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Cascading Radical Cyclization of Bis-Vinyl Ethers: Mechanistic Investigation Reveals a 5-*exo*/3-*exo*/retro-3-*exo*/5-*exo* Pathway

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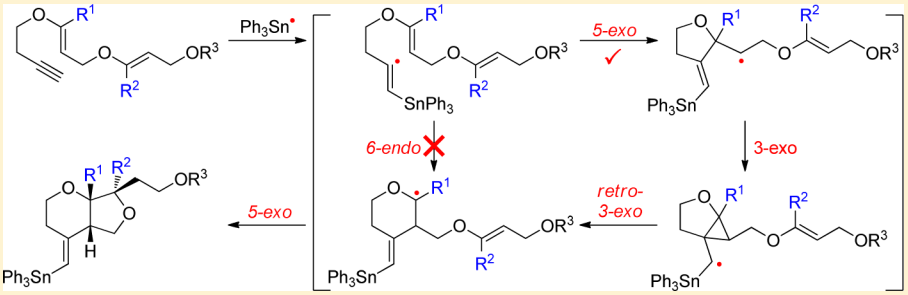
Supporting Information



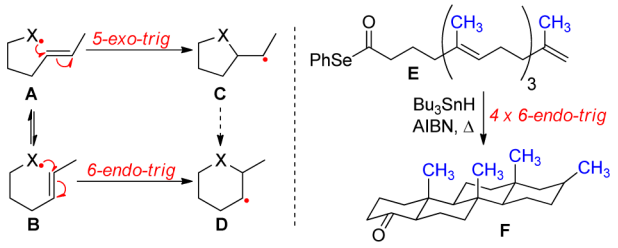
ABSTRACT: We recently described an iterative synthesis of oligo-vinyl ethers, followed by a radical cascade to provide a family of hexahydro-2*H*-furo[3,4-*b*]pyrans. Our results for the radical cascade were consistent with either a direct 6-*endo*-*trig* addition of a vinyl radical onto the first vinyl ether function or an initial 5-*exo*-*trig* addition, followed by rearrangement to the more stable anomeric radical intermediate. In this report, we describe our further mechanistic studies aimed at distinguishing between these two possibilities and conclude that the 5-*exo*/3-*exo*/retro-3-*exo* pathway is dominant.

INTRODUCTION

Reactive centers (anions, cations, or radicals) tethered three atoms away from an alkene acceptor (e.g., an electrophilic alkene to react with an anion, a nucleophilic alkene to react with a cation, or an accessible π system to react with a radical) can engage in either a 5-*exo*-*trig* or 6-*endo*-*trig* cyclization. Both of these reaction trajectories are considered "favored" according to Baldwin's rules (originally intended to describe reactions with anions but now loosely taken as a general guideline for planning all types of cyclizations),[1] although the 5-*exo* process is typically the faster of the two.[2]

Particularly for intramolecular radical additions to alkenes, pioneering work by Beckwith and others showed that the rates of 5-*exo*-*trig* reactions (**A** → **C**, Scheme 1) are usually much faster than the corresponding 6-*endo*-*trig* reactions (**B** → **D**), except in cases where the 5-position is more sterically encumbered.[3] In these cases, the 6-*endo*-*trig* cyclization may predominate. This reversal of regioselectivity in radical cyclizations has been harnessed by several groups in the synthesis of six-membered rings but is particularly notable in the work of Pattenden and co-workers, who developed a series of cascading 6-*endo*-*trig* cyclizations to access steroidlike carbon skeletons (and related structural frameworks) from acyclic precursors (e.g., **E** → **F**, Scheme 1).[4]

Scheme 1. Comparison of 5-*exo*-*trig* and 6-*endo*-*trig* Radical Cyclizations



Interestingly, some apparent 6-*endo*-*trig* radical cyclizations have been revealed upon further study to result from initial 5-*exo*-*trig* cyclizations, followed by rearrangement of the intermediate radical (i.e., **C** → **D**, Scheme 1).[5] This type of rearrangement can occur when the initially reacting radical center (X in Scheme 1) can itself act as a transient radical acceptor. In such cases, intermediate **C** can be converted to intermediate **D** through a 3-*exo*/retro-3-*exo* pathway.[6] Such rearrangements are particularly common when X is part of an aromatic ring, in which case the overall transformation is referred to as a neophyl rearrangement.[5a,d,e,g,h]

On the other hand, many 6-*endo*-*trig* cyclizations—particularly those in which the 5-position is fully substituted, as in the Pattenden examples noted above—have been found to result from direct 6-*endo* cyclization and to not involve any intermediate addition/rearrangement steps.[4,5d,7] Clearly, careful experimentation is required to differentiate between these two mechanistic possibilities.

We recently described an iterative synthesis of oligo-vinyl ethers (e.g., **2**, Scheme 2) from simple alcohol building blocks

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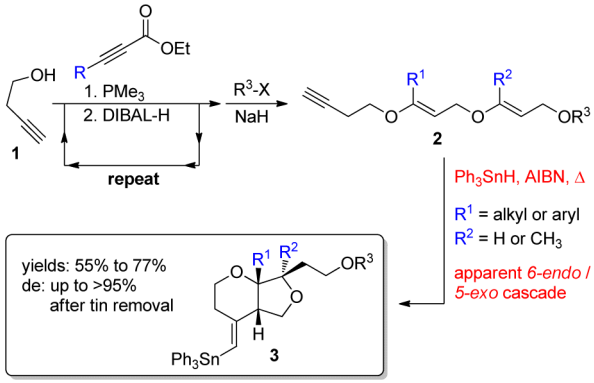
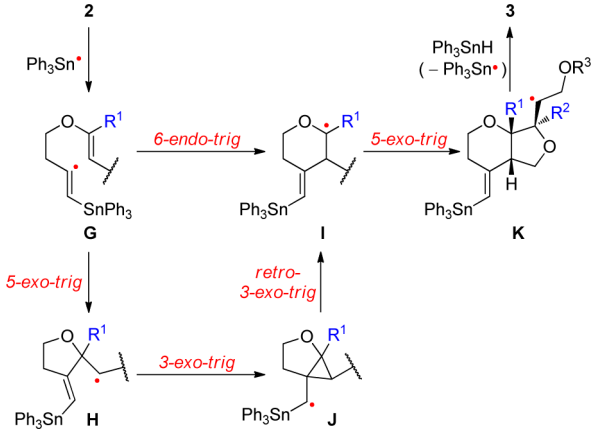
Scheme 2. Iterative Synthesis of Vinyl Ethers and Radical Cascade Reaction



(e.g., **1**) and proposed that chemo-orthogonal cascade reactions across these structures could provide an efficient means to access variously functionalized complex molecules.[8] As a proof of principle for this approach, we reported a cascading 6-*endo*/5-*exo* radical cascade across a selection of bis-vinyl ethers, to afford a series of hexahydro-2*H*-furo[3,4-*b*]pyrans (**3**). To the best of our knowledge, this was the first report of a radical cascade in a bis-vinyl ether system.

In discussing the likely mechanism for the cascade reaction,[8] we noted that we could not conclusively distinguish between a direct 6-*endo*-*trig* cyclization (i.e., **G** → **I**, Scheme 3) and the

Scheme 3. Two Mechanistic Possibilities for Closure of the Six-Membered Ring

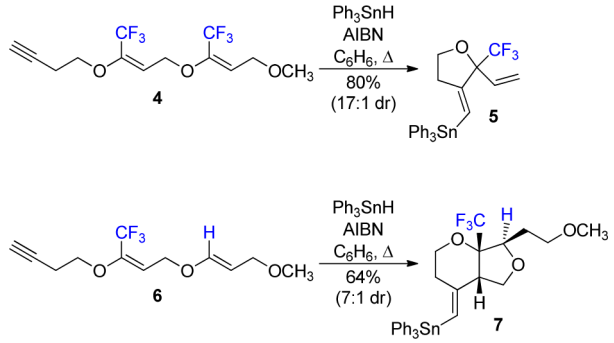


corresponding 5-*exo*/3-*exo*/retro-3-*exo* pathway (i.e., **G** → **H** → **J** → **I**) to close the first ring[9] and promised additional mechanistic studies to resolve this question. In the present report, we describe the results of these mechanistic studies, which confirm the involvement of an initial 5-*exo*-*trig* addition to the first vinyl ether moiety. Understanding the origins of the regiochemical control in this unusual radical cascade will ultimately permit other types of bicycles (and higher order systems) to be accessed from iteratively synthesized precursors.[10]

RESULTS AND DISCUSSION

Our first indication that the 5-*exo*/3-*exo*/retro-3-*exo* pathway might be operative came with an attempt to extend our cyclization methodology toward the preparation of trifluoromethyl-substituted bicycles.[11] As shown in Scheme 4,

Scheme 4. Divergent Reactivity with Trifluoromethyl-Substituted Vinyl Ethers



exposure of the bis-trifluoromethyl-substituted vinyl ether **4** to a source of tin radicals resulted not in the expected 6-*endo*/5-*exo* cascade but in the generation of compound **5** as the sole isolable product.

Compound **5** appeared to result from a 5-*exo*-*trig* cyclization, followed by β-scission. In contrast, bis-vinyl ether **6**, containing a single trifluoromethyl substituent, cyclized to give the usual bicyclic system in good yield. The first vinyl ether group to participate in a radical cyclization reaction is the same for compounds **4** and **6**, and it seemed unlikely that a change in substituents on the *second* vinyl ether could trigger a change in regioselectivity of the initial radical cyclization. A far more likely explanation for the divergent reactivity is that both **4** and **6** reacted through an initial 5-*exo* attack but that the presence of the second trifluoromethyl substituent in compound **4** favored a fast β-scission, essentially trapping intermediate **H** (Scheme 3) before it had a chance to rearrange to the apparent 6-*endo* intermediate **I**.

This single experiment is compelling evidence in favor of a 5-*exo*/3-*exo*/retro-3-*exo* process, but we recognized the possibility that the reactivity displayed by trifluoromethyl-substituted compounds **4** and **6** may not be representative of reactivity in simpler alkyl-substituted vinyl ethers. We therefore sought to install cyclopropane groups into our structures as probes[12] for the presence of radical character at both the 5- and 6-positions (relative to the approaching radical) throughout the cyclization of the six-membered ring.

In designing these reactivity probes, we recognized that building the cyclopropane substituents into bis-vinyl ether substrates was unnecessary, since our early optimization studies had shown that even mono-vinyl ethers (e.g., **8**, Scheme 5) cyclized to give exclusively the six-membered-ring product (e.g., **9**), so long as the vinyl ether function contained an additional substituent on the oxygen-bearing carbon and was not conjugated to an electron-withdrawing function. Less-substituted vinyl ethers (e.g., **10**), as well as those conjugated to esters (e.g., **13**) cyclized to give mixtures of five- and six-membered-ring products. Combining these two structural features, we found that less-substituted vinyl ethers that also contained an electron-withdrawing group (e.g., **16**) cyclized to give exclusively the five-membered-ring product.

Therefore, to test the hypothesis that all of these vinyl ether substrates (**2**, **4**, **6**, **8**, **10**, **13**, and **16**) cyclized through a conserved initial 5-*exo*-*trig* addition, we targeted cyclopropanes **21** and **32** (Schemes 6–8) as mechanistic probes.

Compound **21**, incorporating a cyclopropane substituent on the oxygen-bearing carbon of the vinyl ether function, was accessed by conjugate addition of butynol **1** to the known

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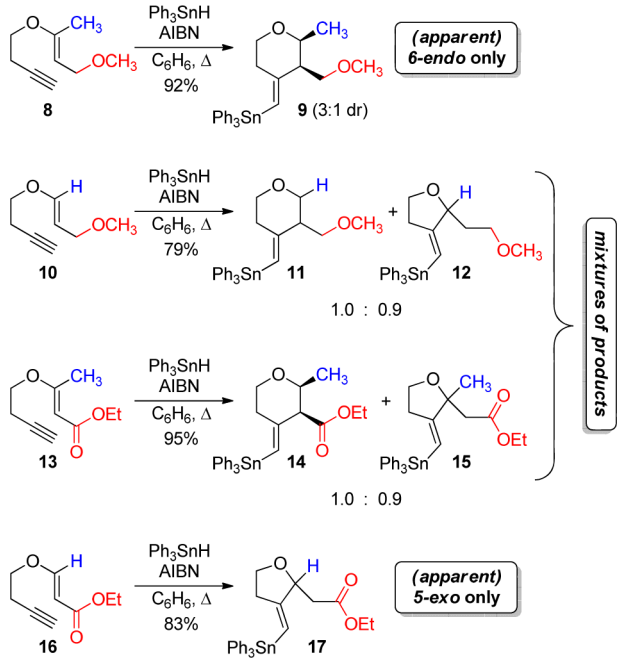
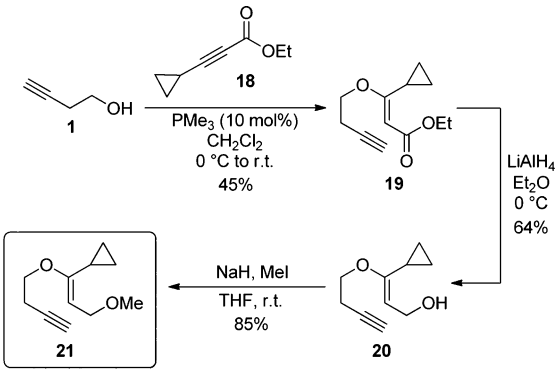
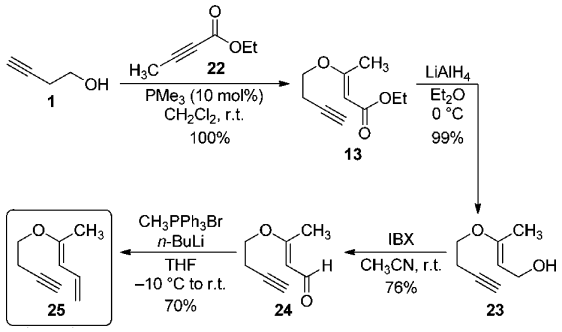
Scheme 5. Cyclizations of Mono-Vinyl Ethers: Substitution Dictates Regioselectivity



Scheme 6. Synthesis of Cyclopropane 21

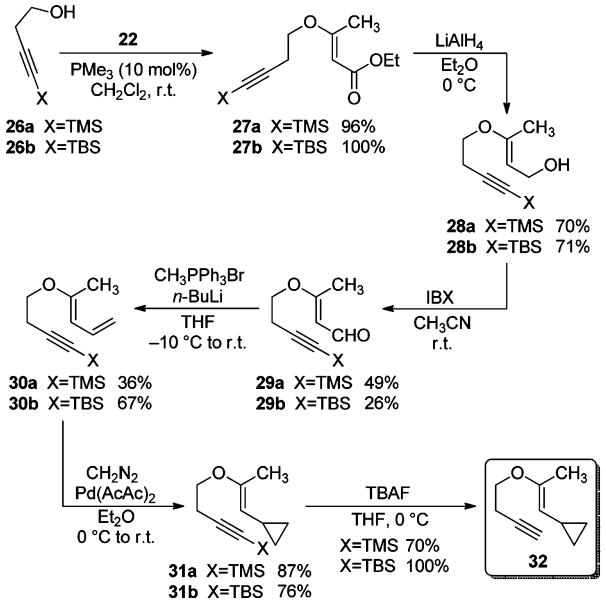


Scheme 7. Synthesis of Diene 25



cyclopropane-containing propynoate **18**,[13] followed by reduction and methylation (Scheme 6). The unexpectedly low yield for the addition step was attributed to the instability of both the reactant (**18**) and the product (**19**). The reduction product (**20**) proved even more unstable, such that we were unable to access it under our usual DIBAL reduction conditions, which require >2 h to proceed to completion. Switching to a more reactive reducing agent ($LiAlH_4$) allowed us to access the

Scheme 8. Synthesis of Cyclopropane 32



unstable alcohol **20** and subject it to methylation conditions before it was able to decompose.

Compound **32**, incorporating a cyclopropane on the non-oxygen-bearing carbon of the vinyl ether function, proved more challenging to synthesize. Inspired by literature precedent showing the selective cyclopropanation of dienyl ethers,[14] we initially hoped to access **32** through a carefully controlled cyclopropanation of diene **25** (Scheme 7). This substrate was prepared by conjugate addition and reduction to access the known alcohol **23**,[8] followed by oxidation with IBX and subsequent olefination.

Unfortunately, we were unable to drive the cyclopropanation of **25** to completion without causing extensive decomposition of the substrate. Control experiments with dienyl ethers lacking alkynes (not shown) were more successful, suggesting that the problem lay in cross-reactivity of the cyclopropanating reagents (several of which were tried in the hopes of exploiting **25**) with the terminal alkyne.

We therefore sought to protect the alkyne throughout the cyclopropanation step. Silyl-protected alkynes **26a,b** were prepared following literature protocols[15] and were subjected to a conjugate addition/reduction sequence (Scheme 8) to afford alcohols **28a,b** in good yield, with no evident migration of the silyl substituents onto the primary alcohol. Oxidation and olefination proceeded in poor yield, but the diene substrates (**30a,b**) could nonetheless be obtained in sufficient quantity to permit evaluation of the cyclopropanation step.

We were pleased to find that both **30a,b** were much better substrates for the cyclopropanation than was unprotected alkyne **25**. Treatment with an excess of freshly generated diazomethane, in the presence of a palladium(II) acetylacetonate catalyst,[16] resulted in good conversion to the corresponding cyclopropane, without inducing decomposition. Finally, both silyl protecting groups could be removed by treatment with a fluoride source, affording **32** (contaminated with a small quantity of **25**, owing to incomplete conversion in the cyclopropanation step) for use in radical cyclization experiments.

As expected, cyclization of compound **21** yielded exclusively the cyclopropane-opened pyran derivative **33** (Scheme 9),

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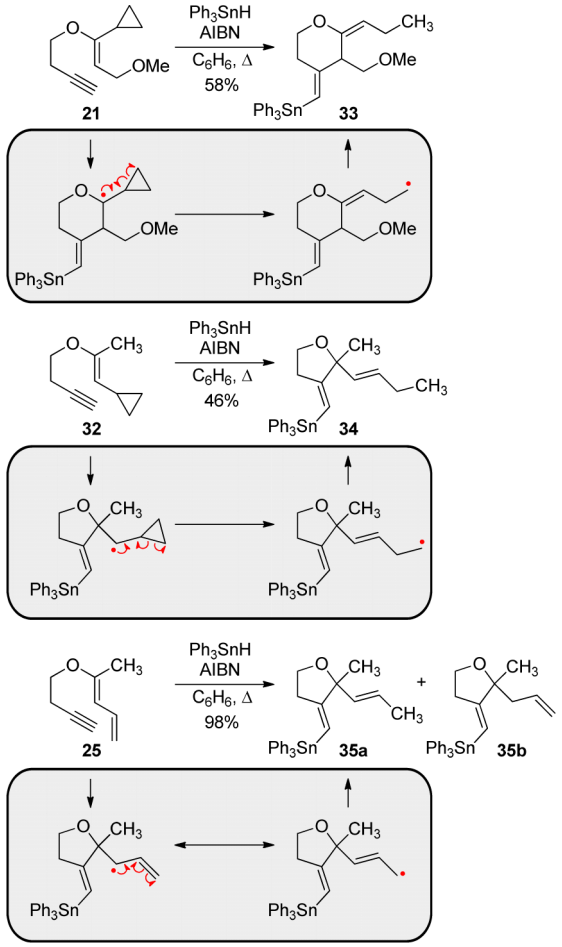
Scheme 9. Probing for the Location of Radical Character during the Cyclization



confirming that the radical character is maintained throughout the cyclization and that the initial vinyl radical resulting from tin addition to the alkyne (**G**, Scheme 3) does not participate in any single-electron-oxidation or -reduction processes prior to cyclization. Although intermediate anions or cations might lead to similar cyclization products, these would not be expected to trigger opening of the cyclopropane in this manner.

Gratifyingly, compound **32** cyclized to provide exclusively the cyclopropane-opened furan derivative **34**, lending considerable support to the hypothesis that 5-*exo*-*trig* cyclization is the initial step in the overall cyclization mechanism leading to bicycle **3**.

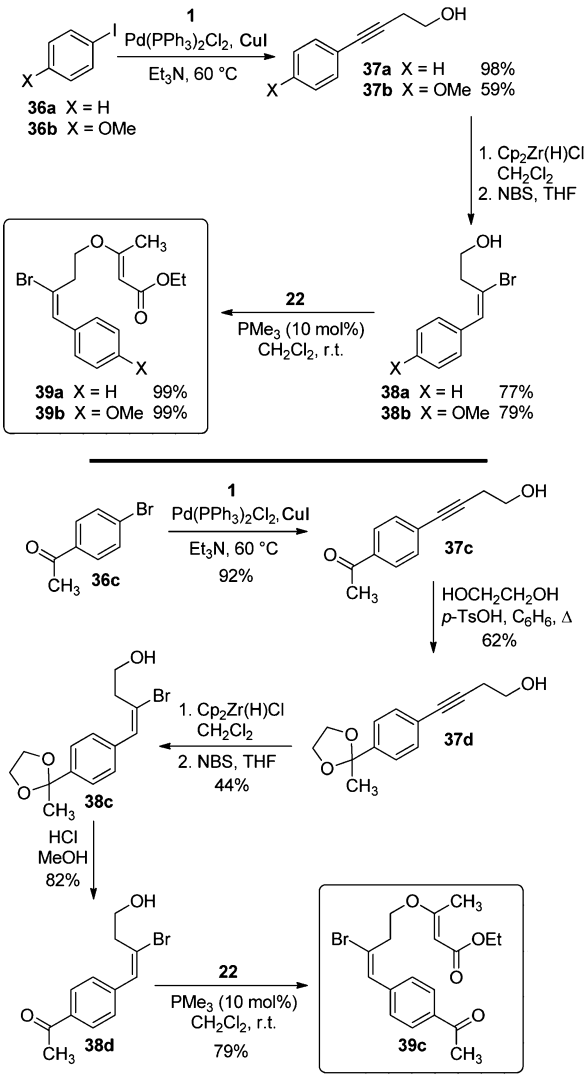
Somewhat surprisingly, even diene **25** cyclized to give only the five-membered-ring products **35a,b** in a 4/1 ratio, lending additional support to this hypothesis. Isomers **35a,b** were not separable by column chromatography, but treatment with $PdCl_2(MeCN)_2$ in refluxing benzene isomerized the terminal olefin in **35b**, affording a clean sample of **35a** for characterization purposes.

The results in Scheme 9 are compelling, but we could not ignore the possibility (however unlikely) that the apparent 5-*exo*-*trig*/*β*-scission products **5**, **34**, and **35** could in fact arise throught initial 6-*endo*-*trig* cyclization, followed by isomerization to the apparent 5-*exo* intermediate and subsequent fragmentation—essentially the exact opposite of our proposed mechanistic pathway!

To probe the order of steps in radical cyclization processes such as these, it is common to repeat the reaction under study at various temperatures, with varying rates of addition of the tin hydride/radical initiator mixture. Whichever product is favored at lower temperatures and faster addition times is understood to correspond to the earlier-formed intermediate in the cyclization reaction. Unfortunately, these types of experiments are not appropriate for the substrates described here, for two important reasons. First, even for simple mono-vinyl ether/alkyne conjugates (e.g., **8**) the cyclization reaction is a multistep process involving first the addition of a tin radical to the alkyne and then cyclization; attempts to add the tin reagent more quickly led mostly to the product of direct Sn−H addition across the alkyne function. Second, for most of the reactions described above, we observed only a single product; a brief survey of alternative reaction conditions failed to yield any other cyclization product that we could use as a basis for comparison.

To resolve these issues and permit the further study of the radical cascade reaction, we targeted compounds **39a−c** (Scheme 10) as probes.[17] We envisioned that these substrates would allow us to generate the vinyl radical intermediate (analogous to **G** in Scheme 3) directly from the vinyl bromide

Scheme 10. Synthesis of Vinyl Bromide Substrates



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function, thereby removing (at least partially) the first problem noted above. The use of an electron-withdrawing group conjugated to the vinyl ether was expected to result in a mixture of pyran and furan products (as previously noted in the cyclization of **13**; Scheme 5), thus resolving the second problem and providing us with two detectable species, the relative concentrations of which might vary in response to applied cyclization conditions. At the same time, the presence of electron-donating (X = OCH_3), electron-neutral (X = H) or electron-withdrawing (X = $C(O)CH_3$) functional groups on the aromatic ring might provide some useful information regarding the energetic barrier associated with the 3-*exo*/retro-3-*exo* isomerization process.

Compounds **39a,b** were synthesized as shown in Scheme 10. The appropriate aryl halide starting material (**36a,b**) was coupled to unprotected alkyne **1** in a Sonogashira reaction. The cross-coupled product (**37**) was then subjected to a hydroxy-directed hydrozirconation,[18] the product of which was reacted with *N*-bromosuccinimide to afford the desired vinyl bromide as a single regio- and stereoisomer (**38**). Conjugate addition proceeded smoothly as expected, to provide the desired cyclization substrates.

Efficient assembly of compound **39c** required that the carbonyl group be unmasked for the Sonogashira step (where an electron-deficient aryl group was advantageous) but be protected for the hydrozirconation step (where a nucleophilic alkene was required for optimal reactivity). A protect/deprotect sequence was therefore included in the synthesis of this substrate.

Vinyl bromides **39a–c** were subjected to our usual radical cyclization conditions. Varying the temperature of the reaction did not provide any useful information: lower temperatures led to no reaction, while higher temperatures resulted only in premature decomposition of the radical initiator. However, varying the rate of addition of the Ph_3SnH/AIBN mixture proved much more informative.

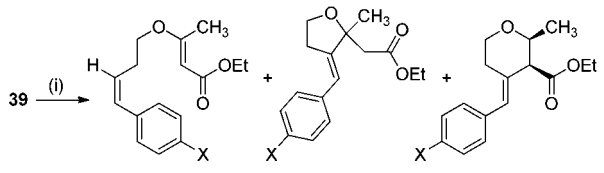
Substrates **39a,b** both cyclized to afford an approximately 1/1 ratio of five-membered- and six-membered-ring products (Table 1, entries 1 and 2) when the Ph_3SnH and AIBN reagents were added over a 6.25 h period. This result agrees very well with the cyclization of **13** (Scheme 5), which was conducted under identical conditions. Compound **39c** did not react under these conditions, presumably because the electron-withdrawing ketone conjugated to the vinyl halide function made the bromide more difficult to abstract.

Changing to a faster addition rate (entries 4 and 5)[19] resulted in a significant increase in the amount of the five-membered-ring product (**41**) relative to the six-membered-ring product (**42**). This result unambiguously confirms the 5-*exo-trig* addition as the first step in the cascade, thus establishing the overall mechanism in the synthesis of bicycle **3** as 5-*exo-trig*/3-*exo-trig*/retro-3-*exo-trig*/5-*exo-trig*.[20]

The fact that the methoxy-substituted vinyl bromide substrate (**39b**) gave a very similar ratio of 5-*exo* and 6-*endo* product to the unsubstituted substrate (**39a**) was somewhat surprising; we had anticipated that the presence of the electron-donating methoxy group would help to stabilize the product of the 3-*exo-trig* cyclization (analogous to intermediate **J** in Scheme 3), thereby reducing the overall barrier to isomerization and favoring the six-membered-ring product **42**. To explain why this did not occur, we turned to DFT calculations[21] to evaluate the relative heats of formation for the various intermediate radical species.[22] As shown in Chart 1, the presence of the methoxy group does not substantially change the relative energies of the 3-*exo* product (**J′**). In fact, the calculated energies for all three cyclic intermediates (relative to that of the original vinyl radical) are essentially identical between the two series. The calculated energies for the five- and six-membered-ring radical intermediates (**H′** and **I′**, respectively) are also quite close together (within about 1 kcal/mol), favoring the formation of a product mixture. This is consistent with the experimental result reported in Table 1, in which compounds **41** and **42** were observed in similar quantities when the tin hydride source was added slowly.

Taken together, our results provide compelling evidence that radical cyclization of each of the vinyl ether species discussed here proceeds through an initial 5-*exo* attack. Viewed from this perspective, however, the results in Scheme 5 were somewhat puzzling. At first glance, the enhanced preference for six-membered-ring products observed for the methyl-substituted vinyl ethers **8** and **13**, relative to that observed for the less-substituted analogues **10** and **16**, *looks* like a classic kinetically controlled regioselectivity bias, where the incoming radical has been directed away from the more-substituted end of the vinyl ether function. But this cannot be the case if all of our

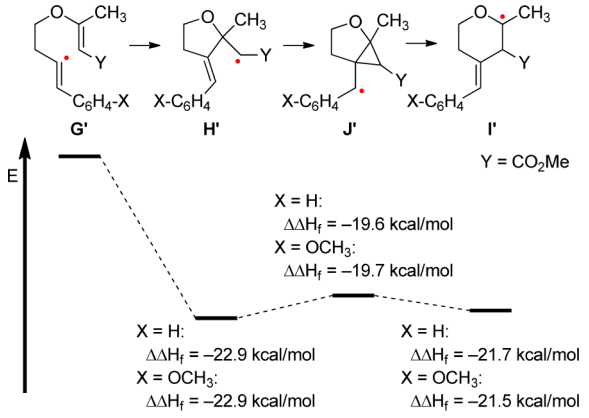
Table 1. Change in Product Distribution with Addition Rate[a]



entry	substrate	X	addition time, h	40/41/42[b]
1	**39a**	H	6.25	0.5/1.0/1.0
2	**39b**	OCH_3	6.25	0.8/1.2/1.0
3	**39c**	$C(O)CH_3$	6.25	*c*
4	**39a**	H	2.50	1.0/1.5/1.0
5	**39b**	OCH_3	2.50	1.3/1.5/1.0

[a]Conditions: (i) Ph_3SnH (1.5 equiv) and AIBN (0.1 equiv) was added to a refluxing solution of **39** (8 mM) in benzene. Heating was continued for 1.5 h prior to workup. [b]Compound **42** was formed as a 1/1 mixture of geometric isomers. [c]Only recovered starting material was observed.

Chart 1. DFT Calculations Investigating the Effect of Substitution on the Aromatic Ring



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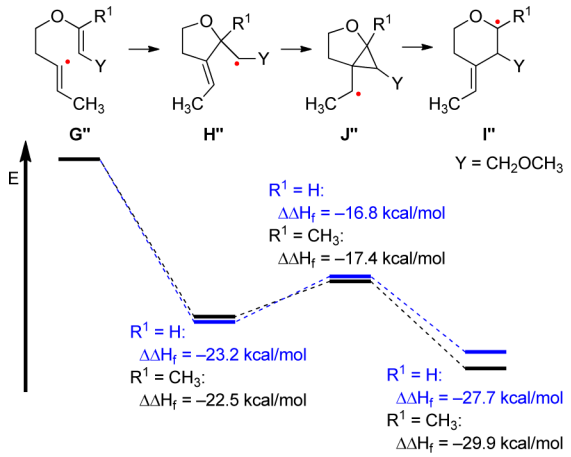
cyclizations in fact proceed through initial 5-*exo* attack. Instead, the regiochemical control must be due either to a change in the rate of the five-membered-ring to six-membered-ring isomerization or to a difference in the thermodynamic preference for the six-membered-ring radical precursor (**I**, Scheme 3) relative to the five-membered-ring radical precursor (**H**, Scheme 3).

To explore the means by which substitution on the vinyl ether dictates the regiochemical outcome for the cyclization reaction, we again turned to DFT calculations[20] to evaluate the relative heats of formation for the intermediate radical species leading to compounds analogous to **9** versus those leading to **11** and **12**. To avoid relativistic effect problems associated with the tin atom, we replaced the triphenyl tin substituent with a methyl group.

As shown in Chart 2, the presence of the methyl group at the R^1 position, relative to a hydrogen atom, both *destabilizes* the 5-

Chart 2. DFT Calculations Investigating the Effect of Substitution on the Vinyl Ether



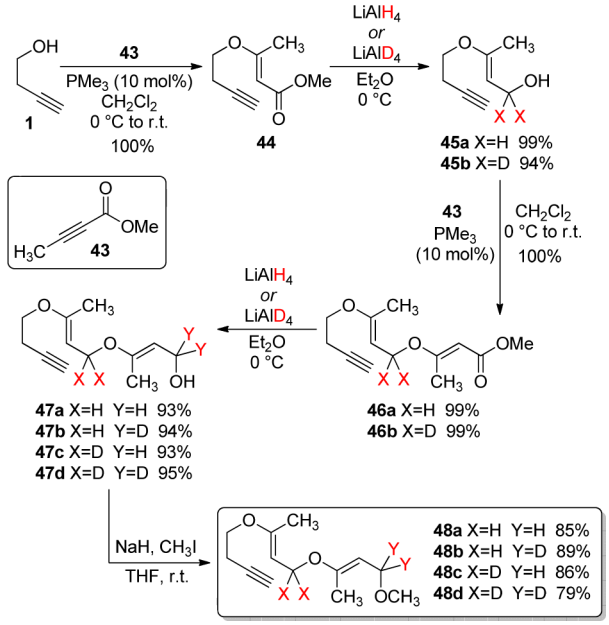
exo radical intermediate **H″** (due to steric strain associated with the introduction of an extra quaternary center) and *stabilizes* the corresponding anomeric radical intermediate **I″** (by incorporating a greater degree of substitution at the radical center). Together, these two effects work to nearly double the degree to which the six-membered-ring radical intermediate is favored (7.4 kcal/mol when $R^1 = CH_3$ vs 4.4 kcal/mol when $R^1 = H$). While this analysis of course omits any discussion of the rate at which these species may be quenched by the incoming hydride donor, it nonetheless provides some explanation for the extent to which substitution on the vinyl ether group can control the regiochemical outcome of the reaction without changing the site of initial radical attack.

The detailed understanding of mechanism developed thus far for the conversion of **2** into **3** should be useful in the design of future radical cascades leading to alternatively fused bicycles and polycycles. However, this will only be true if the various radical intermediates (**G**–**K**) are well-behaved and do not participate in hydrogen atom transfers with other positions on the substrate. In particular, we recognized that two carbon centers on bis-vinyl ether **2** were positioned between alkenes and oxygen atoms. As a result, the C–H bonds at these centers should have relatively low bond strengths (i.e., the resulting radicals would be highly stabilized). If hydrogen atom abstraction from these positions should occur, such that the transferred hydrogen atom quenches a late-stage radical intermediate (**H**, **I**, or **K**) prior to quenching with the desired hydride source (Ph_3SnH), an identical product would result to those described above. However, such a mechanism would undermine the potential utility of future radical cascade reactions, in which these intermediate radical species are required to persist long enough to engage in additional cyclization steps.

To evaluate the likelihood of such unwanted reactions taking place, we synthesized a series of deuterated analogues, by using $LiAlD_4$ in place of the usual reducing agent (either DIBAL or $LiAlH_4$) in the conjugate addition/reduction sequence. In designing these experiments, we intentionally chose a substrate (**48**) that we knew from our previous studies[8] to provide both monocyclic and bicyclic products (**49** and **50**) upon cyclization. In this way, we anticipated being able to isolate and characterize two distinct products deriving from each deuterated substrate, thereby allowing us to more completely probe the stability of the various intermediate radical species. We were particularly interested in interrogating the monocyclic product **50**, since we reasoned that unwanted hydrogen (or deuterium) transfer to the relatively long-lived anomeric radical species **I** was among the more likely of several potential unwanted radical scramblings. If no deuteration were detected at the anomeric position of product **50** following the cyclization of a deuterated substrate, this could be taken as promising evidence against the likelihood of premature quenching through hydrogen atom transfer.

As shown in Scheme 11, the complete series of deuterium-substituted substrates (**48a**–**d**) was accessed efficiently.

Scheme 11. Synthesis of Deuterated Substrates



Gratifyingly, cyclization of these compounds (Table 2, entries 1–4) led to no migration of the deuterium label(s) from the starting locations, in either the fully cyclized (**49**; see Figure 1) or partially cyclized (**50**; see Figure 2) products. No partial deuteration of undeuterated positions could be detected by NMR integration of the purified products, nor could any degree of deuterium erosion be detected from initially deuterated positions. These results were confirmed by MS analysis of the products.

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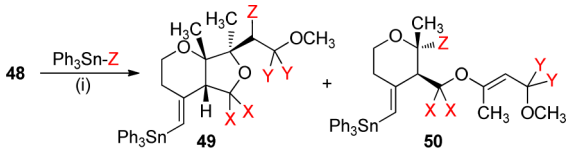
Table 2. Cyclization of Deuterated Substrates[a]



		49				50			
entry	substrate + hydride source	yield, %	X[d]	Y[d]	Z[d]	yield, %	X[d]	Y[d]	Z[d]
1	**48a** + Ph_3Sn–H	55[b] (**49a**)	H (>90)	H (>90)	H (>90)	27 (**50a**)	H (>90)	H (>90)	H (>90)
2	**48b** + Ph_3Sn–H	44 (**49b**)	H (>90)	D (>90)	H (>90)	39 (**50b**)	H (>90)	D (>90)	H (>90)
3	**48c** + Ph_3Sn–H	46 (**49c**)	D (>90)	H (>90)	H (>90)	42 (**50c**)	D (>90)	H (>90)	H (>90)
4	**48d** + Ph_3Sn–H	35 (**49d**)	D (>90)	D (>90)	H (>90)	50 (**50d**)	D (>90)	D (>90)	H (>90)
5	**48a** + Ph_3Sn–D	36 (**49e**)	H (>90)	H (>90)	D[c] (>90)	40 (**50e**)	H (>90)	H (>90)	D (>90)

[a]Conditions: (i) Ph_3SnZ (1.5 equiv) and AIBN (0.1 equiv) were added to a refluxing solution of **48** in benzene. Heating was continued for 1.5 h prior to workup. [b]The reaction shown in entry 1 was run at a lower concentration (1.6 mM) than for the reactions in entries 2–5 (8 mM). This has the effect of increasing the yield of **49**, relative to that of **50**. [c]For product **49e**, two diastereotopic hydrogen atoms can be replaced by deuterium; approximately 50% deuteration was observed at each position. [d]The percent incorporation is given in parentheses.

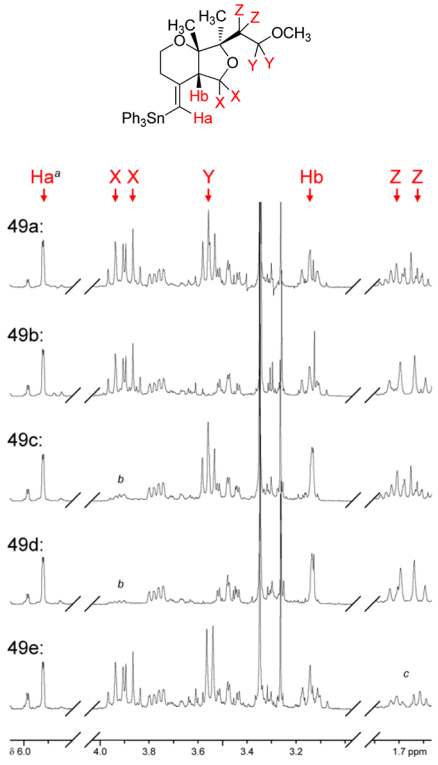


Figure 1. ^{1}H NMR data showing deuteration of bicycle **49**. Legend: (a) compound **49** was formed as a mixture of geometric isomers at the tin-bearing alkene, and tin satellite peaks are also visible in this region; (b) upon deuteration of position X, signals for a proton from the minor isomer are revealed; (c) 50% deuteration at each of the two positions labeled Z was achieved.

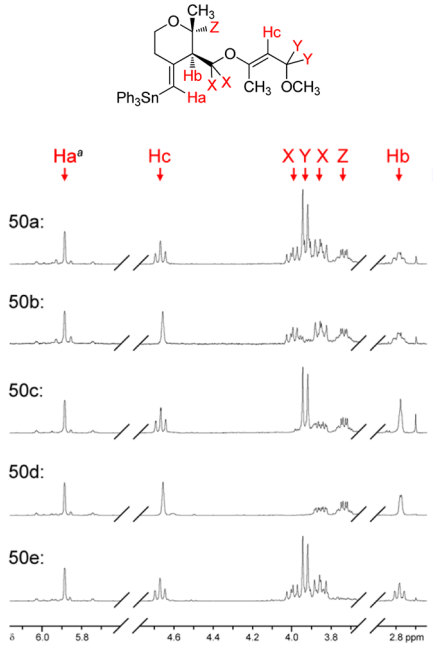


Figure 2. ^{1}H NMR data showing deuteration of monocycle **50**. Legend: (a) compound **50** was formed as a mixture of geometric isomers at the tin-bearing alkene, and tin satellite peaks are also visible in this region.

To complete this series of experiments, we prepared Ph_3Sn-D[23] and used this in a cyclization of the nondeuterated bis-vinyl ether **48a** (Table 2, entry 5). As anticipated, we observed complete deuteration at the anomeric position of **50** (see Figure 2), along with 50% deuteration at each of two diastereotopic positions in bicycle **49** (see Figure 1).

CONCLUSION

Taken together, the experimental results described here strongly support a 5-*exo*-*trig*/3-*exo*-*trig*/retro-3-*exo*-*trig*/5-*exo*-*trig* pathway for the radical cascade leading to the formation of bicycle **3**. This result is further supported by DFT calculations, while a series of experiments with deuterium-substituted cyclization substrates confirmed that the radical intermediates are positionally stable, implying that mechanistically related radical cascades could be used to access an increased diversity of ring structures.

EXPERIMENTAL SECTION

General Methods. All reactions were performed in oven- or flame-dried glassware, under a positive pressure of argon, unless otherwise indicated. Organic solutions were concentrated between 35 and 40 °C by rotary evaporation under vacuum. Analytical thin-layer chromatography (TLC) was performed using aluminum plates precoated with silica gel (0.20 mm, 60 Å pore size, 230–400 mesh, Macherey-Nagel) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light followed by staining with *p*-

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anisaldehyde. Flash column chromatography was performed over silica gel 60 (Caledon, 63−200 μM).

All reagents were used as received, unless otherwise indicated. Bis(cyclopentadienyl)zirconium(IV) chloride hydride was purchased from Strem Chemicals, stored in a glovebox, and used without further purification. Commercial solvents were used as received with the following exceptions. Anhydrous tetrahydrofuran was distilled from sodium/benzophenone prior to use. Acetonitrile, diethyl ether, and dichloromethane were dried by passage through a column of alumina in a commercial solvent purification system (SPS). Triethylamine was distilled over calcium hydride and stored under an inert atmosphere of argon. Benzene was distilled over calcium hydride and degassed by freeze−pump−thaw prior to use.

^{1}H chemical shifts are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$, δ 7.26; $CD_3C(O)CD_3$, δ 2.05; CD_2Cl_2, δ 5.32). Likewise, ^{13}C chemical shifts are referenced to the carbon resonances of the solvent ($CDCl_3$, δ 77.22; $CD_3C(O)CD_3$, δ 29.85). Accurate masses were obtained using an Orbitrap MS. Infrared spectra were collected using an FT-IR spectrometer.

General Procedure for Conjugate Addition. The alkyne (**18**, **22**, **43**, or ethyl propiolate, 1.00 mmol) was added dropwise to a stirred solution of alcohol (**1**, **26**, **38**, or **45**, 1.00 mmol) and trimethylphosphine (1.0 M in THF, 0.10 mmol) in dry dichloromethane (5 mL). The reaction mixture was stirred at room temperature for 18 h. The solvent was then removed under vacuum, and the residue was resuspended in diethyl ether (∼10 mL). The resulting suspension was filtered through a thin layer of basic alumina. The filtrate was concentrated in vacuo and purified by flash column chromatography using silica gel pretreated with 1% triethylamine, to afford the conjugate addition product (**13**, **16**, **19**, **27**, **39**, **44**, or **46**) as clear, colorless to orange oils. Alcohols **39a**,**b** (1.00 mmol) were first washed with saturated $Na_2S_2O_3$(aq) prior to their use in the conjugate addition reaction.

General Procedure for $LiAlH_4$ Reduction. Lithium aluminum hydride (or lithium aluminum deuteride) (2.00 mmol) was added in one portion to a stirred solution of the ester (**13**, **19**, **27**, **44**, or **46**, 1.00 mmol) in anhydrous diethyl ether (10 mL) maintained at 0 °C. After 1.5 h the reaction mixture was diluted with diethyl ether and subsequently quenched with 10% KOH(aq). The two phases were separated, and the aqueous layer was extracted twice with diethyl ether. The combined organic extracts were dried over anhydrous sodium sulfate, filtered, concentrated in vacuo, and purified by flash column chromatography using silica gel pretreated with 1% triethylamine, to afford alcohols **20**, **23**, **28**, **45**, and **47** as clear, colorless to pale yellow oils.

General Procedure for Methylation. Following our procedure reported earlier,[8] iodomethane (3.00 mmol) was added dropwise via syringe to a stirred mixture of alcohol (**20** or **47**, 1.00 mmol) in dry tetrahydrofuran at 0 °C. Sodium hydride (60% w/w in mineral oil, 2.00 mmol) was added in one portion to the reaction mixture, and the resulting slurry was warmed to ambient temperature overnight (∼18 h). The reaction was quenched with saturated NH_4Cl(aq) and 10% KOH(aq) and extracted twice with diethyl ether. The combined organic extracts were dried over anhydrous sodium sulfate, filtered, concentrated in vacuo, and purified by flash column chromatography (1% triethylamine-treated silica gel, hexanes/ethyl acetate, 40/1 to 1/2 gradient), to afford methyl ethers **21** and **48** as clear, colorless to pale yellow oils.

General Procedure for IBX Oxidation. 2-Iodoxybenzoic acid (1.20 mmol) was added in one portion to a stirred solution of alcohol (**23** or **28**, 1.00 mmol) in dry acetonitrile (3.0 mL) at ambient temperature. The progress of the reaction was monitored by TLC. Upon consumption of the alcohol (∼3 h), the reaction was quenched with brine and solids were removed by filtration through a fritted-glass funnel. The two phases were separated, and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were dried over sodium sulfate, filtered, concentrated in vacuo, and purified by flash column chromatography using 1% triethylamine-treated silica gel to afford the corresponding aldehyde. In the case of silyl-protected alkynol **28**, a competing side reaction led to an inseparable mixture of compounds following IBX oxidation. The crude product was therefore taken forward to the Wittig olefination step, at which point diene **30** could be cleanly isolated.

General Procedure for the Wittig Olefination. *n*-Butyllithium (2.0 M in hexanes, 1.10 mmol) was added dropwise to a stirred solution of methyltriphenylphosphonium bromide (1.10 mmol) in anhydrous tetrahydrofuran (6 mL) at −15 °C. The resulting clear, orange solution was kept at −15 °C for 15 min. A solution of aldehyde (**24** or **29**, 1.00 mmol) in anhydrous tetrahydrofuran (2 mL) was added dropwise, via cannula, and the resultant slurry was gradually warmed from −15 °C to room temperature over 2.5 h. The reaction mixture was quenched with water and extracted twice with diethyl ether. The combined organic extracts were dried over sodium sulfate, filtered, concentrated in vacuo, and purified by flash column chromatography using 1% triethylamine-treated silica gel to afford dienes **25** and **30** as clear, colorless to pale yellow oils.

General Procedure for the Cyclopropanation Reaction. Alkene **30a** or **30b** (0.58 mmol) was dissolved in anhydrous diethyl ether (10 mL) and cooled to 0 °C. Palladium(II) acetylacetonate (0.0021 g, 0.0069 mmol) was added to the reaction vessel, followed by 6 mL of diazomethane in ether (∼20 mg of diazomethane/mL of ether). The resulting mixture was warmed to room temperature for 45 min and then cooled to 0 °C. The addition of palladium(II) acetylacetonate followed by diazomethane was repeated a total of six times while cycling through from 0 °C to room temperature after each set of additions. After the sixth addition of reagents, the reaction vessel was gradually warmed to room temperature and the reaction mixture was stirred overnight (∼14 h). The reaction contents were filtered through a plug of Celite, concentrated in vacuo, and then purified by flash column chromatography (1% triethylamine-treated silica gel) to afford cyclopropane **31a** or **31b** (with 8−14% of contaminant **30**, after purification).

General Procedure for the TBAF Deprotection of Cyclopropanes 31. Tetrabutylammonium fluoride (1.10 mmol) was added dropwise to a stirred solution of cyclopropane **31a** or **31b** (1.00 mmol) in anhydrous tetrahydrofuran (27 mL) at 0 °C. The progress of the reaction was monitored by TLC. After complete conversion was indicated by TLC, the reaction mixture was quenched with saturated NH_4Cl(aq) and extracted twice with diethyl ether. The organic extracts were dried over anhydrous sodium sulfate, filtered, concentrated in vacuo, and then purified by flash column chromatography (1% triethylamine-treated silica gel) to afford **32a** or **32b** as a clear, pale yellow oil.

General Procedure for the Sonogoshira Coupling. Bis(triphenylphosphine)palladium(II) dichloride (0.02 mmol), copper(I) iodide (0.01 mmol), aryl halide (1.00 mmol) and 3-butyn-1-ol (**1**; 1.20 mmol) were dissolved in dry triethylamine (∼6 mL) and subsequently heated to reflux. After 2.5 h, the reaction mixture was quenched with an ethyl acetate/water mixture (1/1, 25 mL) and the aqueous and organic phases were separated. The organic layer was washed with water and then brine, dried over anhydrous sodium sulfate, filtered, concentrated in vacuo, and purified by flash column chromatography on silica gel to afford **37a**−**c** as clear, orange oils.

General Procedure for the Hydrozirconation Reaction. A solution of **37a**, **37b**, or **37d** (1.00 mmol) in dry dichloromethane (2.5 mL) was added, via cannula, to a stirred suspension of bis(cyclopentadienyl)zirconium(IV) chloride hydride (3.00 mmol) in dry dichloromethane (3.8 mL) at ambient temperature, followed by rinsing with dichloromethane (2.5 mL). The mixture was stirred in the absence of light for 3 h, forming a clear yellow to orange solution. *N*-Bromosuccinimide (2.00 mmol) in anhydrous tetrahydrofuran (4 mL) was added dropwise to the reaction mixture, which was stirred for an additional 0.5 h. The reaction mixture was quenched by addition of a mixed aqueous solution of saturated $Na_2S_2O_3$ and saturated $NaHCO_3$ (1/1, 20 mL) and diluted with diethyl ether, and the aqueous and organic layers were separated. The aqueous layer was extracted twice with diethyl ether, and the combined organic layers were dried over anhydrous sodium sulfate, filtered, concentrated in vacuo, and purified

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by flash column chromatography to afford **38a**, **38b**, or **38c** as a single regio- and stereoisomer.

Procedure for the Acetal Protection of 37c. *p*-Toluenesulfonic acid (20.8 mg, 0.0710 mmol), **37c** (290.1 mg, 1.541 mmol), and ethylene glycol (0.34 mL, 3.96 mmol) in 30 mL of benzene were heated to reflux with a Dean−Stark apparatus for 25 h. The reaction mixture was cooled to room temperature and washed once with saturated $NaHCO_3$(aq) and twice with brine. The organic layer was dried over anhydrous sodium sulfate, filtered, concentrated in vacuo, and purified by flash column chromatography on silica gel (hexanes/ethyl acetate, 1/1) to afford **37d** (220.3 mg, 0.9484 mmol) as a clear, pale yellow oil.

Procedure for the Acetal Deprotection of 38c. Hydrochloric acid (1.0 M, 0.45 mL) was added to a stirred solution of **38c** (30.5 mg, 0.0974 mmol) in methanol (7.5 mL) at room temperature. After 1 h the solution was diluted with water and methanol was removed by concentration under reduced pressure. The aqueous mixture was extracted twice with diethyl ether, and the organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo to afford **38d** (21.5 mg, 0.0799 mmol) as a clear, yellow-orange oil which was used without further purification.

General Procedure for the Radical Cyclization Reaction. A solution of triphenyltin hydride (1.50 mmol) and azobisisobutyronitrile (0.10 mmol) in deoxygenated benzene (10 mL) was added, via syringe pump, to a refluxing solution of enyne (**8**, **10**, **13**, **16**, **21**, **25**, **32**, or **48**) or vinyl bromide **39** (1.00 mmol) in deoxygenated benzene (115 mL) over 6.25 h. The reaction mixture was maintained at reflux for an additional 1.5 h, cooled to room temperature, concentrated in vacuo, and then purified by flash-column chromatography to afford products **9**, **11**, **12**, **14**, **15**, **17**, **33**, **34**, **35**, **40**, **41**, **42**, **49**, and **50** as clear, colorless to pale yellow oils.

*Triphenyl((2-(trifluoromethyl)-2-vinyldihydrofuran-3(2H)-ylidene)methyl)stannane (**5**):* clear, pale yellow oil (43.9 mg, 80% yield); R_f = 0.78 (hexanes/ethyl acetate, 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60−7.54 (m, 6H), 7.43−7.37 (m, 9H), 6.43 (br s, 1H), 6.08 (dd, J = 16.9, 10.6 Hz, 1H), 5.65 (d, J = 17.2 Hz, 1H), 5.40 (d, J = 10.6 Hz, 1H), 4.06 (td, J = 8.1, 5.9 Hz, 1H), 3.91 (app q, J = 7.7 Hz, 1H), 2.62 (dtd, J = 15.6, 7.7, 2.4 Hz, 1H), 2.49 (dddd, J = 15.9, 7.7, 5.6, 2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1 (C), 137.8 (C), 137.1 (CH), 132.8 (CH), 129.5 (CH), 129.0 (CH), 124.7 (q, J = 287.0 Hz, CF_3), 121.6 (CH), 117.8 (CH_2), 85.3 (q, J = 28.4 Hz, C), 67.8 (CH_2), 35.6 (CH_2); IR (neat, cm^{-1}) 3047 (m), 2915 (s), 1146 (m), 1071 (m), 727 (s), 693 (s); HRMS (ESI) calcd for $C_{26}H_{23}OF_3Sn$ + Na^+ 551.0626, found 551.0635.

*((7-(2-methoxyethyl)-7a-(trifluoromethyl)tetrahydro-2H-furo[3,4-b]pyran-4(3H)-ylidene)methyl)triphenylstannane (**7**):* clear, light yellow oil (23.8 mg, 64% yield, 1.00/0.15/0.06/0.06 dr); R_f = 0.64 (hexanes/ethyl acetate, 2 × 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58−7.46 (m, 6H), 7.38−7.34 (m, 9H), 6.01 (s, 1H), 4.12 (t, J = 8.6 Hz, 1H), 4.00 (d, J = 11.1 Hz, 1H), 3.87−3.83 (m, 1H), 3.76 (t, J = 9.4 Hz, 2H), 3.51−3.46 (m, 2H), 3.33 (s, 3H), 3.31 (t, J = 9.4 Hz, 1H), 2.48 (tdd, J = 13.1, 5.6, 1.1 Hz, 1H), 2.18 (dt, J = 14.7, 3.0 Hz, 1H), 2.07−2.00 (m, 1H), 1.90−1.80 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.1 (C), 138.5 (C), 137.0 (CH), 129.4 (CH), 128.9 (CH), 124.6 (CH), 86.2 (CH), 84.3 (q, J = 27.3 Hz, C), 79.3 (q, J = 285.93 Hz, CF_3), 70.7 (CH_2), 69.8 (CH_2), 65.6 (CH_2), 58.9 (CH_3), 49.3 (CH), 33.1 (CH_2), 29.9 (CH_2); IR (neat, cm^{-1}) 3058 (m), 2913 (s), 1605 (m), 1255 (m), 1071 (s), 727 (s), 697 (s); HRMS (ESI) calcd for $C_{30}H_{31}O_3F_3Sn$ + Na^+ 635.1140, found 635.1125.

*Ethyl 2-methyl-4-((triphenylstannyl)methylene)tetrahydro-2H-pyran-3-carboxylate (**14**):* clear, colorless oil (78.9 mg, 49% yield); R_f = 0.23 (hexanes/dichloromethane/ethyl ether, 10/4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62−7.52 (m, 5H), 7.44−7.32 (m, 10H), 6.02 (d, J = 1.5 Hz, 1H), 4.27 (dq, J = 10.8, 7.1 Hz, 1H), 4.17 (dq, J = 10.8, 7.1 Hz, 1H), 4.01 (ddd, J = 10.8, 6.1, 1.2 Hz, 1H), 3.68 (qd, J = 6.5, 3.4 Hz, 1H), 3.37 (d, J = 3.2 Hz, 1H), 3.31 (ddd, J = 12.5, 10.8, 2.4 Hz, 1H), 3.03 (dddd, J = 13.9, 12.4, 6.0, 1.4 Hz, 1H), 2.12 (ddt, J = 14.0, 2.3, 1.2 Hz, 1H), 1.32 (d, J = 6.4 Hz, 3H), 1.32 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6 (C), 154.4 (C), 138.8 (C), 137.0 (CH), 129.3 (CH), 128.8 (CH), 122.4 (CH), 75.8 (CH), 68.8 (CH_2), 60.7 (CH_2), 59.1 (CH), 34.9 (CH_2), 19.3 (CH_3), 14.5 (CH_3); IR (neat, cm^{-1}) 3064 (m), 2978 (m), 1732 (s), 1609 (m), 1091 (s), 729 (s), 699 (s); HRMS (ESI) calcd for $C_{28}H_{30}O_3Sn$ + H^+ 535.1290, found 535.1301.

*Ethyl 2-(2-methyl-3-((triphenylstannyl)methylene)-tetrahydrofuran-2-yl)acetate (**15**):* clear, colorless oil (73.1 mg, 46% yield); R_f = 0.19 (hexanes/dichloromethane/ethyl ether, 10/4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63−7.54 (m, 5H), 7.44−7.34 (m, 10H), 5.96 (t, J = 2.3 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.95−3.78 (m, 2H), 2.72 (d, J = 18.1 Hz, 1H), 2.68 (d, J = 18.1 Hz, 1H), 2.66−2.43 (m, 2H), 1.49 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5 (C), 168.2 (C), 138.5 (C), 137.1 (CH), 129.3 (CH), 128.9 (CH), 113.1 (CH), 83.4 (C), 65.1 (CH_2), 60.5 (CH_2), 45.5 (CH_2), 35.6 (CH_2), 26.6 (CH_3), 14.4 (CH_3); IR (neat, cm^{-1}) 3064 (m), 2978 (m), 1733 (s), 1622 (w), 1075 (m), 729 (s), 700 (s); HRMS (ESI) calcd for $C_{28}H_{30}O_3Sn$ + Na^+ 557.1109, found 557.1117.

*Ethyl 3-(but-3-yn-1-yloxy)acrylate (**16**):* clear, colorless oil (670.9 mg, 93% yield, 1.00/0.06 *E*/*Z*); R_f = 0.54 (hexanes/dichloromethane/ethyl ether, 5/5/1); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.59 (d, J = 12.6 Hz, 1H), 5.25 (d, J = 12.6 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 2.62 (td, J = 6.5, 2.8 Hz, 2H), 2.46 (t, J = 2.8 Hz, 1H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 167.6 (C), 162.8 (CH), 97.7 (CH), 80.9 (C), 71.5 (CH), 70.1 (CH_2), 60.0 (CH_2), 19.7 (CH_2), 14.7 (CH_3); IR (neat, cm^{-1}) 3296 (s), 3093 (m), 2982 (s), 2951 (s), 2896 (s), 2124 (w), 1708 (s), 1628 (s), 1468 (s), 1045 (s), 970 (s), 825 (s), 646 (s); HRMS (ESI) calcd for $C_9H_{12}O_3$ + Na^+ 191.0679, found 191.0679.

*Ethyl 2-(3-((triphenylstannyl)methylene)tetrahydrofuran-2-yl)-acetate (**17**):* clear, colorless oil (149.0 mg, 83% yield); R_f = 0.54 (hexanes/dichloromethane/ethyl ether, 5/5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59−7.54 (m, 5H), 7.44−7.34 (m, 10H), 6.02 (app q, J = 2.1 Hz, 1H), 4.82−4.74 (m, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.94 (ddd, J = 8.5, 7.6, 5.3 Hz, 1H), 3.75 (app dt, J = 8.3, 7.7 Hz, 1H); 2.75 (dd, J = 15.5, 4.0 Hz, 1H), 2.63 (dd, J = 15.5, 8.7 Hz, 1H), 2.54−2.38 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2 (C), 163.9 (C), 138.3 (C), 137.0 (CH), 129.3 (CH), 128.9 (CH), 113.8 (CH), 79.0 (CH), 67.2 (CH_2), 60.8 (CH_2), 40.7 (CH_2), 35.4 (CH_2), 14.3 (CH_3); IR (neat, cm^{-1}) 3064 (s), 3047 (s), 2980 (s), 2863 (s), 1735 (s), 1625 (m), 1480 (m), 1429 (s), 1163 (s), 1075 (s), 729 (s), 699 (s); HRMS (ESI) calcd for $C_{27}H_{28}O_3Sn$ + Na^+ 543.0953, found 543.0955.

*Ethyl 3-(but-3-yn-1-yloxy)-3-cyclopropylacrylate (**19**):* clear, colorless oil (261.7 mg, 45% yield); R_f = 0.69 (hexanes/ethyl acetate, 4/1); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 5.06 (s, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.88 (t, J = 6.3 Hz, 2H), 3.25 (tt, J = 8.4, 5.0 Hz, 1H), 2.57 (td, J = 6.3, 2.4 Hz, 2H), 2.43 (t, J = 2.7 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H), 0.97 (ddd, J = 6.3, 5.2, 3.4 Hz, 2H), 0.77 (ddd, J = 8.5, 6.4, 3.4 Hz, 2H); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 174.5 (C), 168.3 (C), 91.7 (CH), 81.2 (C), 71.1 (CH), 66.7 (CH_2), 59.5 (CH_2), 19.3 (CH_2), 14.8 (CH_3), 12.0 (CH), 7.4 (CH_2); IR (neat, cm^{-1}) 3300 (s), 3091 (m), 2954 (s), 2123 (w), 1702 (s), 1606 (s), 1146 (s), 1051 (s); HRMS (ESI) calcd for $C_{12}H_{16}O_3$ + H^+ 209.1178, found 209.1177.

*3-(But-3-yn-1-yloxy)-3-cyclopropylprop-2-en-1-ol (**20**):* clear, light yellow oil (323.7 mg, 64% yield); R_f = 0.09 (hexanes/ethyl acetate, 4/1); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 4.71 (t, J = 7.5 Hz, 1H), 4.19 (dd, J = 7.5, 5.5 Hz, 2H), 3.70 (t, J = 6.5 Hz, 2H), 3.31 (t, J = 5.4 Hz, 1H), 2.48 (td, J = 6.5, 2.7 Hz, 2H), 2.38 (t, J = 2.7 Hz, 1H), 1.81 (tt, J = 8.3, 5.0 Hz, 1H), 0.77 (ddd, J = 6.3, 5.0, 3.6 Hz, 2H), 0.56 (ddd, J = 8.4, 6.3, 3.6 Hz, 2H); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 157.4 (C), 98.7 (CH), 81.7 (C), 70.7 (CH), 65.3 (CH_2), 58.1 (CH_2), 19.4 (CH_2), 10.7 (CH), 4.9 (CH_2); IR (neat, cm^{-1}) 3368 (br, s), 3300 (s), 3094 (m), 2928 (s), 2120 (w), 1651 (s), 1102 (s), 1052 (s); HRMS (ESI) calcd for $C_{10}H_{14}0_{O2}$ + Na^+ 189.0891, found 189.0888.

*(1-(But-3-yn-1-yloxy)-3-methoxyprop-1-en-1-yl)cyclopropane (**21**):* clear, light yellow oil (84.8 mg, 85% yield, 1.00/0.13 *E*/*Z*); R_f = 0.57 (hexanes/ethyl acetate, 4/1); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 4.64 (t, J = 7.7 Hz, 1H, major), 4.61 (t, J = 7.7 Hz, 1H, minor), 4.03 (d, J = 7.3 Hz, 2H, major), 4.02 (d, J = 7.3 Hz, 2H, minor), 3.73 (t, J = 6.4 Hz, 2H), 3.24 (s, 3H, major), 3.23 (s, 3H, minor), 2.49 (td, J = 6.5, 2.8 Hz, 2H), 2.37 (t, J = 2.6 Hz, 1H), 1.82 (tt, J = 8.3, 5.0 Hz, 1H),

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0.79 (ddd, J = 6.3, 5.0, 3.6 Hz, 2H), 0.59 (ddd, J = 8.3, 6.1, 3.7 Hz, 2H); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 159.5 (C, minor), 159.2 (C, major), 94.9 (CH, major), 94.3 (CH, minor), 81.7 (C), 70.8 (CH), 68.4 (CH_2, minor), 68.2 (CH_2, major), 65.5 (CH_2), 56.9 (CH_3, major), 56.9 (CH_3, minor), 19.5 (CH_2), 10.9 (CH, major), 10.8 (CH, minor), 5.0 (CH_2, major), 4.9 (CH_2, minor); IR (neat, cm^{-1}) 3308 (s), 3093 (w), 2924 (s), 2122 (w), 1653 (s), 1104 (s), 1083 (s); HRMS (ESI) calcd for $C_{11}H_{16}O_2$ + Na^+ 203.1048, found 203.1049.

*3-(But-3-yn-1-yloxy)but-2-enal (**24**):* clear, light yellow oil (766.0 mg, 76% yield); R_f = 0.25 (hexanes/ethyl ether, 1/2); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 9.80 (d, J = 7.4 Hz, 1H), 5.36 (d, J = 7.4 Hz, 1H), 3.99 (t, J = 6.6 Hz, 2H), 2.65 (td, J = 6.5, 2.7 Hz, 2H), 2.46 (t, J = 2.7 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 190.4 (CH), 176.0 (C), 105.7 (CH), 81.1 (C), 71.4 (CH), 67.5 (CH_2), 19.4 (CH_2), 17.7 (CH_3); IR (neat, cm^{-1}) 3304 (m), 3057 (m), 2958 (m), 2124 (w), 1703 (s), 1138 (m), 1060 (m); HRMS (ESI) calcd for $C_8H_{10}O_2$ + H^+ 139.0759, found 139.0759.

*4-(But-3-yn-1-yloxy)penta-1,3-diene (**25**):* clear, colorless oil (309.7 mg, 70% yield); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 6.44 (dt, J = 16.7, 10.4 Hz, 1H), 5.36 (d, J = 10.7 Hz, 1H), 4.96 (dd, J = 16.7, 2.1 Hz, 1H), 4.76 (dd, J = 10.2, 2.1 Hz, 1H), 3.83 (t, J = 6.7 Hz, 2H), 2.56 (td, J = 6.7, 2.7 Hz, 2H), 2.40 (t, J = 2.7 Hz, 1H), 1.89 (s, 3H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 156.6 (C), 134.0 (CH), 111.4 (CH_2), 102.2 (CH), 81.6 (C), 71.0 (CH), 65.9 (CH_2), 19.7 (CH_2), 16.7 (CH_3); IR (neat, cm^{-1}) 3304 (s), 3086 (w), 3053 (m), 2977 (s), 2123 (w), 1644 (s), 1113 (s), 1073 (s); HRMS (ESI) calcd for $C_9H_{12}O$ + H^+ 137.0966, found 137.0963.

*4-(Trimethylsilyl)but-3-yn-1-ol (**26a**):* clear, colorless oil (5.4068 g, 82% yield); R_f = 0.39 (hexanes/ethyl acetate, 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70 (q, J = 6.1 Hz, 2H), 2.49 (t, J = 6.3 Hz, 2H), 1.94 (t, J = 6.3 Hz, 1H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 103.5 (C), 87.2 (C), 61.1 (CH_2), 24.4 (CH_2), 0.3 (CH_3); IR (neat, cm^{-1}) 3350 (br, s), 2960 (s), 2900 (s), 2178 (s), 1410 (m), 1250 (s), 1055 (s), 1030 (s), 894 (s), 840 (s), 760 (s), 699 (s), 639 (s); HRMS (ESI) calcd for $C_7H_{14}OSi$ + Na^+ 165.0706, found 165.0707.

*4-(tert-Butyldimethylsilyl)but-3-yn-1-ol (**26b**):* clear, yellow oil (1.0938 g, 15% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71 (t, J = 6.3 Hz, 2H), 2.51 (t, J = 6.3 Hz, 2H), 1.88 (br s, 1H), 0.92 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 104.0 (C), 85.4 (C), 61.2 (CH_2), 26.3 (CH_3), 24.5 (CH_2), 16.7 (C), −4.3 (CH_3); IR (neat, cm^{-1}) 3338 (br, m), 2954 (s), 2930 (s), 2858 (s), 2176 (s), 1472 (m), 1250 (s), 1053 (m), 1030 (s), 838 (s), 776 (s), 682 (m); HRMS (ESI) calcd for $C_{10}H_{20}OSi$ + Na^+ 207.1176, found 207.1176.

*Ethyl 3-((4-(trimethylsilyl)but-3-yn-1-yl)oxy)but-2-enoate (**27a**):* clear, colorless oil (8.63 g, 96% yield); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 5.05 (s, 1H), 4.07 (q, J = 7.1 Hz, 2H), 3.93 (t, J = 6.6 Hz, 2H), 2.66 (t, J = 6.7 Hz, 2H), 2.25 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 172.1 (C), 167.8 (C), 103.9 (C), 92.4 (CH), 86.4 (C), 67.0 (CH_2), 59.5 (CH_2), 20.8 (CH_2), 18.8 (CH_3), 14.8 (CH_3), 0.1 (CH_3); IR (neat, cm^{-1}) 2960 (s), 2901 (s), 2181 (s), 1716 (s), 1634 (s), 1271 (s), 1141 (s), 1053 (s), 843 (s), 761 (s), 700 (m); HRMS (ESI) calcd for $C_{13}H_{22}O_3Si$ + H^+ 255.1411, found 255.1411.

*Ethyl 3-((4-(tert-butyldimethylsilyl)but-3-yn-1-yl)oxy)but-2-enoate (**27b**):* clear, pale yellow oil (1.0558 g, 100% yield, 1.00/0.04 E/Z); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 5.05 (s, 1H), 4.06 (q, J = 7.0 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 2.68 (t, J = 6.6 Hz, 2H), 2.25 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H), 0.93 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 172.2 (C), 167.9 (C), 104.8 (C), 92.4 (CH), 84.5 (C), 67.2 (CH_2), 59.6 (CH_2), 26.4 (CH_3), 20.8 (CH_2), 18.9 (CH_3), 17.0 (C), 14.8 (CH_3), −4.4 (CH_3); IR (neat, cm^{-1}) 2954 (s), 2930(s), 2858 (s), 2180 (s), 1714 (s), 1627 (s), 1275 (s), 1251 (s), 1142 (s), 1053 (s), 839 (s), 776 (s), 681 (m); HRMS (ESI) calcd for $C_{16}H_{28}O_3Si$ + H^+ 297.1881, found 297.1880.

*3-((4-(Trimethylsilyl)but-3-yn-1-yl)oxy)but-2-en-1-ol (**28a**):* clear, colorless oil (463.5 mg, 70% yield); R_f = 0.29 (hexanes/ethyl acetate, 2/1); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 4.68 (t, J = 7.4 Hz, 1H), 4.04 (dd, J = 7.4, 5.5 Hz, 2H), 3.74 (t, J = 6.8 Hz, 2H), 3.28 (t, J = 5.5 Hz, 1H), 2.58 (t, J = 6.9 Hz, 2H), 1.79 (s, 3H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 155.8 (C), 104.6 (C), 99.2 (CH), 85.9 (C), 65.5 (CH_2), 58.8 (CH_2), 21.0 (CH_2), 16.3 (CH_3), 0.2 (CH_3); IR (neat, cm^{-1}) 3331 (br, s), 2959 (s), 2980 (m), 2180 (s), 1665 (s), 1250 (s), 842 (s); HRMS (ESI) calcd for $C_{11}H_{20}O_2Si$ + Na^+ 235.1125, found 235.1125.

*3-((4-(tert-Butyldimethylsilyl)but-3-yn-1-yl)oxy)but-2-en-1-ol (**28b**):* clear, colorless oil (500.8 mg, 71% yield); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 4.68 (t, J = 7.4 Hz, 1H), 4.05 (dd, J = 7.3, 5.5 Hz, 2H), 3.76 (t, J = 6.7 Hz, 2H), 3.26 (t, J = 5.5 Hz, 1H), 2.60 (t, J = 6.7 Hz, 2H), 1.79 (s, 3H), 0.93 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 155.8 (C), 105.5 (C), 99.1 (CH), 84.0 (C), 65.6 (CH_2), 58.9 (CH_2), 26.4 (CH_3), 21.0 (CH_2), 17.0 (C), 16.3 (CH_3), −4.3 (CH_3); IR (neat, cm^{-1}) 3332 (s), 2954 (s), 2929 (s), 2857 (s), 2179 (s), 1667 (s), 1472 (m), 1249 (s), 1079 (s), 838 (s); HRMS (ESI) calcd for $C_{14}H_{26}O_2Si$ + Na^+ 277.1594, found 277.1594.

*3-((4-(tert-Butyldimethylsilyl)but-3-yn-1-yl)oxy)but-2-enal (**29b**):* clear, pale yellow oil (98.7 mg, 26% yield); R_f = 0.61 (hexanes-ethyl ether, 1:3); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 9.81 (d, J = 7.6 Hz, 1H), 5.35 (d, J = 7.4 Hz, 1H), 4.00 (t, J = 6.5 Hz, 2H), 2.72 (t, J = 6.5 Hz, 2H), 2.27 (s, 3H), 0.93 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 190.2 (CH), 175.8 (C), 105.7 (CH), 104.6 (C), 84.6 (C), 67.5 (CH_2), 26.4 (CH_3), 20.8 (CH_2), 17.6 (CH_3), 17.0 (C), −4.4 (CH_3); IR (neat, cm^{-1}) 3453 (w), 2954 (s), 2929 (s), 2857 (s), 1667 (s), 1619 (s), 1226 (s), 1060 (m), 839 (s); HRMS (ESI) calcd for $C_{14}H_{24}O_2Si$ + H^+ 253.1619, found 253.1619.

*Trimethyl(4-(penta-2,4-dien-2-yloxy)but-1-yn-1-yl)silane (**30a**):* clear, colorless oil (532.0 mg, 36% yield); R_f = 0.74 (hexanes/ethyl acetate, 9:1); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 6.44 (dt, J = 16.7, 10.4 Hz, 1H), 5.36 (d, J = 10.5 Hz, 1H), 4.96 (dd, J = 16.7, 2.2 Hz, 1H), 4.75 (dd, J = 10.2, 2.1 Hz, 1H), 3.82 (t, J = 6.9 Hz, 2H), 2.60 (t, J = 6.9 Hz, 2H), 1.88 (s, 3H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 156.6 (C), 134.0 (CH), 111.4 (CH_2), 104.6 (C), 102.3 (CH), 65.9 (CH_2), 21.1 (CH_2), 16.7 (CH_3), 0.2 (CH_3); IR (neat, cm^{-1}) 3086 (w), 2960 (s), 2925 (s), 2181 (s), 1651 (s), 1250 (s), 1073 (s), 844 (s), 760 (s); HRMS (ESI) calcd for $C_{12}H_{20}OSi$ + H^+ 209.1356, found 209.1352.

*tert-Butyldimethyl(4-(penta-2,4-dien-2-yloxy)but-1-yn-1-yl)silane (**30b**):* clear, pale yellow oil (66.0 mg, 67% yield); R_f = 0.69 (hexanes/ethyl acetate, 9/1); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 6.44 (dt, J = 16.7, 10.4 Hz, 1H), 5.35 (d, J = 10.6 Hz, 1H), 4.95 (dd, J = 16.7, 2.2 Hz, 1H), 4.75 (dd, J = 10.3, 2.2 Hz, 1H), 3.84 (t, J = 6.7 Hz, 2H), 2.62 (t, J = 6.7 Hz, 2H), 1.88 (s, 3H), 0.93 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 156.6 (C), 134.0 (CH), 111.3 (CH_2), 105.2 (C), 102.2 (CH), 84.1 (C), 65.9 (CH_2), 26.4 (CH_3), 21.1 (CH_2), 17.0 (C), 16.7 (CH_3), −4.3 (CH_3); IR (neat, cm^{-1}) 2954 (s), 2929 (s), 2857 (s), 2179 (s), 1648 (s), 1472 (m), 1218 (s), 838 (s), 776 (s); HRMS (ESI) calcd for $C_{15}H_{26}OSi$ + H^+ 251.1826, found 251.1828.

*(4-((1-Cyclopropylprop-1-en-2-yl)oxy)but-1-yn-1-yl)-trimethylsilane (**31a**):* clear, colorless oil (107.0 mg, 87% yield; 1.00/0.14 **31a**/**30a**); R_f = 0.80 (hexanes/ethyl acetate, 9:1); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.97 (d, J = 7.8 Hz, 1H), 3.64 (t, J = 7.1 Hz, 2H), 2.54 (t, J = 7.1 Hz, 2H), 1.86 (s, 3H), 1.36−1.21 (m, 1H), 0.64 (ddd, J = 8.2, 6.0, 4.0 Hz, 2H), 0.21 (ddd, J = 6.0, 4.8, 4.0 Hz, 2H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 153.1 (C), 104.7 (C), 102.6 (CH), 85.6 (C), 65.5 (CH_2), 21.1 (CH_2), 16.8 (CH_3), 9.4 (CH), 7.1 (CH_2), 0.2 (CH_3); IR (neat, cm^{-1}) 3079 (m), 2958 (s), 2925 (s), 2872 (m), 2180 (s), 1664 (s), 1250 (s), 1151 (s), 843 (s); HRMS (ESI) calcd for $C_{13}H_{22}OSi$ + H^+ 223.1513, found 223.1507.

*tert-Butyl(4-((1-cyclopropylprop-1-en-2-yl)oxy)but-1-yn-1-yl)-dimethylsilane (**31b**):* clear, colorless oil (44.1 mg, 76% yield; 1.00/0.09 **31b**/**30b**); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 4.02 (d, J = 7.8 Hz, 1H), 3.65 (t, J = 6.8 Hz, 2H), 2.56 (t, J = 6.8 Hz, 2H), 1.84 (s, 3H), 1.34−1.26 (m, 1H), 0.93 (s, 9H), 0.63 (ddd, J = 8.2, 6.1, 3.8 Hz, 2H), 0.23−0.18 (m, 2H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 153.2 (C), 105.5 (C), 102.6 (CH), 83.8 (C), 65.5 (CH_2), 26.6 (CH_3), 21.2 (CH_2), 17.0 (C), 16.8 (CH_3), 9.4 (CH), 7.1 (CH_2), −4.3 (CH_3); IR (neat, cm^{-1}) 3079 (w), 2954 (s), 2928 (s), 2857 (s), 2179 (m), 1665 (m), 1250 (m), 1152 (m), 1079 (m), 838 (s), 825 (s); HRMS (ESI) calcd for $C_{16}H_{28}OSi$ + H^+ 265.1982, found 265.1980.

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*(2-(But-3-yn-1-yloxy)prop-1-en-1-yl)cyclopropane (**32**):* clear, pale yellow oil (23.1 mg, 100% yield, 1.00/0.09 **32**/**25**); R_f = 0.55 (hexanes/ethyl ether, 20/1); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 4.03 (d, J = 7.9 Hz, 1H), 3.65 (t, J = 6.7 Hz, 2H), 2.49 (td, J = 6.8, 2.8 Hz, 2H), 2.38 (t, J = 2.6 Hz, 1H), 1.84 (s, 3H), 1.35−1.30 (m, 1H), 0.64 (ddd, J = 8.1, 6.1, 4.0 Hz, 2H), 0.20 (ddd, J = 6.1, 4.7, 4.1 Hz, 2H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 153.2 (C), 102.6 (CH), 81.9 (C), 70.8 (CH), 65.5 (CH_2), 19.7 (CH_2), 16.8 (CH_3), 9.4 (CH), 7.1 (CH_2); IR (neat, cm^{-1}) 3313 (m), 3079 (m), 3002 (s), 2925 (s), 2856 (m), 1663 (m), 1219 (s), 1151 (s), 1079 (s), 837 (s); HRMS (ESI) calcd for $C_{10}H_{14}O$ + Na^+ 173.0937, found 173.0946.

*((3-(Methoxymethyl)-2-propylidenedihydro-2H-pyran-4(3H)-ylidene)methyl)triphenylstannane (**33**):* clear, light yellow oil (115.6 mg, 58% yield); R_f = 0.59 (hexanes/ethyl acetate, 2 × 9/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62−7.50 (m, 6H), 7.37−7.35 (m, 9H), 5.94 (d, J = 0.7 Hz, 1H), 4.63 (t, J = 7.2 Hz, 1H), 4.02 (ddd, J = 10.3, 5.5, 2.9 Hz, 1H), 3.59 (d, J = 7.3 Hz, 2H), 3.43 (ddd, J = 11.4, 10.6, 2.9 Hz, 1H), 3.39 (s, 3H), 3.28 (t, J = 7.5 Hz, 1H), 2.59 (dddd, J = 14.4, 11.5, 5.5, 1.5 Hz, 1H), 2.19 (dtd, J = 14.3, 2.9, 0.7 Hz, 1H), 2.11 (dq, J = 15.5, 7.6 Hz, 1H), 2.05 (dq, J = 15.2, 7.5 Hz, 1H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1 (C), 150.8 (C), 139.1 (C), 137.0 (CH), 129.2 (CH), 128.8 (CH), 119.8 (CH), 112.3 (CH), 74.8 (CH_2), 69.4 (CH_2), 59.0 (CH_3), 54.0 (CH), 34.7 (CH_2), 18.1 (CH_2), 14.9 (CH_3); IR (neat, cm^{-1}) 3049 (m), 2974 (m), 1111 (s), 731 (s), 699 (s); HRMS (ESI) calcd for $C_{29}H_{32}O_2Sn$ + Na^+ 555.1328, found 555.1330.

*((2-(But-1-en-1-yl)-2-methyldihydrofuran-3(2H)-ylidene)methyl)-triphenylstannane (**34**):* clear, colorless oil (76.7 mg, 46% yield, 1.00/0.10 **34**/**35**); R_f = 0.39 (hexanes/dichloromethane/ethyl ether, 20/4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63−7.56 (m, 5H), 7.43−7.35 (m, 10H), 5.95 (t, J = 2.3 Hz, 1H), 5.75 (dt, J = 15.5, 6.3 Hz, 1H), 5.51 (dt, J = 15.5, 1.5 Hz, 1H), 3.88- 3.71 (m, 2H), 2.55- 2.46 (m, 2H), 2.10 (qdd, J = 7.6, 6.1, 1.4 Hz, 2H), 1.46 (s, 3H), 1.03 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6 (C), 138.7 (C), 137.1 (CH), 132.8 (CH), 131.1 (CH), 129.2 (CH), 128.8 (CH), 113.4 (CH), 85.3 (C), 64.4 (CH_2), 35.7 (CH_2), 26.4 (CH_3), 25.4 (CH_2), 13.9 (CH_3); IR (neat, cm^{-1}) 3063 (m), 2970 (m), 2870 (m), 1616 (w), 1480 (w), 1429 (s), 1075 (s), 1059 (m), 971 (m), 728 (s), 699 (s); HRMS (ESI) calcd for $C_{28}H_{30}O_3Sn$ + Na^+ 525.1211, found 525.1214.

*((2-Methyl-2-(prop-1-en-1-yl)dihydrofuran-3(2H)-ylidene)-methyl)triphenylstannane (**35a**):* clear, colorless oil (187.0 mg, 61% yield, 1.00/0.10 **35a**/**35b**); R_f = 0.52 (hexanes/dichloromethane/ethyl ether, 20/4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61−7.55 (m, 5H), 7.42−7.36 (m, 10H), 5.92 (t, J = 2.4 Hz, 1H), 5.69 (dq, J = 15.3, 6.4 Hz, 1H), 5.52 (dq, J = 15.5, 1.6 Hz, 1H), 3.81 (ddd, J = 8.3, 7.9, 5.6 Hz, 1H), 3.74 (dt, J = 8.3, 7.5 Hz, 1H), 2.56−2.40 (m, 2H), 1.72 (dd, J = 6.4, 1.6 Hz, 3H), 1.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6 (C), 138.7 (C), 137.1 (CH), 135.0 (CH), 129.2 (CH), 128.8 (CH), 124.2 (CH), 113.4 (CH), 85.2 (C), 64.5 (CH_2), 35.7 (CH_2), 26.4 (CH_3), 17.9 (CH_3); IR (neat, cm^{-1}) 3063 (m), 2974 (m), 2926 (w), 2858 (w), 1620 (w), 1429 (s), 1075 (s), 1057 (m), 728 (s), 699 (s); HRMS (ESI) calcd for $C_{27}H_{28}OSn$ + Na^+ 511.1054, found 511.1058.

*1-(4-(4-Hydroxybut-1-yn-1-yl)phenyl)ethanone (**37c**):* orange-yellow solid (479.3 mg, 92% yield); R_f = 0.28 (hexanes/ethyl acetate, 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 3.84 (q, J = 6.2 Hz, 2H), 2.73 (t, J = 6.2 Hz, 2H), 2.60 (s, 3H), 1.76 (t, J = 6.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.6 (C), 136.1 (C), 132.0 (CH), 128.6 (C), 128.4 (CH), 90.5 (C), 81.9 (C), 61.2 (CH_2), 26.8 (CH_3), 24.1 (CH_2); IR (KBr, cm^{-1}) 3220 (m), 2952 (w), 2917 (w), 2885 (w), 1680 (s), 1602 (m), 1270 (m), 1045 (m), 834 (s), 594 (m); HRMS (ESI) calcd for $C_{12}H_{12}O_2$ + H^+ 189.0910, found 189.0910.

*4-(4-(2-Methyl-1,3-dioxolan-2-yl)phenyl)but-3-yn-1-ol (**37d**):* clear, pale yellow oil (220.3 mg, 62% yield); R_f = 0.54 (hexanes/ethyl acetate, 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.36 (m, 4H), 4.08−3.97 (m, 2H), 3.81 (q, J = 6.2 Hz, 2H), 3.83−3.69 (m, 2H), 2.69 (t, J = 6.3 Hz, 2H), 1.88 (t, J = 6.3 Hz, 1H), 1.63 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3 (C), 131.7 (CH), 125.5 (CH), 123.0 (C), 108.8 (C), 86.7 (C), 82.5 (C), 64.7 (CH_2), 61.4 (CH_2), 27.6 (CH_3), 24.0 (CH_2); IR (neat, cm^{-1}) 3413 (br, s), 2987 (s), 2958 (s), 2889 (s), 1506 (m), 1374 (s), 1248 (s), 1199 (s), 1039 (s), 839 (s); HRMS (ESI) calcd for $C_{14}H_{16}O_3$ + H^+ 233.1172, found 233.1172.

*3-Bromo-4-phenylbut-3-en-1-ol (**38a**):* clear, colorless oil (53.7 mg, 77% yield); R_f = 0.52 (hexanes/ethyl acetate, 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30−7.17 (m, 5H), 7.08 (s, 1H), 3.85 (t, J = 6.1 Hz, 2H), 2.82 (td, J = 6.1, 0.6 Hz, 2H), 1.62 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2 (C), 135.4 (CH), 128.7 (CH), 128.5 (CH), 127.7 (CH), 126.2 (C), 60.9 (CH_2), 39.3 (CH_2); IR (neat, cm^{-1}) 3350 (br, s), 3057 (m), 3025 (m), 2954 (m), 2884 (m), 1633 (m), 1494 (m), 1446 (m), 1211 (w), 1047 (s), 753 (s), 701 (s).

*3-Bromo-4-(4-methoxyphenyl)but-3-en-1-ol (**38b**):* clear, pale yellow oil (278.7 mg, 79% yield); R_f = 0.20 (hexanes/ethyl acetate, 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 8.5 Hz, 2H), 7.10 (s, 1H), 6.87 (d, J = 8.8 Hz, 2H), 3.94 (q, J = 6.0 Hz, 2H), 3.81 (s, 3H), 2.91 (td, J = 6.1, 0.6 Hz, 2H), 1.55 (t, J = 5.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2 (C), 135.0 (CH), 129.8 (CH), 128.8 (C), 124.7 (C), 114.1 (CH), 61.0 (CH_2), 55.5 (CH_3), 39.3 (CH_2); IR (neat, cm^{-1}) 3413 (br, s), 2955 (w), 2828 (w), 1606 (m), 1511 (s), 1250 (s), 1035 (m), 822 (w); HRMS (ESI) calcd for $C_{11}H_{13}BrO_2$ + Na^+ 278.9991, found 278.9981.

*3-Bromo-4-(4-(2-methyl-1,3-dioxolan-2-yl)phenyl)but-3-en-1-ol (**38c**):* clear, orange oil (63.2 mg, 44% yield); R_f = 0.50 (hexanes/ethyl acetate, 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 7.11 (s, 1H), 4.04−3.98 (m, 2H), 3.91 (q, J = 6.0 Hz, 2H), 3.78−3.72 (m, 2H), 2.88 (td, J = 6.1, 0.6 Hz, 2H), 1.83 (t, J = 6.2 Hz, 1H), 1.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9 (C), 135.8 (C), 135.1 (CH), 128.4 (CH), 126.3 (C), 125.7 (CH), 108.9 (C), 64.7 (CH_2), 61.0 (CH_2), 39.4 (CH_2), 27.7 (CH_3); IR (neat, cm^{-1}) 3433 (m), 2977 (m), 2916 (m), 2885 (m), 1251 (m), 1198 (m), 1039 (s), 871 (m); HRMS (ESI) calcd for $C_{14}H_{17}BrO_3$ + Na^+ 335.0253, found 335.0253.

*1-(4-(2-Bromo-4-hydroxybut-1-en-1-yl)phenyl)ethanone (**38d**):* clear, orange-yellow oil (21.5 mg, 82% yield); R_f = 0.50 (hexanes/ethyl acetate, 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.17 (br s, 1H), 3.96 (t, J = 6.2 Hz, 2H), 2.89 (td, J = 6.1, 0.6 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8 (C), 140.9 (C), 136.1 (C), 134.4 (CH), 128.8 (CH), 128.8 (CH), 128.5 (C), 60.7 (CH_2), 39.5 (CH_2), 26.8 (CH_3); IR (neat, cm^{-1}) 3426 (br, m), 2960 (m), 2917 (m), 2881 (m), 1680 (s), 1602 (s), 1407 (m), 1359 (m), 1268 (s), 1049 (m), 874 (m); HRMS (ESI) calcd for $C_{12}H_{13}BrO_2$ + Na^+ 290.9991, found 290.9992.

*Ethyl 3-((3-bromo-4-phenylbut-3-en-1-yl)oxy)but-2-enoate (**39a**):* colorless solid (135.4 mg, 99% yield); R_f = 0.38 (hexanes/ethyl acetate, 9/1); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.44−7.29 (m, 5H), 7.20 (s, 1H), 5.12 (s, 1H), 4.14 (t, J = 6.1 Hz, 2H), 4.08 (q, J = 7.1 Hz, 2H), 3.07 (td, J = 6.2, 0.9 Hz, 2H), 2.25 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 172.2 (C), 167.8 (C), 136.9 (C), 135.9 (CH), 129.4 (CH), 129.2 (CH), 128.5 (CH), 126.0 (C), 92.5 (CH), 66.5 (CH_2), 59.6 (CH_2), 36.3 (CH_2), 18.9 (CH_3), 14.8 (CH_3); IR (thin film, cm^{-1}) 3058 (w), 3026 (w), 2979 (m), 2935 (m), 1711 (s), 1627 (s), 1274 (m), 1142 (s), 1055 (s), 817 (m), 755 (m), 705 (m); HRMS (ESI) calcd for $C_{16}H_{19}BrO_3$ + Na^+ 361.0410, found 361.0410.

*Ethyl 3-((3-bromo-4-(4-methoxyphenyl)but-3-en-1-yl)oxy)but-2-enoate (**39b**):* clear, pale yellow oil (380.7 mg, 99% yield); R_f = 0.29 (hexanes/ethyl acetate, 9/1); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.35 (d, J = 8.2 Hz, 2H), 7.11 (s, 1H), 6.95 (d, J = 8.8 Hz, 2H), 5.12 (s, 1H), 4.13 (t, J = 6.1 Hz, 2H), 4.08 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 3.07 (td, J = 6.1, 0.6 Hz, 2H), 2.25 (s, 3H), 1.22 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 172.2 (C), 167.8 (C), 160.2 (C), 135.5 (CH), 130.5 (CH), 129.2 (C), 124.3 (C), 114.8 (CH), 92.5 (CH), 66.6 (CH_2), 59.6 (CH_2), 55.6 (CH_3), 36.4 (CH_2), 18.9 (CH_3), 14.8 (CH_3); IR (neat, cm^{-1}) 2977 (w), 2952 (w), 2836 (w), 1710 (s), 1625 (s), 1511 (s), 1251 (s), 1141 (s), 1055 (s), 819 (m); HRMS (ESI) calcd for $C_{17}H_{21}BrO_4$ + H^+ 369.0696, found 369.0696.

*Ethyl 3-((4-(4-acetylphenyl)-3-bromobut-3-en-1-yl)oxy)but-2-enoate (**39c**):* clear, colorless oil (24.1 mg, 79% yield); R_f = 0.11 (hexanes/ethyl acetate, 9/1); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 8.01 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 7.26 (s, 1H), 5.12 (s, 1H), 4.16 (t, J = 5.9 Hz, 2H), 4.07 (q, J = 7.1 Hz, 2H), 3.10 (td, J =

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5.9, 0.6 Hz, 2H), 2.59 (s, 3H), 2.25 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 197.4 (C), 172.1 (C), 167.8 (C), 141.3 (C), 137.2 (C), 135.2 (CH), 129.4 (CH), 129.4 (CH), 128.0 (C), 92.6 (CH), 66.4 (CH_2), 59.6 (CH_2), 36.5 (CH_2), 26.7 (CH_3), 18.9 (CH_3), 14.8 (CH_3); IR (neat, cm^{-1}) 2979 (w), 2936 (w), 2895 (w), 1710 (s), 1685 (s), 1626 (s), 1268 (s), 1143 (s), 1055 (s), 818 (m), 665 (m); HRMS (ESI) calcd for $C_{18}H_{21}BrO_4$ + Na^+ 403.0515, found 403.0515.

*Ethyl 3-((4-phenylbut-3-en-1-yl)oxy)but-2-enoate (**40a**):* clear, colorless oil (5.4 mg, 20% yield); R_f = 0.47 (hexanes/dichloromethane/ethyl ether, 10/4/1); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.45−7.19 (m, 5H), 6.56 (dt, J = 15.8, 1.5 Hz, 1H), 6.34 (dt, J = 15.9, 6.8 Hz, 1H), 5.08 (s, 1H), 4.07 (q, J = 7.1 Hz, 2H), 3.97 (t, J = 6.6 Hz, 2H), 2.64 (qd, J = 6.6, 1.5 Hz, 2H), 2.26 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 172.6 (C), 168.0 (C), 138.4 (C), 133.0 (CH), 129.4 (CH), 128.1 (CH), 126.9 (CH), 126.8 (CH), 92.1 (CH), 68.4 (CH_2), 59.5 (CH_2), 33.0 (CH_2), 19.0 (CH_3), 14.8 (CH_3); IR (neat, cm^{-1}) 3060 (w), 3028 (w), 2979 (m), 2933 (m), 1710 (s), 1624 (s), 1275 (m), 1141 (s), 1053 (s), 965 (m), 818 (m), 730 (m), 694 (m); HRMS (ESI) calcd for $C_{16}H_{20}O_3$ + Na^+ 283.1305, found 283.1305.

*Ethyl 3-((4-(4-methoxyphenyl)but-3-en-1-yl)oxy)but-2-enoate (**40b**):* clear, colorless oil (7.4 mg, 25% yield); R_f = 0.63 (hexanes/dichloromethane/ethyl ether, 5/5/1); ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.34 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.49 (dt, J = 15.8, 1.5 Hz, 1H), 6.17 (dt, J = 15.8, 6.9 Hz, 1H), 5.07 (s, 1H), 4.07 (q, J = 7.1 Hz, 2H), 3.94 (t, J = 6.6 Hz, 2H), 3.78 (s, 3H), 2.60 (qd, J = 6.7, 1.5 Hz, 2H), 2.25 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 172.6 (C), 168.0 (C), 160.1 (C), 132.5 (CH), 131.1 (C), 128.1 (CH), 124.3 (CH), 114.8 (CH), 92.1 (CH), 68.6 (CH_2), 59.5 (CH_2), 55.5 (CH_3), 33.0 (CH_2), 19.0 (CH_3), 14.8 (CH_3); IR (neat, cm^{-1}) 2980 (w), 2952 (m), 2934 (m), 2835 (w), 1709 (s), 1622 (s), 1512 (s), 1276 (s), 1249 (s), 1141 (s), 1052 (s), 967 (m), 821 (m); HRMS (ESI) calcd for $C_{17}H_{22}O_4$ + H^+ 291.1591, found 291.1592.

*Ethyl 2-(3-benzylidene-2-methyltetrahydrofuran-2-yl)acetate (**41a**):* clear, colorless oil (9.5 mg, 35% yield); R_f = 0.17 (hexanes/dichloromethane/ethyl ether, 10/4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.30 (m, 4H), 7.25−7.20 (m, 1H), 6.23 (t, J = 2.4 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 4.06 (ddd, J = 8.3, 7.6, 6.0 Hz, 1H), 3.96 (ddd, J = 8.7, 7.5, 6.8 Hz, 1H), 3.01−2.86 (m, 2H), 2.70 (d, J = 19.1 Hz, 1H), 2.68 (d, J = 19.5 Hz, 1H), 1.51 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4 (C), 147.4 (C), 137.7 (C), 128.6 (CH), 128.4 (CH), 126.9 (CH), 120.7 (CH), 83.2 (C), 65.8 (CH_2), 60.5 (CH_2), 45.6 (CH_2), 31.8 (CH_2), 26.4 (CH_3), 14.5 (CH_3); IR (neat, cm^{-1}) 2979 (m), 2921 (m), 2860 (w), 1733 (s), 1448 (w), 1180 (m), 1034 (m), 695 (s); HRMS (ESI) calcd for $C_{16}H_{20}O_3$ + Na^+ 283.1305, found 283.1303.

*Ethyl 2-(3-(4-methoxybenzylidene)-2-methyltetrahydrofuran-2-yl)acetate (**41b**):* clear, colorless oil (10 mg, 33% yield); R_f = 0.33 (hexanes/dichloromethane/ether, 5/5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.15 (t, J = 2.4 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 4.03 (ddd, J = 8.7, 7.9, 6.0 Hz, 1H), 3.97−3.91 (m, 1H), 3.79 (s, 3H), 2.95−2.81 (m, 2H), 2.66 (d, J = 20.3 Hz, 1H), 2.64 (d, J = 20.3 Hz, 1H), 1.48 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5 (C), 158.6 (C), 145.0 (C), 130.5 (C), 129.6 (CH), 120.1 (CH), 114.0 (CH), 83.2 (C), 65.8 (CH_2), 60.5 (CH_2), 55.5 (CH_3), 45.7 (CH_2), 31.7 (CH_2), 26.3 (CH_3), 14.5 (CH_3); IR (neat, cm^{-1}) 2799 (m), 2917 (m), 1735 (s), 1608 (m), 1512 (s), 1250 (s), 1177 (m), 1033 (m), 826 (w); HRMS (ESI) calcd for $C_{17}H_{22}O_4$ + H^+ 291.1591, found 291.1590.

*Ethyl 4-benzylidene-2-methyltetrahydro-2H-pyran-3-carboxylate (**42a**):* clear, colorless oil (9.1 mg, 34% yield, 1.00/1.00 dr); R_f = 0.22 (hexanes/dichloromethane/ethyl ether, 10/4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.30 (m, 4H), 7.27−7.20 (m, 6H), 6.49 (d, J = 1.2 Hz, 1H), 6.46 (d, J = 1.2 Hz, 1H), 4.27 (q, J = 7.0 Hz, 2H); 4.25−4.13 (m, 3H), 4.10 (dd, J = 11.1, 6.0 Hz, 1H), 3.70 (qd, J = 6.5, 3.6 Hz, 1H), 3.59−3.52 (m, 1H), 3.54 (d, J = 3.2 Hz, 1H), 3.50 (qd, J = 6.4, 3.4 Hz, 1H), 3.38 (ddd, J = 12.3, 11.1, 2.8 Hz, 1H), 3.24−3.12 (m, 1H), 3.17 (d, J = 3.2 Hz, 1H), 2.91 (dddd, J = 14.3, 12.3, 6.3, 2.0 Hz, 1H), 2.66 (dt, J = 14.3, 1.2 Hz, 1H), 2.14 (dt, J = 13.6, 1.2 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H), 1.31 (d, J = 6.4 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.23 (d, J = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2 (C), 171.0 (C), 136.9 (C), 136.6 (C), 135.6 (CH), 135.4 (CH), 129.2 (CH), 128.9 (CH), 128.5 (CH), 128.4 (CH), 127.5 (CH), 127.2 (CH), 127.0 (CH), 126.9 (CH), 75.4 (CH), 75.0 (CH), 69.5 (CH_2), 68.3 (CH_2), 60.7 (CH_2), 60.5 (CH_2), 56.0 (CH), 50.1 (CH), 33.9 (CH_2), 27.3 (CH_2), 19.4 (CH_3), 14.5 (CH_3), 14.5 (CH_3); IR (neat, cm^{-1}) 2978 (m), 2849 (m), 1735 (s), 1447 (m), 1262 (m), 1150 (s), 1092 (s), 1059 (m), 749 (m), 700 (s); HRMS (ESI) calcd for $C_{16}H_{20}O_3$ + H^+ 261.1485, found 261.1484.

*Ethyl 4-(4-methoxybenzylidene)-2-methyltetrahydro-2H-pyran-3-carboxylate (**42b**):* clear, colorless oil (4.7 mg, 16% yield, 1.00/0.62 dr); R_f = 0.44 (hexanes/dichloromethane/ethyl ether, 5/5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, J = 8.7 Hz, 2H, major), 7.16 (d, J = 8.7 Hz, 2H, minor), 6.88 (d, J = 8.7 Hz, 2H, major), 6.86 (d, J = 8.7 Hz, 2H, minor), 6.42 (d, J = 1.2 Hz, 1H, major), 6.39 (d, J = 1.2 Hz, 1H, minor), 4.26 (q, J = 7.2 Hz, 2H, major), 4.23 (q, J = 7.2 Hz, 2H, minor), 4.20−4.12 (m, 1H, major), 4.09 (dd, J = 10.9, 5.8 Hz, 1H, minor), 3.82 (s, 3H, major), 3.81 (s, 3H, minor), 3.69 (qd, J = 6.4, 3.4 Hz, 1H, minor), 3.58−3.52 (m, 2H, major), 3.49 (qd, J = 6.4, 3.4 Hz, 1H, major), 3.37 (ddd, J = 12.7, 11.1, 2.8 Hz, 1H, minor), 3.17−3.08 (m, 1H, major), 3.14 (d, J = 3.2 Hz, 1H, minor), 2.90 (dddd, J = 14.3, 12.3, 6.0, 2.0 Hz, 1H, minor), 2.64 (d, J = 14.3 Hz, 1H, minor), 2.11 (d, J = 13.9 Hz, 1H, major), 1.34 (t, J = 7.2 Hz, 3H, major), 1.30 (d, J = 6.8 Hz, 3H, minor), 1.29 (t, J = 7.2 Hz, 3H, minor), 1.23 (d, J = 6.8 Hz, 3H, major); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4 (C, minor), 171.2 (C, major), 158.7 (C, major), 158.6 (C, minor), 134.1 (C, minor), 133.9 (C, major), 130.4 (CH, minor), 130.2 (CH, major), 129.4 (C, minor), 129.1 (C, major), 127.1 (CH, minor), 126.8 (CH, major), 114.0 (CH, major), 113.8 (CH, minor), 75.4 (CH, minor), 74.9 (CH, major), 69.5 (CH_2, major), 68.3 (CH_2, minor), 60.8 (CH_2, major), 60.6 (CH_2, minor), 56.0 (CH_3, minor), 55.5 (CH_3, major), 50.1 (CH), 33.9 (CH_2, major), 27.3 (CH_2, minor), 19.5 (CH_3, minor), 19.5 (CH_3, major), 14.6 (CH_3, major), 14.6 (CH_3, minor); IR (neat, cm^{-1}) 2975 (m), 2957 (m), 2917 (m), 2849 (m), 1732 (s), 1607 (s), 1511(s), 1296 (m), 1249 (s), 1177 (s), 1149 (s), 1091 (s), 1031 (s), 832 (m), 666 (m); HRMS (ESI) calcd for $C_{17}H_{22}O_4$ + H^+ 291.1591, found 291.1590.

*((7-(2-Methoxyethyl)-7,7a-dimethyltetrahydro-2H-furo[3,4-b]pyran-4(3H)-ylidene)methyl)triphenylstannane (**49a**):* clear, light yellow oil (34.9 mg, 55% yield, 1.00:0.20 dr); R_f = 0.12 (hexanes/ethyl acetate, 2 × 9/1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59−7.48 (m, 6H), 7.38−7.34 (m, 9H), 5.92 (s, 1H), 3.94 (t, J = 9.2 Hz, 1H), 3.87 (t, J = 8.8 Hz, 1H), 3.77 (dd, J = 11.6, 5.0 Hz, 1H), 3.58−3.53 (m, 2H), 3.48 (td, J = 12.2, 2.5 Hz, 1H), 3.35 (s, 3H), 3.15 (t, J = 9.5 Hz, 1H), 2.54 (td, J = 12.8, 6.3 Hz, 1H), 2.03 (d, J = 14.1 Hz, 1H), 1.76−1.70 (m, 1H), 1.66−1.62 (m, 1H), 1.21 (s, 3H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4 (C), 138.9 (C), 137.1 (CH), 129.2 (CH), 128.9 (CH), 122.7 (CH), 87.7 (C), 84.3 (C), 69.3 (CH_2), 68.4 (CH_2), 62.4 (CH_2), 58.9 (CH_3), 56.2 (CH), 36.4 (CH_2), 33.4 (CH_2), 17.8 (CH_3), 14.8 (CH_3); IR (neat, cm^{-1}) 3063 (m), 2931 (s), 1605 (m), 1115 (s), 1041 (s), 728 (s), 699 (s); HRMS (ESI) calcd for $C_{31}H_{36}O_3Sn$ + H^+ 573.1760, found 573.1754.

*((3-(((4-Methoxybut-2-en-2-yl)oxy)methyl)-2-methyldihydro-2H-pyran-4(3H)-ylidene)methyl)triphenylstannane (**50a**):* clear, light yellow oil (17.4 mg, 27% yield, 1.00/0.25 dr); R_f = 0.56 (hexanes/ethyl acetate, 2 × 4/1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61−7.49 (m, 6H), 7.37−7.33 (m, 9H), 5.88 (s, 1H), 4.66 (t, J = 7.5 Hz, 1H), 3.99 (dd, J = 9.6, 6.5 Hz, 1H), 3.92 (dd, J = 7.5, 1.1 Hz, 2H), 3.85 (dd, J = 9.8, 7.7 Hz, 2H), 3.73 (qd, J = 6.7, 2.7 Hz, 1H), 3.31 (s, 3H), 3.31−3.27 (m, 1H), 2.78 (td, J = 7.3, 2.4 Hz, 1H), 2.35 (tdd, J = 12.9, 5.6, 1.0 Hz, 1H), 2.04 (dt, J = 13.7, 2.6 Hz, 1H), 1.84 (s, 3H), 1.21 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.4 (C), 158.0 (C), 139.3 (C), 137.0 (CH), 129.2 (CH), 128.8 (CH), 119.0 (CH), 93.9 (CH), 76.3 (CH), 69.1 (CH_2), 68.6 (CH_2), 64.2 (CH_2), 57.6 (CH_3), 52.8 (CH), 35.0 (CH_2), 18.4 (CH_3), 16.8 (CH_3); IR (neat, cm^{-1}) 3063 (s), 2932 (s), 1662 (m), 1074 (s), 1042 (s), 728 (s), 699 (s); HRMS (ESI) calcd for $C_{31}H_{36}O_3Sn$ + Na^+ 595.1580, found 595.1573.

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*((7-(2,2-Dideuterio-2-methoxyethyl)-7,7a-dimethyltetrahydro-2H-furo[3,4-b]pyran-4(3H)-ylidene)methyl)triphenylstannane (**49b**):* clear, light yellow oil (35.3 mg, 44% yield, 1.00:0.24 dr); R_f = 0.47 (hexanes/ethyl acetate, 2 × 4/1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64−7.44 (m, 6H), 7.38−7.33 (m, 9H), 5.92 (s, 1H), 3.94 (t, J = 9.2 Hz, 1H), 3.87 (t, J = 8.8 Hz, 1H), 3.77 (dd, J = 11.5, 5.0 Hz, 1H), 3.48 (td, J = 12.2, 2.4 Hz, 1H), 3.34 (s, 3H), 3.15 (t, J = 9.2 Hz, 1H), 2.54 (tdd, J = 12.8, 6.2, 1.0 Hz, 1H), 2.02 (dt, J = 13.1, 1.0 Hz, 1H), 1.70 (s, 1H), 1.64 (s, 1H), 1.21 (s, 3H), 1.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.5 (C), 138.97 (C), 137.0 (CH), 129.3 (CH), 128.9 (CH), 122.7 (CH), 87.7 (C), 84.3 (C), 68.4 (CH_2), 62.4 (CH_2), 58.9 (CH_3), 56.2 (CH), 36.2 (CH_2), 33.4 (CH_2), 17.8 (CH_3), 14.8 (CH_3); IR (neat, cm^{-1}) 3058 (m), 2916 (s), 1602 (m), 1093 (m), 1074 (s), 728 (s), 698 (s); HRMS (ESI) calcd for $C_{31}H_{34}O_3D_2Sn$ + H^+ 575.1886, found 575.1893.

*((3-(((4,4-Dideuterio-4-methoxybut-2-en-2-yl)oxy)methyl)-2-methyldihydro-2H-pyran-4(3H)-ylidene)methyl)triphenylstannane (**50b**):* clear, light yellow oil (29.9 mg, 39% yield, 1.00/0.05 dr); R_f = 0.51 (hexanes/ethyl acetate, 2 × 4/1); ^{1}H NMR ($(CD_3)_2CO$, 300 MHz) δ 7.71−7.52 (m, 6H), 7.44−7.37 (m, 9H), 5.95 (s, 1H), 4.69 (s, 1H), 4.06 (dd, J = 10.0, 6.5 Hz, 1H), 3.88 (dd, J = 10.0, 8.0 Hz, 1H), 3.84 (td, J = 5.7, 2.1 Hz, 1H), 3.73 (qd, J = 6.6, 2.7 Hz, 1H), 3.30 (td, J = 11.5, 2.8 Hz, 1H), 3.21 (s, 3H), 2.87 (td, J = 8.0, 2.5 Hz, 1H), 2.41 (tdd, J = 11.7, 5.7, 1.0 Hz, 1H), 2.14 (tdd, J = 12.6, 5.7, 1.0 Hz, 1H), 1.82 (d, J = 0.8 Hz, 3H), 1.21 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($(CD_3)_2CO$, 75 MHz) δ 160.0 (C), 157.7 (C), 139.9 (C), 137.5 (CH), 129.9 (CH), 129.5 (CH), 118.7 (CH), 95.0 (CH), 76.9 (CH), 68.8 (CH_2), 64.8 (CH_2), 56.8 (CH_3), 53.4 (CH), 35.8 (CH_2), 18.6 (CH_3), 16.7 (CH_3); IR (neat, cm^{-1}) 3058 (s), 2918 (s), 1653 (m), 1093 (s), 1071 (s), 728 (s), 698 (s); HRMS (ESI) calcd for $C_{31}H_{34}O_3D_2Sn$ + Na^+ 597.1705, found 597.1696.

*((5,5-Dideuterio-7-(2-methoxyethyl)-7,7a-dimethyltetrahydro-2H-furo[3,4-b]pyran-4(3H)-ylidene)methyl)triphenylstannane (**49c**):* clear, light yellow oil (44.0 mg, 46% yield, 1.00/0.27 dr); R_f = 0.44 (hexanes/ethyl acetate, 2 × 4/1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64−7.44 (m, 6H), 7.38−7.34 (m, 9H), 5.92 (s, 1H), 3.77 (dd, J = 11.5, 5.1 Hz, 1H), 3.56 (t, J = 7.1 Hz, 2H), 3.48 (td, J = 12.3, 2.3 Hz, 1H), 3.35 (s, 3H), 3.13 (s, 1H), 2.52 (tdd, J = 13.1, 6.3, 1.2 Hz, 1H), 2.02 (dt, J = 14.1, 1.2 Hz, 1H), 1.77−1.68 (m, 2H), 1.21 (s, 3H), 1.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.5 (C), 139.0 (C), 137.0 (CH), 129.3 (CH), 128.8 (CH), 122.7 (CH), 87.6 (C), 84.4 (C), 69.4 (CH_2), 62.4 (CH_2), 58.9 (CH_3), 56.0 (CH), 36.5 (CH_2), 33.4 (CH_2), 17.8 (CH_3), 14.8 (CH_3); IR (neat, cm^{-1}) 3063 (m), 2930 (s), 1605 (m), 1095 (s), 1074 (s), 730 (s), 699 (s); HRMS (ESI) calcd for $C_{31}H_{34}O_3D_2Sn$ + H^+ 575.1886, found 575.1887.

*((3-(Dideuterio((4-methoxybut-2-en-2-yl)oxy)methyl)-2-methyldihydro-2H-pyran-4(3H)-ylidene)methyl)triphenylstannane (**50c**):* clear, light yellow oil (40.7 mg, 42% yield, 1.00/0.11 dr); R_f = 0.53 (hexanes/ethyl acetate, 2 × 4/1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66−7.46 (m, 6H), 7.38−7.32 (m, 9H), 5.88 (s, 1H), 4.67 (t, J = 7.5 Hz, 1H), 3.93 (d, J = 7.6 Hz, 2H), 3.86 (ddd, J = 10.9, 5.6, 2.1 Hz, 1H), 3.74 (qd, J = 6.4, 2.7 Hz, 1H), 3.31 (s, 3H), 3.30−3.28 (m, 1H), 2.77 (s, 1H), 2.35 (tdd, J = 12.7, 5.7, 1.0 Hz, 1H), 2.04 (dt, J = 12.7, 3.0 Hz, 1H), 1.85 (s, 3H), 1.21 (d, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.4 (C), 158.0 (C), 139.3 (C), 137.0 (CH), 129.1 (CH), 128.8 (CH), 119.0 (CH), 93.9 (CH), 76.3 (CH), 69.1 (CH_2), 68.6 (CH_2), 57.6 (CH_3), 52.6 (CH), 35.0 (CH_2), 18.6 (CH_3), 16.7 (CH_3); IR (neat, cm^{-1}) 3052 (s), 2984 (s), 1661 (m), 1082 (s), 1075 (s), 733 (s), 703 (s); HRMS (ESI) calcd for $C_{31}H_{34}O_3D_2Sn$ + H^+ 575.1886, found 575.1883.

*((5,5-Dideuterio-7-(2,2-dideuterio-2-methoxyethyl)-7,7a-dimethyltetrahydro-2H-furo[3,4-b]pyran-4(3H)-ylidene)methyl)-triphenylstannane (**49d**):* clear, light yellow oil (31.7 mg, 35% yield, 1.00/0.24 dr); R_f = 0.44 (hexanes/ethyl acetate, 2 × 4:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63−7.44 (m, 6H), 7.38−7.34 (m, 9H), 5.92 (s, 1H), 3.77 (dd, J = 11.5, 5.1 Hz, 1H), 3.47 (td, J = 12.2, 2.3 Hz, 1H), 3.34 (s, 3H), 3.13 (s, 1H), 2.54 (tdd, J = 13.3, 6.2, 1.0 Hz, 1H), 2.03 (dt, J = 14.1, 1.0 Hz, 1H), 1.69 (s, 1H), 1.63 (s, 1H), 1.20 (s, 3H), 1.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.5 (C), 139.0 (C), 137.0 (CH), 129.3 (CH), 128.8 (CH), 122.7 (CH), 87.6 (C), 84.4 (C), 62.4 (CH_2), 58.9 (CH_3), 56.0 (CH), 36.2 (CH_2), 33.4 (CH_2), 17.8 (CH_3), 14.8 (CH_3); IR (neat, cm^{-1}) 3063 (m), 2930 (s), 1605 (m), 1095 (s), 1074 (s), 730 (s), 699 (s); HRMS (ESI) calcd for $C_{31}H_{32}O_3D_4Sn$ + H^+ 577.2011, found 577.2003.

*((3-(Dideutereo((4,4-dideuterio-4-methoxybut-2-en-2-yl)oxy)-methyl)-2-methyldihydro-2H-pyran-4(3H)-ylidene)methyl)-triphenylstannane (**50d**):* clear, light yellow oil (45.2 mg, 50% yield, 1.00/0.20 dr); R_f = 0.50 (hexanes/ethyl acetate, 2 × 4/1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66−7.46 (m, 6H), 7.37−7.33 (m, 9H), 5.88 (s, 1H), 4.66 (s, 1H), 3.85 (ddd, J = 10.9, 5.6, 2.0 Hz, 1H), 3.73 (qd, J = 6.6, 2.6 Hz, 1H), 3.31 (s, 3H), 3.30−3.28 (m, 1H), 2.78 (s, 1H), 2.35 (tdd, J = 12.7, 5.7, 0.9 Hz, 1H), 2.04 (dt, J = 14.0, 2.7 Hz, 1H), 1.85 (s, 3H), 1.21 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.4 (C), 158.1 (C), 139.3 (C), 137.0 (CH), 129.2 (CH), 128.8 (CH), 119.0 (CH), 93.7 (CH), 76.3 (CH), 68.6 (CH_2), 57.5 (CH_3), 52.6 (CH), 35.0 (CH_2), 18.4 (CH_3), 16.8 (CH_3); IR (neat, cm^{-1}) 3058 (s), 2913 (s), 1657 (m), 1095 (s), 1071 (m), 728 (s), 698 (s); HRMS (ESI) calcd for $C_{31}H_{32}O_3D_4Sn$ + H^+ 577.2011, found 577.2023.

*((7-(1-Deuterio-2-methoxyethyl)-7,7a-dimethyltetrahydro-2H-furo[3,4-b]pyran-4(3H)-ylidene)methyl)triphenylstannane (**49e**):* clear, light yellow oil (32.1 mg, 36% yield, 1.00/0.30 dr); R_f = 0.28 (hexanes/ethyl acetate, 2 × 4/1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58−7.55 (m, 6H, minor), 7.54−7.48 (m, 6H, major), 7.38−7.34 (m, 9H, major/minor), 5.98 (s, 1H, minor), 5.92 (s, 1H, major), 3.93 (t, J = 9.2 Hz, 1H, major/minor), 3.87 (t, J = 8.8 Hz, 1H, major/minor), 3.77 (dd, J = 11.4, 6.0 Hz, 1H), 3.55 (d, J = 7.8 Hz, 2H), 3.47 (td, J = 12.0, 2.6 Hz, 1H, major/minor), 3.34 (s, 3H, major), 3.26 (s, 3H, minor), 3.14 (t, J = 9.2 Hz, 1H, major), 3.09 (t, J = 9.2 Hz, 1H, minor), 2.74 (tdd, J = 13.5, 6.0, 1.7 Hz, 1H, minor), 2.74 (tdd, J = 13.5, 6.3, 1.0 Hz, 1H, major), 2.22 (d, J = 13.7 Hz, 1H, minor), 2.02 (d, J = 14.1 Hz, 1H, major), 1.70 (t, J = 7.2 Hz, 0.5H, major/minor), 1.61 (t, J = 7.8 Hz, 0.5H, major/minor), 1.24 (s, 3H, minor), 1.20 (s, 3H, minor), 1.15 (s, 3H, major), 1.09 (s, 3H, minor); ^{1}D NMR ($CHCl_3$) δ 1.67 (s, br); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.1 (C, minor), 154.5 (C, major), 139.0 (C, major), 138.9 (C, minor), 137.1 (CH, minor), 137.0 (CH, major), 129.4 (CH, minor), 129.3 (CH, major), 128.9 (CH, minor), 128.9 (CH, major), 122.7 (CH, major), 122.4 (CH, minor), 87.6 (C), 84.3 (C), 69.3 (CH_2, major), 69.0 (CH_2, minor), 68.4 (CH_2, major), 67.5 (CH_2, minor), 62.7 (CH_2, minor), 62.4 (CH_2, major), 59.0 (CH_3, major), 58.8 (CH_3, minor), 56.2 (CH, major), 53.2 (CH, minor), 33.4 (CHD), 29.9 (CH_2), 17.8 (CH_3, major), 17.6 (CH_3, minor), 14.8 (CH_3, major), 14.4 (CH_3, minor); IR (neat, cm^{-1}) 3051 (s), 2934 (s), 1606 (s), 1074 (s), 1041 (s), 732 (s), 699 (s); HRMS (ESI) calcd for $C_{31}H_{35}O_3DSn$ + Na^+ 596.1624, found 596.1625.

*((2-Deuterio-3-(((4-methoxybut-2-en-2-yl)oxy)methyl)-2-methyldihydro-2H-pyran-4(3H)-ylidene)methyl)triphenylstannane (**50e**):* clear, light yellow oil (28.5 mg, 40% yield, 1.00/0.17 dr); R_f = 0.53 (hexanes/ethyl acetate, 2 × 4/1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66−7.46 (m, 6H), 7.37−7.33 (m, 9H), 5.88 (s, 1H), 4.67 (t, J = 7.6 Hz, 1H), 4.00 (dd, J = 9.7, 6.5 Hz, 1H), 3.93 (d, J = 7.6 Hz, 2H), 3.85 (dd, J = 9.9, 7.6 Hz, 2H), 3.33−3.27 (m, 1H), 3.32 (s, 3H), 2.78 (t, J = 7.2 Hz, 1H), 2.36 (tdd, J = 12.8, 6.0, 1.0 Hz, 1H), 2.05 (dt, J = 12.8, 2.4 Hz, 1H), 1.85 (s, 3H), 1.21 (s, 3H); ^{1}D NMR ($CHCl_3$) δ 3.72 (s, br); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.4 (C), 158.0 (C), 139.3 (C), 137.0 (CH), 129.2 (CH), 128.8 (CH), 119.0 (CH), 93.9 (CH), 75.8 (t, J = 20.7 Hz, CD), 69.1 (CH_2), 68.5 (CH_2), 64.2 (CH_2), 57.6 (CH_3), 52.7 (CH), 35.1 (CH_2), 18.3 (CH_3), 16.7 (CH_3); IR (neat, cm^{-1}) 3051 (s), 2933 (s), 1662 (m), 1074 (s), 1041 (s), 735 (s), 700 (s); HRMS (ESI) calcd for $C_{31}H_{35}O_3DSn$ + Na^+ 596.1624, found 596.1625.

■ ASSOCIATED CONTENT

Supporting Information

Figures and tables giving ^{1}H NMR and ^{13}C NMR spectra for all new compounds and absolute energies and Cartesian coordinates for calculated radical intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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