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CHEMISTRY OF CYCLOPROPYLACYLSILANES I. α-FUNCTIONALIZED ACYLSILANE REAGENTS FOR THE CYCLOPROPANATION OF ELECTROPHILIC ALKENES

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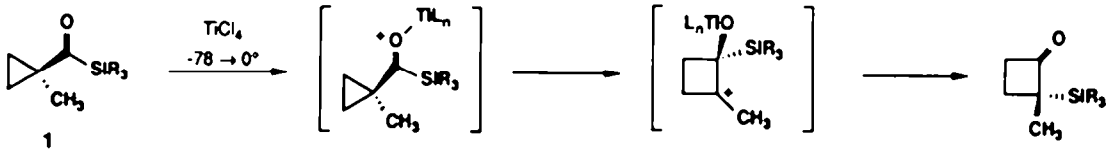
Abstract: Two classes of α-functionalized acylsilane reagents have been developed to effect the cyclopropanation of electrophilic alkenes. The lithium enolate derivatives of the α-haloacylsilanes **14**, **15**, and **17** react with a wide variety of electron-deficient olefins to afford cyclopropylacylsilanes in good yield. In the case of cyclopropanations of α,β-unsaturated carbonyl compounds using the α-chloro reagent **14**, the predominant stereoisomers produced are generally the cyclopropanes in which the acylsilane moiety has a cis stereochemical relationship to the carbonyl group. The synthesis and chemistry of the acylsilane sulfur ylide derivative **33** is also described. This compound has proved particularly useful as a reagent for the cyclopropanation of α,β-unsaturated aldehydes. Efficient syntheses of **33** as well as the α-haloacylsilanes **14**, **15**, and **17** (in 2-4 steps from commercially available starting materials) are also reported.

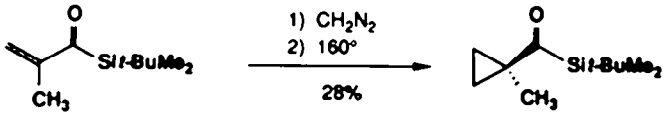
Introduction

Acylsilanes have received considerable attention during the past thirty years due to their unusual spectroscopic features, novel chemical reactivity, and their emerging utility as valuable intermediates for organic synthesis.[2,3] We have recently become interested in exploring the chemistry of *cyclopropylacylsilanes* - a novel class of acylsilane derivatives which we expect will participate in a wide variety of synthetically useful reactions. Of special interest to us are transformations which exploit the well-established reactivity of the strained cyclopropane ring in tandem with the unique chemistry of the acylsilane functional group. Carbocationic rearrangements such as the ring expansion of **1** to **4**[3f] represent one such class of reactions.

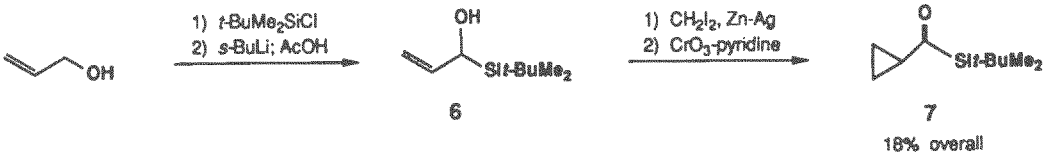


In this rearrangement the powerful ability of the trialkylsilyl substituent to stabilize a β-carbocation operates in conjunction with the high migratory aptitude of this group to make the overall ring expansion an unusually efficient and facile process. Interesting synthetic applications of cyclopropylacylsilanes involving other types of reactive intermediates can also be envisaged. Reactions of particular interest in our laboratory include carbanion-accelerated vinylcyclopropane rearrangements[4] initiated by the Brook rearrangement,[2] and cyclopropylcarbene to cyclobutene ring expansions triggered by the photochemical conversion of acylsilanes to siloxycarbenes.[5]

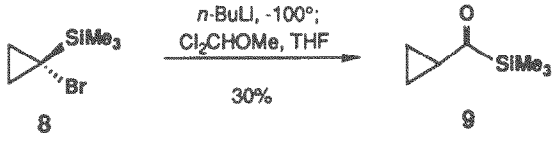
Only four synthetic routes to cyclopropylacylsilanes have previously been recorded. Our synthesis of the cyclopropane **1** in 1985 represented the first report of the preparation of a cyclopropylacylsilane derivative.[3f] Shortly thereafter, Scheller and



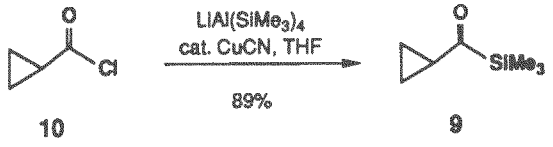
Frei disclosed the results of their investigation of several alternative methods for the synthesis of these compounds.[6] The most successful approach developed in this study involved the Simmons-Smith cyclopropanation of a 1-trialkylsilyl allylic alcohol, followed by Collins oxidation. Four new cyclopropylacylsilanes were prepared by this route in yields ranging from 10 to 85%.



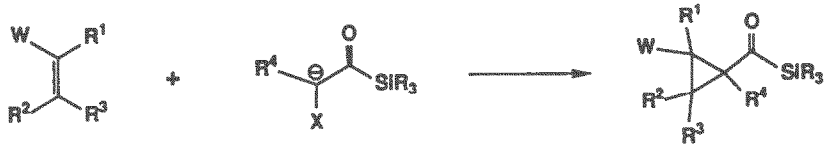
Nakajima and coworkers described a third route to cyclopropylacylsilanes in 1986.[7] This interesting approach (e.g. **8** → **9**) involves a total of three steps (beginning with simple alkenes) and generates the desired acylsilanes in poor to moderate



overall yield. The Nakajima route, unfortunately, is not applicable to the synthesis of 1-substituted cyclopropylacylsilanes such as **1**. Finally, Kang and coworkers have very recently reported a convenient synthesis of the parent cyclopropylacylsilane **9** via the reaction of cyclopropane carboxylic acid chloride with $LiAl(SiMe_3)_4$ in the presence of catalytic CuCN.[8]



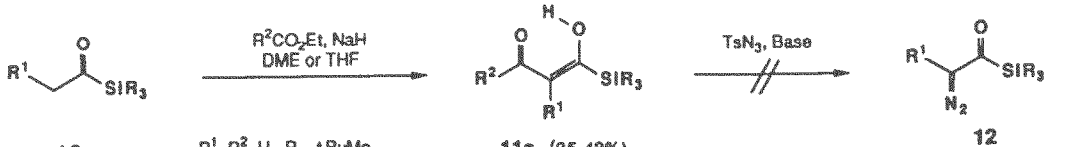
In this paper we describe a general strategy for the synthesis of a variety of bifunctional cyclopropylacylsilanes. As outlined in the following equation, our [2+1] annulation approach involves the reaction of an α-functionalized acylsilane



reagent with an electrophilic alkene. Two complementary versions of the strategy have been developed: one involving α-haloacylsilanes (X = Cl, Br), and a second based on the related sulfur ylide derivatives (X = SMe_2^+).

Results

The α-Diazoacylsilane Approach. The decomposition of α-diazocarbonyl compounds in the presence of activated and unactivated olefins is well established as one of the most efficient and reliable methods for the synthesis of cyclopropyl carbonyl compounds.[9] For our initial studies we consequently focused our attention on the preparation of α-*diazoacylsilanes*. Unfortunately, all of our attempts to isolate a representative of this unknown class of acylsilane derivatives have thus far proved unsuccessful. Most of our efforts in this area have involved the attempted application of the popular diazo group transfer reaction developed by Regitz.[10] Toward this end, the β-oxoacylsilane derivatives **IIa-IId**[11] were prepared in fair to good yield employing standard procedures (eq 1). However, treatment of these acylsilanes with tosyl azide and base under a

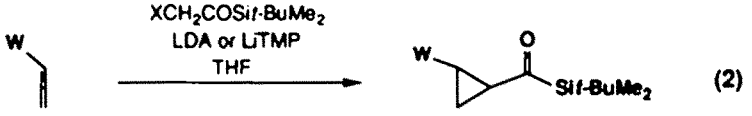


(1)

10a	R^1=R^2=H, R_3=*t*-BuMe$_2$	**11a** (35-48%)
	R^1=H, R^2=OEt, R_3=*t*-BuMe$_2$	**11b** (40%)
10b	R^1=R^2=H, R_3=*t*-BuPh$_2$	**11c** (68-81%)
10c	R^1=Me, R^2=H, R_3=*t*-BuMe$_2$	**11d** (4-20%)

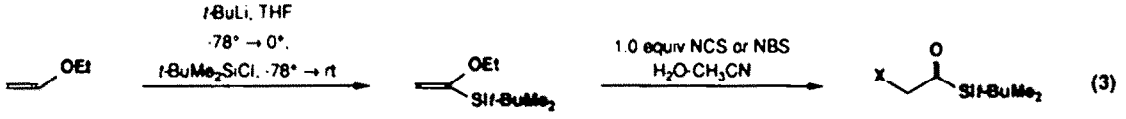
variety of conditions led in every case to the formation of a complex mixture of products. Interestingly, some of these compounds appeared to be derived from silylketene intermediates presumably generated via some type of 1,2-trialkylsilyl group migration. The mechanistic implications of this important observation are considered further in the discussion section of this report.

The α-Haloacylsilane Approach. The reaction of electrophilic olefins with activated α-halocarbanions constitutes one of the most versatile methods available for the synthesis of cyclopropanes,[12] and a number of useful variants of the process have been developed in the years since the groundbreaking studies of the reaction by McCoy.[13,14] The most general strategy we have developed thus far for the synthesis of cyclopropylacylsilanes involves the McCoy-type reaction of lithium enolate derivatives of α-haloacylsilanes with electron deficient alkenes (eq 2; W = electron-withdrawing group, X = Cl or Br).



(2)

For the initial investigation of this cyclopropanation strategy we focused our attention on the α–haloacylsilane reagents **14**, **15**, and **17**. Surprisingly, none of these simple α-haloacylsilanes had been prepared prior to our work, although several more substituted derivatives had been reported previously.[15] Fortunately the requisite α-haloacylsilanes proved to be readily available using the routes outlined in eq 3 and 4. The haloacetyl derivatives **14** and **15** were most conveniently prepared by the

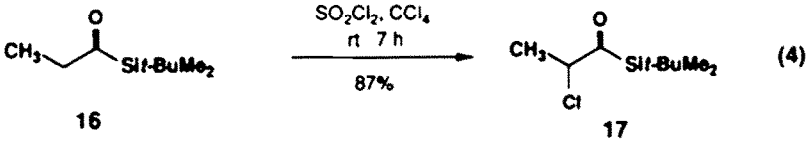


(3)

13

14 (X = Cl)
15 (X = Br)

reaction of the vinyl ether **13**[16] with N-bromo or N-chlorosuccinimide in aqueous acetonitrile. This method proved superior to the direct halogenation of acetyl(*t*-butyldimethyl)silane, which is itself most easily prepared via the hydrolysis of **13**. Aqueous acetonitrile was found to be an especially effective solvent for this halogenation; brominations carried out in other media (e.g. aqueous THF) were complicated by the formation of significant quantities of ethyl (*t*-butyldimethylsilyl)acetate as a byproduct. Under optimal conditions the chloroacetylsilane **14** was obtained in 80% yield after low-temperature recrystallization from pentane; the corresponding bromo derivative was produced in quantitative yield as a bright yellow oil (90-95% purity), which was used in subsequent reactions without further purification. Finally, the 2-chloropropionylsilane **17** was also found to be readily accessible, in this case via the chlorination[18] of **16**[3f] using sulfuryl chloride in carbon tetrachloride (eq 4).



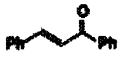
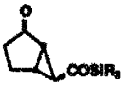
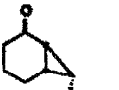
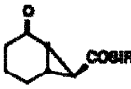
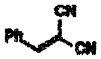
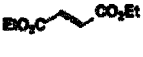
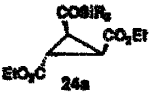
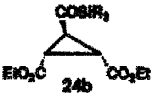
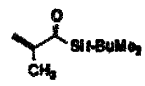
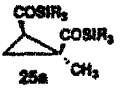
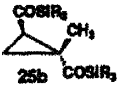
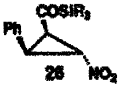
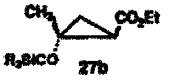
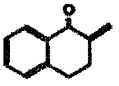
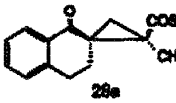
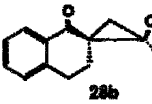
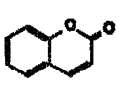
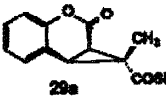
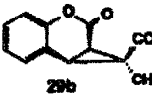
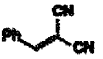
(4)

16 **17**

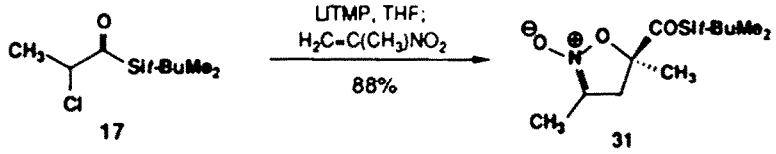
In the past, McCoy reactions have generally been carried out under conditions of thermodynamic enolate generation employing bases such as sodium hydride, potassium *t*-butoxide, or sodium hydroxide in the presence of a phase transfer catalyst.[12-14] However, because of the well-documented sensitivity of the acylsilane moiety to nucleophilic bases, we have focused our studies on the application of lithium dialkylamides to generate the requisite acylsilane enolates. Thus, exposure of the α-haloacylsilanes **14**, **15**, and **17** to 1.05 equiv of lithium diisopropylamide or lithium tetramethylpiperidide[19] in THF at -78 °C for 30 min afforded the corresponding lithium enolates, which were found to combine with a variety of electrophilic alkenes to produce the desired cyclopropylacylsilanes. Table I summarizes our results.

As expected, the cyclopropanation reaction proceeds most efficiently using relatively unhindered Michael acceptors. Cyclic enones participate in the reaction in modest yield, and more highly substituted alkenes (mesityl oxide, 4,4-dimethylcyclohex-2-en-1-one, isopropylidenemalonate) failed to yield significant amounts of the desired cyclopropylacylsilanes. As indicated in Table I, a variety of electrophilic olefins can function as Michael acceptors in the cyclopropanation. Thus, α,β-unsaturated ketones, esters, and acylsilanes all serve as excellent substrates, and certain nitriles and nitro compounds participate smoothly in the reaction as well. Note, however, that the cyclopropanation of nitroolefins using α-haloacylsilanes has not proven to be a general process. Although β-nitrostyrene underwent smooth cyclopropanation with the α-bromo reagent **15**, only trace amounts of the desired cyclopropylacylsilane were obtained using the corresponding α-chloroacylsilane. In addition, 2-nitropropene and 1-nitrocyclohexene reacted anomalously with both α-bromo and α-chloroacylsilanes to form isoxazoline N-oxide derivatives (e.g. **17**→**31**), presumably via intramolecular O-alkylation of the intermediate nitronate Michael adduct.[20]

Table I. Synthesis of Cyclopropylacylsilanes via α-Haloacylsilane Enolates

entry	electrophilic alkene	α-haloacylsilane	products[a] major	products[a] minor	isomer ratio[b]	% yield[c]
1		14	 18a	 18b	1.9 : 1	75-89[d]
2		14	 19a	 19b	3.5 : 1	83[d]
3		14	 20a	 20b	12 : 1	81[d]
4		14	 21a	 21b	2.5 : 1	41[d]
5		14	 22a	 22b	2 : 1	14[e]
6		14	 23a	 23b	1.7 : 1	76[d]
7		14	 24a	 24b	5 : 1	53[e]
8		14	 25a	 25b	10 : 1	57[e]
9		15	 26			60[e]
10		17	 27a	 27b	6 : 1	64[d]
11		17	 28a	 28b	7 : 1	83[d]
12		17	 29a	 29b	3 : 1	34[d]
13		17	 30a	 30b	2.5 : 1	90[d]

[a] $COSiR_3$ = COSi*t*-BuMe$_2$. [b] Isomer ratios were determined by ^{1}H NMR analysis of unpurified reaction products. In entries 1, 7, 8, and 10 ratios were determined on purified products. [c] Isolated yields of products purified by column chromatography. Cyclopropanations were accomplished by sequentially treating the α-haloacylsilane with 1.05 equiv of LDA or LITMP (-78°, 30 min) and then 1.0 - 5.1 equiv of electrophilic alkene (-78 to 25°, 1.5 - 8.5 h); for details see Experimental Section. [d] Lithium tetramethylpiperidide was used as base in this reaction. [e] Lithium diisopropylamide was employed as base in this reaction.

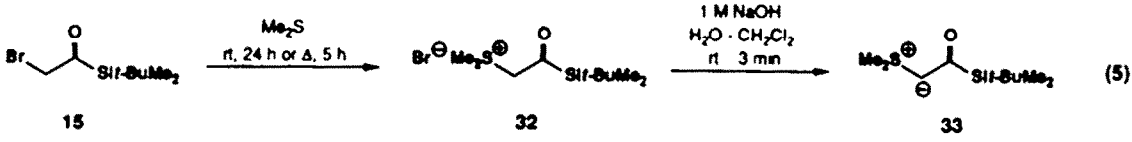


In general, somewhat higher yields of cyclopropylacylsilanes were obtained by employing lithium tetramethylpiperidide as base, and in some cases the yield of the reaction could be further improved by using a larger excess of the electrophilic alkene. In entry 2, for example, increasing the quantity of ethyl acrylate employed from 1.3 to 5.0 equivalents increased the yield of this cyclopropanation from 66 to 83%. In most cases examined, superior results were obtained using the enolate derived from the α-chloroacylsilane **14** rather than the corresponding bromo compound. For example, addition of the bromo derivative **15** to ethyl acrylate proceeded in only 34% yield (compare entry 2), and cyclopropanation of chalcone using **15** produced **20a** in a total yield of only 48%.

It is interesting to note that the stereochemical outcome of the reactions of **14** and **15** also differed. The major products formed in the reactions of the α-chloro derivative are usually the cyclopropane stereoisomers in which the acylsilane group has a cis stereochemical relationship to the carbonyl activating group (vide infra). Reactions involving the α-bromoacylsilane, on the other hand, exhibit a greater degree of trans stereoselectivity. Thus, addition of **15** to ethyl acrylate generated the trans isomer **19b** as the major product (2.5:1 ratio), and in a similar fashion **15** combined with methyl vinyl ketone to afford predominantly (1.7:1) the trans-substituted cyclopropane **18b**. In the case of chalcone (12:1 trans:cis ratio using **14**) the bromoacylsilane produced the trans isomer exclusively.

The Sulfur Ylide Approach. In connection with several projected synthetic applications of cyclopropylacylsilanes, we required a convenient route to derivatives bearing a formyl substituent at the C-2 position of the three-membered ring. Unfortunately, in contrast to the many successful cyclopropanations recorded in Table I, α,β-unsaturated aldehydes react with our α-haloacylsilane reagents to produce complex mixtures of products containing less than 10% of the desired cyclopropanes. Since sulfur ylides are well known to combine with α,β-unsaturated aldehydes to form cyclopropanecarboxaldehydes,[21] we turned our attention to the application of the ylide **33** as a reagent for the synthesis of formyl-substituted cyclopropylacylsilanes.

The sulfur ylide **33** was conveniently prepared from the α-bromoacylsilane **15** via the route outlined in eq 5. Stirring



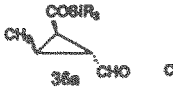
(5)

the unpurified α-bromoacylsilane in dimethylsulfide at room temperature (24 h) or at reflux (5 h) afforded the sulfonium salt **32** in 83% overall yield from the silylated vinyl ether **13**; generation of the desired ylide then proceeded smoothly on shaking **32** in a separatory funnel for 3 min with an ice-cold solution of aqueous NaOH. In this fashion ylide **33** was obtained as a pale yellow solid (95% yield) which was found to be stable to transfer in air and to storage at room temperature for several days. In addition, no significant deterioration of the ylide was observed to take place after several months of storage at -30 °C.

In contrast to its stability in the solid state, the sulfur ylide proved to be relatively unstable in solution, rapidly decomposing ($t_{1/2}$ < 90 min) in benzene, DMSO, and acetonitrile to form dimethylsulfide and a complex mixture of organosilicon compounds. Interestingly, the decomposition of **33** was found to occur significantly more slowly in chloroform: after 90 min ca. 95% of the ylide remained unchanged in this solvent.

In early experiments the relative instability of the sulfur ylide in solution appeared to severely limit its utility as a new cyclopropanation reagent. While a satisfactory yield of the desired cyclopropylacylsilane was obtained in the reaction of **33** with acrolein (Table II, entry 1), addition to less reactive Michael acceptors such as methyl vinyl ketone resulted in low yields (15%) of the expected annulation products, and in some cases (ethyl acrylate, methacrolein) decomposition of the ylide occurred much more rapidly than the desired cyclopropanation. Fortunately a stratagem for extending the scope of the reaction was devised upon further consideration of the peculiar stability of the sulfur ylide in chloroform, which we hypothesized to be due to hydrogen-bonding of the solvent to the acylsilane carbonyl. Support for this hypothesis was obtained from the infrared spectrum of a 0.5 M deuteriochloroform solution of **33**, which revealed a second Cl_3C-D stretching band at 2212 cm^{-1} of

Table II. Synthesis of Cyclopropylacylsilanes via the Sulfur Ylide 33

entry	electrophilic alkene	method[a]	products[b] major	products[b] minor	isomer ratio[c]	% yield[d]
1		A	 34a	 34b	2 : 1	40
2		B	 35a	 35b	2 : 1	89
3		B	 36a 36b 36c		15 : 9 : 1	44
4		B	 18a	 18b	1.2 : 1	55
5		B	 19a	 19b	1.1 : 1	56

[a]Cyclopropanations were performed in CH_3CN at 0 to 25 °C (method A). In method B the cyclopropanation was conducted in the presence of 3.0 equiv of LiOTf at 25 or 40 °C; see Experimental Section for details. [b]$COSiR_3$ = $COSit\text{-}BuMe_2$. [c]Isomer ratios were determined by ^1H NMR analysis of purified (entries 1 and 5) or unpurified (entries 2, 3, and 4) reaction products. [d]Isolated yields of products purified by column chromatography or distillation.

comparable intensity to the normal absorption observed at 2254 cm^{-1}. The low frequency and high intensity of the new band is consistent with the presence of hydrogen-bonded chloroform molecules containing a weakened and more polarized C-D bond.

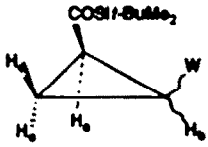
After considerable experimentation we ultimately determined that the lifetime of the sulfur ylide in aprotic solvents could be extended even more effectively by the addition of certain lithium salts.[22] Thus, only 5-10% decomposition of 33 was observed to take place in 0.2 M acetonitrile after 46 h at room temperature when lithium perchlorate (1.0 M) was added to the solution. As expected, the longer lifetime of the sulfur ylide in the presence of Li^+ permitted the extension of our annulation strategy to include several Michael acceptors of lower reactivity than acrolein (Table II). These cyclopropanations were typically carried out in the presence of 3 equiv of lithium triflate (less hazardous than $LiClO_4$) in acetonitrile at either room temperature (entry 2) or 40 °C (entries 3-5). Although α,β-unsaturated aldehydes, ethyl acrylate, and unhindered enones such as MVK participated smoothly in this version of our annulation strategy, less reactive substrates such as mesityl oxide, cyclohexenone, and chalcone failed to afford significant quantities of the desired cyclopropylacylsilanes. In addition, it should be noted that the cyclopropanation of MVK and ethyl acrylate (entries 4 and 5) proceed in lower yield than the corresponding reactions carried out using the α-chloroacylsilane reagent 14 (see Table I). Consequently, we expect the sulfur ylide 33 to find principal use as a reagent for the cyclopropanation of α,β-unsaturated aldehydes.

Discussion

Assignment of Stereochemistry of Cyclopropylacylsilane Annulation Products. ^1H NMR spectroscopy was employed to unambiguously establish the stereochemistry of all of the cyclopropylacylsilane annulation products listed in Tables I and II. Key features of the NMR spectra of these cyclopropanes are summarized in Table III (for complete spectral data, see Experimental Section).

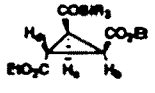
In several cases (Table I, entries 4, 5, 6, 7, and 9) assignments were made based on the well documented rule that in cyclopropane derivatives the vicinal coupling constants for trans protons (J_{trans}) are always smaller than J_{cis}.[23] ^1H NMR Nuclear Overhauser Effect (NOE) experiments permitted the unambiguous determination of the stereochemistry of several other cyclopropylacylsilane annulation products. Specifically, irradiation of methyl and formyl group protons led to significant enhancements in the signals of the cyclopropyl ring protons cis to these substituents; these experiments allowed the assignment of stereochemistry to the products in entries 10, 12, and 13 in Table I, and (in conjunction with analysis of J values) entry 3 in Table II.

Table III. ^{1}H NMR Data for Cyclopropylacylsilane Ring Protons[a]



	H_a	H_b	H_c	H_d
18a	2.72	2.24	1.20	1.72
18b	2.97	2.53	1.33-1.42	1.33-1.42
19a	2.65	2.11	1.13	1.75
19b	2.96	2.19	1.37 (t, 7.5)	1.37 (t, 7.5)
20a	3.58 (dd, 9.9, 5.0)	4.14 (dd, 6.3, 5.0)	3.41 (dd, 9.9, 6.3)	——
20b	3.17 (d, 6.2)	3.17 (d, 6.2)	——	3.36 (t, 6.2)
21a	3.01 (t, 8.4)	not assigned	not assigned	——
21b	2.76 (t, 2.9)	not assigned	——	not assigned
22a	2.95 (t, 8.6)	not assigned	not assigned	——
22b	3.07 (t, 4.1)	2.43 (dd, 7.8, 4.0)	——	not assigned
23a	3.59 (d, 10.5)	——	3.56 (d, 10.5)	——
23b	3.70 (d, 8.1)	——	——	3.63 (d, 8.1)
24a[b]	3.02 (dd, 10, 6)	2.59 (dd, 10, 6)	——	2.83 (t, 6)
24b[b]	3.51 (t, 5.1)	2.48 (d, 5.1)	——	2.48 (d, 5.1)
25a	2.53 (dd, 8.0, 5.5)	——	1.04 (dd, 8.0, 4.1)	1.88 (dd, 5.3, 4.2)
25b	3.20 (dd, 8.1, 6.7)	——	1.24 (8.1, 3.4)	1.44 (6.5, 3.4)
26	3.91 (dd, 11.2, 4.0)	5.39 (t, 4.0)	3.74 (dd, 11.1, 4.9)	——
27a	——	1.73-1.80	1.01 (dd, 9.9, 3.3)	1.73-1.80
27b	——	2.19 (dd, 8.4, 6.4)	1.22 (dd, 6.4, 4.2)	1.45 (dd, 8.5, 4.2)
28a	——	——	0.86 (d, 4.0)	2.18 (d, 4.2)
28b	——	——	1.61 or 1.64 (d, 3.8)	1.64 or 1.61 (d, 3.8)
29a	——	2.94 or 2.79 (d, 8)	——	2.79 or 2.94 (d, 8)
29b	——	2.25 or 2.71 (d, 7.2)	2.71 or 2.25 (d, 7.2)	——
30a	——	——	——	3.77 (s)
30b	——	——	3.08 (s)	——
34a	3.05	2.46	1.46 or 1.53	1.53 or 1.46
34b	3.05	2.12	1.49	1.90
35a	3.02 (dd, 8.3, 6.6)	——	1.38 (dd, 8.4, 4.4)	1.75 (dd, 6.6, 4.5)
35b	2.86 (dd, 7.7, 6.8)	——	1.37 (dd, 8.1,4.5)	2.20 (dd, 6.8, 4.7)
36a	3.20 (dd, 9.5, 4.7)	2.67	2.08	——
36b	2.83 (dd, 8.3, 6.7)	2.20	——	1.96
36c	3.20 (t, 8.9)	2.06	2.06	——

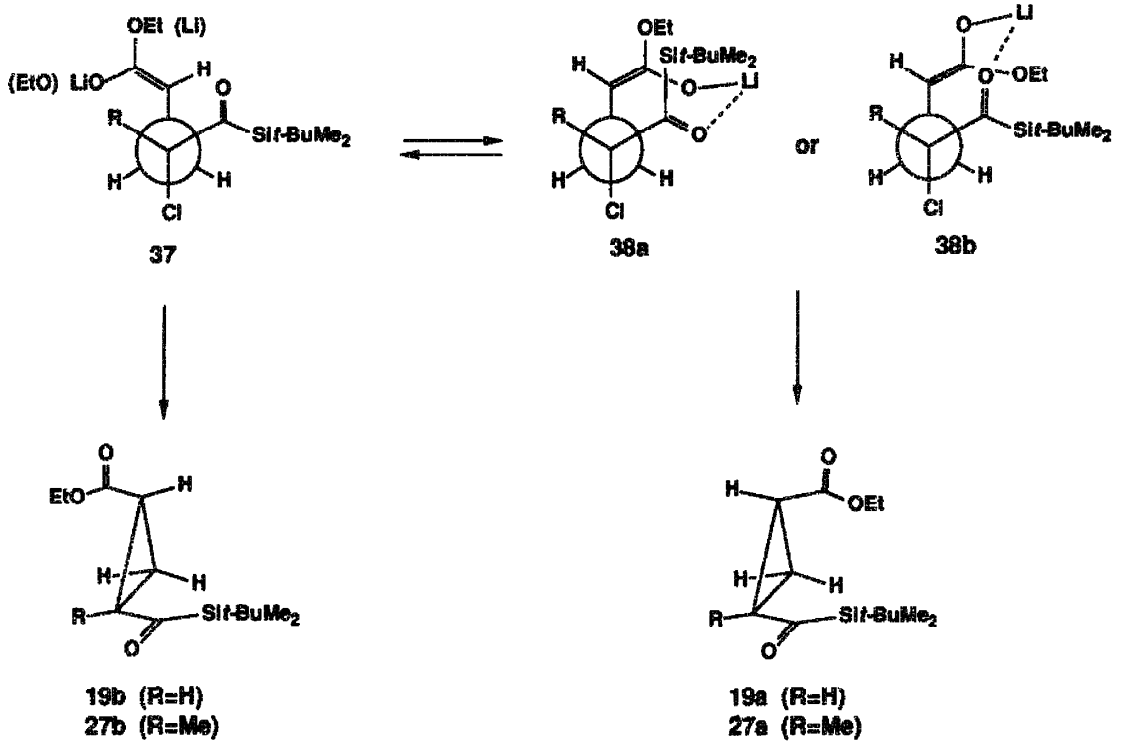
[a]Chemical shifts are expressed in parts per million downfield from tetramethylsilane; coupling constants are reported in Hz. Resonances for which no specific multiplicity is given appeared as multiplets centered at the indicated position. [b]For these compounds the following proton designations are used:

24a: 

24b: 

Anisotropic effects proved useful in assigning structures to the cyclopropylacylsilanes produced in several other reactions (Table I, entries 1, 2, 8, and 11, and Table II, entries 1 and 2). For example, the chemical shift of H_d (see Table III) generally appears 0.5-0.8 ppm downfield relative to H_c in the case of stereoisomers in which *both* carbonyl substituents are situated on the same side of the cyclopropane ring. In the spectra of the corresponding trans isomers, H_c and H_d are observed to resonate at nearly the same frequency. Finally, the stereochemistry of **20a** and **20b** (Table I, entry 3) was determined through a combination of coupling constant analysis, ^{1}H NMR COSY, and homo- and heteronuclear NOE studies. Full details are provided in the Experimental Section.

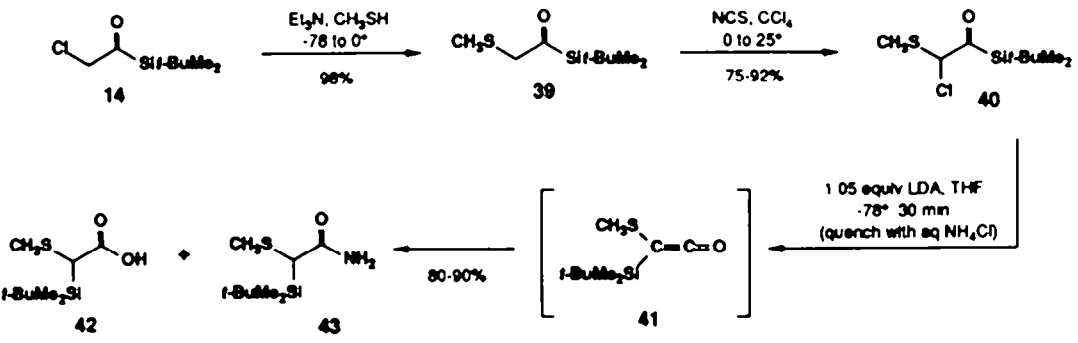
Stereochemical Course of the Cyclopropanation Reaction. The cyclopropanations examined in our study proceed in many cases with useful levels of stereoselectivity. In particular, reactions involving the α-chloroacylsilane reagent **14** and α,β-unsaturated carbonyl compounds lead predominantly to cyclopropanes in which the acylsilane moiety and the alkene-derived carbonyl group are situated on the same side of the new three-membered ring. This preference for the formation of cis-substituted cyclopropane derivatives has been observed in previous studies of the McCoy reaction[13, 14c, 14e, 24] and is generally rationalized in terms of metal-chelated transition states for ring closure. We believe that similar effects direct the stereochemical outcome of our cyclopropanation reactions. For example, the following scheme depicts alternative transition state geometries for the cyclizations leading to cyclopropylacylsilanes **19a,b** and **27a,b** (Table I, entries 2 and 10). Under our



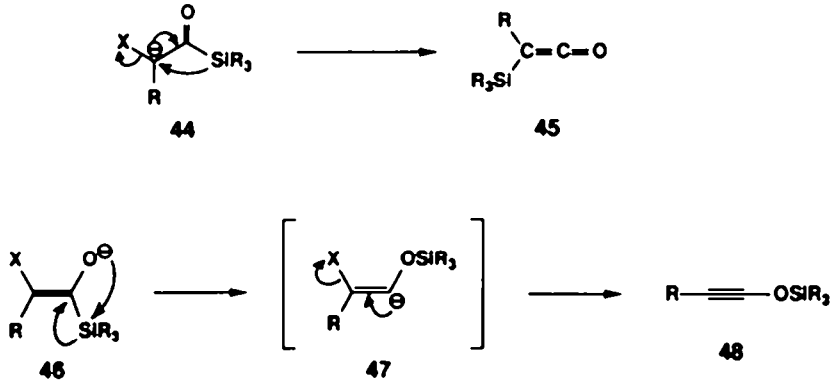
reaction conditions chelated intermediates of type **38a** (or **38b**) are expected to be favored over the non-chelated species **37**; subsequent internal substitution then leads to the predominant formation of cis-substituted cyclopropanes. Note that this model also explains the enhanced selectivity for the formation of cis-substituted cyclopropanes observed in the reaction of ethyl acrylate with the α-chloro*propionyl*silane **17**; in this case additional non-bonded interactions between the enolate moiety and the propionyl methyl group destabilize the non-chelated transition state **37**.

Further examination of Tables I and II reveals other interesting stereochemical features of these cyclopropanation reactions. For example, the reactions of β-substituted electrophilic alkenes with the acetylsilane reagents **14**, **15**, and **33** yield as major products cyclopropanes in which the acylsilane moiety and the substituent derived from the β-position of the Michael acceptor have a cis stereochemical relationship. Unfortunately, we do not at this time have sufficient data to attempt an explanation for the stereochemical course of the complex Michael addition step which controls the relative stereochemistry about these centers. Among the questions that remain to be addressed in order to fully understand the stereochemical course of the reaction are the stereochemical identity of the α-haloacylsilane enolates [E(O) vs. Z(O)], the relative importance of "open" vs. "closed" (chelated) transition states in the Michael addition step, and the question of whether these reactions operate under conditions of kinetic or thermodynamic control.[25,26] Further studies are planned to clarify these issues and thus elucidate the mechanistic basis of the stereochemical course of the McCoy reaction.

Mechanism of the Decomposition of α-Functionalized Acylsilane Reagents. In contrast to the α-haloacylsilanes discussed earlier, the *thiomethyl*-substituted compound **40** did not prove to be a useful reagent for the cyclopropanation of electrophilic alkenes. The enolate derivative of this acylsilane was found to be surprisingly unstable, rapidly decomposing ($t_{1/2}$ ≈ 1 h at -78 °C) to form an unstable ketene **41** which was identified by its conversion to a mixture of the carboxylic acid **42** and amide **43**. The facility with which this acylsilane enolate underwent rearrangement was reminiscent



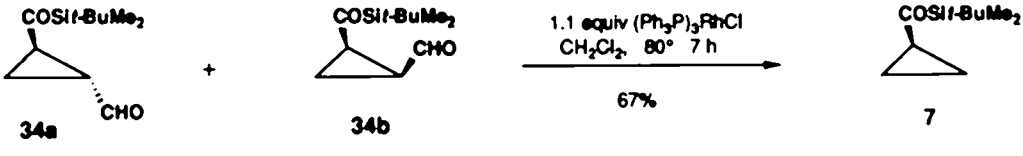
of the instability observed for the α-diazoacylsilanes **12**, suggesting to us that these compounds (as well as the sulfur ylide **33**) might be decomposing via related mechanistic pathways. The following scheme suggests two alternative modes of decomposition which account for our observations.



The *silyl-Wolff rearrangement* of **44** (X = N_2^+) provides a direct pathway for the transformation of this α-functionalized acylsilane derivative to the silylketene **45**, and a similar mechanism can account for the decomposition of the sulfur ylide reagent (X = SMe_2^+) as well. Alternatively, *sp^2-Brook rearrangement* [27] of **46** could generate a carbanion intermediate (**47**) which would be expected to undergo rapid elimination to afford an unstable siloxyacetylene derivative. It has previously been noted[28] that the isomerization of siloxyalkynes to the corresponding silylketenes is often an unusually facile process, and we do not expect that **48** would long survive under the conditions of these reactions.

Finally, it may be noted that the mechanisms outlined above can also account for the increased stability of the sulfur ylide **33** in the presence of lithium salts and hydrogen-bond donor solvents. Regardless of which mechanism operates, the ylide ground state should receive greater stabilization than the transition state for silyl group migration (in which significant charge dispersal has occurred), and consequently the rate of rearrangement and destruction of the reagent is expected to be slower in the presence of these key additives.

Chemistry of Cyclopropylacylsilanes. We anticipate that the various activating groups appended to our cyclopropylacylsilane annulation products will provide the basis for a number of useful synthetic transformations. It should be noted, however, that in some cases these products can also serve as precursors to simple cyclopropylacylsilanes lacking additional functionality. For example, decarbonylation of the annulation products obtained from the reaction of **14** with acrolein using $(Ph_3P)_3RhCl$[29] furnished the parent cyclopropylacylsilane **7** in 67% yield.[30]



In summary, we have developed an efficient annulation route to cyclopropylacylsilanes which provides access for the first time to a wide variety of interesting functionalized derivatives. Further studies are underway in our laboratory aimed at the systematic investigation of the chemistry of these novel cyclopropanes.

Acknowledgment

We thank the National Science Foundation and the National Institutes of Health for generous financial support.

Experimental Section

Instrumentation. Infrared spectra were obtained using a Perkin-Elmer 1320 grating spectrophotometer. ^{1}H NMR spectra were measured with Bruker WM-250 (250 MHz) and Varian XL-300 (300 MHz), XL-400 (400 MHz) and VXR-500 (500 MHz) spectrometers. ^{13}C NMR spectra were determined on Bruker WM-270 (68 MHz) and Varian XL-300 (75 MHz), XL-400 (100 MHz), and VXR-500 (125 MHz) spectrometers. Chemical shifts are expressed in parts per million (δ) downfield from tetramethylsilane. UV spectra were measured on Cary 118 and Varian DMS 100 UV-vis spectrophotometers. Low- and high-resolution electron ionization mass spectra (MS and HRMS) were determined on a Finnegan MAT 8200 instrument using a reduced ionization voltage (24-40 volts). Elemental analyses were performed by Robertson Laboratory, Inc., of Madison, NJ. Melting points and boiling points are uncorrected.

Materials. Commercial grade reagents and solvents were used without further purification except as indicated below. Acetonitrile, carbon tetrachloride, diisopropylamine, dimethylsulfide, ethyl vinyl ether, and 2,2,6,6-tetramethylpiperidine were distilled from calcium hydride. Ethyl formate was distilled from calcium hydride or phosphorus pentoxide. Tetrahydrofuran was distilled from sodium benzophenone ketyl or dianion. All liquid α,β–unsaturated carbonyl compounds were distilled before use; sufficient foreruns were discarded to ensure removal of water azeotropes. N-Bromosuccinimide was recrystallized from distilled water. N-Chlorosuccinimide was recrystallized from benzene. Lithium trifluoromethanesulfonate was dried at 110 °C (0.5 mmHg) for 12 h before use. *n*-Butyllithium was titrated with *sec*-butanol using 1,10-phenanthroline as indicator.[31]

General procedures. All reactions were performed in oven-dried glassware under a positive pressure of argon (with the exception of reactions performed in aqueous solvents). Reaction mixtures were stirred magnetically unless otherwise indicated. Solutions of alkyllithium reagents were transferred by syringe or cannula and were introduced into reaction vessels through rubber septa. Reaction product solutions were concentrated by using a Büchi rotary evaporator at 1-30 mmHg. Column chromatography was performed on Merck or Baker silica gel (230-400 mesh).

***tert*-Butyldimethyl(1-ethoxyvinyl)silane (13).** A 2-L, three-necked, round-bottomed flask was equipped with a thermometer, mechanical stirrer, and an addition funnel fitted with a rubber septum and argon inlet needle. The flask was charged with 500 mL of THF and ethyl vinyl ether (99 mL, 1.04 mol), and then cooled below -75 °C with a dry ice-acetone bath while a solution of *t*-butyllithium (1.7 M in pentane, 500 mL, 0.85 mol) was added dropwise over 2 h. The resulting suspension of yellow precipitate was allowed to slowly warm to -5 °C over the course of 2.5 h, during which time the precipitate dissolved to form a dark yellow solution which was maintained between -5 and 0 °C for 30 min further and then cooled to -78 °C. (CAUTION: an exotherm occurred during the warming to -5 °C. Cooling was necessary to control this exotherm.) A solution of *t*-butylchlorodimethylsilane (104.44 g, 0.6665 mol) in 50 mL of THF was next added over 30 min, and the resulting mixture was allowed to warm to room temperature over 2 h. After 5 h, the flask was cooled in an ice bath, and 500 mL of half-saturated NH_4Cl solution was then added. The aqueous phase was separated and extracted with 250 mL of diethyl ether, and the combined organic layers were washed with 3 L of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. (This crude product was used to prepare the acetylsilane **10a** without further purification as described below.) Anhydrous K_2CO_3 (*ca.* 0.5 g) was added to the residual oil, and remaining solvent and *t*-butyldimethylsilanol were removed by distillation through a 30 cm Vigreux column under reduced pressure. Distillation of the residual oil (57-66 °C, 39 mmHg) afforded 93.55 g (75%) of the vinylsilane **13** as a colorless oil: IR (film) 3094, 2976, 2954, 2928, 2896, 2866, 1631, 1583, 1470, 1462, 1443, 1400, 1389, 1378, 1360, 1254, 1247, 1214, 1153, 1112, 1088, 1051, 1005, 971, 940, 861, 837, 827, 773, 715, 690, and 666 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.62 (d, J = 1.6 Hz, 1 H), 4.26 (d, J = 1.8 Hz, 1 H), 3.67 (q, J = 7.0 Hz, 2 H), 1.27 (t, J = 7.0 Hz, 3 H), 0.91 (s, 9 H), and 0.06 (s, 6 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 168.7, 94.8, 61.7, 26.6, 16.4, 14.5, and -6.7; MS *m/e* 186 (M^+, 2%), 158, 157, 130, 115, 103 (100%), 75, 73, and 57.

1-*tert*-Butyldimethylsilyl-1-ethanone (10a).[32] To a solution of 19.223 g of the crude ethoxyvinylsilane **13** in 80 mL of acetone was added 20 mL of 1 M aqueous HCl. After 30 min, the homogeneous reaction mixture was poured into 100 mL of H_2O and 100 mL of diethyl ether, and the aqueous phase was separated and extracted with one 100-mL and two 30-

mL portions of ether. The combined organic phases were washed with 100 mL of saturated $NaHCO_3$ solution and 200 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to furnish 15.227 g of a yellow oil. Distillation (bp 103.5-106.5 °C, 124 mmHg) afforded 12.554 g of acetylsilane **10a** (67% overall from *tert*-butylchlorodimethylsilane): IR (film) 2955, 2930, 2885, 2855, 1640, 1470, 1465, 1410, 1360, 1340, 1250, 1130, 1005, 940, 835, 820, 805, 775, and 675 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 2.26 (s, 3 H), 0.93 (s, 9 H), and 0.17 (s, 6 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 246.6, 37.4, 26.3, 16.3, and -7.2.

1-*tert*-Butyldiphenylsilyl-1-ethanone (10b). A 25-mL, two-necked, round-bottomed flask equipped with an argon inlet adapter, rubber septum, and magnetic stirring bar was charged with 5 mL of THF and ethyl vinyl ether (0.53 mL, 5.56 mol), and then cooled with a dry ice-acetone bath (-78 °C) while a solution of *t*-butyllithium (1.7 M in pentane, 2.7 mL, 4.6 mmol) was added dropwise over 5 min. The resulting suspension of yellow precipitate was allowed to warm to -2 °C over the course of 100 min, during which time the precipitate dissolved to form a dark yellow solution, which was maintained between -5 and 0 °C for 30 min further and then cooled to -78 °C. A solution of *t*-butylchlorodiphenylsilane (0.963 g, 3.50 mmol) in 1 mL of THF was next added, and the cooling bath was removed. After 4.3 h, the flask was cooled in an ice bath, and a solution of 0.5 mL of concentrated aqueous HCl in 1 mL of H_2O was then added in one portion. After an additional 80 min the reaction mixture was partitioned between 50 mL of H_2O and 50 mL of diethyl ether. The organic phase was washed with 50 mL of saturated $NaHCO_3$ solution and 50 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to afford 1.083 g of a yellow oil. (The major contaminant in the crude acylsilane **10b** is *tert*-butyldiphenylsilanol.) Column chromatography on silica gel (elution with ethyl acetate-hexanes) furnished 0.601 g (61%) of **10b** as a pale yellow oil: IR (film) 3072, 3050, 3016, 2998, 2958, 2932, 2892, 2858, 1643, 1589, 1487, 1472, 1463, 1428, 1392, 1362, 1338, 1256, 1190, 1156, 1126, 1106, 1067, 1028, 1009, 997, 940, 821, 740, 701, and 634 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.63-7.67 (m, 4 H), 7.36-7.49 (m, 6 H), 2.21 (s, 3 H), and 1.14 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 243.9, 136.0, 131.8, 129.7, 127.9, 38.7, 27.6, and 18.5.

3-*tert*-Butyldimethylsilyl-3-hydroxy-*E*-propenal (11a). A 100-mL, three-necked, round-bottomed flask equipped with an argon inlet adapter, addition funnel, rubber septum, and magnetic stirring bar was placed in a water bath (20 °C) and charged with NaH (0.72 g, 30 mmol), 30 mL of ethyl formate, and 30 mL of dimethoxyethane. After gas evolution (resulting from traces of water in the DME) ended, absolute EtOH (0.10 mL, 1.7 mmol) and acetylsilane **10a** (1.57 g, 9.93 mmol) were added to the reaction mixture causing gas evolution to resume and continue for ca. 1 h. After 2.8 h, the reaction mixture was cooled with an ice bath and treated with 20 mL of half-saturated NH_4Cl solution. The aqueous phase was separated and extracted with two 20-mL portions of diethyl ether, and the combined organic phases were extracted with 100 mL of saturated NaCl solution. The aqueous NaCl solution was extracted with an additional 30 mL of ether, and the combined organic phases were then dried over $MgSO_4$, filtered, and concentrated to provide 1.586 g of an orange oil. Column chromatography on silica gel (elution with ethyl acetate-hexanes) afforded 0.883 g (48%) of **11a** as a light orange oil: IR (film) 2500-3200 (br), 2950, 2925, 2880, 2855, 2660, 2560, 2025, 1615, 1555, 1470, 1460, 1410, 1390, 1360, 1345, 1250, 1175, 1120, 1015, 940, 905, 880, 840, 825, 810, 775, and 680 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 14.13 (br s, 1 H), 9.16 (d, J = 1.4 Hz, 1 H), 5.76 (d, J = 1.8 Hz, 1 H), 0.96 (s, 9 H), and 0.17 (s, 6 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 194.2 (s), 191.3 (d), 111.4 (d), 26.3 (q), 16.4 (s), and -7.5 (q); UV max (isooctane) 284 nm (ε = 10,000).

Ethyl 3-*tert*-butyldimethylsilyl-3-hydroxy-*E*-propenoate (11b). A 50-mL, three-necked, round-bottomed flask equipped with an argon inlet adapter, glass stopper, rubber septum, and magnetic stirring bar was placed in a water bath (20 °C) and charged with NaH (0.455 g, 19.0 mmol), 15 mL of diethyl carbonate, 13 mL of THF, absolute EtOH (0.045 mL, 0.77 mmol), and acetylsilane **10a** (0.750 g, 4.74 mmol). After 76 h, the reaction mixture was cooled with an ice bath, 50 mL of half-saturated NH_4Cl solution was added, and the resulting phases were separated. The aqueous phase was extracted with two 50-mL portions of diethyl ether, and the combined organic phases were then extracted with 125 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to give 0.774 g of an orange oil. Column chromatography on silica gel (elution with ethyl acetate-hexanes) afforded 0.438 g (40%) of **11b** as an orange oil: IR (film) 2500-3400 (br), 2960, 2934, 2894, 2862, 1654, 1581, 1474, 1465, 1446, 1399, 1378, 1365, 1354, 1324, 1303, 1252, 1199, 1107, 1035, 1007, 838, 809, 780, 742, 691, and 668 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.78 (s, 1 H), 5.28 (s, 1 H), 4.19 (q, J = 7.3 Hz, 2 H), 1.30 (t, J = 7.2 Hz, 3 H), 0.96 (s, 9 H), and 0.15 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.5, 171.1, 101.1, 59.8, 26.4, 16.4, 14.2, and -7.3; UV max (isooctane) 252 nm (ε = 13,000).

3-*tert*-Butyldiphenylsilyl-3-hydroxy-*E*-propenal (11c). A 10-mL, two-necked, pear-shaped flask equipped with an argon inlet adapter, rubber septum, and magnetic stirring bar was placed in a water bath (22 °C) and charged with NaH

(34 mg, 1.4 mmol), 1 mL of ethyl formate, 1 mL of THF, and acetylsilane **10b** (99 mg, 0.354 mmol). Gas evolution occurred for ca. 1 h. After 105 min, 2 mL of half-saturated NH_4Cl solution was added, and the resulting phases were separated. The aqueous phase was extracted with three 2-mL portions of diethyl ether, and the combined organic phases were extracted with 10 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to give 106 mg of a brown solid. Column chromatography on silica gel (elution with ethyl acetate-hexanes) afforded 89 mg (81%) of **11c** as a yellow solid: mp 73.5-75 °C; IR (CCl_4) 2400-3300 (br), 3080, 3060, 2964, 2942, 2900, 2868,1623, 1554, 1489, 1468, 1432, 1397, 1348, 1298, 1198, 1125, 1113, 1064, 1018, 946, 877, 705, 640 and 610 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 14.38 (br s, 1 H), 9.10 (d, J = 1.5 Hz, 1 H), 7.63-7.67 (m, 4 H), 7.36-7.49 (m, 6 H), 5.59 (d, J = 1.6 Hz, 1 H), and 1.20 (s, 9 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 192.3, 191.4, 136.3, 131.6, 130.0, 128.0, 114.3, 27.9, and 18.4; UV max (isooctane) 287 nm (ε = 12,000) and 217 nm (sh) (ε = 18,000).

3-*tert*-Butyldimethylsilyl-3-hydroxy-2-methyl-*E*-propenal (11d). A 25-mL, two-necked, round-bottomed flask equipped with an argon inlet adapter, rubber septum, and magnetic stirring bar was placed in a water bath (25 °C) and charged with NaH (140 mg, 5.8 mmol), 4 mL of ethyl formate, 4 mL of THF, and propionylsilane **10c** (251 mg, 1.46 mmol).[3f] Gas evolution occurred during the course of the reaction. After 4 h, the reaction mixture was cooled with an ice bath and quenched with 10 mL of half-saturated NH_4Cl solution. The aqueous phase was separated and extracted with two 10-mL portions of diethyl ether, and the combined organic phases were then extracted with 30 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to give 102 mg of a light brown oil which solidified upon standing. Column chromatography on silica gel (elution with ethyl acetate-hexanes) afforded 60 mg (20%) of **11d** as a tan solid: mp 70-71.5 °C; IR (CCl_4) 2100-3700 (br), 2936, 2890, 2862, 2762, 1622, 1543, 1469, 1394, 1366, 1330, 1291, 1256, 1210, 1149, 1063, 1035, 1012, 973, 945, 872, 847, and 691 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 14.71 (s, 1 H), 9.09 (s, 1 H), 1.90 (s, 3 H), 0.97 (s, 9 H), and 0.25 (s, 6 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 194.5, 190.1, 117.6, 26.5, 17.5, 13.2, and -5.6; UV max (isooctane) 304 nm (ε = 9800).

1-*tert*-Butyldimethylsilyl-2-chloro-1-ethanone (14). An ice-cooled, 250-mL, three-necked, round-bottomed flask equipped with an addition funnel and a magnetic stirring bar, was charged with 150 mL of CH_3CN, 50 mL of H_2O, and N-chlorosuccinimide (5.34 g, 40.0 mmol). The vinylsilane **13** (7.45g, 40.0 mmol) was added to this colorless solution over the course of 2 min. The ice bath was removed, and the reaction mixture was allowed to stir at room temperature for 30 min. The resulting homogeneous yellow solution was partitioned between 600 mL of H_2O and 200 mL of pentane, and the organic phase was separated and washed with an additional 800 mL of H_2O. A 50-mL portion of pentane was then used to sequentially wash the 600 and 800 mL aqueous phases, and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated to give a yellow oil, which was recrystallized 5 times from pentane at -78 °C according to the following procedure. A 50-mL, two-necked, pear-shaped flask equipped with an argon inlet and rubber septum was charged with a solution of the crude acetylsilane in 30 mL of pentane and then cooled in a dry ice-acetone bath (-78 °C). After ca. 30 min, as much solvent as possible was removed from the resulting mass of crystals with a pasteur pipet connected to an aspirator, and the bath was removed. (The need for multiple recrystallizations results from incomplete removal of solvent from the porous crystalline mass.) After five such low-temperature recrystallizations, the resulting yellow oil was dried over $MgSO_4$, filtered with the aid of pentane, and concentrated to give 6.18 g (80%) of chloroacetylsilane **14** as a yellow oil (>99% pure by glpc): IR (film) 2952, 2932, 2886, 2858, 1655, 1466, 1392, 1366, 1253, 1152, 1057, 1010, 986, 944, 840, 827, 809, 785, 712, and 673 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.32 (s, 2 H), 0.96 (s, 9 H), and 0.26 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.1, 54.9, 26.2, 16.7, and -6.7; MS *m/e* 194 (^{37}Cl M^+, 0.6%), 192 (^{35}Cl M^+, 1.4%), 143, 115, 99, 95, 93, 75, 74, 73 (100%), 59, 57, 56, 55, 44, 42, and 40; HRMS *m/e* calcd $C_8H_{17}{}^{35}ClOSi$: 192.0737, found: 192.0738.

2-Bromo-1-*tert*-butyldimethylsilyl-1-ethanone (15). A 250-mL, three-necked, round-bottomed flask fitted with a rubber septum, mechanical stirrer, and an argon inlet adapter equipped with a thermometer was charged with 200 mL of CH_3CN, 10 mL of H_2O, and N-bromosuccinimide (7.120 g, 40.00 mmol). The resulting solution was cooled to -40 °C and vigorously stirred (NBS precipitated upon cooling) while the vinylsilane **13** (7.45 g, 40.0 mmol) was added dropwise over 15 min. The solution was maintained at -40 °C for 2 h, allowed to warm to -10 °C over 1 h, and then partitioned between 600 mL of H_2O and 200 mL of pentane. The organic phase was washed with an additional 800 mL portion of H_2O, and a 100-mL portion of pentane was then used to sequentially wash the 600 and 800-mL aqueous phases. This process was repeated with a second 100-mL portion of pentane, and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated to give 9.569 g of bromoacetylsilane **15** as a bright yellow oil (90-95% pure by glpc), which was used for the preparation of the sulfonium salt **32** without further purification. Distillation (87-89 °C, 4 mmHg) provided material of only slightly increased purity which was used in the preparation of **26**:[33] IR (film) 2956, 2932, 2898, 2886, 2960, 1663, 1643, 1471, 1463, 1410,

1383, 1364, 1260, 1251, 1230, 1189, 1150, 1110, 1066, 1006, 940, 843, 825, 808, 779, 678, and 626 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.21 (s, 2 H), 0.95 (s, 9 H), and 0.28 (s, 6 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 232.1, 42.5, 26.3, 16.6, and -6.4; MS *m/e* 238 (^{81}Br M^+, 0.07%), 236 (^{79}Br M^+, 0.07%), 143, 139, 137, 115, 99, 75, 73 (100%), 57, and 56; HRMS *m/e* calcd for $C_8H_{17}{}^{79}BrOSi$: 236.0232, found: 236.0233.

1-*tert*-Butyldimethylsilyl-2-chloro-1-propanone (17). A 100-mL, three-necked, round-bottomed flask was equipped with an argon inlet adapter, magnetic stirring bar, rubber septum, and glass stopper. The reaction flask was charged with 75 mL of CCl_4, SO_2Cl_2 (1.69 mL, 21.0 mmol), and 1-*tert*-butyldimethylsilyl-1-propanone[3f] (2.585 g, 15.00 mmol), and the reaction mixture was stirred at room temperature while the reaction was monitored by glpc. After 7 h, the solvent was removed by rotary evaporation, and the residual yellow oil was purified by column chromatography on silica gel (elution with ethyl acetate-hexanes) to furnish 2.705 g (87%) of the chloropropionylsilane **17** as a yellow oil (98.5% pure by capillary glpc): IR (film) 2956, 2934, 2888, 2860, 1647, 1466, 1445, 1412, 1392, 1367, 1315, 1252, 1227, 1207, 1119, 1055, 1008, 996, 946, 843, 826, 812, 781, 713, 684, and 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.46 (q, J = 6.6 Hz, 1 H), 1.49 (d, J = 6.6 Hz, 3 H), 0.95 (s, 9 H), 0.293 (s, 3 H), and 0.286 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 235.6, 61.9, 26.5, 17.8, 16.9, and -5.9.

(2-*tert*-Butyldimethylsilyl-2-oxoethyl)dimethylsulfonium bromide (32). A one-necked, 100-mL recovery flask equipped with a magnetic stirring bar and a reflux condenser fitted with an argon inlet adapter was charged with the crude bromoacetylsilane **15** prepared in the above reaction (9.569 g) and 50 mL of dimethylsulfide. The reaction mixture was heated at reflux for 5 h[34] and then allowed to cool to room temperature. The sulfonium salt **32** was isolated by filtration, washed with ca. 100 mL of pentane, and dried at 1 mmHg to yield 9.953 g (83% overall from **13**) of the pure sulfonium salt **32** as a fluffy white solid: mp 120-130 °C (dec); IR ($CHCl_3$, freshly prepared solution) 2940, 2862, 1640, 1466, 1414, 1368, 1337, 1255, 1151, 1103, 1050, 1010, 944, 850, 664, and 621 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$, freshly prepared solution) δ 5.80 (s, 2 H), 3.36 (s, 6 H), 0.97 (s, 9 H), and 0.36 (s, 6 H); ^{13}C NMR (68 MHz, CD_3CN, freshly prepared solution) δ 237.5, 62.4, 26.7, 24.9, 17.4, and -6.8; Anal. Calcd for $C_{10}H_{22}BrOSSi$: C, 40.12; H, 7.74. Found: C, 39.75; H, 7.57.

Dimethylsulfonium 2-*tert*-butyldimethylsilyl-2-oxoethylide (33). A solution of the sulfonium salt **32** (9.95 g, 33.2 mmol) in 100 mL of CH_2Cl_2 was shaken for 3 min with 100 mL of ice-cold aqueous NaOH (1.00 M) in a separatory funnel. After (incomplete) phase separation, the organic layer was extracted with 400 mL of saturated NaCl solution. A 100-mL portion of CH_2Cl_2 was then used to sequentially wash the two aqueous layers, the process was repeated with a 50-mL portion of CH_2Cl_2, and then the combined organic layers were dried over $MgSO_4$, filtered, and concentrated to give 6.91 g (95%) of the ylide **33** as a pale yellow solid. (Since the ylide is relatively unstable in solution, the entire period in which the ylide is in solution must be kept to less than 1 h): mp 76-78 °C (dec); IR ($CHCl_3$) 3500-3000 (br), 2950, 2930, 2896, 2858, 1609, 1582, 1454, 1410, 1347, 1317, 1304, 1247, 1215, 1133, 1098, 1053, 1027, 1009, 990, 944, 837, 663, and 621 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 3.99 (s, 1 H), 2.95 (s, 6 H), 0.94 (s, 9 H), and 0.09 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.73, 62.5, 29.0, 26.8, 16.4, and -6.6; UV max (abs EtOH) 273 nm (ε = 10,000); Anal. Calcd for $C_{10}H_{22}OSSi$: C, 54.99; H, 10.15. Found: C, 54.76; H, 10.33.

General Procedure for Cyclopropanation Using Haloenolate Anions. A 25-mL, two-necked, round-bottomed flask equipped with an argon inlet adapter, rubber septum, and magnetic stirring bar was charged with 10 mL of THF and either diisopropylamine (0.154 mL, 1.10 mmol) or 2,2,6,6-tetramethylpiperidine (0.186 mL, 1.10 mmol), and then cooled in an ice bath while *n*-butyllithium solution (1.60 M in hexanes, 0.66 mL, 1.05 mmol) was added rapidly via syringe. After 15 min, the ice bath was replaced with a dry ice-acetone bath (-78 °C), and a solution of 1.00 mmol of haloacylsilane in 0.2 mL of THF was added by microliter syringe over the course of 1 - 2 min (the syringe used for the addition was rinsed with two 0.1-mL portions of THF). After 30 min, 1.0 - 5.1 mmol of the Michael acceptor was added (solid and liquid electrophiles with freezing points much above -78 °C were added in THF solution, other liquids were added neat). The reaction mixture was allowed to warm to room temperature over the course of 1 h (unless otherwise indicated), and then stirred further for 0.5 - 4 h until thin-layer chromatography indicated complete consumption of the haloacylsilane. Half-saturated NH_4Cl solution (8 mL) was then added, and the resulting mixture was partitioned between 50 mL of H_2O and 50 mL of diethyl ether. The organic phase was extracted with 50 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated. Purification was performed as described below.

1-[*cis*-2-(*tert*-Butyldimethylsilyloxomethyl)cyclopropyl]ethan-1-one (18a) and 1-[*trans*-2-(*tert*-butyldimethylsilyloxomethyl)cyclopropyl]ethan-1-one (18b). A 250-mL, three-necked, round-bottomed flask equipped with an argon inlet adapter, rubber septum, magnetic stirring bar, and addition funnel fitted with a rubber septum was charged with 100 mL of THF and 2,2,6,6-tetramethylpiperidine (1.86 mL, 11.0 mmol), and then cooled in an ice bath while *n*-butyllithium solution (1.63 M in hexanes, 6.4 mL, 10.5 mmol) was added rapidly via syringe. After 15 min, the ice bath was replaced with a dry ice-acetone bath (-78 °C), and a solution of chloroacetylsilane **14** (1.928g, 10.00 mmol) in 5 mL of THF was added dropwise via the addition funnel over the course of 15 min. After 30 min, methyl vinyl ketone (1.08 mL, 13.0 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature over the course of 1 h, and then stirred further for 30 min. Half-saturated NH_4Cl solution (100 mL) was then added, and the resulting mixture was partitioned between 100 mL of H_2O and 100 mL of diethyl ether. The aqueous phase was extracted with 50 and 25-mL portions of ether, and the combined organic phases were extracted with 250 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated. Column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.659 g (29%) of **18b** and 1.045 g (46%) of **18a** as pale yellow oils. (When the above reaction was performed on 1/10 of the above scale according to the general procedure for cyclopropanation using haloenolate anions which is described above, 0.069 g (31%) of **18b** and 0.133 g (59%) of **18a** were obtained.) For the trans isomer **18b**: IR (film) 3004, 2956, 2932, 2886, 2860, 1703, 1624, 1465, 1422, 1391, 1355, 1312, 1252, 1171, 1118, 1088, 1065, 1030, 1005, 963, 942, 871, 841, 826, 777, and 675 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.95-3.00 (m, 1 H), 2.50-2.56 (m, 1 H), 2.27 (s, 3 H), 1.33-1.42 (m, 2 H), 0.94 (s, 9 H), and 0.23 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 242.9, 205.7, 36.6, 31.5, 30.7, 26.4, 18.8, 16.5, -7.3, and -7.4; MS *m/e* 226 (M^+, 0.7%) 225 ([M-H]$^+$, 2.8%), 169, 155, 141, 127, 115, 99, 95, 85, 77, 75, 74, 73 (100%), 59, 57, 55, 53, 45, 43, 41, and 39; HRMS *m/e* calcd for $C_{12}H_{21}O_2Si$ ([M-H]$^+$): 225.1311, found: 225.1310; Anal. Calcd for $C_{12}H_{22}O_2Si$: C, 63.67; H, 9.79. Found: C, 63.43; H, 9.97. For the cis isomer **18a**: IR (film) 3006, 2956, 2944, 2890, 2860, 1704, 1626, 1465, 1431, 1381, 1363, 1251, 1197, 1163, 1111, 1064, 1005, 961, 942, 840, 810, 779, and 676 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.68-2.76 (m, 1 H), 2.19-2.27 (m, 1 H), 2.21 (s, 3 H), 1.69-1.75 (m, 1 H), 1.16-1.23 (m, 1 H), 0.95 (s, 9 H), 0.23 (s, 3 H), and 0.20 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 242.6, 204.1, 35.0, 32.4, 30.3, 26.4, 16.6, 13.5, -7.1, and -7.2; MS *m/e* 226 (M^+, 4.9%), 225, 170, 169, 155, 151, 143, 142, 141, 127, 125, 115, 113, 111, 101, 99, 95, 75, 73 (100%), 59; HRMS *m/e* calcd for $C_{12}H_{21}O_2Si$ ([M-H]$^+$): 225.1311, found: 225.1310; Anal. Calcd for $C_{12}H_{22}O_2Si$: C, 63.67; H, 9.79. Found: C, 63.75; H, 10.00.

Ethyl *cis*- and *trans*-2-(*tert*-butyldimethylsilyloxomethyl)cyclopropanecarboxylate (19a and b). Reaction of the chloroacetylsilane **14** (0.193 g, 1.00 mmol) with lithium tetramethylpiperidide produced the corresponding enolate, which was treated with ethyl acrylate (0.55 mL, 5.1 mmol) and allowed to react further for 90 min at room temperature according to the general procedure. Column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.047 g (18%) of **19b** and 0.167 g (65%) **19a** as pale yellow oils. For the trans isomer **19b**: IR (film) 2956, 2934, 2898, 2860, 1728, 1628, 1467, 1404, 1389, 1365, 1313, 1254, 1200, 1182, 1113, 1092, 1053, 1012, 940, 919, 843, 823, 809, 779, and 674 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.15 (q, J = 7.2 Hz, 2 H), 2.92-2.98 (m 1 H), 2.16-2.22 (m, 1 H), 1.37 (appar t, J = 7.5 Hz, 2 H), 1.26 (t, J = 7.1 Hz, 3 H), 0.94 (s, 9 H), 0.24 (s, 3 H), and 0.23 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 242.5, 172.1, 60.9, 34.4, 26.5, 24.3, 17.2, 16.7, 14.3, and -7.2; HRMS *m/e* calcd for $C_{13}H_{23}O_3Si$ ([M-H]$^+$): 255.1417, found: 255.1414. Anal. Calcd for $C_{13}H_{24}O_3Si$: C, 60.89; H, 9.43. Found: C, 60.70; H, 9.64. For the cis isomer **19a**: IR (film) 2958, 2936, 2896, 2862, 1732, 1631, 1467, 1445, 1382, 1366, 1352, 1302, 1253, 1185, 1109, 1064, 1047, 1031, 1007, 943, 844, 811, 781, and 678 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.10 (appar q, J = 7.0 Hz, 1 H), 4.09 (appar q, J = 7.0 Hz, 1 H), 2.61-2.69 (m, 1 H), 2.07-2.15 (m, 1 H), 1.72-1.78 (m, 1 H), 1.23 (t, J = 7.0 Hz, 3 H), 1.11-1.17 (m, 1 H) 0.96 (s, 9 H), 0.22 (s, 3 H), and 0.19 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 241.2, 169.5, 60.7, 32.9, 26.4, 24.5, 16.7, 14.1, 11.8, -7.1, and -7.2; MS *m/e* 256 (M^+, 14%), 255, 227, 211, 200, 199 (100%), 172, 171, 129, 115, 113, 103, 99, 95, 75, 74, 73 (100%), and 55; HRMS *m/e* calcd for $C_{13}H_{23}O_3Si$ ([M-H]$^+$): 255.1417, found 255.1415; Anal. Calcd for $C_{13}H_{24}O_3Si$: C, 60.89; H, 9.43. Found: C, 60.72; H, 9.64.

***tert*-Butyldimethylsilyl[*c*-3-phenyl-*t*-2-(phenyloxomethyl)cyclopropyl]methanone (20a) and *tert*-butyldimethylsilyl[*t*-3-phenyl-*c*-2-(phenyloxomethyl)cyclopropyl]methanone (20b).** Reaction of the chloroacetylsilane **14** (0.193 g, 1.00 mmol) with lithium tetramethylpiperidide produced the corresponding enolate, which was treated with a solution of chalcone (0.208 g, 1.00 mmol) in 0.4 mL THF, and allowed to react further for 1 h at room temperature according to the general procedure. Column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.269 g (74%) of **20a** as a viscous yellow oil which solidified upon standing at -15 °C and 0.026 g (7%) of **20b** a white solid. For the isomer **20a**: mp 53.5-55.5 °C; IR (film) 3062, 3032, 2954, 2932, 2888, 2858, 1668, 1623, 1599, 1581, 1494, 1449, 1410, 1364, 1321, 1285, 1250, 1218, 1180, 1158, 1081, 1050, 1016, 976, 939, 840, 822, 779, 759,

721, 696, 658, and 627 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 8.07 (appar dd, J = 8.4, 1.2 Hz, 2 H), 7.62 (appar tt, J = 7.4, 1.2 Hz, 1 H), 7.52 (appar t, J = 7.7 Hz, 2 H), 7.20-7.28 (m, 5 H), 4.14 (dd, J = 6.3, 5.0 Hz, 1 H), 3.58 (dd, J = 9.9, 5.0 Hz, 1 H), 3.41 (dd, J = 9.9, 6.3 Hz, 1 H), 0.79 (s, 9 H), 0.17 (s, 3 H), and 0.01 (s, 3 H); ^1H NMR NOE experiment: irradiation at δ 8.07 produced an enhancement at 7.52 and 4.14; irradiation at δ 7.20-7.28 produced an enhancement at 4.14 and 3.41; ^1H NMR decoupling experiment: irradiation at δ 7.20-7.28 caused the sharpening of the δ 3.41 doublet of doublets; $^{13}C\{^1H\}$ NOE experiment: irradiation at δ 4.14 in the ^1H spectrum produced large enhancements in the ^{13}C resonances at δ 197 and 138, and a smaller enhancement at 240; irradiation at δ 3.58 in the ^1H spectrum produced a large enhancement in the ^{13}C resonance at δ 240 and a smaller enhancement at 197; irradiation at δ 3.41 produced a large enhancement in the ^{13}C resonance at δ 134, a moderate enhancement at 197, and a small enhancement at 240; ^{13}C NMR (100 MHz, $CDCl_3$) δ 240.4, 197.2, 137.0, 134.1, 133.3, 128.7, 128.6, 128.3, 128.0, 127.0, 46.1, 37.9, 28.7, 26.1, 16.7, -7.4, and -7.5; UV max (isooctane) 243 nm (ε = 17,000) and 202 nm (ε = 30,000); MS *m/e* 364 (M^+, 1.7%), 255, 207, 147, 115, 105, 103, 101, 77, 75, 74, 73 (100%), 59, 44, and 42; HRMS *m/e* calcd for $C_{23}H_{28}O_2Si$: 364.1859, found: 364.1860. For the isomer **20b**: mp 94-95 °C; IR ($CHCl_3$) 3086, 3062, 3026, 3008, 2950, 2928, 2884, 2856, 1678, 1626, 1600, 1582, 1499, 1480, 1464, 1449, 1415, 1392, 1364, 1346, 1317, 1277, 1251, 1226, 1176, 1099, 1080, 1028, 1014, 1004, 974, 941, 840, 694, and 617 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (appar dd, J = 8.0, 1.3 Hz, 2 H), 7.54 (appar tt, J = 7.4, 1.3 Hz, 1 H), 7.44 (appar t, J = 7.6 Hz, 2 H), 7.34 (appar t, J = 7.4 Hz, 2 H), 7.22-7.28 (m, 3 H), 3.36 (t, J = 6.2 Hz, 1 H), 3.17 (d, J = 6.2 Hz, 2 H) 0.90 (s, 9 H), 0.22 (s, 3 H), and 0.13 (s, 3 H); ^1H NMR decoupling experiment: irradiation at δ 7.22-7.28 caused sharpening of the δ 3.36 triplet; ^1H NMR COSY: showed a crosspeak for 7.22-7.28 and 3.36; ^{13}C NMR (100 MHz, $CDCl_3$) δ 240.6 (s), 194.3 (s), 138.8 (s), 137.2 (s), 133.0 (d), 128.7 (d), 128.5 (d), 128.3 (d), 127.0 (d), 126.4 (d), 44.5 (d), 38.2 (d), 30.9 (d), 26.5 (q), 16.8 (s), -6.9 (q), and -7.1 (q); UV max (isooctane) 242 (ε = 15,000) and 201 nm (ε = 31,000); MS *m/e* 364 (M^+, 1.8%) 336, 308, 307, 281, 280, 279 (100%), 249, 233, 203, 202, 201, 187, 91, 77, 75, 73; HRMS *m/e* calcd for $C_{23}H_{28}O_2Si$: 364.1859, found: 364.1853.

***endo*- and *exo*-6-(*tert*-Butyldimethylsilyloxomethyl)-*cis*-bicyclo[3.1.0]hexan-2-one (21a and b).** Reaction of the chloroacetylsilane **14** (0.193 g, 1.00 mmol) with lithium tetramethylpiperidide produced the corresponding enolate, which was treated with a solution of cyclopent-2-en-1-one (0.419 mL, 5.00 mmol) in 0.4 mL of THF, and allowed to react further for 3 h at room temperature according to the general procedure. Evaporation of excess cyclopentenone (25 °C, 0.4 mmHg), followed by column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.028 g (12%) of **21b** (an orange oil) and 0.068 g (28%) **21a** (a pale orange solid). For the exo isomer **21b**: IR (film) 2954, 2932, 2888, 2860, 1729, 1623, 1464, 1413, 1367, 1252, 1184, 1153, 1049, 1008, 964, 943, 917, 863, 841, 828, 780, 736, and 677 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.76 (t, J = 2.9 Hz, 1 H), 2.33-2.38 (m, 2 H), 2.18-2.36 (m, 1 H), 2.06-2.17 (m, 3 H), 0.95 (s, 9 H), 0.26 (s, 3 H), and 0.23 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 239.9, 212.5, 38.5, 37.7, 32.4, 31.6, 26.4, 22.9, 16.7, -7.2, and -7.3. For the endo isomer **21a**: mp 54.5-57.5 °C (sample recrystallized twice from pentane); IR (film) 2952, 2932, 2888, 2858, 1722, 1627, 1463, 1409, 1366, 1301, 1252, 1182, 1150, 1051, 1021, 1007, 972, 943, 922, 840, 800, 782, and 675 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.01 (t, J = 8.4 Hz, 1 H), 2.57-2.65 (m, 1 H), 2.42-2.53 (m, 1 H), 2.18-2.23 (m, 3 H), 1.74-1.82 (m, 1 H), 0.97 (s 9 H), 0.24 (s, 3 H), and 0.22 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 244.7, 213.9, 42.0, 38.5, 36.6, 34.0, 26.4, 19.9, 16.8, -7.1, and -7.3.

***endo*- and *exo*-7-(*tert*-Butyldimethylsilyloxomethyl)-*cis*-bicyclo[4.1.0]heptan-2-one (22a and b).** Reaction of the chloroacetylsilane **14** (0.193 g, 1.00 mmol) with lithium diisopropylamide produced the corresponding enolate, which was treated with cyclohex-2-en-1-one (0.484 mL, 5.00 mmol) and allowed to react further for 4 h at room temperature according to the general procedure. Evaporation of excess cyclohexenone (40 °C, 0.4 mmHg), followed by column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.019 of impure **22b** as a yellow oil, and 0.023 g (9.2%) of **22a** as a pale yellow solid. A volatile contaminant was removed from the exo isomer by evaporation at 0.35 mmHg (25 °C for 15 h followed by 50 °C for 2 h) to give 0.012 g (4.6%) of **22b** as a yellow oil which solidified upon standing at -15 °C. For the exo isomer **22b**: mp 39-41°C (sample recrystallized from pentane); IR (film) 2954, 2934, 2888, 2860, 1696, 1628, 1470, 1450, 1411, 1394, 1366, 1343, 1322, 1279, 1252, 1235, 1192, 1171, 1143, 1089, 1064, 1040, 1007, 953, 941, 898, 881, 843, 779, 740 and 678 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.07 (t, J = 4.1 Hz, 1 H), 2.43 (dd, J = 7.8, 4.0 Hz, 1 H), 2.35 (d of t, J = 18.1, 4.3 Hz, 1 H), 1.92-2.17 (m, 4 H), 1.75-1.91 (m, 1 H), 1.56-1.73 (m, 1 H), 0.94 (s, 9 H), 0.25 (s, 3 H), and 0.22 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 240.1, 205.4, 37.3, 35.7, 35.4, 27.2, 26.4, 20.9, 18.4, 16.8, -7.2, and -7.3; MS *m/e* 252 (M^+, 14%), 237, 209, 197, 196, 195 (100%), 181, 171, 169, 168, 167, 159, 153, 151, 85, 77, 75, 73, and 59; HRMS *m/e* calcd for $C_{14}H_{24}O_2Si$: 252.1546, found: 252.1545. For the endo isomer **22a**: mp 63.5-66 °C (sample recrystallized from pentane); IR ($CHCl_3$) 3004, 2950, 2930, 2860, 1691, 1624, 1471, 1464, 1437, 1410, 1365, 1348, 1329, 1253, 1177, 1144, 1094, 1028, 1001, 941, 886, 839, and 617 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$)

δ 2.95 (t, J = 8.6 Hz, 1 H), 2.61-2.73 (m, 1 H), 2.16-2.31 (m, 2 H), 1.87-2.03 (m, 2 H), 1.61-1.84 (m, 2 H), 1.37-1.48 (m, 1 H), 0.95 (s, 9 H), 0.22 (s, 3 H), and 0.20 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 244.5, 208.5, 41.4, 38.3, 28.3, 27.3, 26.4, 23.5, 18.3, 16.9, -7.0, and -7.3; MS *m/e* (252 M^+, 8.9%), 237, 197, 196, 195 (100%), 181, 169, 168, 167, 155, 151, 75, and 73; HRMS *m/e* calcd for $C_{14}H_{24}O_2Si$: 252.1546, found: 252.1545.

***cis*- and *trans*-2-(*tert*-Butyldimethylsilyloxomethyl)-3-phenylcyclopropanedicarbonitrile (23a and b).** Reaction of the chloroacetylsilane **14** (0.193 g, 1.00 mmol) with lithium tetramethylpiperidide produced the corresponding enolate, which was treated with a solution of benzylidenemalonitrile (0.154 g, 1.00 mmol) in 0.4 mL THF, and allowed to react at -78 °C for 30 min. (Note that in this case decomposition of the product cyclopropylacylsilanes was observed to take place if the reaction mixture was allowed to warm to room temperature.) Half-saturated NH_4Cl solution (8 mL) was then added, and after the reaction mixture was allowed to warm to room temperature, the crude product was isolated as described in the general procedure. Column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.103 g (33%) of **23b** as a white crystalline solid and **23a** (contaminated with a small amount of benzylidenemalonitrile and a trace of **23b**) as a pale yellow oil. Trituration with a mixture of hexanes and pentane provided 0.134 g (43%) of pure **23a** as a white crystalline solid. For the trans isomer **23b**: mp 92.5-95.5 °C (dec); IR ($CHCl_3$) 3028, 2954, 2932, 2886, 2860, 2248, 1643, 1501, 1470, 1466, 1395, 1368, 1328, 1309, 1258, 1100, 1032, 1005, 944, 844, 829, 697, and 618 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41-7.46 (m, 3 H), 7.27-7.30 (m, 2 H), 3.70 (d, AB pattern, J_{AB} = 8.1 Hz, 1 H), 3.63 (d, AB pattern, J_{AB} = 8.1 Hz, 1 H), 1.02 (s, 9 H), 0.38 (s, 3 H), and 0.37 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 234.4, 129.7, 129.5, 129.2, 128.2, 112.3, 111.5, 40.7, 37.6, 26.3, 17.1, 14.8, -7.4, and -7.5; MS *m/e* 310 (M^+, 2.0%), 282, 254, 253, 143, 131, 116, 115, 75, 74, 73 (100%), 45, 43; Anal. Calcd for $C_{18}H_{22}N_2OSi$: C, 69.64; H, 7.14; N, 9.22. Found: C, 69.51; H, 7.10; N, 9.15. For the cis isomer **23a**: mp 102.5-103.5 °C (dec); IR ($CHCl_3$) 3022, 2950, 2928, 2884, 2858, 2244, 1644, 1498, 1469, 1464, 1448, 1394, 1366, 1346, 1255, 1101, 1030, 1021, 1004, 958, 941, 920, 842, 821, 696, and 616 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33-7.38 (m, 3 H), 7.17-7.21 (m, 2 H), 3.59 (d, AB pattern, J_{AB} = 10.5 Hz, 1 H), 3.56 (d, AB pattern, J_{AB} = 10.5 Hz, 1 H), 0.94 (s, 9 H), 0.28 (s, 3 H), and 0.18 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 235.5, 129.2, 129.0, 128.8, 128.2, 115.1, 110.7, 42.7, 39.4, 26.2, 17.0, 11.4, -7.2, and -7.5; MS *m/e* 310 (M^+, 0.6%), 253, 115, 75, 74, 73 (100%); Anal. Calcd for $C_{18}H_{22}N_2OSi$: C, 69.64; H, 7.14; N, 9.02. Found: C, 69.70; H, 7.14; N, 9.22.

Diethyl 3-(*tert*-butyldimethylsilyloxomethyl)-1,2-*trans*-dicarboxylate (24a) and diethyl *t*-3-(*tert*-butyldimethylsilyloxomethyl)-*r*-1,*c*-2-dicarboxylate (24b). Reaction of the chloroacetylsilane **14** (0.193 g, 1.00 mmol) with lithium diisopropylamide produced the corresponding enolate, which was treated with diethyl fumarate (0.21 mL, 1.3 mmol) and allowed to react further for 1 h at room temperature according to the general procedure. Evaporation of excess fumarate (90 °C, 0.7 mmHg), followed by column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.176 g (53%) of a 5:1 mixture of **24a** and **24b** as a yellow oil. For the pure isomer **24a**:[35] IR (film) 2980, 2956, 2934, 2896, 2860, 1728, 1635, 1467, 1392, 1371, 1341, 1296, 1252, 1180, 1113, 1097, 1065, 1034, 1006, 941, 841, 806, 779, and 677; ^1H NMR (300 MHz, $CDCl_3$) δ 4.17 (q, J = 7.2 Hz, 2 H), 4.11 (q, J = 7.2 Hz, 2 H), 3.02 (dd, J = 10, 6 Hz, 1 H), 2.83 (t, J = 6 Hz, 1 H), 2.59 (dd, J = 10, 6 Hz, 1 H), 1.28 (t, J = 7.1 Hz, 3 H), 1.24 (t, J = 7.4 Hz, 3 H), 0.95 (s, 9 H), 0.25 (s, 3 H), and 0.20 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 238.4, 170.7, 167.4, 61.4, 61.3, 39.6, 30.44, 26.3, 25.2, 16.8, 14.1, 14.03, and -7.2; MS *m/e* 313 ($[M-CH_3]^+$, 1.2 %), 272, 271, 256, 255, 227, 115, 99, 95, 75, 74, 73 (100%); HRMS *m/e* calcd for $C_{15}H_{25}O_5Si$ ($[M-CH_3]^+$): 313.1471, found: 313.1471. For the isomer **24b**: ^1H NMR (partial, 400 MHz, $CDCl_3$) δ 3.51 (t, J = 5.1 Hz, 1 H), 2.48 (d, J = 5.1. Hz, 2 H), 0.96 (s, 9 H), 0.27 (s, 6 H).

***tert*-Butyldimethylsilyl[(*c*-2-*tert*-butyldimethylsilyloxomethyl-1-methyl)cyclopropyl]methanone (25a) and *tert*-butyldimethylsilyl[(*t*-2-*tert*-butyldimethylsilyloxomethyl-1-methyl)cyclopropyl]methanone (25b).** A 25-mL, two-necked, round-bottomed flask equipped with an argon inlet adapter, rubber septum, and magnetic stirring bar was charged with 7 mL of THF and diisopropylamine (0.114 mL, 0.78 mmol), and then cooled in an ice bath while *n*-butyllithium solution (1.60 M in hexanes, 0.47 mL, 0.75 mmol) was added via syringe. After 15 min, the ice bath was replaced with a dry ice-acetone bath (-78 °C), and a solution of chloroacetylsilane **14** (0.137 g, 0.71 mmol) in 0.2 mL of THF was added by microliter syringe over the course of 1 - 2 min (the syringe used for the addition was rinsed with two 0.1-mL portions of THF). After 30 min, a solution of 1-*tert*-butyldimethylsilyl-2-methylpropenone[3f] (0.131 g, 0.71 mmol) in 0.3 mL THF was added, and the reaction mixture allowed to warm to room temperature over the course of 1 h, and then stirred further for 5.5 h. Half-saturated NH_4Cl solution (8 mL) was added, and the resulting mixture was partitioned between 50 mL of H_2O and 50 mL of diethyl ether. The organic phase was extracted with 50 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated. Column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.013 g (5.2%) of **25b** and 0.127 g (52%) of **25a** as yellow oils. For the trans isomer **25b**: IR (film) 2956, 2942, 2886, 2858, 1611,

1464, 1411, 1390, 1365, 1251, 1133, 1095, 1039, 1005, 964, 941, 840, 823, 777, and 675 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.20 (dd, J = 6.7, 9.1 Hz, 1 H), 1.44 (dd, J = 3.2, 6.5 Hz, 1 H), 1.37 (s, 3 H), 1.24 (dd, J = 3.4, 8.1 Hz, 1 H), 0.934 (s, 9 H), 0.925 (s, 9 H), 0.25 (s, 6 H), and 0.18 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 244.3, 242.0, 45.3, 38.8, 26.7, 26.6, 21.2, 17.2, 16.9, -4.6, -4.7, and -7.1; MS *m/e* 340 (M^+, 2.9%), 149, 147, 133, 93, 79, 75, and 73 (100%); HRMS *m/e* calcd for $C_{18}H_{35}O_2Si_2$ ([M-H]$^+$): 339.2176, found: 339.2173. For the cis isomer **25a**: IR (film) 2958, 2934, 2892, 2862, 1621, 1465, 1413, 1392, 1365, 1295, 1251, 1090, 1045, 1007, 944, 842, 808, 778, and 680 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.53 (dd, J = 5.5, 8.0 Hz, 1 H), 1.88 (dd, J = 4.2, 5.3 Hz, 1 H), 1.26 (s, 3 H), 1.04 (dd, J = 4.1, 8.0 Hz, 1 H), 0.938 (s, 9 H), 0.928 (s, 9 H), 0.243 (s, 3 H), 0.237 (s, 3 H), 0.227 (s, 3 H), and 0.186 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 243.6, 44.7, 42.7, 26.7, 26.4, 21.3, 20.3, 17.1, 16.8, -4.9, -6.0, -7.1, and -7.3; MS *m/e* 340 (M^+, 3.7%) 283, 149, 147, 133, 117, 115, 89, 83, 75, 73 (100%), 59, 57, 55, 45, 44, 43, 42, and 41; HRMS *m/e* calcd for $C_{18}H_{35}O_2Si_2$ ([M-H]$^+$): 339.2176, found: 339.2172.

***tert*-Butyldimethylsilyl[(*t*-2-nitro-*c*-3-phenyl)cyclopropyl]methanone (26).** Reaction of the bromoacetylsilane **15** (0.237 g, 1.00 mmol) with lithium diisopropylamide produced the corresponding enolate, which was treated with a solution of β-nitrostyrene (0.149 g, 1.00 mmol) in 0.4 mL of THF, and allowed to react further for 30 min at room temperature according to the general procedure. Column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.184 g (60%) of **26** as a viscous yellow oil which solidified upon standing at -15 °C: mp 34-37.5 °C; IR (film) 3054, 3034, 2962, 2932, 2888, 2858, 1630, 1545, 1500, 1465, 1397, 1365, 1251, 1162, 1078, 1043, 1029, 1003, 943, 926, 909, 839, 800, 780, 755, and 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20-7.29 (m, 3 H), 7.10-7.13 (m, 2 H), 5.39 (t, J = 4.0 Hz, 1 H), 3.91 (dd, J = 4.0, 11.2 Hz, 1 H), 3.74 (dd, J = 4.9, 11.1 Hz, 1 H), 0.80 (s, 9 H), 0.18 (s, 3 H), and 0.03 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 237.4, 130.8, 128.5, 128.4, 128.0, 62.3, 44.5, 37.5, 26.1, 16.8, -7.4, and -7.5; MS *m/e* 305 (M^+, 0.6%), 259, 144, 116, 115, 75, and 73 (100%); HRMS *m/e* calcd for $C_{16}H_{23}NO_3Si$: 305.1447, found: 305.1446.

Ethyl *c*-2-(*tert*-butyldimethylsilyloxomethyl)-*t*-2-methylcyclopropanecarboxylate (27a) and Ethyl *t*-2-(*tert*-butyldimethylsilyloxomethyl)-*c*-2-methylcyclopropanecarboxylate (27b). Reaction of the chloropropionylsilane **17** (0.193 g, 1.00 mmol) with lithium tetramethylpiperidide produced the corresponding enolate, which was treated with ethyl acrylate (0.55 mL, 5.1 mmol) and allowed to react further for 30 min at room temperature according to the general procedure. Filtration through a plug of silica gel, followed by column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.043 g (16%) of **27b** (62 mol% pure; contaminated with an acylic byproduct) and 0.147 g (54%) **27a** as pale yellow oils. For the trans isomer **27b**: IR (film) 2956, 2932, 2898, 2862, 1730, 1615, 1464, 1381, 1250, 1180, 841, 824, 812, and 777 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.10-4.20 (m, 2 H), 2.19 (dd, J = 8.4, 6.4 Hz, 1 H), 1.56 (s, 3 H), 1.45 (dd, J = 8.5, 4.2 Hz, 1 H), 1.26 (t, J = 7.0 Hz, 3 H), 1.22 (dd, J = 6.4, 4.2 Hz, 1 H), 0.93 (s, 9 H), and 0.25 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 241.8, 170.7, 60.7, 40.5, 27.3, 26.6, 20.5, 17.0, 14.2, 13.4, -4.9, and -5.0. For the cis isomer **27a**: IR (film) 2958, 2934, 2896, 2860, 1724, 1633, 1463, 1448, 1403, 1383, 1363, 1302, 1250, 1232, 1177, 1094, 1060, 1016, 999, 942, 830, 807, 779, and 678 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.03-4.13 (m, 2 H), 1.73-1.80 (m, 2 H), 1.32 (s, 3 H), 1.24 (t, J = 7.5 Hz, 3 H), 1.01 (dd, J = 3.3, 9.9 Hz, 1 H), 0.94 (s, 9 H), 0.25 (s, 3 H), and 0.21 (s, 3 H); ^1H NMR NOE experiment: irradiation at δ 1.32 produced an enhancement at 1.73-1.80 and 1.01; ^{13}C NMR (100 MHz, $CDCl_3$) δ 242.4, 171.2, 60.6, 40.8, 28.1, 26.6, 20.2, 18.3, 17.0, 14.2, -5.5, and -6.0; MS *m/e* 270 (M^+, 2.9 %), 269, 213, 115, 103, 82, 75, 73 (100%), 59, 55, 45; HRMS *m/e* calcd ([M-H]$^+$): 269.1573, found: 269.1573.

***r*-1-Tetralone-2-spiro-1'-[*c*-2'-(*tert*-butyldimethylsilyloxo)-*t*-2'-methyl]cyclopropane (28a) and *r*-1-tetralone-2-spiro-1'-[*t*-2'-(*tert*-butyldimethylsilyloxo)-*c*-2'-methyl]cyclopropane (28b).** Reaction of the chloropropionylsilane **17** (0.207 g, 1.00 mmol) with lithium tetramethylpiperidide produced the corresponding enolate, which was treated with a solution of 2-methylene-α-tetralone[36] (0.208 g, 1.30 mmol, *ca.* 80% pure) in 0.4 mL THF, and allowed to react further for 30 min at room temperature according to the general procedure. Column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.037 g (11%) of **28b** as a pale yellow oil which solidified upon standing at -15 °C, and 0.239 g (72%) of **28a** as a pale yellow solid. For the isomer **28b**: mp 46.5-48 °C (sample recrystallized from pentane); IR ($CHCl_3$) 3026, 3006, 2952, 2930, 2884, 2846, 1669, 1607, 1463, 1454, 1431, 1365, 1344, 1325, 1290, 1260, 1253, 1229, 1155, 1127, 1100, 978, 911, 837, 825, and 615 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, J = 7.8, 1.4 Hz, 1 H), 7.48 (t of d, J = 7.7, 1.5 Hz, 1 H), 7.32 (appar t, J = 7.4 Hz, 1 H), 7.24 (appar d, J = 7.5 Hz, 1 H), 2.74-2.79 (m, 2 H), 2.18-2.29 (m, 1 H), 1.71 (d of t, J = 14.5, 3.7 Hz, 1 H), 1.64 (d, AB pattern, J_{AB} = 3.8 Hz, 1 H), 1.61 (d, AB pattern, J_{AB} = 3.8 Hz, 1 H), 1.42 (s, 3 H), 0.97 (s, 9 H), 0.21 (s, 3 H), and 0.18 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 244.1, 194.8, 143.8, 133.4, 133.1, 128.9, 127.4, 126.6, 45.8, 41.4, 29.0, 26 8, 26.7, 21.6, 17.3, 14.2, -4.6, and -4.7;

UV max (isooctane) 281 (ε = 2,100), 248 (ε = 14,000), and 205 nm (ε = 23,000); MS *m/e* 329 ([M + H]$^+$), 328 (M$^+$, 23%), 327 ([M-H]$^+$, 44%), 313, 272, 271, 213, 201, 197, 179, 152, 141, 115, 89, 77, 76, 75 (100%), 74, 73, 63, 62, 61, 60, 51, 50, 49, 45, 43, 39, 38, 37, and 36; HRMS *m/e* calcd for $C_{20}H_{27}O_2Si$ ([M-H]$^+$): 327.1780, found: 327.1780. For the isomer **28a**: mp 84-85.5 °C; IR ($CHCl_3$) 3070, 3026, 3000, 2954, 2938, 2890, 2858, 1665, 1627, 1601, 1459, 1434, 1381, 1363, 1340, 1324, 1310, 1249, 1231, 1157, 1117, 988, 965, 912, 838, and 616 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.8, 1.5 Hz, 1 H), 7.45 (t of d, J = 7.4, 1.4 Hz, 1 H), 7.22-7.31 (m, 2 H), 2.92-3.12 (m, 2 H), 2.18 (d, J = 4.2 Hz, 1 H), 2.06-2.23 (m, 2 H), 1.35 (s, 3 H), 0.94 (s, 9 H), 0.86 (d, J = 4.0 Hz, 1 H), 0.20 (s, 3 H), and 0.17 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 243.0, 196.4, 143.5, 133.1, 132.9, 128.3, 127.4, 126.6, 47.0, 38.2, 28.5, 28.1, 26.7, 25.6, 17.4, 15.5, -5.2, and -6.0; UV max (isooctane) 281 (ε = 2,600), 248 (ε = 16,000), and 205 (ε = 29,000) nm; MS *m/e* 328 (M$^+$, 17%), 327 ([M-H]$^+$, 36%), 272, 271 (100%), 244, 243, 213, 197, 185, 184, 179, 153, 115, 75, and 73; HRMS *m/e* calcd for $C_{20}H_{27}O_2Si$ ([M-H]$^+$): 327.1780, found: 327.1779.

4,5-Benzo-*endo*-7-(*tert*-butyldimethylsilyloxomethyl)-*exo*-7-methyl-3-oxa-*cis*-bicyclo[4.1.0]hept-4-en-2-one (29a) and 4,5-benzo-*exo*-7-(*tert*-butyldimethylsilyloxomethyl)-*endo*-7-methyl-3-oxa-*cis*-bicyclo[4.1.0]hept-4-en-2-one (29b). Reaction of the chloropropionylsilane **17** (0.207 g, 1.00 mmol) with lithium tetramethylpiperidide produced the corresponding enolate, which was treated with a solution of coumarin (0.146 g, 1.00 mmol) in 0.4 mL THF, and allowed to react further for 2 h at room temperature according to the general procedure. Unreacted coumarin was removed by shaking a solution of the crude product (in 50 mL of diethyl ether) with 50 mL of 1% aqueous $KMnO_4$ solution. The resulting emulsion was then filtered through Celite and the organic phase was extracted with 50 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated. Column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.083 g (26%) of **29a** as a white solid and 0.026 g (8%) of **29b** as a yellow solid. For the exo isomer **29b**: mp 78.5-80.5 °C; IR ($CHCl_3$) 3030, 2956, 2932, 2884, 2862, 1757, 1732 (sh), 1615, 1588, 1494, 1462, 1408, 1394, 1366, 1340, 1270, 1253, 1185, 1172, 1116, 1073, 1055, 1032, 999, 969, 945, 921, 895, 845, 823, 812, 682, and 618 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (appar t, J = 7 Hz, 2 H), 7.15 (appar t, J = 8 Hz, 1 H), 7.04 (appar d, J = 8 Hz, 1 H), 2.94 (d, AB pattern, J_{AB} = 8 Hz, 1 H), 2.79 (d, AB pattern, J_{AB} = 8 Hz, 1 H), 1.35 (s, 3 H), 0.96 (s, 9 H), 0.32 (s, 3 H), and 0.28 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 239.8, 163.9, 150.9, 129.0, 128.8, 124.7, 117.1, 116.8, 39.2, 32.1, 28.7, 26.5, 17.2, 10.5, -4.7, and -5.1; UV max (isooctane) 275 (ε = 3,100) and 205 nm (ε = 31,000). For the endo isomer **29b**: mp 148-150 °C (sample recrystallized from Et_2O-pentane); IR ($CHCl_3$) 3030, 2954, 2942, 2886, 2862, 1737, 1633, 1587, 1494, 1460, 1383, 1364, 1339, 1268, 1252, 1190, 1150, 1115, 1097, 1035, 985, 961, 901, 841, 822, 682, and 616 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, J = 7.6, 1.8 Hz, 1 H), 7.20 (t of d, J = 7.5, 1.6 Hz, 1 H), 7.06 (t of d, J = 7.7, 2.1 Hz, 1 H), 6.96 (d, J = 7.4 Hz, 1 H), 2.71 (d, J = 7.2 Hz, 1 H), 2.25 (d, J = 7.2 Hz, 1 H), 1.67 (s, 3 H), 0.73 (s, 9 H), 0.25 (s, 3 H), and -0.41 (s, 3 H); ^{1}H NMR NOE experiment: irradiation at δ 1.67 produced enhancement at 2.71 and 2.25; ^{13}C NMR (100 MHz, $CDCl_3$) δ 240.2, 165.8, 150.1, 128.9, 128.8, 123.9, 117.3, 116.0, 46.8, 32.7, 27.1, 26.1, 19.9, 16.9, -6.1, and -7.0; UV max (isooctane) 281 (ε = 2,100) and 203 nm (ε = 26,000).

***r*-2-(*tert*-Butyldimethylsilyloxomethyl)-2-methyl-*t*-3-phenylcyclopropanedicarbonitrile (30a) and *r*-2-(*tert*-butyldimethylsilyloxomethyl)-2-methyl-*c*-3-phenylcyclopropanedicarbonitrile (30b).** Reaction of the chloropropionylsilane **17** (0.207 g, 1.00 mmol) with lithium tetramethylpiperidide produced the corresponding enolate, which was treated with a solution of benzylidenemalonitrile (0.154 g, 1.00 mmol) in 0.4 mL THF, and allowed to react at -78 °C for 30 min. (The reaction mixture was *not* allowed to warm to room temperature.) Half-saturated NH_4Cl solution (8 mL) was then added, the reaction mixture was allowed to warm to room temperature, and the crude product was isolated as described in the general procedure. Column chromatography on silica gel (gradient elution with ethyl acetate-hexanes) afforded 0.212 g (65%) of **30a** and 0.081 g (25%) of **30b** as white crystalline solids. For the trans isomer **30a**: mp 118-119.5 °C (sample recrystallized from benzene-pentane); IR ($CHCl_3$) 3028, 2952, 2930, 2894, 2860, 2242, 1641, 1499, 1464, 1448, 1393, 1266, 1220, 1100, 1081, 1061, 1029, 1012, 1004, 969, 941, 920, 904, 842, 825, 699, and 616 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.42 (m, 3 H), 7.23-7.26 (m, 2 H), 3.77 (s, 1 H), 1.63 (s, 3 H), 1.02 (s, 9 H), 0.404 (s, 3 H), and 0.392 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 236.2, 129.2, 129.1, 128.8, 112.9, 111.5, 49.2, 38.5, 26.5, 17.3, 15.4, 13.6, -5.3, and -5.4; Anal. Calcd for $C_{19}H_{24}N_2OSi$ (sample recrystallized from benzene-pentane): C, 70.33; H, 7.45; N, 8.63. Found: C, 70.25; H, 7.56; N, 8.76. For the cis isomer **30b**: mp 117-118.5 °C (sample recrystallized from benzene-pentane); IR ($CHCl_3$) 3024, 2954, 2932, 2882, 2860, 2238, 1644, 1501, 1465, 1392, 1376, 1262, 1253, 1101, 1032, 1020, 1004, 972, 840, 698, and 618 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.37 (m, 3 H), 7.19-7.23 (m, 2 H), 3.08 (s, 1 H), 1.83 (s, 3 H), 0.90 (s, 9 H), 0.11 (s, 3 H), and -0.05 (s, 3 H); ^{1}H NMR NOE experiment: irradiation at δ 1.83 produced enhancement at 3.08; ^{13}C NMR (100 MHz, $CDCl_3$) δ 236.9, 129.1, 129.0, 128.9, 128.6, 114.2, 111.9, 50.9, 45.9, 26.5, 19.6, 17.4, 15.4,

-5.9, and -6.1; Anal. Calcd for $C_{19}H_{24}N_2OSi$ (sample recrystallized from benzene-pentane): C, 70.33; H, 7.45; N, 8.63. Found: C, 70.13; H, 7.24; N, 8.56.

***trans*-2-(*tert*-Butyldimethylsilyloxomethyl)cyclopropanecarbaldehyde (34a) and *cis*-2-(*tert*-butyldimethylsilyloxomethyl)cyclopropanecarbaldehyde (34b)** An ice-cooled, 25-mL, two-necked, round-bottomed flask equipped with an argon inlet adapter, rubber septum, and magnetic stirring bar was charged with 5 mL of CH_3CN, ylide 33 (0.218 g, 1.00 mmol), and acrolein (0.100 mL, 1.50 mmol). The reaction mixture was allowed to warm to room temperature over the course of 1 h and then maintained at that temperature while the disappearance of the ylide was monitored by UV spectroscopy (in EtOH). After 30 min the reaction mixture was poured into 30 mL of H_2O and 30 mL of diethyl ether, and the aqueous phase was separated and extracted with 30 mL of ether. The combined organic phases were washed with 60 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to afford 0.191 g of a viscous yellow oil. Column chromatography on silica gel (elution with ethyl acetate-hexanes) provided 0.054 g (25%) of **34a** and 0.031 g (15%) of **34b** as pale yellow oils. For the trans isomer **34a**: IR (film) 2956, 2932, 2888, 2860, 2728, 1712, 1628, 1465, 1410, 1394, 1366, 1304, 1252, 1193, 1159, 1071, 1028, 1005, 936, 888, 843, 826, 779, and 678 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.33 (d, J = 4.4 Hz, 1 H), 3.02-3.08 (m, 1 H), 2.42-2.50 (m, 1 H), 1.51-1.56 (m, 1 H), 1.42-1.49 (m, 1 H), 0.94 (s, 9 H), and 0.24 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 241.5, 198.5, 33.7, 32.6, 26.3, 16.6, 16.4, and -7.3; HRMS *m/e* calcd for $C_{11}H_{19}O_2Si$ ($[M-H]^+$): 211.1154, found: 211.1154. For the cis isomer **34b**: IR (film) 2958, 2932, 2892, 2860, 1705, 1627, 1466, 1435, 1410, 1394, 1365, 1316, 1252, 1189, 1166, 1062, 998, 921, 842, 824, 813, 778, 740, and 679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.27 (d, J = 7.3 Hz, 1 H), 3.01-3.10 (m, 1 H), 2.08-2.18 (m, 1 H), 1.87-1.94 (m, 1 H), 1.46-1.53 (m, 1 H), 0.95 (s, 9 H), 0.23 (s, 3 H), and 0.22 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 243.9, 199.8, 35.9, 33.6, 26.4, 16.8, 14.8, and -7.2; HRMS *m/e* calcd for $C_{11}H_{19}O_2Si$ ($[M-H]^+$): 211.1154, found: 211.1153.

***t*-2-(*tert*-Butyldimethylsilyloxomethyl)-1-methyl-*r*-1-cyclopropanecarbaldehyde (35a) and *c*-2-(*tert*-butyldimethylsilyloxomethyl)-1-methyl-*r*-1-cyclopropanecarbaldehyde (35b).** A 100-mL, three-necked, round-bottomed flask equipped with an argon inlet adapter, glass stopper, rubber septum, and magnetic stirring bar was charged with LiOTf (4.7 g, 30 mmol) and 50 mL of CH_3CN. The ylide 33 (2.184 g, 10.00 mmol) and methacrolein (1.08 mL, 13.0 mmol) were then added, and the resulting solution was stirred at room temperature while the disappearance of the ylide was monitored by UV spectroscopy (in EtOH). After 52 h, the reaction mixture was poured into 400 mL of H_2O and 50 mL of diethyl ether, and the aqueous phase was separated and extracted with two 50-mL portions of ether. The combined organic phases were washed with 150 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to furnish 2.178 g of a yellow oil. Column chromatography on silica gel (elution with ethyl acetate-hexanes) afforded 2.021 g (89%) of a 2:1 mixture of **35a** and **b** as a pale yellow oil: IR (film) 2954, 2932, 2886, 2860, 2718, 1710, 1627, 1466, 1366, 1311, 1251, 1090, 1045, 1007, 985, 941, 895, 839, 822, 813, 777, and 676 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$), **35a**: δ 8.91 (s, 1 H) 3.02 (dd J = 6.6, 8.3 Hz, 1 H), 1.75 (dd, J = 4.5, 6.6 Hz, 1 H), 1.35 (dd, J = 4.4, 8.4 Hz, 1 H), 1.19 (s, 3 H), 0.934 (s, 9 H), 0.205 (s, 3 H), and 0.199 (s, 3 H), **35b**: δ 9.14 (s, 1 H), 2.86 (dd, J = 6.8, 7.7 Hz, 1 H), 2.20 (dd, J = 4.7, 6.8 Hz, 1 H), 1.37 (dd, J = 4.5, 8.1 Hz, 1 H), 1.31 (s, 3 H), 0.930 (s, 9 H), 0.217 (s, 3 H), and 0.209 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) **35a**: δ 242.0, 199.5, 26.3, 17.7, 16.8, and 9.8, **35b**: 243.3, 200.5, 26.3, 22.0, 17.6, and 16.8, unassigned (**35a** or **35b**): 43.7, 39.0, 38.7, 36.3, -7.2, -7.3, and -7.4; HRMS *m/e* calcd for $C_{12}H_{21}O_2Si$ ($[M-H]^+$): 225.1311, found: 225.1310.

***t*-2-(*tert*-Butyldimethylsilyloxomethyl)-*t*-3-methyl-*r*-1-cyclopropanecarbaldehyde (36a), *c*-2-(*tert*-butyldimethylsilyloxomethyl)-t-3-methyl-*r*-1-cyclopropanecarbaldehyde (36b), and *c*-2-(*tert*-butyldimethylsilyloxomethyl)-c-3-methyl-*r*-1-cyclopropanecarbaldehyde (36c).** A 25-mL, two-necked, round-bottomed flask equipped with an argon inlet adapter, rubber septum, and magnetic stirring bar was charged with LiOTf (0.47 g, 3.0 mmol) and 5 mL of CH_3CN. The ylide 33 (0.218 g, 1.00 mmol) and crotonaldehyde (0.099 mL, 1.20 mmol) were then added, and the resulting solution was stirred at 40 °C while the disappearance of the ylide was monitored by UV spectroscopy (in EtOH). After 38 h, the reaction mixture was poured into 15 mL of H_2O and 20 mL of diethyl ether, and the aqueous phase was separated and extracted with 10 mL of ether. The combined organic phases were washed with 30 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to give 0.207 g of a yellow oil. Column chromatography on silica gel (elution with ethyl acetate-hexanes) afforded 0.063 g (28%) of **36a**, 0.023 g (10%) of **36b** and 0.0045 g (2.0%) of **36c** as pale yellow oils. Mixed fractions, totalling 0.010 g (4%) were also obtained. For the isomer **36a**: IR (film) 2960, 2936, 2892, 2864, 2726, 1709, 1624, 1465, 1404, 1393, 1380, 1367, 1288, 1253, 1198, 1160, 1142, 1121, 1068, 1039, 1021, 1009, 963, 943, 883, 840, 779, 736, and 679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.40 (d, J = 4.1 Hz, 1 H), 3.20 (dd, J = 4.7, 9.5 Hz, 1 H), 2.64-2.69 (m, 1 H), 2.03-2.13 (m, 1 H), 1.09 (d, J = 6.5 Hz, 3 H), 0.95 (s, 9 H), 0.23 (s, 3 H), and 0.22

(s, 3 H); ^{1}H NMR NOE experiment: irradiation at δ 9.40 produced enhancement at 3.20, 2.64-2.69, and 2.03-2.13 and irradiation at δ 1.09 produced enhancement at 2.64-2.69 and 2.03-2.13; ^{13}C NMR (75 MHz, $CDCl_3$) δ 241.6, 198.7, 40.8, 36.9, 27.0, 26.4, 16.8, 10.7, -7.2, and -7.3; MS m/e 227 (M+1, 0.7%), 155, 125, 115, 99, 97, 75, 73 (100%), 59, 45, 43; HRMS m/e calcd for $C_{11}H_{19}O_2Si$: 211.1154, found: 211.1155. For the isomer **36b**: IR (film) 2958, 2932, 2886, 2860, 2744, 1700, 1623, 1463, 1419, 1393, 1365, 1334, 1253, 1172, 1118, 1092, 1077, 1055, 995, 944, 916, 841, 780, 736, and 677 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.36, (d, J = 7.3 Hz, 1 H), 2.83 (dd, J = 6.7, 8.3 Hz, 1 H), 2.15-2.25 (m, 1 H), 1.93-1.99 (m, 1 H), 1.27 (d, J = 5.7 Hz, 3 H), 0.95 (s, 9 H), 0.24 (s, 3 H), and 0.22 (s, 3 H); ^{1}H NMR NOE *experiment:* irradiation at δ 1.27 produced enhancement at 2.83, 2.15-2.25, and 1.93-1.99 and irradiation at δ 9.36 produced enhancement at 2.15-2.25 and 1.93-1.99; ^{13}C NMR (75 MHz, $CDCl_3$) δ 243.4, 199.3, 45.5, 42.8, 26.4, 24.9, 17.2, 16.8, -7.1, -7.2; MS *m/e* 227 (M+1, 0.6%), 211, 169, 141, 125, 115, 111, 99, 97, 75, 73 (100%), 59; HRMS *m/e* calcd for $C_{11}H_{19}O_2Si$: 211.1154, found: 211.1153. For the isomer **36c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.84 (d, J = 5.8 Hz, 1 H), 3.20 (t, J = 8.9 Hz, 1 H), 2.01-2.11 (m, 2 H), 1.35 (d, J = 7.2 Hz, 3 H), 0.97 (s, 9 H), 0.234 (s, 3 H), and 0.226 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 244.6, 199.9, 43.4, 36.4, 26.5, 25.3, 17.0, 8.0, -7.0, and -7.1.

1-[*cis*-2-(*tert*-Butyldimethylsilyloxomethyl)cyclopropyl]ethan-1-one (18a) and 1-[*trans*-2-(*tert*-butyldimethylsilyloxomethyl)cyclopropyl]ethan-1-one (18b). A 25-mL, two-necked, round-bottomed flask equipped with an argon inlet adapter, rubber septum, and magnetic stirring bar was charged with LiOTf (0.47 g, 3.0 mmol) and 5 mL of CH_3CN. The ylide **33** (0.218 g, 1.00 mmol) and methyl vinyl ketone (0.108 mL, 1.30 mmol) were then added, and the resulting solution was stirred at 40 °C while the disappearance of the ylide was monitored by UV spectroscopy (in EtOH). After 1.5 h, additional methyl vinyl ketone (0.025 mL, 0.3 mmol) was added. After 3 more hours, the reaction mixture was partitioned between 30 mL of H_2O and 30 mL of pentane, and the organic phase was dried over $MgSO_4$, filtered, and concentrated to give 0.164 g of a pale yellow oil. Kugelrohr distillation (80-100 °C, 0.45 mmHg) provided 0.144 g (64%) of a 1.2:1 mixture of **18a** and **b** contaminated with 21 mol % of *tert*-butyldimethylsilanol. (The silanol contaminant can be removed under vacuum at 1 mmHg.)

Ethyl *cis*- and *trans*-2-(*tert*-Butyldimethylsilyloxomethyl)cyclopropanecarboxylate (19a and b). A 5-mL, two-necked round-bottomed flask equipped with an argon inlet adapter, rubber septum and magnetic stirring bar was charged with LiOTf (0.47g, 3.0 mmol) and ylide **33** (0.284 g, 1.30 mmol). The solids were intimately mixed, and ethyl acrylate (0.108 mL, 1.00 mmol) and 0.20 mL of CH_3CN were added, and the resulting paste was heated at 40 °C. After 24 h, the reaction mixture was partitioned between 10 mL of H_2O and 10 mL of diethyl ether, and the aqueous phase was separated and extracted with 10 mL of ether. The combined organic phases were washed with 20 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to give 0.219 mg of a yellow oil. Column chromatography on silica gel (elution with ethyl acetate-hexanes) afforded 0.065 g (25%) of **19b**, 0.010 g (4%) of a mixed fraction, and 0.076 g of **19a** contaminated with *tert*-butyldimethylsilanol. The silanol contaminant was removed under vacuum (1 mmHg, ca. 3 h) to give 0.070 mg (27%) of pure **19a**.

***tert*-Butyldimethylsilyloxomethylcyclopropylmethanone (7).** A sealed tube containing a magnetic stirring bar, 5 mL of CH_2Cl_2, $[(C_6H_5)_3P]_3RhCl$ (0.502 g, 0.543 mmol), and a 2:1 mixture of **34a** and **b** (0.105 g, 0.494 mmol) was heated at 80 °C for 7 h, during which time the color of the solution changed from dark red to orange.[29] The reaction tube was then cooled to room temperature (a large volume of yellow crystals of $[(C_6H_5)_3P]_2Rh(CO)Cl$ precipitated) and the resulting mixture was filtered through a plug of glass wool. Concentration of the filtrate provided 0.402 g of a red oil. Kugelrohr distillation (25-70 °C, 0.5 mmHg) then furnished 0.061 g (67%) of **7** as a yellow oil. Spectral characteristics for this product were identical to those previously reported for this compound.[6]

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