Photochemical Reaction between Tertiary Allylic Amines and Chromium Carbene Complexes: Synthesis of Lactams via a Zwitterion Aza Cope Rearrangement

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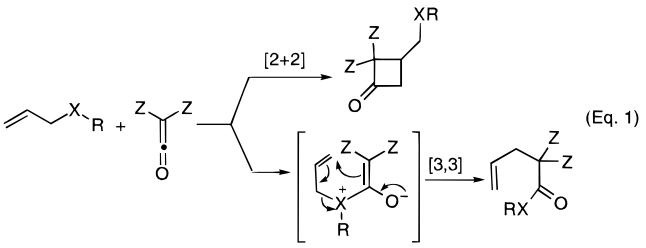
Photolysis of chromium carbene complexes in the presence of tertiary allylic amines resulted in a zwitterionic aza Cope rearrangement to produce unsaturated lactams in fair yield.

Introduction

Ketenes normally undergo reaction with alkenes to produce cyclobutanones[1] in a "concerted" [2 + 2] cycloaddition process.[2] However, alkenes having heteroatoms (O,[3] S,[4] N[5]) at the allylic position can undergo competitive reaction at the heteroatom to form zwitterionic intermediates which undergo [3,3]-sigmatropic rearrangement, particularly in the presence of Lewis acids (eq 1).[6] This "Malherbe−Bellus" variant of the Claisen rearrangement can be quite efficient and has been used to synthesize unsaturated nine-membered lactones.[7] The nitrogen analog (aza-Claisen[8]) has been used to provide unsaturated lactam precursors to indolizidine and quinolizidine ring systems.[5]



(Eq. 1)

Photolysis of chromium carbene complexes (visible light, Pyrex) reversibly produces species with ketene-like reactivity,[9] which can be trapped by imines to give β-lactams,[10] with nucleophiles to give amino acids and peptides,[11] with ylides to give allenes,[12] and with olefins to give cyclobutanones.[13] In the presence of Lewis acids, aldehydes react to produce β-lactones,[14] in strict analogy to standard ketene chemistry.[15] One major difference is that, while most conventional ketene chemistry involves electron poor ketenes (e.g. dichloroketene, diphenylketene), the species generated by photolysis of chromium carbene complexes provide electron rich ketene equivalents (alkoxyketenes, aminoketenes) since these donor groups are required to stabilize the carbene complex itself. To determine if these electron rich ketene species were amenable to the [3,3]-sigmatropic rearrangement pathway with allylic amine substrates, the following experiments were carried out.

Results and Discussion

Studies were initiated with (*S*)-*N*-benzyl-2-vinylpyrrolidine (**2**)[16] as substrate, since this was used in the initial report of the phenomenon.[5] Photolysis of (methoxy)(methyl) chromium carbene complex **1a** with **2** in the absence of a Lewis acid resulted in no reaction at all, not even [2 + 2] cycloaddition to the alkene. Instead unreacted **2** was recovered. The requirement for Lewis acid catalysis in these reactions is potentially problematic, since both the reactants and products can be unstable to Lewis acids.[17] After screening a variety of Lewis acids and conditions, the optimum procedure consisted of photolysis of 1 equiv of carbene complex, 1 equiv of zinc chloride or for less reactive substrates dimethylaluminum chloride, and *3* equiv of amine (1.5 equiv of which were recovered after completion) for 12 h in THF. Under these conditions, a 71% yield of lactam **3a** was obtained (eq 2). The (benzyloxy)carbene complex **1b** was similarly effective, while the more electron rich carbene complexes **1c**−**e**,[18] were much less efficient, giving only low yields of lactams **3c**−**e**, and requiring considerably longer reaction times (18−24 h vs 12 h for **1a** and **1b**).

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(4) (a) Malherbe, R.; Rist, G.; Bellus, D. *J. Org. Chem.* **1983**, *48*, 860. (b) Rosini, G.; Spineti, G. G.; Foresti, E.; Pradella, G. *J. Org. Chem.* **1981**, *46*, 2228. (c) Vedejs, E.; Buchanan, R. A. *J. Org. Chem.* **1984**, *49*, 1841.

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(6) The reaction of dichloroketene, generated by Zn reduction of trichloroacetyl chloride could be altered from [3,3]-sigmatropic manifold to the [2 + 2] cycloaddition manifold by the use of 1,2-dimethoxyethane to complex the Lewis acid zinc chloride: Johnston, B. P.; Czyzewska, E.; Oehlschlager, A. C. *J. Org. Chem.* **1987**, *52*, 3693.

(7) Kling, M. R.; McNaughton-Smith, G. A.; Taylor, R. J. K. *J. Chem. Soc., Chem. Commun.* **1993**, 1593.

(8) (a) Diederich, M.; Nubbemeyer, U. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1026. For related aza Claisen rearrangements of zwitterionic intermediates derived from the addition of tertiary allylic amines to propiolate esters see: (b) Baxter, E. W.; Labaree, D.; Ammon, H. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 7682 and references therein. (c) Vedejs, E.; Gingras, M. *J. Am. Chem. Soc.* **1994**, *116*, 579 and references therein. For Lewis acid-promoted 3-aza Cope rearrangements of *N*-alkyl-*N*-allyl enamines see: Cook, G. R.; Stille, J. R. *Tetrahedron* **1994**, *50*, 4105.

(9) Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.

(10) Dumas, S.; Hegedus, L. S. *J. Org. Chem.* **1994**, *59*, 4967 and references therein.

(11) Hegedus, L. S. *Acc. Chem. Res.* **1995**, *28*, 299 and references therein.

(12) Sestrick, M. R.; Miller, M.; Hegedus, L. S. *J. Am. Chem. Soc.* **1992**, *114*, 4079.

(13) Hegedus, L. S.; Bates, R. W.; Söderberg, B. C. *J. Am. Chem. Soc.* **1991**, *113*, 923.

(14) Colson, P. J.; Hegedus, L. S. *J. Org. Chem.* **1994**, *59*, 4972.

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(16) This material is synthesized from L-proline, see Experimental Section.

(17) This was a major problem in the synthesis of β-lactones, which required Lewis acid catalysis, see reference 14.

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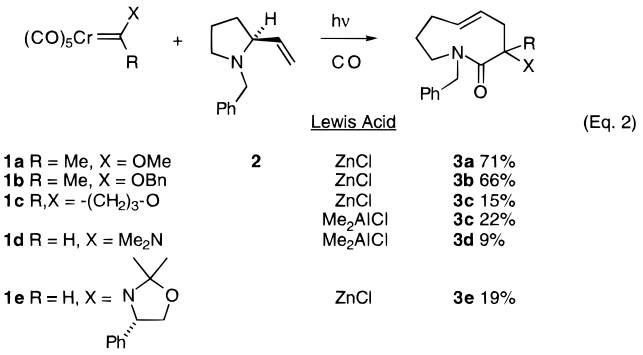
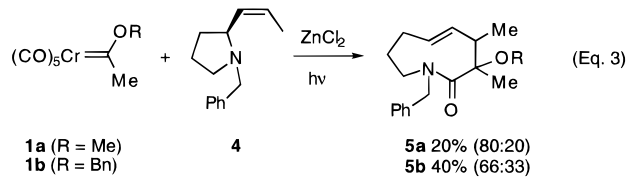
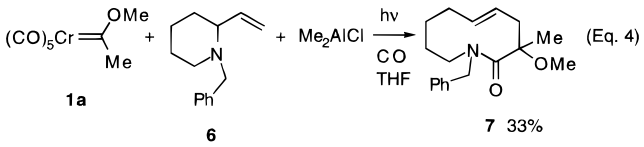


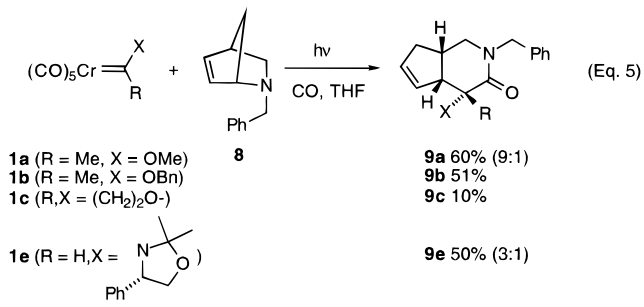
Pyrrolidine **2** is optically active (91:8, 83% ee)[19] and the question of chirality transfer to the product was next addressed. Reduction and ortho-debenzylation of **3b** (H_2 Pd/C) followed by conversion of the thus formed tertiary alcohol to its Mosher's ester showed (^{1}H, ^{19}F NMR) the product to be an 81:19 (62% de) mixture of diastereoisomeric esters,[20] indicating that some loss (≈10%) of stereochemistry had occurred. Carbene complex **1e** is itself optically active, and the chiral auxiliary therein efficiently induces asymmetry in a variety of reactions in which it participates.[11] In its reaction with pyrrolidine **2**, however, it was only marginally more diastereoselective than was the achiral alkoxycarbene complex **1b** (87:13, 74% de for **1e**, vs 81:19, 62% de for **1b**), and the yield of the reaction was quite low as well.

Substitution on the olefinic side chain reduced the overall yield of the reaction, as well as the stereoselectivity of the reaction of the bulky carbene complex **1b** (eq 3), presumably because of increased steric hindrance. Because of the mobility of the flexible nine-membered ring, NOE studies to determine the relative configurations of the two chiral centers were inconclusive.



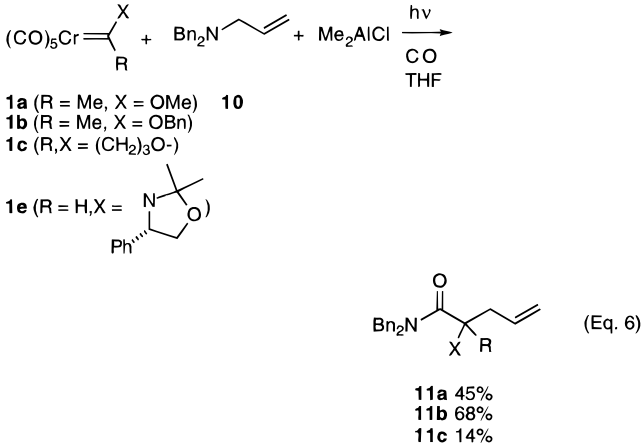
The (racemic) pipecolic acid derived six-membered analog of **2** failed to undergo reaction in the presence of the mild Lewis acid, zinc chloride. With dimethylaluminum chloride a modest yield of lactam **7** was obtained (eq 4). In contrast, the more strained (racemic) bridged bicyclic allyl amine **8** underwent efficient reaction even in the absence of Lewis acids, and even with the much less reactive aminocarbene complex **1e** (eq 5).[21] With





carbene complex **1a**, a 9:1 mixture of diastereoisomers was obtained, while a single diastereoisomer with the relative stereochemistry shown (by NOE) was produced from the reaction of the bulkier carbene complex **1b**. With the optically active carbene complex **1e**, a 3:1 mixture of diastereoisomers was obtained. Since racemic **8** was used, a 1:1 mixture of diastereoisomers would be produced if the chiral auxiliary in **1e** exercised complete control of the stereochemistry of the newly formed center and both enantiomers of **8** underwent reaction with equal efficiency. More than two diastereoisomers would be produced if stereocontrol by the chiral auxiliary were less than complete. The observed formation of only two diastereoisomers, but in a 3:1 ratio, is consistent with complete control of stereochemistry by the chiral auxiliary in **1e** and a modest degree of kinetic resolution (double diastereoselection)[22] of the racemic substrate **8**.

The diminished reactivity of the six-membered amine **6** and the enhanced reactivity of the strained bicyclic amine **8** implied that release of ring strain facilitated the rearrangement.[23] Consonant with this is the observation that acyclic allyl amines failed to react with carbene complexes **1a**−**e**, even in the presence of zinc chloride. The stronger Lewis acid dimethylaluminum chloride did promote the reaction, albeit in modest yield (eq 6).



The above results emphasize the striking similarity in behavior between classically generated ketenes and the

(18) The donor ability of the heteroatom in chromium carbene complexes has been correlated to the ^{53}Cr chemical shift, with better donors appearing at higher field (shielding); see: Hafner, A.; Hegedus, L. S.; deWeck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413. The ^{53}Cr chemical shifts for complexes **1a**−**e** respectively are: **1a** δ 187; **1b** δ 204; **1c** δ 123; **1d** δ 82; **1e** δ 135.

(19) The enantiomeric excess of **2** was determined by reduction and N-debenzylation, conversion to its Mosher's amide, and comparison of the ^{19}F-NMR spectrum of this material to that derived from racemic **2**.

(20) Dale, J. A.; Dull, D. L.; Moser, H. S. *J. Org. Chem.* **1969**, *34*, 2543. When the same reaction was carried out on racemic material, a 1:1 mixture of diastereoisomers was obtained, indicating the correct assignment of peaks for the two diastereoisomers.

(21) For reactions of diphenyl- and dichloroketene with related bicyclic amines, see: (a) Maurya, R.; Pittol, C. A.; Pryce, R. J.; Roberts, S. M. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1617. (b) Cid, M. M.; Eggnauer, U.; Weber, H. P.; Pombo-Villar, E. *Tetrahedron Lett.* **1991**, *32*, 7233.

(22) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1.

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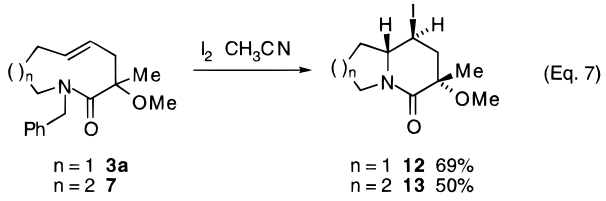
ketene-like species generated by photolysis of chromium carbene complexes. Most of the observed differences can be accommodated by the fact that the chromium-derived ketene species are substantially more electron rich than those typically generated from acid chlorides and thus require more nucleophilic reaction partners. For this reason, the much less nucleophilic allyl benzyl ether, which underwent facile reaction with dichloroketene,[3] failed to react with chromium carbene complexes under a range of conditions. In addition, the chromium-derived ketene species are generated reversibly and in low concentration, making reactions slow and compromising yields when either starting materials or products are sensitive to other reagents present (i.e. Lewis acids).

This reaction of cyclic allyl amines with chromium carbene complexes produces α-alkoxy lactams suitable for cyclization to the indolizidine and the quinolizidine alkaloid ring system, as previously reported for the dichloro analog.[5] Indeed, iodocyclization proceeded smoothly (eq 7), to give compounds **12** and **13**, with the relative stereochemistry shown (by NOE).



(Eq. 7)

Summary

The Malherbe−Bellus variant of the Claisen rearrangement has been extended to include photogenerated ketenes originating from chromium carbene complexes. The use of chromium carbene complexes installs substituents α to the carbonyl carbon other than the dichloro-substituents resulting from dichloroketenes. The reactivity of the tertiary allylic amine in this process increases with increased ring strain. Amines possessing less ring strain will participate only if a Lewis acid is present. When little or no ring strain exists, a strong Lewis acid such as Me_2AlCl is required. When the optically active *N*-benzyl-2-vinylpyrrolidine is employed in this rearrangement, the final product has an ee of 62%, suggesting the transfer of stereochemistry is not complete. The ease with which the nine- and ten-membered ring olefinic lactams are cyclized by the action of electrophiles gives a quick entry to the indolizidine and quinolizidine ring structures.

Experimental Section

General Methods. Chromium carbene complexes **1a**,[24] **1b**,[25] **1c**,[26] **1d**,[27] and **1e**[28] were prepared by previously published literature procedures as was amine **8**.[29] Irradiation of the reaction mixtures was carried out in 20-mL Pyrex pressure tubes placed at a distance of 10 cm from a Conrad-Hanovia 7825 medium-pressure mercury lamp operating at 450 W, which was placed in a water-cooled immersion well. A Conrad-Hanovia 7830-C power supply was used. ^{1}H NMR spectra were run at 300 MHz in $CDCl_3$ and referenced to Me_4Si at 0 ppm. ^{13}C NMR spectra were run at 75 MHz in $CDCl_3$ and referenced to the solvent peak at δ 77.00. Centrifugal radial-layer chromatography (Chromatotron) was performed using glass plates with silica gel 60 PF_{254} (with gypsum, E. Merck Science), and column chromatography was perfomed with ICN 32−63 μm, 60 A silica gel using flash column techniques.

(*S*)-*N*-Benzyl-2-vinylpyrrolidine (2). A 500 mL three-neck flask was equipped with two addition funnels, and H_2O (150 mL) and NaOH (3.48 g, 86.9 mmol) were placed into the flask. After cooling the flask in an ice bath to 0 °C, L-proline (10.0 g, 86.9 mmol) was added. Benzoyl chloride (10.1 mL, 87 mmol) was placed in one of the funnels, and NaOH (3.48 g, 86.9 mmol) in ∼10 mL of H_2O in the other funnel. The contents of both funnels were added simultaneously and dropwise to the flask, and the mixture was stirred at 0 °C for 2 h. The mixture was washed twice with Et_2O (100 mL) and then acidified with cold 6 M HCl (pH = 2). The aqueous layer was extracted three times with EtOAc (100 mL), and the combined EtOAc layers were washed with brine and dried over NaCl. Concentration under reduced pressure gave 17.0 g (89%) of the acid as a sticky oil: ^{1}H NMR δ 1.90 (m, 1 H), 2.05 (m, 1 H), 2.27 (m, 2 H), 3.55 (dd, 2 H, *J* = 6.9, 7.5 Hz), 4.72 (dd, 1 H, *J* = 5.8, 7.6 Hz), 7.40 (m, 3 H), 7.55 (m, 2 H), 8.71 (bs, 1 H).

While under argon, a flask containing 200 mL of dry THF was cooled to 0 °C in an ice bath, and $LiAlH_4$ (9.35 g, 158 mmol) was added in portions to the flask. The acid (27.1 g, 79 mmol) in THF (75 mL) was added over 15 min to the chilled solution, and the resulting slurry was stirred at 0 °C (1 h). The mixture was heated at reflux (16 h) and then cooled to 0 °C. Methanol (20 mL) was added, and then H_2O (10 mL) was added until bubbling ceased. 4 N NaOH (12 mL) and H_2O (40 mL) were added, and the mixture was filtered through Celite. Concentration gave 19.2 g (82%) of the alcohol as a yellow oil: ^{1}H NMR δ 1.65 (m, 2 H), 1.8−1.9 (m, 2 H), 2.27 (q, 1 H, *J* = 7.6 Hz), 2.55 (bs, 1 H), 2.7 (m, 1 H), 2.95 (m, 1 H), 3.34 (d, 1 H, *J* = 13.0 Hz), 3.40 (dd, 1 H, *J* = 2.1, 10.7 Hz), 3.64 (dd, 1 H, *J* = 3.5, 10.7 Hz), 3.95 (d, 1 H, *J* = 13.0 Hz), 7.27 (m, 5 H). This material was used without further purification.

To a 500 mL airless flask filled with argon were added CH_2Cl_2 (250 mL) and DMSO (10.7 mL, 151 mmol), and the flask was cooled to −40 °C. Oxalyl chloride (13.2 mL, 151 mmol) was added over 10 min, and the mixture was stirred for 20 min at −40 °C. The alcohol (19.2 g, 101 mmol) was added over 10 min to the chilled flask, and the mixture was stirred for 15 min. To this mixture, Et_3N (42.1 mL, 302 mmol) was added dropwise, and the resulting slurry was stirred 0.5 h. The reaction mixture was allowed to warm to rt and was washed twice with H_2O. The CH_2Cl_2 layer was dried over $MgSO_4$, and concentration gave a brown oil. The residue was triturated with Et_2O to remove any Et_3NHCl. The Et_2O solution was filtered through Celite and concentrated. The resulting oil was purified via Kugelrohr distillation, giving 15.1 g (79%) of the aldehyde as a yellow oil: ^{1}H NMR δ 1.9 (m, 4 H), 2.38 (q, 1 H, *J* = 8.3 Hz), 2.97 (m, 1 H), 3.08 (m, 1 H), 3.64 (d, 1 H, *J* = 12.9 Hz), 3.73 (d, 1 H, *J* = 12.9 Hz), 7.26 (m, 5 H), 9.28 (d, 1 H, *J* = 4.0 Hz). This material was used without further purification.

n-Butyllithium (53.1 mL, 1.57 M in hexanes) was added to a solution of methyltriphenylphosphonium bromide (29.8 g, 83.3 mmol) in 250 mL of THF at 0 °C under an argon atmosphere, and the resulting red solution was stirred at 0 °C (1 h) and then added dropwise over 1.5 h via a cannula to a flask containing the aldehyde (15.0 g, 79.4 mmol) in THF (100 mL) at 0 °C under an argon atmosphere. The mixture was stirred at 0 °C (0.5 h) and was poured into H_2O (200 mL) and EtOAc (200 mL). The aqueous layer was extracted three times with 150 mL EtOAc. The combined EtOAc layers were washed with brine and dried over $MgSO_4$. Concentration gave the crude olefin and Ph_3PO. The residue was absorbed onto SiO_2 and purifed by column chromatography (5:1 hexane: EtOAc) giving 6.95 (47%) of **2** as a yellow oil: ^{1}H NMR δ 1.7 (m, 3 H), 1.95 (m, 1 H) 2.08 (q, 1 H, *J* = 8.5 Hz), 2.78 (q, 1 H, *J* = 8.3 Hz), 2.92 (dt, 1 H, *J* = 2.7, 9.8 Hz), 3.03 (d, 1 H, *J* =

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(26) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.
(27) Dötz, K. H.; Sturm, W.; Alt, H. G. *Organometallics* **1987**, *6*, 1424.
(28) Imwinkelreid, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702.
(29) Larsen, S. D.; Grieco, P. A. *J. Am. Chem. Soc.* **1985**, *107*, 1768.

13.0 Hz), 4.01 (d, 1 H, J = 13.0 Hz), 5.12 (dd, 1 H, J = 1.9, 10.1 Hz), 5.19 (dd, 1 H, J = 1.8, 17.2 Hz), 5.78 (ddd, 1 H, J = 7.3, 9.1, 17.3 Hz), 7.27 (m, 5 H); ^{13}C NMR δ 22.0, 31.5, 53.3, 58.1, 68.4, 116.4, 128.1, 128.2, 128.9, 139.5, 141.0; IR (film) 1642 cm^{-1}.

Photoreactions: General Procedure. The photoreactions were carried out in oven-dried pressure tubes that were charged with the carbene complex, the tertiary allylic amine as a solution in THF, and the Lewis acid while under a stream of argon. The tube was fitted with a pressure head, purged three times with CO, and placed under 70−80 psi CO, and then photolysis was begun. When complete, the reaction mixture was decanted from any $Cr(CO)_6$ that had precipitated and was partitioned between aqueous saturated $NaHCO_3$ solution and EtOAc. The aqueous layer was extracted twice with EtOAc, the combined EtOAc layers were dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The residue was taken up in 1:1 hexane/EtOAc, air was bubbled through the solution, and it was exposed to light for >12 h to oxidize the remaining chromium(0) compounds. This mixture was filtered through Celite. (For those photoreactions where a Lewis acid was not employed, the base wash was omitted, and the solvent from the crude reaction mixture was removed under vacuum after photolysis.) The products were purified by radial-layer chromatography eluting with 6:1 hexanes/ethyl acetate unless otherwise stated.

8-(Benzylamino)-2-methyl-2-methoxyoct-4-enoic Acid Lactam (3a). The general procedure described above was employed using 250 mg (1.00 mmol) (methyl)(methoxy)chromium carbene complex **1a**, 561 mg (3.00 mmol) of *N*-benzyl-2-vinylpyrolidine (**2**) in ∼10 mL of dry THF, and 1 mL (1.00 mmol) of a 1 M solution of $ZnCl_2$ (in Et_2O). Photolysis for 11 h followed the general workup and radial-layer chromatography (2 mm SiO_2, 15:1 hexane/EtOAc) (recovered 274 mg **2**) gave 195 mg of **3a** (71%) as a waxy white solid (mp 72−78 °C): ^{1}H NMR δ 1.51 (s, 3 H), 1.65 (m, 1 H), 2.02 (m, 2 H), 2.37 (m, 3 H), 3.04 (dd, 1 H, J = 5.3, 14.4 Hz), 3.16 (s, 3 H), 3.87 (d, 1 H, J = 14.6 Hz), 4.44 (dd, 1 H, J = 10.3, 14.5 Hz), 5.27 (d, 1 H, J = 14.6 Hz), 5.44 (ddd, 1 H, J = 3.8, 10.7, 15.0 Hz), 5.70 (ddd, 1H, J = 5.2, 10.6, 15.9 Hz), 7.24 (m, 5 H); ^{13}C NMR δ 24.3, 27.6, 32.0, 41.7, 44.7, 49.0, 51.2, 88.7, 127.0, 128.3, 128.4, 129.7, 132.9, 138.2, 174.3; IR (film) 1615 cm^{-1}. Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 75.16; H, 8.28; N, 5.22.

8-(Benzylamino)-2-methyl-2-(benzyloxy)oct-4-enoic Acid Lactam (3b). The general procedure was followed using 104 mg (0.32 mmol) of the (methyl)(benzyloxy)chromium carbene complex **1b**, 180 mg (0.96 mmol) of allylic amine **2**, and 0.32 mL (0.32 mmol) of 1 M $ZnCl_2$ solution in Et_2O, and the reaction mixture was photolyzed for 12 h. This gave 74 mg (66%) of **3b** as a clear oil: ^{1}H NMR δ 1.60 (m, 1 H), 1.63 (s, 3 H), 1.87 (m, 2 H), 2.05 (m, 1H), 2.33 (dd, 2 H, J = 10.7, 13.0 Hz), 2.50 (dd, 1 H, J = 4.9, 12.8 Hz), 2.92 (dd, 1 H, J = 5.4, 14.5 Hz), 3.86 (d, 1 H, J = 14.6 Hz), 4.14 (d, 1 H, J = 11.3 Hz), 4.41 (dd, 1 H, J = 10.2, 14.6 Hz), 4.58 (d, 1 H, J = 11.3 Hz), 5.31 (d, 1 H, J = 14.6 Hz), 5.46 (ddd, 1 H, J = 3.8, 10.8, 15.1 Hz), 5.77 (ddd, 1 H, J = 5.0, 10.8, 15.8 Hz), 7.25 (m, 10 H); ^{13}C NMR δ 25.3, 27.8, 32.0, 42.0, 45.2, 49.2, 65.6, 88.6, 127.1, 127.2, 127.3, 128.3, 128.4, 128.5, 129.9, 133.0, 138.3, 138.4, 174.4; IR (film) 1618 cm^{-1}. Anal. Calcd for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01. Found C, 78.84; H, 7.99; N, 4.07.

7-Aza-*N*-benzyl-1-oxaspiro[4.8]tridec-11-en-6-one (3c). The general procedure was followed using 140 mg (0.53 mmol) of the cyclic chromium carbene complex **1c**, 50 mg (0.27 mmol) of *N*-benzyl-2-vinylpyrolidine (**2**), 0.27 mL (0.27 mmol) of 1 M Me_2AlCl (in hexanes), and 4 mL of freshly distilled THF. Glass beads were added to the tube, and the reaction mixture was photolyzed for 27 h. This gave 16.5 mg (21%) of **3c** as a white waxy solid: mp = 70−73 °C; ^{1}H NMR δ 1.75 (m, 5 H), 2.1 (ddd, 1 H, J = 7.0, 7.0, 7.0 Hz), 2.26 (dd, 1 H, J = 5.5, 12.5 Hz), 2.37 (m, 1 H), 2.45 (d, 1 H, J = 10.8 Hz), 2.70 (m, 1 H), 3.00 (dd, 1 H, J = 4.9, 14.8 Hz), 3.76 (m, 1 H), 3.87 (d, 1 H, J = 15.0 Hz), 3.93 (m, 1 H), 4.6 (dd, 1 H, J = 10.4, 14.9 Hz), 5.26 (d, 1H, J = 15.0 Hz), 5.46 (ddd, 1 H, J = 3.8, 11.0, 15.1 Hz), 5.77 (ddd, 1 H, J = 5.1, 10.7, 15.8 Hz), 7.25 (m, 5 H); ^{13}C NMR δ 24.5, 28.1, 32.3, 37.8, 39.5, 45.3, 48.8, 68.0, 95.0, 126.9, 127.6, 128.4, 130.3, 132.7, 138.3, 175.5; IR (film) 1608 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91. Found: C, 75.50; H, 7.94; N, 4.83.

8-(Benzylamino)-2-(dimethylamino)oct-4-enoic Acid Lactam (3d). The general procedure was followed using 187 mg (0.75 mmol) of the (dimethylamino)chromium carbene complex **1d**, 70 mg (0.37 mmol) of *N*-benzyl-2-vinylpyrolidine (**2**), 0.37 mL (0.37 mmol) of 1 M Me_2AlCl (in hexanes), and 5 mL of dry THF. Glass beads were added to the reaction mixture, and it was photolyzed 16 h. This gave 9 mg (9.4%) of **3c** as a clear oil: ^{1}H NMR δ 1.70 (m, 1H), 1.91 (m, 1H), 2.08 (m, 1H), 2.15 (s, 6H), 2.33 (m, 2H), 2.59 (m, 1H), 2.88 (dd, 1H, J = 5.4, 14.6 Hz), 3.29 (dd, 1H, J = 2.1, 4.9 Hz), 3.90 (d, 1H, J = 14.4 Hz), 4.89 (dd, 1H, J = 10.6, 14.7 Hz), 5.30 (d, 1H, J = 14.4 Hz), 5.48 (ddd, 1H, J = 3.6, 10.6, 14.9 Hz), 5.68 (ddd, 1H, J = 4.1, 11.2, 15.5 Hz), 7.27 (m, 5H); ^{13}C NMR δ 27.3, 32.2, 32.6, 43.2, 48.2, 80.0, 127.2, 128.4, 128.8, 129.0, 133.1, 138.0, 173.0 (Note: The methyl groups on the nitrogen were not evident in the ^{13}C NMR.); IR (film) 1614.4 cm^{-1}. HRMS for $C_{17}H_{24}N_2O$ M + H, calcd: 273.1967. Found: 273.1963.

8-(Benzylamino)-2-methyl-2-[(5′*S*)-2′,2′-dimethyl-5′-phenyloxazolidinyl]oct-4-enoic Acid Lactam (3e). The general procedure was followed using 122 mg (0.32 mmol) of the amino carbene complex **1e**, 180 mg (0.96 mmol) of *N*-benzyl-2-vinylpyrolidine (**2**), and 0.32 mL (0.32 mmol) of a 1 M solution of $ZnCl_2$ (in Et_2O). The reaction mixture was photolyzed 15 h, giving 24.8 mg (19%) of **3e** as a clear oil after chromatography (9:1 hexanes/ethyl acetate): ^{1}H NMR δ 1.08 (s, 3H), 1.45 (s, 3H), 1.62 (m, 1H), 2.02 (m, 4H), 2.32 (m, 1H), 3.18 (dd, 1H, J = 4.8, 14.4 Hz), 3.43 (dd, 1H, J = 9.9, 14.1 Hz), 3.63 (dd, 1H, J = 9.9, 14.1 Hz), 3.70 (dd, 1H, J = 3.3, 8.1 Hz), 3.91 (d, 1H, J = 14.4 Hz), 4.3 (t, 1H, J = 7.5 Hz), 5.30 (m, 1H), 5.31 (d, 1H, J = 14.1 Hz), 5.45 (m, 1H), 5.76 (dd, 1H, J = 3.3, 6.9 Hz), 7.25 (m, 10H); ^{13}C NMR δ 23.7, 26.2, 27.9, 31.4, 37.9, 44.1, 46.6, 57.6, 60.1, 72.3, 95.4, 126.5, 127.2, 127.3, 128.0, 128.4, 128.4, 129.1, 130.5, 131.9, 137.1, 146.8, 176.8; IR (film) 1628 cm^{-1}. Anal. Calcd for $C_{25}H_{32}N_2O_2$: C, 77.19; H, 7.97; N, 6.92. Found: C, 76.94; H, 7.84; N, 6.87.

Mosher Ester Derived from 3b. In a pressure tube, 36 mg of **3b** was rinsed in using 5 mL of ethanol and a trace amount of ethyl acetate. To this solution, 20 mg of 10% Pd/C was added, and the reaction was placed under 50 psi hydrogen and stirred. The reaction was followed by thin layer chromatography, and at 60 h, the debenzylation was complete. The reaction mixture was filtered through Celite, and the solvent was removed under vacuum. In this manner 20 mg (74%) of the alcohol was obtained as a clear oil which crystallized upon standing. This material was used without further purification: ^{1}H NMR δ 1.34 (m, 1H), 1.43 (s, 3H), 1.69 (m, 3H), 1.93 (m, 2H), 2.17 (m, 1H), 3.16 (d, 1H, J = 15.3 Hz), 3.80 (d, 1H, J = 14.9 Hz), 3.82 (m, 1H), 5.20 (bs, 1H), 5.46 (d, 1H, J = 15.1 Hz), 7.30 (m, 5H).

To a 25 mL airless flask under argon was added 100 mg of 35% KH in mineral oil. This suspension was washed three times with hexanes and was then dried under vacuum, leaving 22 mg of KH as a dry powder. To the KH powder, 12.5 mg of the alcohol from above was added as a solution in ∼3 mL of dry THF, and the mixture was stirred 20 min. To the reaction mixture was added 12 mg of the Mosher acid chloride as a solution in ∼1 mL of THF. The reaction was followed by thin layer chromatography, and within 20 min, the alcohol was consumed. The reaction mixture was taken up in 10 mL of ether. To quench the excess KH, a saturated solution (aqueous) of $NaHCO_3$ was added dropwise until bubbling ceased. The ether layer was collected and washed two times with saturated $NaHCO_3$ solution. The ether layer was dried over $MgSO_4$, and the solvent was removed under vacuum, giving ∼20 mg of the ester as a yellow oil which crystallized upon standing: ^{1}H NMR δ 1.14 (m, 1H), 1.32 (m, 1H), 1.52 (m, 3H), 1.65 (m, 2H), 1.81 (s, 3H), 2.06 (m, 1H), 2.25 (m, 1H), 2.65 (dd, 1H, J = 3.3, 18.7 Hz), 3.40 (s, 3H), 3.75 (m, 1H), 5.51 (m, 1H), 7.28 (m, 10H). ^{19}F NMR (run with external reference $CFCl_3$ at 0.00 ppm). The two diastereomers exhibited a peak at −71.07 ppm and −71.35 ppm, respectively. This work was confirmed using racemic **3b**.

***N*-Benzyl-2(*Z*)-(1′-propenyl)pyrrolidine (4).** *n*-Butyllithium (6.25 mL, 10 mmol, 1.6 M in hexane) was added to 3.71 g (10.0 mmol) of ethyl triphenylphosphonium bromide in 30 mL of THF at 0 °C, and the mixture was stirred 1 h at 0 °C. This solution was added slowly to a solution of amino aldehyde (1.80 g, 9.52 mmol) in 15 mL of THF at 0 °C, and the mixture was stirred 45 min at 0 °C, allowed to warm to room temperature, stirred 30 min, and then placed in a warm water bath and stirred 30 min. The reaction mixture was partitioned between water and EtOAc, the aqueous layer was extracted three times using EtOAc, and the EtOAc layers were combined and dried over $MgSO_4$. The solution was filtered, and the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (5:1 hexanes/ethyl acetate), giving 1.21 g (63%) of **4** as a yellow oil: ^{1}H NMR δ 1.56 (m, 1H), 1.69 (dd, 3H, J = 1.8, 6.9 Hz) 1.70 (m, 2H), 1.92 (m, 1H), 2.09 (q, 1H, J = 9 Hz), 2.93 (dt, 1H, J = 2.7, 8.7 Hz), 3.06 (d, 1H, J = 12.9 Hz), 3.15 (q, 1H, J = 8.7 Hz), 4.0 (d, 1H, J = 12.9 Hz), 5.42 (tq, 1H, J = 1.8, 9.0 Hz), 5.63 (m, 1H), 7.29 (m, 5H). ^{13}C NMR δ 13.3, 22.0, 31.0, 53.1, 58.3, 61.3, 126.3, 126.6, 128.1, 129.0, 133.2, 139.6. This material was used without further purification.

8-(Benzylamino)-2,3-dimethyl-2-methoxyoct-4-enoic Acid Lactam (5a). The general procedure was followed using 50 mg (0.2 mmol) of (methyl)(methoxy)chromium carbene complex **1a**,121 mg (0.6 mmol) of the allylic amine **4**, ∼5 mL of dry THF, and 0.2 mL (0.2 mmol) of 1 M $ZnCl_2$ (in Et_2O) under 80 psi CO, and a 12.5 h photolysis gave 12 mg (20%) of **5a** as an oil (a 2:1 mixture of diastereoisomers): ^{1}H NMR δ 1.09 (d, 3H, J = 6.6 Hz), 1.11 (d, 3H, J = 6.9 Hz), 1.46 (s, 3H), 1.53 (s, 3H), 1.65 (m, 1H), 1.90 (m, 1H), 2.09 (m, 1H), 2.43 (m, 2H), 3.05 (dd, 1H, J = 5.4, 14.1 Hz), 3.15 (s, 3H), 3.18 (s, 3H), 3.85 (d, 1H, J = 14.4), 3.90 (d, 1H, J = 15.0 Hz), 4.48 (dd, 1H, J = 10.5, 14.4 Hz), 5.31 (d, 1H, J = 15.0 Hz), 5.42 (dd, 1H), 5.54 (dd, 1H, J = 9.9, 15.6 Hz), 6.04 (dd, 1H, J = 5.7, 16.5 Hz), 7.26 (m, 5H); ^{13}C NMR δ 12.4, 12.9, 22.0, 22.1, 26.9, 27.7, 31.8, 32.5, 41.5, 44.3, 44.4, 45.2, 48.9, 49.2, 51.1, 51.3, 90.7, 91.8, 102.6, 127.0, 127.1, 127.6, 128.4, 129.2, 135.4, 137.2, 138.3, 176.1; IR (film): 1617 cm^{-1}. Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.23; H, 8.77; N, 4.87. Found: C, 75.11; H, 8.50; N, 4.85.

8-(Benzylamino)-2,3-dimethyl-2-(benzyloxy)oct-4-enoic Acid Lactam (5b). This compound was prepared in the same manner as **5a**. The quantities of reagents used were as follows: 65 mg (0.2 mmol) of (methyl)(benzyloxy)chromium carbene complex **1b**, 121 mg (0.6 mmol) of allylic amine **4**, and 0.2 mL (0.2 mmol) of 1 M $ZnCl_2$ (in Et_2O). This mixture was photolyzed 13 h and gave 28 mg (39%) of **5b** as an oil. It was obtained as a 3:1 mixture of diastereoisomers. By radial chromotography (6:1 hexanes/ethyl acetate) a single diastereoisomer of **5b** was obtained, and the spectral data for this single diastereoisomer is given: ^{1}H NMR δ 1.20 (d, 3H, J = 6.6 Hz), 1.58 (m, 1H), 1.58 (s, 3H), 1.86 (m, 1H), 1.99 (m, 1H), 2.32 (m, 1H), 2.47 (dddd, 1H, J = 6.6, 6.6, 6.6, 9.9 Hz), 2.92 (dd, 1H, J = 5.4, 14.4 Hz), 3.82 (d, 1H, J = 14.7 Hz), 4.16 (d, 1H, J = 14.4 Hz), 4.41 (dd, 1H, J = 10.2, 14.1 Hz), 4.55 (d, 1H, J = 14.4 Hz), 5.35 (d, 1H, J = 14.7 Hz), 5.45 (dd, 1H, J = 3.6, 10.2 Hz), 5.59 (dd, 1H, J = 9.9, 15.9 Hz), 7.30 (m, 10H); ^{13}C NMR δ 13.2, 23.0, 27.0, 31.7, 44.6, 44.9, 49.1, 65.2, 90.5, 126.8, 127.2, 128.2, 128.4, 128.5, 129.2, 137.3, 138.3, 138.8, 176.2; IR (film) 1614 cm^{-1}. Anal. Calcd for $C_{24}H_{29}NO_2$: C, 79.30; H, 8.04; N, 3.85. Found: C, 79.55; H, 7.86; N, 3.92.

N-Benzyl-2-vinylpiperdine (6). This was prepared from D,L-pipecolinic acid following the same procedure that was used to make **2**. Spectral data was identical to that previously reported for this compound.[30]

9-(Benzylamino)-2-methyl-2-methoxynon-4-enoic Acid Lactam (7). The general procedure was followed using 46 mg (0.18 mmol) of the (methyl)(methoxy)chromium carbene complex **1a**, 111 mg (0.55 mmol) of **6**, 0.18 mL (0.18 mmol) of 1 M Me_2AlCl (in hexanes), and ∼4 mL of freshly distilled THF. The mixture was photolyzed for 15.3 h giving 17 mg (33%) of **7** as a clear oil: ^{1}H NMR (peaks were broad because of slow dynamic processes) δ 1.3 (m, 1H), 1.55 (s, 3H), 1.68 (m, 2H), 1.98 (m, 2H), 2.39 (br, 3H), 2.95 (m, 1H), 3.15 (s, 3H), 3.79 (d, 1H, J = 14.6 Hz), 4.95 (br, 1H), 5.65 (br, 3H), 7.29 (m, 5H); ^{13}C NMR δ 22.8, 24.4, 27.5, 33.0, 41.3, 43.9, 46.8, 51.4, 126.1, 126.8, 127.1, 128.2, 128.3, 136.0, 138.0; IR (film) 1621.6 cm^{-1}. This compound was cyclized to **12** and elemental analysis was then carried out.

Bicyclic Lactam 9a. Because a Lewis acid was not necessary for this photoreaction, the modified general procedure was followed using 160 mg (0.64 mmol) of (methyl)(methoxy)chromium carbene complex **1a**, 60 mg (0.32 mmol) of bicyclic allylic amine **8**, and ∼5 mL of dry THF. The reaction mixture was photolyzed 9 h, and 53 mg (60%) **9a** was obtained as a clear oil and a 9:1 mixture of diastereoisomers: ^{1}H NMR δ 1.39 (s, 3H major diastereomer A), 1.45 (s, 3H minor diastereomer B), 1.67 (m, 2H A), 1.95 (m, 1H B), 2.49 (d, 2H, J = 12.5 Hz), 2.64 (m, 2H), 2.89 (dd, 1H, J = 1.3, 12.5 Hz), 2.96 (m, 1H B), 3.14 (s, 3H B), 3.16 (s, 3H B), 3.17 (1H B), 3.97 (dd, 1H A, J = 4.6, 12.5 Hz), 4.47 (d, 1H A, J = 14.3 Hz), 4.59 (d, 1H, J = 14.3 Hz), 5.45 (m, 1H A), 5.64 (m, 2H A and B), 5.77 (m, 1H B), 7.26 (m, 5H A, 5H B); ^{13}C NMR δ 17.6 (major diastereomer A), 18.1 (minor diastereomer B), 33.2 (A), 35.0 (B), 37.4 (B), 39.9 (A), 49.8 (B), 50.2 (A), 50.6 (B), 51.1 (A), 51.2 (A), 51.5 (B), 55.6 (A), 55.9 (B), 80.0, 127.4, 127.5, 128.4, 128.5, 128.7, 128.9, 131.6, 137.4, 170.5; IR (film) 1659.4 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.48; H, 7.66; N, 5.11.

Bicyclic Lactam 9b. The modified general procedure was followed using 209 mg (0.64 mmol) of the (methyl)(benzyloxy)-chromium carbene complex **1b**, 59 mg (0.32 mmol) of the bicyclic, allylic amine **8**, and ∼5 mL of dry THF. The reaction mixture was photolyzed 15 h, and 56 mg (51%) of **9b** was obtained as a clear oil: ^{1}H NMR δ 1.54 (s, 3H), 1.72 (d, 1H, J = 17.1 Hz), 2.52 (ddd, 1H, J = 1.8, 10.2, 17.1 Hz), 2.70 (m, 1H), 2.93 (d, 1H, J = 12.3 Hz), 3.32 (d, 1H, J = 9.3 Hz), 4.04 (dd, 1H, J = 4.5, 12.6 Hz), 4.16 (d, 1H, J = 11.1 Hz), 4.57 (m, 1H), 5.52 (m, 1H), 5.67 (m, 1H), 7.28 (m, 10H); ^{13}C NMR δ 18.4, 33.2, 39.3, 50.4, 51.5, 55.6, 66.1, 80.1, 127.5, 127.6, 127.7, 128.3, 128.4, 128.8, 128.9, 133.7, 137.4, 138.2, 170.7; IR (film): 1658 cm^{-1}. Anal. Calcd for $C_{23}H_{25}NO_2$: C, 79.49; H, 7.25; N, 4.03. Found: C, 79.27; H, 7.23; N, 3.89.

Bicyclic Lactam 9c. The modified general procedure was followed using 168 mg (0.64 mmol) of the cyclic alkoxy carbene **1c**, 59 mg (0.32 mmol) of **8**, and ∼5 mL of dry THF. A photolysis time of 18 h gave 9.1 mg (10%) of **9c** as a clear oil: ^{1}H NMR δ 1.74 (m, 2H), 1.91 (m, 1H), 2.10 (m, 1H), 2.51 (m, 2 H), 2.68 (m, 1H), 2.89 (dd, 1H, J = 3.9, 12.6 Hz), 3.26 (m, 1H), 3.90 (m, 3H), 4.51 (d, 1H, J = 14.4 Hz), 4.59 (d, 1H, J = 14.4 Hz), 5.46 (m, 1H), 5.70 (m, 1H), 7.28 (m, 5H); ^{13}C NMR δ 26.1, 31.6, 33.6, 39.4, 50.1, 50.8, 54.9, 68.5, 85.1, 127.4, 128.2, 128.4, 129.1, 133.6, 137.4, 171.9; IR (film) 1659 cm^{-1}. Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.03; H, 7.61; N, 4.78.

Bicyclic Lactam 9e. The modified procedure was followed using 244 mg (0.64 mmol) of chromium carbene complex **1e**, 59 mg (0.32 mmol) of **8**, and ∼5 mL of dry THF. A 16 h photolysis gave 62 mg (∼50% yield) of **9e** as a clear oil and as a 3:1 mixture of diastereoisomers. Spectral data given is for the single diastereomer that was cleanly separated from the mixture: ^{1}H NMR δ 1.35 (s, 3H), 1.44 (br, 2H), 1.47 (s, 3H), 2.36 (dd, 1H, J = 10.2, 12.0 Hz), 2.59 (m, 1H), 2.90 (d, 1H, J = 13.5 Hz), 3.26 (m, 1H), 3.44 (dd, 1H, J = 4.2, 13.5 Hz), 3.67 (d, 1H, J = 5.1 Hz), 3.77 (d, 1H, J = 7.8 Hz), 4.39 (d, 1H, J = 14.4 Hz), 4.59 (m, 2H), 4.97 (m, 1H), 5.09 (d, 1H, J = 3.6 Hz), 5.34 (m, 1H), 7.26 (m, 10H); ^{13}C NMR δ 23.3, 28.6, 35.2, 39.9, 50.2, 50.3, 51.5, 58.3, 60.8, 73.2, 97.1, 126.2, 126.2, 127.5, 128.1, 128.4, 128.4, 130.0, 130.0, 133.2, 137.6, 147.8, 172.7; IR (film) 1634 cm^{-1}. Anal. Calcd for $C_{21}H_{25}NO_2$: C, 77.99; H, 7.91; N, 4.33. Found: C, 78.10; H, 7.70; N, 4.47.

***N*,*N*-Dibenzyl-2-methyl-2-methoxypent-4-enamide (11a).** The general procedure was followed using 160 mg (0.64 mmol) of (methyl)(methoxy) chromium carbene complex **1a**, 76 mg (0.32 mmol) of *N*,*N*-dibenzyl allyl amine **10**, ∼5 mL of dry THF, and 0.32 mL (0.32 mmol) of 1 M Me_2AlCl (in hexanes). Glass beads were added, and the reaction mixture was photolyzed 10 h. This mixture gave 47 mg (45%) of **11a** as a clear oil: ^{1}H

(30) Vedejs, E.; Arco, M. J.; Powell, D. W.; Renga, J. M.; Singer, S. P. *J. Org. Chem.* **1978**, *43*, 4831.

NMR δ 1.47 (s, 3H), 2.59 (dd, 1H, J = 7.5, 14.7 Hz), 2.73 (dd, 1H, J = 6.6, 14.7 Hz), 3.21 (s, 3H), 4.47 (d, 1H, J = 14.4 Hz), 4.62 (d, 1H, 14.4 Hz), 4.97 (d, 1H, J = 16.5 Hz), 5.10 (m, 3H), 5.81 (m, 1H), 7.26 (m, 10H); ^{13}C NMR δ 22.2, 41.5, 48.5, 49.4, 51.9, 82.3, 118.5, 127.0, 127.2, 127.3, 128.4, 128.6, 128.7, 133.0, 137.1, 137.5, 173.7; IR (film) 1634 cm^{-1}. Anal. Calcd for $C_{21}H_{25}NO_2$: C, 77.99; H, 7.91; N, 4.33. Found: C, 78.10; H, 7.70; N, 4.47.

***N,N*-Dibenzyl-2-methyl-2-(benzyloxy)pent-4-enamide (11b).** The general procedure was followed using 209 mg (0.64 mmol) of the (methyl)(benzyloxy) chromium carbene complex **1b**, 76 mg (0.32 mmol) of the *N,N*-dibenzyl allyl amine **10**, and 0.32 mL (0.32 mmol) of 1 M Me_2AlCl (in hexanes). This mixture was photolyzed 16.5 h which gave 87 mg (68%) of **11b** as a clear oil: ^{1}H NMR δ 1.55 (s, 3H), 2.67 (dd, 1H, J = 7.5, 14.7 Hz), 2.86 (dd, 1H, J = 6.6, 14.7 Hz), 4.39 (s, 2H), 4.49 (d, 1H, J = 14.1 Hz), 4.63 (d, 1H, J = 14.4 Hz), 4.94 (d, 1H, J = 16.8 Hz), 5.04 (d, 1H, J = 16.8 Hz), 5.15 (m, 2H), 5.89, (m, 1H) 7.23 (m, 15H); ^{13}C NMR δ 23.0, 41.8, 48.6, 49.6, 66.1, 82.1, 118.6, 126.8, 127.1, 127.4, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 133.1, 136.9, 137.5, 137.7, 173.7; IR (film): 1634 cm^{-1}; HRMS for $C_{27}H_{29}NO_2$ M + H, calcd: 400.2277. Found: 400.2273.

2-(*N,N*-Dibenzylcarbamoyl)-2-allyltetrahydrofuran (11c). The general procedure was followed using 168 mg (0.64 mmol) of chromium carbene complex **1c**, 76 mg (0.32 mmol) of the *N,N*-dibenzyl allyl amine **10**, and 0.32 mL (0.32 mmol) of 1 M Me_2AlCl (in hexanes). This gave 16 mg (14% yield) of **41** as a clear oil: ^{1}H NMR δ 1.89 (m, 3H), 2.59 (m, 2H), 2.85 (m, 1H), 3.73 (m, 2H), 3.98 (d, 1H, J = 14.4 Hz), 4.40 (d, 1H, J = 15.9 Hz), 5.07 (m, 3H), 5.38 (d, 1H, J = 15.9 Hz), 5.81 (m, 1H), 7.25 (m, 10H); ^{13}C NMR δ 25.3, 35.2, 43.5, 48.8, 50.4, 69.8, 89.0, 118.7, 126.9, 127.1, 127.2, 128.3, 128.4, 128.5, 128.5, 137.7, 137.6, 137.9, 174.3; IR (film) 1632 cm^{-1}. Anal. Calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.59; H, 7.53; N, 4.04.

Bicyclic Lactam 12. In a 25 mL round bottom flask, 100 mg (0.37 mmol) of **3a** was dissolved in ~10 mL of CH_3CN. To this solution, 244 mg of I_2 was added, and the mixture was stirred for 2 h. The reaction mixture was partitioned between EtOAc and a 10% $Na_2S_2O_3$ solution (aqueous), the aqueous layer was extracted twice with EtOAc, the EtOAc layers were combined, dried over $MgSO_4$, filtered through Celite, and the solvent was removed under vacuum yielding a yellow-brown oil. The oil was purified by radial chromatography giving 79 mg (69%) of **12** as yellow-white crystals: mp 45−51 °C; ^{1}H NMR δ 1.35 (s, 3H), 1.57 (m, 1H), 1.78 (m, 1H), 1.97 (m, 1H), 2.25 (t, 1H, J = 13.2 Hz), 2.36 (m, 1H), 2.67 (d, 1H, J = 13.8 Hz), 3.29 (s, 3H), 3.61 (m, 3H), 4.12 (m, 1H); ^{13}C NMR δ 20.6, 21.1, 21.4, 34.4, 46.4, 49.0, 51.8, 67.2, 76.2, 167.4; IR (film) 1644 cm^{-1}. Anal. Calcd for $C_{10}H_{16}NO_2I$: C, 38.85; H, 5.22; N, 4.53. Found: C, 39.00; H, 5.17; N, 4.50.

Bicyclic Lactam 13. In a 10 mL round bottom flask, 17 mg (0.06 mmol) of **3b** was dissolved in ~5 mL of dry CH_3CN. To this flask was added 40 mg (0.16 mmol) of iodine, and the mixture was stirred for 2 h. The reaction mixture was partitioned between EtOAc and a 10% $Na_2S_2O_3$ solution (aqueous), and the aqueous layer was extracted twice with EtOAc. The EtOAc layers were combined, dried over $MgSO_4$, and filtered through Celite, and the solvent was removed under vacuum yielding a clear oil. The oil was purified by radial chromatography, giving 9.6 mg (50%) of **13** as a white crystaline solid: mp 84−85 °C; ^{1}H NMR δ 1.3 (m, 2H), 1.33 (s, 3H), 1.68 (m, 2H), 1.87 (m, 1H), 2.36 (m, 3H), 2.58 (dd, 1H, J = 4.0, 13.6 Hz), 3.26 (s, 3H), 3.48, (ddd, 1H, J = 2.5, 9.2, 11.6 Hz), 4.44 (ddd, 1H, J = 4.0, 9.7, 13.6 Hz), 4.69 (m, 1H); ^{13}C NMR δ 20.2, 23.7, 24.2, 25.5, 33.1, 42.9, 46.9, 51.6, 65.8, 76.4, 167.2; IR (film) 1631 cm^{-1}. Anal. Calcd for $C_{11}H_{18}NO_2I$: C, 40.88; H, 5.61; N, 4.33. Found: C, 40.97; H, 5.56; N, 4.28.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of compounds **3d** and **11b**, and tables of NOE data for compounds **5b**, **9b**, and **12** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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