Synthesis of Indolizidine and Quinolizidine Derivatives via Intramolecular Cyclization of Alkynyltungsten Compounds with *N*-Acyliminium Ion

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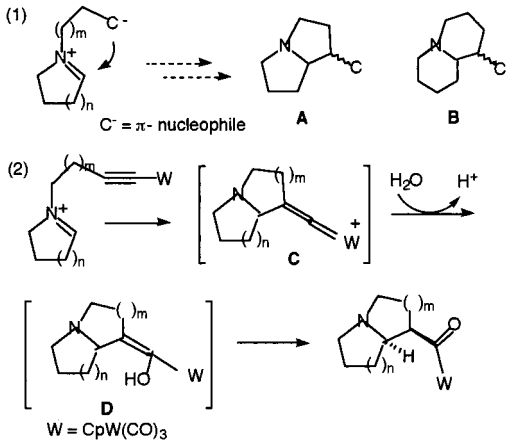
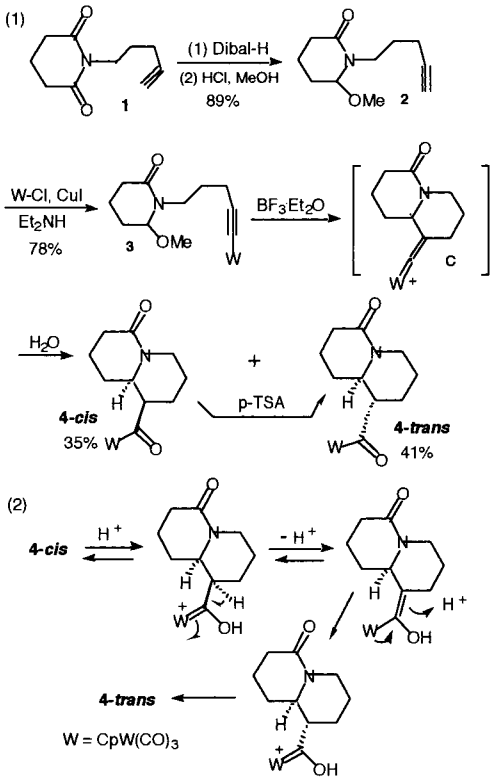
Introduction

Bicyclic indolizidine (**A**) and quinolizidine (**B**) compounds are important structural skeletons for natural alkaloids.[1] A common method to construct these skeletons involves Lewis-acid promoted cyclization of the *N*-acyliminium ion[2,3] with mild π-carbon nucleophiles. Such cyclization involves the use of organometallic π-nucleophiles[4,5] to control the regioselectivity because the metal fragment stabilizes the carbocationic intermediate. Allyl and propargyl organometallics[4,5] of silanes and stannanes underwent regio- and stereocontrolled cyclization with *N*-acyliminium due to the β-effect of silicon and a cyclic transition state in the reaction mechanism. We previously used alkynyltungsten complexes for syntheses of complex oxygen heterocycles via condensation with aldehydes.[6,7] The regiochemistry occurs at the C_β-carbon to yield a tungsten−vinylidenium intermediate.[8] Scheme 1 (eq 2) shows a mechanism speculated for the cyclization of alkynyltungsten complexes with *N*-acyliminium; the alkynyltungsten functionality is considered to be equivalent to an enolate according to this reaction pathway. The *cis*-acyl complex (eq 2, Scheme 1) is envisaged to be the kinetically favored product upon protonation of the enol intermediate (**D**).

Scheme 1



Scheme 2



Results and Discussion

Scheme 2 shows an example of the cyclization of *N*-acyliminium with alkynyltungsten complex **3** that was prepared from N-alkylated glutarimide **1** in two steps (89% overall yield). Treatment of alkynyltungsten complex **3** with $BF_3{\cdot}Et_2O$ (1.1 equiv) in cold diethyl ether slowly deposited a yellow precipitate, presumably a tungsten−vinylidenium intermediate.[6−8] Treatment of this precipitate **C** with water afforded acyltungsten compound **4** as a mixture of cis and trans isomers. ^{1}H NMR spectra shows the crude sample to have a trans/cis ratio ca. 1:1.4. Separation of this mixture on a Et_3N-

(1) *The Alkaloids: Chemistry and Biology*; Cordell, G. A., Ed.; Academic Press: San Diego, 2000; vol 54 and others in this series.

(2) Reviews on *N*-acyliminium cation chemistry, see (a) Speckamp, W. N.; Moolenaar, M. J. *Tetrahedron* **2000**, *56*, 3817. (b) Hiemstra, H.; Speckamp, W. M. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Heathcock, C. H., Eds.; Pergamon: Oxford, 1991; Vol. 2, p 1047. (c) Volkmann, R. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Schreiber, S. L., Eds.; Pergamon: Oxford, 1991; Vol. 1, p 355.

(3) For recent examples, see (a) Okitsu, O.; Suzuki, R.; Kobayashi, S. *J. Org. Chem.* **2001**, *66*, 809. (b) Batey, R. A.; MacKay, B.; Santhakumar, V. *J. Am. Chem. Soc.* **1999**, *121*, 5075. (c) Adelbrecht, J. C.; Craig, D.; Dymock, B. W.; Thorimbert, S. *Synlett* **2000**, 457. (d) Sugisaki, C. H.; Carroll, P. J.; Correia, C. R. D. *Tetrahedron Lett.* **1998**, *39*, 3413. (e) Martin, S. F.; Barr, K. J. *J. Am. Chem. Soc.* **1996**, *118*. 3299.

(4) (a) Hiemstra, H.; Sno, M. H. A. M.; Vijn, R. S.; Speckamp, W. M. *J. Org. Chem.* **1985**, *50*, 4014. (b) Hiemstra, H.; Sno, M. H. A. M.; Vijn, R. S.; Speckamp, W. M. *Tetrahedron Lett.* **1983**, *24*, 1407.

(5) (a) Hart, D. J.; Tsai, Y. M. *Tetrahedron Lett.* **1981**, *22*, 1567. (b) Aratani, M.; Sawada, K.; Hashimoto, M. *Tetrahedron Lett.* **1982**, *23*, 3921. (c) Overman, L. E.; Malone, T. C.; Meier, G. P. *J. Am. Chem. Soc.* **1983**, *105*, 6993.

(6) (a) Liang, K.-W.; Li, W.-T.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1997**, *119*, 4404. (b) Liang, K.-W.; Chandrasekharam, M.; Li, C.-L.; Liu, R.-S. *J. Org. Chem.* **1998**, *63*, 7289. (c) Li. W.-T.; Pan, M.-H.; Wu, Y.-R.; Wang, S.-L.; Liao, F.-L.; Liu, R.-S. *J. Org. Chem.* **2000**, *65*, 3761. (d) Chen, M.-J.; Lo, C.-Y.; Chin, C.-C.; Liu, R.-S. *J. Org. Chem.* **2000**, *65*, 6362. (e) Chen, M.-J.; Lo, C.-Y.; Liu, R.-S. *Synlett* **2000**, 1300.

(7) Li, C.-L.; Liu, R.-S. *Chem. Rev.* **2000**, *100*, 3127.

(8) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311.

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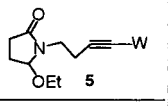
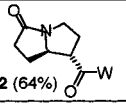
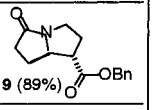
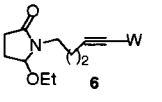
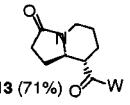
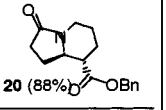
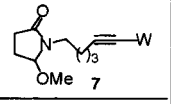
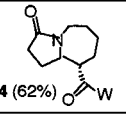
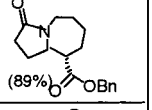
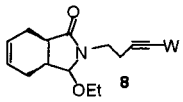
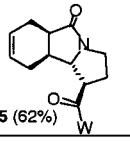
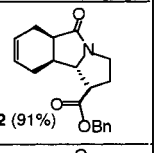
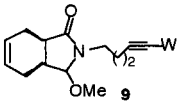
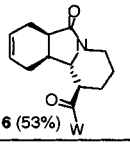
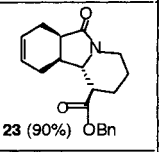
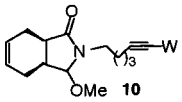
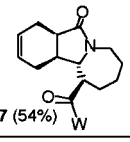
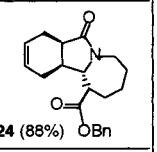
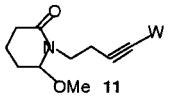
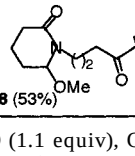
Published on Web 08/15/2001

Table 1. Cyclization and Demetalations Reactions

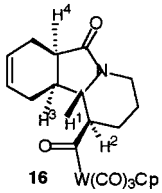
entry	alkynyltungsten	products[a-b]	demetalations[c-d]
1	 **5**	 **12** (64%)	 **19** (89%)
2	 **6**	 **13** (71%)	 **20** (88%)
3	 **7**	 **14** (62%)	 **21** (89%)
4	 **8**	 **15** (62%)	 **22** (91%)
5	 **9**	 **16** (53%)	 **23** (90%)
6	 **10**	 **17** (54%)	 **24** (88%)
7	 **11**	 **18** (53%)	—

W = CpW(CO)$_3$. [a] BF_3·Et_2O (1.1 equiv), CH_2Cl_2 (−78 °C → 23 °C), H_2O. [b] Yields were reported after chromatography from SiO_2 column. [c] BnOH (2.0 equiv), I_2 (1.5 equiv), CH_2Cl_2, (−78 °C → 23 °C) [d] Yields were reported from chromatorgraphy from preparative SiO_2 plate.

pretreated silica column afforded compounds **4-*cis*** and **4-*trans*** in 35% and 41% yields, respectively. The yields of **4-*cis*** and **4-*trans*** became 10% and 66%, respectively, when separation was conducted on a neutral silica column. This phenomenon indicates a cis−trans isomerization of compound **4** in the presence of proton. To confirm this isomerization, compound **4-*cis*** was treated with *p*-toluenesulfonic acid (20 mol %) in CH_2Cl_2 (23 °C, 10 h) to give a **4-*trans*/4-*cis*** ratio of 11.4. An enhanced effect of proton on this isomerization is attributed to formation of a tungsten−oxacarbenium species[6a] **F** that accelerated proton exchange via its increased proton acidity.

We extended these cyclizations to syntheses of bicyclic lactam derivatives of various sizes; the scope is demonstrated in Table 1. Syntheses of alkynyltungsten compounds **5**−**11** followed the same procedures as those for compound **3**; details of their syntheses are provided in Supporting Information. In a typical cyclization, alkynyltungsten compound **5** is treated with BF_3·Et_2O (1.1 equiv) in cold diethyl ether (−78 °C) to yield tungsten vinylidenium salts. After addition of a $NaHCO_3$ solution, the mixture was stirred for 1.0 h at 23 °C to afford acyltungsten compound **12** in a cis/trans ratio 1.0/1.6. Elution of this mixture on a silica column afforded the trans isomer **12** in 62% yield with the cis isomer in trace amount. Attempts to obtain the pure cis isomer were unsuccessful even on a Et_3N-pretreated silica column; in this case, the cis isomer was obtained in small yield (<5%) with contamination of trans isomer. Demetalation of acyltungsten complex **12** with benzyl alcohol (2.0 equiv) and I_2 (1.5 equiv) in CH_2Cl_2 afforded the ester derivative **19** in 89% yield. This cyclization worked well for syntheses of 5,6 and 5,7 bicyclic lactams **13** and **14** for which the yields were 71% and 62%, respectively. Similarly, the corresponding cis isomers of **13** and **14** were not isolable in pure form because of their facile isomerization on a column chromatograph. The trans configurations of compounds **13** and **14** were confirmed by ^{1}H NOE NMR spectra. I_2-induced demetalation of **13** and **14** gave the esters **20** and **21** in good yields (89%). Entry 4 shows a diastereocontrolled cyclization for the synthesis of tricyclic lactam compound **15** in 62% yield. The stereochemistry of compound **15** was determined according to ^{1}H NOE NMR spectra (see Supporting Information). Compound **15** is envisaged to derive from an attack of alkynyltungsten carbon at acyliminium from the less-hindered face. This cyclization was successfully extended to six- and seven-membered analogues **16** and **17** (entries 5 and 6) that were likewise obtained as single diastereomers. The configurations of **16** was confirmed through ^{1}H NOE NMR spectra with the map below (Scheme 3). For **16**, the magnitude of ^{1}H NMR coupling constant J_{12} = 10.2 Hz indicates an axial−axial coupling, confirming our proposed structure. The availability of acyltungsten complexes **15**−**17** provides an easy entry to a tricyclic alkaloid framework via demetalation with I_2 and benzyl alcohol, giving the complex azacycles **22**−**24** in 91−88%.

Scheme 3



16

Irradiations	Intensity (%)
H^1 (δ 4.08)	H^2 (δ 3.22, 0 %), H^3 (δ 1.71, 0%)
H^3 (δ 1.71)	H^4 (δ 2.50, 3.5 %), H^1 (δ 4.08, 0%)

The failure in the cyclization of acyltungsten complex **18** is unexpected because cyclization of the corresponding 6,6 bicyclic lactam **4** proceeded smoothly under similar conditions, and the uncyclized acyltungsten compound **18** was obtained in 53% yield.

Natural (±)-laburnine,[8] (±)-epilupinine,[10,3a] and (±)-lupinine[11] can be prepared from the preceding cyclization

(9) (a) Nagao, Y.; Dai, W.-M.; Ochiai, M.; Tsukagoshi, S.; Fujita, E. *J. Org. Chem.* **1990**, *55*, 1148. (b) Rueger, H.; Benn, M. *Heterocycles* **1982**, *19*, 1677. (c) Rueger, H.; Benn, M. *Heterocycles* **1983**, *20*, 235. (c) Robins, D. J.; Sakdarat, S. *J. Chem. Soc., Chem. Commun.* **1979**, 1181. (d) Hua, D. H.; Miao, S. W.; Bravo, A. A.; Takemoto, D. J. *Synthesis* **1991**, 970. (e) Arai, Y.; Kontani, T.; Koizumi, T. *J. Chem. Soc., Perkin Trans.* **1994**, 15.

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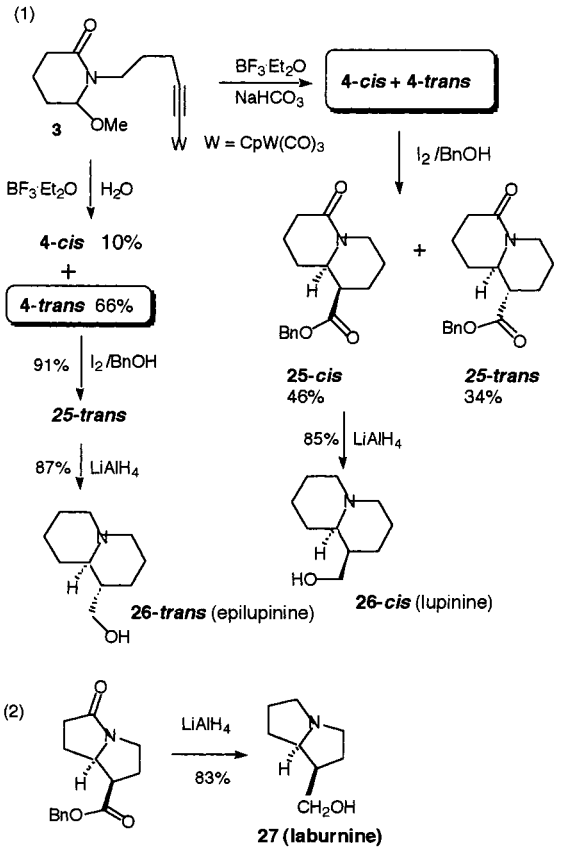
Scheme 4



products; these synthetic procedures are shown in Scheme 4. Toward synthesis of (±)-epilupinine, the crude product of acyltungsten complex **4** was demetalated with I_2 and benzyl alcohol without chromatographic separation of the cis and trans isomers of the acyltungsten compound **4**. The ester **25-*cis*** was obtained in 46% isolated yield based on alkynyltungsten complex **3**. $LiAlH_4$ reduction of this ester in diethyl ether afforded (±)-lupinine **26-*cis*** in 85% yield after workup. As mentioned before, the *trans*-acyltungsten compound **4-*trans*** was obtained in 66% yield via isomerization from its cis isomer ***4*-cis**. The ester **25-*trans*** and epilupinine **26-*trans*** were obtained in 91% and 87% yields, respectively, following the same sequence. Similarly, (±)-laburnine **27** was produced efficiently from $LiAlH_4$ reduction of the corresponding bicyclic ester **19**.

Experimental Section

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 was dried over CaH_2 and distilled before use. $W(CO)_6$, $BF_3{\cdot}Et_2O$, dicyclopentadiene, 3-butyn-1-ol, 4-pentyn-1-ol and 5-hexyn-1-ol, glutarimide succinimide, and sodium were obtained commercially and used without purification. Mass data of tungsten compounds were reported according to ^{184}W. Spectral data of compounds **6**−**10**, **13**−**18**, **20**−**25** in repetitive experiments are provided in Supporting Information.

(1) Synthesis of 1-Pent-4-ynyl-1-piperidine-2,6-dione 1. To a benzene solution (35 mL) of glutarimide[12] (3.50 g, 30.9 mmol) and 4-pentynyl-1-tosylate (7.74 g, 32.5 mmol) were added K_2CO_3 (4.70 g, 34.0 mmol) and 18-crown-6-ether (70 mg). This mixture was refluxed for 16 h and quenched with water. The solution was extracted with diethyl ether, dried over $MgSO_4$, and flashed over a silica column to afford compound **1** as a colorless oil (4.93 g, 27.5 mmol 89%). IR (neat, cm^{-1}): ν(CO) 1780 (s), 1710 (s); ^1H NMR (400 MHz, $CDCl_3$): δ 3.78 (2H, dt, J = 3.2, 9.6 Hz), 2.57 (4H, dt, J = 4, 6.4 Hz), 2.20 (2H, dt, J = 2.8, 5.6 Hz), 1.91−1.86 (3H, m), 1.71−1.66 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 83.4, 68.4, 38.6, 32.6, 26.6, 16.9, 16.1; MS (75 eV *m*/*e*): 179 (M^+). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 43.17; H, 3.45. Found: C, 43.01; H, 3.40; N, 3.33.

(2) Synthesis of 6-Methoxy-1-pent-4-ynyl-piperidin-2-one 2. To a CH_2Cl_2 solution (50 mL) of compound **1** (3.10 g, 17.3 mmol) was added DIBAL-H (1 M, hexane, 19.0 mL) at −78 °C; the mixture was stirred for 0.5 h before addition of MeOH (2.0 mL). The solution was slowly warmed to 23 °C over 8 h, and a saturated NH_4Cl solution (3.0 mL) was added. The solution was treated with HCl solution (2.0 M) with neutralization (pH = 7.0). The solution was extracted with CH_2Cl_2 and chromatographed over a short silica column (ethyl acetate/hexane = 2/1) to afford compound **2** as a colorless oil (2.77 g, 14.2 mmol, 82%). ^1H NMR (400 MHz, $CDCl_3$): δ 4.50 (1H, d, J = 2.4 Hz), 3.63 (1H, m), 3.31 (3H, s), 3.24 (1H, m), 2.41 (1H, m), 2.30−2.13 (3H, m), 2.03−1.92 (3H, m), 1.78 (2H, t, J = 6.8 Hz), 1.68−1.60 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 88.3, 83.6, 68.6, 55.2, 45.1, 32.1, 26.6, 26.1, 15.9, 15.6; MS (75 eV *m*/*e*): 195 (M^+). Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.75; N, 7.21. Found: C, 67.56; H, 8.70; N, 7.11.

(3) Synthesis of Alkynyltungsten Compound 3. To a Et_2-NH solution (15 mL) of $CpW(CO)_3Cl$ (4.78 g, 12.9 mmol) and CuI (0.25 g, 1.13 mmol) was added compound **2** (2.30 g, 11.7 mmol); the mixture was stirred for 4 h before concentration. The residues were chromatographed over a silica column (diethyl ether/ hexane = 1/1) to afford compound **3** as an orange solid (4.47 g, 8.48 mmol, 72%); IR (neat, cm^{-1}): ν (CO) 2014 (s), 1915 (s), 1710 (s); ^1H NMR (400 MHz, $CDCl_3$): δ 5.52 (5H, s), 4.51 (1H, t, J = 3.2 Hz), 3.72 (1H, m), 3.26 (3H, s), 3.15 (1H, m), 2.42−2.30 (3H, m), 2.28−2.19 (1H, m), 2.00−1.90 (2H, m), 1.72−1.57 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 229.9, 212.1, 212.0, 170.0, 127.8, 91.3, 88.1, 55.9, 55.0, 45.3, 32.0, 28.0, 26.0, 19.6, 15.5; MS (75 eV *m*/*e*): 527 (M^+). Anal. Calcd for $C_{19}H_{21}WNO_5$: C, 43.29; H, 4.01; N, 2.67. Found: C, 43.22; H, 4.02; N, 2.55.

(4) Synthesis of Acyltungsten Complex 4. To a diethyl ether (20 mL) of compound **3** (1.26 g, 2.39 mmol) at −78 °C was added $BF_3{\cdot}Et_2O$ (0.33 mL, 2.63 mmol), and the solution was stirred for 3 h and then warmed to 23 °C to deposit yellow precipitates. The diethyl ether was decanted away, and the precipitates were redissolved in CH_2Cl_2 (10 mL). To this solution was added water (3.0 mL) at 23 °C, and the mixtures were stirred for 1 h. The organic layer was separated, concentrated to yield a dark orange precipitate as a mixture of cis and trans isomers (4-cis/4-trans = 1/1.4). Elution of this residue through a Et_3N-pretreated silica column afforded compounds **4-*trans*** (0.50 g, 0.98 mmol, 41%) and **4-*cis*** (0.43 g, 8.36 mmol, 35%), respectively.**Spectral data for 4-*trans***. IR (neat, cm^{-1}): ν (CO) 2018 (s), 1914 (s), 1712 (s); ^1H NMR (400 MHz, $CDCl_3$): δ 5.52 (5H, s), 4.74 (1H, m), 3.67 (1H, m), 3.39−3.21 (2H, m), 2.61 (1H, m), 2.40−2.19 (3H, m), 2.00−1.82 (2H, m), 1.75 (1H, m), 1.62−1.35 (2H, m), 1.23 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 247.3, 225.5, 220.6, 220.2, 169.7, 93.9, 77.8, 58.0, 42.0, 32.8, 28.7, 28.1, 24.2, 18.9; MS (75 eV *m*/*e*): 513 (M^+). Anal. Calcd for $C_{18}H_{19}WNO_5$: C, 37.45; H, 3.73; N, 2.73. Found: C, 37.25; H. 3.71; N. 2.66.

Spectral data for 4-*cis*: IR (neat, cm^{-1}): ν (CO) 2019 (s), 1915 (s), 1711 (s); ^1H NMR (400 MHz, $CDCl_3$): δ 5.46 (5H, s), 4.05 (1H, dt, J = 2.4, 13.2 Hz), 3.53 (1H, m), 3.16 (1H, m), 2.38−2.25 (4H, m), 1.95−1.87 (2H, m), 1.79−1.68 (2H, m), 1.56−1.44 (2H, m), 1.41−1.34 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 243.0, 226.4, 220.9, 220.2, 169.6, 94.0, 71.7, 57.8, 41.8, 32.7, 28.0, 24.6, 20.3, 19.8; MS (75 eV *m*/*e*): 513 (M^+). Anal. Calcd for $C_{18}H_{19}WNO_5$: C, 37.44; H, 3.73; N, 2.73. Found: C, 37.11; H, 3.71; N, 2.50.

(5) Synthesis of Acyltungsten Complex 12. The reaction of alkynyltungsten complex **5** (0.93 g, 1.81 mmol) and $BF_3{\cdot}Et_2O$ (0.25 mL, 1.99 mmol) in cold diethyl ether, followed by quenching with water, afforded crude acyltungsten complex **12**. Purification

(12) Gresson, J. P.; Jacquesy, J. C.; Rambaud, D. *Bull. Chim. Fr.* **1992**, *129*, 227.

of this sample on a silica column afforded the trans isomer **12** (0.56 g, 1.16 mmol) in 64% yield. IR (neat, cm^{-1}): ν (CO) 2021 (s), 1913 (s), 1724 (s); ^1H NMR (300 MHz, $CDCl_3$): δ 5.54 (5H, s), 3.90 (1H, dt, J = 7.1 Hz), 3.49−3.55 (2H, m), 3.01 (1H, m), 2.60 (1H, m), 2.36 (2H, m), 2.21 (1H, m), 1.98 (1H, m), 1.76 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 248.1, 225.2, 220.1, 174.5, 95., 79.8, 63.8, 40.6, 34.8, 32.8, 26.3; MS (75 eV, *m*/*e*): 485 (M^+). Anal. Calcd for $C_{16}H_{15}WNO_5$: C, 39.62; H, 3.12; N, 2.89. Found: C, 39.44; H. 3.06; N. 2.77.

(6) Oxidative Demetalation of Complex 12. To a CH_2Cl_2 solution (5.0 mL) of acyltungsten complex **12** (0.90 g, 1.85 mmol) were added I_2 (0.71 g, 2.78 mmol) and benzyl alcohol (0.18 mL) at −78 °C, and the mixtures were stirred for 1 h before it was warmed to 23 °C. To this solution was added a saturated $Na_2S_2O_3$ solution (3 mL); the organic layer was extracted with diethyl ether to give a yellow oil of **19**. Flash chromatography on a silica column afforded compound **19** as a colorless oil (0.21 g, 0.80 mmol, 89%). IR (neat, cm^{-1}): ν (CO) 1724 (s), 1695 (s); ^1H NMR (400 MHz, $CDCl_3$): δ 7.40−7.30 (5H, s), 5.17 (2H, s), 4.07 (1H, q, J = 9.2 Hz), 3.63 (1H, dt, J = 8.4 Hz, 11.2 Hz), 3.19(1H, dt, J = 3.6, 8.6 Hz), 2.73−2.66 (1H, m), 2.61−2.55 (1H, m), 2.48−2.31 (4H, m), 1.93−1.83 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.8, 171.8, 135.5, 128.6, 128.4, 128.1, 66.8, 64.2, 49.6, 41.1, 34.3, 30.6, 25.9; MS (75 eV *m*/*e*): 259 (M^+). Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.22; H, 6.55; N, 5.33.

(7) Synthesis of (±)-lupinine 26-*cis*. To a THF solution (7.0 mL) of the cis ester **25-*cis*** (150 mg, 0.52 mmol) at 0 °C was added $LiAlH_4$ (2.5 M in THF, 0.63 mL) at 0 °C; the mixture was refluxed for 2 h. To this solution was added HCl (3.0 M) until the solution reached pH = 6.0. The solution was concentrated, extracted with ethyl acetate, and purified on a preparative silica plate (ethyl acetate/hexane = 2/1, 3% Et_3N) to afford (±)-lupinine **26-*cis*** (75.1 mg, 0.44 mmol, 85%) as a colorless solid (mp 168−169°; lit.[11] 168−169°); ^1H NMR (400 MHz, $CDCl_3$): δ 3.68−3.58 (3H, m), 2.86 (2H, t, J = 14.8 Hz), 2.07 (2H, m), 1.93−1.61 (4H, m), 1.58−1.37 (2H, m), 1.28−1.13 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.1, 64.5, 57.1, 56.9, 30.1, 29.9, 28.4, 25.9, 25.3, 24.8; MS (75 eV *m*/*e*): 169 (M^+). Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31; N, 2.37. Found: C, 70.88; H, 11.25; N, 2.55.

(8) Synthesis of (±)-Epilupinine 26-*trans*. $LiAlH_4$ reduction of the *trans*-ester **25-*trans*** (120 mg, 42 mmol, followed by hydrolysis, afforded (±)-epilupinine (61.4 mg, 0.36 mmol, 87%) as a colorless solid (mp 79−80°; lit.[10] 80°); ^1H NMR (400 MHz, $CDCl_3$): δ 4.14 (1H, dd, J = 4.4, 11.6 Hz), 3.68 (1H, d, J = 10.8 Hz), 2.81 (2H, m), 2.13 (2H, m), 2.05 (1H, t, J = 10.0 Hz), 1.86−1.70 (4H, m), 1.60−1.52 (6H, m), 1.30−1.22 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.8, 65.1, 57.0, 53.4, 38.2, 31.2, 29.5, 25.4, 24.6, 22.9; MS (75 eV *m*/*e*): 169 (M^+). Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31; N, 8.28. Found: C, 70.66; H, 11.51; N, 8.22.

(9) Synthesis of (±)-Laburnine. $LiAlH_4$ reduction of the *trans*-ester **19** (110 mg, 4.24 mmol) followed by hydrolysis afforded (±)-laburnine **27** (49.7 mg, 3.52 mmol, 83%) as a colorless solid (mp 115−117°; lit.[9] 117°). ^1H NMR (400 MHz, $CDCl_3$): δ 3.56 (2H, d, J = 5.6 Hz), 3.23(1H, br), 3.16 (1H, q, J = 6.8 Hz), 3.08 (1H, m), 2.91 (1H, dt, J = 6.0 Hz, 10.8 Hz), 2.58−2.46 (2H, m), 2.00−1.88 (2H, m), 1.84−1.79 (1H, m), 1.75−1.67 (1H, m), 1.61−1.55 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 67.7, 65.3, 54.7, 54.4, 48.4, 31.9, 30.0, 25.7; MS (75 eV, *m*/*e*): 141 (M^+). Anal. Calcd for $C_8H_{15}NO$: C, 68.05; H, 10.71; N, 9.92. Found: C, 68.11; H, 10.90; N, 9.88.

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Supporting Information Available: Syntheses and spectral data of compounds **6**−**10**, **13**−**18**, and **20**−**25** in repetitive experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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