Cycloaddition of Heteroatom-Substituted 2-Azaallyl Anions with Alkenes. Synthesis of 1-Pyrrolines and Bridged Azabicyclic Compounds

William H. Pearson* and Erland P. Stevens

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055

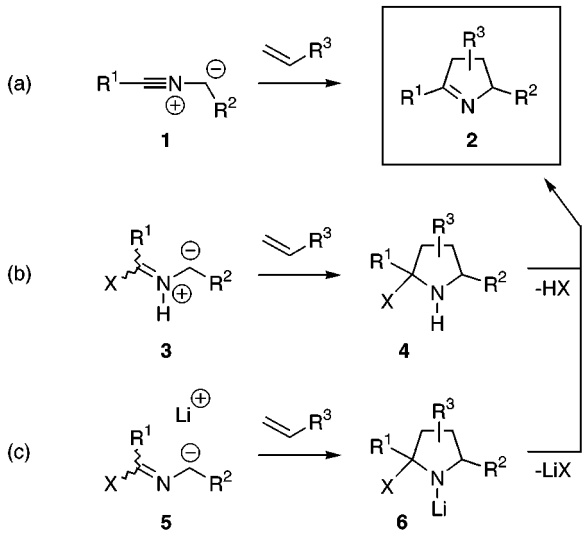
Received July 23, 1998

Nonstabilized 2-azaallyl anions bearing heteroatom substituents [$R^1CHNC(X)R^2(-)Li(+)$, where R^1 and R^2 are hydrogen or alkyl groups and X = OMe, SPh, or NR_2] were generated and found to undergo efficient [3 + 2] cycloadditions with alkenes to provide 1-pyrrolines after loss of LiX. The 2-azaallyl anions were generated by tin−lithium exchange on stannyl imidates, thioimidates, or amidines $R^1CH(SnBu_3)N{=}C(X)R^2$ with *n*-butyllithium. The initially formed 1-pyrrolines were found to be deprotonated under the reaction conditions to afford 1-metalloenamines, which could be quenched with alkyl halides, carbonyl compounds, or MeSSMe to provide further functionalized 1-pyrrolines. Cyclic methoxy-substituted 2-azaallyl anions were generated and were found to undergo cycloadditions with alkenes to afford bridged azabicyclic compounds (1-methoxy-7-azabicyclo[2.2.1]-heptanes and 1-methoxy-8-azabicyclo[3.2.1]octanes). These are the first examples of cyclic nonstabilized 2-azaallyl anions.

Introduction

We have previously described the synthesis of pyrrolidines by the [π4s + π2s] cycloaddition of nonstabilized 2-azaallyl anions with electron-rich alkenes.[1−3] In an effort to expand the scope of this method, we initiated studies aimed at the synthesis of 1-pyrrolines **2** using a [3 + 2] cycloaddition approach.[4] Scheme 1 illustrates three related [3 + 2] cycloadditive approaches to 1-pyrrolines, each involving species with an array of three p-orbitals bearing four π-electrons on a 2-azaallylic fragment. Pathway a is the archetype for the conversion of an alkene to a 1-pyrroline, namely, the cycloaddition of a nitrile ylide **1**.[5] The cycloadditions of aryl-substituted nitrile ylides ArC≡N(+)C(−)HR with electron-poor dipolarophiles have been widely studied. Nitrile ylides without aromatic substitution are rare.[6,7] Pathway b shows the use of heteroatom-substituted azomethine ylides **3** as synthetic equivalents of nitrile ylides in cycloadditions with electron-poor dipolarophiles, requiring loss of the heteroatom after cycloaddition to install

Scheme 1. [3 + 2] Cycloaddition Routes to 1-Pyrrolines



the imine functionality, i.e., **4** → **2**.[8−13] Pathway c shows the proposed use of heteroatom-substituted 2-azaallyl anions **5** to synthesize 1-pyrrolines. The cycloaddition of

(1) For a review of 2-azallyl anion chemistry, see: Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 627−639.

(2) (a) Pearson, W. H.; Szura, D. P.; Harter, W. G. *Tetrahedron Lett* **1988**, *29*, 761−764. (b) Pearson, W. H.; Szura, D. P.; Postich, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1329−1345.

(3) For the most recent work in this area, see: (a) Pearson, W. H.; Mi, Y. *Tetrahedron Lett.* **1997**, *38*, 5441−5444. (b) Pearson, W. H.; Clark, R. B. *Tetrahedron Lett.* **1997**, *38*, 7669−7672.

(4) A portion of this work was reported in communication form: Pearson, W. H.; Stevens, E. P. *Tetrahedron Lett.* **1994**, *35*, 2641−2644.

(5) Hansen, H.-J.; Heimgartner, H. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1; pp 177−290.

(6) (a) Turro, N. J.; Cha, Y.; Gould, I. R.; Padwa, A.; Gasdaska, J. R.; Tomas, M. *J. Org. Chem.* **1985**, *50*, 4415−4417. (b) Padwa, A.; Gasdaska, J. R.; Tomas, M.; Turro, N. J.; Cha, Y.; Gould, I. R. *J. Am. Chem. Soc.* **1986**, *108*, 6739−6746. (c) Padwa, A.; Gasdaska, J. R.; Haffmanns, G.; Rebello, H. *J. Org. Chem.* **1987**, *52*, 1027−1035.

(7) Berrée, F.; Marchand, E.; Morel, G. *Tetrahedron Lett.* **1992**, *33*, 6155−6158.

(8) (a) Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1980**, *102*, 7993−7994. (b) Vedejs, E.; West, F. G. *J. Org. Chem.* **1983**, *48*, 4773−4774. (c) Vedejs, E.; Larsen, S.; West, F. G. *J. Org. Chem.* **1985**, *50*, 2170−2174. (d) Vedejs, E.; West, F. G. *Chem. Rev.* **1986**, *86*, 941−955.

(9) (a) Padwa, A.; Haffmanns, G.; Tomas, M. *Tetrahedron Lett.* **1983**, *24*, 4303−4306. (b) Padwa, A.; Chen, Y.-Y.; Koehler, K. F.; Tomas, M. *Bull. Soc. Chem. Belg.* **1983**, *92*, 811−817. (c) Padwa, A.; Haffmanns, G.; Tomas, M. *J. Org. Chem.* **1984**, *49*, 3314−3322.

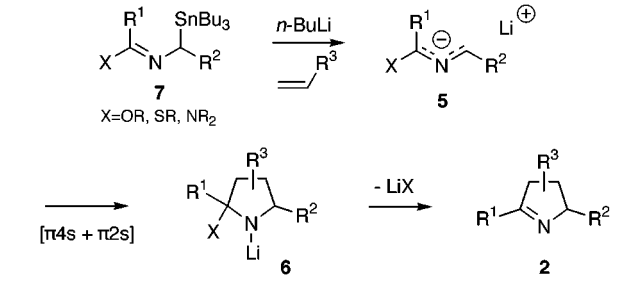
(10) (a) Livinghouse, T.; Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 210−211. (b) Smith, R.; Livinghouse, T. *J. Org. Chem.* **1983**, *48*, 1554−1555. (c) Smith, R.; Livinghouse, T. *Tetrahedron* **1985**, *41*, 3559−3568.

(11) (a) Tsuge, O.; Kanemasa, S.; Matsuda, K. *Chem. Lett.* **1985**, 1411. (b) Tsuge, O.; Kanemasa, S.; Matsuda, K. *J. Org. Chem.* **1986**, *51*, 1997−2004. (c) Tsuge, O.; Kanemasa, S.; Yamada, T.; Matsuda, K. *J. Org. Chem.* **1987**, *52*, 2523−30.

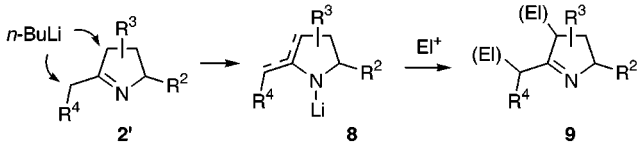
(12) (a) Alanine, A. I. D.; Fishwick, C. W. G. *Tetrahedron Lett.* **1989**, *30*, 4443−4446. (b) Alanine, A. I. D.; Fishwick, C. W. G.; Szantay, C., Jr. *Tetrahedron Lett.* **1989**, *30*, 6573−6576.

10.1021/jo981457i CCC: $15.00
Published on Web 11/25/1998

Scheme 2. Generation and Cycloaddition of Heteroatom-Substituted 2-Azaallyl Anions 5



If pyrroline has acidic hydrogens:



5 with an alkene would produce the 1-lithiopyrrolidine **6**, which should readily β-eliminate to produce the desired 1-pyrroline **2**. The reactions of certain *stabilized* heteroatom-substituted 2-azaallyl anions[11c,14] or *N*-metalloazomethine ylides[6] with carbonyl compounds or electron-poor alkenes have been studied. To complement the approaches to 1-pyrrolines based on nitrile ylides and heteroatom-substituted 1,3-dipoles, both of which require electron-poor alkenes, we have examined the highly reactive nonstabilized 2-azaallyl anions **5** and found them to be successful cycloaddition partners with electron-rich alkenes. This approach also alleviates the requirement for stabilizing groups (e.g., aryl, carboalkoxy) on the 2-azaallyl fragment. In addition, the first examples of *cyclic* 2-azaallyl anions are reported, which undergo cycloadditions with alkenes to afford bridged azabicyclic compounds.

Cycloadditions of Heteroatom-Substituted 2-Azaallyl Anions

As in our previous work on nonstabilized 2-azaallyl anions, tin−lithium exchange was found to be the method of choice for the generation of the heteroatom-substituted anions **5** (Scheme 2). The γ-hetero(2-azaallyl)stannanes **7** were prepared (vide infra), mixed with various anionophiles, and added to *n*-butyllithium (ca. 5 equiv) in THF at −78 °C. After about 30 min, aqueous workup and chromatography afforded the desired pyrrolines **2**. The initially formed 1-lithiopyrrolidine **6** had smoothly eliminated LiX in situ. The use of 1 equiv of *n*-butyllithium resulted in a halving of the typical yield of pyrroline, which was then accompanied by approximately equal amounts of the starting stannane **7**. At the least, 2 equiv of *n*-butyllithium were found to be necessary for adequate yields, although more is typically used. Insight into the requirement for ≥2 equiv of alkyllithium was obtained when the reactions were quenched with electrophiles other than water, producing the pyrrolines **9** where the electrophile had been incorporated at the α-carbon of the imine. Thus, if the pyrroline **2** has enolizable protons (i.e., **2′**), the *final* product of the cycloaddition−elimination sequence is not **2′**, but instead the metalloenamine **8**, the result of deprotonation of **2′** by *n*-butyllithium in competition with tin−lithium exchange. When 1 equiv of *n*-butyllithium is used, the deprotonation of **2′** competes with the initial tin−lithium exchange, resulting in ca. 50% reaction. It was surprising to us that the sequence of cycloaddition, elimination, and deprotonation can compete with tin−lithium exchange, normally a very fast process. Nonetheless, the intermediacy of **8** is potentially useful, since metalloenamines are important nucleophiles in organic synthesis.[15] Thus, the tandem cycloaddition−metalloenamine quench may lead to highly functionalized pyrrolines in a one-pot operation (vide infra).

A. Acyclic Heteroatom-Substituted 2-Azaallyl Anions. Representative cycloadditions of oxygen-, sulfur-, and nitrogen-substituted 2-azaallyl anions are shown in Table 1. In all cases, the reactions were quenched with water, thus masking the chemistry of the intermediate metalloenamines **8**. All amidines and imidates are believed to be the (*E*)-geometrical isomers on the basis of literature precedent and comparison to literature NMR spectroscopic values.[16−18] The thioimidates **14** and **27**, however, were observed to be a mixture of two geometrical isomers. Entries 1−7 in Table 1 illustrate the use of heteroatom-substituted 2-azaallyl anions bearing a single methyl group (entries 1−4 and 6,7, Table 1) or no alkyl group (entry 5, Table 1) in addition to the heteroatom substituent. Although simple 2-unsubstituted 1-pyrrolines are prone to trimerization (e.g., 1-pyrroline itself[19]), the 4-(triethylsilyl)-1-pyrroline **16** was isolated and characterized without difficulty. Vinyl silanes, styrenes, and stilbenes worked well as anionophiles, as we have previously found. Phenyl vinyl sulfide and phenyl vinyl selenide, two of the more synthetically useful anionophiles in our earlier work,[2,3] did not lead to isolable cycloadducts in the current work, perhaps due to instability of the intermediate metalloenamines or the final products themselves. However, these anionophiles did cycloadd with *cyclic* heteroatom-substituted 2-azaallyl anions (vide infra). Entries 8−17 of Table 1 involve anions bearing 1,3-dialkyl substitution, thus requiring tin−lithium exchange on precursors with branching next to the stannyl group. The pyrrolines **22** and **23** derived from either (*Z*)- or (*E*)-stilbene were found to be oxidized easily to 3-hydroxy-1-pyrrolines **24** and **25** upon isolation (entries 10 and 11, Table 1). Note that (*E*)- and (*Z*)-stilbene both give the same four cycloadducts **22**−**25**, perhaps indicating a nonstereospecific cycloaddition proceeding through a stepwise mechanism, as we have observed previously in certain cycloadditions with (*Z*)-stilbene.[20] However, in this case, we believe it is more

(13) (a) Kraus, G. A.; Nagy, J. O. *Tetrahedron* **1985**, *41*, 3537−3545. (b) Jones, R. C. F.; Nichols, J. R.; Cox, M. T. *Tetrahedron Lett.* **1990**, *31*, 2333−2336. (c) Ohno, M.; Komatsu, M.; Miyata, H.; Ohshiro, Y. *Tetrahedron Lett.* **1991**, *32*, 5813−5816. (d) Lerestif, J. M.; Bazureau, J. P.; Hamelin, J. *Tetrahedron Lett.* **1993**, *34*, 4639−4642.

(14) Tsuge, O.; Kanemasa, S.; Matsuda, K. *Chem. Lett.* **1984**, 1827−1830.

(15) (a) Stork, G.; Dowd, S. R. *J. Am. Chem. Soc.* **1963**, *85*, 2178−2179. (b) Wittig, G.; Frommeld, H. D.; Suchanek, P. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 683. (c) Wittig, G.; Hesse, A. In *Organic Syntheses*; Noland, W. E., Ed.; Wiley: New York, 1988; Collect. Vol. VI, pp 901−905.

(16) Lumbroso, H.; Bertin, D. M. *Bull. Soc. Chim. Fr.* **1970**, 1728−1740.

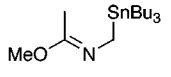
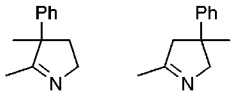
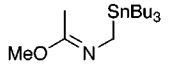
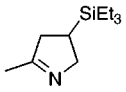
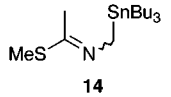
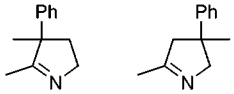
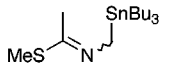
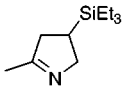
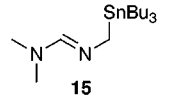
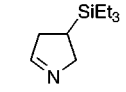
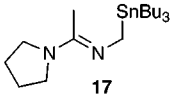
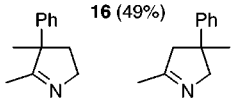
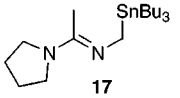
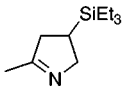
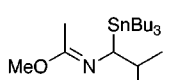
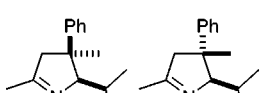
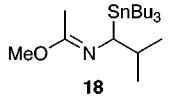
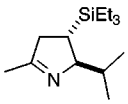
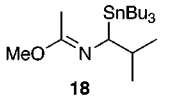
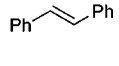
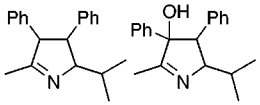
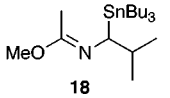
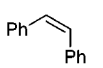
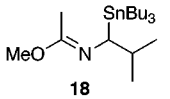
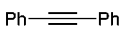
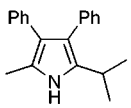
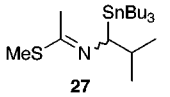
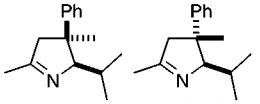
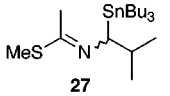
(17) Kandel, M.; Cordes, E. H. *J. Org. Chem.* **1967**, *32*, 3061−3066.

(18) Meese, C. O.; Walter, W.; Berger, M. *J. Am. Chem. Soc.* **1974**, *96*, 2259−2260.

(19) Kraus, G. A.; Neuenschwander, K. *J. Org. Chem.* **1981**, *46*, 4791−4792.

(20) Pearson, W. H.; Postich, M. J. *J. Org. Chem.* **1992**, *57*, 6354−6357.

Table 1. Generation and Cycloaddition of Acyclic Heteroatom-Substituted 2-Azaallyl Anions

Entry	Stannane	Anionophile	Product(s)[a]
no branching next to tin:			
1	 **10**		 **11** **12** 88% (10:1)[b]
2	 **10**		 **13** (12%)
3	 **14**		 **11** **12** 67% (1:4.5)[b]
4	 **14**		 **13** (88%)
5	 **15**		 **16** (49%)
6	 **17**		 **11** **12** 67% (8:1)[b]
7	 **17**		 **13** (56%)
branching next to tin:			
8	 **18**		 **19** **20** 93% (6.2:1)
9	 **18**		 **21** (97%)
10	 **18**		 **22,23** **24,25** 85% (6.8:1.2:5.2:1)[c]
11	 **18**		**22-25** 93% (1:3.0:3.6:2.8)[d] Pd/C xylenes reflux (68%)
12	 **18**		 **26** (33%)
13	 **27**		 **19** (89%) **20** (0%)
14	 **27**		**21** (63%)
15	**28**		**29** (53%)[e]
16	**28**		**30** (75%)
17	**31**		**21** (70%)

likely that the configuration of the center at C(3) in **22** and **23** is scrambled by imine−enamine tautomerization, a well-known process for imines with adjacent aromatic substituents.[21,22] Imine−enamine tautomerization may also explain the ease of oxidation of **22** and **23** to **24** and **25** (i.e., reaction of the enamine form with oxygen). The mixture of four compounds from entry 10 (Table 1) could be converted to a single pyrrole **26** by refluxing in xylene with palladium on carbon, proving the connectivity of **22**−**25**. The use of diphenylacetylene as the anionophile (entry 12, Table 1) led to the direct formation of the pyrrole **26**, albeit in modest yield. Other simple alkynes failed to lead to cyclic products. Anionophiles such as norbornene and ethyl acrylate fail to produce cycloadducts with the anion derived from **18**, as was expected based on our previous experience with simpler nonstabilized 2-azaallyl anions.

Stereoselectivity. The diastereoselectivities of the cycloadditions of heteroatom-substituted 2-azaallyl anions with vinyltriethylsilane (entries 9, 14, 16, and 17,

(21) Burchalter, J. H.; Short, J. H. *J. Org. Chem.* **1958**, *23*, 1278−1281.

(22) Pearson, W. H.; Schkeryantz, J. M. *J. Org. Chem.* **1992**, *57*, 6783−6789.

Scheme 3. Geometry of Heteroatom-Substituted 2-Azaallyl Anions

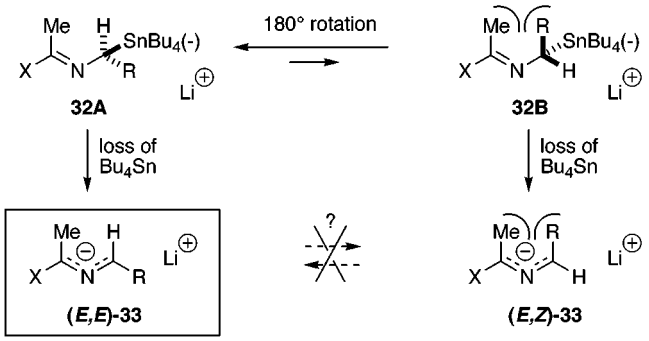


Table 1) and α-methylstyrene (entries 8, 13, and 15, Table 1) were consistent with those observed previously in cycloadditions with simple 2-azaallyl anions.[2] An explanation for the stereoselectivities is complicated by a lack of knowledge of the structure of the heterosubstituted 2-azaallyl anions, particularly with regard to their geometry. Semiempirical molecular orbital calculations (AM1, no counterion or solvent) on the simple anions $CH_3C(X)NCHCH_3(-)$ [X = OCH_3, SCH_3, and $N(CH_3)_2$] revealed little energy difference (<2 kcal/mol) between the four possible geometric isomers of each.[23] Assuming that the (*E*)-geometry of the imidate, thioimidate, or amidine is retained upon transmetalation, examination of conformers **32A** and **32B** of the intermediate pentavalent stannate (Scheme 3), where the C−Sn bond is properly oriented for overlap with the C=N π-system upon release of Bu_4Sn, leads to the prediction that conformation **32A** is more favorable on steric grounds. Thus, loss of Bu_4Sn will produce the *all-E* anion **(*E,E*)-33** rather than the anion **(*E,Z*)-33**. Interconversion of the anions **(*E,E*)-33** and **(*E,Z*)-33** is predicted to be slow on the basis of studies of 1,3-diphenyl-2-azaallylmetals[24,25] and allyllithiums,[26] although equilibration may still favor **(*E,E*)-33** on steric grounds.

Assuming the (*E,E*)-geometry of the heterosubstituted anions, the issue of endo/exo selectivity in the cycloaddition may be addressed (Figure 1). For cycloadditions with vinyltriethylsilane (entries 9, 14, 16, and 17, Table 1), an exo orientation (**35**) is apparently favored over the endo orientation **34** on steric grounds, as shown. For cycloadditions with α-methylstyrene (entries 8, 13, and 15, Table 1), the stereoselectivity may be rationalized by placing the phenyl group in the endo position in the transition state (**36**). Although this seems to be sterically unfavorable, the phenyl ring will be parallel to the 2-azaallyl anion and exerting minimal steric repulsion. There may also be some favorable interaction between the phenyl ring and the anion in this conformation (i.e., secondary orbital interaction). In contrast, the methyl group, regardless of the conformation about the C−CH_3 σ-bond, will always occupy a relatively large volume and thus prefer the exo orientation as in **36**.

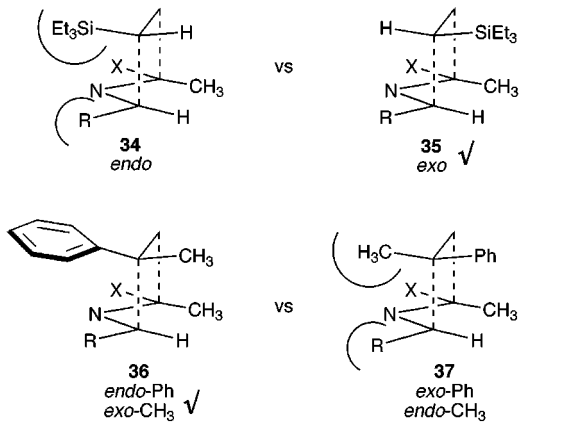


Figure 1. Endo versus exo approach of the anionophile.

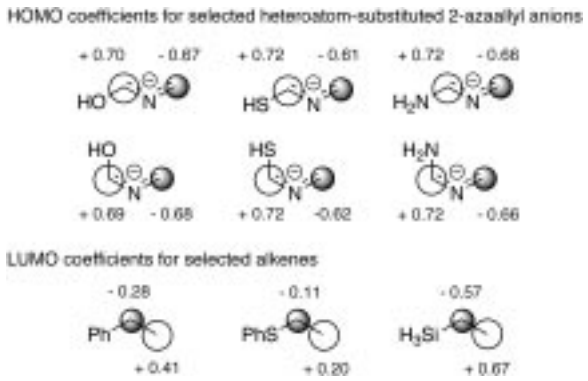
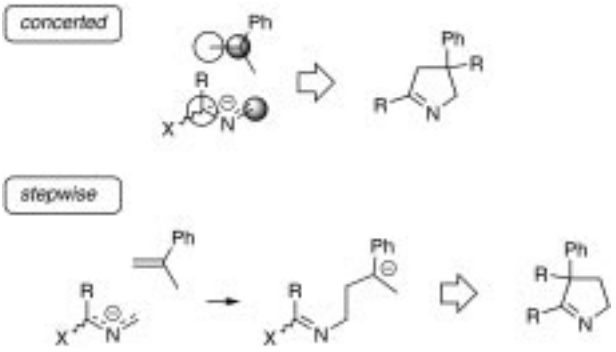


Figure 2. HOMO and LUMO coefficients (AM1).

Regioselectivity. The regioselectivity of the cycloadditions is generally consistent with predictions based on semiempirical calculations[27] of the HOMO and LUMO of the anions and alkenes (Figure 2).[23] These calculations do not consider solvent effects or the anion counterion. Although the calculations were performed on simplified molecules, additional substitution did not significantly change the orbital coefficients. Thus, the activating group on the anionophile (Ph or $SiEt_3$) was placed in the 4-position of the major regioisomeric 1-pyrroline in almost all cases (entries 2−5, 7−9, and 13−17, Table 1).[28,29] Two cycloadditions contradict predictions based on modeling: The imidate **10** and the amidine **17** produce mainly the 3-phenyl-substituted pyrroline **11** upon reaction with α-methylstyrene (entries 1 and 6, Table 1). This reversal in regiochemistry is especially intriguing given that the closely related thioimidate **14** (entry 3, Table 1) gives the "normal" 4-substituted pyrroline **12** as the major product,

(23) Stevens, E. P. Ph.D. Thesis, University of Michigan, 1997.
(24) Young, R. N.; Ahmad, M. A. *J. Chem. Soc., Perkin Trans* **1982**, *2*, 35−8.
(25) (a) Andrews, P. C.; Mulvey, R. E.; Clegg, W.; Reed, D. *J. Organomet. Chem.* **1990**, *386*, 287−297. (b) Andrews, P. C.; Armstrong, D. R.; Baker, D. R.; Mulvey, R. E.; Clegg, W.; Horsburgh, L.; O'Neil, P. A.; Reed, D. *Organometallics* **1995**, *14*, 427−39. (c) Andrews, P. C.; Armstrong, D. R.; Clegg, W.; Craig, F. J.; Dunbar, L.; Mulvey, R. E. *J. Chem. Soc., Chem. Commun.* **1997**, 319−320.
(26) Cabral, J.; Fraenkel, G. *J. Am. Chem. Soc.* **1992**, *114*, 9067−9075.
(27) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.
(28) In recent unpublished results by Michael A. Walters (Parke-Davis Pharmaceutical Research), semiempirical calculations (PM3[28a] modified for lithium[28b]) were performed on the cycloadditions of $MeC(X)NCH_2(-)Li(+)$ (X = OMe, SMe, or NMe_2) with α-methylstyrene. An idealized reaction coordinate involving a concerted cycloaddition was used. The 4-phenylpyrroline was predicted in all three cases. We thank Dr. Walters for sharing his results with us. (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220. (b) Anders, E.; Koch, R.; Freunscht, P. *J. Comput. Chem.* **1993**, *14*, 1301.
(29) For recent ab initio calculations on the cycloaddition of 2-azaallyl anions with alkenes, see: (a) Sauers, R. R. *Tetrahedron Lett.* **1996**, *37*, 7679−7682. (b) Neumann, F.; Lambert, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1998**, *120*, 3357−3370. Note that Schleyer concludes that the cycloaddition of the parent 2-azaallyl anion $CH_2{=}N{-}CH_2(-)Li(+)$ with ethylene proceeds by a stepwise rather than concerted process. We plan to reevaluate our computational results in light of Schleyer's work.

Scheme 4. Concerted versus Stepwise Cycloadditions



and the imidate **18** (entry 8, Table 1) and amidine **28** (entry 15, Table 1) also produce 4-substituted pyrrolines. Attempts to explain the apparently anomalous regiochemistry of **10** and **17** using PM3 semiempirical calculations of the reaction coordinate have not been successful; the 4-phenylpyrroline is predicted for all cases.[28,29]

An alternative explanation is that the anions derived from **10** and **17** undergo reaction via a stepwise mechanism,[29] whereas the anion derived from **14** proceeds by a concerted mechanism involving "normal" cycloaddition regioselectivity (Scheme 4). Thus, for **10** and **17**, nucleophilic addition of the least hindered end of the 2-azaallyl anion to the β-carbon of α-methylstyrene followed by ring closure would produce the 3-phenylpyrroline. We have previously obtained evidence that 2-azaallyl anion cycloadditions may proceed by a stepwise mechanism in cycloadditions with (*Z*)-stilbene,[20] including the present work (see entry 6 of Table 4).

Metalloenamine Trapping. As discussed above, the actual product of the cycloaddition reactions is a 1-metalloenamine (see **8** in Scheme 2). In situ trapping of this 1-metalloenamine with an electrophile would extend the synthetic utility of these cycloadditions. To that end, the stannane **18** was transmetalated with excess *n*-butyllithium in the presence of an anionophile, and the reaction was quenched by the addition of iodomethane, acetone, or the benzylic bromide **42** (Table 2). In each case, trapping of a 2-(lithiomethyl)pyrroline had occurred in a regioselective fashion.

Alternatively, a two-step procedure may be employed, where the cycloadduct (e.g., **21**) is isolated and then subjected to deprotonation and quenching with an electrophile in a separate step (Table 3). The best yields were obtained when *s*-butyllithium was used to deprotonate **21**, allowing a higher yield of alkylated products than the direct quenching method shown in Table 2, where *s*-butyllithium (or other alkyllithiums) is not useful due to poor transmetalation of the (2-azaallyl)stannanes.

B. Cyclic Heteroatom-Substituted 2-Azaallyl Anions. Our efforts to date in the 2-azaallyl anion area have involved inter- or intramolecular cycloadditions of acyclic anions to produce monocyclic pyrrolidines or fused azabicyclic compounds. The generation and cycloaddition of *cyclic* 2-azaallyl anions **45**, heretofore unknown species, would allow the assembly of bridged azabicyclic compounds **47** (Scheme 5).[30] Our initial research in this area

Table 2. Cycloaddition and Quenching with Various Electrophiles

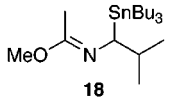
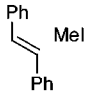
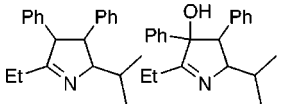
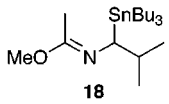
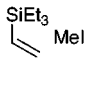
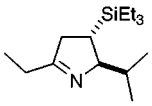
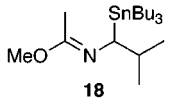
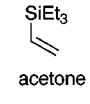
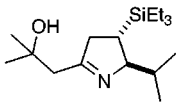
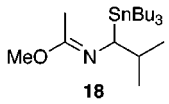
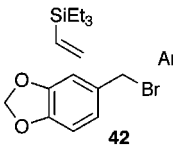
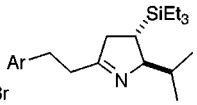
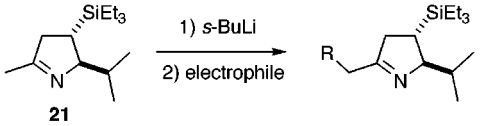
Entry	Stannane	Anionophile and Quench	Product(s)[a]
1	 **18**	 MeI	 **38** (51%)[b] **39** (26%)[b]
2	 **18**	 MeI	 **40** (65%)
3	 **18**	 acetone	 **41** (91%)
4	 **18**	 **42**	 **43** (23%)

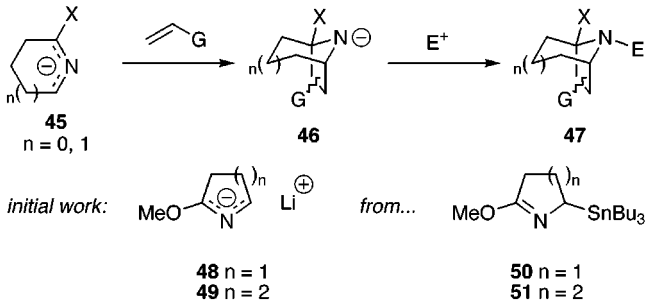
Table 3. Deprotonation and Quenhing of 1-Pyrrolines



21

electrophile	Product	Yield
MeI	**40:** R=Me	93%
42	**43:** R=CH_2Ar	80% (+ 15% **21**)
MeSSMe	**44:** R=SMe	48% (+ 23% **21** + 11% disulfenylated)

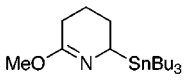
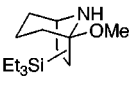
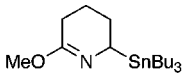
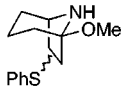
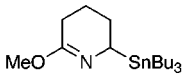
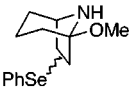
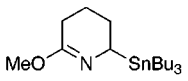
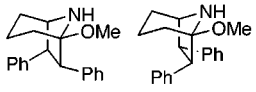
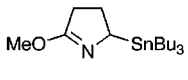
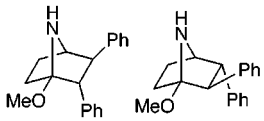
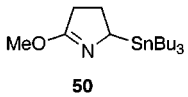
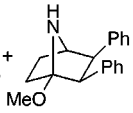
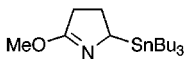
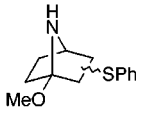
Scheme 5. Generation and Cycloaddition of Cyclic (2-Azaallyl)stannanes



involves the chemistry of the cyclic methoxy-substituted 2-azaallyl anions **48** and **49**, derived from the (2-azaallyl)-stannanes **50** and **51**. In contrast to the chemistry of the acyclic heteroatom-substituted 2-azaallyl anions discussed above, the intermediate *N*-lithiopyrrolidines **46** should not eliminate lithium methoxide, since strained bridgehead imines would result. Thus, we expected that the cycloadditions of the anions **48** and **49** would result

(30) A variety of cyclic azomethine ylides, both stabilized and nonstabilized, have been generated and used in dipolar cycloaddition reactions to afford bridged azabicyclic compounds. For representative examples, see: (a) Kozikowski, A. P.; Araldi, G. L.; Ball, R. G. *J. Org. Chem* **1997**, *62*, 503−509 and references therein. (b) Padwa, A.; Austin, D. J.; Precedo, L.; Zhi, L. *J. Org. Chem.* **1993**, *58*, 1144−50. (c) Pandey, G.; Lakshmaiah, G.; Ghatak, A. *Tetrahedron Lett.* **1993**, *34*, 7301−4. (d) Pandey, G.; Bagul, T. D.; Sahoo, A. K. *J. Org. Chem.* **1998**, *63*, 760−768. (e) Coppola, B. P.; Noe, M. C.; Schwartz, D. J.; Abdon, R. L., II.; Trost, B. M. *Tetrahedron* **1994**, *50*, 93−116.

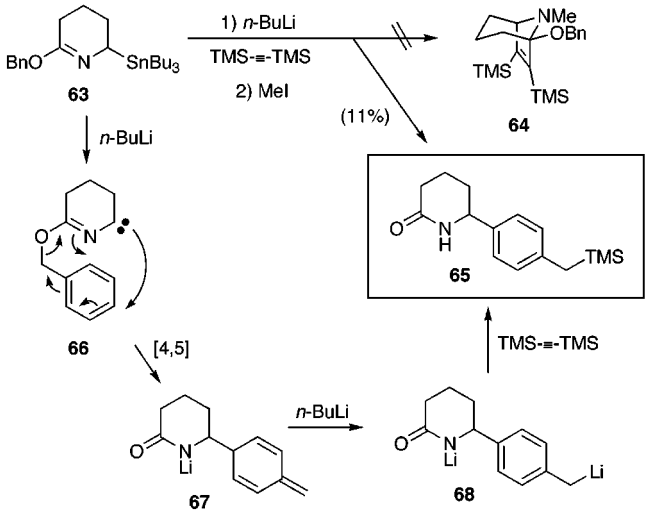
Table 4. Generation and Cycloaddition of Cyclic Heteroatom-Substituted 2-Azaallyl Anions

Entry	Stannane	Anionophile	Product(s)[a]
1	 **51**		 **52** (90%, one isomer)[b]
2	 **51**		 **53** (80%, 4.2:6.4:2.6:1)[c]
3	 **51**		 **54** (94%, 11:8:4:1)[d]
4	 **51**		 **55** (22%)[e] **56** (58%)[e]
5	 **50**		 **57** (44%) **58** (47%)
6	 **50**		**57** + **58** +  (5%) (63%) **59** (5%)
7	 **50**		 **60** (83%, 4.3:2.7:1.2:1)[f]

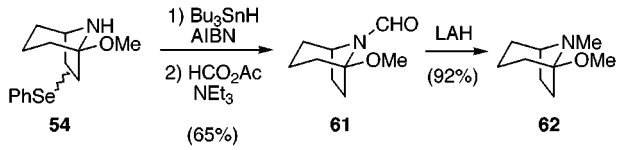
in the formation of the bridgehead-methoxylated azabicyclic compounds **47** (X = methoxy).

Transmetalation of the cyclic stannyl imidates **50** and **51** in the presence of various anionophiles afforded, after quenching with water, the 8-azabicyclo[3.2.1]octanes **52**−**56** and the 7-azabicyclo[2.2.1]heptanes **57**−**60** in good to excellent yields. Indeed, the bridgehead methoxy substituent was retained in all cases. The use of triethylvinylsilane (entry 1, Table 4) afforded a single regio- and stereoisomer of **52**, although we were unable to assign its exact structure. Phenyl vinyl sulfide and phenyl vinyl selenide afforded mixtures of regio- and stereoisomers, as is common for these anionophiles (entries 2, 3, and 7, Table 4). Recall that these two anionophiles did not lead to useful yields of cycloadducts when acyclic heteroatom-substituted 2-azaallyl anions were used (see above). The use of (*E*)-stilbene led to a mixture of endo and exo products where the trans relationship of the phenyl groups had been retained (entries 4 and 5, Table 4). The use of (*Z*)-stilbene, however, led to a nonstereospecific cycloaddition with respect to the alkene geometry, affording the expected cycloadduct **59** (with cis phenyl groups) as the minor product (entry 6, Table 4). The major products were **57** and **58**, both having a trans arrangement of the phenyl groups. We have observed similar nonstereospecific cycloadditions with (*Z*)-stilbene before.[20] The implication from these results is that a nonconcerted cycloaddition pathway is possible for 2-azaallyl anion cycloadditions. Overall, the results presented in Table 4 illustrate that the 2-azaallyl anion method is an efficient one for the synthesis of bridged azabicyclic compounds.

Scheme 6. An anionic [4,5]-Sigmatropic Rearrangement



Given the biological significance of tropane alkaloids (e.g., *N*-methyl-8-azabicyclo[3.2.1]octanes such as cocaine and its analogues),[31] we plan to examine the scope of the 2-azaallyl anion method for the preparation of these compounds. A few simple transformations are shown below. Regarding the installation of an *N*-methyl group,

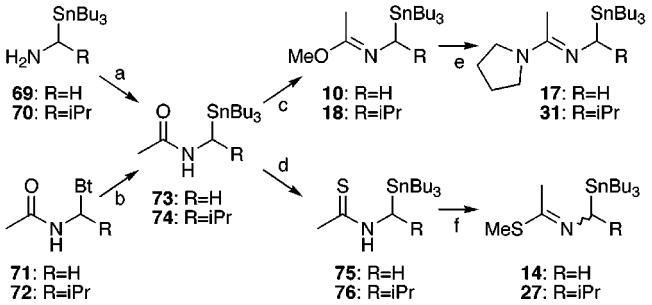


direct quenching of the 2-azaallyl anion cycloadditions with MeI did not afford useful amounts of *N*-methylated products, in contrast to our earlier work.[20,32] However, the four-component mixture of selenides **54** obtained in 94% yield in entry 3 of Table 4 could be deselenated with tri-*n*-butyltin hydride and *N*-formylated to produce **61**, which was reduced to the tropane **62** with $LiAlH_4$. Bridgehead oxygenated tropanes are well-known species (e.g., physoperuvine and the calystegines).[31] In fact, a simple demethylation of **62** would provide physoperuvine, but all attempts at hydrolysis or demethylation of **62** failed.

We are currently exploring the generation of cyclic 2-azaallyl anions with more easily removed heteroatoms (e.g., thio groups) or with no heteroatom substituents at all. With this goal in mind, we prepared the stannane **63**, which bears a benzyloxy group rather than a methoxy group (Scheme 6). During an attempted cycloaddition of the anion **66** with bis(trimethylsilyl)acetylene, the lactam **65** rather than the cycloadduct **64** was observed in low yield. While an intermolecular transfer of the benzyl group to a 2-azaallyl anion might be operative, an anionic [4,5]-sigmatropic rearrangement via **66** → **67** → **68** is an

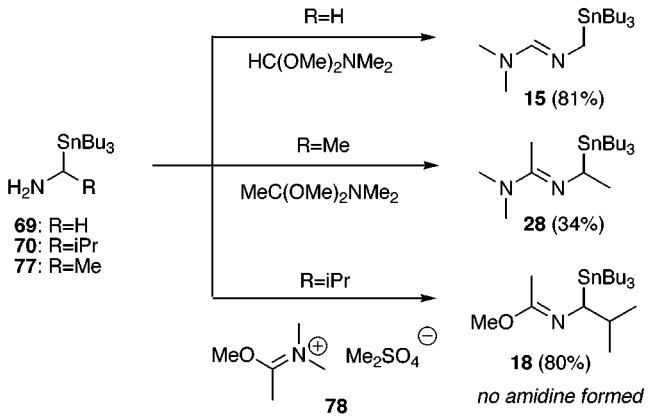
(31) Lounasmaa, M.; Tamminen, T. In *The Alkaloids*; Cordell, G. A., Ed.; Academic Press: New York, 1993; Vol. 44, pp 1−114.
(32) Pearson, W. H.; Szura, D. P.; Postich, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1329−1345.

Scheme 7. Synthesis of Acyclic Heteroatom-Substituted (2-Azaallyl)stannanes

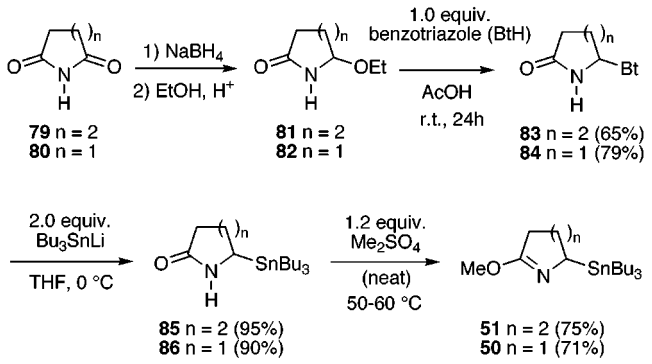


[a]AcCl, NEt_3: **73** (70%), **74** (66%); [b]Bu_3SnLi: **73** (72%), **74** (85%); [c]Me_2SO_4, neat, heat: **10** (61%), **18** (74%); [d]Lawesson's reagent: **75** (49%), **76** (80%); [e]pyrrolidine, $PhCO_2H$, DMF: **17** (90%); pyrrolidine, CF_3CO_2H, MeOH: **31** (9%); [f]Me_2SO_4: **14** (85%); **27** (67%).

Scheme 8. Attempts at Direct Formation of Amidines from Stannyl Amines



Scheme 9. Synthesis of Cyclic Heteroatom-Substituted (2-Azaallyl)stannanes



attractive alternative.[33] Attempts to improve the efficiency and explore the scope of this rearrangement are underway.

Preparation of Anion Precursors

For the current methodology to be useful, simple methods for the synthesis of the requisite stannanes are important. We have developed very convenient routes to these materials, as shown in Schemes 7−9.

For the preparation of the precursors of acyclic heteroatom-substituted 2-azaallyl anions, the stannyl amides **73** and **74** were key intermediates, prepared by two routes (Scheme 7). In the first route, acylation of the readily available α-amino stannanes **69** and **70**[20,34] afforded **73** and **74**. Alternatively, displacement of the benzotriazoles **71** and **72**[35,36] with Bu_3SnLi is an efficient route to these same materials.[37,38] *O*-Alkylation of **73** and **74** with neat methyl sulfate produced the imidates **10** and **18** in an efficient manner. The amidines **17** and **31** could then be prepared from **10** and **18** by an exchange reaction with pyrrolidine. Thionation of **73** and **74** produced the thioamides **75** and **76**, which were *S*-methylated to give the thioimidates **14** and **27**.

An alternate route to stannyl amidines was also examined (Scheme 8). Treatment of the amino stannanes **69** and **77** with an appropriate amide dimethyl acetal afforded the stannyl amidines **15** and **28** as desired. Curiously, similar reactions of the more hindered amino stannane **70** with these reagents failed to produce the desired amidines. Resorting to the iminium salt **78**[39,40] resulted in an efficient reaction, although the desired amidine was not formed. Instead, the imidate **18** was isolated in good yield. Apparently, the highly crowded tetrahedral intermediate eliminates dimethylamine rather than methanol for steric reasons.

The precursors **50** and **51** of cyclic methoxy-substituted 2-azaallyl anions were prepared as shown in Scheme 9. Partial reduction of the imides **79** and **80** followed by exchange with ethanol afforded the known ethoxy lactams **81** and **82**.[41] Exchange of the ethoxy group with benzotriazole afforded the benzotriazolyl lactams **83** and **84**, which were subjected to reaction with Bu_3SnLi as in our previous work[37] to afford the stannyl lactams **85** and **86**. *O*-Methylation as usual gave the desired stannyl imidates **51** and **50**, respectively.

Conclusion

Nonstabilized 2-azaallyl anions bearing heteroatom substituents were generated by tin−lithium exchange and found to undergo efficient [3 + 2] cycloadditions with alkenes to provide 1-pyrrolines after loss of the lithium salt of the heteroatom substituent. Oxygen-, sulfur-, and nitrogen-substituted anions were studied. The initially formed 1-pyrrolines were found to be deprotonated under the reaction conditions to afford 1-metalloenamines, which could be quenched with alkyl halides, carbonyl compounds, or MeSSMe to provide further functionalized 1-pyrrolines. The regio- and stereoselectivities of the cycloadditions were studied and rationalized, although a unified explanation for all cases was not possible, perhaps due to the operation of two cycloaddition mechanisms (i.e., concerted and stepwise). Cyclic methoxy-substituted 2-azaallyl anions were generated and were found to undergo cycloadditions with alkenes to afford

(33) (a) Liard, T.; Ollis, D. W. *J. Chem. Soc., Chem. Commun.* **1973**, 658−660. (b) Ollis, D. W.; Somanathan, R.; Sutherland, I. O. *J. Chem. Soc., Chem. Commun.* **1973**, 661.

(34) Chong, J. M.; Park, S. B. *J. Org. Chem.* **1992**, *57*, 2220−2222.
(35) Katritzky, A. R.; Drewniak, M.; Lue, P. *J. Org. Chem.* **1988**, *53*, 5854−5856.
(36) Katritzky, A. R.; Drewniak, M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2339−2344.
(37) Pearson, W. H.; Stevens, E. P. *Synthesis* **1994**, 904−906.
(38) Katritzky, A. R.; Chang, H.-V.; Wu, J. *Synthesis* **1994**, 907−908.
(39) Weintraub, L.; Oles, S. R.; Kalish, N. *J. Org. Chem.* **1968**, *33*, 1679−1681.
(40) Bredereck, H.; Effenberger, F.; Beyerlin, H. P. *Chem. Ber.* **1964**, *97*, 3076−3080.
(41) Hubert, J. C.; Wijnberg, J. P. B. A.; Speckamp, W. N. *Tetrahedron* **1975**, *31*, 1437−1441.

bridged azabicyclic compounds (1-methoxy-7-azabicyclo-[2.2.1]heptanes and 1-methoxy-8-azabicyclo[3.2.1]octanes). These are the first examples of cyclic nonstabilized 2-azaallyl anions. The current methodology, which involves the use of electron-rich alkenes as cycloaddition partners, offers an attractive alternative to nitrile ylide cycloaddition chemistry, where electron-poor alkenes are generally used. The intermediacy of 1-metalloenamines further enhances the potential synthetic utility of the 2-azaallyl anion route to 1-pyrrolines.

Experimental Section

A. General Methods. Reagents and starting materials were obtained from commercial suppliers and used without further purification unless otherwise noted. Methylene chloride (CH_2Cl_2), triethylamine, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and benzene were distilled from calcium hydride under a nitrogen atmosphere. Methanol (MeOH) was distilled from magnesium turnings under a nitrogen atmosphere. Tetrahydrofuran (THF) and ether were distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. Chloroform was filtered through basic alumina. Alkyllithiums were titrated by the method of Gilman and Haubein[42] or Ronald, Winkle, and Lansinger.[43] All reactions were conducted in oven- or flame-dried glassware under an anhydrous nitrogen atmosphere with standard precautions taken to exclude moisture. Chromatography refers to flash chromatography on silica gel (230−400 mesh) unless otherwise noted. Radial chromatography was performed on a Harrison Research chromatotron with Merck 60 PF254 silica or Merck 60 GF254 aluminum oxide. Thin-layer chromatography (TLC) was performed on 0.25 mm Merck precoated silica plates (60 F-254).

B. Cycloadditions. General Procedure for Cycloadditions. 2,3-Dimethyl-3-phenyl-1-pyrroline (11) and 2,4-Dimethyl-4-phenyl-1-pyrroline (12) from Imidate 10 (Table 1, Entry 1). A solution of the imidate **10** (196 mg, 0.52 mmol) and α-methylstyrene (130 mg, 1.13 mmol) in THF (2 mL) was added dropwise to a solution of *n*-butyllithium (1.2 mL, 2.52 mmol, 2.1 M in hexanes) in THF (2 mL) at −78 °C. After 30 min, saturated aqueous NH_4Cl was added and the mixture was extracted with ether (2×). The organic extracts were combined, dried ($MgSO_4$), filtered, and concentrated. Chromatography of the resultant oil (0−50% EtOAc/hexane gradient) afforded 79 mg (88%) an inseparable 10:1 mixture of **11** and **12** as judged by ^{1}H NMR. Data for **11**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38−7.15 (m, 5 H), 3.85 (br t, 2 H, J = 6.2 Hz), 2.20−2.01 (m, 2 H), 1.80 (s, 3 H) 1.54 (s, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 179.7, 145.0, 128.6, 126.4, 125.9, 57.6, 42.3, 29.9, 22.2, 16.0. Data for **12**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36−7.18 (m, 5 H), 3.99 (br s, 2 H), 2.91 (d, 1 H, J = 16.9 Hz), 2.64 (d, 1 H, J = 17.0 Hz), 2.08 (s, 3 H), 1.37 (s, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 174.4, 148.7, 128.4, 125.8, 125.8, 74.0, 53.4, 46.8, 29.8, 20.2. Data for mixture: IR (in $CHCl_3$) 1644 (m), 1599 (w) cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel intensity) 173 (9), 131 (18), 118 (10), 117 (100); HRMS (EI, 70 eV) calcd for $C_{12}H_{15}N$ M^+ 173.1204, found 173.1204. **From Thioimidate 14 (Table 1, Entry 3).** Using the general procedure, the thioimidate **14** (223 mg, 0.57 mmol) and α-methylstyrene (184 mg, 1.56 mmol) in THF (2 mL) were combined with *n*-butyllithium (1.4 mL, 2.9 mmol, 2.1 M in hexanes) in THF (2 mL) to afford, after chromatography, 66 mg (67%) of a 1:4.5 mixture of **11** and **12** as judged by ^{1}H NMR. **From Amidine 17 (Table 1, Entry 6).** Using the general procedure, the amidine **17** (110 mg, 0.27 mmol) and α-methylstyrene (78 mg, 0.66 mmol) in THF (2 mL) were combined with *n*-butyllithium (0.75 mL, 1.40 mmol, 1.9 M in hexanes) in THF (2 mL) to afford, after chromatography, 31 mg (67%) of an 8:1 mixture of **11** and **12** as judged by ^{1}H NMR.

2-Methyl-4-(triethylsilyl)-1-pyrroline (13) from Imidate 10 (Table 1, Entry 2). Using the general procedure, the imidate **10** (240 mg, 0.63 mmol) and triethylvinylsilane (180 mg, 1.3 mmol) in THF (2 mL) were combined with *n*-butyllithium (1.4 mL, 2.9 mmol, 2.1 M in hexanes) in THF (2 mL) to afford, after chromatography (10−40% EtOAc/hexane gradient), 15 mg (12%) of the title compound as an oil: R_f = 0.12 (50% EtOAc/hexane); IR (neat) 1651 (m), 1457 (m), 1434 (m) (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 4.00 (dd, 1 H, J = 15.0, 9.6 Hz), 3.55 (br t, 1 H, J = 12.3 Hz), 2.62 (dd, 1 H, J = 17.4, 10.8 Hz), 2.30 (br t, J = 13.7 Hz), 2.01 (s, 3 H), 1.46 (pent, 1 H, J = 9.8 Hz), 0.92 (t, 9 H, J = 7.9 Hz), 0.53 (q, 6 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 175.0, 63.3, 41.4, 21.0, 19.5, 7.5, 2.6; MS (CI, NH_3) *m*/*z* (rel intensity) 200 (10), 199 (35), 198 (100, M + H), 196 (4), 168 (12), 156 (7), 132 (10), 104 (5); HRMS (CI, NH_3) calcd for $C_{11}H_{14}NSi$ $(M + H)^+$ 198.1678, found 198.1681. **From Thioimidate 14 (Table 1, Entry 4).** Using the general procedure, the thioimidate **14** (220 mg, 0.56 mmol) and triethylvinylsilane (180 mg, 1.3 mmol) in THF (2 mL) were combined with *n*-butyllithium (1.5 mL, 3.2 mmol, 2.1 M in hexanes) in THF (2 mL) afford, after chromatography, 97 mg (88%) of the title compound. **From Amidine 17 (Table 1, Entry 7).** Using the general procedure, the amidine **17** (103 mg, 0.25 mmol) and triethylvinylsilane (80 mg, 0.56 mmol) in THF (2 mL) were combined with *n*-butyllithium (0.75 mL, 1.40 mmol, 1.9 M in hexanes) in THF (2 mL) to afford, after chromatography, 27 mg (56%) of the title compound.

4-(Triethylsilyl)-1-pyrroline (16) (Table 1, Entry 5). Using the general procedure, the amidine **15** (51 mg, 0.14 mmol) and triethylvinylsilane (65 mg, 0.45 mmol) in THF (2 mL) were combined with *n*-butyllithium (0.50 mL, 0.77 mmol, 1.55 M in hexanes) in THF (2 mL) to afford, after chromatography (0−100% EtOAc/hexane gradient), 12 mg (49%) of the title compound as an oil: R_f = 0.20 (EtOAc); IR (neat) 1654 (w), 1458 (m), 1239 (m), 1203 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.60 (br s, 1 H), 4.16−4.00 (m, 1 H), 3.68−3.52 (m, 1 H), 2.83−2.67 (m, 1 H), 2.42−2.27 (m, 1 H), 1.31 (pent, 1 H, J = 10.3 Hz), 0.92 (t, 9 H, J = 7.9 Hz), 0.53 (q, 6 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 166.9, 63.6, 39.3, 18.3, 7.5, 2.7; MS (EI, 70 eV) *m*/*z* (rel intensity) 183 (14, M), 154 (40), 142 (29), 115 (50), 87 (100); HRMS (EI, 70 eV) calcd for $C_{10}H_{21}NSi$ $(M + H)^+$ 183.1443, found 183.1434.

(4*S,5*R**)-2,4-Dimethyl-5-(1-methylethyl)-4-phenyl-1-pyrroline (19) and (4*R**,5*R**)-2,4-Dimethyl-5-(1-methylethyl)-4-phenyl-1-pyrroline (20) from Imidate 18 (Table 1, Entry 8).** Using the general procedure, the imidate **18** (1.00 g, 2.39 mmol) and α-methylstyrene (0.65 mL, 5.00 mmol) in THF (8 mL) were combined with *n*-butyllithium (5.70 mL, 12.0 mmol, 2.1 M in hexanes) in THF (8 mL) to afford, after chromatography (0−50% EtOAc/hexane gradient), 390 mg (76%) of **19** as an oil and 90 mg (17%) of a 1:5 mixture of **19** and **21**, respectively. The relative configuration was assigned by dNOE experiments. Data for **19**: R_f = 0.17 (50% EtOAc/hexane); IR (in $CHCl_3$) 1732 (m), 1650 (s), 1602 (m), 1497 (s), 1430 (s), 1381 (s), 1317 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33−7.14 (m, 5 H), 3.91−3.87 (m, 1 H), 3.07 (d, 1 H, J = 16.8 Hz), 2.45 (d, 1 H, J = 16.8 Hz), 2.14 (m, 3 H), 1.85−1.70 (m, 1 H), 1.40 (s, 3 H,), 0.93 (d, 3 H, J = 6.9 Hz), 0.45 (d, 3 H, J = 6.6 Hz); dNOE ($CDCl_3$), irradiation at 3.89 ppm (H-5α) produced a 0.3% enhancement of the signal at 7.33−7.14 ppm (Ar−H-4β) and a 1.4% enhancement of the signal at 1.40 ppm (CH_3-4α), irradiation at 1.40 ppm (CH_3-4α) produced a 14.6% enhancement of the signal at 3.91−3.87 ppm (H-5α); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 173.7, 145.7, 128.0, 126.8, 125.8, 87.2, 52.0, 49.5, 32.3, 30.2, 21.5, 20.3, 16.7; MS (EI, 70 eV) *m*/*z* (rel intensity) 215 (23, M), 172 (28); HRMS (EI, 70 eV) calcd for $C_{15}H_{21}N$ M^+ 215.1674, found 215.1685. Data for **20**: R_f = 0.17 (30% EtOAc/hexane); IR (in $CHCl_3$) 1648 (m), 1601 (m), 1498 (m), 1469 (m), 1445 (m), 1431 (m), 1379 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45−7.15 (m, 5 H), 3.78−3.70 (m, 1 H), 2.95 (d, 1 H, J = 17.1 Hz,), 2.55 (d, 1 H, J = 17.1 Hz), 2.06 (d, 3 H, J = 2.1 Hz), 1.98−1.82 (m, 1 H), 1.36 (s, 3 H), 1.17 (d, 3 H, J = 6.5 Hz), 0.63 (d, 3 H, J = 6.6 Hz); dNOE ($CDCl_3$), irradiation at 3.74 ppm (H-5α) produced a 5.0% enhancement of the signal at 7.45−7.15 ppm (Ar−H-4α) and no enhance-

(42) Gilman, H.; Haubein, R. H. *J. Am. Chem. Soc.* **1955**, *66*, 1515.
(43) Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87.

ment of the signal at 1.36 ppm (CH_3-4β), irradiation at 1.36 ppm (CH_3-4β) produced no enhancement of the signal at 3.78−3.70 ppm (H-5α); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 170.8, 148.1, 128.1, 126.1, 125.7, 87.7, 59.1, 49.2, 29.7, 29.4, 22.0, 21.2, 20.3, 20.2; MS (EI, 70 eV) *m*/*z* (rel intensity) 215 (50, M), 172 (52), 131 (21), 129 (13), 115 (14), 97 (96), 82 (100); HRMS (EI, 70 eV) calcd for $C_{15}H_{21}N$ M^+ 215.1674, found 215.1670. **From Thioimidate 27 (Table 1, Entry 13).** Using the general procedure, the thioimidate **27** (240 mg, 0.55 mmol) and α-methylstyrene (160 mg, 1.35 mmol) in THF (2 mL) were combined with *n*-butyllithium (1.40 mL, 2.80 mmol, 2.0 M in hexanes) in THF (2 mL) to afford, after chromatography, 106 mg (89%) of **19** as a single stereoisomer.

(4*S,5*R**)-2-Methyl-5-(1-methylethyl)-4-(triethylsilyl)-1-pyrroline (21) from Imidate 18 (Table 1, Entry 9).** Using the general procedure, the imidate **18** (250 mg, 0.60 mmol) and triethylvinylsilane (192 mg, 1.35 mmol) in THF (2 mL) were combined with *n*-butyllithium (1.40 mL, 2.94 mmol, 2.1 M in hexanes) in THF (2 mL) to afford, after chromatography (0−30% EtOAc/hexane gradient), 138.6 mg (97%) of a single stereoisomer of the title compound as a clear oil. The relative configuration was assigned by dNOE experiments. Data for **21**: R_f = 0.25 (30% EtOAc/hexane); IR (in $CHCl_3$) 1654 (s), 1465 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.96−3.90 (m, 1 H), 2.68 (ddd, 1 H, J = 17.6, 11.3, 3.0 Hz), 2.34 (dd, 1 H, J = 17.7, 7.4 Hz), 2.01 (d, 3 H, J = 1.6 Hz), 1.74 (dhept, 1 H, J = 6.8, 3.8 Hz), 1.26 (pent, 1 H, J = 5.0 Hz), 1.01 (d, 3 H, J = 6.8 Hz), 0.94 (t, 9 H, J = 7.7 Hz), 0.82 (d, 3 H, J = 6.8 Hz), 0.53 (q, 6 H, J = 8.0 Hz); dNOE ($CDCl_3$), irradiation at 3.9 ppm (H-5a) failed to produce an enhancement of the signal at 1.2 ppm (H-4b), irradiation at 1.2 ppm (H-4b) produced a 5.9% enhancement of the signal at 3.9 ppm (H-5a) and a 13% enhancement of the signal at 1.7 ppm (CH-5b); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.8, 80.6, 42.0, 33.7, 22.5, 20.2, 19.2, 17.3, 7.5, 2.6; MS (EI, 70 eV) *m*/*z* (rel intensity) 239 (2, M), 210 (8), 197 (18), 196 (100); HRMS (EI, 70 eV) calcd for $C_{14}H_{29}NSi$ M^+ 239.2069, found 239.2058. **From Thioimidate 27 (Table 1, Entry 14).** Using the general procedure, the thioimidate **27** (290 mg, 0.67 mmol) and triethylvinylsilane (225 mg, 1.59 mmol) in THF (2 mL) were combined with *n*-butyllithium (1.50 mL, 3.75 mmol, 2.5 M in hexanes) in THF (3 mL) to afford, after chromatography, 101 mg (63%) of the title compound as a single stereoisomer. **From Amidine 31 (Table 1, Entry 17).** Using the general procedure, the amidine **31** (92 mg, 0.20 mmol) and triethylvinylsilane (71 mg, 0.50 mmol) in THF (3 mL) were combined with *n*-butyllithium (0.50 mL, 1.25 mmol, 2.5 M in hexanes) in THF (2 mL) to afford, after chromatography, 34 mg (70%) of the title compound as a single stereoisomer.

3,4-Diphenyl-2-methyl-5-(2-methylethyl)-2-pyrroline (22 and 23) and 3,4-Diphenyl-3-hydroxy-2-methyl-5-(2-methylethyl)-2-pyrroline (24 and 25) from *trans*-Stilbene (Table 1, Entry 10). Using the general procedure, the imidate **18** (230 mg, 0.54 mmol) and *trans*-stilbene (206 mg, 1.1 mmol) in THF (1.5 mL) were combined with *n*-butyllithium (1.3 mL, 2.7 mmol, 2.1 M in hexanes) in THF (2 mL) to afford, after chromatography (0−20% EtOAc/hexane gradient), 64 mg (41%) of **22** as a single stereoisomer and 68 mg (44%) of a mixture of at least four stereoisomers and imine−enamine tautomers of **22**−**25**. Assignment of the relative configuration of the isolated isomers was not performed. Data for **22**: R_f = 0.29 (25% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42−7.15 (m, 10 H), 4.05−3.97 (m, 2 H,), 3.47 (dd, 1 H, J = 7.1, 3.9 Hz), 2.04 (d, 3 H, J = 2.0 Hz), 1.70−1.60 (m, 1 H), 1.08 (d, 3 H, J = 6.5 Hz), 0.71 (d, 3 H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 176.0, 142.2, 139.9, 129.0, 128.3, 128.1, 127.5, 127.0, 126.4, 81.6, 66.8, 57.1, 29.0, 20.8, 20.7, 18.9; MS (EI, 70 eV) *m*/*z* (rel intensity) 277 (20, M), 236 (35), 234 (11), 194 (23), 193 (94), 180 (14), 145 (14), 97 (100); HRMS (EI, 70 eV) calcd for $C_{20}H_{23}N$ M^+ 277.1830, found 277.1835. Data for mixture of **22**−**25**: R_f = 0.29−0.10 (25% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.18, 2.05, 1.98, 1.92 (all doublets corresponding to the N=CCH_3 signal for four different isomers). **From *cis*-Stilbene (Table 1, Entry 11).** Using the general procedure, the imidate **18** (222 mg, 0.53 mmol) and *cis*-stilbene (200 mg, 1.1 mmol) in THF (1.5 mL) were combined with *n*-butyllithium (1.3 mL, 2.7 mmol, 2.1 M in hexanes) in THF (2 mL) to afford, after chromatography (0−20% EtOAc/hexane gradient), 14 mg (9%) of **22** as a single stereoisomer, 86 mg (59%) of **23** and **24** as a mixture of stereoisomers and/or imine−enamine tautomers, and 38 mg (25%) of **25** as a single stereoisomer. Data for **25**: R_f = 0.16 (25% EtOAc/hexane); IR (in $CHCl_3$) 3335 (w)1732 (m), 1633 (m), 1494 (m), 1454 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.12−6.98 (m, 8 H), 6.75−7.70 (m, 2 H), 4.01−3.92 (m, 1 H), 3.52 (d, 1 H, J = 5.7 Hz), 2.67 (br s, 1 H), 2.11 (d, 3 H, J = 2.6 Hz), 2.10−1.95 (m, 1 H), 1.30 (d, 3 H, J = 6.5 Hz), 0.60 (d, 3 H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.6, 139.7, 136.9, 130.2, 127.3, 127.1, 126.7, 126.2, 92.1, 80.0, 63.3, 28.8, 22.0, 20.1, 16.5; MS (EI, 70 eV) *m*/*z* (rel intensity) 210 (17), 209 (100), 188 (30), 131 (17), 105 (35), 103 (12); HRMS (CI, NH_3) calcd for $C_{20}H_{24}NO$ $(M + H)^+$ 294.1852, found 294.1856.

3,4-Diphenyl-5-methyl-2-(1-methylethyl)pyrrole (26) from Imidate 18 (Table 1, Entry 12). Using the general procedure, the imidate **18** (230 mg, 0.553 mmol) and diphenylacetylene (230 mg, 1.28 mmol) in THF (2 mL) were combined with *n*-butyllithium (1.30 mL, 2.73 mmol, 2.1 M in hexanes) in THF (2 mL) to afford, after chromatography (0−5% EtOAc/hexane gradient), 50 mg (33%) of the title compound as an orange oil: R_f = 0.58 (25% EtOAc/hexane); IR (in $CHCl_3$) 3464 (s), 1604, 1498, 1444 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.72 (s, 1 H), 7.25−7.00 (m, 10 H), 3.25−3.08 (hept, 1 H, J = 7.0 Hz), 2.32 (s, 3 H), 1.24 (d, 6 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 136.8, 136.5, 133.2, 130.7, 130.5, 127.8, 127.7, 125.4, 125.1, 122.5, 120.9, 119.8, 25.2, 23.3, 12.1; MS (EI, 70 eV) *m*/*z* (rel intensity) 276 (9), 275 (41, M), 261 (21), 260 (100), 244 (11), 230 (6); HRMS (EI, 70 eV) calcd for $C_{20}H_{21}N$ M^+ 275.1674, found 275.1687. **From Pyrrolines 22**−**25.** Pyrrolines **22**−**25** (130 mg, 0.46 mmol) and 30% Pd/C (95 mg, 0.27 mmol) were combined in xylene (5 mL) and heated at reflux. After 4 h, the reaction mixture was concentrated and directly chromatographed (0−10% EtOAc/hexane) to afford 86 mg (68%) of the title compound as a light orange oil.

(4*S,5*R**)-4-Phenyl-2,4,5-trimethyl-1-pyrroline (29) (Table 1, Entry 15).** Using the general procedure, the amidine **28** (208 mg, 0.52 mmol) and α-methylstyrene (150 mg, 1.3 mmol) in THF (2 mL) were combined with 1.0 mL, 2.7 mmol, 2.7 M in hexanes) in THF (3 mL) to afford, after chromatography (0−100% EtOAc/hexane), 51 mg (53%) of the title compound as an oil as well as 14 mg (14%) of an impure mixture of stereoisomeric pyrrolines. The stereochemical assignment was based on comparison to **19**. Data for **29**: R_f = 0.10 (EtOAc); IR (neat) 1646 (m), 1496 (m), 1445 (m), 1430 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.34−7.21 (m, 5 H), 4.08 (q, 1 H, J = 7.0 Hz), 3.12 (d, 1 H, J = 16.6 Hz), 2.58 (d, 1 H, J = 16.7 Hz), 2.10 (s, 3 H), 1.39 (s, 3 H), 0.72 (d, 3 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 173.0, 145.6, 128.0, 126.7, 125.9, 49.8, 29.7, 20.5, 17.3; MS (EI, 70 eV) *m*/*z* (rel intensity) 188 (6), 187 (28, M), 186 (5), 172 (11), 131 (9), 69 (100); HRMS (EI, 70 eV) calcd for $C_{13}H_{17}N$ M^+ 187.1361, found 187.1347.

(4*S,5*R**)-2,5-Dimethyl-4-(triethylsilyl)-1-pyrroline (30) (Table 1, Entry 16).** Using the general procedure, the amidine **28** (199 mg, 0.49 mmol) and triethylvinylsilane (157 mg, 1.10 mmol) in THF (2 mL) were combined with *n*-butyllithium (1.0 mL, 2.7 mmol, 2.7 M in hexanes) in THF (3 mL) to afford, after chromatography (0−100% EtOAc/hexane gradient), 78 mg (75%) of the title compound as a single stereoisomer. The stereochemical assignment was made by comparison to **21**. Data for **30**: R_f = 0.15 (EtOAc); IR (neat) 1654 (m), 1457 (m), 1435 (m), 1416 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 3.95−3.97 (m, 1 H), 2.70 (ddd, 1 H, J = 19.3, 10.6, 2.4 Hz), 2.37 (ddd, 1 H, J = 17.8, 10.6, 2.5 Hz), 1.97 (d, 3 H, J = 1.8 Hz), 1.29 (d, 3 H, J = 6.6 Hz), 1.06−0.98 (m, 1 H), 0.93 (t, 9 H, J = 8.0 Hz), 0.57 (q, 6 H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 173.0, 70.5, 42.6, 29.2, 23.4, 19.4, 7.5, 2.7; MS (EI, 70 eV) *m*/*z* (rel intensity) 211 (17, M), 196 (37), 182 (54), 156 (31), 115 (65), 87 (100); HRMS (EI, 70 eV) calcd for $C_{12}H_{25}NSi$ M^+ 211.1756, found 211.1750.

3,4-Diphenyl-2-ethyl-5-(1-methylethyl)-1-pyrroline (38) and 3,4-Diphenyl-2-ethyl-3-hydroxy-5-(1-methylethyl)-1-

pyrroline (39) (Table 2, Entry 1). A solution of the imidate **18** (205 mg, 0.49 mmol) and *trans*-stilbene (210 mg, 1.17 mmol) in THF (2 mL) was added slowly to a solution of *n*-butyllithium (1.20 mL, 2.52 mmol, 2.1 M in hexanes) in THF (2 mL) at −78 °C. After 30 min, iodomethane (0.18 mL, 3.97 mmol) was added. After warming to room temperature, the reaction was diluted in ether, washed with saturated NH_4Cl (aq), dried ($MgSO_4$), filtered, and concentrated to provide an oil. Chromatography (0−15% EtOAc/hexane gradient) afforded 72 mg (51%) **38** and 37 mg (26%) **39**. The relative configuration of the products was not determined. Data for **38**: $R_f = 0.55$ (35% EtOAc/hexane); IR (neat) 1698 (m), 1643 (m), 1601 (m), 1494 (s), 1453 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.36−7.10 (m, 10 H), 4.15−4.10 (m, 1 H), 4.07−4.00 (m, 1 H), 3.50−3.44 (m, 1 H), 2.43 (dhex, 1 H, J = 7.6, 1.3 Hz), 2.26 (dhex, 1 H, J = 7.6, 2.3 Hz), 1.72−1.61 (m, 1 H), 1.16 (t, 3 H, J = 7.5 Hz), 1.08 (d, 3 H, J = 6.6 Hz), 0.74 (d, 3 H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 179.9, 142.0, 140.2, 128.9, 128.2, 128.1, 127.6, 126.9, 126.3, 81.2, 64.5, 57.0, 29.2, 25.9, 20.8, 20.6, 10.9; MS (EI, 70 eV) *m*/*z* (rel intensity) 291 (18, M), 236 (35), 209 (23), 194 (24), 193 (97), 111 (100); HRMS (EI, 70 eV) calcd for $C_{21}H_{25}N$ M^+ 291.1987, found 291.1974. Data for **39**: $R_f = 0.45$ (35% EtOAc/hex); IR (neat) 1601 (w), 1495 (m), 1448 (s); ^1H NMR (DMSO-d_6, 360 MHz) δ 7.12−7.05 (m, 3 H), 7.02−6.95 (m, 3 H), 6.84−6.78 (m, 2 H), 6.65−6.58 (m, 2 H), 4.01 (d, 1 H, J = 8.1 Hz), 3.88−3.81 (m, 1 H), 3.32 (s, 1 H), 2.50−2.38 (m, 1 H), 2.08−1.99 (m, 1 H), 1.80 (hex, 1 H, J = 6.8 Hz), 1.14 (t, 3 H, J = 7.3 Hz), 0.93 (d, 3 H, J = 6.7 Hz), 0.88 (d, 3 H, J = 6.8 Hz); ^{13}C NMR (DMSO-d_6, 90 MHz) δ 176.5, 138.5, 135.5, 128.7, 127.8, 127.3, 125.9, 125.6, 102.4, 75.1, 52.6, 32.3, 22.4, 20.0, 18.9, 10.1; MS (CI, NH_3) (rel intensity) *m*/*z* (rel intensity) 310 (5), 309 (29), 308 (100, M + H), 306 (5), 292 (15), 209 (8); HRMS (EI, 70 eV) calcd for $C_{21}H_{25}NO$ M^+ 307.1936, found 307.1946.

(4*S,5*R**)-2-Ethyl-5-(1-methylethyl)-4-(triethylsilyl)-1-pyrroline (40) (Table 2, Entry 2).** A solution of the imidate **18** (210 mg, 0.506 mmol) and triethylvinylsilane (150 mg, 1.06 mmol) in THF (2 mL) was added to a solution of *n*-butyllithium (1.40 mL, 2.94 mmol, 2.1 M in hexanes) in THF (2 mL) at −78 °C. After 30 min, iodomethane (0.18 mL, 3.97 mmol) was added. The reaction was allowed to warm to room temperature and water was added. The aqueous layer was extracted with ether (3×). The organic extracts were combined, dried ($MgSO_4$), filtered, and concentrated. Chromatography (0−20% EtOAc/hexane gradient) afforded 84 mg (65%) of the title compound as an oil. The relative configuration was assigned based on analogy to **21**. Data for **40**: R_f = 0.42 (20% EtOAc/hexane); IR (neat) 1652 (m), 1460 (m), 1381 (m), 1365 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 3.97−3.92 (m, 1 H), 2.65 (ddd, 1 H, J = 17.6, 11.4, 3.1 Hz), 2.35−2.25 (m, 3 H,), 1.73 (dpent, 1 H, J = 6.8, 3.9 Hz), 1.19 (pent, 1 H, J = 5.5 Hz), 1.10 (t, 9 H, J = 7.6 Hz), 0.92 (d, 3 H, J = 6.8 Hz), 0.91 (t, 9 H, J = 7.9 Hz), 0.50 (q, 6 H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 177.7, 80.0, 39.5, 33.6, 26.7, 21.3, 19.6, 17.5, 11.2, 7.5, 2.2; MS (CI, CH_4) *m*/*z* (rel intensity) 255 (23), 254 (80, M + H), 252 (29), 224 (67), 211 (26), 210 (100); HRMS (CI, CH_4) calcd for $C_{15}H_{32}NSi$ $(M + H)^+$ 254.2304, found 254.2294. **From Pyrroline 21 by Deprotonation (Table 3, Entry 1).** *s*-Butyllithium (0.60 mL, 0.69 mmol, 1.15 M in cyclohexane) was added to a solution of the pyrroline **21** (155 mg, 0.647 mmol) in THF (1 mL) at −78 °C. After the solution was warmed to −50 °C, iodomethane (0.140 mL, 2.25 mmol) was added slowly, the reaction was warmed to 0 °C, diluted with ether, washed with water, and the organic phase was dried (Na_2SO_4), filtered, and concentrated to give 153 mg (93%) of the title compound of sufficient purity by ^1H NMR so as to make purification unnecessary.

(4*S,5*R**)-2-(2-Hydroxy-2-methylpropyl)-5-(2-methylethyl)-4-(triethylsilyl)-2-pyrroline (41) (Table 2, Entry 3).** A solution of the imidate **18** (200 mg, 0.478 mmol) and triethylvinylsilane (235 mg, 1.65 mmol) in THF (2 mL) was added to a solution of *n*-butyllithium (1.00 mL, 2.50 mmol, 2.5 M in hexanes) in THF (10 mL) at −78 °C. After 30 min, acetone (0.50 mL, 6.81 mmol) was added. After an additional 30 min, saturated aqueous NH_4Cl was added. The mixture was diluted with ether and washed with saturated aqueous NH_4Cl, and the organic layer was dried ($MgSO_4$), filtered, and concentrated. Chromatography (0−20% EtOAc/hexane gradient) afforded 129 mg (91%) of the title compound as a clear oil. The relative configuration was assigned based on analogy with **21** and **40**. Data for **41**: $R_f = 0.30$ (20% EtOAc/hexane); IR (neat) 3374 (br m), 1648 (m), 1466 (m), 1413 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 3.98 (br s, 1 H), 2.69 (ddd, 1 H, J = 18.0, 11.3, 3.0 Hz), 2.38−2.30 (m, 3 H), 1.69 (dpent, 1 H, J = 6.8, 4.0 Hz), 1.26 (s, 3 H), 1.24 (s, 3 H), 1.24−1.13 (m, 1 H), 1.02 (d, 3 H, J = 6.8 Hz), 0.91 (t, 9 H, J = 7.8 Hz), 0.80 (d, 3 H, J = 6.8 Hz), 0.52 (q, 6 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 176.5, 80.5, 69.7, 44.0, 42.8, 33.5, 29.6, 29.5, 20.9, 20.6, 17.1, 7.5, 2.3; MS (CI, NH_3) *m*/*z* (rel intensity) 298 (12, M + H), 280 (15), 241 (21), 240 (100), 196 (48); HRMS (CI, CH_4) calcd for $C_{17}H_{36}NOSi$ $(M + H)^+$ 298.2566, found 298.2567.

(4*S,5*R**)-2-[2-(3,4-Methylenedioxyphenyl)ethyl]-5-(2-methylethyl)-4-(triethylsilyl)-2-pyrroline (43) (Table 2, Entry 4).** A solution of the imidate **18** (1.00 mg, 2.39 mmol) and triethylvinylsilane (500 mg, 3.52 mmol) in THF (5 mL) was added to a solution of *n*-butyllithium (2.90 mL, 7.25 mmol, 2.1 M in hexanes) in THF (10 mL) at −78 °C. After 30 min, 3,4-methylenedioxybenzyl bromide (**42**, 2.05 g, 9.53 mmol) in THF (5 mL) was added. After 30 min, saturated NH_4Cl (aq) was added and the mixture was diluted with ether, washed with saturated NH_4Cl (aq), dried ($MgSO_4$), filtered, and concentrated. Chromatography (0−20% EtOAc/hexane gradient) afforded 201 mg (23%) of the title compound as a clear oil. The relative configuration was assigned based on analogy with **21** and **40**. Data for **43**: $R_f = 0.30$ (20% EtOAc/hexane); IR (neat) 1651 (m), 1504 (s), 1490 (s), 1443 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 6.70−6.62 (m, 3 H), 5.88 (s, 2 H), 3.94 (br s, 1 H), 2.85−2.53 (m, 5 H), 2.31 (dd, 1 H, J = 17.6, 6.1 Hz), 1.72 (dpent, 1 H, J = 6.8, 2.9 Hz), 1.22 (pent, 1 H, J = 5.4 Hz), 0.94 (d, 3 H, J = 6.9 Hz), 0.91 (t, 9 H, J = 7.7 Hz), 0.78 (d, 3 H, J = 6.8 Hz), 0.50 (q, 6 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 175.8, 147.5, 145.7, 135.3, 121.0, 108.8, 108.1, 100.7, 80.2, 40.3, 35.3, 33.6, 32.6, 21.5, 19.8, 17.4, 7.6, 2.3; MS (CI, NH_3) *m*/*z* (rel intensity) 375 (32), 374 (100, M + H), 240 (9); HRMS (CI, NH_3) calcd for $C_{22}H_{36}NO_2Si$ $(M + H)^+$ 374.2515, found 374.2499. **From Pyrroline 21 by Deprotonation (Table 3, Entry 2).** *s*-Butyllithium (0.33 mL, 0.37 mmol, 1.15 M in cyclohexane) was added to a solution of the pyrroline **21** (82 mg, 0.34 mmol) in THF (1 mL) at −78 °C. After the solution was warmed to −50 °C, 3,4-methylenedioxybenzyl bromide (74 mg, 0.39 mmol) was added, the reaction was warmed to 0 °C, diluted with ether, washed with water, and the organic phase was dried (Na_2SO_4), filtered, and concentrated. Chromatography (0−15% EtOAc/hexane) afforded 95 mg of the title compound and 20 mg of a 2.4:1.0 mixture of starting material to the title compound. This corresponds to a total yield of 80% of **43** and 15% recovered **21**.

(4*S,5*R**)-5-(1-Methylethyl)-2-((methylthio)methyl)-4-(triethylsilyl)-1-pyrroline (44).** *s*-Butyllithium (0.65 mL, 0.75 mmol, 1.15 M in cyclohexane) was added to a solution of the pyrroline **21** (158 mg, 0.660 mmol) in THF (1 mL) at −78 °C. After the solution was warmed to −50 °C, methyl disulfide (0.175 mL, 1.94 mmol) was added quickly, the reaction was warmed to 0 °C, diluted with ether, washed with water, and the organic phase was dried (Na_2SO_4), filtered, and concentrated. Chromatography (0−10% EtOAc/hexane) afforded 76 mg of desired product with 50 mg of a 3:1 mixture of starting imine to product and 25 mg of a mixture of disulfenylated products. This corresponds to a total of 48% of **44**, 23% of recovered **21**, and 11% disulfenylated materials. Data for **44**: $R_f = 0.35$ (20% EtOAc/hexane); IR (neat) 1666 (m), 1643 (m), 1464 (m), 1416 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 3.97 (br s, 1 H), 3.28 (q, 2 H, J = 13.7 Hz), 2.88 (ddd, J = 17.7, 11.4, 2.9 Hz), 2.49 (dd, 1 H, J = 17.7, 6.8 Hz), 2.07 (s, 3 H), 1.72 (m, 1 H), 1.26 (dt, 1 H, J = 11.3, 6.2 Hz), 1.00 (d, 3 H, J = 6.8 Hz), 0.93 (t, 9 H, J = 8.0 Hz), 0.81 (d, 3 H, J = 6.8 Hz), 0.53 (q, 6 H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 172.9, 80.7, 38.4, 35.5, 33.3, 21.9, 20.1, 17.3, 15.3, 7.5, 2.3; MS (CI, CH_4) *m*/*z* (rel intensity) 286 (23, M), 239 (35), 208 (15), 197 (22), 196 (100), 195 (14), 194 (62); HRMS (EI, 70 eV) calcd for $C_{15}H_{31}NSSi$ M^+ 286.2025, found 286.2012. Data for disulfe-

nylated material: R_f = 0.50 (20% EtOAc/hexane); MS (CI, NH_3) *m/z* (rel intensity) 332 $(M + H)^+$.

1-Methoxy-6(or 7)−(triethylsilyl)-8-azabicyclo[3.2.1]-octane (52) and 6-[2-(Triethylsilyl)]piperidin-2-one (Table 4, Entry 1). Using the general procedure, the imidate **51** (308 mg, 0.764 mmol) and triethylvinylsilane (275 mg, 1.93 mmol) in THF (2 mL) were combined with *n*-butyllithium (1.70 mL, 3.74 mmol, 2.2 M in hexanes) in THF (3 mL) to afford, after chromatography (0−50% EtOAc/hexane gradient), 175 mg (90%) of **52** as a single diastereomer as judged by TLC and ^{1}H and ^{13}C NMR spectroscopies. The regiochemistry and relative configuration of **52** could not be assigned due to overlapping peaks in the ^{1}H NMR spectrum, regardless of solvent or field strength. 6-[2-(Triethylsilyl)]piperidin-2-one was also isolated in yields as high as 16%. Data for **52**: R_f = 0.28 (30% EtOAc/hexane); IR (neat) 1466 (m), 1392 (m), 1336 (m), 1305 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 3.48 (br s, 1 H), 3.33 (s, 3 H), 1.92−1.58 (m, 7 H), 1.52−1.44 (m, 1 H), 1.39−1.33 (m, 1 H), 1.05 (dd, 1 H, J = 10.4, 7.0 Hz), 0.97 (t, 9 H, J = 7.9 Hz), 0.58 (q, 6 H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 93.9, 55.6, 49.3, 36.9, 34.3, 32.3, 23.7, 18.8, 7.6, 2.4; MS (EI, 70 eV) *m/z* (rel intensity) 255 (17, M), 212 (23), 140 (100); HRMS (EI, 70 eV) calcd for $C_{14}H_{29}NOSi$ M^+ 255.2018, found 255.2015. Data for 6-[2-(triethylsilyl)]piperidin-2-one: R_f = 0.03 (30% EtOAc/hexane); IR (neat) 3395 (m), 1657 (s), 1466 (m), 1417 (m); ^{1}H NMR ($CDCl_3$, 360 MHz) δ 6.01 (s, 1 H), 3.30−3.20 (m, 1 H), 2.39 (dddd, 1 H, J = 17.7, 5.5, 3.6, 1.3 Hz), 2.27 (ddd, 1 H, J = 17.5, 11.8, 5.7 Hz), 1.95−1.87 (m, 2 H), 1.75−1.64 (m, 1 H), 1.50−1.34 (m, 4 H), 0.93 (t, 9 H, J = 7.9 Hz), 0.60−0.41 (m, 8 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 172.3, 55.7, 31.4, 31.1, 28.0, 19.7, 7.3, 6.5, 3.0; MS (EI, 70 eV) *m/z* (rel intensity) 241 (6, M), 213 (30), 212 (100), 115 (29), 98 (99); HRMS (EI, 70 eV) calcd for $C_{13}H_{27}NOSi$ M^+ 241.1862, found 241.1871.

1-Methoxy-6(or 7)-phenylthio-8-azabicyclo[3.2.1]octane (53) (Table 4, Entry 2). Using the general procedure, the imidate **51** (315 mg, 0.78 mmol) and phenyl vinyl sulfide (255 mg, 1.87 mmol) in THF (5 mL) were combined with *n*-butyllithium (2.0 mL, 4.40 mmol, 2.2 M in hexanes) in THF (5 mL) to afford, after chromatography (0−100% EtOAc/hexane gradient), 46 mg (24%) of a 6:1 mixture of isomers A and B and 109 mg (56%) of a 1:9.2:4.2:1.6 mixture of isomers A:B:C:D. This corresponds to a total product ratio of 4.2:6.4:2.6:1 (A:B:C:D) and a combined yield of 80%. The reaction time was 1.5 h rather than the usual 30 min. Data for isomer A: R_f = 0.29 (EtOAc); IR (neat) 3290 (w), 1655 (m), 1584 (m), 1480 (m), 1439 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.35−7.15 (m, 5 H); 3.54 (dd, 1 H, J = 8.3, 4.3 Hz); 3.41 (br s, 1 H,), 3.36 (s, 3 H), 2.23 (dd, 1 H, J = 14.0, 8.5 Hz), 1.95−1.50 (m, 8 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 136.8, 130.3, 129.3, 128.9, 128.7, 126.1, 94.6, 61.5, 50.0, 47.2, 39.6, 35.2, 31.1, 19.2; MS (EI, 70 eV) *m/z* (rel intensity) 249 (25, M), 205 (12), 141 (11), 140 (100); HRMS (EI, 70 eV) calcd for $C_{14}H_{19}NOS$ M^+ 249.1187, found 249.1187. Data for isomer B: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 3.24 (s, 3 H), 2.70 (dt, 1 H, J = 12.8, 7.6 Hz). Data for isomer C: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 3.83 (dd, 1 H, J = 7.9, 4.6 Hz), 3.45 (s, 1 H,). Data for isomer D: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 3.32 (s, 3 H). Data for mixture of all four isomers: R_f = 0.29−0.10 (EtOAc); IR (neat) 3285 (w), 1661 (m), 1593 (m), 1479 (m), 1438 (m) cm^{-1}; MS (EI, 70 eV) *m/z* (rel intensity) 249 (26, M), 205 (11), 140 (27), 126 (39), 123 (11), 113 (67), 98 (100),; HRMS (EI, 70 eV) calcd for $C_{14}H_{19}NOS$ M^+ 249.1187, found 249.1187.

1-Methoxy-6(or 7)-phenylseleno-8-azabicyclo[3.2.1]-octane (54) (Table 4, Entry 3). Using the general procedure, the imidate **51** (3.00 g, 7.44 mmol) and phenyl vinyl selenide (3.08 g, 16.8 mmol) in THF (5 mL) were combined with *n*-butyllithium (16.0 mL, 35.7 mmol, 2.23 M in hexanes) in THF (30 mL) to afford, after chromatography (0−100% EtOAc/hexane gradient), 2.09 g (94%) of **54** as an inseparable 11:8:4:1 mixture of stereo- and/or regioisomers, which were not assigned. Data for the mixture of all four isomers: R_f = 0.40−0.20 (EtOAc); IR (neat) 3285 (br w), 1655 (m), 1578 (m), 1476 (m), 1467 (m) cm^{-1}; partial ^{1}H NMR ($CDCl_3$, 360 MHz, methoxy resonances only, relative integration given) δ 3.44 (s, 3.74), 3.34 (s, 7.94), 3.31 (s, 1.0), 3.22 (s, 10.6); MS (EI, 70 eV) *m/z* (rel intensity) 297 (17), 140 (28), 126 (28), 113 (61), 112 (28), 99 (10), 98 (100); HRMS (EI, 70 eV) calcd for $C_{14}H_{19}NOSe$ M^+ 297.0632, found 297.0620.

(1*R,5*R**,6*S**,7*S**)-6,7-Diphenyl-1-methoxy-8-azabicyclo-[3.2.1]octane (55) and (1*R**,5*R**,6*R**,7*R**)-6,7-Diphenyl-1-methoxy-8-azabicyclo[3.2.1]octane (56) (Table 4, Entry 4).** Using the general procedure, the imidate **51** (302 mg, 0.750 mmol) and *trans*-stilbene (323 mg, 1.79 mmol) in THF (10 mL) were combined with *n*-butyllithium (1.70 mL, 3.74 mmol, 2.2 M in hexanes) in THF (3 mL) to afford, after chromatography (0−100% EtOAc/hexane gradient), 48 mg (22%) of **55** and 128 mg (58%) of **56** as oils. The reaction time was 1.5 h rather than the usual 30 min. Data for **55**: R_f = 0.12 (EtOAc); IR (neat) 3282 (w), 1656 (m), 1601 (m), 1496 (s), 1453 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.49 (dd, 2 H, J = 8.4, 1.4 Hz), 7.35−7.25 (m, 6 H), 7.22−7.14 (m, 2 H), 4.02−3.97 (m, 1 H), 3.94 (t, 1 H, J = 7.4 Hz), 3.62 (d, 1 H, J = 7.7 Hz), 2.98 (s, 3 H), 2.06 (dd, 1 H, J = 11.7, 3.4 Hz), 1.96 (br s, 1 H), 1.79−1.42 (m, 5 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 142.6, 139.5, 129.3, 128.2, 127.8, 127.4, 126.1, 125.4, 94.4, 57.7, 56.3, 52.0, 50.5, 36.2, 26.8, 18.7; MS (EI, 70 eV) *m/z* (rel intensity) 293 (5, M), 114 (9), 113 (100); HRMS (EI, 70 eV) calcd for $C_{20}H_{23}NO$ M^+ 293.1780, found 293.1769. Data for **56**: R_f = 0.17 (20% EtOAc/hexane); IR (neat) 3290 (w), 1657 (w), 1600 (m), 1495 (s), 1454 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.58 (t, 4 H, J = 9.5 Hz), 7.33 (dt, 4 H, J = 7.4, 1.9 Hz), 7.27−7.18 (m, 2 H), 3.64−3.56 (s + m, 5 H), 3.46 (d, 1 H, J = 7.0 Hz), 1.85−1.30 (m, 7 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 147.8, 138.4, 128.6, 128.1, 127.5, 127.0, 126.1, 126.0, 95.4, 60.5, 53.0, 48.0, 47.9, 33.6, 32.9, 17.6; MS (EI, 70 eV) *m/z* (rel intensity) 293 (4, M), 114 (9), 113 (100); HRMS (EI, 70 eV) calcd for $C_{20}H_{23}NO$ M^+ 293.1780, found 293.1771. The stereochemical assignments for **55** and **56** are proposed on the basis of the following assumptions: (1) The phenyl groups at C-6 and C-7 are trans, as has always been observed in 2-azaallyl anion cycloadditions with *trans*-stilbene. (2) The methoxy singlet (^{1}H NMR) for **55** appears at δ = 2.98, while the methoxy singlet for **56** appears at δ = 3.6. By analogy with cycloadducts **57**−**59** (see below), an exo phenyl group nearest the bridgehead methoxy group correlates with a higher field methoxy chemical shift.

(1*R,2*R**,3*R**,4*R**)-2,3-Diphenyl-1-methoxy-7-azabicyclo[2.2.1]-heptane (57), (1*R**,2*S**,3*S**,4*R**)-2,3-Diphenyl-1-methoxy-7-azabicyclo-[2.2.1]heptane (58) and (1*R**,2*S**,3*R**,4*R**)-2,3-Diphenyl-1-methoxy-7-azabicyclo[2.2.1]-heptane (59). Cycloaddition with *trans*-Stilbene (Table 4, Entry 5).** Using the general procedure, the imidate **50** (0.500 g, 1.3 mmol) and *trans*-stilbene (470 mg, 2.6 mmol) in THF (4 mL) were combined with *n*-butyllithium (3.2 mL, 6.4 mmol, 2.0 M in hexanes) in THF (3 mL) to afford, after chromatography (0−80% EtOAc/hexane gradient), 157 mg (44%) of **57** and 168 mg (47%) of **58** as oils. Tentative structural assignments were based upon comparison of coupling constants predictioned by computer-minimized models (vide infra). Many proton assignments were made using two-dimensional COSY experiments. Data for **57**: R_f = 0.37 (EtOAc); IR (in $CHCl_3$) 2959 (s), 1682 (m), 1602 (m), 1496 (s), 1453 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.45−7.18 (m, 10 H), 3.60 (s, 3 H), 3.55 (d, 1 H, J = 4.9 Hz), 3.50 (dd, 1 H, J = 6.4, 2.7 Hz), 3.32 (d, 1 H, J = 6.3 Hz), 2.03−1.94 (m, 1 H), 1.86 (s, 1 H), 1.84−1.70 (m, 2 H), 1.59−1.50 (m, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 145.6, 139.2, 128.7, 128.3, 128.2, 127.0, 126.5, 126.3, 101.3, 58.8, 55.7, 53.7, 52.1, 32.5, 25.4; MS (EI, 70 eV) *m/z* (rel intensity) 279 (7, M), 180 (10), 179 (12), 178 (10), 165 (8), 100 (9), 99 (100); HRMS (EI, 70 eV) calcd for $C_{19}H_{21}NO$ M^+ 279.1623, found 279.1635. Data for **58**: R_f = 0.20 (EtOAc); IR (in $CHCl_3$) 3020 (s), 1602 (m), 1497 (m), 1455 (m), cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.58 (d, 2 H, J = 7.6 Hz), 7.38−7.14 (m, 8 H), 3.79−3.62 (m, 2 H). 3.30 (d, 1 H, J = 6.3 Hz), 3.20 (s, 3 H), 2.13 (br s, 1 H), 1.84−1.67 (m, 4 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 142.6, 140.6, 128.8, 128.4, 128.1, 127.6, 126.4, 126.3, 101.3, 59.2, 56.5, 53.9, 52.4, 32.5, 25.8; MS (EI, 70 eV) *m/z* (rel intensity) 279 (6, M), 180 (5), 179 (7), 178 (7), 115 (5), 100 (8), 99 (100); HRMS (EI, 70 eV) calcd for $C_{19}H_{21}NO$ M^+ 279.1623, found 279.1612. **Cycloaddition with *cis*-Stilbene (Table 4, Entry 6).** Using the general procedure, the imidate

50 (1.00 g, 2.5 mmol) and *cis*-stilbene (944 mg, 5.2 mmol) in THF (6 mL) were combined with *n*-butyllithium (4.0 mL, 8.0 mmol, 2.0 M in hexanes) in THF (6 mL) to afford, after chromatography (0−80% EtOAc/hexane gradient), 36 mg (5%) of **57**, 463 mg (63%) of **58**, and 32 mg (5%) of **59**, all three as oils. Data for **59**: R_f = 0.63 (EtOAc); IR (in $CHCl_3$) 2954 (s), 1602 (m), 1496 (m), 1454 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.15−6.84 (m, 10 H), 3.85 (d, 1 H, J = 4.6 Hz), 3.65 (m, 2 H,), 3.13 (s, 3 H), 2.15−1.70 (m, 5 H); ^{13}C NMR ($CDCl_3$, 90 MHz, JMOD) δ 141.3 (−), 138.2 (−), 130.6 (+), 128.9 (+), 127.2 (+), 126.7 (+), 125.3 (+), 125.2 (+), 100.4 (−), 56.2 (+), 54.8 (+), 54.7 (+), 52.5 (+), 32.9 (−), 32.7 (−); MS (EI, 70 eV) *m*/*z* (rel intensity) 279 (29, M), 250 (15), 202 (29), 180 (21), 179 (30), 178 (21), 165 (15), 99 (100); HRMS (EI, 70 eV) calcd for $C_{19}H_{21}NO$ M^+ 279.1623, found 279.1634. The stereochemical assignments for **57**-**59** are proposed on the basis of the following: (1) The phenyl groups at C-2 and C-3 in **57** and **58** are trans, as has always been observed in 2-azaallyl anion cycloadditions with *trans*-stilbene. This requires **59** to have a *cis*-relationship of the two phenyl rings, since this compound is a diastereomer of both **57** and **58**. By analysis of computer models (MMX), any product that has the 3-phenyl group in the endo position (i.e. **58**) should have a dihedral angle of approximately 45° between 3-H (benzylic) and 4-H (bridgehead). A 45° angle corresponds to a coupling constant of approximately 5 Hz and should lead to a detectable cross-peak in the COSY spectrum. In contrast, the dihedral angle between 3-H and 4-H in the isomers with the 3-phenyl group in the exo position (i.e., **57** and **59**) should be near 85°. This corresponds to a coupling constant of near 0 Hz, which may lead to a small or absent cross-peak in the COSY spectrum. Compound **58** was observed to have a strong cross-peak between H-3 and H-4, consistent with having the 3-phenyl group endo. Compounds **57** and **59** both showed no cross-peak in the COSY spectra, consistent with an exo 3-phenyl group. (3) Compounds with an exo phenyl group at C-2 (**58** and **59**) have methoxy groups that are shifted upfield (δ 3.20 and 3.13, respectively) relative to that in compound **57** (methoxy at δ 3.60), which has an endo phenyl group at C-2. This effect was used above in the assignments of compounds **55** and **56**.

1-Methoxy-2(or 3)-phenylthio-7-azabicyclo[2.2.1]-heptane (60) (Table 4, Entry 7). Using the general procedure, the imidate **50** (490 mg, 1.26 mmol) and phenyl vinyl sulfide (440 mg, 3.21 mmol) in THF (3 mL) were combined with *n*-butyllithium (3.5 mL, 7.00 mmol, 2.0 M in hexanes) in THF (5 mL) to afford, after chromatography (0−100% EtOAc/hexane gradient), all four possible diastereomers. In order of elution, the following components were isolated: Isomer no. 1 {116 mg (39%)}; isomer no. 2 {72 mg (24%)}; isomer no. 3 {26 mg (9%)}; isomer no. 4 {33 mg (11%)}. Assignment of the regiochemistry and relative configuration of the products was not performed. Data for isomer no. 1: R_f = 0.21 (EtOAc); IR (neat) 3270 (w), 1584 (m), 1479 (m), 1439 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.34−7.18 (m, 5 H), 3.56 (dd, 1 H, J = 8.0, 4.3 Hz), 3.45 (s, 3 H), 3.28 (d, 1 H, J = 5.1 Hz), 2.28 (br s, 1 H), 2.22 (dd, 1 H, J = 13.0, 8.1 Hz), 2.00−1.82 (m, 2 H), 1.54−1.38 (m, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 135.7, 130.0, 128.9, 126.4, 98.6, 57.3, 52.3, 50.4, 40.7, 28.3, 28.2; MS (EI, 70 eV) *m*/*z* (rel intensity) 235 (54, M), 126 (100), 115 (20), 99 (86), 49 (62); HRMS (EI, 70 eV) calcd for $C_{13}H_{17}NOS$ M^+ 235.1031, found 235.1039. Data for isomer no. 2: R_f = 0.11 (EtOAc); IR (neat) 3275 (w), 1584 (m), 1480 (m), 1439 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.42−7.14 (m, 5 H), 3.71 (dd, 1 H, J = 7.7, 3.9 Hz), 3.45 (d, 1 H, J = 4.7 Hz), 3.43 (s, 3 H), 2.21 (dd, 1 H, J = 13.5, 7.7 Hz), 2.20 (br s, 1 H), 2.04 (dt, 1 H, J = 11.9, 3.1 Hz), 1.91 (tq, 1 H, J = 11.5, 3.0), 1.81−1.74 (m, 1 H), 1.51−1.38 (m, 2 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 135.7, 130.7, 128.5, 126.0, 99.8, 52.7, 52.0, 51.7, 42.8, 29.8, 27.4; MS (EI, 70 eV) *m*/*z* (rel intensity) 235 (26, M), 220 (16), 175 (18), 123 (15), 112 (52), 99 (72); HRMS (EI, 70 eV) calcd for $C_{13}H_{17}NOS$ M^+ 235.1031, found 235.1030. Data for isomer no. 3: R_f = 0.09 (EtOAc); IR (neat) 1694 (m), 1584 (m), 1480 (s), 1439 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.38−7.16 (m, 5 H), 3.77−3.69 (m, 1 H), 3.50 (br s, 1 H), 3.45 (s, 3 H), 2.35−2.28 (m, 2 H), 1.88 (br s, 1 H), 1.82−1.77 (m, 1 H), 1.61−1.55 (m, 1 H), 1.47 (dd, 1 H, J = 12.4, 5.4 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 135.9, 129.8, 129.0, 126.0, 99.1, 56.4, 52.2, 48.0, 39.7, 30.9, 25.3; MS (EI, 70 eV) *m*/*z* (rel intensity) 235 (100, M), 207 (28), 204 (23), 126 (86), 112 (22); HRMS (EI, 70 eV) calcd for $C_{13}H_{17}NOS$ M^+ 235.1031, found 235.1033. Data for isomer no. 4: R_f = 0.06 (EtOAc); IR (neat) 1694 (m), 1584 (m), 1480 (s), 1439 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.46−7.39 (d, 2 H, J = 7.2 Hz,), 7.30−7.15 (m, 3 H,), 3.56 (ddd, 1 H, J = 11.7, 5.1, 2.8 Hz), 3.47 (t, 1 H, J = 5.1 Hz), 3.37 (s, 3 H), 2.54−2.46 (m, 1 H), 2.33−2.25 (m, 1 H), 1.95−1.85 (m, 1 H), 1.80−1.65 (m, 3 H), 1.56 (dd, 1 H, J = 12.9, 5.2 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 136.3, 130.4, 128.7, 126.3, 101.2, 52.6, 52.2, 48.3, 41.1, 31.4, 26.0; MS (EI, 70 eV) *m*/*z* (rel intensity) 236 (25), 235 (54, M), 221 (25), 220 (54), 175 (59), 126 (32), 123 (27), 112 (71), 99 (72); HRMS (EI, 70 eV) calcd for $C_{13}H_{17}NOS$ M^+ 235.1031, found 235.1040.

***N*-Formyl-1-methoxy-8-azabicyclo[3.2.1]octane (61).** Selenide **54** (355 mg, 1.19 mmol), AIBN (10 mg, 0.06 mmol), and Bu_3SnH (1.00 mL, 3.71 mmol) were dissolved in benzene (25 mL) and heated at reflux. After 2 h, the solution was concentrated to provide an oil, which was dissolved in CH_2Cl_2 (25 mL) and treated with Et_3N (0.50 mL, 6.84 mmol) and acetic−formic anhydride (0.20 mL, 2.04 mmol). After 3 h, the reaction was concentrated, ether was added, and the solution was washed with saturated NH_4Cl (aq) (2×). The organic layer was dried (Na_2SO_4), filtered, and concentrated to provide an oil. Chromatography (0−100% EtOAc/hexane gradient) afforded 132 mg (65%) of the title compound as a white solid: mp 52.0−53.0 °C; R_f = 0.50 (EtOAc); IR (neat) 1658 (s), 1407 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 8.12 (s, 1 H), 4.52 (d, 1 H, J = 7.4 Hz), 3.31 (s, 3 H), 2.11 (ddt, 1 H, J = 12.8, 4.2, 2.1 Hz), 1.96−1.88 (m, 2 H), 1.78−1.70 (m, 4 H), 1.64−1.52 (m, 2 H), 1.42−1.35 (m, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 158.9, 93.7, 51.2, 50.2, 39.6, 29.5, 28.9, 24.0, 18.3; MS (EI, 70 eV) *m*/*z* (rel intensity) 169 (15), 154 (46), 140 (14), 126 (23), 113 (14), 112 (29), 99 (32), 98 (100); HRMS (EI, 70 eV) calcd for $C_9H_{15}NO_2$ M^+ 169.1103, found 169.1102.

1-Methoxy-8-methyl-8-azabicyclo[3.2.1]octane (62). Amide **61** (220 mg, 1.30 mmol) was dissolved in THF (30 mL) and treated with $LiAlH_4$ (0.57 g, 15 mmol). After 1 h, 10% NaOH (2.5 mL) was added. The mixture was diluted in ether and filtered through Celite. The filtrate was washed with water and the organic phase was washed with 5% HCl (aqueous). The acidic extracts were combined and washed with EtOAc. The acidic aqueous phase was neutralized with solid NaOH and extracted with ether (5×). The organic extracts were combined, dried ($MgSO_4$), filtered, and concentrated to provide 188 mg (92%) of the title compound as an oil of sufficient purity by ^1H NMR to not require purification. Data for **62**: IR (neat) 1335 (m), 1257 (m), 1208 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.30−3.23 (m, 4 H), 2.24 (s, 3 H), 2.00−1.74 (m, 4 H), 1.70−1.62 (m, 2 H), 1.60−1.51 (m, 1 H), 1.48−1.40 (m, 1 H), 1.31 (br d, 1 H, J = 11.9 Hz), 1.01 (br d, 1 H, J = 12.8 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 93.1, 59.0, 48.4, 30.1, 28.6, 28.2, 24.7, 18.3; MS (EI, 70 eV) *m*/*z* (rel intensity) 155 (28, M), 140 (27), 126 (20), 113 (32), 112 (100); HRMS (EI, 70 eV) calcd for $C_9H_{17}NO$ M^+ 155.1310, found 155.1308.

6-[(4-Trimethylsilyl)methylphenyl]-2-piperidinone (65). A solution of the imidate **63** (516 mg, 1.08 mmol) and bis(trimethylsilyl)acetylene (400 mg, 2.36 mmol) in THF (3 mL) was added to a solution of *n*-butyllithium (2.70 mL, 5.40 mmol, 2.0 M in hexanes) in THF (3 mL) at −78 °C. After 30 min, iodomethane (0.40 mL, 6.40 mmol) was added in a dropwise fashion. After an additional 10 min, saturated aqueous NH_4Cl was added and the reaction was diluted with ether, washed with saturated aqueous NH_4Cl and 10% NaOH (aqueous), and the organic phase was dried (Na_2SO_4), filtered, and concentrated to provide an oil. Chromatography (0−100% EtOAc/hexane) provided 32 mg (11%) of the title compound as a white solid: mp 99−104 °C; R_f = 0.15 (EtOAc); IR (neat) 3394 (m), 1650 (s), 1462 (m), 1418 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.06 (d, 1 H, J = 8.1 Hz), 6.91 (d, 1 H, J = 8.2 Hz), 5.78 (s, 1 H); 4.41 (dd, 1 H, J = 9.0, 4.4 Hz), 2.42−2.29 (m, 2 H), 2.02 (s, 2 H,); 1.90−1.50 (m, 4 H), −0.10 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.3, 140.4, 137.9, 128.3, 125.9, 57.6,

32.1, 31.2, 26.7, 19.8, −1.9; MS (EI, 70 eV) *m*/*z* (rel intensity) 261 (100, M), 246 (13), 132 (12), 131 (49), 130 (76), 129 (20); HRMS (EI, 70 eV) calcd for $C_{15}H_{23}NOSi$ M^+ 261.1549, found 261.1549.

B. Synthesis of 2-Azaallyl Anion Precursors. *N*-[(Benzotriazol-1-yl)methyl]acetamide (71). Acetamide (1.47 g, 24.9 mmol), *N*-(hydroxymethyl)benzotriazole (3.72 g, 24.9 mmol), and *p*-toluenesulfonic acid (20 mg) were combined in toluene (20 mL) and heated at reflux using a Dean−Stark trap for water removal. After 6 h, the solution was concentrated and the resulting oil was triturated with ether to afford 4.56 g (97%) of the title compound as a white solid: IR (film) 3273 (m), 3228 (m), 1681 (s), 1554 (m), 1454 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 8.01 (dt, 1 H, J = 8.4, 0.9 Hz), 7.95 (dt, 1 H, J = 8.3, 0.9 Hz), 7.53 (ddd, 1 H, J = 8.2, 6.9, 1.0 Hz), 7.41 (s, 1 H), 7.40 (ddd, 1 H, J = 8.4, 7.0, 1.1 Hz), 6.11 (d, 2 H, J = 6.9 Hz), 2.09 (s, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 170.8, 145.8, 132.4, 128.1, 124.5, 119.3, 111.0, 50.9, 23.0; MS (EI, 70 eV) *m*/*z* (rel intensity) 190 (14, M), 120 (34), 119 (100); HRMS (EI, 70 eV) calcd for $C_9H_{10}N_4O$ M^+ 190.0855, found 190.0864. Anal. Calcd. for $C_9H_{10}N_4O$: C, 56.83; H, 5.30; N, 29.46. Found: C, 56.96; H, 5.45; N, 29.54.

***N*-[(Tri-*n*-butylstannyl)methyl]acetamide (73) via Amine 69.** *N*-[(Tri-*n*-butylstannyl)methyl]phthalimide[20] (11.5 g, 26.7 mmol) and hydrazine monohydrate (50 mL, 1.0 mol) were dissolved in EtOH (400 mL, 95%), and the mixture was heated at reflux for 24 h. After cooling, the mixture was concentrated and diluted with ether. The organic phase was washed with water (3×), dried ($MgSO_4$), and concentrated to provide an oil that was dissolved in THF (200 mL) and treated with triethylamine (5.0 mL, 35.7 mmol) followed by acetyl chloride (2.0 mL, 28.1 mmol). After 12 h, the reaction was diluted with ether and washed with water and saturated aqueous NH_4Cl (3×). The organic layer was dried ($MgSO_4$), filtered, and concentrated. Chromatography (0−50% EtOAc/hexane gradient) afforded 6.76 g (70%) of the title compound as a clear, colorless oil: R_f = 0.33 (30% EtOAc/hexane); IR (in $CHCl_3$) 3450 (m), 1650 (s), 1526 (s), 1464 (m); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.95 (br s, 1 H), 2.73 (d, 2 H, J = 4.8 Hz, $^2J(^{117/119}Sn-^1H)$ = 29.6 Hz), 1.92 (s, 3 H), 1.53−1.42 (m, 6 H), 1.32−1.22 (m, 6 H), 1.00−0.75 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 29.1 (20 Hz), 27.3, 24.5, 22.7, 13.6, 10.4; MS (CI, NH_3) *m*/*z* (rel intensity) 364 (15, M + H), 362 (12), 310 (26), 308 (32), 307 (23), 306 (100), 305 (43), 304 (77), 303 (35), 302 (48); HRMS (CI, NH_3) calcd for $C_{15}H_{34}NOSn$ (M + H)$^+$ 364.1662, found 364.1673. Anal. Calcd for $C_{15}H_{33}NOSn$: C, 49.75; H, 9.19; N, 3.87. Found: C, 49.60; H, 8.91; N, 3.96. **Via the Benzotriazole 71.** *n*-Butyllithium (17.7 mL, 31.0 mmol, 1.75 M in hexanes) was added to a solution of diisopropylamine (4.40 mL, 31.4 mmol) in THF (75 mL) at 0 °C. After 30 min, Bu_3SnH (10 mL, 37.2 mmol) was added in a dropwise fashion to afford a pale green-yellow solution. After another 30 min, a solution of **71** (1.90 g, 10 mmol) in THF (50 mL) was added. After 1.5 h at 0 °C, saturated aqueous NH_4Cl was added. The mixture was diluted in ether, and the organic phase was washed with saturated aqueous NH_4Cl and 10% NaOH, dried ($MgSO_4$), filtered, and concentrated. Chromatography (hexane to 50% EtOAc/hexane gradient) afforded 2.60 g (72%) of the title compound.

***N*-[1-(Tri-*n*-butylstannyl)-2-methylpropyl]acetamide (74) via Amine 70.** *N*-[1-(Tri-*n*-butylstannyl)-2-methylpropyl]-phthalimide[20,34] (9.44 g, 19.2 mmol) and hydrazine monohydrate (50 mL, 1.0 mol) were dissolved in EtOH (400 mL, 95%). The mixture was heated at reflux for 24 h and then concentrated and diluted with ether. The organic phase was washed with water (3×), dried ($MgSO_4$), and concentrated. The resultant oil was dissolved in THF (200 mL) and treated with triethylamine (6.0 mL, 42.8 mmol), DMAP (20 mg, 0.16 mmol), and acetyl chloride (1.50 mL, 21.1 mmol). After 12 h, the mixture was diluted with ether and washed with water and saturated aqueous NH_4Cl (3×). The organic phases were combined dried ($MgSO_4$), and concentrated. Chromatography (0−5% EtOAc/hexane gradient) afforded 5.10 g (66%) of the title compound as a white solid: R_f = 0.27 (25% EtOAc/hexane); IR (in $CHCl_3$) 3444 (w), 1667 (s), 1511 (m), 1461 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.76 (d, 1 H, J = 6.7 Hz), 3.10 (t, 1 H, J = 7.7 Hz, ^2J ($^{117/119}Sn-^1H$) = 42.7 Hz), 2.12−1.95 (m, 4 H), 1.60−1.40 (m, 6 H), 1.40−1.25 (m, 6 H), 1.00−0.73 (m, 21 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.2, 49.0, 32.0, 29.5 (19 Hz), 27.5 (56 Hz), 22.9, 21.7, 20.9, 13.5 (92 Hz), 11.0 (310 Hz); MS (CI, NH_3) *m*/*z* (rel intensity) 406 (17, M + H), 404 (14), 352 (24), 350 (22), 349 (22), 348 (100), 347 (43), 346 (76), 345 (35), 344 (47); HRMS (CI, NH_3) calcd for $C_{18}H_{40}NO^{120}Sn$ (M + H)$^+$ 406.2132, found 406.2103. Anal. Calcd for $C_{18}H_{39}NOSn$: C, 53.49; H, 9.73; N, 3.47. Found: C, 53.55; H, 9.44; N, 3.35. **Via the Benzotriazole 72.** *n*-Butyllithium (14.0 mL, 29.4 mmol, 2.1 M in hexanes) was added to a solution of diisopropylamine (4.00 mL, 28.5 mmol) in THF (60 mL) at 0 °C. After 30 min, Bu_3SnH (7.70 mL, 28.6 mmol) was added in a dropwise fashion to afford a pale green-yellow solution. After another 30 min, a solution of **72** (3.14 g, 13.4 mmol)[36] in THF (10 mL) was added. After 2 h at 0 °C, 10% NaOH (aqueous) was added. The organic layer was washed with 10% NaOH (aqueous), saturated aqueous NH_4Cl, and water, dried ($MgSO_4$), and concentrated. Chromatography (0−25% EtOAc/hexane gradient) afforded 4.63 g (85%) of the title compound as a thick, colorless oil.

(*E*)-Methyl *N*-[(Tri-*n*-butylstannyl)methyl]acetimidate (10). Dimethyl sulfate (1.45 mL, 15 mmol) and **73** (5.01 g, 14 mmol) were heated at 50 °C for 24 h. The mixture was diluted with ether and washed with 30% Na_2CO_3 (aqueous), and then the organic extract was dried (Na_2SO_4), filtered, and concentrated. Kugelrohr distillation of the resultant oil (116−120° air bath, 0.18 mmHg) afforded 3.17 g (61%) of of the title compound as a clear, colorless oil: IR ($CHCl_3$) 1672 (s), 1464 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.52 (s, 3 H), 3.25 (s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 40.8), 1.80 (s, 3 H, $^5J(^{117/119}Sn-^1H)$ = 6.5 Hz), 1.55−1.43 (m, 6 H), 1.37−1.22 (m, 6 H), 0.95−0.80 (m, 15 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.3, 51.8, 35.1, 29.2 (19 Hz), 27.4, 13.6, 9.6; MS (CI, NH_3) *m*/*z* (rel intensity) 382 (23), 380 (22), 379 (25), 378 (100, M + H), 377 (44), 376 (38), 374 (51), 308 (22), 306 (17), 304 (10); HRMS (CI, NH_3) calcd for $C_{16}H_{36}NO^{120}Sn$ (M + H)$^+$ 378.1819, found 378.1820. Anal. Calcd for $C_{16}H_{35}NOSn$: C, 51.09; H, 9.38; N, 3.72. Found: C, 51.20; H, 9.38; N, 3.65.

***N*,*N*-Tetramethylene-*N*′-[1-(tri-*n*-butylstannyl)methyl]-acetamidine (17).** Stannane **10** (105 mg, 0.279 mmol), pyrrolidine (29 mg, 0.411 mmol), and benzoic acid (ca. 10 mg) were combined in DMF (2 mL). After 48 h, the mixture was diluted with ether, washed with 10% NaOH (aqueous), dried (Na_2SO_4), filtered, and concentrated to provide 104 mg (90%) of the title compound, which was sufficiently pure to be used without further purification: R_f = 0.80 (MeOH on Al_2O_3); IR (neat) 1619 (s), 1455 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 3.37 (s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 38.1 Hz), 3.30−3.25 (m, 4 H), 1.86 (s, 3 H, $^5J(^{117/119}Sn-^1H)$ = 4.5 Hz), 1.84−1.79 (m, 4 H), 1.52−1.42 (m, 6 H), 1.26 (hex, 6 H, J = 6.3 Hz), 0.97−0.76 (m, 15 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 154.1, 47.0, 36.1, 29.2 (19 Hz), 27.4 (52 Hz), 25.3, 13.7, 9.6; MS (CI, NH_3) *m*/*z* (rel intensity) 417 (5, M + H), 125 (10), 114 (54), 113 (65), 100 (100); HRMS (CI, NH_3) calcd for $C_{19}H_{41}N_2{}^{120}Sn$ (M + H)$^+$ 417.2292, found 417.2288.

(*E*)-Methyl *N*-[1-(Tri-*n*-butylstannyl)-2-methylpropyl]-acetimidate (18) via *O*-Alkylation of 74. Dimethyl sulfate (1.15 mL, 12.1 mmol) and **74** (4.63 g, 11.5 mmol) were mixed and heated neat at 70 °C for 24 h. The mixture was diluted with ether and washed with 50% K_2CO_3 (aqueous). The organic layer was dried ($MgSO_4$), filtered, and concentrated. Kugelrohr distillation of the resultant oil (125 °C air bath, 0.05 mmHg) afforded 3.57 g (74%) of the title compound as a clear colorless oil: IR (in $CHCl_3$) 1672 (s), 1461 (m), 1433 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.56 (s, 3 H), 3.20 (d, 1 H, J = 7.8 Hz, ^2J ($^{117/119}Sn-^1H$) = 23.0 Hz), 2.21−1.92 (m, 1 H), 1.79 (s, 3 H, ^5J ($^{117/119}Sn-^1H$) = 7.1 Hz), 1.60−1.20 (m, 12 H), 0.97−0.74 (m, 21 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 155.0, 60.0, 51.7, 33.6, 29.3 (20 Hz), 27.5 (53 Hz), 22.0, 21.7, 14.1, 13.6, 9.8 (289 Hz); MS (CI, NH_3) *m*/*z* (rel intensity) 424 (26), 422 (12), 421 (26), 420 (100, M + H), 419 (43), 418 (73), 417 (37), 416 (50); HRMS (CI, NH_3) calcd for $C_{19}H_{42}NO^{120}Sn$ (M + H)$^+$ 420.2288, found 420.2289. Anal. Calcd for $C_{19}H_{41}NOSn$: C, 54.57; H, 9.88; N,

3.35. Found: C, 54.43; H, 9.89; N, 3.40. See below for an alternate procedure.

***N,N*-Tetramethylene-*N′*-[1-(tri-*n*-butylstannyl)-2-methylpropyl]acetamidine (31).** Stannane **18** (1.87 g, 4.46 mmol), pyrrolidine (0.95 mL, 11.4 mmol), and trifluoroacetic acid (0.50 mL, 6.49 mmol) were dissolved in MeOH (10 mL) and heated at reflux. After 36 h, solid Na_2CO_3 was added, and the reaction was concentrated to provide an oil. The oil was diluted in ether, washed with 10% NaOH (aqueous), dried (Na_2SO_4), filtered, and concentrated. Chromatography (Al_2O_3, 0−10% MeOH/chloroform) afforded what was presumed to be the conjugate acid of the desired product. This material was diluted in ether, washed with 10% NaOH (aqueous), dried (Na_2SO_4), filtered, and concentrated to afford 184 mg (9%) of the title compound as a colorless oil. Also isolated were 130 mg (7%) of the imidate **18** and 70 mg (4%) of the amide **74**. Data for **31**: R_f = 0.31 (10% MeOH/chloroform); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.38−3.22 (m, 5 H), 2.12−1.98 (m, 1 H), 1.86−1.80 (m, 7 H), 1.56−1.40 (m, 6 H), 1.40−1.27 (m, 6 H), 1.00−0.70 (m, 21 H); MS (CI, NH_3) *m*/*z* (rel intensity) 463 (26), 461 (26), 460 (34), 459 (100, M + H), 458 (54), 457 (80), 456 (41), 455 (53), 388 (41), 386 (31), 167 (98); HRMS (CI, NH_3) calcd for $C_{22}H_{47}N_2{}^{120}Sn$ $(M + H)^+$ 459.2761, found 459.2748. Anal. Calcd. for $C_{22}H_{46}N_2Sn$: C, 57.78; H, 10.14; N, 6.13. Found: C, 57.58; H, 9.81; N, 6.00.

***N*-[(Tri-*n*-butylstannyl)methyl]thioacetamide (75).** Lawesson's reagent (11.7 g, 28.8 mmol) and the amide **73** (5.02 g, 13.9 mmol) were dissolved in THF (75 mL), and the suspension was sonicated at ambient temperature for 3 h. The reaction was diluted with EtOAc, washed with 10% NaOH (aq), dried ($MgSO_4$), filtered, and concentrated to provide a thick, yellow oil. Chromatography (0−15% EtOAc/hexane gradient) afforded 2.56 g (49%) of the title compound as an oil: R_f = 0.54 (30% EtOAc/hexane); IR (in $CHCl_3$) 3397 (s), 1731 (w), 1531 (s), 1464 (m), 1417 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.67 (s, 1 H), 3.39 (d, 2 H, J = 6.3 Hz, $^2J(^{117/119}Sn-^1H)$ = 26.0 Hz), 2.52 (s, 3 H), 1.55−1.47 (m, 6 H), 1.35−1.25 (m, 6 H), 1.03−0.85 (m, 15 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 194.3, 34.3, 32.7, 29.0 (20 Hz), 27.0 (56 Hz), 13.6, 11.1 (317 Hz); MS (CI, NH_3) *m*/*z* (rel intensity) 384 (11), 382 (11), 381 (11), 380 (42, M + H), 379 (21), 378 (35), 377 (16), 376 (21), 322 (14), 320 (11), 90 (100); HRMS (CI, NH_3) calcd for $C_{15}H_{34}NS^{120}Sn$ $(M + H)^+$ 380.1434, found 380.1439.

Methyl *N*-[(Tri-*n*-butylstannyl)methyl]thioacetimidate (14). Thioamide **75** (1.50 g, 3.97 mmol) and dimethyl sulfate (0.40 mL, 4.23 mmol) were mixed at room temperature. After 24 h, the mixture was diluted with 25% Na_2CO_3 (aq) and extracted with ether (2×). The organic extracts were combined, dried (Na_2SO_4), filtered, and concentrated. Kugelrohr distillation of the resultant oil (116−120 °C air bath, 0.2 mmHg) afforded 1.33 g (85%) of the title compound as a 2:1 mixture of isomers about the imine double bond. Assignment of the carbon−nitrogen double bond configuration as *E* or *Z* was not performed for either isomer. Data for the major isomer: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.51 (s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 43.8 Hz), 2.42 (s, 3 H,), 2.21 (s, 3 H, $^5J(^{117/119}Sn-^1H)$ = 16.7 Hz), 1.58−1.40 (m, 6 H), 1.40−1.20 (m, 6 H, 1.20−0.70 (m, 15 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 153.9, 40.5, 29.0, 27.3, 14.2, 13.6, 10.2. Data for minor isomer: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.61 (s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 43.8 Hz), 2.21 (s, 3 H), 1.93 (s, 3 H, $^5J(^{117/119}Sn-^1H)$ = 7.6 Hz), 1.58−1.40 (m, 6 H, 1.40−1.20 (m, 6 H, 1.20−0.70 (m, 15 H,); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 154.9, 39.8, 26.7, 24.6, 13.5, 12.9, 9.6. Data for isomer mixture: IR (neat) 1610 (m), 1464 (m) cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel intensity) 393 (5, M), 336 (44), 291 (42), 235 (73), 233 (57), 179 (97), 177 (85), 175 (56), 55 (100); HRMS (EI, 70 eV) calcd for $C_{16}H_{35}NS^{120}Sn$ M^+ 393.1512, found 393.1512. Anal. Calcd for $C_{16}H_{35}NSSn$: C, 49.00; H, 8.99; N, 3.57. Found: C, 48.63; H, 8.76; N, 3.18.

***N*-[1-(Tri-*n*-butylstannyl)-2-methylpropyl]thioacetamide (76).** Stannane **74** (5.92 g, 14.7 mmol) and Lawesson's reagent (4.41 g, 10.9 mmol) were dissolved in THF (50 mL), and the mixture was sonicated at ambient temperature for 2 h. The mixture was diluted in EtOAc, washed with 5% NaOH (aq), dried ($MgSO_4$), filtered, and concentrated. Chromatography (0−10% EtOAc/hexane gradient) afforded 4.97 g (80%) of the title compound as a nearly colorless oil: R_f = 0.75 (50% EtOAc/hexane); IR (neat) 3384 (m), 1514 (m), 1464 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.45 (br d, 1 H, J = 7.7 Hz), 4.20 (t, 1 H, J = 9.1 Hz), 2.55 (s, 3 H, ^5J ($^{117/119}Sn-^1H$) = 2.5 Hz), 2.28−2.20 (m, 1 H), 1.60−1.40 (m, 6 H), 1.31 (hex, 6 H, J = 7.2 Hz), 0.99 (d, 3 H, J = 6.7 Hz), 0.98 (d, 3 H, J = 6.7 Hz), 0.95−0.87 (m, 15 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 194.5, 57.6, 33.7, 30.8, 29.1 (19 Hz), 27.5, 21.7, 21.2, 13.6, 11.1; MS (CI, NH_3) *m*/*z* (rel intensity) 424 (26), 423 (29), 422 (95, M + H), 421 (50), 420 (82), 419 (39), 418 (51), 364 (27), 308 (26), 160 (60), 132 (100); HRMS (CI, NH_3) calcd for $C_{18}H_{40}NS^{120}Sn$ $(M + H)^+$422.1904, found 422.1903. Anal. Calcd. for $C_{18}H_{39}NSSn$: C, 51.44; H, 9.35; N, 3.33. Found: C, 51.31; H, 9.25; N, 3.38.

Methyl *N*-[1-(Tri-*n*-butylstannyl)-2-methylpropyl]thioacetimidate (27). Stannane **76** (1.72 g, 4.08 mmol) and dimethyl sulfate (0.43 mL, 4.50 mmol) were mixed at room temperature. After 24 h, solid Na_2CO_3 and ether were added. The mixture was washed with 10% Na_2CO_3 (aqueous), and the organic layer was dried (Na_2SO_4), filtered, and concentrated. Kugelrohr distillation of the resultant oil (135−140 °C air bath, 0.05 mmHg) afforded 1.18 g (67%) of the title compound as a 3:2 mixture of geometrical isomers. Assignment of the carbon−nitrogen double bond configuration as *E* or *Z* was not performed for either isomer. Data for major isomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.34 (d, 1 H, J = 9.6 Hz, ^2J = ($^{117/119}Sn-^1H$) = 33.8 Hz), 2.42 (s, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 151.3, 65.6, 33.0. Data for minor isomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.59 (d, 1 H, J = 7.7 Hz, $^2J(^{117/119}Sn-^1H)$ = 25.1 Hz), 1.91 (s, 3 H, $^5J(^{117/119}Sn-^1H)$ = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 152.2, 64.1, 33.5. Data for mixture of both isomers: IR (neat) 1615 (m), 1464 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.59 (d, 0.4 H, J = 7.7 Hz, $^2J(^{117/119}Sn-^1H)$ = 25.1 Hz), 3.34 (d, 0.6 H, J = 9.6 Hz, ^2J = ($^{117/119}Sn-^1H$) = 33.8 Hz), 2.42 (s, 1.8 H), 2.32−2.14 (m, 4 H), 1.91 (s, 1.2 H, $^5J(^{117/119}Sn-^1H)$ = 8.3 Hz), 1.55−1.41 (m, 6 H), 1.34−1.25 (m, 6 H), 0.98−0.80 (m, 21 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 152.2, 151.3, 65.6, 64.1, 33.5, 33.1, 29.2, 27.6, 24.6, 22.6, 22.1, 22.1, 22.0, 19.9, 14.5, 13.7, 12.4, 10.3, 9.9; MS (EI, 70 eV) *m*/*z* (rel intensity) 435 (2, M), 179 (10), 144 (30), 103 (13), 98 (14), 97 (100); HRMS (EI, 70 eV) calcd for $C_{19}H_{41}NS^{120}Sn$ M^+ 435.1982, found 435.1980.

***N,N*-Dimethyl-*N′*-[(tri-*n*-butylstannyl)methyl]formimidamide (15).** *N*-[(Tri-*n*-butylstannyl)methyl]phthalimide (503 mg, 1.11 mmol)[20] and hydrazine monohydrate (2.0 mL, 41 mmol) were dissolved in EtOH (10 mL) and heated at reflux. After 2 h, the mixture was concentrated, diluted with ether, washed with water (4×), dried (Na_2SO_4), filtered, and concentrated to provide 295 mg of the amine **69** an oil (83% crude yield). The oil was dissolved in MeOH (15 mL), and *N,N*-dimethylformamide dimethyl acetal (0.15 mL, 1.05 mmol) was added. After 1 h, the mixture was concentrated to provide 340 mg (81%) of the title compound, which was found by ^{1}H NMR to be sufficiently pure to use without further purification: R_f = 0.55 (10% MeOH/EtOAc, Al_2O_3); IR (neat) 1649 (s), 1463 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.19 (s, 1 H, $^4J(^{117/119}Sn-^1H)$ = 10.8 Hz)), 3.37 (s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 34.3 Hz), 2.77 (s, 6 H), 1.51−1.43 (m, 6 H), 1.31−1.22 (m, 6 H), 0.92−0.78 (m, 15 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ152.5, 40.6, 37.6, 29.2, 27.4, 13.7, 9.1; MS (EI, 70 eV) *m*/*z* (rel intensity) 319 (11, M − C_4H_9), 85 (100); HRMS (CI, NH_3) calcd for $C_{16}H_{27}N_2{}^{120}Sn$ $(M)^+$ 319.1196, found 319.1202.

***N*-[1-(Tri-*n*-butylstannyl)ethyl]phthalimide.** According to the procedure described by Chong for similar compounds,[34] *n*-butyllithium (13.7 mL, 37.1 mmol, 2.7 M in hexanes) was added to a solution of diisopropylamine (5.70 mL, 40.9 mmol) in THF (75 mL) at 0 °C. After 30 min, Bu_3SnH (10.0 mL, 37.1 mmol) was added in a dropwise fashion to afford a pale green-yellow solution. After another 30 min, this solution was cooled to −78 °C and acetaldehyde (7.0 mL, 125 mmol) was added. The reaction was allowed to warm to room temperature. The mixture was diluted with ether, washed with water, dried (Na_2SO_4), filtered, and concentrated. The resultant oil was dissolved in THF (100 mL) and cooled to 0 °C. Phthalimide (6.62 g, 45.0 mmol), triphenylphosphine (11.8 g, 45.0 mmol), and

diisopropyl azodicarboxylate (8.9 mL, 45.2 mmol) were added. Upon warming to room temperature, the mixture was concentrated to provide a thick yellow mass that was triturated with hexane. The washes were concentrated and chromatographed (0−2% EtOAc/hexane gradient) to afford 10.0 g (58%) of the title compound as a yellow-green oil: R_f = 0.20 (5% EtOAc/hexane); IR (neat) 1771 (w), 1706 (s), 1465(w) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.80−7.75 (m, 2 H), 7.67−7.63 (m, 2 H), 3.91 (q, 1 H, J = 7.5 Hz, $^2J(^{117/119}Sn-^1H)$ = 12.8 Hz), 1.59−1.40 (m, 6 H), 1.40−1.22 (m, 6 H), 1.05−0.80 (m, 6 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 168.7, 133.5, 132.3, 122.8, 31.8, 29.0 (18 Hz), 27.4 (56 Hz), 18.8, 13.6, 10.5 (314 Hz); MS (CI, CH_4) m/z (rel intensity) 412 (23), 410 (22), 409 (28), 408 (100, M − C_4H_9), 407 (49), 406 (78), 405 (40), 404 (49), 262 (17), 174 (35), 130 (12); HRMS (CI, CH_4) calcd for $C_{18}H_{26}NO_2{}^{120}Sn$ (M − C_4H_9)$^+$ 408.0986, found 408.0991.

***N*,*N*-Dimethyl-*N*′-[1-(tri-*n*-butylstannyl)ethyl]acetimidine (28).** *N*-[1-(Tri-*n*-butylstannyl)ethyl]phthalimide (3.00 g, 6.46 mmol, see above) and hydrazine monohydrate (5.0 mL, 103 mmol) were dissolved in EtOH (50 mL) and heated at reflux. After 4 h, the mixture was concentrated to provide a white mass, which was diluted with ether. The mixture was washed with water (5×), dried (Na_2SO_4), filtered, and concentrated to give the crude amine **77**, which was diluted with MeOH (50 mL) and treated with *N*,*N*-dimethylacetamide dimethyl acetal (1.05 mL, 7.15 mmol). After 12 h, the mixture was diluted with ether, washed with 10% NaOH (aqueous), dried (Na_2SO_4), filtered, and concentrated. Chromatography (hexane to EtOAc to 10% MeOH/EtOAc gradient on Al_2O_3) afforded 880 mg (34%) of the title compound as an oil: R_f = 0.15 (50% EtOAc/hexane on Al_2O_3); IR (neat) 1616 (s), 1463 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 3.58 (q, 1 H, J = 7.20 Hz), 2.78 (br s, 6 H), 1.82 (br s, 3 H), 1.50−1.32 (m, 9 H), 1.31−1.22 (m, 6 H), 0.90−0.69 (m, 15 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 153.5, 46.0, 38.3, 29.3 (20 Hz), 27.6 (51 Hz), 22.8, 13.7, 12.6, 8.9; MS (CI, NH_3) m/z (rel intensity) 405 (16, M + H), 403 (13), 291 (11), 129 (48), 114 (11), 113 (100); HRMS (CI, NH_3) calcd for $C_{18}H_{41}N_2{}^{120}Sn$ (M + H)$^+$ 405.2292, found 405.2301.

(*E*)-Methyl *N*-[1-(Tri-*n*-butylstannyl)-2-methylpropyl]-acetimidate (18) via Reaction of Amine 70 with Imidate Salt 78. See the above procedure for an alternate preparation. Hydrazine monohydrate (5.0 mL, 103 mmol) was added to a solution of *N*-[(tri-*n*-butylstannyl)-2-methylpropyl]phthalimide (1.02 g, 2.07 mmol)[20,34] in EtOH (20 mL). The mixture was heated at reflux for 18 h, cooled, and diluted with ether. The organic solution was washed with water (5×), dried (Na_2SO_4), filtered through Celite, and concentrated to afford the crude amine **70** as an oil. In a separate flask, Me_2SO_4 (0.20 mL, 2.1 mmol) and *N*,*N*-dimethylacetamide (0.20 mL, 2.2 mmol) were heated neat at 60 °C to form the imidate salt **78**. After 2 h, the mixture was cooled to room temperature, and the amine **70** in CH_2Cl_2 (5 mL) was added in a dropwise fashion. The mixture was heated at reflux for 30 min and then cooled and diluted with CH_2Cl_2. The resultant solution was washed with water, dried (Na_2SO_4), filtered through Celite, and concentrated to provide 0.68 g (80%) of the title compound, which was not purified further. None of the desired amidine was detected by ^1H NMR.

6-(Benzotriazol-1-yl)-2-piperidinone (83). 6-Ethoxy-2-piperidinone (**81**)[41] (9.24 g, 58.0 mmol) and benzotriazole (7.59 g, 63.7 mmol) were dissolved in glacial AcOH (200 mL). After 36 h, the solvent was evaporated, ether was added, and the resulting mixture was cooled. The precipitate was filtered and dried under vacuum to afford 10.0 g (79%) of the title compound as a white solid: mp 126−128 °C. The benzotriazol-2-yl isomer was not detected. Data for **83**: IR (in $CHCl_3$) 3389 (br m), 1679 (s), 1466 (m), 1451 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 8.08 (d, 1 H, J = 8.0 Hz), 7.57 (d, 1 H, J = 8.0 Hz), 7.50 (t, 1 H, J = 8.0 Hz), 7.38 (t, 1 H, J = 8.0 Hz), 7.12 (br s, 1 H,), 6.44 (dt, 1 H, J = 6.7, 2.5 Hz), 2.53 (q, 2 H, J = 7.2 Hz), 2.38 (q, 2 H, J = 6.2 Hz), 2.08 (hept, 1 H, J = 6.8 Hz), 1.91 (hept, 1 H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 172.0, 146.5, 131.5, 127.9, 124.3, 120.4, 109.9, 67.8, 31.4, 28.5, 17.8; MS (EI, 70 eV) m/z (rel intensity) 216 (13, M), 120 (53), 119 (100); HRMS (EI, 70 eV) calcd for $C_{11}H_{12}N_4O$ M$^+$ 216.1011, found 216.1018. Anal. Calcd for $C_{11}H_{12}N_4O$: C, 61.10; H, 5.59; N, 25.91. Found: C, 60.77; H, 5.81; N, 25.72.

5-(Benzotriazolyl)-2-pyrrolidinone (84). 5-Ethoxy-2-pyrrolidinone (**82**)[41] (17.3 g, 119 mmol) and benzotriazole (14.9 g, 125 mmol) were dissolved in glacial AcOH (400 mL). After 18 h, the solvent was evaporated, ether was added, and the mixture was cooled. The resulting precipitate was filtered and dried under vacuum to afford 15.6 g (65%) of the title compound as a white solid: mp 117−128 °C, found to be a 9:1 mixture of benzotriazol-1-yl and -2-yl isomers by ^1H NMR. Data for the benzotriazol-1-yl isomer: ^1H NMR ($CDCl_3$, 200 MHz) δ 8.06 (d, 1 H, J = 8.2 Hz), 6.54 (br d, 1 H, J = 5.5 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 178.5, 146.2, 131.3, 127.9, 124.3, 120.1, 109.3, 68.5, 28.9, 27.5. Data for the benzotriazol-2-yl isomer: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.86−7.80 (m, 2 H), 6.43 (br d, 1 H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 179.0, 144.3, 126.8, 118.2, 74.8, 28.3, 28.0. Data for mixture of regioisomers: IR (in $CHCl_3$) 3220 (br m), 1714 (s), 1452 (m), 1416 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 8.06 (d, 0.9 H, J = 8.2 Hz), 7.86−7.80 (m, 0.2 H), 7.68 (br s, 1 H), 7.60−7.35 (m, 2.9 H), 6.54 (br d, 0.9 H, J = 5.5 Hz), 6.43 (br d, 0.1 H, J = 6.6 Hz), 3.00−2.40 (m, 4 H); MS (EI, 70 eV) m/z (rel intensity) 202 (7, M), 119 (100); HRMS (EI, 70 eV) calcd for $C_{10}H_{10}N_4O$ M$^+$ 202.0855, found 202.0864. Anal. Calcd for $C_{10}H_{10}N_4O$: C, 59.40; H, 4.98; N, 27.71. Found: C, 59.46; H, 5.00; N, 27.41.

6-(Tri-*n*-butylstannyl)-2-piperidinone (85). *n*-Butyllithium (15.0 mL, 30.0 mmol, 2.0 M in hexanes) was added to a solution of diisopropylamine (4.40 mL, 31.4 mmol) in THF (75 mL) at 0 °C. After 30 min, Bu_3SnH (10.0 mL, 37.2 mmol) was added in a dropwise fashion to afford a pale green-yellow solution. After another 30 min, a solution of **83** (2.70 g, 12.4 mmol) in THF (60 mL) was added. After 2 h at 0 °C, 10% NaOH (aqueous) was added. The organic layer was washed with 10% NaOH (aqueous), saturated aqueous NH_4Cl, and water and then dried ($MgSO_4$), filtered, and concentrated. Chromatography (0−100% EtOAc/hexane gradient) afforded 4.32 g (90%) of the title compound as a slightly yellow oil: R_f = 0.10 (50% EtOAc/hexane); IR (neat) 3192 (m), 1657 (s), 1463 (m), 1409 (m); ^1H NMR ($CDCl_3$, 360 MHz) δ 5.80 (s, 1 H), 3.41−3.36 (m, 1 H), 2.43−2.27 (m, 2 H), 2.02−1.66 (m, 4 H), 1.51−1.42 (m, 6 H), 1.34−1.23 (m, 6 H), 1.03−0.85 (m, 15 H); ^{13}C NMR ($CDCl_3$, 360 MHz) δ 171.8, 42.5, 31.5, 29.1 (20 Hz), 27.5, 27.4 (53 Hz), 22.9, 13.6, 8.4; MS (EI, 70 eV) m/z (rel intensity) 389 (7, M), 269 (35), 177 (40), 113 (60), 42 (100); HRMS (EI, 70 eV) calcd for $C_{17}H_{35}NO^{120}Sn$ M$^+$ 389.1741, found 389.1741.

5-(Tri-*n*-butylstannyl)-2-pyrrolidinone (86). *n*-Butyllithium (27.7 mL, 37.4 mmol, 1.85 M in hexanes) was added to a solution of diisopropylamine (9.50 mL, 68.2 mmol) in THF (100 mL) at 0 °C. After 30 min, Bu_3SnH (15.3 mL, 56.9 mmol) was added in a dropwise fashion to afford a pale green-yellow solution. After another 30 min, a solution of **84** (4.63 g, 22.8 mmol) in THF (50 mL) was added. After 2 h at 0 °C, 10% NaOH (aqueous) was added. The organic layer was washed with 10% NaOH (aqueous), saturated aqueous NH_4Cl, and water and then dried ($MgSO_4$), filtered, and concentrated. Chromatography (0−100% EtOAc/hexane gradient) afforded 8.10 g (95%) of the title compound as a colorless oil: R_f = 0.10 (50% EtOAc/hexane); IR (neat) 3432 (m), 1679 (s), 1464 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.20 (br s, 1 H), 3.50 (t, 1 H, J = 7.4 Hz), 2.47−2.15 (m, 4 H), 1.60−1.40 (m, 6 H), 1.40−1.22 (m, 6 H), 1.05−0.84 (m, 15 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 179.0, 42.0, 31.3, 29.0 (21 Hz), 27.3 (53 Hz), 27.0, 13.5, 8.4 (308 Hz); MS (EI, 70 eV) m/z (rel intensity) 375 (31, M), 291 (42), 289 (32), 235 (74), 234 (33), 233 (56), 231 (41), 179 (100), 178 (40), 177 (85), 176 (40), 175 (61); HRMS (EI, 70 eV) calcd for $C_{16}H_{33}NO^{120}Sn$ M$^+$ 375.1584, found 375.1579. Anal. Calcd for $C_{16}H_{33}NOSn$: C, 51.37; H, 8.89; N, 3.74. Found: C, 51.48; H, 8.49; N, 4.04.

2-Methoxy-3,4,5,6-tetrahydro-5-(tri-*n*-butylstannyl)-pyridine (51). Dimethyl sulfate (0.38 mL, 4.02 mmol) and stannane **85** (1.44 g, 3.71 mmol) were mixed and heated at 60 °C. After 24 h, the reaction was cooled and solid Na_2CO_3 was added. The mixture was diluted with ether, washed with 50% Na_2CO_3 (aqueous), dried (Na_2SO_4), filtered, and concentrated

to provide an oil. Kugelrohr distillation (120−125 °C air bath, 0.05 mmHg) afforded 1.06 g (71%) of the title compound as a clear, colorless oil: IR (neat) 1663 (m), 1522 (m), 1458 (m), 1435 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.87−3.79 (m, 1 H), 3.57 (s, 3 H), 2.22−2.11 (m, 2 H), 1.98−1.62 (m, 4 H), 1.63−1.40 (m, 6 H), 1.40−1.27 (m, 6 H), 1.05−0.76 (m, 15 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 158.4, 51.5, 47.0 (368 Hz), 29.3 (18 Hz), 27.5 (51 Hz), 26.7, 25.4 (7 Hz), 21.1 (21 Hz), 13.7, 9.3 (292 Hz); MS (EI, 70 eV) *m*/*z* (rel intensity) 403 (6, M), 235 (43), 234 (47), 233 (43), 232 (36), 179 (60), 177 (55), 175 (37), 112 (100); HRMS (EI, 70 eV) calcd for $C_{18}H_{37}NO^{120}Sn$ M^+ 403.1897, found 403.1913. Anal. Calcd for $C_{18}H_{37}NOSn$: C, 53.76; H, 9.27; N, 3.48. Found: C, 53.46; H, 9.18; N, 3.53.

2-Benzyloxy-3,4,5,6-tetrahydro-6-(tri-*n*-butylstannyl)-pyridine (63). Stannane **85** (1.77 g, 4.55 mmol) was dissolved in CH_2Cl_2 (10 mL) and mixed with diphenylbenzyl sulfonium tetrafluoroborate (2.53 g, 6.95 mmol). The mixture was heated at reflux for 5 h, then cooled and treated with solid Na_2CO_3. After an additional 20 min, the mixture was diluted with CH_2Cl_2, washed with 10% NaOH (aqueous), dried (Na_2SO_4), filtered, and concentrated. Chromatography (hexane) afforded 1.48 g of an oil consisting of 5:1 mixture of the desired product and diphenyl sulfide by ^1H NMR integration. This ratio corresponds to 3.0 mmol of product for a 66% adjusted yield of the title compound: $R_f = 0.50$ (10% EtOAc/hexane); IR (neat) 1666 (s), 1454 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) 7.45−7.20 (m, 5 H), 5.07 (d, 1 H, $J = 12.4$ Hz), 4.93 (d, 1 H, $J = 12.4$ Hz), 3.82 (br s, 1 H), 2.30−2.18 (m, 2 H), 2.00−1.90 (m, 1 H), 1.90−1.60 (m, 3 H), 1.60−1.40 (m, 6 H), 1.40−1.25 (m, 6 H), 0.98−0.80 (m, 15 H); MS (CI, NH_3) *m*/*z* (rel intensity) 480 (39, M + H), 478 (30), 367 (29), 366 (27), 277 (26), 276 (25), 200 (20), 199 (200), 188 (41), 181 (27), 180 (22), 179 (30), 167 (26), 165 (23), 91 (100); HRMS (CI, NH_3) calcd for $C_{24}H_{42}NO^{120}Sn$ $(M + H)^+$ 480.2288, found 480.2296.

2-Methoxy-5-(tri-*n*-butylstannyl)-1-pyrroline (50). Dimethyl sulfate (1.20 mL, 12.7 mmol) and the stannane **86** (4.34 g, 11.1 mmol) were mixed and heated at 50 °C. After 13 h, the solution was cooled and solid Na_2CO_3 was added. This mixture was diluted with ether, washed with 50% K_2CO_3 (aqueous), dried (Na_2SO_4), filtered, and concentrated. Kugelrohr distillation (128−135 °C air bath, 0.10 mmHg) afforded 3.35 g (75%) of the title compound as a clear, colorless oil: IR (in $CHCl_3$) 1632 (s), 1459 (s), 1439 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 4.00−3.88 (m, 1 H), 3.78 (s, 3 H), 2.55−2.30 (m, 3 H), 2.20−2.10 (m, 1 H), 1.60−1.40 (m, 6 H), 1.40−1.24 (m, 6 H), 1.02−0.80 (m, 15 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 168.5, 56.5, 55.0, 31.2, 29.2 (20 Hz), 29.0, 13.6, 8.9 (299 Hz); MS (EI, 70 eV) *m*/*z* (rel intensity) 389 (2, M), 291 (25), 276 (27), 235 (46), 233 (40), 231 (26), 220 (43), 218 (35), 179 (67), 178 (27), 177 (63), 176 (27), 175 (42), 98 (100); HRMS (EI, 70 eV) calcd for $C_{17}H_{35}NO^{120}Sn$ M^+ 389.1741, found 389.1741. Anal. Calcd for $C_{17}H_{35}NOSn$: C, 52.60; H, 9.09; N, 3.61. Found: C, 52.43; H, 8.85; N, 3.79.

Acknowledgment to the National Institutes of Health (GM-52491) for support of this research. We thank Dr. Michael A. Walters (Parke-Davis Pharmaceutical Research) for sharing with us his results on the modeling of the mechanism of 2-azaallyl anion cycloadditions. Acknowledgment is made to Robert Schelkun for preliminary experiments with heteroatom-substituted 2-azaallyl anions.

Supporting Information Available: Photocopies of ^1H NMR and ^{13}C NMR spectra new compounds without elemental analysis (79 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO981457I