Diastereoselective Synthesis of Trisubstituted Cyclopropylstannanes

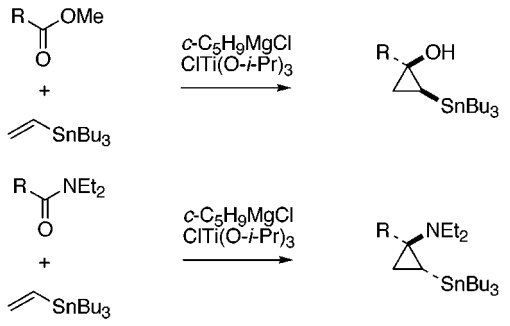
Kwangho Lee, Seok-In Kim, and Jin Kun Cha*

Department of Chemistry, University of Alabama, Tuscaloosa, Alabama 35487

Received August 5, 1998

Cyclopropanes show unique properties and reactivities owing to ring strain and hybridization effects. Typical methods for cyclopropanation involve carbenoid chemistry or 1,3-elimination. On the other hand, the preparation and synthetic applications of stannylated cyclopropane derivatives have so far received little attention.[1,2] Herein we report a convenient and highly diastereoselective synthesis of trisubstituted cyclopropylstannanes by means of Ti(II)-mediated coupling of tributyl(vinyl)tin with carboxylic esters or *N*,*N*-dialkylcarboxamides.[3,4]

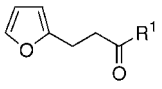
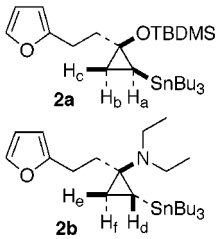
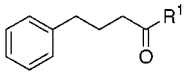
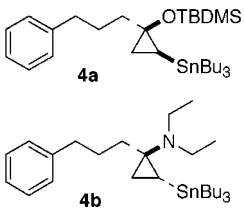
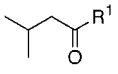
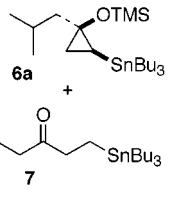
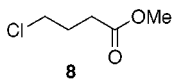
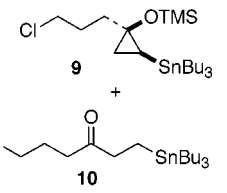
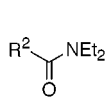
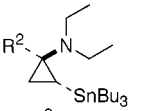
When an excess (4.0−5.0 equiv) of commercially available cyclopentylmagnesium chloride was added slowly (during 30 min) at room temperature to a THF solution of tributyl(vinyl)tin (1.0 equiv), ester (1.0 equiv) [or amide (1.0 equiv)], and ClTi(O-*i*-Pr)$_3$ (1.1 equiv), the corresponding heteroatom-substituted cyclopropylstannanes were obtained, in moderate to good yields, with excellent diastereoselectivity (eq 1). The other stereoisomer was not



(eq 1)

observed within the limits of ^{1}H NMR spectroscopy. As summarized in Table 1, cyclopropanation of carboxamides affords higher yields than that of esters, which can be attributed to greater stability of amides toward competing nucleophilic attack (by the Grignard or related reagents). Moreover, β-stannylcyclopropanols, the initial cyclopropanation products of esters, prove to be labile toward ring-opening, affording β-tributylstannyl ketones during silica gel chromatography. They are best stored as the TMS or TBDMS ethers by protection under standard conditions.

Table 1

starting materials	*products*	*yields*
 **1a**: R^1 = OMe **1b**: R^1 = NEt_2	 **2a** **2b**	51% 68%
 **3a**: R^1 = OMe **3b**: R^1 = NEt_2	 **4a** **4b**	43% 71%
 **5a**: R^1 = OMe **5b**: R^1 = NEt_2	 **6a** + **7** **6b**	14% 30% 66%
 **8**	 **9** + **10**	7% 24%
 **11**: R^2 = H **13**: R^2 = *i*-Pr	 **12**: R^2 = H **14**: R^2 = *i*-Pr	57% 48%

The depicted stereochemistry of the cyclopropanation products is based on ^{1}H−^{1}H COSY spectra and diagnostic difference NOE measurements in representative cases. When the methine proton H$_a$ (δ −0.15) in **2a** was irradiated, for example, the NOE enhancements were

(1) Lautens, M.; Delanghe, P. H. M. *J. Org. Chem.* **1995**, *60*, 2474. (b) Isono, N.; Mori, M. *J. Org. Chem.* **1996**, *61*, 7867 and references therein.

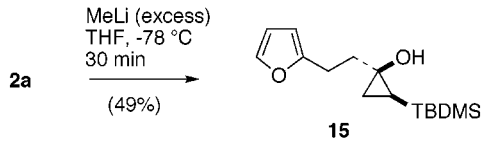
(2) For the synthetic utility of stannylated cyclopropanes, see: (a) Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* **1984**, *25*, 2415. (b) Piers, E.; Jean, M.; Marrs, P. S. *Tetrahedron Lett.* **1987**, *28*, 5075. (c) Schmitz, W. D.; Romo, D. *Tetrahedron Lett.* **1996**, *37*, 4857.

(3) (a) Lee, J.; Kang, C. H.; Kim, H.; Cha, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 291. (b) Lee, J.; Kim, H.; Cha, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 4198. (c) Lee, J.; Kim, Y. G.; Bae, J.; Cha, J. K. *J. Org. Chem.* **1996**, *61*, 4878. (d) Lee, J.; Cha, J. K. *J. Org. Chem.* **1997**, *62*, 1584. (e) Cho, S Y.; Lee, J.; Lammi, R. K.; Cha, J. K. *J. Org. Chem.* **1997**, *62*, 8235. (f) Lee, J.; Ha, J. D.; Cha, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 8127.

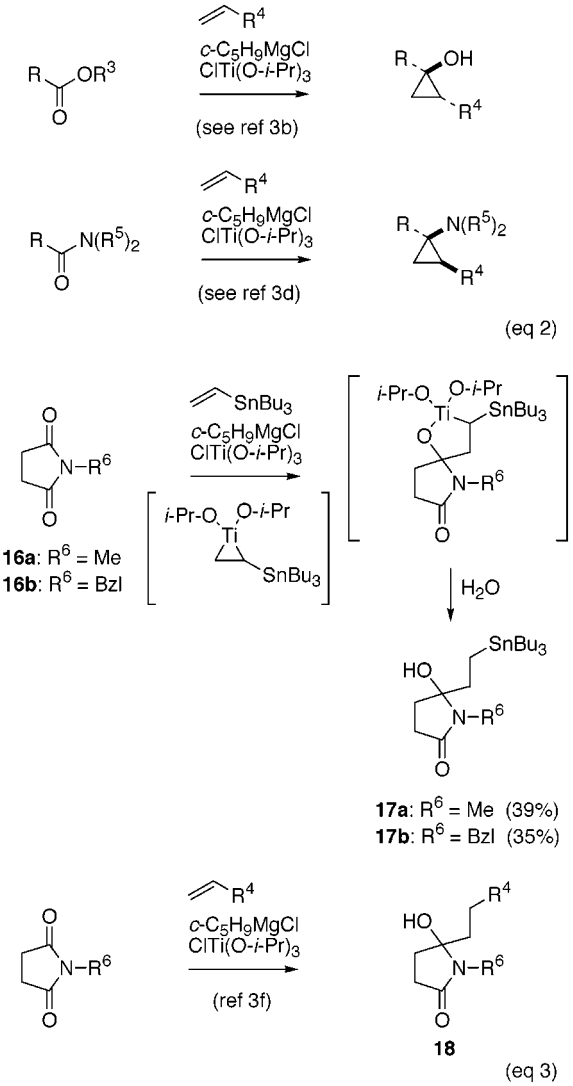
(4) (a) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevskii, D. A.; Prityts kaya, T. S. *Zh. Org. Khim.* **1989**, *25*, 2244. (b) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevskii, D. A.; Savchenko, A. I.; Prityts kaya, T. S. *Zh. Org. Khim.* **1991**, *27*, 294. (c) Kulinkovich, O. G.; Sorokin, V. L.; Kel'in, A. V. *Zh. Org. Khim.* **1993**, *29*, 66. See also: (d) Kasatkin, A.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 6079. (e) Kasatkin, A.; Kobayashi, K.; Okamoto, S.; Sato, F. *Tetrahedron Lett.* **1996**, *37*, 1849 and references therein. (f) Chaplinski, V.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 413.

10.1021/jo9815960 CCC: $15.00
Published on Web 11/11/1998

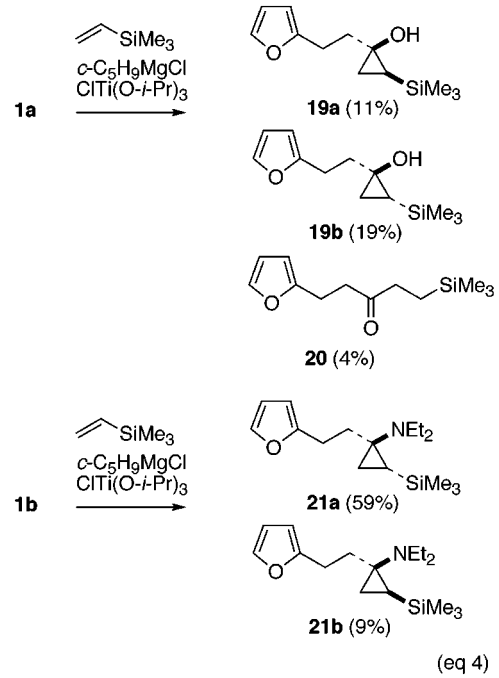
observed for not only the cis proton H_b (δ 0.82; 1.1%), but also both methylene protons [δ 2.71 (1.5%) and 1.33 (0.5%)] in the side chain.[5] In the case of **2b**, irradiation of H_d (δ 0.21) resulted in enhancements at the cis proton H_e (δ 0.97; 3.0%) and the methylene protons [δ 2.62 (1.1%)] of the *N*,*N*-diethyl substituent. This stereochemical assignment was further corroborated by the observation of a reverse-Brook rearrangement: treatment of **2a** with excess MeLi (THF, −78 °C, 30 min) resulted in clean O→C silyl migration affording the silylcyclopropane **15**.[6]



The most striking feature of these cyclopropanations with tributyl(vinyl)tin is that their sense of diastereoselectivity is unexpectedly opposite to that with terminal (alkyl substituted) olefins for both esters and amides (eq 2).[3a−d] The origin for the observed stereochemical outcome might be related to steric effects of the bulky tributylstannyl moiety. To probe whether it exerts a significant electronic influence in the initial formation of the presumed titanaoxacyclopentane intermediates, coupling with succinimides **16a**,**b** was investigated; only single regioisomers **17a**,**b** were obtained in (unoptimized) 39% and 35% yields (eq 3). Both couplings of imides with tributyl(vinyl)tin and terminal olefins are shown to have the identical regioselective insertion to the carbonyl group by the less-substituted carbon and Ti bond of the postulated dialkoxytitanacyclopropane intermediate.[3f] These results suggest that the observed divergent stereochemistry is determined in the subsequent rearrangement step of the titanaoxacyclopentane intermediates, rather than in their formation. Nonetheless, elucidation of the precise origin for the interesting stereochemical outcome in these cyclopropanations must await further studies.



Finally, extension was made to cyclopropanations of vinyltrimethylsilane (eq 4), in view of the demonstrated synthetic utility of silylated cyclopropanes.[7] Treatment of ester **1a** with vinyltrimethylsilane under standard cyclopropanation conditions afforded β-(trimethylsilyl)-1-cyclopropanols **19a** and **19b**, along with the ring-opened ketone **20** (eq 4).[8] Cyclopropanation of amide **1b** gave cyclopropylamine **21a**,**b** with a 6.5:1 diastereomeric ratio in 68% yield, whose stereochemical preference corresponds to that of tributyl(vinyl)tin (vide supra).



In summary, we have developed a new, convenient method for the preparation of β-hydroxy (siloxy) or β-*N*,*N*-dialkylamino-substituted, 1-tributylstannylated, and 1-trimethylsilylated cyclopropanes by Ti(II)-mediated coupling of esters or amides with tributyl(vinyl)tin or vinyltrimethylsilane. The stannyl- and silylcyclopropanations of esters require improvement to be synthetically useful. Further mechanistic and synthetic studies utilizing these new compounds as functionalized metallic cyclopropane derivatives will be reported in due course.

(5) The chemical shifts of the side chain protons are δ 1.33 and 2.47 ppm for the 1′-methylene protons (α to the cyclopropyl group) and 2.71 and 2.96 ppm for the 2′-methylene.

(6) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.
(7) Paquette, L. A. *Chem. Rev.* **1986**, *86*, 733.

(8) These cyclopropanols appear to be more prone to ring opening than the corresponding cyclopropyl stannane derivatives. TLC indicated that ring opening took place even during the cyclopropanation reaction. Thus, the observed product distribution may not reflect the kinetic ratio.

Experimental Section

Typical Procedure for Cyclopropanation of Tributyl(vinyl)tin with Esters or Amides. To a THF solution (7.1 mL) of methyl 3-(2′-furyl)propionate (110 mg, 0.71 mmol), tributyl(vinyl)tin (0.2 mL, 0.71 mmol), and ClTi(O-*i*-Pr)$_3$ (0.8 mL of a 1 M hexane solution) was added slowly (during 30 min) cyclopentylmagnesium chloride (1.4 mL of a 2M Et_2O solution) at room temperature. The reaction mixture was stirred for an additional 1 h and poured into water. The organic layer was separated, and the aqueous layer was extracted three times with ether. The combined extracts were dried over $MgSO_4$ and concentrated in vacuo to afford the crude cyclopropanol. The crude cyclopropanol product was dissolved in 3 mL of anhydrous methylene chloride and 0.17 mL of pyridine (2.1 mmol). The resulting solution was then cooled to 0 °C, and *tert*-butyldimethylsilyl triflate (0.24 mL, 1.0 mmol) was added. After the reaction mixture was stirred at room temperature for 12 h, it was washed with water and dried over $MgSO_4$. Concentration under reduced pressure and purification by column chromatography furnished 0.20 g (51% for two steps) of the silyl ether **2a** as a pale yellow oil: R_f 0.64 (hexane); IR (neat) 2956, 2926, 1463 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.29 (d, J = 1.4 Hz, 1 H), 6.27 (dd, J = 1.4, 3.4 Hz, 1 H), 5.95 (d, J = 3.4 Hz, 1 H), 2.96 (m, 1 H), 2.71 (m, 1 H), 2.47 (m, 1 H), 1.49 (m, 6 H), 1.33 (m, 1 H), 1.32 (sextet, J = 7.3 Hz, 6 H), 0.8−0.92 (m, 24 H), 0.77 (m, 2 H), 0.18 (s, 3 H), 0.06 (s, 3 H), −0.15 (dd, J = 8.5, 11.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ −3.3, −2.8, 9.7, 10.1, 13.8, 18.0, 18.9, 24.9, 26.0, 27.5, 29.2 [29.2 (d, J = 18 Hz)], 39.5, 60.4, 104.5, 110.1, 140.7, 156.5; HRMS (M^+) calcd for $C_{27}H_{52}O_2SiSn$ 556.2759, found 556.2765.

Cyclopropylamine 2b. R_f 0.65 (7:1 hexanes−EtOAc); IR (neat) 2958, 1464 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.28 (d, J = 2.0 Hz, 1 H), 6.27 (dd, J = 2.0, 3.0 Hz, 1 H), 5.93 (d, J = 3.0 Hz, 1 H), 2.77 (m, 2 H), 2.62 (m, 4 H), 2.05 (m, 1 H), 1.48 (m, 6 H), 1.37 (m, 1 H), 1.30 (sextet, J = 7.2 Hz, 6 H), 1.05 (t, J = 7.2 Hz, 6 H), 0.97 (m, 1 H), 0.86 (m, 15 H), 0.43 (dd, J = 4.0, 8.1 Hz, 1 H), 0.22 (dd, J = 8.1, 10.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 9.6, 12.2, 13.7, 15.5, 18.2, 26.7, 27.4 [27.4 (d, J = 54.7 Hz)], 29.2 [29.2 (d, J = 19.4 Hz)], 35.0, 46.0, 46.8, 104.1, 110.0, 140.5, 156.6; HRMS (M^+) calcd for $C_{25}H_{47}NOSn$ 497.2680, found 497.2683.

Cyclopropyl Silyl Ether 4a. R_f 0.80 (hexane); IR (neat) 2928, 2856, 1463 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.23 (m, 5 H), 2.63 (t, J = 5.8 Hz, 2 H), 2.21 (m, 1 H), 1.96 (m, 1 H), 1.75 (m, 1 H), 1.51 (m, 6 H), 1.30 (m, 6 H), 1.02 (m, 1 H), 0.89 (m, 24 H), 0.74 (m, 2 H), 0.10 (d, J = 5.1 Hz, 3 H), 0.04 (d, J = 5.1 Hz, 3 H), −0.16 (m, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ −3.3, −2.9, 9.6, 10.3, 13.7, 18.0, 18.6, 26.0, 27.5, 27.9, 29.2 [29.2 (d, J = 19.5 Hz)], 36.0, 40.2, 60.6, 125.6, 128.2, 128.4, 142.7; HRMS (MH^+) calcd for $C_{30}H_{57}OSiSn$ 581.3201, found 581.3202.

Cyclopropylamine 4b. R_f 0.50 (7:1 hexanes−EtOAc); IR (neat) 2957, 1455 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.23 (m, 5 H), 2.60 (m, 6 H), 1.78 (m, 3 H), 1.48 (m, 6 H), 1.31 (sextet, J = 5.9 Hz, 6 H), 1.06 (m, 1 H), 1.03 (t, J = 7.2 Hz, 6 H), 0.91 (m, 1 H), 0.90 (t, J = 7.2 Hz, 9 H), 0.78 (t, J = 7.9 Hz, 6 H), 0.39 (dd, J = 3.9, 8.1 Hz, 1 H), 0.18 (dd, J = 8.1, 10.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 9.5, 13.1, 13.7, 15.5, 18.4, 27.4, 29.2 [29.2 (d, J = 18.7 Hz)], 30.1, 35.9, 36.8, 46.2, 47.1, 125.7, 128.3, 128.4, 142.5; HRMS (M^+ − butyl) calcd for $C_{24}H_{42}NSn$ 464.2339, found 464.2356.

Cyclopropyl Silyl Ether 6a. R_f 0.60 (hexane); IR (neat) 2955, 2925, 1464 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.23 (dd, J = 4.3 Hz, 1 H), 1.96 (m, 1 H), 1.49 (m, 6 H), 1.31 (sextet, J = 7.3 Hz, 6 H), 0.80−1.00 (m, 21 H), 0.74 (m, 2 H), 0.61 (m, 1 H), 0.10 (s, 9 H), 0.03 (dd, J = 8.5, 10.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 1.5, 9.5, 12.0, 13.7, 17.4, 22.6, 23.9, 25.9, 27.4, 29.2 [29.2 (d, J = 18.0 Hz)], 49.0; HRMS (M^+) calcd for $C_{22}H_{48}OSiSn$ 476.2496, found 476.2517.

Cyclopropylamine 6b. R_f 0.50 (7:1 hexanes−EtOAc); IR (neat) 2956, 2926, 1464 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.64 (m, 2 H), 2.57 (m, 2 H), 2.09 (d, J = 13.8 Hz, 1 H), 1.84 (m, 1 H), 1.47 (m, 6 H), 1.30 (sextet, J = 7.1 Hz, 6 H), 1.29 (m, 1 H), 1.01 (t, J = 7.1 Hz, 6 H), 0.95 (d, J = 7.5 Hz, 6 H), 0.89 (t, J = 7.2 Hz, 9 H), 0.81 (t, J = 8.2 Hz, 6 H), 0.56 (dd, J = 3.7, 4.1 Hz, 1H), 0.46 (dd, J = 4.1, 9.2 Hz, 1 H), 0.10 (dd, J = 3.7, 9.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 9.6, 11.7, 13.7, 15.6, 18.2, 22.8, 24.6, 26.5, 27.4, 29.2, 46.0, 46.1; HRMS (M^+) calcd for $C_{23}H_{49}NSn$ 459.2887, found 459.2858.

Ketone 7. R_f 0.70 (15:1 hexanes−EtOAc); IR (neat) 2956, 1712, 1464 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.55 (t, J = 7.9 Hz, 2 H), 2.28 (d, J = 7.0 Hz, 2 H), 2.14 (m, 1 H), 1.47 (m, 6 H), 1.29 (m, 8 H), 0.70−1.00 (m, 21 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 1.9, 9.1, 13.7, 22.6, 24.7, 27.4 [27.4 (d, J = 53.0 Hz)], 29.2 [29.2 (d, J = 19.4 Hz)], 40.5, 51.1, 212.4; HRMS (M^+ − butyl) calcd for $C_{15}H_{31}OSn$ 347.1397, found 347.1401.

Cyclopropyl Silyl Ether 9. R_f 0.90 (7:1 hexanes−EtOAc 7:1); IR (neat) 2956, 1463 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 3.61 (m, 2 H), 2.30 (m, 1 H), 2.04 (m, 1 H), 1.92 (m, 1 H), 1.48 (m, 6 H), 1.31 (sextet, J = 7.3 Hz, 6 H), 1.15 (m, 1 H), 0.89 (t, J = 7.3 Hz, 9 H), 0.81 (t, J = 8.3 Hz, 6 H), 0.72 (m, 2 H), 0.12 (s, 9 H), −0.10 (dd, J = 8.0, 11.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 1.4, 9.6, 10.7, 13.7, 18.6, 27.4, 27.8, 29.2, 29.5, 37.5, 45.4; HRMS (MH^+ − butyl) calcd for $C_{17}H_{37}ClOSiSn$ 438.1318, found 438.1299.

Ketone 10. R_f 0.68 (7:1 hexanes−EtOAc); IR (neat) 2956, 1714, 1463 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 3.57 (t, J = 4.3 Hz, 2 H), 2.60 (q, J = 7.3 Hz, 4 H), 2.04 (quintet, J = 6.6 Hz, 2 H), 1.45 (m, 6 H), 1.28 (sextet, J = 7.4 Hz, 6 H), 0.78−0.92 (m, 17 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 2.0, 9.0, 13.7, 26.5, 27.4 [27.4 (d, J = 46.4 Hz)], 29.2, 38.4, 40.2, 44.5, 211.2; HRMS (M^+ − butyl) calcd for $C_{14}H_{28}ClOSn$ 367.1001, found 367.0999.

Cyclopropylamine 12. R_f 0.44 (4:1 hexanes−EtOAc); IR (neat) 2958, 2926, 1455 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.69 (m, 4 H), 1.78 (m, 1 H), 1.49 (m, 6 H), 1.30 (sextet, J = 7.1 Hz, 6 H), 1.07 (t, J = 7.2 Hz, 6 H), 0.88 (t, J = 7.3 Hz, 9 H), 0.81 (t, J = 8.0 Hz, 6 H), 0.75 (m, 1 H), 0.49 (m, 1 H), −0.06 (m, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 2.2, 8.7, 11.3, 11.6, 13.7, 27.4 [27.4 (d, J = 52.3 Hz)], 29.1 [29.1 (d, J = 19.9 Hz)], 39.9, 48.4; HRMS (MH^+) calcd for $C_{19}H_{42}NSn$ 402.2333, found: 402.2360.

Cyclopropylamine 14. R_f 0.41 (hexane); IR (neat) 2927, 2925, 1464 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.71 (m, 4 H), 2.01 (septet, J = 6.9 Hz, 1H), 1.50 (m, 6 H), 1.32 (sextet, J = 7.2 Hz, 6 H), 1.03 (dd, J = 2.3, 3.5 Hz, 1H), 0.98 (t, J = 7.2 Hz, 6 H), 0.89 (t, J = 6.7 Hz, 9 H), 0.82 (m, 12 H), 0.53 (dd, J = 3.5, 8.0 Hz, 1 H), −1.33 (dd, J = 2.3, 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 9.1, 10.1, 13.7, 16.2, 17.8, 22.1, 22.2, 27.3, 27.5, 29.2 [29.21 (d, J = 18.4 Hz)], 47.4, 53.2; HRMS (M^+) calcd for $C_{22}H_{47}NSn$ 443.2725, found 443.2754.

Cyclopropanol 15. R_f 0.24 (15:1 hexanes−EtOAc); IR (neat) 3455, 2955, 2925, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.31 (d, J = 1.4 Hz, 1 H), 6.28 (dd, J = 1.4, 3.4 Hz, 1 H), 6.01 (d, J = 3.4 Hz, 1 H), 2.88 (m, 2 H), 1.93 (m, 2 H), 1.56 (br s, 1 H), 0.92 (s, 9 H), 0.70 (m, 2 H), 0.00 (s, 3 H), −0.04 (s, 3 H), −0.23 (dd, J = 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ −5.7, −5.5, 10.2, 16.9, 17.5, 24.9, 26.7, 39.2, 59.8, 104.9, 110.2, 140.8, 155.9; HRMS (M^+) calcd for $C_{15}H_{26}O_2Si$ 266.1702, found 266.1685.

Compound 17a. R_f 0.37 (EtOAc); IR (neat) 3338, 2955, 2925, 1674, 1456 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 3.20 (br s, 1 H), 2.74 (s, 3 H), 2.51 (m, 1 H), 2.30 (m, 2 H), 1.95 (m, 1 H), 1.83 (m, 2 H), 1.46 (m, 6 H), 1.29 (sextet, J = 7.1 Hz, 6 H), 0.87 (m, 15 H), 0.62 (m, 1 H), 0.46 (m, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 1.2, 8.8, 13.7, 23.9, 27.3 [27.3 (d, J = 52.6 Hz)], 29.2 [29.21 (d, J = 20.3 Hz)], 29.5, 31.1, 34.8, 93.6, 174.8; HRMS (M^+ − H_2O) calcd for $C_{19}H_{37}NOSn$ 415.1897, found 415.1920.

Cyclopropanol 19a. R_f 0.69 (7:1 hexanes−EtOAc); IR (neat) 3445, 2953, 1245 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.31 (d, J = 1.3 Hz, 1 H), 6.28 (dd, J = 1.3, 3.1 Hz, 1 H), 6.01 (d, J = 3.1 Hz, 1 H), 2.86 (m, 2 H), 2.00 (m, 1 H), 1.83 (m, 1 H), 1.64 (br s, 1 H), 0.69 (m, 2 H), 0.05 (s, 9 H), −0.28 (dd, J = 8.7, 11.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ −0.7, 13.4, 17.6, 25.0, 39.0, 60.2, 104.9, 110.2, 140.8, 156.0; HRMS (M^+) calcd for $C_{12}H_{20}O_2Si$ 224.1233, found 224.1202.

Cyclopropanol 19b. R_f 0.42 (7:1 hexanes−EtOAc); IR (neat) 3355, 2954, 1255 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.31 (d, J = 1.6 Hz, 1 H), 6.29 (dd, J = 1.6, 3.3 Hz, 1 H), 6.02 (d, J = 3.3 Hz, 1 H), 2.91 (t, J = 8.0 Hz, 2 H), 2.05 (m, 1 H), 2.00 (br s, 1 H), 1.75 (m, 1 H), 0.95 (ddd, J = 1.4, 4.4, 12.0 Hz, 1 H), 0.34 (dd, J = 4.4, 8.6 Hz, 1 H), 0.07 (dd, J = 8.6, 12.0 Hz, 1 H), 0.03 (s, 9 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ −0.9, 14.6, 17.5, 25.1, 35.7, 59.6, 104.9, 110.2, 140.9, 155.9; HRMS (M^+) calcd for $C_{12}H_{20}O_2Si$ 224.1233, found 224.1204.

Ketone 20. R_f 0.75 (7:1 hexanes−EtOAc); IR (neat) 2953, 1717, 1248 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.29 (d, J = 1.4

Hz, 1 H), 6.27 (dd, J = 1.4, 3.0 Hz, 1 H), 5.99 (d, J = 3.0 Hz, 1 H), 2.93 (t, J = 7.8 Hz, 2 H), 2.77 (t, J = 7.8 Hz, 2 H), 2.36 (m, 2 H), 0.76 (m, 2 H), −0.01 (s, 9 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ −1.9, 10.3, 22.4, 37.4, 40.0, 105.1, 110.2, 141.0, 154.7, 210.5; HRMS (M^+) calcd for $C_{12}H_{20}O_2Si$ 224.1233, found 224.1223.

Cyclopropylamine 21a. R_f 0.69 (7:1 hexanes−EtOAc); IR (neat) 2964, 2797, 1249 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.29 (d, J = 1.3 Hz, 1 H), 6.27 (dd, J = 1.3, 2.5 Hz, 1 H), 5.94 (d, J = 2.5 Hz, 1 H), 2.83 (m, 1 H), 2.72 (m, 1 H), 2.61 (m, 4 H), 1.99 (m, 1 H), 1.52 (m, 1 H), 1.04 (t, J = 7.1 Hz, 6 H), 0.91 (m, 1 H), 0.38 (dd, J = 3.9, 8.3 Hz, 1 H), 0.04 (s, 9 H), −0.09 (m, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ −0.5, 14.2, 15.5, 17.9, 26.9, 32.0, 46.8, 47.3, 104.2, 110.0, 140.6, 156.6; HRMS (M^+) calcd for $C_{16}H_{29}NOSi$ 279.2018, found 279.2000.

Cyclopropylamine 21b. R_f 0.91 (7:1 hexanes−EtOAc); IR (neat) 2958, 2927, 1595, 1246 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.28 (d, J = 2.1 Hz, 1 H), 6.26 (dd, J = 2.1, 2.9 Hz, 1 H), 5.94 (d, J = 2.9 Hz, 1 H), 2.75 (m, 4 H), 2.60 (m, 2 H), 1.99 (m, 1 H), 1.78 (m, 1 H), 1.02 (t, J = 7.2 Hz, 6 H), 0.71 (dd, J = 3.5, 10.5 Hz, 1 H), 0.65 (dd, J = 3.5, 8.0 Hz, 1 H), 0.04 (s, 9 H), −0.38 (dd, J = 8.0, 10.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ −0.2, 14.0, 17.8, 26.4, 29.7, 32.2, 47.7, 50.8, 104.2, 110.0, 140.6, 156.5; HRMS (M^+) calcd for $C_{16}H_{29}NOSi$ 279.2018, found 279.2009.

Acknowledgment. We thank the National Institutes of Health (GM35956) for financial support. S.K. thanks KOSEF for a postdoctoral fellowship.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of cyclopropanation products (36 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9815960