, 23.6. MS (75 eV *m*/*e*): 530 (M^+). Anal. Calcd for $C_{20}H_{24}WO_6$: C, 43.04; H, 4.18. Found: C, 43.01; H, 4.16.

CpW(CO)$_2${η^3-π-*anti*-allyl) Complex (20). To an acetone solution (10 mL) of tungsten-π-allyl complex **19** (0.20 g, 0.38 mmol) were added *p*-TSA (0.20 g, 0.38 mmol) and EtCHO (0.30 mL), and the mixture was heated under reflux for 6 h. To this solution was added $NaHCO_3$ (5.0 mL), and the organic layer was extracted with diethyl ether, dried over $MgSO_4$, and concentrated. The residues were chromatographed through a silica column to give a yellow solid (0.15 g, 0.32 mmol, 84%). IR (neat, cm^{-1}): ν (CO) 1945 (s), 1875 (s), 1750 (s), 1725 (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 (5H, s), 4.57 (1H, m), 3.35 (1H, s), 3.07 (1H, d, J = 2.5 Hz), 2.43−2.47 (2H, m), 1.63−1.82 (5H, m), 1.44 (1H, J = 2.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 225.9, 219.1, 201.9, 176.1, 93.6, 83.6, 68.4, 66.6, 43.6, 37.8, 24.3, 21.5; MS (75 eV, *m*/*e*): 472 (M^+). Anal. Calcd for C_{16} $H_{16}WO_5$: C, 40.7; H, 3.42. Found: C, 40.6; H, 3.39.

Synthesis of Bicyclic α-Methylene Butyrolactone (26). To a CH_3CN solution (10.0 mL) of tungsten-π-*syn*-allyl complex **6** (196 mg, 0.42 mmol) at 0 °C was added $NOBF_4$ (56 mg, 0.48 mmol), and the mixture was stirred for 0.50 h before addition of NaI (128 mg, 0.86 mmol). The solution was warmed to 28 °C and kept stirring for 8 h before it was concentrated. The residues were chromatographed through a short silica column to yield a colorless oil of **26** (41 mg, 0.29 mmol, 64%). IR (neat, cm^{-1}): ν (CO) 1746 (s), ν (C=C) 1660 (s); ^{1}H NMR (600 MHz, $CDCl_3$): d, 6.38 (1H, dd, J = 2.2, 0.7 Hz), 5.76 (1H, dd, J = 2.2, 0.7 Hz), 4.89 (1H, m), 4.25 (1H, m), 3.41 (1H, m), 1.87 (1H, m), 1.79 (1H, m), 1.44 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.6, 133.7, 125.9, 81.7, 73.6, 46.6, 31.4, 29.8. MS (75 eV, *m*/*e*): 154 (M^+); HRMS calcd for $C_8H_{10}O_3$, found, 154.1671.

Acknowledgment. The authors thank to National Science Council, Taiwan, for support of this work.

Supporting Information Available: NMR spectra, spectral data, and synthesis of chloropropargyl derivatives **7**, **9**, **11**, **13**, **23**, tungsten-π-allyl complexes **8**, **10**, **12**, **14**, **22, 25**, and bicyclic lactones **27**−**31** as well as semiemperical calculation of the tricyclic transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9909002