Asymmetric Synthesis of Stannanes and Silanes via Reaction of Chiral Imidazolidinone Carbene Complexes with Group 14 Hydrides

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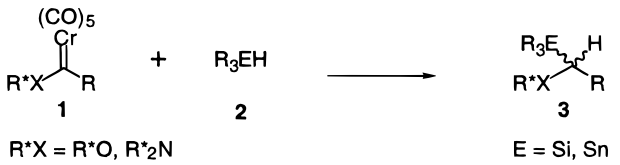
Chiral silanes and stannanes can be obtained with high optical purity from the 1,1-addition reactions of nonchiral silanes and stannanes with Fischer carbene complexes substituted with a chiral imidazolidinone auxiliary. The α-stannyl imidazolidinone products will undergo transmetalation and alkylation with high stereoselection with reactive electrophiles.

The 1,1-additions of silanes, germanes, and stannanes to Fischer carbene complexes have been known since 1972[2a] and subsequently have been investigated in more detail by a number of research groups.[2] However, to our knowledge no asymmetric reactions with chiral Fischer carbene complexes have been reported. We recognized that stereoselective additions of Si−H and Sn−H bonds to enantiomerically pure Fischer carbene complexes would provide a convenient method to prepare optically active silanes and stannanes and also serve as a diagnostic probe into the mechanism of this reaction (Scheme 1).

A number of different chiral carbene complexes have been prepared and evaluated for their effectiveness in a variety of reactions of Fischer carbene complexes.[3] Most of these complexes are chiral at the heteroatom stabilizing substituent of the carbene carbon and thus are derived from either chiral alcohols or amines. We have developed a class of chiral carbene complexes derived from imidazolidinones that have several advantages, including reactivity between that of alkoxy and amino complexes, availability of both antipodes of the chiral auxiliary, and restriction of the conformations of the chiral auxiliary via anchoring to the metal center by coordination of the imidazolidinone carbonyl. We have demonstrated that these complexes can give high asymmetric inductions in aldol reactions,[4] Michael additions,[5] exo selective Diels−Alder reactions,[6] and cyclohexadienone annulations.[7] We now report that these complexes can also provide high asymmetric inductions in their reactions with silanes and stannanes.

Scheme 1



The imidazolidinone complexes **4**, **6**, and **9**[8] were reacted with the silanes and stannanes indicated in Scheme 2 and Table 1. The reactions with silanes were performed in refluxing hexane according to the procedure of Chan,[2f,g] who found that the earlier protocol of Connor[2b−d] that included pyridine was not necessary. The stereoselectivity of the silane additions to the phenyl complex **4** was found to positively correlate with the size of the substituents on the silane, with triphenylsilane giving only one detectable diastereomer. The relative stereochemistry in silane **5a** was determined by X-ray diffraction analysis of a single crystal. The asymmetric induction is not as great for the vinyl carbene complex **6**, where triphenylsilane gave an 85:15 mixture of diastereomers. The reaction of the phenyl complex **4** with tributylstannane required the presence of pyridine, since without it a complex array of materials were formed which were not analyzed. Given the results observed with the silanes shown in Scheme 2, it was surprising that tributylstannane gave a single product upon reaction with complex **4**. The reaction of tributylstannane with complex **6** under the same conditions gave a complex mixture which was not further investigated.

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(2) (a) Fischer, E. O.; Dötz, K. H. *J. Organomet. Chem*. **1972**, *36*, C4. (b) Connor, J. A.; Rose, P. D.; Turner, R. M. *J. Organomet. Chem*. **1973**, *55*, 111. (c) Connor, J. A.; Day, J. P.; Turner, R. M. *J. Chem. Soc., Dalton Trans*. **1976**, 108. (d) Connor, J. A.; Day, J. P.; Turner, R. M. *J. Chem. Soc., Dalton Trans*. **1976**, 283. (e) Nakamura, E.; Tanaka, K.; Aoki, S. *J. Am. Chem. Soc*. **1992**, *114*, 9715. (f) Mak, C. C.; Chan, K. S. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2143. (g) Mak, C. C.; Tse, M. K.; Chan, K. S. *J. Org. Chem*. **1994**, *59*, 3585. (h) Merlic, C. A.; Albaneze, J. *Tetrahedron Lett*. **1995**, *36*, 1011. (i) Merlic, C. A.; Albaneze, J. *Tetrahedron Lett*. **1995**, *36*, 1011.
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(8) Powers, T. S.; Wulff, W. D.; Quinn, J.; Shi, Y.; Jiang, W.; Hsung, R.; Parisi, M. P.; Lau, A. Manuscript in preparation.

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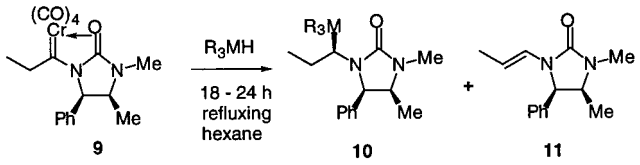
Table 1. Reactions of Alkyl Complex 9 with Silanes and Stannanes[a]



silane/stannane	additive	yield of **10**	yield of **11**
Bu_3SnH (1.5 equiv)	pyridine (3 equiv)	10[b]	34
Bu_3SnH (1.5 equiv)[c]			
Ph_3SiH (2 equiv)			90
none			29[d]

[a] All yields (in percent) are of isolated purified material. [b] One diastereomer by ^1H NMR on crude reaction mixture. [c] Consumption of **9** was complete after 48 h without the formation of any prominent product. [d] Also formed in an equal amount was a compound that was inseparable from **11** and by ^1H NMR was tentatively assigned as resulting from the double bond in **11**.

The reaction of tributyltin hydride with the ethyl complex **9** only gave the 1,1-addition product in 10% yield (one diastereomer). The major product of this reaction is the β-hydride elimination product **11**. It is known that this type of product can be formed by the interaction of alkyl carbene complexes with bases such as pyridine.[9] In the reaction of **9** we found that if the pyridine were omitted from the reaction the amount of β-hydride elimination product was not as prominent. However, the product mixture was quite complicated and its analysis was not further pursued. Surprisingly, the reaction of complex **9** with triphenylsilane gave a 90% yield of the β-hydride elimination product in the absence of pyridine. A control experiment revealed that a simple thermolysis of complex **9** in hexane in the absence of any other reagent did produce the β-hydride elimination product **11**, but not in a clean reaction. The failure of reactions of stannyl hydrides with vinyl and alkyl complexes noted here are in contrast to the observations of Nakamura and Merlic with alkoxycarbene complexes.[2e,h,i] It should be pointed out that the ene urea **11** is of synthetic interest due to the chemistry that has been developed for the corresponding ene carbamates.[10]

The stereochemistry of the 1,1-addition products was determined for the reaction of complex **4** with triphenylsilane with an X-ray crystal structure of **5a**. The stereochemistry of the major products from the rest of the reactions was assumed to also be the 1*S* isomer. We propose the mechanism shown in Scheme 3 to account for the observed stereochemistry.[11] While we have not experimentally probed the mechanism of this reaction, we have observed that the rate of the reaction giving **5a** is slowed by approximately a factor of 4 when the reaction is performed under carbon monoxide instead of argon under the same conditions.[12] If it assumed that the reaction is dissociative with initial loss of a carbon monoxide ligand and that the imidazolidinone carbonyl remains coordinated to the metal, then the stereochemistry can be explained by an approach of the silane or stannane from the side opposite the phenyl group on the imidazolidinone with delivery of hydride to the carbene carbon and of silicon to the metal. Reduction elimination then would give **16** with the observed stereochemistry.

In some synthetic applications of imidazolidinone carbene complexes it would be useful to have a method for the conversion of the carbene complex to an aldehyde. In these situations the chiral center generated upon the 1,1-addition of a silane would be lost, and thus a pure stereoisomer would not be required. Thus, the mixture of diastereomers of silane **5b** was treated with Fleming's procedure[13] for the oxidation of the silicon−carbon bond to give the corresponding alcohol (Scheme 4). Under the acidic reaction conditions, the hemiaminal spontaneously hydrolyzed to benzaldehyde. The highly stereoselective reaction of carbene complex **4** with tributylstannane provides a key intermediate for the transmetalation and trapping of electrophiles. Pearson has shown that similar stannanes generated through a chiral sulfone can be lithiated and then quenched with various electrophiles to construct tertiary or quaternary stereocenters with a high degree of selectivity.[14] We found that tin−lithium exchange and trapping with cyclohexanone occurred with high diastereoselectivity comparable with that reported by Pearson, but trapping with the previously untested ethyl iodide failed to give high diastereoselectivity. The exchange and trapping with cyclohexanone was assumed to proceed with overall retention, in accord with the observations of Pearson.

The process of 1,1-additions of Si−H and Sn−H bonds into chiral Fischer carbene complexes is a simple, effective way to generate chiral silanes and stannanes. The synthetic utility of these complexes has been demonstrated, but other applications of this reaction and further elucidation of its mechanistic details will remain the subject of future study.

Experimental Section

General Considerations. All synthetic reactions were performed in flame-dried glassware under an argon atmosphere. Silane/stannane reactions were run open to the atmosphere. Reactions run under CO atmosphere were performed in sealed Kontes flasks under 1 atm of CO at room temperature. THF was distilled under nitrogen from sodium/benzophenone ketyl. CH_2Cl_2 was distilled under nitrogen from CaH_2. Hexane used in reactions (Optima grade, Fisher Scientific) was stored over 4 Å molecular sieves. (Phenylmethoxy)pentacarbonylchromium(0) and methyl[(4*R*,5*S*)-1,5-dimethyl-4-phenyl-2-imidazolidinone]tetracarbonylchromium(0) were prepared by literature methods. Other reagents were obtained from commercial suppliers and used as received. The preparation of carbene complexes **4**, **6**, and **9** will be described separately.[8]

Representative Procedure for Silylation of Carbene Complexes 4, 6, and 9. Reaction of 4 with Phenyldimethylsilane To Give 5b. Carbene complex **4** (1.327 g, 3.00 mmol) and phenyldimethylsilane (0.818 g, 0.92 mL, 6.00 mmol) were suspended in 20 mL of hexane in a round-bottom flask equipped with a reflux condenser and heated to reflux for 18 h in the presence of air, until the carbene complex had disappeared and green precipitate had formed. The reaction mixture was filtered through Celite to give a yellow-green

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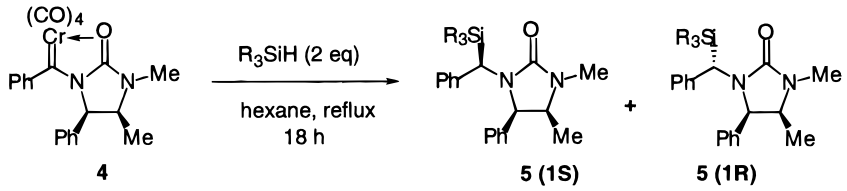
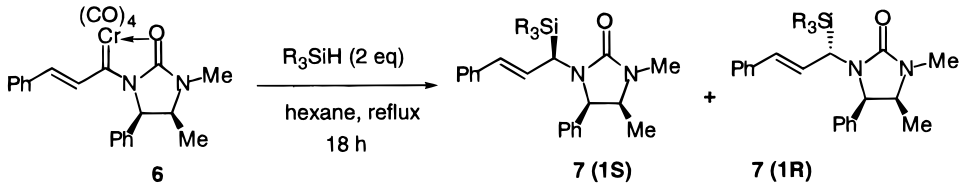
(10) For leading references, see: Reed, A. D.; Hegedus, L. S. *Organometallics* **1997**, *16*, 2313.
(11) For previous mechanistic studies see refs 2c,d.
(12) The reaction flask was sealed at room temperature under 1 atm of CO and then heated to 80 °C.
(13) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229.
(14) Pearson, W. H.; Lindbeck, A. C.; Kampf, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 2622.

Scheme 2



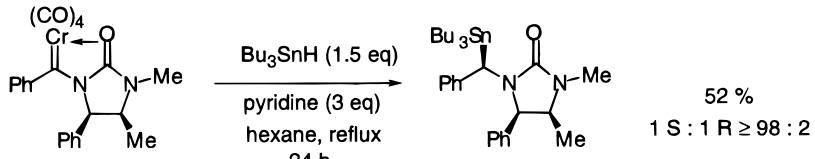
4 **5 (1S)** **5 (1R)**

Product	R_3	Yield	1 S : 1 R
5a	Ph_3	55	≥ 98 : 2
5b	$PhMe_2$	66	67 : 33
5c	Et_3	88	67 : 33



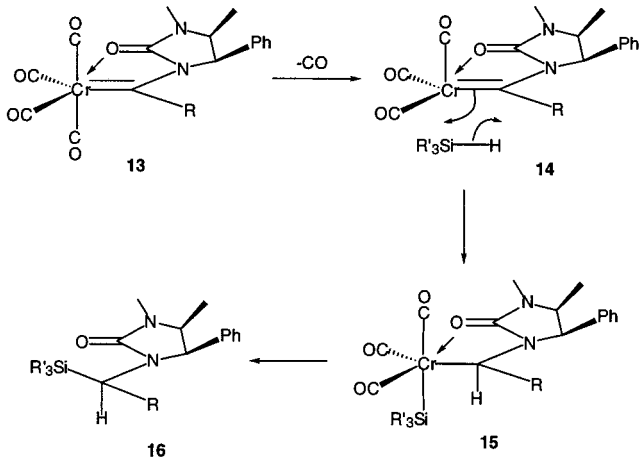
6 **7 (1S)** **7 (1R)**

Product	R_3	Yield	1 S : 1 R
7a	Ph_3	54	85 : 15
7b	$PhMe_2$	57	64 : 36
7c	Et_3	42	64 : 36

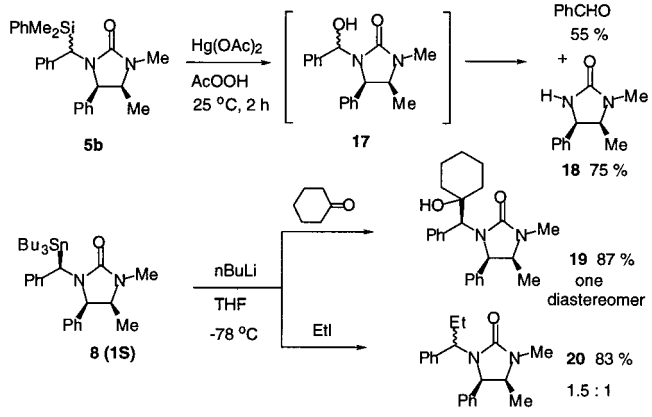


4 **8 (1S)**

Scheme 3



Scheme 4



solution, which was diluted to 150 mL with hexane. Chloroform (2 mL) was added, and the solution was stirred in the air until it was colorless (24 h). The green precipitate was filtered off through Celite, and the solution was concentrated to a white solid. ^{1}H NMR analysis of this solid showed a 2:1 ratio of diastereomers. The solid was purified by chromatography on silica gel (5:1 hexane/EtOAc, PMA/UV visualization). Material at $R_f = 0.5$ was collected and concentrated to a white powdery solid. Yield of **5b**: 816 mg (66%) as mixture of isomers. Minor isomer data are given in italics. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.29 (s, 3H), *0.35 (s, 3H)*, 0.45 (s, 3H), *0.56 (s, 3H)*, 0.61 (d, 3H, J = 6.6 Hz), *0.68 (d, 3H, J = 6.6 Hz)*, 2.69 (s, 3H), *2.80 (s, 3H)*, *3.41 (s, 1H)*, 3.46 (s, 1H), 3.47 (overlapping quintet, 1H, J = 6.6 Hz), *3.66 (quintet, 1H, J = 6.6 Hz)*, *4.33 (d, 1H, J = 9.1 Hz)*, 4.45 (d, 1H, J = 9.1 Hz), 6.90−7.43 (m). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.33, *−3.11*, −2.58, *−2.34*, 14.17, *14.91*, 29.00, *29.10*, 51.67, 54.97, 56.05, 56.29, 61.96, 67.49, 125.40, 126.08, 127.38, 127.51, 127.71, 127.80, 128.00, 128.17, 128.61, 128.66, 128.72, 128.94, 134.39, 134.53, 138.94, 139.15, 156.14, 157.22. IR (neat film): 3105−2800 (w), 1685 (s), 1441 (m), 1260 (w), 1215 (w), 698 (w) cm^{-1}. EI mass spec: m/z 414 (M^+, 100), 399 (20), 337 (27), 295 (38), 192 (30), 135 (86), 118 (24). $R_f = 0.5$ (5:1 hexane/EtOAc), white powder, mp 155−156 °C.

5a: 55% yield, one diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.58 (d, 3H, J = 6.6 Hz), 2.50 (s, 3H), 3.29 (quintet, 1H, J = 2.6 Hz), 4.37−4.41 (m, 2H), 6.96−7.08 (m, 10H), 7.25−7.35 (m, 12H), 7.54 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.62, 29.07, 52.92, 56.18, 67.14, 125.66, 127.51, 127.63, 127.84, 128.72, 128.92, 129.06, 129.23, 135.17, 136.58, 136.77, 140.89, 169.55. IR (neat film): 3100−2650, 1700 (s), 1440 (m), 1429 (m), 1104 (m), 698 (s) cm^{-1}. EI mass spec: m/z 538 (M^+,

100), 279 (29), 259 (71), 240 (20), 181 (18), 132 (15). $R_f = 0.5$ (5:1 hexane/EtOAc), white needlelike crystals, mp 169−170 °C.

5c: 88% yield, 2:1 ratio of diastereomers. Minor isomer data are given in italics. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.67−0.84 (br m, overlap of both isomers), *2.80 (s, 3H)*, 2.83 (s, 3H), *3.37 (s, 1H)*, 3.40 (s, 1H), 3.65 (quintet, 1H, J = 9.1 Hz), *3.76 (quintet, 1H, J = 9.1 Hz)*, 4.34 (d, 1H, J = 9.1 Hz), *4.58 (d, 1H, J = 9.1 Hz)*, 6.99−7.33 (br m, overlap of both isomers). ^{13}C NMR (100 MHz, $CDCl_3$): δ *3.42*, 3.55, *7.19*, 7.36, 14.27, *14.73*, 28.96, *29.14*, 48.52, *51.82*, 55.87, *56.38*, 62.12, *67.52*, 125.22, 125.97, 126.99, 127.69, 127.80, 128.10, 128.19, 128.34, 128.52, 128.63, 128.92, 136.34, 136.42, 141.18, 142.84, 162.09. IR (thin film): 2952−2874, 1701 (s), 1600 (m), 1438 (s), 1257 (s), 1010 (m) cm^{-1}. EI mass spec: m/z 394 (M$^+$, 60), 365 (100), 277 (13), 145 (24), 105 (20), 87 (30). $R_f = 0.55$ (5:1 hexane/EtOAc), colorless oil.

7a: 54% yield, 5.5:1 ratio of separable diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$): major isomer, δ 0.63 (d, 3H, J = 6.5 Hz), 2.46 (s, 3H), 3.23 (quintet, 1H, J = 6.5 Hz), 4.03 (d, 1H, J = 9.3 Hz), 4.25 (d, 1H, J = 9.1 Hz), 5.90 (d, 1H, J = 15.9 Hz), 6.69 (dd, 1H, J = 9.1, 15.9 Hz), 7.03−7.67 (m, 25H); minor isomer, δ 0.58 (d, 3H, J = 6.6 Hz), 2.76 (s, 3H), 3.51 (quintet, 1H, J = 6.5 Hz), 4.36 (d, 1H, J = 9.3 Hz), 4.65 (d, 1H, J = 9.1 Hz), 6.12 (m, 2H), 7.07−7.60 (m, 25H). ^{13}C NMR (125 MHz, $CDCl_3$): major isomer, δ 14.82, 29.12, 50.76, 56.24, 65.83, 126.28, 126.78, 127.62, 127.96, 128.08, 128.22, 128.38, 128.89, 129.38, 129.42, 134.40, 136.50, 136.67, 137.64, 161.27; minor isomer, δ 14.34, 29.02, 48.05, 56.15, 62.57, 126.15, 126.57, 127.64, 127.88, 127.93, 128.18, 128.33, 128.38, 128.45, 129.35, 130.71, 134.54, 136.29, 136.45, 161.45. IR (thin film): 3070−2800 (m), 1698 (s), 1483 (m), 1428 (m), 1400 (m), 1265 (m), 1252 (m), 1108 (m), 730 (s), 700 (s) cm^{-1}. EI mass spec: m/z 564 (M$^+$, 100), 487 (47), 369 (8), 305 (33), 259 (73), 181 (20), 115 (23). $R_f = 0.33$ (major), 0.24 (minor) (5:1 hexane/EtOAc), white semisolid.

7b: 57% yield, 1.8:1 ratio of diastereomers. Minor isomer data are given in italics. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.40 (s, 3H), *0.51 (s, 3H)*, 0.53 (s, 3H), *0.56 (s, 3H)*, *0.64 (d, 3H, J = 6.6 Hz)*, 0.68 (d, 3H, J = 6.6 Hz), *2.69 (s, 3H)*, 2.79 (s, 3H), 3.20 (m, 2H), *3.41 (quintet, 1H, J = 6.5 Hz)*, 3.70 (quintet, 1H, J = 6.5 Hz), *4.20 (d, 1H, J = 8.9 Hz)*, 4.64 (d, 1H, J = 9.0 Hz), *5.84 (d, 1H, J = 15.9 Hz)*, 5.99 (d, 1H, J = 15.9 Hz), 6.11 (dd, 1H, J = 9.0, 15.9 Hz), *6.58 (m, 1H)*, 7.21−7.48 (br m). ^{13}C NMR (125 MHz, $CDCl_3$): δ −3.72, −3.36, −3.15, −0.1, 14.47, 14.58, 28.16, 28.95, 49.67, 52.04, 56.01, 56.31, 62.25, 65.68, 126.09, 126.14, 126.79, 127.05, 127.48, 127.58, 128.01, 128.06, 128.31, 128.34, 128.47, 128.67, 128.77, 129.76, 134.13, 134.26, 136.45, 161.47, 161.77. IR (thin film): 3075−2800 (w), 1699 (s), 1440 (m), 1402 (m), 1251 (m), 817 (m), 701 (s) cm^{-1}. EI mass spec: m/z 440 (M$^+$, 100), 425 (38), 363 (12), 321 (9), 305 (28), 271 (34), 245 (14), 193 (16), 135 (88), 105 (42). $R_f = 0.32$ (5:1 hexane/EtOAc), colorless oil.

7c: 42% yield, 1.8:1 ratio of diastereomers. Minor isomer data are given in italics. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.71−0.80 (m, 9H), 0.92−0.97 (m, 9H), *2.75 (s, 3H)*, 2.80 (s, 3H), 3.14 (d, 1H, J = 8.0 Hz), *3.20 (d, 1H, J = 8.0 Hz)*, 3.72 (quintet, 1H, J = 8.0 Hz), *4.49 (d, 1H, J = 8.7 Hz)*, 4.69 (d, 1H, J = 8.7 Hz), 5.79 (d, 1H, J = 14.0 Hz), 6.11 (m, 1H), 6.56 (m,1H), 7.16−7.37 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$): δ *3.22*, 3.58, *7.53*, 7.73, 14.45, *14.51*, 28.76, *29.04*, 47.45, *49.90*, 55.90, *56.49*, 62.52, *66.05*, 126.06−129.27 (overlapping signals), 136.45, *137.27*, 161.48, *161.71*. IR (thin film): 2965−2875 (s), 2236 (w), 1699 (s), 1447 (s), 1401 (s), 1252 (m), 969 (m), 728 (s) cm^{-1}. EI mass spec: m/z 420 (M$^+$, 100), 405 (34), 391 (69), 329 (14), 305 (28), 273 (12), 205 (22), 115 (56), 105 (65), 103 (67), 75 (54). $R_f = 0.43$ (5:1 hexane/EtOAc), colorless oil.

Representative Procedure for Stannylation of Carbene Complexes 4, 6, and 9. Reaction of 4 with Tributyltin Hydride To Give 8. Carbene complex **4** (2.212 g, 5 mmol) was suspended in 50 mL of hexane. Tributyltin hydride (2.183 g, 2.02 mL, 7.5 mmol) and pyridine (0.791 g, 0.81 mL, 10 mmol) were added, and the reaction mixture was stirred at room temperature. After 18 h, the lemon yellow reaction mixture was filtered through Celite and the filtered solution was concentrated to a thick green oil. Only one diastereomer was seen in the crude ^{1}H NMR. The oil was chromatographed on silica gel (10:1 hexane/EtOAc, UV/PMA visualization) to give the product as a colorless oil. Yield: 1.48 g (52%). Spectral data for **8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.72 (d, 3H, J = 6.5 Hz), 0.77−0.85 (m, 12H), 1.21 (q, 9H, J = 7.3 Hz), 1.28−1.35 (m, 6H), 2.85 (s, 3H), 3.54 (s, 1H), 3.74 (quintet, 1H, J = 2.2 Hz), 4.66 (d, 1H, J = 8.9 Hz), 6.93−7.08 (m, 10H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 12.10, 13.76, 14.30, 27.82, 28.27, 29.35, 51.40, 56.60, 67.63, 124.20, 125.55, 125.64, 127.99, 128.04, 128.10, 129.20, 137.14, 146.37; IR (neat film) 2955 (s), 2920 (s), 2870 (m), 2852 (m), 1691 (s), 1456 (m), 1440 (s), 1403 (m), 1259 (w), 701 (m) cm^{-1}; EI mass spec m/z 570 (M$^+$, 29, ^{120}Sn), 514 (100, ^{120}Sn), 399 (14, ^{120}Sn), 279 (73), 222 (12), 177 (10, ^{120}Sn), 132 (20), 91 (17); $R_f = 0.64$ (10:1 hexane/EtOAc), $[\alpha]_D = -133.16$ (c = 0.01, $CHCl_3$), colorless oil.

10: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.71 (d, 3H, J = 6.5 Hz), 0.81−0.90 (m, 15H), 1.28 (q, 9H, J = 7.4 Hz), 1.43−1.47 (m, 8H), 2.54 (t, 1H, J = 6.6 Hz), 2.70 (s, 3H), 3.69 (quintet, 1H, J = 6.5 Hz), 4.73 (d, 1H, J = 8.8 Hz), 7.14 (m, 2H), 7.30−7.37 (m, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 10.64, 11.51, 12.23, 13.40, 14.32, 23.86, 27.57, 29.20, 42.88, 55.70, 62.60, 127.93, 128.33, 128.42, 136.70, 162.18; IR (neat film) 2955 (s), 2922 (s), 1691 (s), 1440 (m), 1253 (w), 759 (w), 701 (w) cm^{-1}; R_f = 0.38 (10:1 hexane/EtOAc), colorless oil.

11: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.74 (d, 3H, J = 6.6 Hz), 1.52 (d, 3H, J = 6.6 Hz), 2.79 (s, 3H), 3.82 (quintet, 1H, J = 6.6 Hz), 4.30 (dt, 1H, J = 6.6, 14.5 Hz), 4.78 (d, 1H, J = 8.8 Hz), 6.77 (d, 1H, J = 14.5 Hz), 7.10−7.35 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.04, 15.13, 28.70, 55.70, 60.55, 103.05, 124.15, 128.05, 128.52, 135.91, 146.07, 194.07; IR (neat film) 2980−2860 (m), 1700 (s), 1671 (s), 1430 (s), 1258 (m), 1055 (w), 947 (m), 757 (m), 695 (m) cm^{-1}, R_f = 0.4 (2:1 hexane/EtOAc), white crystalline solid, mp 104−105 °C.

Oxidation and Hydrolysis of 5b. Silylated product **5b** (816 mg, 2.00 mmol) was dissolved in 15 mL of peracetic acid solution (30 wt % in dilute acetic acid, Aldrich), and mercury(II) acetate (956 mg, 3.0 mmol) was added in one portion. The reaction mixture was stirred for 2 h and then diluted with 50 mL of water and 150 mL of ether and quenched by adding 2.0 g of $Na_2S_2O_3$ and stirring for 10 min. The mixture was poured into a separatory funnel, and the organic layer was back-extracted with ether (1 × 50 mL). The combined organic layers were washed with $NaHCO_3$ (3 × 50 mL), water (2 × 50 mL), and brine (1 × 50 mL), dried with $MgSO_4$, and concentrated on a rotary evaporator (with care to keep the water bath below 20 °C) to a sticky white solid which yellowed on exposure to air. The solid was washed with pentane, and the pentane was concentrated cold to give benzaldehyde (123 mg, 55%). The remaining yellow solid was dried under high vacuum and then matched by ^{1}H NMR to the imidazolidinone chiral auxiliary **18** (285 mg, 75.0%).

Lithiation and Trapping of 8 with Cyclohexanone. Stannane **8** (569 mg, 1.0 mmol) was dissolved in 10 mL of THF at −78 °C. A solution of ^{n}BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol) was added, and the pale yellow solution of lithiate was stirred for 15 min. Cyclohexanone (98 mg, 0.104 mL, 1.0 mmol) was added neat via syringe, and the yellow color disappeared within 30 s. The reaction mixture was stirred for 30 min and then quenched with HOAc (0.057 mL, 1.0 mmol). The reaction mixture was warmed to room temperature and then diluted with 10 mL of water. This mixture was poured into a separatory funnel and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with $NaHCO_3$ (1 × 20 mL), water (2 × 25 mL), and brine (1 × 20 mL), dried over $MgSO_4$, and concentrated to a thick white semisolid. ^{1}H NMR of the crude product showed only one

diastereomer (benzylic proton). This solid was chromatographed on silica gel (5:1 hexane/EtOAc, PMA visualization) to give the product **19** as a filmy white semisolid. Yield: 331 mg (87.3%). Spectral data for **19**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.74 (d, 3H, $J = 6.6$ Hz), 0.92−1.5 (multiplets corresponding to ring CH_2's, 10H), 2.81 (s, 3H), 3.65 (s, 1H), 3.67 (quintet, 1H, $J = 2.7$ Hz), 4.29 (d, 1H, $J = 9.4$ Hz), 6.71 (s, 1H), 7.21−7.40 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.95, 21.51, 25.93, 28.72, 36.37, 36.64, 56.13, 63.15, 70.71, 71.14, 127.53, 128.10, 128.59, 128.66, 129.75, 135.79, 138.17, 162.09; IR (neat film) 3272 (m), 2932 (m), 1699 (s), 1444 (m), 1264 (m), 992 (m), 700 (m) cm^{-1}; EI mass spec *m*/*z* 378 (M^+, 3), 335 (11), 280 (100), 265 (22), 189 (23), 163 (15), 132 (15), 119 (45), 106 (18), 91 (20); $R_f = 0.32$ (5:1 hexane/EtOAc).

Lithiation and Trapping of 8 with Iodoethane. Stannane **8** (569 mg, 1.0 mmol) was dissolved in 10 mL of THF at −78 °C. A solution of ^{n}BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol) was added, and the pale yellow solution of lithiate was stirred for 15 min. Iodoethane (0.08 mL, 0.156 g, 1.0 mmol) was added neat via syringe, and the reaction mixture was stirred for 30 min. The yellow color faded more slowly than for the cyclohexanone reaction, and the reaction mixture went cloudy. The cold bath was removed, and the reaction mixture was warmed to room temperature with stirring for an additional 30 min and then quenched with HOAc (0.057 mL, 1.0 mmol) and diluted with 10 mL of water.

Aqueous workup as described above gave the crude product as a thick colorless oil, which solidified to white crystals on standing. ^{1}H NMR of the crude product showed a 1.5:1 ratio of diastereomers. The product was chromatographed on silica gel (5:1 hexane/EtOAc, PMA visualization) to give **20** as a colorless oil which solidified on standing. Yield: 256 mg (83.1%). Spectral data for **20**: ^{1}H NMR (1.5:1 mixture of diastereomers) (500 MHz, $CDCl_3$) δ 0.66−0.70 (m, 6H), 0.73 (t, 3H, $J = 7.4$ Hz), 0.92 (t, 3H, $J = 7.4$ Hz), 2.15 (m, 2H), 2.42 (m, 2H), 2.73 (s, 3H), 2.74 (s, 3H), 3.52 (quintet, 1H, $J = 6.5$ Hz), 3.64 (quintet, 1H, $J = 6.6$ Hz), 4.09 (d, 1H, $J = 8.9$ Hz), 4.21 (t, 1H, $J = 9.0$ Hz), 4.46 (d, 1H, $J = 8.9$ Hz), 4.98 (t, 1H, $J = 8$ Hz), 7.02−7.32 (m, 20H); ^{13}C NMR (1.5:1 mixture) (125 MHz, $CDCl_3$) δ 11.43, 11.85, 14.61, 14.64, 22.29, 25.11, 25.24, 28.70, 28.84, 31.64, 56.09, 56.65, 57.33, 59.03, 60.03, 60.14, 61.30, 127.05, 127.45, 127.72, 128.03, 128.10, 128.25, 128.41, 128.53, 136.68, 138.63, 139.68, 140.84, 161.70; IR (neat film) 2968 (m), 2932 (m), 1697 (s), 1428 (s), 1400 (m), 1252 (m), 761 (m), 701 (s) cm^{-1}; EI mass spec *m*/*z* 308 (M^+, 2), 279 (100), 222 (4), 132 (6), 91 (8); $R_f = 0.23$ (5:1 hexane/EtOAc).

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Supporting Information Available: Figures giving ^{1}H NMR spectral data for all new compounds and text and tables giving crystal structure data for **5a**, including atomic parameters, anisotropic thermal parameters, bond distances, and bond angles (21 pages). Ordering information is given on any current masthead page.

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