

Studies on the Base-Promoted Conversion of Conjugated Alkynyl Esters to α -Substituted α -Allenyl Esters

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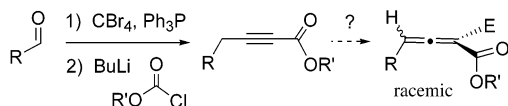
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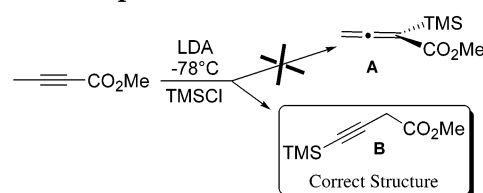
We report the development of an efficient method for the conversion of a variety of conjugated alkynyl esters to α -substituted conjugated allenyl esters (racemic) through the use of strong amide bases. Substantially improved yields over typical enolate formation conditions were observed with the use of 2 equiv of lithium diisopropylamide. Trapping studies indicate that the second equivalent of base likely leads to the dianion intermediate, which upon addition of methyl iodide, trimethylsilyl chloride, or tributyltin chloride gives mixtures of α -substituted conjugated allenyl and β,γ -alkynyl deconjugated esters. Further optimization revealed that additive salts such as LiCl lead primarily to the allenyl product while the use of HMPA as a cosolvent gives the β,γ -alkynyl deconjugated alkylation product. The role of base, base concentration, and electrophile on product yield and selectivity is also discussed.

As part of our plan for the synthesis of bicyclic pyran HIV entry-inhibitors, we required a reliable method to obtain a wide variety of conjugated allenyl carbonyl compounds. In the case of allenyl esters, we envisioned that these compounds could be obtained from the corresponding alkynyl esters using amide bases followed by trapping with various electrophiles. This route to allenyl esters further attracted our attention since a wide variety of alkynyl esters can be readily prepared in two steps by converting aldehydes to the corresponding vinyl dibromides followed by the Corey–Fuchs reaction¹ with use of chloroformates to trap the alkynide.



Allenyl esters substituted at the α -position have been prepared in several ways including the alkoxycarbonylation of allenyl and propynyl halides,² and reaction of phosphorus ylides with ketenes³ and acid chlorides.⁴ Recently, 3-bromo-2-alkynoate methyl ester was converted to the 2-substituted allenyl ester through an organostannane intermediate.⁵ However, methods to convert alkynyl esters to the corresponding α -alkylated allenes have received very little attention despite the potential synthetic utility of this approach. As part of a study involving electrogenerated bases, Tokuda briefly describes the reaction of ethyl 2-butynoate with lithium diisopropylamide (LDA) and methyl iodide yielding both

SCHEME 1. Structure Misassignment in Ainsworth's Paper



allene and deconjugated alkyne products.⁶ However, Tokuda's report gave no reaction yield and provided insufficient experimental detail to repeat the reaction. Ainsworth, following a related procedure,⁷ reported the conversion of methyl 2-butynoate to the corresponding α -trimethylsilyl allenyl ester.⁸ While the procedure of Ainsworth did provide adequate experimental detail, we discovered the ¹H NMR data given in support of the putative α -trimethylsilyl allenyl ester product **A** were in fact from the spectrum of its isomer, deconjugated alkynyl ester **B** (Scheme 1).⁹

Because of conflicting information regarding the strong base-promoted conversion of conjugated alkynyl esters to the corresponding allenes, we undertook a series of studies aimed at identifying and optimizing the important reaction parameters in this transformation.

Effect of Base. We examined a variety of amide bases in their reaction with model compound **1** at low temper-

(6) Tokuda, M.; Nishio, O. *J. Org. Chem.* **1985**, *50*, 1592.

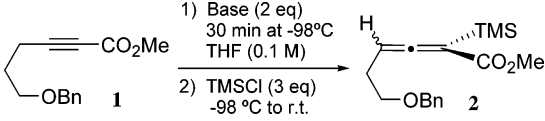
(7) (a) Rathke, M. W.; Sullivan, D. *Tetrahedron Lett.* **1972**, *13*, 4249.

(b) Meyer H. H. *Liebigs Ann. Chem.* **1978**, 327.

(8) Shen, C. C.; Ainsworth, C. *Tetrahedron Lett.* **1979**, *20*, 89.

(9) We prepared compound **B** and characterized this material by mass spectrometry and ¹H and ¹³C NMR analyses. The NMR data (especially ¹³C NMR) clearly demonstrate the existence of the alkyne functionality and the α -methylene groups. Since our ¹H NMR spectrum of **B** exactly matches the spectrum reported by Ainsworth, we conclude that his reported structure for the silylation product resulting from methyl 2-butynoate must be structure **B** and not allenyl ester **A** as reported.

(1) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *36*, 3769.
(2) Nguyen, D. T.; Elsevier: C. J. Vrieze, K. *J. Organomet. Chem.* **1987**, 325 C23.
(3) (a) Hamlet, Z.; Barker, W. D. *Synthesis* **1970**, *2*, 543. (b) Marshall, J. A.; Wolf, M. A.; Wallace, E. M. *J. Org. Chem.* **1997**, *62*, 367.
(4) Lang, von R. W.; Hansen, H. J. *Helv. Chim. Acta* **1980**, *63*, 438.
(5) Winkler, J. D.; Quinn, K. J.; MacKinnon, C. H.; Hiscock, S. D.; McLaughlin, E. C. *Org. Lett.* **2003**, *5*, 1805.

TABLE 1. Effect of Base and Base Equivalents on the Conversion of Alkynyl Ester **1 to TMS-allene **2****


entry	base	equiv	% yield of 2 ^a
2	LDA	1.0	14
3	LDA	1.5	44
4	LDA	2.0	58
5	LDA	2.5	36
6	LDA	3.0	38
7	LiHMDS	2.0	14 ^b
8	NaHMDS	2.0	10 ^b
9	KHMDS	2.0	11 ^b
9	LiTMP	2.0	34

^a Isolated yields. ^b The main byproduct is methyl 6-benzyloxy-hex-3-ynoate.

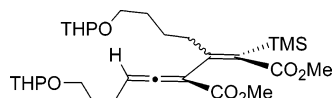
atures (−98 °C) followed by the addition of trimethylsilyl chloride (TMS-Cl) (Table 1). Of the bases used in this reaction, lithium diisopropylamide (LDA) gave the highest yields. Initially, 1 equiv of LDA was used giving allene product **2** although in very low yield (14%).

The use of only 1 equiv of base in this reaction gives mainly a mixture of condensation byproducts.¹⁰ In an attempt to reduce side product formation through the self-condensation mechanism, ester **1** was added slowly to a cold solution of LDA (1 equiv) with the final base concentration in the reaction mixture being 0.1 M. However, this reverse addition approach also failed to give allene **2**. The addition of a second equivalent of LDA dramatically improved the yield of **2** to 58% (Table 1, entry 3), which represents the highest reported yield for this conversion.⁸ More than 2 equiv of LDA gave inferior results.

The use of 1 or 2 equiv of lithium, sodium, and potassium hexamethyl disilyl azide bases gave considerably lower yields of **2** than LDA (Table 1, entries 6–8). These silyl azide bases gave mainly the deconjugated alkynyl ester product (methyl 6-benzyloxy-hex-3-ynoate). The failure of the silyl azide bases to give α-substituted allenes seems more likely to be related to base strength than size since the more bulky lithium tetramethylpiperidide (LiTMP) gave a significantly better yield of allene **2** (Table 1, entry 9).

We next attempted the alkylation reaction of **1** with *tert*-butyllithium (not shown), a considerably stronger base than LDA. We reasoned that this base should rapidly and irreversibly deprotonate **1** and thereby remove the possibility of self-condensation reactions. When *tert*-butyllithium was added to **1**, the only discernible product was the corresponding *tert*-butyl ketone, which was formed in 20% yield.

(10) THF solutions of **1** with 1 equiv of LDA are unstable even at −98 °C. After 30 min, numerous polar compounds were observed by TLC analysis. NMR analysis of these polar compounds reveals a complex mixture of dimers and other unknown products. One of the major dimer byproducts isolated is likely the result of the Michael addition of the anion of **1** with starting alkynyl ester.

**TABLE 2. Effect of Base Reaction Concentration on the Yield of Allene **2** Starting from **1**, Using LDA (2 equiv) and TMS-Cl (3 equiv)**

entry	conc of LDA ^a	% yield of 2 ^b
1	0.05	24
2	0.10	58
3	0.15	42
4	0.20	34
5	0.25	35
6	0.50	27

^a In the reaction mixture. ^b Isolated yields. Reaction conditions: LDA (2 equiv), 30 min at −98 °C, followed by the addition of TMS-Cl (3 equiv), warm to rt over 12 h.

The Effect of Base Concentration. In our experiments involving the use of various bases in the conversion of **1** to **2**, the concentration of base in the reaction was fixed at 0.10 M. An earlier study of a related system⁷ suggested that the optimal base concentration would be 0.4 M. However, after examining a range of concentrations, the optimum appears to be 0.10 M (Table 2, entry 2).

Our initial experiments involving base concentration were conducted with LDA purchased from vendors.¹¹ Since we observed minor differences in the reaction outcomes using these commercial bases, we prepared fresh LDA as a dilute THF solution (approximately 0.15 M) and added it to alkyne **1** at −98 °C bringing the final base concentration in the reaction mixture to 0.10 M. TMS-Cl was then added and the reaction was allowed to warm to room temperature overnight. To our surprise, no product was formed under these conditions; nearly all the starting material was recovered.

In another experiment, a fresh THF solution of LDA was prepared at a much higher concentration (1.0 M) and this was added to a THF solution of alkyne **1** at −98 °C bringing the final base concentration in the reaction mixture to 0.10 M. TMS-Cl was then added and the reaction was allowed to warm to room temperature over the course of several hours. Allene product **2** was obtained under these conditions in yields very similar to those observed with commercially available LDA. In a control experiment, commercially obtained LDA (2.0 M) was diluted with THF to 0.15 M and allowed to stir at room temperature for 2 h. This LDA solution gave no reaction upon its addition to **1** at cold temperatures followed by the addition of TMS-Cl.

Perhaps the preparation of LDA at higher concentrations promotes the formation of higher LDA oligomer complexes that favor the deprotonation of **1** at the γ-position. We presume that these higher oligomers persist at cold temperatures even when diluted by addition to a THF solution of alkynyl ester **1**. Although cyclic dimer complexes have been observed in a wide range of concentrations,¹² the existence of other spectroscopically unobservable complexes has been postulated to explain the chemistry of LDA.¹³

(11) Acros (2.0 M solution in heptane/THF, no. 26883) and Sigma-Aldrich (2.0 M solution in heptane/THF/ethyl benzene, no. 36, 179-8).

(12) Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 794.

(13) Galiano-Roth, A. S.; Collum, D. B. *J. Am. Chem. Soc.* **1989**, *111*, 6772.

TABLE 3. Effect of Additive LiCl on the Yield of Allenylsilane **2** Starting from **1**, Using LDA (2 equiv) and TMS-Cl (3 equiv)

entry	equiv of LiCl	% yield of 2 ^a
1	0	58
2	0.4	59
3	1.0	79
4	2.0	59
5	4.0	56

^a Isolated yields. Reaction conditions: LDA (2 equiv), LiCl, TMS-Cl (3 equiv), -98 °C to rt over 12 h.

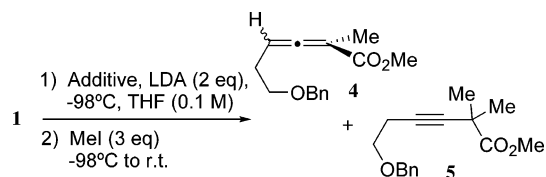
Effect of Metal Halides and Other Additives.

Generally, the addition of a metal halide salt such as LiCl to enolate forming reactions is known to favor the formation a lithio-enolate/LiCl heterodimer over the lithio-enolate homodimer and this mixed dimer is often responsible for enhanced product yields and selectivities.¹⁴ Thus we initially hypothesized that the second equivalent of lithium amide required for the efficient silylation of **1** simply functioned as a source of lithium cation for heterodimer formation. If this were true, then other sources of lithium cation should also give the improved yields observed with the second equivalent of LDA. However, the silylation reaction of alkynyl ester **1** with 1 equiv of both LDA and LiCl gave low yields (10–15%). Interestingly, the use of LiCl, in conjunction with 2 equiv of LDA, gave a significantly improved yield (79%) of allene **2**. To our knowledge, this represents the highest reported yield to date for the conversion of an alkynyl ester to the corresponding α -substituted allenyl ester.

The reaction of **1** with LDA followed by the addition of methyl iodide led to the formation of two alkylation products, allene **4** and deconjugated alkynyl ester **5** (Table 4). As in the case of the silylation reaction, the addition of LiCl improved the overall yield of the methylation reaction by approximately 20%. The added LiCl also seemed to influence the product distribution giving the highest **4**:**5** ratio (14:1) with 2 equiv of LiCl (Table 4, entry 5).

A variety of other salts were investigated for their effect on the ratio of products **4**:**5** in the methylation of alkynyl ester **1** (Table 4). While the lithium salts gave higher yields, the sodium halide series exhibited similar selectivities for allene product **4**. Thus the ratio of **4** to **5** was highest with 1 equiv of the iodide salt (10:1) and decreased as the counteranion changed to bromide, chloride, and fluoride (Table 4, entries 9–11). We also examined the potassium halide series (not shown) which were poorly soluble under the reaction conditions of 0.1 M THF and -98 °C. Not surprisingly, the ratio of **4** to **5** observed with each the potassium salts was the same as if the reaction were performed in the absence of salt (~3:1). The use of other iodide salts such as MgI₂ and Me₄NI also gave diminished ratios of **4** to **5** in the methylation of **1** relative to LiI and NaI.

Substrate Generality. With optimized conditions of 2 equiv of LDA and LiCl (1 equiv) at -98 °C, a variety of methyl alkynoates containing a secondary carbon at the γ -position (Table 5, entries 1–3 and 5) were converted to the corresponding allenylsilanes in synthetically useful

TABLE 4. Effect of Additive Metal Halide (MX) on the Yield and Product Selectivity of the Methylation Reaction of **1**

entry	additive	equiv	ratio 4 : 5 ^a	% yield ^b
1	LiF	1.0	3	62
2	LiF	0	3	47
3	LiF	1.0	4	68
4	LiCl	1.5	7	66
5	LiCl	2.0	14	60
6	LiCl	3.0	7	64
7	LiBr	1.0	3	65
8	LiI	1.0	10	56
9	NaF	1.0	2	42
10	NaCl	1.0	3	56
11	NaBr	1.0	6	53
12	NaI	1.0	10	55
13	MgI ₂	1.0	4	45
14	Me ₄ NI	1.0	3	54

^a Compounds **4** and **5** are isolated as an inseparable mixture and their ratio is determined by ¹H NMR (average of three experiments). ^b Isolated yield of **4** and **5** combined.

TABLE 5. Use of Optimized Conditions (2 equiv of LDA, 1 equiv of LiCl, and 3 equiv of TMS-Cl) in the Alkylative Conversion of Several Alkynes to Allenes

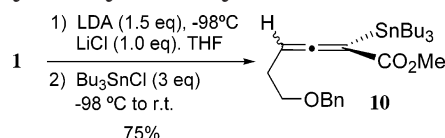
entry	R ₁	R ₂	compound	% yield ^a
1	H	CH ₂ CH ₂ OBn	2	79
2	H	CH ₂ CH ₂ OMEM	3	75
3	H	CH ₂ CH ₂ CH ₂ OTHP	6	71
4	H	CH ₂ OTBDPS	7	22
5	H	CH ₂ Ph	8	75
6	H	Ph	9	41
7		-(CH ₂) ₅ -	-	0 ^b

^a Isolated yields. ^b The allenyl amide was obtained in 48% yield { }

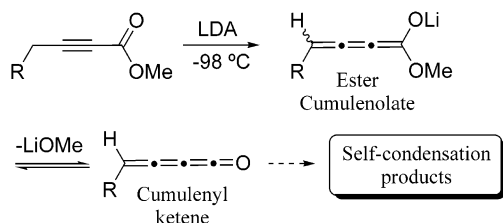
yields (71–79%). The phenyl ester analogue of compound **2** also gives similar yields (not shown). An alkynyl ester containing a δ -silyloxy group gave a low yield of the corresponding allene (entry 4) most likely due to elimination of the silyl oxide under the dianion formation conditions. By contrast, δ -phenyl-substituted alkynyl ester (entry 5) was efficiently converted to the allene. An unexpected low yield was observed in the case of methyl 4-phenylbutynoate even after several attempts to optimize the reaction (entry 6). Finally, an alkynyl ester substrate containing a tertiary carbon at the γ -position failed to give any of the desired allenyl ester product (entry 7). Instead, the major product (41%) from this reaction was the α -trimethylsilyl allenyl amide.

The dianion of alkynyl ester **1** was also reacted under the optimized conditions with a variety of other electrophiles including benzyl bromide, allyl bromide, ethyl

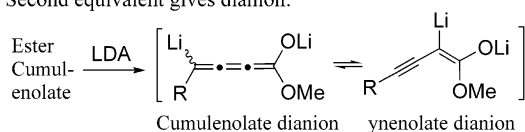
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SCHEME 2. Synthesis of α -Tributylstannyl- α -allenyl Ester 10 from Alkyne 1

SCHEME 3. Proposed Dianion Mechanism

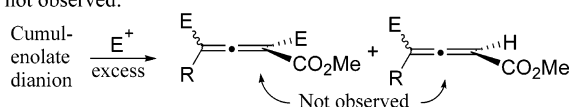
One equivalent of LDA gives condensation products:



Second equivalent gives dianion:



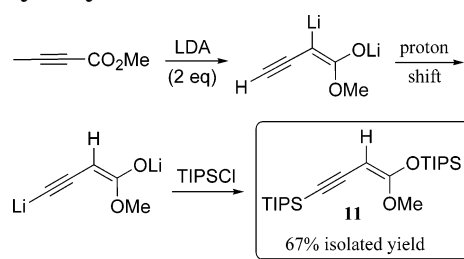
Alkylation products from the cumulenolate dianion are not observed:



iodide, acid chlorides, and tributyltin chloride. In most cases, the major product was the 2,2-disubstituted-3-alkynoate ester (the deconjugated product), which was obtained in low yields.¹⁵ However, with the tin electrophile, allenylstannane **10** was obtained in 75% yield when the amount of LDA was reduced to 1.5 equiv (Scheme 2).

Evidence for a Dianion Intermediate. The use of 1 equiv of base most likely leads to an ester cumulenolate (Scheme 3) analogous to ketone cumulenolates which have been previously described.¹⁶ We believe that the ester cumulenolate is in equilibrium with the cumulenyl ketene, which can react with cumulenolate to form condensation products. Indeed, condensation products are observed immediately following the addition of base even at -98°C . Aliphatic ester enolates have also been shown to undergo a similar self-condensation mechanism although at warmer temperatures.¹⁷

We hypothesize that the addition of a second equivalent of base removes an additional proton from the γ -position of the ester cumulenolate to give a dianion that is less likely to expel LiOMe at -98°C . Others have shown that dianionic intermediates resulting from bis-deprotonation can sometimes be more stable than the

SCHEME 4. Use of TIPS-Cl To Trap the Dianion of Methylbutynoate To Give Ynene 11


monoanion.¹⁸ We have found that THF solutions of alkynyl esters containing 2 equiv of base are stable even at -40°C . We envision that the dianion either may exist as the cumulenolate dianion or may rearrange to the ynenolate dianion, which should be more stable due to improved delocalization (Scheme 3). The ynenolate dianion intermediate most likely reacts with added electrophile at the vinyl anion position. In some cases an additional equivalent of electrophile reacts at the oxygen anionic center to give the ketene acetal, which on subsequent aqueous quenching hydrolyzes to the allene.

Several findings seem to argue for the existence of the ynenolate dianion: (1) Alkynyl esters containing tertiary carbons at the γ -position fail to give the allenyl ester product (Table 5, entry 7). (2) Allenyl ester products alkylated at the γ -position have not been observed throughout the course of this study. (3) Efforts to trap the dianion intermediate resulting from the addition of 2 equiv of LDA to methyl butynoate, using triisopropylsilyl chloride (TIPS-Cl), have led to alkynylketene acetal **11**, which was isolated in 67% yield (Scheme 4).¹⁹ This product is very likely the result of a proton shift from the acidic alkynyl position to the vinyl position immediately following initial dianion formation. (4) Our experiments with TIPS-Cl trapping of the dianion of methyl butynoate to give **11** seem to explain the anomalous product (compound **B**) obtained by Ainsworth (Scheme 1). Trapping of the ynenolate dianion leading to **11** (Scheme 4) with TMS-Cl would lead to a product that should likely hydrolyze to deconjugated product **B** under silica gel chromatography conditions.

Conclusion. We have identified conditions for the alkylative conversion of alkynyl esters to allenyl esters in synthetically useful yields. A key factor in this conversion is the use of 2 equiv of LDA to form a dianion species that upon addition of methyl iodide, trimethylsilyl chloride, or tributyltin chloride gives the α -substituted conjugated allenyl esters. Trapping studies involving methyl 2-butynoate have revealed the likely structure of the dianion intermediate to be a dilithio ynenolate. These studies indicate that the 2-butynoate substrate undergoes a proton shift to give a more stable dianion leading to deconjugated products.

Optimization studies with alkynoic esters containing secondary γ -carbons revealed that additive lithium and

(15) Our current studies indicate that the deconjugated product can be obtained in synthetically useful yields by the addition of HMPA or by the addition of butyllithium to remove the diisopropylamine protons generated during the dianion formation. These and other optimization studies are currently being summarized in a manuscript.

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(19) One-dimensional NOE studies of **11** revealed an enhanced signal for the isopropyl groups of the oxy-TIPS moiety when the sample was irradiated at the resonance frequency of the vinyl proton. The NOE experiment also showed no enhancement of the methoxy signal, thus the double bond geometry of **11** is most likely the *E* configuration.

sodium halide salts lead primarily to the allenyl product while the use of HMPA as a cosolvent gives the β,γ -alkynyl deconjugated alkylation product. The concentration of the base in the reaction mixture was also found to be crucial giving optimal yields at 0.1 M. The optimized conditions resulting from our study of this reaction establish this method as a viable synthetic tool for the production of α -substituted allenyl esters.

Experimental Section

General Methods. THF was dried and freshly distilled under argon from Na/benzophenone. Amide bases and electrophiles were used without further purification. Abbreviations for ^1H NMR are the following: s = singlet, d = doublet, t = triplet, septet = sep, m = multiplet. Reaction progress was monitored by TLC, using silica gel 60 F₂₅₄ precoated plates, visualized by UV light, and stained with KMnO_4 . All NMR spectra were recorded as CDCl_3 solutions on either a Varian 400 or 500 MHz spectrometer.

Representative Procedure: Silylation of Alkynyl Ester 1 to Allene 2. To a 250-mL round-bottom flask containing dry THF (5 mL) was quickly added LiCl (320 mg, 7.55 mmol) to avoid the inclusion of atmospheric water into the salt. Alkynyl ester **1** (1.75 g, 7.55 mmol) was then added to the reaction flask as a THF solution (145 mL). The solution was cooled to -98°C and allowed to stir under nitrogen for 30 min followed by the dropwise addition of LDA (7.6 mL, 2 M, 15.2 mmol) while carefully maintaining the reaction temperature at -98°C . Stirring was continued for an additional 30 min followed by the addition of neat TMS-Cl (5.0 mL, 39.4 mmol). The reaction mixture was maintained at -98°C for 1 h and then allowed to warm to room temperature over the course of 8 h. The reaction was quenched with saturated aqueous NaHCO_3 (200 mL), followed by extraction with ether (200 mL) twice. The combined ether layers were washed with brine, dried over MgSO_4 , and evaporated to leave the crude product, which was purified by column chromatography over silica gel eluting with 2% EtOAc/hexanes to obtain compound **2** as a clear oil (1.81 g, 79%): IR (neat) 1934, 1701 cm^{-1} ; ^1H NMR δ 7.32–7.26 (m, 5H), 5.29 (t, $J = 7.0$ Hz, 1H), 4.50 (s, 2H), 3.68 (s, 3H), 3.54 (t, $J = 6.5$ Hz, 2H), 2.39 (td, $J = 6.25$ Hz, 6.25 Hz, 2H), 0.14 (s, 9H); ^{13}C NMR δ 215.1, 168.2, 138.3, 128.3 (3C), 127.6 (2C), 127.5, 85.1, 72.9, 69.5, 51.9, 27.8, -1.3 (3C). HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3\text{Si}$ 304.1495, found (M + H)⁺ 304.1575.

6-((2-Methoxyethoxy)methoxy)-2-(trimethylsilyl)-hexa-2,3-dienoic Acid Methyl Ester (3). IR (neat) 1936, 1702 cm^{-1} ; ^1H NMR δ 5.28 (t, $J = 7.0$ Hz, 1H), 4.72 (s, 2H), 3.71–3.68 (m, 5H), 3.62 (t, $J = 6.5$ Hz, 2H), 3.57–3.55 (m, 2H), 3.39 (s, 3H), 2.40–2.35 (m, 2H), 0.17 (s, 9H); ^{13}C NMR δ 215.0, 174.3, 95.5, 85.0, 71.7, 67.1, 66.8 (2C), 59.0, 51.9, 27.8, -1.3 (3C). HRMS calcd for $\text{C}_{14}\text{H}_{26}\text{O}_5\text{Si}$ 302.1550, found 302.1340.

6-Benzyloxy-2-methylhexa-2,3-dienoic Acid Methyl Ester (4). IR (neat) 1959, 1723 cm^{-1} ; ^1H NMR δ 7.36–7.27 (m, 5H), 5.52 (m, 1H), 3.58 (t, $J = 6.5$ Hz, 2H), 2.43 (td, $J = 6.25$ Hz, 6.25 Hz, 2H), 1.86 (d, $J = 3.0$ Hz, 3H); ^{13}C NMR δ 210.3, 168.2, 138.2, 128.3 (3C), 127.6 (2C), 127.5, 90.7, 72.9, 69.2, 52.6, 28.5, 27.4; HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$ (M – 45)⁺ 201.1256, found (M – 45)⁺ 201.1289.

6-Benzyloxy-2,2-dimethylhex-3-ynoic Acid Methyl Ester (5). ^1H NMR δ 7.35–7.28 (m, 5H), 4.56 (s, 2H), 3.72 (s, 3H), 3.58 (t, $J = 7.25$ Hz, 2H), 2.51 (t, $J = 7.0$ Hz, 2H), 1.45 (s, 6H); ^{13}C NMR δ 138.4, 128.6 (2C), 127.8 (2C), 127.1, 83.6, 73.1,

68.8, 66.8, 52.9, 38.3, 27.7, 27.6, 20.4; HRMS calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$ 260.1412, found 260.1412.

7-(Tetrahydropyran-2-yloxy)-2-(trimethylsilyl)hepta-2,3-dienoic Acid Methyl Ester (6). IR (neat) 1934, 1704 cm^{-1} ; ^1H NMR δ 5.28–5.24 (m, 1H), 4.54–4.52 (m, 1H), 3.86–3.72 (m, 2H), 3.68 (s, 3H), 3.47–3.37 (m, 2H), 2.20–2.12 (m, 2H), 1.82–1.72 (m, 2H), 1.72–1.64 (m, 4H), 1.55–1.47 (m, 2H), 0.14 (s, 9H); ^{13}C NMR δ 215.1, 168.2, 98.8, 95.5, 87.8, 66.6, 62.2, 51.8, 30.6, 29.2, 25.4, 23.9, 19.6, -1.3 (3C); HRMS calcd for $\text{C}_{16}\text{H}_{28}\text{O}_4\text{Si}$ 312.4766, found 312.1757.

5-(tert-Butyldiphenylsilyloxy)-2-(trimethylsilyl)-penta-2,3-dienoic Acid Methyl Ester (7). IR (neat) 1938, 1710 cm^{-1} ; ^1H NMR δ 7.71–7.68 (m, 4H), 7.46–7.37 (m, 6H), 5.41 (t, $J = 6.0$ Hz, 1H), 4.29 (d, $J = 6.0$ Hz, 2H), 3.72 (s, 3H), 1.05 (s, 9H), 0.21 (s, 9H); ^{13}C NMR δ 214.3, 167.8, 135.7 (4C), 129.7 (4C), 127.6 (4C), 97.0, 89.2, 60.4, 51.9, 26.6 (3C), 19.2, -1.3 (3C); HRMS calcd for $\text{C}_{25}\text{H}_{34}\text{O}_3\text{Si}_2$ 438.2046, found (M – CH_3)⁺ 423.1780.

5-Phenyl-2-(trimethylsilyl)penta-2,3-dienoic Acid Methyl Ester (8). IR (neat) 1936, 1734 cm^{-1} ; ^1H NMR δ 7.24–7.08 (m, 5H), 5.36 (t, $J = 7.1$ Hz, 1H), 3.65 (s, 3H), 3.35 (d, $J = 7.1$ Hz, 2H), 0.04 (s, 9H); ^{13}C NMR δ 215.6, 168.1, 139.3, 128.5 (2C), 128.3 (2C), 126.4, 96.0, 88.1, 51.9, 33.7, -1.3 (3C); HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2\text{Si}$ 260.4036, found 260.1242.

4-Phenyl-2-(trimethylsilyl)buta-2,3-dienoic Acid Methyl Ester (9). IR (neat) 1920, 1734 cm^{-1} ; ^1H NMR δ 7.35–7.21 (m, 5H), 6.31 (s, 1H), 3.75 (s, 3H), 0.26 (s, 9H); ^{13}C NMR δ 217.6, 168.3, 133.5, 129.6 (2C), 128.3 (2C), 126.8, 93.4 (2C), 53.3, 0.0 (3C); HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Si}$ 246.3770, found 246.1082.

6-Benzyloxy-2-(tributylstannanyl)hexa-2,3-dienoic Acid Methyl Ester (10). IR (neat) 1934, 1695 cm^{-1} ; ^1H NMR δ 7.35–7.28 (m, 5H), 5.14 (t, $J = 7.25$ Hz, 1H), 4.52 (s, 2H), 3.69 (s, 3H), 3.58–3.53 (m, 2H), 2.45–2.37 (m, 2H), 1.53–1.47 (m, 6H), 1.34–1.27 (m, 6H), 1.03–0.99 (m, 6H), 0.89 (t, $J = 7.25$ Hz, 9H); ^{13}C NMR δ 211.9, 169.2, 138.3, 128.3 (3C), 127.6 (2C), 127.5, 82.0, 73.0, 69.9, 52.2, 28.8–26.8, 13.0, 10.8; HRMS calcd for $\text{C}_{26}\text{H}_{42}\text{O}_3\text{Sn}$ 521.2077, found (M + H)⁺ 521.2010.

1-Methoxy-4-(triisopropylsilyl)-1-(triisopropylsilyloxy)but-1-en-3-yne (11). ^1H NMR δ 4.92 (s, 1H), 3.67 (s, 3H), 1.31 (sep, $J = 7.5$ Hz, 3H), 1.16–1.11 (m, 3H), 1.09–1.08 (m, 36H); ^{13}C NMR δ 216.6, 81.7, 72.5 (2C), 51.5, 18.8 (6C), 18.4 (6C), 11.8 (6C); HRMS calcd for $\text{C}_{23}\text{H}_{46}\text{O}_2\text{Si}_2$ 410.3036, found (M + H)⁺ 411.3103.

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Supporting Information Available: ^1H NMR spectra for compounds **A** and **B** and compounds **2–11**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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