benzene under argon. The flask was then immersed in a preheated oil bath and refluxed for 50 min. After the solution was cooled, 20 μL of DBU was added and the reaction mixture stirred for 15 min. The solvent was then removed and the mixture purified by flash silica gel chromatography (10–50% EtOAc/hexane) to afford 17.5 mg (0.051 mmol, 84%) of α,β-unsaturated ester **13** as a colorless oil: $R_f$ = 0.6 (50% EtOAc/hexane); $^1$H NMR ($CDCl_3$) δ 7.15 (t, $J$ = 4.1 Hz, 1 H), 4.52–4.47 (m, 1 H), 4.35–4.28 (m, 2 H), 3.74 (s, 3 H), 2.58–2.48 (m, 3 H), 2.29 (ddd, $J$ = 19.3, 4.3, 1.1 Hz, 1 H), 2.04–1.91 (m, 2 H), 0.87 (s, 9 H), 0.07 (s, 3 H), 0.06 (s, 3 H); $^{13}$C NMR ($CDCl_3$) 180.6, 165.8, 141.0, 130.3, 65.9, 63.6, 51.9, 44.0, 39.3, 34.7, 34.2, 25.8, 18.0, -4.8; IR ($CHCl_3$) 1759, 1709 cm$^{-1}$; HRMS $m/e$ ($M^+$ - $t$-Bu) calcd for $C_{17}H_{28}O_5Si$ 283.1002, found 283.1005.

**3-(*tert*-Butyldimethylsiloxy)-2-pyrone.** A 25-mL round-bottomed flask was charged with 125.4 mg (1.12 mmol) of 3-hydroxy-2-pyrone (Aldrich Chemical Co., 2,3-dihydroxypyridine) and dissolved in 3 mL of $CH_2Cl_2$ under argon. To this was added 0.16 mL (1.3 mmol, 1.2 equiv) of 2,6-lutidine followed by 0.31 mL (1.3 mmol, 1.2 equiv) of TBDMS-OTf. This was stirred for 1 h, and then the solvent was removed. Purification by silica gel chromatography (10% EtOAc/hexane) gave 170.2 mg (0.75 mmol, 67%) of the silyl ether as a volatile light yellow oil: $^1$H NMR ($CDCl_3$) δ 7.17 (dd, $J$ = 5.1, 1.8 Hz, 1 H), 6.61 (dd, $J$ = 7.0, 1.8 Hz, 1 H), 6.10 (dd, $J$ = 7.0, 5.1 Hz, 1 H), 0.97 (s, 9 H), 0.24 (s, 6 H); $^{13}$C NMR ($CDCl_3$) δ 160.9, 144.0, 142.4, 122.2, 106.0, 25.5, 18.4, -4.6; IR ($CHCl_3$) 1759, 1709 cm$^{-1}$; HRMS $m/e$ ($M^+$ - $t$-Bu) calcd for $C_{24}H_{34}O_5SSi$ 405.1192, found 405.1186.

**Acknowledgment.** We thank the NIH (Grant GM 30052) for financial support.

**Registry No.** **1**, 98061-54-2; *endo*-**2**, 141510-29-4; *exo*-**2**, 141553-87-9; *endo*-**3**, 141510-30-7; *exo*-**3**, 141553-88-0; *endo*-**4**, 141510-31-8; *exo*-**4**, 141553-89-1; *endo*-**5**, 141510-32-9; *exo*-**5**, 141553-90-4; *endo*-**6**, 141510-33-0; *exo*-**6**, 141553-91-5; *endo*-**7**, 141510-34-1; *exo*-**7**, 141553-92-6; *endo*-**8**, 141510-35-2; *exo*-**8**, 141553-93-7; *endo*-**9**, 141510-36-3; *exo*-**9**, 141553-94-8; *endo*-**10**, 141526-86-5; *exo*-**10**, 141610-01-7; **11**, 141510-37-4; **12**, 141510-38-5; **13**, 141510-39-6; $Ph_2SO_2$, 127-63-9; $PhCO_2Me$, 93-58-3; PhBr, 108-86-1; $Ph_2S$, 139-66-2; $PhOSi(Me)_3$, 1529-17-5; PhOH, 108-95-2; dihydro-3-methylene-2(3*H*)-furanone, 547-65-9; 3-(*tert*-butyldimethylsiloxy)-2-pyrone, 141510-40-9; 3-hydroxy-2-pyrone, 496-64-0; nitroethylene, 3638-64-0; acrylonitrile, 107-13-1; acrolein, 107-02-8; methacrolein, 78-85-3; methyl vinyl ketone, 78-94-4; methyl acrylate, 96-33-3; benzyl acrylate, 2495-35-4; methyl methacrylate, 80-62-6; 3-(*p*-toluenesulfonyl)-2-pyrone, 99268-87-8; 3-carbomethoxy-2-pyrone, 25991-27-9; 3-bromo-2-pyrone, 19978-32-6; 2-pyrone, 504-31-4; benzene, 71-43-2.

**Supplementary Material Available:** Characterization of new compounds by NMR (12 pages). This material is contained in many 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.

# Diels–Alder Cycloadditions Using Nucleophilic 2-Pyridones. Regiocontrolled and Stereocontrolled Synthesis of Unsaturated, Bridged, Bicyclic Lactams

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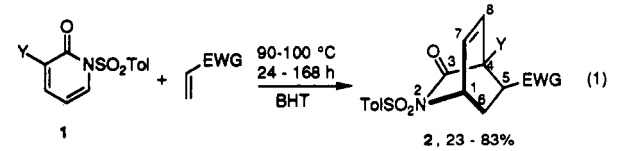
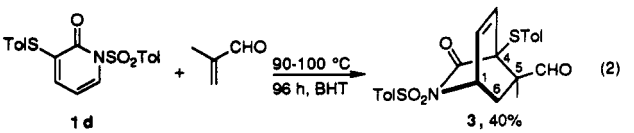
Captodative 3-oxy- and 3-(tolylthio)-1-tosyl-2-pyridones **1a–1d** are shown to be reactive as nucleophilic dienes undergoing 2 + 4-cycloadditions with various electrophilic alkenes under sufficiently *mild thermal conditions* (90–100 °C) that the initial bicylic lactam adducts can be isolated on gram scale in fair to very good yields (23–83%) *without loss of an isocyanate* from the heteroatom bridge. These bicyclic adducts are formed with complete regiocontrol and stereocontrol. For pyridone sulfide **1d**, these Diels–Alder cycloadditions are the first examples of a captodative unsaturated sulfide acting as an enophile. NMR data ($^{13}$C) are presented correlating the electron density in the pyridone diene systems with their Diels–Alder reactivity, and some transformations of the bicyclic lactam adducts are shown to illustrate the value and versatility of these richly functionalized synthetic intermediates.

## Introduction

A few years ago this laboratory reported the first examples of efficient 2 + 4-cycloadditions of electron-poor 1,3-disulfonyl-2-pyridones with electron-rich dienophiles such as vinylic ethers.[1] To complement such *inverse*-electron-demand Diels–Alder reactions, we now report *normal*-electron-demand 2 + 4-cycloadditions of captodative 1,3-disubstituted 2-pyridones under thermal (i.e., not high-pressure) conditions with electron-poor dienophiles such as $CH_2$=C(R)EWG, in which the R group is hydrogen or methyl and the electron-withdrawing-group (EWG) is nitro, aldehyde, ester, or ketone (eqs 1 and 2). These successful cycloadditions, stopping at the initial bicyclic lactam stage without extrusion of an isocyanate from the heteroatom bridge,[2] are *among the few examples*




| Y | EWG |
|---|---|
| a, MeO | g, $NO_2$ |
| b, $PhCH_2O$ | h, CHO |
| c, t-$BuMe_2SiO$ | i, $CO_2Me$ |
| d, TolS | j, COMe |




*in which normally highly aromatic 2-pyridones* (more aromatic than 2-pyrones)[3] *have entered as enophiles into*

(1) Posner, G. H.; Switzer, C. *J. Org. Chem.* **1987**, *52*, 1644 and references therein to 2 + 4-cycloadditions of 2-pyridones.

0022-3263/92/1957-4088$03.00/0 

*thermally mild (90–100 °C) and therefore practical 2 + 4 cycloadditions.*[4] We report also $^{13}C$ NMR chemical shift data for 3-Y-substituted-1-(*p*-toluenesulfonyl)-2-pyridones correlating electron density in the pyridone diene system with 2 + 4 cycloaddition reactivity toward electron-poor dienophiles. The cycloadducts, formed regiospecifically and stereospecifically, are synthetically versatile, unsaturated, bridged, bicyclic lactams. Some transformations of these bicyclic lactams into polyfunctionalized cyclohexenes are presented to illustrate the high value of these synthetic building units.

## Results and Discussion

In Table I are summarized some $^{13}C$ NMR chemical shift data for several 3-Y-1-(*p*-toluenesulfonyl)-2-pyridones; these assignments were made using C–H coupled $^{13}C$ NMR spectroscopy.[5] For comparison, $^{13}C$ NMR data for similarly Y-substituted benzenes are listed.[6]

The data in Table I deserve comment. First, compared to the corresponding 2-pyrones discussed in the accompanying article,[7] these 2-pyridones are considerably more aromatic as expected,[3] with $^{13}C$ NMR chemical shift values differing from those of Y-benzenes by only relatively small amounts. Second, whereas a 3-arenesulfonyl substituent is strongly electron-withdrawing, a 3-oxygen substituent is strongly electron-releasing. Because we already showed that 3-(arenesulfonyl)-2-pyridones cycloadd to *nucleophilic* alkenes,[1] it was our expectation that 3-oxygen-substituted 1-tosyl-2-pyridones would cycloadd to *electrophilic* alkenes. The commercial availability of 3-hydroxy-2-pyridone (2,3-dihydroxypyridine) allowed very convenient access to 3-oxygen-substituted 1-tosyl-2-pyridones **1a** and **1c**, and the commercial availability of 3-bromopyridine enabled easy preparation of 3-(toluenethio)-2-pyridone **1d** (eqs 3–5).

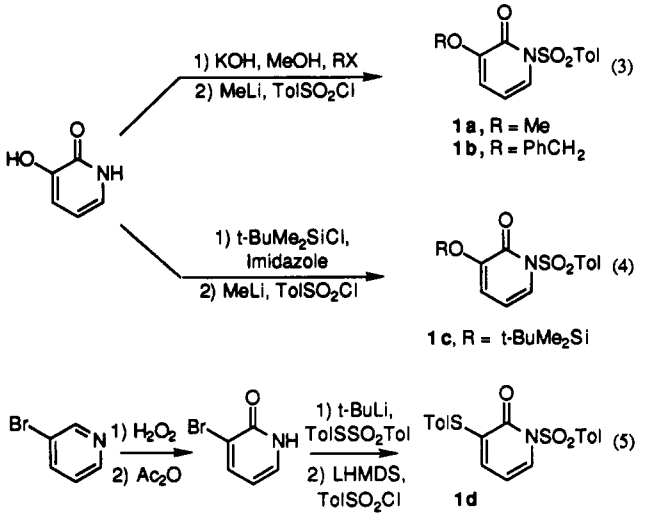
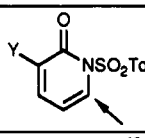
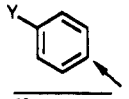



**Table I. $^{13}C$ NMR Chemical Shift Data**

| Y | $^{13}C$ (ppm) | $^{13}C$ (ppm) |
|---|---|---|
| $ArSO_2^-$ | 138.0[a] | 133.6[b] |
| $H^-$ | 131.7 | 128.5 |
| $Br^-$ | 131.3 | 127.0 |
| $ArS^-$ | 126.2[a] | 126.9[b] |
| $RMe_2SiO^-$ | 123.0[c] | 121.4[d] |
| $PhCH_2O^-$ | 123.0 | |
| $MeO^-$ | 122.4 | 120.7 |

[a] Ar = Tol. [b] Ar = Ph. [c] R = *t*-Bu. [d] R = Me.

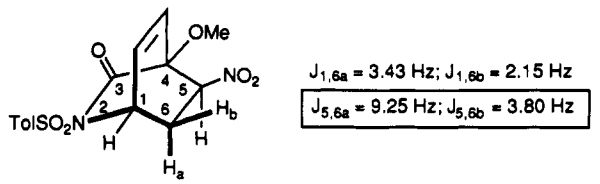
**Table II. Yields (%) of Cycloadduct 2 According to eq 1**

| | EWG | | | |
|---|---|---|---|---|
| Y | $NO_2$ **g** | CHO **h** | $CO_2Me$ **i** | COMe **j** |
| **a**, MeO | 80 | 69 | 57 | 42 |
| **b**, $PhCH_2O$ | 78 | 83 | trace | |
| **c**, *t*-$BuMe_2SiO$ | 69 | 70 | 23 | 56 |
| **d**, TolS | 45 | 42 | trace | |

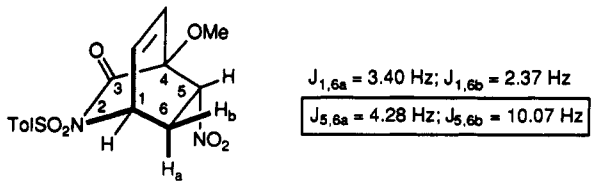
Table II summarizes results of the successful cycloadditions according to eq 1 in which butylated hydroxytoluene (BHT) was used to retard polymerization of the electrophilic alkenes in all cases except with nitroethylene. In every case, bicyclic lactam **2** was formed *exclusively* with the regiochemistry and the stereochemistry shown as determined by 400-MHz $^1H$ NMR spectroscopy of the crude reaction products. Both regiochemistry and stereochemistry were established in analogy with excellent literature precedent[1,8] by $^1H$ NMR spectroscopy showing a 4,5-disubstituted (but not a 4,6-disubstituted) bicyclic lactam with $J_{1,6a}$ larger than $J_{1,6b}$ and $J_{5,6a}$ larger than $J_{5,6b}$; $^1H$ NMR data for nitro lactam methyl ether **2ag** are shown here (in which the nitro group is endo to the 2-carbon olefinic bridge). Furthermore, exposure of this nitro-substituted bicyclic lactam to ammonium formate produced exclusively and quantitatively the epimeric nitro compound (*epi*-**2ag**) with the $^1H$ NMR characteristics shown. Note that $J_{5,6a}$ is smaller than $J_{5,6b}$ in the epimerized *epi*-**2ag**. Analogous results and NMR data were obtained also with bicyclic nitro-bearing benzyloxy lactam **2bg** and tolylthio lactam **2dg** (see Experimental Section). No rationale is obvious at present to explain the unidirectional epimerization of the initially formed *endo*-nitro cycloadducts **2ag**, **2bg**, and **2dg** into the corresponding exo epimers. Interestingly, simply on standing at ambient temperature in $CDCl_3$ for 17 days, *endo*-nitro-substituted bicyclic lactam **2ag** underwent clean and almost complete epimerization into *epi*-**2ag**.[8c]

To examine what effect, if any, a smaller-sized but less electron-withdrawing 1-sulfonyl group would have on the cycloadditions, 1-*mesyl*-3-methoxy-2-pyridone was prepared in the same way as the corresponding 1-*tosyl* derivative. 1-*Mesyl*-3-methoxy-2-pyridone, however, underwent an N → O mesyl shift (50% complete) at 90–100 °C for 40 h, whereas the corresponding 1-*tosyl* system did not rearrange significantly (i.e., <5%) under these conditions.[9,10] A competition experiment between equimolar

(2) Acheson, R. M.; Tasker, P. A. *J. Chem. Soc. C* **1967**, 1542.
(3) (a) Eldridge, J. A.; Jackman, L. M. *J. Chem. Soc.* **1961**, 859. (b) Aihara, J. *J. Am. Chem. Soc.* **1970**, *98*, 2750. (c) Bird, C. W. *Tetrahedron* **1986**, *42*, 89.
(4) (a) Herdeis, C.; Hartke, C. *Heterocycles* **1989**, *29*, 287. (b) Nakano, H.; Tomisawa, H.; Hongo, H. *J. Chem. Soc., Chem. Commun.* **1990**, 1775. (c) Tomisawa, H.; Nakano, H.; Hongo, H. *Heterocycles* **1990**, *30*, 359. For reviews see: (d) Shusherina, N. P. *Russ. Chem. Rev.* **1974**, *43*, 851. (e) Katritzky, A. R.; Dennis, N. *Chem. Rev.* **1989**, *89*, 827.
(5) Imagawa, T.; Haneda, A.; Kawanisi, M. *Org. Magn. Reson.* **1980**, *13*, 244.
(6) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH: Weinheim, FDR, 1987; pp 256–257.
(7) Posner, G. H.; Nelson, T. D.; Kinter, C. M.; Johnson, N. *J. Org. Chem.* **1992**, *57*, accompanying article; for a review of cycloadditions of 2-pyrones and 2-pyridones, see: Afarinkia, K.; Vinader, V.; Nelson, T. D.; Posner, G. H. *Tetrahedron Rep.*, in press.
(8) (a) Harano, K.; Aoki, T.; Eto, M.; Hisano, T. *Chem. Pharm. Bull.* **1990**, *38*, 1182. (b) Herdeis, C.; Hartke-Karger, C. *Liebigs Ann. Chem.*, **1991**, 99. (c) Shusherina, N. P. Pilipenko, V. S.; Kireeva, O. K.; Geller, B. I.; Stepanyants, A. U. *J. Org. Chem. USSR* **1980**, *16*, 2047.
(9) (a) Abramovitch, R. A.; Knaus, G. N. *J. Org. Chem.* **1975**, *40*, 883. See also: (b) Hamer, M.; Lira, E. P. *J. Heterocycl. Chem.* **1972**, *9*, 215.
(10) See also: *Pyridine and Its Derivatives*, Abramovitch, R. A., Ed.; Interscience: New York, 1974; Supplement part III, p 744.




**2ag**



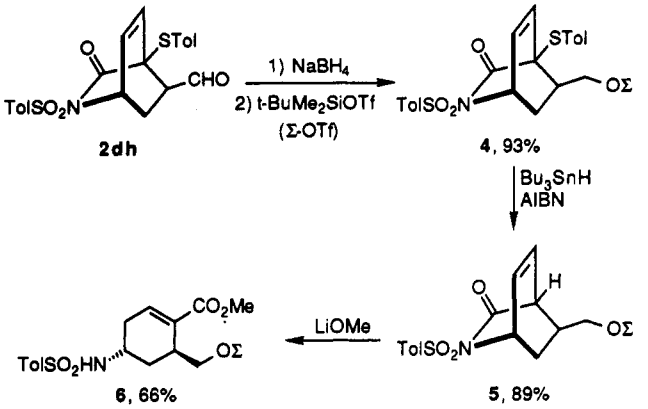

epi-**2ag**

amounts of 1-*mesyl*- and 1-*tosyl*-3-methoxy-2-pyridone with excess methyl vinyl ketone showed a 1.5:1 selectivity for 1-*mesyl*-2-pyridone cycloaddition over 1-*tosyl*-2-pyridone cycloaddition; this small rate advantage in cycloaddition, however, was substantially outweighed by the large N → O rearrangement rate disadvantage using the 1-mesyl-2-pyridone. Rearrangement of the tosyl group from N → O was even more prominent in 3-*unsubstituted* 1-tosyl-2-pyridone; for example, at 133 °C for 21 h, 1-tosyl-2-pyridone rearranged 73% to 2-(tosyloxy)pyridine whereas under these conditions 3-methoxy-1-tosyl-2-pyridone (**1a**) rearranged only 27% to 3-methoxy-2-(tosyloxy)pyridine. Even more striking was the absence of any N → O rearrangement when 3-(tolylthio)- and 3-siloxy-1-tosyl-2-pyridones **1d** and **1c** were subjected to similar reaction conditions. Thus, a large 3-substituent effectively inhibits N → O tosyl migration in 1-tosyl-2-pyridones. In comparison, *N-acyl*-2-pyridones have been reported to undergo rapid N → O rearrangement into 2-acyloxy pyridines even at room temperature.[11]

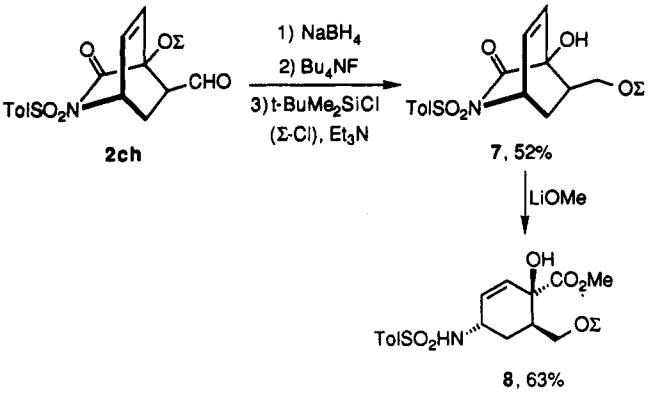
A separate study of steric and electronic effects on cycloaddition rate was done comparing 3-*methoxy*- with 3-*siloxy*-1-tosyl-2-pyridones **1a** and **1c**. Equimolar amounts of these pyridones *reacted at roughly equal rates* with an excess of methyl acrylate and separately with an excess of methyl vinyl ketone at 90–100 °C as judged by $^1$H NMR determination of the ratios of remaining reactant pyridones as well as ratios of cycloadducts. Interestingly, a similar competition experiment comparing 3-*methoxy*- with 3-(*tolylthio*)-2-pyridones **1a** with **1d** showed 3-(tolylthio)-2-pyridone **1d** to react about 1.5 times faster than 3-methoxypyridone **1a** with acrolein. Finally, unlike reactive 3-(*tolylthio*)pyridone **1d**, 3-*bromo*-1-tosyl-2-pyridone was quite unreactive toward electrophilic acrolein.

Several electron-poor alkenes failed to cycloadd with one or more of the 2-pyridones **1a–1d** even upon prolonged heating at 90–100 °C or, in a few cases, even at 130 °C. Examples of such unreactive alkenes include acrylonitrile, 2-chloroacrylonitrile, phenyl vinyl sulfone, α-methylene-γ-butyrolactone, vinyltriphenylphosphonium bromide, diethyl methylenemalonate, 3,3-dimethylacrolein, and maleic anhydride. Also unreactive were 2-pyridones lacking *either* a 1-tosyl group or a 3-heteroatom substituent; for example, 1-*methyl*-3-(tolylthio)-2-pyridone failed to cycloadd with methacrolein whereas the corresponding captodative 1-*tosyl*-3-(tolylthio)-2-pyridone (**1d**) did react (eq 2), and 1-tosyl-2-pyridone failed to cycloadd with

**Scheme I**




**Scheme II**




acrolein whereas the corresponding captodative 1-tosyl-3-(tolylthio)-2-pyridone (**1d**) did react. Even at high pressures (10–11 Kbar)[1] for several days at ambient temperature, 3-(tolylthio)-2-pyridone **1d** failed to cycloadd to α-methylene-γ-butyrolactone, and likewise 3-(benzyloxy)-2-pyridone **1b** failed to cycloadd to methyl acrylate.

1-Tosyl-3-heteroatom-2-pyridones **1a–1d** can be considered as captodative dienes in which $C_3$ is geminally substituted by an electron-donor heteroatom and also an electron-withdrawing carbonyl (amide) group.[12] The successful 2 + 4-cycloadditions shown in Table II, along with those reported in the accompanying 2-pyrone article,[7] represent *the first examples of captodative unsaturated ethers and thioethers acting as enophiles.*[13]

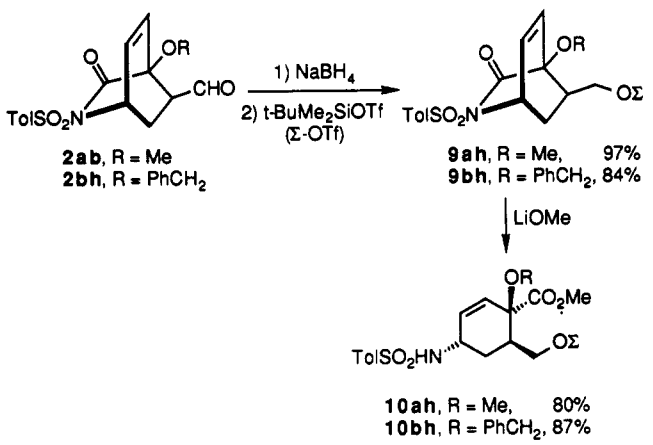
To illustrate the high value and versatility of these bicyclic lactams, formed as single regioisomers and exclusively as endo-diastereomers, several ring-opening transformations were performed. Bicyclic lactam aldehyde **2dh** was reduced and O-silylated to form bicyclic lactam **4** (Scheme I). Reductive removal of the bridgehead tolylthio group under neutral radical conditions was achieved smoothly using tributyltin hydride and azobisisobutyronitrile (AIBN) to form bridgehead-unsubstituted bicyclic lactam **5**; this lactam represents a formal regiospecific cycloaddition of *N*-tosyl-2-pyridone itself to acrolein, a reaction that cannot be achieved thermally because N → O tosyl migration occurs prior to any possible cycloaddition. *Thus, 3-(tolylthio)-N-tosyl-2-pyridone (**1d**) is a highly reactive synthetic equivalent of N-tosyl-2-pyridone in thermal (i.e., not high-pressure) Diels–Alder*

(11) (a) McKillop, A.; Zalesko, M.-T.; Taylor, E. C. *Tetrahedron Lett.* **1968**, 4945. See also: (b) Singth, P. A.; Jonssen, M. J. *Ibid.* **1971**, 4223. (c) See ref 10c, pp 776–784.

(12) (a) Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148. (b) Reyer, A.; Aguilar, R.; Muñoz, A. A.; Zwick, J.-C.; Rubio, M.; Escobar, J.-L.; Soriano, M.; Toscano, R.; Tomariz, R. *J. Org. Chem.* **1990**, *55*, 1024.

(13) For an excellent review with leading references, see: De Lucchi, O.; Pasquato, L. *Tetrahedron* **1988**, *44*, 6755.

**Scheme III**




*cycloadditions with acrolein.* Methanolysis of the lactam bridge converted **5** into regiospecifically and stereospecifically substituted cyclohexene **6** that we are currently converting into a 1$\alpha$-(hydroxymethyl)-3$\beta$-amino vitamin $D_3$ derivative for biological evaluation.[14]

In a similar fashion (Scheme II), bicyclic lactam aldehyde silyl ether **2ch** was reduced, desilylated, and protected selectively as the primary alcohol silyl ether **7** using *tert*-butyldimethylsilyl chloride/4-(dimethylamino)pyridine (DMAP). Methanolysis of the lactam bridge produced regiospecifically and stereospecifically tetrasubstituted cyclohexene **8**. All attempts to deoxygenate tertiary alcohols **7** and **8** were unsuccessful, including, for example, radical reaction of the xanthate derived from bicyclic tertiary alcohol **7**. Likewise, bicyclic tertiary alcohol ethers **9ah** and **9bh** were prepared according to Scheme III. Methanolysis of the bicyclic lactam bridge gave tetrasubstituted cyclohexenes **10ah** and **10bh** as single diastereomers. All attempts to deoxygenate tertiary alcohol ethers **9** and **10** were unsuccessful, including $LiAlH_4/TiCl_4$,[15] $Zn/NH_4Cl$,[16] $LiBH_4$,[17] $LiBEt_3H$,[18] and $HCOONH_4$ using a palladium catalyst.[19]

## Conclusion

1-Tosyl-3-heteroatom-2-pyridones **1a–1d** have been shown for the first time to be reactive captodative dienes that undergo effective thermal 2 + 4-cycloadditions with several unencumbered electron-poor alkenes. Reaction conditions are sufficiently mild so that the bicyclic lactam adducts can be isolated on gram scale in fair to very good yields without loss of an isocyanate from the lactam bridge. These bicycloadducts, formed as single regioisomers and exclusively as endo diastereomers, represent easily prepared, compact, and polyfunctional synthetic intermediates of considerable value.

## Experimental Section

**General Experimental Data.** See ref 7 for details.

**A. Preparation of Pyridones. 3-Methoxy-1-(4′-methylbenzenesulfonyl)-2-pyridone (1a).** To a stirred solution of 3-methoxy-2-pyridone (165 mg, 1.32 mmol) in dry THF (10 mL), maintained at 0 °C under a dry nitrogen atmosphere, was added MeLi (1.4 M solution in $Et_2O$, 1.0 mL, 1.4 mmol). After 20 min, 4-methylbenzenesulfonyl chloride (255 mg, 1.34 mmol) was added as a THF solution (15 mL). After 16 h the solution was poured into water (50 mL) and was extracted with $Et_2O$ (2 × 100 mL). Drying ($Na_2SO_4$) followed by evaporation of solvent under reduced pressure and flash chromatography (silica gel, $Et_2O$) of the residue afforded white solid **1a** (285 mg, 78%): mp 146–147 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 2.42 (3 H, s, $CH_3Ar$), 3.73 (3 H, s, $CH_3O$), 6.18 (1 H, t, $J_{5-6} = J_{5-4} = 7.4$ Hz, pyridone H-5), 6.51 (1 H, dd, $J_{4-5} = 7.4$ Hz, $J_{4-6} = 1.0$ Hz, pyridone H-4), 7.32 (2 H, d, $J = 7.9$ Hz, tosyl H-3), 7.73 (1 H, dd, $J_{6-5} = 7.4$ Hz, $J_{6-4} = 1.0$ Hz, pyridone H-6), 8.02 (2 H, d, $J = 7.9$ Hz, tosyl H-2); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.81 ($CH_3Ar$), 56.20 ($CH_3O$), 105.29 (C-5), 112.52 (C-4), 122.36 (C-6), 129.49 (C-2′), 130.11 (C-3′), 133.35 (C-1′), 146.21 (C-3), 150.94 (C-4′), 156.20 (C-2); IR ($CHCl_3$) 1673 (C=O), 1620 cm$^{-1}$; MS *m/e* (EI) 279 ($M^+$, 13), 215 (39), 214 (20), 124 (27), 96 (26), 92 (22), 91 (100), 65 (24); *m/e* (CI/ammonia) 280 ($MH^+$, 100). Anal. Calcd for $C_{13}H_{13}NO_4S$: C, 55.90; H, 4.69; N, 5.01. Found: C, 55.83; H, 4.72; N, 5.00.

**1-(4′-Methylbenzenesulfonyl)-3-(phenylmethoxy)-2-pyridone (1b).** This compound was prepared in accord with the general procedure described above. Thus, starting from a solution of 3-(benzyloxy)-2-pyridone[20] (1.29 g, 6.41 mmol) in dry THF (75 mL) and using lithium hexamethyldisilazide (LHMDS) (1.0 M solution in hexane, 9.61 mL, 9.61 mmol) and 4-methylbenzenesulfonyl chloride (2.44 g, 12.82 mmol) we obtained after crystallization ($CH_2Cl_2/Et_2O$ (1:2) v/v) white solid **1b** (1.72 g, 76%): mp 160–161 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 2.43 (3 H, s, $CH_3Ar$), 5.00 (2 H, s, $OCH_2$), 6.11 (1 H, t, $J_{5-6} = J_{5-4} = 7.41$ Hz, H-5), 6.55 (1 H, dd, $J_{4-5} = 7.41$ Hz, $J_{4-6} = 1.56$ Hz, H-4), 7.31–7.34 (7 H, m, H-Ar), 7.72 (1 H, dd, $J_{6-5} = 7.41$ Hz, $J_{6-4} = 1.56$ Hz, H-6), 8.02 (2 H, d, $J_{2'-3'} = 8.46$ Hz, H-2′ and H-6′); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.90 ($CH_3$-Ar), 71.14 ($OCH_2$), 105.23 (C-5), 115.33 (C-4), 122.97 (C-6), 127.52, 128.33, 128.72, 129.60, 130.19, 133.45, 135.57, 146.24, 149.86 (C-2); IR ($CHCl_3$) 1672 (C=O), 1619 cm$^{-1}$; MS *m/e* (EI) 355 ($M^+$, 2), 201 (5), 200 (33), 155 (6), 91 (100), 65 (8); HRMS calcd for $C_{19}H_{17}NO_4S$ ($M^+$) 355.0878, found 355.0882.

**3-[(*tert*-Butyldimethylsilyl)oxy]-2-pyridone.** A solution of *tert*-butyldimethylsilyl chloride (TBDMSCl) (305 mg, 2.02 mmol) in anhydrous dimethylformamide (DMF) (5 mL) was delivered to a stirred mixture of 2,3-dihydroxypyridine (220 mg, 2.00 mmol) and imidazole (340 mg, 5.00 mmol) maintained under a dry nitrogen atmosphere. After 3 h, the mixture was poured into $H_2O$ (10 mL) and was extracted with $Et_2O$ (2 × 75 mL). The combined etheral extracts were washed with water (10 mL) and dried over $Na_2SO_4$. Evaporation of solvent afforded a pale brown solid (435 mg, 67%). The crude product can be used directly for the next step; however, an analytically pure sample may be prepared by crystallization ($Et_2O$/hexane (1:10) v/v) as a white solid: mp 117 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 0.25 (6 H, s, $CH_3Si$), 0.99 (9 H, s, $(CH_3)_3Si$), 1.66 (1 H, bs, NH), 6.13 (1 H, t, $J_{5-6} = J_{5-4} =$ 7 Hz, H-5), 6.89 (1 H, dd, $J_{4-5} = 7.0$ Hz, $J_{4-6} = 1.7$ Hz, H-4), 6.97 (1 H, dd, $J_{6-5} = 7.0$ Hz, $J_{6-4} = 1.7$ Hz, H-6); IR ($CHCl_3$) 1653 (C=O), 1621 cm$^{-1}$; MS *m/e* (CI/ammonia) 228 (5), 227 (17), 226 ($MH^+$, 100), 168 ($M^+ - t$-Bu, 19), 129 (4), 113 (3), 112 (62). Anal. Calcd for $C_{11}H_{19}NO_2Si$: C, 58.63; H, 8.50; N, 6.22. Found: C, 58.47; H, 8.52; N, 6.17.

**3-[(*tert*-Butyldimethylsilyl)oxy]-1-(4′-methylbenzenesulfonyl)-2-pyridone (1c).** This compound was prepared in accord with the general procedure described previously. Thus, starting from a solution of 3-[(*tert*-butyldimethylsilyl)oxy]-2-pyridone (4.66 g, 20.7 mmol) in dry $Et_2O$ (150 mL) and using MeLi (1.4 M solution in $Et_2O$, 15.0 mL, 21.0 mmol) and 4-methylbenzenesulfonyl chloride (3.95 g, 20.7 mmol) we obtained after chromatography (silica gel, 10% v/v $Et_2O$ in hexane) white solid **1c** (7.05 g, 90%): mp 78–79 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 0.11 (6 H, s, $CH_3Si$), 0.90 (9 H, s, $(CH_3)_3CSi$), 2.43 (3 H, s, $CH_3Ar$), 6.09 (1 H, t, $J_{5-6} = J_{5-4} = 7.3$ Hz, pyridone H-5), 6.67 (1 H, dd, $J_{4-5} =$ 7.3 Hz, $J_{4-6} = 1.7$ Hz, pyridone H-4), 7.32 (2 H, d, $J = 8.4$ Hz, tosyl H-3′), 7.73 (1 H, dd, $J_{6-5} = 7.3$ Hz, $J_{6-4} = 1.7$ Hz, pyridone H-6), 7.98 (2 H, d, $J = 7.9$ Hz, tosyl H-2′); $^{13}C$ NMR ($CDCl_3$) $\delta$

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−4.59 (2 x $CH_3Si$), 18.49 ($Me_3CSi$), 21.78 ($CH_3Ar$), 25.66 (($C$-$H_3)_3CSi$), 105.59 (C-5), 122.39 (C-4), 123.91 (C-6), 129.45 (C-2′), 129.77 (C-3′), 133.67 (C-1′), 145.97 (C-3), 147.45 (C-4′), 157.90 (C-1); IR ($CHCl_3$) 1674 (C=O), 1620 $cm^{-1}$; MS $m/e$ (EI) 323 (21), 322 ($M^+$ − $t$-Bu, 100), 167 (28), 155 (91), 152 (27), 91 (100), 73 (25); $m/e$ (CI/ammonia) 380 ($MH^+$, 100); HRMS calcd for $C_{14}H_{16}NO_4SSi$ ($M^+$ − $t$-Bu) 322.0570, found 322.0575.

**3-(4″-Methylbenzenesulfenyl)-1-(4′-methylbenzenesulfonyl)-2-pyridone (1d).** This compound was prepared in accord with the general procedure described above. Thus, starting from a solution of 3-(4-methylbenzenesulfenyl)-2-pyridone[1] (432 mg, 1.99 mmol) in dry THF (20 mL) and using LHMDS (1.0 M solution in hexane, 2.45 mL, 2.45 mmol) and 4-methylbenzenesulfonyl chloride (575 mg, 3.02 mmol) we obtained after crystallization ($CH_2Cl_2$/$Et_2O$ (1:2) v/v) pale yellow solid **1d** (516 mg, 70%): mp 165–166 °C; $^1H$ NMR ($CDCl_3$) δ 2.37 (3 H, s, $CH_3$-C4″), 2.44 (3 H, s, $CH_3$-C4′), 6.06 (1 H, t, $J_{5-4} = J_{5-6}$ = 7.19 Hz, H-5), 6.48 (1 H, dd, $J_{4-5}$ = 7.19 Hz, $J_{4-6}$ = 1.35 Hz, H-4), 7.19 (2 H, d, $J_{2''-3''}$ = 7.49 Hz, H-2″ and H-6″), 7.33 (4 H, d, $J$ = 7.93 Hz, H-3′, H-5′, H-3″, and H-5″), 7.86 (1 H, dd, $J_{6-5}$ = 7.19 Hz, $J_{6-4}$ = 1.35 Hz, H-6), 7.91 (2 H, d, $J_{2'-3'}$ = 8.48 Hz, H-2′ and H-6′); $^{13}C$ NMR ($CDCl_3$) δ 21.43 ($CH_3$-C4″), 21.94 ($CH_3$-C4′), 106.56 (C-5), 126.21, 126.91 (C-6), 129.73, 130.18, 130.89, 132.62 (C-4), 133.39, 135.56, 137.34, 140.06 (C-3), 146.40, 158.08 (C-2); IR ($CHCl_3$) 1660, 1601 $cm^{-1}$; MS $m/e$ (EI) 372 ($MH^+$, 11), 371 ($M^+$, 45), 308 (12), 307 (51), 306 (23), 217 (19), 216 (100), 119 (66), 91 (51), 65 (21); HRMS calcd for $C_{19}H_{17}NO_3S_2$ ($M^+$) 371.0650, found 371.0647.

**3-Methoxy-1-(methanesulfonyl)-2-pyridone.** This compound was prepared in accord with the general procedure described above. Thus, starting from a solution of 3-methoxy-2-pyridone (541 mg, 4.33 mmol) in dry THF (40 mL) using MeLi (1.0M solution in $Et_2O$, 5.00 mL, 5.0 mmol) and MsCl (0.5 mL, 6.5 mmol) we obtained after crystallization ($Et_2O$) a white solid (802 mg, 91%): mp 125 °C; $^1H$ NMR ($CDCl_3$) δ 3.56 (3 H, s, $CH_3SO_2$), 3.73 (3 H, s, $CH_3O$), 6.16 (1 H, t, $J_{5-6} = J_{5-4}$ = 7.4 Hz pyridone H-5), 6.58 (1 H, d, $J_{4-5}$ = 7.4 Hz, pyridone H-4), 7.42 (1 H, d, $J_{6-5}$ = 7.4 Hz, pyridone H-6); $^{13}C$ NMR ($CDCl_3$) δ 41.77 ($CH_3SO_2$), 56.31 ($CH_3O$), 105.53 (C-5), 113.21 (C-4), 121.66 (C-6), 150.71 (C-3), 157.19 (C-2); IR ($CHCl_3$) 1671 (C=O), 1619 $cm^{-1}$; MS $m/e$ (EI) 203 ($M^+$, 66), 125 (100), 124 (99), 109 (22), 96 (94), 95 (24), 82 (21), 55 (37), 54 (23); $m/e$ (CI/ammonia) 221 ($MNH_4^+$, 3), 206 (5), 205 (9), 204 ($MH^+$, 100), 126 (39), 125 (6), 96 (6). Anal. Calcd for $C_{13}H_{13}NO_4S$: C, 41.37; H, 4.46; N, 6.89. Found: C, 41.44; H, 4.49; N, 6.86.

**3-[(*tert*-Butyldimethylsilyl)oxy]-1-(methanesulfonyl)-2-pyridone.** This compound was prepared in accord with the general procedure described above. Thus, starting from a solution of 3-[(*tert*-butyldimethylsilyl)oxy]-2-pyridone (1.89 g, 8.40 mmol) in dry $Et_2O$ (40 mL) using methyllithium (1.4 M solution in $Et_2O$, 7.00 mL, 9.8 mmol) and MsCl (1.00 mL, 12.9 mmol) we obtained after flash chromatography (silica gel, 20% v/v diethyl ether in hexane) a white solid (1.77 g, 70%): mp 56 °C dec; $^1H$ NMR ($CDCl_3$) δ 0.24 (6 H, s, $CH_3Si$), 0.98 (9 H, s, $(CH_3)_3CSi$), 3.60 (3 H, s, $CH_3SO_2$), 6.14 (1 H, dd, $J_{6-5}$ = 7.4, $J_{4-5}$ = 7.2 Hz pyridone H-5), 6.67 (1 H, dd, $J_{4-5}$ = 7.2 Hz, $J_{4-6}$ = 1.6 Hz, pyridone H-4), 7.52 (1 H, dd, $J_{6-5}$ = 7.4 Hz, $J_{6-4}$ = 1.6 Hz, pyridone H-6); $^{13}C$ NMR ($CDCl_3$) δ −4.45 (2 x $CH_3Si$), 18.33 ($Me_3CSi$), 25.62 (($CH_3)_3CSi$), 41.21 ($CH_3SO_2$), 123.71 (C-5), 125.02 (C-3), 130.27 (C-6), 139.28 (C-4), 142.98 (C-1); IR ($CHCl_3$) 1667 (C=O), 1619 $cm^{-1}$; MS $m/e$ (EI) 246 (15), 169 (14), 168 (100), 167 (25), 152 (16), 111 (15), 75 (35), 73 (15); $m/e$ (CI/ammonia) 305 (10), 304 (52), 207 (25), 192 (5), 191 (8), 190 (100), 168 (7), 112 (34); HRMS calcd for $C_9H_{12}NO_4SSi$ ($M^+$ − $t$-Bu) 246.0256, found 246.0260.

**1-(Methanesulfonyl)-3-(4′-methylbenzenesulfenyl)-2-pyridone.** This compound was prepared in accord with the general procedure described above. Thus, starting from a solution of 3-(4-methylbenzenesulfenyl)-2-pyridone (500 mg, 2.3 mmol) in dry THF (20 mL) using LHMDS (1.0 M solution in hexane, 2.83 mL, 2.83 mmol) and MsCl (0.270 mL, 3.49 mmol) we obtained after crystallization ($CH_2Cl_2$/$Et_2O$ (1:2) v/v) a pale yellow solid (480 mg, 70%): mp 170–171 °C; $^1H$ NMR ($CDCl_3$) δ 2.24 (3 H, s, $CH_3Ar$), 3.50 (3 H, s, $CH_3SO_2$), 5.96 (1 H, t, $J_{5-6} = J_{5-4}$ = 7.11 Hz, H-5), 6.48 (1 H, dd, $J_{4-5}$ = 7.11 Hz, $J_{4-6}$ = 1.62 Hz, H-4), 7.10 (1 H, d, $J_{2'-3'}$ = 8.19 Hz, H-2′, H-6′), 7.26 (2 H, d, $J_{3'-2'}$ = 8.19 Hz, H-3′, H-5′), 7.50 (1 H, dd, $J_{6-5}$ = 7.11 Hz, $J_{6-4}$ = 1.62 Hz, H-6); $^{13}C$ NMR ($CDCl_3$) δ 21.46 ($CH_3$-C-4′), 42.19 ($CH_3SO_2$), 106.83 (C-5), 125.97, 126.40 (C-6), 131.00, 133.45 (C-4), 135.55, 137.15, 140.22 (C-3), 158.00 (C-2); IR ($CHCl_3$) 1654 (C=O), 1595 $cm^{-1}$; MS $m/e$ (EI) 295 ($M^+$, 29), 218 (13), 217 (100), 216 (64), 184 (17), 119 (17), 91 (12), 48 (70); HRMS calcd for $C_{13}H_{13}NS_2O_3$ ($M^+$) 295.0337, found 295.0341.

**B. Thermal Rearrangement of Pyridones. Typical Procedure.** The corresponding pyridones were dissolved in $CH_2Cl_2$, and the solutions were heated in a sealed hydrolysis tube at 90–100 °C. Periodically, the tube was cooled and the solvent was removed. Ratios of pyridones/pyridinols were determined on the basis of the $^1H$ NMR spectra of the crude materials. The residues were then redissolved and subjected to heat again. At the end of the experiment the rearranged products were separated by preparative thin-layer chromatography (PTLC) and characterized as follows.

**2-[(4′-Methylbenzenesulfonyl)oxy]pyridine**: gum; $^1H$ NMR ($CDCl_3$) δ 2.45 (3 H, s, $CH_3Ar$), 7.17 (1 H, d, $J_{3-4}$ = 8.1 Hz, $J_{3-5}$ = 0.9 Hz, pyridine H-3), 7.21 (1 H, ddd, $J_{4-5}$ = 5.4 Hz, $J_{5-6}$ = 5.0 Hz, $J_{3-5}$ = 0.9 Hz, pyridine H-5), 7.34 (2 H, d, $J$ = 8.0 Hz, tosyl H-3′), 7.77 (1 H, ddd, $J_{3-4}$ = 8.1 Hz, $J_{4-5}$ = 5.4 Hz, $J_{4-6}$ = 2.0 Hz, pyridine H-4), 7.89 (2 H, d, $J$ = 8.0 Hz, tosyl H-2′), 8.26 (1 H, dd, $J_{5-6}$ = 5.0 Hz, $J_{4-6}$ = 2.0 Hz, pyridine H-6); IR ($CHCl_3$) 1592, 1572, 1170 $cm^{-1}$; MS $m/e$ (EI) 186 (7), 185 (55), 184 (41), 157 (26), 92 (8), 91 (100), 65 (27), 63 (7) and 51 (7); $m/e$ (CI/ammonia) 250 (100); HRMS calcd for $C_{12}H_{11}NO$ ($M^+$ − $SO_2$) 185.0837, found 185.0841.

**3-Methoxy-2-[(4′-methylbenzenesulfonyl)oxy]pyridine**: mp 81–82 °C; $^1H$ NMR ($CDCl_3$) δ 2.49 (3 H, s, $CH_3Ar$), 3.85 (3 H, s, $CH_3O$), 7.20 (1 H, dd, $J$ = 8.2 Hz, 4.8 Hz pyridine H-5), 7.27 (1 H, dd, $J$ = 8.2, 1.6 Hz, pyridine H-4), 7.34 (2 H, d, $J$ = 8.3 Hz, tosyl H-3′), 7.82 (1 H, dd, $J$ = 4.8, 1.6 Hz, pyridone H-6), 7.94 (2 H, d, $J$ = 8.3 Hz, tosyl H-2′); $^{13}C$ ($CDCl_3$) δ 21.69 ($CH_3Ar$), 55.93 ($CH_3O$), 120.88 (C-4), 123.59 (C-5), 128.59 (C-2′), 129.52 (C-3′), 134.47 (C-1′), 138.14 (C-6), 144.98 (C-4′), 146.59 (C-3), 147.09 (C-2); IR ($CHCl_3$) 1598, 1574, 1232, 1194, 1181 $cm^{-1}$; MS $m/e$ (EI) 279 (12), 215 (51), 214 (20), 124 (25), 96 (23), 92 (25), 91 (100), 65 (24); $m/e$ (CI/ammonia) 280 (100); HRMS calcd for $C_{13}H_{13}NO_4S$ ($M^+$) 279.0571, found 279.0565.

**3-Methoxy-2-[(methanesulfonyl)oxy]pyridine**: oil; $^1H$ NMR ($CDCl_3$) δ 3.49 (3 H, s, $CH_3SO_2$), 3.90 (3 H, s, $CH_3O$), 7.25 (1 H, dd, $J$ = 8.1, 4.7 Hz, pyridine H-5), 7.33 (1 H, dd, $J$ = 8.1, 1.5 Hz, pyridine H-4), 7.88 (1 H, dd, $J$ = 4.7, 1.5 Hz, pyridone H-6); $^{13}C$ ($CDCl_3$) δ 40.86 ($CH_3SO_2$), 56.08 ($CH_3O$), 121.23 (C-4), 123.77 (C-5), 137.92 (C-6), 146.86 (C-3), 147.90 (C-2); IR (film) 1574, 1229, 1153 $cm^{-1}$; HRMS calcd for $C_7H_9NO_4S$ ($M^+$) 203.0250, found 203.0254.

**3-[(*tert*-Butyldimethylsilyl)oxy]-2-[(methanesulfonyl)oxy]pyridine**: pale yellow liquid; $^1H$ NMR ($CDCl_3$) δ 0.25 (6 H, s, $CH_3Si$), 1.03 (9 H, s, $(CH_3)_3CSi$), 3.50 (3 H, s, $CH_3SO_2$), 7.16 (1 H, dd, $J$ = 8.0, 4.8 Hz, pyridine H-5), 7.29 (1 H, dd, $J$ = 8.0, 1.6 Hz, pyridine H-4), 7.90 (1 H, dd, $J$ = 4.8, 1.6 Hz, pyridone H-6); $^{13}C$ ($CDCl_3$) δ −4.45 ($CH_3Si$), 18.33 (($CH_3)_3CSi$), 25.62 (($C$-$H_3)_3CSi$), 41.21 ($CH_3SO_3$), 123.71 (C-4), 125.03 (C-5), 130.27 (C-6) 139.28 (C-2), 142.98 (C-3); IR ($CHCl_3$) 1571, 1256, 1158 $cm^{-1}$; MS $m/e$ (EI) 246 (17), 210 (3), 169 (12), 168 (100), 167 (24), 152 (13), 73 (19); $m/e$ (CI/ammonia) 306 (9), 305 (19), 304 (100), 226 (6), 168 (12), 112 (3), 102 (4), 96 (4).

**C. Cycloadditions of Pyridones. 4-Methoxy-2-(4′-methylbenzenesulfonyl)-5-*endo*-nitro-3-oxo-2-azabicyclo-[2.2.2]oct-7-ene (2ag).** Nitroethylene[21] (196 mg and 190 mg after 48 h) was added to a solution of **1a** (150 mg, 0.537 mmol) in $CH_2Cl_2$ (2.5 mL) in a sealed tube and was heated at 90 °C for 5 days. Chromatography (silica gel, $Et_2O$) afforded **2ag** as a white solid (151 mg, 80%): mp 155–156 °C; $^1H$ NMR ($CDCl_3$) δ 2.21 (1 H, ddd, $J_{6_{endo}-6_{exo}}$ = 13.98 Hz, $J_{6_{endo}-5}$ = 3.86 Hz, $J_{6_{endo}-1}$ = 2.15 Hz, H-$6_{endo}$), 2.44 (3 H, s, $CH_3Ar$), 2.75 (1 H, ddd, $J_{6_{exo}-6_{endo}}$ = 13.98 Hz, $J_{6_{exo}-5}$ = 9.25 Hz, $J_{6_{exo}-1}$ = 3.45 Hz, H-$6_{exo}$), 3.68 (3 H, s, $CH_3O$), 5.02 (1 H, ddd, $J_{5-6_{exo}}$ = 9.25 Hz, $J_{5-6_{endo}}$ = 3.86 Hz, $J_{5-1}$ = 1.26 Hz, H-5), 5.41 (1 H, m, H-1), 6.31 (1 H, dd, $J_{8-7}$ = 8.13 Hz, $J_{8-1}$ = 1.50 Hz, H-8), 6.69 (1 H, dd, $J_{7-8}$ = 8.13 Hz, $J_{7-1}$ = 6.12 Hz, H-7), 7.33 (2 H, d, $J_{3'-2'}$ = 8.43 Hz, H-3′ and H-5′), 7.84 (2 H, d, $J_{2'-3'}$ = 8.43 Hz, H-2′ and H-6′); $^{13}C$ NMR ($CDCl_3$) δ 21.09 ($CH_3Ar$), 35.47 (C-6), 51.68 ($OCH_3$), 55.05 (C-1), 79.67 (C-5), 84.00 (C-4), 128.19, 129.85, 130.04, 130.13 (C-8), 132.14 (C-7), 146.06, 168.00 (C=O); IR

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($CHCl_3$) 1736, 1560, 1366, 1172 $cm^{-1}$; MS *m/e* (EI) 155 (2), 110 (7), 109 (100), 91 (16), 77 (9); (CI/ammonia) 370 ($MNH_4^+$, 100), 353 ($MH^+$, 84); HRMS calcd for $C_{15}H_{16}N_2O_6S$ ($MH^+$) 353.0807, found 353.0800.

**4-Methoxy-2-(4′-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5-*endo*-carboxaldehyde (2ah).** A solution of acrolein (0.115 mL and 0.110 mL after 24 h) and pyridone **1a** (48 mg, 0.172 mmol) in $CH_2Cl_2$ (0.5 mL) was heated in a sealed tube at 90 °C for 6 days. Removal of solvent followed by chromatography (silica gel, 25–50% $Et_2O$ in hexane) gave **2ah** as a white solid (40 mg, 69%): mp 136 °C dec; $^1H$ NMR ($CDCl_3$) δ 2.11–2.14 (2 H, m, H-6), 2.44 (3 H, s, $CH_3Ar$), 2.92 (1 H, m, H-5), 3.68 (3 H, s, $OCH_3$), 5.38 (1 H, m, H-1), 6.38 (1 H, dd, *J* = 8.2 Hz, 1.4 Hz, H-8), 6.60 (1 H, dd, *J* = 8.2 Hz, 6.1 Hz, H-7), 7.32 (2 H, d, *J* = 8.2 Hz, tosyl H), 7.88 (2 H, d, *J* = 8.2 Hz, tosyl H), 9.65 (1 H, s, CHO); IR ($CHCl_3$) 1728 (C=O's), 1598 (C=C), 1188, 1172 $cm^{-1}$; MS *m/e* (EI) 138 (96), 110 (12), 109 (100), 106 (29), 94 (15), 91 (37), 77 (17), 65 (22); *m/e* (CI/ammonia) 354 ($MNH_4^+$, 19), 353 (100), 337 (19), 336 ($MH^+$, 99), 280 (41), 182 (21), 138 (27), 126 (29). Anal. Calcd for $C_{16}H_{17}NO_5S$: C, 57.30; H, 5.11; N, 4.18. Found: C, 57.23; H, 5.11; N, 4.16.

**Methyl 4-Methoxy-2-(4′-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5-*endo*-carboxylate (2ai). Thermal.** A solution of pyridone **1a** (36.8 mg, 0.132 mmol), methyl acrylate (0.21 mL, 10 equiv), and BHT (2 mg) in $CH_2Cl_2$ (0.5 mL) was heated for 64 h at 130 °C. Chromatography (50% $Et_2O$ in hexane) afforded an inseparable mixture of **2ai** and 3-methoxy-2-[(4-methylbenzenesulfonyl)oxy]pyridine as a pale yellow gum (44 mg, 3:1 in favor of the cycloadduct as determined by $^1H$ NMR). **High Pressure.** Methyl acrylate (0.2 mL, 36 equiv) and $BaCO_3$ (3 mg) were added to a solution of pyridone **1a** (17 mg, 61 μmol) in $CH_2Cl_2$ (0.5 mL), and the mixture was subjected to 10 kbar pressure for 144 h. The resulting gum was taken up in hot methanol and filtered to remove polymeric impurities. Removal of solvent afforded an oil which was purified by preparative thin-layer chromatography ($Et_2O$) to afford **2ai** as a gum (6 mg, 35%): $^1H$ NMR ($CDCl_3$) δ 1.85 (1 H, ddd, *J* = 13.0, 4.9, 1.9 Hz, H-$6_{exo}$), 2.45 (4 H, m, $CH_3$-Ar and H-$6_{endo}$), 3.03 (1 H, ddd, *J* = 9.8, 4.9, 1.1 Hz, H-5), 3.65 (3 H, s, ether $CH_3$), 3.69 (3 H, s, ester $CH_3$), 5.37 (1 H, m, H-1), 6.37 (1 H, dd, *J* = 8.1, 1.4 Hz, H-8), 6.57 (1 H, dd, *J* = 8.1, 4.0 Hz, H-7), 7.31 (2 H, d, *J* = 8.1 Hz, tosyl H), 7.87 (2 H, d, *J* = 8.1 Hz, tosyl H); IR (film) 1733 (C=O), 1598, 1359, 1229, 1172 $cm^{-1}$; MS *m/e* (EI) 366 ($M^+$, 3), 168 (77), 109 (100), 108 (22), 94 (8), 91 (21), 77 (8), 65 (13); *m/e* (CI/ammonia) 366 (100); HRMS calcd for $C_{16}H_{16}NO_5S$ ($M^+$ – OMe) 334.0749, found 334.0752.

**Dimethyl 1β-Methoxy-4α-[(4′-methylbenzenesulfonyl)-amino]cyclohex-5-ene-1,2-dicarboxylate.** *n*-BuLi (0.8 mmol) was added slowly to MeOH (5 mL), and the solution thus obtained was added to the crude mixture of the bicyclic lactam **2ai** (44 mg) at room temperature under dry $N_2$ atmosphere. After 2 h, standard workup procedure followed by purification by flash chromatography (50% $Et_2O$ in hexane) afforded the ring-opened compound as a gummy solid (30 mg, 57% from pyridone): $^1H$ NMR ($CDCl_3$) δ 1.90–2.15 (2 H, m, H-$3_α$ and H-$3_β$), 2.42 (3 H, s, $CH_3Ar$), 3.22 (1 H, dd, *J* = 12.0, 2.6 Hz, H-2), 3.32 (3 H, s, ether $CH_3O$), 3.64 (3 H, s, ester $CH_3O$), 3.77 (3 H, s, ester $CH_3O$), 3.96 (1 H, m, H-4), 5.80–5.83 (1 H, m, H-7 and H-8), 7.30 (2 H, d, *J* = 8.0 Hz, tosyl H), 7.77 (2 H, d, *J* = 8.0 Hz, tosyl H); $^{13}C$ NMR ($CDCl_3$) δ 21.56 ($CH_3Ar$), 26.79 (C-5), 43.30 (C-6), 46.94 (C-4), 52.05 (ether $CH_3$), 52.68 ($CO_2CH_3$), $^{13}C$ NMR ($CO_2CH_3$), 76.52 (C-1), 127.03 (C-3′), 127.72 (C-7/C-8), 129.88 (C-2′), 132.04 (C-7/C-8), 137.61 (C-4′), 143.74 (C-1′), 170.88 ($CO_2Me$), 170.96 ($CO_2Me$); IR (film) 1735 (C=O), 1437, 1161 $cm^{-1}$; HRMS calcd for $C_{17}H_{19}NO_6S$ ($M^+$ – MeOH) 365.0933, found 365.0943.

**5-*endo*-Acetyl-4-methoxy-2-(4′-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene (2aj).** A solution of pyridone **1a** (145 mg, 0.52 mmol), methyl vinyl ketone (0.75 mL, 17.1 equiv), and BHT (30 mg) in $CH_2Cl_2$ (4.0 mL) was heated for 132 h at 90 °C. Chromatography (50% $Et_2O$ in hexane) afforded the starting pyridone (75 mg) and **2aj** as a colorless gum (76 mg, 42%): $^1H$ NMR ($CDCl_3$) δ 1.85 (1 H, ddd, *J* = 12.9, 4.8, 2.0 Hz, H-$6_{exo}$), 2.12 (1 H, ddd, *J* = 12.9, 9.4, 3.7 Hz, H-$6_{endo}$), 2.20 (3 H, s, $CH_3CO$), 2.43 (3 H, s, $CH_3Ar$), 3.01 (1 H, dd, *J* = 9.4, 4.8 Hz, H-5), 3.57 (3 H, s, $CH_3O$), 5.35 (1 H, ddd, *J* = 6.0, 3.8, 2.0 Hz, H-1), 6.32 (1 H, dm, *J* = 8.2 Hz, H-7), 6.60 (1 H, dd, *J* = 8.2, 6.0 Hz, H-8), 7.32 (2 H, d, *J* = 8.5 Hz, tosyl H), 7.87 (2 H, d, *J* = 8.5 Hz, tosyl H); $^{13}C$ NMR ($CDCl_3$) δ 21.75 ($CH_3Ar$), 32.20 ($CH_3CO$), 32.59 (C-6), 47.02 (C-5), 52.83 (C-1), 55.14 ($CH_3O$), 84.24 (C-4), 128.03 (C-2′), 129.63 (C-7/C-8), 129.78 (C-3′), 132.41 (C-7/C-8), 135.42 (C-1′), 145.37 (C-4′), 169.42 (C-3), 206.34 ($CH_3CO$); IR ($CHCl_3$) 1722 (C=O), 1598, 1360, 1171 $cm^{-1}$; MS *m/e* (EI) 152 (16), 137 (20), 110 (9), 109 (100), 94 (8), 91 (23), 77 (8), 65 (13); *m/e* (CI/ammonia) 367 (25), 352 (7), 351 (20), 350 ($MH^+$, 100), 281 (6), 280 (41), 189 95), 152 (9); HRMS calcd for $C_{17}H_{20}NO_5S$ ($MH^+$) 350.1062, found 350.1068.

**4-(Benzyloxy)-2-(4′-methylbenzenesulfonyl)-5-*endo*-nitro-3-oxo-2-azabicyclo[2.2.2]-7-octene (2bg).** A solution of nitroethylene (409 mg and 400 mg after 48 h) and pyridone **1b** (200 mg, 0.561 mmol) in $CH_2Cl_2$ (3 mL) was heated in a sealed tube at 90 °C for 5 days. Removal of solvent followed by preparative thin-layer chromatography (silica gel, 50% EtOAc in hexane, three elutions) afforded **2bg** as a white solid (190 mg, 79%): mp 172–173 °C; $^1H$ NMR ($CDCl_3$) δ 2.22 (1 H, d, $J_{6_{endo}-6_{exo}}$ = 14.0 Hz, $J_{6_{endo}-5}$ = 3.83 Hz, $J_{6_{endo}-1}$ = 2.14 Hz, H-$6_{endo}$), 2.44 (3 H, s, $CH_3$-C4′), 2.79 (1 H, ddd, $J_{6_{exo}-6_{endo}}$ = 14.0 Hz, $J_{6_{exo}-5}$ = 9.35 Hz, $J_{6_{exo}-1}$ = 3.52 Hz, H-$6_{exo}$), 4.89 (1 H, d, *J* = 10.92 Hz, $PhCH_2$), 5.04 (1 H, d, *J* = 10.92 Hz, $PhCH_2$), 5.11 (1 H, ddd, $J_{5-6_{exo}}$ = 9.35 Hz, $J_{5-6_{endo}}$ = 3.83 Hz, $J_{5-1}$ = 1.22 Hz, H-5), 5.44 (1 H, ddd, $J_{1-7}$ = 6.11 Hz, $J_{1-6_{exo}}$ = 3.52 Hz, $J_{1-6_{endo}}$ = 2.14 Hz, H-1), 6.36 (1 H, d, $J_{8-7}$ = 8.11 Hz, H-8), 6.68 (1 H, d, $J_{7-8}$ = 8.11 Hz, $J_{7-1}$ = 6.11 Hz, H-7), 7.28–7.37 (7 H, m, H-Ar), 7.89 (2 H, d, $J_{2′-3′}$ = 8.51 Hz, H-2′ and H-6′); $^{13}C$ NMR ($CDCl_3$) δ 21.70 ($CH_3$-C-4′), 34.25 (C-6), 50.62 (C-1), 70.00 ($CH_2Ph$), 83.90 (C-5), 84.28 (C-4), 127.60, 128.02, 128.55, 128.62, 130.00, 131.60 (C-8), 133.10, 135.60 (C-7), 137.60, 145.78, 160.00; IR ($CHCl_3$) 1736, 1566, 1372, 1166 $cm^{-1}$; MS *m/e* (EI) 185 (10), 184 (3), 155 (10), 91 (100), 77 (20), (CI/ammonia) 446 ($MNH_4^+$, 5); HRMS Calcd for $C_{21}H_{24}N_3O_6S$ ($MNH_4^+$) 446.1386, found 446.1388.

**4-(Benzyloxy)-2-(4′-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5-*endo*-carboxaldehyde (2bh).** A solution of acrolein (0.313 mL and 0.300 mL after 48 h) and pyridone **1b** (200 mg, 0.561 mmol) in $CH_2Cl_2$ (2 mL) was heated in a sealed tube at 90 °C for 5 days. Chromatography (silica gel, 30% EtOAc in hexane) afforded white solid **2bh** (192 mg, 83%). This compound was found to be unstable and was characterized as the corresponding alcohol.

**4-[(*tert*-Butyldimethylsilyl)oxy]-2-(4′-methylbenzenesulfonyl)-5-*endo*-nitro-3-oxo-2-azabicyclo[2.2.2]oct-7-ene (2cg).** A solution of pyridone **1c** (159 mg, 4.20 mmol) and nitroethylene (170 mg, 5.5 equiv, and 205 mg, 6.6 equiv, after 67 h) in $CH_2Cl_2$ (3.0 mL) was heated in a sealed tube for 160 h at 90 °C. Chromatography (50% $Et_2O$/hexane) afforded **2cg** as a white solid: mp 112–113 °C; $^1H$ NMR ($CDCl_3$) δ –0.11 (3 H, s, $CH_3Si$), 0.23 (3 H, s, $CH_3Si$), 0.83 (9 H, s, $(CH_3)_3CSi$), 2.12 (1 H, ddd, *J* = 13.2, 4.3, 1.8 Hz, H-$6_{endo}$), 2.43 (3 H, s, $CH_3Ar$), 2.74 (1 H, ddd, *J* = 13.2, 9.3, 3.6 Hz, H-$6_{exo}$), 4.82 (1 H, ddd, *J* = 9.3, 4.3, 1.2 Hz, H-5), 5.36 (1 H, ddd, *J* = 8.1, 3.6, 1.8 Hz, H-1), 6.10 (1 H, dt, $J_t$ = 8.0 Hz, $J_d$ = 1.4 Hz, H-8), 6.42 (1 H, dd, *J* = 8.0, 6.1 Hz, H-7), 7.32 (2 H, d, *J* = 8.5 Hz, tosyl H), 7.83 (2 H, d, *J* = 8.5 Hz, tosyl H); $^{13}C$ NMR ($CDCl_3$) δ –4.09 ($CH_3Si$), –3.15 ($CH_3Si$), 17.95 ($Me_3CSi$), 21.03 ($CH_3Ar$), 24.67 (($CH_3)_3CSi$), 34.16 (C-6), 51.31 (C-1), 81.48 (C-4), 82.55 (C-5), 127.72 (C-2′), 129.60 (C-3′), 130.80 (C-7/C8), 133.23 (C-7/C-8), 134.57 (C-1′), 145.62 (C-4′), 167.57 (C-3); IR ($CHCl_3$) 1745 (C=O), 1598, 1562, 1370, 1355, 1188, 1172 $cm^{-1}$; MS *m/e* (EI) 395 ($M^+$ – *t*-Bu), 323 (21), 322 (95), 209 (85), 155 (70), 151 (47), 91 (100), 73 (63); *m/e* (CI/ammonia) 453 ($MH^+$, 96), 395 ($M^+$ – *t*-Bu, 51), 380 (47), 322 (100), 209 (70), 155 (55), 91 (39), 73 (37). Anal. Calcd for $C_{20}H_{28}N_2O_6SSi$: C, 53.08; H, 6.26; N, 6.19. Found: C, 53.08; H, 6.23; N, 6.27.

**4-[(*tert*-Butyldimethylsilyl)oxy]-2-(4′-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5-*endo*-carboxaldehyde (2ch).** A solution of pyridone **1c** (1.075 g, 2.84 mmol) and acrolein (4.00 mL, 21 equiv) and BHT (50 mg) in $CH_2Cl_2$ (15 mL) was heated in a sealed tube for 148 h at 90 °C. The desired product **2ch** was isolated by chromatography (silica gel, 10–50% $Et_2O$ in hexane) as a white solid (863 mg, 70%). An analytically pure sample was obtained by crystallization (1:2 v/v $Et_2O$/hexane): mp 121 °C; $^1H$ NMR ($CDCl_3$) δ –0.11 (3 H, s, $CH_3Si$), 0.27 (3 H, s, $CH_3Si$), 0.88 (9 H, s, $(CH_3)_3CSi$), 2.08 (1 H, ddd, *J* = 13.3, 4.8, 2.4 Hz, H-$6_{endo}$), 2.14 (1 H, ddd, *J* = 13.3, 8.9, 3.5 Hz, H-$6_{exo}$), 2.43 (3 H, s, $CH_3Ar$), 2.85 (1 H, ddd, *J* = 8.9, 4.8, 1.0 Hz, H-5),

5.31 (1 H, m, H-1), 6.06 (1 H, d, $J$ = 8.0 Hz, H-8), 6.43 (1 H, dd, $J$ = 8.0, 6.0 Hz, H-7), 7.33 (2 H, d, $J$ = 8.5 Hz, tosyl H), 7.84 (2 H, d, $J$ = 8.5 Hz, tosyl H), 9.77 (1 H, d, $J$ = 1.3 Hz, CHO); $^{13}$C NMR ($CDCl_3$) $\delta$ -3.93 ($CH_3Si$), -2.85 ($CH_3Si$), 18.53 ($Me_3CSi$), 21.66 ($CH_3Ar$), 25.88 (($CH_3)_3CSi$), 28.57 (C-6), 50.37 (C-5), 52.35 (C-1), 81.02 (C-4), 127.86 (C-2'), 129.57 (C-3'), 131.94 (C-1' and C-7), 135.21 (C-8), 145.28 (C-4'), 169.87 (C-3), 200.01 (CHO); IR ($CHCl_3$) 1728 (C=O), 1360, 1188, 1172 cm$^{-1}$; MS $m/e$ (EI) 378 ($M^+$ - $t$-Bu, 11), 322 (96), 167 (26), 155 (82), 152 (24), 151 (26), 91 (100), 73 (38); $m/e$ (CI/ammonia) 453 ($MNH_4^+$, 1), 437 (23), 436 ($MH^+$, 78), 381 (26), 382 (11), 380 (100), 322 (9), 226 (9). Anal. Calcd for $C_{21}H_{21}NO_5SSi$: C, 57.90; H, 6.71; N, 3.22. Found: C, 57.84; H, 6.67; N, 3.24.

**Methyl 4-[(*tert*-Butyldimethylsilyl)oxy]-2-(4'-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5-*endo*-carboxylate (2ci).** A solution of pyridone **1c** (45 mg, 0.12 mmol) and methyl acrylate (0.11 mL, 10 equiv) and BHT (3 mg) in $CH_2Cl_2$ (0.8 mL) was heated in a sealed tube for 110 h at 90 °C. The desired product **2ci** was isolated by chromatography (silica gel, 50–100% $Et_2O$ in hexane) as a white solid (19 mg, 56%): mp 118 °C; $^1$H NMR ($CDCl_3$) $\delta$ -0.14 (3 H, s, $CH_3Si$), 0.21 (3 H, s, $CH_3Si$), 0.84 (9 H, s, $(CH_3)_3CSi$), 1.76 (1 H, ddd, $J$ = 12.9 Hz, 5.2 Hz, 1.93 Hz, H-6$_{endo}$), 2.39 (1 H, ddd, $J$ = 12.9, 9.7, 3.8 Hz, H-6$_{exo}$), 2.43 (3 H, s, $CH_3Ar$), 2.86 (1 H, ddd, $J$ = 9.7, 5.2, 1.1 Hz, H-5), 3.64 (3 H, s, ester $OCH_3$), 5.29 (1 H, ddd, $J$ = 8.0, 3.8, 1.9 Hz, H-1), 6.10 (1 H, dt, $J_t$ = 8.0 Hz, $J_d$ = 1.5 Hz, H-8), 6.42 (1 H, dd, $J$ = 8.0, 6.0 Hz, H-7), 7.30 (2 H, d, $J$ = 8.4 Hz, tosyl H), 7.84 (2 H, d, $J$ = 8.4 Hz, tosyl H); IR (NaCl) 1736 (C=O), 1598, 1437, 1361, 1172 cm$^{-1}$; MS $m/e$ (EI) 408 (41), 322 (100), 268 (21), 211 (90), 155 (62), 151 (47), 91 (91), 73 (51); $m/e$ (CI/ammonia) 468 (13), 467 (30), 466 ($MH^+$, 100), 408 ($M^+$ - $t$-Bu, 4), 380 (9), 322 (5), 226 (3), 211 (6). Anal. Calcd for $C_{22}H_{31}NO_6SSi$: C, 56.75; H, 6.71; N, 3.01. Found: C, 56.62; H, 6.67; N, 3.00.

**5-*endo*-Acetyl-4-[(*tert*-butyldimethylsilyl)oxy]-2-(4-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene (2cj).** A solution of pyridone **1c** (200 mg, 0.528 mmol) and methyl vinyl ketone (0.75 mL, 19.4 equiv) and BHT (10 mg) in $CH_2Cl_2$ (4.0 mL) was heated in a sealed tube for 132 h. The desired product **2cj** was isolated by chromatography (silica gel, 10–50% ether in hexane) as a white solid mass (132 mg, 56%): mp 127–129 °C; $^1$H NMR ($CDCl_3$) $\delta$ -0.19 (3 H, s, $CH_3Si$), 0.19 (3 H, s, $CH_3Si$), 0.85 (9 H, s, $(CH_3)_3CSi$), 1.79 (1 H, ddd, $J$ = 12.8, 5.1, 1.9 Hz, H-6$_{exo}$), 2.21 (1 H, ddm, $J$ = 12.9, 9.2, 3.8 Hz, H-6$_{endo}$), 2.24 (3 H, s, $CH_3CO$), 2.42 (3 H, s, $CH_3Ar$), 3.01 (1 H, dd, $J$ = 9.2, 5.1 Hz, H-5), 5.28 (1 H, ddd, $J$ = 7.8, 3.8, 1.9 Hz, H-1), 5.98 (1 H, dm, $J$ = 8.0 Hz, H-8), 6.42 (1 H, dd, $J$ = 8.0, 6.0 Hz, H-7), 7.29 (2 H, d, $J$ = 8.0 Hz, tosyl H), 7.82 (2 H, d, $J$ = 8.0 Hz, tosyl H); IR ($CHCl_3$) 1738 (C=O), 1721, 1597, 1473, 1360, 1171 cm$^{-1}$; MS $m/e$ (EI) 392 (30), 322 (97), 209 (46), 195 (23), 167 (23), 155 (72), 151 (46), 91 (100), 73 (58); $m/e$ (CI/ammonia) 452 (13), 451 (31), 450 ($MH^+$, 100), 381 (19), 380 (74), 322 (12), 226 (15), 168 (9). Anal. Calcd for $C_{22}H_{31}NO_5SSi$: C, 58.77; H, 6.95; N, 3.12. Found: C, 58.68; H, 6.91; N, 3.19.

**4-(4''-Methylbenzenesulfenyl)-2-(4'-methylbenzenesulfonyl)-5-*endo*-nitro-3-oxo-2-azabicyclo[2.2.2]oct-7-ene (2dg).** A solution of nitroethylene (73 mg and 73 mg after 48 h) and pyridone **1d** (74 mg, 0.199 mmol) in $CH_2Cl_2$ (1 mL) was heated in a sealed tube at 90 °C for 5 days. Removal of solvent and purification by preparative thin-layer chromatography (silica gel, 30% EtOAc in hexane, three elutions) afforded **2dg** as a white solid (40 mg, 45%): mp 159–160 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.35 (3 H, s, $CH_3$-C4''), 2.44 (3 H, s, $CH_3$-C4'), 4.67 (1 H, dd, $J_{5-6_{exo}}$ = 9.08 Hz, $J_{5-6_{endo}}$ = 5.15 Hz, H-5), 5.49 (1 H, ddd, $J_{1-7}$ = 6.81 Hz, $J_{1-6_{exo}}$ = 3.97 Hz, $J_{1-6_{endo}}$ = 1.90 Hz, H-1), 6.20 (1 H, d, $J_{8-7}$ = 7.40 Hz, H-8), 6.62 (1 H, dd, $J_{7-8}$ = 7.40 Hz, $J_{7-1}$ = 6.81 Hz, H-7), 7.19 (2 H, d, $J_{2''-3''}$ = 7.90 Hz, H-2'' and H-6''), 7.35 (2 H, d, $J_{3''-2''}$ = 7.90 Hz, H-3'' and H-5''), 7.50 (2 H, d, $J_{3'-2'}$ = 8.31 Hz, H-3' and H-5'), 7.91 (2 H, d, $J_{2'-3'}$ = 8.31 Hz, H-2' and H-6'), (H-6$_{endo}$ and H-6$_{exo}$ are partially overlapped by the methyl groups); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.45 ($CH_3$-C4''), 21.95 ($CH_3$-C4'), 34.02 (C-6), 51.47 (C-1), 61.87 (C-4), 84.25 (C-5), 128.00, 128.64, 129.85, 130.66, 132.27 (C-8), 132.30, 135.80 (C-7), 138.03, 139.00, 145.73, 168.20 (C=O); IR ($CHCl_3$) 1730, 1562, 1357, 1172 cm$^{-1}$; MS $m/e$ (EI) 247 (3), 217 (32), 216 (71), 202 (10), 201 (64), 200 (11), 155 (13), 124 (18), 123 (19), 119 (43), 91 (100), 79 (14), 77 (14), 65 (39); $m/e$ (CI/ammonia) 462 ($MNH_4^+$, 3), 445 ($MH^+$, 3); HRMS calcd for $C_{21}H_{20}N_2O_5S_2$ ($M^+$) 444.0814, found 444.0811.

**4-(4''-Methylbenzenesulfenyl)-2-(4'-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5-*endo*-carboxaldehyde (2dh).** A solution of acrolein (0.173 mL and 0.173 mL after 48 hours) and pyridone **1d** (100 mg, 0.260 mmol) in $CH_2Cl_2$ (1 mL) was heated in a sealed tube at 90 °C for 5 days. Chromatography (silica gel, 30% EtOAc in hexane) afforded **2dh** as a white solid (47 mg, 42%): mp 134–135 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.03 (1 H, ddd, $J_{6_{endo}-6_{exo}}$ = 13.29 Hz, $J_{6_{endo}-5}$ = 3.84 Hz, $J_{6_{endo}-1}$ = 2.0 Hz, H-6$_{endo}$), 2.32 (3 H, s, $CH_3$-C4''), 2.40 (1 H, m, H-6$_{exo}$), 2.44 (3 H, s, $CH_3$-C4'), 2.74 (1 H, ddd, $J_{5-6_{exo}}$ = 9.63 Hz, $J_{5-6_{exo}}$ = 3.84, $J_{5-CHO}$ = 2.65 Hz, H-5), 5.39 (1 H, ddd, $J_{1-7}$ = 5.97 Hz, $J_{1-6_{exo}}$ = 3.66 Hz, $J_{1-6_{endo}}$ = 2.0 Hz, H-1), 6.01 (1 H, d, $J_{8-7}$ = 7.77 Hz, H-8), 6.64 (1 H, dd, $J_{7-8}$ = 7.77 Hz, $J_{7-1}$ = 5.97 Hz, H-7), 7.09 (2 H, d, $J_{2''-3''}$ = 7.76 Hz, H-2'' and H-6''), 7.31 (2 H, d, $J_{3''-2''}$ = 7.76 Hz, H-3'' and H-5''), 7.48 (2 H, d, $J_{3'-2'}$ = 8.31 Hz, H-3' and H-5'), 7.88 (2 H, d, $J_{2'-3'}$ = 8.31 Hz, H-2' and H-6'), 9.70 (1 H, d, $J_{CHO-5}$ = 2.65 Hz, CHO); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.23 ($CH_3$-C4''), 21.71 ($CH_3$-C4'), 32.53 (C-5), 47.17 (C-6), 52.61 (C-1), 61.21 (C-4), 125.57, 127.97, 128.14, 129.69, 130.03, 132.38 (C-8), 135.09 (C-7), 135.87, 139.68, 145.38, 167.59 (C-3), 198.38 (CHO); IR ($CHCl_3$) 1724, 1597, 1172 cm$^{-1}$; MS $m/e$ (EI) 231 (10), 230 (58), 229 (1), 228 (3), 202 (8), 201 (25), 124 (45), 123 (57), 91 (52), 77 (5), 76 (17), 65 (21), 64 (2), 49 (100), 48 (9); $m/e$ (CI/ammonia) 445 ($MNH_4^+$, 57), 428 ($MH^+$, 74); HRMS calcd for $C_{22}H_{21}NO_4S_2$ ($M^+$) 427.0912, found 427.0915.

**5-Methyl-4-(4''-methylbenzenesulfenyl)-2-(4'-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5-*endo*-carboxaldehyde (3). High Pressure.** Methacrolein (0.223 mL, 27 mmol) was added to a solution of **1d** (100 mg, 0.260 mmol) in $CH_2Cl_2$ (1 mL) in a Teflon sealed tube and was subjected to high pressure (12 kbar) for 5 days. Solvent was removed from the reaction mixture, and the residue was chromatographed (silica gel, 30% EtOAc in hexane) to afford **3** as a white solid (62 mg, 54%). **Thermal.** Methacrolein (0.223 mL and 0.223 mL after 48 h) was added to a solution of **1d** (100 mg, 0.260 mmol) in $CH_2Cl_2$ (1 mL) in a sealed tube and was heated at 90 °C for 96h. Chromatography (silica gel, 30% EtOAc in hexane) afforded **3** as a white solid (46 mg, 40%): mp 134–135 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.93 (3 H, s, $CH_3$-C-5), 1.82 (1 H, dd, $J_{6_{exo}-6_{endo}}$ = 13.26 Hz, $J_{6-1}$ = 3.52 Hz, H-6$_{exo}$), 2.10 (1 H, dd, $J_{6_{endo}-6_{exo}}$ = 13.26 Hz, $J_{6_{endo}-1}$ = 2.07 Hz, H-6$_{endo}$), 2.31 (3 H, s, $CH_3$-C4''), 2.44 (3 H, s, $CH_3$-C4'), 5.37 (1 H, m, H-1), 5.97 (1 H, dd, $J_{8-7}$ = 7.80 Hz, $J_{8-1}$ = 1.73 Hz, H-8), 6.60 (1 H, dd, $J_{8-7}$ = 7.80 Hz, $J_{7-1}$ = 6.07 Hz, H-7), 7.05 (2 H, d, $J_{2''-3''}$ = 7.87 Hz, H-2'' and H-6''), 7.34 (4 H, t, $J$ = 8.41 Hz, H-3'' and H-5'' and H-3' and H-5'), 7.92 (2 H, d, $J_{2'-3'}$ = 8.41 Hz, H-2' and H-6'), 9.52 (1 H, s, CHO); $^{13}$C NMR ($CDCl_3$) $\delta$ 18.87 ($CH_3$-C-5), 21.21 ($CH_3$-C4''), 21.73 ($CH_3$-C4'), 40.94 (C-6), 51.96 (C-5), 52.82 (C-1), 65.76 (C-4), 126.19, 128.45, 130.29, 130.37, 132.55, 134.77, 135.86, 136.17, 139.43, 145.44, 167.49 (C-3), 199.39 (CHO); IR ($CHCl_3$) 2724, 1724, 1597, 1357, 1172 cm$^{-1}$; MS $m/e$ (EI) 245 (2), 244 (13), 216 (26), 215 (9), 124 (14), 123 (21), 91 (46), 77 (1), 65 (14), 64 (2), 49 (11), 41 (100); $m/e$ (CI/ammonia) 459 ($MNH_4^+$, 4), 442 ($MH^+$, 23); HRMS calcd for $C_{23}H_{23}NO_4S_2$ ($M^+$) 441.1069, found 411.1073.

**D. Epimerization of Nitro Bicyclic Adducts. 4-Methoxy-2-(4'-methylbenzenesulfonyl)-5-*exo*-nitro-3-oxo-2-azabicyclo[2.2.2]oct-7-ene (*epi*-2ag).** To a solution of **2ag** (25 mg, 0.07 mmol) in MeOH (1 mL) and $CH_2Cl_2$ (1 mL) was added ammonium formate (8.95 mg, 0.142 mmol) in one portion, and the reaction mixture was stirred for 20 h at room temperature. Removal of the solvent and purification by column chromatography (silica gel, $Et_2O$) gave *epi*-**2ag** as a white solid (23.6 mg, 94%): mp 213–214 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.24 (1 H, ddd, $J_{6_{exo}-6_{endo}}$ = 14.0 Hz, $J_{6_{exo}-5}$ = 4.28 Hz, $J_{6_{exo}-1}$ = 3.40 Hz, H-6$_{exo}$), 2.36 (1 H, ddd, $J_{6_{endo}-6_{exo}}$ = 14.0 Hz, $J_{6_{endo}-5}$ = 10.07 Hz, $J_{6_{endo}-1}$ = 2.37 Hz, H-6$_{endo}$), 2.43 (3 H, s, $CH_3Ar$), 3.68 (3 H, s, $OCH_3$), 4.77 (1 H, dd, $J_{5-6_{endo}}$ = 10.07 Hz, $J_{5-6_{exo}}$ = 4.28 Hz, H-5), 5.49 (1 H, m, H-1), 6.52 (1 H, dd, $J_{8-7}$ = 8.14 Hz, $J_{8-1}$ = 1.69 Hz, H-8), 6.76 (1 H, dd, $J_{7-8}$ = 8.14 Hz, $J_{7-1}$ = 5.93 Hz, H-7), 7.33 (2 H, d, $J_{3'-2'}$ = 8.43 Hz, H-3' and H-5'), 7.95 (2 H, d, $J_{2'-3'}$ = 8.43 Hz, H-2' and H-6'); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.99 ($CH_3$-C-4), 34.29 (C-6), 50.68 ($OCH_3$), 55.47 (C-1), 83.00 (C-4), 84.65 (C-5), 128.58, 129.81, 129.88, 130.89 (C-8), 135.81 (C-7), 145.83, 165.82 (C-3); IR ($CHCl_3$) 1741 (C=O), 1565, 1367, 1172 cm$^{-1}$; MS $m/e$ (EI) 155 (2), 110 (7), 109 (100), 91 (12), 77 (8); $m/e$ (CI/ammonia) 370 ($MNH_4^+$, 100), 353 ($MH^+$, 30); HRMS

calcd for $C_{15}H_{20}N_3O_6S$ ($MNH_4^+$) 370.1073, found 370.1080.

**4-(Benzyloxy)-2-(4′-methylbenzenesulfonyl)-5-*exo*-nitro-3-oxo-2-azabicyclo[2.2.2]oct-7-ene (*epi*-2bg).** To a solution of **2bg** (50 mg, 0.101 mmol) in MeOH (1 mL) and $CH_2Cl_2$ (1 mL) was added ammonium formate (12.7 mg, 0.202 mmol) in one portion, and the reaction mixture was stirred for 60 h at room temperature. Removal of the solvent and purification by column chromatography (30% EtOAc in hexane) gave 38.5 mg (89%) of *epi*-**2bg** as a white solid: mp 195–196 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 2.26 (1 H, dt $J_{6_{exo}-6_{endo}}$ = 14.0 Hz, $J_{6_{exo}-5}$ = 4.28 Hz, $J_{6_{exo}-1}$ = 3.66 Hz, H-$6_{exo}$), 2.35 (1 H, ddd, $J_{6_{endo}-6_{exo}}$ = 14.0 Hz, $J_{6_{endo}-5}$ = 10.07 Hz, $J_{6_{endo}-1}$ = 2.38 Hz, H-$6_{endo}$), 2.45 (3 H, s, $CH_3$-C-4′), 4.73 (1 H, d, $J$ = 11.49 Hz, $PhCH_2$), 4.85 (1 H, dd, $J_{5-6_{endo}}$ = 10.07 Hz, $J_{5-6_{exo}}$ = 4.28 Hz, H-5), 5.21 (1 H, d, $J$ = 11.49 Hz, $PhCH_2$), 5.51 (1 H, m, H-1), 6.49 (1 H, dd, $J_{8-7}$ = 8.11 Hz, $J_{8-1}$ = 1.59 Hz, H-8), 6.76 (1 H, dd, $J_{7-8}$ = 8.11 Hz, $J_{7-1}$ = 5.93 Hz, H-7), 7.27–7.37 (7 H, m, H-Ar), 7.96 (2 H, d, $J_{2'-3'}$ = 8.37 Hz, H-2′ and H-6′); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.84 ($CH_3$-C-4′), 34.29 (C-6), 50.70 (C-1), 69.83 ($CH_2Ph$), 84.23 (C-4), 84.88 (C-5), 127.30, 128.02, 128.51, 128.62, 129.90, 131.57 (C-8), 135.06, 135.74 (C-7), 137.54, 145.80, 157.03 (C-3); IR ($CHCl_3$) 1740 (C=O), 1565, 1366, 1354 1166 $cm^{-1}$; MS *m/e* (EI) 185 (9), 184 (2), 155 (6), 91 (100), 77 (3); *m/e* (CI/ammonia) 446 ($MNH_4^+$, 4); HRMS calcd for $C_{21}H_{24}N_3O_6S$ ($MNH_4^+$) 446.1386, found 446.1392.

**4-(4″-Methylbenzenesulfenyl)-2-(4′-methylbenzenesulfonyl)-5-*exo*-nitro-3-oxo-2-azabicyclo[2.2.2]-7-octene (*epi*-2dg).** To a solution of **2dg** (131 mg, 0.295 mmol) in MeOH (1 mL) and $CH_2Cl_2$ (2 mL) was added ammonium formate (38.36 mg, 0.59 mmol) in one portion, and the reaction mixture was stirred for 20 h at room temperature. Removal of the solvent and purification by flash column chromatography (30% EtOAc in hexane) afforded *epi*-**2dg** as a white solid (125 mg, 95%): mp 165–166 °C (from $CH_2Cl_2/Et_2O$ (1:2) v/v); $^1H$ NMR ($CDCl_3$) $\delta$ 2.36 (3 H, s, $CH_3$-C4″), 2.44 (3 H, s, $CH_3$-C-4′), 4.67 (1 H, dd, $J_{5-6_{exo}}$ = 8.98 Hz, $J_{5-6_{endo}}$ = 5.15 Hz, H-5), 5.48 (1 H, m, $J_{1-7}$ = 5.93 Hz, $J_{1-6_{exo}}$ = 4.28 Hz, $J_{1-6_{endo}}$ = 2.41 Hz, $J_{1-8}$ = 1.80 Hz, H-1), 6.19 (1 H, dd, $J_{8-7}$ = 7.76 Hz, $J_{8-1}$ = 1.80 Hz, H-8), 6.61 (1 H, dd, $J_{7-8}$ = 7.76 Hz, $J_{7-1}$ = 5.93 Hz, H-7), 7.18 (2 H, d, $J_{2''-3''}$ = 8.0 Hz, H-2″ and H-6″), 7.34 (2 H, d, $J_{3''-2''}$ = 8.0 Hz, H-3″ and H-5″), 7.51 (2 H, d, $J_{3'-2'}$ = 8.34 Hz, H-3′ and H-5′), 7.91 (2 H, d, $J_{2'-3'}$ = 8.34 Hz, H-2′ and H-6′); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.42 ($CH_3$-C4″), 21.95 ($CH_3$-C4′), 35.00 (C-6), 51.11 (C-1), 61.87 (C-4), 84.62 (C-5), 123.90, 128.62, 129.85, 130.65, 132.72 (C-8), 135.41 (C-7), 138.01, 140.97, 189.58 (C-3); IR ($CHCl_3$) 1725 (C=O), 1560, 1354, 1166 $cm^{-1}$; MS *m/e* (EI) 247 (2), 217 (12), 216 (36), 201 (37), 155 (7), 124 (13), 123 (100), 119 (33), 91 (90), 79 (14), 77 (16), 65 (49); *m/e* (CI/ammonia) 462 ($MNH_4^+$, 7), 445 ($MH^+$, 12); HRMS calcd for $C_{21}H_{20}N_2O_5S_2$ ($MH^+$) 444.0892, found 444.0898.

**E. Chemical Manipulation of 1-Azabicyclo[2.2.2]octanes. 5-*endo*-(Hydroxymethyl)-4-(4″-methylbenzenesulfenyl)-2-(4′-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene.** $NaBH_4$ (19.35 mg) was added to a solution of **2dh** (218.5 mg, 0.511 mmol) in $CH_2Cl_2$ (3 mL) and methanol (5 mL) at 0 °C, and the reaction mixture was stirred for 15 min and then poured into $H_2O$ (25 mL) and extracted with $CH_2Cl_2$ (3 × 50 mL), dried ($MgSO_4$), filtered, and concentrated. Purification of the residue by flash column chromatography (silica gel, EtOAc) afforded *epi*-**2dh** as a clear oil (203.9 mg, 93%): $^1H$ NMR ($CDCl_3$) $\delta$ 1.59 (1 H, ddd, $J_{6_{endo}-6_{exo}}$ = 13.0 Hz, $J_{6_{endo}-5}$ = 4.24 Hz, $J_{6_{endo}-1}$ = 2.0 Hz, H-$6_{endo}$), 1.75 (1 H, bs, OH), 2.15 (1 H, m, H-5), 2.32 (3 H, s, $CH_3$-C4″), 2.36 (1 H, m, H-$6_{exo}$), 2.44 (3 H, s, $CH_3$-C4′), 3.42 (1 H, dd, $J_{9a-9b}$ = 11.34 Hz, $J_{9a-5}$ = 6.94 Hz, $-CH_{9a}H_{9b}OH$), 3.92 (1 H, dd, $J_{9b-9a}$ = 11.34 Hz, $J_{9b-5}$ = 5.17 Hz, $-CH_{9a}H_{9b}OH$), 5.30 (1 H, ddd, $J_{1-7}$ = 6.02 Hz, $J_{1-6_{exo}}$ = 3.48 Hz, $J_{1-6endo}$ = 2.0 Hz, H-1), 5.92 (1 H, d, $J_{8-7}$ = 7.80 Hz, H-8), 6.50 (1 H, ddd, $J_{7-8}$ = 7.80 Hz, $J_{7-1}$ = 6.02 Hz, H-7), 7.05 (2 H, d, $J_{2''-3''}$ = 8.0 Hz, H-2″, H-6″), 7.30 (2 H, d, $J_{3''-2''}$ = 8.0 Hz, H-3″ and H-5″), 7.39 (2 H, d, $J_{3'-2'}$ = 8.37 Hz, H-3′ and H-5′), 7.89 (2 H, d, $J_{2'-3'}$ = 8.37 Hz, H-2′ and H-6′); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.29 ($CH_3$-C-4″), 21.81 ($CH_3$-C-4′), 33.65 (C-5), 38.96 (C-6), 52.43 (C-1), 63.75 (C-4), 64.38 (C-9), 127.07, 128.27, 129.69, 129.92, 132.79, 132.06, 134.81, 135.45, 138.84, 145.19, 169.29 (C-3); IR ($CHCl_3$) 3612, 3518, 1713, 1595, 1354, 1172 $cm^{-1}$; MS *m/e* (EI) 232 ($M^+$ – TsNCO, 3), 155 (2), 123 (4), 109 (8), 91 (8), 42 (7), 41 (100); *m/e* (CI/ammonia) 447 ($MNH_4^+$, 3), 430 ($MH^+$, 21); HRMS calcd for $C_{22}H_{24}NO_4S_2$ ($MH^+$) 430.1147, found 430.1141.

**5-*endo*-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-4-(4″-methylbenzenesulfenyl)-2-(4′-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene (4).** Triethylamine (0.019 mL, 0.151 mmol) was added to the solution of 5-(hydroxymethyl)-4-(4″-methylbenzenesulfenyl)-2-(4′-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene (54.4 mg, 0.126 mmol) in $CH_2Cl_2$ (2 mL) at 0 °C. After 5 min, TBDMSOTf (0.034 mL, 0.151 mmol) was added via syringe. After 5 min the reaction mixture was quenched with $H_2O$ (5 mL) and extracted with $Et_2O$ (3 × 75 mL), dried ($MgSO_4$), filtered, and concentrated to give a residue which was purified by columm chromatography (silica gel, 30% EtOAc in hexane) to give **4** as a clear oil (65 mg, 95%): $^1H$ NMR ($CDCl_3$) $\delta$ –0.01 (3 H, s, $CH_3Si$), 0.05 (3 H, s, $CH_3Si$), 0.89 (9 H, s, $(CH_3)_3CSi$), 1.82 (1 H, ddd, $J_{6_{endo}-6_{exo}}$ = 12.92 Hz, $J_{6_{endo}-5}$ = 4.09 Hz, $J_{6_{endo}-1}$ = 2.01 Hz, H-$6_{endo}$), 2.11 (1 H, m, H-5), 2.35 (1 H, m, H-$6_{exo}$), 2.37 (3 H, s, $CH_3$-C4″), 2.50 (3 H, s, $CH_3$-C4′), 3.46 (1 H, dd, $J_{9a-9b}$ = 10.0 Hz, $J_{9a-5}$ = 8.37 Hz, $-CH_{9a}H_{9b}OSi$), 3.97 (1 H, dd, $J_{9b-9a}$ = 10.0 Hz, $J_{9b-5}$ = 4.08 Hz, $-CH_{9a}H_{9b}OSi$), 5.35 (1 H, ddd, $J_{1-7}$ = 5.97 Hz, $J_{1-6exo}$ = 4.05 Hz, $J_{1-6_{endo}}$ = 2.01 Hz, H-1), 5.92 (1 H, d, $J_{8-7}$ = 7.8 Hz, H-8), 6.51 (1 H, dd, $J_{7-8}$ = 7.80 Hz, $J_{7-1}$ = 5.97 Hz, H-7), 7.09 (2 H, d, $J_{2''-3''}$ = 8.0 Hz, H-2″ and H-6″), 7.35 (2 H, d, $J_{3''-2''}$ = 8.0 Hz, H-3″ and H-5″), 7.44 (2 H, d, $J_{3'-2'}$ = 8.41 Hz, H-3′ and H-5′), 7.49 (2 H, d, $J_{2'-3'}$ = 8.41 Hz, H-2′ and H-6′); $^{13}C$ NMR ($CDCl_3$) $\delta$ –5.34 ($CH_3Si$), –5.25 ($CH_3Si$), 18.20 (($C-H_3)_3CSi$), 21.27 ($CH_3$-C4″), 21.82 ($CH_3$-C4′), 25.90 (($CH_3)_3CSi$), 33.02 (C-5), 38.37 (C-6), 52.56 (C-1), 63.22 (C-4), 63.94 (C-9), 127.65, 128.30, 129.63, 129.81, 132.33, 133.29, 134.52, 135.57, 138.43, 145.02, 169.52 (C-3); IR ($CHCl_3$), 3036, 2954, 1719 (C=O), 1595, 1354, 1249, 1166, 1096 $cm^{-1}$; MS *m/e* (EI) 544 ($MH^+$, 100), 390 (13), 347 (15), 289 (4), 229 (18), 155 (2), 91 (8), 58 (4); *m/e* (CI/ammonia) 486 ($M^+$ – *t*-Bu, 2); HRMS calcd for $C_{24}H_{28}NO_4S_2Si$ ($M^+$ – *t*-Bu) 486.1229, found 486.1232.

**5-*endo*-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-2-(4′-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene (5).** $Bu_3SnH$ (0.076 mL, 0.283 mmol) and azobisisobutyronitrile (AIBN) (46.4 mg, 0.283 mmol) were added to the solution of compound **4** (70 mg, 0.128 mmol) in anhydrous benzene (3 mL), the mixture was heated at reflux temperature for 2 h, another 0.283 mmol of AIBN was added via syringe in benzene (0.5 mL), after 2 h reflux the reaction mixture was cooled down to room temperature, the solvent was removed under reduced pressure, and the resultant residue was purified by PTLC (silica gel, 20% EtOAc in hexane, three elutions) to give **5** (48 mg, 89%) as a clear oil: $^1H$ NMR ($CDCl_3$) $\delta$ –0.01 (6 H, s, $CH_3$-Si), 0.84 (9 H, s, $(CH_3)_3CSi$), 0.97 (1 H, m, H-5), 1.24–1.38 (2 H, m, H-$6_{endo}$ and H-4), 2.18 (1 H, ddd, $J_{6_{exo}-6_{endo}}$ = 14.0 Hz, $J_{6_{exo}-5}$ = 9.26 Hz, $J_{6_{exo}-1}$ = 3.66 Hz, H-$6_{exo}$), 2.40 (3 H, s, $CH_3$-C4′), 3.11 (1 H, t, $J_{9a-9b}$ = 10.0 Hz, $J_{9a-5}$ = 10.0 Hz $-CH_{9a}H_{9b}OSi$), 3.41 (1 H, dd, $J_{9b-9a}$ = 10.0 Hz, $J_{9b-5}$ = 5.26 Hz, $-CH_{9a}H_{9b}OSi$), 5.31 (1 H, ddd, $J_{1-7}$ = 5.8 Hz, $J_{1-6_{exo}}$ = 3.66 Hz, $J_{1-6_{endo}}$ = 1.41 Hz, H-1), 6.14 (1 H, ddd, $J_{8-4}$ = 7.87 Hz, $J_{8-7}$ = 7.52 Hz, $J_{8-1}$ = 1.66 Hz, H-8), 6.50 (1 H, ddd, $J_{7-8}$ = 7.52 Hz, $J_{7-1}$ = 5.8 Hz, $J_{7-4}$ = 1.53 Hz, H-7), 7.27 (2 H, d, $J_{3'-2'}$ = 8.35 Hz, H-3′ and H-5′), 7.84 (2 H, d, $J_{2'-3'}$ = 8.35 Hz, H-2′ and H-6′); $^{13}C$ NMR ($CDCl_3$) $\delta$ –5.37 ($CH_3Si$), –5.25 ($CH_3Si$), 21.75 ($CH_3$-C4′), 25.34 (($CH_3)_3CSi$), 25.97 (($CH_3)_3CSi$), 30.37 (C-5), 35.40 (C-6), 47.32 (C-4), 53.86 (C-1), 64.81 (C-9), 128.11, 129.61, 129.72 (C-8), 129.83, 133.35 (C-7), 144.72, 171.27 (C-3); IR ($CHCl_3$) 1713 (C=O), 1595, 1354, 1255, 1102, 1090 $cm^{-1}$; MS *m/e* (EI) 422 ($MH^+$, 2), 364 ($M^+$ – *t*-Bu, 24), 167 (46), 155 (21), 152 (41), 115 (7), 100 (5), 91 (72), 59 (15), 57 (4); *m/e* (CI/ammonia) 439 ($MNH_4^+$, 5), 422 ($MH^+$, 100), 364 ($M^+$ – *t*-Bu, 4); HRMS calcd for $C_{21}H_{32}NO_4SSi$ ($MH^+$) 422.1821, found 422.1818.

**Methyl 6α-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-4β-[(4′-methylbenzenesulfonyl)amino]cyclohexene-1-carboxylate (6).** To a solution of LiOMe (0.32 mL of *n*-BuLi 1.6M in hexanes in 5 mL of anhydrous MeOH) at 0 °C, a solution of compound **5** (11 mg, 0.026 mmol) in $CH_2Cl_2$ (0.5 mL) was added via cannula. The reaction mixture was warmed to room temperature and stirred for 4 h, quenched with saturated aqueous $NH_4Cl$ (5 mL), extracted with $CH_2Cl_2$ (4 × 20 mL), dried ($MgSO_4$), filtered, and concentrated. The resultant residue was purified by ptlc (30% EtOAc in hexanes) to give **6** as a clear oil (7.7 mg, 66%): $^1H$ NMR ($CDCl_3$) $\delta$ –0.07 (3 H, s, $CH_3Si$), –0.03 (3 H, s, $CH_3Si$), 0.82 (9 H, s, $(CH_3)_3CSi$), 1.25 (1 H, m, H-5α), 1.44 (1 H, m, H-5β), 1.97–2.04 (1 H, m, H-6), 2.42 (3 H, s, $CH_3$-C4′), 2.52 (2 H, m, H-3α,β), 2.76 (1 H, m, H-4), 3.47 (1 H, dd, $J_{7a-7b}$ = 10.0

Hz, $J_{7a-6}$ = 7.02 Hz, -C$H_{7a}$H$_{7b}$OSi), 3.61 (1 H, dd, $J_{7b-7a}$ = 10.0 Hz, $J_{7b-6}$ = 3.29 Hz, -CH$_{7a}$H$_{7b}$OSi), 3.70 (3 H, s, $CH_3O$), 4.47 (1 H, d, NH, $J$ = 8.0 Hz), 6.86 (1 H, t, $J$ = 3.35 Hz, H-2), 7.25 (2 H, d, $J_{3'-2'}$ = 8.31 Hz, H-3' and H-5'), 7.77 (2 H, d, $J_{2'-3'}$ = 8.31 Hz, H-2' and H-6'); $^{13}$C NMR ($CDCl_3$) $\delta$ -5.47 ($CH_3Si$), -5.37 ($CH_3Si$), 17.83 (($CH_3)_3CSi$), 21.72 ($CH_3$-C4'), 26.02 (($CH_3)_3CSi$), 32.30, 34.12, 37.01, 46.04 ($OCH_3$), 51.83 (C-3), 64.81 (C-7), 127.17, 129.93, 130.13, 138.36 (C-1), 139.27 (C-2), 143.35, 166.98 ($CO_2Me$); IR ($CHCl_3$) 1707, 1648, 1595, 1255, 1155, 1078 cm$^{-1}$; MS $m/e$ (EI) 397 (24), 396 ($M^+$ - $t$-Bu, 100), 226 (18), 225 (99), 155 (7), 115 (6), 91 (40), 89 (64) 59 (14), 58 (5), 57 (4), HRMS calcd for $C_{18}H_{26}NO_5SSi$ ($M^+$ - $t$-Bu) 396.1301, found 396.1305.

**4-[(*tert*-Butyldimethylsilyl)oxy]-5-*endo*-(hydroxymethyl)-2-(4'-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene.** $NaBH_4$ (49 mg, 1.29 mmol) was added to a solution of **2ch** (561 mg, 1.29 mmol) in $CH_3OH$ (10 mL) at room temperature. The reaction mixture was stirred for 15 min and then poured into $H_2O$ (10 mL) and was extracted with $CH_2Cl_2$ (3 × 50 mL) and dried ($Na_2SO_4$). Removal of solvent followed by flash columm chromatography (silica gel, 50–100% $Et_2O$ in hexane) afforded a gummy solid (563 mg, 100%): $^1$H NMR ($CDCl_3$) $\delta$ -0.14 (3 H, s, $CH_3Si$), 0.24 (3 H, s, $CH_3Si$), 0.89 (9 H, s, $(CH_3)_3CSi$), 1.09 (1 H, ddd, $J$ = 13.0, 4.8, 1.9 Hz, H-6$_{endo}$), 2.14 (1 H, m, H-5), 2.27 (1 H, ddd, $J$ = 13.0, 9.5, 3.6 Hz, H-6$_{exo}$), 2.42 (3 H, s, $CH_3Ar$), 3.39 (1 H, dd, $J$ = 11.3, 4.6 Hz, C$H_2$OH), 3.69 (1 H, dd, $J$ = 11.3, 8.1 Hz, C$H_2$OH), 5.20 (1 H, m, H-1), 6.07 (1 H, d, $J$ = 8.0 Hz, H-8), 6.39 (1 H, dd, $J$ = 8.0, 6.0 Hz, H-7), 7.29 (2 H, d, $J$ = 8.5 Hz, tosyl H), 7.83 (2 H, d, $J$ = 8.5 Hz, tosyl H); $^{13}$C NMR ($CDCl_3$) $\delta$ -3.88 ($CH_3Si$), -2.89 ($CH_3Si$), 18.41 ($Me_3CSi$), 21.63 ($CH_3Ar$), 25.96 (($CH_3)_3CSi$), 30.98 (C-6), 39.71 (C-5), 52.04 (C-1), 64.85 ($CH_2OH$), 83.05 (C-4), 127.82 (C-2'), 129.47 (C-3'), 130.58 (C-4' and C-7), 135.04 (C-8), 135.39 (C-1'), 171.02 (C-3); IR ($CHCl_3$) 1736 (C=O), 1598, 1472, 1361, 1188, 1121, 1090 cm$^{-1}$. Anal. Calcd for $C_{21}H_{31}NO_5SSi$: C, 57.64; H, 7.14; N, 3.20. Found: C, 57.71; H, 7.15; N, 3.16.

**4-Hydroxy-5-*endo*-(hydroxymethyl)-2-(4'-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene.** The alcohol from the above preparation (73 mg, 0.167 mmol) was dissolved in THF, and tetra-$n$-butylammonium fluoride (TBAF) (1 M solution in THF, 1 mL) was added at room temperature. After 20 min, the solvent was evaporated and the residue was chromatographed directly ($Et_2O$) to afford a white solid (32 mg, 60%): mp 174 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.10 (1 H, ddd, $J$ = 13.0, 4.95, 1.9 Hz, H-6$_{endo}$), 2.02 (1 H, m, H-5), 2.31 (1 H, ddd, $J$ = 13.0, 9.8, 3.8 Hz, H-6$_{exo}$), 2.44 (3 H, s, $CH_3Ar$), 3.45 (1 H, m, C$H_2$OH), 3.76 (1 H, dd, $J$ = 11.4, 9.4 Hz, C$H_2$OH), 5.28 (1 H, ddd, $J$ = 7.5, 3.8, 1.9 Hz, H-1), 6.20 (1 H, d, $J$ = 6.0 Hz, H-8), 6.43 (1 H, dd, $J$ = 7.5, 6.0 Hz, H-7), 7.32 (2 H, d, $J$ = 8.0 Hz, tosyl H), 7.84 (2 H, d, $J$ = 8.0 Hz, tosyl H); IR ($CHCl_3$) 3483, 1723, 1596, 1519, 1174 cm$^{-1}$. Anal. Calcd for $C_{15}H_{17}NO_5S$: C, 55.72; H, 5.30; N, 4.33. Found: C, 55.61; H, 5.32; N, 4.28.

This bis-alcohol is sensitive to chromatography. Therefore, for the next step, the crude product obtained after standard aqueous workup was used.

**4-Hydroxy-5-*endo*-[[(*tert*-butyldimethylsilyl)oxy]methyl]-2-(4'-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene (7).** To a $CH_2Cl_2$ (5 mL) solution of crude bis-alcohol, prepared as described previously by addition of TBAF (1 M solution in THF, 2 mL) to alcohol (430 mg, 0.98 mmol), was added TBDMSCl (150 mg, 1.0 mmol) and triethylamine (0.15 mL, 1.08 mmol). After 8 h, the solution was poured into water (10 ml) and was extracted with $CH_2Cl_2$ (2 × 50 mL). Evaporation of solvent followed by chromatography (15–50% $Et_2O$ in hexane) afforded white solid 7 (360 mg, 80% over two steps): mp 113 °C; $^1$H NMR ($CDCl_3$) $\delta$ -0.01 (6 H, s, $(CH_3)_2Si$), 0.84 (9 H, s, $(CH_3)_3CSi$), 1.48 (1 H, ddd, $J$ = 13.1, 4.6, 1.95 Hz, H-6$_{endo}$), 2.00 (1 H, m, H-5), 2.26 (1 H, ddd, $J$ = 13.1, 9.4, 3.7 Hz, H-6$_{exo}$), 2.42 (3 H, s, $CH_3Ar$), 3.49 (1 H, dd, $J$ = 9.9, 7.2 Hz, C$H_2$OSi), 3.76 (1 H, dd, $J$ = 9.9, 5.6 Hz, C$H_2$OSi), 5.27 (1 H, ddd, $J$ = 6.0, 3.7, 1.95 Hz, H-1), 6.08 (1 H, d, $J$ = 8.0 Hz, H-8), 6.35 (1 H, dd, $J$ = 8.0, 6.0 Hz, H-7), 7.30 (2 H, d, $J$ = 8.5 Hz, tosyl H), 7.85 (2 H, d, $J$ = 8.5 Hz, tosyl H); $^{13}$C NMR ($CDCl_3$) $\delta$ -5.41 ($CH_3Si$), -5.40 ($CH_3Si$), 18.11 ($Me_3CSi$), 21.67 ($CH_3Ar$), 25.77 (($CH_3)_3CSi$), 31.36 (C-6), 39.53 (C-5), 52.81 (C-1), 63.57 ($CH_2OSi$), 78.63 (C-4), 127.96 (C-2'), 129.63 (C-3'), 129.94 (C8/C-7), 135.37 (C-4'), 135.65 (C-8/C-7), 145.24 (C-1'), 172.43 (C-3); IR ($CHCl_3$) 1721 (C=O), 1598, 1472, 1361 1188, 1172, 1089 cm$^{-1}$. Anal. Calcd for $C_{21}H_{31}NO_5SSi$: C, 57.64; H, 7.14; N, 3.20. Found: C, 57.51; H, 7.08; N, 3.18.

**Methyl 6$\beta$-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-1$\beta$-hydroxy-4$\alpha$-(4'-methylbenzenesulfonamido)cyclohex-2-enecarboxylate (8).** $n$-BuLi (3.2 mmol) was added slowly to MeOH (10 mL), and the solution thus obtained was added to bicyclic lactam (360 mg, 0.822 mmol) at room temperature under dry $N_2$ atmosphere. After 2 h, a workup procedure as described above followed by purification by flash chromatography (50% $Et_2O$ in hexane) afforded 8 as a gummy solid (260 mg, 81%): $^1$H NMR ($CDCl_3$) $\delta$ 0.00 (3 H, s, $CH_3Si$), 0.01 (3 H, s, $CH_3Si$), 0.85 (9 H, s, $(CH_3)_3CSi$), 1.25 (1 H, m, H-6), 1.55 (1 H, dm, $J$ = 13.0 Hz, H-5$_\beta$), 1.67 (1 H, dt, $J_t$ = 4.4 Hz, $J_d$ = 11.5 Hz, H-5$_\alpha$), 2.43 (3 H, s, $CH_3$-Ar), 3.43 (1 H, dd, $J$ = 4.7, 9.9 Hz, $CH_2OSi$), 3.61 (1 H, dd, $J$ = 8.7, 9.9 Hz, $CH_2OSi$), 3.74 (3 H, s, $CO_2CH_3$), 3.87 (1 H, m, H-4), 4.81 (1 H, bd, $J$ = 8.0 Hz, NH), 5.60 (2 H, d, $J$ = 10.0 Hz, H-2), 5.64 (1 H, dd, $J$ = 4.0, 10 Hz, H-3), 7.31 (2 H, d, $J$ = 8.0 Hz, ArH), 7.78 (2 H, d, $J$ = 8.0 Hz, ArH); $^{13}$C NMR ($CDCl_3$) $\delta$ -5.64 ($CH_3Si$), 18.31 ($Me_3C$), 21.48 ($CH_3Ar$), 25.85 (($CH_3)_3C$), 27.41 (C-5), 37.58 (C-6), 47.12 (C-4), 52.93 (ester $CH_3$), 62.59 ($CH_2O$), 71.45 (C-1), 126.92 (C-2'), 128.51 (C-2/C-3), 129.75 (C-3'), 131.56 (C-2/C-3), 137.90 (C-4'), 143.46 (C-1'), 176.13 ($CO_2Me$); IR (film) 3273 (OH and NH), 2929, 1735 (C=O), 1437, 1250, 1086 cm$^{-1}$; HRMS calcd for $C_{18}H_{26}NO_6SSi$ ($M^+$ - $t$-Bu) 412.1250, found 412.1259.

**5-*endo*-(Hydroxymethyl)-4-methoxy-2-(4'-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene.** This compound was prepared in accordance with the general procedure described previously. Thus, starting from a solution of aldehyde (357 mg, 1.07 mmol) in MeOH (10 mL) and $NaBH_4$ (38 mg, 1.0 mmol), we obtained a waxy solid (313 mg, 94%): $^1$H NMR ($CDCl_3$) $\delta$ 1.02 (1 H, ddd, $J$ = 12.6, 4.4, 1.8 Hz, H-6$_{endo}$), 2.14 (1 H, m, H-5), 2.22 (1 H, ddd, $J$ = 12.6, 9.7, 3.7 Hz, H-6$_{exo}$), 2.44 (3 H, s, $CH_3Ar$), 3.32 (1 H, dd, $J$ = 11.4, 4.1 Hz, C$H_2$OH), 3.54 (1 H, dd, $J$ = 11.4, 8.5 Hz, C$H_2$OH), 3.65 (3 H, s, $CH_3O$), 5.26 (1 H, ddd, $J$ = 6.0, 3.7, 1.8 Hz, H-1), 6.43 (1 H, dd, $J$ = 8.2, 1.4 Hz, H-8), 6.58 (1 H, dd, $J$ = 8.2, 6.0 Hz, H-7), 7.32 (2 H, d, $J$ = 8.3 Hz, tosyl H), 7.88 (2 H, d, $J$ = 8.3 Hz, tosyl H); IR (film) 3522 (OH), 1726 (C=O), 1597 (C=C), 1355, 1170, 1089 cm$^{-1}$; HRMS calcd for $C_{16}H_{20}NO_5S$ ($MH^+$) 338.1062, found 338.1069.

**4-(Benzyloxy)-5-*endo*-(hydroxymethyl)-2-(4'-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene.** $NaBH_4$ (17.67 mg) was added to a solution of **2bh** (192 mg, 0.467 mmol) in $CH_2Cl_2$ (3 mL) and MeOH (5 mL) at 0 °C, and the reaction mixture was stirred at this temperature for 15 min, poured into 25 mL of $H_2O$, extracted with $CH_2Cl_2$ (3 × 50 mL), dried ($MgSO_4$), filtered, and concentrated. Purification by columm chromatography (silica gel, 50% EtOAc in hexane) gave a white solid (149 mg, 86%): mp 105–106 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.11 (1 H, m, H-6$_{endo}$), 2.20–2.28 (2 H m, H-5 and H-6$_{exo}$), 2.44 (3 H, s, $CH_3Ar$), 2.78 (1 H, s broad, OH), 3.35 (1 H, t, $J$ = 11.36 Hz, -C$H_{9a}$H$_{9b}$OH), 3.63 (1 H, dd, $J_{9b-9a}$ = 11.36 Hz, $J_{9b-5}$ = 8.0 Hz, -CH$_{9a}$H$_{9b}$OH), 4.68 (1 H, d, $J$ = 12.03 Hz, $PhCH_2$), 5.11 (1 H, d, $J$ = 12.03 Hz, $PhCH_2$), 5.28 (1 H, ddd, $J_{1-7}$ = 6.04 Hz, $J_{1-6_{exo}}$ = 3.34 Hz, $J_{1-6_{endo}}$ = 1.76 Hz, H-1), 6.46 (1 H, d, $J_{8-7}$ = 8.21 Hz, H-8), 6.56 (1 H, dd, $J_{7-8}$ = 8.21 Hz, $J_{7-1}$ = 6.04 Hz, H-7), 7.30–7.40 (7 H, m, H-Ar), 7.90 (2 H, d, $J_{2'-3'}$ = 8.34 Hz, H-2' and H-6'); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.85 ($CH_3Ar$), 31.55 (C-5), 38.88 (C-6), 52.39 (C-1), 64.62 ($PhCH_2$), 69.97 ($OCH_2$), 86.17 (C-4), 127.80, 128.08, 128.18, 128.75, 129.09, 131.09 (C-8), 132.54 (C-7), 135.64, 137.66, 145.45, 170.37 (C=O); IR ($CHCl_3$) 3671, 3542, 1725, 1596, 1225, 1172 cm$^{-1}$; MS $m/e$ (EI) 217 (2), 216 ($M^+$ - TsNCO, 13), 155 (2), 125 (2), 91 (100); $m/e$ (CI/ammonia) 431 ($MNH_4^+$, 23), 414 ($MH^+$, 100); HRMS calcd for $C_{22}H_{24}NO_5S$ ($MH^+$) 414.1375, found 414.1378.

**5-*endo*-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-4-methoxy-2-(4'-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene (9ah).** This compound was prepared in accordance with the general procedure described previously. Thus, starting from a solution of alcohol (313 mg, 0.929 mmol) in $CH_2Cl_2$ (15 mL), TBDMSTf (0.5 mL), and $Et_3N$ (0.25 mL), we obtained **9ah** as gummy solid (383 mg, 91%): $^1$H NMR ($CDCl_3$) $\delta$ -0.02 (3 H, s, $CH_3Si$), 0.00 (3 H, s, $CH_3Si$), 0.83 (9 H, s, $(CH_3)_3CSi$), 1.63 (1 H, ddd, $J$ = 13.1, 4.6, 1.9 Hz, H-6$_{endo}$), 2.18 (2 H, m, H-5 and H-6$_{exo}$), 2.43 (3 H, s, $CH_3Ar$), 3.33 (1 H, dd, $J$ = 9.9, 7.5 Hz, C$H_2$OSi), 3.58 (3 H, s, $CH_3O$), 3.73 (1 H, dd, $J$ = 9.7, 3.9 Hz, C$H_2$OSi), 5.25 (1 H, m, H-1), 6.21 (1 H, dd, $J$ = 8.2, 1.8 Hz, H-8),

6.44 (1 H, dd, $J$ = 8.2, 5.9 Hz, H-7), 7.29 (2 H, d, $J$ = 8.6 Hz, tosyl H), 7.86 (2 H, d, $J$ = 8.6 Hz, tosyl H); $^{13}$C NMR ($CDCl_3$) $\delta$ –5.40 ($CH_3Si$), 18.15 ($Me_3CSi$), 21.78 ($CH_3Ar$), 25.85 (($CH_3)_3CSi$), 31.57 (C-6), 38.04 (C-5), 52.56 (C-1), 54.25 ($CH_3O$), 62.09 ($CH_2OSi$), 83.20 (C-4), 128.02 (C-2′), 129.64 (C-3′), 131.03 (C8/C-7), 135.58 (C-4′), 132.01 (C-8/C-7), 145.04 (C-1′), 172.40 (C-3); IR ($CHCl_3$) 1728 (C=O) 1598, 1472, 1360, 1262, 1172, 1081 cm$^{-1}$; MS $m/e$ (EI) 394 ($M^+$ – $t$-Bu, 20), 197 (30), 122 (100), 109 (38), 91 (32), 89 (41), 85 (34), 73 (45); $m/e$ (CI/ammonia) 469 ($MNH_4^+$, 10), 453 (31), 452 ($MH^+$, 100), 355 (14), 338 (50), 140 (10), 122 (22), 79 (20); HRMS calcd for $C_{18}H_{24}NO_5SSi$ ($M^+$ – $t$-Bu) 394.1145, found 394.1152.

**4-(Benzyloxy)-5-*endo*-[(*tert*-butyldimethylsiloxy)-methyl]-2-(4′-methylbenzenesulfonyl)-3-oxo-2-azabicyclo-[2.2.2]oct-7-ene (9bh).** Triethylamine (0.027 mL, 0.274 mmol) was added to the solution of 4-(benzyloxy)-5-*endo*-(hydroxymethyl)-2-(4′-methylbenzenesulfonyl)-3-oxo-2-azabicyclo[2.2.2]-oct-7-ene (103 mg, 0.249 mmol) in $CH_2Cl_2$ (3 mL) at 0 °C, and after 5 min TBDMSTf (0.038 mL, 0.299 mmol) was added via syringe. The reaction mixture was quenched with $H_2O$ (5 mL) after 5 min and was extracted with $Et_2O$ (3 × 75 mL), dried ($MgSO_4$), filtered, and concentrated to give a residue which was purified by column chromatography (silica gel 50% EtOAc in hexane) to give the title compound as a clear oil (128 mg, 98%): $^1$H NMR ($CDCl_3$) $\delta$ –0.01 (3 H, s, $CH_3Si$), 0.02 (3 H, s, $CH_3Si$), 0.85 (9 H, s, $(CH_3)_3CSi$), 1.67–1.73 (2 H, m, H-6$_{exo}$, H-5), 2.22–2.26 (1 H, m, H-6$_{endo}$), 2.43 (3 H, s, $CH_3$-C4′), 3.49 (1 H, dd, $J_{9a-9b}$ = 10.0 Hz, $J_{9a-5}$ = 6.84 Hz, $-CH_{9a}H_{9b}OSi$), 3.80 (1 H, dd, $J_{9b-9a}$ = 10.0 Hz, $J_{9b-5}$ = 2.73 Hz, $-CH_{9a}H_{9b}OSi$), 4.77 (1 H, d, $J$ = 11.62 Hz, $PhCH_2$), 4.98 (1 H, d, $J$ = 11.62 Hz, $PhCH_2$), 5.29 (1 H, m, H-1), 6.27 (1 H, d, $J_{8-7}$ = 7.59 Hz, H-8), 6.46 (1 H, dd, $J_{7-8}$ = 7.59 Hz, $J_{7-1}$ = 6.15 Hz H-7), 7.27–7.43 (7 H, m, ArH), 7.90 (2 H, d, $J_{2'-3'}$ = 8.04 Hz, H-2′ and H-6′); $^{13}$C NMR ($CDCl_3$) $\delta$ –5.36 ($CH_3Si$), –5.33 ($CH_3Si$), 18.50 (($CH_3)_3CSi$), 21.79 ($CH_3$-C4′), 25.92 (($CH_3)_3CSi$), 31.58 (C-5), 38.59 (C-6), 52.62 (C-1), 62.69 (C-9), 68.84 (C-10), 84.41 (C-4), 127.51, 127.69, 128.05, 128.46, 129.75, 131.02 (C-8), 132.49 (C-7), 135.83, 138.58, 145.10, 171.16 (C-3); IR ($CHCl_3$) 1725 (C=O), 1595, 1472, 1360, 1090 cm$^{-1}$; MS $m/e$ (EI) 229 (27), 189 (19), 187 (4), 155 (1), 115 (21), 113 (100), 91 (60), 57 (10); $m/e$ (CI/ammonia) 545 ($MNH_4^+$, 1), 528 ($MH^+$, 25); HRMS calcd for $C_{28}H_{41}N_2O_5SSi$ ($MNH_4^+$) 545.2505, found 545.2499.

**Methyl 6$\beta$-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-1$\beta$-methoxy-4$\alpha$-[(4′-methylbenzenesulfonyl)amino]cyclohex-2-enecarboxylate (10ah).** $n$-BuLi (4.8 mmol) was added slowly to MeOH (15 mL), and the solution thus obtained was added to bicyclic lactam **9ah** (380 mg, 0.842 mmol) at room temperature under dry $N_2$ atmosphere. After 2 h, a workup procedure as described above followed by purification by flash chromatography (50% $Et_2O$ in hexane) afforded **10ah** as a white solid (368 mg, 90%): mp 106 °C; $^1$H NMR ($CDCl_3$) $\delta$ –0.01 (6 H, s, 2 × $CH_3Si$), 0.85 (9 H, s, $(CH_3)_3CSi$], 1.64 (1 H, dt, $J$ = 14.0, 3.1 Hz, H-5$_\beta$), 1.79 (1 H, ddd, $J$ = 5.3, 11.5, 5.3 Hz, H-5$_\alpha$), 2.25 (1 H, m, H-6), 2.43 (3 H, s, $CH_3Ar$), 3.29 (3 H, s, $CH_3O$), 3.33 (1 H, dd, $J$ = 10.3, 7.9 Hz, $CH_2OSi$), 3.69 (1 H, dd, $J$ = 10.3, 6.2 Hz, $CH_2OSi$), 3.73 (3 H, s, $CO_2CH_3$), 3.94 (1 H, m, H-4), 4.61 (1 H, bd, $J$ = 9.0 Hz, NH), 5.83 (2 H, m, H-2 and H-3), 7.31 (2 H, d, $J$ = 8.0 Hz, tosyl H), 7.77 (2 H, d, $J$ = 8.0 Hz, tosyl H); $^{13}$C ($CDCl_3$) $\delta$ –5.40 ($CH_3Si$), 18.38 ($Me_3C$), 21.53 ($CH_3Ar$), 25.99 (($CH_3)_3C$), 27.79 (C-5), 39.75 (C-6), 47.22 (C-4), 52.20 (ester $CH_3$), 53.00 (ether $CH_3$), 62.11 ($CH_2O$), 76.52 (C-1), 127.02 (C-2′), 128.60 (C-2/C-3), 129.78 (C-3′), 131.96 (C-2/C-3), 138.14 (C-4′), 143.36 (C-1′), 173.22 ($CO_2Me$); IR ($CHCl_3$) 3382 (NH), 1744 (C=O), 1596 (C=C), 1413, 1337, 1221, 1160, 1091 cm$^{-1}$. Anal. Calcd for $C_{22}H_{38}NO_6SSi$: C, 57.11; H, 7.71; N, 2.90. Found: C, 56.98; H, 7.75; N, 2.94.

**Methyl 1$\beta$-(Benzyloxy)-6$\beta$-[[(*tert*-butyldimethylsilyl)-oxy]methyl]-4$\alpha$-(4′-methylbenzenesulfonamido)cyclohex-2-enecarboxylate (10bh).** To a solution of LiOMe (2.26 mL of $n$-BuLi 1.6 M in hexanes in 15 mL of anhydrous MeOH) at 0 °C was added a solution of compound **9bh** (128 mg, 0.242 mmol) in $CH_2Cl_2$ (2 mL) via cannula. The reaction mixture was warmed to room temperature and stirred for 16 h, quenched with saturated aqueous $NH_4Cl$ (5 mL), extracted with $CH_2Cl_2$ (3 × 50 mL), dried ($MgSO_4$), filtered, and concentrated, and the resultant residue was purified by column chromatography (30% EtOAc in hexanes) to give **10bh** as a clear oil (117.3 mg, 87%): $^1$H NMR ($CDCl_3$) $\delta$ –0.02 (3 H, s, $CH_3Si$), –0.016 (3 H, s, $CH_3Si$), 0.84 (9 H, s, $(CH_3)_3CSi$), 1.60 (1 H, m, H-5$\beta$), 1.84 (1 H, ddd, $J_{5\alpha-5\beta}$ = 13.8 Hz, $J_{5\alpha-4}$ = 12.1 Hz, $J_{5\alpha-6}$ = 5.29 Hz, H-5$\alpha$), 2.30–2.37 (1 H, m, H-6), 2.44 (3 H, s, $CH_3$-C4′), 3.36 (1 H, dd, $J_{7a-7b}$ = 10.17 Hz, $J_{7a-6}$ = 7.32 Hz, $-CH_{7a}H_{7b}OSi$), 3.72 (3 H, s, $CH_3O$), 3.77 (1 H, dd, $J_{7b-7a}$ = 10.17 Hz, $J_{7b-6}$ = 6.78 Hz, $-CH_{7a}H_{7b}OSi$), 3.94 (1 H, m, H-4), 4.39 (1 H, d, $J$ = 10.78 Hz, $PhCH_2$), 4.69 (1 H, d, $J$ = 8.62 Hz, NH), 4.70 (1 H, d, $J$ = 10.78 Hz, $PhCH_2$), 5.83 (1 H, ddd, $J_{3-2}$, 9.91 Hz, $J_{3-4}$ = 4.44 Hz, $J_{3-5\beta}$ = 3.53 Hz, H-3), 5.96 (1 H, dd, $J_{2-3}$ = 9.91 Hz, $J_{2-4}$ = 1.46 Hz, H-2), 7.27–7.31 (7 H, m), 7.77 (2 H, d, $J_{2'-3'}$ = 8.31 Hz, H-2′ and H-6′); $^{13}$C NMR ($CDCl_3$) $\delta$ –5.44 ($CH_3Si$), –5.31 ($CH_3Si$), 18.06 (($CH_3)_3CSi$), 21.66 ($CH_3$-C4′), 26.10 (($CH_3)_3CSi$), 27.45 (C-5), 40.05, 47.40 (C-4, C-6), 52.29 ($CH_3O$), 62.56 ($CH_2OSi$), 67.23 ($CH_2OPh$), 76.13 (C-1), 127.16, 127.45, 127.49, 128.27, 129.27 (C-3), 129.93, 131.95 (C-2), 138.07, 139.24, 143.58, 172.99 (C=O); IR ($CHCl_3$) 1742, 1595, 1337, 1225, 1155 cm$^{-1}$; MS $m/e$ (EI) 503 (2), 502 ($M^+$ – $t$-Bu, 4), 395 (2), 394 (4), 171 (14), 155 (3), 115 (13), 113 (25), 107 (2), 91 (100), 59 (17), 57 (20); $m/e$ (CI/ammonia) 577 ($MNH_4^+$, 4), 560 ($MH^+$, 8); HRMS calcd for $C_{25}H_{32}NO_6SSi$ ($M^+$ – $t$-Bu) 502.1720, found 502.1722.

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**Registry No.** **1a**, 141667-29-0; **1b**, 141667-30-3; **1c**, 141667-31-4; **1d**, 141667-32-5; **2a** (EWG = $CH_2OH$), 141667-33-6; **2ag**, 141667-34-7; *epi*-**2ag**, 141725-48-6; **2ah**, 141667-35-8; **2ai**, 141667-36-9; **2aj**, 141667-37-0; **2b** (EWG = $CH_2OH$), 141667-38-1; **2bg**, 141667-39-2; *epi*-**2bg**, 141725-49-7; **2bh**, 141667-40-5; **2c** (EWG = $CH_2OH$), 141667-41-6; **2cg**, 141667-42-7; **2ch**, 141667-43-8; **2ci**, 141667-44-9; **2cj**, 141667-45-0; **2dg**, 141667-46-1; *epi*-**2dg**, 141725-50-0; **2dh**, 141667-47-2; **3**, 141667-48-3; **3** (EWG = $CH_2OH$), 141667-49-4; **4**, 141667-50-7; **5**, 141667-51-8; **6**, 141667-52-9; **7**, 141667-53-0; **7** ($\Sigma$ = H), 141667-54-1; **8**, 141667-55-2; **9ah**, 141667-56-3; **9bh**, 141667-57-4; **10ah**, 141684-41-5; **10bh**, 141684-42-6; 3-(benzyloxy)-2-pyridone, 94475-64-6; 3-[(*tert*-butyldimethylsilyl)oxy]-2-pyridone, 141667-58-5; 3-(4-methylbenzenesulfenyl)-2-pyridone, 107383-65-3; 3-methoxy-1-(methanesulfonyl)-2-pyridone, 141667-59-6; 3-[(*tert*-butyldimethylsilyl)oxy]-1-(methanesulfonyl)-2-pyridone, 141667-60-9; 1-(methanesulfonyl)-3-(4′-methylbenzenesulfenyl)-2-pyridone, 141667-61-0; 2-[(4′-methylbenzenesulfonyl)oxy]pyridine, 57785-86-1; 3-methoxy-2-[(4′-methylbenzenesulfonyl)oxy]pyridine, 141667-62-1; 3-methoxy-2-[(methanesulfonyl)oxy]pyridine, 141667-63-2; 3-[(*tert*-butyldimethylsilyl)oxy]-2-[(methanesulfonyl)oxy]pyridine, 141667-64-3; dimethyl 1$\beta$-methoxy-4$\alpha$-[(4′-methylbenzenesulfonyl)amino]cyclohex-5-ene-1,2-dicarboxylate, 141667-65-4; 3-methoxy-2-pyridone, 20928-63-6; 2,3-dihydroxypyridine, 16867-04-2; nitroethylene, 3638-64-0; acrolein, 107-02-8; methyl acrylate, 96-33-3; methyl vinyl ketone, 78-94-4; methacrolein, 78-85-3.

**Supplementary Material Available:** Characterization of new compounds by NMR (41 pages). This material is contained in many 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.