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Development of the Copper-Catalyzed Olefin Aziridination Reaction

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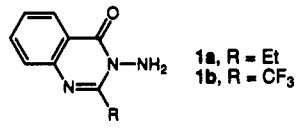
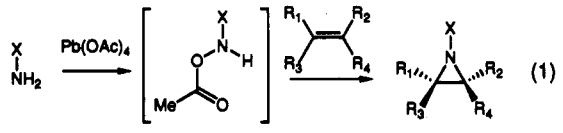
Abstract: Soluble Cu(I) and Cu(II) triflate and perchlorate salts are efficient catalysts for the aziridination of olefins employing (*N*-(*p*-tolylsulfonyl)imino)phenyliodinane, PhI=NTs, as the nitrene precursor. Electron-rich as well as electron-deficient olefins undergo aziridination with this reagent in 55–95% yields, at temperatures ranging from –20 °C to +25 °C. The catalyzed nitrogen atom-transfer reaction to enol silanes and silylketene acetals has also been developed to provide facile syntheses of α-amino ketones. Other metal complexes were found to be less effective at catalyzing the reaction, while PhI=NTs proved to be superior to other imido group donors as the nitrene precursor. Reaction rates and yields are enhanced in polar aprotic solvents such as MeCN and $MeNO_2$. Reaction stereospecificity in the aziridination of *cis* and *trans* disubstituted olefins was evaluated and found to be both catalyst and substrate dependent. Intermolecular competition experiments between pairs of mono- and disubstituted olefins indicate that the olefin selectivity profile for the reaction is independent of the oxidation state of the copper catalyst employed. It is concluded that these reactions are proceeding through the 2+ catalyst oxidation state under the conditions employed in this study.

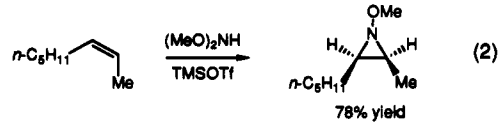
Introduction

Considerable attention has been devoted to the development of reactions that effect catalytic atom transfer to olefins. Due to the utility of these processes in organic synthesis, such reactions have been extensively refined for both epoxidation[1] and cyclopropanation.[2] On the other hand, the analogous nitrogen atom-transfer processes, particularly metal-catalyzed variants, have been less developed in spite of the fact that the broad utility of aziridines as electrophiles has been amply demonstrated.[3,4]

Although the formation of aziridines from the addition of thermally or photochemically generated nitrenes to olefins is a well-known reaction, its utility is limited by low yields due to competing hydrogen abstraction and insertion processes.[5] Two of the most general olefin aziridinations are illustrated below (eqs 1 and 2). The oxidation of a variety of heteroatom-substituted

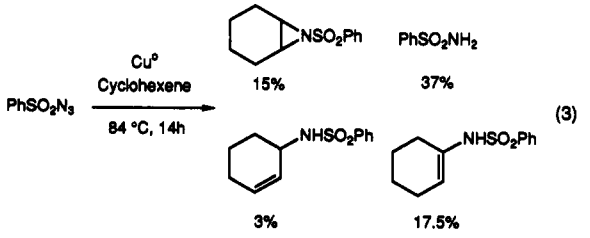






amines with $Pb(OAc)_4$ in the presence of olefins has been found to provide a stereospecific route to aziridines of some generality (eq 1).[6,7] While these reactions have traditionally been postulated to proceed through nitrenes, this point has not been unequivocally established. Atkinson has proposed that the isolable intermediate *N*-acetoxyamide **2b** functions mechanistically as a peracid equivalent, thus bypassing the nitrene manifold,[6b] and has also documented that olefin aziridination via **2** is hydroxyl-directed as are peracid epoxidations.[6c] In related studies, Rudchenko has demonstrated the utility of dimethoxyamine, in conjunction with BF_3·OEt_2 catalysis, as a stereospecific aziridination reagent,[8a] and Vedejs has recently reported that TMSOTf appears to be even more efficient in promoting the reaction (eq 2).[8b]

The first metal-catalyzed nitrogen atom-transfer process was reported by Kwart and Kahn, who demonstrated that copper powder promoted the decomposition of benzenesulfonyl azide when heated in cyclohexene (eq 3).[9] The resulting distribution of products is consistent with the intervention of nitrene (or metal nitrenoid) intermediates.



In 1983, Groves reported an example of the stoichiometric activation and transfer of nitrogen from a nitridomanganese(V)

• Abstract published in *Advance ACS Abstracts,* March 1, 1994.

(1) For a recent review on the metal-catalyzed epoxidation reaction, see: Jorgensen, K. A. *Chem. Rev.* **1989**, *89*, 431–458.

(2) For a recent review on the metal-catalyzed cyclopropanation reaction, see: Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919–939.

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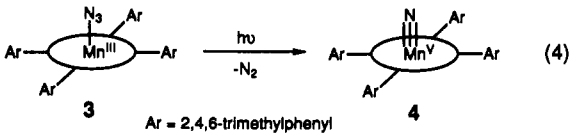
Table 1. Olefin Aziridination with Mn(III) and Fe(III) Porphyrin Catalysts (Eq 6)

entry	catalyst[a]	olefin	yield,%[b]
1	Mn(TPP)Cl[c]	Ph	80
2	Mn(TDCPP)ClO_4[d]	*n*-Bu	23
3	Fe(TDCPP)ClO_4	Ph, Ph	36
4	Fe(TDCPP)ClO_4	Ph, Ph	43[e]
5	Mn(TDCPP)ClO_4		0[f]

[a] All reactions were performed in CH_2Cl_2 with 5 mol % catalyst and 100 equiv of olefin at 25 °C. [b] Based on 1 equiv of PhI=NTs. [c] TPP = tetraphenylporphyrin. [d] TDCPP = tetrakis(2,6-dichlorophenyl)porphyrin. [e] Product isolated as the *trans*-1,2-diphenylaziridine only. [f] The product of allylic insertion was obtained, see eq 7.

porphyrin complex to an olefin.[10] Irradiation of **3** afforded the manganese nitrido complex **4**, which was isolated in 80% yield (eq 4). Treatment of **4** with trifluoroacetic anhydride (TFAA, 1.2 equiv) in the presence of cyclooctene (11 equiv) provided the *N*-(trifluoroacetyl)-protected aziridine in 82–94% yield, apparently through the intermediacy of the manganese(V) imido complex **5** (eq 5).



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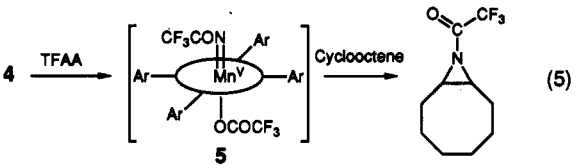
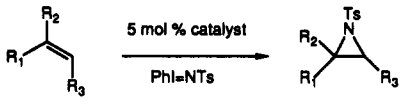


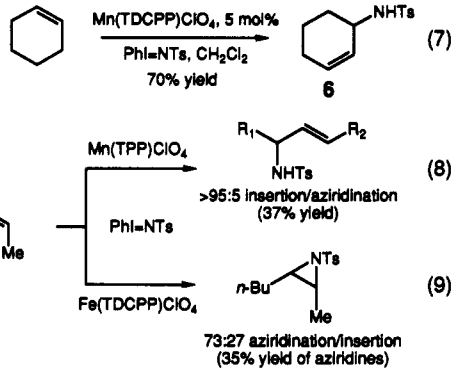
(5)

Prior to the present investigation, the only study addressing the scope of metal-catalyzed nitrogen atom transfer to olefins had been reported by Mansuy.[11] In this investigation, Fe(III)- and Mn(III)-derived porphyrin catalysts were employed in the aziridination of olefins, employing the nitrene precursor (*N*-(*p*-tolylsulfonyl)imino)phenyliodinane, PhI=NTs, (eq 6, Table 1).[12] Catalysts derived from tetraphenylporphyrin (TPP) and tetrakis-(2,6-dichlorophenyl)porphyrin (TDCPP) were utilized.

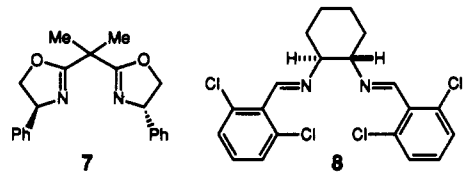


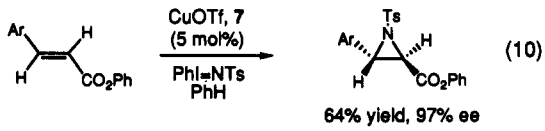
(6)

Although the Mn(TPP)Cl-catalyzed reaction of PhI=NTs with styrene afforded the derived aziridine in 80% yield (entry 1), significantly lower yields were obtained with other olefins, even with optimized catalysts (entries 2–4). Nitrogen atom transfer to *cis*-stilbene catalyzed by Fe(TDCPP)ClO_4 was not stereospecific, yielding only the *trans*-2,3-diphenylaziridine (entry 4). Allylic insertion by the metal nitrenoid is frequently the major side reaction encountered during olefin aziridination. In fact, the equally useful allylic amination process can be amplified into the dominant process with proper catalyst selection (eqs 7–9).[11b]



The present investigation was initiated[13] with the objective of finding metal catalysts which might extend the scope of the aziridination process and ultimately developing enantioselective reaction variants. Preliminary results which document the realization of this latter objective have recently been published in independent investigations from this and the Jacobsen laboratories, where chiral, copper-based catalysts were used (eqs 10 and 11).[14–16]





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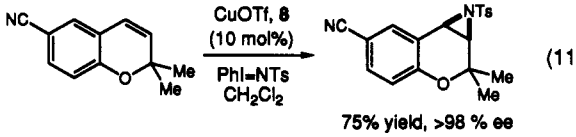

(11)

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(7) Atkinson, R. S.; Tughan, G. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2803–2807. Atkinson, R. S.; Tughan, G. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2787–2796. Chilmonczyk, Z.; Egli, M.; Behringer, C.; Dreiding, A. S. *Helv. Chim. Acta* **1989**, *72*, 1095–1106. Kapron, J. T.; Santarsiero, B. D.; Vederas, J. C. *J. Chem. Soc., Chem. Commun.* **1993**, 1074–1076.

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(10) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073–2074.

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Table 2. Transition-Metal Catalysts in the Aziridination of Styrene and Cyclohexene (Eqs 12 and 13)

entry	catalyst[a]	yield 9, %[b]	yield 10, %[b,c]
1	$CuClO_4$	90	54
2	CuOTf	92	50
3	CuCl	61	nd
4	CuBr	56	nd
5	$Cu(acac)_2$	95	30
6	$Cu(OTf)_2$	92[c]	60
7	Mn(TPP)Cl	71	0[d]
8	$Mn(OTf)_2$	30[c]	5[e]
9	Fe(TPP)Cl	31	0[d]
10	$Fe(OTf)_2$	63[c]	21[e]
11	$Co(OTf)_2$	38[c]	0
12	$Rh_2(OAc)_4$	48	0
13	$Rh(PPh_3)Cl$	10	0
14	$Ni(acac)_2$	9	0
15	$Ni(OTf)_2$	12[c]	0
16	$Pd(acac)_2$	12	0

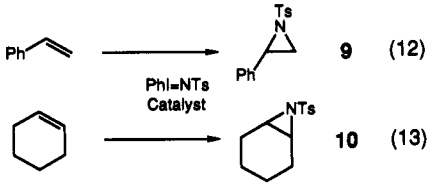
[a] All reactions were performed with 5 mol % catalyst and 5 equiv of olefin in CH_2Cl_2 unless otherwise noted. Experiments which were not performed are denoted by nd. [b] Based on 1 equiv of PhI=NTs. [c] Reaction run in MeCN. [d] Reaction provided insertion product (see text). [e] Reaction provided product of insertion in addition to aziridination (see text).

Results and Discussion

Mn(III) and Fe(III) catalysts are commonly employed in olefin epoxidation, while Cu(I) and Rh(II) complexes are among the best metal catalysts for cyclopropanation. In conjunction with the present investigation, it was of interest to determine whether an analogy might be drawn between aziridination and either of the other two atom-transfer processes since such a correlation might provide a useful vehicle for catalyst selection.

During the course of our studies on asymmetric cyclopropanation with Cu(I) catalysts,[14c] we were presented with the opportunity of evaluating the aziridination ↔ cyclopropanation analogy for the two group-transfer processes. This analogy led us to screen soluble copper catalysts early in this study. Our subsequent survey of a range of other metal complexes has confirmed that copper-based catalysts are superior to those catalysts which one normally associates with oxo-transfer processes.

Catalyst Development. We initially screened a variety of Cu(I) and Cu(II) salts and later compared their catalytic competency to that of other metal complexes which have been employed in both cyclopropanation[2,17] and epoxidation[1] reactions. All experiments were performed at 25 °C with 5–10 mol % catalyst in CH_2Cl_2 or MeCN containing 5 equiv of olefin and 1 equiv of PhI=NTs (eqs 12 and 13, Table 2). Metal complexes were



initially screened in the aziridination of styrene since this olefin affords good yields of product in the Mansuy experiments (eq 12, Table 2). The styrene studies were then followed up with the analogous experiments with cyclohexene (eq 13, Table 2), which was chosen as a representative aliphatic disubstituted olefin (*vide infra*). Unless specified, the catalyzed reaction of olefin and nitrene reagent, PhI=NTs, afforded the desired *N*-tosylaziridine along with benzenesulfonamide. In those instances where other side reactions such as allylic insertion were encountered, these reactions are specifically mentioned in the following discussion.

(17) Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssié, P. *J. Org. Chem.* **1980**, *45*, 695–702.

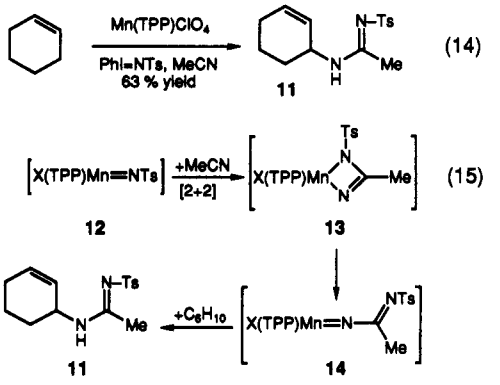
Styrene. Our results indicate that Cu(I) and Cu(II) salts are optimal for this substrate (entries 1–5), providing **9** in 56–95% yield. The cationic Cu(I) salts, $Cu(MeCN)_4ClO_4$ ($CuClO_4$)[18] and CuOTf·$^1/_2$PhH (CuOTf)[19] (Table 2, entries 1 and 2) were more efficient catalysts than the Cu(I) halides (entries 3 and 4). The use of $CuClO_4$ is preferred to CuOTf since it is more easily prepared and less air sensitive. We have also used $Cu(MeCN)_4PF_6$[18] as a catalyst in isolated cases. In contrast to olefin cyclopropanation, Cu(II) catalysts have been found to be competent in the aziridination reaction (entry 5). The use of Cu(II) salts as catalysts is particularly attractive as these complexes are both commercially available and air stable.

Among the selection of metal complexes screened, Mn(TPP)Cl, as expected, also proved to be a competent catalyst, (71% **9**, entry 7).[20] This result is to be contrasted with the lower yield obtained with the $Mn(OTf)_2$[21]-catalyzed process (31% **9**, entry 8). In contrast, the iron-derived complex Fe(TPP)Cl provided only a 31% yield of **9** (entry 9), whereas the $Fe(OTf)_2$ catalyst[22] afforded a 63% yield of aziridine (entry 10). It is evident from these four cases that no generalizations can be made between ligand architecture and catalytic efficiency in comparisons between Mn and Fe-derived catalysts.

$Co(OTf)_2$ afforded a moderate yield of the aziridine (entry 11). $Rh_2(OAc)_4$, which has previously been shown to be an effective catalyst for intramolecular nitrenoid insertions,[23] afforded a 48% yield of product (entry 12). The poor performance of this excellent cyclopropanation catalyst indicates that the aziridination ↔ cyclopropanation analogy does not extend to rhodium. Finally, $Rh(PPh_3)Cl$, $Ni(acac)_2$, $Ni(OTf)_2$,[21] and $Pd(acac)_2$ were all uniformly poor catalysts in the aziridination reaction, affording low yields of **9** after prolonged reaction times (entries 13–16).

Cyclohexene. The metal complexes listed in Table 2 were also screened against this less reactive olefin (eq 13), a substrate which also presents the opportunity for allylic insertion. In general, reactions carried out in CH_2Cl_2 afforded very low yields of aziridine **10**. Reactions performed in MeCN provided higher yields of aziridine, and consequently all metals were screened in this solvent. *For the metals listed in Table 2, the copper catalysts were unique in affording no competing allylic insertion.* As with styrene, the best catalysts for the reaction were copper salts with dissociable counterions (entries 1, 2, and 6).

The Mn(TPP)Cl and Fe(TPP)Cl catalysts afforded primarily insertion products with cyclohexene. In exploring the role of solvent with these catalysts, the mechanistically interesting insertion product **11** was produced in good yield (eq 14). A rationale for this transformation is presented below (eq 15).The



important step is suggested to involve solvent trapping of the

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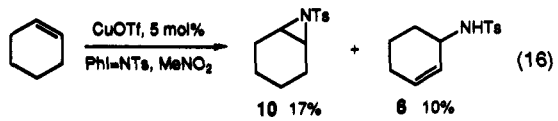
Table 3. Lewis Acid-Catalyzed Aziridination of *trans*-β-Methylstyrene (Eq 18)

entry	catalyst[a]	yield **17**, %[b]
1	SmI_2(O-*t*-Bu)	76[c]
2	$Sm(OTf)_3$	<5
3	$Mg(OTf)_2$	18
4	$Zn(OTf)_2$	21
5	$Sn(OTf)_2$	17

[a] All reactions were performed in MeCN at 25 °C with 5 mol % catalyst and 5 equiv of olefin. [b] Based on 1 equiv of PhI=NTs. [c] Isolated as a 9:1 mixture of *trans* and *cis* aziridines, respectively.

initially generated metal–imido intermediate **12**[24] and the subsequent **13** → **14** rearrangement prior to allylic insertion. This reaction affords a 63% yield of **11** when Mn(TPP)ClO_4 is used as catalyst (eq 14), in contrast to a 27% yield with Mn(TPP)Cl and a 41% yield with Fe(TPP)Cl. A mixture of aziridine (21%) and allylic insertion product **11** (20%) was also obtained when the $Fe(OTf)_2$ catalyst was employed (entry 10). A mixture of aziridination (5%) and insertion (6%) was also observed with $Mn(OTf)_2$ but in low overall yield (entry 8). The remainder of the metal complexes provided at best only traces of either aziridination or insertion products.

In general, copper catalysts exhibit a low propensity for C–H insertion. In the current study we have observed only two cases in which an insertion product was produced. The Cu(I)-catalyzed aziridination of cyclohexene in $MeNO_2$ provided a mixture of the aziridine **10** and the allylic sulfonamide **6** (eq 16), while the reaction of methyl cinnamyl ether catalyzed by $CuClO_4$ afforded the aziridine **15** in 31% yield as well as 20% of the imine **16** (eq 17). Presumably **16** arises from allylic insertion followed by elimination of MeOH. This reaction is metal-catalyzed although an analogous uncatalyzed C–H insertion adjacent to oxygen has been observed with tetrahydrofuran (*vide infra*).



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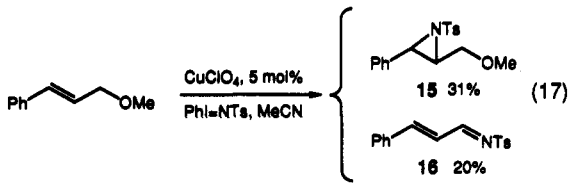
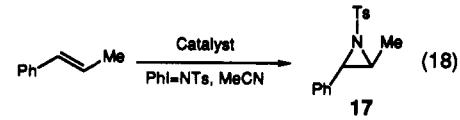


(17)

Lewis Acid Catalysis. During the initial phases of catalyst screening, the choice of metals was guided by epoxidation and cyclopropanation precedents which are generally believed to proceed through metal oxo and carbenoid intermediates, respectively. However, we have subsequently discovered that the reaction can be catalyzed to some extent by a variety of Lewis acids that are unlikely to participate in redox pathways.[25] Table 3 lists those metal complexes falling into this category that have been screened during the course of this study in the aziridination of *trans*-β-methylstyrene (eq 18).

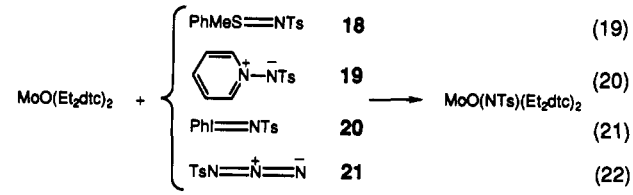


(18)

SmI_2(O-*t*-Bu)[26] (5 mol %) was found to be a good reaction catalyst, providing a 76% yield of the aziridine **17** (entry 1). The Lewis acid-catalyzed aziridinations proceeded in higher yield in MeCN than in CH_2Cl_2. Substantially lower yields were provided by the Mg(II), Zn(II), and Sn(II) triflate catalysts (entries 3–5). It came as a surprise that the reaction catalyzed by SmI_2(O-*t*-Bu) afforded, in addition to the expected *trans* adduct, some of the *cis* aziridine (*trans*/*cis* = 9). Circumstantial evidence that this contaminant was produced through a product isomerization pathway was provided by the following experiment. A sample of the pure *trans* aziridine which was treated with 5 mol % SmI_2(O-*t*-Bu) in MeCN (24 h, 25 °C) reproduced the observed 9:1 ratio of *trans* and *cis* aziridines. Independently, treatment of the pure *cis* aziridine under identical conditions failed to promote any isomerization. As SmI_2(O-*t*-Bu) proved to be an efficient catalyst of the reaction with *trans*-β-methylstyrene, it was screened against other olefins in order to determine the scope of the reaction. In the reaction of styrene, competitive olefin polymerization accounted for a low yield of aziridine (11%), while the analogous reaction with cyclohexene provided a 21% yield of the allylic insertion product **6**. Finally, electron-poor olefins are not good substrates for the reaction. For example, no aziridine was isolated from the attempted aziridination of *trans*-methyl cinnamate.

In summary, these Lewis acid catalysts, while raising intriguing questions with respect to mechanism, do not exhibit the efficiency and generality of copper catalysts (*vide infra*).

Nitrogen Atom Sources. Subsequent to catalyst screening, we examined alternative nitrogen atom-transfer reagents. In a recent report by Holm,[27] compounds **18–21** were found to function as imido group donors to *N,N*-diethyldithiocarbamate (Et_2dtc) complexes of molybdenum (eqs 19–22). As this was the most



(19)
(20)
(21)
(22)

comprehensive list of compounds reported to undergo imido group transfer, it provided a useful starting point for our study.[28] Compounds **18–21** were examined in the aziridination of styrene (100 equiv) using 5 mol % CuOTf. Among the illustrated nitrene precursors, PhI=NTs proved to be the best, providing a 96% yield of **9** in <5 min at 25 °C. No reaction occurred in the absence of catalyst. Tosyl azide (**21**) was less effective, affording only 12% of **9** after 12 h at 65 °C.[29] Finally, compounds **18** and **19** gave no reaction.

Solvent Effects. The copper-catalyzed aziridination of styrene with PhI=NTs provided excellent yields of aziridine **9** in both polar and nonpolar media. Under standard conditions, the reaction afforded the indicated yields of **9** in the following solvents: benzene (99%), CH_2Cl_2 (92%), $MeNO_2$ (90%), and MeCN (92%); however, these observations did not extend to other olefins. For less reactive substrates, both the reaction rate and the efficiency are enhanced when more polar solvents, such as MeCN and $MeNO_2$, are employed. In solvents of lower polarity such as CH_2Cl_2, the reactions are substantially slower and in

(20) The yields that we obtained for the aziridination of styrene with Mn(TPP)Cl and Fe(TPP)Cl are lower than those reported by Mansuy (ref 11a), who employed 100 equiv of styrene.

(21) Fujinaga, T.; Sakamoto, I. J. *Electroanal. Chem. Interfac. Electrochem.* **1976**, *73*, 235–246.

(22) Haynes, J. S.; Sams, J. R.; Thompson, R. C. *Can. J. Chem.* **1981**, *59*, 669–678.

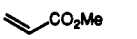
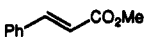
(23) Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1983**, 105, 6728–6729.

(24) Apparent [2 + 2] reactions of a zirconium nitrenoid with alkynes have been reported: Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729–8731.

(25) For studies of Lewis acid-catalyzed epoxidation of olefins employing iodosylbenzene, see: Yang, Y.; Diederich, F.; Valentine, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 7195–7205.

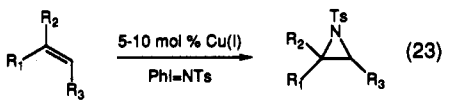
(26) Namy, J. L.; Souppe, J.; Collin, J.; Kagan, H. B. *J. Org. Chem.* **1984**, *49*, 2045–2049.

Table 4. Effect of Solvent on the Cu-Catalyzed Aziridination of Olefins (Eq 23)

entry	olefin[a]	yield,%[b] CH_2Cl_2	yield,%[b] MeCN
1		45	66
2		30	54
3		35	45
4		70	69

[a] All reactions were performed with 5–10 mol % $CuClO_4$ and 5 equiv of olefin at 25 °C. [b] Isolated yield of aziridine based on 1 equiv of PhI=NTs.

some cases provide moderately lower yields of products (eq 23, Table 4). For example, 1-hexene afforded a 45% yield of aziridine



(23)

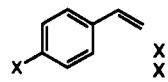
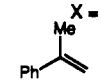
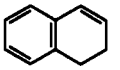
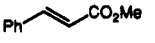
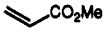
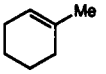
after 2 h at room temperature in CH_2Cl_2. In contrast, this same reaction when carried out in MeCN at 25 °C proceeded to completion within 5 min and gave a 66% yield of the derived aziridine (entry 1). Cyclohexene and methyl acrylate behaved similarly (entries 2–3). *trans*-Methyl cinnamate provided the same yield in the two solvents; however, the reaction rate was also significantly enhanced in MeCN (entry 4). Some solvents are incompatible with the reaction conditions. Not unexpectedly, hydroxylic solvents afford only *p*-tolylsulfonamide, presumably as a consequence of solvent trapping.[30] The oxidation of DMSO by PhI=NTs has been reported,[12] and we have found that PhI=NTs readily reacts with THF in the absence of metals to afford the α-insertion product.

The preceding results show that, with Cu(I) and Cu(II) complexes, acetonitrile is the optimal solvent for the the aziridination of a variety of olefins with PhI=NTs. In the following discussion, the scope of the process is explored.

Reaction Scope. The results obtained for the aziridination of a representative selection of olefins with $CuClO_4$, $Cu(acac)_2$, and $Cu(OTf)_2$ in MeCN are summarized in Table 5.[31] Under the "standard conditions" (MeCN, 5–10 mol % catalyst, 1 equiv of PhI=NTs, 5 equiv of olefin, 25 °C), good yields of aziridines were obtained from either electron-rich or electron-deficient olefins. PhI=NTs, like its oxygen analogue PhI=O,[32] is insoluble in a variety of solvents, including MeCN, and the course of the reaction may be followed by monitoring the dissolution of this reagent.

$CuClO_4$, rather than CuOTf, was utilized in this study due to its greater air stability and associated convenience in handling. $CuClO_4$ and $Cu(acac)_2$ afforded similar yields of aziridine

Table 5. Cu-Catalyzed Aziridination of Representative Olefins

entry	olefin[a]	catalyst	yield,%[b]
1	 X = H	$CuClO_4$	89
		$Cu(acac)_2$	95
		$Cu(OTf)_2$	92
	X = OMe	$CuClO_4$	78
	X = Me	$CuClO_4$	83
	X = Cl	$CuClO_4$	90
	X = NO_2	$CuClO_4$	89
2		$CuClO_4$	78
		$Cu(acac)_2$	72 (66)[c]
		$Cu(OTf)_2$	73
3		$CuClO_4$	71
		$Cu(acac)_2$	73
		$Cu(OTf)_2$	73
4		$CuClO_4$	69
		$Cu(acac)_2$	36
		$Cu(OTf)_2$	75
5		$CuClO_4$	45
		$Cu(acac)_2$	32
		$Cu(OTf)_2$	40
6		$CuClO_4$	90[d]
		$Cu(acac)_2$	95[d]
		$Cu(OTf)_2$	50[d]
7		$CuClO_4$	66
		$Cu(acac)_2$	39
		$Cu(OTf)_2$	62
8		$CuClO_4$	54 (77, -20 °C)
		$Cu(acac)_2$	30
		$Cu(OTf)_2$	60
9		$CuClO_4$	46 (66, -20 °C)
		$Cu(acac)_2$	32
		$Cu(OTf)_2$	51

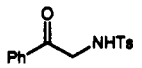
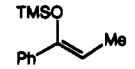
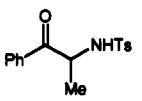
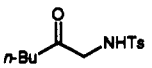
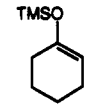
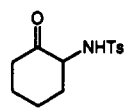
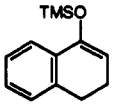
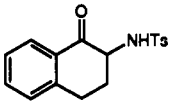
[a] All reactions were performed in MeCN with 5–10 mol % catalyst and 5 equiv of olefin at 25 °C unless otherwise noted. [b] Isolated yield of aziridine based on 1 equiv of PhI=NTs. [c] Value in parentheses for $Cu(acac)_2$ reaction carried out open to the air. [d] Three equivalents of olefin were used; the *exo* isomer was the exclusive product.

products for many olefins examined.[33] However, for those cases where $Cu(acac)_2$ is inferior, the utilization of $Cu(OTf)_2$ provided yields comparable to those obtained with $CuClO_4$. It appears that for reactive olefins, $Cu(acac)_2$ is as suitable in the reaction as $CuClO_4$, whereas for less reactive olefins, $Cu(acac)_2$ provides somewhat lower yields of aziridine. For these less reactive olefins, Cu(II) catalysts with dissociable counterions afford higher yields of aziridines. Although all reactions were initially performed under an atmosphere of nitrogen, this is an unnecessary precaution for $Cu(acac)_2$. For example, α-methylstyrene affords a 66% yield of aziridine when the reaction is carried out open to the air (entry 2).

The results listed in Table 5 indicate that mono-, di-, and trisubstituted olefins are aziridinated successfully in MeCN using $Cu(acac)_2$, $CuClO_4$, or $Cu(OTf)_2$ as catalysts. All phenyl-substituted olefins afford high yields of aziridines (entries 1–3). The low yield of the *p*-methoxystyrene-derived aziridine was due to decomposition of the product during isolation. α,β-Unsaturated esters such as *trans*-methyl cinnamate and methyl acrylate are also good substrates for the reaction (entries 4 and 5). When the following cinnamate esters were employed under the standard conditions using $CuClO_4$, the indicated yields were obtained: Me (69%, entry 4), *i*-Pr (67%), *t*-Bu (61%), Bn (62%), Ph (64%). These results indicate that competing C–H insertion adjacent to the alkyl oxygen moiety is not a problem (see eq 17). Not surprisingly, unsaturated ketones appear to be much less reactive; cyclohexenone provides only trace amounts of aziridination product. The copper-catalyzed aziridination of norbornene by PhI=NTs was found to provide the *exo* adduct in high yield

(27) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186–193.
(28) Preparations of imido group donors: (a) *S*-Methyl-*S*-phenyl-*N*-tosylsulfilimine. Tsujihara, K.; Furukawa, N.; Oae, K.; Oae, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2631–2635. (b) *N*-1-Pyridinium sulfonamidate. Balasubramian, A.; McIntosh, J. M.; Snieckus, V. *J. Org. Chem.* **1970**, *35*, 433–438. (c) (*N*-(*p*-Tolylsulfonyl)imino)phenyliodinane. See ref 12. (d) Tosyl azide. Doering, W. von E.; DePuy, C. H. *J. Am. Chem. Soc.* **1953**, *75*, 5955–5957.
(29) The decompostion of azides by transition metals to provide aziridines has been reported, although elevated temperatures are required and yields are low: (a) Reference 9. (b) Migita, T.; Chiba, M.; Takahashi, K.; Saitoh, N.; Nakaido, S.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3943–3944.
(30) The reaction of PhI=NTs catalyzed by cytochrome P-450 in MeOH has been shown to provide *p*-tolylsulfonamide: White, R. E. *Inorg. Chem.* **1987**, *26*, 3916–3919.
(31) CuOTf gave the same results as $Cu(MeCN)_4ClO_4$ for all olefins reported in Table 5.
(32) The existence of iodosylbenzene in a polymeric form, $(PhI{=}O)_n$, has been reported: Siebert, H.; Handrich, M. *Z. Anorg. Chem.* **1976**, *426*, 173.
(33) In our initial communication of these results (ref 13), some experiments had inadvertently been run with catalysts possessing a bis(oxazoline) ligand.

Table 6. Copper-Catalyzed Aziridination of Enol Silanes (Eq 25)

entry	enolsilane[a]	product	yield,%[b]
1			75
2			58[c]
3			70
4			64[d]
5			53[c]

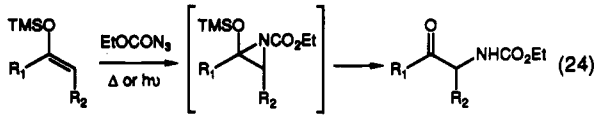
[a] All reactions were performed in MeCN with 5–10 mol % $CuClO_4$ and 1.5 equiv of enol silane at –20 °C unless otherwise indicated. [b] Isolated yield of α-amino ketone based on 1 equiv of PhI=NTs. [c] Reaction performed at 0 °C. [d] Reaction performed at –20 °C.

(>90%) with both $CuClO_4$ and $Cu(acac)_2$, although, surprisingly, the reaction provides a substantially lower yield with $Cu(OTf)_2$ (entry 6).[34]

The $CuClO_4$-catalyzed aziridination of alkyl-substituted olefins affords higher yields of aziridines when the reaction is carried out at lower temperatures (entries 8 and 9). For example, aziridination of cyclohexene at –20 °C gave a 77% yield of aziridine compared to the 54% yield obtained at room temperature.

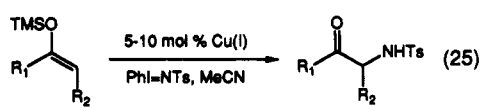
The use of excess olefin (5 equiv relative to PhI=NTs) is unnecessary if the reactions are run at relatively high concentrations. For example, when equimolar quantities of cyclohexene and PhI=NTs were employed at 1 M in MeCN with $CuClO_4$ as the catalyst, a 58% yield of the aziridine was obtained at 25 °C, while at –20 °C, a 69% yield could be obtained. Under the same conditions at 25 °C, 1-methylcyclohexene provided a 45% yield of the corresponding aziridine.

Amination of Enol Silanes. The direct amination of enol silanes in 35–60% yields[35]p and silyl ketene acetals in 21–38% yields[36] by either thermolysis or photolysis of azidoformates has been reported (eq 24).



(24)

As an extension of the present study, we have evaluated this reaction as an approach to the synthesis of α-amino acids and ketones (eq 25, Table 6). All of the reactions were carried out



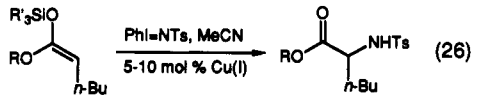
(25)

in MeCN at either 0 or –20 °C with 5–10 mol % $CuClO_4$, 1 equiv of PhI=NTs, and 1.5 equiv of enol silane,[37] conditions which provide the α-amino ketones in 53–75% yield based on nitrene precursor as the limiting reagent.

A comparison of the Cu(I) and Cu(II) catalysts using 1-trimethylsilyloxy)cyclohexene at room temperature showed that with $Cu(acac)_2$ the derived α-amino ketone could be obtained in 35% yield, while $CuClO_4$ afforded a 47% yield of the expected product at the same temperature. The major side reaction observed in these aziridinations is the substrate oxidation product cyclohexenone. In view of the the greater nucleophilicity of these enol ethers, it is reasonable to speculate that metal catalysis might be unnecessary. However, in the absence of catalyst, 1-((trimethylsilyl)oxy)cyclohexene reacted very slowly in the presence of PhI=NTs and provided none of the expected α-amino ketone adduct.

The influence of the silyl moiety on reaction yields was also evaluated. The $CuClO_4$ catalyzed amination of 1-((*tert*-butyldimethylsilyl)oxy)cyclohexene with PhI=NTs in MeCN at –20° C gave a 65% yield of the α-amino ketone, which was comparable to the 64% yield obtained when the trimethylsilyl protecting group was employed (Table 6, entry 4).

The copper-catalyzed amination of silylketene acetals has also been examined (eq 26, Table 7).[38] All reactions were carried out



(26)

in MeCN at 25 °C or –20 °C with 5–10 mol % $CuClO_4$, 1 equiv of PhI=NTs, and 1.5 equiv of substrate and provided the corresponding *N*-(*p*-tolylsulfonyl)-α-amino esters in the indicated yields. The yield of the reaction varied depending on the ester and silyl groups employed. When the trimethylsilylketene acetal derived from phenyl hexanoate was employed, a 50% yield of product was obtained (entry 2), which was significantly greater than the 10% yield afforded by the analogous derivative of methyl hexanoate (entry 1). (Trimethylsilyl)- and (*tert*-butyldimethylsilyl)ketene acetals afforded similar yields of α-amino esters (entries 2 and 3), while no reaction was observed with a (phenyldimethylsilyl)ketene acetal (entry 4). A control experiment indicated that the uncatalyzed reaction between silylketene acetals and PhI=NTs is slow and provides no α-tosylamino ester products. We thus conclude that the enol amination of silylketene acetals under these conditions does not represent a practical approach to the synthesis of α-amino esters.

Table 7. Cu-Catalyzed Aziridination of Silylketene Acetals (Eq 26)

entry	R	R'_3	yield, %[b]
1	Me	Me_3	27 (10)[c]
2	Ph	Me_3	43 (50)[c]
3	Ph	*t*-$BuMe_2$	45
4	Ph	$PhMe_2$	0

[a] All reactions were performed in MeCN with 5–10 mol % $CuClO_4$ and 1.5 equiv of silylketene acetal at 25 °C unless otherwise noted. [b] Isolated yield of α-amino ester based on 1 equiv of PhI=NTs. [c] Values in parentheses for reactions performed at –20 °C.

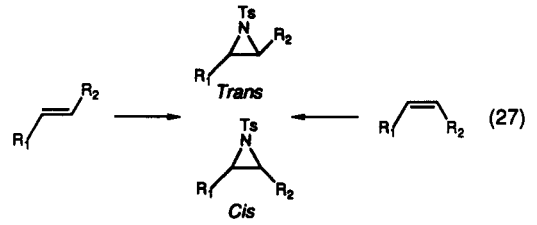
Observations Pertaining to Mechanism

Reaction Stereospecificity. The issue of reaction stereospecificity was addressed in the aziridination of *cis* and *trans* 1,2-disubstituted olefins (eq 27, Table 8). All *trans* 1,2-disubstituted olefins gave the derived *trans* 2,3-disubstituted aziridines in high yields (entries 1, 3, and 5). On the other hand, the aziridination of *cis*-stilbene was not stereospecific (entry 2). At 0 °C, the $CuClO_4$-catalyzed reaction provided a 73% yield of a 83:17 *cis/trans* ratio of 2,3-diphenylaziridines, while the same reaction at –20 °C afforded an 80% yield of an improved 90:10 *cis/trans* product ratio. When $Cu(acac)_2$ was employed as the catalyst at 25 °C, a 54% yield of a 40:60 *cis/trans* ratio of aziridines was

(34) The *exo* adduct was assigned by comparison to spectral data previously reported for the phenylsulfonyl adduct: Franz, J. E.; Osuch, C.; Dietrich, M. W. *J. Org. Chem.* **1964**, *29*, 2922–2927.

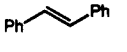
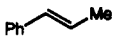
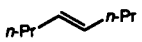
(35) Lociuro, S.; Pellacani, L.; Tardella, P. A. *Tetrahedron Lett.* **1983**, *24*, 593–596.

(36) Cipollone, A.; Loreto, M. A.; Pellacani, L.; Tardella, P. A. *J. Org. Chem.* **1987**, *52*, 2584–2586.



obtained. When $Cu(OTf)_2$ was utilized at −20 °C, the reaction provided a 67% yield of a 90:10 *cis/trans* ratio of aziridines. These results are to be contrasted with the Mn(TPP)Cl- or Fe(TPP)-Cl-catalyzed aziridination of *cis*-stilbene, which affords exclusively *trans*-2,3-diphenylaziridine.[11c]

Table 8. Aziridination of *Cis* and *Trans* Disubstituted Olefins (Eq 27)

entry	olefin[a]	catalyst	temp,°C	aziridine trans : cis[b]	yield,%[c,d]
1		$CuClO_4$	25	>95 : 5	56[e]
		$Cu(acac)_2$	25	>95 : 5	50[e]
2		$CuClO_4$	0	17 : 83	73
		$CuClO_4$	-20	10 : 90	80
		$Cu(acac)_2$	25	60 : 40	54
		$Cu(OTf)_2$	-20	10 : 90	67
3		$CuClO_4$	25	>95 : 5	81
		$Cu(acac)_2$	25	>95 : 5	75
4		$CuClO_4$	25	7 : 93	87
		$CuClO_4$	-20	7 : 93	89
		$Cu(acac)_2$	25	74 : 26	64
		$Cu(ClO_4)_2$	25	<5 : 95[f]	76
		$CuBr_2$	25	70 : 30	40
5		$CuClO_4$	-20	>95 : 5	64
6		$CuClO_4$	-20	<5 : 95[e]	78

[a] All reactions were performed in MeCN with 5–10 mol % catalyst and 5 equiv of olefin unless otherwise noted. [b] Ratios determined by 500-MHz NMR. [c] Isolated yield of aziridine based on 1 equiv of PhI=NTs. [d] For the *cis*-olefins the yields reported are for the *cis* and *trans* disubstituted aziridines combined. [e] Reaction performed in CH_2Cl_2. [f] No *trans* aziridine detected by 500-MHz NMR.

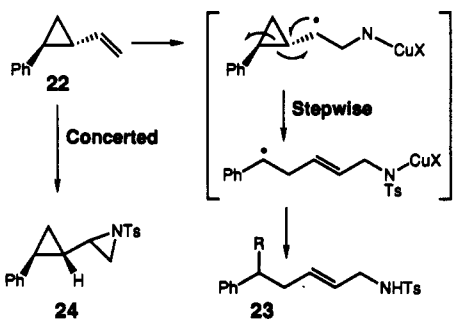
The aziridination of *cis*-β-methylstyrene[39] afforded varying ratios of *cis* and *trans* aziridines depending on the nature of the copper catalyst employed (Table 8, entry 4). At −20 °C, $CuClO_4$ gave an 89% yield of a 93:7 *cis/trans* ratio of aziridines. With Cu(II) catalysts, the reaction selectivity was dependent on the nature of the ligand. With $Cu(ClO_4)_2$, the reaction exhibited apparent stereospecificity, giving a 76% yield of the *cis* aziridine uncontaminated by its *trans* diastereomer. However, reactions catalyzed by $CuBr_2$ and $Cu(acac)_2$ afforded predominantly the *trans* adduct. Examination of recovered β-methylstyrene from reactions run to partial conversion showed that, for the $CuClO_4$-(−20 °C) and $Cu(ClO_4)_2$-catalyzed (−20 °C) processes, no loss of olefin geometry occurred (Table 9). However, those reactions catalyzed by $Cu(acac)_2$ and $CuBr_2$ exhibited 3–5% loss of olefin stereochemistry (entries 3 and 5). In the absence of PhI=NTs, no isomerization of *cis*-β-methylstyrene was observed with either Cu(I) or Cu(II) catalysts. Furthermore, no isomerization of *cis*-*N*-(*p*-tolylsulfonyl)-2-methyl-3-phenylaziridine was observed when it was stirred with $CuClO_4$ or $Cu(acac)_2$ in MeCN at room temperature.

Table 9. Stereochemistry of Recovered *cis*-β-Methylstyrene

olefin[a]	entry	catalyst	temp,°C	olefin trans : cis[b]
 1 : 99	1	$CuClO_4$	25	4 : 96
	2	$CuClO_4$	-20	1 : 99
	3	$Cu(acac)_2$	25	3 : 97
	4	$Cu(ClO_4)_2$	25	1 : 99
	5	$CuBr_2$	25	5 : 95

[a] All reactions were performed in CH_3CN with 5–10 mol % catalyst and 1 equiv of PhI=NTs. [b] Ratios were determined by capillary GLC.

Scheme 1



Phenyl substitution on the olefin seems to alter the process from a stereospecific to a nonstereospecific reaction manifold. This point is highlighted by the observation that the $CuClO_4$-catalyzed aziridination of *cis*-4-octene by PhI=NTs was stereospecific, providing exclusively the *cis*-di-*n*-propylaziridine in 78% yield (Table 8, entry 6). On the other hand, in the aziridination of *cis*-stilbene ($CuClO_4$, 0 °C) the *trans* aziridine is formed to a moderate extent (*trans/cis* = 17:83). If the reaction proceeds through a charged intermediate, during the reaction of styrene one would expect charge accumulation at the benzylic position. Accordingly, the relative rates of aziridination of styrene and *p*-nitrostyrene were determined (5 equiv of each olefin, 8 mol % $CuClO_4$, 1 equiv of PhI=NTs, 25 °C) in both MeCN and CH_2Cl_2. In MeCN, styrene is only 1.4 times as reactive as *p*-nitrostyrene, while in CH_2Cl_2, the rate difference is only 1.1. It is thus concluded that the intervention-charged intermediates in this process is unlikely.

For unfunctionalized alkyl-substituted olefins such as *cis*-4-octene (Table 8, entry 6), the observed stereospecificity of the reaction supports a concerted mechanism. However, a stepwise process in which the rate of ring closure is fast relative to the rate of C–C bond rotation is also possible. To probe for the possible intermediacy of radical intermediates in alkyl-substituted olefins, we examined the aziridination of *trans*-2-phenyl-1-vinylcyclopropane (**22**)[40,41] to determine whether any radical intermediates might be intercepted through cyclopropylcarbinyl rearrangement (Scheme 1).[42] The aziridination of **22** (1 equiv of PhI=NTs, MeCN, 25 °C) using the $CuClO_4$ catalyst afforded, in addition to aziridines **24** (43%) and recovered starting material, no products derived from cyclopropyl ring-opening based on analysis of the unpurified reaction mixture.[43] The formation of **24** in conjunction with the absence of rearrangement products provides added support for the concerted mechanism for the aziridination of alkyl-substituted olefins. This conclusion is consistent with our

(37) Enolsilanes were prepared from the corresponding ketones according to the reported procedure: House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324–2336.

(38) Silyl ketene acetals were synthesized from the corresponding esters according to the reported procedures: (a) Ainsworth, C.; Chen, F.; Kuo, Y.-N. *J. Organomet. Chem.* **1972**, *46*, 59–71. (b) Slougui, N.; Rousseau, G.; Conia, J. M. *Synthesis* **1982**, 58–60. (b) Slougui, N.; Rousseau, G. *Synth. Commun.* **1987**, *17*, 1–11.

(39) Davies, D. E.; Gilchrist, T. L.; Roberts, T. G. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1275–1281.

(40) (a) Marvell, E. N.; Lin, C. *J. Am. Chem. Soc.* **1978**, *100*, 877–883. (b) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042–4053.

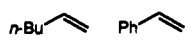
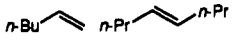
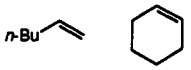
(41) (a) Fu, H.; Look, G. C.; Zhang, W.; Jacobsen, E. N.; Wong, C.-H. *J. Org. Chem.* **1991**, *56*, 6497–6500. (b) Feldman, K. S.; Ruckle, R. E., Jr.; Romanelli, A. L. *Tetrahedron Lett.* **1989**, *30*, 5845–5848. (c) Feldman, K. S.; Simpson, R. E. *Tetrahedron Lett.* **1989**, *30*, 6985–6988. (d) Feldman, K. S.; Simpson, R. E. *J. Am. Chem. Soc.* **1989**, *111*, 4878–4886.

(42) (a) He, G.-X.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 2747–2753. (b) Newcomb, M.; Manek, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 9662–9663.

observation that *cis* disubstituted olefins such as *cis*-4-octene are transformed to the derived *N*-tosylaziridine without detectable isomerization.

Competition Experiments. Competition experiments were carried out to assess relative olefin reactivity with both Cu(I) and Cu(II) catalysts. If the two catalyst oxidation states are maintained during the course of the reaction, one might anticipate that Cu(I) catalysts, which coordinate well with olefins,[20a] might exhibit a different selectivity profile than Cu(II) catalysts, which show a low tendency to coordinate olefins except under special circumstances.[44] The results of the study are presented in Table 10. All reactions were carried out under identical conditions (MeCN, 5–10 mol % catalyst, 1 equiv of PhI=NTs and 5 equiv of each olefin at −20 °C). Two conclusions may be drawn from the data. First, the modest difference in reactivity between styrene and 1-hexene (entry 1) is again inconsistent with the intervention of polar intermediates during the aziridination process. Second, the comparable selectivity profiles for the three olefin pairs for Cu(I) and Cu(II) catalysts suggests that a common catalyst oxidation state is being accessed in both instances.

Table 10. Relative Olefin Reactivity with Various Cu Catalysts[a]

entry	olefin A	olefin B	ratio, olefin B/olefin A		
			$CuClO_4$	CuOTf	$Cu(OTf)_2$
1			5	5	5
2			2	1.5	1.5
3			7	6	6

[a] All reactions were performed in MeCN with 5–10 mol % catalyst and 5 equiv of each olefin at −20 °C. Ratios were determined by capillary GLC using internal standards.

Catalyst Oxidation State. The preceding experiments provide strong circumstantial evidence for a common catalyst oxidation state irrespective of the oxidation state of the copper complex employed. *In view of the fact that iodine(III) reagents are oxidants, it is reasonable to conclude that these reactions are being catalyzed through Cu(II) rather than Cu(I) as originally presumed.* Supporting evidence that PhI=NTs will promote catalyst oxidation was obtained with the chiral complex derived from CuOTf and the bis(oxazoline) ligand **7**. When an acetonitrile solution of this ligand and CuOTf was treated with PhI=NTs, the solution became green. The UV–vis spectrum of this solution is nearly indistinguishable from a spectrum of a solution of $Cu(OTf)_2$ complexed with this bis(oxazoline) ligand in the same solvent. It thus appears that a similar catalytically active metal complex is accessible from either oxidation state, at least in MeCN at 25 °C. In spite of these observations, it is not clear whether the 2+ oxidation state of the catalyst is being accessed at low temperature (−78 °C) and in less polar solvents, conditions reported by Jacobsen in his asymmetric aziridination study.[14a]

Conclusions

This study has demonstrated that soluble Cu(I) and Cu(II) complexes are the most efficient catalysts yet discovered for olefin aziridination using PhI=NTs. With these catalysts, the reaction scope has been significantly extended to include both electron-rich and electron-deficient olefins. Solvent optimization studies have also contributed significantly to both yield improvement and rate acceleration, and the polar aprotic solvent MeCN appears to be the optimal choice for preparative reactions. Examination of *cis* and *trans* disubstituted olefins reveals that the derived aziridination reactions can be rendered either highly stereoselective or stereospecific with the proper choice of catalyst. These results should be contrasted to previous observations that aziridination of *cis*-stilbene catalyzed by Fe(TPP)Cl affords exclusively *trans*-2,3-diphenylaziridine.[11c]

The intervention of radical intermediates through cyclopropyl-based radical traps was probed, and results obtained with *trans*-2-phenyl-1-vinylcyclopropane support a concerted process for unfunctionalized alkyl-substituted olefins.

Experimental Section

General. Infrared spectra were recorded on a Nicolet 5SX or 5PC FT-IR spectrometer. ^1H NMR spectra were recorded on Bruker AM-500 (500 MHz) and AM-400 (400 MHz) spectrometers at ambient temperature. Data are reported as follows: chemical shift in ppm from internal standard tetramethylsilane on the δ scale, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, coupling constant (Hz), and assignment. ^{13}C NMR were recorded on Bruker AM-500 (126 MHz) and AM-400 (101 MHz) spectrometers at ambient temperature. Chemical shifts are reported in ppm from tetramethylsilane on the δ scale, with the solvent resonance employed as the internal standard (deuteriochloroform at 77.0 ppm, DMSO-d_6 at 39.5 ppm and benzene-d_6 at 128.5 ppm). Combustion analyses were performed by Spang Microanalytical Laboratory (Eagle Harbor, MI) and Galbraith Microanalytical Laboratory (Knoxville, TN). High-resolution mass spectra were obtained on Jeol AX-505 or SX-102 spectrometers in the Harvard University Mass Spectrometry Laboratory. Analytical thin-layer chromatography was performed on EM Reagent 0.25-mm silica gel 60-F plates. Visualization was accomplished with UV light and aqueous ceric ammonium molybdate solution followed by heating. Purification of reaction products was carried out by medium-pressure liquid chromatography using Michel-Miller columns (Ace Glass, Inc.) dry-packed with 230–400 mesh silica gel or by conventional flash column chromatography.[45] All reactions were carried out under an atmosphere of nitrogen in glassware that had been flame-dried under a stream of nitrogen. When necessary, solvents and reagents were purified prior to use. Dichloromethane and acetonitrile were distilled from calcium hydride under nitrogen. $CuClO_4$[18] and CuOTf[19] were handled in the drybox under an atmosphere of nitrogen. $Cu(OTf)_2$ and $Cu(acac)_2$ were purchased from the Aldrich Chemical Co. All olefins were distilled prior to use.

Representative Experimental Details for the Aziridination Reaction Catalyzed by $Cu(acac)_2$. $Cu(acac)_2$ (10 mol %) was added to a suspension of the olefin (5 equiv) and PhI=NTs (1 equiv) in 10 mL of MeCN at room temperature. When all the PhI=NTs had been drawn into solution, the reaction was filtered through a plug of silica with EtOAc as eluent. The solvent was removed *in vacuo* to give an oil that was purified by MPLC or flash column chromatography.

Representative Experimental Details for the Aziridination Reaction Catalyzed by $Cu(MeCN)_4ClO_4$. $Cu(MeCN)_4ClO_4$ (5–10 mol %) in 5 mL of MeCN was added under nitrogen to a suspension of olefin (5 equiv) and PhI=NTs (1 equiv) in 5 mL of MeCN. When all the PhI=NTs had been drawn into solution, the reaction was filtered through a plug of silica with 200 mL of EtOAc as eluent. The solvent was removed *in vacuo* to give an oil that was purified by MPLC or flash column chromatography.

Representative Experimental Details for the Aziridination Reaction Catalyzed by $Cu(OTf)_2$. To $Cu(OTf)_2$ (5–10 mol %) in 5 mL of MeCN under nitrogen were added olefin (5 equiv) and PhI=NTs (1 equiv) under a flow of N_2. When all the PhI=NTs had been drawn into solution, the reaction was filtered through a plug of silica with 50 mL of EtOAc as eluent. The solvent was removed *in vacuo* to give an oil that was purified by MPLC or flash column chromatography.

Competition Experiments. The competition experiments were carried out according to the general procedure. When complete, the reactions were filtered through a plug of silica and the ratios determined quantitatively by capillary GLC (DB-1, 4 psi, 200 °C) employing *n*-docosane as the internal standard. The relative retention times of the

(43) One of the referees has suggested that, one must consider that copper(II) will oxidize carbon radicals with ligand transfer at diffusion controlled rates (Kochi). Thus failure to see ring-opened products may just reflect a kinetic victory for the three-membered ring closure to give the aziridine even in the face of the so-called hypersensitive radical probe. The authors concur with this qualification to the radical trapping experiments illustrated in Scheme 1.

(44) Zelonka, R. A.; Baird, M. C. *J. Organomet. Chem.* **1971**, *33*, 267–272.

(45) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

products are as follows: *N*-(*p*-tolylsulfonyl)-2-*n*-butylaziridine (t_RR*t* = 5.2 min); *N*-(*p*-tolylsulfonyl)-2-phenylaziridine (t_R = 10.9 min); *trans*-*N*-(*p*-tolylsulfonyl)-2,3-di-*n*-propylaziridine (t_R = 6.5 min); *N*-(*p*-tolylsulfonyl)-7-azabicyclo[4.1.0]heptane (t_R = 6.5 min).

***N*-(*p*-Tolylsulfonyl)-2-phenylaziridine (9).** The general procedure was followed using 103 mg (0.276 mmol) of PhI=NTs, 5.0 mg (0.014 mmol) of $Cu(OTf)_2$, and 0.160 mL (0.145 g, 1.40 mmol) of styrene in 1 mL of MeCN. Reaction time: 1 h at room temperature. Flash column chromatography (2- × 18-cm silica, 4:1 hexane/EtOAc) afforded 69 mg (92%) of the aziridine as a crystalline solid: mp 88–89 °C (lit. mp 88–89 °C);[46] TLC R_f 0.62 (2:1 hexane:EtOAc); IR ($CHCl_3$) 3017, 1327, 1217, 1161, 916, 783, 769, 715, 696, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.27 (m, 7H, Ar-*H*), 3.77 (dd, 1H, J_{cis} = 7.2 Hz, J_{trans} = 4.5 Hz, C*H*Ph), 2.98 (d, 1H, J = 7.8 Hz, *cis*-C*H*-aziridine), 2.43 (s, 3H, Ar-Me), 2.38 (d, 1H, J = 4.4 Hz, *trans*-C*H*-aziridine); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 144.5, 134.9, 129.6, 128.4, 128.1, 127.8, 126.4, 40.9, 35.7, 21.4; HRMS (FAB, MNBA) exact mass calcd for $C_{15}H_{15}NO_2S$ (M + H)$^+$ 274.0902, found 274.0916. Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12. Found: C, 65.79; H, 5.46; N, 5.08.

***N*-(*p*-Tolylsulfonyl)-2-(*p*-methoxyphenyl)aziridine.** The general procedure was followed using 600 mg (1.60 mmol) of PhI=NTs, 33 mg (0.089 mmol) of $Cu(MeCN)_4ClO_4$, and 0.32 mL (0.32 g, 2.4 mmol) of *p*-methoxystyrene. Reaction time: 15 min at room temperature. Direct crystallization of the product aziridine from the reaction mixture using hexane:EtOAc as solvent provided 254 mg (54%) of aziridine, and an additonal 127 mg (26%) of product was obtained by flash chromatography (SiO_2, 2 × 16 cm^2, 4:1:0.2 hexane:EtOAc:Et_3N). Overall yield 381 mg (78%) of aziridine as a white crystalline solid: mp 87–88 °C; TLC R_f 0.4 (4:1 hexane:EtOAc); IR (CH_2Cl_2) 3056, 3002, 2960, 2838, 1614, 1600, 1515, 1460, 1380, 1322, 1304, 1246, 1158, 1092, 1030, 910, 832, 811, 689, 665, 656 cm^{-1}; ^{1}H NMR (benzene-d_6, 500 MHz) δ 7.94 (d, 2H, J = 8.3 Hz, Ar-*H*), 6.94 (d, 2H, J = 8.6 Hz, Ar-*H*), 6.75 (d, 2H, J = 8.0 Hz, Ar-*H*), 6.64 (d, 2H, J = 8.7 Hz, Ar-*H*), 3.77 (dd, 1H, J_{cis} = 4.4 Hz, J_{trans} = 7.1 Hz, C*H*Ph-aziridine), 3.24 (s, 3H, OCH_3), 2.79 (d, 1H, J = 7.1 Hz, *trans*-C*H*-aziridine), 1.93 (d, 1H, J = 4.4 Hz, *cis*-C*H*-aziridine), 1.84 (s, 3H, Ar-CH_3); ^{13}C NMR (benzene-d_6, 126 MHz) δ 160.1, 151.3, 144.0, 136.8, 129.7, 128.2, 127.8, 114.3, 54.8, 41.0, 35.6, 21.1.

***N*-(*p*-Tolylsulfonyl)-2-(*p*-methylphenyl)aziridine.** The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 16 mg (0.043 mmol) of $Cu(MeCN)_4ClO_4$ and 0.44 mL (0.39 g, 3.3 mmol) of *p*-methylstyrene. Reaction time: 1 h at room temperature. MPLC purification was carried out by elution with hexane:EtOAc (6:1) to give 159 mg (83%) of aziridine as a white crystalline solid: mp 136–137 °C; TLC R_f 0.28 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3034, 1600, 1516, 1380, 1322, 1158, 1092, 1018, 978, 911, 814, 716, 708, 692, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.86 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.31 (d, 2H, J = 7.9 Hz, Ar-*H*), 7.09 (s, 4H, Ar-*H*), 3.73 (dd, 1H, J_{cis} = 7.2 Hz, J_{trans} = 4.5 Hz, C*H*Ph-aziridine), 2.96 (d, 1H, J = 7.2 Hz, *cis*-C*H*-aziridine), 2.42 (s, 3H, Ar-CH_3), 2.36 (d, 1H, J = 4.5 Hz, *trans*-C*H*-aziridine), 2.3 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 144.4, 138.0, 135.1, 132.0, 129.6, 129.1, 127.8, 126.4, 41.0, 35.6, 21.5, 21.0; HRMS (FAB, MNBA) exact mass calcd for $C_{16}H_{17}NO_2S$ (M + Na)$^+$ 310.0878, found 310.0894.

***N*-(*p*-Tolylsulfonyl)-2-(*p*-chlorophenyl)aziridine.** The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 20 mg (0.054 mmol) of $Cu(MeCN)_4ClO_4$, and 0.40 mL (0.46 g, 3.3 mmol) of *p*-chlorostyrene. Reaction time: 1 h at room temperature. MPLC purification was carried out by elution with hexane:EtOAc (6:1) to give 186 mg (90%) of aziridine as a white crystalline solid: mp 115–116 °C; TLC R_f 0.25 (4:1 hexane:EtOAc); IR (CH_2Cl_2) 3056, 1600, 1494, 1462, 1376, 1325, 1185, 1160, 1190, 1014, 980, 908, 812, 688, 667 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.85 (d, 2H, J = 8.2 Hz, Ar-*H*), 7.33 (d, 2H, J = 8.1 Hz, Ar-*H*), 7.26 (d, 2H, J = 8.4 Hz, Ar-*H*), 7.15 (d, 2H, J = 8.4 Hz, Ar-*H*), 3.73 (dd, 1H, J_{cis} = 7.1 Hz, J_{trans} = 4.3 Hz, C*H*Ph-aziridine), 2.97 (d, 1H, J = 7.1 Hz, *trans*-C*H*-aziridine), 2.44 (s, 3H, Ar-CH_3), 2.34 (d, 1H, J = 4.3 Hz, C*H*-aziridine); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 144.8, 134.8, 134.2, 133.6, 129.8, 128.7, 127.9, 127.8, 40.2, 36.0, 21.6; HRMS (FAB, MNBA) exact mass calcd for $C_{15}H_{14}ClNO_2S$ (M + H)$^+$ 308.0512, found 308.0516. Anal. Calcd for $C_{15}H_{14}ClNO_2S$: C, 58.53; H, 4.58; N, 4.55. Found: C, 58.15; H, 4.64; N, 4.39.

***N*-(*p*-Tolylsulfonyl)-2-(*p*-nitrophenyl)aziridine.** The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 17 mg (0.046 mmol) of $Cu(MeCN)_4ClO_4$, and 0.50 g (3.3 mmol) of *p*-nitrostyrene.[47] Reaction time: 2 h at room temperature. MPLC purification was carried out by elution with hexane:EtOAc (6:1) to give 190 mg (89%) of aziridine as a white crystalline solid: mp 116–117 °C; TLC R_f 0.13 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3028, 1606, 1624, 1346, 1330, 1186, 1160, 1112, 1092, 980, 908, 854, 812, 715, 688, 659 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.16 (d, 2H, J = 8.6 Hz, Ar-*H*), 7.87 (d, 2H, J = 8.2 Hz, Ar-*H*), 7.40 (d, 2H, J = 8.7 Hz, Ar-*H*), 7.35 (d, 2H, J = 8.3 Hz, Ar-*H*), 3.84 (dd, 1H, J_{cis} = 4.4 Hz, J_{trans} = 7.3 Hz, C*H*Ph-aziridine), 3.05 (d, 1H, J_{trans} = 7.3 Hz, *trans*-C*H*-aziridine), 2.44 (s, 3H, Ar-CH_3), 2.37 (d, 1H, J = 4.4 Hz, *cis*-C*H*-aziridine); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 147.7, 145.1, 142.4, 134.3, 129.8, 127.9, 127.4, 123.7, 39.6, 36.4, 21.6; HRMS (FAB, MNBA) exact mass calcd for $C_{15}H_{14}N_2O_4S$ (M + H)$^+$ 319.0752, found 319.0761. Anal. Calcd for $C_{15}H_{14}N_2O_4S$: C, 56.59; H, 4.43; N, 8.80. Found: C, 56.51; H, 4.46; N, 8.64.

***trans*-*N*-(*p*-Tolylsulfonyl)-2,3-diphenylaziridine.** The general procedure was followed with the exception of the use of 5 mL of CH_2Cl_2 as solvent. The reaction was run using 400 mg (1.07 mmol) of PhI=NTs, 18 mg (0.055 mmol) of $Cu(MeCN)_4ClO_4$, and 0.965 g (5.35 mmol) of *trans*-stilbene. Reaction time: 2 h at room temperature. Flash column chromatography (3 × 18-cm silica, 1:1 hexane/CH_2Cl_2) afforded 210 mg (56%) of *trans*-aziridine as a white crystalline solid: mp 139–139 °C (lit.[46] mp 139 °C; TLC R_f 0.19 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3031, 3019, 1327, 1306, 1215, 1161, 1088, 930, 910, 814, 745, 741, 708, 698, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.62 (d, 2H, J = 8.2 Hz, Ar-*H*), 7.42–7.32 (m, 10H, Ar-*H*), 7.19 (d, 2H, J = 8.2 Hz, Ar-*H*), 4.26 (s, 2H, C*H*-aziridine), 2.38 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 143.9, 137.0, 133.0, 129.4, 128.7, 128.4, 128.3, 127.5, 50.3, 21.5; HRMS (FAB, MNBA) exact mass calcd for $C_{21}H_{19}NO_2S$ (M + H)$^+$ 350.1215, found 350.1222. Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found: C, 71.90; H, 5.57; N, 4.02.

***cis*-*N*-(*p*-Tolylsulfonyl)-2,3-diphenylaziridine.** The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 18 mg (0.048 mmol) of $Cu(MeCN)_4ClO_4$, and 0.60 mL (0.60 g, 3.3 mmol) of *cis*-stilbene. Reaction time: 3 h at −20 °C. MPLC purification was carried out by elution with hexane:EtOAc (6:1) to give 187 mg (80%) of *cis* and *trans* aziridines in a 9.0:1.0 ratio as determined by 500-MHz ^{1}H NMR. The aziridines can be separated by MPLC gradient elution with hexane:CH_2Cl_2 (2:1) to hexane:CH_2Cl_2 (1:1): mp 155–156 °C; TLC R_f 0.19 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3034, 1599, 1495, 1329, 1306, 1186, 1161, 1092, 1026, 909, 814, 801, 698, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (d, 2H, J = 8.1 Hz, Ar-*H*), 7.35 (d, 2H, J = 8.1 Hz, Ar-*H*), 7.11–7.03 (m, 10H, Ar-*H*), 4.22 (s, 2H, C*H*-aziridine), 2.43 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 144.7, 134.9, 132.0, 129.8, 128.0, 127.9, 127.8, 127.7, 47.4, 21.6; HRMS (FAB, MNBA) exact mass calcd for $C_{21}H_{19}NO_2S$ (M + H)$^+$ 350.1215, found 350.1213. Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found: C, 72.29; H, 5.34; N, 4.14.

***trans*-*N*-(*p*-Tolylsulfonyl)-2-methyl-3-phenylaziridine (18).** The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 19 mg (0.051 mmol) of $Cu(MeCN)_4ClO_4$, and 0.40 mL (0.40 g, 3.3 mmol) of *trans*-β-methylstyrene. Reaction time: 1.5 h at room temperature. MPLC purification was carried out by elution with hexane:EtOAc (6:1) to give 156 mg (81%) of aziridine as a white cyrstalline solid: mp 72–74 °C; TLC R_f 0.25 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3031, 1458, 1321, 1306, 1291, 1217, 1159, 1090, 1038, 974, 891, 814, 772, 743, 710, 698, 687, 667 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.26–7.20 (m, 5H, Ar-*H*), 7.13 (d, 2H, J = 7.9 Hz, Ar-*H*), 3.79 (d, 1H, J = 4.3 Hz, C*H*Ph), 2.9 (dq, 1H, J = 6.0, 4.4 Hz, C*H*CH_3), 2.37 (s, 3H, Ar-CH_3), 1.83 (d, 3H, J = 6.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 143.8, 137.9, 135.5, 129.5, 128.4, 128.0, 127.1, 126.2, 49.1, 21.5, 14.1; HRMS (FAB, MNBA) exact mass calcd for $C_{16}H_{17}NO_2S$ (M + Na)$^+$ 310.0878, found 310.0887. Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 67.06; H, 5.88; N, 4.90.

Catalysis Employing SmI_2(O-*t*-Bu).[26] To 1.0 mL of a 0.1 M solution of SmI_2 (0.10 mmol) under nitrogen was added 10 μL (8.0 mg, 0.054 mmol) of *tert*-butyl peroxide. After 20 min, the resulting yellow mixture was concentrated *in vacuo*. The residue was then redissolved in 3 mL of MeCN. A 10-mL flask under N_2 was charged with a 1-mL aliquot of the SmI_2(O-*t*-Bu) solution. To this solution were added *trans*-β-methylstyrene and PhI=NTs. After 6 h, the homogeneous reaction was filtered through a plug of silica and washed with EtOAc. Purification by flash chromatography (2- × 18-cm silica gel, 5:1 hexane/EtOAc) afforded 145 mg (76%) of the aziridine.

(46) Seden, T. P.; Turner, T. W. *J. Chem. Soc. (C)* **1968**, 876–878.

(47) Broos, R.; Anteunis, M. *Synth. Commun.* **1976**, *6*, 53–57.

***cis*-*N*-(*p*-Tolylsulfonyl)-2-methyl-3-phenylaziridine.** The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 12 mg (0.032 mmol) of $Cu(MeCN)_4ClO_4$, and 0.40 mL (0.40 g, 3.3 mmol) of *cis*-β-methylstyrene.[40] Reaction time: 1 h at −20 °C. MPLC purification was carried out by elution with hexane:EtOAc (6:1) to give 170 mg (89%) of *cis* and *trans* aziridines in a 13:1 ratio as determined by 500-MHz ^{1}H NMR: TLC R_f 0.25 (4:1 hexane:EtOAc); IR (neat) 3065, 3035, 2936, 1600, 1585, 1498, 1452, 1404, 1321, 1240, 1160, 1090, 1042, 984, 880, 760, 728, 698, 670 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.33–7.19 (m, 7H, Ar-*H*), 3.92 (d, 1H, J = 7.3 Hz, C*H*Ph), 3.18 (dq, 1H, J = 7.3, 5.8 Hz, C*H*CH_3), 2.41 (s, 3H, Ar-CH_3), 1.0 (d, 3H, J = 5.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 144.4, 135.1, 132.6, 129.6, 129.4, 128.2, 127.7, 127.4, 45.9, 41.5, 21.5, 11.8; HRMS (FAB, MNBA) exact mass calcd for $C_{16}H_{17}NO_2S$ (M + Na)$^+$ 310.0878, found 310.0875. Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.85; H, 5.86; N, 4.83.

***trans*-*N*-(*p*-Tolylsulfonyl)-2-(carbomethoxy)-3-phenylaziridine.** The general procedure was followed using 400 mg (1.07 mmol) of PhI=NTs, 20 mg (0.055 mmol) of $Cu(OTf)_2$, and 0.870 g (5.37 mmol) of *trans*-methyl cinnamate. Reaction time: 1 h at room temperature. Purification by flash column chromatography (3- × 18-cm silica, 6:1 hexane/EtOAc) afforded 267 mg (75%) of *trans*-aziridine as a white crystalline solid: mp 44.2–44.6 °C; TLC R_f 0.21 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3068, 3021, 2960, 1750, 1600, 1498, 1456, 1440, 1412, 1338, 1306, 1292, 1161, 1086, 1081, 1004, 938, 906, 834, 812, 709, 692, 646 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.31–7.24 (m, 7H, Ar-*H*), 4.44 (d, 1 H, J = 3.9 Hz, C*H*-aziridine), 3.85 (s, 3H, OCH_3), 3.53 (d, 1H, J = 4.0 Hz, C*H*-aziridine), 2.41 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 166.2, 144.3, 136.9, 132.5, 129.5, 128.9, 128.5, 127.4, 127.3, 53.1, 47.6, 46.7, 21.6; HRMS (FAB, MNBA) exact mass calcd for $C_{17}H_{17}NO_4S$ (M + Na)$^+$ 354.0776, found 354.0765. Anal. Calcd for $C_{17}H_{17}NO_4S$: C, 61.61; H, 5.17; N, 4.23. Found: C, 61.65; H, 5.01; N, 4.30.

***N*-(*p*-Tolylsulfonyl)-2-methyl-2-phenylaziridine.** The general procedure was followed using 300 mg (0.804 mmol) of PhI=NTs, 21 mg (0.080 mmol) of $Cu(acac)_2$, and 0.52 mL (0.47 g, 4.0 mmol) of α-methylstyrene. Reaction time: 1 h at room temperature. MPLC purification was carried out by elution with hexane:EtOAc (6:1) to give 165 mg (72%) of aziridine as a white crystalline solid: mp 83–84 °C; TLC R_f 0.26 (4:1 hexane:EtOAc); IR (CCl_4) 3060, 3028, 2992, 2930, 1600, 1449, 1330, 1267, 1160, 1128, 1089, 1027, 939, 870, 715, 694, 680, 650 cm^{-1}; ^{1}H NMR (benzene-d_6, 400 MHz) δ 8.03 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.38–7.12 (m, 5H, Ar-*H*), 6.92 (d, 2H, J = 8.4 Hz, Ar-*H*), 2.81 (s, 1H, C*H*-aziridine), 2.16 (s, 1H, C*H*-aziridine), 2.08 (s, 3H, CH_3), 2.01 (s, 3H, CH_3); ^{13}C NMR (benzene-d_6, 101 MHz) δ 144.4, 142.5, 139.7, 130.4, 129.3, 128.8, 128.5, 127.6, 52.2, 42.7, 21.9, 21.5; HRMS (FAB, MNBA) exact mass calcd for $C_{16}H_{17}NO_2S$ (M + Na)$^+$ 310.0878, found 310.0889.

***trans*-*N*-(*p*-Tolylsulfonyl)-2-(methoxymethyl)-3-phenylaziridine (15).** The general procedure was followed using 373 mg (1.00 mmol) of PhI=NTs, 16 mg (0.050 mmol) of $Cu(MeCN)_4ClO_4$, and 0.148 g (1.00 mmol) of *trans*-methyl cinnamyl ether. Reaction time: 30 min at room temperature. Flash column purification was carried out by elution (2- × 18-cm silica) with hexane:EtOAc (5:1) to give 77 mg of the *trans* aziridine **15** as a colorless oil. Repurification of the other fractions under identical conditions afforded 20 mg of aziridine (97 mg total, 31%) and 56 mg of the imine **16** (20%) as a crystalline solid.

15: TLC R_f 0.28 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3023, 3018, 2930, 1599, 1498, 1458, 1440, 1322, 1216, 1160, 1102, 1089, 911 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.28–7.24 (m, 5H, Ar-*H*), 7.20-7.17 (m, 2H, Ar-*H*), 4.16 (dd, 1 H, J = 5.4, 10.9 Hz, CH_2-OMe), 3.96 (dd, 1H, J = 6.6, 10.9, CH_2-OMe), 3.91 (d, 1H, J = 4.3 Hz, C*H*-aziridine), 3.44 (s, 3H, -OCH_3), 3.13–3.09 (m, 1H, C*H*-aziridine), 2.40 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 144.1, 137.1, 134.5, 129.5, 128.5, 128.3, 127.4, 126.7, 69.3, 59.1, 50.4, 47.1, 21.6; HRMS (FAB, MNBA) exact mass calcd for $C_{17}H_{20}NO_3S$ (M + H)$^+$ 318.1164, found 318.1171.

***N*-(*p*-Tolylsulfonyl)cinnamaldehyde imine (16)**: mp 120–121 °C; TLC R_f 0.22 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3022, 1622, 1583, 1451, 1361, 1320, 1170, 1156, 1090, 965 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.78 (d, 1H, J = 8.3, imine-C*H*) 7.86 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.56–7.40 (m, 6H, Ar-*H*), 7.34 (d, 2H, J = 8.4 Hz, Ar-*H*), 6.98 (dd, 1 H, J = 9.4, 15.8 Hz, vinyl-C*H*), 2.43 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.8, 153.7, 144.4, 135.3, 134.1, 131.6, 129.7, 129.1, 128.6, 127.9, 124.7, 21.6; HRMS (CI, NH_3) exact mass calcd for $C_{16}H_{16}NO_2S$ (M + H)$^+$ 286.0902, found 286.0901.

***N*-(*p*-Tolylsulfonyl)-2-*n*-butylaziridine.**[11c] The general procedure was followed using 400 mg (0.670 mmol) of PhI=NTs, 20 mg (0.055 mmol) of $Cu(OTf)_2$, and 0.670 mL (0.451 g, 5.36 mmol) of 1-hexene. Reaction time: 1 h at room temperature. Flash column chromatography (3- × 18-cm silica, 4:1 hexane/EtOAC) afforded 167 mg (62%) of the aziridine as a colorless oil: TLC R_f 0.42 (4:1 hexane:EtOAc); IR (thin film) 2959, 2932, 1456, 1325, 1306, 1291, 1233, 1163, 1092, 957, 943, 924, 866, 816, 716, 694, 662 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.33 (d, 2H, J = 8.3 Hz, Ar-*H*), 2.70 (m, 1H, C*H*-aziridine), 2.61 (d, 1H, J = 7.0 Hz, *cis*-C*H*-aziridine), 2.42 (s, 3H, Ar-CH_3), 2.05 (d, 1H, J = 4.6 Hz, *trans*-C*H*-aziridine), 1.54 (m, 1H, aliphatic), 1.34–1.18 (m, 5H, aliphatic), 0.8 (t, 3H, J = 7 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 144.1, 134.9, 129.3, 127.7, 40.0, 33.4, 30.6, 28.6, 21.8, 21.2, 13.5; HRMS (EI) exact mass calcd for $C_{13}H_{19}NO_2S$ (M)$^+$ 253.1136, found 253.1119. Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53. Found: C, 61.80; H, 7.41; N, 5.68.

***trans*-*N*-(*p*-Tolylsulfonyl)-2,3-di-*n*-propylaziridine.** The general procedure was followed using 400 mg (1.07 mmol) of PhI=NTs, 32 mg (0.086 mmol) of $Cu(MeCN)_4ClO_4$, and 0.84 mL (0.60 g, 5.4 mmol) of *trans*-4-octene. Reaction time: 5 h at −20 °C. MPLC purification was carried out by elution with hexane:EtOAc (9:1) to give 191 mg (64%) of the *trans* aziridine as a colorless oil: TLC R_f 0.32 (4:1 hexane:EtOAc); IR (neat) 2968, 2940, 2880, 1602, 1470, 1322, 1316, 1249, 1160, 1092, 984, 930, 816, 710, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.83 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.30 (d, 2H, J = 8.4 Hz, Ar-*H*), 2.66 (m, 2H, *cis*-C*H*), 2.43 (s, 3H, Ar-CH_3), 1.78–1.62 (m, 4H, CH_2Et), 1.40–1.31 (m, 4H, CH_2-CH_3), 0.9 (t, 6H, J = 7.4 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 143.6, 137.9, 129.3, 127.3, 49.5, 31.8, 21.5, 20.7, 13.6; HRMS (FAB, MNBA) exact mass calcd for $C_{15}H_{23}NO_2S$ (M + Na)$^+$ 304.1347, found 304.1333. Anal. Calcd for $C_{15}H_{23}NO_2S$: C, 64.02; H, 8.24; N, 4.98. Found: C, 64.18; H, 8.14; N, 5.06.

***cis*-*N*-(*p*-Tolylsulfonyl)-2,3-di-*n*-propylaziridine.** The general procedure was followed using 400 mg (1.07 mmol) of PhI=NTs, 22 mg (0.059 mmol) of $Cu(MeCN)_4ClO_4$, and 0.84 mL (0.60 g, 5.4 mmol) of *cis*-oct-4-ene.[7] Reaction time: 5 h at −20 °C. MPLC purification was carried out by elution with hexane:EtOAc (9:1) to give 235 mg (78%) of *cis*-aziridine. No *trans* isomer was detected by 500-MHz ^{1}H NMR. Capillary GLC (DB-1, 5 psi, 160 °C) indicated >96:4 ratio of aziridines: TLC R_f 0.32 (4:1 hexane:EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.32 (d, 2H, J = 8.2 Hz, Ar-*H*), 2.79 (m, 2H, *trans*-C*H*), 2.44 (s, 3H, Ar-CH_3), 1.49–1.24 (m, 8H, CH_2CH_2-CH_3), 0.89 (t, 6H, J = 7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 144.1, 135.4, 129.4, 127.9, 127.3, 44.9, 28.7, 21.6, 20.7, 20.5, 13.7; HRMS (FAB, MNBA) exact mass calcd for $C_{15}H_{23}NO_2S$ (M + Na)$^+$ 304.1347, found 304.1334. Anal. Calcd for $C_{15}H_{23}NO_2S$: C, 64.02; H, 8.24; N, 4.98. Found: C, 64.21; H, 8.07; N, 5.06.

***N*-(*p*-Tolylsulfonyl)-2-(carbomethoxy)aziridine.** The general procedure was followed using 400 mg (1.07 mmol) of PhI=NTs, 20 mg (0.055 mmol) of $Cu(OTf)_2$, and 0.485 mL (0.464 g, 5.39 mmol) of methyl acrylate. Reaction time: 1 h at room temperature. Purification by flash column chromatography (3- × 18-cm silica, 3:1 hexane/EtOAc) afforded 110 mg (40%) of the aziridine as a colorless oil: TLC R_f 0.35 (3:1 hexane:EtOAc); IR (thin film) 2950, 1752, 1441, 1395, 1333, 1306, 1292, 1233, 1209, 1186, 1165, 1096, 909, 816, 781, 733, 710, 692, 642 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.84 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.36 (d, 2H, J = 8.2 Hz, Ar-*H*), 3.73 (s, 3H, OCH_3), 3.34 (dd, 1H, J = 7.1, 4.1 Hz, C*H*CO_2Me), 2.76 (d, 1H, J = 7.1 Hz, *cis*-C*H*-aziridine), 2.56 (d, 1H, J = 4.1 Hz, *trans*-C*H*-aziridine), 2.45 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 167.1, 145.2, 133.9, 129.8, 128.1, 52.7, 35.6, 31.9, 21.5; HRMS (FAB, MNBA) exact mass calcd for $C_{11}H_{13}NO_4S$ (M + Na)$^+$ 278.0463, found 278.0482. Anal. Calcd for $C_{11}H_{13}NO_4S$: C, 51.75; H, 5.13; N, 5.49. Found: C, 51.82; H, 5.30; N, 5.50.

***N*-(*p*-Tolylsulfonyl)-3-azatricyclo[3.2.1.0.^{2,4exo}]octane.** The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 25 mg (0.067 mmol) of $Cu(MeCN)_4ClO_4$, and 0.19 g (2.0 mmol) of norbornene. Reaction time: 30 min at room temperature. MPLC purification was carried out by elution with hexane:EtOAc (6:1) to give 158 mg (90%) of aziridine as a white crystalline solid: mp 123–124 °C; TLC R_f 0.22 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3017, 1310, 1296, 1277, 1138, 1080, 961, 895, 858, 770, 741, 725, 656 cm^{-1}; ^{1}H NMR (benzene-d_6, 400 MHz) δ 7.97 (d, 2H, J = 8.3 Hz, Ar-*H*), 6.77 (d, 2H, J = 7.9 Hz, Ar-*H*), 2.87 (s, 2H, H_2, H_3), 1.98 (s, 2H, H_1,H_4), 1.86 (s, 3H, Ar-CH_3), 1.45 (dt, 1H, J = 2.0, 9.9 Hz, syn-H_7), 0.97–0.92 (m, 2H, H_5, H_6), 0.77–0.71 (m, 2H, H_5, H_6), 0.32 (d, 1H, J = 9.9 Hz, anti-H_7); ^{13}C NMR ($CDCl_3$, 126 MHz)

δ 144.0, 135.9, 129.5, 127.6, 41.9, 35.8, 28.2, 25.6, 21.6; HRMS (FAB, MNBA) exact mass calcd for $C_{14}H_{17}NO_2S$ (M + Na)$^+$ 286.0878, found 286.0870.

N-(p-Tolylsulfonyl)amino)-1,2,3,4-tetrahydronaphthalen-1,2-imine. The general procedure was followed using 300 mg (0.804 mmol) of PhI=NTs, 20 mg (0.080 mmol) of $Cu(acac)_2$, and 0.52 mL (0.52 g, 4.0 mmol) of 1,2-dihydronaphthalene. Reaction time: 1 h. MPLC purification was carried out by elution with hexane:EtOAc (6:1) to give 176 mg (73%) of aziridine as a crystalline solid: mp 123–124 °C; TLC R_f 0.2 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3029, 1599, 1495, 1399, 1321, 1306, 1291, 1229, 1217, 1198, 1174, 1157, 1092, 990, 947, 909, 878, 816, 781, 762 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.80 (d, 2H, J = 8.2 Hz, Ar-*H*), 7.28–7.01 (m, 6H, Ar-*H*), 3.8 (d, 1H, J_{cis} = 7 Hz, C*H*-aziridine), 3.52 (d, 1H, J_{cis} = 6.9 Hz, C*H*-aziridine), 2.72 (dt, 1H, J = 14.5, 6.2 Hz, PhC*H*), 2.51 (dd, 1H, J = 15.5, 5.2 Hz, PhC*H*), 2.36 (s, 3H, Ar-CH_3), 2.21 (dd, 1H, J = 14.2, 6.3 Hz, $PhCH_2CH$), 1.62 (dt, 1H, J = 13.7, 5.4 Hz, $PhCH_2CH$); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 144.1, 136.4, 135.4, 129.8, 129.5, 129.2, 128.4, 128.2, 127.4, 126.1, 41.8, 41.6, 24.5, 21.4, 19.8; HRMS (FAB, MNBA) exact mass calcd for $C_{17}H_{17}NO_2S$ (M + Na)$^+$ 322.0878, found 322.0886. Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68. Found: C, 68.09; H, 5.75; N, 4.64.

N-(p-Tolylsulfonyl)-7-azabicyclo[4.1.0]heptane (10). The general procedure was followed using 400 mg (1.07 mmol) of PhI=NTs, 20 mg (0.055 mmol) of $Cu(OTf)_2$, and 0.540 mL (0.438 g, 5.33 mmol) of cyclohexene. Reaction time: 1 h at room temperature. Flash column chromatography (3- × 18-cm silica, 4:1 hexane/EtOAc) provided 161 mg (60%) of the aziridine as a white crystalline solid: mp 55.3–55.9 °C; TLC R_f 0.32 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3020, 2950, 2860, 1600, 1440, 1395, 1315, 1305, 1155, 1090, 965, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.33 (d, 2H, J = 8.0 Hz, Ar-*H*), 2.98 (t, 2H, J = 1.4 Hz, C*H*-aziridine), 2.44 (s, 3H, Ar-CH_3), 1.79 (m, 4H, ring-C*H*), 1.43–1.36 (m, 2H, ring-C*H*), 1.26–1.19 (m, 2H, ring-C*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 144.0, 135.8, 129.5, 127.5, 39.7, 22.7, 21.6, 19.4; HRMS (FAB, MNBA) exact mass calcd for $C_{13}H_{17}NO_2S$ (M + Na)$^+$ 274.0878, found 274.0872. Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 62.14; H, 6.79; N, 5.65.

N-(p-Tolylsulfonyl)-1-methyl-7-azabicyclo[4.1.0]heptane. The general procedure was followed using 400 mg (1.07 mmol) of PhI=NTs, 20 mg (0.055 mmol) of $Cu(OTf)_2$, and 0.635 mL (0.516 g, 5.37 mmol) of 1-methyl-1-cyclohexene. Reaction time: 1 h at room temperature. Flash column chromatography (2- × 18-cm silica, 4:1 hexane/EtOAc) afforded 145 mg (51%) of the aziridine: mp 84.4–85.2 °C; TLC R_f 0.30 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3010, 2940, 2860, 1600, 1455, 1450, 1435, 1400, 1310, 1300, 1175, 1150, 1090, 1035, 975, 940 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, 2H, J = 8.3 Hz, Ar-*H*), 7.30 (d, 2H, J = 8.1 Hz, Ar-*H*), 3.05 (d, 1H, J = 5.1 Hz, C*H*-aziridine), 2.42 (s, 3H, Ar-CH_3), 2.05 (ddd, J = 4.3, 5.0, 14.4 Hz, 1H, C*H*-aziridine), 1.86–1.78 (m, 1H, ring-C*H*), 1.71 (s, 3H, CH_3), 1.59–1.49 (m, 2H, ring-C*H*), 1.45–1.25 (m, 3H, ring-C*H*), 1.16–1.08 (m, 1H, ring-C*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 143.3, 138.9, 129.3, 126.9, 51.2, 47.2, 33.0, 22.8, 21.5, 20.4, 19.7, 19.5; HRMS (FAB, MNBA) exact mass calcd for $C_{14}H_{19}NO_2S$ (M + Na)$^+$ 288.1034, found 288.1031. Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.37; H, 7.22; N, 5.28. Found: C, 63.18; H, 7.29; N, 5.29.

2-(N-(p-Tolylsulfonyl)amino)cyclohexanone. The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 22 mg (0.059 mmol) of $Cu(MeCN)_4ClO_4$, and 0.20 mL (0.17 g, 1.0 mmol) of (1-cyclohexenyloxy)trimethylsilane.[37] Reaction time: 1.5 h at −20 °C. MPLC purification was carried out by elution with hexane:EtOAc (5:1) to give 115 mg (64%) of aziridine: mp 133–135 °C; TLC R_f 0.28 (2:1 hexane:EtOAc); IR ($CHCl_3$) 3350, 1694, 1345, 1296, 1219, 1163, 1094, 781, 748, 743, 687, 671 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72 (d, 2H, J = 8.2 Hz, Ar-*H*), 7.28 (d, 2H, J = 8.4 Hz, Ar-*H*), 5.79 (bd, 1H, J = 4.3 Hz, N*H*Ts), 3.76 (m, 1H, C*H*NHTs), 2.54–2.42 (m, 2H, ring-C*H*), 2.41 (s, 3H, Ar-CH_3), 2.22 (dt, 1H, J = 1.0, 10.6 Hz, ring-C*H*), 2.07 (m, 1H, ring-C*H*), 1.86 (m, 1H, ring-C*H*), 1.71–1.48 (m, 3H, ring-C*H*); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 205.6, 143.5, 137.0, 129.7, 126.9, 60.6, 40.7, 36.8, 27.4, 23.9, 21.4; HRMS (FAB, MNBA) exact mass calcd for $C_{13}H_{17}NO_3S$ (M + H)$^+$ 268.1007, found 268.1003. Anal. Calcd for $C_{13}H_{17}NO_3S$: C, 58.41; H, 6.41; N, 5.24. Found: C, 58.2; H, 6.33; N, 5.32.

2-(N-(p-Tolylsulfonyl)amino)acetophenone. The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 18 mg (0.048 mmol) $Cu(MeCN)_4ClO_4$ and 0.20 mL (0.19 g, 1.0 mmol) (1-styrenyloxy)-trimethylsilane. Reaction time: 3 h at −20 °C. MPLC purification was carried out by elution with hexane:EtOAc (5:1) to give 146 mg (76%): mp 112–114 °C; TLC R_f 0.25 (2:1 hexane:EtOAc); IR ($CHCl_3$) 3350, 1694, 1344, 1296, 1219, 1163, 1094, 781, 748, 743, 687, 671 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.85 (d, 2H, J = 7.3 Hz, Ar-*H*), 7.78 (d, 2H, J = 8.2 Hz, Ar-*H*), 7.61 (t, 1H, J = 7.6, 7.3 Hz, Ar-*H*), 7.47 (t, 2H, J = 7.6, 7.9 Hz, Ar-*H*), 7.29 (d, 2H, J = 8.1 Hz, Ar-*H*), 5.64 (bs, 1H, N*H*Ts), 4.46 (d, 2H, J = 4.6 Hz, CH_2CO), 2.39 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 192.5, 143.7, 136.2, 134.4, 133.8, 129.8, 129.0, 127.8, 127.2, 48.6, 21.5; HRMS (FAB, MNBA) exact mass calcd for $C_{15}H_{15}NO_3S$ (M + Na)$^+$ 312.0670, found 312.0687. Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.27; H, 5.23; N, 4.84. Found: C, 62.35; H, 5.07; N, 4.88.

2-(N-(p-Tolylsulfonyl)amino)tetralone. The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 20 mg (0.053 mmol) of $Cu(MeCN)_4ClO_4$ and 0.22 g (4.2 mmol) of (1-naphthalenyloxy)-trimethylsilane. Reaction time: 90 min at 0 °C. MPLC purification was carried out by elution with hexane:EtOAc (5:1) to give 111 mg (53%) of aziridine. mp 106.2–106.8 °C; TLC R_f 0.27 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3660–3120, 3025, 1690, 1605, 1460, 1405, 1360, 1338, 1295, 1165, 1098, 1005, 960, 815, 679 cm^{-1}; ^{1}H NMR (benzene-d_6, 500 MHz) δ 7.95 (d, 1H, J = 7.8 Hz, Ar-*H*), 7.86 (d, 2H, J = 8.1 Hz, Ar-*H*), 6.98 (t, 1H, J = 7.5, 7.4 Hz, Ar-*H*), 6.84 (t, 1H, J = 7.5, 7.5 Hz, Ar-*H*), 6.80 (d, 2H, J = 7.9 Hz, Ar-*H*), 6.60 (d, 2H, J = 7.6 Hz, Ar-*H*), 6.29 (s, 1H, N*H*Ts), 3.82 (dd, 1H, J = 4.6, 13.6 Hz, COC*H*), 2.63 (bd, 1H, J = 12.9 Hz, ring-C*H*), 2.40 (dt, 1H, J = 4.0, 13.0 Hz, ring-C*H*), 2.23 (bd, 1H, J = 17.0 Hz, ring-C*H*), 1.89 (s, 3H, Ar-CH_3), 1.67 (dq, 1H, J = 4.2, 13.3 Hz, ring-C*H*); ^{13}C NMR (benzene-d_6, 126 MHz) δ 194.4, 144.7, 143.8, 134.6, 130.5, 129.6, 128.9, 128.7, 128.6, 128.2, 127.4, 60.1, 32.8, 28.5, 21.7; HRMS (FAB, MNBA) exact mass calcd for $C_{17}H_{17}NO_3S$ (M + Na)$^+$ 338.0827, found 338.0836. Anal. Calcd for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43; N, 4.44. Found: C, 64.80; H, 5.47; N, 4.51.

2-(N-(p-Tolylsulfonyl)amino)propiophenone. The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 30 mg (0.08 mmol) of $Cu(MeCN)_4ClO_4$, and 0.22 g (1.0 mmol) of 2-methyl-1-styrenyloxy)trimethylsilane. Reaction time: 15 min at 0 °C. MPLC purification was carried out by elution with hexane:EtOAc (5:1) to give 118 mg (58%): mp 112.2–114.8 °C; TLC R_f 0.26 (2:1 hexane:EtOAc); IR ($CHCl_3$) 3400–3220, 3117, 1690, 1494, 1451, 1342, 1278, 1165, 1095, 972, 814, 701, 674 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76 (d, 2H, J = 7.3 Hz, Ar-*H*), 7.69 (d, 2H, J = 8.2, Ar-*H*), 7.58 (t, 1H, J = 1.1, 7.5 Hz, Ar-*H*), 7.43 (t, 2H, J = 7.6 Hz, Ar-*H*), 7.16 (d, 2H, J = 8.1 Hz, Ar-*H*), 5.79 (bs, 1H, N*H*Ts), 4.93 (m, 1H, C*H*CH$_3$), 2.31 (s, 3H, Ar-CH_3), 1.39 (d, 3H, J = 7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 198.1, 143.5, 137.1, 134.0, 133.4, 129.6, 128.8, 128.4, 127.0, 53.3, 21.4, 21.1; HRMS (FAB, MNBA) exact mass calcd for $C_{16}H_{17}NO_3S$ (M + Na)$^+$: 326.0827, found 326.0826. Anal. Calcd for $C_{16}H_{17}NO_3S$: C, 63.35; H, 5.65; N, 4.62. Found: C, 63.40; H, 5.48; N, 4.68.

1-(N-(p-Tolylsulfonyl)amino)-2-hexanone. The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 30 mg (0.080 mmol) of $Cu(MeCN)_4ClO_4$, and 0.17 g (1.0 mmol) of (2-hexenyloxy)-trimethylsilane. Reaction time: 90 min at 0 °C. MPLC purification was carried out by elution with hexane:EtOAc (5:1) to give 111 mg (53%) of aziridine: mp 78.8–79.5 °C; TLC R_f 0.27 (4:1 hexane:EtOAc); IR ($CHCl_3$) 3660–3160, 3018, 2964, 2918, 2880, 1730, 1588, 1495, 1400, 1342, 1300, 1160, 1120, 1048, 812, 662 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73 (d, 2H, J = 8.2 Hz, Ar-*H*), 7.30 (d, 2H, J = 8.2 Hz, Ar-*H*), 5.34 (bs, 1H, N*H*Ts), 3.83 (d, 2H, J = 4.6 Hz, CH_2CO), 2.42 (s, 3H, Ar-CH_3), 2.33 (t, 2H, J = 7.4 Hz, CH_2CH_2CO), 1.61–1.45 (m, 2H, CH_2), 1.25–1.17 (m, 2H, CH_2), 0.85 (t, 3H, J = 7.4 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 203.8, 143.7, 136.1, 129.7, 127.2, 51.3, 39.8, 25.6, 22.1, 21.5, 13.6; HRMS (FAB, MNBA) exact mass calcd for $C_{13}H_{19}NO_3S$ (M + Na)$^+$ 292.0983, found, 292.0990. Anal. Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11; N, 5.2. Found: C, 58.08; H, 7.13; N, 5.21.

2-(N-(p-Tolylsulfonyl)amino)phenylhexanoate. The general procedure was followed using 250 mg (0.670 mmol) of PhI=NTs, 29 mg (0.080 mmol) of $Cu(MeCN)_4ClO_4$, and 0.26 g (1.0 mmol) of 1-phenoxy-2-*n*-butyl-1-(*tert*-butyldimethylsiloxy)ethene. Reaction time: 1 h at −20 °C. MPLC purification was carried out by elution with hexane:EtOAc (5:1) to give 120 mg (50%) of the α-amino ester as a white crystalline solid: mp 98–99 °C; TLC R_f of 0.34 (2:1 hexane:EtOAc); IR ($CHCl_3$) 3020, 2964, 2938, 1760, 1494, 1349, 1090, 1060, 1032, 964, 816, 688, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, 2H, J = 8.2 Hz, Ar-*H*), 7.24–7.10 (m, 5H, Ar-*H*), 6.66 (d, 2H, J = 7.5 Hz, Ar-*H*), 5.33 (d, 1H, J = 9.6 Hz, N*H*Ts), 4.05 (m, 1H, C*H*CO), 2.33 (s, 3H, Ar-CH_3), 1.86–1.65 (m, 2H, CH_2), 1.37–1.22 (m, 4H, $CH_2CH_2CH_3$), 0.81 (t, 3H, J = 7.2

Hz, CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.5, 149.9, 143.7, 136.7, 129.7, 129.3, 127.3, 126.1, 120.8, 55.7, 33.0, 27.0, 21.9, 21.4, 13.7; HRMS (FAB, MNBA) exact mass calcd for $C_{19}H_{23}NO_4S$ $(M + Na)^+$ 384.1245, found 384.1262.

***N*-(*p*-Tolylsulfonyl)-*N*-(1-cyclohex-2-ene)acetamidine (11).** A flame-dried 25-mL flask under N_2 was charged with 143 mg (0.383 mmol) of PhI=NTs. MeCN (3 mL) was added followed by addition of cyclohexene (3.90 mL) (3.16 g, 38.4 mmol). $Mn(TPP)ClO_4$ dissolved in 1 mL of MeCN was added. After 2 h, the homogenous solution was filtered through a plug of silica (wash with EtOAc). Purification by flash column chromatography (2- × 16-cm silica) afforded 60.3 mg (63%) of allylic insertion product **11**: TLC R_f 0.18 (1:1 hexane:EtOAc); IR ($CHCl_3$) 3432, 3307, 3020, 2975, 2929, 1565, 1533, 1444, 1276, 1147, 1095, 1042 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.71 (d, 1H, J = 7.2 Hz, N*H*), 7.66 (d, 2H, J = 8.1 Hz, Ar-*H*), 7.33 (d, 2H, J = 8.2 Hz, Ar-*H*), 5.86–5.83 (m, 1H, vinyl-C*H*), 5.54 (dd, 1H, J = 2.3, 10.0 Hz, vinyl-C*H*), 4.36–4.35 (bm, 1H, allyl-C*H*), 2.36 (s, 3H), 2.19 (s, 3H), 1.99–1.96 (m, 2H), 1.82–1.76 (m, 1H), 1.68–1.64 (m, 1H), 1.55–1.46 (m, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 164.8, 141.5, 141.2, 130.5, 129.2, 126.6, 125.7, 46.4, 27.6, 24.3, 20.9, 19.8, 19.4; HRMS (CI, NH_3) exact mass calcd for $C_{15}H_{21}N_2O_2S$ $(M + H)^+$ 293.1324, found 293.1323.

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