Configurational Stability of Chiral, Nonconjugated Nitrogen-Substituted Organolithium Compounds Generated by Tin–Lithium Exchange of *N*-[(1-Tri-*n*-butylstannyl)alkyl]imidazolidin-2-ones and -oxazolidin-2-ones

William H. Pearson,* Aline C. Lindbeck, and Jeff W. Kampf[1]

Contribution from the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

Received October 30, 1992

Abstract: Chiral, nonracemic, nonconjugated, acyclic nitrogen-substituted organolithium compounds were generated in order to study the configurational stability of such species. The organolithium compounds were generated by tin–lithium exchange on *N*-[(1-tri-*n*-butylstannyl)alkyl]imidazolidin-2-ones and *N*-[(1-tri-*n*-butylstannyl)alkyl]-oxazolidin-2-ones. Varying degrees of epimerization were observed, depending on the structure of the heterocycle and the reaction conditions. When the nitrogen was part of an imidazolidinone ring, the epimerization was sufficiently slow to be observed at low temperature, thus allowing the configurational stability of nonconjugated, acyclic nitrogen-substituted organolithium compounds to be evaluated for the first time. Addition of the coordinating solvent TMEDA caused a much more rapid epimerization. When the nitrogen was part of an oxazolidinone ring, the rate of epimerization was too fast to observe, even at low temperature. Reaction of these species with electrophiles such as DCl, Bu_3SnCl, aldehydes, and ketones proceeded with retention of configuration. A novel method for the synthesis of the chiral stannanes was developed. Condensation of carbamates (cyclic and acyclic) or imidazolidin-2-ones with sodium *p*-toluenesulfinate, an aldehyde, and formic acid produced *N*-sulfonylalkylated materials (the Engberts method), which were treated with tri-*n*-butylstannyl anions to give *N*-[(1-tri-*n*-butylstannyl)alkyl]carbamates, -oxazolidin-2-ones, and -imidazolidin-2-ones. When chiral imidazolidin-2-ones were used in the sulfonylalkylation reaction, a single diastereomeric sulfone was produced. Displacement of the sulfone with (tri-*n*-butylstannyl)lithium proceeded with complete retention of stereochemistry. Evidence for the formation and stereoselective reaction of a nitrogen-substituted radical intermediate was obtained.

Nitrogen-substituted organolithium compounds have been widely studied and have become useful intermediates for the synthesis of amines and their derivatives.[2] Chiral, conjugated versions of these species have seen considerable research activity.[3-6] Several stereochemical studies have been reported on racemic, nonconjugated systems where a conformational bias was present.[7-12] Prior to the work described herein,[13] Walborsky[14] and Gawley[5c] had published the only examples of chiral, *nonracemic*, nonconjugated nitrogen-substituted organolithiums. Both cases involved cyclic systems, where small-ring strain[14,15] or conformational considerations[5c] affected the configuration of the carbanion. The configurational stability of acyclic nitrogen-substituted organolithiums had not been studied, and there had been no reports on the generation of chiral, nonracemic, acyclic, nonconjugated systems, although closely related acyclic benzylic organolithiums have been recently studied by Gawley.[5a] We chose to study the transmetalation of N-acylated α-aminostannanes **1** (eq 1) for the following reasons: (1) a chiral auxiliary could be easily attached to serve as an internal stereochemical reference; (2) the resultant organolithium **2** would be internally chelated ("dipole-stabilized"),[2] providing a degree of conformational rigidity; and (3) deprotection to provide an optically active primary amine **3** should be possible. We wish to report that the tin–lithium exchange method allows the generation of such organ-

(1) Author to whom correspondence regarding the X-ray crystallographic determinations should be directed.

(2) (a) Beak, P.; Zajdel, W. J.; Reitz, D. B. *Chem. Rev.* **1984**, *84*, 471–523. (b) Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275. (c) Gawley, R. E.; Rein, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 1, pp 459–485. (d) Gawley, R. E.; Rein, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, pp 65–83. (e) Hart, D. J. In *Alkaloids: Chemical and Biological Perspectives*; Pelletier, S. W., Ed.; Wiley: New York, 1988, Vol. 6, pp 227–296.

(3) (a) Highsmith, T. K.; Meyers, A. I. In *Advances in Heterocyclic Natural Product Synthesis*; Pearson, W. H., Ed.; JAI: Greenwich, CT, 1990; Vol. 1, pp 95–135. (b) Meyers, A. I. *Aldrichimica Acta* **1985**, *18*, 59. (c) For a study of the configurational stability of chiral lithioformamidines, see: Meyers, A. I.; Guiles, J.; Warmus, J. S.; Gonzalez, M. A. *Tetrahedron Lett.* **1991**, *32*, 5505–5508.

(4) Roder, H.; Helmchen, G.; Peter, E.-M.; Peters, K.; von Schnering, H.-G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 898.

(5) (a) Gawley, R. E.; Rein, K.; Chemburkar, S. *J. Org. Chem.* **1989**, *54*, 3002–3004. (b) Rein, K.; Goicoechea-Pappas, M.; Anklekar, T. V.; Hart, G. C.; Smith, G. A.; Gawley, R. E. *J. Am. Chem. Soc.* **1989**, *111*, 2211–2217. (c) Gawley, R. E.; Hart, G. C.; Bartolotti, L. J. *J. Org. Chem.* **1989**, *54*, 175–181.

(6) Häner, R.; Olano, B.; Seebach, D. *Helv. Chim. Acta* **1987**, *70*, 1676–1693.

(7) (a) Seebach, D.; Wykypiel, W.; Lubosch, D.; Kalinowski, H.-O. *Helv. Chim. Acta* **1978**, *61*, 3100–3102. (b) Renger, B.; Kalinowski, H.-O.; Seebach, D. *Chem. Ber.* **1977**, *110*, 1866–1878. (c) Seebach, D.; Enders, D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 15.

(8) Fraser, R. R.; Grindley, T. B.; Passannanti, S. *Can. J. Chem.* **1975**, *53*, 2473–2480.

(9) Lyle, R. E.; Saavedra, J. E.; Lyle, G. G.; Fribush, H. M.; Marshall, J. L.; Lijinsky, W.; Singer, G. M. *Tetrahedron Lett.* **1976**, 4431–4434.

(10) (a) Beak, P.; Lee, W. K. *J. Org. Chem.* **1990**, *55*, 2578–2580. (b) Peak, P.; Zajdel, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 1010.

(11) (a) Meyers, A. I.; Edwards, P. D.; Rieker, W. F.; Bailey, T. R. *J. Am. Chem. Soc.* **1984**, *106*, 3270–3276. (b) Shawe, T. T.; Meyers, A. I. *J. Org. Chem.* **1991**, *56*, 2751–2755.

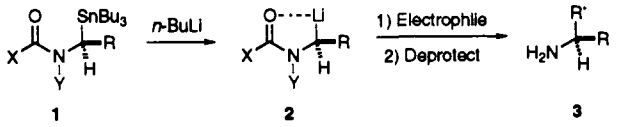
(12) Sanner, M. A. *Tetrahedron Lett.* **1989**, *30*, 1909–1912.

(13) Portions of this work have been published as a communication: Pearson, W. H.; Lindbeck, A. C. *J. Am. Chem. Soc.* **1991**, *113*, 8546–8548.

(14) (a) Periasamy, M. P.; Walborsky, H. M. *J. Am. Chem. Soc.* **1977**, *99*, 2631. (b) Walborsky, H. M.; Periasamy, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 3711.

(15) Seebach has studied a chiral, nonracemic, configurationally stable 2-lithioaziridine.[6] Even though the anion is substituted by a thioester, the small ring prevents epimerization.

0002-7863/93/1515-2622$04.00/0

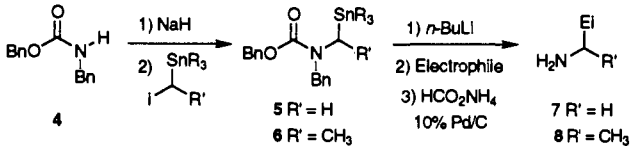


(1)

olithium compounds, which undergo highly stereoselective reactions with electrophiles.[13] Evidence for configurational stability was obtained. Related stereochemical studies on nonracemic cyclic[16] and acyclic[17] nonconjugated nitrogen-substituted organolithiums have recently appeared from other laboratories.

Results and Discussion

We recently reported that nonconjugated (racemic or achiral) dipole-stabilized nitrogen-substituted organolithium compounds could be generated from protected α-aminostannane derivatives **5** and **6** by tin–lithium exchange (eq 2),[18] allowing access to

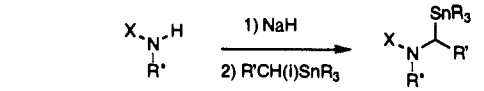


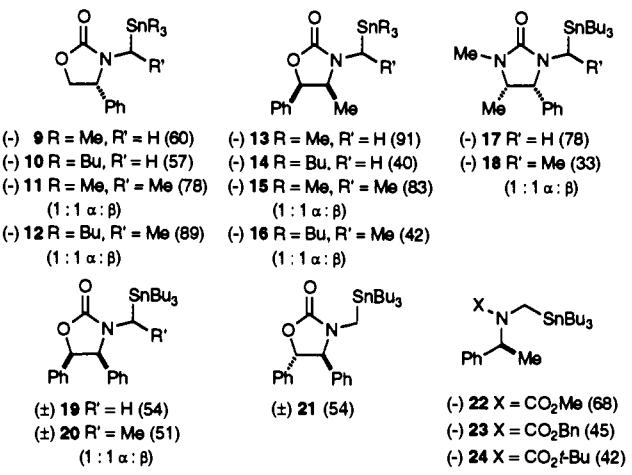
(2)

primary amines **7** and **8** after reaction with electrophiles and deprotection.[17,19-21] The stannanes were prepared by N-alkylation of carbamate **4**. We now wish to report the details of the transmetalation of chiral nonracemic versions of these stannanes and the stereoselective reactions of the resultant organolithiums.[22,23]

Preparation of N-Acylated α-Aminostannanes. A simple method for the synthesis of N-acylated α-aminostannanes is the alkylation of the sodium salt of a carbamate or urea with an α-iodoalkylstannane (e.g., **4** → **5**, **6**; eq 2).[18] However, this method has several problems. First, α-iodoalkylstannanes other than (iodomethyl)trialkylstannanes and (1-iodoethyl)trialkylstannanes are not readily available.[24] Second, elimination is often a problem. Finally, the optically active (1-iodoethyl)trialkylstannanes are not available.[25] Despite these deficiencies, this method was useful for the preparation of a variety of chiral N-acylated α-aminostannanes, both branched and unbranched (Table I). Alkylation of chiral oxazolidin-2-ones, an imidazolidin-2-one, and an acyclic carbamate provided stannanes **9–24** in moderate to high yield. Alkylation with racemic (1-iodoethyl)trialkylstannanes produced equal amounts of both diastereomers (e.g., **11**), which were separable in each case.

Table I. Chiral *N*-((Trialkylstannyl)alkyl)carbamates and -Ureas Prepared by N-Alkylation with (1-Iodoalkyl)stannanes (Cf, Eq 2)[a]

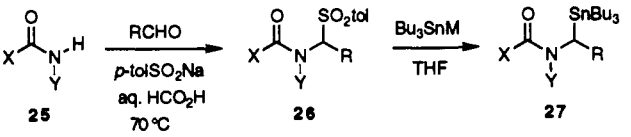




(-) **9** R = Me, R' = H (60)
(-) **10** R = Bu, R' = H (57)
(-) **11** R = Me, R' = Me (78) (1 : 1 α : β)
(-) **12** R = Bu, R' = Me (89) (1 : 1 α : β)
(-) **13** R = Me, R' = H (91)
(-) **14** R = Bu, R' = H (40)
(-) **15** R = Me, R' = Me (83) (1 : 1 α : β)
(-) **16** R = Bu, R' = Me (42) (1 : 1 α : β)
(-) **17** R' = H (78)
(-) **18** R' = Me (33) (1 : 1 α : β)
(±) **19** R' = H (54)
(±) **20** R' = Me (51) (1 : 1 α : β)
(±) **21** (54)
(-) **22** X = CO_2Me (68)
(-) **23** X = CO_2Bn (45)
(-) **24** X = CO_2t-Bu (42)

[a] Isolated yields in parentheses. [b] α and β refer to the disposition of the R' group when the molecule is drawn in the conformation shown.

In order to prepare stannanes with other side chains, it was necessary to examine new routes to these compounds. A successful solution to this problem is shown in eq 3. Condensation of various

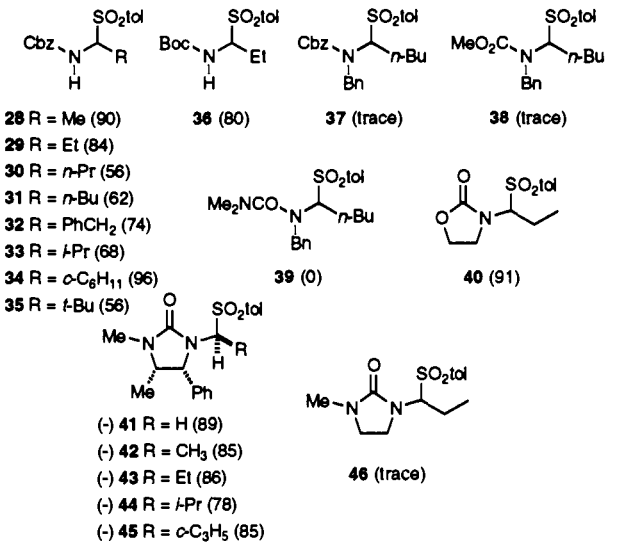


(3)

N-acylated amines **25** with aldehydes and sodium *p*-toluenesulfinate in the presence of formic acid according to the method of Engberts[26] gave crystalline sulfones **26** in good yield. Examples of the reaction of sulfones such as **26** with various nucleophiles have been reported.[27] We found that displacement of these sulfones with tributyltin anions gave the stannanes **27**.[28] This

(16) Kerrick, S. T.; Beak, P. *J. Am. Chem. Soc.* **1991**, *113*, 9708–9710.
(17) Chong, J. M.; Park, S. B. *J. Org. Chem.* **1992**, *57*, 2220–2222.
(18) Pearson, W. H.; Lindbeck, A. C. *J. Org. Chem.* **1989**, *54*, 5651–5654.
(19) Tin–lithium exchange has been used to generate α-*amino* carbanions: (a) Peterson, D. J. *J. Organomet. Chem.* **1970**, *21*, 63. (b) Peterson, D. J. *J. Organomet. Chem.* **1974**, *66*, 209. (c) Peterson, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 159. (d) Pereyre, 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. (e) Peyeyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987. (f) Elissondo, B.; Verlhac, J.-B.; Quintard, J.-P.; Pereyre, M. *J. Organomet. Chem.* **1988**, *339*, 267–275 and earlier references cited therein.
(20) Sulfur–lithium exchange is also useful for the generation of branched nonconjugated nitrogen-substituted carbanions: (a) Tsunoda, T.; Fujiwara, K.; Yamamoto, Y.; Itô, S. *Tetrahedron Lett.* **1991**, *32*, 1975–1978. (b) See also: Broka, C. A.; Shen, T. *J. Am. Chem. Soc.* **1989**, *111*, 2981–2984. (c) Tellurium–lithium exchange: Hiiro, T.; Atarashi, Y.; Kambe, N.; Fujiwara, S.-I.; Ogawa, A.; Ryu, I.; Sonoda, N. *Organometallics* **1990**, *9*, 1355–1357.
(21) For a novel method for the preparation of branched, nonconjugated nitrogen-substituted organosamarium anions, see: Murakami, M.; Hayashi, M.; Ito, Y. *J. Org. Chem.* **1992**, *57*, 793–794.
(22) For the use of carbamates in the formation of dipole-stabilized carbanions, see refs 5a, 10a, and: (a) Seebach, D.; Hassel, T. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 274. (b) Armande, J. C.; Pandit, U. K. *Tetrahedron Lett.* **1977**, 897. (c) Macdonald, T. L.; Narayanan, B. A. *J. Chem. Res. Synop.* **1983**, *48*, 1129. (d) Macdonald, T. L. *J. Org. Chem.* **1980**, *45*, 193. (e) Comins, D. L.; Weglarz, M. A. *J. Org. Chem.* **1988**, *52*, 4437. (f) Comins, D. L.; LaMungon, P. H. *Tetrahedron Lett.* **1989**, *30*, 5053–5056. (g) Beak, P.; Lee, W. K. *Tetrahedron Lett.* **1989**, *30*, 1197–1200. (h) For the transmetalation of stannanes in the presence of a more remote carbamate substituent, see: Zidani, A.; Vaultier, M. *Tetrahedron Lett.* **1986**, *27*, 857–860.
(23) For the use of ureas in the formation of dipole-stabilized carbanions, see ref 4 and: (a) Hassel, T.; Seebach, D. *Helv. Chim. Acta* **1978**, *61*, 2237. (b) Hassel, T.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 399.
(24) (a) Seyferth, D.; Andrews, S. B. *J. Organomet. Chem.* **1971**, *30*, 151–166. (b) Seyferth, D.; Andrews, S. B.; Lambert, R. L. *J. Organomet. Chem.* **1972**, *37*, 69–76.
(25) For a solution to this problem using optically active (1-hydroxyalkyl)-stannanes in a Mitsunobu reaction with carbamates, see ref 17.
(26) (a) Engberts, J. B. F. N.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 942–950. (b) Engberts, J. B. F. N.; Olijnsma, T.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 1211–1222.
(27) (a) Brown, D. S.; Hansson, T.; Ley, S. V. *Synlett* **1990**, 48–49. (b) Morton, J.; Rahim, A.; Walker, E. R. H. *Tetrahedron Lett.* **1982**, *23*, 4123–4126. (c) Kobayashi, T.; Ishida, N.; Hiraoka, T. *J. Chem. Soc., Chem. Commun.* **1980**, 736. (d) Olijnsma, T.; Engberts, J. B. F. N.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 1281–1287.
(28) While this work was in progress, a similar method was used by Quayle to prepare 4-(tributylstannyl)azetidin-2-ones: (a) MacLeod, C.; Quayle, P.; Davies, G. M. *Tetrahedron Lett.* **1990**, *31*, 4927–4930. These stannanes were also transmetalated. For a related synthesis of 4-(tributylstannyl)azetidin-2-ones based on the displacement of 4-acetoxyazetidinones with tin anions, see: (b) Nativi, C.; Ricci, A.; Taddei, M. *Tetrahedron Lett.* **1990**, *31*, 2637–2640.

Table II. *N*-((*p*-Tolylsulfonyl)alkyl)carbamates and -Ureas Prepared by N-Sulfonylalkylation of Carbamates and Ureas (e.g., **25** → **26**; eq 3)[a]



[a] Isolated yields in parentheses.

route is similar in concept to existing methods for the preparation of α-aminostannanes from iminium ions or their precursors.[19]

Table II shows examples of sulfones prepared by the sulfonylalkylation reaction. For acyclic systems, carbamates bearing no N-substituent were excellent partners in the reaction, producing sulfones **28–36** in good yield. These reactions are simple to run, producing analytically pure products after simply filtering the reaction mixture to afford the crystalline sulfones. Branched aldehydes were successful in the condensation reaction, even pivalaldehyde. However, cyclohexanone, cinnamaldehyde, furfural, and benzaldehyde failed to produce the desired sulfones, consistent with observations by Engberts.[26] Carbamates or ureas bearing an N-alkyl group did not produce significant quantities of the sulfones **37–39**. In contrast, related cyclic systems were often successful in the reaction. Oxazolidin-2-one **40** and the imidazolidin-2-ones **41–45** were prepared in high yield, despite the presence of an N-alkyl substituent. The imidazolidin-2-one **46** could not be prepared by this method. The product was detected in considerable quantities by ^{1}H NMR analysis, but since crystallization did not ensue, it was not possible to isolate the product in pure form. Chromatography of these sulfones led to decomposition. Crystallization from the reaction mixture appears to be a necessity for a successful sulfonylalkylation reaction.

The *N*-[1-(*p*-tolylsulfonyl)alkyl]imidazolidin-2-ones **41–45** were formed as single diastereomers. The stereochemistry of **42** was assigned by X-ray crystallography (Figure 1). The stereochemical assignments of **41**, **43**, **44**, and **45** were made by analogy to **42**. The conformation of **42** in the crystal structure is interesting, since the tolyl substituent is oriented above the plane of the imidazole ring. While this may be due to forces in the crystal, the same conformation was found to be the lowest energy using molecular mechanics calculations.[29] A possible explanation is a favorable alignment of the N1–Cα and S(O)(O) dipoles.

The stereochemistry of the sulfonylalkylation reaction may be rationalized by consideration of the two possible iminium ions **48**-(*E*) and **48**-(*Z*) that may be formed from the imidazolidinone **47** (Scheme I). The *Z*-isomer should be disfavored due to 1,3-allylic strain.[30,31] Attack of *p*-toluenesulfinic acid from least hindered β-face of **48**-(*E*) would produce the observed sulfone **49**. Indeed, molecular mechanics calculations[29] found **48**-(*Z*)

(29) Lipton, M.; Still, W. C. *J. Comput. Chem.* **1988**, *9*, 343–355.
(30) Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841–1860.

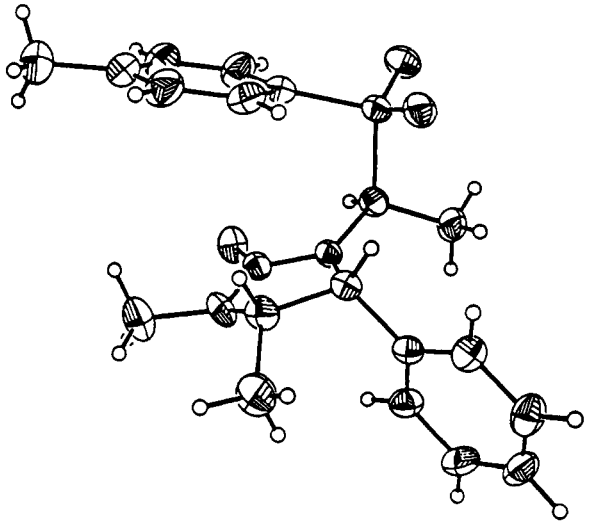
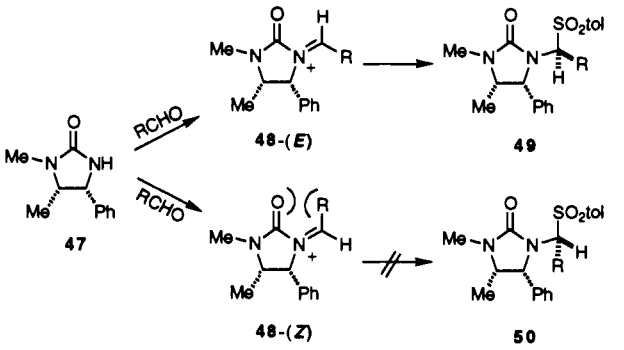
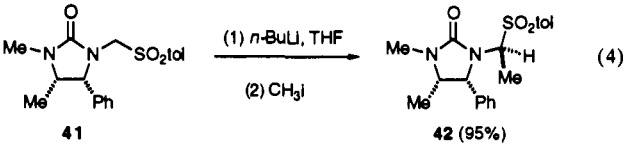


Figure 1. X-ray crystal structure of sulfone **42**.

Scheme I



(R = Et) to be 1.6 kcal/mol higher in energy than **48**-(*E*). It is also possible that the addition reaction is reversible and that diastereomer **49** is simply more stable than **50**. Molecular mechanics calculations on **49** and **50** (R = CH_3) indicated that **49** was more stable, but only by 0.5 kcal/mol, indicating that some of **50** should have been produced. All attempts to prepare the other diastereomer of sulfones **49** were unsuccessful, thus preventing studies that might prove or disprove the equilibration hypothesis. For example, attempted epimerization of these sulfones with a variety of bases led to recovery of the starting material. We also attempted to synthesize a mixture of sulfone diastereomers by deprotonation of the unsubstituted sulfone **41** and quenching with electrophiles. An example is shown in eq 4, where quenching with methyl iodide afforded **42** as a single diastereomer. While this experiment did not provide us with a sample of the other diastereomer, it does illustrate another potentially useful route to these sulfones.

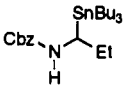
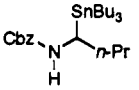
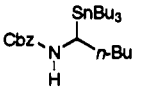
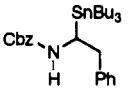
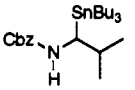
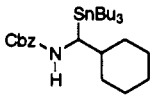
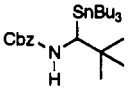
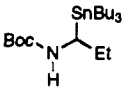
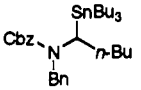
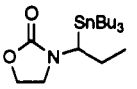
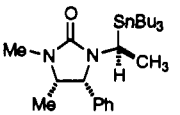
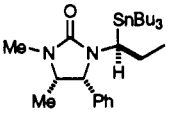
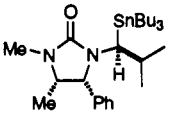
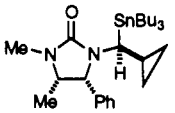


(4)

With the sulfones in hand, their use as electrophiles in reactions with tributyltin anions was examined (Table III). For the acyclic substrates, bis(tri-*n*-butylstannyl)zinc was the best reagent for

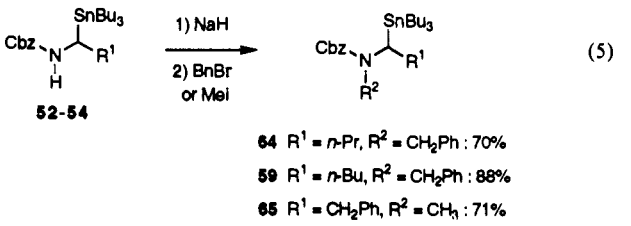
(31) This rationale has been used to explain other stereoselective reactions of iminium ions. For example, see: (a) Hart, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 397–398. (b) Hart, D. J.; Kanai, K. *J. Org. Chem.* **1982**, *47*, 1555–1560. (c) Hart, D. J.; Kanai, K. *J. Am. Chem. Soc.* **1983**, *105*, 1255–1263. (d) Polniaszek, R. P.; McKee, J. A. *Tetrahedron Lett.* **1987**, *28*, 4511–4514. (e) Polniaszek, R. P.; Kaufman, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 4859–4863. (f) Polniaszek, R. P.; Kaufman, C. R. *Tetrahedron Lett.* **1990**, *31*, 797–800.

Table III. *N*-((Tri-*n*-butylstannyl)alkyl)carbamates and -Ureas Prepared by Substitution of Sulfones (e.g., **26** → **27**; eq 3)

Sulfone	Reagent	Product	(% yield)
29	$(Bu_3Sn)_2Zn$		**51** (85)
29	$Bu_3SnMgCl$		**51** (32)
30	$(Bu_3Sn)_2Zn$		**52** (60)
30	$Bu_3SnMgCl$		**52** (31)
30	$Bu_3SnZnBr$		**52** (<10)[a]
31	$(Bu_3Sn)_2Zn$		**53** (63)
31	$Bu_3SnMgCl$		**53** (10)
31	Bu_3SnLi		**53** (45)
32	$(Bu_3Sn)_2Zn$		**54** (75)
32	$Bu_3SnMgCl$		**54** (28)
33	$(Bu_3Sn)_2Zn$		**55** (64)
33	$Bu_3SnMgCl$		**55** (29)
33	$Bu_3SnZnBr$		**55** (<10)
34	$(Bu_3Sn)_2Zn$		**56** (64)
34	$Bu_3SnMgCl$		**56** (30)
35	$(Bu_3Sn)_2Zn$		**57** (7)[b]
35	Bu_3SnLi		**57** (34)
36	$(Bu_3Sn)_2Zn$		**58** (<10)
36	$Bu_3SnMgCl$		**58** (<10)
36	Bu_3SnLi		**58** (<10)
37	$Bu_3SnMgCl$		**59** (0)[c]
40	$(Bu_3Sn)_2Zn$		**60** (0)[d]
40	Bu_3SnLi		**60** (0)[d]
42	Bu_3SnLi		**18β** (59)
43	Bu_3SnLi		**61** (76)
43	$(Bu_3Sn)_2Zn$		**61** (27)
43	$Bu_3SnMgCl$		**61** (<10)
43	$Bu_3SnZnBr$		**61** (<10)
43	$Bu_3SnLiCuCN$		**61** (<5)[e]
43	$Bu_3SnCuCN_2ThLi_2$		**61** (<10)[e]
44	Bu_3SnLi		**62** (65)
45	Bu_3SnLi		**63** (17)[f]

[a] Plus 78% of the reduction product *N*-(carbobenzyloxy)-*n*-butylamine. [b] Plus 78% of the reduction product *N*-(carbobenzyloxy)neopentylamine. [c] In THF, no reaction was observed. In ether, the major product was reduction to *N*-benzyl-*N*-(carbobenzyloxy)-*n*-pentylamine. [d] Starting material was recovered. [e] Plus reduction and elimination products. [f] Plus ring-opened product. See eq 7.

the displacement, affording stannanes **51–56** in good yield. The magnesium and lithium reagents were less effective, except in the displacement of the pivalaldehyde-derived sulfone **35**, where (tri-*n*-butylstannyl)lithium was preferred, producing **57** in modest yield. In several cases, a reductive desulfonylation was observed (see Table III, footnotes a–c, e). Two equivalents of the tin anions were necessary for the best yields, which may indicate an elimination–addition mechanism proceeding through an *N*-acylimine. An alternative radical mechanism is also possible (vide infra). To our surprise, changing the protecting group from a carbobenzyloxy group to a *tert*-butoxycarbonyl group provided the stannane **58** in only trace amounts. Displacement of N-alkyl-substituted carbamates was also difficult, as evidenced by the attempted synthesis of **59** from **37**. However, these compounds could be prepared in high yield by N-alkylation of the unsubstituted stannanes (eq 5). Displacement of the *N*-(sulfonylalkyl)-



(5)

oxazolidinone **40** was also unsuccessful. Starting material was recovered in high yield, even after extended treatment with various tin anions. In contrast, the *N*-(sulfonylalkyl)imidazolidinones **42–45** were successful partners in the displacement, affording *single diastereomers* of the stannanes **18β** and **61–63**. (Tri-*n*-butylstannyl)lithium was the reagent of choice in these cases. Again, 2 equiv of the anion gave the best yields, even though an elimination–addition mechanism is not possible in these systems. The difference in reactivity between the oxazolidinone and imidazolidinone systems is surprising, and we do not have an explanation for this observation at this time.

In order to speculate on the origin of the high stereoselectivity of the displacement of the sulfones in the imidazolidinone series, it was first necessary to determine the stereochemistry of these compounds. Fortunately, stannane **61** was crystalline, and its structure was determined by X-ray crystallography (Figure 2). *It was found that the displacement had occurred with retention of configuration.* The stereochemistry of the other stannyl imidazolidinones was assigned by analogy with **61**.

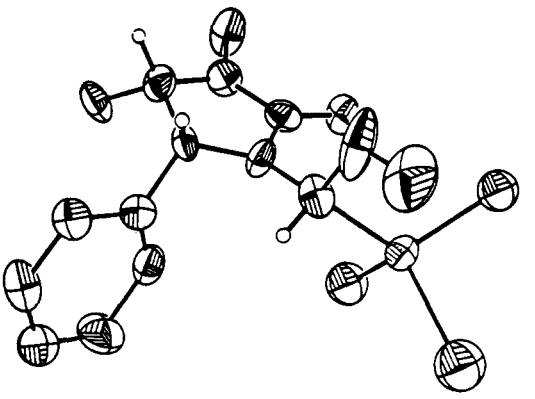
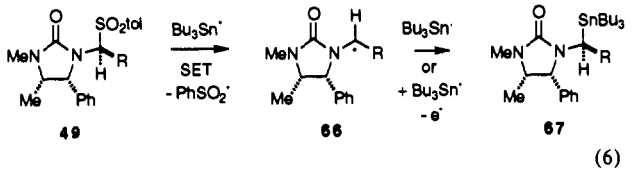


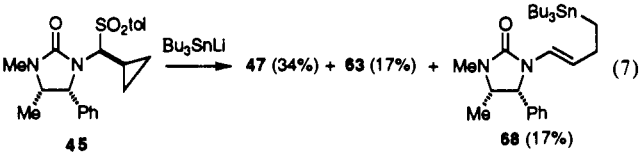
Figure 2. X-ray crystal structure of stannane **61**. *n*-Butyl groups omitted for clarity.

The observation of retention of configuration rules out a simple S_N2 mechanism. The two most likely remaining mechanisms are (1) ionization of the sulfinate group to provide the iminium ion (e.g. **48**), which is captured by the tin anion with high diastereofacial selectivity (i.e., an S_N1 reaction), and (2) a single-electron-transfer mechanism, proceeding through the nitrogen-substituted radical **66**, which reacts diastereoselectively to produce the stannane **67** (eq 6). We favor the latter pathway for the following reasons. First, it is unlikely that an S_N1 process involving a sulfinate leaving group will occur at a reasonable rate at −78 °C in THF. Second, the observation of reductive desulfonylation



49 66 67 (6)

in some cases in Table III is consistent with abstraction of a hydrogen atom from the solvent by an intermediate radical. Third, the products from the displacement of the cyclopropyl-substituted sulfone **45** with (tributylstannyl)lithium are consistent with a radical mechanism (eq 7). The products were the heterocycle



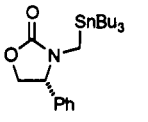
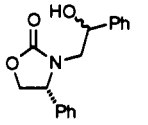
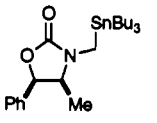
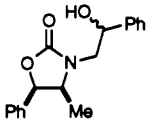
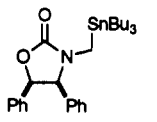
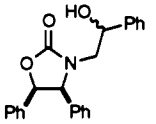
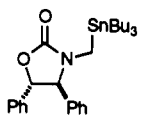
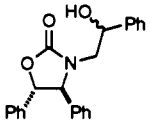
45 68 (17%) (7)

47, the expected cyclopropyl stannane **63**, and the ring-opened homoallylic stannane **68**. The presence of **68** is evidence for a cyclopropylcarbinyl radical intermediate (e.g. **66**, R = *c*-C_3H_7).[32] While an iminium ion intermediate (e.g. **48**, R = *c*-C_3H_7) could also undergo cyclopropylcarbinyl cation ring opening, it is unlikely under these conditions. For example, the cyclopropyl sulfone **45** was prepared in good yield under aqueous acidic conditions by a reaction which presumably involves the iminium ion **48**, and no ring-opened products were observed. The presence of **47** in the stannyl anion reaction may be a result of partial hydrolysis of **68** upon workup or chromatography. The high stereoselectivity of the radical reaction is very significant. The radical **66** is expected to be relatively planar and should exist mainly in the conformation shown to avoid excessive allylic strain while enjoying a favorable electronic interaction with the urea π-system. Reaction from the least hindered β-face then proceeds stereoselectively. We are currently studying the use of these chiral nitrogen-substituted radicals in other applications.

Transmetalation of Chiral N-Acylated α-Aminostannanes. With the chiral stannanes in hand, we then studied their transmetalation and reaction with electrophiles. While the main thrust of this research was to investigate the configurational stability of nitrogen-substituted carbanions, the unbranched stannanes **10**, **14**, **19**, and **21** were also examined to see if a chiral $NH_2CH_2(-)$ synthon could be developed that would provide stereocontrol in reactions with aldehydes. Transmetalation and reaction with benzaldehyde produced the adducts **69–72** in moderate to good yield, but with low stereoselectivity (Table IV). In principle, these adducts could be separated and deprotected[18] to provide optically pure amino alcohols, but this was not deemed worthwhile due to the low stereoselectivity. While the intermediate organolithium species may have a defined five-membered-ring chelate structure, the aldehyde may approach the C–Li bond along a variety of trajectories, thus avoiding interactions with the remote chiral center that would be necessary for stereoselectivity.

The transmetalation of *branched* chiral stannanes with *n*-BuLi at –78 °C in THF and quenching with various electrophiles led to the products shown in Table V. Quenching the anion derived from stannane **18β** with Bu_3SnCl regenerated **18β** exclusively. Thus, the transmetalation and quenching of **18β** had occurred with complete retention of stereochemistry. The presence of TMEDA did not affect this stereoselectivity, although the yield was slightly higher. To prove that the anion was formed and that

Table IV. Transmetalation of Unbranched Chiral Stannanes and Reaction with Benzaldehyde[a]

Stannane	Products	Yield (%)	Ratio[b]
 (-)-**10**	 **69**	50	1.5 : 1
 (-)-**14**	 **70**	80	1.1 : 1
 (±)-**19**	 **71**	60	1.3 : 1
 (±)-**21**	 **72**	41	1.3 : 1

[a] Stannane treated with *n*-BuLi in THF at –78 °C and then quenched with PhCHO. [b] Not separated. Stereochemistry not determined.

the isolation of **18β** was not just the result of incomplete transmetalation, the reaction was run under identical conditions except that the anion was quenched with DCl/D_2O. Complete transmetalation was observed, and a single stereoisomeric product was isolated, which was assigned as **73** by analogy with the formation of **18β** with complete retention of configuration.

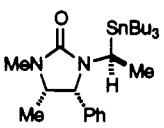
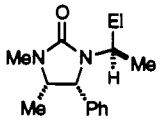
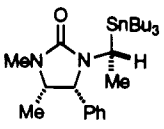
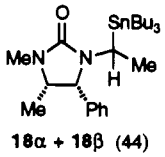
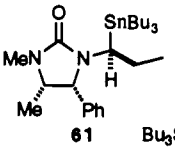
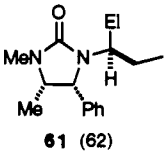
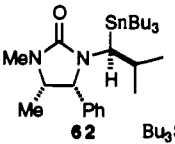
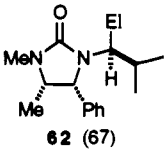
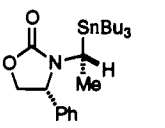
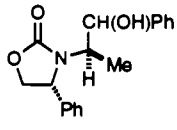
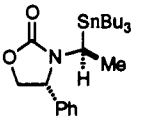
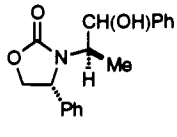
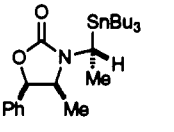
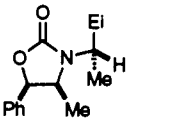
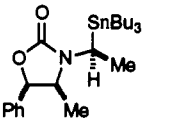
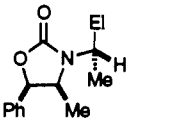
The observation of retention of configuration in the transmetalation and quenching of **18β** does not provide evidence for the configurational stability of the carbanion. However, transmetalation of the epimeric stannane **18α** does provide such information. Quenching the anion derived from **18α** with Bu_3SnCl after 5 min at –78 °C gave a 2.4:1 mixture of **18α** and **18β**, showing that some retention of configuration had occurred. Again, control experiments showed that transmetalation was complete under these conditions. Table VI summarizes the stereochemical outcome of the transmetalation of **18α** and **18β** as a function of time at –78 °C before quenching with Bu_3SnCl. The stereoselectivity of the reaction of the anion derived from **18β** was found to be independent of time, whereas the selectivity of the reaction of the anion derived from **18α** varied from mostly retention after 5 min to mostly inversion after 45 min at –78 °C. Presumably, complete inversion would be observed if the anion were kept for a sufficiently long time before quenching, but this was not possible in practice, since anion decomposition limited the time scale of these experiments.

An explanation for these observation is shown in Figure 3. Transmetalation of the stannane with relative configuration **83** proceeds with retention of configuration[33] to give **85**. This

(32) Use of cyclopropylcarbinyl radicals as a mechanistic probe: (a) Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734–1736. (b) Newcomb, M. In *Advances in Detailed Reaction Mechanisms*; Coxon, J. M., Ed.; JAI: Greenwich, CT, 1991; Vol. 1. For a leading reference on the generation and use of α-acylamino radicals, see: (c) Choi, J.-K.; Ha, D.-C.; Hart, D. J.; Lee, C.-S.; Ramesh, S.; Wu, S. *J. Org. Chem.* **1989**, *54*, 279–290.

(33) Retention of stereochemistry in tin–lithium exchange reactions is well-known for the generation of α-heterosubstituted organometallics. See ref 19e and the following representative examples: (a) Still, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 1201–1202. (b) Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* **1987**, *109*, 4930. (c) Sawyer, J. S.; Kucerovy, A.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 842–853. (d) McDougal, P. G.; Condon, B. D.; Laffosse, M. D.; Lauro, A. M.; VanDerveer, D. *Tetrahedron Lett.* **1988**, *29*, 2547–2550. (e) Marshall, J. A.; Gung, W. Y. *Tetrahedron Lett.* **1988**, *29*, 1657. (f) Matteson, D. S.; Tripathy, P. B.; Sarkar, A.; Sadhu, K. M. *J. Am. Chem. Soc.* **1989**, *111*, 4399–4402. (g) Chan, P. C.-M.; Chong, J. M. *Tetrahedron Lett.* **1990**, *31*, 1985–1988 and earlier references cited therein.

Table V. Transmetalation of Branched Chiral Stannanes and Reaction with Electrophiles[a]

Stannane	Electrophile	Product (% yield)[b]	El	% α / % β [b,c]
				
18β	Bu_3SnCl	**18β** (46)	$SnBu_3$	0 / 100
18β	Bu_3SnCl [d]	**18β** (55)	$SnBu_3$	0 / 100
18β	DCl/D_2O	**73** (63)	D	0 / 100
				
18α	Bu_3SnCl	**18α** + **18β** (44)	–	71 / 29[e]
18α	Bu_3SnCl [d]	**18β** (48)	–	0 / 100[e]
				
61	Bu_3SnCl	**61** (62)	$SnBu_3$	0 / 100
61	DCl/D_2O	**74** (72)	D	0 / 100
61	DCl/D_2O	**74** (85)[f]	D	0 / 100
61	cyclohexanone	**75** (78)	$C(OH)(CH_2)_5$	0 / 100
61	PhCHO	**76** (88)	CH(OH)Ph	0 / 100[g]
61	*i*-PrCHO	**77** (91)	CH(OH)*i*-Pr	0 / 100[h]
61	$ClCO_2Et$	**78α** + **78β** (83)	CO_2Et	8 / 92
				
62	Bu_3SnCl	**62** (67)	$SnBu_3$	0 / 100
62	D_2O	**79** (56)	D	0 / 100
				
12α	PhCHO	**80** (76)	-	0 / 100[i]
				
12β	PhCHO	**80** (69)	-	0 / 100[i]
				
16α	Bu_3SnCl	**16α** (76)	$SnBu_3$	100 / 0
16α	PhCHO	**81** (82)	CH(OH)Ph	100 / 0[j]
16α	cyclohexanone	**82** (32)	$C(OH)(CH_2)_5$	100 / 0
				
16β	Bu_3SnCl	**16α** (52)	$SnBu_3$	100 / 0
16β	PhCHO	**81** (50)	CH(OH)Ph	100 / 0[j]
16β	cyclohexanone	**82** (39)	$C(OH)(CH_2)_5$	100 / 0

[a] Stannane treated with *n*-BuLi in THF at −78 °C, and then quenched with the electrophile shown. [b] α and β refer to the orientation of the original alkyl chain in the representation as shown. [c] A value of 0/100 indicates that only one stereoisomer was detected by 300-MHz ^1H NMR. [d] TMEDA added before transmetalation. [e] Ratio obtained by quenching anion after 5 min at −78 °C. See Figure 3 for ratios at other times. [f] Run at −95 °C, whereas other entries were run at −78 °C. [g] The β isomer was a 1.7:1 mixture of diastereomers at the carbinol center; the stereochemistry was not assigned. [h] The β isomer was a 1.5:1 mixture of diastereomers at the carbinol center; the stereochemistry was not assigned. [i] The β isomer was a 1:1 mixture of diastereomers at the carbinol center; the stereochemistry was not assigned. [j] The α isomer was a 1:1 mixture of diastereomers at the carbinol center; the stereochemistry was not assigned.

Table VI. Results of Tin-Lithium Exchange on Stannanes **18α** and **18β** after Quenching with Bu_3SnCl after Varying Lengths of Time

starting material	time at −78 °C before quench with Bu_3SnCl (min)	ratio of **18α**:**18β** recovered
18α	5	2.4:1
18α	15	1.2:1
18α	30	1:2.4
18α	45	1:6.7
18β	5	1:59
18β	15	**18β** only
18β	30	**18β** only
18β	45	**18β** only

diastereomer is the most stable one, and quenching with electrophiles occurs with retention of configuration to produce a single diastereomer of the observed products. Transmetalation of the opposite diastereomeric stannane **84** also proceeds with retention of configuration to give **86**, but steric problems (as indicated) destabilize this diastereomer with respect to **85**.[34] Therefore, the anion slowly epimerizes to produce the more stable diastereomer **85**. This epimerization is sufficiently slow to observe varying ratios of products as a function of time. *These studies show for the first time that acyclic, nonconjugated nitrogen-substituted carbanions have observable configurational stability at −78 °C.* These results also lead to the conclusion that, even in the absence of a stereochemical bias (i.e., the chiral centers in the heterocyclic ring), configurational stability should be observable. That is, since we can observe configurational stability in a system that is biased *against* this phenomenon (e.g., the anion from **18α** or the anion **86** in general), that configurational stability may be even greater in a system which lacks this bias (vide infra[17]).

The effect of additives was also examined. When the transmetalation of **18α** was carried out with TMEDA present, no evidence for configurational stability was observed. Only **18β** was produced after quenching with Bu_3SnCl after 5 min at −78 °C, in contrast to the results in THF. The ligating ability of TMEDA may disrupt the chelate **86**, allowing a more rapid equilibration to **85**.[35]

(34) Semiempirical MNDO calculations[a] were carried out with MOPAC[b] on diethyl ether-solvated diastereomeric anions **85** and **86** derived from **18β** and **18α**, respectively, and showed that **85** was more stable by 1.44 kcal/mol. (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907. (b) Stewart, J. J. P. *Quantum Chemistry Program Exchange* No. 455, Version 6.0. For other studies on the theoretical and experimental structures of similar anions, see ref 5a,b and: (c) Rondan, N. G.; Houk, K. N.; Beak, P.; Zajdel, W. J.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1981**, *46*, 4108–4110. (d) Bach, R. D.; Braden, M. L.; Wolber, G. J. *J. Org. Chem.* **1983**, *48*, 1509–1514. (e) Bartolotti, L. J.; Gawley, R. E. *J. Org. Chem.* **1989**, *54*, 2980–2982. (f) Seebach, D.; Hansen, J.; Seiler, P.; Gromek, J. M. *J. Organomet. Chem.* **1985**, *285*, 1–13.

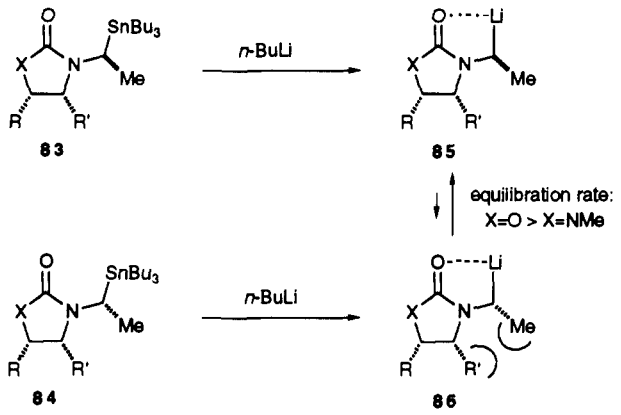
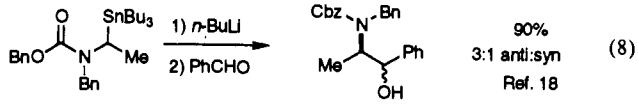
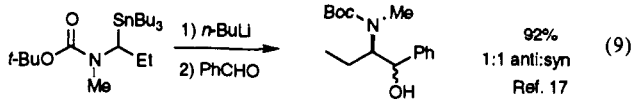


Figure 3. Proposed equilibration of anions.

The use of carbonyl compounds as electrophiles led to the efficient and stereoselective formation of β-amino alcohol derivatives **75–77** and an α-amino ester derivative **78**. The stereochemistry of these compounds is based on the assumption that the carbonyl addition occurred with retention of configuration at the carbanionic center, as for the other electrophiles. When aldehydes were used, two of the four possible stereoisomers were formed, presumably with high stereoselectivity at the carbanionic center coupled with modest facial selectivity with respect to the aldehyde. Previous observations on the addition of nitrogen-substituted carbanions to aldehydes show that the syn/anti selectivities vary widely.[2,3,5-7,10-12,17,18] Examples are shown in eqs 8 and 9. The formation of **78** may provide a new method for the synthesis of optically pure α-amino acids.[17]



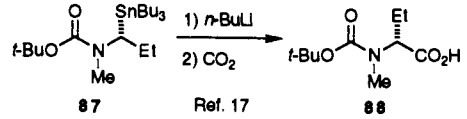
(8)



(9)

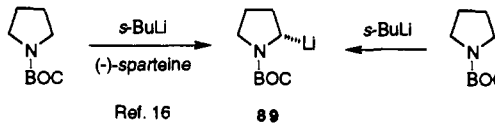
Oxazolidinones **12** and **16** were also useful in achieving high levels of stereoselection (Table V). However, no evidence for the configurational stability of the organolithium species derived from **12α** or **16β** was obtained, even when these were quenched after 5 min at −78 °C. All of the oxazolidinone transmetalations produced products derived from the most stable organolithium diastereomer. This is in sharp contrast to the transmetalation of the imidazolidinone **18α**. Evidently, equilibration of the "crowded" oxazolidinones **86** (Figure 3, X = O) is faster than that of the imidazolidinones (X = NCH_3), perhaps due to the poorer lithium-ligating ability of a carbamate carbonyl oxygen versus a urea carbonyl oxygen. A looser chelate would be expected to allow easier inversion. The stereochemical outcome of these reactions is also consistent with recent work by Gawley, who studied acyclic benzylic anions derived from the deprotonation of chiral *N*-benzyloxazolidinones.[5a]

Since the preliminary publication of these results,[13] Chong has reported similar studies which examine the configurational stability of carbamate-substituted carbanions such as those in our original work,[18] except in optically active form.[17] For example, transmetalation of optically active **87** and quenching with CO_2 gave **88**, whose enantiomeric excess depended on the time and temperature at which the anion was kept before quenching (eq 10). These results are consistent with our observations on the



(10)

stannyl imidazolidinones described above. Chong also found that the configurational stability of these anions was diminished by the presence of a strong chelating agent, HMPA. In addition, Beak recently reported the formation of cyclic, nonracemic, nonconjugated carbamate-substituted carbanions **89** and found that the configurational stability of these anions depended dramatically on the presence or absence of diamine ligands (eq 11).[16]



(11)

Conclusion

Data on the configurational stability of nitrogen-substituted organolithium compounds was obtained in systems were the anion center was neither conjugated nor subject to the conformational restraints of being in a ring. Moderate conformational stability was observed at low temperatures in a system where steric hindrance actually favored epimerization (c.f. **86**, X = NCH_3). The presence of a coordinating ligand such as TMEDA promoted rapid equilibration even at low temperatures, resulting in the exclusive formation of the most stable diastereomeric species (e.g. **85**). Slight variation in the structure of the N-acyl group in these systems had a dramatic effect on configurational stability. For example, organolithiums derived from the transmetalation of oxazolidinones **83/84** (X = O) epimerized to the more stable diastereomer too quickly to observe, whereas those derived from imidazolidinones **83/84** (X = NCH_3) epimerized at a much slower (and observable) rate. The observation of configurational stability in anions such as **86** (X = NCH_3), where steric congestion favors epimerization, allows the prediction that systems with no such bias should have even higher configurational stability. Recent studies by Chong support this conclusion.[17]

From a synthetic standpoint, the equilibration of diastereomeric nitrogen-substituted organolithiums to a single isomer is useful, since the resultant single species reacts stereoselectively with a variety of electrophiles, producing optically pure derivatives of β-amino alcohols and α-amino acids.[36]

Another significant finding from this work is the development of a new method for the synthesis of N-acylated α-aminostannanes. The displacement of Engberts' sulfonylalkylated carbamates and ureas with tin nucleophiles is a convenient route to these compounds. The formation of a single diastereomer of the stannanes **18β**, **61**, **62**, and **63** in the displacement of the sulfones **42–45** is surprising and may reflect the generation of a chiral nitrogen-substituted radical which reacts in a diastereofacially selective manner.

The observation of moderate configurational stability in nitrogen-substituted organolithium compounds bearing an N-acyl group is significant but does not provide an answer to the question of the configurational stability of simple nonconjugated, acyclic α-*amino* anions. Studies on the latter systems are now underway in our laboratories.

(35) The role of TMEDA in the structure of anions is not straightforward: Collum, D. B. *Acc. Chem. Res.*, in press. For example, Reich has recently found that TMEDA may increase the configurational stability of carbanions (H. J. Reich, personal communication). Similar observations have been made by Beak.[16]

(36) The synthetic utility of these anions will depend on the ease of deprotection of the products. While oxazolidinones related to **71** may be easily cleaved to amino alcohols by hydrogenolysis,[18] deprotection of imidazolidinones such as those shown in Table V has proved resistant to hydrogenolysis and hydrolysis under a variety of conditions. More practical systems are currently being investigated.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry nitrogen in flame-dried glassware equipped with a tightly fitted rubber septum, with the exception of tin–lithium transmetalation reactions, which were carried out under an atmosphere of dry argon. RT refers to room temperature. Unless otherwise specified, solvents were freshly distilled prior to use. Tetrahydrofuran (THF) and ether were distilled from sodium and benzophenone. Benzene, toluene, hexane, pyridine, dimethyl sulfoxide (DMSO), dichloromethane, chloroform, diisopropylamine, triethylamine, and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were distilled from powdered calcium hydride. Dimethylformamide (DMF) was distilled from barium oxide at reduced pressure. Commercial *n*-BuLi and methyllithium were titrated with diphenylacetic acid prior to use. Tributyltin hydride was made according to the method of Hayashi.[37] Sodium *p*-toluenesulfinate dihydrate was prepared according to the method of Whitmore.[38] (Iodomethyl)-tri-*n*-butylstannane was prepared according to the method of Seitz.[29] (Iodomethyl)trimethylstannane, (1-iodoethyl)trimethylstannane, and (1-iodoethyl)tri-*n*-butylstannane were prepared according to the method of Seyferth.[24] Zinc bromide was prepared according to the method of Ley.[27a] All other reagents were obtained commercially and distilled or recrystallized prior to use. Unless otherwise noted, chromatography was performed according to the procedure described by Still using 230–400 mesh silica gel.[40] Analytical HPLC was performed on Rainin Microsorb silica gel or C18 columns. Preparative HPLC was carried out with a Rainin Dynamax silica gel column. For the ^{1}H NMR spectra of tin compounds, the average of the ^{117}Sn and ^{119}Sn satellite couplings is reported where measurable. Mass spectra were obtained via electron impact at 70 eV unless otherwise noted. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI; by Galbraith Laboratories Inc., Knoxville, TN; or by the microanalytical laboratory run by the Department of Chemistry at the University of Michigan.

General Procedure for Stannylalkylation of Oxazolidinones, Imidazolidinones, and Carbamates: (4*R*,1'*R*)-3-[1-(Tri-*n*-butylstannyl)ethyl]-4-phenyloxazolidin-2-one (12α) and (4*R*,1'*S*)-3-[1-(Tri-*n*-butylstannyl)ethyl]-4-phenyloxazolidin-2-one (12β). Sodium hydride (120 mg of a 60% dispersion in mineral oil, 3.00 mmol) was added in portions at RT to a solution of (*R*)-4-phenyl-2-oxazolidinone[41] (0.40 g, 2.45 mmol) in DMF (12 mL). After 30 min, (1-iodoethyl)tri-*n*-butylstannane[24] (1.35 g, 3.03 mmol) was added in a dropwise fashion. After 4.5 h, the solution was diluted with water (50 mL) and extracted with EtOAc (3 × 40 mL). The combined organic layers were washed with water (5 × 50 mL), dried ($MgSO_4$), and concentrated. Chromatography (5% EtOAc/hexane) gave 1.05 g (89%) of a mixture of the title compounds as a colorless oil. ^{1}H NMR showed the material to be a 1:1 ratio of diastereomers. Rechromatography using the same solvent system allowed collection of pure fractions of each diastereomer. See the text for a discussion of the stereochemical assignment of each diastereomer. **12α**: R_f = 0.26 (10% EtOAc/hexane); $[\alpha]^{23}_D$ −47.0° (*c* 0.64, $CHCl_3$); IR (neat) 2955 (m), 2923 (m), 1740 (s), 1454 (m), 1421 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45–7.33 (m, 5 H), 4.62–4.52 (m, 2 H), 4.16, 4.13 (ABq, J_{AB} = 5.5 Hz, 1 H), 2.78 (q, *J* = 7.5 Hz, 1 H), 1.53–1.21 (m, 12 H), 1.17 (d, *J* = 7.5 Hz, 3 H), 0.90–0.76 (m, 15 H); MS (EI, 70 eV) *m/z* (relative intensity) 481 (M^+, 6), 424 (100), 422 (78), 421 (36), 420 (47), 380 (22), 320 (14), 276 (12), 235 (9), 220 (6), 190 (7), 84 (26); HRMS calcd for $C_{23}H_{39}NO_2{}^{120}Sn$ 481.2003, found 481.2001. Anal. Calcd for $C_{23}H_{39}NO_2Sn$: C, 57.52; H, 8.19; N, 2.92. Found: C, 57.59; H, 8.23; N, 2.85. **12β**: R_f = 0.20 (10% EtOAc/hexane); $[\alpha]^{23}_D$ −39.3° (*c* 0.89, $CHCl_3$); IR (neat) 2954 (m), 2920 (m), 1741 (s), 1456 (m), 1420 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45–7.35 (m, 5 H), 4.93 (t, *J* = 8.1 Hz, 1 H), 4.58 (t, *J* = 8.8 Hz, 1 H), 4.07, 4.03 (ABq, J_{AB} = 8.1 Hz, 1 H), 2.57 (q, *J* = 7.2 Hz, 1 H), 1.50–1.17 (m, 12 H), 1.28 (d, *J* = 7.2 Hz, 3 H), 1.00–0.78 (m, 15 H); MS (EI, 70 eV) *m/z* (relative intensity) 481 (M^+, 2), 424 (100), 422 (78), 421 (35), 420 (47), 380 (9), 320 (7), 276 (6), 235 (6), 190 (5); HRMS calcd for $C_{23}H_{39}NO_2{}^{120}Sn$ 481.2003, found 481.2002. Anal. Calcd for $C_{23}H_{39}NO_2Sn$: C, 57.52; H, 8.19; N, 2.92. Found: C, 57.62; H, 8.13; N, 2.81.

(4*S*,5*R*,1'*R*)-3-[1-(Tri-*n*-butylstannyl)ethyl]-4-methyl-5-phenyloxazolidin-2-one (16α) and (4*S*,5*R*,1'*S*)-3-[1-(Tri-*n*-butylstannyl)ethyl]-4-methyl-5-phenyloxazolidin-2-one (16β). Sodium hydride (48.0 mg of a 60% dispersion in mineral oil, 1.20 mmol), (4*S*,5*R*)-4-methyl-5-phenyloxazolidin-2-one[42] (0.18 g, 1.01 mmol), and (1-iodoethyl)tri-*n*-butylstannyl[24] (0.49 g, 1.10 mmol) were stirred for 3.5 h in DMF (5 mL) according to the general procedure. Workup and chromatography (5% EtOAc/hexane) gave 0.23 g (42%) of a mixture of the title compounds as a colorless oil. ^{1}H NMR showed the material to be a 1:1 ratio of diastereomers. Rechromatography using the same solvent system allowed collection of pure fractions of each diastereomer. See the text for a discussion of the stereochemical assignment of each diastereomer. **16α**: R_f = 0.36 (10% EtOAc/hexane); $[\alpha]^{23}_D$ −60.5° (*c* 1.1, $CHCl_3$); IR (neat) 2954 (s), 2361 (s), 1740 (s), 1456 (m), 1425 (m), 1331 (m), 699 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42–7.21 (m, 5 H), 5.49 (d, *J* = 8.4 Hz, 1 H), 4.03 (dq, *J* = 8.4, 6.5 Hz, 1 H), 2.91 (q, *J* = 7.2 Hz, 1 H), 1.63–1.26 (m, 15 H), 1.08–0.86 (m, 15 H), 0.83 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 157.6, 135.6, 128.4, 128.3, 126.2, 78.3, 58.8, 38.4, 29.1, 27.5, 19.5, 16.2, 13.7, 10.3; MS (CI, NH_3) *m/z* (relative intensity) 495 (M + 1, 4), 438 (92), 394 (4), 382 (6), 324 (10), 291 (10), 276 (5), 252 (5), 235 (19), 211 (6), 179 (24), 160 (100), 132 (5), 117 (25), 105 (7), 91 (19); HRMS calcd for $C_{20}H_{32}NO_2{}^{120}Sn$ [(M − C_4H_9)$^+$] 438.1455, found 438.1458. Anal. Calcd for $C_{24}H_{41}NO_2Sn$: C, 58.32; H, 8.36; N, 2.83. Found: C, 58.44; H, 8.57; N, 2.68. **16β**: R_f = 0.24 (10% EtOAc/hexane); $[\alpha]^{23}_D$ −26.4° (*c* 1.3, $CHCl_3$); IR (neat) 2955 (s), 2921 (s), 1738 (s), 1456 (m), 1423 (m), 1332 (w), 699 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.49–7.21 (m, 5 H), 5.51 (d, *J* = 8.4 Hz, 1 H), 4.22 (dq, *J* = 8.4, 6.6 Hz, 1 H), 2.83 (q, *J* = 7.4 Hz, 1 H), 1.61–1.23 (m, 15 H), 1.07–0.82 (m, 15 H), 0.76 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 158.4, 135.7, 128.4, 126.2, 78.2, 54.3, 34.8, 29.2, 27.5, 16.6, 14.6, 13.7, 10.8; MS (CI, NH_3) *m/z* (relative intensity) 495 (M + 1, 2), 438 (100), 394 (3), 382 (4), 324 (7), 291 (6), 269 (4), 252 (4), 235 (12), 211 (5), 179 (15), 160 (77), 132 (4), 117 (20), 105 (6), 91 (15), 84 (25); HRMS calcd for $C_{20}H_{32}NO_2{}^{120}Sn$ [(M − C_4H_9)$^+$] 438.1455, found 438.1457. Anal. Calcd for $C_{24}H_{41}NO_2Sn$: C, 58.32; H, 8.36; N, 2.83. Found: C, 58.51; H, 8.59; N, 2.74.

(4*R*,5*S*,1'*R*)-1-Methyl-3-[1-tri-*n*-butylstannyl)ethyl]-4-phenyl-5-methylimidazolidin-2-one (18α) and (4*R*,5*S*,1'*S*)-1-Methyl-3-[1-(tri-*n*-butylstannyl)ethyl]-4-phenyl-5-methylimidazolidin-2-one (18β). Sodium hydride (0.48 g of a 60% dispersion in mineral oil, 12.0 mmol), (4*R*,5*S*)-1-methyl-4-phenyl-5-methylimidazolidin-2-one (**47**)[43] (1.90 g, 10.0 mmol), and (1-iodoethyl)tri-*n*-butylstannane[24] (4.45 g, 10.0 mmol) were stirred for 2 h in DMF (60 mL) according to the general procedure. Workup and chromatography (2.5% EtOAc/hexane) gave 1.67 g (33%) of a mixture of the title compounds as a thick, colorless oil, R_f = 0.45 (15% EtOAc/hexane). ^{1}H NMR showed the material to be a 1:1 ratio of diastereomers. The two diastereomers were separated by preparative HPLC (5% EtOAc/hexane, silica gel column, flow rate = 12 mL/min) to give **18α** (retention time = 38.4 min) and **18β** (retention time = 46.0 min). **18α**: $[\alpha]^{23}_D$ −21.9° (*c* 0.90, $CHCl_3$); IR (neat) 2955 (s), 1697 (s), 1440 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.42–7.23 (m, 5 H), 4.41 (d, *J* = 8.9 Hz, 1 H), 3.64 (dq, *J* = 8.8, 6.6 Hz, 1 H), 2.78 (q, *J* = 7.4 Hz, 1 H), 2.71 (s, 3 H), 1.58–1.17 (m, 15 H), 0.99–0.78 (m, 15 H), 0.75 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 154.5, 138.3, 128.7, 128.3, 128.2, 66.2, 56.7, 40.1, 29.3, 29.2, 27.6, 19.7, 14.6, 13.7, 10.5. **18β**: $[\alpha]^{23}_D$ −28.5° (*c* 2.4, $CHCl_3$); IR (neat) 2953 (s), 2359 (s), 1694 (s), 1480 (s), 1441 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.39–7.12 (m, 5 H), 4.79 (d, *J* = 8.8 Hz, 1 H), 3.67 (dq, *J* = 8.8, 6.6 Hz, 1 H), 2.75 (s, 3 H), 2.59 (q, *J* = 7.2 Hz, 1 H), 1.60–1.25 (m, 12 H), 1.21 (d, *J* = 7.2 Hz, 3 H), 0.99–0.79 (m, 15 H), 0.72 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 161.7, 136.5, 128.2, 127.9, 61.7, 55.8, 35.2, 29.3, 29.2, 27.6, 16.4, 14.6, 13.7, 11.00; MS (EI, 70 eV) *m/z* (relative intensity) 451 [(M − C_4H_9)$^+$, 41], 309 (8), 217 (100), 174 (11), 160 (11), 148 (9), 117 (12), 105 (12), 91 (8), 84 (11), 56 (7), 49 (17); HRMS calcd for $C_{21}H_{35}N_2O^{120}Sn$ [(M − C_4H_9)$^+$] 451.1771, found 451.1760. Anal. Calcd for $C_{25}H_{44}N_2OSn$: C, 59.19; H, 8.74; N, 5.52. Found: C, 59.04; H, 8.76; N, 5.37. The stereochemistry of **18β** was determined by comparison to an authentic sample (vide infra).

General Procedure for Sulfonylalkylation of Carbamates, Oxazolidinones, and Imidazolidinones: Benzyl *N*-[1-((*p*-Methylphenyl)sulfonyl)-ethyl]carbamate (28). Freshly distilled acetaldehyde (13.2 g, 300 mmol) in methanol (10 mL) was added to a solution of benzyl carbamate (15.1

(37) Hayashi, K.; Iyoda, J.; Shiihara, I. *J. Organomet. Chem.* **1967**, *10*, 81–94.
(38) Whitmore, F. C.; Hamilton, F. H. In *Organic Syntheses*; Gilman, H., Ed.; John Wiley & Sons: New York, 1941; Collect. Vol. 1, pp 492–494.
(39) Seitz, D. E.; Carroll, J. J.; Cartaya, C. P.; Lee, S.-H.; Zapata, A. *Synth. Commun.* **1983**, *13*, 129–134.
(40) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
(41) Pirkle, W. H.; Simmons, K. A. *J. Org. Chem.* **1983**, *48*, 2520–2527.
(42) (a) Evans, D. A.; Mathre, D. J. *J. Org. Chem.* **1985**, *50*, 1830–1835. (b) Fodor, G.; Stefanovsky, J. N.; Kurtev, B. J. *Monatsh. Chem.* **1967**, *98*, 1027–1040.
(43) Close, W. J. *J. Org. Chem.* **1950**, *15*, 1131–1134.

g, 100 mmol) and sodium *p*-toluenesulfinate dihydrate (21.4 g, 100 mmol) in water (100 mL). The pH was adjusted to approximately 2 with 88% formic acid (ca. 20 mL), and the mixture was stirred for 12 h at RT. The resulting white precipitate was filtered and washed sequentially with water and petroleum ether, giving 30.0 g (90%) of **28** as analytically pure white crystals which required no further purification: mp 78.0–80.0 °C; IR ($CHCl_3$) 3426 (w), 1730 (s), 1504 (m), 1317 (s), 1145 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.74 (d, J = 8.2 Hz, 2 H), 7.37–7.06 (m, 7 H), 5.79 (d, J = 10.4 Hz, 1 H), 5.06–4.95 (m, 1 H), 4.95–4.82 (m, 2 H), 2.39 (s, 3 H), 1.58 (d, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 154.6, 144.9, 135.8, 133.4, 129.6, 129.2, 128.4, 128.2, 128.1, 128.0, 127.9, 67.4, 67.1, 21.5, 13.1; MS (CI, NH_3) m/z (relative intensity) 351 [$(M + NH_4)^+$, 95], 334 (M + 1, 2), 221 (2), 195 (100), 189 (6), 178 (32), 174 (54), 169 (9), 156 (2), 134 (43), 125 (4), 108 (8); HRMS calcd for $C_{17}H_{19}NO_4SH$ (M + 1) 334.1113, found 334.1107. Anal. Calcd for $C_{17}H_{19}NO_4S$: C, 61.24; H, 5.74; N, 4.20. Found: C, 60.97; H, 5.47; N, 4.54.

Benzyl *N*-[1-((*p*-Methylphenyl)sulfonyl)propyl]carbamate (29). Propionaldehyde (6.39 g, 110 mmol), methanol (10 mL), benzyl carbamate (15.1 g, 100 mmol), sodium *p*-toluenesulfinate dihydrate (21.4 g, 100 mmol), water (100 mL), and 88% formic acid (ca. 20 mL) were combined according to the general procedure above, except that the mixture was heated at 70 °C for 1 h. After cooling, the white crystals were filtered and washed sequentially with water and petroleum ether to give 29.0 g (84%) of analytically pure **29**: mp 109.0–114.0 °C; R_f = 0.20 (25% EtOAc/hexane); IR ($CHCl_3$) 3424 (m), 1731 (s), 1506 (s), 1315 (s), 1143 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.73 (d, J = 8.2 Hz, 2 H), 7.38–7.10 (m, 7 H), 5.73 (d, J = 10.7 Hz, 1 H), 4.99–4.75 (m, 3 H), 2.39 (s, 3 H), 2.33–2.21 (m, 1 H), 1.85–1.68 (m, 1 H), 1.04 (t, J = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 155.1, 144.8, 135.8, 133.8, 129.6, 129.1, 128.4, 128.1, 127.9, 127.8, 72.7, 67.1, 21.5, 20.2, 9.8; MS (CI, NH_3) m/z (relative intensity) 365 [$(M + NH_4)^+$, 46], 209 (100), 192 (66), 174 (20), 169 (12), 148 (40), 136 (48), 108 (7), 75 (8); HRMS calcd for $C_{18}H_{21}NO_4SNH_4$ [$(M + NH_4)^+$] 365.1535, found 365.1515. Anal. Calcd for $C_{18}H_{21}NO_4S$: C, 62.23; H, 6.09; N, 4.03. Found: C, 61.90; H, 6.09; N, 4.13.

Benzyl *N*-[1-((*p*-Methylphenyl)sulfonyl)butyl]carbamate (30). Butyraldehyde (13.2 g, 74.2 mmol), methanol (7 mL) benzyl carbamate (10.2 g, 67.5 mmol), sodium *p*-toluenesulfinate dihydrate (14.5 g, 67.5 mmol), water (70 mL), and 88% formic acid (ca. 14 mL) were combined according to the general procedure above, except that the mixture was heated at 70 °C for 1 h. After cooling, the white crystals were filtered and washed sequentially with water and petroleum ether to give 20.4 g (56%) of analytically pure **30**: mp 118.0–140.0 °C dec; R_f = 0.16 (15% EtOAc/hexane); IR ($CHCl_3$) 3424 (w), 1730 (s), 1507 (m), 1316 (s), 1143 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.73 (d, J = 8.2 Hz, 2 H), 7.35–7.07 (m, 7 H), 5.52 (d, J = 10.6 Hz, 1 H), 4.94–4.78 (m, 3 H), 2.39 (s, 3 H), 2.25–2.12 (m, 1 H), 1.81–1.67 (m, 1 H), 1.62–1.48 (m, 1 H), 1.47–1.32 (m, 1 H), 0.95 (app t, J = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 154.9, 144.8, 135.8, 133.8, 129.6, 129.1, 128.4, 128.2, 127.9, 71.1, 67.2, 28.5, 21.6, 18.6, 13.3; MS (CI, NH_3) m/z (relative intensity) 379 [$(M + NH_4)^+$, 32], 223 (70), 206 (100), 189 (7), 174 (23), 169 (4), 162 (43), 136 (59), 125 (3), 108 (8), 89 (5); HRMS calcd for $C_{19}H_{23}NO_4SNH_4$ [$(M + NH_4)^+$] 379.1691, found 379.1677. Anal. Calcd for $C_{19}H_{23}NO_4S$: C, 63.14; H, 6.41; N, 3.88. Found: C, 63.10; H, 6.47; N, 3.83.

Benzyl *N*-[1-((*p*-Methylphenyl)sulfonyl)pentyl]carbamate (31). Valeraldehyde (9.47 g, 110 mmol), methanol (10 mL), benzyl carbamate (15.1 g, 100 mmol), sodium *p*-toluenesulfinate dihydrate (21.4 g, 100 mmol), water (100 mL), and 88% formic acid (ca. 20 mL) were combined according to the general procedure above, except that the mixture was heated at 70 °C for 1 h. After cooling, the white crystals were filtered and washed sequentially with water and petroleum ether to give 23.4 g (62%) of analytically pure **31**: mp 126.0–128.0 °C; R_f = 0.32 (25% EtOAc/hexane); IR ($CHCl_3$) 3425 (w), 2961 (w), 1731 (s), 1506 (s), 1315 (s), 1143 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.73 (d, J = 8.2 Hz, 2 H), 7.32–7.05 (m, 7 H), 5.87 (d, J = 10.6 Hz, 1 H), 4.95–4.75 (m, 3 H), 2.37 (s, 3 H), 2.25–2.12 (m, 1 H), 1.80–1.65 (m, 1 H), 1.50–1.18 (m, 4 H), 0.88 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 159.9, 144.7, 135.8, 133.6, 129.5, 129.0, 128.3, 128.0, 127.8, 72.3, 71.4, 67.3, 66.9, 27.2, 25.9, 21.9, 21.5, 13.6 (extra peaks due to rotamers); MS (CI, NH_3) m/z (relative intensity) 393 [$(M + NH_4)^+$, 33], 376 (M + 1, 2), 327 (4), 305 (5), 288 (2), 237 (75), 220 (59), 176 (100), 174 (68), 169 (8), 156 (9), 139 (14), 108 (19), 86 (41); HRMS calcd for $C_{20}H_{25}NO_4S$ (M + 1) 376.1583, found 376.1565. Anal. Calcd for $C_{20}H_{25}NO_4S$: C, 63.98; H, 6.71; N, 3.73. Found: C, 64.00; H, 6.76; N, 3.98.

Benzyl *N*-[1-((*p*-Methylphenyl)sulfonyl)-2-phenylethyl]carbamate (32). Phenylacetaldehyde (13.2 g, 110 mmol), methanol (10 mL), benzyl carbamate (15.1 g, 100 mmol), sodium *p*-toluenesulfinate dihydrate (21.4 g, 100 mmol), water (100 mL), and 88% formic acid (ca. 20 mL) were combined according to the general procedure above, except that the mixture was heated at 70 °C for 1 h. After cooling, the white crystals were filtered and washed sequentially with water and petroleum ether to give 30.3 g (74%) of analytically pure **32**: mp 142.0–150.0 °C; R_f = 0.27 (25% EtOAc/hexane); IR ($CHCl_3$) 3424 (w), 1731 (s), 1504 (m), 1317 (m), 1144 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.77 (d, J = 8.2 Hz, 2 H), 7.38–6.95 (m, 12 H), 5.88 (d, J = 10.6 Hz, 1 H), 5.16 (app dt, J = 3.3, 11.0 Hz, 1 H), 4.77, 4.71 (ABq, J_{AB} = 12.4 Hz, 2 H), 3.61 (dd, J = 14.4, 3.3 Hz, 1 H), 3.02 (dd, J = 14.4, 11.4 Hz, 1 H), 2.38 (s, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 156.8, 154.7, 145.0, 135.8, 134.7, 133.5, 129.7, 129.2, 128.6, 128.4, 128.3, 128.0, 127.7, 127.1, 72.0, 66.9, 66.8, 32.6, 21.6 (extra peaks due to rotamers); MS (CI, NH_3) m/z (relative intensity) 300 (11), 254 (27), 210 (23), 193 (7), 157 (7), 139 (16), 118 (7), 108 (6), 91 (100). Anal. Calcd for $C_{23}H_{23}NO_4S$: C, 67.46; H, 5.66; N, 3.42. Found: C, 67.47; H, 5.74; N, 3.73.

Benzyl *N*-[1-((*p*-Methylphenyl)sulfonyl)-2-methylpropyl]carbamate (33). Isobutyraldehyde (7.93 g, 110 mmol), methanol (10 mL), benzyl carbamate (15.1 g, 100 mmol), sodium *p*-toluenesulfinate dihydrate (21.4 g, 100 mmol), water (100 mL), and 88% formic acid (ca. 20 mL) were combined according to the general procedure above, except that the mixture was heated at 70 °C for 1 h. After cooling, the white crystals were filtered and washed sequentially with water and petroleum ether to give 24.7 g (68%) of analytically pure **33**: mp 92.5–97.0 °C; R_f = 0.15 (15% EtOAc/hexane); IR ($CHCl_3$) 3429 (w), 1731 (s), 1505 (m), 1315 (m), 1143 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.71 (d, J = 8.2 Hz, 2 H), 7.38–7.08 (m, 7 H), 5.63 (d, J = 11.2 Hz, 1 H), 4.93, 4.84 (ABq, J_{AB} = 12.2 Hz, 2 H), 4.76 (dd, J = 11.2, 3.6 Hz, 1 H), 2.75 (m, 1 H), 2.38 (s, 3 H), 1.11 (d, J = 6.8 Hz, 3 H), 1.07 (d, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 155.2, 144.6, 135.8, 134.9, 129.6, 128.8, 128.4, 128.2, 128.0, 128.0, 127.9, 127.6, 75.0, 67.2, 66.7, 26.9, 21.5, 20.6, 16.8; MS (CI, NH_3) m/z (relative intensity) 379 [$(M + NH_4)^+$, 8], 223 (25), 206 (34), 174 (9), 169 (100), 162 (8), 136 (8), 125 (3), 108 (6); HRMS calcd for $C_{19}H_{23}NO_4SNH_4$ [$(M + NH_4)^+$] 379.1691, found 379.1682. Anal. Calcd for $C_{19}H_{23}NO_4S$: C, 63.14; H, 6.41; N, 3.88. Found: C, 63.02; H, 6.42; N, 4.30.

Benzyl *N*-[((*p*-Methylphenyl)sulfonyl)cyclohexylmethyl]carbamate (34). Cyclohexanecarboxaldehyde (6.17 g, 55.0 mmol), methanol (5 mL), benzyl carbamate (7.56 g, 50.0 mmol), sodium *p*-toluenesulfinate dihydrate (10.7 g, 50.0 mmol), water (50 mL), and 88% formic acid (ca. 10 mL) were combined according to the general procedure above, except that the mixture was heated at 70 °C for 1 h. After cooling, the white crystals were filtered and washed sequentially with water and petroleum ether to give 19.3 g (96%) of analytically pure **34**: mp 141.0–142.0 °C; R_f = 0.18 (15% EtOAc/hexane); IR ($CHCl_3$) 3430 (w), 1730 (s), 1504 (s), 1318 (m), 1303 (m), 1140 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.70 (d, J = 8.2 Hz, 2 H), 7.45–7.10 (m, 7 H), 5.58 (d, J = 11.2 Hz, 1 H), 4.92, 4.82 (ABq, J_{AB} = 12.2 Hz, 2 H), 4.72 (app dd, J = 11.2, 3.7 Hz, 1 H), 2.39 (s, 3 H), 2.25–1.55 (m, 5 H), 1.54–0.99 (m, 6 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 155.1, 144.7, 135.8, 134.9, 129.6, 128.9, 128.8, 128.4, 128.2, 128.0, 74.9, 67.2, 36.5, 30.6, 27.3, 25.9, 25.7, 25.6, 21.6; MS (CI, NH_3) m/z (relative intensity) 419 [$(M + NH_4)^+$, 5], 402 (M + 1, 1), 263 (16), 246 (100), 202 (14), 189 (6), 174 (16), 136 (42); HRMS calcd for $C_{22}H_{27}NO_4SNH_4$ [$(M + NH_4)^+$] 419.2005, found 419.2001. Anal. Calcd for $C_{22}H_{27}NO_4S$: C, 65.81; H, 6.78; N, 3.49. Found: C, 65.47; H, 6.72; N, 3.52.

Benzyl *N*-[1-((*p*-Methylphenyl)sulfonyl)-2,2-dimethylpropyl]carbamate (35). Trimethylacetaldehyde (4.74 g, 55 mmol), methanol (5 mL), benzyl carbamate (7.56 g, 50.0 mmol), sodium *p*-toluenesulfinate dihydrate (10.7 g, 50.0 mmol), water (50 mL), and 88% formic acid (ca. 10 mL) were combined according to the general procedure above, except that the mixture was heated at 70 °C for 2 h. After cooling, the white crystals were filtered and washed sequentially with water and petroleum ether to give 10.5 g (56%) of analytically pure **35**: mp 83.0–88.5 °C; R_f = 0.19 (15% EtOAc/hexane); IR ($CHCl_3$) 3431 (w), 1730 (s), 1504 (m), 1317 (m), 1142 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.71 (d, J = 8.1 Hz, 2 H), 7.44–7.07 (m, 7 H), 5.66, 4.64 (2 doublets due to rotamers, J = 11.3 Hz, J = 11.3 Hz, respectively, 1 H total), 5.10 (s, 1 H), 4.92–4.76 (m, 2 H), 2.38 (s, 3 H), 1.25 (s, 9 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 155.0, 144.4, 136.3, 136.2, 135.7, 129.4, 128.9, 128.8, 128.5, 128.3, 128.1, 128.1, 128.0, 127.8, 77.6, 67.2, 66.9, 36.7, 27.4, 21.6; MS (CI, NH_3) m/z (relative intensity) 393 [$(M + NH_4)^+$, 6], 237 (6), 220 (75), 176 (14), 169 (100), 136 (12); HRMS calcd for $C_{20}H_{25}NO_4SNH_4$ [(M

+ NH_4)1+] 393.1848, found 393.1856. Anal. Calcd for $C_{20}H_{25}NO_4S$: C, 63.98; H, 6.71; N, 3.73. Found: C, 63.76; H, 6.52; N, 3.96.

***tert*-Butyl *N*-[1-((*p*-Methylphenyl)sulfonyl)propyl]carbamate (36).** Propionaldehyde (1.91 g, 33 mmol), methanol (3 mL), *tert*-butyl carbamate (3.51 g, 30.0 mmol), sodium *p*-toluenesulfinate dihydrate (5.35 g, 30.0 mmol), water (30 mL), and 88% formic acid (ca. 9 mL) were combined according to the general procedure above, except that the mixture was heated at 70 °C for 1 h. After cooling, the white crystals were filtered and washed sequentially with water and petroleum ether to give 7.5 g (80%) of **36**: mp 114–115 °C; IR (KBr) 3346 (s), 2977 (s), 1719 (s), 1518 (s), 1315 (s), 1139 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.73 (d, J = 8 Hz, 2 H), 7.34 (d, J = 8 Hz, 2 H), 4.90 (d, J = 10 Hz, 1 H), 4.75 (m, 1 H), 2.41 (s, 3 H), 2.4–2.25 (m, 1 H), 1.7–1.65 (m, 1 H), 1.25 (s, 9 H), 1.05 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.2, 144.8, 134.9, 129.6, 129.1, 80.9, 72.1, 27.9, 21.4, 20.4, 9.78; MS (CI, NH_3) m/z (relative intensity) 331 [($M + NH_4$)$^+$, 8], 314 (M + 1, 2.8), 296 (3), 275 (8), 175 (17), 174 (41), 159 (11), 158 (100), 139 (15), 136 (18), 75 (27); HRMS calcd for $C_{15}H_{23}NO_4SH$ ($M + H$)$^+$ 314.1430, found 314.1426.

1-[1-((*p*-Methylphenyl)sulfonyl)propyl]oxazolidin-2-one (40). Propionaldehyde (1.28 g, 22.0 mmol), methanol (2 mL), oxazolidin-2-one (1.74 g, 20.0 mmol), sodium *p*-toluenesulfinate dihydrate (4.28 g, 20.0 mmol), water (20 mL), and 88% formic acid (ca. 4 mL) were stirred according to the general procedure above, except that the mixture was heated at 70 °C for 2 h. After cooling, the white crystals were filtered and washed sequentially with water and petroleum ether to give 5.18 g (91%) of analytically pure **40**: mp 111.0–113.0 °C; IR ($CHCl_3$) 1759 (s), 1417 (m), 1318 (m), 1146 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.77 (d, J = 8.1 Hz, 2 H), 7.37 (d, J = 8.1 Hz, 2 H), 4.87 (dd, J = 11.6, 3.5 Hz, 1 H), 4.42–4.21 (m, 2 H), 4.08–3.94 (m, 1 H), 3.59 (q, J = 8.5 Hz, 1 H), 2.45 (s, 3 H), 2.39–2.21 (m, 1 H), 2.07–1.88 (m, 1 H), 1.01 (t, J = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 157.4, 145.7, 133.8, 130.1, 128.7, 74.3, 62.7, 40.1, 21.7, 17.1, 10.1; MS (CI, NH_3) m/z (relative intensity) 301 [($M + NH_4$)$^+$, 100], 284 (M + 1, 0.4), 223 (2), 188 (1), 174 (2), 162 (3), 153 (2), 145 (51), 136 (91), 105 (15), 94 (3), 77 (7); HRMS calcd for $C_{13}H_{17}NO_4SNH_4$ [($M + NH_4$)$^+$] 301.1222, found 301.1212. Anal. Calcd for $C_{13}H_{17}NO_4S$: C, 55.11; H, 6.05; N, 4.94. Found: C, 55.06; H, 5.95; N, 4.79.

(4*R*,5*S*)-1-Methyl-3-[1-((*p*-methylphenyl)sulfonyl)methyl]-4-phenyl-5-methylimidazolidin-2-one (41). Formaldehyde (4.10 g of a 37% aqueous solution, 50.0 mmol), (4*S*,5*S*)-1-methyl-4-phenyl-5-methylimidazolidin-2-one[43] (1.90 g, 10.0 mmol), sodium *p*-toluenesulfinate dihydrate (2.14 g, 10.0 mmol), water (5 mL), and 88% formic acid (7.0 mL) were stirred at RT for 24 h according to the general procedure above to give 3.19 g (89%) of analytically pure **41** as a white solid. Note that methanol was not used in this procedure: mp 146.0–148.5 °C; $[\alpha]^{23}_D$ –101.8° (c 0.50, $CHCl_3$); IR ($CHCl_3$) 1711 (s), 1436 (s), 1406 (s), 1322 (m), 1282 (w), 1147 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.79 (d, J = 8.3 Hz, 2 H), 7.40–7.31 (m, 5 H), 7.13–7.03 (m, 2 H), 5.12 (d, J = 8.7 Hz, 1 H), 5.12, 3.82 (ABq, J_{AB} = 14.3 Hz, 2 H), 3.90–3.79 (m, 1 H), 2.67 (s, 3 H), 2.45 (s, 3 H), 0.79 (d, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 159.1, 144.9, 134.6, 134.3, 129.7, 128.7, 128.5, 128.2, 63.3, 61.4, 55.4, 28.6, 21.6, 14.7; MS m/z (relative intensity) 376 [($M + NH_4$)$^+$, 100], 359 (M + 1, 26), 220 (24), 203 [($M - SO_2$tol)$^+$, 8], 136 (80); HRMS calcd for $C_{19}H_{23}N_2O_3S$ (M + 1) 359.1429, found 359.1403. Anal. Calcd for $C_{19}H_{22}N_2O_3S$: C, 63.66; H, 6.19; N, 7.81. Found: C, 61.56; H, 6.14; N, 7.25.

(4*R*,5*S*,1′*S*)-1-Methyl-3-[1-((*p*-methylphenyl)sulfonyl)ethyl]-4-phenyl-5-methylimidazolidin-2-one (42). Method A (Sulfonylalkylation): Freshly distilled acetaldehyde (1.10 g, 25.0 mmol), methanol (0.5 mL), (4*R*,5*S*)-1-methyl-4-phenyl-5-methylimidazolidin-2-one[43] (0.96 g, 5.00 mmol), sodium *p*-toluenesulfinate dihydrate (1.17 g, 5.50 mmol), water (5 mL), and 88% formic acid (1.3 mL) were stirred at RT for 15 min according to the general procedure above to give 1.58 g (85%) of analytically pure **42** as a white solid: mp 115.5–116.5 °C; $[\alpha]^{23}_D$ –130.9° (c 2.5, $CHCl_3$); IR ($CHCl_3$) 1707 (w), 1518 (w), 1320 (w), 1193 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.84 (d, J = 8.3 Hz, 2 H), 7.37 (d, J = 8.3 Hz, 2 H), 7.35–7.08 (m, 5 H), 5.44 (q, J = 7.2 Hz, 1 H), 5.15 (d, J = 8.5 Hz, 1 H), 3.70 (dq, J = 8.5 Hz, 6.6 Hz, 1 H), 2.46 (s, 3 H), 2.44 (s, 3 H), 1.18 (d, J = 7.2 Hz, 3 H), 0.70 (d, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 159.8, 144.8, 138.2, 134.2, 129.5, 129.1, 128.4, 128.2, 69.4, 58.5, 56.6, 28.6, 21.5, 14.5, 11.6; MS m/z (relative intensity) 217 [($M - SO_2$tol)$^+$, 100], 104 (27), 91 (54), 77 (17), 65 (35), 56 (23), 51 (12), 42 (34). Anal. Calcd for $C_{20}H_{24}N_2O_3S$: C, 64.49; H, 6.49; N, 7.52. Found: C, 64.25; H, 6.55; N, 7.61. **Method B (Deprotonation and Alkylation of 41):** A solution of **41** (1.08 g, 3.00 mmol) in THF (40 mL) was cooled to –78 °C, and *n*-BuLi (1.40 mL of a 2.14 M solution in hexane, 3.00 mmol) was added dropwise to the white slurry. After 20 min at –78 °C, methyl iodide (0.57 g, 4.00 mmol) was added to the clear yellow solution and the mixture was allowed to warm to RT. After 3 h, the mixture was concentrated, water was added, and the resultant white solid was collected, washed with more water, and dried under vacuum to give 1.05 g (95%) of **42**, which showed the same physical and spectral properties reported above. ^1H NMR showed a single diastereomer.

(4*R*,5*S*,1′*S*)-1-Methyl-3-[1-((*p*-methylphenyl)sulfonyl)propyl]-4-phenyl-5-methylimidazolidin-2-one (43). Propionaldehyde (1.28 g, 22.0 mmol), methanol (1 mL), (4*R*,5*S*)-1-methyl-4-phenyl-5-methylimidazolidin-2-one[43] (3.81 g, 20.0 mmol), sodium *p*-toluenesulfinate dihydrate (4.28 g, 20.0 mmol), water (20 mL), and 88% formic acid (4.0 mL) were stirred at RT for 2 h according to the general procedure above to give 6.61 g (86%) of analytically pure **43** as a white solid: mp 134.0–135.0 °C; $[\alpha]^{23}_D$ –124.6° (c 2.5, $CHCl_3$); IR ($CHCl_3$) 2955 (s), 2920 (s), 2852 (m), 1689 (s), 1440 (m), 1377 (m), 1285 (m), 1253 (m), 1071 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.84 (d, J = 8.2 Hz, 2 H), 7.39–7.12 (m, 7 H), 5.18 (dd, J = 10.0, 4.1 Hz, 1 H), 5.11 (d, J = 8.7 Hz, 1 H), 3.69 (dq, J = 8.7, 6.6 Hz, 1 H), 2.50 (s, 3 H), 2.44 (s, 3 H), 1.98–1.85 (m, 1 H), 1.51–1.37 (m, 1 H), 0.77 (d, J = 6.6 Hz, 3 H), 0.62 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 161.0, 144.8, 138.0, 135.1, 129.6, 129.0, 128.3, 128.2, 128.0, 76.3, 58.9, 56.8, 28.8, 21.6, 19.1, 14.6, 10.7; MS m/z (relative intensity) 278 (19), 270 (12), 230 (59), 215 (14), 190 (20), 175 (54), 139 (54), 118 (50), 91 (89), 77 (33), 65 (48), 58 (100). Anal. Calcd for $C_{21}H_{26}N_2O_3S$: C, 65.26; H, 6.78; N, 7.25. Found: C, 65.21; H, 7.31; N, 7.75.

(4*R*,5*S*,1′*S*)-1-Methyl-3-[1-((*p*-methylphenyl)sulfonyl)-2-methylpropyl]-4-phenyl-5-methylimidazolidin-2-one (44). Isobutyraldehyde (1.59 g, 22.0 mmol), methanol (2 mL), (4*R*,5*S*)-1-methyl-4-phenyl-5-methylimidazolidin-2-one[43] (3.81 g, 20.0 mmol), sodium *p*-toluenesulfinate dihydrate (4.28 g, 20.0 mmol), water (20 mL), and 88% formic acid (4.0 mL) were stirred at RT for 2 h according to the general procedure above to give 6.26 g (78%) of analytically pure **44** as a white solid: mp 101.0–103.0 °C; $[\alpha]^{23}_D$ –118.3° (c 2.5, $CHCl_3$); IR ($CHCl_3$) 1693 (w), 1529 (w), 1333 (w), 1139 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.84 (d, J = 8.2 Hz, 2 H), 7.39–7.16 (m, 7 H), 5.18 (d, J = 9.1 Hz, 1 H), 5.02 (d, J = 8.6 Hz, 1 H), 3.63 (dq, J = 8.6, 6.7 Hz, 1 H), 2.52 (s, 3 H), 2.44 (s, 3 H), 2.09–1.98 (m, 1 H), 0.97 (d, J = 6.7 Hz, 3 H), 0.71 (d, J = 6.6 Hz, 3 H), 0.65 (d, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 161.9, 144.4, 137.7, 136.9, 129.5, 129.3, 128.3, 128.2, 80.7, 59.6, 56.9, 28.9, 27.9, 21.5, 20.6, 19.8, 14.6; MS (CI, NH_3) m/z (relative intensity) 418 [($M + NH_4$)$^+$, 3], 401 (M + 1, 1), 245 [($M - SO_2$tol)$^+$, 100], 208 (5), 191 (5), 174 (9), 136 (10). Anal. Calcd for $C_{20}H_{24}N_2O_3S$: C, 65.97; H, 7.05; N, 6.99. Found: C, 65.90; H, 7.00; N, 6.73.

(4*R*,5*S*,1′*S*)-1-Methyl-3-[1-((*p*-methylphenyl)sulfonyl)cyclopropylmethyl]-4-phenyl-5-methylimidazolidin-2-one (45). Cyclopropanecarboxaldehyde (0.70 g, 10.0 mmol), (4*R*,5*S*)-1-methyl-4-phenyl-5-methylimidazolidin-2-one[43] (1.90 g, 10.0 mmol), sodium *p*-toluenesulfinate dihydrate (2.14 g, 10.0 mmol), water (10 mL), and 88% formic acid (2.0 mL) were stirred at RT for 3 h according to the general procedure above to give 3.39 g (85%) of analytically pure **45** as a white solid. Note that no methanol was used: mp 149.0–151.0 °C; $[\alpha]^{23}_D$ –147.5° (c 1.2, $CHCl_3$); IR ($CHCl_3$) 1704 (s), 1431 (s), 1403 (s), 1318 (m), 1288 (m), 1140 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.83 (d, J = 8.3 Hz, 2 H), 7.39–7.15 (m, 7 H), 5.22 (d, J = 8.7 Hz, 1 H), 4.47 (d, J = 11.0 Hz, 1 H), 3.75 (dq, J = 8.7, 6.6 Hz, 1 H), 2.55 (s, 3 H), 2.44 (s, 3 H), 0.89–0.71 (m, 1 H), 0.75 (d, J = 6.6 Hz, 3 H), 0.65–0.52 (m, 1 H), 0.33–0.22 (m, 1 H), 0.13–0.02 (m, 1 H), –0.21 to –0.33 (m, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 160.2, 144.8, 137.9, 134.2, 129.6, 129.1, 128.2, 128.1, 78.9, 59.4, 56.6, 28.8, 21.6, 14.7, 8.9, 7.5, 4.3; MS (CI, NH_3) m/z (relative intensity) 399 (M + 1, 9), 279 (9), 243 [($M - SO_2$tol)$^+$, 100], 209 (19), 192 (5), 136 (17). Anal. Calcd for $C_{22}H_{26}N_2O_3S$: C, 66.31; H, 6.58; N, 7.03. Found: C, 65.90; H, 6.43; N, 6.76.

General Procedure for the Displacement of Sulfones by $(Bu_3Sn)_2Zn$: Benzyl *N*-[1-(Tri-*n*-butylstannyl)propyl]carbamate (51). Tri-*n*-butyltin hydride (0.58 g, 2.00 mmol) in ether (5 mL) was cooled to 0 °C, and isopropylmagnesium chloride (1.32 mL of a 1.52 M solution in ether, 2.00 mmol) was added dropwise over a period of 5 min. The reaction was warmed to RT and heated to reflux for 2 h. After cooling to RT, THF (5 mL) and anhydrous $ZnBr_2$ (1.25 mL of a 0.96 M solution in THF, 1.20 mmol) were added. After resultant black solution was stirred for 30 min, a solution of the sulfone **29** (0.35 g, 1.00 mmol) in THF (5 mL) was added. After 2 h, the mixture was quenched with 10% aqueous HCl (20 mL) and extracted with ether (3 × 25 mL). The combined organic phases were washed with 10% aqueous HCl (75 mL), saturated

aqueous $NaHCO_3$ (1 × 75 mL), and brine (1 × 100 mL) and then dried ($MgSO_4$) and concentrated. Chromatography (hexane, then 5% EtOAc/hexane) gave 0.41 g (85%) of **51** as a thick oil: R_f = 0.63 (25% EtOAc/hexane); IR (neat) 3329 (w, br), 2955 (s), 2923 (s), 1701 (s), 1507 (m), 1456 (m), 1245 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.42–7.25 (m, 5 H), 5.11, 5.06 (ABq, J_{AB} = 12.3 Hz, 2 H), 4.94 (d, J = 7.8 Hz, 1 H), 3.20 (q, J = 7.4 Hz, 1 H), 1.83–1.61 (m, 2 H), 1.60–1.15 (m, 12 H), 1.09–0.72 (m, 18 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 156.6, 136.9, 128.4, 128.0, 127.9, 66.5, 43.4, 30.5, 29.2, 27.9, 27.4, 13.6, 12.7, 10.2, 9.8 (extra peaks due to rotamers); MS (CI, NH_3) m/z (relative intensity) 482 (M^+, 3), 426 [$(M - C_4H_9)^+$, 80], 393 (73), 364 (49), 335 (31), 308 (100), 291 (84), 252 (71), 235 (31), 196 (53), 148 (31), 138 (58), 126 (43), 108 (72), 91 (95); HRMS calcd for $C_{19}H_{32}NO_2{}^{120}Sn$ [$(M - C_4H_9)^+$] 426.1455, found 426.1474. Anal. Calcd for $C_{23}H_{41}NO_2Sn$: C, 57.28; H, 8.57; N, 2.90. Found: C, 56.84; H, 8.65; N, 2.68.

Benzyl *N*-[1-(Tri-*n*-butylstannyl)butyl]carbamate (52). Tri-*n*-butyltin hydride (2.91 g, 10.0 mmol), ether (5 mL), isopropylmagnesium chloride (6.60 mL of a 1.52 M solution in ether, 10.0 mmol), $ZnBr_2$ (6.25 mL of a 0.96 M solution in THF, 6.00 mmol), THF (30 mL), and the sulfone **30** (1.81 g, 5.00 mmol) in THF (20 mL) were combined according to the general procedure (reaction time 1 h) to give 1.49 g (60%) of **52** as a thick oil after chromatography (hexane, then 5% EtOAc/hexane): R_f = 0.78 (15% EtOAc/hexane); IR (neat) 3330 (w, br), 2955 (s), 2924 (s), 2870 (m), 1698 (s), 1506 (m), 1456 (m), 1251 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.39–7.25 (m, 5 H), 5.10, 5.05 (ABq, J_{AB} = 12.3 Hz, 2 H), 4.94 (d, J = 7.6 Hz, 1 H), 3.32–3.22 (m, 1 H), 1.78–1.20 (m, 16 H), 1.04–0.75 (m, 18 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 156.5, 136.9, 128.4, 128.0, 127.9, 66.5, 41.2, 37.2, 30.5, 29.1, 27.4, 21.2, 13.6, 9.7; MS m/z (relative intensity) 440 [$(M - C_4H_9)^+$, 28], 362 (5), 291 (8), 269 (21), 235 (12), 211 (5), 177 (25), 162 (27), 155 (7), 121 (15), 91 (100), 84 (46), 49 (81), 41 (20); HRMS calcd for $C_{20}H_{34}NO_2{}^{120}Sn$ [$(M - C_4H_9)^+$] 440.1612, found 440.1610. Anal. Calcd for $C_{24}H_{43}NO_2Sn$: C, 58.08; H, 8.73; N, 2.82. Found: C, 57.83; H, 8.90; N, 2.91.

Benzyl *N*-[1-(Tri-*n*-butylstannyl)pentyl]carbamate (53). Tri-*n*-butyltin hydride (2.91 g, 10.0 mmol), ether (5 mL), isopropylmagnesium chloride (6.60 mL of a 1.52 M solution in ether, 10.0 mmol), $ZnBr_2$ (6.25 mL of a 0.96 M solution in THF, 6.00 mmol), THF (30 mL), and the sulfone **31** (1.88 g, 5.00 mmol) in THF (20 mL) were combined according to the general procedure (reaction time 1 h) to give 1.60 g (63%) of **53** as a thick oil after chromatography (hexane, then 5% EtOAc/hexane): R_f = 0.66 (15% EtOAc/hexane); IR (neat) 3324 (m, br), 2955 (s), 2923 (s), 2870 (s), 2853 (s), 1708 (s), 1510 (m), 1455 (m), 1252 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.50–7.26 (m, 5 H), 5.10, 5.05 (ABq, J_{AB} = 12.3 Hz, 2 H), 4.92 (d, J = 7.6 Hz, 1 H), 3.26 (q, J = 8.1 Hz, 1 H), 1.75–1.17 (m, 18 H), 0.98–0.75 (m, 18 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 156.5, 136.9, 128.5, 128.3, 128.0, 66.5, 41.4, 34.6, 30.3, 29.2, 27.5, 22.4, 17.5, 13.9, 13.7, 9.8 (extra peaks due to rotamers); MS (CI, NH_3) m/z (relative intensity) 454 [$(M - C_4H_9)^+$, 12], 308 (6), 291 (38), 269 (43), 235 (22), 196 (8), 180 (17), 155 (10), 138 (19), 121 (12), 108 (30), 91 (100); HRMS calcd for $C_{21}H_{36}NO_2{}^{120}Sn$ [$(M - C_4H_9)^+$] 454.1768, found 454.1772.

Benzyl *N*-[1-(Tri-*n*-butylstannyl)-2-phenylethyl]carbamate (54). Tri-*n*-butyltin hydride (2.91 g, 10.0 mmol), ether (5 mL), isopropylmagnesium chloride (6.60 mL of a 1.52 M solution in ether, 10.0 mmol), $ZnBr_2$ (6.25 mL of a 0.96 M solution in THF, 6.00 mmol), THF (30 mL), and the sulfone **32** (2.05 g, 5.00 mmol) in THF (20 mL) were combined according to the general procedure (reaction time 40 min) to give 2.05 g (75%) of **54** as a thick oil after chromatography (hexane, then 5% EtOAc/hexane): R_f = 0.63 (15% EtOAc/hexane); IR (neat) 3398 (m, br), 2954 (s), 2921 (s), 2869 (m), 2851 (m), 1710 (s), 1508 (s), 1454 (m), 1239 (s), 1125 (w), 697 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.40–7.05 (m, 10 H), 5.10, 5.05 (ABq, J_{AB} = 12.3 Hz, 2 H), 4.92 (d, J = 6.4 Hz, 1 H), 3.30, 3.27 (2 triplets due to rotamers, J = 6.1 Hz, J = 6.1 Hz, respectively, 1 H total), 3.02–2.84 (m, 2 H), 1.58–1.17 (m, 12 H), 0.98–0.72 (m, 15 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 156.8, 140.6, 136.9, 128.8, 128.5, 128.4, 128.0, 126.3, 66.5, 42.5, 40.6, 29.1, 27.4, 13.7, 10.2 (extra peaks due to rotamers); MS (CI, NH_3) m/z (relative intensity) 488 [$(M - C_4H_9)^+$, 93], 455 (5), 410 (19), 380 (11), 355 (5), 308 (11), 291 (35), 235 (29), 210 (44), 179 (17), 138 (17), 108 (26), 91 (100); HRMS calcd for $C_{24}H_{34}NO_2{}^{120}Sn$ [$(M - C_4H_9)^+$] 488.1612, found 488.1610. Anal. Calcd for $C_{28}H_{43}NO_2Sn$: C, 61.78; H, 7.96; N, 2.57. Found: C, 61.76; H, 8.04; N, 2.33.

Benzyl *N*-[1-(Tri-*n*-butylstannyl)-2-methylpropyl]carbamate (55). Tri-*n*-butyltin hydride (2.91 g, 10.0 mmol), ether (5 mL), isopropylmagnesium chloride (6.60 mL of a 1.52 M solution in ether, 10.0 mmol), $ZnBr_2$ (6.25 mL of a 0.96 M solution in THF, 6.00 mmol), THF (30 mL), and the sulfone **33** (1.81 g, 5.00 mmol) in THF (20 mL) were combined according to the general procedure (reaction time 1 h) to give 1.58 g (64%) of **55** as a thick oil after chromatography (hexane, then 5% EtOAc/hexane): R_f = 0.72 (15% EtOAc/hexane); IR (neat) 3330 (w, br), 2955 (s), 2924 (s), 1704 (m), 1506 (m), 1456 (m), 1246 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.42–7.25 (m, 5 H), 5.10, 5.06 (ABq, J_{AB} = 12.2 Hz, 2 H), 4.99 (d, J = 8.4 Hz, 1 H), 3.14 (t, J = 7.9 Hz, 1 H), 2.11–1.90 (m, 1 H), 1.72–1.18 (m, 12 H), 1.08–0.76 (m, 21 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 156.6, 136.9, 128.4, 128.0, 66.5, 49.7, 32.6, 29.2, 27.5, 21.5, 20.8, 17.5, 13.6, 10.3 (extra peaks due to rotamers); MS m/z (relative intensity) 440 [$(M - C_4H_9)^+$, 19], 362 (5), 291 (8), 269 (16), 235 (11), 211 (4), 177 (24), 162 (24), 155 (7), 121 (15), 91 (100), 57 (9), 41 (15); HRMS calcd for $C_{20}H_{34}NO_2{}^{120}Sn$ [$(M - C_4H_9)^+$] 440.1612, found 1604. Anal. Calcd for $C_{24}H_{43}NO_2Sn$: C, 58.08; H, 8.73; N, 2.82. Found: C, 57.84; H, 8.91; N, 2.76.

Benzyl *N*-[(Tri-*n*-butylstannyl)cyclohexylmethyl]carbamate (56). Tri-*n*-butyltin hydride (2.91 g, 10.0 mmol), ether (5 mL), isopropylmagnesium chloride (6.60 mL of a 1.52 M solution in ether, 10.0 mmol), $ZnBr_2$ (6.25 mL of a 0.96 M solution in THF, 6.00 mmol), THF (30 mL), and the sulfone **34** (2.01 g, 5.00 mmol) in THF (20 mL) were combined according to the general procedure (reaction time 1 h) to give 1.47 g (64%) of **56** as a thick oil after chromatography (hexane, then 5% EtOAc/hexane): R_f = 0.74 (15% EtOAc/hexane); IR (neat) 3328 (w, br), 2954 (m), 2922 (s), 1701 (m), 1507 (m), 1456 (m), 1248 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.47–7.25 (m, 5 H), 5.10, 5.05 (ABq, J_{AB} = 12.2 Hz, 2 H), 4.97 (d, J = 8.5 Hz, 1 H), 3.15 (t, J = 8.0 Hz, 1 H), 1.85–0.75 (m, 38 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 156.6, 137.0, 128.5, 128.0, 66.6, 48.7, 42.3, 32.3, 31.5, 29.2, 27.5, 26.4, 26.2, 17.5, 13.6, 10.4; MS m/z (relative intensity) 480 [$(M - C_4H_9)^+$, 8], 402 (3), 291 (12), 269 (100), 253 (8), 235 (9), 213 (35), 202 (8), 177 (33), 155 (26), 121 (15), 108 (5), 91 (21), 57 (38), 41 (30); HRMS calcd for $C_{23}H_{38}NO_2{}^{120}Sn$ [$(M - C_4H_9)^+$] 480.1925, found 480.1921.

Benzyl *N*-[1-(Tri-*n*-butylstannyl)-2,2-dimethylpropyl]carbamate (57). Tri-*n*-butyltin hydride (2.91 g, 10.0 mmol), ether (5 mL), isopropylmagnesium chloride (6.60 mL of a 1.52 M solution in ether, 10.0 mmol), $ZnBr_2$ (6.25 mL of a 0.96 M solution in THF, 6.00 mmol), THF (30 mL), and the sulfone **35** (1.88 g, 5.00 mmol) in THF (20 mL) were combined according to the general procedure (reaction time 2 h) to give 0.18 g (7%) of **57** as a thick oil after chromatography (hexane, then 5% EtOAc/hexane): R_f = 0.57 (15% EtOAc/hexane); IR (neat) 3379 (w, br), 2956 (s), 2923 (s), 2871 (m), 2854 (m), 1710 (m), 1463 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.39–7.27 (m, 5 H), 5.19–5.05 (m, 2 H), 4.94 (d, J = 9.6 Hz, 1 H), 3.33 (d, J = 9.8 Hz, 1 H), 1.78–1.17 (m, 12 H), 1.02–0.78 (m, 24 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 156.6, 137.0, 128.5, 128.4, 128.2, 128.0, 127.9, 66.6, 54.8, 36.5, 30.5, 29.1, 27.8, 26.8, 17.5, 13.5, 11.1; MS m/z (relative intensity) 454 [$(M - C_4H_9)^+$, 2], 291 (10), 269 (100), 234 (4), 213 (20), 177 (20), 155 (18), 121 (8), 91 (12), 84 (5), 57 (29), 49 (4), 41 (20); HRMS calcd for $C_{21}H_{36}NO_2{}^{120}Sn$ [$(M - C_4H_9)^+$] 454.1768, found 454.1762. Anal. Calcd for $C_{25}H_{45}NO_2Sn$: C, 58.84; H, 8.89; N, 2.74. Found: C, 58.84; H, 9.03; N, 3.01. The major product from this reaction was assigned as *N*-benzyl-*N*-(carbobenzyloxy)-*n*-pentylamine by examination of the ^1H NMR spectrum of the crude reaction mixture.

(4*R*,5*S*,1′*S*)-1-Methyl-3-[1-(tri-*n*-butylstannyl)propyl]-4-phenyl-5-methylimidazolidin-2-one (61). Tri-*n*-butyltin hydride (0.58 g, 2.00 mmol), ether (5 mL), isopropylmagnesium chloride (1.32 mL of a 1.52 M solution in ether, 2.00 mmol), $ZnBr_2$ (1.25 mL of a 0.96 M solution in THF, 1.20 mmol), THF (5 mL), and the sulfone **43** (0.39 g, 1.00 mmol) in THF (5 mL) were combined according to the general procedure (reaction time 24 h) to give 0.14 g (27%) of **61** as a thick oil after chromatography (hexane, then 5% EtOAc/hexane): R_f = 0.48 (15% EtOAc/hexane); $[\alpha]^{23}_D$ −33.9° (*c* 2.0, $CHCl_3$); IR (neat) 1707 (s), 1430 (m), 1402 (m), 1140 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.39–7.10 (m, 5 H), 4.73 (d, J = 8.8 Hz, 1 H), 3.70 (dq, J = 8.8, 6.5 Hz, 1 H), 2.75 (s, 3 H), 2.57 (t, J = 5.8 Hz, 1 H), 1.75–1.17 (m, 14 H), 1.01–0.65 (m, 21 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 162.1, 136.7, 128.4, 128.0, 63.3, 55.9, 43.6, 29.3, 27.9, 27.6, 24.4, 14.6, 13.6, 12.7, 11.6; MS m/z (relative intensity) 465 [$(M - C_4H_9)^+$, 100], 351 (5), 309 (9), 291 (3), 269 (33), 231 (44), 213 (9), 177 (10), 155 (8), 121 (5), 84 (17), 57 (11), 49 (21), 41 (12); HRMS calcd for $C_{22}H_{37}N_2O^{120}Sn$ [$(M - C_4H_9)^+$] 465.1928, found 465.1933. Examination of the crude reaction mixture by ^1H NMR showed a single diastereomer of **61**.

General Procedure for the Displacement of Sulfones by $Bu_3SnMgCl$: Benzyl *N*-[1-(Tri-*n*-butylstannyl)propyl]carbamate (51). Tri-*n*-butyltin hydride (2.91 g, 10.0 mmol) in ether (10 mL) was cooled to 0 °C, and isopropylmagnesium chloride (6.41 mL of a 1.56 M solution in ether,

10.0 mmol) was added dropwise over a period of 5 min. The reaction was warmed to RT and then heated to reflux for 2 h. After the reaction mixture was cooled to RT, a solution of sulfone **29** (3.47 g, 10.0 mmol) in THF (50 mL) was added. After 1 h, the mixture was quenched with 10% aqueous HCl (20 mL) and extracted with ether (3 × 50 mL). The combined organic phases were washed with 10% aqueous HCl (75 mL), saturated aqueous $NaHCO_3$ (1 × 75 mL), and brine (1 × 100 mL) and then dried (Na_2SO_4) and concentrated. Chromatography (hexane, then 2.5% EtOAc/hexane) gave 1.55 g (32%) of **51**, which had physical and spectral properties identical to those reported above.

Benzyl *N*-[1-(Tri-*n*-butylstannyl)butyl]carbamate (52). Following the general procedure, sulfone **30** (3.61 g, 10.0 mmol) gave 1.54 g (31%) of **52**, which had physical and spectral properties identical to those reported above. Chromatography: hexane, then 2.5% EtOAc/hexane.

Benzyl *N*-[1-(Tri-*n*-butylstannyl)pentyl]carbamate (53). Following the general procedure, tri-*n*-butyltin hydride (5.82 g, 20.0 mmol), ether (20 mL), isopropylmagnesium chloride (12.82 mL of a 1.56 M solution in ether, 20.0 mmol), and the sulfone **31** (3.61 g, 10.0 mmol) in THF (100 mL) were combined for 1 h to give 1.03 g (10%) of **53**, which had physical and spectral properties identical to those reported above. Chromatography: hexane, then 2.5% EtOAc/hexane.

Benzyl *N*-[1-(Tri-*n*-butylstannyl)-2-phenylethyl]carbamate (54). Following the general procedure, sulfone **32** (4.10 g, 10.0 mmol) gave 1.52 g (28%) of **54**, which had physical and spectral properties identical to those reported above. Chromatography: hexane, then 2.5% EtOAc/hexane.

Benzyl *N*-[1-(Tri-*n*-butylstannyl)-2-methylpropyl]carbamate (55). Following the general procedure, sulfone **33** (3.61 g, 10.0 mmol) gave 1.42 g (29%) of **55**, which had physical and spectral properties identical to those reported above. Chromatography: hexane, then 2.5% EtOAc/hexane.

Benzyl *N*-[(Tri-*n*-butylstannyl)cyclohexylmethyl]carbamate (56). Following the general procedure, sulfone **34** (4.02 g, 10.0 mmol) gave 1.60 g (30%) of **56**, which had physical and spectral properties identical to those reported. Chromatography: hexane, then 2.5% EtOAc/hexane.

General Procedure for the Displacement of Sulfones by Bu_3SnLi: Benzyl *N*-[1-(Tri-*n*-butylstannyl)pentyl]carbamate (53). The sulfone **31** (1.88 g, 5.00 mmol) in THF (40 mL) was added to a solution of (tri-*n*-butylstannyl)lithium[44] (5.00 mmol in 10 mL of THF) at −78 °C. After 20 min, the bright-yellow solution was allowed to warm to 0 °C. After 1.5 h, water (25 mL) was added, the THF was removed under reduced pressure, and the resultant mixture was extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed with 10% aqueous HCl (2 × 30 mL), saturated aqueous $NaHCO_3$ (1 × 30 mL), and brine (1 × 30 mL) and then dried ($MgSO_4$) and concentrated. Chromatography (hexane, then 5% EtOAc/hexane) gave 1.15 g (45%) of **53**, which had physical and spectral properties identical to those reported above.

Benzyl *N*-[1-(Tri-*n*-butylstannyl)-2,2-dimethylpropyl]carbamate (57). Following the general procedure, sulfone **35** (1.88 g, 5.00 mmol) gave 0.86 g (34%) of **57**, which had physical and spectral properties identical to those reported above. Chromatography: hexane, then 5% EtOAc/hexane.

(4*R*,5*S*,1′*S*)-1-Methyl-3-[1-(tri-*n*-butylstannyl)ethyl]-4-phenyl-5-methylimidazolidin-2-one (18β). Following the general procedure, sulfone **42** (1.86 g, 5.00 mmol) gave 1.49 g (59%) of **18β** as a thick oil (reaction time 2 h), which had physical and spectral properties identical to those reported above. Chromatography: hexane, then 5% EtOAc/hexane. The stereochemistry was determined by analogy with **61** (see below).

(4*R*,5*S*,1′*S*)-1-Methyl-3-[1-(tri-*n*-butylstannyl)propyl]-4-phenyl-5-methylimidazolidin-2-one (61). Following the general procedure, sulfone **43** (3.87 g, 10.0 mmol) in THF (75 mL) and (tributylstannyl)lithium[44] (10.0 mmol in 25 mL of THF) gave 3.97 g (76%) of **61** as a thick oil (reaction time 2 h), which had physical and spectral properties identical to those reported above. Chromatography: hexane, then 5% EtOAc/hexane. Upon standing, this compound crystallized to give colorless needles suitable for X-ray diffraction, mp 49.5–52.5 °C. Anal. Calcd for $C_{26}H_{46}N_2OSn$: C, 59.90; H, 8.89; N, 5.37. Found: C, 59.94; H, 8.62; N, 4.99.

(4*R*,5*S*,1′*S*)-1-Methyl-3-[1-(tri-*n*-butylstannyl)-2-methylpropyl]-4-phenyl-5-methylimidazolidin-2-one (62). Following the general procedure, sulfone **44** (4.01 g, 10.0 mmol) in THF (80 mL) and (tributylstannyl)-lithium[44] (10.0 mmol in 20 mL of THF) gave 3.49 g (65%) of **62** as a thick oil (reaction time 1 h), which had physical and spectral properties identical to those reported above. Chromatography: hexane, then 5% EtOAc/hexane: R_f = 0.33 (15% EtOAc/hexane); $[\alpha]^{23}_D$ −24.1° (*c* 2.2, $CHCl_3$); IR (neat) 2953 (s), 2869 (s), 1692 (s), 1441 (s), 1403 (s), 1257 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.38–7.12 (m, 5 H), 4.74 (d, *J* = 8.9 Hz, 1 H), 3.73 (dq, *J* = 8.9, 6.6 Hz, 1 H), 2.75 (s, 3 H), 2.44 (d, *J* = 7.1 Hz, 1 H), 2.19 (app sextuplet, *J* = 6.8 Hz, 1 H), 1.53–1.20 (m, 12 H), 1.02–0.79 (m, 21 H), 0.76 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 162.1, 136.5, 128.6, 128.3, 128.1, 64.8, 56.0, 49.6, 31.7, 29.4, 29.3, 27.6, 21.9, 21.6, 14.7, 13.7, 12.3; MS *m/z* (relative intensity) 479 [$(M - C_4H_9)^+$, 34], 309 (9), 245 (100), 173 (9), 148 (8), 117 (11), 91 (12), 55 (15), 41 (10); HRMS Calcd for $C_{23}H_{39}N_2O^{120}Sn$ [$(M - C_4H_9)^+$] 479.2084, found 479.2096. The stereochemistry was determined by analogy with **61** (see above).

(4*R*,5*S*,1′*S*)-1-Methyl-3-[(tri-*n*-butylstannyl)cyclopropylmethyl]-4-phenyl-5-methylimidazolidin-2-one (63) and (1′*E*)-(4*R*,5*S*)-1-Methyl-3-[4-(tri-*n*-butylstannyl)but-1-enyl]-4-phenyl-5-methylimidazolidin-2-one (68). Following the general procedure, sulfone **45** (0.40 g, 1.00 mmol) in THF (8 mL) and (tributylstannyl)lithium[44] (1.00 mmol in 2 mL of THF) were stirred for 2.25 h to give 90.0 mg (17%) of **63**, 90.0 mg (17%) of **68**, and 65.0 mg (34%) of (4*R*,5*S*)-1-methyl-4-phenyl-5-methylimidazolidin-2-one **47**. Chromatography: hexane, then 5% EtOAc/hexane. **63**: Colorless oil, R_f = 0.47 (15% EtOAc/hexane); $[\alpha]^{23}_D$ −24.1° (*c* 2.2, $CHCl_3$); IR (neat) 2954 (s), 2921 (s), 2869 (m), 1691 (s), 1440 (m), 1402 (m), 1375 (m), 1255 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.38–7.09 (m, 5 H), 5.05 (d, *J* = 8.8 Hz, 1 H), 3.72 (dq, *J* = 8.8, 6.6 Hz, 1 H), 2.79 (s, 3 H), 1.87 (d, *J* = 10.9 Hz, 1 H), 1.70–1.21 (m, 12 H), 1.05–0.77 (m, 16 H), 0.70 (d, *J* = 6.6 Hz, 3 H), 0.54–0.46 (m, 1 H), 0.36–0.27 (m, 1 H), −0.01 to −0.09 (m, 1 H), −0.14 to −0.23 (m, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 161.7, 136.4, 128.4, 128.2, 127.9, 63.4, 55.7, 46.7, 29.3, 29.0, 27.6, 14.3, 13.7, 13.0, 11.6, 8.3, 1.5; MS *m/z* (relative intensity) 477 [$(M - C_4H_9)^+$, 20] 475 (15), 309 (9), 243 (100), 177 (9), 149 (9), 117 (7), 105 (6), 41 (6); HRMS Calcd for $C_{23}H_{37}N_2O^{120}$-Sn [$(M - C_4H_9)^+$] 477.1928, found 477.1934. The stereochemistry was determined by analogy with **56** (see above). **68**: R_f = 0.26 (15% EtOAc/hexane); $[\alpha]^{23}_D$ −17.6° (*c* 0.58, $CHCl_3$); IR (neat) 2955 (s), 2924 (s), 2870 (s), 1709 (s), 1597 (m), 1430 (s), 1400 (s), 1285 (m), 1257 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.38–7.06 (m, 5 H), 6.76 (d, *J* = 14.5 Hz, 1 H), 4.78 (d, *J* = 8.9 Hz, 1 H), 4.37 (dt, *J* = 14.5, 6.8 Hz, 1 H), 3.82 (dq, *J* = 8.9, 6.6 Hz, 1 H), 2.79 (s, 3 H), 2.07 (q, *J* = 7.3 Hz, 2 H), 1.68–1.59 (m, 2 H), 1.51–1.20 (m, 12 H), 0.99–0.62 (m, 18 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 158.1, 135.7, 128.4, 127.9, 127.5, 122.5, 112.1, 60.6, 55.7, 29.2, 28.7, 27.3, 17.5, 15.1, 13.7, 9.7, 8.8; MS *m/z* (relative intensity) 477 [$(M - C_4H_9)^+$, 30] 258 (59), 243 (34), 215 (14), 190 (47), 175 (100), 167 (22), 149 (61), 132 (35), 117 (38), 105 (27), 91 (31), 77 (22), 58 (65), 42 (34); HRMS Calcd for $C_{23}H_{37}N_2O^{120}Sn$ [$(M - C_4H_9)^+$] 477.1928, found 477.1933.

Transmetalation of 18β. A. Quenching with Bu_3SnCl. Recovery of (4*R*,5*S*,1′*S*)-1-Methyl-3-[1-(tri-*n*-butylstannyl)ethyl]-4-phenyl-5-methylimidazolidin-2-one (18β). A solution of imidazolidinone **18β** (100 mg, 0.197 mmol) in THF (2 mL) was cooled to −78 °C, and *n*-BuLi (0.092 mL of a 2.14 M solution in hexane, 0.197 mmol) was added dropwise. After 5 min at −78 °C, tributyltin chloride (64.0 mg, 0.197 mmol) was added. After 30 min, a solution of acetic acid in THF (1.0 mL of a 20% solution) was added, and the mixture was warmed to RT and then diluted with water (2 mL) and extracted with EtOAc (3 × 5 mL). The combined organic phases were washed with brine (3 × 5 mL), dried ($MgSO_4$), and concentrated. Examination of the crude reaction mixture by 300-MHz ^1H NMR showed a 59:1 mixture of diastereomers **18β**/**18α**. Chromatography (hexane, then 5% EtOAc/hexane) gave 45.7 mg (46%) of **18β**/**18α** (same ratio). See above for the spectral and physical properties of **18β** and below for the characteristics of **18α**.

B. Time Dependence. Three additional experiments were run under the same conditions, except that the anion was kept for increasingly longer times at −78 °C before Bu_3SnCl was added. Again, the crude reaction mixtures as well as the chromatographed products were examined by NMR to determine the stereochemical outcome. The following results were obtained (reported as mmol of **18β** used, time before addition of Bu_3SnCl, yield of **18β** isolated by chromatography, ratio of **18β**/**18α** observed by 300-MHz ^1H NMR). Run #1: 0.197 mmol, 15 min, 41%, **18β** only. Run #2: 0.36 mmol, 30 min, 33% **18β** only. Run #3: 0.31 mmol, 45 min, 33%, **18β** only. The lack of detection of any **18α** in these experiments as compared to the 59:1 ratio of **18β**/**18α** described above may be due to differing signal-to-noise ratios in the NMR spectra.

C. With TMEDA. A solution of **18β** (101 mg, 0.20 mmol) and TMEDA (33.7 mg, 0.29 mmol) in THF (2 mL) was cooled to −78 °C, and *n*-BuLi (0.095 mL of a 2.10 M solution in hexane, 0.20 mmol) was added dropwise. After 15 min at −78 °C, tributyltin chloride (65.0 mg,

(44) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481–1487.

0.20 mmol) was added and the mixture was worked up and purified as above to give 55.5 mg (55%) of **18β** as a single diastereomer by examination of both the crude and purified product by 300-MHz ^{1}H NMR.

D. Quenching with DCl. (4*R*,5*S*,1′*S*)-1-Methyl-3-(1-deuterioethyl)-4-phenyl-5-methylimidazolidin-2-one (73). Transmetalation of **18β** (100 mg, 0.20 mmol) in THF (2 mL) with *n*-BuLi (0.092 mL of a 2.14 M solution in hexane, 0.20 mmol) was carried out as described above. After 15 min at −78 °C, DCl (80 μL of a 20 wt % solution in D_2O, 0.40 mmol) was added. After 15 min, the mixture was worked up as described above to give 27.4 mg (63%) of **73** after chromatography (25% EtOAc/hexane), which was found to be a single diastereomer by examination of the ^{1}H NMR spectra of both the crude and purified product: R_f = 0.11; $[\alpha]^{23}_D$ −16.4° (*c* 1.07, $CHCl_3$); IR ($CHCl_3$) 1685 (s), 1439 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.48–7.12 (m, 5 H), 4.63 (d, *J* = 8.6 Hz, 1 H), 3.72 (dq, *J* = 8.6, 6.6 Hz, 1 H), 2.76 (s, 3 H), 2.77–2.64 (m, 1 H), 1.01 (d, *J* = 7.1 Hz, 3 H), 0.75 (d, *J* = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 161.5, 136.1, 128.4, 128.1, 61.3, 56.0, 36.0 (t, J_{C-D} = 22 Hz), 28.9, 14.6, 12.5; MS *m*/*z* (relative intensity) 219 (M^+, 35), 204 (100), 149 (14), 142 (17), 132 (41), 119 (35), 105 (18), 91 (29), 83 (20), 77 (25), 58 (45), 51 (10), 42 (32); HRMS Calcd for $C_{13}H_{17}N_2OD$ 219.1482, found 219.1472.

Transmetalation of 18α. A. Quenching with Bu_3SnCl. Recovery of (4*R*,5*S*,1′*R*)- and (4*R*,5*S*,1′*S*)-1-Methyl-3-[1-(tri-*n*-butylstannyl)ethyl]-4-phenyl-5-methylimidazolidin-2-one (18α and 18β). Four experiments were run under the exact same conditions as those for the transmetalation of **18β**, varying the time the anion was kept at −78 °C before Bu_3SnCl was added. The crude reaction mixtures as well as the chromatographed products were examined by NMR to determine the stereochemical outcome. The following results were obtained (reported as mmol of **18α** used, time before addition of Bu_3SnCl, yield of **18α** + **18β** isolated by chromatography, ratio of **18α**/**18β** observed by 300-MHz ^{1}H NMR). Run #1: 0.197 mmol, 5 min, 44%, 2.4:1. Run #2: 0.099 mmol, 15 min, 29% 1.2:1. Run #3: 0.099 mmol, 30 min, 26%, 1:2.4. Run #4: 0.100 mmol, 45 min, 24%, 1:6.7.

B. With TMEDA. A solution of **18α** (61.0 mg, 0.120 mmol) and TMEDA (16.7 mg, 0.14 mmol) in THF (2 mL) was cooled to −78 °C, and *n*-BuLi (0.057 mL of a 2.10 M solution in hexane, 0.12 mmol) was added dropwise. After 15 min at −78 °C, tributyltin chloride (39.1 mg, 0.12 mmol) was added and the mixture was worked up and purified as above to give 29.3 mg (48%) of **18β** as a single diastereomer by examination of both the crude and purified product by 300-MHz ^{1}H NMR.

Transmetalation of 61. A. Quenching with Bu_3SnCl. Recovery of (4*R*,5*S*,1′*S*)-1-Methyl-3-[1-(tri-*n*-butylstannyl)propyl]-4-phenyl-5-methylimidazolidin-2-one (61). Transmetalation of **61** (300 mg, 0.58 mmol) in THF (5 mL) with *n*-BuLi (0.271 mL of a 2.14 M solution in hexane, 0.58 mmol) at −78 °C for 15 min followed by quenching with Bu_3SnCl (190 mg, 0.58 mmol) was carried out as described above for **18β** to give 186 mg (62% chromatographed yield) of a single diastereomer of **61** by examination of both the crude and purified product by 300-MHz ^{1}H NMR.

B. Quenching with DCl. (4*R*,5*S*,1′*S*)-1-Methyl-3-(1-deuteriopropyl)-4-phenyl-5-methylimidazolidin-2-one (74). Transmetalation of **61** (310 mg, 0.59 mmol) in THF (6 mL) with *n*-BuLi (0.276 mL of a 2.14 M solution in hexane, 0.59 mmol) was carried out as described above. After 20 min at −78 °C, DCl (240 μL of a 20 wt % solution in D_2O, 1.2 mmol) was added. After 15 min, the mixture was worked up as described above to give 100 mg (72%) of **74** after chromatography (25% EtOAc/hexane), which was found to be a single diastereomer by examination of the ^{1}H NMR spectra of both the crude and purified product: R_f = 0.14; $[\alpha]^{23}_D$ −3.0° (*c* 1.06, $CHCl_3$); IR ($CHCl_3$) 2962 (m), 2932 (m), 2874 (m), 1699 (s), 1439 (s), 1402 (s), 1382 (m), 1365 (m), 1350 (m), 1257 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.43–7.08 (m, 5 H), 4.58 (d, *J* = 8.6 Hz, 1 H), 3.73 (dq, *J* = 8.6, 6.6 Hz, 1 H), 2.75 (s, 3 H), 2.58 (br t, *J* = 6.2 Hz, 1 H), 1.50–1.34 (m, 2 H), 0.84 (t, *J* = 7.4 Hz, 3 H), 0.76 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 161.8, 136.2, 128.4, 128.1, 128.0, 61.9, 56.1, 43.1 (t, J_{C-D} = 18 Hz), 29.0, 20.7, 14.6, 11.1; MS *m*/*z* (relative intensity) 233 (M^+, 17), 218 (8), 204 (100), 174 (5), 147 (8), 132 (6), 119 (12), 105 (21), 92 (25), 77 (9), 58 (6), 42 (8); HRMS Calcd for $C_{14}H_{19}N_2OD$ 233.1638, found 233.1629. A similar experiment on 260 mg (0.50 mmol) of **61** was run at −95 °C for 20 min, affording 100 mg (85%) of **74** after chromatography, again as a single diastereomer.

C. Quenching with Cyclohexanone. (4*R*,5*S*,1′*R*)-1-Methyl-3-[1-(1-hydroxycyclohexyl)propyl]-4-phenyl-5-methylimidazolidin-2-one (75). Transmetalation of **61** (1.03 g, 1.97 mmol) in THF (15 mL) with *n*-BuLi (0.940 mL of a 2.10 M solution in hexane, 1.97 mmol) was carried out as described above. After 15 min at −78 °C, cyclohexanone (193 mg, 1.97 mmol) was added. After 30 min, the mixture was worked up as described above to give 505 mg (78%) of **75** after chromatography (25% EtOAc/hexane), which was found to be a single diastereomer by examination of the ^{1}H NMR spectra of both the crude and purified product: R_f = 0.14; $[\alpha]^{23}_D$ +15.9° (*c* 1.3, $CHCl_3$); IR ($CHCl_3$) 3311 (w, br), 2932 (m), 2855 (m), 1672 (s), 1480 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.45–7.19 (m, 5 H), 5.19 (br s, 1 H), 4.61 (d, *J* = 8.9 Hz, 1 H), 3.97–3.85 (m, 2 H), 2.76 (s, 3 H), 1.90–1.18 (m, 10 H), 1.05–0.90 (m, 4 H), 0.84 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 162.8, 136.7, 129.2, 128.4, 128.1, 72.3, 67.6, 67.1, 65.4, 57.1, 36.4, 28.9, 25.7, 21.9, 21.6, 20.4, 14.7, 12.8; MS *m*/*z* (relative intensity) 330 (M^+, 1), 287 (8), 231 (100), 217 (10), 203 (85), 189 (9), 174 (10), 118 (72), 105 (14), 91 (22), 71 (36), 58 (23), 43 (34); HRMS Calcd for $C_{20}H_{30}N_2O_2$ 330.2307, found 330.2303.

D. Quenching with Benzaldehyde. (4*R*,5*S*,1′*R*,2′*R*)- and (4*R*,5*S*,1′*R*,-2′*S*)-1-Methyl-3-[1-(phenylhydroxymethyl)propyl]-4-phenyl-5-methylimidazolidin-2-one (76). Transmetalation of **61** (500 mg, 0.96 mmol) in THF (10 mL) with *n*-BuLi (0.457 mL of a 2.10 M solution in hexane, 0.96 mmol) was carried out as described above. After 15 min at −78 °C, benzaldehyde (102 mg, 0.96 mmol) was added. After 15 min, the mixture was worked up as described above to give 281 mg (88%) of **76** after chromatography (25% EtOAc/hexane, all product fractions combined), which was found to be a 1.7:1 mixture of diastereomers by examination of the ^{1}H NMR spectra of both the crude and purified product. Rechromatography with the same solvent system allowed separation of the two diastereomers (stereochemistry not assigned). Major diastereomer: R_f = 0.21; $[\alpha]^{23}_D$ −59.3° (*c* 0.68, $CHCl_3$); IR ($CHCl_3$) 3289 (w, br), 2967 (w), 2874 (w), 1669 (s), 1487 (m), 1449 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.58–6.85 (m, 10 H), 6.37 (br s, 1 H), 5.01 (s, 1 H), 4.58 (d, *J* = 9.0 Hz, 1 H), 3.90 (dq, *J* = 9.0, 6.6 Hz, 1 H), 2.91 (dd, *J* = 3.7, 10.9 Hz, 1 H), 2.80 (s, 3 H), 2.18–2.02 (m, 1 H), 1.52–1.38 (m, 1 H), 0.97–0.73 (m, 5 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 162.4, 142.5, 136.5, 128.7, 128.6, 127.8, 126.6, 125.7, 76.9, 66.5, 65.7, 56.5, 28.6, 17.6, 14.6, 11.7; HRMS Calcd for $C_{21}H_{27}N_2O_2$ (M + 1) 339.2073, found 339.2067. Minor diastereomer: R_f = 0.10; $[\alpha]^{23}_D$ −151.5° (*c* 0.66, $CHCl_3$); IR ($CHCl_3$) 3321 (w, br), 2959 (w), 1672 (s), 1485 (m), 1454 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.39–6.90 (m, 10 H), 4.80 (br s, 1 H), 4.65 (d, *J* = 8.7 Hz, 1 H), 3.70 (dq, *J* = 8.7, 6.6 Hz, 1 H), 2.88 (quint, *J* = 4.7 Hz, 1 H), 2.79 (s, 3 H), 2.14–1.98 (m, 1 H), 1.77–1.63 (m, 1 H), 1.00 (t, *J* = 7.4 Hz, 3 H), 0.53 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 162.5, 143.8, 135.0, 128.1, 127.8, 127.7, 126.8, 126.7, 73.3, 63.7, 63.2, 56.9, 28.6, 20.5, 13.9, 11.4; MS (Cl, NH_3) *m*/*z* (relative intensity) 339 (M + 1, 100), 245 (1), 231 (10), 191 (2), 136 (54); HRMS Calcd for $C_{21}H_{27}N_2O_2$ (M + 1) 339.2073, found 339.2060.

E. Quenching with Isobutyraldehyde. (4*R*,5*S*,1′*R*,2′*R*)- and (4*R*,5*S*,-1′*R*,2′*S*)-1-Methyl-3-(1-ethyl-2-hydroxy-3-methylbutyl)-4-phenyl-5-methylimidazolidin-2-one (77). Transmetalation of **61** (705 mg, 1.35 mmol) in THF (14 mL) with *n*-BuLi (0.643 mL of a 2.10 M solution in hexane, 1.35 mmol) was carried out as described above. After 20 min at −78 °C, isobutyraldehyde (107 mg, 1.49 mmol) was added. After 25 min, the mixture was worked up as described above to give 376 mg (91%) of **77** after chromatography (25% EtOAc/hexane, all product fractions combined), which was found to be a 1.5:1 mixture of diastereomers by examination of the ^{1}H NMR spectra of both the crude and purified product. Rechromatography with the same solvent system allowed separation of the two diastereomers (stereochemistry not assigned). Major diastereomer: R_f = 0.59 (50% EtOAc/hexane); $[\alpha]^{23}_D$ −4.1° (*c* 0.51, $CHCl_3$); IR ($CHCl_3$) 3414 (s, br), 2956 (w), 1659 (s), 1443 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.40–7.16 (m, 5 H), 5.87 (s, 1 H, OH), 4.59 (d, *J* = 9.0 Hz, 1 H), 3.88 (dq, *J* = 9.0, 6.6 Hz, 1 H), 3.36 (d, *J* = 9.2 Hz, 1 H), 2.87 (dd, *J* = 3.2, 10.9 Hz, 1 H), 2.76 (s, 3 H), 2.14–1.96 (m, 1 H), 1.58–1.42 (m, 1 H), 1.01 (t, *J* = 7.4 Hz, 3 H), 0.86 (d, *J* = 6.6 Hz, 3 H), 0.82 (d, *J* = 6.6 Hz, 3 H), 0.35 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 162.3, 136.3, 128.7, 128.3, 80.9, 66.6, 60.5, 56.4, 31.3, 28.5, 19.6, 19.3, 18.9, 14.5, 11.9; MS (Cl, NH_3) *m*/*z* (relative intensity) 305 (M + 1, 100), 261 (2), 231 (13), 191 (7), 136 (13); HRMS Calcd for $C_{18}H_{29}N_2O_2$ (M + 1) 305.2229, found 305.2224. Minor diastereomer: R_f = 0.45 (50% EtOAc/hexane); $[\alpha]^{23}_D$ +6.0° (*c* 0.53, $CHCl_3$); IR ($CHCl_3$) 3420 (s, br), 2945 (w), 1662 (s), 1440 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.39–7.17 (m, 5 H), 4.96 (br d, *J* = 8.1 Hz, 1 H, OH), 4.61 (d, *J* = 9.0 Hz, 1 H), 3.88 (dq, *J* = 9.0, 6.6 Hz, 1 H), 3.21–3.10 (m, 2 H), 2.74 (s, 3 H), 1.80–1.52 (m, 2 H), 0.96 (d, *J* = 6.6 Hz, 3 H), 0.90 (t, *J* = 7.4 Hz, 3 H), 0.82 (d, *J* = 6.6 Hz, 3 H), 0.40 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 162.6, 137.2, 128.7, 128.1, 76.5, 63.6, 59.6, 57.1, 30.7, 28.9, 22.8, 19.7, 18.5, 14.8, 11.2.

F. Quenching with Ethyl Chloroformate. (4*R*,5*S*,1′*S*)- and (4*R*,5*S*,1′*R*)-1-Methyl-3-(1-(ethoxycarbonyl)propyl)-4-phenyl-5-methylimidazolidin-2-one (78α and 78β). Transmetalation of **61** (762 mg, 1.46 mmol) in THF (15 mL) with *n*-BuLi (0.695 mL of a 2.10 M solution in hexane, 1.46 mmol) was carried out as described above. After 20 min at −78 °C, ethyl chloroformate (0.32 g, 2.92 mmol) was added. After 25 min, the mixture was worked up as described above to give 367 mg (83%) of **78** after chromatography (25% EtOAc/hexane), which was found to be a 11.5:1 mixture of diastereomers **78β** and **78α** by examination of the ^{1}H NMR spectra of both the crude and purified product. The diastereomers were not separable by chromatography. Mixture of **78α** and **78β**: R_f = 0.30 (50% EtOAc/hexane); $[\alpha]^{23}_D$ −1.4° (*c* 0.51, $CHCl_3$); IR (neat) 2973 (w), 1736 (s), 1702 (s), 1432 (m), 1401 (w), 1254 (w), 1200 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz, major isomer) δ 7.41–7.09 (m, 5 H), 4.74 (d, *J* = 8.8 Hz, 1 H), 4.35 (dd, *J* = 6.9, 8.0 Hz, 1 H), 4.19 (q, *J* = 7.1 Hz, 2 H), 3.88 (dq, *J* = 8.8, 6.6 Hz, 1 H), 2.74 (s, 3 H), 1.73–1.58 (m, 1 H), 1.44–1.31 (m, 1 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 0.78–0.69 (m, 5 H); partial ^{1}H NMR ($CDCl_3$, 360 MHz, minor isomer) δ 3.84–3.76 (m, 1 H), 2.80 (s, 3 H), 1.15 (t, *J* = 7.1 Hz, 3 H), 0.99 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 172.1, 162.1, 138.2, 128.3, 128.1, 127.9, 60.9, 60.8, 58.0, 56.9, 28.4, 23.2, 20.7, 14.7, 14.1, 11.0; MS *m*/*z* (relative intensity) 304 (M^+, 1), 231 (100), 203 (9), 189 (35), 174 (11), 146 (8), 132 (11), 117 (11), 105 (7), 91 (17), 77 (6), 58 (11), 42 (8); HRMS Calcd for $C_{17}H_{24}N_2O_3$ 304.1787, found 304.1778.

Transmetalation of 62. A. Quenching with Bu_3SnCl. Recovery of (4*R*,5*S*,1′*S*)-1-Methyl-3-[1-(tri-*n*-butylstannyl)-2-methylpropyl]-4-phenyl-5-methylimidazolidin-2-one (62). Transmetalation of **62** (370 mg, 0.69 mmol) in THF (7 mL) with *n*-BuLi (0.329 mL of a 2.10 M solution in hexane, 0.69 mmol) at −78 °C for 15 min followed by quenching with Bu_3SnCl (224 mg, 0.69 mmol) was carried out as described above for **18β** to give 245 mg (67% chromatographed yield) of a single diastereomer of **62** by examination of both the crude and purified product by 300-MHz ^{1}H NMR. Chromatography was accomplished with hexane followed by 5% EtOAc/hexane: R_f 0.33 (15% EtOAc/hexane).

B. Quenching with DCl. (4*R*,5*S*,1′*S*)-1-Methyl-3-(1-deuterio-2-methylpropyl)-4-phenyl-5-methylimidazolidin-2-one (79). Transmetalation of **62** (307 mg, 0.57 mmol) in THF (6 mL) with *n*-BuLi (0.271 mL of a 2.10 M solution in hexane, 0.57 mmol) was carried out as described above. After 15 min at −78 °C, D_2O (0.25 mL) was added and the mixture was worked up as described above to give 79.0 mg (56%) of **79** after chromatography (25% EtOAc/hexane) as a white solid, which was found to be a single diastereomer by examination of the ^{1}H NMR spectra of both the crude and purified product: R_f = 0.16; $[\alpha]^{23}_D$ +9.0° (*c* 0.73, $CHCl_3$); IR ($CHCl_3$) 2954 (w), 1683 (s), 1436 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.40–7.07 (m, 5 H), 4.56 (d, *J* = 8.5 Hz, 1 H), 3.74 (dq, *J* = 8.5, 6.5 Hz, 1 H), 2.75 (s, 3 H), 2.40 (d, *J* = 5.6 Hz, 1 H), 1.84–1.69 (m, 1 H), 0.88 (d, *J* = 6.7 Hz, 3 H), 0.82 (d, *J* = 6.7 Hz, 3 H), 0.77 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 162.0, 135.9, 128.4, 128.1, 62.4, 56.0, 48.7 (t, J_{C-D} = 18 Hz), 29.1, 26.7, 20.2, 19.8, 14.7; MS *m*/*z* (relative intensity) 247 (M^+, 13), 204 (100), 190 (3), 174 (5), 147 (7), 132 (4), 117 (7), 106 (10), 92 (29), 77 (7), 56 (6), 42 (8); HRMS Calcd for $C_{15}H_{21}N_2OD$ 247.1795, found 247.1809.

Transmetalation of 12α. Preparation of (4*R*,1′*R*,2′*R*)- and (4*R*,1′*R*,2′*S*)-3-(1-Methyl-2-hydroxy-2-phenylethyl)-4-phenyloxazolidin-2-one (80). Transmetalation of **12α** (59.4 mg, 0.12 mmol) in THF (1.2 mL) with *n*-BuLi (0.099 mL of a 1.21 M solution in hexane, 0.12 mmol) was carried out as described above. After 15 min at −78 °C, benzaldehyde (12.5 mg, 0.12 mmol) was added. After 15 min, the mixture was worked up as described above to give 27.1 mg (76%) of **80** after chromatography (25% EtOAc/hexane, all product fractions combined), which was found to be a 1:1 mixture of diastereomers by examination of the ^{1}H NMR spectra of both the crude and purified product. Rechromatography with the same solvent system allowed separation of the two diastereomers (stereochemistry not assigned). Less polar diastereomer: R_f = 0.55 (50% EtOAc/hexane); IR ($CHCl_3$) 3404 (m, br), 1714 (s) cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.48–6.95 (m, 10 H), 5.05 (s, 1 H), 4.81 (t, *J* = 8.2 Hz, 1 H), 4.63 (dt, *J* = 1.4, 8.9 Hz, 1 H), 4.19 (dt, *J* = 1.4, 8.2 Hz, 1 H), 3.24 (dq, *J* = 2.4, 7.0 Hz, 1 H), 1.13 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.4, 141.8, 138.0, 129.3, 129.2, 128.1, 127.3, 127.2, 125.7, 76.0, 70.7, 61.6, 57.2, 9.3; MS (Cl, NH_3) *m*/*z* (relative intensity) 298 (M + 1, 100), 280 (33), 216 (9), 199 (15), 190 (9), 136 (25), 104 (31), 88 (11); HRMS Calcd for $C_{18}H_{20}NO_3$ (M + 1) 298.1443, found 298.1445. More polar diastereomer: R_f = 0.38 (50% EtOAc/hexane); IR ($CHCl_3$) 3402 (m, br), 1722 (s) cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.47–6.81 (m, 10 H), 4.88–4.75 (m, 2 H), 4.75–4.67 (br m, 1 H), 4.58 (dt, *J* = 0.9, 8.8 Hz, 1 H), 4.02 (dt, *J* = 0.9, 8.6 Hz, 1 H), 3.52 (quint, *J* = 6.6 Hz, 1 H), 1.13 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.8, 142.0, 137.6, 129.0, 128.9, 128.4, 127.5, 127.4, 126.3, 76.0, 70.9, 60.6, 56.2, 14.3; MS (Cl, NH_3) *m*/*z* (relative intensity) 298 (M + 1, 100), 280 (21), 136 (11), 104 (9); HRMS Calcd for $C_{18}H_{20}NO_3$ (M + 1) 298.1443, found 298.1442.

Transmetalation of 12β. Preparation of (4*R*,1′*R*,2′*R*)- and (4*R*,1′*R*,2′*S*)-3-(1-Methyl-2-hydroxy-2-phenylethyl)-4-phenyloxazolidin-2-one (80). Transmetalation of **12β** (41.0 mg, 0.09 mmol) in THF (1.0 mL) with *n*-BuLi (0.070 mL of a 1.21 M solution in hexane, 0.09 mmol) was carried out as described above. After 15 min at −78 °C, benzaldehyde (9.0 mg, 0.09 mmol) was added. After 15 min, the mixture was worked up as described above to give 13.8 mg (69%) of **80** after chromatography (25% EtOAc/hexane, all product fractions combined), which was found to be a 1:1 mixture of diastereomers by examination of the ^{1}H NMR spectra of both the crude and purified product. See above for characterization.

Transmetalation of 16α. A. Quenching with Bu_3SnCl. Recovery of (4*S*,5*R*,1′*R*)-3-[1-(Tri-*n*-butylstannyl)ethyl]-4-methyl-5-phenyloxazolidin-2-one (16α). Transmetalation of **16α** (108 mg, 0.22 mmol) in THF (2 mL) with *n*-BuLi (0.105 mL of a 2.10 M solution in hexane, 0.22 mmol) at −78 °C for 15 min followed by quenching with Bu_3SnCl (71.6 mg, 0.22 mmol) was carried out as described above for **18β** to give 81.3 mg (76% chromatographed yield) of a single diastereomer of **16α** by examination of both the crude and purified product by 300-MHz ^{1}H NMR. Chromatography was accomplished with hexane followed by 5% EtOAc/hexane: R_f = 0.24 (10% EtOAc/hexane).

B. Quenching with Benzaldehyde. (4*S*,5*R*,1′*S*,2′*R*)- and (4*S*,5*R*,1′*S*,2′*S*)-3-(1-Methyl-2-hydroxy-2-phenylethyl)-4-methyl-5-phenyloxazolidin-2-one (81). Transmetalation of **16α** (96.9 mg, 0.20 mmol) in THF (2 mL) with *n*-BuLi (0.095 mL of a 2.10 M solution in hexane, 0.20 mmol) was carried out as described above. After 15 min at −78 °C, benzaldehyde (21.2 mg, 0.20 mmol) was added. After 15 min, the mixture was worked up as described above to give 50.8 mg (82%) of **81** after chromatography (25% EtOAc/hexane, all product fractions combined), which was found to be a 1:1 mixture of diastereomers by examination of the ^{1}H NMR spectra of both the crude and purified product. Rechromatography with the same solvent system allowed separation of the two diastereomers (stereochemistry not assigned). Less polar diastereomer: R_f = 0.47 (50% EtOAc/hexane); $[\alpha]^{23}_D$ −8.7° (*c* 0.15, $CHCl_3$); IR ($CHCl_3$) 3361 (w, br), 1708 (s), 1456 (m), 1430 (m), 1359 (m), 1250 (m), 1096 (m) cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.48–7.09 (m, 10 H), 5.54 (d, *J* = 8.3 Hz, 1 H), 5.20 (br d, *J* = 2.8 Hz, 2 H), 4.27 (s, 1 H, OH), 4.10 (dq, *J* = 8.3, 6.6 Hz, 1 H), 3.48 (dq, *J* = 3.7, 6.9 Hz, 1 H), 1.35 (d, *J* = 6.9 Hz, 3 H), 0.73 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 158.4, 142.1, 134.9, 128.6, 128.5, 128.3, 127.7, 126.3, 126.2, 79.6, 76.4, 57.2, 56.5, 15.7, 11.1; MS (Cl, NH_3) *m*/*z* (relative intensity) 312 (M + 1, 100), 294 (10), 221 (15), 204 (11), 195 (38), 178 (12), 160 (15), 136 (86); HRMS Calcd for $C_{19}H_{22}NO_3$ (M + 1) 312.1600, found 312.1599. More polar diastereomer: R_f = 0.38 (50% EtOAc/hexane); $[\alpha]^{23}_D$ +51.7° (*c* 0.12, $CHCl_3$); IR ($CHCl_3$) 3362 (w, br), 1709 (s), 1446 (m), 1430 (m), 1359 (m), 1250 (m), 1097 (m) cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.45–7.13 (m, 8 H), 7.00–6.90 (m, 2 H), 5.48 (d, *J* = 8.5 Hz, 1 H), 5.02 (d, *J* = 8.6 Hz, 1 H), 4.90 (dd, *J* = 8.6, 5.7 Hz, 1 H), 4.08 (dq, *J* = 8.5, 6.6 Hz, 1 H), 3.61 (dq, *J* = 5.7, 7.0 Hz, 1 H), 1.43 (d, *J* = 7.0 Hz, 3 H), 0.39 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 158.8, 142.5, 128.6, 128.4, 127.6, 126.5, 126.0, 80.2, 76.1, 56.4, 55.7, 15.4, 14.8; MS (Cl, NH_3) *m*/*z* (relative intensity) 312 (M + 1, 100), 294 (8), 221 (17), 204 (10), 195 (32), 178 (9), 160 (19), 136 (87); HRMS Calcd for $C_{19}H_{22}NO_3$ (M + 1) 312.1600, found 312.1598.

C. Quenching with Cyclohexanone. (4*S*,5*R*,1′*S*)-3-[1-(Hydroxycyclohexyl)ethyl]-4-methyl-5-phenyloxazolidin-2-one (82). Transmetalation of **16α** (109 mg, 0.22 mmol) in THF (2 mL) with *n*-BuLi (0.105 mL of a 2.10 M solution in hexane, 0.22 mmol) was carried out as described above. After 15 min at −78 °C, cyclohexanone (21.6 mg, 0.22 mmol) was added. After 15 min, the mixture was worked up as described above to give 21.3 mg (32%) of **82** after chromatography (15% EtOAc/hexane, then 25% EtOAc/hexane): R_f = 0.41 (50% EtOAc/hexane); $[\alpha]^{23}_D$ −34.1° (*c* 0.58, $CHCl_3$); IR ($CHCl_3$) 3350 (w, br), 2935 (m), 1717 (s) cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.45–7.19 (m, 5 H), 5.61 (d, *J* = 8.5 Hz, 1 H), 4.29–4.19 (m, 2 H), 3.20 (q, *J* = 7.0 Hz, 1 H), 1.82–1.45 (m, 7 H), 1.34 (d, *J* = 7.0 Hz, 3 H), 1.30–1.09 (m, 3 H), 0.81 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.0, 135.2, 128.5, 126.3, 126.2, 79.9, 72.3, 58.8, 56.3, 36.5, 35.8, 25.7, 21.8, 16.1, 11.9; MS (Cl, NH_3) *m*/*z* (relative intensity) 304 (M + 1, 49), 237 (5), 223 (100), 206 (83), 186 (6), 136 (30), 118 (4); HRMS Calcd for $C_{18}H_{26}NO_3$ (M + 1) 304.1913, found 304.1904.

Transmetalation of 16β. A. Quenching with Bu_3SnCl. (4S,5R,1′R)-3-[1-(Tri-n-butylstannyl)ethyl]-4-methyl-5-phenyloxazolidin-2-one (16α). Transmetalation of **16β** (100 mg, 0.20 mmol) in THF (2 mL) with *n*-BuLi (0.095 mL of a 2.10 M solution in hexane, 0.20 mmol) at −78 °C for 15 min followed by quenching with Bu_3SnCl (65.1 mg, 0.20 mmol) was carried out as described above for **16β** to give 51.7 mg (52% chromatographed yield) of a single diastereomer of **16α** by examination of both the crude and purified product by 300-MHz ^1H NMR. Chromatography was accomplished with hexane followed by 5% EtOAc/hexane: R_f = 0.24 (10% EtOAc/hexane).

B. Quenching with Benzaldehyde. (4S,5R,1′S,2′R)- and (4S,5R,1′S,-2′S)-3-(1-Methyl-2-hydroxy-2-phenylethyl)-4-methyl-5-phenyloxazolidin-2-one (81). Transmetalation of **16β** (104.1 mg, 0.21 mmol) in THF (2 mL) with *n*-BuLi (0.100 mL of a 2.10 M solution in hexane, 0.21 mmol) was carried out as described above. After 15 min at −78 °C, benzaldehyde (22.3 mg, 0.21 mmol) was added. After 15 min, the mixture was worked up as described above to give 32.5 mg (50%) of **81** after chromatography (25% EtOAc/hexane, all product fractions combined), which was found to be a 1:1 mixture of diastereomers by examination of the ^1H NMR spectra of both the crude and purified product. Rechromatography with the same solvent system allowed separation of the two diastereomers (stereochemistry not assigned). The physical and spectral properties matched those reported above.

C. Quenching with Cyclohexanone. (4S,5R,1′S)-3-[1-(Hydroxycyclohexyl)ethyl]-4-methyl-5-phenyloxazolidin-2-one (82). Transmetalation of **16β** (99.1 mg, 0.20 mmol) in THF (2 mL) with *n*-BuLi (0.095 mL of a 2.10 M solution in hexane, 0.20 mmol) was carried out as described above. After 15 min at −78 °C, cyclohexanone (19.6 mg, 0.20 mmol) was added. After 15 min, the mixture was worked up as described above to give 23.6 mg (39%) of **82** after chromatography (15% EtOAc/hexane, then 25% EtOAc/hexane). The physical and spectral properties matched those reported above.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Michigan (Gomberg, Riggs, Sokol and Dow-Britton fellowships to A.C.L.) for support of this work.

Note Added in Proof: Chong has recently reported studies on the configurational stability of α-aminoorganolithiums derived from tin–lithium exchange on α-aminoorganostannanes: Burchat, A. F.; Chong, J. M.; Park, S. B. *J. Org. Chem.* **1993**, *34*, 51–54.

Supplementary Material Available: Experimental procedures and characterization for compounds **9–11**, **13–15**, **17**, **19–24**, **59**, **64**, **65**, **69–72**, methyl (*S*)-*N*-(α-methylbenzyl)carbamate, benzyl (*S*)-*N*-(α-methylbenzyl)carbamate, and *tert*-butyl (*S*)-*N*-(α-methylbenzyl)carbamate and Ortep drawings and tables listing atomic coordinates, thermal parameters, bond lengths, bond angles, and torsion angles for compounds **42** and **61** (36 pages); listings of structure factors for compounds **42** and **61** (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS. Ordering information is available on any current masthead page.