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Synthesis, Reactivity and Demetallation of Tungsten–Azacyclic Carbeniums via Cycloalkenation of Tungsten–Alkynylamine Compounds

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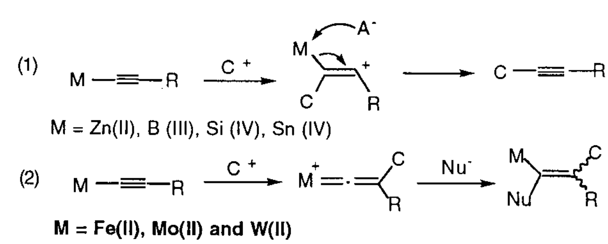
Abstract—Treatment of tungsten–η^1-α,δ-alkynylamine compounds with aldehyde and $BF_3 \cdot Et_2O$ led to cycloalkenation reaction, giving good yields of tungsten–η^1-pyrrolylidium salts. These azacyclic carbeniums provide a short synthesis of α-alkylidene-γ-lactam via oxidation with *m*-CPBA. In contrast with tungsten–η^1-oxacyclic carbenium, this salt reacts with one molecule of organometallic reagents such as $NaBH_3CN$, CH_3MgBr and Me_2CuLi to give tungsten–η^1-4,5-dihydropyrrole complexes. An alternative use of this cyclialkenation is to provide a short synthesis of 3-vinyl-Δ^2-pyrrolines.

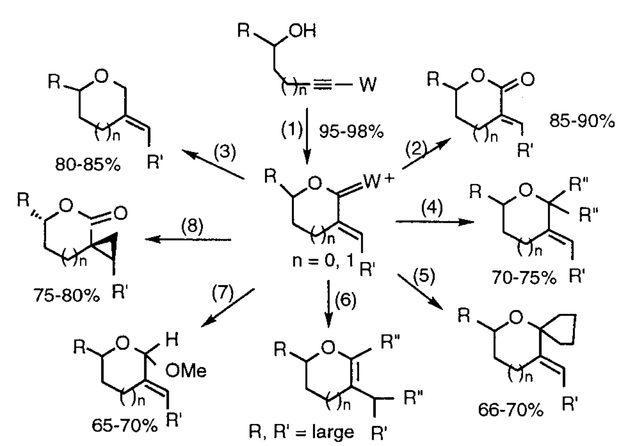
Introduction

Alkynyl complexes of silanes, stannanes, boranes, zinc and titanium[1] are not as useful as their allyl, allenyl and propargyl complexes.[2,3] As shown in Scheme 1, these alkynyl organometallics react with carbon electrophiles at the C_α-carbon to form unstable vinyl cation that is easily destroyed by any basic species to afford functionalized alkynyl compounds.[1] Transition metal–alkynyl compounds react with carbon electrophiles at the C_β-carbon to form metal–allenylidenium cations which are fairly kinetically stable.[4] Nucleophilic attack at cations of these types proceeds with regiochemistry at their C_α-carbons to effect a 1,2-addition.

To highlight the synthetic utility of these allenylidenium species, we recently reported that tungsten–η^1-alkynol compounds underwent Lewis acid-catalyzed cycloalkenation reaction with aldehydes to form tungsten–oxacarbenium salts.[5] The reaction works well for both five- and six-membered ring systems. In contrast with conventional transition-metal–carbeniums, these oxacyclic carbeniums function as a dication equivalent upon treatment with suitable nucleophiles.[6] Scheme 2 shows the protocol to utilize this unique reactivity for synthesis of various oxygen heterocycles. Treatment of this carbenium salt with water and air produced the α-alkylidene γ- and ϵ-lectones exclusively (Eq (2)). $NaBH_3CN$ and RMgBr effected α,α-double addition of the salt to afford β-alkylidene furan and pyran derivatives (Eqs. (3) and (4)). A noticeable example is the reaction with di-Grignard reagent $MgBr(CH_2)_4MgBr$ to give spirofuran and -pyran compounds in 66–70% yields (Eq.



Scheme 1.



Scheme 2. (1) $R'CHO/BF_3 \cdot Et_2O$, (2) H_2O/air, (3) $NaBH_3CN$, (4) $R''MgBr$, (5) $MgBr(CH_2)_4MgBr$, (6) R''_2CuLi, (7) $NaBH(OMe)_3/MeOH$, (8) CH_2N_2, H_2O.

Keywords: cycloalkenations; tungsten–azacyclic carbeniums; azacyclic compounds.

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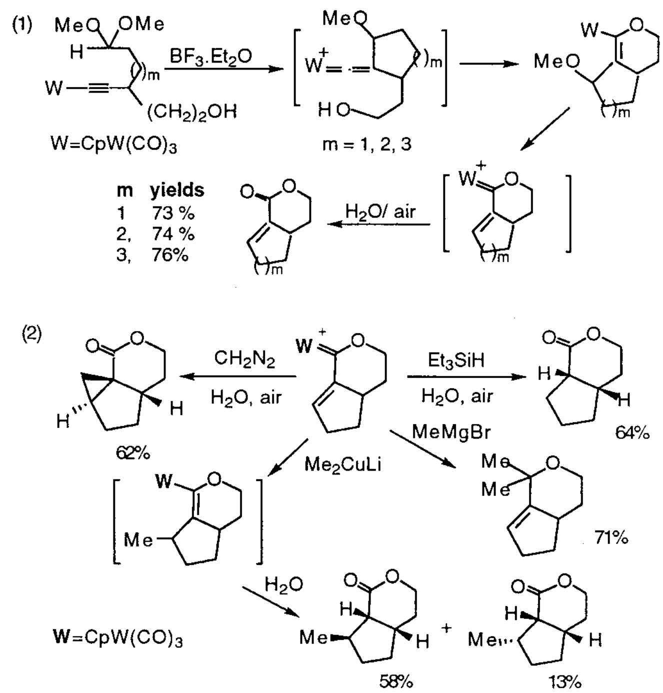


Scheme 3.

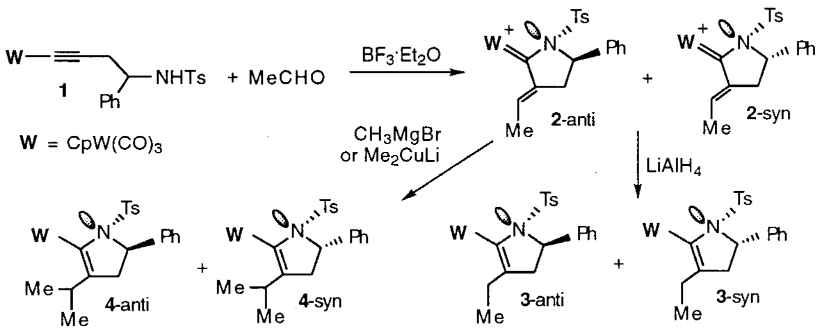
(5)). Organocuperate R_2CuLi effected 1,3-addition reaction of the salt in the cases that the sizes of R and R′ substituents are large (Eq. (6)). If a MeOH solution of $NaBH_4$ was used in the reaction, five- and six-membered lactols were formed exclusively (Eq. (7)). Finally, treatment of this salt with CH_2N_2 led to cyclopropanation reaction with excellent diastereoselectivities, yielding a single diastereomeric product (Eq. (8)).[5]

In a subsequent study, we employed this cycloalkenation in intramolecular system for synthesis of various unsaturated bicyclic lactones,[6] and the reaction protocol is shown in Scheme 3. The reaction not only works well for tungsten–η^1-alkynols tethered with dimethoxymethane, and also efficiently for those bearing a tethered ketone and trimethoxymethane group. With alternation of lengths of the alcohol and electrophile chains, various sizes of bicyclic lactones can be prepared in good yields including the medium ring compounds [4.6.0] and [5.5.0]-bicyclic lactones. Since the bicyclic tungsten–oxacyclic carbeniums can be isolated, they are useful for synthesis of various oxygen heterocycles via treatment with CH_2N_2, Et_3SiH and MeMgBr to effect cyclopropanation, reduction of C=C bond and α,α-dialkylation reaction. A summary of the products is given in Eq. (2), and the yields exceeded 62%. This synthetic method is also applicable to a short synthesis of natural bicyclic lactones such as mitsugashiwalactone and onikulactone. Addition of Me_2CuLi to this bicyclic oxacarbenium, followed by demetallation with hydrolysis, affords mitsugashiwalactone and onikulactone in 56 and 13% yields[6], respectively, based on starting tungsten–alkynol species.

Nitrogen heterocycles are equally important as oxygen heterocycles in synthetic organic chemistry. The fact that the preceding tungsten–oxacarbenium salts can be elaborated for various oxygen heterocycles, it is desired to extend this cycloalkenation reaction to tungsten–η^1-alkynyl amines to afford tungsten–azacyclic carbeniums. In this article, we report the preparation and the use of such salts for the synthesis of nitrogen hetrocycles.

Results and Discussion

The tungsten–η^1-α,δ-alkynylamine **1** was easily prepared from $CpW(CO)_3Cl$, Et_2NH and CuI catalysts; the yield was 64%.[7] Treatment of compound **1** with MeCHO and $BF_3{\cdot}Et_2O$ (1.0 equiv.) in cold diethyl ether deposited a dark red precipitate, characterized as tungsten–η^1-pyrrolylidenium salt. In contrast with its η^1-oxacyclic carbenium, ^1H NMR spectra of this azacarbenium salt (−30°C) showed the presence of two conformational isomers **2**-*anti* and **2**-*syn* (**2**-*anti*/**2**-*syn*=4:1) which are distinguishable by different orientations of their lone pair electrons to the phenyl group. Both species showed the diagnostic carbene ^{13}C NMR resonances at 259.9 and 262.0 ppm, respectively, in addition to NMR resonances assignable to ethylidene group. The ^1H NMR resonances of these two isomers became broad as the temperatures were warmed to 40°C. Unfortunately, we could not measure the coalescing temperatures to obtain the activation energy because the sample decomposed abruptly above 40°C. This structural assignment is further supported by structural characterization of the tungsten–η^1-2,3-dihydropyrrolyl complex **3**-*anti* and **3**-*syn* produced from $LiAlH_4$-reduction of the salt **2**. Although tungsten–η^1-oxacyclic carbenium undergoes double addition reaction upon treatment with $NaBH_3CN$, RMgBr and R_2CuLi, the azacarbenium salt **2a** and **2b** only undergoes single addition with organometallic reagents. $NaBH_3CN$ was ineffective for reduction of the salt even if excess amount was used. The reaction of this salt



Scheme 4.

with $LiAlH_4$ gave two conformers **3**-*anti* and **3**-*syn* which were indicated by low-temperature ^1H and ^{13}C NMR spectra. The ^1H NMR resonances of these two species became broad and eventually coalesced as the temperatures were raised; the energy barrier was calculated to be 13.6 kcal/mol. The reaction of the salt **2** with excess MeMgBr and Me_2CuLi led to single addition to give a mixture of two conformers **4**-*anti* and **4**-*syn*; the yields were 72 and 69%, respectively (Scheme 4). ^1H NMR signals of **3**-*anti* and **3**-*syn* also coalesced into one resonance as the temperatures were raised. No cyclopropanation took place for the reaction of these salts with CH_2N_2 over a prolonged reaction period. Fig. 1 shows the ORTEP drawing of the molecular structure of compound **3** in which the tosylate and the phenyl group are *trans* to each other, i.e. the molecule adopts an *anti*-conformation. Notably, this five-membered pyrrolyl ring is coplanar to the plane defined by C16–W1–C2 atoms, similar to those of tungsten–oxacarbenium salts. This structural arrangement is very favorable for overlap of the C16-p-orbital with tungsten-d_{xy}-orbital (SHOMO).[6] However, this arrangement renders it very difficult for the pyrrolyl nitrogen to undergo inversion of configuration because it will force a steric interaction between the tosylate and cyclopentadienyl groups.

The synthetic utility of this cycloalkenation is best manifested by a short and efficient synthesis of α-alkylidene-γ-lactam. The results are shown in Table 1; the yields exceed 54%. In a typical operation, tungsten–η^1-α,γ-alkynylamine was treated with aldehyde and $BF_3{\cdot}Et_2O$ in cold diethyl ether to deposit a red precipitate which was isolated by filtration for oxidative demetallation with *m*-chloroperbenzoic acid or Me_3NO in CH_2Cl_2. Unlike their oxacarbenium salts, treatment of these pyrrolylidenium salts with water and air did not effect oxidative demetallations. The synthesis of α-alkylidene-γ-lactam works well for both aliphatic and aromatic aldehydes. In addition to tosylamine, tethered mesyl amine and aliphatic amide are also very efficient to give good yields of γ-lactams as shown in entries 3–5. Attempts to prepare larger nitrogen heterocycles such as α-alkylidene-δ-lactams from tungsten–η^1-alk-1-yn-1-yl-4-tosylamines were unsuccessful and their reactions with aldehydes and $BF_3{\cdot}Et_2O$ failed to give the desired azacyclic carbenium salt in cold diethyl ether.

An alternative use of tungsten–azacarbenium salt is to provide a convenient synthesis of 3-vinyl Δ^2-pyrrolines, and synthesis of compounds of this class was reported to involve a long sequence of procedures.[8] As shown in

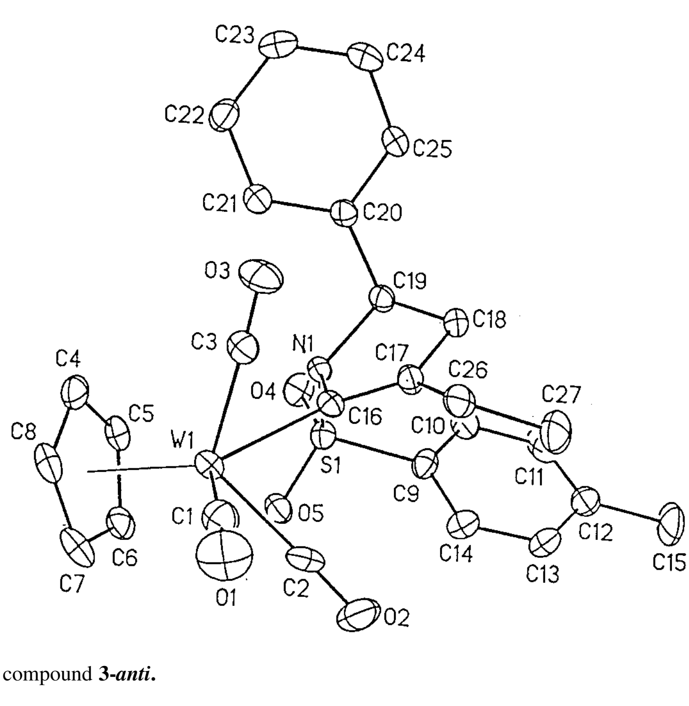


Figure 1. The molecular structure of compound **3-*anti*.**

Table 1. Direct synthesis of α-alkylidene-γ-lactam

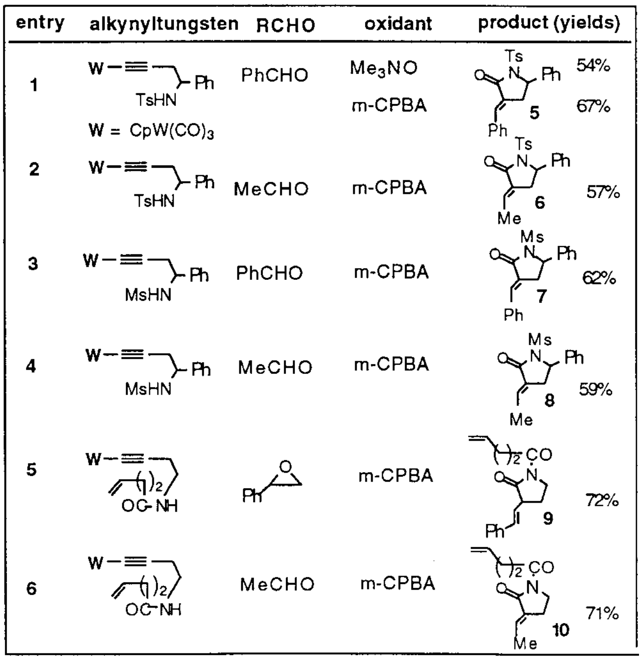
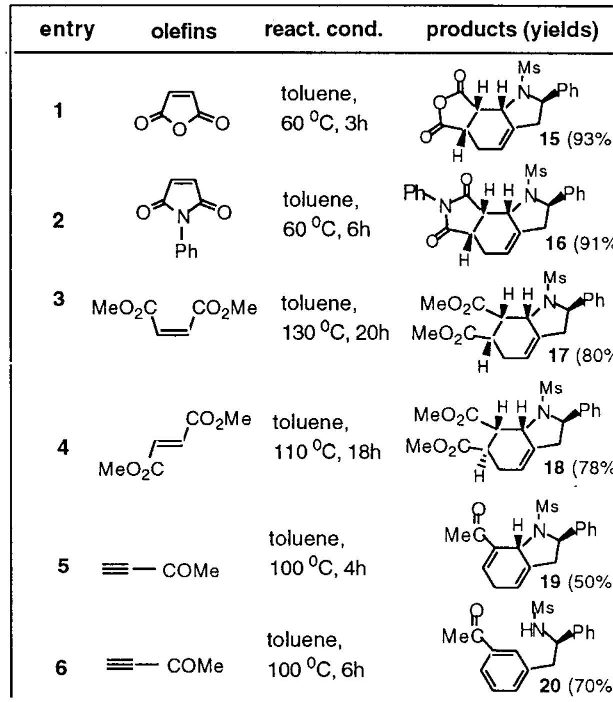


Table 2. Cycloadditions of 3-vinyl-Δ^2-prolline (**14**)

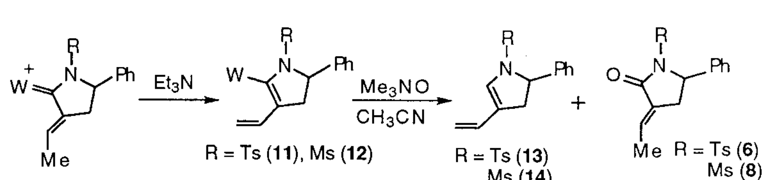


Scheme 5, treatment of these salts with Et_3N led to deprotonation to yield tungsten–4,5-dihydropyrroles **11** and **12** in 91% and 89% respectively. Hydrodemetallation of compounds **11** and **12** was achieved smoothly via treatment with anhydrous Me_3NO in CH_3CN (23°C, 12 h). Under this circumstance, 3-vinyl Δ^2-pyrrolines **13** and **14** were obtained in 46% and 39% yields respectively in addition to α-ethylidene-γ-lactams **6** and **8** in 18 and 19% yields. Solvents are very critical to obtain good yields of azacyclic dienes. If CH_2Cl_2 was used as the solvent, pyrrolines **13** and **14** were obtained in 21 and 20% yields respectively whereas α-ethylidene-γ-lactams **6** and **8** were increased to 45 and 42% yields, respectively. We believe that CH_3CN is a better proton source than CH_2Cl_2 in the hydrodemetallation reaction.

Cycloaddition reactions of simple dienamines has been studied extensively over last two decades. Considerable attentions have focused on the Diels–Alder reaction of azacyclic dienes for the synthesis of pericyclic nitrogen compounds.[8–11] Boeckman and corworkers has studied the cycloaddition of 3-vinyl-Δ^2-pyrrolines as an approach to Amaryllidaceae alkaloid lycorine.[8] 3-Vinyl-Δ^2-pyrrolines **13** and **14** with an additional substituent seem to be more challenging because the cycloaddition may form additional diastereomeric products. Table 2 shows the results for cycloadditions of 3-vinyl-Δ^2-pyrroline **14** with electron-deficient olefins. The cycloaddition proceeds very rapidly for maleic anhydride and *N*-phenylmaleimide (entries 1 and 2) to afford only *endo*-addition products **15** and **16** in 93 and 91% yields, respectively. The stereochemistries of **15** and **16** were determined by proton NOE spectra. In this manner, dienophiles preferably approach the diene from endo face opposite the phenyl substituent. The reactions with dimethyl maleate and dimethyl fumarate (entries 3 and 4) require higher temperatures and longer reaction time for completion, giving only *endo*-addition products **17** and **18** in 80 and 78%, respectively. Determination of the stereochemistries of **17** and **18** relied on ^1H NMR NOE effect. Azacyclic diene **14** also reacted well with 3-butyn-2-one to affod the cycloadduct **19** in 50% yield in addition to aromatic compound **20** (13%). Over a prolonged heating, compound **20** will undergo substantial aromatization to yield the amine **20** (70% yield) exclusively.

Experimental

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere in oven dried glassware using standard syringe, cannula and septa apparatus. Benzene, diethyl ether, tetrahydrofuran and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane



Scheme 5.

was dried over CaH_2 and distilled before use. $W(CO)_6$, sodium, dicyclopentadiene, propargyl bromide, methanesulfonamide, p-toluenesulphonamide and benzaldehyde were obtained commercially and used without purification.

Tungsten–η¹-4-phenyl-4-tosylamino-but-1-yn-1-yl (1). To a diethylamine solution (25 mL) of $CpW(CO)_3Cl$ (3.00 g, 8.15 mmol), CuI (0.16 g, 0.82 mmol) was added 4-phenyl-3-tosylamino-1-butyne (2.31 g, 7.74 mmol), and the mixtures were stirred at 23°C for 6 h. The solution was concentrated to ca. 3.0 mL, and eluted through a silica column to yield a yellow band that afforded compound **1** as a yellow solid (3.18 g, 5.03 mmol, 65%). IR (neat, cm^{-1}): ν(CO) 2027(vs), 1934(vs), $\nu(SO_2)$ 1349(s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10–7.56 (9H, m) 5.50 (5H, s) 5.31 (s, br s) 4.38 (1H, dd, *J*=11.8, 4.9 Hz) 2.71 (2H, m, *J*=15 Hz), 2.34 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 228.9, 212.2, 212.1, 142.9, 140.4, 137.5, 129.3, 127.9, 127.2, 127.0, 126.7, 122.5, 91.4, 63.9, 56.7, 31.3, 21.4. MS (EI, *m/z*): 631 (M^+), 603 (M^+-CO), 547 (M^+-3CO). Anal. Calcd for $WC_{25}H_{21}SO_5N$: C, 47.54; H, 3.25; N, 2.23. Found: C, 47.54; H, 3.52; N, 2.29.

Tungsten–η¹-pyrrolylidenium salt (2). To a diethyl ether solution of alkynyltungsten compound **1** (0.80 g, 1.27 mmol) at −78°C was added acetaldehyde (1.0 mL) and $BF_3{\cdot}Et_2O$ (0.16 mL, 1.30 mmol), and the solution was warmed to 23°C over a period of 8 h. During this period, red precipitate of tungsten–η¹-azacyclic carbenium salt **2** was slowly deposited, collected by filtration and washed with diethyl ether. The yield was 91% (0.86 g, 1.15 mmol). IR (neat, cm^{-1}): ν(CO) 1991(vs), 1920(s); ^{1}H NMR (400 MHz, $CDCl_3$, −40°C): δ *anti*-form, 7.50–6.90 (10H, m), 6.01 (5H, s), 4.89 (1H, dd, *J*=9.4, 4.9 Hz), 3.63 (1H, dd, *J*=15.9, 9.4 Hz), 2.74 (1H, dd, *J*=15.9, 4.9 Hz), 2.65 (3H, s), 2.10 (3H, d, *J*=6.3 Hz), *syn*-form, δ 7.50–6.90 (10H, m), 6.06 (5H, s), 5.39 (1H, dd, *J*=9.4, 4.9 Hz), 3.48 (1H, dd, *J*=15.9, 9.4 Hz), 3.10 (1H, dd, *J*=15.9, 4.9 Hz), 2.35 (3H, s), 2.10 (3H, d, *J*=6.3Hz); ^{13}C NMR (100 MHz, $CDCl_3$, −30°C): *anti*-form δ 259.9, 235.5, 230.2, 228.5, 152.6, 150.1, 148.4, 147.3, 136.9, 131.2, 129.4, 127.9, 127.2, 126.8, 94.8, 69.6, 38.2, 22.3, 18.4, *syn*-form, δ 262.0, 235.5, 234.6, 231.5, 152.7, 146.3, 146.1, 130.1, 128.9, 128.4, 127.6, 127.0, 124.2, 94.4, 69.2, 37.4, 21.9, 18.7. Anal. Calcd for $C_{27}H_{24}WSNO_6BF_3$: C, 43.66; H, 3.26; N, 1.89. Found: C, 43.61; H, 3.25; N, 1.86.

$LiAlH_4$-reduction of the salt 2. To a CH_2Cl_2 solution (10 mL) of azacyclic carbenium salt **2** (0.30 g, 0.40 mmol) was added a THF solution of $LiAlH_4$ (51 mg, 1.20 mmol) and the solution was stirred for 0.5 h. Monitoring of the solution by silica-TLC showed the presence of a yellow band. The solution was filtered through a thin silica bed to yield a yellow solid of tungsten–η¹-4,5-dihydropyrrolyl complex **3** (0.14 g, 0.21 mmol, 53%). IR (neat, cm^{-1}): ν(CO) 2023(vs), 1926(s); ^{1}H NMR (400 MHz, $CDCl_3$, −20°C): *anti*-form δ 7.04–7.85 (9H, m), 5.66 (5H, s) 4.93 (1H, dd, *J*=9.4, 4.9 Hz), 2.41 (3H, s), 1.74–2.05 (4H, m), 0.70 (3H, t, *J*=5.5 Hz), *syn*-form, δ 7.04–7.85 (9H, m), 5.70 (5H, s), 4.93 (1H, dd, *J*=9.4, 4.9 Hz), 2.38 (3H, s), 1.74–2.05 (4H, m), 0.85 (3H, t, *J*=5.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): *anti*-form δ 229.5, 215.9, 214.7, 155.7, 143.6, 141.9, 135.8, 134.2, 129.3, 128.1, 127.5, 126.9, 118.1, 92.7, 64.5, 41.7, 27.5, 21.7, 11.6. *syn*-form, 218.9, 218.3, 151.8, 143.5, 142.2, 141.9, 128.1, 128.0, 127.5, 126.7 125.8, 116.1, 93.6, 64.5, 39.1, 22.2, 21.7, 12.2. MS (EI, *m/z*): 659.4 (M^+) 631.4 (M^+-CO).

Reaction of 2 with MeMgBr. To a CH_2Cl_2 solution of azacyclic carbenium salt **2** (0.30 g, 0.40 mmol) was added MeMgBr (ca. 1.2 mmol) at −78°C, and the solution was stirred for 2 h before treatment with a saturated NH_4Cl solution. The organic layer was extracted with diethyl ether, and eluted through a silica column to afford compound **4** as a yellow solid (0.16 g, 0.30 mmol, 76%). IR (neat, cm^{-1}): ν(CO) 2023(vs), 1921(s), $\nu(SO_2)$ 1333(s); ^{1}H NMR (400 MHz, $CDCl_3$, −20°C): *anti*-form δ 7.14–7.36 (9H, m) 5.63 (5H, s) 5.21(1H, d, *J*=7.8 Hz), 3.24 (1H, m), 2.50 (1H, m) 2.26 (1H, m), *syn*-form δ 7.14–7.36 (9H, m), 5.86 (5H, s), 5.21 (1H, d, *J*=7.5 Hz), 3.05 (1H, m), 2.50 (1H, m), 2.18 (1H, m); MS (EI, *m/z*): 549 (M^+), 521 (M^+-CO). Anal Calcd for $WC_{22}H_{23}SO_5N$: C, 48.15; H, 4.22; N, 2.55. Found: C, 48.99; H, 4.16; N, 2.32.

1-Tosyl-3-benzylidene-5-phenyl-γ-lactam (5). To a diethyl ether solution of alkynyltungsten compound **1** (0.80 g, 1.27 mmol) at −78°C was added benzaldehyde (1 mL) and $BF_3{\cdot}Et_2O$ (0.16 mL, 1.30 mmol) at −78°C, and the solution was stirred and warmed to 23°C over a period of 6 h. The resulting red precipitate was collected by filtration and washed with diethyl ether. The precipitate was redissolved in CH_2Cl_2 (15 mL) and to this solution was added m-chloroperbenzoic acid (1.31g, 50%, 7.62 mmol). The mixtures were stirred for 6 h at 23°C, concentrated and eluted through a preparative silica TLC to afford γ-lactam **5** as a colorless oil (0.35 g, 0.86 mmol, 67%). IR (neat, cm^{-1}): ν(CO) 1719(vs), ν(C=C) 1648(m), $\nu(SO_2)$ 1354(s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (1H, s), 7.07–7.45 (9H, m), 5.50 (1H, d, *J*=9.2 Hz), 3.60 (1H, m, *J*=17.4, 9.2 Hz) 3.04 (1H, d, *J*=17.4 Hz) 2.34 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 144.7, 140.9, 134.6, 130.1, 129.7, 129.1, 128.8, 128.5, 128.3, 127.6, 126.5, 135.9, 59.8, 35.1, 21.6. HRMS (*m/z*): Calcd for $C_{24}H_{21}O_3SN$: 403.1242; found 403.1243.

1-Tosyl-3-ethylidene-5-phenyl-γ-lactam (6). This compound was prepared according to the procedure for the synthesis of **5**; the yield was 57%. IR (neat, cm^{-1}): ν(CO) 1719(vs), ν(C=C) 1675(m), $\nu(SO_2)$ 1361(s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04–7.40 (9H, m, 2 Ph) 6.76 (1H, m), 5.39 (1H, t, *J*=9.5 Hz) 5.15 (1H, m, *J*=15.9, 9.5 Hz), 2.62 (1H, m, *J*=15.9 Hz, 6.2 Hz) 2.32 (3H, s), 1.82 (3H, d, *J*=6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1, 144.5, 141.3, 135.5, 129.9, 128.8, 128.7, 128.3, 128.3, 127.8, 134.5, 59.7, 32.4, 21.5, 14.9. HRMS (*m/z*): Calcd for $C_{19}H_{19}O_3NS$, 341.1086; found 341.1085.

1-Mesyl-3-benzylidene-5-phenyl-γ-lactam (7). This compound was prepared according to the procedure for the synthesis of **5**; the yield was 62%. IR (neat, cm^{-1}) ν(CO) 1719(vs), ν(C=C) 1648(m), $\nu(SO_2)$ 1354(s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (1H, m) 7.27–7.51 (10H, m), 5.30 (1H, dd, *J*=9.4, 1.8 Hz), 3.67 (1H, dd, *J*=15.5, 9.4 Hz), 3.12 (1H, dd, *J*=15.5, 1.8 Hz), 3.01 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2, 140.9, 136.2, 134.4, 130.3, 129.2, 129.1, 128.9, 128.6, 127.2, 126.1, 59.4, 41.5, 34.9; HRMS: Calcd for $C_{18}H_{17}SO_3N$: 327.0929; found: 327.0929.

1-Mesyl-3-ethylidene-5-phenyl-γ-lactam (8). This compound was prepared according to the procedure for the synthesis of **5**; the yield was 59%. IR (neat, cm^{-1}): ν(CO) 1719(vs), ν(C=C) 1655(m), $\nu(SO_2)$ 1354(s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22–7.37 (5H, m, Ph), 6.89 (1H, m), 5.28 (1H, dd, *J*=9.2, 1.8 Hz), 3.20 (1H, m, *J*=16.0, 9.2 Hz), 2.91 (3H, s), 2.71 (1H, dd, *J*=16.0, 1.8 Hz), 1.81 (3H, d, *J*=2.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9, 141.2, 135.5, 129.6, 125.9, 129.1, 128.4, 59.2, 41.4, 32.3, 15.1. HRMS: Calcd for $C_{13}H_{15}SO_3N$, 265.0784; found 265.0772.

1-(But-3-enoyl)-3-(phenylethenyl)-γ-lactam (9). This compound was prepared according to the procedure for the synthesis of **5**; the yield was 72%. IR (neat, cm^{-1}): 1750(s), 1711(s), 1647(m); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (5H, m), 6.53 (1H, dd, *J*=16.0, 1.6 Hz), 6.25 (1H, dd, *J*=16.0, 6.4 Hz), 5.85 (1H, m), 5.06 (1H, dd, *J*=10.4, 3.6 Hz), 4.99 (1H, dd, *J*=10.4, 2.8 Hz), 3.95 (1H, m), 3.65 (1H, m), 3.47 (1H, m), 3.03 (2H, t, *J*=7.2 Hz), 2.37 (3H, m), 2.02 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): 175.1, 173.7, 137.0, 136.4, 133.2, 128.6, 127.8, 126.4, 124.8, 115.4, 47.7, 43.4, 36.2, 28.1, 24.4. HRMS Calcd for $C_{17}H_{18}NO_2$: 269.1416, found: 269.1418.

1-(But-3-enoyl)-3-(ethylidene)-γ-lactam (10). This compound was prepared according to the procedure for the synthesis of **5**; the yield was 71%. IR (neat, cm^{-1}): 1750(s), 1711(s), 1647(m); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.76 (dq, *J*=7.6, 2.4 Hz), 5.86 (1H, m), 5.06 (1H, ddd, *J*=9.6, 2.4, 1.6 Hz), 4.97 (1H, dd, *J*=9.6, 2.4 Hz), 3.78 (1H, t, *J*=7.6 Hz), 3.07 (2H, t, *J*=7.6 Hz), 2.65 (2H, m), 2.40 (2H, m), 1.82 (3H, dt, *J*=7.6, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 174.3, 167.7, 137.2, 134.1, 132.6, 115.3, 42.0, 36.2, 28.2, 20.3, 15.0. HRMS: Calcd for $C_{11}H_{15}NO_2$: 193.1103; found: 193.1095.

CpW(CO)$_3$(η^1-1-tosyl-3-vinyl-5-phenyl-4,5-dihydropyrrol-2-yl) (11). To a CH_2Cl_2 solution of azacyclic carbenium salt **2** (0.30 g, 0.40 mmol) was added Et_3N (0.081 mL, 0.80 mmol) at 0°C, and the mixtures were stirred for 1 h. The residues were chromatographed through a short alumina column to give a yellow band to afford **11** as a yellow solid (0.23 g, 0.36 mmol, 89%). IR (neat, cm^{-1}): ν(CO) 2025(vs) 1922(s), $\nu(SO_2)$ 1332(s); ^{1}H NMR (400 MHz, $CDCl_3$, −40°C): *anti*-form δ 7.04–7.40 (9H, m, 2 Ph), 6.50 (1H, dd, *J*=17.0, 10.8 Hz), 5.58 (5H, s), 5.30 (1H, dd, *J*=8.3, 7.5 Hz), 5.14 (1H, d, *J*=10.8 Hz), 5.01 (1H, d, *J*=17.1 Hz), 3.30 (1H, m, *J*=8.3 Hz), 2.87 (3H, s), 2.51 (1H, d, *J*=7.5 Hz), *syn*-form 7.12–7.47 (5H, m), 6.43 (1H, dd, *J*=17.4, 10.7 Hz), 5.69 (5H, s), 5.30 (1H, overlapped with that of *anti* isomer), 5.08 (2H, m), 3.16 (1H, m), 2.82 (3H, s), 2.69 (1H, m); MS (EI, *m/e*): 657. Anal. Calcd for $C_{27}H_{23}WNSO_5$: C, 49.31; H, 3.53; Found: C, 49.04; H, 3.66.

CpW(CO)$_3$(η^1-1-mesyl-3-vinyl-5-phenyl-4,5-dihydropyrrol-2-yl) (12). This compound was prepared according to the procedure for synthesis of compound **11**; the yield was 91%. IR (neat, cm^{-1}): ν(CO) 2025(vs), 1922(s); $\nu(SO_2)$ 1332(s); ^{1}H NMR(400 MHz, $CDCl_3$, −40°C): *anti*-form δ 7.12–7.37 (5H, m), 6.64 (1H,dd, *J*=17.1, 10.8 Hz), 5.60 (5H, s), 5.32 (1H, dd, *J*=8.3, 7.5 Hz), 5.10 (1H, d, *J*=10.8 Hz), 5.01(1H, d, *J*=17.1 Hz), 3.39 (1H, m, *J*=8.3 Hz), 2.88 (3H, s), 2.44 (1H, d, *J*=7.5 Hz), *syn*-form 7.12–7.37 (5H, m), 6.40 (1H, dd, *J*=17.4, 10.7 Hz), 5.68 (5H, s), 5.32 (1H, overlapped with that of *anti* isomer), 5.07 (2H, m), 3.18 (1H, m), 2.80 (3H, s), 2.63 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$, −20°C): δ 228.3, 215.6, 149.1, 142.8, 128.3, 126.9, 125.4, 135.6, 128.4, 114.7, 92.8, 64.5, 39.8, 25.7; MS (EI, *m/e*): 581 (M^+). Anal Calcd for $WC_{21}H_{19}SO_5N$: C, 43.39; H, 3.29; N, 2.41; found C: 43.23; H, 3.55; N, 2.20.

1-Tosyl-3-vinyl-5-phenyl-4,5-dihydropyrrole (13). To a CH_3CN solution of compound **11** (0.33 g, 0.50 mmol) was added Me_3NO (75 mg, 1.00 mmol), and the mixtures were stirred for 6 h. The solution was concentrated and eluted through a preparative silica plate to afford compound **13** as a colorless oil (74 mg, 0.23 mmol, 46%). IR(neat, cm^{-1}): ν(C=C) 1638(m), $\nu(SO_2)$ 1341(s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18–7.58 (9H, m, 2 Ph), 6.58 (1H, s), 6.46 (1H, dd, *J*=17.3, 10.6 Hz), 4.97 (1H, d, *J*=10.7 Hz), 4.80–4.84 (2H, m), 3.04 (1H, m, *J*=15.9, 9.2 Hz), 2.54 (1H, dd, *J*=15.9, 6.4 Hz), 2.39 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.8, 142.3, 129.7, 129.4, 128.9, 128.6, 128.4, 127.6, 126.4, 126.4, 113.4, 63.6, 39.5, 21.6; HRMS: Calcd for $C_{19}H_{19}SO_2N$, 325.1136; found 325.1142.

1-Mesyl-3-vinyl-5-phenyl-4,5-dihydropyrrole (14). This compound was prepared according to the procedure for synthesis of compound **13**. IR (neat, cm^{-1}): ν(C=C) 1638(m), $\nu(SO_2)$ 1341(s); ^{1}H NMR (400 MHz, $CDCl_3$, −40°C): *anti*-form, δ 7.12–7.37 (5H, m) 6.64 (1H, dd, *J*=17.1 Hz, 10.8 Hz), 5.60 (5H, s), 5.32 (1H, dd, *J*=8.3, 7.5 Hz), 5.10 (1H, d, *J*=10.8 Hz), 5.01 (1H, d, *J*=17.1 Hz), 3.39 (1H, m, *J*=8.3 Hz), 2.88 (3H, s) 2.44 (1H, m, *J*=7.5 Hz), *syn*-form, 7.12–7.37 (5H, m), 6.40 (1H, dd, *J*=17.4, 10.7 Hz), 5.68 (5H, s), 5.32 (1H, dd, *J*=8.3, 7.5 Hz), 5.07 (2H, m), 3.18 (1H, m), 2.80 (3H, s), 2.63 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$, −20°C): δ 228.3, 215.6, 149.1, 142.8, 128.3, 126.9, 125.4, 135.6, 128.4, 114.7, 92.8, 64.5, 39.8, 25.7; MS (EI, *m/z*): 581 (M^+). Anal. Calcd for $WC_{21}H_{19}SO_5N$: C, 43.39; H, 3.29; N, 2.41; found C, 43.23; H, 3.55; N, 2.24.

1-(Methylsulfonyl)-2-phenyl-2,3,5,5a,6,8,8a,8b-octahydro-1*H*-furo[3,4-*g*]indole-6,8-dione (15). To a d_8-toluene solution (1.0 mL) of diene 14 (30 mg, 0.12 mmol) was added maleic anhydride (13 mg, 0.132 mmol) in a sealed NMR tube, and the NMR sample was heated at 60°C for 2 h. NMR spectra of this solution showed the completion of reaction. The solution was concentrated and eluted through a preparative silica TLC-plate to afford compound **14** as a colorless solid (38 mg, 0.11 mmol, 92%). IR (neat, cm^{-1}): ν(C=O) 1767(vs); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (5H, m), 5.84 (1H, m), 5.04 (1H, dd, *J*=8.0, 3.6 Hz), 4.31 (2H, t, *J*=6.4 Hz), 3.37 (1H, m), 3.06 (1H, dd, *J*=17.2, 8.0 Hz), 2.78 (2H, m), 2.38 (3H, s), 2.34 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 170.0, 143.2, 140.6, 128.9, 128.7, 127.7, 118.3, 64.9, 59.3, 45.1, 40.8, 39.9, 38.2, 25.9. HRMS: Calcd for $C_{17}H_{17}NO_5S$, 347.0827; found 347.0831.

1-(Methylsulfonyl)-2,7-diphenyl-1,2,3,5,5a,6,7,8,8a,8b-deca-hydropyrrolo[3,4-*g*]indole-6,8-dione (16). This compound was prepared similarly from compound **14** and *N*-phenylmaleimide; the yield was 91%. IR (neat, cm^{-1}): ν(C=O) 1767(s); ^1H NMR (300 MHz, $CDCl_3$): δ 7.38 (10 H, m), 5.81 (1H, m), 4.89 (1H, dd, *J*=9.9, 8.0 Hz), 4.66 (1H, d, *J*=8.2 Hz), 4.04 (1H, t, *J*=8.2, 7.4 Hz), 3.32 (1H, t, *J*=7.4 Hz), 3.14 (1H, dd, *J*=17.2, 8.0 Hz), 2.93 (1H, dd, *J*=14.6, 7.4 Hz), 2.67 (1H, dd, *J*=17.2, 9.9 Hz), 2.60 (3H, s), 2.27 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.3, 175.1, 139.5, 139.0, 132.0, 129.3, 128.9, 128.8, 128.5, 128.4, 126.6, 118.1, 65.1, 60.2, 43.1, 42.8, 40.7, 39.7, 25.2. HRMS: Calcd for $C_{23}H_{22}N_2O_4S$, 422.1300; found 422.1298.

Dimethyl 1-(methylsulfonyl)-2-phenyl-2,3,5,6,7,7a-hexa-hydro-1*H*-6,7-indole-dicarboxylate (17). This compound was prepared similarly from compound **14** and dimethyl maleate; the yield was 80%. IR (neat, cm^{-1}): ν(C=O) 1735(s); ^1H NMR (400 MHz,$CDCl_3$): δ 7.32 (5H, m, Ph), 5.60 (1H, s), 4.90 (1H, t, *J*=7.2 Hz), 4.41 (1H, d, *J*=4.0 Hz), 4.10 (1H, t, *J*=4.0 Hz), 3.68 (3H, s), 3.58 (3H, s), 2.34~3.00 (5H, m), 2.21 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 169.8, 139.6, 134.6, 128.7, 128.6, 128.5, 119.1, 80.8, 64.,1 52.2, 51.7, 45.0, 41.0, 40.2, 39.3, 24.9. HRMS: Calcd for $C_{19}H_{23}NO_6S$: 393.1246; found 393.1242.

Dimethyl 1-(methylsulfonyl)-2-phenyl-2,3,5,6,7,7a-hexa-hydro-1*H*-6,7-indoledicarboxylate (18). This compound was prepared similarly from compound **14** and dimethyl furmate; the yield was 78%. IR (neat, cm^{-1}): ν(C=O) 1733(vs); ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (5H, m, Ph), 5.47 (1H, t, *J*=3.5 Hz), 5.16 (1H, d, *J*=8.9 Hz), 4.54 (1H, d, *J*=8.8 Hz), 3.71 (3H, s), 3.63 (3H, s), 3.05 (1H, dd, *J*=9.8, 8.8 Hz), 2.98 (1H, m,), 2.81 (3H, s), 2.21 (1H, dd, *J*=11.6, 9.8 Hz), 2.48 (2H, m), 2.08 (1H, ddd, *J*=18.2, 11.6, 3.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 173.3, 141.6, 135.7, 128.7, 127.4, 125.9, 121.1, 62.3, 60.4, 52.3, 52.2, 48.9, 41.5, 40.3, 40.2, 28.4. HRMS: Calcd for $C_{19}H_{23}NO_6S$, 393.1246; found 393.1243.

1-[1-(Methylsulfonyl)-2-phenyl-2,3,5,7a-tetrahydro-1*H*-7-indolyl]-1-ethanone (19). This compound was prepared by heating a toluene solution of compound **14** with dimethyl furmate (100°C, 4 h); the yield was 50%. IR (neat, cm^{-1}): ν(C=O) 1715(s), ν(C=C) 1635(w); ^1H NMR (300 MHz, $CDCl_3$): δ 7.22 (5H, m), 6.66 (1H, m), 5.60 (1H, m), 5.12 (2H, m), 3.06 (3H, s), 2.46~2.92 (4H, m), 2.40 (3 H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.8, 142.8, 139.6, 137.0, 134.1, 128.3, 127.1, 125.8, 118.7, 62.0, 54.3, 40.3, 38.9, 28.1, 27.9. HRMS: Calcd for $C_{17}H_{19}NO_3S$: 317.1086; found 317.1084.

[2-(3-Acetylphenyl)-1-phenylethyl]methanesulfonamide (20). This compound was prepared by heating a toluene solution of compound **14** with dimethyl furmate (100°C, 6 h); the yield was 70%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (1H, d, *J*=7.4 Hz), 7.60 (1H, s), 7.32 (7H, m, Ph), 4.90 (1H, d, *J*=7.2 Hz), 4.73 (1H, dd, *J*=14.5, 7.3 Hz), 3.14 (2H, d, *J*=7.2 Hz), 2.51 (3H, s), 2.45 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.9, 140.3, 137.3, 137.1, 134.1, 129.4, 128.9, 128.8, 128.3, 127.1, 126.8, 59.2, 43.8, 41.8, 26.6. HRMS: Calcd for $C_{17}H_{19}NO_3S$, 317.1086; found 317.1099.

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References

1. (a) Lozar, L. D.; Clark, R. D.; Heathcock, C. H. *J. Org. Chem.* **1977**, *42*, 1386. (b) Johnson, W. S.; Yarnell, T. M.; Myers, R. F.; Morton, D. R. *Tetrahedron Lett.* **1978**, *26*, 1201. (c) Johnson, W. S.; Yarnell, T. M.; Myers, R. F.; Morton, D. R.; Boots, D. R. *J. Org. Chem.* **1980**, *45*, 1254.
2. (a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (b) Masse, C.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293. (c) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375. (d) Weinreb, S. M. *J. Heterocyclic. Chem.* **1996**, *33*, 1429. (e) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31.
3. (a) Herndon, J. W.; Wu, C. *Synlett* **1990**, *1*, 411. (b) Danheiser, R. L.; Takahashi, T.; Bertok, R.; Dixon, B. R. *Tetrahedron Lett.* **1993**, *34*, 3845. (c) Danheiser, R. L.; Ksasigroch, C. A.; Tsai, Y. M. *J. Am. Chem. Soc.* **1985**, *107*, 7233. (d) Panek, J. S.; Yang, M. *J. Am. Chem. Soc.* **1991**, *113*, 9868.
4. (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 257. (b) Davidson, A.; Solar, J. P. *J. Organomet. Chem.* **1979**, *166*, c13.
5. Liang, K.-W.; Li, W.-T.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1997**, *119*, 4404.
6. Liang, K.-W.; Chandrasekharam, M.; Li, C.-L.; Liu, R.-S. *J. Org. Chem.* **1998**, *63*, 7289.
7. Bruce, M. L.; Humphrey, M. G.; Mattisons, J. G.; Roy, S.; Swincer, A. G. *Aust. J. Chem.* **1984**, 1041.
8. Boeckman Jr., R. K.; Breining, S. R.; Arvanitis, A. *Tetrahedron* **1997**, *53*, 8941.
9. Brosius, A. D.; Overman, L. E.; Schwink, L. *J. Am. Chem. Soc.* **1999**, *121*, 700.
10. Ha, J. D.; Kang, C. H.; Belmore, K. A.; Cha, J. K. *J. Org. Chem.* **1998**, *63*, 3810.
11. (a) Hickmott, P. W. *Tetrahedron* **1984**, *40*, 2989. (b) Houk, K. N.; Wu, T. C. *Tetrahedron Lett.* **1985**, *26*, 2293.