Reaction of Allylstannanes with α,β-Unsaturated Acyliron Complexes: Stereoselective Synthesis of Cyclopentane Derivatives†,[1]

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The reaction between allylstannanes and α,β-unsaturated acyliron complexes has been examined. When the reaction is conducted in the presence of Lewis acids, [3 + 2] cycloaddition products are obtained with extremely high degrees of stereoselectivity. If the iron complex is alkylated prior to addition of the allylstannane, products resulting from the Michael addition of allyl anion are obtained. The [3 + 2] cycloadducts contain acyliron and organotin functionalities. The acyliron group is easily converted to the corresponding ester by treatment with *N*-bromosuccinimide in the presence of alcohols. The tributyltin group can be converted to a hydroxy group by treatment with bromine followed by treatment with peracids and amine bases; this transformation occurs with complete retention of stereochemistry. The high stereoselectivity can be explained by reaction through a synclinal orientation of allylstannane and the acyliron complex. The question of allylation vs cycloaddition has been attributed to the relative reactivity of the intermediate enolate derivatives.

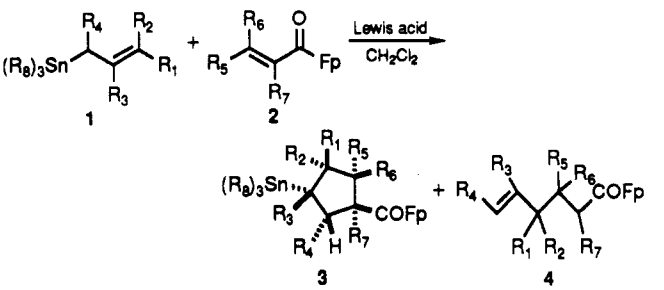
Introduction

Cycloaddition reactions have provided synthetic organic chemists with a highly versatile and convergent method for the construction of ring systems, the classical example being the Diels–Alder reaction for the construction of six-membered rings. Until recently, cycloaddition reactions only existed for the formation of three-, four-, and six-membered all-carbon ring systems, while few reactions existed for the synthesis of five-membered ring systems. Over the last 10 years, exciting developments in this area have been reported, highlighted by the discovery of reactions that allow for cycloaddition-type construction of cyclopentane rings in a single step.[2] In addition to these developments, numerous reports of cycloaddition schemes involving more than one step have also been reported.[2]

Recently, we reported that the reaction of allylstannane derivatives with α,β-unsaturated acyliron complexes leads to the formation of cyclopentane derivatives **3** in fair yield with excellent control of stereoselectivity (Scheme I),[1a] sometimes accompanied by allylation products **4**. The reaction in Scheme I represents a [3 + 2] cycloaddition approach for the synthesis of five-membered rings. Allylstannanes typically react with α,β-unsaturated carbonyl compounds to provide allylation products (e.g. **4**) and not cycloaddition products (e.g. **3**).[3] The formation of **3** is more reminiscent of the chemistry of allyltransition-metal complexes,[4–6] and prior to the initiation of these studies allenylsilanes[7] were the only class of main-group allylmetal compounds known to undergo [3 + 2] cycloaddition reactions. Unlike most of the reactions in ref 2, the cyclopentane ring formed in these reactions contains only sp^3 carbons, and this is a rare example of this type where the five-membered ring is formed with a high degree of stereoselectivity.

The newly formed five-membered ring contains tetraalkyltin and acyliron functionalities. In order for this reaction to be useful for organic synthesis, successful methods must be developed for the cleavage of these substituents. Also, the stereochemical assignments suggested in the original communication of this reaction were based on conformational preferences in five-membered rings, which may not be reliable. By conversion of these organometallic compounds to simpler organic derivatives, a more reliable assignment of the stereochemistry might now be possible. In this paper, we report a detailed investigation into the scope, limitations, mechanism, and

Scheme I



allylstannanes (**1**)

A: R_8 = Bu; R_1, R_2, R_3, R_4 = H
B: R_8 = Bu; R_1 = Ph; R_2, R_3, R_4 = H
C: R_8 = Bu; R_3 = CH_3; R_1, R_2, R_4 = H
D: R_8 = Bu; R_1 = CH_3; R_2, R_3, R_4 = H
E: R_8 = Bu; R_2, R_4 = $-CH_2CH_2-$; R_1, R_3 = H
F: R_8 = Bu; R_1, R_4 = CH_3; R_2, R_3 = H
G: R_8 = CH_3; R_1, R_2, R_3, R_4 = H
H: R_8 = Ph; R_1, R_2, R_3, R_4 = H

acyliron complexes (**2**)

A: R_5, R_6, R_7 = H
B: R_7 = CH_3; R_5, R_6 = H
C: R_5 = CH_3; R_6, R_7 = H
D: R_6 = CH_3; R_5, R_7 = H
E: R_5, R_6 = CH_3; R_7 = H

adducts **3**, **4**, **6–8**, **14**, **15**

A: R_8 = Bu; R_1, R_2, R_3, R_4, R_5, R_6, R_7 = H
B: R_8 = Bu; R_1 = Ph; R_2, R_3, R_4, R_5, R_6, R_7 = H
C: R_8 = Bu; R_3 = CH_3; R_1, R_2, R_4, R_5, R_6, R_7 = H
D: R_8 = Bu; R_1 = CH_3; R_2, R_3, R_4, R_5, R_6, R_7 = H
E: R_8 = Bu; R_2–R_4 = $-CH_2CH_2-$; R_1, R_3, R_5, R_6, R_7 = H
F: R_8 = Bu; R_1, R_4, R_5 = CH_3; R_2, R_3, R_6, R_7 = H
G: R_8 = CH_3; R_1, R_2, R_3, R_4, R_5, R_6, R_7 = H
H: R_8 = Ph; R_1, R_2, R_3, R_4, R_5, R_6, R_7 = H
I: R_8 = Bu; R_7 = CH_3; R_1, R_2, R_3, R_4, R_5, R_6 = H
J: R_8 = Bu; R_5 = CH_3; R_1, R_2, R_3, R_4, R_6, R_7 = H
K: R_8 = Bu; R_6 = CH_3; R_1, R_2, R_3, R_4, R_5, R_7 = H
L: R_8 = Bu; R_5, R_6 = CH_3; R_1, R_2, R_3, R_4, R_7 = H
M: R_8 = Bu; R_1 = Ph; R_7 = CH_3; R_2, R_3, R_4, R_5, R_6 = H
N: R_8 = Bu; R_1, R_7 = CH_3; R_2, R_3, R_4, R_5, R_6 = H
O: R_8 = Bu; R_1,R_5 = CH_3; R_2, R_3, R_4, R_6, R_7 = H

† Dedicated to the memory of Professor John K. Stille.

(1) Some of these studies have been reported in preliminary form: (a) Herndon, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 3165–3166. (b) Herndon, J. W.; Wu, C. *Tetrahedron Lett.* **1989**, *30*, 5745–5746. (c) Herndon, J. W.; Wu, C. *Tetrahedron Lett.* **1989**, *30*, 6461–6464. (d) Herndon, J. W.; Wu, C. *Synlett* **1990**, *1*, 411–413.

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Table I. Lewis-Acid-Catalyzed Reactions between Allylstannanes and Acyliron Complexes

entry no.	allylstannane	acyliron complex	Lewis acid	temp/time[a]	substituents 3, 4	yield 3,[b] %	yield of 4, %
1	**1A**	**2A**	Et_2AlCl	25 °C/24 h	**A**	0	0
2	**1A**	**2A**	$EtAlCl_2$	0 °C/0.5 h	**A**	40	0
3	**1A**	**2A**	$MeAlCl_2$	0 °C/0.5 h	**A**	37	0
4	**1A**	**2A**	$AlCl_3$	0 °C/0.5 min	**A**	42	3
5	**1A**	**2A**	$AlBr_3$	−42 °C/2 h	**A**	25	7
6	**1A**	**2A**	$Me_3Al_2Cl_3$	25 °C/24 h	**A**	64 (74)	2
7	**1A**	**2B**	$AlCl_3$	0 °C/5 min	**I**	66 (91)	0
8	**1A**	**2B**	$EtAlCl_2$	25 °C/6 h	**I**	32 (86)	0
9	**1A**	**2B**	$Me_3Al_2Cl_3$	25 °C/24 h	**I**	13 (75)	0
10	**1A**	**2C**	$AlCl_3$	25 °C/2 h	**J**	41 (58)	5
11	**1A**	**2C**	$EtAlCl_2$	25 °C/12 h	**J**	22 (63)	4
12	**1A**	**2D**	$AlCl_3$	0 °C/10 min	**K**	23 (62)	11
13	**1A**	**2E**	$AlCl_3$	25 °C/12 h	**L**	0	0
14	**1B**	**2A**	$AlCl_3$	25 °C/24 h	**B**	34 (57)	0
15	**1B**	**2B**	$AlCl_3$	25 °C/24 h	**M**	0	0
16	**1C**	**2A**	$AlCl_3$	−78 °C/5 min	**C**	0	11
17	**1D**[c]	**2A**	$AlCl_3$	25 °C/1 h	**D**	52 (56)	trace
18	**1D**[c]	**2B**	$AlCl_3$	25 °C/2 h	**N**	51 (87)	0
19	**1E**	**2A**	$AlCl_3$	−78 °C/1 h	**E**	27 (40)	0
20	**1F**	**2C**	$EtAlCl_2$	25 °C/40 min	**F**	25 (52)	0
21	**1G**	**2A**	$AlCl_3$	0 °C/1.5 h	**G**	27	0
22	**1H**	**2A**	$AlCl_3$	25 °C/24 h	**H**	8 (15)	0

[a] All reactions were allowed to proceed to completion or until no further progress as diagnosed by TLC analysis. [b] The yield in parentheses refers to the yield based on recovered complex **2**. [c] A 65:35 trans–cis mixture was employed.

demetalation studies of this potentially highly useful cycloaddition reaction.

Results

Reaction of Allyltributyltin with α,β-Unsaturated Acyliron Complexes. The reaction of allylstannanes with a variety of α,β-unsaturated acyliron complexes and Lewis acids has been examined; the results are presented in Table I. The reaction of the two unsubstituted partners allyltributyltin (**1A**) and α,β-unsaturated acyliron complex **2A** and ethylaluminum dichloride provided compound **3A** as a single stereoisomer in 40% yield. The cycloadduct was assigned as the isomer in which the substituents are trans, for reasons that will be outlined below; this assignment is opposite to that suggested in ref 1a. An even faster reaction occurred with freshly sublimed aluminum chloride as the catalyst to produce compound **3A** in 42% yield, accompanied by a small amount (3%) of open-chain product **4A**. Diethylaluminum chloride was not an effective catalyst for the reaction, but methylaluminum sesquichloride was the optimal catalyst for the reaction, leading to compound **3A** in 64% yield. Apparently, the low yields of the reaction are due to decomposition of the allylstannane, perhaps through a transmetalation reaction with the Lewis acid.[8] Cycloadduct **3A** slowly decomposes upon prolonged exposure to the aluminum chloride and reacts exothermically with untreated (1% triethylamine) silica gel. A variety of other Lewis acids were tested in the cycloaddition reaction. Titanium tetrachloride, boron trifluoride etherate, tin tetrachloride, zinc chloride, cerium trichloride, magnesium chloride, dimethylaluminum chloride, and trimethylsilyl triflate all failed to catalyze the reaction between **1A** and **2A** to any extent, while aluminum bromide and methylaluminum dichloride were effective catalysts but less efficient than aluminum chloride.

Reaction of allyltributyltin with the methacryloyliron complex **2B** was considerably slower than the corresponding reaction involving the acryloyliron complex **2A**. Although the reaction was slower, the overall yield in these systems was typically better; the starting iron complex and the product did not suffer from decomposition reactions, and the yields based on recovered starting material were respectable. This reaction also led exclusively to the isomer where the tributylstannyl and acyliron groups were trans. Methylaluminum sesquichloride was not an effective catalyst for the reaction between complex **2B** and allyltributyltin.

The reaction employing crotonyliron complexes **2C** and **2D** was equally sluggish; however, this cycloadduct appeared to be subject to decomposition reactions, as was the case with acryloyliron complex **2A**. The yield based on recovered starting material was also poor when complexes **2C,D** were employed. When these reactions were performed at 25 °C for short times (5 min), they were stereospecific, and the relative configurations between acyliron and $R_{5,6}$ were identical in the reactants and the product. When the reaction between allyltributyltin and complex **2D** was performed at 25 °C for an extended period (1 h), mixtures of **3J,K** were obtained. Aluminum chloride induced the conversion of **2D** to **2C**, which might account for the loss of stereospecificity seen at longer reaction times. In both of these reactions, a single stereoisomer at tin was obtained. Further substitution of the double bond of the acyliron complex produced a complex (e.g. **2E**) that is unreactive to allylstannanes. When one of the CO ligands at iron was replaced by a triphenylphosphine, the resulting complex was no longer reactive to allyltributyltin and aluminum chloride.

(2) See: Hudlicky, T.; Fleming, A.; Radesca, L. *J. Am. Chem. Soc.* **1989**, *111*, 6691–6707 and references therein.
(3) Yamamoto, Y.; Nishii, S. *J. Org. Chem.* **1988**, *53*, 3597–3603.
(4) For examples using iron, see: (a) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495–3507. (b) Bucheister, A.; Klemarczyk, P.; Rosenblum, M. *Organometallics* **1982**, *1*, 1679–1684. (c) Raseta, M. E.; Cawood, S. A.; Welker, M. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8268–8270.
(5) For examples using group 6 and 7 metals, see: (a) William, J. P.; Wojcicki, A. *Inorg. Chem.* **1977**, *16*, 3116–3124. (b) Bell, P.; Wojcicki, A. *Inorg. Chem.* **1981**, *20*, 1585–1592. (c) Lee, G.-H.; Peng, S.-M.; Yang, G.-M.; Lush, S.-F.; Liu, R. S. *Organometallics* **1989**, *8*, 1106–1111.
(6) For an example using platinum, see: Calligaris, M.; Nardin, G.; Carturan, G.; Wojcicki, A. *Inorg. Chim. Acta* **1981**, *54*, L285–286.
(7) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935–947.
(8) Transmetalation of allyltributyltin with $SnCl_4$, a weaker Lewis acid than $AlCl_3$, is very rapid at −78 °C: Denmark, S. E.; Wilson, T.; Wilson, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 984–986. Precomplexation of the carbonyl group with the Lewis acid appears to suppress this process: Keck, G. E.; Andrus, M. B.; Castellino, S. *J. Am. Chem. Soc.* **1989**, *111*, 8136–8141.

Table II. Reaction of Allylstannanes with Cationic α,β-Unsaturated Acyliron Complexes

entry no.	allylstannane	acyliron complex	substituents 4	yield of 4,[a] %	yield of 6, %	anti:syn
1	1A	2C	J	48 (63)	89	
2	1D	2C	O	47 (62)		75:25
3	1D	2D	O	64 (77)	69	75:25
4	1A	2B	I	45 (71)	94	

[a] The yield in parentheses refers to the yield based on recovered starting material.

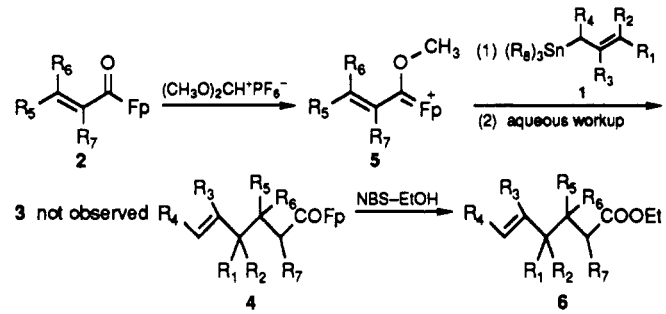
Substitution of the Allylstannane. Reaction of crotyltributyltin (**1D**; 65/35 trans/cis) with acryloyliron complex **2A** led to the five-membered ring adduct **3D** as a single stereoisomer. The reaction of cinnamyltributyltin (**1B**) with complex **2A** was considerably more sluggish, but a single stereoisomer (**3B**) was obtained from the reaction in this case as well. The reaction of methallyltributyltin (**1C**) with complex **2A** produced only the open-chain compound **4C** in 10% yield. Cyclopentenyltributyltin (**1E**) was highly reactive with acryloyliron complex **1A**, producing the single isomer **3E** in low yield. Predominately (>80%) a single compound was obtained from the reaction between allylstannane **1F** and the crotonyliron complex **2C**.

Reaction of Allylstannanes with Cationic Alkoxycarbene–Iron Complexes. Electrophilic activation of acyliron complexes can also be achieved by alkylation of the oxygen atom and conversion to the cationic alkoxycarbene–iron complex (**5**). Unlike simple acylcyclopentadienyldicarbonyliron complexes, the α,β-unsaturated acyliron complexes were not converted to the corresponding methoxycarbene complexes upon treatment with methyl triflate.[9] The more reactive alkylating agent dimethoxycarbenium hexafluorophosphate provided the corresponding carbene complexes upon stirring at 0 °C for 15 min.[10] Reaction of allylstannanes with these complexes did not lead to five-membered ring products but rather to open-chain products **4** after treatment with sodium iodide/aqueous acetone. This reaction appears to be quite general in the examples studied (Table II). The diastereoselectivity of the reaction between crotyltributyltin (**1D**) and the *trans*-crotonyliron complex **2C** was mediocre, giving compound **4O** as a 75:25 mixture of diastereomers; the major diastereomer was assigned as anti by comparison of the ^{1}H NMR spectrum of ethyl ester **6O** (mixture of both isomers) with that reported by Yamamoto.[3] The diastereoselectivity is comparable to that observed by Yamamoto in the reaction of crotyltributyltin with 3-penten-2-one, catalyzed by titanium tetrachloride.[3]

Variation of the Metal. Allyltributyltin was the superior reagent to effect [3 + 2] cycloaddition. Allyltrimethyltin underwent the [3 + 2] cycloaddition reaction at a considerably lower rate and gave much lower yields of cycloadduct. Allyltriphenyltin was hardly reactive at all, and reaction with iron complex **2A** and aluminum chloride gave only a trace amount of the [3 + 2] cycloadduct.

A brief examination of the effect of metals was also undertaken. Reaction of allyltrimethylsilane with acyliron complex **2A** and aluminum chloride led to hexenoyliron complex **4A** in low yield (35%). Reaction of **2A** with the silicon analogue was noticeably slower than the analogous

Scheme II



Scheme III

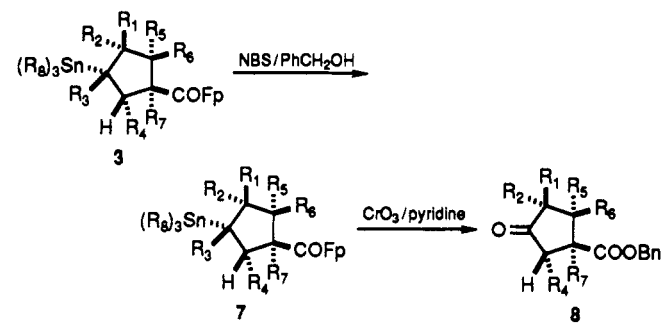


Table III. Reaction of the [3 + 2] Cycloadducts (7) with CrO_3–Pyridine

entry no.	starting stannane	yield of 7, %	yield of 8, %
1	3A	91	21
2	3I	61	14
3	3J	70	18
4	9		34 (4-phenyl-2-butanone)

reaction with allyltributyltin (**1A**). The analogous reaction with allyltributylgermane afforded a mixture of the five-membered-ring germanium analogue of **3A** (20%) and open-chain product **4A** (5%). The combination of allyltriphenyllead or allylphenylmercury, complex **2A**, and aluminum chloride led only to decomposition of the allylmetal species.

Demetalation Reactions. Although the acyliron functionality was easily converted to an ester by treatment with *N*-bromosuccinimide and alcohols, the tributylstannyl group was considerably more difficult to cleave. There is a paucity of methods for conversion of a tributyltin group at an unactivated carbon atom into a simple organic group.[11] Among the methods known are oxidation with a large excess of chromic anhydride–pyridine to produce ketones[12] and intramolecular reactions with carbocations in which a three-[13] or five-membered[14] ring is formed. The

(9) (a) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761–3762. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258–264.

(10) (a) Bodnar, T. W.; Cutler, A. R. *Synth. React. Inorg. Met.-Org. Chem.* **1985**, *15*, 31–42. (b) Knors, C. J.; Brinkman, K.; Helquist, P. *Abstracts of Papers*, 193rd National Meeting of the American Chemical Society, Denver, CO; American Chemical Society: Washington, DC, 1987; ORGN 149. (c) Addition of other nucleophiles to **6** has been observed in: Knors, C. J. Ph.D. Dissertation, University of Notre Dame, 1987.

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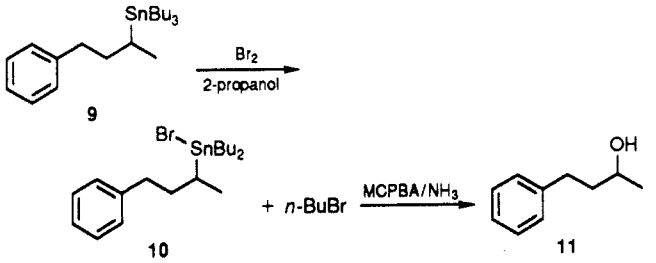
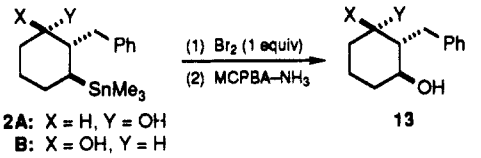
(13) (a) Nicolau, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704–3706. (b) Peterson, D. J.; Robbins, M. D. *Tetrahedron Lett.* **1972**, 2135–2138. (c) Fleming, I.; Urch, C. J. *Tetrahedron Lett.* **1983**, *24*, 4591–4594. (d) Johnson, C. R.; Kadow, J. F. *J. Org. Chem.* **1988**, *52*, 1493–1500.

(14) For leading references, see: MacDonald, T. L.; Delahunty, C. M.; Mead, K.; O'Dell, D. E. *Tetrahedron Lett.* **1989**, *30*, 1473–1476.

Scheme IV



Scheme V



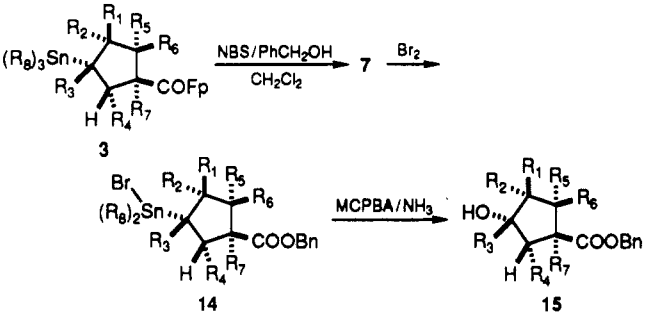
tributyltin group can in theory react with electrophiles such as bromine to effect cleavage of a carbon–tin bond; however, butyl group cleavage is known to proceed faster than cleavage of a secondary alkyl group.[15] Also, successive cleavage reactions of the bromotrialkylstannanes are known to proceed less readily than those for the tetraalkylstannanes.

The reaction of the stannane–ester compounds 7 with chromium trioxide–pyridine afforded the corresponding cyclopentanone derivatives (8) in low yield (Table III). Although this method does lead to cleavage of the carbon–tin bond, low yields were obtained and the stereoselectivity features of the reaction are now lost since the tributyltin-bearing carbon is converted to an sp^2-hybridized carbon.

Methods for the conversion of a triorganosilyl group into an alcohol with retention of configuration have recently been presented.[16] While this work was in progress, a method for the conversion of a trimethylstannyl group to an alcohol was presented with use of hypervalent iodine chemistry.[17] Taking advantage of the ease of cleavage of a butyl group at tin relative to a secondary alkyl group, we felt that the above method for silyl group cleavage might also be feasible for the cleavage of a tributyltin group. Thus, treatment of tetraalkylstannane **9** with bromine led to formation of bromotrialkylstannane **10**. When this reaction was conducted in 2-propanol, only cleavage of the *n*-butyl groups was detected. Subsequent treatment of bromotrialkylstanane **10** with *m*-chloroperoxybenzoic acid (mCPBA) and ammonia provided the alcohol **11** in 86% yield. Substitution of triethylamine for ammonia led to lower yields (61%) of alcohol **11**. Substitution of peroxyacetic acid for mCPBA also led to lower yields (48%) of alcohol **11**.

Compounds **12A,B** were synthesized and subsquently treated with bromine and then mCPBA/ammonia (Scheme V). In both of these cases, the corresponding alcohols **13A,B** were obtained with retention of configuration. A variety of the tetraalkylstannanes obtained from the [3 + 2] cycloaddition reaction were subjected to complete demetalation (NBS–ROH, followed by Br_2, followed by mCPBA) to provide the corresponding alcohols. The

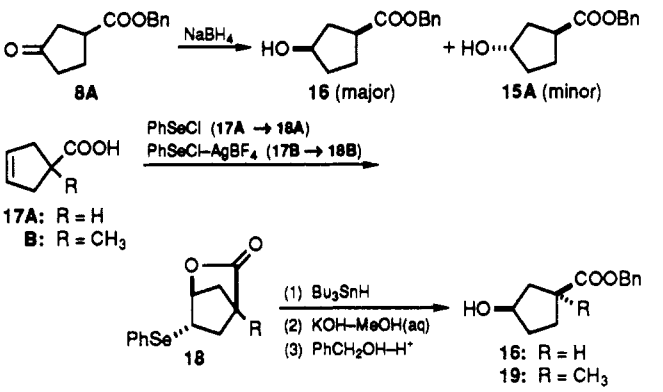
Table IV. Complete Demetalation of the [3 + 2] Cycloadducts



entry no.	stannane	yield of 7, %	yield of 14,[a] %	yield of 15, %
1	**3A**	91		55
2	**3D**	86		67
3	**3I**	61	84	79[b]
4	**3J**	70	77	59[b]
5	**3F**	67	82	55[b]

[a] If no number appears in this column, the trialkylstannyl bromide was not isolated but immediately converted to the corresponding alcohol. [b] The yield is for the conversion of **7** to **15**.

Scheme VI



results are summarized in Table IV. Subsequent stereochemical determinations were performed on the alcohols (**15**) derived from the initial [3 + 2] cycloadducts (**3**) (see below).

Discussion

Stereochemical Assignments. Having established that the conversion of tributylin groups to alcohols proceeds with retention of configuration, we can now assign the stereochemistry of the cycloadducts. The adduct from allyltributyltin and acryloyliron complex **3A** was subjected to the destannylation procedure to provide the alcohol **15A** in 50% overall yield. Alcohol **15A** was identical with the minor isomer obtained from reduction of cyclopentenone **8A**. The sequence of reactions outlined in Scheme VI (**17A** → **16**) provided the major isomer obtained from reduction of cyclopentanone **8A**. Thus, we conclude that compound **3A** had the tributylstannyl and acyliron groups in the trans orientation. A similar approach was used to determine the stereochemistry of cyclopentane **3I**, obtained from allyltributyltin and methacryloyliron complex **2B**. The sequence of reactions in Scheme VI (**17B** → **19**) provided a compound not identical with compound **15I**, suggesting that **15I** has the carbonyl and alcohol groups in the trans position, as in compound **15A**. Reaction of crotyltributyltin with acryloyliron complex **2A** led to a single stereoisomer (**3D**), which subsequently affords a single alcohol stereoisomer (**15D**) upon destannylation. In com-

(15) (a) Boue, S.; Gielen, M.; Nasielski, J.; Lieutenant, J.-P.; Spielmann, R. *Bull. Soc. Chim. Belg.* **1969**, *78*, 135–146. (b) Gielen, M. *Acc. Chem. Res.* **1973**, *6*, 198–202.

(16) (a) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983–990. (b) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229–4232.

(17) Ochiai, M.; Iwaki, S.; Ukita, T.; Matsuura, Y.; Shiro, M.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4606–4610.

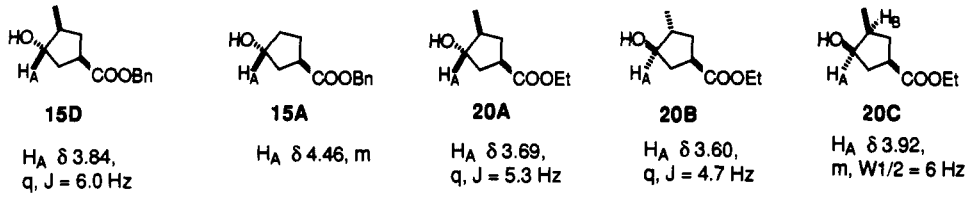


Figure 1. Spectral comparison for compound **15D** and selected compounds.

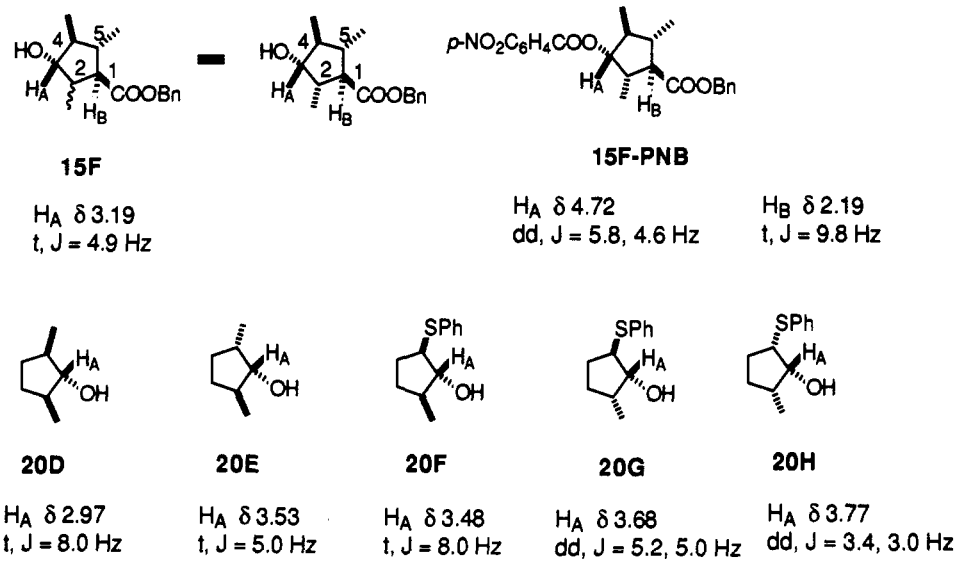


Figure 2. Spectral comparison of compound **15F** and selected compounds.

pound **15D**, H_A appears as a quartet with a coupling constant of 6 Hz, similar to closely related compounds **20A,B**[18a,b] in Figure 1. We have assumed that the alcohol is trans to the carbonyl group as in compounds **15A,I**.

Assuming that the previously established trends hold true for compound **15F**, the only ambiguity in **15F** is the configuration of the methyl group at the 2-position (Figure 2). All evidence suggests that this group is cis to the hydroxy group. In the *p*-nitrobenzoate ester (**15F-PNB**) of **15F**, H_B appears as a triplet at δ 2.19 (overlapping with a 1 H multiplet) with a coupling constant of 9.8 Hz, suggesting that the methyl groups at C_2 and C_5 are cis to each other and trans to the carbonyl group.[18c,d] Comparison of the coupling patterns of H_B of **15F-PNB** and H_A in compounds **20D,F** support this assignment. In compounds **15F** and **15F-PNB**, H_A appears as a doublet of doublets with coupling constants of 5.8 and 4.6 Hz, which is similar to H_A in compounds **20E,G**.

In two cases, **3B,E**, stereochemical information can be obtained from the tin compounds. In norbornene derivative **3E**, the ^{13}C–^{119}Sn coupling constant between C_A and Sn is 48 Hz. According to previous results by Kuivila,[19] a large coupling constant (maximum 66 Hz) between C_A and Sn would be predicted if acyliron and tributyltin are trans, while a small value (0 Hz) would be predicted if they are cis (Figure 3). The value of 48 Hz is far more consistent with the trans isomer. That the acyliron substituent was exo is suggested by the pattern for the H at C_A, a doublet of doublets with values of 7.8 and 4.8 Hz.[20] In

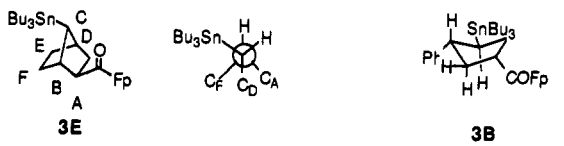
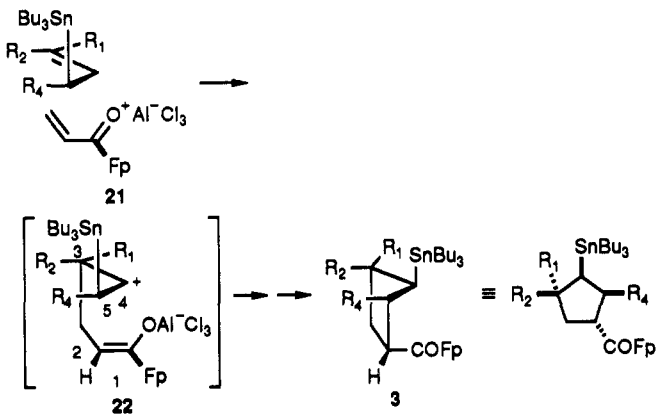


Figure 3. Assignment of stereochemistry in compounds **3B,E**.

Scheme VII



the case of **3B**, the benzylic H appears as a doublet of doublets of doublets with coupling constants of 12.1, 10.6, and 6.6 Hz. Only in certain cases where the H's are in a trans diaxial relationship does the coupling constant in a cyclopentane system exceed 10 Hz,[21] therefore suggesting that phenyl and tributylstannyl are trans. This is the same stereochemistry observed in **3D,N**.

Rationale for the Stereoselectivity. The transition-state model depicted in Scheme VII explains the stereoselectivity observed in the cycloaddition reaction. We have

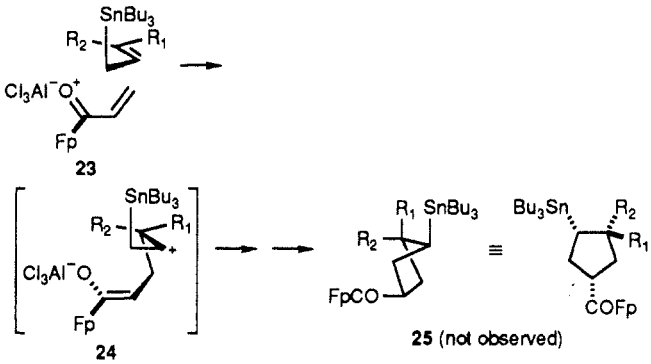
(18) (a) Melchiorre, C.; Giannella, M.; Giardira, D.; Gualtieri, F. *Synth. Commun.* **1975**, *5*, 95–100. (b) Gualtieri, F.; Angeli, P.; Giannella, M.; Melchiorre, C. *Synth. Commun.* **1976**, *6*, 63–68. (c) Rei, M.-H. *J. Org. Chem.* **1978**, *43*, 2173–2178. (d) Harada, T.; Akiba, E.; Tsujimoto, K.; Oku, A. *Tetrahedron Lett.* **1985**, *26*, 4483–4486.

(19) Kuivila, H. G.; Considine, J. L.; Sarma, R. H.; Mynott, R. J. *J. Organomet. Chem.* **1976**, *111*, 179–196.

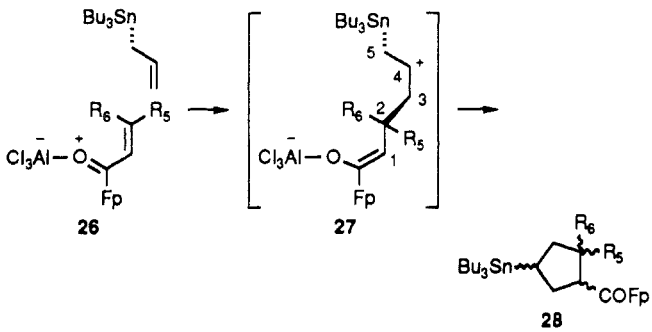
(20) For assignment of stereochemistry in a related system, see: Herndon, J. W. *J. Org. Chem.* **1986**, *51*, 2853–2855.

(21) (a) Miyano, M.; Dorn, C. R.; Mueller, R. A. *J. Org. Chem.* **1972**, *37*, 1810–1818. (b) Miyano, M.; Dorn, C. R. *J. Org. Chem.* **1972**, *37*, 1818–1823.

Scheme VIII



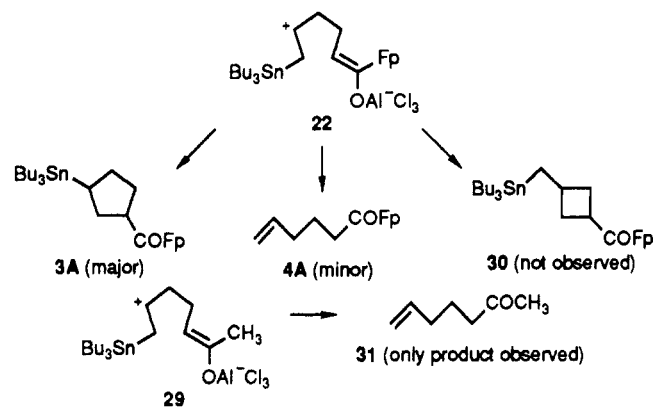
Scheme IX



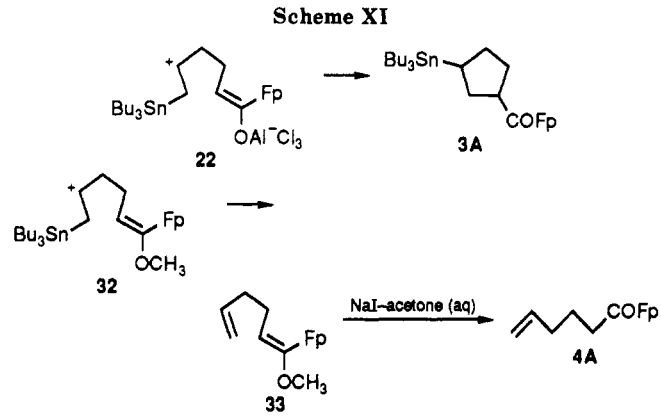
assumed a conformation of the allylstannane where the carbon–tin bond overlaps with the p orbitals of the alkene π-bond and have assumed that the incoming electrophile (acyliron complex) approaches from the side anti to tin (depicted by structure **21**). Similar results have been observed by Kitching in the reaction of allylstannanes with various electrophiles.[22] We have assumed that the acyliron complex exists predominately in the s-cis form by analogy to the results of Liebeskind and Davies.[23] Initial electrophilic attack from this orientation leads to the intermediate hyperconjugatively stabilized carbocation **22**, which upon reaction with the enolate concomitant with 1,2-migration of tin leads to the cyclopentane derivative **3**, which has the tin and acyliron groups in the trans relative configuration. There are a variety of other reasons for the choice of this transition state. The intermediate carbocation has maximum stabilization due to a favorable Coulombic interaction with the negatively charged aluminum enolate;[24] the alternate synclinal mode of attack does not have this stabilization (Scheme VIII) and predicts that the tributylstannyl and acyliron groups will be cis (compound **25**). We have chosen a synclinal transition state[25] over an anticlinal transition (Scheme IX, structure **26**) state because the reaction appears to proceed with retention of configuration of the carbon–carbon double bond in the α,β-unsaturated acyliron complexes. A synclinal transition state allows for the rapid formation of the C_1–C_5 bond and requires no rotation about carbon–carbon bonds for ring closure to occur. In an anticlinal transition state, the zwitterionic intermediate has the reacting centers (C_1 and C_5) considerably far apart, and the retention of stereochemistry can only be explained if C_1–C_5 bond formation occurs faster than rotation about

(22) Kitching, W.; Laycock, B.; Maynard, I.; Penman, K. *J. Chem. Soc., Chem. Commun.* **1986**, 954–955.
(23) (a) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328–6343. (b) Davies, S. G.; Walker, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 609–610.
(24) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 119–124.
(25) Denmark, S. E.; Henke, B. R.; Weber, E. *J. Am. Chem. Soc.* **1987**, *109*, 2512–2514.

Scheme X



Scheme XI



the C_1–C_2 bond. The intermediate carbocation **27** lacks dipole stabilization from the aluminum enolate, and it is difficult to see how the relative stereochemistry between acyliron and *tin* is controlled from an anticlinal transition state.

In the limited number of examples studied, R_1 ends up trans to tin (Table I, entries 14, 17, and 18), while R_2 ends up cis to tin (Table I, entry 19). Such a stereochemical outcome is easily explained by the orientation depicted by structure **21**. In the case of crotyltributyltin, a mixture of allylstannane stereoisomers leads to a single compound. This implies that only one of these isomers is reactive in the cycloaddition reaction or that isomerization occurs under the conditions of the reaction to produce a single diastereomer.[26] The stereochemistry in the product of the reaction must arise from *trans*-crotyltributyltin. In another case, reaction of tributyl(pent-3-en-2-yl)stannane (**1F**) with the *trans*-crotonyliron complex **2C**, predominately a single diastereomer was produced from a mixture of allylstannane stereoisomers. The stereoselectivity in this system is best explained by the relative orientation/conformation depicted in Scheme VII involving also the trans alkene isomer. To avoid steric interactions between R_4 and the acyliron group, the conformation where R_4 is in the orientation depicted in structure **21** is preferred.

Cycloaddition vs Allylation. In the results presented, there is a competition between cycloaddition and allylation. Zwitterionic intermediate **22** has three possible reaction pathways available (Scheme X): ring closure to form a four-membered ring (**30**), ring closure to form a five-membered ring (**3A**), and destannylation to form the net product from Michael addition of allyl anion (**4A**). Only the last two processes have been observed. Presumably

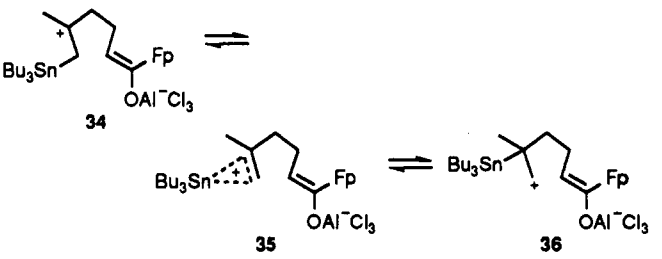
(26) Crotyltributylstannane undergoes a facile cis–trans isomerization upon treatment with Lewis acids: Denmark, S. E.; Weber, E. J.; Wilson, T. M.; Wilson, T. M. *Tetrahedron* **1989**, *45*, 1053–1065.

there is a kinetic preference for formation of the five-membered ring over the four-membered ring; in related reactions studied by Danheiser,[7] Rosenblum,[4] and Wojcicki,[5,6] only five-membered-ring formation or allylation was observed.

In the reaction of allylstannanes with α,β-unsaturated carbonyl compounds, typically only the allylation products are observed.[3] There are two cases where cycloaddition products have been observed with use of allylstannanes, this case and the reaction of allystannanes with quinones.[27] On the basis of previous results by others, the fact that allylstannanes react with α,β-unsaturated acyliron complexes at all is surprising.[3] Lewis-acid-catalyzed allylation reactions from allylstannanes have been observed only for α,β-unsaturated ketones and for alkenes having two electron-withdrawing groups on the same carbon. This reaction is also known to fail when the ketone is replaced by less electrophilic carbonyl groups such as esters and amides. Although no direct determination of the electron-withdrawing power of these acyliron groups has been determined, they are weaker ortho–para directors than the corresponding esters in Diels–Alder reactions.[28] We suggest that the reaction works in the case of α,β-unsaturated acyliron complexes due to the basicity of the acyl oxygen, which is now more receptive to the Lewis acid. The Lewis-acid-activated α,β-unsaturated acyliron complex now reacts to produce zwitterionic intermediate **22**. The difference between intermediate **22** and the analogous zwitterion derived from an α,β-unsaturated ketone (**29**) lies in the enolate portions of these molecules. The enolate portion of **22** should be more reactive than that of **29**, thus allowing cyclization to compete more favorably with destannylation. A similar comparison of the enolate portion of **22** and that of **32**, derived from reaction of allyltributyltin and α,β-unsaturated carbene complex **5A**, suggests that more destannylation should be observed with intermediate **32**, and this is the only pathway observed from these systems. In the Lewis-acid-catalyzed reactions between α,β-unsaturated acyliron complexes and allylstannanes, the proportion of allylation product increases if poor-quality aluminum chloride was used in the reaction. This is presumably due to the presence of chloride ion, which would facilitate the destannylation reaction. Allylation products have never been observed in reactions involving methacryloyl complex **2B**. This is perhaps due to the increased nucleophilicity of the enolate due to the electron-donating methyl group.

Five-membered-ring formation requires either that the tributyltin group undergoes a 1,2-migration in intermediate carbocation **22** or that significant hyperconjugative stabilization of the intermediate carbocation leads to a situation where both C_4 and C_5 are electrophilic. The intermediate carbocation **22** is undoubtedly stabilized by hyperconjugative interaction with the tributyltin group.[29] In systems where this hyperconjugative interaction is diminished, allylation products predominate. For example, allyltrimethylsilane gave only open-chain products, whereas allyltributylgermane led to mixtures of allylation and cycloaddition products. The proportion of cycloaddition products correlates with carbocation stability, which proceeds in the order $Bu_3SnCH_2CH_2^+ >$ $Bu_3GeCH_2CH_2^+ > Me_3SiCH_2CH_2^+$.[30] In a recent example, the Lewis-acid-catalyzed reaction of enones and allylsilanes was found to produce low yields of cycloaddition products.[31] In another case, reaction of methallyltributyltin with acyliron complexes, only allylation products were observed. In this case, the hyperconjugative stabilization by tributyltin would be diminished since the carbocation is now tertiary (**34**, Scheme XII) and thus the demand for stabilization is diminished. Without hyperconjugative stabilization, there is no way for C_5 to become electrophilic, and thus the cyclization step does not occur. Also, a 1,2-tributyltin migration would be thermodynamically unfavorable in this system. The failure of the cycloaddition reaction was also noted in the reaction of methallyliron complexes with chlorosulfonyl isocyanate.[4]

Scheme XII



Conclusion

A thorough examination of the reaction between allylstannanes and α,β-unsaturated acyliron complexes has been undertaken in our laboratories. This reaction produces five-membered rings with a very high degree of stereoselectivity, substituted by an acyliron and a tributyltin group. The acyliron group is easily converted to an ester, while the tributyltin group can be converted to an alcohol with retention of configuration. The reaction proceeds in modest yields of 40–60% but provides a very rapid and stereoselective method to generate highly substituted cyclopentane derivatives. This is one of only a few five-membered-ring-forming cycloaddition reactions that provides only sp^3 carbons in the newly formed ring.

Experimental Section

General Considerations. ^1H NMR spectra were obtained at 200 MHz on a Bruker AF-200 spectrometer or at 400 MHz on a IBM AM-400 spectrometer, as indicated. ^{13}C NMR spectra were obtained at 50 MHz on a Bruker AF-200 spectrometer. The chemical shifts are reported in ppm downfield from internal tetramethylsilane. Coupling constants are given in hertz (Hz). Spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). IR spectra were obtained on a Perkin-Elmer 281 infrared spectrophotometer or on a Nicolet 5DXC FT-IR spectrometer. Mass spectroscopic data were obtained on a VG 7070E spectrometer using electron ionization or chemical ionization. For low-resolution spectra, the data are expressed with the nominal fragment weight followed in parentheses by the percent intensity (taking the base peak as 100%). For high-resolution spectra, only the parent ion is reported to establish the accurate molecular weight; for compounds containing tin, ^{120}Sn was used to determine elemental composition. Elemental analyses were obtained from Galbraith Laboratories Inc., Knoxville, TN. Routine thin-layer chromatography (TLC) was effected by using precoated 250-μm silica gel plates with fluorescence indicator purchased from Whatman. Preparative TLC was effected by using precoated 250–2000-μm silica gel plates silica gel plate purchased from American Scientific

(27) Maruyama, K.; Matano, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3877–3885.
(28) The acyliron group is less electron-withdrawing than the analogous carbethoxy group, as evidenced by the reduced regioselectivity in Diels–Alder reactions between α,β-unsaturated acyliron complexes and isoprene.[20]
(29) Lambert, J. B.; Wang, J.; Teramura, D. H. *J. Org. Chem.* **1988**, *53*, 5422–5428.
(30) Traylor, T. G.; Berwin, H. J.; Jerkunica, J. M.; Hall, M. L. *Pure Appl. Chem.* **1972**, *30*, 599–606.
(31) Knölker, H.-J.; Jones, P. G.; Pannek, J.-B. *Synlett* **1990**, *1*, 429–430.

Products. Routine flash column chromatography was effected by using 230–400 mesh ASTM silica gel purchased from American Scientific Products. Ether solvents were dried by distillation from sodium benzophenone ketyl under nitrogen. Dichloromethane was dried by distillation from calcium hydride and used immediately. Diisopropylamine was purified by distillation from calcium hydride under nitrogen and stored over molecular sieves. Reactions involving organolithium reagents were carried out under dry nitrogen in oven-dried glassware. The term "short-path distillation" refers to the process in which the entire distillation apparatus (a tube closed at one end, held horizontally with the exception of the receiver) was slowly heated in an air bath from 25 to 150 °C under vacuum; the distillate was collected at 0 °C, and boiling points for fractions refer to the bath temperature range. All boiling points are uncorrected. All melting points are uncorrected. The term "pressure bottle" refers to a thick-wall glass flask with thread that can be sealed with a polypropylene stopper.

Materials. Allylstannanes. Allyltributyltin (**1A**),[32] cinnamyltributyltin (**1B**),[33] methallyltributyltin (**1C**),[33] crotyltributyltin (**1D**),[34] (cyclopent-2-en-1-yl)tributyltin (**1E**),[35] (pent-3-en-2-yl)-tributyltin (**1F**),[36] and allyltrimethyltin (**1G**)[32] were obtained with use of literature procedures. Allyltriphenyltin (**1H**) was purchased from Strem Chemical Co.

Acyliron Complexes. Acryloyliron complex **2A**,[37] methacryloyliron complex **2B**,[9] and *trans*-crotonyliron complex **2C**[38] were prepared according to a modified literature procedure.[37] *cis*-Crotonyliron complex **2D** was prepared according to the procedure outlined below.

Lewis Acids. Ethylaluminum dichloride (1.0 M solution in hexane), methylaluminum sesquichloride (1.0 M solution in toluene), methylaluminum dichloride (1.0 M solution in hexane), aluminum bromide (1.0 M solution in dibromomethane), and diethylaluminum chloride (1.0 M solution in hexane) were purchased from Aldrich Chemical Co. and used without further purification. Aluminum chloride was purchased from Aldrich Chemical Co. and sublimed at 15 mmHg prior to use.

General Procedure I: Preparation of α,β-Unsaturated Acyliron Complexes. To a solution of cyclopentadienyliron dicarbonyl dimer[39] (1.0 equiv) in dry THF (0.5 M) was added 6% Na–Hg (2.5 equiv). The mixture was stirred vigorously at 25 °C for 2 h. During this period the color of the solution changed from dark brown to deep red. The mixture was then cooled to −78 °C, and acid chloride (2.1 equiv) was added via syringe. The mixture was stirred at −78 °C for 30 min and then warmed to 25 °C gradually over 2 h. All the volatiles were then removed on a rotary evaporator, and the resulting brown residue was dissolved in dichloromethane and the solution washed with water. The organic extracts were filtered through alumina. After the solvent was removed on a rotary evaporator, the crude product was purified by flash column chromatography on silica gel or by vacuum distillation (<0.1 mmHg). This is a modification of a literature procedure where gravity column chromatography on alumina was used as the final purification step; considerably higher yields were obtained with this procedure.

Preparation of Acryloyliron Complex 2A. General procedure I was followed with cyclopentadienyliron dicarbonyl dimer (2.45 g, 6.92 mmol), 6% Na–Hg (6.50 g, 17.0 mmol), and acryloyl chloride (1.20 mL, 14.8 mmol). The crude product was purified by short-path distillation under vacuum (85–90 °C/0.1 mmHg). Complex **2A** was obtained as a brown oil (2.05 g, 64%). The spectral data were in agreement with those reported previously for this compound.[37]

Preparation of Methacryloyliron Complex 2B. General procedure I was followed with cyclopentadienyliron dicarbonyl dimer (3.20 g, 9.04 mmol), 6% Na–Hg (9.50 g, 24.8 mmol), and methacryloyl chloride (2.0 mL, 20 mmol). The crude product was purified by short-path distillation under vacuum (90–95 °C/0.1 mmHg). The distillation could not be performed unless liquid nitrogen was used in the vacuum trap; when dry ice–acetone was employed, the pressure would not drop to an acceptable level. Complex **2B** was obtained as a yellow oil (3.19 g, 72%). The spectral data were in agreement with those reported previously for this compound.[9]

Preparation of *trans*-Crotonyliron Complex 2C and *cis*-Crotonyliron Complex 2D. General procedure I was followed with cyclopentadienyliron dicarbonyl dimer (7.5 g, 21 mmol), 6% Na–Hg (21.5 g, 55 mmol), and *trans*-crotonyl chloride (4.7 mL, 50 mmol). The crude product was purified by short-path distillation under vacuum (90–98 °C/0.1 mmHg). A mixture of complexes **2C,D** was obtained as a yellow oil (6.3 g, 62%). These two compounds were separated by flash column chromatography on silica gel with 4:1 hexane–ethyl acetate as eluent. Complexes **2C** (2.61 g, 25%, R_f 0.45) and **2D** (2.91 g, 29%, R_f 0.30) were obtained as yellow oils. The spectral data for **2C** were in agreement with those reported previously.[38] Spectral data for **2D**: ^{1}H NMR ($CDCl_3$) δ 6.38 (dq, J = 10.8, 1.6 Hz, 1 H), 5.00 (dq, J = 10.8, 7.1 Hz, 1 H), 4.81 (s, 5 H), 1.72 (dd, J = 7.1, 1.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 152.4, 214.0, 143.1, 122.9, 86.4, 15.0; IR (CH_2Cl_2) 2005 (s), 1960 (vs), 1622 (s), 1600 (m), 1322 (m), 1213 (m), 1180 (m), 970 (w), 828 (m) cm^{-1}; MS (EI) m/e 246 (M^+, 8), 217 (25), 204 (43), 185 (100), 161 (31), 148 (6), 120 (39); HRMS calcd for $C_{11}H_{10}FeO_3$ m/e 245.9979, found 245.9986.

General Procedure II: [3 + 2] Cycloaddition Reaction between an α,β-Unsaturated Acyliron Complex and Allyltrialkylstannane. To a mixture of $AlCl_3$ (1.0 equiv) or $EtAlCl_2$ (1.0 equiv) in dried dichloromethane (0.05 M) at 0 or 25 °C was added a solution of α,β-unsaturated acyliron complex (1.0 equiv) in dichloromethane (0.05 M). The mixture was stirred at this temperature for 15 min; then allyltrialkylstannane (1.0 equiv, neat) was added via syringe. After the mixture was stirred for 30 min to 2 h, saturated sodium carbonate solution (excess) was added. The resulting mixture was extracted with dichloromethane, and the organic extracts were dried over Na_2SO_4 and filtered through alumina. The filtrate was concentrated on a rotary evaporator, and the resulting yellow oil was separated by flash column chromatography on silica gel (slurry-packed with 99:1 hexane–triethylamine). Elution with hexane gave a trialkylstannyl residue, and elution with 9:1 hexane–ethyl acetate afforded the open-chain adduct and the cycloadduct separately. Elution with 4:1 hexane–ethyl acetate afforded unreacted acyliron complex.

Preparation of (1β,3α)-(±)-((3-(Tributylstannyl)cyclopentyl)carbonyl)cyclopentadienyldicarbonyliron (3A). $AlCl_3$ Catalyzed. General procedure II was followed with acryloyliron complex **2A** (0.056 g, 0.24 mmol), $AlCl_3$ (0.034 g, 0.25 mmol), and allyltributyltin (**1A**; 0.080 g, 0.24 mmol). The reaction was conducted at 0 °C for 30 min. Compound **3A** was obtained as a yellow oil (0.056 mg, 42%): ^{1}H NMR ($CDCl_3$) δ 4.83 (s, 5 H), 3.42 (13-line pattern, 1 H), 1.10–2.20 (m, 19 H), 0.70–0.95 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 253.8, 215.8, 215.6, 86.5, 74.2, 34.8, 32.4, 30.8, 29.8, 27.9, 22.9, 13.9, 8.6; IR (neat) 2952 (m), 2923 (m), 2009 (s), 1955 (s), 1660 (s) cm^{-1}; MS (EI) m/e 536 (M − CO, 1), 507 (1), 440 (5), 291 (31), 242 (33), 205 (100), 177 (59). Anal. Calcd for $C_{25}H_{40}FeO_3Sn$: C, 53.32; H, 7.16; Fe, 9.92. Found: C, 53.23; H, 7.28; Fe, 9.49. A trace amount of compound **4A** (0.0018 g, 3%) was isolated from the reaction.

Preparation of (1β,3α)-(±)-((3-(Tributylstannyl)cyclopentyl)carbonyl)cyclopentadienyldicarbonyliron (3A). $Me_3Al_2Cl_3$ Catalyzed. General procedure II was followed with acryloyliron complex **2A** (0.050 g, 0.20 mmol), $Me_3Al_2Cl_3$ (0.20 mL of a 1.0 M hexane solution, 0.20 mmol), and allyltributylstannane (**1A**; 0.083 g, 0.25 mmol). The reaction was conducted at 25 °C for 24 h. Compound **3A** was obtained as a yellow oil (0.067 g, 64%), accompanied by unreacted complex **2A** (0.005 g, 11%). A trace amount of compound **4A** (0.0015 g, 2%) was isolated from the reaction.

Preparation of (1β,3β,4α)-(±)-((3-Phenyl-4-(tributylstannyl)cyclopentyl)carbonyl)cyclopentadienyldicarbonyliron (3B). General procedure II was followed with

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acryloyliron complex **2A** (0.069 g, 0.30 mmol), $AlCl_3$ (0.039 g, 0.29 mmol), and *trans*-cinnamyltributylstannane (**1B**; 0.118 g, 0.29 mmol). The reaction was conducted at 25 °C for 24 h. Unreacted complex **2A** (0.018 g, 26%) was obtained from the reaction. Compound **3B** was obtained as a yellow oil (0.064 g, 34%): ^1H NMR ($CDCl_3$) δ 7.25 (m, 5 H), 4.84 (s, 5 H), 3.67 (11-line pattern, 1 H), 2.85 (ddd, J = 12.1, 10.6, 6.6 Hz, 1 H), 2.25 (m, 2 H), 1.45–1.85 (m, 3 H), 1.25 (m, 12 H), 0.85 (br t, J = 7.1 Hz, 9 H), 0.59 (br t, J = 7.1 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 255.0, 214.6, 214.4, 144.5, 128.2, 127.4, 126.2, 86.4, 74.6, 52.1, 46.1, 34.4, 32.4, 29.1, 24.7, 13.5, 8.3; IR (neat) 2965 (s), 2920 (s), 2010 (s), 1950 (s), 1630 (s) cm^{-1}; MS (EI) m/e 610 (M - CO, 1), 583 (5), 554 (3), 377 (5), 318 (12), 291 (42), 265 (75), 235 (27), 205 (100), 179 (37). Anal. Calcd for $C_{31}H_{44}FeO_3Sn$: C, 58.25; H, 6.94; Fe, 8.74. Found: C, 57.84; H, 7.09; Fe, 8.54.

Preparation of (1β,3β,4α)-(±)-((3-Methyl-4-(tributylstannyl)cyclopentyl)carbonyl)cyclopentadienyldicarbonyliron (3D). General procedure II was followed with acryloyliron complex **2A** (0.135 g, 0.58 mmol), $AlCl_3$ (0.081 g, 0.61 mmol), and crotyltributylstannane (**1D**; 0.203 mg, 0.59 mmol). The reaction was conducted from 0 to 25 °C for 1 h. Unreacted complex **2A** (0.010 g, 7%) was obtained from the reaction. Compound **3D** was obtained as a yellow oil (0.174 g, 52%): ^1H NMR ($CDCl_3$) δ 4.83 (s, 5 H), 3.53 (8-line pattern, 1 H), 2.01 (m, 2 H), 1.85 (m, 2 H), 1.10–1.75 (m, 14 H), 1.06 (d, J = 8.6 Hz, 3 H), 0.70–1.00 (m, 15 H); ^{13}C NMR (C_6D_6) δ 254.0, 215.5, 86.5, 75.0, 40.8, 39.8, 35.0, 32.7, 29.8, 27.8, 20.0, 13.8, 8.7; IR (neat) 2960 (s), 2921 (s), 2010 (s), 1950 (s), 1641 (s) cm^{-1}; MS (EI) m/e 550 (M - CO, 1), 521 (1), 493 (1), 440 (2), 411 (1), 291 (58), 235 (60), 204 (86), 175 (100), 120 (64). Anal. Calcd for $C_{26}H_{42}FeO_3Sn$: C, 54.12; H, 7.34; Fe, 9.68. Found: C, 53.94; H, 7.51; Fe, 9.51. A trace amount of compound **4D** (<0.002 g) was isolated from the reaction.

Preparation of ((*anti*-7-(Tributylstannyl)-*exo*-2-norbornyl)carbonyl)cyclopentadienyldicarbonyliron (3E). General procedure II was followed with acryloyliron complex **2A** (0.054 g, 0.23 mmol), $AlCl_3$ (0.031 g, 0.23 mmol), and (2-cyclopentenyl)tributylstannane (**1E**; 0.082 g, 0.23 mmol). The reaction was conducted at 0 °C for 1 h. Unreacted complex **2A** (0.018 g, 47%) was recovered from the reaction. Compound **3E** was obtained as a yellow oil (0.037 g, 27%): ^1H NMR ($CDCl_3$) δ 4.84 (s, 5 H), 3.09 (dd, J = 7.8, 4.8 Hz, 1 H), 2.69 (m, 1 H), 2.39 (m, 1 H), 1.00–1.60 (m, 19 H), 0.98 (t, J = 7.2 Hz, 6 H), 0.92 (t, J = 7.2 Hz, 9 H); ^{13}C NMR (C_6D_6) δ 256.9, 214.9, 214.8, 86.5, 77.5, 43.9, 40.7, 35.7, 34.3, 30.3, 29.6, 29.3, 27.5, 13.7, 9.3; IR (neat) 2960 (s), 2921 (s), 2054 (m), 2008 (s), 1955 (s), 1635 (s) cm^{-1}; MS (EI) m/e 562 (M - CO, 1), 533 (1), 505 (1), 411 (8), 324 (40), 291 (62), 235 (52), 204 (52), 177 (91), 66 (100). Anal. Calcd for $C_{27}H_{42}FeO_3Sn$: C, 55.04; H, 7.19; Fe, 9.48. Found: C, 55.45; H, 7.57; Fe, 9.49.

Preparation of (1β,2α,3β,4α,5α)-(±)-((2,3,5-Trimethyl-4-(tributylstannyl)cyclopentyl)carbonyl)cyclopentadienyldicarbonyliron (3F). General procedure II was followed with *trans*-crotonyl complex **2C** (0.533 g, 2.17 mmol), $EtAlCl_2$ (2.20 mL of a 1 M solution in hexane, 2.20 mmol), and (pent-3-en-2-yl)tributylstannane (**1F**; 0.790 mg, 2.20 mmol). The reaction was conducted at 25 °C for 40 min. Unreacted complex **2C** (0.281 g, 53%) was recovered from the reaction. Compound **3F** was obtained as a yellow oil (0.328 g, 25%): ^1H NMR ($CDCl_3$) δ 4.83 (s, 5 H), 2.92 (m, 1 H), 2.00–2.25 (m, 2 H), 1.22–1.70 (m, 14 H), 1.08 (d, J = 7.2 Hz, 3 H), 0.70–1.05 (m, 21 H); ^{13}C NMR ($CDCl_3$) δ 261.0, 214.9, 214.7, 90.5, 86.6, 42.8, 42.5, 40.4, 40.2, 29.3, 27.5, 21.5, 16.8, 15.4, 13.6, 8.4; IR (CH_2Cl_2) 2960 (s), 2925 (s), 2015 (vs), 1955 (vs), 1640 (s) cm^{-1}; MS (CI) m/e 606 (M, 3.5), 578 (3.5), 549 (13), 521 (1.5), 492 (3.5), 387 (25), 291 (60), 235 (39), 205 (100), 177 (13), 109 (37); HRMS calcd for $C_{28}H_{46}FeO_3Sn$ m/e 606.1818, found 606.1864. Additional singlets at δ 4.80–4.90 were noted, the largest one being integrated for 10% of the area of the peak at δ 4.84.

Preparation of (1β,4α)-(±)-((3-Trimethylstannyl)cyclopentyl)carbonyl)cyclopentadienyldicarbonyliron (3G). General procedure II was followed with acryloyliron complex **2A** (0.050 g, 0.22 mmol), $AlCl_3$ (0.029 g, 0.22 mmol), and allyltrimethylstannane (**1G**; 0.045 g, 0.22 mmol). The reaction was conducted at 0 °C for 1.5 h. Compound **3G** was obtained as a yellow oil (0.026 g, 27%): ^1H NMR ($CDCl_3$) δ 4.83 (s, 5 H), 3.41 (13-line pattern, 1 H), 1.10–2.20 (m, 7 H), 0.02 (s, 9 H); ^{13}C NMR (C_6D_6) δ 254.0, 215.6, 86.5, 74.2, 34.4, 31.7, 30.8, 23.4, -11.4; IR (neat) 2010 (s), 1950 (s), 1640 (s) cm^{-1}; MS (EI) m/e 437 (M, <1), 286 (18), 205 (100), 187 (28), 177 (24), 165 (28), 149 (18); HRMS calcd for $C_{16}H_{22}FeO_3Sn$ m/e 437.9940, found 437.9928.

Preparation of (1β,4α)-(±)-((3-(Triphenylstannyl)cyclopentyl)carbonyl)cyclopentadienyldicarbonyliron (3H). General procedure II was followed with acryloyliron complex **2A** (0.050 g, 0.22 mmol), $AlCl_3$ (0.030 g, 0.22 mmol), and allyltriphenylstannane (**2H**; 0.084 g, 8%). The reaction was conducted at 25 °C for 24 h. Unreacted complex **2A** (0.023 g, 45%) was recovered from the reaction. Compound **3H** was obtained as a yellow solid (0.011 g, 8%): ^1H NMR ($CDCl_3$) δ 7.55 (m, 6 H), 7.40 (m, 9 H), 4.85 (s, 5 H), 3.51 (14-line pattern, 1 H), 2.40 (m, 2 H), 1.50–2.20 (m, 5 H); IR ($CHCl_3$) 2010 (s), 1951 (s), 1639 (s). This compound was not characterized further due to the paucity of compound.

Preparation of (1α,3α)-(±)-((1-Methyl-3-(tributylstannyl)-1β-cyclopentyl)carbonyl)cyclopentadienyldicarbonyliron (3I). General procedure II was followed with methacryloyliron complex **2B** (0.085 g, 0.35 mmol), $AlCl_3$ (0.048 g, 0.36 mmol), and allyltributylstannane (**1A**; 0.116 g, 0.35 mmol). The reaction was conducted at 0 °C for 5 min. Unreacted complex **2B** (0.023 g, 23%) was recovered from the reaction. Compound **3I** was obtained as a yellow oil (0.133 g, 66%): ^1H NMR ($CDCl_3$) δ 4.82 (s, 5 H), 2.41 (6-line pattern, 1 H), 1.96 (dd, J = 10.4, 8.2, Hz, 1 H) overlapping with 1.92 (m, 1 H), 1.36–1.75 (m, 16 H), 1.19 (s, 3 H), 0.75–0.95 (m, 15 H); ^{13}C NMR (C_6D_6) δ 255.4, 216.6, 216.3, 86.7, 71.2, 42.7, 38.7, 31.3, 29.8; IR (neat) 2953 (m), 2920 (m), 2009 (s), 1955 (s), 1660 (s) cm^{-1}; MS (EI) m/e 536 (M - CO, 1), 507 (1), 440 (5), 291 (31), 242 (33), 205 (100), 177 (59). Anal. Calcd for $C_{25}H_{40}FeO_3Sn$: C, 53.32; H, 7.16; Fe, 9.92. Found: C, 53.23; H, 7.28; Fe, 9.49.

Preparation of (1β,2α,4α)-(±)-((2-Methyl-4-(tributylstannyl)cyclopentyl)carbonyl)cyclopentadienyldicarbonyliron (3J). General procedure II was followed with *trans*-crotonyliron complex **2C** (0.112 g, 0.46 mmol), $AlCl_3$ (0.063 mg, 0.47 mmol), and allyltributylstannane (**1A**; 0.155 g, 0.47 mmol). The reaction was conducted at 25 °C for 2 h. Unreacted complex **2C** (0.032 g, 28%) was recovered from the reaction. Compound **3J** was obtained as a yellow oil (0.109 g, 41%): ^1H NMR ($CDCl_3$) δ 4.83 (s, 5 H), 3.07 (q, J = 7.5 Hz, 1 H), 1.80–2.15 (m, 5 H), 1.42 (m, 7 H), 1.26 (m, 6 H), 0.97 (d, J = 6.9 Hz, 3 H), 0.65–0.89 (m, 15 H); ^{13}C NMR (C_6D_6) δ 253.9, 215.5, 86.7, 83.1, 41.7, 39.3, 34.9, 29.9, 29.8, 27.8, 22.1, 13.8, 8.6; IR (neat) 2950 (m), 2920 (m), 2010 (s), 1950 (s), 1644 (s) cm^{-1}; MS (EI) m/e 550 (M - CO, 1), 521 (1), 493 (1), 411 (2), 311 (4), 291 (75), 235 (53), 205 (100), 175 (60), 121 (73). Anal. Calcd for $C_{26}H_{42}FeO_3Sn$: C, 54.12; H, 7.51; Fe, 9.51. Found: C, 54.35; H, 7.23; Fe, 9.77. Compound **4J(K)** (0.006 g, 5%) was also isolated from the reaction.

Preparation of (1β,2β,4α)-(±)-((2-Methyl-4-(tributylstannyl)cyclopentyl)carbonyl)cyclopentadienyldicarbonyliron (3K). General procedure II was followed with *cis*-crotonyliron complex **2D** (0.125 g, 0.51 mmol), $AlCl_3$ (0.070 g, 0.52 mmol), and allyltributylstannane (**1A**; 0.172 g, 0.52 mmol). The reaction was conducted at 25 °C for 10 min. Unreacted complex **2D** (0.078 g, 63%) was recovered from the reaction. Compound **3K** was obtained as a yellow oil (0.068 g, 23%): ^1H NMR ($CDCl_3$): δ 4.75 (s, 5 H), 3.51 (q, J = 7.0 Hz, 1 H), 2.32 (m, 1 H), 2.07 (m, 1 H), 1.12–1.71 (m, 16 H), 0.70–0.88 (m, 18 H); ^{13}C NMR ($CDCl_3$) δ 259.1, 214.8, 214.6, 86.5, 79.0, 38.9, 38.1, 32.8, 29.3, 27.4, 18.5, 16.2, 11.3, 8.3; IR (neat) 2958 (s), 2921 (s), 2005 (s), 1952 (s), 1625 (s) cm^{-1}; MS (CI) m/e 578 (M^+, 63), 520 (12), 492 (2.5), 439 (11), 410 (2.1), 291 (26), 271 (27), 205 (100), 177 (16), 121 (5.8); HRMS (EI) calcd for $C_{23}H_{42}FeO_2Sn$ (M - CO) m/e 550.1556, found 550.1523. Compound **4K(J)** (0.014 g, 11%) was also isolated from the reaction.

Preparation of (1β,3β,4α)-(±)-((1,3-Dimethyl-4-(tributylstannyl)cyclopentyl)carbonyl)cyclopentadienyldicarbonyliron (3N). General procedure II was followed with methacryloyliron complex **2B** (0.064 g, 0.26 mmol), $AlCl_3$ (0.036 g, 0.27 mmol), and crotyltributylstannane (**1D**; 0.090 g, 0.26 mmol). The reaction was conducted at 25 °C for 1 h. Unreacted complex **2B** (0.027 g, 42%) was recovered from the reaction. Compound **3N** was obtained as a yellow oil (0.078 g, 51%): ^1H NMR ($CDCl_3$) δ 4.81 (s, 5 H), 2.42 (dd, J = 13.0, 8.2 Hz, 1 H) overlapping with 2.35 (m, 2 H), 1.95 (m, 1 H), 1.10–1.80 (m, 14 H), overlapping with 1.18 (s, 3 H), 0.96 (d, J = 6.7 Hz, 3 H), 0.70–0.92 (m, 15 H); ^{13}C

NMR ($CDCl_3$) δ 253.8, 215.5, 215.4, 86.5, 71.4, 47.3, 42.7, 39.1, 33.5, 29.3, 27.4, 27.1, 20.1, 13.6, 8.4; IR (CH_2Cl_2) 2960 (s), 2923 (s), 2010 (s), 1950 (s), 1634 (s) cm^{-1}; MS (EI) *m/e* 564 (M − CO, 1), 535 (1), 359 (1), 354 (1), 329 (6), 291 (22), 235 (28), 205 (100), 177 (42), 121 (24). Anal. Calcd. for $C_{27}H_{44}FeO_3Sn$: C, 54.86; H, 7.51; Fe, 9.45. Found: C, 54.70; H, 7.95; Fe, 9.41.

Preparation of Complex 4A by Reaction of Complex 2A with Allyltrimethylsilane. General procedure II was followed with acryloyliron complex **2A** (0.100 g, 0.43 mmol), $EtAlCl_2$ (0.43 mL of 1.0 M solution in hexane, 0.43 mmol), and allyltrimethylsilane (0.068 g, 0.60 mmol). The reaction was conducted at 25 °C for 24 h. Compound **4A** was obtained as a yellow oil (0.036 g, 31%): ^1H NMR ($CDCl_3$) δ 4.84 (s, 5 H), 4.82 (br s, 1 H), 4.79 (br s, 1 H), 3.02 (sextet, *J* = 6.7 Hz, 1 H), 1.97 (br t, *J* = 6.4 Hz, 1 H), 1.79 (br s, 3 H), 1.30–1.40 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 243.0, 214.3, 138.1, 114.7, 86.2, 65.6, 32.9, 24.2; IR (CH_2Cl_2) 2952 (m), 2915 (w), 2008 (s), 1953 (vs), 1630 (s), 1067 (m), 1023 (m), 822 (m) cm^{-1}; MS (CI) *m/e* 275 (M + 1); HRMS *m/e* calcd for $C_{13}H_{15}FeO_3$ (M + 1) 275.0371, found 275.0371.

Preparation of (1β,3α)-(±)-((3-(Tributylgermanyl)cyclopentyl)carbonyl)cyclopentadienyldicarbonyliron. General procedure II was followed with acryloyliron complex **2A** (0.050 g, 0.22 mmol), $AlCl_3$ (0.030 g, 0.22 mmol), and allyltributylgermane[41] (0.114 g, 0.40 mmol). The reaction was conducted at 25 °C for 6 h. The compound was obtained as a yellow oil (0.023 g, 20%): ^1H NMR ($CDCl_3$) δ 4.83 (s, 5 H), 3.45 (m, 1 H), 1.10–2.20 (m, 19 H), 0.60–0.90 (m, 15 H); IR (neat) 2952 (m), 2923 (m), 2009 (s), 1955 (s), 1660 (s) cm^{-1}; MS (EI) *m/e* 489 (M − CO, <1), 461 (<1), 432 (3), 394 (15), 310 (8), 252 (9), 245 (43), 205 (59), 189 (100), 176 (80), 133 (59), 121 (38); HRMS *m/e* calcd for $C_{24}H_{40}FeO_2Ge$ (M − CO) 490.1589, found 490.1590. Compound **4A** (0.004 g, 5%) was also isolated from the reaction.

Attempted Reaction of Allyltriphenyllead and *trans*-Crotonyliron Complex 2C. General procedure II was followed with *trans*-crotonyliron complex **2C** (0.086 g, 0.35 mmol), $EtAlCl_2$ (0.30 mL of a 1.0 M solution in hexane, 0.30 mmol), and allyltriphenyllead[42] (0.250 g, 0.52 mmol). The reaction was conducted at 0 °C for 2 h. No addition product was found after this period, and allyltriphenyllead had decomposed, as diagnosed by TLC.

Attempted Reaction of Allylphenylmercury and *trans*-Crotonyliron Complex 2C. General procedure II was followed with *trans*-crotonyliron complex **2C** (0.086 g, 0.35 mmol), $EtAlCl_2$ (0.30 mL of a 1.0 M solution in hexane, 0.30 mmol), and allylphenylmercury[43] (0.112 g, 0.35 mmol). The reaction was conducted at 0 °C for 2 h. No addition product was found after this period, and allylphenylmercury had decomposed, as diagnosed by TLC.

General Procedure III: Michael Addition Reaction of an α,β-Unsaturated Acyliron Complex and Allyltrialkylstannane. To a solution of triphenylcarbenium hexafluorophosphate (2.0 equiv)[10a] in dry dichloromethane (0.1 M) was added trimethyl orthoformate (3.0 equiv). The mixture was stirred at 25 °C for 10 min before a solution of α,β-unsaturated acyliron complex (1.0 equiv, 0.05 M in dichloromethane) was added via syringe. The mixture was stirred for 30–60 min (period I) at 25 °C before allyltrialkylstannane (1.2 equiv, neat) was added via syringe. The resulting mixture was stirred for an additional 30 min to 2 h (period II). After period II was over, a saturated solution of sodium iodide (excess) in 10% aqueous acetone was added. The mixture was stirred for 10 min; then all the volatiles were removed on a rotary evaporator. The residue was dissolved in dichloromethane and filtered through alumina. After the solvent was removed on a rotary evaporator, the brown residue was separated by flash column chromatography on silica gel. Elution with hexane gave trialkylstannyl residue, and elution with 9:1 hexane–ethyl acetate afforded the Michael addition product.

Preparation of Complex 4I. General procedure III was followed with triphenylcarbenium hexafluorophosphate (0.272 g, 0.824 mmol), trimethyl orthoformate (0.133 g, 1.23 mmol), methacryloyliron complex **2B** (0.100 g, 0.406 mmol), and allyltributylstannane **1A**; 0.161 g, 0.487 mmol). The reaction times for periods I and II were 30 min and 2 h, respectively. Unreacted complex **2B** (0.037 g, 37%) was recovered from the reaction. Complex **4I** was obtained as a yellow oil (0.052 g, 45%): ^1H NMR ($CDCl_3$) δ 5.80 (ddt, *J* = 16.7, 9.2, 6.4 Hz, 1 H), 5.01 (dq, *J* = 16.7, 1.4 Hz, 1 H), 4.97 (dq, *J* = 9.2, 1.1 Hz, 1 H), 4.86 (s, 5 H), 3.04 (sextet, *J* = 7.1 Hz, 1 H), 2.05 (m, 2 H), 1.77 (m, 1 H), 1.22 (m, 1 H), 0.98 (d, *j* = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 253.2, 214.7, 138.5, 114.6, 86.5, 67.9, 32.0, 31.4, 15.8; IR (CH_2Cl_2) 2960 (w), 2008 (s), 1950 (vs), 1643 (s), 1070 (m), 1028 (m), 824 (m) cm^{-1}; MS (CI) *m/e* 289 (M + 1, 66), 232 (23), 205 (100), 177 (34), 149 (6), 121 (22); HRMS *m/e* calcd for $C_{14}H_{17}FeO_3$ (M + 1) 289.0526, found 289.0534.

Preparation of Complex 4J. General procedure III was followed with triphenylcarbenium hexafluorophosphate (0.700 g, 2.12 mmol), trimethyl orthoformate (0.330 g, 3.06 mmol), *trans*-crotonyliron complex **2C** (0.250 g, 1.02 mmol), and allyltributylstannane **1A**; 0.410 g, 1.24 mmol). The reaction times for periods I and II were 1 h and 30 min, respectively. Unreacted complex **2C** (0.064 g, 26%) was recovered from the reaction. Complex **4J** was obtained as a yellow oil (0.141 g, 48%): ^1H NMR ($CDCl_3$) δ 5.70 (ddt, *J* = 17.8, 8.9, 6.2 Hz, 1 H), 4.98 (m, 1 H), 4.92 (m, 1 H), 4.80 (s, 5 H), 2.88 (dd, *J* = 16.4, 5.4 Hz, 1 H), 2.71 (dd, *J* = 16.4, 7.2 Hz, 1 H), 1.75–2.13 (m, 2 H), 0.80 (d, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 257.8, 214.4, 136.9, 116.0, 86.4, 73.4, 40.8, 29.7, 19.6; IR (CH_2Cl_2) 2955 (w), 2915 (w), 2008 (s), 1955 (vs), 1633 (s), 1430 (w), 824 (m) cm^{-1}; MS (CI) *m/e* 289 (M + 1, 10), 232 (62), 204 (93), 177 (27), 162 (37), 149 (20), 121 (100). This complex was not further characterized but converted to the known ethyl ester (see below).

Preparation of Complex 4O. General procedure III was followed with triphenylcarbenium hexafluorophosphate (0.350 g, 1.06 mmol), trimethyl orthoformate (0.175 g, 1.62 mmol), *cis*-crotonyliron complex **2D** (0.120 g, 0.488 mmol), and crotyltributylstannane (**1D**; 0.193 g, 0.56 mmol). The reaction times for periods I and II were 30 and 40 min, respectively. Unreacted complex **2C** (from isomerization of **2D**, 0.020 g, 17%) was recovered from the reaction. Complex **4O** was obtained as a 75:25 anti–syn mixture (0.095 g, 64%): ^1H NMR ($CDCl_3$) major isomer δ 2.94 (dd, *J* = 16.7, 5.5 Hz, 1 H), 2.73 (dd, *J* = 16.7, 8.1 Hz, 1 H), 0.94 (d, *J* = 7.1 Hz, 3 H), 0.79 (d, *J* = 6.8 Hz), minor isomer δ 2.98 (dd, *J* = 16.5, 4.3 Hz, 1 H), 2.73 (dd, *J* = 16.5, 9.0 Hz, 1 H), 0.93 (d, *J* = 7.0 Hz, 3 H), 0.80 (d, *J* = 6.8 Hz), for both isomers δ 5.70 (m, 1 H), 5.00 (m, 1 H), 4.95 (m, 1 H), 4.83 (s, 5 H), 1.94–2.15 (m, 2 H): IR (CH_2Cl_2) 2952 (m), 2915 (w), 2008 (s), 1953 (vs), 1630 (s), 1067 (m), 1023 (m), 822 (m) cm^{-1}; MS (CI) *m/e* 303 (M + 1, 100), 275 (5), 246 (24), 218 (36), 205 (29), 177 (22), 163 (18). This complex was not further characterized but converted to the known ethyl ester (see below).

General Procedure IV: Oxidative Cleavage of the Acyliron Moiety to Ester. To a solution of acyliron complex (1.0 equiv, 0.05 M) and alcohol (5.0–20 equiv) in dichloromethane at −23 °C was added dropwise a solution of *N*-bromosuccinimide (ca. 1.5 equiv) in dichloromethane. The mixture was stirred at −23 °C for 1 h; during this period the solution changed gradually from yellow to red-brown. It was then warmed to room temperature and stirred for an additional 2 h. The resulting mixture was then filtered through silica gel. Removal of dichloromethane on a rotary evaporator left a dark brown oil, which was separated by flash column chromatography on silica gel with 9:1 hexane–ethyl acetate as the eluent to give the product.

General Procedure V: Transformation of Tetraalkylstannanes to Monobromostannanes. To a 0.05 M solution of tetraalkylstannane (1.0 equiv) in 2-propanol and dichloromethane (5:1) at 25 °C was added dropwise a 0.1 M bromine (1–4 equiv) solution in 2-propanol over a period of 5 min. The mixture was stirred at this temperature in the dark for 3 h. All volatile materials were then removed on a rotary evaporator with the bath temperature below 40 °C. The crude product was used without purification and characterization unless otherwise indicated.

General Procedure VI: Conversion of Monobromostannanes to Alcohols by Peracid Oxidation. To a 0.05 M solution of monobromostannane (1.0 equiv) and peracid (1.5–6 equiv) in dichloromethane at 0 °C was added a base. The mixture was stirred at this temperature for 1 h and then warmed to 25 °C and stirred for 12 h. The resulting solution was extracted with

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saturated sodium carbonate solution three times. The combined organic extracts were concentrated on a rotary evaporator, and the residue was separated by flash column chromatography on silica gel.

Preparation of (1β,3α)-(±)-1-Carbethoxy-3-(tributylstannyl)cyclopentane (7A, Ethyl Ester). General procedure IV was followed with complex **3A** (0.330 g, 0.587 mmol), NBS (0.160 g, 0.899 mmol, 1.53 equiv), and ethanol (2.0 mL, 34 mmol). Stannane **7A** (ethyl ester) was obtained as a colorless oil (0.169 g, 67%): ^{1}H NMR ($CDCl_3$) δ 4.05 (q, J = 7.2 Hz, 2 H), 2.70 (m, 1 H), 2.12 (m, 1 H), 1.93 (m, 1 H), 1.70 (m, 1 H), 1.13–1.55 (m, 19 H), 0.70–0.90 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 177.1, 60.1, 43.9, 35.1, 32.0, 31.5, 29.3, 27.4, 22.6, 14.2, 13.6, 8.2; IR (CH_2Cl_2) 2965 (s), 2926 (s), 2870 (s), 2853 (s), 1725 (s), 1382 (m), 1262 (m), 1182 (s), 1155 (s) cm^{-1}. This compound was not further characterized but subjected to further manipulations (see below).

Preparation of (1β,3α)-(±)-1-Carbobenzoxy-3-(tributylstannyl)cyclopentane (7A). General procedure IV was followed with complex **3A** (0.678 g, 1.18 mmol), NBS (0.315 g, 1.77 mmol), and benzyl alcohol (2.0 mL, 19 mmol). Stannane **7A** was obtained as a colorless oil (0.532 g, 91%): ^{1}H NMR ($CDCl_3$) δ 7.35 (br s, 5 H), 5.12 (s, 2 H), 2.85 (m, 1 H), 2.20 (m, 1 H), 2.00 (m, 2 H), 1.20–1.87 (m, 16 H), 0.75–0.97 (m, 15 H); ^{13}C NMR ($CDCl_3$ δ 176.8, 136.3, 128.4, 127.9, 65.9, 43.8, 35.1, 31.9, 29.3, 27.4, 22.6, 17.2, 13.6, 8.2; IR (CH_2Cl_2) 2962 (s), 2925 (s), 2870 (s), 2850 (s), 1722 (s), 1455 (m), 1380 (m), 1262 (m), 1180 (s), 1157 (s) cm^{-1}. This compound was converted to **15A** without further characterization.

Preparation of (1β,3α)-(±)-1-Carbethoxy-1-methyl-3-(tributylstannyl)cyclopentane (7I, Ethyl Ester). General procedure IV was followed with complex **3I** (1.780 g, 3.08 mmol), NBS (0.822 g, 4.62 mmol), and ethanol (5.0 mL, 85 mmol). Complex **7I** (ethyl ester) was obtained as a colorless oil (1.180 g, 86%): ^{1}H NMR ($CDCl_3$) δ 4.07 (q, J = 7.2 Hz, 2 H), 2.39 (m, 1 H), 1.85–2.13 (m, 2 H), 1.15–1.65 (m, 22 H), 0.70–0.95 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 178.8, 60.2, 50.0, 44.1, 39.0, 30.8, 29.3, 27.4, 25.6, 23.4, 14.1, 13.6, 8.2; IR (CH_2Cl_2) 2961 (s), 2923 (s), 2869 (s), 2852 (s), 1724 (s), 1378 (m), 1262 (m), 1183 (s), 1157 (s) cm^{-1}. This compound was not further characterized but subjected to further manipulations (see below).

Preparation of (1β,3α)-(±)-1-Carbobenzoxy-1-methyl-3-(tributylstannyl)cyclopentane (7I). General procedure IV was followed with complex **3I** (2.250 g, 3.90 mmol), NBS (0.800 g, 4.49 mmol), and benzyl alcohol (5.0 mL, 48 mmol). Stannane **7I** was obtained as a colorless oil (1.200 g, 61%): ^{1}H NMR ($CDCl_3$) δ 7.33 (br s, 5 H), 5.12 (s, 2 H), 2.47 (m, 1 H), 2.15 (m, 1 H), 2.00 (m, 1 H), 1.20–1.70 (m, 19 H), 0.75–0.95 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 178.6, 136.6, 128.4, 127.9, 127.6, 66.0, 50.1, 44.2, 39.1, 30.8, 29.3, 27.4, 25.6, 23.4, 13.6, 8.2; IR (CH_2Cl_2) 2963 (s), 2924 (s), 2872 (s), 2851 (s), 1725 (s), 1454 (m), 1382 (m), 1262 (m), 1179 (s), 1157 (s) cm^{-1}. This compound was converted to **15I** without further characterization.

Preparation of (1β,2α,4α)-(±)-1-Carbobenzoxy-2-methyl-4-(tributylstannyl)cyclopentane (7J). General procedure IV was followed with complex **3J** (0.582 g, 1.01 mmol), NBS (0.250 g, 1.40 mmol), and benzyl alcohol (2.0 mL, 19 mmol). Stannane **7J** was obtained as a colorless oil (0.357 g, 70%): ^{1}H NMR ($CDCl_3$) δ 7.35 (br s, 5 H), 5.13 (s, 2 H), 1.75–2.45 (m, 5 H), 1.15–1.65 (m, 14 H), 1.10 (d, J = 7.2 Hz, 3 H), 0.75–0.95 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 176.6, 136.4, 128.4, 127.9, 65.9, 52.0, 41.6, 41.4, 34.8, 29.3, 27.4, 22.6, 19.3, 13.6, 8.2; IR (CH_2Cl_2) 2960 (s), 2930 (s), 2875 (s), 2852 (s), 1722 (s), 1458 (m), 1380 (m), 1261 (m), 1180 (s), 1157 (s), 1060 (m), 1000 (m) cm^{-1}; MS (CI) m/e 508 (M^+, 0.6), 451 (100), 395 (12), 259 (15), 291 (48), 235 (51), 179 (36); HRMS m/e calcd for $C_{26}H_{44}O_2Sn$ 508.2363, found 508.2371.

Preparation of (1β,2β,4α)-(±)-1-Carbobenzoxy-2-methyl-4-(tributylstannyl)cyclopentane (7K). General procedure IV was followed with complex **3K** (0.144 g, 0.250 mmol), NBS (0.160 g, 0.899 mmol), and benzyl alcohol (1.5 mL, 14 mmol). Stannane **7K** was obtained as a colorless oil (0.112 g, 88%): ^{1}H NMR ($CDCl_3$) δ 7.35 (br s, 5 H), 5.10 (s, 2 H), 2.95 (m, 1 H), 2.45 (m, 1 H), 2.18 (m, 2 H), 1.15–1.90 (m, 18 H), 0.75–0.95 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 175.8, 136.0, 128.9, 128.4, 128.2, 65.9, 48.7, 37.7, 37.5, 31.5, 29.3, 27.4, 24.2, 18.7, 13.6, 8.2; IR (CH_2Cl_2) 2960 (s), 2932 (s), 2874 (s), 2852 (s), 1725 (s), 1460 (m), 1380 (m), 1263 (m), 1182 (s), 1157 (s), 1058 (m), 1002 (m) cm^{-1}. This compound was converted to **15K** without further characterization.

Preparation of (1β,3β,4α)-(±)-1-Carbobenzoxy-3-methyl-4-(tributylstannyl)cyclopentane (7D). General procedure IV was followed with **3D** (0.460 g, 0.797 mmol), NBS (0.220 g, 1.24 mmol), and benzyl alcohol (1.5 mL, 14 mmol). Stannane **7D** was obtained as a colorless oil (0.348 g, 86%): ^{1}H NMR ($CDCl_3$) δ 7.30 (br s, 5 H), 5.08 (s, 2 H), 2.84 (m, 1 H), 1.75–2.28 (m, 4 H), 1.05–1.65 (m, 14 H), 1.00 (d, J = 7.2 Hz, 3 H), 0.75–0.95 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 176.9, 136.4, 128.4, 128.0, 66.0, 44.4, 40.7, 40.1, 35.2, 32.2, 29.3, 27.5, 19.8, 13.6, 8.3; IR (CH_2Cl_2) 2961 (s), 2930 (s), 2872 (s), 2850 (s), 1724 (s), 1461 (m), 1382 (m), 1261 (m), 1182 (s), 1155 (s), 1060 (m), 1002 (m) cm^{-1}. This compound was converted to **15D** without further characterization.

Preparation of (1β,2α,3β,4α,5α)-(±)-1-Carbobenzoxy-4-(tributylstannyl)-2,3,5-trimethylcyclopentane (7F). General procedure IV was followed with complex **3F** (0.165 g, 0.273 mmol), NBS (0.058 g, 0.33 mmol), and benzyl alcohol (0.50 mL, 4.8 mmol). Stannane **7F** was obtained as a colorless oil (0.098 g, 67%): ^{1}H NMR ($CDCl_3$) δ 7.33 (br s, 5 H), 5.12 (s, 2 H), 1.93–2.40 (m, 3 H), 1.20–1.70 (m, 14 H), 0.75–0.95 (m, 24 H); ^{13}C NMR ($CDCl_3$) δ 175.9, 136.5, 128.5, 127.9, 65.9, 60.1, 43.7, 42.7, 41.0, 40.5, 29.3, 27.5, 20.1, 17.9, 14.8, 13.6, 8.5; IR (CH_2Cl_2) 2962 (s), 2932 (s), 2873 (s), 2852 (s), 1723 (s), 1460 (m), 1380 (m), 1260 (m), 1180 (s), 1155 (s), 1059 (m) 1003 (m) cm^{-1}. This compound was converted to **15F** without further characterization.

Preparation of Ethyl 3-Methyl-5-hexenecarboxylate (6J). General procedure IV was followed with complex **3J** (0.102 g, 0.354 mmol), NBS (0.070 g, 0.393 mmol), and ethanol (0.50 mL, 8.5 mmol). Ester **6J** was obtained as a colorless oil (0.069 g, 89%): ^{1}H NMR ($CDCl_3$) δ 5.03 (br s, 1 H), 4.96 (m, 1 H), 4.17 (q, 2 H, J = 7.0 Hz), 2.38 (m, 1 H), 1.95–2.22 (m, 3 H), 1.16 (t, 3 H, J = 7.0 Hz), 0.93 (d, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.9, 136.3, 136.2, 128.5, 128.2, 116.6, 66.0, 41.0, 40.9, 30.2, 19.6; IR (CH_2Cl_2) 2962 (m), 2930 (w), 1725 (s), 1458 (m), 1380 (m), 1265 (m), 1225 (m), 1178 (s), 1000 (m) cm^{-1}. The spectral data were in agreement with those previously reported for this compound.[44]

Preparation of Ethyl 3,4-Dimethyl-5-hexenecarboxylate (6O, Anti and Syn). General procedure IV was followed with a 3:1 anti–syn mixture of complex **4O** (0.085 g, 0.281 mmol), NBS (0.063 g, 0.354 mmol), and ethanol (1.0 mL, 16 mmol). Ester **6O** was obtained as a colorless liquid (0.027 g, 56%): ^{1}H NMR ($CDCl_3$) of **6O**-*anti* (major isomer) δ 0.96 (d, J = 6.7 Hz, 3 H), 0.86 (d, J = 6.5 Hz, 3 H); ^{1}H NMR ($CDCl_3$) of **6O**-*syn* (minor isomer) δ 0.94 (d, J = 6.6 Hz, 3 H), 0.87 (d, J = 6.3 Hz, 3 H); ^{1}H NMR signals in both isomers δ 5.68 (m, 1 H), 5.00 (m, 1 H), 4.93 (m, 1 H), 4.10 (q, J = 7.1 Hz, 2 H), 2.35 (m, 1 H), 1.85–2.15 (m, 2 H), 1.22 (t, J = 7.1 Hz, 3 H); IR (CH_2Cl_2) 2960 (m), 2930 (w), 1730 (s), 1455 (w), 1380 (w), 1265 (w), 1185 (m), 1030 (w) cm^{-1}. The spectral data matched those of the anti and syn isomers, respectively, as reported by Yamamoto.[3]

Preparation of 4-Phenyl-2-(tributylstannyl)butane (9). To a flask containing potassium hydride (1.83 g of 35% KH in mineral oil, 16.0 mmol, prewashed with hexane) was added, in sequence, 15 mL of THF, 1.5 mL of HMPA, and tributylstannyl hydride (4.50 mL, 16.7 mmol). Hydrogen gas evolved instantaneously upon the addition of tributylstannyl hydride. The solution changed gradually to green. The evolution of hydrogen ceased in 15 min, and the solution was transferred to a solution of 4-phenyl-2-bromobutane (3.17 g, 14.9 mmol)[46] in THF (20 mL) at −78 °C via a cannula. The mixture was stirred for 1 h at this temperature and was then warmed to 25 °C and stirred for 4 h. The resulting mixture was then poured into 20 mL of water and extracted with diethyl ether (2 × 50 mL). The organic extracts were dried (Na_2SO_4), and the solvent was removed on a rotary evaporator. The residue was separated by fractional distillation under vacuum. Two fractions were collected. The first fraction (3.86 g, colorless liquid) was a mixture of the starting bromide and tributylstannyl residue. The second fraction (2.85 g, 45%, 150–165 °C/0.05 mmHg, colorless liquid) was the desired product

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9: ^{1}H NMR ($CDCl_3$) δ 7.05–7.25 (m, 5 H), 2.55 (m, 2 H), 1.80 (m, 2 H), 1.10–1.60 (m, 16 H), 0.80–0.90 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 142.9, 128.4, 128.3, 125.6, 38.5, 36.0, 29.4, 27.6, 19.7, 18.6, 13.7, 8.4; IR (CH_2Cl_2) 2958 (s), 2927 (s), 2870 (m), 2856 (s), 1495 (w), 1465 (w), 1455 (w), 1180 (w) cm^{-1}; MS (EI) m/e 367 (M – C_4H_9, 100), 353 (13), 291 (44), 235 (35), 121 (30); HRMS m/e calcd for $C_{18}H_{31}Sn$ (M – C_4H_9) 367.1448, found 367.1447.[45]

Preparation of 4-Phenyl-2-butanone from Stannane 9. General procedure V was followed with stannane **9** (0.125 g, 0.296 mmol) and chromic anhydride–pyridine (1.53 g, 5.93 mmol, 20 equiv). The reaction was allowed to proceed for 36 h, and the final purification was achieved by silica gel preparative TLC with 9:1 hexane–ethyl acetate as the eluent. 4-Phenyl-2-butanone was obtained as a colorless oil (0.015 g, 34%). The spectral data were in agreement with those reported previously for this compound.[46]

Preparation of 1-Carbobenzoxy-3-oxocyclopentane (8A). General procedure V was followed with **7A** (0.150 g, 0.304 mmol) and chromic anhydride–pyridine (1.80 g, 7.03 mmol, 23 equiv). The reaction was conducted at 25 °C for 48 h, and the final purification was achieved by flash column chromatography on silica gel with 4:1 hexane–ethyl acetate as eluent. Ketone **8A** was obtained as a colorless oil (0.027 g, 41%): ^{1}H NMR ($CDCl_3$) δ 7.31 (br s, 5 H), 5.12 (s, 2 H), 3.12 (tt, J = 8.1, 7.1 Hz, 1 H), 2.45 (dd, J = 8.6, 7.1 Hz, 1 H), 1.98–2.37 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 216.3, 173.8, 135.4, 128.4, 128.1, 128.0, 66.4, 40.8, 37.1, 26.3; IR (CH_2Cl_2) 3075 (w), 3040 (w), 2960 (w), 1735 (s), 1485 (m), 1460 (m), 1410 (m), 1195 (s), 1160 (s), 1010 (w), 982 (w) cm^{-1}; MS (EI) m/e 218 (M$^+$, 5.5), 190 (7.3), 175 (2.3), 165 (2.2), 107 (8.8), 91 (100), 84 (24), 77 (14), 65 (19); HRMS m/e calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0944.

Preparation of 1-Carbobenzoxy-1-methyl-3-oxocyclopentane (8I). General procedure V was followed with **7I** (0.065 g, 0.128 mmol) and chromic anhydride–pyridine (0.920 g, 3.56 mmol, 27 equiv). The reaction was conducted at 25 °C for 24 h, and the final purification was achieved by silica gel preparative TLC with 4:1 hexane–ethyl acetate as eluent. Ketone **8I** was obtained as a colorless oil (0.004 g, 14%): ^{1}H NMR ($CDCl_3$) δ 7.29 (br s, 5 H), 5.09 (s, 2 H), 2.74 (d, J = 18 Hz, 1 H), 2.22–2.43 (m, 3 H), 2.08 (d, J = 18 Hz), 1.88 (m, 1 H), 1.37 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 216.9, 176.4, 136.0, 128.9, 128.6, 128.2, 67.1, 49.4, 46.7, 37.0, 34.0, 24.1; IR (CH_2Cl_2) 3062 (w), 2980 (w), 1740 (s, br), 1500 (w), 1458 (m), 1410 (m), 1190 (s), 1160 (s), 1010 (w), 982 (w) cm^{-1}; MS (CI) m/e 233 (M + 1, 26), 215 (1.7), 204 (2.4), 181 (0.8), 131 (2.2), 91 (100); HRMS m/e calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1108.

Preparation of (1β,2α)-(±)-1-Carbobenzoxy-2-methyl-4-oxocyclopentane (8J). General procedure V was followed with **7J** (0.086 g, 0.170 mmol) and chromic anhydride–pyridine (1.10 g, 4.25 mmol, 25 equiv). The reaction was conducted at 25 °C for 48 h, and the final purification was achieved by silica gel preparative TLC with 4:1 hexane–ethyl acetate as eluent. Complex **8J** was obtained as a colorless oil (0.007 g, 18%): ^{1}H NMR ($CDCl_3$) δ 7.34 (br s, 5 H), 5.16 (s, 2 H), 2.40–2.80 (m, 5 H), 1.88 (m, 1 H), 1.18 (d, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 215.5, 173.7, 135.6 128.6, 128.4, 128.2, 66.8, 48.6, 46.2, 42.2, 35.5, 19.3; IR (CH_2Cl_2) 3075 (w), 3040 (w), 2960 (w), 1735 (s), 1485 (m), 1460 (m), 1410 (m), 1195 (s), 1160 (s), 1010 (w), 982 (w) cm^{-1}; MS (EI) m/e 232 (M$^+$, 2.4), 214 (1.4), 204 (17), 141 (3.1), 107 (17), 91 (100), 77 (9.0), 65 (24); HRMS m/e calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1104.

Preparation of 4-Phenyl-2-(bromodibutylstannyl)butane (10). General procedure VI was followed with stannane **9** (0.820 g, 1.94 mmol) and bromine (0.950 g, 5.94 mmol, 3.06 equiv). The yellow residue obtained after the removal of solvents was redissolved in dichloromethane–hexane and filtered through silica gel (2.5 × 4 cm). Elution with hexane gave the unreacted stannane **9** (0.067 g, 7.0%). Elution with ethyl acetate afforded bromotrialkylstannane **10** (0.727 g, 84%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.08–7.25 (m, 5 H), 2.65 (m, 2 H), 1.89 (m, 2 H), 1.52 (m, 4 H), 1.25 (m, 8 H), 1.10 (m, 1 H), 0.88 (m, 9 H); IR (CH_2Cl_2) 2960 (s), 2931 (s), 2658 (s), 1462 (m), 1458 (m) cm^{-1}; MS (EI) m/e 444 (M$^+$, 28), 387 (65), 367 (18), 313 (45), 257 (16), 199 (32), 177 (49); HRMS m/e calcd for $C_{14}H_{23}BrSn$ (M – C_4H_9) 390.0005, found 390.0028.[45]

Preparation of (1β,4α)-(±)-1-Carbobenzoxy-3-(bromodibutylstannyl)-1-methylcyclopentane (14I). General procedure VI was followed with stannane **7I** (0.416 g, 0.820 mmol) and bromine (0.450 g, 2.81 mmol, 3.43 equiv). The yellow residue obtained after the removal of solvents was redissolved in dichloromethane–hexane and filtered through silica gel (2.5 × 4 cm). Elution with hexane gave the unreacted **7I**. Elution with ethyl acetate afforded bromotrialkylstannane **14I** (0.365 g, 84%) as a colorless oil: ^{1}H NMR ($CDCl_3$ δ 7.27 (br s, 5 H), 5.05 (s, 2 H), 2.46 (br dd, J = 12.9, 7.4 Hz, 1 H), 1.90–2.18 (m, 2 H), 1.65–1.72 (m, 3 H), 1.47–1.63 (m, 5 H), 1.13–1.45 (m, 11 H), 0.86 (t, J = 7.5 Hz, 6 H). This compound was not characterized further but was converted to **15I** (see below).

Preparation of (1β,2β,4α)-(±)-1-Carbobenzoxy-4-(bromodibutylstannyl)-2-methylcyclopentane (14J). General procedure VI was followed with stannane **7J** (0.112 g, 0.221 mmol) and bromine (0.104 g, 0.650 mmol, 2.94 equiv). The yellow residue obtained after the removal of solvents was redissolved in dichloromethane–hexane and filtered through silica gel (2.5 × 4 cm). Elution with hexane gave the unreacted **7J**. Elution with ethyl acetate afforded **14J** (0.090 g, 77%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.35 (br s, 5 H), 5.10 (s, 2 H), 2.96 (m, 1 H), 2.30–2.55 (m, 2 H), 1.92–2.25 (m, 3 H), 1.80 (m, 1 H), 1.63 (m, 4 H), 1.15–1.45 (m, 11 H), 0.90 (t, J = 7.2 Hz, 6 H). This compound was not characterized further but was converted to **15J** (see below).

Preparation of (1β,2α,3β,4α,5α)-(±)-1-Carbobenzoxy-4-(bromodibutylstannyl)-2,3,5-trimethylcyclopentane (14F). General procedure VI was followed with stannane **7F** (0.098 g, 0.183 mmol) and bromine (0.150 g, 0.938 mmol, 5.12 equiv). The yellow residue obtained after the removal of solvents was redissolved in dichloromethane–hexane and filtered through silica gel (2.5 × 4 cm). Elution with ethyl acetate afforded **14F** (0.084 g, 82%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.32 (br s, 5 H), 5.12 (s, 2 H), 2.38 (m, 2 H), 2.02 (m, 1 H), 1.60 (m, 4 H), 1.20–1.48 (m, 10 H), 1.09 (d, J = 7.2 Hz, 3 H), 0.80–1.0 (m, 12 H). This compound was not characterized further but was converted to **15F** (see below).

Conversion of 4-Phenyl-2-(bromodibutylstannyl)butane (10) to 4-Phenyl-2-butanol (11). Method A. General procedure VI was followed with stannane **10** 0.050 g, 0.11 mmol), MCPBA (0.065 g, 0.38 mmol, 3.4 equiv), and triethylamine (0.20 mL, 1.4 mmol, 13 equiv). The final purification was achieved by preparative TLC with 3:2 hexane–ethyl acetate as eluent. A colorless oil identified as alcohol **11** was obtained (0.010 g, 61%).

Method B. General procedure VI was followed with stannane **10** (0.255 g, 0.572 mmol), MCPBA (0.247 g, 1.43 mmol, 2.5 equiv), and NH_3 (gaseous ammonia was allowed to pass through the reaction mixture for 15 min). The final purification was achieved by flash column chromatography on silica gel with 4:1 hexane–ethyl acetate as eluent (0.074 g, 86%).

Method C. General procedure VI was followed with stannane **10** (0.125 g, 0.28 mmol), peracetic acid (0.20 mL of a 32% solution in acetic acid, 0.84 mmol, 3.0 equiv), and triethylamine (0.50 mL, 3.6 mmol, 13 equiv). The final purification was achieved by flash column chromatography on silica gel with 3:2 hexane–ethyl acetate as eluent (0.019 g, 46%). The spectral data were in agreement with those reported previously for this compound.[46]

Preparation of (1β,3α)-(±)-1-Carbobenzoxy-3-hydroxycyclopentane (15A). General procedures V and VI were followed with stannane **7A** (0.187 g, 0.380 mmol), bromine (0.112 g, 0.700 mmol, 1.84 equiv), MCPBA (0.150 g, 0.870 mmol, 2.29 equiv), and NH_3 (gaseous ammonia was allowed to pass through the reaction mixture for 15 min). The intermediate monobromide was used without purification and characterization. The purification of the final product was achieved by silica gel preparative TLC with 3:2 hexane–ethyl acetate as the eluent. Alcohol **15A** was obtained as a colorless oil (0.045 g, 55%): ^{1}H NMR ($CDCl_3$) δ 7.36 (br s, 5 H), 5.11 (s, 2 H), 4.46 (m, 1 H), 3.12 (m, 1 H), 1.70–2.22 (m, 6 H), 1.65 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 176.2, 136.2, 128.5, 128.1, 128.0, 73.5, 66.2, 41.7, 39.3, 35.0, 27.4; IR (CH_2Cl_2) 3606 (w), 3580 (w, br), 2955 (m), 1729 (s), 1460 (m), 1385 (m), 1350 (m), 1185 (s), 1176 (s) cm^{-1}; MS (EI) m/e 220 (M$^+$, 1.3), 192 (1.1), 174 (1.5), 129 (4.7), 113 (10), 107 (6.4), 91 (100), 77 (10); HRMS m/e calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1107.

Preparation of (1β,3α)-(±)-1-Carbobenzoxy-3-hydroxy-1-methylcyclopentane (15I). General procedure VI was followed with bromotrialkylstannane **14I** (0.365 g, 0.689 mmol), MCPBA (0.212 g, 1.23 mmol, 1.78 equiv), and NH_3 (gaseous ammonia was

allowed to pass through the reaction mixture for 15 min). The final purification was achieved by silica gel preparative TLC with 3:2 hexane–ethyl acetate as the eluent. Alcohol **15I** was obtained as a colorless oil (0.152 g, 94%): ^{1}H NMR ($CDCl_3$) δ 7.33 (br s, 5 H), 5.08 (s, 2 H), 4.40 (tt, J = 6.0, 3.9 Hz, 1 H), 2.52 (dd, J = 14.0, 6.0 Hz, 1 H), 1.63–2.20 (m, 5 H), 1.49 (dd, J = 14.0, 3.9 Hz, 1 H), 1.40 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 178.0, 136.2, 128.5, 128.0, 127.7, 73.7, 66.3, 48.6, 46.7, 35.9, 35.2, 26.2; IR (CH_2Cl_2) 3608 (w), 2970 (m), 2950 (m), 1724 (s), 1456 (m), 1384 (w), 1350 (m), 1162 (s), 909 (m) cm^{-1}; MS (EI) m/e 234 (M^+, 1.6), 154 (2.6), 143 (2.6), 127 (3.2), 107 (5.2), 99 (2.5), 91 (46), 84 (100), 77 (23); HRMS m/e calcd for $C_{14}H_{18}O_3$ 234.1256, found 234.1269.

Preparation of (1β,2α,4α)-(±)-1-Carbobenzoxy-4-hydroxy-2-methylcyclopentane (15J). General procedures V and VI were followed with stannane **7J** (0.152 g, 0.300 mmol), bromine (0.150 g, 0.938 mmol, 3.12 equiv), MCPBA (0.105 g, 0.609 mmol, 2.03 equiv), and NH_3 (gaseous ammonia was allowed to pass through the reaction mixture for 15 min). The intermediate monobromide was used without purification and characterization. The purification of the final product was achieved by silica gel preparative TLC with 3:2 hexane–ethyl acetate as the eluent. Alcohol **15J** was obtained as a colorless oil (0.041 g, 59%): ^{1}H NMR ($CDCl_3$) δ 7.38 (br s, 5 H), 5.16 (s, 2 H), 4.42 (m, 1 H), 2.70 (q, J = 9.3 Hz, 1 H), 1.88–2.40 (m, 5 H), 1.30 (m, 1 H), 1.17 (d, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 175.4, 136.2, 128.5, 128.1, 127.9, 72.6, 66.1, 49.8, 44.1, 39.9, 37.5, 20.3; IR (CH_2Cl_2) 3607 (w), 3450 (w, br), 2961 (m), 2933 (m), 1728 (s), 1456 (m), 1384 (w), 1350 (m), 1160 (s), 905 (w) cm^{-1}; MS (CI) m/e 235 (M + 1, 35), 217 (14), 199 (2.9), 159 (9.6), 143 (77), 127 (30), 99 (20), 91 (62), 82 (100), 77 (4); HRMS (CI) m/e calcd for $C_{14}H_{19}O_3$ 235.1334, found 235.1318.

Preparation of (1β,2β,4α)-(±)-1-Carbobenzoxy-4-hydroxy-2-methylcyclopentane (15K). General procedure VI was followed with bromostannane **14K** (0.090 g, 0.17 mmol), MCPBA (0.070 g, 0.41 mmol, 2.4 equiv), and NH_3 (gaseous ammonia was allowed to pass through the reaction mixture for 15 min). The final product was separated by silica gel preparative TLC with 3:2 hexane–ethyl acetate as the eluent. Alcohol **15K** was obtained as a colorless oil (0.031 g, 76%): ^{1}H NMR ($CDCl_3$) δ 7.30 (br s, 5 H), 5.05 (s, 2 H), 4.45 (m, 1 H), 2.60 (m, 1 H), 1.50–2.40 (m, 6 H), 0.84 (d, J = 7.2 Hz, 3 H); IR (CH_2Cl_2) 3605 (w), 3445 (w, br), 2959 (m), 2933 (m), 1731 (s), 1450 (m), 1388 (w), 1350 (m), 1160 (s), 910 (w) cm^{-1}; MS (CI) m/e 235 (M + 1, 21), 217 (8.5), 188 (11), 171 (9.3), 143 (69), 127 (73), 99 (58), 91 (100), 82 (100), 78 (73); HRMS (CI) m/e calcd for $C_{14}H_{19}O_3$ 235.1334, found 235.1334.

Preparation of (1β,3β,4α)-(±)-1-Carbobenzoxy-4-hydroxy-3-methylcyclopentane (15D). General procedures V and VI were followed with stannane **7D** (0.146 g, 0.287 mmol), bromine (0.070 g, 0.436 mmol, 1.52 equiv), MCPBA (0.100 g, 0.580 mmol, 2.02 equiv), and NH_3 (gaseous ammonia was allowed to pass through the reaction mixture for 15 min). The intermediate monobromide was used without purification and characterization. The purification of the final product was achieved by silica gel preparative TLC with 3:2 hexane–ethyl acetate as the eluent. Alcohol **15D** was obtained as a colorless oil (0.045 g, 67%): ^{1}H NMR ($CDCl_3$) δ 7.34 (br s, 5 H), 5.10 (s, 2 H), 3.84 (br q, J = 6.0 Hz, 1 H), 3.04 (tt, J = 10.4, 7.4 Hz, 1 H), 2.20 (dt, J = 10.4, 7.4 Hz, 2 H), 1.83 (m, 2 H), 1.22–1.50 (m, 2 H), 1.01 (d, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 175.9, 136.2, 128.5, 128.1, 128.0, 79.4, 66.2, 42.8, 40.6, 37.5, 35.8, 17.9; IR (CH_2Cl_2) 3604 (w), 3450 (w, br), 2952 (m), 2931 (m), 1730 (s), 1456 (m), 1384 (w), 1350 (w), 1168 (s), 910 (w) cm^{-1}; MS (EI) m/e 234 (M, 3.5), 143 (16), 127 (17), 99 (6.2), 91 (100), 81 (31), 77 (16); HRMS m/e calcd for $C_{14}H_{18}O_3$ 234.1256, found 234.1271.

Preparation of (1β,2α,3β,4α,5α)-(±)-1-Carbobenzoxy-4-hydroxy-2,3,5-trimethylcyclopentane (15F). General procedure VI was followed with stannane **7F** (0.084 g, 0.15 mmol), MCPBA (0.080 g, 0.46 mmol, 3.1 equiv), and NH_3 (gaseous ammonia was allowed to pass through the reaction mixture for 15 min). The final product was separated by silica gel preparative TLC with 3:2 hexane–ethyl acetate as the eluent. Alcohol **15F** was obtained as a colorless oil (0.026 g, 67%): ^{1}H NMR ($CDCl_3$) δ 7.38 (br s, 5 H), 5.09 (s, 2 H), 3.19 (br t, J = 4.9 Hz, 1 H), 2.36 (m, 1 H), 1.82–2.04 (m, 3 H), 1.07 (d, J = 7.2 Hz, 3 H), 0.90 (d, J = 7.2 Hz, 3 H), 0.88 (d, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 175.2, 136.3, 128.5, 128.1, 128.0, 85.0, 66.2, 56.6, 45.7, 37.1, 17.3, 16.4, 13.2; IR (CH_2Cl_2) 3610 (w), 3455 (w, br), 2962 (m), 2931 (m), 1725 (s), 1460 (m), 1387 (w), 1365 (w), 1164 (s), 910 (w) cm^{-1}; MS (CI) m/e 263 (M + 1, 100), 245 (15), 227 (12), 215 (6.1), 199 (7.0), 172 (10), 153 (7.0), 138 (8.4), 125 (5.2), 109 (50), 91 (66); HRMS m/e calcd for $C_{16}H_{23}O_3$ 263.1647, found 263.1625.

Preparation of (2β,3α)-(±)-2-Benzyl-3-(trimethylstannyl)cyclohexanone. *Small deviations from the following procedure led to no formation of the desired product!* To a solution of hexamethylditin (1.875 g, 5.751 mmol) in THF (10 mL) at 0 °C was added a solution of methyllithium (3.50 mL of a 1.5 M diethyl ether solution, 5.30 mmol). The yellow-green mixture was stirred at 0 °C for 15 min, after which time a solution of 2-cyclohexenone (0.367 g, 3.83 mmol) in THF (4 mL) was added. The mixture was stirred at 0 °C for 1 h before benzyl bromide (0.783 g, 0.56 mL, 4.57 mmol) was added. Stirring was continued at 0 °C for 20 min. The solution was then poured into 50 mL of H_2O and extracted with diethyl ether (3 × 25 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated on a rotary evaporator. The residue was separated by flash column chromatography on silica gel. Elution with hexane gave trimethylstannyl residue and unreacted benzyl bromide. Elution with 9:1 hexane–ethyl acetate afforded 2-benzyl-3-(trimethylstannyl)cyclohexanone (1.067 g, 80%): ^{1}H NMR ($CDCl_3$) δ 7.20–7.40 (m, 5 H), 3.04 (dd, J = 13.5, 10.0 Hz, 1 H), 2.78 (td, J = 10.0, 3.0 Hz, 1 H), 2.42 (dd, J = 13.5, 3.0 Hz, 1 H), 2.42 (m, 2 H), 2.05–2.30 (m, 2 H), 1.65–2.00 (m, 3 H), 0.18 (s, 9 H); ^{13}C NMR ($CDCL_3$) δ 212.9, 140.7, 129.0, 128.1, 125.8, 56.4, 42.7, 37.0, 34.4, 32.3, 29.7, -9.8; IR (CH_2Cl_2) 2966 (m), 2932 (s), 2863 (m), 1704 (vs), 1496 (m), 1454 (m) cm^{-1}; MS (CI) m/e 351 (M + 1, 1.5), 337 (20), 313 (11), 286 (7.5), 261 (50), 186 (37), 165 (73), 135 (17), 108 (45), 86 (100); HRMS m/e calcd for $C_{16}H_{24}OSn$ (M) 352.0849, found 351.0846.

Preparation of (1β,2β,3α)-(±)-2-Benzyl-3-(trimethylstannyl)-1-cyclohexanol (12A,B). To a flask containing sodium borohydride (0.059 g, 1.53 mmol) at 0 °C was added slowly a solution of (2β,3α)-(±)-2-benzyl-3-(trimethylstannyl)cyclohexanone (see above; 0.420 g, 1.20 mmol) in methanol. Gas evolution was observed immediately. The mixture was stirred at this temperature for 30 min before 0.1 N HCl (10 mL) was added. It was then extracted with diethyl ether (3 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated on a rotary evaporator. The residue was redissolved in dichloromethane and the solution filtered through alumina. After dichloromethane was removed from the filtrate, the crude product was obtained as a colorless oil (0.225 g, 53%). ^{1}H NMR spectroscopy showed the crude product was a mixture of two isomers in a 1:1 rfatio. This material was separated by silica gel preparative TLC with 7:3 hexane–ethyl acetate as eluent. The two isomers were separated partially, and 0.028 g of pure isomer **12A** and 0.006 g of pure isomer **12B** were obtained. The less polar product was identified as **12A**: ^{1}H NMR ($CDCl_3$) δ 7.10–7.25 (m, 5 H), 3.47 (q, J = 2.3 Hz, 1 H), 2.45–2.63 (m, 2 H), 1.15–1.90 (m, 9 H), 0.05 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 140.6, 129.1, 128.3, 125.9, 66.2, 46.8, 39.6, 33.3, 30.4, 25.9, 21.9, 11.3, -10.2; IR (CH_2Cl_2) 3612 (m), 2979 (m), 2927 (s), 2858 (m), 1602 (w), 1500 (w), 1455 (w), 910 (s) cm^{-1}; MS (EI) m/e 339 (M - CH_3, 24), 319 (6), 183 (7), 172 (28), 165 (73), 135 (21), 104 (54), 91 (100); HRMS m/e calcd for $C_{15}H_{23}OSn$ (M - CH_3) 339.0771, found 339.0770.[45] This compound was assigned as **12A** due to the smaller couplings to the C*H*OH proton, which would be expected for an equatorial H. The more polar product was identified as **12B**: ^{1}H NMR ($CDCl_3$) δ 7.10–7.30 (m, 5 H), 3.39 (m, $w_{1/2}$ = 24 Hz, 1 H), 3.01 (dd, J = 14.0, 3.8 Hz, 1 H), 2.48 (dd, J = 14.0, 7.1 Hz, 1 H), 1.55–1.95 (m, 4 H), 1.10–1.40 (m, 4 H), 0.10 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 140.3, 129.3, 128.5, 126.2, 75.2, 48.8, 41.3, 35.0, 30.5, 29.7, 26.6, -9.7; IR (CCl_4) 3400 (s, br), 3025 (w), 2955 (m), 2920 (m), 2840 (m), 1600 (w), 1455 (w), 1385 (m), 1240 (m), 1135 (s) cm^{-1}; MS (EI) m/e 339 (M - CH_3, 24) 319 (6), 183 (8), 172 (28), 165 (74), 135 (21), 104 (54), 91 (100); HRMS m/e calcd for $C_{15}H_{23}OSn$ (M - CH_3) 339.0771, found 339.0771.[45] This compound was assigned as **12B** because of the larger couplings to the C*H*OH proton, which would be expected for an axial H.

Preparation of (1α,2β,3β)-(±)-2-Benzyl-1,3-cyclohexanediol (13A). General procedures V and VI were followed with stannane **12A** (0.060 g, 0.17 mmol), bromine (0.028 g, 0.18 mmol), MCPBA

(0.080 g, 0.46 mmol), and NH_3, except that general procedure VI was conducted at 0 °C. The intermediate monobromide was used without purification and characterization. The final product was purified by silica gel preparative TLC (2:1) hexane–ethyl acetate) as a colorless oil (0.029 g, 82%): ^1H NMR ($CDCl_3$) δ 7.10–7.30 (m, 5 H), 3.65–3.80 (m, 2 H), 3.11 (dd, J = 13.5, 4.1 Hz, 1 H), 2.63 (dd, J = 13.5, 11.0 Hz, 1 H), 1.10–2.05 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 140.8, 129.2, 128.4, 125.9, 70.3, 67.4, 51.0, 35.3, 33.9, 32.9, 18.8; IR (CH_2Cl_2) 3617 (m), 3060 (w), 2938 (m), 1364 (m), 1223 (m), 1034 (w), 909 (m) cm^{-1}; MS (EI) m/e 206 (M, 4.6), 188 (55), 170 (17), 144 (17), 129 (37), 117 (27), 91 (100); HRMS m/e calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1318.

Preparation of (1α,2β,3α)-(±)-2-Benzyl-1,3-cyclohexanediol (13B). General procedures V and VI were followed with stannane **12B** (0.006 g, 0.02 mmol), bromine (0.003 g, 0.02 mmol), MCPBA (0.008 g, 0.05 mmol), and NH_3, except that general procedure VI was conducted at 0 °C. The intermediate monobromide was used without purification and characterization. The final product was purified by silica gel preparative TLC (2:1 hexane–ethyl acetate) as a colorless oil (0.001 g, 30%): ^1H NMR ($CDCl_3$) δ 7.10–7.30 (m, 5 H), 3.48 (m, 2 H, $w_{1/2}$ = 21.4 Hz), 2.89 (d, 2 H, J = 6.4 Hz), 1.30–1.90 (m, 9 H). Due to the paucity of material, this compound could not be characterized further.

Preparation of (1β,3α)- and (1β,3β)-(±)-1-Carbobenzoxy-3-hydroxycyclopentane (15A and 16) from 8A. A solution of 3-oxocyclopentanecarboxylic acid[48] (2.10 g, 16 mmol), benzyl alcohol (1.80 g, 16 mmol), and concentrated H_2SO_4 (0.10 mL) in benzene (25 mL) was heated to reflux. The water produced during the reaction was separated with a Dean-Stark trap. After the mixture was refluxed for 2 h, about 0.3 mL (16 mmol) of water was removed. The mixture was then washed with saturated Na_2CO_3 solution (2 × 25 mL), and the solvent was removed on a rotary evaporator. The crude product was purified by short-path distillation (120–135 °C/0.05 mmHg), and 3.1 g of benzyl 3-oxocyclopentanecarboxylate (1-carbobenzoxy-3-oxocyclopentane, **8A**) was obtained. This material was dissolved in methanol (25 mL) and added to a flask containing $NaBH_4$ (0.400 g, 10.5 mmol) and methanol (25 mL) at 0 °C. The mixture was stirred at this temperature for 30 min and then poured into a mixture of 2 mL of 37% HCl, 10 mL of acetone, and 50 mL of water. After 10 min of stirring, methanol was removed on a rotary evaporator. The residue was extracted with diethyl ether (3 × 30 mL), and the combined organic extracts were dried (Na_2SO_4) and concentrated. After short-path distillation, 2.75 g of colorless material was obtained. It was determined to be a mixture of **15A** and **16** in 1:3 ratio by ^1H NMR spectroscopy.

Preparation of 3-Oxo-6-(phenylseleno)-2-oxabicyclo-[2.2.1]heptane (18A). To a solution of carboxylic acid **17A**[49] (0.650 g, 5.80 mmol) in dry dichloromethane (25 mL) at −78 °C was added dropwise a solution of phenylselenyl chloride (1.11 g, 5.80 mmol) in dichloromethane (3 mL) over a 5-min period. An instantaneous reaction was observed as the color of phenylselenyl chloride disappeared upon contact with the solution of **17A**. After the addition was complete, the mixture was stirred at −78 °C for 30 min and then warmed to room temperature over a period of 30 min. After the solvent was removed on a rotary evaporator, the light yellow solid residue was separated by flash column chromatography on silica gel. Elution with dichloromethane afforded **18A** (1.21 g, 78%) as white crystals: mp 72–73 °C (hexane–ethyl acetate); ^1H NMR ($CDCl_3$) δ 7.45 (m, 2 H), 7.25 (m, 3 H), 4.65 (br s, 1 H), 3.52 (m, 1 H), 2.85 (m, 1 H), 2.00–2.35 (m, 3 H), 1.73 (dt, J = 14.1, 5.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 176.9, 133.6, 129.4, 128.8, 128.0, 83.5, 41.8, 39.4, 37.1, 30.7; IR (CH_2Cl_2) 3060 (w), 2962 (w), 1790 (s), 1781 (s), 1480 (w), 1440 (w), 1322 (w), 1092 (m), 918 (m) cm^{-1}. This compound was converted to **16** without further characterization.

Preparation of (1β,3β)-(±)-1-Carbobenzoxy-3-hydroxycyclopentane (16) from 18A. Tributylstannyl hydride (1.50 g, 5.1 mmol), selenide **18A** (1.21 g, 4.52 mmol), and AIBN (0.020 g, 0.12 mmol) were dissolved in benzene (20 mL). The mixture was heated to reflux for a period of 4 h. The solution was cooled to 25 °C after this period, and benzyl alcohol (510 mg, 4.72 mmol) and p-toluenesulfonic acid (0.050 g, 0.29 mmol) were added. The resulting mixture was heated to 70 °C with stirring for a period of 10 h. After this period, the solvent was then removed on a rotary evaporator, and the residue was separated by flash column chromatography on silica gel. Elution with 19:1 hexane–ethyl acetate gave the tributylstannyl residue. Elution with 7:3 hexane–ethyl acetate afforded compound **16** (0.655 g, 66%): ^1H NMR ($CDCl_3$) δ 7.35 (br s, 5 H), 5.13 (s, 2 H), 4.33 (m, 1 H), 2.92 (m, 1 H), 1.95–2.17 (m, 5 H), 1.80 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 177.4, 135.8, 128.5, 128.2, 128.1, 66.6, 60.8, 42.0, 38.7, 35.6, 27.7; IR (CH_2Cl_2) 3606 (w), 3480 (w, br), 2955 (m), 1729 (s), 1460 (w), 1385 (w), 1353 (w), 1187 (s), 1174 (s), 905 (m) cm^{-1}; MS (EI) m/e 220 (M^+, 7.8), 202 (3.2), 192 (5.7), 174 (4.8), 108 (35), 91 (100), 77 (28); HRMS m/e calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1101.

Preparation of Benzyl 3-Cyclopentenecarboxylate. A solution of 3-cyclopentenecarboxylic acid[49] (1.85 g, 16.5 mmol), benzyl alcohol (2.20 g, 20.4 mmol), and concentrated H_2SO_4 (0.10 mL) in benzene (25 mL) was heated to reflux. The water produced during the reaction was separated with a Dean-Stark trap. After the solution was refluxed for 2 h, about 0.30 mL (16.5 mmol) of water was removed. The mixture was then washed with saturated Na_2CO_3 solution (2 × 25 mL), and the solvent was removed on a rotary evaporator. The crude product was purified by short-path distillation, and benzyl 3-cyclopentenecarboxylate was obtained as a colorless liquid (2.81 g, 84%): ^1H NMR ($CDCl_3$) δ 7.38 (br s, 5 H), 5.68 (br s, 2 H), 5.17 (s, 2 H), 3.20 (tt, J = 9.1, 8.1 Hz, 1 H), 2.67–2.73 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 175.6, 136.0, 128.7, 128.3, 127.8, 127.7, 66.0, 41.3, 36.0; IR (CH_2Cl_2) 3064 (w), 2945 (w, br), 2859 (w), 1730 (s), 1498 (w), 1455 (m), 1381 (w), 1350 (w), 1273 (m), 1192 (s), 1164 (s), 1023 (m), 909 (m) cm^{-1}. This compound was converted to the benzyl ester of **17B** without further characterization.

Preparation of Benzyl 1-Methyl-3-cyclopentenecarboxylate (17B, Benzyl Ester). To a solution of benzyl 3-cyclopentenecarboxylate (2.50 g, 12.4 mmol) in dry THF (20 mL) at −78 °C was added dropwise a solution of LDA (18.6 mmol) in THF (10 mL). The mixture was stirred at this temperature for 1 h. After this period methyl iodide (1.20 mL, 19.3 mmol) was added via syringe. The resulting mixture was stirred at this temperature for 30 min and then slowly warmed to 25 °C over a period of 2 h. After the solvent was removed on a rotary evaporator, the residue was redissolved in ethyl ether (30 mL) and washed with H_2O (2 × 10 mL). The organic extracts were dried (Na_2SO_4), and the solvent was removed on a rotary evaporator. The crude product was purified by short-path distillation. Benzyl 1-methyl-3-cyclopentenecarboxylate was obtained as a colorless liquid (2.01 g, 75%): ^1H NMR ($CDCl_3$) δ 7.30 (br s, 5 H), 5.57 (br s, 2 H), 5.10 (s, 2 H), 2.90 (br d, J = 15.5 Hz, 2 H), 2.20 (br d, J = 15.5 Hz, 2 H), 1.29 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 177.8, 136.3, 128.4, 128.2, 127.9, 127.7, 66.1, 47.8, 44.5, 25.9; IR (CH_2Cl_2) 2968 (w), 2934 (w), 1726 (s), 1456 (m), 1214 (m), 1198 (m), 1118 (m) cm^{-1}. This compound was converted to carboxylic acid **17B** without further characterization.

Preparation of 1-Methyl-3-cyclopentenecarboxylic Acid (17B). A mixture of benzyl 1-methyl-3-cyclopentenecarboxylate (0.500 g, 2.31 mmol) and KOH (1.8 g, 46 mmol) in benzene (10 mL) and H_2O (10 mL) was heated to 80 °C and stirred for 24 h. After this period the mixture was cooled to 25 °C, and the aqueous layer was separated. To this solution was added dropwise 37% HCl until the pH value was below 0. The resulting mixture was then extracted with ethyl ether (3 × 10 mL), the combined organic extracts were dried (Na_2SO_4), and the solvent was removed on a rotary evaporator. Compound **15B** was obtained as a white solid (0.267 g, 92%): ^1H NMR ($CDCl_3$) δ 11.85 (br s, 1 H), 5.48 (br s, 2 H), 2.82 (br d, J = 15.5 Hz, 2 H), 2.11 (br d, J = 15.5 Hz, 2 H), 1.20 (s, 3 H). This compound was converted to **18B** without further characterization.

Preparation of 4-Methyl-3-oxo-6-(phenylseleno)-2-oxabicyclo[2.2.1]heptane (18B). To a solution of compound **17B** (0.267 g, 2.12 mmol) in dry dichloromethane (15 mL) at −78 °C was added dropwise a solution of phenylselenyl chloride (0.410 g, 2.14 mmol) in dichloromethane (2 mL) over a 5-min period. An instantaneous reaction was observed as the color of phenylselenyl chloride disappeared upon its contact with the solution of **17B**. After the addition was complete, the mixture was stirred at −78 °C for 30 min and then warmed to 25 °C over a period of 30 min. After the solvent was removed on a rotary evaporator,

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the light yellow solid residue was separated by flash column chromatography on silica gel. Elution with 9:1 hexane–ethyl acetate afforded a mixture of isomers of 4-chloro-1-methyl-3-(phenylseleno)cyclopentanecarboxylic acid (0.550 g, 81%) as a white solid. No attempt was made to separate these compounds: ^{1}H NMR ($CDCl_3$): δ 11.90 (br s, 1 H), 7.58 (m, 2 H), 7.30 (m, 3 H), 4.20 (m, 1 H), 3.78 (m, 1 H), 3.07 (m, 1 H), 2.68 and 2.52 (dd, J = 14.6, 5.6 Hz, 1 H), 2.38 and 2.33 (dd, J = 14.6, 5.6 Hz, 1 H), 1.92 and 1.68 (dd, J = 14.6, 6.0 Hz, 1 H), 1.48 and 1.34 (s, 3 H). This mixture was converted into compound **18B**. A solution of this mixture (0.550 g, 1.73 mmol) and silver tetrafluoroborate (0.500 g, 2.57 mmol) in dichloromethane (10 mL) was stirred at 25 °C for 4 h. The mixture changed quickly from brown to black. After this period the mixture was filtered through silica gel with dichloromethane as eluent. After the solvent was removed from the filtrate, a yellow solid was obtained, which was separated by column chromatography on silica gel. Elution with 9:1 hexane–ethyl acetate afforded unreacted 4-chloro-1-methyl-3-(phenylseleno)cyclopentanecarboxylic acid (0.232 g, 0.73 mmol) and compound **18B** (0.186 g, 38%). Compound **18B** was a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 7.52 (m, 2 H), 7.29 (m, 3 H), 4.62 (br s, 1 H), 3.60 (m, 1 H), 2.14–2.30 (m, 2 H), 2.03 (m, 1 H), 1.61 (dd, J = 14.1, 5.1 Hz, 1 H), 1.33 (s, 3 H); IR (CH_2Cl_2) 3060 (w), 2962 (w), 1785 (s), 1482 (w), 1440 (w), 1322 (w), 1090 (m), 915 (m) cm^{-1}. This compound was converted to alcohol **19** without further purification.

Preparation of (1β,3β)-(±)-1-Carbobenzoxy-3-hydroxy-1-methylcyclopentane (19) from 18B. Tributylstannyl hydride (0.280 g, 0.96 mmol), selenide **18B** (0.186 g, 0.66 mmol), and AIBN (0.005 g, 0.03 mmol) were dissolved in benzene (5 mL). The mixture was heated to reflux for a period of 2 h. The solution was cooled to 25 °C after this period, and benzyl alcohol (0.180 g, 1.67 mmol) and *p*-toluenesulfonic acid (0.010 g, 0.06 mmol) were added. The resulting mixture was heated to 70 °C with stirring for a period of 10 h. After this period, the solvent was removed on a rotary evaporator, and the residue was separated by silica gel preparative TLC with 7:3 hexane–ethyl acetate as eluent. Alcohol **19** was obtained as a colorless oil (0.075 g, 48%): ^{1}H NMR ($CDCl_3$) δ 7.33 (br s, 5 H), 5.13 (s, 2 H), 4.32 (m, 1 H), 2.18–2.45 (m, 2 H), 1.95 (m, 1 H), 1.75 (m, 1 H) overlapping with 1.73 (dd, J = 15.2, 6.0 Hz, 1 H), 1.47–1.62 (m, 2 H), 1.30 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 179.1, 136.0, 128.6, 128.2, 127.9, 74.0, 66.7, 48.4, 47.2, 36.5, 35.4, 25.4; IR (CH_2Cl_2) 3605 (w), 2972 (m), 1723 (s), 1435 (w), 1220 (w), 1162 (m, br), 1050 (m) cm^{-1}; MS (CI) m/e 235 (M + 1, 17), 217 (15), 204 (7.2), 188 (17), 171 (9.8), 143 (92), 127 (98), 105 (92), 97 (100); HRMS m/e calcd for $C_{14}H_{19}O_3$ 235.1334, found 235.1326.

Preparation of (1β,2α,3β,4α,5α)-(±)-1-Carbobenzoxy-4-(carbo-*p*-nitrobenzoxy)-2,3,5-trimethylcyclopentane (15F-PNB). To a solution of alcohol **15F** (0.005 g, 0.019 mmol) in pyridine (1.0 mL) was added 4-nitrobenzoyl chloride (0.020 g, 0.11 mmol). The mixture was stirred at 25 °C for 12 h. After the solvent was removed on a rotary evaporator, the residue was separated by silica gel preparative TLC with 3:2 hexane–ethyl acetate as eluent. Compound **15F-PNB** was obtained as a yellow oil (0.007 g, 91%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.21 (m, 2 H), 8.13 (m, 2 H), 7.30 (m, 5 H), 5.11 (s, 2 H), 4.72 (dd, J = 5.8, 4.6 Hz, 1 H), 2.51 (m, 1 H), 2.40 (m, 1 H), 2.20 (m, 1 H) overlapping with 2.19 (t, J = 9.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 174.7, 164.6, 150.5, 136.0, 135.7, 130.7, 128.6, 128.2, 128.0, 123.5, 88.2, 66.5, 56.3, 44.1, 42.7, 39.1, 18.3, 14.9, 12.9; MS (CI) m/e 412 (M + 1, 4.6), 382 (26), 262 (4.5), 245 (13), 227 (10), 215 (7.6), 199 (5.2), 153 (16), 137 (100), 120 (82), 109 (35), 91 (40); HRMS m/e calcd for $C_{23}H_{26}NO_6$ 412.1760, found 412.1765.

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Stereoselective Reaction of an Enolate with Chiral α-Halo Boronic Acid Esters[1]

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Reaction of *tert*-butyl *trans*-lithiopropionate (**6**) with (*S*,*S*)-diisopropylethanediol ("DIPED") (1*R*)-(1-bromopentyl)boronate (**9a**) yielded semipurified *tert*-butyl (2*S*,3*S*)-3-hydroxy-2-methylheptanoate (**11a**) ("threo") in a 60:1 ratio to the "erythro" diastereomer. Other threo/erythro ratios included DIPED (1*R*)-(1-bromo-2-methylpropyl)boronate (**9b**) to crude **11b**, 15:1, DIPED (α-bromobenzyl)boronate (**9c**) to crude **11c**, 8:1; (3*S*,4*S*)-2,5-dimethoxy-2,5-dimethyl-3,4-hexanediol (1*R*)-(1-bromo-pentyl)boronate (**9d**) to semipurified **11a**, 10:1; and pinacol (1-bromopentyl)boronate (**5**) via **7** to semipurified racemic **11a**, >100:1. These reactions are sluggish, and α-bromo boronic acid esters generally give better yields than the corresponding chloro compounds. Less hindered ester enolates appear to undergo Claisen condensation under the reaction conditions, and only the *tert*-butyl ester proved useful. An efficient synthesis of (3*S*,4*S*)-2,5-dimethoxy-2,5-dimethyl-3,4-hexanediol (**16**) and its use as a chiral director for chain extension of boronic acid esters are described.

Introduction

Displacement reactions of enolates such as diethyl sodiomalonate or methyl sodiocyanoacetate with (iodomethyl)boronic acid esters have been reported,[2] as well as those of *tert*-butyl lithioacetate with pinacol (1-chloroallyl)boronate,[3] (*R*)-pinanediol (1*R*)-(1-chloroethyl)boronate,[4] and pinacol (iodomethyl)boronate.[5] In view of the

(1) Dedicated to the memory of John K. Stille.

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