system with DDB-FlLi, reactivities of S^- and R^- dimer anions are similar. However, the propagating dimer anion contains a larger amount of S^- dimer anion than R^- dimer anion. In the next step and thereafter, SS^- trimer anion and the higher isotactic oligomer anions with *SSS*--- configuration predominantly propagate to a polymer of *SSS*--- configuration. In the system with PMP-FlLi, the propagation of unimer anion to dimer anion is slower than in the other two systems. The stereochemistry of propagation in this system is similar to that in the DDB-FlLi system, and a polymer of *SSS*--- configuration is produced. In the systems with DBB-FlLi and PMP-FlLi, acceleration of polymerization occurs when the oligomer anion grows to DP ~7. The difference in the stereochemistry of propagation with the three initiator systems must be related to the stereostructure of the complexes of oligomer anions with chiral ligands.

Though the absolute configuration of asymmetric carbons in the main chain of the polymer obtained with Sp-FlLi is opposite that of the polymers obtained with DDB-FlLi and PMP-FlLi, all the polymers possess the same helicity. The two isotactic polymer chains of the same helicity with opposite absolute configurations are regarded as diastereomers, particularly when DP is low, because the influence of the α and ω end groups cannot be ignored. Therefore, the stereostructure of the helices in the vicinity of the chain ends may slightly differ depending on the absolute configuration. This may be the reason why a stable helix starts at different DP in the above polymerization systems. The helix with *SSS*--- configuration may be more stable than that with the opposite configuration, since the helix starts at lower DP (~7), and polymerization is much faster in the systems with DDB-FlLi and PMP-FlLi than in the system with Sp-FlLi.

There exist few examples of studies on polymerization with stereochemical investigation of each addition step of a monomer including the absolute configuration of the main chain as done in the present study. Pino and co-workers briefly reported such a study of polypropylene produced with an optically active zirconium catalyst.[32] The present report may be the first example of assignment of absolute configuration of the main chain of polymethacrylate, and we could show that th polymer chains produced with the chiral initiator systems have exclusively either *RRR*--- or *SSS*--- absolute configuration.

Acknowledgment. We thank Dr. K. Ute and Mr. Y. Terawaki (Osaka University) for their help in measuring two-dimensional NMR spectra and Dr. E. Yashima (Nagoya University) for fruitful discussions.

Registry No. (±)-MMA, 138180-98-0; (±)-*m*-MMA (dimer), 138181-02-9; (±)-*r*-MMA (dimer), 125078-68-4; (±)-*mm*-MMA (trimer), 138181-03-0; (±)-*rr*-MMA (trimer), 138256-49-2; (±)-*mr*-MMA (trimer), 138181-04-1; (*S*,*S*)-MMA (dimer), 138256-50-5; (*R*,*R*)-MMA (dimer), 138256-51-6; (*R*,*S*)-MMA (dimer), 138257-63-3; (*S*,*R*)-MMA (dimer), 138256-52-7; FlLi·SP, 138180-99-1; FlLi·DDP, 138181-00-7; FlLi·PMP, 138181-01-8; TrMA (homopolymer), 27497-74-1; (*R*,*R*)-$HO_2CCH(CH_3)CH_2CH(CH_3)CO_2H$, 24018-75-5; *meso*-$HO_2CCH(CH_3)CH_2CH(CH_3)CO_2H$, 2121-67-7; (±)-$MeO_2CCH(CH_3)CH_2CH(CH_3)CO_2Me$, 2121-68-8; (*R*,*R*)-$MeO_2CCH(CH_3)CH_2CH(CH_3)CO_2Me$, 85717-93-7; 9-(iodomethyl)fluorene, 73283-56-4; 9-fluorenylmethanol, 24324-17-2.

Supplementary Material Available: Tables of ^1H NMR chemical shifts of MMA dimer, trimer, pentamer, hexamer, heptamer, and octamer (4 pages). Ordering information is given on any current masthead page.

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Generation of 2-Azaallyl Anions by the Transmetalation of *N*-(Trialkylstannyl)methanimines. Pyrrolidine Synthesis by [3 + 2] Cycloadditions with Alkenes

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Abstract: Treatment of *N*-(trimethylstannyl)methanimines or *N*-(tri-*n*-butylstannyl)methanimines with methyllithium or *n*-butyllithium, respectively, affords 2-azaallyl anions by tin-lithium exchange. These anions undergo intermolecular or intramolecular [π4s + π2s] cycloadditions with alkenes and alkynes to generate pyrrolidines or pyrrolines after quenching with water or other electrophiles. The tin-lithium exchange method allows unstabilized 2-azaallyl anions to be generated for the first time. The lifetime of the anions is limited by a competing intermolecular side reaction. Therefore, relatively reactive alkenes and alkynes must be used, such as stilbene, styrenes, enynes, diphenylacetylene, vinyl sulfides, vinyl selenides, and vinyl silanes. The latter three types of anionophiles afford functionalized cycloadducts which may be transformed into more useful pyrrolidines by reduction, elimination, or oxidation. A synthesis of the alkaloid (±)-mesembrane was accomplished using an intramolecular 2-azaallyl anion cycloaddition.

The pyrrolidine ring is a common feature of many interesting natural and unnatural compounds. Synthetic methods which allow the rapid construction of the pyrrolidine ring would be very useful. In particular, methods which make more than one ring bond in a single operation would be the most efficient, and such reactions generally fall into the cycloaddition category. Whereas the Diels-Alder reaction has been of major importance in the synthesis of both carbocyclic and heterocyclic six-membered rings,[1] cycloaddition reactions which form five-membered heterocyclic rings have only recently gained similar popularity. Of particular utility is the cycloaddition of 1,3-dipolar species, leading to a variety of five-membered ring heterocycles.[2] The cycloaddition of azomethine ylides **1** with alkenes has proven to be effective for the assembly of a variety of pyrrolidines **2**.[3] A related, but less well

(1) (a) Boger, D. L.; Weinreb, S. N. *Hetero Diels-Alder Methodology in Organic Synthesis*; Academic Press: San Diego, 1987. (b) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1990.

(2) Padwa, A. *1,3-Dipolar Cycloaddition Chemistry*; Wiley-Interscience: New York, 1984; Vols. 1 and 2.

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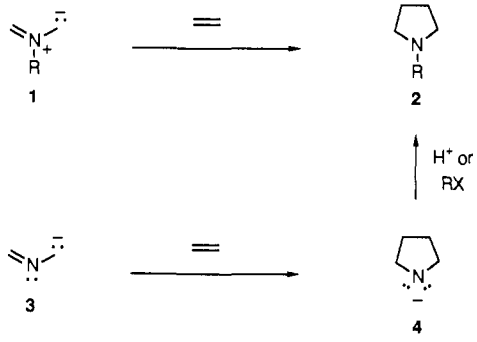
developed, method for the preparation of pyrrolidines is the cycloaddition of 2-azaallyl anions **3** with alkenes to provide anions **4**, which may be protonated or alkylated to provide pyrrolidines **2**.[3b,4] In principle, this method would serve as a complement to



azomethine ylide chemistry. However, the scope of 2-azaallyl anion cycloadditions has been limited by the methods available for the preparation of these anions. We wish to report a new method for the generation and cycloaddition of 2-azaallyl anions that increases the scope of this synthetic method considerably.[5]

Background

The cycloaddition of a three-atom fragment bearing four π-electrons (i.e., an allylic anion) with a two-atom, two π-electron component has long been recognized as a potential method for the generation of five-membered rings. Whereas allyl anions themselves are generally reluctant to undergo concerted cycloaddition reactions with alkenes,[6] the replacement of the central carbon atom with a more electronegative nitrogen atom has a favorable effect on the cycloaddition, since the reaction proceeds with a shift of electron density from the carbon termini of the 2-azaallyl anion to the central nitrogen atom (**3** → **4**). While 2-azaallyl anions have been studied since the early studies of Ingold in 1929,[7] it was Kauffmann in 1970 who first demonstrated the ability of these anions to undergo cycloaddition with alkenes and other "anionophiles", culminating in a review article in 1974.[4] For example, (1,3-diphenyl-2-azaallyl)lithium underwent cycloaddition with *cis*- or *trans*-stilbene, providing diastereomers of 2,3,4,5-tetraphenylpyrrolidine.[8] On the basis of the stereospecificity of the reaction with respect to the alkene, the reaction was proposed to be a concerted one.

Despite the potential utility of 2-azaallyl anion cycloadditions for the assembly of pyrrolidines, this reaction has not borne fruit as a useful synthetic method.[3b] The major barrier to its development has been the difficulty associated with the generation of these anions. The two most common methods for anion generation are the deprotonation of imines with a strong base and the conrotatory ring opening of *N*-metalloaziridines.[4] These methods for anion generation are generally limited to those examples bearing two or more aryl groups or those bearing an anion-stabilizing group (e.g., CO_2R, CN, etc.). The limitations of the former anions are obvious, since polyaryl pyrrolidines are of limited interest. In the latter case, strong electron-withdrawing groups attenuate the reactivity of the anions to such a degree that electron-deficient alkenes must be used for successful cycloaddition.[9] We recently reported that monoaryl-substituted anions could be generated by imine deprotonation or by cycloreversion of *N*-lithioimidazolidines, thus extending the scope of the reaction further, but we could not extend any of these methods to anions bearing simple alkyl groups.[3b,10] An alternative method for anion generation based on the desilylation of *N*-(trimethylsilyl)methanimines has recently been studied by Achiwa[9h,l] and Tsuge.[11] The desilylation method was useful for the generation and cycloaddition of anions bearing electron-withdrawing and/or aryl groups. However, attempts to generate alkyl-substituted anions were unsuccessful due to very sluggish desilylation,[3b,5,11] except in cases where a sulfur substituent was present.[11a] We report herein that the transmetalation of *N*-(trialkylstannyl)methanimines provides a convenient route to unstabilized 2-azaallyl anions and that these anions undergo cycloaddition reactions with a variety of alkenes.[5]

Table I. Synthesis of 2-Azaallylstannanes **5**

azide	R	R′	R″	stannane **5** (%)[a]
8a	Me	Ph	H	**5a** (92)
8b	*n*-Bu	Ph	H	**5b** (92)
8a	Me	*o*-OMePh	H	**5c** (74)
8b	*n*-Bu	2-pyridyl	H	**5d** (80)[b]
8a	Me	Me	H	**5e** (71)
8a	Me	*n*-Pr	H	**5f** (66)
8b	*n*-Bu	*n*-Pr	H	**5g** (86)
8a	Me	*i*-Pr	H	**5h** (84)
8b	*n*-Bu	*i*-Pr	H	**5i** (80)[b,c]
8a	Me	cyclopropyl	H	**5j** (70)
8a	Me	*t*-Bu	H	**5k** (71)
8b	*n*-Bu	*t*-Bu	H	**5l** (65)[b]
8a	Me	Me	Me	**5m** (90)[d]
8a	Me	$-CH_2(CH_2)_3CH_2-$		**5n** (51)

[a] Isolated yields of pure, distilled materials unless otherwise indicated. [b] Not distilled. Yield determined by ^1H NMR versus an internal DMF standard. [c] Shown to be *E* geometry by DNOE spectroscopy. [d] Crude yield, used without further purification.

Results and Discussion

The transmetalation of organostannanes with alkyllithium reagents to afford new alkyllithium compounds is an important method for the generation of carbanions.[12] For the generation and cycloaddition of 2-azaallyl anions using this method, a process such as that shown below was envisioned. Transmetalation of

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(5) A portion of this work was previously communicated: Pearson, W. H.; Szura, D. P.; Harter, W. G. *Tetrahedron Lett.* **1988**, *29*, 761–764.
(6) (a) Eidenschink, R.; Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1972**, 292. (b) Böche, G.; Martens, D. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 724. (c) Ford, W. T.; Luteri, G. F. *J. Am. Chem. Soc.* **1977**, *99*, 5330 and earlier work cited therein. (d) Kauffmann, T. *Top. Curr. Chem.* **1980**, *92*, 109 and references cited therein. Stepwise reactions are more common, for example: (e) Kempf, D. J.; Wilson, K. D.; Beak, P. *J. Org. Chem.* **1982**, *47*, 1610–1612. (f) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1985**, *26*, 4455. (g) Padwa, A.; Yeske, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 1617–1618. (h) Beak, P.; Burg, D. A. *J. Org. Chem.* **1989**, *54*, 1647–1654 and references cited therein. For the cycloaddition of a π-allyl nickel species, see: (i) Hoberg, H.; Heger, G.; Kruger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1988**, *348*, 261–278.
(7) Ingold, C. K.; Shoppee, C. W. *J. Chem. Soc.* **1929**, 1199.
(8) (a) Kauffmann, T.; Koppelmann, E.; Berg, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 163. (b) Kauffmann, T.; Berg, H.; Koppelmann, E. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 380.
(9) (a) Kanemasa, S.; Uchida, O.; Wada, E.; Yamamoto, H. *Chem. Lett.* **1990**, 105–108. (b) Kanemasa, S.; Yoshioka, M.; Tsuge, O. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 869–874 and 2196–2200. (c) Amornaraksa, K.; Barr, D. G.; Donegan, G.; Grigg, R.; Ratanankul, P.; Sridharan, V. *Tetrahedron* **1989**, *45*, 4649–4668. (d) Barr, D. A.; Grigg, R.; Sridharan, V. *Tetrahedron Lett.* **1989**, *30*, 4727–4730. (e) Barr, D. A.; Grigg, R.; Gunaratne, H. Q. N.; Kemp, J.; McMeekin, P.; Sridharan, V. *Tetrahedron* **1988**, *44*, 557–570. (f) Tsuge, O.; Kanemasa, S.; Yoshioka, M. *J. Org. Chem.* **1988**, *53*, 1384–1391. (g) Dehnel, A.; Kanabus-Kaminska, E. J. M. *Can. J. Chem.* **1988**, *66*, 310–318. (h) Imai, N.; Achiwa, K. *Chem. Pharm. Bull.* **1987**, *35*, 2646–2655. (i) Tsuge, O.; Ueno, K.; Kanemasa, S.; Yorozu, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3347. (j) Grigg, R.; Devlin, J. *J. Chem. Soc., Chem. Commun.* **1986**, 631. (k) Parker, K. A.; Cohen, I. D.; Babine, R. E. *Tetrahedron Lett.* **1984**, *25*, 3543–3546. (l) Achiwa, K.; Imai, N.; Inaoka, T.; Sekiya, M. *Chem. Pharm. Bull.* **1984**, *32*, 2878. (m) Grigg, R.; Gunaratne, H. Q. N. *J. Chem. Soc., Chem. Commun.* **1982**, 384. (n) Rabilla, C.; Dehnel, A.; Lavielle, G. *Can. J. Chem.* **1982**, *60*, 926. (o) Fouchet, B.; Joucla, M.; Hamelin, J. *Tetrahedron Lett.* **1981**, *22*, 3397–3400. (p) Grigg, R.; Kemp, J.; Malone, J.; Tangthongkum, A. *J. Chem. Soc., Chem. Commun.* **1980**, 648–650. (q) Dehnel, A.; Lavielle, G. *Tetrahedron Lett.* **1980**, *21*, 1315. (r) Grigg, R.; Kemp, J.; Sheldrick, G.; Trotter, J. *J. Chem. Soc., Chem. Commun.* **1978**, 109.
(10) (a) Pearson, W. H.; Walters, M. A.; Oswell, K. D. *J. Am. Chem. Soc.* **1986**, *108*, 2769–2771. (b) Pearson, W. H.; Harter, W. G. Unpublished results.
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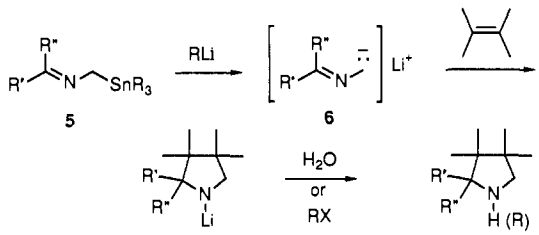
(12) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987.

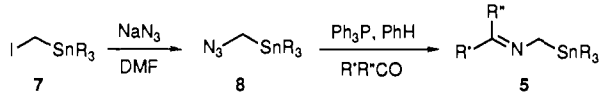
imines **5** with an alkyllithium reagent may produce 2-azaallyl anions **6**, which may then undergo a [π4s + π2s] cycloaddition reaction with an anionophile, leading to a pyrrolidine anion. The success of the tin to lithium exchange approach for the generation of α-amino anions[12-15] and allyl anions[16] provided good precedent for this process.



5 6

Synthesis of *N*-(Trialkylstannyl)methanimines. The obvious approach for the preparation of imines **5** is the condensation of a carbonyl compound with an (aminomethyl)trialkylstannane.[17] While tertiary (aminomethyl)trialkylstannanes are stable,[12-14] attempts at generating primary amines of this type by a variety of methods[18] failed, presumably due to their instability. This sensitivity is mirrored by the behavior of (hydroxymethyl)trialkylstannanes, which are best handled as their ethers.[12,19]

An alternate approach is the "aza-Wittig" reaction[20] of a carbonyl compound with an iminophosphorane, generated by the reaction of a phosphine with an azide **8**, as outlined below. Azides **8** were prepared from the known (iodomethyl)trialkylstannanes **7a** and **7b**[21] by displacement with sodium azide. For optimum

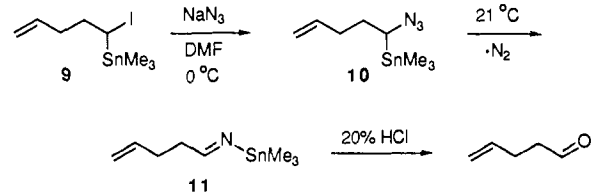


7 8 5

a: R = Me
b: R = nBu

yields in the condensation reaction, the azides were freshly prepared since they decomposed upon prolonged storage at room temperature (vide infra). Reaction of **8** with triphenylphosphine in benzene generated a yellow iminophosphorane, which afforded the (2-azaallyl)stannanes **5** upon condensation with a carbonyl compound (Table I). Most of the imines were purified by vacuum distillation, although the reactions were sufficiently clean that trituration with hexane to remove triphenylphosphine oxide provided materials of sufficient purity to use in subsequent transmetalation reactions.

A limitation of this method was encountered upon the attempted synthesis of more substituted (2-azaallyl)stannanes. For example, displacement of (1-iodoethyl)tributylstannane with sodium azide produced (1-azidoethyl)tributylstannane, but this compound afforded only minor amounts of imine upon condensation with aldehydes. The problem was traced to the instability of the azide, as evidenced by the following study. Displacement of iodide **9**[22] with sodium azide was complete in 15 min at 0 °C, and the α-azido stannane **10** was observed as the major product in the reaction mixture by ^{1}H NMR spectroscopy. Upon standing at room temperature, **10** decomposed with nitrogen evolution to afford a compound assigned as the *N*-(trimethylstannyl)imine **11** by ^{1}H NMR spectroscopy. Attempts at isolating **11** were unsuccessful,



9 10 11

which is not surprising in light of the known sensitivity of such compounds.[23] Further evidence for the structure of **11** was obtained by acid hydrolysis to 4-pentenal. This rearrangement of **10** to **11** is an extremely facile example of the Stieglitz rearrangement.[24] The fact that this rearrangement occurs at room temperature is in contrast to similar rearrangements of alkyl azides and α-thioalkyl azides, which require temperatures well in excess of 100 °C to rearrange.[25] The unsubstituted α-azido stannanes **8** were more stable, but they also underwent thermal decomposition after storage for extended periods at room temperature. Therefore, it is advisable that **8** be used shortly after preparation or stored in a freezer.

Generation and Cycloaddition of 2-Azaallyl Anions. With the (2-azaallyl)stannanes in **5** in hand, we then turn to their transmetalation to 2-azaallyl anions. Initial studies focused on the use of alkenes with an aromatic substituent, since these were likely to be good anionophiles in the cycloaddition reaction. The reactions were carried out by adding a mixture of the imine **5** with the anionophile in THF to 1.1 equiv of either methyllithium or *n*-butyllithium (depending on the tin substituent R) at −78 °C. After warming to room temperature, the reactions were quenched with water or methyl iodide, providing pyrrolidines with or without an N-substituent.

The results of these cyclizations are illustrated in Table II. Entries 1–9 show that the reaction of monoaryl-substituted 2-azaallyl anions may be quite efficient in cycloadditions with stilbene, styrene, and diphenylacetylene. The reaction was stereospecific with respect to the alkene geometry (cf. entries 1 and 7). Entry 5 shows that the cycloaddition is very rapid when a good anionophile such as stilbene is used. In this case, a 70% yield of the cycloadduct **12** was obtained when water was added to the reaction after 5 min at −78 °C, indicating that warming to room temperature is probably unnecessary. Entries 10–17 demonstrate that 2-azaallyl anions bearing no stabilizing group may be generated and used in cycloadditions. These are the first examples of the generation of simple alkyl-substituted anions, a process that is not possible using the deprotonation technique or other methods for anion generation that have been previously reported. Entry 17 shows that enynes undergo a chemo- and regioselective cycloaddition at the alkene rather than the alkyne.

While these cycloadditions are a significant advance in 2-azaallyl anion chemistry, entries 18–21 illustrate a limitation of

(13) (a) Peterson, D. J. *J. Organomet. Chem.* **1970**, *21*, P63. (b) Peterson, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 4027. (c) Peterson, D. J. *J. Organomet. Chem.* **1974**, *66*, 209. (d) Peterson, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 159.

(14) (a) Quintard, J.-P.; Elissondo, B.; Jousseaume, B. *Synthesis* **1984**, 495. (b) Peryere, M.; Elissondo, B.; Quintard, J.-P. In *Selectivity—A Goal for Synthetic Efficiency*; Bartmann, W., Trost, B. M., Eds.; Verlag Chemie: Weinheim, Germany, 1984; pp 191–212. (c) Elissondo, B.; Verlhac, J.-B.; Quintard, J.-P.; Pereyre, M. *J. Organomet. Chem.* **1988**, *339*, 267–275 and earlier references cited therein.

(15) Pearson, W. H.; Lindbeck, A. C. *J. Org. Chem.* **1989**, *54*, 5651–5654.

(16) (a) Seyferth, D.; Weiner, M. A. *J. Org. Chem.* **1961**, *26*, 4797. (b) Seyferth, D.; Mammarella, R. *J. Organomet. Chem.* **1977**, *137*, C17.

(17) Prior to our work, the only *N*-(trialkylstannyl)methanimine which had been reported in the literature was prepared by the stannylation of a 2-azaallyl anion, itself prepared by a deprotonation reaction. See: Popowski, E.; Hahn, A.; Kelling, H. *J. Organomet. Chem.* **1976**, *110*, 295.

(18) For example, the reduction of tributyltin cyanide and (azidomethyl)tributylstannane with a variety of reagents was unsuccessful.

(19) (a) Seebach, D.; Meyer, N. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 438. (b) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481. (c) Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 1290. (d) Sawyer, J. S.; Kucerovy, A.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 842 and earlier references cited therein. (e) Linderman, R. J.; Ghannam, A. *J. Am. Chem. Soc.* **1990**, *112*, 2392 and references cited therein. (f) Marshall, J. A.; Gung, W. Y. *Tetrahedron* **1989**, *45*, 1043–1052. (f) Chan, P. C.-M.; Chong, J. M. *Tetrahedron Lett.* **1990**, *31*, 1985–1988 and earlier references cited therein.

(20) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635.

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(22) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1986**, *27*, 1043–1046.

(23) (a) Chan, L.-H.; Rochow, E. G. *J. Organomet. Chem.* **1967**, *9*, 231. (b) Jappy, J.; Preston, P. N. *Tetrahedron Lett.* **1970**, 1157. (c) Harrison, P. G. *J. Chem. Soc., Perkin Trans. 1* **1972**, 130. (d) Lappert, M. F.; McMeeking, J.; Palmer, E. *J. Chem. Soc., Dalton Trans.* **1973**, 151.

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(25) Jarvis, B.; Nicholas, P.; Midiwo, J. *J. Am. Chem. Soc.* **1981**, *103*, 3878.

Table II. Cyclization of 2-Azaallylstannanes **5** with Anionophiles

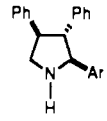
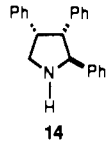
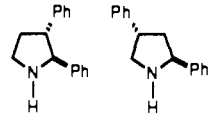
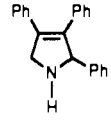
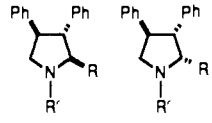
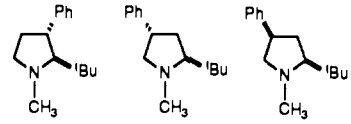
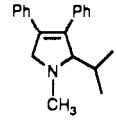
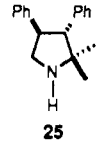
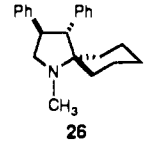
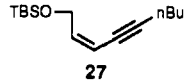
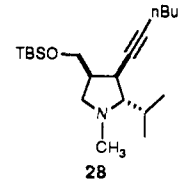
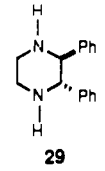
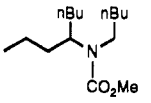
entry	imine[a]	anionophile	product(s) structure(s)	product(s) substituent(s)	% yield (ratio)[b]
1	**5a**	*trans*-stilbene		**12**: Ar = Ph	83
2	**5a**	*trans*-stilbene			25[c]
3	**5a**	*trans*-stilbene			65[d]
4	**5b**	*trans*-stilbene			84
5	**5b**	*trans*-stilbene			70[e]
6	**5c**	*trans*-stilbene		**13**: Ar = *o*-OMePh	76
7	**5a**	*cis*-stilbene	 **14**		65
8	**5a**	styrene	 **15** **16**		74 (10:1)
9	**5a**	PhCCPh	 **17**		73
10	**5g**	*trans*-stilbene	 **a** **b**	**18a,b**: R = *n*-Pr, R′ = H	62 (1.2:1)
11	**5h**	*trans*-stilbene		**19a,b**: R = *i*-Pr, R′ = Me	70 (1.4:1)
12	**5j**	*trans*-stilbene		**20a,b**: R = c-C_3H_5, R′ = H	65 (1.4:1)
13	**5k**	styrene	 **21** **22** **23**		75 (3:2:1)
14	**5h**	PhCCPh	 **24**		31
15	**5m**	*trans*-stilbene	 **25**		39
16	**5n**	*trans*-stilbene	 **26**		59
17	**5i**	 **27**	 **28**		44
18	**5b**	cyclohexene	 **29**		13[f]
19	**5f**	norbornene	*f*		
20	**5g**	1-hexene	*f*		

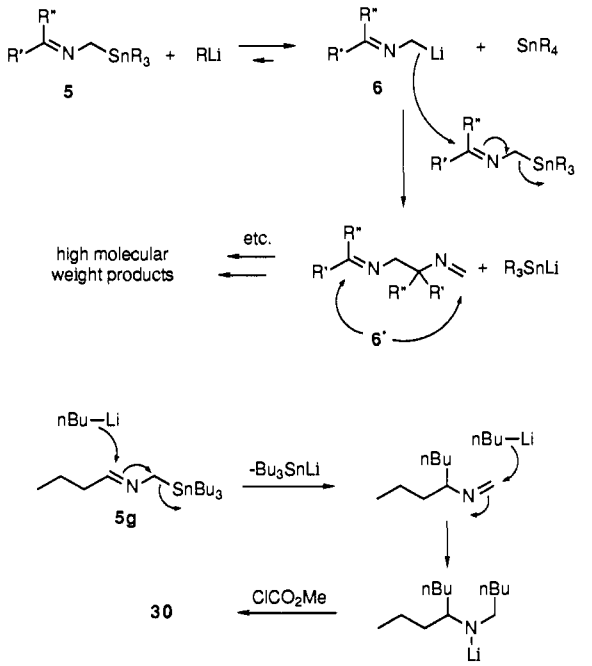
Table II (Continued)

entry	imine[a]	anionophile	product(s) structure(s)	substituent(s)	% yield (ratio)[b]
21	**5g**	1-hexene	 **30**		40[g]

[a] Transmetalation was accomplished at −78 °C in THF using MeLi or nBuLi for trimethylstannyl or tributylstannyl imines, respectively. [b] Yields are of isolated, purified materials. Stereochemical assignments are presented in the Experimental Section. Unless otherwise indicated, all reactions were run by adding a mixture of imine and anionophile to the alkyllithium reagent (1.1 equiv) at −78 °C in THF. After warming to room temperature, the reaction was quenched with water. If MeI was used to quench the reaction, it was added before warming to room temperature. [c] The imine was added to MeLi (1.1 equiv) at −78 °C, and the anionophile was added after 5 min. [d] The imine was added to MeLi (5 equiv) at −78 °C, and the anionophile was added after 5 min. [e] Reaction was run as in entry 4, but quenched with water after 5 min at −78 °C rather than warming to room temperature first. [f] The remaining material was recovered alkene and high molecular weight materials derived from oligomerization of the imine. [g] Reaction carried out in hexane and quenched with methyl chloroformate.

the method. Unactivated alkenes such as cyclohexene, hexene, and norbornene did not undergo cycloaddition. Instead, high molecular weight materials derived from oligomerization of the 2-azaallyl fragment were found to be the major products by mass spectroscopy. On the basis of this observation and others (vide infra), it became clear that the 2-azaallyl anions had a relatively short lifetime at −78 °C. If a good anionophile is present at the outset, cycloaddition competes well with this decomposition pathway, allowing good yields of pyrrolidines to be realized. If the anionophile is not as reactive (i.e., a simple alkene), the cycloaddition rate is not competitive. Even with a good anionophile, the order of mixing of reagents is important. For example, addition of imine **5a** to methyllithium in THF at low temperature followed by addition of stilbene after 15 min led to a diminished yield of pyrrolidine **12** as compared to the same experiment performed by addition of the imine and stilbene simultaneously (cf. entries 1 and 2).[26] The major products from entry 2 were oligomeric byproducts. Occasionally, the dimer **29** was observed in low yields, reminiscent of the dimerization of azomethine ylides.[27]

A possible mechanism for the decomposition pathway is shown below. The transmetalation of organostannanes to organolithium reagents is an equilibrium process, with the position of the equilibrium depending on the relative stability of the organolithium species.[12,19d,28] In the present case, it is possible that the equilibrium does not lie entirely on the side of the anion **6**.[29] A bimolecular reaction of **5** with the 2-azaallyl anion **6** may then occur, leading to high molecular weight products. A possible bimolecular reaction is shown below.[30] Support for this process is provided by entry 21 of Table II, where a 40% yield of **30** (based on imine **5g**) was obtained when the transmetalation was carried out with 1.2 equiv of *n*-BuLi in hexane rather than THF, a solvent which is known to slow Sn → Li transmetalations.[19d] An



equivalent amount of tributyltin hydride was observed by gas chromatography. A reasonable mechanism is the addition of *n*-BuLi to the imine with a concomitant loss of tributyltin anion, followed by addition of *n*-BuLi to the newly formed imine. If the equilibrium between **5** and **6** is the problem, an excess of alkyllithium reagent should force the equilibrium further in the direction of **6**. Indeed, mixing **5a** with 5 equiv of MeLi followed by the addition of stilbene after 15 min led to an improvement in the yield of **12** from 25% (entry 2, Table II) to 65% (entry 3), although it did not approach the 83% yield obtained when the stilbene was present from the beginning. In any event, the

(26) In a similar fashion, quenching with benzaldehyde after 15 min gave none of the addition product. In contrast, transmetalation of 1,3-diphenyl-1-(trimethylstannyl)-2-azaprop-2-ene with methyllithium followed by quenching with benzaldehyde and hydrolysis with aqueous hydrochloric acid gave an 89% yield of a 1.8:1 mixture of *threo*- and *erythro*-1,2-diphenyl-2-aminoethan-1-ol.

(27) (a) Huisgen, R.; Scheer, W.; Szeimies, G.; Huber, H. *Tetrahedron Lett.* **1966**, 397. (b) Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917. (c) Beugelmans, R.; Benadjila-Iguertsira, L.; Roussi, G. *J. Chem. Soc., Chem. Commun.* **1982**, 544. (d) Padwa, A.; Dent, W.; Nimmesgern, H.; Venkattramanan, M. K.; Wong, G. *Chem. Ber.* **1986**, *119*, 813. (e) Chastenet, J.; Roussi, G. *J. Org. Chem.* **1988**, *53*, 3808.

(28) (a) Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 1290. (b) Anderson, N. H.; McGrae, D. A.; Grotjahn, D. B.; Gable, S.; Theodore, L. J.; Ippolito, R. M.; Sarkar, T. K. *Tetrahedron* **1981**, *37*, 4069. (c) Newman-Evans, R. H.; Carpenter, B. K. *Tetrahedron Lett.* **1985**, *26*, 1141. (d) Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102–2103 and references cited therein. (e) Zideni, A.; Vaultier, M. *Tetrahedron Lett.* **1986**, *27*, 857. (f) Matteson, D. S.; Tripathy, P. B.; Sarkar, A.; Sadhu, K. M. *J. Am. Chem. Soc.* **1989**, *111*, 4399–4402 and references cited therein.

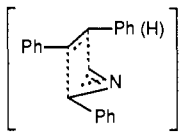
(29) While we expected that transmetalation would be favorable due to resonance stabilization and the presence of the electronegative nitrogen atom in the 2-azaallyl anion, Wiberg has recently presented evidence that resonance stabilization in allyl and 2-azaallyl anions is not significant. This may explain why the transmetalation equilibrium is not as biased as we had hoped. See: Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61.

(30) While the evidence points to a bimolecular reaction, other possible pathways available for decomposition have not been ruled out completely. These include a 1,4-hydrogen shift (see: Fishwick, C. W. G.; Jones, A. D.; Mitchell, M. B. *Tetrahedron Lett.* **1989**, *30*, 4447), an acid–base reaction of **6** with α-protons on the R′ group of **5** (both processes leading to 1-azaallyl anion formation), the cycloaddition of **6** with the imine π-bond of **5**,[4] and simple thermal instability. Thermal instability seems an unlikely explanation, since monoaryl 2-azaallyl anions have been shown to cycloadd with simple alkenes when they are generated by deprotonation or imidazolidine fragmentation,[10] whereas monoaryl 2-azaallyl anions generated by stannane transmetalation display the short lifetime typical of this method, resulting in a failure to cycloadd with unactivated alkenes. Furthermore, the stability of 2-azaallyl anions is predicted to be approximately the same as that of allyl anions.[29]

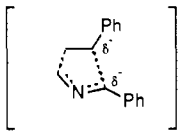
available evidence points to an incomplete transmetalation, which allows decomposition of the 2-azaallyl anion by a bimolecular process. Varying the solvent, concentration, and the tin substituents have not afforded a solution to this problem. Related examples of incomplete transmetalation of α-alkoxy stannanes have been recently reported.[19d,28f]

The possibility that the species undergoing reaction is a biradical anion[31] is addressed in entry 12, Table II. A cyclopropane-substituted 2-azaallyl anion was generated in the presence of stilbene. Cycloadducts **20a,b** were obtained with the cyclopropane ring intact in approximately the same yield as in entry 11 where an isopropyl substituent was used. No evidence for products derived from ring opening of the cyclopropane was observed, as is often the case when a cyclopropylcarbinyl radical is formed.[32]

The stereochemistry of the cycloadditions shown in Table II is consistent with a transition state **31** involving the *E* geometry of the 2-azaallyl anion.[33,34] Minimization of steric interactions produces the major stereoisomers in all cases. The stereochemistry of the products was determined by difference NOE spectroscopy (see the Experimental Section). The regiochemistry of the cycloaddition reactions with styrene bears comment. Entry 8 shows a clear preference for the 2,3-disubstituted pyrrolidine **15** over the 2,4-disubstituted isomer **16**. The production of the presumably more sterically crowded regioisomer may be evidence for a concerted but nonsynchronous cycloaddition reaction where there is considerable buildup of negative charge on the two benzylic carbons in the transition state (i.e., **32**). Evidence for the concerted nature of the cycloaddition comes from the stereospecificity of the cycloaddition with respect to the anionophile (entries 1 and 7), although a stepwise reaction cannot be ruled out if the second bond closure is faster than rotation about a single bond. Simple frontier molecular orbital considerations also predict the predominance of **15** over **16**.[35] Entry 13 shows a 1:1 mixture of 2,3- and 2,4-disubstituted products. The lower regioselectivity is reasonable, considering that the termini of the 2-azaallyl anion derived from imine **5k** are electronically very similar.



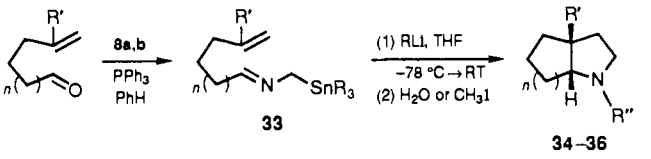
31



32

Intramolecular cyclizations were also examined (Table III). It was hoped that the entropic advantage of an intramolecular cyclization would allow the use of unactivated alkenes in the cycloaddition reactions. We have previously reported that monoaryl-substituted 2-azaallyl anions obtained by imine deprotonation undergo intramolecular cycloadditions with unactivated alkenes, providing tetrahydrocyclopenta[*b*]pyrroles and perhydroindoles in reasonable yield.[10a] Treatment of imine **33b**, which bears a styrene-like anionophile, with nBuLi afforded a high yield of the tetrahydrocyclopenta[*b*]pyrrole **35**. However, treatment of the closely related imine **33c** with methyllithium gave a considerably lower yield of the same cycloadduct. This is consistent with the equilibrium picture of transmetalation, since a higher concentration of the 2-azaallyl anion would be expected from **33b**/*n*-BuLi than from **33c**/MeLi on the basis of the relative stabilities of the two alkyllithium reagents.[19d] When a simple alkene was used as the acceptor as in imine **33a**, none of the corresponding cycloadduct **34** was isolated. Surprisingly, even styrene-like acceptors gave low yields of cycloadducts if the tether connecting them to the 2-azaallyl anion was only one carbon longer. Thus, imines **33d,e** gave low yields of perhydroindole **36**, even when an excess of the alkyllithium reagent was used. With the exception of **35**, oligomeric materials with the alkene portion of the molecule still intact were observed as the major products in all entries of Table III. These results provide further evidence that unstabilized 2-azaallyl anions generated by the tin method are susceptible to a competing decomposition pathway, especially when contrasted with the successful use of unactivated alkenes in our previous work on intramolecular cycloadditions of aryl-substituted 2-azaallyl anions.[10a] Hence, the anionophile must be sufficiently reactive (e.g., styrene and stilbene) to compete effectively with this decomposition pathway.

Table III. Intramolecular Cyclizations



33 **34–36**

n	R	R'	R''	**33** (%)[a]	RLi (equiv)	cycloadduct (%)[b]
1	nBu	H	H	**33a** (90)	nBuLi (1.1–5)[c]	**34** (0)[d]
1	nBu	Ph	H	**33b** (94)	nBuLi (1.1)	**35** (83/94)[e]
1	Me	Ph	H	**33c** (91)	MeLi (1.1)	**35** (30)[d]
2	Me	3,4-diOMePh	Me	**33d** (92)	MeLi (1.1–5)[c]	**36** (4)[d]
2	nBu	3,4-diOMePh	Me	**33e** (92)	nBuLi (1.1–5)[c]	**36** (15)[d]

[a] Yields determined by ^{1}H NMR versus internal DMF standard. [b] Isolated, purified yields. [c] Yield did not vary significantly as a function of amount of alkyllithium reagent. [d] Oligomeric materials formed. [e] Yield determined by GC relative to an internal decane standard, corrected for relative response factors.

While the use of reactive anionophiles such as styrene and stilbene provided good yields of cycloadducts, the synthetic utility of the reaction needed improvement. We therefore embarked on a search for anionophiles which would be more synthetically useful. These anionophiles had to meet several requirements. First, they had to be compatible with the presence of alkyllithium reagents, since the (2-azaallyl)stannane and anionophile must be mixed before addition to the alkyllithium reagent. Second, the rate of reaction with the 2-azaallyl anion had to be competitive with the rate of decomposition of the anion. Finally, the anionophile had to carry a synthetically useful functionality. To this end, we examined the use of heteroatom-substituted alkenes as anionophiles.

Kauffman[36] found that phenyl vinyl sulfide and phenyl vinyl selenide underwent cycloaddition with (1,3-diphenyl-2-azaallyl)lithium and that these reactions proceeded faster than analogous cycloadditions with stilbene. The rate increase was attributed to the ability of sulfur and selenium to stabilize a partial negative charge in the transition state of an asynchronous concerted reaction. Popowski[37] found that vinyltrimethylsilane also underwent a successful cycloaddition reaction with (1,3-diphenyl-2-azaallyl)lithium.

(31) A biradical anion pathway would explain the formation of **29** as well as the competing oligomerization pathway which leads to consumption of the anion in the absence of a good trap. Biradical forms of 1,3-dipoles have often been implicated in the literature.[2,27]

(32) Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734–1736.

(33) Although the geometry of monosubstituted 2-azaallyl has not been studied directly, 1-substituted allyl anions prefer the *E* geometry. See: (a) Freedman, H. H.; Sandel, V. R.; Thill, B. P. *J. Am. Chem. Soc.* **1967**, *89*, 1762. (b) Sandel, V. R.; McKinley, S. V.; Freedman, H. H. *J. Am. Chem. Soc.* **1968**, *90*, 495. (c) Schosser, M.; Hartman, J. *J. Am. Chem. Soc.* **1976**, *98*, 4674. (d) Bartmess, J. E.; Hehre, W. J.; McIver, R. T.; Overman, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 1976. (1,3-Diphenyl-2-azaallyl)lithium prefers the *E,E* geometry. See: (e) Eidenschink, R.; Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 292. (f) Young, R. N.; Ahmad, M. A. *J. Chem. Soc., Perkin Trans. 2* **1982**, 35. X-ray of sodium salt: (g) Andrews, P. C.; Mulvey, R. E.; Clegg, W.; Reed, D. *J. Organomet. Chem.* **1990**, *386*, 287–297.

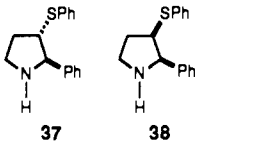
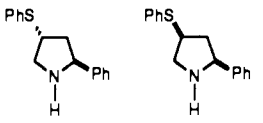
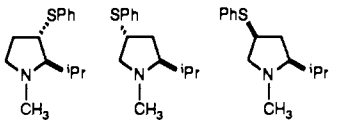
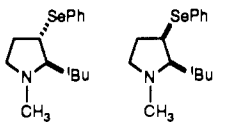
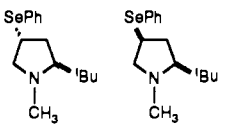
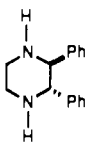
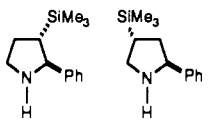
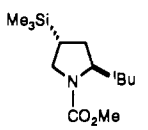
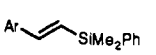
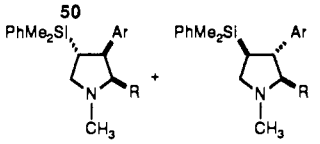
(34) Stannane **5i** prefers the *E* geometry, as shown by DNOE spectroscopy (Experimental Section).

(35) The regiochemistry of the cycloaddition of azomethine ylides has been treated by frontier molecular orbital theory.[35a–c] An analogy may be drawn between azomethine ylides and 2-azaallyl anions, since both systems have a similar set of allylic anion orbitals. (a) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361. (b) Huisgen, R. in ref 2, Vol. 1, Chapter 1. (c) Houk, K. N.; Yamaguchi, K. in ref 2, Vol. 2, Chapter 13.

(36) (a) Kauffmann, T.; Ahlers, H.; Hamsen, A.; Schultz, H.; Tilhard, H.-J.; Vahrenhorst, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 119. (b) Kauffmann, T.; Ahlers, H.; Echsler, K.-J.; Schultz, H.; Tilhard, H.-J. *Chem. Ber.* **1985**, *118*, 4496.

(37) Popowski, E. *Z. Chem.* **1974**, *14*, 360.

Table IV. Cyclization of 2-Azaallylstannanes **5** with Functionalized Anionophiles

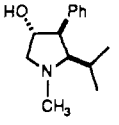
entry	imine[a]	anionophile	product(s)	% yield (ratio)[b]
1	**5a**	CH_2=CHSPh	 **37** **38**  **39** **40**	73 (6.9:1:4.8:2.3)
2	**5h**	CH_2=CHSPh	 **41** **42** **43**	88 (1.5:1:1)[c]
3	**5k**	CH_2=CHSePh	 **44** **45**  **46** **47**	71 (3.0:1:3.9:5.3)[c]
4	**5a**	CH_2=CHOEt	 **29**	7[d]
5	**5a**	CH_2=CHSiMe_3	 **48** **49**	79 (3.2:1)
6	**5l**	CH_2=CHSiMe_3	 **50**	91[e]
				
7	**5h**	**51**: Ar = Ph	**52** + **53**: R = iPr, Ar = Ph	75 (1.3:1)[c]
8	**5i**	**54**: Ar = MDP[f]	**55** + **56**: R = iPr, Ar = MDP	59 (13:1)[c]
9	**5b**	**54**: Ar = MDP	**57** + **58**: R = Ph, Ar = MDP	76 (1:1)[c]

[a] Transmetalation was accomplished at −78 °C in THF using MeLi or nBuLi for trimethylstannyl or tributylstannyl imines, respectively. [b] Yields are of isolated, purified materials. Stereochemical assignments are presented in the Experimental Section. [c] Quenched with MeI. [d] Remainder of material was oligomeric products derived from the imine. [e] Quenched with $ClCO_2Me$. [f] MDP = 3,4-(methylenedioxy)phenyl.

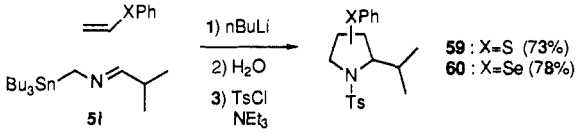
The reactions of these and other anionophiles with tin-derived 2-azaallyl anions are shown in Table IV. Indeed, the cycloaddition reactions with phenyl vinyl sulfide and phenyl vinyl selenide were very rapid at −78 °C, affording stereo- and regiochemical mixtures of sulfur- and selenium-substituted pyrrolidines in good yield. While the low regioselectivity of entries 2 and 3 was not surprising given the similar electron density at the two termini of the 2-azaallyl anion, the low regioselectivity in entry 1 was not expected. The greater ability of sulfur to stabilize negative charge in the transition state would lead to a prediction that the 2,3-disubstituted pyrrolidines **37** and **38** would be the major products with a phenyl-substituted 2-azaallyl anion (cf. entry 8 in Table II). Enol ethers were not useful in the cycloaddition (e.g., entry 4). Vinylsilanes proved to be good anionophiles (entries 5–9) and led to improved regio- and stereoselectivity. Silicon is also known to stabilize negative charge,[38] which may explain the success of these reactions. Hence, sulfur-, selenium-, and silicon-substituted alkenes are good anionophiles in the reaction with tin-derived 2-azaallyl anions.

(38) Blumenkopf, T. A.; Overman, L. E. *Chem. Rev.* **1986**, *86*, 857.

Table V. Transformations of Cycloadducts

substrate	conditions	product(s)	% yield (ratio)
59	Ra(Ni), EtOH	 **61**	82
60	Bu_3SnH, AIBN, PhH, reflux	 **61**	99
59	(1) *m*-CPBA (2) Ac_2O, NaOAc, reflux	 **62**	45
60	(1) *m*-CPBA (2) iPr_2NH, hexane, reflux	 **62**  **63**	91 (3:1)
52	(1) HBF_4 (2) H_2O_2, KF	 **64**	32

In addition to facilitating the cycloaddition reaction, these heterosubstituted alkenes afford functionalized pyrrolidines that are synthetically useful. Some transformations of these pyrrolidines are illustrated in Table V. The cycloadditions of phenyl vinyl sulfide and phenyl vinyl selenide were repeated, and the crude reaction products were tosylated to provide protected pyrrolidines **59** and **60** so that the compounds would be easier to manipulate.

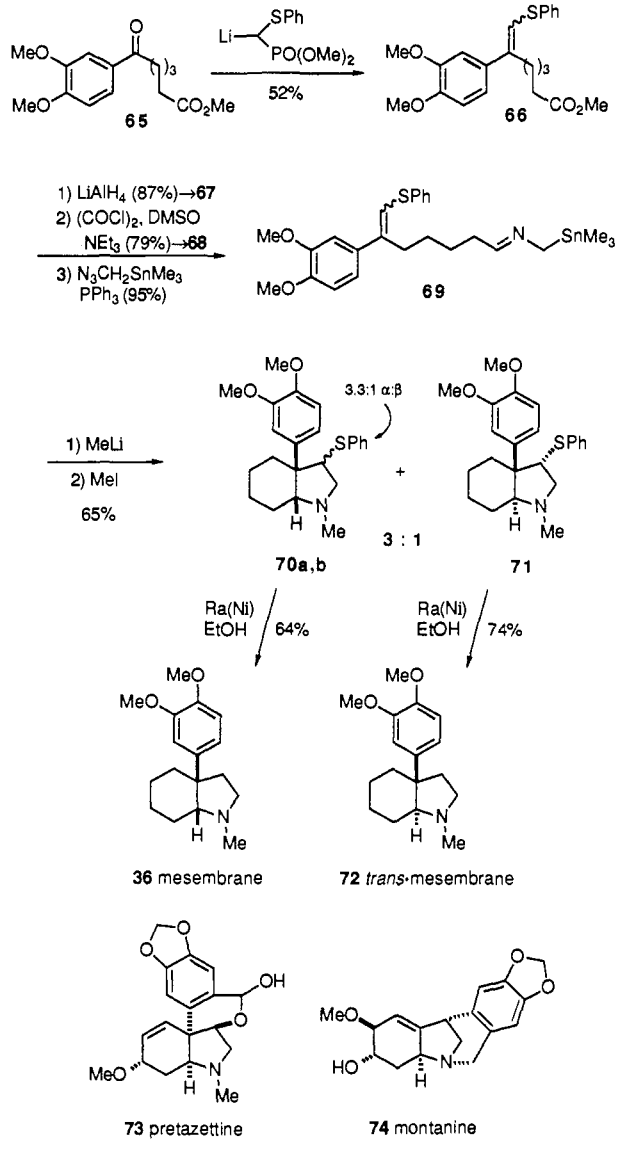


These pyrrolidines were a mixture of regio- and stereoisomers, similar to the ratios from Table IV, entries 2 and 3. Tosylation after workup of the anions was preferred, since direct quenching of the cycloaddition reactions with *p*-TsCl led to low yields of sulfonamides. Raney nickel reduction of the mixture of pyrrolidines **59** provided a good yield of a single pyrrolidine **61**. Access to **61** is the result of a formal cycloaddition of ethylene to the 2-azaallyl anion, a process which would not be possible directly. Raney nickel could also be used to remove the phenylseleno group of **60**, but reduction with tri-*n*-butyltin hydride was found to be more effective, affording **61** in near-quantitative yield. Oxidation of **59** to the sulfoxide followed by heating with acetic anhydride in an attempt to carry out a Pummerer rearrangement[39] gave the 3-pyrroline **62** instead, the result of sulfoxide elimination. The regiochemistry of the elimination is expected, since sulfoxides and selenoxides are known to prefer elimination away from heteroatoms, rather than toward them.[40] The production of **62** is the result of a formal cycloaddition of acetylene with the 2-azaallyl anion. Preparation of the selenoxides of **60** followed by heating smoothly afforded the 3-pyrroline **62** and the 2-pyrroline **63** in good yields. Again, elimination away from the heteroatom was the major process. Finally, the use of dimethylphenylsilyl-substituted alkenes (Table IV, entries 7–9) allows access to hydroxypyrrolidines, since this type of carbon–silicon bond may be oxidized to a carbon–oxygen bond according to Fleming.[41] In this particular case, pyrrolidine **52** was oxidized according to the procedure of Overman[42] to afford **64** in modest yield. A single stereoisomer was produced, with complete retention of configuration. This process is the synthetic equivalent of a cycloaddition of a 2-azaallyl anion with an enol, a process which is not otherwise possible.

The use of sulfur-, selenium-, and silicon-substituted alkenes as anionophiles in cycloaddition reactions with 2-azaallyl anions greatly extends the synthetic utility of this route to pyrrolidines. The resultant heterosubstituted pyrrolidines may be transformed in a second operation to pyrrolidines, pyrrolines, or hydroxypyrrolidines. The production of a mixture of isomeric pyrrolidines in these intermolecular cycloadditions is not necessarily a problem, since reduction or elimination of the mixture of compounds may lead to a single pyrrolidine or pyrroline. Intramolecular examples (vide infra) should eliminate the regioselectivity problem.

Hence, the reliance upon aromatic groups on the 2-azaallyl anion and/or the anionophile is no longer a necessity. This chemistry is complementary to azomethine ylide cycloadditions, where access to alkyl-substituted pyrrolidines and pyrrolines such

Scheme I



(39) Iriuchijima, S.; Maniwa, K.; Tsuchihashi, G. *J. Am. Chem. Soc.* **1974**, *96*, 4280.

(40) For example: (a) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1974**, *95*, 2697. (b) Haraguchi, K.; Tanaka, H.; Maeda, H.; Itoh, Y.; Saito, S.; Miyasaka, T. *J. Org. Chem.* **1991**, *56*, 5401–5408 and references therein.

(41) (a) Fleming, I.; Henning, R.; Plant, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29. (b) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229.

(42) Overman, L. E.; Wild, H. *Tetrahedron Lett.* **1989**, *30*, 647.

as those found in Table V are limited. Roussi's method involving the deprotonation of amine *N*-oxides in the presence of simple alkenes appears to be the only azomethine ylide route that does not require aromatic groups or other activating groups on the ylide or the dipolarophile to be successful.[43]

The ability to produce functionalized pyrrolidines from 2-azaallyl anions should allow access to natural products. A simple example is illustrated by the synthesis of mesembrane **36**[44] in Scheme I. The (2-azaallyl)stannane **69** was readily assembled from the known keto ester **65**. Generation of the 2-azaallyl anion, intramolecular cycloaddition, and quenching with methyl iodide afforded the cycloadducts **70a,b** and **71** in 65% yield. This compares favorably with the cyclizations that were carried out on the substrates which lacked the phenylthio group (Table III, imines **33d** and **33e**, 4% and 15% yields, respectively). The major product of the cycloaddition was **70a,b**, with the cis ring juncture. This is similar to our earlier work on intramolecular cycloadditions of 2-azaallyl anions[10a] and is also precedented in azomethine ylide chemistry as well.[3b] Attempts to separate the *E* and *Z* isomers of the vinyl sulfides **66–69** were unsuccessful, preventing a study of the relationship of the alkene geometry to the ring-juncture stereochemistry of the cycloadducts **70a,b** and **71**. Raney nickel reduction of **70a,b** afforded (±)-mesembrane **36**. Reduction of **71** produced (±)-*trans*-mesembrane **72**. While the heteroatom substituent is used only to increase the reactivity of the alkene as an anionophile in this case, natural products such as pretazettine **73**[42,45] and montanine **74**[46] are ideally suited to this chemistry, since the heteroatom functionality may be used to install the hydroxy group of **73** by silane oxidation and the double bond of **74** by selenoxide elimination. Synthetic efforts along these lines are currently underway.

Conclusion

Unstabilized 2-azaallyl anions bearing a single alkyl or aryl group have been generated by the transmetalation of (2-azaallyl)stannanes. These anions undergo efficient [3 + 2] cycloadditions with alkenes and alkynes, providing access to pyrrolidines and 3-pyrrolines. Cycloaddition with heteroatom-substituted alkenes provides a convenient route to functionalized pyrrolidines which may be useful for the synthesis of natural products.

Experimental Section

General. All reactions were carried out under an atmosphere of dry argon or nitrogen in flame-dried glassware equipped with a tightly fitted rubber septum. Benzene, toluene, pyridine, dimethyl sulfoxide (DMSO), triethylamine, dichloromethane, and diisopropylamine were distilled from powdered calcium hydride. Dimethylformamide (DMF) was distilled at reduced pressure from barium oxide. Tetrahydrofuran (THF) and diethyl ether were distilled under nitrogen from sodium/benzophenone ketyl. Commercial *n*-butyllithium and methyllithium were titrated with diphenylacetic acid prior to use. The aldehydes and ketones used in the preparation of *N*-(trialkylstannyl)methanimines were purified by distillation. Raney nickel (W-2) was freshly prepared before use according to the literature procedure.[47] All other commercial reagents were ACS reagent grade and were used as obtained. Cycloaddition reactions were monitored by gas chromatography (5-m 530-μm methyl silicone column, FID 60–200 °C, 20 °C/min temperature program) and by TLC (SiO_2 plates). Product yields for some cycloaddition reactions were determined by GC analysis using a known amount of decane as an internal standard and were corrected by determination of relative response factors. Chromatography refers to liquid chromatography according to the method of Still[48] unless otherwise noted. It was often found that isomeric mixtures of cycloadducts could not be completely separated by column chromatography in one pass. Thus, for reactions in which two or more isomeric pyrrolidines were formed, all fractions containing one or more of the isomers were combined to determine the overall yield for the reaction. In order to obtain analytically pure samples of each isomer for characterization, the mixture was rechromatographed using the same solvent system, and column fractions containing pure isomers were collected. Several of the *N*-(trialkylstannyl)methanimines were purified by Kugelrohr distillation. In these cases, the temperature reported for the distillation refers to the temperature of the oven. For ^1H NMR resonances which exhibit satellite peaks due to coupling with ^{117}Sn and ^{119}Sn, the average of the two couplings is reported when measurable. ^1H NMR assignments were made on the basis of homonuclear decoupling experiments or 2D-COSY spectroscopy when possible. Stereochemical assignments were made using difference nuclear Overhauser effect (DNOE) experiments, which were performed at ambient temperature on thoroughly degassed samples. Otherwise, stereochemical assignments were made on the basis of comparison with analogous compounds reported in the literature. Mass spectra were obtained via electron impact at 70 eV unless otherwise noted. RT refers to room temperature.

(Azidomethyl)trimethylstannane (8a). A solution of (iodomethyl)trimethylstannane (**7a**)[21] (5.10 g, 16.8 mmol) in 10 mL of freshly distilled DMF was cooled to 0 °C and treated with 3.0 equiv of sodium azide (2.71 g, 41.7 mmol). After the mixture was stirred for 5 min, a white precipitate (sodium iodide) began to form. Analysis (TLC) of the reaction mixture after 15 min indicated that the reaction was complete. The mixture was poured into water and pentane, and the organic layer was washed with water (4×) and brine, dried ($MgSO_4$), and concentrated in vacuo to give 2.83 g (77%) of the title compound as a clear, colorless liquid, which was used immediately without further purification. While storage in a freezer was possible for several days, the product decomposed slowly at room temperature with evolution of nitrogen. **8a**: IR (neat) 2089 (s), 1422 (w), 1284 (s), 1189 (w), 1177 (w), 1111 (w) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 3.02 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 26.0 Hz], 0.23 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 55.2 Hz]; ^{13}C NMR (90 MHz, $CDCl_3$) δ 36.4, 3.9. Attempts to obtain mass spectral data for this compound (low and high resolution) were unsuccessful.

(Azidomethyl)tri-*n*-butylstannane (8b). A solution of (iodomethyl)tri-*n*-butylstannane (**7b**)[21] (2.36 g, 5.47 mmol) in 10 mL of freshly distilled DMF was cooled to 0 °C and treated with 3.0 equiv of sodium azide (1.07 g, 16.4 mmol). The reaction mixture was allowed to warm to room temperature, and a white precipitate (sodium iodide) began to form in the reaction flask after 30 min. Analysis (TLC) of the reaction mixture after 1 h indicated that the displacement was complete. Workup as for **8a** afforded 1.60 g (85%) of the title compound as a clear, colorless oil, which was used without further purification. While storage in a freezer was possible for several days, the product decomposed slowly at room temperature with evolution of nitrogen. **8b**: IR (neat) 2086 (s), 1464 (w), 1418 (w), 1376 (w), 1287 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.02 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 22.3 Hz], 1.50 (m, 6 H), 1.31 (m, 6 H), 0.90 (m, 15 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 35.3, 29.0, 27.3, 13.6, 9.7. Attempts to obtain mass spectral data for this compound (low and high resolution) were unsuccessful.

General Procedure for the Synthesis of *N*-(Trialkylstannyl)methanimines. Triphenylphosphine (0.9–1.0 equiv) was added to a cooled (0 °C) solution of **8a** or **8b** (1.0 equiv) in benzene (0.5–1.5 M). The mixture was allowed to warm to room temperature and was stirred until TLC analysis showed that the azide had been consumed (ca. 2 h for **8a**, 5 h for **8b**). The resulting bright yellow solution containing the iminophosphorane was then cooled back to 0 °C and treated with the appropriate aldehyde or ketone (0.9–1.0 equiv). The reaction mixture was stirred at room temperature until the yellow color had discharged (10 min to 12 h). The benzene was removed in vacuo to give a semi-solid (imine and triphenylphosphine oxide). After trituration with pentane, the solid precipitate (triphenylphosphine oxide) was removed by filtration, and the filtrate was concentrated in vacuo. When possible, the residue was vacuum distilled using a Kugelrohr apparatus to give the pure imine as an oil. Those imines which were not able to be distilled were used without further purification, after determination of the purity of an aliquot by ^1H NMR analysis with dimethylformamide as an internal standard.

***N*-[(Trimethylstannyl)methyl]benzaldimine (5a)** was prepared from **8a** (1.87 g, 8.51 mmol), PPh_3 (2.22 g, 8.48 mmol), and benzaldehyde (0.90 g, 8.47 mol) in benzene (6 mL) at RT (3 h). Kugelrohr distillation gave 2.21 g (92%) of the title compound as a clear colorless oil: bp 90–95 °C

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(44) (a) Popelak, A.; Lettenbauer, G.; Haack, E.; Springer, H. *Naturwissenschaften* **1960**, *47*, 231. (b) Oh-ishi, T.; Kugita, H. *Tetrahedron Lett.* **1968**, 5445. (c) Jeffs, P. W.; Hawks, R. L.; Farrier, D. S. *J. Am. Chem. Soc.* **1969**, *91*, 3831. (d) Capps, T. M.; Hargrave, K. D.; Jeffs, P. W.; McPhail, A. T. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1098. (e) Oh-ishi, T.; Kugita, H. *Chem. Pharm. Bull.* **1979**, *18*, 291. (f) Nagashima, H.; Ken-ichi, A.; Wakamatsu, H.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1985**, 518.

(45) (a) Martin, S. F.; Davidsen, S. K.; Puckette, T. A. *J. Org. Chem.* **1987**, *52*, 1962–1972 and references cited therein. (b) Danishefsky, S.; Morris, J.; Mullen, G.; Gammill, R. *J. Am. Chem. Soc.* **1982**, *104*, 7591–7599 and references therein.

(46) Martin, S. F. In *The Alkaloids: Chemistry and Physiology*; Brossi, A., Ed.; Academic Press: New York, 1987; Vol. 30, Chapter 3.

(47) Mozingo, R. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 181.

(48) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 4923.

(air bath) at 0.5 mmHg; IR (neat) 1626 (s), 1494 (w), 1450 (s), 1425 (w), 1365 (w), 1006 (s), 766 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 [s, 1 H, $^4J(^{117/119}Sn-^1H)$ = 19.8 Hz], 7.6–7.3 (m, 5 H), 3.82 [d, 2 H, J = 1.1 Hz, $^2J(^{117/119}Sn-^1H)$ = 51.8 Hz], 0.16 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 54.0 Hz]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 137.2, 129.5, 128.6, 127.3, 49.6, −10.0; MS m/z (rel intensity) 282 (13, M + 1), 268 (2), 165 (29), 150 (3), 135 (8), 118 (56), 91 (100), 77 (6), 65 (18); HRMS calcd for $C_{11}H_{16}N^{120}Sn$ (M − H^+) 282.0305, found 282.0315.

***N*-[(Tri-*n*-butylstannyl)methyl]benzaldimine (5b)** was prepared from **8b** (1.47 g, 4.24 mmol), PPh_3 (1.11 g, 4.24 mmol), and benzaldehyde (0.45 g, 4.24 mmol) in benzene (20 mL) at RT (6 h). Kugelrohr distillation gave 1.59 g (92%) of the title compound as a clear colorless oil: bp 145–155 °C (air bath) at 0.1 mmHg; IR (neat) 1600 (w), 1464 (m), 1457 (w), 1451 (w), 755 (m), 693 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 [s, 1 H, $^4J(^{117/119}Sn-^1H)$ = 17.5 Hz], 7.60 (m, 2 H), 7.30 (m, 3 H), 3.84 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 45.2 Hz], 1.52 (m, 6 H), 1.25 (m, 6 H), 0.85 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 137.5, 129.3, 128.5, 127.2, 48.4, 29.1, 27.3, 16.4, 9.6; MS m/z (rel intensity) 409 (M^+, 1.1), 352 (3.7), 291 (16.8), 235 (35.1), 183 (13.5), 179 (59.4), 118 (75.5), 91 (100); HRMS (CI, butane) calcd for $C_{20}H_{36}N^{120}Sn$ (MH^+) 410.1870, found 410.1873.

***N*-[(Trimethylstannyl)methyl]-2-methoxybenzaldimine (5c)** was prepared from **8a** (0.84 g, 3.82 mmol), PPh_3 (1.01 g, 3.82 mmol), and *p*-methoxybenzaldehyde (0.47 g, 3.44 mmol) in benzene (6 mL) at RT (12 h). Kugelrohr distillation gave 0.75 g (74%) of the title compound as a clear colorless oil: bp 110–120 °C (air bath) at 1.0 mmHg; IR (neat) 1617 (s), 1464 (s), 1437 (w), 1367 (w), 1247 (s), 1028 (s), 754 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.55 [s, 1 H, $^4J(^{117/119}Sn-^1H)$ = 20.6 Hz], 7.8 (m, 1 H), 7.25 (m, 1 H), 6.9–7.0 (m, 2 H), 3.85 (m, 6 H), 0.16 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 53.6 Hz]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 151.8, 130.5, 125.5, 126.7, 120.8, 111.0, 55.5, 50.4, −10.0; MS m/z (rel intensity) 314 (1, M + 1), 312 (11), 277 (13), 199 (2), 183 (3), 165 (20), 148 (99), 133 (15), 121 (100), 105 (10), 91 (23); HRMS (CI, ammonia) calcd for $C_{12}H_{20}NO^{120}Sn$ (MH^+) 314.0567, found 314.0555.

***N*-[(Tri-*n*-butylstannyl)methyl]-2-pyridinecarboxaldimine (5d)** was prepared from **8b** (5.84 g, 16.87 mmol), PPh_3 (4.12 g, 15.7 mmol), and 2-pyridinecarboxaldehyde (1.67 g, 15.6 mmol) in benzene (30 mL) at RT (10 h). The fluorescent pink oil obtained from the workup was determined by ^1H NMR (DMF internal standard) to contain 5.1 g (80%) of the title compound, which was used without further purification: IR (neat) 1623 (w), 1585 (s), 1566 (m), 1466 (s), 1434 (s), 1376 (m), 1345 (m), 1290 (w), 1180 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.58 (m, 1 H), 8.26 [s, 1 H, $^4J(^{117/119}Sn-^1H)$ = 17.6 Hz], 7.9 (m, 1 H), 7.7 (m, 1 H), 7.2 (m, 1 H), 3.93 [d, 2 H, J = 1.1 Hz, $^2J(^{117/119}Sn-^1H)$ = 46.2 Hz], 1.41 (m, 6 H), 1.30 (m, 6 H), 0.90 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 155.6, 149.2, 136.2, 123.5, 120.1, 48.7, 29.0, 27.3, 13.6, 9.8; MS m/z (rel intensity) 410 (M^+, 3.0), 369 (0.6), 353 (2.1), 339 (1.6), 227 (6.2), 235 (3.5), 179 (10.2), 119 (100), 92 (7.2); HRMS calcd for $C_{19}H_{34}N_2{}^{120}Sn$ (M^+) 410.1744, found 410.1743.

***N*-[(Trimethylstannyl)methyl]ethanimine (5e)** was prepared from **8a** (2.31 g, 9.50 mmol), PPh_3 (2.51 g, 9.50 mmol), and excess acetaldehyde (>10 equiv, freshly distilled) in benzene (15 mL) at RT (30 min). Kugelrohr distillation gave 1.49 g (71%) of the title compound as a clear colorless oil: bp 55–58 °C (air bath) at 55 mmHg; IR (neat) 1655 (s), 1435 (m), 1377 (w), 1188 (w), 1032 (w), 770 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (q, 1 H, J = 4.9 Hz), 3.49 [d, 2 H, J = 0.9 Hz, $^2J(^{117/119}Sn-^1H)$ = 48.2 Hz], 1.90 [d, 3 H, J = 4.9 Hz, $^5J(^{117/119}Sn-^1H)$ = 19.4 Hz], 0.09 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 54.0 Hz]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 48.2, 21.8, −10.3; MS (CI, NH_3) m/z (rel intensity) 222 (100, M + 1), 206 (17), 182 (29), 165 (14), 152 (4), 135 (5), 113 (4), 99 (5); HRMS (CI, NH_3) calcd for $C_6H_{16}N^{120}Sn$ (MH^+) 222.0305, found 222.0299.

***N*-[(Trimethylstannyl)methyl]butanimine (5f)** was prepared from **8a** (2.61 g, 11.9 mmol), PPh_3 (3.11 g, 11.9 mmol), and freshly distilled *n*-butyraldehyde (4.3 g, 59.4 mmol) in benzene (75 mL) at RT (14 h). Kugelrohr distillation gave 1.94 g (66%) of the title compound as a clear colorless oil: bp 110–120 °C (air bath) at 110 mmHg; IR (neat) 1685 (w), 1653 (s), 1457 (s), 1188 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, 1 H, J = 5.0 Hz), 3.50 [d, 2 H, J = 0.9 Hz, $^2J(^{117/119}Sn-^1H)$ = 48.4 Hz], 2.15 (m, 2 H), 1.49 (m, 2 H), 0.92 (t, 3 H, J = 7.4 Hz), 0.11 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 54.0 Hz]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 48.3, 37.2, 20.0, 13.8, −10.3; MS (CI, isobutane) m/z (rel intensity) 250 (100, M + 1), 234 (11), 208 (2), 183 (7), 158 (5), 140 (3), 126 (3), 115 (1), 97 (2), 86 (25); HRMS (CI, isobutane) calcd for $C_8H_{20}N^{120}Sn$ (MH^+) 250.0618, found 250.0610.

***N*-[(Tri-*n*-butylstannyl)methyl]butanimine (5g)** was prepared from **8b** (0.82 g, 2.36 mmol), PPh_3 (0.62 g, 2.36 mmol), and freshly distilled butyraldehyde (0.20 g, 2.84 mmol) in benzene (14 mL) at RT (10 h). The clear, colorless oil obtained from the workup was determined by ^1H NMR (DMF internal standard) to contain 0.76 g (86% yield) of the title compound, which was used without further purification: ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, 1 H, J = 5.0 Hz), 3.52 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 43.4 Hz], 2.13 (m, 2 H), 1.46 (m, 6 H), 1.28 (m, 6 H), 0.86 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 46.9, 37.8, 29.1, 27.4, 20.0, 13.9, 13.7, 9.2; MS (CI, isobutane) m/z (rel intensity) 376 (M + 1, 0.4), 318 (11.5), 235 (24.7), 206 (16.0), 179 (49.4), 148 (2.1), 12.1 (20.4), 84 (100), 55 (17.1); HRMS (CI, isobutane) calcd for $C_{17}H_{38}N_2{}^{120}Sn$ (MH^+) 376.2026, found 376.2025.

***N*-[(Trimethylstannyl)methyl]-2-methylpropanimine (5h)** was prepared from **8a** (1.71 g, 7.75 mmol), PPh_3 (1.85 g, 7.06 mmol), and isobutyraldehyde (2.55 g, 35.3 mmol) in benzene (15 mL) at RT (1 h). Kugelrohr distillation gave 1.46 g (84%) of the title compound as a clear colorless oil: bp 57–58 °C (air bath) at 12 mmHg; IR (neat) 1651 (s), 1466 (s), 1422 (w), 1384 (w), 1362 (w), 1004 (s), 767 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, 1 H, J = 5.1 Hz), 3.47 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 48.6 Hz], 2.34 (m, 1 H), 1.00 (d, 6 H, J = 6.9 Hz), 0.07 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 53.8 Hz]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 47.9, 33.8, 19.8 (2), −10.4; MS (CI, NH_3) m/z (rel intensity) 250 (100, M + 1), 234 (9), 208 (30), 196 (3), 182 (97), 165 (13), 152 (3), 126 (7), 86 (21); HRMS (CI, NH_3) calcd for $C_8H_{20}N^{120}Sn$ (MH^+) 250.0618, found 250.0609.

***N*-[(Tri-*n*-butylstannyl)methyl]-2-methylpropanimine (5i)** was prepared from **8b** (1.46 g, 4.22 mmol), PPh_3 (1.11 g, 4.22 mmol), and isobutyraldehyde (1.53 g, 21.15 mmol) in benzene (10 mL) at RT (4 h). The clear, colorless oil obtained from the workup was determined by ^1H NMR (DMF internal standard) to contain 1.27 g (80% yield) of the title compound, which was used without further purification: IR (neat) 1650 (m), 1464 (s), 1434 (m), 1418 (w), 1376 (m), 1072 (w), 1002 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, 1 H, J = 5.0 Hz), 3.53 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 43.4 Hz], 2.36 (m, 1 H), 1.45 (m, 6 H), 1.30 (m, 6 H), 1.03 (d, 6 H, J = 6.9 Hz), 0.80 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 46.7, 33.9, 30.7, 29.1, 27.4, 19.7, 13.7, 9.2; MS m/z (rel intensity) 375 (M^+, 1.1), 332 (12.8), 318 (40.9), 291 (36.9), 235 (73.9), 206 (28.0), 179 (100), 121 (34.0), 56 (32.4); HRMS (CI, CH_4) calcd for $C_{17}H_{38}N^{120}Sn$ (MH^+) 376.2026, found 376.2038. DNOE: Irradiation at 3.53 ppm led to an 8.6% enhancement for the signal for the imine proton at 7.38 ppm, but did not enhance the intensity of the multiplet at 2.36 or the doublet at 1.03 ppm. Irradiation at 1.03 ppm enhanced the signal at 2.36 ppm by 37% and that of the signal at 7.38 by 6.6%, but did not result in an enhancement for the signal at 3.53 ppm. This is consistent with the *E* configuration of the imine.

***N*-[(Trimethylstannyl)methyl]cyclopropanecarboxaldimine (5j)** was prepared from **8a** (1.87 g, 8.50 mmol), PPh_3 (2.12 g, 8.1 mmol), and cyclopropanecarboxaldehyde (0.90 g, 1.28 mmol) in benzene (10 mL) at RT (9 h). Kugelrohr distillation gave 1.39 g (70%) of the title compound as a clear colorless oil: bp 65 °C (air bath) at 10 mmHg; IR (neat) 1652 (s), 1567 (bw), 1479 (w), 1436 (s), 1401 (m), 1186 (bs), 938 (s), 767 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.89 (d, 1 H, J = 7.3 Hz), 3.49 [d, 2 H, J = 0.7 Hz, $^2J(^{117/119}Sn-^1H)$ = 47.8 Hz], 1.63 (m, 1 H), 0.80 (m, 2 H), 0.60 (m, 2 H), 0.11 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 53.8 Hz]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8, 48.1, 15.8, 5.7, −10.4; MS (CI, NH_3) m/z (rel intensity) 282 (13, M + 1), 248 (100, M + 1), 208 (10), 186 (19), 180 (72), 165 (7), 84 (28); HRMS (CI, NH_3) calcd for $C_8H_{18}N^{120}Sn$ (MH^+) 248.0461, found 248.0453.

***N*-[(Trimethylstannyl)methyl]-2,2-dimethylpropanimine (5k)** was prepared from **8a** (2.09 g, 9.52 mmol), PPh_3 (2.40 g, 9.04 mmol), and trimethylacetaldehyde (2.33 g, 27.0 mmol) in benzene (20 mL) at RT (5 h) then 60 °C (3 h). Kugelrohr distillation gave 1.68 g (71%) of the title compound as a clear colorless oil: bp 50 °C (air bath) at 10 mmHg; IR (neat) 1649 (s), 1436 (s), 1362 (s), 1244 (s), 768 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 [s, 1 H, $^4J(^{117/119}Sn-^1H)$ = 19.1 Hz], 3.51 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 52.6 Hz], 1.02 (s, 9 H), 0.10 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 53.4 Hz]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 40.6, 28.6, 17.6, −9.7; MS (CI, NH_3) m/z (rel intensity) 236 (10, M + 1), 208 (6), 200 (3), 196 (16), 180 (11), 170 (1), 136 (100), 119 (3), 100 (28); HRMS (CI, NH_3) calcd for $C_9H_{22}N^{120}Sn$ (MH^+) 236.0461, found 236.0461.

***N*-[(Tri-*n*-butylstannyl)methyl]-2,2-dimethylpropanimine (5l)** was prepared from **8b** (1.05 g, 3.04 mmol), PPh_3 (0.80 g, 3.05 mmol), and trimethylacetaldehyde (2.36 g, 9.15 mmol) in benzene (15 mL) at RT (24 h). The pale yellow oil obtained from the workup was determined by ^1H NMR (DMF internal standard) to contain 1.88 g (65% yield) of the title compound, which was used without further purification: IR (neat) 1649 (bw), 1464 (m), 1418 (w), 1376 (w), 1362 (w), 1072 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 [s, 1 H, $^4J(^{117/119}Sn-^1H)$ = 16.4 Hz], 3.53 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 43.8 Hz], 1.5 (m, 6 H), 1.3 (m, 6 H), 1.03 (s, 9 H), 0.9 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 46.7, 35.8, 29.1, 27.4, 27.3, 13.6, 9.2; MS (CI, CH_4) m/z (rel intensity) 390 (MH^+, 59.1), 350 (9.4), 332 (100), 291 (45.0), 249 (47.7),

185 (15.3), 136 (30.4), 119 (54.2); HRMS (CI, CH_4) calcd for $C_{18}H_{40}N^{120}Sn$ (MH^+) 390.2183, found 390.2164.

***N*-[(Trimethylstannyl)methyl]-1-methylethanimine (5m)** was prepared from **8a** (414 mg, 1.36 mmol), PPh_3 (360 mg, 1.36 mmol), and acetone (72.0 mg, 1.24 mmol) in benzene (3 mL) at RT (2 h). Workup gave 256 mg (90% crude yield) of the imine as a clear oil. A portion of the crude product was Kugelrohr distilled: bp 50–55 °C (air bath) at 50 mmHg; IR (neat) 1649 (s), 1435 (m), 1362 (m), 1243 (w), 1187 (w), 1086 (w), 768 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.43 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 52.5 Hz], 1.95 [s, 3 H, $^5J(^{117/119}Sn-^1H)$ = 20.2 Hz], 1.71 [s, 3 H, $^5J(^{117/119}Sn-^1H)$ = 10.9 Hz], 0.08 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 53.4 Hz]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 40.6, 28.6, 17.6, −9.7; MS (CI, NH_3) *m/z* (rel intensity) 236 (M + 1, 10.3), 208 (6.3), 196 (15.8), 180 (11.3), 136 (100), 100 (28.2); HRMS (CI, NH_3) calcd for $C_7H_{18}N^{120}Sn$ (MH^+) 236.0461, found 236.0461.

***N*-[(Trimethylstannyl)methyl]cyclohexanimine (5n)** was prepared from **8a** (1.16 g, 5.27 mmol), PPh_3 (1.24 g, 4.73 mmol), and cyclohexanone (0.44 g, 4.48 mmol) in benzene (10 mL) at 60 °C (5 h). Kugelrohr distillation gave 0.63 g (51%) of the title compound as a clear pale yellow oil: bp 70 °C (air bath) at 10 mmHg; IR (neat) 1644 (s), 1448 (m), 1431 (w), 1346 (w), 1312 (w), 1185 (w), 1066 (m), 769 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.50 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 52.0 Hz], 2.20 (m, 4 H), 1.63 (broad m, 6 H), 0.09 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 52.5 Hz]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 39.4, 39.3, 27.7, 27.5, 26.5, 26.1, −9.7; MS (CI, NH_3) *m/z* (rel intensity) 236, 290 (M + 15, 1.5), 276 (M + 1, 22.8), 207 (4.7), 182 (7.9), 167 (2.1), 136 (100), 116 (2.8); HRMS (CI, NH_3) calcd for $C_{10}H_{22}N^{120}Sn$ (MH^+) 276.0774, found 276.0766.

5-Azido-5-(trimethylstannyl)-1-pentene (10). A solution of **9** (1.43 g, 3.97 mmol; see the supplementary material) in DMF (12 mL) was cooled to 0 °C and treated with sodium azide (0.774 g, 11.9 mmol). After the reaction was stirred for 5 min, a white precipitate (sodium iodide) began to form. Analysis (TLC) of the reaction mixture after 15 min indicated that the reaction was complete. The mixture was poured into water and pentane, and the organic layer was washed with water (4×) and brine, dried ($MgSO_4$), and concentrated in vacuo to give 0.92 g (85%) of the title compound as a clear, colorless liquid, which was used immediately without further purification. This compound rapidly evolves N_2 at room temperature (see text). **10**: IR (neat) 2084 (s), 1641 (m), 1447 (w), 1416 (w), 1264 (m), 1242 (w), 1193 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.80 (m, 1 H), 5.05 (m, 2 H), 3.18 (m, 1 H), 2.13 (m, 2 H), 1.85 (m, 1 H), 1.74 (m, 1 H), 0.20 [s, 9 H, $^2J(Sn^{117/119}-^1H)$ = 55.9 Hz]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 115.6, 51.2, 32.6, 32.4, 4.2. Attempts to obtain mass spectral data for this compound (low and high resolution) were unsuccessful. A sample of **10** was dissolved in $CDCl_3$ and was allowed to stand at room temperature. After 30 min, a new multiplet at 7.5 and a new singlet at 0.5 ppm appeared in the ^1H NMR spectrum, each with characteristic $^{117}Sn/^{119}Sn-^1H$ satellite peaks. This new compound was assigned as the rearranged imine **11**. Gas evolution was also observed. After ca. 4 h, all of **9** had been converted to **11**. The imine **11** was then stirred with 20% HCl, affording 4-pentenal[49] after isolation by extraction.

General Procedures for Cycloadditions. Procedure A. A mixture of imine **5** and an alkene or alkyne in THF was added dropwise via syringe to a solution of *n*-butyllithium or methyllithium in THF at −78 °C. Decane was used as an internal standard in some cases and was mixed with **5** and the trap prior to addition. After stirring for 10 min, the solution was warmed to RT, quenched with water, and diluted with ether. The organic phase was washed with water, saturated aqueous sodium bicarbonate, and brine, dried over magnesium sulfate, and concentrated in vacuo. After analysis by ^1H NMR to determine isomer ratios, chromatography of the residue provided the pure cycloadducts.

Procedure B. Same as Procedure A, except the cycloaddition was kept at −78 °C and iodomethane or methyl chloroformate was added. The solution was warmed to RT and worked up as for Procedure A.

Procedure C (for intramolecular cycloadditions): The imine in THF was added in a dropwise fashion via syringe to a solution of *n*-butyllithium or methyllithium in THF at −78 °C. In some cases, decane was mixed with the imine for use as an internal standard. If iodomethane was used to quench, it was added at −78 °C and the solution was then allowed to warm to RT. If water was used to quench, the cycloaddition was warmed to room temperature before quenching. In both cases, the workup was the same as for Procedure A.

2β,3α,4β-Triphenylpyrrolidine (12). According to Procedure A, **5b** (540 mg, 1.32 mmol), decane (180 mg, 1.27 mmol), and *trans*-stilbene (229 mg, 1.27 mmol) in THF (5 mL) were added to *n*-butyllithium (0.62 mL of a 2.6 M solution in hexane, 1.60 mmol) in THF (10 mL) over 5 min. After 10 min, the mixture was warmed to RT for 16 h and worked up to give a pale yellow oil, which was shown to be a single diastereomer by ^1H NMR. Chromatography (1% NH_4OH/9% MeOH/90% $CHCl_3$) afforded 316 mg (84%) of the title compound as a white crystalline solid (97% GC yield versus decane): mp 73–76 °C (lit. mp[11b] 64–67 °C); R_f = 0.61; ^1H NMR (300 MHz, $CDCl_3$) δ 7.0–7.3 (m, 15 H), 4.42 (d, 1 H, *J* = 9.5 Hz, H-2α), 3.74 (dd, 1 H, *J* = 9.6, 8.2 Hz, H-5), 3.64 (m, 1 H, H-4α), 3.46 (dd, 1 H, *J* = 9.6, 7.5 Hz, H-5), 3.22 (t, 1 H, *J* = 9.6 Hz, H-3β), 2.10 (broad s, 1 H, NH) (DNOE: Irradiation at 3.22 ppm (H-3β) failed to enhance the signals at either 4.42 ppm (H-2α) or 3.64 ppm (H-4α); irradiation at 4.42 ppm (H-2α) failed to enhance the signal at 3.22 ppm (H-3β)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 142.7, 140.6, 128.5, 128.4, 128.0, 127.4, 127.1, 126.7 (2), 126.5, 126.4, 71.2, 63.1, 54.8, 54.3; MS *m/z* (rel intensity) 299 (M^+, 0.4), 205 (0.2), 193 (0.5), 178 (3.0), 165 (2.1), 152 (0.9), 119 (100), 118 (93.1), 91 (8.4), 77 (2.5).

2β-(2-Methoxyphenyl)-3α,4β-diphenylpyrrolidine (13). According to Procedure A, **5c** (130 mg, 0.44 mmol) and *trans*-stilbene (82 mg, 0.44 mmol) in THF (1.5 mL) were added to methyllithium (0.30 mL of a 1.6 M solution in ether, 0.5 mmol) in THF (2 mL) over 3 min. After 15 min, the mixture was warmed to RT for 3 h and worked up to give 142 mg of a yellow semi-solid, which was shown to be a single diastereomer by ^1H NMR. Chromatography (10% EtOAc/hexane followed by 1% NH_4OH/9% MeOH/90% $CHCl_3$) afforded 110 mg (76%) of the title compound as a pale yellow liquid: R_f = 0.45 (1% NH_4OH/9% MeOH/90% $CHCl_3$); IR (neat) 1601 (s), 1585 (m), 1492 (s), 1462 (s), 1453 (m), 1393 (w), 1357 (w), 1281 (w), 1244 (s), 1027 (s) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.0–7.3 (m, 11 H), 6.8–6.9 (m, 3 H), 4.71 (d, 1 H, *J* = 9.7 Hz, H-2), 3.70 (s, 3 H), 3.68 (m, 1 H), 3.60 (m, 1 H), 3.50 (t, 1 H, *J* = 9.7 Hz), 3.45 (dd, 1 H, *J* = 9.9, 7.7 Hz), stereochemistry was the same as for **12** based on the similarity of their ^1H NMR spectra; ^{13}C NMR (90 MHz, $CDCl_3$) δ 157.5, 141.4, 139.9, 128.9, 128.8, 128.5, 128.2, 127.8, 127.4 (2), 126.6, 126.5, 120.8, 110.9, 66.6, 59.3, 55.3, 53.6, 29.7; MS (CI, CH_4) *m/z* (rel intensity) 330 (M + 1, 1), 312 (0.1), 179 (6), 165 (6), 149 (100), 148 (56), 1118 (20), 91 (19), 77 (9); HRMS calcd for $C_{23}H_{24}NO$ (MH^+) 330.1858, found 330.1848.

2β,3α,4α-Triphenylpyrrolidine (14). According to Procedure A, **5a** (276 mg, 0.98 mmol) and *cis*-stilbene (350 mg, 1.96 mmol) in THF (2 mL) were added to methyllithium (0.93 mL of a 1.37 M solution in ether, 1.27 mmol) in THF (10 mL) over 2 min. After 10 min, the mixture was warmed to RT and immediately worked up to give a yellow semi-solid, which was shown to be a single diastereomer by ^1H NMR. Chromatography (1% NH_4OH/9% MeOH/90% $CHCl_3$) afforded 193 mg (65%) of the title compound as a pale yellow solid: mp 68–71 °C; R_f = 0.71; IR (neat) 1602 (m), 1495 (s), 1412 (w), 1072 (w), 1028 (w), 699 (s) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 6.7–7.5 (m, 15 H), 4.74 (d, 1 H, *J* = 7.4 Hz, H-2α), 3.82 (m, 2 H), 3.65 (m, 2 H, contains H-3β), 2.30 (broad s, 1 H, NH) (DNOE: irradiation at 4.74 ppm (H-2α) failed to enhance the intensities of any other signals in the ^1H NMR spectrum); ^{13}C NMR (90 MHz, $CDCl_3$) δ 144.2, 140.4, 139.5, 128.9, 128.7, 128.4, 127.6, 127.5, 127.0, 126.6, 126.0, 66.6, 58.8, 51.9, 50.4; MS *m/z* (rel intensity) 299 (M^+, 1.5), 191 (1.1), 178 (6.0), 165 (3.8), 118 (100), 103 (1.8), 91 (10.5), 77 (3.5). Anal. Calcd for $C_{22}H_{21}N$: C, 88.25; H, 7.07; N, 4.68. Found: C, 88.27; H, 6.93; N, 4.76.

2β,3α-Diphenylpyrrolidine (15) and 2β,4α-Diphenylpyrrolidine (16). According to Procedure A, **5a** (326 mg, 1.16 mmol) and styrene (123 mg, 1.17 mmol) in THF (2 mL) were added to methyllithium (1.0 mL of a 1.4 M solution in ether, 1.4 mmol) in THF (3 mL) over 2 min. After 3 h, the mixture was warmed to RT and immediately worked up to give 285 mg a yellow oil, which was shown to be a 10:1 mixture of diastereomers **15** and **16** by ^1H NMR and GC analysis. Chromatography (1% NH_4OH/9% MeOH/90% $CHCl_3$) afforded 191 mg (74%) of an identical 10:1 mixture of **15** and **16** as a clear, colorless oil. The mixture was rechromatographed (same solvent system) in order to isolate each isomer for characterization (**15**, white solid, mp 42–44 °C, R_f = 0.42; **16**, colorless oil, R_f = 0.56). Data for **15**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.1–7.4 (m, 10 H), 4.12 (d, 1 H, *J* = 8.9 Hz, H-2α), 3.36 (m, 2 H, H-5), 3.12 (q, 1 H, *J* = 8.9 Hz, H-3β), 2.41 (m, 1 H, H-4β), 2.25 (broad s, 1 H, NH), 2.10 (m, 1 H, H-4α) (DNOE: irradiation at 3.12 ppm (H-3β) produced a 5.0% enhancement in the signal at 2.41 ppm (H-4β), but no enhancement for the signal at 4.12 (H-2α)); ^{13}C NMR (90 MHz, $CDCl_3$) δ 142.9, 142.7, 128.3, 128.2, 127.6, 127.0, 126.7, 126.2, 70.8, 54.0, 46.6, 35.2; MS *m/z* (rel intensity) 223 (M^+, 2.0), 178 (1.3), 165 (0.7), 119 (62.8), 118 (100), 104 (4.7), 91 (13.3), 77 (5.6); HRMS calcd for $C_{16}H_{17}N$ 223.1361, found 223.1345. Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 85.67; H, 7.78; N, 6.25. Data for **16**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.2–7.4 (m, 10 H), 4.47 (t, 1 H, *J* = 7.6 Hz, H-2α), 3.60 (dd, 1 H, *J* = 10.0, 7.4 Hz, H-5β), 3.47 (m, 1 H, H-4β), 3.07 (dd, 1 H, *J* = 10.0, 7.3 Hz, H-5α), 2.2–2.4 (m, 2 H, H-3), 1.9 (broad s, 1 H, NH) (DNOE: irradiation at 4.47 ppm (H-2α) produced a 2.5% enhancement for the signal at 3.07 ppm (H-5α); irradiation at 3.07 ppm (H-5α) had no effect on the signal at 3.47 ppm (H-4β)); ^{13}C

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NMR (90 MHz, $CDCl_3$) δ 145.1, 144.1, 128.5 (2), 127.3, 127.0, 126.5, 126.3, 62.6, 55.6, 44.8, 42.5; MS *m/z* (rel intensity) 223 (M^+, 15.6), 222 (19.3), 193 (12.0), 179 (6.8), 165 (1.7), 146 (3.2), 119 (57.3), 118 (100), 104 (9.1), 91 (20.0), 77 (11.9); HRMS calcd for $C_{16}H_{17}N$ 223.1361, found 223.1345. Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 85.67; H, 7.78; N, 6.25. Data for mixture of **15** and **16**: IR (neat) 1602 (m), 1493 (s), 1453 (s), 1395 (bs), 1099 (w), 1070 (w), 1028 (m) cm^{-1}.

2,3,4-Triphenyl-2,5-dihydro-1*H*-pyrrole (17). According to Procedure A, **5a** (581 mg, 2.06 mmol) and diphenylacetylene (730 mg, 4.12 mmol) in THF (10 mL) were added to methyllithium (1.8 mL of a 1.37 M solution in ether, 2.5 mmol) in THF (15 mL) over 2 min. After 10 min, the mixture was warmed to RT for 10 min and worked up to give 979 mg of a yellow oil. Chromatography (1% NH_4OH/9% MeOH/90% $CHCl_3$) afforded 447 mg (73%) of the title compound as a white solid: mp 88–91 °C; R_f = 0.63; IR ($CHCl_3$) 1599 (s), 1574 (w), 1490 (s), 1454 (s), 1443 (s), 1405 (w), 1073 (s), 1028 (w) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 6.9–7.3 (m, 15 H), 5.40 (dd, 1 H, *J* = 5.0, 2.5 Hz), 4.56 (dd, 1 H, *J* = 14.2, 5.0 Hz), 4.27 (dd, 1 H, *J* = 14.2, 2.5 Hz), 2.2 (broad s, 1 H, NH); ^{13}C NMR (90 MHz, $CDCl_3$) δ 143.9, 138.5, 136.4, 135.7, 135.3, 128.7, 128.6, 128.3, 128.1, 128.0, 127.5, 127.4, 127.3, 127.0, 74.8, 57.8; MS *m/z* (rel intensity) 297 (M^+, 30.6), 296 (12.2), 220 (100), 202 (2.6), 191 (6.6), 178 (5.7), 165 (4.0), 118 (14.6), 115 (11.5), 91 (8.0); HRMS calcd for $C_{22}N_{19}N$ 297.1517, found 297.1517.

3α,4β-Diphenyl-2β-propylpyrrolidine (18a) and 3α,4β-Diphenyl-2α-propylpyrrolidine (18b). According to Procedure A, **5g** (0.95 g, 3.83 mmol) and *trans*-stilbene (0.63 g, 3.49 mmol) in THF (12 mL) were added to *n*-butyllithium (1.75 mL of a 2.4 M solution in hexane, 4.2 mmol) in THF (22 mL) over 2 min. After 4 h, the mixture was warmed to RT for 14 h and worked up to give a yellow oil, which was determined by ^1H NMR to contain a 1.2:1.0 mixture of the title compounds **18a** and **18b**, respectively. Chromatography (1% NH_4OH/9% MeOH/90% $CHCl_3$) afforded 0.52 g (62.2%) of the title compounds as a clear, colorless oil. The mixture was rechromatographed (same solvent system) in order to isolate each isomer for characterization (R_f(**18a**) = 0.28, R_f(**18b**) = 0.23). Data for **18a**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.1–7.3 (m, 10 H), 3.55–3.75 (m, 2 H), 3.46 (t, 1 H, *J* = 7.9 Hz), 3.12 (dd, 1 H, *J* = 8.3, 10.1 Hz), 0.7–1.5 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 140.6, 128.9, 128.6, 128.3, 127.4, 126.5, 126.4, 63.4, 56.3, 54.1, 51.2, 34.1, 20.4, 14.0; MS *m/z* (rel intensity) 265 (M^+, 5.6), 222 (22.9), 193 (1.4), 178 (3.6), 165 (2.2), 115 (6.5), 91 (11.8), 85 (100), 70 (96.4). Data for **18b**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.1–7.3 (m, 10 H), 3.65 (dd, 1 H, *J* = 10.7, 8.2 Hz), 3.4–3.5 (m, 2 H), 3.31 (dd, 1 H, *J* = 10.7, 8.5 Hz), 2.87 (t, 1 H, *J* = 10.0 Hz), 1.3–1.5 (m, 3 H), 0.86 (t, 3 H, *J* = 7.2 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 14.17, 140.6, 128.6, 128.5, 128.0, 127.4, 126.8, 126.6, 67.0, 60.9, 54.4, 53.4, 36.5, 20.4, 14.1; MS *m/z* (rel intensity) 265 (M^+, 6.8), 222 (24.5), 193 (1.4), 178 (3.4), 130 (2.5), 115 (6.8), 91 (12.6), 85 (100), 70 (92.5). Data for mixture of **18a** and **18b**: IR (neat) 1602 (w), 1495 (s), 1453 (s), 1417 (bw), 1400 (w), 1078 (w), 1032 (w) cm^{-1}; HRMS calcd for $C_{19}H_{23}N$ 265.1830, found 265.1827.

1-Methyl-3α,4β-diphenyl-2β-(1-methylethyl)pyrrolidine (19a) and 1-Methyl-3α,4β-diphenyl-2α-(1-methylethyl)pyrrolidine (19b). According to Procedure B, **5h** (132 mg, 0.53 mmol) and *trans*-stilbene (193 mg, 1.07 mol) in THF (3 mL) were added to methyllithium (0.51 mL of a 1.25 M solution in ether, 0.64 mmol) in THF (4 mL) over 2 min. After 15 min, CH_3I (98 mg, 0.69 mmol) was added, and the solution was warmed to RT and immediately worked up to give a yellow oil, which was determined by ^1H NMR to contain a 1.4:1.0 mixture of the title compounds **19a** and **19b**, respectively. Chromatography (30% EtOAc/hex) afforded 105 mg (70%) of an identical 1.4:1.0 mixture of **19a** and **19b** as a clear, colorless oil. The mixture was rechromatographed (same solvent system) in order to isolate each isomer for characterization (R_f(**19a**) = 0.63, R_f(**19b**) = 0.45). Data for **19a**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.1–7.3 (m, 10 H), 3.25 (dd, 1 H, *J* = 9.7, 4.2 Hz, H-5), 3.15 (m, 1 H, H-4β), 3.05 (t, 1 H, *J* = 8.9 Hz, H-3α), 2.97 (t, 1 H, *J* = 8.9 Hz, H-5), 2.55 (dd, 1 H, *J* = 8.9, 3.2 Hz, H-2β), 2.45 (s, 3 H, NCH_3), 1.95 (m, 1 H, H-2′), 0.96 (d, 3 H, *J* = 7.0 Hz), 0.67 (d, 3 H, *J* = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 144.8, 128.4, 128.3, 127.4 (2), 126.1, 126.0, 79.1, 64.3, 57.6, 52.7, 42.2, 29.0, 19.6, 17.6; MS *m/z* (rel intensity) 279 (M^+, 0.1), 236 (100), 193 (1.2), 178 (2.1), 144 (6.4), 117 (6.1), 99 (4.1), 91 (14.1), 84 (11.8). Data for **19b**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.1–7.3 (m, 10 H), 3.5–3.7 (m, 3 H), 2.72 (dd, 1 H, *J* = 8.6, 4.6 Hz, H-2α), 2.50 (s, 3 H, NCH_3), 1.63 (m, 1 H, H-2′), 0.84 (d, 3 H, *J* = 6.8 Hz), 0.60 (d, 3 H, *J* = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 141.7, 129.8, 128.4, 127.9, 127.6, 126.3, 126.1, 75.5, 66.0, 55.1, 49.3, 44.2, 29.8, 21.0, 18.8; MS *m/z* (rel intensity) 278 (M − 1, 0.3), 236 (100), 193 (1.4), 178 (3.0), 158 (3.8), 144 (7.5), 130 (2.0), 115 (7.6), 99 (10.4), 91 (17.4), 84 (30.4), 77 (4.2), 71 (3.0). Data for mixture of **19a** and **19b**: IR (neat) 1601 (m), 1495 (s), 1453 (s), 1387 (w), 1365 (w), 1351 (w), 1225 (w), 1154 (w), 1031 (w) cm^{-1}. Anal. Calcd for $C_{20}H_{25}N$: C, 85.97; H, 9.02; N, 5.01. Found: C, 86.00; H, 9.16; N, 4.93.

2β-Cyclopropyl-3α,4β-diphenylpyrrolidine (20a) and 2α-Cyclopropyl-3α,4β-diphenylpyrrolidine (20b). According to Procedure A, **5j** (162 mg, 0.66 mmol) and *trans*-stilbene (244 mg, 1.32 mmol), in THF (2 mL) were added to methyllithium (0.63 mL of a 1.37 M solution in ether, 0.83 mmol) in THF (5 mL) over 2 min. After 15 min, the mixture was warmed to RT over 20 min and worked up to give 261 mg of a white semi-solid, which was determined by ^1H NMR to contain a 1.4:1.0 mixture of the title compounds **20a** and **20b**, respectively. Chromatography (1% NH_4OH/9% MeOH/90% $CHCl_3$) afforded 113 mg (65%) of a 1.4:1.0 mixture of the title compounds as a clear, colorless oil. The mixture was rechromatographed (same solvent system) in order to isolate each isomer for characterization (R_f(**20a**) = 0.40, R_f(**20b**) = 0.34). Data for **20a**: ^1H NMR (360 MHz, $CDCl_3$) δ 7.1–7.3 (m, 10 H), 3.57 (dd, 1 H, *J* = 9.8, 8.2 Hz, H-5), 3.50 (m, 1 H, H-4α), 3.40 (broad s, 1 H, NH), 3.28 (dd, 1 H, *J* = 9.9, 8.2 Hz, H-5), 3.10 (t, 1 H, *J* = 9.5 Hz, H-3β), 2.76 (dd, 1 H, *J* = 9.0, 8.2 Hz, H-2α), 0.94 (m, 1 H, H-2′), 0.43 (m, 1 H), 0.23 (m, 2 H), −0.17 (m, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 141.9, 141.3, 128.4, 128.3, 127.9, 127.3 (2), 126.4, 71.6, 60.6, 54.1, 53.6, 14.8, 2.4, 2.1; MS *m/z* (rel intensity) (M^+, 5.1), 193 (1.2), 179 (4.8), 178 (4.6), 128 (3.4), 115 (8.9), 91 (13.1), 83 (100), 82 (97.9), 68 (89.2); HRMS calcd for $C_{19}H_{21}N$ 263.1673, found: 263.1666. Anal. Calcd for $C_{19}H_{21}N$: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.88; H, 8.00; N, 5.19. Data for **20b**: ^1H NMR (360 MHz, $CDCl_3$) δ 7.1–7.3 (m, 10 H), 3.67 (m, 2 H, H-4α and H-5), 3.51 (t, 1 H, *J* = 8.8 Hz, H-3β), 3.05 (m, 1 H, H-5), 2.92 (broad s, 1 H, NH), 2.79 (t, 1 H, *J* = 8.8 Hz, H-2β), 0.43 (m, 1 H, H-2′), 0.37 (m, 1 H), 0.18 (m, 1 H), 0.0 (m, 1 H), −0.17 (m, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 142.5, 140.7, 128.9 (2), 128.4 (2), 127.9 (2), 127.4 (2), 126.3, 126.1, 69.2, 56.0, 54.4, 50.2, 13.5, 3.3, 3.2; MS *m/z* (rel intensity) 263 (M^+, 4.1), 193 (1.3), 178 (5.1), 165 (3.4), 128 (2.9), 115 (9.2), 103 (4.0), 91 (12.8), 83 (100), 82 (99.7), 68 (91.0); HRMS calcd for $C_{19}H_{21}N$ 263.1673, found: 263.1659. Data for mixture of **20a** and **20b**: IR (neat) 1602 (s), 1494 (s), 1452 (s), 1426 (w), 1076 (w), 1031 (w), 757 (s) cm^{-1}.

1-Methyl-2β-(1,1-dimethylethyl)-3α-phenylpyrrolidine (21), 1-Methyl-2β-(1,1-dimethylethyl)-4α-phenylpyrrolidine (22), and 1-Methyl-2β-(1,1-dimethylethyl)-4β-phenylpyrrolidine (23). According to Procedure B, **5k** (205 mg, 0.783 mmol) and styrene (163 mg, 1.57 mmol) in THF (4 mL) were added to methyllithium (0.73 mL of a 1.24 M solution in ether, 0.94 mmol) in THF (4 mL) over 2 min. After 20 min, CH_3I (144 mg, 1.02 mmol) was added, and the solution was warmed to RT and immediately worked up to give 166 mg of a pale yellow oil, which was determined by ^1H NMR to contain a 3:3:1 mixture of the title compounds **21**, **22**, and **23**, respectively. Chromatography (10% to 50% EtOAc/hexane gradient) afforded 127 mg (75%) of a pale oil containing all three isomers. The mixture was rechromatographed (same solvent system) in order to isolate each isomer for characterization (R_f(**21**) = 0.24, R_f(**22**) = 0.58, R_f(**23**) = 0.32, 50% EtOAc/hexane). Data for **21**: ^1H NMR (360 MHz, $CDCl_3$) δ 7.2–7.5 (m, 5 H), 3.17 (dt, 1 H, *J* = 8.0, 5.3 Hz, H-3β), 3.10 (dt, 1 H, *J* = 10.3, 6.1 Hz, H-5α), 2.78 (m, 1 H, H-5β), 2.64 (s, 3 H), 2.53 (d, 1 H, *J* = 5.8 Hz, H-2α), 2.13 (m, 1 H, H-4β), 1.79 (m, 1 H, H-4α), 0.90 (s, 9 H) (DNOE: irradiation of the signal at 3.17 ppm (H-3β) produced enhancements for the signals at 2.13 (H-4β) and 2.78 ppm (H-5β) of 9.2 and 13.5%, respectively, but failed to enhance the signal at 2.53 ppm (H-2α); irradiation at 2.53 ppm did not produce an enhancement for the signal at 3.17 ppm (H-3β)); MS *m/z* (rel intensity) 218 (M + 1, 0.2), 202 (2.0), 160 (100), 143 (2.85), 129 (3.6), 117 (20.8), 98 (10.1), 91 (18.7), 42 (35.4). Data for **22**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.2–7.4 (m, 5 H), 3.42 (m, 1 H, H-5), 3.27 (m, 1 H, H-4β), 2.51 (s, 3 H, NCH_3), 2.47 (dd, 1 H, *J* = 11.4, 8.7 Hz, H-5), 2.36 (dd, 1 H, *J* = 10.2, 3.1 Hz, H-2α), 2.08 (m, 1 H, H-3β), 1.99 (m, 1 H, H-3α), 0.94 (s, 9 H) (DNOE: irradiation of the signal at 1.99 ppm (H-3α) produced an 8.5% enhancement for the signal at 2.36 ppm (H-2α); irradiation of the signal at 2.08 ppm (H-3β) produced an 11.5% enhancement for the multiplet at 3.27 ppm (H-4β)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 128.3, 127.2, 126.2, 74.9, 66.3, 45.7, 35.6 (2), 27.1 (3 C); MS *m/z* (rel intensity) 218 (M + 1, 0.8), 202 (5.4), 186 (0.7), 160 (100), 144 (3.0), 129 (8.4), 115 (4.3), 104 (3.9), 91 (10.4), 42 (34.5). Anal. Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.44. Found: C, 82.66; H, 10.62; N, 6.18. Data for **23**: ^1H NMR (360 MHz, $CDCl_3$) δ 7.2–7.5 (m, 5 H), 3.30 (m, 1 H, H-4α), 2.8–3.0 (m, 2 H, H-5), 2.54 (s, 3 H, NCH_3), 2.50 (m, 1 H, H-2α), 2.23 (m, 1 H, H-3α), 1.72 (m, 1 H, H-3β), 0.95 (s, 9 H). Data for the mixture of **21**, **22**, and **23**: IR (neat) 1603 (w), 1495 (m), 1481 (m), 1452 (m), 1390 (m), 1361 (m), 1262 (w), 1169 (w), 699 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.44. Found: C, 82.87; H, 10.56; N, 6.40.

1-Methyl-2-(1-methylethyl)-3,4-diphenyl-2,5-dihydro-1*H*-pyrrole (24). According to Procedure B, **5h** (74 mg, 0.30 mmol) and diphenylacetylene

(110 mg, 0.59 mmol) in THF (2 mL) were added to methyllithium (0.29 mL of a 1.23 M solution in ether, 0.36 mmol) in THF (4 mL) over 2 min. After 10 min, CH_3I (55 mg, 0.39 mmol) was added, and the solution was warmed to RT and immediately worked up to give 135 mg of a colorless oil. Chromatography (10% to 50% EtOAc/hexane gradient) afforded 26 mg (31%) of the title compound as a clear colorless oil: R_f = 0.55 (50% EtOAc/hexane); IR (film) 1599 (m), 1575 (w), 1498 (m), 1491 (m), 1453 (m), 1444 (s), 1361 (m), 1120 (bm), 1029 (m) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.1–7.3 (m, 10 H), 4.53 (dd, 1 H, J = 14.8, 5.2 Hz), 3.89 (m, 1 H, H-2), 3.60 (dd, 1 H, J = 14.8, 2.3 Hz), 2.62 (s, 3 H, NCH_3), 1.75 (m, 1 H, H-2′), 1.00 (d, 3 H, J = 6.8 Hz), 0.79 (d, 3 H, J = 6.8 Hz); ^{13}C NMR (360 MHz, $CDCl_3$) δ 137.7, 136.8, 135.4, 133.3, 128.8, 128.4, 128.1, 127.7, 126.9, 83.7, 67.9, 46.6, 31.1, 20.2, 16.1; MS m/z (rel intensity) 276 (M − 1, 1.9), 275 (5.8), 260 (10.4), 234 (100), 219 (7.2), 202 (1.8), 191 (2.7), 178 (2.7), 115 (6.1), 91 (4.9); HRMS (CI, CH_4) calcd for $C_{20}H_{24}N$ (MH^+) 278.1909, found 278.1904.

2,2-Dimethyl-3α,4β-diphenylpyrrolidine (25). According to Procedure A, **5m** (60.2 mg, 0.26 mmol) and *trans*-stilbene (47.8 mg, 0.26 mmol) in THF (2 mL) were added to methyllithium (0.54 mL of a 1.6 M solution in ether, 0.86 mmol) in THF (1.5 mL) over 2 min. After 5 min, the mixture was warmed to RT and worked up immediately to give a yellow solid. Chromatography (1% NH_4OH/9% MeOH/90% $CHCl_3$) afforded 24.7 mg (39%) of the title compound as a pale yellow solid: mp 118–119 °C; R_f = 0.42; IR ($CDCl_3$) 1602 (m), 1496 (s), 1452 (m), 1382 (m), 1365 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.5–6.7 (m, 10 H), 3.25 (m, 1 H), 3.04 (dd, 1 H, J = 11.4, 8.6 Hz), 2.80 (broad s, 1 H, NH), 2.60 (dd, 1 H, J = 11.4, 8.6 Hz), 2.56 (d, 1 H, J = 11.7 Hz, H-3), 0.79 (s, 3 H), 0.35 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 138.6, 128.8 (2), 128.4, 128.1 (2), 127.4 (2), 126.6, 126.3 (2), 63.0, 52.4, 49.5, 29.0, 24.5; MS m/z (rel intensity) 251 (M^+, 6.1), 236 (3.0), 178 (5.2), 158 (1.0), 128 (1.5), 115 (7.6), 103 (2.6), 91 (9.7), 71 (100), 56 (6.9); HRMS calcd for $C_{18}H_{21}N$ 251.1674, found 251.1679.

1-Methyl-3β,4α-diphenyl-1-azaspiro[4.5]decane (26). According to Procedure B, **5n** (261 mg, 0.95 mmol) and *trans*-stilbene (340 mg, 1.90 mmol) in THF (3 mL) were added to methyllithium (0.92 mL of 1.24 M solution in ether, 1.14 mmol) in THF (4 mL) over 2 min. After 10 min, CH_3I (176 mg, 1.24 mmol) was added, and the solution was warmed to RT and immediately worked up to give 445 mg of a semi-solid. Chromatography (50% EtOAc/hexane) afforded 171 mg (59%) of the title compound as a yellow solid: mp 223–225 °C dec; R_f = 0.24; IR (neat) 1601 (w), 1494 (s), 1454 (s), 1350 (w), 1294 (w), 1240 (w), 1143 (w), 1076 (w), 1031 (w), 699 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.2–7.4 (m, 10 H), 3.63 (q, 1 H, J = 8.2 Hz), 3.44 (dd, 1 H, J = 9.5, 7.8 Hz), 3.22 (d, 1 H, J = 8.6 Hz), 3.00 (t, 1 H, J = 9.8 Hz), 2.50 (s, 3 H, NCH_3), 1.0–1.9 (m, 9 H), 0.70 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 143.2, 129.9 (2), 128.3 (2), 127.8 (2), 127.3 (2), 126.2, 126.1, 65.7, 61.9, 60.2, 52.4, 34.9, 31.5, 30.4, 25.8, 22.8, 22.1; MS m/z (rel intensity) 305 (M^+, 11.5), 276 (0.7), 262 (32.6), 248 (1.6), 172 (4.8), 158 (2.1), 144 (2.5), 125 (100), 124 (52.2), 110 (7.6), 97 (11.0), 91 (10.4). Anal. Calcd for $C_{22}H_{27}N$: C, 86.51; H, 8.91; N, 4.59. Found: C, 86.45; H, 8.93; N, 4.54.

1-Methyl-2α-(1-methylethyl)-3β-(1-hexynyl)-4β-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]methyl]pyrrolidine (28). According to Procedure B, **5i** (0.20 g, 0.53 mmol) and enyne **27** (0.27 g, 1.1 mmol) in THF (1 mL) were added to *n*-butyllithium (0.31 mL, 2.10 M solution in hexane) in THF (5 mL) over 5 min. After 15 min, CH_3I (0.10 g, 0.69 mmol) was added, and the solution was warmed to RT and immediately worked up. Chromatography (2–20% EtOAc/hexane gradient) afforded 0.08 g (44%) of the title compound as a pale yellow oil: R_f = 0.54 (30% EtOAc/hexane); IR (neat) 1462 (m), 1251 (m), 1082 (s), 854 (s) cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 4.05 (dd, 1 H, J = 9.8, 5.8 Hz), 3.87 (dd, 1 H, J = 9.8, 5.8 Hz), 3.25 (dd, 1 H, J = 8.0, 5.5 Hz), 2.92–2.85 (m, 1 H), 2.49–2.27 (m, 3 H), 2.22 (s, 3 H), 2.10–2.05 (m, 2 H), 1.88–1.77 (m, 1 H), 1.40–1.35 (m, 4 H), 1.08 (d, 3 H, J = 6.8 Hz), 1.01 (s, 9 H), 0.92 (d, 3 H, J = 6.8 Hz), 0.86–0.82 (m, 3 H), 0.12 (s, 6 H) (NOE experiments: all assignments made from a two-dimensional NOESY ^1H NMR spectrum); ^{13}C NMR (90 MHz, $CDCl_3$) δ 83.1, 80.4, 79.1, 64.4, 61.0, 41.8, 32.5, 31.2, 29.4, 25.9, 21.9, 19.9, 18.5, 18.3, 16.8, 13.6, −5.3; MS (CI, NH_3) m/z (rel intensity) 352 [100, $(M + H)^+$], 309 (20), 308 (59), 294 (6), 267 (2), 243 (2), 193 (3), 181 (6), 176 (5), 131 (21); HRMS (CI, NH_3) calcd for $C_{21}H_{42}NOSi$ (MH^+) 352.3036, found 352.3040.

***N*-[(Tri-*n*-butylstannyl)methyl]-5-phenyl-5-hexenimine (33b)** was prepared from **8b** (0.479 g, 1.38 mmol), PPh_3 (0.367 g, 1.38 mmol), and 5-phenyl-5-hexenal (0.240 g, 1.38 mmol; see the supplementary material for preparation) in benzene (7 mL) at RT (20 h) according to the general procedure above. The clear, colorless oil obtained from the workup was determined by ^1H NMR (DMF internal standard) to contain 0.620 g (94%) of the title compound, which was used without further purification: IR (neat) 2870 (m), 2852 (m), 1651 (w), 1600 (w), 1463 (m), 1376 (w), 777 (w) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.49 [s, 1 H, $^4J(^{117/119}Sn-^1H)$ = 9.8 Hz], 7.2–7.4 (m, 5 H), 5.28 (d, 1 H, J = 1.4 H), 5.06 (d, 1 H, J = 1.4 Hz), 3.53 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 43.5 Hz], 2.54 (m, 2 H), 2.20 (m, 2 H), 1.65 (m, 2 H), 1.45 (m, 6 H), 1.30 (m, 6 H), 0.87 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 148.1, 141.2, 128.2, 127.3, 126.1, 112.4, 46.8, 35.3, 35.0, 29.0, 27.3, 25.1, 13.6, 9.1; MS m/z (rel intensity) 477 (M^+, 0.6), 434 (8.8), 420 (9.5), 308 (31.7), 235 (47.4), 179 (98.2), 157 (38.6), 121 (35.7), 91 (100); HRMS (CI, isobutane) calcd for $C_{25}H_{44}N^{120}Sn$ (MH^+) 478.2496, found 478.2468.

***N*-[(Trimethylstannyl)methyl]-5-phenyl-5-hexenimine (33c)** was prepared from **8a** (0.497 g, 2.26 mmol), PPh_3 (0.557 g, 2.10 mmol), and 5-phenyl-5-hexenal (0.367 g, 2.10 mmol; see the supplementary material for preparation) in benzene (10 mL) at RT (21 h) according to the general procedure above. The clear, colorless oil obtained from the workup was determined by ^1H NMR (DMF internal standard) to contain 0.667 g (91% yield) of the title compound, which was used without further purification: IR (neat) 2933 (s), 2861 (m), 1652 (m), 1627 (w), 1495 (m), 1443 (bw), 1364 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 [broad s, 1 H, $^4J(^{117/119}Sn-^1H)$ = 10.4 Hz], 7.2–7.4 (m, 5 H), 5.28 (d, 1 H, J = 1.2 Hz), 5.07 (d, 1 H, J = 1.2 Hz), 3.51 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 48.5 Hz], 2.54 (m, 2 H), 2.23 (m, 2 H), 1.66 (m, 2 H), 0.10 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 52.9 Hz]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 148.7, 141.2, 128.2, 127.3, 126.1, 112.5, 48.3, 35.2, 34.9, 25.2, −3.6; MS m/z (rel intensity) 350 (M − 1, 0.3), 308 (11.7), 244 (3.6), 206 (3.1), 186 (5.6), 161 (51.5), 163 (40.7), 91 (100), 41 (58.6); HRMS (CI, isobutane) calcd for $C_{16}H_{26}N^{120}Sn$ (MH^+) 352.1087, found 352.1097.

***N*-[(Trimethylstannyl)methyl]-6-(3,4-dimethoxyphenyl)-6-heptenimine (33d)** was prepared from **8a** (192 mg, 0.87 mmol), PPh_3 (230 mg, 0.87 mmol), and 6-(3,4-dimethoxyphenyl)-6-heptenal (216 mg, 0.87 mmol; see the supplementary material for preparation) in benzene (9 mL) at RT (17 h) according to the general procedure above. The clear, colorless oil obtained from the workup was determined by ^1H NMR (DMF internal standard) to contain 338 mg (92%) of the title compound, which was used without further purification: IR (neat) 1652 (m), 1576 (w), 1615 (s), 1464 (m), 1254 (s), 1227 (m), 1143 (m), 1078 (m), 767 (m) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.48 [t, 1 H, J = 1.0 Hz, $^4J(^{117/119}Sn-^1H)$ = 10.0 Hz], 6.8–7.0 (m, 3 H), 5.20 (d, 1 H, J = 1.4 Hz), 5.00 (d, 1 H, J = 1.4 Hz), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.51 [d, 2 H, J = 0.90 Hz, $^2J(^{117/119}Sn-^1H)$ = 48.4 Hz], 2.49 (apparent t, 2 H, J = 6.9 Hz), 2.20 (m, 2 H), 1.50 (m, 4 H), 0.10 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 53.0 Hz]; ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.5, 148.6, 148.5, 147.9, 134.1, 118.4, 110.9, 110.8, 109.6, 55.8 (2), 48.1, 35.4, 35.1, 27.9, 26.2, 4.4; MS (CI, NH_3) m/z (rel intensity) 426 (MH^+, 49.1), 345 (8.4), 279 (97.6), 262 (78.7), 249 (100), 209 (84.0), 181 (85.2), 163 (54.0); HRMS (CI, CH_4) calcd for $C_{19}H_{32}NO_2{}^{120}Sn$ (MH^+) 426.1455, found 426.1479.

***N*-[(Tri-*n*-butylstannyl)methyl]-6-(3,4-dimethoxyphenyl)-6-heptenimine (33e)** was prepared from **8b** (475 mg, 1.37 mmol), PPh_3 (343 mg, 1.31 mmol), and 6-(3,4-dimethoxyphenyl)-6-heptenal (235 mg, 1.27 mmol; see the supplementary material for preparation) in benzene (10 mL) at RT (24 h) according to the general procedure above. The clear, pale yellow oil obtained from the workup was determined by ^1H NMR (DMF internal standard) to contain 372 mg (95%) of the title compound, which was used without further purification: IR (neat) 1652 (w), 1602 (w), 1579 (w), 1515 (s), 1463 (m), 1414 (w), 1254 (m), 1227 (w), 1143 (w), 1050 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 [s, 1 H, $^4J(^{117/119}Sn-^1H)$ = 10 Hz], 6.8–7.0 (m, 3 H), 5.2 (d, 1 H, J = 1.4 Hz), 4.99 (d, 1 H, J = 1.4 Hz), 3.90 (s, 3 H), 3.88 (s, 3 H), 3.53 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 48 Hz], 2.49 (m, 2 H), 2.18 (m, 2 H), 1.4 (m, 8 H), 1.3 (m, 6 H), 0.8 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 148.8 (2), 147.9, 134.3, 118.4, 111.0, 110.9, 109.8, 55.9 (2), 46.8, 35.5, 35.2, 29.0, 28.0, 27.3, 26.2, 13.6, 9.2; MS m/z (rel intensity) 550 (M − 1, 1.0), 494 (24.3), 382 (25.3), 277 (60.2), 260 (75.3), 235 (53.0), 179 (100), 151 (32.9), 96 (73.6); HRMS (CI, CH_4) calcd for $C_{28}H_{50}NO_2{}^{120}Sn$ (MH^+) 552.2864, found 552.2862.

(3aβ,6aβ)-3a-Phenyloctahydrocyclopenta[*b*]pyrrole (35). According to Procedure C, **33b** (1.3 g, 2.72 mmol) and decane (0.39 g, 2.74 mmol) in THF (9 mL) were added to *n*-butyllithium (1.3 mL of a 2.6 M solution in hexane, 3.3 mmol) in THF (20 mL) over 10 min. After 30 min, the reaction was warmed to RT for 22 h. Analysis of the crude reaction mixture by GC indicated a 94% yield of the title compound versus decane. Workup and purification by acid/base extraction (20% HCl; 20% NaOH; ether extraction) gave 425 mg (84%) of the title compound as a pale yellow oil: IR (neat) 3187 (bw), 2868 (s), 2733 (bw), 1599 (w), 1494 (m), 1445 (m), 1401 (w), 1332 (w), 923 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.1–7.3 (m, 5 H), 3.90 (dd, 1 H, J = 7.2, 2.6 Hz, H-6a), 3.00 (m, 2 H), 2.50 (broad s, 1 H, NH), 1.6–2.1 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 128.4, 125.9, 125.8, 69.1, 58.7, 46.0, 41.5, 40.9, 33.8, 24.8; MS m/z (rel intensity) 187 (M^+, 24.3), 158 (23.1), 144 (100), 130 (16.5), 115 (23.7), 91 (15.9), 82 (23.9), 77 (16.3), 56 (19.5); HRMS calcd for $C_{13}H_{17}N$ 187.1361, found 187.1357.

(3aβ,7aβ)-3a-(3,4-Dimethoxyphenyl)-1-methyloctahydroindole (Mesembrane, 36). From 33e. See also the preparation of mesembrane from **70a,b**. According to Procedure C, **33e** (2.12 g, 3.86 mmol) in THF (5 mL) was added to *n*-butyllithium (7.6 mL of a 2.55 M solution in hexane, 19.3 mmol) in THF (200 mL) over 5 min. After 10 min, CH_3I (2.85 g, 20.1 mmol) was added, and the solution was warmed to RT and immediately worked up to give 2.69 g of a viscous yellow oil. The ^1H NMR spectrum of the residue indicated the presence of the title compound along with tetrabutyltin and a considerable amount of an unidentifiable polymeric material. Chromatography (1% NH_4OH/9% MeOH/90% $CHCl_3$) afforded 0.163 g (15%) of the title compound as a clear, colorless oil, R_f = 0.3 (0.25% NH_4OH/2.5% MeOH/97.25% $CHCl_3$). The spectral properties for **33c** matched those that were incompletely reported in the literature:[44d] IR (neat) 3382 (bw), 2932 (s), 2853 (s), 2831 (s), 2779 (s), 1605 (w), 1588 (w), 1519 (s), 1462 (s), 1449 (s), 1409 (w), 1335 (w), 1253 (s), 1448 (s), 1029 (s) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 6.7–6.9 (m, 3 H), 3.85 (s, 3 H), 3.84 (s, 3 H), 3.26 (dt, 1 H, J = 9.1, 4.8 Hz, H-2), 2.60 (broad t, 1 H, H-7a, $w_{1/2}$ = 7.1 Hz), 2.33 (s, 3 H), 2.30 (m, 1 H), 1.0–2.0 (10 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 148.7, 147.0, 140.3, 118.9, 111.0, 110.9, 68.7, 56.0, 55.9, 54.3, 47.5, 41.0, 40.6, 35.9, 23.6, 22.9, 20.3; MS m/z (rel intensity) 275 (M^+, 60.3), 274 (100), 260 (24.4), 232 (27.3), 219 (34.4), 218 (66.7), 204 (36.3), 201 (11.7), 187 (5.2), 174 (6.9), 137 (31.2), 109 (22.7), 96 (34.9), 70 (32.1); HRMS (CI, CH_4) calcd for $C_{17}H_{26}NO_2$ (MH^+) 276.1963, found 276.1949.

2β-Phenyl-3α-(phenylthio)pyrrolidine (37), 2β-Phenyl-3β-(phenylthio)pyrrolidine (38), 2β-Phenyl-4α-(phenylthio)pyrrolidine (39), and 2β-Phenyl-4β-(phenylthio)pyrrolidine (40). According to Procedure A, **5a** (289 mg, 1.03 mmol) and phenyl vinyl sulfide (210 mg, 1.54 mmol) in THF (2 mL) were added to methyllithium (0.82 mL of a 1.37 M solution in ether, 1.13 mmol) in THF (2 mL) over 2 min. After 15 min, the mixture was worked up without warming to RT to give 261 mg of a dark yellow oil, which was shown to be a 6.9:1.0:4.8:2.3 mixture of diastereomers **37**, **38**, **39**, and **40** by ^1H NMR analysis. Chromatography (1% NH_4OH/9% MeOH/90% $CHCl_3$) afforded 191 mg (73%) the title compounds as a pale yellow oil. The mixture was rechromatographed (same solvent system) in order to isolate each isomer for characterization (R_f(**37**) = 0.33, R_f(**38**) = 0.28, R_f(**39**) = 0.39, R_f(**40**) = 0.44). Data for **37**: IR (neat) 3334 (bs), 1602 (w), 1583 (s), 1480 (s), 1453 (s), 1438 (s), 1092 (s), 1026 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.2–7.4 (m, 10 H), 4.10 (d, 1 H, J = 5.7 Hz, H-2α), 3.60 (m, 1 H, H-3β), 3.22 (m, 2 H, H-5), 2.34 (m, 1 H, H-4β), 2.05 (broad s, 1 H, NH), 1.95 (m, 1 H, H-4α) (DNOE: irradiation at 4.10 ppm (H-2α) had no effect on the signal at 3.60 (H-3β) and produced a 3.0% enhancement at 1.95 ppm (H-4α); irradiation at 3.60 ppm (H-3β) had no effect on the signal at 4.10 ppm (H-2α) and produced a 12.6% enhancement for the signal at 2.34 ppm (H-4β)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 135.8, 131.0, 128.9, 128.4, 127.3, 126.7, 126.6, 62.4, 53.8, 46.0, 33.8; MS m/z (rel intensity) 256 (M + 1, 2.1), 255 (1.2), 177 (0.7), 145 (17.4), 118 (100), 104 (8.8), 91 (40.9), 77 (20.1), 65 (16.0). Data for **38**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.1–7.4 (m, 10 H), 4.52 (d, 1 H, J = 5.7 Hz, H-2), 4.05 (m, 1 H, H-3), 3.40 (m, 1 H), 3.10 (m, 1 H), 2.35 (m, 1 H), 2.10 (m, 1 H), 2.1 (broad s, 1 H, NH). Data for **39**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.2–7.4 (m, 10 H), 4.43 (t, 1 H, J = 7.8 Hz, H-2α), 3.87 (m, 1 H, H-4β), 3.55 (dd, 1 H, J = 11.4, 6.6 Hz, H-5), 3.02 (dd, 1 H, J = 11.4, 5.4 Hz, H-5), 2.1–2.3 (m, 2 H, H-3), 1.95 (broad s, 1 H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 136.1, 130.3, 128.9, 128.4, 127.0, 126.4 (2), 61.3, 54.0, 45.7, 42.0; MS m/z (rel intensity) 255 (M^+, 1.7), 238 (0.8), 177 (1.3), 146 (79.6), 129 (5.3), 118 (100), 109 (10.0), 104 (16.6), 91 (37.8), 77 (23.6), 68 (28.6). Anal. Calcd for $C_{16}H_{17}NS$: C, 75.25; H, 6.17; N, 5.48. Found: C, 75.56; H, 6.69; N, 5.56. Data for **40**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.2–7.4 (m, 10 H), 4.16 (t, 1 H, J = 7.5 Hz, H-2α), 3.90 (m, 1 H, H-4α), 3.33 (dd, 1 H, J = 11.7, 6.7 Hz, H-5), 3.15 (m, 1 H, H-5), 2.69 (dt, 1 H, J = 13.4, 7.4 Hz, H-3α), 1.74 (ddd, 1 H, J = 12.7, 9.3, 7.5 Hz, H-3β); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 136.2, 130.4, 129.0, 128.5, 127.3, 126.7, 126.5, 63.3, 54.4, 46.0, 41.6. Data from the mixture of all four isomers: IR (neat) 3334 (bm), 1598 (w), 1581 (s), 1489 (m), 1480 (s), 1454 (s), 1432 (s), 1090 (m), 1020 (m) cm^{-1}; HRMS calcd for $C_{16}H_{17}NS$ 255.1082, found 255.1076.

1-Methyl-2β-(1-methylethyl)-3α-(phenylthio)pyrrolidine (41), 1-Methyl-2β-(1-methylethyl)-4α-(phenylthio)pyrrolidine (42), and 1-Methyl-2β-(1-methylethyl)-4β-(phenylthio)pyrrolidine (43). According to Procedure B, **5h** (262 mg, 1.06 mmol) and phenyl vinyl sulfide (288 mg, 2.12 mmol) in THF (3 mL) were added to methyllithium (1.08 mL of a 1.24 M solution in ether, 1.33 mmol) in THF (10 mL) over 3 min. After 10 min, CH_3I (196 mg, 1.38 mmol) was added, and the solution was warmed to RT and immediately worked up to give 497 mg of a pale yellow oil, which was determined by ^1H NMR to contain a 1.5:1:1 mixture of the title compounds **41**, **42**, and **43**, respectively. Chromatography (10–30% EtOAc/hex gradient) afforded 219 mg (88%) of the cycloadducts as a clear, colorless oil. The mixture was rechromatographed (same solvent system) in order to isolate each isomer for characterization. Data for **41**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.1–7.3 (m, 5 H), 3.50 (m, 1 H, H-3), 3.04 (m, 1 H, H-5), 2.56 (m, 1 H, H-5), 2.38 (s, 3 H, NCH_3), 2.0–2.1 (m, 2 H, H-2α and H-4), 1.90 (m, 1 H, H2′), 1.77 (m, 1 H, H-4), 1.00 (d, 3 H, J = 6.9 Hz), 0.92 (d, 3 H, J = 6.9 Hz) (DNOE experiments were inconclusive due to the overlap of signals for H-2 and H-4; the trans arrangement for the isopropyl and phenyl groups was assigned on the basis of the upfield shift of H-2α, which is shielded by the adjacent *cis*-phenylthio group); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9, 130.1, 128.9, 126.7, 76.9, 55.6, 46.7, 42.1, 33.0, 30.1, 20.0, 17.3; MS m/z (rel intensity) 235 (M^+, 0.9), 192 (100), 161 (1.2), 135 (2.2), 123 (1.2), 96 (7.4), 91 (1.6), 82 (93.6), 67 (7.7), 55 (6.3). Data for **42** (which could not be completely separated from **43**): ^1H NMR (360 MHz, $CDCl_3$) δ 7.1–7.4 (m, 5 H), 3.65 (m, 1 H, H-4β), 3.44 (dd, 1 H, J = 9.3, 6.7 Hz, H-5), 2.2–2.3 (m, 2 H, H-5 and H-2α), 2.27 (s, 3 H, NCH_3), 2.09 (m, 1 H), 1.89 (m, 1 H, H-2′), 1.68 (m, 1 H, H-3), 0.85 (m, 6 H); ^{13}C NMR (360 MHz, $CDCl_3$) δ 136.4, 129.7, 128.8, 126.1, 70.1, 64.3, 41.4, 40.3, 33.1, 27.9, 20.2, 15.1; MS m/z (rel intensity) 235 (M^+, 0.8), 192 (95.0), 135 (1.5), 109 (4.8), 96 (5.4) 91 (1.4), 82 (100), 77 (2.1), 67 (8.5), 55 (8.6), 42 (39.8). Data for **43**: ^1H NMR (360 MHz, $CDCl_3$) δ 7.1–7.4 (m, 5 H), 3.66 (m, 1 H, H-2α), 3.13 (dd, 1 H, J = 10.3, 2.2 Hz, H-5), 2.60 (dd, 1 H, J = 10.3, 7.0 Hz, H-5), 2.25 (s, 3 H, NCH_3), 2.19 (m, 1 H, H-3), 2.09 (m, 1 H, H-2), 1.92 (m, 1 H, H-2′), 1.58 (m, 1 H, H-3), 0.88 (d, 6 H, J = 6.8 Hz) (DNOE experiments: irradiation at 1.58 (H-3β) ppm enhanced the signal for the geminal H-3α proton at (2.19 ppm) by 19.3%, but failed to enhance the signals at 3.66 (H-4α) or 2.09 (H-2α) ppm; irradiation at 2.19 (H-3α) ppm resulted in a 19.3% enhancement for the geminal H-3β proton signal (1.58 ppm) and a 10.0% enhancement of the signal at 3.66 (H-4α) (the effect on H-2α could not be accurately determined due to the proximity of this proton to the site of irradiation)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 129.3, 128.8, 125.7, 71.6, 64.1, 41.3, 40.4, 32.9, 27.7, 20.3, 15.1; MS m/z (rel intensity) 235 (M^+, 0.8), 192 (100), 135 (1.5), 126 (1.0), 109 (4.5), 96 (5.4), 91 (1.3), 82 (93.8), 69 (5.4), 55 (7.7), 42 (52.9). Data for the mixture of **41**, **42**, and **43**: IR (neat) 1585 (m), 1450 (m), 1466 (m), 1438 (m), 1386 (w), 1368 (w), 1225 (w) cm^{-1}. Anal. Calcd for $C_{14}H_{21}NS$: C, 71.44; H, 8.99; N, 5.95. Found: C, 71.56; H, 8.74; N, 6.09.

1-Methyl-2β-(1,1-dimethylethyl)-3α-(phenylseleno)pyrrolidine (44), 1-Methyl-2β-(1,1-dimethylethyl)-3β-(phenylseleno)pyrrolidine (45), 1-Methyl-2β-(1,1-dimethylethyl)-4α-(phenylseleno)pyrrolidine (46), and 1-Methyl-2β-(1,1-dimethylethyl)-4β-(phenylseleno)pyrrolidine (47). According to Procedure B, **5k** (307 mg, 1.17 mmol) and phenyl vinyl selenide (428 mg, 2.34 mmol) in THF (2 mL) were added to methyllithium (1.18 mL of a 1.24 M solution in ether, 1.44 mmol) in THF (10 mL) over 3 min. After 10 min, CH_3I (216 mg, 1.52 mmol) was added, and the solution was warmed to RT and immediately worked up to give 283 mg of a clear, colorless oil, which was determined by ^1H NMR to contain a 3.0:1:3.9:5.3 mixture of the title compounds **44**, **45**, **46**, and **47**, respectively. Chromatography (10–30% EtOAc/hex gradient) afforded 245 mg (71%) of the cycloadducts as a clear, colorless oil. The mixture was rechromatographed (same solvent system) in order to isolate each isomer for characterization. Data for **44** (which could not be separated completely from **46**): ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.25 (m, 3 H), 3.62 (m, 1 H, H-3), 3.09 (broad m, 1 H, H-5), 2.85 (m, 1 H, H-5), 2.23 (d, 1 H, J = 2.0 Hz, H-2), 1.75 (m, 1 H, H-4), 0.88 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.3, 131.0, 129.1, 127.5, 81.2, 56.8, 46.4, 44.6, 36.5, 33.1, 26.8. Data for **45**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.25 (m, 3 H), 3.68 (q, 1 H, J = 5.8 Hz, H-3α), 3.38 (broad m, 1 H, H-5), 2.45 (m, 4 H, NCH_3 and H-2α), 2.34 (m, 1 H, H-5), 2.0–2.2 (m, 2 H, H-4), 1.13 (s, 9 H) (DNOE: irradiation at 3.68 (H-3α) ppm caused a 3.0% enhancement for the signal at 2.45 (H-2α) ppm); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.6, 129.0, 128.4, 127.0, 78.0, 55.9, 46.5, 45.5, 35.3, 33.3, 28.5. Data for **46**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.26 (m, 3 H), 3.59 (m, 1 H, H-4β), 3.40 (dd, 1 H, J = 9.6, 6.0 Hz, H-5), 2.50 (t, 1 H, J = 9.6 Hz, H-5), 2.46 (s, 3 H, NCH_3), 2.30 (dd, 1 H, J = 9.6, 4.1 Hz, H-2α), 2.09 (m, 1 H, H-3β), 1.90 (dt, 1 H, J = 9.6, 13.3 Hz, H-3α), 0.87 (s, 9 H) (DNOE: irradiation at 3.59 ppm (H-4β) produced a 4.0% enhancement for the signal at 2.09 (H-3β) ppm. Irradiation at 2.09 (H-3β) ppm produced a 4.7% enhancement at 3.59 (H-4β) ppm and a 7.2% enhancement at 1.90 ppm (H-3α), but failed to enhance the signal at 2.30 (H-2α) ppm; irradiation at 1.90 (H-3α) ppm produced a 3.9% enhancement for the signal at 2.30 (H-2α) ppm and a 4.8% enhancement for the signal at 2.09 ppm (H-3β)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.6, 129.0, 128.3, 127.1, 74.8, 65.9, 45.8, 38.4, 36.0, 35.2, 27.0. Data for **47**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (m, 2 H), 7.25 (m, 3 H), 3.59 (m, 1 H), 2.90 (m, 2 H), 2.43 (s, 3 H, NCH_3), 2.30 (m, 2 H), 1.61 (m, 1 H), 0.86 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.0, 129.7, 128.9, 127.2, 64.6, 47.2,

37.4, 36.4, 34.8, 26.6 (one carbon under $CDCl_3$ peak). Data for the mixture of all four isomers: IR (neat) 2778 (m), 1577 (m), 1479 (s), 1436 (m), 1389 (w), 1359 (m), 1295 (w), 1299 (w), 1239 (w), 1201 (w), 1158 (w) cm^{-1}; MS m/z (rel intensity) 296 (M^+, 0.1), 282 (0.8), 242 (11.4), 240 (58.3), 238 (31.4), 157 (2.6), 110 (1.0), 82 (100), 67 (7.7), 55 (10.9), 42 (63.8). Anal. Calcd for $C_{15}H_{23}NSe$: C, 60.80; H, 7.82; N, 4.73. Found: C, 60.85; H, 8.01; N, 4.80.

2β-Phenyl-3α-(trimethylsilyl)pyrrolidine (48) and 2β-Phenyl-4α-(trimethylsilyl)pyrrolidine (49). According to Procedure A, **5a** (298 mg, 1.06 mmol) and vinyltrimethylsilane (212 mg, 2.12 mmol) in THF (2 mL) were added to methyllithium (0.92 mL of a 1.37 M solution in ether, 1.27 mmol) in THF (2 mL) over 2 min. After 5 min, the mixture was warmed to RT and worked up immediately to give 188 mg of a yellow liquid, which was shown to be a 3.2:1 mixture of diastereomers **48** and **49** by ^1H NMR analysis. Chromatography (1% NH_4OH/9% MeOH/90% $CHCl_3$) afforded 183 mg (79%) of the cycloadducts. The mixture was rechromatographed (same solvent system) in order to isolate each isomer for characterization (R_f(**48**) = 0.24, R_f(**49**) = 0.42). Data for **48**: IR (neat) 3286 (bw), 1602 (w), 1492 (w), 1454 (s), 1403 (bw), 1249 (s), 839 (s) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.1–7.4 (m, 5 H), 3.89 (d, 1 H, J = 10.2 Hz, H-2α), 3.18 (dt, 1 H, J = 10.0, 7.1 Hz, H-5), 3.01 (m, 1 H, H-5), 2.2 (broad s, NH), 2.10 (m, 1 H, H-4), 1.73 (m, 1 H, H-4), 1.27 (q, 1 H, J = 10.2 Hz, H-3β), −0.12 (s, 9 H) (DNOE: irradiation at 3.89 (H-2α) ppm did not enhance the signal at 1.27 (H-3β) ppm); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0, 128.4, 127.3, 127.1, 65.9, 47.4, 35.2, 29.6, −2.6; MS m/z (rel intensity) 220 (M + 1, 21.4), 204 (9.2), 142 (40.7), 118 (100), 102 (9.5), 91 (20.2), 73 (85.8), 68 (36.1), 59 (43.8), 45 (48.8). Anal. Calcd for $C_{13}H_{21}NSi$: C, 71.17; H, 9.65; N, 6.38. Found: C, 70.96; H, 9.55; N, 6.38. Data for **49**: IR (neat) 3322 (bw), 1603 (w), 1492 (w), 1451 (m), 1249 (s), 1029 (w), 835 (s), 700 (s) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.0–7.4 (m, 5 H), 4.16 (dd, 1 H, J = 8.6, 5.8 Hz, H-2α), 3.32 (dd, 1 H, J = 10.1, 8.0 Hz, H-5), 2.80 (dd, 1 H, J = 11.2, 10.2 Hz, H-5), 2.02 (m, 1 H, H-3α), 1.87 (m, 1 H, H-3β), 1.38 (m, 1 H, H-4), 0.02 (s, 9 H) (DNOE: irradiation at 4.16 (H-2α) ppm produced a 3.0% enhancement for the signal at 2.02 (H-3α) ppm; irradiation at 2.02 (H-3α) ppm produced a 4.9% enhancement for the signal at 4.16 ppm (H-2α) but did not enhance the signal at 1.38 (H-4β) ppm); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 128.3, 126.8, 126.5, 62.8, 49.7, 36.3, 25.6, −2.9; MS m/z (rel intensity) 220 (MH^+, 6.7), 219 (M^+, 12.0), 204 (5.1), 178 (32.3), 146 (30.0), 129 (2.6), 118 (46.4), 106 (53.7), 91 (12.5), 73 (100), 68 (9.0), 59 (29.9); HRMS calcd for $C_{13}H_{21}NSi$ 219.1444, found 219.1433.

1-(Methoxycarbonyl)-2β-(1,1-dimethylethyl)-4α-(trimethylsilyl)pyrrolidine (50). According to Procedure B, **5l** (537 mg, 1.44 mmol) and vinyltrimethylsilane (288 mg, 2.87 mmol) in THF (3 mL) were added to n-butyllithium (0.68 mL of a 2.55 M solution in hexane, 1.72 mmol) in THF (15 mL) over 3 min. After 15 min, methyl chloroformate (163 mg, 1.72 mmol) was added, and the solution was warmed to RT and immediately worked up to give 1.07 g of a clear oil, which was determined by ^1H NMR to contain only one product. Chromatography (10% EtOAc/hexane) afforded 336 mg (91%) of the title compound as colorless, opaque crystals: mp 51–52 °C; R_f = 0.32; IR ($CHCl_3$) 1683 (s), 1478 (w), 1448 (s), 1377 (s), 1354 (m), 1290 (w), 1252 (m), 1212 (s), 1120 (m), 838 (s), 735 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.77 (broad d, 1 H, J = 6.2 Hz, H-2), 3.67 (s, 3 H, OCH_3), 3.41 (broad m, 2 H, H-5), 1.87 (broad dd, 1 H, J = 12.7, 7.6 Hz, H-3), 1.60 (dt, 1 H, J = 12.7, 8.4 Hz, H-3), 1.43 (m, 1 H, H-4), 0.89 (s, 9 H), −0.24 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 66.7, 52.2, 49.9, 36.6, 28.8, 27.5 (3), 24.5, −3.3 (3); MS m/z (rel intensity) 258 (M + 1, 8.9), 242 (8.0), 200 (100), 126 (11.36), 105 (56.7), 96 (81.4), 89 (21.8), 73 (93.5), 69 (86.2), 59 (39.3). Anal. Calcd for $C_{13}H_{27}NO_2Si$: C, 60.65; H, 10.57; N, 5.44. Found: C, 60.62; H, 10.22; N, 5.25.

1-Methyl-2β-(1-methylethyl)-4α-(dimethylphenylsilyl)-3β-phenylpyrrolidine (52) and 1-Methyl-2β-(1-methylethyl)-4α-(dimethylphenylsilyl)-3α-phenylpyrrolidine (53). According to Procedure B, **5h** (509 mg, 2.05 mmol) and (*E*)-β-(dimethylphenylsilyl)styrene (**51**)[50] (1.23 g, 5.15 mmol) in THF (7 mL) were added to methyllithium (2.45 mL of a 1.24 M solution in ether, 3.04 mmol) in THF (20 mL) over 5 min. After 10 min, CH_3I (500 mg, 3.5 mmol) was added, and the solution was warmed to RT and immediately worked up to give 1.39 g of a yellow oil, which was determined by ^1H NMR to contain a 1.3:1 mixture of the title compounds **52** and **53**, respectively. Chromatography (25–100% EtOAc/hex gradient) afforded 519 mg (75%) of the same 1.3:1 mixture of cycloadducts as a clear, colorless oil. The mixture was rechromatographed (same solvent system) in order to isolate each isomer for characterization (R_f(**52**) = 0.45, R_f(**53**) = 0.21, 50% EtOAc/hexane). Data for **52**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.0–7.5 (m, 10 H), 3.30 (t, 1 H, J = 8.5 Hz, H-5), 3.17 (t, 1 H, J = 7.6 Hz, H-3α), 2.30 (s, 3 H, NCH_3), 2.17 (dd, 1 H, J = 11.3, 9.3 Hz, H-5α), 2.00 (dd, 1 H, J = 7.6, 5.6 Hz, H-2α), 1.84 (dt, 1 H, J = 11.0, 7.8 Hz, H-4), 1.63 (m, 1 H, H-2′), 0.82 (d, 3 H, J = 6.9 Hz), 0.39 (d, 3 H, J = 6.9 Hz), 0.21 (s, 3 H), 0.18 (s, 3 H) (DNOE: irradiation at 2.00 ppm (H-2α) produced a 4.5% enhancement for the signal at 3.17 ppm (H-3α), a 5.2% enhancement for the signal at 2.17 ppm (H-5α), and a 5.7% enhancement for the signal at 1.63 ppm (H-2′); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0, 138.0, 134.0, 130.1, 129.0, 127.7 (2), 126.0, 76.3, 59.9, 50.8, 42.9, 32.2, 28.8, 19.8, 19.3, −3.9, −4.5; MS m/z (rel intensity) 336 (M − 1, 0.3), 294 (84.1), 216 (3.0), 202 (2.1), 158 (17.7), 135 (100), 117 (17.4), 84 (14.3); HRMS (CI, CH_4) calcd for $C_{22}H_{32}NSi$ (MH^+) 338.2304, found 338.2319. Data for **53**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.0–7.5 (m, 10 H), 3.09 (dd, 1 H, J = 10.0, 6.9 Hz, H-5), 2.95 (t, 1 H, J = 9.2 Hz, H-3β), 2.74 (t, 1 H, J = 9.5 Hz, H-5), 2.37 (s, 3 H, NCH_3), 2.35 (m, 1 H, H-2α), 1.82 (m, 1 H, H-2′), 1.65 (m, 1 H, H-4α), 0.89 (d, 3 H, J = 6.9 Hz), 0.63 (d, 3 H, J = 6.9 Hz), 0.22 (s, 3 H), 0.12 (s, 3 H) (DNOE: irradiation of the signal at 2.95 ppm (H-3β) produced a 2.2% enhancement for the signal at 3.09 ppm (H-5β); no other enhancements were observed); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 138.4, 133.9 (2), 128.8, 128.4 (2), 128.1 (2), 127.6 (2), 125.8, 80.7, 59.1, 50.2, 42.7, 33.2, 29.2, 19.4, 18.0, −3.7, −4.6; MS m/z (rel intensity) 336 (M − 1, 0.3), 294 (92.1), 216 (3.5), 158 (18.7), 135 (100), 117 (12.4), 107 (6.7), 91 (6.6), 84 (9.5); HRMS (CI, CH_4) calcd for $C_{22}H_{32}NSi$ (MH^+) 338.2304, found 338.2304. Data for the mixture of **52** and **53**: IR (neat) 2769 (s), 1602 (w), 1490 (m), 1453 (m), 1427 (w), 1364 (w), 1355 (w), 1249 (s), 1113 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{31}NSi$: C, 78.28; H, 9.26; N, 4.15. Found: C, 78.48; H, 9.12; N, 4.06.

1-Methyl-2β-(1-methylethyl)-4α-(dimethylphenylsilyl)-3β-[3,4-(methylenedioxy)phenyl]pyrrolidine (55) and 1-Methyl-2β-(1-methylethyl)-4β-(dimethylphenylsilyl)-3α-[3,4-(methylenedioxy)phenyl]pyrrolidine (56). According to Procedure B, **5i** (0.20 g, 0.53 mmol) and vinylsilane **54** (0.30 g, 1.07 mmol) in THF (2 mL) were added to n-butyllithium (0.31 mL, 2.10 M solution in hexane) in THF (4.3 mL) over 5 min. After 15 min, CH_3I (0.11 g, 0.75 mmol) was added, and the solution was warmed to RT and immediately worked up to give an oil, which was determined by ^1H NMR to consist of a 13:1 mixture of the title compounds **55** and **56**, respectively. Chromatography (10–100% EtOAc/hex gradient) afforded 0.12 g (59%) of the title compounds as an inseparable mixture of diastereomers (13:1) as shown by ^1H NMR, R_f = 0.36 (50% EtOAc/hexane). Data for **55**: IR (neat) 1485 (s), 1246 (s), 1041 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2 H), 7.34–7.30 (m, 3 H), 6.86 (s, 1 H), 6.64 (s, 1 H), 5.91 (s, 2 H), 3.28 (t, 1 H, J = 8.7 Hz), 3.09 (t, 1 H, J = 7.5 Hz), 2.28 (s, 3 H), 2.12 (dd, 1 H, J = 10.9, 9.4 Hz), 1.94 (dist t, 1 H, J = 6.8 Hz), 1.74 (dt, 1 H, J = 10.9, 7.8 Hz), 1.65 (m, 1 H), 0.84 (d, 3 H, J = 6.9 Hz), 0.45 (d, 3 H, J = 6.9 Hz), 0.22 (s, 3 H), 0.20 (s, 3 H) (DNOE: irradiation at 1.74 ppm (H-4β) produced a 3.5% enhancement for the signal at 2.12 ppm (H-5β); irradiation at 1.94 ppm (H-2α) produced a 5.4% enhancement for the signal at 3.09 ppm (H-3α), while irradiation at 3.09 ppm (H-3α) produced a 3.5% enhancement for the signal at 1.94 ppm (H-2α) and failed to produce an enhancement for the signal at 1.65 ppm (H-4β)); ^{13}C NMR (90 MHz, $CDCl_3$) δ 147.2, 145.9, 139.0, 137.9, 134.0, 129.0, 127.7, 122.8, 110.5, 107.3, 100.7, 76.3, 59.7, 50.4, 42.7, 32.4, 28.7, 19.9, 19.5, −4.0, −4.5; MS (CI, NH_3) m/z (rel intensity) 382 [100, (M + H)$^+$], 339 (4), 338 (15), 244 (3), 202 (2), 179 (9), 177 (14), 152 (8), 136 (27), 84 (2); HRMS (CI, NH_3) calcd for $C_{23}H_{32}NO_2Si$ (M + H)$^+$ 382.2202, found 382.2181. Partial data for **56**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.29 (d, 6 H, J = 6.9 Hz). The identity and stereochemistry of **56** are tentative, since it was present in such a small amount and could not be separated from **55**.

1-Methyl-2β-phenyl-4α-(dimethylphenylsilyl)-3β-[3,4-(methylenedioxy)phenyl]pyrrolidine (57) and 1-Methyl-2β-phenyl-4β-(dimethylphenylsilyl)-3α-[3,4-(methylenedioxy)phenyl]pyrrolidine (58). According to Procedure B, **5b** (0.10 g, 0.25 mmol) and vinylsilane **54** (0.14 g, 0.49 mmol) in THF (1 mL) were added to n-butyllithium (0.14 mL, 2.10 M solution in hexane) in THF (2 mL) over 5 min. After 15 min, CH_3I (0.05 g, 0.34 mmol) was added, and the solution was warmed to RT and immediately worked up to give an oil, which was determined by ^1H NMR to consist of a 1:1 mixture of the title compounds **57** and **58**, respectively. Chromatography (5–20% EtOAc/hex gradient) afforded 0.08 g (76%) of the title pyrrolidines as a pale yellow oil. The mixture was rechromatographed (same solvent system) to isolate pure fractions of each diastereomer for characterization, R_f(**57**) = 0.43, R_f(**58**) = 0.53 (30% EtOAc/hexane). Data for **57**: IR (neat) 2776 (m), 1441 (m), 1490 (s), 1246 (s), 1114 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50–7.46 (m, 2 H), 7.37–7.32 (m, 3 H), 7.07–6.92 (m, 5 H), 6.51 (d, 1 H, J = 1.6 Hz), 6.40 (d, 1 H, J = 8.0 Hz), 6.32 (dd, 1 H, J = 8.0, 1.6 Hz), 5.78 (s, 2 H), 3.40 (dd, 1 H, J = 9.0, 8.0 Hz), 3.35–3.26 (m, 2 H), 2.32 (dd, 1 H, J = 11.2, 9.2 Hz), 2.19 (s, 3 H), 1.99–1.90 (m, 1 H), 0.28 (s, 3 H), 0.23 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 146.8, 145.4, 137.8, 134.0, 129.1, 128.4,

(50) Seki, Y.; Takeshita, K.; Kawamoto, S.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 928.

128.1, 127.8, 127.4, 126.2, 122.4, 109.8, 107.0, 100.4, 76.6, 59.1, 53.7, 40.9, 32.5, 29.7, -3.8, -4.5; MS m/z (rel intensity) 415 (29, M^+), 296 (14), 205 (41), 161 (17), 133 (100), 132 (84), 131 (21), 105 (19), 103 (16), 91 (18); HRMS calcd for $C_{26}H_{29}NO_2Si$ (M^+) 415.1968, found 415.1970. Data for **58**: IR (neat) 2776 (m), 1485 (s), 1441 (m), 1246 (s), 1114 (m), 1041 (s) cm^{-1}; ^1H NMR (360 MHz, C_6D_6) δ 7.52–7.49 (m, 2 H), 7.26–7.08 (m, 10 H), 6.70 (d, 1 H, J = 1.7 Hz), 6.52 (d, 1 H, J = 7.9 Hz), 6.26 (dd, 1 H, J = 7.9, 1.7 Hz), 5.33 (d, 1 H, J = 1.7 Hz), 5.31 (d, 1 H, J = 1.7 Hz), 3.35 (dd, 1 H, J = 9.2, 4.0 Hz), 3.15 (d, 1 H, J = 9.0 Hz), 3.06 (app t, 1 H, J_{app} = 9.0 Hz), 2.71 (dd, 1 H, J = 10.8, 9.2 Hz), 2.15 (s, 3 H), 1.78–1.71 (m, 1 H), 0.39 (s, 3 H), 0.22 (s, 3 H), all assignments were made from a 2D-NOESY experiment (DNOE: irradiation at 3.15 ppm (H-2α) produced a -5.6% enhancement for the signal at 3.35 ppm (H-5α); irradiation at 3.06 ppm (H-3β) failed to produce an enhancement for the signal at 3.35 ppm (H-5α) and for the signal at 1.78–1.71 ppm (H-4α); irradiation at 1.75 ppm (H-4α) produced a -5.6% enhancement for the signal at 3.35 ppm (H-5α) and failed to produce an enhancement for the signal at 3.06 ppm (*H*-3β); irradiation at 3.35 ppm (H-5α) produced a -3.8% enhancement for the signal at 3.15 ppm (H-2α), a -3.3% enhancement for the signal at 1.78–1.71 ppm (H-4α), and a 16.4% enhancement for the signal at 2.71 ppm (*H*-5β)); ^{13}C NMR (90 MHz, $CDCl_3$) δ 147.4, 146.0, 138.1, 133.9, 128.9, 128.1, 127.9, 127.7, 127.1, 121.6, 108.1, 107.8, 100.7, 81.3, 58.2, 57.7, 40.4, 31.7, 29.7, -3.8, -4.8; MS m/z (rel intensity) 415 (26, M^+), 296 (11), 205 (37), 161 (15), 135 (69), 133 (100), 132 (86), 131 (18), 103 (12), 91 (14); HRMS calcd for $C_{26}H_{29}NO_2Si$ (M^+) 415.1968, found 415.1974.

Preparation of 2-Isopropyl-1-(*p*-tolylsulfonyl)pyrrolidine (61) by Desulfurization of 59. According to Procedure A, **5i** (0.96 g, 1.93 mmol) and phenyl vinyl sulfide (0.61 g, 4.48 mmol) in THF (5 mL) were added to *n*-butyllithium (0.83 mL of a 2.55 M solution in hexane, 2.12 mmol) in THF (15 mL) over 3 min. After 15 min, water was added and the mixture was worked up to give 1.40 g of a yellow oil containing the cycloadducts along with tetrabutyltin and unreacted vinyl sulfide. The crude product was passed through a plug of silica gel (eluted first with $CHCl_3$ then 1% NH_4OH/9% MeOH/90% $CHCl_3$) to give 425 mg (100%) of a mixture of diastereomeric pyrrolidines. The product was dissolved in THF (20 mL), mixed with triethylamine (317 mg, 3.13 mmol), cooled to 0 °C, and treated with *p*-toluenesulfonyl chloride (447 mg, 2.34 mmol) in THF (5 mL). After warming to RT for 13 h, the mixture was diluted with water and extracted with EtOAc. The organic layer was washed successively with 1 N H_2SO_4, water, aqueous 5% $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated in vacuo to give a dark yellow oil. Chromatography (10–50% EtOAc/hexane gradient) gave 525 mg (73% from **5i**) of **59** as a mixture of diastereomers. The entire product (1.40 mmol) was dissolved in absolute ethanol (10 mL) and treated with W-2 Raney nickel (2.5 g, 42 mmol) at 85 °C for 45 min. The mixture was cooled, filtered, and concentrated in vacuo to give 337 mg of a dark yellow solid. Chromatography (10% ethyl acetate/hexane) afforded 311 mg (82%) of the title compound as a pale yellow solid: mp 87–89 °C; R_f = 0.57; IR ($CDCl_3$) 1599 (w), 1468 (m), 1427 (m), 1340 (s), 1274 (s), 1254 (s), 1093 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, 2 H, J = 8.2 Hz), 7.30 (d, 2 H, J = 8.2 Hz), 3.50 (m, 1 H), 3.29 (m, 2 H), 2.41 (s, 3 H), 2.16 (m, 1 H), 1.64 (m, 2 H), 1.3–1.5 (m, 2 H), 0.92 (d, 3 H, J = 6.8 Hz), 0.87 (d, 3 H, J = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 135.6, 129.6, 127.6, 65.7, 49.5, 32.1, 26.3, 24.6, 21.5, 19.8, 16.6; MS m/z (rel intensity) 267 (M^+, 0.3), 224 (100), 155 (78.7), 117 (141), 92 (10.3), 91 (87.0), 70 (8.0), 65 (19.8), 41 (21.3). Anal. Calcd for $C_{14}H_{21}NO_2S$: C, 62.89; H, 7.92; N, 5.24. Found: C, 63.11; H, 7.85; N, 5.14.

Preparation of 2-Isopropyl-1-(*p*-tolylsulfonyl)pyrrolidine (61) by Desulfurization of 60. According to Procedure A, **5i** (656 mg, 1.31 mmol) and phenyl vinyl selenide (480 mg, 2.62 mmol) in THF (5 mL) were added to *n*-butyllithium (0.57 mL of a 2.55 M solution in hexane, 1.44 mmol) in THF (15 mL) over 3 min. After 15 min, water was added and the mixture was worked up to give 1.13 g of a yellow oil containing the cycloadducts along with tetrabutyltin and unreacted vinyl selenide. The crude product was passed through a plug of silica gel (eluted first with $CHCl_3$ then 1% NH_4OH/9% MeOH/90% $CHCl_3$) to give 350 mg (99%) of a mixture of diastereomeric pyrrolidines. The product was dissolved in THF (15 mL), mixed with triethylamine (211 mg, 2.09 mmol), cooled to 0 °C, and treated with *p*-toluenesulfonyl chloride (299 mg, 1.57 mmol). After warming to RT for 13 h, the mixture was diluted with water and extracted with EtOAc. The organic layer was washed successively with 1 N H_2SO_4, water, aqueous 5% $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated in vacuo to give a dark yellow oil. Chromatography (10–50% EtOAc/hexane gradient) gave 434 mg (78% from **5i**) of **60** as a mixture of diastereomers (colorless oil). The mixture of sulfonamides **60** (215 mg, 0.51 mmol) was dissolved in benzene (15 mL) along with tributyltin hydride (220 mg, 0.76 mmol) and AIBN (12 mg, 0.08 mmol). The solution was heated to reflux for 15 h and then cooled to RT and diluted with ether. The organic solution was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to give a yellow oil. Chromatography of the residue (25% EtOAc/hexane) afforded 136 mg (99%) of the title compound as a pale yellow solid; see above for characterization.

Preparation of 2-(1-Methylethyl)-1-(*p*-tolylsulfonyl)-2,5-dihydro-1*H*-pyrrole (62) from 59. The method of Umezawa was followed.[51] A solution of **59** (527 mg, 1.40 mmol, prepared as above) in CH_2Cl_2 (50 mL) was cooled to -30 °C and treated with *m*-CPBA (242 mg, 1.40 mmol). The resultant peach colored solution was stirred at -30 °C for 30 min and then treated with 10 mL of 10% NaOH and warmed to RT. The organic layer was separated, washed with brine, dried ($MgSO_4$), and concentrated in vacuo to give 528 mg of a dark yellow oil containing an isomeric mixture of sulfoxides. The crude mixture of sulfoxides was taken up in acetic anhydride (18 mL), along with sodium acetate (300 mg, 3.6 mmol), and heated to reflux for 7 h. The yellow-orange reaction mixture was cooled to RT and diluted with ether. The ethereal solution was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to give 363 mg of a dark brown oil. Column chromatography (25% EtOAc/hexane) afforded 167 mg (45% overall yield from **59**) of the title compound as a pale yellow solid: mp 91–94 °C; R_f = 0.58; IR ($CDCl_3$) 1599 (w), 1422 (s), 1340 (m), 1274 (s), 1250 (s), 1162 (s), 1092 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, 2 H, J = 8.2 Hz), 7.26 (d, 1 H, J = 8.2 Hz), 5.65 (m, 1 H), 5.53 (m, 1 H), 4.37 (m, 1 H), 4.08 (m, 2 H), 2.40 (s, 3 H), 2.23 (m, 1 H), 0.93 (d, 3 H, J = 7.0 Hz), 0.82 (d, 3 H, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 135.3, 129.7, 127.5, 126.9, 126.0, 72.8, 56.2, 33.2, 21.5, 19.0, 16.2; MS m/z (rel intensity) 265 (M^+, 0.1), 222 (63.0), 155 (54.7), 139 (2.3), 94 (1.4), 91 (100), 65 (21.2), 51 (2.1). Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.37; H, 7.22; N, 5.28. Found: C, 63.26; H, 7.33; N, 4.92.

5-(1-Methylethyl)-1-(*p*-tolylsulfonyl)-3-pyrroline (62) and 5-(1-Methylethyl)-1-(*p*-tolylsulfonyl)-2-pyrroline (63) from 60. The method of Reich[52] for the elimination of selenoxides was followed. An isomeric mixture of **60** (249 mg, 0.59 mmol) prepared as described above was dissolved in CH_2Cl_2 (5 mL) and cooled to 0 °C. *m*-CPBA (102 mg, 0.588 mmol) was added, and the mixture was stirred for 30 min at 0 °C. Diisopropylamine (119 mg, 1.18 mmol) was added, and the reaction mixture was transferred via a cannula into a reaction vessel containing refluxing hexane. The solution was refluxed for 30 min, cooled to room temperature, washed successively with 10% KOH, water, and brine, dried (Na_2SO_4), and concentrated in vacuo to give 218 mg of a dark orange oil. The ^1H NMR spectrum of the crude residue indicated that it consisted of 3:1 mixture of **62** and **63**. Chromatography (25% EtOAc/hexane) afforded 128 mg (91%) of the same 3:1 mixture of title compounds as a yellow oil. The mixture was rechromatographed (same solvent system) to isolate a pure sample of **63** as a pale yellow solid, mp 95–96 °C, R_f = 0.54. See above for characterization of **62**. Data for **63**: IR ($CDCl_3$) 1622 (w), 1598 (w), 1494 (w), 1466 (m), 1346 (s), 1285 (m), 1167 (s), 1114 (m), 1090 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (m, 2 H), 7.30 (m, 2 H), 6.31 (m, 1 H), 5.07 (m, 1 H), 3.62 (m, 1 H), 2.42 (s, 3 H), 2.18 (m, 3 H), 0.88 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 136.4, 134.1, 131.0, 130.1, 129.4, 127.6, 112.5, 64.8, 32.0, 30.6, 21.5, 18.3, 15.3; MS m/e (rel intensity) 265 (M^+, 13.2), 222 (83.7), 155 (89.6), 139 (2.3), 110 (4.6), 91 (100), 68 (22.8), 65 (28.1), 55 (7.8); HRMS calcd for $C_{14}H_{19}NO_2S$ 265.1136, found 265.1125.

4α-Hydroxy-1-methyl-2β-(1-methylethyl)-3β-phenylpyrrolidine (64). The method of Overman[42] was used for the oxidation of **52**. A solution of pyrrolidine **52** (222 mg, 0.66 mmol) in CH_2Cl_2 (20 mL) was cooled to 0 °C, treated with a tetrafluoroboric acid–diethyl ether complex (1.4 mL of an 85% solution), and stirred for 5 min. The yellow reaction mixture was then allowed to warm to RT. After 8 h, GC analysis indicated that the reaction was only 50% complete. An additional 1.4 mL of tetrafluoroboric acid–ether complex was added, and the mixture was allowed to stir at RT overnight. The reaction was cooled to 0 °C, and ether (40 mL) was added followed by an equal volume of saturated $NaHCO_3$. The organic layer was dried (Na_2SO_4) and concentrated in vacuo to give 148 mg of a yellow oil. ^1H NMR analysis indicated that it contained the desired fluorosilane intermediate along with a small amount of unreacted starting material (80.7% crude yield). The crude fluorosilane and potassium fluoride (160 mg, 2.65 mmol) were taken up in DMF (15 mL) and stirred for 5 min at 0 °C. Hydrogen peroxide (1.0 mL of a 30% aqueous solution, 12 mmol) was then added, and the mixture was heated to 60 °C for 10 h and then cooled to 0 °C and diluted with 30% EtOAc/hexane solution. The organic layer was washed with saturated aqueous sodium sulfite, saturated $NaHCO_3$, and brine, dried

(51) Nishimura, Y.; Kondo, S.; Umezawa, H. *J. Org. Chem.* **1985**, *50*, 5210.

(52) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *J. Org. Chem.* **1978**, *43*, 1697.

(Na_2SO_4), and concentrated in vacuo to give 82 mg of a pale yellow oil. Analysis of the crude oil by ^1H NMR indicated that it contained the desired alcohol along with a small amount of DMF (73.4% crude yield). Chromatography (NH_4OH/MeOH/$CHCl_3$ gradient) afforded 47 mg (32% based on starting pyrrolidine, 40% based on 80% conversion to the fluorosilane) of the title compound as a colorless oil: R_f = 0.40 (1% NH_4OH/9% MeOH/90% $CHCl_3$); IR (neat) 3345 (bs), 1602 (w), 1494 (m), 1454 (s), 1418 (w), 1388 (w), 1363 (m), 1030 (m), 703 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.2–7.3 (m, 5 H), 4.32 (m, 1 H, H-4β), 3.71 (dd, 1 H, J = 10.8, 5.6 Hz, H-5), 3.22 (dd, 1 H, J = 7.2, 3.4 Hz, H-3α), 2.77 (t, 1 H, J = 6.9 Hz, H-2α), 2.52 (s, 3 H, NCH_3), 2.45 (dd, 1 H, J = 10.8, 4.2 Hz, H-5), 1.77 (m, 1 H, H-2′), 0.90 (d, 3 H, J = 6.8 Hz), 0.49 (d, 3 H, J = 6.8 Hz) (DNOE: irradiation of the signal at 3.22 ppm (H-3α) produced a 7.3% enhancement in the signal at 2.77 ppm (H-2α) and a 6.0% enhancement for the signal at 1.77 ppm (H-2′)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0 (2), 129.5 (2), 128.1, 126.4, 76.3, 74.0, 65.0, 57.9, 44.4, 28.8, 19.8, 19.6; MS m/z (rel intensity) 220 (M + 1, 100), 218 (18.4), 202 (36.2), 176 (15.6), 163 (2.9), 136 (29.8), 119 (25.0), 101 (4.1), 91 (5.1); HRMS (CI, CH_4) calcd for $C_{14}H_{22}NO$ (MH^+) 220.1701; found 220.1698.

N-[(Trimethylstannyl)methyl]-(*E*)-6-(3,4-dimethoxyphenyl)-7-(phenylthio)-6-heptenimine (*E*-69) and N-[(trimethylstannyl)methyl]-(*Z*)-6-(3,4-dimethoxyphenyl)-7-(phenylthio)-6-heptenimine (*Z*-69) were prepared from **8a** (0.73 g, 3.29 mmol), PPh_3 (0.77 g, 2.95 mmol), and the aldehyde **68** (0.86 g, 2.41 mmol, 3:1 mixture of E/Z isomers; see the supplementary material) in benzene (13 mL) at RT (13 h) according to the general procedure. Workup afforded 1.37 g of a clear, colorless oil. Analysis of the oil by ^1H NMR (DMF internal standard) indicated that it consisted of 1.25 g (95% yield) of a 3:1 mixture of the title imines *E*-**69** and *Z*-**69**, which was used without further purification: IR (neat) 1650 (w), 1602 (w), 1579 (w), 1514 (s), 1463 (m), 1413 (w), 1254 (s), 1227 (m), 1028 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) *E*-**69** δ 7.43 (t, 1 H, J = 3.7 Hz), 7.4–7.2 (m, 5 H), 6.9–6.7 (m, 3 H), 6.36 (s, 1 H), 3.84 (s, 3 H), 3.83 (s, 1 H), 3.46 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 52.3 Hz], 2.71 (m, 2 H), 2.16 (m, 2 H), 1.47 (m, 4 H), 0.05 [s, 9 H, $^2J(^{117/119}Sn-^1H)$ = 52.5 Hz], partial data for *Z*-**69** δ 6.18 (s, 1 H), 2.49 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 148.9, 148.6, 143.1, 136.7, 134.0, 128.9, 128.7, 126.1, 119.6, 118.5, 111.2, 109.6, 55.8 (2), 48.1, 35.4, 31.7, 27.9, 26.4, −10.4; MS (CI, CH_4) m/z (rel intensity) 534 (MH^+, 24.5), 518 (8.8), 424 (6.6), 368 (18.7), 260 (7.5), 231 (6.2), 165 (18.8), 111 (100), 91 (6.7); HRMS (CI, CH_4) calcd for $C_{25}H_{36}NO_2SSn$ (MH^+) 534.1489, found 534.1465.

(3α,3aβ,7aβ)-3-(Phenylthio)-3a-(3,4-dimethoxyphenyl)-1-methyloctahydroindole (70a), (3β,3aβ,7aβ)-3-(Phenylthio)-3a-(3,4-dimethoxyphenyl)-1-methyloctahydroindole (70b), and (3α,3aβ,7aα)-3-(Phenylthio)-3a-(3,4-dimethoxyphenyl)-1-methyloctahydroindole (71). According to Procedure C, **69** (486 mg, 0.91 mmol, 3:1 mixture of E/Z isomers) in THF (5 mL) was added to methyllithium (1.05 mL of a 1.24 M solution in ether, 1.30 mmol) in THF (60 mL) over 10 min. After 10 min, CH_3I (192 mg, 1.37 mmol) was added, and the solution was slowly warmed to RT over 1 h and worked up to give 394 mg of a viscous yellow oil. Analysis by ^1H NMR spectroscopy and GC indicated a 3.3:1:1.5 ratio of **70a**, **70b**, and **71**. Chromatography (50% EtOAc/hexane) afforded 0.226 g (65%) of a mixture of the title cycloadducts as a clear, colorless oil. The mixture was rechromatographed (same solvent system) to isolate fractions of each isomer uncontaminated by the others for further characterization (R_f(**71**) = 0.51, R_f(**70b**) = 0.25, R_f(**70a**) = 0.20). Data for **70a**: IR (neat) 1604 (w), 1584 (m), 1519 (s), 1462 (s), 1440 (s), 1324 (m), 1257 (s), 1149 (s), 1027 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.0–7.1 (m, 7 H), 6.80 (d, 1 H, J = 8.5 Hz), 3.87 (s, 3 H), 3.84 (s, 3 H), 3.54 (dd, 1 H, J = 10.2, 6.8 Hz), 3.37 (dd, 1 H, J = 10.2, 7.0 Hz), 2.98 (t, 1 H, J = 10.2 Hz), 2.92 (broad t, 1 H, H-7a, $w_{1/2}$ = 6 Hz), 3.35 (s, 3 H, NCH_3), 2.26 (d, 1 H, J = 13.3 Hz), 2.04 (dt, 1 H, J = 13.4, 3.4 Hz), 1.80 (distorted d, 1 H, J = 13.7 Hz), 1.1–1.7 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 147.6, 136.8, 136.0, 130.3, 128.7, 126.0, 119.3, 111.1, 111.0, 70.0, 62.7, 58.7, 56.1, 55.9, 50.4, 40.4, 28.3, 23.5, 22.5, 20.0; MS m/z (rel intensity) 383 (M^+, 2.5), 382 (1.4), 275 (100), 243 (23.0), 217 (4.7), 202 (3.6), 187 (3.1), 177 (14.4), 165 (6.9), 151 (6.8), 109 (4.0); HRMS (CI) calcd for $C_{23}H_{29}NO_2S$ 383.1919, found 383.1905. Data for **70b**: IR (neat) 1604 (w), 1584 (m), 1519 (s), 1463 (s), 1440 (s), 1410 (m), 1256 (s), 1148 (s), 1027 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.7–7.2 (m, 8 H), 3.87 (s, 3 H), 3.79 (s, 3 H), 3.78 (m, 1 H), 3.66 (dd, 1 H, J = 7.3, 5.0 Hz), 3.08 (broad t, 1 H, H-7a, $w_{1/2}$ = 6 Hz), 2.44 (dd, 1 H, J = 10.7, 5.0 Hz), 2.37 (s, 3 H, NCH_3), 1.0–2.1 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 147.6, 136.7, 133.7, 130.3, 128.5, 125.9, 121.1, 112.5, 110.3, 65.7, 63.2, 55.9, 55.8, 52.2, 40.6, 35.6, 23.3, 22.7, 20.3; HRMS calcd for $C_{23}H_{29}NO_2S$ 383.1919, found 383.1891. Data for **71**: IR (neat) 1603 (w), 1583 (m), 1514 (s), 1463 (s), 1409 (w), 1325 (w), 1259 (s), 1233 (s), 1149 (s) 1029 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.1–7.5 (m, 7 H), 6.80 (d, 1 H, J = 8.6 Hz), 3.87 (s, 3 H), 3.80 (s, 3 H), 3.70 (m, 2 H), 2.52 (dd, 1 H, J = 11.2, 4.4 Hz, H-7a), 2.38 (s, 3 H, NCH_3), 2.20 (m, 2 H), 1.96 (dt, 1 H, J = 13.2, 3.4 Hz), 1.6–1.8 (m, 3 H), 1.3–1.5 (m, 2 H), 1.10 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 146.9, 138.1, 137.4, 129.4, 128.8, 125.9, 121.2, 113.0, 110.8, 73.5, 61.9, 55.9, 55.7, 55.0, 53.6, 41.2, 33.7, 25.2, 24.2, 22.1; MS m/z (rel intensity) 283 (M^+, 5.6), 382 (2.6), 274 (100), 243 (55.0), 228 (5.10), 217 (6.20), 201 (5.7), 177 (28.5), 151 (9.3), 136 (9.2), 84 (17.9); HRMS calcd for $C_{23}H_{29}NO_2S$ 383.1891, found 181.1900.

(3aβ,7aβ)-3a-(3,4-Dimethoxyphenyl)-1-methyloctahydroindole (36) by Desulfurization of 70a and 70b. A solution containing an 11.5:1.0 mixture of pyrrolidines **70a** and **70b** (69.1 mg, 0.18 mmol) and W-2 Raney nickel (210 mg, 3.6 mmol) in 10 mL of absolute ethanol was heated to reflux for 7 h. The mixture was cooled, filtered, and concentrated in vacuo to give a pale purple oil. Chromatography (0.25% NH_4OH/2.5% MeOH/97.5% $CHCl_3$) afforded 31.7 mg (64%) of the title compound as a colorless oil. See above for characterization.

(3aα,7aβ)-3a-(3,4-Dimethoxyphenyl)-1-methyloctahydroindole (72). A mixture of **71** (44.1 mg, 0.12 mmol) and W-2 Raney nickel (135 mg, 2.3 mmol) in 10 mL of absolute ethanol was heated to reflux for 3 h. The mixture was cooled, filtered, and concentrated in vacuo to give 33.3 mg of a yellow oil. Chromatography (0.25% NH_4OH/2.5% MeOH/97.5% $CHCl_3$) afforded 23.4 mg (74%) of the title compound as a colorless oil: R_f = 0.55; IR (neat) 1604 (m), 1582 (m), 1514 (s), 1454 (s), 1409 (m), 1336 (m), 1340 (m), 1257 (s), 1230 (s), 1151 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, 1 H, J = 2.1 Hz), 7.26 (m, 1 H), 6.79 (d, 1 H, J = 8.5 Hz), 3.86 (s, 3 H), 3.84 (s, 3 H), 3.10 (dt, 1 H, J = 10.0, 8.2 Hz, H-2), 2.60 (broad d, 1 H, J = 12.7 Hz, H-7a), 2.35 (s, 3 H, NCH_3), 2.49 (dt, 1 H, J = 10.3, 2.8 Hz), 2.16 (dd, 1 H, J = 11.2, 4.0 Hz), 1.1–1.7 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 146.7, 138.5, 121.1, 113.9, 111.1, 77.2, 56.1, 55.9, 53.4, 50.0, 41.4, 40.1, 38.0, 25.8, 24.3, 22.3; MS m/z (rel intensity) 274 (100), 260 (23), 232 (22), 219 (25), 218 (51), 204 (18), 137 (19), 96 (21), 84 (10), 70 (34), 57 (22), 44 (77); HRMS (CI, CH_4) calcd for $C_{17}H_{26}NO_2$ (MH^+) 276.1963, found 276.1952.

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Supplementary Material Available: Experimental procedures for **9**, **27**, **54**, **66**, **67**, and **68** (8 pages). Ordering information is given on any current masthead page.