Allylmetal-directed addition of $^1O_2$: Scope, mechanism and synthetic utility

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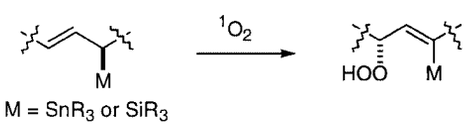
Allylic silyl and stannyl groups strongly influence the regio- and stereochemistry of alkene oxygenations by $^1O_2$, even within functionalized systems. Allylstannanes undergo *anti*-S_E2' oxygenation to form both *Z*-stannylalkenyl hydroperoxides and 4-stannyl-1,2-dioxolanes; the ene-like reaction is generally preferred unless limited by allylic strain. The alkenylstannane products, as well as the derived iodides, are effective substrates for palladium-mediated cross-couplings, additions, carbonylations, and acylations to form peroxydienes, peroxyenones, and peroxyenoates. Allylsilanes are less effective directing groups, possessing reactivity surprisingly similar to simple alkenes, and undergoing oxidation to form regioisomeric mixtures of hydroperoxides. The different reactivities and product distributions observed for allylstannanes and allylsilanes reflect different nucleophilicities of the ground state alkenes as well as variable polarization of the developing perepoxides by the neighboring C–Sn or C–Si bond. The observed selectivity for production of *Z*-alkenylmetals appears to result from the preferential formation of a single perepoxide pyramidal isomer and the tendency for this perepoxide to abstract the *inside* hydrogen on the metal-bearing carbon at a rate which is faster than either perepoxide inversion or single bond rotation to deliver the *outside* hydrogen for abstraction.

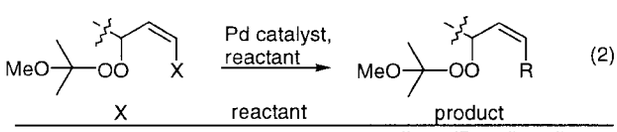
Introduction

The addition of singlet oxygen ($^1O_2$) to alkenes remains among the most efficient of methods for allylic oxidation and synthesis of unsaturated hydroperoxides.[1–3] However, $^1O_2$ is a small, achiral, and highly reactive molecule which reacts with simple alkenes to provide racemic mixtures of regioisomers. A variety of approaches have been explored in an effort to control the regio- and/or stereoselectivity of oxygenation.[2] Modest regioselection is sometimes possible for abstractions from the more crowded side of an alkene (*cis* effect) while higher selectivity is possible for alkenes bearing geminal functional groups or in which allylic strain limits abstraction of particular hydrogens.[4] Altered regioselectivity has been observed upon oxygenation within inclusion complexes or zeolite cavities.[5–8] Attempts to control the stereoselectivity of addition have involved the use of chiral inclusion complexes,[5,6,9] neighboring chiral centers or chiral auxiliaries,[2] and hydrogen-bonding with neighboring alcohols, amines, or carboxy groups.[2] In preliminary work, we reported a new route for the synthesis of enantiomerically enriched hydroperoxides through oxygenation of chiral allylstannanes.[10] We now describe a general investigation into the use of allylsilanes and -stannanes as regio- and/or stereochemical directing groups for addition of $^1O_2$ (eqn. 1). Our



(1)

results, which shed new light on the formation and reactivity of the intermediate perepoxides, demonstrate stannanes to be highly effective regio- and stereochemical directing groups; silanes are less effective. Depending upon electron density and the presence or absence of allylic strain, oxygenation of allylstannanes can produce allyl hydroperoxides, allylstannyl peroxides, or 1,2-dioxolanes. The stannylalkene oxygenation products provide excellent substrates for construction of more functionalized peroxides through Pd-mediated couplings (eqn. 2).



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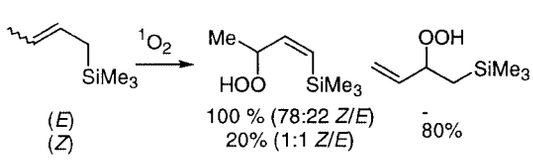
X	reactant	product
$SnBu_3$	vinyl halide	diene (R = alkenyl)
	acid chloride	enone (R = acyl)
I	CO, MeOH	ester (R = CO_2Me)
	alkenylstannane	diene (R = alkenyl)
	enone	dienone (R = enone)

Our interest was prompted by a series of reports (eqn. 3 and 4). Addition of $^1O_2$ to *E*-allylsilanes was shown to favor abstrac-



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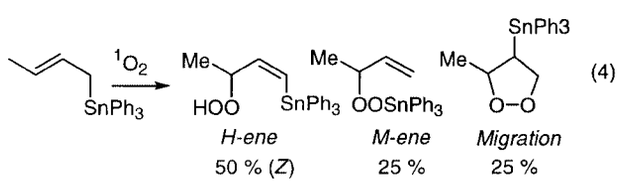
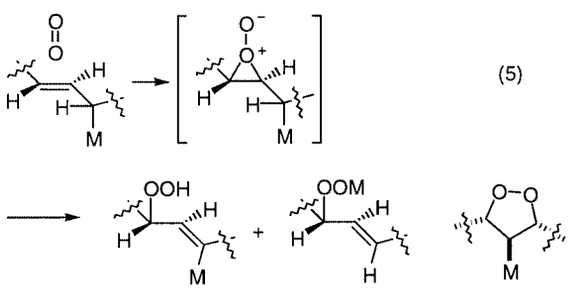


(4)

tion of hydrogen adjacent to silicon and to favor production of *Z*-silylalkenyl hydroperoxides (eqn. 3).[11] The corresponding *Z*-allylsilane was found to give less of the 1-silylalkene product (formed as an equal mixture of *E* and *Z* isomers), instead favoring abstraction of hydrogen from the allylic methyl.[12] Allylstannanes, in contrast, were observed to react through three manifolds (eqn. 4):[13–15] abstraction of the hydrogen from

the tin-bearing carbon to afford *Z*-stannylalkenyl hydroperoxides (H-ene pathway), abstraction of tin to form a stannylated allyl hydroperoxide (M-ene) or 1,2-migration of tin to the developing perepoxide to form 1,2-dioxolanes. The selectivity between the three pathways was sensitive to the substituents on tin as well as solvent polarity.

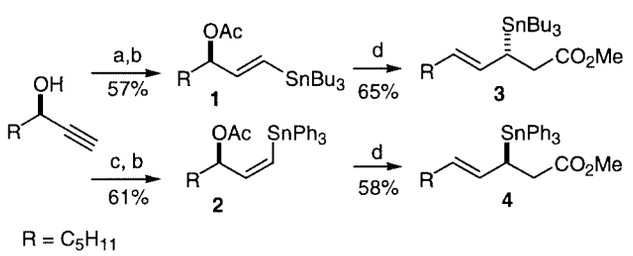
We were attracted by the synthetic potential of allylsilanes and allylstannanes as "activating" auxiliaries able to direct the regiochemistry of oxygen introduction and also, by virtue of the electronic acceleration imparted by the silyl or stannyl group,[11,16,17] to direct selective oxygenations within polyunsaturated and other functionalized systems. The preference of chiral allylsilanes and stannanes to undergo addition of electrophiles through an *anti*-S_E2' transition state implied that addition of $^1O_2$ to a chiral allylsilane or -stannane should proceed *via* a single perepoxide to produce products of a single absolute stereochemistry, regardless of whether the reaction proceeded *via* the H-ene, M-ene, or dioxolane pathways (eqn. 5). This is similar to a hypothesis advanced by Davies to explain



the *Z*-selectivity of the stannane oxygenations.[13,14] Finally, the resulting silylalkenyl or stannylalkenyl peroxides held promise as synthons for a modular peroxide synthesis based upon Pd-mediated reactions (eqn. 2).

Results and discussion

The synthesis of initial substrates, **3** and **4**, began with (*R*)-oct-1-yn-3-ol, available in 80–85% ee through asymmetric reduction of oct-1-yn-3-one (Scheme 1).[18] Radical addition of tributyltin

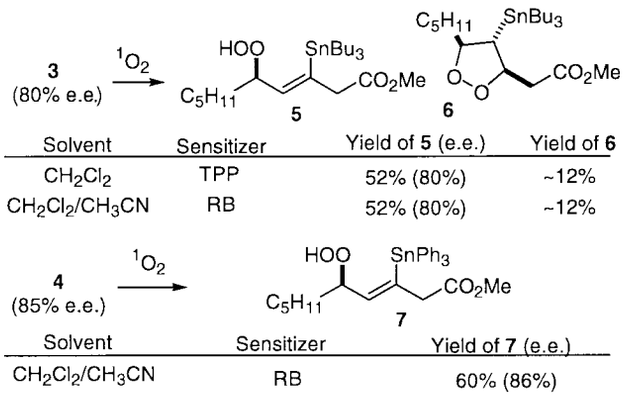


Scheme 1 Synthesis of allylstannanes. *Reagents and conditions*: (a) $HSnBu_3$, AIBN, 90 °C; (b) AcCl; (c) $HSnPh_3$, Et_3B; (d) (i) $KN(TMS)_2$, TMSCl, (ii) H_2O, (iii) CH_2N_2.

hydride furnished a 4:1 mixture of *E*- and *Z*-alkenyltributylstannanes from which the *E* isomer could be separated by chromatography (Scheme 1). The Et_3B-catalyzed addition of triphenyltin hydride to the propargyl alcohol (prop-2-ynyl alcohol) furnished a *Z*-alkenyltriphenylstannane.[19] The corresponding acetates **1** and **2** were subjected to ester enolate Claisen rearrangement conditions to produce optically active allylstannanes **3** and **4**.[20]

Oxygenation of stannylenoates

Photooxygenation of tributylstannyl enoate **3** using visible light and either tetraphenylporphyrin (TPP) or Rose Bengal (RB) as a sensitizer (see Experimental section for details) yielded as the major product, β-stannyl hydroperoxide **5**, accompanied by

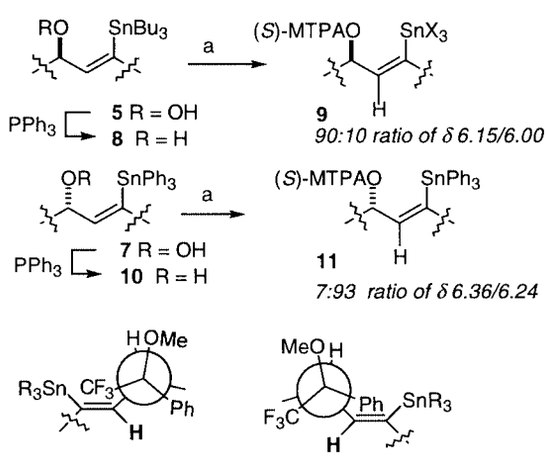


Scheme 2 Oxidation of allylstannanes.

smaller amounts of a 1,2-dioxolane (**6**) arising from migration of the tributyltin group (Scheme 2). In contrast, oxygenation of the triphenylstannyl enoate furnished only the H-ene product (**7**), presumably reflecting the relative migratory aptitudes of the triphenylstannyl and tributylstannyl groups.[15] In contrast to previous reports describing oxygenation of allylstannanes, no metallo-ene products were isolated.[14,15] Although it is possible that small amounts of stannyl peroxides were hydrolyzed and overlooked during workup and chromatographic purification, it would appear more likely that the M-ene pathway is less significant for acyclic secondary allylstannanes.

The *Z*-configuration of the stannylalkenes was established by olefinic Sn–H couplings of 112 Hz for **5** and 150 Hz for **7**. The *trans* $^3J_{Sn-H}$ has been reported to range between 120 and 150 Hz while the corresponding *cis* coupling is typically 40 to 60 Hz.[21,22] The stereochemical assignment was supported by the observation of a 17% NOE enhancement between the vinyl hydrogen and the neighboring methylene for compound **5**.

Enantiomeric excesses were determined through reduction to the alcohols and formation of the (−)-methoxytrifluorophenylacetic (MTPA, Mosher) esters (Scheme 3).[23] The ^1H NMR



Scheme 3 Stereochemical determination. *Reagents and conditions*: (a) (*S*)-methoxytrifluoromethylphenylacetyl chloride, DMAP, pyridine.

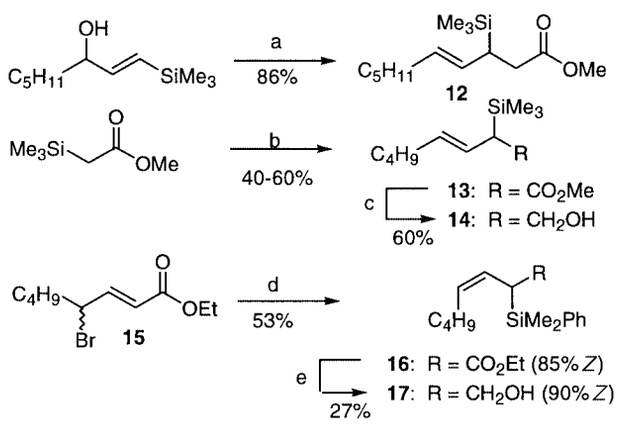
spectrum of **9** displayed a 90:10 ratio of doublets at δ d 6.15 and 6.00 ppm, indicating that alcohol **8**, and therefore hydroperoxide **5**, was formed in 80% ee. The corresponding spectra of **11** displayed a 7:93 ratio of doublets at 6.36 and 6.24 ppm, indicating a purity of 86% ee for the parent hydroperoxide. The results demonstrate complete transfer of chirality from the allylstannane to the product hydroperoxide *via* the intermediate perepoxide.

Assignment of absolute stereochemistry was based upon correlations developed for MTPA esters of secondary alcohols.[24] The diastereomeric esters formed upon reaction of

(*S*)-MTPA acid chloride with an epimeric mixture of secondary alcohols place the shielding benzene ring in proximity to different hydrogen atoms, resulting in a characteristic set of upfield and downfield shifts. The absolute stereochemistry indicated by this correlation supports the proposed stannyl-directed *anti*-S_E2' addition of $^1O_2$ to the allylstannane to form a single perepoxide which undergoes abstraction of hydrogen adjacent to tin to form the hydroperoxy *Z*-vinylstannane (eqn. 5). It is interesting to note that whereas other methods for stereoselective oxygenation result in the formation of diastereomeric products, the oxygenation of allylstannanes proceeds with transfer of the original stereocenter to furnish enantiomeric products.[2]

Oxygenation of silylenoates

The ability of allylic stannanes to control the regio- and stereoselection of oxygenation led us to investigate an extension of the strategy to functionalized allylsilanes (Scheme 4). The silicon

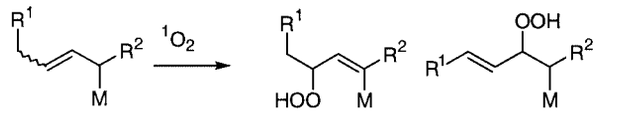


Scheme 4 Synthesis of functionalised allylsilanes (a) $CH_3C(OMe)_3$; (b) 1. LDA, 2. $NiBr_2$/*n*-BuLi, I-CH=CHBu; (c) LAH; (d) $CuCN(SiMe_2Ph)_2Li_2$, $BF_3{\cdot}OEt_2$; (e) DIBAL-H.

analog (**12**) of the initial stannyl substrate was prepared through orthoester Claisen rearrangement of (1*E*)-1-trimethylsilyloct-1-en-3-ol.[25,26] Several methods were investigated for preparation of silyl- or stannyl-substituted β,γ-unsaturated esters, anticipated to be effective precursors to synthetically useful γ-peroxy-α,β-unsaturated carbonyls.[27,28] Racemic α-silyl β,γ-enoate **13** could be prepared with good *E*-selectivity *via* a capricious nickel mediated coupling between a vinyl iodide and the lithium enolate of trimethylsilylacetate.[29] However, attempts to perform a similar coupling with ethyl tributylstannylacetate were unsuccessful.[30] An alternate approach to α-(stannyl- or silyl)-β,γ-enoates was based on Lewis-acid mediated S_N2' displacements of γ-mesyloxy and γ-bromo α,β-enoates.[31,32] Displacement of allylic bromide **15** with the higher order silylcuprate developed by Fleming produced allylsilane **16** in good yield as an 85:15 *Z*:*E* mixture,[32,33] a surprising stereochemical outcome given the typical *E*-selectivity of S_N2' cuprate displacements.[34] Reduction of compounds **13** and **16** provided silyl alkenols **14** and **17**. Unfortunately, we were unable to prepare the corresponding stannyl enoates by this strategy.

Photooxygenation of **12** under similar conditions as employed for **1** or **2** furnished as the major product *Z*-silylalkenyl hydroperoxide **18** derived from "H-ene" decomposition of the intermediate perepoxide (Table 1). The isolation of significant amounts of a regioisomeric hydroperoxide (**19**) testified to the reduced influence of the silane group on the intermediate perepoxide. Silylenoate **13** underwent photooxygenation to produce the desired hydroperoxyenoate **20** in modest yield. The corresponding alcohol **14** reacted with $^1O_2$ to produce hydroperoxy vinylsilane **21** in substantially higher yield (Table 1, Entry 3). Neighboring hydroxy groups have been reported to

Table 1 Allylsilane photooxygenation

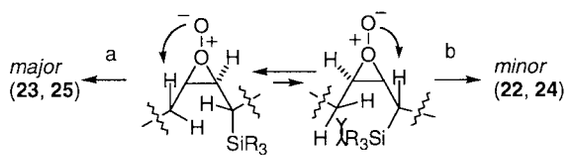


Silane	R^1	R^2	M	*Z*-Vinylsilane	*E*-Alkene
12	C_4H_9	CH_2CO_2Me	$SiMe_3$	40% (**18**)	12% (**19**)
13	C_3H_7	CO_2Me	$SiMe_3$	38% (**20**)	—
14	C_3H_7	CH_2OH	$SiMe_3$	60% (**21**)	—
16	C_3H_7	CO_2Et	$SiPhMe_2$	15% (**22**)[a]	45% (**23**)[a]
17	C_3H_7	CH_2OH	$SiPhMe_2$	14% (**24**)	44% (**25**)

[a] Isolated as alcohol after reduction.

greatly influence $^1O_2$ reactions[35] and it was initially believed that the increase in the yield compared to the ester might reflect a directing influence of the homoallylic hydroxy group. However, little difference was observed between enoate **16** and the corresponding alcohol **17**, both of which reacted with $^1O_2$ to produce mixtures of regioisomeric allylic hydroperoxides favoring the products derived from abstraction of hydrogen at the non-silicon bearing carbon. The hydroperoxides derived from **16** were analyzed following reduction to the corresponding alcohols, **22** and **23**.

The reversal in regioselectivity in the oxygenations of *Z*-allylsilanes **16** and **17** relative to the corresponding *E*-isomers **13** and **14** demonstrates the influence of 1,3-allylic strain (Scheme 5). Formation of an allyl hydroperoxide requires

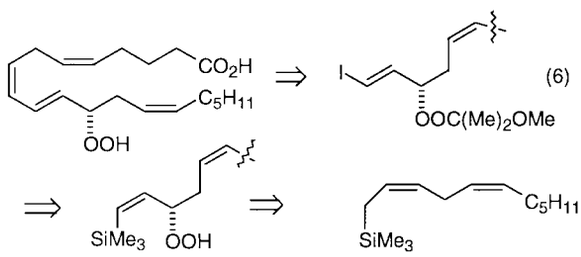


Scheme 5 Reversal of regioselectivity of *Z*-allylsilanes.

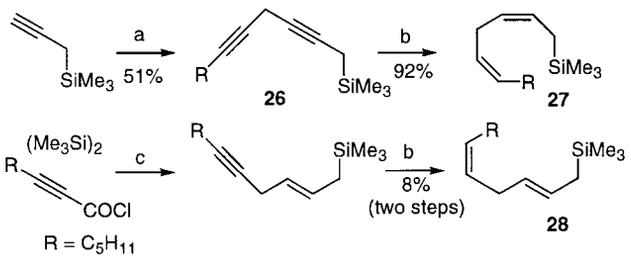
alignment of the perepoxide with a neighboring C–H. For a perepoxide derived from a *Z*-alkene, the conformer required for formation of the 1-silylalkene (pathway b) eclipses the *cis*-methylene with either the alkyl or trialkylsilyl groups. The transition state required for production of the other regioisomer (pathway a) can be attained with much less steric strain. Similar observations have been reported for oxygenations of simple allylsilanes.[11]

Oxygenation of silicon-substituted 1,4-dienes

We next investigated photooxygenation of dienylsilanes. Selective photooxygenation within a polyunsaturated system, combined with the possibility of converting the product vinylsilanes to vinyl iodides with either retention or inversion of alkene configuration was hoped to set the stage for a variety of palladium-mediated C–C bond forming reactions (*vida infra*) as a new approach to polyunsaturated peroxide natural products (eqn. 6).[16,36]



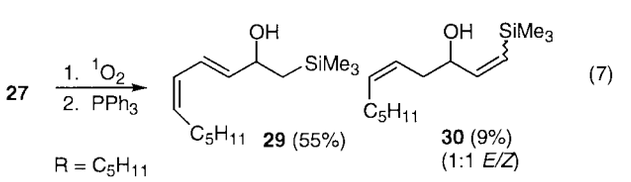
Alkylation of lithiated trimethylsilylpropyne with 1-iodooct-2-yne furnished diynylsilane **26** (Scheme 6),[37] which was rapidly subjected to semihydrogenation with P2-nickel to produce the



Scheme 6 Synthesis of silyldienes (a) *n*-BuLi, 1-iodoct-2-yne (b) P2 Ni, H_2; (c) $Pd_2(dba)_3$, butadiene.

Z,Z-diene **27** in high yield.[38] Preparation of the corresponding *Z,E*-dienylsilane was based upon the formation of silylenynes during palladium catalyzed 1,4-carbosilylation.[39] Decarbonylative coupling of oct-2-ynoyl chloride[40] with butadiene and hexamethyldisilane in a pressure tube yielded an unstable enyne, which was immediately reduced to provide compound **28** in low yield.

Based upon the results observed earlier for the *Z*-allylsilanes **16** and **17**, the perepoxide derived from dienylsilane **27** was anticipated to abstract hydrogen from both neighboring positions. Photooxygenation yielded a regioisomeric mixture of hydroperoxides both derived from attack of $^1O_2$ on the alk-2-ene; the products were analyzed as the corresponding alcohols (eqn. 7). Decoupling experiments revealed the major product **29**



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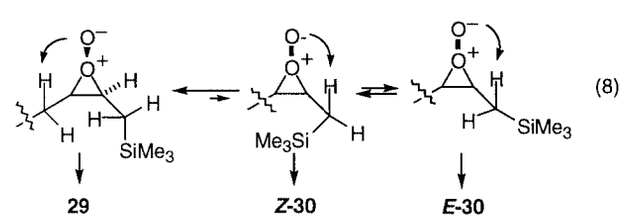
to be the conjugated diene derived from selective abstraction of hydrogen from the internal methylene; the minor product **30** was the *Z*-silylalkenyl hydroperoxide derived from abstraction of hydrogen adjacent to silicon. Traces of the regioisomeric diene hydroperoxides resulting from oxygenation of the alk-5-ene were also observed.

Photooxygenation of 1,4-dienes normally displays little bias towards formation of conjugated dienes.[41] It is likely that the electronic influence of the silyl group leads to selective formation of the perepoxide of the alk-2-ene but that the conformation required for abstraction to form the *Z*-alkenylsilane **30** is disfavored by allylic strain. Consequently, the major product (**29**) is derived through abstraction of hydrogen from the internal methylene (eqn. 8). Furthermore, the little alk-1-



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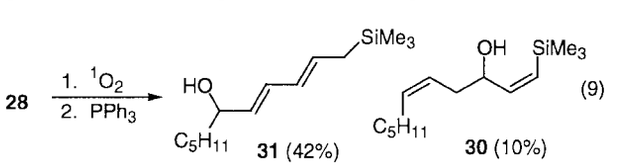
enylsilane observed is formed as a mixture of *E*- and *Z*-geometric isomers.

Photooxygenation of *Z,E*-diene **28** produced a mixture of hydroperoxides, which were directly reduced to the corresponding alcohols (eqn. 9). The major product was the con-



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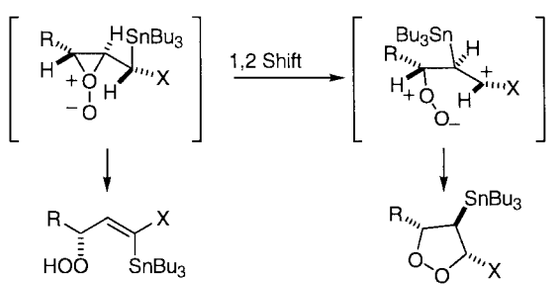
jugated dienol (**31**) arising from attack on the (5*Z*)-alkene while the minor product was the "expected" *Z*-alkenylsilane **30**; the lowered reactivity of the *E*-allylsilane moiety of **28** apparently allows predominant formation of the perepoxide from the simple *Z*-alkene. Although the reduced reactivity of *E*-alkenes towards $^1O_2$ is well known,[1] the results were surprising in light of reported relative rates for oxygenation of simple alkenes and allylsilanes.[11]

Synthesis of 1,2-dioxolanes

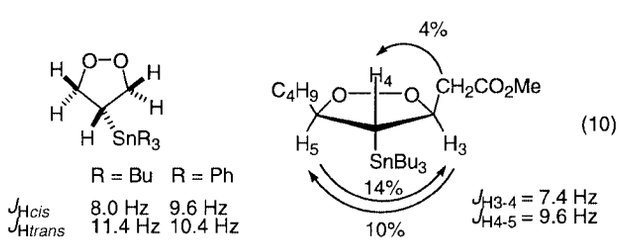
Dang and Davies had reported that, along with ene products, the oxygenation of simple allylstannanes also produced 1,2-dioxolanes in a process that was sensitive to structure and solvent polarity.[15] Our preliminary investigations had demonstrated photooxygenation of allylstannane **3** to furnish, along with the major ene product, a diastereomerically pure 1,2-dioxolane **6**. The existence of a little explored family of 1,2-dioxolane natural products combined with the lack of stereoselective methods for dioxolane synthesis,[42] led us to investigate methods for deliberately enhancing this migration/cyclization pathway during oxygenations of allylstannanes. Our initial efforts were based on the assumption that the two pathways (H-ene and dioxolane) shared a common perepoxide intermediate (Scheme 7).[43] Migration of hydrogen (H-ene) to the perepoxide oxygen



Scheme 7 Relationship of ene and dioxolane pathways.

yields the allylic hydroperoxide while 1,2-migration of the stannyl group with concomitant ring opening of the perepoxide produces a zwitterion which closes to the 4-stannyl-1,2-dioxolane without loss of stereochemistry.

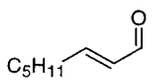
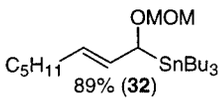
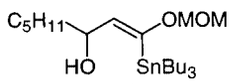
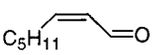
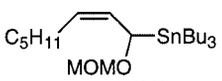
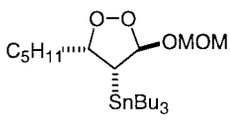
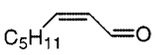
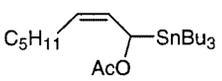
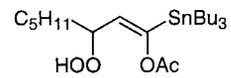
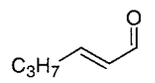
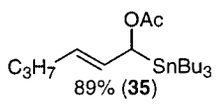
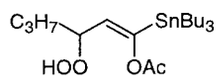
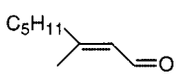
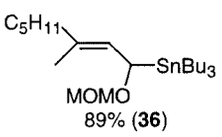
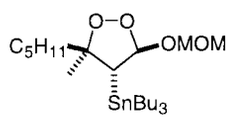
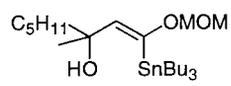
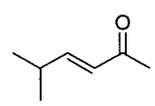
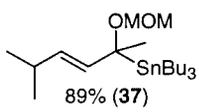
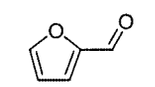
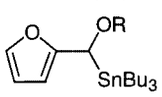
This mechanism was supported by spectroscopic studies on the initial 1,2-dioxolane product (**6**). The configuration of C_3,C_5 disubstituted dioxolanes has been previously assigned based upon geminal coupling constants.[44–46] However, in the case of **6**, the $^3J_{3-4}$ and $^3J_{4-5}$ coupling constants did not allow a clear determination of stereochemistry. Definitive assignment of the relative stereochemistry was achieved through NOE experiments (eqn. 10). Irradiation of H_3 resulted in 10–14%



(10)

enhancement of H_5, demonstrating the *cis*-relative stereochemistry of these two hydrogens. In addition, irradiation of the methylene group on the acetate sidechain resulted in a 4% enhancement of H_4. Together, these observations support the 3,4-*trans*, 4,5-*trans* relative stereochemistry (3,5-*cis*-1,2-dioxolane), in agreement with the mechanism outlined above. Attempts to establish the absolute stereochemistry of the dioxolane through reduction were abandoned after the observation of allylic alcohol byproducts raised the possibility of

Table 2 Photooxygenation of alkoxystannanes

Starting material	Substrate	Oxygenation conditions	Dioxolane	H-ene
	 89% (**32**)	TPP, $CHCl_3$	—	 39% (**40**)
	 89% (**33**)	RB, $CDCl_3$	 58% (**41**)	—
	 89% (**34**)	RB, $CHCl_3$	—	 38% (**42**)
	 89% (**35**)	RB, MeCN CH_2Cl_2	—	 33% (**43**)
	 89% (**36**)	TPP, $CHCl_3$	 46% (**44**)	 37% (**45**)
		TPP, CCl_4	—	89% (**45**)
	 89% (**37**)	TPP, CCl_4 RB, $CDCl_3$	—	—
	 **38** R = MOM **39** R = Ac	RB or TPP $CDCl_3$	—	—

initial isomerization to a hydroxyketone, a problem also encountered by others.[47–50]

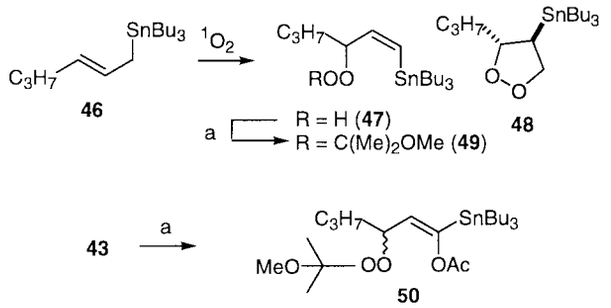
α-Alkoxyallylstannanes were investigated as readily available substrates which might favor dioxolane formation due to stabilization of the developing cation in the transition state for 1,2-stannyl migration. In addition, the availability of methodology for asymmetric synthesis of alkoxystannanes would allow extension of any successful route to the synthesis of enantiomerically enriched dioxolanes.[51] Alkoxy allylstannanes **32**–**39** were obtained through 1,2-addition of tributylstannyllithium to unsaturated aldehydes or ketones, followed by trapping of the stannylmethanol with chloromethyl methyl ether or acetic anhydride to form the methoxymethyl ether or acetate, respectively (Table 2).[52,53]

Photooxygenation of α-alkoxyallylstannane **32** produced none of the expected dioxolane, instead yielding a hydroperoxy *Z*-vinylstannane which was isolated after reduction to the corresponding alcohol (**40**). The configuration of the vinylstannanes was assigned on the basis of the olefinic $^3J_{Sn-H}$ (86 Hz). The inability to enhance dioxolane formation solely upon incorporation of electron-releasing groups led us to investigate the application of allylic strain. *Z*-Allylstannanes **33** and **34** were expected to form a perepoxide with appropriate alignment for backside stannyl migration but in which the H-ene reaction would be disfavored by steric interactions between the stannyl group and the alkyl sidechain.

Z-Alkoxyallylstannane **33** underwent photooxygenation to produce the dioxolane as the exclusive product. Conversely, the corresponding acetoxystannane (**34**) afforded only the hydroperoxy vinylstannane product, **42**. Presumably, the reduced electron donating ability of the acetate sufficiently disfavors 1,2-migration to overcome the stereoelectronic bias against ene reaction. As expected, photooxygenation of the *E*-allylstannane **35** also produced an *E*-vinylstannane **43** ($^3J_{Sn-H}$ = 86). A trisubstituted allylstannane, **36** underwent photooxygenation in chloroform to produce a mixture of dioxolane **44** and an unstable H-ene product, which decomposed during chromatographic purification. Conducting the reaction in the less polar solvent CCl_4 resulted in exclusive formation of the ene product, which could be characterized as the corresponding alcohol, **45**. Allylstannane **37**, lacking an abstractable hydrogen geminal to tin, reacted to form a complex mixture devoid of dioxolanes. The oxygenation of furans is a well known method for the synthesis of bicyclic ozonides 2,3,7-trioxabicyclo[2.2.1]hept-5-enes and alkoxyhydroperoxides.[54,55] We investigated the oxygenation of α-alkoxy-α-stannylfurans to determine whether the presence of an "allylic" stannane would alter the normal course of the reaction. Unfortunately, photooxygenation of **38** and **39** resulted in the formation of complex mixtures in which no dioxolanes could be detected.

Functionalization of substrates

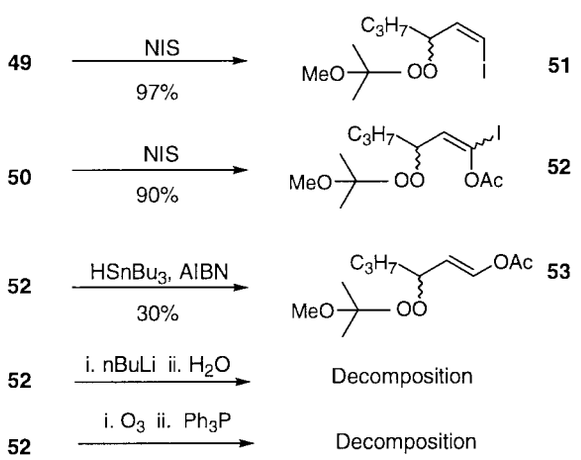
The versatility of vinylstannanes and related species as synthetic reagents and intermediates led us to investigate synthetic transformations of the ene oxidation products.[36] Initial investigations focused on protection of the hydroperoxide products (Scheme 8). The first substrate was prepared from allylstannane **46**, available from S_N2 displacement of the mesylate derived



Scheme 8 Synthesis of protected allyl hydroperoxides (a) 2-methoxypropene, cat. PPTS.

from (*E*)-hex-3-en-1-ol.[56] Reaction with $^1O_2$ produced the hydroperoxy *Z*-vinylstannane **47** as the major product, accompanied by small amounts of a 1,2-dioxolane (**48**). Although Dang and Davies had reported decomposition of both H-ene and dioxolane products during purification, both **47** and **48** were stable to chromatographic purification.[15] Conversely, we did not isolate the metallo-ene product observed in the earlier work; if a stannyl peroxide was formed, it may have decomposed during workup to form a volatile hydroperoxide. Acid-catalyzed reaction of **47** with 2-methoxypropene furnished the protected peroxyketal **49**.[57] The hydroperoxy *E*-vinylstannane **43** was similarly protected to furnish peroxyketal **50**.

We next investigated synthetic manipulations of the protected hydroperoxides (Scheme 9).[58] Oxidation of stannanes



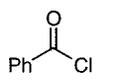
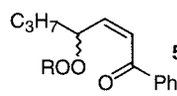
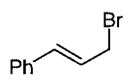
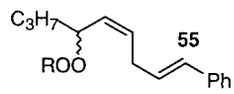
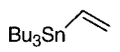
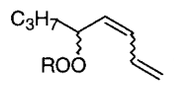
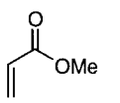
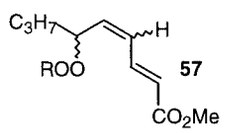
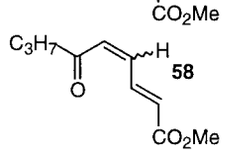
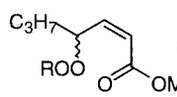
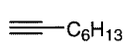
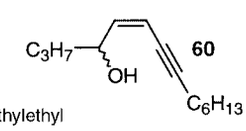
Scheme 9 Functionalization of vinylstannanes.

49 or **50** with *n*-iodosuccinimide produced vinyl iodides **51** and **52** in excellent yield.[59] While the conversion of **49** to **51** was stereospecific, compound **52** was produced as an *E*/*Z* mixture. Chemoselective radical reduction of the vinyl iodide **52** could be achieved in modest yield with tributyltin hydride to produce compound **53**. An alternative approach to reduction *via* transmetalation and protonation of the resulting vinyllithium species resulted in decomposition of the peroxide. Oxidative cleavage of **52** was attempted as a route to α-peroxy aldehydes, useful synthons for production of new unsaturated peroxides.[27,57] However, ozonolysis resulted only in formation of low molecular weight materials.

Palladium-mediated couplings involving vinylstannanes, vinyl halides and related species are powerful methods for C–C bond formation.[36] The surprising tolerance of the protected hydroperoxide toward tributyltin hydride, combined with the ability to efficiently form peroxy vinyl iodide compounds from peroxy vinylstannanes prompted us to investigate palladium-mediated cross-coupling reactions as an unprecedented modular approach to peroxide synthesis (eqn. 2 and Table 3).

Successful cross-coupling of vinylstannane **49** with an acid chloride was achieved in the presence of the catalyst complex

Table 3 Cross-couplings of peroxide products

Substrates	Conditions[a]	Product	Yield
49	 A	 **54**	69%
49	 B	 **55**	55%
51	 C	 **56**	77% 1:9
51	 D	 **57**	46% 1:5.8
		 **58**	22% 3.5:1
51	CO, MeOH E	 **59**	37%
51	 F	 **60**	49%

R = 1-methoxy-1-methylethyl

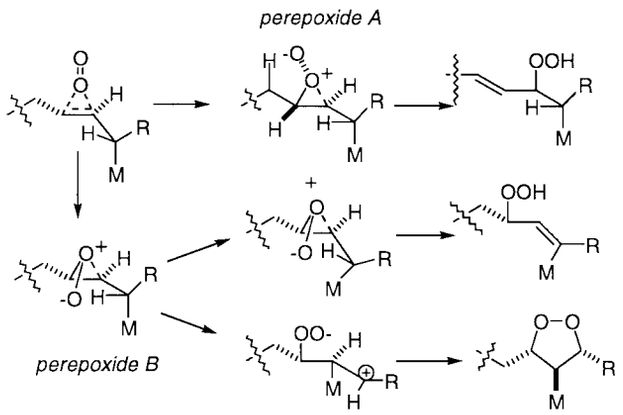
[a] (A) 5 mol% Pd_2dba_2, 10 mol% $(furyl)_3P$, RT, THF; (B) same as A except 60 °C; (C) 10–20 mol% $Pd(PPh_3)_3Cl_2$, 45 °C, THF; (D) 10–15 mol% $Pd(OAc)_2$, K_2CO_3, *n*-Bu_4NBr, excess methyl acrylate; (E) 10 mol% $Pd(OAc)_2$, 20 mol% PPh_3, 2 equiv. Et_3N, CO (1 atm), MeOH–DMF, 60 °C; (F) 10 mol% $Pd(Ph_3P)_4$, 2 mol% CuI, *n*-$BuNH_2$ (1 equiv.), C_6H_6, RT.

formed from $Pd(dba)_3$ and tri(2-furyl)phosphine[60] to produce the *Z*-enone **54** in good yield. Palladium-mediated allylation with cinnamyl bromide furnished diene **55**. Both reactions were stereospecific and proceeded without formation of any detectable products of peroxide fragmentation. The corresponding vinyl iodide (**51**) underwent Stille reaction with vinyltributyltin to produce the conjugated diene peroxide **56** in good yield.[61] In this case, a slight loss of stereochemical integrity was observed. The palladium-mediated alkenylation of **51** with methyl acrylate under mild phase transfer conditions produced dienoate **57**, predominantly as the *Z*, *E* isomer,[62,63] accompanied by small amounts of an oxodienoate byproduct (**58**) derived from base-mediated fragmentation of either the starting material or the coupled peroxide.

Palladium-mediated carbonylation of vinyl iodide **51** was anticipated to provide a route to synthetically versatile peroxyenoates.[64] Carbonylation of **51** in the presence of methanol provided a modest yield of *Z*-peroxyenoate **59**. The palladium-mediated Sonogashira coupling of terminal alkynes with vinyl electrophiles appeared to offer an attractive entry to peroxyalk-2-en-4-ynes.[65] Given our previous success with chemoselective hydrogenation in the presence of a peroxide group, peroxyenynes would be useful intermediates for the synthesis of polyene hydroperoxides. However, the reaction of **51** with oct-1-yne under standard conditions[66] furnished enynol **60**, indicating the reduction of the peroxide group under the reaction conditions. The Sonogashira reaction, unlike the previous reactions, utilizes copper(I) which may be the cause of the peroxide decomposition.

Mechanism

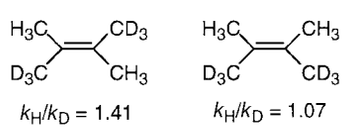
The mechanistic picture that emerges from these studies involves *anti*-S_E2' addition of $^1O_2$ to the allylmetal to form a polarized perepoxide, possibly as a single pyramidal isomer, in which the vicinal C–O bond hyperconjugatively interacts to varying extents with the neighboring C–M bond (Scheme 10).



Scheme 10 Proposed mechanism of oxygenation.

The different product distributions observed from oxygenation of allylstannanes and allylsilanes reflects differences in the extent of this hyperconjugation. For perepoxides derived from allylstannanes, the interaction is strong and two competing pathways are available: ring-opening to a zwitterion through 1,2-migration of trialkylstannyl or abstraction of a hydrogen atom from the tin-bearing carbon to afford a stannylalkenyl hydroperoxide. For perepoxides derived from allylsilanes, the interaction is weaker. No 1,2-migration is observed and abstraction of hydrogen can occur from either neighboring carbon. Similar migrations have been observed in reactions of allyl- and allenylsilanes with *N*-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and Lewis acid-activated carbonyl groups.[14,67–69]

The complete regioselectivity observed in formation of stannylalkenes could reflect formation of a single perepoxide able to abstract hydrogen from the tin-bearing carbon at a rate greater than that of pyramidal inversion. The reduced regioselectivity for allylsilane oxidations would therefore result from a reduced selectivity for formation of a single pyramidal perepoxide. This mechanistic possibility, also discussed by Davies,[13] is supported by kinetic isotope effects observed by Stephenson during the oxygenation of *E*- and *Z*-2,3-di(trideuteromethyl)-but-2-ene (eqn. 11). Oxygenation of the *E*-isomer proceeds *via*



(11)

a single perepoxide which must choose between abstraction of deuterium or hydrogen. Oxygenation of the *Z*-isomer produces isomeric perepoxides, one of which decomposes mainly through abstraction of deuterium, the other through abstraction of hydrogen. The observation of substantially smaller isotope effects for the *Z*-isomer would seem to indicate that abstraction is faster than inversion.[70]

Another possibility is that hyperconjugative interaction of the carbon–metal bond with the vicinal perepoxide C–O might strongly favor the transition state for abstraction of hydrogen geminal to the metal. The difference in regioselectivity between allylstannanes and allylsilanes might therefore simply reflect the difference in the strength of hyperconjugation. However, variable polarization of the C–O bond does not account for the highly selective formation of *both* the 1-(silyl- or stannyl-)-alkenyl hydroperoxides as the less stable *Z*-isomer. Formation of the *Z*- or *E*-isomers from an intermediate perepoxide requires inward (*Z*) or outward (*E*) rotation of the metal-bearing methylene; both rotations are energetically feasible for perepoxides derived from *E*-allylmetals. *anti*-S_E2' addition of $^1O_2$ would produce perepoxides in which the pro-*Z* hydrogen was initially much closer to the perepoxide than the pro-*E*. The selective formation of the *Z*-alkene may reflect a favorable interaction between the terminal perepoxide oxygen and the pro-*Z* hydrogen; interaction of a developing perepoxide with allylic hydrogens has been invoked as the basis for selective abstraction of hydrogen from the more crowded side of trisubstituted alkenes (*cis* effect).[71,72]

Alternatively, selective formation of the *Z*-alkenylmetals might simply reflect the relative rotational barriers for achieving appropriate alignment of the pro-*Z* and pro-*E* hydrogen atoms; correlation of regioselectivity with rotational barriers of allylic groups has been previously proposed but also disputed.[73–75] However, rotational correlations cannot account for the oxygenation of *Z*-allylsilanes, in which nearly equal amounts of *E*- and *Z*-alk-1-enylsilanes were observed despite the substantial allylic strain involved in any rotation attempting to bring the pro-*Z* hydrogen in alignment with the perepoxide.

Concluding remarks

Allylstannanes and allylsilanes are shown to be directing groups for control of regio- and/or stereoselectivity in a variety of singlet oxygen addition reactions. Allylstannanes are stronger directing groups, directing *anti*-S_E2' addition of $^1O_2$ with complete transfer of stereochemistry. The resulting perepoxide favors decomposition *via* abstraction of the *inside* hydrogen attached to the tin-bearing carbon, except where the transition state for this abstraction is blocked by allylic strain, whereupon 1,2-migration of tin results in ring opening and dioxolane synthesis. The presence or absence of allylic strain is the primary factor controlling the competition between ene and dioxolane formation, although the distribution can be altered through the presence of an electron-donating oxygen. Allylsilanes are only slightly more reactive towards $^1O_2$ than simple alkenes. The perepoxides derived from oxygenation of allylsilanes undergo decomposition exclusively *via* ene reactions; no dioxolanes are observed. The formation of dioxolanes from the allylstannanes, as well as the regioselectivity in formation of the alkenylmetal products, both demonstrate the strong interaction of the neighboring C–Si and C–Sn bonds with the neighboring bond of the developing perepoxide. In addition, the selective formation of *Z*-alkenylmetals from allylstannanes demonstrates the preference for formation of the perepoxide as a single pyramidal isomer having a strong interaction between the terminal oxygen and the "inside" hydrogen of the allylmetal. Finally, the ability to apply Pd mediated couplings to the resulting vinylstannanes or vinyl iodides provides a new method for synthesis of functionalized peroxides.

Safety. As in any work involving peroxides, standard precautions (safety shields, avoidance of heat, light, or metals salts, use of minimal scale whenever possible) should be faithfully observed.[76–78]

Experimental

All reagents and solvents were used as supplied commercially, except THF and CH_2Cl_2, which were distilled from Na–Ph_2CO and CaH_2, respectively. ^1H, ^{13}C and ^{19}F spectra were recorded on 200–, 300-, 360- or 500-MHz spectrometers in $CDCl_3$ unless otherwise specified; individual peaks are reported as (multiplicity, number of hydrogens, coupling constant in Hz). Infrared spectra were recorded on an FT-IR spectrophotometer as neat films unless otherwise stated. Selected absorbances are

reported in wavenumber (cm^{-1}). Thin layer chromatographic (TLC) analyses were done on 250 micron plates containing a fluorescent indicator. Progress of reactions involving peroxides were monitored by TLC, using an *N*,*N*′-dimethyl-*p*-phenylenediamine indicator; hydroperoxides and peracids yield an immediate reddish-pink spot while perketals or peresters exhibit a pink or green-red color after mild charring.[79] TLC plates were also monitored with a handheld UV light source or after staining/charring with a solution of 1% ceric sulfate–2.5% ammonium molybdate in 10% sulfuric acid. Hydroperoxides were stabilized with a few drops of 1% solution of 2,6-di-*tert*-butyl-4-methylphenol (BHT) in CH_2Cl_2 prior to concentration. Much of the chromatography was performed with ethyl acetate–hexane (EA–hex) recycled and quantified by a reported procedure.[80] Elemental analyses were obtained from M-H-W Laboratories (Phoenix, Arizona, USA); Desert Analytics in (Tucson, Arizona, USA), or Quantitative Technologies, Inc. (New Jersey, USA).

(3*R*,1*Z*)-1-Tributylstannylocten-3-yl acetate (1)

Compound **1** was prepared in three steps from oct-1-yn-3-one. Asymmetric reduction furnished (+)-(*R*)-oct-1-yn-3-ol of 80% ee based upon Mosher ester analysis.[18,23] Hydrostannylation of the propargyl alcohol[20] furnished the corresponding alcohol which was converted to the acetate upon treatment with acetyl chloride and pyridine: $[a]_D^{25} = +38.3$ ($c = 9.5$, $CHCl_3$) (lit., (S) = −22.5, $c = 1.1$).[81]

(3*R*,1*Z*)-1-Triphenylstannylocten-3-yl acetate (2)

To a solution of (+)-oct-1-yn-3-ol (1.0 g, 7.9 mmol, 86% ee) and triphenyltin hydride (3.2 g, 9.1 mmol) in benzene (50 mL) at 25 °C under N_2 atmosphere was added triethylborane (0.79 mL of a 1.0 M *n*-hexane solution). After stirring for 50 min at 25 °C the reaction mixture was poured into water and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The concentrate was purified by flash chromatography to yield 2.5 g (66%) of *Z*-alkenol: $R_f = 0.30$ (10% EA–hex); $[a]_D^{25} = -31.0$ ($c = 1.34$, CH_2Cl_2, 86% ee assumed based upon optical purity of (+)-(3*R*)-oct-1-yn-3-ol); ^{1}H NMR (300 MHz) δ 7.65–7.41 (m, 15H), 6.87 (dd, 1H, $J = 12.4$, 4.3, $^3J_{Sn-H} = 175$), 6.33 (dd, 1H, $J = 12.4$, 1.7, $^2J_{Sn-H} = 45$), 4.23 (tdd, 1H, $J = 4.8$, 12.0, 1.9), 1.60–0.80 (11H); ^{13}C NMR (50 MHz) δ 152.0, 141.1, 136.8, 128.6, 128.4, 124.5, 73,6, 37.2, 31.6, 24.8, 22.5, 13.9; IR 3569, 3423, 3062, 2856 cm^{-1}. Anal. Calcd. for $C_{26}H_{30}OSn$: C, 65.44; H, 6.34. Found C, 65.68; H, 6.38%.

Into a 0 °C solution of the allylic alcohol (2.0 g, 4.2 mmol) in methylene chloride (10 mL) and pyridine (1.3 mL, 16 mmol) was dropwise added acetyl chloride (0.45 mL, 6.3 mmol). After 1 h the reaction mixture was poured into water and extracted with methylene chloride (3 × 15 mL). The organic extracts were washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography (10% EA–hex) to yield 2.1 g (93%) of acetate **2**: $R_f = 0.48$ (10% EA–hex); $[a]_D^{25} = -4.94$ ($c = 1.8$, CH_2Cl_2, 86% ee assumed based upon optical purity of (+)-(3*R*)-oct-1-yn-3-ol); ^{1}H NMR (300 MHz) δ 7.65–7.41 (m, 15H), 6.77 (dd, 1H, $J = 7.2$, 12.9), 6.39 (dd, 1H, $J = 12.9$, 0.9), 5.21 (tdd, 1H, $J = 7.2$, 5.7, 0.9), 1.76 (s, 3H), 1.60–0.81 (11H); ^{13}C NMR (50 MHz) δ 170.0, 149.6, 137.1, 136.9, 128.,9, 128.4, 127.5, 75.8, 34.8, 31.4, 24.5, 22.4, 21.1, 13.9; IR 3049, 2956, 2860, 1749, 1429 cm^{-1}. Anal. Calcd. for $C_{28}H_{32}O_2Sn$: C, 64.77; H, 6.21. Found C, 64.56; H, 6.14%.

Methyl (3*R*,4*E*)-3-tributylstannyldec-4-enoate (3)

To a −78 °C solution of **1** (950 mg, 2.07 mmol, 80% ee*) in THF (30 mL) was added potassium bis(trimethylsilyl)amide (4.8 mL of a 0.48 M solution in toluene) over a 15 min period. After an additional 3 min, a solution of trimethylsilyl chloride (1.0 mL, 7.9 mmol) in THF (5.0 mL) was added and the reaction was allowed to warm to room temperature. After 3 h the reaction mixture was poured into water (20 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was dried over Na_2SO_4 and concentrated. The crude carboxylic acid was dissolved in ethyl ether (3 mL) and treated with an excess of an ethereal solution of diazomethane to give 640 mg (65%) of methyl ester **3**: $R_f = 0.52$ (5% EA–hex); $[a]_D^{25} = +20.3$ ($c = 1.05$, CH_2Cl_2, assumed 80% ee based on the optical purity of **1**; ^{1}H NMR (300 MHz) δ 5.50 (ddt, 1H, $J = 15.1$, 8.6, 1.2), 5.14 (dtd, 1H, $J = 15.1$, 6.8, 1.2), 3.64 (s, 3H), 2.59 (m, 2H), 2.40 (m, 1H), 1.94 (m, 2H), 1.55–0.81 (m, 9H); ^{13}C NMR (50 MHz) δ 174.4, 132.6, 124.7, 51.4, 36.7, 32.7, 31.3, 29.8, 29.1, 27.5, 26.0, 22.6, 14.1, 13.7, 9.0; IR 2956, 2871, 1739, 1463 cm^{-1}. Anal. Calcd. for $C_{23}H_{46}O_2Sn$: C, 58.36; H, 9.80. Found C, 58.10; H, 9.67%.

Methyl (3*S*,4*E*)-3-triphenylstannyldec-4-enoate (4)

Compound **4** was prepared from acetate **2** (1.1 g, 2.11 mmol) by a similar procedure in 53% yield (600 mg): $R_f = 0.51$ (10% EA–hex); $[a]_D^{25} = -8.75$ ($c = 1.42$, CH_2Cl_2, assumed 86% ee based upon optical purity of (+)-(3*R*)-oct-1-yn-3-ol); ^{1}H NMR (300 MHz) δ 7.64–7.42 (m, 15H), 5.79 (dd, 1H, $J = 8.6$, 15.3), 5.41 (td, 1H, $J = 6.9$, 15.3), 3.52 (s, 3H), 3.19 (td, 1H, $J = 7.4$, 7.9), 2.89 (d, 2H, $J = 7.9$), 2.02 (q, 2H, $J = 6.9$), 1.35–0.85 (9H); ^{13}C NMR (50 MHz) δ 173.9, 138.6, 137.3, 131.2, 128.8, 128.5, 127.5, 51.4, 36.6, 32.5, 31.2, 29.3, 28.8, 22.5, 14.0; IR 3047, 2952, 1735, 1429 cm^{-1}. Anal. Calcd. for $C_{29}H_{34}O_2Sn$: C, 65.32; H, 6.43. Found C, 65.25; H, 6.30%.

Photooxygenation of allylstannanes and allylsilanes—*general procedure*

Oxygen was bubbled into a jacketed cell containing a solution of allylstannane or allylsilane and sensitizer (Rose Bengal or TPP in CH_3CN, CCl_4, $CHCl_3$ or CH_2Cl_2). The solution was irradiated with a high intensity visible illuminator (Fiber-lite™ series 180, Dolan-Jenner Industries, Inc.) at 0–12 °C from a distance of 3–10 cm until complete conversion of the alkene was observed by TLC or ^{1}H NMR. The solvent was removed under reduced pressure and the oily residue was purified by flash chromatography on silica gel. The product ratio was determined by the isolated yield or ^{1}H NMR.

Methyl (5*R*,3*Z*)-3-tributylstannyl-5-hydroperoxydec-3-enoate (5) and (3*S*,4*R*,5*R*)-3-methoxycarbonylmethyl-5-pentyl-4-tributylstannyl-1,2-dioxolane (6). Oxygenation of allylstannane **3** (110 mg, 0.23 mmol) in TPP–CH_2Cl_2 (5 mL) under standard conditions was complete according to TLC in ~30 min. The solvent was removed under reduced pressure and the oily residue was purified by flash chromatography on silica gel to yield 18 mg (15%) of **6** and 68 mg (58%) of **5**:

Compound **5**: $R_f = 0.38$ (10% EA–hex); $[a]_D^{25} = -5.0$ ($c = 1.24$, CH_2Cl_2, 80% ee assumed on optical purity of (+)-(3*R*)-oct-1-yn-3-ol); ^{1}H NMR (360 MHz) δ 7.88 (s, 1H), 5.99 (d, 1H, $J = 8.95$, $^3J_{Sn-H} = 112$), 4.20 (m, 1H, $J = 9.0$, 12.3), 3.65 (s, 3H), 3.25 (d, 2H, $J = 0.93$), 1.65–0.80 (m, 38H); ^{13}C NMR (50 MHz) δ 172.9, 143.4, 87.2, 51.8, 45.2, 32.9, 31.9, 29.0, 28.0, 27.4, 25.1, 22.5, 14.0, 13.6, 10.8; IR (neat) 3408, 2956, 1739 cm^{-1}.

Compound **6**: $R_f = 0.55$ (10% EA–hex); $[a]_D^{25} = +7.50$ ($c = 1.40$, CH_2Cl_2); ^{1}H NMR (360 MHz) δ 4.63 (td, 1H, $J = 7.6$, 4.5), 4.16 (dd, 1H, $J = 7.9$, 9.5), 3.68 (s, 3H), 2.65 (dd, 1H, J =15.7, 7.9), 2.49 (dd, 1H, $J = 15.7$, 4.5), 1.70 (dd, 1H, $J = 9.5$, 7.6), 1.60–0.80 (38H); ^{13}C NMR (50 MHz) δ 170.8, 85.7, 81.8, 51.8, 43.5, 40.4, 33.0, 31.8, 29.1, 27.4, 26.4, 22.4, 14.0, 13.6, 8.7; IR 2954, 2869, 1741 cm^{-1}. Anal. Calcd. for $C_{23}H_{46}O_4Sn$: C, 54.67; H, 9.18. Found C, 54.70; H, 9.27%.

Methyl (5*S*,3*Z*)-3-triphenylstannyl-5-hydroperoxydec-3-enoate (7). Oxygenation of allylstannane **4** (58 mg, 0.11 mmol) in TPP–CH_2Cl_2 (2 mL) under standard conditions was com-

plete according to TLC in ~80 min. Solvent was removed under reduced pressure and the oily residue was purified by flash chromatography on silica gel to yield 34 mg (74%) of **7**: $R_f = 0.44$ (20% EA–hex); $[a]_D^{25} = -10.9$ ($c = 1.39$, CH_2Cl_2) (86% ee assumed on the optical purity of MTPA ester); ^{1}H NMR (300 MHz) δ 7.65–7.39 (m, 15H), 6.29 (d, 1H, $J = 7.7$, $^3J_{Sn-H} = 150$), 4.26 (m, 1H), 3.38 (d, 2H, $J = 0.9$), 3.34 (s, 3H), 1.65–0.80 (11H); ^{13}C NMR (50 MHz) δ 172.4, 145.3, 139.9, 137.3, 137.1, 129.0, 128.5, 86.6, 51.6, 45.1, 33.0, 31.7, 24.6, 22.4, 13.9; IR 3417, 3062, 2950, 1728 cm^{-1}.

Methyl (5*R*,3*Z*)-3-tributylstannyl-5-hydroxydec-3-enoate (8). To a solution of **5** (90 mg, 0.18 mmol) in CH_2Cl_2 was added triphenylphosphine (51 mg, 0.2 mmol). The mixture stirred until the reaction was complete by TLC. The concentrated material was purified by flash chromatography (10% EA–hex) to yield 75 mg (86%) of **8**: $R_f = 0.20$ (10% EA–hex); $[a]_D^{25} = +6.47$ ($c = 1.72$, CH_2Cl_2) (80% ee based upon NMR integration of (*R*,*R*)-MTPA ester **9**); ^{1}H NMR (360 MHz) δ 6.06 (d, 1H, $J = 8.3$), 3.91 (m, 1H), 3.64 (s, 3H), 3.20 (d, 2H, $J = 1.0$), 1.60–0.80 (m, 38H); ^{13}C NMR (50 MHz) δ 172.8, 146.9, 139.5, 74.3, 51.7, 45.1, 37.3, 31.8, 29.1, 29.0, 27.4, 25.2, 22.6, 14.0, 13.6, 10.9. Anal. Calcd. for $C_{23}H_{46}O_3Sn$: C, 56.46; H, 9.48. Found C, 56.48; H, 9.38%.

Methyl (5*R*,3*Z*)-3-tributylstannyl-5-(1-methoxy-1-trifluoromethylphenylacetoxy)dec-3-enoate (9). To a solution of alcohol **8** (13.5 mg, 0.028 mmol) and pyridine (0.1 mL) in 0.2 mL of CH_2Cl_2 was added (*S*)-(+)-MTPA chloride (5.68 mL, 0.03 mmol), and the mixture was allowed to stir at room temperature for 12 h. Excess N^1,N^3-dimethylpropane-1,3-diamine was added, and after 10 min the solvent was evaporated. The residue was subjected to flash chromatography, affording 13 mg (67%) of the (*R*)-MTPA ester **8**: $R_f = 0.68$ (10% EA–hex); ^{1}H NMR (360 MHz) δ 7.55–7.50 (m, 2H), 7.4–7.35 (m, 3H), 6.12 (d, 1H, $J = 9.6$), 5.45–5.35 (m, 1H), 3.64 (s, 3H), 3.49 (s, 3H), 3.22 (s, 2H), 1.60–0.80 (m, 38H). The diastereomer ratio was assigned based uopn the relative integration of the signals at δ 6.12 (major) and 6.00 (minor).

Methyl (5*S*,3*Z*)-3-triphenylstannyl-5-hydroxydec-3-enoate (10). To a solution of **7** (50 mg, 0.08 mmol) in CH_2Cl_2 was added triphenylphosphine (26 mg 0.1 mmol). The mixture was stirred until the reaction was complete by TLC and the contents were concentrated. The crude residue was purified by flash chromatography (10% EA–hex) to yield 45 mg (93%) of **10**: $R_f = 0.43$ (20% EA–hex); $[a]_D^{25} = +8.1$ ($c = 1.50$, CH_2Cl_2) (86% ee the optical purity was determined by NMR integration of the derived (*R*,*S*)-MTPA ester **11**); ^{1}H NMR (300 MHz) δ 7.65–7.37 (m, 15H), 6.40 (d, 1H, $J = 5.7$, $^3J_{Sn-H} = 150$), 3.36 (s, 3H + 2H), 1.51–0.80 (11H); ^{13}C NMR (75 MHz) δ 172.7, 148.1, 137.3, 137.0, 128.3, 72.9, 51.5, 44.5, 37.1, 31.5, 24.8, 22.4, 14.9. Anal. Calcd. for $C_{29}H_{34}O_3Sn$: C, 63.41; H, 6.24. Found C, 63.25; H, 6.18%.

Methyl (5*S*,3*Z*)-3-(triphenylstannyl)-5-(1-methoxy-1-trifluoromethylphenylacetoxy)dec-3-enoate (11). A solution of alcohol (15 mg, 0.027 mmol) and pyridine (0.1 mL) in CH_2Cl_2 (0.2 mL) was treated with (*S*)-(+)-MTPA chloride (15 mL, 0.082 mmol), and the mixture was allowed to stir at room temperature overnight. After the reaction was complete, excess N^1,N^3-dimethylpropane-1,3-diamine was added. The mixture was allowed to stand for 10 min. The mixture was diluted with ether, washed with water and dried over $MgSO_4$. The filtered solution was concentrated and the residue was subjected to flash chromatography to afford 16 mg (79%) of ester **11**: ^{1}H NMR (360 MHz) δ 7.80–7.30 (m, 10H), 6.25 (d, 1H), 5.40–5.3 (m, 1H), 3.48 (s, 3H), 3.35 (s, 3H), 3.35–3.25 (m, 2H), 1.4–0.80 (m, 11H). The ratio of diastereomers was based upon the relative integration of signals at δ 6.25 (major) and 6.05 (minor).

Methyl (4*E*)-3-trimethylsilyldec-4-enoate (12). A solution of (1*E*)-1-trimethylsilyoct-1-en-3-ol[82] (950 mg, 4.80 mmol) in trimethyl orthoacetate (7 mL) was heated to reflux for 6 hours. The reaction was cooled to room temperature and the mixture was purified by flash chromatography to yield 1.1 g (86%) of **12**: $R_f = 0.63$ (5% EA–hex); ^{1}H NMR (300 MHz) δ 5.25–5.20 (m, 2H), 3.58 (s, 3H), 2.40–2.20 (m, 2H), 1.98–1.85 (m, 2H), 0.83 (t, 3H, $J = 6.9$), −0.06 (s, 9H); ^{13}C NMR (75 MHz) δ 174.1, 129.1, 129.0, 51.3, 34.3, 32.6, 31.1, 29.5, 29.2, 22.4, 14.0, −3.5; IR 2946, 1756, 1436 cm^{-1}.

Methyl (3*E*)-2-trimethylsilyloct-3-enoate (13). Compound **13** was prepared from trimethylsilyl acetate, 1-iodohex-1-ene and $NiBr_2$ according to the procedure of Rathke.[29] The crude mixture was purified by flash chromatography (5% EA–hex) to yield 532 mg (42%) of **13**: $R_f = 0.50$ (5% EA–hex); ^{1}H NMR (500 MHz) δ 5.50 (dd, 1H, $J = 15.3$, 10.1), 5.19 (dt, 1H, $J = 15.3$, 6.9), 3.53 (s, 3H), 2.72 (d, 1H, $J = 10.1$), 1.91 (q, 2H, $J = 6.5$), 1.21 (m, 4H), 0.77 (t, 3H, $J = 7.3$), −0.05 (s, 9H); ^{13}C NMR (125 MHz) δ 130.0, 124.1, 51.0, 43.4, 32.3, 31.8, 22.2, 13.9, −2.9; IR 2969, 2850, 1725, 1428, 1255 cm^{-1}. Anal. Calcd. for $C_{12}H_{24}O_2Si$: C, 63.11; H, 10.59. Found C, 63.23; H, 10.69%.

(3*E*)-2-Trimethylsilyloct-3-en-1-ol (14). To a solution of **13** (320 mg, 1.40 mmol) in THF (20 mL) at 0 °C was added lithium aluminium hydride (57 mg, 1.50 mmol). After 60 min the reaction was quenched with ice–H_2O. The organic layer was removed and the aqueous layer was extracted with EA–hex (50%). The combined organic layers were dried, filtered through Celite, and concentrated. The residue was purified by flash chromatography (10% EA–hex) to yield 168 mg (60%) of **14**: $R_f = 0.22$ (10% EA–hex); ^{1}H NMR (500 MHz) δ 5.42 (dt, 1H, $J = 14.9$, 6.4), 5.23 (dd, 1H, $J = 14.9$, 5.2), 3.71–3.57 (m, 2H), 2.05–2.00 (dt, 2H, $J = 6.9$, 6.4), 1.80 (td, 1H, $J = 10.5$, 4.0), 1.34–1.28 (m, 4H), 0.89–0.86 (t, 3H, $J = 6.9$), −0.02 (s, 9H); ^{13}C NMR (125 MHz) δ 132.2, 127.7, 64.5, 38.3, 32.5, 32.0, 22.1, 13.9, −3.0; IR 3408, 3390, 2952, 2925, 1690, 1247 cm^{-1}. Anal. Calcd. for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07. Found C, 65.86; H, 11.79%.

Ethyl (2*E*)-4-bromooct-2-enoate (15). A solution of ethyl oct-2-enoate (1.50 g, 8.8 mmol) in carbon tetrachloride (5 mL) containing *N*-bromosuccinimide (NBS) (1.67 g, 9.26 mmol) was heated to reflux for 5 h. The mixture was cooled to room temperature and poured into an aqueous solution of $NaHSO_3$ (10%). The organic layer was removed and the aqueous layer was extracted with ether. The combined organic layers were dried with $MgSO_4$, filtered through Celite and concentrated. The residue was purified by flash chromatography (5% EA–hex) to yield 1.53 g (70%) of **15**: $R_f = 0.49$ (5% EA–hex); ^{1}H NMR (500 MHz) δ 6.92 (dd, 1H, $J = 15.3$, 9.3), 5.90 (d, 1H, $J = 15.3$), 4.50–4.48 (m, 1H), 4.19–4.15 (m, 2H), 1.95–1.8 (m, 2H), 1.45–1.15 (m, 7H), 0.90 (t, 3H); ^{13}C NMR (125 MHz) δ 167.0, 146.5, 121.8, 60.6, 51.2, 37.6, 29.5, 21.9, 14.1, 13.7.

Ethyl (3*Z*/*E*)-2-phenyldimethylsilyloct-3-enoate (16). Compound **16** was prepared from **15** in 53% yield as an 85:15 *Z*/*E* mixture according to the procedure of Bloch.[32] $R_f = 0.70$ (5% EA–hex); ^{1}H NMR (500 MHz) δ 7.55–7.45 (m, 2H), 7.40–7.35 (m, 3H), 5.61 (tt, 1H, $J = 11.3$, 1.6), 5.30 (dt, 1H, $J = 10.9$, 6.9), 4.00–3.95 (m, 2H), 4.05–3.95 (q, 2H), 3.35 (d, 1H, $J = 10.9$), 1.83–1.75 (m, 2H), 1.34–1.25 (m, 4H), 1.12–1.09 (t, 3H, $J = 7.3$), 0.84–0.81, (t, 3H, $J = 7.3$), 0.39 (s, 6H); ^{13}C NMR (75 MHz) δ 173.0, 133.9, 133.8, 129.5, 129.0, 128.7, 128.0, 59.9, 39.1, 33.0, 31.5, 27.2, 14.1, −4.5; IR 2954, 1716 cm^{-1}.

(3*Z*/*E*)-2-Phenyldimethylsilyloct-3-en-1-ol (17). To a solution of **16** (401 mg, 1.30 mmol) in THF (45 mL) at 0 °C was added diisobutylaluminium hydride (3.9 mL of a 1.0 M solution in hex). After 3 h the reaction was quenched with excess 10% HCl.

The organic layer was removed and the aqueous layer extracted with EA. The combined organic layers were dried with $MgSO_4$, filtered through Celite and concentrated. The residue was purified by flash chromatography to yield 94 mg (27%) of **17** as an inseparable 90:10 *Z*/*E* mixture: $R_f = 0.13$ (5% EA–hex); ^{1}H NMR (500 MHz) δ 7.50–7.48 (m, 2H), 7.36–7.34 (m, 3H), 5.54 (dt, 1H, $J = 10.9, 7.3$), 5.19 (apparent t, 1H, $J = 10.9$), 3.70 (dd, 1H, $J = 10.5, 4.0$), 3.55 (apparent t, 1H, $J = 10.5$), 2.45–2.40 (td, 1H, $J = 10.9, 4.3$), 2.05–2.00 (m, 1H), 1.90–1.85 (m, 1H), 1.30–1.24 (m, 4H), 0.87, (t, 3H, $J = 7.3$), 0.30 (s, 6H); ^{13}C NMR (125 MHz) δ 133.9, 132.6, 129.2, 127.7, 127.0, 63.3, 33.5, 31.9, 27.3, 22.4, 13.9, −4.2, −4.9; IR 3443, 2999 cm^{-1}. Anal. Calcd. for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98. Found C, 72.41; H, 10.18%.

Methyl (3*Z*)-5-hydroperoxy-3-trimethylsilyldec-3-enoate (18) and methyl (5*E*/*Z*)-4-hydroperoxy-3-trimethylsilyldec-5-enoate (19). Oxygenation of allylsilane **12** (110 mg, 0.23 mmol) in 4:1 CH_2Cl_2–MeCN (15 mL) containing Rose Bengal under standard conditions was complete according to TLC in 5 h. The solvent was removed under reduced pressure and the oily residue was purified by flash column chromatography (20% EA–hex) to yield 14 mg (12%) of **19** and 47 mg (40%) of **18**:

Compound **18**: $R_f = 0.46$ (20% EA–hex); ^{1}H NMR (300 MHz) δ 8.28 (s, 1H), 5.92 (d, 1H, $J = 9.8$), 4.7–4.55 (m, 1H), 3.67 (s, 3H), 3.15 (s, 2H), 1.80–1.20 (m, 10H), 0.85 (t, 3H, $J = 7.3$), 0.49 (s, 9H); ^{13}C NMR (75 MHz) δ 173.2, 145.4, 139.5, 83.9, 51.9, 43.1, 32.7, 31.8, 24.9, 22.5, 13.9, 0.2; FT-IR (neat) 3419, 2874, 1718 cm^{-1}. HRMS (M + Na) calcd 311.1654, found 311.1653.

Compound **19** was formed as a 72:28 *E*–*Z* mixture. The following data is for the major (*E*) isomer: $R_f = 0.52$ (20% EA–hex); ^{1}H NMR (300 MHz) δ 9.5 (s, 1H), 5.82 (dt, 1H, $J = 15.5, 6.7$), 5.29 (dd, 1H, $J = 15.3, 8.34$), 4.54 (dd, 1H, $J = 8.3, 4.1$), 3.70 (s, 3H), 2.5–2.01 (m, 4H), 1.45–1.20 (m, 4H), 0.89 (t, 3H, $J = 6.9$), 0.02 (s, 9H); ^{13}C NMR (75 MHz) δ 170.0, 138.8, 123.9, 86.7, 52.5, 32.3, 31.5, 30.9, 29.0, 24.5, 22.4, 13.9, −2.3; IR 3391, 2955, 1740 cm^{-1}; HRMS (M + Na) calcd 311.1654, found 311.1653.

Methyl (2*Z*)-4-hydroperoxy-2-trimethylsilyloct-2-enoate (20). Oxygenation of allylsilane **13** (74 mg, 0.32 mmol) in TPP–CCl_4 (50 mL) under standard conditions was complete according to TLC in 75 min. The solvent was removed under reduced pressure and the oily residue was purified by flash chromatography on silica gel (10% EA–hex) to yield 32 mg (39%) of **20**: $R_f = 0.40$ (10% EA–hex); ^{1}H NMR (300 MHz) δ 8.25 (s, 1H), 6.94 (d, 1H, $J = 9.3$), 4.8–4.7 (m, 1H), 3.75 (s, 3H), 1.65–1.20 (m, 6H), 0.95 (t, 3H), 0.06 (s, 9H); ^{13}C NMR (75 MHz) δ 153.5, 119.0, 83.0, 62.1, 51.7, 32.3, 27.3, 22.7, 13.9, 0.63; IR 3425, 2955, 1757 cm^{-1}. Anal. Calcd. for $C_{12}H_{24}O_4Si$: C, 55.35; H, 9.29. Found C, 55.66; H, 9.20%.

(2*Z*)-4-Hydroperoxy-2-trimethylsilyloct-2-en-1-ol (21). Oxygenation of allylsilane **14** (50 mg, 0.25 mmol) in TPP–CCl_4 (5 mL) under standard conditions was complete according to TLC in 75 min. The solvent was removed under reduced pressure and the oily residue was purified by flash chromatography on silica gel (20% EA–hex) to yield 33 mg (58%) of **21**: $R_f = 0.27$ (30% EA–hex); ^{1}H NMR (500 MHz) δ 6.10 (d, $J = 9.7$, NOE 11% with C*H*$_2$OH), 4.66–4.62 (m, 1H), 4.25–4.14 (m, 2H), 1.65–1.28 (m, 6H), 0.92–0.87 (t, 3H, $J = 6.9$), 0.19 (s, 9H); ^{13}C NMR (125 MHz) δ 145.2, 140.9, 83.9, 67.9, 32.8, 27.5, 22.8, 13.9, 0.25; IR 3333, 3265, 2948 cm^{-1}.

Ethyl (2*Z*)-4-hydroxy-2-phenyldimethylsilyloct-2-enoate (22) and ethyl (4*E*)-3-hydroxy-2-phenyldimethylsilyloct-4-enoate (23). Oxygenation of allylsilane **16** (538 mg, 1.78 mmol) in 4:1 CH_2Cl_2–MeCN and Rose Bengal (20 mL) under standard conditions was complete according to TLC in 2 h. The solvent was removed under reduced pressure and the oily residue was diluted in EA (20 mL) and triphenylphosphine (276 mg, 1.06 mmol) was added to reduce the hydroperoxide to the alcohol. Concentration and flash chromatography of the resulting alcohols on silica gel (5% EA–hex) yielded 253 mg (45%) of **23** and 85 mg (15%) of **22**:

Compound **22**: $R_f = 0.27$ (5% EA–hex); ^{1}H NMR (500 MHz) δ 7.56–7.54 (m, 2H), 7.36–7.35 (m, 3H), 6.92 (d, 1H, $J = 9.3$), 4.14 (q, 2H, $J = 7.3$), 4.07–4.01 (m, 1H), 2.16 (s, 1H), 1.28–1.14 (m, 9H), 0.81 (t, 3H, $J = 7.3$), 0.49 (s, 6H); ^{13}C NMR (125 MHz) δ 139.0, 134.9, 133.6, 129. 4, 128.1, 125.0, 69.7, 60.7, 36.1, 27.2, 22.5, 14.1, 13.9, −0.87; IR 3443, 2956, 1711 cm^{-1}.

Compound **23**: $R_f = 0.17$ (5% EA–hex); ^{1}H NMR (500 MHz) δ 7.60–7.58 (m, 2H), 7.40–7.35 (m, 3H), 5.54 (dt, 1H, $J = 15.3, 6.9$), 5.40 (dd, 1H, $J = 15.3, 6.4$), 4.26 (br s, 1H), 4.05–3.98 (m, 2H), 2.45 (d, 1H, $J = 5.2$), 1.90 (dd, 2H, J =7.3, 6.9), 1.34–1.29 (m, 2H), 1.13 (t, 3H, $J = 6.9$), 0.85 (t, 3H, $J = 7.7$), 0.50 (s, 6H); ^{13}C NMR (125 MHz) δ 174.8, 134.0, 133.0, 131.9, 129.6, 129.5, 127.9, 71.3, 60.1, 44.7, 34.1, 22.0, 14.1, 13.6, 0.05; IR 3404, 3360, 1717 cm^{-1}. Anal. Calcd. for $C_{18}H_{28}O_3Si$: C, 67.46; H, 8.81. Found C, 67.38; H, 9.34%.

(2*Z*)-4-Hydroperoxy-2-phenyldimethylsilyloct-2-en-1-ol (24) and (4*E*)-3-hydroperoxy-2-phenyldimethylsilyloct-4-en-1-ol (25). Oxygenation of allylsilane **17** (95 mg, 0.36 mmol) in 4:1 CH_2Cl_2–MeCN (12 mL) and Rose Bengal under standard conditions was complete according to TLC in 2 h. The solvent was removed under reduced pressure and the oily residue was purified by flash chromatography (20% EA–hex) to yield 39 mg (44%) of **25** and 12 mg (14%) of **24**:

Compound **24**: $R_f = 0.23$ (25% EA–hex); ^{1}H NMR (500 MHz) δ 7.85 (s, 1H), 7.55–7.53 (m, 2H), 7.36–7.34 (m, 3H), 6.16 (d, 1H, $J = 9.7$), 4.44–4.39 (m, 1H), 4.25 and 4.19 ($dd_{ABX'}$, 2H, $J = 13.3, 1.2$), 1.50–1.15 (m, 4H), 0.79 (t, 3H, $J = 7.3$), 0.57 (s, 3H), 0.45 (s, 3H); ^{13}C NMR (125 MHz) δ 144.5, 142.2, 133.9, 129.3, 128.0, 127.8, 83.9, 68.3, 32.5, 27.3, 22.6, 13.9, −1.33.

Compound **25**: $R_f = 0.28$ (25% EA–hex); ^{1}H NMR (500 MHz) δ 8.15 (br s, 1H), 7.50–7.30 (m, 5H), 5.67 (dt, 1H, $J = 15.3, 6.9$), 5.30 (dd, 1H, $J = 15.3, 8.5$), 4.43 (t, 1H, $J = 9.3$), 3.90–3.75 (m, 2H), 1.96–1.93 (m, 2H), 1.58–1.55 (m, 1H), 1.37–1.29 (m, 2H), 0.89 (t, 3H, $J = 7.7$), 0.34 (s, 3H), 0.33 (s, 3H); ^{13}C NMR (125 MHz) δ 137.6, 137.2, 133.8, 129.2, 128.4, 127.8, 89.0, 62.4, 35.6, 34.3, 21.8, 13.8, −2.5, −2.8; IR 3204, 3196, 2973 cm^{-1}.

1-Trimethyl(undeca-2,5-diynyl)silane (26). To a −78 °C solution of propargyl silane (200 mg, 1.78 mmol) in THF (5.0 mL) was added *n*-BuLi (0.91 mL, 1.96 M soln in hexane). After 60 min 1-iodoct-2-yne[37] was added and the reaction was stirred at −78 °C for 10 min. The reaction was warmed to room temperature and then refluxed for 60 min. The reaction was quenched with H_2O and the organic layer removed. The aqueous layer was extracted (10% EA–hex), dried with $MgSO_4$, filtered through Celite, and concentrated. Flash chromatography yielded 178 mg (51%) of diyne **26**: $R_f = 0.40$ (100% hex); ^{1}H NMR (300 MHz) δ 3.06 (t, 2H, $J = 2.6$), 2.14–2.08 (m, 2H), 1.60–1.24 (m, 8H), 0.86 (t, 3H, $J = 6.7$), 0.10 (s, 9H); ^{13}C NMR (75 MHz) δ 80.0, 77.7, 74.9, 73.2, 31.0, 28.4, 22.1, 18.6, 13.9, 9.7, 6.8, −2.2.

(2*Z*,5*Z*)-1-Trimethyl(undeca-2,5-dienyl)silane (27). To a solution of nickel acetate tetrahydrate (637 mg, 2.56 mmol) in ethanol (30 mL) under 1 atm of H_2 was added sodium borohydride (97 mg, 2.56 mmol) in ethanol (10 mL). After stirring for 15 min ethylenediamine (481 mg, 8.0 mmol) was added followed by compound **26** (587 mg, 2.67 mmol). After 2 h the reaction was vented and the crude mixture was filtered through Celite, extracted (5% EA–hex), dried with $MgSO_4$, and concentrated. The concentrate was immediately subjected to flash chromatography to yield 542 mg (92%) of **27**: $R_f = 0.64$ (100% hex); ^{1}H NMR (500 MHz) δ 5.46–5.18 (m, 4H, $J = 10.7, 10.5$), 2.75–2.65 (apparent t, 2H, $J = 6.4$), 2.06 (apparent q, 2H, $J = 6.6$), 1.50–1.45 (d, 2H, $J = 8.6$), 1.4–1.2 (m, 6H), 0.89 (t,

3H, $J = 6.9$), 0.0 (s, 9H); ^{13}C NMR (125 MHz) δ 130.0, 128.2, 125.8, 125.8, 31.5, 29.4, 27.2, 25.4, 22.6, 18.5, 14.0, −1.8.

(2*E*,5*Z*)-1-Trimethyl(undeca-2,5-dienyl)silane (28). Compound **28** was prepared according to the procedure of Tsuji.[39] A solution of tris(dibenzylideneacetone)–dipalladium(0)–chloroform adduct (122 mg, 0.12 mmol), hexamethyldisilane (344 mg, 2.35 mmol), oct-2-ynoyl chloride[40] (372 mg, 2.35 mmol), and butadiene (4.4 mL of a 1.6 M toluene solution) in toluene (9 mL) were placed in a pressure tube. The contents were flushed several times with a strong stream of nitrogen. The tube was sealed and heated to 80 °C with stirring. After 4 h the reaction vessel was cooled in ice–water and vented. The contents were passed through a 4 cm Florisil column (100–200 mesh) and concentrated to afford crude (2*E*)-1-trimethyl[undec-2-en-4-ynyl]silane, which was used without further purification: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.62 (dt, 1H, $J = 14.9$, 8.1), 5.23 (dt, 1H, $J = 14.9$, 5.6), 2.85–2.84 (m, 2H), 2.20–2.12 (m, 2H), 1.50–1.25 (m, 6H), 0.89 (t, 3H, $J = 7.3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 127.7, 123.1, 89.0, 74.0, 31.0, 28.7, 22.4, 22.15, 18.6, 13.9, −2.1. Into a suspension of nickel acetate (421 mg, 1.69 mmol) in ethanol (25 mL) under 1 atm H_2 was added sodium borohydride (64 mg, 1.69 mmol) in ethanol (8 mL) whereupon the solution became dark. After stirring for 15 min ethylenediamine (338 mg, 5.60 mmol) was added followed by (2*E*)-1-trimethyl[undec-2-en-4-ynyl]silane (residue) (144 mmol) in ethanol (5 mL). Reaction progress was monitored by TLC (100% hex). The reaction was stopped after 2 h by removing the H_2 atmosphere. The crude reaction mixture was filtered through Celite, extracted (5% EA–hex), dried with $MgSO_4$, and concentrated. The concentrate was immediately subjected to flash chromatography to yield 40 mg (8%, two steps) of (2*E*,4*Z*)-1-trimethylsilylundeca-2,4-diene (**28**): $R_f = 0.44$ (100% hex); ^{1}H NMR (500 MHz) δ 5.45–5.15 (m, 4H, $J = 15.3$), 2.71 (t, 2H, $J = 6.0$), 2.0 (dt, 2H, $J = 6.2$, 6.7), 1.41–1.38 (d, 2H, $J = 7.9$), 1.31–1.25 (m, 6H), 0.88 (t, 3H, $J = 6.7$), 0.0 (s, 9H); ^{13}C NMR (125 MHz) δ 130.2, 128.1, 126.9, 126.4, 31.5, 30.6, 29.4, 27.0, 22.6, 22.6, 14.0, −2.0.

(3*E*,5*Z*)-1-Trimethylsilylundeca-3,5-dien-2-ol (29) and (1*E*/*Z*,5*Z*)-1-trimethylsilylundeca-1,5-dien-3-ol (30). Oxygenation of compound **39** (152 mg, 0.63 mmol) in TPP–CH_2Cl_2 (15 mL) under standard conditions was complete within 1 h according to TLC analysis. The solvent was removed under reduced pressure and the oily residue was dissolved in ethyl acetate (20 mL) and reduced to the alcohol by the addition of triphenylphosphine (170 mg, 0.65 mmol). Flash chromatography on silica gel (5% EA–hex) yielded 125 mg (77%) of a mixture of regioisomeric dienols enriched in **29**. High performance liquid chromatography of a sample (2.5% EA–hex, 1 mL min^{-1}) afforded 6.9 mg of **30** and 17 mg of **29**:

Compound **29** $R_f = 0.27$ (5% EA–hex); ^{1}H NMR (500 MHz, $CDCl_3$) d 6.43 (dd, 1H, $J = 15.3$, 11.3), 5.94 (apparent t, 1H, $J = 10.9$), 6.92 (d, 1H, $J = 9.3$), 5.65 (dd, 1H, $J = 15.3$, 7.3), 5.45 (dt, 1H, $J = 10.9$, 7.7), 4.38–4.30 (apparent q, 1H, $J = 7.26$), 2.20–2.13 (m, 2H), 1.45–1.20 (m, 6H), 1.06 and 0.95 ($dd_{ABX'}$, 2H, $J = 12$, 7), 0.85 (t, 3H, $J = 6.9$).

Compound **30**: $R_f = 0.27$ (5% EA–hex); ^{1}H NMR (500 MHz) δ 6.25 (dd, 1H, $J = 14.1$, 8.5), 6.06 (dd, 1H, $J = 18.5$, 5.2), 5.89 (dd, 1H, $J = 18.9$, 1.61), 5.66 (d, 1H, $J = 14.1$), 5.57 (m, 1H), 5.39–5.35 (m, 1H), 4.28–4.22 (apparent q, 1H, $J = 7.7$, 6.0), 4.1–4.15 (apparent q, 2H), 2.40–2.20 (m, 2H), 2.10–2.00 (m, 2H), 1.4–1.20 (m, 6H), 0.89 (t, 3H).

(2*E*,4*E*/*Z*)-1-Trimethylsilylundeca-2,4-dien-6-ol (31). Oxygenation of compound **28** (36 mg, 0.16 mmol) in 4:1 CH_2Cl_2–MeCN (1 mL) containing TPP under standard conditions was complete in 2 h. The solvent was removed under vacuum and the crude residue was dissolved in ethyl acetate (20 mL) and reduced to the alcohol with triphenylphosphine (47 mg, 0.18 mmol). Flash chromatography of the resulting alcohols on silica gel (5% EA–hex) yielded 4 mg of a 90:10 *Z*/*E* mixture of compound **31** and 16 mg (42%) of **30**:

Compound **31**: $R_f = 0.27$ (5% EA–hex); ^{1}H NMR (500 MHz) δ 6.15 (dd, 1H, $J = 15.3$, 10.5), 5.88 (dd, 1H, $J = 14.9$, 10.9), 5.69 (dt, 1H, $J = 15.3$, 8.1), 5.47 (dd, 1H, $J = 14.9$, 6.9), 4.10–4.05 (apparent q, 1H, $J = 6.9$, 6.4), 1.53 (d, 2H, $J = 8.1$), 1.45–1.20 (m, 6H), 0.85 (t, 3H, $J = 6.9$).

Preparation of tributylstannyllithium

To a −78 °C solution of diisopropylamine (3.1 mL, 22.4 mmol) in THF (100 mL) was added *n*-BuLi (7.5 mL, 2.5 M in hex). After stirring for 10 minutes at 0 °C tributyltin hydride (5.0 g, 17.2 mmol) was added and this mixture was stirred for 20 min to form tributylstannyllithium as an approximately 17 mM solution in THF.

[(2*E*)-1-(Methoxymethoxy)oct-2-enyl]tributylstannane (32). To a 0 °C solution of tributylstannyllithium (17.2 mmol) in THF (100 mL) was added (*E*)-oct-2-enal (1.68 g, 17.2 mmol). The reaction was allowed to warm to room temperature and then was quenched with sat. ammonium chloride (20 mL) after 2 h. The separated aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was dissolved in dry CH_2Cl_2 (75 mL) and cooled to 0 °C, whereupon *N*,*N*-diisopropylethylamine (3.89 mL, 22.4 mmol), and methoxymethyl chloride (MOMCl) (1.4 mL, 18.9 mmol) were added. After stirring for 3 h the reaction was quenched with water (50 mL). The organic layer was removed and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (5% EA–hex) to yield 6.58 g (83%) of **32**: $R_f = 0.71$ (10% EA–hex); ^{1}H NMR (500 MHz) δ 5.53 (dd, 1H, $J = 7.3$, 15.3), 5.37 (dtd, 1H, $J = 1.2$, 6.9, 15.3), 4.65 (d, 1H, $J = 6.4$), 4.55 (d, 1H, $J = 7.3$), 4.47 (d, 1H, $J = 6.5$), 3.32 (s, 3H), 1.98 (apparent q, 2H, $J = 7.3$), 1.48 (m, 6H), 1.35 (q, 2H, 7.3), 1.29 (m, 6H), 0.9 (m, 10H), 0.87 (t, 12H, $J = 7.3$); ^{13}C NMR (75 MHz) δ 131, 125, 95, 72, 55, 34, 29, 27, 22, 13 and 9; IR 2956, 1463, 1155 cm^{-1}. Anal. Calcd. for $C_{22}H_{46}O_2Sn$: C, 57.28; H, 10.06. Found C, 57.31; H, 9.86.

[(2*Z*)-1-(Methoxymethoxy)oct-2-enyl]tributylstannane (33). To a −78 °C solution of oxalyl chloride (5.96 g, 47.3 mmol) in CH_2Cl_2 (200 mL) was added dimethyl sulfoxide (5.71 g, 73.2 mmol) followed by *cis*-oct-2-en-1-ol (5.51 g, 43.1 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred for 1 h prior to the addition of triethylamine (43.58 g, 430.7 mmol). After stirring for an additional hour at −78 °C the mixture was warmed to room temperature and then quenched with water (200 mL). The organic layer was removed and the aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The crude (2*Z*)-oct-2-enal was redissolved in THF (15 mL) and then transferred *via* cannula into a solution of tributylstannyllithium (43.1 mmol) at −78 °C. The mixture was allowed to stir for 30 minutes at 0 °C then water (50 mL) was added to quench the reaction. The organic layer was removed and the aqueous layer was extracted with ethyl acetate (2 × 100 mL). The combined organic layers were dried over Na_2SO_4 and the stannylmethanol was concentrated. The crude methanol was redissolved in CH_2Cl_2 (200 mL), at −78 °C and reacted with *N*,*N*-diisopropylethylamine (7.12 g, 56.5 mmol), and methoxymethyl chloride (4.52 g, 56.5 mmol). The reaction was brought to 0 °C and stirred for 2.5 h, whereupon it was quenched with water (50 mL). The organic layer was removed and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to yield 10.52 g (53%) of **33**: $R_f = 0.71$ (10% EA–hex); ^{1}H NMR (300 MHz) δ 5.65 (t, 1H,

J = 10.7, 1.7), 5.19 (dt, 1H), 4.87 (d, 1H, J = 10.5), 4.60–4.41 (d_{AB} 1H, J_{AB} = 6.2, 6.4), 3.57 (s, 3H), 2.05–1.95 (m, 2H), 1.6–0.80 (m, 36H); ^{13}C NMR (75 MHz) δ 131.1, 126.3, 95.3, 68.7, 55.1, 31.6, 29.5, 29.1, 27.7, 27.4, 22.6, 14.0, 13.6, 9.0; IR 2956, 1463 cm^{-1}. Anal. Calcd. for $C_{22}H_{46}O_2Sn$: C, 57.28; H, 10.05. Found C, 57.31; H, 9.86%.

(2*Z*)-1-(Tributylstannyl)oct-2-en-1-yl acetate (34). To a 0 °C THF (75 mL) solution of the tributylstannyl methanol derived as described above from (*Z*)-oct-2-enal (1.87 g, 14.6 mmol) was added dimethylaminopyridine (DMAP) (25 mg, 0.21 mmol), *N*,*N*-diisopropylethylamine (2.2 g, 17.4 mmol), and acetic anhydride (1.77 g, 17.4 mmol). The reaction was stirred for 3 h at room temperature and then quenched with water (50 mL). The organic layer was removed and the aqueous layer was extracted with ether (2 × 25 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to yield 3.75 g (56%, 3 steps) of **28**: R_f = 0.72 (10% EA–hex); ^{1}H NMR (500 MHz) δ 5.66 (apparent t, 1H, J = 10.5), 5.56 (d, 1H, J = 10.5), 5.17 (dt, 1H, J = 10.9, 7.3), 2.0 (s, 3H), 1.95–1.85 (m, 2H), 1.65–1.58 (m, 16H), 0.9–0.83 (m, 20H); ^{13}C NMR (125 MHz) δ 170.8, 128.7, 125.8, 69.8, 31.6, 29.3, 28.9, 27.9, 27.4, 22.5, 20.9, 14.0, 13.6, 10.0; IR 3012, 1720, 1417, 1292. Anal. Calcd. for $C_{22}H_{44}O_2Sn$: C, 57.53; H, 9.66. Found C, 57.73; H, 9.52%.

(2*E*)-1-(Tributylstannyl)hex-2-en-1-yl acetate (35). By a similar procedure as **28** (*E*)-hex-2-enal (2.0 g, 20.4 mmol) was converted to 6.68 g (76%) of **30**: R_f = 0.65 (10% EA–hex); ^{1}H NMR (300 MHz) δ 5.63 (dd, 1H, J = 15.3, 7.2), 5.35 (dt, 1H, J = 15.3, 6.7), 5.27 (d, 1H, J = 7.2), 2.03 (s, 3H), 2.0–1.96 (m, 2H), 1.58–1.21 (m, 14H), 0.97–0.80 (m, 18H); ^{13}C NMR (75 MHz) δ 170.8, 129.6, 125.8, 72.0, 34.5, 28.9, 27.4, 22.8, 21.0, 13.6, 9.9.

(2*E*)-[3-Methyl-1-(methoxymethoxy)oct-2-enyl]tributylstannane (36). To a −78 °C solution of oxalyl chloride (1.06 g, 8.4 mmol) in CH_2Cl_2 (150 mL) was slowly added DMSO (1.01 g, 13.0 mmol). After 10 min a solution of (2*E*)-3-methyloct-2-en-1-ol[83] (1.09 g, 7.60 mmol) in CH_2Cl_2 (20 ml) was added dropwise. The reaction mixture was stirred for 1 h and triethylamine (30 mL, 214 mmol) was added. The reaction was allowed to warm to room temperature over a period of 2 h and was quenched with water (200 mL). The organic layer was removed and the aqueous layer was extracted with dichloromethane (1 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated on a rotary evaporator. The residue was purified by flash chromatography on silica gel (10% EA–hex) to yield 968 mg (91%) of (2*E*)-3-methyloct-2-enal: R_f = 0.4 (12% EA–hex); ^{1}H NMR (300 MHz) δ 9.9 (d, 1H, J = 8.1), 5.8 (dt, 1H, J = 8.1, 1.1), 2.1 (t, 2H, J = 6.6), 2.13 (d, 3H, J = 1.1), 1.19–1.54 (m, 5H), 0.86 (t, 3H, J = 6.6); ^{13}C NMR (75 MHz) δ 191.1, 164.2, 127.1, 40.4, 31.2, 26.6, 22.3, 17.3, 13.7; IR 2956, 1675 cm^{-1}. Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.49. Found C, 76.89; H, 11.30%.

By a similar procedure as **33** (2*E*)-3-methyloct-2-en-1-ol was converted to 2.71 g (70%) of **36**: R_f = 0.74 (10% EA–hex); ^{1}H NMR (300 MHz) δ 5.33 (dd, 1H, J = 1.2, 10.5), 4.81 (d, 1H, J = 10.7), 4.60–4.41 (dd, 2H, J = 6.2, 6.4), 3.30 (s, 3H), 1.95 (t, 2H, J = 7.15), 1.15–0.80 (m, 39H); ^{13}C NMR (75 MHz) δ 132.5, 126.1, 94.9, 68.9, 55.1, 39.6, 31.5, 29.1, 27.7, 27.4, 22.5, 16.4, 14.0, 13.6 and 9.1; IR 2956, 2871, 1463 cm^{-1}. Anal. Calcd. for $C_{23}H_{48}O_2Sn$: C, 58.12; H, 10.17. Found C, 58.24; H, 10.26%.

(3*E*)-[2-(Methoxymethoxy)-5-methylhex-3-enyl]tributylstannane (37). By a similar procedure as **33** 5-methylhex-3-en-2-one (1.7 g, 15.2 mmol) was converted to 407 mg (6%) of alkoxystannane **37**: R_f = 0.71 (2% EA–hex); ^{1}H NMR (500 MHz) δ 5.63 (d, 1H, J = 15.7), 5.19 (dd, 1H, J = 15.7, 7.0), 4.71, 4.41 (d, 2H, J_{AB} = 6.9), 3.34 (s, 3H), 2.30–2.20 (m, 1H), 1.55–1.44 (m, 8H), 1.33–1.25 (m, 8H), 1.0–0.80 (m, 20H); IR 2871, 1463, 1376, 1135. Anal. Calcd. for $C_{21}H_{44}O_2Sn$: C, 56.39; H, 9.91. Found C, 56.12; H, 10.01%.

[Furan-2-yl(methoxymethoxy)methyl]tributylstannane (38). To a 0 °C solution of tributylstannyllithium (12.0 mmol) in THF (40 mL) was added 2-furaldehyde (0.5 mL, 6.0 mmol). After 30 min, the reaction was quenched with sat. aq. ammonium chloride (20 mL). The organic layer was removed, dried over Na_2SO_4, and concentrated. The residue was redissolved in CH_2Cl_2 (15 mL) and cooled to 0 °C. *N*,*N*-Diisopropylethylamine (2.0 mL, 12 mmol) was added, followed by methoxymethyl chloride (MOMCl) (1.0 mL, 13 mmol). The reaction was stirred for 1 h and slowly warmed to room temperature before quenching with water (20 mL). The organic layer was removed, dried over Na_2SO_4, and concentrated. The oily residue was purified by flash chromatography (5% EA–hex) to yield 1.75 g (34%) of **36**: R_f = 0.86 (10% EA–hex); ^{1}H NMR (300 MHz) δ 7.3 (dd, 1H, J = 0.7, 1.8), 6.2 (dd, 1H, J = 1.9, 3.1), 6.0 (d, 1H, J = 3.1), 4.9 (s, 1H, $^3J_{Sn-H}$ = 32), 4.5 (d, 1H, J = 6.5), 4.4 (d, 1H, J = 6.4), 3.3 (s, 3H), 1.4 (m, 6H), 1.2 (m, 6H), 0.9 (m, 6H), 0.75 (t, 9H, J = 7.2); ^{13}C NMR (75 MHz) δ 156, 141, 110, 105, 95, 65, 55, 28, 27, 13, 9. Anal. Calcd. for $C_{19}H_{36}O_3Sn$: C, 52.92; H, 8.41. Found C, 52.80; H, 8.25%.

Acetic acid, α-(tributylstannyl)furan-2-ylmethyl ester (39). To a 0 °C solution of tributylstannyllithium (16.0 mmol) in THF (100 mL) was added 2-furaldehyde (1.40 g, 14.6 mmol). After 30 min, the reaction was quenched with sat. aq. ammonium chloride (20 mL). The organic layer was removed, dried over Na_2SO_4, and concentrated. The residue was redissolved in CH_2Cl_2 (15 mL) and cooled to 0 °C. To the solution of dimethylaminopyridine (DMAP) (25 mg, 0.21 mmol), *N*,*N*-diisopropylethylamine (2.2 g, 17.4 mmol), and acetic anhydride (1.63 g, 16.0 mmol) were added. The reaction was stirred for 3 h at room temperature, then quenched with water (20 mL) and the organic layer was removed. The aqueous layer was extracted with ether (3 × 100 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated. The crude residue was purified by flash chromatography (5% EA–hex) to yield 2.6 g (42%) of **39**: R_f = 0.75 (10% EA–hex); ^{1}H NMR (300 MHz) δ 7.3 (d, 1H, J = 1.9), 6.3 (dd, 1H, J = 1.9, 3.1), 6.1 (d, 1H, J = 3.1), 5.7 (s, 1H), 2.0 (s, 3H), 1.5–1.2 (m, 12H), 0.95–0.80 (m, 15H), 0.75 (t, 9H, J = 7.2); ^{13}C NMR (75 MHz) δ 170.8, 155.0, 141.9, 110.5, 106.3, 65.0, 28.7, 27.3, 20.9, 13.6, 10.5; IR 2844, 1731, 1500, 1367, 1187 cm^{-1}.

(1*Z*)-1-Methoxymethoxy-1-tributylstannyloct-1-en-3-ol (40). Oxygenation of allylstannane **32** (910 mg, 2.0 mmol) in TPP–CCl_4 (50 mL) under standard conditions was complete according to TLC in 45 min. The solvent was removed under reduced pressure and the oily residue was rediluted in THF (25 mL) and reduced to the alcohol with lithium aluminium hydride. Water was added and the organic layer was removed. The aqueous layer was extracted with ethyl acetate and the combined organic layers were concentrated. The concentrate was purified by flash chromatography on silica gel to yield 372 mg (39%) of alcohol **40**: R_f = 0.21 (10% EA–hex); ^{1}H NMR (300 MHz) δ 5.45 (d, 1H, J = 9.0, $^3J_{Sn-H}$ = 86.1), 4.88 (s, 2H), 3.85–3.78 (m, 1H), 3.4 (s, 3H), 1.65–1.20 (m, 21H), 1.05–0.80 (m, 18H); ^{13}C NMR (300 MHz) δ 167.3, 119.6, 94.1, 72.2, 55.8, 38.3, 31.8, 29.0, 27.2, 25.6, 22.6, 13.9, 13.6, 10.8; IR 3411, 2857, 1076 cm^{-1}. Anal. Calcd. for $C_{22}H_{46}O_3Sn$: C, 55.36; H, 9.71. Found C, 55.19; H, 9.75%.

[3-Methoxymethoxy-5-pentyl-1,2-dioxolan-4-yl]tributylstannane (41). Oxygenation of allylstannane **33** (15 mg, 0.030 mmol) under standard conditions ($CDCl_3$, Rose Bengal) was complete in 25 min according to ^{1}H NMR. The solvent was removed under reduced pressure and the residue was purified by chromatography (5% EA–hex) to yield 9.3 mg (58%) of dioxolane **41**: R_f = 0.30 (5% EA–hex); ^{1}H NMR (300 MHz) δ 5.44 (d, 1H, J = 2.6), 4.91 (d, 2H, J = 6.9), 4.56 (d, 1H,

$J = 7.1$), 4.55–4.45 (m, 1H), 3.40 (s, 3H), 2.50 (dd, 1H, $J = 6.7$, 2.4), 1.60–0.80 (m, 38H); IR 2956, 1685, 1589 cm^{-1}.

(1*E*)-1-Acetoxy-3-hydroperoxy-1-tributylstannyloct-1-ene (42). Oxygenation of allylstannane **34** (100 mg, 0.22 mmol) in $CHCl_3$ (10 mL) containing Rose Bengal under standard conditions was complete according to TLC in 15 min. The solvent was removed under reduced pressure and the oily residue was purified by flash column chromatography (20% EA–hex) to yield 38 mg (38%) of hydroperoxide **42**: $R_f = 0.36$ (10% EA–hex); ^{1}H NMR (300 MHz) δ 8.25 (s, 1H), 5.78 (d, 1H, $J = 9.8$, $^3J_{Sn-H} = 68.4$), 4.30–4.28 (m, 1H), 2.10 (s, 3H), 1.7–1.2 (m, 20H), 1.5–0.9 (18H); ^{13}C NMR (75 MHz) δ 170.3, 164.5, 130.6, 83.3, 33.2, 31.8, 28.8, 27.3, 25.0, 22.5, 20.7, 13.9, 13.6, 86.6; IR 3376, 2854, 1714, 1683 cm^{-1}.

(1*E*)-1-Acetoxy-3-hydroperoxy-1-tributylstannylhex-1-ene (43). Oxygenation of allylstannane **35** (3.66 g, 7.90 mmol) in 4:1 CH_2Cl_2–MeCN (50 mL) and Rose Bengal under standard conditions was complete according to TLC in 5 h. The solvent was removed under reduced pressure and the oily residue was purified by flash chromatography (20% EA–hex) to yield 1.23 g (33%) of hydroperoxide **43**: $R_f = 0.41$ (15% EA–hex); ^{1}H NMR (300 MHz) δ 8.0 (s, 1H), 5.78 (d, 1H, $J = 9.8$, $^3J_{Sn-H} = 68.4$), 4.30–4.28 (m, 1H), 2.10 (s, 3H), 1.7–1.2 (m, 16H), 1.5–0.9 (m, 18H); ^{13}C NMR (75 MHz) δ 170.3, 164.5, 130.4, 83.2, 83.1, 35.3, 29.0, 27.3, 20.8, 14.1, 13.6, 11.8; IR 3442, 2975, 1737, 1465, 1240 cm^{-1}. Anal. Calcd. for $C_{20}H_{40}O_4Sn$: C, 51.86; H, 8.7. Found C, 51.66; H, 8.48%.

[1-(Methoxymethoxy-5-methyl-5-pentyl-1,2-dioxolan-4-yl]-tributylstannane (44). Oxygenation of allylstannane **36** (200 mg, 0.42 mmol) in $CHCl_3$ (12 mL) and Rose Bengal under standard conditions was complete according to TLC in 10 min. Immediately after the photooxygenation, ^{1}H NMR indicated a 55:45 ratio of 1,2-dioxolane (**44**) to the allylic hydroperoxide precursor of **45**. The solvent was removed under reduced pressure and the oily residue was purified by flash chromatography on silica gel. Purification of the oily residue by flash chromatography on silica gel led to selective decomposition of the allylic hydroperoxide and isolation of 98 mg (46%) of 1,2-dioxolane **44**: $R_f = 0.7$ (10% EA–hex); ^{1}H NMR (500 MHz) δ 5.72 (d, 1H, $J = 3.7$, $^3J_{Sn-H} = 32$), 5.05 (d, 1H, $J = 6.9$), 4.47 (d, 1H, $J = 6.9$), 3.23 (s, 3H), 2.58 (d, 1H, $J = 3.5$, $^{1,2}J_{Sn-H} = 42$), 1.75–0.80 (m, 38H); ^{13}C NMR (125 MHz) δ 104, 93, 88, 56, 49, 37, 32, 28, 27, 25, 24, 22, 13.9, 13.6, 9; IR 2956, 1464, 1292 cm^{-1}. Anal. Calcd. for $C_{23}H_{48}O_4Sn$: C, 54.45; H, 9.53. Found C, 54.17; H, 9.75%.

(1*E*)-1-Methoxymethoxy-1-tributylstannyl-3-methyloct-1-en-3-ol (45). Oxygenation of allylstannane **36** (110 mg, 0.23 mmol) in TPP–CCl_4 (12 mL) under standard conditions was complete according to TLC in 15 min. The solvent was removed under reduced pressure. Thin layer chromatography and ^{1}H NMR showed the presence of only allylic hydroperoxide (H-ene) and not the 1,2-dioxolane. The residue was dissolved in THF (20 mL) and cooled to −78 °C, whereupon lithium aluminium hydride (10.5 mg, 0.27 mmol) was added. The reaction was allowed to warm to 0 °C and stirred for 1 h before quenching with sat. $NaHCO_3$ (20 mL). The organic layer was removed and the aqueous layer was extracted with ethyl acetate (1 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The concentrate was purified by flash chromatography to yield 98 mg (86%) of **45**: $R_f = 0.6$ (10% EA–hex); ^{1}H NMR (300 MHz) δ 5.5 (s, 1H, $^3J_{Sn-H} = 94$), 4.83 (s, 2H), 3.35 (s, 3H), 1.55 (br s, 1H), 1.5 (m, 8H), 1.28 (m, 12H), 1.23 (s, 3H), 0.88 (m, 9H), 0.86 (t, 9H, $J = 7.3$); ^{13}C NMR (75 MHz) δ 163.3, 123.6, 94.3, 73.0, 55.5, 44.8, 32.9, 30.9, 29.2, 27.4, 23.7, 22.6, 13.9, 13.7, 12.1; IR 3469, 2958, 2871, 1463 cm^{-1}. Anal. Calcd. for $C_{23}H_{48}O_3Sn$: C, 56.22; H, 9.84. Found C, 56.2; H, 10.04%.

(2*E*)-1-Tributyl(hex-2-enyl)stannane (46). A solution of (*E*)-hex-2-en-1-ol (1.70 g, 17.0 mmol) in ether (70 mL) was cooled to 0 °C. Triethylamine (1.89 g, 18.7 mmol) was added and the mixture was stirred for 15 min. Slow addition of methanesulfonyl chloride (2.14 g, 18.7 mmol) produced a white slurry, which was allowed to warm to room temperature and quenched after 2 h by the addition of water. The organic layer was diluted with 50% EA–hex (50 mL) and washed twice with water (30 mL). The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure to yield 2.62 g of crude mesylate (86%).

Diisopropylamine was diluted in THF (70 mL) and cooled to −78 °C. A solution of *n*-BuLi (9.71 mL, nominally 2.1 M solution in hexane) was added and the mixture was allowed to warm to 0 °C. After 20 min tributyltin hydride (0.36 g, 12.5 mmol) was added dropwise and the resulting solution stirred at 0 °C for 20 min. A solution of the mesylate in THF (30 mL) was slowly added *via* a cannula to the reaction. The mixture was allowed to reach room temperature and stirred for 18 h. The reaction was quenched with a saturated solution of ammonium chloride and extracted with 5% EA–hex. The combined organic layers were dried with $MgSO_4$, filtered through Celite and concentrated under reduced pressure. The concentrate was purified by column chromatography (100% hex) to yield 1.35 g (69%) of allylstannane **46**: $R_f = 0.71$ (hex); ^{1}H NMR (500 MHz) δ 5.27 (dt, 1H, $J = 14.9$, 8.5), 5.22 (dt, 1H, $J = 14.9$, 5.6), 1.93 (apparent q, 2H, $J = 7.8$), 1.69 (d, 2H, $J = 8.1$), 1.52–1.47 (m, 6H), 1.37–1.27 (m, 14H), 0.91–0.84 (m, 18H); ^{13}C NMR (125 MHz) δ 129.1, 125.8, 34.9, 29.3, 27.4, 23.3, 14.2, 13.7, 10.0, 9.2; IR 2842, 1486 cm^{-1}.

(1*Z*)-3-Hydroperoxy-1-tributylstannylhex-1-ene (47) and (3-propyl-1,2-dioxolan-4-yl)tributylstannane (48). Oxygenation of allylstannane **45** (3.41 g, 9.14 mmol) in TPP–CCl_4 (100 mL) under standard conditions was complete by TLC in 75 min. The reaction mixture was concentrated and directly subjected to flash chromatography (20% EA–hex) to yield 440 mg (12%) of dioxolane **48** and 1.35 g (36%) of hydroperoxide **47**: $R_f = 0.60$ in (20% EA–hex); ^{1}H NMR (500 MHz) δ 7.63 (s, 1H), 6.41 (dd, 1H, $J = 12.9$, 8.5, $^2J_{Sn-H} = 60$) 6.23 (d, 1H, $J = 12.9$), 4.17–4.14 (m, 1H), 1.72–1.58 (m, 2H), 1.53–1.28 (m, 14H), 0.96–0.87 (m, 18H); ^{13}C NMR (125 MHz) δ 146.7, 136.0, 88.8, 35.0, 29.1, 27.3, 18.6, 14.2, 13.6, 10.6; IR 3400, 2959, 2924, 2841, 1464 cm^{-1}.

Compound **48**: $R_f = 0.63$ (5% EA–hex); ^{1}H NMR (300 MHz) δ 4.29 (dd, 1H, $J = 7.6$, 6.4), 4.13 (td, 1H, $J = 10.0$, 7.2, 4.3), 3.93 (dd, 1H, $J = 11.2$, 7.2), 2.11–1.94 (m, 1H), 1.6–1.25 (m, 14H), 0.95–0.86 (m, 18H); ^{13}C NMR (125 MHz) δ 84.1, 74.1, 38.7, 36.0, 29.1, 27.4, 20.1, 14.1, 13.6, 8.6; IR 2964, 2934, 1465 cm^{-1}.

(1*Z*)-[3-(Methoxy-1-methylethyl)peroxyhex-1-enyl]tributylstannane (49). To a solution of **47** (1.76 g, 4.34 mmol) in CH_2Cl_2 (50 mL) was added 2-methoxypropene (0.31g, 4.34 mmol) and pyridinium toluene-*p*-sulfonate (0.10 g, 0.40 mmol). After 45 min the reaction was washed with water and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography to yield 1.95 g (94%) of peroxyketal **49**: $R_f = 0.75$ (20% EA–hex); ^{1}H NMR (500 MHz) δ 6.47 (dd, 1H, $J = 12.9$, 8.9, $^3J_{Sn-H} = 62$), 6.06 (d, 1H, $J = 12.9$), 4.17–4.12 (m, 1H), 3.16 (s, 3H), 1.49–1.48 (m, 2H), 1.39 (s, 3H), 1.33 (s, 3H), 1.32–1.28 (m, 14H), 0.95–0.87 (m, 18H); ^{13}C NMR (125 MHz) δ 148.9, 131.4, 104.2, 86.8, 49.2, 35.8, 29.1, 27.4, 23.1, 22.7, 18.9, 14.2, 13.7, 10.5; IR 2956, 2852, 1463 cm^{-1}. Anal. Calcd. for $C_{22}H_{46}O_3Sn$: C, 55.36; H, 9.71. Found C, 55.37; H, 9.85%.

(1*Z*)-3-[(1-Methoxy-1-methylethyl)peroxy]-1-tributylstannyl-1-acetoxyhex-1-ene (50). By a similar procedure as **49** compound **43** (1.23 g, 2.65 mmol) was converted to 837 mg (59%) of

50: R_f = 0.46 (10% EA–hex); ^{1}H NMR (500 MHz) δ 5.85 (d, 1H, J = 10.1, $^3J_{Sn-H}$ = 71.3), 4.32–4.28 (m, 1H), 3.28 (s, 3H), 2.10 (s, 3H), 1.55–1.45 (m, 2H), 1.39–1.25 (m, 22H), 1.39 (s, 3H), 1.34 (s, 3H), 1.02–0.98 (t, 3H), 0.93–0.88 (m, 18H); ^{13}C NMR (125 MHz) δ 194.8, 162.0, 132.0, 105.0, 80.8, 49.1, 36.3, 28.8, 27.3, 23.0, 22.8, 20.7, 18.9, 14.1, 13.6, 11.8; IR 2931, 1733, 1463 cm^{-1}. Anal. calcd. For $C_{24}H_{48}O_5Sn$: C, 53.85; H, 9.04. Found C, 54.26; H, 9.17%.

(1*Z*)-1-Iodo-3-[(1-methoxy-1-methylethyl)peroxy]hex-1-ene (51). To a −78 °C solution of **49** (0.16 g, 0.34 mmol) in THF (1.5 mL) was added a solution of *N*-iodosuccinimide (120 mg, 0.54 mmol) in THF (3.0 mL). After 90 min the reaction was concentrated and the residue was purified by flash chromatography (5% EA–hex) to yield 1.02 g (97%) of iodide **51**: R_f = 0.44 (5% EA–hex); ^{1}H NMR (500 MHz) δ 6.38 (d, J = 7.7), 6.30 (apparent t, J = 7.7, 1H), 4.74–4.70 (m, 1H), 3.30 (s, 3H), 1.63–1.60 (m, 2H), 1.47–1.40 (m, 3H), 1.39 (s, 3H), 1.37 (s, 3H), 0.93 (t, 3H, J = 7.3); ^{13}C NMR (125 MHz) δ 141.6, 104.9, 85.6, 82.9, 49.4, 34.0, 23.0, 22.7, 18.5, 14.0; IR 2992, 2874, 2830, 1613 cm^{-1}. Anal. Calcd. for $C_{10}H_{19}O_3I$: C, 38.23; H, 6.10. Found C, 38.82; H, 6.28%.

(1*E*/*Z*)-1-Acetoxy-1-iodo-3-[(1-methoxy-1-methylethyl)-peroxy]hex-1-ene (52). To a solution of **50** (62 mg, 0.120 mmol) in THF (3 mL) at −78 °C was slowly added *N*-iodosuccinimide (26 mg, 120 mmol) in THF (3 ml), whereupon the solution took on a yellow color. The reaction was monitored by TLC (5% EA–hex) and was concentrated after 22 h. The residue was purified by flash chromatography (5% EA–hex) to give 39 mg (90%) of **52** as a mixture of (*E*,*Z*) isomers: R_f = 0.27 (5% EA–hex); ^{1}H NMR (500 MHz) δ 5.86 (d, 1H, J = 8.9), 5.62–5.60 (d, 1H, J = 8.5), 3.32 (s, 3H), 3.30 (s, 3H), 4.6 (m, 1H), 4.5 (m, 1H), 2.16 (s, 3H), 1.71–1.63 (m, 2H), 1.55–1.40 (m, 2H), 1.39 (s, 3H), 1.36 (s, 3H), 0.97–0.98 (t, 3H, J = 7.3); ^{13}C NMR (125 MHz) δ 136.0, 129.9, 84.4, 78.9, 49.42, 34.5, 23.0, 22.9, 22.8, 21.2, 18.4, 14.0; IR 2956, 1779, 1369, 1209 cm^{-1}. Anal. Calcd. for $C_{12}H_{21}O_5I$: C, 38.77; H, 5.69. Found C, 38.51; H, 5.88%.

(1*E*)-Acetoxy-3-[(1-methoxy-1-methylethyl)peroxy]hex-1-ene (53). To a solution of compound **30** (39 mg, 0.11 mmol) and tributyltin hydride (92 mg, 0.32 mmol) in benzene (10 mL) was added AIBN (10 mg). The mixture was heated to 80 °C for 2 h. The mixture was cooled to room temperature and the contents were concentrated under vacuum. The residue was purified by flash chromatography (5% EA–hex) to yield 8 mg (30%) of **53**: R_f = 0.38 (5% EA–hex); ^{1}H NMR (360 MHz) δ 7.32 (d, 1H, J = 12.5), 5.40 (dd, 1H, J = 12.5, 8.9), 4.35 (dt, 1H, J = 8.7, 6.9), 3.24 (s, 3H), 2.11 (s, 3H), 2.70–2.55 (m, 2H), 1.47–1.32 (m, 2H), 0.92–0.87 (t, 3H, J = 6.9); ^{13}C NMR (125 MHz) δ 138.2, 135.7, 114.3, 80.8, 50.0, 35.3, 27.8, 18.6, 18.5, 17.5, 13.5; IR 2960, 1762, 1675, 1464, 1370 cm^{-1}. Anal. Calcd. for $C_{12}H_{22}O_5$: C, 58.52; H, 9.00. Found C, 59.58; H, 9.22%.

(2*Z*)-4-[(1-Methoxy-1-methylethyl)peroxy]-1-phenylhept-2-enone (54). Benzoyl chloride (77 mg, 0.55 mmol), Pd_2dba_3-$CHCl_3$ (27 mg, 0.026 mmol), and tri(2-furyl)phosphine (12 mg, 0.052 mmol) were dissolved in THF (5 mL) and stirred for 10 min, after which was added stannane **49** (215 mg, 0.45 mmol). After 4 hours, ether (50 mL) was added and the organic layer was washed with 10% NH_4OH. The organic layer was removed and the aqueous layer was extracted with ether–hex. The combined organic layers were dried with $MgSO_4$, filtered and concentrated. The concentrate was purified by flash chromatography (5% EA–hex) to yield 91 mg (69%) of peroxyenone **54**: R_f = 0.21 (5% EA–hex); ^{1}H NMR (300 MHz) δ 7.93 (d, 2H, J = 7.3), 7.54 (apparent t, 1H, J = 7.3), 7.47 (apparent t, 2H, J = 7.7), 6.91 (d, 1H, J = 11.7), 6.43 (dd, 1H, J = 11.7, 8.1), 5.44 (td, 1H, J = 8.1, 4.8), 3.29 (s, 3H), 1.66–1.5 (m, 4H), 1.32 (d, 6H, J = 5.2), 0.95 (t, 2H, J = 7.3); ^{13}C NMR (75 MHz) δ 191.3, 150.4, 138.0, 132.9, 128.6, 128.4, 124.4, 104.8, 80.8, 49.2, 34.5, 23.0, 22.6, 18.9, 14.0; IR 2998, 1673, 1622, 1582, 1234, 1074 cm^{-1}. HRMS (M + Li) calcd 299.1834, found 299.1841.

(5*Z*,8*E*)-4-[(1-Methoxy-1-methylethyl)peroxy]-9-phenyl-nona-5,8-diene (55). Cinnamyl bromide (40 mg, 0.22 mmol), $Pd_2(dba)_3CHCl_3$ (15 mg, 0.011 mmol), and tri(2-furyl)phosphine (5 mg, 0.022 mmol) were dissolved in THF (5 mL) and stirred for 10 min, after which was added **49** (196 mg, 0.42 mmol). The mixture was heated to 60 °C for 6 h and then cooled to room temperature. Ether (50 mL) was added and the organic layer was washed with 10% NH_4OH. The organic layer was removed and the aqueous layer was extracted with ether–hex. The combined organic layers were dried with $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (5% EA–hex) to yield 37 mg (55%) of peroxydiene **55**: R_f = 0.52 (5% EA–hex); ^{1}H NMR (300 MHz) δ 7.34–7.16 (m, 5H), 6.41 (d, 1H, J = 15.7), 6.19 (dt, 1H, J = 16.0, 6.4), 5.7 (dt, 1H, J = 11.0, 7.4), 5.48 (dd, 1H, J = 9.3, 10.7), 4.80 (m, 1H), 3.30 (s, 3H), 3.00 (apparent q, 2H, J = 6.4, 7.4), 1.71–1.33 (m, 10H), 0.92 (t, 3H, J = 7.4); ^{13}C NMR (75 MHz) δ 137.5, 131.0, 130.6, 128.5, 127.0, 126.0, 104.5, 78.9, 49.2, 35.2, 31.2, 23.0, 22.9, 18.6, 14.1; IR 2994, 2875, 1496 cm^{-1}.

(3*Z*)-5-[(1-Methoxy-1-methylethyl)peroxy]octa-1,3-diene (56). A solution of **51** (195 mg, 0.62 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.10 mmol) and vinyltributyltin (317 mg, 1.0 mmol) in THF (10 mL) was heated to 45 °C for 16 h. The reaction was allowed to cool, ether (75 mL) was added and the organic layer was washed with 10% NH_4OH. The organic layer was dried with $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography to yield 102 mg (77%) of diene **56** as an inseparable 9 : 1 *Z*/*E* mixture: R_f = 0.50 (5% EA–hex); ^{1}H NMR (500 MHz) δ 6.67 (dt, 1H, J = 16.9, 11.3), 6.13 (apparent t, 1H, J = 11.3), 5.42 (apparent t, 1H, J = 9.7), 5.23 (d, 1H, J = 16.9), 5.15 (d, 1H, J = 10.1), 4.88 (m, 1H), 3.28 (s, 3H), 1.67–1.38 (m, 10H), 0.9 (t, 3H, J = 7.3) (major isomer); ^{13}C NMR (125 MHz) δ 132.1, 131.9, 131.8, 118.9, 104.6, 79.2, 49.2, 35.3, 22.97, 22.78, 18.6, 14.0 (major isomer); IR 2993, 1598, 1463 cm^{-1}.

Methyl (2*Z*,4*E*)- and (2*E*,4*E*)-6-[(1-methoxy-1-methylethyl)-peroxy]nona-2,4-dienoate (57) and methyl (2*Z*,4*E*) and (2*E*, 4*E*)-6-oxonona-2,4-dienoate (58). To a solution of **51** (163 mg, 0.52 mmol) in methyl acrylate (4 mL) was added a solution of K_2CO_3 (165 mg, 1.20 mmol), *n*-Bu_4NBr (258 mg, 0.80 mmol) and $Pd(OAc)_2$ (18 mg, 0.08 mmol) in methyl acrylate (6 mL). The mixture was stirred at room temperature for 6 h. The reaction mixture was diluted with ether (100 mL) and filtered though a pad of Celite. The filtrate was concentrated and purified by flash chromatography (5% EA–hex) to yield 21 mg (22%) of oxodienoate **58** as a 3.5 : 1 *E*,*E* and *Z*,*E* mixture followed by 65 mg (46%) of peroxydienoate **57** as a 5.8 : 1 2*Z*, 4*E*/2*E*, 4*E* mixture:

Compound **57**: R_f = 0.21 (5% EA–hex); ^{1}H NMR (300 MHz) δ 7.60 (dd, 0.85H, J = 15.3, 11.9), 7.25 (dd, 0.15H, J = 11.0, 15.5), 6.31 (dd, 0.15H, J = 15.5, 11.0), 6.23 (t, 0.85H, J = 11.2), 6.06 (dd, 0.15H, J = 7.15, 15.3), 5.89 (d, 0.85H, J = 15.3), 5.87 (d, 0.15H, J = 15.3), 5.78 (t, 0.85H, J = 10.02), 4.94 (apparent q, 0.85H, J = 6.2), 4.45 (apparent q, 0.15H, J = 7.15), 3.72 (s, 2.55H), 3.71 (s, 0.45H), 3.25 (s, 2.55H), 3.24 (s, 0.45H), 1.67–1.29 (m, 10H), 0.89 (t, 3H, J = 7.16); ^{13}C NMR (75 MHz) δ 167.2, 140.0, 139.1, 128.5, 122.5, 104.7, 79.0, 51.5, 49.2, 35.1, 22.8, 22.7, 18.5, 13.9 (major isomer); IR 2992, 2875, 1724, 1646, 1610 cm^{-1}. HRMS *m*/*z* calcd 295.1521, found 295.1530.

Compound **58**: R_f = 0.22 (5% EA–hex); ^{1}H NMR (300 MHz) δ 8.28 (dd, 0.22H, J = 15.7, 11.3), 7.30 (dd, 0.78H, J = 15.3, 11.3), 7.16 (dd, 0.78H, J = 15.7, 11.3), 6.45 (apparent t, 0.22H, J = 11.3), 6.42 (d, 0.78H, J = 15.3), 6.26 (d, 0.22H, J = 11.3), 6.21 (d, 0.78H, J = 15.3), 6.07 (d, 0.22H, J = 15.3), 3.76 (s,

2.34H), 3.75 (s, 0.66H), 2.56, (t, 1.56, $J = 7.2$), 2.49 (t, 0.44H, $J = 7.2$), 1.65 (m, 2H), 0.93 (t, 3H, $J = 7.4$); ^{13}C NMR (75 MHz) δ 200.0, 166.2, 141.6, 138.0, 135.5, 128.3, 51.9, 43.1, 17.4, 13.7 (major); IR 2954, 1708, 1687, 1591 cm^{-1}.

Methyl (2*Z*)-4-[(1-methoxy-1-methylethyl)peroxy]hept-2-enoate (59). A solution of **51** (195 mg, 0.62 mmol), $Pd(OAc)_2$ (14 mg, 0.062 mmol), triphenylphosphine (33 mg, 0.12 mmol) and triethylamine (0.17 mL, 1.24 mmol) in 20 mL of a 2.3 : 1 mixture of DMF–MeOH was placed under a balloon of carbon monoxide and purged twice. The contents were heated to 60 °C for 3 h. After cooling, water was added and the mixture was extracted with ether–hex. The organic layer was dried with $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (5% EA–hex) to yield 57 mg (37%) of enoate **59**: $R_f = 0.39$ (5% EA–hex); ^{1}H NMR (500 MHz) δ 6.34 (dd, 1H, $J = 11.7$, 8.1), 5.83 (dd, 1H, $J = 11.7$, 1.2), 5.57 (td, $J = 2.4$, 8.1), 3.70 (s, 3H), 3.26 (s, 3H), 1.65–1.4 (m, 4H), 1.38 (s, 6H), 0.92 (t, 3H, $J = 7.25$); ^{13}C NMR (125 MHz) δ 166.2, 151.6, 119.6, 104.8, 79.9, 51.2, 49.2, 34.6, 23.0, 22.7, 18.7, 13.9; IR 2997, 2878, 1727, 1652 cm^{-1}.

(5*Z*)-4-Hydroxytetradec-5-en-7-yne (60). To a solution of **51** (200 mg, 0.64 mmol) and $Pd(PPh_3)_4$ (74 mg, 0.064 mmol) in dry benzene (5 mL) was added copper iodide (24 mg, 0.014 mmol), *n*-butylamine (47 mg, 0.64 mmol), and oct-1-yne (72 mg, 0.65 mmol). The reaction was stirred for 10 h at room temperature. The reaction was quenched with NH_4Cl and extracted with ether. The organic phase was dried with $MgSO_4$, filtered and concentrated. The concentrate was purified by flash chromatography to yield 42 mg (49%) of enynol **60:** $R_f = 0.51$ (5% EA–hex); ^{1}H NMR (500 MHz) δ 5.79 (dd, 1H, $J = 10.7$, 8.1), 5.51 (d, 1H, $J = 11.0$), 4.64 (apparent q, 1H, $J = 6.5$), 2.31 (td, 2H, $J = 6.7$, 1.9), 1.86 (s, 1H), 1.59–1.26 (m, 12H), 0.95–0.85 (m, 6H); ^{13}C NMR (125 MHz) δ 143.9, 110.4, 96.2, 76.4, 69.8, 38.7, 31.3, 28.6, 28.5, 22.5, 19.5, 18.4, 14.0, 13.9; IR 3352, 3028, 2939, 2877, 2219 cm^{-1}.

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