JOC The Journal of Organic Chemistry

Article

Diastereoselective Syntheses of (E)-#-Trialkylsilyl-#,#-Unsaturated Esters, #-Silane Substituted Conjugated Silyl Ketene Acetals, and #,#-Substituted Allyl Silanes

David A. Johnson, Amanda J. Mueller Hendrix, and Michael Paul Jennings

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b01209 • Publication Date (Web): 25 Jul 2018

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

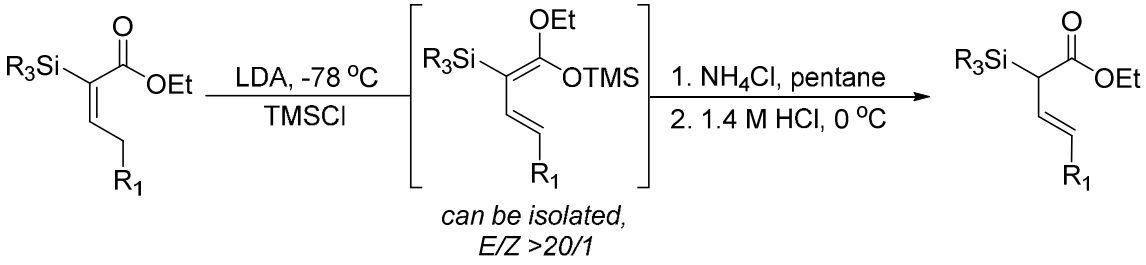
Diastereoselective Syntheses of (*E*)-α-Trialkylsilyl-α,β-Unsaturated Esters, α-Silane Substituted Conjugated Silyl Ketene Acetals, and α,γ-Substituted Allyl Silanes

*David A. Johnson, Amanda J. Mueller Hendrix, and Michael P. Jennings**

Department of Chemistry, 250 Hackberry Lane, The University of Alabama, Tuscaloosa, AL 35487-0336

jenningm@ua.edu

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)



ABSTRACT:

The vicinal functionalization of propiolate esters *via* a catalytic carbocupration-silicon group migration sequence has been further investigated to include the syntheses of a wide variety of β-alkyl and aryl substituted (*E*)-α-silyl-α,β-unsaturated esters. The ester substrates were transformed into their β,γ-unsaturated isomers by means of an LDA mediated γ-deprotonation, extended silyl ketene acetal formation, and final α-protonation sequence. The silyl ketene acetal intermediates were also isolated and

their stereochemistries were established by nOe. The isolation of the intermediate extended silyl ketene acetals afforded further understanding of the lithium extended dienolate structure and furnished additional support for Snieckus' proposed cyclic eight-membered transition state in the deprotonation of (*Z*)-α,β-unsaturated carbonyls with metallo-dialkylamides.

INTRODUCTION:

The application of silicon-based reagents in organic synthesis has been well documented for more than 60 years.[1] More specifically, a couple subgroups of organosilanes have received a majority of the attention of synthetic chemists.

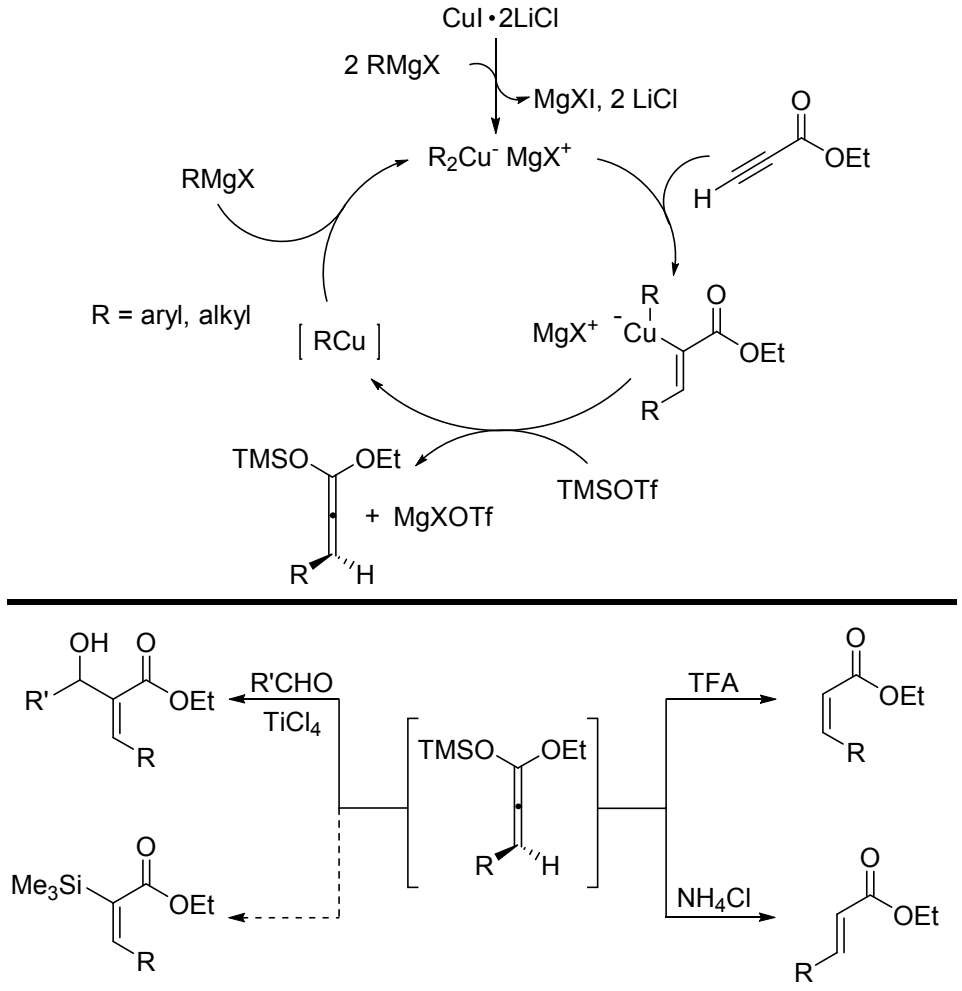


Figure 1. TMS-allenolate formation via catalytic carbocupration of ethyl propiolate (**1a**)

Both allyl-and vinyl silanes have been utilized in a variety of such synthetic strategies ranging from broadly defined Hosomi-Sakurai reactions to Pd-catalyzed Hiyama cross-couplings.[2,3] In addition, silyl ketene acetals, enol ethers, oxyallenes, and allenolates have been shown to be exceedingly useful organic synthons extending from Mukaiyama-type aldol reactions, Diels-Alder cyclizations, and α-acylvinyl anion equivalents.[4-6] Due to the frequent usage of such reagents, the development of methods that provide stereodefined organosilanes remains a significant area of research.[7,8] Coupled with our interest in the aforementioned silane reagents for target based organic synthesis, we have been concomitantly involved in developing a *catalytic* carbocupration of propiolate electrophilic substrates utilizing Kharasch reagents combined with further manipulation of the expected TMS-allenolate intermediate.[9,10] Our general hypothesis for the catalytic cycle is detailed in Figure 1. Thus, the addition of substoichiometric amounts (5-15 mol%) of CuI•2LiCl and 2 equiv. of Grignard reagent (aryl and/or alkyl) with respect to the electrophilic substrate should allow for the formation of the *in-situ* formed Kharasch Reagent.[11] An ensuing *syn*-carbocupration at low temp. (-78 ^{o}C) of ethyl propiolate (**1a**) with the diaryl(or dialkyl) magnesiocuprate should afford the moderately stable stereodefined vinyl cuprate. In order to complete the turnover of the Cu-catalyst, the vinyl cuprate would then be transformed into the TMS allenolate, *via* addition of TMSOTf, coupled with a simultaneous liberation of the organocuprate.[12] Seemingly, the by-product aryl(or alkyl) cuprate would then be re-transformed into the reactive diaryl(or dialkyl) magnesiocuprate by means of RMgX addition and, in turn, complete the Cu(I) catalytic cycle while providing the intermediate TMS allenolate product which could be manipulated *in situ* into other products. In order for the catalytic cycle to be feasible, a couple of noteworthy conditions must be met. The first is that the Cu(I) catalyst turnover must be faster than any side reactions that the Grignard reagent might undergo (i.e. nucleophilic addition to the ester functionality, deprotonation of the acetylenic C-H bond of **1a**, or addition to TMSOTf). The second condition centers on the stability of the intermediate TMS allenolate product under the reaction conditions. We have observed that both the Cu(I) turnover is very rapid leading to minimal side

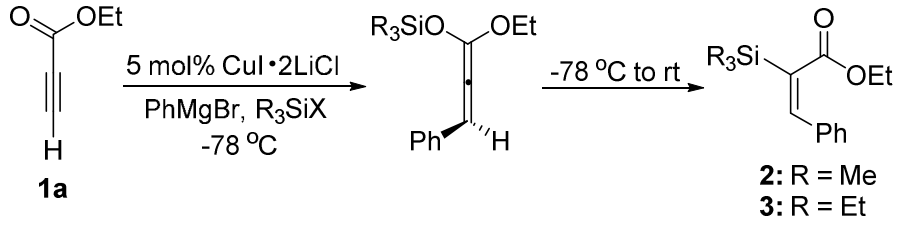
reactions with excess Grignard reagent. In addition, the TMS allenolate is stable under the reaction conditions and can be further manipulated into other final products, *vide infra*.

With these thoughts in mind, we have recently described the divergent synthesis of both *E* and *Z*-α,β-unsaturated esters by means of the above hypothesized catalytic carbocupration reaction process. Interestingly, the diastereoselectivity deviates from a presumed common TMS allenolate contingent on specific reaction conditions.[13] In addition, we extended the scope of utilizing the TMS allenolate as a nucleophile by establishing a vicinal functionalization of propiolate esters by means of a catalytic carbocupration-Mukaiyama aldol reaction protocol.[14] During this sequence, a tautomerization was detected of the TMS allenolate intermediate into a stereodefined α-TMS-α,β-unsaturated ester upon the addition of excess TMSOTf.[15] Equipped with this intriguing silyl group migration, we elected to further explore the reaction scope and limitations. Our complete results with respect to the synthesis of a variety of α-silyl-α,β-unsaturated esters and their further transformations into stereodefined allylsilanes and silyl ketene acetals are reported herein.[16]

RESULTS AND DISCUSSION

Synthesis of vinyl silanes. Before embarking on the synthetic utility of the mentioned α-TMS-α,β-unsaturated esters as precursors to more complex allyl silanes and silyl ketene acetals, a few key questions with respect to the catalytic carbocupration/silyl migration observation remained. The catalytic carbocupration (5 mol% CuI•2LiCl) of ethyl propiolate (**1a**) and PhMgBr (1.2 equiv) coupled with TMSOTf (1.3 equiv) afforded a 43% yield of the desired vinyl silane **2** with a d.r. of >20:1 for the *E* isomer.[15] Increasing the amount of TMSOTf from 1.3→3.3 equiv. provided better yields (86% and 92%) of vinyl silane **2,** while preserving the d.r. of >20:1. Moreover, portionwise addition of TMSOTf did not have a significant influence on the yield of **2** (see table 1, entries 4 and 5) or the diastereoselectivity as delineated in Table 1.

Table 1. Vicinal functionalization of **1a** via a catalytic carbocupration-silicon group migration sequence with various silane promoters.



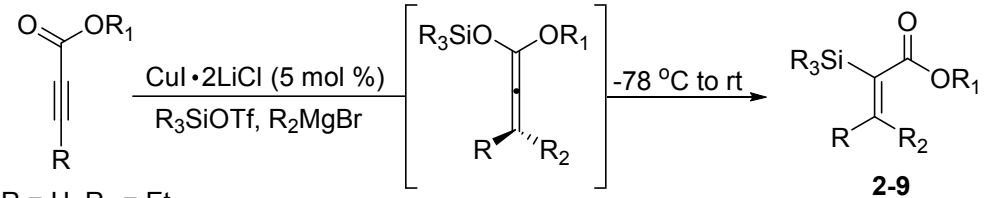
entry	R_3SiX Equiv.	R_3SiX	Yield%[a]	*E/Z*[b]
1	1.3	TMSOTf	43[c]	>20/1
2	2.3	TMSOTf	86	>20/1
3	3.3	TMSOTf	92	>20/1
4	1.3 then 1	TMSOTf	72[c]	>20/1
5	1.3 then 2	TMSOTf	90	>20/1
6	3.3	TMSCl	67[c]	>20/1
7	3.3	TMSBr	80	>20/1
8	3.3	TMSI	89	>20/1
9	3.3	TESOTf	88	>20/1
10	3.3	TESCl	32[c]	>20/1

(a) purified, isolated yield of vinyl silane. (b) *E/Z* ratio determined by ^{1}H NMR (360 or 500 MHz) from the crude reaction mixture. (c) remaining mass balance was the α,β-unsaturated ester from the proton quench of the TMS allenolate or decomposed material.

In addition, the TMS halide Lewis acids ranging in acidity from TMSCl→TMSI (3.3 equiv.) provided yields ranging from 67 to 89% for product **2**. Furthermore, catalytic carbocupration exploiting both TESCl or TESOTf afforded assorted results with respect to the TES group migration and ultimately to the final product vinyl silane **2**. The yields of the α-TES-α,β-unsaturated ester **3** varied from 32% to 88%, however with mutually identical levels of diastereoselectivity (>20:1). Unfortunately, other silane halides or triflates (i.e. TBSOTf and TBSCl) furnished no corresponding vinyl silane product and returned mainly decomposed starting material **1a**.

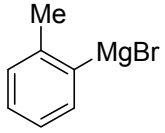
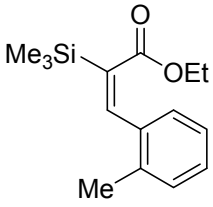
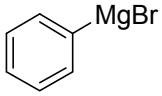
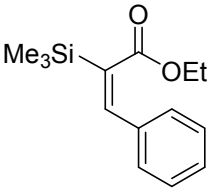
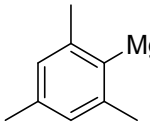
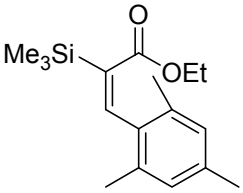
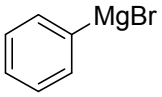
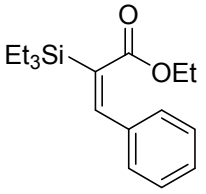
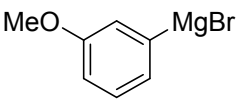
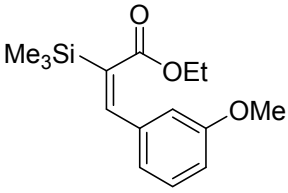
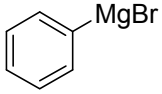
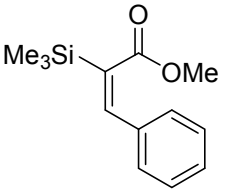
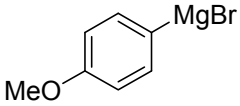
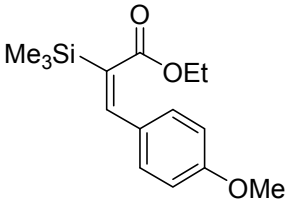
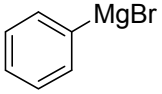
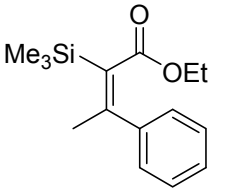
Given the synthetic value of α-trialkylsilyl-α,β-unsaturated ester products, we were optimistic for a *general stereoselective* synthetic process, as they have evaded organic chemists.[17] With the scope somewhat defined in Table 1, additional exploration of the above mentioned reaction with a series of aromatic Grignard reagents coupled with esters **1a, 1b,** and **1c** was undertaken. The catalytic carbocupration/TMS-tautomerization of **1a** readily progressed with 5 mol% of the CuI•2LiCl catalyst and TMSOTf (3.3 equiv.) with a variety of steric and electronic diverse aromatic Grignard reagents (1.2 equiv) to furnish compounds **4-7** in virtually identical high yields (88-92%) as highlighted in Table 2. Furthermore, all of the β-aromatic-α-TMS-α,β-unsaturated esters (**4-7**) were isolated as a single stereoisomer, >20:1 for the *E* diastereomer. In addition, the catalytic carbocupration-TMS tautomerization of methyl propiolate (**1b**) with PhMgBr furnished the α-TMS-β-phenyl-α,β-unsaturated methyl ester **8** in 90% yield as a single diastereomer under identical conditions to that of **1a**. Likewise, we subsequently investigated ethyl 2-butynoate (**1c**) as a more sterically diverse electrophilic coupling partner under the above noted reaction conditions with PhMgBr. Pleasantly, the catalytic carbocupration of **1c** under the above described reaction conditions afforded the presumed initial TMS allenolate intermediate and ensuing tautomerization provided the tetrasusbtituted silyl ester **9** in 85 % yield as a single diastereomer (>20:1 for the *E*-isomer).[18] Unfortunately, both alkenyl and alkynyl Grignard reagents were not compatible under reaction conditions and afforded only decomposed starting material.

Table 2. Vicinal functionalization of **1a, 1b,** and **1c** *via* a catalytic carbocupration-silicon group migration sequence with various aryl Grignard reagents and R_3SiOTf.[a,b]



1a: R = H, R_1 = Et
1b: R = H, R_1 = Me
1c: R = Me, R_1 = Et

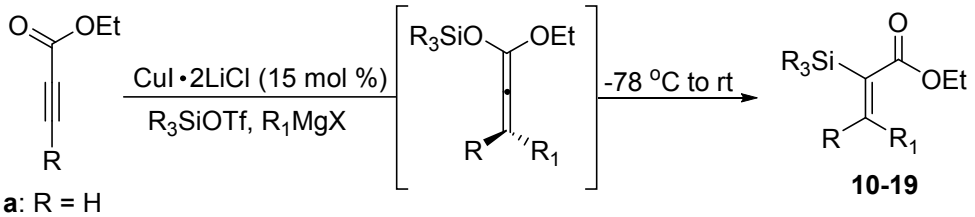
2-9

Grignard reagent	product yield, (*E/Z*)	Grignard reagent	product yield, (*E/Z*)
	 **4**: 88% (*E/Z* > 20/1)		 **2**: 92% (*E/Z* > 20/1)
	 **5**: 92% (*E/Z* > 20/1)		 **3**: 83% (*E/Z* > 20/1)
	 **6**: 88% (*E/Z* > 20/1)		 **8**: 90% (*E/Z* > 20/1)
	 **7**: 90% (*E/Z* > 20/1)		 **9**: 85% (*E/Z* > 20/1)

(a) *E/Z* ratio determined by ^{1}H NMR (360 or 500 MHz) from the crude reaction mixture. (b) yields are of the isolated, pure compounds.

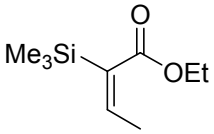
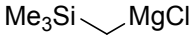
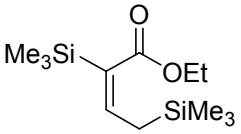
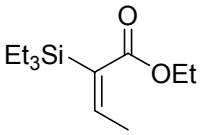
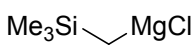
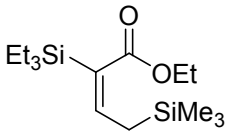
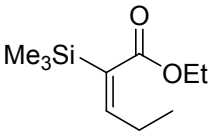
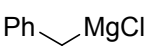
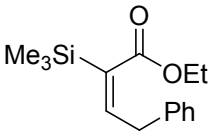
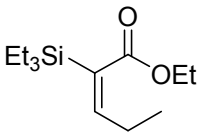
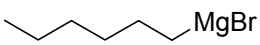
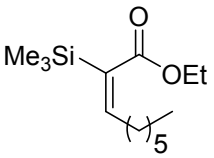
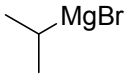
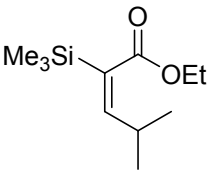
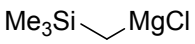
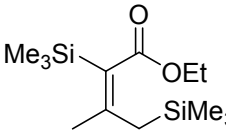
Building on the successful catalytic carbocupration/TMS-tautomerization of **1a** with aromatic Grignard reagents as noted in Table 2, we looked to expand the reaction scope by investigating aliphatic Grignard reagents under similar reaction conditions. Initially, the addition of MeMgBr to **1a** in the presence of 5 mol% of the CuI•2LiCl catalyst and 3.3 equiv of TMSOTf afforded the corresponding product **10** in ~50% yield with a diastereoselectivity of >20:1 for the *E* isomer. Similarly, EtMgBr mirrored the reactivity and outcome to that of the methyl derived Grignard reagent with **1a** and provided synthon **12** in 51% yield as a single *E* isomer as well. Based on these two results, it was hypothesized that the Cu(I) turnover was more sluggish with respect to the less reactive aliphatic Grignard regents to that of the aromatic ones. Thus, we increased the catalyst loading from 5 to 15 mol% while maintaining the 3.3 equiv of TMSOTf and observed an increase in yield from ~50% to 75% for both α-TMS-α,β-unsaturated esters **10** and **12** as delineated in Table 3. With the updated reaction conditions, we further investigated a diverse series of aliphatic Grignard reagents. Much to our delight, catalytic carbocupartiation/silyl migration utilizing 15 mol% of CuI•2LiCl of **1a** with *i*PrMgCl, Me_3SiCH_2MgCl, benzylMgCl, octylMgBr (1.3 equiv. for all Grignard reagents) and TMSOTf (3.3 equiv.) readily provided the corresponding α-TMS-α,β-unsaturated esters **14, 15, 17,** and **18** with yields ranging from 70-90% with diastereoselectivities of >20:1 strongly favoring the *E* isomer in all examples. The lowest isolated yield of 70% was observed for benzyl ester **17** and due to the Grignard reagent catalyzing a SET polymerization of the THF solvent, thus making isolation/purification of the product more problematic. Similar to ester **3** from Table 1, silyl migration/tautomerization utilizing TESOTf in place of TMSOTf was also successful with MeMgBr, EtMgBr, and Me_3SiCH_2MgCl upon catalytic carbocupration of **1a** to afford α-TES-α,β-unsaturated esters **11, 13,** and **16** with yields ranging from 33-75% with diastereoselectivities of >20:1 strongly favoring the *E* isomer in all examples.

Table 3. Vicinal functionalization of **1a** and **1b** via a catalytic carbocupration-silicon group migration sequence with various aliphatic Grignard reagents and R_3SiOTf.[a,b]



1a: R = H
1b: R = Me

10-19

Grignard reagent	product yield, (*E/Z*)	Grignard reagent	product yield, (*E/Z*)
MeMgBr			
	10: 75% (*E/Z* > 20/1)		**15**: 90% (*E/Z* > 20/1)
MeMgBr			
	11: 33% (*E/Z* > 20/1)		**16**: 75% (*E/Z* > 20/1)
EtMgBr			
	12: 75% (*E/Z* > 20/1)		**17**: 70% (*E/Z* > 20/1)
EtMgBr			
	13: 44% (*E/Z* > 20/1)		**18**: 88% (*E/Z* > 20/1)
			
	14: 82% (*E/Z* > 20/1)		**19**: 33% (*E/Z* > 20/1)

(a) *E/Z* ratio determined by ^{1}H NMR (360 or 500 MHz) from the crude reaction mixture. (b) yields are of the isolated, pure compounds.

It is worth noting that yields are lower across the board (i.e. **2** vs **3**, **10** vs **11**, **12** vs **13**, and **15** vs **16**) when TESOTf is used in place of TMSOTf. Lastly, catalytic carbocupration/silyl migration of **1b** with Me_3SiCH_2MgCl under the standard reactions conditions did proceed, but unfortunately, only provided a 33% isolated yield of the tetrasubstituted α-TMS-α,β-unsaturated ester **19** with a >20:1 diastereoselectivity favoring the *E* isomer. An assessment of Tables 2 and 3 have revealed that both aromatic and aliphatic Grignard regents readily undergo catalytic carbocupration/silyl group migration (5-15 mol % of CuI•2LiCl and 3.3 equiv of R_3SiOTf) of **1a** to afford α-TMS(or TES)-α,β-unsaturated ester products in modest to outstanding yields coupled with excellent levels of diastereocontrol over the olefin geometry. Generally, the aromatic Grignard reagents led to higher yields with a slightly lower catalyst loading.

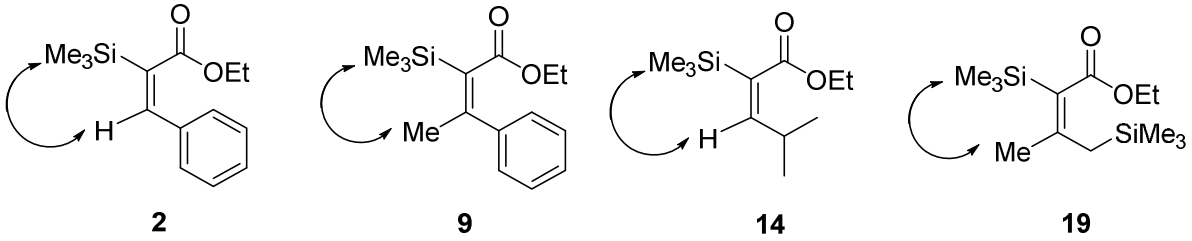


Figure 2. Key nOe enhancements of aryl- and alkyl vinyl silanes for assigning olefin geometry

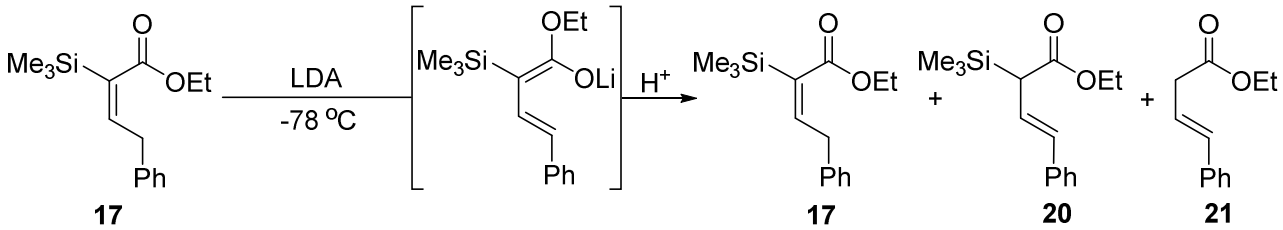
As described in Figure 2, the geometry of vinyl silane products **2, 9, 14,** and **19** were determined by means of 1D nOe spectroscopy. As shown above, the strong couplet from the protons resident on the TMS moieties and the β-vinylic positions afforded convincing evidence for the assigned *E*-olefin geometry. Furthermore, the ^{1}H NMR chemical shifts of **2-19** emulate that of structurally comparable silane products as conveyed by Zweifel.[16b] Based on the noted nOe results for **2, 9, 14,** and **19**, the stereochemistry of the remaining silane products, as described in tables 2 and 3, were designated as the *E*-isomer.

Kinetic deconjugation of α-TMS-(*E*)-α,β-unsaturated esters. Zweifel and co-workers previously described a four step synthetic process, including deconjugation of α-TMS-(*Z*)-α,β-unsaturated esters, to obtain three higher order allylic silanes with the inconvenient dependency of HMPA as a co-solvent.[16b] Likewise, they also reported a five step reaction sequence, devoid of HMPA, which included isomerization of olefin stereochemistry (from *Z*→*E*) followed by deconjugation of α-TMS-(*E*)-α,β-unsaturated esters, to obtain two stereochemically pure conjugated silyl ketene acetal products. However, the enolate olefin geometries were not fully established. In addition, no further reactions of the isolated silyl ketenes acetals were investigated. With our new method for the direct one-pot selective formation of α-TMS-(*E*)-α,β-unsaturated esters, we chose to investigate the further scope and limitations of the deconjugation of the afore mentioned esters with the hopes of building a diverse set functionalized allyl and crotyl-type silane reagents over a two-step process, while eliminating the reliance on HMPA. Initially, we elected to examine the LDA-mediated deprotonation of ester **17** followed by direct protonation of the Li-extended enolate intermediate with the anticipation of forming allyl silane **20**. Ester **17** was selected due to the fact that the anticipated product (**20**) would most likely contain a labile carbon-silicon bond due to the ease of forming a further extended enolate upon anion mediated desilylation, thus potentially making the isolation of **20** somewhat challenging.

As described in Table 4, LDA (1.1 equiv) mediated kinetic deprotonation (-78 ^{o}C in THF) of **17** at the γ-position seemingly formed the extended Li-enolate and subsequent protonation with 1M HCl provided a product ratio of 21:42:37 for compounds **17**, **20**, and **21** as determined by ^{1}H NMR in a combined 85% yield of the crude material as further purification was not required. A few key points merit further discussion from entry 1. The esters **20** and **21** were isolated with an excellent dr of >20:1 for the *E* isomer of the newly formed β,γ-olefin as determined by ^{1}H NMR and were a consequence of α-protonation of the extended enolate. Secondly, desilylation of the α-TMS group occurred during the work-up, post protonation, providing a significant amount of ester **21** as we initially surmised might transpire. Lastly, a significant amount of starting material ester **17** was recovered and attributed to

either incomplete deprotonation, γ-protonation of the extended enolate, or possible olefin isomerization of **20**→**17**.

Table 4. LDA mediated deprotonation/Brönsted acid reprotonation of α-TMS-α,β-unsaturated ester **17**



17 **17** **20** **21**

Entry	H^+ source	Temp., °C	Product Ratio (%) **17:20:21**[a]	Combined Yield %[b]
1	HCl (1M)	-78	21:42:37	85
2	HCl (1M)	-40	6:57:37	85
3	HCl (1M)	-20	0:61:39	90
4	TFA (2 eq.)	-20	4:16:80	90
5	AcOH (2 eq.)	-20	9:0:91	95
6	CSA (2 eq.)	-20	4:22:74	80
7	PTSA (2 eq.)	-20	0:0:100	90
8	37% HCl (2 eq.)	-20	0:9:91	90
9	H_2SO_4 (2 eq.)	-20	9:0:91	80
10	H_3PO_4 (2 eq.)	-20	0:0:100	60
11	48% HBF_4 (2 eq.)	-20	0:0:100	80
12	NH_4Cl (sat.)	-20	0:0:100	80
13	HBr (1.4 M)	-20	11:44:45	92

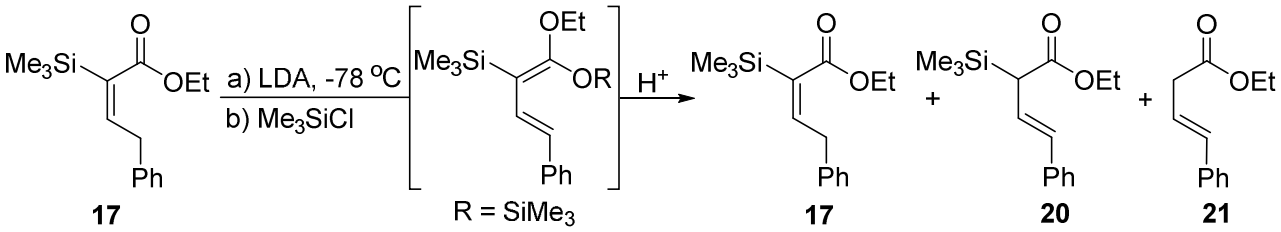
(a) product ratio determined by ^{1}H NMR (360 or 500 MHz) from the crude reaction mixture. (b) crude combined yield of **17**, **20**, and **21** as further purification was not required.

We subsequently varied the protonation (1M HCl) temperatures from -78 °C to -40 °C then further to -20 °C and observed significantly less product **17** (6% at -40 and ~0% at -20) while slightly improving

the ratio of **20:21** (up to 61:39) while maintaining ~85-90% overall yield (entries 2 and 3). It should be noted that only the *E* alkene isomer was detected in esters **20** and **21**. We were pleased that complete deprotonation of **17** had taken place and a large majority of α-protonation products (**20** and **21**) were identified, while being able to rule out olefin isomerization of **20→17**. While holding the protonation temperature at -20 ^{o}C, a series of Brönsted acids were examined and provided mixed results. Most all of the acid reagents provided deconjugated esters **20** and/or **21** (>20:1 for the *E* isomer) in 60-90% yields with little to no starting material **17**. Unfortunately, the major product (75-100%) in entries 4-12 was the desilylated ester **21**, thus highlighting the lability of the α-TMS moiety resident in ester **20** during a direct protonation of the lithium extended enolate.

Unfortunately, direct protonation of the Li-extended enolate afforded a large majority of the desilyled ester product **21** due to a combination of the strongly basic/nucleophilic nature of the conjugate bases and labile silicon-carbon bond α-to the carbonyl moiety. In an attempt to circumvent these issues, we envisaged trapping the extended lithium enolate with TMSCl as a silyl ketene acetal consequently affording a softer and more regioselective mechanism for protonation, thus leading to the delivery of ester **20** *in lieu* of **21**.[19] As shown in Table 5, LDA (1.1 equiv) mediated kinetic deprotonation (-78 ^{o}C in THF) of **17** at the γ-position followed by subsequent trapping of the presumed extended enolate with TMSCl afforded the intermediate silyl ketene acetal. Ensuing protonation at -20 ^{o}C with NH_4Cl furnished a product ratio of 4:9:87 for compounds **17**, **20**, and **21** as determined by ^{1}H NMR in a combined 60% yield of the crude material.

Table 5. LDA mediated deprotonation/silyl ketene formation/Brönsted acid protonation of α-TMS-α,β-unsaturated ester **17.**



Entry	H^+ source	Temp., °C	Product Ratio (%) **17:20:21**[a]	Combined Yield %[b]
1	NH_4Cl (sat.)	-20	4:9:87	60
2	TFA (2 eq.)	-20	0:65:35	90
3	HCl (1.4 M)	-20	13:37:50	80
4	HCl (1.4 M)[c]	-78	8:77:15	85
5	TFA (2 eq.)[c]	-78	33:51:16	80
6	HCl (1.4 M)[d]	-78	27:61:12	85
7	HCl (1.4 M)[e]	-78	8:80:12	90
8	HCl (1.4 M)	-78→rt	9:0:91	58
9	HCl (1.4 M)[f]	-78	8:77:15	88
10	HBr (1.4 M)[e]	-78	4:83:13	86
11	HI (1.4 M)[e]	-78	65:32:3	85
12	HBr (1.4 M)[g]	-78	8:77:15	90

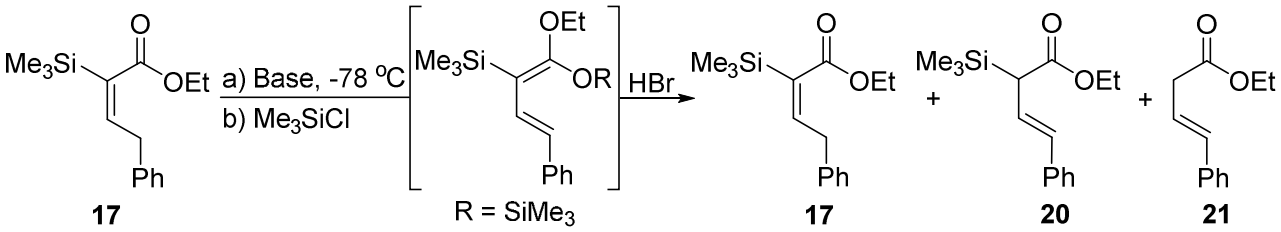
(a) product ratio determined by ^{1}H NMR (360 or 500 MHz) from the crude reaction mixture. (b) crude combined yield of **17**, **20**, and **21** as further purification was not required. (c) reaction stirred for 15 min. post addition of proton source (d) reverse quench (e) reaction stirred for 2 min. post addition of proton source (f) 1.5 equiv of LDA used (g) TMSOTf was used to form the silyl ketene acetal in place of TMSCl.

As noted before in Table 5, the olefin stereochemistry of both **20** and **21** were >20:1 for the *E*-isomer Exchanging the proton source from NH_4Cl to TFA provided for the first time a majority of the desired deconjugated ester **20** (~2:1 ratio) in a 90% yield under the formerly described reaction conditions at -20 °C. As shown in entry 5, lowering the temperature from -20 to -78 °C for the TFA quench of the

intermediate silyl ketene acetal did improve the product **20:21** ratio to roughly 3:1, however a significant of the γ-protonated product (i.e. ester **17**) was isolated as well. Much to our delight, utilizing HCl or HBr (entries 4, 7, 9, 10 and 12) as the proton source, while maintaining the reaction and quench temperature at -78 ^{o}C, provided a ~5:1 ratios of the α-TMS ester **20** to the desilylated analogue **21** in 85-90% yields while minimizing ester **17** formation via a γ-protonation (<10%). Overall, lower temperatures allowed for higher α-regioselecivity protonations and lower amounts of desilylation with HCl but higher γ-regioselectivity with TFA. A reverse quench with HCl resulted in higher γ-regioselectivity (entry 6), while warming the protonation from -78 ^{o}C to rt afforded no desired silylated ester **20** (entry 8).

Based on the observation that protonation of the silyl ketene acetal derived from ester **17** with HCl or HBr at -78 ^{o}C in THF provided a maximum product ratio (~5:1) for the silylated ester **20** *in lieu* of product **21**, we elected to investigate the effect of non-polar solvents and sterically diverse Li-amide bases on final product ratios of **20:21**. An initial examination of solvent effects revealed little variance between Et_2O and THF with repect to α- versus γ-protonation, however 5 fold greater levels of γ-protonation was obseved with MTBE leading to ester **17** (entry 3) as delineated in Table 6. Interestingly, hydrocarbon solvents, such as toluene or pentane, afforded the highest levels of regioselectivity for the α-protonated product and nearly suppressed desilylation (entries 4 and 5) while providing yields ranging from 89-95% for ester **20**.

Table 6. LDA mediated deprotonation/silyl ketene formation/HBr protonation of α-TMS-α,β-unsaturated ester **17.**

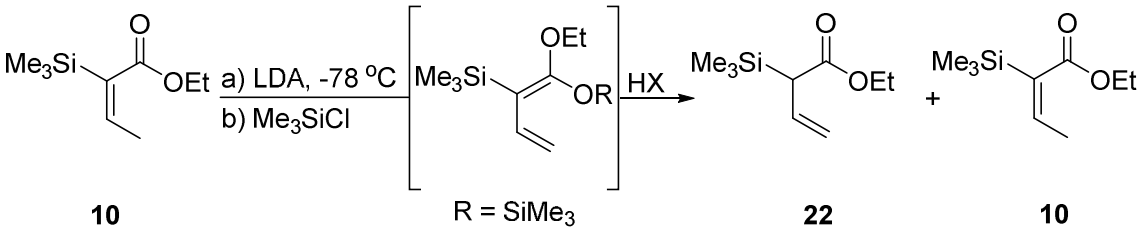


Entry	Solvent	Li-amide base	Product Ratio (%) **17:20:21**[a]	Combined Yield %[b]
1	THF	LDA	4:83:13	86
2	Et_2O	LDA	4:80:16	62
3	MTBE	LDA	19:74:7	90
4	pentane	LDA	4:87:9	95
5	toluene	LDA	4:91:5	89
6	toluene	LiCA	0:87:13	90
7	toluene	LiTMP	71:21:7	90
8	toluene	LiHMDS	77:23:0	90

(a) product ratio determined by ^{1}H NMR (360 or 500 MHz) from the crude reaction mixture. (b) crude combined yield of **17**, **20**, and **21** as further purification was not required.

An ensuing examination of a few Li-amide based revealed that LDA afforded the highest α-regioselective pronation, however LiCA afforded a slightly greater amount of the deconjugated/desilylated product **21**. Finally, both LiHMDS and LiTMP appeared to be either insufficient to appreciably deprotonate ester **17** under standard reaction conditions and/or promoted a significant amount of γ-protonation, thus leading to re-isolation of a substantial amount (71-77%) of starting material (entries 7 and 8).

Table 7. LDA mediated deprotonation/silyl ketene formation/protonation of α-TMS-α,β-unsaturated ester **10.**



10 R = $SiMe_3$ **22** **10**

Entry	Solvent	Temp., °C of H^+ addn.	H^+ source/workup	Product Ratio (%) **22**:**10**[a]	Yield %[b]
1	pentane	-78	HBr (1.4 M)	2:1	80
2	THF	-78	HBr (1.4 M)	2:1	81
3	THF	0	HCl (1.4 M)	2:1	95
4	THF	0	NH_4Cl, pentane, H_2O extraction, then HCl (1.4 M)	15:1	80
5	pentane	0	NH_4Cl, pentane, H_2O extraction, then HCl (1.4 M)	2:1	62

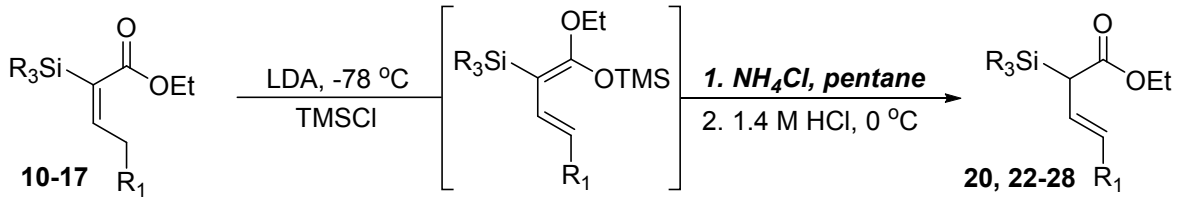
(a) product ratio determined by ^1H NMR (360 or 500 MHz) from the crude reaction mixture. (b) crude combined yield of **22** and **10** as further purification was not required.

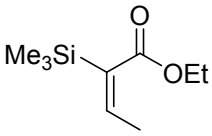
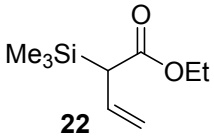
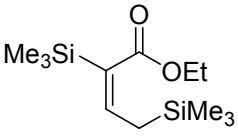
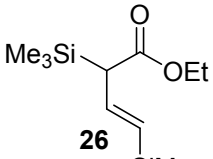
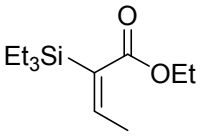
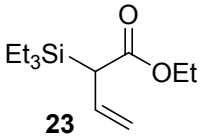
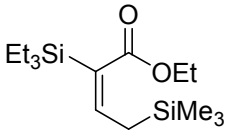
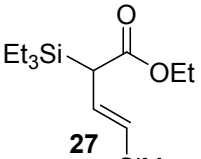
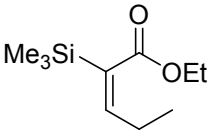
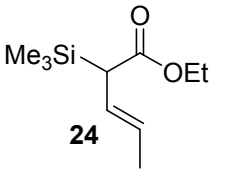
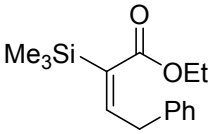
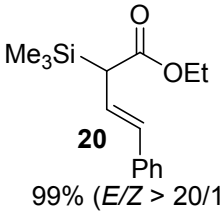
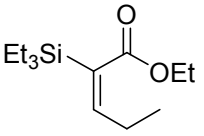
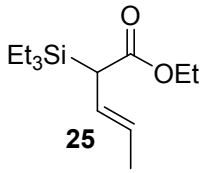
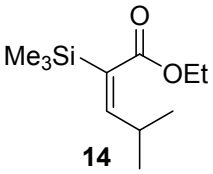
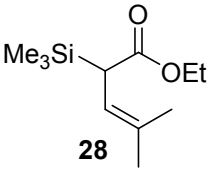
Based on the standardized reaction condition for the deconjugation of ester **17**, we sought to further investigate the identical reaction process on aliphatic α-TMS-α,β-unsaturated esters. Thus, LDA (1.1 equiv) mediated kinetic deprotonation (-78 °C in pentane) of **10** at the γ-position followed by ensuing trapping of the presumed extended enolate with TMSCl afforded the intermediate silyl ketene acetal. Subsequent protonation at -78 °C with HBr furnished a substandard 2:1 product ratio for compounds **22** and **10** as determined by ^1H NMR in a combined 80% yield of the crude material. However, no desilylated product was observed with ester **10** as the substrate. As described in Table 7, exchanging the reaction solvent from pentane to THF while holding the other reaction variables constant (equivalents, temperature, and proton source) also afforded a 2:1 ratio of the deconjugated product (**22**) to that of the starting material (**10**) in roughly the same yield (~81%). Perplexed by these two results, the reaction medium (THF) was warmed to 0 °C, post deprotonation at -78 °C, and quenched with HCl to provide the identical product ratio of 2:1 with a slightly greater yield of 95%. The poor α-

protonation regioselectivities were much lower than those reported by Zweifel (although this exact substrate was not investigated) for the protonation of silyl ketene acetals derived from (Z)-α-silyl-α,β-unsaturated esters.[16b] As noted by Zweifel, their γ-deprotonation-α-protonation sequence with LDA required the use of HMPA as a co-solvent. Thus, prior to protonation with 1.4M HCl, a specific reaction workup and extraction was reported in order to remove HMPA. Intrigued by this subtle technique, we repeated the deconjugation of **10** in THF, followed the H_2O/pentane work-up as noted above, and observed a significant enhancement of α-protonation of the silyl ketene acetal (15:1/α versus γ) with 1.4M HCl leading to the desired volatile deconjugated ester **22** in 80% yield (entry 4). Unfortunately, the repeat of entry 4 with exclusively using pentane as the solvent accompanied by the identical brief work-up process afforded a ~2:1 ratio (similar to entries 1-3) of products **22** and **10** in a lower yield of 60%. Pleased that the brief work-up with pentane and H_2O provided high levels of α-protonation with 1.4M HCl leading to the desired product **22**, we chose to further investigate the scope of the LDA-mediated deconjugation/protonation reaction sequence to include a variety of α-silylated-α,β-unsaturated esters.

As delineated in Table 8, LDA (1.1 equiv) mediated kinetic deprotonation (-78 ^{o}C in THF) of **11** at the γ-position followed by ensuing trapping of the presumed extended enolate with TMSCl afforded the intermediate silyl ketene acetal. Subsequent H_2O/pentane work-up, as noted above, followed by slow addition of 1.4 M HCl at 0 ^{o}C to the organic phase provided the desired deconjugated ester **23** in nearly quantitative yield (~99%) with no purification required of the crude material. Likewise, under identical reaction conditions, esters **12** and **13** readily underwent deconjugation to afford the trimethyl and triethyl allylic silanes **24** and **25** in 80 and ~99% yields, respectively. In addition, only the *E* isomer of the newly formed olefin moiety (>20:1, J = 15.2 Hz) was detected by ^{1}H NMR of the crude material.

Table 8. LDA mediated deprotonation/silyl ketene formation/protonation of a variety of α-silyl-α,β-unsaturated esters.



vinyl silane	product yield, (*E/Z*)	vinyl silane	product yield, (*E/Z*)
 **10**	 **22** 80%	 **15**	 **26** 99% (*E/Z* > 20/1)
 **11**	 **23** 99%	 **16**	 **27** 99% (*E/Z* > 20/1)
 **12**	 **24** 80% (*E/Z* > 20/1)	 **17**	 **20** 99% (*E/Z* > 20/1)
 **13**	 **25** 99% (*E/Z* > 20/1)	 **14**	 **28** 90%[c]

(a) *E/Z* ratio determined by ^{1}H NMR (360 or 500 MHz) from the crude reaction mixture. (b) yields are of the isolated, pure compounds. (c) deprotonation carried out at -40 °C.

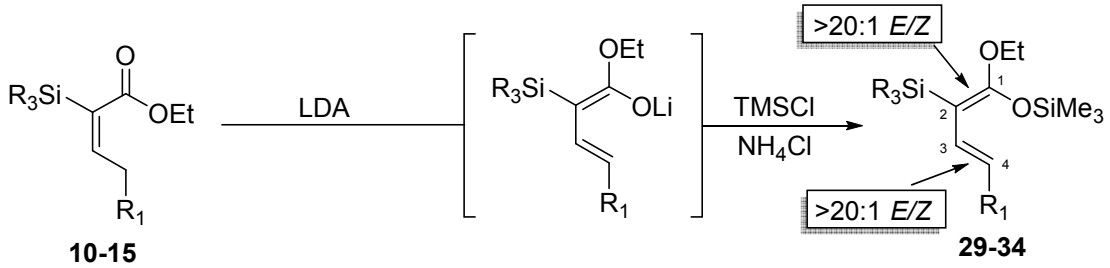
As noted above, the crude esters **24** and **25** were sufficiently pure and did not require any type of further purification. In addition, LDA mediated γ-deprotonation of bis-silyl esters **15** and **16** provided the corresponding silyl ketene acetal intermediates upon addition of TMSCl and an ensuing brief pentane-H_2O workup/HCl protonation furnished the vinyl silyl-deconjugated esters **26** and **27** in nearly quantitative yields with only a single olefin isomer (>20:1, *E*) observed by ^{1}H NMR. Much to our delight, the current procedure also afforded the sought after TMS-deconjugated product ester **20** in

~99% as a single diastereomer post deprotonation/work-up/α-protonation of starting material **17**. Lastly, the (*E*)-α-TMS-β-isopropyl ester **14** readily underwent LDA deprotonation at -40 °C (the reaction was quite sluggish when carried out at -78 °C) and subsequent work-up/α-protonation provided the *gem*-dimethyl allyl silane ester **28** in 90% isolated yield. Interestingly, Zweifel had noted previously that a similar *Z*-isomer (β-cyclohexyl versus β-isopropyl ester **14**) variant which contained a tertiary allylic hydrogen could not be deprotonated with LDA and HMPA.[16b] As noted above, no further purification was required of the product esters **20**, **22-28** and yields were consistently high at 80-99%.

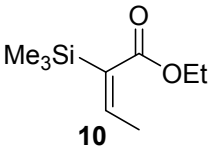
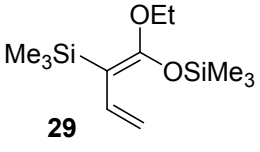
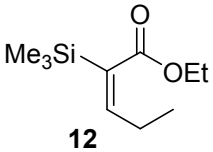
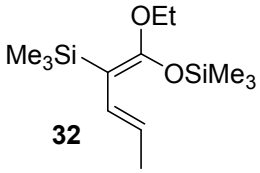
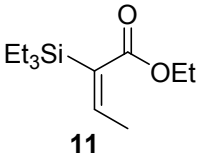
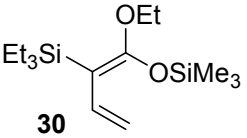
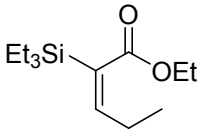
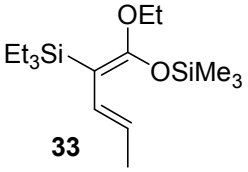
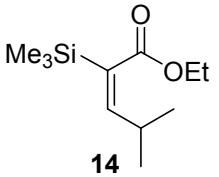
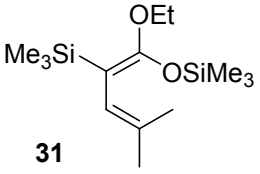
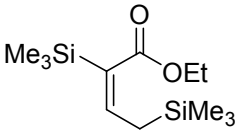
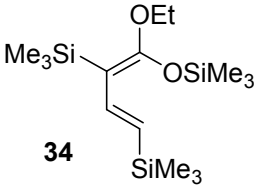
Synthesis and isolation of α-silane substituted conjugated silyl ketene acetals. Zweifel and coworkers were able to isolate two silyl ketene acetal intermediates derived from the deprotonation of (*E*)-α-trimethylsilyl-α,β-unsaturated esters in the absence of HMPA with a non-aqueous workup.[16b] Moreover, only one stereoisomer was detected and the enolate geometry tentatively assigned (but not confirmed) as C_1-C_2-*E*, C_3-C_4-*E* based on a previously reported extended silyl ketene acetal. Along this line, we unexpectedly isolated a 3:1 ratio, as determined by ^{1}H NMR integration, of the intermediate silyl ketene acetal and product allyl silane **28** due to an incomplete acidic hydrolysis post the standard pentane/H_2O work up starting from ester **14**. Based on this observation, we chose to investigate the possibility of isolating the extended silyl ketene intermediates prior to acidic hydrolysis with the anticipation of confirming the enolate stereochemistry by 1D nOe.

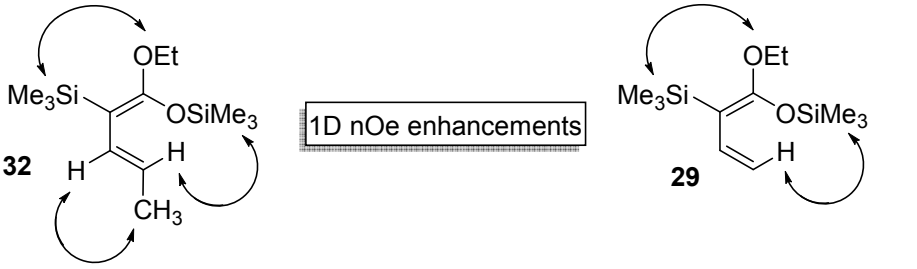
As shown in Table 9, the deprotonation of (*E*)-α-trimethylsilyl-α,β-unsaturated ester **10** with LDA in THF at -78 °C followed by an ensuing trapping of the pendent enolate with TMSCl afforded the crude extended silyl ketene acetal intermediate. A subsequent quench and work-up with NH_4Cl, pentane, and H_2O furnished the pure acetal **29** a single diastereomer as observed by ^{1}H NMR in 93% isolated yield. As noted above with respect to the allyl silanes in Table 8, no further purification was required. Likewise, treatment of the triethyl silyl ester variant **11** under identical reaction and work-up conditions provided the extended conjugated silyl ketene acetal **30** in 85% yield with a dr of >20:1.

Table 9. LDA mediated deprotonation and isolation of extended silyl ketene acetals from a variety of α-silyl-α,β-unsaturated esters.[a,b]



10-15 **29-34**

vinyl silane	product yield, (*E/Z*)	vinyl silane	product yield, (*E/Z*)
 **10**	 **29** 93% (C_1-C_2: *E/Z* > 20/1)	 **12**	 **32** 91% (C_1-C_2: *E/Z* > 20/1)
 **11**	 **30** 85% (C_1-C_2: *E/Z* > 20/1)	 **13**	 **33** 89% (C_1-C_2: *E/Z* > 20/1)
 **14**	 **31** 99% (C_1-C_2: *E/Z* > 20/1)	 **15**	 **34** 91% (C_1-C_2: *E/Z* > 20/1)



(a) C_1-C_2 and C_3-C_4 olefin *E/Z* ratios determined by ^{1}H NMR (360 or 500 MHz) from the crude reaction mixture. (b) yields are of the isolated, pure compounds.

Additionally, deprotonation of ester **14** with LDA at -40 ^{o}C followed by addition of TMSCl afforded the silyl ketene acetal **31** in quantitative yield while maintaining the >20:1 *E/Z* ratio of the newly

formed tetra substituted alkene moiety after the standard work-up process. Similar to esters **10** and **11**, deprotonation of esters **12**, **13**, and **15** with LDA at -78 ^{o}C furnished the extended dienolate intermediates followed by an ensuing addition of TMSCl provided silyl ketene acetals **32**, **33**, and **34** in very good yields ranging from 89-91% while affording very high levels of dr (>20:1) for both the C_1-C_2 and C_3-C_4 olefin moieties.

As shown in Table 9, the C_1-C_2 and C_3-C_4 olefin geometries of silyl ketene acetal **32** were determined by means of ^{1}H NMR. The strong 1D nOe couplet for the C_2-silane methyl groups and ethoxy protons resident on C_1 provided convincing proof for the assigned C_1-C_2 enolate (*E*)-olefin geometry. Additionally, a strong 1D nOe signal for the vinylic proton on C_3 and the terminal methyl group on C_4 furnished persuasive evidence (combined with a C_3-C_4 J = 16.0 Hz) of the C_3-C_4-(*E*)-alkene stereochemical assignment. Furthermore, the C_1-C_2 olefin geometry of silyl ketene acetal **29** was also investigated and based on the compelling nOe data, the stereochemistry of the C_1-C_2 olefin was assigned as the *E*-isomer. Based on the nOe experimental results for **29** and **32**, the C_1-C_2 (and additional C_3-C_4, where applicable) stereochemistries of the remaining extended silyl ketene acetals **30**, **31**, **33**, and **34** were assigned as the *E*-isomer by analogy, thus confirming Zweifel's previous tentative stereochemical assignments.[16b]

A few key observations from Tables 7-9 merit further discussion. It has been established that an β,γ-unsaturated ester product is a consequence of a selective α-protonation typically under kinetic conditions of an extended enolate or silyl ketene acetal.[19] The α-positions of the extended silyl ketene acetals (i.e. **29-34**) derived from substrates **10-19** are more sterically hindered and less accessible than that of the γ-position. However, the α-position is significantly more nucleophilic based on the tetra-substitution patterns of the C_1-C_2 carbon atoms coupled with anion stabilization by the silyl group *via* negative hyperconjugation.[20] Thus, the competition of steric hindrance versus electronic effects during the process of protonation of the intermediate silyl ketene acetals was quite sensitive depending on reaction conditions. Direct protonation of the intermediate extended silyl ketene acetals in THF at either -78 or 0 ^{o}C was believed to be nearly instantaneous and provided a significant amount of the

thermodynamically more stable product as shown in Table 7, entries 2 and 3. It would appear, based on the results, that the sterically more accessible γ-carbon site was preferred under homogenous protonation conditions irrespective of temperature. As noted above, Zweifel and coworkers utilized an aqueous workup prior to protonation in order to remove the HPMA co-solvent.[16b] In actuality, the extraction step (pentane, NH_4Cl, and H_2O) is critically essential to exert kinetic control over the regioselective protonation, due to the fact that it functioned as a method of both purification and significant dilution of the extended silyl ketene acetal. At the conclusion of the reaction prior to protonation, the crude reaction mixture was partition between aqueous and hydrocarbon layers. Most likely, a large majority of THF, LiCl, and *i*Pr_2NH were drawn into the aqueous layer leaving the crude, but considerably pure, extended silyl ketene acetal with a trace amount of THF in the hydrocarbon (pentane) layer. The removal of iPr_2NH during the partition helped to clarify the truly active proton donor (HCl versus *i*Pr_2NH-HCl). Moreover, upon addition of an aqueous 1.4M HCl solution to the hydrocarbon phase, the presence of trace amounts of THF most likely operated as a phase transfer catalyst, shuttling protons into the hydrocarbon layer. Thus, this heterogeneous process allowed the protonations to proceed under highly dilute concentrations and proved to be quite regioselective for the α-position of the extended silyl ketene acetal intermediates leading to the observed α-trialkylsilyl-β,γ-unsaturated ester products in high yield (nearly quantitative in most examples) as delineated in Table 8.

The complexed-induced proximity effect (CIPE), initially introduced by Beak and Meyers, has been used to explain deprotonations/lithiations occurring at remote positions in relation to Lewis basic functional groups capable of an initial coordination.[21,22] Typically, a deprotonation/substitution sequence involves an association of the organolihium or lithium amide species with the substrate to provide the prelithiation complex followed by a subsequent remote deprotonation of an acidic hydrogen. This in turn would furnish a new lithiated species which can further undergo an ensuing transformation with an electrophile. The CIPE model has been cited for chemoselective deprotonations of *Z*-α,β-unsaturated carbonyls, particularly the high kinetic preference for γ-*Z* deprotonations over γ-*E* deprotonations when the β-position was disubstituted.[22,23] Under such kinetic conditions,

deprotonations of *Z*-α,β-unsaturated carbonyls generally provide C_1-C_2-(*Z*) and C_3-C_4-(*E*) extended dienolates. Thus, Snieckus proposed eight membered transitions states to help rationalize the observed stereoselectivities for both C_1-C_2 and C_3-C_4 olefins.[23,24]

Based on the observed products derived from the deprotonation of (*E*)-α-trimethylsilyl-α,β-unsaturated esters, we envisaged two possible transition states that would account for high levels of dr for both the C_1-C_2 and C_3-C_4 olefins as highlighted in Figure 3. Constructed from the Snieckus model utilizing an eight membered transition state, the initial olefin C_2-C_3 stereochemistry of ester **12** should facilitate a CIPE intramolecular deprotonation at the γ-position (C_4) thus providing the C_1-C_2-(*E*)-enolate stereochemistry in both **TS1** and **TS2**. Without the CIPE, one would most likely expect a mixture of C_1-C_2 enolate geometries and/or competitive Michael addition of LDA in the absence of HMPA, which was not observed experimentally. The cyclic eight-membered transition state ensures high diastereoselectivity of the C_1-C_2-olefin. In addition, the stereochemistry of the C_3-C_4 olefin was established during the CIPE deprotonation. The selectivity for the C_3-C_4 olefin can be depicted as a competition between two transition states (**TS1** and **TS2**) with respect to A1,3 and A1,2 strain.

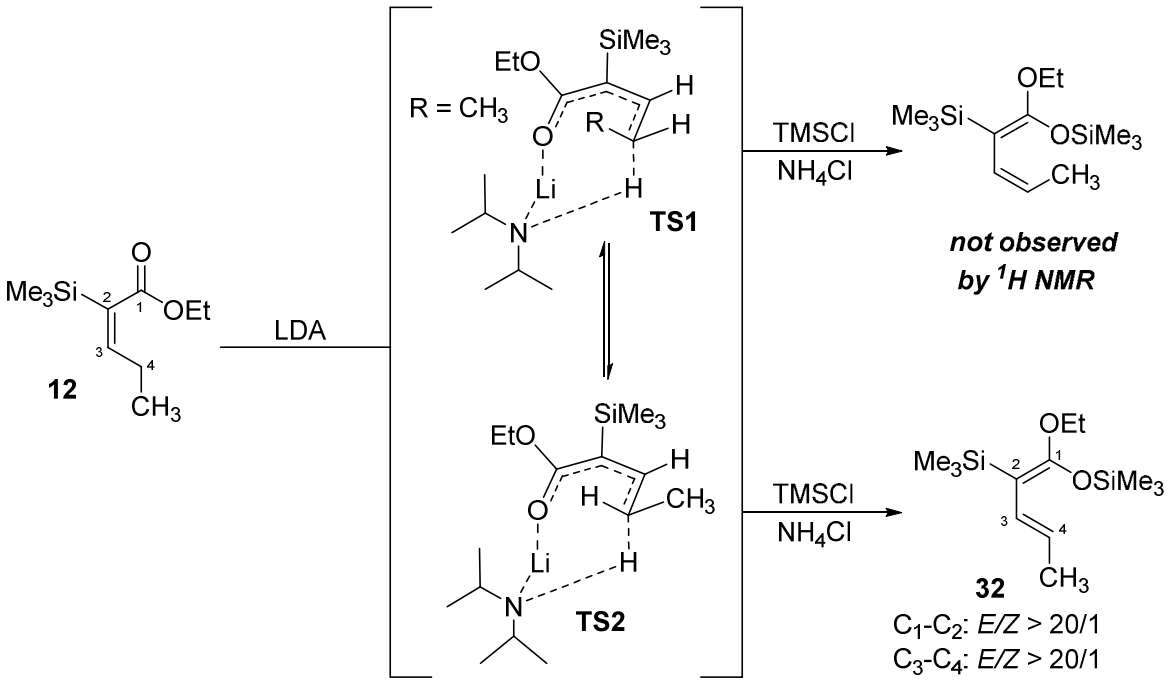


Figure 3. Competing transition states during the deprotonation of ester **12** leading to stereochemically pure extended silyl ketene acetal **32.**

As shown in **TS1**, the methyl group resident on C_4 of ester **12** would eclipse the π-system causing significant A1,3-strain (but minimal A1,2 strain *via* eclipsing H atoms) during the deprotonation leading to the C_3-C_4-(*Z*) stereochemistry (which was not detected in the final product silyl ketene acetal). However in the competing **TS2,** the H atom on C_4 of ester **12** would eclipse the π-system minimizing A1,3-strain during deprotonation while the methyl group would eclipse the H atom on C_3 leading to A1,2 strain and thus afford the C_3-C_4-(*E*) stereochemistry of the final product **32** (as observed in a >20:1 E/Z ratio). Based on the experimental ratios of *E/Z* for the C_1-C_2 and C_3-C_4 olefin geometries in all of the isolated silyl ketene acetals **24-30**, it appears that **TS2** (in lieu of **TS1**) must be in operation during the CIPE γ-deprotonations of (*E*)-α-trimethylsilyl-α,β-unsaturated esters.

CONCLUSION

In conclusion, we have presented an expansion of the scope for the catalytic carbocupration of alkynoates in the presence of excess trialkylsilyl triflates to include several β-alkyl substituted (*E*)-α-silyl-α,β-unsaturated esters. These substrates were converted to their β,γ-unsaturated constitutional isomers *via* a γ-deprotonation-α-protonation sequence. Kinetic protonations with aq. HCl of the intermediate silyl ketene acetals in a biphasic solution were required to illicit high levels of regioselectivity. The extended silyl ketene acetal intermediates were also isolated and their stereochemistries were confirmed by nOe to be C_1-C_2-(*E*), C_3-C_4-(*E*). The observed stereochemistry provided insight into the lithium extended dienolate structure resulting from CIPE deprotonations and afforded additional support for an eight-membered transition state in the deprotonation of (*Z*)-α,β-unsaturated carbonyls with metallo dialkylamides. Future directions of investigation will include further utilization of both the prepared allyl silanes and extended silyl ketene acetals in target driven synthesis. In addition, a novel approach to enantioenriched allyl silanes by means of a chiral protonation of the

described extended silyl ketene acetal intermediates is currently ongoing. Results from these studies will be reported in due course.

EXPERIMENTAL SECTION

All of the reactions were performed under Ar in flame-dried glassware. Anhydrous tetrahydrofuran (THF) was obtained from a commercial source and used without purification. Copper(I) iodide (98% purity) and lithium chloride (LiCl, 99%+, ACS) were used without any purification. The NMR spectra were recorded with either a 360 or 500 MHz Bruker spectrometer. ^{1}H spectra were obtained using $CDCl_3$ or C_6D_6 as the solvent with chloroform ($CHCl_3$: $\delta = 7.26$ ppm) or benzene (C_6H_6: $\delta = 7.16$ ppm) as the internal standard. ^{13}C spectra were obtained using $CDCl_3$ or C_6D_6 as the solvent with chloroform ($CDCl_3$: $\delta = 77.0$ ppm) or benzene (C_6D_6: $\delta = 128.1$ ppm) as the internal standard. High-resolution mass spectra were recorded on an EBE sector instrument using electron ionization (EI) at 70 eV. Column chromatography was performed using 60-200 μm silica gel. Analytical thin layer chromatography was performed on silica coated glass plates with F-254 indicator. Visualization was accomplished by UV light (254 nm) and $KMnO_4$.

General Experimental Procedure for the TMSOTf-Promoted Catalytic Carbocupration of 1a with aromatic Grignard Reagents: CuI (0.029 g, 0.15 mmol) and LiCl (0.013 g, 0.30 mmol) was placed in a 100 mL round bottom flask (flame dried under vacuum) under Ar. Dry THF (20 mL) was added and the mixture was stirred at rt for a period of 0.5 h until complete dissolution had occurred. The clear, light yellow homogeneous solution was cooled to –78 °C, and **1a** (0.294 g, 3.0 mmol) was added, followed by TMSOTf (3.3 eq., 1.8 mL, 9.9 mmol). After 5 minutes at –78 °C, the aryl Grignard reagent (1.2 eq., 1.2 mL, 3.6 mmol) was added dropwise via syringe, and the solution was stirred at –78 °C for 1 h and allowed to warm to rt. The reaction was quenched with H_2O and the product extracted with Et_2O (3 X 25 mL), and the combined organic layers were washed with deionized H_2O followed by saturated NH_4Cl. The organic layer was separated, dried with $MgSO_4$, and concentrated *in vacuo* to

give the crude product, which was then analyzed by ^{1}H NMR spectroscopy to determine diastereoselectivity. Column chromatography of the crude material (3% ethyl acetate in hexanes) afforded the pure vinyl silane products.

Ethyl-(*E*)-3-phenyl-2-(trimethylsilyl)acrylate (**2**): Yield: 0.684 g, 92%: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (m, 5H), 6.77 (s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.19 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 141.3, 138.7, 136.6, 128.4, 128.3, 128.1, 60.4, 14.1, -1.7. IR (CH_2Cl_2): 2954, 1711, 1601, 1490, 1213, 1028, 852, 753, 696 cm^{-1}. R_f = 0.66, 20% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{14}H_{20}O_2Si$ 248.1233; Found: 248.1239.

Ethyl-(*E*)-3-phenyl-2-(triethylsilyl)acrylate (**3**): Yield: 0.722 g, 83%: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.31 (m, 5H), 6.79 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.6 Hz, 9H), 0.75 (q, *J* = 7.6 Hz, 6H). ^{13}C NMR (125MHz, $CDCl_3$) δ 172.1, 142.1, 136.7, 136.1, 128.3, 128.3, 128.1, 60.3, 14.0, 7.1, 3.0. IR (CH_2Cl_2): 2957, 2872, 1708, 1601, 1456, 1190, 1006, 740, 696 cm^{-1}. R_f = 0.77, 20% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M\text{-}C_2H_5]^+$ Calcd for $C_{17}H_{26}O_2Si$ 261.1311; Found 261.1312.

Ethyl-(*E*)-3-(*o*-tolyl)-2-(trimethylsilyl)acrylate (**4**): Yield: 0.692 g, 88%: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (m, 4H), 7.03 (s, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.25 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 142.2, 139.5, 136.7, 135.7, 129.9, 128.1, 127.6, 125.6, 60.1, 19.6, 14.0, -1.5. IR (CH_2Cl_2): 2958, 1703, 1605, 1369, 1198, 1030, 760, 669cm^{-1}. R_f = 0.81, 20% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{15}H_{22}O_2Si$ 262.1389; Found 262.1392.

Ethyl-(*E*)-3-mesityl-2-(trimethylsilyl)acrylate (**5**): Yield: 0.801 g, 92%: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.80 (s, 2H), 3.95 (q, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 2.14 (s, 6H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.26 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 146.1, 140.8, 136.3, 134.8, 134.5, 127.7, 59.7, 21.0, 20.0, 13.9, -1.3. IR (CH_2Cl_2): 2957, 2912, 1712, 1605, 1442, 1327, 1242, 1190, 1043, 855 cm^{-1}. R_f =

0.77, 20% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{17}H_{26}O_2Si$ 290.1702; Found 290.1707.

Ethyl-(*E*)-3-(3-methoxyphenyl)-2-(trimethylsilyl)acrylate (**6**): Yield: 0.734 g, 88%: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.89 (s, 1H), 6.83 (dd, *J* = 8.3, 3.0 Hz, 1H), 6.78 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.24 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 159.5, 141.0, 139.0, 138.0, 129.3, 120.7, 114.5, 113.1, 60.4, 55.2, 14.2, -1.7. IR (CH_2Cl_2): 2961, 2898, 1704, 1597, 1579, 1468, 1250, 1194, 1035, 847, 777, 688 cm^{-1}. R_f = 0.68, 20% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{15}H_{22}O_3Si$ 278.1338; Found 278.1338.

Ethyl-(*E*)-3-(4-methoxyphenyl)-2-(trimethylsilyl)acrylate (**7**): Yield: 0.751 g, 90%: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.74 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.23 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 159.8, 140.9, 135.8, 129.8, 129.2, 113.7, 60.3, 55.2, 14.2, -1.6. IR (CH_2Cl_2): 2961, 2894, 1704, 1608, 1509, 1257, 1202, 1039, 995, 851 cm^{-1}. R_f = 0.68, 20% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{15}H_{22}O_3Si$ 278.1338; Found 278.1346.

Methyl-(*E*)-3-phenyl-2-(trimethylsilyl)acrylate (**8**): Yield: 0.632 g, 90%: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 5H), 6.82 (s, 1H), 3.71 (s, 3H), 0.24 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 141.5, 138.2, 136.5, 128.4, 128.3, 128.0, 51.4, -1.8. IR (CH_2Cl_2): 2957, 1716, 1605, 1428, 1209, 1021, 946, 843, 758, 696 cm^{-1}. R_f = 0.73, 20% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{13}H_{18}O_2Si$ 234.1076; Found 234.1085.

Ethyl-(*E*)-3-phenyl-2-(trimethylsilyl)but-2-enoate (**9**): Yield: 0.668 g, 85%: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 5H), 3.86 (q, *J* = 7.2 Hz, 2H), 2.19 (s, 3H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.28 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 152.0, 144.2, 135.0, 128.0, 127.3, 126.6, 59.9, 24.0, 13.9, -0.24. IR (CH_2Cl_2): 2961, 2902, 1704, 1597, 1442, 1261, 1209, 1091, 1035, 839, 754, 702 cm^{-1}. R_f = 0.48, 20%

EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{15}H_{22}O_2Si$ 262.1389; Found 262.1387.

General Experimental Procedure for the TMSOTf-Promoted Catalytic Carbocupration of 1a with aliphatic Grignard Reagents: CuI (0.11 g, 0.6 mmol) and LiCl (0.050 g, 1.2 mmol) was flame dried under vacuum in a 100 mL round bottom flask under Ar. Dry THF (20 mL) was added and the mixture was stirred at RT for a period of 0.5 h until complete dissolution had occurred. The clear, light yellow homogeneous solution was cooled to – 78 °C, and **1a** (0.39 g, 0.40 mL, 4.0 mmol) was added, followed by TMSOTf (3.3 equiv, 2.4 mL, 13.2 mmol). After 10 minutes at – 78 °C, the aliphatic Grignard Reagent (1.4 equiv, 5.6 mmol) was added dropwise via syringe, and the solution was stirred at –78 °C for 2 hr and allowed to warm to RT for 2 hrs. The reaction was quenched with H_2O and the product extracted with Et_2O (3x25 mL), and the combined organic layers were washed with brine. The organic layer was separated, dried with $MgSO_4$, and concentrated *in vacuo* to give the crude product, which was then analyzed by ^1H NMR spectroscopy to determine diastereoselectivity. The crude material was then submitted to column chromatography and purified using 1% diethyl ether in hexane.

Ethyl-(*E*)-2-(trimethylsilyl)but-2-enoate (**10**): Yield: 0.558 g, 75%: ^1H NMR (360 MHz, $CDCl_3$) 6.30 (q, J = 6.8 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 1.97 (d, J = 6.8 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 0.13 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 146.2, 137.0, 59.6, 17.4, 14.2, -1.6. IR (CH_2Cl_2): 2957, 1716, 1612, 1339, 1198, 1032, 847 cm^{-1}. R_f = 0.53, 20% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M\text{-}CH_3]^+$ Calcd for $C_8H_{15}O_2Si$ 171.0841; Found 171.0839.

Ethyl-(*E*)-2-(triethylsilyl)but-2-enoate (**11**)[25]: Yield: 0.301 g, 33%: ^1H NMR (360 MHz, $CDCl_3$) δ 6.22 (q, J = 6.7 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 1.94 (d, J = 6.6 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 8.0 Hz, 9H), 0.64 (q, J = 8.0 Hz, 6H).

Ethyl-(*E*)-2-(trimethylsilyl)pent-2-enoate (**12**): Yield: 0.600 g, 75%: ^1H NMR (500 MHz, $CDCl_3$) δ 6.14 (t, J = 7.1 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.37 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.6 Hz, 3H), 0.13 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 153.0, 135.5, 59.9, 25.0, 14.4, 13.5, -

1.3 ppm. IR: (Pentane) 2964, 1713, 1608, 1366, 1249, 1196, 1140, 1037, 840, 625 cm^{-1}. R_f: 0.64, 10% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M-H]^+$ Calcd for $C_{10}H_{19}O_2Si$ 199.1233; Found 199.1161.

Ethyl-(*E*)-2-(triethylsilyl)pent-2-enoate (**13**): Yield: 0.427 g, 44%: ^1H NMR (360 MHz, $CDCl_3$) δ 6.06 (t, *J* = 7.1 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.33 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.6 Hz, 3H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.64 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 152.8, 132.7, 59.9, 25.1, 14.3, 13.7, 7.2, 3.2 ppm. IR: (Pentane) 2956, 2876, 1713, 1607, 1459, 1417, 1366, 1348, 1307, 1195, 1137, 1037, 1006, 721 cm^{-1}. R_f: 0.61, 10% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M- C_2H_5]^+$ Calcd for $C_{11}H_{21}O_2Si$ 213.1311; Found: 213.1311.

Ethyl-(*E*)-4-methyl-2-(trimethylsilyl)pent-2-enoate (**14**): Yield: 0.702 g, 82%: ^1H NMR (360 MHz, $CDCl_3$) δ 5.89 (d, *J* = 9.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.92 (m, 1H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 6H), 0.13 (s, 9H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 170.6, 157.4, 133.5, 59.9, 30.6, 22.4, 14.4, –1.3. IR: (Pentane) 2962, 2870, 1714, 1608, 1467, 1366, 1249, 1198, 1150, 1037, 996, 841, 694, 628 cm^{-1}. R_f = 0.70, 10% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{11}H_{22}O_2Si$ 214.1389; Found: 214.1398.

Ethyl-(*E*)-2,4-bis(trimethylsilyl)but-2-enoate (**15**): Yield: 0.929 g, 90%: ^1H NMR (360 MHz, $CDCl_3$) δ 6.41 (t, *J* = 9.1 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.22 (d, *J* = 9.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.12 (s, 9H), 0.03 (s, 9H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 170.1, 152.5, 131.2, 59.4, 25.4, 14.4, -1.0, -1.7 ppm. IR: (Pentane) 2955, 2899, 1708, 1589, 1367, 1249, 1198, 1126, 1049, 840, 751, 693, 629 cm^{-1}. R_f: 0.70, 10% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{12}H_{26}O_2Si_2$ 258.1471; Found 258.1469.

Ethyl-(*E*)-2-(triethylsilyl)-4-(trimethylsilyl)but-2-enoate (**16**): Yield: 0.901 g, 75%: ^1H NMR (500 MHz, $CDCl_3$) δ 6.32 (t, *J* = 9.0 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.18 (d, *J* = 8.8 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.64 (q, *J* = 7.9 Hz, 6H), 0.03 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ170.5, 152.4, 128.3, 59.5, 25.4, 14.3, 7.3, 3.5, -1.6 ppm. IR: (Pentane) 2954, 2875, 1706,

1588, 1460, 1416, 1366, 1349, 1249, 1195, 1127, 1047, 1006, 854, 728cm^{-1}. R_f: 0.67, 10% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{15}H_{32}O_2Si_2$ 300.1941; Found 300.1930.

Ethyl-(*E*)-4-phenyl-2-(trimethylsilyl)but-2-enoate (**17**): Yield: 0.734 g, 70%: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.27 (m, 5H), 6.30 (t, *J* = 7.0 Hz, 1H), 4.27 (q, *J* = 7.0 Hz, 2H), 3.74 (d, J = 7.0 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 0.18 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ170.3, 149.1, 139.7, 136.8, 128.8, 128.7, 126.3, 60.2, 38.0, 14.5, -1.2 ppm. IR (CH_2Cl_2): 2956, 1714, 1601, 1493, 1215, 1023, 852, 757, 695 cm^{-1}. R_f = 0.64, 20% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{15}H_{22}O_2Si$ 262.1389; Found 262.1383.

Ethyl-(*E*)-2-(trimethylsilyl)non-2-enoate (**18**): Yield: 0.902 g, 88%: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.15 (t, *J* = 6.9 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.35 (q, *J* = 7.6 Hz, 2H), 1.42 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.29 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 5, 3H), 0.13 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 151.8, 135.9, 59.9, 31.6, 31.6, 29.0, 29.0, 22.5, 14.4, 14.0, -1.3. IR (CH_2Cl_2): 2962, 1711, 1373, 1183, 1042, 669 cm^{-1}. R_f = 0.88, 20% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M\text{-}CH_3]^+$ Calcd for $C_{13}H_{25}O_2Si$ 241.1624; Found 241.1622.

Ethyl-(*E*)-3-methyl-2,4-bis(trimethylsilyl)but-2-enoate (**19**): Yield: 0.359 g, 33%: ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.12 (q, *J* = 7.1 Hz, 2H), 1.83 (s, 3H), 1.81 (s, 2H), 1.28 (t, *J* = 7.0 Hz, 3H), 0.17 (s, 9H), 0.05 (s, 9H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 172.9, 153.5, 127.9, 59.8, 30.3, 24.8, 14.4, 0.1, -0.8 ppm. IR: (Pentane) 2955, 1710, 1599, 1249, 1211, 1151, 1041, 841cm^{-1}. R_f: 0.65, 10% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{13}H_{28}O_2Si_2$ 272.1628; Found 272.1629.

General Experimental Procedure for the Syntheses of (*E*)-α-trialkylsilyl-β,γ-unsaturated esters: Freshly distilled (^{i}Pr)$_2$NH (0.07g, 0.1 mL, 0.65 mmol) in dry THF (1.4 mL) was placed into a flame dried 25 mL round bottom flask and cooled to 0 °C. *n*-Butyllithium (2.2 M, 0.29 mL, 0.65 mmol) was added to the solution dropwise *via* syringe and allowed stir for 30 min. The solution was cooled to -78 °C and a representative α-TMS-(*E*)-α,β-unsaturated ester (0.83 equiv., 0.54 mmol) was added dropwise. The reaction was stirred for 2 hrs and TMSCl (0.07g, 0.08 mL, 0.65 mmol) was added and

further stirring continued for 0.5 hr. The reaction was poured into an Erlenmeyer flask containing pentane (6 mL), saturated NH_4Cl (6 mL), and crushed ice (~ 20 g) and transferred to a separatory funnel. The organic layer was separated and the aqueous layer was extracted with pentane (20 mL). The organic extracts were placed in an Erlenmeyer flask, lowered to 0 °C, stirred vigorously with 5% HCl (6 mL) for 15 min. The reaction mixture was then placed into another separatory funnel, the organic layer was removed, and the aqueous layer was washed with pentane (10 mL). The organic extracts were washed with brine, dried with $MgSO_4$, and concentrated.

Ethyl-2-(trimethylsilyl)but-3-enoate (**22**)[26]: Yield: 0.080 g, 80%: ^{1}H NMR: (360 MHz, $CDCl_3$) δ 6.03 (ddd, *J* = 17.3, 10.2, 1.7 Hz, 1H), 4.94 (ddd, *J* = 10.2, 1.7, 0.7 Hz, 1H), 4.88 (ddd, *J* = 17.3, 1.7, 0.8 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.91 (d, *J* = 10.2 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.09 (s, 9H).

Ethyl-2-(triethylsilyl)but-3-enoate (**23**): Yield: 0.122 g, 99%: ^{1}H NMR: (360 MHz, $CDCl_3$) δ 6.06 (ddd, *J* = 17.3 Hz, 10.2 Hz, 10.2 Hz, 1H), 4.91 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.02 (d, *J* = 10.2 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.8 Hz, 9H), 0.64 (q, *J* = 7.5 Hz, 6H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 173.2, 133.5, 113.1, 59.9, 42.2, 14.3, 7.1, 2.4 ppm. IR: (Pentane) 2955, 2913, 2878, 1719, 1631, 1460, 1415, 1366, 1304, 1285, 1238, 1170, 1131, 1073, 1038, 1007, 900, 801, 710 cm^{-1}. R_f: 0.67, 10% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{12}H_{24}O_2Si$ 228.1546; Found 228.1550.

Ethyl-(*E*)-2-(trimethylsilyl)pent-3-enoate (**24**)[16a] : Yield: 0.087 g, 80%: ^{1}H NMR: (360 MHz, $CDCl_3$) δ 5.63 (ddq, *J* = 15.2, 10.2, 1.6 Hz, 1H), 5.30 (dq, *J* = 15.2, 6.4 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.82 (d, *J* = 10.2 Hz, 1H), 1.68 (dd, J = 6.5, 1.7 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.06 (s, 9H).

Ethyl-(*E*)-2-(triethylsilyl)pent-3-enoate (**25**): Yield: 0.129 g, 99%: ^{1}H NMR: 360 MHz, $CDCl_3$) δ 5.65 (ddq, *J* = 15.2, 10.4, 1.6 Hz, 1H), 5.28 (dq, *J* = 15.2, 6.4 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 2.92 (d, *J* = 10.4 Hz, 1H), 1.66 (dd, *J* = 6.4, 1.6 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.8 Hz, 9H), 0.59 (q, *J* = 7.6 Hz, 6H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 173.7, 125.6, 123.9, 59.8, 40.4, 17.9, 14.3, 7.0, 2.5 ppm. IR: (Pentane) 2955, 2878, 1720, 1583, 1549, 1334, 1259, 1150, 1007, 969, 731cm^{-1}. R_f: 0.68,

10% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{13}H_{26}O_2Si$ 242.1702; Found 242.1695.

Ethyl-(*E*)-2,4-bis(trimethylsilyl)but-3-enoate (**26**): Yield: 0.138 g, 99%: ^{1}H NMR: (500 MHz, $CDCl_3$) δ 6.21 (dd, *J* = 18.7, 9.6 Hz, 1H), 5.47 (dd, *J* = 18.6, 0.8 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.97 (dd, *J* = 9.5, 0.8 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.07 (s, 9H), 0.05 (s, 9H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 172.7, 140.8, 128.9, 59.9, 48.6, 14.5, -1.2, -2.9 ppm. IR: (Pentane) 2956, 2926, 2854, 1719, 1604, 1367, 1323, 1300, 1249, 1217, 1180, 1137, 1061, 996, 842, 730, 692, 641 cm^{-1}. R_f: 0.71, 10% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{12}H_{26}O_2Si_2$ 258.1471; Found 258.1474.

Ethyl-(*E*)-2-(triethylsilyl)-4-(trimethylsilyl)but-3-enoate (**27**): Yield: 0.160 g, 99%: ^{1}H NMR: (500 MHz, $CDCl_3$) δ 6.25 (dd, *J* = 18.6, 9.8 Hz, 1H), 5.46 (dd, *J* = 18.6, 0.9 Hz, 1H), 4.09 (*J* = 7.1 Hz, 2H), 3.08 (dd, *J* = 9.8, 0.9 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.9 Hz, 6H), 0.04 (s, 9H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 173.0, 141.1, 128.5, 59.9, 45.7, 14.3, 7.1, 2.4, -1.2 ppm. IR: (Pentane) 2954, 2878, 1719, 1603, 1414, 1367, 1322, 1300, 1248, 1216, 1179, 1137, 1005, 867, 840, 715 cm^{-1}. R_f: 0.71, 10% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{15}H_{32}O_2Si_2$ 300.1941; Found 300.1951.

Ethyl-(*E*)-4-phenyl-2-(trimethylsilyl)but-3-enoate (**20**)[16b]: Yield: 0.140 g, 99%: ^{1}H NMR: (360 MHz, $CDCl_3$) δ 7.33 (m, 5H), 6.52 (dd, *J* = 15.9, 10.0 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 3.13 (dd, *J* = 10.0, 0.7 Hz, 1H), 1.35 (t, *J* = 7.2 Hz, 3H), 0.21 (s, 9H).

Ethyl-4-methyl-2-(trimethylsilyl)pent-3-enoate (**28**): Yield: 0.104 g, 90%: ^{1}H NMR: (360 MHz, $CDCl_3$) δ 5.40 (dm, *J* = 10.9 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.05 (d, *J* = 10.9 Hz, 1H), 1.71 (d, *J* = 1.4 Hz, 3H), 1.53 (d, *J* = 1.1 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.03 (s, 9H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ173.5, 129.9, 118.7, 59.8, 39.5, 25.7, 18.2, 14.4, -2.7 ppm. IR: (Pentane) 2965, 1718, 1367, 1294, 1250, 1202, 1145, 1041, 844, 757 cm^{-1}. R_f: 0.63, 10% EtOAc in hexanes. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{11}H_{22}O_2Si$ 214.1389; Found 214.1390.

General Experimental Procedure for the Syntheses of Conjugated Silyl Ketene Acetals : Freshly

distilled (^{i}Pr)$_2$NH (0.07g, 0.1 mL, 0.65 mmol) in dry THF (1.4 mL) was placed into a flame dried 25 mL round bottom flask and cooled to 0 °C. *n*-Butyllithium (2.2 M, 0.29 mL, 0.65 mmol) was added to the solution dropwise *via* syringe and allowed stir for 30 min. The solution was cooled to -78 °C and a representative α-TMS-(*E*)-α,β-unsaturated ester (0.83 equiv., 0.54 mmol) was added dropwise. The reaction was stirred for 2 hr and TMSCl (0.07g, 0.08 mL, 0.65 mmol) was added and further stirring continued for 0.5 hr. The reaction was poured into an Erlenmeyer flask containing pentane (6 mL), saturated NH_4Cl (6 mL), and crushed ice (~20 g) and transferred to a separatory funnel. The organic layer was separated and the aqueous layer was extracted with pentane (20 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, and concentrated.

(*E*)-(1-ethoxy-1-((trimethylsilyl)oxy)buta-1,3-dien-2-yl)trimethylsilane (**29**): Yield: 0.130 g, 93%: ^{1}H NMR: (360 MHz, $CDCl_3$) δ 6.40 (dd, *J* = 17.9, 11.4 Hz, 1H), 4.98 (dd, *J* = 17.9, 2.0 Hz, 1H), 4.83 (dd, *J* = 11.1, 2.0 Hz, 1H), 3.85 (q, *J* = 7.0 Hz, 2H), 1.25 (t, *J* = 6.9 Hz, 3H), 0.26 (s, 9H), 0.17 (s, 9H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.7, 136.0, 111.5, 93.1, 63.4, 14.6, 0.9, 0.2 ppm. IR: (Pentane): 2958, 1722, 1612, 1582, 1390, 1245, 1082, 845, 762, 689, 631 cm^{-1}. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{12}H_{26}O_2Si_2$ 258.1471; Found 258.1481.

(*E*)-(1-ethoxy-1-((trimethylsilyl)oxy)buta-1,3-dien-2-yl)triethylsilane (**30**): Yield: 0.138 g, 85%: ^{1}H NMR: (500 MHz, $CDCl_3$) δ 6.37 (dd, *J* = 18.0, 11.4 Hz, 1H), 4.95 (dd, *J* = 18.0, 2.2 Hz, 1H), 4.81 (dd, *J* = 11.2, 2.0 Hz, 1H), 3.82 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H), 0.25 (s, 9H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 159.0, 136.5, 111.6, 89.7, 63.3, 14.6, 7.6, 4.4, 0.3 ppm. IR: (Pentane) 2954, 2874, 1612, 1580, 1389, 1254, 1152, 1081, 1002, 876, 849, 755, 730 cm^{-1}. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{15}H_{32}O_2Si_2$ 300.1941; Found 300.1929.

(*E*)-(1-ethoxy-4-methyl-1-((trimethylsilyl)oxy)penta-1,3-dien-2-yl)trimethylsilane (**31**): Yield: 0.153 g, 99%: ^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.40 (m, 1H), 3.79 (q, *J* = 7.1 Hz, 2H), 1.70 (d, *J* = 1.3 Hz, 3H), 1.51 (d, *J* = 1.3 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.15 (s, 9H), 0.04 (s, 9H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 155.5, 131.9, 122.6, 90.2, 62.7, 25.3, 19.5, 14.7, 0.0, -0.2 ppm. IR: (Pentane) 2960, 1722,

1612, 1252, 1218, 1077, 836, 754 cm^{-1}. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{14}H_{30}O_2Si_2$ 286.1784; Found 286.1791.

((1*E*,3*E*)-1-ethoxy-1-((trimethylsilyl)oxy)penta-1,3-dien-2-yl)trimethylsilane (**32**): Yield: 0.134 g, 91%: ^1H NMR: (500 MHz, $CDCl_3$) δ 5.99 (dq, *J* = 15.9, 1.7 Hz, 1H), 5.40 (dq, *J* = 16.0, 6.5 Hz, 1H), 3.80 (q, *J* = 7.1 Hz, 2H), 1.71 (dd, *J* = 6.5, 1.7 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.23 (s, 9H), 0.12 (s, 9H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 157.5, 129.5, 122.9, 92.4, 63.4, 19.0, 14.6, 0.9, 0.2 ppm. IR: (Pentane): 2960, 2349, 1721, 1589, 1443, 1366, 1252, 1150, 1062, 970, 846, 755, 631 cm^{-1}. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{13}H_{28}O_2Si_2$ 272.1628; Found 272.1630.

((1*E*,3*E*)-1-ethoxy-1-((trimethylsilyl)oxy)penta-1,3-dien-2-yl)triethylsilane (**33**): Yield: 0.151 g, 89%: ^1H NMR: (500 MHz, C_6D_6) δ 6.25 (dq, *J* = 15.8, 1.6 Hz, 1H), 5.58 (dq, *J* = 15.8, 6.5 Hz, 1H), 3.69 (q, *J* = 7.0 Hz, 2H), 1.76 (dd, *J* = 6.5, 1.6 Hz, 3H), 1.16 (t, *J* = 7.9 Hz, 9H), 1.05 (t, *J* = 7.0 Hz, 3H), 0.90 (q, *J* = 7.9 Hz, 6H), 0.18 (s, 9H). ^{13}C NMR: (125 MHz, C_6D_6) δ 158.5, 130.8, 123.3, 88.9, 63.3, 19.1, 14.7, 8.2, 5.1, 0.29 ppm. IR: (Pentane) 2954, 2874, 1589, 1481, 1462, 1389, 1253, 1107, 1063, 1003, 967, 849, 733 cm^{-1}. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{16}H_{34}O_2Si_2$ 314.2097; Found 314.2099.

((1*E*,3*E*)-4-ethoxy-4-((trimethylsilyl)oxy)buta-1,3-diene-1,3-diyl)bis(trimethylsilane) (**34**): Yield: 0.162 g, 91%: ^1H NMR: (500 MHz, C_6D_6) δ 7.00 (d, *J* = 19.5 Hz, 1H), 5.89 (d, *J* = 19.5 Hz, 1H), 3.67 (q, *J* = 7.1 Hz, 2H), 1.02 (t, *J* = 7.1 Hz, 3H), 0.41 (s, 9H), 0.21 (s, 9H), 0.18 (s, 9H). ^{13}C NMR: (125 MHz, C_6D_6) δ 159.5, 144.8, 126.5, 95.8, 63.5, 14.6, 1.5, 0.3, - 0.6 ppm. IR: (Pentane) 2955, 2898, 1582, 1553, 1482, 1468, 1389, 1366, 1246, 1207, 1145, 1070, 993, 841, 757, 688, 631 cm^{-1}. HRMS (EI-EBE Sector) m/z: $[M]^+$ Calcd for $C_{15}H_{34}O_2Si_3$ 330.1867; Found 330.1872.

ASSOCIATED CONTENT

Supporting Information Available. Full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author:

jenningm@ua.edu

ORCID:

Michael P. Jennings: 0000-0002-1069-6246

Notes:

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Partial support for this project was provided by the University of Alabama and the National Science Foundation CAREER program under CHE-0845011.

REFERENCES

1. (a) Fleming, I.; Dunogués, J.; Smithers, R. The Electrophilic Substitution of Allylsilanes and Vinylsilanes. *Org. React.* **1989**, *37*, 57-575. (b) Majetich, G. Allylsilanes in Organic Synthesis. In *Organic Synthesis: Theory and Application;* **1989;** Vol. 1**,** p 173-240. (c) Yamamoto, Y.; Asao, N. Selective Reactions Using Allylic Metals. *Chem. Rev.* **1993**, *93*, 2207-2239. (d) Denmark, S. E.; Almstead, N. G. Stereochemical Studies on the Addition of Allylsilanes to Aldehydes. The SE' Component. *J. Mex. Chem. Soc*. **2009**, *53*, 174-192.

2. For a few reviews on the Hosomi-Sakurai reaction, see: (a) Lade, J. J.; Pardeshi, S. D.; Vadagaonkar, K. S.; Murugan, K.; Chaskar, A. C. The Remarkable Journey of Catalysts From Stoichiometric to Catalytic Quantity for Allyltrimethylsilane Inspired Allylation of Acetals, Ketals, Aldehydes and Ketones. *RSC Adv*. **2017**, *7*, 8011-8033. (b) Hosomi, A.; Miura, K. Development of New Reagents Containing Silicon and Related Metals and Application to

Practical Organic Syntheses. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 835-851. (c) Marko, I. E.; Mekhalfia, A.; Murphy, F.; Bayston, D. J.; Bailey, M.; Janoouusek, Z.; Dolan, S. Multicomponent Cyclizations. Efficient Methodologies for the Preparation of Complex Natural Products. *Pure Appl. Chem*. **1997**, *69*, 565-570. For the initial disclosure paper, see: (d) Hosomi, A.; Sakurai, H. Chemistry of Organosilicon Compounds. 89. Syntheses of γ,δ-Unsaturated Alcohols from Allylsilanes and Carbonyl Compounds in the Presence of Titanium Tetrachloride. *Tetrahedron Lett*. **1976**, *17*, 1295-1298.

3. For a couple of reviews that focus solely on the Hiyama coupling, see: (a) Teizeira, R. R.; Barbosa, L. C. A.; Pilo-Veloso, D. Palladium Catalyzed Cross Coupling Reactions of Organosilicon Compounds: Historical, Synthetic and Mechanistic Aspects. *Quim. Nova* **2007**, *30*, 1704-1720. (b) Hiyama, T. How I Came Across the Silicon-Based Cross-Coupling Reaction. *J. Organomet. Chem.* **2002**, *653*, 58-61. For recent reviews that include the Hiyama coupling, see: (c) Grimaud, L.; Jutand, A. Role of Fluoride Ions in Palladium-Catalyzed Cross-Coupling Reactions. *Synthesis* **2017**, *49*, 1182-1189. (d) Yang, H.; Yang, X.; Tang, W. Transition-metal Catalyzed Asymmetric Carbon-Carbon Cross-Coupling With Chiral Ligands. *Tetrahedron.* **2016**, *72*, 6143-6174. (e) Glorius, F. Asymmetric Cross-Coupling of Non-Activated Secondary Alkyl Halides. *Angew. Chem. Int. Ed*. **2008**, *47*, 8347-8349.

4. For a series of reviews, see: (a) Hosokawa, S. Recent Development of Vinylogous Mukaiyama Aldol Reactions. *Tetrahedron Lett.* **2018**, *59*, 77-88. (b) Gati, W.; Yamamoto, H. Second Generation of Aldol Reaction. *Acc. Chem. Res*. **2016**, *49*, 1757-1768. (c) Averill, D. J.; Allen, M. J. Tools for Studying Aqueous Enantioselective Lanthanide-Catalyzed Mukaiyama Aldol Reactions. *Catal. Sci. Technol.* **2014**, *4*, 4129-4137. (d) Kalesse, M.; Cordes, M.; Symkenberg, G.; Lu, H.-H. The Vinylogous Mukaiyama Aldol Reaction (VMAR) in Natural Product Synthesis. *Nat. Prod. Rep.* **2014**, *31*, 563-594. (e) Roiban, G.-D.; Ilie, A.; Reetz, M. T. The Chelation-Controlled Mukaiyama Aldol Reaction of Chiral α- and β-Alkoxy Aldehydes. *Chem. Lett*. **2014**, *43*, 2-10. (f) Sutar, R. L.; Joshi, N. N. Base-Catalyzed Mukaiyama-Type Aldol

Additions, A Continued Quest for Stereoselectivity. *Tetrahedron: Asymmetry*. **2013**, *24*, 1345-1363. (g) Beutner, G. L.; Denmark, S. E. Lewis Base Catalysis of the Mukaiyama Directed Aldol Reaction: 40 Years of Inspiration and Advances. *Angew. Chem. Int. Ed*. **2013**, *52*, 9086-9096. (h) Kan, S. B. J.; Ng, K. K.-H.; Paterson, I. The Impact of the Mukaiyama Aldol Reaction in Total Synthesis. *Angew. Chem. Int. Ed*. **2013**, *52*, 9097-9108. (i) Matsuo, J.-i.; Murakami, M. The Mukaiyama Aldol Reaction: 40 Years of Continuous Development. *Angew. Chem. Int. Ed*. **2013**, *52*, 9109-9118.

5. For a recent review, see: (a) Koshvandi, T. k. A.; Heravi, M. M. Applications of Danishefsky's Dienes in Asymmetric Oxo-Diels-Alder Reactions. *Tetrahedron: Asymmetry*. **2017**, *28*, 1506-1556. and references therein. (b) Li, Y.; Hu, Y.; Zhang, S.; Sun, J.; Li, L.; Zha, Z.; Wang, Z. Copper-Catalyzed Enantioselective Hetero-Diels-Alder Reaction of Danishefsky's Diene with Glyoxals. *J. Org. Chem*. **2016**, *81*, 2993-2999. (c) Takeda, Y.; Hisakuni, D.; Lin, C.-H.; Minakata, S. 2-Halogenoimidazolium Salt Catalyzed Aza-Diels-Alder Reaction Through Halogen-Bond Formation. *Org. Lett*. **2015**, *17*, 318-321. (d) Zhao, B.; Loh, T.-P. Asymmetric Hetero-Diels-Alder Reaction of Danishefsky's Dienes with α-Carbonyl Esters Catalyzed by an Indium(III)-PyBox Complex. *Org. Lett*. **2013**, *15*, 2914-2917.

6. For some leading references, see: (a) Reynolds, T. E.; Scheidt, K. A. Catalytic Enantioselective α-Acylvinyl Addition Reactions of Silyloxyallenes. *Angew. Chem. Int. Ed*. **2007**, *46*, 7806-7809. (b) Reynolds, T. E.; Stern, C. A.; Scheidt, K. A. N-Heterocyclic Carbene-Initiated α-Acylvinyl Anion Reactivity: Additions of α-Hydroxypropargylsilanes to Aldehydes. *Org. Lett*. **2007**, *9*, 2581-2584. (c) Reynolds, T. E.; Bharadwaj, A. R.; Scheidt, K. A. Stereoselective Lewis Acid-Catalyzed α-Acylvinyl Additions. *J. Am. Chem. Soc*. **2006**, *128*, 15382-15383. (d) Crimmins, M. T.; Nantermet, P. G. Addition of Zinc Homoenolates to Acetlyenic Esters: A Formal [3+2] Cycloaddition. *J. Org. Chem*. **1990**, *55*, 4235-4237.

7. (a) Wu, J.; Zhu, K.-C.; Yuan, P.-W.; Panek, J. S. Bifunctional Homoallylic Carbamates From Chiral Silane Additions to in situ Generated N-acyl Iminium Ions. *Org. Lett*. **2012**, *14*, 3624-3627 and references therein. (b) Kim, D.; Lee, J. S.; Lozano, L.; Kong, S. B.; Han, H. Enantioenriched Bifunctional Crotylsilanes for the Asymmetric Synthesis of Orthogonally Protected 2-Methyl-1,3-diols. *Org. Lett*. **2013**, *15*, 5142-5145. (c) Chai, G.; Zeng, R.; Fu, C.; Ma, S. Iron-Catalyzed Diastereoselective Synthesis of α-(Methoxycarbonyl)allylsilanes. *Eur. J. Org. Chem*. **2013**, 148-154. (d) Chen, D.; Zhu, D.-X.; Xu, M.-H. Rhodium(I)-Catalyzed Highly Enantioselective Insertion of Carbenoid into Si–H: Efficient Access to Functional Chiral Silanes. *J. Am. Chem. Soc*. **2016**, *138*, 1498-1501.

8. (a) Shimizu, K.; Takimoto, M.; Sato, Y.; Mori, M. Nickel-Catalyzed Regioselective Synthesis of Tetrasubstituted Alkene Using Alkylative Carboxylation of Disubstituted Alkyne. *Org. Lett*. **2005**, *7*, 195-197. (b) Sumida, Y.; Kato, T.; Yost, S.; Hosoya, T. Palladium-Catalyzed Regio- and Stereoselective Hydrosilylation of Electron-Deficient Alkynes. *Org. Lett*. **2012**, *14*, 1552-1555. (c) Rooke, D. A.; Menard, Z. A.; Ferreira, E. M. An Analysis of the Influences Dictating Regioselectivity in Platinum-Catalyzed Hydrosilylations of Internal Alkynes. *Tetrahedron Lett*. **2014**, *70*, 4232-4244.

9. Kharasch, M. S.; Tawney, P. O. Factors Determining the Course and Mechanisms of Grignard Reactions. II. The Effect of Metallic Compounds on the Reaction Between Isophorone and Methylmagnesium Bromide. *J. Am. Chem. Soc*. **1941**, *63*, 2308-2315.

10. For some leading references, see: (a) Nakamura, E; Mori, S. Wherefore Art Thou Copper? Structures and Reaction Mechanisms of Organocuprate Clusters in Organic Chemistry *Angew. Chem. Int. Ed*. **2000**, *39*, 3750-3771. (b) Woodward, S. Decoding the 'Black Box' Reactivity That is Organocuprate Conjugate Addition Chemistry. *Chem. Soc. Rev*. **2000**, *29*, 393-401. (c) Corey, E. J.; Katzenellenbogen, J. A. Stereospecific Synthesis of Trisubstituted and Tetrasubstituted Olefins. Conjugate Addition of Dialkylcopper-lithium Reagents to α,β-Acetylenic Esters. *J. Am. Chem. Soc.* **1969,** *91*, 1851-1852.

11. Reetz, M. T.; Kindler, A. The Kharasch Reaction Revisited: CuX_3Li_2-Catalyzed Conjugate Addition Reactions of Grignard Reagents. *J. Organomet. Chem*. **1995**, *502*, C5-C7.

12. (a) Nakamura, E.; Kuwajima, I. Copper Catalyzed Acylation and Conjugate Addition of Zinc Homoenolate. Synthesis of 4-and 6-Oxo Esters. *J. Am. Chem. Soc*. **1984**, *106*, 3368-3370. (b) Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino H.; Kuwajima, I. Carbon-Carbon Bond-Forming Reactions of Zinc Homoenolate of Esters. A Novel Three-Carbon Nucleophile with General Synthetic Utility. *J. Am. Chem. Soc*. **1987**, *109*, 8056-8066. (c) Frantz, D. E.; Singleton, D. A. Isotope Effects and the Mechanism of Chlorotrimethylsilane-Mediated Addition of Cuprates to Enones. *J. Am. Chem. Soc*. **2000**, *122*, 3288-3295. (d) Nilsson, K.; Andersson, T.; Ullenius, C. π-Complexation Between a Mixed Methylalkenylcuprate and an Alkyne. Further Insight into the Mechanism of Organcopper Additions to Ynoates. *J. Organomet. Chem*. **1997**, *545-546*, 591-595. (e) Nilsson, K.; Andersson, T.; Ullenius, C.; Gerold, A.; Krause, N. NMR Spectroscopic Investigation of the Adducts Formed by Addition of Cuprates to Ynoates and Ynones: Alkenylcuprates or Allenoates? *Chem. Eur. J*. **1998**, *4*, 2051-2058. (f) Klein, J.; Levene, R. Two Different Structures for Copper and Lithium Derivatives of Vinylic Enolates. Effect of Structure on the Direction of Electrophilic Attack." *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1971-1978. (g) Marino, J. P.; Linderman, R. J. Chemistry of Substituted [α-(Carboethoxy)vinyl]cuprates and Their Synthetic Application to Cyclopentenone Annulation. *J. Org. Chem*. **1981**, *46*, 3696-3702.

13. (a) Mueller, A. J.; Jennings, M. P. A Highly Stereoselective TMSOTf-Mediated Catalytic Carbocupration of Alkynoates. *Org. Lett*. **2007**, *9*, 5327-5329. (b) Jennings, M. P.; Sawant, K. B. TMSCl-Mediated Catalytic Carbocupration of Alkynoates: An Unprecedented and Remarkable Effect of Catalyst Loading on Highly Selective Stereochemical Induction via a TMS-allenoate Intermediate. *Eur. J. Org. Chem*. **2004**, 3201-3204.

14. Mueller, A. J.; Jennings, M. P. Vicinal Functionalization of Propiolate Esters via a Tandem Catalytic Carbocupration-Mukaiyama Aldol Reaction Sequence. *Org. Lett.* **2008**, *10,* 1649-1652.

15. Mueller Hendrix, A. J.; Jennings, M. P. Vicinal Functionalization of Propiolate Esters via Catalytic Carbocupration: Stereoselective Formation of Substituted Vinyl Silanes. *Org. Lett.* **2010**, *12*, 2750-2753.

16. (a) Albaugh-Robertson, P.; Katzenellenbogen, J. A. Selective γ-Substitution of α,β-Unsaturated Esters via α-Trimethylsilyl β,γ-Unsaturated Esters. *J. Org. Chem*. **1983**, *48*, 5288-5302. (b) Najafi, M. R.; Wang, M.-L.; Zweifel, G. (*Z*)-α-(trimethylsilyl)-α,β-Unsaturated Esters. Their Stereoselective Conversion into α,β- and β,γ-Unsaturated Esters and β,γ-Unsaturated Ketene Acetals. *J. Org. Chem.* **1990**, *56*, 2468-2476.

17. (a) Hartzell, S. L.; Rathke, M. W. The Preparation and Reactions of Lithio *tert*-Butylbis(trimethylsilyl)acetate. A Synthesis of α-Silylated Vinyl Esters. *Tetrahedron Lett*. **1976**, *17*, 2737-2740. (b) Sato, Y.; Takeuchi, S. α-Substitution of 2-Alkenoic Esters via α-Carbanion Intermediates. *Synthesis*. **1983**, *9*, 734-735. (c) Boeckman, Jr., R. K.; Chinn, R. L. Counterion Effects on Geometric Control in the Peterson Reaction of Bistrimethylsilyl Esters: Synthetic Scope and Mechanistic Implications. *Tetrahedron Lett*. **1985**, *26*, 5005-5008.

18. Yeh, M. C. P.; Knochel, P. The Reactivity of the Highly Functionalized Copper, Zinc Reagents RCu(CN)ZnI Toward 1-Haloalkynes and Acetylenic Esters. *Tetrahedron Lett*. **1989**, *30*, 4799-4802.

19. (a) Bunnell, C. A.; Fuchs, P. L. Synthesis of β,γ-Unsaturated Esters. Direct Generation of Ester Dienolates From β-Keto Ester Tosylhydrazone Trianions. *J. Am. Chem. Soc*. **1977**, *99*, 5184-5187. (b) Fehr, C.; Stempf, I.; Galindo, J. Highly Enantioselective Protonation of Thiol Ester Enolates. *Angew. Chem. Int. Ed. Engl*. **1993**, *32,* 1042-1044. (c) Piers, E.; Gavai, A. Stereospecific Deconjugation of Alkyl (*E*)- and (*Z*)-3-Trimethylstannyl-2-Alkenoates. *J. Org.*

Chem. **1990**, *55*, 2374-2379. (d) Kende, A. S.; Toder, B. H. Stereochemistry of Deconjugative Alkylation of Ester Dienolates. Stereospecific Total Synthesis of the Litsenolides. *J. Org. Chem*. **1982**, *47*, 163-167. (e) Ikeda, Y.; Ukai, J.; Ikeda, N.; Yamamoto, H. Selective Proton Transfer of Unsaturated Esters. Syntheses of a Trail-Following Pheromone for Subterranean Termites and Megatomoic Acid. *Tetrahedron* **1987**, *43*, 743-753. (f) Mayo, P. D.; Silk, P. J.; Abeysekera, S. D.; MaGee, D. I. Synthesis of Three Putative Kairomones of the Beech Leaf-Mining Weevil Orchestes fagi (L.). *Synth Commun*. **2016**, *46*, 1124-1132. (g) Fehr, C.; Galindo, J. Syntheses of the Enantiomers of γ-Cyclogeranic acid, γ-Cyclocitral, and γ-Damascone: Enantioselective Protonation of Enolates *Helv. Chim. Acta* **1995**, *78*, 539-552. (h) Nakai, K.; Miyamoto, S.; Sasuga, D.; Doi, T.; Takahashi, T. The Synthesis of the CD Ring of Paclitaxel. *Tetrahedron Lett*. **2001**, *42*, 7859-7862. (i) Ihara, M.; Suzuki, S.; Taniguchi, N.; Fukumoto, K. Deconjugation of α,β-Unsaturated Esters and an Intramolecular Michael Reaction of Bis-α,β-Unsaturated Esters with Trialkylsilyl Trifluoromethanesulfonate in the Presence of Tertiary Amine: Synthesis of (±)-Ricciocarpin A. *J. Chem. Soc. Perkin. Trans. 1*. **1993**, 2251-2258.

20. Schleyer, P. V. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. Structures and Stabilities of α-Hetero-substituted Organolithium and Organosodium Compounds. Energetic Unimportance of d-Orbital Effects. *J. Am. Chem. Soc*. **1984**, *106*, 6467-6475.

21. Beak, P.; Meyers, A. I. Stereo-and Regiocontrol By Complex Induced Proximity Effects: Reactions of Organolithium Compounds. *Acc. Chem. Res*. **1986**, *19*, 356-363.

22. Whisler, M. C.; MacNeil, S.; Snieckus, V.; Beak, P. Beyond Thermodynamic Acidity: A Perspective on the Complex-Induced Proximity Effect (CIPE) in Deprotonation Reactions. *Angew. Chem. Int. Ed*. **2004**, *43*, 2206-2225.

23. Green, J. R.; Majewski, M.; Snieckus, V. Deprotonation of β,β-Disubstituted α,β-Unsaturated Amides-Mechanism and Stereochemical Consequences. *Can. J. Chem*. **2006**, *84*, 1397-1410.

24. Majewski, M.; Green, J. R.; Snieckus, V. Stereoselective Deprotonation of α,β-Unsaturated Amides. *Tetrahedron Lett*. **1986**, *27*, 531-534.

25. Planellas, M.; Guo, W.; Alonso, F.; Yus, M.; Shafir, A.; Pleixats, R.; Parella, T. Hydrosilylation of Internal Alkynes Catalyzed by Tris-Imidazolium Salt-Sstabilized Palladium Nanoparticles. *Adv. Synth. Catal.* **2014**, *356*, 179-188.

26. Morizawa, Y.; Kanemoto, S.; Oshima, K.; Nozaki, H. Regioselective Coupling of Allylic Ethers With Ethyl 2-Trimethylsilyl-3-Butenoate. *Tetrahedron Lett*. **1982**, *23*, 2953-2954.