analysis of the mother liquor showed no other isomer present.

Other Reducing Agents. $NaBH_4$ in Acetic Acid (Entry 1 in Table I). Six portions of 95 mg (2.5 mmol) of sodium borohydride were added under slight cooling to a suspension of 0.444 g (1 mmol) of 1 in a mixture of 5 mL of acetic acid and 1 mL of dichloromethane during a period of 3 h. The reaction mixture was stirred for 18 h at room temperature. An aliquot of the reaction mixture was worked up (as described in the procedure for the preparation of amino ester 2) and analyzed by HPLC.

$NaCNBH_3$ in Trifluoroacetic Acid (Entry 3 in Table I). To a stirred solution of 0.444 g (1 mmol) of 1 in 2 mL of trifluoroacetic acid was added 0.126 g (2 mmol) of sodium cyanoborohydride at 0 °C. The reaction mixture was stirred for 1 h at 0 °C, and then an aliquot was worked up (as described in the procedure for the preparation of 4) and analyzed by HPLC.

$(CH_3)_2PhSiH$ in Trifluoroacetic Acid (Entry 7 in Table I). To a solution of 0.444 (1 mmol) of 1 in 5 mL of trifluoroacetic acid was added 0.409 g (3 mmol, 0.46 mL) of dimethylphenylsilane. The reaction mixture was stirred for 18 h at room temperature. An aliquot of the reaction mixture was worked up (as described in the procedure for the preparation of 4) and analyzed by HPLC.

Single-Crystal X-ray Structure Determination of Amino Ester 4. Crystals suitable for X-ray diffraction analysis were grown from ethanol. The crystal used for data collection was a colorless, transparent needle prism measuring 0.075 × 0.175 × 0.625 mm. Lattice constants and intensity data were measured at 297 K on an Enraf-Nonius Cad-4 automated diffractometer using graphite-monochromatized Cu Kα radiation. Unit cell dimensions were obtained by least-squares methods from the adjusted angular settings of 25 large-angle reflections. The crystal data are as follows: $C_{27}H_{30}N_2O_4$, M_r = 446.55; triclinic space group $P\bar{1}$; a = 5.8241 (6) Å, b = 13.0620 (20) Å, c = 15.3812 (16) Å, α = 95.990 (11)°, β = 93.392 (9)°, γ = 95.633 (11)°, V = 1155.24 Å^3, Z = 2, ρ_c = 1.284 g/cm^3, μ(Cu Kα) = 6.6 cm^{-1}. Data collection was attempted to θ < 65° in the ω-2θ scanning mode. A total of 4083 reflections were collected ($\pm h,\pm k,+l$) yielding 4083 unique intensities and 3199 reflections with $I > 3.0\sigma(I)$. This set of reflections was used in the structure solution. Data reduction included corrections for background, Lorentz and polarization effects, extinction, and absorption by a semiempirical method.[11]

By direct methods (MULTAN)[12] 31 out of 33 non-hydrogen atoms were located, the missing two non-hydrogen atoms by difference Fourier methods. The positions of the hydrogen atoms were calculated geometrically or in the case of the methyl H atoms located from Fourier difference maps. Full-matrix least-squares refinement was carried out with anisotropic temperature factors for non-H atoms and isotropic factors for H atoms, using all reflections with $I > 3.0\sigma(I)$ and sin θ/λ < 0.5 Å^{-1}. The final R_1 (2160 reflections, 419 variables) was 0.037. The final difference Fourier map was featureless. The following programs were used: Enraf-Nonius SDP[13] and ORTEP.[14]

Supplementary Material Available: Tables of bond distances, bond angles, atomic positional parameters, and atomic thermal parameters for amino ester 4 (6 pages). Ordering information is given on any current masthead page.

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The Chemistry of *N*-Sulfonyl Enamines

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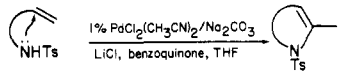
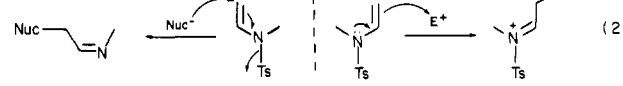
N-Tosyl enamines are available in multigram quantities using a palladium(II)-catalyzed cyclization process. This unusual class of compounds has limited nucleophilic character at the β-position, undergoing protonation and halogenation by *N*-halosuccinimides. The 3-iodo compound is subject to a number of palladium(0)-catalyzed insertion processes leading to conjugated dienes having an electron donor at one terminus and an electron acceptor at the other. *N*-Tosyl enamines are inert to nucleophilic attack at the β-position. The 3-iodo compound is cleaved to the alkyne by *n*-butyllithium.

Transition metal catalyzed processes have been developed for the synthesis of heterocyclic systems not readily available by conventional heterocyclic preparative methods.[1] One such class of heterocyclic compounds is the *N*-sulfonyl enamines, many of which are easily prepared by a palladium-catalyzed procedure (eq 1)[2] but not readily available by more standard synthetic routes. The recent



(1)

development of this cyclization reaction on a preparative scale (10–15 g)[3] made usable quantities of these compounds available for further study. *N*-Tosyl enamines are potentially "ambiphilic" and may be reactive toward both electrophiles (depending on the availability of the lone pair of electrons on nitrogen) and nucleophiles (depending on the ease of displacement of the sulfinate group) (eq 2).



(2)

Both modes of reactivity have been observed.[2] For example, both the acid-catalyzed hydrolysis to the *N*-tosyl amino ketone and the acid-assisted reduction by cyanoborohydride to the saturated *sulfonamide* clearly involved in-

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(2) For more details and important limitations of this reaction, see: Hegedus, L. S.; McKearin, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 2444.
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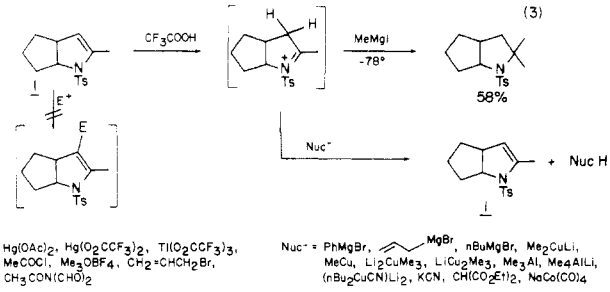
0022-3263/86/1951-1171$01.50/0

itial protonation of the β-position of the enamide followed by nucleophilic attack (H_2O or H^-) at the α-position. In contrast, the reduction of the *N*-tosyl enamine to the free cyclic secondary *amine* by bis(2-methoxyethoxy)aluminum hydride (Red-Al) appears to have involved initial *nucleophilic* attack at the β-position, followed by reduction of the resulting imine. The results of studies to probe the generality of these two types of processes are presented below.

Results and Discussion

The *N*-sulfonyl enamine chosen to be studied, *cis*-N-tosyl-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (1) was synthesized by the multistep process previously reported,[2,3] on a 15–20-g scale in excellent yield. Since the reduction of 1 by Red-Al to give the saturated bicyclic amine was thought to proceed by "hydride" attack at the β-position of the enamine with displacement of the sulfinate group, followed by reduction of the resulting imine (eq 2), reactions of 1 with other nucleophilic species were studied. Remarkably, 1 proved inert to methyllithium, *n*-butyllithium, trimethylaluminum, triethylaluminum, and even the methyl analogue of Red-Al, $Li[AlMe_2(OCH_2CH_2OCH_3)_2]$. Thus, the reduction of 1 by Red-Al is likely to be more complex than as shown in eq 2, and nucleophilic attack at the β-position of 1 seems unlikely.

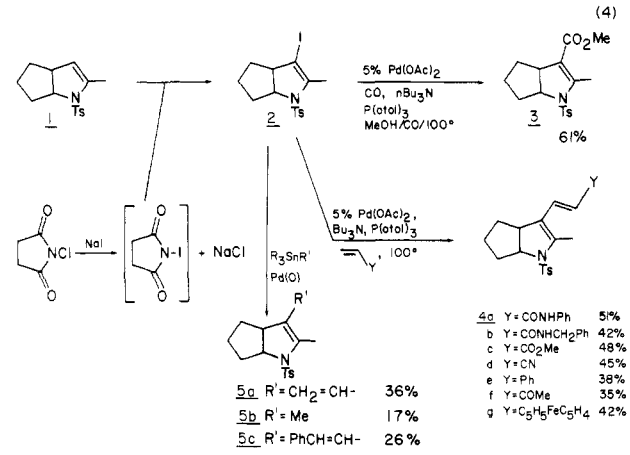
Enamines themselves can be protonated at the β-carbon, and the resulting immonium ions are reactive toward a range of nucleophiles.[4] Treatment of 1 with 1 equiv of trifluoroacetic acid followed by methylmagnesium iodide at −78 °C resulted in α-methylation, presumably by the route shown in eq 3. However, this was not a general



process, and a variety of other nucleophiles failed to atack the α-position but rather reabstracted a β-proton, regenerating starting compound 1. Compound 1 also proved to be inert toward a variety of other electrophiles.

N-Tosyl enamine 1 did undergo reaction with *N*-bromosuccinimide, producing the corresponding 3-bromo compound in fair (58%) yield. However this compound was very stable. It failed to form the Grignard reagent with activated magnesium[5] and was also unreactive toward a variety of palladium(0)-catalyzed processes which involve oxidative addition of organic halides as a first step (e.g., Heck reactions).[6]

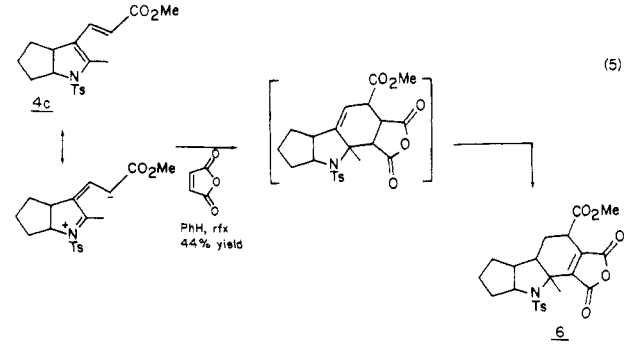
Previous studies in these laboratories[7] had indicated that 3-iodo-*N*-tosylindoles underwent a variety of useful palladium(0)-catalyzed processes. Accordingly, compound 1 was iodinated with *N*-iodosuccinimide (generated in situ from NCS and sodium iodide[8]) to produce iodo compound 2. This compound was relatively unstable, and was subjected without purification to a variety of palladium(0)-catalyzed processes (eq 4).



Both carbonylation and insertion of unsubstituted electron deficient olefins proceeded in modest yield, giving 3-substituted products in 40–60% overall yield from the *N*-tosyl enamine 1. As is typical of olefin insertion processes, α- or β-substitution on the olefin drastically reduced the efficiency of the reaction. In this system, methyl methacrylate, dimethyl fumarate, dimethyl maleate, and methyl crotonate failed to undergo insertion in usuable yields. Somewhat more surprising was the observation that electron-rich olefins, such as *N*-vinyl phthalimide and *N*-vinyl acetamide, as well as allyl alcohol, *N*-phthalimido-1-butene, and 1,1-dimethylbut-3-en-1-ol also failed to insert, even though these olefins are normally reactive in "Heck-type" insertions. Thus, with β-iodo-*N*-tosyl enamines, insertion is limited to unsubstituted electron deficient olefins.

Tin-to-palladium transmetalation processes have recently been developed as a method to alkylate aryl and vinyl halides.[9] Attempts to apply this process to compound 1 were only minimally successful (eq 4). Under the standard conditions for these tin reactions (THF, 50 °C, preformed Pd(0) catalyst) *no* alkylation was observed. Only when conditions were identical with those used in the successful insertion reactions ($Pd(OAc)_2$, n-Bu_3N, P(*o*-tol)$_3$, 100 °C, neat) did alkylation occur, and then only in poor yield. Thus functionalization of 1 by this procedure is inefficient.

The products (4) from olefin insertion are unusual dienes, having electron-withdrawing groups (e.g., CO_2R, COR, CN) at one terminus and a weak electron-donating group (NTs) at the other. It was expected that they would undergo either a stepwise or a concerted cycloaddition with dienophiles (eq 5). Indeed, exposure of acrylate adduct



4c to maleic anhydride (benzene at reflux, 44 h) led to a

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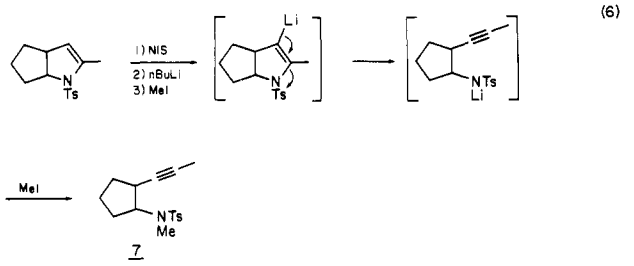
(7) Harrington, P. J.; Hegedus, L. S. *J. Org. Chem.* **1984**, *49*, 2657.
(8) Vankar, Y. D.; Kumaravel, G. *Tetrahedron Lett.* **1984**, *25*, 233.
(9) (a) Labadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6129. (b) Goure, W. F.; Wright, M. E.; Davis, P. D.; Labadie, S. S.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 6417. (c) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. (d) Crisp, G. T.; Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7500.

modest yield of the cycloadduct **6**, in which the double bond has rearranged into conjugation with the maleic anhydride carbonyl groups.

Finally, β-lithiation/alkylation of **1** by halogen metal exchange was attempted[10] (eq 6). Rather than the expected 2,3-dimethyl compound, the product was the N-methylated ring-opened alkyne **7**, produced by fragmentation of the initial lithiation product, promoted by the leaving ability of the *N*-tosyl group.[11]



(6)

7

Summary

N-Tosyl enamines are available in multigram quantities using a palladium(II)-catalyzed cyclization process. This unusual class of compounds has limited nucleophilic character at the β-position, undergoing protonation and halogenation by *N*-halosuccinimides. The 3-iodo compound is subject to a number of palladium(0) catalyzed insertion processes leading to conjugated dienes having an electron donor at one terminus and an electron acceptor at the other. *N*-Tosyl enamines are inert to nucleophilic attack at the β-position. The 3-iodo compound is cleaved to the alkyne by *n*-butyllithium.

Experimental Section

General. All articles of glassware used in reactions done under an inert atmosphere were oven-dried prior to use. Nuclear magnetic resonance spectra were recorded on a Bruker WP-270 SY (270 MHz) or Nicolet NTC-FT 1180 (360 MHz) instrument in $CDCl_3$ with tetramethylsilane as an internal standard. Melting points were recorded on a Laboratory Devices Mel-Temp apparatus in a sealed tube and are uncorrected. Infrared spectra were recorded on a Beckman Model 4200 spectrometer. Preparative thin-layer chromatography was performed on 20 cm × 20 cm plates, with a layer of Kieselgel 60 PF-254 silica gel 1.5 mm thick, and visualization was accomplished with I_2 or UV light. Compounds were then removed from the silica gel with ethyl acetate. The use of a chromatotron refers to the device marketed by Harrison Research, Palo Alto, CA. In vacuo distillation refers to the use of a Kugelrohr apparatus. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Materials. *N*-Chlorosuccinimide was recrystallized quickly from benzene. Methanol was fractionally distilled and stored over molecular sieves. Benzene and carbon tetrachloride were fractionally distilled and stored over molecular sieves under argon. Acetone was dried ($CaSO_4$), distilled, and stored over molecular sieves. Tetrahydrofuran was distilled from sodium benzophenone ketyl immediately prior to use. Tri-*n*-butylamine was dried (CaH_2), distilled under reduced pressure, and stored under argon. Benzoquinone was sublimed [60 °C (15 mm)] and stored under argon. $PdCl_2(MeCN)_2$ was formed by stirring 8.00 g of $PdCl_2$ in 200 mL of acetonitrile for 2 days. The complex (11.43 g, 97.8%) was collected by filtration, washed, and dried. *N*-Tosyl enamine **1** was prepared as in ref 3. Other materials were obtained from commercial sources and used as supplied.

***cis*-*N*-Tosyl-4-iodo-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (2).** A solution of NaI (81 mg, 0.54 mmol) dissolved in 1 mL of dry acetone was added to a stirred solution of *N*-chlorosuccinimide (72 mg, 0.54 mmol) dissolved in 1 mL of dry acetone. After 10 min, 2 mL of acetone were added to precipitate the NaCl, and the mixture was filtered into a 25-mL round-bottomed flask. The solvent was removed in vacuo to yield *N*-iodosuccinimide. *cis*-*N*-tosyl-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (100 mg, 0.36 mmol) and 5 mL of dry CCl_4 were added, and the heterogeneous solution was stirred for 1 h and then filtered and the solvent removed in vacuo. The residue was dissolved in 25 mL of Et_2O and then washed with 10 mL of a saturated aqueous $Na_2S_2O_3$ solution. The organic layer was separated, dried ($MgSO_4$), and filtered and the solvent removed in vacuo to yield **2** as an off-white semisolid. This material was used directly in further reactions.

^1H NMR (270 MHz, $CDCl_3$) δ: 1.3–2.2 (m, 6 H, CH_2), 2.18 (d, 3 H, J = 2.2 Hz, $=CCH_3$), 2.44 (s, 3 H, $ArCH_3$), 3.1 (m, 1 H, CH), 4.35 (m, 1 H, CH), 7.32 (d, 2 H, J = 8 Hz, Ar H), 7.63 (d, 2 H, J = 8 Hz, Ar H).

***cis*-*N*-Tosyl-4-carbomethoxy-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (3).** The β-iodo-*N*-tosyl enamine **2** (prepared as described above from 100 mg, 0.36 mmol, of **1** and *N*-iodosuccinimide), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol, 5.0 mol %), $P(o\text{-tol})_3$ (22 mg, 0.072 mmol), and n-Bu_3N (83 mg, 0.45 mmol) were heated, in a 25-mL sealed tube, at 100 °C in 10 mL of methanol under an atmosphere of CO for 48 h. The solvent was removed in vacuo and the residue taken up in 50 mL of Et_2O. This solution was washed with 10 mL of H_2O and then 100 mL of saturated brine. The organic layer was dried ($MgSO_4$) and filtered and the solvent removed in vacuo. Preparative TLC (3:1 hexane–EtOAc; R_f 0.43) followed by recrystallization from hexanes yielded the product as a white solid (74 mg, 61%), mp 97–98 °C.

^1H NMR (360 MHz, $CDCl_3$) δ: 1.55 (m), 1.65 (m), 1.83 (m), 2.05 (m), 2.10 (m, 6 H, CH_2S), 2.43 (s, 3 H, $ArCH_3$), 2.44 (d, 3 H, J = 1.6 Hz, $=CCH_3$), 3.38 (m, 1 H, CH), 3.68 (s, 3 H, CO_2CH_3), 4.47 (m, 1 H, CH), 7.31 (d, 2 H, J = 8.2 Hz, Ar H), 7.69 (d, 2 H, J = 8.2 Hz, Ar H). IR (KBr): 1696 (C=O), 1629, 1432, 1347, 1159 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_4S$: C, 60.88; H, 6.31; N, 4.18. Found: C, 60.90; H, 6.30; N, 4.18.

Formation of Olefin Insertion Products. General Procedure. The β-iodo-*N*-tosyl enamine **2** (prepared as described above from 100 mg, 0.36 mmol, of **21** and *N*-iodosuccinimide), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol, 5.0 mol %), $P(o\text{-tol})_3$ (22 mg, 0.072 mmol), n-Bu_3N (83 mg, 0.45 mmol), and the olefin (0.45 mmol) were placed in a 2-mL acylation tube. The system was placed under argon, sealed, and heated at 100 °C for 24 h. The mixture was allowed to cool and was dissolved in 15 mL of CH_2Cl_2. This was washed with 10 mL of H_2O, and then the organic layer was separated, dried ($MgSO_4$), and filtered and the solvent removed in vacuo to yield the crude product.

***cis*-*N*-Tosyl-4-(2-(*N*-phenylcarbamoyl)ethen-1-yl)-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (4a).** The reaction employing 66 mg (0.45 mmol) of *N*-phenylacrylamide yielded, upon purification by chromatotron (1:1 hexane–EtOAc; R_f 0.20) followed by recrystallization from acetone/ether, 77 mg (51%) of **4a** as a white solid, mp 116–118 °C.

^1H NMR (270 MHz, $CDCl_3$) δ: 1.5 (m), 1.7 (m), 2.0 (m, 6 H, CH_2), 2.12 (d, 3 H, J = 1 Hz, $=CCH_3$), 2.42 (s, 3 H, $ArCH_3$), 3.2 (m, 1 H, CH), 4.4 (m, 1 H, CH), 5.76 (d, 1 H, J = 15 Hz, =CH), 7.0–7.6 (m, 5 H, N-Ar H), 7.29 (d, 2 H, J = 8 Hz, Ar H), 7.46 (d, 1 H, J = 15 Hz, =CH), 7.64 (d, 2 H, J = 8 Hz, Ar H), 7.85 (br s, 1 H, NH). IR (KBr): 3700–3200 (N–H), 1595 (C=O) cm^{-1}. Anal. Calcd for $C_{24}H_{26}N_2O_3S$: C, 68.22; H, 6.20; N, 6.63. Found: C, 68.28; H, 6.46; N, 6.40.

***cis*-*N*-Tosyl-4-(2-(*N*-benzylcarbamoyl)ethen-1-yl)-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (4b).** The reaction employing 72 mg (0.45 mmol) of *N*-benzylacrylamide yielded, upon purification by chromatotron (1:1 hexane–EtOAc; R_f 0.19), 66 mg (42%) of **4b** as a white solid, mp 73–74 °C.

^1H NMR (270 MHz, $CDCl_3$) δ: 1.5 (m), 1.7 (m), 2.0 (m, 6 H, CH_2), 2.16 (s, 3 H, $=CCH_3$), 2.41 (s, 3 H, $ArCH_3$), 3.2 (m, 1 H, CH), 4.4 (m, 1 H, CH), 4.47 (d of d, 2 H, J = 5, 2 Hz, $PhCH_2$), 5.60 (d, 1 H, J = 15 Hz, =CH), 6.15 (br s, 1 H, NH), 7.20–7.35 (m, 7 H, Ar H), 7.37 (d, 1 H, J = 15 Hz, =CH), 7.62 (d, 2 H, J = 8 Hz, Ar H). IR (KBr): 3650–3100 (N–H), 1598 (C=O), 1345, 1158 cm^{-1}. Anal. Calcd for $C_{26}H_{28}N_2O_3S$: C, 68.78; H, 6.46; N, 6.42. Found: C, 68.87; H, 6.68; N, 6.32.

***cis*-*N*-tosyl-4-(2-carbomethoxyethen-1-yl)-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (4c).** The reaction employing 39 mg

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(0.45 mmol) of methyl acrylate yielded, upon purification by preparative TLC (3:1 hexane–EtOAc; R_f 0.25), 63 mg (48%) of **4c** as a clear, colorless oil.

^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.5 (m), 1.8 (m), 2.0 (m, 6 H, CH_2), 2.20 (s, 3 H, $=CCH_3$), 2.42 (s, 3 H, $ArCH_3$), 3.25 (m, 1 H, CH), 3.72 (s, 3 H, CO_2CH_3), 4.45 (m, 1 H, CH), 5.57 (d, 1 H, J = 15 Hz, =CH), 7.30 (d, 2 H, J = 8 Hz, Ar H), 7.43 (d, 1 H, J = 15 Hz, =CH), 7.66 (d, 2 H, J = 8 Hz, Ar H). IR ($CHCl_3$): 1698 (C=O), 1615, 1493, 1349, 1160 cm^{-1}. Anal. Calcd for $C_{19}H_{23}NO_4S$: C, 63.14; H, 6.41; N, 3.88. Found: C, 63.20; H, 6.47; N, 4.03.

***cis*-*N*-Tosyl-4-(2-cyanoethen-1-yl)-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (4d).** The reaction employing 24 mg (0.45 mmol) of acrylonitrile yielded, upon purification by chromatotron (3:1 hexane–EtOAc; R_f 0.24), 54 mg (45%) of **4d** as a clear pale yellow oil.

^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.5 (m), 1.7 (m), 2.0 (m, 6 H, CH_2), 2.16 (d, 3 H, J = 1 Hz, $=CCH_3$), 2.43 (s, 3 H, $ArCH_3$), 3.25 (m, 1 H, CH), 4.5 (m, 1 H, CH), 4.93 (d, 1 H, J = 16 Hz, =CH), 7.09 (d, 1 H, J = 16 Hz, =CH), 7.32 (d, 2 H, J = 8 Hz, Ar H), 7.66 (d, 2 H, J = 8 Hz, Ar H). IR ($CHCl_3$): 2195 (C≡N), 1612, 1492, 1351, 1160 cm^{-1}. Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.64; H, 6.31; N, 8.31.

***cis*-*N*-Tosyl-4-(2-phenylethen-1-yl)-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (4e).** The reaction employing 47 mg (0.45 mmol) of styrene yielded, upon purification by preparative TLC (3 × 9:1 hexane–EtOAc; R_f 0.44), 52 mg (38%) of **4e** as a white semisolid.

^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.5 (m), 1.7 (m), 1.85 (m), 2.1 (m, 6 H, CH_2), 2.21 (d, 3 H, J = 2 Hz, $=CCH_3$), 2.40 (s, 3 H, $ArCH_3$), 3.35 (m, 1 H, CH), 4.35 (m, 1 H, CH), 6.24 (d, 1 H, J = 16 Hz, =CH), 6.80 (d, 1 H, J = 16 Hz, =CH), 7.1–7.4 (m, 7 H, Ar H), 7.66 (d, 2 H, J = 8 Hz, Ar H). IR ($CHCl_3$): 1632, 1595, 1493, 1345, 1162 cm^{-1}. Anal. Calcd for $C_{23}H_{25}NO_2S$: C, 72.79; H, 6.64; N, 3.69. Found: C, 72.56; H, 6.88; N, 3.49.

***cis*-*N*-Tosyl-4-(2-acetylethen-1-yl)-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (4f).** The reaction employing 32 mg (0.45 mmol) of methyl vinyl ketone yielded, upon purification by chromatotron (3:1 hexane–EtOAc; R_f 0.13), 44 mg (35%) of **4f** as a pale yellow oil.

^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.5 (m), 1.8 (m), 2.0 (m, 6 H, CH_2), 2.22 (d, 3 H, J = 1 Hz, $=CCH_3$), 2.25 (s, 3 H, $O=CCH_3$), 2.43 (s, 3 H, $ArCH_3$), 3.3 (m, 1 H, CH), 4.45 (m, 1 H, CH), 5.90 (d, 1 H, J = 16 Hz, =CH), 7.25–7.33 (m, 3 H, Ar H, =CH), 7.67 (d, 2 H, J = 8 Hz, Ar H). IR ($CDCl_3$): 1685–1640 (C=O), 1605, 1570, 1486, 1351, 1160 cm^{-1}. Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.05. Found: C, 65.80; H, 6.66; N, 3.98.

***cis*-*N*-Tosyl-4-(2-ferrocenylethen-1-yl)-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (4g).** The reaction employing 95 mg (0.45 mmol) of vinylferrocene yielded, upon purification by chromatotron (3:1 hexane–EtOAc; R_f 0.46), followed by recrystallization from ether/hexanes, 74 mg (42%) of **4g** as a red solid, mp 109–111 °C.

^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.55 (m), 1.7 (m), 1.85 (m), 2.05 (m, 6 H, CH_2), 2.13 (d, 3 H, J = 2 Hz, $=CCH_3$), 2.40 (s, 3 H, $ArCH_3$), 3.25 (m, 1 H, CH), 4.35 (s, 5 H, Cp H), 4.20–4.45 (m, 5 H, Cp H, CH), 5.97 (d, 1 H, J = 16 Hz, =CH), 6.33 (d, 1 H, J = 16 Hz, =CH), 7.27 (d, 2 H, J = 8 Hz, Ar H), 7.65 (d, 2 H, J = 8 Hz, Ar H). IR (KBr): 1626, 1591, 1485, 1349, 1161 cm^{-1}. Anal. Calcd for $C_{27}H_{29}FeNO_2S$: C, 66.53; H, 6.00; N, 2.87. Found: C, 66.35; H, 6.13; N, 2.60.

Formation of Tin-to-Palladium Transmetalation Products. General Procedure. The β-iodo-N-tosyl enamine **2** (prepared as described above from 100 mg, 0.36 mmol, of **1** and *N*-iodosuccinimide), $Pd(OAc)_2$ (8.0 mg, 0.036 mmol, 10 mol %), $P(o\text{-tol})_3$ (44 mg, 0.14 mmol), n-Bu_3N (166 mg, 0.90 mmol), and the tin reagent (0.80 mmol) were placed in a 2-mL acylation tube. The system was placed under argon, sealed, and heated at 100 °C for 24 h. The mixture was allowed to cool and was taken up in 25 mL of Et_2O. This was washed with 10 mL of H_2O and then 10 mL of saturated brine. The organic layer was separated, dried ($MgSO_4$) and filtered and the solvent removed in vacuo to yield the crude product.

***cis*-*N*-Tosyl-4-vinyl-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (5a). Method a.** The reaction employing 252 mg (0.80 mmol) of tributylvinyltin yielded, upon purification by preparative TLC (2 × 9:1 hexane–EtOAc; R_f 0.42), 40 mg (36%) of **5a** as a clear, colorless oil.

Method b. The reaction employing 153 mg (0.80 mmol) of trimethylvinyltin yielded, upon purification as above, 31 mg (28%) of **5a** as a clear, colorless oil.

^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.5 (m), 1.75 (m), 2.0 (m, 6 H, CH_2), 2.10 (d, 3 H, J = 1 Hz, $=CCH_3$), 2.41 (s, 3 H, $ArCH_3$), 3.2 (m, 1 H, CH), 4.3 (m, 1 H, CH), 4.90 (d, 1 H, J = 17 Hz), 4.97 (d, 1 H, J = 11 Hz, $=CH_2$), 6.38 (d of d, 1 H, J = 17, 11 Hz, =CH), 7.28 (d, 2 H, J = 8 Hz, Ar H), 7.65 (d, 2 H, J = 8 Hz, Ar H). IR ($CHCl_3$): 1635, 1592, 1488, 1340, 1155 cm^{-1}. This compound was not sufficiently stable to obtain an elemental analysis.

***cis*-*N*-Tosyl-3,4-dimethyl-2-azabicyclo[3.3.0]oct-3-ene (5b).** The reaction employing 143 mg (0.80 mmol) of tetramethyltin and 49 mg (0.36 mmol) of zinc chloride yielded, upon purification by chromatotron (3:1 hexane–EtOAc; R_f 0.44), 18 mg (17%) of **5b** as a white semisolid. This material was identical with that reported in the literature.[2]

***cis*-*N*-Tosyl-4-(2-phenylethen-1-yl)-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (5c).** The reaction employing 315 mg (0.80 mmol) of (*E*)-β-styryltributyltin yielded, upon purification by chromatotron (3:1 hexane–EtOAc; R_f 0.43), 36 mg (26%) of **5c** as a white semisolid. This material was identical with that obained above (compound **4e**), from the insertion reaction with styrene.

Cycloaddition Product of 4c and Maleic Anhydride (6). A solution of **4c** (49 mg, 0.14 mmol) and maleic anhydride (150 mg, 1.5 mmol) in 1 mL of benzene was heated at reflux for 44 h. The mixture was cooled and immediately subjected to purification by chromatotron (1:1 hexane–EtOAc: R_f 0.28) to yield **6** (24 mg, 39%) as a white semisolid.

^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.9 (m), 1.2–1.4 (m), 1.6 (m), 1.85 (m, 8 H, CH_2), 1.25 (s, 3 H, CCH_3), 2.43 (s, 3 H, $ArCH_3$), 3.0 (m, 2 H, CH), 3.5–3.9 (m, 1 H, CH), 3.71 (s, 3 H, CO_2CH_3), 4.3 (m, 1 H, CH), 7.31 (d, 2 H, J = 8 Hz, Ar H), 7.61 (d, 2 H, J = 8 Hz, Ar H). IR ($CDCl_3$): 1848, 1780 (O=COC=O), 1730 (CO_2Me), 1594, 1485, 1350, 1161 cm^{-1}. Anal. Calcd for $C_{23}H_{25}NO_7S$: C, 60.12; H, 5.48; N, 3.05. Found: C, 59.98; H, 5.59; N, 2.94.

***cis*-*N*-Methyl-*N*-tosyl-2-propyn-1-ylcyclopentylamine (7).** *n*-Butyllithium (151 μL of a 2.7 M solution in hexanes, 0.38 mmol) was added to a solution of the β-iodo compound **2** (prepared as described above from 100 mg, 0.36 mmol, of **1** and *N*-iodosuccinimide) in 10 mL of THF cooled to −78 °C. After 1.5 h, methyl iodide (71 mg, 0.50 mmol) was added, and the solution was allowed to warm to room temperature. The reaction mixture was quenched with 2 mL of a saturated aqueous Na_2CO_3 solution, diluted with 50 mL of Et_2O, and then washed with 10 mL of saturated brine. The organic layer was dried ($MgSO_4$) and the solvent removed in vacuo. Purification by chromatotron (3:1 hexane–EtOAc; R_f 0.36) gave **7** (67 mg, 64%) as a clear, colorless oil.

^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.30–1.95 (m, 6 H, CH_2), 1.67 (d, 3 H, J = 2 Hz, CCH_3), 2.42 (s, 3 H, $ArCH_3$), 2.9 (m, 1 H, CH), 2.94 (s, 3 H, NCH_3), 4.23 (q, 1 H, J = 9 Hz, CH), 7.28 (d, 2 H, J = 8 Hz, Ar H), 7.71 (d, 2 H, J = 8 Hz, Ar H). IR ($CHCl_3$): 1493, 1399, 1357, 1159 cm^{-1}. Anal. Calcd for $C_{16}H_{21}NO_2S$: C, 65.95; H, 7.26; N, 4.81. Found: C, 65.84; H, 7.41; N, 4.71.

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Registry No. **1**, 100899-20-5; **2**, 100899-21-6; **3**, 100899-22-7; **4a**, 100899-23-8; **4b**, 100899-24-9; **4c**, 100899-25-0; **4d**, 100899-26-1; **4e**, 100899-27-2; **4f**, 100899-28-3; **4g**, 100909-00-0; **5a**, 100899-29-4; **5b**, 100899-30-7; **5c**, 100899-27-2; **6**, 100899-31-8; **7**, 100899-32-9; H_2C=CHCONHPh, 2210-24-4; H_2C=CHCONHCHCH_2Ph, 13304-62-6; H_2C=CHCO_2Me, 96-33-3; H_2C=CHCN, 107-13-1; H_2C=CHPh, 100-42-5; H_2C=CHCOMe, 78-94-4; H_2C=CH$C_5H_4FeC_5H$, 1271-51-8; H_2C=CH$SnBu_3$, 7486-35-3; H_2C=CH$SiMe_3$, 754-06-3; $SnMe_4$, 594-27-4; (*E*)-PhCH=CH$SnBu_3$, 66680-88-4; *N*-tosyl-3,3-dimethyl-2-azabicyclo[3.3.0]octane, 100899-33-0; maleic anhydride, 1121-34-2.