Synthesis of Pyrrolidines and Piperidines via Palladium-Catalyzed Coupling of Vinylic Halides and Olefinic Sulfonamides

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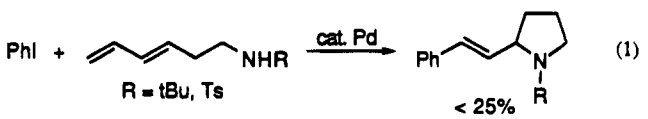
Received November 29, 1993®

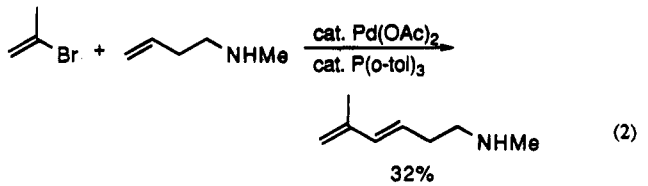
The palladium-catalyzed coupling of vinylic halides and olefinic sulfonamides affords good yields of 2-(1-alkenyl)pyrrolidine and -piperidine sulfonamides via vinylpalladium addition to the olefin, regioselective rearrangement to a π-allylpalladium intermediate, and subsequent intramolecular nucleophilic displacement of palladium.

The pyrrolidine and piperidine ring systems are prevalent in nature and present a worthy target for new synthetic methodology.[1,2] While the palladium-catalyzed coupling of iodobenzene and 3,5-hexadienylamine derivatives produce unsaturated pyrrolidines, the yields are less than 25% (eq 1).[3] Heck has previously examined the



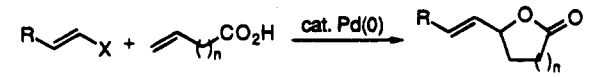
(1)

cross-coupling of vinylic halides and olefinic amines as a possible route to pyrrolidines, but only a low yield of an alkadienyl amine was obtained (eq 2).[4,5] Our prior

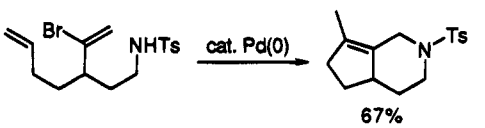


(2)

experience with the palladium-catalyzed coupling of vinylic halides with alkenoic acids (eq 3)[6] and intramolecular versions of this type of process using olefinic tosylamides (eq 4)[7,8] to form unsaturated lactones and



(3)



(4)

polycyclic tosylamides, respectively, suggested that the analogous coupling of vinylic halides and simple olefinic sulfonamides should provide a convenient new route to these important ring systems. We report here the success of that approach.

Independently, three different experimental procedures have been developed: procedure A, 2:1 vinylic halide:sulfonamide, 5 mol % $Pd(OAc)_2$, 10 mol % $P(o\text{-}tol)_3$, 2 equiv of nBu_4NCl, 2 equiv of Na_2CO_3 in MeCN (0.1 M in sulfonamide); procedure B, 1:2 vinylic halide:sulfonamide, 5 mol % $Pd(OAc)_2$, 1 equiv of nBu_4NCl, 4.5 equiv of Na_2CO_3 in MeCN (0.5 M in sulfonamide); procedure C, 1:2 vinylic halide:sulfonamide, 5 mol % $Pd(OAc)_2$, 1 equiv of nBu_4NCl, 4.5 equiv of $KHCO_3$ in MeCN (0.5 M in sulfonamide). Using these procedures, vinylic halides can be cross-coupled in good yields with a variety of olefinic sulfonamides to produce the corresponding five- and six-membered ring nitrogen heterocycles as summarized in Table 1.

A wide variety of vinylic halides can be employed in this process, including bromides and iodides with a range

® Abstract published in *Advance ACS Abstracts,* July 1, 1994.

(1) For periodic reports on these alkaloids, see: (a) *Alkaloids: Chemical and Biological Perspectives*; Pelletier, S. W., Ed.; J. Wiley and Sons: New York. (b) *The Alkaloids, Specialist Periodical Reports*; The Royal Society of Chemistry: London. (c) *The Alkaloids*, Brossi, A., Ed.; Academic Press: New York. (d) *Nat. Prod. Rep.*; The Royal Society of Chemistry: London.

(2) For some recent references, see: (a) Rubiralta, M.; Giralt, E.; Diez, A. *Piperidine: Structure, Preparation, Reactivity, and Synthetic Applications of Piperidine and its Derivatives*; Elsevier: Amsterdam-Oxford-New York-Tokyo, 1991. (b) Jego, J.-M.; Carboni, B.; Youssofi, A.; Vaultier, M. *Synlett* **1993**, 595. (c) Jefford, C. W.; Wang, J. B. *Tetrahedron Lett.* **1993**, *34*, 2911. (d) Enders, D.; Tiebes, J. *Liebigs Ann. Chem.* **1993**, 173. (e) Wang, C.-L. J.; Wuonola, M. A. *Org. Prep. Proc. Int.* **1992**, *24*, 583. (f) Tawara, J. N.; Blokhin, A.; Foderaro, T. A.; Stermitz, F. R. *J. Org. Chem.* **1993**, *58*, 4813. (g) Davies, I. W.; Scopes, D. I. C.; Gallagher, T. *Synlett* **1993**, 85. (h) Fujita, H.; Tokuda, M.; Nitta, M.; Suginome, H. *Tetrahedron Lett.* **1992**, *33*, 6359. (i) Lygo, B. *Synlett* **1993**, 764. (j) Kim, M.-J.; Lee, I. S. *Synlett* **1993**, 767.

(3) Harrington, P. J.; DiFiore, K. A. Unpublished results cited in Harrington, P. *Transition Metals in Total Synthesis*; Wiley: New York, 1990; p 67.

(4) Shi, L.; Narula, C. K.; Mak, K. T.; Kao, L.; Xu, Y.; Heck, R. F. *J. Org. Chem.* **1983**, *48*, 3894.

(5) For examples of the more successful *intramolecular* coupling of vinylic halides, olefins and secondary amines, see ref 4 and: (a) Narula, C. K.; Mak, K. T.; Heck, R. F. *J. Org. Chem.* **1983**, *48*, 2792. (b) Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 3898.

(6) Larock, R. C.; Leuck, D. J.; Harrison, L. W. *Tetrahedron Lett.* **1988**, *29*, 6399.

(7) (a) Harris, G. D., Jr.; Herr, R. J.; Weinreb, S. M. *J. Org. Chem.* **1992**, *57*, 2528. (b) Harris, G. D., Jr.; Herr, R. J.; Weinreb, S. M. *J. Org. Chem.* **1993**, *58*, 5452.

(8) For other examples of π-allylpalladium displacements by tosylamides, see: (a) Larock, R. C.; Berrios-Peña, N. G.; Fried, C. A.; Yum, E. K.; Tu, C.; Leong, W. *J. Org. Chem.* **1993**, *58*, 4509. (b) Larock, R. C.; Yum, E. K. *Synlett* **1990**, 529. (c) Larock, R. C.; Berrios-Peña, N. G.; Fried, C. A. *J. Org. Chem.* **1990**, *56*, 2615. (d) Larock, R. C.; Berrios-Peña, N.; Narayanan, K. *J. Org. Chem.* **1990**, *55*, 3447. (e) Inoue, Y.; Taguchi, M.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2721. (f) Byström, S. E.; Aslanian, R.; Bäckvall, J.-E. *Tetrahedron Lett.* **1985**, *26*, 1749. (g) Stolle, A.; Ollivier, J.; Piras, P. P.; Salaün, J.; de Meijere, A. *J. Am. Chem. Soc.* **1992**, *114*, 4051. (h) Uozumi, Y.; Tanahashi, A.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 6826.

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of substitution patterns. As anticipated (see the later discussion of mechanism), *E*- and *Z*-1-halo-1-alkenes both give exclusively the *E*-substituted products. The more hindered the halide, in general, the lower the yield is. Although vinylic iodides are generally more reactive in Pd(0)-catalyzed processes, the yields from vinylic bromides and iodides are generally comparable. Reactions employing cyclohexenyl triflate have afforded mixed results. *N*-(3-Butenyl)tosylamide (**1**) afforded a 67% yield of the expected pyrrolidine product (entry 16), while only diene was obtained from *N*-(4-pentenyl)tosylamide (**2**) (entries 22 and 23).

Both *N*-(3-alkenyl)- and *N*-(4-alkenyl)tosylamides afford good to excellent yields of the expected pyrrolidines and piperidines. However, *N*-(4-pentenyl)triflamide (**3**) gave consistently higher yields than the corresponding tosylamide, once the procedure was modified to obtain optimal results (cf. entries 20, 24, and 25).

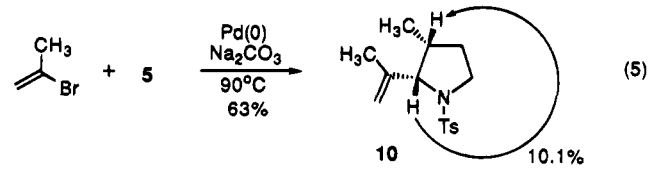
Procedures A and B for the cyclization of tosylamides were developed independently and neither seems consistently superior (cf. entries 1 and 2, 5 and 6, 9 and 10, and 18 and 19). For piperidine formation, it appears that procedure A with tosylamides and vinylic bromides is superior to procedure B (cf. entries 18 and 19), but better results can usually be obtained using triflamides and procedure C (cf. entries 20, 24, and 25; and 27 and 28).

These reactions undoubtedly proceed according to the mechanism outlined in Scheme 1. The individual steps (i.e., the regioselective formation and subsequent nucleophilic displacement of π-allylpalladium intermediates) in the process are well known.[6,7,9] The exclusive formation of *E*-substituted products from either *E*- or *Z*-1-halo-1-alkenes is the result of the thermodynamic preference for *syn,syn*-π-allylpalladium formation. No seven- or eight-membered ring products have been observed in any of these reactions.

We decided to investigate whether alkyl-substituted olefinic sulfonamides would undergo intermolecular coupling reactions with vinylic halides to produce heterocycles stereoselectively. The methyl-substituted precursors **5** and **7** were synthesized by conventional chemistry from readily available starting materials (Scheme 2). 3-Methyl-3-butenol (**4**) was converted to the corresponding iodide and was reacted with potassium *p*-toluenesulfonamide to produce *N*-(3-methyl-3-butenyl)-*p*-toluenesulfonamide (**5**) in 68% overall yield. Wittig olefination of 3-acetyl-1-propanol (**6**) provided 4-methyl-4-pentenol[10] which was converted to the corresponding iodide. Amidation with potassium *p*-toluenesulfonamide produced *N*-(4-methyl-4-pentenyl)-*p*-toluenesulfonamide (**7**) in 46% overall yield from the starting ketone.

The reaction of tosylamide **7** with 2-bromopropene at 115 °C for 48 h in DMF (procedure A) proceeded smoothly to produce *cis*-*N*-tosyl-2-isopropenyl-3-methylpiperidine (**9**) in 64% yield as a single stereoisomer (Scheme 3). The *cis* stereochemical assignment is based on ^{1}H NMR decoupling and NOE experiments, with enhancements for the piperidine derivative **9** as shown in Scheme 3. This selectivity may be due to the intermediate π-allylpalladium complex **8** adopting a pseudoaxial geometry to avoid developing $A^{1,2}$ strain in the transition state for ring closure.

Likewise, tosylamide **5** reacted with 2-bromopropene at 90 °C for 72 h (procedure A) to produce the single stereoisomer *cis*-*N*-tosyl-2-isopropenyl-3-methylpyrrolidine (**10**) in 63% yield (eq 5). The stereochemistry of **10** was also determined by ^{1}H NMR decoupling and NOE experiments.



(5)

When *cis*-*N*-(2-ethenylcyclopentyl)-*p*-toluenesulfonamide (**11**)[11] was reacted with 2-bromopropene at 115 °C for 24 h (procedure A), a 67% yield of the isopropenyl bicyclic pyrrolidine **13** was obtained as a single isomer (Scheme 4). We attribute this stereoselectivity to the regioselective formation of the intermediate **12**, in which the π-allylpalladium moiety adopts a conformation which minimizes steric interactions. The stereochemical assignment of **13** is again based on homodecoupling and NOE ^{1}H NMR experiments, with enhancements as shown.

The chemistry outlined here provides a simple, direct method for the synthesis of functionalized pyrrolidines and piperidines via palladium-catalyzed coupling of readily available vinylic halides and unactivated olefinic sulfonamide precursors. We are currently investigating applications of this methodology to alkaloid total synthesis.

Experimental Section

General. All proton and carbon NMR spectra were recorded at 300 and 75.5 MHz, respectively. TLC was performed using commercially prepared 60-mesh silica gel plates, and visualization was effected with short wavelength UV light (254 nm) or basic potassium permanganate solution.

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Palladium acetate was donated to R.C.L. by Johnson Matthey, Inc. and Kawaken Fine Chemicals Co., Ltd. All vinylic halides,[12] *N*-(3-butenyl)-*p*-toluenesulfonamide (**1**),[13,14] *N*-(4-pentenyl)-*p*-toluenesulfonamide (**2**),[14,15] *N*-(4-pentenyl)trifluoromethanesulfonamide (**3**)[15,16] and *cis*-*N*-(2-ethenylcyclopentyl)-*p*-toluenesulfonamide (**11**)[11] were synthesized by literature procedures.

Procedure A for the Palladium-Catalyzed Reactions. To a mixture of 5 mol % of $Pd(OAc)_2$, 10 mol % of P(o-tol)$_3$, 2.0

(9) For reviews of π-allylpalladium chemistry see: (a) Hegedus, L. S. Nucleophilic Attack on Transition Metal Organometallic Compounds. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, p 401. (b) Tsuji, J. η^3-Allylpalladium Complexes. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 3, p 163. (c) Pearson, A. J. Transition Metal-Stabilized Carbocations in Organic Synthesis. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 4, p 889. (d) Godleski, S. A. Nucleophiles with Allyl-Metal Complexes. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Semmelhack, M. F., Eds.; Pergamon: Elmsford, New York, 1991; Vol. 4, p 585. (e) Frost, C. G.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089.

(10) Padwa, A.; Kulkarni, Y. S.; Zhang, Z. *J. Org. Chem.* **1990**, *55*, 4144.

(11) Hegedus, L. S.; McKearin, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 2444.

(12) (A) Kim, J. I.; Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1981**, *46*, 1067. (b) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786. (c) MacLeod, A. J.; Rossiter, J. T. *J. Chem. Soc., Perkin Trans. 1* **1983**, 717. (d) Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *102*, 2753. (e) Kamiya, N.; Chikami, Y.; Ishii, Y. *Synlett* **1990**, 675.

(13) Yoon, N. M.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 2927.

(14) Ratcliffe, J. *J. Chem. Soc.* **1951**, 1140.

(15) Sheehan, J. C.; Bolhofer, W. A. *J. Am. Chem. Soc.* **1950**, *72*, 2786.

(16) Bergeron, R.; Sternbach, D. D.; Hendrickson, J. B. *Tetrahedron* **1975**, *31*, 2517.

Table 1. Synthesis of Pyrrolidines and Piperidines from Sulfonamides and Vinylic Halides

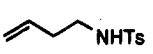
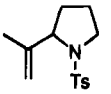
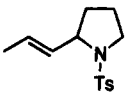
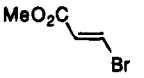
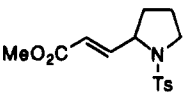
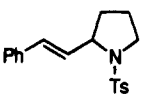
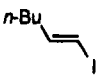
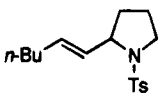
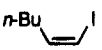
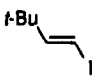
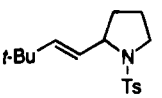
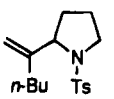
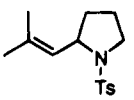
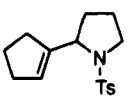
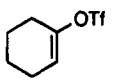
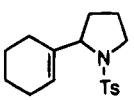
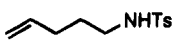
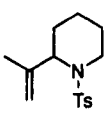
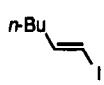
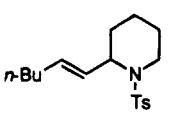
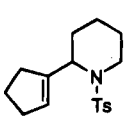
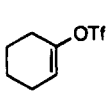
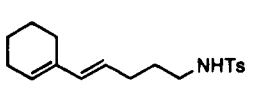
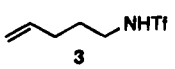
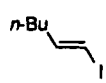
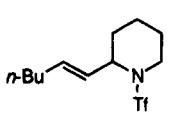
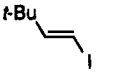
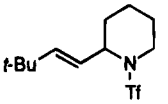
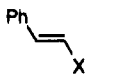
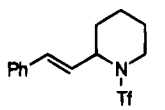
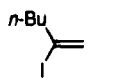
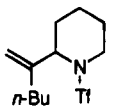
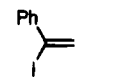
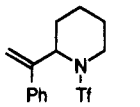
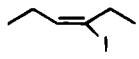
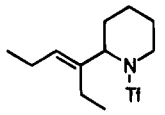
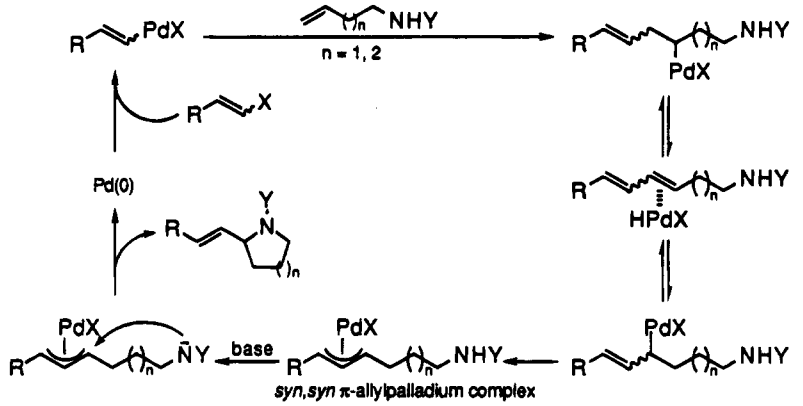
entry	sulfonamide	vinylic halide	cyclization product [a]	procedure [b]; conditions	% isolated yield
1	 1			A; 90 °C, 24 h	88
2				B; 100 °C, 60 h	83
3				A; 90 °C, 40 h	74
4				B; 100 °C, 48 h	60
					
5		X = Br		A; 90 °C, 24 h	28
6		Br		B; 100 °C, 60 h	69
7		I		B; 100 °C, 26 h	66
8				B; 100 °C, 48 h	53
9				A; 90 °C, 24 h	16
10				B; 100 °C, 60 h	61
11				B; 100 °C, 42 h	61
12				B; 100 °C, 42 h	63
13				B; 100 °C, 36 h	48
14				B; 100 °C, 26 h	57
15				A; 90 °C, 48 h	93
16				A; 90 °C, 48 h	67
17				B; 100 °C, 72 h	40
18	 2			A; 100 °C, 48 h	74
19				B; 100 °C, 60 h	21
20				C; 100 °C, 24 h	44
21				A; 100 °C, 48 h	78
22				A; 100 °C, 48 h	54
23				B; 100 °C, 70 h	61
24	 3			A; 100 °C, 24 h	19
25				C; 100 °C, 24 h	77

Table 1 (Continued)

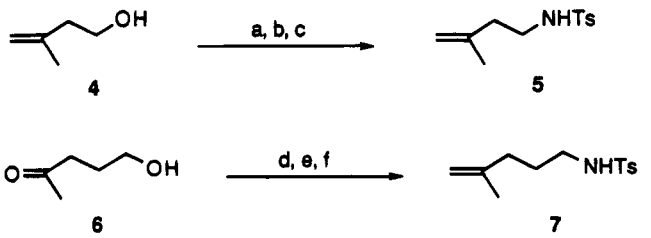
entry	sulfonamide	vinylic halide	cyclization product [a]	procedure [b]; conditions	% isolated yield
26				C; 100 °C, 24 h	69
		 X = Br			
27				A; 100 °C, 24 h	20
28		Br		C; 100 °C, 24 h	63
29		I		C; 100 °C, 24 h	69
30				C; 100 °C, 24 h	62
31				C; 100 °C, 24 h	43
32				C; 100 °C, 24 h	31
33				C; 100 °C, 24 h	48

[a] All products gave satisfactory ^1H and ^{13}C NMR, IR, and mass spectral data. [b] See text and the Experimental Section for procedures.

Scheme 1



Scheme 2[a]



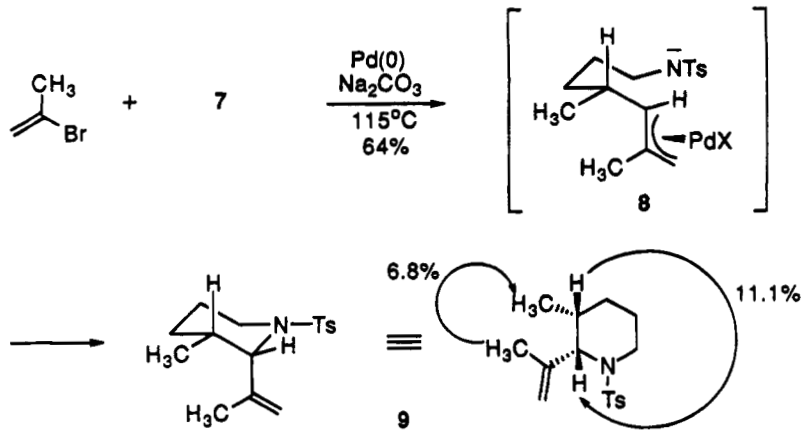
[a] Key: (a) TsCl, Et_3N, CH_2Cl_2, 0 °C, 98%; (b) NaI, acetone, 96%; (c) p-$TsNH_2$, KOH/DMSO, 50 °C, 72%; (d) (1) Ph_3PCH_3Br/nBuLi, THF/HMPA, (2) TsCl, Et_3N, CH_2Cl_2, 0 °C, 64%; (e) NaI, acetone, 86%; (f) p-$TsNH_2$, KOH/DMSO, 50 °C, 83%.

equiv of anhydrous Na_2CO_3, 2.0 equiv of anhydrous nBu_4NCl, and 1.0 equiv of the olefinic sulfonamide in dry MeCN (as a 0.1 M solution of the sulfonamide) in a resealable tube was added 2.0 equiv of the vinylic halide. The mixture was sealed under high vacuum at −78 °C, warmed to rt, and heated for the time and the temperature listed in Table 1. The mixture was then filtered through a plug of silica gel eluting with 30% ethyl acetate/hexanes; the solvent was removed under reduced pressure and the residue was purified by preparative TLC, eluting with 30% ethyl acetate/hexanes, to produce the *N*-tosylpyrrolidine or -piperidine.

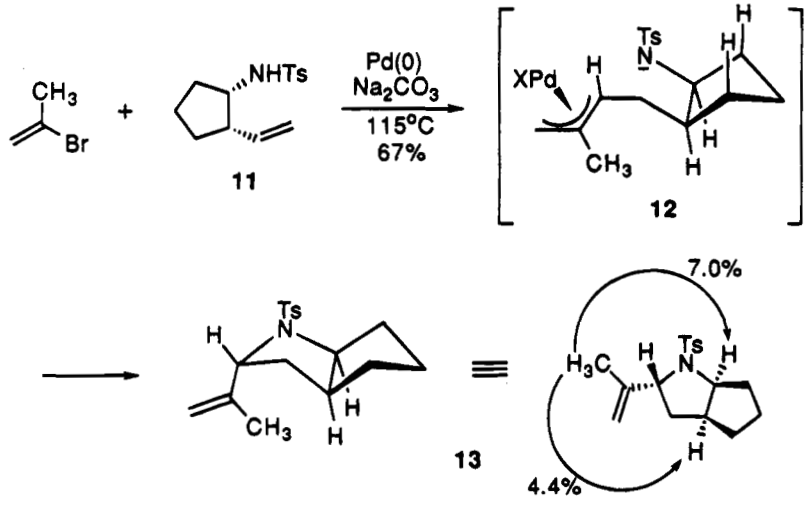
Procedure B. To a 1 dram vial were added the $Pd(OAc)_2$ (0.0125 mmol, 5 mol %), the corresponding vinylic halide (0.25 mmol), Na_2CO_3 (1.125 mmol), nBu_4NCl (0.25 mmol), MeCN (1 mL), and *N*-(3-butenyl)-*p*-toluenesulfonamide (0.5 mmol). The vial was capped with a screw-cap containing a Teflon liner. After heating at 100 °C for the appropriate time, the reaction mixture was diluted with ether and washed with saturated NH_4Cl, followed by water. The organic layer was then dried over $MgSO_4$, concentrated, and purified by flash column chromatography (silica gel, hexane/EtOAc as eluents).

Procedure C. To a 1 dram vial were added the $Pd(OAc)_2$ (0.0125 mmol, 5 mol %), the corresponding vinylic halide (0.25 mmol), $KHCO_3$ (1.125 mmol), nBu_4NCl (0.25 mmol), MeCN (1 mL), and *N*-(4-pentenyl)trifluoromethanesulfonamide (0.5 mmol). The vial was capped with a screw-cap containing a Teflon liner. After heating at 100 °C for 24 h, the reaction

Scheme 3



Scheme 4



mixture was diluted with ether and washed with saturated NH_4Cl, followed by water. The organic layer was then dried over $MgSO_4$, concentrated, and purified via flash column chromatography (silica gel, hexane/EtOAc as eluents).

***N*-(3-Butenyl)-*p*-toluenesulfonamide (1):** IR ($CDCl_3$) 911, 3363 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00 (qt, 2 H, J = 6.9, 0.9 Hz), 2.43 (s, 3 H), 2.98–3.05 (m, 2 H), 4.43 (s, 1 H), 5.00–5.10 (m, 2 H), 5.62 (ddt, 1 H, J = 17.1, 10.5, 6.9 Hz), 7.31 (d, 2 H, J = 8.1 Hz), 7.74 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 21.5, 33.6, 42.1, 118.0, 127.1, 129.7, 134.1, 136.9, 143.4; HRMS M^+ (calcd for $C_{11}H_{15}NO_2S$) 225.0829, found 225.0829.

***N*-(4-Pentenyl)-*p*-toluenesulfonamide (2):** IR ($CDCl_3$) 3282 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.51–1.61 (m, 2 H), 2.02 (q, 2 H, J = 6.9 Hz), 2.41 (s, 3 H), 2.91 (q, 2 H, J = 6.9 Hz), 4.90–4.98 (m, 2 H), 5.24 (t, 1 H, J = 6.0 Hz), 5.68 (ddt, 1 H, J = 17.1, 10.2, 6. Hz), 7.30 (d, 2 H, J = 7.8 Hz), 7.77 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 21.5, 28.6, 30.6, 42.5, 115.4, 127.0, 129.6, 136.9, 137.2, 143.2; HRMS M^+ (calcd for $C_{12}H_{17}NO_2S$) 239.0980, found 239.0987.

***N*-(4-Pentenyl)trifluoromethanesulfonamide (3):** IR ($CDCl_3$) 1189, 3317 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.68–1.77 (m, 2 H), 2.15 (q, 2 H, J = 7.2 Hz), 3.32 (q, 2 H, J = 6.9 Hz), 4.88 (br s, 1 H), 5.03–5.12 (m, 2 H), 5.78 (ddt, 1 H, J = 17.1, 10.2, 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 29.2, 30.4, 44.0, 116.2, 117.0, 136.7; HRMS M^+ (calcd for $C_6H_{10}F_3NO_2S$) 217.0384, found 217.0379.

***N*-Tosyl-2-(isopropenyl)pyrrolidine (entry 1):** ^1H NMR (200 MHz, $CDCl_3$) δ 1.55–1.85 (m, 4H), 1.73 (s, 3H), 2.43 (s, 3H), 3.27 (m, 1H), 3.45 (m, 1H), 4.03 (m, 1H), 4.86 (s, 1H), 5.00 (s, 1H), 7.30 (d, 2H, J = 8.4 Hz), 7.72 (d, 2H, J = 8.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.6, 21.5, 24.0, 31.4, 49.3, 64.9, 111.8, 127.5, 129.6, 143.2, 145.1; EI MS *m/z* 265(M^+), 224, 155, 91; HRMS M^+ (calcd for $C_{14}H_{19}NO_2S$) 265.1136, found 265.1131.

***N*-Tosyl-2-(*trans*-1-propenyl)pyrrolidine (entry 3):** ^1H NMR (360 MHz, $CDCl_3$) δ 1.60–1.85 (m, 7H), 2.40 (s, 3H), 3.24 (m, 1H), 3.43 (m, 1H), 4.07 (m, 1H), 5.36 (m, 1H), 5.65 (m, 1H), 7.33 (d, 2H, J = 8.1 Hz), 7.71 (d, 2H, J = 8.1 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 17.5, 21.5, 23.8, 32.7, 48.6, 61.5, 126.5, 127.5, 129.4, 131.5, 135.5, 143.0; CI MS *m/z* 266(M^+ + 1), 224, 110.

Methyl (*E*)-β-[2-(*N*-tosylpyrrolidinyl)]acrylate (entry 4): TLC (2:1 hexane/EtOAc), R_f = 0.22; IR ($CDCl_3$) 1435, 1595, 1724, 3023 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56–1.87 (m, 4 H), 2.43 (s, 3 H), 3.19–3.52 (m, 2 H), 3.73 (s, 3 H), 4.26–4.32 (m, 1 H), 6.07 (dd, 1 H, J = 15.3, 0.9 Hz), 6.85 (dd, 1 H, J = 15.6, 5.7 Hz), 7.32 (d, 2 H, J = 8.1 Hz), 7.71 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 21.6, 23.9, 31.9, 48.9, 51.6, 60.1, 121.5, 127.5, 129.7, 134.6, 143.6, 147.9, 166.7; HRMS M^+ (calcd for $C_{15}H_{19}NO_4S$) 309.1035, found 309.1032.

***N*-Tosyl-2-((*E*)-2-phenylethenyl)pyrrolidine (entries 5–8):** TLC (2:1 hexane/EtOAc), R_f = 0.4; mp 113–116 °C; IR ($CDCl_3$) 1448, 1597, 3080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.58–1.96 (m, 4 H), 2.39 (s, 3 H), 3.29–3.55 (m, 2 H), 4.34 (q, 1 H, J = 3.9 Hz), 6.05 (dd, 1 H, J = 15.9, 7.2 Hz), 6.54 (dd, 1 H, J = 15.9, 0.9 Hz), 7.24–7.30 (m, 7 H), 7.72 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 21.5, 24.0, 32.8, 48.7, 61.7, 126.5, 127.6, 128.4, 129.5, 130.0, 130.2, 135.6, 136.6, 143.1; HRMS M^+ (calcd for $C_{15}H_{21}NO_2S$) 327.1293, found 327.1287.

***N*-Tosyl-2-((*E*)-1-hexenyl)pyrrolidine (entries 9–11):** TLC (5:1 hexane/EtOAc), R_f = 0.30; IR ($CDCl_3$) 1456, 1597, 3060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 6.6 Hz), 1.20–1.40 (m, 4 H), 1.55–1.85 (m, 4 H), 2.00 (q, 2 H, J = 7.2 Hz), 2.42 (s, 3 H), 3.20–3.45 (m, 2 H), 4.05–4.15 (m, 1 H), 5.33 (ddt, 1 H, J = 15.3, 6.6, 1.2 Hz), 5.63 (dt, 1 H, J = 15.0, 6.9 Hz), 7.29 (d, 2 H, J = 8.1 Hz), 7.70 (d, 2 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0, 21.5, 22.3, 23.9, 31.3, 31.7, 32.8, 48.6, 61.6, 127.5, 129.4, 130.1, 131.9, 135.6, 143.0; HRMS M^+ (calcd for $C_{17}H_{25}NO_2S$) 307.1606, found 307.1599.

***N*-Tosyl-2-((*E*)-3,3-dimethyl-1-butenyl)pyrrolidine (entry 12):** TLC (5:1 hexane/EtOAc), R_f = 0.35; IR ($CDCl_3$) 1459, 1596, 3025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (s, 9 H), 1.60–1.90 (m, 4 H), 2.42 (s, 3 H), 3.28–3.45 (m, 2 H), 4.13 (m, 1 H), 5.21 (dd, 1 H, J = 15.6, 6.6 Hz), 5.61 (dd, 1 H, J = 15.6, 1.2 Hz), 7.28 (d, 2 H, J = 8.4 Hz), 7.71 (d, 2 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 21.5, 23.9, 29.4, 32.7, 33.0, 48.6, 61.8, 125.0, 127.5, 129.4, 136.0, 142.6, 143.0; HRMS M^+ (calcd for $C_{17}H_{25}NO_2S$) 307.1606, found 307.1611.

***N*-Tosyl-2-(2-hexenyl)pyrrolidine (entry 13):** TLC (5:1 hexane/EtOAc), R_f = 0.32; IR ($CDCl_3$) 1455, 1595, 1648, 3082 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 7.2 Hz), 1.10–2.10 (m, 10 H), 2.40 (s, 3 H), 3.20–3.47 (m, 2 H), 4.07 (t, 1 H, J = 5.7 Hz), 4.83 (s, 1 H), 5.02 (s, 1 H), 7.27 (d, 2 H, J = 8.1 Hz), 7.68 (d, 2 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 21.6, 22.6, 23.9, 29.9, 31.6, 32.0, 49.1, 64.2, 109.8, 127.5, 129.5, 136.1, 143.2, 149.3; HRMS M^+ (calcd for $C_{17}H_{25}NO_2S$) 307.1606, found 307.1613.

***N*-Tosyl-2-(2-methyl-1-propenyl)pyrrolidine (entry 14):** TLC (5:1 hexane/EtOAc), R_f = 0.26; mp 68–69 °C; IR ($CDCl_3$) 1447, 1596, 1673, 2970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53–1.61 (m, 2 H), 1.65 (d, 3 H, J = 0.9 Hz), 1.70 (d, 3 H, J = 0.90 Hz), 1.79–1.90 (m, 2 H), 2.42 (s, 3 H), 3.28–3.42 (m, 2 H), 4.30–4.38 (m, 1 H), 5.02–5.07 (m, 1 H), 7.28 (d, 2 H, J = 8.7 Hz), 7.68 (d, 2 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 18.1, 21.5, 24.2, 25.8, 33.5, 48.5, 58.0, 125.8, 127.5, 129.3, 133.0, 136.0, 142.9; HRMS M^+ (calcd for $C_{15}H_{21}NO_2S$) 279.1293, found 279.1288.

***N*-Tosyl-2-(1-cyclopentenyl)pyrrolidine (entry 15):** ^1H NMR (360 MHz, $CDCl_3$) δ 1.55–1.95 (m, 6H), 2.15–2.35 (m, 4H), 2.43 (s, 3H), 3.27 (m, 1H), 3.43 (m, 1H), 4.31 (s, 1H), 5.57 (s, 1H), 7.27 (d, 2H, J = 8.1 Hz), 7.68 (d, 2H, J = 8.1 Hz); CI MS m/z 292 (M^++1), 224, 136, 91.

***N*-Tosyl-2-(1-cyclohexenyl)pyrrolidine (entry 16):** ^1H NMR (360 MHz, $CDCl_3$) δ 1.45–1.60 (m, 4H), 1.68 (m, 4H), 1.85–1.98 (m, 4H), 2.43 (s, 3H), 3.37 (m, 2H), 3.98 (m, 1H), 5.60 (s, 1H), 7.27 (d, 2H, J = 8.0 Hz), 7.71 (d, 2H, J = 8.0 Hz); CI MS m/z 306 (M^+ + 1), 224, 150, 91.

***N*-Tosyl-2-(isopropenyl)piperidine (entry 18):** ^1H NMR (200 MHz, $CDCl_3$) δ 1.23 (m, 1H), 1.48 (m, 4H), 1.69 (s, 3H), 1.87 (m, 1H), 2.41 (s, 3H), 2.99 (m, 1H), 3.70 (m, 1H), 4.48 (s, 1H), 4.98 (s, 1H), 5.02 (s, 1H), 7.28 (d, 2H, J = 8.1 Hz), 7.73 (d, 2H, J = 8.1 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 19.2, 21.1, 21.5, 24.3, 25.9, 41.8, 57.0, 113.4, 127.0, 129.6, 138.8, 141.9, 142.8; EI MS m/z 279(M^+), 238, 155, 91; HRMS M^+ (calcd for $C_{15}H_{21}SO_2N$) 279.1293, found 279.1283.

***N*-Tosyl-2-((*E*)-1-hexenyl)piperidine (entry 20):** TLC (5:1 hexane/EtOAc), R_f = 0.36; IR ($CDCl_3$) 1184, 3060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, 3 H, J = 6.9 Hz), 1.21–1.68 (m, 12 H), 1.90 (q, 2 H, J = 6.3 Hz), 2.40 (s, 3 H), 2.89–2.99 (m, 1 H), 3.68 (d, 1 H, J = 13.2 Hz), 4.55 (br s, 1 H), 5.30 (ddt, 1 H, J = 15.6, 6.3, 1.2 Hz), 5.51 (dtd, 1 H, J = 15.6, 6.6, 1.2 Hz), 7.24 (d, 2 H, J = 8.4 Hz), 7.66 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0, 19.1, 21.5, 22.3, 25.3, 30.6, 31.1, 32.0, 41.6, 54.7, 126.1, 127.4, 129.3, 133.5, 137.9, 142.6; HRMS M^+ (calcd for $C_{18}H_{27}O_2NS$) 321.1763, found 321.1768.

***N*-Tosyl-2-(1-cyclopentenyl)piperidine (entry 21):** ^1H NMR (360 MHz, $CDCl_3$) δ 1.47 (m, 4H), 1.83 (m, 4H), 2.21 (m, 1H), 2.34 (m, 1H), 2.43 (s, 3H), 3.02 (m, 1H), 3.73 (m, 1H), 4.63 (s, 1H), 5.48 (s, 1H), 7.23 (d, 2H, J = 8.3 Hz), 7.70 (d, 2H, J = 8.3 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 19.4, 21.5, 23.3, 24.5, 27.0, 32.7, 33.7, 41.8, 53.6, 127.0, 127.7, 129.5, 138.8, 141.7, 142.7; CI MS m/z 306(M^+ + 1), 280, 238, 150, 83.

***N*-(Trifluoromethanesulfonyl)-2-((*E*)-1-hexenyl)piperidine (entry 25):** TLC (20:1 hexane/EtOAc), R_f = 0.36; IR ($CDCl_3$) 1183, 2981 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H, J = 6.6 Hz), 1.25–1.82 (m, 12 H), 2.08 (q, 2 H, J = 6.9 Hz), 3.22 (t, 1 H, J = 12.3 Hz), 3.76 (d, 1 H, J = 13.8 Hz), 4.61 (br s, 1 H), 5.49 (dd, 1 H, J = 15.3, 4.2 Hz), 5.69 (dtd, 1 H, J = 15.3, 6.6, 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ 13.9, 18.6, 22.2, 25.6, 29.8, 31.2, 32.1, 43.0, 56.1, 135.0; HRMS M^+ (calcd for $C_{12}H_{20}O_2NSF_3$) 299.1167, found 299.1166.

***N*-(Trifluoromethanesulfonyl)-2-((*E*)-3,3-dimethyl-1-butenyl)piperidine (entry 26):** TLC (20:1 hexane/EtOAc), R_f = 0.35; IR ($CDCl_3$) 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (s, 9 H), 1.45–1.80 (m, 6 H), 3.14 (br t, 1 H, J = 12.3 Hz), 3.70 (br d, 1 H, J = 14.4 Hz) 4.55 (br d, 1 H, J = 2.7 Hz), 5.25–5.45 (m, 1 H), 5.64 (dd, 1 H, J = 15.9, 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 18.6, 25.7, 29.4, 30.3, 33.2, 43.0, 56.3, 145.7; HRMS M^+ (calcd for $C_{12}H_{20}F_3NO_2S$) 299.1167, found 299.1170.

***N*-(Trifluoromethanesulfonyl)-2-((*E*)-β-styryl)piperidine (entries 27–30):** TLC (20:1 hexane/EtOAc), R_f = 0.26; IR ($CDCl_3$) 1184, 2947 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56–2.01 (m, 6 H), 3.30 (t, 1 H, J = 12.3 Hz), 3.83 (d, 1 H, J = 13.8 Hz), 4.83 (br s, 1 H), 6.22 (dd, 1 H, J = 15.9, 5.1 Hz), 6.59 (dd, 1 H, J = 16.2, 1.5 Hz), 7.25–7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.8, 25.4, 29.7, 43.3, 56.3, 126.6, 128.1, 128.7, 133.4, 136.1; HRMS M^+ (calcd for $C_{14}H_{16}F_3NO_2S$) 319.0854, found 319.0845.

***N*-(Trifluoromethanesulfonyl)-2-(2-hexenyl)piperidine (entry 31):** TLC (20:1 hexane/EtOAc), R_f = 0.38; IR ($CDCl_3$) 1189, 2954 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, 3 H, J = 7.2 Hz), 1.28–1.80 (m, 10 H), 1.90–2.14 (m, 2 H), 3.23 (td, 1 H, J = 12.0, 2.1 Hz), 3.79 (d, 1 H, J = 14.7 Hz), 4.55 (br s, 1 H), 5.04 (s, 1 H), 5.15 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 18.8, 22.5, 25.2, 26.7, 30.0, 33.3, 43.7, 58.3, 112.8, 144.2; HRMS M^+ (calcd for $C_{12}H_{20}F_3NO_2S$) 299.1167, found 299.1165.

***N*-(Trifluoromethanesulfonyl)-2-(1-phenylethenyl)-piperidine (entry 32):** TLC (20:1 hexane/EtOAc), R_f = 0.25; IR ($CDCl_3$) 1194, 2958 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–1.90 (m, 6 H), 3.44 (td, 1 H, J = 13.2, 2.1 Hz), 3.87 (dd, 1 H, J = 14.1, 2.7 Hz), 5.13 (br s, 1 H), 5.32 (d, 1 H, J = 2.1 Hz), 5.40 (d, 1 H, J = 2.1 Hz), 7.25–7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.4, 25.2, 27.5, 43.7, 57.9, 116.2, 127.1, 127.9, 128.5, 140.1, 145.8; HRMS M^+ (calcd for $C_{14}H_{16}F_3NO_2S$) 319.0854, found 319.0858.

***N*-(Trifluoromethanesulfonyl)-2-((*E*)-3-hexenyl)piperidine (entry 33):** TLC (20:1 hexane/EtOAc), R_f = 0.40; IR ($CDCl_3$) 1189, 2956 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (t, 3 H, J = 7.2 Hz), 1.01 (t, 3 H, J = 7.2 Hz), 1.52–1.80 (m, 6 H), 2.01–2.18 (m, 4 H), 3.10–3.25 (m, 1 H), 3.77 (d, 1 H, J = 13.2 Hz), 4.55 (m, 1 H), 5.37 (td, 1 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 13.3, 13.5, 14.5, 18.9, 21.3, 25.3, 26.6, 43.7, 58.0, 129.9, 134.9; HRMS M^+ (calcd for $C_{12}H_{20}F_3NO_2S$) 299.1167, found 299.1167.

***N*-(3-Methyl-3-butenyl)-*p*-toluenesulfonamide (5).** To a solution of 5.0 mL (49.5 mmol) of 3-methyl-3-buten-1-ol (**4**) and 8.3 mL (59.4 mmol) of triethylamine in 100 mL of dry CH_2Cl_2 at 0 °C under argon was added portionwise 10.4 g (54.5 mmol) of *p*-toluenesulfonyl chloride. The mixture was stirred at 0 °C for 1 h and warmed to rt. After the mixture had stirred for 12 h, 100 mL of saturated $NaHCO_3$ solution was added and the solution was extracted three times with 50 mL portions of CH_2Cl_2. The combined organic extracts were washed with water and brine and dried over $MgSO_4$. The solvents were removed *in vacuo* and the crude product was purified by flash chromatography, eluting with ethyl acetate/hexanes (1:9), to produce 3-methyl-3-butenol tosylate as a yellow oil (11.7 g, 98%): ^1H NMR (200 MHz, $CDCl_3$) δ 1.64 (s, 3H), 2.33 (t, 2H, J = 6.2 Hz), 2.43 (s, 3H), 4.12 (t, 2H, J = 6.9 Hz), 4.67 (s, 1H), 4.78 (s, 1H), 7.37 (d, 2H, J = 8.2 Hz), 7.78 (d, 2H, J = 8.2 Hz); CI MS m/z 241(M^+ + 1), 213, 173, 155, 137, 91.

To a solution of 33.9 g (226 mmol) of sodium iodide in 200 mL of dry acetone under argon was added 13.6 g (56.6 mmol) of the above 3-methyl-3-butenol tosylate. After the mixture had stirred for 24 h, 100 mL of water was added and the solution was extracted three times with 50 mL portions of hexanes. The combined organic extracts were washed with water and brine and dried over $MgSO_4$. The solvents were removed *in vacuo* to produce 1-iodo-3-methyl-3-butene as a colorless oil which was suitable for use without further purification (10.7 g, 96%): ^1H NMR (360 MHz, $CDCl_3$) δ 1.77 (s, 3H), 2.69 (t, 2H, J = 7.6 Hz), 3.26 (t, 2H, J = 7.6 Hz), 4.76 (s, 1H), 4.87 (s, 1H); EI MS m/z 196 (M^+), 155, 139, 127, 69.

A solution of 2.94 g (52.4 mmol) of KOH and 15.9 g (92.7 mmol) of *p*-toluenesulfonamide in 50 mL of dry DMSO was heated at 50 °C under argon for 2 h, after which 7.9 g (40.3 mmol) of the above 1-iodo-3-methyl-3-butene was added. After the mixture had stirred at 50 °C for 1 h, the mixture was cooled to rt, diluted with 100 mL of ice water, and extracted three times with 50 mL portions of CH_2Cl_2. The combined organic extracts were washed with 15% KOH solution, water and brine and dried over $MgSO_4$. The solvents were removed *in vacuo* and the crude product was purified by flash chromatography, eluting with ethyl acetate/hexanes (1:9), to produce *N*-(3-

methyl-3-butenyl)-*p*-toluenesulfonamide (**5**) as a yellow oil (6.95 g, 72%): ^{1}H NMR (200 Mhz, Cdcl$_3$) δ 1.56 (s, 3H), 2.11 (t, 2H, J = 6.7 Hz), 2.39 (s, 3H), 3.00 (d, 2H, J = 6.2 Hz), 4.62 (s, 1H), 4.77 (s, 1H), 7.30 (d, 2H, J = 8.3 Hz), 7.74 (d, 2H, J = 8.3 Hz); ^{13}C NMR (90 MHz, CDCl$_3$) δ 21.4, 21.8, 37.2, 40.9, 112.7, 127.1, 139.6, 136.9, 141.6, 143.2; EI MS *m/z* 239 (M$^+$), 184, 155, 91; HRMS M$^+$ (calcd for $C_{12}H_{17}SO_2N$) 239.0980, found 239.0990.

***cis*-*N*-Tosyl-2-isopropenyl-3-methylpyrrolidine (10).** Using procedure A (90 °C, 72 h), from 0.0472 g (0.24 mmol) of *N*-(3-methyl-3-butenyl)-*p*-toluenesulfonamide (**5**) was obtained 0.0345 g (63% yield) of **10**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.73 (d, 3H, J = 6.6 Hz), 1.11 (m, 1H), 1.76 (s, 3H), 1.95 (m, 2H), 2.44 (s, 3H), 3.35 (d, 1H, J = 6.6 Hz), 3.46 (m, 2H), 4.90 (d, 2H, J = 8.3 Hz), 7.32 (d, 2H, J = 8.3 Hz), 7.71 (d, 2H, J = 8.3 Hz); ^{13}C NMR (75 Hz, CDCl$_3$) δ 17.4, 17.7, 21.5, 31.9, 38.4, 48.4, 73.0, 112.6, 127.5, 129.5, 134.7, 143.2, 144.4; EI MS *m/z* 279 (M$^+$), 238, 155, 124, 91, 82, 28; HRMS M$^+$ (calcd for $C_{15}H_{21}NO_2S$) 279.1293, found 279.1281.

***N*-(4-Methyl-4-pentenyl)-*p*-toluenesulfonamide (7).** To a solution of 27.3 g (19.1 mmol) of methyltriphenylphosphonium bromide and 11.3 mL (16.2 mmol) of HMPA in 100 mL of dry THF under argon was added 28.2 mL (17.6 mmol) of *n*-butyllithium (2.5 M solution in hexanes) and the mixture was stirred for 10 min before 1.5 g (14.7 mmol) of 3-acetyl-1-propanol (**6**) was added dropwise. After the mixture had stirred for 12 h, the solvent was removed *in vacuo* and the crude residue diluted with 100 mL of water and extracted three times with 50 mL portions of ether. The combined organic extracts were washed with water and brine and dried over MgSO$_4$. The solvent was removed *in vacuo* and the crude olefinic alcohol was diluted with 100 mL of dry CH$_2$Cl$_2$ and placed under argon at 0 °C.

To the stirring solution were added 9.8 mL (17.6 mmol) of triethylamine and 12.3 g (16.2 mmol) of *p*-toluenesulfonyl chloride and the mixture was warmed to rt and stirred for 12 h. The mixture was diluted with 100 mL of saturated NaHCO$_3$ solution and was extracted three times with 50 mL portions of CH$_2$Cl$_2$. The combined organic extracts were washed with water, brine and dried over MgSO$_4$. The solvents were removed *in vacuo* and the crude product was purified by flash chromatography, eluting with ethyl acetate/hexanes (1:9), to produce 4-methyl-4-pentenol tosylate as a yellow oil (2.4 g, 64%): ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.64 (s, 3H), 1.76 (m, 2H), 2.01 (t, 2H, J = 8.1 Hz), 2.43 (s, 3H), 4.02 (t, 2H, J = 6.5 Hz), 4.57 (s, 1H), 4.68 (s, 1H), 7.34 (d, 2H, J = 8.3 Hz), 7.80 (d, 2H, J = 8.3 Hz); CI MS *m/z* 255(M$^+$ + 1), 229, 213, 173, 83.

To a solution of 8.3 g (55 mmol) of sodium iodide in 50 mL of dry acetone under argon was added 3.5 g (13.8 mmol) of the above 4-methyl-4-pentenol tosylate. After the mixture had stirred for 24 h, 50 mL of water was added and the solution was extracted three times with 50 mL portions of hexanes. The combined organic extracts were washed with water and brine and dried over MgSO$_4$. The solvents were removed *in vacuo* to produce 1-iodo-4-methyl-4-pentene a colorless oil which was suitable for use without further purification (2.5 g, 86%): ^{1}H NMR (360 MHz, CDCl$_3$) δ 1.72 (s, 3H), 1.96 (m, 2H), 2.12 (t, 2H, J = 7.7 Hz), 3.18 (t, 2H, J = 6.9 Hz), 4.73 (s, 1H), 4.77 (s, 1H); CI MS *m/z* 211(M$^+$ + 1), 157, 139, 83.

A solution of 0.64 g (11.4 mmol) of KOH and 3.47 g (20.3 mmol) of *p*-toluenesulfonamide in 30 mL of dry DMSO was heated at 50 °C under argon for 2 h, after which 1.85 g (8.8 mmol) of the above 1-iodo-4-methyl-4-pentene was added. After the mixture had stirred at 50 °C for 1 h, the mixture was cooled to rt, diluted with 50 mL of ice–water, and extracted three times with 50 mL portions of CH$_2$Cl$_2$. The combined organic extracts were washed with 15% KOH solution, water, and brine and dried over MgSO$_4$. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography, eluting with ethyl acetate/hexanes (1:9), to produce *N*-(4-methyl-4-pentenyl)-*p*-toluenesulfonamide (**7**) as a yellow oil (1.85 g, 83%): ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.53 (m, 2H), 1.56 (s, 3H), 1.95 (t, 2H, J = 7.6 Hz), 2.40 (s, 3H), 2.89 (t, 2H, J = 6.5 Hz), 4.58 (s, 1H), 4.65 (s, 1H), 7.29 (d, 2H, J = 8.3 Hz), 7.75 (d, 2H, J = 8.3 Hz); ^{13}C NMR (90 MHz, CDCl$_3$) δ 21.4, 22.1, 27.3, 34.6, 42.8, 110.5, 127.0, 129.6, 137.0, 143.2, 144.4; EI MS *m/z* 253 (M$^+$), 184, 155, 98, 97; HRMS M$^+$ (calcd for $C_{13}H_{19}SO_2N$) 253.1136, found 253.1120.

***cis*-*N*-Tosyl-2-*trans*-isopropenyl-3-methylpiperidine (9).** Using procedure A (155 °C, 48 h, in DMF), from 0.196 g (0.77 mmol) of *N*-(4-methyl-4-pentenyl)-*p*-toluenesulfonamide (**7**) was obtained 0.145 g (64% yield) of **9**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.94 (d, 3H, J = 6.9 Hz), 1.21 (m, 1H), 1.36 (m, 1H), 1.64 (m, 2H), 1.72 (s, 3H), 2.08 (m, 1H), 2.42 (s, 3H), 3.17 (m, 1H), 3.47 (m, 1H), 4.01 (s, 1H), 4.77 (s, 1H), 4.94 (s, 1H), 7.28 (d, 2H, J = 8.0 Hz), 7.72 (d, 2H, J = 8.0 Hz); ^{13}C NMR (50 MHz, CDCl$_3$) δ 18.6, 20.3, 20.7, 21.5, 26.1, 29.0, 42.5, 64.8, 113.8, 127.3, 129.3, 137.9, 142.6, 142.7; EI MS *m/z* 293 (M$^+$), 252, 155, 138, 91; HRMS M$^+$ (calcd for $C_{16}H_{23}SO_2N$) 293.1449, found 293.1468.

***N*-Tosyl-3-*trans*-isopropenyl-2-*cis*-azabicyclo[3.3.0]-octane (13).** Using procedure A (115 °C, 24 h), from 0.0825 g (0.23 mmol) of *cis*-*N*-(2-ethenylcyclopentyl)-*p*-toluenesulfonamide (**11**)[11] was obtained 0.0465 g (67% yield) of **13**: ^{1}H NMR (360 MHz, CDCl$_3$) δ 1.45–1.65 (m, 4H), 1.74 (m, 1H), 1.82 (s, 3H), 1.87 (m, 2H), 2.08 (m, 1H), 2.34 (m, 1H), 2.45 (s, 3H), 3.68 (dd, 1H, J = 3.9, 10.1 Hz), 3.95 (dt, 1H, J = 3.8, 8.4 Hz), 4.86 (s, 1H), 4.94 (s, 1H), 7.32 (d, 2H, J = 8.3 Hz), 7.70 (d, 2H, J = 8.3 Hz); ^{13}C NMR (90 MHz, CDCl$_3$) δ 16.5, 21.5, 23.8, 31.5, 35.1, 37.6, 40.8, 67.0, 68.6, 112.1, 128.1, 129.4, 133.6, 143.3, 145.0; CI MS *m/z* 306 (M$^+$+1), 279, 172, 155, 91.

Acknowledgment. The Larock group gratefully acknowledges the donors of the Petroleum Research Fund administered by the American Chemical Society for their generous financial support of this work and Johnson Matthey, Inc. and Kawaken Fine Chemicals Co., Ltd. for the palladium acetate. The Weinreb group thanks the National Science Foundation (CHE 9202848) for support.

Supplementary Material Available: Copies of ^{1}H-NMR spectral data for all new compounds (56 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.